JOC Article

An Experimental and Theoretical Study on the Interaction of *N*-Heterocyclic Carbene-Derived 1,3-Dipoles with Methoxycarbonylallenes: Highly Regio- and Stereoselective [3+2]-Cycloadditions Controlled by the Structures of *N*-Heterocycles of 1,3-Dipoles

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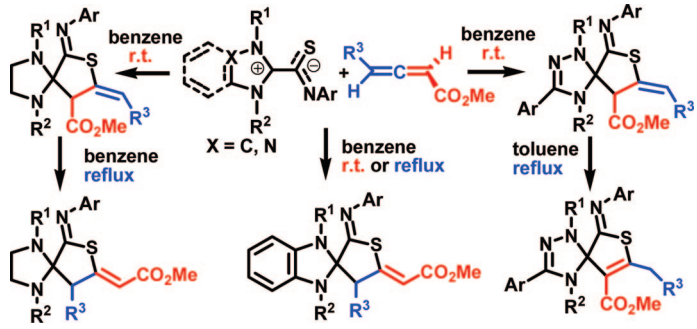

The reactions of *N*-heterocyclic carbene-derived 1,3-dipoles with methoxycarbonylallenes were studied systematically by means of experimental and theoretical approach. The regioselectivity of [3+2]-cycloaddition of 1,3-dipoles toward the ester-substituted (activated) or alkyl-substituted (less activated) carbon−carbon double bond of methoxycarbonylallenes was strongly governed by the structures of *N*-heterocycles of 1,3-dipoles. In addition, the reaction temperature played an important part in regulating the regioselectivity of [3+2]-cycloaddition in some cases. While the reaction between benzimidazole carbene-derived 2-thiocarbamoyl benzimidazolium inner salts **5** and methoxycarbonylallenes **6** with or without heating gave predominantly adducts of C^+-C-S^- moiety to the alkyl-substituted double bond of methoxycarbonylallenes, triazole carbene-derived triazolium salts **14** underwent mainly its [3+2]-cycloaddition of C^+-C-S^- dipoles to the ester-substituted double bond of methoxycarbonylallenes. In the case of imidazoline carbene-derived 1,3-dipoles **10**, the cycloaddition occurred between the C^+-C-S^- fragment and the activated double bond at room temperature, while in refluxing benzene, however, the same reaction yielded cycloadducts from the addition of **10** to the less activated double bond of methoxycarbonylallenes. DFT calculation revealed asynchronous cycloaddition mechanisms for the reactions of benzimidazole and imidazoline carbene-derived 1,3-dipoles with methoxycarbonylallenes, and a concerted mechanism for the reaction of triazole carbene-derived dipoles. The different regioselectivity of the reaction originated from the combination of electronic and steric effects of the reactants and the stability of the final products.

Introduction

Allenes are versatile building blocks in organic synthesis,[1] especially in the construction of numerous cyclic compounds via cycloaddition reactions.[2] The [3+2] cycloadditions of allenes have attracted considerable interest from both synthetic[3] and theoretical[4] chemists, because they present a number of synthetic and mechanistic possibilities. Allenes can play either as the three-carbon or two-carbon species in different [3+2] cycloadditions. In the former reactions, allenes are converted into dipolar intermediates by the action of a nucleophilic phosphine,[5] while in the latter cases, allenes behave as dipolarophiles to cyclize with 1,3-dipoles, using one carbon−carbon double of 1,2-

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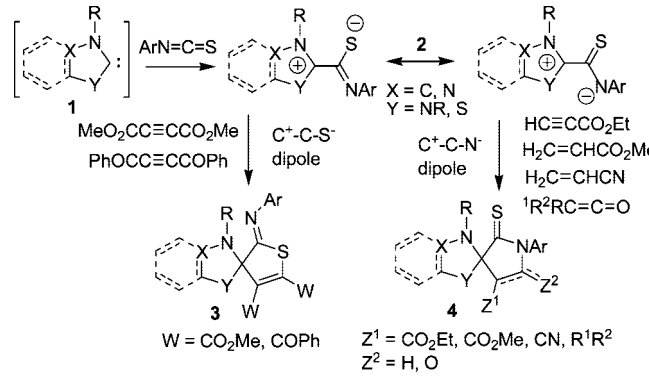
propadiene.[6,7] The [3+2] cycloadditions of electron-deficient allenes with various 1,3-dipoles such as nitrones,[6a−c] nitrile oxide,[6d−f] aromatic *N*-oxides,[6g−i] diazoalkanes,[6j,k] nitrilimines,[6f] and azides[6f,l] have been investigated. In most reactions,[6] it is the electron-deficient double bond of the allene that undergoes the 1,3-dipolar cycloaddition reaction, since the electron-withdrawing group lowers the LUMO energy level of allenes which favored the dipole HOMO−dipolarophile LUMO interaction.

Nucleophilic *N*-heterocyclic carbenes **1**, including benzimidazole, imidazoline, imidazole, triazole, and thiazole carbenes, are known to react with aryl isothiocyanates to form the corresponding stable zwitterionic products **2**, 2-thiocarbamoyl benzimidazolium, -imidazolinium, -imidazolium, -triazolium, and -thiazolium inner salts, respectively.[8] In 2006, we found for the first time that the zwitterions derived from *N*-heterocyclic carbenes and aryl isothiocyanates are unique ambident bis-dipolar compounds.[9a] Our experimental and theoretical studies indicated that these ambident 1,3-dipoles can act as either C^+-C-S^- or C^+-C-N^- dipolar species toward electron-deficient alkynes, alkenes, and ketenes to produce [3+2] cycloadducts, spiro-thiophenes **3** or spiro-pyrroles **4** as products or reaction intermediates (Scheme 1).[9] The chem-selectivity between C−C−S and C−C−N cycloaddition is dependent upon both the electronic and steric effects of dipolarophiles. For example, these ambident 1,3-dipoles acted as C^+-C-S^- dipoles toward dimethyl acetylenedicarboxylate and dibenzoylacetylene to afford spiro-thiophenes **3**. On the other hand, upon treatment with ethyl propiolate, methyl acrylate, acrylonitrile, or ketenes, they behaved as C^+-C-N^- species and produced spiro-pyrrole derivatives **4**. In the cases of imidazole and thiazole carbene-derived dipoles, the spiro-thiophene or spiro-pyrrole intermediates were not stable, being able to transform to mono or fused thiophene or pyrrole derivatives through different ring transformations.[9e,f] Very recently, we studied the three-component reaction of benzimidazole carbenes, isothiocyanates, and methoxycarbonylallenes.[10] We found that the reaction proceeds in a highly chem- and regioselective manner to produce predominantly spiro[benzimidazoline-2,3′-tetrahydrothiophene] derivatives via a tandem nucleophilic addition of carbenes to isothiocyanates followed by a [3+2] cycloaddition of C^+-C-S^- dipolar species of 2-thiocarbamoyl benzimidazolium salts to the less activated (electron-rich) carbon−carbon double bond of methoxycarbonylallenes. Interestingly, the regioselectivity of this reaction is in sharp contrast to that of most 1,3-dipolar cycloadditions of electron-deficient allenes that are documented in the literature.[6] To gain a full understanding of the chemistry of [3+2] cycloadditions between *N*-heterocyclic carbene-derived ambident dipoles and allenes, we undertook the systematic investigation on the reactions of 2-arylthiocarbamoyl benzimidazolium, -imidazolinium, and -triazolium inner salts with methoxycarbonylallenes by means of experimental and theoretical approaches.

SCHEME 1. The Reactions between *N*-Heterocyclic Carbene-Derived Ambident Dipoles and Electron-Deficient Alkynes, Alkenes, and Ketenes



Results and Discussion

Experimental Study on the Reaction of *N*-Heterocyclic Carbene-Derived 1,3-Dipoles with Methoxycarbonylallenes. Having observed an unusual regioselectivity of cycloaddition between 2-thiocarbamoyl benzimidazolium salts and methoxycarbonylallenes that was involved in the three-component reaction of benzimidazole carbenes with isothiocyanates and methoxycarbonylallenes in the presence of NaH,[10] the first issue of the current study was to investigate the effect of the neutral reaction media on the regioselectivity. Thus, the reaction of 1,3-dibenzyl-2-*N*-phenylthiocarbamoyl benzimidazolium salt **5a** with 4-benzylallenecarboxylate **6a** was examined under different conditions. It was found that the reaction conditions including ratio of starting materials, solvent, temperature, and reaction time affected slightly the yield of major product **7a**, but did not influence the regioselectivity. As shown in Table 1, under all neutral reaction conditions examined, ambident dipole **5a** acted as a C^+-C-S^- dipolar specie selectively to cyclize with the less activated C(2)−C(3) double bond of allene **6a** giving

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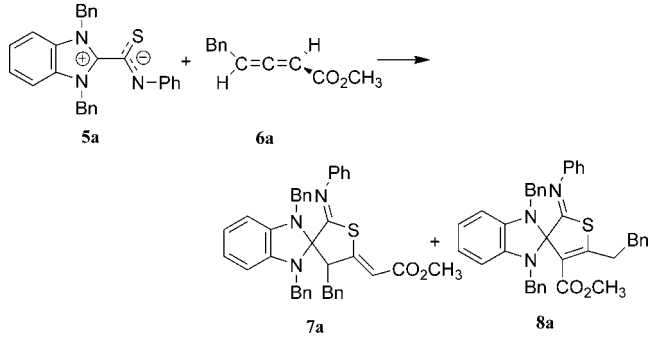
TABLE 1. The Reaction of 1,3-Dibenzyl-2-*N*-phenylthiocarbamoyl Benzimidazolium Salt 5a with 4-Benzylallenecarboxylate 6a under Different Conditions



5a **6a** **7a** **8a**

		reaction conditions				yield (%)	
entry	starting materials	**5a**:**6a**	solvent	temp (°C)	time (h)	**7a**	**8a**
1	**5a**, **6a**	1:1	acetonitrile	20−30	24	79	4
2	**5a**, **6a**	1:1	butanone	20−30	24	79	6
3	**5a**, **6a**	1:1	1,2-dichloroethane	20−30	24	80	*a*
4	**5a**, **6a**	1:1	1,4-dioxane	20−30	24	77	*a*
5	**5a**, **6a**	1:1.5	THF	50−60	2	72	*a*
6	**5a**, **6a**	1:1	benzene	20−30	24	81	*a*
7	**5a**, **6a**	1:1.5	benzene	20−30	24	90	*a*
8	**5a**, **6a**	1:1.5	benzene	50−60	4	82	*a*
9	**5a**, **6a**	1:1.5	benzene	80	4	82	*a*

a No or a tiny amount of byproduct was observed.

