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Alkenylation of thiophenes and furans at the 2-position and a synthesis of allenes conjugated with α,β-unsaturated ester with magnesium alkylidene carbenoids

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ABSTRACT

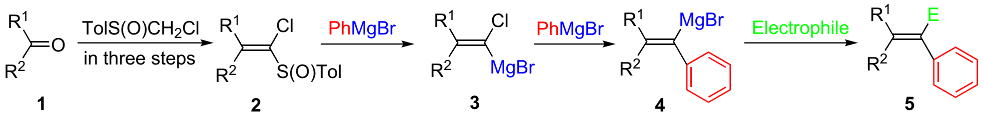
The reaction of 1-chlorovinyl *p*-tolyl sulfoxides, derived from ketones and chloromethyl *p*-tolyl sulfoxide, with *i*-PrMgCl at −78 °C gave magnesium alkylidene carbenoids. Treatment of the magnesium carbenoids with 2-lithiothiophenes and 2-lithiofurans resulted in the formation of 2-alkenylated thiophenes and furans, respectively, in good to high yields. The intermediates of these reactions were found to be alkenylmagnesium, which could be trapped with several electrophiles to afford thiophenes and furans bearing a fully substituted alkene at the 2-position. Treatment of the magnesium alkylidene carbenoids with 2-lithio-5-methoxyfuran afforded allenes conjugated with α,β-unsaturated methyl ester in moderate yields. These procedures offer a new and versatile one-pot synthesis of 2-alkenylthiophenes, 2-alkenylfurans, and allenes conjugated with α,β-unsaturated methyl ester from 1-chlorovinyl *p*-tolyl sulfoxides.

1. Introduction

Carbenes and carbenoids are obviously one of the most interesting highly reactive carbon species in organic synthesis; however, in particular case, they are too reactive to be controlled.[1] In fact, methylene must be classed as the most indiscriminate reactive species known in organic chemistry.[2] In this decade, we have studied the chemistry of magnesium carbenoids as more stable carbenoid species and we have reviewed our work.[3]

For example, as shown in Scheme 1, treatment of 1-chlorovinyl *p*-tolyl sulfoxides **2**, derived from ketones **1** and chloromethyl *p*-tolyl sulfoxide, with phenylmagnesium bromide resulted in the formation of magnesium alkylidene carbenoids **3** by the sulfoxide–magnesium exchange reaction. The magnesium alkylidene carbenoids **3** were found to be stable at low temperature[4,5] and reacted with phenylmagnesium bromide to give phenylated alkenylmagnesium intermediate **4**, which was able to be trapped with electrophiles to afford fully substituted styrene derivatives **5** in good yields.[5]

In continuation of our interest in the chemistry of magnesium alkylidene carbenoids in organic synthesis, we investigated the reaction of **3** with lithiated heteroaromatic compounds and found that the reaction of **3** with 2-lithiothiophenes and 2-lithiofurans gave alkenylmagnesium intermediates bearing thiophenes and furans, respectively, **6** in good to high yields (Scheme 2).[6] These intermediates were found to be trapped with several electrophiles to afford thiophenes and furans **7** bearing fully substituted olefins at the 2-position in good yields. Very interesting reaction was found from the reaction of **3** with 2-lithio-5-methoxyfuran. Thus, the reaction gave alkenylmagnesium intermediate **8**, which afforded allenes conjugated with α,β-unsaturated methyl ester **9** in moderate to good yields. In this paper, we report in detail the above-mentioned reactions.



Scheme 1.

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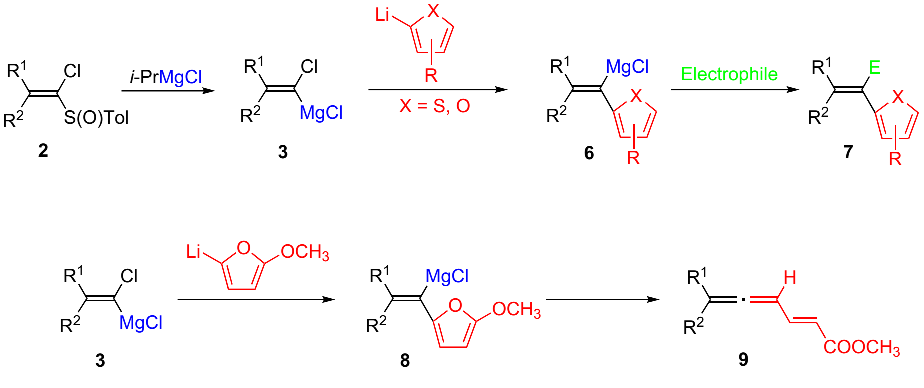
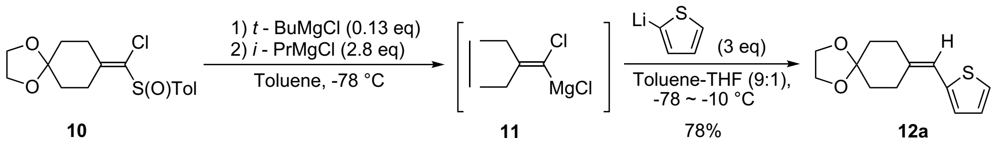


Scheme 2.



Scheme 3.

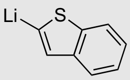
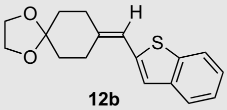
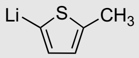
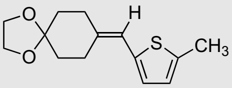
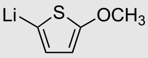
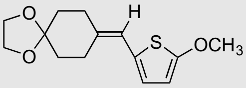
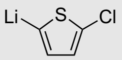
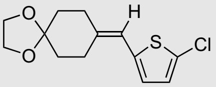
2. Results and discussion

2.1. Alkenylation of thiophenes at the 2-position with magnesium alkylidene carbenoids

At first, 1-chlorovinyl *p*-tolyl sulfoxide **10** was synthesized from cyclohexane-1,4-dione mono ethylene ketal in three steps in high overall yield (Scheme 3).[5,7] To a solution of **10** in THF was added *t*-BuMgCl (0.13 equiv) to remove a trace of moisture in the reaction mixture. To this solution was added *i*-PrMgCl (2.8 equiv) at −78 °C. Magnesium alkylidene carbenoid **11** was generated instantaneously. A solution of 2-lithiothiophene (3 equiv), generated from thiophene with *n*-BuLi in THF, was added to a solution of the magnesium alkylidene carbenoid through a cannula and the reaction mixture was slowly allowed to warm to −10 °C. Fortunately, the desired reaction took place to afford 2-alkenylthiophene **12a** in 60% yield.

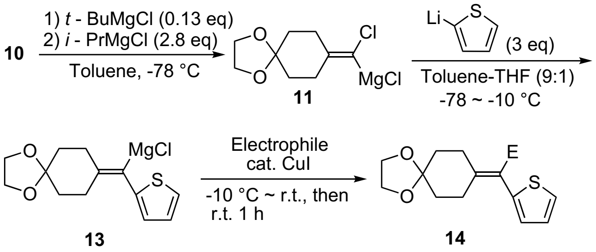
In order to improve the yield of the product **12a**, amount of *i*-PrMgCl, solvent, and additive were investigated as reported in the preliminary letter[6] and a mixture of toluene–THF (9:1) was found to be the solvent of choice and use of 2.8 equiv of *i*-PrMgCl was found to be suitable to the reaction and alkenylated thiophene **12a** was obtained in 78% yield (Scheme 3). As the methods for obtaining alkenylated thiophenes are quite limited,[8] the procedure presented herein was thought to be useful to a synthesis of 2-alkenylthiophenes. We investigated the generality of this reaction by using the above-mentioned conditions, and the results are summarized in Table 1.

Table 1
Reaction of magnesium alkylidene carbenoid **11** with 2-lithiothiophenes

Entry	2-Lithiothiophene[a]	Product/**12**	Yield/%
1		 **12b**	67[b]
2		 **12c**	77
3		 **12d**	80
4		 **12e**	80

[a] All 2-lithiothiophenes were generated from the corresponding thiophenes with *n*-BuLi.
[b] 2-Lithiobenzothiophene was generated with *t*-BuLi.

Table 2
Reaction of alkenylmagnesium intermediate **13** with electrophiles to give thiophenes bearing a fully substituted olefin at the 2-position **14**

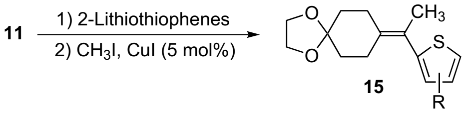


Entry	Electrophile (equiv)	CuI (mol %)	**14**		
			E	Yield/%	
1	CH_3OD	None	D	**14a**	78[a]
2	CH_3I (3)	5	CH_3	**14b**	72
3	CH_3CH_2I (10)	5	CH_2CH_3	**14c**	69[b]
4	$CH_2{=}CHCH_2I$ (3)	5	$CH_2CH{=}CH_2$	**14d**	67
5	$(CH_3)_2CHI$ (10)	5	$CH(CH_3)_2$	—[c]	
6	$PhCH_2Br$ (3)	5	CH_2Ph	**14e**	72
7	$ClCOOC_2H_5$ (10)	None	$COOC_2H_5$	**14f**	70
8	I_2 (10)	None	I	**14g**	71

[a] Deuterium content 97%.
[b] The reaction mixture was stirred at room temperature for 3 h.
[c] Compound **12a** was obtained as a main product.

