Chapter 2 – Catalytic Rearrangements of Cyclopropenes

Acknowledgment: The author would like to thank Stuart MacGregor *and his group for the calculations carried out in Figure 1 and Figure 2.*

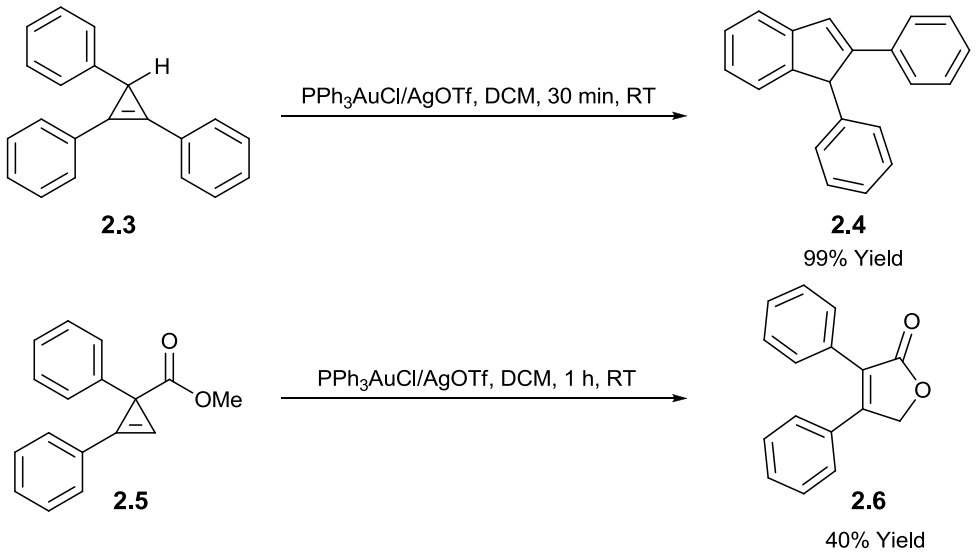
2.1 Introduction

The first confirmed report of cyclopropene synthesis was in 1922 by Dem'yanov and Doyarenko who thermally decomposed trimethylcyclopropylammonium hydroxide on platinised clay at approximately 300 ^{o}C.[1] Since then, cyclopropenes and their derivatives have been widely sought after due to their unique reactivities through increased angular strain on the sp^2 centres[2] which enable cyclopropenes to deliver products that typical olefins cannot.[3, 4] Even though some extensive investigations on cyclopropenes have been carried out, when our investigations began, there were no reactions involving gold(I) catalysts. The initial aim if this PhD project was thus to explore the chemistry of gold(I) catalysis with cyclopropenes and in particular to develop any novel reactions that may result from our study.

In 2008 the first report in this area was published by Shi and they found that gold(I) catalysts can selectively form the isomeric indene **2.2** from **2.1** selectively when DBU is added as an additive (Scheme 1).[5] It was suggested that in addition to eliminating traces of any Brønsted acids present (TfOH or $HSbF_6$ formed from the respective silver salts), DBU could also have a weak coordinating effect with gold(I), enhancing the selectivity of the reaction, which indeed drops when DBU is not present.

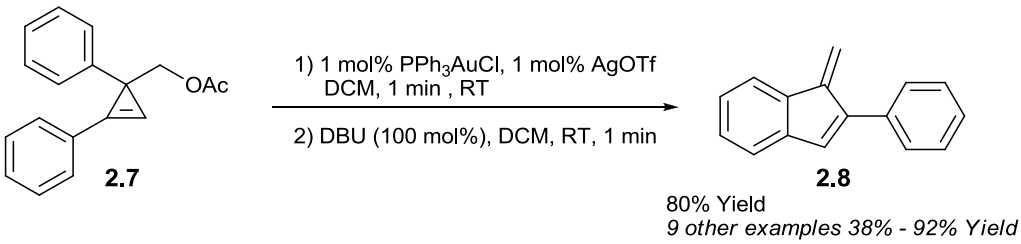
Scheme 1 Gold(I)-Catalysed Rearrangement of Cyclopropenes

Soon after the publication from Shi, we presented our initial results on the formation of butenolides and indenes described in this chapter (*vide infra*)[6] which was followed by complementary and independent work by Wang and co-workers.[7] Wang's initial studies utilising gold(I) to rearrange cyclopropene **2.3** resulted in the formation of indene **2.4**. However, with an ester substituent in **2.5**, butenolides **2.6** became the major product (Scheme 2).



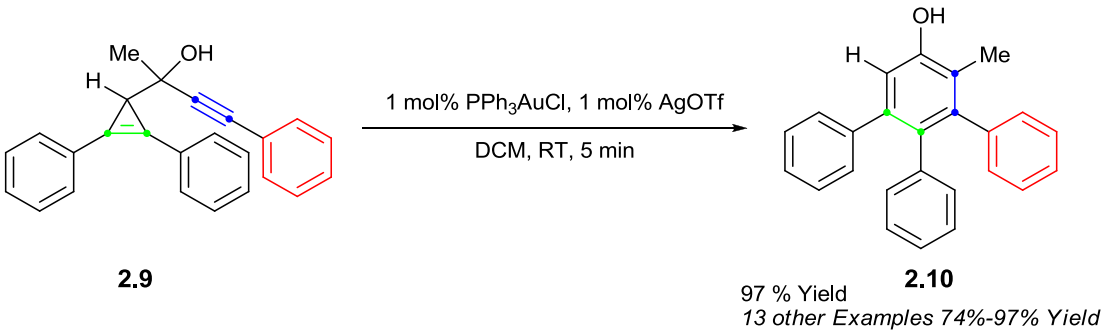
Scheme 2 Gold (I) Catalysed Indene and Butenolide Formation

In an attempt to increase the yield of the indene product, the ester group in **2.5** was reduced and then protected to form **2.7**, which resulted in successfully limiting the butenolide product and with the addition of DBU, increased the yields of the preferred product, the indene **2.8** (Scheme 3).



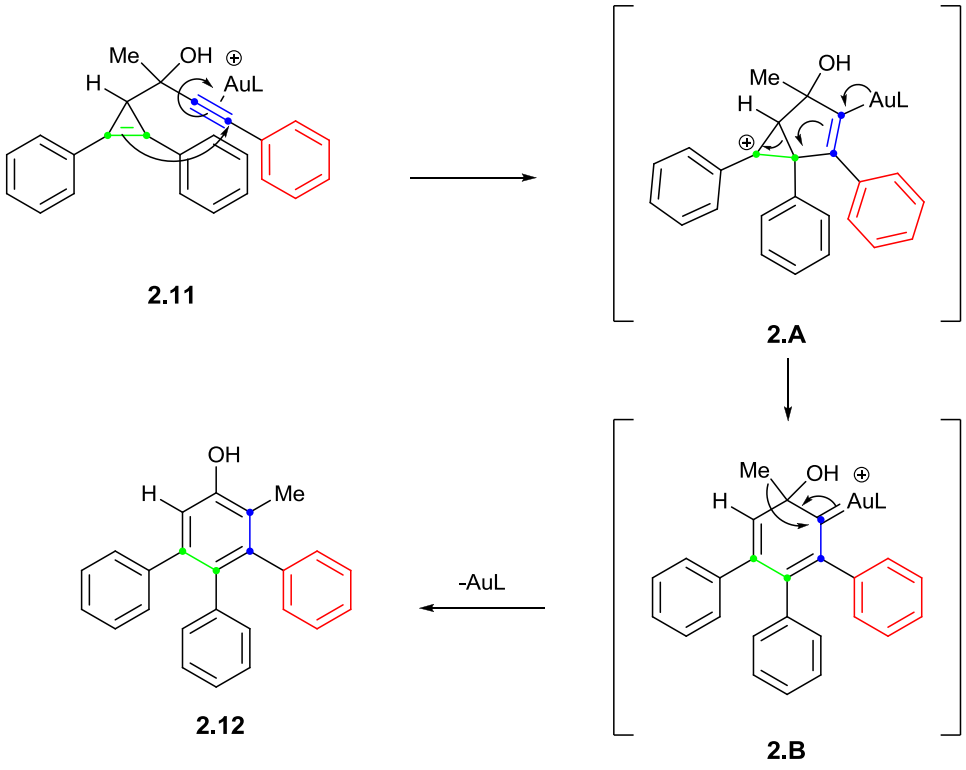
Scheme 3 Gold (I) Catalysed Indene Formation

In 2010, Wang and co-workers followed up their investigations in this area by looking into gold-catalysed cycloisomerisation of propargyl cyclopropenes (Scheme 4).[8] Gold(I) catalyses the skeletal rearrangement of propargyl cyclopropenes **2.9** to form phenol derivatives **2.10**.



