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Ring-Opening Reaction of Vinylidenecyclopropanediesters Catalyzed by $Re_2(CO)_{10}$ or $Yb(OTf)_3$

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Ring-opening reaction of vinylidenecyclopropanediesters catalyzed by $Re_2(CO)_{10}$ or $Yb(OTf)_3$ afforded 2*H*-pyran-2-one derivatives or α,β-unsaturated ketones in moderate to good yields through a highly regioselective carbon–carbon bond cleavage pathway. The substituents at the cyclopropane mainly determine the regioselectivity of the carbon–carbon bond cleavage, providing different products of tandem ring-opening and rearrangement reactions.

Introduction

Vinylidenecyclopropanes (VDCPs),[1] containing an allene moiety and a connected cyclopropane ring in their structural motif, are one of the most fascinating organic compounds in the chemistry of highly strained small rings. It is already known that these highly strained cyclopropanes are easily available, thermally stable, and yet reactive substances, which can easily undergo a variety of novel intramolecular rearrangements or intermolecular reactions with many electrophiles either upon heating and photoirradiation[2] or catalyzed by a variety of Lewis or Brønsted acids.[3–5] It is quite clear that the release of the highly strained energy associated with the ring opening of a cyclopropane moiety in an organic molecule can lead to novel tandem transformations, and the reaction pathway highly depends on the electronic properties of the substituents on the cyclopropane ring as well as the functional groups connected to the cyclopropane.[6,7] We anticipated that the geminal installation of two electron-withdrawing groups (EWGs) at the cyclopropane ring connected with an allene moiety might further promote carbon–carbon bond cleavage of cyclopropane, leading to a highly regioselective ring-opening reaction.[8] In our previous work on the reactivity of VDCP-diesters, we found that they could undergo interesting cycloaddition reactions with 1,3-dipoles to afford the corresponding cycloadducts in good yields under mild conditions.[9,10] These results have stimulated us to further explore other novel reactions of VDCP-diesters in the presence of Lewis acids or transition metals. During our ongoing investigations, we realized that the transition metal rhenium has very special catalytic properties. Most rhenium complexes are stable with different oxidation states and are moisture- and air-tolerant, resulting in their diverse application in catalytic organic reactions as homogeneous catalysts.[11] Herein, we wish to report an interesting intramolecular ring-opening reaction of VDCP-diesters through a regioselective carbon–carbon bond cleavage catalyzed by $Re_2(CO)_{10}$ or $Yb(OTf)_3$ to produce the corresponding 2*H*-pyran-2-one derivatives or α,β-unsaturated ketones, substantially enriching the chemistry of highly strained small rings as well as rhenium-catalyzed reactions.

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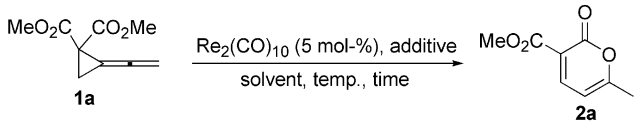
Results and Discussion

Initial experiments were carried out by using VDCP-diester **1a** as the substrate in the presence of a series of catalysts at 110 °C in toluene to determine the most effective catalyst. We found that the reaction was complete within 3 d, giving 2*H*-pyran-2-one **2a** in 40% yield in the presence of $Re_2(CO)_{10}$ (5 mol-%) (Table 1, Entry 1). Adding $LiOH·H_2O$ (1.2 equiv.) to assist the hydrolysis of the ester groups of **1a** afforded complex product mixtures (Table 1, Entry 2). Other commonly used transition metals such as $Ru_3(CO)_{12}$ and $Ru(PPh_3)_2Cp^*Cl$ as well as Lewis acids such as $PtCl_2$, Ph_3PAu^I, $Yb(OTf)_3$, $In(OTf)_3$, $Sc(OTf)_3$, $BF_3·OEt_2$, $Fe(OTf)_2·2CH_3CN$, $Cu(OTf)_2$, $Zn(OTf)_2$ and the Brønsted acid trifluoromethanesulfonic acid TfOH were not effective catalysts in this reaction, leading to either complex product mixtures or no reaction. On the basis of catalyst screening, it was found that only $Re_2(CO)_{10}$ was a suitable catalyst in this reaction and this is the first example of a $Re_2(CO)_{10}$-catalyzed intramolecular cyclization of VDCP-diesters as far as we know. The carbonyl complex $Ru_3(CO)_{12}$ has no catalytic activity for this reaction.

We next examined solvent effects of this reaction by using $Re_2(CO)_{10}$ as the catalyst, and the results of these experiments are summarized in Table 1. Examination of the

Table 1. Optimization of the reaction conditions.



