

# Supporting Information

## Rhodium Porphyrin Catalyzed Regioselective Transfer Hydrogenolysis of C–C $\sigma$ -Bonds in Cyclopropanes with $i$ PrOH

*Chen Chen, Shiyu Feng and Kin Shing Chan\**

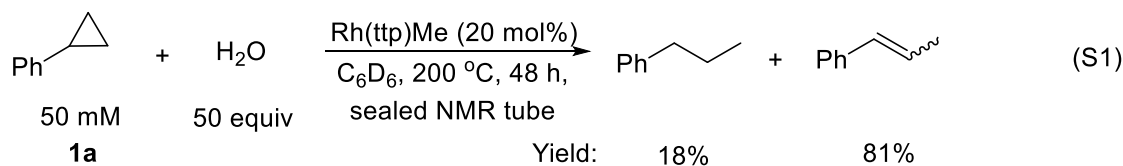
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

Email: [ksc@cuhk.edu.hk](mailto:ksc@cuhk.edu.hk)

### Table of Contents

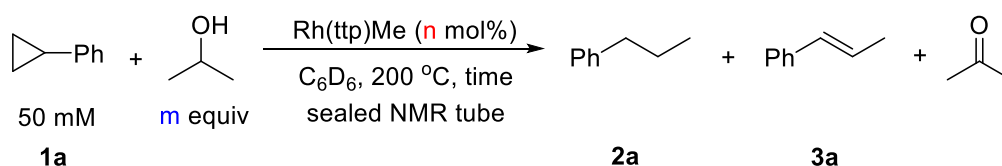
1	Reaction for Attempted Transfer Hydrogenolysis with H <sub>2</sub> O	S1
2	Reaction Conditions Optimization	S1
3	Thermal Decarboxylation and Transesterification of Diethyl Ethylmalonate ( <b>2e</b> )	S1
4	Reaction Time Profile for the Hydrogenolysis of Rh(ttp)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph with $i$ PrOH at 180 °C	S2
5	Computed Bond Dissociation Energies of Cyclopropane Ring C–C $\sigma$ -Bonds	S3
6	Experimental Section	S11
7	References	S18
8	List of NMR Spectra	S19
9	GC-MS Chromatogram Spectra	S24
10	X-ray Data	S26

## 1. Attempted Transfer Hydrogenolysis of Cyclopropylbenzene with H<sub>2</sub>O



## 2. Reaction Conditions Optimization

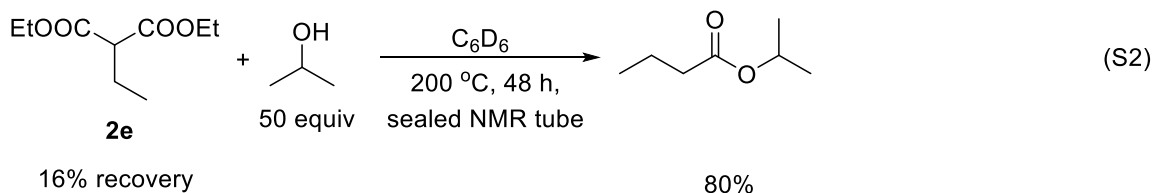
**Table S1** Reaction Conditions Optimization



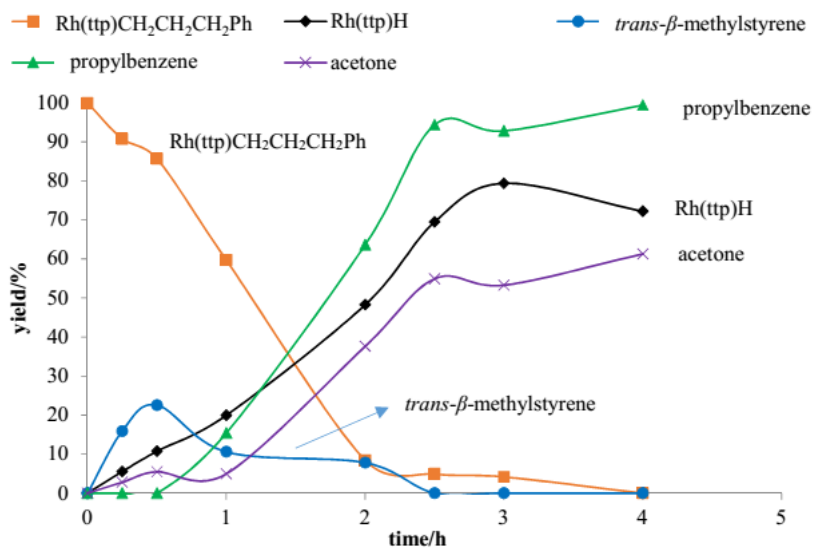
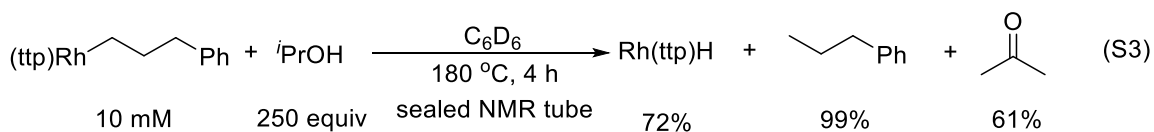
Entry <sup>a</sup>	n	m	time	<b>1a</b> Recovery%	<b>2a</b> Yield%	<b>3a</b> Yield%	( <b>1a</b> + <b>2a</b> + <b>3a</b> ) Yield%	Acetone Yield%
1	0	50	5 d	100	0	0	100	0
2	10	50	5 d	36	24	38	98	40
3	20	50	12 h	0	100	0	100	99
4	20	25	24 h	0	100	0	100	92

<sup>a</sup>NMR yield.

## 3. Thermal decarboxylation and transesterification of diethyl ethylmalonate (2e)



#### 4. Reaction Time Profile for the Hydrogenolysis of Rh(tp) $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ with $i\text{PrOH}$ at 180 °C

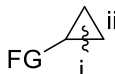
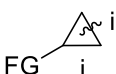


**Figure S1** Reaction Time Profile for the Reduction of Rh(tp) $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  with  $i\text{PrOH}$  at 180 °C (eq S3).

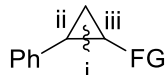
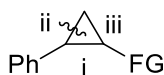
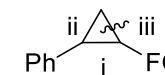
## 5. Computed B.D.E of Cyclopropane Ring C-C $\sigma$ -Bond

The bond dissociation energy (B.D.E) of ring C-C  $\sigma$ -bonds in cyclopropanes is estimated based on the method employed by Jones.<sup>1</sup>  $\Delta H_f^\circ$  calculated with HF/6-31G\*/T1 method using Spartan 2018.

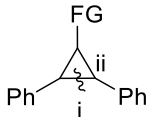
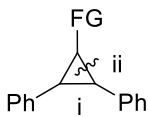
**Table S2** Calculated B.D.E of Ring C-C  $\sigma$ -Bonds of Monosubstituted Cyclopropanes

<div style="display: inline-block; transform: rotate(-45deg);">                     B.D.E (kcal/mol) FG                 </div>		
Ph ( <b>1a</b> )	44.6	55.6
C(O)Ph ( <b>1b</b> )	53.8	58.8
COOEt ( <b>1c</b> )	55.9	65.4
CN ( <b>1d</b> )	49.6	50.8
(COOEt) <sub>2</sub> ( <b>1e</b> )	53.6	58.3

**Table S3** Calculated B.D.E of Ring C-C  $\sigma$ -Bonds of 1,2-Disubstituted Cyclopropanes

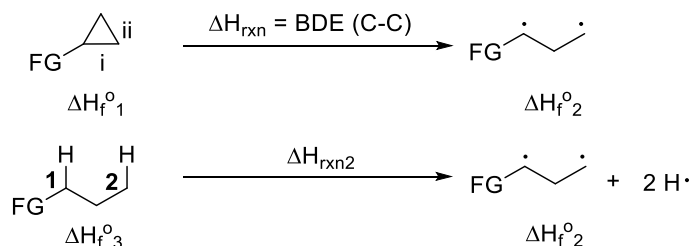
<div style="display: inline-block; transform: rotate(-45deg);">                     B.D.E (kcal/mol) FG                 </div>			
Ph ( <i>trans</i> ) ( <i>trans</i> - <b>1f</b> )	32.4	43.1	43.1
C(O)Ph ( <i>trans</i> ) ( <i>trans</i> - <b>1g</b> )	43.5	46.5	54.6
COOEt ( <i>trans</i> ) ( <i>trans</i> - <b>1h</b> )	45.6	45.7	56.7
CN ( <i>trans</i> ) ( <i>trans</i> - <b>1i</b> )	41.0	41.6	52.9

**Table S4** Calculated B.D.E of Ring C-C  $\sigma$ -Bonds of 1,2,3-Trisubstituted Cyclopropanes

<div style="display: inline-block; transform: rotate(-45deg);">                     B.D.E (kcal/mol) FG                 </div>		
COOEt ( <i>cis,trans</i> ) ( <b>1k</b> )	34.2	43.0
C(O)Ph ( <i>trans,trans</i> ) ( <b>1j</b> )	38.1	43.4

## Calculation Process

### Monosubstituted Cyclopropanes



$$\Delta H_{\text{rxn}2} = \text{BDE (bond 1)} + \text{BDE (bond 2)}$$

$$= \Delta H_f^{\circ 2} + 2 \times \Delta H_f^{\circ}(\text{H} \cdot) - \Delta H_f^{\circ 3}$$

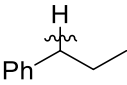
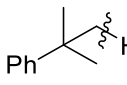
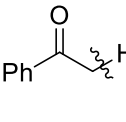
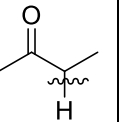
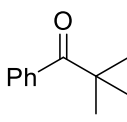
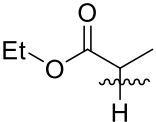
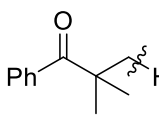

