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SYNTHESIS OF 3-METHYLENEPYRROLIDINES BY PALLADIUM-CATALYZED [3+2] CYCLOADDITION OF ALKYLIDENE-CYCLOPROPANES WITH IMINES

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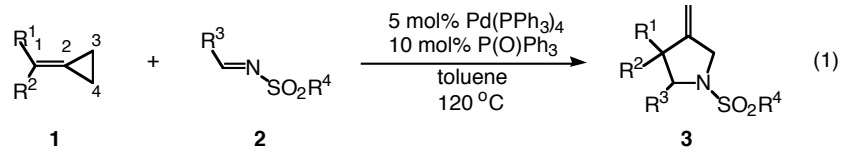
Abstract-Alkylidenecyclopropanes react with *N*-tosylimines in toluene in the presence of a catalytic amount of $Pd(PPh_3)_4$ and triphenylphosphine oxide to afford the corresponding [3+2] cycloaddition products, pyrrolidine derivatives, in good to excellent yields.

Introduction

Transition metal catalyzed [3+2] cycloaddition reactions are one of the the most useful methods for constructing five-membered carbo- and hetero-cycles.[1] Especially, methylenecyclopropanes are very useful "three-carbon component" for [3+2] cycloaddition reaction.[2] The synthesis of carbocycles *via* the intermolecular [3+2] cycloaddition reaction of methylenecyclopropanes with carbon-carbon multiple bond[1,2] and its intramolecular version has been reported by several groups.[3] However, catalytic hetero [3+2] cycloaddition of methylenecyclopropanes with a carbon-hetero atom multiple bond is limited to the reaction with heterocumulenes such as carbon dioxide[4] and keteneimines.[5] Recently, we reported the palladium catalyzed [3+2] cycloadditon of methylenecyclopropanes with aldehydes.[6] More recently, we

reported that the reaction of methylenecyclopropanes (**1**) with *N*-tosylimines (**2**) in the presence of 5 mol% of $Pd(PPh_3)_4$ and 10 mol% of triphenylphosphine oxide at 120 °C gives the corresponding [3+2] cycloadducts, the pyrrolidine derivatives (**3**) (eq. 1).[7] Herein, we report the detailed study for the palladium-catalyzed reaction of alkylidenecyclopropanes (**1**) with *N*-sulfonylimines (**2**).



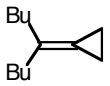
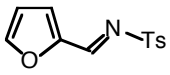
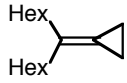
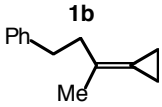
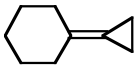
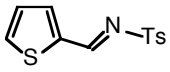
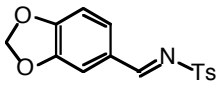
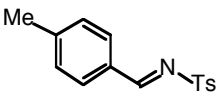
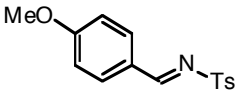
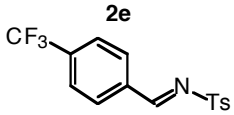
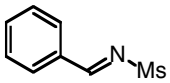
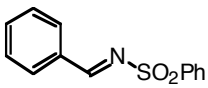
1 2 3 (1)

