이학석사 학위논문

Palladium-Catalyzed Cycloisomerization of 1,6-Enynes

팔라듐 촉매를 이용한 1,6인아인의

고리이성질화 반응

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오 혜 미

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Abstract

A palladium-catalyzed cycloisomerization of 1,6-enynes, which can provide a variety of cyclic compounds, has been studied, The reaction pathway is highly dependent upon a leaving group of 1,6-enynes. Enynes with a phosphate leaving group gave rise to 5.7-bicyclic trienes and by an alkoxy group yielded monocyclic trienes. We also observed a Pd(Ⅱ)-catalyzed cycloisomerizaiotn of 1,6-enynes to bicyclo[4.1.0]heptenes in good yields under optimized conditions.

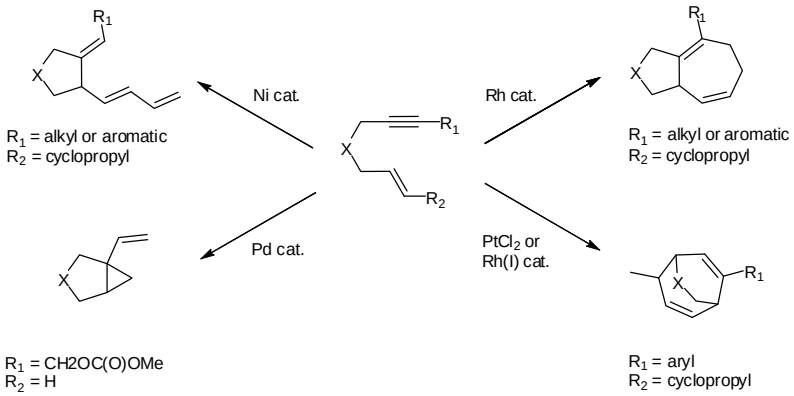
Keywords: Palladium, Catalysis, Trienes, Bicyclo[4.1.0]heptenes, Vinyl cyclopropane, Cycloisomerization

Contents

Introduction

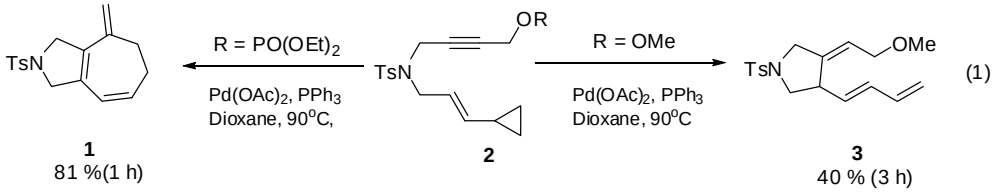
The transition metal-catalyzed cycloisomerization reactions have attracted a great deal of attention[1] because they can easily provide a variety of cyclic compounds.[2] For example, cyclopropyl groups engage in many rearrangement reactions including a vinylcyclopropane rearrangement and a divinylcyclopropane-cycloheptadiene rearrangement.[3] Cyclopropyl groups also participate in cycloaddition reactions such as a formal [5+2] cycloaddition.[4] Vinyl cyclopropanes (VCPs) are considered to be particularly suitable C_5 building blocks in the formal [5+2] cycloaddion. Thus, a variety of transition-metal-catalyzed cyclizations have been developed over the past decades.[5] In particular, Wender[6] has demonstrated that VCP is a very versatile strained cyclic synthon in the rhodium-catalyzed [5+2] cyclizations of cyclopropylen-ynes. However, the reaction products in the transition-metal-catalyzed reaction of cyclopropylen-ynes seem to be rather dependent upon a catalyst and the identity of the substituent on the alkyne. For example, Louie et al. found[7] a size effect, due to the substituent on the alkyne, on the heterocyclic product formed in a $Ni(COD)_2$/SIPr-catalyzed reaction, although employment of $Ni(COD)_2$/I*t*Bu as a catalytic system solved the selectivity problem (Scheme 1). Pimm reported[8] the formation of alk-1-enyl-(3-aza)bicyclo[3.1.0]hexanes in the palladium-catalyzed cyclization of olefinic propargylic carbonates. Recently, we reported[8] that a consecutive reactions of platinum- and rhodium-catalyzed cycloisomerization of enynes bearing a cyclopropyl and aryl group in

the alkene and alkyne termini, respectively, afforded azabicyclo[3.2.2]nona-2,8-dienes in high yields.

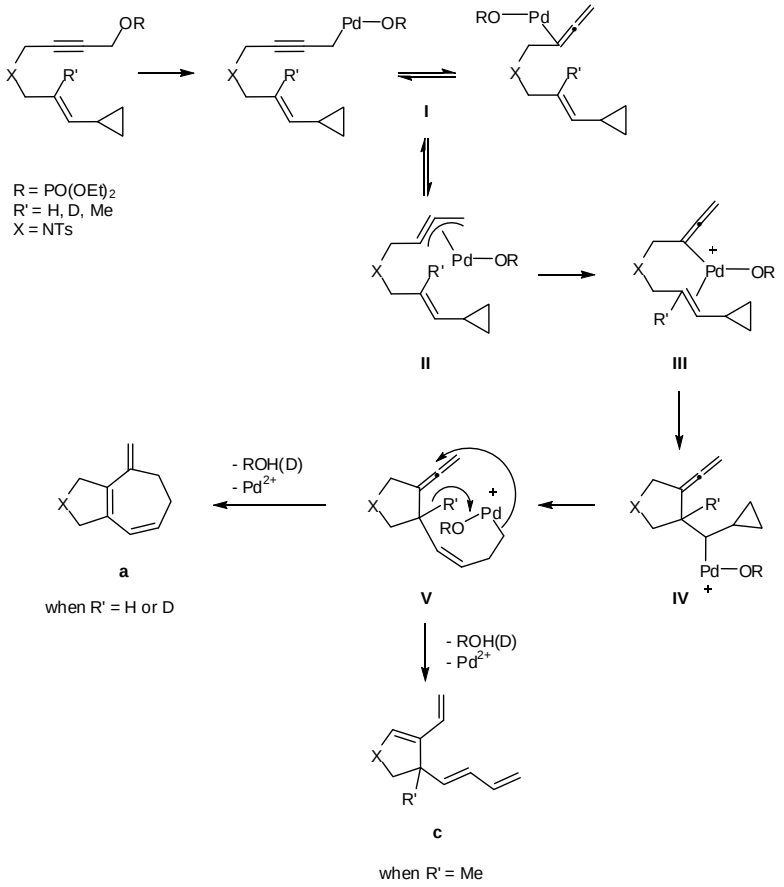


Scheme 1. Metal-catalyzed cycloisomerization

Based on the previous studies, we envisioned that palladium-catalyzed cyclization of cyclopropyl-substituted 1,6-enynes proceeded in two ways depending upon the presence or absence of a leaving group. In the presence of the leaving group, 5.7-bicyclic trienes were obtained as the sole product; in the absence of the leaving group monocyclic trienes were isolated [Eq. (1)]. Based on the experimental observations, a plausible reaction mechanism for formation of **1** has been proposed (Scheme 2).



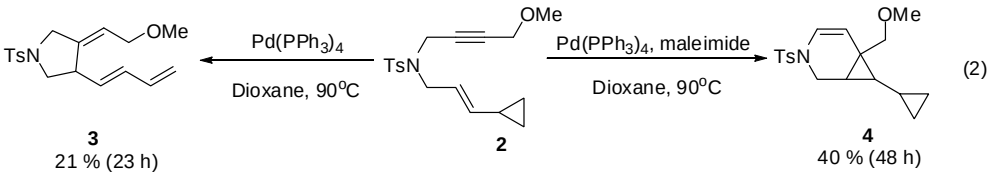
(1)



Scheme 2. Proposed mechanism for the Pd catalyzed formation of 5.7-Bicyclic Trienes

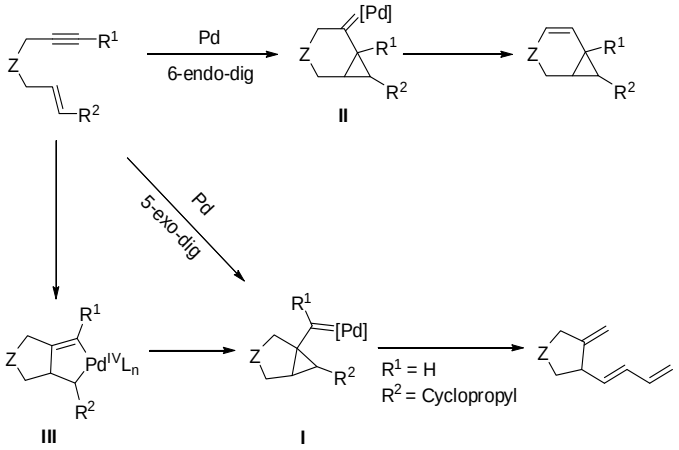
Next, we tested whether **3** (1-((*E*)-buta-1,3-dienyl)-2-methylenecyclopentane) undergo Dielse-Alder reacation with maleimide(dienophile). However, when **3** (0.3 mmol) was treated with 5 mol% $Pd(OAc)_2$, 10 mol% PPh_3, and 1.3 equiv maleimide in 3 mL 1,4 – dioxane at 90°C, no Diels-Alder-type product was isolated. Instead, a bicyclo[4.1.0]heptene compound (**4**) was isolated in 40% yield [Eq. (2)]. To the best of our knowledge, there has been no

report on the formation of bicyclo[4.1.0]heptenes in the presence of palladium catalysts. The formation of bicyclo[4.1.0]heptenes has been recognized for Pt,[9] Au,[10] Ir,[11] and Rh[12]-catalyzed cycloisomerization of 1,6-enynes.



(2)

Typically, cyclizaion of 1,6-enynes in palladium system proceeded 5 -exo type cyclization. Thus, the palladium-catalyzed formation of bicyclo[4.1.0]hept-2-enes is unprecedented. So, we proposed a plausible mechanism (Scheme 3).



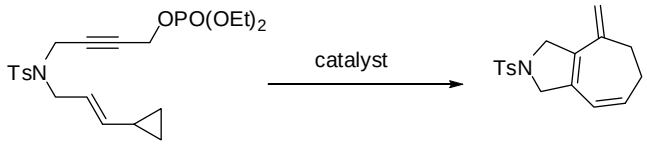
Scheme 3. Plausible mechanism for Pd-catalyzed cycloisomerization of 1,6-enynes.

Results and Discussion

1. Palladium-Catalyzed Cyclization of Cyclopropyl-Substituted 1,6-Enynes to 5.7-Bicyclic Trienes or Monocyclic Trienes Depending Upon a Leaving Group.

Initial treatment of olefinic propargylic diethyl phosphate **1** with a catalytic amount of $[Pd_2(dba)_3]$ in dioxane at 90 °C for one day gave bicyclic triene **1a** in 17% yield with 67% recovery of the reactant (Scheme 2). The structure of **1a** was confirmed by ^{1}H and ^{13}C NMR studies. It has a 4-methylene-1,2,3,4,5,6-hexahydroazulene skeleton, which can be considered to be an important building block because it may participate in a variety of functionalizations and tandem carbon-carbon bond-forming processes. The formation of **1a** suggests that the phosphate acts as a leaving group. Encouraged by the observation of the formation of **1a**, we also screened other palladium compounds (Table 1, entries 1-8). Among them, the best yield (81%) was observed in the presence of 5 mol% $Pd(OAc)_2$/10 mol% Ph_3P in dioxane for one hour. The yield of the reaction was highly sensitive to the reaction medium (entries 9 and 10). We also screened nickel compounds such as $Ni(acac)_2/Ph_3P$ (1:2) and $Ni(OAc)_2/Ph_3P$ (1:2) as potential catalysts. However, no reaction was observed with the nickel systems. We were able to establish the following optimized reaction conditions: 5 mol% $Pd(OAc)_2$, 10 mol% Ph_3P, in dioxane, at 90 °C for 1 hour.

Table 1. Reaction of **1** under Various Reaction Conditions



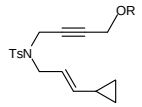
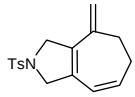
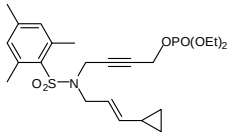
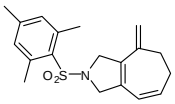
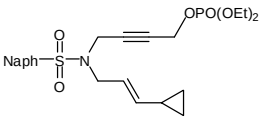
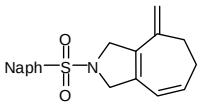
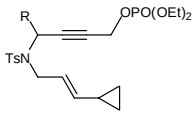
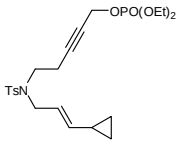
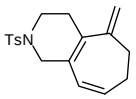
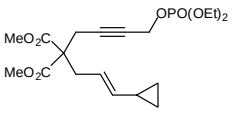
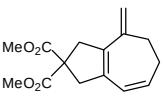
1 **2**

Entry	catalyst	Solvent	Temp(^{o}C)	Time (h)	Yield (%)[c]
1[a]	$Pd_2(dba)_3$	Dioxane	90	24	17
2[a]	$Pd(PPh_3)_4$	Dioxane	90	24	42
3[a]	$Pd(OAc)_2$	Dioxane	90	24	13
4[a]	$Pd(OAc)_2$/dppp(1:1)	dioxane	90	24	28
5[a]	$Pd(OAc)_2$/dppp(1:1)	dioxane	25	24	41
6[a]	$Pd(OAc)_2$/dppe(1:1)	dioxane	70	2	71
7[a]	$Pd(OAc)_2$/P(*o*-toly)$_3$(1:2)	dioxane	80	24	23(52)[d]
8[b]	$Pd(OAc)_2/PPh_3$(1:2)	dioxane	100	1	81
9[b]	$Pd(OAc)_2/PPh_3$(1:2)	DCE	90	22	33
10[b]	$Pd(OAc)_2/PPh_3$(1:2)	toluene	90	1	39
11[b,e]	$Pd(OAc)_2/PPh_3$(1:2)	THF-MeOH	70	21	63
12[b]	$Ni(acac)_2/PPh_3$(1:2)	dioxane	90	24	n.r.[f]
13[b]	$Ni(OAc)_2/PPh_3$(1:2)	dioxane	90	24	n.r.[f]

[a] Reaction conditions: Pd catalyst (10 mol%), enyne (0.22 g, 0.5 mmol), solvent (5 mL).
[b]. Reaction conditions: Pd catalyst (5 mol %), enyne (0.22 g, 0.5 mmol), solvent (5 mL).
[c]. Isolated yield.
[d] .Yields in parenthesis are the reactant recovered.
[e] .Reaction conditions: enyne (0.22 g, 0.5 mmol), $Pd(OAc)_2$ (5 mol%), THF (5 mL), MeOH (0.5 mL), CO (1 atm).
[f] .n.r. = No reaction

