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Synthesis of Primitive Dendrimer Systems Bearing Bicyclo[3,2,0] Hept-6-en-6-yl Groups *via* Unique Au-catalyzed [2+2] Cyclization

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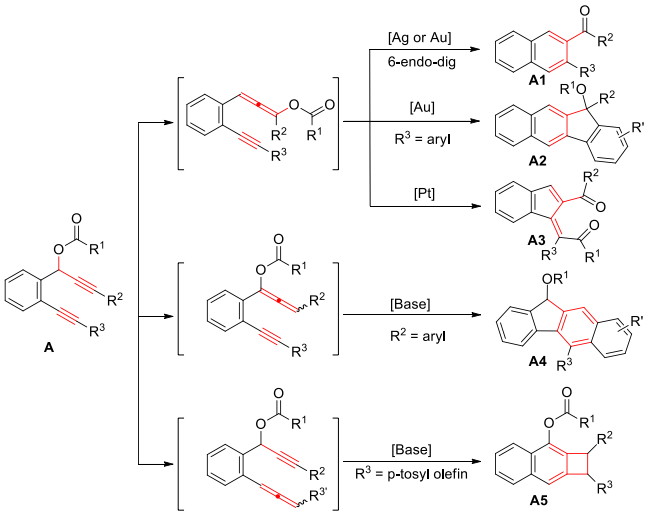
Propargylic pivaloates bearing an alkynyl group at a three-carbon tether under the gold catalysis would undergo [3,3] rearrangements of propargylic pivaloates followed by tandem [2+2] cyclization to give the corresponding 6-acylbicyclo[3,2,0]hept-6-ens. In continuing work, we prepared various substrates bearing two arms of alkyne-propargylic pivaloates to explore primitive dendrimer concept bicyclic compounds. Finally, we could obtain a series of diasteromeric compounds bearing two arms of 6-acylbicyclo[3,2,0] hept-6-ene groups in high yields.

Keywords: Gold catalyst, [2+2] cyclization, Propargylic carboxylate, Bicyclo[3,2,0]heptane