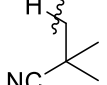
$$= \Delta H_f^{\circ 2} + 2 \times (52.1) - \Delta H_f^{\circ 3}$$

$$\Delta H_f^{\circ 2} = \text{BDE (bond 1)} + \text{BDE (bond 2)} + \Delta H_f^{\circ 3} - 104.2$$

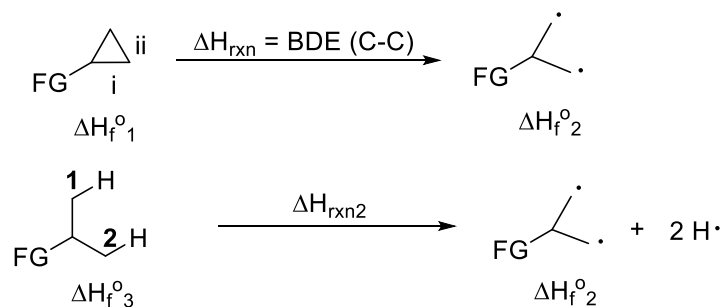
$$\text{BDE (C-C)} = \Delta H_f^{\circ 2} - \Delta H_f^{\circ 1}$$

$$= \text{BDE (bond 1)} + \text{BDE (bond 2)} + \Delta H_f^{\circ 3} - \Delta H_f^{\circ 1} - 104.2$$

**Table S5** Calculations on B.D.E of Proximal Ring C–C  $\sigma$ -Bonds of Monosubstituted Cyclopropanes

FG	$\Delta H_f^{\circ 1}$ (kcal/mol)	$\Delta H_f^{\circ 3}$ (kcal/mol)	Bond 1 (kcal/mol) <sup>2</sup>		Bond 2 (kcal/mol) <sup>2</sup>		BDE (C-C) /kcal/mol
Ph ( <b>1a</b> )	37.00	0.43		86.7		98.7	44.6
C(O)Ph ( <b>1b</b> )	2.79	-30.93	 or 	93		98.8	53.88
COOEt ( <b>1c</b> )	-80.94	-115.19		95.6		98.8	55.95
CN ( <b>1d</b> )	45.29	8.81		94		96.3	49.62

(COOEt) <sub>2</sub> ( <b>1e</b> )	-172.74	-205.20		91.5		98.8	53.64
---------------------------------------	---------	---------	--	------	--	------	-------



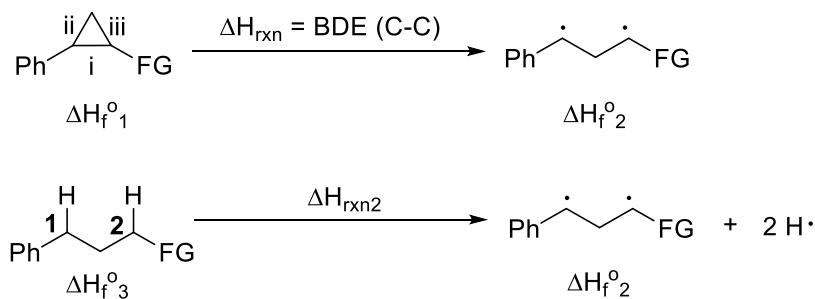
$$\text{BDE (C-C)} = \Delta H_{\text{f}}^{\circ} 2 - \Delta H_{\text{f}}^{\circ} 1$$

$$= \text{BDE (bond 1)} + \text{BDE (bond 2)} + \Delta H_{\text{f}}^{\circ} 3 - \Delta H_{\text{f}}^{\circ} 1 - 104.2$$

**Table S6** Calculations on B.D.E of Distal Ring C–C  $\sigma$ -Bonds of Monosubstituted Cyclopropanes

FG	$\Delta H_{\text{f}}^{\circ} 1$ (kcal/mol)	$\Delta H_{\text{f}}^{\circ} 3$ (kcal/mol)	Bond 1 (kcal/mol) <sup>2</sup>		Bond 2 (kcal/mol) <sup>2</sup>		BDE (C-C) /kcal/mol
Ph ( <b>1a</b> )	37.00	-0.57		98.7		98.7	55.63
C(O)Ph ( <b>1b</b> )	2.79	-31.78		98.8		98.8	58.83
COOEt ( <b>1c</b> )	-80.94	-108.93		98.8		98.8	65.41
CN ( <b>1d</b> )	45.29	7.78		96.3		96.3	50.89
(COOEt) <sub>2</sub> ( <b>1e</b> )	-172.74	-207.77		98.8		98.8	58.37

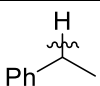

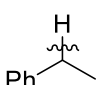
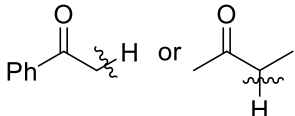
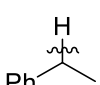
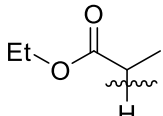
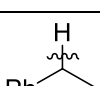

## 1,2-Disubstituted Cyclopropanes



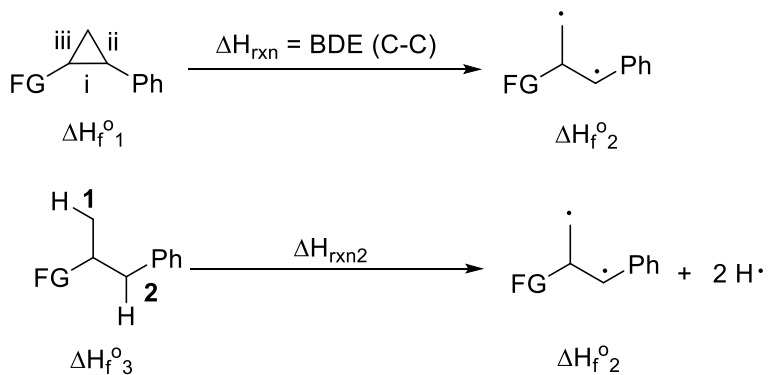
$$\text{BDE (C-C)} = \Delta H_f^\circ 2 - \Delta H_f^\circ 1$$

$$= \text{BDE (bond 1)} + \text{BDE (bond 2)} + \Delta H_f^\circ 3 - \Delta H_f^\circ 1 - 104.2$$

**Table S7** Calculations on B.D.E of Bond i of 1,2-Disubstituted Cyclopropanes

FG	$\Delta H_f^\circ 1$ (kcal/mol)	$\Delta H_f^\circ 3$ (kcal/mol)	Bond 1 (kcal/mol) <sup>2</sup>		Bond 2 (kcal/mol) <sup>2</sup>		BDE (C-C) /kcal/mol
Ph ( <i>trans</i> - <b>1f</b> )	59.89	25.7		85.4		85.4	32.41
(CO)Ph ( <i>trans</i> - <b>1g</b> )	25.67	-5.03		85.4		93	43.5
COOEt ( <i>trans</i> - <b>1h</b> )	-58.74	-89.88		85.4		95.6	45.66
CN ( <i>trans</i> - <b>1i</b> )	68.69	34.49		85.4		94	41

## 1,2-Disubstituted Cyclopropanes



$$\text{BDE (C-C)} = \Delta H_f^\circ_2 - \Delta H_f^\circ_1$$

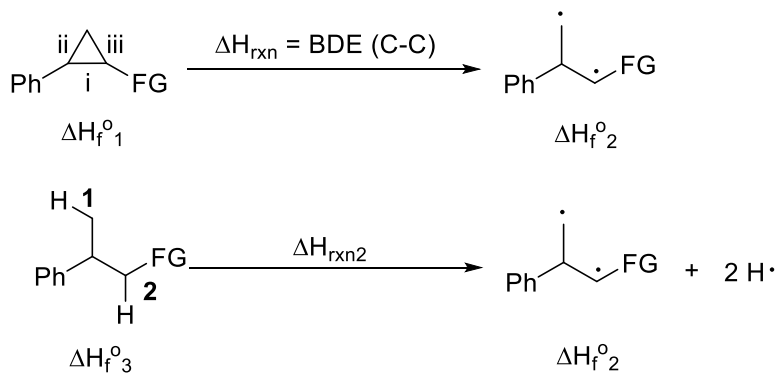
$$= \text{BDE (bond 1)} + \text{BDE (bond 2)} + \Delta H_f^\circ_3 - \Delta H_f^\circ_1 - 104.2$$

**Table S8** Calculations on B.D.E of Bond ii of 1,2-Disubstituted Cyclopropanes

FG	$\Delta H_f^\circ_1$ (kcal/mol)	$\Delta H_f^\circ_3$ (kcal/mol)	Bond 1 (kcal/mol) <sup>2</sup>		Bond 2 (kcal/mol) <sup>2</sup>		BDE (C-C) /kcal/mol
Ph ( <i>trans</i> - <b>1f</b> )	59.89	23.15		98.7		85.4	43.16
(CO)Ph ( <i>trans</i> - <b>1g</b> )	25.67	-7.82		98.8		85.4	46.51
COOEt ( <i>trans</i> - <b>1h</b> )	-58.74	-92.97		98.8		85.4	45.77
CN ( <i>trans</i> - <b>1i</b> )	68.69	32.79		96.3		85.4	41.6



## 1,2-Disubstituted Cyclopropanes



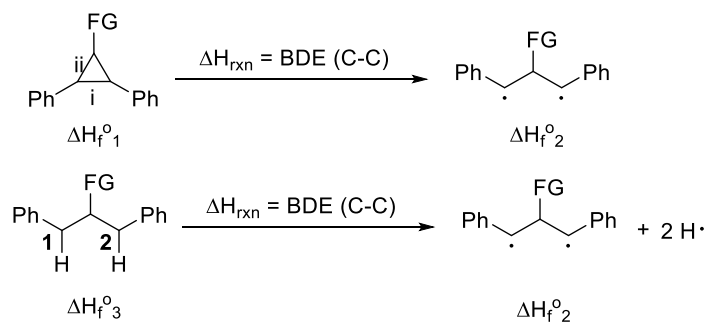
$$\text{BDE (C-C)} = \Delta H_f^\circ_2 - \Delta H_f^\circ_1$$

$$= \text{BDE (bond 1)} + \text{BDE (bond 2)} + \Delta H_f^\circ_3 - \Delta H_f^\circ_1 - 104.2$$

