Dual Visible Light Photoredox and Gold-Catalyzed Arylative Ring Expansion

Xing-zhong Shu,[a] Miao Zhang,[b] Ying He,[a,c] Heinz Frei,*[,b] F. Dean Toste*[, a]

[a] Department of Chemistry, University of California, Berkeley, California 94720, and Chemical Sciences Divisions, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

[b] Physical Biosciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

[c] Institute of Chemistry and BioMedical Sciences, Nanjing University, Nanjing 210046, P. R. China

Supporting Information

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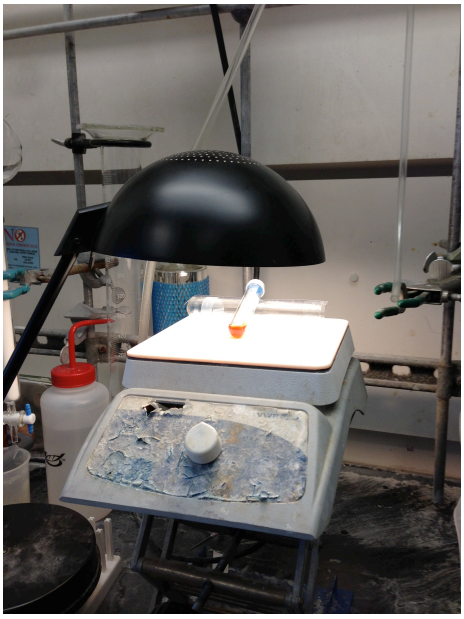
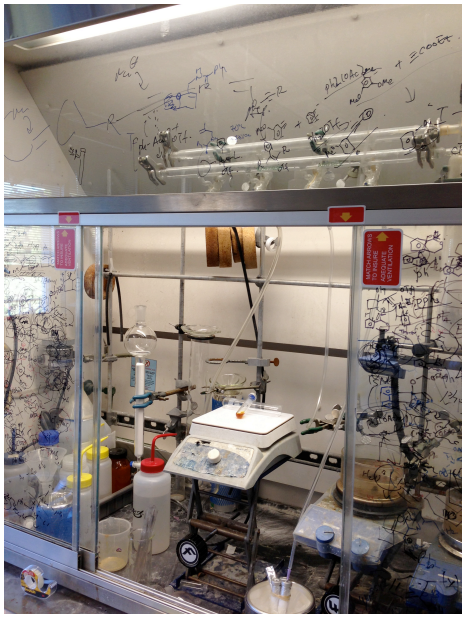
1. General Information

Unless otherwise noted, reagents were obtained commercially and used without further purification. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates using UV light, ceric ammonium molybdate stain, potassium permanganate stain, and/or I_2 to visualize the reaction components. Flash chromatography was carried out on ICN SiliTech 32-63 D 60 Å silica gel according to standard procedures. Solvents used for chromatographic purification procedures (HPLC grade hexane and ethyl acetate) were obtained from Fisher Scientific. Unless otherwise noted, ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature with Bruker AV-300, AVB-400, AVQ-400, DRX-500, AV-500, and AV-600 spectrometers and were referenced to residual protium in the NMR solvent ($CHCl_3$, δ = 7.26 ppm; CH_3CN, δ = 1.96 ppm) for 1H spectra and to carbon resonance of the NMR solvent (center line: $CHCl_3$, δ = 77.2 ppm; CH_3CN, δ = 1.79, 118.26 ppm) for ^{13}C spectra. ^{19}F and ^{31}P NMR spectra were recorded at ambient temperature with Bruker AVQ-400 spectrometers operating at 376.441 and 161.967 MHz respectively. Mass spectral and analytical data were obtained via the QB3/Chemistry Mass Spectrometry Facility operated by the QB3 Institute and the College of Chemistry, University of California, Berkeley. Electrospray ionization (ESI) mass spectra were recorded on a Finnigan LTQ FT mass spectrometer. GC-MS data were obtained on an Agilent Technologies 6890N/5973 GC-MS with HP-5MS column of 30 m length and 0.25 mm diameter.

Visible light source:



(Light Source A)



(Light Source B)

Light Source A: Using 26 W Fluorescent light bulb.

Source B: Using 32 W Fluorescent light bulb installed in hood.

Synthesis of substrates.

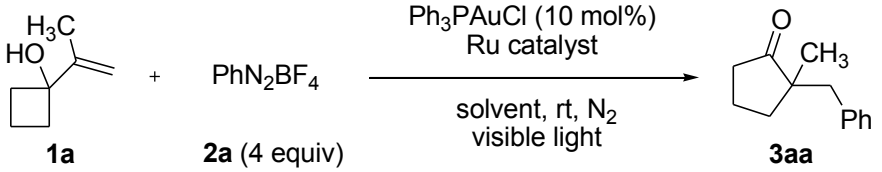
Aryldiazonium salts were prepared according to the procedure of Bunnett.[1] $[Ru(bpy)_3](PF_6)_2$ was prepared according to the procedure of Meggers.[2] The syntheses of the following compounds have been previously described elsewhere: 1-(prop-1-en-2-yl)cyclobutanol (**1a**)[3], 1-(1-phenylpropa-1,2-dienyl)cyclopropanol (**12a**)[4], 1-(1-*p*-Tolylpropa-1,2-dienyl)cyclopropanol (**12c**)[4], 1-(1-Cyclohexylpropa-1,2-dienyl)cyclopropanol (**12d**)[4], 1-(5-Phenylpenta-1,2-dien-3-yl)cyclopropanol (**12e**)[4]. The syntheses of the remaining substrates are given below:

2. Optimization of reaction conditions:

2.1 Effect of photocatalyst, solvents and visible light sources.

Initial studies on the screening of various solvents revealed that the reaction of vinylcyclobutanol **1a** with PhN_2BF_4 **2a** (4 equiv) in the presence of Ph_3PAuCl (10 mol %), $[Ru(bpy)_3]Cl_2·6H_2O$ (5 mol %) and visible light (Source A) in degassed MeOH (0.04 M) gave 36% yield of product **3aa** (Table S1, entries 1-8). The use of $[Ru(bpy)_3]·2(PF_6)$ improved the reactivity and the photocatalyst loading could be reduced to 2.5% (entries 9-10). The use of mixed solvents is helpfull (entries 11-19), affording the best result in MeOH/CH_3CN (3:1) (entry 13). The switchness of visible light source and decrease in diazonium loading efficiently improved the reactivity, affording **3aa** in 87% isolated yield (entries 14 and 15).

Table S1. Effect of various solvents, Ru catalysts and visible light source.[a]



1a **2a** (4 equiv) **3aa**

entry	Ru catalyst (mol)	solvent	yield% of **3aa**[b]
1	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	CH_2Cl_2	0
2	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	THF	0
3	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	Toluene	0
4	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	CH_3CO_2Et	0
5	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	Acetone	21
6	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	CH_3CN	26
7	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	MeOH	36
8	$[Ru(bpy)_3]Cl_2·6H_2O$ (5%)	EtOH	15
9	$[Ru(bpy)_3]·2(PF_6)$ (5%)	MeOH	50
10	$[Ru(bpy)_3]·2(PF_6)$ (2.5%)	MeOH	51
11	$[Ru(bpy)_3]·2(PF_6)$ (2.5%)	MeOH/CH_3CN (10:1)	58
12	$[Ru(bpy)_3]·2(PF_6)$ (2.5%)	MeOH/CH_3CN (6:1)	63

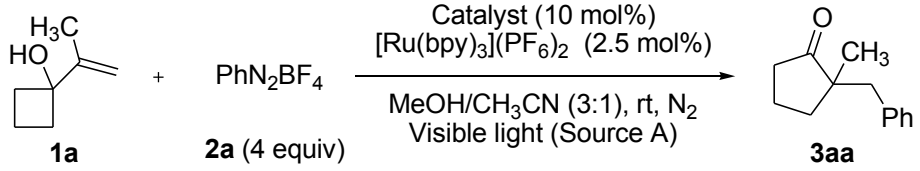
13	$[Ru(bpy)_3]\cdot 2(PF_6)$ (2.5%)	MeOH/CH_3CN (3:1)	73
14[c]	$[Ru(bpy)_3]\cdot 2(PF_6)$ (2.5%)	MeOH/CH_3CN (3:1)	83
15[c,d]	$[Ru(bpy)_3]\cdot 2(PF_6)$ (2.5%)	MeOH/CH_3CN (3:1)	93 (87)[e]
16	$[Ru(bpy)_3]\cdot 2(PF_6)$ (2.5%)	MeOH/CH_3CN (1:1)	43
17	$[Ru(bpy)_3]\cdot 2(PF_6)$ (2.5%)	MeOH/CH_3CN (1:3)	57
18	$[Ru(bpy)_3]\cdot 2(PF_6)$ (2.5%)	MeOH/CH_3CN (1:6)	61
19	$[Ru(bpy)_3]\cdot 2(PF_6)$ (2.5%)	MeOH/CH_3CN (1:10)	49

[a.] Reaction works at rt using **1a** (0.2 mmol), Ph_3PAuCl (10 mol %), Ru catalyst (2.5-5 mol %), PhN_2BF_4 (**2a**, 4 equiv) in degassed solvent (0.04 M) under visible light (Source A) overnight. [b.] Yields were calculated based on ^1H NMR using internal standard. [c.] visible light (Source B) was used. [d.] visible light (Source B) and PhN_2BF_4 (3 equiv) were used. [e.] Isolated yield.

2.2 Effect of various transition metal catalysts

The reaction proceeded smoothly when either electron poor or rich triaryl phosphine ligand was used (Table S2 entries 1-5). However, the reactivity was dramatically reduced when sterically hindered ligand was employed (entry 6). Low conversion of **1a** were observed when both alkyl and bidentate phosphine ligands were used (entries 7-13). Low yield of **3aa** were also obtained when Au-Me, Au-Ph complex as well as cationic gold(I) compounds were used (entries 14-18). Only trace of desired product was obtained when the reaction proceeded in the presence of non-phosphine ligand or no ligand (entries 19-21). The reaction failed to be catalyzed by several other transition metal catalysts and acid (entries 22-26).

Table S2. Effect of various gold and transition metal catalysts.[a]



entry	catalyst	yield% of **3aa**[b]
1	Ph_3PAuCl	73
2	Ph_3PAuBr	68

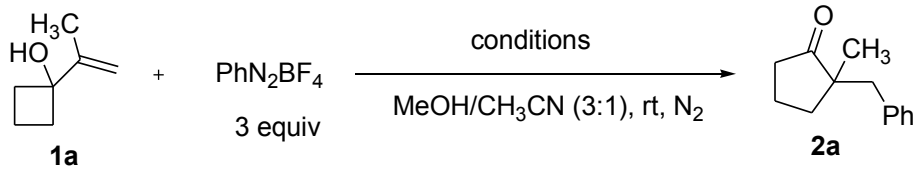
3	$(4\text{-F-Ph})_3PAuBr$	68
4	$(4\text{-}CF_3\text{-Ph})_3PAuBr$	57
5	$(4\text{-}CH_3\text{-Ph})_3PAuCl$	74
6	$(2\text{-}CH_3\text{-Ph})_3PAuCl$	9
7	$PhP(Me)_2AuCl$	46
8	Me_3PAuCl	28
9	Cy_2(*o*-biphenyl)PAuCl	18
10	$dppm(AuBr)_2$	24
11	$dppp(AuBr)_2$	23
12	$PNP(AuCl)_2$	10
13	$BINAP(AuCl)_2$	2
14	Ph_3PAuMe	28
15	Ph_3PAuPh	24
16	$Ph_3PAuN(Tf)_2$	18
17	Ph_3PAuBF_4	25
18	$Ph_3PAuSbF_6$	20
19	IPrAuCl	2
20	$AuCl_3$	0
21	AuCl	2
22	$AgSbF_6$	0
23	$Cu(OAc)_2$	0
24	$Pd(OAc)_2$	0
25	$Rh(PPh_3)_3Cl$	0
26	TfOH	0

[a.] Reaction works at rt using **1a** (0.2 mmol), catalyst (10 mol%), $Ru(bpy)_3(PF_6)_2$ (2.5 mol%), PhN_2BF_4 (4 equiv) in degassed MeOH/CH_3CN (3:1, 5 mL) under visible light (source A) overnight. [b.] Yields were calculated based on ^1H NMR using internal standard.

2.3 Control experiments

The controlled experiments revealed that only trace amount of product was detected by ^{1}H NMR when the reaction proceeded in the absence of light, photocatalyst or gold catalyst (Table S3, entries 1-3). No reaction was observed when PPh_3 was used instead of gold catalyst (entry 4). Thus the use of vinylcyclobutanol **1a** (1 equiv), PhN_2BF_4 **2a** (3 equiv), Ph_3PAuCl (10 mol %), $Ru(bpy)_3(PF_6)_2$ (2.5 mol %) in degassed MeOH/CH_3CN (3:1, 0.04 M) in the presence of visible light (Source B) was used as standard condition as Method A.

