■ **Supporting Information**

# Prostereogenic Face and Orientational Selective Oxidative Coupling Reaction between Methyl Methacrylate and 2,5-Dihydrofuran Catalyzed by a Ruthenium(0) Compound

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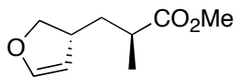
## Experimental

### General procedures

All manipulations were carried out under dry nitrogen using standard Schlenk and vacuum line techniques. Benzene, THF and pentane were dried over anhydrous calcium chloride and then distilled from sodium wire under nitrogen with benzophenone ketyl as an indicator. Methyl methacrylate (MMA) and MeCN was dried over calcium chloride and distilled over calcium hydride under nitrogen. Ru($\eta^6$-naphthalene)($\eta^4$-1,5-COD) (**1**) was prepared according to the literature method.[1] 2,5-dihydrofuran was dried over anhydrous $Na_2SO_4$ and purified by value-to-value distillation under reduced pressure. 2,2-Dimethyl-2,5-dihydrofuran was prepared according to the reported methods.[2] Other substituted olefins were degassed by freeze-pump-thaw cycles. Deuterated solvents for use in NMR experiments were purchased from Kanto Chemical and dried over sodium wire for $C_6D_6$, and was directly vacuum-transferred into an NMR tube. NMR spectra were recorded on a JEOL LA300, ECX400P or ECA600 spectrometers (300.4 MHz, 399.8 MHz, 596.5 MHz for $^1$H) with chemical shifts reported in ppm downfield from TMS for $^1$H and from 85% $H_3PO_4$ in $D_2O$ for $^{31}$P NMR. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer using KBr disks. GLC analysis was performed on a Shimadzu GC-14B with FID detector equipped with a capillary column (Inertcap-wax, 0.25 mmf x 30 m). GLC conditions: injector: 220 ˚C, detector 220 ˚C, Initial temp.: 50 ˚C, Initial time: 5 min, program rate: 10 ˚C/min, final temp.: 220 ˚C. GC-MS spectra were performed on a Shimadzu QP2010 equipped with a capillary column (TC-wax, 0.25 mmf x 30 m). The elemental analysis was performed by a Perkin-Elmer 2400 Series II CHN analyzer.

**Preparation and characterization of 2a and 2b.** MMA (270 μL, 2.54 mmol) and 2,5-dihydrofuran (950 μL, 12.6 mmol) were added into **1 (**42.0 mg, 0.124 mmol) in Schlenk tube by the valve-to-valve distillation under reduced pressure. The mixture was stirred at 30 ˚C for 24 hour. Products were determined quantity by GLC using $CHPh_3$ as initial standard. Then, all volatile matters were removed under reduced pressure. After quenching of the catalyst by exposure to air, silicagel column chromatography of the residue (Merck Kieselgel 60; hexane/ethyl acetate = 5/1) gave mixture of *rac*-(2*S*)-3-[(3*R*)-2,3-dihydrofuran-3-yl]-2-methylpropionate (**2a**) and methyl 3-(2,3-dihydrofuran-3-yl)-2-methylacrylate (**2b**) (**2a**/**2b** = 88/12, 203.0 mg, 47%) as a viscous colorless oil. Since **2a** and **2b** could not be separated, **2a** and **2b** were characterized by the spectroscopic mechod as shown in Fig. S1. **2a** is moderately air sensitive. In this reaction, the remaining 2,5-dihydrofuran was isomerized to 2,3-dihydrofuran.

**2a**: *rac*-(2*S*)-3-[(3*R*)-2,3-dihydrofuran-3-yl]-2-methylpropionate:



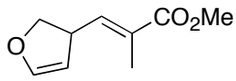
$^1$H NMR (400 MHz, r.t., $C_6D_6$): δ 0.95 (d, *J* = 6.9 Hz, 3H, *Me*), 1.18 (dt, *J* = 13.3, 6.6 Hz, 1H, C*H*$_2$), 1.74 (dt, *J* = 13.8, 6.4 Hz, 1H, C*H*$_2$), 2.23 (sext., *J* = 6.8 Hz, 1H, C*H*), 2.72 (t quint., *J* = 1.8, 7.8 Hz, 1H, C*H*), 3.30 (s, 3H, O*Me*), 3.74 (dd, *J* = 8.7, 6.9 Hz, 1H, OC*H*$_2$), 4.13 (t, *J* = 9.2 Hz, 1H, OC*H*$_2$), 4.67 (t, *J* = 2.7 Hz, 1H, =C*H*), 6.19 (t, *J* = 2.7 Hz, 1H, =C*H*).

$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $C_6D_6$): δ 17.38 (s, *Me*), 37.76 (s, *C*H$_2$), 39.93 (s, *C*H), 40.49 (s, *C*H), 51.04 (s, O*Me*), 74.99 (s, O*C*H$_2$), 103.79 (s, C=*C*H-C), 146.42 (C=*C*H-O), 176.13 (s, *C*=O).

GC-MS(EI): *m*/*z* = 170 (M$^+$), 155 (M$^+$-Me), 139 (M$^+$-OMe), 110 (M$^+$-HCO$_2$Me).

The elemental analysis was measured by use of a 87/13 mixture of **2a** and **2b**. Calcd for a 87/13 mixture of **2a** and **2b**: C, 63.61; H, 8.15. Found: 63.03; H, 7.68.