**Table S9** Calculations on B.D.E of Bond iii of 1,2-Disubstituted Cyclopropanes

FG	$\Delta H_f^\circ_1$ (kcal/mol)	$\Delta H_f^\circ_3$ (kcal/mol)	Bond 1 (kcal/mol) <sup>2</sup>		Bond 2 (kcal/mol) <sup>2</sup>		BDE (C-C) /kcal/mol
Ph ( <i>trans</i> - <b>1f</b> )	59.89	23.15		98.7		85.4	43.16
(CO)Ph ( <i>trans</i> - <b>1g</b> )	25.67	-7.18		98.7		93	54.65
COOEt ( <i>trans</i> - <b>1h</b> )	-58.74	-92.09		98.7		95.6	56.75
CN ( <i>trans</i> - <b>1i</b> )	68.69	33.18		98.7		94	52.99

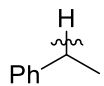
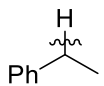
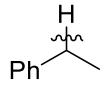
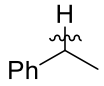
## 1,2,3-Trisubstituted Cyclopropanes



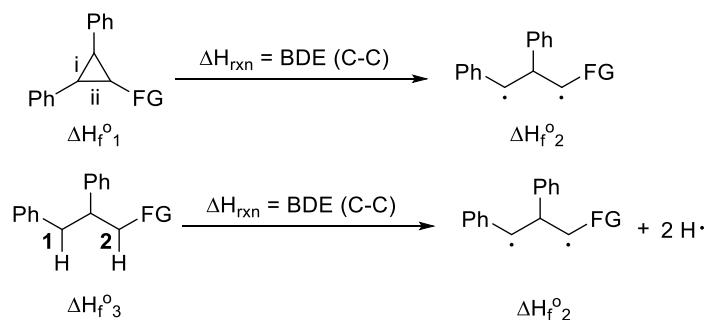
$$\text{BDE (C-C)} = \Delta H_{\text{f}}^{\circ}_2 - \Delta H_{\text{f}}^{\circ}_1$$

$$= \text{BDE (bond 1)} + \text{BDE (bond 2)} + \Delta H_{\text{f}}^{\circ}_3 - \Delta H_{\text{f}}^{\circ}_1 - 104.2$$

**Table S10** Calculations on B.D.E of Bond i of 1,2,3-Trisubstituted Cyclopropanes

FG	$\Delta H_{\text{f}}^{\circ}_1$ (kcal/mol)	$\Delta H_{\text{f}}^{\circ}_3$ (kcal/mol)	Bond <b>1</b> (kcal/mol)		Bond <b>2</b> (kcal/mol)		BDE (C-C) /kcal/mol
COOEt <b>(1j)</b>	-34.95	-63.41		85.4		85.4	38.14
(CO)Ph <b>(1k)</b>	47.02	14.71		85.4		85.4	34.29

## 1,2,3-Trisubstituted Cyclopropanes



**Table S11** Calculations on B.D.E of Bond ii of 1,2,3-Trisubstituted Cyclopropanes

FG	$\Delta H_{\text{f}}^{\circ} \text{1}$ (kcal/mol)	$\Delta H_{\text{f}}^{\circ} \text{3}$ (kcal/mol)	Bond 1 (kcal/mol)		Bond 2 (kcal/mol)		BDE (C-C) /kcal/mol
COOEt ( <b>1j</b> )	-34.95	-68.29		85.4		95.6	43.46
(CO)Ph ( <b>1k</b> )	47.02	15.85		85.4		93	43.03

## 6. Experimental Section

### General Procedures

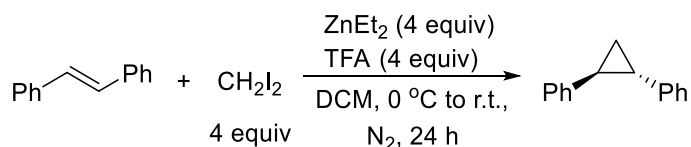
Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Benzene was distilled over sodium under nitrogen. Thin-layer chromatography was performed on precoated silica gel 60 F<sub>254</sub> plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used in column chromatography to isolate. Neutral alumina (Merck, 90 active neutral, 70-230 mesh)/H<sub>2</sub>O (~10:1 v/v) was used in column chromatography to isolate. For the reaction conducted in a sealed NMR tube, the mixture was degassed by three freeze (77 K)-pump (0.005 mmg)-thaw cycles, and then flame-sealed under vacuum, heated in oven in dark and wrapped with alumina foil to protect from exposure to room light before <sup>1</sup>H NMR measurements. The NMR yields were calculated using benzene residue or excess <sup>i</sup>PrOH as internal standard. *trans*-1,2-Diphenyl cyclopropane (*trans*-**1f**),<sup>3</sup> *trans*-1-benzoyl-2-phenylcyclopropane (*trans*-**1g**),<sup>4</sup> 2-phenyl-cyclopropanecarboxylic acid ethyl ester (**1h**),<sup>5</sup> *trans*-2-phenylcyclopropanecarbonitrile (*trans*-**1i**),<sup>6</sup> *trans,cis*-2,3-diphenyl-1-cyclopropanecarboxylic acid ethyl ester (**1j**)<sup>7</sup> and *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**1k**)<sup>8</sup> have been characterized and were prepared according to the literature process.

<sup>1</sup>H NMR spectra was recorded on a Bruker AV-400 instrument at 400 MHz. Chemical shifts were referenced with the residual solvent protons in CDCl<sub>3</sub> ( $\delta$  7.26 ppm), C<sub>6</sub>D<sub>6</sub> ( $\delta$  7.15ppm). Chemical shifts ( $\delta$ ) are reported as parts per million (ppm) in  $\delta$  scale downfield from TMS. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectrometry (HRMS) was performed on Bruker Autoflex speed MALDI-TOF instrument using a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix and CH<sub>2</sub>Cl<sub>2</sub> as the solvent. GC-MS analyses were conducted on a GCMS-QP2010 Plus system using an Rtx-5MS column (30 m  $\times$  0.25 mm). Details of the GC program are as follows. The column oven temperature and injection temperature were 100 and 250 °C. Helium was used as the carrier gas. The flow control mode was chosen as linear velocity (36.3 cm s<sup>-1</sup>) with a pressure of 68.8 kPa. The total flow, column flow, and purge flow were 13.5, 0.95, and 3.0 mL min<sup>-1</sup>, respectively. Split

mode injection with a split ratio of 10.0 was applied. After injection, the column oven temperature was kept at 100 °C for 2 min and was then elevated at a rate of 30 °C min<sup>-1</sup> for 5 min until 250 °C. The temperature of 250 °C was kept for 4 min. The retention time and mass spectrum of organic products obtained were identical with those of commercially available authentic samples.

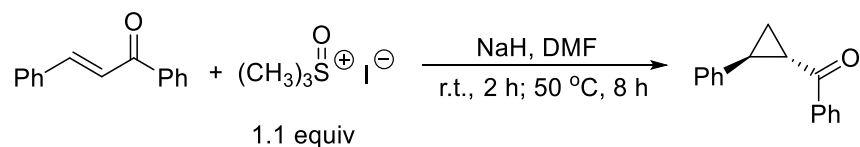
### Preparation of Cyclopropane Substrates.

#### *trans*-1,2-Diphenylcyclopropane (*trans*-**1f**)<sup>3</sup>



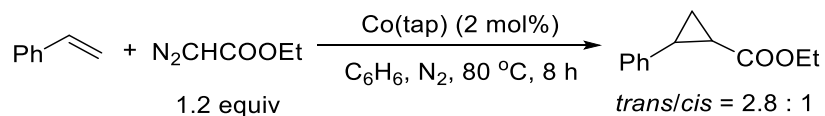
A solution of trifluoroacetic acid (620  $\mu\text{L}$ , 8 mmol) in 2 mL dry dichloromethane was added very slowly at 0 °C to a solution of diethyl zinc (1.0 M in hexane, 8 mL, 8 mmol) in 4 mL dry dichloromethane under N<sub>2</sub>. The mixture was further stirred for 30 min to give solid attached on the side of flask. A solution of diiodomethane (700  $\mu\text{L}$ , 8 mmol) in 2 mL dry DCM was added to the reaction mixture at 0 °C over 30 min and further stirred for 30 min. A solution of *trans*-stilbene (365 mg, 2 mmol) in 2 mL dry DCM was added to the reaction mixture at 0 °C and was stirred at r.t. for 24 h. The reaction was quenched with sat. NH<sub>4</sub>Cl (aq) (15 mL) and extracted with DCM (3×30 mL). The organic layers were combined and washed with sat. NaHCO<sub>3</sub> (aq) (2×15 mL), water (15 mL) and brine (2×15 mL). The resulting organic layer was further dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated with rotary evaporator. The resulting yellow oil was dissolved in DCM (10 mL). *m*CPBA (350 mg, 2 mmol) was added to the reaction mixture and the resulted mixture was stirred at r.t. overnight. The reaction was quenched with sat. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq) (20 mL) and extracted with DCM (2×20 mL). The organic layer was washed with sat. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq) (2×20 mL) and brine (20 mL). The resulting organic layer was further dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated with rotary evaporator. The residue was purified with column chromatography on silica gel and using hexane as eluent to afford *trans*-1,2-diphenylcyclopropane (*trans*-**1f**) as a colorless oil in 52% yield (202 mg, 1.01 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.45 (t, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 2 H), 2.17 (t, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, 2 H), 7.13-7.20 (m, 6 H), 7.27-7.31 (m, 4 H).