Scheme 4 Gold(I) Catalysed Rearrangements of Propargyl Cyclopropenes

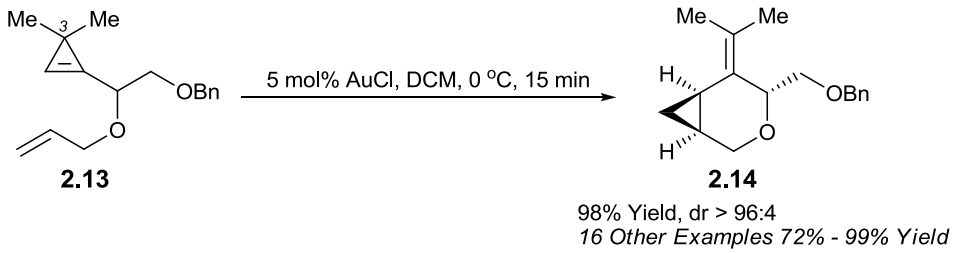
The proposed mechanism for the reaction presented in Scheme 4 differs from the "normal" cyclopropene ring-opening pathway (*vide infra*, Scheme 11) as gold(I) activation of the alkyne is followed by intramolecular attack from the cyclopropene (Scheme 5).



Scheme 5 Mechanism of the Gold(I) Catalysed Rearrangement of Propargyl Cyclopropenes

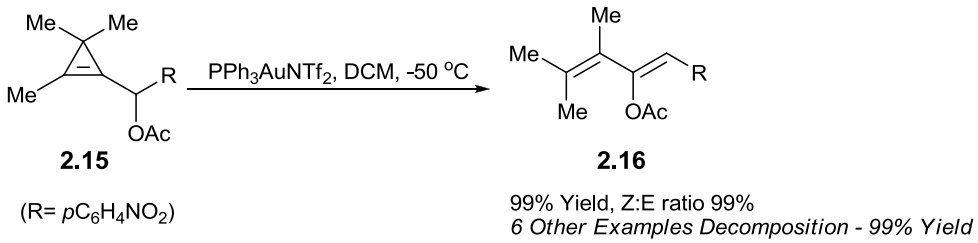
More recently Meyer, Cossy and co-workers demonstrated that gold-catalysed cyclopropanation reactions with cyclopropenes perform intramolecular cyclosiomerisations (Scheme 6).[9] Several 3-oxa- and 3-azabicyclo[4.1.0]heptanes (e.g. **2.14**) were synthesised in excellent yields and remarkable diastereoselectivities

from a series of allylic ether cyclopropenes (e.g. **2.13**). The *bis*-substitution at C-3 was found to be crucial for substrate stability and the *gem*-dimethyl group is also proposed to have a marked influence on the regio- and diastereoselectivity of the reaction, since substitution at C-2 instead of C-3 results in both lower regio- and diastereoselectivities.



Scheme 6 Gold(I) Catalysed 3-oxabicyclo[4.1.0]heptane Formation

Highly strained cyclopropene homologues of propargylic acetates can also undergo gold(I) catalysis.[10] Hyland and co-workers found that cyclopropenylmethyl acetates **2.15** rearrange to the *Z*-acetoxy dienes **2.16** in good yields and *Z*:*E* selectivities when R = Ph or Ar with an electron-withdrawing substituent (Scheme 7).



Scheme 7 Gold(I) Catalysed Rearrangement of Cyclopropene Propargylic Acetates

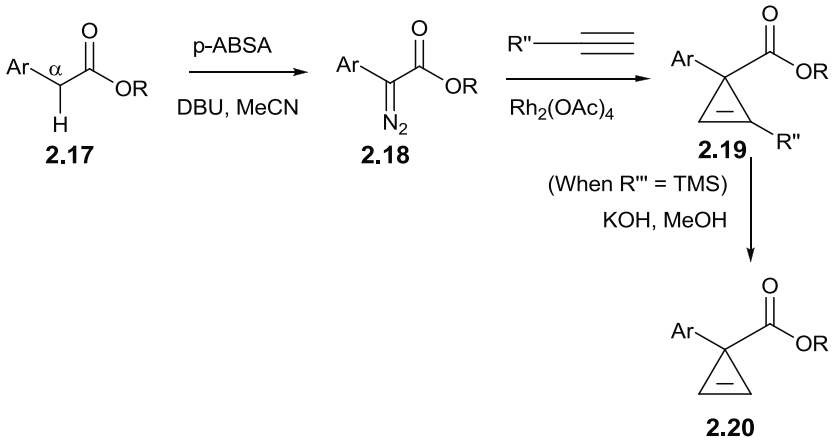
While the reaction with an electron rich aryl substituent (R = tol) also underwent the rearrangement, the corresponding diene product rapidly decomposed whereas alkyl R substituents provide noticeably poorer *Z*:*E* ratios (1.8:1).

The gold(I) activation of cyclopropenes is now somewhat established[11] however, the ease in which the species described above can rearrange mean that an external nucleophile would struggle to react with any of those substrates. Although the rearrangement reactions are interesting and important, it would be synthetically advantageous to be able to perform *inter*molecular reactions.

2.2 Results and Discussion

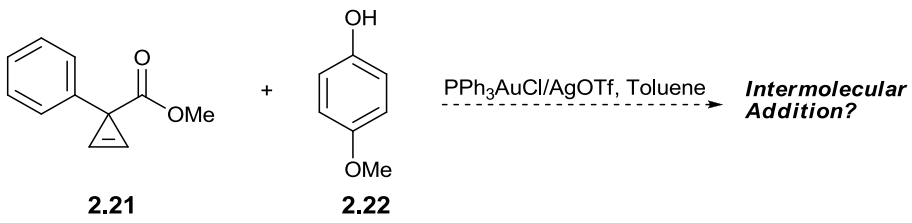
When this study began there were no gold(I) catalysed reactions involving cyclopropenes present in the literature. Our initial aim was thus to synthesise quick and easily accessible starting cyclopropene substrates and to explore the reactivity of these substrates with gold catalysts.

