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Rui Liu, Laurent Giordano, Alphonse Tenaglia. Ruthenium-Catalyzed [2+2+2] Cycloaddition of 1,6-Enynes and Unactivated Alkynes: Access to Ring-Fused Cyclohexadienes. *Chemistry - An Asian Journal*, 2017, 12 (17), pp.2245-2257. 10.1002/asia.201700642 . hal-01682722

HAL Id: hal-01682722

<https://hal.science/hal-01682722>

Submitted on 16 Apr 2018

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Ruthenium-Catalyzed [2+2+2] Cycloaddition of 1,6-Enynes and Unactivated Alkynes: Access to Ring-Fused Cyclohexadienes

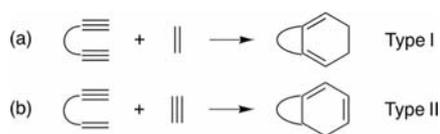
Rui Liu, Laurent Giordano, and Alphonse Tenaglia*^[a]

Abstract: The [2+2+2] intermolecular carbocyclization reactions between 1,6-enynes and alkynes catalyzed by [RuCl(cod)(Cp*)] (cod = 1,5-cyclooctadiene, Cp* = pentamethylcyclopentadienyl) are reported to provide bicyclohexa-1,3-dienes. The presented reaction conditions are compatible

with internal and terminal alkynes and the chemo- and regioselectivity issues are controlled by the presence of substituents at the propargyl carbon center of the alkyne(s) partner(s).

Introduction

The development of synthetic strategies and methodologies based on transition-metal-catalyzed transformations to construct complex molecular structures from readily available starting materials is an intensive area of research.^[1] The generation of ring systems through cycloaddition reactions is representative of multiple-bond- and/or stereocenter-forming synthetic methods that preserve atom economy.^[2] Thus, the [2+2+2] intermolecular carbocyclization reactions between two alkynes and one alkene conceptually represent a straightforward route to cyclohexa-1,3-dienes.^[3] To this end, two main options have been devised to form type I and II bicyclic cyclohexa-1,3-dienes from a) reactions between diynes and alkenes, and b) reactions between enynes and alkynes (Scheme 1). Early



Scheme 1. Substrate topology for cyclohexadiene synthesis through crossed intermolecular [2+2+2] carbocyclization.

examples illustrating routes a^[4] and b^[5] (Scheme 1) were reported by Vollhardt and co-workers, who made use of stoichiometric cobalt-mediated processes. Rhodium-,^[6] cobalt-,^[7] and ruthenium-based^[8] complexes proved to be catalysts of choice, among other transition-metal complexes,^[9] for reactions that

gave rise to type I products. These reactions were, however, restricted to electron-deficient^[6a,7b,8,9c,d] or strained^[7a,c] alkenes and, despite their use in large excess, substantial alkyne trimerization, leading to aromatic compounds, was observed when the alkyne functions were unsubstituted at the terminal position. This approach offered opportunities for the enantioselective construction of quaternary carbon stereocenters,^[8b,10] and DFT calculations,^[11] kinetic studies, and characterization of a rhoda(III)cyclopentadiene intermediate^[12] supported similar reaction paths for the cobalt-, rhodium-, and ruthenium-catalyzed reactions.

An alternative strategy, consisting of the combination of 1,6-enynes and alkynes (Scheme 1b), was scarcely investigated in recent decades and presented major challenges.^[13] First, the competitive self-carbocyclization of enynes has long hampered the success of such an event.^[6,13b,f,14] To circumvent this issue, a large excess of alkynes (up to 10 equiv) is often required. Second, specific structural requirements, such as internal, terminal, electron-poor, or unactivated alkynes and enynes featuring internal alkyne framework, are often mandatory, depending on the nature of the catalyst. To date, a general sketch of this simple assembly of reactants remains to be established. Recent developments by the groups of Shibata and Evans based on the use of cationic rhodium catalysts were dedicated to the enantioselective synthesis of chiral bicyclohexadienes containing one quaternary stereocenter generated at the ring-fused position.^[13g,15] Despite the ability of ruthenium complexes to catalyze a myriad of [2+2+2] cycloadditions of 1,6-diynes with alkynes^[16] or electron-deficient carbon-heteroatom multiple-bond compounds,^[17] to the best of our knowledge, the intermolecular cross-carbocyclization of enynes with alkynes, leading to type II compounds, has not yet been described. Herein, we have achieved the intermolecular carbocyclization of enynes with unactivated alkynes by using a neutral ruthenium catalyst to provide ready access to cyclohexa-1,3-diene frameworks. Importantly, selectivity and regioselectivity issues can be controlled through the appropriate choice of substituents

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at the propargyl carbon atom of one or both alkyne(s) partner(s).

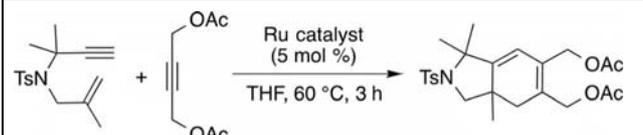
Results and Discussion

We recently disclosed the ruthenium-catalyzed hydroalkynylative cyclizations of enynes.^[18] These transformations generate five-membered cyclic compounds that feature a 1,5-enyne subunit through the formation of C(sp²)-H and C(sp³)-C(sp) bonds. During these studies, we observed few cases of self-coupling of enynes as a result of [2+2+2] cycloaddition; this suggested that cross-cycloaddition between enynes and alkynes would be possible. Based on these observations, an initial examination of the carbocyclization of enynes with alkynes was performed by using nitrogen-tethered enynes **1 a/1 b** and but-2-yne-1,4-diyl diacetate (**2 a**) in the presence of 5 mol% [RuCl(cod)(Cp*)] (cod = 1,5-cyclooctadiene, Cp* = pentamethylcyclopentadienyl) in tetrahydrofuran (THF) at 60 °C. To our delight, the target bicyclodiene **3 a a** was isolated from **1 a** in 44% yield, along with cyclodimer **4 a**^[18] (47%) as a 4.8/1 mixture of regioisomers (the major isomer is depicted in Scheme 2). The reaction involving enyne **1 b**, with methyl substituents at the propargyl carbon atom, exclusively led to **3 b a** in almost quantitative yield. At this stage, it seemed clear that the competitive insertion of two different alkynes into the putative ruthenacyclopentene generated by the oxidative coupling of enyne **1** could be oriented towards cross-coupling product **3** by minimizing the nonbonded interactions between the metal ligands and substituents at the propargyl position of the alkynes.

Having identified **1 b** as the ideal enyne, we studied the [2+2+2] cycloaddition of **2 a** with a series of structurally similar ruthenium complexes as catalysts. The screening results are summarized in Table 1.

These results showed that the [2+2+2] cycloaddition was best performed with electron-rich ruthenium complexes containing a Cp* ligand rather than the Cp ligand (compare Table 1, entries 1/2 and 3/4). Cationic complexes, such as [Ru(CH₃CN)₃(Cp*)]PF₆ (Table 1, entry 4), appeared to be less effective than the neutral ones (Table 1, entries 2 and 5). This result was supported by the reaction carried out with a catalyst combining [Ru(CH₃CN)₃(Cp*)]PF₆ with *n*Bu₄NCl to generate the neutral complex [Ru(CH₃CN)₂Cl(Cp*)],^[19] which restored the performance level to 91% yield (Table 1, entry 7). Owing to the more labile bidentate cod ligand, compared with triphenylphosphine, [RuCl(cod)(Cp*)] gave the best result (Table 1, entries 2 and 5). The [RuCl(cod)(Cp*)] catalyst loading can be low-

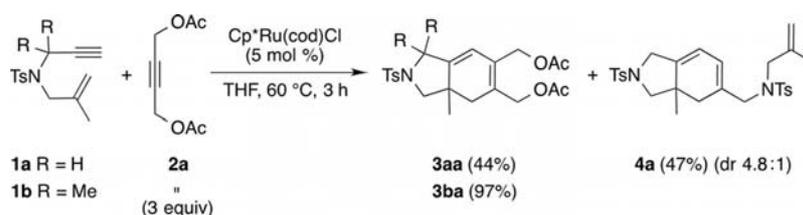
Table 1. Results of the screening of ruthenium catalysts.^[a]



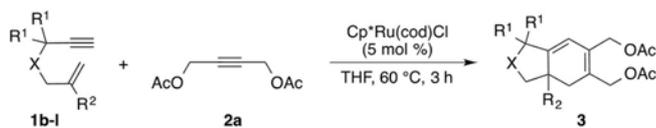
Entry	Ru catalyst	Yield ^[b] [%]
1	[RuCl(Cp)(PPh ₃) ₂]	15 ^[c]
2	[RuCl(Cp*)(PPh ₃) ₂]	85
3	[Ru(CH ₃ CN) ₃ (Cp)]PF ₆	9 ^[d]
4	[Ru(CH ₃ CN) ₃ (Cp*)]PF ₆	61
5	[RuCl(cod)(Cp*)]	97
6	[RuCl(cod)(Cp*)] ^[e]	89 ^[f]
7	[Ru(CH ₃ CN) ₃ (Cp*)]PF ₆ / <i>n</i> Bu ₄ NCl ^[g]	91

[a] Reaction conditions: [Ru] cat. (5 mol%), **1 b** (1 equiv), **2 a** (3 equiv), 60 °C, 3 h, *c* = 0.1 M. Cp = cyclopentadienyl. [b] Yields of products isolated. [c] 70% of **1 b** was recovered. [d] 62% of **1 b** was recovered. [e] 2.5 mol%. [f] Reaction time: 24 h. [g] 10 mol% of *n*Bu₄NCl.

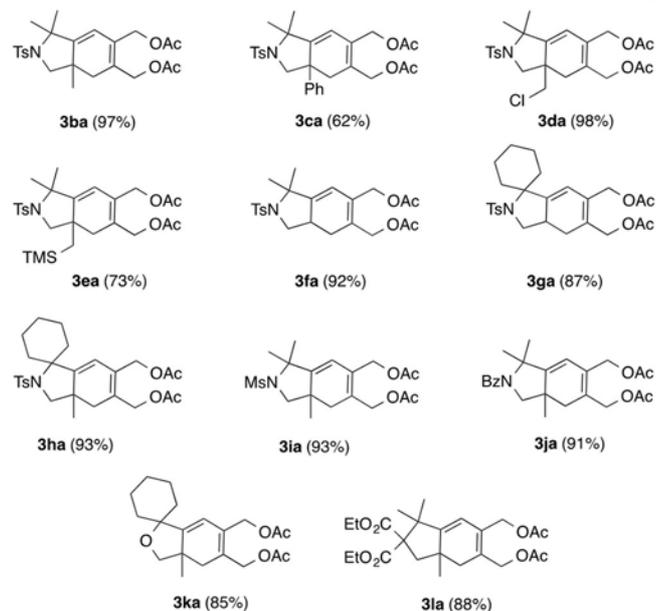
ered to 2.5 mol% to give 89% yield of **3 b a**; however, the reaction requires 24 h (instead of 3 h) for complete conversion (Table 1, entry 6). The examination of the solvent effect on the carbocyclization reaction with [RuCl(cod)(Cp*)] as the catalyst revealed that the polarity of the solvent had no major influence on the catalyst efficiency. For instance, ethyl acetate (92%), acetone (90%), 1,2-dichloroethane (88%), or toluene (86%) could be used, albeit slightly decreased yields of **3 b a** were observed relative to the reaction performed in THF (97%). However, when protic solvents such as MeOH were used, the yield of **3 b a** dramatically dropped (61%). Under these conditions, an in situ generated cationic ruthenium complex was likely to be formed and the yield of **3 b a** matched that observed with a cationic catalyst (Table 1, entry 4). Interestingly, water as cosolvent with THF (1/1 v/v) was not detrimental to the reaction because **3 b a** was isolated in 95% yield. We found that a **1 b/2 a** ratio of 1/3 was convenient to obtain **3 b a** in high yields and to suppress the homo-hydroalkynylative cyclization of 1,6-enyne.^[18] Indeed, carrying out the reaction with a 1/1 molar ratio of **1 b/2 a** resulted in the formation of **3 b a** with lower yield (52%). Most of the excess of **2 a** was recovered unchanged and isolated by chromatography for recycling. Cyclotrimer was not detected in the crude reaction mixture by ¹H NMR spectroscopy.



