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Catalytic Nucleophilic Addition Reaction to (2-Furyl)carbene Intermediates Generated from Carbonyl–Ene–Ynes

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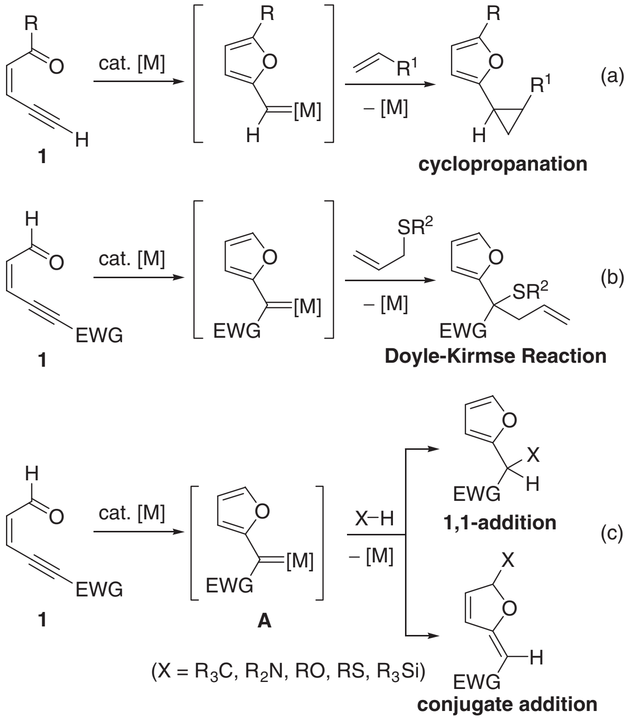
Rhodium- and chromium-catalyzed addition reactions of various σ-bonds, such as C–H, N–H, O–H, Si–H, and S–H bonds, to (2-furyl)carbenoids in situ generated from conjugated carbonyl–ene–yne compounds having electron-withdrawing groups on an alkyne terminus are described. 2-Alkoxy-2,5-dihydrofuran was obtained from the chromium-catalyzed addition reaction of an alcohol with the (2-furyl)carbene chromium intermediates in a conjugate manner.

Nucleophilic addition reactions of either activated or inactivated σ-bonds, such as C–H, N–H, O–H, Si–H, and S–H bonds to transient electrophilic carbenoid species serve as one of the most powerful σ-bond construction reactions.[1] Transition-metal-catalyzed intra- and intermolecular addition reactions to a C=M bond of carbenoid species generated from diazo compounds have been intensively investigated to provide a direct entry to σ-bond construction.[2–7] We, and other researchers, have explored the generation of carbenoid species with activation of alkynes using transition-metal complexes.[8] We have already developed catalytic carbene-transfer reactions involving the in situ generation of (2-furyl)carbenoids from carbonyl–ene–yne compounds and their application to catalytic cyclopropanation reactions and the Doyle–Kirmse reaction, which is a formal C–S bond insertion reaction via an ylide rearrangement (Schemes 1a and 1b).[8b,8c,9] In the course of our continuous study, we have also found that electron-withdrawing groups introduced at the alkyne terminus of **1** enhance the electrophilicity of the intermediary carbenoid species.[9,10] Herein, we report on rhodium-catalyzed nucleophilic addition reactions of Xsp^3–H bonds (where X = C, N, O, S, and Si), as well as a unique chromium-catalyzed addition reaction to the intermediary (2-furyl)carbene complexes with methanol (Scheme 1c).



Scheme 1.

Results and Discussion

Rhodium-Catalyzed Addition Reactions of C–H Bonds. First, we attempted to carry out the addition reaction of a C–H bond of cyclohexa-1,4-diene to a (2-furyl)carbene intermediate generated from the carbonyl–ene–yne compound **1a**, which is a good (2-furyl)carbene precursor for the catalytic cyclopropanation reaction,[8b,8c] in the presence of a catalytic amount of [$Rh_2(OAc)_4$]. However, no reaction occurred. On the other hand, when the rhodium-catalyzed reaction of **1b** having an electron-withdrawing benzoyl group at an alkyne terminus, which was expected to enhance the electrophilicity of the intermediary carbenoid species to an allylic C–H bond was carried out, 3-furfurylcyclohexa-1,4-diene derivative **2b** was obtained in 20% yield (eq 1). The acetyl compound **1c** was more reactive for the allylic C–H bond addition reaction and afforded the corresponding product **2c** in 35% yield. Notably, the reaction of **1d** having a methoxycarbonyl moiety with cyclohexa-1,4-diene took place at room temperature. Moreover, **1e**, which has a phenoxycarbonyl moiety, reacted with cyclohexa-1,4-diene more smoothly to give the corresponding adduct **2e** in higher yield. The results of the addition reactions using **1e** with selected compounds are summarized in Table 1. Cyclohexa-1,3-diene gave the adduct **3e** with an allylic C–H bond of cyclohexa-1,3-diene in 47% yield as a mixture of diastereomers (dr = 80/20). Cycloheptatriene also reacted

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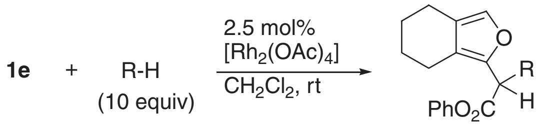
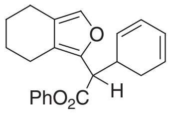
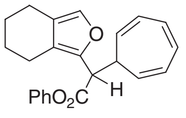
Table 1. Rh-Catalyzed Addition Reactions of sp^3 C–H Bond to Carbenes Generated from **1e**[a)]

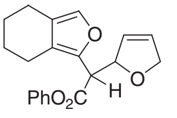




3e 47% (80/20)

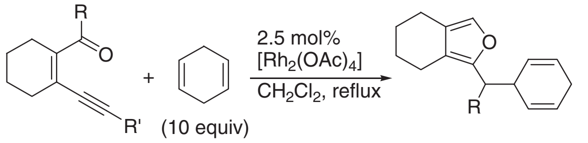


4e 38%



5e 68% (67/33)

a) Reactions of **1e** (0.2 mmol) with cyclic olefin (2.0 mmol) in CH_2Cl_2 (1 mL) were carried out in the presence of $[Rh_2(OAc)_4]$ (0.005 mmol) at room temperature under N_2. Diastereomeric ratios were determined by ^1H NMR.



