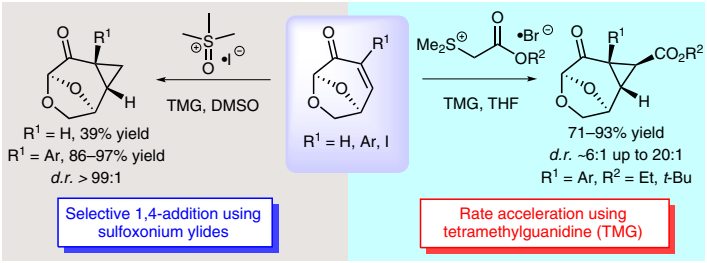
Synthesis E. T. Ledingham et al. Paper

Stereoselective Cyclopropanation of (–)-Levoglucosenone Derivatives Using Sulfonium and Sulfoxonium Ylides

Edward T. Ledingham[a]
Christopher J. Merritt[a]
Christopher J. Sumby[b]
Michelle K. Taylor[a]
Ben W. Greatrex*[a]

[a] School of Science and Technology, University of New England, Armidale, New South Wales, 2351, Australia
ben.greatrex@une.edu.au
[b] Department of Chemistry, School of Physical Sciences, The University of Adelaide, Adelaide, South Australia, 5005, Australia



Received: 26.01.2017
Accepted after revision: 20.02.2017
Published online: 17.03.2017
DOI: 10.1055/s-0036-1588971; Art ID: ss-2017-t0052-op

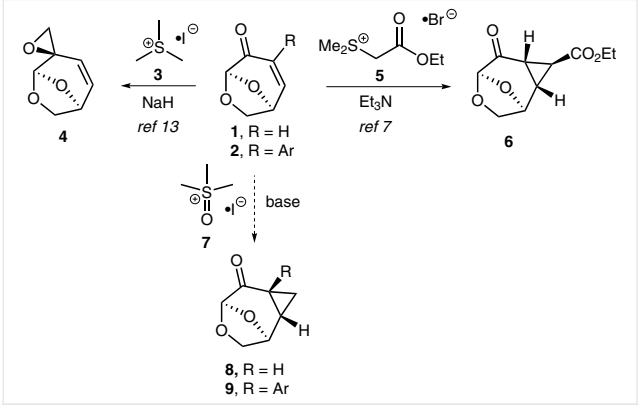
Abstract The synthesis of tri- and tetrasubstituted cyclopropanes from 3-aryl-substituted levoglucosenones (LGO) has been developed. In contrast to the unstabilised ylide dimethylsulfonium methylide which gives epoxides from LGO via 1,2-addition, we have found that the soft nucleophile dimethylsulfoxonium methylide affords cyclopropanes in moderate yields from LGO and in excellent yields and stereoselectivity with 3-aryl LGO derivatives. The use of 1,1,3,3-tetramethylguanidine as base in DMSO to generate the ylide provided the best yields and shortest reaction times. Ester stabilised sulfonium ylides could also be used to generate tetrasubstituted cyclopropane derivatives. One of the products was converted into a cyclopropyl lactone via Baeyer–Villiger oxidation to demonstrate the utility of applying cyclopropanation chemistry to LGO.

Key words levoglucosenone, cyclopropane, ylide, enone, conjugate addition

(–)-Levoglucosenone (**1**, LGO) is a readily available and versatile chiral synthon derived from abundant lignocellulose in a single step.[1] Although carbohydrate-derived, **1** lacks the multiple chiral centres that can reduce the general utility of carbohydrates in synthesis. The attraction of **1** as a biorenewable synthon has stimulated the development of a variety of chemistries for the enone functionality including metal-mediated coupling reactions,[2] conjugate addition,[3] cycloadditions,[4,5] as well as cyclopropanation reactions.[5] Cyclopropanation of the double bond in **1** is attractive due to the versatility of the cyclopropane in synthesis and as it could enable the synthesis of a variety of chiral bioactive cyclopropane derivatives.[6] Previous strategies for the cyclopropanation of the alkene in **1** have employed diazomethane[5] and sulfonium ylide chemistry[7] as well as Michael-initiated ring-closure reactions with diethyl bromomalonate,[8] however, the substitution patterns of products accessible from **1** are still limited.

We have recently reported Heck and Suzuki–Miyaura arylation reactions using **1**,[2] producing species such as **2**, and envisaged that these products could be used to prepare cyclopropane-containing bioactives. We have previously approached these targets starting with **1** using an intramolecular ring-closure reaction on an epoxide derivative.[9] The epoxide ring-closure approach has also been used by Doris et al. for the synthesis of levomilnacipran,[10] while we were able to complete a formal synthesis of PCCG-4 and some $GABA_C$ agonists using **1**.[9] The Johnson–Corey–Chaykovsky reaction[11,12] was considered as an alternative reaction to expand the types of products that can be accessed starting with **1**.

The Johnson–Corey–Chaykovsky reaction of **1** with dimethylsulfonium methylide generated from iodide **3** is known to generate epoxide **4** in 50% yield through 1,2-at-



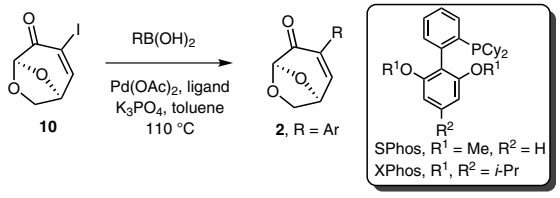
Scheme 1 Reactions of **1** and **2** with sulfonium and sulfoxonium ylides

tack with insignificant formation of cyclopropane via 1,4-addition (Scheme 1).[13] A report by Samet et al. detailed the reactions of **1** with stabilised ylides, generated by reaction of the corresponding bromide salt **5** with triethylamine.[7] These reactions afforded cyclopropyl derivatives **6** exclusively and the reactions were highly diastereoselective. As found in the reactions of **1** with other nucleophiles,[3] conjugate addition occurred on the least hindered α-face. The products were then converted into chiral γ-butyrolactones via a Baeyer–Villiger oxidation further demonstrating the utility of **1** as a chiral starting material.[14] These reports are consistent with previous reactions of sulfonium ylides with α,β-unsaturated enones; the unstabilised reagent **3** prefers 1,2-addition leading to epoxides and the stabilised reagents, such as **5**, prefer 1,4-addition affording cyclopropanes.[11] The dimethylsulfoxonium cation is a more effective stabilising group than the dimethylsulfonium group and cyclopropanation of enones occurs more readily using ylides generated from trimethylsulfoxonium iodide (**7**) compared to **3**.[11] However, no literature reports have examined the reactions of **1** or derivatives such as **2** with the methylide generated from **7**. Previously reported X-ray structures suggested that the aryl group in **2b** and **2c** twists out of plane with the enone to avoid unfavourable steric interactions.[2] We theorised that the twisted arene would block the carbonyl and promote 1,4-addition instead of 1,2-attack. We now report our investigations on the cyclopropanation of **1** and aryl derivatives **2a–g** using sulfoxonium and ester stabilised sulfur ylides.

The preparation of 3-aryl derivatives **2a–g** proceeded in good yield via the Suzuki–Miyaura reaction of iodide **10** with boronic acids using Buchwald ligands (Table 1). Our previous report on the preparation of these adducts used conventional heating,[2] however, there is ample evidence that microwave irradiation drastically shortens reaction times for Pd-catalysed cross-coupling reactions.[15] We have modified the conditions using microwave irradiation and have found a large reduction in the reaction times with comparable yields. For reference, the results are presented in Table 1. In these modified conditions, Cs_2CO_3 was replaced with K_3PO_4 which contributed to the higher yield obtained for the parent arene **2a**.

The reactions of dimethylsulfoxonium methylide with substrates **1**, **2a–g**, and **10** are shown in Table 2. Cyclopropane **8** has previously been synthesised from **1** by Novikov et al. in a 3 step process, which involved Luche reduction of the ketone in **1** followed by reaction with diazomethane and then oxidation to regenerate the ketone.[5] The cyclopropanation of **1** with sulfoxonium methylide generated from **7** using NaH afforded mainly oligomeric products. 1,1,3,3-Tetramethylguanidine (TMG) in acetonitrile/water has been reported as an effective promoter of cyclopropanation reactions using the stabilised sulfonium salt **5** and so we attempted the reaction of **7** and enone **1** using this base.[16]

Table 1 Synthesis of 3-Aryldioxabicyclo[3.2.1]oct-2-en-ones **2a–i** Using Microwave Irradiation[a]



Entry	R	Ligand	Time (min) [ref 2]	Product	Yield (%) [ref 2]
1[b]	Ph	XPhos	80	**2a**	60
2[c]		SPhos	60 [18 h]	**2a**	90 [61]
3	4-$MeOC_6H_4$	XPhos	10	**2b**	84
4		SPhos	10 [1.5 h]	**2b**	88 [89]
5	3,4-$(OCH_2O)C_6H_4$	SPhos	30 [1.5 h]	**2c**	72 [85]
6	2-FC_6H_4	SPhos	10 [16 h]	**2d**	75 [88]
7	2,3,4-$F_3C_6H_2$	SPhos	40 [3 h]	**2e**	63 [74]
8	4-$F_3CC_6H_4$	SPhos	40	**2f**	72
9[d]	2-$HC(O)C_6H_4$	SPhos	90 [24 h]	**2g**	49 [53]
10	4-MeC_6H_4	SPhos	30	**2h**	74
11	2-naphthyl	SPhos	30	**2i**	94

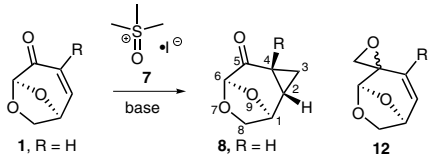
[a] Conditions: **10** (1.5 mmol), $RB(OH)_2$ (1.5 equiv), K_3PO_4 (2 equiv), $Pd(OAc)_2$ (1 mol%), ligand (2 mol%), solvent (100 mg/mL).
[b] $RB(OH)_2$ (1.2 equiv).
[c] Reaction scaled up to **10** (6.0 mmol).
[d] $Pd(OAc)_2$ (5 mol%) and SPhos (10 mol%).