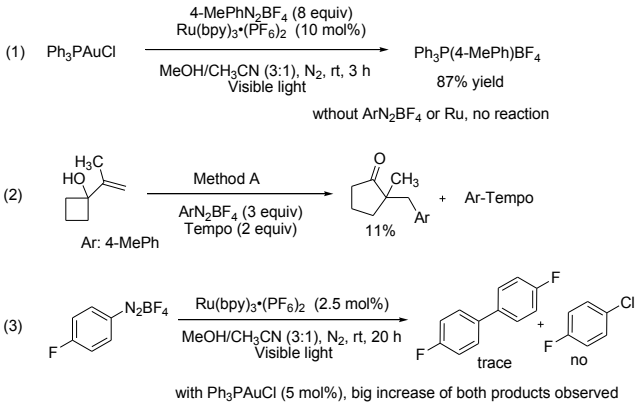
Table S3. Control experiments[a]



entry	conditions	yield of **2a**
1	Ph_3PAuCl (10 mol %)	4
2	$Ru(bpy)_3{\cdot}(PF_6)_2$ (2.5 mol %)	2
3	Ph_3PAuCl (10 mol %), $Ru(bpy)_3(PF_6)_2$ (2.5 mol %) in dark	1
4	Ph_3P (10 mol%), $Ru(bpy)_3(PF_6)_2$ (2.5 mol %)	0
5	Ph_3PAuCl (10 mol%), $Ru(bpy)_3(PF_6)_2$ (2.5 mol%), visible light	93 (87)[b]

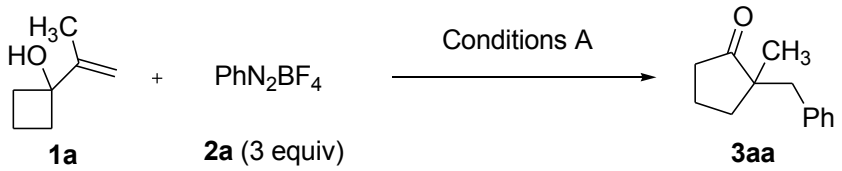
[a.] Reaction works at rt using **1a** (0.2 mmol), PhN_2BF_4 (3 equiv) in degassed MeOH/CH_3CN (3:1, 5 mL) under controlled conditions. Yields were calculated based on ^{1}H NMR using internal standard. [b.] Isolated yield.

3. Mechanism study



To gain further insights for the mechanism of this dual catalytic process, we monitored the reaction progress by ^{31}P NMR spectroscopy (Figure S1). Ph_3PAuCl with signal at 32.97 was the dominant gold species in solution during the catalytic reaction (Minor peaks were also observed at ^{31}P NMR: 38.4, 44.5). Thus we believe it is part of the catalytic cycle. Upon consumption of alkene substrate, this species was fast converted to $[Ph_3P\text{-}Ph]^+$ with a signal at 22.95. In the absence of gold catalyst, this signal was not observed from Ph_3P alone (Table S3, entry 4). Ph_3PAuCl reacted efficiently with 4-$MePhN_2BF_4$ under photoredox conditions, but no reaction was observed in the absence of diazonium or Ru catalyst (eq. 1). The isolated Ph_3P(4-MePh)BF_4 did not show any reactivity towards alkene substrate. The conversion of phosphine to phosphonium could be slowed down by addition of Tempo (Figure S4). The observed Tempo-Ar compound supports the presence of Ar· during the reaction. The oxidative arylation of **1a** was also significantly decreased by Tempo addition (eq. 2). We then hypothesized that the reaction of Ar· with Ph_3PAuCl should give an active gold species, which has great reactivity towards alkene substrate.

3.1 In situ monitoring of the reaction of 1a with 2a under standard conditions by ^{1}H NMR and ^{31}P NMR spectroscopy.



The reaction of alkene **1a** (0.05 mmol) with diazonium salt **2a** in deuterated MeOH/CH_3CN (3:1, 1.2 mL) was conducted under the standard conditions of Method A in J Young NMR tube. It was measured by ^{1}H NMR and ^{31}P NMR in 30 min, 2 h, 3 h and 5 h. The reaction proceeded efficiently in 2h. During this time, most **1a** was transferred to **3aa** and Ph_3PAuCl with signal at 32.97 was the dominant gold species in solution. Ph_4P^+ with signal at 22.95 was not observed at this time. A significant increase in Ph_4P^+ with Ph_3PAuCl decreasing was observed when alkene **1a** was gone in 3h. A total conversion was observed in 5h.

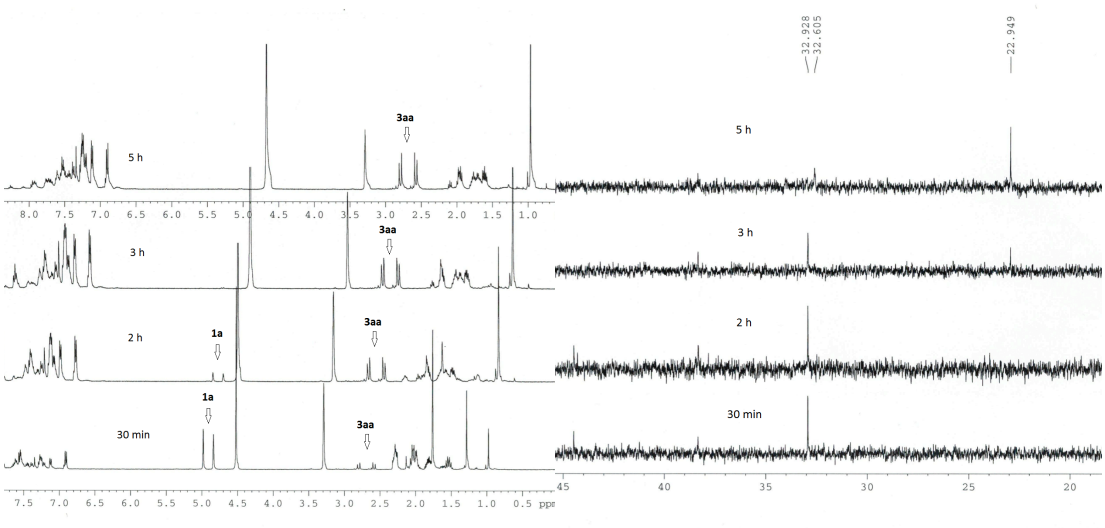
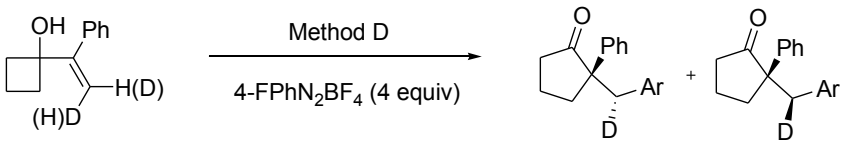


Figure S1

3.2 Stereochemistry of the reaction of deuterated-1f and the *in situ* monitoring experiments

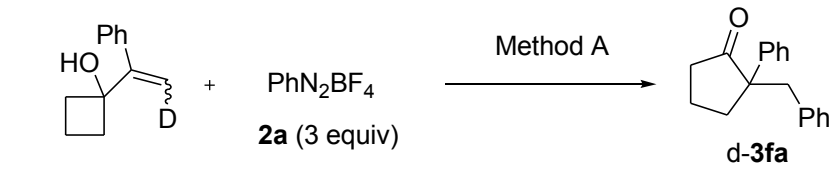
3.2.1 Stereochemistry of the reaction of deuterated-1f



dr (*cis* **d-1f**/*trans* **d-1f**) = 3:1

a) (4-CF_3-Ph)$_3$PAuCl (10 mol%) — 73% yield, dr (**d-3fb-1**/**d-3fb-2**) = 2.2:1
b) no gold catalyst — 21% yield, dr (**d-3fb-1**/**d-3fb-2**) = 1:1

3.2.2 Monitoring of the reaction of deuterated-1f with 2a under standard conditions.



(mixture of **1f**, *cis*-d-**1f** and *trans*-d-**1f**)

The reaction of styrene substrate (0.05 mmol) and diazonium salt **2a** in deuterated MeOH/CH_3CN (3:1, 1.2 mL) was conducted under the standard conditions of Method A in J Young NMR tube. It was measured by ^{1}H NMR and ^{31}P NMR in 2 h. Most substrate remained unreacted in 2 h, whereas most Ph_3PAuCl was already transferred to Ph_4P^+.

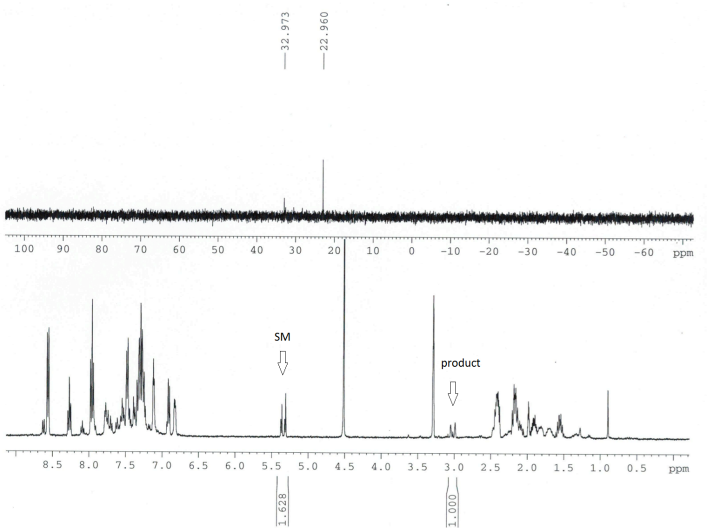


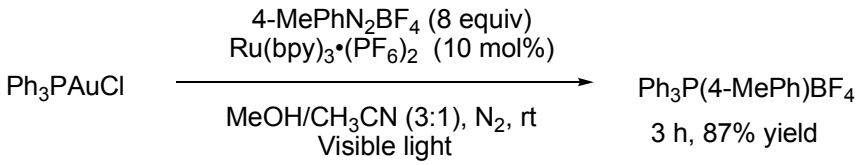
Figure S2

3.3. Controlled reactions of Ph_3PAuCl with diazoniums

Table S4. List of observed phosphoniums

entry	phosphonium	^{31}P NMR (d-MeOH/d-CH_3CN, 3:1)	HRMS
1	$[Ph_3PPh]^+$	22.95	339.1293
2	$[Ph_3P(4\text{-}MePh)]^+$	22.71	353.1448
3	$[Ph_3P(4\text{-}FPh)]^+$	22.64	357.1198

3.3.1. Synthesis of $[Ph_3P(4\text{-}MePh)]BF_4$ compound



Ph_3PAuCl (20 mg, 0.04 mmol, 1 equiv), $Ru(bpy)_3(PF_6)_2$ (3.5 mg, 10 mol%) and 4-$MePhN_2BF_4$ (65 mg, 8 equiv) were added to a microwave vial. MeOH/CH_3CN (3:1, 6 mL) was then added to the sealed vial in the absence of light at -78°C. The mixture was degassed and then refilled with N_2 for three times. The reaction mixture was then warmed to room temperature and stirred under irradiation from visible light source B. Most solvent was removed under reduced pressure after 5 h. The residue was dissolved with DCM (2 mL) and the remaining 4-$MePhN_2BF_4$ was precipitated by addition of 8 mL of diethyl ether. The mixture was filtered though a pad of celite. The solvent of filtrate was removed under educed pressure. The residue was washed with ether and recrystallized with THF/Ether to give $Ph_3P(4\text{-}MePh)BF_4$ (15 mg) in 87% yield. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.93-7.89 (m, 3H), 7.75-7.72 (m, 6H), 7.64-7.47 (m, 10H), 2.54 (s, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.6 (d, *J* = 2.5 Hz), 135.6 (d, *J* = 3.8 Hz), 134.40 (d, *J* = 11.3 Hz), 134.38 (d, *J* = 11.3 Hz), 131.3 (d, *J* = 13.9 Hz), 130.5 (d, *J* = 13.9 Hz), 117.9 (d, *J* = 90.7 Hz), 113.7 (d, *J* = 92.0 Hz), 21,7 (d, *J* = 1.3 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 23.0. HRMS (ESI) calc for $C_{25}H_{22}P_1$ $[M]^+$: m/z 353.1454, found 353.1444. HRMS (ESI) calc for BF_4 $[M]^-$: m/z 87.0035, found 87.0034.

To further confirm the anion of the formed phosphonium salt is BF_4^-, both ^1H NMR and ^{19}F NMR experiments were taken with PhF as the added external standard. The ratio of PhF/$[Ph_3P(4\text{-MePh})]^+$ is 2.75:1 based on ^1H NMR, and the ratio of PhF/BF_4^- is 2.83:1 based on ^{19}F NMR (Figure S3). The two numbers are consistent with the structure of $Ph_3P(4\text{-MePh})BF_4$.

