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이학석사 학위논문

Rearrangement Reaction of  
Bicyclo[4.1.0]heptenes:  
Using Rh-catalyzed and  
Thermal rearrangement reactions

바이싸이클로[4.1.0]헵틴의 재배열반응:  
로듐 촉매와 열적 재배열 반응을 이용

2012 년 8 월

서울대학교 대학원

화학부 무기화학전공

손 소 리

Rearrangement Reaction of  
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이 논문을 이학석사 학위논문으로 제출함  
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## Abstract

A PtCl<sub>2</sub>-catalyzed cycloisomerization, thermal rearrangement, and rhodium(I)-catalyzed rearrangement reactions of 1,6-enynes led to the construction of various molecular structures. In these reactions, 1-aryl-tetrahydro-1H-indenes, 3-methylene-4-vinylcyclohex-1-enes, and aryl-hexahydroisoquinolines are generated from 1,6-enynes: Depending upon the substituent(s) and tether group of the enynes, the PtCl<sub>2</sub>-catalyzed cycloisomerization products, bicyclo[4.1.0]hept-2-enes, undergo vinylcyclopropanes-cyclopentene rearrangement, 1,5-hydrogen shift, and newly cyclization.

**Keywords:** Platinum dichloride, Rhodium, Bicyclo[4.1.0]heptenes, cyclopropane, rearrangement

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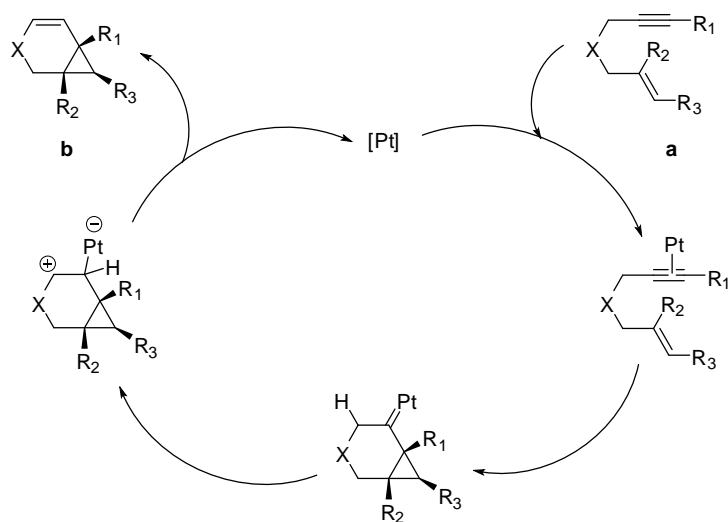
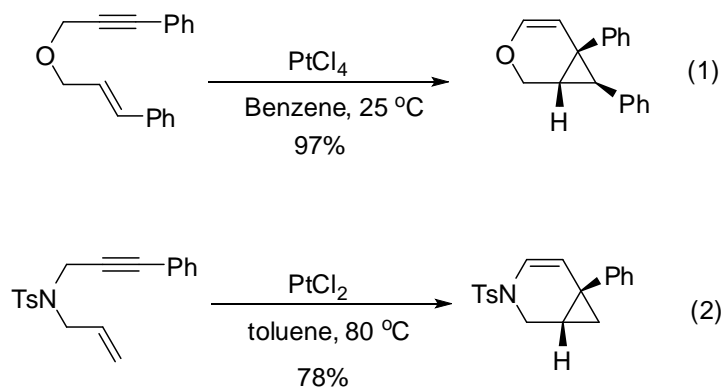
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## Introduction

Bicyclo[4.1.0]hept-2-ene derivatives are a class of the products which can be readily obtained by transition metal-catalyzed cycloisomerization.<sup>[1]</sup> They have synthetic potential originated from their unique structure. They are very stable even at high temperature but they have a strained cyclopropane ring connected to cyclohexene which can be easily broken to give rise to another sequential rearrangement if it has a substituent(s) activating the rupture of cyclopropane ring. Moreover, the geometry of the products can be controlled by restricted frame of bicyclo[4.1.0]heptenes. Despite of their synthetic potential, their use in the organic synthesis of more complex compounds is still quite rare. The scarcity of their use in organic synthesis stimulated us to explore the possible utilization of bicyclo[4.1.0] heptenes in organic synthesis.<sup>[2]</sup>

Among various transition metals catalyzing the transformation of bicyclization of 1,6-enynes, we chose platinum dichloride as catalyst because it is very stable in air and moisture, and there is no need to generate catalyst or to synthesize ligands. The first example of formation of bicyclo[4.1.0]heptenes by platinum-catalyzed cycloisomerization of 1,6-enyne was reported in 1995 by Blum and coworkers [Eq.(1)].<sup>[3]</sup> They reported PtCl<sub>4</sub>-catalyzed cycloisomerization of allyl propargyl ether into 3-oxabicyclo[4.1.0]heptenes, but mechanistic rationale was not provided at that time. In 2000, Fürstner<sup>[4]</sup> found that PtCl<sub>2</sub> is an

effective catalyst for transformation of nitrogen tethered 1,6-enynes to the corresponding 3-azabicyclo[4.1.0]heptenes [Eq. (2)]. Using computational methods, Soriano et al<sup>[5]</sup> proposed the mechanism of this transformation later (Scheme 1).

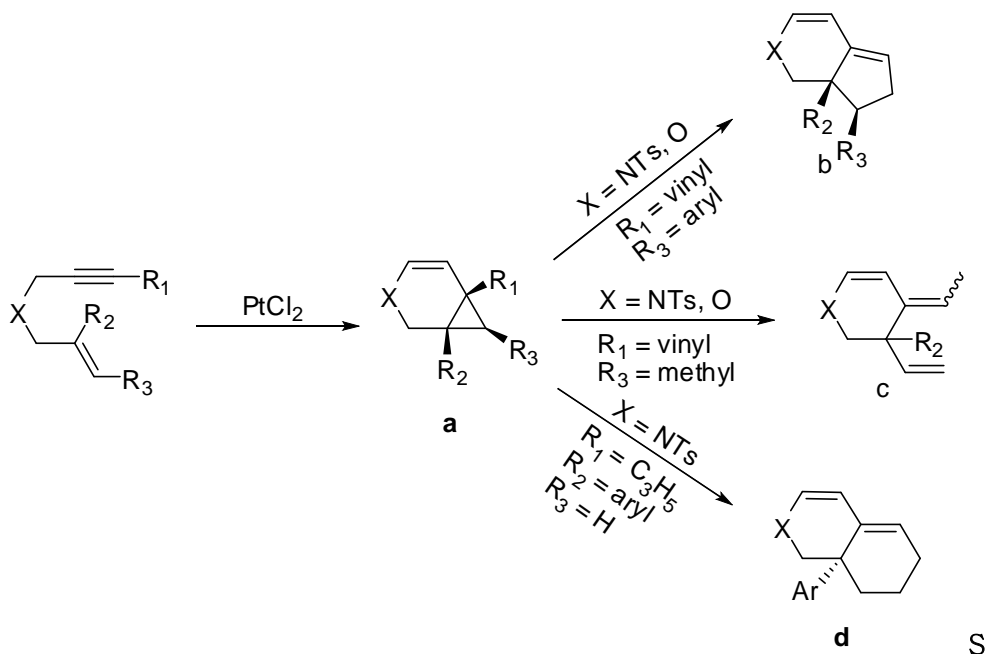


**Scheme 1. Proposed mechanism for the Pt catalyzed formation of bicyclo[4.1.0]heptene**

Based on the previous studies, we envisioned that  $\text{PtCl}_2$  catalyzed cycloisomerization of modified enynes would lead to



bicyclo[4.1.0]heptenes and subsequently rearranged products depending upon the substituents (Scheme 2). Tandem reactions have advantages of that unexpected complex molecular structures can be generated by combining common reactions. This approach might improve a scope of reactions or provide methods for structural frames which are not possible through a catalytic reaction.



**Scheme 2.** Platinum catalyzed cycloisomerization, thermal rearrangement and  $\text{Rh}^{\text{I}}$  catalyzed rearrangement of 1,6-enynes.

First, we found that bicyclo[4.1.0]hept-2-ene derivatives can selectively undergo a [1,5]hydrogen shift, or a vinylcyclopropane rearrangement depending upon the substituent(s) and tether group in the enynes substrates. As these reactions take place with high stereochemical fidelity, a wide variety of cyclic and acyclic products

containing several stereocenters could be obtained.

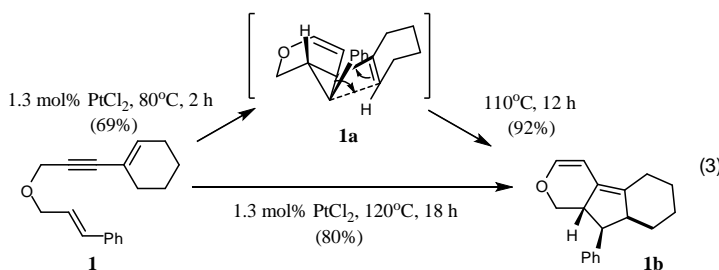
The syntheses of 1-aryl-tetrahydro-1H-indenes and 3-methylene-4-vinylcyclohex-1-enes were achieved through this strategy.

These observations urged us to study a transformation of bicyclo[4.1.0]heptenes bearing cyclopropyl and aryl groups in 1- and 6-positions, respectively, which usually had no reactivity toward transition metal catalyst.<sup>[6f]</sup> However, we recently found that they were activated in the presence of cationic rhodium compounds to give a new cyclization product, aryl-hexahydroisoquinoline.

## Result and Discussion

### 1. Thermal rearrangement reaction of Bicyclo[4.1.0]heptenes.

We initially studied a  $\text{PtCl}_2$ -catalyzed reaction of oxygen-tethered enynes bearing an aryl group at the terminal position of the alkene. A  $(E)$ -(3-(3-cyclohexenylprop-2-ynoxy)prop-1-enyl)benzene **1** was treated with 1.3 mol%  $\text{PtCl}_2$  in toluene at  $80^\circ\text{C}$  for 2 h, a cyclopropanated **1a** instead of a dienal<sup>[7]</sup> was isolated in 69% yield. Heating the isolated **1a** in toluene at  $110^\circ\text{C}$  for 12 h without catalyst result in 9-phenyloctahydroindeno[2,1-*c*]pyran **1b** in 92% yield [Eq. (3)]

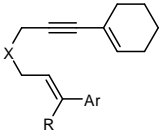
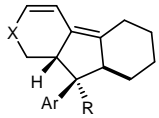
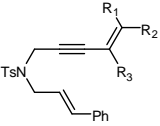
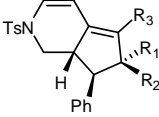


The second thermal rearrangement is probably conceived of as a vinylcyclopropanes-cyclopentene rearrangement. It has been reported<sup>[8a-8b]</sup> that aryl substituents at alkene moiety influence largely on the thermal rearrangement of vinylcyclopropanes.

We investigated a consecutive reaction of  $\text{PtCl}_2$ -catalysed cycloisomerization and thermal reaction in a one-pot reaction. When the same reaction was carried out at  $120^\circ\text{C}$ , the total yield was improved to 80%. We further screened the consecutive reactions of  $\text{PtCl}_2$ -catalyzed cycloisomerization and vinyl-cyclopropane

rearrangement with a variety of dienyne having a phenyl group at the terminal carbon of an alkene moiety. The results are compiled in Table 1.

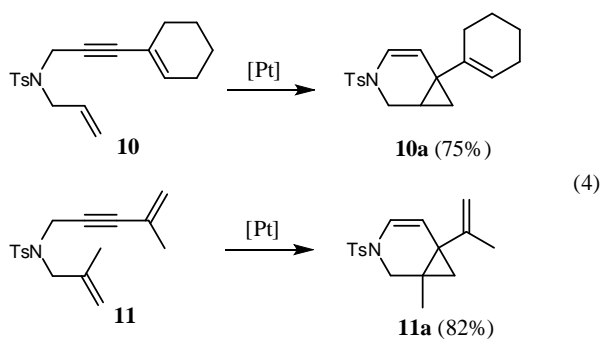
**Table 1.** A consecutive reaction of PtCl<sub>2</sub>-catalyzed cycloisomerization and vinylcyclopropane rearrangement<sup>[a]</sup>

Entry	Substrate	Time (h)	Product <sup>[b]</sup> (Yield)
			
	X      Ar      R		
1	<b>1</b> O      Ph      H	18	<b>1b</b> (80)
2	<b>2</b> NTs      Ph      H	24	<b>2b</b> (80)
3	<b>3</b> O      Ph      Me	24	<b>3b</b> (34)
4	<b>4</b> NTs <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> H	24	<b>4b</b> (68)
5	<b>5</b> NTs <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> H	24	<b>5b</b> (74)
			
	R <sub>1</sub> R <sub>2</sub> R <sub>3</sub>		
6	<b>6</b> H      H      Me	22	<b>6b</b> (59) <sup>[c]</sup>
7	<b>7</b> H      Me      Me	24	<b>7b</b> (36) <sup>[d]</sup>
8	<b>8</b> Ph      Ph      H	18	<b>8b</b> (57)
9	<b>9</b> H      Ph      H	3	<b>9b</b> (48) <sup>[e]</sup>

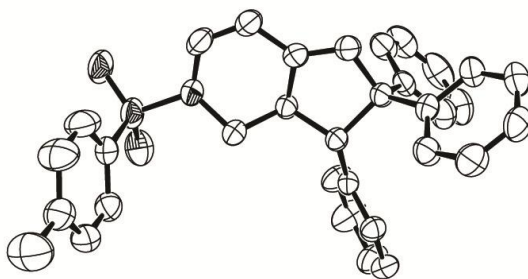
<sup>[a]</sup> Reaction conditions: 0.3 mmol of substrate and 5 mol% PtCl<sub>2</sub> were reacted in 6 mL toluene at 120°C. <sup>[b]</sup> Isolated yield. <sup>[c]</sup> Isolated as a mixture with **6** in 10% yield. <sup>[d]</sup> Isolated as a mixture with **7** in 36% yield. <sup>[e]</sup> Isolated as a mixture with **9** in 19% yield.

As the table shows, the reactants gave the expected products in reasonable to high yield (36%–80%). The best yield was obtained when a nitrogen or an oxygen tethered enyne having a cyclohexene moiety was used as a substrate (entries 1 and 2, 80%). However methyl substitution to vinyl group of enynes rather reduced the yields (entries 6 and 7). It is noted that substitution at the inner

position of vinyl group prevents the cyclopentene formation.<sup>[9b]</sup> When two phenyl groups were introduced to the terminal of vinyl (entry 8), the reaction time was shortened to 15 h. When only one phenyl group was added to the end of the vinyl, the reaction time was significantly shortened but there was no improvement in the yield of **b** (48%). It seems that this rearrangement is insensitive to the electronic effect of the aryl group (entries 8 and 9). An enyne bearing *p*-MeOC<sub>6</sub>H<sub>4</sub> and tolyl group instead of a phenyl gave a reasonable yields (68% and 74%) at 120°C. The structure of **8b** was confirmed by X-ray diffraction analysis (Figure 1).<sup>[10]</sup>



However, dienynes bearing no phenyl group at the terminal carbon of an alkene group gave only cyclopropanated products in high yields (**10** and **11**: [Eq. (4)]). Interestingly, phenyl group placed at the C-3 position of vinylcyclopropanes rather than C-2 could not activate the thermal rearrangement. Thus the 2-aryl substituent on the vinylcyclopropanes group may exert an effect on such a rearrangement.

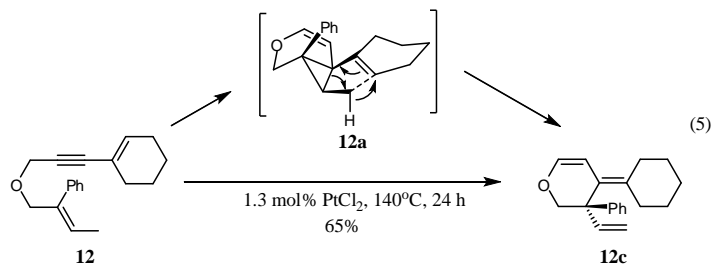


**Figure 2.** X-ray crystal structure of **8b**.

<b>8b</b>	
Empirical formula	C <sub>33</sub> H <sub>29</sub> NO <sub>2</sub> S
Formula weight	503.63
Crystal system	Monoclinic
Space group	P 21
a ( Å )	10.0826 (10)
b ( Å )	14.1675 (8)
c ( Å )	10.2547 (11)
$\alpha$	90
$\beta$	14.729 (3)
$\gamma$	90
Volume ( Å <sup>3</sup> )	1330.5 (2)
Z, d (calcd), Mg/cm <sup>3</sup>	2, 1.257
no. tot. collection	4840
no. unique data	4132
final R indices [ I>sigma (I) ]	R1 = 0.0392, wR2 = 0.0891
R indices (all data)	R1 = 0.0500, wR2 = 0.0943

We next investigated a PtCl<sub>2</sub>-catalyzed reaction of O-tethered dienynes bearing a methyl group at the olefinic terminal carbon. We expected that this type of the substrate would be transformed to the 2,4-dienal,<sup>[7]</sup> but when substrate **12** was reacted with 1.3 mol% of

PtCl<sub>2</sub> in xylene at 140°C for 24 h, a methylene-4-vinylcyclohex-ene derivative, **12c**, was isolated in 65% yield [Eq. (5)].



