Gold(I)-catalysed Hydroarylations of Alkynes for the Synthesis of Inherently Chiral Calix[4]arenes

Gabriele Giovanardi,[a] Gabriele Scarica,[a] Valentina Pirovano,[b] Andrea Secchi,*[a] and Gianpiero Cera*[a]

We describe the first gold(I)-catalysed intramolecular hydroarylation of alkynes for the straightforward synthesis of inherently chiral calix[4]arenes. This step- and atom-economical approach, which exploits a formal *meta*-functionalisation of the calix[4]arene macrocycle, is able to deliver an ample family of *N*-heterocyclic, chiral compounds in high yields and functional group tolerance.

Introduction

Calix[n]arenes represent a fascinating class of organic molecules which have been thoroughly exploited for many uses.[1] Particularly, their defined cavity, three-dimensional shape and facile synthesis opened access to their use as synthetic receptors,[2] prototypes of molecular machines and nanodevices[3] and as catalysts.[4] Among these structures, particular attention has been drawn by inherently chiral calix[4]arene (ICCs) compounds.[5] In fact, the introduction of an element of chirality on these macrocycles paves the way for the construction of a new generation of asymmetric molecules with potential applications in enantioselective recognition or catalysis. Common synthetic routes to ICCs are constituted by multistep sequences that involve the asymmetric functionalisations at the upper- or lower-rim of the calix[4]arene scaffold, as in example.[6] In this context, stoichiometric *meta*-functionalisations of calix[4]arenes emerged as a viable alternative to introduce an element of chirality.[7,8] Hence, this approach was thoroughly exploited to promote several synthetic manipulations of calix[4]arene macrocycles at their *meta* position, representing a "*state-of-the-art*" method to synthesize ICCs (Figure 1, a).[9] Disapprovingly, this synthetic route often requires the use of of toxic and environmentally hazardous mercury salts as reagents. In this scenario, it appears to be highly demanding to introduce novel catalytic methods to afford ICCs in the safest way and, possibly, by devising atom- and step-economical approaches to such molecularly complex entities. As an example, palladium-catalyzed C-H functionalisations are among the most powerful techniques to synthesize organic molecules.[10] Recently, this method has been exploited to construct ICC derivatives in asymmetric manner. Intramolecular C-H arylations[11] or transannular, dehydrogenative arene-arene coupling[12] were made accessible in high yields and enantioselectivities by a judicious choice of reaction conditions (Figure 1, b).

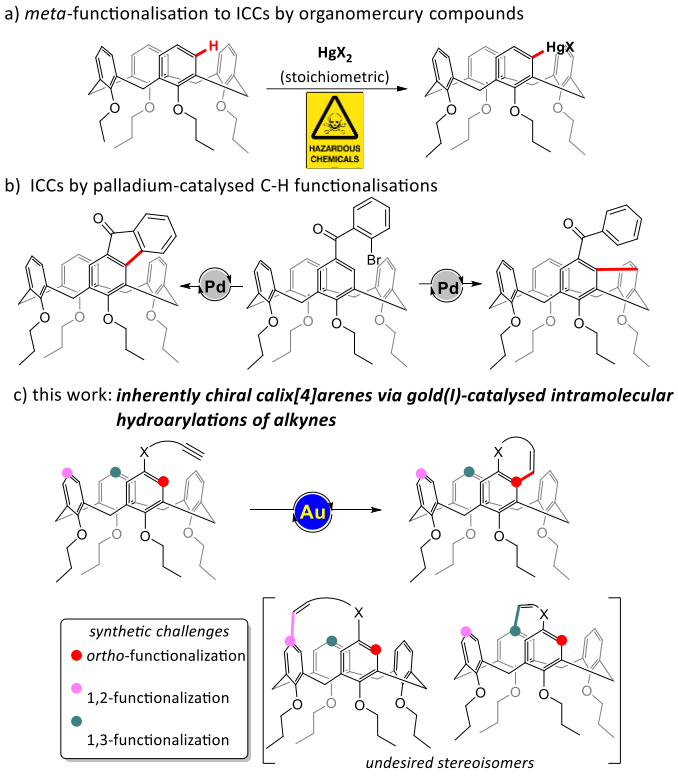


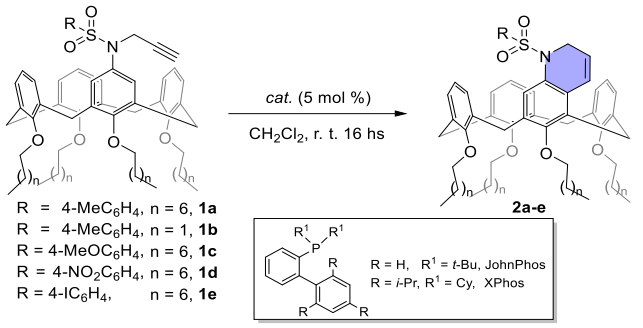
Figure 1. Comparing synthetic routes to ICCs via meta functionalization.

Parallelly, gold(I)-catalysed hydroarylations of alkynes represent an established and sustainable method, as well.[13,14] Indeed, simple phosphine-gold(I) catalysts already proved their versatility to promote intramolecular cyclisations of arenes for the formation of 6-membered heterocycles.[15] With these premises, we reasoned on the possibility to exploit the reactivity of gold catalysts in the presence of simple calix[4]arene alkyne derivatives to form ICCs (Figure 1, c). Important synthetic challenges are represented by the presence of multiple reactive sites towards electrophilic aromatic substitutions. In fact, while *ortho*-hydroarylations are entropically favored, 1,2 functionalisations of the proximal phenolic rings[16] could become accessible by the conformational mobility of the macrocycle.[17] Further, remote 1,3-functionalisations would lead to "bridged" yet achiral macrocyclic compounds.

Results and Discussion

At the outset of the investigation, we submitted alkyne **1a** to typical reaction conditions for gold(I) catalysis using PPh_3AuCl (5 mol %) and $AgSbF_6$ as the chloride scavenger. Delightedly, calix[4]dihydroquinoline **2a** was delivered as the only product in high yields as a racemic mixture (Table 1, entry 1).

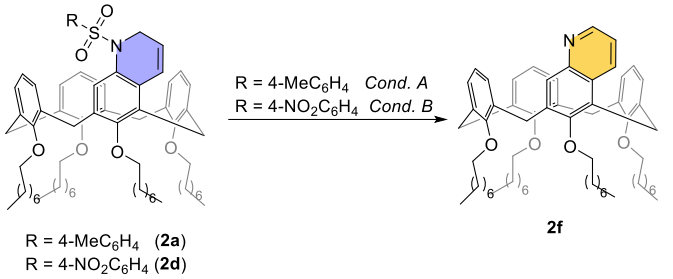
Table 1. Optimisation of reaction conditions.



Entry[a]	1	[M]	[Ag]	**2** [%]
1	**1a**	PPh_3AuCl	$AgSbF_6$	82
2	**1a**	--	$AgSbF_6$	--
3	**1a**	(*rac*)-BINAP(AuCl)$_2$	$AgSbF_6$	46
4	**1a**	XPhosAuCl	$AgSbF_6$	63
5	**1a**	JohnPhosAu(NCCH$_3$)SbF$_6$	--	95
6	**1b**	JohnPhosAu(NCCH$_3$)SbF$_6$	--	94
7	**1b**	$InOTf_3$	--	--
8	**1b**	AgOTf	--	--
9	**1b**	CuI	--	--
10	**1b**	$FeCl_3$	--	--
11[b]	**1c**	JohnPhosAu(NCCH$_3$)SbF$_6$	--	85
12[b]	**1d**	JohnPhosAu(NCCH$_3$)SbF$_6$	--	74
13[b]	**1e**	JohnPhosAu(NCCH$_3$)SbF$_6$	--	73

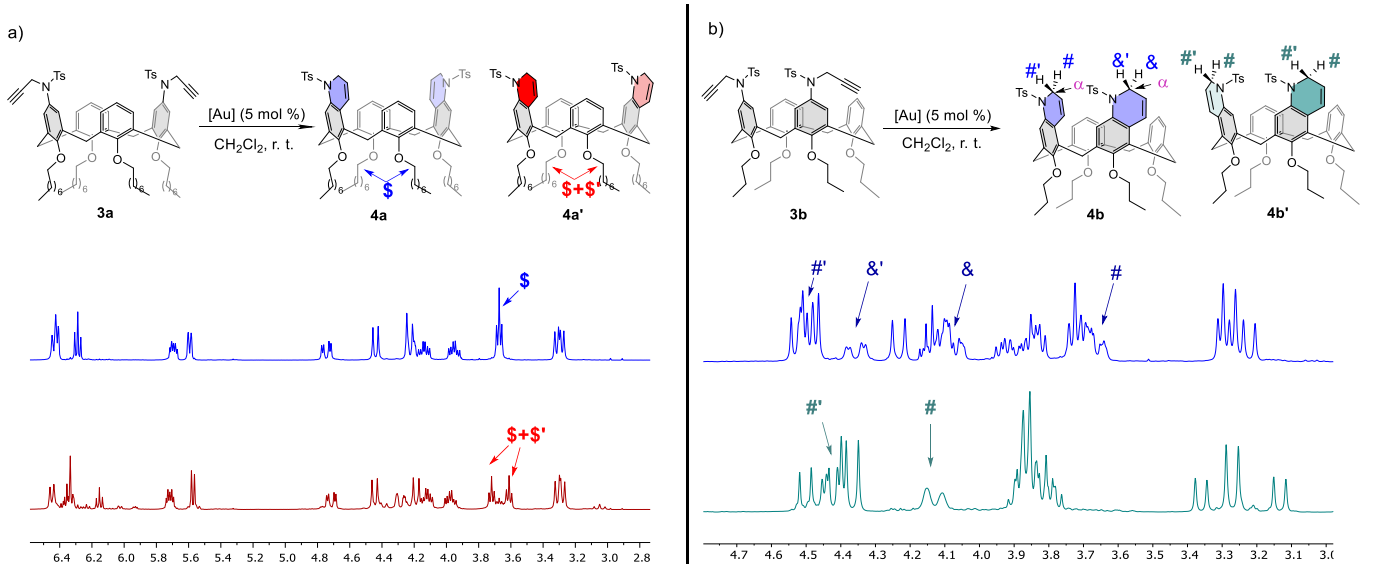
[a]Reaction conditions: 1 (0.05 mmol), solvent (1.0 ml), r. t., 16 hs, isolated yields. [b]1,2-DCE (1.0 ml) as the solvent, 80 °C, 16 hs.

