Regio- and Stereoselective Reductive Coupling of Bicyclic Alkenes with Propiolates Catalyzed by Nickel Complexes: A Novel Route to Functionalized 1,2-Dihydroarenes and γ-Lactones

Dinesh Kumar Rayabarapu and Chien-Hong Cheng*[a]

Abstract: 7-Oxabenzonorbornadienes derivatives **1a–d** underwent reductive coupling with alkyl propiolates $CH_3C{\equiv}CCO_2CH_3$ (**2a**), $PhC{\equiv}CCO_2Et$ (**2b**), $CH_3(CH_2)_3C{\equiv}CCO_2CH_3$ (**2c**), $CH_3(CH_2)_4C{\equiv}CCO_2CH_3$ (**2d**), $TMSC{\equiv}CCO_2Et$ (**2e**), $(CH_3)_3C{\equiv}CCO_2CH_3$ (**2f**) and $HC{\equiv}CCO_2Et$ (**2g**) in the presence of $[NiBr_2(dppe)]$ ($dppe = Ph_2PCH_2CH_2PPh_2$), H_2O and zinc powder in acetonitrile at room temperature to afford the corresponding 2-alkenyl-1,2-dihydronapthalen-1-ol derivatives **3a–n** with remarkable regio- and diastereoselectivity in good to excellent yields. Similarly, the reaction of 7-azabenzonorbornadienes derivative **1e** with propiolates **2a**, **b** and **d** proceeded smoothly to afford reductive coupling products 2-alkenyl-1,2-dihydronapthalene carbamates **3o–p** in good yields with high regio- and stereoselectivity. This nickel-catalyzed reductive coupling can be further extended to the reaction of 7-oxabenzonorbornene derivatives. Thus, 5,6-di(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**4**) reacted with **2a** and **2d** to furnish cyclohexenol derivatives bearing four *cis* substituents **5a** and **b** in 81 and 84% yield, respectively. In contrast to the results of **4** with **2**, the reaction of dimethyl 7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylate (**6**) with propiolates **2a–d** afforded the corresponding reductive coupling/cyclization products, bicyclo[3.2.1]γ-lactones **7a–d** in good yields. The reaction provides a convenient one-pot synthesis of γ-lactones with remarkably high regio- and stereoselectivity.

Keywords: alkenes · cyclization · lactones · nickel · reductive coupling

Introduction

Ring opening addition reaction of bicyclic alkenes is an efficient method for the synthesis of cyclic and acyclic compounds with multiple stereocenters.[1, 2] Nucleophilic ring opening of oxabicyclic alkenes using nucleophiles is well known.[3, 4] Lautens et al. have reported metal-mediated enantioselective ring opening of oxabicyclic alkenes with DIBAL-H, Grignard, organolithium, organozinc and organoboronic acid reagents.[5–8] Previously, we successfully used electrophilic aryl, alkenyl and alkyl halides as reagents for the ring-opening addition of oxabicyclic alkenes in the presence of a palladium[9] or nickel catalysts.[10] In addition, we have shown that terminal acetylenes add to bicyclic alkenes effectively in the presence of nickel complexes to give ring opening addition products.[11] However, to date, no report has appeared on the reductive coupling of alkynes and bicyclic alkenes to afford the ring opening addition products. Very recently, we observed a nickel-catalyzed novel cyclization of oxanorbornadienes with propiolates to give benzocoumarin derivatives (Scheme 1).[12] In an effort to extend this chemistry, we observed a novel reductive coupling of oxa- or azabicyclic alkenes with propiolates in the presence of nickel complexes and zinc metal to give ring opening addition products with remarkable regio- and diastereoselectivity. The reaction is highly atom-economical,[13] an important consideration of modern synthetic chemistry. Moreover, the dihydronapthalene skeleton was found in a wide range of naturally occurring compounds that exhibit diverse biological activities.[14]

Scheme 1.

Results and Discussion

The reaction of 7-oxabenzonorbornadiene (**1a**) with methyl-2-butynoate (**2a**) in the presence of $[NiBr_2(dppe)]$ and zinc powder in acetonitrile at room temperature gave 2-alkenyl-

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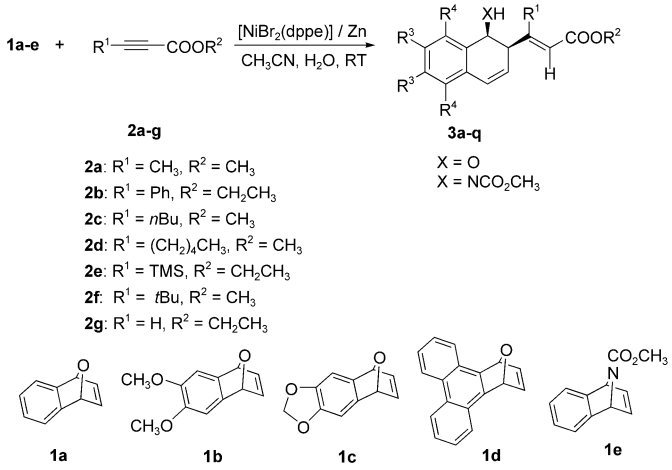
1,2-dihydronapthalen-1-ol (**3a**) in 60% yield. Addition of water (1.5 equiv) greatly increases the yield to 91% (Scheme 2). This new interesting reductive coupling reaction is remarkably regio- and stereoselective. The propiolate moiety is added to **1a** exclusively at the face *cis* to the oxygen atom and the C–C bond formation occurs specifically at the triple bond carbon distal to the ester group of the propiolate.



Scheme 2.

