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Substrate-Controlled and Site-Selective [3+2] Cycloadditions of N-Heterocyclic Carbene Derived Ambident Dipoles

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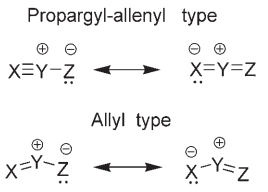
Abstract: 2-Aryl thiocarbamoyl benzimidazolium and imidazolinium inner salts derived from benzimidazole and imidazoline carbenes are unique ambident C-C-S and C-C-N 1,3-dipolar systems, which undergo highly efficient and site-selective cycloaddition reactions with dimethyl acetylenedicarboxylate or dibenzoylacetylene to furnish spiro(imidazole-2,3′-thiophene) derivatives in excellent yields. When treated with ethyl propiolate, methyl acrylate or acrylonitrile, spiro(imidazole-2,3′-pyrrole) derivatives were formed in good yields. Theoretical studies revealed an asynchronous concerted mechanism for both the C-C-S and C-C-N 1,3-dipolar cycloaddition reactions. The site selectivity in the [3+2] cycloaddition reaction of ambident 1,3-dipoles was predictably regulated by both the electronic and steric effects of dipolarophiles.

Keywords: 1,3-dipoles · carbenes · cycloaddition · heterocycles · site selectivity

Introduction

1,3-Dipolar cycloaddition reactions constitute one of the most powerful protocols in organic synthesis.[1] Most 1,3-dipolar cycloaddition reactions proceed through a concerted mechanism,[1a] although two-stage reactions through zwitterionic intermediates have also been reported.[2] The interaction between unsymmetrical reagents in a 1,3-dipolar cycloaddition reaction can give two isomeric adducts depending on the relative position of the substituent in the cycloadduct. The development of 1,3-dipolar cycloaddition reactions has in recent years entered into a new stage in terms of controlling regio-[2c,3] and stereoselectivity.[4] An important method for the regulation of regio- and stereoselectivity in 1,3-dipolar cycloadditions is to change the electronic and steric effects of the reactants with Lewis acid catalysts. This approach has been exemplified by the excellent work of Palomo et al.,[5] in which the perfect combination of both regio- and stereoselectivity was achieved in the $Cu(OTf)_2$-mediated (OTf = triflate) 1,3-dipolar cycloaddition reaction of α′-hydroxy enones and nitrones. Another strategy to control regio- and stereoselectivity is the application of a well-defined nanosized environment. For example, Ye and coworkers recently reported a successful regioselective 1,3-dipolar cycloaddition reaction of azides with alkynes using molecularly imprinted polymers as regioselective nanoreactors.[3a] Most of the 1,3-dipolar systems reported to date are either of the propargyl–allenyl type, including diazoalkanes, azides, dinitrogen oxide, nitrile ylides, nitrile imines and nitrile oxides, or allyl type, such as azomethine ylides, azomethine imines, nitrones, carbonyl ylides, carbonyl imines and carbonyl oxides (Scheme 1). All of these dipolar compounds share two common structural features: first, they are all heteroatom-centred dipoles; second, they each contain only one dipolar component. The carbon-centred 1,3-dipoles, and compounds that can act as two or more different 1,3-dipoles, have scarcely been explored.



Scheme 1. General structures of 1,3-dipoles.

Imidazoline and benzimidazole carbenes, or their dimers, were reported to react with isothiocyanates to form [1+1] adducts, namely, 2-aryl thiocarbamoyl imidazolinium[6] and benzimidazolium inner salts,[7] or [1+2] adducts (i.e., dithiohydantoins),[6b,8] under different reaction conditions. The 2-aryl thiocarbamoyl imidazolinium and benzimidazolium

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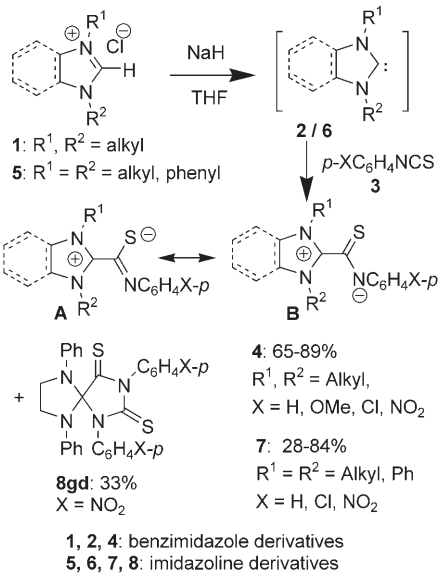
inner salts can have two different 1,3-dipolar resonance canonical forms: C-C-S 1,3-dipole **A** and C-C-N 1,3-dipole **B** (Scheme 2). Winberg and Coffman[6a] and Regitz et al.[6b]



Scheme 2. Preparation of 2-aryl thiocarbamoyl benzimidazolium and imidazolinium inner salts.

claimed, respectively, that *N*,*N*′-diethyl-2-thiocarbamoyl imidazolinium and *N*,*N*′-diphenyl-2-thiocarbamoyl imidazolinium salts behaved as the C-C-N 1,3-dipoles in all cycloaddition reactions with dimethyl acetylenedicarboxylate (DMAD), dibenzoylacetylene and other electron-deficient alkenes to give spiro(tetrahydroimidazole-2,3′-pyrrole) derivatives. Recently, we found for the first time that the 2-aryl thiocarbamoyl benzimidazolium and imidazolinium inner salts actually behaved as the novel ambident C-C-S or C-C-N 1,3-dipolar components.[9] These salts underwent highly site-selective 1,3-dipolar cycloaddition reactions with DMAD or ethyl propiolate to furnish imidazole–spiro(thiophene) or imidazole–spiro(pyrrole) derivatives, respectively, in good-to-excellent yields. It was the reactivity of these new 1,3-dipolar systems and the site-selectivity of their [3+2] cycloadditions with different dipolarophiles that intrigued us. The control or regulation of the site selectivity should be of great importance. To explore the reactivity and selectivity, or the applications, of the C-C-S and C-C-N 1,3-dipolar components and obtain deep insight into the reaction mechanism, we systematically investigated the 1,3-dipolar cycloaddition reactions of 2-aryl thiocarbamoyl benzimidazolium and imidazolinium inner salts with different electron-deficient acetylene and olefin derivatives by means of experimental and theoretical approaches.

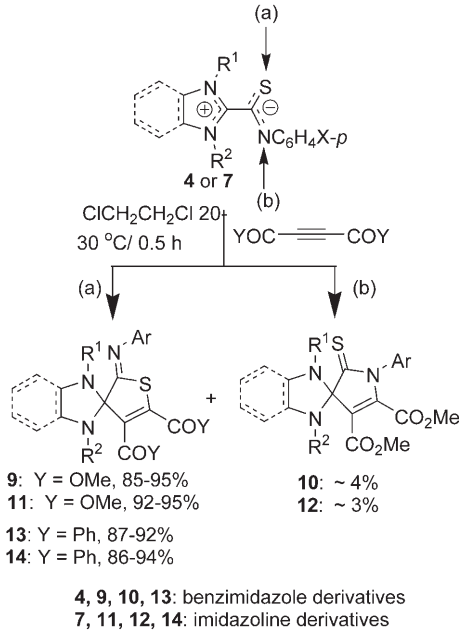
Results and Discussion

Preparation of 2-aryl thiocarbamoyl benzimidazolium and imidazolinium inner salts: Herein, 2-aryl thiocarbamoyl benzimidazolium inner salts **4** or imidazolinium inner salts **7** were prepared from the reactions of benzimidazole carbenes **2** or imidazoline carbenes **6** with aryl isocyanates at 0–20 °C. Carbenes **2** and **6** were generated in situ by the deprotonation of the corresponding benzimidazolium salts **1** or imidazolinium salts **5** with sodium hydride. All the *N*,*N*′-dialkyl benzimidazolium salts **4** or imidazolinium salts **7** were obtained as sole products in 65–89 % yield. In the case of the *N*,*N*′-diaryl imidazoline carbene **6g**, *N*,*N*′-diaryl imidazolinium salt **7gd** (28 %) was obtained along with dithiohydantoin **8gd** (33 %; Scheme 2). The latter product **8gd** was most likely derived from the cycloaddition reaction of **7gd** with another equivalent of isothiocyanate. The different outcomes between *N*,*N*′-dialkyl imidazoline carbenes and *N*,*N*′-diaryl imidazoline carbenes were most probably due to the different stabilities of the imidazolinium inner salts **7**. These carbene-derived 1,3-dipoles are stabilised by delocalisation of the positive charge of the cation centre on the adjacent nitrogen atoms and the negative charge on the sulfur atom and aryl amino substituent. Because of this electronic effect, an alkyl-substituted amino group is a stronger electron donor than a phenyl-substituted amino group; therefore, the *N*,*N*′-dialkyl imidazolinium salt should be more stable than the *N*,*N*′-diaryl substituted analogue.

Reaction of 2-aryl thiocarbamoyl benzimidazolium salts 4 and imidazolinium salts 7 with DMAD or dibenzoylacetylene: We initially examined the reaction of **4** and **7** with the highly electron-deficient agent DMAD as the dipolarophile. When treated with one equivalent of DMAD in 1,2-dichloroethane at ambient temperature, the zwitterion **4** was very rapidly transformed into the red–purple spiro(benzimidazoline-2,3′-dihydrothiophenes) **9** in 85–95 % yield, and a small amount (4 %) of dark green spiro(benzimidazoline-2,3′-dihydropyrrole) **10** was also obtained (Scheme 3). Neither the substituent effect on the dipoles (Table 1, entries 5–9) nor the reaction conditions (Table 1, entries 1–5) altered the reaction pathway. 2-Phenylthiocarbamoyl imidazolinium salts **7** acted in a similar manner to their benzimidazolium analogues **4** on reaction with DMAD. Under identical conditions, the zwitterionic adducts **7** derived from imidazoline carbenes were found to behave predominantly as the C-C-S rather than the C-C-N 1,3-dipolar systems, thus forming spiro(imidazoline-2,3′-dihydrothiophene) cycloproducts **11** in excellent yields, although a tiny amount of by-product spiro(imidazoline-2,3′-dihydropyrrole) **12** was isolated.

Following the reaction with DMAD, the interaction between zwitterions **4** or **7** and dibenzoylacetylene was explored. Under identical conditions as those for the reaction with DMAD, both **4** and **7** reacted with dibenzoylacetylene quickly and efficiently to afford C-C-S cycloaddition product spiro(benzimidazoline-2,3′-dihydrothiophene) **13** or spiro(imidazoline-2,3′-dihydrothiophene) derivatives **14** in 86–94 % yield. It is worth noting that the imidazole–spiro(pyrrole)-type products were not detected (see Scheme 3 and Table 2).

The structures of all the products were fully characterised by spectroscopic studies and microanalysis. This characteri-



Scheme 3. Reaction of 1,3-dipoles **4** and **7** with DMAD or dibenzoylacetylene.

Table 1. The 1,3-dipolar cycloaddition reactions between **4** or **7** and DMAD.