The effect of the silver salt was subsequently evaluated. Hence, no conversion of the starting material was observed (entry 2), proving the gold(I) catalysis manifold. A dinuclear gold(I) catalyst was poorly effective in the transformation, with **2a** isolated in low yields (entry 3, 46 %). A sterically congested Buchwald ligand such as XPhos was found applicable although with diminished efficacy compared to PPh_3AuCl. Interestingly, the well-established, silver-free JohnPhosAu(NCCH$_3$)SbF$_6$ catalyst led to the formation of product **2a** in nearly quantitative yields (entry 5). The effect of the length of the alkyl chain appended on the calix[4]arene scaffold was subsequently evaluated. As expected, smaller alkyl chains as for substrate **1b** did not impact the catalysis, delivering the corresponding product **2b** in comparable high yields (94%, entry 6). The reactivity of substrate **1b** was further tested in the presence of other common Lewis acid catalysts (entries 7,10) whose reactivity was already exploited in intramolecular hydroarylations of alkynes.[18] In all cases, only traces of product **2b** were detected by NMR analysis of the crude mixture. We next probed different sulfonamide-based tethering units, as for **1c**-**e**. Particularly, their reactivities could be unlocked only by running the catalysis at a higher temperature (80 °C, 1,2-dichloroethane as the solvent). Under these reaction conditions, **2c**-**e** could all be delivered in high yields (entries 9-11). Noteworthy, sulfonyl groups could be deprotected under mild reaction conditions leading to the formation of the corresponding calix[4]quinoline scaffold **2f** in good yields (Scheme 2 and Experimental Section for more details).[19]



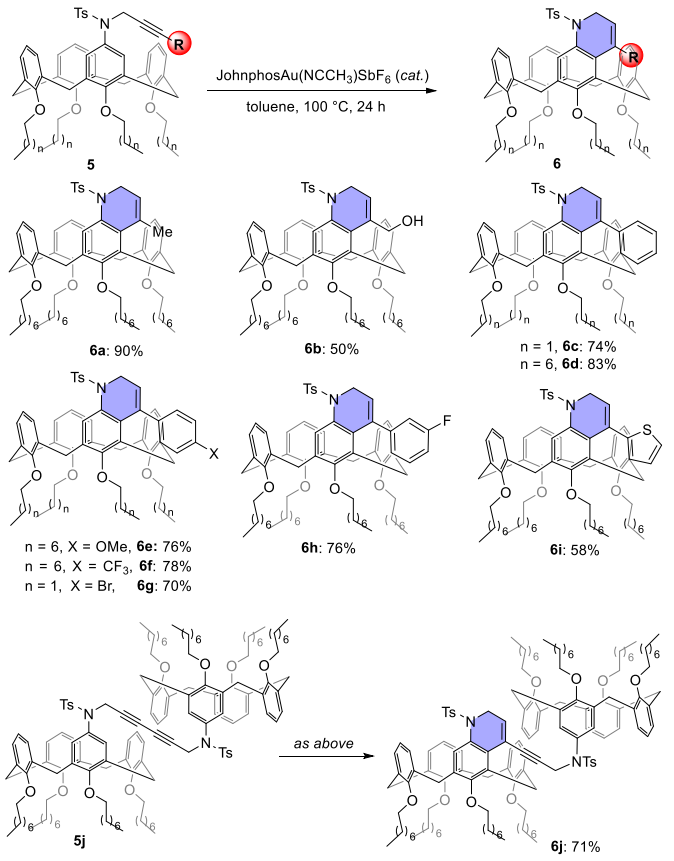
Scheme 2. Synthesis of **2f** via deprotection of sulfonyl groups.

To further investigate the regioselectivity of the transformation, we subsequently synthesized a bis-alkyne substrate **3a** from the corresponding 1,3-diamino calix[4]arenes (Scheme 3a). Hence, **3a** smoothly reacted under the optimised reaction conditions (see entry 5, Table 1) delivering two different products in comparable yields (**4a**: 46 % and **4a**': 40%). Noteworthy, these compounds could be easily isolated by column chromatography on silica gel. The structure of the first spot **4a** was assigned to a chiral compound, in its racemic form, with a C2 symmetry axis while, the second one **4a'**, to an achiral *meso*-compound. The most important difference that could be observed between these structures at NMR, is the presence of a single resonance at 3.67 ppm (blue $) corresponding to the methylenes of the octyloxy groups appended at the unfunctionalised phenolic rings of the calix[4]arene. This signal shifts into two resonances at 3.72 and 3.61 ppm (red $+$') in the second isomer **4a'** suggesting the presence of a plane of symmetry passing through the unfunctionalised phenolic units. Analogously, **3b** was converted into a mixture of products, the assignment of those was more challenging to realize due to the higher complexity of the system. The first compound was attributed to the racemic, chiral compound **4b** (43%) with C1 symmetry. Here, the most notable NMR features are four doublets for the diastereotopic methylene C-H bonds (#,&) on the α-position of the dihydroquinoline scaffold (Scheme 3b). The second compound revealed to be a meso isomer **4b'** (26 %), which is formed from the intramolecular hydroarylations of both alkyne fragments occurring at the diametral positions of the two adjacent phenolic rings (see Scheme 3b and ESI for assignement of **4b'**).



Scheme 3. Synthesis of **4a** and **4a'** and their midfield expanded region of stacked plot ^{1}H-NMR spectra (blue: **4a** and red: **4a'**) (400 MHz, 298K, $CDCl_3$) (a); Synthesis of **4b** and **4b'** and their midfield expanded region of stacked plot ^{1}H-NMR spectra (blue: **4b** and green: **4b'**) (400 MHz, 298 K, $CDCl_3$) showing their diastereo- and enantiotopic methylene-gem protons & and # (b).

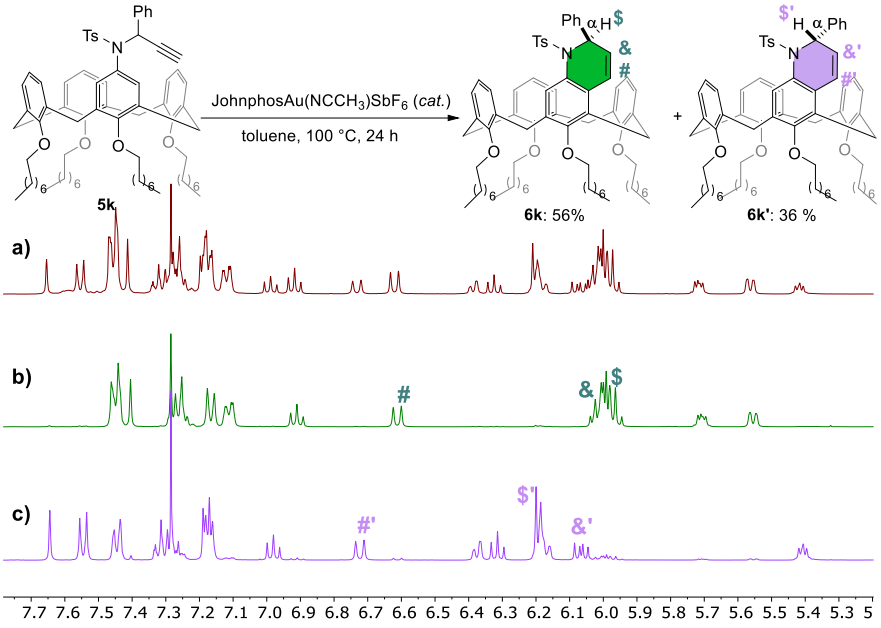
Having now more detailed information about the reactivity of these compounds, we attempted to prove further the scope of the methodology (Scheme 4). Particularly, also internal alkyne derivatives were prone to the transformation although requiring higher temperatures. Indeed, a 2-butyne derivative (**5a**) could be converted into the corresponding product **6a** in good yields, while a propargylic alcohol analogue was also amenable to the transformation into **6b**. Substitution with aryl groups was tolerated as well. Therefore, ICCs **6c**-**h** bearing an aryl ring functionalized with different electron-donating and withdrawing groups at the *para* and *meta* positions, were all delivered with high efficacy (50-90%). Noteworthy, the presence of a heterocyclic thiophene ring did not impact the outcome of the catalysis with product **6i** delivered in synthetically useful yields (58%). To prove the chemoselectivity of the transformation, a dimeric 1,3-diyne starting material **5j** was synthesized and submitted to the catalysis. Hence, the gold(I)-catalysed hydroarylation occurred selectively at only one of the alkyne fragments providing the highly functionalised macrocyclic structure **6j** in 71% yield. Disappointingly, the hydroarylation on the second alkyne fragment did not occur, probably because of sterics.



Scheme 4. Substrate Scope.

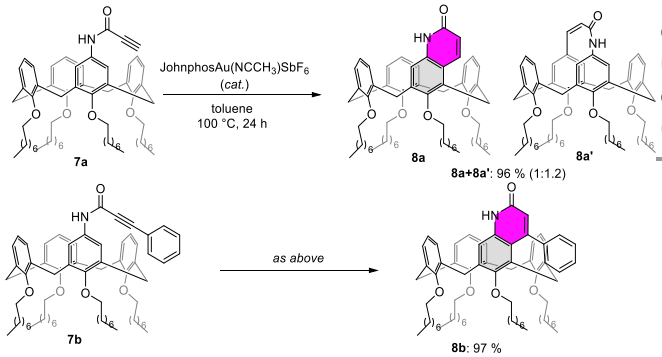
We next evaluated the reactivity of a chiral, racemic propargyl substrate **5k**. Interestingly, NMR analysis of the crude reaction mixture revealed the formation of two diastereoisomeric products **6k** and **6k'** (1.6:1) with the phenyl ring pointing outside and inside the cavity, respectively (Scheme 5). A notable feature of their NMR is represented by the different resonances of the C-H bonds in the α position of the heterocyclic ring. In fact, in

compound **6k'**, **$'** is downfield shifted of 0.2 ppm with respect **$**, suggesting that this latter suffers a more shielded enviroment as a consequence of its proximity to the aromatic calix[4]arene cavity. This finding suggests that the macrocycle plays a role in influencing the stereochemical outcome of the gold(I)-catalysed hydroarylation. Furthermore, compounds **6k** and **6k'** could be easily isolated by column chromatography on silica gel (56% and 36%, respectively).