No products were obtained using acetonitrile as solvent, however, the reaction in DMSO afforded 39% of the target cyclopropane **8** confirmed by matching the spectroscopic data with the literature (Table 2, entry 1).[5] This single step synthesis of **8** does not compare to the 83% overall yield reported by Novikov et al. although it does avoid the hazardous preparation of diazomethane and is faster.

The majority of the reactions used to determine optimal conditions for the cyclopropanation reaction using **7** were carried out on **2a** (Table 2). A dramatic solvent dependence was observed with low yields of cyclopropane obtained in THF and toluene and in contrast to the reactions of **1**, the reaction of **2a** gave a good yield in acetonitrile. Again, reaction outcomes were superior in DMSO in terms of speed and yield (entries 2, 3, 6, and 7 vs. 8 and 9). The choice of base was found to be important and TMG gave better yields of **9a** than NaOH and NaH (not shown), which both led to a second epoxidation step following cyclopropanation, especially if **7** was used in excess (entries 4 and 5). Applying these optimised conditions to the enone series **2b–g** afforded excellent yields (86–97%) for all cyclopropyl products. Pleasingly, even vinyl iodide **10** afforded cyclopropane **11** albeit in lower yield. No epoxide **12** was observed in any of the reactions involving **7** and TMG in DMSO. The reactions were highly stereoselective due to the preferential addition of the ylide to the α-face and no diastereomers were seen in any reactions involving sulfoxonium salt **7**. The product stereochemistry was confirmed using the single-crystal X-ray structure of cyclopropane **9b** (Figure 1).

The importance of using the sulfoxonium ylide derived from **7** can be seen when contrasted with the reaction of trimethylsulfonium ylide derived from **3** with **2a**. Epoxide **12a** formed through 1,2-addition was not observed using the sulfoxonium ylide; however, the reaction of **2a** with **3** and NaH was dominated by epoxide **12a** (R = Ph) and only

Table 2 Cyclopropanation of **1**, **2**, and **10** Using Sulfoxonium Ylide Generated from **7**[a]



1, R = H
2, R = Ar
10, R = I

8, R = H
9, R = Ar
11, R = I

12

Entry	Substrate	R	Base	Solvent	Temp (°C)	Time (h)	Product	Yield (%)
1[b]	**1**	H	TMG	DMSO	50	2	**8**	39
2[c,d]	**2a**	Ph	TMG	toluene	110	8	**9a**	11
3			TMG	THF	25	3.5		<5[e]
4[c]			NaOH	THF	70	60		17
5[d,f]			NaOH	THF	70	3		32
6			TMG	acetone	25	95[g]		40
7			TMG	MeCN	25	73		73
8			TMG	DMSO	25	2.25		97
9[h]			TMG	DMSO	25	3.25		95
10[d,f]	**2b**	4-MeOC$_6$H$_4$	NaOH	THF	70	2.5	**9b**	37
11[b]			NaH	THF	70	36		50
12			TMG	DMSO	25	2		96
13	**2c**	3,4-(OCH$_2$O)C$_6$H$_4$	TMG	DMSO	25	2	**9c**	86
14	**2d**	2-FC$_6$H$_4$	TMG	DMSO	25	2.5	**9d**	95
15	**2e**	2,3,4-F$_3$C$_6$H$_2$	TMG	DMSO	25	2.5	**9e**	90
16	**2f**	4-F$_3$CC$_6$H$_4$	TMG	DMSO	25	3.5	**9f**	97
17	**2h**	4-MeC$_6$H$_4$	TMG	DMSO	25	2	**9h**	91
18	**2i**	2-naphthyl	TMG	DMSO	25	2	**9i**	94
19	**10**	I	TMG	DMSO	25	2	**11**	46

[a] Conditions: **2** or **10** (0.43 mmol), **7** (1.1 equiv), base (1.1 equiv), solvent (3 mL), 25 °C, under N$_2$.
[b] **1** (0.86 mmol) in DMSO (5 mL).
[c] Base (1.5 equiv) and **7** (1.5 equiv).
[d] Microwave irradiation used.
[e] Percentage composition based on GC spectrum.
[f] Base (1.05 equiv) and **7** (1.05 equiv).
[g] Reaction terminated before completion.
[h] Reaction scaled up to 2.5 mmol of **2a**.

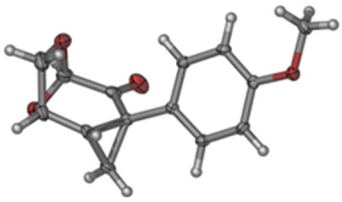
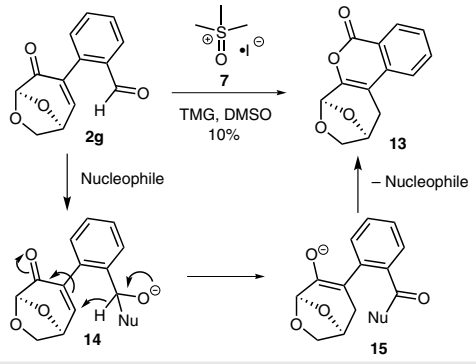


Figure 1 Single-crystal X-ray structure (50% probability ellipsoids) of **9b**

small amounts of cyclopropane **9a** were observed [23:67 **9a**/**12** (R = Ph)].

The reaction of aromatic aldehyde **2g** with sulfoxonium salt **7** and TMG afforded lactone **13** and no observed cyclopropane (Scheme 2). The reaction product presumably resulted from a nucleophilic addition to the aromatic aldehyde in **2g** giving intermediate **14**. An intramolecular hydride transfer from **14** gave an activated ester **15** which reacted with the enolate oxygen affording the observed product **13**. There is literature precedence for this type of reaction which can also be catalysed by N-heterocyclic carbenes and cyanide.[17]



Scheme 2 Formation of lactone **13** from **2g**

The possible nucleophilic species in the reaction include the sulfoxonium ylide, iodide, DMSO, TMG, or possibly the compound itself. The omission of **7** from the mixture did not improve the yield of **13** ruling out TMG and DMSO while sodium iodide in DMSO also failed to catalyse the formation of **13**. Attempted catalysis using cyanide gave only trace amounts of **13** and so we have not been able to identify the nucleophile in this reaction.

Cyclopropanation reactions of **2a–g** with the stabilised sulfur ylides derived from **5** and **20** are shown in Table 3. Although there is literature precedence for this type of reaction using **1**, there are no examples in the literature using more substituted derivatives.[7] The reaction of **2a** with **5** promoted by triethylamine proved sluggish with only 7% conversion to **16a** (by GCMS) after 29 h at 70 °C (entry 1). A significant increase in reaction rate was observed upon switching from triethylamine to TMG, providing a 93% yield of **16a** in 18 h (Table 3, entry 3). The minor isomer visible in crude reaction mixtures of ethyl ester **5** resulted from approach of the enone to the more hindered β-face. Performing the reaction with microwave heating at 110 °C in THF at 2.5 bars afforded cyclopropane **16a** in low yield and greatly reduced time as well as the byproduct ethyl 2-(methylthio)acetate (**21**) (entry 2). When the temperature was reduced to 70 °C using conventional heating, a negligible quantity of **21** was detected. Payne has suggested that the formation of **21** is due to decomposition of the in situ generated ylide which shows considerable thermal instability.[18]

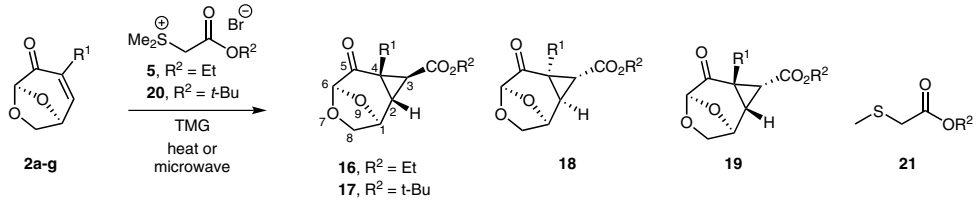
In addition to facial selectivity, two possible stereoisomers can result from the ring-closure step of the cyclopropanation reaction. The ratio depends on which face of the ylide approaches the enone, the relative stability and rate of epimerisation for the intermediates and the rate of ring-closure. To determine whether steric bulk played a role in the reaction outcome, the *tert*-butyl ester **20**[19] was prepared and used in the reactions using microwave heating giving cyclopropanes **17a–g** in good to excellent yields.

A change in the minor isomer was observed in some of the reactions of **2a** with the bulky *tert*-butyl ylide precursor **20**. The major and minor products obtained from reactions of **2a–e** with bulky **20** were both derived from approach of the ylide to the less-hindered α-face. Interestingly, the reactions of **2f** and **2g** with **20** resulted in minor isomers that were assigned as **18f** and **18g** on the basis of the observed small coupling constants (*vide infra*). We conclude that the *tert*-butyl ester group generally promoted reaction at the less hindered α-face. Furthermore, reactions of stabilised sulfonium ylides were much faster using microwave irradiation.

The stereochemistry of the ester group at C3 in **16a–c** and **17a–g** was assigned on the basis of small coupling constants (~4.8 Hz) between H2 and H3 in the ^{1}H NMR spectra consistent with a *trans*-relationship. Supporting the stereochemical assignment, the 2D NOESY NMR of **17f** was found to be consistent with the major isomers. A crosspeak was observed between H2 (δ = 2.56) with the *ortho*-protons of the aromatic ring (δ = 7.42) and H8-β (δ = 4.28) confirming the relative stereochemistry at C2 and C4. NOESY crosspeaks between the *tert*-butyl group (δ = 1.20) with H2 and the *ortho*-protons of the aromatic ring confirmed the relative conformation of C3.