Entry	Starting material				Reaction conditions	Product	Yield [%]
	Compd	R^1	R^2	Ar			
1	**4ba**	*n*Bu	*n*Bu	Ph	DCE, 50–60 °C, 0.5 h	**9ba**	90
						10ba	5
2	**4ba**	*n*Bu	*n*Bu	Ph	CH_3CN, 50–60 °C, 0.5 h	**9ba**	78
						10ba	–[a]
3	**4ba**	*n*Bu	*n*Bu	Ph	THF, 50–60 °C, 0.5 h	**9ba**	64
						10ba	8
4	**4ba**	*n*Bu	*n*Bu	Ph	acetone, 50–60 °C, 0.5 h	**9ba**	85
						10ba	6
5	**4ba**	*n*Bu	*n*Bu	Ph	DCE, RT, 0.5 h	**9ba**	90
						10ba	4
6	**4ca**	Bz	Bz	Ph	DCE, RT, 0.5 h	**9ca**	95
						10ca	–[a]
7	**4cb**	Bz	Bz	*p*-$MeOC_6H_4$	DCE, RT, 0.5 h	**9cb**	88
						10cb	–[a]
8	**4cc**	Bz	Bz	*p*-ClC_6H_4	DCE, RT, 0.5 h	**9cc**	87
						10cc	–[a]
9	**4cd**	Bz	Bz	*p*-$NO_2C_6H_4$	DCE, RT, 0.5 h	**9cd**	85
						10cd	–[a]
10	**7aa**	Et	Et	Ph	DCE, RT, 0.5 h	**11aa**	95
						12aa	–[a]
11	**7da**	Bz	Bz	Ph	DCE, RT, 0.5 h	**11da**	92
						12da	3

[a] A tiny amount of minor product was observed. DCE = 1,2-dicholorethane.

sation indicated that **9**–**14** were the [1+1] adducts of the two starting materials. To identify the isomers beyond doubt, the structures of **9ca** and **10ba** were determined unambiguously by single-crystal X-ray diffraction studies.[10] It is worth noting that in the ^{13}C NMR spectra the diagnostic C=N signals for the dihydrothiophene products **9, 11, 13** and **14** were at $\delta = 165$–175 ppm and the C=S signals for the dihydropyrroles **10** and **12** were in the downfield range $\delta =$ 200–210 ppm. These spectroscopic characteristics are very useful for the differentiation of the imidazole–spiro(thiophene) and imidazole–spiro(pyrrole) products in the latter studies.

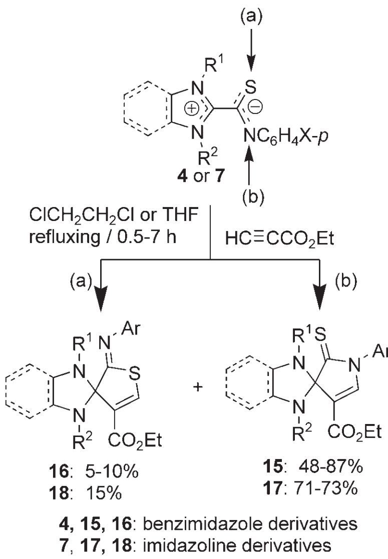
Table 2. The 1,3-dipolar cycloaddition reactions between **4** or **7** and dibenzoylacetylene.[a]

Entry	Starting material				Product	Yield [%]
	Compd	R^1	R^2	Ar		
1	**4ba**	*n*Bu	*n*Bu	Ph	**13ba**	89
2	**4ca**	Bz	Bz	Ph	**13ca**	92
3	**4cb**	Bz	Bz	*p*-$MeOC_6H_4$	**13cb**	92
4	**4cc**	Bz	Bz	*p*-ClC_6H_4	**13cc**	90
5	**4cd**	Bz	Bz	*p*-$NO_2C_6H_4$	**13cd**	91
6	**4da**	Et	*n*Bu	Ph	**13da**	91
7	**4fa**	Et	Bz	Ph	**13fa**	88
8	**4ga**	*n*Bu	Bz	Ph	**13ga**	87
9	**7da**	Bz	Bz	Ph	**14da**	93
10	**7ea**	*p*-MeOBz	*p*-MeOBz	Ph	**14ea**	86
11	**7gd**	Ph	Ph	*p*-$NO_2C_6H_4$	**14gd**	94

[a] Reaction conditions: 1,2-dichloroethane, RT, 0.5 h.

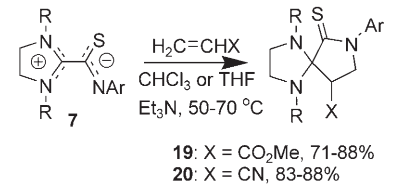
The aforementioned results clearly indicated that the zwitterions **4** and **7** act predominantly as the powerful C-C-S dipolar component towards DMAD and dibenzoylacetylene. It should be noted that these results are in sharp contrast to those previously reported.[6a,b] Clearly, the structures of **11aa** and **14gd** were wrongly assigned in these earlier reports.

Reaction of 2-aryl thiocarbamoyl benzimidazolium salts 4 and imidazolinium salts 7 with ethyl propiolate, methyl acrylate or acrylonitrile: A quite different reaction pathway was encountered when ethyl propiolate was used as the dipolarophile in reaction with **4** and **7**. Under identical conditions as those for the reaction of DMAD and dibenzoylacetylene with **4** and **7**, the reaction of **4** with ethyl propiolate proceeded very slowly. Only at elevated temperatures and with excess amounts of ethyl propiolate did the reactions go to completion. At reflux in 1,2-dichloroethane or THF, all the zwitterions **4** and **7**, except 2-*para*-nitrophenylthiocarbamoyl benzimidazolium **4cd**, reacted with five equivalents of ethyl propiolate to furnish **15** and **17** as the major products, respectively, in 73–82% yield within 0.5–1.5 h, along with **16** and **18** in 5–15% yield (see Scheme 4 and Table 3). Most surprisingly, however, the major products **15** and **17** were imidazole–spiro(pyrrole) products. This outcome clearly indicated that **4** and **7** be-



Scheme 4. Reaction of dipoles **4** and **7** with ethyl propiolate.

vious on reaction with electron-deficient alkenes, such as methyl acrylate and acrylonitrile. The reaction of benzimidazolium salts **4** with methyl acrylate or acrylonitrile was totally inefficient under all the reaction conditions employed. On the contrary, however, in $CHCl_3$ or THF at reflux and in the presence of a large excess of the dipolarophile, imidazolinium **7** acted as the C-C-N 1,3-dipolar component in the smooth addition to methyl acrylate or acrylonitrile, thus producing tetrahydropyrrole derivatives **19**[10] or **20**, respectively, in good yields (see Scheme 5 and Table 4). Apparently,



Scheme 5. The cycloaddition reactions between **7** and methyl acrylate or acrylonitrile.

Table 3. The 1,3-dipolar cycloaddition reactions between **4** or **7** and ethyl propiolate.

Entry	Starting material				Reaction conditions	Product	Yield [%]
	Compd	R^1	R^2	Ar			
1	**4cb**	Bz	Bz	*p*-$MeOC_6H_4$	DCE, reflux for 20 min	**15cb**	81
						16cb	10
2	**4cc**	Bz	Bz	*p*-ClC_6H_4	DCE, reflux for 1.5 h	**15cc**	81
						16cc	5
3	**4cd**	Bz	Bz	*p*-$NO_2C_6H_4$	DCE, reflux for 7 h	**15cd**	48
						16cd	–
4	**7da**	Bz	Bz	Ph	THF, reflux for 1.5 h	**17da**	73
						18da	15
5	**7ea**	*p*-MeOBz	*p*-MeOBz	Ph	THF, reflux for 1.5 h	**17ea**	71
						18ea	15

the zwitterions **4** were less active than **7**, as an aromatic benzimidazoline cation should be more stable than an aliphatic tetrahydroimidazole cation. It was interesting to note that an organic base can promote the reaction process. Thus, improved chemical yields were achieved in the presence of triethylamine (See Table 4, entries 3 and 4). Zwitterion **7** was not very stable at an elevated temperature and underwent intramolecular cyclisation to form spiro(tetrahydroimidazole-2,3′-indoline-2-thione). Zwitterion **7** was stabilised in the presence of an organic base probably because of the interaction of a base with the cation centre, and therefore its tendency to intramolecular cyclisation with the phenyl moiety was alleviated.

haved mainly as C-C-N 1,3-dipolar components in the addition to ethyl propiolate. The reaction of **4 cd** with ethyl propiolate took a longer time (7 h) and gave a lower yield (48%) of product **15 cd**. It is not difficult to understand why **4 cd** gave a lower yield of the C-C-N cycloaddition product as its C-C-N dipolar component has the weakest nucleophilicity among the 1,3-dipoles employed.

Table 4. The 1,3-dipolar cycloaddition reactions between **7** and methyl acrylate or acrylonitrile.

Entry	Starting materials				Reaction conditions	Product	Yield [%]
	7	R	Ar				
1	**7da**	Bz	Ph	methyl acrylate	$CHCl_3$, Et_3N 60°C, 7 h	**19da**	84
2	**7ea**	*p*-MeOBz	Ph	methyl acrylate	$CHCl_3$, Et_3N 60°C, 8 h	**19ea**	88
3	**7ec**	*p*-MeOBz	*p*-ClC_6H_4	methyl acrylate	$CHCl_3$, Et_3N refluxing, 10 h	**19ec**	71
4	**7ec**	*p*-MeOBz	*p*-ClC_6H_4	methyl acrylate	$CHCl_3$, refluxing, 15 h	**19ec**	38
5	**7fc**	*p*-ClBz	*p*-ClC_6H_4	methyl acrylate	$CHCl_3$, Et_3N refluxing, 22 h	**19fc**	88
6	**7da**	Bz	Ph	acrylonitrile[a]	THF, Et_3N, refluxing, 12 h	**20da**	83
7	**7ea**	*p*-MeOBz	Ph	acrylonitrile	THF, Et_3N, reflux, 9 h	**20ea**	88
8	**7ec**	*p*-MeOBz	*p*-ClC_6H_4	acrylonitrile	THF, Et_3N, reflux, 14 h	**20ec**	86

[a] Acrylonitrile is a carcinogenic compound.

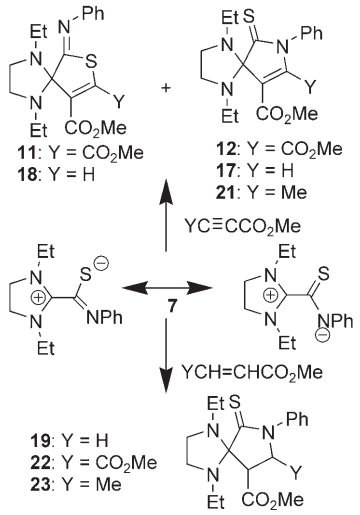
The ambident reactivity of the benzimidazolium and imidazolinium species and their completely opposite site-selective cycloaddition reactions were intriguing. To examine the generality of the site selectivity in the 1,3-dipolar cycloaddition reactions of the ambident 1,3-dipolar components, other dipolarophiles were tested.

Although both the benzimidazolium and imidazolinium dipolar systems showed almost identical reactivities towards the electron-deficient alkynes, different reactivities were ob-

It should be pointed out that other α,β-unsaturated alkyne and alkenes, including methyl 2-butynoate, methyl crotonate, diethyl fumarate, diethyl maleate and fumaroni-

trile, were not good 1,3-dipolarophiles towards benzimidazolium and imidazolinium inner salts. No reaction was observed under various conditions.

