Cationic Gold-Catalyzed Regioselective Hydration of 1-Arylalkynes through Carbonyl Group Participation

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Abstract: The unsymmetrically substituted internal alkynes were regioselectively hydrated through carbonyl-group participation using cationic gold catalyst where the nature and position of carbonyl functionalities play a key role in governing the regioselectivity of products as well as facilitating the reaction. A new atom-economical, cationic gold-catalyzed regioselective hydration of 1-arylalkynes substituted with various functionalities in the absence of any toxic catalyst, strong acid, or other additives have been reported.

Key words: catalysis, regioselectivity, internal alkynes, hydration

The alkyne hydration reaction, leading to the formation of carbonyl derivatives, is of prime interest considering the wide availability of alkynyl substrates and the fundamental importance of the carbonyl motif in modern organic synthesis.[1] Although this reaction has been known since the 19th century, its potential in organic synthesis and industrial processes has yet to be fully exploited.[2,3] Traditional alkyne hydration suffers drawback regarding harsh reaction conditions such as the use of toxic catalysts as well as strong and dangerous reagents (H_2SO_4, BF_3).[4]

Until recent date, several groups attempted atom-economic approach toward hydration of terminal alkynes resulting in excellent selectivity while regioselective hydration of internal alkynes still remains a challenge to be explored further. Carriedo and co-workers developed the Au-catalyzed hydration of a terminal alkyne[5] in the presence of H_2SO_4 at high temperature whereas Leyva developed a progressive Au-catalyzed hydration at room temperature in the absence of acidic cocatalysts.[6]

A major drawback associated with the hydration of an internal alkyne is the lack of regioselectivity resulting in a mixture of ketones.[7] Tanaka et al. reported the Au–acid cocatalyzed hydration of internal alkynes leading to a mixture of ketones.[8] A recent report by Nolan described the Au–acid co-catalyzed hydration of symmetrical internal alkynes.[9] According to Kaspar, hydroamination of an unsymmetrically substituted internal alkyne can regioselectively give an anti-Markovnikov ketone.[10] There are rare reports on mild and regioselective hydration of an internal alkyne which inspired us for the investigation of appropriate reaction conditions in order to develop an efficient methodology. Herein we report an operationally simple, efficient, and nonhazardous method for the regioselective hydration of internal alkynes in substituted 1-arylalkynes to obtain regioselectively hydrated products in good to excellent yield.

The initial attempt to hydrate internal alkynes was carried out with the *ortho*-alkynylaryl aldehyde **1a** as substrate which has been repeatedly used in our lab previously for the gold-catalyzed cyclization to obtain fused substituted cycloheptanones.[11] The reaction conditions for the regioselective hydration were optimized with substrate **1a** by screening various metal catalysts in different solvents at varying temperature and time in the presence of water (Table 1). The amount of water was found to be crucial in dictating the product. $PtCl_2$ mostly facilitated cyclization resulting in the products **1c** and **1d**, rather than alkyne hydration in toluene with excess water both at room temperature as well as elevated temperature. Although the change in solvent from toluene to 1,4-dioxane was able to provide the desired hydrated product **1b** in 46% yield, but the decrease in the amount of water from 20 equivalents to 10 equivalents in the reaction led to the cyclized product **1c** even in 1,4-dioxane. Improved yields of hydrated products resulted when platinum was replaced with gold catalysts. $AuBr_3$ alone was found to be effective in regioselective hydration of internal alkynes. Most striking observation directing to remarkable yield of the regioselectively hydrated product was achieved when the catalytic system $AuCl(PPh_3)$–AgOTf was used in 1,4-dioxane. This led to the formation of **1b** in 87% yield at room temperature in two hours. The change of AgOTf to $AgSbF_6$ resulted in the declination of product yield from 87% to 70% while the removal of silver from the catalytic system led to total recovery of starting material after two hours (Table 1, entry 8). Delighted and enlightened with the optimized outcome, we proceeded further with various other similar substrates.