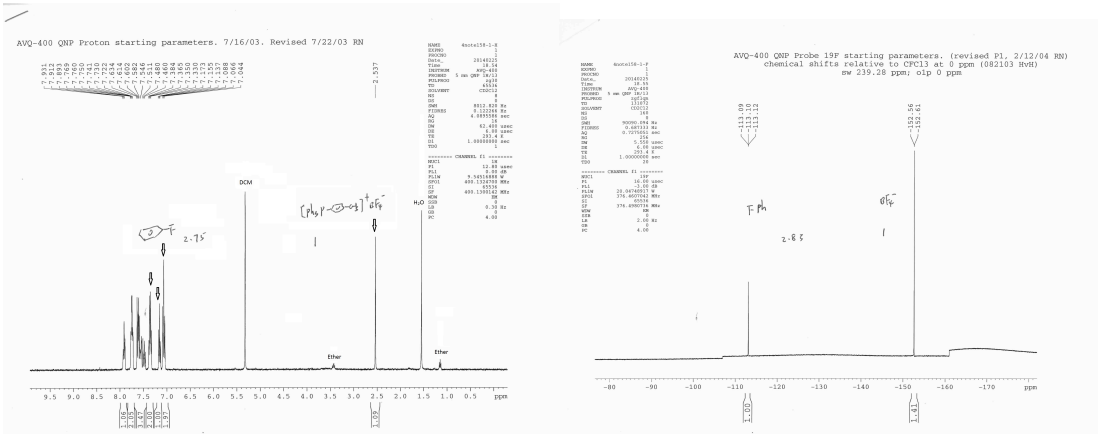
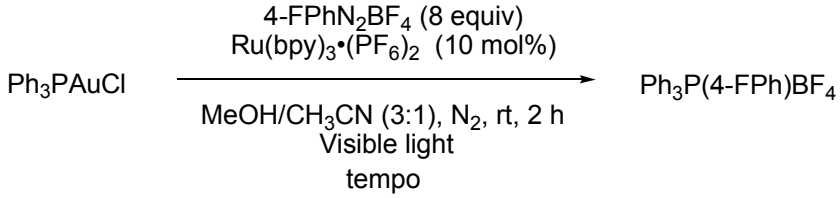


Figure S3

3.3.2. Effect of tempo on the reaction of Ph_3PAuCl to phosphonium.



The reaction of phosphine ligand to phosphonium (31 P NMR: 22.64) is significantly slowed down by addition of tempo.

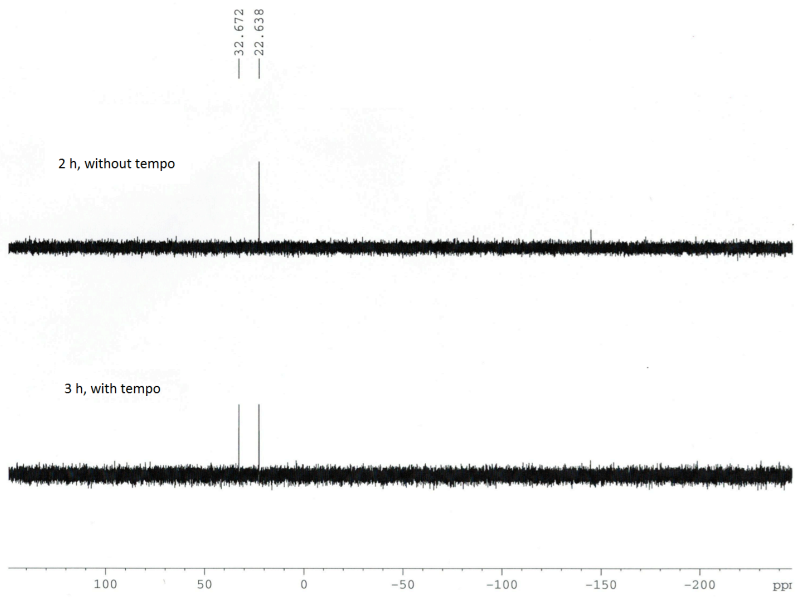
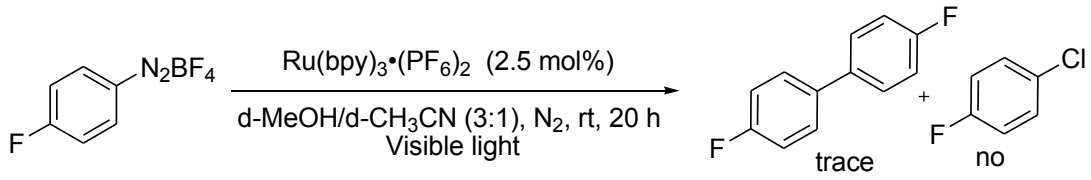


Figure S4

3.3.3. Effect of gold catalyst on the formation of biaryl compound



with Ph_3PAuCl (5 mol%), big increase of both products observed

The amount of homocoupling product (4-F)Ph-Ph(4-F) is significantly increased when Ph_3PAuCl was added to 4-$FPhN_2BF_4$ in photocatalysis conditions. The observed deuterated biaryl compound is formed by the reaction of 4-$FPhN_2BF_4$ with d-Ar, which is generated by radical process in deuterated solvent.

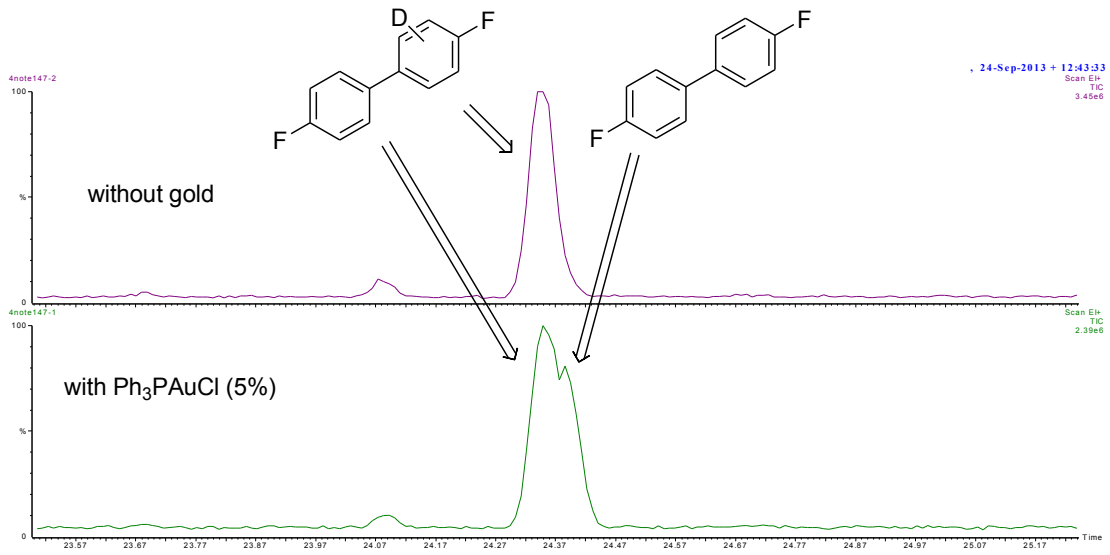
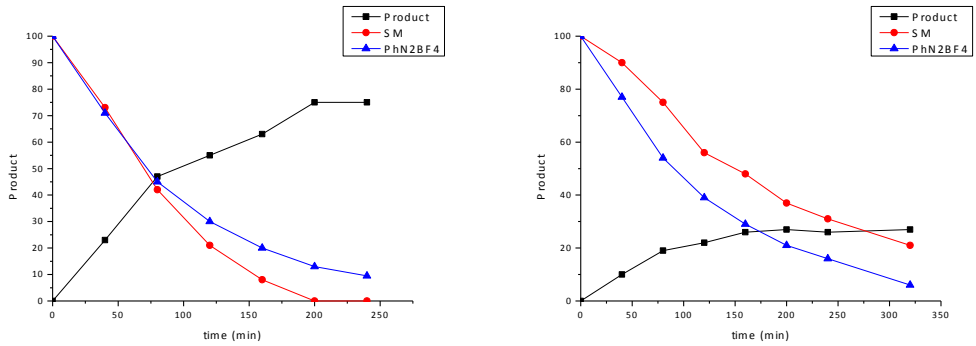


Figure S5

4. Comparing the catalytic reactivity of Ph_3PAuCl and Ph_3PAuBF_4 catalysts

The reaction of alkene **1a** (0.05 mmol) with diazonium salt **2a** in deuterated MeOH/CH_3CN (3:1, 1.2 mL) was conducted under the standard conditions of Method A in J Young NMR tube. The reaction was monitored by ^1H NMR spectroscopy.



(Ph_3PAuCl catalysis) (Ph_3PAuBF_4 catalysis)

Figure S6

5. Time-resolved rapid-scan FT-IR spectroscopy

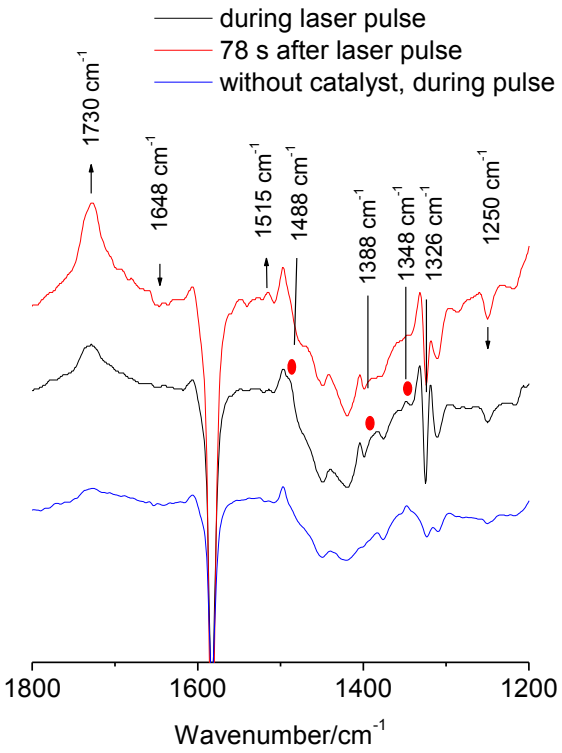
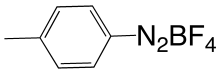
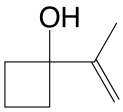
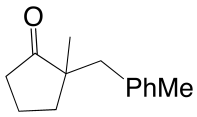


Figure S7. The rapid-scan FTIR spectra (difference spectra, with the spectrum before reaction as background) of the reaction system during the laser pulse (black, 12 s illumination) and 78 s after the end of the laser pulse (red). Blue trace: The control system without gold catalyst (but with $Ru(bpy)_3$ sensitizer) during the laser pulse (12 s illumination). In addition to the 1488 cm^{-1} band mentioned in the main text, another two intermediate bands at 1388 cm^{-1} and 1348 cm^{-1} were also observed.

Table S5. IR absorption bands of authentic samples of reactants and product.

compound	ν (cm^{-1})
	2272, 1583,* 1323, 1309, 1188, 1090, 815
	3092, 1648, 1250,* 1149, 1106, 960, 895, 831
$(CF_3Ph)_3PAuCl$	1610, 1326, 1173, 1131, 1063, 1027, 1016, 784, 708, 700
$Ru(bpy)_3^{2+}$,**	1603, 1465, 1445, 1424, 1313, 1270, 1245, 1165, 1124, 1068, 1025, 1010, 969, 902, 773, 733, 659

$Ru(bpy)^{3+,**}$	1606, 1496, 1472, 1452, 1322, 1167, 1047, 1036, 1022, 862
	1730,* 1515,* 1460, 1406, 1369, 1152, 1062

* The underlined frequencies are used to represent the temporal behavior for kinetic analysis.

** The data listed for these compounds originate from ref. 11. In this work, the absorption bands of $Ru(bpy)_3$ complexes were not observed because of the low concentration.

An Attenuated Total Reflection (ATR) accessory featuring a 3 mm diameter diamond plate with three reflections was used for the time-resolved FT-IR experiments (ASI Systems). Sample solutions containing **1a** (20 mM), **2b** (60 mM), $(4\text{-}CF_3Ph)_3PAuCl$ (2 mM) and $[Ru(bpy)_3](PF_6)_2$ (0.5 mM) in $MeOH/CH_3CN$ (3:1) were degassed prior to start of the measurement. For each rapid-scan experiment, 0.1 mL solution was held atop the diamond plate in a homemade Teflon liquid cell featuring a quartz window for access of the laser beam. A N_2 atmosphere was maintained throughout the experiment. For initiation of catalysis by excitation of the $[Ru(bpy)_3]^{2+}$ sensitizer, a laser pulse of 12 s duration was generated by intercepting the continuous emission of an Ar ion laser at 458 nm (150 mW, area 7 mm^2) (Coherent model Innova 90 C) with a mechanical shutter (UniBlitz model D122). The sample was discarded after each pulse.

Time-resolved rapid scan FT-IR spectra were recorded on a Bruker model Vertex 80 spectrometer equipped with a HgCdTe PV detector (Kolmar Technologies model KMPV11-1-J2, 14 micron band gap). The mirror velocity was 160 kHz and the spectral resolution was 4 cm^{-1}. Data were recorded in double-sided/forward-backward mode. For each sample, 1000 spectra were recorded in the dark before the photolysis and averaged. The resulting spectrum served as background. The protocol for obtaining the transient spectra consisted of

the recording of 80 interferograms following the arrival of the laser pulse. Consequently, eighty spectral time slices at 1.2 s time resolution were extracted, resulting in final absorbance spectra with midpoints at 0.6 s, 1.8 s, 3 s, 4.2 s etc., up to 95.4 s. Slices were averaged in groups of three to yield slices with 3.6 s time resolution. The result of 17 such experiments was averaged for further S/N improvement. Further details of the time-resolved ATR FT-IR technique are presented in a previous paper[5].

