Synthesis of [m,7,n]-Tricycles via Platinum-Catalyzed Cyclization of Conjugated Enynals with a Pendant Alkene

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Abstract: Conjugated enynals anchored to cycloalkenes, in the presence of platinum catalysts, were cyclized to the corresponding [m,7,n]-tricarbocycles, which are valuable skeletons in biologically active natural products like taxoids.

Key words: platinum, enynal, catalyst, cyclization, tetracycle

The promising anticancer activity of taxol and related compounds has attracted considerable attention from organic and medicinal chemists toward the development of efficient synthetic methods for taxoids and more active analogues (Figure 1).[1]

Conjugated enynals may serve as versatile substrates for [m,7,n]-tricyclic skeletons via metal-catalyzed reactions. In fact, conjugated enynals with certain alkynophilic metal cations are known to form metal–pyrylium intermediates which undergo cycloaddition with a pendent unsaturated bond.[2] Recently, we reported [3+2] cycloaddition of Rh-carbenoid dipolar carbonyl ylides derived from enynals with a pendant double bond.[3] Yamamoto and co-workers reported a gold-catalyzed benzannulation of *o*-alkynylbenzaldehydes with alkynes involving a [4+2] cycloaddition of Au-pyrylium intermediates with dienophiles such as alkynes and enol ethers at high temperature.[4] In this context, we reported Au-catalyzed cyclization of diynals **1** to dihydrobenzo[*f*]azulen-4(1*H*)-ones **2** via [3+2] cycloaddition and Pt-catalyzed cyclization to 2,3-dihydrophenanthren-4(1*H*)-ones **3** via [4+2] cycloaddition (Scheme 1).[5]

Continuing our interest in cycloisomerization involving Huisgen-type [3+2] cycloadditions, we have paid attention to metal–pyrylium intermediates derived from an aliphatic anchor.[6] Similar to gold, platinum is alkynophilic and prone to form Pt–carbene complexes. Combining properties associated with platinum cations, we could

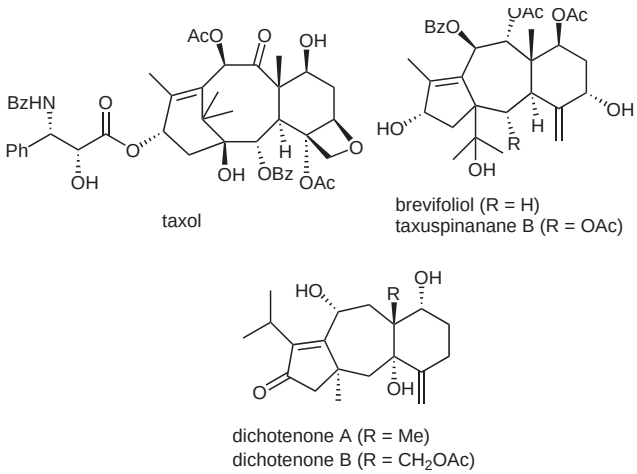
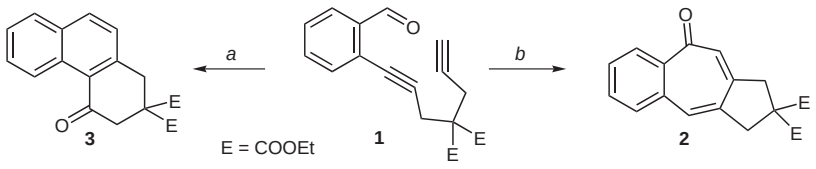


Figure 1

postulate their powerful catalytic activities toward enynals to form reactive pyrylium intermediates which could undergo cycloaddition via either [4+2] or [3+2] route. Herein we wish to report Pt-catalyzed synthesis of [m,7,n]-tricyclic skeletons having an oxygen bridge in the seven-membered ring from conjugated enynals with a pendent double bond (Scheme 2).

In order to exploit this transformation, we first prepared a substrate **4a** by known procedures.[7] At first, cyclization of enynal **4a** was attempted with $AuBr_3$, AuCl, and $AuCl(PPh_3)$, but the substrate **4a** was dimerized within an hour. Thus we changed catalysts from gold compounds to less reactive platinum compounds (Table 1).