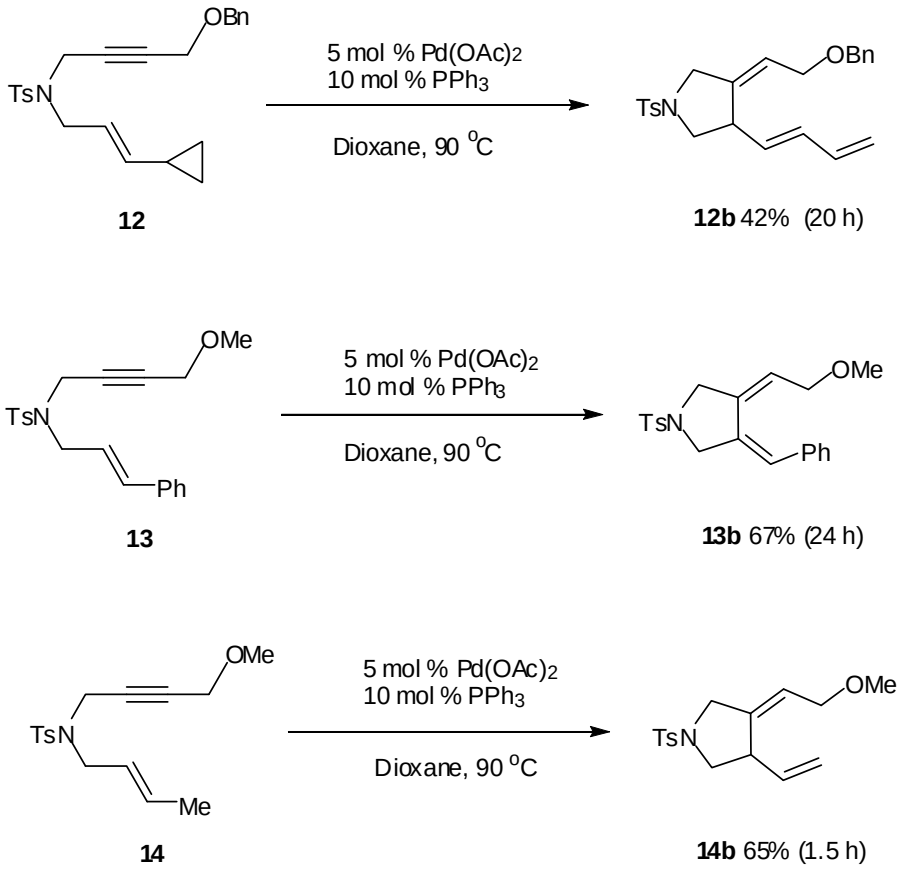
We first examined whether the phosphate was the best leaving group or not under the optimized reaction conditions (Table 2). Olefinic propargylic compounds (entries 2 and 3) having an acetoxy or carbonate as a leaving group afforded the expected **1a** in rather lower yields (40% and 49%, respectively) under our reaction conditions. In the case of the carbonate, when the reaction was carried out in the presence of 5 mol% $Pd(OAc)_2$ and 5 mol% dppp under 1 atm of CO, a higher yield (63%) was observed. The leaving group has a dramatic effect on the yield of the reaction and the best yield (81%) was observed with the phosphate group. Therefore, we examined the scope of substrates bearing a phosphate group under our reaction conditions. As the steric bulkiness of N-tether groups increased (entry **4** vs **5**), the yield decreased. The number of internal substituents (entry **6** vs **8**) and the identity of the substituents (entry **6** vs **7**) affected the yield of the reaction. The use of a 1,7-enyne substrate did not affect the reaction (entry **9**). A carbon-tethered substrate (entry **10**) also underwent the reaction. When a substrate (**11**) was treated in dioxane in the presence of the standard catalytic conditions, a monocyclic triene (**11b**), 1-((*E*)-buta-1,3-dienyl)-2-methylenecyclopentane, was isolated in 40% yield[Eq. (1)].

Table 2 Palladium-Catalyzed Cyclization of Cyclopropyl-Substituted 1,6-Enynes to 5.7-Bicyclic Trienes[a]

Entry	Substrate	Time (h)	Product Yield (%)[b]
			
1	**1** R = $PO(OEt)_2$	1	**1a** 81
2	**2** R = COMe	1	**1a** 81
3[c]	**3** R = CO_2Me	1	**1a** 63
4		4	
	4		**4a** 65
5		5	
	5		**5a** 35
			
6	**6** R = Me	20	**6a** 93
7	**7** R = Et	4	**7a** 60
8	**8** R = gem-dimethyl	3	**8a** 43
9		20	
	9		**9a** 50
10		4	
	10		**10a** 47

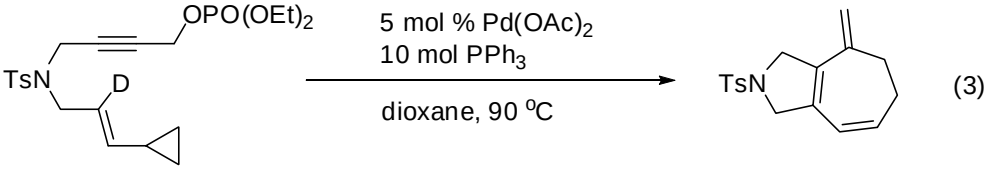
[a] Reaction conditions: substrate (0.3 mmol), $Pd(OAc)_2$ (5 mol%), Ph_3P (10 mol%), dioxane (3 mL), 90 °C. [b] Isolated yield. [c] Under 1 atm CO.

Zuo and Louie reported[5a] a similar reaction in the presence of $Ni(cod)_2$/NHC. To ascertain whether this rearrangement was typical, a range of substrates **12** – **14** were prepared and tested (Scheme 4).



Scheme 4 Palladium-catalyzed cyclization of cyclopropyl-substituted 1,6-enynes to monocyclic trienes.

With substrate **12** containing the cyclopropyl group, monocyclic triene **12b** was isolated in 42% yield. With a phenyl (**13**) or methyl group (**14**) instead of a cyclopropyl group, monocyclic dienes **13b** and **14b** were isolated in 67 and 65% yields, respectively. Thus, the formation of cyclopentane derivatives was quite general for the palladium-catalyzed reaction of enyne substrates not bearing a leaving group. In the formation of a bicyclic triene from a substrate, both the leaving group and one of the hydrogen atoms were lost. To gain some information on the formation of bicyclic trienes, deuterated compound **1**-D was reacted under the standard reaction conditions [Eq. (3)]. When the product of the reaction was isolated, the deuterium was not found in the product. This observation suggested that the disappearing hydrogen atom was from the inner position of an alkene moiety.

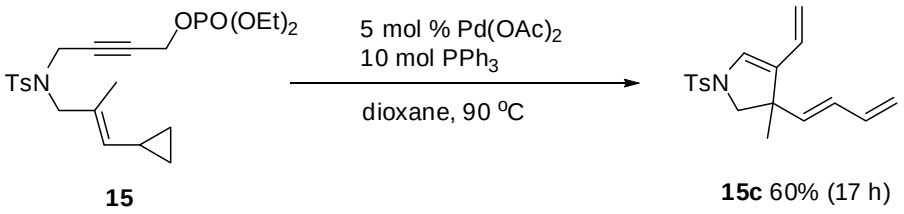


(3)

1-D **1a** 81% (1.5 h)

Moreover, when a methyl group was introduced into the same position as that of the deuterium in **1**-D, a new cyclopentene derivative, **15c**, produced by the isomerization of an allene to a diene, instead of a bicyclic triene, was isolated in 60% yield [Eq. (4)]. A similar reaction product was obtained in the palladium-catalyzed carbocyclization of aza-enallenes.[13] It seems that the presence of a

methyl group might block the formation of a seven-memered ring compound.



15 **15c** 60% (17 h) (4)

Based on the experimental observations, a plausible reaction mechanism for the formation of **a** has been proposed (Scheme 2). In the presence of a palladium catalyst, an equilibrium mixture of η^1-allenic and propargylic intermediate **I** forms,[13] which may be in equilibrium with η^3- propargyl intermediate **II**.[14] Both intermediates can be transformed into a (π-olefin)(σ-allenyl)palladium intermediate **III**. Carbon–carbon bond formation followed by ring-opening of the allyl group leads to intermediate **V**. The allyl group then attacks the central carbon of the allene group to form a seven-membered ring and regenerate the catalytic species to reenter the catalytic cycle. When the final step is blocked, **c** instead of **a** is formed.

2. Palladium-Catalyzed Cycloisomerization of Enynes to Bicyclo[4.1.0]hept-2-enes.

Our initial study began with a reaction of an enyne (**1a**) in the presence of 5 mol% $Pd(OAc)_2$ and 10 mol% of PPh_3 in 1,4-dioxane at 90°C. After work-up, a monocyclic triene compound (**1b**) was isolated in 40% yield. In order to use the in situ generated triene in the Diels-Alder-type reaction, 1.3 equiv maleimide was added from the beginning. However, no Diels-Alder-type product was isolated. Instead, a bicyclo[4.1.0]heptene compound (**1d**) was isolated in 40% yield. As far as we are aware, this was the first observation of the formation of bicyclo[4.1.0]heptene in the palladium-catalyzed cycloisomerization of 1,6-enynes. When the same substrate was reacted in the presence of 10 mol% $PtCl_2$ in 1,4-dioxane at 90°C for 1 h, **1d** was obtained in 45% yield. Although maleimide did not participate in the reaction product, it had to play some role in the reaction. In order to obtain a maximum yield of **1d**, we optimized the reaction conditions, including the palladium precursor, the additive (ligand), the reaction solvent, the reaction temperature, and the reaction time (Table 1). The use of $Pd(OAc)_2$ as a catalyst in the presence of PPh_3 afforded **1b** in low yield (25%) (entry 1). When $Pd_2(dba)_3$ was used as a catalyst precursor in dioxane, no reaction was observed (entry 3). Our screening showed that the use of an additive: Pd ratio of 1: 4 was found to be optimal for this catalytic system.[15] When $Pd(PPh_3)_4$ in presence of maleimide was used as a catalyst in toluene at 90°C for 16 h, **1d** was isolated in 62% yield (entry 4).

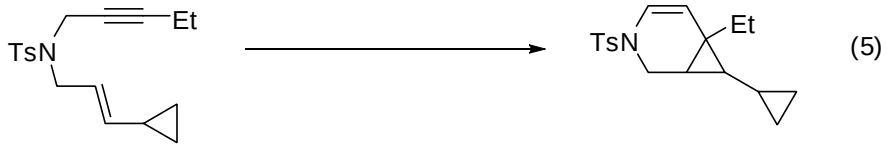
Table 3. Palladium-catalyzed cycloisomerization of 1,6-enynes 16 and 17

Entry	Pd complex (mol %)	Ligand (mol %)	Solvent	Temp (^{o}C)	Time (h)	Yield of b(%)	Yield of c(%)
1	$Pd(OAc)_2$ (10)	PPh_3 (20)	dioxane	90	6	0	25
2	$Pd_2(dba)_3$ (5)	maleimide (40)	dioxane	90	24	0	0
3	$Pd(PPh_3)_4$ (10)	maleimide (40)	dioxane	90	24	9	0
4	$Pd(PPh_3)_4$ (10)	maleimide (40)	toluene	90	16	62	0
5	$Pd(PPh_3)_4$ (10)	maleimide (130)	dioxane	90	48	0	40
6	$Pd(PPh_3)_4$ (10)	succinamide (40)	toluene	90	20	44	0
7	$Pd(PPh_3)_4$ (10)	imidazole (40)	toluene	90	24	0	0
8	$Pd(PPh_3)_4$ (10)	benzoquinone (40)	toluene	90	24	0	10
9	$Pd(PPh_3)_4$ (10)	furan-2,5-dione (40)	toluene	90	24	0	29
10	$Pd(PPh_3)_4$ (10)	cyclopent-4-ene-1,3 dione (40)	toluene	90	16	0	16
11	$Pd(PPh_3)_4$ (10)	1,2-cyclohexane dione(40)	toluene	90	5	0	37
12	Pd(maleimide)$_2$(PPh_3)$_2$ (10)	-	THF	50	7	9	0
13	Pd(maleimide)$_2$(PPh_3)$_2$ (10)	-	DCE	70	7	6	82
14	Pd(maleimide)$_2$(PPh_3)$_2$ (10)	-	dioxane	90	7	13	13

Entry	Pd complex (mol %)	Ligand (mol %)	Solvent	Temp (^oC)	Time (h)	Yield of b(%)	Yield of c(%)
15	Pd(maleimide)$_2$(PPh$_3$)$_2$ (10)	-	toluene	130	7	60	40
16	Pd(maleimide)$_2$(PPh$_3$)$_2$ (10)	-	xylene	150	7	17	18
17	Pd(MeCN)$_2$Cl$_2$(10)	-	toluene	130	24	0	0
18	Pd(MeCN)$_2$Cl$_2$(10)	triphenyl phosphite(40)	toluene	130	24	0	56
19	Pd(MeCN)$_2$Cl$_2$(10)	tris-2-furylphosphine(40)	toluene	130	24	15	9
20	Pd(MeCN)$_2$Cl$_2$(10)	tricyclohexyl phosphine(40)	toluene	130	24	5	30
21	Pd(MeCN)$_2$Cl$_2$(10)	tris(4-fluorophenyl) phosphine(40)	toluene	130	24	22	17
22	Pd(MeCN)$_2$Cl$_2$(10)	tri-o-tolyphoshpine(40)	toluene	130	24	18	15
23	Pd(MeCN)$_2$Cl$_2$(10)	triphenyl phosphite(40)	DCE	70	24	0	0
24	Pd(MeCN)$_2$Cl$_2$(10)	triphenyl phosphite(40)	dioxane	90	24	0	0
25	Pd(MeCN)$_2$Cl$_2$(10)	triphenyl phosphite(40)	xylene	150	7	0	30

[a] Entries **1-15** used compound **16.** [b] Pd($C_4H_2NO_2$)$_2$(PPh$_3$)$_2$ was prepared according to the literaure.[16] [c] Entries **16-24** used compound **17**

When succinic imide was used instead of maleimide in toluene, **1c** was isolated in 44% yield (entry 6). Interestingly, when imidazole (entry 7) or N-phenylmaleimide was used instead of maleimide, no reaction was observed. Moreover, when benzoquinone, furan-2,5-dione, cyclopent-4-ene-1,3-dienone, or 1,2-cyclohexanedione was used instead of maleimide (entries 8-11), only **1b** was isolated in low yields (10 %, 29 %, 16 %, and 37% yields, respectively). These observations suggested that maleimide acted as a ligand to produce a Pd(II) species, Pd(maleimidate)$_2$(PPh$_3$)$_2$ (maleimidate = $C_4H_2NO_2$). Thus, Pd($C_4H_2NO_2$)$_2$(PPh$_3$)$_2$ was prepared and used as a catalyst in the reaction. Using Pd($C_4H_2NO_2$)$_2$(PPh$_3$)$_2$ as a catalyst, the reaction solvent was screened (entries 12-16). The reaction was highly dependent upon the solvent and the best result was obtained in toluene. Thus, we established the optimum reaction conditions as follows: 10 mol% Pd($C_4H_2NO_2$)$_2$(PPh$_3$)$_2$ (or 10 mol% of Pd(PPh$_3$)$_4$ and 40 mol% of maleimide) in toluene at 130°C for 7 h. We also had to find another set of optimum reaction conditions because the established reaction conditions were not good enough for some substrates. For example, when (*E*)-*N*-(3-cyclopropyallyl)-4-methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide, **2a**, was used as a substrate, **2c** was isolated in just 17% yield [Eq. (5)].