6. Kinetic analysis based on the time-resolved FTIR spectroscopy

Starting with a fixed reservoir of 1-vinylcyclobutanol and 4-methyl benzyl diazonium, the kinetic behavior of the reactants, intermediates and products according to Scheme I is described by the following set of differential equations (in terms of concentrations)

Scheme I

$$R \xrightarrow{k_1} I \xrightarrow{k_2} P$$

$$\frac{d[R]}{dt} = -k_1[R] \quad (1)$$

$$\frac{d[I]}{dt} = k_1[R] - k_2[I] \quad (2)$$

$$\frac{d[P]}{dt} = k_2[I] \quad (3)$$

Integration of the differential equations 1-3 gives

$$[R] = [R]_0 e^{-k_1 t} \quad (4)$$

$$[I] = \frac{k_1[R]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (5)$$

$$[P] = [R]_0\left(1 + \frac{1}{k_2 - k_1}\left[k_1 e^{-k_2 t} - k_2 e^{-k_1 \cdot t}\right]\right) \quad (6)$$

Expressed in absorbance units:

$$A^R = A_0^R e^{-k_1 t} \quad (4')$$

$$A^I = A_\infty^P \frac{\varepsilon^I}{\varepsilon^P} \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (5')$$

$$A^P = A_\infty^P (1 + \frac{1}{k_2 - k_1} [k_1 e^{-k_2 t} - k_2 e^{-k_1 \cdot t}]) \quad (6')$$

(A_0^R is the reactant absorbance before photolysis; ε^R, ε^I, ε^P are the extinction coefficients of reactant, intermediate and product infrared absorptions, respectively.)

As calculated from the experimental data with above equations, we obtained:

k_1= 0.160±0.012 s^{-1},

k_2 = 0.055±0.013 s^{-1},

A_0^R = 0.000150±0.

A_∞^P = 0.0000396±0.0000047

E_P = 0.778±0.046. ($E_P = \frac{\varepsilon^I}{\varepsilon^P}$)

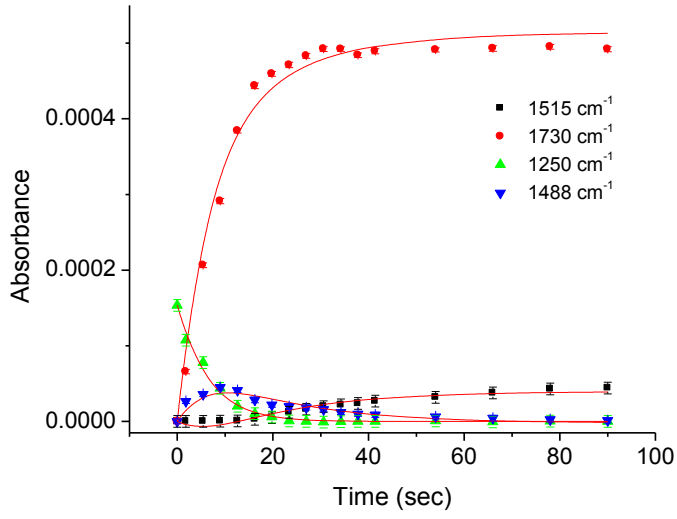


Figure S8 Results of curve fitting for the IR absorption bands. The points

represent the experimentally measured absorbance. The red lines for the 1515, 1250 and 1488 cm^{-1} bands are the least squares fit curves for the simultaneous fit of equations (4')-(6') using the 5 parameters k_1, k_2, A_0^R, A_P, and E_P.

The kinetic curve for 1730 cm^{-1} was simulated as

$$A_{1730} = A_{1488} * \frac{\varepsilon_{1730}}{\varepsilon_{1488}} + A_{1515} * \frac{\varepsilon_{1730}}{\varepsilon_{1515}}$$

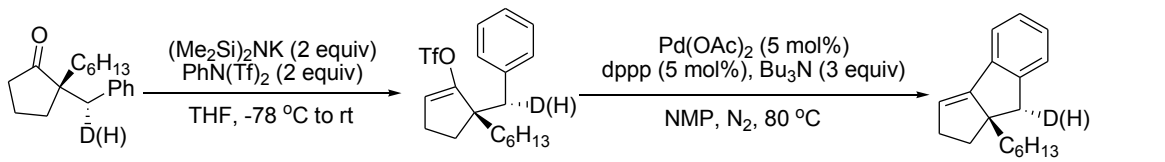
$$= A_{1488} * \frac{\varepsilon_{1730}}{\varepsilon_{1515} * E_p} + A_{1515} * \frac{\varepsilon_{1730}}{\varepsilon_{1515}}$$

$$= A_{1488} * \frac{A_{\infty}^{1730}}{A_{\infty}^{1515} * E_p} + A_{1515} * \frac{A_{\infty}^{1730}}{A_{\infty}^{1515}}$$

As shown in the Figure S8, the simulated curve of 1730 cm^{-1}, predicted on the basis of the 1488, 1515 and 1250 cm^{-1} bands, fits well with the experimental data, which strongly suggests that the absorption at 1730 cm^{-1} belongs to both the intermediate and the product.

7. Stereochemical determination

7.1 Synthesis of derivates 3ba-2 and 6-2



6 (D)
3ba (H)

6-1 (D)
3ba-1 (H), 72% yield

6-2 (D)
3ba-2 (H), 83% yield

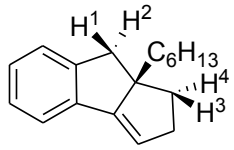
The stereochemistry of **6** was determined by comparing ^{1}H NMR spectroscopy of **6-2** with **3ba-2**. Compound **3ba-2** was prepared according to previous procedure.[6]

To a stirred solution of *N*-phenylbis(trifluormethanesulphonimide) (214 mg, 0.6 mmol)

and ketone **3ba** (77 mg, 0.3 mmol) in dry THF (4 mL) was dropwise added a solution of potassium hexamethyldisilazide (0.5 M in toluene, 1.2 mL, 0.6 mmol) over 20 min at -78 ^{o}C. The reaction mixture was stirred at this temperature for 1 hour then it was warmed to room temperature and stirred for 6 h. The mixture was diluted with hexane (30 mL), washed with water (30 mL), 10% aqueous solution of NaOH (20 mL) and then brine (30 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was further purified by flash chromatography to give the desired triflate **3ba-1** (85 mg, 72% yield).

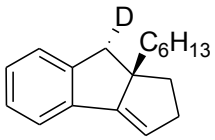
To a stirred solution of triflate **3ba-1** (78 mg, 0.2 mmol), palladium acetate (2.2 mg, 5 mol%) and 1,3-bis(diphenylphosphino)propane (4.1 mg, 5 mol%) in 2 mL of dry NMP was added tri-*n*-butylamine (111 mg, 3 equiv) under an atmosphere of nitrogen.

The solution was then heated at 80 ^{o}C for 12 hours. The reaction mixture was cooled to room temperature and diluted with diethyl ether (20 mL). The mixture was washed with 1 M HCl (20 mL), water (20 mL) and then brine (20 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was further purified by flash chromatography to give the desired tricycle **3ba-2** (40 mg, 83% yield).



8a-hexyl-1,2,8,8a-tetrahydrocyclopenta[a]indene (3ba-2)

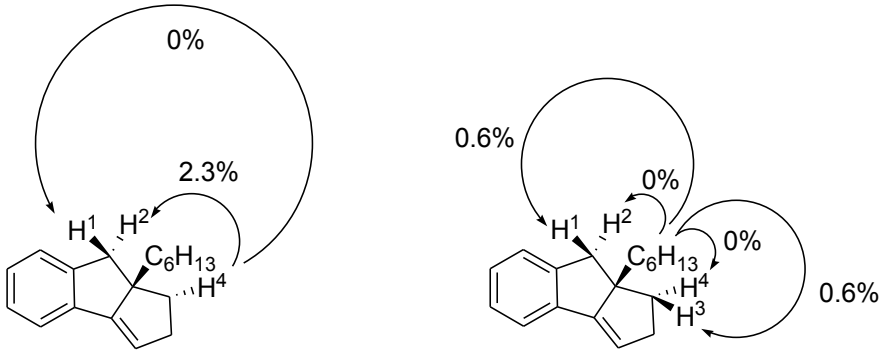
^{1}H NMR (400 MHz, C_6D_6) δ 7.41 – 7.32 (m, 1H), 7.13 – 7.01 (m, 3H), 5.65 (s, 1H), 2.85 – 2.75 (m, 1H), 2.74 (d, J = 15.2 Hz, 1H, H^1), 2.52 (d, J = 14.8 Hz, 1H, H^2), 2.50 – 2.40 (m, 1H), 1.99 (dd, J = 12.0, 6.0 Hz, 1H, H^3), 1.80 – 1.63 (m, 1H, H^4), 1.41 (t, J = 8.0 Hz, 2H), 1.34 – 1.03 (m, 8H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 157.2, 148.7, 136.5, 127.6, 126.6, 125.8, 122.1, 116.7, 59.3, 42.5, 37.1, 37.0, 36.3, 31.9, 30.2, 25.7, 22.7, 14.0. HRMS (EI) calc for $C_{18}H_{24}$: m/z 240.1878, found 240.1880.



[*S*(*R*), *R*(*S*)]-deuterated-8a-hexyl-1,2,8,8a-tetrahydrocyclopenta[a]indene (6-2)

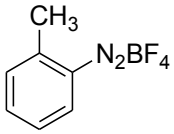
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.0 Hz, 1H), 7.27 – 7.15 (m, 3H), 5.74 (s, 1H), 2.90 – 2.78 (m, 1H), 2.83 (s, 1H), 2.60 (ddd, *J* = 16.5, 8.5, 3.0 Hz, 1H), 2.11 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.88 – 1.75 (m, 1H), 1.43 – 1.15 (m, 10H), 0.95 – 0.80 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 148.8, 136.4, 127.5, 126.5, 126.0, 122.0, 117.1, 59.3, 42.0 (t, *J* = 19.5 Hz), 37.0, 36.8, 36.3, 31.92, 30.2, 25.7, 22.7, 14.2. HRMS (EI) calc for $C_{18}H_{23}D$: m/z 241.1941, found 241.1945.

7.2 NOE experiment of tricycle 3ba-2



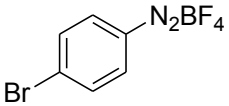
8. General procedure for the synthesis of diazonium salts.

To a stirred solution of appropriate aniline (10 mmol) in a mixture of 50% fluoroboric acid (3 mL) and distilled water (3 mL), was added a solution of sodium nitrite (690 mg) in water (3 mL) at 0 ^{o}C. The mixture was stirred for 30 minutes and the thick precipitate was collected and re-dissolved in acetone. The diazonium tetrafluoroborate was then precipitated by the addition of diethyl ether.



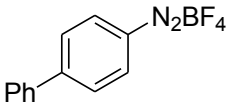
2d

Compound **2d** (1.1 g) was obtained in 53% yield from appropriate aniline. ^{1}H NMR (300 MHz, d-acetone) δ 8.73 (d, *J* = 8.4 Hz, 1 H), 8.23 (t, *J* = 7.5 Hz, 1 H), 7.93 (d, *J* = 7.8 Hz, 1 H), 7.85 (d, *J* = 7.8 Hz, 1 H), 2.92 (s, 3 H); ^{13}C NMR (125 MHz, d-acetone) δ 144.8, 141.2, 132.9, 132.7, 129.2, 115.6, 17.9.



2h

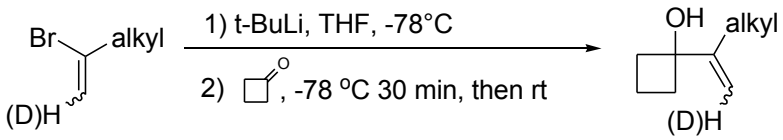
Compound **2h** (2.05 g) was obtained in 76% yield from appropriate aniline. ^{1}H NMR (300 MHz, d-acetone) δ 8.73 (d, *J* = 9.0 Hz, 2 H), 8.30 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (125 MHz, d-acetone) δ 137.6, 135.1, 134.1, 114.7.



2i

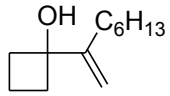
Compound **2i** (2.38 g) was obtained in 89% yield from appropriate aniline. ^{1}H NMR (600 MHz, CD_3CN) δ 8.53 (d, *J* = 9.0 Hz, 2 H), 8.18 (d, *J* = 9.0 Hz, 2 H), 7.83 (m, 2 H), 7.60 (m, 3 H); ^{13}C NMR (125 MHz, CD_3CN) δ 154.0, 136.7, 133.1, 131.1, 129.9, 129.6, 128.2, 111.6.

9. General procedure for the synthesis of alkyl substituted and deuterated allylic cyclobutanols



To a solution of 2-bromooct-1-ene (760 mg, 4.0 mmol, 1.0 equiv) in THF (20 mL) was added a solution of *t*-BuLi (1.7 M in pentane, 4.7 mL, 8.0 mmol, 2.0 equiv) at -78 °C under argon for 10 min. The solution was stirred at the same temperature for 1 h. A solution of cyclobutanone (364 mg, 5.2 mmol, 1.3 equiv) in THF (5 mL) was then added. The reaction mixture was stirred at -78 °C for 0.5 h, then allowed warm to

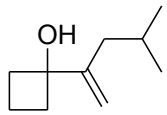
room temperature. When the reaction was completed as determined by TLC analysis, the reaction mixture was quenched with H_2O and extracted with ethyl acetate (2×40 mL). The combined organic layers were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (40:1 Hex/EtOAc) to obtain the desired cyclobutanol **1b** (626 mg, 3.44 mmol) in 86% yield as an oil.