The regioselective hydration of internal alkynes in general needs a directing group nearby which helps in the formation of cyclic intermediate followed by nucleophilic attack with water. In this context, we proposed that the triple bond in 1-arylalkene substrates **S** may be activated by a metal catalyst forming intermediate **B**. The nearby oxygen from carbonyl functionality can act as nucleophile and attack the metal-activated alkyne to form either a five- or six-membered ring intermediate **C** or **D** via *5-exo-* or *6-endo*-dig mode of cyclization. Subsequent attack by water

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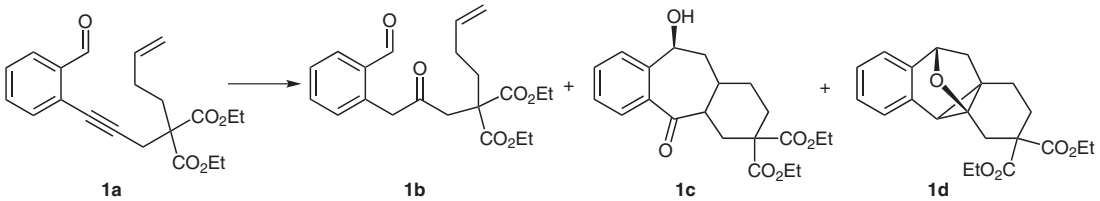
Table 1 Optimization of Reaction Conditions for the Regioselective Hydration of Substituted *ortho*-Alkynylaryl Aldehyde **1a**



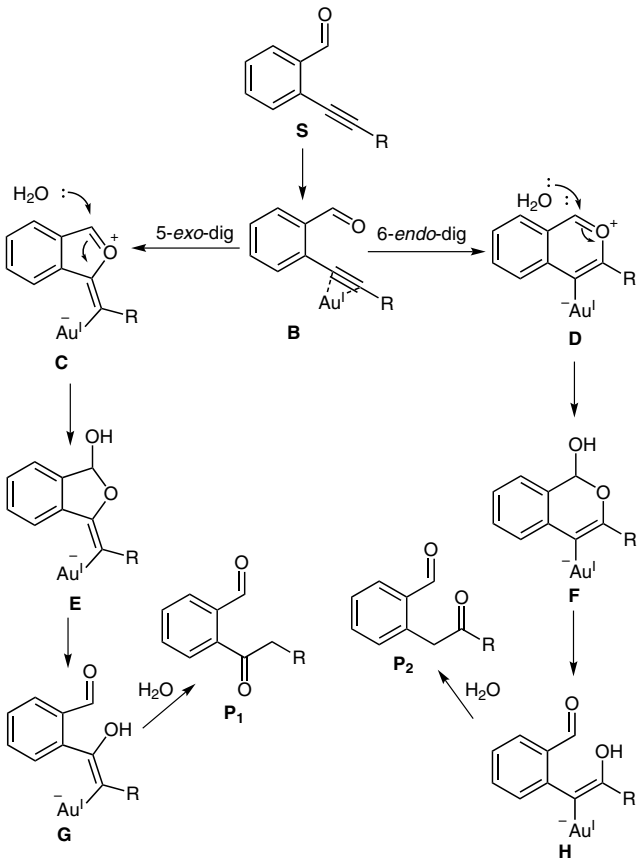
Entry	Catalyst (mol%)	Additive (mol%)	H_2O (equiv)	Solvent	Temp (°C)	Time (h)	Yield of **1b** (%)[a]	Yield of **1c** (%)[a]	Yield of **1d** (%)[a]
1	$PtCl_2$ (5)	–	20	toluene	25	18	–	20	15
2	$PtCl_2$ (5)	–	20	toluene	80	2	–	30	27
3	$PtCl_2$ (5)	–	20	1,4-dioxane	25	2	46	–	–
4	$PtCl_2$ (5)	–	10	1,4-dioxane	60	2	–	39	–
5	$AuCl(PPh_3)$ (1)	AgOTf (1)	3	1,4-dioxane	25	2	87	–	–
6	$AuCl(PPh_3)$ (1)	$AgSbF_6$ (1)	3	1,4-dioxane	25	2	70	–	–
7	$AuBr_3$ (5)	–	5	1,4-dioxane	25	2	76	–	–
8	$AuCl(PPh_3)$ (2)	–	5	1,4-dioxane	25	2	–	–	–

[a] Yields were determined by ^1H NMR integration.

at the carbonyl center may afford the internediates **E** and **F**.