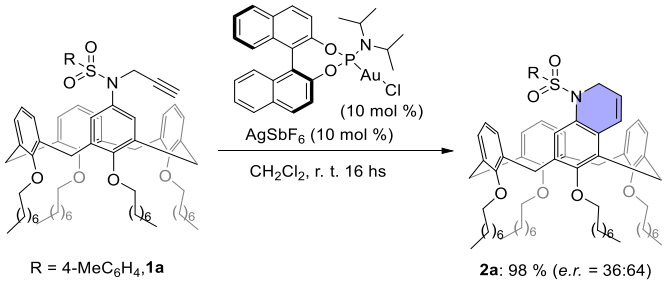
Scheme 5. Synthesis of **6k** and **6k'** and stack plot ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) crude reaction mixture, (b) **6k** (c) **6k'**.

Further, we also evaluated the modification of the tethering unit by synthesizing an amide of type **7a** (Scheme 6).



Scheme 6. Variation of the heterocyclic scaffold.

Hence, we observed the quantitative formation of an inseparable mixture of products, namely a chiral isoquinolone **8a** and its achiral isomer **8a'** (~ 1:1.2). Unfortunately, the use of other gold(I) catalysts or by changing key reaction parameters such as solvent or temperature (see Supporting Information) did not lead to a substantial improvement in the regioselectivity of the gold-catalysed transformation. This outcome underlines that, in principle, all the phenolic rings of the calix[4]arene scaffold are feasible for the functionalization and that the tethering unit is crucial to dictate the regioselectivity of the transformation. This issue could be overcome by increasing the steric hindrance of the alkyne fragment, as for substrate **7b**. In this case, under virtually the same reaction conditions, the corresponding inherently chiral calix[4]isoquinolone **8b** was delivered in excellent yields. Finally, we performed a few explorative experiments to control the construction of these chiral entities via gold(I) catalysis.[20] To this end, a set of commercially available phosphine ligands was tested using model substrate **1a** and promising results were obtained only in the presence of a phosphoramidite ligand (98%, *e.r.* = 36:64, Scheme 7).



Scheme 7. Asymmetric gold(I)-catalyzed hydroarylation of **1a**.

Although just preliminary, this finding opens new perspectives in designing new enantioselective, gold(I)-catalysed methods for ICCs.

Conclusion

In summary, we developed the first catalytic approach to synthesize ICCs via gold(I)-catalysis. Commercially available catalysts promoted highly regioselective 6-endo-dig cyclizations for the synthesis of diversely decorated, chiral

macrocycles. This atom- and step-economical method, which stands as a sustainable alternative to stepwise synthetic routes to ICCs opens new perspectives in this field. Particularly, gold(I)-catalysed functionalisations of unsaturated macrocyclic substrates could be, in principle, applied for the synthesis of novel chiral macrocyclic receptors[21] with higher levels of stereoinduction. These compounds, with preorganised binding sites, finds important applications in the recognition and enantioselective separation of chiral organic molecules, as in example.[5b] Further, their chiroptical properties could be exploited for the design of novel organic materials for optoelecronic devices.[22]

Experimental Section

General Procedure for catalytic reactions. Into a Schlenk flask, under nitrogen atmosphere, the corresponding substrate (50.0 mg) and [JohnPhosAu(I)ACN]$^+$SbF$_6^-$ (5-10 mol %) were dissolved in a dry solvent (1.0 mL) and the mixture stirred at the desired temperature for 16 hrs. After completion, the mixture was diluted with CH_2Cl_2 (10 ml) and filtered through a pad of celite that was washed with an additional 20 ml of CH_2Cl_2. The solvent was removed under low pressure and the crude was purified by column chromatography on silica gel (n-Hex: EtOAc 95:5), obtaining the desired product.

2a. Representative procedure was followed using **1a** (50 mg, 0.046 mmol), [JohnPhosAu(I)ACN]$^+$SbF$_6^-$ (5 mol %), CH_2Cl_2 (1.0 ml) as the solvent and stirring the reaction at 25 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **2a** (47.6 mg, 95 %) as a white solid. **M.p.** = 142 – 143 °C. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.06 (m, 4H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.45 – 6.39 (m, 2H), 6.36 (t, *J* = 7.4 Hz, 1H), 6.27 – 6.18 (m, 3H), 5.68 (dt, *J* = 9.3, 4.3 Hz, 1H), 5.62 – 5.53 (m, 1H), 4.71 (dd, *J* = 17.9, 5.0 Hz, 1H), 4.53 – 4.40 (m, 3H), 4.30 – 4.17 (m, 2H), 4.14 (td, *J* = 11.0, 5.4 Hz, 1H), 4.10 – 4.03 (m, 2H), 3.96 (td, *J* = 10.9, 5.5 Hz, 1H), 3.75 (td, *J* = 6.7, 3.2 Hz, 2H), 3.70 (t, *J* = 6.7 Hz, 2H), 3.34 – 3.25 (m, 2H), 3.23 – 3.12 (m, 2H), 2.38 (s, 3H), 2.16 – 1.76 (m, 8H), 1.66 – 1.48 (m, 4H), 1.48 – 1.18 (m, 36H), 0.93 (t, *J* = 6.6 Hz, 12H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ = 157.8 (C_q), 156.4 (C_q), 155.5 (C_q), 155.4 (C_q), 143.1 (C_q), 137.0 (C_q), 136.9 (C_q), 136.6 (C_q), 136.6 (C_q), 133.5 (C_q), 133.4 (C_q), 133.1 (C_q), 132.9 (C_q), 132.8 (C_q), 129.2 (C_q), 129.0 (CH), 128.9 (CH), 128.7 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.0 (C_q), 127.0 (CH), 126.8 (CH), 123.9 (CH), 123.1 (CH), 122.0 (CH), 121.9 (CH), 121.7 (CH), 75.5 (CH_2), 75.3 (CH_2), 75.2 (CH_2), 75.0 (CH_2), 45.1 (CH_2), 32.0 ($2CH_2$), 31.1 ($2CH_2$), 31.0 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.2 (CH_2), 30.1 ($2CH_2$), 29.8 ($2CH_2$), 29.5 ($2CH_2$), 26.7 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 24.5 (CH_2), 22.8 (CH_2), 22.7 ($2CH_2$), 21.6 (CH_3), 14.1 ($2CH_3$). **LC-MS:** *m/z* [M+NH$_4$]$^+$ calculated for $C_{70}H_{101}N_2O_6S$: 1097.74; found: 1097.49. **HR-MS** (ESI) *m/z*: [M+K]$^+$ calcd. for $C_{70}H_{97}KNO_6S$ 1118.6674; found 1118.6682.

2b. Representative procedure was followed using **1b** (50.0 mg, 0.062 mmol), [JohnPhosAu(I)ACN]$^+$SbF$_6^-$ (5 mol %), CH_2Cl_2 (1.0 ml) as the solvent and stirring the reaction at 25 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **2b** (47.1 mg, 94 %) as a white solid. **M.p.** = 148 – 149 °C. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.07 (m, 4H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.44 – 6.39 (m, 2H), 6.36 (t, *J* = 7.4 Hz, 1H), 6.29 – 6.18 (m, 3H), 5.73 – 5.64 (m, 1H), 5.57 (t, *J* = 4.7 Hz, 1H), 4.75 – 4.65 (m, 1H), 4.52 – 4.38 (m, 3H), 4.26 (d, *J* = 14.1 Hz, 1H), 4.20 (ddd, *J* = 17.9, 3.6, 2.1 Hz, 1H), 4.10 (td, *J* = 10.6, 5.6 Hz, 1H), 4.05 – 3.99 (m, 2H), 3.92 (td, *J* = 10.6, 5.8 Hz, 1H), 3.73 (td, *J* = 6.9, 3.4 Hz, 2H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.35 – 3.24 (m, 2H), 3.23 – 3.14 (m, 2H), 2.38 (s, 3H), 2.09 – 1.80 (m, 8H), 1.13 (t, *J* = 7.4 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H), 0.99 – 0.88 (m, 6H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ = 157.9 (C_q), 156.5 (C_q), 155.4 (C_q), 155.3 (C_q), 143.1 (C_q), 136.9 (C_q), 136.8 (C_q), 136.6 (C_q), 136.5 (C_q), 133.5 (C_q), 133.4 (C_q), 133.1 (C_q), 132.9 (C_q), 132.8 (C_q), 129.2 (C_q), 129.0 (CH), 128.9 (CH), 128.7 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.0 (C_q), 127.0 (CH), 126.8 (CH), 123.8 (CH), 123.1 (CH), 122.0 (CH), 121.9 (CH), 121.8 (CH), 76.8 (CH_2), 76.5 (CH_2), 45.1 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 24.5 (CH_2), 23.5 (CH_2), 23.4 (CH_2), 23.0 (CH_2), 22.9 (CH_2), 21.6 (CH_3), 10.8 (CH_3), 10.7 (CH_3), 10.0 (CH_3), 9.9 (CH_3). **LC-MS:** *m/z* [M+Na]$^+$ calculated for $C_{50}H_{57}NNaO_6S$: 822.38; found: 822.86. **HR-MS** (ESI) *m/z*: [M+K]$^+$ calcd. for $C_{50}H_{57}KNO_6S$ 838.3544; found 838.3538.