The quickest route to making cyclopropenes is to form the diazo species **2.18** from deprotonation of the alpha acidic hydrogen of an ester **2.17**, followed by rhodium catalysed carbene addition to an alkyne, which was the method used to produce all the cyclopropenes in this chapter (Scheme 8).[12]



Scheme 8 Cyclopropene Formation

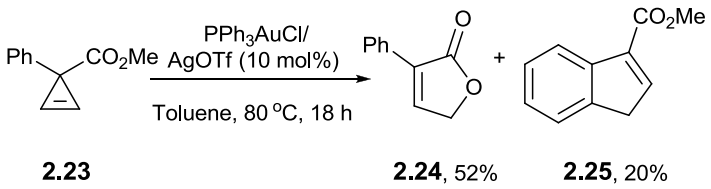
With the cyclopropene **2.21**, in hand, we aimed to activate the unsaturated double bond in the ring with a gold(I) catalyst, which would allow nucleophilic addition of a nucleophile such as phenol (Scheme 9).[13]



Scheme 9 Attempted Gold(I) Catalysed Addition of Phenol to Cyclopropene

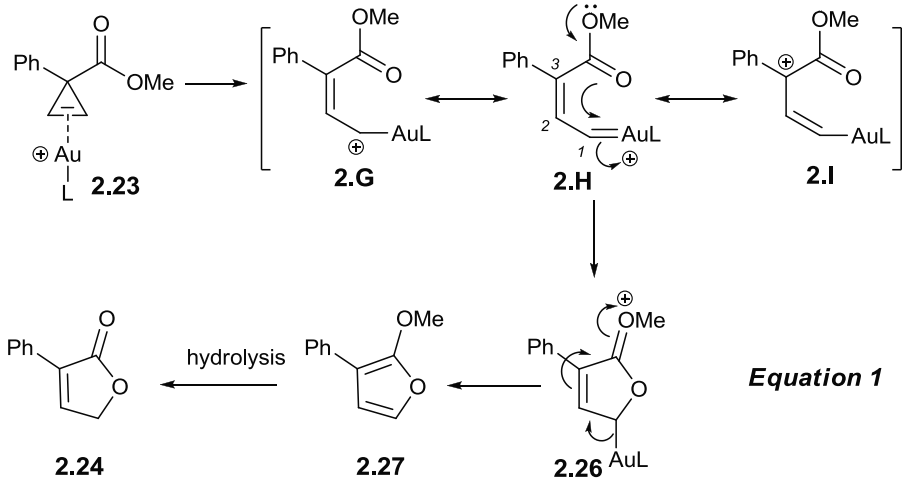
From ^{1}H-NMR analysis it was clear that the structure of the major product formed in the reaction (Scheme 9) was a rearrangement product that did not contain the phenol moiety

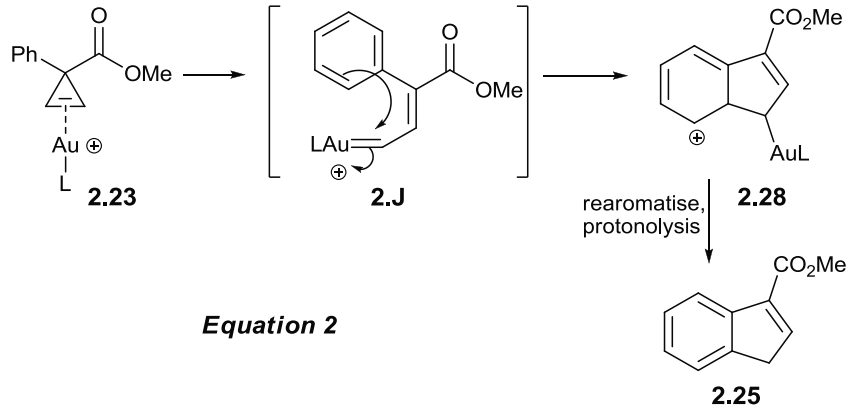
and further reactions employing a variety of phenols and carboxylic acids as nucleophiles did not deliver the desired intermolecular addition. The reaction was then repeated without any external nucleophile present resulting in the same intramolecular rearrangement major product, butenolide **2.24** (Scheme 10). In addition, the indene **2.25**, was observed as a side-product.



Scheme 10 Gold(I)-Catalysed Intramolecular Rearrangement

With this result in hand, we proposed a plausible mechanism for the gold(I) catalysed rearrangement of cyclopropene **2.23** (Scheme 11). Gold activates the strained double bond causing it to ring-open to the stereoisomeric intermediates **2.H** and **2.J**. The gold(I) catalysed ring opening of the cyclopropene that we propose in Scheme 11 is also applicable to the reactions described in the introduction at the beginning of this chapter (Chapter 2.1).[11] Attack of the ester group being held close to the reactive site (C-1) in **2.H** furnishes the butenolide **2.24** (Equation 1, Scheme 11). In the isomeric intermediate **2.J**, the aromatic ring attacks instead to give the side product, indene **2.25** (Equation 2, Scheme 11). The rearrangement occurs more quickly than the intermolecular reaction with phenol; hence even when the phenol is present, the butenolide **2.24** is still observed as the major product.





Scheme 11 Proposed Mechanism for the Gold (I) Catalysed Cyclopropene Rearrangement

The nature of intermediates **2.H** and **2.J** in terms of the issue of carbocation *vs.* gold carbene mesomeric structures is of some interest due to the true nature being extensively debated in the literature at the time of this study (see Chapter 1). In order to study the cationic/carbene nature of C-*1* in intermediates **2.H** and **2.J**, our theoretical collaborators compared the computed C-*1*-Au bond lengths with single C-Au and double C-Au bond lengths respectively (Figure 1).[14]

The calculated C-*1*-Au bond lengths of 2.02 Å fall between the values of a single (2.07 Å) and double (1.95 Å) C-Au bond. Thus, the C-*1*-Au bond in **2.H** and **2.J** exhibits both single and double bond character and their cationic/carbene nature cannot be decided by bond length alone.[15]

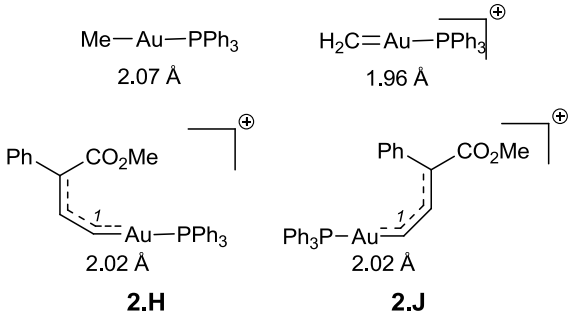


Figure 1 Calculated Bond Lengths for Intermediates 2.H and 2.J

As the calculated C-*1*-Au bond lengths do not provide evidence for either a single or a double bond, natural charges were calculated to determine where most of the positive partial charge resides (Figure 2). The results indicate that most of the partial

positive charge resides on Au, thus suggesting some degree of gold carbene structure for intermediates **2.H** and **2.J**.

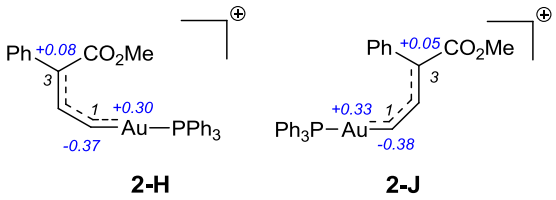
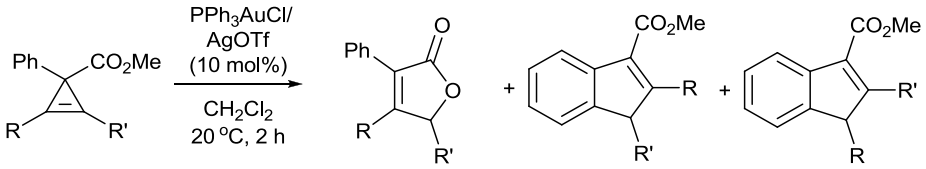


Figure 2 Partial charge distributions for intermediates 2.H and 2.J

Investigations into the effect of substitution on the cyclopropene substrate (Table 1) followed the initial observations with the Ph-substituted cyclopropene **2.29** undergoing rearrangement under milder conditions to furnish the butenolide **2.35** in 53% yield (Entry 1). The rearrangement of cyclopropene **2.29** regioselectively forms the butenolide **2.35**, whereas the indene by-products (18%) are formed in a 1:1 regioisomeric ratio of **2.39** and **2.43**.