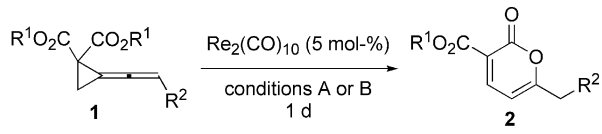
Entry[a]	Additive	Solvent	Temperature [°C]	Time [d]	Yield [%][b]
1	–	toluene	110	3	40
2	$LiOH·H_2O$ (1.2 equiv.)	toluene	110	3	complex
3	–	xylene	130	3	trace
4	–	DMF	110	3	nr
5	–	dioxane	110	3	trace
6	–	TCE	110	3	36
7	–	chlorobenzene	130	1	45
8	H_2O (10 equiv.)	chlorobenzene	130	1	64
9	H_2O (20 equiv.)	chlorobenzene	130	1	70
10	H_2O (10 equiv.)	*ortho*-dichlorobenzene	110	1	78
11	MeOH (10 equiv.)	*ortho*-dichlorobenzene	110	1	56

[a] All reactions were carried out with VDCP-diester **1a** (0.2 mmol), $Re_2(CO)_{10}$ (5 mol-%), and the additives upon heating in the solvent (2.0 mL), and the reaction was monitored by TLC unless otherwise specified. [b] Isolated yield.

reaction temperature indicated that the ring-opening reaction could only take place at >100 °C, perhaps due to the high energy required for carbon–carbon bond cleavage. Screening of several solvents with high boiling points revealed that the use of chlorobenzene afforded **2a** in 45% yield at 130 °C within 1 d, and other solvents such as xylene, *N*,*N*-dimethylformamide (DMF), dioxane, and 1,1,2,2-tetrachloroethane (TCE) were not suitable for this reaction (Table 1, Entries 3–7). In the presence of 10 and 20 equiv. of H_2O, **2a** could be formed in 64 and 70% yield, respectively (Table 1, Entries 8 and 9). These results suggest that the extra proton source can accelerate the reaction, giving the cyclized product in higher yield. Moreover, in *ortho*-dichlorobenzene with the addition of 10 equiv. of H_2O at 110 °C, the reaction proceeded more smoothly, affording **2a** in 78% yield within 1 d (Table 1, Entry 10). The use of MeOH as the proton source gave no improvement (Table 1, Entry 11). Therefore, the best reaction conditions involve the use of chlorobenzene as the solvent at 130 °C with the addition of 20 equiv. of H_2O (conditions A) or the use of *ortho*-dichlorobenzene as the solvent at 110 °C with the addition of 10 equiv. of H_2O (conditions B) both in the presence of $Re_2(CO)_{10}$ (5 mol-%).

With these optimal reaction conditions in hand, we further investigated the scope of this interesting intramolecular cyclization reaction with respect to various VDCP-diesters **1**, and the results are summarized in Table 2. As for VDCP-diesters **1** in which R^2 = H or alkyl, the reactions proceeded smoothly to afford desired products **2** in moderate to good yields under conditions A or B (Table 2, Entries 1–5). In the case of VDCP-diester **1g** in which R^2 = phenyl, we found that this substrate was sensitive to the extra proton source, leading to nucleophilic attack of H_2O at the cyclopropane. The corresponding cyclized product could be obtained in 51 and 46% yield under conditions A and B, respectively, without the addition of H_2O (Table 2, Entry 6).

Table 2. $Re_2(CO)_{10}$-catalyzed intramolecular reactions of VDCP-diesters **1**.[a]



Entry[b]	Substrate	R^1	R^2	Product, Yield [%][c]
1	**1b**	Bn	H	**2b**, 70 (74)
2	**1c**	Me	*n*Pr	**2c**, 68 (70)
3	**1d**	Me	Bn	**2d**, 61 (55)
4	**1e**	Me	*i*Pr	**2e**, 62 (62)
5	**1f**	Me	nC_5H_{11}	**2f**, 70 (73)
6[d]	**1g**	Me	Ph	**2g**, 51 (46)

[a] Conditions A: At 130 °C in chlorobenzene (2.0 mL) with the addition of H_2O (20 equiv.). Conditions B: At 110 °C in *ortho*-dichlorobenzene (2.0 mL) with the addition of H_2O (10 equiv.). [b] All reactions were carried out with VDCP-diester **1** (0.2 mmol) and $Re_2(CO)_{10}$ (5 mol-%) under conditions A or B, and the reaction was monitored by TLC unless otherwise specified. [c] Isolated yield. Yield of the product obtained under conditions B is given in parentheses. [d] The reaction was carried out with VDCP-diester **1g** (0.2 mmol) in the presence of $Re_2(CO)_{10}$ (5 mol-%) in chlorobenzene (2.0 mL) at 130 °C or in *ortho*-dichlorobenzene (2.0 mL) at 110 °C without the addition of H_2O.

The structure of compound **2e** was further established by a single-crystal X-ray diffraction (Figure 1).[12]

To identify the effect of H_2O in the reaction, we carried out an isotopic labeling control experiment (Scheme 1). Under the standard reaction conditions (conditions A), using D_2O to replace H_2O, desired product **2b**-*d* was obtained in 67% yield along with 76%D incorporation, indicating that H_2O did play an important role in this reaction.

