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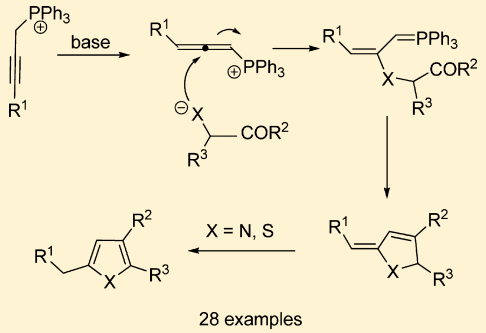
Synthesis of Cyclopentenes, Pyrroles, and Thiophenes via a Sequence of Propargyl−Allenyl Isomerizations, Michael Additions, and Intramolecular Wittig Reactions

Guoqing Zhao, Qianyun Zhang, and Hongwei Zhou*

Department of Chemistry, Zhejiang University (Campus Xixi), Hangzhou 310028, People's Republic of China

Supporting Information

ABSTRACT: Allenylphosphonium species, reactive Michael acceptors, could be generated from simple, readily available propargylphosphonium salts through propargyl−allenyl isomerization. We developed an efficient synthesis for cyclopentenes, pyrroles, and thiophenes via a sequence of propargyl−allenyl isomerizations, Michael additions, and intramolecular Wittig reactions.



INTRODUCTION

Five-membered cycles are common structural motifs found in a broad range of natural products, drug molecules, and useful materials.[1−3] Among this group of compounds, cyclopentenes, pyrroles, and thiophenes are considered to be important targets because of intrinsic properties such as drug activity, photobiological activity, redox activity, and electron transport.[4−6]

Since the use of phosphorus ylides in 1953, reported by George Wittig, Wittig olefination has been employed extensively in organic syntheses.[7] Correspondingly, the intramolecular Wittig reactions were applied in the formation of cyclic compounds.[8] The classic strategy for the construction of the suitable ylide is the introduction of a carbonyl group and halide moiety into the same substrate and treatment of the substrate with triphenylphosphine/trialkylphosphine (Scheme 1a).[9] In the 1960s, Schweizer continued to develop a general approach to cyclic compounds using vinylphosphonium salts as the Michael acceptors followed by an intramolecular Wittig reaction.[10a−j] McEwen applied Schweizer's procedure to the further development of the synthesis of 1,2,5-trisubstituted pyrroles,[10k] and Murphy developed a domino reaction utilizing an *in situ* vinylphosphonium intermediate generated from the treatment of acetylene dicarboxylate with Ph_3P[10l] (Scheme 1b). Recently, Lin's group developed a series of intramolecular Wittig reactions via *in situ*-generated phosphorus ylides, using designed acceptors and suitable trapping reagents (Scheme 1c). During our study of propargyl−allenyl isomerization,[11] we found that the allenylphosphonium species, which was generated *in situ* from base-promoted propargyl−allenyl isomerization of propargylphosphonium salts,[11g] could be attacked by mild nucleophiles. We anticipate that the allenylphosphonium species might react easily with a nucleophile containing a carbonyl group to produce *in situ* an allyl ylide, which could undergo an intramolecular Wittig reaction to complete the cylization (Scheme 1d).

RESULTS AND DISCUSSION

Stimulated by this proposal, we prepared propargylphosphonium bromide (**1a**) as the starting material, which could be synthesized readily via the treatment of (3-bromoprop-1-ynyl)benzene with triphenylphosphine in toluene. We initiated our study by testing the reaction of **1a** with 1,1-diethyl 2-methylethane-1,1,2-tricarboxylate (**2a**) and examining the effects of base, solvent, and temperature. TEA (triethylamine), DIEA (*N*,*N*-diisopropylethylamine), and K_2CO_3 could initiate the propargyl−allenyl isomerization; NaH and KH could trigger the following Michael addition and Wittig reaction, affording cyclopentene (**3a**) as the sole product. At the same time, a significant solvent effect was observed (Table 1).

The stereochemistry of **3a** was established by a NOESY experiment, which clearly showed an NOE effect between the aromatic protons and the proton on the cyclic double bond.

Under the optimized conditions, the scope of this reaction was further examined. The reacion was successful for various triphenyl(3-substituted prop-2-ynyl)phosphonium bromides. The R^1 group can be an alkyl group or optionally substituted aryl group, and the carbonyl moiety, reacting intramolecularly with the ylide, can be an aliphatic ketone (Table 2, entries 3−8), an aromatic ketone (Table 2, entries 9−11), or an ester (Table 2, entries 1 and 2).