(1)

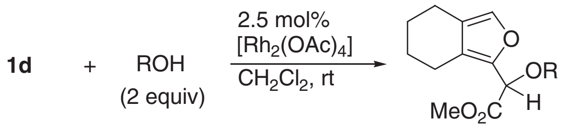
1a (R = Ph, R' = H)
1b (R = H, R' = COPh)
1c (R = H, R' = COMe)
1d (R = H, R' = CO_2Me)
1e (R = H, R' = CO_2Ph)

2a 0% (24 h)
2b 20% (72 h)
2c 35% (8 h)
2d 57% (rt, 48 h)
2e 67% (rt, 12 h)

with **1e** to give the cyclohepta-2,4,6-trienyl adduct **4e** in 38% yield. The reaction with 2,5-dihydrofuran also produced the adduct **5e** in 68% yield as a mixture of diastereomers (dr = 67/33). However, no addition reaction of a C–H bond occurred with cyclohexene, tetrahydrofuran, cyclopentadiene,[11] or penta-1,4-diene. These results indicate that highly activated C–H bonds at a doubly allylic position, or at an allylic position adjacent to a heteroatom in a cyclic structure are required for the nucleophilic addition reactions using **1e** as a furylcarbene precursor. Davies and co-workers reported that phenylcarbene intermediates in situ generated from phenyldiazoacetates inserted into C–H bonds at a double allylic position as well as at a C–H bond of cyclohexane.[3c] They mentioned that a C–H bond at a double allylic position of cyclohexa-1,4-diene is almost 10 times as reactive to a carbene intermediate than a C–H bond next to the oxygen atom of tetrahydrofuran. Since an electron-rich furan ring generated from a carbonyl–ene–yne moiety decreases the electrophilicity of a (2-furyl)carbene carbon to attack C–H bonds, it seems that phenylcarbene intermediates generated from phenyldiazoacetates are much more reactive than the present (2-furyl)carbenoid generated from **1e** in the addition reactions to C–H bonds.

Rhodium-Catalyzed Addition Reactions of Heteroatom–Hydrogen Bonds (X–H, where X = N, O, Si, or S). Addition reactions of alcohols or phenols to carbenoid species generated from diazoalkanes have been well investigated.[4] Therefore, we carried out the rhodium-catalyzed addition reaction of several alcohols and phenols with methoxycarbonyl analogue **1d** as a furylcarbene precursor. The results are shown in Table 2. The reaction of **1d** with methanol gave the furfuryl methyl ether **6d** in 82% yield (Entry 1). Reactions of **1d** with ethanol and benzyl alcohol also gave the corresponding furfuryl ethers **7d** and **8d** in 63% and 42% yields, respectively (Entries 2 and 3). Secondary alcohol also reacted with **1d** to give the adduct **9d** in 54% yield (Entry 4). However, no reaction occurred with *tert*-butyl alcohol, probably because of its bulkiness (Entry 5). The reaction with phenol and *p*-methoxyphenol gave a complex mixture, while the reaction with *p*-nitrophenol produced the adduct **10d** in 44% yield (Entries 6–8). These are unexpected results, because it is known that electrophilic carbene complexes generated from diazo compounds react with more electron-rich phenols smoothly to give adducts.[4i]

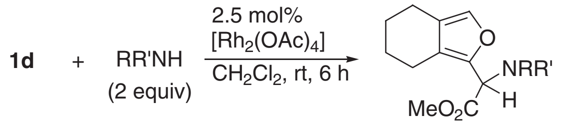
Table 2. Rh-Catalyzed Addition Reactions of Alcohols or Phenols with **1d**[a)]



Entry	ROH	Time/h	Product	Yield/%[b)]
1	MeOH	4	**6d**	82
2	EtOH	4	**7d**	63
3	BnOH	4	**8d**	42
4	^{i}PrOH	4	**9d**	54
5	^{t}BuOH	12	—	—
6	PhOH	12	—	trace
7	p-$MeOC_6H_4OH$	12	—	—
8	p-$NO_2C_6H_4OH$	8	**10d**	44

a) Reactions of **1d** (0.2 mmol) with alcohol or phenol (0.4 mmol) in CH_2Cl_2 (1 mL) were carried out in the presence of $[Rh_2(OAc)_4]$ (0.005 mmol) at room temperature under N_2. b) Isolated yield.

Table 3. Rh-Catalyzed Addition Reactions of N–H Bond to Furylcarbene Species Using **1d**[a)]

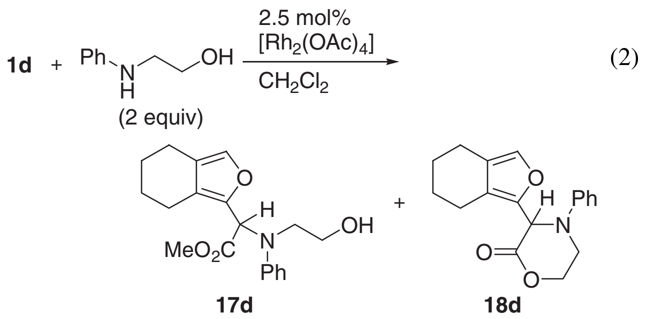


Entry	RR′NH	Product	Yield/%[b)]
1	Et_2NH	—	—
2	Ph(Me)NH	**11d**	69
3	Ph_2NH	**12d**	45
4	$PhNH_2$	**13d**	46
5	p-$MeOC_6H_4NH_2$	**14d**	12
6	p-$NO_2C_6H_4NH_2$	**15d**	62
7	CH_3CONH_2	—	—
8	$TsNH_2$	**16d**	51

a) Reactions of **1d** (0.2 mmol) with amine or amide (0.4 mmol) in CH_2Cl_2 (1 mL) were carried out in the presence of $[Rh_2(OAc)_4]$ (0.005 mmol) at room temperature under N_2. b) Isolated yield.

To examine the addition reactions of heteroatom–hydrogen bonds, the reaction of **1d** with several amines and amides was carried out,[5] and the results are summarized in Table 3. Although several researchers have reported that alkyl amines are applicable to the addition reaction of phenylcarbenoids generated from phenyldiazoacetates,[5c,5d] the reaction of **1d** with diethylamine gave no adduct (Entry 1). On the other hand, *N*-methylaniline and diphenylamine gave α-amino acid esters **11d** and **12d** in 69% and 45% yields, respectively (Entries 2 and 3). The carbene precursor **1d** underwent an addition reaction to only one of two N–H bonds of anilines to give **13d** (Entry 4). These results indicate that at least one aryl group on the nitrogen atom is essential for the present addition reactions of N–H bonds to (2-furyl)carbene intermediates. *p*-Methoxyaniline gave the corresponding α-amino acid ester **14d** in a lower yield, while *p*-nitroaniline afforded **15d** in a higher yield (Entries 5 and 6). The propensity of the reactivity of p-substituted anilines was consistent with that of phenol derivatives (vide supra). The reaction with acetamide gave no adduct, while the reaction with *p*-toluenesulfonamide yielded the corresponding adduct **16d** in a moderate yield (Entries 7 and 8).