1b

1-(oct-1-en-2-yl)cyclobutanol (1b)

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.06 (s, 1H), 4.87 (s, 1H), 2.35 – 2.30 (m, 2H), 2.15 – 1.99 (m, 4H), 1.97 – 1.85 (m, 1H), 1.64 (s, 1H), 1.61 – 1.53 (m, 1H), 1.52 – 1.41 (m, 2H), 1.40 – 1.22 (m, 6H), 0.89 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 107.9, 78.6, 34.7, 31.8, 30.2, 29.3, 28.4, 22.6, 14.1, 13.1. IR (film): ν 1144, 1246, 1465, 1643, 2858, 2927, 3335 cm^{-1}. HRMS (EI) calc for $C_{12}H_{22}O$: m/z 182.1671, found 182.1669.

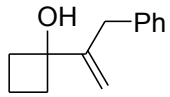


1c

1-(4-methylpent-1-en-2-yl)cyclobutanol (1c)

Compound **1c** (548 mg, 3.56 mmol) was prepared in 89% yield from 2-bromo-4-methylpent-1-ene[7] according to procedures described for **1b**.

Oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.12 (s, 1H), 4.86 (d, *J* = 1.2 Hz, 1H), 2.38 – 2.27 (m, 2H), 2.09 – 2.00 (m, 2H), 1.98 (d, *J* = 7.2 Hz, 2H), 1.96 – 1.82 (m, 2H), 1.65 – 1.52 (m, 1H), 1.60 (s, 1 H), 0.92 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 109.4, 78.7, 40.2, 34.7, 26.4, 22.7, 13.3. IR (film): ν 1145, 1365, 1465, 1641, 2953, 3342 cm^{-1}. HRMS (EI) calc for $C_{10}H_{18}O$: m/z 154.1358, found 154.1362.

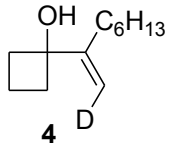


1d

1-(1-phenylprop-2-en-2-yl)cyclobutanol (1d)

Compound **1d** (586 mg, 3.12 mmol) was prepared in 78% yield from 1-(2-bromoallyl)benzene[7] according to procedures described for **1b**.

Oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.27 – 7.19 (m, 3H), 5.18 (s, 1H), 4.71 (d, *J* = 1.0 Hz, 1H), 3.48 (s, 2H), 2.42 – 2.31 (m, 2H), 2.14 – 2.03 (m, 2H), 1.99 – 1.88 (m, 1H), 1.69 (s, 1H), 1.65 – 1.57 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 140.0, 129.4, 128.4, 126.1, 111.1, 78.5, 37.3, 34.9, 13.2. IR (film): ν 1141, 1247, 1495, 1642, 2947, 2986, 3341 cm^{-1}. HRMS (EI) calc for $C_{13}H_{16}O$: m/z 188.1201, found 188.1202.

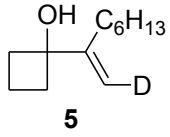


4

***Cis*-deuterated-1-(oct-1-en-2-yl)cyclobutanol (4)**

Compound **4** (615 mg, 3.36 mmol) was prepared in 84% yield from (*Z*)-1-deuterio-2-bromo-1-octene[8] according to procedures described for **1b**.

Oil, D = 94%, with 1% of *trans* **5**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (s, 1H), 2.40 – 2.27 (m, 2H), 2.15 – 2.00 (m, 4H), 1.97 – 1.84 (m, 1H), 1.63 (s, 1H), 1.61 – 1.43 (m, 3H), 1.38 – 1.23 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 107.7 (t, *J* = 23.7 Hz), 78.6, 34.7, 31.9, 30.2, 29.4, 28.4, 22.7, 14.1, 13.2. IR (film): ν 1140, 1248, 1464, 1621, 2858, 2927, 3335 cm^{-1}. HRMS (EI) calc for $C_{12}H_{21}DO$: m/z 183.1733, found 183.1736.



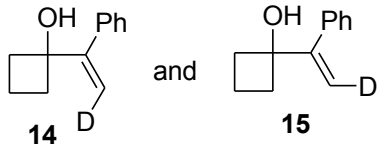
5

***Trans*-deuterated-1-(oct-1-en-2-yl)cyclobutanol (5)**

Compound **5** (600 mg, 3.28 mmol) was prepared in 82% yield from (*E*)-1-deuterio-2-bromo-1-octene[8] according to procedures described for **1b**.

Oil, D = 99%, with 1.4% of *cis* **4**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.05 (s, 1H), 2.38 – 2.28 (m, 2H), 2.14 – 2.01 (m, 4H), 1.97 – 1.86 (m, 1H), 1.66 – 1.53 (m, 2H), 1.53 – 1.43 (m, 2H), 1.39 – 1.23 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 107.7 (t, *J* = 23.3 Hz), 78.5, 34.6, 31.8, 30.1, 29.4, 28.4, 22.6, 14.1,

13.1. IR (film): ν 1134, 1247, 1460, 1621, 2858, 2927, 3336 cm^{-1}. HRMS (EI) calc for $C_{12}H_{21}DO$: m/z 183.1733, found 183.1737.



14 **15**

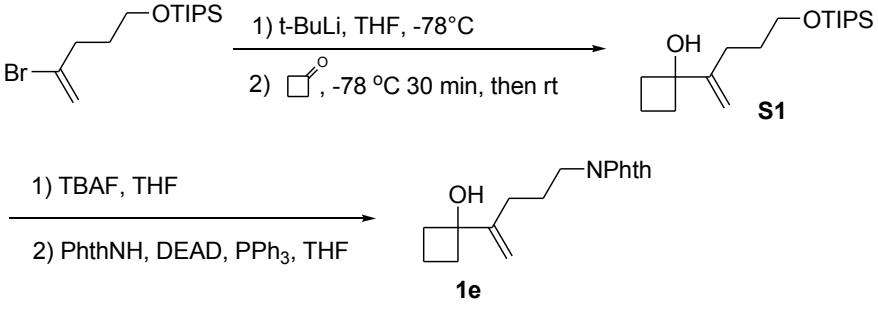
***Cis*-deuterated -1-(1-phenylvinyl)cyclobutanol (14)**

***trans*-deuterated -1-(1-phenylvinyl)cyclobutanol (15)**

Compounds **14** and **15** (322 mg, 1.84 mmol) was prepared in a 3:1 mixture in 46% yield from β-deuterio-α-bromostyrene (Z/E = 4.5:1, D = 85%)[8] according to procedures described for **1b**.

The mixture of (**14**/**15** = 3:1, D = 81%). ^{1}H NMR (600 MHz, MeOD, **14**) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.31 (s, 1H), 2.48 – 2.35 (m, 2H), 2.18 (ddd, *J* = 12.0, 9.6, 7.2 Hz, 2H), 1.97 – 1.88 (m, 1H), 1.62 – 1.50 (m, 1H); ^{1}H NMR (600 MHz, MeOD, **15**) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.37 (s, 1H), 2.48 – 2.35 (m, 2H), 2.18 (ddd, *J* = 12.0, 9.6, 7.2 Hz, 2H), 1.97 – 1.88 (m, 1H), 1.62 – 1.50 (m, 1H); ^{13}C NMR (126 MHz, MeOD) mixture of **1f**, **14** and **15**.

10. General procedure for the synthesis of cyclobutanol 1e

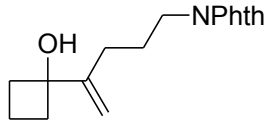


Compound **S1** (1.06 g, 3.4 mmol) was prepared in 85% yield from (4-bromopent-4-enyloxy)triisopropylsilane[9] according to procedures described for **1b**.

To a stirred solution of **S1** (624 mg, 2 mmol) in THF (10 mL) was added a solution of tetrabutylammonium fluoride (3 mL, 3 mmol, 1.0M in THF) at 0 °C. The mixture was

stirred at room temperature for 4 h. Diethyl ether (30 mL) was added. The mixed solution was washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude diol for the next step without purification.

To a solution of above crude diol in THF (20 ml) at 0 °C was added PPh_3 (786 mg, 3 mmol, 1.5 equiv), followed by phthalimide (323 mg, 2.2 mmol, 1.1 equiv). A solution of DEAD in toluene (40% w/w, 1.3 g, 3.0 mmol, 1.5 eq.) was added dropwise to the reaction mixture. The reaction was allowed to slowly warm to rt over 2.5 h, then the solvents were removed *in vacuo*. Purification by chromatography on silica provided imide **1e** (421 mg, 74% for 2 steps) as a solid.

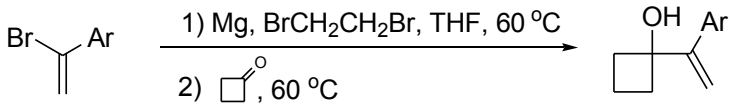


1e

2-(4-(1-hydroxycyclobutyl)pent-4-enyl)isoindoline-1,3-dione (1e)

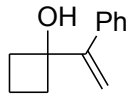
Mp: 53-55 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.13 (s, 1H), 4.94 (s, 1H), 3.74 (t, *J* = 7.5 Hz, 2H), 2.43 – 2.27 (m, 2H), 2.27 – 2.15 (m, 2H), 2.13 – 2.01 (m, 2H), 1.99 – 1.72 (m, 4H), 1.63 – 1.50 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 150.6, 133.9, 132.1, 123.2, 108.8, 78.3, 37.7, 34.7, 27.2, 26.9, 13.1. IR (film): ν 1362, 1395, 1643, 1701, 2940, 3462 cm^{-1}. HRMS (EI) calc for $C_{17}H_{19}NO_3$: m/z 285.1365, found 285.1369.

11. General procedure for the synthesis of aryl substituted allylic cyclobutanols



To a solution of Mg (288 mg, 12 mmol, 3 equiv) in THF (20 mL) was added a crystal of iodine under N_2 atmosphere. A solution of 1,2-dibromoethane (300 mg, 0.4 equiv) in THF (2 mL) was added. The solution was stirred when small bubble was observed. A solution of α-bromostyrene (728 mg, 4 mmol, 1 equiv) in THF (3 mL) was then added. When the mixed solution was stirred at 60 °C for 1 h, a solution of

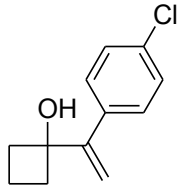
cyclobutanone (392 mg, 5.6 mmol, 1.4 equiv) in THF (3 mL) was added. After stirring at the same temperature for 5 h, the reaction mixture was quenched with H_2O and extracted with ethyl acetate (2×40 mL). The combined organic layers were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (15:1 Hex/EtOAc) to obtain the desired cyclobutanol **1f** (430 mg, 2.48 mmol) in 62% yield as an oil.



1f

1-(1-phenylvinyl)cyclobutanol (1f)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.0 Hz, 2H), 7.41 – 7.29 (m, 3H), 5.40 (s, 1H), 5.38 (s, 1H), 2.58 – 2.40 (m, 2H), 2.36 – 2.16 (m, 2H), 2.08 – 1.90 (m, 2H), 1.74 – 1.53 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 139.1, 128.2, 127.6, 127.6, 112.9, 78.1, 35.7, 13.4. IR (film): ν 1249, 1493, 1626, 2948, 2986, 3373 cm^{-1}. HRMS (EI) calc for $C_{12}H_{14}O$: m/z 174.1045, found 174.1047.

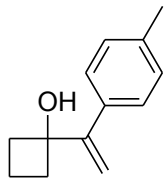


1g

1-(1-(4-chlorophenyl)vinyl)cyclobutanol (1g)

Compound **1g** (432 mg, 2.08 mmol) was prepared in 52% yield from α-bromo-4-chlorostyrene according to procedures described for **1f**.

Oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.38 (s, 1H), 5.36 (s, 1H), 2.43 (dd, *J* = 14.4, 10.8 Hz, 2H), 2.22 (dd, *J* = 18.0, 9.6 Hz, 2H), 2.04 – 1.94 (m, 1H), 1.84 (s, 1H), 1.67 – 1.56 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3, 137.5, 133.4, 128.9, 128.2, 113.3, 78.0, 35.6, 13.3. IR (film): ν 1092, 1248, 1489, 1624, 2947, 2987, 3354 cm^{-1}. HRMS (EI) calc for $C_{12}H_{13}ClO$: m/z 208.0655, found 208.0658.

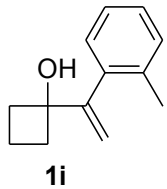


1h

1-(1-p-tolylvinyl)cyclobutanol (1h)

Compound **1h** (360 mg, 1.92 mmol) was prepared in 48% yield from α-bromo-4-methylstyrene[10] according to procedures described for **1f**.

Oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.36 (s, 2H), 2.56 – 2.45 (m, 2H), 2.37 (s, 3H), 2.32 – 2.21 (m, 2H), 2.07 – 1.88 (m, 2H), 1.73 – 1.55 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 137.3, 136.0, 128.9, 127.4, 112.1, 78.1, 35.7, 21.1, 13.3. IR (film): ν 1248, 1511, 1672, 2946, 2986, 3375 cm^{-1}. HRMS (EI) calc for $C_{13}H_{16}O$: m/z 188.1201, found 188.1200.



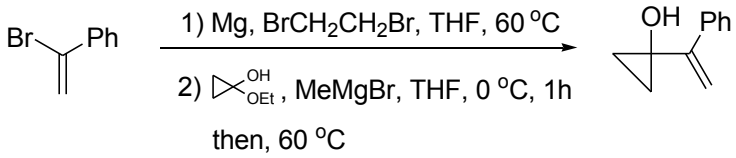
1i

1-(1-o-tolylvinyl)cyclobutanol (1i)

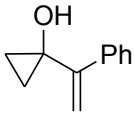
Compound **1i** (428 mg, 2.28 mmol) was prepared in 57% yield from α-bromo-2-methylstyrene[10] according to procedures described for **1f**.

Oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 4H), 5.54 (s, 1H), 4.99 (s, 1H), 2.47 – 2.37 (m, 2H), 2.29 (s, 3H), 2.10 (dd, *J* = 17.2, 10.4 Hz, 2H), 2.02 – 1.90 (m, 1H), 1.69 (s, 1H), 1.64 – 1.53 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 139.8, 136.3, 130.2, 129.0, 127.3, 125.2, 113.6, 78.5, 35.5, 20.5, 13.6. IR (film): ν 1248, 1487, 1632, 2947, 2987, 3362 cm^{-1}. HRMS (EI) calc for $C_{13}H_{16}O$: m/z 188.1201, found 188.1205.

12. General procedure for the synthesis of aryl substituted allylic cyclopropanol 1j



To a solution of Mg (288 mg, 12 mmol, 3 equiv) in THF (20 mL) was added a crystal of iodine under N_2 atmosphere. A solution of 1,2-dibromoethane (300 mg, 0.4 equiv) in THF (2 mL) was added. The solution was stirred when small bubble was observed. A solution of α-bromostyrene (728 mg, 4 mmol, 1 equiv) in THF (3 mL) was then added and the mixed solution was stirred at 60 °C for 1 h. In a separate flask, a solution of 1-ethoxycyclopropanol[2] (571 mg, 5.6 mmol, 1.4 equiv) in THF (5 ml) was added dropwise to MeMgBr in Et_2O (3.0 M, 1.9 ml, 5.7 mmol, 1.01 eq.) at 0 °C. The resulting white suspension was stirred at 0 °C for 30 min, then it was added to above grignard reagent via syringe. After stirring at 60 °C for 5 h, the reaction mixture was quenched with H_2O and extracted with ethyl acetate (2×40 mL). The combined organic layers were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (15:1 Hex/EtOAc) to obtain the desired cyclopropanol **1j** (428 mg, 2.68 mmol) in 67% yield as an oil.



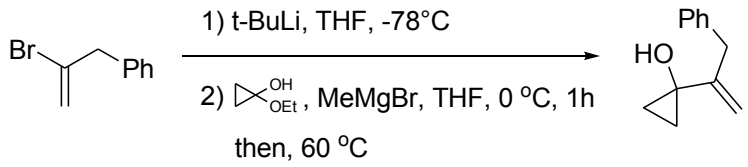
1j

1-(1-phenylvinyl)cyclopropanol (1j)

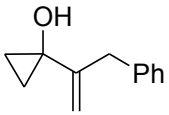
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 5.37 (s, 1H), 5.31 (s, 1H), 2.17 (s, 1H), 1.12 (t, *J* = 6.0 Hz, 2H), 1.00 – 0.83 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 138.8, 128.4, 127.9, 127.1, 112.4, 57.7, 14.0. IR (film): ν 1233, 1494, 1626, 3087, 3359 cm^{-1}. HRMS (EI) calc for $C_{11}H_{12}O$: m/z 160.0888, found 160.0889.

13. General procedure for the synthesis of alkyl substituted

allylic cyclopropanol 1k



To a solution of 1-(2-bromoallyl)benzene[7] (760 mg, 4.0 mmol, 1.0 equiv) in THF (20 mL) was added a solution of *t*-BuLi (1.7 M in pentane, 4.7 mL, 8.0 mmol, 2.0 equiv) at -78 °C under argon for 10 min. The solution was stirred at the same temperature for 1 h. In a separate flask, a solution of 1-ethoxycyclopropanol[4] (571 mg, 5.6 mmol, 1.4 equiv) in THF (5 ml) was added dropwise to MeMgBr in Et_2O (3.0 M, 1.9 ml, 5.7 mmol, 1.01 eq.) at 0 °C. The resulting white suspension was stirred at 0 °C for 30 min, then it was added to above lithium reagent via syringe at -78 °C. After stirring at the same temperature for 1 h, the reaction was warmed to rt and stirred for another 5 h. The reaction mixture was quenched with H_2O and extracted with ethyl acetate (2×40 mL). The combined organic layers were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (15:1 Hex/EtOAc) to obtain the desired cyclopropanol **1k** (508 mg, 2.92 mmol) in 73% yield as an oil.



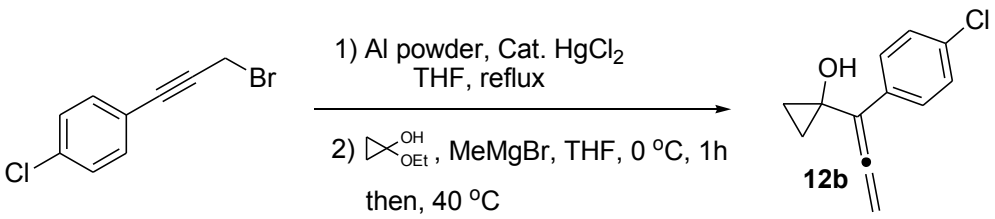
1k

1-(1-phenylprop-2-en-2-yl)cyclopropanol (1k)

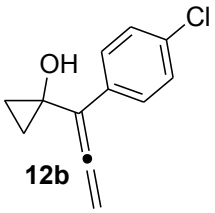
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.27 – 7.20 (m, 3H), 5.16 (s, 1H), 4.75 (d, *J* = 1.0 Hz, 1H), 3.45 (s, 2H), 2.01 (s, 1H), 0.91 (dd, *J* = 7.5, 5.0 Hz, 2H), 0.80 (dd, *J* = 7.5, 5.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 139.6, 129.1, 128.4, 126.2, 111.2, 58.1, 39.5, 14.6. IR (film): ν 1231, 1494, 1633, 3027, 3086, 3312 cm^{-1}. HRMS (EI) calc for $C_{12}H_{14}O$: m/z 174.1045, found 174.1048.

14. General procedure for the synthesis of

1-Allenylcyclopropanol 12b.[4]



A suspension of powdered aluminum (89 mg, 3.2 mmol, 0.8 eq.) and catalytic $HgCl_2$ (22 mg, 0.08 mmol, 0.02 eq.) in anhydrous THF (2 ml) was heated to reflux for 30 min. After cooling to rt, a solution of 1-(3-bromoprop-1-ynyl)-4-chlorobenzene (912 mg, 4 mmol) in THF (2 ml) was added dropwise. The reaction was stirred at reflux for 1 h, during which time most of the aluminum powder disappeared. The resulting yellowish mixture was allowed to cool to rt. In a separate flask, a solution of 1-ethoxycyclopropanol (571 mg, 5.6 mmol, 1.4 equiv) in THF (5 ml) was added dropwise to MeMgBr in Et_2O (3.0 M, 1.9 ml, 5.7 mmol, 1.01 eq.) at 0 °C. The resulting white suspension was stirred at 0 °C for 30 min, then the solution of the propargyl aluminum reagent prepared above was added via syringe to the suspension. The resulting mixture was stirred at 40 °C for 14 h. After addition of saturated aqueous Rochelle salt solution (50 ml) and aqueous pH 7 buffer (30 ml), the biphasic system was vigorously stirred at rt for 0.5 h. The phases were separated, and the aqueous layer was extracted with Et_2O (2 x 30 ml). The combined organic phases were washed with saturated aqueous NaCl (50 ml), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel (hexane : EtOAc 9:1 to 6:1 gradient) provided 1-allenylcyclopropanol **12b** (428 g, 2.08 mmol) in 52% yield as a solid.



1-(1-(4-chlorophenyl)propa-1,2-dienyl)cyclopropanol (12b)

Mp: 59-61 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4

Hz, 2H), 5.15 (s, 2H), 2.22 (s, 1H), 1.14 (t, J = 6.0 Hz, 2H), 0.88 (t, J = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.6, 132.8, 132.7, 128.6, 128.4, 107.6, 79.4, 54.8, 15.0. IR (film): ν 1014, 1090, 1229, 1489, 1591, 1710, 3336 cm^{-1}. HRMS (EI) calc for $C_{12}H_{11}ClO$: m/z 206.0498, found 206.0501.

15. General procedures for visible light photoredox promoted gold-catalyzed ring-expansion arylation reactions

Method A:

Ph_3PAuCl (10 mg, 10 mol%), $Ru(bpy)_3(PF_6)_2$ (4 mg, 2.5 mol%) and ArN_2BF_4 (3 equiv) were added to a microwave vial. A solution of substrate (0.2 mmol) in MeOH/CH_3CN (3:1, 5 mL) was then added to the sealed vial in the absence of light at -78^{o}C. The vial was evacuated and then refilled with N_2 for three times. The reaction mixture was then warmed to room temperature and stirred under irradiation from visible light source B until the reaction was complete as determined by TLC analysis. Ether (15 mL) was added to precipitate remaining diazonium. The mixture was filtered with a pad of silica gel and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to give desired arylation product.

Method B:

Same procedure with Method A but $Ir(ppy)_3$ (3.3 mg, 2.5 mol%) was used instead of $Ru(bpy)_3(PF_6)_2$.

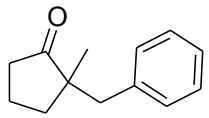
Method C:

Same procedure with Method A but $(4\text{-}CF_3Ph)_3PAuCl$ (14 mg, 10 mol%) was used instead of Ph_3PAuCl.

Method D:

Same procedure with Method A but $(4\text{-}CF_3Ph)_3PAuCl$ (14 mg, 10 mol%), $Ir(ppy)_3$ (3.3 mg, 2.5 mol%) and ArN_2BF_4 (4 equiv) was used.

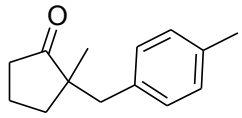
16. Characterization data of products



3aa

2-benzyl-2-methylcyclopentanone (3aa)

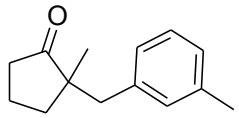
Oil, 33 mg, 87% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 2.88 (d, *J* = 13.5 Hz, 1H), 2.62 (d, *J* = 13.5 Hz, 1H), 2.31 (ddd, *J* = 18.5, 8.0, 5.0 Hz, 1H), 2.15 – 2.03 (m, 1H), 1.98 (dt, *J* = 13.0, 7.5 Hz, 1H), 1.87 – 1.69 (m, 2H), 1.69 – 1.56 (m, 1H), 1.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.4, 138.0, 130.3, 128.1, 126.4, 49.8, 42.6, 38.0, 34.6, 22.7, 18.6. IR (film): ν 1077, 1160, 1405, 1453, 1733, 2960 cm^{-1}. HRMS (EI) calc for $C_{13}H_{16}O$: m/z 188.1201, found 188.1204.



3ab

2-(4-methylbenzyl)-2-methylcyclopentanone (3ab)

Oil, 35 mg, 87% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.84 (d, *J* = 13.5 Hz, 1H), 2.57 (d, *J* = 13.5 Hz, 1H), 2.33 (s, 3H), 2.32 – 2.24 (m, 1H), 2.15 – 2.03 (m, 1H), 1.98 (dt, *J* = 13.0, 7.5 Hz, 1H), 1.86 – 1.69 (m, 2H), 1.64 (dt, *J* = 12.5, 6.0 Hz, 1H), 1.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.6, 135.9, 134.8, 130.1, 128.8, 49.8, 42.2, 38.1, 34.6, 22.7, 21.0, 18.7. IR (film): ν 1062, 1160, 1514, 1735, 2924, 2960 cm^{-1}. HRMS (EI) calc for $C_{14}H_{18}O$: m/z 202.1358, found 202.1359.

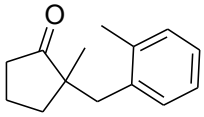


3ac

2-(3-methylbenzyl)-2-methylcyclopentanone (3ac)

Oil, 29 mg, 73% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 2.84 (d, *J* = 13.5 Hz, 1H), 2.57 (d, *J* = 13.5 Hz, 1H), 2.34 (s, 3H), 2.33 – 2.25 (m, 1H), 2.15 – 2.03 (m, 1H), 1.98 (dt, *J* = 13.0, 7.5 Hz, 1H), 1.88 – 1.69 (m, 2H), 1.68 – 1.62 (m, 1H), 1.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.5, 137.9, 137.7, 131.0, 128.0, 127.3,

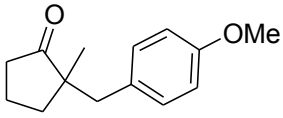
127.1, 49.8, 42.5, 38.1, 34.6, 22.7, 21.5, 18.7. IR (film): ν 1062, 1160, 1456, 1734, 2924, 2960 cm^{-1}. HRMS (EI) calc for $C_{14}H_{18}O$: m/z 202.1358, found 202.1358.