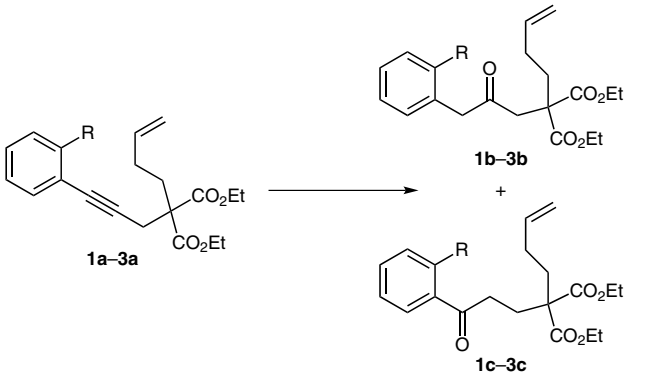
The ring opening of particularly six-membered-ring intermediate **F** to form intermediate **H** may have finally resulted in the regioselective formation of 1,5-dicarbonyl compound $\mathbf{P_2}$ which was found in the case of *ortho*-alkynylaryl aldehydes (Scheme 1).

To test this hypothesis, we compared the reactivity of internal alkynes bearing a carbonyl functionality (**1a** and **3a**) with that of the substrate lacking it (**2a**, Table 2). The substrate **2a** (Table 2) lacking carbonyl functionality failed to react at all under the optimized reaction conditions even after 24 hours at room temperature which was fully in agreement with the proposed hypothesis where neighboring-group participation was mandatory and supposed to be the driving force for the reaction. Thus, the substrate **1a** yielded 87% of the product **1b**. However, the product **3c** obtained from alkyne **3a** bearing a keto functionality was found to have altered regioselectivity as compared to that obtained from *ortho*-alkynylaryl aldehyde **1a**. Further, numerous internal alkyne substrates **4a**–**7a** containing various carbonyl functionalities apart from aldehydes and ketones were screened (Table 3). The alkyne substrate with hydroxy functionality **8a** was also tested out of curiosity and found to furnish cyclized product **8b**. With the substrate **4a** containing a carbonate functionality, the formation of hydrated product was comparatively much slower and resulted in 50% yield of the desired ketone derivative **4b** in 24 hours at room temperature. The homologated carbonate substrate **5a**, when subjected to the Au–Ag co-catalyzed reaction, did not afford the hydrated product, and instead the entire starting material was recovered even after 24 hours.



Scheme 1 Plausible mechanism for the regioselective hydration of 1-arylalkynes **S** assisted by a carbonyl functionality

Table 2 Comparative Study of Hydration of Internal Alkynes with and without Aldehyde and Ketone Functionalities[a]



Entry	R	Time (h)	Product	Yield (%)[b]
1	**1a** CHO	2	**1b**	87
2	**2a** H	24	n.r.[c]	–
3	**3a** COMe	2	**3c**	85

[a] Substrate (0.30 mmol), Au(PPh$_3$)Cl (1 mol%), AgOTf (1 mol%), H_2O (1.0 mmol), 1,4-dioxane, r.t.
[b] Isolated yield.
[c] n.r. = no reaction.