***trans*-1-Benzoyl-2-phenylcyclopropane (*trans*-1g)<sup>4</sup>**



Trimethylsulfoxonium iodide (893.6 mg, 4.1 mmol) and NaH (492 mg, 20.6 mmol) were added into a 25 mL two-necked round-bottom flask, refilled with N<sub>2</sub> for 3 times. Dry DMF (4 mL) was added to the flask through syringe. A solution of (*E*)-chalcone (765.3 mg, 3.7 mmol) in dry DMF (1 mL) was added to the flask at 0 °C. The reaction mixture was warmed up to r.t. and stirred for 2 h, then further warmed up to 50 °C and stirred for another 8 h. Water (10 mL) was added to quench the reaction and DCM (10×3 mL) was used to extract the product for 3 times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using EA/hexane (v/v: 2% ~ 5%) as eluent to get the target product in 53% yield (429.1 mg, 1.93 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.53-1.58 (m, 1 H), 1.90-1.95 (m, 1 H), 2.67-2.72 (m, 1 H), 2.88-2.92 (m, 1 H), 7.17-7.33 (m, 5 H), 7.44-7.58 (m, 3 H), 7.98-8.00 (m, 2 H). Lit<sup>9</sup> IR (neat) 2980, 1711, 1627, 1272, 1164 cm<sup>-1</sup>.

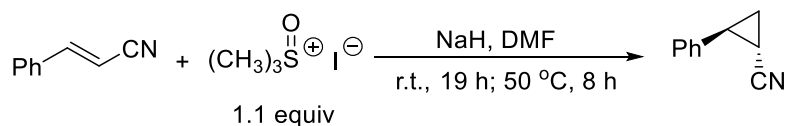
**2-Phenyl-cyclopropanecarboxylic acid ethyl ester (1h)<sup>5</sup>**



Styrene (60 μL, 0.52 mmol), ethyl diazoacetate (66 μL, 0.63 mmol), Co(tap) (8.0 mg, 0.010 mmol) and 2 mL benzene were added into a Teflon crew capped reaction tube. The mixture was degassed by three freeze-pump-thaw cycles and heated to 80 °C for 8 h. The resulting mixture was concentrated and purified by column chromatography on silica gel to give the product in 95% yield (*trans* : *cis* = 2.8 : 1; 94.5 mg, 0.50 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *trans*-isomer: δ 1.27 (t, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, 3 H), 1.28-1.33 (m, 1 H), 1.57-1.62 (m, 1 H), 1.87-1.92 (m, 1 H), 2.49-2.54 (m, 1 H), 4.17 (q, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, 2 H), 7.08-7.29 (m, 5 H). *cis*-isomer: δ 0.96 (t, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, 3 H), 1.31-1.35 (m, 1 H), 1.69-1.73 (m, 1 H), 2.04-2.10 (m, 1 H), 2.58 (q, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 1 H), 3.86 (q, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, 2 H), 7.08-7.29 (m, 5 H). Lit<sup>9</sup> IR (neat) 3060, 1662, 1600, 1283, 1223, 1012 cm<sup>-1</sup> **CAUTION!!!**

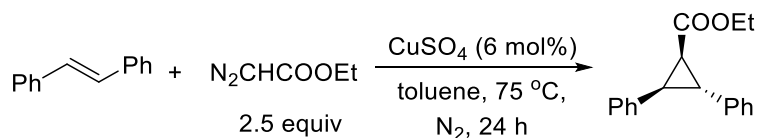
**Diazo compounds are toxic and potentially explosive. They should be stored in refrigerator and handled with caution in a fume hood.**

***trans*-2-Phenylcyclopropanecarbonitrile (*trans*-1i)<sup>6</sup>**



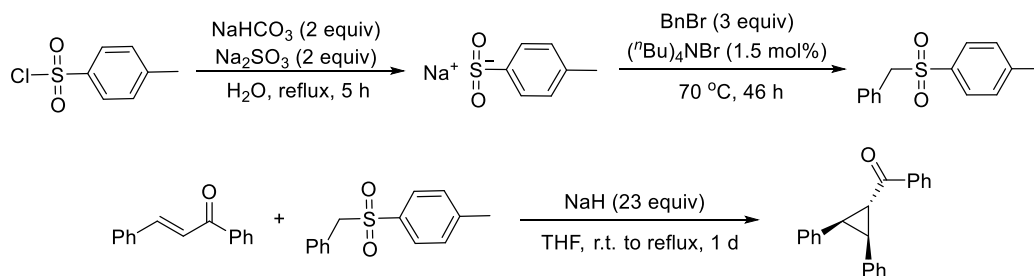
Trimethylsulfoxonium iodide (920.0 mg, 4.2 mmol) and NaH (480 mg, 20.0 mmol) were added in to a 25 mL two-necked round-bottom flask, refilled with N<sub>2</sub> for 3 times. Dry DMF (4 mL) was added to the flask through syringe. A solution of (*E*)-cinnamionitrile (480  $\mu$ L, 3.8 mmol) in dry DMF (1 mL) was added to the flask at 0 °C. The reaction mixture was warmed up to r.t. and stirred for 19 h, then further warmed up to 50 °C for another 8 h. Water was added to quench the reaction and DCM (10 $\times$ 3 mL) was used to extract the product for 3 times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using EA/hexane (v/v: 2% ~ 4%) as eluent to get the target product in 5% yield (28.3 mg, 0.2 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.43-1.48 (m, 1 H), 1.53-1.58 (m, 1 H), 1.60-1.64 (m, 1 H), 2.61-2.66 (m, 1 H), 7.09-7.33 (m, 5 H).

***trans, cis*-2,3-Diphenyl-1-cyclopropanecarboxylic acid ethyl ester (1j)<sup>7</sup>**



*trans*-Stilbene (1.0 g, 5.5 mmol), CuSO<sub>4</sub> (53 mg, 0.33 mmol) and toluene (6 mL) were added to a dried 3-necked flask under N<sub>2</sub>. The mixture was heated up to 75 °C and a solution of ethyl diazoacetate (1.46 mL, 13.8 mmol) in 4.5 mL toluene was added very slowly over a period of 5 h. The reaction mixture was further stirred for 24 h at 75 °C. The resulting mixture was concentrated and purified by column chromatography on silica gel to give the desired product in 34% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.05 (t, <sup>3</sup>J<sub>H-H</sub> = 7.16 Hz, 3 H), 2.41-2.45 (m, 1 H), 2.93-2.97 (m, 1 H), 3.22-3.25 (m, 1 H), 3.93-4.01 (m, 2 H), 7.23-7.37 (m, 10 H).<sup>7</sup>

***trans, trans*-2,3-Diphenyl-1-benzoylcyclopropane (1k)**<sup>8</sup>



*Preparation of 1-(benzylsulfonyl)-4-methylbenzene.* *p*-Toluenesulfonyl chloride (1.0 g, 5.3 mmol), sodium sulfite (1.3 g, 10.7 mmol), NaHCO<sub>3</sub> (976 mg, 11.6 mmol) and 50 mL water were added into a 100 mL round bottom flask. The reaction mixture was heated to reflux for 3 h. Benzyl bromide (1.95 mL, 16.3 mmol) and (*n*-Bu)<sub>4</sub>NBr (25.5 mg, 0.08 mmol) were added to the reaction mixture. The reaction temperature was cooled to 70 °C and stirred overnight. The mixture was extracted with DCM (20×3 mL). The organic layers were combined, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated with vacuo. The resulting residue was purified with column chromatography on silica gel using ethyl acetate/hexane (v/v: 10%) as eluent to get the target product as a white solid in 82% yield (1.06 g, 4.3 mmol).<sup>8a</sup>

*Preparation of trans, trans*-2,3-diphenyl-1-benzoylcyclopropane (**1k**). 1-(Benzylsulfonyl)-4-methylbenzene (252.4 mg, 1.02 mmol), (*E*)-chalcone (215.6 mg, 1.03 mmol), sodium hydride (547.9 mg, 22.9 mmol) and dried THF (10 mL) were added to a 25 mL round bottom flask under N<sub>2</sub>. The reaction mixture was heated to reflux for 1 d. 1 mL water was added to quench the reaction. Solvent THF was removed under reduced pressure. The residue was diluted with water and extracted with DCM (10×3 mL). The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated to afford crude product. Purification on silica gel using ethyl acetate/hexane (v/v: 10%) as eluent to get the target product as a white solid in 57% yield (176.5 mg, 0.59 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.31 (d, <sup>3</sup>J<sub>H-H</sub> = 5.2 Hz, 2 H), 3.54 (t, <sup>3</sup>J<sub>H-H</sub> = 5.2 Hz, 1 H), 7.00-7.02 (m, 4 H), 7.12-7.18 (m, 6 H), 7.50-7.53 (m, 2 H), 7.58-7.62 (m, 1 H), 8.09-8.11 (m, 2 H).<sup>8b</sup> Lit<sup>10</sup> IR (KBr) 1660, 1600, 1580, 1500, 1010, 880 cm<sup>-1</sup>



### Attempted Transfer Hydrogenolysis of Cyclopropylbenzene with H<sub>2</sub>O

Cyclopropylbenzene (**1a**; 3.1  $\mu$ L, 0.025 mmol), H<sub>2</sub>O (25  $\mu$ L, 1.38 mmol), Rh(*ttp*)Me (4.0 mg, 0.005 mmol) and 415  $\mu$ L C<sub>6</sub>D<sub>6</sub> were added into a Teflon crew head stoppered NMR tube, degassed by three freeze-pump-thaw cycles, and then flame-sealed under vacuum, heated in oven in dark at 200 °C for 48 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy at particular time interval. 18% propylbenzene (**2a**; 0.004 mmol) and 81% *trans*- $\beta$ -methylstyrene (**3a**; 0.02 mmol) were obtained. The yield was determined through GC-MS analysis using naphthalene as internal standard.