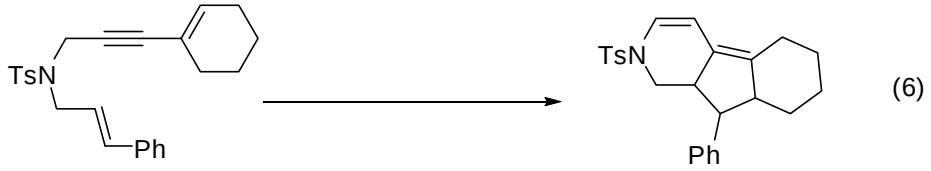
17 **17d** (40 %) (5)

Thus, we had to find another set of optimum conditiona to obtain the maximum yield of **2c**. We examined $Pd(MeCN)_2Cl_2$ with phosphine or phosphite as catalyst (entries 17−25) for Eq 2 because $Pd(MeCN)_2Cl_2$ has been widely used as a palladium(II) catalyst or precursor in diverse catalytic reactions.[17] When $Pd(MeCN)_2Cl_2$ was used as a catalyst in the absence of any additive (entry 17), no reaction was observed. However, in the presence of phosphite or phosphine, a mixture of **2b** and **2c** in various ratios was isolated (entries 18−22). Among the phosphines and phophites used, the best result was observed with $P(OPh)_3$. We attempted to synthesize $[Pd\{P(OPh)_3\}_2Cl_2]$ and use it as a catalyst. However, it was too hydrophilic to isolate. Thus, we had to use $Pd(MeCN)_2Cl_2$ with $P(OPh)_3$ (1: 4) as catalyst. We also examined the effect of solvent on the yield of **2c** (entries 18 and 23−25) and discovered that the yield of **2c** was highly sensitive to the solvent. The best result was observed in toluene (entry 18), but, strangely no reaction was observed in DCE or dioxane (entries 23 and 24). We also examined a diphosphine such as BINAP as an additive in the presence of $Pd(MeCN)_2Cl_2$. However, we failed to isolate a major product because there were too many spots in the tlc plate. Thus, we established two sets of optimal reaction conditions using $Pd(C_4H_2NO_2)_2(PPh_3)_2$ and $Pd(MeCN)_2Cl_2$ with $P(OPh)_3$ (1: 4), respectively, and could use one of them according to the substrate.

We next examined the scope of a substrate under our optimal reaction conditions (Table 2). Most substrates gave rise to bicyclo[4.1.0]hepenes as single diastereomers in reasonable to high

yields. An Alder-ene-type reaction may take place in some cases (entries 18, 20, and 21). Fortunately, the formation of an Alder-ene-type product (**b**) was not observed in the other cases. When the yield of **d** was not good enough, no isolable major compounds were formed. The yield of **d** was highly dependent upon the substituent on the alkyne and alkene moieties. Enynes with a terminal alkyne (entry 18), or with a sterically bulky substituent on the alkyne (entry 31) were poor or inert substrates under our reaction conditions. When enynes (entries 31-34, 38, and 40) having a cyclopropyl group at the terminal position of an olefin were used as a substrate, the yield was highly sensitive to the substituent at the terminal position of an alkyne in the following order H << cyclohexenyl ≈ Et < CH_2OMe < Me <cyclopropyl. In the case of enynes (entries 13-19) bearing a 4-$MeOC_6H_4$ group at the terminal position of an olefin, the yield was highly sensitive to the substituent at the terminal position of an alkyne in the following order cyclobutyl < C_6H_4-OMe-4 < ^nPr ≈ Me < cyclopropyl < Et. For enynes (19, 20, 21, and 28) with a methyl group at the terminal position of an alkyne, the yield was highly sensitive to the substituent at the terminal position of an alkene in the following order Me < Ph < cyclopropyl ≈ 4-$MeOC_6H_4$. Substrates **19** and **22** having a methyl and a cyclopropyl group at the different terminal positions of an alkyne and an olefin, gave quite different yields (72% and 53% yield, respectively). Enynes (entries 35 and 37) having an aryl group at the internal carbon of the olefin moiety were better substrates than those (entries 24 and 28) bearing an aryl group at the terminal

position of an olefin. In the cases of enynes (entry 35 *vs.* 36; 37 *vs.* 38) having an aryl group at the internal carbon of the olefin moiety, the electronic effect of a substituent on the aromatic ring might exert on the yield: an electron-withdrawing group diminishes the yield of a reaction. Interestingly, a compound having a cyclopenta[*c*]pyridine skeleton was obtained in 41% and 31% yields, respectively, in entries 11 and 12 [Eq. (6)].



(6)

26 **26d** (41 %)

The same kind of transformation was previously found[18a] in the consecutive reactions of a $PtCl_2$-catalyzed cycloisomerization of dienynes having a phenyl group at the terminal carbon of an alkene moiety, followed by vinylcyclopropane rearrangement. The structure of the bicyclo[4.1.0]heptene skeleton was confirmed by X-ray crystallographic analyses of **17d** and **34d** (Figure 1, 2).

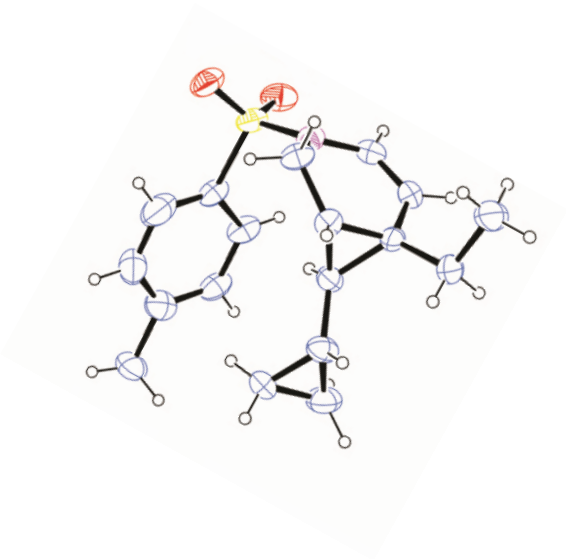


Figure 1. X-ray crystallography of **17d**

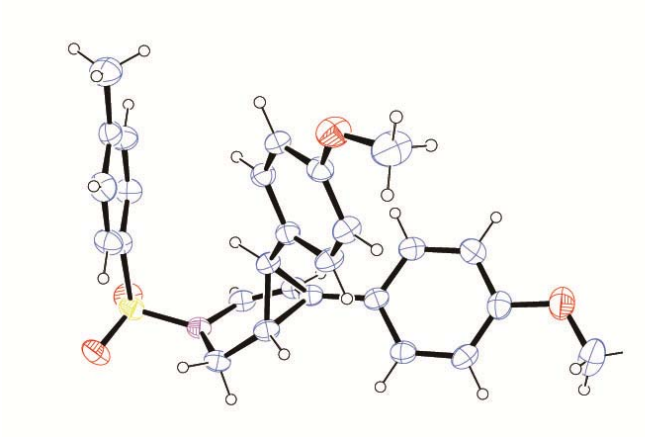
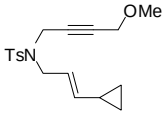
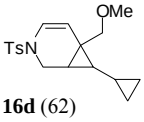
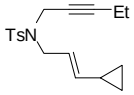
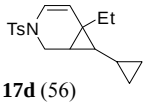
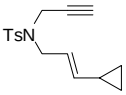
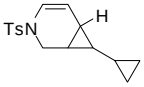
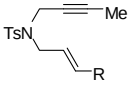
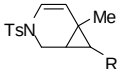
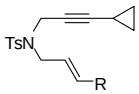
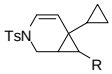
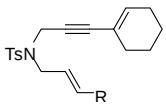
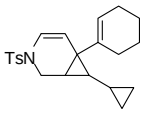
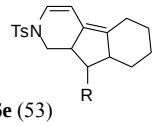
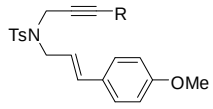
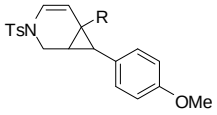
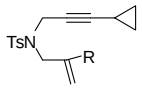
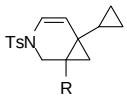
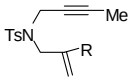
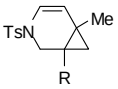
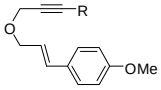
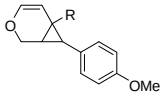


Figure 2. X-ray crystallography of **34d**

Unlike N-Ts tethered enynes, oxygen-tethered 1,6-enynes were not good substrates.[19] A similar observation was made in the Ir-catalyzed cycloisomerization of 1,6-enynes. When O-tethered enynes were reacted in the presence of $Pd(MeCN)_2Cl_2$ with $P(OPh)_3$ (1: 4), full conversion was observed, but too many spots were observed in the tlc plate. Thus, the same reaction was conducted in the presence of $Pd(PPh_3)_4$ and maleic imide. However, the expected reaction products were cleanly isolated in relatively low yields (entries 39 and 40: 37% and 20% yield, respectively). We next wanted to use a reaction of enynes with a carbon tether to investigate whether this palladium-catalyzed cycloisomerization was effective or not. Unfortunately, no reaction was observed. Thus, the formation of cyclopropanes takes place only with heteratom-tethered enynes, with other transition metal-catalyzed reactions.[20]

Table 2. Scope of Pd-catalyzed cycloisomerization.[a]

Entry	Substrate	*t* [h]	Product Yield [%][b]
16	 **16**	19	 **16d** (62)
17	 **17**	24	 **17d** (56)
18[c]	 **18**	24	 **18d** (4)
			
19	**19** (R = cyclopropyl)	24	**19d** (72)
20[c]	**20** (R = Me)	24	**20d** (10)
21	**21** (R = C_6H_5)	24	**21d**(53)
			
22[c]	**22** (R = Me)	24	**22d** (53)
23[d]	**23** (R = cyclopropyl)	24	**23d** (84)
24	**24** (R = C_6H_5)	24	**24d** (45)
			
25	**25** (R = cyclopropyl)	24	**25d** (53)[e] 
26	**26** (R = C_6H_5)	24	**26e** (53)
27	**27** (R = 4-$MeOC_6H_4$)	24	**27e** (31)[f]

				
28	**28** (R = Me)		24	**28d** (72)
29	**29** (R = Et)		24	**29d** (89)
30	**30** (R = *n*-Pr)		24	**30d** (71)
31	**31** (R = *t*-Bu)		24	**31d** (0)[g]
32	**32** (R = cyclopropyl)		24	**32d** (77)
33	**33** (R = cyclobutyl)		24	**33d** (56)
34	**34** (R = $MeOC_6H_4$)		24	**34d** (63)[h]
				
35[j]	**35** (R = C_6H_5)			**35d** (83)
36[j]	**36** (R = FC_6H_4)	12 12		**36d** (79)
				
37	**37** (R = $MeOC_6H_4$)	12		**37d** (79)
38	**38** (R = $CF_3C_6H_4$)	12		**38d** (50)
				
39[i]	**39** (R = Et)	48		**39d** (37)
40[i]	**40** (R = *n*-Pr)	48		**40d** (20)

[a] Reaction conditions: 10 mol% $Pd(MeCN)_2Cl_2$/ 40 mol% $P(OPh)_3$, toluene, 130°C, 24 h (or 10 mol% of $Pd(PPh_3)_4$/40 mol% maleimide, dichloroethane, 70°C, 7 h). [b] Yield of the isolated product. [c] **3b**, **5b**, and **7b** were isolated in 16%, 8%, and 8% yields, respectively. [d] 15 mol% $Pd(MeCN)_2Cl_2$ was used. [e] Compound **10** was recovered in 30%. [f] Compound **12** was recovered in 18 %. [g] No reaction was observed. [h] Reactions were carried out at 90°C [i] Reactions were carried out at 80°C. Compounds **24** and **25** were recovered in 36% and 11%, respectively

Initially, we envisioned that mechanisms for the cycloisomerization reactions of enynes catalyzed by Pt(II) and Pd(II) might be different to each other. However, other previous studies proposed that the cyclization of enynes (intramolecular reaction of enol ethers with alkynes) with Pt^{II}, Pd^{II}, Au^{III}, and Cu^{I} (in methanol) take place by a common mechanism.[21] In the methoxy- or hydroxycyclization reactions of enynes, palladium-catalyzed reactions showed selectivities similar to those observed with Pt^{II} complexes.[22] Furthermore, our experimental results also suggested that the palladium-catalyzed reaction is closely related to the electrophilic metal-catalyzed reactions. Thus, a mechanism similar to that proposed for Pt^{II}-catalyzed reactions[23] can also be postulated for the process catalyzed by palladium. Complexation of Pd(II) renders the alkyne susceptible to nucleophilic attack by the tethered alkene. The nucleophilic attack can occur by 5-exo-dig or 6-endo-dig pathways to give cyclopropylcarbenes **I** and **II**, respectively. Cyclopropyl palladium complexes have been proposed by Trost[24] and Murai[25] as intermediates for the reaction of some enynes which give cyclopropane derivatives. The intermediates **I** and **II** stabilize along different pathways. The preference for either of these processes may ultimately depend on which one gains more stabilization via the heteroatom in the tether. It is well-known[2d,26] that the electron-deficient palladium catalysts are effective in the enyne methathesis reactions In this case, metallacyclopentene derivatives (**III**) are proposed as the key intermediates of a Pd(II)/Pd(IV) manifold.[27] However, a metallacyclopetene-

metallacyclopropane rearrangement takes place during the Pd(II)-catalyzed cycloisomerization reactions of vinyl-substituted enynes[24] and of allylpropargy ether.[28] An Alder-ene-type reaction may take place as a secondary process in some cases.[29]

Conclusion

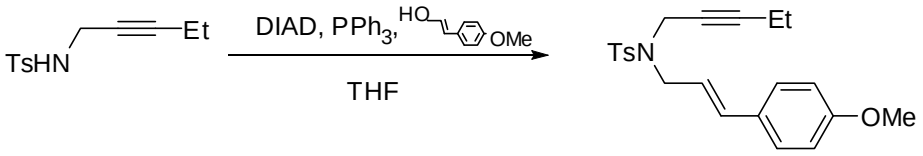
In conclusion, we have demonstrated that palladium-catalyzed reactions of nitrogen- and oxygen-bridged 1,6-enynes that affords 3-aza- and 3-oxabicyclo[4.1.0]heptenes in reasonable to high yields and 1,6-enynes bearing a cyclopropyl moiety at the alkene affords bicyclic or monocyclic trienes as products depending on the presence or absence of a leaving group. The bicyclic or monocyclic trienes can form a class of important building blocks because they possess three double bonds that may be used for further derivatization. And current efforts are directed at gaining a deeper understanding of some of the fundamental principles dictating the reactivity of the substrates, as well as extending their utility by expanding the substrate scope. Further experiments have to be carried out to corroborate the proposed mechanism. A report on the full scope and limitations of the new cycloisomerization process will be available in due time. We envision that the reaction developed in this study will be easily accessible to many synthetic chemists and of use to them in near future.