Computational study of the mechanism, reactivity and site selectivity of the reactions: The highly site-selective 1,3-dipolar cycloaddition reactions of the 2-aryl thiocarbamoyl benzimidazolium and imidazolinium inner salts are remarkable. In particular, their clear-cut cycloaddition reaction pathways between the C-C-S and C-C-N 1,3-dipolar systems when treated with different alkynes and alkenes are intriguing. Our experimental studies show that neither the substituent effect on dipoles **4** and **7** nor the reaction conditions can change the reaction pathway. It is the structure of the dipolarophile that affects the reactivity of the dipole and switches the site selectivity of the reaction. To shed light on the different selectivity of the zwitterionic species towards different dipolarophiles, density functional theory B3LYP/6–31G* was employed to investigate the mechanisms of the reactions depicted in Scheme 6. The calculation indicated that



Scheme 6. Computational reactions of **7aa** with DMAD, methyl propiolate, methyl 2-butynoate, methyl acrylate, dimethyl fumarate and methyl crotonate.

the cycloaddition of **7aa** with DMAD or methyl propiolate can proceed through two different reaction pathways by using both the C-C-S and C-C-N dipoles, respectively. Compound **7aa** only acted as a C-C-N 1,3-dipole to α,β-unsaturated alkyne and alkenes, including methyl 2-butynoate, methyl acrylate, dimethyl fumarate or methyl crotonate, as the transition states for the C-C-S 1,3-dipolar reactions could not be located; therefore, such reactions are probably not favoured under the present conditions. Eight transition states have been located for the reactions in Scheme 6 (Figure 1). In each transition state, the two bonds that are forming have quite different lengths, but no intermediate could be located between the reactants and the final product. Therefore, the reaction proceeded most likely through a concerted but asynchronous mechanism. The activation barriers, activation enthalpies, activation entropies and activation free energies, which were obtained by using the B3LYP/6–31G* method, are summarised in Table 5.

In the reaction of **7aa** with DMAD at 298 K, the relative free energy in the C-C-S cycloaddition is 0.98 kcal mol^{-1} more favourable than that of the C-C-N cycloaddition. On the contrary, however, the activation free energy of the C-C-N 1,3-dipolar reaction is about 2 kcal mol^{-1} less than that of the C-C-S pathway in the case of the reaction between **7aa** and methyl propiolate. The results of these calculations are in good agreement with the experimental observations. In each of the transition states illustrated in Figure 1, the C–S or C–N bond being formed was shorter than the C–C bond being formed, thus indicating that the nucleophilic attack of the sulfur or nitrogen atom on the unsaturated carbon atom initiated this cycloaddition reaction. As indicated in Table 5, both the C-C-S and C-C-N reaction pathways of **7aa** with DMAD have lower activation barriers, enthalpies and free energies because DMAD is the most electrophilic and active 1,3-dipolarophile among those on which we performed calculations. Although two transition states for the C-C-S and C-C-N 1,3-dipolar cycloaddition reactions (Table 5, entries 1 and 2) have almost the same activation barriers and activation enthalpies, the contribution of entropy to the free energy caused a difference of about 1 kcal mol^{-1} in the activation free energy. This entropy effect led to the competition of two reaction processes, and the C-C-S cycloaddition is, therefore, the predominant process. The disfavoured C-C-N pathway in this case is most probably due to a strong steric repulsion between the phenyl group on the nitrogen atom and the carboxylate group in the C-C-N reaction process. When the reaction was carried out in dichloroethane, single-point SCRF-B3LYP/6–31G* calculations showed that the difference in free energy increased to 1.6 kcal mol^{-1}, thus leading to the formation of the major and minor products in a ratio of 93:7. In the reaction of **7aa** with methyl propiolate, calculations showed the C-C-N 1,3-dipolar cycloaddition to be the favoured path way and the calculated ratio of the C-C-N/C-C-S products is 97:3. It is interesting to note that the reaction transition state of **7aa** with methyl acrylate has a much higher activation barrier, enthalpy and free energy (Table 5, entry 6), which is in good agreement with the experimental observation that **7** was a much less reactive 1,3-dipole to methyl acrylate or acrylonitrile.

The theoretical calculations indicate a steric effect that plays a determinant role in the C-C-N cycloaddition process. For example, the reactions of **7aa** with methyl acrylate and methyl 2-butynoate have similar activation barriers, enthalpies and free energies (Table 5, entries 5 and 6), but actually the latter reaction did not take place under the conditions employed as result of the unfavourable steric effect in the C-C-N cycloaddition reaction. The dimethyl fumarate, an alkene substituted by two electron-withdrawing groups, should be a more reactive dipolarophile than methyl acry-

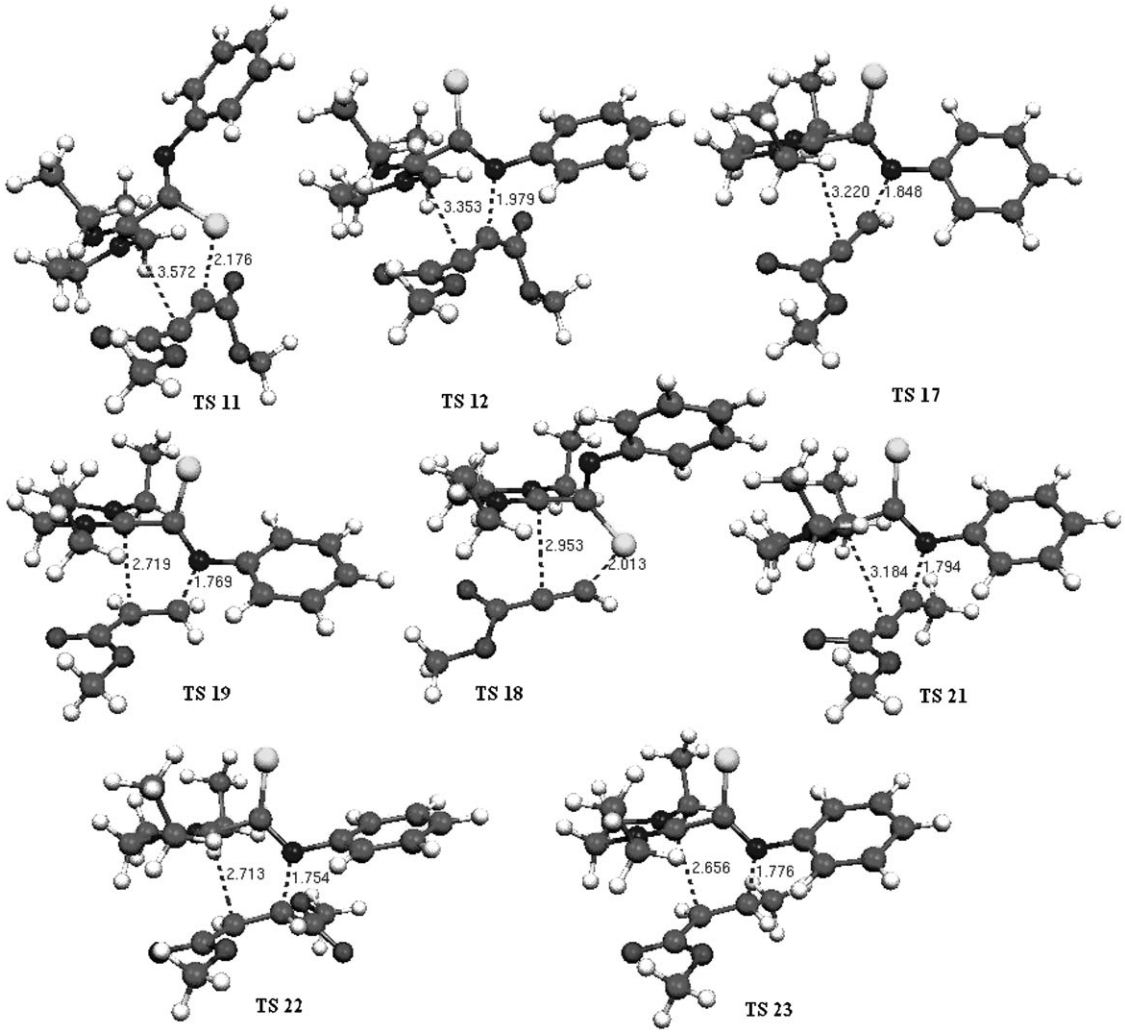


Figure 1. Optimised (B3LYP/6–31G*) transition structures (TS; bond lengths in Å) for the reactions between **7aa** and DMAD, methyl propiolate, methyl 2-butynoate, methyl acrylate, dimethyl fumarate or methyl crotonate.

Table 5. The calculated activation barriers, activation enthalpies, activation entropies and activation free energies of 1,3-dipolar cycloaddition reactions between **7aa** and different alkynes and alkenes based on the B3LYP/6–31G* method.

Entry	Reaction	$\Delta E^{\neq}$[a] (298 K) [kcal mol^{-1}]	$\Delta H^{\neq}$ (298 K) [kcal mol^{-1}]	$\Delta S^{\neq}$ (298 K) [cal mol^{-1} K^{-1}]	$\Delta G^{\neq}$ (298 K) [kcal mol^{-1}]
1	**7aa** + $MeCO_2C{\equiv}CCO_2Me$ → **11**	6.2	6.5	−49.0	21.1
2	**7aa** + $MeCO_2C{\equiv}CCO_2Me$ → **12**	6.1	6.6	−52.0	22.1
3	**7aa** + $HC{\equiv}CCO_2Me$ → **17**	8.5	9.4	−45.0	22.9
4	**7aa** + $HC{\equiv}CCO_2Me$ → **18**	12.5	12.1	−42.8	24.8
5	**7aa** + $MeC{\equiv}CCO_2Me$ → **21**	15.9	16.4	−53.1	32.2
6	**7aa** + $H_2C{=}CHCO_2Me$ → **19**	15.0	15.7	−49.7	30.5
7	**7aa** + $MeO_2CHC{=}CHCO_2Me$ → **22**	19.1	19.9	−51.4	35.0
8	**7aa** + $MeHC{=}CHCO_2Me$ → **23**	18.5	19.6	−53.9	35.4

[a] The activation barrier without zero-point energy correction.

late. On the contrary, however, the reaction of **7aa** with dimethyl fumarate has much high activation barrier, enthalpy and free energy than with methyl acrylate. The steric factors clearly counterbalance the electronic preference in these reactions.

The reactivity of ambident benzimidazolium and imidazolinium 1,3-dipoles and the site selectivity of the [3+2] cycloaddition reactions are best interpreted by both the electronic and steric effects of the dipolarophiles. When dipoles **4** or **7** were treated with strong electrophilic dipolarophiles, such as DMAD and dibenzoylacetylene, both the C-C-S and C-C-N cycloaddition pathways appear favourable as a result of the low activation free energies. However, the huge steric hindrance in the C-C-N process drove the reaction to follow the C-C-S pathway. On the other hand, the C-C-N cycloaddition reaction should be a generally preferred process in the reactions with less active dipolarophiles. If the dipolarophiles, such as ethyl propiolate, methyl

acrylate and acrylonitrile, have less steric hindrance in their approach to the C-C-N dipoles, the reaction will afford the C-C-N cycloaddition product as the major or sole product. Less reactive and sterically bulky dipolarophiles are not favoured in a C-C-N cycloaddition process, and they inhibit the 1,3-dipolar cycloaddition.