2c. Representative procedure was followed using **1c** (50.0 mg, 0.046 mmol), [JohnPhosAu(I)ACN]$^+$SbF$_6^-$ (5 mol %), 1,2-dichloroethane (1.0 ml) as the solvent and stirring the reaction at 80 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **2c** (42.6 mg, 85 %) as a yellowish oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.56 (s, 1H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.10 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.08 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 9.8 Hz, 1H), 6.41 – 6.31 (m, 2H), 6.28 – 6.18 (m, 3H), 5.74 – 5.65 (m, 1H), 5.60 (dd, *J* = 6.6, 2.7 Hz, 1H), 4.68 (dd, *J* = 17.9, 5.0 Hz, 1H), 4.50 – 4.41 (m, 3H), 4.30 – 4.17 (m, 2H), 4.12 (td, *J* = 11.0, 5.5 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.95 (td, *J* = 10.9, 5.5 Hz, 1H), 3.81 (s, 3H), 3.74 (td, *J* = 6.7, 3.5 Hz, 2H), 3.69 (t, *J* = 6.7 Hz, 2H), 3.34 – 3.23 (m, 2H), 3.22 – 3.13 (m, 2H), 2.12 – 1.79 (m, 8H), 1.66 – 1.48 (m, 4H), 1.47 – 1.21 (m, 36H), 0.96 – 0.87 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 162.8 (C_q), 157.8 (C_q), 156.4 (C_q), 155.4 (C_q), 155.3 (C_q), 137.0 (C_q), 136.9 (C_q), 136.6 (C_q), 133.5 (C_q), 133.5 (C_q), 133.2 (C_q), 132.9 (C_q), 132.8 (C_q), 131.3 (C_q), 129.8 (CH), 129.3 (C_q), 128.9 (CH), 128.7 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.0 (CH), 126.9 (C_q), 126.8 (CH), 123.9 (CH), 123.1 (CH), 122.0 (CH), 121.9 (CH), 121.8 (CH), 113.4 (CH), 75.5 (CH_2), 75.3 (CH_2), 75.2 (CH_2), 75.0 (CH_2), 55.5 (CH_3), 45.1 (CH_2), 32.0 ($2CH_2$), 31.1 (CH_2), 31.0 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 24.5 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 14.1 ($2CH_3$). **LC-MS:** *m/z* [M+Na]$^+$ calculated for $C_{50}H_{57}NaO_7S$: 1118.69; found: 1118.59. **HR-MS** (ESI) *m/z*: [M+K]$^+$ calcd. for $C_{70}H_{97}KNO_7S$ 1134.6623; found 1134.6618.

2d. Representative procedure was followed using **1d** (50.0 mg, 0.045 mmol), [JohnPhosAu(I)ACN]$^+$SbF$_6^-$ (5 mol %), 1,2-dichloroethane (1.0 ml) as the solvent and stirring the reaction at 80 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **2d** (37.2 mg, 74 %) as a yellowish oil.

^{1}H NMR: (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.51 (s, 1H), 7.07 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.03 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.49 – 6.37 (m, 3H), 6.36 – 6.23 (m, 3H), 5.70 – 5.58 (m, 2H), 4.57 (dd, *J* = 18.0, 4.6 Hz, 1H), 4.53 – 4.41 (m, 3H), 4.33 (ddd, *J* = 17.9, 4.1, 1.8 Hz, 1H), 4.27 (d, *J* = 14.0 Hz, 1H), 4.14 (td, *J* = 10.7, 5.4 Hz, 1H), 4.03 (m, 2H), 3.97 (dt, *J* = 10.7, 5.4 Hz, 1H), 3.84 – 3.73 (m, 2H), 3.71 (t, *J* = 6.8 Hz, 2H), 3.34 – 3.23 (m, 2H), 3.23 – 3.14 (m, 2H), 1.93 (m, 8H), 1.66 – 1.24 (m, 40H), 0.92 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 157.6 (C_q), 157.0 (C_q), 155.6 (C_q), 155.5 (C_q), 149.8 (C_q), 145.1 (C_q), 136.9 (C_q), 136.7 (C_q), 136.6 (C_q), 134.0 (C_q), 133.9 (C_q), 133.4 (C_q), 132.7 (C_q), 132.7 (C_q), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.2 (C_q), 128.1 (CH), 128.0 (CH), 127.4 (CH), 127.0 (CH), 126.8 (C_q), 126.6 (CH), 124.3 (CH), 123.4 (CH), 122.7 (CH), 122.1 (CH), 122.0 (CH), 121.7 (CH), 75.6 (CH_2), 75.4 (CH_2), 75.3 (CH_2), 75.3 (CH_2), 45.3 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.4 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 24.9 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 14.1 ($2CH_3$). **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{69}H_{95}N_2O_8S$: 1111.68; found: 1111.20. **HR-MS** (ESI) *m/z*: $[M+K]^+$ calcd. for $C_{69}H_{94}KN_2O_8S$ 1149.6368; found 1149.6362.

2e. Representative procedure was followed using **1e** (50.0 mg, 0.042 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (5 mol %), 1,2-dichloroethane (1.0 ml) as the solvent and stirring the reaction at 80 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **2e** (36.4 mg, 73 %), as a colourless oil. **^{1}H NMR**: (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.5 Hz, 2H), 7.54 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.14 – 7.05 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.49 – 6.42 (m, 1H), 6.40 – 6.32 (m, 3H), 6.32 – 6.22 (m, 2H), 5.74 – 5.66 (m, 1H), 5.59 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.66 (dd, *J* = 17.9, 4.9 Hz, 1H), 4.51 – 4.41 (m, 3H), 4.30 – 4.18 (m, 2H), 4.13 (td, *J* = 10.8, 5.4 Hz, 1H), 4.09 – 4.02 (m, 2H), 3.96 (td, *J* = 10.8, 5.5 Hz, 1H), 3.78 – 3.72 (m, 2H), 3.70 (t, *J* = 6.8 Hz, 2H), 3.35 – 3.25 (m, 2H), 3.22 – 3.14 (m, 2H), 2.07 – 1.80 (m, 8H), 1.62 – 1.47 (m, 4H), 1.47 – 1.20 (m, 36H), 1.01 – 0.85 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 157.7 (C_q), 156.7 (C_q), 155.4 ($2C_q$), 139.1 (C_q), 137.5 (CH), 136.9 (C_q), 136.8 (C_q), 136.8 (C_q), 133.7 (C_q), 133.6 (C_q), 133.4 (C_q), 132.8 (C_q), 132.8 (C_q), 129.1 (CH), 128.9 (CH), 128.7 (C_q), 128.7 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 126.9 (C_q), 126.9 (CH), 126.7 (CH), 124.2 (CH), 122.9 (CH), 122.0 (CH), 121.9 (CH), 99.7 (C_q), 75.5 (CH_2), 75.3 (CH_2), 75.3 (CH_2), 75.1 (CH_2), 45.2 (CH_2), 32.0 ($2CH_2$), 31.1 ($2CH_2$), 31.0 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.2 (CH_2), 30.1 ($2CH_2$), 29.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 24.6 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 14.1 ($2CH_3$). **LC-MS:** *m/z* $[M+H_3O]^+$ calculated for $C_{69}H_{97}NIO_7S$: 1210.60; found: 1210.05. **HR-MS** (ESI) *m/z*: $[M+K]^+$ calcd. for $C_{69}H_{94}IKNO_6S$ 1230.5484; found 1230.5488.

2f. Method A: Into a Schlenk, trifluoromethasulphonic acid (2 eq., 0.093 mmol) was added to a solution of **2a** (50 mg, 0.046 mmol) in 1,2-DCE (1 ml) at 0 °C. After 10 minutes, the ice-bath was removed, and the mixture was left stirring at r.t. overnight. The reaction was monitored by TLC (n-Hex:EtOAc 9:1). Once the reaction was completed, water and DCM were added to the residue, the organic phase was separated and washed with water (2x 30 mL) and brine (30 mL), dried over Na_2SO_4 and filtered. The crude was purified by column chromatography on silica gel (n-Hex:EtOAc 9:1), obtaining the desired product **2f** (30.1 mg, 71 %) as a colourless oil. **Method B:** Into a two-necked round bottom flask, under nitrogen atmosphere, thiophenol (1.2 eq., 0.054 mmol) was added to a suspension of **2d** (50.0 mg, 0.045 mmol) and K_2CO_3 (3 eq., 0.130 mmol) in dry acetonitrile (1.5 mL). The mixture was left stirring at r.t. overnight. The reaction was monitored by TLC (n-Hex:EtOAc 9:1). Once the reaction was completed, the solvent was removed under reduced pressure. Water and EtOAc were added to the residue, the organic phase was separated and washed with water (2x 30 mL) and brine (30 mL), dried over Na_2SO_4 and filtered. The crude was purified by column chromatography on silica gel (n-Hex:EtOAc 9:1), obtaining the desired product **2f** (24.3 mg, 59 %) as a colourless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 8.81 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.44 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.81 (s, 1H), 7.37 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.00 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.29 – 6.15 (m, 5H), 6.05 – 5.97 (m, 1H), 4.70 – 4.59 (m, 2H), 4.53 – 4.42 (m, 2H), 4.20 (td, *J* = 10.7, 5.6 Hz, 1H), 4.13 – 4.00 (m, 3H), 3.96 (d, *J* = 14.2 Hz, 1H), 3.89 – 3.74 (m, 4H), 3.46 (d, *J* = 13.3 Hz, 1H), 3.17 (d, *J* = 13.4 Hz, 2H), 2.06 – 1.84 (m, 8H), 1.62 – 1.50 (m, 4H), 1.47 – 1.23 (m, 36H), 1.01 – 0.85 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 157.6 (C_q), 156.0 (C_q), 155.7 (C_q), 155.6 (C_q), 147.9 (CH), 145.4 (C_q), 144.4 (Cq), 141.2 (C_q), 136.8 (C_q), 136.7 (C_q), 133.9 ($2C_q$), 133.3 (C_q), 132.4 (C_q), 132.0 (CH), 130.2 (C_q), 128.8 (CH), 128.7 (CH), 128.5 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 126.9 (CH), 122.1 (CH), 122.1 (CH), 121.8 (CH), 120.1 (CH), 75.5 (CH_2), 75.4 (CH_2), 75.3 (CH_2), 75.0 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.2 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 26.6 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 24.3 (CH_2), 22.8 (CH_2), 22.7 ($2CH_2$), 14.1 ($2CH_3$). **LC-MS:** *m/z* $[M+Na]^+$ calculated for $C_{63}H_{89}NNaO_4$: 946.67; found: 946.83. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{63}H_{89}KNO_4$: 962.6429; found: 964.6423.