In addition to [$NiBr_2$(dppe)], several other nickel complexes were tested which also showed substantial catalytic activity. [$NiCl_2$(dppe)] and [NiI_2(dppe)] exhibit similar catalytic activity as that of [$NiBr_2$(dppe)] giving **3a** in 87 and 80%, respectively, while [$NiBr_2(PPh_3)_2$], [$NiBr_2$(dppb)], and [$NiBr_2$(dppp)] were less active affording **3a** in 63, 46 and 53% yields, respectively (Table 1, entries 7, 12 and 13). Other nickel complexes [$NiBr_2(nBu_3P)_2$], and [$NiBr_2$(dppf)] gave only a trace of desired product (entries 10 and 11). The solvent used is also crucial in the present catalytic reaction. Among several solvents examined, namely dichloromethane, DMF, THF, toluene and acetonitrile, the latter turned out to be most effective, producing compound **3a** in the highest yield (entries 2–6).

Table 1. Effects of ligands and solvent on the reaction of 7-oxabenzonorbornadiene (**1a**) with methyl but-2-ynoate (**2a**).[a]

	Catalyst	Solvent	Yield [%][b]
1	–	CH_3CN	0
2	[$NiBr_2$(dppe)]	THF	trace
3	[$NiBr_2$(dppe)]	toluene	0
4	[$NiBr_2$(dppe)]	CH_2Cl_2	trace
5	[$NiBr_2$(dppe)]	DMF	0
6	[$NiBr_2$(dppe)]	CH_3CN	95
7	[$NiBr_2(PPh_3)_2$]	CH_3CN	63
8	[$NiCl_2PPh_3)_2$]	toluene	0
9	[$NiCl_2(PPh_3)_2$]	CH_3CN	60
10	[$NiCl_2(nBu_3P)_2$]	CH_3CN	trace
11	[$NiBr_2$(dppf)]	CH_3CN	trace
12	[$NiBr_2$(dppb)]	CH_3CN	46
13	[$NiBr_2$(dppp)]	CH_3CN	53
14	[$NiCl_2$(dppe)]	CH_3CN	87
15	[NiI_2(dppe)]	CH_3CN	80

[a] Unless stated otherwise, all reactions were carried out using Ni catalyst (0.0500 mmol), Zn (2.75 mmol), **1a** (1.0 mmol), **2a** (1.5 mmol), H_2O (1.5 mmol) and solvent (3.0 mL) at room temperature for 16 h under 1 atm N_2. [b] Yields were determined by ^1H NMR spectroscopy with mesitylene as an internal standard.

Under similar reaction conditions, **1a** also underwent reductive coupling with various propiolates ($R^1C{\equiv}CCO_2R^2$). Table 2 summarizes the results of these reactions. Thus, **1a** reacted smoothly with **2b–g** with a phenyl, *n*-butyl, *n*-pentyl, trimethylsilyl, *tert*-butyl or hydrogen group attached to the triple bond of the propiolate, respectively, (Table 1, Scheme 2) to give the corresponding *cis*-1,2-dihydronapthalene derivatives **3b–g** in 59–93% yields. In a similar way, treatment of substituted 7-oxabenzonorbornadienes **1b** and **1c** with different propiolates provided the corresponding reductive coupling products in good to excellent yields (entries 8–12). Furthermore, the reductive coupling can also be applied to the reaction of phenanthrene derivative **1d** with **2a** and **2e** affording *cis*-1,2-dihydrotriphenylenes **3m** and **3n** in 81% and 72% yields, respectively (entries 13 and 14).

Similar to 7-oxabenzonorbornadienes **1a–d**, azabenzonorbornadiene **1e** coupled with propiolates cleanly in the presence of [$NiBr_2$(dppe)], Zn and water to give *cis*-1-aza-2-hydronapthalene derivatives **3o–q** in fair to good yields (entries 15–17). In all these reactions the products show *trans* geometry on the alkenyl groups. The *trans* stereochemistry was established based on the results of NOE experiments and on the coupling constant ($J = 16$ Hz) of the two olefinic protons of product **3g**.

The present catalytic reaction is successfully extended to substituted 7-oxanorbornenes. The reaction of oxabicyclic alkene **4** with **2a** in acetonitrile proceeded efficiently with complete regio- and stereoselectivity to give cyclohexene derivative **5a** with the four substituents on the cyclohexene ring *cis* to each other in 81% yield at room temperature (Scheme 3). Four stereocenters are readily constructed in a single step in this catalytic reaction. Similarly, **4** underwent reductive coupling with propiolate **2d** to give corresponding cyclohexenol derivative **5b** in 84% yield.

Treatment of oxabicyclic alkene **6** bearing two ester groups with propiolate **2a** under similar conditions did not afford the anticipated reductive coupling product, but gave instead a bicyclic γ-lactone **7a** in 87% (Scheme 4, Table 3, entry 1). The structure of this product was characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectra and by the single crystal X-ray diffraction method. The structure determination further confirms the *trans* geometry on the alkenyl substituent. Presumably, the formation of **7a** proceeded via the expected reductive coupling and subsequent lactonization (Scheme 4). Other substituted propiolates **2b–d** also reacted with **6** under similar conditions to afford the corresponding bicyclic γ-lactones **7b–d** in 75–89% yields. It is noteworthy that the skeleton of these bicyclic γ-lactones are useful intermediates in the synthesis of natural products.[15]

The mechanism for this unprecedented reductive en-yne coupling is appealing in view of the observed novel regio- and stereoselectivity.[16] On the basis of the above results and known nickel chemistry, the key pathways are proposed as shown in Scheme 5. The catalysis is initiated by the reduction[17] of Ni^{II} to Ni^0 by zinc powder. *Exo* coordination of 7-oxabenzonorbornadiene and propiolate to the Ni^0 center