Scheme 2. Initial studies on the carbocyclization of enynes with alkynes.

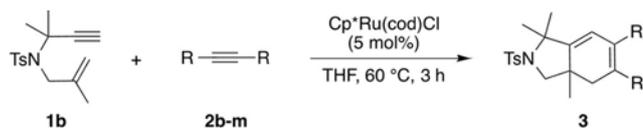


b X = NTs, R¹ = R² = Me
c X = NTs, R¹ = Me, R² = Ph
d X = NTs, R¹ = Me, R² = CH₂Cl
e X = NTs, R¹ = Me, R² = CH₂TMS
f X = NTs, R¹ = Me, R² = H
g X = NTs, R¹, R² = (CH₂)₅, R² = H
h X = NTs, R¹, R² = (CH₂)₅, R² = Me
i X = NMs, R¹ = R² = Me
j X = NBz, R¹ = R² = Me
k X = O, R¹, R² = (CH₂)₅, R² = Me
l X = C(CO₂Et)₂, R¹ = R² = Me

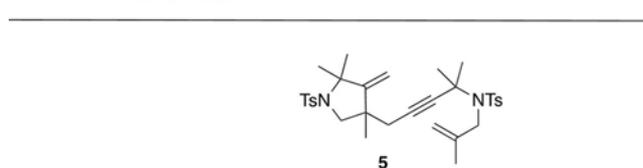


Scheme 3. Ruthenium-catalyzed [2+2+2] cycloaddition of 1,6-enynes **1b-l** and alkyne **2a**. Ts = toluenesulfonyl, Ms = methanesulfonyl, Bz = benzoyl.

Having the optimal conditions in hand, we then investigated the scope of enyne substrates. As shown in Scheme 3, a variety of bicyclic dienes **3** were easily prepared in good to excellent yields with this simple protocol. Interestingly, the homodimerization of enynes (< 5%) was observed in a few cases, as determined by ¹H NMR spectroscopic analysis of the crude reaction mixture. First, variation of the substituent of the double bond of the enyne (R²) showed that an electrophilic (**1d**) or nucleophilic (**1e**) functional group was tolerated for the [2+2+2] cycloaddition, providing azabicycles **3da** (98%) and **3ea** (73%), respectively. Interestingly, the sterically demanding phenyl group, compared with the methyl group, can be introduced at the ring junction of bicycle **3ca**, although the yield dramatically dropped to 62%. Enynes **1f-g**, which lacked substituent R², were also good candidates, and gave adducts such as **3fa** (92%) and **3ga** (87%). Variation of substitution at the propargyl carbon center of the enyne (**3g**, **3h**, **3k**) and groups on the nitrogen atom (**3i**, **3j**) did not impact significantly on the formation of the corresponding adducts. Oxygen- and carbon-containing tethered enynes could also be employed; thus providing oxabicyclo[4.3.0]nonadiene **3ka** (85%) and bicyclo[4.3.0]nonadiene **3la** (88%), respectively.

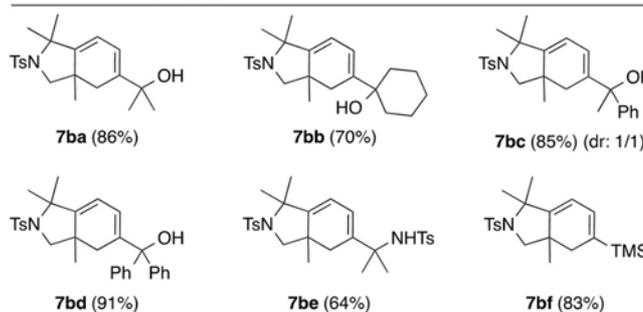
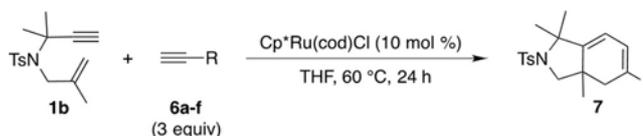


b R = CH₂OCO₂Me
c R = CH₂OMe
d R = CH₂OBn
e R = CH₂OBoc
f R = CH₂OCbz
g R = CH₂OCOC₆H₄pNO₂
h R = CH₂OCOC₆H₄pOMe
i R = CH₂OH
j R = CH₂Cl
k R = Et
l R = Ph
m R = TMS



Scheme 4. Ruthenium-catalyzed [2+2+2] cycloaddition of **1b** and symmetrical alkynes **2b-m**. Bn = benzyl, Boc = *tert*-butyloxycarbonyl, Cbz = carboxybenzyl, TMS = trimethylsilyl.

To expand the scope of the intermolecular carbocyclization, the reaction of **1b** with various functionalized internal alkynes **2** was performed under the optimized conditions (Scheme 4). Bicyclic dienes **3bb-bk** were obtained in very good to excellent yields and protecting groups for the hydroxyl group, such as esters, mixed carbonates, or ethers, are compatible with our conditions. Even functional groups such as free alcohol and chloride are satisfactorily tolerated and an unactivated alkyne, such as hex-3-yne (**2k**), afforded **3bk** in almost quantitative yield. Interestingly, diphenylacetylene **2l** allowed the formation of **3bl**, albeit in modest yield (21%), which was in contrast with similar rhodium-catalyzed carbocyclization reactions.^[13h] In this case, the major product (61%) was the alkynylative cyclized adduct **5**.^[18] Similarly, bis-trimethylsilylethyne **2m**, which is an excellent partner in cobalt-catalyzed cycloadditions,^[20] did not provide the expected adduct; instead, dienyne **5** was formed as the sole product in 86% yield.

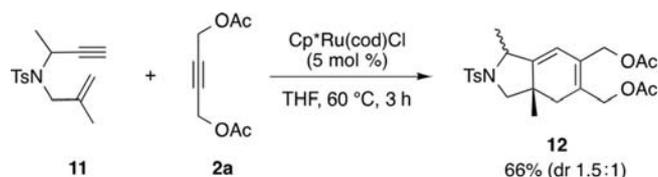


Scheme 5. Regioselective ruthenium-catalyzed [2+2+2] cycloaddition of **1b** and terminal alkynes **6a-f**.

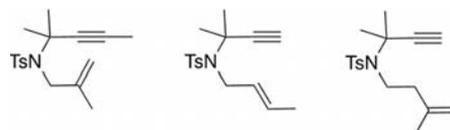
Interestingly, not only internal alkynes took part in the [2+2+2] cycloaddition reaction, but also terminal alkynes participated as well under similar reaction conditions, providing that a twofold catalyst charge (10 mol%) was used (Scheme 5).

On the basis of our previous observations,^[18] we thought that increasing the steric bulk at the propargyl carbon atom of **6** could impact on the regioselectivity, even though the selectivity of the reaction (self-coupling versus cross-coupling) might be eroded. Gratifyingly, tertiary propargyl alcohols **6 a–d** afforded adducts **7 ba–bd** as single regioisomers, although the reactions required 24 h for complete conversion. This trend was also observed with tertiary propargyl sulfonamide **6 e**^[21] and alkyne **6 f**, featuring the bulky TMS group, which afforded **7 be** (64%) and dienyne **7 bf**^[18] (83%). We wondered about the regioselectivity observed in these reactions, especially for cases involving tertiary propargyl alcohols, insofar as the coordination of the free hydroxyl group to ruthenium being invoked in a number of catalytic reactions involving this class of substrates.^[22] Indeed, performing the reaction of 3-methoxy-3-methylbut-1-yne (**6 g**)^[23] with **1 b** resulted in loss of both regio- and chemoselectivity; thus leading to bicyclic dienes **7 bg/7 bg'** (63%, 0.83/1 ratio of regioisomers) and 1,5-enyne **8** (34%), which arose from the alkynylative coupling reaction^[18] (Scheme 6). The structure of regioisomer **7 bg'** was confirmed by single-crystal XRD analysis.^[24]

Further scope of the reaction was examined with variation of substitution on either the enyne or alkyne. Loss of regioselectivity was observed in coupling reactions involving phenylethyne **6 h** and primary propargyl alcohols **6 i** and **9** (Scheme 7). The pair of regioisomers **7 bi/7 bi'** and **10/10'** were separated by chromatography and fully characterized by spectroscopic means. Enyne **11**,^[25] with monosubstitution at the propargyl carbon, participated equally in the coupling reaction with **2 a**



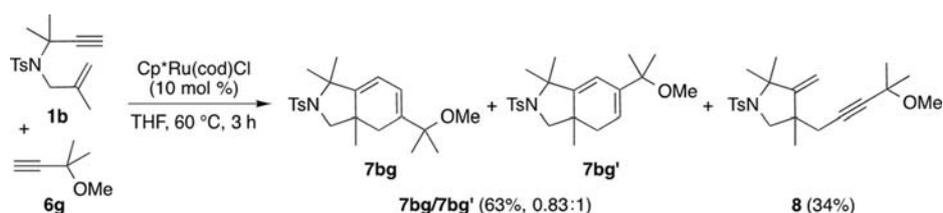
Scheme 8. Ruthenium-catalyzed [2+2+2] cycloaddition of **11** with **2 a**.



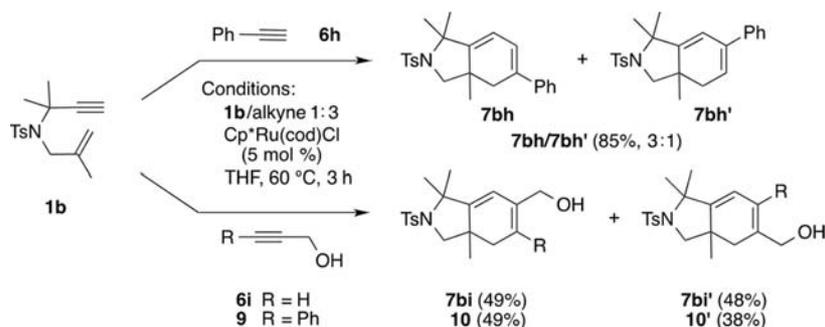
Scheme 9. Unsuitable enynes for ruthenium-catalyzed [2+2+2] cycloaddition.

and yielded bicyclohexadiene **12** with poor diastereoselectivity (Scheme 8). Examination of enynes featuring an internal alkyne or 1,2-disubstituted alkene, as well as 1,7-enyne, failed to give cycloadducts with **2 a**. Representative examples of such substrates are given in Scheme 9.

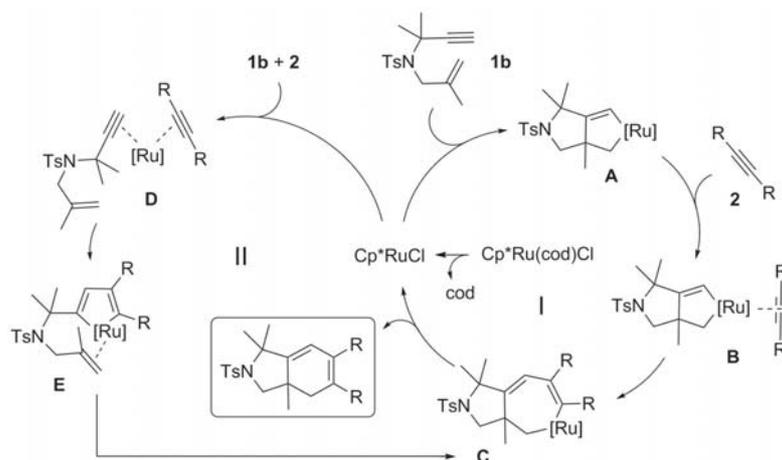
A mechanism rationale involving ruthenacycles as intermediates is depicted in Scheme 10. Catalytic cycle I starts with the dissociation of the weakly coordinated cod ligand from ruthenium, which allows intramolecular coordination of both triple and double bonds of enyne. Oxidative cyclization gives bicyclic ruthenacyclopentene intermediate **A**, which, upon coordination of alkyne **2** to the ruthenium centre (**B**), followed by its insertion, generates ruthenacycloheptadiene **C**. Finally, reductive elimination releases the bicyclic product and regenerates the active metal species. An alternative mechanism (II), leading to



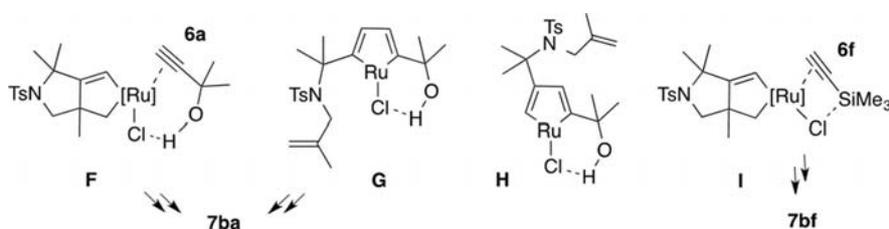
Scheme 6. Ruthenium-catalyzed coupling of **1 b** and **6 g**.



