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Supporting Information

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Gold Catalysis: Benzylic C-H-activation at room temperature

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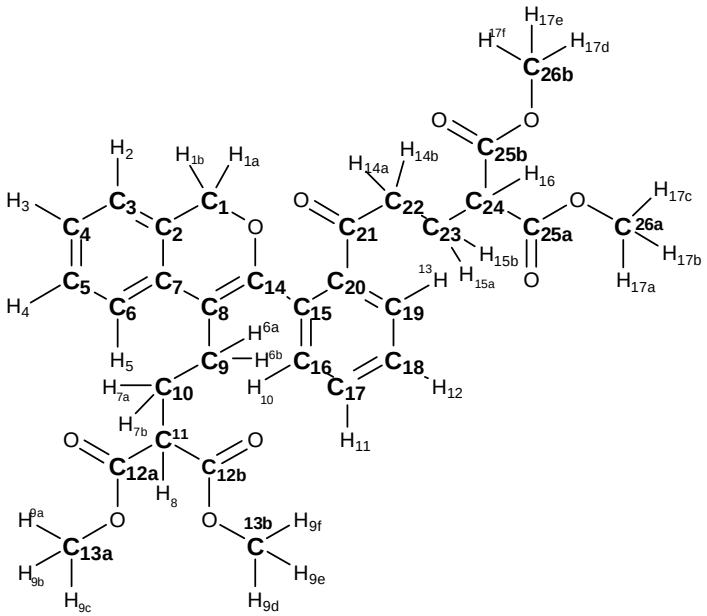
Dimethyl (1*H*-isochromen-3-ylmethyl)malonate (2g), dimethyl [3-(2-{4-[4-methoxy-3-(methoxycarbonyl)-4-oxobutyl]1*H*-isochromen-3-yl}phenyl)-3-oxopropyl]malonate (3g). In a Schlenk tube 104 mg (376 µmol) **1g** was dissolved in 0.3 ml dry acetonitrile under an atmosphere of nitrogen and 5.71 mg (18.8 µmol) $AuCl_3$ (5 mol%) were added. The reaction was monitored by TLC (hexanes/EtOAc). After 24 hours at room temperature 20.9 mg (75.6 µmol, 20%) **2g** as a colourless oil and 81.0 mg (29.4 µmol, 78%) **3g** as a yellow oil were obtained after purification by column chromatography.

2g. R_f (hexanes: ethyl acetate, 2:1) = 0.45. IR (film): $\tilde{\nu}$ = 2953 cm^{-1}, 2843, 1732, 1649, 1435, 1233, 1201, 1152, 1024, 755. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.74 (d, ^3J(H,H)= 7.7 Hz, 2H), 3.69 (s, 6H), 3.79 (t, ^3J(H,H)= 7.5 Hz, 1H), 4.99 (s, 2H), 5.78 (s, 1H), 6.94-7.21 (m, 4H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 34.4 (t), 51.5 (d), 53.8 (q, 2C), 70.1 (t), 104.4 (d), 124.2 (d), 125.4 (d), 127.9 (d) 129.1 (s), 129.8 (d), 132.8 (s), 156.0 (s), 170.7(s, 2C). MS (EI, 70 eV): *m/z* (%): 276 (45) [M^+], 245 (8), 216 (14), 145 (18), 144 (100), 129 (12), 77 (9). HRMS (EI, 70eV): $C_{15}H_{16}O_5$; calcd. 276.0998; found 276.0997.

3g. R_f (hexanes: ethyl acetate, 2:1) = 0.20. IR (film): $\tilde{\nu}$ = 2953 cm^{-1}, 1729, 1694, 1434, 1198, 1102, 761, 604. ^{1}H NMR (CD_3CN, 500 MHz): δ = 1.91 ("q"*, ^3J(H,H)= 7.3 Hz, 2H), 2.15 (q, ^3J(H,H)= 7.5 Hz, 2H), 2.51 ("t"*, ^3J(H,H)= 7.0 Hz, 2H), 2.95 (t, ^3J(H,H)= 7.5 Hz, 2H), 3.45 (t, ^3J(H,H)= 7.4 Hz, 1H), 3.47 (s, 6H), 3.53 (t, ^3J(H,H)= 7.4 Hz, 1H), 3.68 (s, 6H), 5.00 (s, 2H), 7.15-7.68 (m, 8 H). ^{13}C NMR ($CDCl_3$, 63.9 MHz): δ = 24.1 (t), 24.9 (t), 29.0 (t), 39.4 (t), 51.2 (d), 51.4 (d), 52.9 (q, 2C), 53.1 (q, 2C), 70.2 (t), 114.0 (s), 125.3 (d), 123.9 (d), 127.9 (d), 128.7 (d), 129.1 (d), 130.2 (d), 130.6 (s), 131.6 (d), 132.3 (d), 132.7 (s), 134.3 (s), 141.8 (s), 152.5 (s), 170.6 (s, 2C), 170.7 (s, 2C), 205.0 (s). MS (EI, 70 eV): *m/z* (%): 552 (100) [M^+], 393 (60), 261 (50), 159 (80), 145 (70), 113 (35), 31 (90). $C_{30}H_{32}O_{10}$ (552.56): calcd. C 65.31, H 5.84; found C 65.58, H 5.78.