It was not possible to isolate the minor isomers **18** or **19** although they were visible by NMR in crude reaction mixtures prior to chromatography. The relative stereochemistry of the minor isomers **18** and **19** were assigned using $J_{H2\text{-}H3}$ values in crude NMRs. The minor isomer **18** had a small *trans* $J_{H2\text{-}H3}$ coupling, the same as **16** and **17**, from which we concluded that approach of the nucleophile had occurred from the β-face. The minor isomers from reactions of *tert*-butyl ester **20** with **2a–e** had relatively large $J_{H2\text{-}H3}$ couplings, from which we concluded that they were epimeric

Table 3 Cyclopropanation of **2a–g** Using Stabilised Sulfonium Ylides Derived from **5** and **20**[a]

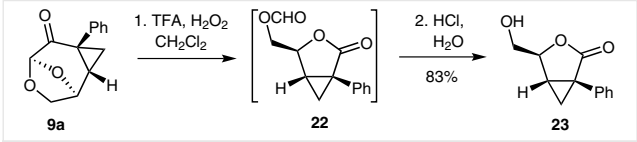


Entry	Substrate	R^1	R^2	Temp (°C)	Time (h)	Yield (%)	Ratio[b]
1[c]	**2a**	Ph	Et	70	29	7	–[d], **16a**/**18a**
2[e]			Et	110	0.8	34	92:8, **16a**/**18a**
3			Et	70	18	93	90:10, **16a**/**18a**
4[e,f]			*t*-Bu	110	0.7	81	90:10, **17a**/**19a**
5	**2b**	4-$MeOC_6H_4$	Et	70	18	76	87:13, **16b**/**18b**
6[e,g]			*t*-Bu	70	0.8	84	95:5, **17b**/**19b**
7	**2c**	3,4-$(OCH_2O)C_6H_4$	Et	70	18	64	92:8, **16c**/**18c**
8[e]			*t*-Bu	70	0.2	71	89:11, **17c**/**19c**
9[e,h]	**2d**	2-FC_6H_4	*t*-Bu	70	0.8	85	87:13, **17d**/**19d**
10[e]	**2e**	2,3,4-$F_3C_6H_2$	*t*-Bu	70	0.5	89	86:14, **17e**/**19e**
11[e]	**2f**	4-$F_3CC_6H_4$	*t*-Bu	70	0.5	91	89:11, **17f**/**18f**
12[e,h]	**2g**	2-$HC(O)C_6H_4$	*t*-Bu	70	1	36	92:8, **17g**/**18g**

[a] Conditions: **2a–g** (0.43 mmol), **5** or **20** (1.5 equiv), TMG (1.5 equiv), THF (3 mL), N_2 atmosphere.
[b] Ratios were determined from crude NMR spectra.
[c] Et_3N was used as base.
[d] Not determined.
[e] Microwave irradiation used.
[f] Sulfonium salt **20** (1.5 equiv total) was added portionwise every 10 min.
[g] Sulfonium salt **20** (1.8 equiv) was used.
[h] Sulfonium salt **20** (2.5 equiv) was used.

to the major isomers only at C3. For example, **19d** from the reaction of **2d** with **20** was fairly well resolved and exhibited a large coupling ($J_{H2\text{-}H3}$ = 8.6 Hz) in the ^1H NMR spectrum which was consistent with a *cis*-relationship between H2 and H3.

In order to demonstrate the utility of the cyclopropanation chemistry, the Baeyer–Villiger reaction of cyclopropane **9a** to give a 2-cyclopropyl-γ-butyrolactone **23** was examined (Scheme 3). Baeyer–Villiger oxidations of dioxabicyclo[3.2.1]octan-4-ones requires the removal of residual peroxide followed by the addition of acid to cleave the intermediate formyl ester **22** which can be complicated when the solubility of the product in water is high. The mild workup we have developed for these reactions involves the addition of a Pd/C hydrogenation catalyst which acts as a surface to slowly and cleanly decompose the peroxyacid and hydrogen peroxide. Subsequent filtration and treatment with a dilute solution of HCl which can be removed under reduced pressure affords the hydroxymethyl lactone. Cyclopropane **9a** was fairly unreactive with peracetic acid due to the hindered ketone, however, the powerful oxidant trifluoroperacetic acid generated in situ from hydrogen peroxide and trifluoroacetic acid afforded lactone **23** in an excellent yield of 83%. Derivatives of the 1-aryl-1-carboxycyclopropane motif in the product are found in CNS active compounds[6b] such as (+)-MR200[20] and milnacipran[10] demonstrating possible uses for this chemistry.



Scheme 3 Preparation of lactone **23** from cyclopropane **9a**

In conclusion, we have developed conditions for a high yielding and enantioselective synthesis of cyclopropyl derivatives from LGO. The use of DMSO and TMG was critical to achieve high yields and short reaction times and the sulfoxonium salt was found to be highly selective for 1,4-addition. This work has extended the use of TMG as an efficient base for the Johnson–Corey–Chaykovsky cyclopropanation to sulfoxonium salt **7**. We have shown proof of principle conversion through to the aryl-substituted cyclopropyl lactone **23** and are now examining the use of these compounds for the preparation of bioactive targets.

Solvents were dried using literature procedures.[21] Levoglucosenone (**1**) was obtained from Circa Group (Melbourne, Australia). All other reagents are commercially available and were used as purchased. ^{1}H NMR spectra were referenced to TMS δ = 0.0 and ^{13}C NMR were referenced to solvent $CDCl_3$, δ = 77.0; DMSO-d_6, δ = 39.5.[22] Melting points are uncorrected. HRMS were recorded in positive ASAP or ESI mode. NMR were assigned using COSY, NOESY, HSQC, and HMBC experiments. The synthesis of **2a–e** and **2g** has been previously described.[2] Sulfonium and sulfoxonium halides **3**,[11,23] **5**,[7,24] **7**,[11,25] and **20**[19] were prepared using literature procedures. Microwave reactions were carried out using an Anton-Paar Monowave 300 at set temperature.

Suzuki Reactions Promoted by Microwave Irradiation; General Procedure

Iodide **10** (1.5 mmol), boronic acid (2.25 mmol), K_3PO_4 (3.0 mmol), $Pd(OAc)_2$ (0.015 mmol), SPhos (0.03 mmol), toluene (3.80 mL), and an internal standard *n*-hexadecane (100 μL) were sealed in a 10-mL microwave pressure vessel and heated using microwave irradiation for 10 min intervals as specified in Table 1 until all starting material was consumed (GC/MS). The mixture was filtered then concentrated under reduced pressure and the product purified as specified.

(1*S*,5*R*)-3-[4-(Trifluoromethyl)phenyl]-6,8-dioxabicyclo[3.2.1]oct-2-en-4-one (2f)

Purified via flash column chromatography (EtOAc/hexanes, 3:17) then recrystallized (*i*-Pr_2O) to afford light brown crystals (296 mg, 72%); R_f = 0.27 (EtOAc/hexanes, 3:17); mp 105–107 °C; $[\alpha]_D^{20}$ –209 (*c* 0.55, $CHCl_3$).

FT-IR (neat): 2967, 2903, 2327, 1692, 1613, 1475, 1411, 1359, 1324, 1276, 1163, 1105, 1063, 1034, 1013, 988, 892, 838 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.65–7.53 (m, 4 H), 7.34 (d, *J* = 4.9 Hz, 1 H), 5.52 (s, 1 H), 5.19 (dd, *J* = 4.9, 4.7 Hz, 1 H), 3.98 (dd, *J* = 6.9, 4.7 Hz, 1 H), 3.88 (d, *J* = 6.9 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 187.3, 144.2, 136.7, 136.1, 130.7 (q, *J* = 32.6 Hz), 128.6, 125.3 (q, *J* = 3.8 Hz), 125.0, 101.6, 72.5, 66.6.

MS (EI): *m*/*z* (%) = 242 (64), 197 (100), 196 (34), 183 (27), 177 (100), 171 (42), 129.1 (66), 128.1 (57), 127 (27), 115 (44).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}O_3F_3$: 271.0577; found: 271.0593.

(1*S*,5*R*)-3-(*p*-Tolyl)-6,8-dioxabicyclo[3.2.1]oct-2-en-4-one (2h)

Purified via flash column chromatography (EtOAc/hexanes, 1:4) then recrystallized (*i*-Pr_2O) to afford fine white crystals (240 mg, 74%); R_f = 0.47 (EtOAc/hexanes, 1:4); mp 121–123 °C; $[\alpha]_D^{29}$ –223 (*c* 1.8, $CHCl_3$).

FT-IR (neat): 3034, 2989, 2954, 2893, 1700, 1507, 1358, 1337, 1306, 1285, 1105, 1072, 1032, 985, 828 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.33–7.31 (m, 2 H), 7.24 (d, *J* = 4.8 Hz, 1 H), 7.20–7.18 (m, 2 H), 5.49 (s, 1 H), 5.14 (dd, *J* = 4.8, 4.7 Hz, 1 H), 3.94 (dd, *J* = 6.8, 4.7 Hz, 1 H), 3.85 (d, *J* = 6.8 Hz, 1 H), 2.36 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 188.1, 142.2, 138.7, 136.9, 130.3, 129.1, 128.0, 101.8, 72.6, 66.7, 21.2.

MS (EI): *m*/*z* (%) = 188.1 (18), 171.1 (22), 144.1 (22), 143.1 (100), 142.1 (26), 141.1 (28), 129.1 (37), 128.1 (59), 127.1 (23), 115.1 (40).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_3$: 217.0859; found: 217.0870.