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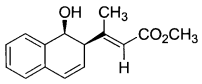
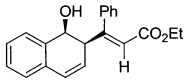
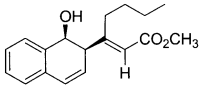
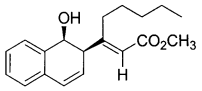
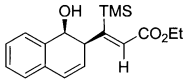
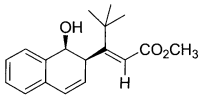
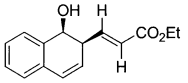
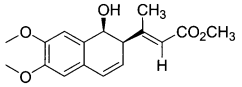
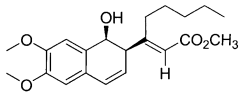
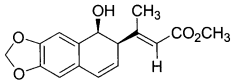
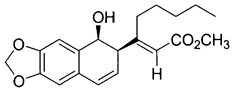
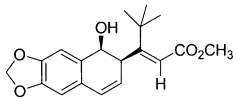
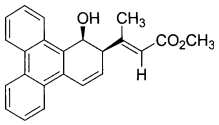
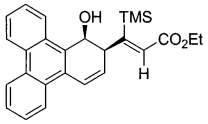
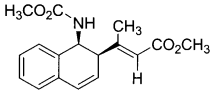
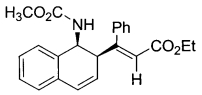
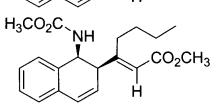
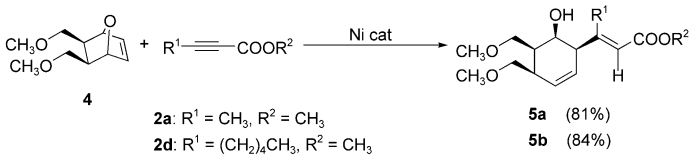
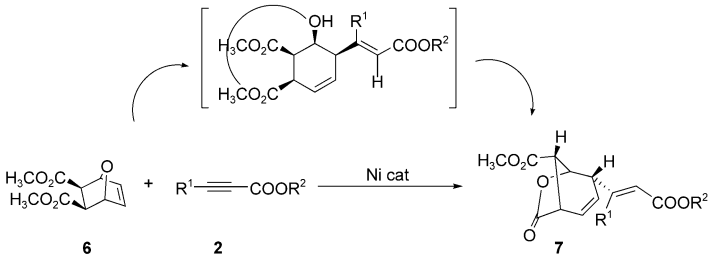
Table 2. Results of nickel-catalyzed reductive coupling of 7-oxa-and 7-azabenzonorbornadienes **1** with propiolates **2**.[a]

	Bicyclic alkene	Alkyl propiolate	Product		Yield [%][b]
1	**1a**	**2a**		**3a**	91
2	**1a**	**2b**		**3b**	70
3	**1a**	**2c**		**3c**	86
4	**1a**	**2d**		**3d**	93
5	**1a**	**2e**		**3e**	76
6	**1a**	**2f**		**3f**	81
7	**1a**	**2g**		**3g**	59
8	**1b**	**2a**		**3h**	85
9	**1b**	**2d**		**3i**	89
10	**1c**	**2a**		**3j**	78
11	**1c**	**2d**		**3k**	80
12	**1c**	**2f**		**3l**	73
13	**1d**	**2a**		**3m**	81
14	**1d**	**2e**		**3n**	72
15	**1e**	**2a**		**3o**	78
16	**1e**	**2b**		**3p**	52
17	**1e**	**2c**		**3q**	74

[a] Unless stated otherwise, all reactions were carried out by using [$NiBr_2$(dppe)] (0.0500 mmol), Zn (2.75 mmol), **1** (1.0 mmol), **2** (1.2–2.0 mmol), H_2O (1.5 mmol) and CH_3CN (3.0 mL) at room temperature for 16 h under 1 atm N_2. [b] Isolated yield.

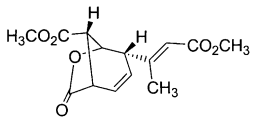
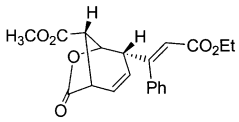
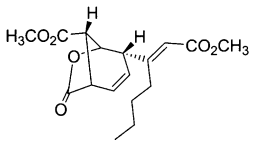
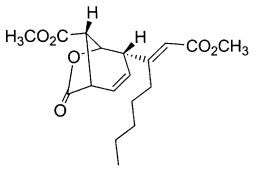


Scheme 3.



Scheme 4.

Table 3. Results of nickel-catalyzed cyclization of bicyclic alkene **6** with propiolates **2**.[a]

	Bicyclic alkene	Alkyl propiolate	Product		Yield [%][b]
1	**6**	**2a**		**7a**	87
2	**6**	**2b**		**7b**	75
3	**6**	**2c**		**7c**	89
4	**6**	**2d**		**7d**	83

[a] Unless stated otherwise, all reactions were carried out using conditions mentioned in Table 2. [b] Isolated yield.

followed by regioselective oxidative coupling of the bicyclic alkene and alkyne ligands leads to the formation of a nickelacyclopentene[18] intermediate **8**. Subsequent β-heteroatom elimination[19] and protonation afford the final product **3** and Ni^{II} species. The latter is then reduced by Zn to regenerate the Ni^0 species. This mechanism accurately accounts for the *cis* stereochemistry of the hydroxy and alkenyl groups and the *trans* geometry on the alkenyl moiety. Support for the protonation of **9** comes from the requirement of water in the reaction. In addition, an isotope labeling experiment using D_2O (99.5%) to replace H_2O in the synthesis of compound **3a** from **1a** and **2a** shows by ^1H NMR analysis that