*:signal of higher order. No exact analysis possible.

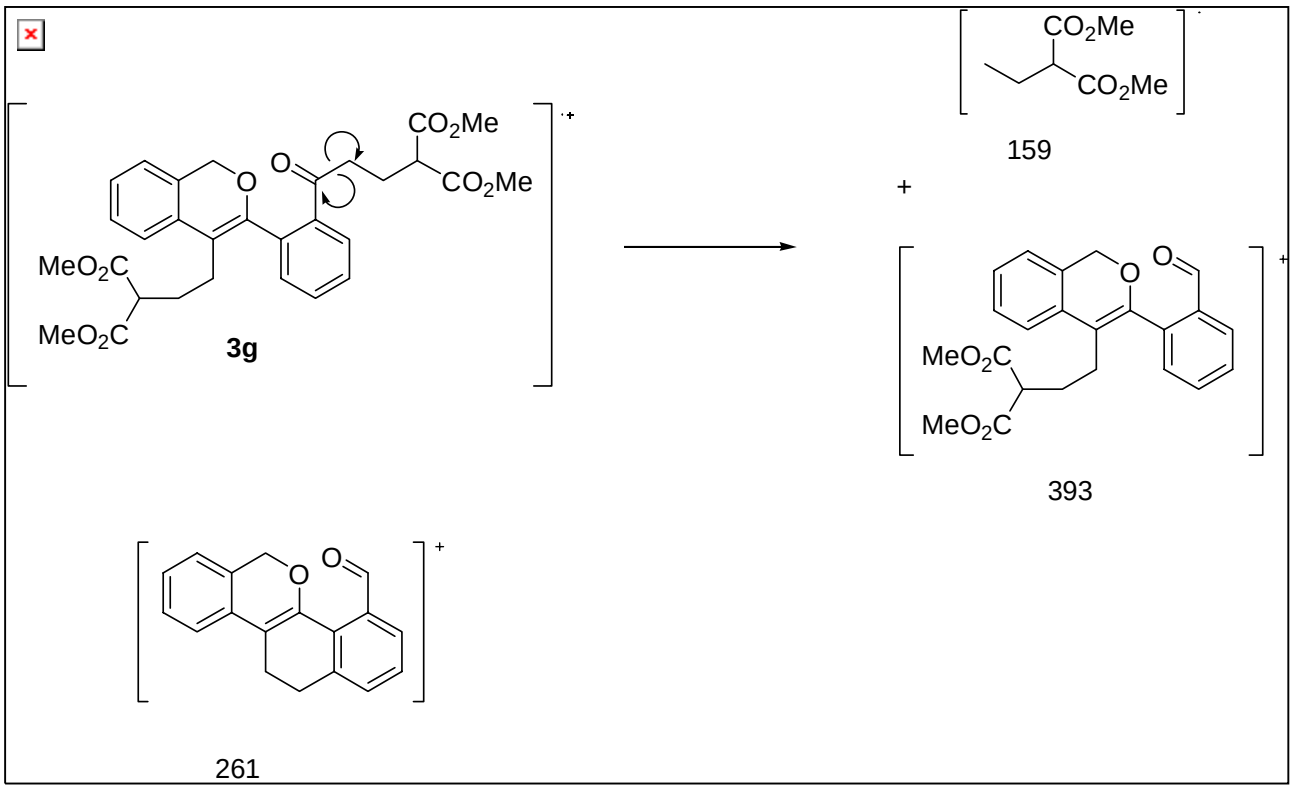


Scheme 8. Numbering of the positions in **3g**.

