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Tandem reactions of α-diazo ketones with macrocyclic olefins: diastereoselective synthesis of oxanorbornane fused macrocyclic lactones

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Abstract—Tandem cyclization–cycloaddition reactions of α-diazo ketones with macrocyclic olefins in the presence of rhodium(II) acetate catalyst led to the oxanorbornane fused macrocyclic di- or tetralactone ring systems in moderate yield. This forms the first example of 1,3-dipolar cycloaddition reactions with a macrocyclic olefin as a dipolarophile, affording a variety of new oxanorbornane fused macrocycles with diastereoselectivity.

1. Introduction

α-Diazocarbonyl compounds continue to be a subject of considerable interest and intensive investigation in synthetic organic chemistry[1] as they undergo very useful transformations, such as cyclopropanation, insertion, and ylide formation. Intramolecular carbenoid–carbonyl group cyclization has been recognized as one of the most effective methods for generating carbonyl ylides; subsequent 1,3-dipolar cycloadditions with π-bonds of C=C or C=O bonds to construct carbo/heterocyclic ring systems are well documented.[2] As a result, there has been growing interest in the use of rhodium(II)-generated carbonyl ylides as 1,3-dipoles for the synthesis of many bioactive natural products such as brevicomin,[3] illudins,[4] epoxysorbicillinol,[5] zaragozic acid,[6] and various alkaloids.[7] Thus, the selection of dipolarophile for reactivity and selectivity is of considerable interest in carbonyl ylides cycloaddition reactions. Synthesis[8] and studies[9] of the macrocyclic dilactones are impressive in organic chemistry due to their biological as well as ion-selective properties and application in the perfume industry. However, there is no literature available for the reactivity and selectivity of a macrocyclic olefin as a dipolarophile. As a part of our ongoing research on the carbonyl ylide[10] and supramolecular systems,[11] herein we report the tandem cyclization–cycloaddition reactions of α-diazo ketones with macrocyclic olefins using $Rh_2(OAc)_4$ as a catalyst.

2. Results and discussion

To perform the tandem cyclization–cycloaddition reactions, the required α-diazo ketones **1** (Fig. 1) having a mono- or disubstituent on the diazocarbonyl carbon were prepared based on the reported method.[11] We have also synthesized several symmetrical macrocyclic dilactones **2a**–**c** and tetralactones **2d**–**h** (Fig. 2) having olefin functionalities. Initially, the synthesis of macrocycles having oxyethylene units was performed. To this end, the reaction of maleic anhydride or maleic acid with tri(ethylene glycol) under reflux conditions using a catalytic amount of PTSA–H_2SO_4 afforded a mixture of di- and tetralactones (dimer) **2a**,**g** (ratio 1:1.5, Fig. 2). These lactones were separated by column chromatography and characterized by NMR and mass spectra. Similarly, the reaction of maleic anhydride and tetra(ethylene glycol) afforded a mixture of macrocyclic di- and tetralactones **2b**,**h** (ratio 1:1.4) holding 17,34 atoms in the cyclic core, respectively. Subsequently, di(ethylene glycol) with maleic anhydride afforded tetralactone **2e**. The tetralactone

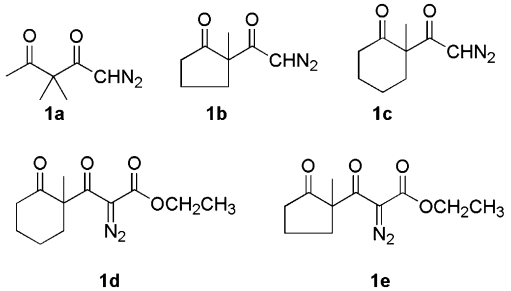

Figure 1. Synthesized α-diazo ketones.

Keywords: Carbonyl ylide; Cycloaddition; Diazo ketones; Macrocycles; Rhodium(II) acetate.
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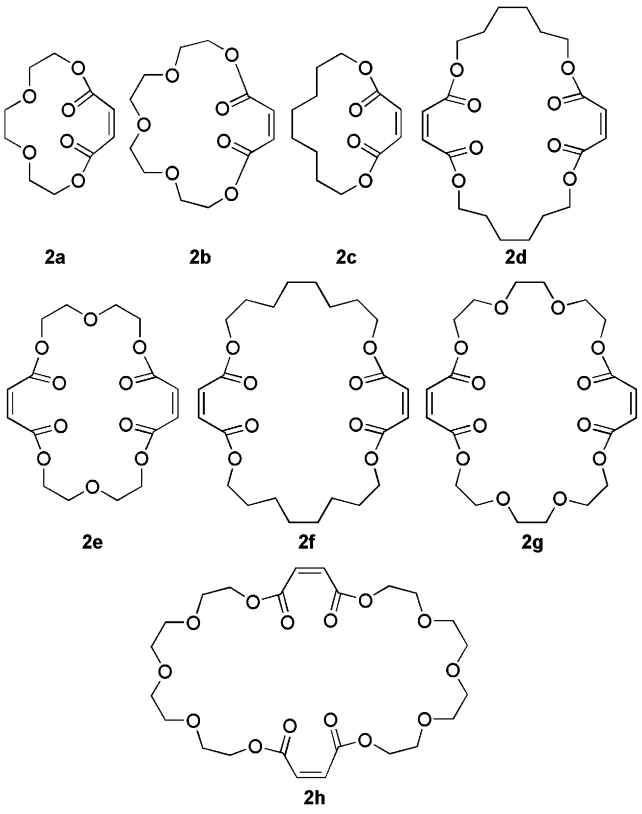
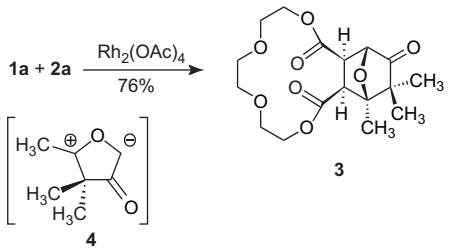


Figure 2. Synthesized macrocyclic olefins **2**.

2e was obtained as a selective single product when the spacer length is shorter. Next, we planned to synthesize macrocycles having an alkane spacer. Toward this, reaction of maleic anhydride and 1,8-octanediol afforded the respective symmetrical di- and tetralactones **2c**,**f** (ratio 1:1) having an octane spacer. The reaction of 1,6-hexanediol and maleic anhydride under similar conditions afforded the macrocyclic tetralactone **2d** as a single product in 35% yield.