As mentioned above, because VDCP-diester **1g** was quite sensitive to H_2O, it was found that it could easily undergo nucleophilic attack by H_2O (20 equiv.) in chlorobenzene at

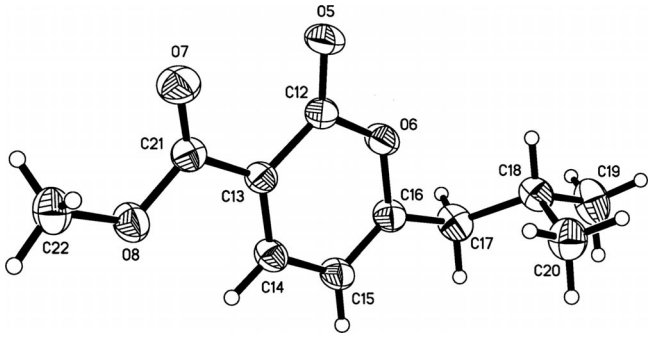
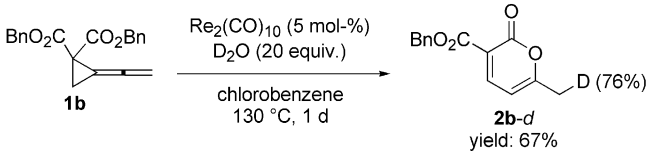
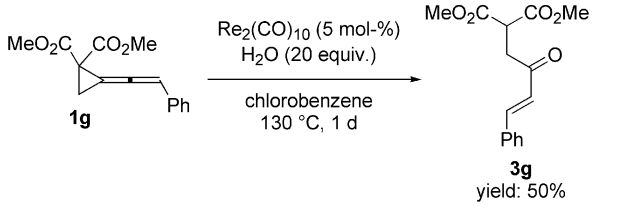


Figure 1. ORTEP drawing of **2e**.



Scheme 1. Isotopic labeling control experiment.

130 °C to give the corresponding α,β-unsaturated ketone **3g** in 50% yield in the presence of $Re_2(CO)_{10}$, disfavoring the formation of 2*H*-pyran-2-one **2g** (Scheme 2). Decreasing the amount of H_2O to 10 equiv. and lowering the reaction temperature to 110 °C produced **3g** in 51% yield (Table 3, Entry 1). the use of VDCP-diesters **1h**–**j** having an aromatic ring at the terminus of the allene moiety gave similar results in the presence of $Re_2(CO)_{10}$ (5 mol-%) and H_2O (10 equiv.) in chlorobenzene at 110 °C, affording **3h**–**j** in 30–46% yield (Table 3, Entries 3, 5, and 7). Similar results were obtained with the addition of 4 Å molecular sieves (MS), suggesting that their use as an additive did not devoid the reaction system of water. Furthermore, we found that by using $Yb(OTf)_3$ (10 mol-%) as the catalyst in this reaction, the corresponding α,β-unsaturated ketones **3g**–**j** could be formed in higher yields in chlorobenzene or toluene (Table 3, Entries 2, 4, 6, and 8).

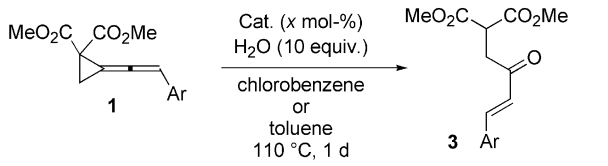


Scheme 2. $Re_2(CO)_{10}$-catalyzed reaction of VDCP-diesters **1g** with H_2O.

In the case of VDCP-diester **1k**, the intramolecular ring-opening reaction took place in a different way, affording products **4k**, **5k**, and **6k** in 86% total yield under the standard conditions, probably because the *i*Pr substituent at the cyclopropane ring activates the C1–C3 bond to make it more sensitive to cleavage than the C1–C2 bond under these reaction conditions (Scheme 3).

The mechanism of this unprecedented reaction has not been unequivocally established, but on the basis of the outcome of the above reaction, plausible mechanisms for the formation of these ring-opening products are tentatively outlined in Schemes 4–6. As for VDCP-diester **1**, in which R^2 = H or alkyl, we believe that the rhenium catalyst can coordinate with the carbonyl group and the allene moiety simultaneously, although the active rhenium species is not clear. Cleavage of the C1–C2 bond takes place to give intermediate **A**, in which the oxygen anion is bonded to the rhenium catalyst, and then intermediate **A** undergoes 1,2-H shift to afford intermediate **B** and its resonance-stabilized intermediate **C** along with the regeneration of the rhenium catalyst. Cyclization of intermediate **C** gives intermediate **D**, which undergoes nucleophilic attack with H_2O to provide intermediates **E** and **F**. Then, elimination of R^1OH affords final product **2** (Scheme 4).

Table 3. Reaction of VDCP-diesters **1** with H_2O.