Introduction

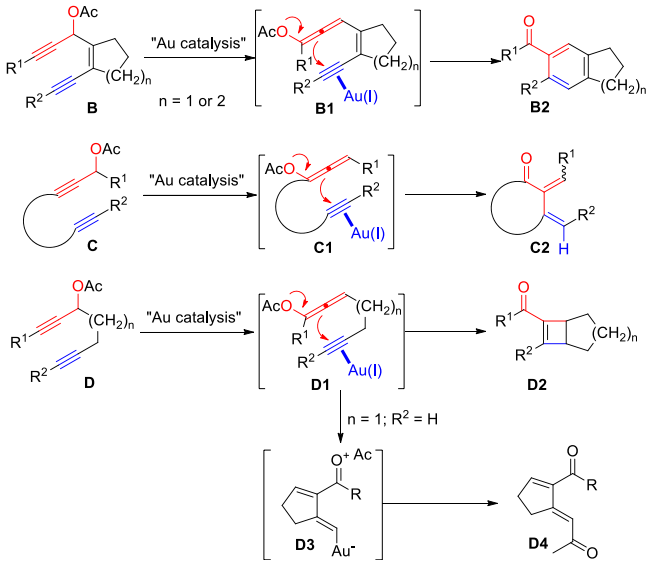
Gold-catalyzed rearrangement reactions of propargylic esters offer a highly significant synthetic strategy for their synthetic utility in a wide variety of fascinating transformations and to construct complex polycyclic compounds.[1] This is mainly due to the excellent alkynophilicity of gold cations (I or III) towards propargylic carboxylates. A propargylic carboxylate upon treatment with the gold cation has been known to undergo 1,2- and/or 1,3-shift of the carboxylate selectively depending mainly on the types of substrates.[2] Propargylic carboxylates with a terminal alkyne form the gold-carbene complexes by 1,2-carboxylate shift,[3] those with an internal alkyne form the allenoates by 1,3-carboxylate shift.[4] Scheme 1 shows a schematic summary for cyclization of propargylic carboxylates (substrate **A**). **A1–A3** shows the result of the cyclizative products with 1,3-carboxylate shift under metal-catalyzed conditions. And **A4–A5** shows non-shift-cyclization under non-metal and base catalyzed condition. It has been assumed that acyl migration was occurred only under [Au and Pt] catalyzed conditions. Toste *et al.* reported silver-catalyzed 1,3-acyl migration of a nonterminal propargylic esters (Type **A**) to the highly functionalized aromatic compounds (Type **A1**).[5] In the same year, we reported gold-catalyzed allene formation via 1,3-acyl migration of a nonterminal propargylic esters (Type **A**), followed by Myers–Saito-type (C^2–C^7) enyne–allene cyclization to form the highly functionalized aromatic compounds (Type **A1**) via *6-endo-dig*.[6] Next, Liu group has reported about a gold-catalyzed allene formation via 1,3-acyl migration of a propargyl carbonates (Type **A1**).[7] Here the resulting oxocarbenium ion formed in the gold-catalyzed *6-endo-dig* cyclization step could be further attacked by the aryl moiety, giving rise to a second cyclization reaction leading to the tetracycles (Type **A2**). In 2014, Chen *et al.* reported benzofulvenes via 1,3-acyl migration strategy (Type **A3**) through a Schmittel-type (C^2–C^6) enyne–allene cyclization by platinum-catalyzed reaction.[8] It has been postulated that Au(I)-catalyzed [3,3]-rearrangement of propargylic esters are reversible processes that take place via Au(I)-coordinated cationic intermediates and subsequent formation of the allenes, which can then undergo further transformations.[9] Recently, *Liu* groups reported base catalyzed Schmittel enyne–allene cyclization (Type **A4**).[10] As expected, under non-metal condition, non-shift cyclization was occurred. In the same year, *Zhou et al.* reported that p-tosyl alkenyl substituted (R^3) propargylic carboxylates were transformed to 1,2-dihydrocyclobuta-[b]naphthyl structures under base catalysts via non-shift [2+2] cycloaddition (Type **A5**).[11]



Scheme 1. Three types of cyclization of propargylic carboxylate.

Propargylic carboxylates with an alkynyl group linked with an alkyl tether have been valuable substrates for various gold-catalyzed transformations as summarized in

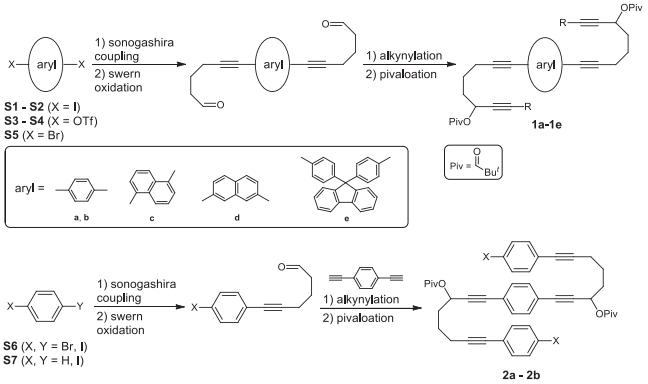
Scheme 2. In continuing our study, we further extended our methodology to alkynes-propargylic acetates, **B** and **C**, for facile synthesis of benzene derivatives **B2** and 2,3-bisalkylidenecyclohexanones **C2.** We observed that similar pathways of **A** to **A1** (1,3-sigmatropic acyl shift, *6-endo-dig* cyclization, and acyl elimination) to afford the corresponding dienes **B2** and **C2.**[12] During our study, the standard conditions towards alkynes-propargylic acetates like **D** did not afford the expected diene products, but exhibited a different mode of reactions to give the [*n*,2,0]bicyclic products like **D2**. This unprecedent Au-catalyzed [2+2] cyclization of alkyne-propargylic pivaloates to transform into [3,2,0]bicyclic compounds was quite general with a wide scope of substrates.[13] We have shortly extended this reaction towards several substrates which have two sets of alkyne-propargylic pivaloate groups in a molecule linked by a aryl group to explore a very primitive dendrimer concept.[14] If more substituted alkyl chain was linked (longer and more alkynyl groups), more bicyclic units were appeared in the occurred macro molecule. In this context, Fensterbank *et al.* reported a Schmittel-type 5-*exo*-dig enyne–allene cyclization of hepta-1,6-diyn-3-yl esters like **D**. Of particular interest, hydrative cyclizations of (*Z*)-hepta-4-ene-1,6-diyn-3-yl esters led to aromatic ketones after 1,3-sigmatropic acyloxy shift, 6-*endo*-dig cyclization, and acyl elimination where the acylium ion could be trapped by the nucleophilic Au—C bond of **D3**, a new kind of cycloisomerization product **D4** would ensue.[15] This could be an efficient method for the preparation of δ-diketones like **D4** based on an Au-triggered 1,5-acyl shift.[4o]