The same trend of reactivity was observed with the corresponding OAc-substituted alkyne **6a** where the C=O functionality of the OAc group was unable to initiate the reaction through neighboring-group participation. The probable reason for inertness of substrates **5a** and **6a** toward hydration reaction can be the requirement of intermediate ring formation through neighboring-group participation which may be unfavorable in this case. The ester-substituted internal alkyne **7a** was found to be reactive enough to produce a mixture of hydrated and cyclized products **7b** and **7c** in almost 1:1 ratio in two hours at room temperature. In the literature, 3-alkynoates and 2-alkynoates are reported to afford γ- and β-keto esters regioselectively through neighboring carbonyl-group participation,[12] the facile cyclization leading to the formation of a six-membered ring is also possible in addition to hydration, which results in the formation of significant amount of cyclized product **7c** along with the hydrated product **7b**. The substrate **8a** underwent cyclization much more rapidly than hydration leading to the formation of substituted furan derivative **8b** in 68% yield.[13] Thus it was obvious that the *ortho*-alkynylaryl aldehydes among all other 1-arylalkyne substrates underwent an efficient, clean, and fast hydration resulting in the regioselective formation of the desired hydrated products in good to excellent yields.

Table 3 Hydration of Internal Alkynes Bearing Various Functionalities[a]

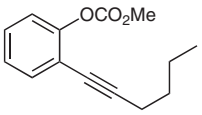
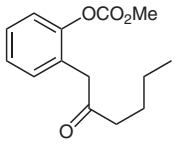
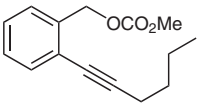
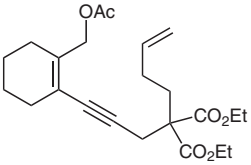
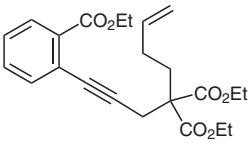
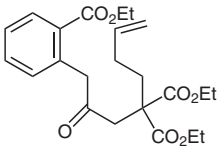
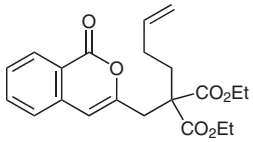
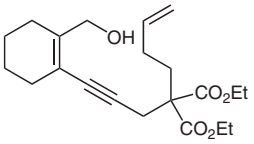
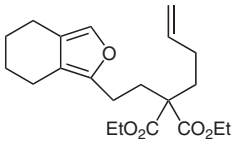
Entry	Substrates	Time (h)	Product	Yield (%)[b]
1	 **4a**	24	 **4b**	50
2	 **5a**	24	n.r.[c]	–
3	 **6a**	24	n.r.[c]	–
4	 **7a**	2	 **7b**  **7c**	44 39

Table 3 Hydration of Internal Alkynes Bearing Various Functionalities[a] (continued)

Entry	Substrates	Time (h)	Product	Yield (%)[b]
5	 **8a**	2	 **8b**	68

[a] Substrate (0.3 mmol), $Au(PPh_3)Cl$ (1 mol%), AgOTf (1 mol%), H_2O (1.0 mmol), 1,4-dioxane, r.t.
[b] Isolated yield.
[c] n.r. = no reaction.

The developed methodology was further illustrated with a number of *ortho*-alkynylaryl aldehydes to prove its generality as described in Table 4. The simple internal alkyne **9a** with alkyl side chain afforded the desired ketone compound **9b** in 51% yield after two hours at room temperature while the substrate **10a** with substituted alkene side chain afforded 50% of product **10b**. The hydration reaction of substrate **11a** where the side chain is substituted with diester functionality afforded the product **11b** in 63% yield. When the substituent on the side chain possesses an OTBS functionality, a maximum yield of 95% of the desired ketone product **12b** was obtained. The *O*-benzyl-substituted pyridine substrate **13a** also afforded the desired hydrated product **13b** in 74% yield. Although **14a** afforded the corresponding ketone product **14b** in somewhat lower yield (58%) but the substrates **15a** and **16a** afforded the desired products **15b** and **16b** in better yields. When the substrate **17a** containing two alkyne functionalities was subjected to the hydration reaction, the regioselective product **17b** was formed in good yield where the alkyne close to the aldehyde functionality was specifically hydrated leaving the other alkyne intact. Thus the methodology has been found to work efficiently with a wide range of substrates retaining its generality.