Conclusion

We have demonstrated experimentally and theoretically that the 2-aryl thiocarbamoyl benzimidazolium and imidazolinium inner salts derived from N-heterocyclic carbenes are a unique type of ambident C-C-S and C-C-N 1,3-dipolar systems. These compounds acted predominately as C-C-S dipoles in cycloaddition reactions with alkynes bearing two electron-withdrawing groups to furnish spiro(imidazole-2,3′-thiophene) compounds in excellent yields. When treated with alkynes and alkenes substituted with one electron-withdrawing group, they behaved as a C-C-N 1,3-dipolar component to produce good yields of spiro(imidazole-2,3′-pyrrole) derivatives as products. Both the C-C-S and C-C-N 1,3-dipolar cycloaddition reactions proceeded through an asynchronous concerted mechanism. This study has revealed the regularity of the reactivity of an ambident bis(1,3-dipolar) system and the site selectivity in [3+2] cycloaddition reactions. The site selectivity of the cycloaddition reactions was predictably controlled by both the electronic and steric effects of the dipolarophiles. The applications of these ambident 1,3-dipolar systems in cycloaddition reactions provide very simple synthetic approaches to complex cyclic systems, which are not easily prepared by other synthetic methods.

Experimental Section

The melting points are uncorrected. Column chromatography was performed on 200–300-mesh silica gel. The experimental procedure for preparation of 2-aryl thiocarbamoyl benzimidazolium inner salts **4** and imidazolinium inner salts **7**, full characterisation of **4** and **7** and the computational calculated data are given in the Supporting Information.

General procedure for the reaction of 4 and 7 with DMAD or dibenzoylacetylene: A solution of DMAD or dibenzoylacetylene (1 mmol) in 1,2-dichloroethane (10 mL) was added dropwise to a solution of benzimidazolium salt **4** (1 mmol) or imidazolinium salt **7** (1 mmol) in 1,2-dichloroethane (20 mL) at ambient temperature (20–30 °C). The reaction mixture was then stirred at room temperature for 0.5 h. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether (30–60 °C)/ethyl acetate (5:1) as the eulant to afford **9** and **10**, **11** and **12**, and **13** or **14**, respectively.

Dimethyl 1,3-dibutyl-2′-phenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-dicarboxylate (9ba): 90% yield; m.p. 70–71 °C, IR (KBr): $\tilde{\nu}$ = 1740, 1720, 1644, 1593, 1501 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.21 (t, ^3J(H,H) = 7.8 Hz, 2H), 7.14 (d, ^3J(H,H) = 7.6 Hz, 2H), 7.02 (t, ^3J(H,H) = 7.3 Hz, 1H), 6.89 (dd, ^3J(H,H) = 5.2 and 3.1 Hz, 2H), 6.51 (dd, ^3J(H,H) = 5.1 and 3.2 Hz, 2H), 3.39–3.49 (m, 4H), 3.43 (s, 3H), 3.30 (s, 3H), 1.79–1.93 (m, 4H), 1.36–1.41 (m, 4H), 0.93 ppm (t, ^3J(H,H) = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 163.8, 161.6, 150.9, 139.6, 132.4, 131.5, 129.3, 125.9, 119.3, 118.2, 112.8, 103.3, 53.4, 52.6, 45.1, 31.2, 20.6, 14.0 ppm; MS (MALDI-TOF): *m*/*z* (%): 506 [*M*−1]/507 [*M*$^+$]/508 [*M*+1]; elemental analysis calcd (%) for $C_{28}H_{33}N_3O_4S$: C 66.25, H 6.55, N 8.28; found: C 66.32, H 6.43, N 8.20.

Dimethyl 1,3-dibutyl-1′-phenyl-2′,3′-dihydrospiro(benzimidazoline-2,3′-pyrrole)-2′-thione-4′,5′-dicarboxylate (10ba): 5% yield; m.p. 122–123 °C, IR (KBr): $\tilde{\nu}$ = 1755, 1702, 1646, 1595, 1497 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.55 (m, 3H), 7.28 (d, ^3J(H,H) = 7.3 Hz, 2H), 6.61 (dd, ^3J(H,H) = 5.4 and 3.2 Hz, 2H), 6.32 (dd, ^3J(H,H) = 5.4 and 3.2 Hz, 2H), 3.74 (s, 3H), 3.67 (s, 3H), 3.15 (qt, ^3J(H,H) = 7.3 Hz, 2H), 3.02 (qt, ^3J(H,H) = 7.2 Hz, 2H), 1.60 (qt, ^3J(H,H) = 7.4 Hz, 4H), 1.38 (m, 4H), 0.94 ppm (t, ^3J(H,H) = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.5, 161.5, 160.9, 147.1, 140.0, 135.7, 129.8, 127.4, 117.8, 113.6, 103.1, 97.6, 53.5, 52.0, 44.8, 31.0, 20.5, 14.0 ppm; MS (MALDI-TOF): *m*/*z* (%): 506 [*M*−1]; elemental analysis calcd (%) for $C_{28}H_{33}N_3O_4S$: C 66.25, H 6.55, N 8.28; found: C 66.41, H 6.85, N 8.38.

Dimethyl 1,3-dibenzyl-2′-phenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-dicarboxylate (9ca): 95% yield; m.p. 123–124 °C; IR (KBr): $\tilde{\nu}$ = 1739, 1734, 1640, 1495 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.63 (d, ^3J(H,H) = 7.4 Hz, 4H), 7.23 (t, ^3J(H,H) = 7.6 Hz, 4H), 7.11–7.18 (m, 4H), 6.98 (t, ^3J(H,H) = 7.4 Hz, 1H), 6.75 (d, ^3J(H,H) = 7.6 Hz, 2H), 6.66 (dd, ^3J(H,H) = 5.4 and 3.2 Hz, 2H), 6.32 (dd, ^3J(H,H) = 5.4 and 3.2 Hz, 2H), 4.74 (d, ^3J(H,H) = 16.2 Hz, 2H), 4.60 (d, ^3J(H,H) = 16.2 Hz, 2H), 3.42 (s, 3H), 3.30 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.4, 163.7, 161.6, 150.6, 139.5, 137.6, 134.8, 129.8, 129.1, 128.7, 128.1, 127.6, 127.3, 125.8, 119.3, 118.8, 113.5, 104.9, 53.4, 52.7, 49.1 ppm; MS (ESI): *m*/*z* (%): 576 [*M*+1]; elemental analysis calcd (%) for $C_{34}H_{29}N_3O_4S$: C 70.94, H 5.08, N 7.30; found: C 70.92, H 5.19, N 7.59.

Dimethyl 1,3-dibenzyl-2′-*para*-methoxyphenylimino-2′,3′-dihydrospiro-(benzimidazoline-2,3′-thiophene)-4′,5′-dicarboxylate (9cb): 88% yield; m.p. 134–135 °C; IR (KBr): $\tilde{\nu}$ = 1735, 1719, 1635, 1597, 1503 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, ^3J(H,H) = 7.3 Hz, 4H), 7.33 (t, ^3J(H,H) = 7.6 Hz, 4H), 7.28 (t, ^3J(H,H) = 7.2 Hz, 2H), 6.82 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.64 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.52 (d, ^3J(H,H) = 2.8 Hz, 2H), 6.11 (dd, ^3J(H,H) = 5.1, 3.1 Hz, 2H), 4.54 (d, ^3J(H,H) = 16.0 Hz, 2H), 4.38 (d, ^3J(H,H) = 16.0 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.67 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.8, 163.1, 161.7, 157.9, 143.3, 139.6, 137.6, 135.1, 129.7, 129.1, 128.1, 127.6, 127.2, 126.1, 121.4, 118.8, 114.3, 113.5, 104.8, 102.1, 55.4, 53.4, 52.7, 49.1 ppm; MS (ESI): *m*/*z* (%): 606 [*M*+1]; elemental analysis calcd (%) for $C_{35}H_{31}N_3O_5S$: C 69.40, H 5.16, N 6.94; found: C 69.41, H 5.18, N 6.85.

Dimethyl 1,3-Dibenzyl-2′-*para*-chlorophenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-dicarboxylate (9cc): 87% yield; m.p. 119–120 °C; IR (KBr): $\tilde{\nu}$ = 1739, 1721, 1636, 1598, 1496 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, ^3J(H,H) = 7.2 Hz, 4H), 7.34 (t, ^3J(H,H) = 7.0 Hz, 4H), 7.34 (t, ^3J(H,H) = 8.5 Hz, 2H), 7.21 (d, ^3J(H,H) = 8.6 Hz, 2H), 6.54 (dd, ^3J(H,H) = 5.2, 3.1 Hz, 2H), 6.41 (d, ^3J(H,H) = 8.6 Hz, 2H), 6.15 (dd, ^3J(H,H) = 5.2, 3.2 Hz, 2H), 4.58 (d, ^3J(H,H) = 16.3 Hz, 2H), 4.37 (d, ^3J(H,H) = 16.1 Hz, 2H), 3.88 (s, 3H), 3.67 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 163.6, 161.4, 148.9, 139.3, 137.5, 134.2, 131.2, 129.9, 129.2, 129.1, 128.5, 128.1, 127.6, 127.3, 126.1, 120.7, 118.9, 113.5, 104.7, 102.0, 53.5, 52.8, 50.5, 49.0 ppm; MS (ESI): *m*/*z* (%): 610 [*M*+1]; elemental analysis calcd (%) for $C_{34}H_{28}ClN_3O_4S$: C 66.93, H 4.63, N 6.89; found: C 66.91, H 4.87, N 6.93.

Dimethyl 1,3-Dibenzyl-2′-*para*-nitrophenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-dicarboxylate (9cd): 85% yield; m.p. 140–141 °C; IR (KBr): $\tilde{\nu}$ = 1745, 1703, 1648, 1601, 1587, 1519, 1497 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.50 (d, ^3J(H,H) = 6.8 Hz, 4H), 7.32–7.37 (m, 6H), 6.59 (dd, ^3J(H,H) = 5.4, 3.2 Hz, 2H), 6.33 (d, ^3J(H,H) = 8.9 Hz, 2H), 6.23 (dd, ^3J(H,H) = 5.4, 3.2 Hz, 2H), 4.65 (d, ^3J(H,H) = 16.3 Hz, 2H), 4.36 (d, ^3J(H,H) = 16.3 Hz, 2H), 3.90 (s, 3H), 3.69 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.5, 163.5, 161.0, 156.0, 145.2, 139.0, 137.5, 132.9, 130.3, 128.6, 127.7, 127.5, 125.1, 119.4, 119.1, 104.7, 102.2, 53.6, 53.0, 48.8 ppm; MS (ESI): *m*/*z* (%): 621 [*M*+1]; elemental analysis calcd (%) for $C_{34}H_{28}N_4O_6S$: C 65.80, H 4.55, N 9.03; found: C 65.90, H 4.45, N 8.89.