### Reaction Conditions Optimization

*Without Rh(*ttp*)Me catalyst in the presence of 50 equiv <sup>i</sup>PrOH.* Cyclopropylbenzene (**1a**; 3.1  $\mu$ L, 0.025 mmol), <sup>i</sup>PrOH (95  $\mu$ L, 1.24 mmol) and 400  $\mu$ L C<sub>6</sub>D<sub>6</sub> were added into a Teflon screw head stoppered NMR tube, degassed by three freeze-pump-thaw cycles, and then flame-sealed under vacuum, heated in oven in dark at 200 °C for 5 d. The reaction was monitored by <sup>1</sup>H NMR spectroscopy at particular time interval. Cyclopropylbenzene (**1a**) was recovered quantitatively.

*With 10 mol% Rh(*ttp*)Me catalyst in the presence of 50 equiv <sup>i</sup>PrOH.* Cyclopropylbenzene (**1a**; 3.1  $\mu$ L, 0.025 mmol), <sup>i</sup>PrOH (95  $\mu$ L, 1.24 mmol), Rh(*ttp*)Me (2.0 mg, 0.0025 mmol) and 400  $\mu$ L C<sub>6</sub>D<sub>6</sub> were added into a Teflon screw head stoppered NMR tube, degassed by three freeze-pump-thaw cycles, and then flame-sealed under vacuum, heated in oven in dark at 200 °C for 5 d. The reaction was monitored by <sup>1</sup>H NMR spectroscopy at particular time interval. 24% of propylbenzene (**2a**; 0.006 mmol), 38% of *trans*- $\beta$ -methylstyrene (**3a**; 0.009 mmol), 40% of acetone were obtained with 36% of cyclopropylbenzene (**1a**) recovered.

*With 20 mol% Rh(*ttp*)Me catalyst in the presence of 25 equiv <sup>i</sup>PrOH.* Cyclopropylbenzene (**1a**; 3.1  $\mu$ L, 0.025 mmol), <sup>i</sup>PrOH (48  $\mu$ L, 0.63 mmol), Rh(*ttp*)Me (3.9 mg, 0.005 mmol) and 400  $\mu$ L C<sub>6</sub>D<sub>6</sub> were added into a Teflon screw head stoppered NMR tube, degassed by three freeze-pump-thaw cycles, and then flame-sealed under vacuum, heated in oven in dark at 200 °C for 24 h. The reaction was monitored by <sup>1</sup>H NMR spectroscopy at particular time interval. 100% of propylbenzene (**2a**; 0.025 mmol) and 92% of acetone were obtained.

### **Thermal Decarboxylation and Transesterification of Ethyl Diethylmalonate (2e)**

Diethyl ethylmalonate (**2e**; 4.7  $\mu\text{L}$ , 0.025 mmol),  $i\text{PrOH}$  (95  $\mu\text{L}$ , 1.24 mmol) and 400  $\mu\text{L}$   $\text{C}_6\text{D}_6$  were added into a Teflon screw head stoppered NMR tube, degassed by three freeze-pump-thaw cycles, and then flame-sealed under vacuum, heated in oven in dark at 200  $^\circ\text{C}$  for 2 d. The reaction was monitored by  $^1\text{H}$  NMR spectroscopy at particular time interval. 80% yield of isopropyl butyrate (0.02 mmol) and 16% yield of recovered diethyl ethylmalonate were achieved after reaction.

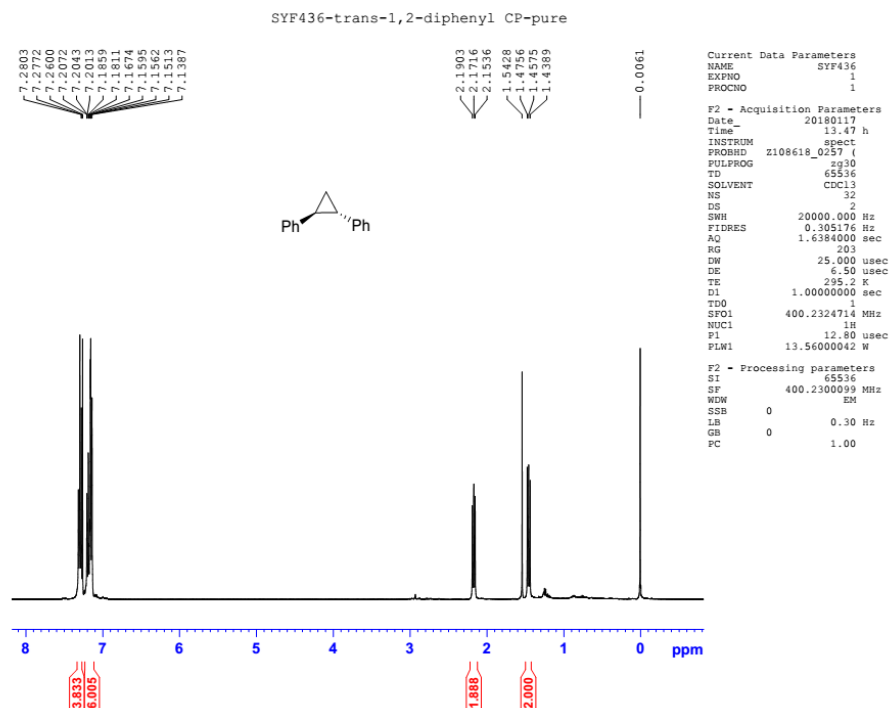
## 7. References

1. Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Simhai, N.; Iverson, C. N.; Müller, C.; Satoh, T.; Jones, W. D. Cleavage of the Carbon–Carbon Bond in Biphenylene using Transition Metals. *J. Mol. Catal. A: Chem.* **2002**, *189*, 157-168.
2. Luo, Y. R. *Handbook of Bond Dissociation Energies in Organic Compounds*, CRC Press: Boca Raton, FL, 2002.
3. Cahard, E.; Schoenebeck, F.; Garnier, J.; Cutulic, S. P. Y.; Zhou, S.; Murphy, J. A. Electron Transfer to Benzenes by Photoactivated Neutral Organic Electron Donor Molecules. *Angew. Chem. Int. Ed.* **2012**, *51*, 3673-3676.
4. Yusuke, A.; Ren, T.; Gaku, A.; Takashi, K.; Munetaka, A. Oxydifluoromethylation of Alkenes by Photoredox Catalysis: Simple Synthesis of CF<sub>2</sub>H-Containing Alcohols. *Chem. Eur. J.* **2016**, *22*, 1262-1265.
5. Huang, L.; Chen, Y.; Gao, G.-Y.; Zhang, X. P. Diastereoselective and Enantioselective Cyclopropanation of Alkenes Catalyzed by Cobalt Porphyrins. *J. Org. Chem.* **2003**, *68*, 8179-8184.
6. Wang, M.-X.; Feng, G.-Q. A Novel Approach to Eantiopure Cyclopropane Compounds from Biotransformation of Nitriles. *New J. Chem.* **2002**, *26*, 1575-1583.
7. Scholz, S. O.; Farney, E. P.; Kim, S.; Bates, D. M.; Yoon, T. P. Spin-Selective Generation of Triplet Nitrenes: Olefin Aziridination through Visible-Light Photosensitization of Azidoformates. *Angew. Chem. Int. Ed.* **2016**, *55*, 2239-2242.
8. (a) Laha, J. K.; Jethava, K. P.; Dayal, N. Palladium-Catalyzed Intramolecular Oxidative Coupling Involving Double C(sp<sup>2</sup>)–H Bonds for the Synthesis of Annulated Biaryl Sultams. *J. Org. Chem.* **2014**, *79*, 8010-8019. (b) Chang, M.-Y.; Chen, Y.-C.; Chan, C.-K. One-pot Synthesis of Multifunctionalized Cyclopropanes. *Tetrahedron* **2014**, *70*, 2257-2263.
9. Davi, M.; Lebel, H. One-pot Approach for the Synthesis of *trans*-Cyclopropyl Compounds from Aldehydes. Application to the Synthesis of GPR40 Receptor Agonists. *Chem. Commun.* **2008**, 4974-4976.
10. Stahl, I.; Schomburg, S.; Kalinowski, H. O. Diastereomere Cyclopropane aus Benzyldisulfuranen und Chalkonen. *Chem. Ber.* **1984**, *117*, 2247-2260.