Thus, a subtle change in the substitution leads to a quite different reaction product. The product was derived from cycloisomerization followed by [1,5] hydrogen shift (retro-ene reaction).<sup>[11]</sup> For cis-disubstituted vinylcyclopropanes, because the formation of retro-ene product is kinetically favored over the ring expansion product<sup>[12]</sup>, we observed only the former in this reaction. The scope of the reaction was further studied with a variety of dienyne having a methyl group at the olefin terminal carbon (Table 2). The reaction temperature was highly dependent upon the substrate. In the case of **18**, a reaction temperature of 80°C was chosen. In some cases, a reaction temperature of 140°C was required, in order to enhance the thermal reaction. When significant decomposition of the products was observed at 140°C, 100°C was chosen as the reaction temperature. The yield found to be highly dependant upon the substituent at the alkene's inner carbon and on the concentration of the catalyst. When a substrate **13** in entry 2 was reacted in the presence of 1.3 mol% PtCl<sub>2</sub>, no reaction was observed, but 57% of

the expected product **13c** was isolated with a 33% recovery of **13**. In the presence of 5.0 mol% of PtCl<sub>2</sub> all of the reactants were decomposed, that is, no isolable compound was observed. Interestingly, for oxygen-tethered substrates (**12** and **22**), a higher yield was observed when 1.3 mol% PtCl<sub>2</sub> was used instead of 5.0 mol% PtCl<sub>2</sub> (entries 1 and 11). Higher yields (> 80%) were observed with enynes having an aryl group at the alkene's inner position (entries 6 and 7). This observation is consistent with the acceleration of 1,5-homodienyl hydrogen migrations due to electron-withdrawing aryl substituents.<sup>[13]</sup> Dienenynes substrates (entries 2, 5 and 8) without in substituent an the alkene's inner position gave the expected product in reasonable yields (57–65%).

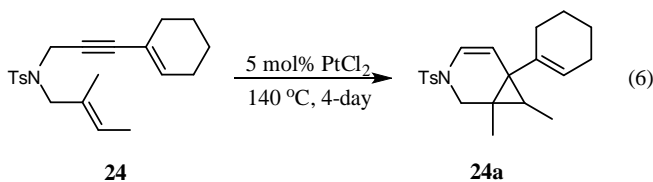


**Table 2.** A consecutive reaction of PtCl<sub>2</sub>-catalyzed cycloisomerization and [1,5]-hydrogen shift<sup>[a]</sup>

Entry	Substrate	Time (h)	Temp (°C)	Product <sup>[b]</sup> (Yield)	
	X      R <sub>1</sub> R <sub>2</sub>				
1	<b>12</b> <sup>[c]</sup> O      Ph      H	24	140	<b>12c</b> (65)	
2	<b>13</b> O      H      Me	48	140	<b>13c</b> (57) <sup>[e]</sup>	
3	<b>14</b> NTs      Ph      H	24	140	<b>14c</b> (78)	
4	<b>15</b> NTs <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> H	24	140	<b>15c</b> (69)	
5	<b>16</b> NTs      H      H	48	100	<b>16c</b> (63)	
	X      R <sub>1</sub> R <sub>2</sub> R <sub>3</sub>				
6	<b>17</b> NTs      H      H      Ph	24	140	<b>17c</b> (83)	
7	<b>18</b> <sup>[d]</sup> NTs      H      Me      Ph	48	80	<b>18c</b> (87)	
8	<b>19</b> NTs      H      Me      H	8	140	<b>19c</b> (65) <sup>[f]</sup>	
9	<b>20</b> NTs      Me      Me      Ph	24	100	<b>20c</b> (48)	
10	<b>21</b> O      H      Ph      Ph	24	140	<b>21c</b> (41)	
11	<b>22</b> <sup>[c]</sup> O      Ph      H      Ph	8	140	<b>22c</b> (58)	
12		<b>23</b> <sup>[d]</sup>	20	140	<b>23c</b> (41) <sup>[g]</sup>

<sup>[a]</sup> Reaction conditions: 0.3mmol of substrate and 5 mol% PtCl<sub>2</sub> were reacted in 6 mL xylene at presented temperature. <sup>[b]</sup> Isolated yield. <sup>[c]</sup> 1.3 mol% PtCl<sub>2</sub> was used. <sup>[d]</sup> 10 mol% PtCl<sub>2</sub> was used. <sup>[e]</sup> 33% of **13** was recovered. <sup>[f]</sup> Isolated as a mixture with **19a** in 9% yield. <sup>[g]</sup> 9% of **23** was recovered.

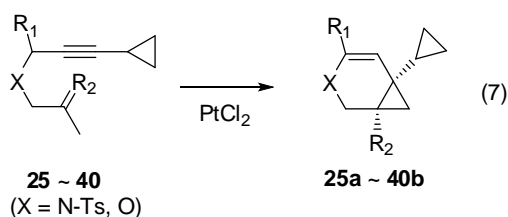
However, when a substrate bearing a methyl group at the alkene's inner position (**24** in [Eq. (6)]) was reacted at 140°C over a 4-day of a reaction period, compound **24a** was isolated in 78% with a trace amount of **24c**.



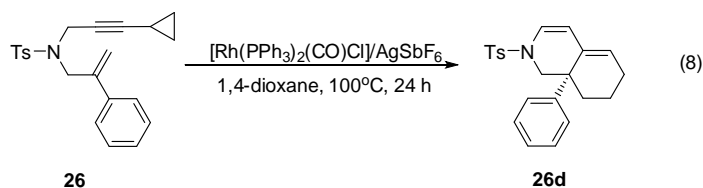
Thus it seems that the electronic effect of the substituent at the alkene's inner position has a profound effect on the yield of the reaction. When a dienyne **23** having an ethyl group instead of the methyl at the olefinic terminal carbon was used as a substrate (entry 12), the expected reaction occurred, but the yield decreased to 41 %. Oxygen-tethered dienynes with a methyl group at the olefinic terminal carbon (entries 1, 2, 10 and 11) gave the expected products at slightly lower yields (41–65%) than those of N-Ts-tethered dienynes. It has been well documented<sup>[14a]</sup> that a [1,5] hydrogen shift pathway competes with a vinylcyclopropanes rearrangement when the 2-cis substituted groups at vinylcyclopropanes contain at least one hydrogen atom at the  $\alpha$ -position. However, our study shows that the 1,5-hydrogen shift is unique to dienyne substrates having a methyl group at the terminal carbon of the alkene moiety and is much preferred when dienynes have an aryl group at the inner position of an alkene.

## 2. Rhodium–Catalyzed rearrangement of Bicyclo[4.1.0]heptenes.

Bicyclo[4.1.0]heptenes derivatives were easily obtained from cyclopropyl-enynes by transition metal-catalyzed cycloisomerization reactions.<sup>[6g, 15]</sup> 1-Cyclopropylbicyclo[4.1.0]hept-2-ene derivatives (**25a** – **40a**) used in this study were easily obtained by PtCl<sub>2</sub>-catalyzed cycloisomerization of the corresponding enynes (**25** – **40**) ([Eq. (7) and Table 3].

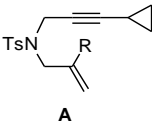
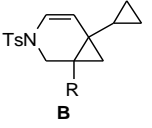
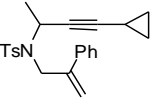
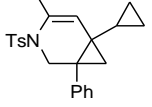
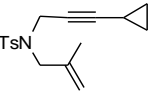
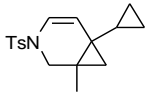
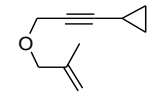
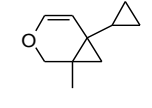


In hope of finding a new transformation of bis-cyclopropane compounds into other compounds, we treated **25** (X = NTs, R<sub>1</sub> = H, R<sub>2</sub> = Me) with a cationic rhodium catalyst Rh(PPh<sub>3</sub>)(CO)Cl/AgSbF<sub>6</sub>. However, intractable compounds were obtained. When **26** (X = NTs, R<sub>1</sub> = H, R<sub>2</sub> = Ph) was reacted with Rh(PPh<sub>3</sub>)(CO)Cl/AgSbF<sub>6</sub> in 1,4-dioxane at 100°C for 24 h, we could confirm the formation of a new cyclic compound **26d** in 20% yield [Eq. (8)].



Encouraged by this observation, we screened reaction conditions including a rhodium species, a counteranion, a reaction solvent, a reaction time, and a reaction temperature (Table 4).

**Table 3.** Platinum-Catalyzed Rearrangement Reaction<sup>[a]</sup>

Entry		Substrate	t (h)	Product (%) <sup>[b]</sup>
				
		<b>A</b>		<b>B</b>
		R		
1	<b>26</b>	C <sub>6</sub> H <sub>5</sub>	7	83
2	<b>27</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4	85
3	<b>28</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4	84
4	<b>29</b>	4-ClC <sub>6</sub> H <sub>4</sub>	4	79
5	<b>30</b>	4-FC <sub>6</sub> H <sub>4</sub>	4	80
6	<b>31</b>	4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	4	80
7	<b>32</b>	tert-butylbenzene	5	59
8	<b>33</b>	3-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4	77
9	<b>34</b>	3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	3	80
10	<b>35</b>	3-ClC <sub>6</sub> H <sub>4</sub>	4	71
11	<b>36</b>	m-xylene	4	60
12	<b>37</b>	naphthyl	4	79>
13	<b>38</b>	mesitylene	5	62
14	<b>39</b>		19	
15	<b>25</b>		4	
16	<b>40</b>		4	

[a] Reaction conditions: substrate and 5 mol% PtCl<sub>2</sub> were reacted in toluene at 80 °C. [b] Isolated yield.

**Table 4.** Variety of Rhodium-Catalyzed Rearrangement Reaction of **a**

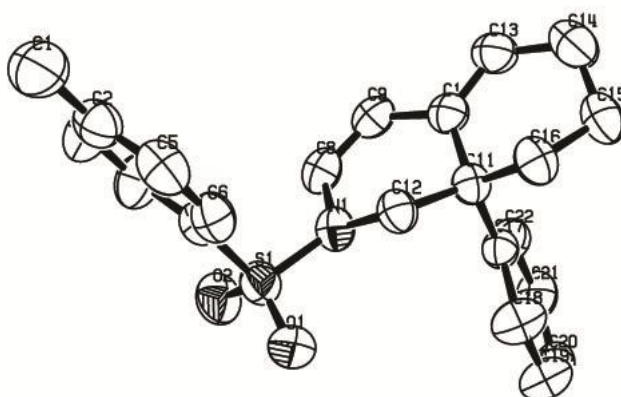
Entry	Catalysts (mol%)	Solvent	Time (h)	Temp (°C)	Product (%) <sup>[a]</sup>
1	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgSbF <sub>6</sub> (12)	1,4-dioxane	4	100	36
2	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgSbF <sub>6</sub> (12)	1,2-DCE	4	80	68
3	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (5) / AgSbF <sub>6</sub> (9)	1,4-dioxane	24	100	trace
4	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (20) / AgSbF <sub>6</sub> (24)	1,4-dioxane	1	100	54
5 <sup>[b]</sup>	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgSbF <sub>6</sub> (12)	1,2-DCE	4	80	24
6	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgNO <sub>3</sub> (12)	1,2-DCE	24	80	no reaction
7	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgPF <sub>6</sub> (12)	1,2-DCE	24	80	no reaction
8 <sup>[c]</sup>	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgClO <sub>4</sub> (12)	1,2-DCE	1	80	14
9 <sup>[d]</sup>	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgOTf (12)	1,2-DCE	1	80	10
10	Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> Cl (10) / AgBF <sub>4</sub> (12)	1,2-DCE	4	80	74
11	RhCl(CO)(dppe) (10) / AgSbF <sub>6</sub> (12)	1,4-dioxane	24	100	no reaction
12	[RhCl(COD)] <sub>2</sub> (10)	Toluene	17	100	trace
13	[RhCl(COD)] <sub>2</sub> (10) / AgSbF <sub>6</sub>	Toluene	24	100	no reaction
14	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5) / P(4-FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> (20) / AgSbF <sub>6</sub> (12)	1,2-DCE	24	80	no reaction
15	[PPN][Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (4) / AgSbF <sub>6</sub> (8)	CH <sub>2</sub> Cl <sub>2</sub>	24	30	no reaction
16	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5)	THF	24	60	no reaction
17 <sup>[e]</sup>	[RhCl(CO)(dppp)] <sub>2</sub> (10)	1,2-DCE	24	80	no reaction

[a] Isolated yield. [b] Under CO(g) 1 atm. [c] 16% of reactant was remained. [d] 14% of reactant was remained. [e] CO 13 atm.

Yields of the reaction were highly sensitive to the reaction solvent. When 1,2-dichloroethane was used instead of 1,4-dioxane, the yield was dramatically increased to 36% (entry 2). As the amount of the catalyst used was increased, the yield was also increased (entries 3 and 4). The reaction conditions with an atmosphere of carbon monoxide were detrimental to the yield (entry 5). The yield of the reaction was highly dependent upon the counteranion (entries 2 and 6–10). When the counteranion was NO<sub>3</sub><sup>−</sup> or PF<sub>6</sub><sup>−</sup> (entries 6 and 7), no reaction was observed. Moreover, in case of ClO<sub>4</sub><sup>−</sup> and OTf<sup>−</sup> (entries 8 and 9), very poor yields (14 and 10% yields, respectively) were observed. The BF<sub>4</sub><sup>−</sup> anion (entry 10) was found to give the best yield (74%) in 1,2-dichloroethane. We also screened other neutral and cationic rhodium compounds, such as a [Rh(CO)Cl(dppe)]<sub>2</sub>/AgSbF<sub>6</sub>, [RhCl(COD)]<sub>2</sub>, [RhCl(COD)]<sub>2</sub>/AgSbF<sub>6</sub>, [RhCl(COD)]<sub>2</sub>/P(4-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>/AgSbF<sub>6</sub>, [PPN][Rh(CO)<sub>2</sub>Cl]<sub>2</sub>/AgSbF<sub>6</sub>,

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$  under carbon monoxide and  $[\text{RhCl}(\text{CO})(\text{dppp})]_2$  under 13 atmosphere carbon monoxide. (Entries 12–17). Unfortunately, they are ineffective. Thus, we established that  $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}/\text{AgBF}_4$  in 1,2-dichloroethane was the best catalyst system in respect to the yield. Formation of **26d** was confirmed by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopic investigations, high resolution mass spectrometry, and X-ray crystallographic structure (Figure 2). This was the first exposure of the skeleton of aryl-hexahydroisoquinolines.

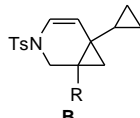
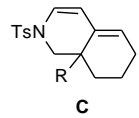
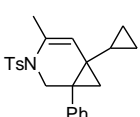
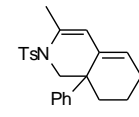
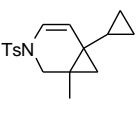
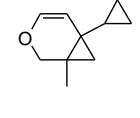
Using  $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}/\text{AgBF}_4$  as a catalyst, we investigated the  $\text{Rh}^{\text{I}}$ -catalyzed transformation of various N-Ts tethered enynes to aryl-hexahydroisoquinolines (Table 5). All the reaction went to completion within 4 hours. Reasonable to high yields were observed for all enynes bearing an aryl with an electron-withdrawing (entries 4–6 and 10) or -donating group (entries 2, 3, 7, 8 and 9).