Next, the effect of electronics on the aryl substituent was probed (Table 1). Changing the electronics on the aryl ring appears not to effect the butenolide to indene ratios (Entries 1-3), although it does seem to switch the respective indene side-product isomeric ratios (Entries 2 and 3). The TMS-substituted cyclopropene **2.32** undergoes rearrangement as expected however during the work up the TMS group is lost through hydrolysis to yield the unsubstituted products **2.24** and **2.25** (Entry 4). Finally, the electron-deficient and sterically encumbered cyclopropenes **2.33** and **2.34** (Entries 5 and 6) did not produce any of the expected rearrangement products under gold(I) catalysis, even at elevated temperatures and extended reaction time (70 ^{o}C, 24 h), presumably due to steric reasons.



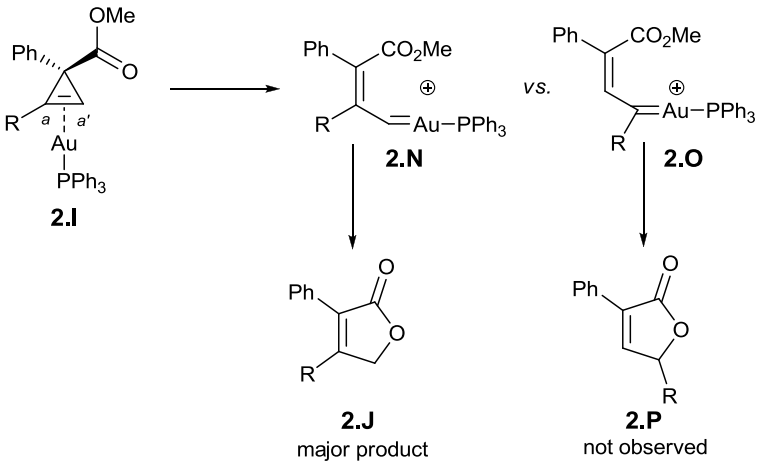
2.I **2.K** **(2.24,2.35-2.37)** **2.L** **(2.25,2.38-2.40)** **2.M** **(2.25,2.41-2.43)**

Entry	R	R'	Yield **K**[a]	Yield **L+M**[a]	Ratio **L:M**[b]
1	Ph	H	53%	18%	1:1
	(2.29)		**(2.35)**	**(2.38, 2.41)**	
2	*p*OMeC_6H_4	H	50%	20%	2.6:1
	(2.30)		**(2.36)**	**(2.39, 2.42)**	
3	*p*FC_6H_4	H	50%	18%	1:3
	(2.31)		**(2.37)**	**(2.40, 2.43)**	
4	TMS	H	39%	37%	N/A
	(2.32)		**(2.24)**	**(2.25)**	
5[c]	Ph	*p*$NO_2C_6H_4$	-	-	N/A
	(2.33)				
6[c]	Ph	Ph	-	-	N/A
	(2.34)				

[a]Isolated yields. [b]Determined by ^{1}H-NMR analysis. [c]Reaction was heated at 70 °C for 24 h in dichloroethane; no reaction was observed by TLC or ^{1}H-NMR analysis of the crude reaction mixture.

Table 1 The Effect of Substitution and Electronics on Gold (I) Catalysed Cyclopropene Rearrangement Reaction

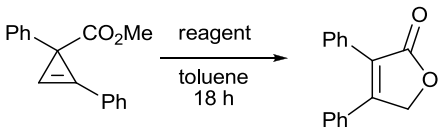
The selectivity of the major butenolide product **2.K** can be explained by steric reasons, whereby gold(I) prefers to be delivered to the less hindered centre (a' *vs.* a) producing **2.N** and thus **2.K** (Scheme 12).



Scheme 12 Butenolide Selectivity

In order to ascertain whether gold(I) is actually catalysing the rearrangement reaction, several control experiments were carried out with cyclopropene **2.29** (Table 2). These are particularly important as several apparently gold(I) catalysed reactions have been shown to proceed in catalytic amounts of Brønsted acid, which is usually present in trace amounts when AgOTf is used as a catalyst or co-catalyst.[16]

Should traces of TfOH be present in the gold-catalysed reaction (Scheme 10) then we would expect at the very most, only 10 mol% to be present. However, our controls show that 1 mol% or 10 mol% of TfOH does not catalyse the reaction (Etntries 1 and 2). Silver catalysts have been shown to catalyse similar reactions however in this case, the use of AgOTf as the sole catalyst also produces no appreciable rearrangement (Entry 3). These results confirm that the rearrangement in the presence of PPh_3AuCl/AgOTf is thus truly catalysed by gold(I). It should be noted, however, that *stoichiometric* amounts of TfOH can indeed mediate the rearrangement of cyclopropene **2.29** to form butenolide **2.35**, though in noticeably lower yields compared to gold(I) (Entry 5). Intrigued by this, several other Brønsted acids were screened as stoichiometric reagents (Entries 5-10).[17] Strong Brønsted acids such as TfOH and 2,4-dinitrobenzenesulfonic acid (DNBA) were capable of mediating the rearrangement of **2.29** to **2.35** in low to moderate yields (Entries 5-7). Weaker Brønsted acids, such as camphor-10-sulfonic acid, trifluoroacetic acid and *bis*(trifluoromethane)sulfonimide did not produce appreciable conversions (Entries 8-10). These results imply that only very strong Brønsted acids are capable of mediating the rearrangement, and then only in stoichiometric amounts.



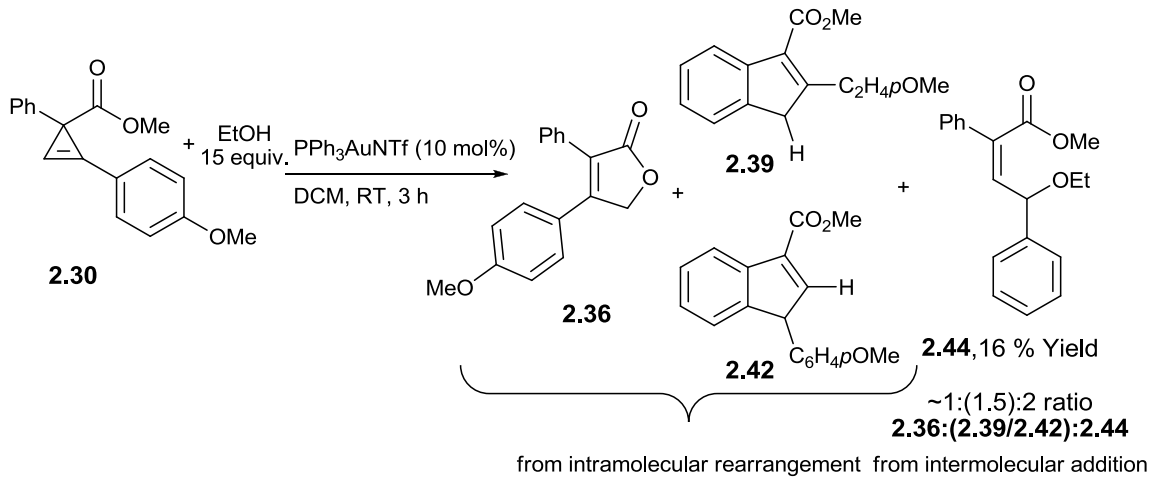
2.29 **2.35**

Entry	Reagent	Equiv.	Temp (^{o}C)	Yield **2-19** (%)[a]
1	TfOH	1 mol%	80	<5%
2	TfOH	10 mol%	80	<5%
3[b]	AgOTf	10 mol%	25	<5%
4[b]	AgOTf	10 mol%	70	Complex mix
5	TfOH	1 equiv.	30	36%[c]
6	TfOH	1 equiv.	50	35%[c]
7	DNBA	1 equiv.	80	41%[c]
8	CSA	1 equiv.	80	<5%
9	TFA	1 equiv.	80	<5%
10	HNTf2	1 equiv.	80	<5%

[a]Isolated yields; <5% implies product not detected by ^{1}H-NMR analysis of crude reaction mixture. [b]Dichloroethane used as solvent. [c]As with gold(I) catalysed reactions, indenes **8a** and **9a** were also detected as minor by-products but were not isolated in these cases.