Scheme 2. Mechanistic four-pathways of substrates via Au-catalyzed cyclization.

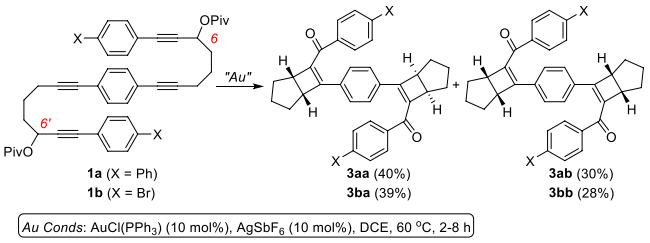
Results and Discussion

In this paper, we wish to explore our recent accomplishment in which various substrates bearing two sets of a propargylic carboxylate and an internal triple bond could undergo sequential gold-catalyzed cyclizations of 1,3-sigmatropic acyloxy shift, [2+2] cycloaddition, and acyl elimination to afford the corresponding dendrimer type compounds having two arms of a bicyclo[3,2,0]heptane unit. These are very useful dendrimer application in macromolecule system. Initially we have prepared substrates for our study as the following well-known sequences: Sonogashira cross-coupling, oxidation, alkynylation, and esterification to the pivaloates **1a–e** (Scheme 3).[16]



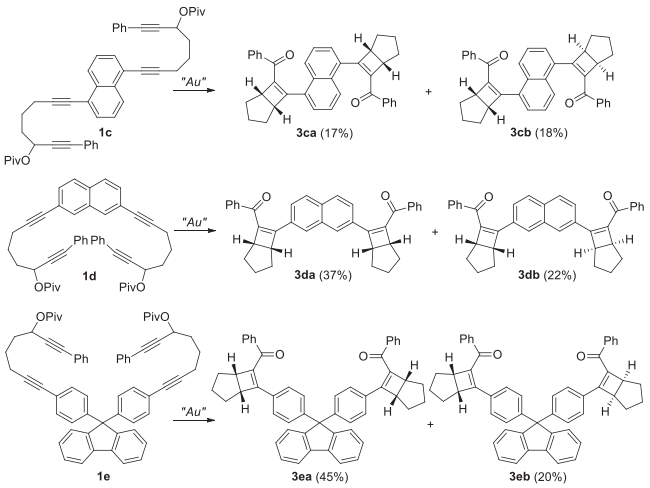
Scheme 3. General procedure for preparing substrates.

Next, we have carried out gold-catalyzed reaction of **1a** to explore the optimal conditions affording to the product **3aa** and **3ab** (Scheme 4). In our previous study, we have established gold-catalyzed cyclization of one propargylic pivaloate in to a [3,2,0]bicyclic compounds. Here to improve the importance of method to application part, we started our study towards bis-propargylic pivaloates and internal alkynes to obtain bis[3,2,0] bicyclic compounds with our standard condition (10 mol % of chloro(triphenylphosphine)gold (I) and 10 mol% of silver hexaflouroantimonate(V) in 1,2-dichloroethane). In fact, these two propargylic compounds have two chiral centers, so they produce at least two diastereomeric bicyclic compounds. As a result, since substrate **1a** is also a diastereomeric mixture, the corresponding products should be a diastereomeric mixture. Diastereomeric mixture of **3aa** and **3ab** obtained by the reaction of **1a** with Au-catalyst in 8 h with 70% as shown in Scheme 4. Thus, we have separated its diastereomers by using preparative HPLC to give **3aa** and **3ab** in a ratio of 40 and 30% yields, respectively. The proton NMR of the compound **3aa** appears two different magnetically nonequivalents of chiral protons due to the center of symmetry and C_2-axis of symmetry whereas **3ab** appears 4 non equivalents of chiral proton signals due to the lack of symmetry. The substrate **1b**, possessing somewhat labile a —Br substituent, successfully proceeded this reaction in 3 h to give **3ba** and **3bb** in 39 and 28% yields, respectively.