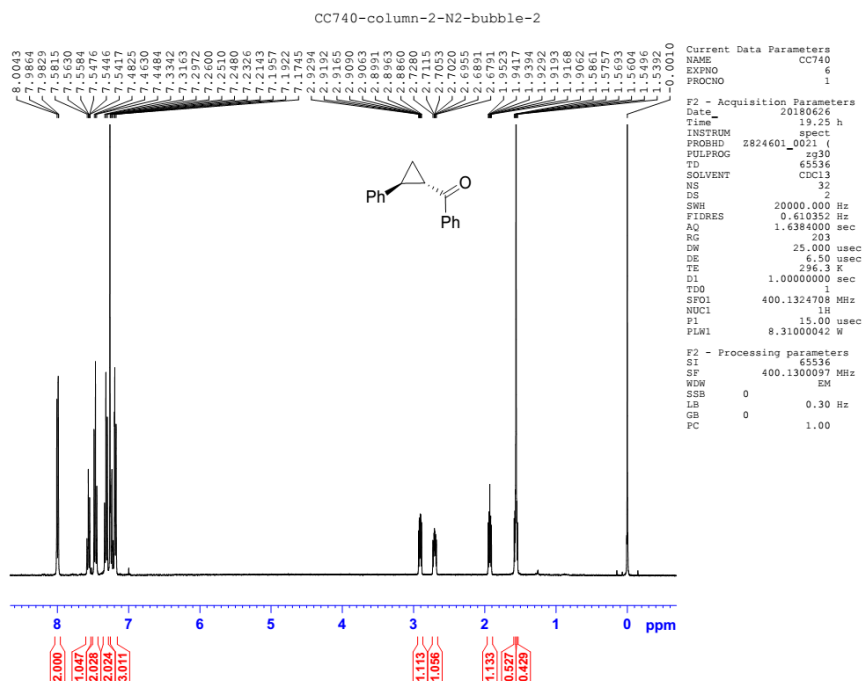
## 8. List of NMR Spectra

No.	Spectra	Page
1	<sup>1</sup> H NMR spectrum of <i>trans</i> -1,2-diphenylcyclopropane ( <i>trans</i> - <b>1f</b> )	S20
2	<sup>1</sup> H NMR spectrum of <i>trans</i> -1-benzoyl-2-phenylcyclopropane ( <i>trans</i> - <b>1g</b> )	S20
3	<sup>1</sup> H NMR spectrum of 2-phenylcyclopropanecarboxylic acid ethyl ester ( <i>cis&amp;trans</i> - <b>1h</b> )	S21
4	<sup>1</sup> H NMR spectrum of <i>trans</i> -2-phenylcyclopropanecarbonitrile ( <i>trans</i> - <b>1i</b> )	S21
5	<sup>1</sup> H NMR spectrum of <i>trans, cis</i> -2,3-diphenyl-1-cyclopropanecarboxylic acid ethyl ester ( <b>1j</b> )	S22
6	<sup>1</sup> H NMR spectrum of <i>trans, trans</i> -2,3-diphenyl-1-benzoylcyclopropane ( <b>1k</b> )	S22
7	<sup>1</sup> H NMR spectrum of Rh(ttp)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	S23
8	<sup>13</sup> C NMR spectrum of Rh(ttp)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	S23

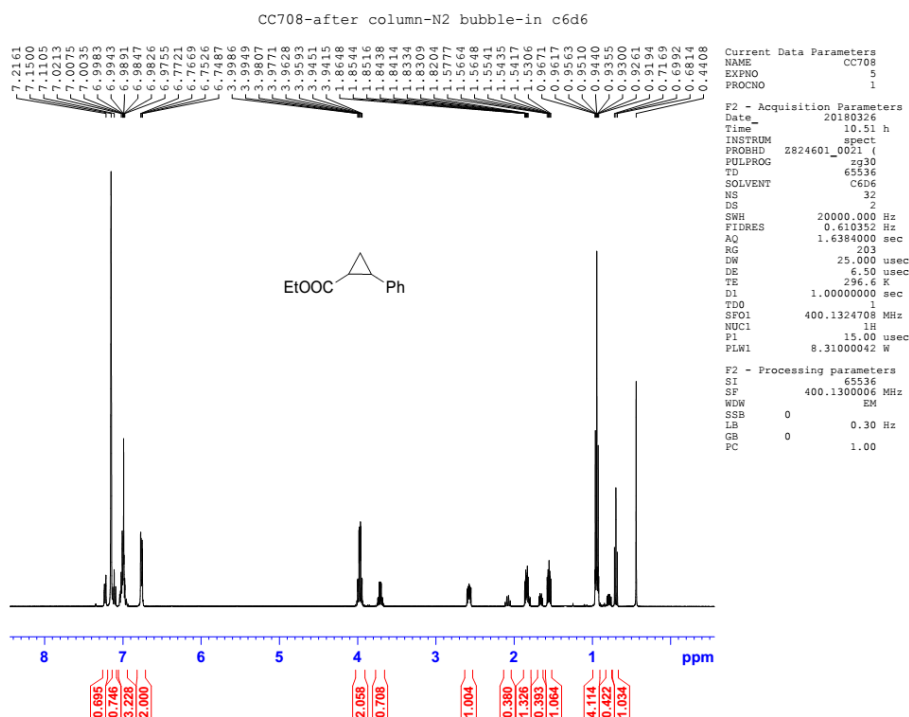
**Figure S2**  $^1\text{H}$  NMR spectrum of *trans*-1,2-diphenylcyclopropane (*trans*-**1f**) ( $\text{CDCl}_3$ , 400MHz, 295K)



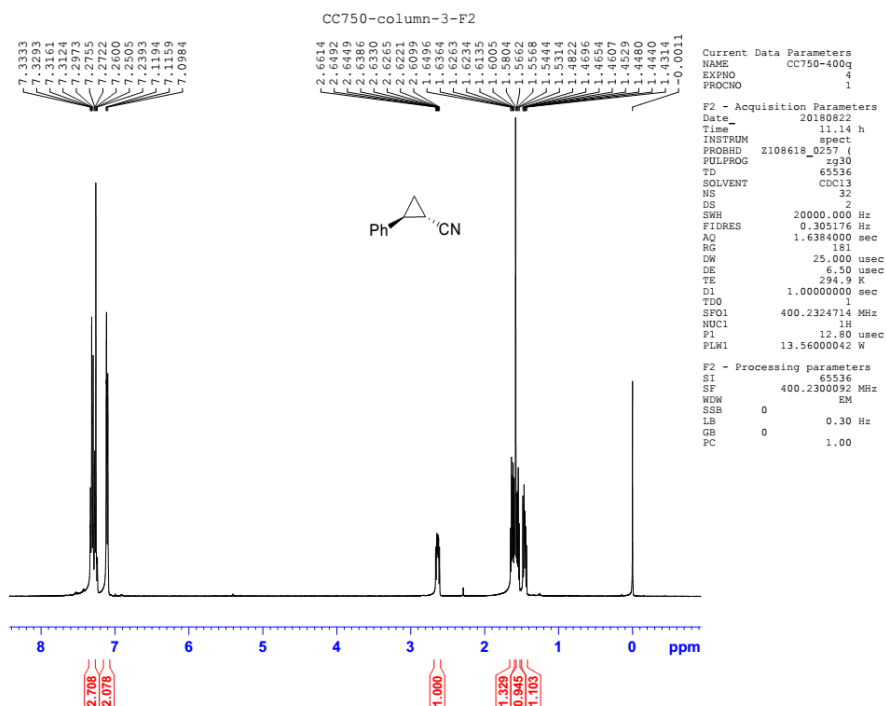
**Figure S3**  $^1\text{H}$  NMR spectrum of *trans*-1-benzoyl-2-phenylcyclopropane (*trans*-**1g**) ( $\text{CDCl}_3$ , 400MHz, 296K)



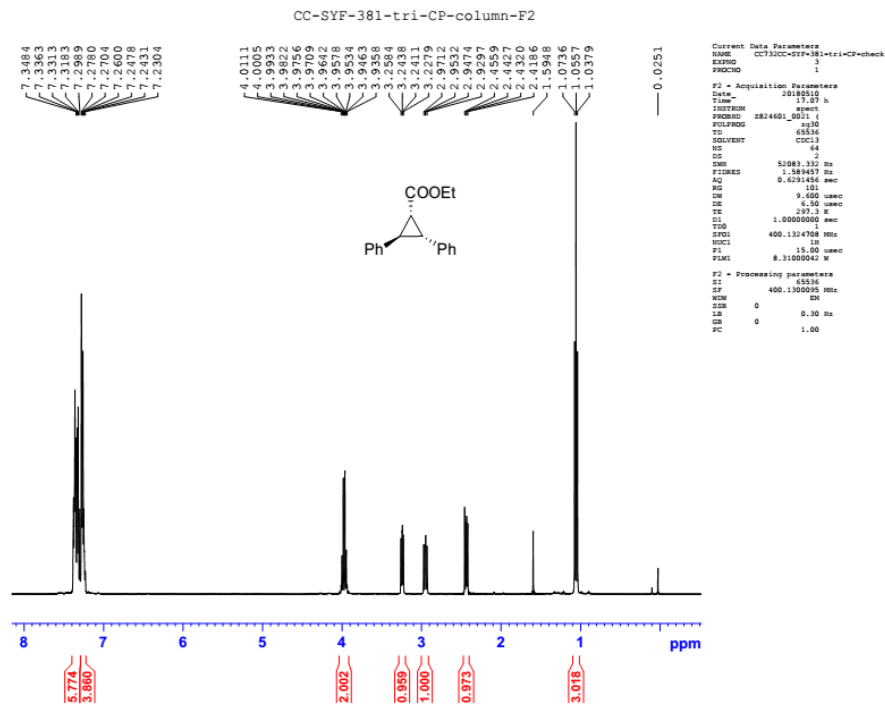
**Figure S4**  $^1\text{H}$  NMR spectrum of 2-phenylcyclopropanecarboxylic acid ethyl ester (**1h**) ( $\text{C}_6\text{D}_6$ , 400MHz, 296K)



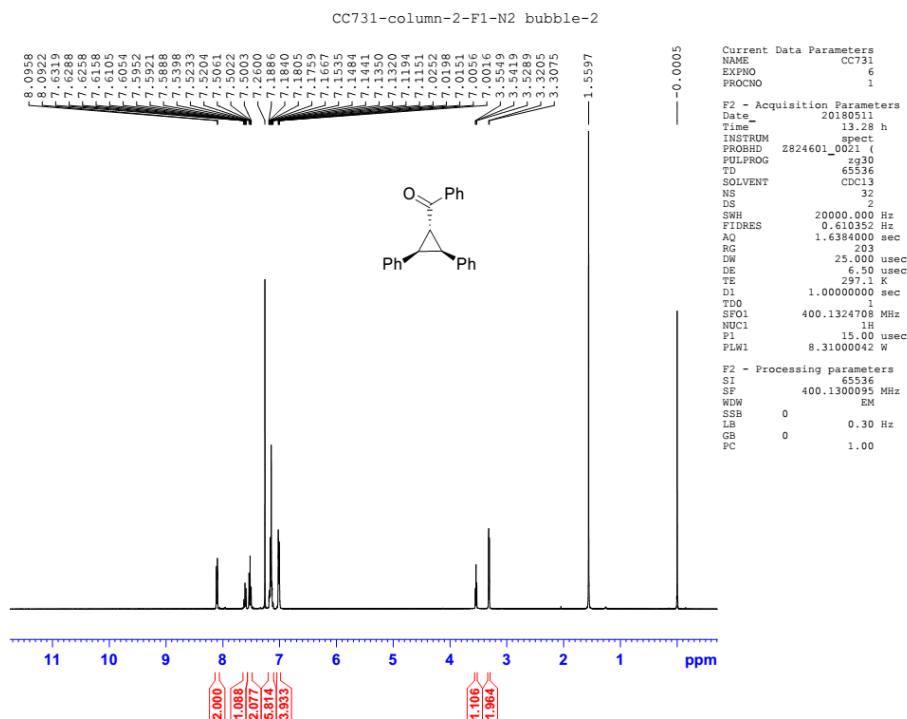
**Figure S5**  $^1\text{H}$  NMR spectrum of *trans*-2-phenylcyclopropanecarbonitrile (*trans*-**1i**) ( $\text{CDCl}_3$ , 400MHz, 295K)