TABLE 2. The Reaction of 2-Thiocarbamoyl Benzimidazolium Salts 5 with Methoxycarbonylallenes 6 in Benzene

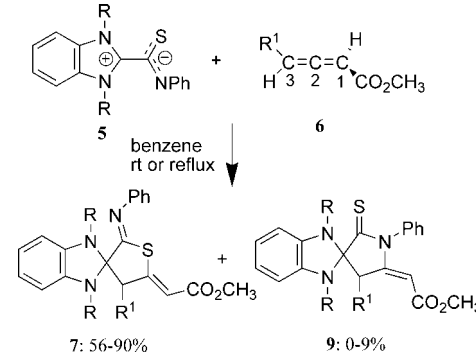
	starting materials		reaction conditions[a]		yield (%)	
entry	**5**: R	**6**: R^1	temp (°C)	time (h)	**7**	**9**
1	**5a**: Bn	**6a**: Bn	20−30	24	**7a**: 90	*b*
2	**5b**: *p*-CH_3OBn	**6a**: Bn	20−30	24	**7b**: 75	*b*
3	**5c**: *p*-ClBn	**6a**: Bn	20−30	48	**7c**: 83	*b*
4	**5a**: Bn	**6b**: Me	20−30	24	**7d**: 56	*b*
5	**5a**: Bn	**6c**: Et	20−30	24	**7e**: 63	*b*
6	**5d**: Et	**6a**: Bn	20−30	24	**7f**: 82	*b*
7	**5e**: *n*-Bu	**6a**: Bn	20−30	24	**7g**: 87	*b*
8	**5a**: Bn	**6a**: Bn	reflux	4	**7a**: 82	*b*
9	**5b**: *p*-CH_3OBn	**6a**: Bn	reflux	3	**7b**: 69	*b*
10	**5c**: *p*-ClBn	**6a**: Bn	reflux	2	**7c**: 80	*b*
11	**5a**: Bn	**6b**: Me	reflux	2	**7d**: 70	**9d**: 9
12	**5a**: Bn	**6c**: Et	reflux	2	**7e**: 82	*b*

[a] **5**:**6** = 1:1.5. *b* No or a tiny amount of byproduct was observed.

the benzimidazole-spiro-thiophene **7a** in high yields (72−90%). The byproduct **8a**, another spiro-thiophene yielded from cycloaddition of the C^+-C-S^- dipole of **5a** with the electron-deficient C(1)−C(2) double bond of **6a**, was isolated only in 4−6% yields from the reactions performed in acetonitrile and in butanone (Table 1, entries 1 and 2).

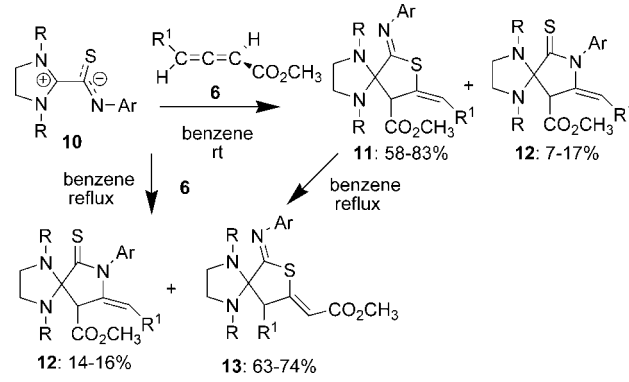
The scope of the reaction was then studied under optimal conditions by using dipoles **5** and allenes **6** that bear different substituents. As evidenced by the results summarized in Table 2, the reaction showed tolerance for the substituent on the reactants. At room temperature and in benzene, all reactions proceeded smoothly to afford products **7** in 56−90% yields in 24−48 h (Scheme 2 and Table 2, entries 1−7). At an elevated temperature such as 80−90 °C, the reactions of dipoles **5** with allenes **6** were completed within 2−3 h to afford benzimidazole-spiro-thiophenes **7** in 69−82% yields. A trace amount of benzimidazole-spiro-pyrroles **9** that were derived from cycloaddition of C^+-C-N^- dipoles of **5** with the C(2)−C(3) double

SCHEME 2. The Reaction of 2-Thiocarbamoyl Benzimidazolium Salts 5 with Methoxycarbonylallenes 6



5 **6** **7**: 56-90% **9**: 0-9%

SCHEME 3. The Reaction of 2-Thiocarbamoyl Imidazolinium Salts 10 with Allenes 6



10 **11**: 58-83% **12**: 7-17% **12**: 14-16% **13**: 63-74%

bond of allenes **6** was also detected in some cases (0−9%) (Scheme 2 and Table 2, entries 8−12).

To examine the generality of the reaction, we then extended the 1,3-dipolar substrates to 2-thiocarbamoyl imidazolinium salts **10**. At ambient temperature in benzene, the reaction of imidazoline carbene-derived dipoles **10** with allenes **6** produced imidazoline-spiro-thiophenes **11** as major products in 58−83% yields, while the byproducts imidazoline-spiro-pyrroles **12** were also isolated in 7−17% yields (Scheme 3; Table 3, entries 1−7). To our surprise, in sharp contrast to the reaction of **5** that yielded benzimidazole-spiro-thiophenes **7** from cycloaddition of dipoles **5** with the electron-rich C(2)−C(3) double bond of methoxycarbonylallenes **6**, X-ray diffraction analysis demonstrated that either major products **11** or minor products **12** were derived from cycloaddition of the electron-deficient C(1)−C(2) double bond of methoxycarbonylallenes **6** with the C^+-C-S^- or C^+-C-N^- dipolar species of **10**, respectively.

However, imidazoline-spiro-thiophenes **11** were found unstable under warm condition. When heated in solvent, they were astonishingly transformed into the constitutional isomers imidazoline-spiro-thiophenes **13** that were virtually the cycloadducts of dipoles **10** with the C(2)−C(3) double bond of allenes **6**. Intrigued by this observation, we examined again the reaction of dipoles **10** with allenes **6** in refluxing benzene. The reaction proceeded rapidly to form spiro-thiophenes **11** initially, and products **11** were then converted almost completely into their isomers **13** after heating in benzene for a prolonged time (Scheme 3; Table 3, entries 8−11).

To further examine the effect of the structure of the *N*-heterocycle on the regioselectivity, we then studied the reaction of 2-thiocarbamoyl triazolium salts **14** with methoxycarbonylallenes **6** at ambient and at elevated temperatures. As

TABLE 3. The Reaction of 2-Thiocarbamoyl Imidazolinium Salts 10 with Allenes 6 in Benzene

	starting materials			reaction conditions[a]		yield (%)		
entry	**10**: R	Ar	**6**: R^1	temp (°C)	time (h)	**11**	**12**	**13**
1	**10a**: Bn	Ph	**6a**: Bn	20−30	24	**11a**: 75	**12a**: 16	
2	**10b**: *p*-CH_3OBn	Ph	**6a**: Bn	20−30	24	**11b**: 65	**12b**: 12	
3	**10c**: *p*-ClBn	Ph	**6a**: Bn	20−30	24	**11c**: 63	**12c**: 17	
4	**10d**: *p*-ClBn	*p*-BrC_6H_5	**6a**: Bn	20−30	24	**11d**: 83	**12d**: 11	
5	**10e**: *p*-ClBn	3,4-$Cl_2C_6H_4$	**6a**: Bn	20−30	24	**11e**: 60	**12e**: 7	
6	**10a**: Bn	Ph	**6c**: Et	20−30	24	**11f**: 58	**12f**: 17	
7	**10a**: Bn	Ph	**6d**: *iso*-Pr	20−30	24	**11g**: 63	**12g**: 17	
8	**10a**: Bn	Ph	**6a**: Bn	reflux	6		**12a**: 16	**13a**: 74
9	**10b**: *p*-CH_3OBn	Ph	**6a**: Bn	reflux	2		**12b**: 14	**13b**: 70
10	**10c**: *p*-ClBn	Ph	**6a**: Bn	reflux	12		[b]	**13c**: 71
11	**10e**: *p*-ClBn	3,4-$Cl_2C_6H_4$	**6a**: Bn	reflux	13		[b]	**13e**: 63

[a] **10**: **6** = 1:1.5. [b] Byproduct was observed without isolation.