Results and Discussion

The results are summarized in Table 1. In the presence of catalytic amounts of $Pd(PPh_3)_4$ (5 mol%) and triphenylphosphine oxide (10 mol%), the reaction of 2-butylpenthylidenecyclopropane (**1a**) (1 mmol) and 2-furyl-*N*-tosylimine (**2a**) (0.5 mmol) in toluene at 120 °C for 16 h gave the corresponding cycloadduct (**3a**) in 89% yield (entry 1). The use of other solvents, such as THF, DMF, 1,4-dioxane and CH_3CN, also gave the cycloaddition product (**3a**) in good and moderate yields, while the use of CH_2Cl_2 as a solvent did not afford the cyclized product. Without a palladium catalyst, the reaction of **1a** and **2a** did not proceed at all. The catalytic system such as $Pd(dba)_2/PPh_3$ was less effective, and $Pd_2(dba)_3CHCl_3$ or $Pd(PPh_3)_2Cl_2$ didn't promote the reaction of **1a** and **2a** at all. The combination of $Pd(PPh_3)_4$ with phosphine ligands such as PPh_3, $P(O)Bu_3$, P(*o*-tolyl)$_3$ gave **3a** in high to good yields. However, even in the presence of $Pd(PPh_3)_4$ catalyst, if bidentate ligands such as bis(diphenylphosphanyl)methane (dppm), 1,2-bis(diphenylphosphanyl)ethane (dppe) and 1,1'-bis(diphenylphosphanyl)ferrocene (dppf) were used as a ligand, only trace amounts of **3a** were obtained. The reaction of 2-hexylheptylidenecyclopropane (**1b**) with **2a**, and 2-methyl-4-phenylbutylidenecyclopropane (**1c**) with **2a** afforded **3b** and **3c** in yields of 88% and 91%, respectively (entries 2 and 3). The spiro compound (**3d**) was obtained in 71% yield from the reaction of **1d** with **2a** (entry 4). The reaction of **1a** with **2b** proceeded smoothly and the corresponding cycloadduct (**3e**) was produced in 91% yield (entry 5). The aryl imines (**2c-f**), having an electron-donating or electron-withdrawing group at the para-position, also reacted smoothly to give **3f-i** in

excellent yields (entries 6-9). Methanesufonylimide (**2g**) and benzenesulfonylimide (**2h**) reacted with **1a** and the corresponding pyrrolidine derivatives (**3j**) and (**3k**) were obtained in excellent yields (entries 10 and 11).

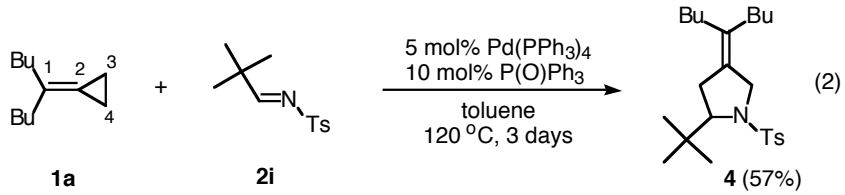
Table 1. Palladium-catalyzed [3+2] cycloaddition of alkylidenecyclopropanes (**1**) and imines (**2**)[a]

entry	1	2	time / h	3	yield / %[b]
1	 **1a**	 **2a**	16	**3a**	89
2	 **1b**	**2a**	18	**3b**	88
3	 **1c**	**2a**	13	**3c**	91 (56:44)[c]
4	 **1d**	**2a**	20	**3d**	71
5	**1a**	 **2b**	17	**3e**	91
6	**1a**	 **2c**	16	**3f**	93
7	**1a**	 **2d**	12	**3g**	91
8	**1a**	 **2e**	9	**3h**	94
9	**1a**	 **2f**	24	**3i**	88
10	**1a**	 **2g**	12	**3j**	97
11	**1a**	 **2h**	18	**3k**	94

[a]The reaction of **1** (1 mmol) and **2** (0.5 mmol) was carried out in the presence of 5 mol% of $Pd(PPh_3)_4$ and 10 mol% of triphenylphosphine oxide in toluene at 120 °C. [b]Isolated yield based on **2**. [c]The diastereomeric ratio of **3c**.

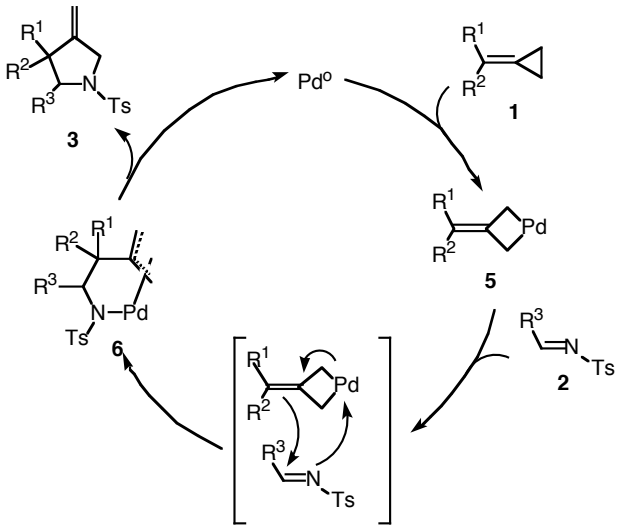
Interestingly, the reaction of **1a** with *t*-butyl-*N*-tosylimine (**2i**) gave the regioisomeric [3+2] cycloadduct (**4**) in 57% yield, in which the three carbon component was derived from the C-2,3,4 carbons of the