Experimental Section

General remarks. All solvents were dried and distilled according to standard methods before use. Toluene, Dioxane were distilled from sodium. $Pd_2(dba)_3$, $Pd(PPh_3)_4$, $Pd(OAc)_2$, $Ni(acac)_2$, and $Ni(OAc)_2$ were purchased from Strem Chemical Co. $Pd(MeCN)_2Cl_2$ was prepared according to the literaure.[30] Reactions were carried out in a microwave tube equipped with a stirring bar and sealed with a rubber septum, unless otherwise indicated. Elevated temperatures were maintained in thermostat-controlled oil baths. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and acidic *p*-anisaldehyde, and heat as a developing agent. Flash chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^1H and ^{13}C NMR spectra were recorded with Bruker (300 MHz) spectrometer, Varian spectrometer (400 MHz), and Varian spectrometer (500 MHz). ^1H NMR spectra were referenced to residual TMS (0.0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.00 ppm). Mass data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Single crystal data for **17d** and **34d** were collected on an Enraf-Nonius CCD single crystal X-ray diffractometer at room temperature using graphite-monochromated Mo Kα radiation (λ = 0.71073Å). Structures were

solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97. Compounds **2 – 6**,[31] **7**,[32] **11 – 12**,[33] **13**,[34] **20 – 21**,[35] **22**,[36] **23**,[31] **2c – 6c**,[31] **5b**,[37] **7c**,[32] **11d – 12d**,[33] **13c**,[34] **20c – 21c**,[35] **22c**,[36] and **23c**[31] were known.

Representative procedure for preparation of (*E*)-N-(3-(4-methoxyphenyl)allyl)-4-methyl-N-(pent-2-ynyl)benzenesulfonamide (29)



To a solution of N-(3-cyclopropylprop-2-ynyl)-4-methylbenzenesulfonamide (0.872 g, 3.5 mmol) and PPh_3 (0.92 g, 3.5 mmol) in THF (30 mL) was added DIAD (diisopropyl azodicarboxylate) (0.68 mL, 3.5 mmol) at room temperature. To the above solution, (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol was added. The reaction mixture was stirred for 24 h at room temperature. After the solvent was removed by a rotary evaporator, the residue was purified by flash column chromatography eluting with Hexane/EtOAc(15:1).

General procedure for palladium-catalyzed reactions (a, b,c): To a flame-dried 10 mL Schlenk flask capped with a rubber septum, dioxane (2 mL), $Pd(OAc)_2$ (5 mol%), and Ph_3P (10 mol%) were

added under N_2 flow. Compound **1** (0.3 mmol) was added to the flask under N_2. The mixture was heated at 90 ℃ and the progress of the reaction was monitored by TLC. The mixture was cooled to room temperature, filtered, and the solvent was evaporated under reduced pressure. The product was purified by flash chromatography on a silica gel column (*n*–hexane–ethyl acetate, 10:1).

General procedure for palladium–catalyzed reactions (d,e,f): 10 mol % $Pd(MeCN)_2Cl_2$, 40 mol % Triphenyl phosphite and toluene (2 mL) were added to a microwave tube equipped with a stirring bar and capped with a rubber septum. After 5 min, The solution was stirred for 5 min. A substrate (0.3 mmol) and toluene (1 mL) were added to the tube reactor and the resulting solution was heated. The resulting mixture was reacted until the substrate was completely consumed (reaction monitored by TLC). The product was purified by flash chromatography on a silica gel column by eluting with n–hexane/ethyl acetate.

Characterization of New compounds

1: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2 H), 6.98 (d, *J* = 8.1 Hz, 2 H), 5.08 – 4.97 (m, 1 H), 4.88 (dd, *J* = 8.6, 15.2 Hz, 1H), 4.06 (d, *J* = 9.6 Hz, 2 H), 3.82 – 3.71 (m, 6 H), 3.39 (d, *J* = 6.6 Hz, 2 H), 2.10 (s, 3 H), 1.00 (t, *J* = 7.0 Hz, 7 H), 0.37 – 0.33 (m, 2 H), 0.02 – 0.00 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 140.9, 136.2, 129.6, 127.9, 120.5, 80.9, 79.5, 64.2, 64.1, 54.98, 54.92, 48.5, 35.8, 21.6, 16.3, 16.2, 13.5, 7.0 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{21}H_{30}NO_6SP_1$: 456.1610, found: 456.1613.

2: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.43 – 5.33 (m, 1H), 5.20 (dd, *J* = 8.6, 15.3 Hz, 1 H), 4.38 (s, 2 H), 4.10 (s, 2 H), 3.72 (d, *J* = 6.7 Hz, 2 H), 2.43 (s, 3 H), 2.05 (s, 3 H), 1.41 – 1.33 (m, 1H), 0.74 – 0.67 (m, 2H), 0.37 – 0.33 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 143.6, 141.0, 136.2, 129.5, 128.0, 120.6, 79.9, 79.5, 52.0, 48.6, 35.9, 21.7, 20.8, 13.5, 7.0 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}NO_4S$: 362.1426, found: 362.1425.

3 :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 5.43 – 5.33 (m, 1 H), 5.20 (dd, *J* = 8.6, 15.3 Hz, 1 H),. 4.44 (s, 2 H), 4.11 (s, 2 H), 3.80 (s, 3 H), 3.71 (d, *J* = 6.8 Hz, 2 H), 2.42 (s, 3 H), 1.41 – 1.32 (m, 1 H), 0.73 – 0.67 (m, 2 H), 0.37 – 0.32 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 143.7,

141.0, 136.1, 129.6, 128.0, 120.5, 80.7, 78.9, 55.4, 55.3, 48.6, 35.8, 21.7, 13.6, 7.0 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}NO_5S$: 378.1375, found: 378.1378

4: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (s, 2 H), 5.37 – 5.28 (m, 1 H), 5.22 – 5.15 (dd, *J* = 8.5, 15.2 Hz, 1 H), 4.63 (d, *J* = 9.7 Hz, 2 H), 4.17 – 4.08 (m, 4 H), 4.03 (s, 2 H), 3.73 (d, *J* = 6.6 Hz, 2 H), 2.59(s, 6 H), 2.30 (s, 3 H), 1.34 (t, *J* = 6.9 Hz, 7 H), 0.70 – 0.68 (m, 2 H), 0.34 – 0.33 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 141.1, 140.5, 132.6, 132.2, 120.7, 82.0, 78.8, 64.3, 64.2, 55.37, 55.30, 47.7, 34.5, 23.0, 21.1, 16.3, 16.2, 13.6, 7.0 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{23}H_{34}NO_6SP_1$: 484.1923, found: 484.1920.

5: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1 H), 7.97 – 7.95 (m, 2 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.82 (dd, *J* = 1.7, 8.7 Hz, 1 H), 7.65 – 7.58 (m, 2 H), 5.41 – 5.35 (m, 1 H), 5.21 (dd, *J* = 8.8, 15.2 Hz, 1 H), 4.188– 4.186 (d, *J* = 1.0 Hz, 3 H), 4.16 (d, *J* = 1.6 Hz, 1 H), 4.05 – 3.99 (m, 4 H), 3.79 (d, *J* = 6.8 Hz, 2 H), 1.36 – 1.32 (m, 1 H), 1.28 (dt, *J* = 1.0, 7.1 Hz, 6 H), 0.70 –0.66 (m, 2H), 0.33 – 0.30 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 136.1, 135.0, 132.2, 129.4, 129.3, 129.2, 129.0, 128.0, 127.6, 127.6, 123.2, 120.5, 80.8, 79.7, 64.2, 64.1, 54.8, 54.7, 48.7, 35.9, 16.2, 13.5, 7.0 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{24}H_{30}NO_6SP_1$: 492.1610, found: 492.1612.

6: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 7.8 Hz, 2 H), 5.50 (d, *J* = 7.2 Hz, 1 H), 5.16 (dd, *J* = 8.7, 15.3 Hz, 1 H), 4.92 (d, *J* = 7.1 Hz, 1 H), 4.46 (dd, *J* = 1.6, 9.4 Hz, 2 H), 4.11 (d, *J* = 7.2 Hz, 4 H), 3.86 (dd, *J* = 5.1, 15.9 Hz, 1 H), 3.66 (dd, *J* = 7.4, 15.9 Hz, 1 H), 2.42 (s, 3 H), 1.43 (d, *J* = 7.1 Hz, 3 H), 1.33 (t, *J* = 7.0 Hz, 7 H), 0.70 – 0.67 (m, 2 H), 0.36 – 0.31 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ143.5, 138.0, 136.8, 129.6, 127.8, 124.5, 85.6, 79.2, 64.3, 64.2, 55.1, 55.0, 47.0, 46.2, 22.5, 21.7, 16.3, 16.2, 13.5, 6.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{22}H_{32}NO_6SP_1$: 470.1766, found: 470.1768.

7 :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 5.57 – 5.47 (m, 1 H), 5.16 (dd, *J* = 8.5, 15.3 Hz, 1 H), 4.65 (t, *J* = 7.7 Hz, 1 H), 4.46 (d, *J* = 9.3 Hz, 2 H), 4.14 – 4.05 (m, 4 H), 3.86 – 3.79 (m, 1 H), 3.61 (dd, *J* = 7.7, 15.8 Hz, 1 H), 2.43 (s, 3 H), 1.80 – 1.70 (m, 2 H), 1.35 – 1. 31 (m, 7 H), 1.00 (t, *J* = 7.3 Hz, 3 H), 0.68 (dd, *J* = 3.6, 9.8 Hz, 2 H), 0.34 – 0. 30 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 137.7, 136.6, 129.3, 127.6, 124.1, 84.6, 77.4, 64.0, 63.9, 54.9, 52.3, 47.0, 28.7, 21.5, 16.1, 16.0, 13.2, 10.7, 6.5, 6.4 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{23}H_{34}NO_6SP_1$: 484.1923, found: 484.1924.

8 :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 7.7 Hz, 2 H), 5.67 (dd, *J* = 6.4, 15.1 Hz, 1 H), 5.19 (dd, *J* = 8.7, 15.3 Hz, 1 H), 4.54 (d, *J* = 9.6 Hz, 2 H), 4.11 (m, 6 H), 2.41 (s, 3

H), 1.66 (s, 6 H), 1.41 – 1.25 (m, 7 H), 0.73 – 0.67 (m, 2 H), 0.37 – 0.35 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 139.8, 137.7, 129.2, 127.2, 125.3, 90.1, 77.6, 64.0, 63.9, 56.1, 55.1, 55.0, 49.5, 30.4, 21.4, 16.1, 16.0, 13.3, 6.5 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{23}H_{34}NO_6SP_1$: 294.1164, found: 294.1161.

9 :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2 H), 7.31 (d, *J* = 7.7 Hz, 2 H), 5.34 – 5.24 (m, 1 H), 5.10 (dd, *J* = 8.6, 15.1 Hz, 1 H), 4.62 (d, *J* = 9.2 Hz, 2 H), 4.16 – 4.11 (m, 4 H), 3.76 (d, *J* = 6.4 Hz, 2 H), 3.25 (t, *J* = 7.3 Hz, 2 H), 2.51 (s, 2 H), 2.47 (s, 3 H), 1.35 (t, *J* = 6.9 Hz, 7 H), 0.70 (d, *J* = 6.3 Hz, 2 H), 0.32 (d, *J* = 3.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.1, 137.1, 129.9, 127.4, 121.6, 85.2, 76.2, 64.29, 64.21, 55.6, 50.7, 45.6, 21.7, 20.0, 16.3, 16.2, 13.5, 7.0 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{22}H_{32}NO_6SP_1$: 470.1766, found: 470.1768.

10 :^{1}H NMR (300 MHz, $CDCl_3$) δ 5.30 – 5.20 (m, 1 H), 5.14 – 5.04 (m, 1 H), 4.61 (d, *J* = 9.7 Hz, 2 H), 4.19 – 4.07 (m, 4 H), 3.72 (s, 6 H), 2.84 (s, 2 H), 2.68 (d, *J* = 7.3 Hz, 2 H), 1.36 – 1.31 (m, 6 H), 1.26 – 1.21 (m, 1 H), 0.69 – 0.63 (m, 2 H), 0.31 – 0.27 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 140.0, 120.2, 83.0, 77.4, 64.2, 64.1, 57.3, 55.6, 52.9, 35.5, 23.1, 16.3, 16.2, 13.8, 6.8 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{29}O_8P_1$: 417.1678, found: 417.1680.

11 :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2 H), 7.29 (d,

J = 8.3 Hz, 2 H,) 5.39 (dd, *J* = 7.2, 14.6 Hz, 1 H), 5.20 (dd, *J* = 8.7, 15.2 Hz, 1 H), 4.12 (s, 2 H), 3.83 (s, 2 H), 3.74 (d, *J* = 6.6 Hz, 2 H), 3.19 (s, 3 H), 2.42 (s, 3 H), 1.38 – 1.31 (m, 1 H), 0.71 (d, *J* = 7.1 Hz, 2 H), 0.34 (d, *J* = 3.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.8, 136.4, 129.9, 129.6, 128.0, 120.8, 81.3, 79.6, 59.8, 57.6, 48.6, 35.9, 21.7, 13.6, 7.1 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}NO_3S$: 334.1477, found: 334.1476.