SCHEME 4. The Reaction of 2-Thiocarbamoyl Triazolium Salts 14 with Methoxycarbonylallenes 6

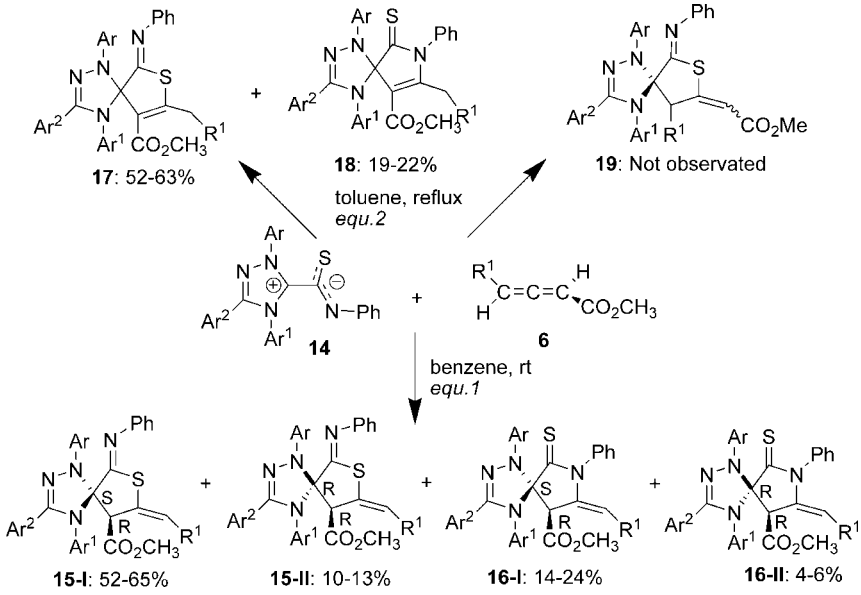


TABLE 4. The Reaction of 2-Thiocarbamoyl Triazolium Salts 14 with Methoxycarbonylallenes 6

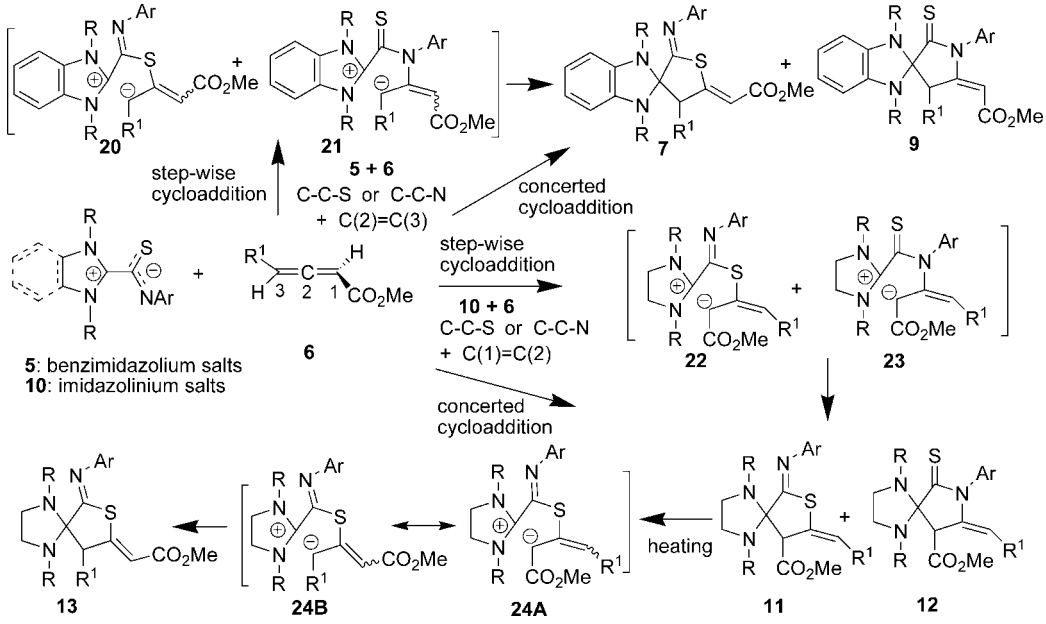
	starting materials			yield (%)			
entry	**14**: Ar, AR^1, Ar^2	**6**: R^1	reaction conditions[a]	**15-I** or **17**	**15-II**	**16-I** or **18**	**16-II**
1	**14a**: Ph, Ph, Ph	**6a**: Bn	benzene, rt, 24 h	**15a-I**: 65	**15a-II**: 13	**16a-I**: 15	**16a-II**: 5
2	**14b**: Ph, *p*-$CH_3OC_6H_4$, Ph	**6a**: Bn	benzene, rt, 15 h	**15b-I**: 61	**15b-II**: 11	**16b-I**: 17	**16b-II**: 6
3	**14c**: Ph, Ph, *p*-$CH_3C_6H_4$	**6a**: Bn	benzene, rt, 23 h	**15c-I**: 54	**15c-II**: 12	**16c-I**: 14	**16c-II**: 4
4	**14a**: Ph, Ph, Ph	**6c**: Et	benzene, rt, 24 h	**15d-I**: 52	**15d-II**: 10	**16d-I**: 24	**16d-II**: 6
5	**14a**: Ph, Ph, Ph	**6d**: *i*-Pr	benzene, rt, 15 h	**15e-I**: 58	**15e-II**: 12	**16e-I**: 20	**16e-II**: 5
6	**14a**: Ph, Ph, Ph	**6a**: Bn	toluene, reflux, 12 h	**17a**: 62		**18a**: 22	
7	**14b**: Ph, *p*-$CH_3OC_6H_4$, Ph	**6a**: Bn	toluene, reflux, 2 h	**17b**: 63		**18b**: 20	
8	**14c**: Ph, Ph, *p*-$CH_3C_6H_4$	**6a**: Bn	toluene, reflux, 9 h	**17c**: 60		**18c**: 20	
9	**14a**: Ph, Ph, Ph	**6c**: Et	toluene, reflux, 7 h	**17d**: 54		**18d**: 22	
10	**14a**: Ph, Ph, Ph	**6d**: *iso*-Pr	toluene, reflux, 2 h	**17e**: 52		**18e**: 19	

[a] **10**:**6** = 1:1.5.

illustrated in Scheme 4 and Table 4, at ambient temperature, the reaction of 2-thiocarbamoyl-1,3,4-triaryltriazolium salts **14** with methoxycarbonylallenes **6** produced two pairs of diastereomers, triazole-spiro-thiophenes **15-I** and **15-II** and triazole-spiro-pyrroles **16-I** and **16-II**. Diastereomers **15-I** and **15-II** were isolated in the yields of 52−65% and 10−13%, while **16-I** and **16-II** were obtained in 14−24% and 4−6% yields, respectively (Table 4, entries 1−5). X-ray diffraction analysis indicated that both major diastereomers **15-I** and **16-I** of the two pairs of diastereomers have the (*S*,*R*) or (*R*,*S*) configurations at chiral centers (vide infra). Similar to the 2-thiocarbamoyl imidazolinium salts **10**, at ambient temperature, either C^+-C-S^- or C^+-C-N^- dipolar species of triazolium salts **14** cyclized with the electron-deficient C(1)−C(2) double bond of allenes **6** to give **15** or **16**, respectively (Scheme 4, eq 1).

Since an isomerization from imidazoline-spiro-thiophenes **11** to their constitutional isomers **13** was observed at higher temperature (Scheme 3), the reaction between triazolium salts **14** and allenes **6** was also examined in refluxing benzene. It was observed that the four products **15-I**, **15-II**, **16-I**, and **16-II** formed at ambient temperature were converted into two new compounds **17** and **18** at 80 °C. However, the transformation

SCHEME 5. The Proposed Mechanisms for the Reactions of Dipoles 5 and 10 with Methoxycarbonylallenes 6

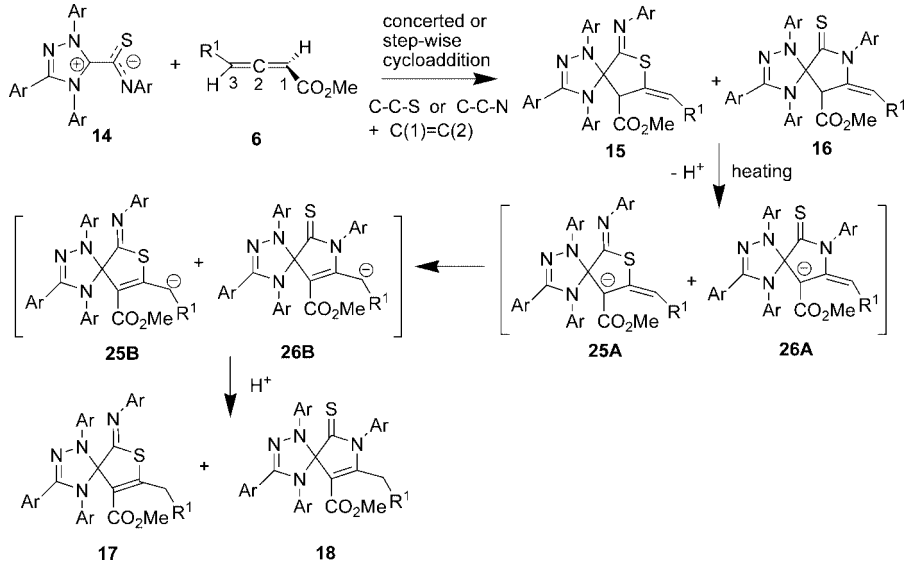


was not completed under those conditions. To promote the transformation, the reaction temperature was increased to 110 °C. In refluxing toluene, the reaction of triazolium salts **14** with allenes **6** finally produced products **17** and **18**, via intermediates **15** and **16**, in 52−63% and 19−22% yields, respectively (Scheme 4, eq 2; Table 4, entries 6−10). Although triazole-spiro-thiophenes **15** were similar to imidazoline-spiro-thiophenes **11** that underwent isomerization at high temperature, the structures of products were out of our expectation. Instead of isomerizing into the constitutional isomers **19**, spiro-tetrahydrothiophenes **15** isomerized into spiro-dihydrothiophenes **17** under heating condition. A similar isomerization was also observed during the transformation of spiro-tetrahydropyrroles **16** to spiro-dihydropyrroles **18**. Besides the reactions of 2-thiocarbamoyl 1,3,4-triaryltriazolium salts **14a−c** with allenes **6**, we also tried the reaction between 1,3-dibenzyl-2-thiocarbamoyl triazolium salt **14d** (Ar = Ar^1 = Bn; Ar^2 = H) and allene **6a**, but finally gave up because the products were unstable in the processes of chromatography and recrystallization.