cyclopropyl group of **1a** (eq. 2). This is in marked contrast to the ordinary [3+2] cycloaddtion shown in eq. 1, in which the three carbon component is derived from the C-1,2,3 carbons of **1a**. The formation of the ordinary [3+2] cycloadduct was not detected in the reaction of **2i**.

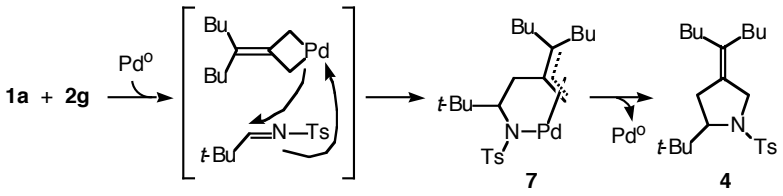


1a **2i** **4** (57%)

A plausible mechanism for the ordinary [3+2] cycloaddition is illustrated in Scheme 1. Oxidative addition of palladium(0) to a distal bond of the alkylidenecyclopropane (**1**) leads to the palladacyclobutane complex (**5**),[8] which reacts with the imine (**2**) to give the π-allylpalladium complex (**6**). Reductive elimination of palladium(0) gives the [3+2] cycloadduct (**3**). In this case, the π-allylpalladium complex (**5**) reacts with the imine (**2**) in the manner similar to the ordinary allylic organometallics such as allylic stannanes; **5** reacts at the γ-position of the allylic unit. On the other hand, the formation of the regioisomeric [3+2] cycloaduct (**4**) in the case of *t*-butyl-*N*-tosylimine (**2g**) can be explained if **5** reacts with the imine (**2g**) at the α-position of the allylic unit (Scheme 2). The reaction at the α-position leads to the π-allylpalladium intermediate (**7**), which gives **4** upon reductive elimination of Pd(0). Perhaps, the steric hindrance of *t*-butyl group of **2g** would force the allylation reaction to take an alternative pathway through the γ-addition.



Scheme 1. A plausible mechanism for the palladium-catalyzed [3+2] cycloaddition of alkylidenecyclopropanes (**1**) with imines (**2**).



Scheme 2. A plausible mechanism for the palladium-catalyzed [3+2] cycloaddition of **1a** with **2g**.

The thermal [3+2] cycloaddition reactions of methylenecyclopropane ketals with aldehydes[9] and imines[10] were reported recently. However, these reactions require the use of highly activated methylenecyclopropane derivatives. Meanwhile, the [3+2] cycloaddition of electron-deficient imines with trimethylenemethane(TMM), generated *in situ* from 2-acetoxymethyl-3-allyltrimethylsilane and palladium catalyst was reported by Trost and Marrs.[11] While an actual role of phosphine oxide is not clear, this ligand perhaps promotes the generation of coordinatively unsaturated palladium species, because of it labile characteristics in comparison with PPh_3.[12]

Conclusion

We have developed a novel and efficient route to pyrrolidine derivatives through the palladium-catalyzed [3+2] cycloaddition between methylenecyclopropanes and imines. The present atom-economical reaction may be potentially useful for constructing biologically important pyrrolidine skeletons.

EXPERIMENTAL

General. Spectroscopic measurements were carried out with the following instrument: JEOL JMMAL-300, JEOL JNM LA-300, JEOL JNM □-500 (^{1}H and ^{13}C NMR). SHIMADZU FTIR-8200A (FT-IR). Hitachi M-2500S, JEOL JMS-AX500, JEOL JMS-DX303 (high-resolution mass spectra). All tosyl imines (**2**) were synthesized according to the method in the literature.[10]

General procedure for the cycloaddition of alkylidenecyclopropanes (1) with imines (2). To a mixture of $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol) and triphenylphosphine oxide (10.9 mg, 0.05 mmol) were added the imines (**2**) (1.0 mmol) and the alkylidenecyclopropanes (**1**) (0.5 mmol) under Ar atmosphere in

a pressure vial. After heating at 120 ºC for 9-24 h, the reaction mixture was filtered through a silica-gel column using ethyl acetate as an eluent. Separation by passing through a silica gel column and purification by middle-pressure liquid column chromatography (SI) and recrystallization afforded the cycloadducts (**3**).