Dimethyl 1,3-diethyl-2′-phenylimino-2′,3′-dihydrospiro(imidazolidine-2,3′-thiophene)-4′,5′-dicarboxylate (11aa): 95% yield; m.p. 140–141 °C; IR (KBr): $\tilde{\nu}$ = 1740, 1644, 1593 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (t,

^3J(H,H) = 7.7 Hz, 2H), 7.19 (t, ^3J(H,H) = 7.4 Hz, 2H), 6.98 (d, ^3J(H,H) = 7.4 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 3.45–3.46 (m, 2H), 3.19–3.21 (m, 2H), 2.80–2.86 (m, 2H), 2.63–2.68 (m, 2H), 1.16 ppm (t, ^3J(H,H) = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.3, 164.6, 161.0, 151.2, 138.7, 131.7, 129.3, 125.4, 119.7, 98.1, 53.1, 52.6, 47.9, 43.3, 14.2 ppm; MS (EI): *m/z*: 241 (80), 300 (100), 404 [*M*+1, 45%]; elemental analysis calcd (%) for $C_{20}H_{25}N_3O_4S$: C 59.53, H 6.25, N 10.41; found: C 59.54, H 6.55, N 10.37.

Dimethyl 1,3-dibenzyl-2′-phenylimino-2′,3′-dihydrospiro(imidazolidine-2,3′-thiophene)-4′,5′-dicarboxylate (11da): 92% yield; m.p. 177°C (decomp); IR (KBr): $\tilde{\nu}$ = 1737, 1725, 1640 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.49 (m, 6H), 7.35 (t, ^3J(H,H) = 7.3 Hz, 4H), 7.26–7.29 (m, 3H), 7.14 (d, ^3J(H,H) = 7.5 Hz, 2H), 4.16 (d, ^3J(H,H) = 12.7 Hz, 2H), 3.99 (s, 3H), 3.85 (s, 3H), 3.69 (d, ^3J(H,H) = 12.7 Hz, 2H), 3.20–3.21 (m, 2H), 3.11–3.12 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 164.6, 161.0, 151.0, 138.6, 137.6, 133.4, 129.5, 128.7, 128.2, 127.1, 125.8, 119.9, 97.8, 53.5, 53.2, 52.6, 48.3 ppm; MS (ESI): *m/z* (%): 528 [*M*+1]; elemental analysis calcd (%) for $C_{30}H_{29}N_3O_4S$: C 68.29, H 5.54, N 7.96; found: C 68.00, H 5.90, N 7.86.

Dimethyl 1,3-dibenzyl-1′-phenyl-2′,3′-dihydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione-4′,5′-dicarboxylate (12da): 3% yield; m.p. 147–148°C; IR (KBr): $\tilde{\nu}$ = 1751, 1724, 1639, 1495 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.60 (d, ^3J(H,H) = 7.4 Hz, 4H), 7.31 (t, ^3J(H,H) = 7.4 Hz, 4H), 7.22 (t, ^3J(H,H) = 7.3 Hz, 2H), 7.12–7.16 (m, 4H), 7.06–7.09 (m, 1H), 4.23 (d, ^3J(H,H) = 13.2 Hz, 2H), 4.06 (d, ^3J(H,H) = 13.2 Hz, 2H), 3.64 (s, 3H), 3.53–3.55 (m, 2H), 3.25–3.27 (m, 2H), 3.25 ppm (s, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ = 209.2, 161.8, 160.5, 147.0, 139.1, 136.7, 129.1, 129.0, 128.9,128.4, 127.2, 116.5, 95.1, 53.5, 52.2, 51.3, 47.9 ppm; MS (ESI): *m/z* (%): 528 [*M*+1]; elemental analysis calcd (%) for $C_{30}H_{29}N_3O_4S$: C 68.29, H 5.54, N 7.96; found: C 68.21, H 5.62, N 7.99.

1,3-Dibutyl-2′-phenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13ba): 89% yield; m.p. 117–118°C; IR (KBr): $\tilde{\nu}$ = 1652, 1594, 1507 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.48 (m, 8H), 7.21–7.27 (m, 3H), 7.18 (t, ^3J(H,H) = 7.4 Hz, 2H), 7.05 (d, ^3J(H,H) = 7.5 Hz, 2H), 6.58 (dd, ^3J(H,H) = 5.0, 3.1 Hz, 2H), 6.31 (dd, ^3J(H,H) = 5.2, 3.2 Hz, 2H), 3.43–3.49 (m, 2H), 3.31–3.37 (m, 2H), 1.79 (qt, ^3J(H,H) = 7.5 Hz, 4H), 1.42–1.51 (m, 4H), 0.99 ppm (t, ^3J(H,H) = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.1, 190.4, 166.7, 151.0, 142.2, 139.6, 138.1, 136.1, 134.0, 133.7, 133.0, 129.4, 128.7, 128.6, 128.2, 125.9, 119.5, 118.0, 104.4, 103.1, 45.5, 31.0, 20.8, 14.0 ppm; MS (ESI): *m/z* (%): 600 [M+1], 638 [*M*+K]$^+$; elemental analysis calcd (%) for $C_{38}H_{37}N_3O_2S$: C 76.10, H 6.22, N 7.01; found: C 76.03, H 6.21, N 7.04.

1,3-Dibenzyl-2′-phenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13ca): 92% yield; m.p. 135–136°C; IR (KBr): $\tilde{\nu}$ = 1648, 1596, 1501 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, ^3J(H,H) = 7.1 Hz, 4H), 7.45 (t, ^3J(H,H) = 7.3 Hz, 1H), 7.34 (t, ^3J(H,H) = 6.8 Hz, 4H), 7.24–7.31 (m, 9H), 7.18–7.21 (m, 3H), 7.04 (t, ^3J(H,H) = 7.9 Hz, 2H), 6.78 (d, ^3J(H,H) = 7.5 Hz, 2H), 6.51 (dd, ^3J(H,H) = 5.2, 3.1 Hz, 2H), 6.11 (dd, ^3J(H,H) = 5.2, 3.2 Hz, 2H), 4.77 (d, ^3J(H,H) = 16.3 Hz, 2H), 4.71 ppm (d, ^3J(H,H) = 16.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.7, 190.5, 165.7, 150.8, 144.1, 139.7, 138.2, 137.4, 135.9, 134.1, 132.9, 129.3, 128.7, 128.6 (d), 128.2, 127.4, 127.3, 125.9, 119.5, 118.7, 104.5, 104.1, 49.7 ppm; MS (ESI): *m/z* (%): 668 [*M*+1], 706 [*M*+K]$^+$; elemental analysis calcd (%) for $C_{44}H_{33}N_3O_2S$: C 79.14, H 4.98, N 6.29; found: C 78.80, H 5.29, N 6.30.

1,3-Dibenzyl-2′-*para*-methoxyphenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13cb): 92% yield; m.p. 148–149°C; IR (KBr): $\tilde{\nu}$ = 1648, 1597, 1579, 1502 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, ^3J(H,H) = 7.2 Hz, 4H), 7.45 (t, ^3J(H,H) = 7.4 Hz, 1H), 7.35 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.20–7.29 (m, 11H), 7.03 (t, ^3J(H,H) = 7.8 Hz, 2H), 6.88 (d, ^3J(H,H) = 8.9 Hz, 2H), 6.81 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.50 (brs, 2H), 6.10 (dd, ^3J(H,H) = 5.1, 3.2 Hz, 2H), 4.75 (d, ^3J(H,H) = 16.3 Hz, 2H), 4.68 (d, ^3J(H,H) = 16.3 Hz, 2H), 3.83 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.8, 190.6, 163.2, 157.9, 144.3, 143.5, 139.8, 138.3, 137.5, 136.0, 134.0, 132.8, 128.7, 128.60, 128.57, 128.49, 128.1, 127.4, 127.2, 121.6, 118.6, 114.3, 104.4, 104.3, 55.5, 49.7 ppm; MS (ESI): *m/z* (%): 698 [*M*+1]; elemental analysis calcd (%) for $C_{45}H_{35}N_3O_3S$: C 77.45, H 5.06, N 6.02; found: C 77.16, H 5.32, N 5.96.

1,3-Dibenzyl-2′-*para*-chlorophenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13cc): 90% yield; m.p. 136–137°C; IR (KBr): $\tilde{\nu}$ = 1650, 1641, 1597, 1580, 1497 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, ^3J(H,H) = 7.0 Hz, 4H), 7.47 (t, ^3J(H,H) = 7.5 Hz, 1H), 7.36 (d, ^3J(H,H) = 7.0 Hz, 2H), 7.25–7.33 (m, 11H), 7.22 (t, ^3J(H,H) = 8.0 Hz, 2H), 7.05 (t, ^3J(H,H) = 7.5 Hz, 2H), 6.62 (d, ^3J(H,H) = 8.5 Hz, 2H), 6.53 (brs, 2H), 6.13 (dd, ^3J(H,H) = 5.0, 3.0 Hz, 2H), 4.77 (d, ^3J(H,H) = 16.0 Hz, 2H), 4.67 ppm (d, ^3J(H,H) = 16.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.5, 190.4, 166.8, 149.1, 143.5, 139.6, 138.1, 137.4, 135.9, 134.1, 133.0, 131.3, 129.3, 128.7, 128.5, 128.2, 127.4, 127.3, 121.0, 118.7, 104.4, 49.5 ppm; MS (ESI): *m/z* (%): 702 [*M*+1]; elemental analysis calcd (%) for $C_{44}H_{32}ClN_3O_2S$: C 75.25, H 4.59, N 5.98; found: C 75.10, H 4.86, N 5.94.

1,3-Dibenzyl-2′-*para*-nitrophenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13cd): 91% yield; m.p. 138–139°C; IR (KBr): $\tilde{\nu}$ = 1650, 1597, 1585, 1500 cm^{-1}; ^{1}H MNR (500 MHz, $CDCl_3$): δ = 8.16 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.50 (d, ^3J(H,H) = 6.8 Hz, 4H), 7.48 (t, ^3J(H,H) = 7.6 Hz, 1H), 7.38 (d, ^3J(H,H) = 7.7 Hz, 2H), 7.34 (t, ^3J(H,H) = 7.4 Hz, 1H), 7.29–7.31 (m, 8H), 7.24 (t, ^3J(H,H) = 7.5 Hz, 2H), 7.08 (t, ^3J(H,H) = 7.5 Hz, 2H), 6.57 (d, ^3J(H,H) = 8.3 Hz, 4H), 6.19 (d, ^3J(H,H) = 3.4 Hz, 2H), 4.82 (d, ^3J(H,H) = 16.4 Hz, 2H), 4.66 ppm (d, ^3J(H,H) = 16.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.2 (2 C=O), 169.6, 156.2, 145.2, 142.5, 139.3, 137.9, 137.3, 135.8, 134.3, 133.2, 128.7, 128.6, 128.5, 128.3, 127.5, 127.4, 125.2, 119.7, 118.9, 104.5, 49.4 ppm; MS (ESI): *m/z* (%): 713 [*M*+1]; elemental analysis calcd (%) for $C_{44}H_{32}N_4O_4S$: C 74.14, H 4.53, N 7.86; found: C 74.15, H 4.66, N 7.72.