Scheme 7. Ruthenium-catalyzed [2+2+2] cycloaddition of **1 b** with terminal arylalkyne **6 h** or primary propargyl alcohols **6 i** and **9**.



Scheme 10. Mechanism of the [2+2+2] intermolecular carbocyclization.

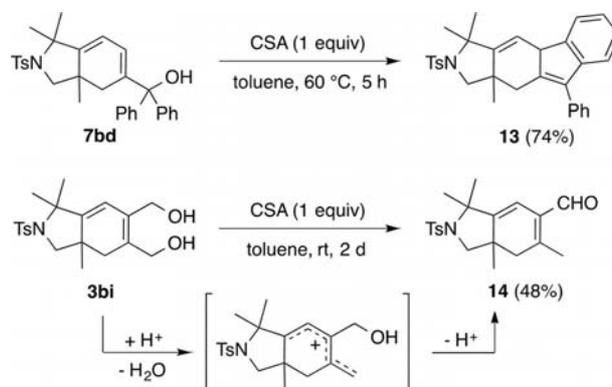


Scheme 11. Possible intermediates for the control of regioselectivity.

intermediate **C**, might first involve intermolecular coordination of the alkyne reactants (**D**) to form ruthenacyclopentadiene **E** and subsequent insertion of the pendant olefin. At this point, it is not clear which of the two pathways is dominant. However, on the basis of the hydroalkynylative cyclization of enyne **1b**,^[18] which is achieved in the absence of **2a**, we are inclined to favor the mechanism of path I.

The origin of the regioselectivity observed with tertiary propargylic alcohols (Scheme 5) can be ascribed to the idea of interligand interactions through hydrogen bonding of the hydroxyl proton to a chloride ligand of the {RuCl} fragment, as recently introduced by Fürstner et al.^[26b-d] (Scheme 11). This allows control of the orientation of alkynol insertion within the ruthenacycle (**B**→**C**, Scheme 10). According to the mechanisms depicted in Scheme 10, intermediates **F**–**H** can be considered from the initial couplings of enyne **1b** and **6a**, but only **F** and **G** might lead to the formation of cycloadduct **7ba** (Scheme 11). Because the less congested ruthenacyclopentadiene **H**, relative to **G**, is catalytically inoperative, again we are inclined to favor the mechanism via ruthenacyclopentene. Analogous with intermediate **F**, the interaction between the chloride of the {RuCl} fragment with the TMS group of alkyne **6f**^[26] might explain the formation of **7bf**.

To gain insights into initial intermediates formed in the coupling reactions, we attempted the stoichiometric reaction of **1b** with **6b** and one molar equivalent of [RuCl(cod)(Cp*)]. Unfortunately, no metalacycle intermediate was detected and we observed the fast formation of **7bb** immediately after data acquisition by NMR spectroscopy.



Scheme 12. Synthetic transformations of cycloadducts **3bi** and **7bd**. CSA = camphorsulfonic acid.

Chemical transformations into more complex ring-fused polycycles were briefly examined (Scheme 12). Thus, the treatment of adduct **7bd** in toluene with CSA at 60 °C provided the tetracyclic structure **13** in 74% yield through the dehydrative cyclization of a pentadienyl-like cation intermediate. Additionally, conversion of diol **3bi** into the conjugated aldehyde **14** (48%) occurred smoothly at room temperature in the presence of CSA. The location of the formyl group was ascertained by NOESY experiments. Interestingly, the formation of **14** as a single regioisomer could be rationalized on the basis of the preferred generation of a pentadienyl cation intermediate and subsequent release of a proton.

Conclusion

Crossed intermolecular ruthenium-catalyzed [2+2+2] carbocyclization reactions between 1,6-enynes with alkynes has been developed. This catalytic reaction provided facile access to bicyclohexadienes containing a quaternary center at the ring junction and tolerated a wide range of functional groups. The chemo- and regioselectivity of the reaction was controlled by the choice of substituents at the propargyl carbon(s) atom(s) of the reactants. The latent functions within these bicyclic building blocks provide opportunities for chemical transformations into more complex and/or functionalized polycyclic molecules in a limited number of steps, as illustrated with the generation of tetracycle **13** and aldehyde **14**.

Experimental Section

General

All reactions, unless otherwise stated, were carried out under an argon atmosphere in oven-dried (120 °C) glassware. Reaction solvents were purified according to standard procedures^[27] and degassed before use. All ruthenium complexes were purchased and used as received. ¹H NMR spectra were measured with 300 and 400 MHz spectrometers as solutions in CDCl₃, unless otherwise indicated. Chemical shifts are given in ppm (δ) downfield from tetramethylsilane by using the residual solvent signal (CHCl₃ δ = 7.26 ppm) as an internal standard. ¹H NMR spectroscopy data is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept, septet; m, multiplet), coupling constant(s) (*J*) in Hz, number of protons. ¹³C NMR spectra are reported in ppm (δ) relative to residual CHCl₃ (δ = 77.4 ppm), unless otherwise noted. Ruthenium complexes and alkynes **2c** and **2i-m** were obtained from commercial sources. HRMS was performed at the Spectropôle of Aix-Marseille Université.

Compound **2b**^[28]

Methyl chloroformate (2.27 g, 24 mmol) was added dropwise to a solution of 2-butyne-1,4-diol (861 mg, 10 mmol), 4-dimethylaminopyridine (122 mg, 1 mmol), and triethylamine (4 g, 40 mmol) in dry dichloromethane (50 mL) at 0 °C. The mixture was stirred at room temperature overnight, washed with a 10% solution of HCl (50 mL) and brine (30 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **2b** as a white semisolid (1.8 g, 91%). *R_f* (petroleum ether (PE)/Et₂O 4/6) = 0.35; ¹H NMR (400 MHz, CDCl₃): δ = 4.77 (m, 4H), 3.81 ppm (m, 6H); ¹³C NMR (101 MHz, CDCl₃): δ = 155.1 (C), 80.9 (C), 55.2 (CH₃), 55.1 ppm (CH₂).

Compound **2d**^[29]

2-Butyne-1,4-diol (861 mg, 10 mmol) was added dropwise to a suspension of NaH (880 mg, 22 mmol, 60% dispersion in mineral oil) in dry THF (50 mL) at 0 °C. The mixture was stirred for 1 h, and then benzyl bromide (4.1 g, 24 mmol) was added dropwise. The mixture was warmed to RT and stirred until completion (monitoring by TLC), diluted with a saturated aqueous solution of NH₄Cl (30 mL), and extracted with diethyl ether (3 × 15 mL). The combined extracts were washed with brine (30 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **2d** as a colorless oil (1.7 g,

65%). *R_f* (PE/Et₂O 4/1) = 0.45; ¹H NMR (300 MHz, CDCl₃): δ = 7.47–7.28 (m, 10H), 4.64 (s, 4H), 4.27 ppm (s, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 137.6 (C), 128.6 (CH), 128.2 (CH), 128.0 (CH), 82.8 (C), 71.8 (CH₂), 57.6 ppm (CH₂).

Compound **2e**^[30]

A solution of di-*tert*-butyl dicarbonate (5.24 g, 24 mmol) in dichloromethane (25 mL) was added to a solution of 2-butyne-1,4-diol (861 mg, 10 mmol), 4-dimethylaminopyridine (122 mg, 1 mmol), and triethylamine (4 g, 40 mmol) in dichloromethane (50 mL). The mixture was stirred overnight, washed with a 10% solution of HCl (50 mL) and brine (30 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **2e** as a colorless oil (2.1 g, 73%). *R_f* (PE/Et₂O 1/1) = 0.35; ¹H NMR (300 MHz, CDCl₃): δ = 4.68 (s, 4H), 1.47 ppm (s, 18H); ¹³C NMR (101 MHz, CDCl₃): δ = 152.9 (C), 83.0 (C), 81.1 (C), 54.6 (CH₂), 27.8 ppm (CH₃).

Compound **2f**

Benzyl chloroformate (4.09 g, 24 mmol) was added to a solution of 2-butyne-1,4-diol (861 mg, 10 mmol), 4-dimethylaminopyridine (122 mg, 1 mmol), and triethylamine (4 g, 40 mmol) in dichloromethane (50 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature, washed with a 10% aqueous solution of HCl (50 mL) and brine (30 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **2f** as a white solid (2.4 g, 69%). M.p. 74–75 °C; *R_f* (PE/Et₂O 3/2) = 0.45; IR (neat): $\tilde{\nu}$ = 3034, 2955, 1744, 1497, 1389, 1223, 1153, 932, 910, 751, 694, 576 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.40–7.31 (m, 10H), 5.19 (s, 4H), 4.78 ppm (s, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.8 (C), 135.2 (C), 128.9 (CH), 128.9 (CH), 128.6 (CH), 81.3 (C), 70.4 (CH₂), 55.7 ppm (CH₂); HRMS (ESI-MS): *m/z* calcd for C₂₀H₂₂NO₆⁺ [*M*+NH₄]⁺: 372.1442; found: 372.1442.

General Procedure for Acylation of 2-butyne-1,4-diol (**A**)

Acyl chloride (24 mmol) was added dropwise to a solution of 2-butyne-1,4-diol (861 mg, 10 mmol), 4-dimethylaminopyridine (122 mg, 1 mmol), and triethylamine (4 g, 40 mmol) in dry dichloromethane (50 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature, washed with a 10% solution of HCl (50 mL) and brine (30 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel.

Compound **2g**

Procedure A afforded **2g** as a white solid (2.8 g, 72%). M.p. 148–149 °C; *R_f* (Et₂O) = 0.40; IR (neat): $\tilde{\nu}$ = 3113, 2913, 1729, 1522, 1344, 1262, 1094, 944, 878, 718 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.31 (d, *J* = 8.9 Hz, 4H), 8.25 (d, *J* = 9.0 Hz, 4H), 5.05 ppm (s, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 164.2 (C), 151.1 (C), 135.0 (C), 131.3 (CH), 123.9 (CH), 81.3 (C), 53.6 ppm (CH₂); HRMS (ESI-MS): *m/z* calcd for C₁₈H₁₆N₃O₈⁺ [*M*+NH₄]⁺: 402.0932; found: 402.0928.

Compound **2h**

Procedure A afforded **2h** as a white solid (2.9 g, 82%). M.p. 117–118 °C; *R_f* (PE/AcOEt 4/1) = 0.35; IR (neat): $\tilde{\nu}$ = 2933, 2846, 1701, 1606, 1512, 1444, 1310, 1269, 1260, 1161, 1101, 842, 765, 693, 615 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.02 (d, *J* = 8.4 Hz, 4H),

6.92 (d, $J=8.4$ Hz, 4H), 4.96 (s, 4H), 3.86 ppm (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=164.9$ (C), 163.0 (C), 131.3 (CH), 121.2 (C), 113.1 (CH), 80.4 (C), 54.8 (CH_3), 51.7 ppm (CH_2); HRMS (ESI-MS): m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_6^+$ [$M+\text{H}$] $^+$: 355.1176; found: 355.1172.

General Procedure for the Ruthenium(II)-Catalyzed Coupling Reaction of Enynes and Alkynes (B)

A solution of 1,6-enyne (0.2 mmol) and alkyne (0.6 mmol) in THF (0.5 mL) was added to a solution of $[\text{RuCl}(\text{cod})(\text{Cp}^*)]$ (3.80 mg, 0.01 mmol) in THF (0.5 mL). The mixture was stirred at 60 °C until completion of the reaction (monitoring by TLC), cooled to room temperature, filtered through Celite, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel.