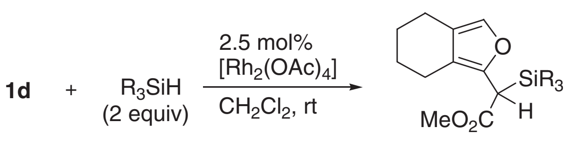
A competition experiment, in which 2-anilinoethanol with **1d** was reacted at room temperature, led exclusively to the formation of N-adducts **17d** and *N*-phenylmorpholin-2-one **18d** (eq 2).[12] This tendency, where a (2-furyl)carbenoid intermediate favors a nitrogen nucleophile rather than an oxygen nucleophile, is similar to the reported result of the competition reaction of diazo compounds with aniline and phenol to give 2-phenylaminoacetates in rhodium catalysis.[4e]



(2)

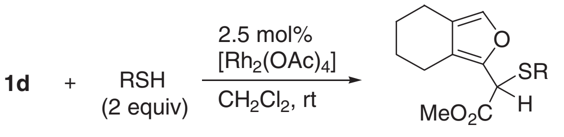
temp.	time/h	17d	18d
rt	6	90%	6%
reflux	19	31%	17%

Finally, we examined the addition reactions of Si–H and S–H bonds with **1d** in the presence of a Rh catalyst. Since silanes are known as good acceptors of carbene intermediates generated from diazoalkanes,[6] the reactions of **1d** with triethylsilane or triphenylsilane were carried out. Expectedly, the rhodium-catalyzed addition reaction proceeded to give **19d** (67% yield) and **20d** (20% yield), respectively (eq 3). Reactions of **1d** with alkanethiol and benzenethiol gave sulfides **21d** (35% yield) and **22d** (59% yield), respectively (eq 4). To the best of our knowledge, only a few catalytic addition reactions of S–H bonds to carbene species generated from diazoalkanes have been reported.[7] Interestingly, arenethiols gave the corresponding adducts **23d** and **24d** in good yields, irrespective of the electronic nature of the substituents.



(3)

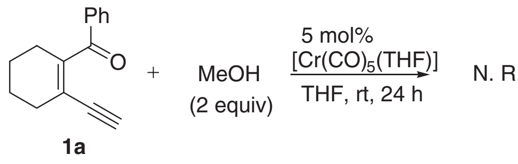
R = Et	**19d** 67% (2 h)
Ph	**20d** 20% (8 h)



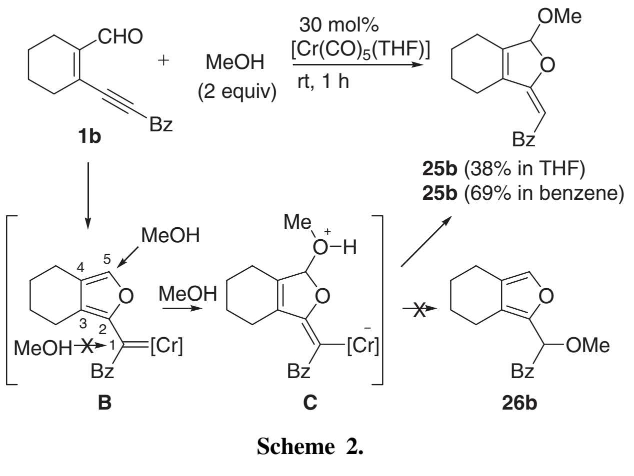
(4)

R = *n*-Bu	**21d** 35% (24 h)
Ph	**22d** 59% (8 h)
p-MeOC$_6$H$_4$	**23d** 73% (8 h)
p-NO$_2$C$_6$H$_4$	**24d** 80% (4 h)

Chromium-Catalyzed Conjugate Addition Reactions of Alcoholic O–H Bonds. Since we found the generation of (2-furyl)carbene complexes from carbonyl–ene–ynes and a chromium carbonyl compound,[8a–8c] we attempted to carry out the addition reactions of an alcohol in the presence of chromium catalyst. The reaction of **1a** with MeOH (2 equiv) in THF was carried out at room temperature in the presence of 5 mol % of [Cr(CO)$_5$(THF)], but no adducts were obtained (eq 5). On the other hand, the reaction of the carbonyl–ene–yne compound **1b** afforded the unexpected 2-alkoxy-5-alkylidene-2,5-dihydrofuran **25b** in 38% yield instead of the typical adduct **26b** (Scheme 2).[13] Barluenga and co-workers reported that the nucleophilic conjugate addition reactions of organolithium reagents to Fischer carbene complexes led to the formation of 2,3-dihydrofurans.[14,15] To the best of our knowledge, the present reaction is the first example of the conjugate addition of methanol to arylcarbene complexes. Among the other solvents examined for this chromium-mediated conjugate addition reaction, benzene was revealed to be the best solvent of choice (69% yield). Secondary alcohols were less reactive under identical conditions, giving the corresponding adducts in 10%–20% yields, while *tert*-butyl alcohol gave no adducts at all. Interestingly, adduct **25b** was gradually isomerized into thermodynamically stable **25b′** at room temperature under slightly acidic conditions (eq 6).[13] This indicates that the more hindered chromium moiety rather than the benzoyl group is oriented towards the less hindered oxygen in order to avoid steric repulsion from the cyclohexane ring in intermediate **B** and transient structure **C**.

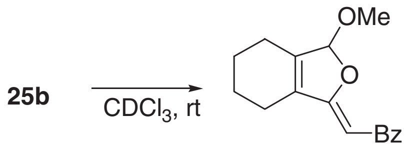


(5)



25b (38% in THF)
25b (69% in benzene)

Scheme 2.



25b'

(6)

In conclusion, we have demonstrated the rhodium- and chromium-catalyzed addition reactions of various σ-bonds, such as C–H, N–H, O–H, Si–H, and S–H, based on the in situ generation of (2-furyl)carbenoids from conjugated carbonyl–ene–yne compounds. We also found that carbonyl–ene–yne compounds having electron-withdrawing groups on an alkyne terminus act as a strongly electrophilic carbenoid precursor for Rh- and Cr-catalyzed reactions. In the case of chromium-catalyzed reactions, the addition of an alcohol to the (2-furyl)carbene chromium intermediates takes place in a conjugate manner to afford 2-alkoxy-5-alkylidene-2,5-dihydrofuran. These results strongly support the generation of (2-furyl)carbene species from conjugated carbonyl–ene–ynes. These nucleophilic addition reactions of O–H, N–H, O–H, Si–H, and S–H σ-bonds to carbene complex intermediates will be applicable to asymmetric synthesis.

Experimental

General Procedures. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. NMR spectra were measured for solutions in $CDCl_3$ with $SiMe_4$ as an internal standard or CD_2Cl_2 (^1H and ^{13}C): the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL, JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. All new compounds prepared were fully characterized. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon, and other solvents were dried by the usual methods and distilled before use.