Table 2 Brønsted Acid Catalysed Cyclopropene Rearrangement

Although the gold(I) catalysed rearrangements of cyclopropenes are mechanistically interesting and we were able to prove that the cyclopropene was indeed activated by gold(I), our initial target to *inter*molecularly add nucleophiles to cyclopropenes still remained as a major aim. In an intriguing preliminary result, the ether **2.44** was observed when cyclopropene **2.30** was reacted with 15 equivalents of ethanol (Scheme 13). This result clearly shows that intermolecular alcohol addition is possible, but the issue of competition from the intramolecular rearrangement needs to be tackled.



Scheme 13 Signs of Ether Product

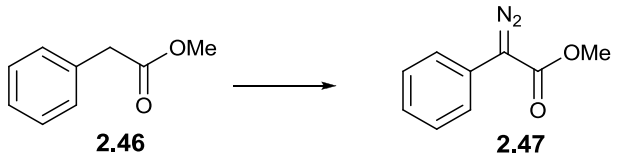
In order to successfully achieve intermolecular additions to cyclopropenes, it appears that the ester functional group needs to be replaced with a substituent which is less prone to rearrangement *via* the mechanism shown in Scheme 11. As such, 3,3-dialkyl substituted cyclopropenes were investigated next and the results are presented in Chapter 3.

2.3 Experimental

General Experimental

^{1}H NMR spectra were recorded on Bruker AC 200, DPX 400 and AV 400 spectrometers at 200 and 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectra were recorded at 50 and 100 MHz on the same spectrometers. Chemical shift data are quoted in parts per million (δ in ppm), J values are given in Hz and s, d, dd, t, q and m represent singlet, doublet, doublet of doublet, triplet, quartet and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 pre-coated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic $KMnO_4$ or aqueous acidic ammonium molybdate as appropriate. Chemicals were purchased from Aldrich and Fisher chemical companies and used without further purification unless otherwise stated. Acetonitrile was dried by distillation from CaH under nitrogen and stored in a inert atmosphere over 4 Å molecular sieves. Dichloromethane and chloroform were stored over 4 Å molecular sieves.

2.47, Methyl 2-diazo-2-phenylacetate[22]

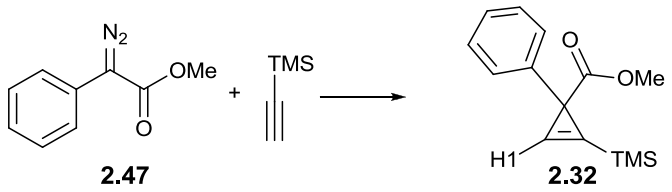


2.46 **2.47**

Methyl 2-phenylacetate **2.46** (7 ml, 49.7 mmol) was added to a slurry of 4-acetamidobenzenesulfonyl azide (14.3 g, 59.5 mmol) in MeCN (60 ml). DBU (8.8 ml, 59.5 mmol) was added drop-wise (over 20 min) to the resulting solution at 0 ^{o}C. Upon completion the slurry was allowed to stir at RT for 18 hours. The reaction mixture was diluted with diethyl ether and quenched with saturated NH_4Cl. The aqueous layer was separated and extracted with diethyl ether (3x). The combined organic layers were washed with NaOH (10%), brine and dried ($MgSO_4$) and concentrated under reduced pressure. The resulting oil was purified by column chromatography (50:1 hexane/diethyl ether) to yield the product **2.47** (5.8 g, 67%) as an amber oil.

ν_{max}/cm^{-1} 2082 md (N=N=C), 1709 st (C=O), 1153 st (C-O); δ_H (200 MHz, $CDCl_3$) 7.40-7.22 (5H, m, Ar-*H*), 3.73 (3H, s, OC*H*$_3$); δ_C (200 MHz, $CDCl_3$) 166.8 (O=*C*), 129.8 (Ar-*C*), 129.1 (2x Ar-*C*-H), 126.0 (Ar-*C*-H), 125.6 (N_2=*C*), 124.1 (2x Ar-*C*-H), 52.1 (O*C*H$_3$); LR-EI: m/z = 176 [M$^+$] ($C_9H_8N_2O_2$).

2.32, Methyl 1-phenyl-2-(trimethylsilyl)cycloprop-2-enecarboxylate[23]

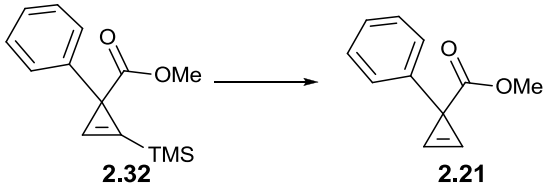


2.47 **2.32**

A solution of $Rh_2(OAc_2)_4$ (2.5 mg, 0.01 mol%) in dry ethynltrimethylsilane (10 ml) was heated to reflux. Diazo **2.47** (1.0 g, 5.7 mmol) in dry ethynltrimethylsilane (1 ml) was added dropwise to this refluxing mixture over a period of 20 hours using an injection pump. On completion of addition, the syringe was washed with solvent (1 ml) and the resulting mixture was allowed to stir for a further hour. The crude product was then filtered through a plug of silica, concentrated and purified using column chromatography (10:1 hexane/diethyl ether) to yield the product **2.32** as a yellow oil (727 mg, 52%).

ν_{max}/cm^{-1} 2954 st (C-H), 1728 md (C=O), 1702 st (C=C), 1528, 1494, 1433 md (Ar-C), 1250 shp (Si-CH_3), 1219 st(C-O); δ_H (200 MHz, $CDCl_3$) 7.44 (1H, s, *H-1*), 7.35-7.10 (5H, m, Ar-*H*), 3.65, (3H, s), 0.20 (9H, s, Si-(CH_3)$_3$); δ_C (200 MHz, $CDCl_3$) 176.3 (O=*C*), 142.6 (Ar-*C*), 128.5 (2x Ar-*C*-H), 128.1 (2x Ar-*C*-H), 126.2 (Ar-*C*-H), 120.4 (^{1}H-*C*=), 116.0 (=*C*-TMS), 52.1 (O*C*H_3), 31.5 (Ph-*C*-CO_2Me), -1.3 (Si-(*C*H_3)$_3$); LR-EI: m/z = 246 [M^+] ($C_{14}H_{18}O_2Si$).

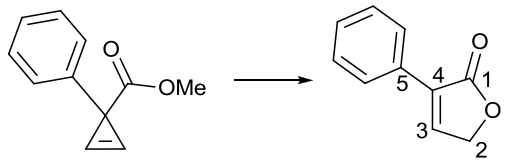
2.21, Methyl 1-phenylcycloprop-2-enecarboxylate[24]



A solution of methyl 1-phenyl-2-(trimethylsilyl)cycloprop-2-enecarboxylate **2.32** (730 mg, 3mmol) in MeOH (30 ml) was stirred and cooled to 0 ^{o}C. KOH (830 mg, 14.8 mmol) was added and the resulting mixture was allowed to stir for 20 min at 0 ^{o}C. The reaction was allowed to warm to RT and stir for 18 hour. The solution was diluted with DCM and washed with water. The aqueous layer was then extracted twice with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated and purified by column chromatography (3:1 hexane/diethyl ether) to yield the product **2.21** as a yellow oil (483 mg, 94%).