Compound 3aa

Procedure B afforded **3aa** as a colorless oil (38.1 mg, 44%). R_f (PE/ Et_2O 1/1)=0.30; IR (neat): $\tilde{\nu}=2960, 2862, 1734, 1376, 1221, 1161, 1092, 1021, 817, 711, 664, 601, 549$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=7.70$ (d, $J=8.2$ Hz, 2H), 7.33 (d, $J=7.9$ Hz, 2H), 5.70 (t, $J=2.1$ Hz, 1H), 4.77 (d, $J=12.5$ Hz, 1H), 4.70 (d, $J=12.4$ Hz, 1H), 4.62 (d, $J=12.4$ Hz, 1H), 4.54 (d, $J=12.5$ Hz, 1H), 4.20 (dd, $J=15.6, 2.1$ Hz, 1H), 3.75 (d, $J=15.6$ Hz, 1H), 3.54 (d, $J=9.0$ Hz, 1H), 2.78 (d, $J=9.0$ Hz, 1H), 2.43 (s, 3H), 2.20 (s, 2H), 2.03 (s, 3H), 2.02 (s, 3H), 0.99 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=171.1$ (C), 144.1 (C), 144.0 (C), 133.2 (C), 130.1 (CH), 129.2 (C), 128.7 (C), 128.0 (CH), 116.9 (CH), 63.4 (CH_2), 62.1 (CH_2), 62.0 (CH_2), 50.2 (CH_2), 41.5 (C), 37.6 (CH_2), 21.9 (CH_3), 21.6 (CH_3), 21.2 (CH_3), 21.1 ppm (CH_3); HRMS (ESI-MS): m/z calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_6\text{S}^+$ [$M+\text{H}$] $^+$: 434.1632; found: 434.1627.

Compound 3ba

Procedure B afforded **3ba** as a colorless oil (89.5 mg, 97%). R_f (PE/ Et_2O 4/6)=0.35; IR (neat): $\tilde{\nu}=3055, 2979, 2254, 1733, 1353, 1264, 1091, 907, 727$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=7.74$ (d, $J=8.3$ Hz, 2H), 7.27 (d, $J=8.9$ Hz, 2H), 5.65 (s, 1H), 4.80 (d, $J=12.5$ Hz, 1H), 4.74 (d, $J=12.4$ Hz, 1H), 4.66 (d, $J=12.4$ Hz, 1H), 4.57 (d, $J=12.5$ Hz, 1H), 3.40 (d, $J=9.2$ Hz, 1H), 3.01 (d, $J=9.2$ Hz, 1H), 2.41 (s, 3H), 2.20–2.14 (m, 2H), 2.04 (s, 3H), 2.03 (s, 3H), 1.69 (s, 3H), 1.46 (s, 3H), 0.96 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=171.0$ (C), 156.6 (C), 143.2 (C), 138.2 (C), 129.6 (CH), 129.4 (C), 128.7 (C), 127.7 (CH), 115.3 (CH), 67.3 (C), 63.3 (CH_2), 62.1 (CH_2), 60.8 (CH_2), 39.5 (C), 38.4 (CH_2), 31.1 (CH_3), 28.4 (CH_3), 21.9 (CH_3), 21.7 (CH_3), 21.1 (CH_3), 20.9 ppm (CH_3); HRMS (ESI-MS): m/z calcd for $\text{C}_{24}\text{H}_{32}\text{NO}_6\text{S}^+$ [$M+\text{H}$] $^+$: 462.1945; found: 462.1947.

Compound 3ca

Procedure B afforded **3ca** as a colorless oil (64.9 mg, 62%). R_f (PE/ Et_2O 4/6)=0.43; IR (neat): $\tilde{\nu}=2932, 2868, 2252, 1734, 1218, 1090, 1023, 728, 581$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=7.28$ (d, $J=8.3$ Hz, 2H), 7.19–7.11 (m, 5H), 6.99 (d, $J=8.0$ Hz, 2H), 6.11 (s, 1H), 4.79 (d, $J=12.4$ Hz, 1H), 4.69 (d, $J=12.4$ Hz, 1H), 4.56 (d, $J=12.5$ Hz, 1H), 4.31 (d, $J=12.5$ Hz, 1H), 4.16 (d, $J=10.0$ Hz, 1H), 3.49 (d, $J=10.0$ Hz, 1H), 2.57 (d, $J=16.1$ Hz, 1H), 2.52 (d, $J=16.1$ Hz, 1H), 2.32 (s, 3H), 2.05 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H), 1.53 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=170.9$ (C), 170.5 (C), 152.7 (C), 142.8 (C), 140.7 (C), 138.6 (C), 130.6 (C), 129.3 (CH), 129.1 (C), 128.3 (CH), 127.1 (CH), 127.1 (CH), 127.0 (CH), 119.4 (CH), 66.8 (C), 62.6 (CH_2), 61.9 (CH_2), 61.4 (CH_2), 48.0 (C), 40.4 (CH_2), 29.1 (CH_3), 29.0 (CH_3), 21.6 (CH_3), 21.1 (CH_3), 20.7 ppm (CH_3); HRMS (ESI-MS): m/z calcd for $\text{C}_{29}\text{H}_{34}\text{NO}_6\text{S}^+$ [$M+\text{H}$] $^+$: 524.2101; found: 524.2101.

Compound 3da

Procedure B afforded **3da** (as a colorless oil 97.2 mg, 98%). R_f (PE/ Et_2O 4/6)=0.35; IR (neat): $\tilde{\nu}=2975, 2871, 1735, 1364, 1220, 1150, 1112, 1089, 991, 728, 576$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=7.74$ (d, $J=8.3$ Hz, 2H), 7.28 (d, $J=8.0$ Hz, 2H), 5.81 (s, 1H), 4.83 (d, $J=12.7$ Hz, 1H), 4.76 (dd, $J=12.5, 1.7$ Hz, 1H), 4.67 (d, $J=12.5$ Hz, 1H), 4.51 (d, $J=12.7$ Hz, 1H), 3.91 (d, $J=10.2$ Hz, 1H), 3.22 (dd, $J=10.9, 1.6$ Hz, 1H), 3.17 (d, $J=10.9$ Hz, 1H), 2.97 (dd, $J=10.2, 1.6$ Hz, 1H), 2.78 (d, $J=17.0$ Hz, 1H), 2.41 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (brs, 1H), 1.61 (s, 3H), 1.49 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=171.0$ (C), 170.9 (C), 152.3 (C), 143.5 (C), 138.4 (C), 129.8 (CH), 129.6 (C), 129.5 (C), 127.4 (CH), 118.8 (CH), 66.9 (C), 62.6 (CH_2), 61.9 (CH_2), 56.0 (CH_2), 44.7 (C), 44.2 (CH_2), 32.4 (CH_2), 30.3 (CH_3), 28.9 (CH_3), 21.7 (CH_3), 21.2 (CH_3), 21.1 ppm (CH_3); HRMS (ESI-MS): m/z calcd for $\text{C}_{24}\text{H}_{31}\text{ClNO}_6\text{S}^+$ [$M+\text{H}$] $^+$: 496.1555; found: 496.1553.

Compound 3ea

Procedure B afforded **3ea** as a colorless oil (77.9 mg, 73%). R_f (PE/ Et_2O 4/6)=0.38; IR (neat): $\tilde{\nu}=2976, 2869, 2257, 1733, 1364, 1221, 1141, 1023, 959, 729$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=7.75$ (d, $J=8.3$ Hz, 2H), 7.28 (d, $J=8.0$ Hz, 2H), 5.59 (s, 1H), 4.71–4.69 (m, 4H), 3.45 (d, $J=9.3$ Hz, 1H), 2.94 (dd, $J=9.3, 2.0$ Hz, 1H), 2.40 (s, 3H), 2.32 (d, $J=16.9$ Hz, 1H), 2.20 (d, $J=16.9$ Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 1.76 (s, 3H), 1.47 (s, 3H), 0.88 (dd, $J=14.9, 2.0$ Hz, 1H), 0.72 (dd, $J=14.9, 1.3$ Hz, 1H), -0.12 ppm (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=171.0$ (C), 171.0 (C), 158.5 (C), 143.4 (C), 138.1 (C), 130.1 (C), 129.7 (CH), 128.4 (C), 127.9 (CH), 114.3 (CH), 67.0 (C), 63.7 (CH_2), 62.3 (CH_2), 59.8 (CH_2), 41.9 (C), 38.1 (CH_2), 31.4 (CH_3), 28.7 (CH_3), 23.1 (CH_2), 21.7 (CH_3), 21.1 (CH_3), 0.7 ppm (CH_3); HRMS (ESI-MS): m/z calcd for $\text{C}_{27}\text{H}_{40}\text{NO}_6\text{Si}^+$ [$M+\text{H}$] $^+$: 534.2340; found: 534.2339.

Compound 3fa

Procedure B afforded **3fa** as a colorless oil (82.3 mg, 92%). R_f (PE/ Et_2O 2/3)=0.37; IR (neat): $\tilde{\nu}=2995, 2938, 1717, 1410, 1229, 1159, 1086, 723, 589$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta=7.73$ (d, $J=8.3$ Hz, 2H), 7.27 (d, $J=8.0$ Hz, 2H), 5.69 (d, $J=2.7$ Hz, 1H), 4.79 (d, $J=12.6$ Hz, 1H), 4.72 (dd, $J=12.4, 1.4$ Hz, 1H), 4.65 (d, $J=12.4$ Hz, 1H), 4.57 (d, $J=12.6$ Hz, 1H), 3.82 (t, $J=7.8$ Hz, 1H), 3.01–2.88 (m, 2H), 2.41 (s, 4H), 2.04 (s, 6H), 2.02–1.99 (m, 1H), 1.59 (s, 3H), 1.53 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=171.0$ (C), 171.0 (C), 151.8 (C), 143.3 (C), 138.3 (C), 130.4 (C), 129.7 (CH), 129.6 (C), 127.6 (CH), 115.8 (CH), 67.3 (C), 63.2 (CH_2), 62.2 (CH_2), 54.0 (CH_2), 36.0 (CH), 30.6 (CH_2), 30.5 (CH_2), 27.3 (CH_2), 21.7 (CH_3), 21.1 ppm (CH_3); HRMS (ESI-MS): m/z calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_6\text{SNa}^+$ [$M+\text{Na}$] $^+$: 470.1608; found: 470.1607.

Compound 3ga

Procedure B afforded **3ga** as a colorless oil (84.8 mg, 87%). R_f (PE/ Et_2O 4/6)=0.33; IR (neat): $\tilde{\nu}=2925, 2869, 1736, 1376, 1221, 1155, 1044, 663, 588$ cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): $\delta=7.65$ (d, $J=8.0$ Hz, 2H), 7.19 (d, $J=7.9$ Hz, 2H), 6.07 (s, 1H), 4.74–4.49 (m, 4H), 3.70 (t, $J=8.1$ Hz, 1H), 2.95–2.77 (m, 2H), 2.55–2.45 (td, $J=12.5, 4.6$ Hz, 2H), 2.34 (s, 3H), 2.30–2.25 (m, 1H), 1.98 (s, 3H), 1.97 (s, 3H), 1.80–1.75 (m, 1H), 1.67–1.41 (m, 7H), 1.35–1.19 ppm (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=171.1$ (C), 149.6 (C), 143.1 (C), 139.2 (C), 130.6 (C), 129.7 (CH), 129.5 (C), 127.5 (CH), 118.5 (CH), 70.9 (C), 63.2 (CH_2), 62.5 (CH_2), 53.8 (CH_2), 36.7 (CH), 36.1 (CH_2), 35.2 (CH_2), 30.7 (CH_2), 24.7 (CH_2), 22.9 (CH_2), 21.8 (CH_3), 21.2 (CH_3), 21.2 ppm (CH_3); HRMS (ESI-MS): m/z calcd for $\text{C}_{26}\text{H}_{37}\text{N}_2\text{O}_6\text{S}^+$ [$M+\text{NH}_4$] $^+$: 505.2367; found: 505.2368.