$AuBr_3$ in 1,2-dichloroethane (DCE) and toluene completely converted **4a** within one hour at room temperature and 0 °C, respectively, but afforded a complex dimeric compound, the structure of which is still under



Scheme 1 *Reagent and conditions*: (a) $PtCl_2$ or $PtCl_4$ (3 mol%), DCE, 80 °C, 3 h, **3** (40–43%); (b) $AuBr_3$ (3 mol%), DCE, r.t., 8 h, **2** (80%).

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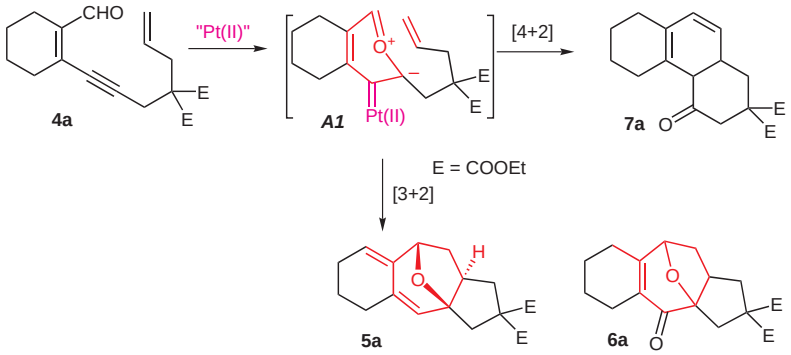
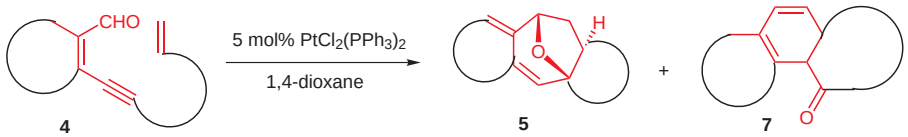


Scheme 2

Table 1 Metal-Catalyzed Reactions of Enynal **4a**

Entry	Catalysts (5 mol%)	Solvent	Temp (°C), time (h)	Product (%yield)
1	$AuBr_3$	DCE	r.t., 1	dimer (89)
2	$AuBr_3$	toluene	0, 1	dimer (82)
3	AuCl	CH_2Cl_2	r.t., 0.5	dimer (71)
4	$AuCl(PPh_3)$	CH_2Cl_2	r.t., 1	dimer (79)
5	$PtCl_2$	toluene	110, 48	**5a** (30), **6a** (12)
6	$PtCl_2(PPh_3)_2$	toluene	100, 12	**5a** (47), **6a** (11)
7	$PtCl_2(PPh_3)_2$	DCE	80, 12	**5a** (44), **6a** (38)
8	$PtCl_2(PPh_3)_2$	DMF	100, 12	dec.
9	$PtCl_2(PPh_3)_2$	dioxane	100, 12	**5a** (86)

Table 2 Pt-Catalyzed Cyclizations of Enynals **4**[10]



Entry	Substrates	Temp (°C), time (h)	Products	Yields (%)
1	**4b**	100, 2	**5b**	78
2	**4c**	100, 24	**5c**	72
3	**4d**	100, 4	**5d**	65
4	**4e**	100, 4	**5e**	77
5	**4f**	120, 15	**7f**	66
6	**4g**	100, 2	**5g**	80
7	**4h**	100, 2	**5h**	86
8	**4i**	100, 15	**5i**	64
9	**4j**	100, 1	**5j**	–
10	**4k**	100, 24	**5k**	–

characterization (entries 1 and 2). AuCl and $AuCl(PPh_3)$ also afforded the same dimeric product (entries 3 and 4). Pt(+2) is isoelectronic with Au(+3). Both $PtCl_2$ and $PtCl_2(PPh_3)_2$ catalyzed cycloisomerization of **4a** to **5a** as the major product along with **6a** (entries 5 and 6).[8] The present reaction in DCE was a little better in terms of the combined yield (82%) of **5a** and **6a**, but DMF as solvent did not work (entries 7 and 8). It is noteworthy that the