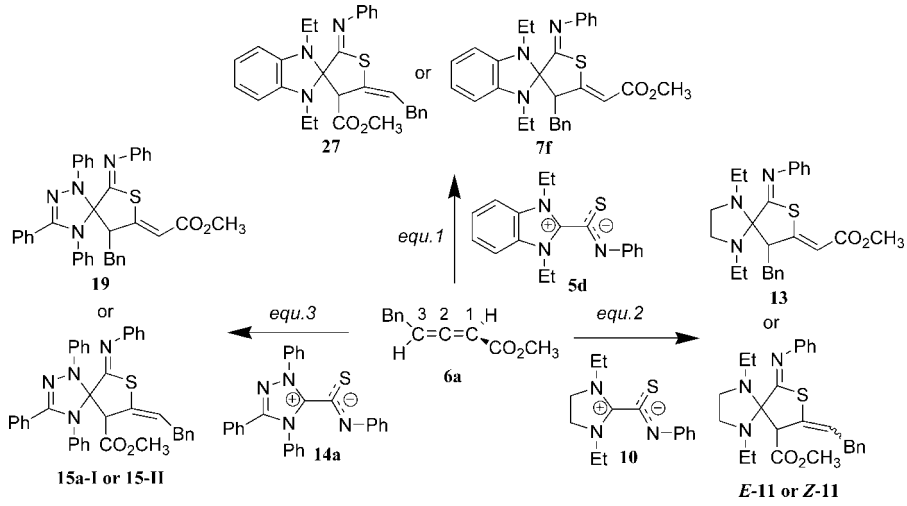
The structures of products were elucidated on the basis of spectroscopic data and microanalysis. The NMR spectra, mass data, and elemental analyses indicated all products being derived from 1+1 addition of dipoles and allenes. To identify the isomeric products beyond doubt, the structures of **7a**, **11a**, **12g**, **13a**, **15e-I**, **16e-I**, **16e-II**, and **17e** were determined unambiguously by single-crystal X-ray diffraction analysis. Interestingly, it was found that the exocyclic C=C bond of spiro-thiophenes **7** and **13** derived from the C(2)−C(3) double bond of allenes **6** is a *Z*-configuration, while the C=C bond of spiro-thiophenes **11** and **15** derived from the C(1)−C(2) double bond of **6** is a *E*-configuration. It is worth noting that different types of isomeric products show distinctly different ^{13}C NMR and ^{1}H NMR spectra, and they can be used in turn as diagnostics to differentiate isomers. First, major products spiro-thiophenes can be differentiated from the byproduct spiro-pyrroles by using ^{13}C NMR spectra, since all spiro-thiophenes **7**, **11**, **13**, **15**, and **17** gave their diagnostic C=N carbon signals around 160−170 ppm, while C=S carbon signals of spiro-pyrroles **9**, **12**, **16**, and **18** appeared at lower field around 190−210 ppm. Second, the constitutional isomers imidazoline-spiro-thiophenes **11** and **13** can be easily identified by the ^{1}H NMR spectra, because the vinyl protons of **11** were coupled with the adjacent CH_2 or CH protons to give triplet or doublet signals, respectively, while vinyl protons of **13** have no adjacent protons and therefore appeared as singlet signals. In addition, the isomeric triazole-spiro-thiophenes **15** and **17**, or triazole-spiro-pyrroles **16** and **18**, can be differentiated by their ^{1}H NMR spectra, because the isomer **15** or **16** has two signals around 4−6 ppm corresponding to the exocyclic vinyl proton and the proton of thiophene or pyrrole ring adjacent to the ester group whereas the isomer **17** or **18** containing an endocyclic C=C bond has no signals appearing in that region. Finally, the diastereomers **15-I** and **15-II**, or **16-I** and **16-II**, also showed a difference between their thiophene or pyrrole ring protons in the ^{1}H NMR spectra. The protons of thiophene or pyrrole rings of all (*S*,*R*)- or (*R*,*S*)-**15-I** or **16-I** resonated at 4.8−5.0 ppm, while those ring-protons of (*R*,*R*)- or (*S*,*S*)-**15-II** or **16-II** appeared at slightly higher field around 4.3−4.5 ppm.

The formation of all products can be explained by a concerted or a stepwise [3+2] cycloaddition reaction pathway (Schemes 5 and 6). At room temperature, the ambident 1,3-dipolar compounds **5**, **10**, and **14** acted predominately as the C^+-C-S^- 1,3-dipoles to react selectively with the C(2)−C(3) or C(1)−C(2) double bond of methoxycarbonylallenes **6** to produce spiro-tetrahydrothiophenes **7**, **11**, or **15**, respectively. In turn, they behaved as the C^+-C-N^- 1,3-dipolar species to add to the C(2)−C(3) or C(1)−C(2) double bond of allenes **6** giving rise to the byproduct, spiro-tetrahydropyrroles **9**, **12**, or **16**. Under heating conditions, the unstable imidazoline-spiro-thiophenes **11** underwent isomerization to give the constitutional isomers **13** via ring-opening and reclosure of the thiophene rings (Scheme 5). The isomerization of triazole-spiro-tetrahydrothiophenes **15** or triazole-spiro-tetrahydropyrroles **16** took place apparently through shifting the exocyclic carbon−carbon double bond to the endocyclic double bond to give the thermodynamically more stable conjugated products **17** or **18**. Since a concerted suprafacial 1,3-H shift is a symmetry-forbidden process, the isomerization of **15** or **16** to **17** or **18** was most probably through an allyl anion intermediate **25A** or **26A** by deprotonation of the acidic proton adjacent to the

SCHEME 6. The Proposed Mechanism for the Reaction between Dipoles 14 and Methoxycarbonylallenes 6



SCHEME 7. Computational Reactions of 2-Arylthiocarbamoyl Benzimidazolium 5d, -imidazolinium 10, and -triazolium Salt 14a with 4-Benzylallenecarboxylate 6a



carbonyl group in the presence of basic triazole compounds. Rearrangement of **25A** and **26A** to **25B** and **26B** by shifting the exocyclic double bond to the endocyclic double bond and protonation of anions **25B** and **26B** afforded spiro-dihydrothiophenes **17** and spiro-dihydropyrrole **18**, respectively (Scheme 6).

Computational Study on the Mechanism and Selectivity of the Reaction. The chem-, regio-, and stereoselective [3+2] cycloaddition reactions of 2-arylthiocarbamoyl benzimidazolium, -imidazolinium, and -triazolium salts with methoxycarbonylallenes are remarkable. The most interesting and intriguing feature of the reaction is the substrate regulated regioselectivity. Our experimental studies have shown that it was the structure of the heterocycle of 1,3-dipole that controlled the regioselectivity. In the meantime, the reaction temperature also affected the outcomes of the reactions. To shed light on the different selectivities of different *N*-heterocyclic carbene-derived 1,3-dipoles toward allenes, density functional theory B3LYP/6-31G* was employed to investigate the mechanisms of the reactions. First, the reactions between C^+-C-S^- dipoles and methoxycarbonylallenes were studied to understand the regioselectivity and stereoselectivity in the reaction of formation of major products spiro-thiophenes (Scheme 7).

We started the theoretical study with the reaction between 2-arylthiocarbamoyl benzimidazolium salt **5d** and allene **6a**. The calculation indicated that cycloaddition of the C^+-C-S^- dipolar specie of **5d** with **6a** could take place either at the C(2)−C(3) or the C(1)−C(2) double bond of allene **6** to form two different adducts **7f** or **27** (see eq 1 in Scheme 7 and Figure 1). In the former reaction, the formation of the C−S bond is much faster than that of the C−C bond (2.168 vs. 3.303 Å in transition state $\mathbf{TS_{A1}}$) and an intermediate $\mathbf{INT_{A1}}$ is located, therefore the formation of **7f** was via a stepwise mechanism (path A in Figure 1). In the latter case, the asynchronicity in transition state $\mathbf{TS_{B1}}$ is not as big as that in $\mathbf{TS_{A1}}$, and hence a concerted pathway was characterized for compound **27** (path B in Figure 2). Generally, the ester carbonyl substituted C(1)−C(2) double bond should be more active than the benzyl substituted C(2)−C(3) double bond toward nucleophilic additions due to the electronic preference. However, we observed a reversed selectivity in the reaction of benzimidazolium salts **5** with allenes **6**. This unusual regioselectivity can be well explained with our calculation

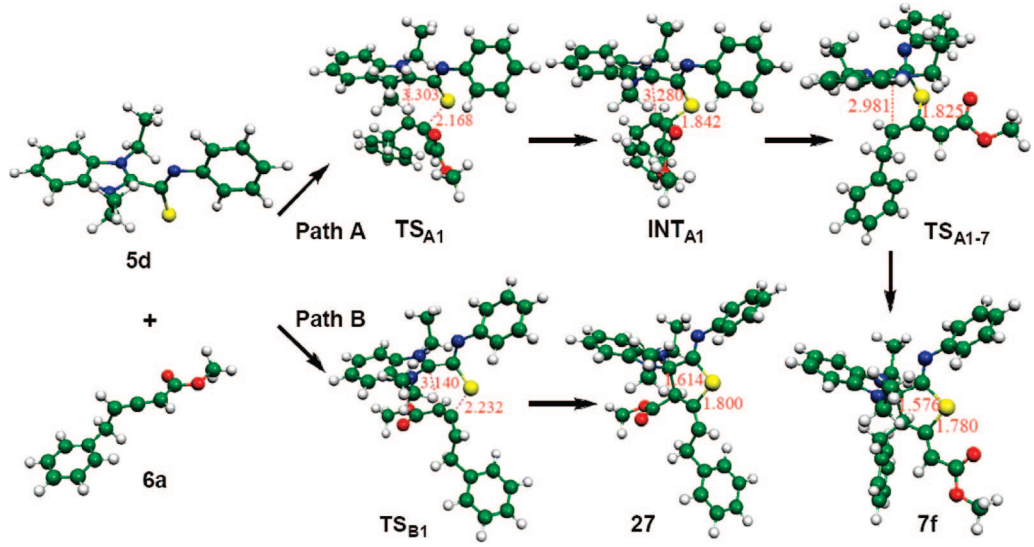


FIGURE 1. The obtained reaction pathways for **5d** + **6a** → **7f** and **5d** + **6a** → **27**, along with the bond lengths (Å) for the main reaction coordinates.