Subsequently, the reaction of five-membered cyclic carbonyl ylide **4** derived from α-diazo ketone **1a** and the 14-membered macrocyclic olefin **2a** having the oxyethylene spacer in the presence of 2 mol % of rhodium(II) acetate dimer was carried out affording the macrocyclic dilactone having the oxanorbornane fused macrocyclic system **3a** in 76% yield (Scheme 1). The structure of the product **3a** with complete diastereoselectivity was confirmed by spectroscopic analysis. Encouraged by the above result via the tandem cyclization–cycloaddition, the reaction of **1a** was performed with macrocyclic dilactone **2b** and stirred for 6 h at room temperature to furnish the corresponding oxanorbornane fused macrocyclic dilactone **3b** in 74% yield (Table 1, entry b). Next, we investigated the reactions of fused five-membered cyclic carbonyl ylides **5** generated from the α-diazo ketones tethered on cycloalkanes in the presence of a macrocyclic olefin. Therefore, reaction of α-diazo ketone **1b** and macrocyclic olefin **2a** or **2b** was carried out to afford the oxanorbornane fused macrocyclic dilactone **3c** or **3d** (Scheme 2, Table 1, entries c and d) with diastereoselectivity possessing five stereocenters. Similar reaction of α-diazo ketone **1c** tethered on a cyclohexane ring, and **2b** afforded the cycloadduct having the macrocyclic dilactone **3e** (Table 1, entry e).

The 1,3-dipolar cycloaddition reaction of α-diazo ketone **1c** and the macrocyclic olefin **2c** having the octane spacer was carried out furnishing the corresponding oxanorbornane fused macrocyclic dilactone **3f**.



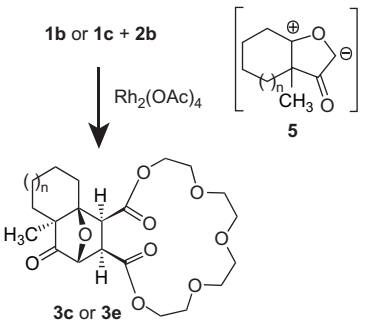
Scheme 1. Reaction of α-diazo ketones with macrocyclic olefin.

Further, we investigated these reactions with five-membered-ring carbonyl ylides generated from the α-diazo ketones tethered on cycloalkanes having an ester substituent at the diazo functional group. To this end, α-diazo ketone **1d** with macrocyclic dilactones **2a**,**b** under reflux conditions afforded the corresponding oxanorbornane fused macrocyclic dilactones **3g**,**h**.

Next, our attention turned to perform the tandem cyclization–1,3-dipolar cycloaddition reaction with a macrocyclic tetralactone having olefin functional groups. Consequently, the reaction of equimolar quantity of α-diazo ketone **1d** and macrocyclic tetralactone **2d** was performed under reflux conditions for 6 h in dry benzene to yield the monocycloaddition product **3i** in 65% yield.

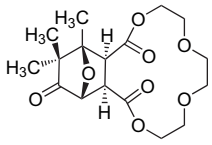
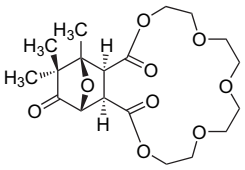
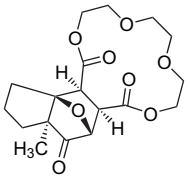
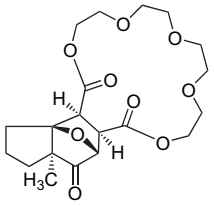
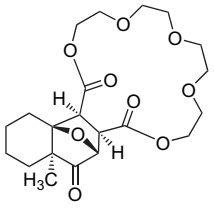
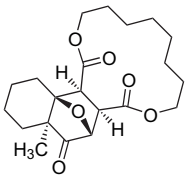
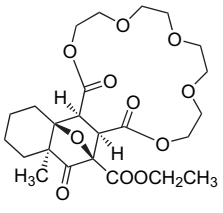
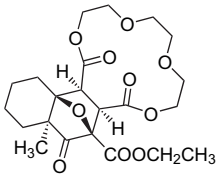
Similar reaction of **1e** and **2d** afforded the oxanorbornane fused macrocyclic tetralactone **3j** in moderate yield. Further, these reactions were extended by changing the spacer in the macrocyclic tetralactones. To this end, the reactions of **1b**,**c** and macrocyclic tetralactones **2d**,**e** having diolefins were performed obtaining the respective monocycloadducts **3k**–**m**.

The diastereoselective monocycloadducts **3** were clearly confirmed by the spectroscopy as well as our earlier studies.[12,13] Interestingly, the assignment of macrocyclic part as *exo*-addition in products **3** was made upon inspection of ^{1}H NMR spectra, where the bridgehead OCH-proton showed[13] a singlet without any coupling.



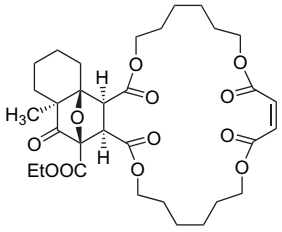
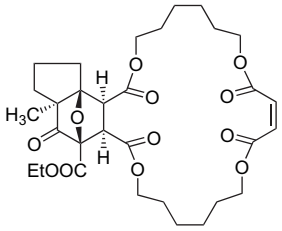
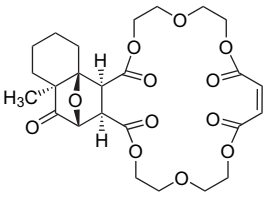
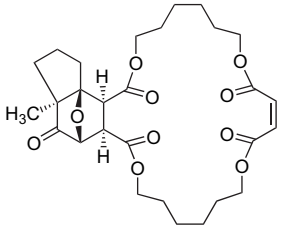
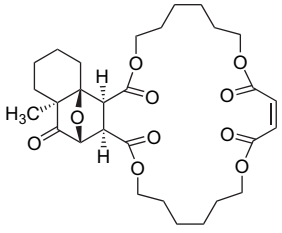
Scheme 2. Reaction of cycloalkane fused α-diazo ketones with macrocyclic olefin.