Table 4 Regioselective Alkyne Hydration of Various *ortho*-Alkynylaryl Aldehydes[a]

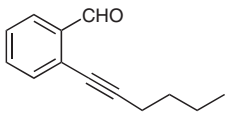
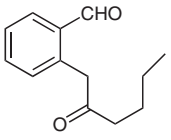
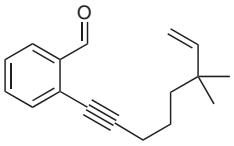
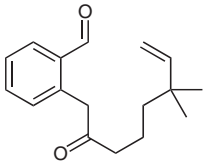
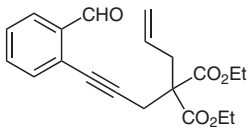
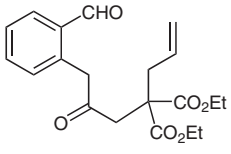
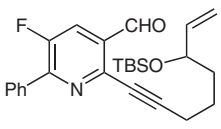
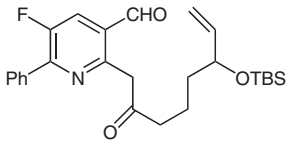
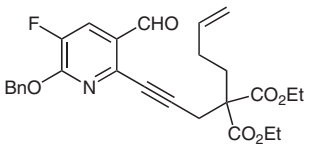
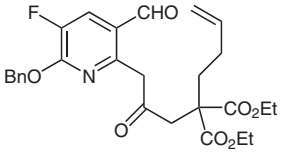
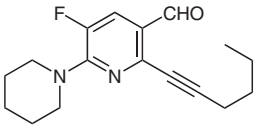
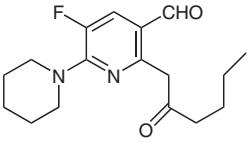
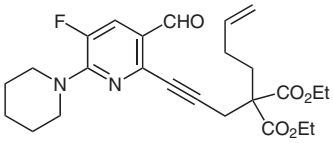
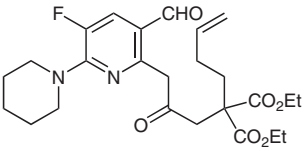
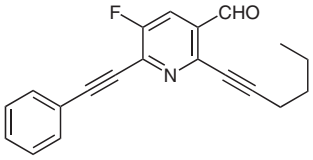
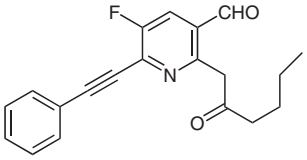
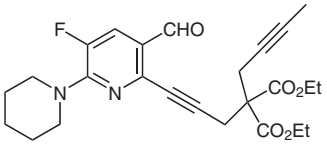
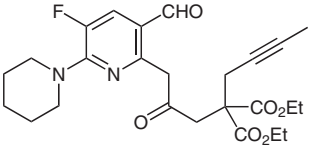
Entry	Substrates	Products	Yield (%)[b]
1	 **9a**	 **9b**	51
2	 **10a**	 **10b**	50
3	 **11a**	 **11b**	63
4	 **12a**	 **12b**	95

Table 4 Regioselective Alkyne Hydration of Various *ortho*-Alkynylaryl Aldehydes[a] (continued)

Entry	Substrates	Products	Yield (%)[b]
5	 **13a**	 **13b**	74
6	 **14a**	 **14b**	58
7	 **15a**	 **15b**	71
8	 **16a**	 **16b**	75
9	 **17a**	 **17b**	68

[a] Substrate (0.3 mmol), $Au(PPh_3)Cl$ (1 mol%), AgOTf (1 mol%), H_2O (1.0 mmol), 1,4-dioxane, 2 h, r.t.
[b] Isolated yield.