Synthesis of 1. Compounds **1a**–**1d** were prepared by reported procedures.[9]

Ene–Yne–Carbonyl Compound 1e. Ene–yne–carbonyl compound **1e** was prepared by the same procedure for the synthesis of **1d**[9] using phenyl chloroformate instead of methyl chloroformate to introduce a phenyloxycarbonyl moiety at an alkyne terminus. A yellow solid (0.52 g, 2.04 mmol, 68% yield for 2 steps); mp 53.8–54.0 °C; IR (KBr) 495, 694, 733, 758, 846, 939, 1063, 1127, 1161, 1215, 1254, 1366, 1426, 1455, 1491, 1588, 1682 (C=O), 1720 (C=O), 2215 (C≡C), 2840, 2864, 2939, 3062, 3346, 3441 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.60–1.81 (m, 4H), 2.25–2.38 (m, 2H), 2.43–2.55 (m, 2H), 7.15 (d, $J = 7.2$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.41 (dd, $J = 7.2$, 7.2 Hz, 2H), 10.1 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.5, 21.4, 22.3, 31.0, 84.4, 87.5, 121.2, 126.5, 129.5, 135.2, 148.4, 149.9, 151.5, 191.2. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55%. Found: C, 75.12; H, 5.58%. HRMS (FAB) Calcd for $C_{16}H_{15}O_3$ ($M + H^+$): 255.1021. Found: 255.1024.

Typical Procedure for Rh-Catalyzed Reaction of 1 with Allylic C–H Bonds. To a solution of **1** (0.20 mmol) and diene or triene (2 mmol) in dry and deoxygenated CH_2Cl_2 (1.0 mL) in a flame dried Schlenk flask was added $[Rh_2(OAc)_4]$ (2.2 mg, 0.005 mmol) at room temperature under N_2. After the reaction was complete, the organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 20/1) as an eluent to afford the corresponding products.

3-Furfurylcyclohexa-1,4-diene 2b. A colorless oil (12.5 mg, 0.039 mmol, 20% yield); IR (neat) 544, 599, 699, 759, 800, 1026, 1094, 1260, 1446, 1596, 1681, 1773 (C=O), 2817, 2853, 2921, 3028, 3400, 2855, 2931, 3073 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.60–1.62 (m, 4H), 2.35–2.56 (m, 4H), 2.65–2.70 (m, 2H), 3.83–3.86 (m, 1H), 4.51 (d, $J = 10.8$ Hz, 1H), 5.36 (d, $J = 10.8$ Hz, 1H), 5.67–5.77 (m, 3H), 7.07 (s, 1H), 7.41 (dd, $J = 7.2$, 7.2 Hz, 2H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.95 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.2, 20.6, 23.0, 23.2, 26.4, 35.4, 53.0, 119.3, 122.4, 125.5, 125.6, 126.6, 127.1, 128.4, 128.4, 132.8, 136.6, 136.9, 142.5, 195.3. HRMS (FAB) Calcd for $C_{22}H_{23}O_2$ ($M + H^+$): 319.1698. Found: 319.1698.

3-Furfurylcyclohexa-1,4-diene 2c. A yellow oil (31.3 mg, 0.070 mmol, 35% yield); IR (neat) 402, 701, 742, 791, 849, 1112, 1152, 1260, 1353, 1416, 1443, 1556, 1634, 1722 (C=O), 2857, 2954, 3029, 3428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.59–1.67 (m, 4H), 2.08 (s, 3H), 2.41–2.44 (m, 2H), 2.50–2.53 (m, 2H), 2.59–2.63 (m, 2H), 3.56–3.58 (m, 2H), 5.32 (d, $J = 10.0$ Hz, 1H), 5.67–5.70 (m, 2H), 5.75–5.78 (m, 1H), 7.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.2, 20.4, 23.1, 23.2, 26.3, 29.3, 34.7, 58.4, 119.7, 122.3, 125.4, 125.7, 126.3, 126.8, 136.6, 142.8, 204.5. Anal. Calcd for $C_{17}H_{20}O_2$: C, 74.97; H, 7.40%. Found: C, 74.48; H, 7.62%. HRMS (FAB) Calcd for $C_{17}H_{21}O_2$ ($M + H^+$): 257.1542. Found: 257.1547.

3-Furfurylcyclohexa-1,4-diene 2d. A colorless oil (31.3 mg, 0.11 mmol, 57% yield); IR (neat) 608, 708, 738, 761, 889, 919, 989, 1020, 1113, 1155, 1255, 1321, 1384, 1434, 1556, 1635, 1739 (C=O), 2855, 2931, 3028, 3478 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.65–1.68 (m, 4H), 2.45–2.50 (m, 4H), 2.62–2.64 (m, 2H), 3.57–3.59 (m, 1H), 3.70 (s, 3H), 5.33–5.36 (m, 1H), 5.67–5.73 (m, 2H), 5.78–5.82 (m, 1H), 7.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.2, 20.3, 23.1, 23.2, 26.3, 35.9, 50.5, 52.0, 119.2, 122.1, 125.7, 125.8, 126.1, 126.3, 136.3, 142.7, 171.0. HRMS (FAB) Calcd for $C_{17}H_{21}O_3$ ($M + H^+$): 273.1491. Found: 273.1488.

3-Furfurylcyclohexa-1,4-diene 2e. A colorless oil (44.9 mg, 0.13 mmol, 67% yield); IR (neat) 689, 707, 739, 942, 1024, 1070, 1123, 1162, 1193, 1318, 1492, 1592, 1637, 1758 (C=O), 2857, 2932, 3030, 3450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.68–1.70 (m, 4H), 2.51–2.53 (m, 4H), 2.67 (dd, $J = 4.0$, 4.0 Hz, 2H), 3.66–3.73 (m, 1H), 3.76 (d, $J = 10.0$ Hz, 1H), 5.43–5.45 (m, 1H), 5.75–5.78 (m, 1H), 5.84–5.87 (m, 2H), 7.04 (d, $J = 7.2$ Hz, 2H), 7.14 (s, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.34 (dd, $J = 7.2$, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.2, 20.4, 23.2, 23.2, 26.4, 36.0, 50.7, 119.5, 121.4, 122.2, 125.6, 125.7, 125.9, 126.1, 126.4, 129.2, 136.6, 142.3, 150.6, 168.9. Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63%. Found: C, 79.09; H, 6.84%.

4-Furfurylcyclohexa-1,3-diene 3e. A colorless oil (31.4 mg, 0.093 mmol, 47% yield, dr = 80/20); IR (neat) 411, 502, 689, 734, 1024, 1094, 1118, 1384, 1441, 1493, 1593, 1748 (C=O), 2851, 2925, 3040, 3412 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): major isomer, δ 1.67–1.74 (m, 4H), 1.89 (ddd, $J = 5.2$, 6.4, 17.6 Hz, 1H), 2.19–2.20 (m, 1H), 2.50–2.56 (m, 4H), 3.10–3.18 (m, 1H), 3.98 (d, $J = 10.8$ Hz, 1H), 5.76 (dd, $J = 4.8$, 9.6 Hz, 1H), 5.95–6.00 (m, 2H), 6.07 (dd, $J = 4.8$, 9.6 Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 2H), 7.16 (s, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.37 (dd, $J = 7.6$, 7.6 Hz, 2H); minor isomer, δ 1.67–1.74 (m, 4H), 2.21–2.23 (m, 1H), 2.45–2.56 (m, 5H), 3.22–3.31 (m, 1H), 3.96 (d, $J = 10.8$ Hz, 1H), 5.50 (dd, $J = 4.0$, 8.8 Hz, 1H), 5.85–5.89 (m, 1H), 5.95–5.97 (m, 2H), 7.03 (d, $J = 7.6$ Hz, 2H), 7.16 (s, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.37 (dd, $J = 7.6$, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): major isomer, δ 20.7, 20.7, 23.6, 23.6, 25.9, 33.2, 46.8, 121.8, 122.0, 122.7, 124.3, 125.5, 125.7, 126.0, 128.2, 129.6, 136.9, 142.9, 151.1, 169.7; minor isomer, δ 20.5, 20.5, 23.5, 23.5, 27.5, 33.6, 47.1, 121.8, 121.9, 123.1, 124.5, 125.5, 125.9, 126.2, 127.8, 129.7, 136.5, 143.2, 151.6, 169.8. Anal. Calcd for $C_{22}H_{22}O_3$ (a mixture of isomers): C, 79.02; H, 6.63%. Found: C, 78.95; H, 6.88%.