3,3-Dibutyl-2-furan-2-yl-4-methylene-1-(4-toluenesulfonyl)pyrrolidine (3a). White solid: IR (KBr) 2956-2864, 1654, 1596, 1460, 1380, 1342, 1161, 1099, 1068, 1014, 883, 754, 667 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) 0.55 (t, *J* = 13.1 Hz, 1H), 0.73 (t, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 6.9 Hz, 3H), 1.08-1.57 (m, 11H), 2.36 (s, 3H), 3.95 (td, *J* = 13.2, 2.5 Hz, 1H), 4.20 (td, *J* = 13.2, 2.5 Hz, 1H), 4.73 (s, 1H), 4.76 (t, *J* = 2.1Hz, 1H), 5.01 (t, *J* = 2.1 Hz, 1H), 6.11 (d, *J* = 3.3 Hz, 1H), 6.17 (dd, *J* = 3.3, 1.8 Hz, 1H), 7.02 (s, 1H), 7.13 (d, *J* = 4.8 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.76, 13.99, 21.44, 22.85, 23.18, 25.53, 26.03, 29.50, 34.31, 51.29, 53.05, 66.26, 106.98, 108.66, 109.73, 127.03, 129.20, 135.66, 141.51, 142.61, 149.62, 152.63. Anal. Calcd for $C_{24}H_{33}NO_3S$ (415.59): C, 69.36; H, 8.00; N, 3.37; S, 7.72. Found: C, 69.26; H, 8.33; N, 3.36; S, 7.76. HRMS (EI) Calcd for $C_{24}H_{33}NO_3S$: m/z 415.2179. Found: m/z 415.2181.

3,3-Dihexyl-2-furan-2-yl-4-methylene-1-(4-toluenesulfonyl)pyrrolidine (3b). Pale yellow oil: IR (neat) 2929-2858, 1662, 1598, 1463, 1348, 1163, 1099, 1068, 1012, 813, 732, 665 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) 0.54 (t, *J* = 7.2 Hz, 3H), 0.80-1.50 (m, 23H), 2.36 (s, 3H), 3.95 (d, *J* = 13.5 Hz, 1H), 4.19 (d, *J* = 13.5 Hz, 1H), 4.74 (d, *J* = 7.8 Hz, 2H), 5.01 (s, 1H), 6.10 (d, *J* = 3.3 Hz, 1H), 6.17-6.19 (m, 1H), 7.03 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.96, 14.03, 21.41, 22.47, 22.66, 23.27, 23.78, 29.45, 29.78, 29.86, 31.42, 31.68, 34.58, 51.28, 53.14, 66.26, 106.94, 108.60, 109.72, 127.03, 129.19, 135.67, 141.48, 142.57, 149.63, 152.66. HRMS (EI) Calcd for $C_{28}H_{41}NO_3S$: m/z 471.2808. Found: m/z 471.2809.

2-Furan-2-yl-3-methyl-4-methylene-3-phenethyl-1-(4-toluenesulfonyl)pyrrolidine (3c). *anti*: yellow solid : IR (KBr) 3028-2873, 1726, 1662, 1600, 1496, 1456, 1340, 1166, 1097, 1058, 881, 738, 665 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz) 0.80 (s, 3H), 1.53-1.59 (m, 1H), 1.64-1.70 (m, 1H), 2.31 (s, 3H), 2.48-2.52 (m, 2H), 4.06 (dt, *J* = 13.5, 1.5 Hz, 1H), 4.24 (d, *J* = 13.5, 1.5 Hz, 1H), 4.73 (s, 1H), 4.87 (t, *J* = 2.5 Hz, 1H), 5.08 (t, *J* = 2.5 Hz, 1H), 6.15 (dd, *J* = 3.2, 1.0 Hz, 1H), 6.21 (dd, *J* = 3.2, 1.0 Hz, 1H), 7.05-7.06 (m, 2H), 7.07 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.16-7.19 (m, 1H), 7.24-7.27 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) 18.07, 21.44, 30.82, 41.66, 50.44, 51.32, 55.95, 107.12, 108.47, 109.82, 125.80, 127.04, 128.27, 128.34, 129.28, 135.39, 141.65, 141.78, 142.82, 150.17, 152.96. HRMS (EI) Calcd for $C_{25}H_{27}NO_3S$: m/z 421.1712. Found: m/z 421.1706.