(1*S*,5*R*)-3-(Naphthalen-2-yl)-6,8-dioxabicyclo[3.2.1]oct-2-en-4-one (2i)

Purified via flash column chromatography (EtOAc/hexanes, 3:7) then recrystallized (*i*-Pr_2O) to afford a tan powder (356 mg, 94%); R_f = 0.55 (EtOAc/hexanes, 1:4); mp 70–72 °C; $[\alpha]_D^{31}$ –140 (*c* 1.7, $CHCl_3$).

FT-IR (neat): 3052, 2966, 2909, 1688, 1592, 1502, 1350, 1333, 1105, 1070, 877, 852, 813, 739, 640 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.98 (br s, 1 H), 7.87–7.83 (m, 3 H), 7.51–7.49 (m, 3 H), 7.39 (d, *J* = 4.9 Hz, 1 H), 5.56 (s, 1 H), 5.21 (dd, *J* = 4.9, 4.5 Hz, 1 H), 3.99 (dd, *J* = 6.7, 4.5 Hz, 1 H), 3.91 (d, *J* = 6.7 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 188.1, 143.2, 137.0, 133.2, 133.1, 130.6, 128.4, 128.0, 127.8, 127.6, 126.6, 126.3, 125.6, 101.8, 72.7, 66.7.

MS (EI): *m*/*z* (%) = 252.1 (11) [M]$^+$, 221.1 (11), 195.1 (9), 180.1 (16), 179.1 (100), 178.1 (41), 177.1 (12), 167.1 (14), 165.1 (28), 152.1 (21).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{16}H_{11}O_3$: 251.0714; found: 251.0713.

(1*S*,2*S*,4*R*,6*R*)-7,9-Dioxatricyclo[4.2.1.0^{2,4}]nonan-5-one (8)[5]

To a stirred solution of trimethylsulfoxonium iodide (**7**, 212 mg, 0.96 mmol) in dry DMSO (3 mL) under a N_2 atmosphere was added TMG (122 μL, 0.97 mmol). After 10 min the temperature was raised to 50 °C by immersion of the flask into a heated oil bath and LGO **1** (84 μL, 0.86 mmol) dissolved in DMSO (2 mL) was added dropwise over 2 min. After stirring for 4 h, the product was isolated via repeated flash column chromatography (EtOAc/hexanes, 1:4) to afford a colourless oil (47 mg, 39%); R_f = 0.62 (EtOAc/hexanes, 3:7).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.96 (s, 1 H), 4.86 (d, *J* = 4.6 Hz, 1 H), 4.02 (d, *J* = 7.0 Hz, 1 H), 3.88 (dd, *J* = 7.0, 4.9 Hz, 1 H), 1.72 (br ddd, *J* = 10.7, 7.0, 4.9 Hz, 1 H), 1.54 (dddd, *J* = 7.0, 7.0, 5.1, 1.2 Hz, 1 H), 1.44 (ddd, *J* = 5.1, 4.9, 4.9 Hz, 1 H), 1.14 (ddd, *J* = 10.7, 7.0, 4.7 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 197.3, 100.0, 71.4, 68.6, 20.1, 14.9, 9.2.

MS (EI): *m*/*z* (%) = 94.1 (47), 81.1 (24), 70.1 (33), 67.1 (36), 66.1 (100), 65.1 (26), 55.1 (72), 53.1 (43), 41.1 (33), 39.1 (42).

Cyclopropanation Reactions of 2a–i Using 7; General Procedure

To a stirred solution of enone **2** (0.43 mmol) and trimethylsulfoxonium iodide (**7**, 0.48 mmol) in DMSO (3 mL) under N_2 was added TMG (0.48 mmol). After 3 h, when no starting material remained (GC/MS), the solution was diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic fractions were then combined and dried ($MgSO_4$), concentrated under reduced pressure, and the product was further purified as specified.

(1*S*,2*S*,4*R*,6*R*)-4-Phenyl-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonan-5-one (9a)

Purified via flash column chromatography (EtOAc/hexanes, 3:17) then dried under reduced pressure. Recrystallization (*i*-Pr_2O) afforded clear colourless crystals (0.508 g, 2.35 mmol, 95%); R_f = 0.33 (EtOAc/hexanes, 3:17); mp 92–94 °C; $[\alpha]_D^{20}$ –173 (*c* 0.48, $CHCl_3$).

FT-IR (neat): 2960, 2900, 1717, 1604, 1498, 1447, 1380, 1350, 1321, 1259, 1160, 1116, 1093, 1080, 1060, 1011, 934, 902 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.34–7.26 (m, 5 H), 5.11 (s, 1 H), 4.96 (dd, *J* = 4.6, 1.4 Hz, 1 H), 4.24 (d, *J* = 6.9 Hz, 1 H), 3.99 (dd, *J* = 6.9, 4.6 Hz, 1 H), 1.82 (br dd, *J* = 5.2, 5.2 Hz, 1 H), 1.73 (br ddd, *J* = 7.6, 5.2, 1.4 Hz, 1 H), 1.55 (br dd, *J* = 7.6, 5.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 196.7, 137.7, 129.5, 128.5, 127.6, 99.9, 72.0, 68.9, 34.8, 23.0, 14.7.

MS (EI): *m*/*z* (%) = 170.1 (32), 143.1 (25), 142.1 (100), 141.1 (96), 129.1 (41), 128.1 (52), 115.1 (44), 103.1 (27), 91.1 (28), 77.1 (23).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_3$: 217.0865; found: 217.0870.

(1*S*,2*S*,4*R*,6*R*)-4-(4-Methoxyphenyl)-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonan-5-one (9b)

Purified via flash column chromatography (EtOAc/hexanes, 1:4) then recrystallized (*i*-Pr_2O) to afford light yellow crystals (102.0 mg, 96%); R_f = 0.59 (EtOAc/hexanes, 1:4); mp 110–111 °C; $[\alpha]_D^{20}$ –243 (*c* 0.7, $CHCl_3$).

FT-IR (neat): 2966, 2914, 2848, 1719, 1609, 1514, 1467, 1440, 1348, 1331, 1288, 1246, 1179, 1161, 1115, 1094, 1063, 1023, 1002, 930 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.19–7.17 (m, 2 H), 6.84–6.86 (m, 2 H), 5.10 (s, 1 H), 4.95 (dd, *J* = 4.5, 1.3 Hz, 1 H), 4.22 (d, *J* = 6.9 Hz, 1 H), 3.98 (dd, *J* = 6.9, 4.5 Hz, 1 H), 3.78 (s, 3 H), 1.79 (dd, *J* = 5.3, 4.9 Hz, 1 H), 1.70 (ddd, 7.6, 5.3, 1.3 Hz, 1 H), 1.50 (dd, *J* = 7.6, 4.9 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 197.2, 159.0, 130.7, 129.8, 113.9, 99.8, 72.0, 68.9, 55.3, 34.2, 23.0, 15.0.

MS (EI): *m*/*z* (%) = 246.1 (87) [M]$^+$, 200.1 (59), 173.1 (79), 172.1 (100), 159.1 (58), 158.1 (52), 157.1 (62), 129.1 (61), 128.1 (53), 115.1 (60).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}O_4$: 247.0965; found: 247.0969.

(1*S*,2*S*,4*R*,6*R*)-4-(1,3-Benzodioxol-4-yl)-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonan-5-one (9c)

Purified via flash column chromatography (EtOAc/hexanes, 3:17) to afford an amber waxy solid (96 mg, 86%); R_f = 0.28 (EtOAc/hexanes, 3:17); $[\alpha]_D^{20}$ –140 (*c* 0.8, $CHCl_3$).

FT-IR (neat): 2967, 2898, 1714, 1607, 1503, 1489, 1442, 1377, 1349, 1331, 1311, 1247, 1222, 1168, 1116, 1034, 1011, 929, 901 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.75–6.70 (m, 3 H), 5.93 (s, 2 H), 5.08 (s, 1 H), 4.93 (br d, *J* = 4.2 Hz, 1 H), 4.20 (d, *J* = 6.9 Hz, 1 H), 3.97 (br dd, *J* = 6.9, 4.2 Hz, 1 H), 1.77 (br dd, *J* = 5.3, 4.6 Hz, 1 H), 1.69 (br dd, *J* = 7.1, 4.6 Hz, 1 H), 1.48 (br dd, *J* = 7.1, 5.3 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 196.9, 147.6, 147.1, 131.5, 122.8, 110.3, 108.1, 101.1, 99.8, 71.9, 68.9, 34.6, 23.1, 15.0.

MS (EI): *m*/*z* (%) = 260.1 (100), 187.1 (37), 186.1 (100), 185.1 (57), 173.1 (37), 145.1 (34), 143.1 (37), 129.1 (44), 128.1 (85), 115.1 (70).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}O_5$: 261.0763; found: 261.0764.

(1*S*,2*S*,4*R*,6*R*)-4-(2-Fluorophenyl)-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonan-5-one (9d)

Purified via flash column chromatography (EtOAc/hexanes, 3:17) then recrystallized (*i*-Pr_2O) to give light yellow crystals (96.0 mg, 95%); R_f = 0.31 (EtOAc/hexanes, 3:17); mp 142–143 °C; $[\alpha]_D^{20}$ –195 (*c* 0.8, $CHCl_3$).