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Scheme 1. Proposed Cyclization via Propargyl−Allenyl Isomerization, Michael Addition, and Intramolecular Wittig Reaction

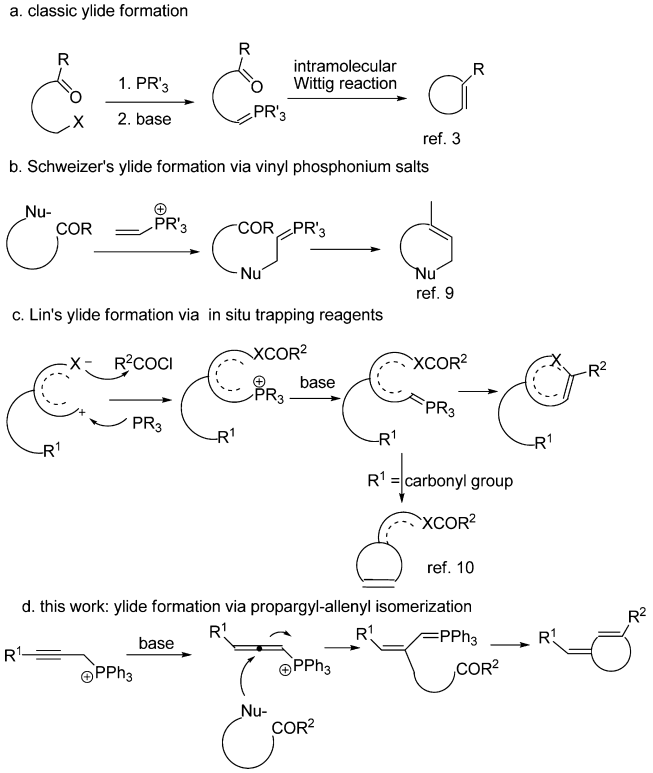
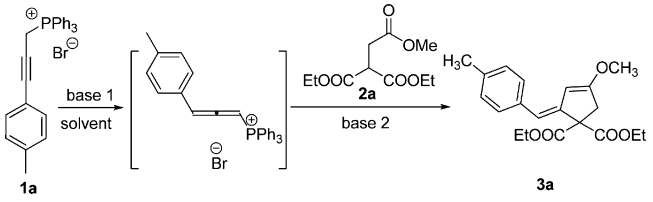


Table 1. Base, Solvent, and Temperature Effects[a]

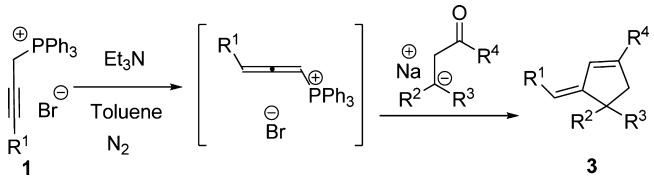


entry	base 1	base 2	solvent	T (°C)	yield (%)
1	*t*-BuOK	*t*-BuOK	toluene	rt	0
2	DBU	NaH	toluene	rt	7
3	DBN	NaH	toluene	rt	6
4	DIEA	NaH	toluene	rt	45
5	DIEA	LiH	toluene	rt	20
6	K_2CO_3	NaH	toluene	rt	48
7	TEA	NaH	toluene	rt	62
8	TEA	NaH	MeCN	rt	0
9	TEA	NaH	1,4-dioxane	rt	trace
10	DIEA	NaH	THF	rt	8
11	TEA	NaH	THF	rt	12
12	TEA	KH	toluene	rt	60
13	TEA	LiH	toluene	rt	32
14	**TEA**	**NaH**	**toluene**	**40**	**78**
15	TEA	NaH	toluene	60	72
16	TEA	NaH	toluene	80	74

[a]The reaction was conducted using **1a** (0.5 mmol), base 1 (1.5 mmol), **2a** (0.4 mmol), and base 2 (0.48 mmol) in solvent (3 mL) under N_2.

Then our attention was diverted to the synthesis of pyrroles. The reactive allenylphosphonium intermediate might be attacked by a nitrogen anion, and the desired cyclic products might undergo an aromatization to give highly substituted pyrroles. The expected reactions proceeded smoothly under similar conditions and afforded pyrroles in moderate to good yields (Table 3).

Table 2. Synthesis of Cyclopentenes[a]



entry	R^1	R^2/R^3	R^4	**3**/yield (%)
1	*p*-Tol	CO_2Et/CO_2Et	OMe	**3a**/78
2	*p*-Cl-C_6H_4	CO_2Et/CO_2Et	OMe	**3b**/55
3	*p*-Tol	CO_2Et/CO_2Et	Me	**3c**/61
4	Ph	CO_2Et/CO_2Et	Me	**3d**/57
5	*n*-C_4H_9	CO_2Et/CO_2Et	Me	**3e**/67
6	*n*-C_4H_9	CO_2Et/MeCO	Me	**3f**/73
7	*p*-Tol	CO_2Et/MeCO	Me	**3g**/83
8	Ph	CO_2Et/MeCO	Me	**3h**/81
9	*p*-Tol	CN/CN	Ph	**3i**/62
10	*p*-Cl-C_6H_4	CN/CN	Ph	**3j**/54
11	*n*-C_4H_9	CN/CN	Ph	**3k**/59

[a]The reaction was conducted using **1** (0.5 mmol), Et_3N (1.5 mmol), **2** (0.4 mmol), and NaH (0.48 mmol) in toluene (3 mL) under N_2.

Generally, a sulfur anion is a better nucleophile for the Michael addition than a nitrogen anion; it is a reasonable inference that the thiophenes could be synthesized via this strategy. The experimental results proved this out, and the thiophenes were obtained in moderate yields (Table 4).