Table 3

Reaction of magnesium alkylidene carbenoid **11** with 2-lithiothiophenes followed by iodomethane to give thiophenes having a fully substituted olefin at the 2-position **15**



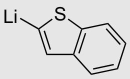
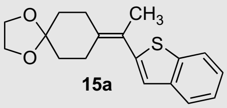
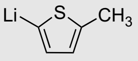
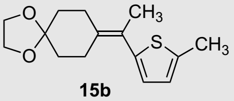
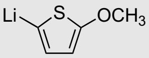
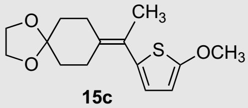
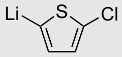
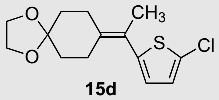
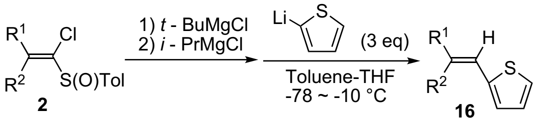
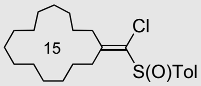
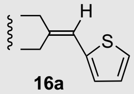
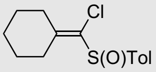
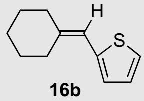
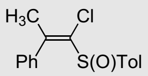
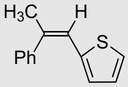
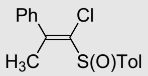
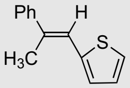
Entry	2-Lithiothiophene	15	
			Yield/%
1		 **15a**	58
2		 **15b**	75
3		 **15c**	70
4		 **15d**	77

Table 4

Synthesis of 2-alkenylthiophenes **16** from 1-chlorovinyl *p*-tolyl sulfoxides **2** with 2-lithiothiophene



Entry	1-Chlorovinyl *p*-tolyl sulfoxide	2-Alkenylthiophene 16		
			E/*Z*	Yield/%
1	 **2a**	 **16a**	—	63
2	 **2b**	 **16b**	—	72
3	 **2c** (*E*)	 **16c** (*Z*)	34/66	60
4	 **2d** (*Z*)	 **16d** (*E*)	81/19	73

2-Lithiobenzothiophene was generated from benzothiophene with *t*-BuLi in a mixture of toluene–THF, and it was treated with magnesium alkylidene carbenoid **11**, generated from **10** with *i*-PrMgCl in toluene, to give the desired 2-alkenylated benzothiophene **12b** in 67% yield (entry 1). 2-Lithiothiophenes bearing an electron-donating group at the 5-position gave the desired products **12c** and **12d** in about 80% yields (entries 2 and 3). 2-Lithiothiophene bearing a chlorine atom at the 5-position gave the desired product **12e** without any problem (entry 4). From these results, generality of this reaction was thought to be verified.

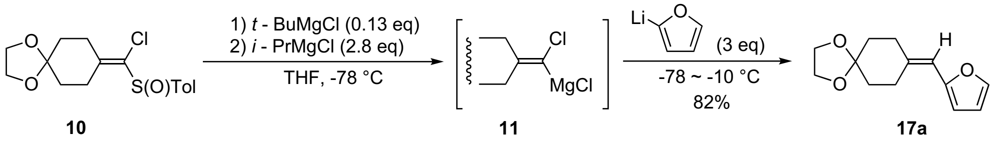
On the bases of our previous investigations,[5,9] the intermediate of this reaction was thought to be alkenylmagnesium **13** (Table 2). To ascertain that the intermediate was the expected alkenylmagnesium, the reaction of magnesium alkylidene carbenoid **11** with 2-lithiothiophene was quenched with CH_3OD. This reaction afforded 2-alkenylthiophene bearing a deuterium at the olefin carbon **14a** (E=D) in 78% yield with 97% deuterium incorporation (Table 2, entry 1). From this result, the intermediate of this reaction was confirmed to be alkenylmagnesium **13**.

It was thought that if this alkenylmagnesium intermediate **13** could be trapped with electrophiles, a new method for a synthesis of thiophenes bearing a fully substituted olefin would be achieved. To this end, iodomethane (10 equiv) was added to the reaction mixture. This reaction gave the methylated product **14b** ($E{=}CH_3$); however, the yield was not satisfactory (54%). After some investigations, Cu(I) iodide was found to be the effective catalyst in this reaction. Thus, after generation of the intermediate **13**, Cu(I) iodide (5 mol %) followed by iodomethane (3 equiv) was added to the reaction mixture at -10 °C and the reaction mixture was slowly allowed to warm to room temperature. The stirring was continued for 1 h at room temperature to give the desired methylated product **14b** in much better 72% yield (entry 2).

The ethylation reaction required 10 equiv of iodoethane and much longer reaction time to give the desired product **14c** in 69% yield (entry 3). Allyl iodide, benzyl bromide worked well; however, 2-iodopropane did not give the desired product at all (entries 4–6). Ethyl chloroformate and iodine gave ethoxycarbonylated and iodinated products, **14f** and **14g**, respectively, in good yields (entries 7 and 8). Unfortunately, benzaldehyde and acetone did not afford the expected adduct but the protonated product **12a**. The reaction with benzoyl chloride gave a complex mixture.

In order to verify that this procedure could be applicable to other thiophenes, the reaction of magnesium alkylidene carbenoid **11** with 2-lithiothiophenes followed by iodomethane was carried out and the results are summarized in Table 3. Comparing the results in Table 3 with those in Table 1, the yields for the methylation of **11** with iodomethane giving **15a**–**15d** are high (86–97%). From the results shown in Table 3, it is verified that the method mentioned above is applicable to various thiophenes.

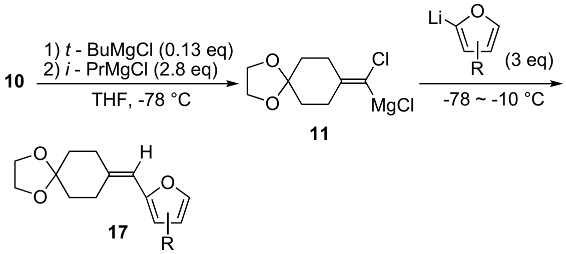
Next, generality of this reaction was investigated using various 1-chlorovinyl *p*-tolyl sulfoxides with 2-lithiothiophene and the results are summarized in Table 4. 1-Chlorovinyl *p*-tolyl sulfoxides prepared from cyclopentadecanone and cyclohexanone gave the desired products **16a** and **16b**, respectively, in good yields (entries 1 and 2). Low stereospecificity was observed in the reaction with geometrical isomers **2c** and **2d** (entries 3 and 4). *E*-Vinyl sulfoxide **2c** gave *Z*-olefin **16c** as main product. In contrast to this, *Z*-vinyl sulfoxide **2d** mainly gave *E*-olefin **16d**.

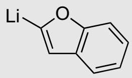
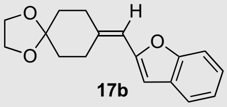
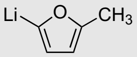
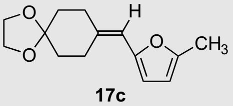
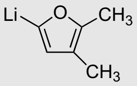
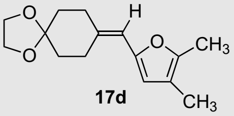
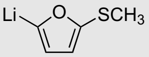
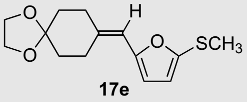
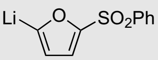
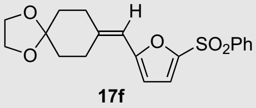


10 **11** **17a**

Scheme 4.

Table 5
Reaction of 1-chlorovinyl *p*-tolyl sulfoxide **10** with Grignard reagents followed by 2-lithiofurans to give furans bearing an olefin at the 2-position **17**



Entry	2-Lithiofuran	Product/**17**	Yield/%
1		 **17b**	72
2		 **17c**	68
3		 **17d**	60
4[a]		 **17e**	62
5[b]		 **17f**	44

[a] 2-Methylthiofuran was synthesized by Cohen's procedure; Nolan, S. M.; Cohen, T. *J. Org. Chem.* **1981**, *46*, 2473.

[b] 2-Phenylsulfonylfuran was derived from 2-phenylthiofuran with *m*-CPBA.