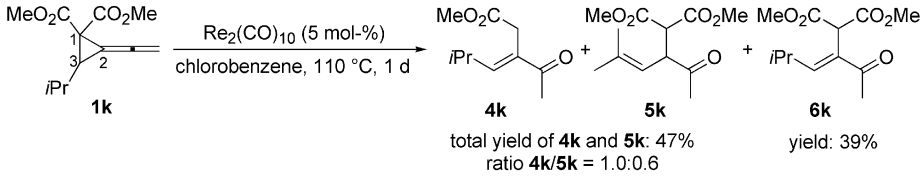


Entry[a]	**1**, Ar	Cat. (*x* mol-%)	**3**	Yield of **3** [%][b]
1	**1g**, Ph	$Re_2(CO)_{10}$ (5)	**3g**	51
2	**1g**, Ph	$Yb(OTf)_3$ (10)	**3g**	88 (92)[c]
3	**1h**, *p*-MeC_6H_4	$Re_2(CO)_{10}$ (5)	**3h**	46
4	**1h**, *p*-MeC_6H_4	$Yb(OTf)_3$ (10)	**3h**	85 (86)[c]
5	**1i**, *p*-ClC_6H_4	$Re_2(CO)_{10}$ (5)	**3i**	30
6	**1i**, *p*-ClC_6H_4	$Yb(OTf)_3$ (10)	**3i**	78 (72)[c]
7	**1j**, *p*-BrC_6H_4	$Re_2(CO)_{10}$ (5)	**3j**	30
8	**1j**, *p*-BrC_6H_4	$Yb(OTf)_3$ (10)	**3j**	81 (85)[c]

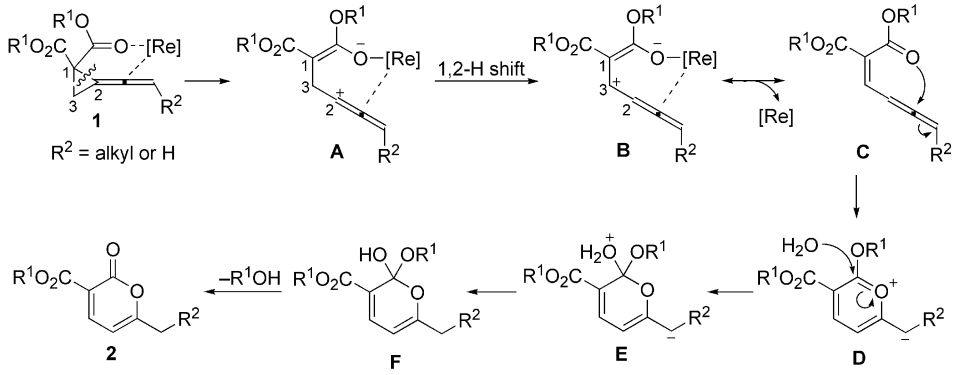
[a] All reactions were carried out with VDCP-diesters **1** (0.2 mmol), the catalyst $Re_2(CO)_{10}$ (5 mol-%) or $Yb(OTf)_3$ (10 mol-%), and H_2O (10 equiv.) in chlorobenzene or toluene (2.0 mL) at 110 °C, and the reaction was monitored by TLC unless otherwise specified. [b] Isolated yield. [c] Yield of the product obtained for the reaction conducted in toluene is given in parentheses.

Cyclopropane has significant π character,[13] providing the kinetic opportunity to initiate the release of strain. In 1,1-cyclopropanediesters, this ring bond can be polarized and further weakened by coordination of a Lewis acid to one or both of the ester moieties.[14] As for VDCP-diester **1** having an aromatic ring at the terminus of the allene moiety, the C–C cyclopropane bond is initially activated by $Yb(OTf)_3$ through coordination with the ester moieties; it can then easily undergo nucleophilic attack by H_2O to give intermediate **G** through C1–C2 bond cleavage, indicating that this vinylidenecyclopropane substrate is more sensitive to H_2O. Intermediate **G** can tautomerize to corresponding product **3** through intermediate **H** (Scheme 5).

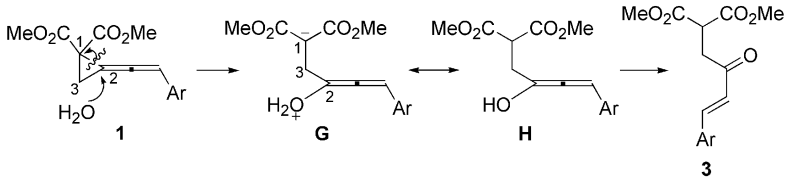
In the case of VDCP-diester **1k** having an *i*Pr group at the cyclopropane ring, its reaction mechanism is partially similar to the cyclopropane ring opening of VDCP-diester **1a** as described in Scheme 4. The carbonyl group and allene moiety coordinate with the rhenium catalyst at the same time, but the ring opening takes place through a different path involving nucleophilic attack of H_2O at the middle carbon atom of the allene moiety along with C1–C3 bond



Scheme 3. $Re_2(CO)_{10}$-catalyzed reaction of VDCP-diester **1k**.



Scheme 4. A plausible reaction mechanism for the formation of 2*H*-pyran-2-one **2**.