Notably, these reactions could not offer any isolatable products when only the second base NaH was charged, indicating that the presence of triethylamine is essential for triggering the propargyl−allenyl isomerization. We therefore propose the plausible mechanism shown in Scheme 2. First, the base-assisted propargyl−allenyl isomerization of triphenyl-(prop-2-ynyl)phosphonium salt gives triphenyl allenylphosphonium salt,[11g,12] which is attacked by the nucleophile to afford *in situ* an allyl ylide. A subsequent Wittig process yields the cyclopentenes, 2-methylene-2,5-dihydropyrroles, or 2-methylene-2,5-dihydrothiophenes; the latter two species may undergo an aromatization to afford pyrroles or thiophenes.

As a simple route to five-membered cycles, the usefulness of this protocol should be demonstrated on a gram-scale preparation. We thus conducted the reaction of **1a** with **2a** on a 2 g scale and obtained **3a** in 72% yield (Scheme 3).

CONCLUSION

In summary, we have reported an efficient synthesis for cyclopentenes, pyrroles, and thiophenes via a sequence of propargyl−allenyl isomerizations, Michael additions, and intramolecular Wittig reactions. Further studies of the applications and expansions of this reaction are ongoing in our laboratory.

EXPERIMENTAL SECTION

Typical Procedure for the Synthesis of 3a (0.5 mmol scale). To a solution of **1a** (236 mg, 0.5 mmol) and Et_3N (152 mg, 1.5 mmol) in dry toluene (2.0 mL) at room temperature was added a mixture of **2a** (93 mg, 0.4 mmol) and NaH (16 mg, 0.48 mmol, w = 70%) in dry toluene (1.0 mL). The reaction mixture was stirred at 40 °C for 12 h. Upon completion, the reaction was quenched with a saturated aqueous

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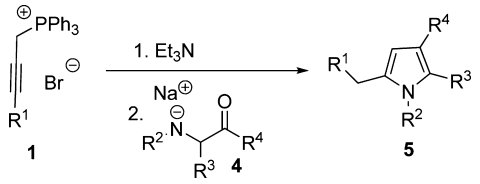
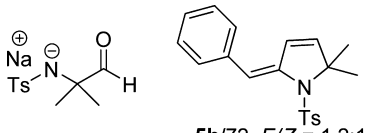
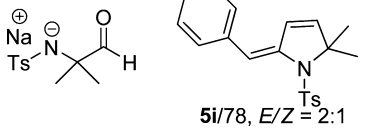
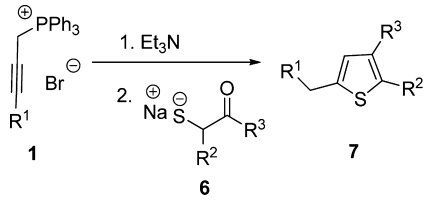
Table 3. Synthesis of Pyrroles[a]



Entry	R^1	$R^2/R^3/R^4$	5/Yield
1	Ph	Ts/H/OEt	**5a**/ 60
2	*p*-Tol	Ts/H/OEt	**5b**/55
3	*p*-Cl-C_6H_4-	Ts/H/OEt	**5c**/53
4	*n*-C_4H_9-	Ts/Me/OEt	**5d**/58
5	*n*-C_4H_9-	Ts/H/OEt	**5e**/62
6	*t*-Bu-	Ts/H/OEt	**5f**/55
7	*n*-C_4H_9-	Ms/Bn/OEt	**5g**/53
8	Ph		**5h**/72, *E*/*Z* = 1.2:1
9	*p*-Cl-C_6H_4-		**5i**/78, *E*/*Z* = 2:1

[a]The reaction was conducted using **1** (0.5 mmol), Et_3N (1.5 mmol), **4** (0.4 mmol), and NaH (0.48 mmol) in toluene (3 mL) under N_2.

Table 4. Synthesis of Thiophenes[a]

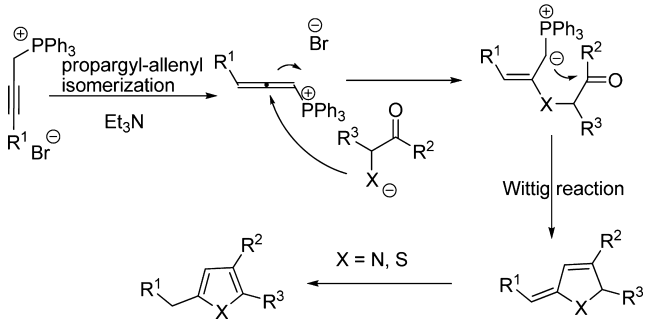


entry	R^1	R^2/R^3	7/yield (%)
1	Ph	H/OMe	**7a**/65
2	Ph	Me/OEt	**7b**/54
3	*p*-Tol	H/OMe	**7c**/57
4	*p*-Tol	Me/OEt	**7d**/54
5	*p*-Cl-C_6H_4	H/OMe	**7e**/63
6	*p*-Cl-C_6H_4	Me/OEt	**7f**/55
7	*n*-C_4H_9	H/OMe	**7g**/63
8	*n*-C_4H_9	Me/OEt	**7h**/55

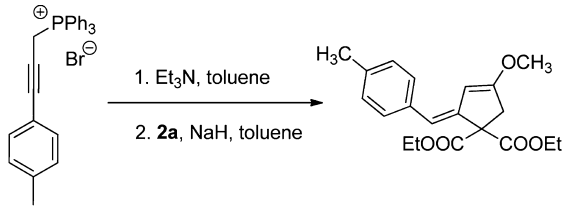
[a]The reaction was conducted using **1** (0.5 mmol), Et_3N (1.5 mmol), **6** (0.4 mmol), and NaH (0.48 mmol) in toluene (3 mL) under N_2.