Table 1. Synthesis of oxanorbornane fused macrocyclic lactones **3**

Entry	α-Diazo ketone	Macrocyclic olefin	Oxanorbornane fused macrocycles **3**	Yield[a] (%)
a	**1a**	**2a**		76
b	**1a**	**2b**		74
c	**1b**	**2a**		64
d	**1b**	**2b**		68
e	**1c**	**2b**		72
f	**1c**	**2c**		74
g	**1d**	**2b**		70
h	**1d**	**2c**		76

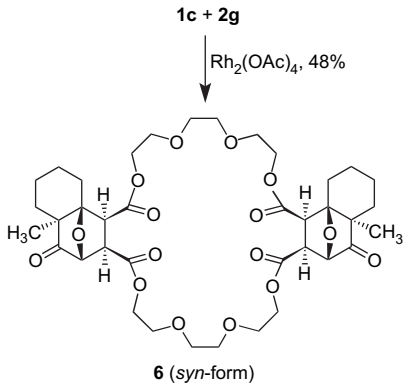
(*continued*)

Table 1. (*continued*)

Entry	α-Diazo ketone	Macrocyclic olefin	Oxanorbornane fused macrocycles **3**	Yield[a] (%)
i	**1d**	**2d**		65
j	**1e**	**2d**		60
k	**1c**	**2e**		60
l	**1b**	**2d**		60
m	**1c**	**2d**		64

[a] Yields are unoptimized and refer to isolated pure compounds **3**.

Finally, a bis-tandem cyclization–cycloaddition reaction was planned with the macrocyclic tetralactone **2g**. To this end, the reaction of an excess amount of α-diazo ketone **1c** with 1 equiv of 28-membered macrocyclic tetralactone **2g** having a diolefin functionality afforded the bis-oxanorbornane fused macrocyclic tetralactone **6** having 10 stereocenters in 48% yield (Scheme 3). The product **6** was obtained as a single isomer based on the NMR and mass spectra. The bis-oxanorbornane product **6** might exist as a mixture of *meso* and *dl* compounds; based on the reaction of macrocycle **2g** with the same or opposite enantiomers of carbonyl ylide **5**, respectively. Based on the MM2 force field calculations, the product **6** perhaps exist as *syn*-form (Fig. 3), which is having relatively less energy (≈6 kcal/mol) than *anti*-form (Fig. 4).



Scheme 3. Bis-cycloaddition reaction of cycloalkane fused α-diazo ketones with macrocyclic olefin.

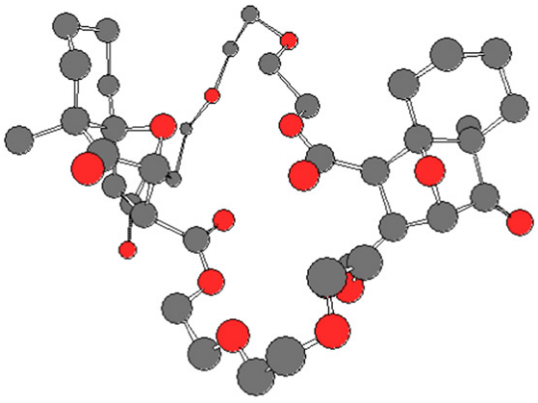


Figure 3. Energy minimized structures of *syn*-form of **6** at MM2 level.

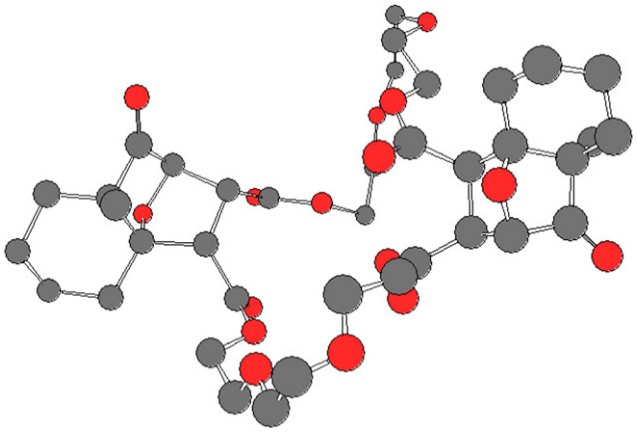


Figure 4. Energy minimized structures of *anti*-form of **6** at MM2 level.

3. Conclusion

In conclusion, we have disclosed the first example of 1,3-dipolar cycloaddition reaction of carbonyl ylides with macrocyclic olefins. The tandem cyclization–cycloaddition methodology afforded various oxanorbornane or bis-oxanorbornane fused macrocyclic di- and tetralactones having an oxyethylene or alkane spacer with complete diastereoselectivity.

4. Experimental section

4.1. General

All reactions were carried out in oven-dried glassware under an atmosphere of argon. All solvents were freshly purified by distillation. All the materials used are purchased from Aldrich. α-Diazo ketones are prepared as described in the literature.[12] IR spectra were recorded using CH_2Cl_2 on a Perkin–Elmer Spectrum GX FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded (200 and 50.3 MHz, respectively) on a Bruker Avance DPX 200 spectrometer using $CDCl_3$. Chemical shifts for proton and carbon resonances are reported in parts per million (δ) relative to tetramethylsilane (δ 0.00) and chloroform (δ 77), respectively. Multiplicities are indicated by singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Coupling constants (J) were reported in Hertz (Hz). Carbon types were determined from ^{13}C NMR and DEPT experiments. High-resolution mass analyses were performed using electrospray ionization (ESI) technique on a Waters QTof-micro mass spectrometer. Analytical thin layer chromatography (TLC) was performed on silica and components were visualized by observation under iodine, UV-light, or sulfuric acid charring. Column chromatography was performed on a silica-gel (100–200 mesh) column.

4.2. General experimental procedure for the synthesis of compounds 2, 3, and 6

4.2.1. Method A for the synthesis of macrocyclic olefins 2. To an oven-dried flask, a solution containing maleic anhydride or maleic acid (10 mmol) and dihydroxy compound (10 mmol) in dry benzene was added a catalytic amount of PTSA–H_2SO_4 under nitrogen atmosphere. Initially, maleic anhydride or maleic acid was insoluble, but a clear solution was obtained after refluxing the reaction mixture for 1–2 h duration. The reaction mixture was evaporated after refluxing for 12 h. Water was added to the residue and extracted with DCM (3×100 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated. The residue was subjected to 100–200 mesh silica-gel column chromatography to afford macrocyclic dilactone (30% EtOAc–hexane) and macrocyclic tetralactone (60% EtOAc–hexane or only EtOAc).