**Figure 2.** X-ray crystallography of **26d**

<b>26d</b>	
Empirical formula	C <sub>22</sub> H <sub>23</sub> NO <sub>2</sub> S
Formula weight	365.48
Crystal system	Orthorhombic
Space group	P cab
a ( Å )	13.4556 (11)
b ( Å )	13.6408 (10)
c ( Å )	21.0602 (12)
<i>α</i>	90.0
<i>β</i>	90
<i>γ</i>	90
Volume ( Å <sup>3</sup> )	3865.5
Z, d (calcd), Mg/cm <sup>3</sup>	8, 1.25
no. tot. collection	8093
no. unique data	4407
final R indices [ I>sigma (I) ]	R1 = 0.156, wR2 = 0.125
R indeces (all data)	R1 = 0.059, wR2 = 0.0975

**Table 5.** Rhodium-Catalyzed Rearrangement Reaction<sup>[a]</sup>

Entry	Substrate	t (h)	Product (%) <sup>[b]</sup>
	 <b>B</b>		 <b>C</b>
	R		
1	<b>26</b> C <sub>6</sub> H <sub>5</sub>	4	74
2	<b>27</b> 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	5	72
3	<b>28</b> 4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4	70
4	<b>29</b> 4-ClC <sub>6</sub> H <sub>4</sub>	4	73
5	<b>30</b> 4-FC <sub>6</sub> H <sub>4</sub>	4	72
6	<b>31</b> 4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	4	79
7	<b>32</b> tert-butylbenzene	4	60
8	<b>33</b> 3-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	67
9	<b>34</b> 3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4	62
10	<b>35</b> 3-ClC <sub>6</sub> H <sub>4</sub>	4	58
11	<b>36</b> m-xylene	4	50
12	<b>37</b> naphthyl	-	-
13	<b>38</b> mesitylene	-	-
14	<b>39</b> 	4	 70
15	<b>25</b> 	-	-
16	<b>40</b> 	-	decomposed

[a] Reaction conditions: substrate, 10 mol% [Rh(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl] and 12 mol% AgBF<sub>4</sub> were reacted in 1,2-DCE at 80 °C. [b] Isolated yield.

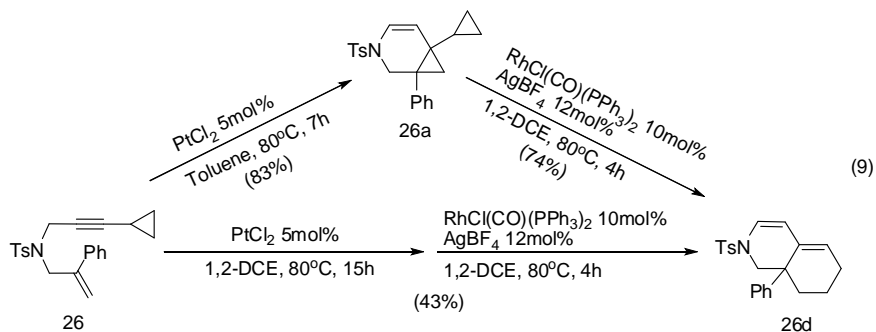
It seems that the electronic nature of a substituent on the aryl ring does not exert any noticeable influence on the yield of the reaction. However, the position of the substituent (3- vs. 4- position: entry 2 vs. 8, 3 vs. 9, and 4 vs. 10) has a slight influence on the yield of



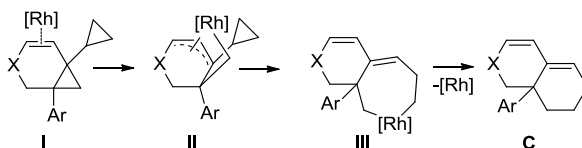
the reaction. Substrates with a substituent at the 4-position produce 10% higher yields than those of the 3-position. Interestingly, in the case of the *tert*-butyl group (entry 7), a rather low yield (60%) is obtained even the substituent is located at the 4-position. As expected, a substituent at the 2-position would exert a dramatic effect on the yield of the reaction. Thus, enynes having an aryl with ortho substituents did not give any products (entries 12 and 13). The reactant was recovered intact. Introduction of a methyl group to the  $\alpha$ -position of the N-Ts group did not have any effect on the yield of the reaction (entry 15). Unfortunately, all attempts with O-tethered substrate **40a** were unsuccessful. The substrate **40a** readily decomposed in the presence of the catalytic system. Thus, no characterizable products were isolated. Thus, the transformation of the bis-cyclopropanyls to hexa-hydronaphthalenes is unique to the N-Ts tethered substrates.

Next we investigated the possibility of integrating the platinum- and rhodium-catalyzed reactions into a "one-pot" transformation. However, all attempts were not successful presumably due to the different reaction conditions of each catalyzed reaction. The first step was usually carried out in toluene and the second step in 1,2-dichloroethane. When the second step was carried out in toluene, the yield of the second step was 36%. Thus, we had to find out a solvent which could be used in both steps. After much experimentation, 1,2-dichloroethane was chosen as a solvent. However, the integration of the two reactions in 1,2-dichloroethane afforded the

expected product in up to 43% yield [Eq. (9)]



A plausible reaction mechanism (Scheme 3) is proposed as follows. Although little mechanistic information has been obtained, a plausible mechanism is proposed on the basis of the above results and previous studies. The pre-coordination of the  $\text{Rh}^{\text{I}}$  center to the double bond (**I**) leads to the formation of a  $(\pi\text{-allyl})(\sigma\text{-alkyl})\text{Rh}^{\text{III}}$  intermediate (**II**). The intermediate **III** may be stabilized by the coordination of an aryl group.<sup>[16]</sup> A successive insertion leading to the metallacycle **IV**, followed by a reductive elimination allows the formation of the product.



Scheme 3. Proposed mechanism for the Rh catalyzed formation of aryl-hexahydroisoquinolines.

## Conclusion

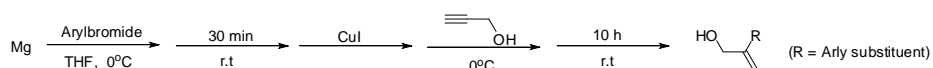
In conclusion, we have demonstrated the usefulness of a PtCl<sub>2</sub>-catalyzed cycloisomerization and three different rearrangements leading to compounds which are difficult to prepare by conventional synthetic pathways: we have discovered synthetic pathway of bicyclo[4.1.0]hept-2-enes to 1-aryl-tetrahydro-1H-indenes, 3-methylene-4-vinylcyclohex-1-enes, or aryl-hexahydroisoquinolines. The reaction pathways are highly sensitive to the identity and position of substituents at the alkene moiety. However, each reaction pathway favours a special frame. Readily available enynes are used as starting materials for the reaction. Moreover, the experimental simplicity is noteworthy. Recently, transition-metal-catalyzed cyclopropanation has been widely developed. Thus, the methodology developed in this study could become a highly versatile tool for obtaining cycloaddition products that cannot be easily attained by other methods. Further research into the synthetic utility of the reactions is in progress.

## Experimental Section

**General remarks.** All solvents were dried and distilled according to standard methods before use.  $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$  was prepared according to the literature procedures.<sup>[17]</sup> Platinum dichloride ( $\text{PtCl}_2$ ) was purchased from Strem Chemicals, Inc., and Silver tetrafluoroborate ( $\text{AgBF}_4$ ) was purchased from Acros Organics. Reactions were carried out in flame-dried glassware equipped with a stirring bar and sealed with a rubber septum under  $\text{N}_2$ , unless otherwise indicated. Elevated temperatures were maintained in thermostat-controlled oil baths. Reactions were monitored by thin-layer chromatography 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).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with Bruker (300 MHz) spectrometer.  $^1\text{H}$  NMR spectra were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Chemical shifts of the  $^{13}\text{C}$  NMR spectra were measured relative to  $\text{CDCl}_3$  (75.00 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Single crystal data for **8d**, **22d** were collected on an Enraf-Nonius CCD single crystal X-ray diffractometer at room temperature using graphite-monochromated Mo K  $\alpha$  radiation ( $\lambda =$

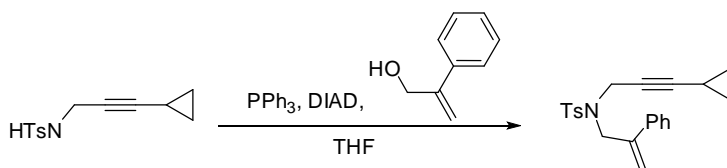
0.71073 Å). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97.

### Preparation of 2-arylprop-2-en-1-ol



Magnesium turnings (1.24 g, 51 mmol) were dissolved in THF (20 mL) in a round-bottomed flask equipped with a stirrer. After aryl bromide (51 mmol) was added to the solution at 0°C, the resulting solution was stirred for 30 min. Then, copper iodide (0.16 g, 0.8 mmol) was also added. After propargyl alcohol (1 mL, 17 mmol) was dropwisely added to the solution at 0°C, then resulting solution was stirred at room temperature for 10 h. The reaction mixture was quenched with NH<sub>4</sub>Cl solution. The reaction product was extracted with ethyl acetate. The extract was dried over anhydrous MgSO<sub>4</sub>, and was evaporated to give a crude product. Flash chromatography on a silica gel eluting with hexane and ethyl acetate (v/v, 9:1) afforded 2-arylprop-2-en-1-ol.

### Representative procedure for preparation of N-(3-cyclopropylprop-2-ynyl)-4-methyl-N-(2-phenylallyl)benzenesulfonamide (25)



To a solution of *N*-(3-cyclopropylprop-2-ynyl)-4-methylbenzenesulfonamide (0.872 g, 3.5 mmol) and PPh<sub>3</sub> (0.92 g, 3.5 mmol) in THF (30 mL) was added DIAD (DiisopropylAzodicarboxylate) (0.68 mL, 3.5 mmol) at room temperature. To the solution, 2-phenylprop-2-en-1-ol was added. The reaction mixture was stirred for 20 h at room temperature. After the solvent was removed by a rotary evaporator, the residue was purified by flash column chromatography eluting with 10% EtOAc in hexane.

**Representative procedure for platinum dichloride-catalyzed cycloisomerization and thermal rearrangement of dienyne. (b, c)**

PtCl<sub>2</sub> and toluene (2 mL) were added to a tube-type Schlenk flask equipped with a stirring bar and capped with a rubber septum. Then a substrate and toluene (4 mL) were added to the flask. The resulting mixture was stirred until the substrate was completely disappeared (as checked by TLC) at corresponding temperature. The reaction product(s) was (were) purified by flash chromatography on a silica gel column eluting with *n*-hexane/ethyl acetate (v/v = 7/1 or 50/1).

**Representative procedure for Rh(I)-catalyzed cycloisomerization reaction of bicyclo[4.1.0]heptenes (d)**

[Rh(PPh<sub>3</sub>)(CO)Cl], AgBF<sub>4</sub>, and 1,2-dichloroethane (2 mL) were added to a Schlenk flask equipped with a stirring bar and capped with a rubber septum. The reaction mixture was stirred at room

temperature for 5 min. Then a substrate and 1,2-dichloroethane were added to the Schlenk flask. The resulting mixture was stirred until the substrate completely disappeared at 80°C. The reaction mixture was purified by flash chromatography on a silica gel column eluting with *n*-hexane/ethyl acetate (v/v = 20/1).

### Characterization of New compounds

**1:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.63 (ddd, *J* = 11.3, 7.2, 2.7 Hz, 4 H), 2.10–2.15 (m, 4 H), 4.25 (dd, *J* = 6.1, 1.1 Hz, 2 H), 4.33 (s, 2 H), 6.16 (s, 1 H), 6.31 (dt, *J* = 15.9, 6.2 Hz, 1 H), 6.66 (d, *J* = 15.9 Hz, 1 H), 7.23–7.42 (m, 5 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 21.4, 22.2, 25.6, 29.1, 57.9, 70.0, 82.2, 88.3, 120.1, 125.5, 126.5, 127.7, 128.5, 133.0, 135.4, 136.6 ppm. HRMS (EI) calc. for [C<sub>18</sub>H<sub>20</sub>O]: 252.1514, found: 252.1511.

**2:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.54–1.61 (m, 4 H), 1.82 (br s, 2 H), 2.02 (br s, 2 H), 2.42 (s, 3 H), 3.98 (d, *J* = 6.8 Hz, 2 H), 4.22 (s, 2 H), 5.79 (s, 1 H), 6.12 (dt, *J* = 15.0, 7.5 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 21.3, 21.5, 22.1, 25.5, 28.9, 36.8, 48.6, 78.8, 87.6, 119.7, 123.2, 126.5, 127.8, 127.9, 128.5, 129.4, 134.6, 135.1, 136.0, 136.2, 143.3 ppm. HRMS (FAB) calc. for [C<sub>25</sub>H<sub>27</sub>NO<sub>2</sub>S]<sup>+</sup>: 406.1841, found: 406.1837.

**3:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.57–1.64 (m, 4 H), 2.09–2.13 (m, 7 H), 4.28 (s, 2 H), 4.31 (d, *J* = 3.0 Hz, 2 H), 5.94 (t, *J* = 6.7 Hz, 1

H), 6.14 (s, 1 H), 7.52–7.34 (m, 3 H), 7.41 (d,  $J = 7.1$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  16.2, 21.4, 22.3, 25.6, 29.1, 58.0, 66.3, 88.4, 88.2, 120.2, 123.6, 125.8, 127.3, 128.2, 135.4, 139.2, 142.9 ppm. HRMS (EI) calc. for  $[\text{C}_{19}\text{H}_{22}\text{O}]$ : 266.1671, found: 266.1673.

**4:** According to  $^1\text{H}$  NMR, the ratio of *E:Z* isomer was 5:1. (*E*-isomer)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.46–1.48 (m, 4 H), 1.75 (br s, 2 H), 1.95 (br s, 2 H), 2.34 (s, 3 H), 3.73 (s, 3 H), 3.88 (d,  $J = 6.8$  Hz, 2 H), 4.14 (s, 2 H), 5.72 (s, 1 H), 5.89 (dt,  $J = 15.7, 6.9$  Hz, 1 H), 6.43 (d,  $J = 15.7$  Hz, 1 H), 6.77 (d,  $J = 8.7$  Hz, 2 H), 7.19 (d,  $J = 6.4$  Hz, 2 H), 7.22 (d,  $J = 5.8$  Hz, 2 H), 7.69 (d,  $J = 8.2$  Hz, 2 H) ppm. (*Z*-isomer):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.47–1.55 (m, 6 H), 1.95 (br s, 2 H), 2.40 (s, 3 H), 3.79 (s, 3 H), 4.11 (d,  $J = 6.6$  Hz, 2 H), 4.20 (s, 2 H), 5.49–5.58 (m, 2 H), 6.59 (d,  $J = 11.7$  Hz, 1 H), 6.84 (d,  $J = 8.0$  Hz, 2 H), 7.16–7.20 (m, 4 H), 7.71 (d,  $J = 8.0$  Hz, 2 H) ppm. (*E and Z*-isomers):  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  15.2, 21.3, 21.5, 22.05, 22.12, 25.4, 25.5, 28.6, 28.9, 36.7, 37.0, 44.2, 48.7, 55.1, 55.3, 65.8, 77.2, 78.6, 78.9, 87.5, 113.5, 113.9, 119.6, 119.8, 120.8, 124.5, 127.1, 127.5, 127.7, 127.8, 128.6, 129.0, 129.4, 129.6, 130.1, 133.2, 134.2, 134.8, 135.1, 135.9, 136.1, 143.2, 158.7, 159.4 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{29}\text{NO}_3\text{S}]$ : 435.1868, found: 435.1866.

**5:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.54–1.59 (m, 4 H), 1.83 (br s, 2 H), 2.03 (br s, 2 H), 2.34 (s, 3 H), 2.43 (s, 3 H), 3.97 (d,  $J = 6.8$  Hz,



2 H), 4.22 (s, 2 H), 5.79 (s, 1 H), 6.01–6.11 (m, 1 H), 6.54 (d,  $J = 15.8$  Hz, 1 H), 7.12 (d,  $J = 7.9$  Hz, 2 H), 7.24 (d,  $J = 8.0$  Hz, 2 H), 7.30 (d,  $J = 8.1$  Hz, 2 H), 7.77 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.2, 21.4, 21.5, 22.2, 25.5, 28.9, 36.8, 48.7, 78.9, 87.6, 119.8, 122.1, 126.4, 127.9, 129.3, 129.5, 133.5, 134.6, 135.2, 136.1, 137.9, 143.3 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{29}\text{NO}_2\text{S}]$ : 419.1919, found: 419.1916.

**6:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.70 (s, 3 H), 2.45 (s, 3 H), 4.02 (d,  $J = 6.7$  Hz, 2 H), 4.28 (s, 2 H), 5.03 (s, 1 H), 5.17 (s, 1 H), 6.16 (dt,  $J = 15.7, 6.8$  Hz, 1 H), 6.62 (d,  $J = 15.8$  Hz, 1 H), 7.29–7.40 (m, 7 H), 7.81 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.5, 23.1, 36.8, 48.8, 80.8, 87.0, 122.1, 123.1, 125.9, 126.6, 127.8, 128.1, 128.6, 129.5, 134.8, 136.0, 136.2, 143.5 ppm. HRMS (FAB) calc. for  $[\text{C}_{22}\text{H}_{23}\text{NO}_2\text{S}]^+$ : 366.1449, found: 366.1450.

**7:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.66 (s, 3 H), 1.75 (d,  $J = 6.9$  Hz, 3 H), 2.41 (s, 3 H), 3.99 (d,  $J = 6.7$  Hz, 2 H), 4.27 (s, 2 H), 5.01 (s, 1 H), 6.11 (dt,  $J = 15.7, 6.8$  Hz, 1 H), 6.57 (d,  $J = 15.8$  Hz, 1 H), 7.27–7.32 (m, 7 H), 7.76 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.0, 21.5, 24.7, 37.0, 48.6, 83.6, 83.8, 104.4, 123.3, 126.6, 127.8, 128.0, 128.6, 129.5, 134.7, 136.16, 136.21, 143.4, 149.0 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 379.1603.