1-Butyl-3-ethyl-2′-phenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13da): 91% yield; m.p. 116–117°C; IR (KBr): $\tilde{\nu}$ = 1655, 1644, 1595, 1503 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.49 (m, 8H), 7.21–7.27 (m, 3H), 7.18 (t, ^3J(H,H) = 7.6 Hz, 2H), 7.04 (d, ^3J(H,H) = 7.6 Hz, 2H), 6.57–6.59 (m, 2H), 6.30–6.34 (m, 2H), 3.51–3.57 (m, 1H), 3.42–3.49 (m, 2H), 3.36–3.40 (m, 1H), 1.81 (qt, ^3J(H,H) = 7.5 Hz, 2H), 1.46–1.51 (m, 2H), 1.39 (t, ^3J(H,H) = 7.2 Hz, 3H), 1.00 ppm (t, ^3J(H,H) = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.1, 190.5, 166.7, 151.0, 141.9, 139.7, 139.0, 138.1, 136.1, 134.0, 133.8, 133.0, 129.4, 128.7, 128.6 (d), 128.3, 125.9, 119.5, 118.0 (d), 104.2, 103.1, 103.0, 45.5, 39.6, 31.0, 20.8, 14.1, 14.0 ppm; MS (ESI): *m/z* (%): 572 [*M*+1]; elemental analysis calcd (%) for $C_{36}H_{33}N_3O_2S$: C 75.63, H 5.82, N 7.35; found: C 75.50, H 6.14, N 7.46.

1-Benzyl-3-ethyl-2′-phenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13fa): 88% yield; m.p. 132–133°C; IR (KBr): $\tilde{\nu}$ = 1655, 1595, 1502 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.50 (m, 3H), 7.36–7.41 (m, 7H), 7.20–7.27 (m, 6H), 7.12 (t, ^3J(H,H) = 7.4 Hz, 2H), 6.89 (d, ^3J(H,H) = 7.4 Hz, 2H), 6.61 (t, ^3J(H,H) = 7.3 Hz, 1H), 6.48 (t, ^3J(H,H) = 7.3 Hz, 1H), 6.36 (d, ^3J(H,H) = 7.3 Hz, 1H), 6.07 (d, ^3J(H,H) = 7.3 Hz, 1H), 4.79 (d, ^3J(H,H) = 16.3 Hz, 1H), 4.65 (d, ^3J(H,H) = 16.3 Hz, 1H), 3.57–3.59 (m, 1H), 3.48–3.52 (m, 1H), 1.44 ppm (t, ^3J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.8, 190.5, 166.2, 150.9, 142.7, 139.6, 139.3, 138.1, 137.5, 136.0, 134.0, 133.4, 132.9, 129.3, 128.7, 128.6, 128.5, 128.2, 127.3, 127.2, 125.9, 119.4, 118.7, 117.9, 104.5, 104.1, 103.0, 49.4, 39.8, 14.1 ppm; MS (ESI): *m/z* (%): 606 [*M*+1]; elemental analysis calcd (%) for $C_{39}H_{31}N_3O_2S$: C 77.33, H 5.16, N 6.94; found: C 77.35, H 5.40, N 6.84.

1-Benzyl-3-butyl-2′-phenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′,5′-diylbisphenylmethanone (13ga): 87% yield; m.p. 129–130°C; IR (KBr): $\tilde{\nu}$ = 1648, 1596, 1501 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, ^3J(H,H) = 6.8 Hz, 2H), 7.45 (d, ^3J(H,H) = 7.5 Hz, 1H), 7.33–7.40 (m, 7H), 7.19–7.28 (m, 6H), 7.11 (t, ^3J(H,H) = 7.7 Hz, 2H), 6.89 (d, ^3J(H,H) = 7.6 Hz, 2H), 6.61 (t, ^3J(H,H) = 7.5 Hz, 1H), 6.48 (t, ^3J(H,H) = 7.5 Hz, 1H), 6.36 (d, ^3J(H,H) = 7.4 Hz, 1H), 6.05 (d, ^3J(H,H) = 7.3 Hz, 1H), 4.75 (d, ^3J(H,H) = 16.3 Hz, 1H), 4.64 (d, ^3J(H,H) = 16.3 Hz, 1H), 3.46–3.52 (m, 1H), 3.38–3.43 (m, 1H), 1.84 (qt, ^3J(H,H) = 7.7 Hz, 2H), 1.47–1.53 (m, 2H), 1.00 ppm (t, ^3J(H,H) = 7.4 Hz, 3, H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.9, 190.4, 166.3, 150.9, 143.1, 139.9, 139.5, 138.2, 137.5, 136.0, 134.0, 133.4, 133.0, 129.3, 128.7, 128.6, 128.5, 128.2, 127.3, 127.2, 125.9, 119.5, 118.8, 118.0, 104.5, 104.2, 103.2, 49.5, 45.7, 31.0, 20.8, 14.0 ppm; MS (ESI): *m/z* (%): 634 [*M*+1], 672 [*M*+K]$^+$; elemental

analysis calcd (%) for $C_{41}H_{35}N_3O_2S$: C 77.70, H 5.57, N 6.63; found: C 77.64, H 5.83, N 6.75.

1,3-Dibenzyl-2′-phenylimino-2′,3′-dihydrospiro(imidazolidine-2,3′-thiophene)-4′,5′- diylbisphenylmethanone (14da): 93% yield; m.p. 139–140°C; IR (KBr): $\tilde{\nu}$ = 1653, 1595, 1578, 1485 cm^{-1}, 1447; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.51 (d, ^3J(H,H) = 7.1 Hz, 2H), 7.48 (d, ^3J(H,H) = 7.6 Hz, 2H), 7.39 (t, ^3J(H,H) = 7.3 Hz, 1H), 7.35 (d, ^3J(H,H) = 6.5 Hz, 4H), 7.17–7.28 (m, 14H), 4.46 (d, ^3J-(H,H) = 13.3 Hz, 2H), 4.08 (d, ^3J(H,H) = 13.3 Hz, 2H), 3.22 (brs, 2H), 3.14 ppm (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.1, 190.6, 167.8, 151.4, 142.6, 139.4, 138.6, 138.4, 136.2, 133.8, 133.0, 129.5, 129.0, 128.9, 128.5, 128.3, 128.2, 127.1, 125.7, 119.9, 99.9, 53.9, 48.6 ppm; MS (ESI): *m*/*z* (%): 620 [*M*+1]; elemental analysis calcd (%) for $C_{40}H_{33}N_3O_2S$: C 77.52, H 5.37, N 6.78; found: C 77.03, H 5.74, N 6.49.

1,3-Di(*para*-methoxy)benzyl-2′-phenylimino-2′,3′-dihydrospiro(imidazolidine-2,3′-thiophene)-4′,5′- diylbisphenylmethanone (14ea): 86% yield; m.p. 143–144°C; IR (KBr): $\tilde{\nu}$ = 1698, 1634, 1596, 1544, 1499, 1469 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.47–7.52 (m, 5H), 7.41 (t, ^3J(H,H) = 7.3 Hz, 1H), 9.19–7.29 (m, 11H), 6.78 (d, ^3J-(H,H) = 8.4 Hz, 4H), 4.39 (d, ^3J(H,H) = 13.0 Hz, 2H), 3.98 (d, ^3J(H,H) = 13.0 Hz, 2H), 3.79 (s, 3H), 3.16 (brs, 2H), 3.08 (brs, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.0, 190.6, 167.8, 158.7, 151.4, 142.4, 139.5, 138.4, 136.2, 133.8, 133.0, 130.8, 129.6, 129.4, 129.3, 129.0, 128.9, 128.5, 128.3, 125.6, 119.9, 113.6, 99.8, 55.2, 53.2, 48.4 ppm; MS (ESI): *m*/*z* (%): 680 [*M*+1]; elemental analysis calcd (%) for $C_{42}H_{37}N_3O_4S$: C 74.20, H 5.49, N 6.18; found: C 74.14, H 5.93, N 6.14.

1,3-Diphenyl-2′-*para*-nitrophenylimino-2′,3′-dihydrospiro(imidazolidine-2,3′-thiophene)-4′,5′- diylbisphenylmethanone (14gd): 94% yield; m.p. 172–173°C; IR (KBr): $\tilde{\nu}$ = 1657, 1596, 1586, 1519, 1496 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.42 (t, ^3J(H,H) = 7.5 Hz, 4H), 7.34 (t, ^3J(H,H) = 7.4 Hz, 1H), 7.26 (t, ^3J(H,H) = 7.3 Hz, 1H), 7.16 (d, ^3J(H,H) = 8.0 Hz, 4H), 7.03–7.06 (m, 4H), 7.01 (d, ^3J(H,H) = 7.9 Hz, 2H), 6.98 (d, ^3J(H,H) = 8.1 Hz, 2H), 6.80 (d, ^3J(H,H) = 8.1 Hz, 2H), 6.74 (d, ^3J(H,H) = 7.5 Hz, 2H), 4.16 (brs, 2H), 3.94 ppm (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.2, 190.1, 173.1, 156.7, 145.8, 145.2, 144.6, 139.2, 137.2, 136.1, 133.8, 132.6, 129.4, 128.54, 128.49, 128.2, 128.1, 125.4, 120.9, 119.4, 117.0, 96.4, 47.2 ppm; MS (ESI): *m*/*z* (%): 637 [*M*+1]; elemental analysis calcd (%) for $C_{38}H_{28}N_4O_4S$: C 71.68, H 4.43, N 8.80; found: C 71.60, H 4.58, N 8.68.

General procedure for the reaction of 2-thiocarbamoyl benzimidazolium 4 or imidazolinium inner salts 7 with ethyl propiolate: Ethyl propiolate (5 mmol) was mixed with benzimidazolium salts **4** (1 mmol) or imidazolinium salts **7** (1 mmol) in 1,2-dichloroethane or THF (20 mL) at ambient temperature. The reaction mixture was stirred at reflux for a period of time. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether (30–60°C)/ethyl acetate (5:1) as the eulant. The green-crystalline products **15** and red by-products **16** or orange-crystalline products **17** and colourless crystalline by-products **18** were isolated.

Ethyl 1,3-dibenzyl-1′-*para*-methoxyphenyl-2′,3′-dihydrospiro(benzimidazoline-2,3′-pyrrole)-2′-thione-4′-carboxylate (15cb): 81% yield; m.p. 169–170°C; IR (KBr): $\tilde{\nu}$ = 1711, 1698, 1626, 1601, 1510, 1495 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.47 (s, 1H), 7.43 (d, ^3J(H,H) = 6.3 Hz, 4H), 7.29–7.31 (m, 6H), 7.17 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.97 (d, ^3J-(H,H) = 8.2 Hz, 2H), 6.53 (brs, 2H), 6.14 (brs, 2H), 4.31 (d, ^3J(H,H) = 15.5 Hz, 2H), 4.14–4.20 (m, 4H), 3.85 (s, 3H), 1.13 ppm (t, ^3J(H,H) = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 204.8, 161.4, 159.4, 145.9, 140.5, 137.5, 130.3, 128.3, 127.9, 127.3, 126.3, 118.4, 117.1, 114.6, 104.9, 98.2, 60.4, 55.6, 49.3, 14.0 ppm; MS (ESI): *m*/*z* (%): 562 [*M*+1]; elemental analysis calcd (%) for $C_{34}H_{31}N_3O_3S$: C 72.70, H 5.56, N 7.48; found: C 72.60, H 5.71, N 7.39.