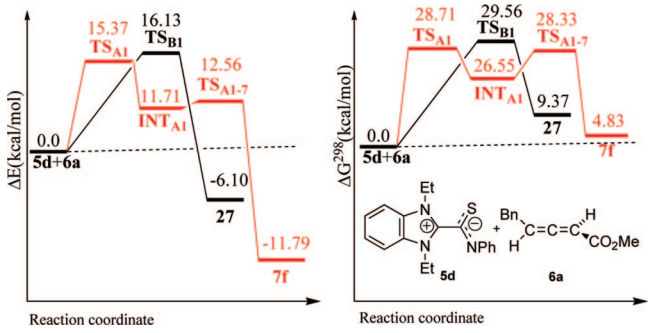


FIGURE 2. The energy profiles (ΔE and ΔG^{298}) for the reactions of **5d** + **6a** → **7f** and **5d** + **6a** → **27**.

results. As indicated by the energy profiles in Figure 2, **TS$_{A1}$** is a little bit more stable than **TS$_{B1}$**. The lower stability of **TS$_{B1}$** than **TS$_{A1}$** is most probably due to the repulsion between the phenyl ring of benzimidazolium **5d** and the ester carbonyl group of **6a** (see Figure 1, **TS$_{B1}$**). That means the steric effect counterbalances the electronic preference in the formation of transition states. From energy profiles in Figure 2, we can observe that the energy barrier to form **INT$_{A1}$** is 15.34 kcal/mol, and the energy barrier from **INT$_{A1}$** to **7f** in the second step is just 0.85 kcal/mol. The energy of **7f** is about 5.7 kcal/mol lower than that for **27**, which is most likely attributed to both the conjugative stability of **7f** and the steric repulsion of **27** as mentioned above. The tendency of ΔG^{298} is similar to that of ΔE, and the relative free energy of product **27** at 298 K is higher than those of the two starting materials (**5d** + **6a**) (see right column of Figure 2). From the ΔE and ΔG^{298} indicated in Figure 2, it is clear that **7f** is both a kinetically and a thermodynamically favorable product. In addition to the regioselectivity, the reaction of benzimidazolium salts **5** with allenes **6** is so highly stereoselective that only *Z*-**7f** was detected. This stereoselectivity can be easily explained by the Molekel drawing of structures for experimental product *Z*-**7f** and the fancy isomer of *E*-**7f** (see Supporting Information, Figure S2). Apparently, the reaction preferred to form *Z*-**7f** because of *E*-**7f** having a huge steric repulsion between the carbonyl and the benzyl group bearing to the thiophene ring.

The reaction pathways for the interaction between 2-arylthiocarbamoyl imidazolinium salt **10** and **6a** are more complicated (Scheme 7, eq 2). Experimentally, products *E*-**11** and **13** were isolated respectively from the reaction of **10** with **6** at ambient and at higher temperature. In these two reactions, the asynchronicity of cycloaddition is explicit because the C−S and C−C bonds of the thiophene ring were bonded respectively before and after the formation of intermediate **INT$_{A2}$** or **INT$_{B2}$** (see Figure 3, paths A and B), indicating both the formation of *E*-**11** and **13** proceeded in two-step processes. As shown in Figure 4, the first energy barriers for transition states **TS$_{B2}$** and **TS$_{A2}$** are 8.44 and 14.89 kcal/mol, respectively, and the relative free energy of **TS$_{B2}$** is about 3 kcal/mol lower than that of **TS$_{A2}$**. Therefore, the compound *E*-**11** formed from addition of **10** to the C(1)═C(2) bond of **6** at room temperature is a kinetically favored product. At higher temperature, the reaction is controlled by thermodynamic aspect. The calculation shows that product *E*-**11** can break the C−C bond of the thiophene ring to return to **INT$_{B2}$** with an energy barrier of about 15.1 kcal/mol. Then intermediate **INT$_{B2}$** is transformed into **INT$_{A2}$** that is easier to form the more stable product **13** by overcoming the energy barrier of 6 kcal/mol of **TS$_{B2-A2}$** (see the left column in Figure 4). The curvature of the ΔG^{298} profile is similar to that of ΔE with a shift-up of about 5−18 kcal/mol (see the right column in Figure 4). Hence, the same conclusion has been obtained from both ΔE and ΔG^{298}. The theoretical study has revealed that product *E*-**11** is the kinetically controlled product while **13** is the thermodynamically controlled one. These results can well explain our experimental observations.

On the contrary to the *Z*-configurational products **7** and **13** derived from reactions of dipoles **5** and **10** with the C(1)═C(2) bond of allenes **6**, the products **11** formed from cycloaddition of **10** with the C(1)═C(2) bond of allenes **6** have a trans C═C bond. This stereoselectivity was out of our expectation, because *Z*-**11** looked more stable than *E*-**11** due to the repulsion between carbonyl and alkyl group attached to the C═C bond. To clarify the stereoselectivity, the reaction of imidazolinium **10** with **6a** to form fancy isomer *Z*-**11** was also calculated (See Figure 3, path C). From the energy profiles in Figure 4, it was found that the energy and free energy of *Z*-**11** are slight lower than those of *E*-**11**, which means *Z*-**11** is a litter bit more stable than *E*-**11**. However, both ΔE and ΔG^{298} of **TS′$_{B2}$** (green line in Figure 4) that will transform to *Z*-**11** are higher than those of **TS$_{B2}$** (blue

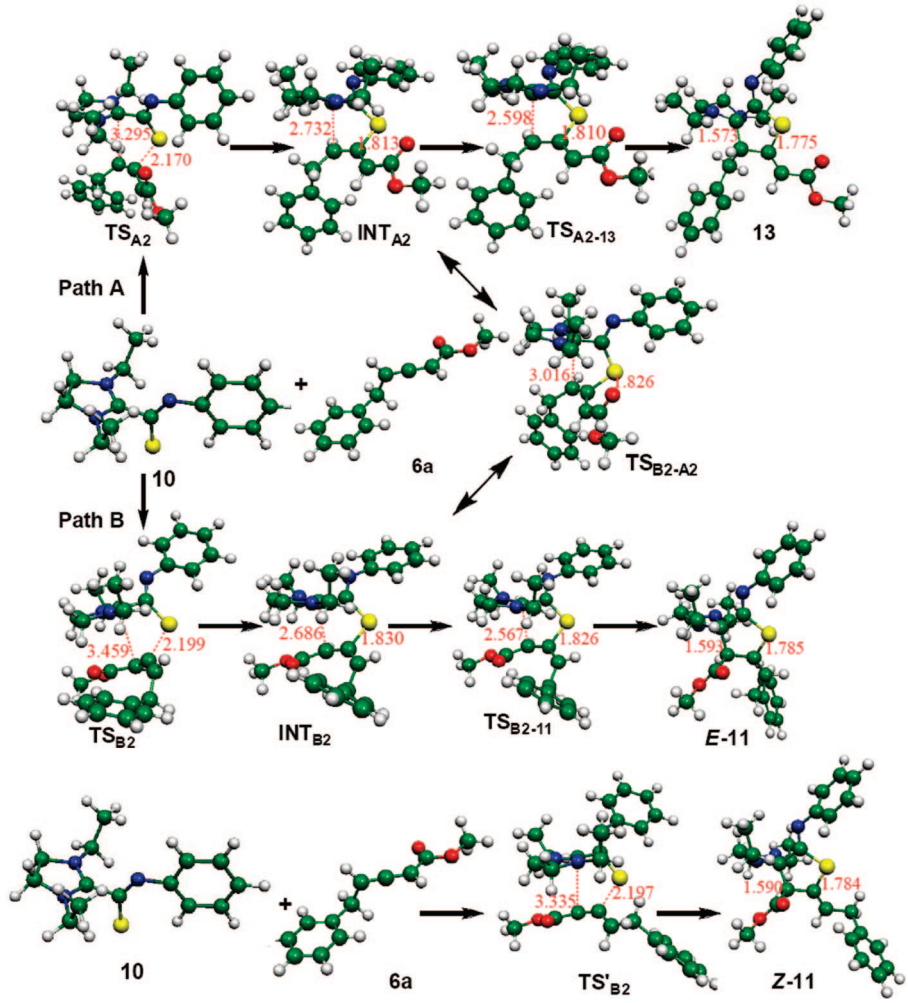


FIGURE 3. The reaction pathways for **10** + **6a** → *E*-**11** and *Z*-**11**, and **10** + **6a** → **13**, along with the bond lengths (Å) for the main reaction coordinates.

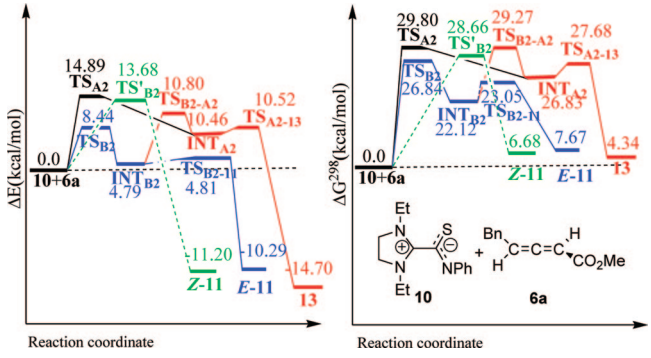


FIGURE 4. The energy profiles (ΔE and ΔG^{298}) for the reactions of **10** + **6a** → *E*-**11** and *Z*-**11**, and **10** + **6a** → **13**.

line) due to the repulsion between the benzyl of allene **6a** and *N*-ethyl bearing to the imidazoline ring of **10** in **TS′$_{B2}$**. Thus, the formation of *E*-**11** is a kinetically favored process.