3ad

2-(2-methylbenzyl)-2-methylcyclopentanone (3ad)

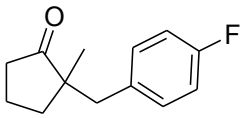
Oil, 29 mg, 72% yield from Method A. ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.03 (m, 4H), 2.91 (d, *J* = 14.0 Hz, 1H), 2.79 (d, *J* = 14.0 Hz, 1H), 2.39 – 2.25 (m, 1H), 2.32 (s, 3H), 2.11 – 1.95 (m, 1H), 1.94 – 1.76 (m, 3H), 1.76 – 1.68 (m, 1H), 1.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.5, 137.0, 136.8, 130.6, 130.4, 126.4, 125.8, 50.6, 38.5, 38.1, 34.5, 23.1, 20.3, 18.8. IR (film): ν 1063, 1159, 1457, 1734, 2925, 2958 cm^{-1}. HRMS (EI) calc for $C_{14}H_{18}O$: m/z 202.1358, found 202.1360.



3ae

2-(4-methoxybenzyl)-2-methylcyclopentanone (3ae)

Oil, 22 mg, 51% yield from Method C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.5 Hz, 2H), 3.80 (s, 3H), 2.82 (d, *J* = 13.5 Hz, 1H), 2.55 (d, *J* = 13.5 Hz, 1H), 2.36 – 2.23 (m, 1H), 2.14 – 2.02 (m, 1H), 2.01 – 1.91 (m, 1H), 1.87 – 1.68 (m, 2H), 1.67 – 1.62 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.6, 158.2, 131.2, 123.0, 113.5, 55.2, 49.9, 41.8, 38.1, 34.6, 22.7, 18.7. IR (film): ν 1244, 1457, 1511, 1732, 2958 cm^{-1}. HRMS (EI) calc for $C_{14}H_{18}O_2$: m/z 218.1307, found 218.1308.

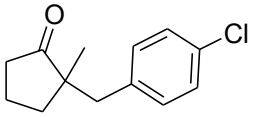


3af

2-(4-fluorobenzyl)-2-methylcyclopentanone (3af)

Oil, 31 mg, 76% yield from Method A. ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.96 (dd, *J* = 8.5, 8.5 Hz, 2H), 2.85 (d, *J* = 13.5 Hz, 1H), 2.59 (d, *J* = 13.5 Hz, 1H), 2.32 (ddd, *J* = 18.5, 8.0, 5.0 Hz, 1H), 2.11 – 1.99 (m, 1H), 1.94 (dt, *J* = 12.5, 8.0 Hz, 1H), 1.88 – 1.70 (m, 2H), 1.69 – 1.56 (m, 1H), 1.03 (s, 3H); ^{13}C NMR

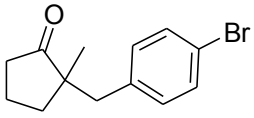
(126 MHz, $CDCl_3$) δ 223.1, 161.7 (d, J = 244.5 Hz), 133.6 (d, J = 3.4 Hz), 131.6 (d, J = 7.9 Hz), 115.0 (d, J = 21.0 Hz), 49.8, 41.8, 38.0, 34.5, 22.7, 18.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.9 – -115.2 (m, 1F). IR (film): ν 1158, 1220, 1508, 1733, 2962 cm^{-1}. HRMS (EI) calc for $C_{13}H_{15}FO$: m/z 206.1107, found 206.1109.



3ag

2-(4-chlorobenzyl)-2-methylcyclopentanone (3ag)

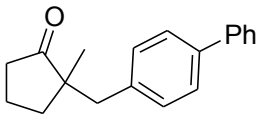
Oil, 27 mg, 62% yield from Method A. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 2.85 (d, J = 13.5 Hz, 1H), 2.59 (d, J = 13.5 Hz, 1H), 2.32 (ddd, J = 18.5, 8.0, 5.0 Hz, 1H), 2.13 – 1.99 (m, 1H), 1.92 (dt, J = 12.5, 8.0 Hz, 1H), 1.87 – 1.71 (m, 2H), 1.69 – 1.59 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.0, 136.5, 132.3, 131.6, 128.3, 49.7, 41.9, 38.0, 34.5, 22.7, 18.6. IR (film): ν 1094, 1160, 1406, 1490, 1734, 2925, 2959 cm^{-1}. HRMS (EI) calc for $C_{13}H_{15}ClO$: m/z 222.0811, found 222.0815.



3ah

2-(4-bromobenzyl)-2-methylcyclopentanone (3ah)

Oil, 34 mg, 64% yield from Method A. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 2.83 (d, J = 13.5 Hz, 1H), 2.58 (d, J = 13.5 Hz, 1H), 2.33 (ddd, J = 18.5, 8.0, 5.0 Hz, 1H), 2.14 – 1.99 (m, 1H), 1.98 – 1.70 (m, 3H), 1.68 – 1.61 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 222.9, 137.0, 132.0, 131.3, 120.4, 49.7, 40.0, 38.0, 34.5, 22.7, 18.6. IR (film): ν 1064, 1404, 1487, 1734, 2927, 2961 cm^{-1}. HRMS (EI) calc for $C_{13}H_{15}BrO$: m/z 266.0306, found 266.0309.

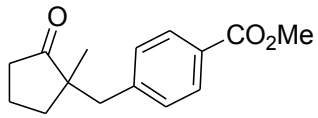


3ai

2-(4-phenylbenzyl)-2-methylcyclopentanone (3ai)

Oil, 40 mg, 75% yield from Method A. ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H),

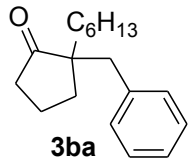
7.21 (d, *J* = 8.0 Hz, 2H), 2.92 (d, *J* = 13.5 Hz, 1H), 2.67 (d, *J* = 13.5 Hz, 1H), 2.34 (ddd, *J* = 18.5, 8.0, 5.0 Hz, 1H), 2.19 – 2.07 (m, 1H), 2.03 (dt, *J* = 13.0, 7.5 Hz, 1H), 1.92 – 1.74 (m, 2H), 1.74 – 1.65 (m, 1H), 1.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.4, 140.8, 139.2, 137.1, 130.7, 128.8, 127.2, 127.0, 126.8, 49.9, 42.3, 38.1, 34.7, 22.7, 18.7. IR (film): ν 1104, 1278, 1435, 1610, 1719, 2957 cm^{-1}. HRMS (EI) calc for $C_{19}H_{20}O$: m/z 264.1514, found 264.1514.



3aj

methyl 4-((1-methyl-2-oxocyclopentyl)methyl)benzoate (3aj)

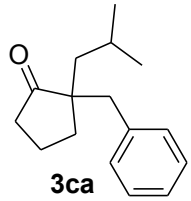
Mixed with 5% of methyl benzoate, Oil, 24 mg, 48% yield from Method B. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 2.93 (d, *J* = 13.0 Hz, 1H), 2.69 (d, *J* = 13.0 Hz, 1H), 2.33 (ddd, *J* = 18.5, 8.0, 4.5 Hz, 1H), 2.13 – 1.98 (m, 1H), 1.93 (dt, *J* = 12.5, 8.0 Hz, 1H), 1.87 – 1.71 (m, 2H), 1.69 – 1.63 (m, 1H), 1.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 222.8, 167.1, 143.6, 130.3, 129.5, 128.4, 52.1, 49.8, 42.6, 37.9, 34.6, 22.7, 18.6. IR (film): ν 1062, 1160, 1407, 1487, 1733, 2927, 2960 cm^{-1}. HRMS (EI) calc for $C_{15}H_{18}O_3$: m/z 246.1256, found 246.1259.



3ba

2-benzyl-2-hexylcyclopentanone (3ba)

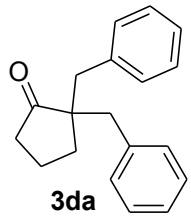
Oil, 46 mg, 90% yield from Method A. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 2.89 (d, *J* = 13.2 Hz, 1H), 2.59 (d, *J* = 13.2 Hz, 1H), 2.17 (dt, *J* = 18.0, 7.2 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.85 – 1.68 (m, 2H), 1.54 – 1.36 (m, 3H), 1.36 – 1.16 (m, 8H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.7, 138.1, 130.3, 128.2, 126.4, 53.4, 41.7, 38.9, 36.6, 31.7, 31.7, 29.9, 24.3, 22.7, 18.7, 14.1. IR (film): ν 1143, 1212, 1405, 1453, 1733, 2856, 2929 cm^{-1}. HRMS (EI) calc for $C_{18}H_{26}O$: m/z 258.1984, found 258.1990.



3ca

2-benzyl-2-isobutylcyclopentanone (3ca)

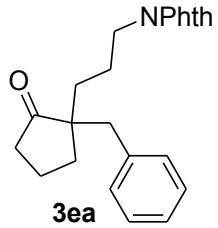
Oil, 37 mg, 81% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 3H), 7.11 (d, *J* = 7.0 Hz, 2H), 2.90 (d, *J* = 13.5 Hz, 1H), 2.59 (d, *J* = 13.5 Hz, 1H), 2.23 (ddd, *J* = 18.5, 8.5, 7.0 Hz, 1H), 2.06 – 1.84 (m, 3H), 1.84 – 1.71 (m, 2H), 1.54 – 1.40 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.9, 137.9, 130.4, 128.2, 126.4, 53.5, 45.0, 42.4, 38.6, 31.4, 25.0, 24.7, 24.1, 18.6. IR (film): ν 1110, 1156, 1405, 1453, 1732, 2956 cm^{-1}. HRMS (EI) calc for $C_{16}H_{22}O$: m/z 230.1671, found 230.1668.



3da

2,2-dibenzylcyclopentanone (3da)

Oil, 44 mg, 83% yield from Method A. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.2 Hz, 4H), 7.24 – 7.19 (m, 2H), 7.14 – 7.07 (m, 4H), 3.02 (d, *J* = 13.2 Hz, 2H), 2.59 (d, *J* = 13.2 Hz, 2H), 1.95 – 1.81 (m, 4H), 1.39 – 1.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.8, 137.6, 130.5, 128.3, 126.6, 54.7, 42.9, 39.5, 29.9, 18.7. IR (film): ν 1147, 1453, 1494, 1731, 2916, 2959 cm^{-1}. HRMS (EI) calc for $C_{19}H_{20}O$: m/z 264.1514, found 264.1516.

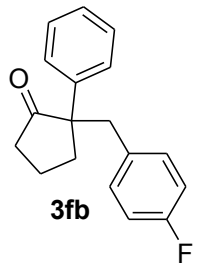


3ea

2-(3-(1-benzyl-2-oxocyclopentyl)propyl)isoindoline-1,3-dione (3ea)

Oil, 58 mg, 80% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.25 – 7.14 (m, 3H), 7.08 (d, *J* = 7.5

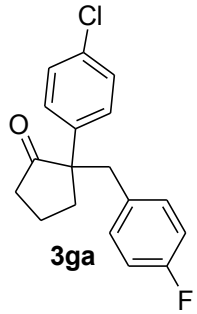
Hz, 2H), 3.66 (t, *J* = 7.0 Hz, 2H), 2.87 (d, *J* = 13.5 Hz, 1H), 2.61 (d, *J* = 13.5 Hz, 1H), 2.19 (dt, *J* = 18.5, 8.0 Hz, 1H), 2.06 – 1.89 (m, 2H), 1.85 – 1.63 (m, 4H), 1.56 – 1.43 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 222.8, 168.4, 137.6, 134.0, 132.1, 130.2, 128.2, 126.5, 123.3, 52.8, 41.3, 38.7, 38.2, 33.2, 32.1, 23.6, 18.6. IR (film): ν 1031, 1361, 1396, 1707, 2952 cm^{-1}. HRMS (EI) calc for $[C_{23}H_{24}NO_3]^+$ ($[M]^+$): m/z 362.1751, found 362.1750.



3fb

2-(4-fluorobenzyl)-2-phenylcyclopentanone (3fb)

Oil, 38 mg, 71% yield from Method D. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 5H), 6.85 (dd, *J* = 8.5, 8.5 Hz, 2H), 6.78 (dd, *J* = 8.5, 5.5 Hz, 2H), 3.06 (d, *J* = 13.5 Hz, 1H), 3.02 (d, *J* = 13.5 Hz, 1H), 2.53 – 2.40 (m, 1H), 2.40 – 2.26 (m, 1H), 2.26 – 2.12 (m, 1H), 2.02 (ddd, *J* = 13.5, 11.0, 6.5 Hz, 1H), 1.91 – 1.68 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.0, 161.6 (d, *J* = 244.4 Hz), 138.8, 133.2 (d, *J* = 3.2 Hz), 131.6 (d, *J* = 7.8 Hz), 128.6, 127.1, 127.1, 114.7 (d, *J* = 21.1 Hz), 58.1, 44.2, 37.6, 32.7, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.9 – -116.1 (m, 1F). IR (film): ν 1155, 1220, 1508, 1601, 1732, 2885, 2963 cm^{-1}. HRMS (EI) calc for $C_{18}H_{17}FO$: m/z 268.1263, found 268.1266.