NH_4Cl solution, and the mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. After evaporation, chromatography on silica gel (50:1 petroleum ether/ethyl acetate) of the reaction mixture afforded **3a** as a yellow amorphous solid (107 mg, 78%).

Scheme 2. Plausible Mechanism



Scheme 3. Gram-Scale Preparation



1a: 5.6g 12mmol
Et_3N: 3.6g, 36 mmol
2a: 2.3g 10 mmol
NaH (70%): 0.4g 12 mmol
toluene: 60 mL

3a: 2.5g, 72%

Typical Procedure for the Synthesis of 3a (2 g scale). To a solution of **1a** (5.6 g, 12 mmol) and Et_3N (3.6 g, 36 mmol) in dry toluene (30 mL) at room temperature was added a mixture of **2a** (2.3 g, 10 mmol) and NaH (0.4 g, 12 mmol, *w* = 70%) in dry toluene (30 mL). The reaction mixture was stirred at 40 °C for 18 h. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution, and the mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. After evaporation, chromatography on silica gel (50:1 petroleum ether/ethyl acetate) of the reaction mixture afforded **3a** as a yellow amorphous solid (2.5 g, 72%).

*(E)-Diethyl 4-Methoxy-2-(4-methylbenzylidene)cyclopent-3-ene-1,1-dicarboxylate (**3a**).* Yellow amorphous solid (107 mg, 78% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.34 (s, 1 H), 5.75 (s, 1 H), 4.23–4.28 (m, 4 H), 3.73 (s, 3 H), 3.21 (s, 2 H), 2.33 (s, 3 H), 1.29 (t, *J* = 7.6 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 166.7, 139.7, 135.7, 135.6, 128.9, 127.9, 119.6, 97.5, 61.8, 61.3, 57.6, 39.6, 21.1, 14.0; IR (neat) 1727, 1237, 1176, 1093, 1042 cm^{-1}; HRMS (EI-TOF) calcd for $C_{20}H_{24}O_5$ (M^+) 344.1624, found 344.1616.

*(E)-Diethyl 2-(4-Chlorobenzylidene)-4-methoxycyclopent-3-ene-1,1-dicarboxylate (**3b**).* Yellow oil (80 mg, 55% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.29 (m, 4 H), 6.32 (s, 1 H), 5.71 (s, 1 H), 4.26–4.31 (q, *J* = 6.7 Hz, 4 H), 3.77 (s, 3 H), 3.23 (s, 2 H), 1.32 (t, *J* = 6.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 167.8, 141.2, 137.1, 131.4, 129.3, 128.4, 118.3, 97.2, 61.9, 61.4, 57.7, 39.7, 14.0; IR (neat) 1730, 1616, 1361, 1240, 1094 cm^{-1}; HRMS (EI-TOF) calcd for $C_{19}H_{21}ClO_5$ (M^+) 364.1078, found 364.1071.

*(E)-Diethyl 4-Methyl-2-(4-methylbenzylidene)cyclopent-3-ene-1,1-dicarboxylate (**3c**).* Amorphous solid (80 mg, 61% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.0 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 6.40 (s, 1 H), 6.31 (s, 1 H), 4.14–4.20 (m, 4 H), 3.03 (s, 2 H), 2.26 (s, 3 H), 1.84 (s, 3 H), 1.20 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 147.7, 142.7, 136.1, 135.3, 128.9, 128.3, 124.8, 122.3, 63.7, 61.6, 45.0, 21.1, 17.1, 14.0; IR (neat) 2911, 1729, 1443, 1240, 1177, 1067 cm^{-1}; HRMS (EI-TOF) calcd for $C_{20}H_{24}O_4$ (M^+) 328.1675, found 328.1680.

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*(E)-Diethyl 2-Benzylidene-4-methylcyclopent-3-ene-1,1-dicarboxylate (**3d**).* Yellow oil (72 mg, 57% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.35 (m, 4 H), 7.27−7.31 (m, 1 H), 6.51 (s, 1 H), 6.40 (s, 1 H), 4.22−4.28 (m, 4 H), 3.12 (s, 2 H), 1.92 (s, 3 H), 1.29 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 148.3, 143.4, 138.2, 128.3, 128.2, 126.4, 124.7, 122.3, 63.7, 61.7, 45.0, 17.1, 14.0; IR (neat) 2938, 1726, 1242, 1129 cm^{-1}; HRMS (EI-TOF) calcd for $C_{19}H_{22}O_4$ (M^+) 314.1518, found 314.1522.