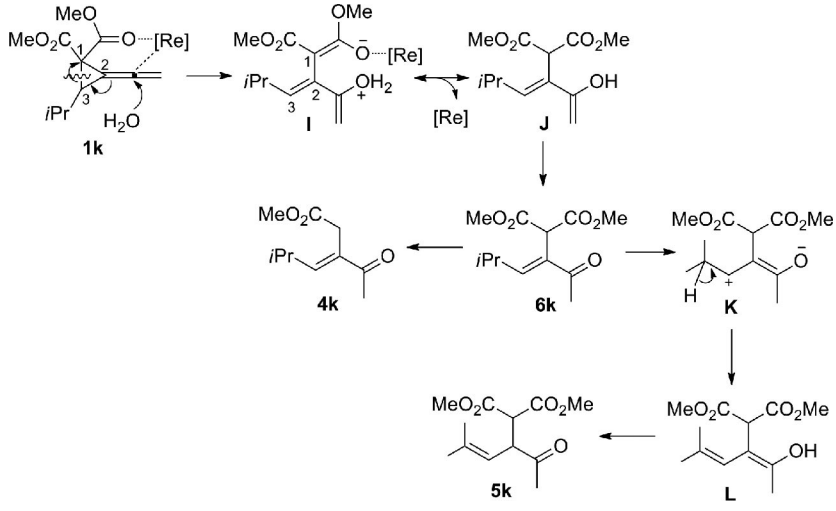


Scheme 5. A plausible reaction mechanism for the formation of α,β-unsaturated ketone **3**.

cleavage to afford intermediate **I**. Intermediate **I** can produce intermediate **J**, leading to corresponding product **6k** along with the regeneration of the rhenium catalyst. Decarboxylation of **6k** under the reaction conditions produces product **4k**. Proton transfer of **6k** can give intermediate **L** via intermediate **K**, which undergoes tautomerization to give product **5k** (Scheme 6).

Conclusions

In summary, we have reported an interesting ring-opening reaction of vinylidenecyclopropanediesters through a highly regioselective carbon–carbon bond cleavage pathway catalyzed by $Re_2(CO)_{10}$ or $Yb(OTf)_3$ to produce 2*H*-pyran-2-one derivatives or α,β-unsaturated ketones in moderate to



Scheme 6. A plausible reaction mechanism for the ring-opening reaction of VDCP-diester **1k**.

good yields. The geminal installation of two EWGs at the cyclopropane ring significantly facilitates C–C bond cleavage, which exclusively takes place at C1–C2, leading to the tandem ring-opening reaction. However, introduction of another substituent at the cyclopropane ring causes exclusive C1–C3 bond cleavage, affording different reaction products. The outcome of the reactions is mainly dependent on the electronic properties of the substituents at the cyclopropane ring as well as at the terminus of allene moiety. Clarification of the reaction mechanism and further application of this chemistry are in progress.

Experimental Section

General Remarks: Melting points were determined with a digital melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. LRMS and HRMS were recorded by the EI method. Employed solvents were dried by standard procedures. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out by using 300–400 mesh silica gel at increased pressure. Because VDCP-diesters and some products are unstable and quite labile, the obtainment of elemental analytic data was difficult and only HRMS data are given.

General Procedure for the Reaction of VDCP-diesters under Standard Reaction Conditions: Under an Ar atmosphere, VDCP-diester **1** (0.2 mmol, 1.0 equiv.), $Re_2(CO)_{10}$ (5 mol-%) or $Yb(OTf)_3$ (10 mol-%), H_2O (10 or 20 equiv.), and chlorobenzene or *ortho*-dichlorobenzene (2.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 110 or 130 °C for 1–3 d and monitored by TLC until the reaction was complete. Then, the reaction mixture was directly applied to a silica gel column to give the corresponding product.

VDCP-diesters **1a**–**d**,[9] **1g**–**k**,[9] and product **3g**[9] are known compounds.

VDCP-Diester 1e: Yield: 29 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.03 (d, J = 6.8 Hz, 6 H, $2CH_3$), 2.40–2.48 (m, 3 H, CH, CH_2), 3.75 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 5.66–5.70 (m, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 19.4, 21.78, 21.83, 28.6, 34.6, 52.5, 52.6, 85.7, 107.7, 167.6, 167.7, 186.9 ppm. IR (NaCl): $\tilde{\nu}$ = 2959, 2870, 1738, 1436, 1313, 1275, 1235, 1193, 1108 cm^{-1}. MS (EI): *m*/*z* (%) = 224 (14) $[M]^+$, 177 (11), 165 (51), 149 (15), 133 (37), 105 (56), 86 (66), 84 (100), 59 (33). HRMS: calcd. for $C_{12}H_{16}O_4$ 224.1049; found 224.1050.