ν_{max}/cm^{-1} 1720 st (C=O), 1661 md (C=C), 1601, 1494, 1434 md (C-Ar), 1216 st (C-O);δ_H (200 MHz, $CDCl_3$) 7.36-7.25 (5H, m, Ar-*H*), 7.23-7.26 (2H, m, *H*-C=C-*H*), 3.72 (3H, s, O-C*H*$_3$); δ_C (200 MHz, $CDCl_3$) 175.6 (O=*C*), 141.5 (Ar-*C*), 128.3 (2x Ar-*C*-H), 128.2 (2x Ar-*C*-H), 126.7 (Ar-*C*-H), 107.7 (*C*=*C*), 52.3 (O-*C*H$_3$), 30.6 (Ph-*C*-CO_2Me). LR-EI: m/z = 174 [M^+] ($C_{11}H_{10}O_2$).

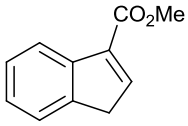
2.24, 3-phenylfuran-2(5H)-one[18]



2.23 **2.24**

A solution of AgOTf (18.8 mg, 0.07 mmol) and PPh_3AuCl (36.1 mg, 0.07 mmol) in toluene (0.2 ml) was added to a solution of cyclopropene **2.23** (50 mg, 0.29 mmol) toluene (0.3 ml). The reaction mixture was allowed to stir at 80 ^oC and the reaction monitored using TLC (1:1 hex/ether). Upon completion of the reaction the product was purified using column chromatography (1:1 hex/ether) to yield the product **2.24** (24 mg, 52%) as an amorphous orange solid.

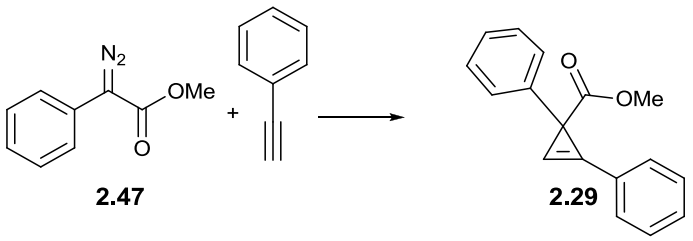
δ_H (200 MHz, $CDCl_3$) 7.90-7.76 (2H, m Ar-H), 7.63 (1H, t, *J* 2.0, H-3), 7.46-7.34 (3H, m, Ar-H), 4.91 (2H, d, *J* 2.0, H-2); δ_C (200 MHz, $CDCl_3$) 172.4 (<u>*C*</u>-1) 144.5 (<u>*C*</u>-4), 131.8 (<u>*C*</u>-5), 129.5 (<u>*C*</u>-3), 129.5 (2xAr-<u>*C*</u>), 128.9 (2xAr-<u>*C*</u>), 127.1 (Ar-<u>*C*</u>), 69.7 (<u>*C*</u>-2); LR-EI: m/z = 160 [M^+] ($C_{10}H_8O_2$).



2.25

The methyl 1H-indene-3-carboxylate, **2.25**[21], was also formed as a minor product in 20 % yield; δ_H (200 MHz, $CDCl_3$); - 8.03 (1H, dt, *J* 7.8, 0.6, C-H), 7.40 (4H, m, Ar-<u>*H*</u>), 3.89 (3H, s, O-C<u>*H*</u>$_3$), 3.51 (2H, d, *J* 2.0, C<u>*H*</u>$_2$); δ_C (50 MHz, $CDCl_3$) 164.5 (C), 144.7 (CH), 143.4 (C), 140.8 (C), 136.1 (C), 126.7 (CH), 125.6 (CH), 123.8 (CH), 122.5 (CH), 51.7 (CH_3), 38.5 (CH_2) LR-EI: m/z = 174 [M^+] ($C_{11}H_{10}O_2$).

2.29, Methyl 1,2-diphenylcycloprop-2-enecarboxylate[22]

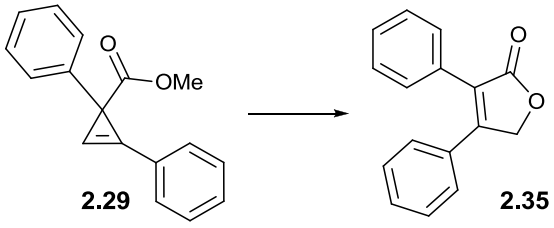


2.47 **2.29**

A solution of $Rh_2(OAc_2)_4$ (43.3 mg, 1 mol%) and phenylacetylene (3.3ml, 29.8 mmol) in DCM (11 ml) was allowed to stir at RT. Diazo **2.47** (1.7 g, 9.8 mmol) in DCM (9 ml) was added dropwise to the mixture at RT over a period of 20 hours using an injection pump. On completion of addition, the syringe was washed with solvent (1 ml) and the resulting mixture was allowed to stir for a further hour. The crude product was then filtered through a plug of silica, concentrated and purified using column chromatography (10:1 hexane/EtOAc) to yield the product **2.29** as a yellow oil (1.62 g, 66%).

δ_H (200 MHz, $CDCl_3$) 7.76-7.22 (11H, m, Ar-*H* and *H*-C=C), 3.74 (3H, s, O-C*H*$_3$); δ_C (200 MHz, $CDCl_3$) 175.3 (*C*=O), 141.0 (Ar-*C*), 130.2 (Ar-*C*-H), 130.1 (2x Ar-*C*-H), 129.1 (2x Ar-*C*-H), 128.4 (2x Ar-*C*-H), 128.3 (2x Ar-*C*-H), 126.7 (Ar-*C*-H), 125.6 (*C*-Ar), 117.5 (=*C*-Ph), 100.5 (=*C*-H), 52.4 (O-*C*H$_3$), 33.7 (Ph-*C*-CO_2Me). LR-EI: m/z = 250 [M^+] ($C_{17}H_{14}O_2$).

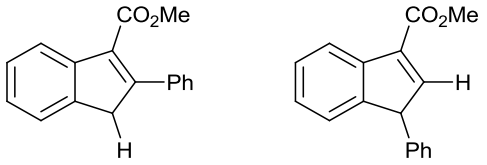
2.35, 3,4-diphenylfuran-2(5H)-one[19]



2.29 **2.35**

A solution of AgOTf (2.0 mg, 0.008 mmol) and PPh_3AuCl (3.7 mg, 0.008 mmol) in DCM (0.2 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **2.29** (20 mg, 0.08 mmol) in DCM (0.3 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx 1 h) the crude mixture was purified using column chromatography (1:1 hex/ether) to yield the product 3,4-diphenylfuran-2(5H)-one **2.35** as an amber oil (10 mg, 53%).

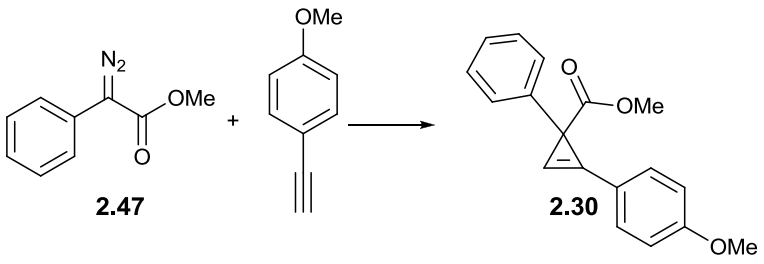
δ_H (200 MHz, $CDCl_3$) 7.46-7.28 (10H, m, Ar-H), 5.17 (2H, s, O-CH_2); δ_C (100 MHz, $CDCl_3$) 173.4 (C), 156.1 (C), 130.8 (C), 130.6 (CH), 130.1 (C), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 127.5 (CH), 126.2 (C), 70.6 (CH_2); LR-EI: m/z = 236 [M^+] ($C_{16}H_{12}O_2$).