Ethyl 1,3-dibenzyl-2′-*para*-methoxyphenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′-carboxylate (16cb): 10% yield; m.p. 156–157°C; IR (KBr): $\tilde{\nu}$ = 1687, 1642, 1584, 1504 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 8.46 (d, ^3J(H,H) = 7.2 Hz, 4H), 7.26–7.33 (m, 6H), 6.83 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.64 (d, ^3J(H,H) = 8.7 Hz, 2H), 6.54 (dd, ^3J(H,H) = 5.1, 3.2 Hz, 2H), 6.15 (dd, ^3J(H,H) = 5.1, 3.2 Hz, 2H), 4.37 (d, ^3J(H,H) = 16.2 Hz, 2H), 4.31 (d, ^3J(H,H) = 16.2 Hz, 2H), 4.12 (q, ^3J-(H,H) = 7.1 Hz, 2H), 3.81 (s, 3H), 1.03 ppm (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 161.3, 157.6, 143.6, 140.7, 140.1, 138.1, 129.1, 128.4, 127.9, 127.5, 127.1, 125.8, 124.3, 121.2, 118.2, 114.2, 113.4, 103.7, 97.4, 60.8, 55.4, 48.8, 13.7 ppm; MS (ESI): *m*/*z* (%): 562 [*M*+1]; elemental analysis calcd (%) for $C_{34}H_{31}N_3O_3S$: C 72.70, H 5.56, N 7.48; found: C 72.31, H 5.82, N 7.47.

Ethyl 1,3-dibenzyl-1′-*para*-chlorophenyl-2′,3′-dihydrospiro(benzimidazoline-2,3′-pyrrole)-2′-thione-4′-carboxylate (15cc): 81% yield; m.p. 168–169°C; IR (KBr): $\tilde{\nu}$ = 1689, 1625, 1603, 1494 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.47 (s, 1H), 7.43 (d, ^3J(H,H) = 8.6 Hz, 2H), 7.40 (d, ^3J-(H,H) = 7.1 Hz, 4H), 7.26–7.31 (m, 6H), 7.18 (d, ^3J(H,H) = 8.5 Hz, 4H), 6.55 (brs, 2H), 6.16–6.18 (m, 2H), 4.29 (d, ^3J(H,H) = 15.7 Hz, 2H), 4.20 (d, ^3J(H,H) = 15.7 Hz, 2H), 4.16 (q, ^3J(H,H) = 7.1 Hz, 2H), 1.13 ppm (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.0, 161.3, 144.8, 140.3, 137.3, 135.8, 134.3, 129.6, 128.4, 128.0, 127.4, 126.2, 118.5, 117.6, 104.9, 98.2, 60.5, 49.2, 14.0 ppm; MS (ESI): *m*/*z* (%): 566 [*M*+1]; elemental analysis calcd (%) for $C_{33}H_{28}ClN_3O_2S$: C 70.01, H 4.99, N 7.42; found: 69.80, H 5.27, N 7.31.

Ethyl 1,3-dibenzyl-2′-*para*-chlorophenylimino-2′,3′-dihydrospiro(benzimidazoline-2,3′-thiophene)-4′-carboxylate (16cc): 5% yield; m.p. 153–154°C; IR (KBr): $\tilde{\nu}$ = 1685, 1642, 1597, 1584, 1508 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 8.45 (d, ^3J(H,H) = 7.1 Hz, 4H), 7.27–7.33 (m, 6H), 7.23 (d, ^3J(H,H) = 8.4 Hz, 2H), 6.56 (brs, 2H), 6.43 (d, ^3J-(H,H) = 8.3 Hz, 2H), 6.18–6.20 (m, 2H), 4.40 (d, ^3J(H,H) = 16.2 Hz, 2H), 4.31 (d, ^3J(H,H) = 16.2 Hz, 2H), 4.12 (q, ^3J(H,H) = 7.1 Hz, 2H), 1.02 ppm (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 161.2, 149.1, 140.0, 139.9, 138.0, 131.0, 129.2, 128.5, 127.6, 127.2, 124.5, 120.7, 118.4, 103.7, 97.4, 60.9, 48.7, 13.7 ppm; MS (ESI): *m*/*z* (%): 566 [*M*+1]; elemental analysis calcd (%) for $C_{33}H_{28}ClN_3O_2S$: C 70.01, H 4.99, N 7.42; found: 69.91, H 5.21, N 7.39.

Ethyl 1,3-dibenzyl-1′-*para*-nitrophenyl-2′,3′-dihydrospiro(benzimidazoline-2,3′-pyrrole)-2′-thione-4′-carboxylate (15 cd): 48% yield; m.p. 167–168°C; IR (KBr): $\tilde{\nu}$ = 1697, 1636, 1595, 1525, 1494 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.52 (s, 1H), 7.44 (d, ^3J(H,H) = 9.0 Hz, 2H), 7.38 (d, ^3J(H,H) = 5.5 Hz, 4H), 7.26–7.30 (m, 6H), 6.59–6.60 (m, 2H), 6.21–6.23 (m, 2H), 4.28 (d, ^3J(H,H) = 16.2 Hz, 2H), 4.25 (d, ^3J(H,H) = 17.6 Hz, 2H), 4.17 (q, ^3J(H,H) = 7.1 Hz, 2H), 1.13 (t, ^3J(H,H) = 7.1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.3, 161.1, 146.6, 143.5, 142.4, 140.1, 137.1, 128.4, 128.1, 127.5, 125.2, 124.8, 118.7, 118.2, 104.9, 98.3, 60.8, 49.2, 13.9 ppm; MS (ESI): *m*/*z* (%): 577 [M+1]; elemental analysis calcd (%) for $C_{33}H_{28}N_4O_4S$: C 68.73, H 4.89, N 9.72; found C 68.74, H 5.10, N 9.58.

Ethyl 1,3-dibenzyl-1′-phenyl-2′,3′-dihydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione-4′-carboxylate (17da): 73% yield; m.p. 134–135°C; IR (KBr): $\tilde{\nu}$ = 1692, 1628, 1589 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.48 (s, 1H), 7.48 (t, ^3J(H,H) = 8.2 Hz, 2H), 7.37–7.41 (m, 6H), 7.28–7.30 (m, 5H), 7.24 (d, ^3J(H,H) = 7.1 Hz, 2H), 4.36 (q, ^3J(H,H) = 7.1 Hz, 2H), 3.84 (d, ^3J(H,H) = 13.6 Hz, 2H), 3.78 (d, ^3J(H,H) = 13.6 Hz, 2H), 3.42–3.45 (m, 2H), 3.23–3.26 (m, 2H), 1.41 ppm (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, C6D6): δ = 209.7, 161.4, 145.4, 139.6, 138.1, 128.9, 128.8, 128.3, 128.0, 127.0, 125.3, 118.0, 95.2, 59.7, 53.4, 48.2, 14.4 ppm; MS (ESI): *m*/*z* (%): 484 [*M*+1]; elemental analysis calcd (%) for $C_{29}H_{29}N_3O_2S$: C 72.02, H 6.04, N 8.69; found: C 72.10, H 6.11, N 8.71.

Ethyl 1,3-dibenzyl-2′-phenylimino-2′,3′-dihydrospiro(imidazolidine-2,3′-thiophene)-4′-carboxylate (18da): 15% yield; m.p. 102–103°C; IR (KBr): $\tilde{\nu}$ = 3057, 1696, 1640, 1582 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.78 (s, 1H), 7.41–7.45 (m, 6H), 7.32 (t, ^3J(H,H) = 7.2 Hz, 4H), 7.24–7.27 (m, 3H), 7.08 (d, ^3J(H,H) = 7.6 Hz, 2H), 4.37 (q, ^3J(H,H) = 7.1 Hz, 2H), 3.94 (d, ^3J(H,H) = 13.6 Hz, 2H), 3.80 (d, ^3J(H,H) = 13.4 Hz, 2H), 3.29 (brs, 4H), 1.42 ppm (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 161.7, 151.4, 140.7, 139.4, 129.3, 128.4, 128.2, 127.5, 126.9, 125.4, 119.8, 93.1, 60.4, 53.4, 48.9, 14.5 ppm; MS (ESI): *m*/*z* (%): 484 [*M*+1]; elemental analysis calcd (%) for $C_{29}H_{29}N_3O_2S$: C 72.02, H 6.04, N 8.69; found: C 72.00, H 6.00, N 8.62.

Ethyl 1,3-di(*para*-methoxy)benzyl-1′-phenyl-2′,3′-dihydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione-4′-carboxylate (17ea): 71% yield; m.p. 116–117°C; IR (KBr): $\tilde{\nu}$ = 1717, 1616, 1512 cm^{-1}; ^1H NMR (500 MHz, C_6D_6): δ = 7.54 (d, ^3J(H,H) = 8.4 Hz, 4H), 7.26 (s, 1H), 7.06–7.14 (m, 5H), 6.92

(d, ^3J(H,H) = 8.4 Hz, 4H), 4.36 (q, ^3J(H,H) = 7.1 Hz, 2H), 4.03 (d, ^3J-(H,H) = 13.2 Hz, 2H), 3.99 (d, ^3J(H,H) = 13.2 Hz, 2H), 3.65 (brs, 2H), 3.42 (s, 8H), 1.27 ppm (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ = 209.9, 161.5, 159.2, 145.3, 138.2, 131.5, 130.0, 128.9, 127.7, 125.4, 118.2, 113.8, 95.1, 59.7, 54.6, 52.9, 48.3, 14.5 ppm; MS (ESI): *m*/*z* (%): 544 [*M*+1]; elemental analysis calcd (%) for $C_{31}H_{33}N_3O_4S$: C 68.48, H 6.12, N 7.73; found: C 68.66, H 6.53, N 8.12.

Ethyl 1,3-di(*para*-methoxy)benzyl-2′-phenylimino-2′,3′-dihydrospiro(imidazolidine-2,3′-thiophene)-4′-carboxylate (18ea): 15% yield; m.p. 119–120 °C; IR (KBr): $\tilde{\nu}$ = 1726, 1634, 1610, 1579 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.44 (t, ^3J(H,H) = 7.7 Hz, 2H), 7.30 (d, ^3J-(H,H) = 8.3 Hz, 4H), 7.24 (t, ^3J(H,H) = 7.3 Hz, 1H), 7.07 (d, ^3J(H,H) = 7.5 Hz, 2H), 6.85 (d, ^3J(H,H) = 8.4 Hz, 4H), 4.35 (q, ^3J(H,H) = 7.0 Hz, 2H), 3.86 (d, ^3J(H,H) = 13.3 Hz, 2H), 3.82 (s, 6H), 3.72 (d, ^3J(H,H) = 13.2 Hz, 2H), 3.24 (brs, 4H), 1.41 ppm (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 161.7, 158.7, 151.4, 140.4, 140.4, 131.5, 129.5, 129.3, 125.3, 119.8, 113.6, 92.9, 60.4, 55.3, 52.7, 48.8, 14.5 ppm; MS (ESI): *m*/*z* (%): 544 [*M*+1]; elemental analysis calcd (%) for $C_{31}H_{33}N_3O_4S$: C 68.48, H 6.12, N 7.73; found: C 68.23, H 6.24, N 7.69.

General procedure for the reaction of 2-thiocarbamoyl benzimidazolium 4 or imidazolinium inner salts 7 with methyl acrylate or acrylonitrile: Imidazolinium salt **7** (100 mg) was mixed with redistilled methyl acrylate (2 mL) or acrylonitrile (2 mL) in solution with triethylamine (1 mL) and $CHCl_3$ (10 mL) at ambient temperature. The reaction mixture was heated to reflux for a period of time. The pale yellow crystalline products **19** or **20** were isolated from the reaction by chromatography on silica gel with petroleum ether (60–90 °C)/ethyl acetate (5:1) as the eluant.