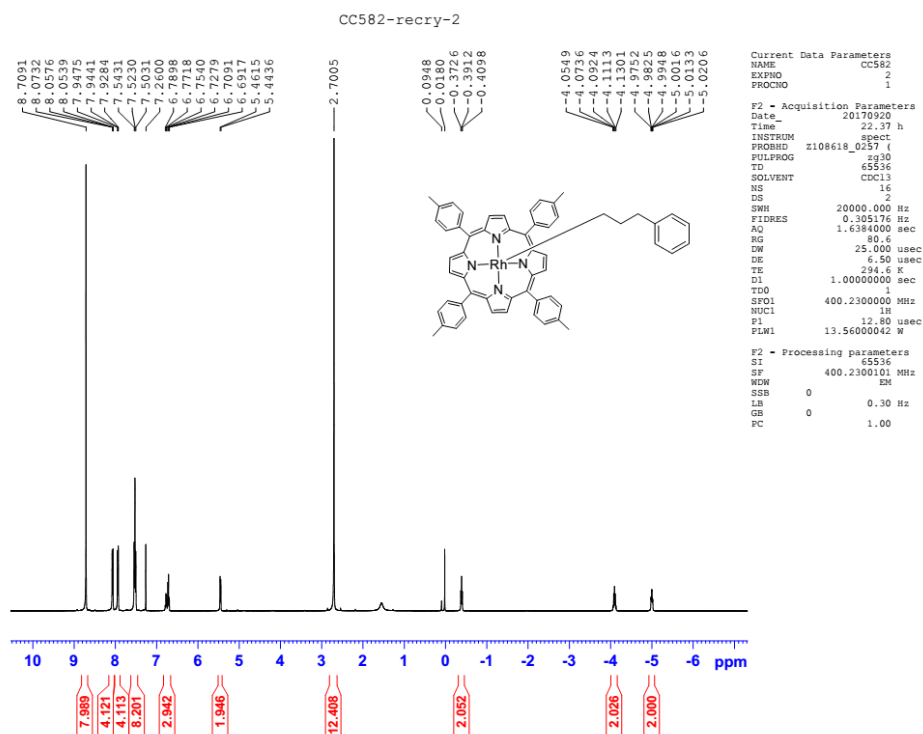
**Figure S6**  $^1\text{H}$  NMR spectrum of *trans, cis*-2,3-diphenyl-1-cyclopropanecarboxylic acid ethyl ester (**1j**) ( $\text{CDCl}_3$ , 400MHz, 297K)



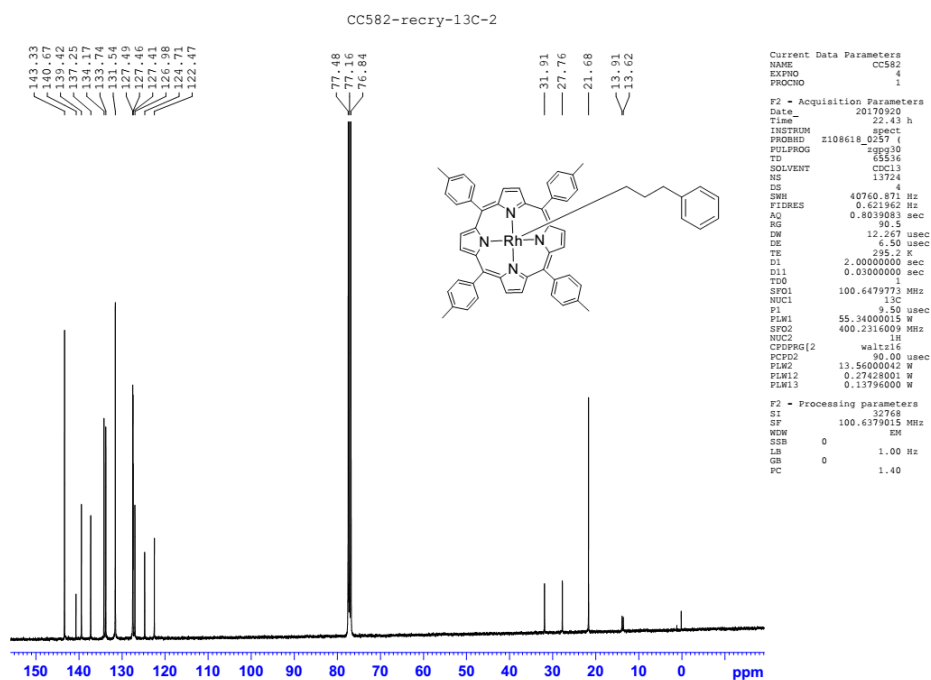
**Figure S7**  $^1\text{H}$  NMR spectrum of *trans, trans*-2,3-diphenyl-1-benzoylcyclopropane (**1k**) ( $\text{CDCl}_3$ , 400MHz, 297K)



**Figure S8**  $^1\text{H}$  NMR spectrum of  $\text{Rh}(\text{ttp})\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  ( $\text{CDCl}_3$ , 400MHz, 295K)



**Figure S9**  $^{13}\text{C}$  NMR spectrum of  $\text{Rh}(\text{ttp})\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  ( $\text{CDCl}_3$ , 100MHz, 295K)



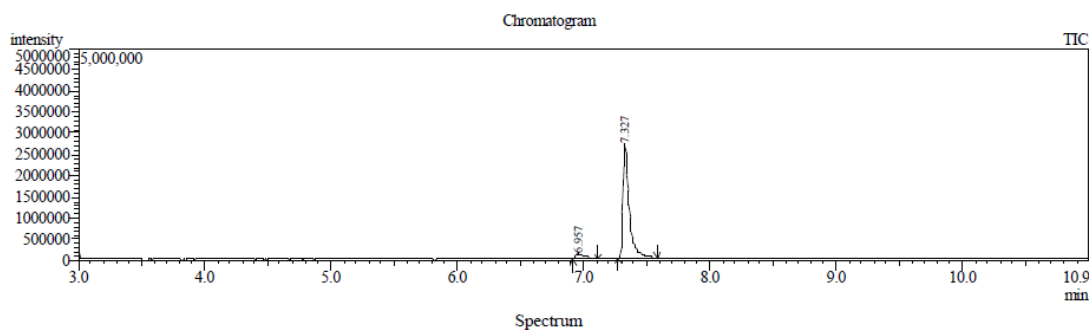


## 9. GC-MS Chromatogram Spectra.

**Figure S10** GC-MS Chromatogram Spectrum for *trans*-1,2-Diphenylcyclopropane (*trans*-**1f**) (*trans*-*cis* isomerization of **1f** occurred at high temperature in GC oven)

Quantitative Result Table

Name	ID#	R.Time	m/z	Area
cis-1,2-Diphenylcyclopropane	1	6.963	115.00	91749
trans-1,2-Diphenylcyclopropane	2	7.327	115.00	1267615