4.2.2. Method B for the synthesis of oxanorbornane fused macrocyclic di- and tetralactones 3 and 6. To an oven-dried flask, a solution containing the appropriate macrocyclic olefin (1 mmol) and α-diazo ketone (1 mmol) in dry DCM under inert atmosphere was added 2.0 mol % of rhodium(II) acetate dimer and stirred for 6 h at room temperature. The reaction was monitored by TLC. After the decomposition of all diazocarbonyl compounds, the reaction mixture was evaporated and subjected to 100–200 mesh silica-gel column chromatography (EtOAc–hexane) to afford the respective oxanorbornane fused macrocyclic product. An excess amount of α-diazo ketone **1c** was taken for the bis-cycloaddition reaction.

4.2.3. Method C for the synthesis of oxanorbornane fused macrocyclic di- and tetralactones 3. To an oven-dried flask, a solution containing the appropriate macrocyclic olefin (1 mmol) and α-diazo ketone (1 mmol) in dry benzene

under inert atmosphere was added 2.0 mol % of rhodium(II) acetate dimer and stirred for 6 h at reflux. The reaction was monitored by TLC. After the decomposition of all diazocarbonyl compounds, the reaction mixture was evaporated and subjected to 100–200 mesh silica-gel column chromatography (EtOAc–hexane) to afford the respective oxanorbornane fused macrocyclic product **3**. Reactions utilizing α-diazo ketones **1d**,**e** (when R^1=COOEt) were performed in dry benzene (dried over sodium) at reflux.

4.2.4. Method D for the synthesis of bis-oxanorbornane fused macrocyclic tetralactones 6. To an oven-dried flask, a solution containing the appropriate macrocyclic olefin (1 mmol) and α-diazo ketone (2.4 mmol) in dry DCM under inert atmosphere was added 2.0 mol % of rhodium(II) acetate dimer and stirred for 6 h at room temperature. The reaction was monitored by TLC. After the decomposition of all diazocarbonyl compounds, the reaction mixture was evaporated and subjected to 100–200 mesh silica-gel column chromatography (70:30 EtOAc–hexane) to afford the respective bis-oxanorbornane fused macrocyclic product.

4.3. Characterization data of new compounds

4.3.1. Macrocyclic dilactone (2a) and tetralactone (2g). Maleic anhydride (0.98 g, 10 mmol), tri(ethylene glycol) (1.5 g, 10 mmol), and a catalytic amount of *p*-toluene sulfonic acid–H_2SO_4 in dry benzene were allowed to reflux under nitrogen atmosphere for 12 h. Workup and purification according to method A afford macrocyclic dilactone **2a** (20%) and macrocyclic tetralactone **2g** (30%).

Dilactone **2a**: colorless thick oil. IR (neat): ν 2944, 2868, 1755, 1449, 1323, 1254, 1207, 1027, 1004, 736 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.28 (s, 2H, =C*H*), 4.37 (t, 4H, OCH_2, J=6.0 Hz), 3.77 (t, 4H, OCH_2, J=6.0 Hz), 3.65 (s, 4H, OCH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 164.7 (*C*=O), 129.4 (=*C*H), 69.2 (O*C*H_2), 68.4 (O*C*H_2), 63.5 (O*C*H_2). HRMS (ESI^+) Calcd for $C_{10}H_{14}O_6Na$ $(M+Na)^+$: 253.0688, found: 253.0627.

Tetralactone **2g**: colorless thick oil. IR (neat): ν 2944, 2868, 1755, 1449, 1323, 1254, 1207, 1027, 1004, 736 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.28 (s, 4H, =C*H*), 4.37 (t, 8H, OCH_2, J=6.0 Hz), 3.77 (t, 8H, OCH_2, J=6.0 Hz), 3.65 (s, 8H, OCH_2). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 164.9 (*C*=O), 129.4 (=*C*H), 69.2 (O*C*H_2), 68.4 (O*C*H_2), 63.6 (O*C*H_2). HRMS (ESI^+) Calcd for $C_{20}H_{28}O_{12}Na$ $(M+Na)^+$: 483.1478, found: 483.1410.

4.3.2. Macrocyclic dilactone (2b) and tetralactone (2h). Maleic anhydride (0.98 g, 10 mmol), tetra(ethylene glycol) (1.94 g, 10 mmol), and a catalytic amount of *p*-toluene sulfonic acid–H_2SO_4 in dry benzene were allowed to reflux under nitrogen atmosphere for 12 h. Workup and purification according to method A afford macrocyclic dilactone **2b** (25%) and macrocyclic tetralactone **2h** (34%).

Dilactone **2b**: colorless thick oil. IR (neat): ν 2952, 2873, 1748, 1642, 1452, 1337, 1218, 1171, 1141, 1055 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.29 (s, 2H, =C*H*), 4.36 (t, 4H, OCH_2, J=6.0 Hz), 3.78 (t, 4H, OCH_2, J=6.0 Hz), 3.65 (s, 8H, OCH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 164.6 (*C*=O), 129.3 (=*C*H), 70.5 (O*C*H_2), 70.1 (O*C*H_2), 68.4 (O*C*H_2), 64.0 (O*C*H_2). HRMS (ESI^+) Calcd for $C_{12}H_{18}O_7Na$ $(M+Na)^+$: 297.0950, found: 297.0910.

Tetralactone **2h**: colorless thick oil. IR (neat): ν 2952, 2873, 1748, 1452, 1337, 1218, 1171, 1141, 1055 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.29 (s, 4H, =C*H*), 4.35 (t, 8H, OCH_2, J=6.0 Hz), 3.77 (t, 8H, OCH_2, J=6.0 Hz), 3.64 (s, 16H, OCH_2). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 164.6 (*C*=O), 129.3 (=*C*H), 70.5 (O*C*H_2), 70.1 (O*C*H_2), 68.4 (O*C*H_2), 64.0 (O*C*H_2). HRMS (ESI^+) Calcd for $C_{24}H_{36}O_{14}Na$ $(M+Na)^+$: 571.2003, found: 571.2067.