12 :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2 H), 7.37 – 7.29 (m, 3 H), 7.27 – 7.21 (m, 4 H), 5.45 – 5.35 (m, 1 H), 5.24 – 5.16 (dd, *J* = 8.7, 15.2 Hz, 1 H), 4.38 (s, 2 H), 4.14 (s, 2 H), 3.91 (s, 2 H), 3.75 (d, *J* = 6.7 Hz, 2 H), 2.33 (s, 3 H), 1.40 – 1.32 (m, 1 H), 0.72 – 0.66 (m, 2 H), 0.35 – 0.30 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.8, 137.4, 136.4, 129.6, 128.1, 128.0, 127.9, 120.8, 81.4, 79.6, 71.5, 57.2, 48.6, 36.0, 21.6, 13.6, 7.1 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{24}H_{27}NO_3S$: 410.1790, found: 410.1794.

13 :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2 H), 7.31 – 7.24 (m, 7 H), 6.56 (d, *J* = 15.8 Hz, 1 H), 6.13 – 6.03 (m, 1 H), 4.17 (s, 2 H), 3.98 (d, *J* = 6.7 Hz, 2 H), 3.85 (s, 2 H), 3.20 (s, 3 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.3, 135.0, 129.7, 128.8, 128.3, 128.0, 126.7, 123.2, 81.7, 79.4, 59.8, 57.6, 49.0, 36.4, 21.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}NO_3S$: 370.1477, found: 370.1480.

14: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 5.78 – 5.64 (m, 1 H), 5.41 – 5.32 (m, 1 H), 4.12 (s, 2 H), 3.83 (s, 2 H), 3.75 (d, *J* = 6.7 Hz, 2 H), 3.19 (s, 3 H), 2.42 (s, 3 H), 1.69 (d, *J* = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 136.4, 131.7, 129.5, 127.9, 124.8, 81.3, 79.5, 59.7, 48.6, 35.9, 21.7, 17.9 HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}NO_3S$: 308.1320, found: 308.1318.

1-D: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 5.19 (d, *J* = 8.6 Hz, 1 H), 4.39 (d, *J* = 9.4 Hz, 2 H), 4.15 – 4.05 (m, 6 H), 3.71 (s, 2 H), 2.43 (s, 3 H), 1.34 (t, *J* = 7.0 Hz, 7 H), 0.74 – 0.68 (m, 2 H) 0.37 – 0.32 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 140.9, 136.2, 129.6, 127.9, 120.6, 80.9, 79.6, 64.3, 64.2, 55.0, 54.9, 48.6, 35.8, 21.7, 16.3, 16.2, 13.5, 7.0 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{21}H_{29}D_1NO_6SP_1$: 457.1672, found: 457.1674.

15: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 2 H), 4.75 (d, *J* = 9.4 Hz, 1 H), 4.33 (d, *J* = 9.1 Hz, 2 H), 4.11 – 4.04 (m, 6 H), 3.62 (s, 2 H), 2.43 (s, 3 H), 1.75 (s, 3 H), 1.50 – 1.47 (m, 1 H), 1.33 (t, *J* = 6.9 Hz, 6 H), 0.74 (d, *J* = 7.3 Hz, 2 H), 0.30 (d, *J* = 3.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.2, 135.4, 129.5, 128.0, 127.2, 80.8, 79.6, 64.2, 64.2, 54.9, 54.5, 35.5, 21.7, 16.3, 16.2, 14.4, 10.3, 7.1 ppm HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{22}H_{32}NO_6SP_1$: 470.1766, found: 470.1768.

16: H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H,) 5.39 (dd, *J* = 7.2, 14.6 Hz, 1 H), 5.20 (dd, *J* = 8.7, 15.2 Hz, 1 H), 4.12 (s, 2 H), 3.83 (s, 2 H), 3.74 (d, *J* = 6.6 Hz, 2 H), 3.19 (s, 3 H), 2.42 (s, 3 H), 1.38 – 1.31 (m, 1 H), 0.71 (d, *J* = 7.1 Hz, 2 H), 0.34 (d, *J* = 3.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.8, 136.4, 129.9, 129.6, 128.0, 120.8, 81.3, 79.6, 59.8, 57.6, 48.6, 35.9, 21.7, 13.6, 7.1 ppm. HRMS (FAB) Calcd for $[C_{18}H_{23}NO_3S]$: 334.1477, found: 334.1476.

17 : ^1H NMR (300 MHz, $CDCl_3$) δ. 7.73 (d, *J* = 8.1 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 5.43 – 5.36 (m, 1 H), 5.20 (dd, *J* = 8.6, 15.3Hz, 1 H), 4.03 (s, 2 H), 3.72 (d, *J* = 6.7 Hz, 2 H), 2.41 (s, 3 H), 1.91 (q, *J* = 7.4 Hz, 2 H), 1.36 (dt, *J* = 3.7, 8.2 Hz, 1 H), 0.90 (t, *J* = 7.4 Hz, 3 H), 0.71 – 0.67 (m, 2 H), 0.35 – 0.32 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 140.4, 136.5, 129.4, 128.0, 121.0, 87.4, 72.0, 48.2, 36.1, 21.6, 13.7, 13.5, 12.2, 6.9 ppm.

18 : ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8 2 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 5.44 – 5.34 (m, 1 H) 5.21 (dd, *J* = 8.6, 15.3 Hz, 1 H), 4.08 (d, *J* = 2.3 Hz, 2 H), 3.75 (d, *J* = 6.7 Hz, 2 H) 2.42 (s, 3 H), 1.98 (t, *J* = 2.3, 1 H) 1.41 – 1.31 (m, 1 H), 0.74 – 0.68 (m, 2 H), 0.37 – 0.32 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 141.0, 136.3, 129.6, 127.9, 120.6, 76.9, 73.7, 48.4, 35.6, 21.7, 13.6, 7.0 ppm.

19: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H). 5.43 – 5.34 (m, 1 H), 5.19 (dd, *J* = 8.8, 15.0 Hz, 1 H), 4.00 (s, 2 H), 3.71 (d, *J* = 6.5 Hz, 2 H), 2.42 (s, 3 H), 1.53 (s, 3 H), 1.39 – 1.19 (m, 1 H), 0.71 – 0.68 (m, 2 H), 0.35 – 0.33 (m, 2 H) ppm ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 135.0, 129.9,127.2, 119.9, 118.3, 40.6, 32.5, 25.3, 21.7, 17.3, 16.4, 13.1 ppm.

20: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 5.72 – 5.64 (m ,1 H), 5.40 – 5.29 (m, 1 H), 4.00 (d, *J* = 2.0 Hz, 2 H), 3.72 (d, *J* = 6.7 Hz, 2 H), 2.42 (s, 3 H), 1.68 (d, 3 H), 1.54 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 136.3, 131.1, 129.4, 129.1, 127.8, 124.8, 81.3, 71.8, 48.2, 35.9, 21.4, 17.6, 3.2 ppm.

21: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2 H), 7.32 – 7.29 (m, 7 H), 6.55 (d, *J* = 15.8 Hz, 1 H), 6.13 – 6.03 (m, 1 H), 4.05 (s, 2 H), 3.96 (d, *J* = 6.7 Hz, 2 H), 2.42 (s, 3 H), 1.58 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 136.4, 134.6, 129.4, 128.8, 128.1, 126.7, 123.5, 81.8, 71.9, 48.7 36.6, 21.7, 3.5 ppm.

22: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2 H), 7.29 (d, *J* = 7.9 Hz, 2 H), 5.74 – 5.62 (m, 1 H), 5.40 – 5.31 (m, 1 H), 4.00 (s, 2 H), 3.71 (d, *J* = 6.6 Hz, 2 H), 2.43 (s, 3 H), 1.68 (d, *J* = 6.0 Hz, 3 H), 0.95 – 0.94 (d, *J* = 4.8 Hz, 1 H), 0.63 – 0.59 (m, 2 H), 0.32 –

0.29 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 1316.4, 131.3, 129.4, 127.9, 124.9, 89.2, 67.8, 48.3, 36.1, 21.6, 17.8, 7.9, −0.7 ppm.

23: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 5.44 – 5.35 (m, 1 H), 5.19 (dd, *J* = 8.6, 15.2 Hz, 1 H), 4.01 (d, *J* = 1.6 Hz, 2 H), 3.71 (d, *J* = 6.7 Hz, 2 H), 2.43 (s, 3 H), 1.43 – 1.25 (m, 1 H), 0.97 – 0.91 (m, 1 H), 0.72 – 0.67 (td, *J* = 4.4, 6.1 Hz, 2 H), 0.61 (td, *J* = 4.1, 6.4 Hz, 2 H), 0.37 −0.27 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 140.4, 136.5, 129.5, 128.0, 121.0, 89.2, 68.0, 48.3, 36.2, 21.7, 13.6, 8.0, 7.0, −0.6 ppm. HRMS (FAB) calc. for [$C_{19}H_{23}NO_2S$]:329.1149, found:329.1152

24: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2 H), 7.32 (dd, *J* = 3.4, 7.3 Hz, 7 H), 6.55 (d, *J* = 15.8 Hz, 1 H), 6.09 (td, *J* = 6.8, 15.7 Hz, 1 H), 4.06 (d, *J* = 1.5 Hz, 2 H), 3.96 (d, *J* = 6.7 Hz, 2 H), 2.44 (s, 3 H), 1.01 – 0.95 (m, 1 H), 0.66 – 0.60 (m, 2 H), 0.37−0.31 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3. 136.2(2). 136.2(1), 134.4, 129.3, 128.5, 127.9, 127.7, 126.4, 123.2, 89.3, 77.3, 77.0, 76.7, 67.7, 48.5, 36.5, 21.5, 7.8, −0.8

25: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 6.5 Hz, 2 H), 5.76 −5.73 (m, 1 H), 5.47 −5.30 (m, 1 H), 5.24 – 5.16 (dd, *J* = 8.7, 15.2 Hz, 1 H), 4.17 (s, 2 H), 3.73 (d, *J* = 6.7 Hz, 2 H), 2.40 (s, 3 H), 2.00(8) – 2.00(3) (m, 2 H), 1.79 – 1.85 (m, 2

H), 1.53 – 1.51 (m, 2 H), 1.37 – 1.28 (m, 1 H), 0.73 – 0.66 (m, 2 H), 0.37 – 0.27 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 140.6, 136.4, 135.1, 129.5, 128.0, 120.9, 120.0, 87.5, 79.2, 48.4, 36.5, 29.1, 25.7, 22.3,21.6, 21.5, 13.5, 7.0 ppm. HRMS (EI) calc. for [$C_{22}H_{27}NO_2S$]:369.1792, found: 369.1802

26: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54−1.61 (m, 4 H), 1.82 (br s, 2 H), 2.02 (br s, 2 H), 2.41 (s, 3 H), 3.98 (d, *J* = 6.8 Hz, 2 H), 4.22 (s, 2 H), 5.79 (s, 1 H), 6.11 (dt, *J* = 15.7, 6.9 Hz, 1 H), 6.57 (d, *J* = 15.8 Hz, 1 H), 7.24−7.33 (m, 7 H), 7.76 (d, *J* = 7.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 136.2, 135.1, 134.6, 129.4, 128.5, 127.9, 127.8, 126.5, 123.2, 119.7, 87.6, 78.8, 48.6, 36.8, 28.9, 25.5, 22.1, 21.5, 21.3 ppm.

27: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.28 (dd, *J* = 6.1, 7.9 Hz, 4 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 6.51 (d, *J* = 15.8 Hz, 1 H), 6.01 – 5.91 (m, 1 H), 5.78 (bs, 1 H), 4.22 (s, 2 H), 3.95 (d, *J* = .8 Hz, 2 H), 3.81 (s, 3 H), 2.42 (s, 3 H), 2.03 (bs, 2 H), 1.83 (bs, 2 H), 1.57 – 1.54 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 143.4, 136.4, 135.3, 134.4, 129.6, 129.2, 128.0, 127.9, 121.0, 120.0, 114.2, 87.7, 79.2, 55.5, 48.9, 36.9, 29.1, 25.7, 22.3, 21.7, 21.6 ppm.

28: H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2 H), 7.28 (t, *J* = 8.9 Hz, 4 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 6.49 (d, *J* = 15.8 Hz, 1 H), 5.98 – 5.88 (m, 1 H), 4.04 (d, *J* = 2.1 Hz, 2 H), 3.93 (d, *J* = 6.7 Hz, 2 H), 3.80 (s, 3 H), 2.43 (s, 3 H), 1.56 (s, 3 H) ppm. ^{13}C NMR (75

MHz, $CDCl_3$) δ 159.4, 143.2, 136.2, 134.0, 129.2, 129.0, 127.9, 127.7, 120.9, 113.9, 81.5, 71.7, 55.3, 48.6, 36.3, 21.5, 3.3 ppm.

29: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2 H), 7.28 (t, *J* = 8.0 Hz, 4 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 6.50 (d, *J* = 15. 8Hz, 1 H), 5.99 – 5.89 (m, 1 H), 4.08 (s, 2 H), 3.94 (d, *J* = 6.7 Hz, 2 H), 3.80 (s, 3 H), 2.42 (s, 3 H), 1.94 (dd, *J* = 7.4, 14.9 Hz, 2 H), 0.93 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 143.2, 136.3, 124.0, 129.3, 129.0, 127.8, 127.7, 120.9, 114.0, 87.5, 71.9, 55.3, 48.5, 36.3, 21.4, 13.5, 12.1 ppm. HRMS (EI) calc. for $[C_{22}H_{25}NO_3S]$:383.1555, found: 383.1554

30: ^{1}H NMR (300 MHz, $CDCl_3$ δ 7.76 (d, *J* = 8.2 Hz, 2 H), 7.29 – 7.25 (m, 4 H), 6.84 (d, *J* = 8.7 Hz, 2 H) 6.50 (d, *J* = 15.8 Hz, 1 H), 5.95 (td, *J* = 6.8, 15.7, 1 H), 4.09 (s, 2 H), 3.95 (d, *J* = 6 8 Hz, 2 H), 3.79 (s, 3 H), 2.41 (s, 3 H), 1.91 (dd, *J* = 4.6, 9.4 Hz, 2 H), 1.35 – 1.23 (m, 2 H), 0.85 – 0.81 (t, *J* = 7.3 Hz, 3 H) ppm. δ 159.6, 143.4, 136.5, 134.2, 129.5, 129.2, 128.0, 127.9, 121.1, 114.1, 86.3, 72.8, 55.5, 48.7, 36.5, 22.0, 21.6, 20.6, 13.6 ppm HRMS (EI) calc. for $[C_{23}H_{27}NO_3S]$: 397.1712, found: 396.1628

31: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2 H), 7.31 – 7.25 (m, 4 H), 6.85 (d, *J* = 8.6 Hz, 2 H), 6.51 (d, *J* = 15.8 Hz, 1 H), 6.0 – 5.91 (m, 1 H), 4.10 (s, 2 H), 3.95 (d, *J* = 6.8 Hz, 2 H), 3.81 (s, 3 H), 2.42 (s, 3 H), 1.00 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 143.4, 136.6, 134.4, 129.7, 129.3, 128.0, 127.9, 121.0, 114.2,