Compound 3ha

Procedure B afforded **3ha** as a colorless oil (93.3 mg, 93%). R_f (PE/Et₂O 2/3)=0.33; IR (neat): $\tilde{\nu}$ =2931, 2872, 2255, 1733, 1225, 1154, 905, 724, 603 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.74 (d, J =8.3 Hz, 2H), 7.26 (d, J =8.0 Hz, 2H), 6.10 (s, 1H), 4.79 (d, J =12.5 Hz, 1H), 4.74 (d, J =12.4 Hz, 1H), 4.69 (d, J =12.4 Hz, 1H), 4.56 (d, J =12.5 Hz, 1H), 3.26 (d, J =9.3 Hz, 1H), 3.10 (d, J =9.3 Hz, 1H), 2.87–2.79 (m, 1H), 2.47–2.42 (m, 1H), 2.40 (s, 3H), 2.22 (d, J =16.3 Hz, 1H), 2.10 (d, J =16.3 Hz, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 1.85 (d, J =13.0 Hz, 1H), 1.74–1.59 (m, 6H), 1.42–1.33 (m, 1H), 0.86 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =171.0 (C), 170.9 (C), 154.4 (C), 143.1 (C), 138.8 (C), 129.6 (C), 129.6 (CH), 128.6 (C), 127.5 (CH), 117.9 (CH), 70.8 (C), 63.2 (CH₂), 62.4 (CH₂), 60.3 (CH₂), 40.2 (C), 38.3 (CH₂), 36.3 (CH₂), 36.1 (CH₂), 24.5 (CH₂), 22.7 (CH₂), 22.2 (CH₂), 22.1 (CH₃), 21.7 (CH₃), 21.1 (CH₃), 20.9 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₂₇H₃₆NO₆S⁺ [M+H]⁺: 502.2258; found: 502.2258.

Compound 3ia

Procedure B afforded **3ia** as a colorless oil (71.7 mg, 93%). R_f (PE/Et₂O 3/7)=0.35; IR (neat): $\tilde{\nu}$ =2998, 2819, 2254, 1761, 1395, 1210, 1159, 1034, 719, 537 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =5.70 (s, 1H), 4.83 (d, J =12.5 Hz, 1H), 4.78 (d, J =12.4 Hz, 1H), 4.69 (d, J =12.4 Hz, 1H), 4.60 (d, J =12.5 Hz, 1H), 3.53 (d, J =9.2 Hz, 1H), 3.10 (d, J =9.2 Hz, 1H), 2.91 (s, 3H), 2.29 (d, J =16.4 Hz, 1H), 2.24 (d, J =16.4 Hz, 1H), 2.05 (s, 3H), 2.05 (s, 3H), 1.64 (s, 3H), 1.52 (s, 3H), 1.12 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =171.0 (C), 156.2 (C), 129.4 (C), 128.8 (C), 115.7 (CH), 66.6 (C), 63.3 (CH₂), 62.1 (CH₂), 61.1 (CH₂), 40.3 (CH₃), 39.4 (C), 38.4 (CH₂), 30.9 (CH₃), 28.2 (CH₃), 22.2 (CH₃), 21.1 (CH₃), 21.0 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₁₈H₃₁N₂O₆S⁺ [M+NH₄]⁺: 403.1897; found: 403.1897.

Compound 3ja

Procedure B afforded **3ja** as a colorless oil (74.9 mg, 91%). R_f (PE/Et₂O 1/1)=0.36; IR (neat): $\tilde{\nu}$ =2974, 2891, 2252, 1734, 1628, 1445, 1225, 904, 723, 647 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.37 (s, 5H), 5.76 (s, 1H), 4.81 (d, J =12.5 Hz, 1H), 4.78 (d, J =12.4 Hz, 1H), 4.69 (d, J =12.4 Hz, 1H), 4.58 (d, J =12.5 Hz, 1H), 3.49–3.44 (m, 1H), 3.20 (d, J =10.7 Hz, 1H), 2.23 (d, J =16.4 Hz, 1H), 2.13 (d, J =16.4 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 1.83 (s, 3H), 1.64 (s, 3H), 1.09 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =170.9 (C), 170.9 (C), 170.2 (C), 157.1 (C), 138.9 (C), 129.4 (C), 129.3 (CH), 128.6 (CH), 128.2 (C), 126.3 (CH), 115.1 (CH), 64.6 (C), 63.3 (CH₂), 62.9 (CH₂), 62.1 (CH₂), 39.7 (C), 38.4 (CH₂), 29.2 (CH₃), 26.1 (CH₃), 22.1 (CH₃), 21.0 (CH₃), 20.8 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₂₄H₃₀NO₅⁺ [M+H]⁺: 412.2118; found: 412.2118.

Compound 3ka

Procedure B afforded **3ka** as a colorless oil (59.2 mg, 85%). R_f (PE/Et₂O 4/1)=0.45; IR (neat): $\tilde{\nu}$ =2932, 2855, 2255, 1734, 1375, 1221, 1021, 959, 727 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =5.64 (s, 1H), 4.83 (d, J =12.4 Hz, 1H), 4.79 (dd, J =12.3, 1.3 Hz, 1H), 4.70 (d, J =12.3 Hz, 1H), 4.61 (d, J =12.4 Hz, 1H), 3.83 (d, J =8.3 Hz, 1H), 3.51 (d, J =8.3 Hz, 1H), 2.25 (d, J =16.4 Hz, 1H), 2.16 (d, J =16.4 Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 1.80–1.51 (m, 8H), 1.30–1.21 (m, 2H), 1.06 ppm (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ =170.7 (C), 170.7 (C), 157.3 (C), 129.5 (C), 128.1 (C), 113.6 (CH), 82.3 (C), 77.8 (CH₂), 63.2 (CH₂), 62.0 (CH₂), 42.1 (C), 38.4 (CH₂), 37.1 (CH₂), 35.5 (CH₂), 25.2 (CH₂), 22.4 (CH₂), 22.1 (CH₂), 21.2 (CH₃), 20.8 (CH₃), 20.7 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₂₀H₃₂NO₅⁺ [M+NH₄]⁺: 366.2275; found: 366.2275.

Compound 3la

Procedure B afforded **3la** as a colorless oil (79.3 mg, 88%). R_f (PE/Et₂O 3/1)=0.40; IR (neat): $\tilde{\nu}$ =2913, 2900, 1796, 1431, 1185, 1025, 997, 835, 775, 564 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =5.61 (s, 1H), 4.81 (d, J =12.5 Hz, 1H), 4.75–4.68 (m, 2H), 4.50 (d, J =12.5 Hz, 1H), 4.22 (q, J =7.1 Hz, 2H), 4.10 (qd, J =7.2, 1.5 Hz, 2H), 2.60–2.54 (m, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (d, J =16.4 Hz, 1H), 1.98 (d, J =16.4 Hz, 1H), 1.38 (s, 3H), 1.29 (t, J =7.1 Hz, 3H), 1.22–1.13 ppm (m, 9H); ¹³C NMR (75 MHz, CDCl₃): δ =171.8 (C), 171.19 (C), 171.15 (C), 170.7 (C), 158.5 (C), 129.8 (C), 129.6 (C), 114.8 (CH), 68.0 (C), 63.5 (CH₂), 62.4 (CH₂), 61.3 (CH₂), 61.2 (CH₂), 48.3 (C), 44.3 (CH₂), 41.6 (CH₂), 38.8 (C), 26.5 (CH₃), 25.9 (CH₃), 23.2 (CH₃), 21.3 (CH₃), 21.1 (CH₃), 14.4 (CH₃), 14.2 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₂₄H₃₈NO₈⁺ [M+NH₄]⁺: 468.2592; found: 468.2593.

Compound 3bb

Procedure B afforded **3bb** as a colorless oil (93.8 mg, 95%). R_f (PE/Et₂O 1/1)=0.30; IR (neat): $\tilde{\nu}$ =2998, 2890, 1710, 1495, 1220, 1106, 895, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.73 (d, J =8.3 Hz, 2H), 7.27 (d, J =8.1 Hz, 2H), 5.69 (s, 1H), 4.88 (d, J =12.5 Hz, 1H), 4.85 (d, J =12.3 Hz, 1H), 4.73 (d, J =12.3 Hz, 1H), 4.63 (d, J =12.5 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.40 (d, J =9.2 Hz, 1H), 3.00 (d, J =9.2 Hz, 1H), 2.40 (s, 3H), 2.23 (s, 2H), 1.68 (s, 3H), 1.45 (s, 3H), 0.96 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =157.2 (C), 155.9 (C), 155.8 (C), 143.3 (C), 138.2 (C), 129.7 (CH), 129.5 (C), 128.7 (C), 127.7 (CH), 115.0 (CH), 67.4 (C), 66.6 (CH₂), 65.4 (CH₂), 60.7 (CH₂), 55.2 (CH₃), 39.4 (C), 38.2 (CH₂), 31.0 (CH₃), 28.4 (CH₃), 21.9 (CH₃), 21.7 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₂₄H₃₂NO₈S⁺ [M+H]⁺: 494.1843; found: 494.1842.

Compound 3bc

Procedure B afforded **3bc** as a colorless oil (76.2 mg, 94%). R_f (PE/Et₂O 4/6)=0.37; IR (neat): $\tilde{\nu}$ =3441, 2926, 2819, 1726, 1598, 1379, 1156, 1089, 663, 549 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.74 (d, J =8.2 Hz, 2H), 7.27 (d, J =8.2 Hz, 2H), 5.71 (s, 1H), 4.05 (d, J =12.0 Hz, 1H), 4.04 (dd, J =11.6, 1.7 Hz, 1H), 3.98 (d, J =11.6 Hz, 1H), 3.92 (d, J =12.0 Hz, 1H), 3.40 (d, J =9.1 Hz, 1H), 3.27 (s, 3H), 3.26 (s, 3H), 3.01 (d, J =9.1 Hz, 1H), 2.41 (s, 3H), 2.27 (d, J =16.4 Hz, 1H), 2.24 (d, J =16.4 Hz, 1H), 1.70 (s, 3H), 1.46 (s, 3H), 1.00 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =155.3 (C), 143.2 (C), 138.4 (C), 130.0 (C), 129.9 (C), 129.7 (CH), 127.7 (CH), 115.7 (CH), 71.1 (CH₂), 70.1 (CH₂), 67.5 (C), 61.1 (CH₂), 58.1 (CH₂), 39.5 (C), 38.3 (CH₂), 31.1 (CH₃), 28.6 (CH₃), 22.4 (CH₃), 21.7 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₂₂H₃₂NO₄S⁺ [M+H]⁺: 406.2047; found: 406.2047.

Compound 3bd

Procedure B afforded **3bd** as a colorless oil (103 mg, 92%). R_f (PE/Et₂O 6/4)=0.45; IR (neat): $\tilde{\nu}$ =2919, 2893, 2230, 1317, 1153, 1094, 1039, 721, 544 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.76 (d, J =8.3 Hz, 2H), 7.36–7.26 (m, 12H), 5.76 (s, 1H), 4.43 (dd, J =11.8, 5.0 Hz, 2H), 4.37 (dd, J =11.8, 2.7 Hz, 2H), 4.11 (d, J =11.8 Hz, 1H), 4.09 (dd, J =11.5, 1.5 Hz, 1H), 4.03 (d, J =11.5 Hz, 1H), 3.98 (d, J =11.8 Hz, 1H), 3.42 (d, J =9.1 Hz, 1H), 3.03 (d, J =9.1 Hz, 1H), 2.42 (s, 3H), 2.34 (d, J =16.5 Hz, 1H), 2.20 (d, J =16.5 Hz, 1H), 1.72 (s, 3H), 1.47 (s, 3H), 1.04 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =155.3 (C), 143.2 (C), 138.6 (C), 138.4 (C), 138.4 (C), 130.2 (C), 130.0 (C), 129.7 (CH), 128.7 (CH), 128.7 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 115.9 (CH), 72.2 (CH₂), 72.1 (CH₂), 68.7 (CH₂), 67.5 (CH₂), 67.5 (C), 61.1 (CH₂), 39.6 (C), 38.5 (CH₂), 31.2 (CH₃),

28.6 (CH₃), 22.5 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₄H₄₃N₂O₄S⁺ [*M*+NH₄]⁺: 575.2938; found: 575.2938.