**8:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.39 (s, 3 H), 3.72 (d,  $J = 6.7$  Hz, 2 H), 4.19 (d,  $J = 1.9$  Hz, 2 H), 5.79 (s, 1 H), 5.93–6.03 (m, 1 H),

6.20 (d,  $J = 15.8$  Hz, 1 H), 7.18–7.32 (m, 17 H), 7.73 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.5, 36.9, 48.4, 84.7, 86.1, 21.5, 36.9, 48.4, 84.7, 86.1, 106.2, 122.8, 126.5, 127.7, 127.9, 127.96, 128.01, 128.2, 128.3, 128.47, 128.54, 129.4, 129.7, 134.8, 135.9, 136.1, 139.1, 140.8, 143.5, 152.9 ppm. HRMS (EI) calc. for  $[\text{C}_{33}\text{H}_{29}\text{NO}_2\text{S}]$ : 503.1919, found: 503.1917.

**9**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.38 (s, 3 H), 4.01 (d,  $J = 6.7$  Hz, 2 H), 4.28 (s, 2 H), 5.88 (d,  $J = 16.3$  Hz, 1 H), 6.12 (dt,  $J = 15.7, 6.8$  Hz, 1 H), 6.56 (d,  $J = 5.2$  Hz, 1 H), 6.61 (d,  $J = 4.7$  Hz, 1 H), 7.24–7.36 (m, 12 H), 7.80 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.5, 37.1, 49.0, 84.1, 85.0, 107.1, 123.2, 126.2, 126.6, 239.0, 128.1, 128.7, 128.8, 128.9, 129.6, 134.8, 135.9, 136.1, 136.2, 141.8, 143.6 ppm. HRMS (EI) calc. for  $[\text{C}_{27}\text{H}_{25}\text{NO}_2\text{S}]$ : 427.1606, found: 427.1608.

**10**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.52–1.54 (m, 4 H), 1.79 (br s, 2 H), 2.01 (br s, 2 H), 2.41 (s, 3 H), 3.81 (d,  $J = 6.3$  Hz, 2 H), 4.19 (s, 2 H), 5.23 (d,  $J = 10.2$  Hz, 1 H), 5.29 (d,  $J = 17.2$  Hz, 1 H), 5.69–5.82 (m, 2 H), 7.29 (d,  $J = 8.3$  Hz, 2 H), 7.74 (d,  $J = 7.9$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.3, 21.5, 22.2, 25.5, 28.9, 36.7, 49.0, 78.7, 87.5, 119.8, 127.8, 129.4, 129.6, 132.1, 135.1, 136.0, 143.3 ppm. HRMS (EI) calc. for  $[\text{C}_{19}\text{H}_{23}\text{NO}_2\text{S}]$ : 329.1450, found: 329.1451.

**11**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.61 (s, 3 H), 1.78 (s, 3 H), 2.40 (s, 3 H), 3.72 (s, 2 H), 4.15 (s, 2 H), 4.93 (s, 1 H), 4.97 (s, 2 H),

5.09 (s, 1 H), 7.29 (d,  $J = 8.1$  Hz, 2 H), 7.74 (d,  $J = 8.1$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  19.7, 21.5, 23.0, 36.2, 52.5, 80.6, 86.9, 115.4, 121.9, 125.9, 127.8, 129.4, 136.0, 139.2, 143.3 ppm. HRMS (EI) calc. for  $[\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}]$ : 303.1293, found: 303.1290.

**12:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.57–1.64 (m, 4 H), 1.68 (d,  $J = 6.9$  Hz, 3 H), 2.09–2.11 (m, 4 H), 4.25 (s, 2 H), 4.28 (s, 2 H), 5.89 (q,  $J = 6.9$  Hz, 1 H), 6.11 (s, 1 H), 7.24–7.28 (m, 3 H), 7.32–7.37 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.7, 21.5, 22.3, 25.6, 29.2, 57.5, 74.4, 82.3, 88.1, 120.2, 126.2, 126.9, 128.1, 128.7, 135.2, 137.4, 138.7 ppm. HRMS (EI) calc. for  $[\text{C}_{19}\text{H}_{22}\text{O}]$ : 266.1671, found: 266.2671.

**13:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.53 (dd,  $J = 11.0, 5.6$  Hz, 4 H), 1.64 (s, 3 H), 1.68 (s, 3 H), 2.03 (dd,  $J = 6.2, 12.2$  Hz, 4 H), 3.98 (d,  $J = 7.0$  Hz, 2 H), 4.16 (s, 2 H), 5.28 (t,  $J = 7.0$  Hz, 1 H), 6.04 (s, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  18.0, 21.5, 22.3, 25.6, 25.8, 29.1, 57.6, 65.7, 82.6, 87.9, 120.2, 120.5, 135.1, 138.0 ppm. HRMS (EI) calc. for  $[\text{C}_{14}\text{H}_{20}\text{O}]$ : 204.1514, found: 204.1512.

**14:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.52–1.54 (m, 4 H), 1.66 (d,  $J = 6.9$  Hz, 3 H), 1.79 (br s, 2 H), 2.01 (br s, 2 H), 2.38 (s, 3 H), 4.09 (s, 2 H), 4.12 (s, 2 H), 5.76 (s, 1 H), 5.85 (q,  $J = 6.8$  Hz, 1 H), 7.20–7.25 (m, 5 H), 7.31 (dd,  $J = 15.4, 7.9$  Hz, 2 H), 7.65 (d,  $J = 8.1$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.8, 21.4, 21.5, 22.2, 25.5, 28.9, 36.4, 52.8, 78.9, 87.7, 119.9, 126.8, 127.2, 127.8, 128.2, 128.8, 129.3, 134.9, 135.0, 136.1, 137.7, 143.1 ppm. HRMS (EI)

calc. for [C<sub>26</sub>H<sub>29</sub>NO<sub>2</sub>S]: 419.1919, found: 419.1918.

**15:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.53–1.55 (m, 4 H), 1.68 (d, *J* = 6.9 Hz, 3 H), 1.79 (br s, 2 H), 2.02 (br s, 2 H), 2.40 (s, 3 H), 3.82 (s, 3 H), 4.06 (s, 2 H), 4.10 (s, 2 H), 5.76 (s, 1 H), 5.80 (d, *J* = 7.0 Hz, 1 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 7.16 (d, *J* = 8.6 Hz, 2 H), 7.24 (d, *J* = 8.1 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.9, 21.4, 21.5, 22.2, 25.5, 28.9, 36.3, 52.9, 55.2, 79.0, 87.6, 113.6, 119.9, 126.4, 127.8, 129.3, 129.8, 129.9, 134.3, 135.0, 136.2, 143.1, 158.6 ppm. HRMS (EI) calc. for [C<sub>26</sub>H<sub>29</sub>NO<sub>3</sub>S]: 435.1868, found: 435.1866.

**16:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.52–1.53 (m, 4 H), 1.69 (d, *J* = 6.1 Hz, 3 H), 1.79 (br s, 2 H), 2.01 (br s, 2 H), 2.41 (s, 3 H), 3.74 (d, *J* = 6.7 Hz, 2 H), 4.17 (s, 2 H), 5.34–5.43 (m, 1 H), 5.64–5.74 (m, 1 H), 5.76 (s, 1 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 17.8, 21.4, 21.5, 22.2, 25.5, 28.9, 36.4, 48.3, 79.0, 87.3, 119.9, 124.7, 127.82, 129.3, 131.4, 135.0, 143.2 ppm. HRMS (EI) calc. for [C<sub>20</sub>H<sub>25</sub>NO<sub>2</sub>S]: 343.1606, found: 343.1606.

**17:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.67 (d, *J* = 6.9 Hz, 3 H), 2.39 (s, 3 H), 4.09 (s, 2 H), 4.12 (s, 2 H), 5.31 (dd, *J* = 17.1, 2.5 Hz, 1 H), 5.36 (dd, *J* = 11.3, 2.5 Hz, 1 H), 5.51 (dd, *J* = 17.0, 11.3 Hz, 1 H), 5.85 (q, *J* = 6.9 Hz, 1 H), 7.22 (dd, *J* = 15.2, 6.9 Hz, 5 H), 7.32 (dd, *J* = 14.6, 7.2 Hz, 2 H), 7.64 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.9, 21.5, 36.3, 53.0, 82.7, 84.3, 116.3, 127.0, 127.2,

127.8, 128.2, 128.7, 129.3, 134.9, 136.0, 137.6, 143.2 ppm. HRMS (EI) calc. for  $[C_{21}H_{23}NO_2S]$ : 365.1449, found: 365.1449.

**18:**  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  1.64 (s, 2 H), 1.67 (d,  $J = 6.9$  Hz, 4 H), 2.37 (s, 3 H), 4.09 (s, 2 H), 4.13 (s, 2 H), 4.96 (s, 1 H), 5.10 (m, 1 H), 5.85 (q,  $J = 6.9$  Hz, 1 H), 7.20–7.25 (m, 5 H), 7.32 (dd,  $J = 15.3, 7.9$  Hz, 2 H), 7.66 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  14.9, 21.5, 23.1, 36.3, 52.9, 81.0, 87.0, 122.0, 126.0, 127.0, 127.2, 127.8, 128.2, 128.7, 129.4, 134.9, 136.0, 137.6, 143.3 ppm. HRMS (EI) calc. for  $[C_{23}H_{25}NO_2S]$ : 379.1606, found: 379.1605.

**19:**  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  1.69 (d,  $J = 6.4$  Hz, 3 H), 2.40 (s, 3 H), 3.73 (d,  $J = 6.8$  Hz, 2 H), 4.17 (s, 2 H), 5.23–5.54 (m, 4 H), 5.69 (dd,  $J = 15.1, 6.6$  Hz, 1 H), 7.27 (d,  $J = 9.4$  Hz, 2 H), 7.73 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  17.8, 21.5, 36.2, 48.5, 82.6, 84.1, 116.3, 124.6, 127.2, 129.4, 131.6, 136.0, 143.3 ppm. HRMS (FAB) calc. for  $[C_{16}H_{19}NO_2S]^+$ : 290.1215, found: 290.1211.

**20:**  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  1.41 (d,  $J = 9.4$  Hz, 3 H), 1.49 (d,  $J = 6.9$  Hz, 3 H), 1.55 (d,  $J = 6.7$  Hz, 3 H), 2.25 (s, 3 H), 4.01 (d,  $J = 4.6$  Hz, 4 H), 5.46 (d,  $J = 6.9$  Hz, 1 H), 5.75 (q,  $J = 6.6$  Hz, 1 H), 7.10–7.15 (m, 5 H), 7.19–7.23 (m, 2 H), 7.55 (d,  $J = 7.9$  Hz, 2 H) ppm.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  14.0, 14.9, 16.5, 21.5, 36.4, 52.9, 77.9, 89.0, 117.6, 126.9, 127.2, 127.8, 128.2, 128.8, 129.4, 132.8, 135.0, 136.2, 137.7, 143.2 ppm. HRMS (EI) calc. for  $[C_{24}H_{27}NO_2S]$ : 393.1762, found: 393.1762.

**21:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.69 (d,  $J = 6.8$  Hz, 3 H), 4.35 (s, 2 H), 4.37 (s, 2 H), 5.67 (s, 1 H), 5.93 (s, 2 H), 7.27 (d,  $J = 6.2$  Hz, 2 H), 7.34 (d,  $J = 7.3$  Hz, 4 H), 7.63 (d,  $J = 7.3$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.7, 57.5, 74.7, 85.4, 86.8, 121.1, 125.8, 126.0, 126.6, 127.0, 128.2, 128.4, 128.7, 130.1, 137.0, 137.4, 138.6 ppm. HRMS (EI) calc. for  $[\text{C}_{21}\text{H}_{20}\text{O}]$ : 288.1514, found: 288.1512.

**22:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.60 (d,  $J = 6.9$  Hz, 3 H), 4.32 (s, 4 H), 5.92 (q,  $J = 6.9$  Hz, 1 H), 6.17 (dt,  $J = 16.2, 1.7$  Hz, 1 H), 6.95 (d,  $J = 16.3$  Hz, 1 H), 7.26–7.39 (m, 8 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.7, 57.7, 74.7, 85.5, 87.6, 107.6, 126.27, 126.36, 126.9, 128.2, 128.65, 128.69, 128.72, 128.70, 136.1, 137.4, 138.6, 141.7 ppm. HRMS (EI) calc. for  $[\text{C}_{21}\text{H}_{20}\text{O}]$ : 288.1514, found: 288.1512.

**23:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.94 (t,  $J = 7.5$  Hz, 3 H), 1.53–1.55 (m, 4 H), 1.80 (br s, 2 H), 2.01 (br s, 2 H), 2.01–2.11 (q,  $J = 7.4$  Hz, 2 H), 2.40 (s, 3 H), 4.08 (s, 2 H), 4.13 (s, 2 H), 5.74 (d,  $J = 7.4$  Hz, 1 H), 5.76–5.78 (m, 1 H), 7.19–7.25 (m, 5 H), 7.32 (d,  $J = 13.6, 6.3$  Hz, 2 H), 7.66 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.4, 21.4, 21.5, 22.2, 22.3, 25.5, 28.9, 36.3, 52.8, 79.0, 87.6, 119.9, 127.2, 127.8, 128.2, 128.6, 129.3, 133.3, 134.4, 135.0, 136.1, 138.0, 143.1 ppm. HRMS (EI) calc. for  $[\text{C}_{27}\text{H}_{32}\text{NO}_2\text{S}]$ : 433.2075, found: 433.2075.

**24:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.44–1.46 (m, 4 H), 1.55 (d,  $J = 6.7$  Hz, 3 H), 1.59 (s, 3 H), 1.68 (br s, 2 H), 1.93 (br s, 2 H), 2.33

(s, 3 H), 3.60 (s, 2 H), 4.01 (s, 2 H), 5.39 (q,  $J = 6.5$  Hz, 1 H), 5.64 (br s, 1 H), 7.20 (d,  $J = 8.1$  Hz, 2 H), 7.66 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 13.6, 21.4, 21.5, 22.2, 25.5, 28.9, 36.0, 54.2, 78.9, 87.4, 120.0, 124.9, 127.8, 129.3, 129.8, 134.9, 136.2, 143.1 ppm. HRMS (EI) calc. for  $[\text{C}_{21}\text{H}_{27}\text{NO}_2\text{S}]$ : 357.1762, found: 357.1762.

**25:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.2$  Hz, 2 H), 7.30 (d,  $J = 8.4$  Hz, 2 H), 4.95 (s, 2 H), 3.982 (s, 1 H), 3.976 (s, 1 H), 3.70 (s, 2 H), 2.44 (s, 3 H), 1.76 (s, 3 H), 0.85 – 0.96 (m, 1 H), 0.56 – 0.63 (m, 2 H), 0.26 – 0.31 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.22, 139.40, 136.28, 129.30, 127.81, 115.20, 89.26, 67.52, 52.31, 36.02, 21.52, 19.74, 7.82, –0.94 ppm. HRMS (EI) calc. for  $[\text{C}_{17}\text{H}_{21}\text{O}_2\text{SN}]$ : 303.1293, found 303.1293.

**26:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  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.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  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. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{23}\text{NO}_2\text{S}]$ : 365.1450, found: 365.1447.

**27:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 7.9$  Hz, 2 H), 7.43 (d,

$J = 7.8$  Hz, 2 H), 7.31 (d,  $J = 7.8$  Hz, 2 H), 7.15 (d,  $J = 7.6$  Hz, 2 H), 5.52 (s, 1 H), 5.26 (s, 1 H), 4.20 (s, 2 H), 3.92 (s, 2 H), 2.45 (s, 3 H), 2.35 (s, 3 H), 0.93 (br s, 1 H), 0.60 (d,  $J = 6.1$  Hz, 2 H), 0.27 (d,  $J = 2.3$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.30, 141.22, 137.95, 135.85, 134.87, 129.31, 129.11, 128.00, 126.29, 116.14, 89.62, 67.39, 49.95, 36.03, 21.53, 21.15, 7.83,  $-0.95$  ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 379.1610.

**28:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.3$  Hz, 2 H), 7.50 (d,  $J = 8.8$  Hz, 2 H), 7.32 (d,  $J = 8.1$  Hz, 2 H), 6.88 (d,  $J = 8.8$  Hz, 2 H), 5.48 (s, 1 H), 5.21 (s, 1 H), 4.19 (s, 2 H), 3.91 (d,  $J = 1.8$  Hz, 2 H), 3.81 (s, 3 H), 2.45 (s, 3 H), 0.88 – 0.97 (m, 1 H), 0.56 – 0.63 (m, 2 H), 0.24 – 0.29 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.53, 143.32, 140.58, 135.76, 130.07, 129.30, 128.00, 127.59, 115.35, 113.76, 89.62, 67.31, 55.26, 50.03, 35.95, 21.51, 7.81,  $-0.97$  ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 395.1555, found: 395.1555.