product **6a** could be formed with a trace of water present in the reaction solvents. 1,4-Dioxane turned out to be the best among the solvents we tested, where ^{1}H NMR of the crude reaction mixture indicated the exclusive formation of **5a** (entry 8). Structure of the product **5a** was fully characterized by 1D and 2D NMR studies. ^{1}H NMR, ^{13}C NMR, DEPT, COSY, and HMQC spectra of **5a** revealed the proposed structure. The proton connections of **5a** were further confirmed by 1D TOCSY data. HMBC data showed the overall skeleton by long-range coupling and NOE studies confirmed its relative stereochemistry based on the proximity among protons.[9] With this initial success, we examined the scope of this reaction toward various enynals (Table 2, Figure 2). Overall, the present cyclizations turned out to be quite general as long as the structural blocking was not severe. Five- and seven-membered enynals **4b**, **4c**, and **4d** under our conditions afforded **5b**, **5c**, and **5d** in 78%, 72% and 65% yields, respectively. As the ring size increased from five to seven, the reactions required longer time to complete. The enynal **4c** with a methyl substituent on the olefinic position required much longer reaction time but afforded the expected product **5c** in 72% yield.

The substrate **4e**, a homologue of **4b**, was an important substrate since it afforded a different type of ring skeleton. The reaction proceeded well to give [5,7,6]-carbocycle **5e** in 77% yield. Sterically bulky substrate **4f**, however, underwent cyclization in a different mode, via [4+2], to afford the [6,6,6]-tricyclic product **7f** in 66% yield after deprotection of the TBS group. Nitrogen-tethered substrates **4g**, **4h**, and **4i** were converted more readily in the same way. Six- and five-membered enynals **4g** and **4h** gave the corresponding [6,7,5]- and [5,7,5]-tricycles **5g**

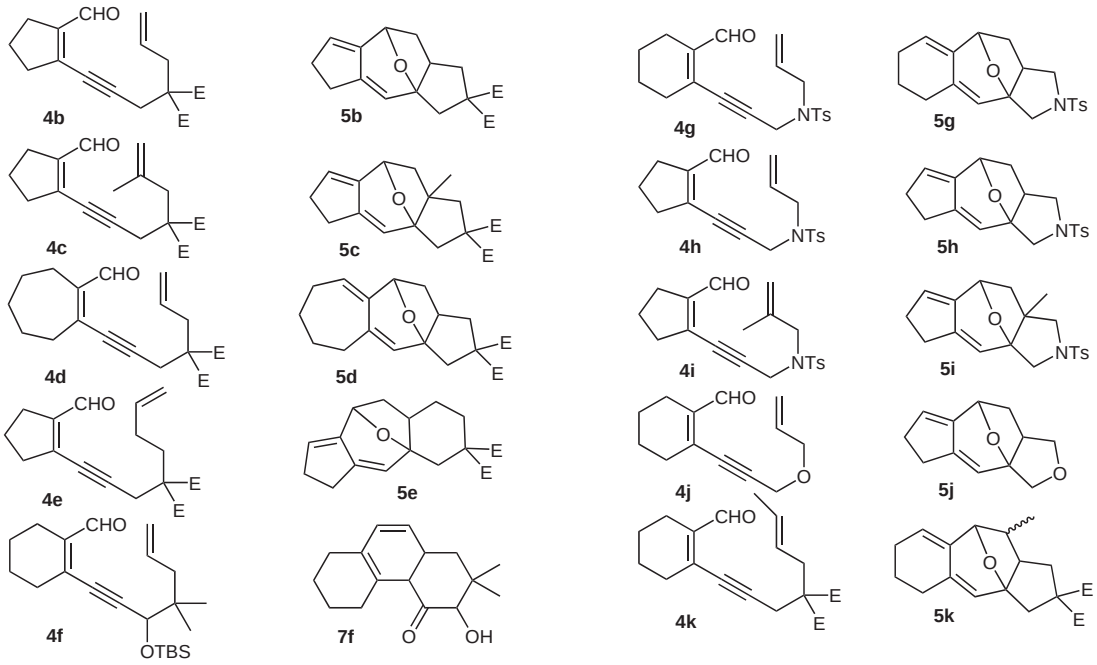
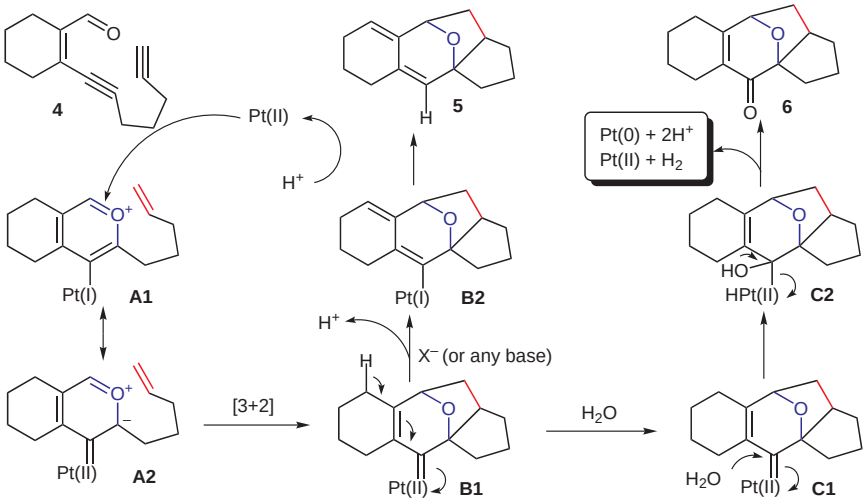