Experimentally, two diastereoisomeric spiro-thiophenes **15-I** and **15-II** were isolated from the cycloaddition between C$^+$−C−S$^-$ dipoles of 1,3,4-triaryltriazolium salts **14** with C(1)═C(2) bonds of methoxycarbonylallenes **6** due to the unsymmetrical structures of triazolium salts **14**. The calculation showed that no intermediate was located in the cycloadditions of the C$^+$−C−S$^-$dipole of **14a** with the two double bonds of allene **6a**, which means all reactions followed concerted processes (Figure 5). Comparing the energy profiles in Figure 6 with that in Figures 2 and 4, the energy barriers of transition states **TS$_{A3}$**, **TS′$_{A3}$**, and **TS$_{B3}$** in the reactions between triazolium salt **14a** and **6a** are much higher than those energies of the reactions between benzimidazolium salt **5d** or imidazolinium salt **10** and **6a**. These results indicated that triazolium salt **14a** is less active than benzimidazolium salt **5d** or imidazolinium salt **10** toward allene **6a**. The lower reactivity of **14** with **6** was most probably due to the steric hindrance of three phenyl substituents in the triazole ring. As shown in Figure 6, the energy and free energy of **TS$_{A3}$** and **TS′$_{A3}$** are much lower than those of **TS$_{B3}$**, which indicated the formation of products **15a-I** and **15a-II** rather than **19** at room temperature was controlled by the kinetic effect. Between the two stereoisomeric products **15-I** and **15-II**, **15-I** is the major product. This stereoselectivity can be explained by the energy or free energy of transition state **TS$_{A3}$**, **TS′$_{A3}$** and product **15a-I**, **15a-II** (Figure 6, blue and red lines). The lower energy or free energy of **TS$_{A3}$** and **15a-I** than that of **TS′$_{A3}$** and **15a-II** demonstrated that **15a-I** is both a kinetically and thermodynamically favored product compared to its diastereoisomers **15a-II**. Although compound **19** that was formed from the cycloaddition of dipole **14a** with the C(1)═C(2) bond of **6a** is thermodynamically more stable than **15a-I** and **15a-II** (Figures 5 and 6), products **15a** could not be converted into **19** at higher temperature, because no intermediate that plays

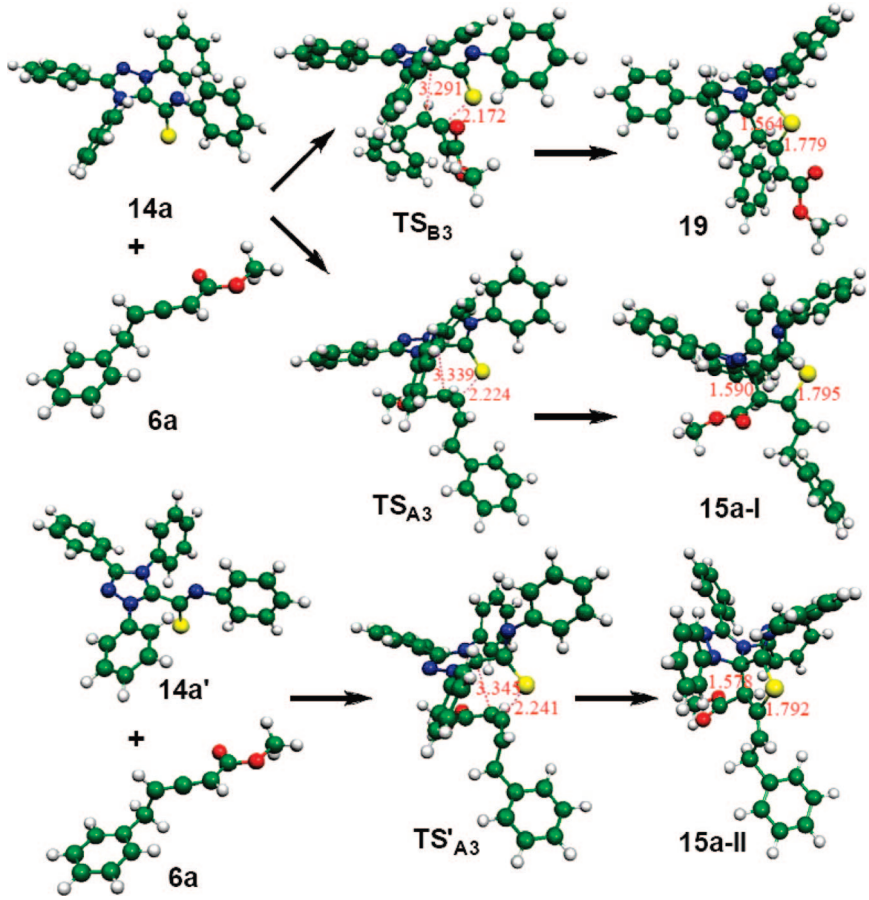


FIGURE 5. The reaction pathways for **14a** + **6a** → **15a-I** and **14a′** + **6a** → **15a-II**, and **14a** + **6a** → **19**, along with the bond lengths (Å) for the main reaction coordinates.

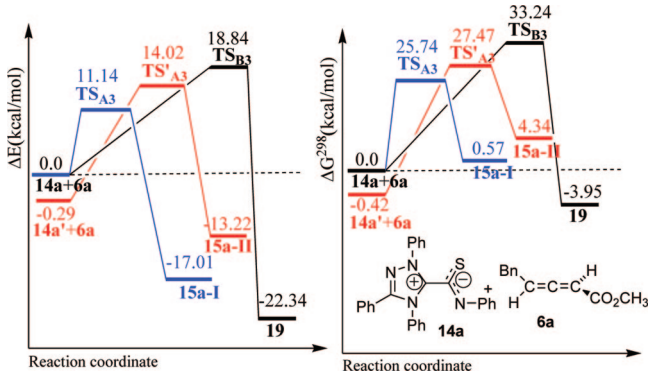


FIGURE 6. The energy profiles (Δ*E* and Δ*G*^{298}) for the reactions of **14a** + **6a** → **15a-I** and **14a′** + **6a** → **15a-II**, and **14a** + **6a** → **19**.

a bridge for the transformation between **15a** and **19** has been located. All of the theoretical studies are in good agreement with our experiment observations.

In addition to the high regio- and stereoselectivity, the reactions between 2-arylthiocarbamoyl benzimidazolium, -imidazolinium, and -triazolium salts with methoxycarbonylallenes also show chemselectivity. Our experimental studies indicated that all inner salts **5**, **10**, and **14** acted predominately as C^+-C-S^- dipoles toward methoxycarbonylallenes to form spiro-thiophenes products. This chemselectivity is in agreement with our previous studies on the ambident reactivity of *N*-heterocyclic carbene-derived 1,3-dipoles toward electron-deficient alkynes, alkenes, and ketenes.[9a–c] We have demonstrated that the sterically hindered and strongly electrophilic 1,3-dipolarphiles prefer to react with the C−C−S dipolar component, whereas the dipolarophiles with less steric hindrance favor the reaction with the C−C−N moiety.[9a–c] In the current reactions, the predominate C−C−S cycloaddition is most probably due to the steric hindrance between the aryl group bearing to thiocarbamoyl of dipoles **5**, **10**, or **14** and the two substituents of allenes that disfavored the C−C−N pathway. To support our supposition, the cycloaddition reactions between the C^+-C-N^- dipolar species of **5d**, **10**, **14a**, and methoxycarbonylallene **6a** that produced the byproduct **9f**, **12**, or **16a-I** were calculated. The calculation indicated that all C−C−N cycloadditions between dipoles **5d**, **10**, **14a**, and allene **6a** have higher Δ*E* and Δ*G* than that of the corresponding C−C−S cycloadditions. However, the spiro-pyrroles **9f**, **12**, and **16a-I** derived from C−C−N cycloadditions are more stable than the C−C−S adducts spiro-thiophenes **7f**, **11**, and **15a-I**, respectively (see the Supporting Information, Figures S3−S8). Therefore, it is the kinetic effects that controlled the predominate formation of C−C−S cycloadducts.

Conclusion

In summary, we have shown that *N*-heterocyclic carbene-derived 1,3-dipoles are useful reactive intermediates able to undergo [3+2] cycloaddition reactions with methoxycarbonylallenes. The reaction regioselectivity, namely addition of C^+-C-S^- dipoles to the ester-substituted carbon−carbon double bond or alkyl-substituted carbon−carbon double bond of methoxycarbonylallenes, depended on the heterocycle structures of the 1,3-dipoles. Benzimidazole carbene-derived 2-thio-

carbamoyl benzimidazolium inner salts **5** reacted with the alkyl-substituted carbon−carbon double bond of methoxycarbonylallenes **6** at room temperature or in refluxing benzene yielding benzimidazole-spiro-thiophenes **7** as the major products, whereas triazole carbene-derived triazolium inner salts **14** underwent [3+2] cycloaddition to the ester-substituted double bond predominantly at room temperature to afford exoalkylidene-substituted triazole-spiro-tetrahydrothiophene adducts **15**, which underwent exo-to-endo carbon−carbon double bond isomerization to furnish triazole-spiro-dihydrothiophene **17** at higher temperature. In some cases, the reaction temperature played an important role in regulating the regioselectivity of [3+2]-cycloaddition. The reaction of imidazoline carbene-derived imidazolinium salts **10** with methoxycarbonylallenes **6** at ambient temperature yielded almost all adducts of C^+-C-S^- dipoles to the ester-substituted double bond of **6**. The same reaction performed in refluxing benzene led to the formation of adducts of the alkyl-substituted double bond of methoxycarbonylallenes. Computational study with DFT (B3LYP/6-31G*) revealed asynchronous cycloaddition mechanisms for the reactions of benzimidazole and imidazoline carbene-derived 1,3-dipoles, and a concerted mechanism for the reaction of triazole carbene-derived dipoles. The unusual regioselectivity in the reaction of benzimidazolium salts **5** with methoxycarbonylallenes **6** may be due to the repulsion between the fused benzene moiety of benzimidazolium salts **5** and the ester carbonyl group of allenes **6** in the transition state of reaction. The kinetically favored adducts **11** or **15** from [3+2]-cycloaddition between imidazolinium salts **10** or triazolium salts **14** and the activated ester-substituted double bond of methoxycarbonylallenes at room temperature underwent transformation to products **13** or **17**, respectively, at a high temperature because of the thermodynamical stability of the products. The easy availability of various of *N*-heterocyclic carbene-derived 1,3-dipoles and the predictable high selectivity of the reaction toward allenes should render the protocol valuable for the construction of complex spiro heterocyclic compounds.