4a + 4a' Representative procedure was followed using **3a** (50.0 mg, 0.039 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (5 mol %), CH_2Cl_2 (1.0 ml) as the solvent and stirring the reaction at 25 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **4a** (23.1 mg, 46 %) and **4a'** (19.8 mg, 40 %) as colourless oils. **4a. ^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.64 (s, 2H), 7.45 (d, *J* = 8.1 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 4H), 6.47 – 6.38 (m, 4H), 6.29 (t, *J* = 7.6 Hz, 2H), 5.75 – 5.65 (m, 2H), 5.59 (dd, *J* = 7.6, 1.7 Hz, 2H), 4.75 (dd, *J* = 18.0, 5.1 Hz, 2H), 4.44 (d, *J* = 13.2 Hz, 2H), 4.28 – 4.18 (m, 4H), 4.14 (td, *J* = 11.1, 5.2 Hz, 2H), 3.95 (td, *J* = 11.0, 5.4 Hz, 2H), 3.67 (t, *J* = 6.6 Hz, 4H), 3.35 – 3.25 (m, 4H), 2.40 (s, 6H), 2.10 – 1.99 (m, 2H), 1.99 – 1.90 (m, 2H), 1.90 – 1.80 (m, 4H), 1.54 (t, *J* = 7.7 Hz, 4H), 1.44 – 1.22 (m, 36H), 0.92 (td, *J* = 6.7, 4.1 Hz, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 156.5 (C_q), 155.3 (C_q), 143.2 (C_q), 136.7 (C_q), 136.6 (C_q), 133.3 (C_q), 132.9 (C_q), 132.8 (C_q), 129.2 (C_q), 128.9 (CH), 127.8 (CH), 127.7 (CH), 127.1 (CH), 127.1 (C_q), 126.8 CH), 123.7 (CH), 123.4 (CH), 121.8 (CH), 75.4 (CH_2), 75.3 (CH_2), 45.1 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.2 (CH_2), 30.6 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 26.7 (CH_2), 26.1 (CH_2), 24.1 (CH_2), 22.8 (CH_2),

22.7 (CH_2), 21.7 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{80}H_{107}N_2O_8S_2$: 1287.75; found: 1287.27. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{80}H_{106}KN_2O_8S_2$: 1325.7028; found: 1325.7024.

4a'. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.64 (s, 2H), 7.47 (d, *J* = 8.3 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 4H), 6.45 (d, *J* = 9.8 Hz, 2H), 6.34 (m, 3H), 6.15 (t, *J* = 7.6 Hz, 1H), 5.72 (dt, *J* = 9.4, 4.3 Hz, 2H), 5.57 (d, *J* = 7.6 Hz, 2H), 4.71 (dd, *J* = 18.0, 4.9 Hz, 2H), 4.45 (d, *J* = 13.3 Hz, 2H), 4.29 (ddd, *J* = 18.0, 3.8, 2.0 Hz, 2H), 4.19 (d, *J* = 14.0 Hz, 2H), 4.12 (td, *J* = 11.0, 5.3 Hz, 2H), 3.97 (td, *J* = 11.0, 5.5 Hz, 2H), 3.72 (t, *J* = 6.5 Hz, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 3.35 – 3.24 (m, 4H), 2.40 (s, 6H), 2.08 – 1.76 (m, 8H), 1.57 – 1.47 (m, 4H), 1.44 – 1.22 (m, 36H), 0.92 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 156.6 (C_q), 155.4 (C_q), 155.2 (C_q), 143.0 (C_q), 136.8 (C_q), 136.7 (C_q), 133.4 (C_q), 133.0 (C_q), 132.7 (C_q), 129.2 (C_q), 128.8 (CH), 127.8 (CH), 127.6 (CH), 127.2 (CH), 126.9 (C_q), 126.7 (CH), 123.6 (CH), 123.4 (CH), 122.0 (CH), 121.7 (CH), 75.5 (CH_2), 75.2 (CH_2), 45.1 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.1 (CH_2), 30.7 (CH_2), 30.5 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.1 (CH_2), 24.2 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 21.6 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{80}H_{107}N_2O_8S_2^+$: 1287.75; found: 1287.34. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{80}H_{106}KN_2O_8S_2$: 1325.7028; found: 1325.7021.

4b+4b'. Representative procedure was followed using **3b** (50.0 mg, 0.039 mmol), [JohnPhosAu(I)ACN]$^+$$SbF_6^-$ (5 mol %), CH_2Cl_2 (1.0 ml) as the solvent and stirring the reaction at 25 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **4b** (21.5 mg, 43 %) as colourless oil and **4b'** (13.2 mg, 26% as a white solid. **M.p.:** 140 – 141 °C. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.23 – 7.15 (m, 5H), 7.11 – 7.01 (m, 5H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.81 (s, 1H), 6.43 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.36 (t, *J* = 7.5 Hz, 1H), 6.24 (dd, *J* = 9.8, 2.4 Hz, 1H), 6.18 (d, *J* = 9.8 Hz, 1H), 5.92 (d, *J* = 7.4 Hz, 1H), 5.41 – 5.30 (m, 2H), 4.57 – 4.44 (m, 4H), 4.36 (dd, *J* = 17.7, 4.9 Hz, 1H), 4.23 (d, *J* = 14.5 Hz, 1H), 4.18 – 4.03 (m, 3H), 3.97 – 3.80 (m, 3H), 3.76 – 3.62 (m, 4H), 3.33 – 3.25 (m, 3H), 3.22 (d, *J* = 13.4 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 1.92 (m, 8H), 1.12 (t, *J* = 7.4 Hz, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 157.3 (C_q), 156.3 (C_q), 156.0 (C_q), 155.2 (C_q), 143.2 (C_q), 143.1 (C_q), 136.7 (C_q), 136.6 (C_q), 136.3 (C_q), 135.4 (C_q), 134.2 (C_q), 134.1 (C_q), 133.7 (C_q), 133.3 (C_q), 132.7 (C_q), 132.6 (C_q), 129.7 (C_q), 129.1 (CH), 128.9 (CH), 128.8 (C_q), 128.8 (CH), 128.6 (CH), 128.2 (CH), 128.0 (CH), 127.5 (CH), 127.1 (CH), 126.9 (CH), 126.9 (C_q), 126.8 (CH), 126.5 (C_q), 124.4 (CH), 123.3 (CH), 122.7 (CH), 122.5 (CH), 121.5 (CH), 121.4 (CH), 76.9 (CH_2), 76.7 (CH_2), 76.3 (CH_2), 44.7 (CH_2), 44.3 (CH_2), 31.2 (CH_2), 30.7 (CH_2), 28.7 (CH_2), 25.4 (CH_2), 23.4 (CH_2), 23.3 (CH_2), 23.1 (CH_2), 22.5 (CH_2), 21.6 (CH_3), 10.8 (CH_3), 10.6 (CH_3), 10.1 (CH_3), 9.9 (CH_3). **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{80}H_{107}N_2O_8S_2$: 1287.75; found: 1287.33. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{80}H_{106}KN_2O_8S_2$: 1325.7028; found: 1325.7034.

4b'. **^{1}H NMR :** (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.2 Hz, 4H), 7.21 (s, 2H), 7.09 (d, *J* = 8.1 Hz, 4H), 6.52 – 6.46 (m, 2H), 6.43 (t, *J* = 7.4 Hz, 2H), 6.28 – 6.22 (m, 2H), 6.19 (d, *J* = 9.9 Hz, 2H), 5.46 (dt, *J* = 9.3, 4.3 Hz, 2H), 4.50 (d, *J* = 13.4 Hz, 1H), 4.47 – 4.39 (m, 3H), 4.37 (d, *J* = 14.0 Hz, 2H), 4.18 – 4.08 (m, 2H), 3.94 – 3.72 (m, 8H), 3.36 (d, *J* = 13.4 Hz, 1H), 3.27 (d, *J* = 14.1 Hz, 2H), 3.13 (d, *J* = 14.0 Hz, 1H), 2.37 (s, 6H), 1.99 – 1.90 (m, 4H), 1.90 – 1.80 (m, 4H), 1.04 (t, *J* = 7.4 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 156.7 (C_q), 155.7 (C_q), 142.8 (C_q), 136.7 (C_q), 135.2 (C_q), 134.1 (C_q), 133.9 (C_q), 131.2 (C_q), 129.7 (C_q), 128.7 (2 x CH), 127.9 (CH), 127.8 (CH), 127.0 (C_q), 126.9 (CH), 124.1 (CH), 121.6 (CH), 121.3 (CH), 77.2 (CH_2), 76.3 (CH_2), 44.8 (CH_2), 31.4 (CH_2), 30.9 (CH_2), 27.0 (CH_2), 23.3 (CH_2), 22.8 (CH_2), 21.6 (CH_3), 10.4 (CH_3), 10.2 (CH_3). **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{80}H_{107}N_2O_8S_2$: 1287.75; found: 1287.42. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{80}H_{106}KN_2O_8S_2$: 1325.7028; found: 1325.7021.

6a. Representative procedure was followed using **5a** (50.0 mg, 0.046 mmol), [JohnPhosAu(I)ACN]$^+$$SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6a** (44.9 mg, 90 %) as a yellowish solid. **M.p.** = 100 – 101 °C. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.55 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.06 (m, 4H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.36 – 6.21 (m, 2H), 6.15 – 6.07 (m, 2H), 5.99 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.54 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.43 – 5.35 (m, 1H), 4.46 – 4.33 (m, 4H), 4.29 (d, *J* = 14.3 Hz, 1H), 4.17 – 3.98 (m, 5H), 3.70 (td, *J* = 6.5, 2.9 Hz, 2H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.47 (d, *J* = 14.4 Hz, 1H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.20 – 3.08 (m, 2H), 2.35 (s, 3H), 1.89 (m 8H), 1.62 (s, 3H), 1.56 (m, 4H), 1.46 – 1.17 (m, 36H), 0.96 – 0.84 (m, 12H). **^{13}C NMR**: (101 MHz, $CDCl_3$) δ = 158.3 (C_q), 158.1 (C_q), 155.2 (C_q), 155.2 (C_q), 142.8 (C_q), 137.3 (C_q), 137.2 (C_q), 136.9 (C_q), 136.3 (C_q), 134.1 (C_q), 133.6 (C_q), 133.4 (C_q), 133.4 (C_q), 133.0 (C_q), 132.5 (C_q), 131.6 (C_q), 130.5 (C_q), 128.9 (CH), 128.8 (CH), 128.7 (CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 126.2 (CH), 122.8 (CH), 122.2 (CH), 122.1 (CH), 121.8 (CH), 75.3 (CH_2), 75.2 (CH_2), 75.1 (CH_2), 74.8 (CH_2), 45.4 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 27.6 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 22.0 (CH_3), 21.5 (CH_3), 14.1 (CH_3). **LC-MS:** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{71}H_{100}NO_6S$ 1094.72; found 1099.79. **HR-MS** (ESI) *m/z*: $[M+K]^+$ calcd. for $C_{71}H_{99}KNO_6S$ 1132.6830; found 1132.6827.