VDCP-Diester 1f: Yield: 34 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.89 (t, J = 6.8 Hz, 3 H, CH_3), 1.29–1.33 (m, 4 H, $2CH_2$), 1.39–1.46 (m, 2 H, CH_2), 2.09–2.14 (m, 2 H, CH_2), 2.42–2.43 (m, 2 H, CH_2), 3.75 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 5.64–5.69 (m, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.8, 19.3, 22.2, 28.0, 28.8, 31.0, 34.5, 52.5, 52.6, 84.6, 100.5, 167.61, 167.66, 188.0 ppm. IR (NaCl): $\tilde{\nu}$ = 2955, 2929, 2858, 1736, 1436, 1276, 1241, 1107 cm^{-1}. MS (EI): *m*/*z* (%) = 252 (2) $[M]^+$, 196 (71), 164 (100), 137 (41), 121 (51), 105 (57), 91 (36), 79 (24), 59 (36), 55 (22). HRMS: calcd. for $C_{14}H_{20}O_4$ 252.1362; found 252.1364.

Compound 2a: Yield: 26 mg, 78%; yellow solid; m.p. 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.34 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 6.16 (dd, J = 7.2, 0.8 Hz, 1 H, CH=), 8.18 (d, J = 7.2 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 20.6, 52.6, 103.7, 113.7, 150.2, 158.3, 164.1, 169.1 ppm. IR (NaCl): $\tilde{\nu}$ = 3083, 2956, 2923, 2852, 1753, 1626, 1562, 1430, 1364, 1266, 1096, 792 cm^{-1}. MS (EI): *m*/*z* (%) = 168 (70) $[M]^+$, 140 (75), 137 (58), 109 (100), 85 (54), 84 (72), 49 (85). HRMS: calcd. for $C_8H_8O_4$ 168.0423; found 168.0425.

Compound 2b: Yield: 36 mg, 74%; yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.32 (s, 3 H, CH_3), 5.33 (s, 2 H, OCH_2), 6.12 (dd, J = 7.2, 0.8 Hz, 1 H, CH =), 7.30–7.39 (m, 3 H, Ar), 7.43–7.45 (m, 2 H, Ar), 8.15 (d, J = 7.2 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 20.6, 67.0, 103,5, 113.6, 128.15, 128.24, 128.5, 135.6, 149.9, 158.1, 163.1, 169.1 ppm. IR (NaCl): $\tilde{\nu}$ = 3064, 3034, 2955, 2926, 1756, 1628, 1556, 1278, 1109, 788, 739, 698 cm^{-1}. MS (EI): *m*/*z* (%) = 244 (6) $[M]^+$, 226 (6), 138 (39), 110 (62), 91 (100), 71 (5), 65 (18), 43 (15). HRMS: calcd. for $C_{14}H_{12}O_4$ 244.0736; found 244.0733.

Compound 2c: Yield: 29 mg, 70%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.94 (t, J = 7.6 Hz, 3 H, CH_3), 1.36–1.41 (m, 2 H, CH_2), 1.64–1.72 (m, 2 H, CH_2), 2.56 (t, J = 7.6 Hz, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 6.14 (d, J = 7.2 Hz, 1 H, CH=), 8.18 (d, J = 7.2 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.6, 22.1, 28.8, 34.0, 52.6, 102.9, 113.8, 150.1, 158.4, 164.2, 172.9 ppm. IR (NaCl): $\tilde{\nu}$ = 2956, 2919, 2852, 1745, 1619, 1553, 1272, 1109, 1002, 784 cm^{-1}. MS (EI): *m*/*z* (%) = 210 (8) $[M]^+$, 197 (3), 169 (6), 153 (22), 127 (14), 113 (19), 99 (24), 85 (78), 71 (78), 57 (100). HRMS: calcd. for $C_{11}H_{14}O_4$ 210.0892; found 210.0895.

Compound 2d: Yield: 31 mg, 61%; light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.86 (t, J = 7.2 Hz, 2 H, CH_2), 3.02 (t, J = 7.2 Hz, 2 H, CH_2), 3.89 (s, 3 H, OCH_3), 6.04 (d, J = 7.2 Hz, 1 H, CH=), 7.15–7.31 (m, 5 H, Ar), 8.12 (d, J = 7.2 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 32.8, 36.0, 52.6, 103.5, 114.0, 126.6, 128.2, 128.6, 139.3, 150.0, 158.2, 164.0, 171.2 ppm. IR (NaCl): $\tilde{\nu}$ = 3027, 2953, 2926, 2854, 1753, 1627, 1556, 1435, 1287, 1113, 1009, 791, 700 cm^{-1}. MS (EI): *m*/*z* (%) = 258 (11) $[M]^+$, 153 (5), 139 (2), 115 (2), 104 (2), 91 (100), 71 (4), 65 (6), 49 (9). HRMS: calcd. for $C_{15}H_{14}O_4$ 258.0892; found 258.0896.