syn : yellow oil: IR (neat) 3026-2869, 1728, 1664, 1598, 1496, 1456, 1346, 1163, 1097, 1062, 815, 665 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) 1.14-1.19 (m, 1H), 1.29 (s, 3H), 1.69-1.76 (m, 1H), 2.36 (s, 3H), 2.43-2.49 (m, 2H), 2.55-2.60 (m, 1H), 3.99 (dt, *J* = 13.5, 2.0 Hz, 1H), 4.33 (dd, *J* = 13.5, 2.0 Hz, 1H), 4.81 (s, 1H), 4.83 (t, *J* = 2.0 Hz, 1H), 4.92 (t, *J* = 2.0 Hz, 1H), 6.23-6.25 (m, 2H) 6.90 (d, *J* = 7.0 Hz, 2H), 7.01-7.20(m, 6H), 7.41 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) 21.43, 25.41, 30.82, 36.77, 49.48, 51.01, 65.82, 105.21, 109.19, 109.84, 125.76, 127.10, 128.17, 128.27, 129.22, 135.38, 141.84, 142.23, 142.69, 151.99, 152.14. HRMS (EI) Calcd for $C_{25}H_{27}NO_3S$: m/z 421.1712. Found: m/z 421.1706.

The stereochemistries of two diastereomers of **3c** were determined by NOE experiments as shown in Figure 1.

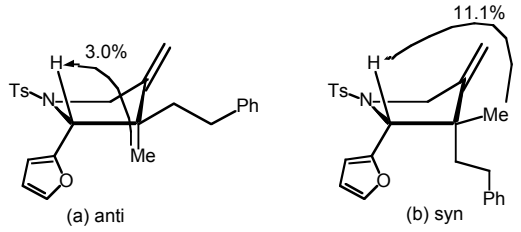


Figure 1. NOE experiment of **3c** (a) anti (b) syn

1-Furan-2-yl-4-methylene-2-(4-toluenesulfonyl)-2-azaspiro[4.5]decane (3d). White solid: IR (KBr) 2983-2862, 1660, 1598. 1502, 1454, 1340, 1161, 1097, 877, 812, 661 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.90 (d, *J* = 11.7 Hz, 1H), 1.06-1.74 (m, 9H), 2.40 (s, 3H), 3.95 (d, *J* = 13.2 Hz, 1H), 4.19 (td, *J* = 13.2, 2.4 Hz, 1H), 4.87 (d, *J* = 2.4 Hz, 1H), 4.93 (s, 1H), 5.04 (s, 1H), 6.15-6.19 (m, 2H), 7.02 (s, 1H), 7.12 (d,

J = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 21.40, 22.83, 33.04, 25.69, 29.66, 36.59, 50.44, 50.78, 62.22, 104.99, 108.65, 109.64, 126.95, 129.15, 135.62, 141.63, 142.54, 152.48, 152.78. HRMS (EI) Calcd for $C_{21}H_{25}NO_3S$: m/z 371.1555. Found: m/z 371.1554.