6b. Representative procedure was followed using **5b** (50.0 mg, 0.045 mmol), [JohnPhosAu(I)ACN]$^+$$SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6b** (24.8 mg, 50 %) as a yellowish oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.14 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.35 – 6.26 (m, 2H), 6.18 – 6.07 (m, 2H), 6.02 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.85 – 5.78 (m, 1H), 5.58 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.67 (dd, *J* = 17.1, 6.1 Hz, 1H), 4.51 – 4.33 (m, 4H), 4.17 – 3.99 (m, 7H), 3.78 – 3.68 (m, 2H), 3.65 (t, *J* = 6.6 Hz, 2H), 3.30 (d, *J* = 13.5 Hz, 1H), 3.24 – 3.09 (m, 3H), 2.42 (s, 3H), 2.06 – 1.78 (m, 8H), 1.63 – 1.50 (m, 4H), 1.41 – 1.21 (m, 36H), 1.00 – 0.85 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4 (C_q), 158.0 (C_q), 155.2 ($2C_q$), 143.5 (C_q), 138.3 (C_q), 137.5 (C_q), 137.3 (C_q), 137.1 (C_q), 136.8 (C_q), 133.8 (C_q), 133.5 (C_q), 133.5 (C_q), 133.3 (C_q), 132.3 (C_q), 130.2 (C_q), 129.1 (C_q), 128.9 (CH), 128.8 (CH), 128.8 (CH), 128.3 (CH), 127.9 (CH), 127.6 (CH), 127.4 (CH), 127.1 (CH),

126.0 (CH), 122.6 (CH), 122.2 (CH), 122.1 (CH), 121.8 (CH), 75.3 (CH_2), 75.2 (CH_2), 75.1 (CH_2), 74.9 (CH_2), 64.2 (CH_2), 45.1 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 27.9 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 22.7, (CH_2) 21.4 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{71}H_{100}NO_7S$: 1110.72; found: 1110.59. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{71}H_{99K}NO_7S$: 1148.6779; found: 1148.6772.

6c. Representative procedure was followed using **5c** (50.0 mg, 0.057 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6c** (36.8 mg, 74 %), as a colourless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.48 – 7.41 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.21 – 7.12 (m, 2H), 7.10 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.03 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.96 – 6.85 (m, 3H), 6.38 – 6.31 (m, 2H), 6.15 (dd, *J* = 5.9, 3.5 Hz, 1H), 6.08 (t, *J* = 7.6 Hz, 1H), 5.94 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.69 (dd, *J* = 6.6, 3.7 Hz, 1H), 5.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.01 (dd, *J* = 16.9, 6.6 Hz, 1H), 4.50 (d, *J* = 13.4 Hz, 1H), 4.44 (d, *J* = 13.3 Hz, 1H), 4.32 (d, *J* = 13.5 Hz, 1H), 4.13 – 3.88 (m, 5H), 3.77 – 3.68 (m, 2H), 3.64 (d, *J* = 14.6 Hz, 1H), 3.52 – 3.43 (m, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.20 – 3.12 (m, 2H), 3.05 (d, *J* = 13.6 Hz, 1H), 2.56 (d, *J* = 14.6 Hz, 1H), 2.20 (s, 3H), 2.01 – 1.86 (m, 6H), 1.67 – 1.53 (m, 2H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.95 – 0.82 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.6 (C_q), 158.1 (C_q), 155.2 (C_q), 155.0 (C_q), 143.0 (C_q), 141.1 (C_q), 139.3 (C_q), 137.1 (C_q), 137.0 (C_q), 136.8 (C_q), 136.8 (C_q), 135.1 (C_q), 133.7 (C_q), 133.5 (C_q), 133.3 (C_q), 132.5 (C_q), 131.1 (C_q), 130.3 (C_q), 129.6 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.2 (CH), 127.1 (CH), 126.8 (CH), 126.5 (CH), 125.7 (CH), 122.8 (CH), 122.3 (CH), 122.0 (CH), 121.7 (CH), 76.9 (CH_2), 76.5 (CH_2), 76.5 (CH_2), 76.2 (CH_2), 45.7 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 30.8 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 23.5 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 23.0 (CH_2), 21.3 (CH_3), 10.9 (CH_3), 10.8 (CH_3), 10.4 (CH_3), 9.9 (CH_3). **LC-MS:** *m/z* $[M+Na]^+$ calculated for $C_{56}H_{61}NNaO_6S$: 898.41; found: 898.73. **HR-MS:** *m/z* $[M+H]^+$ calculated for $C_{56}H_{61}NKO_6S$: 914.3857; found: 914.3863.

6d. Representative procedure was followed using **5d** (50.0 mg, 0.043 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6d** (41.4 mg, 83 %) as a colourless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.07 (m, 5H), 7.03 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 – 6.86 (m, 4H), 6.37 – 6.30 (m, 2H), 6.15 (dd, *J* = 6.3, 3.1 Hz, 1H), 6.07 (t, *J* = 7.6 Hz, 1H), 5.94 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.69 (dd, *J* = 6.6, 3.7 Hz, 1H), 5.56 (dd, *J* = 7.5, 1.7 Hz, 1H), 5.02 (dd, *J* = 16.9, 6.6 Hz, 1H), 4.48 (d, *J* = 13.4 Hz, 1H), 4.43 (d, *J* = 13.3 Hz, 1H), 4.31 (d, *J* = 13.5 Hz, 1H), 4.17 – 3.90 (m, 5H), 3.74 (td, *J* = 6.6, 2.9 Hz, 2H), 3.63 (d, *J* = 14.6 Hz, 1H), 3.49 (dt, *J* = 9.4, 6.3 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.23 – 3.13 (m, 2H), 3.05 (d, *J* = 13.6 Hz, 1H), 2.55 (d, *J* = 14.6 Hz, 1H), 2.20 (s, 3H), 1.98 – 1.82 (m, 8H), 1.67 – 1.51 (m, 4H), 1.51 – 1.17 (m, 36H), 0.97 – 0.90 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 158.3 (C_q), 158.1 (C_q), 155.3 (C_q), 155.1 (C_q), 143.0 (C_q), 141.1 (C_q), 139.2 (C_q), 137.1 (C_q), 137.1 (C_q), 137.0 (C_q), 136.8 (C_q), 135.3 (C_q), 133.7 (C_q), 133.5 (C_q), 133.3 (C_q), 132.5 (C_q), 131.1 (C_q), 130.3 (C_q), 128.9 (CH), 128.8 (CH), 128.7 (CH), 127.6 (CH), 127.6 (CH), 127.6 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 125.7 (CH), 122.8 (CH), 122.3 (CH), 122.0 (CH), 121.7 (CH), 75.3 (CH_2), 75.0 (CH_2), 74.8 (CH_2), 74.5 (CH_2), 45.7 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.5 (2CH_2), 29.5 (CH_2), 26.7 (CH_2), 26.5 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 21.3 (CH_3), 14.2 (CH_3), 14.2 (CH_3), 14.1 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+NH_4]^+$ calculated for $C_{76}H_{105}N_2O_6S$: 1173.77; found: 1173.33. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{76}H_{101}KNO_6S$: 1194.6987; found: 1194.6994.

6e. Representative procedure was followed using **5e** (50.0 mg, 0.042 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6e** (38.2 mg, 76 %) as a yellowish oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.60 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.09 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 – 6.86 (m, 3H), 6.72 – 6.66 (m, 3H), 6.39 – 6.29 (m, 3H), 6.16 (dd, *J* = 6.6, 2.7 Hz, 1H), 6.08 (t, *J* = 7.6 Hz, 1H), 5.95 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.62 (dd, *J* = 6.6, 3.8 Hz, 1H), 5.57 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.98 (dd, *J* = 16.8, 6.6 Hz, 1H), 4.48 (d, *J* = 13.5 Hz, 1H), 4.43 (d, *J* = 13.3 Hz, 1H), 4.32 (d, *J* = 13.5 Hz, 1H), 4.12 – 3.94 (m, 4H), 3.80 (s, 3H), 3.78 – 3.71 (m, 2H), 3.67 (d, *J* = 14.5 Hz, 1H), 3.51 (dt, *J* = 9.4, 6.3 Hz, 1H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.24 (dt, *J* = 9.4, 6.6 Hz, 2H), 3.17 (d, *J* = 13.4 Hz, 1H), 3.05 (d, *J* = 13.6 Hz, 1H), 2.64 (d, *J* = 14.5 Hz, 1H), 2.21 (s, 3H), 1.98 – 1.84 (m, 8H), 1.67 – 1.54 (m, 4H), 1.39 – 1.21 (m, 36H), 0.97 – 0.88 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 158.7 (C_q), 158.3 (C_q), 158.0 (C_q), 155.3 (C_q), 155.1 (C_q), 142.8 (C_q), 138.7 (C_q), 137.1 (C_q), 137.0 (C_q), 136.8 (C_q), 136.8 (C_q), 135.3 (C_q), 133.7 (C_q), 133.7 (C_q), 133.5 (C_q), 133.4 (C_q), 132.5 (C_q), 131.2 (C_q), 130.4 (C_q), 128.9 (CH), 128.8 (CH), 128.7 (CH), 127.9 (CH), 127.6 (CH), 127.6 (CH), 127.6 (CH), 127.2 (CH), 127.0 (CH), 125.8 (CH), 122.3 (CH), 122.0 (CH), 121.7 (CH), 121.7 (CH), 113.1 (CH), 75.3 (CH_2), 75.0 (CH_2), 74.8 (CH_2), 74.6 (CH_2), 55.2 (CH_3), 45.7 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 31.0 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.2 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 26.7 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 21.3 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+NH_4]^+$ calculated for $C_{77}H_{107}N_2O_7S$: 1203.78; found: 1204.23. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{77}H_{103}KNO_7S$: 1224.7092; found: 1224.7088.