Compound 2e: Yield: 26 mg, 62%; yellow solid; m.p. 95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.97 (d, J = 6.8 Hz, 6 H, 2 CH_3), 2.09–2.19 (m, 1 H, CH), 2.42 (d, J = 6.8 Hz, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 6.15 (d, J = 6.8 Hz, 1 H, CH=), 8.19 (d, J = 6.8 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 22.1, 27.0, 43.2, 52.5, 103.9, 113.7, 149.9, 158.4, 164.1, 172.0 ppm. IR (NaCl): $\tilde{\nu}$ = 2958, 2928, 1766, 1714, 1626, 1557, 1435, 1291, 1111, 1007, 789 cm^{-1}. MS (EI): *m*/*z* (%) = 210 (34) $[M]^+$, 182 (10), 168 (17), 153 (75), 136 (100), 125 (16), 111 (13), 85 (65), 71 (47), 57 (78). HRMS: calcd. for $C_{11}H_{14}O_4$ 210.0892; found 210.0894.

Compound 2f: Yield: 35 mg, 73%; light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.89 (t, J = 6.8 Hz, 3 H, CH_3), 1.26–1.36 (m, 6 H, $3CH_2$), 1.65–1.73 (m, 2 H, CH_2), 2.56 (t, J = 7.6 Hz, 2 H, CH_2), 3.90 (s, 3 H, OCH_3), 6.15 (d, J = 7.2 Hz, 1 H, CH=), 8.18 (d, J = 7.2 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.9, 22.4, 26.7, 28.6, 31.3, 34.2, 52.5, 102.9, 113.7, 150.1, 158.4, 164.1, 172.9 ppm. IR (NaCl): $\tilde{\nu}$ = 2955, 2929, 2858, 1759, 1626, 1556, 1436, 1287, 1113, 1009, 791 cm^{-1}. MS (EI): *m*/*z* (%) = 238 (26) $[M]^+$, 207 (14), 188 (15), 168 (23), 153 (100), 136 (73), 125 (9), 108 (8), 84 (41), 59 (17). HRMS: calcd. for $C_{13}H_{18}O_4$ 238.1205; found 238.1207.

Compound 2g: Yield: 25 mg, 51%; light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 3.86 (s, 2 H, CH_2), 3.89 (s, 3 H, OCH_3), 6.00 (dd, J = 7.2, 1.2 Hz, 1 H, CH=), 7.25–7.38 (m, 5 H, Ar), 8.14 (d, J = 7.2 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 40.4, 52.6, 103.4, 114.1, 127.7, 129.0, 129.3,

134.0, 150.0, 158.0, 164.0, 171.0 ppm. IR (NaCl): $\tilde{\nu}$ = 3030, 2954, 2925, 2854, 1755, 1627, 1556, 1277, 1111, 789, 700 cm^{-1}. MS (EI): *m/z* (%) = 244 (25) $[M]^+$, 213 (5), 153 (100), 128 (6), 125 (4), 85 (34), 84 (10), 65 (10), 49 (14). HRMS: calcd. for $C_{14}H_{12}O_4$ 244.0736; found 244.0731.

Compound 3h: Yield: 50 mg, 86%; light yellow oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.38 (s, 3 H, CH_3), 3.34 (d, J = 6.8 Hz, 2 H, CH_2), 3.78 (s, 6 H, $2OCH_3$), 4.02 (t, J = 6.8 Hz, 1 H, CH), 6.71 (d, J = 16.4 Hz, 1 H, CH=), 7.21 (d, J = 8.0 Hz, 2 H, Ar), 7.45 (d, J = 8.0 Hz, 2 H, Ar), 7.59 (d, J = 16.4 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.5, 39.3, 46.6, 52.8, 124.3, 128.4, 129.7, 131.4, 141.3, 143.8, 169.4, 196.2 ppm. IR (NaCl): $\tilde{\nu}$ = 3003, 2954, 2925, 2854, 1738, 1691, 1665, 1613, 1513, 1436, 1281, 978, 802, 543 cm^{-1}. MS (EI): *m/z* (%) = 210 (6) $[M]^+$, 275 (11), 259 (5), 227 (5), 158 (18), 145 (100), 115 (30), 91 (14), 71 (7), 55 (6). HRMS: calcd. for $C_{16}H_{18}O_5$ 290.1154; found 290.1151.

Compound 3i: Yield: 49 mg, 78%; light yellow oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 3.34 (d, J = 6.8 Hz, 2 H, CH_2), 3.78 (s, 6 H, $2OCH_3$), 4.02 (t, J = 6.8 Hz, 1 H, CH), 6.72 (d, J = 16.4 Hz, 1 H, CH=), 7.38 (d, J = 8.4 Hz, 2 H, Ar), 7.48 (d, J = 8.4 Hz, 2 H, Ar), 7.56 (d, J = 16.4 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 39.5, 46.6, 52.9, 125.6, 129.3, 129.5, 132.6, 136.7, 142.2, 169.3, 196.0 ppm. IR (NaCl): $\tilde{\nu}$ = 2955, 2925, 2854, 1744, 1696, 1613, 1489, 1435, 1012, 962 cm^{-1}. MS (EI): *m/z* (%) = 244 (16), 165 (47), 152 (23), 139 (57), 105 (100), 91 (19), 77 (42). HRMS: calcd. for $C_{15}H_{15}ClO_5$ 310.0608; found 310.0606.