4.3.3. Macrocyclic dilactone (2c) and tetralactone (2f). Maleic anhydride (0.98 g, 10 mmol), 1,8-octanediol (1.46 g, 10 mmol), and a catalytic amount of *p*-toluene sulfonic acid–H_2SO_4 in dry benzene were allowed to reflux under nitrogen atmosphere for 12 h. Workup and purification according to method A afford macrocyclic dilactone **2c** (30%) and macrocyclic tetralactone **2f** (28%).

Dilactone **2c**: colorless thick oil. IR (neat): ν 2948, 2866, 1748, 1641, 1472, 1322, 1172, 1012, 735 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.23 (s, 2H, =C*H*), 4.17 (t, 4H, OCH_2, J=6.0 Hz), 1.66–1.33 (m, 12H, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 169.1 (*C*=O), 129.7 (=*C*H), 65.2 (O*C*H_2), 29.0 (*C*H_2), 28.3 (*C*H_2), 25.7 (*C*H_2). HRMS (ESI^+) Calcd for $C_{12}H_{18}O_4Na$ $(M+Na)^+$: 249.1103, found: 249.1148.

Tetralactone **2f**: colorless thick oil. IR (neat): ν 2949, 2867, 1746, 1642, 1472, 1322, 1172, 1012, 736. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.23 (s, 4H, =C*H*), 4.17 (t, 8H, OCH_2, J=6.0 Hz), 1.66–1.33 (m, 24H, CH_2). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 169.2 (*C*=O), 129.7 (=*C*H), 65.2 (O*C*H_2), 29.0 (*C*H_2), 28.3 (*C*H_2), 25.7 (*C*H_2). HRMS (ESI^+) Calcd for $C_{24}H_{36}O_8Na$ $(M+Na)^+$: 475.2308, found: 475.2378.

4.3.4. Macrocyclic tetralactone (2d). Maleic anhydride (0.98 g, 10 mmol), 1,6-hexanediol (1.18 g, 10 mmol), and a catalytic amount of *p*-toluene sulfonic acid–H_2SO_4 in dry benzene were allowed to reflux under nitrogen atmosphere for 12 h. Workup and purification according to method A afford macrocyclic tetralactone **2d** (35%) as a colorless thick oil. IR (neat): ν 2934, 2864, 1732, 1641, 1464, 1371, 1070, 1016, 732 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.23 (s, 4H, =C*H*), 4.19 (t, 8H, OCH_2, J=6.0 Hz), 1.69–1.41 (m, 16H, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 165.2 (*C*=O), 129.5 (=*C*H), 65.1 (O*C*H_2), 28.4 (*C*H_2), 25.4 (*C*H_2). HRMS (ESI^+) Calcd for $C_{20}H_{28}O_8Na$ $(M+Na)^+$: 419.1682, found: 419.1642.

4.3.5. Macrocyclic tetralactone (2e). Maleic anhydride (0.98 g, 10 mmol), di(ethylene glycol) (1.22 g, 10 mmol), and a catalytic amount of *p*-toluene sulfonic acid–H_2SO_4 in dry benzene were allowed to reflux under nitrogen atmosphere for 12 h. Workup and purification according to method A afford macrocyclic tetralactone **2e** (28%) as a colorless thick oil. IR (neat): ν 2944, 2872, 1740, 1641, 1447, 1323, 1255, 1205, 1027, 1004, 735 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.31 (s, 4H, =C*H*), 4.36 (t, 8H, OCH_2, J=6.0 Hz), 3.76 (t, 8H, OCH_2, J=6.0 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 165.1 (*C*=O), 129.7 (=*C*H),

68.5 (O*C*H$_2$), 64.1 (O*C*H$_2$). HRMS (ESI$^+$) Calcd for $C_{16}H_{20}O_{10}Na$ (M+Na)$^+$: 395.0954, found: 395.0910.

4.3.6. Macrocyclic dilactone (3a). A mixture of α-diazo ketone **1a** (154 mg, 1 mmol) and macrocyclic olefin **2a** (230 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (40:60 EtOAc–hexane) to afford **3a** (270 mg, 76%) as a colorless oil. IR (neat): ν 2950, 2914, 2871, 1746, 1451, 1392, 1337, 1268, 1216, 1142, 737 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.93 (s, 1H, OC*H*), 4.40–4.36 (m, 4H, OCH_2), 3.86–3.71 (m, 4H, OCH_2), 3.64–3.50 (m, 5H, OCH_2, C*H*), 3.02 (d, 1H, C*H*, *J*=10.0 Hz), 1.36 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.05 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 215.4 (*C*=O), 170.6 (*C*OOEt), 168.8 (*C*OOEt), 91.0 (*quat-C*), 81.0 (O*C*H), 69.4 (O*C*H$_2$), 68.5 (O*C*H$_2$), 63.7 (O*C*H$_2$), 51.2 (*quat-C*), 50.2 (*C*H), 47.9 (*C*H), 20.7 (*C*H$_3$), 19.6 (*C*H$_3$), 13.7 (*C*H$_3$). HRMS (ESI$^+$) Calcd for $C_{17}H_{24}O_8Na$ (M+Na)$^+$: 379.1369, found: 379.1311.

4.3.7. Macrocyclic dilactone (3b). A mixture of α-diazo ketone **1a** (154 mg, 1 mmol) and macrocyclic olefin **2b** (274 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (40:60 EtOAc–hexane) to afford **3b** (296 mg, 74%) as a colorless oil. IR (neat): ν 2948, 2916, 2870, 1740, 1450, 1392, 1337, 1268, 1216, 1142, 737 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.93 (s, 1H, OC*H*), 4.73–4.05 (m, 4H, OCH_2), 3.99–3.80 (m, 4H, OCH_2), 3.72–3.51 (m, 9H, OCH_2, C*H*), 3.03 (d, 1H, C*H*, *J*=10.0 Hz), 1.36 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.05 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 215.4 (*C*=O), 170.4 (*C*OOEt), 168.6 (*C*OOEt), 91.0 (*quat-C*), 81.1 (O*C*H), 70.3 (O*C*H$_2$), 70.0 (O*C*H$_2$), 68.4 (O*C*H$_2$), 63.5 (O*C*H$_2$), 51.2 (*quat-C*), 50.2 (*C*H), 47.9 (*C*H), 20.7 (*C*H$_3$), 19.6 (*C*H$_3$), 13.7 (*C*H$_3$). HRMS (ESI$^+$) Calcd for $C_{19}H_{28}O_9Na$ (M+Na)$^+$: 423.1631, found: 423.1691.