6f. Representative procedure was followed using **5f** (50.0 mg, 0.041 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6f** (39.2 mg, 78 %) as a white solid. **M.p.** = 152 – 153 °C. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.09 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 – 6.86 (m, 4H), 6.40 – 6.32 (m, 3H), 6.19 (dd, *J* = 5.6, 3.8 Hz, 1H), 6.09 (t, *J* = 7.6 Hz, 1H), 5.98 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.76 (dd, *J* = 6.6, 3.8 Hz, 1H), 5.55 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.04 (dd, *J* = 17.0, 6.6 Hz, 1H), 4.50 (d, *J* = 13.4 Hz, 1H), 4.44 (d, *J*

= 13.3 Hz, 1H), 4.32 (d, *J* = 13.5 Hz, 1H), 4.16 – 3.90 (m, 5H), 3.82 – 3.72 (m, 2H), 3.69 (d, *J* = 14.4 Hz, 1H), 3.52 (dt, *J* = 9.5, 6.4 Hz, 1H), 3.34 (d, *J* = 13.5 Hz, 1H), 3.24 – 3.14 (m, 2H), 3.06 (d, *J* = 13.6 Hz, 1H), 2.44 (d, *J* = 14.5 Hz, 1H), 2.18 (s, 3H), 1.97 – 1.83 (m, 8H), 1.66 – 1.52 (m, 4H), 1.52 – 1.20 (m, 36H), 1.03 – 0.88 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 158.4 (C_q), 158.0 (C_q), 155.3 (C_q), 155.1 (C_q), 144.6 (d, $J_{C\text{-}F}$ = 1.4 Hz, C_q), 143.1 (C_q), 138.0 (C_q), 137.5 (C_q), 137.0 (C_q), 136.9 (C_q), 136.9 (C_q), 134.8 (C_q), 133.6 (C_q), 133.6 (C_q), 133.2 (C_q), 132.4 (C_q), 131.2 (C_q), 129.5 (C_q), 129.2 (C_q), 129.0 (CH), 128.8 (CH), 128.6 (CH), 127.8 (CH), 127.8 (CH), 127.6 (CH), 127.3 (CH), 127.2 (CH), 126.9 (CH), 125.6 (CH), 124.7 (2CH), 124.1 (q, $J_{C\text{-}F}$ = 271 Hz, C_q), 122.3 (CH), 122.0 (CH), 121.8 (CH), 75.3 (CH_2), 75.1 (CH_2), 74.9 (CH_2), 74.7 (CH_2), 45.6 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.0 (CH_2), 31.0 (2CH_2), 30.6 (CH_2), 30.2 (CH_2), 30.2 (CH_2), 30.2 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (2CH_2), 21.2 (CH_3), 14.1 (2CH_3), 14.1 (CH_3), 14.1 (CH_3). **^{19}F NMR**: (565 MHz, $CDCl_3$) δ = -62.5. **LC-MS:** *m/z* $[M+Na]^+$ calculated for $C_{77}H_{100}F_3NNaO_6S$: 1246.71; found: 1246.31. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{77}H_{100}F_3KNO_6S$: 1262.6861; found: 1262.6866.

6g. Representative procedure was followed using **5g** (50.0 mg, 0.040 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6g** (35.0 mg, 70 %) as an orange solid. **M.p.** = 127 – 128 °C. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.59 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.08 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.01 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.39 – 6.31 (m, 4H), 6.18 (t, *J* = 4.7 Hz, 1H), 6.08 (t, *J* = 7.6 Hz, 1H), 5.97 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.68 (dd, *J* = 6.6, 3.8 Hz, 1H), 5.58 – 5.50 (m, 1H), 5.00 (dd, *J* = 16.9, 6.7 Hz, 1H), 4.50 (d, *J* = 13.5 Hz, 1H), 4.44 (d, *J* = 13.3 Hz, 1H), 4.33 (d, *J* = 13.5 Hz, 1H), 4.11 – 4.01 (m, 1H), 4.01 – 3.89 (m, 4H), 3.78 – 3.66 (m, 3H), 3.54 (dt, *J* = 9.5, 6.5 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.23 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.18 (d, *J* = 13.5 Hz, 1H), 3.07 (d, *J* = 13.6 Hz, 1H), 2.53 (d, *J* = 14.5 Hz, 1H), 2.23 (s, 3H), 2.02 – 1.82 (m, 8H), 1.72 – 1.54 (m, 4H), 1.13 (t, *J* = 7.4 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 158.6 (C_q), 158.0 (C_q), 155.2 (C_q), 155.1 (C_q), 143.1 (C_q), 140.0 (C_q), 138.1 (C_q), 137.1 (C_q), 137.0 (C_q), 136.9 (C_q), 136.8 (C_q), 134.8 (C_q), 133.6 (C_q), 133.5 (C_q), 133.4 (C_q), 132.4 (C_q), 131.2 (C_q), 130.9 (CH), 129.8 (C_q), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.3 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 127.2 (CH), 125.7 (CH), 123.5 (CH), 122.3 (CH), 122.0 (CH), 121.7 (CH), 120.7 (C_q), 76.9 (CH_2), 76.6 (CH_2), 76.5 (CH_2), 76.3 (CH_2), 45.6 (CH_2), 31.0 (CH_2), 31.0 (CH_2), 30.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 23.5 (CH_2), 23.3 (CH_2), 23.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 21.3 (CH_3), 10.8 (CH_3), 10.7 (CH_3), 10.4 (CH_3), 9.9 (CH_3). **LC-MS:** *m/z* $[M+Na]^+$ calculated for $C_{56}H_{60}BrNNaO_6S$: 976.32; found: 976.67. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{56}H_{60}BrKNO_6S$: 992.2962; found: 992.2968.

6h. Representative procedure was followed using **5h** (50.0 mg, 0.043 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6h** (38.1 mg, 76 %) as a colourless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.64 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.06 (m, 3H), 7.03 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.97 – 6.85 (m, 5H), 6.36 – 6.30 (m, 2H), 6.15 (dd, *J* = 5.6, 3.8 Hz, 1H), 6.07 (t, *J* = 7.6 Hz, 1H), 5.95 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.73 (dd, *J* = 6.6, 3.8 Hz, 1H), 5.54 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.04 (dd, *J* = 16.9, 6.6 Hz, 1H), 4.49 (d, *J* = 13.4 Hz, 1H), 4.43 (d, *J* = 13.3 Hz, 1H), 4.32 (d, *J* = 13.5 Hz, 1H), 4.16 – 3.91 (m, 4H), 3.78 – 3.66 (m, 4H), 3.52 (dt, *J* = 9.4, 6.3 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.25 – 3.20 (m, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 3.05 (d, *J* = 13.5 Hz, 1H), 2.52 (d, *J* = 14.5 Hz, 1H), 2.22 (s, 3H), 1.98 – 1.84 (m, 8H), 1.68 – 1.54 (m, 4H), 1.39 – 1.20 (m, 36H), 0.97 – 0.87 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 161.2 (d, $J_{C\text{-}F}$ = 249 Hz, C_q), 158.4 (C_q), 158.1 (C_q), 155.3 (C_q), 155.1 (C_q), 143.4 (d, $J_{C\text{-}F}$ = 8Hz, C_q), 143.3 (C_q), 138.2 (d, $J_{C\text{-}F}$ = 3 Hz, C_q), 137.4 (C_q), 137.1 (C_q), 137.0 (C_q), 136.7 (C_q), 135.1 (C_q), 133.5 (C_q), 133.4 (C_q), 133.4 (C_q), 132.4 (C_q), 131.0 (C_q), 129.8 (C_q), 129.4 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 127.7 (d, $J_{C\text{-}F}$ = 2 Hz, CH), 127.7 (CH), 127.6 (CH), 127.2 (CH), 127.1 (d, $J_{C\text{-}F}$ = 4 Hz, CH), 125.6 (CH), 123.6 (CH), 122.3 (CH), 122.2 (d, $J_{C\text{-}F}$ = 24 Hz, CH), 121.7 (CH), 113.6 (d, $J_{C\text{-}F}$ = 21 Hz, CH), 75.3 (CH_2), 75.1 (CH_2), 74.8 (CH_2), 74.6 (CH_2), 45.7 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (2CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 26.5 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.7 (2CH_2), 22.7 (CH_2), 21.1 (CH_3), 14.2 (CH_3), 14.1 (CH_3), 14.1 (CH_3). **^{19}F NMR**: (565 MHz, $CDCl_3$) δ = -113.7. **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{76}H_{101}FNO_6S$: 1174.73; found: 1175.12. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{76}H_{100}FKNO_6S$: 1212.6892; found: 1212.6896.

6i. Representative procedure was followed using **5i** (50.0 mg, 0.043 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6i** (28.8 mg, 58 %) as a yellowish oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.57 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.13 – 7.06 (m, 2H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.83 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.45 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.39 – 6.31 (m, 2H), 6.18 (dd, *J* = 6.5, 3.0 Hz, 1H), 6.08 (t, *J* = 7.6 Hz, 1H), 5.96 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.72 (dd, *J* = 6.6, 4.0 Hz, 1H), 5.57 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.93 (dd, *J* = 16.9, 6.7 Hz, 1H), 4.49 (d, *J* = 13.3 Hz, 1H), 4.44 (d, *J* = 13.3 Hz, 1H), 4.34 (d, *J* = 13.4 Hz, 1H), 4.17 (td, *J* = 10.4, 6.2 Hz, 1H), 4.09 – 3.91 (m, 4H), 3.89 (d, *J* = 14.4 Hz, 1H), 3.74 (td, *J* = 6.7, 3.8 Hz, 2H), 3.56 (dt, *J* = 9.4, 6.3 Hz, 1H), 3.38 – 3.27 (m, 2H), 3.17 (d, *J* = 13.4 Hz, 1H), 3.07 (d, *J* = 13.6 Hz, 1H), 2.84 (d, *J* = 14.5 Hz, 1H), 2.21 (s, 3H), 2.01 – 1.83 (m, 8H), 1.73 – 1.52 (m, 4H), 1.47 – 1.27 (m, 36H), 1.02 – 0.89 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 158.5 (C_q), 158.0 (C_q), 155.3 (C_q), 155.2 (C_q), 143.5 (C_q), 143.1 (C_q), 137.2 (C_q), 137.1 (C_q), 137.0 (C_q), 136.8 (C_q), 135.2 (C_q), 133.6 (C_q), 133.6 (C_q), 133.4 (C_q), 132.5 (C_q), 132.4 (C_q), 131.1 (C_q), 130.2 (C_q), 129.0 (CH), 128.8 (CH), 128.7 (CH), 127.7 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 127.1 (CH), 126.3 (CH), 125.8 (CH), 124.6 (CH), 124.1 (CH), 122.7 (CH), 122.3 (CH), 122.0 (CH), 121.7 (CH), 75.3 (CH_2), 75.0 (2CH_2), 74.6 (CH_2), 45.5 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.3 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2),

26.7 (CH_2), 26.5 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 21.4 (CH_3), 14.2 (CH_3), 14.2 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+NH_4]^+$ calculated for $C_{74}H_{103}N_2O_6S_2$: 1179.73; found: 1179.64. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{74}H_{99}KNO_6S_2$: 1200.6551; found: 1200.6557.