*(E)-Diethyl 4-Methyl-2-pentylidenecyclopent-3-ene-1,1-dicarboxylate (**3e**).* Yellow oil (79 mg, 67% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 1 H), 5.45 (t, J = 7.6 Hz, 1 H), 4.17−4.22 (m, 4 H), 3.03 (s, 2 H), 2.17 (q, J = 7.1 Hz, 2 H), 1.86 (s, 3 H), 1.31−1.4 (m, 2 H), 1.23−1.27 (m, 8 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 143.8, 141.7, 123.9, 123.6, 62.5, 61.5, 45.2, 31.9, 29.2, 22.2, 16.8, 14.0, 13.9; IR (neat) 2960, 2931, 1731, 1460, 1369, 1260 cm^{-1}; HRMS (EI-TOF) calcd for $C_{17}H_{26}O_4$ (M^+) 294.1831, found 294.1827.

*(E)-Ethyl 1-Acetyl-4-methyl-2-pentylidenecyclopent-3-enecarboxylate (**3f**).* Yellow oil (77 mg, 73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 1 H), 5.38 (t, J = 7.6 Hz, 1 H), 4.17−4.23 (m, 2 H), 3.12 (d, J = 17.6 Hz, 1 H), 2.79 (d, J = 17.6 Hz, 1 H), 2.13−2.19 (m, 5 H), 1.86 (s, 3 H), 1.29−1.39 (m, 4 H), 1.25 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 171.2, 144.5, 142.1, 124.2, 123.8, 69.4, 61.4, 43.9, 31.8, 29.2, 25.6, 22.2, 16.8, 13.98, 13.89; IR (neat) 2959, 2932, 1710, 1444, 1359, 1245 cm^{-1}; HRMS (EI-TOF) calcd for $C_{16}H_{24}O_3$ (M^+) 264.1725, found 264.1734.

*(E)-Ethyl 1-Acetyl-4-methyl-2-(4-methylbenzylidene)cyclopent-3-enecarboxylate (**3g**).* Yellow oil (99 mg, 83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 6.44 (s, 1 H), 6.41 (s, 1 H), 4.24−4.30 (m, 2 H), 3.25 (d, J = 18.0 Hz, 1 H), 2.85 (d, J = 18.4 Hz, 1 H), 2.34 (s, 3 H), 2.25 (s, 3 H), 1.94 (s, 3 H), 1.31 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 170.7, 148.5, 142.9, 136.3, 135.0, 129.0, 128.1, 125.2, 122.3, 70.5, 61.6, 43.6, 25.7, 21.1, 17.1, 14.0; IR (neat) 2979, 1711, 1442, 1356, 1243, 1097 cm^{-1}; HRMS (EI-TOF) calcd for $C_{19}H_{22}O_3$ (M^+) 298.1569, found 298.1566.

*(E)-Ethyl 1-Acetyl-2-benzylidene-4-methylcyclopent-3-enecarboxylate (**3h**).* Yellow oil (92 mg, 81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 4.8 Hz, 4 H), 7.20−7.23 (m, 1 H), 6.44 (s, 2 H), 4.24−4.30 (m, 2 H), 3.25 (d, J = 18.4 Hz, 1 H), 2.85 (d, J = 18.4 Hz, 1 H), 2.25 (s, 3 H), 1.94 (s, 3 H), 1.31 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 170.7, 149.0, 143.7, 137.9, 128.3, 128.2, 126.6, 125.1, 122.4, 70.5, 61.6, 43.6, 25.7, 17.1, 14.0; IR (neat) 2979, 1710, 1444, 1356, 1243, 1217 cm^{-1}; HRMS (EI-TOF) calcd for $C_{18}H_{20}O_3$ (M^+) 284.1412, found 284.1409.

*(E)-2-(4-Methylbenzylidene)-4-phenylcyclopent-3-ene-1,1-dicarbonitrile (**3i**).* Yellow oil (73 mg, 62% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.46 (m, 5 H), 7.33 (d, J = 8.4 Hz, 2 H), 7.23 (d, J = 8.4 Hz, 2 H), 7.17 (s, 1 H), 6.83 (s, 1 H), 3.71 (s, 2 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 138.6, 138.4, 132.9, 132.7, 129.7, 129.5, 128.9, 128.5, 126.0, 125.9, 122.3, 115.9, 44.2, 37.1, 21.3; IR (neat) 1496, 1445, 1264, 1080, 1031 cm^{-1}; HRMS (EI-TOF) calcd for $C_{21}H_{16}N_2$ (M^+) 296.1313, found 296.1310.

*(E)-2-(4-Chlorobenzylidene)-4-phenylcyclopent-3-ene-1,1-dicarbonitrile (**3j**).* Amorphous solid (68 mg, 54% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.49 (m, 2 H), 7.35−7.45 (m, 7 H), 7.12 (s, 1 H), 6.81 (s, 1 H), 3.74 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 139.9, 134.3, 134.0, 132.7, 130.1, 129.7, 129.0, 126.1, 124.5, 121.7, 115.6, 44.3, 37.1; IR (neat) 1737, 1488, 1442, 1265, 1086 cm^{-1}; HRMS (EI-TOF) calcd for $C_{20}H_{13}ClN_2$ (M^+) 316.0767, found 316.0767.