Compound 3be

Procedure B afforded **3be** as a colorless oil (103 mg, 89%). *R_f* (PE/Et₂O 7/3)=0.48; IR (neat): $\tilde{\nu}$ =2980, 2259, 1737, 1270, 1149, 906, 725 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.73 (d, *J*=8.3 Hz, 2H), 7.27 (d, *J*=8.0 Hz, 2H), 5.68 (s, 1H), 4.81 (d, *J*=12.5 Hz, 1H), 4.77 (d, *J*=12.3 Hz, 1H), 4.65 (d, *J*=12.3 Hz, 1H), 4.53 (d, *J*=12.5 Hz, 1H), 3.38 (d, *J*=9.2 Hz, 1H), 2.99 (d, *J*=9.2 Hz, 1H), 2.41 (s, 3H), 2.24 (d, *J*=16.7 Hz, 1H), 2.19 (d, *J*=16.7 Hz, 1H), 1.68 (s, 3H), 1.46 (s, 9H), 1.44 (s, 12H), 0.96 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =156.7 (C), 153.7 (C), 153.7 (C), 143.3 (C), 138.3 (C), 129.7 (CH), 129.5 (C), 128.8 (C), 127.7 (CH), 115.3 (CH), 82.6 (C), 82.5 (C), 67.5 (C), 65.7 (CH₂), 64.5 (CH₂), 60.8 (CH₂), 39.5 (C), 38.2 (CH₂), 31.1 (CH₃), 28.5 (CH₃), 28.1 (CH₃), 21.9 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₀H₄₇N₂O₈S⁺ [*M*+NH₄]⁺: 595.3048; found: 595.3052.

Compound 3bf

Procedure B afforded **3bf** as a white waxy oil (112 mg, 87%). *R_f* (PE/Et₂O 1/1)=0.53; IR (neat): $\tilde{\nu}$ =3086, 2916, 2230, 1711, 1236, 1244, 945, 726, 684 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ =7.76 (d, *J*=7.3 Hz, 2H), 7.45–7.26 (m, 12H), 5.69 (s, 1H), 5.15 (s, 4H), 4.91 (d, *J*=12.4 Hz, 1H), 4.87 (d, *J*=12.2 Hz, 1H), 4.77 (d, *J*=12.2 Hz, 1H), 4.66 (d, *J*=12.4 Hz, 1H), 3.40 (d, *J*=8.7 Hz, 1H), 3.01 (d, *J*=8.7 Hz, 1H), 2.44 (s, 3H), 2.22 (s, 2H), 1.68 (s, 3H), 1.46 (s, 3H), 0.92 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =157.2 (C), 155.3 (C), 155.2 (C), 143.2 (C), 138.2 (C), 135.4 (C), 129.7 (CH), 129.5 (C), 128.9 (CH), 128.6 (C), 128.6 (CH), 127.7 (CH), 115.0 (CH), 70.0 (CH₂), 67.4 (C), 66.7 (CH₂), 65.5 (CH₂), 60.7 (CH₂), 39.4 (C), 38.1 (CH₂), 31.0 (CH₃), 28.4 (CH₃), 21.8 (CH₃), 21.7 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₆H₄₃N₂O₈S⁺ [*M*+NH₄]⁺: 663.2735; found: 663.2734.

Compound 3bg

Procedure B afforded **3bg** as a white solid (112 mg, 83%). M.p. 156–158 °C; *R_f* (PE/Et₂O 4/6)=0.50; IR (neat): $\tilde{\nu}$ =3639, 3020, 2257, 1755, 1558, 1298, 1178, 1091, 862, 731, 647 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ =8.26 (d, *J*=8.7 Hz, 4H), 8.14 (d, *J*=8.7 Hz, 4H), 7.74 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=7.2 Hz, 2H), 5.78 (s, 1H), 5.22 (d, *J*=12.5 Hz, 1H), 5.14 (d, *J*=12.5 Hz, 1H), 5.07 (d, *J*=12.5 Hz, 1H), 4.94 (d, *J*=12.5 Hz, 1H), 3.42 (d, *J*=9.2 Hz, 1H), 3.06 (d, *J*=9.2 Hz, 1H), 2.41 (s, 3H), 2.35 (d, *J*=6.4 Hz, 2H), 1.70 (s, 3H), 1.51 (s, 3H), 0.99 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =164.8 (C), 164.7 (C), 157.9 (C), 151.0 (C), 151.0 (C), 143.5 (C), 138.2 (C), 135.5 (C), 135.5 (C), 131.0 (CH), 131.0 (CH), 129.98 (C), 129.8 (CH), 128.8 (C), 127.7 (CH), 124.0 (CH), 123.9 (CH), 115.2 (CH), 67.4 (C), 64.8 (CH₂), 63.6 (CH₂), 60.7 (CH₂), 39.7 (C), 38.6 (CH₂), 31.2 (CH₃), 28.5 (CH₃), 22.1 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₄H₃₄N₃O₁₀S⁺ [*M*+H]⁺: 676.1959; found: 676.1959.

Compound 3bh

Procedure B afforded **3bh** as a colorless oil (120 mg, 93%). *R_f* (PE/Et₂O 4/6)=0.32; IR (neat): $\tilde{\nu}$ =2967, 2865, 1701, 1604, 1510, 1249, 1164, 1087, 815, 608, 549 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.93 (d, *J*=9.0 Hz, 4H), 7.73 (d, *J*=8.3 Hz, 2H), 7.27 (d, *J*=8.0 Hz, 2H), 6.88 (d, *J*=1.7 Hz, 2H), 6.86 (d, *J*=1.7 Hz, 2H), 5.77 (s, 1H), 5.10 (d, *J*=12.5 Hz, 1H), 5.03 (d, *J*=12.4 Hz, 1H), 4.97 (d, *J*=12.4 Hz, 1H), 4.85 (d, *J*=12.5 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.40 (d, *J*=9.2 Hz, 1H), 3.03 (d, *J*=9.2 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 2H), 1.69 (s, 3H), 1.48 (s, 3H), 1.00 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =

166.3 (C), 163.8 (C), 163.7 (C), 156.6 (C), 143.2 (C), 138.2 (C), 131.9 (CH), 131.9 (CH), 129.9 (C), 129.7 (CH), 129.2 (C), 127.7 (CH), 122.7 (C), 122.6 (C), 115.6 (CH), 114.0 (CH), 113.9 (CH), 67.4 (C), 63.7 (CH₂), 62.6 (CH₂), 60.8 (CH₂), 55.7 (CH₃), 39.6 (C), 38.6 (CH₂), 31.2 (CH₃), 28.5 (CH₃), 22.0 (CH₃), 21.7 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₆H₄₃N₂O₈S⁺ [*M*+NH₄]⁺: 663.2735; found: 663.2739.

Compound 3bi

Procedure B afforded **3bi** as a colorless oil (64.9 mg, 86%). *R_f* (AcOEt)=0.36; IR (neat): $\tilde{\nu}$ =3516, 3086, 2965, 1680, 1236, 1185, 1055, 980, 796, 663, 544 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.74 (d, *J*=8.3 Hz, 2H), 7.28 (d, *J*=8.0 Hz, 2H), 5.69 (s, 1H), 4.26–4.08 (m, 4H), 3.38 (d, *J*=9.1 Hz, 1H), 3.00 (d, *J*=9.1 Hz, 1H), 2.41 (brs, 5H; CH₃+2OH), 2.26 (d, *J*=16.6 Hz, 1H), 2.20 (d, *J*=16.6 Hz, 1H), 1.68 (s, 3H), 1.45 (s, 3H), 0.98 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =155.6 (C), 143.4 (C), 138.3 (C), 131.8 (C), 129.8 (CH), 127.7 (CH), 116.3 (CH), 67.5 (C), 62.4 (CH₂), 61.3 (CH₂), 61.1 (CH₂), 39.6 (C), 39.1 (CH₂), 31.2 (CH₃), 28.6 (CH₃), 22.1 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₀H₂₇NO₄SN⁺ [*M*+Na]⁺: 400.1553; found: 400.1553.

Compound 3bj

Procedure B afforded **3bj** as a colorless oil (73.7 mg, 89%). *R_f* (PE/Et₂O 7/3)=0.38; IR (neat): $\tilde{\nu}$ =2931, 2878, 2255, 1733, 1375, 1225, 1154, 905, 724, 588 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ =7.75 (d, *J*=8.2 Hz, 2H), 7.28 (d, *J*=8.2 Hz, 2H), 5.68 (s, 1H), 4.30 (d, *J*=11.5 Hz, 1H), 4.19 (d, *J*=11.6 Hz, 1H), 4.11 (d, *J*=11.6 Hz, 1H), 4.06 (d, *J*=11.5 Hz, 1H), 3.43 (d, *J*=9.2 Hz, 1H), 3.04 (d, *J*=9.2 Hz, 1H), 2.41 (s, 3H), 2.33 (d, *J*=16.4 Hz, 1H), 2.23 (d, *J*=16.4 Hz, 1H), 1.71 (s, 3H), 1.49 (s, 3H), 1.02 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =157.8 (C), 143.4 (C), 138.2 (C), 130.8 (C), 129.7 (CH), 129.4 (C), 127.7 (CH), 115.3 (CH₂), 67.4 (C), 60.7 (CH₂), 43.9 (CH₂), 41.6 (CH₂), 39.8 (C), 38.9 (CH₂), 31.1 (CH₃), 28.5 (CH₃), 22.4 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₀H₂₆NO₂SCl₂⁺ [*M*+H]⁺: 414.1056; found: 414.1056.

Compound 3bk

Procedure B afforded **3bk** as a colorless oil (73.2 mg, 98%). *R_f* (PE/Et₂O 8/2)=0.55; IR (neat): $\tilde{\nu}$ =2963, 2867, 1598, 1362, 1288 1148, 1014, 926, 799, 709, 548 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.68 (d, *J*=8.3 Hz, 2H), 7.20 (d, *J*=7.2 Hz, 2H), 5.41 (s, 1H), 3.31 (d, *J*=9.0 Hz, 1H), 2.91 (d, *J*=9.0 Hz, 1H), 2.34 (s, 3H), 2.15–2.03 (m, 3H), 1.99–1.81 (m, 3H), 1.60 (s, 3H), 1.38 (s, 3H), 0.90–0.84 ppm (m, 9H); ¹³C NMR (75 MHz, CDCl₃): δ =152.5 (C), 143.1 (C), 138.6 (C), 129.9 (C), 129.7 (C), 129.6 (CH), 127.8 (CH), 117.7 (CH), 67.5 (C), 61.3 (CH₂), 40.2 (CH₂), 39.9 (C), 31.4 (CH₃), 28.7 (CH₃), 25.9 (CH₂), 24.4 (CH₂), 22.0 (CH₃), 21.8 (CH₃), 14.3 (CH₃), 13.0 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₂H₃₂NO₂S⁺ [*M*+H]⁺: 374.2148; found: 374.2146.

Compound 3bl

Procedure B afforded **3bl** as a colorless oil (19.7 mg, 21%). *R_f* (PE/Et₂O 8/2)=0.45; IR (neat): $\tilde{\nu}$ =2965, 2918, 1612, 1497, 1381, 1153, 1036, 930, 723, 706, 528 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ =7.79 (d, *J*=8.2 Hz, 2H), 7.30 (d, *J*=8.1 Hz, 2H), 7.16–7.08 (m, 6H), 7.01–6.96 (m, 4H), 5.88 (s, 1H), 3.49 (d, *J*=9.1 Hz, 1H), 3.14 (d, *J*=9.1 Hz, 1H), 2.76 (d, *J*=16.1 Hz, 1H), 2.48 (d, *J*=16.1 Hz, 1H), 2.43 (s, 3H), 1.76 (s, 3H), 1.56 (s, 3H), 1.21 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =155.0 (C), 143.3 (C), 142.5 (C), 141.2 (C), 138.4 (C), 132.9 (C), 131.2 (C), 129.8 (CH), 129.4 (CH), 129.1 (CH), 128.3 (CH), 128.3 (CH), 127.8 (CH), 126.8 (CH), 126.7 (CH), 119.1 (CH), 67.67 (C), 61.1

(CH₂), 43.2 (CH₂), 40.1 (CH₃), 31.4 (CH₃), 28.7 (CH₃), 22.1 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₀H₃₂NO₂S⁺ [M+H]⁺: 470.2148; found: 470.2146.