2.38 **2.41**

The indene products **2.38** and **2.41** (ratio ~1:1) were collected as a mixture (3.6 mg, 18%). δ_H (400 MHz, $CDCl_3$); - 7.58-7.18 (9H+10H', m, Ar-H and C=CH), 4.84 (1H', s, C=CHC*H*Ar), 3.58 (2H, s, CH_2), 3.81, (3H, s, OCH_3), 3.62 (3H', s, OCH_3); HRMS mz = 268.1337 $[M+NH_4]^+$ (calc. for $C_{17}H_{14}O_2$ = 268.1332 $[M+NH_4]^+$).

2.30, Methyl 2-(4-methoxyphenyl)-1-phenylcycloprop-2-enecarboxylate[23]

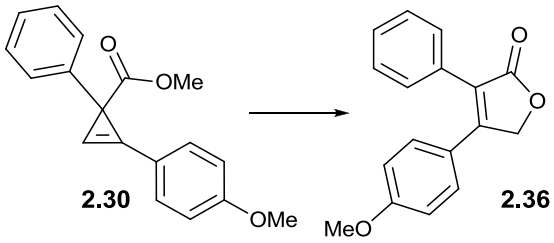


2.47 **2.30**

A solution of $Rh_2(OAc_2)_4$ (20.3 mg, 1 mol%) and 4-ethynylanisole (1.0 ml, 7.71 mmol) in DCM (1 ml) was allowed to stir at RT. Diazo **2.47** (579.0 mg, 2.63 mmol) in DCM (5 ml) was added dropwise to the mixture at RT over a period of 20 hours using an injection pump. On completion of addition, the syringe was washed with solvent (1 ml) and the resulting mixture was allowed to stir for a further hour. The crude product was then filtered through a plug of silica, concentrated and purified using column chromatography (7:1 hexane/Et_2O) to yield the product **2.30** as a yellow oil (456.2 mg, 62%).

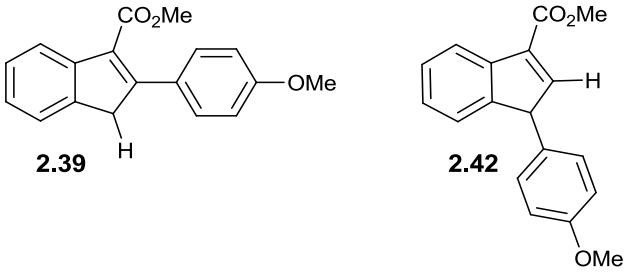
δ_H (200 MHz, $CDCl_3$) 7.57 (2H, m, Ar-*H*), 7.45-7.15 (5H, m, Ar-*H*), 7.07 (1H, s, C=C-*H*), 6.95 (2H, m, Ar-*H*), 3.84 (3H, s, O-C*H*$_3$), 3.73 (3H, s, O-C*H*$_3$); δ_C (200 MHz, $CDCl_3$) 175.3 (*C*=O), 161.0 (Ar-*C*), 141.1 (Ar-*C*), 131.5 (Ar-*C*-H), 128.2 (Ar-*C*-H), 128.0 (Ar-*C*-H), 127.7 (Ar-*C*-H), 126.4 (Ar-*C*-H), 118.0 (Ar-*C*), 114.4 (C=*C*-Ar), 97.5 (C=*C*-H), 52.4 (O-*C*H_3), 52.1 (O-*C*H_3), 33.4 (Ph-*C*-CO_2Me). LR-EI: m/z = 280 [M^+] ($C_{18}H_{16}O_2$)

2.36, 4-(4-Methoxyphenyl)-3-phenylfuran-2(5H)-one[22]



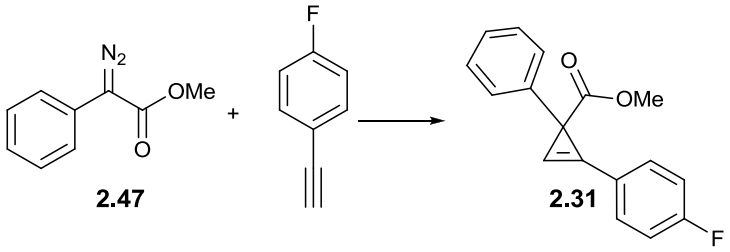
A solution of AgOTf (4.6 mg, 0.018 mmol) and PPh_3AuCl (8.9 mg, 0.018 mmol) in DCM (0.4 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **2.30** (50 mg, 0.18 mmol) in DCM (0.8 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx 2 h) the crude mixture was purified using column chromatography (5:1 hex/ether) to yield the product 4-(4-methoxyphenyl)-3-phenylfuran-2(5H)-one **2.36** as a yellow solid (24 mg, 50%).

δ_H (200 MHz, $CDCl_3$); 7.48-7.35 (5H, m, Ph-H), 7.28 (2H, d, *J* = 8.3, Ar-H), 6.83 (2H, d, *J* = 8.3, Ar-H), 5.16 (2H, s, CH_2), 3.81 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 173.8 (C), 161.4 (C), 155.6 (C), 130.7 (C), 129.4 (CH), 129.1(CH), 128.7 (CH), 128.6 (CH), 124.3 (C), 123.1 (C), 114.4 (CH), 70.4 (CH_2), 55.4 (CH_3); LR-EI: m/z = 266 [M^+] ($C_{17}H_{14}O_3$).



The indene products **2.39** and **2.42** (ratio 2.6:1) were collected as a mixture (10 mg, 20%). δ_H (200 MHz, $CDCl_3$); 7.48-6.80 (8H+9H', m, Ar-H and C=CH), 4.73 (1H', s, C=CHC*H*Ar), 3.78 (8H, overlapping s, CH_2, 2xOCH_3), 3.76, (3H, s, OCH_3), 3.56 (3H', s, OCH_3).

2.31, Methyl 2-(4-fluorophenyl)-1-phenylcycloprop-2-enecarboxylate[6]

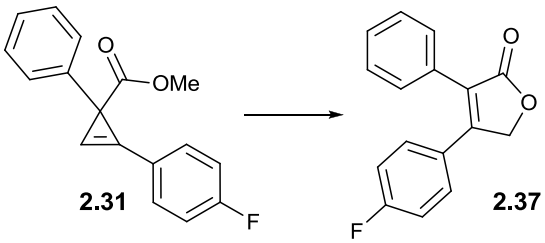


2.47 **2.31**

A solution of $Rh_2(OAc_2)_4$ (7.2 mg, 1 mol%) and ethynyl-4-flourobenzene (0.91 ml, 7.94 mmol) in DCM (2 ml) was allowed to stir at RT. Diazo **2.47** (276.8 mg, 1.59 mmol) in DCM (4 ml) was added dropwise to the mixture at RT over a period of 20 hours using an injection pump. On completion of addition, the syringe was washed with solvent (1 ml) and the resulting mixture was allowed to stir for a further hour. The crude product was then filtered through a plug of silica, concentrated and purified using column chromatography (8:1 hexane/Et_2O) to yield the product **2.31** as a yellow oil (80.6 mg, 19%).