In conclusion, we have developed a new, convenient, atom-economic, and mild method toward the regioselective hydration of 1-arylalkynes in the presence of gold catalysts where the use of toxic strong acid or other additives can be avoided. A series of internal alkynes having diverse carbonyl functionalities were screened for the effective hydration which can be further explored and utilized in near future. The developed method is efficient enough to be applied to a wide range of substituted alkynes showing tolerance toward numerous functionalities.

The substrate (0.3 mmol) was dissolved in distilled 1,4-dioxane (1.0 mL) in a test tube and treated with catalysts (1–3 mol%). Water (1.0 mmol) was incorporated with a microsyringe. After a quick purge of argon gas, the reaction mixtures were stirred for 1–24 h either at r.t. or preheated oil bath (60–80 °C) as given conditions. Upon completion of the reaction (as indicated by TLC), the solvent was removed under vacuum, and flash column chromatography of the residue afforded the pure products.

Spectral Data of Compounds

Compound **1b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, 6 H, *J* = 7.0 Hz), 2.05–2.11 (m, 4 H), 3.37 (s, 2 H), 4.14–4.19 (m, 6 H), 4.95–5.06 (m, 2 H), 5.70–5.83 (m, 1 H), 7.22 (d, 1 H, *J* = 6.4 Hz), 7.49–7.55 (m, 2 H), 7.80 (d, 1 H, *J* = 7.2 Hz), 9.99 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 29.1, 32.3, 45.1, 47.8, 55.3, 61.6, 115.2, 127.9, 132.9, 133.8, 134.2, 135.3, 135.4, 137.7, 170.8, 193.3, 203.9.

Compound **1c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23–1.29 (m, 6 H), 1.47–1.57 (m, 1 H), 2.04–2.14 (m, 1 H), 2.19–2.27 (m, 1 H) 2.45–2.49 (m, 1 H), 2.57–2.65 (m, 2 H), 2.79–2.85 (m, 1 H), 3.06–3.10 (m, 1 H), 4.16–4.25 (m, 4 H), 5.69–5.67 (m, 1 H), 7.51–7.55 (m, 2 H), 7.65–7.71 (m, 1 H), 7.88 (d, 1 H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 29.8, 30.2, 36.0, 45.7, 46.0, 57.8, 61.9, 80.4, 121.9, 125.5, 125.7, 129.2, 134.2, 150.2, 170.0, 170.3, 207.5.

Compound **3b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, 6 H, *J* = 7.2 Hz), 2.00 (m, 4 H), 2.36–2.41 (m, 2 H), 2.55 (s, 3 H), 2.74–2.78 (m, 2 H), 4.19 (q, 4 H, *J* = 6.8 Hz), 4.96 (d, 1 H, *J* = 10.0 Hz), 5.04 (d, 1 H, *J* = 17.2 Hz), 5.73–5.81 (m, 1 H), 7.45–7.47 (m, 1 H), 7.51–7.57 (m, 2 H), 7.64–7.66 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 26.9, 28.1, 28.3, 32.5, 36.9, 56.6, 61.2, 115.0, 127.1, 128.3, 130.5, 131.6, 137.5, 138.1, 140.4, 171.3, 200.5, 203.8.

Compound **4b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, *J* = 7.2 Hz), 1.24–1.35 (m. 2 H), 1.51–1.58 (m, 2 H), 2.44 (t, 2 H, *J* = 7.6 Hz), 3.66 (s, 2 H), 3.90 (s, 3 H), 7.20–7.26 (m, 3 H), 7.29–7.34 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 22.2, 25.8, 41.8, 44.4, 55.5, 122.0, 126.4, 126.8, 128.4, 131.5, 149.4, 153.8, 207.3.