Mass spectrometry showed the product **3g** to be a dimer of two substrate molecules with the molcular weight of 552.2 Da, which refers to the sum formula $C_{30}H_{32}O_{10}$ and 15 double-bond equivalents. In the aromatic region the proton NMR shows two independent spin systems of a 1,2-disubstituted benzene ring. In the aliphatic region two independent 3,3-bis(carbonylmethoxy)propanyl chains could be observed. At 5 ppm only one singulett signal for two protons is found, which is similar to the correspondig signal of the "monomer" isochromene **2g** and to the products described in the literature [C. Castro, R. Havlin, V. Honwad, A. Malte, S. Moje, *J. Am. Chem. Soc.* **1969**, *91*, 6464-6470. A. Padwa, K. Krumpe, M. Weingarten, *J. Org. Chem.* **1995**, *60*, 5595-5603.]. This shows that only one benzylic position is remaining in the dimer **3g**. Via H,H-COSY the tripletts for $H^{6a,b}$, $H^{14a,b}$, the quartetts for $H^{7a,b}$, $H^{15a,b}$ and the tripletts for $H^{7a,b}$, $H^{15a,b}$ could be assigned. In each malonyl ester fragment, the methoxy groups show only one signal in the ^{1}H NMR. In the ^{13}C NMR only two ester carbonyl and two OCH_3-signals are observed. This shows that the molecule **3g** has no stereogenic center and the positions C_9 and C_{22} are completely hydrogenated. The product **3g** has to be a planar molecule. In the sp^3-region the ^{13}C NMR shows singnals of two OCH_3 groups and two independent propanyl chain structures. In the sp^2-region eight C-H-signals and six signals for quaternary carbon atoms are observed. The signals at 152 ppm and 114 ppm belong to the isochromene ring, which is substituted in the position 8. The OCH_2-signal is found at 70.2 ppm. One cabonyl signal is found at 205 ppm. The connection between the propanyl-chains and the ring system was determined, using an HMBC-spectrum. The carbonyl carbon at 205 ppm shows three

crosspeaks. The crosspeaks connect the C=O signal with the *ortho*-arene dublett at deeper field, the α-CH_2 at 2.95 ppm and the β-CH_2 at 2.15 ppm of one of the propanyl chains. The second valence at the second arene ring has to be an acyl group. This explains why the signals for the α and the β-methylen signals of the 3,3-bis(carbonylmethoxy)propyl chains compared with the similar signals of 3,3-bis(carbonylmethoxy)propyl chain, connected to the isochromene ring, is shifted to to deeper field ($\Delta\delta$ 0.44 ppm for the α-methylene signals and $\Delta\delta$ 0.24 ppm for the β-methylene signals). Via HMBC C-2 and C-3 could be identified. With this information, one arene ring could be assigned to the isochromene ring. Beyond this, C-9, C-10, C-22 and C-23 could be assigned. Via C,H-COSY the assignment of 9-H, 10-H and 22-H and 23-H are possible. The characteristic sequence of the signals in the proton NMR support this assumption. The ^2J-crosspeak to the H-atoms at C-9 shows that one propyl chain has to be connected to C-8. With the crosspeaks of C-20 to 16-H, 18-H and 19-H in the HMBC allowed an assignment of the second propyl chain to an aren ring. The position of the carbonyl function could also be verified by HMBC. Because of the sum formula and one missing unsaturation besides the two arene rings and the carbonyl groups, another ring has to be in the molecule. As the position of the two propyl chains and the arene rings are determined, the connection between the two molecule parts has to be between C-14 and C-15. These C-atoms are assigned to their signals via HMBC.

The product **3g** is formed of two molecule parts. These two parts are former substrate molecules but with a striking change of functionalities. The former alkyne-C turned to a keton (C-21). The corresponding C-atom (C-8) of the other substrate forms an unsaturated bridge to the former benzylic position of the molecule part, carrying the keton. The heterocycle with a condensed benzene ring is also found in the monomer. But in the dimer, only one heterocycle is found. The propyl chain is also found in the monomer, but not connected to the C-8 corresponding C-atom but connected to C-14. The mass spectrum shows some characteristic singals and serves as an independent method to confirm the structure determination. The signals at 159 (80%) and 393 (58%) show the existence of the 3,3-bis(carbonylmethoxy)propayl chains. The scaffold of the molecule could be assigned to the signal 261 (40%).



Scheme 9. Fragmentation of **3g** under EI MS conditions.

Table 3: Assignment of the H-atoms.