7-Furfurylcyclohepta-1,3,5-triene 4e. A colorless oil (26.2 mg, 0.076 mmol, 38% yield); IR (neat) 500, 701, 742, 935, 1023, 1070, 1123, 1162, 1195, 1243, 1399, 1441, 1492, 1592, 1759 (C=O), 2855, 2932, 3017, 3478 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.60–1.75 (m, 4H), 2.42–2.59 (m, 4H), 3.03 (ddd, $J = 6.3$, 6.3, 11.1 Hz, 1H), 4.10 (d, $J = 11.1$ Hz, 1H), 5.24 (dd, $J = 6.3$, 9.3 Hz, 1H), 5.47 (dd, $J = 6.3$, 9.3 Hz, 1H), 6.20 (ddd, $J = 2.4$, 3.6, 9.3 Hz, 1H), 6.30 (ddd, $J = 2.4$, 3.6, 9.3 Hz, 1H), 6.63–6.75 (m, 2H), 7.02 (d, $J = 7.8$ Hz, 2H), 7.11 (s, 1H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.33 (dd, $J = 7.8$, 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.1, 20.3, 23.0, 23.1, 39.3, 45.1, 119.9, 121.4, 121.5, 122.2, 123.1, 123.8, 125.7, 125.7, 125.8, 129.2, 130.8, 136.8, 142.7, 150.7, 169.2. Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40%. Found: C, 79.48; H, 6.61%.

2-Furfuryl-2,5-dihydrofuran 5e. A colorless oil (44.0 mg, 0.14 mmol, 68% yield, dr = 67/33); IR (neat) 501, 608, 690, 751, 818, 900, 1022, 1074, 1141, 1162, 1193, 1254, 1441, 1492, 1592, 1758 (C=O), 2855, 2932, 3081, 3478 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): major isomer, δ 1.69–1.71 (m, 4H), 2.53–2.55 (m, 4H), 4.01 (d, $J = 7.2$ Hz, 1H), 4.61 (d, $J = 4.4$ Hz, 2H), 5.44–5.48 (m, 1H), 5.99–6.01 (m, 2H), 7.03 (d, $J = 7.6$ Hz, 2H), 7.15 (s, 1H), 7.23 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.37 (dd, $J = 7.6$, 7.6 Hz, 2H); minor isomer, δ 1.69–1.71 (m, 4H), 2.54–2.56 (m, 4H), 3.96 (d, $J = 8.7$ Hz, 1H), 4.65–4.69 (m, 2H), 5.52–5.58 (m, 1H), 5.68–5.72 (m, 1H), 5.94–5.96 (m, 1H), 7.06 (d, $J = 7.6$ Hz, 2H), 7.15 (s, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.37 (dd, $J = 7.6$, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): major isomer, δ 20.5, 20.7, 23.5, 23.6, 50.1, 75.8, 85.6, 120.1, 121.7, 122.8, 126.2, 127.7, 128.9, 129.6, 136.8, 142.3, 150.9, 168.5; minor isomer, δ 20.4, 23.5, 23.5, 51.3, 75.9, 85.6, 120.1, 121.9, 122.9, 126.2, 127.8, 128.8, 129.7, 137.2, 141.8, 151.2, 168.8. Anal. Calcd for $C_{20}H_{20}O_4$ (a mixture of isomers): C, 74.06; H, 6.21%. Found: C, 73.80; H, 6.19%.

Furfuryl Methyl Ether 6d. A colorless oil (36.6 mg, 0.16 mmol, 82% yield); IR (neat) 602, 763, 850, 920, 947, 1009, 1109, 1194, 1270, 1335, 1439, 1581, 1758 (C=O), 2856, 2932, 3437 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.68–1.70 (m, 4H), 2.52–2.55 (m, 4H), 3.37 (s, 3H), 3.79 (s, 3H), 4.84 (s, 1H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.1, 20.1, 23.0, 23.0, 52.5, 57.0, 74.5, 121.8, 122.3, 137.6, 141.8, 169.1. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%. Found: C, 63.99; H, 7.23%.

Ethyl Furfuryl Ether 7d. A colorless oil (30.1 mg, 0.12 mmol, 63% yield); IR (neat) 613, 727, 760, 935, 987, 1024, 1052, 1113, 1203, 1236, 1269, 1332, 1436, 1651, 1751 (C=O), 2862, 2938, 3467 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.25 (t, $J = 7.2$ Hz, 3H), 1.67–1.71 (m, 4H), 2.46–2.60 (m, 4H), 3.51 (q, $J = 7.2$ Hz, 1H), 3.54 (q, $J = 7.2$ Hz, 1H), 3.77 (s, 3H), 4.94 (s, 1H), 7.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 15.0, 20.0, 20.1, 22.9, 22.9, 52.4, 64.8, 73.0, 121.3, 122.2, 137.3, 142.2, 169.4. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%. Found: C, 65.76; H, 7.69%.

Benzyl Furfuryl Ether 8d. A colorless oil (25.2 mg, 0.084 mmol, 42% yield); IR (neat) 401, 699, 747, 934, 1026, 1093, 1204, 1263, 1384, 1435, 1681, 1739 (C=O), 2339, 2359, 2859, 2932, 3458 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.59–1.66 (m, 4H), 2.30–2.37 (m, 1H), 2.46–2.50 (m, 3H), 3.76 (s, 3H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.62 (d, $J = 12.0$ Hz, 1H), 4.97 (s, 1H), 7.12 (s, 1H), 7.25–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 19.9, 20.0, 22.8, 22.8, 52.4, 70.7, 71.6, 121.9, 122.3, 127.8, 128.0, 128.3, 137.0, 137.6, 142.0, 169.3. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%. Found: C, 71.70; H, 6.77%.