2.2. Alkenylation of furans at the 2-position with magnesium alkylidene carbenoids

As an extension of the above-mentioned chemistry, we investigated the reaction of magnesium alkylidene carbenoid **11** with 2-lithiofurans (Scheme 4). Thus, 1-chlorovinyl *p*-tolyl sulfoxide **10** was treated with *t*-BuMgCl followed by *i*-PrMgCl in THF at −78 °C to give magnesium alkylidene carbenoid **11**. A solution of 2-lithiofuran (generated from furan with *n*-BuLi in THF; 3 equiv) was added to the solution of **11** and the temperature of the reaction mixture was slowly allowed to warm to −10 °C. This reaction gave the desired 2-alkenylfuran **17a** in 82% yield. We investigated to find the better conditions for the formation of **17a**; however, the reaction conditions carried out at the first time proved to be the best.

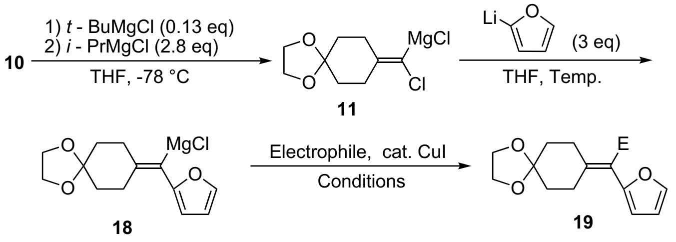
Next, generality of this reaction was studied by using various 2-lithiofurans and the results are summarized in Table 5. All 2-lithiofurans were generated easily with *n*-BuLi. As shown in Table 5, benzofuran and the furans having an electron-donating group gave the desired products **17b**–**17e** in 60–70% yields (entries 1–4). On the other hand, 2-lithiofuran bearing an electron-withdrawing group gave the product **17f** in much worse yield (entry 5). Comparing the results in Table 5 with those in Table 3, 2-lithiothiophenes gave somewhat better yields in this reaction.

The intermediate of this reaction was again found to be the alkenylmagnesium **18** (Table 6). Thus, quenching the reaction of **11** with 2-lithiofuran with CH_3OD gave deuterated alkenylfuran **19a** in 78% yield with 96% deuterium content (Table 6, entry 1). In the same way described above, the intermediate **18** could be trapped with various electrophiles to afford furans bearing a fully substituted alkene at the 2-position. The reaction conditions and the results are summarized in Table 6.

Alkylation of **18** with haloalkanes proceeded well in the presence of Cu(I) iodide to afford **19b**–**19e** in good yields (entries 2–5). Benzaldehyde gave the adduct **19g** in 73% yield. Ethyl chloroformate gave the desired product **19f** in moderate yield (entry 6); however, benzoyl chloride only gave a complex mixture (entry 8). The reaction with iodine gave the desired alkenyl iodide **19h** in good yield (entry 9).

Finally, generality of the reaction of magnesium alkylidene carbenoids with 2-lithiofurans was investigated by using some

Table 6
Reaction of alkenylmagnesium intermediate **18** with electrophiles to give furans bearing a fully substituted olefin **19**



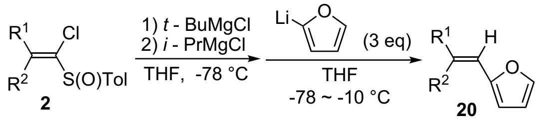
Entry	Electrophile (equiv)	CuI (mol %)	E	Temp	Conditions	**19**	
						Yield/%	
1	CH_3OD	None	D	−78 to −10 °C	−10 °C to rt, 1 h	**19a**	78[a]
2	CH_3I (6)	5	CH_3	−78 to −10 °C	−10 °C to rt, 1 h	**19b**	79
3	CH_3CH_2I (6)	5	CH_2CH_3	−78 to −10 °C	−10 °C to rt, 2 h	**19c**	67
4	$CH_2{=}CHCH_2I$ (3)	5	$CH_2CH{=}CH_2$	−78 to −10 °C	−10 °C to rt, 1 h	**19d**	75
5	$PhCH_2Br$ (6)	5	CH_2Ph	−78 to −30 °C	−30 °C to rt, 1 h	**19e**	73
6	$ClCOOC_2H_5$ (10)	None	$COOC_2H_5$	−78 to −30 °C	−30 °C to rt, 2 h	**19f**	62
7	PhCHO (10)	None	CH(Ph)OH	−78 to −30 °C	−30 to −15 °C, 20 min	**19g**	73
8	PhCOCl (10)	None	COPh	−78 to −10 °C	−10 °C to rt, 1 h		—[b]
9	I_2 (10)	None	I	−78 to −10 °C	−10 °C to rt, 1 h	**19h**	70

[a] Deuterium content 96%.

[b] A complex mixture was obtained.

Table 7

Synthesis of 2-alkenylfurans **20** from 1-chlorovinyl *p*-tolyl sulfoxides **2** with 2-lithiofuran



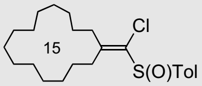
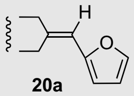
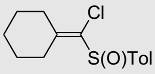
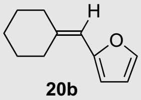
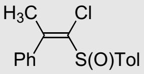
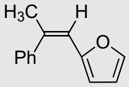
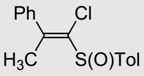
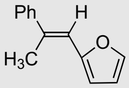
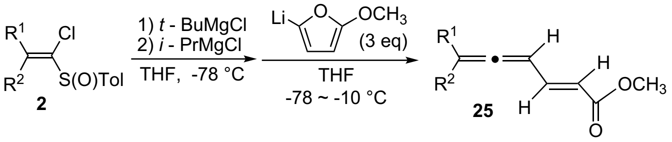
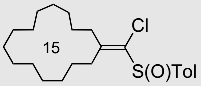
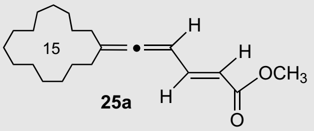
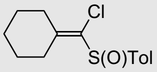
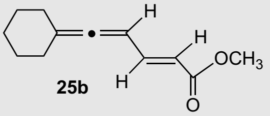
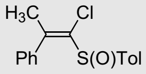
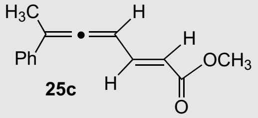
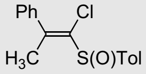
Entry	1-Chlorovinyl *p*-tolyl sulfoxide	2-Alkenylfuran **20**		
			E/*Z*	Yield/%
1	 **2a**	 **20a**	—	57
2	 **2b**	 **20b**	—	56
3	 **2c** (*E*)	 **20c** (*Z*)	42/58	74
4	 **2d** (*Z*)	 **20d** (*E*)	82/18	73

Table 8

Synthesis of allenes conjugated with α,β-unsaturated methyl esters **25** from 1-chlorovinyl *p*-tolyl sulfoxides **2** with 2-lithio-5-methoxyfuran



Entry	1-Chlorovinyl *p*-tolyl sulfoxide	Allene **25**	
			Yield/%
1	 **2a**	 **25a**	54
2	 **2b**	 **25b**	54
3	 **2c** (*E*)	 **25c**	45
4	 **2d** (*Z*)	**25c**	40

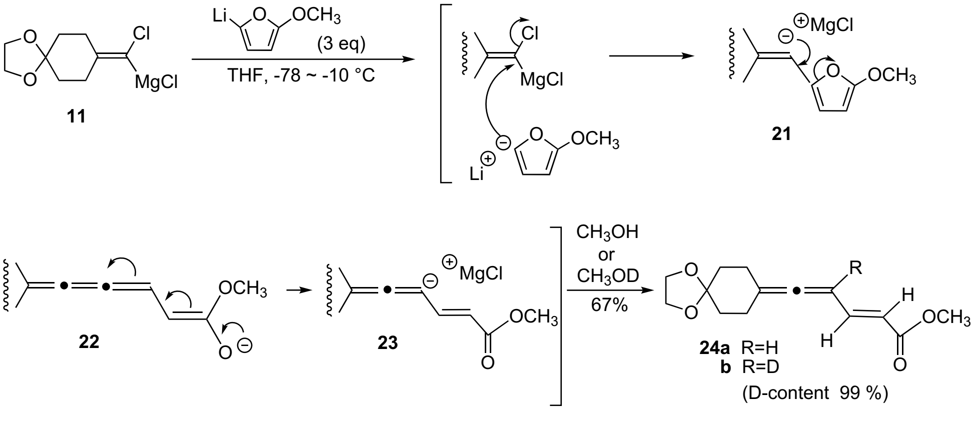
1-chlorovinyl *p*-tolyl sulfoxides and 2-lithiofuran and the results are summarized in Table 7. Quite similar stereospecificity was observed in the reaction with **2c** and **2d** (entries 3 and 4; compare the results in Table 4).