FT-IR (neat): 2969, 2900, 1715, 1614, 1578, 1490, 1445, 1377, 1346, 1324, 1271, 1252, 1209, 1162, 1117, 1106, 1059, 1031, 1012, 776 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.30–7.25 (m, 2 H), 7.11 (br dd, *J* = 7.5, 7.5 Hz, 1 H), 7.03 (br dd, *J* = 9.1, 9.1 Hz, 1 H), 5.11 (s, 1 H), 4.95 (br d, *J* = 4.4 Hz, 1 H), 4.33 (d, *J* = 6.7 Hz, 1 H), 3.98 (br dd, *J* = 6.7, 4.4 Hz, 1 H), 1.95 (br dd, *J* = 5.4, 4.8 Hz, 1 H), 1.77 (br dd, *J* = 7.1, 4.8 Hz, 1 H), 1.54 (br dd, *J* = 7.1, 5.4 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 196.1, 161.8 (d, J_{CF} = 247 Hz), 132.2 (d, J_{CF} = 3.1 Hz), 129.7 (d, J_{CF} = 8.4 Hz), 125.0 (d, J_{CF} = 14.2 Hz), 124.0 (d, J_{CF} = 3.6 Hz), 115.5 (d, J_{CF} = 21.4 Hz), 99.7, 71.8, 68.2, 30.2 (d, J_{CF} = 1.3 Hz), 22.7, 14.9.

MS (EI): *m*/*z* (%) = 204 (14) [M – CH_2O]$^+$, 186.1 (14), 157.9 (100), 145 (35), 134.1 (13), 133.3 (12), 131.9 (23), 120.2 (15), 119.4 (16), 107.7 (20).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{12}O_3F$: 235.0765; found: 235.0779.

(1*S*,2*S*,4*R*,6*R*)-4-(2,3,4-Trifluorophenyl)-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonan-5-one (9e)

Purified via flash column chromatography (EtOAc/hexanes, 1:4) to afford an amber oil (104 mg, 90%); R_f = 0.41 (EtOAc/hexanes, 1:4); $[\alpha]_D^{20}$ –143 (*c* 0.91, $CHCl_3$).

FT-IR (neat): 2971, 2903, 1718, 1630, 1611, 1513, 1478, 1379, 1350, 1327, 1292, 1280, 1268, 1234, 1202, 1154, 1115, 1081, 1040, 1016, 998, 905 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.00–6.91 (m, 2 H), 5.10 (s, 1 H), 4.95 (br d, *J* = 4.2 Hz, 1 H), 4.29 (d, *J* = 6.9 Hz, 1 H), 3.98 (br dd, *J* = 6.9, 4.2 Hz, 1 H), 1.97 (br dd, *J* = 5.5, 4.5 Hz, 1 H), 1.79 (br dd, *J* = 7.1, 4.5 Hz, 1 H), 1.50 (br dd *J* = 7.1, 5.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 195.2, 151.7 (ddd, J_{CF} = 26.2, 9.9, 3.2 Hz), 149.7 (ddd, J_{CF} = 26.2, 9.9, 3.2 Hz), 139.7 (ddd, J_{CF} = 250.4, 15.2, 15.2 Hz), 125.5 (ddd, J_{CF} = 7.9, 3.8, 3.8 Hz), 122.4 (dd, J_{CF} = 11.7, 3.6 Hz), 111.9 (dd, J_{CF} = 17.5, 3.8 Hz), 99.5, 71.6, 68.2, 29.7, 22.6, 15.0.

MS (EI): *m*/*z* (%) = 239.5 (33) [M – CH_2O]$^+$, 195.8 (35), 193.8 (100), 193.6 (50), 182.1 (37), 180.5 (69), 175.3 (32), 167.4 (56), 154.9 (55), 143.8 (78).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}O_3F_3$: 271.0577; found: 271.0581.

(1*S*,2*S*,4*R*,6*R*)-4-[4-(Trifluoromethyl)phenyl]-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonan-5-one (9f)

Purified via flash column chromatography (EtOAc/hexanes, 3:17) to afford an amber oil (119 mg, 97%); R_f = 0.26 (EtOAc/hexanes, 3:17); $[\alpha]_D^{20}$ –120 (*c* 2.0, $CHCl_3$).

FT-IR (neat): 2968, 2908, 1724, 1617, 1408, 1322, 1255, 1161, 1112, 1069, 1011 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.59–7.57 (m, 2 H), 7.39–7.37 (m, 2 H), 5.12 (s, 1 H), 4.97 (br, d, *J* = 3.9 Hz, 1 H), 4.22 (d, *J* = 6.9 Hz, 1 H), 4.00 (br dd, *J* = 6.9, 3.9 Hz, 1 H), 1.88 (br dd, *J* = 5.9, 4.9 Hz, 1 H), 1.76 (br dd, *J* = 6.9, 4.9 Hz, 1 H), 1.56 (br dd, *J* = 6.9, 5.9 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 195.8, 141.5, 129.9, 129.8 (q, J_{CF} = 32.5 Hz), 125.5 (q, J_{CF} = 3.8 Hz), 124.0 (q, J_{CF} = 272 Hz), 99.8, 71.8, 68.9, 34.4, 23.0, 14.9.

MS (EI): *m*/*z* (%) = 253.3 (14) [M – CH_2O]$^+$, 235.6 (21), 207.9 (100), 175.3 (18), 169.3 (18), 157.3 (21), 149.6 (16), 139.9 (44), 127.1 (18), 126.3 (17).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{12}O_3F_3$: 285.0739; found: 285.0749.

(1*S*,2*S*,4*R*,6*R*)-4-(*p*-Tolyl)-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonan-5-one (9h)

Purified via flash column chromatography (EtOAc/hexanes, 1:4) then recrystallized (*i*-Pr_2O) to afford fine white crystals (90.5 mg, 91%); R_f = 0.47 (EtOAc/hexanes, 1:4); mp 121–123 °C; $[\alpha]_D^{29}$ –223 (*c* 1.80, $CHCl_3$).

FT-IR (neat): 3034, 2989, 2954, 2893, 1700, 1507, 1358, 1337, 1306, 1285, 1105, 1072, 1032, 985, 828 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.16–7.12 (m, 4 H), 5.10 (s, 1 H), 4.94 (br dd, *J* = 4.5, 1.5 Hz, 1 H), 4.22 (d, *J* = 6.9 Hz, 1 H), 3.98 (dd, *J* = 6. 9, 4.5 Hz, 1 H), 2.32 (s, 3 H), 1.80 (br dd, *J* = 5.3, 5.0 Hz, 1 H), 1.70 (br ddd, *J* = 7.6, 5.3, 1.5 Hz, 1 H), 1.52 (dd, *J* = 7.6, 5.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 197.0, 137.4, 134.7, 129.4, 129.2, 99.9, 72.0, 68.9, 34.5, 23.0, 21.1, 14.8.

MS (EI): *m*/*z* (%) = 188.1 (18), 171.1 (22), 144.1 (22), 143.1 (100), 142.1 (26), 141.1 (28), 129.1 (37), 128.1 (59), 127.1 (23), 115.1 (40).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}O_3$: 231.1016; found: 231.1030.

(1*S*,2*S*,4*R*,6*R*)-4-(Naphthalen-2-yl)-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonan-5-one (9i)

Purified via flash column chromatography (EtOAc/hexanes, 3:7) then recrystallized (*i*-Pr_2O) to afford a tan powder (108 mg, 94%); R_f = 0.55 (EtOAc/hexanes, 1:4); mp 70–72 °C; $[\alpha]_D^{31}$ –140 (*c* 1.7, $CHCl_3$).

FT-IR (neat): 3052, 2966, 2909, 1688, 1592, 1502, 1350, 1333, 1105, 1070, 877, 852, 813, 739, 640 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.81–7.78 (m, 3 H), 7.68 (s, 1 H), 7.47–7.45 (m, 2 H), 7.39 (dd, *J* = 8.5, 1.6 Hz, 1 H), 5.15 (s, 1 H), 4.98 (br d, *J* = 4.3 Hz, 1 H), 4.30 (d, *J* = 6.9 Hz, 1 H), 4.02 (dd, *J* = 6. 9, 4.3 Hz, 1 H), 1.89 (br dd, *J* = 5.2, 5.0 Hz, 1 H), 1.79 (br ddd, *J* = 7.6, 5.2, 1.5 Hz, 1 H), 1.68 (dd, *J* = 7.6, 5.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 196.9, 135.2, 133.2, 132.7, 128.3, 128.1, 127.8, 127.6, 127.6, 126.3, 126.2, 99.9, 72.1, 69.0, 35.0, 23.2, 14.8.

MS (EI): *m*/*z* (%) = 252.1 (11) [M]$^+$, 221.1 (11), 195.1 (9), 180.1 (16), 179.1 (100), 178.1 (41), 177.1 (12), 167.1 (14), 165.1 (28), 152.1 (21).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{15}O_3$: 267.1016; found: 267.1015.

(1*S*,2*R*,4*S*,6*R*)-4-Iodo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonan-5-one (11)

Purified via flash column chromatography (EtOAc/hexanes, 1:3) to afford an amber oil (52 mg, 46%); R_f = 0.61 (EtOAc/hexanes, 1:3); $[\alpha]_D^{23}$ –119 (*c* 0.77, $CHCl_3$).

FT-IR (neat): 2964, 2900, 1723, 1329, 1276, 1172, 1114, 1067, 1007, 925, 901 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.22 (s, 1 H), 4.80 (br d, *J* = 4.7 Hz, 1 H), 4.15 (dd, *J* = 7.0 Hz, 1 H), 3.90 (dd, *J* = 7.0, 4.7 Hz, 1 H), 1.98 (ddd, *J* = 7.8, 6.0, 1.4 Hz, 1 H), 1.93 (dd, *J* = 6.2, 6.0 Hz, 1 H), 1.53 (dd, *J* = 7.8, 6.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 191.8, 97.8, 71.2, 68.2, 27.75, 21.1, –1.32.

MS (EI): *m*/*z* (%) = 139.1 (100) [M – I]$^+$, 126.9 (23), 111.1 (22), 93.1 (80), 83.1 (51), 66.1 (19), 65.1 (74), 55.1 (72), 53.1 (37), 39.1 (51).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_7H_8O_3I$: 266.9513; found: 266.9525.