Furfuryl *i*-Propyl Ether 9d. A colorless oil (27.0 mg, 0.11 mmol, 54% yield); IR (neat) 601, 667, 758, 919, 990, 1019, 1090, 1174, 1197, 1264, 1384, 1435, 1633, 1760 (C=O), 2351, 2856, 2929, 3390 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.18 (d, $J = 6.0$ Hz, 3H), 1.22 (d, $J = 6.0$ Hz, 3H), 1.66–1.69 (m, 4H), 2.44–2.61 (m, 4H), 3.65 (sep, $J = 6.0$ Hz, 1H), 3.76 (s, 3H), 5.02 (s, 1H), 7.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.0, 20.1, 21.9, 21.9, 22.9, 22.9, 52.3, 70.6, 70.9, 120.9, 122.3, 137.3, 142.8, 170.0. HRMS (FAB) Calcd for $C_{14}H_{21}O_4$ ($M + H^+$): 253.1440. Found: 253.1442.

Furfuryl *p*-Nitrophenyl Ether 10d. A yellow oil (29.1 mg, 0.087 mmol, 44% yield); IR (neat) 640, 688, 733, 751, 763, 845, 877, 912, 969, 1039, 1112, 1202, 1243, 1299, 1340, 1384, 1436, 1516, 1592, 1760 (C=O), 2857, 2932 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.62–1.70 (m, 4H), 2.48–2.58 (m, 4H), 3.82 (s, 3H), 5.74 (s, 1H), 7.00 (d, $J = 9.3$ Hz, 2H), 7.18 (s, 1H), 8.19 (d, $J = 9.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 19.9, 20.0, 22.6, 22.6, 53.0, 71.6, 115.3, 122.9, 122.9, 125.8, 138.3, 139.8, 142.3, 161.8, 167.3. Anal. Calcd for $C_{17}H_{17}NO_6$: C, 61.63; H, 5.17; N, 4.23%. Found: C, 61.71; H, 5.20; N, 3.94%.

α-Amino Acid Ester 11d. A colorless oil (45.1 mg, 0.13 mmol, 69% yield); IR (neat) 691, 750, 920, 949, 997, 1033, 1111, 1196, 1307, 1366, 1435, 1504, 1598, 1751 (C=O), 2854, 2931, 3025 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.60–1.78 (m, 4H), 2.21–2.35 (m, 1H), 2.40–2.53 (m, 3H), 2.84 (s, 3H), 3.75 (s, 3H), 5.54 (s, 1H), 6.76 (d, $J = 7.5$ Hz, 2H), 6.79 (t, $J = 7.5$ Hz, 1H), 7.13 (s, 1H), 7.24 (dd, $J = 7.5$, 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.1, 20.1, 22.9, 22.9, 34.2, 52.3, 59.3, 113.3, 117.9, 120.9, 122.4, 129.2, 137.0, 142.1, 149.3, 170.7. Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68%. Found: C, 72.39; H, 7.34; N, 4.61%.

α-Amino Acid Ester 12d. A colorless oil (32.8 mg, 0.090 mmol, 45% yield); IR (neat) 601, 701, 745, 908, 921, 988, 1039, 1073, 1095, 1271, 1359, 1447, 1494, 1590, 1754 (C=O), 2855, 2933, 3059 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.37–1.53 (m, 4H), 1.90–1.98 (m, 1H), 2.05–2.17 (m, 1H), 2.35–2.41 (m, 2H), 3.80 (s, 3H), 5.73 (s, 1H), 6.83 (d, $J = 7.5$ Hz, 4H), 6.95 (dd, $J = 7.5$, 7.5 Hz, 2H), 6.97 (s, 1H), 7.18 (dd, $J = 7.5$, 7.5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 19.9, 19.9, 22.7, 22.7, 52.5, 59.4, 122.0, 122.2, 122.2, 122.2, 128.8, 136.8, 140.8, 146.0, 170.6. Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88%. Found: C, 76.34; H, 6.45; N, 3.77%.

α-Amino Acid Ester 13d. A colorless oil (26.4 mg, 0.091 mmol, 46% yield); IR (neat) 408, 507, 551, 602, 692, 749, 818, 849, 920, 988, 1074, 1147, 1176, 1202, 1256, 1311, 1385, 1434, 1504, 1603, 1738 (C=O), 2854, 2934, 3022, 3051, 3405 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.66–1.80 (m, 4H), 2.48–2.53 (m, 4H), 3.75 (s, 3H), 4.76 (d, $J = 7.3$ Hz, 1H), 5.13 (d, $J = 7.3$ Hz, 1H), 6.61 (d, $J = 7.3$ Hz, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 7.09 (s, 1H), 7.15 (dd, $J = 7.3$, 7.3 Hz, 2H); ^{13}C NMR (67.5 MHz, CDCl$_3$, 25 °C) δ 20.1, 20.2, 22.9, 23.8, 52.8, 54.0, 113.3, 118.4, 119.4, 122.4, 129.1, 136.8, 142.4, 145.8, 170.5. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91%. Found: C, 71.31; H, 6.83; N, 5.18%.

α-Amino Acid Ester 14d. A colorless oil (7.8 mg, 0.024 mmol, 12% yield); IR (neat) 401, 606, 671, 692, 732, 803, 892, 919, 1044, 1093, 1203, 1351, 1442, 1481, 1526, 1583, 1739 (C=O), 2874, 2931, 3092, 3377 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 1.55–1.67 (m, 4H), 2.49–2.52 (m, 4H), 3.73 (s, 3H), 3.74 (s, 3H), 4.50 (d, $J = 5.6$ Hz, 1H), 5.06 (d, $J = 5.6$ Hz, 1H), 6.59 (d, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 8.8$ Hz, 2H), 7.09 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) δ 20.1, 20.2, 22.9, 23.0, 52.7, 55.0, 55.6, 114.7, 115.0, 119.4, 122.4, 136.8, 140.0, 142.6, 152.7, 170.7. HRMS (FAB) Calcd for $C_{18}H_{21}NO_4$ (M$^+$): 315.1471. Found: 315.1472.

α-Amino Acid Ester 15d. A yellow solid (41.2 mg, 0.12 mmol, 62% yield); mp 131.2–131.8 °C; IR (KBr) 497, 696, 754, 763, 842, 1004, 1115, 1149, 1185, 1218, 1252, 1292, 1317, 1474, 1500, 1523, 1597, 1728 (C=O), 2855, 2935, 3385 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 1.58–1.69 (m, 4H), 2.39–2.51 (m, 4H), 3.80 (s, 3H), 5.18 (d, $J = 6.4$ Hz, 1H), 5.59 (d, $J = 6.4$ Hz, 1H), 6.55 (d, $J = 9.2$ Hz, 2H), 7.10 (s, 1H), 8.07 (d, $J = 9.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) δ 20.0, 20.1, 22.8, 22.8, 53.1, 53.3, 111.7, 120.2, 122.7, 126.1, 137.3, 138.9, 140.9, 150.7, 169.3. Anal. Calcd for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.49; N, 8.48%. Found: C, 61.66; H, 5.53; N, 8.29%.