94.8, 71.1, 55.5, 48.7, 36.5, 30.9, 27.3, 21.7 ppm. HRMS (EI) calc. for [$C_{24}H_{29}NO_3S$]: 411.1868, found: 411.1864

32: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2 H), 7.31 – 7.26 (m, 5 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 6.49 (d, *J* = 15.8 Hz, 1 H), 5.94 (td, *J* = 6.8, 15.7 Hz 1 H), 4.05 (s, 2 H), 3.93 (d, *J* = 6.8 Hz, 2 H), 3.81 (s, 3 H), 2.44 (s, 3 H), 1.00 – 0.97 (m, 1 H), 0.66 −0.59 (m, 1 H), 0.36 – 0.31 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 143.5, 136.5, 134.2, 129.6, 129.2, 127.9, 121.2, 114.2, 89.5, 68.0, 55.5, 48.8, 36.6, 21.7, 8.1, −0.6 ppm. HRMS (EI) calc. for [$C_{23}H_{25}NO_3S$] : 395.1555, found: 394.1480

33: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 4 H), 6.86 (d, *J* = 8.3 Hz, 2 H), 6.50 (d, *J* = 15.7 Hz, 1 H) 6.00 – 5.91 (m, 1 H), 4.11 (s, 2 H), 3.95 (d, *J* = 6.6 Hz, 2 H), 3.81 (s, 3 H), 2.76 – 2.74 (m, 1 H), 2.43 (s, 3 H), 2.09 (d, J=7.7Hz, 2 H), 1.85 – 1.74 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 143.5, 136.6, 134.3, 129.6, 129.3, 128.1, 128.0, 121.2, 114.2, 90.2, 73.6, 55.5, 48.9, 36.7, 31.2, 29.8, 24.9, 21.8, 19.3 ppm. HRMS (FAB) $[M + H]^+$calc. for [$C_{24}H_{27}NO_3S$]:, 409.1712 found: 410.1791

34: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2 H), 7.19 (t, *J* = 6.6 Hz, 4 H), 6.94 (d, *J* = 8.5 Hz, 2 H), 6.73 (dd, *J* = 8.5, 21.7 Hz, 4 H), 6.46 (d, *J* = 15.7 Hz, 1 H) 5.96 −5.87 (m, 1 H), 4.23 (s, 2 H), 3.93 (d, *J* = 6.7 Hz, 2 H), 3.72 (s, 6 H), 2.28 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 159.6, 143.5, 136.2, 134.4, 133.1, 129.6,

128.0, 127.9, 120.9, 114.1, 113.9, 85.7, 80.5, 55.4, 49.0, 36.9, 21.6 ppm.

35: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2 H), 7.53 (d, J = 6.8 Hz, 2 H), 7.25 – 7.37 (m, 5 H), 5.56 (s, 1 H), 5.32 (s, 1 H), 4.22 (s, 2 H), 3.93 (s, 2 H), 2.45 (s, 3 H), 0.89 – 0.95 (m, 1 H), 0.57 – 0.63 (m, 2 H), 0.25 – 0.30 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.39, 141.45, 137.84, 135.82, 129.36, 128.44, 128.12, 127.99, 126.43, 116.99, 89.73, 67.36, 49.93, 36.10, 21.55, 7.86, −0.82 ppm.

36: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2 H), 7.54 (dd, J = 5.4, 8.7 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.04 (t, J = 8.7 Hz, 2 H), 5.53 (s, 1 H), 5.31 (s, 1 H), 4.21 (s, 2 H), 3.92 (d, J = 1.5 Hz, 2 H), 2.46 (s, 3 H), 0.90 – 0.96 (m, 1 H), 0.58 – 0.65 (m, 2 H), 0.25 – 0.31 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.50, 140.37, 135.63, 129.38, 128.22, 128.11, 127.95, 117.04, 115.43, 115.14, 89.84, 67.11, 50.04, 36.03, 21.54, 7.86, −0.96 ppm.

37: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2 H), 7.48 – 7.46 (m, 2 H), 7.29 (d, J = 8.2 Hz, 2 H), 6.86 (d, J = 8.9 Hz, 2 H), 5.46 (s, 1 H), 5.20 (s, 1 H), 4.17 (s, 2 H), 3.89 (q, J = 2.1 Hz, 2 H), 3.80 (s, 3 H), 2.42 (s, 3 H), 1.48 (t, J = 2.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 143.1, 140.7, 135.7, 130.1, 129.1, 128.0, 127.5, 115.2, 113.7, 81.7, 71.3, 55.2, 50.1, 35.9, 21.4, 3.1 ppm.

38 : ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2 H), 7.61 (q, *J* = 8.6 Hz, 4 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 5.63 (s, 1 H), 5.43 (s, 1 H), 4.24 (s, 2 H), 3.91 (d, *J* = 2.2 Hz, 2 H), 2.44 (s, 3 H), 1.51 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 141.3, 140.7, 135.6, 129.2, 128.0, 126.7, 125.3(9), 125.3(3), 119.0,82.1, 71.0, 49.9 ,36.1, 21.4, 3.1 ppm.

39 :H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2 H), 6.85 (d, *J* = 8.6 Hz, 2 H), 6.57 (d, *J* = 15.9 Hz, 1 H), 6.15 (td, *J* = 6.3, 15.8 Hz, 1 H), 4.19 – 4.16 (m, 4 H), 3.81 (s, 3 H), 2.28 – 2.17 (m, 2 H), 1.16 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 132.7, 129.4, 127.7, 123.1, 113.9, 88.3, 75.2, 70.2, 57.5, 55.2, 13.8, 12.4 ppm. HRMS (EI) calc. for [$C_{15}H_{18}O_2$]: 230.1307, found: 230.1411

40 : ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 6.58 (d, *J* = 15.9 Hz, 1 H), 6.19 −6.10 (m, 1 H), 4.19 (d, *J* = 6.6 Hz, 4 H), 3.81 (s, 3 H), 2.22 (t, *J* = 6.9 Hz, 2 H), 1.58 – 1.51 (m, 2 H), 1.00 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 132.7, 129.4, 127.7, 123.2, 113.9, 86.9, 76.1, 57.5, 55.2, 22.0, 20.7, 13.5 ppm. HRMS (FAB) calc. for [$C_{16}H_{20}O_2$]: 244.1463, found: 244.1461

1a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.02 (dd, *J* = 5.4, 11.1 Hz, 1 H), 5.67 (d, *J* = 11.0 Hz, 1 H), 4.84 (s, 1 H), 4.73 (s, 1 H), 4.34 (d, *J* = 3.4 Hz, 2 H),

4.21 (d, *J* = 3.3 Hz, 2 H), 2.43 (s, 5 H), 2.31 (t, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 142.6, 136.8, 134.0, 132.1, 130.7, 129.9, 127.6, 121.9, 114.3, 58.8, 56.8, 34.0, 28.5, 21.6 ppm HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{19}NO_2S$: 301.1137, found: 301.1142.

4a :^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (s, 2 H), 6.06 (dd, *J* = 5.8, 10.8 Hz, 1 H), 5.70 (d, *J* = 11.1 Hz, 1 H), 4.85 (s, 1 H), 4.73 (s, 1 H), 4.35 (d, *J* = 3.4 Hz, 2 H), 4.19 (s, 2 H), 2.65 (s, 6 H), 2.49 – 2.46 (m, 2 H), 2.38–2.36 (m, 2 H), 2.32 (d, *J* = 8.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.7, 140.3, 136.8, 136.7, 132.6, 132.5, 132.1, 130.7, 122.1, 114.3, 57.7, 55.6, 34.1, 28.6, 23.1, 21.1 ppm. **HRMS** HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}NO_2S$: 330.1528, found: 330.1530.

5a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1 H), 7.99 (d, *J* = 8.0 Hz, 2 H), 7.93 – 7.84 (m, 2 H), 7.64 (s, 2 H), 6.04 – 5.99 (m, 1 H), 5.66 (d, *J* = 11.1 Hz, 1 H), 4.83 (s, 1 H), 4.74 (s, 1 H), 4.43 (s, 2 H), 4.29 (s, 2 H), 2.40 (d, *J* = 3.8 Hz, 2 H), 2.29 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 137.0, 135.1, 134.2, 132.2, 130.7, 129.6, 129.5, 128.9, 128.1, 127.7, 123.1, 121.9, 114.5, 59.0, 57.0, 34.1, 28.6 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{19}NO_2S$: 337.1136, found: 337.1139.

6a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 2 H), 7.27 (d, *J* = 7.3 Hz, 2 H), 5.97 – 5.94 (m, 1 H), 5.62 (d, *J* = 10.3 Hz, 1 H),

4.90 (s, 1 H), 4.81 (s, 1 H), 4.30 – 4.06 (m, 3 H), 2.40 – 2.32 (m, 7 H), 1.47 (d, J = 6.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 142.3, 138.0, 136.6, 135.5, 129.8, 129.5, 127.4, 121.8, 115.2, 64.9, 57.8, 34.3, 29.3, 22.3, 21.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}NO_2S$: 316.1371, found: 316.1367.

7a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 5.99 – 5.91 (m, 1 H), 5.64 – 5.59 (m, 1 H), 4.95 (s, 1 H), 4.86 (d, J = 15.3 Hz, 1 H), 4.31 – 4.05 (m, 3 H), 2.41 – 2.34 (m, 4 H), 2.20 – 2.14 (m, 1 H), 2.00 – 1.92 (m, 1 H) 1.85 – 1.76 (m, 1 H), 1.64 (s, 1 H), 1.26 (s, 1 H), 0.88 – 0.79 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 142.4, 136.4, 135.7, 130.6, 129.8, 127.4, 121.6, 115.2, 69.9, 58.9, 34.1, 29.7, 27.1, 21.7, 8.3 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}NO_2S$: 330.1528, found: 330.1532.

8a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 8.6 Hz, 2 H), 5.96 (d, J = 11.3 Hz, 1 H), 5.66 – 5.58 (m, 1 H), 5.16 (s, 1 H), 4.95 (s, 1 H), 4.10 (s, 2 H), 2.41 (s, 7 H), 1.74 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 142.3, 140.9, 138.4, 136.5, 129.6, 127.8, 127.5, 121.3, 115.4, 75.5, 56.8, 36.0, 32.0, 27.5, 21.6 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}NO_2S$: 330.1528, found: 330.1525.

9a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.32 (d, J

= 7.9 Hz, 2 H), 5.88 – 5.84 (m, 1 H), 5.41 (d, *J* = 12.1 Hz, 1 H), 5.01 (s, 1 H), 4.86 (s, 1 H), 3.59 (s, 2 H), 3.15 (t, *J* = 5.7 Hz, 2 H), 2.48 – 2.45 (m, 3 H), 2.42 (s, 4 H), 2.32 – 2.30 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 143.8, 134.4, 132.4, 129.8, 128.0, 127.9, 126.5, 125.8, 114.4, 50.0, 43.0, 35.3, 31.4, 29.3, 21.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}NO_2S$: 316.1371, found: 316.1369.

10a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (dd, *J* = 5.4, 11.1 Hz, 1 H), 5.80 (d, *J* = 11.1 Hz, 1 H), 4.88 (s, 1 H), 4.82 (s, 1 H), 3.75 (s, 6 H), 3.34 (s, 2 H), 3.24 (s, 2 H), 2.49 – 2.45 (m, 2 H), 2.37 – 2.33 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 144.7, 134.9, 134.6, 133.0, 124.8, 113.6, 56.6, 52.9, 46.2, 43.4, 34.3, 28.6 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{18}O_4$: 262.1205, found: 262.1201.

11b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 6.31 – 6.19 (m, 1 H), 6.09 (dd, *J* = 10.5, 15.0 Hz, 1 H), 5.34 (dd, *J* = 8.5, 14.9 Hz, 2 H), 5.17 (d, *J* = 16.7 Hz, 1 H), 5.06 (d, *J* = 9.7 Hz, 1 H), 4.01 (d, *J* = 14.6 Hz, 1 H), 3.82 (d, *J* = 6.2 Hz, 2 H), 3.73 (d, *J* = 14.5 Hz, 1 H), 3.63 – 3.58 (m, 1 H), 3.29 (s, 4 H), 2.78 (t, *J* = 9.2 Hz, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 141.5, 136.2, 134.4 ,132.6, 131.1, 129.9, 128.0, 120.6, 117.5, 69.7, 58.5, 53.0, 49.6, 46.9, 21.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}NO_3S$: 333.1399, found:

333.1397.

12b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 2 H), 7.32 – 7.26 (m, 7 H), 6.31 – 6.24 (m, 1 H), 6.12 – 6.03 (m, 1 H), 5.36 – 5.31 (m, 2 H), 5.16 (d, *J* = 16.8 Hz, 1 H), 5.06 (d, *J* = 9.8 Hz, 1 H), 4.45 (s, 2 H), 3.98 (d, *J* = 14.7 Hz, 1 H), 3.91 – 3.90 (m, 2 H), 3.69 (d, *J* = 14.4 Hz, 1 H), 3.60 (t, *J* = 8.3 Hz, 1 H), 3.30 – 3.28 (m, 1 H), 2.76 (t, *J* = 8.9 Hz 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 141.5, 138.0, 136.3, 134.4, 132.6, 131.1, 129.9, 128.6, 128.0, 120.7, 117.5, 72.9, 67.4, 53.0, 49.7, 47.0, 21.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{24}H_{27}NO_3S$: 410.1790, found: 410.1788.

13b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2 H), 7.37 – 7.26 (m, 5 H), 7.19 (d, *J* = 7.3 Hz, 2 H), 6.78 (s, 1 H), 6.04 (s, 1 H), 4.28 (s, 2 H), 4.03 (s, 2 H), 3.99 (d, *J* = 6.3 Hz, 2 H), 3.35 (s, 3 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 138.0, 136.2, 133.9, 133.0, 130.1, 130.0, 128.9, 127.9, 121.6, 117.1, 69.9, 58.6, 51.9, 49.9, 21.7ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}NO_3S$: 370.1477, found: 370.1474.

14b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 5.54 – 5.42 (m, 1 H), 5.35 (dd, *J* = 3.9, 6.3 Hz, 1 H), 5.14 (s, 1 H), 5.09 (d, *J* = 7.4 Hz, 1 H), 4.02 – 3.89 (m, 2 H), 3.82 (d, *J* = 6.5 Hz, 2 H), 3.75 – 3.70 (m, 1 H), 3.63 – 3.58 (m, 1 H),

3.28 (d, J = 3.6 Hz, 3 H), 2.79 (t, J = 9.2 Hz, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ144.0, 141.3, 135.7, 132.6, 129.9, 128.0, 120.5, 118.6, 69.7, 58.5, 52.8, 49.6, 48.0, 21.7 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}NO_3S$: 308.1320, found: 308.1317.