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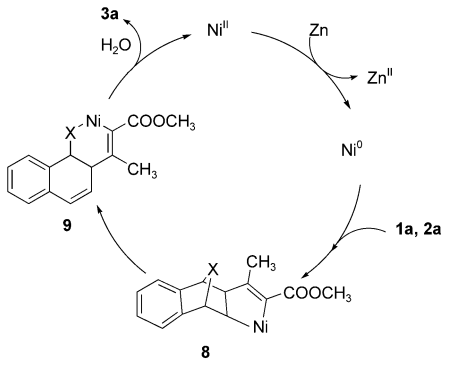
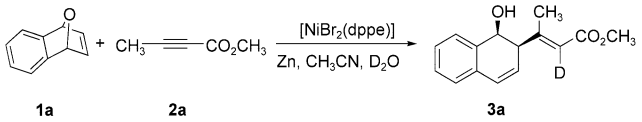


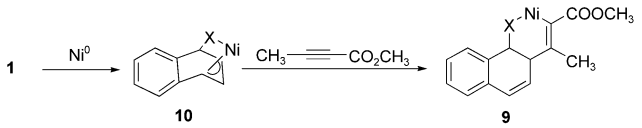
Scheme 5.



Scheme 6.

3a is labeled at the olefinic proton with deuterium-isotope abundance of 75% (Scheme 6).

An alternative pathway involving the formation of key Ni^{II}-(π-allyl) intermediate from oxidative addition of **1** to Ni^0, followed by regioselective insertion of propiolate moiety to π-allyl species and further protonation (Scheme 7) cannot be



Scheme 7.

ruled out completely.[20a] It is known that Ni^{II}-(π-allyl) species can behave as nucleophiles. Michael addition of the π-allyl group on a propiolate leads to the observed regiochemistry. A weak point of this alternative pathway is the stereochemistry of oxidative addition of **1** to Ni^0. In order to obtain the observed stereochemistry of the reductive coupling products, the nickel center should be *cis* to the oxygen atom as shown in intermediate **10**. Most oxidation additions known today, however, show the reverse stereochemistry.[16, 20]

It should be noted that the reaction of **1** with **2** in the presence of [$NiBr_2$(dppe)] and zinc powder in acetonitrile without additional water gave the corresponding coumarin (Scheme 1), if the reaction was carried out at 80 °C instead of room temperature. Studies on the present catalytic reaction of **1** with **2** at ambient temperature (Scheme 2) were originally aimed at detection and isolation of the intermediate for coumarin formation reaction. The observation of reductive coupling product **3** from the reaction of **1** with **2** raises the possibility of **3** as the intermediate for the coumarin formation. However, attempts to convert **3a** into the corresponding coumarin (Scheme 1, $R^1 = Me$) by heating compound **3a** in acetonitrile or under conditions similar to those for the coumarin formation at 80 °C did not give the expected coumarin product. At the present moment, we assume that both coumarin formation (Scheme 1) and reductive coupling (Scheme 2) share the same intermediates that is **8** (or **10**) and **9**. On protonation of intermediate **9**, the reductive coupling product **3** is obtained. In the absence of proper proton source, intermediate **9** will undergo rearrangement and cyclization to give the coumarin product. However, once the reductive coupling product **3** is formed, conversion to the corresponding coumarin does not occur under the catalytic reaction conditions. Further studies on the catalytic mechanisms by isotope labeling experiments and isolation of the catalytic intermediates are currently underway.

Conclusion

In summary, we have developed a novel nickel-catalyzed reductive coupling of bicyclic alkenes with alkynes producing functionalized cyclohexenols and 1,2-dihydroarenes in fair to excellent yields with complete regio- and stereoselectivity. In addition, the reaction proceeds under very mild conditions with high atom economy. Studies on the asymmetric version of this nickel-catalyzed reaction, the scope and application in organic synthesis are in progress.

Experimental Section

All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line by using purified deoxygenated solvents and standard inert atmosphere techniques, unless otherwise stated. Reagents and chemicals were used as purchased without further purification. Oxa- and azabenzonorbornadienes (**1a–e**, **4**, **6**) and alkyl propiolates (**2c**, **f**) were prepared following literature procedures.[21–23] [$NiBr_2$(dppe)$_2$] was synthesized according to a reported procedure.[24]

General procedure for the reductive coupling of 7-oxa and 7-aza benzonorbornadienes 1 with alkyl propiolates 2: A round-bottom side-arm flask (25 mL) containing **1** (1.00 mmol), [$NiBr_2$(dppe)] (0.0500 mmol) and zinc powder (2.50 mmol) was evacuated and purged with nitrogen gas three times. To the flask was added freshly distilled CH_3CN (3.0 mL) and the system was stirred at room temperature until green color appeared in the reaction mixture. Compound **2** (1.2–2.0 mmol) and then water (1.5 mmol) were added and the reaction mixture was further stirred at room temperature for another 16 h. The mixture was then diluted with dichloromethane (20 mL) and stirred in the air for 15 min. The mixture was filtered through a Celite and silica gel pad and washed with dichloromethane. The filtrate was concentrated and the residue was purified on a silica gel column using hexanes/ethyl acetate as eluent to afford the desired reductive coupling products **3**.

Important spectral data for all new compounds are as follows.