**29:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.2$  Hz, 2 H), 7.48 (d,  $J = 8.6$  Hz, 2 H), 7.30 – 7.33 (m, 4 H), 5.55 (s, 1 H), 5.33 (s, 1 H), 4.19 (s, 2 H), 3.90 (d,  $J = 1.7$  Hz, 2 H), 2.46 (s, 3 H), 0.93 (dd,  $J = 4.0, 9.1$  Hz, 1 H), 0.57 – 0.64 (m, 2 H), 0.24 – 0.29 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.51, 140.42, 136.10, 135.64, 134.01, 129.39, 128.61, 127.97, 127.78, 117.61, 89.84, 67.13, 49.90, 36.05, 21.56, 7.87,  $-0.96$  ppm. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{22}\text{NO}_2\text{ClS}]$ : 399.1060, found: 399.1060.



**30:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.2$  Hz, 2 H), 7.54 (m, 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, 1H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  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. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{22}\text{FNO}_2\text{S}]$ : 383.1355, found: 383.1359.

**31:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.2$  Hz, 2 H), 7.67 (d,  $J = 8.3$  Hz, 2 H), 7.59 (d,  $J = 8.4$  Hz, 2 H), 7.32 (d,  $J = 8.1$  Hz, 2 H), 5.65 (s, 1 H), 5.44 (s, 1 H), 4.25 (s, 2 H), 3.91 (d,  $J = 1.3$  Hz, 2 H), 2.44 (s, 3 H), 0.91 – 0.95 (m, 1 H), 0.68 – 0.64 (m, 2 H), 0.25 – 0.29 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.66, 140.45, 135.53, 129.43, 127.92, 126.81, 125.42, 125.36, 125.31, 119.26, 90.07, 66.91, 49.86, 36.10, 21.46, 7.85, –1.00 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{22}\text{F}_3\text{NO}_2\text{S}]$ : 433.1323, found: 433.1325.

**32:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 8.2$  Hz, 2 H), 7.42 (d,  $J = 8.4$  Hz, 2 H), 7.23 – 7.31 (m, 4 H), 5.48 (s, 1 H), 5.20 (s, 1 H), 4.14 (s, 2 H), 3.86 (d,  $J = 1.5$  Hz, 2 H), 2.38 (s, 3 H), 1.25 (s, 9 H), 0.82 – 0.86 (m, 1 H), 0.51 – 0.54 (m, 2 H), 0.19 – 0.22 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  151.12, 143.34, 141.02, 135.84, 134.82, 129.33, 128.02, 126.06, 125.37, 116.30, 89.67, 67.42, 49.94, 36.08, 34.56, 31.29, 21.55, 7.85, –0.93 ppm. HRMS (EI)

calc. for [C<sub>26</sub>H<sub>31</sub>NO<sub>2</sub>S]: 421.2076, found: 421.2074.

**33:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.2 Hz, 2 H), 7.32 (br s, 2 H), 7.10 – 7.32 (m, 4 H), 5.53 (s, 1 H), 5.30 (s, 1 H), 4.20 (s, 2 H), 3.94 (d, *J* = 1.6 Hz, 2 H), 2.45 (s, 3 H), 2.36 (s, 3 H), 0.90 – 1.01 (m, 1 H), 0.57 – 0.64 (m, 2 H), 0.26 – 0.31 (m, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 143.29, 141.58, 137.91, 135.91, 129.49, 129.31, 128.84, 128.29, 127.95, 127.16, 123.52, 116.66, 89.63, 67.45, 49.90, 36.10, 21.51, 21.47, 7.82, –0.95 ppm. HRMS (EI) calc. for [C<sub>23</sub>H<sub>25</sub>NO<sub>2</sub>S]: 379.1606, found: 379.1606.

**34:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.1 Hz, 2 H), 7.23 – 7.33 (m, 4 H), 7.12 (d, *J* = 6.4 Hz, 1 H), 6.86 (d, *J* = 7.1 Hz, 1 H), 5.58 (s, 1 H), 5.32 (s, 1 H), 4.21 (s, 2 H), 3.94 (s, 2 H), 3.84 (s, 3 H), 2.45 (s, 3 H), 0.91 – 0.94 (m, 1 H), 0.57 – 0.63 (m, 2 H), 0.25 – 0.30 (m, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.63, 143.37, 141.28, 139.25, 135.85, 129.35 (Ts carbon + 3-MeO carbon), 127.96, 118.78, 117.15, 114.08, 111.86, 89.74, 67.34, 55.36, 49.97, 36.11, 21.54, 7.86, –0.93 ppm. HRMS (EI) calc. for [C<sub>23</sub>H<sub>25</sub>NO<sub>3</sub>S]: 395.1555, found: 395.1552.

**35:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.2 Hz, 2 H), 7.42 – 7.45 (m, 1 H), 7.27 – 7.33 (m, 5 H), 5.56 (s, 1 H), 5.37 (s, 1 H), 4.19 (s, 2 H), 3.93 (d, *J* = 1.6 Hz, 2 H), 2.45 (s, 3 H), 0.87 – 0.99 (m, 1 H), 0.61 (dt, *J* = 4.1, 6.7 Hz, 2 H), 0.26 – 0.32 (m, 2 H) ppm.

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.50, 140.51, 139.80, 135.72, 134.32, 129.74, 129.40, 128.13, 127.96, 126.57, 124.781, 118.09, 89.90, 67.24, 49.79, 36.19, 21.56, 7.89,  $-0.93$  ppm. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{22}\text{NO}_2\text{SCl}]$ : 399.1060, found: 399.1060.

**36:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.2$  Hz, 2 H), 7.30 (d,  $J = 8.0$  Hz, 2 H), 7.12 (s, 2 H), 6.94 (s, 1 H), 5.51 (s, 1 H), 5.28 (s, 1 H), 4.19 (s, 2 H), 3.94 (s, 2 H), 2.44 (s, 3 H), 2.32 (s, 6 H), 0.91  $- 0.99$  (m, 1 H), 0.57  $- 0.64$  (m, 2 H), 0.27  $- 0.32$  (m, 2 H) ppm.  $^{13}\text{C}$

NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.29, 141.74, 138.01, 137.83, 136.01, 129.76, 129.33, 127.97, 124.33, 116.43, 89.63, 67.58, 49.94, 36.16, 21.55, 21.37, 7.87,  $-0.90$  ppm. HRMS (EI) calc. for  $[\text{C}_{24}\text{H}_{27}\text{NO}_2\text{S}]$ : 393.1763, found: 393.1759.

**37:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00  $- 8.03$  (m, 1 H), 7.83  $- 7.86$  (m, 1 H), 7.78 (d,  $J = 8.1$  Hz, 1 H), 7.63 (d,  $J = 8.2$  Hz, 2 H), 7.45  $- 7.48$  (m, 2 H), 7.41 (d,  $J = 8.0$  Hz, 1 H), 7.31 (d,  $J = 6.9$  Hz, 1 H), 7.18 (d,  $J = 8.1$  Hz, 2 H), 5.74 (s, 1 H), 5.35 (s, 1 H), 4.18  $- 4.20$  (m, 4 H), 2.37 (s, 3 H), 0.92  $- 1.00$  (m, 1 H), 0.59 (dt,  $J = 4.1, 6.6$  Hz, 2 H), 0.27  $- 0.32$  (m, 2 H) ppm.  $^{13}\text{C}$

NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.22, 142.13, 137.95, 136.23, 133.71, 131.28, 129.29, 128.40, 127.93, 127.66, 126.18, 125.81, 125.24, 117.89, 89.75, 67.83, 51.63, 36.92, 21.49, 7.88,  $-0.88$  ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{25}\text{NO}_2\text{S}]$ : 415.1606, found: 415.1608.

**38:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 8.2$  Hz, 2 H), 7.25 (d,

$J = 8.0$  Hz, 2 H), 6.87 (s, 2 H), 5.58 (s, 1 H), 5.02 (s, 1 H), 4.21 (s, 2 H), 3.84 (s, 2 H), 2.40 (s, 3 H), 2.27 (s, 3 H), 2.23 (s, 6 H), 0.87 (dd,  $J = 4.7, 11.6$  Hz, 1 H), 0.54 – 0.60 (m, 2 H), 0.23 – 0.28 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.26, 142.24, 136.89, 136.42, 135.80, 129.32, 128.23, 127.69, 114.14, 89.63, 67.99, 49.96, 37.23, 31.61, 22.67, 21.49, 20.97, 19.53, 14.14, 7.81,  $-0.96$  ppm. HRMS (EI) calc. for  $[\text{C}_{25}\text{H}_{29}\text{NO}_2\text{S}]$ : 407.1919, found: 407.1915.

**39:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 8.2$  Hz, 2 H), 7.47 (m, 2 H), 7.25 – 7.37 (m, 5 H), 5.49 (d,  $J = 5.0$  Hz, 2 H), 4.81 (q,  $J = 6.9$  Hz, 1 H), 4.39 (d,  $J = 16.8$  Hz, 1 H), 3.98 (d,  $J = 16.8$  Hz, 1 H), 2.43 (s, 3 H), 1.28 (d,  $J = 7.1$  Hz, 3 H), 0.93 – 1.02 (m, 1 H), 0.61 (dd,  $J = 2.3, 8.3$  Hz, 2 H), 0.25 – 0.30 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.78, 143.28, 139.26, 135.97, 129.35, 128.36, 127.85, 126.46, 115.28, 89.03, 72.17, 48.40, 47.15, 22.83, 21.52, 7.97, 7.89,  $-0.94$  ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 397.1609.

**40:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 7.6$  Hz, 2 H), 7.28 – 7.36 (m, 3 H), 5.53 (s, 1 H), 5.36 (s, 1 H), 4.44 (s, 2 H), 4.14 (s, 2 H), 1.24 – 1.30 (m, 1 H), 0.75 – 0.83 (m, 2 H), 0.67 – 0.73 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.61, 138.62, 128.35, 127.78, 126.06, 115.03, 90.35, 86.48, 71.15, 57.61, 8.22,  $-0.51$  ppm. HRMS (EI) calc. for  $[\text{C}_{15}\text{H}_{16}\text{O}]$ : 212.1201, found 212.1200.

**10a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.50–0.53 (m, 1 H), 0.96 (dd,  $J = 8.7, 4.4$  Hz, 1 H), 1.47–1.50 (m, 5 H), 1.87 (br s, 2 H), 1.94 (br s, 2 H), 2.42 (s, 3 H), 3.04 (dd,  $J = 11.6, 2.5$  Hz, 1 H), 3.91 (d,  $J = 11.6$  Hz, 1 H), 5.30 (d,  $J = 8.2$  Hz, 1 H), 5.45 (s, 1 H), 6.36 (d,  $J = 8.2$  Hz, 2 H), 7.31 (d,  $J = 8.1$  Hz, 2 H), 7.65 (d,  $J = 8.2$  Hz, 2 H) ppm.

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  19.1, 21.5, 22.3, 22.9, 23.2, 25.0, 25.1, 26.5, 41.0, 114.6, 120.7, 122.1, 127.0, 129.7, 134.9, 138.4, 143.6 ppm. HRMS (EI) calc. for  $[\text{C}_{19}\text{H}_{23}\text{NO}_2\text{S}]$ : 329.1450, found: 329.1488.

**11a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.66 (d,  $J = 4.6$  Hz, 1 H), 0.78 (d,  $J = 4.6$  Hz, 1 H), 0.95 (s, 3 H), 1.59 (s, 3 H), 2.35 (s, 3 H), 2.65 (d,  $J = 11.6$  Hz, 1 H), 3.78 (d,  $J = 11.6$  Hz, 1 H), 4.63 (s, 1 H), 4.81 (s, 1 H), 5.12 (d,  $J = 8.0$  Hz, 1 H), 6.29 (d,  $J = 8.0$  Hz, 1 H), 7.24 (d,  $J = 8.0$  Hz, 2 H), 7.59 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  17.2, 21.6, 22.4, 23.3, 29.7, 30.9, 46.5, 113.2, 115.8, 121.0, 127.0, 129.8, 135.1, 143.7, 144.5 ppm. HRMS (EI) calc. for  $[\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}]$ : 303.1293, found: 303.1291.

**14a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (s, 4 H), 0.94 (s, 3 H), 1.45–1.46 (m, 5 H), 1.73–1.77 (m, 2 H), 1.89 (br s, 2 H), 2.35 (s, 3 H), 2.57 (d,  $J = 11.3$  Hz, 1 H), 3.71 (d,  $J = 11.3$  Hz, 1 H), 5.10 (d,  $J = 8.0$  Hz, 1 H), 5.38 (s, 1 H), 6.18 (d,  $J = 8.0$  Hz, 1 H), 7.23 (d,  $J = 8.0$  Hz, 2 H), 7.57 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  11.0, 14.2, 21.6, 22.3, 23.1, 25.3, 27.3, 27.8, 30.7, 32.3, 47.2, 119.2, 120.0, 126.9, 127.0, 129.7, 134.9, 135.1, 143.6 ppm. HRMS (EI) calc. for  $[\text{C}_{21}\text{H}_{27}\text{NO}_2\text{S}]$ : 357.1762, found: 357.1761.

**25a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 8.2$  Hz, 2 H), 7.16 (d,  $J = 8.1$  Hz, 2 H), 6.12 (d,  $J = 8.0$  Hz, 1 H), 5.15 (d,  $J = 8.0$  Hz, 1 H), 3.64 (d,  $J = 11.3$  Hz, 1 H), 2.55 (d,  $J = 11.3$  Hz, 1 H), 2.27 (s, 3 H), 1.02 (s, 3 H), 0.65 – 0.74 (m, 1 H), 0.35 – 0.41 (m, 1 H), 0.31 (d,  $J = 4.6$  Hz, 1 H), 0.22 – 0.28 (m, 1 H), 0.16 (d,  $J = 4.4$  Hz, 1 H), 0.01 (dd,  $J = 1.4, 4.7$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.59, 134.98, 129.74, 127.03, 120.12, 117.06, 46.67, 30.30, 23.58, 22.06, 21.55, 17.31, 12.40, 5.00, 2.83 ppm. HRMS (EI) calc. for  $[\text{C}_{17}\text{H}_{21}\text{O}_2\text{SN}]$ : 303.1293, found 303.1293.

**26a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.66 (m, 2 H), 7.31 (d,  $J = 8.0$  Hz, 2 H), 7.25 – 7.29 (m, 5 H), 6.40 (dd,  $J = 1.0, 8.1$  Hz, 1 H), 5.34 (d,  $J = 8.1$  Hz, 1 H), 3.96 (dd,  $J = 1.0, 11.5$  Hz, 1 H), 2.99 (d,  $J = 11.5$  Hz, 1 H), 2.43 (s, 3 H), 1.00 (d,  $J = 4.9$  Hz, 1 H), 0.94 (d,  $J = 4.9$  Hz, 1 H), 0.50 (m, 1 H), 0.33 – 0.42 (m, 1 H), 0.09 – 0.18 (m, 1 H), –0.14 – –0.05 (m, 1 H), –0.20 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.72, 139.21, 134.94, 129.91, 129.82, 128.34, 127.09, 127.02, 121.23, 115.68, 48.09, 24.13, 21.58, 20.48, 13.82, 2.84 ppm. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{23}\text{NO}_2\text{S}]$ : 365.1450, found: 365.1448.

**27a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 8.2$  Hz, 2 H), 7.30 (d,  $J = 8.1$  Hz, 2 H), 7.16 (d,  $J = 8.0$  Hz, 2 H), 7.09 (d,  $J = 8.0$  Hz, 2 H), 6.38 (d,  $J = 8.1$  Hz, 1 H), 5.31 (d,  $J = 8.1$  Hz, 1 H), 3.94 (d,  $J = 11.3$  Hz, 1 H), 2.95 (d,  $J = 11.5$  Hz, 1 H), 2.43 (s, 3 H), 2.32 (s, 3

H), 1.00 (d,  $J = 4.8$  Hz, 1 H), 0.92 (d,  $J = 4.8$  Hz, 1 H), 0.49 (qd,  $J = 5.2, 8.2$  Hz, 1 H), 0.33 – 0.42 (m, 1 H), 0.13 (m, 1 H), –0.07 (m, 1 H), –0.17 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.69, 136.66, 136.17, 134.92, 129.80, 129.76, 129.04, 127.09, 121.15, 115.60, 48.12, 39.71, 24.08, 21.08, 21.14, 20.60, 13.83, 2.88, 2.82 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 379.1605.