Scheme 4. Gold reaction of substrates **1a** and **1b.**

We became to know that the **1c** was also composed of one enantiomeric pair (**1ca**) and one meso isomer. These two **1cb** compounds were exactly same because of having a center of symmetry, C_2 symmetry group (Figure 1). And all other substrates have a symmetry plane. Consequently we could obtain totally three compounds via cyclization, two enantiomeric compounds and one diastereromeric compound. Scheme 5 shows substrates **1c–e** and the corresponding products obtained from the present Au-catalyzed reactions. The substrates **1a–e** are aromatic compounds conjugated with two alkynyl groups, each of which has a remote propargyl carboxylate group in 6 and 6′-positions.



Scheme 5. Substrates scope of gold reaction.

The substrate **1c**, under standard conditions, took 2 h at room temperature to form two diastereomeric products **3ca** and **3cb** in 17 and 18% yields, respectively. The substrates **1d**, 2, 7-disubstituted naphthalene, underwent the present transformation for 3 h at 60 °C into **3da** and **3db** in 37 and 22% yields, respectively. The substrates **1e** underwent the present transformation into **3ea** and **3eb** in 45 and 20% yields, respectively.

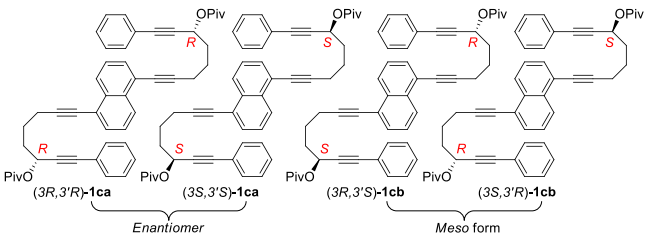
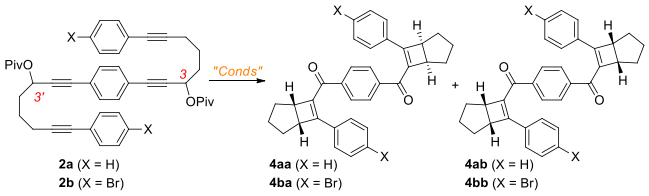


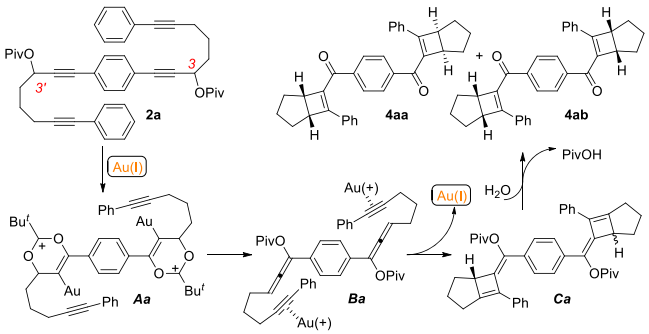
Figure 1. Structural analysis of diastereomeric substrate **1c**.

Next, we have prepared two more substrates (Scheme 6). The substrates **2a** and **2b** are 1,4-disubstituted benzenes conjugated with two propargyl pivaloates in 3- and 3′-position, each of which has a remote triple bond in 7- and 7′-position. These substrates were important to confirm the mechanistic process including 1,3-migration of cyclization. Overall, these substrates under our conditions proceeded smoothly into the corresponding products for 5–6 h at 60 °C. Thus **2a** gave **4aa** and **4ab** in 45 and 25% yields; **2b** gave **4ba** and **4bb** in 22 and 37% yields, respectively. Again, the bromide group was intact during this reaction.