Methyl (*E*)-3-[(1*S,2*R**)-1-hydroxy-1,2-dihydro-2-naphthalenyl]-2-butenoate (3a)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.24$ (d, $J = 1.2$ Hz, 3H), 3.29–3.31 (m, 1H), 3.68 (s, 3H), 4.80 (d, $J = 4.6$ Hz, 1H), 5.88 (dd, $J = 2.8$, 9.6 Hz, 1H), 5.93 (d, $J = 0.8$ Hz, 1H), 6.63 (dd, $J = 2.8$, 9.6 Hz, 1H), 7.12 (dd, $J = 1.2$, 7.2 Hz, 1H), 7.25–7.29 (m, 2H), 7.36 (dd, $J = 1.6$, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 18.5$, 50.9, 51.0, 69.2, 118.2, 126.6, 127.0, 127.0, 128.0, 128.4, 128.6, 131.9, 135.7, 157.2, 166.8; HRMS: *m*/*z*: calcd for $C_{15}H_{16}O_3$: 244.1099; found: 244.1098.

Ethyl (*Z*)-3-[(1*S,2*R**)-1-hydroxy-1,2-dihydro-2-naphthalenyl]-3-phenyl-2-propenoate (3b)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.07$ (t, $J =$ 7.2 Hz, 3H), 3.67–3.68 (m, 1H), 3.98–4.02 (m, 2H), 4.45 (dd, $J = 1.2$, 4.6 Hz, 1H), 6.08 (dd, $J = 2.8$, 9.6 Hz, 1H), 6.18 (d, $J = 0.8$ Hz, 1H), 6.69 (dd, $J = 2.8$, 9.6 Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 1H), 7.21–7.30 (m, 5H), 7.35–7.38 (m, 3H,); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 13.8$, 50.5, 59.9, 67.9, 120.3, 126.7, 126.8, 127.4, 127.8, 127.9, 128.0, 128.1, 128.5, 128.8, 131.8, 135.3,

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139.8, 156.5, 165.9; HRMS: m/z: calcd for $C_{21}H_{20}O_3$: 320.1412; found: 320.1411.

Methyl (*E*)-3-[(1*S,2*R**)-1-hydroxy-1,2-dihydro-2-naphthalenyl]-2-heptenoate (3c)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 7.2$ Hz, 3H), 1.35 – 1.40 (m, 2H), 1.45 – 1.51 (m, 2H), 2.26 – 2.35 (m, 1H), 3.07 – 3.15 (m, 1H), 3.37 – 3.39 (m, 1H), 3.67 (s, 3H), 4.70 (d, $J = 4.6$ Hz, 1H), 5.83 (ddd, $J = 0.8$, 2.8, 9.6 Hz, 1H), 5.91 (s, 1H), 6.62 (dd, $J = 2.8$, 9.6 Hz, 1H), 7.13 (dd, $J = 1.6$, 7.2 Hz, 1H), 7.24 – 7.31 (m, 2H), 7.34 (dd, $J = 1.6$, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 13.7$, 22.9, 31.0, 32.2, 49.0, 50.8, 68.6, 118.0, 126.6, 127.6, 127.8, 127.9, 128.2, 128.6, 131.9, 135.3, 161.7, 166.4; HRMS: m/z: calcd for $C_{18}H_{22}O_3$: 286.1568; found: 286.1568.

Methyl (*E*)-3-[(1*S,2*R**)-1-hydroxy-1,2-dihydro-2-naphthalenyl]-2-octenoate (3d)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 3.2$ Hz, 3H), 1.30 – 1.34 (m, 4H), 1.50 – 1.53 (m, 2H), 1.79 (d, $J = 6.4$ Hz, 1H), 2.23 – 2.34 (m, 1H), 3.07 – 3.15 (m, 1H), 3.39 – 3.42 (m, 1H), 3.69 (s, 3H), 4.71 (t, $J =$ 5.6 Hz, 1H), 5.86 (ddd, $J = 1.2$, 2.8, 9.6 Hz, 1H), 5.92 (s, 1H), 6.64 (dd, $J =$ 2.8, 9.6 Hz, 1H), 7.14 (dd, $J = 1.6$, 7.2 Hz, 1H), 7.25 – 7.35 (m, 2H), 7.37(dd, $J = 1.6$, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 13.9$, 22.3, 28.7, 32.1, 32.5, 49.1, 50.9, 68.6, 118.1, 126.7, 127.7, 127.9, 128.0, 128.3, 128.8, 132.0, 135.2, 161.8, 166.4; HRMS m/z: calcd for $C_{19}H_{24}O_3$: 300.1726; found: 300.1725.

Ethyl (*Z*)-3-[(1*S,2*S**)-1-hydroxy-1,2-dihydro-2-naphthalenyl]-3-(1,1,1-trimethylsilyl)-2-propenoate (3e)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.28$ (s, 9H), 1.30 (t, $J = 6.8$ Hz, 3H), 1.59 (m, 1H), 3.81 (m, 1H), 4.17 – 4.21 (m, 2H), 4.54 (m, 1H), 5.88 (dd, $J = 2.8$, 9.6 Hz, 1H), 6.58 (s, 1H), 6.66 (dd, $J =$ 2.8, 9.6 Hz, 1H), 7.16 (d, $J = 7.2$ Hz, 1H), 7.25 – 7.36 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = -0.15$, 14.1, 47.7, 60.3, 68.8, 126.7, 127.9, 127.9, 128.1, 128.9, 129.6, 132.0, 133.2, 134.6, 162.2, 166.3; HRMS: m/z: calcd for $C_{18}H_{24}O_3Si$: 316.1494; found: 316.1496.

Methyl (*Z*)-3-[(1*S,2*R**)-1-hydroxy-1,2-dihydro-2-naphthalenyl]-4,4-dimethyl-2-pentenoate (3f)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.27$ (s, 9H), 1.94 (d, $J = 6.2$ Hz, 1H,), 3.64 – 3.65 (m, 1H), 3.71 (s, 3H), 4.63 (m, 1H), 5.89 (dd, $J = 2.8$, 9.6 Hz, 1H), 5.92 (s, 1H), 6.58 (dd, $J = 2.8$, 9.6 Hz, 1H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.25 – 7.33 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 29.1$, 37.5, 45.0, 51.5, 69.0, 119.6, 126.6, 127.2, 127.9, 128.2, 128.8, 131.3, 131.8, 134.6, 156.6, 169.0; HRMS: m/z: calcd for $C_{18}H_{22}O_3$: 286.1568; found: 286.1568.