Figure 2



Scheme 3

and **5h** in 80% and 86% yields, respectively. The methyl substituent on the olefinic position of **4i** again did not affect the present reaction leading to **5i**. Enynals with an oxygen linker (**4j**) and an internal olefin (**4j**), unfortunately, did not proceed to the corresponding products. It is noteworthy that the key skeletons of [m,7,n]-tricycles fused with an oxygen bridge are found in many biologically active natural products such as barbatusol, pisiterin, faveline, and xochitlone;[11] therefore this study would have a high potential in synthetic organic chemistry.

Mechanistically, the proposed intermediate **A1** is stabilized by a resonance form **A2** (Scheme 3). The intermediate **A2** would undergo [3+2] cycloaddition to platinum-carbene **B1**. Any basic species could deprotonate from **B1** to form **B2** followed by protolysis to give the product **5**. In the presence of water, however, **B1** is expected to form **C2**, which would be further transformed to **6** with releasing either Pt(II)-H_2 or Pt(0)-$2H^+$. Formation of **7f** can be understood via the intramolecular [4+2] cycloaddition of **A1** followed by the base-promoted fragmentation.[4a,5a]

In conclusion, conjugated enynals **4** anchored to cycloalkenes were successfully cyclized to the corresponding fused tetracyclic compounds **5**, which would be valuable skeletons in many complex natural products. This transformation is highly selective, atom-economical, and an environmentally benign technique. Synthetic applications to natural products and further exploration by using other transition metal catalysts are currently underway.

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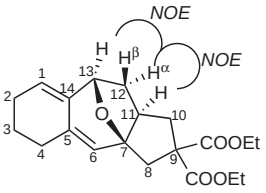
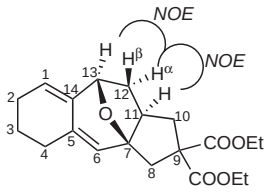
(9) The structure of product **5a** was fully characterized by 1D and 2D NMR studies. ^{1}H NMR, ^{13}C NMR, DEPT, COSY, and HMQC spectra of **5a** revealed the proposed structure. The proton connections of **5a** were further confirmed by 1D TOCSY data. HMBC data showed the overall skeleton by long-range coupling and NOE studies confirmed its relative stereochemistry based on the proximity of H^α at C-12 with both H-11 and H-13 as shown in Table 3.

Table 3



C#	δ ^{1}H NMR, COSY, TOCSY	δ ^{13}C NMR, DEPT, HMQC	HMBC (H → C#)
1	5.49 (td, *J* = 1.6, 4.0 Hz)	121.53 (CH)	2, 13, 14
2	2.07 (m, 2 H)	25.31 (CH_2)	1, 3, 4
3	1.70 (m, 1 H), 1.56 (m, 1 H)	22.76 (CH_2)	4, 2, 1, 5
4	2.24 (m, 2 H)	29.16 (CH_2)	2, 5, 6, 14
5		133.06	
6	5.72 (s)	127.12 (CH)	11, 7, 5, 4
7		90.82	
8	2.66 (d, *J* = 14.4 Hz), 2.51(d, *J* = 14.4 Hz)	42.14 (CH_2)	9, 6, 7, COO^-
9		62.77	

Table 3 (continued)