H-atoms	δ (ppm)	multiplicity	coupling (Hz)
1-H	5.00	s	-
3-H	7.14	df	^3J(3-H, 4-H) = 7.4
4-H	7.24	td	^3J(4-H, 3-H) = ^3J(4-H, 5 H) = 7.3
			^4J(4-H, 6-H) = 1.4
5-H	7.34	td	^3J(5-H, 4-H) = ^3J(5-H, 6-H) = 7.5
			^4J(5-H, 3-H) = 1.5
6-H	7.28	dd	^3J(6-H, 5-H) = 7.8
			^4J(6-H, 4-H) = 1.5
9-H_2	2.51	"t"*	^3J = 7.0
10-H_2	1.91	"q"*	^3J = 7.3
11-H	3.53	t	^3J(11-H, 10-H_2) = 7.4
13a-H_3	3.47	s	-
13b-H_3	3.47	s	-
16-H	7.40	m**	-
17-H	7.53	m**	-
18-H	7.50	m**	-
19-H	7.67	m**	-
22-H_2	2.95	t	^3J(22-H_2, 23-H_2) = 7.5
23-H_2	2.15	q	^3J(23-H_2, 22-H_2) = ^3J(23-H_2, 24-H)= 7.5
24-H	3.45	t	^3J(24-H, 23- H_2) = 7.4
26a-H_3	3.68	s	-
26b-H_3	3.68	s	-

*: signal of higher order. Exact analysis not possible.

**: full symmetric spectrum AMNX; chemical shift of the middle of the multipletts is given.

Table 4: Assignment of the C-atoms.

C-atoms	δ (ppm)	multiplicity (DEPT)	assignment via
C-1	70.20	CH_2	^{13}C / C,H-COSY / HMBC
C-2	130.58	C	HMBC
C-3	125.21	CH	^{13}C / C,H-COSY / HMBC
C-4	127.86	CH	^{13}C / C,H-COSY / HMBC
C-5	129.11	CH	^{13}C / C,H-COSY / HMBC
C-6	122.08	CH	^{13}C / C,H-COSY / HMBC
C-7	132.72	C	HMBC
C-8	114.00	C	HMBC
C-9	24.92	CH_2	^{13}C / C,H-COSY / HMBC
C-10	28.96	CH_2	^{13}C / C,H-COSY / HMBC
C-11	51.16	CH	^{13}C / C,H-COSY / HMBC
C-12a, b	170.73	C	^{13}C/ HMBC
C-13a, b	52.87	CH_3	^{13}C / C,H-COSY / HMBC
C-14	152.53	C	HMBC
C-15	134.26	C	HMBC
C-16	132.28	CH	^{13}C / C,H-COSY / HMBC
C-17	131.64*	CH	^{13}C / C,H-COSY / HMBC
C-18	130.19*	CH	^{13}C / C,H-COSY / HMBC
C-19	128.72	CH	^{13}C / C,H-COSY / HMBC
C-20	141.84	C	HMBC
C-21	205.00	C	HMBC
C-22	39.37	CH_2	^{13}C / C,H-COSY / HMBC
C-23	24.07	CH_2	^{13}C / C,H-COSY / HMBC
C-24	51.37	CH	^{13}C / C,H-COSY / HMBC
C-25a, b	170.55	C	^{13}C / HMBC
C-26a, b	53.12	CH_3	^{13}C / C,H-COSY / HMBC

*: here the assignment could be the other way around, too.

Table 5: HMBC crosspeaks.

C-atoms	HMBC-crosspeak	
	via ^2J	via ^3J
C-1	-	3-H
C-2	-	4-H / 6-H
C-3	-	5-H / 6-H
C-4	-	-
C-5	-	3-H
C-6	5-H (w)	4-H
C-7	-	3-H / 5-H
C-8	-	1-H (w) / 6-H / 10-H_2
C-9	10-H_2 (w)	10-H_2
C-10	9-H_2/ 11-H	-
C-11	10-H_2	9-H_2
C-12a, b	-	13a, b-H / 10-H_2
C-13a, b	-	-
C-14	-	1-H / 9-H / 16-H
C-15	16-H (w)	17-H / 19-H (w)
C-16	17-H	18-H
C-17	-	-
C-18	-	-
C-19	18-H	17-H
C-20	19-H (w)	16-H / 18-H
C-21	22-H_2	19-H
C-22	23-H_2	24-H (w)
C-23	22-H_2/ 24-H	-
C-24	23-H_2	22-H_2
C-25a, b	-	23-H_2 / 26a, b-H
C-26a, b	-	-

The INADEQUATE spectrum then again proofs the assignment shown above, expecially the connectivity in the array of seven quaternary carbon atoms in the center of the molecule and its connection to the sourrinding methine and methylene groups is conveniently shown:
cross peak from **C2** to C3, from **C2** to C1 and from **C2** to C7
cross peak from **C7** to C6 and from **C7** to C8
cross peak from **C8** to C9 and from **C8** to C14
cross peak from **C14** to C15
cross peak from **C15** to C16 and from **C15** to C20
cross peak from **C20** to C19 and from **C20** to C21
cross peak from **C21** to C22