Compound 7ba

Procedure B, with 10 mol% [RuCl(cod)(Cp*)], afforded **7ba** as a colorless oil (64.6 mg, 86%). *R_f* (PE/Et₂O 1/1) = 0.23; IR (neat): $\tilde{\nu}$ = 3510, 3054, 2304, 1670, 1421, 1264, 1158, 730, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.95 (dd, *J* = 5.5, 2.9 Hz, 1H), 5.63 (d, *J* = 5.5 Hz, 1H), 3.41 (d, *J* = 9.1 Hz, 1H), 3.03 (d, *J* = 9.1 Hz, 1H), 2.41 (s, 3H), 2.19 (d, *J* = 16.1 Hz, 1H), 2.09 (dd, *J* = 16.1, 2.9 Hz, 1H), 1.67 (s, 3H), 1.45 (s, 3H), 1.37 (s, 1H), 1.33 (s, 3H), 1.31 (s, 3H), 0.98 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.8 (C), 143.2 (C), 142.3 (C), 138.3 (C), 129.7 (CH), 127.7 (CH), 115.7 (CH), 113.8 (CH), 72.6 (C), 67.4 (C), 61.1 (CH₂), 40.0 (C), 35.8 (CH₂), 31.2 (CH₃), 28.6 (CH₃), 28.6 (CH₃), 28.4 (CH₃), 21.8 (CH₃), 21.6 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₁H₃₀NO₃S⁺ [M+H]⁺: 376.1941; found: 376.1938.

Compound 7bb

Procedure B, with 10 mol% [RuCl(cod)(Cp*)], afforded **7bb** as a white solid (58.2 mg, 70%). M.p. 71–73 °C; *R_f* (PE/Et₂O 1/1) = 0.41; IR (neat): $\tilde{\nu}$ = 2918, 2877, 2271, 1310, 1125, 1076, 959, 749, 544 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.96 (dd, *J* = 5.5, 2.9 Hz, 1H), 5.63 (d, *J* = 5.5 Hz, 1H), 3.41 (d, *J* = 9.1 Hz, 1H), 3.03 (d, *J* = 9.1 Hz, 1H), 2.41 (s, 3H), 2.24 (d, *J* = 16.0 Hz, 1H), 2.06 (dd, *J* = 16.0, 2.9 Hz, 1H), 1.67 (s, 3H), 1.65–1.51 (m, 9H), 1.45 (s, 3H), 1.26–1.13 (s, 2H), 0.98 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.9 (C), 143.2 (C), 142.5 (C), 138.4 (C), 129.7 (CH), 127.8 (CH), 116.5 (CH), 113.9 (CH), 73.3 (C), 67.4 (C), 61.2 (CH₂), 40.0 (C), 35.7 (CH₂), 35.6 (CH₂), 35.5 (CH₂), 31.2 (CH₃), 28.6 (CH₃), 25.9 (CH₂), 22.2 (CH₂), 22.1 (CH₂), 21.8 (CH₃), 21.5 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₄H₃₄NO₃S⁺ [M+H]⁺: 416.2254; found: 416.2254.

Compound 7bc

Procedure B, with 10 mol% [RuCl(cod)(Cp*)], afforded **7bc** as a white solid in a 1:1 mixture of diastereomers (74.4 mg, 85%). M.p. 75–76 °C; *R_f* (PE/Et₂O 1/1) = 0.54; IR (neat): $\tilde{\nu}$ = 2997, 2868, 2253, 1373, 1150, 1121, 904, 701, 593, 549 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.69 (d, *J* = 8.2 Hz, 2H), 7.39–7.36 (m, 2H), 7.34–7.27 (m, 2H), 7.25–7.20 (m, 3H), 6.17 (dd, *J* = 5.5, 2.9 Hz, 0.5H), 6.11 (dd, *J* = 5.5, 2.9 Hz, 0.5H), 5.67 (dd, *J* = 5.4, 2.4 Hz, 1H), 3.28 (d, *J* = 9.0 Hz, 0.5H), 3.25 (d, *J* = 9.1 Hz, 0.5H), 2.91 (d, *J* = 9.2 Hz, 0.5H), 2.88 (d, *J* = 9.1 Hz, 0.5H), 2.39 (s, 3H), 1.97–1.80 (m, 2H), 1.78 (s, 0.5H), 1.76 (s, 0.5H), 1.71–1.66 (m, 6H), 1.44 (s, 1.5H), 1.43 (s, 1.5H), 0.82 (s, 1.5H), 0.73 ppm (s, 1.5H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.3 (C × 0.5), 154.1 (C × 0.5), 145.6 (C × 0.5), 145.4 (C × 0.5), 143.1 (C), 141.0 (C × 0.5), 140.8 (C × 0.5), 138.3 (C × 0.5), 138.2 (C × 0.5), 129.6 (CH × 2), 128.4 (CH × 2), 127.7 (CH × 2 × 0.5), 127.7 (CH × 2 × 0.5), 127.3 (CH × 0.5), 127.2 (CH × 0.5), 125.81 (CH × 2 × 0.5), 125.7 (CH × 2 × 0.5), 117.5 (CH₂ × 0.5), 117.2 (CH₂ × 0.5), 113.6 (CH₂ × 0.5), 113.59 (CH₂ × 0.5), 76.6 (C × 0.5), 76.2 (C × 0.5), 67.3 (C), 61.0 (CH₂ × 0.5), 60.95 (CH₂ × 0.5), 40.0 (C × 0.5), 39.9 (C × 0.5), 35.8 (CH₂ × 0.5), 35.7 (CH₂ × 0.5), 31.4 (CH₃ × 0.5), 31.2 (CH₃ × 0.5), 28.6 (CH₃), 28.5 (CH₃ × 0.5), 28.1 (CH₃ × 0.5), 22.2 (CH₃ × 0.5), 21.8 (CH₃ × 0.5), 21.7 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₆H₃₂NO₃S⁺ [M+H]⁺: 438.2097; found: 438.2096.

Compound 7bd

Procedure B, with 10 mol% [RuCl(cod)(Cp*)], afforded **7bd** as a white solid (90.9 mg, 91%). M.p. 112–113 °C; *R_f* (PE/Et₂O 1/1) = 0.60; IR (neat): $\tilde{\nu}$ = 3018, 2947, 1610, 1508, 1485, 1112, 1023, 742, 712 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 8.3 Hz, 2H), 7.28–7.23 (m, 8H), 7.23–7.19 (m, 2H), 7.19–7.17 (m, 2H), 5.58 (dd, *J* = 5.5, 2.7 Hz, 1H), 5.52 (d, *J* = 5.5 Hz, 1H), 3.24 (d, *J* = 9.1 Hz, 1H), 2.86 (d, *J* = 9.1 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 1H), 2.08 (d, *J* = 16.3 Hz, 1H), 1.98 (dd, *J* = 16.3, 2.7 Hz, 1H), 1.59 (s, 3H), 1.37 (s, 3H), 0.84 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.7 (C), 144.6 (C), 144.6 (C), 143.2 (C), 140.3 (C), 138.3 (C), 129.7 (CH), 128.3 (CH), 128.25 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.7 (CH), 122.2 (CH), 113.6 (CH), 82.6 (C), 67.3 (C), 61.1 (CH₂), 40.3 (C), 36.5 (CH₂), 31.3 (CH₃), 28.5 (CH₃), 22.5 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₁H₃₄NO₃S⁺ [M+H]⁺: 500.2254; found: 500.2256.

Compound 7be

Procedure B afforded **7be** as a pale yellow solid (67.6 mg, 64%). M.p. 58–59 °C; *R_f* (PE/Et₂O 4/6) = 0.33; IR (neat): $\tilde{\nu}$ = 3276, 2977, 1598, 1450, 1382, 1146, 1090, 909, 661, 548 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.88 (dd, *J* = 5.5, 2.8 Hz, 1H), 5.58 (d, *J* = 5.5 Hz, 1H), 4.43 (s, 1H), 3.38 (d, *J* = 9.1 Hz, 1H), 2.89 (d, *J* = 9.1 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H), 2.07 (d, *J* = 16.1 Hz, 1H), 1.79 (dd, *J* = 16.1, 2.8 Hz, 1H), 1.66 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.28 (s, 3H), 0.96 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 153.6 (C), 142.3 (C), 142.2 (C), 139.3 (C), 138.8 (C), 137.3 (C), 128.8 (CH), 128.7 (CH), 126.8 (CH), 126.4 (CH), 117.1 (CH), 112.6 (CH), 66.3 (C), 60.1 (CH₂), 58.1 (C), 39.1 (C), 34.4 (CH₂), 30.3 (CH₃), 27.5 (CH₃), 27.0 (CH₃), 25.3 (CH₃), 20.8 (CH₃), 20.7 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₈H₃₇N₂O₄S₂⁺ [M+H]⁺: 529.2189; found: 529.2188.

Compound 7bg

Procedure B afforded **7bg** as a colorless oil (22.3 mg, 29%). *R_f* (PE/Et₂O 3/1) = 0.44; IR (neat): $\tilde{\nu}$ = 3018, 2932, 1698, 1454, 1214, 1156, 1090, 940, 751, 667, 570 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.86 (dd, *J* = 5.5, 3.0 Hz, 1H), 5.62 (d, *J* = 5.5 Hz, 1H), 3.42 (d, *J* = 9.0 Hz, 1H), 3.05 (s, 3H), 3.02 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 3H), 2.28 (d, *J* = 16.3 Hz, 1H), 1.95 (dd, *J* = 16.3, 2.9 Hz, 1H), 1.69 (s, 3H), 1.46 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H), 1.00 ppm (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 154.5 (C), 143.2 (C), 139.9 (C), 138.3 (C), 129.7 (CH), 127.8 (CH), 119.2 (CH), 113.6 (CH), 76.8 (C), 67.4 (C), 61.3 (CH₂), 50.8 (CH₃), 40.1 (C), 35.0 (CH₂), 31.3 (CH₃), 28.6 (CH₃), 25.4 (CH₃), 25.1 (CH₃), 22.4 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₂H₃₂NO₃S [M+H]⁺: 390.2097; found: 390.2097.

Compound 7bg'

Procedure B afforded **7bg'** as a white solid (26.8 mg, 34%). M.p. 56–57 °C; *R_f* (PE/Et₂O 1/1) = 0.60; IR (neat): $\tilde{\nu}$ = 2975, 2821, 1599, 1451, 1271, 1223, 1074, 951, 903, 784, 598 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.82 (s, 1H), 5.50 (t, *J* = 4.5 Hz, 1H), 3.41 (d, *J* = 9.1 Hz, 1H), 3.01 (d, *J* = 9.1 Hz, 1H), 2.99 (s, 3H), 2.41 (s, 3H), 2.14 (d, *J* = 4.5 Hz, 2H), 1.70 (s, 3H), 1.48 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H), 1.00 ppm (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 155.7 (C), 143.2 (C), 140.3 (C), 138.4 (C), 129.7 (CH), 127.8 (CH), 1178.0 (CH), 113.4 (CH), 76.1 (C), 67.6 (C), 61.2 (CH₂), 50.7 (CH₃), 39.3 (C), 35.6 (CH₂), 31.4 (CH₃), 28.7 (CH₃),

25.9 (CH₃), 25.5 (CH₃), 22.1 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₂H₃₂NO₃S [M+H]⁺: 390.2097; found: 390.2097.

Slow evaporation of a solution of **7bg'** in petroleum ether yielded good single crystals for X-ray analysis. Crystal data: C₂₂H₃₁NO₃S, *M_r* = 389.54, monoclinic, *P*1211, *a* = 6.4533(5) Å, *b* = 8.1500(5) Å, *c* = 20.626(2) Å, β = 93.939(8)°, *V* = 1082.25(16) Å³, *Z* = 2, ρ_{calcd} = 1.195 g cm⁻³, *R* = 0.0684 (*R_w* = 0.1905) for 3537 reflections with *I* > 2.00σ(*I*) and 251 variable parameters.^[24]

Compound 7bi

Procedure B afforded **7bi** as a colorless oil (34.1 mg, 49%). *R_f* (PE/Et₂O 4/6) = 0.30; IR (neat): $\tilde{\nu}$ = 3490, 2929, 2899, 1738, 1318, 1209, 953, 749, 559 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.57–5.54 (m, 1H), 5.66 (s, 1H), 4.14–4.07 (m, 2H), 3.37 (d, *J* = 9.1 Hz, 1H), 3.00 (d, *J* = 9.1 Hz, 1H), 2.41 (s, 3H), 2.14 (d, *J* = 4.4 Hz, 2H), 1.69 (s, 3H), 1.47 (s, 3H), 1.42 (brs, 1H), 1.01 ppm (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 156.2 (C), 143.3 (C), 138.3 (C), 135.8 (C), 129.7 (CH), 127.8 (CH), 119.1 (CH), 113.9 (CH), 67.4 (C), 65.5 (CH₂), 61.1 (CH₂), 39.6 (C), 35.3 (CH₂), 31.2 (CH₃), 28.7 (CH₃), 22.3 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₁₉H₂₆NO₃S⁺ [M+H]⁺: 348.1628; found: 348.1630.