Compounds **7b** and **7c** (inseparable mixture): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21–1.28 (m, 12 H), 1.35 (t, 3 H, *J* = 7.2 Hz), 1.98–2.15 (m, 8 H), 3.19 (s, 2 H), 3.31 (s, 2 H), 4.10 (s, 2 H), 4.14–4.31 (m, 10 H), 4.93–5.08 (m, 4 H), 5.73–5.82 (m, 2 H), 6.3 (s, 1 H), 7.18 (d, 1 H, *J* = 7.6 Hz), 7.32–7.36 (m, 2 H), 7.44–7.49 (m, 2 H), 7.66–7.69 (m, 1 H), 8.01–8.03 (m, 1 H), 8.23 (d, 1 H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 28.5, 28.9, 31.5, 32.0, 36.5, 44.2, 48.9, 55.1, 56.8, 60.8, 61.4, 61.7, 106.1, 114.9, 115.4, 125.3, 127.3, 128.2, 129.6, 130.9, 132.29, 132.6, 134.7, 136.3, 136.9, 137.1, 137.7, 153.2, 161.9, 166.8, 170.4, 170.7, 204.2.

Compound **8b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, 6 H, *J* = 7.4 Hz), 1.66–1.67 (m, 4 H), 1.98–2.02 (m, 6 H), 2.18–2.22 (m, 2 H), 2.39–2.51 (m, 4 H), 4.18 (q, 4 H, *J* = 7.2 Hz), 4.96–5.05 (m, 2 H), 5.75–5.79 (m, 1 H), 7.02 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.2, 20.3, 21.4, 23.3, 23.4, 28.4, 30.7, 31.6, 50.9, 61.2, 115.1, 116.0, 122.1, 135.0, 137.6, 148.0, 171.3.

Compound **9b**: ^{1}H NMR (400 MHz,$CDCl_3$): δ = 0.92 (t, 3 H *J* = 7.4 Hz), 1.35 (q, 2 H, *J* = 7.2 Hz), 1.62 (quint, 2 H, *J* = 7.6 Hz), 2.62 (t, 2 H, *J* = 7.6 Hz), 4.13 (s, 2 H), 7.22 (d, 1 H, *J* = 7.2 Hz), 7.48–7.57 (m, 2 H), 7.81 (d, 1 H, *J* = 7.6 Hz), 10.02 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.4, 25.9, 42.6, 47.6, 127.6, 127.7, 132.7, 133.8, 135.2, 193.4, 207.5.

Compound **10b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 6 H), 1.26–1.30 (m, 2 H), 1.53–1.57 (m, 2 H), 2.59 (t, 2 H, *J* = 7.2 Hz), 4.11 (s, 2 H), 4.88–4.92 (m, 2 H), 5.72–5.79 (m, 1 H), 7.21 (d, 1 H, *J* = 7.2 Hz), 7.47–7.57 (m, 2 H), 7.81 (d, 1 H, *J* = 7.4 Hz), 10.01 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 26.8, 36.7, 42.2, 43.5, 47.6, 110.6, 127.8, 132.8, 133.8, 134.4, 135.3, 136.2, 148.3, 193.5, 207.4.

Compound **11b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, 6 H, *J* = 7.0 Hz), 2.79 (d, 2 H, *J* = 7.2 Hz), 3.34 (s, 2 H), 4.13–4.19 (m, 6 H), 5.12 (d, 2 H, *J* = 12.0 Hz), 5.68–5.76 (m, 2 H), 7.21 (d, 1 H, *J* = 7.2 Hz), 7.49–7.55 (m, 2 H), 7.80 (d, 1 H, *J* = 6.0 Hz), 9.99 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 37.6, 44.9, 47.9, 55.3, 61.7, 119.6, 127.9, 132.9, 133.1, 133.8, 134.3, 135.3, 135.5, 170.4, 193.3, 203.9.

Compound **12b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (s, 9 H), 1.51–1.55 (m, 2 H), 1.66–1.72 (m, 2 H), 2.67 (t, 2 H, *J* = 7.6 Hz), 4.09–4.13 (m, 1 H), 4.38 (s, 2 H), 5.03 (d, 1 H, *J* = 10.4 Hz), 5.14 (d, 1 H, *J* = 17.2 Hz), 5.74–5.83 (m, 1 H), 7.49–7.52 (m, 3 H), 7.91 (d, 1 H, *J* = 10.8 Hz), 8.04–8.06 (m, 2 H), 10.04 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 19.5, 26.0, 37.5, 43.3, 49.9, 73.7, 114.0, 127.1, 127.3, 128.7, 129.1, 129.4, 129.5, 129.9, 130.5, 130.8, 134.3, 134.3, 141.5, 151.6, 151.6, 155.4, 158.0, 189.9, 206.4.