Experimental Section

General Procedure for the Reaction of 2-Arylthiocarbamoyl Benzimidazolium Salts 5 with Methoxycarbonylallenes 6. 2-Arylthiocarbamoyl benzimidazolium salts **5** (1 mmol) were mixed with methoxycarbonylallenes **6** (1.5 mmol) in dry benzene (40 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature (20−30 °C) for 24−48 h or at the refluxing temperature of benzene for 2−4 h. After removal of the solvent under vacuum, the residue was chromatographied on a silica gel column eluting with a mixture of petroleum ether (30−60 °C) and ethyl acetate (8:1) to afford benzimidazole-spiro-thiophenes **7** in 56−90% yields from the reaction at room temperature (69−82% from the reaction in refluxing benzene). In some cases, a tiny amount of byproduct were also detected, but only benzimidazole-spiro-pyrrole **9d** (9%) was full characterized.

(*Z*,*Z*)-Methyl 2-[4′-benzyl-1,3,4′,5′-tetrahydro-1,3-bis(4-methoxybenzyl)-2′-(phenylimino)spiro[2*H*-benzo[*d*]imidazole-2,3′(2′*H*)-thiophen]-5′-ylidene]acetate (7b): 510 mg, 75%, yellow crystals (dichloromethane and petroleum ether), mp 168−170 °C; IR υ (cm^{-1}) 1708, 1610, 1512, 1494; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.33−7.37 (m, 6H), 7.16−7.17 (m, 4H), 6.89 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.77 (t, J = 3.4 Hz, 2H), 6.61 (t, J = 7.5 Hz, 1H), 6.55 (t, J = 7.0 Hz, 1H), 6.32 (d, J = 7.3 Hz, 1H), 6.15 (d, J = 7.4 Hz, 1H), 5.87 (d, J = 2.2 Hz, 1H), 4.82 (d, J = 16.8 Hz, 1H), 4.54 (d, J = 16.3 Hz, 1H), 4.46 (d, J = 16.9 Hz, 1H), 4.42 (d, J = 16.3 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.74 (d, J = 15.6 Hz, 1H), 3.64 (s, 3H), 3.53 (d, J = 10.0 Hz, 1H), 2.88 (dd, J = 15.9, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 166.4, 164.8, 159.0, 158.9, 157.8, 150.2, 141.2, 139.8, 138.8, 130.7, 129.5, 129.2, 128.9, 128.8, 128.7, 128.4, 128.3, 128.0, 126.4, 125.4, 119.9, 118.9, 118.4, 114.3, 114.0, 113.8, 111.6, 105.3, 104.1, 98.4, 55.4, 55.3, 51.5, 50.9, 49.1, 48.8, 33.3; MS (ESI) 682 (M + 1). Anal. Calcd for $C_{42}H_{39}N_3O_4S$: C 73.98, H 5.77, N 6.16. Found: C 73.98, H 5.95, N 6.05.

General Procedure for the Reaction of 2-Arylthiocarbamoyl Imidazolinium Salts 10 with Methoxycarbonylallenes 6. 2-Arylthiocarbamoyl imidazolinium salts **10** (1 mmol) were mixed with methoxycarbonylallenes **6** (1.5 mmol) in dry benzene (40 mL) under nitrogen atmosphere. The reaction mixture was stirred at ambient temperature (20−30 °C) for 24 h or in refluxing benzene for 2−13 h. For the reaction at ambient temperature, solvent benzene was evaporated under vacuum at 30−35 °C, and the products **11** (58−83%) and **12** (7−17%) were isolated by chromatography on a neutral Al_2O_3 column eluting with a mixture of petroleum ether (30−60 °C) and ethyl acetate (30:1) followed by evaporating solvents at room temperature. For the reaction in refluxing benzene, products **13** (63−74%) and **12** (11−14%) were isolated by chromatography on a silica gel column eluting with a mixture of petroleum ether (30−60 °C) and ethyl acetate (30:1).

(2′*Z*,5′*E*)-Methyl 1,3-dibenzyl-4′,5′-dihydro-5′-(2-phenylethylidene)-2′-(phenylimino)spiro[imidazolidine-2,3′(2′*H*)-thiophene]-4′-carboxylate (11a): 430 mg, 75%, white crystals (ethyl acetate and petroleum ether), mp 136−137 °C; IR υ (cm^{-1}) 1738, 1643, 1619, 1591; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.49 (d, J = 7.4 Hz, 2H), 7.45 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.18−7.30 (m, 6H), 7.14 (d, J = 10.1 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 5.71 (t, J = 6.4 Hz, 1H), 4.52 (d, J = 13.6 Hz, 1H), 4.40 (s, 1H), 4.16 (d, J = 13.7 Hz, 1H), 3.86 (d, J = 13.8 Hz, 1H), 3.80 (d, J = 13.6 Hz, 1H), 3.72 (s, 3H), 3.40−3.47 (m, 2H), 3.21−3.25 (m, 1H), 3.08−3.13 (m, 2H), 2.90−2.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 169.5, 168.1, 151.8, 139.4, 139.3, 139.0, 131.0, 129.4, 128.6, 128.5, 128.4, 128.35, 128.25, 128.2, 127.2, 126.8, 126.4, 125.0, 124.8, 120.0, 95.7, 55.4, 55.1, 53.2, 52.6, 50.6, 49.0, 35.9; MS (MALDI-TOF) 573 (M^+). Anal. Calcd for $C_{36}H_{35}N_3O_2S$: C 75.36, H 6.15, N 7.32. Found: C 75.27, H 6.42, N 7.23.

(*E*)-Methyl 1,3-dibenzyl-1′-phenyl-5′-(2-phenylethylidene)-2′-thioxospiro[imidazolidine-2,3′-pyrrolidine]-4′-carboxylate (12a): 92 mg, 16%, yellow crystals (ethyl acetate and petroleum ether), mp 165−166 °C; IR υ (cm^{-1}) 1744, 1681, 1602, 1494; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.58 (t, J = 7.4 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.38−7.43 (m, 4H), 7.30−7.35 (m, 4H), 7.22−7.29 (m, 4H), 7.18 (t, J = 6.9 Hz, 1H), 7.08 (d, J = 7.4 Hz, 2H), 4.86 (t, J = 7.8 Hz, 1H), 4.42 (s, 1H), 4.32 (d, J = 13.1 Hz, 1H), 4.10 (d, J = 13.9 Hz, 1H), 3.98 (d, J = 13.9 Hz, 1H), 3.87 (d, J = 13.1 Hz, 1H), 3.77 (s, 3H), 3.29−3.35 (m, 2H), 3.14−3.24 (m, 3H), 3.07−3.10 (m, 1H); ^{13}C NMR (125 MHz) δ (ppm) 197.8, 169.0, 141.6, 139.5, 138.9, 138.8, 137.4, 130.1, 129.3, 128.9, 128.55, 128.48, 128.44, 128.3, 128.2, 127.2, 126.9, 126.4, 109.1, 94.8, 54.3, 52.7, 51.7, 50.2, 48.9, 33.9; MS (MALDI-TOF) 573 (M^+). Anal. Calcd for $C_{36}H_{35}N_3O_2S$: C 75.36, H 6.15, N 7.32. Found: C 75.07, H 6.58, N 7.24.

(*Z*,*Z*)-Methyl 2-[1,3,4′-tribenzyl-4′,5′-dihydro-2′-(phenylimino)-spiro[imidazolidine-2,3′(2′*H*)-thiophen]-5′-ylidene]acetate (13a): 424 mg, 74%, white crystals (ethyl acetate and petroleum ether), mp 101−102 °C; IR υ (cm^{-1}) 1711, 1638, 1593; ^1H NMR (400 MHz, CD_3COCD_3) 7.39 (d, J = 7.4 Hz, 2H), 7.31−7.36 (m, 4H), 7.27 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.14−7.22 (m, 5H), 7.07−7.12 (m, 3H), 7.03 (dd, J = 8.2, 1.2 Hz, 2H), 5.95 (d, J = 2.3 Hz, 1H), 4.36 (d, J = 14.4 Hz, 1H), 3.99 (d, J = 12.8 Hz, 1H), 3.90 (d, J = 14.4 Hz, 1H), 3.78 (d, J = 9.4 Hz, 1H), 3.73 (d, J = 15.8 Hz, 1H), 3.43 (d, J = 13.0 Hz, 1H), 3.41 (s, 3H), 3.08−3.14 (m, 2H), 2.91−2.96 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.0, 166.6, 161.2, 150.9, 140.8, 139.4, 138.4, 129.5, 128.9, 128.6, 128.5, 128.4, 128.2, 128.1, 127.3, 127.0, 126.3,

125.1, 120.0, 110.3, 90.9, 54.1, 53.9, 51.4, 50.1, 49.8, 48.1, 33.2; MS (ESI): 574 (M + 1). Anal. Calcd for $C_{36}H_{35}N_3O_2S$: C 75.36, H 6.15, N 7.32. Found: C 75.23, H 6.31, N 7.14.

General Procedure for the Reaction of 2-Arylthiocarbamoyl Triazolium Salts 14 with Methoxycarbonylallenes 6. 2-Arylthiocarbamoyl triazolium salts **14** (2 mmol) were mixed with methoxycarbonylallenes **6** (3 mmol) in dry benzene or toluene (60 mL) under nitrogen atmosphere. The reaction mixture in benzene was stirred at ambient temperature (20−30 °C) for 15−24 h or in refluxing toluene for 2−12 h. For the reaction at ambient temperature, solvent benzene was evaporated under vacuum at 30−35 °C, and the products **15-I** (52−65%), **15-II** (10−13%) and **16-I** (14−24%), **16-II** (4−6%) were isolated by chromatography on a silica gel column eluting with a mixture of petroleum ether (30−60 °C) and ethyl acetate (15:1) followed by evaporating solvents at room temperature. For the reaction in refluxing toluene, products **17** (52−63%) and **18** (19−22%) were isolated by chromatography on a silica gel column eluting with a mixture of petroleum ether (30−60 °C) and ethyl acetate (15:1).