15c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.4 Hz, 2 H), 7.33 (d, J = 7.9 Hz, 2 H), 6.44 (s, 1 H), 6.19 (td, J = 10.2, 17.0 Hz, 1 H), 6.09 (dd, J = 11.3, 17.8 Hz, 1 H), 5.91 (dd, J = 10.3, 15.5 Hz, 1 H), 5.53 (d, J = 15.6 Hz, 1 H), 5.15 – 5.07 (m, 2 H), 5.03 (d, J = 10.1 Hz, 1 H), 4.93 (d, J = 11.3 Hz, 1 H), 3.37 (dd, J = 1.0, 10.3 Hz, 1 H), 3.30 (d, J = 10.3 Hz, 1 H), 2.44 (s, 3 H), 1.24 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 138.7, 136.6, 130.5, 130.2, 130.0, 128.6, 128.1, 128.1, 127.8, 117.2, 114.1, 62.1, 49.0, 23.4, 21.8 ppm. HRMS (FAB) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}NO_2S$: 316.1371, found: 316,1373.

16d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 7.9 Hz, 2 H), 7.34 (d, J = 7.9 Hz, 2 H), 6.38 (d, J = 8.1 Hz, 1 H), 5.52 (d, J = 8.1 Hz, 1 H), 3.94 (d, J = 11.8 Hz, 1 H), 3.54 (d, J = 10.1 Hz, 1 H), 3.38 (d, J = 16.1 Hz, 4 H), 3.02 (d, J = 11.7 Hz, 1 H), 2.47 (s, 3 H), 1.37 (s, 1 H), 0.54 – 0.52 (m, 1 H) 0.45 (t, J = 8.5 Hz, 3 H), −0.00 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 129.7, 129.6, 126.9, 120.7, 114.9, 74.4, 58.7, 40.0, 34.2, 29.3, 21.4, 8.5, 6.8, 4.7, 4.6 ppm. HRMS (FAB) Calcd for $[C_{18}H_{23}NO_3S]$: 333.1399, found: 333.1397

17b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 13.9 Hz, 2 H), 6.32 (ddd, *J* = 8.8, 13.5, 18.6 Hz, 1 H), 6.19 – 6.13 (m, 2 H), 5.44 (dd, *J* = 8.3, 15.1 Hz, 1 H), 5.21 (d, *J* = 16.9 Hz, 1 H), 5.10 (d, *J* = 10.2 Hz, 1 H), 4.32 (dd, *J* = 1.0, 14.6 Hz, 1 H), 4.00 (dd, *J* = 1.8, 15.0 Hz, 1 H), 3.64 – 3.61 (m, 1 H), 3.47 – 3.45 (m, 1 H), 2.85 (t, *J* = 8.7 Hz, 1 H), 2.42 (s, 3 H), 2.03 (d, *J* = 8.9 Hz, 2 H), 0.89 – 0.82 (m, 3 H) ppm ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 134.7, 129.6, 128.2, 127.8, 127.7, 127.3, 126.7, 118.6, 116.7, 54.9, 49.7, 47.8, 21.4, 20.0, 12.6 ppm. HRMS (EI) calc. for [$C_{18}H_{23}NO_2S$]: 317.1450, found: 317.1447

17c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 2 H), 7.19 (d, *J* = 7.6 Hz, 2 H), 6.20 (d, *J* = 8.0 Hz, 1 H), 5.20 (d, *J* = 8.1 Hz, 1 H), 3.74 (d, *J* = 11.9 Hz, 1 H), 2.87 (d, *J* = 11.7 Hz, 1 H), 2.32 (s, 3 H), 1.39 (dd, *J* = 7.2, 14.3 Hz, 1 H), 1.32 – 1.23 (m, 1 H), 0.94 (bs, 1 H), 0.83 (t, *J* = 7.2 Hz, 3 H), 0.29 – 0.22 (m, 3 H), −0.05 (bs, 1 H), −0.21 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 135.2, 129.9, 127.2, 120.6, 117.0, 40.7, 35.6, 30.2, 25.4, 23.4, 21.7, 12.0, 9.0, 5.0, 4.8 ppm.

18b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 7.7 Hz, 2 H) , 6.27 (td, *J* = 10.2, 16.8 Hz, 1 H), 6.09 (dd, *J* = 10.5, 15.0 Hz, 1 H), 5.39 – 5.30 (m, 1 H), 5.17 (d, *J* = 16.6 Hz, 1 H), 5.06 (d, *J* = 10.6 H z, 1 H), 4.97 (d, *J* = 2.1 Hz, 1 H), 4.86 (dd, *J* = 2.2, 4.5 Hz, 1 H), 4.0 1 (d, *J* = 14.5 Hz, 1 H), 3.72 (dd, *J* = 1.8, 14.2

Hz, 1 H), 3.63 (dd, *J* = 8.0, 9.3 Hz, 1 H), 3.31 – 3.21 (m, 1 H), 2.85 (t, *J* = 9.1 Hz, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 136.1, 133.9, 131.0, 129.7, 127.8, 127.4, 117.2, 114.9, 108.4, 53.3, 51.8, 46.6, 21.5 ppm. HRMS (EI) calc. for [$C_{16}H_{19}NO_2S$]: 289.1137, found: 289.1133

18d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.48 (dd, *J* = 5.5, 7.9 Hz, 1 H), 3.93 (d, *J* = 11.7 Hz, 1 H), 3.04 (dd, *J* = 2.8, 11.8 Hz, 1 H), 2.50 (s, 3 H), 1.39 – 1.32 (m, 1 H), 1.03 −0.97 (m, 1 H), 0.67 – 0.60 (m, 1 H), 0.55 – 0.51 (m, 1 H), 0.39 (d, *J* = 8.2 Hz, 2 H), −0.01 (d, *J* = 4.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 135.0, 129.9, 127.2, 120.9, 112.4, 40.6, 29.8, 24.3, 21.2, 13.4, 11.7, 3.6, 3.4 ppm.

19d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2 H), 7.38 (d, *J* = 7.9 Hz, 2 H), 6.33 (d, *J* = 8.1 Hz, 1 H), 5.32 (d, *J* = 8.1 Hz, 1 H), 3.91 (d, *J* = 11.8 Hz, 1 H), 3.07 (dd, *J* = 2.3, 11.8 Hz, 1 H), 2.51 (s, 3 H), 1.23 (s, 3 H), 1.11 – 1.0 (m, 1 H), 0.50 (bs, 2 H), 0.45 – 0.42 (m, 1 H), 0.25 – 0.24 (m, 1 H), 0.00 – −0.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 135.0, 129.8, 127.1, 119.6, 118.9, 40.4, 34.9, 30.8, 21.7, 18.1, 8.9, 4.7, 4.5 ppm.

20b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 5.45 (ddd, *J* = 8.3, 10.9 , 16.2 Hz, 1 H), 5.22 –

5.17 (m, 1 H), 5.07 (s, 1 H), 5.04 (dd, *J* = 0.9, 7.3 Hz, 1 H), 3.93 – 3.88 (m, 1 H), 3.66 (dd, *J* = 1.5, 14.1 Hz, 1 H), 3.57 (dd, *J* = 7.6, 9.3 Hz, 1 H), 3.21 – 3.16 (m, 1 H), 2.78 (t, *J* = 9.0 Hz, 1 H) , 2.42 (s, 3 H), 1.53 (ddd, *J* =2 .0, 3.7, 4.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 137.8, 136.3, 132.7, 129.6, 127.8, 118.4, 117.5, 53.1, 49.4, 47.5, 21.5, 14.4 ppm.

20d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 6.24 (d, *J* = 8.2 Hz, 1 H), 5.18 (d, *J* = 8.2 Hz, 1 H), 3.86 (d, *J* = 11.3 Hz, 1 H), 2.91 (dd, *J* = 2.7, 11.4 Hz, 1 H), 2.40 (s, 3 H), 1.03 (s, 3 H), 0.93 (d, *J* = 6.3 Hz, 6 H), 0.85 – 0.83 (m, 1 H), 0.63 – 0.57 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 135.0. 129.9, 127.2, 119.9, 118,3 40.6, 32.5, 26.3, 21.7, 17.3, 16.4, 13.1 ppm.

20f :^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2 H), 7.32 (d, *J* = 7.8 Hz, 2 H), 6.45 (dd, *J* = 10.9, 17.5 Hz, 1 H), 5.11 (d, *J* = 10.9 Hz, 1 H), 4.96 (d, *J* = 17.5 Hz, 1 H), 4.21 (s, 2 H), 4.09 (s, 2 H), 2.43 (s, 3 H), 2.17 (dd, *J* = 7.51, 15.1 Hz, 2 H), 0.96 (t, *J* = 7.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 137.3, 135.2, 134.1, 129.7, 128.6, 127.4, 115.2, 57.2, 54.8, 21.5, 19.4, 12.5 ppm. HRMS (EI) calc. for [$C_{15}H_{19}NO_2S$]:277.1137, found: 277.1134

21d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2 H) 7.31 – 7.96 (m, 5 H), 6.98 (d, *J* = 7.2 Hz, 2 H), 6.41 (d, *J* = 8.1 Hz, 1 H), 5.31 (d, *J* = 8.1 Hz, 1 H), 4.03 (d, *J* 11.6 Hz, 1 H), 3.14 (dd, *J* = 2.6,

11.6 Hz, 1 H), 2.40 (s, 3 H), 1.90 (d, *J* = 5.9 Hz, 1 H), 1.81 (s, 1 H), 0.85 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 137.4, 134.9, 130.0,128.8, 128.2, 127.2, 126.3, 120.8, 117.5, 40.5, 36.0, 29.5, 21.7, 20.5, 17.7 ppm.

22b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 5.70 (ddd, *J* = 7.1, 12.1, 17.2, 1H), 5.07 (dd, *J* = 9.8, 13.5Hz, 3 H), 4.10 (d, *J* = 14.6 Hz, 1 H), 3.80 (d, *J* = 13.8 Hz, 1 H), 3.49 (t, *J* = 6.5 Hz, 1 H), 3.50 – 3.38 (m, 1 H), 3.16 (dd, *J* = 6.7, 9.4 Hz, 1 H), 2.45 (s, 3 H), 1.49 – 1.43 (m, 1 H), 0.78 – 0.69 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 135.2, 132.2, 129.7, 127.9, 127.4, 115.8, 52.9, 50.1, 46.6, 21.5, 15.3, 5.8, 5.3 ppm. HRMS (FAB) calc. for [$C_{17}H_{21}NO_2S$]: 303.1293, found: 329.1452–

22d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2 H), 7.23 (d, *J* = 8.1 Hz, 2 H), 6.17 (d, *J* = 8.2 Hz, 1 H), 5.18 (d, *J* = 8.2 Hz, 1 H), 3.81 (d, *J* = 11.4 Hz, 1 H), 2.69 (dd, *J* = 2.3, 11.5 Hz, 1 H), 2.35 (s, 3 H), 0.95 (d, *J* = 6.3 Hz, 3 H), 0.84 (d, *J* = 4.9 Hz, 1 H), 0.78 – 0.77 (m, 1 H), 0.64 (dd, *J* = 6.0, 11.8 Hz, 1 H), 0.41– 0.26 (m, 2 H), 0.01 – 0.00 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 135.0, 129.8, 127.2, 1198, 116.9, 40.7, 30.1, 26.2, 22.3, 21.7, 13.0, 11.8, 3.8, 2.7 ppm.

23d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 6.21 (d, *J* = 8.2 Hz, 1 H), 5.27 (d, *J* = 8.2 Hz, 1 H), 3.82 (d, *J* = 11.9 Hz, 1 H), 2.83 (dd, *J* = 2.5, 12.0 Hz, 1 H), 2.41 (s,

3 H), 1.06 – 1.05 (m, 1 H), 1.02 – 0.95 (m, 1 H), 0.54 – 0.28 (m, 6 H), 0.14 – 0.07 (m, 2 H), −0.07 – −0.17 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 135.1, 129.8, 127.1, 119.7, 117.4, 40.5, 36.1, 29.3, 21.6, 12.5, 9.1, 5.1, 4.6, 3.7, 3.1 ppm. HRMS (FAB) calc. for [$C_{19}H_{23}NO_2S$]: 329.1441, found: 329.1452

24d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 7.5 Hz, 3 H), 6.85 (d, *J* = 7.1 Hz, 2 H), 6.21 (d, *J* = 8.2 Hz, 1 H), 5.09 (d, *J* = 8.2 Hz, 1 H), 3.85 (d, *J* = 11.6 Hz, 1 H), 2.83 (dd, *J* = 2.3, 11.7 Hz, 1 H), 2.22 (s, 3 H), 1.75 (d, *J* = 5.9 Hz, 1 H), 1.67 (bs, 1 H), 0.33 – 0.27 (m, 1 H), 0.14 (dd, *J* = 6.0, 13.4 Hz, 1 H) , −0.02 – −0.03 (m, 2 H), −0.06 – −0.10 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 137.6, 134.9, 130.0, 128.9, 1280, 127.2, 126.1, 120.9, 115.3, 40.6, 36.8, 29.4, 25.9, 21.7, 12.6, 4.2, 2.8 ppm.

25d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 6.26 (d, *J* = 8.1 Hz, 1 H), 5.43 – 5.39 (m, 2 H), 3.95 (d, *J* = 11.9 Hz, 1 H), 3.00 (dd, *J* = 2.1, 11.9 Hz, 1 H), 2.42 (s, 3 H), 2.20 – 2.15 (m, 1 H), 1.96 (s, 3 H), 1.54 – 1.52 (m, 6 H), 0.34 0.28 (m, 2 H), 0.25 – 0.21 (m, 1H) −0.12 – −0.13 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.7, 135.0, 129.9, 127.2, 124.4, 119.5, 116.2, 40.5, 36.7, 29.0, 27.5, 25.4, 23.1, 22.6, 21.6, 9.6, 5.0, 3.9 ppm.