2.3. Synthesis of allenes conjugated with α,β-unsaturated methyl ester by the reaction of magnesium alkylidene carbenoids with 2-lithio-5-methoxyfuran

Very interesting reaction was found from the reaction of magnesium alkylidene carbenoid with 2-lithio-5-methoxyfuran (Scheme 5). Thus, the reaction of magnesium alkylidene carbenoid **11** with 2-lithio-5-methoxyfuran under the same conditions as described above gave an unexpected product in 67% yield. Infrared absorption of the product showed 1947 cm^{-1} (allene) and 1709 cm^{-1} (carbonyl absorption for an α,β-unsaturated ester). ^{13}C NMR showed signals at δ 206.5 (allene) and δ 167.2 (ester carbonyl). ^{1}H NMR showed three olefinic protons δ 5.82 (1H, m), 5.85 (1H, d, J=15.6 Hz), 7.18 (1H, dd, J=15.6, 11.0 Hz). From the spectral data, an allene conjugated with α,β-unsaturated methyl ester was determined to be the structure of the product **24a**.

A plausible mechanism for the reaction is shown in Scheme 5. Thus, 2-lithio-5-methoxyfuran attacks the carbenoid carbon to give alkenylmagnesium intermediate **21**. The anion would cleave the C–O bond of the furan ring[10] to afford 1,2,3-triene conjugated with enolate **22**. This triene intermediate must be unstable and transfer of the charge on the oxygen to the allenic carbon gives intermediate **23**, which is protonated to give product **24a**. When this reaction was quenched with CH_3OD, deuterated allene **24b** was obtained with perfect deuterium incorporation.

As we recognized that this reaction is quite useful for a synthesis of allenes conjugated with α,β-unsaturated esters, generality of this



Scheme 5.

reaction was investigated and the results are summarized in Table 8. Both magnesium alkylidene carbenoids derived from **2a** (having a large cyclic chain) and **2b** (having a medium sized cyclic chain) gave expected allenes **25a** and **25b**, respectively, in the same moderate yields (entries 1 and 2). The reaction of the magnesium alkylidene carbenoids derived from the geometrical isomers **2c** and **2d** gave the same allene **25c** in somewhat lower yields (entries 3 and 4). Although the yields of allenes **25** are not satisfactory, this method is very useful for a short synthesis of allenes conjugated with α,β-unsaturated methyl ester.

3. Conclusion

In conclusion, we have developed a new method for alkenylation of thiophenes and furans at the 2-position from 1-chlorovinyl *p*-tolyl sulfoxide with 2-lithiothiophenes and 2-lithiofurans in one-pot. This method could be expanded to a synthesis of thiophenes and furans bearing a fully substituted olefin at the 2-position. Moreover, a new method for a synthesis of allenes conjugated with α,β-unsaturated methyl esters was developed by the reaction of magnesium alkylidene carbenoids with 2-lithio-5-methoxyfuran. We believe that the method presented herein will contribute to the synthesis of the products mentioned above and to the chemistry of magnesium carbenoids.

4. Experimental

4.1. General

All melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 300, 500, BRUKER DPX 400, and AV 600 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion by HITACHI M-80B mass spectrometer. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR instrument. Silica gel 60 N containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiment requiring a dry solvent and reagent, diisopropylamine and toluene were distilled from CaH_2, and THF was distilled from diphenylketyl. Compounds **2a**, **2b**, **2c**, **2d** and **10** are known.[5]

*4.1.1. 8-Thiophen-2-ylmethylene-1,4-dioxaspiro[4.5]decane (**12a**)*

To a solution of **10** (98.0 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.04 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to the reaction mixture to give magnesium alkylidene carbenoid **11**. In another flask, *n*-BuLi (1.65 M solution in hexane, 0.6 mL; 0.99 mmol) was added dropwise to a solution of thiophene (0.072 mL; 0.9 mmol) in a mixture of 3 mL of dry toluene and 1 mL of THF at −78 °C under argon atmosphere to give 2-lithiothiophene. After 30 min, this solution was added to a solution of carbenoid **11** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give **12a** (55 mg; 78%) as colorless oil. IR (neat) 3104, 2949, 2881, 1648, 1432, 1120, 1082, 907, 761, 693 cm^{-1}; ^{1}H NMR δ 1.76 (4H, dt, *J*=6.5, 5.5 Hz), 2.42 (2H, t, *J*=6.6 Hz), 2.70 (2H, t, *J*=6.6 Hz), 3.99 (4H, s), 6.36 (1H, s), 6.89 (1H, d, *J*=3.4 Hz), 6.97 (1H, dd, *J*=5.1, 3.5 Hz), 7.19 (1H, d, *J*=5.1 Hz). MS *m*/*z* (%) 236 (M$^+$, 100), 207 (40), 192 (9), 191 (13), 174 (17), 163 (10), 149 (12), 135 (30), 121 (14), 97 (19), 91 (14), 77 (8), 55 (8), 42 (11). Calcd for $C_{13}H_{16}O_2S$: M, 236.0869. Found: *m*/*z* 236.0864.

*4.1.2. 8-Benzo[b]thiophen-2-ylmethylene-1,4-dioxaspiro[4.5]decane (**12b**)*

Colorless crystals; mp 112–112.5 °C (AcOEt–hexane); IR (KBr) 2949, 2881, 2865, 1643, 1431, 1379, 1228, 1139, 1116, 1079, 1036, 907, 877, 741, 726 cm^{-1}; ^{1}H NMR δ 1.77 (2H, t, *J*=6.1 Hz), 1.81 (2H, t, *J*=6.2 Hz), 2.47 (2H, t, *J*=6.6 Hz), 2.77 (2H, t, *J*=6.6 Hz), 4.00 (4H, s), 6.43 (1H, s), 7.09 (1H, s), 7.23–7.34 (2H, m), 7.69 (1H, d, *J*=7.1 Hz), 7.76 (1H, d, *J*=7.5 Hz). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; S, 11.20. Found: C, 71.12; H, 6.15; S, 11.14.

*4.1.3. 8-(5-Methylthiophen-2-ylmethylene)-1,4-dioxaspiro[4.5]decane (**12c**)*

Yellow oil; IR (neat) 2948, 2880, 1648, 1441, 1382, 1233, 1119, 1080, 1034, 906, 794, 685 cm^{-1}; ^{1}H NMR δ 1.71–1.79 (4H, m), 2.39 (2H, t, *J*=6.6 Hz), 2.45 (3H, s), 2.67 (2H, t, *J*=6.4 Hz), 3.98 (4H, s), 6.27 (1H, s), 6.61 (1H, dd, *J*=3.5, 1.1 Hz), 6.68 (1H, d, *J*=3.4 Hz). MS *m*/*z* (%) 250 (M$^+$, 100), 221 (25), 206 (9), 205 (18), 189 (22), 177 (9), 163 (28), 149 (34), 135 (18), 111 (21), 99 (21), 91 (13), 77 (9), 59 (9). Calcd for $C_{14}H_{18}O_2S$: M, 250.1026. Found: *m*/*z* 250.1020.

*4.1.4. 8-(5-Methoxythiophen-2-ylmethylene)-1,4-dioxaspiro[4.5]decane (**12d**)*

Yellow oil; IR (neat) 2948, 2881, 1548, 1489, 1430, 1207, 1119, 1080, 1034, 906, 769, 684 cm^{-1}; ^{1}H NMR δ 1.73 (2H, t, *J*=7.5 Hz), 1.75 (2H, t, *J*=7.7 Hz), 2.38 (2H, t, *J*=6.6 Hz), 2.63 (2H, t, *J*=6.4 Hz), 3.87 (3H, s), 3.98 (4H, s), 6.06 (1H, d, *J*=4.0 Hz), 6.16 (1H, s), 6.50 (1H, d, *J*=4.0 Hz). MS *m*/*z* (%) 266 (M$^+$, 100), 251 (14), 221 (22), 207 (10), 205 (32), 170 (25), 165 (13), 151 (10), 137 (14), 127 (22), 109 (7), 99 (19), 91 (11), 77 (9), 55 (10), 42 (9). Calcd for $C_{14}H_{18}O_3S$: M, 266.0975. Found: *m*/*z* 266.0975.

*4.1.5. 8-(5-Chlorothiophen-2-ylmethylene)-1,4-dioxaspiro[4.5]decane (**12e**)*

Colorless oil; IR (neat) 2950, 2881, 1646, 1437, 1120, 1081, 907, 758, 686 cm^{-1}; ^{1}H NMR δ 1.73 (2H, t, *J*=6.2 Hz), 1.77 (2H, t, *J*=6.2 Hz), 2.40 (2H, t, *J*=6.6 Hz), 2.62 (2H, t, *J*=6.6 Hz), 3.99 (4H, s), 6.20 (1H, s), 6.64 (1H, d, *J*=3.8 Hz), 6.78 (1H, d, *J*=3.9 Hz). MS *m*/*z* (%) 270 (M$^+$, 100), 241 (40), 225 (20), 209 (13), 197 (12), 183 (22), 173 (21), 163 (22), 149 (25), 134 (23), 121 (28), 99 (25), 86 (21), 77 (12), 55 (13), 42 (17). Calcd for $C_{13}H_{15}O_2ClS$: M, 270.0479. Found: *m*/*z* 270.0476.