Scheme 6. Gold reaction of substrates **2a** and **2b**.

The proposed mechanism for the conversion of **2a** into **4aa** and **4ab** is as follows (Scheme 6). The first step would be Au-catalyzed activation of propargyl group to **Aa**; then proceed 1,3-pivaloyl shift into **Ba**, in which Au(+) would activate the other triple bond in order to help [2+2] cycloaddition to **Ca**. The two reactive sites of **2a** might proceed sequentially not simultaneously. Finally, the presence of water upon exposure to workup caused to hydrolyze the **Ca** into the products **4aa** and **4ab** in a different ratio depending on their stabilities. During hydrolysis of **Ca**, diastereomeric ratio would be gained into **4aa** and **4ab** (Scheme 7).



Scheme 7. Specific mechanism of Au-catalyzed [2+2] cycloaddition.

Conclusion

In conclusion, we have synthesized a series of dendrimer type compounds bearing two arms of 7-acylbicyclo[3,2,0]-hept-6-en-6-yl via rare Au-catalyzed [2+2] cycloaddition. The tandem gold-catalyzed sequences are composed of 1,3-

acyl migration, [2+2] cyclization, and hydrolysis of the resulting enloates.

Experimental

Typical Procedure of Gold-catalyzed Reaction (1a-2b to 3aa-4bb). To a new sealed tube equipped with a stirring bar a solution of bis-alkyne-propargylic pivaloate (**1a–2b**, 0.10 mmol) in dried 1,2-dichloroethane (1.0 mL) were added chlorotriphenylphosphine(I) ($AuCl(PPh_3)$) (0.01 mmol) and silver hexaflouroantimonate(V) ($AgSbF_6$) (0.01 mmol). The resulting mixture was stirred at 60 °C for 2–8 h. Without extraction, the solvent was removed under reduced pressure and the crude residue was purified by column chromatography (ethyl acetate: hexane = 1:10) to afford the diastereomeric mixtures as a clear oil. These mixtures were separated by HPLC (ethyl acetate: hexane = 1:10) as a clear oil **(3aa–4bb).**

3aa. IR (NaCl, cm^{-1}) 2946, 2855, 2249, 1745, 1631, 1601, 1287, 1232, 1119; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 4H), 7.63–7.60 (m, 8H), 7.55 (s, 4H), 7.47–7.43 (m, 4H), 7.40 (d, *J* = 7.6 Hz, 2H), 3.68–3.45 (m, 2H), 3.57–3.55 (m, 2H), 1.83–1.79 (m, 4H), 1.73–1.67 (m, 5H), 1.43–1.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 153.0, 145.4, 140.2, 137.7, 136.8, 133.6, 129.8, 129.1, 128.8, 128.3, 127.4, 127.37, 46.3, 44.7, 31.8, 26.7, 26.5, 23.5, 22.8, 14.3; HRMS (ESI) [M + Na] $^+$ calculated for $C_{46}H_{38}O_2Na^+$: 645.2764, found 645.2764.

3ab. IR (NaCl, cm^{-1}): 2952, 2851, 2247, 1757, 1612, 1313, 1287, 1187. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.65–7.58(m, 7H), 7.54(d, *J* = 8.4 Hz, 2H), 7.48–7.39(m, 5H), 7.37–7.30(m, 4H), 7.27–7.25(m, 2H), 3.83(t, *J* = 6.8 Hz, 1H), 3.70(dd, *J* = 3.2 Hz, *J* = 4 Hz, 1H), 3.58(dd, *J* = 3.6 Hz, *J* = 3.8 Hz, 1H), 3.09–3.05(m, 1H), 2.13–2.08(m, 1H), 1.93–1.63(m, 8H), 1.44–1.33(m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 190.4, 169.9, 153.0, 145.2, 140.7, 140.5, 140.1, 139.9, 138.1, 137.9, 136.7, 136.1, 134.2, 134.0, 133.6, 131.9, 131.0, 50.6, 46.5, 46.3, 44.5, 30.0, 26.6, 26.5, 26.3, 24.2, 23.3. HRMS (ESI) [M + Na]$^+$ calculated for $C_{46}H_{38}O_2Na^+$: 645.2764, found 645.2764.