Furfurylsulfonamide 16d. A colorless oil (37.1 mg, 0.10 mmol, 51% yield); IR (neat) 402, 558, 671, 704, 736, 815, 1010, 1034, 1090, 1162, 1269, 1288, 1337, 1384, 1438, 1598, 1721, 1746 (C=O), 2857, 2934, 3279 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 1.56–1.59 (m, 4H), 2.34–2.37 (m, 7H), 3.64 (s, 3H), 5.11 (d, $J = 7.6$ Hz, 1H), 5.63 (d, $J = 7.6$ Hz, 1H), 6.88 (s, 1H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) δ 19.7, 19.9, 21.5, 22.7, 22.8, 52.0, 53.1, 120.7, 122.1, 126.8, 129.1, 136.9, 137.0, 140.3, 143.0, 168.3. Anal. Calcd for $C_{18}H_{21}NO_5S$: C, 59.49; H, 5.82; N, 3.85%. Found: C, 59.34; H, 5.79; N, 3.67%.

α-Amino Acid Ester 17d. A colorless oil (59.8 mg, 0.18 mmol, 90% yield); IR (neat) 693, 749, 1007, 1038, 1095, 1110, 1165, 1204, 1276, 1383, 1436, 1504, 1598, 1738 (C=O), 2856, 2932, 3437 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ 1.56–1.78 (m, 4H), 2.15–2.30 (m, 1H), 2.41–2.60 (m, 3H), 3.08 (br s, 1H), 3.24 (ddd, $J = 3.4$, 3.9, 15.1 Hz, 1H, N–CH$_2$), 3.48 (ddd, $J = 3.9$, 4.9, 11.2 Hz, 1H, O–CH$_2$), 3.56 (ddd, $J = 3.9$, 4.9, 15.1 Hz, 1H, N–CH$_2$), 3.67 (ddd, $J = 3.4$, 3.9, 11.2 Hz, 1H, O–CH$_2$), 3.82 (s, 3H), 5.46 (s, 1H), 6.80 (d, $J = 7.8$ Hz, 2H), 6.83 (t, $J = 7.8$ Hz, 1H), 7.15 (s, 1H), 7.25 (dd, $J = 7.8$, 7.8 Hz, 2H) (The peaks between 3.24–3.67 ppm were assigned by using D$_2$O experiments, see the Supporting Information); ^{13}C NMR (75.5 MHz, CDCl$_3$, 25 °C) δ 20.0, 20.1, 22.8, 22.9, 49.1, 52.9, 59.8, 60.3, 114.7, 118.9, 121.7, 122.6, 129.3, 137.4, 141.3, 147.7, 172.3. HRMS (FAB) Calcd for $C_{19}H_{24}NO_4$ (M + H$^+$): 330.1705. Found: 330.1710.

***N*-Phenylmorpholin-2-one 18d.** A colorless oil (9.8 mg, 0.033 mmol, 17% yield); IR (neat) 692, 733, 910, 1075, 1204, 1278, 1378, 1468, 1504, 1600, 1753 (C=O), 2854, 2931 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 1.60–1.75 (m, 4H), 2.39–2.65 (m, 4H), 3.61 (ddd, $J = 3.6$, 10.0, 11.6 Hz, 1H), 3.68 (ddd, $J = 3.2$, 3.6, 11.6 Hz, 1H), 4.56 (ddd, $J = 3.2$, 3.6, 11.6 Hz, 1H), 4.85 (ddd, $J = 3.6$, 10.0, 11.6 Hz, 1H), 5.42 (s, 1H), 6.70 (d, $J = 7.6$ Hz, 2H), 6.86 (t, $J = 7.6$ Hz, 1H), 7.10 (s, 1H), 7.26 (dd, $J = 7.6$, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) δ 20.1, 20.4, 22.9, 23.0, 43.1, 58.2, 65.8, 112.9, 119.2, 120.3, 122.7, 129.4, 137.2, 142.0, 147.1, 166.6. HRMS (FAB) Calcd for $C_{18}H_{20}NO_3$ (M + H$^+$): 298.1443. Found: 298.1443.

Triethyl(furfuryl)silane 19d. A colorless oil (41.1 mg, 0.13 mmol, 67% yield); IR (neat) 732, 772, 806, 836, 944, 972, 1007, 1072, 1163, 1240, 1435, 1650, 1712 (C=O), 1769, 2877, 2951, 3450 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ 0.64 (q, $J = 7.8$ Hz, 6H), 0.92 (t, $J = 7.8$ Hz, 9H), 1.58–1.65 (m, 4H), 2.32–2.40 (m, 2H), 2.49–2.52 (m, 2H), 3.47 (s, 1H), 3.65 (s, 3H), 7.08 (s, 1H); ^{13}C NMR (67.5 MHz, CDCl$_3$, 25 °C) δ 3.3, 6.9, 20.2, 20.5, 23.2, 23.3, 33.8, 51.5, 116.7, 121.9, 135.6, 143.8, 172.2. Anal. Calcd for $C_{17}H_{28}O_3Si$: C, 66.19; H, 9.15%. Found: C, 65.98; H, 8.94%.

Furfuryltriphenylsilane 20d. A white solid (17.8 mg, 0.039 mmol, 20% yield); mp 111.2–111.6 °C; IR (KBr) 479, 503, 699, 740, 847, 986, 1114, 1175, 1189, 1276, 1308, 1335, 1428, 1731 (C=O), 2848, 2917, 2937, 3071, 3427 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 1.46–1.62 (m, 4H), 2.05–2.12 (m, 1H), 2.21–2.27 (m, 1H), 2.39–2.41 (m, 2H), 3.38 (s, 3H), 4.28 (s, 1H), 6.91 (s, 1H), 7.32 (dd, $J = 7.2$, 7.2 Hz, 6H), 7.39 (t, $J = 7.2$ Hz, 3H), 7.49 (d, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) δ 20.2, 20.5, 23.1, 23.2, 36.4, 51.6, 118.2, 121.9, 127.5, 129.6, 132.7, 135.8, 136.0, 142.1, 171.3. Anal. Calcd for $C_{29}H_{28}O_3Si$: C, 76.95; H, 6.24%. Found: C, 76.53; H, 6.33%. HRMS (FAB) Calcd for $C_{29}H_{28}O_3Si$ (M$^+$): 452.1808. Found: 452.1808.

***n*-Butyl Furfuryl Sulfide 21d.** A colorless oil (19.5 mg, 0.069 mmol, 35% yield); IR (neat) 480, 535, 606, 671, 692, 732, 803, 845, 892, 919, 1045, 1093, 1166, 1202, 1351, 1440, 1481, 1529, 1538, 1620, 1693, 1735 (C=O), 1972, 2436, 2872, 2931, 3091, 3383 cm^{-1}; ^{1}H NMR (270 MHz, CD$_2$Cl$_2$, 25 °C) δ 0.80 (t, $J = 7.3$ Hz, 3H), 1.29 (tq, $J = 7.3$, 7.3 Hz, 2H), 1.42 (tq, $J = 7.3$, 7.3 Hz, 2H), 1.58–1.60 (m, 4H), 2.41–2.46 (m, 7H), 3.63 (s, 3H), 4.59 (s, 1H), 7.02 (s, 1H); ^{13}C NMR (67.5 MHz, CD$_2$Cl$_2$, 25 °C) δ 20.4, 20.7, 22.3, 23.4, 23.4, 31.6, 31.7, 32.1, 44.8, 53.0, 120.3, 122.9, 137.1, 142.0, 169.4. HRMS (FAB) Calcd for $C_{15}H_{22}O_3S$ (M$^+$): 282.1290. Found: 282.1296.