6j. Representative procedure was followed using **5j** (50.0 mg, 0.023 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6j** (35.5mg, 71 %) as a colourless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 5.9 Hz, 2H), 7.39 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 1H), 7.02 – 6.92 (m, 3H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.74 (d, *J* = 2.7 Hz, 1H), 6.41 – 6.36 (m, 1H), 6.36 – 6.26 (m, 6H), 6.24 – 6.15 (m, 2H), 6.10 – 6.04 (m, 2H), 5.83 (d, *J* = 7.2 Hz, 1H), 5.75 (t, *J* = 5.1 Hz, 1H), 4.52 – 4.42 (m, 6H), 4.38 (dd, *J* = 13.3, 3.4 Hz, 2H), 4.33 – 4.18 (m, 6H), 4.10 – 3.94 (m, 8H), 3.82 – 3.59 (m, 8H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.22 – 3.11 (m, 5H), 2.99 (d, *J* = 10.3 Hz, 1H), 2.96 (d, *J* = 10.3 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H), 2.05 – 1.77 (m, 16H), 1.61 – 1.45 (m, 8H), 1.41 – 1.26 (m, 72H), 0.97 – 0.88 (m, 24H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 157.8 (C_q), 157.5 (C_q), 157.5 (C_q), 157.2 (C_q), 155.7 (C_q), 155.6 (C_q), 155.6 (C_q), 155.5 (C_q), 143.5 (C_q), 143.3 (C_q), 137.2 (C_q), 136.9 (C_q), 136.8 ($2C_q$), 136.4 (C_q), 136.0 (C_q), 135.7 (C_q), 134.7 (C_q), 134.0 (C_q), 133.9 (C_q), 133.5 (C_q), 133.3 (C_q), 133.1 (C_q), 133.1 (C_q), 132.9 (C_q), 132.7 (C_q), 132.0 (CH), 130.0 (C_q), 129.2 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 126.6 (C_q), 122.1 (CH), 122.0 (CH), 121.9 (CH), 121.9 (CH), 121.8 (CH), 121.6 (CH), 120.2 (C_q), 86.1 (C_q), 83.7 (C_q), 75.4 (CH_2), 75.3 (CH_2), 75.3 (CH_2), 75.3 (CH_2), 75.1 (CH_2), 75.0 (CH_2), 45.1 (CH_2), 41.9 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.1 ($3CH_2$), 29.9 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 21.6 (CH_3), 14.1 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+2K]^{2+}$ calculated for $C_{140}H_{192}K_2N_2O_{12}S_2$: 1117.65; found: 1117.82. **HR-MS** (ESI) *m/z*: $[M+2K]^+$ calcd. for $C_{140}H_{192}K_2N_2O_{12}S_2$: 1117.6595; found: 1117.6588.

6k+6k'. Representative procedure was followed using **5k** (50.0 mg, 0.043 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **6k** (27.9 mg, 56 %) as a waxy oil and **6k'** (18.1 mg, 36 %) as a white solid. **M.p.** = 160 – 161 °C.

6k. ^{1}H NMR: (400 MHz, $CDCl_3$) δ = 7.48 – 7.42 (m, 4H), 7.40 (s, 1H), 7.28 – 7.23 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 7.4, 2.2 Hz, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 9.5 Hz, 1H), 6.05 – 5.93 (m, 6H), 5.71 (dd, *J* = 6.0, 3.4 Hz, 1H), 5.55 (dd, *J* = 7.6, 1.9 Hz, 1H), 4.45 – 4.35 (m, 3H), 4.25 (d, *J* = 13.7 Hz, 1H), 4.16 (td, *J* = 10.8, 5.4 Hz, 1H), 4.07 – 3.94 (m, 3H), 3.72 – 3.61 (m, 4H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.17 (d, *J* = 13.5 Hz, 1H), 3.12 (d, *J* = 13.3 Hz, 2H), 2.43 (s, 3H), 2.05 – 1.90 (m, 4H), 1.90 – 1.79 (m, 4H), 1.64 – 1.52 (m, 4H), 1.47 – 1.17 (m, 36H), 0.99 – 0.87 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 157.9 (C_q), 157.2 (C_q), 155.1 (C_q), 154.9 (C_q), 143.1 (C_q), 138.8 (C_q), 137.3 (C_q), 137.2 (C_q), 136.8 (C_q), 136.7 (C_q), 133.2 ($2C_q$), 132.4 (C_q), 132.2 (C_q), 129.9 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.1 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 127.3 (CH), 127.2 (C_q), 127.1 (C_q), 127.0 (CH), 126.8 (CH), 126.5 (CH), 123.6 (CH), 122.1 (CH), 121.9 (CH), 121.7 (CH), 75.2 (CH_2), 75.2 (CH_2), 75.1 (CH_2), 74.8 (CH_2), 56.3 (CH), 32.1 (CH_2), 32.0 ($2CH_2$), 31.0 (CH_2), 31.0 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 ($2CH_2$), 26.7 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 24.6 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 21.6 (CH_3), 14.1 (CH_3), 14.1 ($2CH_3$). **LC-MS:** *m/z* $[M+NH_4]^+$ calculated for $C_{76}H_{105}N_2O_6S$: 1173.77; found: 1174.22. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{76}H_{101}KNO_6S$: 1194.6987; found: 1194.6883.

6k'. ^{1}H NMR: (400 MHz, $CDCl_3$) δ = 7.64 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 (dd, *J* = 7.8, 3.5 Hz, 4H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 9.8 Hz, 1H), 6.38 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.31 (t, *J* = 7.5 Hz, 1H), 6.22 – 6.14 (m, 4H), 6.07 (dd, *J* = 9.8, 6.2 Hz, 1H), 5.41 (dd, *J* = 5.5, 3.8 Hz, 1H), 4.50 – 4.42 (m, 2H), 4.37 (d, *J* = 13.2 Hz, 1H), 4.22 (d, *J* = 14.0 Hz, 1H), 4.14 – 4.03 (m, 3H), 3.88 (td, *J* = 11.1, 5.3 Hz, 1H), 3.74 – 3.61 (m, 4H), 3.37 (d, *J* = 14.0 Hz, 1H), 3.24 – 3.14 (m, 3H), 2.39 (s, 3H), 2.08 – 1.91 (m, 4H), 1.91 – 1.78 (m, 4H), 1.66 – 1.50 (m, 4H), 1.45 – 1.16 (m, 36H), 0.99 – 0.85 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 158.0 (C_q), 156.2 (C_q), 155.3 (C_q), 155.2 (C_q), 143.1 (C_q), 138.8 (C_q), 137.2 (C_q), 137.2 (C_q), 137.0 (C_q), 136.3 (C_q), 133.3 (C_q), 133.1 (C_q), 133.1 (C_q), 132.9 (C_q), 132.7 (C_q), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.3 (2CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 127.0 (C_q), 126.6 (CH), 126.0 (C_q), 125.8 (CH), 123.5 (CH), 121.9 (CH), 121.8 (CH), 121.7 (CH), 75.4 (CH_2), 75.3 (CH_2), 75.1 (CH_2), 75.0 (CH_2), 56.3 (CH), 32.0 (CH_2), 31.2 (CH_2), 31.1 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.6 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.8 ($2CH_2$), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 24.0 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 21.6 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+H]^+$ calculated for $C_{76}H_{102}NO_6S$: 1156.74; found: 1156.32. **HR-MS:** *m/z* $[M+K]^+$ calculated for $C_{76}H_{101}KNO_6S$: 1194.6987; found: 1194.6892.

8b Representative procedure was followed using **7b** (50.0 mg, 0.049 mmol), $[JohnPhosAu(I)ACN]^+SbF_6^-$ (10 mol %), toluene (1.0 ml) as the solvent and stirring the reaction at 100 °C. Purification by column chromatography on silica gel (n-Hexane/EtOAc 95:5) yielded **8b** (48.6 mg, 97 %), isolated as a colourless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ = 7.56 – 7.51 (m, 1H), 7.46 – 7.37 (m, 4H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.14 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.29 – 6.22 (m, 2H), 6.08 (dd, *J* = 6.3, 3.0 Hz, 1H), 6.03 (t, *J* = 7.6 Hz, 1H), 5.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 5.49 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.52 (d, *J* = 13.1 Hz, 1H), 4.42 (d, *J* = 13.3 Hz, 1H), 4.34 (d, *J* = 13.4 Hz, 1H), 4.11 (td, *J* = 10.9, 5.4 Hz, 1H), 4.07 – 3.95 (m, 3H), 3.90 (d, *J* = 14.8 Hz, 1H), 3.70 (t, *J* = 6.5 Hz, 2H), 3.50 (dt, *J* = 9.4, 6.3 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 3.22 – 3.12 (m, 2H), 3.06 (d, *J* = 13.6 Hz, 1H), 2.84 (d, *J* = 14.9 Hz, 1H), 2.11 – 1.75 (m, 8H), 1.73 – 1.63 (m, 2H), 1.63 – 1.54 (m, 2H), 1.51 – 1.27 (m, 36H), 1.04 – 0.85 (m, 12H). **^{13}C NMR:** (101 MHz, $CDCl_3$) δ = 158.2 (C_q), 155.9 (C_q), 155.1 ($2C_q$), 154.9 (C_q), 141.8 (C_q), 141.7 (C_q), 137.4 (C_q), 137.3 (C_q), 135.3 (C_q), 135.0 (C_q), 134.0 (C_q), 133.4 (C_q), 133.1 ($2C_q$), 131.4 (C_q), 129.3

(2CH), 128.8 (2CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.1 (CH), 127.0 (CH), 126.8 (CH), 125.6 (CH), 122.3 (CH), 122.2 (CH), 121.7 (CH), 119.5 (C_q), 116.6 (CH), 75.7 (CH_2), 75.3 (CH_2), 75.0 (CH_2), 74.5 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 31.0 (CH_2), 30.8 (CH_2), 30.6 (CH_2), 30.3 (CH_2), 30.1 ($2CH_2$), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 28.1 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 26.0 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3), 14.1 (CH_3). **LC-MS:** *m/z* $[M+NH_4]^+$ calculated for $C_{69}H_{97}N_2O_5$: 1033.74; found: 1033.37. **HR-MS** (ESI) *m/z*: $[M+K]^+$ calcd. for $C_{69}H_{93}KNO_5$ 1054.6691; found 1054.6685.

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