Compound 7bi'

Procedure B afforded **7bi'** as a colorless oil (33.4 mg, 48%). *R_f* (PE/Et₂O 4/6) = 0.28; IR (neat): $\tilde{\nu}$ = 3501, 2917, 2900, 1696, 1299, 1152, 949, 687, 660, 593 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.92–5.89 (m, 1H), 5.62 (d, *J* = 5.4 Hz, 1H), 4.13–4.05 (m, 2H), 3.39 (d, *J* = 9.1 Hz, 1H), 3.03 (d, *J* = 9.1 Hz, 1H), 2.41 (s, 3H), 2.19–2.11 (m, 1H), 2.06 (d, *J* = 16.4 Hz, 1H), 1.68 (s, 3H), 1.45 (s, 3H), 1.41 (brs, 1H), 1.00 ppm (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 154.6 (C), 143.3 (C), 138.3 (C), 135.4 (C), 129.7 (CH), 127.8 (CH), 119.2 (CH), 113.5 (CH), 67.4 (C), 66.4 (CH₂), 61.0 (CH₂), 39.9 (C), 36.6 (CH₂), 31.2 (CH₃), 28.7 (CH₃), 22.2 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₁₉H₂₆NO₃S⁺ [M+H]⁺: 348.1628; found: 348.1631.

Compound 8

Procedure B afforded **8** as a colorless oil (26.5 mg, 34%). *R_f* (PE/Et₂O 7/3) = 0.35; IR (neat): $\tilde{\nu}$ = 3019, 2911, 1599, 1447, 1214, 1156, 1091, 930, 744, 667, 566, 550 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.89 (s, 1H), 4.87 (s, 1H), 3.37 (d, *J* = 9.7 Hz, 1H), 3.25 (s, 3H), 3.10 (d, *J* = 9.7 Hz, 1H), 2.41 (s, 3H), 2.30 (d, *J* = 16.7 Hz, 1H), 2.19 (d, *J* = 16.7 Hz, 1H), 1.55 (s, 3H), 1.53 (s, 3H), 1.35 (s, 6H), 1.17 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 162.6 (C), 142.3 (C), 137.4 (C), 128.7 (CH), 126.8 (CH), 104.3 (CH₂), 83.5 (C), 80.4 (C), 69.8 (C), 67.7 (C), 56.3 (CH₂), 50.8 (CH₃), 43.1 (C), 29.1 (CH₂), 28.6 (CH₃), 28.5 (CH₃), 27.9 (CH₃), 27.8 (CH₃), 23.7 (CH₃), 20.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₂H₃₂NO₃S [M+H]⁺: 390.2097; found: 390.2097.

Compound 10

Procedure B afforded **10** as a white solid (41.5 mg, 49%). M.p. 61–62 °C; *R_f* (PE/Et₂O 1/1) = 0.42; IR (neat): $\tilde{\nu}$ = 3520, 2974, 2929, 1598, 136, 1149, 1090, 1028, 703, 572, 549 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 8.2 Hz, 2H), 7.36–7.26 (m, 5H), 7.15 (d, *J* = 7.2 Hz, 2H), 5.93 (s, 1H), 4.16 (d, *J* = 5.5 Hz, 2H), 3.43 (d, *J* = 9.2 Hz, 1H), 3.06 (d, *J* = 9.2 Hz, 1H), 2.60 (d, *J* = 16.2 Hz, 1H), 2.42 (s, 3H), 2.34 (d, *J* = 16.2 Hz, 1H), 1.75 (s, 3H), 1.54 (s, 3H), 1.24 (t, *J* = 5.4 Hz, 1H), 1.13 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 155.1 (C), 143.2 (C), 141.3 (C), 138.3 (C), 132.8 (C), 130.6 (C), 129.7 (CH), 128.6

(CH), 128.2 (CH), 127.7 (CH), 127.5 (CH), 115.9 (CH), 67.6 (C), 62.0 (CH₂), 61.0 (CH₂), 42.8 (CH₂), 39.9 (C), 31.3 (CH₃), 28.7 (CH₃), 22.1 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₅H₂₉NO₃Na⁺ [M+Na]⁺: 446.1760; found: 446.1759.

Compound 10'

Procedure B afforded **10'** as a white solid (32.2 mg, 38%). M.p. 68–69 °C; *R_f* (PE/Et₂O 1/1) = 0.40; IR (neat): $\tilde{\nu}$ = 3515, 2972, 2927, 1598, 1363, 1224, 1147, 973, 780, 701, 581 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 8.2 Hz, 2H), 7.37–7.26 (m, 5H), 7.14 (d, *J* = 7.0 Hz, 2H), 5.72 (s, 1H), 4.19 (d, *J* = 11.7 Hz, 1H), 4.04 (d, *J* = 11.7 Hz, 1H), 3.47 (d, *J* = 9.2 Hz, 1H), 3.11 (d, *J* = 9.2 Hz, 1H), 2.44 (d, *J* = 16.3 Hz, 1H), 2.43 (s, 3H), 2.34 (d, *J* = 16.3 Hz, 1H), 1.70 (s, 3H), 1.50 (s, 3H), 1.22 (dt, *J* = 6.9, 4.3 Hz, 1H), 1.11 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 155.3 (C), 143.3 (C), 140.1 (C), 138.4 (C), 134.1 (C), 129.8 (C), 129.7 (CH), 128.6 (CH), 128.5 (CH), 127.8 (CH), 127.5 (CH), 118.0 (CH), 67.6 (C), 63.2 (CH₂), 61.1 (CH₂), 39.7 (C), 38.0 (CH₂), 31.2 (CH₃), 28.7 (CH₃), 22.2 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₅H₂₉NO₃Na⁺ [M+Na]⁺: 446.1760; found: 446.1757.

Compound 12

Procedure B afforded **12** as a colorless oil (59.1 mg, 66%, 15:1 md). *R_f* (PE/Et₂O 6/4) = 0.35; IR (neat): $\tilde{\nu}$ = 2972, 2869, 1736, 1376, 1223, 1162, 1048, 915, 712, 549 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.1 Hz, 0.8H), 7.69 (d, *J* = 8.1 Hz, 1.2H), 7.33 (d, *J* = 8.0 Hz, 1.2H), 7.30 (d, *J* = 8.0 Hz, 0.8H), 5.66–5.64 (m, 1H), 4.79–4.51 (m, 4H), 4.44 (q, *J* = 6.6 Hz, 0.4H), 3.89 (q, *J* = 6.6 Hz, 0.6H), 3.59 (d, *J* = 8.6 Hz, 0.6H), 3.56 (d, *J* = 10.8 Hz, 0.4H), 3.20 (d, *J* = 10.8 Hz, 0.4H), 2.65 (d, *J* = 8.6 Hz, 0.6H), 2.44 (s, 1.8H), 2.41 (s, 1.2H), 2.27–2.08 (m, 2H), 2.04–2.02 (m, 6H), 1.60 (d, *J* = 6.6 Hz, 1.8H), 1.45 (d, *J* = 6.6 Hz, 1.2H), 1.15 (s, 1.8H), 0.51 ppm (s, 1.2H); ¹³C NMR (75 MHz, CDCl₃): δ = 171.0 (C), 150.9 (C), 150.7 (C), 144.1 (C), 143.7 (C), 136.8 (C), 132.6 (C), 130.0 (CH), 129.9 (CH), 129.2 (C), 129.1 (C), 128.9 (C), 128.8 (C), 128.4 (CH), 127.6 (CH), 116.7 (CH), 116.4 (CH), 63.4 (CH₂), 63.3 (CH₂), 62.2 (CH₂), 62.1 (CH₂), 61.0 (CH₂), 58.8 (CH), 57.4 (CH), 41.4 (C), 39.5 (C), 38.3 (CH₂), 38.1 (CH₂), 24.8 (CH₃), 22.6 (CH₃), 21.8 (CH₃), 21.7 (CH₃), 21.6 (CH₃), 21.2 (CH₃), 21.1 (CH₃), 21.0 (CH₃), 20.9 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₂₃H₃₀NO₆S⁺ [M+H]⁺: 448.1788; found: 448.1786.

Compound 13

CSA (55.7 mg, 0.24 mmol) was added to a solution of **7bd** (99.9 mg, 0.2 mmol) in toluene (10 mL). The mixture was stirred for 5 h at 60 °C and then concentrated in vacuo. The crude residue was purified by flash chromatography on silica gel to give **13** as a white solid (69.4 mg, 74%). M.p. 113–114 °C; *R_f* (PE/Et₂O 2/3) = 0.28; IR (neat): $\tilde{\nu}$ = 3025, 2930, 1598, 1363, 1156, 1038, 1015, 939, 702, 658, 546 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.73 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.48–7.34 (m, 5H), 7.30–7.22 (m, 5H), 5.92 (d, *J* = 3.8 Hz, 1H), 4.07 (d, *J* = 3.8 Hz, 1H), 3.20 (d, *J* = 9.1 Hz, 1H), 3.07 (d, *J* = 9.1 Hz, 1H), 2.79 (d, *J* = 12.2 Hz, 1H), 2.47 (d, *J* = 12.2 Hz, 1H), 2.40 (s, 3H), 1.62 (s, 3H), 1.59 (s, 3H), 0.71 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.1 (C), 145.1 (C), 144.6 (C), 143.9 (C), 143.2 (C), 139.1 (C), 138.4 (C), 134.8 (C), 129.7 (CH), 129.4 (CH), 128.9 (CH), 127.7 (CH), 127.2 (CH), 125.0 (CH), 123.0 (CH), 120.5 (CH), 115.9 (CH), 67.0 (C), 59.1 (CH₂), 50.9 (CH), 46.2 (C), 35.8 (CH₂), 30.7 (CH₃), 29.0 (CH₃), 26.7 (CH₃), 21.8 ppm (CH₃); HRMS (ESI-MS): *m/z* calcd for C₃₁H₃₂NO₂S⁺ [M+H]⁺: 482.2148; found: 482.2148.

Compound 14

CSA (46.4 mg, 0.2 mmol) was added to a solution of **3bi** (75.5 mg, 0.2 mmol) in toluene (10 mL). The mixture was stirred for 2 days at RT and then concentrated in vacuo. The crude residue was purified by flash chromatography to give **14** as a yellow solid (34.5 mg, 48%). M.p. 144–145 °C; R_f (PE/Et₂O 1/1)=0.37; IR (neat): $\tilde{\nu}$ =3019, 2975, 2866, 1668, 1449, 1214, 1150, 1121, 1033, 747, 667, 540 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =10.08 (s, 1H), 7.75 (d, J =8.3 Hz, 2H), 7.28 (d, J =8.0 Hz, 2H), 6.18 (s, 1H), 3.42 (d, J =9.2 Hz, 1H), 3.02 (d, J =9.2 Hz, 1H), 2.43 (d, J =17.3 Hz, 1H), 2.41 (s, 3H), 2.24 (d, J =1.4 Hz, 3H), 2.14 (d, J =17.3 Hz, 1H), 1.70 (s, 3H), 1.47 (s, 3H), 0.98 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =187.9 (CH), 154.3 (C), 152.3 (C), 143.3 (C), 138.2 (C), 130.9 (C), 129.7 (CH), 127.7 (CH), 109.8 (CH), 67.5 (C), 60.7 (CH₂), 44.8 (CH₂), 39.1 (C), 31.0 (CH₃), 28.5 (CH₃), 22.7 (CH₃), 21.8 (CH₃), 19.1 ppm (CH₃); HRMS (ESI-MS): m/z calcd for C₂₀H₂₆NO₃S⁺ [M+H]⁺: 360.1628; found: 360.1628.

Acknowledgements

We thank the Centre National de la Recherche Scientifique (CNRS) and the Ministère de l'Enseignement Supérieur et de la Recherche (MESR) for financial support. R.L. is grateful for a Ph.D. fellowship from the China Scholarship Council (CSC). We thank Dr. I. DeRiggi (ECM) for help with NMR spectra analysis, Dr. M. Giorgi (Aix-Marseille Université) for X-ray structural analysis, Dr. H. Clavier for help with the X-ray data, and Dr V. Monnier (Aix-Marseille Université) for HRMS assistance.

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