(5*S*,4′*R*,2′*Z*,5′*E*) or (5*R*,4′*S*,2′*Z*,5′*E*)-methyl 1,4,4′,5′-tetrahydro-1,3,4-triphenyl-5′-(2-phenylethylidene)-2′-(phenylimino)spiro[3*H*-1,2,4-triazole-5,3′(2′*H*)-thiophene]-4′-carboxylate (15a-I): 806 mg, 65%, yellow solid (without recrystallization), mp 96−97 °C; IR υ (cm^{-1}) 1744, 1626, 1593, 1492; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.59 (dd, J = 7.3, 1.5 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.26−7.32 (m, 9H), 7.23−7.24 (m, 5H), 7.14−7.18 (m, 4H), 7.07 (t, J = 7.5 Hz, 1H), 6.97 (t, J = 7.0 Hz, 1H), 6.08 (d, J = 7.5 Hz, 2H), 5.88 (dt, J = 6.1, 2.6 Hz, 1H), 4.91 (t, J = 1.1 Hz, 1H), 3.67 (s, 3H), 3.48 (dd, J = 16.1, 6.2 Hz, 1H), 3.30 (dd, J = 16.2, 8.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 169.8, 165.0, 151.5, 147.5, 140.8, 139.4, 139.0, 129.24, 129.20, 129.0, 128.7, 128.6, 128.44, 128.38, 127.8, 127.7, 127.4, 127.2, 126.60, 126.56, 125.0, 119.9, 118.5, 114.7, 98.1, 53.4, 52.9, 36.6; HRMS (TOF-EI) 620.2252, $C_{39}H_{32}N_4O_2S$ required 620.2246.

(5*R*,4′*R*,2′*Z*,5′*E*)- or (5*S*,4′*S*,2′*Z*,5′*E*)-methyl 1,4,4′,5′-tetrahydro-1,3,4-triphenyl-5′-(2-phenylethylidene)-2′-(phenylimino)spiro[3*H*-1,2,4-triazole-5,3′(2′*H*)-thiophene]-4′-carboxylate (15a-II): 81 mg, 13%, yellow crystals, mp 153−154 °C; IR υ (cm^{-1}) 1750, 1633, 1592, 1487; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.55 (d, J = 7.2 Hz, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.23−7.35 (m, 10H), 7.13−7.21 (m, 7H), 7.00−7.06 (m, 2H), 6.20 (d, J = 7.7 Hz, 2H), 5.86 (t, J = 6.8 Hz, 1H), 4.58 (s, 1H), 3.64 (s, 3H), 3.49 (dd, J = 16.2, 6.6 Hz, 1H), 3.35 (dd, J = 16.1, 8.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 168.7, 166.1, 151.6, 149.5, 143.7, 139.0, 138.5, 129.4, 129.2, 129.1, 128.7, 128.44, 128.39, 128.3, 128.22, 127.8, 127.1, 127.0, 126.5, 124.9, 122.0, 119.5, 118.5, 99.8, 57.0, 52.9, 36.2; MS (-c ESI): 619 (M − 1). Anal. Calcd for $C_{39}H_{32}N_4O_2S$: C 75.46, H 5.20, N 9.03. Found: C 75.62, H 5.38, N 8.74.

(5*S*,4′*R*,*E*)- or (5*R*,4′*S*,*E*)-methyl 1,4-dihydro-1,1′,3,4-tetraphenyl-5′-(2-phenylethylidene)-2′-thioxospiro[3*H*-1,2,4-triazole-5,3′-pyrrolidine]-4′-carboxylate (16a-I): 93 mg, 15%, yellow crystals, mp 177−178 °C; IR υ (cm^{-1}) 1746, 1594, 1492; ^1H NMR (500 MHz) δ (ppm) 7.56 (d, J = 7.3 Hz, 2H), 7.53 (br s, 1H), 7.41 (br s, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.20−7.32 (m, 14H), 7.17 (d, J = 7.7 Hz, 2H), 6.99 (t, J = 7.2 Hz, 1H), 6.66 (br s, 1H), 5.19 (t, J = 7.0 Hz, 1H), 5.03 (s, 1H), 3.57 (s, 3H), 3.48 (dd, J = 16.5, 7.0 Hz, 1H), 3.24 (dd, J = 16.4, 8.1 Hz, 1H); ^{13}C NMR (125 MHz) δ (ppm) 190.4, 169.2, 147.5, 141.3, 139.3, 139.1, 138.9, 137.3, 130.2, 129.4, 129.3, 129.2, 128.6, 128.4, 128.0, 127.7, 127.0, 126.5, 126.4, 120.6, 115.6, 112.2, 97.2, 52.8, 49.4, 34.3; MS (-c ESI): 619 (M − 1). Anal. Calcd for $C_{39}H_{32}N_4O_2S$: C 75.46, H 5.20, N 9.03. Found: C 75.29, H 5.40, N 8.92.

(5*R*,4′*R*,*E*)- or (5*S*,4′*S*,*E*)-methyl 1,4-dihydro-1,1′,3,4-tetraphenyl-5′-(2-phenylethylidene)-2′-thioxospiro[3*H*-1,2,4-triazole-5,3′-pyrrolidine]-4′-carboxylate (16a-II): 31 mg, 5%, yellow crystals, mp 164−165 °C; IR υ (cm^{-1}) 1748, 1593, 1493; ^1H NMR (500 MHz) δ (ppm) 7.49 (t, J = 7.3 Hz, 4H), 7.43 (d, J = 7.1 Hz, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.26−7.36 (m, 10H), 7.22 (t, J = 6.9 Hz, 2H), 7.18 (t, J = 7.0 Hz, 1H), 6.99−7.03 (m, 5H), 5.10 (t, J = 7.6 Hz, 1H), 4.43 (s, 1H), 3.77 (s, 3H), 3.40 (dd, J = 16.7, 6.9 Hz, 1H), 3.16 (dd, J = 16.4, 8.2 Hz, 1H); ^{13}C NMR (125 MHz) δ (ppm) 193.1, 168.1, 149.9, 143.6, 139.4, 139.3, 137.9, 137.3, 130.2, 129.5, 129.3, 128.5, 128.3, 128.2, 127.7, 127.2, 126.3, 122.4, 119.3, 111.6, 99.0, 52.9, 51.3, 33.9; MS (-c ESI) 619 (M − 1). Anal. Calcd for $C_{39}H_{32}N_4O_2S$: C 75.46, H 5.20, N 9.03. Found: C 75.16, H 5.42, N 8.78.

(*Z*)-Methyl 1,4-dihydro-5′-phenethyl-1,3,4-triphenyl-2′-(phenylimino)spiro[3*H*-1,2,4-triazole-5,3′(2′*H*)-thiophene]-4′-carboxylate (17a): 384 mg, 62%, red crystals, mp 110−111 °C; IR υ (cm^{-1}) 1699, 1641, 1593, 1493; ^1H NMR (500 MHz) δ (ppm) 7.54 (d, J = 6.7 Hz, 2H), 7.22−7.32 (m, 15H), 7.11−7.13 (m, 3H), 7.04 (d, J = 6.5 Hz, 2H), 6.88 (t, J = 6.7 Hz, 1H), 6.50 (d, J = 7.3 Hz, 2H), 3.72 (s, 3H), 3.21−3.27 (m, 2H), 2.82 (t, J = 7.8 Hz, 2H); ^{13}C NMR (125 MHz) δ (ppm) 166.6, 162.4, 159.8, 151.2, 147.3, 143.0, 140.0, 138.6, 129.6, 129.2, 129.1, 128.7, 128.6, 128.3, 128.2, 128.0, 127.5, 126.6, 126.5, 125.6, 120.1, 119.9, 118.8, 114.7, 98.0, 51.8, 34.3, 34.1; MS (-c ESI) 619 (M − 1). Anal. Calcd for $C_{39}H_{32}N_4O_2S$: C 75.46, H 5.20, N 9.03. Found: C 75.57, H 5.32, N 8.98.

Methyl 1,4-dihydro-5′-phenethyl-1,1′,3,4-tetraphenyl-2′-thioxospiro[3*H*-1,2,4-triazole-5,3′(2′*H*)-pyrrole]-4′-carboxylate (18a): 273 mg, 22%, green crystals, mp 167−168 °C; IR υ (cm^{-1}) 1705, 1629, 1594, 1492; ^1H NMR (500 MHz) δ (ppm) 7.57−7.61 (m, 3H), 7.54 (d, J = 7.3 Hz, 2H), 7.23−7.34 (m, 8H), 7.15−7.21 (m, 4H), 7.12 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 7.5 Hz, 2H), 6.88 (t, J = 6.8 Hz, 2H), 6.84 (d, J = 7.0 Hz, 2H), 3.74 (s, 3H), 2.91−2.97 (m, 1H), 2.82−2.87 (m, 1H), 2.53 (t, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz) δ (ppm) 207.4, 162.5, 160.4, 147.4, 143.2, 139.9, 138.1, 135.9, 130.2, 130.1, 129.9, 129.1, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 127.8, 127.5, 126.9, 126.5, 120.1, 114.8, 111.2, 95.2, 51.4, 33.4, 29.2; MS (-c ESI) 619 (M − 1). Anal. Calcd for $C_{39}H_{32}N_4O_2S$: C 75.46, H 5.20, N 9.03. Found: C 75.16, H 5.42, N 8.79.

Computational Methods. Density functional calculations have been performed with the Gaussian 03 program package.[11] The geometric parameters of the possible transition states, reactants and products are optimized with B3LYP/6−31G* method, and verified with the number of imaginary frequencies. In order to confirm whether the reactions proceed in a concerted or a stepwise way, Intrinsic Reaction Coordiates (IRC)[12] have been traced for the relevant reaction paths.

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Supporting Information Available: The experimental procedures for the reactions of 2-arylthiocarbamoyl benzimidazolium salts **5**, imidazolinium salts **1,0** and triazolium salts **14** with methoxycarbonylallenes **6**, full characterization for products **7**, **11**, **12**, **13**, **15**, **16**, **17**, and **18** excluding those byproducts without isolation, copies of ^1H NMR and ^{13}C NMR spectra of products **7**, **11**, **12**, **13**, **15**, **16**, **17**, and **18**, as well as single crystal data of **7a**, **11a**, **12g**, **13a**, **15e-I**, **16e-I**, **16e-II**, and **17e** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) See the Supporting Information.

(12) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523–5527.