*(E)-2-Pentylidene-4-phenylcyclopent-3-ene-1,1-dicarbonitrile (**3k**).* Yellow oil (62 mg, 59% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.46 (m, 5 H), 6.82 (d, J = 1.6 Hz, 1 H), 5.96 (t, J = 7.8 Hz, 1 H), 3.66 (s, 2 H), 2.30−2.36 (q, J = 7.6 Hz, 2 H), 1.47−1.52 (m, 2 H), 1.37−1.42 (m, 2 H), 0.95 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 139.1, 133.1, 129.4, 128.9, 128.5, 125.8, 121.5, 116.1, 44.7, 35.9, 31.2, 29.3, 22.2, 13.8; IR (neat) 2958, 2928, 1495, 1344, 1261 cm^{-1}; HRMS (EI-TOF) calcd for $C_{18}H_{18}N_2$ (M^+) 262.1470, found 262.1471.

*2-Benzyl-4-ethoxy-1-tosyl-1H-pyrrole (**5a**).* Yellow oil (85 mg, 60% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.54 (m, 2 H), 7.19−7.21 (m, 5 H), 7.06 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 2 H), 6.73 (d, J = 2.0 Hz, 1 H), 5.54−5.55 (m, 1 H), 4.03 (s, 2 H), 3.85 (q, J = 6.9 Hz, 2 H), 2.39 (s, 3 H), 1.33 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 144.4, 138.0, 136.2, 134.0, 129.7, 129.0, 128.3, 126.6, 126.3, 107.9, 102.2, 65.8, 33.7, 21.5, 14.7; IR (neat) 2928, 1743, 1614, 1166, 1086 cm^{-1}; HRMS (EI-TOF) calcd for $C_{20}H_{21}NO_3S$ (M^+) 355.1242, found 355.1239.

*4-Ethoxy-2-(4-methylbenzyl)-1-tosyl-1H-pyrrole (**5b**).* Yellow oil (81 mg, 55% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.01 (d, J = 8.0 Hz, 2 H), 6.94 (d, J = 8.0 Hz, 2 H), 6.73 (d, J = 2.0 Hz, 1 H), 5.54−5.55 (m, 1 H), 3.99 (s, 2 H), 3.85 (q, J = 7.0 Hz, 2 H), 2.40 (s, 3 H), 2.31 (s, 3 H), 1.33 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 144.3, 136.3, 135.9, 134.9, 134.4, 129.7, 128.94, 128.86, 126.5, 107.8, 102.2, 65.7, 33.3, 21.5, 21.0, 14.7; IR (neat) 2921, 1743, 1701, 1364, 1166, 1087 cm^{-1}; HRMS (EI-TOF) calcd for $C_{21}H_{23}NO_3S$ (M^+) 369.1399, found 369.1402.

*2-(4-Chlorobenzyl)-4-ethoxy-1-tosyl-1H-pyrrole (**5c**).* Yellow oil (82 mg, 53% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.47 (m, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 7.12−7.14 (m, 2 H), 6.94−6.96 (m, 2 H), 6.75 (d, J = 2.0 Hz, 1 H), 5.61−5.62 (m, 1 H), 4.00 (s, 2 H), 3.87 (q, J = 7.1 Hz, 2 H), 2.39 (s, 3 H), 1.34 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 144.5, 136.5, 136.1, 133.0, 132.2, 130.2, 129.7, 128.3, 126.4, 108.1, 102.5, 65.8, 32.9, 21.5, 14.6; IR (neat) 1742, 1703, 1364, 1166, 1067 cm^{-1}; HRMS (EI-TOF) calcd for $C_{20}H_{20}ClNO_3S$ (M^+) 389.0852, found 389.0847.

*3-Ethoxy-2-methyl-5-pentyl-1-tosyl-1H-pyrrole (**5d**).* Yellow oil (81 mg, 58% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 2 H), 5.86 (s, 1 H), 3.88 (q, J = 6.9 Hz, 2 H), 2.76 (t, J = 7.6 Hz, 2 H), 2.38 (s, 3 H), 2.25 (s, 3 H), 1.57−1.61 (m, 2 H), 1.25−1.33 (m, 7 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.1, 137.4, 135.3, 129.8, 125.9, 116.0, 104.1, 67.1, 31.5, 29.0, 28.9, 22.5, 21.5, 15.1, 14.0, 10.8; IR (neat) 2958, 2923, 1701, 1357, 1162, 1090 cm^{-1}; HRMS (EI-TOF) calcd for $C_{19}H_{27}NO_3S$ (M^+) 349.1712, found 349.1716.

*4-Ethoxy-2-pentyl-1-tosyl-1H-pyrrole (**5e**).* Yellow oil (83 mg, 62% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 6.68 (d, J = 2.0 Hz, 1 H), 5.76 (m, 1 H), 3.87 (q, J = 6.9 Hz, 2 H), 2.62 (t, J = 7.8 Hz, 2 H), 2.39 (s, 3 H), 1.49−1.54 (m, 2 H), 1.35 (t, J = 7.2 Hz, 3 H), 1.25−1.28 (m, 4 H), 0.84−0.87 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 144.4, 136.5, 135.8, 129.8, 126.4, 105.7, 101.7, 65.7, 31.3, 28.3, 27.4, 22.4, 21.5, 14.7, 13.9; IR (neat) 2929, 2870, 1705, 1597, 1347 cm^{-1}; HRMS (EI-TOF) calcd for $C_{18}H_{25}NO_3S$ (M^+) 335.1555, found 335.1558.