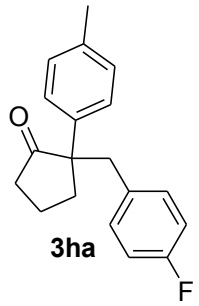


3ga

2-(4-fluorobenzyl)-2-(4-chlorophenyl)cyclopentanone (3ga)

Oil, 40 mg, 67% yield from Method D. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.86 (dd, *J* = 8.5, 8.5 Hz, 2H), 6.76 (dd, *J* = 8.5, 5.5 Hz, 2H), 3.02 (d, *J* = 13.5 Hz, 1H), 2.98 (d, *J* = 13.5 Hz, 1H), 2.48 – 2.28 (m, 2H),

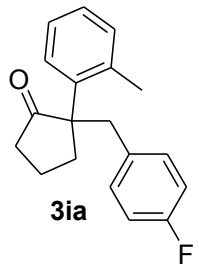
2.28 – 2.15 (m, 1H), 2.04 (ddd, *J* = 13.5, 10.0, 6.5 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.81 – 1.68 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.6, 161.7 (d, *J* = 244.8 Hz), 137.4, 133.1, 132.8 (d, *J* = 3.3 Hz), 131.5 (d, *J* = 7.9 Hz), 128.6, 128.6, 114.8 (d, *J* = 21.0 Hz), 57.5, 44.1, 37.6, 32.8, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.5 – -115.8 (m, 1F). IR (film): ν 1156, 1220, 1401, 1508, 1601, 1733, 2922, 2963, 3004 cm^{-1}. HRMS (EI) calc for $C_{18}H_{16}ClFO$: m/z 302.0874, found 302.0878.



3ha

2-(4-fluorobenzyl)-2-p-tolylcyclopentanone (3ha)

Oil, 45 mg, 80% yield from Method D. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.89 – 6.74 (m, 4H), 3.03 (d, *J* = 13.6 Hz, 1H), 2.99 (d, *J* = 13.6 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.34 (s, 3H), 2.29 (ddd, *J* = 9.2, 3.2, 1.6 Hz, 1H), 2.22 – 2.08 (m, 1H), 1.97 (ddd, *J* = 13.2, 11.2, 6.4 Hz, 1H), 1.90 – 1.66 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.1, 161.6 (d, *J* = 244.5 Hz), 136.8, 135.7, 133.4 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 7.8 Hz), 129.3, 127.0, 114.6 (d, *J* = 21.0 Hz), 57.8, 44.1, 37.5, 32.7, 21.0, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.0 – -116.3 (m, 1F). IR (film): ν 1155, 1219, 1508, 1601, 1732, 2885, 2963 cm^{-1}. HRMS (EI) calc for $C_{19}H_{19}FO$: m/z 282.1420, found 282.1423.

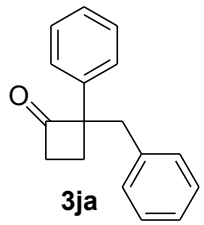


3ia

2-(4-fluorobenzyl)-2-o-tolylcyclopentanone (3ia)

Oil, 18 mg, 32% yield from Method D. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 7.16 – 7.09 (m, 2H), 7.03 – 6.96 (m, 2H), 6.95 – 6.88 (m, 2H), 3.23 (d, *J* = 14.0 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.55 – 2.42 (m, 4H), 2.41 – 2.30 (m, 1H), 2.12 –

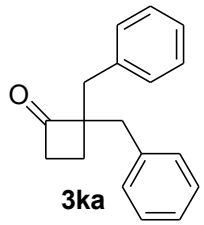
2.00 (m, 2H), 1.74 – 1.60 (m, 1H), 1.54 – 1.42 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.3, 161.7 (d, *J* = 244.3 Hz), 139.1, 136.4, 133.6 (d, *J* = 2.9 Hz), 133.2, 131.8 (d, *J* = 7.8 Hz), 127.4, 127.1, 126.0, 114.9 (d, *J* = 21.0 Hz), 59.2, 41.1, 37.9, 34.0, 22.1, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.8 – -115.9 (m, 1F). IR (film): ν 1157, 1221, 1451, 1508, 1734, 2884, 2963 cm^{-1}. HRMS (EI) calc for $C_{19}H_{19}FO$: m/z 282.1420, found 282.1427.



3ja

2-benzyl-2-phenylcyclobutanone (3ja)

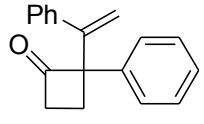
Oil, 31 mg, 67% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.13 (m, 8H), 7.00 – 6.87 (m, 2H), 3.22 (d, *J* = 13.5 Hz, 1H), 3.02 (d, *J* = 13.5 Hz, 1H), 2.98 – 2.86 (m, 1H), 2.82 – 2.68 (m, 1H), 2.49 – 2.32 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.8, 140.8, 136.5, 130.2, 128.4, 128.1, 126.9, 126.7, 126.6, 73.0, 45.8, 42.7, 21.8. IR (film): ν 1070, 1446, 1495, 1771, 2920, 2961 cm^{-1}. HRMS (EI) calc for $C_{17}H_{16}O$: m/z 236.1201, found 236.1202.



3ka

2,2-dibenzylcyclobutanone (3ka)

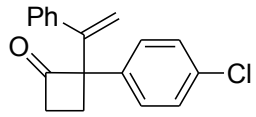
Oil, 26 mg, 51% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 6H), 7.18 (d, *J* = 7.0 Hz, 4H), 3.06 (d, *J* = 13.5 Hz, 2H), 2.75 (d, *J* = 13.5 Hz, 2H), 2.33 (t, *J* = 8.5 Hz, 2H), 1.95 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.6, 137.3, 130.1, 128.4, 126.6, 69.8, 43.4, 41.3, 19.4. IR (film): ν 1061, 1453, 1494, 1769, 2848, 2916, 3028 cm^{-1}. HRMS (EI) calc for $C_{18}H_{18}O$: m/z 250.1358, found 250.1362.



13a

2-phenyl-2-(1-phenylvinyl)cyclobutanone (13a)

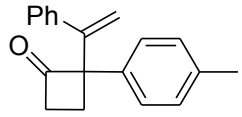
Oil, 15 mg, 62% yield from Method E. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.37 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.33 – 7.18 (m, 4H), 7.18 – 7.07 (m, 2H), 5.56 (s, 1H), 5.48 (s, 1H), 3.19 (ddd, *J* = 18.0, 10.8, 7.2 Hz, 1H), 3.13 – 2.98 (m, 1H), 2.76 (ddd, *J* = 11.6, 10.0, 7.2 Hz, 1H), 2.42 – 2.22 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 147.5, 139.4, 138.5, 128.7, 128.1, 127.7, 127.6, 127.1, 126.6, 115.2, 77.0, 42.9, 22.8. IR (film): ν 1075, 1493, 1597, 1615, 1774, 2966, 3022, 3056 cm^{-1}. HRMS (EI) calc for $C_{18}H_{16}O$: m/z 248.1201, found 248.1205.



13b

2-(4-chlorophenyl)-2-(1-phenylvinyl)cyclobutanone (13b)

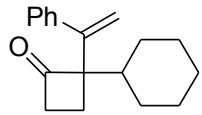
Oil, 15 mg, 52% yield from Method E. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.17 (m, 3H), 7.15 – 7.04 (m, 2H), 5.55 (s, 1H), 5.50 (s, 1H), 3.23 (ddd, *J* = 18.5, 11.0, 7.5 Hz, 1H), 3.14 – 2.97 (m, 1H), 2.79 – 2.62 (m, 1H), 2.37 (td, *J* = 11.5, 6.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.9, 147.3, 139.0, 137.1, 133.1, 128.8, 128.2, 128.1, 127.8, 127.6, 115.4, 76.5, 43.0, 22.8. IR (film): ν 1072, 1396, 1490, 1615, 1775, 2926, 2968, 3055 cm^{-1}. HRMS (EI) calc for $C_{18}H_{15}ClO$: m/z 282.0811, found 282.0815.



13c

2-(1-phenylvinyl)-2-p-tolylcyclobutanone (13c)

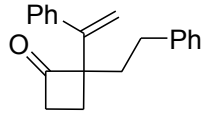
Oil, 11 mg, 43% yield from Method E. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.08 (m, 7H), 5.55 (s, 1H), 5.48 (s, 1H), 3.17 (ddd, *J* = 18.0, 11.0, 7.0 Hz, 1H), 3.11 – 2.97 (m, 1H), 2.73 (ddd, *J* = 11.5, 10.0, 7.0 Hz, 1H), 2.34 (s, 3H), 2.37 – 2.24 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.8, 147.5, 139.4, 136.8, 135.5, 129.4, 128.1, 127.7, 127.6, 126.5, 115.1, 76.7, 42.8, 22.9, 21.1. IR (film): ν 1073, 1443, 1510, 1615, 1775, 2923, 2967, 3023 cm^{-1}. HRMS (EI) calc for $C_{19}H_{18}O$: m/z 262.1358, found 262.1363.



13d

2-cyclohexyl-2-(1-phenylvinyl)cyclobutanone (13d)

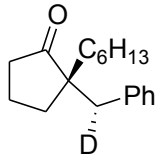
Oil, 18 mg, 72% yield from Method E. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 5.38 (s, 1H), 5.32 (s, 1H), 3.00 (ddd, *J* = 17.5, 11.0, 6.5 Hz, 1H), 2.92 – 2.75 (m, 1H), 2.38 – 2.24 (m, 1H), 2.20 (td, *J* = 11.5, 7.0 Hz, 1H), 1.87 (d, *J* = 12.0 Hz, 1H), 1.82 – 1.60 (m, 5H), 1.36 – 0.95 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.5, 147.0, 140.5, 128.1, 127.8, 127.4, 115.3, 77.5, 43.3, 41.5, 28.4, 28.2, 26.6, 26.4, 26.2, 20.9. IR (film): ν 1056, 1448, 1613, 1771, 2852, 2927 cm^{-1}. HRMS (EI) calc for $C_{18}H_{22}O$: m/z 254.1671, found 254.1675.



13e

2-phenethyl-2-(1-phenylvinyl)cyclobutanone (13e)

Oil, 17 mg, 61% yield from Method E. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 2H), 5.48 (s, 1H), 5.39 (s, 1H), 3.11 (t, *J* = 8.0 Hz, 2H), 2.71 (qd, *J* = 13.5, 6.5 Hz, 1H), 2.62 – 2.48 (m, 1H), 2.39 (dt, *J* = 11.5, 8.5 Hz, 1H), 2.18 – 2.03 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 146.6, 141.7, 139.9, 128.4, 128.3, 128.3, 127.6, 127.6, 125.9, 115.4, 72.6, 42.7, 37.8, 31.2, 24.5. IR (film): ν 1057, 1443, 1494, 1602, 1770, 2861, 2926, 2949, 3025 cm^{-1}. HRMS (EI) calc for $C_{20}H_{20}O$: m/z 276.1514, found 276.1515.

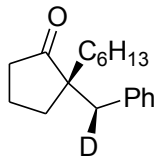


6

[*S*(*R*), *S*(*R*)]-deuterated-2-benzyl-2-hexylcyclopentanone (6)

Oil, D = 94%, with 1.2% of **7**, 46 mg, 88% yield from Method A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.11 (d, *J* = 7.0 Hz, 2H), 2.89 (s, 1H), 2.19 (ddd, *J* = 18.5, 8.5, 6.5 Hz, 1H), 2.05 – 1.87 (m, 2H), 1.87 – 1.68 (m, 2H), 1.58 – 1.38 (m, 3H), 1.38 – 1.14 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR

(126 MHz, $CDCl_3$) δ 223.7, 138.0, 130.2, 128.1, 126.3, 53.2, 41.3 (t, *J* = 19.7 Hz), 38.9, 36.5, 31.7, 31.6, 29.9, 24.2, 22.6, 18.7, 14.1. IR (film): ν 1158, 1451, 1733, 2856, 2929 cm^{-1}. HRMS (EI) calc for $C_{18}H_{25}DO$: m/z 259.2046, found 259.2049.



7

[*S*(*R*), *R*(*S*)]-deuterated-2-benzyl-2-hexylcyclopentanone (7)

Oil, D = 99%, with 1.6% of **6**, 45 mg, 87% yield from Method A. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.24 – 7.19 (m, 1H), 7.15 – 7.08 (m, 2H), 2.59 (s, 1H), 2.19 (ddd, *J* = 18.0, 8.5, 6.5 Hz, 1H), 2.04 – 1.87 (m, 2H), 1.77 (m, 2H), 1.55 – 1.38 (m, 3H), 1.38 – 1.17 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.7, 138.0, 130.2, 128.1, 126.3, 53.2, 41.3 (t, *J* = 20.7 Hz), 38.9, 36.5, 31.7, 31.6, 29.9, 24.2, 22.6, 18.7, 14.1. IR (film): ν 1155, 1451, 1495, 1732, 2856, 2928 cm^{-1}. HRMS (EI) calc for $C_{18}H_{25}DO$: m/z 259.2046, found 259.2047.

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