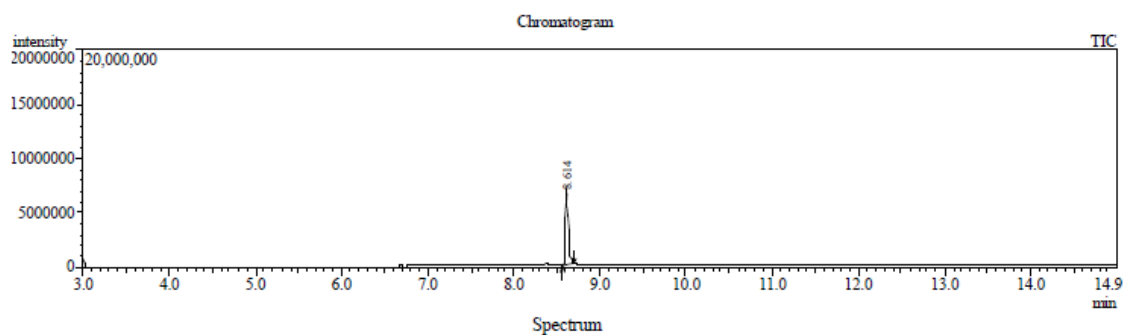


**Figure S11** GC-MS Chromatogram Spectrum of *trans*-1-Benzoyl-2-phenylcyclopropane (*trans*-**1g**)

Quantitative Result Table

Name	ID#	R.Time	m/z	Area
RT:8.617	1	8.614	105.00	5322280

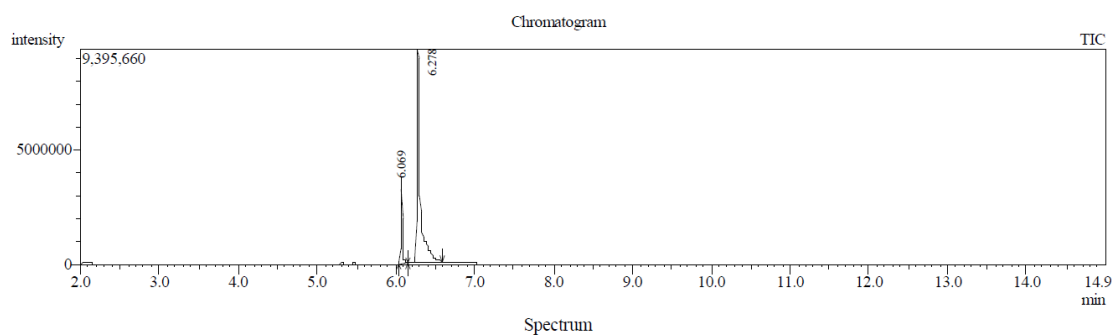
trans-1-benzoyl-2-phenylcyclopropane



**Figure S12** GC-MS Chromatogram Spectrum of 2-Phenyl-cyclopropanecarboxylic Acid Ethyl Ester (**1h**)

Quantitative Result Table

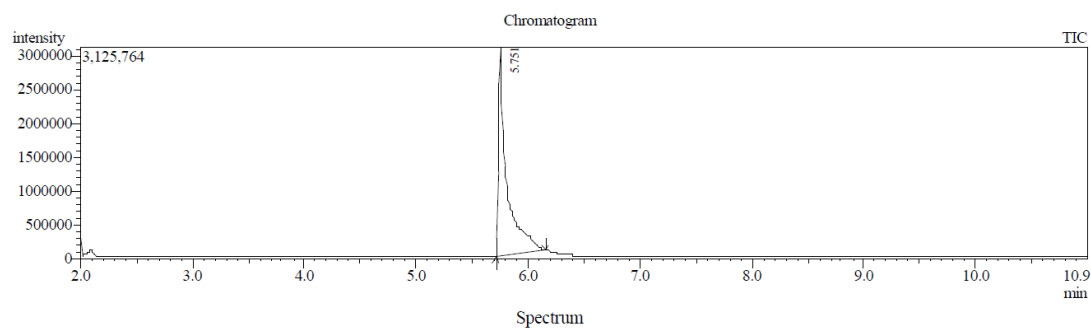
Name	ID#	R.Time	m/z	Area
cis-1-Carbethoxy-2-phenylcyclopropane	1	6.069	117.00	1572960
trans-1-Carbethoxy-2-phenylcyclopropane	2	6.278	117.00	6614208



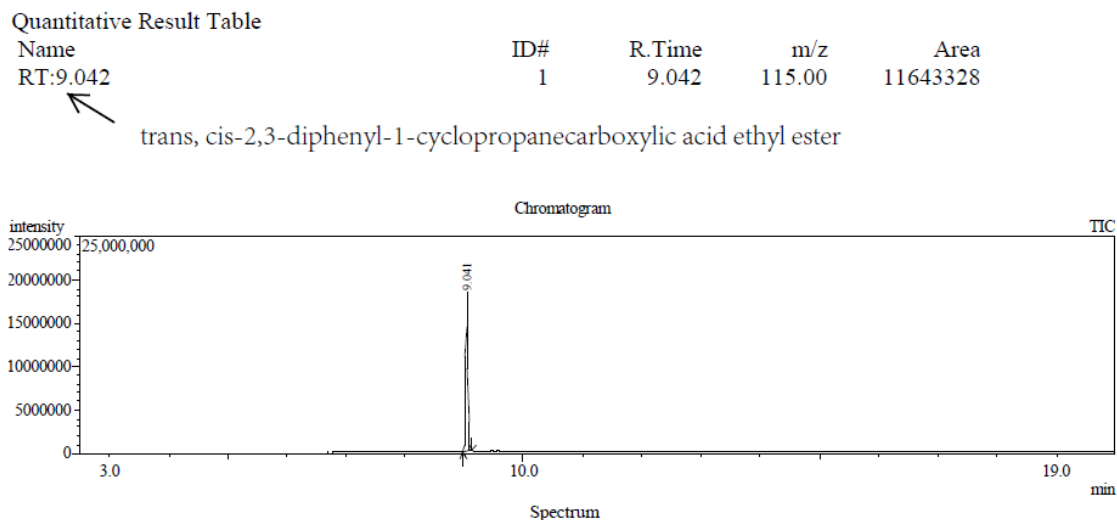
**Figure S13** GC-MS Chromatogram Spectrum of *trans*-2-Phenylcyclopropanecarbonitrile (*trans*-**1i**)

Quantitative Result Table

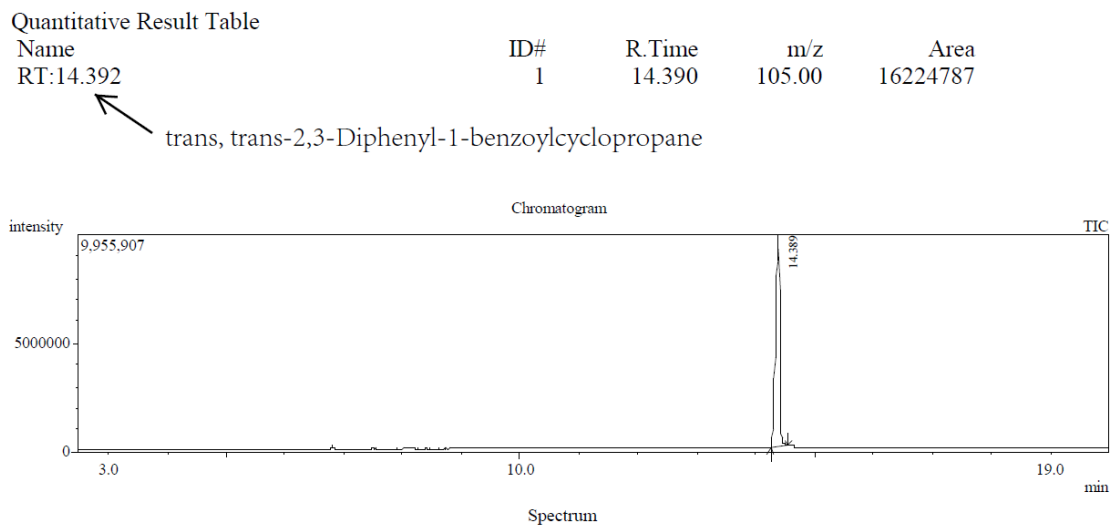
Name	ID#	R.Time	m/z	Area
Cyclopropanecarbonitrile, 2-phenyl-, trans-	1	5.751	115.00	3253753



**Figure S14** GC-MS Chromatogram Spectrum of *trans*, *cis*-2,3-Diphenyl-1-cyclopropanecarboxylic acid ethyl ester (**1j**)



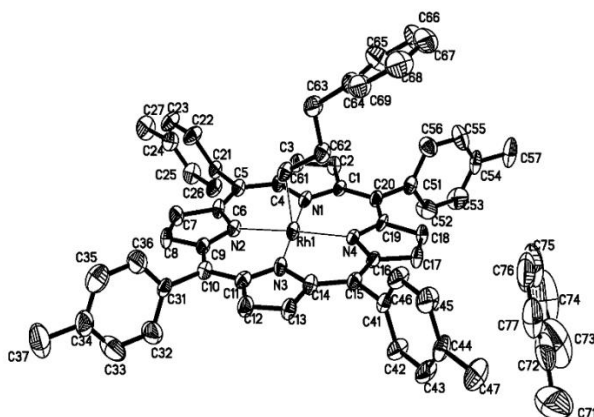
**Figure S15** GC-MS Chromatogram Spectrum of *trans*, *trans*-2,3-Diphenyl-1-benzoylcyclopropane (**1k**)



## 10. X-ray Data

X-ray Crystallographic Data and Structure of Rh(ttp)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph·PhCH<sub>3</sub>. Data were collected on a Bruker D8Venture diffractometer with a Mo K $\alpha$  microfocus source ( $\lambda = 0.71073$  Å) at 299 K, using phi scan mode with an increment of 0.5°. Unit cell parameters were obtained from 60 frames. The collected frames were integrated with the unit cell

parameters. Apex2 software was used for collecting frames of data, indexing reflections and determination of lattice constants; integration of intensity of reflections and scaling; and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.



**Figure S16** ORTEP presentation of the molecular structure with numbering scheme for Rh(ttp)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph·PhCH<sub>3</sub> with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Rh(ttp)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph·PhCH<sub>3</sub> selected bond length (Å): Rh(1)-N(4): 2.018(7); Rh(1)-C(61): 2.081(10); N(1)-C(1): 1.357(12); C(1)-C(20): 1.408(12); C(1)-C(2): 1.417(13). Bond angles (°): N(4)-Rh(1)-N(2): 176.8(3); N(4)-Rh(1)-N(3): 91.2(3); N(4)-Rh(1)-C(61): 97.3(4).

**Table S12** Crystal Data and Structure Refinement for Rh(ttp)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph·PhCH<sub>3</sub>

Compound	Rh(ttp)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph·PhCH <sub>3</sub>
Empirical formula	C <sub>64</sub> H <sub>55</sub> N <sub>4</sub> Rh
Formula weight	983.03
Temperature	299(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic
Unit cell dimensions	a = 11.288(2) Å α = 108.423(6)°. b = 13.288(3) Å β = 99.541(8)°. c = 20.809(5) Å γ = 99.110(6)°.
Volume	2845.2(11) Å <sup>3</sup>

Z, Calculated density	2, 1.147 Mg/m <sup>3</sup>
Absorption coefficient	0.340 mm <sup>-1</sup>
F(000)	1024
Crystal size	0.500 x 0.400 x 0.300 mm <sup>3</sup>
Theta range for data collection	2.207 to 25.247°.
Index ranges	-13<=h<=13, -15<=k<=15, -24<=l<=24
Reflections collected / Independent reflections	38133 / 10066 [R(int) = 0.0817]
Completeness to theta = 25.242 deg	97.6 %
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.4568
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	10066 / 7 / 622
Goodness-of-fit on F <sup>2</sup>	1.068
Final R indices [I>2sigma(I)]	R1 = 0.1288, wR2 = 0.3074
R indices (all data)	R1 = 0.1596, wR2 = 0.3195
Largest diff. peak and hole	1.622 and -2.588 e.Å <sup>-3</sup>