**28a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.62 (m, 2 H), 7.27 (d,  $J = 8.0$  Hz, 2 H), 7.13 – 7.17 (m, 2 H), 6.76 – 6.81 (m, 2 H), 6.34 (dd,  $J = 1.0, 8.1$  Hz, 1 H), 5.28 (d,  $J = 8.1$  Hz, 1 H), 3.91 (dd,  $J = 1.0, 11.5$  Hz, 1 H), 3.75 (s, 3 H), 2.90 (d,  $J = 11.3$  Hz, 1 H), 2.40 (s, 3 H), 0.95 (d,  $J = 4.9$  Hz, 1 H), 0.86 (d,  $J = 5.2$  Hz, 1 H), 0.46 (tt,  $J = 5.2, 8.2$  Hz, 1 H), 0.30 – 0.39 (m, 1H), 0.08 (m, 1 H), –0.12 – –0.06 (m, 1 H), –0.26 – –0.17 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.51, 143.68, 134.93, 131.31, 130.93, 129.80, 127.08, 121.09, 115.64, 113.69, 55.22, 48.11, 39.35, 24.14, 20.68, 13.78, 2.83, 0.00 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_3\text{S}]$ : 395.1555, found: 395.1558.

**29a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.2$  Hz, 2 H), 7.32 (d,  $J = 8.1$  Hz, 2 H), 7.19 – 7.27 (m, 4 H), 6.39 (d,  $J = 8.1$  Hz, 1 H), 5.33 (d,  $J = 8.1$  Hz, 1 H), 3.93 (d,  $J = 11.5$  Hz, 1 H), 2.93 (d,  $J = 11.5$  Hz, 1 H), 2.44 (s, 3 H), 1.01 (d,  $J = 5.0$  Hz, 1 H), 0.90 (d,  $J = 4.9$  Hz, 1 H), 0.44 – 0.53 (m, 1 H), 0.40 (m, 1 H), 0.13 (m, 1 H), –0.11 – –0.03 (m, 1H) –0.21 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,

CDCl<sub>3</sub>)  $\delta$  143.84, 137.76, 134.79, 131.26, 129.87, 128.59, 127.07, 121.38, 115.47, 47.91, 39.29, 24.23, 21.60, 20.41, 13.74, 2.97, 2.91 ppm. HRMS (EI) calc. for [C<sub>22</sub>H<sub>22</sub>NO<sub>2</sub>SCl]: 399.1060, found: 399.1060.

**30a:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.23 (dd, *J* = 6.1, 9.3 Hz, 2 H), 6.97 (t, *J* = 8.7 Hz, 2 H), 6.39 (d, *J* = 8.2 Hz, 1 H), 5.33 (d, *J* = 8.1 Hz, 1 H), 3.94 (d, *J* = 11.4 Hz, 1 H), 2.94 (d, *J* = 11.5 Hz, 1 H), 2.43 (s, 3 H), 0.99 (d, *J* = 4.9 Hz, 1 H), 0.89 (d, *J* = 5.3 Hz, 1 H), 0.49 (td, *J* = 4.1, 3.4 Hz, 1 H), 0.35 – 0.44 (m, 1 H), 0.13 (m, 1 H), –0.07 (m, 1 H), –0.22 (m, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  143.78, 134.89, 131.50, 131.39, 129.85, 127.06, 121.30, 115.56, 115.40, 48.05, 39.24, 24.20, 21.58, 20.55, 13.74, 2.88 ppm. HRMS (EI) calc. for [C<sub>22</sub>H<sub>22</sub>NO<sub>2</sub>FS]: 383.1355, found: 383.1358.

**31a:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, *J* = 8.2 Hz, 2 H), 7.55 (d, *J* = 8.1 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 6.42 (d, *J* = 8.1 Hz, 1 H), 5.35 (d, *J* = 8.1 Hz, 1 H), 3.94 (d, *J* = 11.5 Hz, 1 H), 2.98 (d, *J* = 11.5 Hz, 1 H), 2.44 (s, 3 H), 1.07 (d, *J* = 5.1 Hz, 1 H), 0.96 (d, *J* = 5.0 Hz, 1 H), 0.36 – 0.51 (m, 2 H), 0.15 (m, 1 H), –0.08 (m, 1 H), –0.22 (m, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  143.90, 143.32, 134.80, 130.27, 129.89, 127.08, 125.40, 125.35, 121.63, 115.26, 47.87, 39.56, 24.33, 21.59, 20.40, 13.77, 2.95 ppm. HRMS (EI) calc. for [C<sub>23</sub>H<sub>22</sub>F<sub>3</sub>NO<sub>2</sub>S]: 433.1323, found: 433.1320.



**32a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.6$  Hz, 2 H), 7.27 – 7.32 (m, 4 H), 7.18 (d,  $J = 7.5$  Hz, 2 H), 6.38 (d,  $J = 7.9$  Hz, 1 H), 5.30 (d,  $J = 8.0$  Hz, 1 H), 3.96 (d,  $J = 11.4$  Hz, 1 H), 2.97 (d,  $J = 11.4$  Hz, 1 H), 2.43 (s, 3 H), 1.30 (s, 9 H), 1.00 (br s, 1 H), 0.95 (br s, 1 H), 0.42 (m, 2 H), 0.14 (d,  $J = 4.1$  Hz, 1 H),  $-0.16 - -0.07$  (m, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.88, 143.66, 136.01, 134.98, 129.79, 129.48, 127.09, 125.15, 121.15, 115.47, 48.04, 39.69, 34.47, 31.35, 24.03, 21.58, 20.74, 13.83, 2.78 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{31}\text{NO}_2\text{S}]$ : 421.2076, found: 421.2074.

**33a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.2$  Hz, 2 H), 7.46 (d,  $J = 8.0$  Hz, 2 H), 7.25 – 7.35 (m, 2 H), 7.21 (t,  $J = 7.9$  Hz, 2 H), 6.55 (d,  $J = 8.1$  Hz, 1 H), 5.48 (d,  $J = 8.1$  Hz, 1 H), 4.12 (d,  $J = 11.5$  Hz, 1 H), 3.14 (d,  $J = 11.5$  Hz, 1 H), 2.58 (s, 3 H), 2.47 (s, 3 H) 1.15 (d,  $J = 4.8$  Hz, 1 H), 1.09 (d,  $J = 4.7$  Hz, 1 H), 0.61 – 0.70 (m, 1 H), 0.49 – 0.58 (m, 1 H), 0.29 (m, 1 H) 0.06 – 0.14 (m, 1 H),  $-0.03 - 0.04$  (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.75, 139.13, 137.93, 134.99, 130.63, 129.85, 128.23, 127.81, 127.10, 126.96, 121.22, 115.64, 48.17, 40.09, 24.11, 21.60, 21.43, 20.66, 13.89, 2.87 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 379.1606.

**34a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.1$  Hz, 2 H), 7.45 (d,  $J = 8.1$  Hz, 2 H), 7.34 (t,  $J = 7.9$  Hz, 1 H), 7.00 (d,  $J = 7.6$  Hz, 1 H), 6.92 (dd,  $J = 3.6, 11.8$  Hz, 2 H), 6.54 (d,  $J = 8.1$  Hz, 1 H), 5.46 (d,  $J$

= 8.1 Hz, 1 H), 4.10 (d,  $J = 11.5$  Hz, 1 H), 3.91 (s, 3 H), 3.13 (d,  $J = 11.5$  Hz, 1 H), 2.56 (s, 3 H), 1.14 (d,  $J = 4.8$  Hz, 1 H), 1.08 (d,  $J = 4.8$  Hz, 1 H), 0.61 – 0.70 (m, 1 H), 0.48 – 0.57 (m, 1 H), 0.27 (m, 1 H), 0.07 – 0.12 (m, 1 H), –0.03 – 0.04 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.52, 143.77, 140.76, 134.92, 129.85, 129.35, 127.07, 122.29, 121.29, 115.79, 115.57, 112.24, 55.24, 48.03, 40.10, 24.25, 21.59, 20.68, 13.84, 2.86 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_3\text{S}]$ : 395.1555, found: 395.1558.

**35a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.2$  Hz, 2 H), 7.23 – 7.34 (m, 4 H), 7.16 – 7.25 (m, 2 H), 6.40 (d,  $J = 8.1$  Hz, 1 H), 5.34 (d,  $J = 8.1$  Hz, 1 H), 3.94 (d,  $J = 11.5$  Hz, 1 H), 2.97 (d,  $J = 11.5$  Hz, 1 H), 2.44 (s, 3 H), 1.00 (d,  $J = 5.0$  Hz, 1 H), 0.92 (d,  $J = 5.0$  Hz, 1 H), 0.47 – 0.56 (m, 1 H), 0.37 – 0.46 (m, 1 H), 0.14 (dt,  $J = 5.4, 9.6$  Hz, 1 H), –0.05 (m, 1 H), –0.20 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.86, 141.29, 134.86, 134.04, 130.01, 129.90, 129.70, 128.13, 127.32, 127.05, 121.45, 115.42, 47.84, 39.64, 24.31, 21.60, 20.43, 13.73, 2.92 ppm. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{22}\text{NO}_2\text{SCl}]$ : 399.1060, found: 399.1062.

**36a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.2$  Hz, 2 H), 7.30 (d,  $J = 8.1$  Hz, 2 H), 6.87 (d,  $J = 5.0$  Hz, 3 H), 6.38 (d,  $J = 8.1$  Hz, 1 H), 5.30 (d,  $J = 8.1$  Hz, 1 H), 3.94 (d,  $J = 11.4$  Hz, 1 H), 2.96 (d,  $J = 11.5$  Hz, 1 H), 2.43 (s, 3 H), 2.27 (s, 6 H), 1.00 (d,  $J = 4.8$  Hz, 1 H), 0.92 (d,  $J = 4.8$  Hz, 1 H), 0.43 – 0.51 (m, 1 H), 0.33 – 0.42 (m, 1 H),

0.14 (m, 1 H), -0.07 - -0.01 (m, 1 H), -0.16 - -0.09 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.64, 139.06, 137.73, 135.07, 129.79, 128.65, 127.69, 127.10, 121.16, 115.46, 48.17, 40.09, 24.01, 21.57, 21.25, 20.78, 13.88, 2.75 ppm. HRMS (EI) calc. for  $[\text{C}_{24}\text{H}_{27}\text{NO}_2\text{S}]$ : 393.1763, found: 393.1759.

**37a**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 9.5$  Hz, 2 H), 7.76 (m, 2 H), 7.63 (d,  $J = 8.1$  Hz, 2 H), 7.41 (d,  $J = 5.1$  Hz, 3 H), 7.28 (d,  $J = 8.2$  Hz, 2 H), 6.56 (d,  $J = 8.2$  Hz, 1 H), 5.42 (d,  $J = 8.1$  Hz, 1 H), 3.88 (d,  $J = 11.9$  Hz, 1 H), 3.40 (d,  $J = 11.9$  Hz, 1 H), 2.42 (s, 3 H), 1.07 (s, 2 H), 0.39 - 0.43 (m, 1 H), 0.07 - 0.23 (m, 2 H), -0.41 - -0.24 (m, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.79, 136.58, 134.95, 134.00, 132.05, 129.87, 128.70, 128.42, 128.07, 127.19, 127.06, 125.87, 125.68, 125.57, 121.35, 114.34, 46.49, 38.18, 25.26, 21.61, 21.14, 13.60, 3.12, 2.63 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{25}\text{NO}_2\text{S}]$ : 415.1606, found: 415.1608.

**38a**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 8.1$  Hz, 2 H), 7.22 (d,  $J = 8.0$  Hz, 2 H), 6.72 (s, 2 H), 6.35 (d,  $J = 8.1$  Hz, 1 H), 5.16 (d,  $J = 8.1$  Hz, 1 H), 3.74 (d,  $J = 12.0$  Hz, 1 H), 2.84 (d,  $J = 12.0$  Hz, 1 H), 2.34 (s, 3 H), 2.17 (d,  $J = 12.1$  Hz, 6 H), 2.13 (s, 3 H), 0.97 (d,  $J = 5.0$  Hz, 1 H), 0.58 (d,  $J = 4.7$  Hz, 1 H), 0.42 - 0.51 (m, 1 H), 0.25 - 0.34 (m, 1 H), 0.07 - 0.16 (m, 1 H), -0.07 (dd,  $J = 4.4, 9.8$  Hz, 1 H), -0.31 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.73, 138.67, 138.55, 136.45, 135.02, 129.78, 129.56, 129.08, 127.07,

121.11, 114.55, 44.73, 37.46, 25.27, 22.77, 21.59, 20.85, 20.38, 13.11, 3.65, 1.84 ppm. HRMS (EI) calc. for [C<sub>25</sub>H<sub>29</sub>NO<sub>2</sub>S]: 407.1919, found: 407.1921.

**39a:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 8.2 Hz, 2 H), 7.22 (m, 7 H), 5.34 (s, 1 H), 4.18 (d, *J* = 12.8 Hz, 1 H), 3.11 (d, *J* = 12.8 Hz, 1 H), 2.34 (s, 3 H), 1.86 (s, 3 H), 1.07 (d, *J* = 5.3 Hz, 1 H), 0.88 (d, *J* = 5.2 Hz, 1 H), 0.45 – 0.54 (m, 1 H), 0.28 – 0.37 (m, 1 H), 0.07 (m, 1 H), –0.15 (m, 1 H), –0.27 – –0.21 (m, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 143.10, 139.16, 138.73, 130.03, 129.88, 129.63, 128.31, 126.89, 126.62, 120.52, 50.46, 41.67, 24.92, 21.51, 20.77, 18.76, 14.21, 2.98 ppm. HRMS (EI) calc. for [C<sub>23</sub>H<sub>25</sub>NO<sub>2</sub>S]: 379.1606, found: 379.1608.

**40a:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.24 – 7.39 (m, 5 H), 6.23 (d, *J* = 5.9 Hz, 1 H), 5.17 (d, *J* = 5.9 Hz, 1 H), 4.07 (d, *J* = 10.5 Hz, 1 H), 3.80 (d, *J* = 10.5 Hz, 1 H), 1.31 (d, *J* = 4.5 Hz, 1 H), 1.10 (d, *J* = 4.4 Hz, 1 H), 0.52 (m, 1 H), 0.39 – 0.43 (m, 1 H), 0.21 (m, 1 H), –0.10 – –0.01 (m, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 141.55, 138.85, 130.11, 128.27, 126.80, 109.74, 68.47, 38.76, 23.11, 20.61, 13.77, 2.65, 2.47 ppm. HRMS (EI) calc. for [C<sub>15</sub>H<sub>16</sub>O]: 212.1201, found 212.1200.

**1b:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.89–0.98 (m, 1 H), 1.12–1.18 (m, 2 H), 1.66–1.89 (m, 4 H), 2.31 (t, *J* = 9.2 Hz, 1 H), 2.52 (d, *J* = 11.6 Hz, 2 H), 3.03 (t, *J* = 10.6 Hz, 1 H), 3.50–3.57 (m, 1 H), 4.22 (dd, *J* = 9.9, 5.0 Hz, 1 H), 5.45 (d, *J* = 5.9 Hz, 1 H), 6.39 (d, *J* = 5.9

Hz, 1 H), 7.11–7.25 (m, 5 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  25.5, 25.9, 33.9, 48.9, 53.4, 56.8, 72.1, 98.9, 124.0, 126.5, 127.77, 127.81, 128.5, 132.7, 142.9, 145.4 ppm. HRMS (EI) calc. for  $[\text{C}_{18}\text{H}_{20}\text{O}]$ : 252.1514, found: 252.1515.

**2b**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86–0.98 (m, 1 H), 1.18–1.26 (m, 2 H), 1.70–1.88 (m, 4 H), 2.29 (t,  $J = 9.2$  Hz, 1 H), 2.42 (s, 3 H), 2.53–2.59 (m, 2 H), 2.63 (d,  $J = 11.5$  Hz, 1 H), 2.77 (br s, 1 H), 4.03 (dd,  $J = 10.9, 4.5$  Hz, 1 H), 5.69 (d,  $J = 8.0$  Hz, 1 H), 6.69 (d,  $J = 7.9$  Hz, 1 H), 7.14 (d,  $J = 6.9$  Hz, 2 H), 7.24–7.33 (m, 5 H), 7.60 (d,  $J = 8.1$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 25.3, 25.6, 25.7, 33.6, 48.0, 49.5, 53.8, 57.6, 104.0, 124.6, 125.3, 126.6, 127.0, 127.7, 128.5, 129.8, 134.9, 136.0, 142.0, 143.7 ppm. HRMS (EI) calc. for  $[\text{C}_{25}\text{H}_{27}\text{NO}_2\text{S}]$ : 405.1763, found: 405.1759.