*4.1.6. 8-(1-Thiophen-2-ylethylidene)-1,4-dioxaspiro[4.5]decane (**14b**)*

To a solution of **10** (98 mg; 0.3 mmol) in 6 mL of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.04 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to the reaction mixture to give magnesium alkylidene carbenoid **11**. In another flask, *n*-BuLi (1.65 M solution in hexane, 0.6 mL; 0.99 mmol) was added dropwise to a solution of thiophene (0.072 mL; 0.9 mmol) in a mixture of 3 mL of dry toluene and 1 mL of THF at −78 °C under argon atmosphere to give 2-lithiothiophene. After 30 min, this solution was added to a solution of carbenoid **11** through a cannula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. Copper iodide (2.9 mg; 0.015 mmol) was added to the reaction mixture and was stirred for 10 min. Iodomethane (0.056 mL; 0.9 mmol) was added dropwise to the reaction mixture. The reaction mixture was gradually allowed to warm to room temperature, and then was stirred for 1 h at room temperature. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give **14b** (53.9 mg; 72%) as colorless crystals; mp 54.0–54.5 °C (AcOEt–hexane). IR (KBr) 2947, 2880, 1438, 1364, 1232, 1124, 1097, 1034, 900, 764, 693 cm^{-1}; ^{1}H NMR δ 1.64 (2H, t, *J*=6.5 Hz), 1.76 (2H, t, *J*=6.7 Hz), 2.04 (3H, s), 2.40 (2H, t, *J*=6.6 Hz), 2.47 (2H, t, *J*=6.6 Hz), 3.97 (4H, s), 6.76 (1H, dd, *J*=3.5, 1.2 Hz), 6.96 (1H, dd, *J*=5.1, 3.5 Hz), 7.20 (1H, dd, *J*=5.1, 1.1 Hz). MS *m*/*z* (%) 250 (M$^+$, 100), 235 (21), 221 (26), 205 (15), 191 (25), 173 (15), 163 (22), 149 (47), 135 (27), 121 (12), 99 (23), 86 (18), 77 (11), 55 (10). Calcd for $C_{14}H_{18}O_2S$: M, 250.1025. Found: *m*/*z* 250.1024. Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25; S, 12.81. Found: C, 67.13; H, 7.23; S, 12.78.

4.1.7. 8-(1-Thiophen-2-ylpropylidene)-1,4-dioxaspiro[4.5]-decane (*14c*)

Colorless crystals; mp 40–40.5 °C (AcOEt–hexane); IR (KBr) 2960, 2875, 1366, 1124, 1101, 1035, 694 cm^{-1}; ^{1}H NMR δ 0.96 (3H, t, *J*=7.5 Hz), 1.64 (2H, t, *J*=6.4 Hz), 1.76 (2H, t, *J*=6.2 Hz), 2.29–2.47 (6H, m), 3.97 (4H, s), 6.73 (1H, dd, *J*=3.4, 1.1 Hz), 6.96 (1H, dd, *J*=5.1, 3.4 Hz), 7.21 (1H, dd, *J*=5.1, 1.1 Hz). Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62; S, 12.13. Found: C, 67.50; H, 7.56; S, 11.98.

4.1.8. 8-(1-Thiophen-2-ylbut-3-enylidene)-1,4-dioxaspiro[4.5]decane (*14d*)

Colorless oil; IR (neat) 2949, 2880, 1637, 1440, 1247, 1233, 1124, 1100, 1035, 909, 695 cm^{-1}; ^{1}H NMR δ 1.66 (2H, t, *J*=6.4 Hz), 1.75 (2H, t, *J*=6.4 Hz), 2.39 (2H, t, *J*=6.5 Hz), 2.45 (2H, t, *J*=6.5 Hz), 3.14 (2H, d, *J*=6.0 Hz), 3.97 (4H, s), 4.97–5.07 (2H, m), 5.72–5.85 (1H, m), 6.75 (1H, dd, *J*=3.5, 1.2 Hz), 6.95 (1H, dd, *J*=5.0, 3.4 Hz), 7.19 (1H, dd, *J*=5.3, 1.1 Hz). MS *m*/*z* (%) 276 (M$^+$, 100), 235 (35), 231 (12), 215 (12), 191 (26), 175 (25), 161 (37), 149 (36), 135 (23), 115 (15), 99 (37), 86 (21), 77 (15), 55 (15), 42 (13). Calcd for $C_{16}H_{20}O_2S$: M, 276.1182. Found: *m*/*z* 276.1175.

4.1.9. 8-(2-Phenyl-1-thiophen-2-ylethylidene)-1,4-dioxaspiro[4.5]decane (*14e*)

Colorless oil; IR (neat) 2950, 2882, 1494, 1453, 1367, 1246, 1232, 1123, 1094, 1034, 944, 904, 850, 756, 697 cm^{-1}; ^{1}H NMR δ 1.70 (2H, t, *J*=6.4 Hz), 1.79 (2H, t, *J*=6.4 Hz), 2.44 (2H, t, *J*=6.4 Hz), 2.57 (2H, t, *J*=6.4 Hz), 3.77 (2H, s), 3.98 (4H, s), 6.62 (1H, dd, *J*=3.5, 1.3 Hz), 6.88 (1H, dd, *J*=5.0, 3.5 Hz), 7.10–7.24 (6H, m). MS *m*/*z* (%) 326 (M$^+$, 100), 235 (59), 211 (45), 191 (30), 173 (15), 149 (32), 99 (32), 91 (39). Calcd for $C_{20}H_{22}O_2S$: M, 326.1340. Found: *m*/*z* 326.1341.

4.1.10. (1,4-Dioxaspiro[4.5]dec-8-ylidene)thiophen-2-ylacetic acid ethyl ester (*14f*)

Yellow oil; IR (neat) 3103, 2953, 2883, 1718, 1624, 1445, 1207, 1089, 700 cm^{-1}; ^{1}H NMR δ 1.26 (3H, t, *J*=7.2 Hz), 1.72 (2H, t, *J*=6.8 Hz), 1.83 (2H, t, *J*=6.8 Hz), 2.44 (2H, t, *J*=6.8 Hz), 2.69 (2H, t, *J*=6.8 Hz), 3.97 (4H, s), 4.21 (2H, q, *J*=7.2 Hz), 6.88 (1H, dd, *J*=3.5, 1.2 Hz), 7.00 (1H, dd, *J*=5.1, 3.5 Hz), 7.29 (1H, dd, *J*=5.1, 1.2 Hz). MS *m*/*z* (%) 308 (M$^+$, 13), 279 (14), 262 (100), 235 (33), 222 (5), 217 (25), 200 (10), 189 (13), 173 (12), 161 (10), 149 (24), 135 (15), 121 (18), 99 (21), 86 (23), 77 (10). Calcd for $C_{16}H_{20}O_4S$: M, 308.1080. Found: *m*/*z* 308.1080.

4.1.11. 8-(Iodothiophen-2-ylmethylene)-1,4-dioxaspiro[4.5]-decane (*14g*)

Colorless crystals; mp 118.5–119 °C (AcOEt–hexane); IR (KBr) 3100, 2942, 2880, 2348, 1425, 1364, 1335, 1232, 1211, 1121, 1076, 1031, 942, 908, 764, 731 cm^{-1}; ^{1}H NMR δ 1.60 (2H, t, *J*=6.6 Hz), 1.80 (2H, t, *J*=6.6 Hz), 2.49 (2H, t, *J*=6.6 Hz), 2.72 (2H, t, *J*=6.8 Hz), 3.98 (4H, s), 6.92–6.95 (2H, m), 7.26–7.29 (1H, m). MS *m*/*z* (%) 362 (M$^+$, 10), 235 (100), 191 (9), 173 (10), 149 (50), 121 (22), 77 (9), 55 (9). Calcd for $C_{13}H_{15}O_2SI$: M, 361.9838. Found: *m*/*z* 361.9839. Anal. Calcd for $C_{13}H_{15}O_2SI$: C, 43.11; H, 4.17; I, 35.03; S, 8.72. Found: C, 43.15; H, 4.08; I, 34.99; S, 8.72.

4.1.12. 8-(1-Benzo[b]thiophen-2-ylethylidene)-1,4-dioxaspiro[4.5]decane (*15a*)

Colorless crystals; mp 94.5–95 °C (AcOEt–hexane); IR (KBr) 2960, 2934, 2897, 2850, 1438, 1367, 1236, 1179, 1127, 1113, 1087, 1029, 939, 897, 822, 754, 728 cm^{-1}; ^{1}H NMR δ 1.65 (2H, t, *J*=6.5 Hz), 1.78 (2H, t, *J*=6.5 Hz), 2.09 (3H, s), 2.44 (2H, t, *J*=6.1 Hz), 2.50 (2H, t, *J*=6.5 Hz), 3.98 (4H, s), 6.96 (1H, s), 7.24–7.35 (2H, m), 7.70 (1H, d, *J*=7.2 Hz), 7.78 (1H, d, *J*=7.9 Hz). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71; S, 10.67. Found: C, 71.99; H, 6.73; S, 10.66.