Ethyl (*E*)-3-[(1*S,2*R**)-1-hydroxy-1,2-dihydro-2-naphthalenl]-2-propenoate (3g)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.27$ (td, $J = 1.2$, 7.2 Hz, 3H), 3.91 (m, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 4.86 (d, $J = 4.8$ Hz, 1H), 5.88 (ddd, $J = 1.2$, 2.4, 9.6 Hz, 1H,), 6.05 (d, $J = 16$ Hz, 1H), 6.60 (dd, $J = 2.4$, 9.6 Hz, 1H), 7.02 (dd, $J = 6.8$, 16.0 Hz, 1H), 7.11 – 7.13 (m, 1H), 7.26 – 7.28 (m, 2H), 7.38 – 7.41 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 14.4$, 44.3, 60.6, 70.6, 124.5, 126.5, 126.8, 126.9, 128.4, 128.6, 128.7, 132.3, 136.3, 145.5, 166.3; HRMS: m/z: calcd for $C_{15}H_{16}O_3$: 244.1099; found: 244.1101.

Methyl (*E*)-3-[(1*S,2*R**)-1-hydroxy-6,7-dimethoxy-1,2-dihydro-2-naphthalenyl]-2-butenoate (3h)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.69$ (m, 1H), 2.27 (s, 3H), 3.26 – 3.29 (m, 1H), 3.69 (s, 3H), 3.87 (s, 3H), 3.90 (s, 3H), 4.72 (t, $J = 6.4$ Hz, 1H), 5.79 (dd, $J = 2.8$, 9.2 Hz, 1H), 5.94 (s, 1H), 6.54 (dd, $J = 2.8$, 9.2 Hz, 1H), 6.67 (s, 1H), 6.92 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 18.7$, 50.9, 51.3, 56.0, 69.1, 110.1, 110.9, 118.2, 125.0, 125.0, 127.9, 128.4, 148.6, 148.9, 157.5, 166.8; HRMS: m/z: calcd for $C_{17}H_{20}O_5$: 304.1311; found: 304.1311.

Methyl (*E*)-3-[(1*S,2*R**)-1-hydroxy-6,7-dimethoxy-1,2-dihydro-2-naphthalenyl]-2-octenoate (3i)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.84$ (t, $J = 7.2$ Hz, 3H), 1.21 – 1.33 (m, 4H), 1.46 – 1.50 (m, 2H), 2.23 – 2.26 (m, 1H), 3.04 – 3.07 (m, 1H), 3.33 (m, 1H), 3.65 (s, 3H), 3.84 (s, 3H), 3.86 (s, 3H), 4.60 (t, $J = 5.2$ Hz, 1H), 5.71 (dd, $J = 2.4$ Hz, 9.6 Hz, 1H), 5.89 (s, 1H), 6.50 (dd, $J = 2.4$, 9.6 Hz, 1H), 6.64 (s, 1H), 6.88 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 13.8$, 22.3, 28.6, 32.0, 32.5, 49.3, 50.8, 55.9, 68.5, 110.1, 111.4, 118.0, 125.0, 125.9, 127.8, 128.0, 148.5, 149.0, 162.0, 166.6; HRMS: m/z: calcd for $C_{21}H_{28}O_5$: 360.1937; found: 342.1826 $[M - H_2O]^+$.

Methyl (*E*)-3-[(5*S,6*R**)-5-hydroxy-5,6-dihydronaphtho[2,3-*d*][1,3]dioxol-6-yl]-2-butenoate (3j)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.99$ (m, 1H), 2.21 (s, 3H), 3.20 – 3.22 (m, 1H), 3.65 (s, 3H), 4.63 (t, $J = 5.2$ Hz, 1H), 5.74 (dd, $J = 2.8$, 9.6 Hz, 1H), 5.88 (s, 1H), 5.89 (s, 2H), 6.46 (dd, $J = 2.8$, 9.6 Hz, 1H), 6.58 (s, 1H), 6.82 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta =$ 18.6, 50.8, 51.0, 69.2, 101.0, 107.1, 108.2, 118.1, 125.1, 126.3, 128.0, 129.9, 146.9, 147.4, 157.3, 166.8; HRMS: m/z: calcd for $C_{16}H_{16}O_5$: 288.0997; found: 270.0892 $[M - H_2O]^+$.

Methyl (*E*)-3-[(5*S,6*R**)-5-hydroxy-5,6-dihydronaphtho[2,3-*d*][1,3]dioxol-6-yl]-2-octenoate (3k)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.86$ (t, $J = 7.2$ Hz, 3H), 1.27 – 1.33 (m, 4H), 1.45 – 1.50 (m, 2H), 2.21 – 2.24 (m, 1H), 3.03 – 3.06 (m, 1H), 3.31 (m, 1H), 3.65 (s, 3H), 4.55 (t, $J = 4.8$ Hz, 1H), 5.71 (dd, $J = 2.4$, 9.6 Hz, 1H), 5.88 (s, 1H), 5.90 (s, 2H), 6.47 (dd, $J = 2.4$, 9.6 Hz, 1H), 6.59 (s, 1H), 6.82 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 13.9$, 22.3, 28.6, 32.0, 32.5, 49.1, 50.8, 68.7, 101.0, 107.1, 108.7, 118.0, 126.0, 126.4, 127.9, 129.5, 146.8, 147.6, 161.8, 166.4; HRMS: m/z: calcd for $C_{20}H_{24}O_5$: 344.1623; found: 344.1625.