(2*S*,5*R*)-2,3-Dihydro-1*H*-2,5-epoxyoxepino[3,4-*c*]isochromen-7(5*H*)-one (13)

Purified via repeated flash column chromatography (EtOAc/hexanes, 3:7 then EtOAc/PhMe, 1:19) then recrystallized (*i*-Pr_2O) to give clear colourless crystals (9.8 mg, 10%); R_f = 0.13 (EtOAc/PhMe, 1:19); mp 152–153 °C; $[\alpha]_D^{20}$ –27 (*c* 0.82, $CHCl_3$).

FT-IR (neat): 3055, 2970, 2908, 1735, 1660, 1605, 1490, 1454, 1388, 1315, 1298, 1241, 1194, 1160, 1103, 1058, 1041, 1023, 1005, 759, 688 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.33 (d, *J* = 7.9 Hz, 1 H), 7.77 (dd, *J* = 7.9, 7.6 Hz, 1 H), 7.55 (t, *J* = 7.6, 7.9 Hz, 1 H), 7.40 (d, *J* = 7.9 Hz, 1 H), 5.78 (s, 1 H), 5.02–4.99 (m, 1 H), 4.10 (ddd, *J* = 7.7, 6.0, 1.7 Hz, 1 H), 3.75 (dd, *J* = 7.7, 1.7 Hz, 1 H), 3.28 (ddd, *J* = 16.0, 4.7, 1.7, 1 H), 2.45 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 161.2, 149.8, 136.5, 135.0, 130.4, 128.5, 121.7, 121.5, 104.4, 96.1, 72.0, 68.4, 29.2.

MS (EI): *m*/*z* (%) = 230 (87) [M]$^+$, 174.1 (35), 171 (62), 158.1 (29), 144 (31), 130.1 (29), 129.1 (80), 128.1 (62), 115.1 (100), 102.1 (33).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}O_4$: 231.0657; found: 231.0646.

Ester-Stabilised Cyclopropanation; General Procedure

Enone **2** (0.43 mmol), TMG (0.65 mmol), **5** or **20** (0.65 mmol), and THF (3 mL) were sealed in a 10-mL microwave vial and heated at 70 °C using microwave irradiation while stirring for 10 min intervals until no starting material remained (via GC/MS). The solution was concentrated under reduced pressure and further purified as specified.

Ethyl (1*S*,2*S*,3*S*,4*S*,6*R*)-5-Oxo-4-phenyl-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonane-3-carboxylate (16a)

Purified via flash column chromatography (EtOAc/PhMe, 1:19) to yield a light yellow oil (86 mg, 93%); R_f = 0.17 (EtOAc/PhMe, 1:19); $[\alpha]_D^{20}$ –148 (*c* 0.56, $CHCl_3$).

FT-IR (neat): 2977, 2904, 1720, 1497, 1446, 1368, 1342, 1268, 1242, 1223, 1180, 1151, 1116, 1092, 1033, 1015 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.31–7.25 (m, 5 H), 5.13 (s, 1 H), 5.02 (br dd, *J* = 4.5, 1.5 Hz, 1 H), 4.30 (d, *J* = 7.1 Hz, 1 H), 4.01 (dd, *J* = 7.1, 4.5 Hz, 1 H), 3.96–3.85 (m, 2 H), 2.83 (d, *J* = 4.9 Hz, 1 H), 2.61 (dd, *J* = 4.9, 1.5 Hz, 1 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 192.1, 167.6, 132.4, 130.1, 128.2, 128.2, 99.9, 71.2, 68.9, 61.2, 40.7, 28.4, 25.1, 13.9.

MS (EI): *m*/*z* (%) = 203 (33), 201.1 (90), 173 (100), 169 (25), 141 (55), 129 (24), 128 (28), 127 (15), 115 (46), 91 (18).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}O_5$: 289.1076; found: 289.1080.

tert-Butyl (1*S*,2*S*,3*S*,4*S*,6*R*)-5-Oxo-4-phenyl-7,9-dioxatricyclo-[4.2.1.0^{2,4}]nonane-3-carboxylate (17a)

Purified via flash column chromatography (EtOAc/PhMe, 1:19) and recrystallized (*i*-Pr_2O) to give light yellow crystals (110 mg, 81%); R_f = 0.30 (EtOAc/PhMe, 1:19); mp 146–147 °C; $[\alpha]_D^{20}$ –91 (*c* 1.3, $CHCl_3$).

FT-IR (neat): 2973, 2908, 1730, 1697, 1497, 1446, 1366, 1343, 1294, 1221, 1152, 1119, 1096, 1083, 1066, 1029, 1017, 978 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.31–7.27 (m, 5 H), 5.12 (s, 1 H), 5.02 (br dd, *J* = 4.6, 1.8 Hz, 1 H), 4.28 (d, *J* = 7.1 Hz, 1 H), 4.00 (dd, *J* = 7.1, 4.6 Hz, 1 H), 2.74 (d, *J* = 4.9 Hz, 1 H), 2.54 (dd, *J* = 4.9, 1.8 Hz, 1 H), 1.20 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 192.3, 166.5, 132.4, 130.4, 128.1, 128.1, 99.9, 81.7, 71.3, 68.9, 40.6, 29.4, 27.7, 24.9.

MS (EI): *m*/*z* (%) = 174.1 (12), 173 (100), 169.1 (10), 142.1 (10), 141 (23), 115 (17), 57.1 (36), 56 (17), 41.1 (34), 39 (16).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{21}O_5$: 317.1384; found: 317.1388.

Ethyl (1*S*,2*S*,3*S*,4*S*,6*R*)-4-(4-Methoxyphenyl)-5-oxo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (16b)

Purified via flash column chromatography (EtOAc/PhMe, 1:19) to afford an amber oil (104 mg, 76%); R_f = 0.25 (EtOAc/PhMe, 1:19); $[\alpha]_D^{20}$ –141 (*c* 5.65, $CHCl_3$).

FT-IR (neat): 2975, 2904, 2846, 1721, 1610, 1581, 1514, 1442, 1368, 1343, 1293, 1268, 1244, 1223, 1176, 1152, 1111, 1032 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.17–7.16 (m, 2 H), 6.84–6.82 (m, 2 H), 5.12 (s, 1 H), 5.01 (br s, 1 H), 4.28 (d, *J* = 7.2 Hz, 1 H), 4.00 (dd, *J* = 7.2, 4.4 Hz, 1 H), 3.97–3.89 (m, 2 H), 3.77 (s, 3 H), 2.80 (d, *J* = 4.8 Hz, 1 H), 2.57 (br dd, *J* = 4.8, 1.8 Hz, 1 H), 1.06 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 192.6, 167.6, 159.4, 131.2, 124.5, 113.7, 99.9, 71.2, 68.9, 61.3, 55.2, 40.0, 28.5, 25.3, 14.0.

MS (EI): *m*/*z* (%) = 318.1 (24) [M]$^+$, 231.1 (100), 203 (88), 199 (23), 187.1 (20), 172.1 (21), 171.1 (64), 135 (28), 128 (26), 115 (24).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}O_6$: 319.1176; found: 319.1192.

***tert*-Butyl (1*S*,2*S*,3*S*,4*S*,6*R*)-4-(4-Methoxyphenyl)-5-oxo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (17b)**

Purified via repeated flash column chromatography (EtOAc/PhMe, 1:19 then EtOAc/hexanes, 3:7) and recrystallized (*i*-Pr_2O) to give colourless crystals (125 mg, 84%); R_f = 0.58 (EtOAc/hexanes, 3:7); mp 148–149 °C; $[\alpha]_D^{20}$ –148 (*c* 0.66, $CHCl_3$).

FT-IR (neat): 2959, 1722, 1703, 1609, 1513, 1475, 1458, 1393, 1368, 1333, 1300, 1260, 1240, 1179, 1157, 1109, 1064, 1022, 976 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.20–7.19 (m, 2 H), 6.84–6.83 (m, 2 H), 5.11 (s, 1 H), 5.00 (dd, *J* = 4.4, 1.7 Hz, 1 H), 4.26 (d, *J* = 7.1 Hz, 1 H), 3.99 (dd, *J* = 7.1, 4.4 Hz, 1 H), 3.77 (s, 3 H), 2.71 (d, *J* = 4.9 Hz, 1 H), 2.50 (dd, *J* = 4.9, 1.7 Hz, 1 H), 1.23 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 192.8, 166.6, 159.3, 131.4, 124.5, 113.6, 99.9, 81.7, 71.3, 68.9, 55.2, 40.0, 29.5, 27.8, 25.1.

MS (EI): *m*/*z* (%) = 290.1 (22), 216.1 (14), 204.1 (14), 203 (100), 172.1 (14), 171 (22), 135 (14), 57.1 (27), 56.1 (16), 41.1 (31).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{19}H_{21}O_6$: 345.1344; found: 345.1326.

Ethyl (1*S*,2*S*,3*S*,4*S*,6*R*)-4-(1,3-Benzodioxol-5-yl)-5-oxo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (16c)

Purified via flash column chromatography (EtOAc/PhMe, 3:7) to afford a yellow oil (92 mg, 64%); R_f = 0.25 (EtOAc/PhMe, 3:7); $[\alpha]_D^{20}$ –107 (*c* 1.6, $CHCl_3$).

FT-IR (neat): 2976, 2916, 2853, 1776, 1720, 1490, 1442, 1373, 1332, 1242, 121, 1181, 1116, 1034 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.75–6.69 (m, 3 H), 5.93 (s, 2 H), 5.12 (s, 1 H), 4.99 (dd, *J* = 4.4, 1.7 Hz, 1 H), 4.26 (d, *J* = 7.1 Hz, 1 H), 4.03–3.93 (m, 3 H), 2.78 (d, *J* = 4.9 Hz, 1 H), 2.54 (dd, *J* = 4.9, 1.7 Hz, 1 H), 1.11 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 192.3, 167.6, 147.5, 147.4, 126.0, 123.6, 110.6, 108.1, 101.2, 99.9, 71.2, 68.9, 61.4, 40.4, 28.5, 25.6, 14.0.