4.3.8. Macrocyclic dilactone (3c). A mixture of α-diazo ketone **1b** (166 mg, 1 mmol) and macrocyclic olefin **2a** (230 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (50:50 EtOAc–hexane) to afford **3c** (235 mg, 64%) as a colorless oil. IR (neat): ν 2948, 2872, 1746, 1450, 1336, 1265, 1133 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.96 (s, 1H, OC*H*), 4.42–4.32 (m, 4H, OCH_2), 3.88–3.71 (m, 4H, OCH_2), 3.62–3.48 (m, 5H, OCH_2, C*H*), 3.01 (d, 1H, C*H*, *J*=10.0 Hz), 2.46–1.43 (m, 6H, CH_2), 1.16 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 215.2 (*C*=O), 170.3 (*C*OOEt), 168.7 (*C*OOEt), 101.0 (*quat-C*), 81.2 (O*C*H), 69.3 (O*C*H$_2$), 68.6 (O*C*H$_2$), 63.6 (O*C*H$_2$), 58.5 (*quat-C*), 48.6 (*C*H), 46.8 (*C*H), 33.7 (*C*H$_2$), 27.8 (*C*H$_2$), 22.8 (*C*H$_2$), 19.3 (*C*H$_3$). HRMS (ESI$^+$) Calcd for $C_{18}H_{24}O_8Na$ (M+Na)$^+$: 391.1369, found: 391.1374.

4.3.9. Macrocyclic dilactone (3d). A mixture of α-diazo ketone **1b** (166 mg, 1 mmol) and macrocyclic olefin **2b** (274 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (60:40 EtOAc–hexane) to afford **3d** (280 mg, 68%) as a colorless oil. IR (neat): ν 2955, 2876, 1748, 1451, 1336, 1267, 1217, 1133, 735 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.97 (s, 1H, OC*H*), 4.74–4.25 (m, 4H, OCH_2), 3.99–3.72 (m, 12H, OCH_2), 3.56 (d, 1H, C*H*, *J*=10.0 Hz), 3.23 (d, 1H, C*H*, *J*=10.0 Hz), 2.44–1.59 (m, 6H, CH_2), 1.15 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 212.9 (*C*=O), 170.1 (*C*OOEt), 169.0 (*C*OOEt), 101.1 (*quat-C*), 81.0 (O*C*H), 70.9 (O*C*H$_2$), 70.5 (O*C*H$_2$), 69.0 (O*C*H$_2$), 64.8 (O*C*H$_2$), 58.6 (*quat-C*), 48.7 (*C*H), 46.9 (*C*H), 33.9 (*C*H$_2$), 27.9 (*C*H$_2$), 22.7 (*C*H$_2$), 19.2 (*C*H$_3$). HRMS (ESI$^+$) Calcd for $C_{20}H_{28}O_9Na$ (M+Na)$^+$: 435.1631, found: 435.1601.

4.3.10. Macrocyclic dilactone (3e). A mixture of α-diazo ketone **1c** (180 mg, 1 mmol) and macrocyclic olefin **2b** (274 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (50:50 EtOAc–hexane) to afford **3e** (306 mg, 72%) as a colorless oil. IR (neat): ν 2946, 2870, 1748, 1330, 1217, 1024, 737 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.01 (s, 1H, OC*H*), 4.72–4.22 (m, 4H, OCH_2), 3.96–3.68 (m, 12H, OCH_2), 3.54 (d, 1H, *C*H, *J*=10.0 Hz), 3.03 (d, 1H, C*H*, *J*=10.0 Hz), 1.94–1.20 (m, 8H, CH_2), 1.12 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 215.2 (*C*=O), 170.4 (*C*OOEt), 168.7 (*C*OOEt), 90.3 (*quat-C*), 81.7 (O*C*H), 70.6 (O*C*H$_2$), 70.2 (O*C*H$_2$), 69.2 (O*C*H$_2$), 64.8 (O*C*H$_2$), 50.6 (*C*H), 50.2 (*quat-C*), 48.2 (*C*H), 30.3 (*C*H$_2$), 25.5 (*C*H$_2$), 22.0 (*C*H$_2$), 19.8 (*C*H$_2$), 16.4 (*C*H$_3$). HRMS (ESI$^+$) Calcd for $C_{21}H_{30}O_9Na$ (M+Na)$^+$: 449.1788, found: 449.1794.

4.3.11. Macrocyclic dilactone (3f). A mixture of α-diazo ketone **1c** (180 mg, 1 mmol) and macrocyclic olefin **2c** (226 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (60:40 EtOAc–hexane) to afford **3f** (279 mg, 74%) as a colorless oil. IR (neat): ν 2942, 2866, 1740, 1468, 1325, 1174, 1076, 1014, 732 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.00 (s, 1H, OC*H*), 4.21–3.96 (m, 4H, OCH_2), 3.35 (d, 1H, C*H*, *J*=8.0 Hz), 2.96 (d, 1H, C*H*, *J*=8.0 Hz), 1.87–1.33 (m, 20H, CH_2), 1.09 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 215.5 (*C*=O), 170.1 (*C*OOEt), 169.1 (*C*OOEt), 90.3 (*quat-C*), 87.7 (O*C*H), 65.6 (O*C*H$_2$), 65.2 (O*C*H$_2$), 50.9 (*C*H), 50.2 (*quat-C*), 48.4 (*C*H), 30.4 (*C*H$_2$), 29.0 (*C*H$_2$), 28.3 (*C*H$_2$), 25.7 (*C*H$_2$), 25.6 (*C*H$_2$), 22.0 (*C*H$_2$), 19.9 (*C*H$_2$), 16.5 (*C*H$_3$). HRMS (ESI$^+$) Calcd for $C_{21}H_{30}O_6Na$ (M+Na)$^+$: 401.1940, found: 401.1970.