Compound 3j: Yield: 60 mg, 85%; yellow solid; m.p. 120–122 °C. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 3.33 (d, J = 6.8 Hz, 2 H, CH_2), 3.78 (s, 6 H, 2 OCH_3), 4.02 (t, J = 6.8 Hz, 1 H, CH), 6.73 (d, J = 16.4 Hz, 1 H, CH=), 7.41 (d, J = 8.4 Hz, 2 H, Ar), 7.53 (d, J = 8.4 Hz, 2 H, Ar), 7.54 (d, J = 16.4 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 39.5, 46.6, 52.8, 125.0, 125.7, 129.7, 132.2, 133.1, 142.2, 169.3, 195.9 ppm. IR (NaCl): $\tilde{\nu}$ = 2954, 2925, 2853, 1732, 1689, 1611, 1585, 1487, 1434, 1262, 1160, 1009, 973, 802 cm^{-1}. MS (EI): *m/z* (%) = 211 (41), 209 (40), 181 (8), 155 (6), 113 (16), 102 (64), 85 (42), 71 (55), 57 (100), 43 (91). HRMS: calcd. for $C_{15}H_{15}BrO_5$ 354.0103; found 354.0101.

Compounds 4k/5k: Ratio = 1.0:0.6. Yield: 20 mg, 47%; light yellow oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.08 (d, J = 6.8 Hz, 6 H, 2 CH_3, **4k**), 2.34 (s, 3 H, CH_3, **4k**), 2.59–2.71 (m, 1 H, CH, **4k**), 3.34 (s, 2 H, CH_2, **4k**), 3.66 (s, 3 H, OCH_3, **4k**), 6.58 (d, J = 10.0 Hz, 1 H, CH=, **4k**), 1.74 (s, 1.8 H, CH_3, **5k**), 1.80 (s, 1.8 H, CH_3, **5k**), 2.19 (s, 1.8 H, CH_3, **5k**), 3.67 (s, 1.8 H, OCH_3, **5k**), 3.71 (s, 1.8 H, OCH_3, **5k**), 3.90 (d, J = 10.4 Hz, 0.6 H, CH=, **5k**), 4.14 (t, J = 10.4 Hz, 0.6 H, CH=, **5k**), 4.85 (d, J = 10.4 Hz, 0.6 H, CH=, **5k**) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS, **4k**/**5k**): δ = 18.2, 22.0, 25.1, 25.9, 28.8, 28.9, 30.8, 51.9, 52.7, 53.0, 117.8, 139.8, 152.9, 168.5, 168.7, 206.4 ppm. IR (NaCl): $\tilde{\nu}$ = 2955, 2931, 2859, 1737, 1717, 1434, 1347, 1149, 1029 cm^{-1}. MS (GC–EI, **4k**): *m/z* = 152 $[M - CH_3OH]^+$, 125, 109, 99, 81, 67, 59. MS (GC–EI, **5k**): *m/z* = 242 $[M]^+$, 200, 179, 167, 140, 125, 109, 99, 81, 67, 59.

Compound 6k: Yield: 19 mg, 39%; light yellow oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.08 (d, J = 6.4 Hz, 6 H, 2 CH_3), 2.37 (s, 3 H, CH_3), 2.64–2.70 (m, 1 H, CH), 3.74 (s, 6 H, 2 OCH_3), 4.82 (s, 1 H, CH), 6.65 (d, J = 10.4 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.6, 25.1, 29.4, 48.2, 52.7, 132.8, 155.0, 168.5, 197.4 ppm. IR (NaCl): $\tilde{\nu}$ = 2957, 2924, 2853, 1738, 1670, 1641, 1435, 1193, 758 cm^{-1}. MS (EI): *m/z* (%) = 242 (12) $[M]^+$, 210 (6), 178 (19), 155 (8), 141 (10), 127 (7), 113 (18), 99 (24), 71 (73), 57 (100), 43 (96). HRMS: calcd. for $C_{12}H_{18}O_5$ 242.1154; found 242.1150.

Supporting Information (see footnote on the first page of this article): ^1H NMR and ^{13}C NMR spectra of VDCP-diesters **1e** and **1f** and compounds **2**, **3**, **4k**, **5k** and **6k** and crystallographic data of **2e**.

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[12] CCDC-783105 (for **2e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Empirical formula: $C_{11}H_{14}O_4$; formula weight: 210.22; crystal color, habit: colorless, prismatic; crystal system: triclinic; lattice type: primitive; crystal size: $0.413 \times 0.369 \times 0.307$; lattice parameters: a = 9.0256(9) Å, b = 11.2232(12) Å, c = 11.7436(12) Å, α = 102.157(2)°, β = 107.425(2)°, γ = 90.063(2)°, V = 1106.9(2) Å^3; space group: $P\bar{1}$; Z = 4; $D_{calcd.}$ = 1.261 g/cm^3; $F(000)$ = 448; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0543, 0.1435.

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