MS (EI): *m*/*z* (%) = 332.1 (82) [M]$^+$, 258.1 (31), 245.1 (66), 217 (100), 213 (34), 199 (33), 186.1 (34), 185.1 (82), 149 (29), 115.1 (39).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}O_7$: 333.0969; found: 333.0974.

***tert*-Butyl (1*S*,2*S*,3*S*,4*S*,6*R*)-4-(1,3-Benzodioxol-5-yl)-5-oxo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (17c)**

Purified via repeated flash column chromatography (EtOAc/PhMe, 1:19 then EtOAc/hexanes, 3:7) to afford an amber oil (110 mg, 71%); R_f = 0.25 (EtOAc/PhMe, 1:19); $[\alpha]_D^{20}$ –103 (*c* 3.1, $CHCl_3$).

FT-IR (neat): 2967, 2921, 2853, 1720, 1504, 1490, 1442, 1367, 1245, 1221, 1151, 1116, 1035, 800 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.76–6.72 (m, 3 H), 5.93–5.92 (m, 2 H), 5.10 (s, 1 H), 4.99 (br dd, *J* = 4.4, 1.6 Hz, 1 H), 4.24 (d, *J* = 7.1 Hz, 1 H), 3.98 (dd, *J* = 7.1, 4.4 Hz, 1 H), 2.69 (d, *J* = 4.9 Hz, 1 H), 2.46 (dd, *J* = 4.9, 1.6 Hz, 1 H), 1.28 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 192.5, 166.5, 147.4, 147.3, 126.1, 123.7, 111.0, 107.9, 101.1, 99.9, 81.9, 71.2, 68.9, 40.3, 29.5, 27.8, 25.4.

MS (EI): *m*/*z* (%) = 304 (42) [M – $C(CH_3)_3$]$^+$, 230 (94), 217 (100), 186 (27), 185 (66), 115.1 (30), 57.1 (68), 56.1 (39), 41.1 (79), 39 (33).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{19}H_{19}O_7$: 359.1136; found: 359.1123.

***tert*-Butyl (1*S*,2*S*,3*S*,4*S*,6*R*)-4-(2-Fluorophenyl)-5-oxo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (17d)**

Purified via flash column chromatography (EtOAc/hexanes, 1:4) then recrystallized (EtOH) to afford colourless crystals (122 mg, 85%); R_f = 0.61 (EtOAc/hexanes, 1:9); mp 145–148 °C; $[\alpha]_D^{23}$ –137 (*c* 0.93, $CHCl_3$).

FT-IR (neat): 2976, 2905, 1719, 1494, 1453, 1368, 1278, 1245, 1221, 1144, 1117, 755 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.30–7.22 (m, 2 H), 7.11–7.08 (m, 1 H), 7.05–7.01 (m, 1 H), 5.13 (s, 1 H), 5.01 (br d, *J* = 4.3 Hz, 1 H), 4.39 (br d, *J* = 6.7 Hz, 1 H), 3.97 (dd, *J* = 6.7, 4.3 Hz, 1 H), 2.84 (br d, *J* = 4.9 Hz, 1 H), 2.52 (br d, *J* = 4.3 Hz, 1 H), 1.27 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 191.7, 166.9, 162.8, 160.8, 132.9, 129.9 (d, *J* = 8.5 Hz), 123.8 (d, *J* = 3.5 Hz), 120.2 (d, *J* = 13.8 Hz), 115.5 (d, *J* = 21.8 Hz), 99.7, 81.9, 71.2, 68.3, 28.9, 27.7, 26.0.

MS (EI): *m*/*z* (%) = 250.1 (11), 204.1 (7), 192.1 (12), 191.1 (100), 160.1 (7), 159.1 (11), 146.1 (6), 133.1 (10), 57.1 (27), 41.1 (9).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{18}H_{18}O_5F$: 333.1144; found: 333.1136.

***tert*-Butyl (1*S*,2*S*,3*S*,4*S*,6*R*)-5-Oxo-4-(2,3,4-trifluorophenyl)-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (17e)**

Purified via repeated flash column chromatography (EtOAc/PhMe, 1:19 then EtOAc/hexanes, 1:9) to afford a yellow oil (141 mg, 89%); R_f = 0.68 (EtOAc/hexanes, 3:7); $[\alpha]_D^{20}$ –111 (*c* 3.2, $CHCl_3$).

FT-IR (neat): 2978, 2916, 1719, 1613, 1513, 1482, 1394, 1368, 1277, 1245, 1205, 1157, 1141, 1117, 1085, 1040, 1005, 731 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.96–6.89 (m, 2 H), 5.13 (s, 1 H), 5.01 (br dd, *J* = 4.5, 1.6 Hz, 1 H), 4.33 (d, *J* = 7.1 Hz, 1 H), 3.98 (dd, *J* = 7.1, 4.5 Hz, 1 H), 2.84 (br dd, *J* = 4.6, 1.6 Hz, 1 H), 2.49 (br d, *J* = 4.6 Hz, 1 H), 1.32 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 190.9, 166.7, 152.0 (ddd, J_{CF} = 249.8, 9.8, 9.8 Hz), 150.9 (ddd, J_{CF} = 249.5, 9.7, 9.7 Hz),, 139.9 (ddd, J_{CF} = 250.3, 15.4, 15.4 Hz), 126.1, 118.1 (d, J_{CF} = 12.2 Hz), 111.7 (dd, J_{CF} = 17.5, 3.7 Hz), 99.6, 82.4, 71.0, 68.3, 35.4, 28.7, 27.7, 26.0.

MS (EI): *m*/*z* (%) = 228 (32), 207 (30), 184 (11), 183 (100), 182 (40), 169 (44), 156 (28), 151.1 (30), 145.1 (14), 133 (28).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{18}O_5F_3$: 371.1101; found: 371.1102.

tert-Butyl (1*S*,2*S*,3*S*,4*S*,6*R*)-5-Oxo-4-[4-(trifluoromethyl)phenyl]-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (17f)

Purified via flash column chromatography (EtOAc/hexanes, 3:7) then recrystallized (*i*-Pr_2O) to yield small colourless crystals (181 mg, 91%); R_f = 0.67 (EtOAc/hexanes, 3:7); mp 121–122 °C; $[\alpha]_D^{20}$ –113 (*c* 2.1, $CHCl_3$).

FT-IR (neat): 2977, 2904, 1717, 1619, 1480, 1410, 1393, 1368, 1324, 1271, 1250, 1231, 1157, 1109, 1069, 1018 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.59–7.57 (m, 2 H), 7.41–7.40 (m, 2 H), 5.14 (s, 1 H), 5.04 (br dd, *J* = 4.5, 1.7 Hz, 1 H), 4.28 (d, *J* = 7.2 Hz, 1 H), 4.02 (dd, *J* = 7.2, 4.5 Hz, 1 H), 2.79 (d, *J* = 4.9 Hz, 1 H), 2.56 (dd, *J* = 4.9, 1.7 Hz, 1 H), 1.20 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 191.5, 166.2, 136.4, 130.8, 130.3 (q, J_{CF} = 32.4 Hz), 125.0 (q, J_{CF} = 3.6 Hz), 124.0 (q, J_{CF} = 272.5), 99.8, 82.2, 711, 68.9, 40.2, 29.4, 27.7, 25.0.

MS (EI): *m*/*z* (%) = 328 (6), 300 (7), 254 (8), 242 (13), 241 (100), 210 (6), 209 (9), 183 (5), 57.1 (38), 41.1 (9).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{19}O_5F_3Na$: 407.1082; found: 407.1098.

tert-Butyl (1*S*,2*S*,3*S*,4*S*,6*R*)-4-(2-Formylphenyl)-5-oxo-7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-3-carboxylate (17g)

Purified via repeated flash column chromatography (EtOAc/hexanes, 3:7 then EtOAc/PhMe, 1:19) to afford a yellow oil (53 mg, 36%); R_f = 0.59 (EtOAc/hexanes, 3:7); $[\alpha]_D^{20}$ –130 (*c* 0.47, $CHCl_3$).

FT-IR (neat): 2973, 2921, 2851, 2165, 2023, 1715, 1691, 1598, 1479, 1457, 1395, 1368, 1280, 1263, 1246, 1199, 1144, 1118, 1100, 1024 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 10.18 (s, 1 H), 8.00 (br d, *J* = 7.6 Hz, 1 H), 7.56 (br ddd, *J* = 7.6, 7.5, 1.4 Hz, 1 H), 7.46 (br dd, *J* = 7.6, 7.5 Hz, 1 H), 7.26 (br d, *J* = 7.6 Hz, 1 H), 5.18 (s, 1 H), 5.11 (br d, *J* = 4.5 Hz, 1 H), 4.34 (d, *J* = 7.2 Hz, 1 H), 4.05 (br dd, *J* = 7.2, 4.5 Hz, 1 H), 2.95 (d, *J* = 4.9 Hz, 1 H), 2.67 (br dd, *J* = 4.9, 1.5 Hz, 1 H), 1.16 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 191.3, 190.9, 166.1, 136.3, 134.5, 133.6, 130.1, 128.8, 128.1, 99.7, 82.8, 71.2, 68.9, 38.0, 30.6, 27.5, 24.9.

MS (EI): *m*/*z* (%) = 243.1 (24), 215.1 (100), 197.1 (21), 170.1 (24), 169.1 (25), 141.1 (35), 128.1 (20), 115.1 (33), 57.1 (68), 41.1 (26).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{19}H_{19}O_6$: 343.1187; found: 343.1174.