4.3.12. Macrocyclic dilactone (3g). A mixture of α-diazo ketone **1d** (252 mg, 1 mmol) and macrocyclic olefin **2b** (274 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry benzene (50 mL) for 6 h at reflux condition under an argon atmosphere according to the general method C followed by chromatographic

purification (EtOAc) to afford **3g** (348 mg, 70%) as a colorless oil. IR (neat): ν 2944, 2870, 1752, 1447, 1376, 1323, 1299, 1204, 1131, 1028, 735 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 4.40–4.16 (m, 6H, OCH_2), 3.81–3.73 (m, 4H, OCH_2), 3.67 (s, 8H, OCH_2), 3.52 (d, 1H, CH, J=10.0 Hz), 3.39 (d, 1H, CH, J=10.0 Hz), 1.92–1.40 (m, 8H, CH_2), 1.35–1.28 (t, 3H, CH_3), 1.19 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 209.1 (*C*=O), 169.1 (*C*OOEt), 167.6 (*C*OOEt), 89.6 (*quat-C*), 88.5 (*quat-C*), 70.0 (OCH_2), 70.6 (OCH_2), 69.0 (OCH_2), 65.3 (OCH_2), 61.6 (OCH_2), 51.7 (*C*H), 50.5 (*quat-C*), 50.0 (*C*H), 30.5 (CH_2), 24.9 (CH_2), 21.6 (CH_2), 19.6 (CH_2), 16.3 (CH_3), 13.9 (CH_3). HRMS (ESI^+) Calcd for $C_{24}H_{34}O_{11}Na$ $(M+Na)^+$: 521.1999, found: 521.1976.

4.3.13. Macrocyclic dilactone (3h). A mixture of α-diazo ketone **1d** (252 mg, 1 mmol) and macrocyclic olefin **2a** (230 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry benzene (50 mL) for 6 h at reflux condition under an argon atmosphere according to the general method C followed by chromatographic purification (EtOAc) to afford **3h** (345 mg, 76%) as a colorless oil. IR (neat): ν 2948, 2868, 1750, 1372, 1204, 1128 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 4.91 (q, 2H, OCH_2, J= 10.0 Hz), 4.40–3.46 (m, 13H, OCH_2, *C*H), 3.37 (d, 1H, *C*H, J=8.0 Hz), 2.05–1.29 (m, 11H, CH_2, CH_3), 1.16 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 209.0 (*C*=O), 169.1 (*C*OOEt), 167.3 (*C*OOEt), 89.4 (*quat-C*), 88.4 (*quat-C*), 70.2 (OCH_2), 69.2 (OCH_2), 68.8 (OCH_2), 67.9 (OCH_2), 64.5 (OCH_2), 63.3 (OCH_2), 61.6 (OCH_2), 50.7 (*C*H), 50.3 (*quat-C*), 50.0 (*C*H), 30.5 (CH_2), 24.8 (CH_2), 21.5 (CH_2), 19.6 (CH_2), 16.3 (CH_3), 13.9 (CH_3). HRMS (ESI^+) Calcd for $C_{22}H_{30}O_{10}Na$ $(M+Na)^+$: 477.1737, found: 477.1741.

4.3.14. Macrocyclic tetralactone (3i). A mixture of α-diazo ketone **1d** (252 mg, 1 mmol) and macrocyclic olefin **2d** (396 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry benzene (50 mL) for 6 h at reflux condition under an argon atmosphere according to the general method C followed by chromatographic purification (80:20 EtOAc–hexane) to afford **3i** (403 mg, 65%) as a colorless oil. IR (neat): ν 2931, 2864, 1729, 1641, 1466, 1373, 1070, 1016, 915, 732 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.25 (s, 2H, =C*H*), 4.39–4.29 (q, 2H, OCH_2), 4.26–3.87 (m, 8H, OCH_2), 3.41 (d, 1H, *C*H, J=10 Hz), 3.33 (d, 1H, *C*H, J=10 Hz), 2.04–1.26 (m, 27H, CH_2, CH_3), 1.20 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 209.0 (*C*=O), 168.9 (*C*OOEt), 167.5 (*C*OOEt), 165.1 (*C*OOEt), 165.0 (*C*OOEt), 129.6 (=*C*H), 89.5 (*quat-C*), 88.3 (*quat-C*), 65.3 (OCH_2), 65.0 (OCH_2), 64.9 (OCH_2), 64.7 (OCH_2), 61.5 (OCH_2), 50.7 (*C*H), 50.3 (*quat-C*), 50.1 (*C*H), 30.4 (CH_2), 28.1 (CH_2), 25.4 (CH_2), 25.1 (CH_2), 24.7 (CH_2), 21.5 (CH_2), 19.5 (CH_2), 16.2 (CH_3), 13.9 (CH_3). HRMS (ESI^+) Calcd for $C_{32}H_{44}O_{12}Na$ $(M+Na)^+$: 643.2730, found: 643.2792.

4.3.15. Macrocyclic tetralactone (3j). A mixture of α-diazo ketone **1e** (238 mg, 1 mmol) and macrocyclic olefin **2d** (396 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at reflux under an argon atmosphere according to the general method B followed by chromatographic purification (80:20 EtOAc–hexane) to afford **3j** (363 mg, 60%) as a colorless oil. IR (neat): ν 2936, 2872, 1745, 1656, 1466, 1373, 1072, 1020, 735 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.24 (s, 2H, =C*H*), 4.35–4.28 (q, 2H, OCH_2, J=8 Hz), 4.26–4.00 (m, 8H, OCH_2), 3.50 (d, 1H, *C*H, J=8 Hz), 3.42 (d, 1H, *C*H, J=8 Hz), 2.17–1.20 (m, 25H, CH_2, CH_3), 1.16 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 212.9 (*C*=O), 169.7 (*C*OOEt), 168.5 (*C*OOEt), 130.3 (=*C*H), 130.0 (=*C*H), 99.6 (*quat-C*), 91.1 (*quat-C*), 65.7 (OCH_2), 65.5 (OCH_2), 62.4 (OCH_2), 59.3 (OCH_2), 51.9 (*C*H), 48.4 (*C*H), 34.9 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 28.4 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 23.3 (CH_2), 19.4 (CH_3), 14.6 (CH_3). HRMS (ESI^+) Calcd for $C_{31}H_{42}O_{12}Na$ $(M+Na)^+$: 629.2574, found: 629.2594.