Compound **13b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, 6 H, *J* = 7.2 Hz), 2.01–2.04 (m, 2 H), 2.10–2.12 (m, 2 H), 3.33 (s, 2 H), 4.18 (q, 4 H, *J* = 7.6 Hz), 4.26 (s, 2 H), 4.97 (d, 1 H, *J* = 9.6 Hz), 5.02 (d, 1 H, *J* = 17.2 Hz), 5.52 (s, 2 H), 5.73–5.80 (m, 1 H), 7.34–7.47 (m, 5 H), 7.75 (d, 1 H, *J* = 9.6 Hz), 9.91 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 29.2, 32.6, 45.5, 49.6, 55.5, 61.8, 69.2, 115.4, 125.2, 125.4, 128.5, 128.5, 128.7, 135.9, 137.5, 170.7, 189.0, 203.0.

Compound **14b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, 3 H, *J* = 7.4 Hz), 1.32–1.36 (m, 2 H), 1.57–1.71 (m, 8 H), 2.58 (t, 2 H, *J* = 7.4 Hz), 3.73–3.75 (m, 4 H), 4.11 (s, 2 H), 7.52 (d, 1 H, *J* = 14.0 Hz), 9.79 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.4, 24.8, 25.9, 26.3, 42.9, 48.1, 48.2, 49.5, 121.0, 124.9, 125.1, 145.3, 147.8, 150.3, 152.3, 188.3, 207.3.

Compound **15b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, 6 H, *J* = 7.2 Hz), 1.65–1.68 (m, 10 H), 1.98–2.02 (m, 2 H), 2.09–2.13 (m, 2 H), 3.31 (s, 2 H), 3.73–3.76 (m, 4 H), 4.13 (s, 2 H), 4.17 (q, 4 H, *J* = 7.2 Hz), 4.94–5.03 (m, 2 H), 5.70–5.80 (m, 1 H), 7.51 (d, 1 H, *J* = 14.0 Hz), 9.77 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 24.8, 26.2, 29.1, 32.4, 45.3, 48.2, 55.2, 61.6, 115.2, 120.9, 125.3, 137.6, 145.3, 150.2, 151.4, 170.7, 188.2, 203.5.

Compound **16b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, 3 H, *J* = 7.2 Hz), 1.25–1.45 (m, 2 H), 1.57–1.69 (m, 2 H), 2.67 (t, 2 H, *J* = 7.6 Hz), 4.37 (s, 2 H), 7.26–7.43 (m, 3 H), 7.64–7.61 (m, 2 H), 7.88 (d, 1 H, *J* = 8.0 Hz), 9.99 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 22.3, 25.6, 42.9, 49.5, 82.5, 98.9, 121.2, 125.3, 125.5, 128.5, 129.9, 132.2, 135.9, 136.0, 152.1, 157.9, 160.5, 189.2, 206.1.

Compound **17b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, 6 H, *J* = 7.2 Hz), 1.66–1.70 (m, 6 H), 1.74 (t, 3 H, *J* = 2.4 Hz), 2.91 (d, 2 H, *J* = 2.0 Hz), 3.45 (s, 2 H), 3.75–3.76 (m, 4 H), 4.15–4.20 (m, 6 H), 7.52 (d, 1 H, *J* = 14.4 Hz), 9.79 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.5, 13.9, 23.6, 24.7, 26.1, 44.7, 48.1, 49.6, 54.8, 61.8, 73.8, 78.9, 120.9, 124.5, 124.7, 169.3, 187.9, 203.8.

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