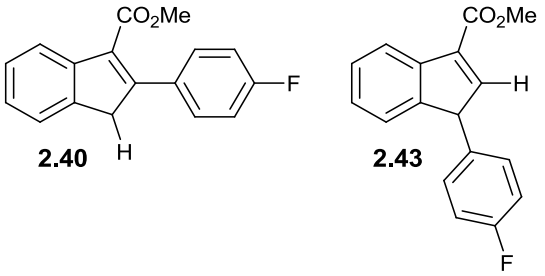
δ_H (200 MHz, $CDCl_3$) 7.69 (2H, dd, *J* = 8.8, 5.3 F-Ar-*H*), 7.48-7.16 (8H, m, Ar-*H* + C=C-*H*), 3.81 (3H, s, O-C*H*$_3$); δ_C (200 MHz, $CDCl_3$) 174.8 (*C*=O), 163.5 (d, *J* = 251.5, F-*C*-Ar), 140.6 (Ar-*C*), 131.8 (d, *J* = 8.5, Ar-*C*-H), 128.1 (Ar-*C*-H), 128.0 (Ar-*C*-H), 126.6 (Ar-*C*-H), 121.7 (d, *J* = 2.8, Ar-*C*), 116.5 (Ar-*C*=C), 116.2 (d, *J* = 22.6, Ar-*H*), 99.7 (C=*C*-H), 52.2 (O-*C*H_3), 33.6 (Ph-*C*-CO_2Me). LR-EI: m/z = 268 [M^+] ($C_{17}H_{13}FO_2$).

2.37, 4-(4-Fluorophenyl)-3-phenylfuran-2(5H)-one[6]



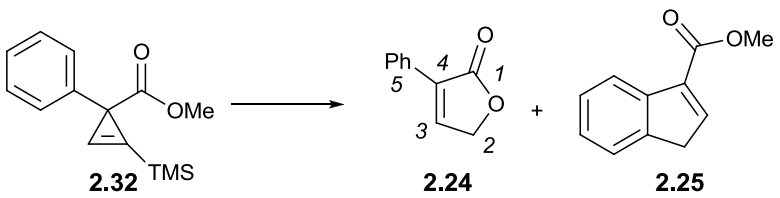
A solution of AgOTf (4.8 mg, 0.019 mmol) and PPh_3AuCl (9.3 mg, 0.019 mmol) in DCM (0.4 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **2.31** (50 mg, 0.187 mmol) in DCM (0.8 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx 2 h) the crude mixture was purified using column chromatography (3:1 hex/ether) to yield the product 4-(4-fluorophenyl)-3-phenylfuran-2(5H)-one **2.37** as a yellow solid (24 mg, 50%).

δ_H (400 MHz, $CDCl_3$); 7.43-7.36 (5H, m, Ph-H), 7.32 (2H, dd, *J* 9.0, 5.2, Ar-H), 7.32 (2H, dd, *J* 9.0, 8.4, Ar-H), 5.16 (2H, s, CH_2); δ_C (100 MHz, $CDCl_3$) 173.3 (C), 163.8 (d, *J* 253 Hz, C), 154.8 (C), 130.0 (C), 129.6 (d, *J* 8 Hz, CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 127.0 (C), 126.2 (C), 116.3 (d, *J* 22 Hz, CH), 70.4 (CH_2); LR-EI: m/z = 254 [M^+]. HRMS m/z = 254.0736 [M^+] (calc. for $C_{16}H_{11}O_2F$ 254.0738).



The indene products **2.40** and **2.43** (ratio 1:3) were collected as a mixture (8.8 mg, 18%). δ_H (400 MHz, $CDCl_3$); 7.55-7.02 (8H+9H', m, Ar-H and C=CH), 4.80 (1H', s, C=CHC*H*Ar), 3.85 (2H, s, CH_2), 3.82, (3H, s, OCH_3), 3.63 (3H', s, OCH_3).

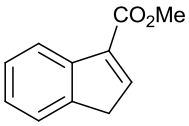
Catalytic Rearrangement of methyl 1-phenyl-2-(trimethylsilyl) cycloprop-2-enecarboxylate, 2.32



2.32 **2.24** **2.25**

A solution of AgOTf (2.0 mg, 0.008 mmol) and PPh_3AuCl (4 mg, 0.008 mmol) in DCM (0.2 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **2.32** (20 mg, 0.08 mmol) in DCM (0.3 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of reaction the mixture was purified using column chromatography (1:1 hex/ether) to produce two products 3-phenylfuran-2(5H)-one **2.24**[18] (5.0 mg, 39%) and methyl 1H-indene-3-carboxylate[21] **2.25** (5.1mg, 37%).

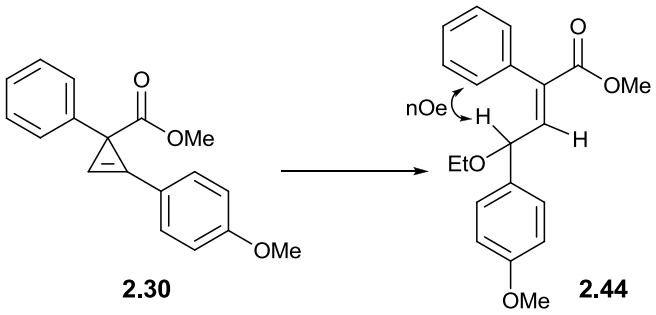
δ_H (200 MHz, $CDCl_3$) 7.90-7.76 (2H, m Ar-H), 7.63 (1H, t, *J* 2.0, H-3), 7.46-7.34 (3H, m, Ar-H), 4.91 (2H, d, *J* 2, H-2); δ_C (200 MHz, $CDCl_3$) 172.4 (*C*-1) 144.5 (*C*-4), 131.8 (*C*-5), 129.5 (*C*-3), 129.5 (2xAr-*C*), 128.9 (2xAr-*C*), 127.1 (Ar-*C*), 69.7 (*C*-2); LR-EI: m/z = 160 [M^+] ($C_{10}H_8O_2$).



2.25

Methyl 1H-indene-3-carboxylate, **2.25**[21]; δ_H (200 MHz, $CDCl_3$); - 8.03 (1H, app. dt, *J* = 7.8, 0.6, C=C-*H*), 7.40 (4H, m, Ar-*H*), 3.89 (3H, s, O-C*H*$_3$), 3.51 (2H, d, *J* 2.0, C*H*$_2$); δ_C (50 MHz, $CDCl_3$) 164.5 (C), 144.7 (CH), 143.4 (C), 140.8 (C), 136.1 (C), 126.7 (CH), 125.6 (CH), 123.8 (CH), 122.5 (CH), 51.7 (CH_3), 38.5 (CH_2) LR-EI: m/z = 174 [M^+] ($C_{11}H_{10}O_2$).

2.44, (Z)-methyl 4-ethoxy-2,4-diphenylbut-2-enoate



2.30 **2.44**

A solution of PPh_3AuNTf_2 (8.4 mg, 0.011 mmol) and EtOH (0.09 mL, 1.6 mmol) in DCM (0.2 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **2.30** (30 mg, 0.11 mmol) in DCM (0.3 mL) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx. 3 h) the crude mixture was filtered through a plug of silica (eluent:ether). The product, **2.44**, was identified by 1H-NMR (400 MHz, $CDCl_3$) analysis of the crude mixture.

δ_H(400 MHz, $CDCl_3$); - 7.25-7.28 (5H, m, Ph-*H*), 7.06 (2H, d, *J* 8.9, Ar-*H*), 6.73 (2H, d, *J* 8.9, Ar-*H*), 6.38 (1H, s, C=C*H*), 4.96 (1H, s, tOCC*H*), 3.98-3.84 (2H, m, OCH_2), 3.74 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 1.28 (3H, t, *J* = 7.1, OCH_2CH_3); δ_C(100 MHz, $CDCl_3$) 173.3 (C), 158.3 (C), 144.9 (CH), 137.6 (C), 131.1 (C), 129.2 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 117.1 (C), 113.5 (CH), 68.3 (CH_2), 55.2 (CH_3), 52.0 (CH_3), 51.5 (CH), 15.3 (CH_3).

2.4 References

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