3ba. IR (NaCl, cm^{-1}): 2932, 2850, 2252, 1736, 1633, 1585, 1288, 1228; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.8 Hz, 4H), 7.65 (d, *J* = 7.2, Hz, 4H), 7.54 (d, *J* = 7.2 Hz, 4H), 3.62–3.60 (m, 2H), 3.57–3.55 (m, 2H), 1.83–1.60 (m, 10H), 1.43–1.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 154.0, 137.1, 136.9, 133.6, 132.0, 130.7, 128.8, 127.8, 46.2, 44.8, 29.9, 27.2, 26.7, 26.5, 23.4. HRMS (ESI) [M + Na]$^+$ calculated for $C_{34}H_{28}Br_2O_2Na^+$: 649.0338, found 649.0335.

3bb. IR (NaCl, cm^{-1}) 2952, 2867, 2250, 1695, 1633, 1584, 1484, 1340, 1229; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.57 (dd, *J* = 10.4, 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.82–3.79 (m, 1H), 3.65–3.63 (m, 1H), 3.57–3.55 (m, 1H), 3.07–3.04 (m, 1H), 2.94–2.05 (m, 1H), 1.90–1.30 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 189.6, 170.3, 154.0, 139.4, 137.4, 136.6, 136.3, 133.5, 131.7, 131.6, 131.0, 130.9, 130.4, 128.7, 127.6, 122.2, 50.5, 46.6, 46.1, 44.7, 30.0, 29.9, 29.6, 26.5, 26.2, 24.2, 23.3; HRMS (ESI) [M + Na]$^+$ calculated for $C_{34}H_{28}Br_2O_2Na^+$: 649.0338, found 649.0335.

3ca. IR (NaCl, cm^{-1}): 2943, 2855, 1633, 1597, 1577, 1504, 1446, 1333, 1288, 1233; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.86 (m, 2H), 7.56 (d, *J* = 8 Hz, 4H), 7.22–7.13 (m, 6H), 6.95 (dd, *J* = 7.6 6.4 Hz, 4H), 3.82–3.78 (m, 2H), 3.67–3.64 (m, 2H), 2.28–2.24 (m, 2H), 1.80–1.73 (m, 4H), 1.58–1.48 (m, 4H), 1.42–1.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 154.6, 154.4, 139.3, 137.4, 137.4, 132.2, 132.0, 132.0, 130.8, 130.7, 128.6, 127.7, 127.1, 127.0, 126.2, 126.1, 125.3, 48.9, 48.8, 45.8, 45.7, 26.8, 25.5, 25.4, 23.4. HRMS (ESI) [M + Na]$^+$ calculated for $C_{38}H_{32}O_2Na^+$: 543.2295, found 543.2296.

3cb. IR (NaCl, cm^{-1}): 3865, 3744, 1700, 1652, 1558, 1539, 1506, 1456; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.92 (d, *J* = 8.8 Hz, 1H), 7.52–7.48 (m, 4H), 7.29–7.28 (m, 2H), 7.13–7.09 (m, 7H), 6.91–6.86 (m, 2H), 3.84–3.82 (m, 1H), 3.75–3.68 (m, 2H), 3.15–3.12 (m, 1H), 2.30–2.17 (m, 2H), 1.95–1.80 (m, 3H), 1.66–1.65 (m, 2H), 1.52–1.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5, 191.7, 191.6, 142.9, 139.9, 137.9, 137.8, 132.2, 128.9, 128.2, 127.8, 127.2, 126.3, 125.9, 125.5, 50.9, 49.0, 45.9, 31.0, 29.1, 27.1, 25.9, 24.2, 23.9. HRMS (ESI) [M + Na]$^+$ calculated for $C_{38}H_{32}O_2Na^+$: 543.2295, found 543.2296.