C#	δ ^{1}H NMR, COSY, TOCSY	δ ^{13}C NMR, DEPT, HMQC	HMBC (H → C#)
10	2.31 (dd, *J* = 7.6, 13.6 Hz), 2.28 (dd, *J* = 4.4, 13.6 Hz)	41.09 (CH_2)	8, 9, 11, COO^-
11	2.67 (ddd, *J* = 4.4, 7.2, 8.8 Hz)	52.59 (CH)	7, 10, 12
12	2.13 (ddd, *J* = 3.4, 7.2, 12.4 Hz), 1.89 (ddd, *J* = 0.8, 8.8, 12.4 Hz)	40.82 (CH_2)	14
13	4.70 (d, *J* = 7.6 Hz)	81.18 (CH)	11, 7, 1, 5
14		137.79	

(10) **General Experimental Procedure for Cyclization**: In a new 5 mL test tube, enynals **4a–i** (0.3 mmol), $PtCl_2(PPh_3)_2$ (5 mol%), and anhyd 1,4-dioxane (0.5 mL) were charged at 0 °C and the reaction mixture was kept under an argon atmosphere. The resulting mixture was stirred for 1–24 h in a preheated oil-bath (100 °C) with periodic monitoring of the reaction (TLC). Upon completion, the solvent was removed under vacuum and the crude product was subjected to flash column chromatography to afford the pure products **5a–e** and **5g–i**. In the case of substrate **4f**, the reaction mixture was cooled to 0 °C and treated with a 1.0 M TBAF solution in THF (1.0 mmol). Extractive work-up and flash chromatography gave the desilylated **7f** in 66% yield.

5a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.72 (s, 1 H), 5.49 (td, *J* = 1.6, 4.0 Hz, 1 H), 4.70 (d, *J* = 7.6 Hz, 1 H), 4.09–4.25 (m, 4 H), 2.67 (ddd, *J* = 4.4, 7.2, 8.8 Hz, 1 H), 2.66 (d, *J* = 14.4 Hz, 1 H), 2.51 (d, *J* = 14.4 Hz, 1 H), 2.31 (dd, *J* = 7.6, 13.6 Hz, 1 H), 2.28 (dd, *J* = 4.4, 13.6 Hz, 1 H), 2.24 (m, 2 H), 2.13 (ddd, *J* = 3.4, 7.2, 12.4 Hz, 1 H), 2.07 (m, 2 H), 1.89 (ddd, *J* = 0.8, 8.8, 12.4 Hz, 1 H), 1.70 (m, 1 H), 1.56 (m, 1 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.27, 171.15, 137.79, 133.06, 127.12, 121.53, 90.82, 81.18, 62.77, 61.57, 61.35, 52.59, 42.14, 41.09, 40.82, 29.16, 25.31, 22.76, 14.03, 14.00. IR (NaCl): 1739, 1673, 1598 cm^{-1}. HRMS: *m*/*z* calcd for $C_{20}H_{26}NaO_5$: 369.1678; found: 369.1683.

6a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.52 (d, *J* = 6.4 Hz, 1 H), 4.13–4.27 (m, 4 H), 3.15 (d, *J* = 14.4 Hz, 1 H), 2.59 (m, 1 H), 2.56 (d, *J* = 14.4 Hz, 1 H), 2.43 (dd, *J* = 4.8, 13.6 Hz, 1 H), 2.38 (dd, *J* = 9.6, 13.6 Hz, 1 H), 2.17–2.31 (m, 2 H), 2.14 (ddd, *J* = 5.2, 6.8, 12.4 Hz, 1 H), 2.02–2.11 (m, 2 H), 1.99 (dd, *J* = 9.2, 12.4 Hz, 1 H), 1.67–1.81 (m, 2 H), 1.40–1.55 (m, 2 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.06, 171.37, 171.25, 159.49, 129.00, 96.80, 80.08, 62.42, 61.94, 61.73, 44.92, 39.49, 37.36, 36.93, 26.97, 21.81, 21.72, 21.03, 14.28, 14.22. IR (NaCl): 1739, 1678, 1636 cm^{-1}. HRMS: *m*/*z* calcd for $C_{20}H_{26}NaO_6$: 385.1627; found: 385.1625.