**3b**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.09 (s, 3 H), 1.19–1.35 (m, 3 H), 1.76–1.91 (m, 4 H), 2.64 (d,  $J = 14.4$ , 1 H), 2.81 (br s, 1 H), 3.16–3.20 (m, 1 H), 3.78 (dd,  $J = 12.3, 10.0$  Hz, 1 H), 4.36 (dd,  $J = 9.9, 4.7$  Hz, 1 H), 5.60 (d,  $J = 5.8$  Hz, 3 H), 6.52 (d,  $J = 5.8$  Hz, 1 H), 7.21 (t,  $J = 7.2$  Hz, 1 H), 7.33 (t,  $J = 7.6$  Hz, 2 H), 7.43 (d,  $J = 7.6$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  18.6, 25.4, 25.6, 26.7, 49.8, 51.1, 56.9, 68.7, 99.8, 122.8, 125.9, 126.1, 128.3, 130.6, 145.4, 149.6 ppm. HRMS (EI) calc. for  $[\text{C}_{19}\text{H}_{22}\text{O}]$ : 266.1671, found: 266.1668.

**4b**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86–0.97 (m, 1 H), 1.16–1.26 (m, 2 H), 1.64–1.87 (m, 4 H), 2.24 (m, 1 H), 2.42 (s, 3 H), 2.47–2.63

(m, 2 H), 2.59 (dd,  $J = 12.0, 10.8$  Hz, 1 H), 2.69–2.76 (m, 1 H), 3.81 (s, 3 H), 4.02 (dd,  $J = 10.8, 4.4$  Hz, 1 H), 5.68 (d,  $J = 8.0$  Hz, 1 H), 6.69 (d,  $J = 8.0$  Hz, 1 H), 6.84 (d,  $J = 8.5$  Hz, 2 H), 7.06 (d,  $J = 8.5$  Hz, 2 H), 7.27 (d,  $J = 8.2$  Hz, 2 H), 7.60 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 25.3, 25.6, 25.7, 33.6, 48.0, 49.6, 53.8, 55.3, 56.9, 104.0, 113.9, 124.7, 125.2, 127.0, 128.6, 129.8, 134.0, 135.0, 136.0, 143.7, 158.3 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{29}\text{NO}_3\text{S}]$ : 435.1868, found: 435.1873.

**5b**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.77–0.88 (m, 1 H), 1.04–1.12 (m, 2 H), 1.60–1.83 (m, 4 H), 2.18 (m, 1 H), 2.25 (s, 3 H), 2.32 (s, 3 H), 2.39–2.49 (m, 2 H), 2.51 (dd,  $J = 11.9, 11.0$  Hz, 1 H), 2.65–2.68 (m, 1 H), 3.95 (dd,  $J = 11.0, 4.7$  Hz, 1 H), 5.59 (d,  $J = 8.0$  Hz, 1 H), 6.61 (d,  $J = 8.0$  Hz, 1 H), 6.95 (d,  $J = 7.9$  Hz, 2 H), 7.03 (d,  $J = 7.9$  Hz, 2 H), 7.18 (d,  $J = 8.1$  Hz, 2 H), 7.51 (d,  $J = 8.1$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  20.9, 21.5, 25.2, 25.5, 25.6, 33.5, 47.7, 49.4, 53.7, 57.1, 103.9, 124.6, 125.1, 126.9, 127.5, 129.0, 129.7, 134.8, 135.8, 136.0, 138.8, 143.6 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{29}\text{NO}_2\text{S}]$ : 419.1919, found: 419.1917

**6b**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.71 (s, 3 H), 2.42 (s, 3 H), 2.57–2.67 (m, 3 H), 2.75–2.90 (m, 2 H), 4.06 (dd,  $J = 11.0, 4.3$  Hz, 1 H), 5.69 (d,  $J = 8.0$  Hz, 1 H), 6.70 (d,  $J = 8.0$  Hz, 1 H), 7.17 (d,  $J = 7.0$  Hz, 2 H), 7.23–7.33 (m, 5 H), 7.60 (d,  $J = 8.1$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.6, 21.5, 46.3, 48.7, 49.4, 104.2, 125.1, 126.6, 127.0, 127.3, 127.8, 128.5, 129.8, 130.7, 134.9, 142.7, 143.7

ppm. HRMS (EI) calc. for [C<sub>22</sub>H<sub>23</sub>NO<sub>2</sub>S]: 365.1449, found: 365.1451.

**7b:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.95 (d, *J* = 6.8 Hz, 3 H), 1.67 (s, 3 H), 2.18 (dd, *J* = 10.9, 8.2 Hz, 1 H), 2.43 (s, 3 H), 2.48 (t, *J* = 11.6 Hz, 1 H), 2.69–2.71 (m, 2 H), 3.99 (dd, *J* = 10.9, 4.5 Hz, 1 H), 5.69 (d, *J* = 8.0 Hz, 1 H), 6.70 (d, *J* = 7.9 Hz, 1 H), 7.15 (d, *J* = 6.7 Hz, 2 H), 7.23–7.34 (m, 5 H), 7.59 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 11.6, 17.0, 21.6, 47.7, 49.3, 51.2, 58.8, 104.3, 125.3, 126.7, 126.9, 127.1, 127.9, 128.4, 129.8, 134.1, 134.8, 141.6, 143.7 ppm. HRMS (EI) calc. for [C<sub>23</sub>H<sub>25</sub>NO<sub>2</sub>S]: 379.1606, found: 379.1607.

**8b:** <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>) δ 2.42 (s, 3 H), 2.68 (d, *J* = 11.3 Hz, 1 H), 2.81–2.88 (m, 1 H), 3.81 (d, *J* = 10.3 Hz, 1 H), 3.88 (dd, *J* = 11.0, 4.8 Hz, 1 H), 5.75 (s, 1 H), 5.82 (d, *J* = 7.9 Hz, 1 H), 6.55 (d, *J* = 7.5 Hz, 2 H), 6.65 (d, *J* = 7.7 Hz, 2 H), 6.86 (d, *J* = 7.9 Hz, 1 H), 7.01–7.19 (m, 7 H), 7.23–7.29 (m, 4 H), 7.38 (d, *J* = 7.4 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H) ppm. <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>) δ 21.6, 45.8, 48.6, 59.1, 65.7, 105.3, 126.1, 126.4, 126.9, 127.0, 127.4, 127.6, 127.9, 128.2, 128.3, 129.5, 129.6, 129.9, 134.6, 135.0, 138.2, 142.9, 144.0, 147.2 ppm. HRMS (EI) calc. for [C<sub>33</sub>H<sub>29</sub>NO<sub>2</sub>S]: 503.1919, found: 503.1916.

**9b:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.44 (s, 3 H), 2.65–2.71 (m, 2 H), 2.93–3.00 (m, 1 H), 4.00 (d, *J* = 9.6 Hz, 1 H), 4.01–4.07 (m, 1 H), 5.49 (s, 1 H), 5.75 (d, *J* = 8.0 Hz, 1 H), 6.82 (d, *J* = 7.9 Hz, 1 H), 6.92–6.94 (m, 2 H), 7.01–7.03 (m, 2 H), 7.17 (d, *J* = 6.8 Hz, 3 H),

7.25 (d,  $J = 6.9$  Hz, 3 H), 7.29 (d,  $J = 8.0$  Hz, 2 H), 7.62 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 48.1, 49.0, 59.3, 61.7, 105.2, 124.6, 126.6, 126.9, 127.0, 127.4, 127.5, 127.9, 128.3, 128.5, 130.0, 134.8, 135.7, 140.4, 143.6, 144.0 ppm. HRMS (EI) calc. for  $[\text{C}_{27}\text{H}_{25}\text{NO}_2\text{S}]$ : 427.1606, found: 427.1603.

**12c**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.36–1.49 (m, 2 H), 1.51–1.68 (m, 6 H), 2.23–2.42 (m, 2 H), 3.80 (d,  $J = 11.0$  Hz, 1 H), 3.90 (d,  $J = 11.0$  Hz, 1 H), 5.27 (d,  $J = 17.3$  Hz, 1 H), 5.35 (d,  $J = 10.7$  Hz, 1 H), 5.81 (d,  $J = 6.3$  Hz, 1 H), 6.20 (dd,  $J = 17.3, 10.6$  Hz, 1 H), 6.47 (d,  $J = 6.3$  Hz, 1 H), 7.18–7.35 (m, 5 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  26.5, 26.7, 28.0, 30.7, 33.3, 51.1, 75.4, 103.8, 116.3, 124.7, 126.4, 127.3, 128.4, 135.2, 139.0, 143.2, 144.4 ppm. HRMS (EI) calc. for  $[\text{C}_{19}\text{H}_{22}\text{O}]$ : 266.1671, found: 266.1672.

**13c**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.43–1.59 (m, 6 H), 1.83 (s, 3 H), 1.99–2.24 (m, 3 H), 2.33–2.39 (m, 1 H), 3.17 (s, 1 H), 3.90 (dd,  $J = 10.8, 3.2$  Hz, 1 H), 4.29 (dd,  $J = 10.8, 1.3$  Hz, 1 H), 4.76 (s, 1 H), 4.87 (s, 1 H), 5.64 (dd,  $J = 6.3, 0.9$  Hz, 1 H), 6.37 (d,  $J = 6.3$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.3, 26.9, 27.9, 28.0, 29.5, 30.0, 43.3, 69.0, 120.6, 112.3, 120.3, 133.3, 143.7, 144.2 ppm. HRMS (EI) calc. for  $[\text{C}_{14}\text{H}_{20}\text{O}]$ : 204.1514, found: 204.1512.

**14c**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.05–1.14 (m, 2 H), 1.34–1.61 (m, 6 H), 2.18–2.26 (m, 1 H), 2.34–2.44 (m, 1 H), 2.40 (s, 3 H), 2.90 (d,  $J = 11.6$  Hz, 1 H), 3.59 (d,  $J = 11.4$  Hz, 1 H), 5.19 (d,  $J = 17.4$  Hz, 1 H), 5.27 (d,  $J = 10.6$  Hz, 1 H), 5.96 (d,  $J = 8.5$  Hz, 1 H),



6.09 (dd,  $J = 17.3, 10.6$  Hz, 1 H), 6.59 (d,  $J = 8.5$  Hz, 1 H), 7.16–7.21 (m, 1 H), 7.25–7.26 (m, 6 H), 7.59 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 26.4, 26.7, 28.0, 31.2, 33.7, 50.9, 55.5, 108.6, 117.2, 122.6, 125.5, 126.4, 127.0, 127.1, 128.4, 129.8, 134.8, 138.5, 138.7, 143.8, 145.4 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{29}\text{NO}_2\text{S}]$ : 419.1919, found: 419.1919.

**15c**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.06 (br s, 2 H), 1.27–1.59 (m, 7 H), 2.09–2.17 (m, 1 H), 2.40 (s, 3 H), 2.82 (d,  $J = 11.7$  Hz, 1 H), 3.46 (d,  $J = 11.6$  Hz, 1 H), 3.70 (s, 3 H), 5.10 (d,  $J = 17.4$  Hz, 1 H), 5.17 (d,  $J = 10.6$  Hz, 1 H), 5.86 (d,  $J = 8.5$  Hz, 1 H), 6.00 (dd,  $J = 17.2, 10.6$  Hz, 1 H), 6.51 (d,  $J = 8.5$  Hz, 1 H), 6.71 (d,  $J = 8.4$  Hz, 2 H), 7.07 (d,  $J = 8.5$  Hz, 2 H), 7.17 (d,  $J = 7.8$  Hz, 2 H), 7.51 (d,  $J = 7.9$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 26.4, 26.9, 28.1, 31.3, 33.6, 50.2, 55.2, 55.5, 108.6, 113.7, 116.9, 122.5, 125.6, 127.1, 128.0, 129.7, 134.8, 137.3, 138.7, 139.0, 143.7, 158.0 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{29}\text{NO}_3\text{S}]$ : 435.1868, found: 435.1866.

**16c**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.45 (br s, 6 H), 1.99–2.09 (m, 3 H), 2.23–2.27 (m, 1 H), 2.34 (s, 3 H), 2.83 (dd,  $J = 11.4, 3.3$  Hz, 1 H), 3.36 (br s, 1 H), 3.82 (d,  $J = 11.3$  Hz, 1 H), 4.84 (d,  $J = 10.4$  Hz, 1 H), 4.89 (d,  $J = 17.3$  Hz, 1 H), 5.54 (ddd,  $J = 17.2, 10.6, 5.9$  Hz, 1 H), 5.64 (d,  $J = 8.5$  Hz, 1 H), 6.51 (d,  $J = 8.4$  Hz, 1 H), 7.22 (d,  $J = 8.1$  Hz, 2 H), 7.59 (d,  $J = 8.2$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 26.7, 27.9, 28.0, 29.8, 30.1, 38.4, 48.5, 105.8, 115.4, 120.4, 123.1, 127.2, 129.7, 134.9, 136.1, 137.0, 143.7 ppm. HRMS

(EI) calc. for [C<sub>20</sub>H<sub>25</sub>NO<sub>2</sub>S]: 343.1606, found: 343.1605.

**17c:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.64 (d, *J* = 7.1 Hz, 3 H), 2.33 (s, 3 H), 3.24 (d, *J* = 11.6 Hz, 1 H), 3.70 (d, *J* = 11.6 Hz, 1 H), 4.67 (dd, *J* = 17.3, 0.6 Hz, 1 H), 4.98 (q, *J* = 6.9 Hz, 1 H), 5.10 (d, *J* = 11.2 Hz, 1 H), 5.68 (d, *J* = 2.5 Hz, 1 H), 5.73 (dd, *J* = 14.5, 7.7 Hz, 1 H), 6.55 (d, *J* = 8.3 Hz, 1 H), 7.09–7.19 (m, 7 H), 7.52 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 12.9, 21.6, 50.6, 52.0, 105.2, 117.6, 122.4, 124.4, 126.8, 127.1, 128.0, 128.4, 129.8, 133.9, 134.9, 140.9, 140.6, 143.9 ppm. HRMS (EI) calc. for [C<sub>21</sub>H<sub>23</sub>NO<sub>2</sub>S]: 365.1449, found: 365.1449.

**18c:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.02 (s, 3 H), 1.73 (s, 3 H), 2.32 (s, 3 H), 2.87 (d, *J* = 11.7 Hz, 1 H), 3.52 (d, *J* = 11.7 Hz, 1 H), 5.04 (d, *J* = 17.3 Hz, 1 H), 5.17 (d, *J* = 10.6 Hz, 1 H), 5.80 (d, *J* = 8.5 Hz, 1 H), 5.98 (dd, *J* = 17.3, 10.6 Hz, 1 H), 6.51 (d, *J* = 8.4 Hz, 1 H), 7.11–7.20 (m, 7 H), 7.52 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 21.6, 24.0, 51.0, 55.4, 109.2, 117.1, 122.2, 126.4, 126.5, 127.2, 127.7, 128.5, 129.7, 130.4, 134.9, 138.1, 143.7, 145.0 ppm. HRMS (EI) calc. for [C<sub>23</sub>H<sub>25</sub>NO<sub>2</sub>S]: 379.1606, found: 379.1606.

**19c:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.66 (d, *J* = 7.0 Hz, 3 H), 2.42 (s, 3 H), 2.74 (br s, 1 H), 3.33 (ddd, *J* = 18.7, 11.4, 5.7 Hz, 2 H), 5.03 (s, 1 H), 5.08 (d, *J* = 7.9 Hz, 1 H), 5.12–5.16 (m, 1 H), 5.57 (ddd, *J* = 17.5, 10.2, 7.6 Hz, 1 H), 5.69 (d, *J* = 8.3 Hz, 1 H), 6.70 (d, *J* = 8.2 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.67 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 12.8, 21.6, 43.3, 48.3, 76.6, 105.2,

117.0, 120.1, 124.8, 127.1, 129.7, 129.9, 137.0, 143.9 ppm. HRMS (EI) calc. for [C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub>S]: 289.1163, found: 289.1161.

**20c**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.41–0.46 (m, 3 H), 1.42–1.50 (m, 2 H), 1.70 (s, 3 H), 2.31 (s, 3 H), 2.93 (d, *J* = 11.7 Hz, 1 H), 3.46 (d, *J* = 11.7 Hz, 1 H), 5.01 (d, *J* = 17.3 Hz, 1 H), 5.16 (d, *J* = 10.6 Hz, 1 H), 5.79 (d, *J* = 8.4 Hz, 1 H), 6.00 (dd, *J* = 17.2, 10.6 Hz, 1 H), 6.52 (d, *J* = 8.4 Hz, 1 H), 7.17 (d, *J* = 5.8 Hz, 7 H), 7.51 (d, *J* = 8.0 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 10.8, 18.1, 21.6, 29.5, 51.3, 55.5, 110.0, 117.1, 122.5, 126.5, 127.1, 127.2, 127.7, 128.4, 130.0, 134.8, 135.4, 138.8, 143.8, 145.0 ppm. HRMS (EI) calc. for [C<sub>24</sub>H<sub>27</sub>NO<sub>2</sub>S]: 393.1762, found: 393.1762.