*4-Ethoxy-2-neopentyl-1-tosyl-1H-pyrrole (**5f**).* Yellow oil (74 mg, 55% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 6.64 (d, J = 2.0 Hz, 1 H), 5.78 (d, J = 2.0 Hz, 1 H), 3.85 (q, J = 6.9 Hz, 2 H), 2.67 (s, 2 H), 2.38 (s, 3 H), 1.34 (t, J = 7.0 Hz, 3 H), 0.93 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 144.3, 136.4, 134.0, 129.6, 126.3, 109.0, 102.3, 65.7, 39.7, 32.2, 29.3, 21.5, 14.6; IR (neat) 2958, 1705, 1596, 1363, 1164, 1085 cm^{-1}; HRMS (EI-TOF) calcd for $C_{18}H_{25}NO_3S$ (M^+) 335.1555, found 335.1551.

*2-Benzyl-3-ethoxy-1-(methylsulfonyl)-5-pentyl-1H-pyrrole (**5g**).* Yellow oil (74 mg, 53% yield): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.22−7.26 (m, 4 H), 7.14−7.17 (m, 1 H), 5.99 (s, 1 H), 4.15 (s, 2 H), 4.01 (q, J = 7.1 Hz, 2 H), 2.71 (t, J = 7.8 Hz, 2 H), 2.43 (s, 3 H), 1.59−1.64 (m, 2 H), 1.33−1.38 (m, 7 H), 0.88−0.92 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.9, 140.4, 135.1, 128.7, 128.2, 125.9, 118.2, 103.1, 66.9, 41.4, 31.5, 29.6, 28.9, 28.8, 22.5, 15.3, 14.0; IR (neat): 2930, 2969, 1728, 1636, 1356, 1155 cm^{-1}; HRMS (EI-TOF) calcd for $C_{19}H_{27}NO_3S$ (M^+): 349.1712, found: 349.1702.

*5-Benzylidene-2,2-dimethyl-1-tosyl-2,5-dihydro-1H-pyrrole (1.2:1 E:Z) (**5h**).* Gum (106 mg, 72% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.79 (m, 4 H), 7.30−7.38 (m, 8 H), 7.20−7.25 (m, 4 H), 6.50 (d, J = 7.6 Hz, 0.8 H), 6.45 (d, J = 7.6 Hz, 1 H), 5.72 (d, J = 7.2 Hz, 0.8 H), 5.63 (d, J = 7.6 Hz, 1 H), 5.23 (d, J = 8.4 Hz, 1.8 H), 2.35 (s, 5.5 H), 1.48 (s, 6 H), 1.42 (s, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.63, 160.60, 157.8, 157.6, 143.03, 143.00, 139.8, 139.7, 136.3,

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136.1, 129.5, 129.4, 128.7, 128.6, 128.20, 128.16, 127.8, 127.7, 127.3, 127.2, 115.5, 115.2, 109.9, 109.8, 57.6, 57.5, 28.7, 28.4, 21.44, 21.40; IR (neat) 1569, 1323, 1147, 1093 cm^{-1}; HRMS (EI-TOF) calcd for $C_{20}H_{21}NO_2S$ (M^+) 339.1293, found 339.1302.

*5-(4-Chlorobenzylidene)-2,2-dimethyl-1-tosyl-2,5-dihydro-1H-pyrrole (2:1 E:Z) (**5i**).* Yellow oil (116 mg, 78% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.76−7.79 (m, 3 H), 7.22−7.30 (m, 9 H), 6.45 (d, J = 7.6 Hz, 0.5 H), 6.41 (d, J = 7.6 Hz, 1 H), 5.77 (d, J = 7.2 Hz, 0.5 H), 5.67 (d, J = 7.6 Hz, 1 H), 5.08 (br, 1.5 H), 2.37 (s, 4.5 H), 1.48 (s, 6 H), 1.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 157.6, 143.2, 143.1, 139.8, 139.7, 134.8, 134.0, 132.6, 129.51, 129.48, 129.0, 128.9, 128.86, 128.81, 128.7, 127.3, 127.2, 116.5, 116.1, 108.6, 108.5, 57.7, 57.5, 28.6, 28.4, 21.5; IR (neat) 1595, 1491, 1324, 1152, 1092 cm^{-1}; HRMS (EI-TOF) calcd for $C_{20}H_{20}ClNO_2S$ (M^+) 373.0903, found 373.0910.

*2-Benzyl-4-methoxythiophene (**7a**).* Yellow oil (53 mg, 65% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.27−7.31 (m, 2 H), 7.21−7.23 (m, 3 H), 6.47−6.48 (m, 1 H), 6.02 (d, J = 1.6 Hz, 1 H), 4.02 (s, 2 H), 3.73 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 143.2, 139.8, 128.6, 128.5, 126.5, 117.8, 94.8, 56.9, 36.6; IR (neat) 1562, 1480, 1390, 1203, 1149 cm^{-1}; HRMS (EI-TOF) calcd for $C_{12}H_{12}OS$ (M^+) 204.0609, found 204.0613.