5b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73 (d, *J* = 1.2 Hz, 1 H), 5.63 (d, *J* = 2.0 Hz, 1 H), 4.99 (d, *J* = 8.4 Hz, 1 H), 4.10–4.26 (m, 4 H), 2.70 (d, *J* = 14.0 Hz, 1 H), 2.68 (ddd, *J* = 4.4, 7.2, 8.8 Hz, 1 H), 2.49 (d, *J* = 14.0 Hz, 1 H), 2.46 (m, 2 H), 2.44 (m, 2 H), 2.33 (dd, *J* = 7.2, 13.4 Hz, 1 H), 2.26 (dd, *J* = 9.2, 13.4 Hz, 1 H), 2.16 (ddd, *J* = 3.6, 7.2, 12.0 Hz, 1 H), 1.95 (ddd, *J* = 0.8, 8.8, 12.0 Hz, 1 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.38, 171.20, 145.59, 144.45, 126.36, 120.74, 90.23, 80.15, 62.39, 61.56, 61.33, 52.37, 42.03, 41.08, 40.98, 31.36, 26.39, 14.02, 14.00. IR (NaCl): 1741, 1670, 1593 cm^{-1}. HRMS: *m*/*z* calcd for $C_{19}H_{24}NaO_5$: 355.1521; found: 355.1517.

5c: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.62 (d, *J* = 2.0 Hz, 1 H), 5.54 (d, *J* = 1.2 Hz, 1 H), 4.84 (d, *J* = 7.2 Hz, 1 H), 4.10–4.28 (m, 4 H), 2.82 (dd, *J* = 10.8, 13.6 Hz, 2 H), 2.45–2.55 (m, 6 H), 1.97 (d, *J* = 14.0 Hz, 1 H), 1.55 (dd, *J* = 1.4, 12.2 Hz, 1 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.09 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.54, 171.56, 146.59, 144.99, 126.22, 117.86, 91.62, 74.80, 61.57, 61.35, 59.97, 57.70, 49.49, 49.16, 40.76, 31.31, 26.42, 25.94, 13.98 (2 × C). IR (NaCl): 1740, 1675, 1595 cm^{-1}. HRMS: *m*/*z* calcd for $C_{20}H_{26}NaO_5$: 369.1678; found: 369.1674.

5d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.80 (s, 1 H), 5.48 (dd, *J* = 5.2, 6.0 Hz, 1 H), 4.66 (d, *J* = 7.2 Hz, 1 H), 4.10–4.26 (m, 4 H), 2.65 (d, *J* = 14.4 Hz, 1 H), 2.64 (ddd, *J* = 3.0, 8.4, 16.4 Hz, 1 H), 2.49 (d, *J* = 14.4 Hz, 1 H), 2.35 (m, 2 H), 2.17–2.31 (m, 4 H), 2.10 (ddd, *J* = 3.2, 7.6, 12.4 Hz, 1 H), 1.85 (ddd, *J* = 0.8, 8.4, 12.4 Hz, 1 H), 1.61–1.75 (m, 4 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.30, 171.16, 139.96, 137.25, 130.01, 125.71, 90.27, 83.11, 62.46, 61.57, 61.35, 52.46, 41.65, 40.68, 40.52, 34.16, 27.62, 26.46, 25.89, 14.02, 14.00. IR (NaCl): 1731, 1448 cm^{-1}. HRMS: *m*/*z* calcd for $C_{21}H_{28}NaO_5$: 383.1834; found: 383.1833.

5e: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.58 (s, 1 H), 5.42 (dd, *J* = 0.8, 2.0 Hz, 1 H), 4.85 (dd, *J* = 4.4, 5.6 Hz, 1 H), 4.30 (dq, *J* = 7.2, 12.0 Hz, 1 H), 4.19 (dq, *J* = 7.2, 14.4 Hz, 1 H), 4.15 (dq, *J* = 7.2, 14.4 Hz, 1 H), 4.08 (dq, *J* = 7.2, 12.0 Hz, 1 H), 2.78 (dd, *J* = 2.0, 15.2 Hz, 1 H), 2.37–2.53 (m, 4 H), 2.31 (dq, *J* = 1.6, 13.6 Hz, 1 H), 2.21 (d, *J* = 15.2 Hz, 1 H), 2.07 (m, 1 H), 1.80 (m, 2 H), 1.65 (m, 2 H), 1.47 (m, 1 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.81, 170.86, 145.55, 144.20, 124.17, 122.90, 78.65, 72.91, 61.48, 60.96, 51.88, 43.90, 40.08, 36.03, 31.23, 29.46, 28.08, 26.53, 14.00, 13.95. IR (NaCl): 1737, 1670, 1599 cm^{-1}. HRMS: *m*/*z* calcd for $C_{20}H_{26}NaO_5$: 369.1678; found: 369.1680.