4.3.16. Macrocyclic tetralactone (3k). A mixture of α-diazo ketone **1c** (180 mg, 1 mmol) and macrocyclic olefin **2e** (372 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (EtOAc) to afford **3k** (314 mg, 60%) as a colorless oil. IR (neat): ν 2944, 2872, 1746, 1447, 1334, 1267, 1217, 1204, 1027, 1004, 735 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.28 (s, 2H, =C*H*), 5.02 (s, 1H, OC*H*), 4.44–4.34 (m, 8H, OCH_2), 3.77–3.65 (m, 8H, OCH_2), 3.43 (d, 1H, *C*H, J=10 Hz), 3.02 (d, 1H, *C*H, J=10 Hz), 1.93–1.20 (m, 8H, CH_2), 1.13 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 215.3 (*C*=O), 170.1 (*C*OOEt), 168.8 (*C*OOEt), 165.0 (*C*OOEt), 129.8 (=*C*H), 129.6 (=*C*H), 90.4 (*quat-C*), 81.7 (O*C*H), 68.7 (OCH_2), 68.5 (OCH_2), 64.5 (OCH_2), 64.1 (OCH_2), 50.7 (*C*H), 50.3 (*quat-C*), 48.1 (*C*H), 30.4 (CH_2), 25.5 (CH_2), 22.0 (CH_2), 19.9 (CH_2), 16.5 (CH_3). HRMS (ESI^+) Calcd for $C_{25}H_{32}O_{12}Na$ $(M+Na)^+$: 547.1791, found: 547.1711.

4.3.17. Macrocyclic tetralactone (3l). A mixture of α-diazo ketone **1b** (166 mg, 1 mmol) and macrocyclic olefin **2d** (396 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (80:20 EtOAc–hexane) to afford **3l** (320 mg, 60%) as a colorless oil. IR (neat): ν 2946, 2870, 1748, 1662, 1370, 1082, 738 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.24 (s, 2H, =C*H*), 4.97 (s, 1H, OC*H*), 4.26–3.99 (m, 8H, OCH_2), 3.48 (d, 1H, *C*H, J=10 Hz), 3.40 (d, 1H, *C*H, J=10 Hz), 2.17–1.20 (m, 22H, CH_2), 1.15 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 212.9 (*C*=O), 169.8 (*C*OOEt), 167.8 (COOEt), 130.2 (=*C*H), 130.0 (=*C*H), 101.0 (*quat-C*), 81.2 (O*C*H), 65.7 (OCH_2), 65.5 (OCH_2), 58.6 (*quat-C*), 51.7 (*C*H), 48.3 (*C*H), 34.9 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 28.4 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 23.3 (CH_2), 19.3 (CH_3). HRMS (ESI^+) Calcd for $C_{28}H_{38}O_{10}Na$ $(M+Na)^+$: 557.2363, found: 557.2393.

4.3.18. Macrocyclic tetralactone (3m). A mixture of α-diazo ketone **1c** (180 mg, 1 mmol) and macrocyclic olefin **2d** (396 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (50 mL) for 6 h at room temperature under an argon atmosphere according to the general method B followed by chromatographic purification (80:20 EtOAc–hexane) to afford **3m** (350 mg, 64%) as a colorless oil. IR (neat): ν 2936, 2868, 1732, 1646, 1464,

1378, 1074, 732 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.24 (s, 2H, =C*H*), 5.00 (s, 1H, OC*H*), 4.26–3.84 (m, 8H, OCH_2), 3.42 (d, 1H, C*H*, *J*=10 Hz), 3.32 (d, 1H, CH, *J*=10 Hz), 2.04–1.20 (m, 24H, CH_2), 1.21 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 209.2 (C=O), 168.9 (COOEt), 167.5 (COOEt), 129.5 (=*C*H), 90.2 (*quat-C*), 81.3 (O*C*H), 65.5 (O*C*H_2), 65.2 (O*C*H_2), 50.5 (*C*H), 50.2 (*quat-C*), 48.3 (*C*H), 30.2 (*C*H_2), 28.0 (*C*H_2), 25.4 (*C*H_2), 25.0 (*C*H_2), 24.8 (*C*H_2), 21.4 (*C*H_2), 19.2 (*C*H_2), 16.2 (*C*H_3). HRMS (ESI^+) Calcd for $C_{29}H_{40}O_{10}Na$ $(M+Na)^+$: 571.2519, found: 571.2522.

4.3.19. Macrocyclic tetralactone (6). A mixture of α-diazo ketone **1c** (432 mg, 2.4 mmol) and macrocyclic olefin **2g** (460 mg, 1 mmol) was allowed to react with 2 mol % of rhodium(II) acetate dimer (8.6 mg) in dry DCM (100 mL) for 6 h at room temperature under an argon atmosphere according to the general method D followed by chromatographic purification (EtOAc) to afford **6** (366 mg, 48%) as a colorless oil. IR (neat): ν 2954, 2872, 1746, 1452, 1269, 1217, 1168, 735 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.01 (s, 2H, OC*H*), 4.36–4.07 (m, 8H, OCH_2), 3.85–3.48 (m, 18H, OCH_2, C*H*), 2.99 (d, 2H, C*H*, *J*=8 Hz), 2.04–1.22 (m, 16H, CH_2), 1.12 (s, 6H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 215.4 (*C*=O), 170.2 (*C*OOEt), 168.9 (*C*OOEt), 90.4 (*quat-C*), 81.6 (O*C*H), 70.4 (O*C*H_2), 69.4 (O*C*H_2), 69.0 (O*C*H_2), 68.2 (O*C*H_2), 64.6 (O*C*H_2), 63.5 (O*C*H_2), 50.6 (*C*H), 50.2 (*quat-C*), 47.9 (*C*H), 30.4 (*C*H_2), 25.5 (*C*H_2), 22.0 (*C*H_2), 19.9 (*C*H_2), 16.4 (*C*H_3). HRMS (ESI^+) Calcd for $C_{38}H_{52}O_{16}Na$ $(M+Na)^+$: 787.3153, found: 787.3011.

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