**21c**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.36 (s, 3 H), 3.88 (q, *J* = 11.0 Hz, 2 H), 5.27–5.39 (m, 3 H), 6.24 (dd, *J* = 17.0, 11.0 Hz, 2 H), 7.18 (t, *J* = 7.5 Hz, 4 H), 7.26–7.33 (m, 4 H), 7.38 (d, *J* = 7.5 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 23.4, 50.9, 75.3, 106.3, 117.0, 126.6, 126.7, 127.4, 128.2, 128.3, 128.6, 128.7, 128.9, 129.7, 137.8, 143.2, 143.6 ppm. HRMS (EI) calc. for [C<sub>21</sub>H<sub>20</sub>O]: 288.1514, found: 288.1514.

**22c**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.72 (ddd, *J* = 23.5, 16.6, 7.5 Hz, 2 H), 3.87 (q, *J* = 11.0 Hz, 2 H), 5.32 (d, *J* = 12.3 Hz, 1 H), 5.41 (dd, *J* = 14.1, 7.7 Hz, 2 H), 6.61 (dd, *J* = 17.3, 10.6 Hz, 1 H), 6.36 (d, *J* = 5.9 Hz, 1 H), 6.85 (d, *J* = 7.1 Hz, 2 H), 7.08 (dd, *J* = 15.2, 7.3 Hz, 2 H), 7.14–7.19 (m, 2 H), 7.25 (t, *J* = 7.4 Hz, 2 H), 7.34 (d, *J* = 7.3 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 35.6, 50.9, 74.7,

109.2, 117.1, 125.9, 126.2, 127.0, 127.8, 128.3, 128.6, 133.9, 138.3, 140.9, 142.6, 143.4 ppm. HRMS (EI) calc. for [C<sub>21</sub>H<sub>20</sub>O]: 288.1514, found: 288.1514.

**23c:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.18–1.52 (m, 8 H), 1.63 (d, *J* = 5.8 Hz, 3 H), 2.15–2.18 (m, 1 H), 2.27–2.30 (m, 1 H), 2.330 (s, 3 H), 2.85 (d, *J* = 11.7 Hz, 1 H), 3.45 (d, *J* = 11.7 Hz, 1 H), 5.48 (q, *J* = 6.0 Hz, 1 H), 5.57 (d, *J* = 16.0 Hz, 1 H), 5.86 (d, *J* = 8.5 Hz, 1 H), 6.52 (d, *J* = 8.5 Hz, 1 H), 7.08–7.12 (m, 1 H), 7.16–7.19 (m, 6 H), 7.52 (d, *J* = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 18.4, 21.6, 26.5, 26.7, 28.0, 31.2, 33.7, 50.1, 55.8, 108.4, 122.5, 126.2, 126.3, 127.1, 127.5, 128.3, 129.7, 131.6, 135.0, 138.1, 143.6, 146.1 ppm. HRMS (EI) calc. for [C<sub>27</sub>H<sub>32</sub>NO<sub>2</sub>S]: 433.2075, found: 433.2075.

**26d:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 8.1 Hz, 2 H), 7.15 – 7.17 (m, 7 H), 6.44 (d, *J* = 8.0 Hz, 1 H), 5.71 (t, *J* = 3.7 Hz, 1 H), 5.49 (d, *J* = 8.1 Hz, 1 H), 4.26 (d, *J* = 11.6 Hz, 1 H), 2.83 (d, *J* = 11.6 Hz, 1 H), 2.39 (s, 3 H), 2.14 (dd, *J* = 3.5, 7.7 Hz, 2 H), 1.82 – 1.87 (m, 1 H), 1.41 – 1.51 (m, 2 H), 1.26 – 1.27 (d, *J* = 4.5 Hz, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 143.42, 142.53, 135.25, 132.73, 129.61, 127.97, 127.40, 126.89, 126.21, 124.43, 123.80, 109.76, 54.28, 42.17, 34.81, 25.52, 21.52, 17.51 ppm. HRMS (EI) calc. for [C<sub>22</sub>H<sub>23</sub>NO<sub>2</sub>S]: 365.1450, found: 365.1446.

**27d:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 8.1 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.96 (d, *J* = 8.1 Hz, 2 H), 6.45 (d, *J* = 8.0 Hz, 1 H), 5.69 (t, *J* = 3.6 Hz, 1 H), 5.48 (d, *J* = 8.0

Hz, 1 H), 4.23 (d,  $J = 11.6$  Hz, 1 H), 2.82 (d,  $J = 11.6$  Hz, 1 H), 2.39 (s, 3 H), 2.29 (s, 3 H), 2.11 – 2.14 (m, 2 H), 1.82 (td,  $J = 3.6$ , 5.5 Hz, 1 H), 1.39 – 1.48 (m, 2 H), 1.25 (t,  $J = 11.3$  Hz, 1 H) ppm.

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.29, 139.46, 135.68, 135.39, 132.88, 129.51, 128.64, 127.24, 126.88, 124.28, 123.72, 109.78, 54.34, 41.82, 34.77, 25.53, 21.56, 20.99, 17.55 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 379.1604.

**28d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.3$  Hz, 2 H), 7.08 (d,  $J = 8.0$  Hz, 2 H), 6.98 (d,  $J = 8.9$  Hz, 2 H), 6.61 (d,  $J = 8.9$  Hz, 2 H), 6.40 (d,  $J = 8.0$  Hz, 1 H), 5.61 (t,  $J = 3.8$  Hz, 1 H), 5.41 (d,  $J = 8.1$  Hz, 1 H), 4.12 (d,  $J = 11.6$  Hz, 1 H), 3.70 (s, 3 H), 2.76 (d,  $J = 11.7$  Hz, 1 H), 2.32 (s, 3 H), 2.06 (dd,  $J = 3.9$ , 8.1 Hz, 2 H), 1.07 – 1.75 (m, 1 H), 1.32 – 1.43 (m, 2 H), 1.19 – 1.20 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  157.96, 143.34, 135.47, 134.36, 132.96, 129.53, 128.39, 126.82, 124.28, 123.71, 113.25, 109.77, 55.08, 54.44, 41.51, 34.76, 25.54, 21.50, 17.52 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_3\text{S}]$ : 395.1555, found: 395.1552.

**29d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.3$  Hz, 2 H), 7.16 (d,  $J = 8.1$  Hz, 2 H), 7.00 – 7.06 (m, 4 H), 6.53 (d,  $J = 8.0$  Hz, 1 H), 5.72 (t,  $J = 3.7$  Hz, 1 H), 5.50 (d,  $J = 8.0$  Hz, 1 H), 4.16 (d,  $J = 12.0$  Hz, 1 H), 2.93 (d,  $J = 12.0$  Hz, 1 H), 2.43 (s, 3 H), 2.11 – 2.15 (m, 2 H), 1.79 – 1.84 (m, 1 H), 1.43 – 1.52 (m, 2 H), 1.10 – 1.19 (m,

1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.62, 141.16, 135.56, 132.34, 132.17, 129.56, 128.83, 127.96, 126.64, 124.72, 123.91, 109.39, 54.35, 41.85, 34.50, 25.46, 21.61, 17.49 ppm. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{22}\text{NO}_2\text{SCI}]$ : 399.1060, found: 399.1062.

**30d**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 8.2$  Hz, 2 H), 7.08 (d,  $J = 8.1$  Hz, 2 H), 7.00 (dd,  $J = 5.4, 8.7$  Hz, 2 H), 6.71 (t,  $J = 8.7$  Hz, 2 H), 6.43 (d,  $J = 8.0$  Hz, 1 H), 5.62 (t,  $J = 3.7$  Hz, 1 H), 5.42 (d,  $J = 8.0$  Hz, 1 H), 4.10 (d,  $J = 11.7$  Hz, 1 H), 2.80 (d,  $J = 11.8$  Hz, 1 H), 2.32 (s, 3 H), 2.04 – 2.07 (m, 2 H), 1.72 – 1.76 (m, 1 H), 1.34 – 1.43 (m, 2 H), 1.05 – 1.18 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.56, 135.52, 132.63, 129.58, 129.03, 128.92, 126.73, 124.57, 123.88, 114.77, 114.49, 109.55, 54.47, 41.72, 34.69, 25.47, 21.45, 17.45 ppm. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{22}\text{NO}_2\text{FS}]$ : 383.1355, found: 383.1353.

**31d**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 8.3$  Hz, 2 H), 7.28 (d,  $J = 8.8$  Hz, 2 H), 7.16 (d,  $J = 8.3$  Hz, 2 H), 7.06 (d,  $J = 8.1$  Hz, 2 H), 6.44 (d,  $J = 8.0$  Hz, 1 H), 5.67 (t,  $J = 3.6$  Hz, 1 H), 5.43 (d,  $J = 8.1$  Hz, 1 H), 4.16 (d,  $J = 11.9$  Hz, 1 H), 2.87 (d,  $J = 11.9$  Hz, 1 H), 2.29 (s, 3 H), 2.05 – 2.08 (m, 2 H), 1.75 – 1.79 (m, 1 H), 1.32 – 1.51 (m, 2 H), 0.98 – 1.11 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.71, 135.40, 132.09, 129.58, 127.82, 126.70, 124.91, 124.83, 124.78, 124.73, 124.00, 109.24, 54.14, 42.30, 34.58, 25.40, 21.36, 17.44 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{22}\text{F}_3\text{NO}_2\text{S}]$ : 433.1323, found:

133.1326.

**32d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 8.2$  Hz, 2 H), 7.12 – 7.16 (m, 4 H), 7.03 (d,  $J = 8.4$  Hz, 2 H), 6.33 (d,  $J = 8.0$  Hz, 1 H), 5.62 (t,  $J = 3.6$  Hz, 1 H), 5.40 (d,  $J = 8.1$  Hz, 1 H), 4.21 (d,  $J = 11.3$  Hz, 1 H), 2.69 (d,  $J = 11.4$  Hz, 1 H), 2.32 (s, 3 H), 2.05 – 2.07 (m, 2 H), 1.70 – 1.75 (m, 1 H), 1.32 – 1.43 (m, 2 H), 1.23 (s, 9 H), 1.23 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  148.82, 143.37, 139.30, 135.08, 132.88, 129.62, 127.09, 126.98, 124.81, 124.15, 123.70, 109.76, 71.35, 54.00, 42.63, 41.74, 35.02, 34.27, 31.43, 25.53, 21.57, 17.52 ppm. HRMS (EI) calc. for  $[\text{C}_{26}\text{H}_{31}\text{NO}_2\text{S}]$ : 421.2076, found: 421.2079.

**33d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.2$  Hz, 2 H), 7.07 (d,  $J = 8.1$  Hz, 2 H), 6.98 (d,  $J = 7.7$  Hz, 1 H), 6.85 – 6.90 (m, 3 H), 6.39 (d,  $J = 8.0$  Hz, 1 H), 5.62 (t,  $J = 3.6$  Hz, 1 H), 5.43 (d,  $J = 8.1$  Hz, 1 H), 4.16 (d,  $J = 11.6$  Hz, 1 H), 2.77 (d,  $J = 11.6$  Hz, 1 H), 2.31 (s, 3 H), 2.17 (s, 3 H), 2.04 – 2.07 (m, 2 H), 1.75 – 1.80 (m, 1 H), 1.32 – 1.42 (m, 2 H), 1.13 – 1.20 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.27, 142.57, 137.21, 135.38, 132.83, 129.51, 128.01, 127.79, 127.02, 126.79, 124.60, 124.40, 123.70, 109.90, 54.48, 42.07, 34.79, 25.55, 21.67, 21.52, 17.58 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 379.1607.

**34d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.2$  Hz, 2 H), 7.00 – 7.09 (m, 3 H), 6.71 (d,  $J = 7.5$  Hz, 1 H), 6.59 (d,  $J = 7.5$  Hz, 2 H),

6.40 (d,  $J = 8.0$  Hz, 1 H), 5.62 (t,  $J = 3.5$  Hz, 1 H), 5.42 (d,  $J = 8.0$  Hz, 1 H), 4.16 (d,  $J = 11.6$  Hz, 1 H), 3.66 (s, 3 H), 2.76 (d,  $J = 11.6$  Hz, 1 H), 2.30 (s, 3 H), 2.05 – 2.06 (m, 2 H), 1.79 (dd,  $J = 3.5, 12.7$  Hz, 1 H), 1.32 – 1.41 (m, 2 H), 1.19 (dd,  $J = 8.7, 11.6$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.14, 144.40, 143.36, 135.31, 132.74, 129.56, 128.88, 126.81, 124.50, 123.74, 119.74, 114.04, 111.13, 109.81, 55.03, 54.37, 42.22, 34.67, 25.51, 21.53, 17.55 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_3\text{S}]$ : 395.1555, found: 395.1559.

**35d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 8.2$  Hz, 2 H), 7.16 (d,  $J = 8.1$  Hz, 2 H), 7.03 – 7.07 (m, 4 H), 6.52 (d,  $J = 8.0$  Hz, 1 H), 5.72 (t,  $J = 3.7$  Hz, 1 H), 5.51 (d,  $J = 8.1$  Hz, 1 H), 4.16 (d,  $J = 11.8$  Hz, 1 H), 2.90 (d,  $J = 11.9$  Hz, 1 H), 2.39 (s, 3 H), 2.12 – 2.15 (m, 2 H), 1.81 – 1.86 (m, 1 H), 1.42 – 1.52 (m, 2 H), 1.11 – 1.22 (m, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.07, 143.52, 135.31, 133.80, 132.14, 129.61, 129.26, 127.90, 126.67, 126.46, 125.49, 124.92, 123.93, 109.51, 54.35, 42.18, 34.55, 25.44, 21.55, 17.49 ppm. HRMS (EI) calc. for  $[\text{C}_{22}\text{H}_{22}\text{NO}_2\text{SCl}]$ : 399.1060, found: 399.1062.

**36d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 8.2$  Hz, 2 H), 7.15 (d,  $J = 8.1$  Hz, 2 H), 6.74 (m + s, 3 H), 6.51 (d,  $J = 8.0$  Hz, 1 H), 5.71 (t,  $J = 3.4$  Hz, 1 H), 5.54 (d,  $J = 8.0$  Hz, 1 H), 4.24 (d,  $J = 11.7$  Hz, 1 H), 2.89 (d,  $J = 11.7$  Hz, 1 H), 2.40 (s, 3 H), 2.23 (s, 6 H), 2.14 –



2.17 (m, 2 H), 1.86 – 1.91 (m, 1 H), 1.40 – 1.49 (m, 2 H), 1.30 (br s, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.12, 142.62, 136.98, 135.56, 132.96, 129.35, 127.98, 126.68, 125.24, 124.38, 123.60, 110.07, 54.72, 41.98, 34.74, 25.58, 21.52, 17.64, 1.04 ppm. HRMS (EI) calc. for  $[\text{C}_{24}\text{H}_{27}\text{NO}_2\text{S}]$ : 393.1763, found: 393.1765.

**39d:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 – 7.27 (m, 5 H), 6.91 – 6.98 (m, 4 H), 5.54 (t,  $J = 3.5$  Hz, 1 H), 5.24 (s, 1 H), 4.78 (d,  $J = 12.2$  Hz, 1 H), 3.13 (d,  $J = 12.2$  Hz, 1 H), 2.26 (s, 3 H), 2.08 – 2.10 (m, 2 H), 1.91 (dd,  $J = 3.1, 12.0$  Hz, 1 H), 1.73 (s, 3 H), 1.47 (t,  $J = 5.6$  Hz, 2 H), 1.42 (dd,  $J = 6.1, 9.1$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.13, 144.00, 138.73, 134.46, 132.83, 129.49, 128.22, 128.16, 126.94, 126.42, 122.38, 111.29, 56.57, 42.75, 34.26, 25.40, 21.43, 20.94, 17.75 ppm. HRMS (EI) calc. for  $[\text{C}_{23}\text{H}_{25}\text{NO}_2\text{S}]$ : 379.1606, found: 379.1608.

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[10] The Synthetic procedures and spectroscopic data are provided in the Experimental Section. CCDC 778495 (**8b**), CCDC 882216 (**25d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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## 국문초록

염화 백금 촉매를 이용한 고리화 반응, 열적 재배열반응 그리고 로듐(I) 촉매를 이용한 재배열 반응으로 1,6-인아인으로부터 다양한 분자 구조를 합성해낼 수 있었다. 이러한 반응에 의해 일반적인 1,6-인아인으로부터 1-아릴-테트라하이드로-1H-인덴, 3-메틸렌-4-바이닐사이클로헥센, 그리고 아릴-헥사하이드로아이소퀴놀린이 생성됨을 관찰하였다; 인아인의 치환기와 연결기에 따라 염화 백금을 이용한 고리화 반응에 의한 생성물, 바이사이클로 [4.1.0] 헵텐은 바이닐사이클로프로판-사이클로펜텐 재배열, 1,5-수소 재배열, 그리고 새로운 고리화 반응이 진행되었다.

주요어 : 염화 백금, 로듐, 바이사이클로 [4.1.0] 헵텐, 싸이클로프로판, 재배열

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