(1*R*,4*S*,5*S*)-4-(Hydroxymethyl)-1-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (23)

To a stirred solution of TFA (0.50 mL, 6.53 mmol) and 30% H_2O_2 (0.50 mL, 6.39 mmol) was added a solution of **9a** (50 mg, 0.23 mmol) in CH_2Cl_2 (1.0 mL). The mixture was stirred at 25 °C for 8 h and then 10% Pd/C (0.05 g) was added and stirring continued until the evolution of O_2 had ceased and a negative test for peroxides was obtained. The solution was then filtered through celite and concentrated under reduced pressure. The residue containing a mixture of **22** and **23** was then stirred vigorously with 32% HCl (2 mL, 27.6 mmol) for 8 h, concentrated under reduced pressure and purified via flash column chromatography (EtOAc/hexanes, 7:3) to give **23** as a light yellow oil that crystallized upon standing to afford a white solid (39 mg, 83%); R_f = 0.67 (EtOAc/hexanes, 7:3); mp 66–68 °C; $[\alpha]_D^{20}$ +82 (*c* 0.15, $CHCl_3$).

FT-IR (neat): 3419, 2933, 1746, 1603, 1502, 1446, 1343, 1247, 1137, 1109, 1068, 1042, 1003 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.45–7.41 (m, 2 H), 7.34–7.25 (m, 3 H), 4.48 (dd, *J* = 3.5, 3.5 Hz, 1 H), 3.99 (br d, *J* = 12.1 Hz, 1 H), 3.80 (br d, *J* = 12.1, Hz, 1 H), 2.40 (dd, *J* = 7.7, 4.7 Hz, 1 H), 2.31 (br s, 1 H), 1.64 (dd, *J*= 7.7, 4.9 Hz, 1 H), 1.35 (dd, *J* = 4.9, 4.7 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 176.5, 133.9, 129.0, 128.4, 127.8, 79.9, 64.0, 32.4, 26.8, 18.2.

MS (EI): *m*/*z* (%) = 204.1 (33) [M]$^+$, 174.1 (35), 173.1 (52), 145.1 (66), 127.1 (34), 117.1 (72), 116.1 (35), 115.1 (100), 103.1 (22), 91.1 (29).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}O_3$: 205.0865; found: 205.0870.

Single Crystal X-ray Crystallography

A single crystal was mounted in paratone-N oil on a plastic loop and X-ray diffraction data were collected at 150(2) K on an Oxford X-calibur single crystal diffractometer using Mo Kα radiation. The data set was corrected for absorption using a multi-scan method, and the structure solved by direct methods using SHELXS-2014 and refined by full-matrix least squares on F2 by SHELXL-2014,[26] interfaced through the program X-Seed.[27] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. An ORTEP representation of the structure (ellipsoids at 50% occupancy), along with tables of bond lengths and angles generated using OLEX2[28] are included in the supporting information.

Crystal data for **9b**:[29] $C_{14}H_{14}O_4$, FW 246.25, monoclinic, $P2_1$, a = 6.1695(3), b = 7.0249(4), c = 13.5028(6) Å, β = 97.135(4)°, V = 580.68(5) Å^3, Z = 2, D_{calc} = 1.408 Mg/m^3, μ = 0.103 mm^{-1}, F(000) 260, crystal size = 0.66 × 0.35 × 0.17 mm^3, θ range for data collection 3.33 to 29.14°, Reflns coll. 6990, Obs. reflns 2311, R_{int} = 0.0401, GoF = 1.032, R_1 [I > 2σ(I)] = 0.0433, wR_2 (all data) = 0.0916, largest diff. peak and hole 0.286 and –0.198 e Å^{-3}.

Acknowledgment

We kindly thank Dr Warwick Raverty and Mr Tony Duncan for the kind donation of **1**. E.T.L. thanks the Australian government for an APA scholarship.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588971.

References

(1) (a) Halpern, Y.; Riffer, R.; Broido, A. *J. Org. Chem.* **1973**, *38*, 204. For reviews on the chemistry of LGO see: (b) Sarotti, A.; Zanardi, M.; Spanevello, R. A.; Suarez, A. G. *Curr. Org. Synth.* **2012**, *9*, 439. (c) *Levoglucosenone and Levoglucosans: Chemistry and Applications*; Witczak, Z. J., Ed.; ATL Press: Mount Prospect USA, **1994**. For recent synthetic applications see: (d) Ma, X.; Anderson, N.; White, L.; Bae, S.; Raverty, W.; Willis, A. C.; Banwell, M. *Aust. J.*

Chem. **2015**, *68*, 593. (e) Giordano, E. D.; Frinchaboy, A.; Suárez, A. G.; Spanevello, R. A. *Org. Lett.* **2012**, *14*, 4602. (f) Witczak, Z. J.; Kaplan, P.; Dey, P. M. *Carbohydr. Res.* **2003**, *338*, 11.
(2) Stockton, K. P.; Merritt, C. J.; Sumby, C. J.; Greatrex, B. W. *Eur. J. Org. Chem.* **2015**, 6999.
(3) (a) Becker, B.; Thimm, J.; Thiem, J. *J. Carbohydr. Chem.* **1996**, *15*, 1179. (b) Awad, L.; Demange, R.; Zhu, Y.-H.; Vogel, P. *Carbohydr. Res.* **2006**, *341*, 1235.
(4) (a) Ward, D. D.; Shafizadeh, F. *Carbohydr. Res.* **1981**, *95*, 155. (b) Sarotti, A. M.; Joullié, M. M.; Spanevello, R. A.; Suárez, A. G. *Org. Lett.* **2006**, *8*, 5561.
(5) Novikov, R. A.; Rafikov, R. R.; Shulishov, E. V.; Konyushkin, L. D.; Semenov, V. V.; Tomilov, Y. V. *Russ. Chem. Bull.* **2009**, *58*, 327.
(6) (a) Wong, H. N.; Hon, M. Y.; Tse, C. W.; Yip, Y. C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (b) For a recent review on the cyclopropane in bioactive discovery see: Talele, T. *J. Med. Chem.* **2016**, *59*, 8712.
(7) Samet, A. V.; Shestopalov, A. M.; Lutov, D. N.; Rodinovskaya, L. A.; Shestopalov, A. A.; Semenov, V. V. *Tetrahedron: Asymmetry* **2007**, *18*, 1986.
(8) (a) Valeev, F. A.; Gorobets, E. V.; Miftakhov, M. S. *Russ. Chem. Bull.* **1997**, *46*, 1192. (b) Gorobets, E. V.; Spirikhin, L. V.; Tzypysheva, I. P.; Miftakhov, M. S.; Valeev, F. A. *Russ. J. Org. Chem.* **2001**, *37*, 1088.
(9) Stockton, K. P.; Greatrex, B. W. *Org. Biomol. Chem.* **2016**, *14*, 7520.
(10) Alliot, J.; Gravel, E.; Pillon, F.; Buisson, D.-A.; Nicolas, M.; Doris, E. *Chem. Commun.* **2012**, *48*, 8111.
(11) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
(12) Johnson, A. W.; LaCount, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 417.
(13) Gelas-Mialhe, Y.; Gelas, J. *Carbohydr. Res.* **1990**, *199*, 243.
(14) Samet, A. V.; Lutov, D. N.; Konyushkin, L. D.; Strelenko, Y. A.; Semenov, V. V. *Tetrahedron: Asymmetry* **2008**, *19*, 691.
(15) (a) Dongamanti, A.; Bommidi, V. L.; Madderla, S. *Lett. Org. Chem.* **2016**, *13*, 76. (b) Namboodiri, V. V.; Varma, R. S. *Green Chem.* **2001**, *3*, 146.
(16) Zhang, F.; Moher, E. D.; Zhang, T. Y. *Tetrahedron Lett.* **2007**, *48*, 3277.
(17) (a) De Frutos, O.; Atienza, C.; Echavarren, A. M. *Eur. J. Org. Chem.* **2001**, 163. (b) Gerbino, D. C.; Augner, D.; Slavov, N.; Schmalz, H.-G. *Org. Lett.* **2012**, *14*, 2338.
(18) Payne, G. B. *J. Org. Chem.* **1967**, *32*, 3351.
(19) Amador, A. G.; Sherbrook, E. M.; Yoon, T. P. *J. Am. Chem. Soc.* **2016**, *138*, 4722.
(20) (a) Prezzavento, O.; Parenti, C.; Marrazzo, A.; Ronsisvalle, S.; Vittorio, F.; Aricò, G.; Scoto, G. M.; Ronsisvalle, G. *Life Sci.* **2008**, *82*, 549. (b) Moison, D.; De Deurwaerdere, P.; Cagnotto, A.; Marrazzo, A.; Prezzavento, O.; Ronsisvalle, G.; Mennini, T.; Spampinato, U. *Neuropharmacology* **2003**, *45*, 945.
(21) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, **2013**.
(22) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.
(23) Fischer, S.; Huwyler, N.; Wolfrum, S.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2016**, *55*, 2555.
(24) Nikolaev, D. N.; Davidovich, P. B.; Piotrovskii, L. B. *Russ. J. Org. Chem.* **2016**, *52*, 1050.
(25) Duarte-Ruiz, A.; Nunez-Dallos, N.; Garzon-Tovar, L.; Wurst, K.; Avella-Moreno, E.; Gomez-Baquero, F. *Chem. Commun.* **2011**, *47*, 7110.
(26) (a) Sheldrick, G. M. *SHELXS and SHELXL-2014*; University of Göttingen: Germany, **2014**. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112. (c) Sheldrick, G. M. *Acta Crystallogr., Sect. C* **2015**, *71*, 3.
(27) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189.
(28) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
(29) CCDC 1526675 (**9b**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.