Methyl 1,3-dibenzyl-1′-phenyl-2′,3′,4′,5′-tetrahydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione-4′-carboxylate (19da): 83% yield; m.p. 157–158 °C; IR (KBr): $\tilde{\nu}$ = 1726, 1497, 1440 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.52–7.53 (m, 4H), 7.37–7.41 (m, 5H), 7.33 (t, ^3J(H,H) = 7.6 Hz, 2H), 7.22–7.29 (m, 2H), 4.67 (dd, ^3J(H,H) = 11.7, 9.2 Hz, 1H), 4.15 (s, 2H), 4.10 (d, ^3J(H,H) = 11.9 Hz, 1H), 3.99 (dd, ^3J(H,H) = 11.7, 9.6 Hz, 1H), 3.79 (t, ^3J(H,H) = 9.3 Hz, 1H), 3.70 (d, ^3J-(H,H) = 11.9 Hz, 1H), 3.29–3.31 (m, 1H), 3.14–3.19 (m, 2H), 2.97–2.99 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.9, 170.2, 140.6, 139.5, 138.5, 129.5, 128.9, 128.4, 128.3, 128.20, 128.17, 127.1, 127.0, 125.3, 96.7, 55.7, 54.0, 52.7, 52.5, 49.5, 48.9, 46.6 ppm; MS (EI): 55 (100), 91 (95), 471 ([M^+], 6%); elemental analysis calcd (%) for $C_{28}H_{29}N_3O_2S$: C 71.30, H 6.20, N 8.91; found: C 71.21, H 6.32, N 8.96.

Methyl 1,3-di(*para*-methoxy)benzyl-1′-phenyl-2′,3′,4′,5′-tetrahydrospiro-(imidazolidine-2,3′-pyrrole)-2′-thione-4′-carboxylate (19ea): 88% yield; m.p. 134–135 °C; IR (KBr): $\tilde{\nu}$ = 1725, 1611, 1512, 1439 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.54 (m, 6H), 7.40–7.41 (m, 1H), 7.31 (d, ^3J-(H,H) = 8.5 Hz, 2H), 6.92 (d, ^3J(H,H) = 8.6 Hz, 2H), 6.87 (d, ^3J(H,H) = 8.6 Hz, 2H), 4.67 (dd, ^3J(H,H) = 11.6, 9.2 Hz, 1H), 4.07 (s, 2H), 3.95–4.02 (m, 2H), 3.94 (s, 3H), 3.78 (t, ^3J(H,H) = 9.3 Hz, 1H), 3.63 (d, ^3J(H,H) = 11.7 Hz, 1H), 3.25–3.29 (m, 1H), 3.10–3.14 (m, 2H), 2.90–2.94 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.0, 170.3, 158.74, 158.69, 140.6, 131.5, 130.6, 130.1, 129.5, 129.3, 128.2, 125.3, 113.7, 113.6, 96.4, 55.7, 55.3, 55.2, 53.3, 52.5, 52.0, 49.3, 48.8, 46.5 ppm; MS (ESI): *m*/*z* (%): 532 [*M*+1]; elemental analysis calcd (%) for $C_{30}H_{33}N_3O_4S$: C 67.77, H 6.26, N 7.90; found: C 67.39, H 5.98, N 7.66.

Methyl 1,3-di(*para*-methoxy)benzyl-1′-*para*-chlorophenyl-2′,3′,4′,5′-tetrahydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione-4′-carboxylate (19ec): 71% yield; m.p. 123–124 °C; IR (KBr): $\tilde{\nu}$ = 1724, 1612, 1512, 1494, 1437 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (brs, 6H), 7.29 (d, ^3J-(H,H) = 7.5 Hz, 2H), 6.91 (d, ^3J(H,H) = 8.5 Hz, 2H), 6.86 (d, ^3J(H,H) = 8.5 Hz, 2H), 4.65 (dd, ^3J(H,H) = 11.4, 9.3 Hz, 1H), 4.04 (s, 2H), 3.92–4.04 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.77 (t, ^3J(H,H) = 9.3 Hz, 1H), 3.58 (d, ^3J(H,H) = 11.6 Hz, 1H), 3.24–3.25 (m, 1H), 3.08–3.13 (m, 2H), 2.89–2.92 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 170.1, 158.8, 158.7, 139.0, 133.7, 131.3, 130.4, 130.0, 139.6, 129.3, 126.5, 113.7, 113.6, 96.3, 55.5, 55.3, 55.2, 53.3, 52.5, 52.0, 49.3, 48.7, 46.3 ppm; MS (ESI): *m*/*z* (%): 566 [*M*+1]; elemental analysis calcd (%) for $C_{30}H_{32}ClN_3O_4S$: C 63.65, H 5.70, N 7.42; found: C 63.60, H 6.15, N 7.16.

Methyl 1,3-di(*para*-chloro)benzyl-1′-*para*-chlorophenyl-2′,3′,4′,5′-tetrahydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione-4′-carboxylate (19fc): 88% yield; m.p. 98–99 °C; IR (KBr): $\tilde{\nu}$ = 1739, 1490, 1436 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49–7.51 (m, 6H), 7.34 (d, ^3J(H,H) = 7.5 Hz, 2H), 7.30 (s, 4H), 4.65 (dd, ^3J(H,H) = 11.5, 9.3 Hz, 1H), 4.06 (s, 2H), 3.99 (d, ^3J(H,H) = 11.7 Hz, 2H), 3.84 (s, 3H), 3.72 (t, ^3J(H,H) = 9.3 Hz, 1H), 3.60 (d, ^3J(H,H) = 12.0 Hz, 1H), 3.24–3.27 (m, 1H), 3.07–3.15 (m, 2H), 2.91–2.94 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.8, 170.0, 138.7, 137.73, 136.66, 133.8, 133.0, 132.7, 130.2, 129.7, 129.4, 128.5, 128.4, 126.4, 96.4, 55.4, 53.4, 52.6, 52.0, 49.4, 48.7, 46.4 ppm; MS (ESI): *m*/*z* (%): 574 [*M*+1]; elemental analysis calcd (%) for $C_{28}H_{26}Cl_3N_3O_2S$: C 58.49, H 4.56, N 7.31; found: C 58.74, H 4.33, N 7.25.

1,3-Dibenzyl-4′-cyano-1′-phenyl-2′,3′,4′,5′-tetrahydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione (20da): 83% yield; m.p. 149–150 °C; IR (KBr): $\tilde{\nu}$ = 2250, 1597, 1496, 1454, 1434 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) ?δ? = 7.66 (d, ^3J(H,H) = 7.4 Hz, 2H), 7.54 (t, ^3J(H,H) = 7.8 Hz, 2H), 7.44–7.47 (m, 5H), 7.39 (t, ^3J(H,H) = 8.1 Hz, 4H), 7.30–7.33 (m, 2H), 4.24 (t, ^3J(H,H) = 9.5 Hz, 1H), 4.08–4.22 (m, 4H), 3.81 (t, ^3J(H,H) = 9.5 Hz, 1H), 3.78 (d, ^3J-(H,H) = 11.9 Hz, 1H), 3.31–3.36 (m, 2H), 3.19–3.23 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.8, 139.8, 138.6, 137.5, 129.7, 129.1, 128.7, 128.6, 128.5, 127.9, 127.6, 127.4, 125.2, 116.9, 95.5, 55.4, 53.9, 52.6, 49.6, 49.4, 34.5 ppm; MS (ESI): *m*/*z* (%): 439 [*M*+1]; elemental analysis calcd (%) for $C_{27}H_{26}N_4S$: C 73.94, H 5.98, N 12.77; found: C 73.83, H 6.24, N 12.57.

1,3-Di(*para*-methoxy)benzyl-4′-cyano-1′-phenyl-2′,3′,4′,5′-tetrahydrospiro-(imidazolidine-2,3′-pyrrole)-2′-thione (20ea): 88% yield; m.p. 134–135 °C; IR (KBr): $\tilde{\nu}$ = 2247, 1612, 1586, 1513, 1497 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.53 (d, ^3J(H,H) = 7.8 Hz, 2H), 7.42–7.45 (m, 3H), 7.36 (d, ^3J(H,H) = 8.5 Hz, 2H), 6.92 (d, ^3J-(H,H) = 8.3 Hz, 2H), 4.23 (t, ^3J(H,H) = 9.5 Hz, 1H), 4.13 (t, ^3J(H,H) = 9.9 Hz, 1H), 4.05 (d, ^3J(H,H) = 14.3 Hz, 1H), 4.01 (t, ^3J(H,H) = 9.6 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.79 (t, ^3J(H,H) = 9.5 Hz, 1H), 3.70 (d, ^3J-(H,H) = 11.9 Hz, 1H), 3.31–3.34 (m, 1H), 3.25–3.30 (m, 1H), 3.15–3.20 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.8, 159.1, 159.0, 139.8, 130.5, 130.2, 129.7, 129.1, 128.7, 125.3, 117.0, 114.4, 114.0, 113.8, 95.2, 55.5, 55.33, 55.29, 53.2, 52.0, 49.5, 49.2, 34.5 ppm; MS (ESI): *m*/*z* (%): 499 [*M*+1]; elemental analysis calcd (%) for $C_{29}H_{30}N_4O_2S$: C 69.85, H 6.06, N 11.24; found: C 69.80, H 6.18, N 11.14.

1,3-Di(*para*-methoxy)benzyl-4′-cyano-1′-*para*-chlorophenyl-2′,3′,4′,5′-tetrahydrospiro(imidazolidine-2,3′-pyrrole)-2′-thione (20ec): 86% yield; m.p. 129–130 °C; IR (KBr): $\tilde{\nu}$ = 2244, 1611, 1512, 1491 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.50 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.41 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.35 (d, ^3J(H,H) = 8.4 Hz, 2H), 6.91 (d, ^3J(H,H) = 7.4 Hz, 4H), 4.20 (t, ^3J(H,H) = 9.5 Hz, 1H), 4.12 (t, ^3J(H,H) = 9.9 Hz, 1H), 3.98–4.04 (m, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.78 (t, ^3J(H,H) = 9.5 Hz, 1H), 3.66 (d, ^3J(H,H) = 11.9 Hz, 1H), 3.26–3.32 (m, 2H), 3.16–3.18 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.1, 159.1, 159.0, 138.1, 134.3, 130.4, 130.2, 129.9, 129.5, 129.1, 126.5, 116.9, 114.0, 113.8, 95.2, 55.33, 55.29, 55.2, 53.2, 52.0, 49.5, 49.2, 34.4 ppm; MS (ESI): *m*/*z* (%): 533 [*M*+1]; elemental analysis calcd (%) for $C_{29}H_{29}ClN_4O_2S$: C 65.34, H 5.48, N 10.51; found: C 65.57, H 5.31, N 10.75.

Computational methods: Density functional calculations were performed with the Gaussian 03 program package (see the Supporting Information). The geometric parameters of the possible transition states, reactants and products were optimised with B3LYP/6–31G* method and verified with the number of imaginary frequencies. To mimic real experimental conditions, a single-point polarised continuum model (PCM)[11] and the solvent 1,2-dichloroethane (dielectric constant ε = 10.36, 298.15 K) were employed to investigate some of reactions, which is denoted as SCRF-B3LYP/6–31G*.

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