Methyl (*Z*)-3-[(5*S,6*R**)-5-hydroxy-5,6-dihydronaphtho[2,3-*d*][1,3]dioxol-6-yl]-4,4-dimethyl-2-pentenoate (3l)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.24$ (s, 9H), 2.15 (s, 1H), 3.56 – 3.58 (m, 1H), 3.69 (s, 3H), 4.48 (t, $J =$ 4.8 Hz, 1H), 5.66 (dt, $J = 1.2$, 9.6 Hz, 1H), 5.90 (s, 1H), 5.93 (s, 2H), 6.46(dd, $J = 2.4$, 9.6 Hz, 1H), 6.61 (s, 1H), 6.83 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 29.0$, 37.4, 45.1, 51.4, 69.1, 101.0, 107.0, 109.0, 119.6, 126.3, 126.9, 128.8, 129.6, 146.8, 147.6, 156.6, 169.1; HRMS: m/z: calcd for $C_{19}H_{22}O_5$: 330.1467; found: 330.1466.

Methyl (*E*)-3-[(1*S,2*R**)-1-hydroxy-1,2-dihydro-2-triphenylenyl]-2-butenoate (3m)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.92$ (d, $J = 6.8$ Hz, 1H), 2.44 (s, 3H), 3.30 (m, 1H), 3.74 (s, 3H), 5.40 (t, $J = 5.6$ Hz, 1H), 6.15 (s, 1H), 6.17 (dd, $J = 2.4$, 9.6 Hz, 1H), 7.39(dd, $J = 2.4$, 9.2 Hz, 1H), 7.61 – 7.68 (m, 4H), 8.16 – 8.27 (m, 2H), 8.64 – 8.68 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 19.3$, 50.9, 51.1, 65.1, 118.2, 122.9, 122.9, 123.5, 123.5, 123.8, 125.9, 126.4, 126.8, 127.0, 127.2, 128.2, 128.3, 128.5, 129.4, 130.4, 130.5, 157.7, 166.9; HRMS: m/z: calcd for $C_{23}H_{20}O_3$: 344.1413; found: 344.1411.

Ethyl (*Z*)-3-[(1*S,2*S**)-1-hydroxy-1,2-dihydro-2-triphenylenyl]-3-(1,1,1-trimethylsilyl)-2-propenoate (3n)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.34 (s, 9H), 1.33 (t, $J = 6.8$ Hz, 3H), 1.74 (m, 1H), 3.87 – 3.88 (m, 1H), 4.22 – 4.26 (m, 2H), 5.30 (s, 1H), 6.24 (dd, $J = 2.8$, 9.2 Hz, 1H), 6.78 (s, 1H), 7.50 (dd, $J = 2.8$, 9.6 Hz, 1H), 7.63 – 7.69 (m, 4H), 8.23(td, $J = 1.2$, 7.2 Hz, 2H), 8.73 (dt, $J = 1.2$, 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 0.1$, 14.5, 48.3, 60.6, 64.7, 123.3, 123.3, 123.7, 123.8, 124.2, 126.2, 126.7, 127.1, 127.6, 128.7, 128.8, 130.0, 130.8, 130.9, 131.4, 133.8, 162.7, 166.9; HRMS: m/z: calcd for $C_{26}H_{28}O_3Si$: 416.1808; found: 416.1807.

Methyl (*E*)-3-(1*S,2*R**)-1-[(methoxycarbonyl)amino]-1,2-dihydro-2-naphthalenyl-2-butenoate (3o)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.14$ (s, 3H), 3.37 (s, 1H), 3.60 (s, 3H), 3.75 (s, 3H), 4.96 – 5.02 (m, 1H), 5.11 – 5.18 (m, 1H), 5.80 (s, 1H), 5.88 (dd, $J = 2.8$, 9.6 Hz, 1H), 6.61 (dd, $J = 2.8$, 9.6 Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 7.21 – 7.25 (m, 2H), 7.30(d, $J = 7.2$ Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 18.2$, 48.9, 50.5, 50.8, 52.1, 118.2, 126.2, 126.6, 127.1, 128.1,128.3, 129.1, 132.1, 134.5, 156.4, 156.7, 166.5; HRMS: m/z: calcd for $C_{17}H_{19}NO_4$: 301.1314; found: 301.1312.

Ethyl (*Z*)-3-(1*S,2*R**)-1-[(methoxycarbonyl)amino]-1,2-dihydro-2-naphthalenyl-3-phenyl-2-propenoate (3p)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.01$ (t, $J = 6.8$ Hz, 3H), 3.58 (s, 3H), 3.75 – 3.77 (m, 1H), 3.95 (q, $J =$ 6.8 Hz, 2H), 4.81 – 4.83 (m, 1H), 5.07 (dd, $J = 2.8$, 9.6 Hz, 1H), 6.00 (s, 1H), 6.04 (dd, $J = 2.8$, 9.2 Hz, 1H), 6.67 (dd, $J = 2.4$, 7.2 Hz, 1H), 6.93 – 6.95 (m, 1H), 7.08 – 7.24 (m, 5H), 7.30 – 7.36 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 13.8$, 48.6, 50.1, 52.0, 59.9, 66.1, 120.4, 125.0, 126.7, 127.0, 127.4, 127.9, 128.3, 129.5, 131.7, 134.6, 139.6, 143.9, 156.1, 165.8; HRMS: m/z: calcd for $C_{23}H_{23}NO_4$: 377.1627; found: 377.1624.