4.1.13. 8-[1-(5-Methylthiophen-2-yl)ethylidene]-1,4-dioxaspiro[4.5]decane (*15b*)

Yellow oil; IR (neat) 3061, 2947, 2880, 1443, 1364, 1232, 1124, 1096, 1035, 945, 901, 800, 759, 690 cm^{-1}; ^{1}H NMR δ 1.64 (2H, t, *J*=6.5 Hz), 1.74 (2H, t, *J*=6.5 Hz), 2.00 (3H, s), 2.41–2.47 (7H, m), 3.97 (4H, s), 6.54 (1H, d, *J*=3.4 Hz), 6.59–6.60 (1H, m). MS *m*/*z* (%) 264 (M$^+$, 100), 249 (20), 235 (16), 220 (29), 219 (23), 205 (23), 187 (17), 177 (30), 163 (60), 149 (32), 125 (20), 111 (14), 99 (35), 86 (21), 77 (13), 55 (14), 42 (13). Calcd for $C_{15}H_{20}O_2S$: M, 264.1183. Found: *m*/*z* 264.1187.

4.1.14. 8-[1-(5-Methoxythiophen-2-yl)ethylidene]-1,4-dioxaspiro[4.5]decane (*15c*)

Yellow oil; IR (neat) 2947, 2882, 1718, 1650, 1553, 1500, 1431, 1364, 1277, 1204, 1124, 1096, 1034, 945, 901, 761 cm^{-1}; ^{1}H NMR δ 1.64 (2H, t, *J*=6.5 Hz), 1.73 (2H, t, *J*=6.5 Hz), 1.98 (3H, s), 2.43 (2H, t, *J*=6.0 Hz), 2.45 (2H, t, *J*=5.3 Hz), 3.86 (3H, s), 3.97 (4H, s), 6.04 (1H, d, *J*=3.8 Hz), 6.36 (1H, d, *J*=3.8 Hz). MS *m*/*z* (%) 280 (M$^+$, 100), 265 (20), 235 (20), 221 (13), 219 (30), 193 (20), 179 (31), 165 (13), 151 (14), 141 (17), 127 (8), 115 (7), 99 (28), 91 (13), 77 (9), 55 (13), 42 (10). Calcd for $C_{15}H_{20}O_3S$: M, 280.1131. Found: *m*/*z* 280.1126.

4.1.15. 8-[1-(5-Chlorothiophen-2-yl)ethylidene]-1,4-dioxaspiro[4.5]decane (*15d*)

Colorless oil; IR (neat) 2948, 2880, 1446, 1365, 1230, 1124, 1096, 1035, 945, 900, 796 cm^{-1}; ^{1}H NMR δ 1.63 (2H, t, *J*=6.6 Hz), 1.74 (2H, t, *J*=6.6 Hz), 1.99 (3H, s), 2.39 (2H, t, *J*=6.8 Hz), 2.44 (2H, t, *J*=6.7 Hz), 3.97 (4H, s), 6.51 (1H, d, *J*=3.8 Hz), 6.76 (1H, d, *J*=3.8 Hz). MS *m*/*z* (%) 284 (M$^+$, 100), 269 (22), 255 (18), 240 (34), 225 (32), 207 (16), 197 (22), 138 (38), 169 (14), 163 (29), 149 (23), 134 (22), 115 (14), 99 (38), 86 (27), 55 (18), 42 (21). Calcd for $C_{14}H_{17}O_2ClS$: M, 284.0637. Found: *m*/*z* 284.0648.

4.1.16. 2-(Cyclopentadecylidenemethyl)thiophene (*16a*)

Colorless oil; IR (neat) 2929, 2856, 1459, 1349, 854, 689 cm^{-1}; ^{1}H NMR δ 1.34–1.53 (24H, m), 2.17 (2H, t, *J*=8.1 Hz), 2.38 (2H, t, *J*=8.1 Hz), 6.39 (1H, s), 6.88 (1H, d, *J*=3.4 Hz), 6.97 (1H, dd, *J*=5.2, 3.5 Hz), 7.17 (1H, d, *J*=5.1 Hz). MS *m*/*z* (%) 304 (M$^+$, 100), 151 (8), 137 (22), 123 (28), 110 (27), 97 (37), 91 (9), 69 (7), 55 (17), 41 (23), 28 (30), 18 (9). Calcd for $C_{20}H_{32}S$: M, 304.2223. Found: *m*/*z* 304.2229.

4.1.17. 2-(Cyclohexylidenemethyl)thiophene (*16b*)

Colorless oil; IR (neat) 2928, 2853, 1446, 1343, 1237, 851, 690 cm^{-1}; ^{1}H NMR δ 1.60–1.61 (6H, m), 2.23–2.29 (2H, m), 2.54 (2H, m), 6.29 (1H, s), 6.87 (1H, d, *J*=3.4 Hz), 6.96 (1H, dd, *J*=5.1, 3.6 Hz), 7.16 (1H, dd, *J*=5.1, 1.1 Hz). MS *m*/*z* (%) 178 (M$^+$, 100), 177 (8), 150 (9), 149 (18), 135 (32), 110 (84), 97 (59), 91 (21), 79 (21), 65 (10), 39 (20). Calcd for $C_{11}H_{14}S$: M, 178.0815. Found: *m*/*z* 178.0812.

4.1.18. 8-Furan-2-ylmethylene-1,4-dioxaspiro[4.5]decane (*17a*)

To a solution of **10** (98 mg; 0.3 mmol) in 6 mL of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.04 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to the reaction mixture to give magnesium alkylidene carbenoid **11**. In another flask, *n*-BuLi (1.65 M solution in hexane, 0.6 mL; 0.99 mmol) was added dropwise to a solution of furan (0.065 mL; 0.9 mmol) in 4 mL of dry THF at −50 °C and the reaction mixture was allowed to warm to −10 °C under argon atmosphere to give 2-lithiofuran. This solution was added to a solution of carbenoid **11** through a cannula at −78 °C. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give **17a** (54 mg; 82%) as a colorless oil. IR (neat) 2949, 2884, 1717, 1683, 1622, 1445, 1371, 1275, 1120, 1083, 1034, 906, 735 cm^{-1}; ^1H NMR δ 1.75 (2H, t, *J*=6.6 Hz), 1.77 (2H, t, *J*=6.6 Hz), 2.40 (2H, t, *J*=6.6 Hz), 2.77 (2H, t, *J*=6.6 Hz), 3.99 (4H, s), 6.03 (1H, s), 6.17 (1H, d, *J*=3.4 Hz), 6.36 (1H, dd, *J*=3.1, 1.8 Hz), 7.34 (1H, d, *J*=1.8 Hz). MS *m*/*z* (%) 220 (M^+, 100), 191 (43), 158 (17), 133 (25), 99 (51), 77 (15), 55 (21). Calcd for $C_{13}H_{16}O_3$: M, 220.1098. Found: *m*/*z* 220.1098.

*4.1.19. 8-Benzofuran-2-ylmethylene-1,4-dioxaspiro[4.5]decane (**17b**)*

Colorless crystals; mp 60–61 °C (hexane); IR (KBr) 2949, 2863, 1658, 1455, 1378, 1260, 1228, 1183, 1139, 1117, 1080, 1037, 942, 740 cm^{-1}; ^1H NMR δ 1.80 (2H, t, *J*=7.6 Hz), 1.81 (2H, t, *J*=7.6 Hz), 2.47 (2H, t, *J*=6.6 Hz), 2.92 (2H, t, *J*=6.6 Hz), 4.01 (4H, s), 6.17 (1H, s), 6.52 (1H, s), 7.17–7.24 (2H, m), 7.43 (1H, d, *J*=7.3 Hz), 7.50 (1H, d, *J*=7.6 Hz). MS *m*/*z* (%) 270 (M^+, 100), 241 (20), 225 (13), 208 (18), 197 (13), 183 (30), 169 (20), 131 (21), 115 (13), 99 (12), 28 (31). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.37; H, 6.68.

*4.1.20. 8-(5-Methylfuran-2-ylmethylene)-1,4-dioxaspiro[4.5]decane (**17c**)*

Colorless oil; IR (neat) 2947, 2882, 1596, 1538, 1444, 1275, 1230, 1120, 1084, 1034, 906, 779, 685 cm^{-1}; ^1H NMR δ 1.74 (2H, t, *J*=6.7 Hz), 1.76 (2H, t, *J*=6.7 Hz), 2.29 (3H, s), 2.38 (2H, t, *J*=6.5 Hz), 2.75 (2H, t, *J*=6.5 Hz), 3.99 (4H, s), 5.94 (1H, dd, *J*=3.2, 1.2 Hz), 5.96 (1H, s), 6.06 (1H, d, *J*=3.1 Hz). MS *m*/*z* (%) 234 (M^+, 100), 205 (25), 189 (18), 173 (23), 147 (37), 133 (17), 119 (14), 95 (29), 43 (39). Calcd for $C_{14}H_{18}O_3$: M, 234.1255. Found: *m*/*z* 234.1262.