3da. IR (NaCl, cm^{-1}): 2950, 2866, 2248, 1694, 1632, 1596, 1445, 1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.92 (d, *J* = 8 Hz, 2H), 7.86 (s, 1H), 7.64 (dd, *J* = 2.4, 1.6 Hz, 1H), 7.62 (s, 1H), 7.60–7.56 (m, 1H), 7.53–7.49 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.29–7.27 (m, 3H), 7.24–7.20 (m, 3H), 3.97–3.93 (m, 1H), 3.71–3.69 (m, 2H), 3.14–3.10 (m, 1H), 2.16–2.11 (m, 1H), 1.95–1.65 (m, 8H), 1.43–1.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 191.5, 170.7, 153.6, 140.8, 138.3, 137.4, 133.9, 133.4, 132.8, 132.2, 130.8, 129.7, 129.2, 129.1, 129.0, 128.7, 128.9, 127.7, 127.6, 50.76, 46.9, 46.8, 46.2, 46.0, 44.7, 30.2, 26.7, 26.4, 24.3, 23.4. HRMS (ESI) [M + Na]$^+$ calculated for $C_{38}H_{32}O_2Na^+$: 543.2295, found 543.2295.

3db. IR (NaCl, cm^{-1}): IR(NaCl cm^{-1}): 2947, 1743, 1635, 1601, 1313, 1287, 1232; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.04(d, *J* = 8.4 Hz, 2H), 7.93–7.91(d, *J* = 7.6 Hz, 4H), 7.63–7.56 (m, 4H), 7.53–7.49 (m, 2H), 7.41–7.37(m, 4H), 3.70–3.68(m, 4H), 1.92–1.89 (m, 2H), 1.85–1.80 (m, 2H), 1.76–1.69 (m, 4H), 1.60–1.55 (m, 2H), 1.44–1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 153.9, 153.9, 138.4, 137.0, 137.0, 134.1, 132.7, 132.6, 130.6, 130.6, 129.4, 129.1, 128.6, 127.6, 127.4, 46.0, 44.7, 26.8, 26.4, 23.4; HRMS (ESI) [M + Na]$^+$ calculated for $C_{38}H_{32}O_2Na^+$: 543.2295, found 543.2295.

3ea. IR (NaCl, cm^{-1}): 3059, 2948, 2864, 1694, 1446, 1230, 913; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 3H), 7.37–7.34 (m, 5H), 7.32–7.23 (m, 8H),

7.18 (d, J = 8.4 Hz, 2H), 7.15–7.13 (m, 2H), 7.05 (dd, J = 6, 2.8 Hz, 2H), 3.79–3.76 (m, 1H), 3.61 (dd, J = 2.8, 4.0 Hz, 1H), 3.49 (dd, J = 4.0, 3.6 Hz, 1H), 3.04–3.00 (m, 1H), 2.09–2.05 (m, 1H), 1.86–1.57 (m, 7H), 1.49–1.28 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 191.0, 169.7, 154.0, 150.2, 147.2, 147.1, 140.1, 138.2, 136.2, 133.1, 132.7, 132.2, 131.2, 129.3, 128.9, 128.8, 128.6, 128.4, 128.3, 128.0, 128.8, 127.7, 127.7, 126.0, 120.2, 65.2, 50.4, 46.1, 45.8, 44.4, 30.0, 29.9, 26.5, 26.2, 24.1, 23.2. HRMS (ESI) [M + Na] $^+$ calculated for $C_{53}H_{42}O_2Na^+$: 733.3077, found 733.3080.

3eb. IR(NaCl, cm^{-1}); 2943, 2855, 1632, 1598, 1501,1323, 1230, 912; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 6.8 Hz, 4H), 7.74 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 8.4 Hz, 6H), 7.35 (t, J = 7.4 Hz, 8H), 7.29–7.23 (m, 2H), 7.04 (d, J = 8.4 Hz, 4H), 3.62–3.59 (m, 2H), 3.51–3.48 (m, 2H), 1.83–1.78 (m, 2H), 1.75–1.63 (m, 6H), 1.47–1.41 (m, 2H), 1.36–1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 153.9, 150.3, 147.1, 140.1, 138.2, 136.1, 132.2, 131.1, 128.8, 128.6, 128.3, 127.9, 127.7, 126.1, 120.2, 65.3, 45.7, 44.2, 26.5, 26.3, 23.2. HRMS (ESI) [M + Na]$^+$ calculated for $C_{53}H_{42}O_2Na^+$: 733.3077, found 733.3080.