7f: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (s, 1 H), 5.43 (d, *J* = 4.4 Hz, 1 H), 4.16 (d, *J* = 5.6 Hz, 1 H), 3.26 (d, *J* = 4.8 Hz, 1 H), 2.75 (dq, *J* = 2.4, 12.0 Hz, 1 H), 2.05–2.34 (m, 7 H), 1.86 (m, 1 H), 1.68–1.77 (m, 2 H), 1.55–1.64 (m, 1 H), 1.22 (s, 3 H), 0.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.13, 134.61, 130.00, 122.96, 121.56, 80.57, 53.80, 44.42, 36.95, 33.12, 32.97, 31.35, 29.48, 26.09, 25.37, 23.01. IR (NaCl): 3465, 1753, 1663 cm^{-1}. HRMS: *m*/*z* calcd for $C_{16}H_{22}NaO_2$: 269.1517; found: 269.1520.

5g: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.57 (s, 1 H), 5.51 (dd, *J* = 0.8, 4.4 Hz, 1 H), 4.65 (d, *J* = 8.8 Hz, 1 H), 3.69 (dd, *J* = 7.6, 8.0 Hz, 1 H), 3.51 (s, 2 H), 3.50 (m, 1 H), 2.70–2.83 (m, 2 H), 2.43 (s, 3 H), 2.23 (m, 2 H), 2.08 (m, 2 H), 1.98 (ddd, *J* = 1.6, 7.2, 12.8 Hz, 1 H), 1.77 (ddd, *J* = 1.2, 8.0, 12.8 Hz, 1 H), 1.68 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.37, 143.21, 142.00, 129.64, 127.62, 123.43, 122.19, 118.67, 89.17, 80.82, 55.14, 54.34, 52.12, 36.89, 28.80, 24.94, 21.55. IR (NaCl): 1598, 1472 cm^{-1}. HRMS: *m*/*z* calcd for $C_{20}H_{23}NNaSO_3S$: 380.1296; found: 380.1294.

5h: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 5.65 (d, *J* = 1.2 Hz, 1 H), 5.59 (dd, *J* = 1.4, 3.2 Hz, 1 H), 4.97 (d, *J* = 6.8 Hz, 1 H), 3.68 (dd, *J* = 7.6, 8.0 Hz, 1 H), 3.50 (ABq, Δδ = 13.2 Hz, *J* = 11.2 Hz,

2 H), 2.79 (ddd, *J* = 2.4, 8.8, 16.4 Hz, 1 H), 2.75 (dd, *J* = 9.2, 16.4 Hz, 1 H), 2.40–2.47 (m, 4 H), 2.43 (s, 3 H), 1.99 (ddd, *J* = 2.0, 7.6, 12.8 Hz, 1 H), 1.82 (ddd, *J* = 1.6, 8.0, 12.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.10, 143.82, 143.47, 133.24, 129.64, 127.66, 127.15, 117.64, 94.45, 88.90, 55.32, 54.60, 52.31, 37.42, 31.36, 26.44, 21.57. IR (NaCl): 1597, 1457 cm^{-1}. HRMS: *m*/*z* calcd for $C_{19}H_{21}NNaSO_3S$: 366.1140; found: 366.1144.

5i: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 5.63 (d, *J* = 2.0 Hz, 1 H), 5.45 (s, 1 H), 4.83 (d, *J* = 6.8 Hz, 1 H), 3.53 (ABq, Δδ = 16.0 Hz, *J* = 12.0 Hz, 2 H), 3.40 (d, *J* = 8.8 Hz, 1 H), 3.06 (d, *J* = 8.8 Hz, 1 H), 2.47 (m, 4 H), 2.42 (s, 3 H), 2.25 (dd, *J* = 7.6, 12.4 Hz, 1 H), 1.42 (dd, *J* = 1.2, 12.8 Hz, 1 H), 1.12 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.95, 144.43, 143.26, 133.66, 129.55, 127.48, 126.72, 115.02, 89.95, 75.18, 60.72, 57.91, 54.20, 43.90, 31.26, 26.49, 21.52, 21.01. IR (NaCl): 1599, 1455 cm^{-1}. HRMS: *m*/*z* calcd for $C_{20}H_{23}NNaSO_3S$: 380.1296; found: 380.1298.

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