Furfuryl Phenyl Sulfide 22d. A colorless oil (35.6 mg, 0.12 mmol, 59% yield); IR (neat) 404, 692, 738, 798, 900, 947, 977, 1008, 1047, 1143, 1163, 1268, 1295, 1384, 1435, 1640, 1692, 1708 (C=O), 2859, 2943, 3412 cm^{-1}; ^{1}H NMR (300 MHz, C$_4$D$_8$O, 25 °C) δ 1.54–1.57 (m, 4H), 2.33–2.47 (m, 4H), 3.63 (s, 3H), 5.04 (s, 1H), 7.09 (s, 1H), 7.22–7.33 (m, 5H); ^{13}C NMR (75 MHz, C$_4$D$_8$O, 25 °C) δ 20.9, 20.9, 23.9, 23.9, 50.3, 52.6, 121.4, 123.1, 128.7, 129.3, 129.5, 134.5, 137.8, 142.5, 168.7. HRMS (FAB) Calcd for $C_{17}H_{19}O_3S$ (M + H$^+$): 303.1055. Found: 303.1048.

Furfuryl *p*-Methoxyphenyl Sulfide 23d. A colorless oil (48.7 mg, 0.14 mmol, 73% yield); IR (neat) 418, 527, 606, 639, 671, 692, 732, 803, 831, 892, 919, 1044, 1093, 1149, 1173, 1288, 1351, 1441, 1481, 1493, 1525, 1569, 1620, 1692, 1732 (C=O), 2868, 2933, 3091, 3352 cm^{-1}; ^{1}H NMR (270 MHz, CD$_2$Cl$_2$, 25 °C) δ 1.54–1.68 (m, 4H), 1.83–1.95 (m, 1H), 2.24–2.32 (m, 1H), 2.45–2.48 (m, 2H), 3.69 (s, 3H), 3.78 (s, 3H), 4.82 (s, 1H), 6.80 (d, $J = 8.9$ Hz, 2H), 7.11 (s, 1H), 7.24 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (65 MHz, CD$_2$Cl$_2$, 25 °C) δ 20.3, 20.4, 23.3, 23.3, 50.5, 55.6, 114.5, 121.5, 122.8, 123.2, 137.2, 137.3, 141.3, 160.7, 168.7. HRMS (FAB) Calcd for $C_{18}H_{20}O_4S$ (M$^+$): 332.1082. Found: 332.1801.

Furfuryl *p*-Nitrophenyl Sulfide 24d. A yellow oil (55.5 mg, 0.16 mmol, 80% yield); IR (neat) 411, 473, 539, 622, 638, 723, 740, 761, 801, 825, 853, 902, 948, 985, 1009, 1047, 1110, 1143, 1218, 1296, 1347, 1397, 1433, 1477, 1579, 1595, 1633, 1644, 1681, 1743 (C=O), 2856, 2927, 3097 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.61–1.67 (m, 4H), 2.46–2.49 (m, 4H), 3.68 (s, 3H), 5.49 (s, 1H), 7.13 (s, 1H), 7.40 (d, $J = 9.0$ Hz, 2H), 8.06 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 19.9, 20.3, 23.0, 23.0, 49.7, 52.2, 120.8, 122.5, 123.4, 124.1, 133.6, 137.4, 141.5, 145.7, 168.4. HRMS (FAB) Calcd for $C_{17}H_{17}NO_5S$ (M^+): 347.0827. Found: 347.0827.

Cr-Catalyzed Addition Reaction of 1b with MeOH. A solution of $[Cr(CO)_6]$ (66 mg, 0.30 mmol) and THF (24 µL, 0.30 mmol) in benzene (10 mL) in flame-dried Schlenk tube under N_2 was irradiated by Hg lamp (450 W, 350 nm) at room temperature for 2 h. After N_2 blowing bubbles into the yellow solution, to the yellow solution were added **1b** (60 mg, 0.25 mmol) and MeOH (20 µL, 0.50 mmol) at room temperature. The color of the reaction mixture gradually changed from deep blue to yellowish brown as the reaction proceeded. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt as an eluent to afford a white solid **25b** (48 mg, 69% yield); mp 68.3–69.8 °C; IR (KBr) 706, 937, 965, 1069, 1081, 1207, 1391, 1573, 1591, 1651 (C=O), 2933 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60–1.79 (m, 4H), 2.20–2.28 (m, 2H), 2.47–2.62 (m, 1H), 2.62–2.78 (m, 1H), 3.47 (s, 3H), 5.74 (s, 1H), 6.46 (s, 1H), 7.39–7.54 (m, 3H), 7.92–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 22.3, 22.8, 24.0, 54.8, 97.4, 107.8, 128.0, 128.2, 131.9, 134.2, 139.3, 149.2, 170.6, 189.2. HRMS (FAB) Calcd for $C_{17}H_{19}O_3$ ($M + H^+$): 271.1334. Found: 271.1327. **25b** was gradually isomerized under slightly acidic conditions (e.g. in $CDCl_3$ at room temperature) to afford the thermodynamically more stable diastereoisomer **25b′** quantitatively: A white solid; mp 82.7–83.4 °C; IR (KBr) 629, 705, 715, 772, 854, 935, 1004, 1218, 1317, 1569, 1600, 1650 (C=O), 2860, 2930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.63–1.78 (m, 4H), 2.20–2.25 (m, 4H), 3.55 (s, 3H), 5.92 (s, 1H), 5.94 (s, 1H), 7.39–7.52 (m, 3H), 7.92 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 20.3, 21.7, 21.7, 22.1, 56.0, 92.0, 111.1, 127.7, 128.1, 131.5, 134.6, 139.8, 146.8, 168.4, 188.9.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Deposition numbers CCDC-687434 for compound **25b** and CCDC-687435 for compound **25b′**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information

^{1}H and ^{13}C NMR spectra of **1e**, **2b–2d**, **9d**, **14d**, **17c**, **18c**, **20d**, **21d**, **22d**, and **23d**, and also X-ray crystallographic data of **25b** and **25b′** (CCDC #687434 (**25b**) and #687435 (**25b′**), respectively). This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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11 The reaction of **1e** with 10 equivalents of cyclopentadiene at room temperature afforded mono-cyclopropanated product in 88% yield for 1.5 h.

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13 5-Alkylidene-2,5-dihydrofuran **25b** was kinetically obtained as a primary product. The structure of **25b** and **25b′** were determined by X-ray crystallography. See Supporting Information.

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