3,3-Dibutyl-4-methylene-2-thiophen-2-yl-1-(4-toluenesulfonyl)pyrrolidine (3e). White solid: IR (KBr) 2937-2860, 1660, 1596, 1456, 1334, 1166, 1099, 1068, 885, 702, 667 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.68 (t, *J* = 7.2 Hz, 3H), 0.76-1.60 (m, 15H), 2.32 (s, 3H), 3.87 (d, *J* = 13.5 Hz, 1H), 4.21 (d, *J* = 13.5 Hz, 1H), 4.86 (s, 1H), 5.01 (s, 1H), 5.13(s, 1H), 6.78-6.82 (m, 2H), 7.03-7.08 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.54, 13.91, 21.34, 22.80, 22.99, 25.74, 25.79, 28.76, 33.89, 50.55, 53.07, 68.63, 109.04, 125.01, 125.45, 126.54, 126.80, 128.99, 135.95, 142.07, 142.55, 148.79. Anal. Calcd for $C_{24}H_{33}NO_2S_2$: C, 69.78; H, 7.71; N, 3.25; S, 14.86. Found: C, 69.73; H, 8.07; N, 3.21; S, 15.09. HRMS (EI) Calcd for $C_{24}H_{33}NO_2S_2$: m/z 431.1953. Found: m/z 431.1956.

2-Benzo[1,3]dioxol-5-yi-3,3-dibutyl-4-methylene-1-(4-toluenesulfonyl)pyrrolidine (3f). Yellow solid: IR (KBr) 2956-2866, 1662, 1598, 1488, 1440, 1344, 1245, 1166, 1097, 1041, 931, 813, 663 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.65 (t, *J* = 6.9 Hz, 3H), 0.72-1.14 (m, 13H), 1.36-1.43 (m, 2H), 2.35 (s, 3H), 4.00 (d, *J* = 13.5 Hz, 1H), 4.19 (d, *J* = 13.5 Hz, 1H), 4.49 (s, 1H), 4.82 (s, 1H) 5.12 (s, 1H), 5.87 (d, *J* = 10.5 Hz, 2H), 6.38 (s, 1H), 6.61-6.65 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.55, 13.85, 21.34, 22.75, 22.96, 25.37, 25.43, 28.81, 34.50, 51.79, 52.72, 73.14, 100.79, 107.35, 108.01, 122.07, 126.96, 129.00, 133.55, 135.77, 142.66, 146.65, 147.18, 149.49. Anal. Calcd for $C_{27}H_{35}NO_4S$ (469.64): C, 69.05; H, 7.51; N, 2.98; S, 6.82. Found: C, 69.07; H, 7.87; N, 3.00; S, 6.79. HRMS (EI) Calcd for $C_{27}H_{35}NO_4S$: m/z 469.2287. Found: m/z 469.2293.

3,3-Dibutyl-4-methylene-1-(4-toluenesulfonyl)-2-*p*-tolylpyrrolidine (3g). White solid: IR (KBr) 2962-2862, 1658, 1598, 1465, 1348, 1163, 1101, 1070, 916, 862, 813 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) 0.59-1.64 (m, 15H), 2.28 (s, 3H), 2.34 (s, 3H), 4.01 (d, *J* = 13.5 Hz, 1H), 4.19 (d, *J* = 13.5 Hz, 1H), 4.80 (s, 1H), 4.80 (s, 1H), 5.10 (s, 1H), 6.91 (dd, *J* = 8.1, 11.1 Hz, 4H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.45, 13.77, 20.93, 21.23, 22.67, 22.82, 25.28, 25.32, 28.78,

34.37, 51.76, 52.59, 73.07, 107.67, 126.88, 127.76, 128.29, 128.90, 135.57, 136.41, 136.64, 142.49, 149.57. HRMS (EI) Calcd for $C_{26}H_{36}NO_2S$: m/z 439.2545. Found: m/z 439.2540.

3,3-Dibutyl-2-(4-methoxyphenyl)-4-methylene-1-(4-toluenesulfonyl)pyrrolidine (3h). White solid: IR (KBr) 2933-2860, 1662, 1612, 1514, 1460, 1348, 1249, 1163, 1097, 1058, 1039, 661 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) 0.61 (t, *J* = 6.9 Hz, 3H), 0.78-1.43 (m, 15H), 2.33 (s, 3H), 3.76 (s, 3H), 3.99 (d, *J* = 13.2 Hz, 1H), 4.19 (d, *J* = 13.2 Hz, 1H), 4.53 (s, 1H), 4.80 (s, 1H), 5.10 (s, 1H), 6.66 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.51,13.84, 21.30, 22.75, 22.90, 25.36, 25.40, 28.91, 34.49, 51.73, 52.69, 55.14, 72.86, 107.72, 113.12, 126.98, 128.98, 129.08, 131.79, 135.80, 142.52, 149.78, 158.76. HRMS (EI) Calcd for $C_{27}H_{37}NO_3S$: m/z 455.2494. Found: m/z 455.2502.