4aa. IR (NaCl, cm^{-1}) 2943, 2854, 1632, 1562, 1489, 1227; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 0.8 Hz, 4H), 7.60 (t, J = 5.8 Hz, 4H), 7.31–7.26 (m, 6H), 3.62–3.57 (m, 4H), 1.84 (dt, J = 12.4, 5.8 Hz, 2H), 1.78–1.59 (m, 6H), 1.53–1.45 (m, 2H), 1.41–1.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 155.8, 141.2, 141.1, 135.9, 132.5, 130.1, 129.0, 128.4, 45.7, 44.9, 44.9, 26.6, 26.6, 26.4, 23.4; HRMS (ESI) [M + Na]$^+$ calculated for M $C_{34}H_{30}O_2Na^+$: 493.2138, found 493.2138.

4ab. IR (NaCl, cm^{-1}): 3059, 2950, 2866, 2248, 1697, 1631, 1602, 1346, 1231; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, J = 4.8, 3.6 Hz, 2H), 7.57–7.61 (m, 2H), 7.22–7.33 (m, 10H), 3.83–3.87 (m, 1H), 3.54–3.63 (m, 2H), 3.06–3.09 (m, 1H), 2.12–2.07 (m, 1H), 1.94–1.64 (m, 7H), 1.57–1.44 (m, 2H), 1.42–1.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 191.3, 172.7, 154.1, 139.6, 137.3, 137.0, 136.6, 135.0, 132.8, 130.0, 129.9, 129.2, 128.9, 128.9, 128.8, 128.4, 50.9, 47.1, 46.0, 45.9, 44.7, 30.3, 30.2, 26.8, 26.7, 26.6, 26.5, 24.4, 23.5. HRMS (ESI) [M + Na]$^+$ calculated for M $C_{34}H_{30}O_2Na^+$: 493.2138, found 493.2138.

4ba. IR (NaCl, cm^{-1}): 3069, 2945, 2856, 1745, 1633, 1582, 1482, 1273; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 4H), 7.59–7.55 (m, 4H), 7.43 (d, J = 8.8 Hz, 4H), 3.63–3.60 (m, 2H), 3.58–3.56 (m, 2H), 1.83–1.57 (m, 10H), 1.42–1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 154.9, 141.0, 136.3, 131.6, 131.1, 130.4, 128.8, 124.5, 45.8, 44.7, 27.2, 27.0, 26.5, 26.4, 26.2, 23.2; HRMS (ESI) [M + Na] $^+$ calculated for M $C_{34}H_{30}O_2Na^+$: 493.2138, found 493.2138.

4bb. IR (NaCl, cm^{-1}): 3054, 2879, 2845, 2013, 1763, 1577, 1541, 1462, 1380, 1239. ^{1}H NMR (400 Hz, $CDCl_3$): δ 7.86–7.82 (m, 2H), 7.56–7.42 (m, 8H), 7.14–7.12 (m, 2H), 3.84–3.80 (m, 1H), 3.64–3.61 (m, 1H), 3.56–3.52 (m, 1H), 3.10–3.07 (m, 1H), 2.11–2.08 (m, 1H), 1.95–1.86 (m, 1H), 1.80–1.60 (m, 6H), 1.53–1.45 (m, 2H), 1.41–1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 154.9, 141.0, 136.3, 131.6, 131.1, 130.4, 128.8, 124.5, 45.8, 44.7, 27.2, 27.0, 26.5, 26.4, 26.1, 23.2. HRMS (ESI) [M + Na]$^+$ calculated for M $C_{34}H_{30}O_2Na^+$: 493.2138, found 493.2138.

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Supporting Information. Supplementary data (Copies of ^{1}H and ^{13}C NMR spectra for all compounds associated with this article can be found in the online version).

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