Methyl (*E*)-3-(1*S,2*R**)-1-[(methoxycarbonyl)amino]-1,2-dihydro-2-naphthalenyl-2-octenoate (3q)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.8$ Hz, 3H), 1.24 – 1.30 (m, 4H), 1.40 – 1.44 (m, 2H), 2.18 – 2.22 (m, 1H), 3.02 – 3.07 (m, 1H), 3.44 (m, 1H), 3.57 (s, 3H), 3.65 (s, 3H), 4.96 (d, $J = 7.6$ Hz, 1H), 5.02 – 5.06 (m, 1H), 5.73 (s, 1H), 5.84 (dd, $J = 3.2$, 9.6 Hz, 1H), 6.60 (dd, $J = 3.2$, 9.6 Hz, 1H), 7.09 (dd, $J = 1.6$, 7.2 Hz, 1H), 7.21 – 7.31 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 13.9$, 22.3, 28.7, 32.0, 32.5, 46.9, 50.5, 50.9, 52.1, 117.7, 126.6, 127.0, 128.1, 128.3, 129.0, 132.0, 134.3, 156.3, 161.7, 166.3; HRMS: m/z: calcd for $C_{21}H_{27}NO_4$: 357.1941; found: 357.1940.

Methyl (*E*)-3-[(1*R,4*R**,5*S**,6*S**)-6-hydroxy-4,5-di(methoxymethyl)-2-cyclohexenyl]-2-octenoate (5b)**: oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 7.2$ Hz, 3H), 1.23 – 1.35 (m, 4H), 1.41 – 1.47 (m, 2H), 2.12 – 2.19 (m, 1H), 2.35 (m, 1H), 2.52 – 2.55 (m, 1H), 2.97 (s, 1H), 3.01 – 3.08 (m, 1H), 3.33 (s, 3H), 3.35 (s, 3H), 3.39 (d, $J = 3.6$ Hz, 2H), 3.52 (dd, $J = 2.4$, 6.8 Hz, 2H), 3.64 (s, 3H), 3.91 (m, 1H), 5.54 (dd, $J = 2.8$, 9.2 Hz, 1H), 5.60 (s, 1H), 5.74 (dt, $J = 2.8$, 9.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 14.0$, 22.5, 28.6, 32.2, 32.4, 36.0, 41.7, 49.4, 50.7, 58.8, 64.2, 70.9, 72.8, 117.1, 127.9, 129.3, 164.3, 166.8; HRMS: m/z: calcd for $C_{19}H_{32}O_5$: 340.2250; found: 340.2249.

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Methyl (1*R,4*R**,5*S**,8*R**)-4-[(*E*)-3-methoxy-1-methyl-3-oxo-1-propenyl]-7-oxo-6-oxabicyclo[3.2.1]oct-2-ene-8-carboxylate (7a)**: solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.21$ (s, 3H), 3.06 (s, 1H), 3.27–3.32 (m, 2H), 3.64 (s, 3H), 3.73 (s, 3H), 5.06 (s, 1H), 5.65 (s, 1H), 5.73 (dt, $J = 2.4$, 9.6 Hz, 1H), 6.21 (ddd, $J = 2.4$, 7.2, 9.6 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta =$ 18.0, 39.6, 50.9, 51.1, 51.7, 52.7, 78.5, 118.5, 126.6, 129.4, 153.3, 166.3, 170.1, 173.7; HRMS: *m*/*z*: calcd for $C_{14}H_{16}O_6$: 280.0946; found: 280.0946.

Methyl (1*R,4*R**,5*S**,8*R**)-4-[(*E*)-1-butyl-3-methoxy-3-oxo-1-propenyl]-7-oxo-6-oxabicyclo[3.2.1]oct-2-ene-8-carboxylate (7c)**: solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7.2$ Hz, 3H), 1.38–1.45 (m, 4H), 2.18–2.21 (m, 1H), 3.00–3.06 (m, 1H), 3.08 (s, 1H), 3.30–3.35 (m, 2H), 3.64 (s, 3H), 3.74 (s, 3H), 5.03 (s, 1H), 5.60 (s, 1H), 5.70 (dd, $J = 2.4$, 9.6 Hz, 1H), 6.21 (ddd, $J = 2.4$, 7.2, 9.6 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta =$ 13.8, 22.9, 31.0, 31.4, 39.6, 49.2, 50.9, 51.9, 52.8, 78.0, 118.4, 126.5, 130.0, 157.2, 166.1, 170.1, 173.8; HRMS: *m*/*z*: calcd for $C_{17}H_{22}O_6$: 322.1416; found: 322.1416.

Methyl (1*R,4*R**,5*S**,8*R**)-4-[(*E*)-3-methoxy-3-oxo-1-pentyl-1-propenyl]-7-oxo-6-oxabicyclo[3.2.1]oct-2-ene-8-carboxylate (7d)**: solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 6.8$ Hz, 3H), 1.31–1.34 (m, 4H), 1.41–1.44 (m, 2H), 2.18–2.24 (m, 1H), 3.01–3.06 (m, 1H), 3.08 (s, 1H), 3.30–3.35 (m, 2H), 3.64 (s, 3H), 3.74 (s, 3H), 5.03 (s, 1H), 5.60 (s, 1H), 5.71 (dd, $J = 2.4$, 9.2 Hz, 1H), 6.21 (ddd, $J = 2.4$, 7.6, 9.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta =$ 13.9, 22.3, 28.6, 31.6, 32.0, 39.6, 49.2, 50.9, 51.9, 52.8, 78.0, 118.4, 126.5, 130.0, 157.2, 166.1, 170.1, 173.7; HRMS: *m*/*z*: calcd for $C_{18}H_{24}O_6$: 336.1572; found: 336.1570.

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[25] CCDC-202107 (**7a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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