*4.1.21. 8-(4,5-Dimethylfuran-2-ylmethylene)-1,4-dioxaspiro[4.5]decane (**17d**)*

Colorless oil; IR (neat) 2946, 2880, 1629, 1444, 1247, 1228, 1119, 1083, 1034, 945, 906 cm^{-1}; ^1H NMR δ 1.71–1.77 (4H, m), 1.92 (3H, s), 2.20 (3H, s), 2.37 (2H, t, *J*=6.4 Hz), 2.73 (2H, t, *J*=6.4 Hz), 3.98 (4H, s), 5.92 (1H, s), 5.97 (1H, s). MS *m*/*z* (%) 248 (M^+, 100), 219 (17), 203 (13), 187 (30), 161 (24), 147 (13), 133 (11), 109 (28), 99 (19), 77 (9), 55 (9), 43 (39). Calcd for $C_{15}H_{20}O_3$: M, 248.1411. Found: *m*/*z* 248.1403.

*4.1.22. 8-(5-Methylsulfanylfuran-2-ylmethylene)-1,4-dioxaspiro[4.5]decane (**17e**)*

Colorless oil; IR (neat) 2948, 2881, 1658, 1485, 1435, 1120, 1083, 1034, 906, 783 cm^{-1}; ^1H NMR δ 1.75 (2H, t, *J*=6.0 Hz), 1.77 (2H, t, *J*=6.0 Hz), 2.41 (5H, m), 2.76 (2H, t, *J*=6.5 Hz), 3.99 (4H, s), 5.99 (1H, s), 6.14 (1H, d, *J*=3.3 Hz), 6.40 (1H, d, *J*=3.3 Hz). MS *m*/*z* (%) 266 (M^+, 100), 222 (14), 205 (27), 147 (13), 142 (30), 127 (15), 99 (74), 86 (23), 55 (18), 32 (17). Calcd for $C_{14}H_{18}O_3S$: M, 266.0976. Found: *m*/*z* 266.0975.

*4.1.23. 8-(5-Benzenesulfonylfuran-2-ylmethylene)-1,4-dioxaspiro[4.5]decane (**17f**)*

Colorless oil; IR (neat) 2950, 1691, 1655, 1482, 1447, 1330, 1170, 1145, 1083, 1032, 942, 906, 725 cm^{-1}; ^1H NMR δ 1.72 (2H, t, *J*=6.6 Hz), 1.75 (2H, t, *J*=6.6 Hz), 2.40 (2H, t, *J*=6.6 Hz), 2.68 (2H, t, *J*=6.6 Hz), 3.99 (4H, s), 6.00 (1H, s), 6.24 (1H, d, *J*=3.4 Hz), 7.16 (1H, d, *J*=7.2 Hz), 7.52–7.60 (2H, m), 7.60–7.63 (1H, m), 7.99–8.01 (2H, m). MS *m*/*z* (%) 360 (M^+, 62), 331 (17), 316 (100), 219 (48), 191 (94), 174 (21), 125 (80), 99 (41), 77 (97), 51 (55). Calcd for $C_{19}H_{20}O_5S$: M, 360.1029. Found: *m*/*z* 360.1029.

*4.1.24. 8-(1-Furan-2-ylethylidene)-1,4-dioxaspiro[4.5]decane (**19b**)*

To a solution of **10** (98 mg; 0.3 mmol) in 6 mL of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (1.0 M solution in THF, 0.04 mL; 0.04 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (2.0 M solution in THF, 0.42 mL; 0.84 mmol) was added dropwise to the reaction mixture to give magnesium alkylidene carbenoid **11**. In an another flask, *n*-BuLi (1.65 M solution in hexane, 0.6 mL; 0.99 mmol) was added dropwise to a solution of furan (0.065 mL; 0.9 mmol) in 4 mL of THF at −50 °C and the reaction mixture was allowed to warm to −10 °C under argon atmosphere to give 2-lithiofuran. This solution was added to a solution of carbenoid **11** through a cannula at −78 °C. Temperature of the reaction mixture was gradually allowed to warm to −10 °C. Copper iodide (2.9 mg; 0.015 mmol) was added to the reaction mixture and was stirred for 10 min. Iodomethane (0.112 mL; 1.8 mmol) was added dropwise to the reaction mixture. The reaction mixture was gradually allowed to warm to room temperature, and then was stirred for 1 h at room temperature. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give **19b** (55.7 mg; 79%) as colorless oil. IR (neat) 2947, 2881, 1496, 1445, 1124, 1099, 1013, 917, 897, 734 cm^{-1}; ^1H NMR δ 1.70 (2H, t, *J*=6.4 Hz), 1.75 (2H, t, *J*=6.4 Hz), 1.98 (3H, s), 2.47 (2H, t, *J*=6.5 Hz), 2.61 (2H, t, *J*=6.0 Hz), 3.98 (4H, s), 6.14 (1H, d, *J*=3.0 Hz), 6.37 (1H, dd, *J*=3.3, 2.0 Hz), 7.36 (1H, d, *J*=1.8 Hz). MS *m*/*z* (%) 234 (M^+, 100), 220 (10), 219 (21), 205 (20), 189 (15), 175 (30), 157 (18), 147 (22), 133 (27), 119 (20), 99 (28), 91 (38). Calcd for $C_{14}H_{18}O_3$: M, 234.1255. Found: *m*/*z* 234.1259.

*4.1.25. 8-(1-Furan-2-ylpropylidene)-1,4-dioxaspiro[4.5]decane (**19c**)*

Colorless oil; IR (neat) 2957, 2878, 1718, 1444, 1366, 1274, 1231, 1124, 1102, 1035, 914, 734 cm^{-1}; ^1H NMR δ 0.95 (3H, t, *J*=7.5 Hz), 1.69 (2H, t, *J*=6.4 Hz), 1.75 (2H, t, *J*=6.8 Hz), 2.37–2.55 (6H, m), 3.98 (4H, s), 6.13 (1H, dd, *J*=3.2, 0.6 Hz), 6.37 (1H, dd, *J*=3.3, 1.7 Hz), 7.36 (1H, dd, *J*=1.7, 0.8 Hz). MS *m*/*z* (%) 248 (M^+, 100), 219 (82), 175 (35), 153 (33), 99 (40), 86 (32). Calcd for $C_{15}H_{20}O_3$: M, 248.1412. Found: *m*/*z* 248.1413.

*4.1.26. 8-(1-Furan-2-ylbut-3-enylidene)-1,4-dioxaspiro[4.5]decane (**19d**)*

Colorless oil; IR (neat) 2950, 2882, 1719, 1637, 1496, 1445, 1366, 1275, 1235, 1123, 1035, 944, 907, 751 cm^{-1}; ^1H NMR δ 1.69–1.77 (4H, m), 2.44 (2H, t, *J*=6.4 Hz), 2.60 (2H, t, *J*=6.4 Hz), 3.16 (2H, d, *J*=5.9 Hz), 3.98 (4H, s), 4.93–5.04 (2H, m), 5.72–5.85 (1H, m), 6.16 (1H, d, *J*=3.2 Hz), 6.36 (1H, dd, *J*=3.3, 1.9 Hz), 7.36 (1H, d, *J*=1.9 Hz). MS *m*/*z* (%) 260 (M^+, 100), 219 (33), 175 (26), 145 (19), 99 (18), 91 (20). Calcd for $C_{16}H_{20}O_3$: M, 260.1413. Found: *m*/*z* 260.1411.

*4.1.27. 8-(1-Furan-2-yl-2-phenylethylidene)-1,4-dioxaspiro[4.5]decane (**19e**)*

Colorless crystals; mp 64.5–65 °C (AcOEt–hexane); IR (KBr) 3149, 3118, 3025, 2970, 2951, 2929, 2881, 2847, 1600, 1494, 1446, 1424, 1356, 1233, 1197, 1134, 1099, 1082, 1032, 945, 904, 728 cm^{-1}; ^1H NMR δ 1.70–1.77 (4H, m), 2.51 (2H, t, *J*=6.4 Hz), 2.65 (2H, t, *J*=6.4 Hz), 3.80 (2H, s), 3.98 (4H, s), 6.08 (1H, dd, *J*=3.3, 0.7 Hz), 6.31 (1H, dd, *J*=3.3, 1.8 Hz), 7.10–7.24 (5H, m), 7.33 (1H, dd, *J*=1.8, 0.7 Hz). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.38; H, 7.10. Found: C, 77.39; H, 7.14.