*5-Benzyl-3-ethoxy-2-methylthiophene (**7b**).* Yellow oil (50 mg, 54% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.21−7.24 (m, 2 H), 7.15−7.17 (m, 3 H), 6.42 (s, 1 H), 3.93 (s, 2 H), 3.88 (q, J = 6.9 Hz, 2 H), 2.13 (s, 3 H), 1.24 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 140.2, 137.9, 128.6, 128.5, 126.5, 116.5, 115.6, 67.4, 36.7, 15.3, 10.6; IR (neat) 2977, 2919, 1577, 1493, 1449 cm^{-1}; HRMS (EI-TOF) calcd for $C_{14}H_{16}OS$ (M^+) 232.0922, found 232.0924.

*4-Methoxy-2-(4-methylbenzyl)thiophene (**7c**).* Yellow oil (50 mg, 57% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.13−7.17 (m, 4 H), 6.51 (s, 1 H), 6.06 (s, 1 H), 4.03 (s, 2 H), 3.77 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 143.6, 136.7, 136.0, 129.2, 128.5, 117.6, 94.7, 56.9, 36.2, 21.0; IR (neat) 1562, 1513, 1480, 1369, 1203 cm^{-1}; HRMS (EI-TOF) calcd for $C_{13}H_{14}OS$ (M^+) 218.0765, found 218.0768.

*3-Ethoxy-2-methyl-5-(4-methylbenzyl)thiophene (**7d**).* Yellow oil (53 mg, 54% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.12−7.16 (m, 4 H), 6.51 (s, 1 H), 3.95−4.01 (m, 4 H), 2.35 (s, 3 H), 2.23 (s, 3 H), 1.34 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 138.3, 137.1, 136.0, 129.2, 128.4, 116.4, 115.5, 67.3, 36.3, 21.0, 15.3, 10.6; IR (neat) 2977, 2917, 1577, 1513, 1362, 1399 cm^{-1}; HRMS (EI-TOF) calcd for $C_{15}H_{18}OS$ (M^+) 246.1078, found 246.1077.

*2-(4-Chlorobenzyl)-4-methoxythiophene (**7e**).* Yellow oil (60 mg, 63% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.17−7.20 (m, 2 H), 7.07−7.09 (m, 2 H), 6.38−6.39 (m, 1 H), 5.96−5.97 (m, 1 H), 3.92 (s, 2 H), 3.67 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 142.5, 138.3, 132.4, 129.9, 128.6, 118.0, 95.1, 57.0, 36.0; IR (neat) 1635, 1481, 1440, 1202 cm^{-1}; HRMS (EI-TOF) calcd for $C_{12}H_{11}ClOS$ (M^+) 238.0219, found 238.0216.

*5-(4-Chlorobenzyl)-3-ethoxy-2-methylthiophene (**7f**).* Yellow oil (58 mg, 55% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.18−7.20 (m, 2 H), 7.07−7.09 (m, 2 H), 6.40 (s, 1 H), 3.86−3.91 (m, 4 H), 2.14 (s, 3 H), 1.24 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 138.6, 137.2, 132.3, 129.9, 128.6, 116.7, 115.9, 67.4, 36.1, 15.3, 10.6; IR (neat) 2975, 2919, 1577, 1489, 1384 cm^{-1}; HRMS (EI-TOF) calcd for $C_{14}H_{15}ClOS$ (M^+) 266.0532, found 266.0536.

*4-Methoxy-2-pentylthiophene (**7g**).*[13] Yellow oil (46 mg, 63% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 (m, 1 H), 6.01 (d, J = 1.6 Hz, 1 H), 3.78 (s, 3 H), 2.69−2.73 (m, 2 H), 1.64−1.67 (m, 2 H), 1.33−1.37 (m, 4 H), 0.89−0.93 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 145.0, 116.6, 93.6, 56.9, 31.2, 30.9, 30.5, 22.4, 14.0; IR (neat) 2929, 2856, 1564, 1459, 1391, 1204 cm^{-1}; HRMS (EI-TOF) calcd for $C_{10}H_{16}OS$ (M^+) 184.0922, found 184.0927.

*3-Ethoxy-2-methyl-5-pentylthiophene (**7h**).* Yellow oil (47 mg, 55% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 (s, 1 H), 3.98 (q, J = 7.1 Hz, 2 H), 2.66 (t, J = 7.6 Hz, 2 H), 2.23 (s, 3 H), 1.58−1.64 (m, 2 H), 1.31−1.36 (m, 7 H), 0.90 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 139.7, 115.4, 114.3, 67.3, 31.2, 31.1, 30.6, 22.4, 15.4, 14.0, 10.6; IR (neat) 2926, 2858, 1579, 1458, 1383, 1150 cm^{-1}; HRMS (EI-TOF) calcd for $C_{12}H_{20}OS$ (M^+) 212.1235, found 212.1232.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Proton and carbon NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhouhw@zju.edu.cn. Fax: (+ 86)-571-8892-0271.

Notes

The authors declare no competing financial interest.

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