3,3-Dibutyl-4-methylene-1-(4-toluenesulfonyl)-2-(4-trifluoromethylphenyl)pyrrolidine (3i). White solid: IR (KBr) 2950-2871, 1558, 1456, 1348, 1330, 1163, 1109, 1068, 663 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) 0.50-0.61 (m, 4H), 0.78-1.47 (m, 14H), 2.32 (s, 3H), 4.08 (d, *J* = 13.5 Hz, 1H), 4.25 (d, *J* = 13.5 Hz, 1H), 4.60 (s, 1H), 4.84 (s, 1H), 5.16 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.37 (dd, *J* = 8.1, 2.7 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.48, 13.91, 21.31, 22.79, 22.87, 25.38, 25.45, 28.84, 34.58, 52.06, 52.96, 72.64, 108.52, 124.69, 124.74, 124.79, 126.82, 128.37, 129.20, 135.55, 143.09, 143.55, 149.11. HRMS (EI) Calcd for $C_{27}H_{37}NO_3S$: m/z 493.2262. Found: m/z 493.2293.

3,3-Dibutyl-2-phenyl-4-methylene-1-(methanesulfonyl)pyrrolidine (3j). White solid: IR (neat) 3084-2857, 1660, 1455, 1335. 1144, 1081, 969, 897, 761 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) 0.59 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.71-1.74 (m, 12H), 2.26 (s, 3H), 4.07 (d, *J* = 13.5 Hz, 1H), 4.39 (d, *J* = 13.5 Hz, 1H), 4.60 (s, 1H), 4.94 (s, 1H), 5.22 (s, 1H), 7.19-7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) 13.42, 14.11, 22.89, 25.36, 25.68, 29.00, 35.10, 38.56, 51.87, 52.68, 72.90, 108.00, 127.90, 128.36, 139.02, 150.04. HRMS (EI) Calcd for $C_{20}H_{31}NO_2S$: m/z 349.2075. Found: m/z 349.2070.

3,3-Dibutyl-2-phenyl-4-methylene-1-(benzenesulfonyl)pyrrolidine (3j). White solid: IR (neat) 3084-2857, 1970, 1899, 1803, 1654, 1585, 1344, 1163, 1094, 900 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) 0.59 (t,

J = 7.0 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H), 0.60-1.56 (m, 12H), 4.03 (d, *J* = 13.4 Hz, 1H), 4.26 (d, *J* = 13.4 Hz, 1H), 4.61 (s, 1H), 4.83 (s, 1H), 5.13 (s, 1H), 6.99-7.45 (m, 10H). HRMS (EI) Calcd for $C_{25}H_{33}NO_2S$: m/z 411.2232. Found: m/z 411.2227.

2-*tert*-Butyl-4-(1-butyl-pentylidene)-1-(4-toluenesulfonyl)pyrrolidine (4). Pale yellow oil: IR (KBr) 2956-2871, 1598, 1467, 1346, 1163, 1091, 667 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) 0.80-1.22 (m, 23H), 1.77-1.78 (m, 5H), 2.25 (d, *J* = 16.5 Hz, 1H), 2.40 (s, 3H), 3.73 (d, *J* = 9.0 Hz, 1H), 3.88 (d, *J* = 16.5 Hz, 1H), 4.12 (d, *J* = 16.5 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) 14.04, 14.06, 21.47, 22.61, 22.68, 26.85, 29.63, 29.76, 29.90, 32.38, 32.50, 35.93, 51.91, 69.33, 127.42, 129.54, 130.51, 131.60, 135.76, 143.13. HRMS (EI) Calcd for $C_{24}H_{39}NO_2S$: m/z 405.2701. Found: m/z 405.2696.

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