4.1.28. *(1,4-Dioxaspiro[4.5]dec-8-ylidene)furan-2-ylacetic acid ethyl ester (**19f**)*

Colorless oil; IR (neat) 2955, 2885, 1719, 1638, 1446, 1367, 1281, 1245, 1212, 1089, 1033, 946, 927, 901, 752 cm^{-1}; ^1H NMR δ 1.28 (3H, t, J=7.2 Hz), 1.77 (2H, t, J=6.4 Hz), 1.82 (2H, t, J=6.4 Hz), 2.59 (2H, t, J=6.6 Hz), 2.64 (2H, t, J=6.6 Hz), 3.98 (4H, s), 4.25 (2H, q, J=7.2 Hz), 6.25 (1H, dd, J=3.3, 0.8 Hz), 6.40 (1H, dd, J=3.3, 1.8 Hz), 7.40 (1H, dd, J=1.8, 0.8 Hz). MS m/z (%) 292 (M^+, 25), 246 (100), 219 (37), 201 (21), 184 (11), 157 (18), 133 (11), 86 (17). Calcd for $C_{16}H_{20}O_5$: M, 292.1310. Found: m/z 292.1312.

4.1.29. *2-(1,4-Dioxaspiro[4.5]dec-8-ylidene)-2-furan-2-yl-1-phenylethanol (**19g**)*

Colorless oil; IR (neat) 3430, 2940, 2921, 1648, 1495, 1448, 1236, 1201, 1080, 1058, 1034, 905, 738 cm^{-1}; ^1H NMR δ 1.68–1.86 (4H, m), 2.33 (1H, t, J=7.8 Hz), 2.41 (2H, t, J=6.5 Hz), 2.58–2.65 (2H, m), 3.98 (4H, s), 5.92–5.94 (2H, m), 6.28 (1H, dd, J=3.2, 1.9 Hz), 7.20–7.34 (6H, m). MS m/z (%) 326 (M^+, 45), 308 (100), 236 (23), 222 (96), 133 (33), 105 (80), 91 (40), 77 (80), 55 (30), 42 (22). Calcd for $C_{20}H_{22}O_4$: M, 326.1517. Found: m/z 326.1521.

4.1.30. *8-(Furan-2-yl-iodomethylene)-1,4-dioxaspiro[4.5]-decane (**19h**)*

Colorless oil; IR (neat) 2951, 2882, 1366, 1217, 1122, 1086, 1034, 907, 785, 739 cm^{-1}; ^1H NMR δ 1.64 (2H, t, J=6.5 Hz), 1.79 (2H, t, J=6.5 Hz), 2.61 (2H, t, J=6.5 Hz), 2.72 (2H, t, J=6.5 Hz), 3.98 (4H, s), 6.32 (1H, dd, J=3.3, 0.8 Hz), 6.38 (1H, dd, J=3.3, 1.9 Hz), 7.41 (1H, dd, J=1.9, 0.8 Hz). MS m/z (%) 346 (M^+, 25), 219 (100), 175 (13), 147 (10), 133 (27), 105 (12), 99 (12), 86 (12), 77 (8), 28 (20). Calcd for $C_{13}H_{15}O_3I$: M, 346.0066. Found: m/z 346.0067.

4.1.31. *2-(Cyclopentadecylidenemethyl)furan (**20a**)*

Colorless oil; IR (neat) 2927, 2857, 1652, 1460, 1015, 726 cm^{-1}; ^1H NMR δ 1.33–1.58 (24H, m), 2.15 (2H, t, J=7.3 Hz), 2.38 (2H, t, J=7.7 Hz), 6.06 (1H, s), 6.16 (1H, d, J=3.3 Hz), 6.37 (1H, dd, J=3.3, 1.8 Hz), 7.33 (1H, d, J=1.3 Hz). MS m/z (%) 288 (M^+, 100), 135 (12), 121 (21), 94 (37), 81 (23), 79 (12), 55 (16), 41 (22), 28 (38). Calcd for $C_{20}H_{32}O$: M, 288.2452. Found: m/z 288.2457.

4.1.32. *2-(Cyclohexylidenemethyl)furan (**20b**)*

Colorless oil; IR (neat) 2928, 2853, 1658, 1447, 1149, 1014, 926, 848, 727 cm^{-1}; ^1H NMR δ 1.55–1.59 (6H, m), 2.21–2.29 (2H, m), 2.59 (2H, m), 5.96 (1H, s), 6.15 (1H, d, J=3.4 Hz), 6.36 (1H, dd, J=3.3, 1.5 Hz), 7.23 (1H, d, J=1.5 Hz). MS m/z (%) 162 (M^+, 76), 133 (12), 120 (13), 94 (100), 81 (43), 79 (26), 55 (15), 39 (23), 28 (72). Calcd for $C_{11}H_{14}O$: M, 162.1044. Found: m/z 162.1040.

4.1.33. *5-(1,4-Dioxaspiro[4.5]dec-8-ylidene)-penta-2,4-dienoic acid methyl ester (**24a**)*

Colorless crystals; mp 95–96 °C (AcOEt–hexane); IR (KBr) 2956, 1947, 1709, 1633, 1429, 1306, 1259, 1187, 1163, 1122, 1067, 1030, 981, 897, 866 cm^{-1}; ^1H NMR δ 1.77 (4H, t, J=6.6 Hz), 2.30–2.39 (4H, m), 3.74 (3H, s), 3.97 (4H, s), 5.82 (1H, m), 5.85 (1H, dd, J=15.6, 0.6 Hz), 7.18 (1H, dd, J=15.6, 11.0 Hz); ^{13}C NMR δ 206.48 (C, allene), 167.17 (CO), 143.56 (CH), 118.62 (CH), 107.87 (C), 101.86 (C), 91.29 (CH), 64.25 ($2CH_2$), 51.36 (CH_3), 35.04 ($2CH_2$), 27.87 ($2CH_2$). MS m/z (%) 250 (M^+, 58), 219 (16), 205 (10), 191 (19), 177 (13), 163 (16), 147 (10), 124 (16), 119 (10), 99 (54), 86 (100), 77 (20), 55 (19), 42 (18). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.15; H, 7.19. Found: C, 67.18; H, 7.25.

4.1.34. *5-Cyclopentadecylidenepenta-2,4-dienoic acid methyl ester (**25a**)*

Colorless oil; IR (neat) 2929, 2857, 1941, 1721, 1627, 1459, 1440, 1301, 1260, 1171, 1113, 982, 868 cm^{-1}; ^1H NMR δ 1.34–1.37 (20H, m), 1.47 (4H, t, J=6.8 Hz), 2.05 (4H, dt, J=6.8, 2.5 Hz), 3.73 (3H, s), 5.84 (1H, d, J=15.4 Hz), 5.87–5.89 (1H, m), 7.18 (1H, dd, J=15.4, 11.1 Hz). MS m/z (%) 318 (M^+, 50), 287 (12), 259 (22), 219 (12), 178 (9), 152 (92), 137 (30), 105 (53), 93 (100), 41 (78). Calcd for $C_{21}H_{34}O_2$: M, 318.2559. Found: m/z 318.2555.

4.1.35. *5-Cyclohexylidenepenta-2,4-dienoic acid methyl ester (**25b**)*

Colorless oil; IR (neat) 2932, 2855, 1945, 1716, 1628, 1440, 1299, 1273, 1246, 1193, 1165, 1119, 983, 868 cm^{-1}; ^1H NMR δ 1.51–1.66 (6H, m), 2.13–2.17 (4H, m), 3.74 (3H, s), 5.76–5.80 (1H, m), 5.83 (1H, dd, J=15.4, 0.6 Hz), 7.19 (1H, dd, J=15.4, 11.0 Hz). MS m/z (%) 192 (M^+, 76), 191 (12), 163 (18), 133 (33), 117 (19), 105 (30), 91 (100), 77 (30), 65 (21), 39 (27), 27 (12). Calcd for $C_{12}H_{16}O_2$: M, 192.1148. Found: m/z 192.1145.

4.1.36. *6-Phenylhepta-2,4,5-trienoic acid methyl ester (**25c**)*

Colorless oil; IR (neat) 3026, 2988, 2950, 1930, 1719, 1627, 1598, 1494, 1436, 1302, 1267, 1246, 1167, 1114, 1066, 1027, 981, 872, 760, 693 cm^{-1}; ^1H NMR δ 2.15 (3H, s), 3.74 (3H, s), 5.96 (1H, d, J=15.4 Hz), 6.23 (1H, d, J=10.9 Hz), 7.25 (1H, dd, J=15.4, 10.9 Hz), 7.25–7.38 (5H, m). MS m/z (%) 214 (M^+, 100), 183 (25), 171 (43), 155 (70), 128 (61), 105 (49), 91 (12), 77 (49), 76 (10), 51 (19), 43 (14). Calcd for $C_{14}H_{14}O_2$: M, 214.0994. Found: m/z 214.0993.

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