26e: ^{1}H NMR (300 MHz, $CDCl_3$) δ7.60 (d, *J* = 8.1 Hz, 2 H), 7.24–7.33 (m, 5 H), 7.14 (d, *J* = 6.9 Hz, 2 H, 0.86–0.98 (m, 1 H), 1.18–1.26 (m, 2 H), 6.69 (d, *J* = 7.9 Hz, 1 H), 5.69 (d, *J* = 8.0 Hz, 1 H), 4.03 (dd, *J* = 10.9, 4.5 Hz, 1 H), 2.75 (br s, 1 H), 2.61 (dd, *J* = 11.8, 11.0 Hz, 1 H), 2.53–2.59 (m, 2 H), 2.42 (s, 3 H), 2.29 (dd, *J* = ~9.3, ~9.0 Hz, 1 H), 1.70–1.88 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 142.0, 135.9, 129.8, 128.6, 128.4, 127.7, 126.9, 126.6, 125.2, 124.6, 103.9, 57.6, 53.7, 49.5, 47.9, 33.6, 25.7, 25.5, 25.3, 21.5

27e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 7.9 Hz, 2 H), 7.06 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.5 Hz, 2 H), 6.69 (d, *J* = 7.9 Hz, 1 H), 5.68 (d, *J* = 8.0 Hz, 1 H), 4.02 (dd, *J* = 4.5, 10.8 Hz, 1 H), 3.82 (s, 3 H), 2.71 (d, *J* = 9.7 Hz, 1 H), 2.59 (t, *J* = 11.4 Hz, 1 H), 2.43 (s, 1 H) , 2.24 (t, 1H, J=9.2Hz) , 1.81 (m, 1H) , 1.21 (dd, J=8.6Hz, J=19.1Hz, 1H) , 0.89 (t, J=9.1Hz, 1H) ppm.^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 143.8, 136.1, 135.2, 134.1, 130.0, 128.8, 127.2, 125.4, 124.9, 114.0, 104.1, 57.1, 55.5, 53.9, 49.7, 48.2, 33.8, 25.9, 25.7, 25.5, 21.7 ppm.

28d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 6.90 (d, *J* = 8.6 Hz, 2 H), 6.78 (d, *J* = 8.6 Hz, 2 H), 6.39 (d, *J* = 8.1 Hz, 1 H), 5.30 (d, *J* = 8.1 Hz, 1 H), 4.02 (d, *J* = 11.5 Hz, 1 H), 3.78 (s, 3 H), 3.12 (dd, *J* = 2.6, 11.5 Hz, 1 H), 2.40 (s, 3 H), 1.85 (d, *J* = 5.8 Hz, 1 H), 1.71 (d, *J* = 5.2 Hz, 1 H), 0.84 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 143.9, 134.9, 130.0,

129.8, 129.5, 127.3, 120.7, 11736, 113.7, 55.4, 40.6, 35.3, 29.7, 21.7 20.2, 17.8 ppm.

29d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2 H), 7.29 (d, *J* = 7.7 Hz, 2 H), 6.90 (d, *J* = 8.1 Hz, 2 H), 6.76 (d, *J* = 7.9 Hz, 2 H), 6.46 (d, *J* = 8.1 Hz, 1 H), 5.36 (d, *J* = 8.1 Hz, 1 H), 4.03 (d, *J* = 11.6 Hz, 1 H), 3.77 (s, 3 H), 3.10 (d, *J* = 11.5 Hz, 1 H), 2.39 (s, 3 H), 1.84 (d, *J* = 5.5 Hz, 1 H), 1.76 (s, 1 H), 1.25 −1.18 (m, 1 H), 0.94 (m, 0.97 – 0.90, 1 H), 0.73 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm. HRMS (EI) calc. for [$C_{22}H_{25}NO_3S$]: 383.1555, found: 383.1552

30d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J=7.7Hz, 2 H) 7.28 (d, *J* = 7.9 Hz, 2 H), 6.89 (d, *J* = 8.1 Hz, 2 H), 6.77 (d, *J* = 7.9 Hz, 2 H), 6.44 (d, *J* = 8.0 Hz, 1 H), 5.34 (d, *J* = 8.1 Hz, 1 H), 4.04 (d, *J* = 11.6 Hz, 1 H), 3.76 (s, 3 H), 3.11 (d, *J* = 11.6 Hz, 1 H), 2.39 (s, 3H), 1.78 – 1.76 (m, 2 H), 1.22 (s, 4 H), 0. 71 – 0.67 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 143.9, 135.1, 130.0, 129.7, 129.5, 127.2, 121.4, 116.4, 113.6, 55.4, 40.7, 35.4, 40.7, 35.4, 33.7, 29.0, 25.0, 21.7, 20.6, 14.3 ppm. HRMS (EI) calc. for [$C_{23}H_{27}NO_3S$]: 397.1712, found: 397.1712

32d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 2 H), 7.34 (d, *J* = 7.8 Hz, 2 H), 7.00 (d, *J* = 8.1 Hz, 2 H), 6.81 (d, *J* = 7.8 Hz, 2 H), 6.41 (d, *J* = 8.2 Hz, 1 H), 5.30 (d, *J* = 8.2 Hz, 1 H), 4.07 (d, *J* = 11.5 Hz, 1 H), 3.81 (s, 3 H), 3.04 (dd, *J* = 1.8 Hz, 11.5 Hz, 1 H), 2.44 (s, 3 H), 1.93 (d, *J* = 5.8 Hz, 1 H), 1.81 (d, *J*=4.9 Hz, 1 H),

0.51 – 0.47 (m, 1 H), 0.37 −0.33 (m, 1 H), 0.23 – 0.19 (m, 2 H), 0.13 – 0.09 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 143.9, 135.0, 130.0, 129.9, 129.6, 127.2, 120.8, 115.3, 113.5, 55.4, 40.6, 36.1, 29.4, 25.5, 21.7, 12.7, 4.1, 2.8 ppm. HRMS (EI) calc. for [$C_{23}H_{25}NO_3S$]: 395.1555, found: 395.1558

33d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 6.92 (d, *J* = 8.3 Hz, 2 H), 6.75 (d, *J* = 8.4 Hz, 2 H), 6.50 (d, *J* = 8.2 Hz, 1 H), 5.62 (d, *J* = 8.2 Hz, 1 H), 4.03 (d, *J* = 11.3Hz, 1H), 3.78 (s, 3 H), 3.09 (dd, *J* = 2.1, 11.4 Hz, 1 H), 2.39 (s, 3 H), 1.90 – 1.78 (m, 5 H), 1.61 (d, *J* = 9.5 Hz, 2 H), 1.55 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 143.9, 135.0, 130.0(6), 130.0(1), 129.5, 127.2, 121.8, 113.5, 113.3, 55.4, 40.9, 37.7, 35.5, 28.6, 27.0, 25.7, 24.7, 21.7, 18.4 ppm. HRMS (FAB) $[M + H]^+$ calc. for [$C_{24}H_{27}NO_3S$] :409.1712, found: 410.1791

34d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2 H). 7.33 (d, *J* = 8.2 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 6.64 (d, *J* = 8.6 Hz, 2 H), 6.54 (d, *J* = 8.7 Hz, 2 H), 6.41 – 6.38 (m, 3 H),. 5.43 (d, *J* = 8.1 Hz, 1 H), 4.17 (d, *J* = 11.9 Hz, 1 H), 3.69 (s, 3 H), 3.66 (s, 3 H), 3.30 (dd, *J* = 2.4, 12.0 Hz, 1 H), 2.44 (s, 3 H), 2.32 (d, *J* = 5.8 Hz, 1 H), 1.94 (d, *J* = 6.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 157.6, 143.8, 134.7, 131.4, 130.7, 129.9, 129.0, 128.3, 127.0, 119.7, 118.0, 113.6, 113.0, 55.0(9), 55.0(6), 40.2, 37.1, 31.0(7), 31.0(0), 21.5 ppm. HRMS (EI) calc. for [$C_{27}H_{27}NO_4S$]: 461.1661, found:

461.1659

35d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J*= 8.2 Hz, 2 H), 7.51 – 7.46 (m, 7 H), 6.59 (d, *J* = 8.1 Hz, 1 H), 5.54 (d, *J* = 8.1 Hz, 1 H), 4.16 (d, *J* = 11.5 Hz, 1 H), 3.19 (d, *J* = 11.5 Hz, 1 H), 2.61 (s, 3 H), 1.19 (d, *J* = 4.8 Hz, 1 H), 1.14 (d, *J* = 4.6 Hz, 1 H), 0.72 – 0.65 (m, 1 H), 0.59 −0.54 (m, 1 H), 0.34 – 0.28 (m, 1 H), 0.12 – 0.06 (m, 1 H), 0.04 – −0.03 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 139.3, 135.0, 130.0(8), 130.0(6), 128.5, 127.2, 121.4, 115.8, 48.2, 40.2, 24.3, 21.7, 20.6, 14.0, 3.0 ppm.

36d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.23 – 7.19 (m, 2). 6.95 (t, *J* = 8.6Hz, 2 H), 6.38 (d, *J* = 8.1 Hz, 1 H), 5.32 (d, *J* = 8.1 Hz, 1 H), 3.92 (d, *J* = 11.6 Hz, 1 H), 2.94 (d, *J* = 11.6 Hz, 1 H), 2.41 (s, 3 H), 0.96 (d, *J* = 4.9 Hz, 1 H), 0.88 – 0.86 (m, 1 H), 0.49 – 0.44 (m, 1 H), 0.40 – 0.33 (m, 1 H), 0.14 – 0.08 (m, 1 H), −0.05 – −0.13 (m, 1 H), −0.20 – −0.26 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 134.8, 131.4, 131.3, 129.8, 127.0, 121.2, 115.5, 115.3, 115.1, 48.0, 39.2, 24.1, 21.5, 20.5, 13.7, 2.8(6), 2.8(5) ppm.

37c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.5 Hz, 2 H), 6.83 (d, *J* = 8.5 Hz, 2 H), 6.35 (d, *J* = 8.0 Hz, 1 H), 5.34 (d, *J* = 8.0 Hz, 1 H), 3.94 (d, *J* = 11.4 Hz, 1 H), 3.78 (s, 3 H), 2.92 (d, *J* = 11.4 Hz, 1 H), 2.43 (s, 3 H), 1.18 (d, *J* = 4.5 Hz, 1 H), 0.91 (d, *J* = 4.4 Hz, 1 H), 0.85 (s, 3

H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 143.9, 135.0, 131.1, 131.0, 129.9, 127.2, 120.8, 118.3, 114.0, 55.4, 48.3, 39.1, 24.4, 21.7, 20.9, 18.9 ppm.

38c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.23 – 7.19 (m, 2 H), 6.95 (ddd, *J* = 2.5, 5.9, 10.7 Hz, 2 H), 6.37 (dd, *J* = 0.9, 8.1 Hz, 1 H), 5.32 (d, *J* = 8.1 Hz, 1 H), 3.92 (dd, *J* = 1.0, 11.6 Hz, 1 H), 2.93 (d, *J* = 11.6 Hz, 1 H), 2.41 (s, 3 H), 0.96 (d, *J* = 4.9 Hz, 1 H), 0.88 (d, *J* = 4.9 Hz, 1 H), 0.51 – 0.44 (m, 1 H), 0.40 – 0.33 (m, 1H) 0.11 (td, *J* = 5.6, 9.4Hz, 1 H), −0.07 – −0.12 (m, 1 H), −0.25 – 0.26 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 134.8, 131.4, 131.3, 129.8, 127.0, 121.2, 115.5, 115.3, 115.1, 48.0, 39.2, 24.1, 21.5, 20.5, 13.7 ppm

39d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.5 Hz, 2 H), 6.74 (d, *J* = 8.4 Hz, 2 H), 6.19 (d, *J* = 6.0 Hz, 1 H), 5.11 (d, *J* = 6.0 Hz, 1 H), 4.17 (d, *J* = 10.3 Hz, 1 H), 3.78 (d, *J* = 10.3 Hz, 1 H) 3.71 (s, 3 H), 2.34 (d, *J* = 5.7 Hz, 1 H), 1.63 (d, *J* = 5.3 Hz, 1 H), 1.23 – 1.16 (m, 1 H), 0.94 – 0.85 (m, 1 H), 0.75 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 142.0, 130.3, 129.9, 113.6, 109.8, 62.1, 55.4, 35.3, 27.9, 24.7, 11.4 ppm. HRMS (FAB) calc. for [$C_{15}H_{16}O_2$]: 230.1307, found: 230.1301

40d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.4 Hz, 2 H), 6.82 (d, *J* = 8.4 Hz, 2 H), 6.24 (d, *J* = 5.9 Hz, 1 H), 5.17 (d, *J* = 5.9 Hz, 1 H),

4.25 (d, J = 10.3 Hz, 1 H), 3.87 (d, J = 10.3 Hz, 1 H), 3.79 (s, 3 H), 2.38 (d, J = 5.6 Hz, 1 H), 1.72 (d, J = 4.9 Hz, 1 H), 1.37 – 1.26 (m, 4 H), 0.78 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 141.7, 130.3, 129.9, 113.6, 110.3, 62.0, 55.4, 35.0, 33.9, 28.4, 20.6, 14.3 ppm. HRMS (FAB) calc. for [$C_{16}H_{20}O_2$]: 244.1463, found:244. 1458

X-ray analysis

Single crystal diffraction data were measured by a Bruker-Nonius CCD single-crystal X-ray diffractometer at room temperature by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO. The structure was

solved by direct methods using SHELXS-97, and refined by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were treated as idealized contributions.

Crystal data for **17d**: $C_{18}H_{23}NO_2S$ (293K). M = 503.63, triclinic, space group P1, a = 10.4402 (9) Å, b = 12.7247(11) Å, c = 13.2229(9) Å, β = 84.852(5)°, V = 1711.9(2) Å^3, Z = 4, $\rho_{calc.}$ = 1.232 g/cm^{-3}, absorption coefficient = 0.196 mm^{-1}, total reflections collected 7763, unique 3134 (R_{int} = 0.0000), GOF = 1.101, R_1 = 0.0994, R_w = 0.3239 (I>2σ(I)).

Crystal data for **34d**: $C_{27}H_{27}NO_4S$ (293K). M = 503.63, monoclinic, space group P21/c, a = 14.3764(5) Å, b = 6.4364(3) Å, c = 25.7893(11) Å, β = 91.356(2)°, V = 2385.67 (17) Å^3, Z = 4, $\rho_{calc.}$ = 1.285 g/cm^{-3}, absorption coefficient = 0.169 mm^{-1}, total reflections collected 5285, unique 2962 (R_{int} = 0.0348), GOF = 1.017, R_1 = 0.0501, R_w = 0.1170 (I>2σ(I)).

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국문초록

팔라듐을 촉매로 한 1,6-인아인 물질에 대한 고리이성질화 반응은 꾸준히 연구되어 오고 있다. 그 물질들은 다양한 고리화물질들로 쉽게 합성될 수 있다. 우리는 바이닐 사이클로 프로필기가 치환된 1,6인아인 물질의 이탈기에 따른 고리화반응을 연구하였다. 포스페이트 이탈기가 치환된 인아인은 5.7-바이사이클릭트라이엔, 알콕시 이탈기가 치환된 인아인은 모노사이클릭 트라이엔 반응이 진행되었다. 그리고 1,6-인아인이 팔라듐 존재하에 좋은 수득률로 바이사이클로[4.1.0]헵테인으로 고리이성질화되는 것을 연구하였다

주요어 : 팔라듐, 촉매, 바이사이클로[4.1.0]헵텐, 싸이클로프로판, 바이닐사이클로프로페, 고리이성질화

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