**2b**: methyl 3-(2,3-dihydrofuran-3-yl)-2-methylacrylate:



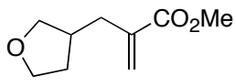
$^1$H NMR (400 MHz, r.t., $C_6D_6$): δ 1.69 (s, 3H, *Me*), 3.39 (s, 3H,O*Me*), 3.46 (m, 1H, C*H*), 3.73 (overlapped with **2a**, 1H, OC*H*$_2$), 4.03 (t, 9.6 Hz, 1H, OC*H*$_2$), 4.52 (m, 1H, =C*H*),6.16 (m, 1H, OC*H*=), 6.71 (d, *J* = 9.2 Hz, 1H, =C*H*).

$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $C_6D_6$): δ 12.63 (s, *Me*), 41.59 (s, *C*H), 51.32 (s, O*Me*), 74.44 (s, *C*H$_2$), 101.88 (s, =*C*H), 128.59 (s, =C), 142.84 (s, =*C*H), 147.44 (s, O*C*H=), 167.76 (s, *C*=O).

GC-MS(EI): *m*/*z* = 168 (M$^+$), 153 (M$^+$-Me), 136 (M$^+$-MeOH), 109 (M$^+$-CO$_2$Me).

**Preparation and characterization of 2c and *E*-2d and *Z*-2d.** MMA (65 μL, 0.61 mmol), 2,5-dihydrofuran (230 μL, 3.05 mmol) and MeCN 1 ml were heated at 30 ˚C for 4 h in the presence of **1** (10.1 mg, 0.0299 mmol) to give a mixture of products. Then, all volatile matters were removed under reduced pressure. After quenching of the catalyst by exposure to air, silicagel column chromatography of the residue (Merck Kieselgel 60; pentane/diethyl ether = 5/1 then 1/1) gave a mixture of **2a** and **2b** (**2a**/**2b** = 94/6, 10.4 mg, 10%) as a viscous colorless oil and mixture of methyl 2-(tetrahydrofuran-3-ylmethyl)acrylate (**2c**) and *E*- and *Z*- methyl 2-methyl-3-(tetrahydrofuran-3-yl)acrylate (**2d**) (**2c**/*E*-**2d**/*Z*-**2d** = 14/78/8, 32.8 mg, 32%) as a viscous colorless oil. The stereochemistry of **2d** was estimated by the isomerization from *Z*-**2d** to *E*-**2d** was confirmed by use of GLC analysis. Since **2c** and **2d** could not be separated, **2c** and **2d** were characterized spectroscopically as shown in Fig. S2-S5.

**2c**: methyl 2-(tetrahydrofuran-3-ylmethyl)acrylate:

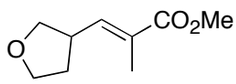



$^1$H NMR (400 MHz, r.t., $C_6D_6$): δ 1.20 (overlapped with *E*-**2d**, 1H, C$H_2$), 1.60 (overlapped with *E*-**2d**, 1H, C$H_2$), 2.21 (d, *J* = 7.8 Hz, 2H, C$H_2$), 2.25 (m, 1H, C*H*), 3.31 (m, 1H, OC$H_2$CH), 3.36 (s, 3H, O*Me*), 3.48 (overlapped with **2d**, 1H, OC$H_2$CH$_2$), 3.68 (overlapped with *E*-**2d**, 1H, OC$H_2$CH$_2$), 3.70 (overlapped with *E*-**2d**, 1H, OC$H_2$CH), 5.13 (s, 1H, =C$H_2$), 6.09 (s, 1H, =C$H_2$).

$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $C_6D_6$): δ 32.1 (s, *C*H$_2$), 36.0 (s, =C*C*H), 38.0 (s, *C*H), 50.9 (s, O*Me*), 67.5 (s, O*C*H$_2$CH$_2$), 72.8 (s, O*C*H$_2$CH), 125.4 (s, =*C*H$_2$), 139.8 (s, =C), 167.0 (s, *C*=O).

GC-MS(EI): *m*/*z* = 171 (M+H$^+$), 155 (M$^+$-Me), 140 (M$^+$-MeOH), 110 (M$^+$-HCO$_2$Me).

*E*-**2d**: methyl (*E*)-2-methyl-3-(tetrahydrofuran-3-yl)acrylate:

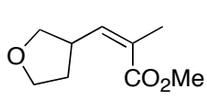



$^1$H NMR (400 MHz, r.t., $C_6D_6$): δ 1.24 (dq, *J* = 11.9, 7.8 Hz, 1H, C$H_2$), 1.58 (ddt, *J* = 12.4, 7.3, 5.0 Hz, 1H, C$H_2$), 1.74 (d, *J* = 1.4 Hz, 3H, *Me*), 2.67 (dqui, *J* = 9.3, 7.3 Hz, 1H, C*H*), 3.25 (t, *J* = 8.2 Hz, 1H, OC$H_2$CH), 3.42 (s, 3H, O*Me*), 3.51 (q, *J* = 7.8 Hz, 1H, OC$H_2$CH$_2$), 3.62 (q, *J* = 8.2 Hz, 1H, OC$H_2$CH$_2$), 3.68 (t, *J* = 7.3 Hz, 1H, OC$H_2$CH), 6.71 (dq, *J* = 10.1, 1.4 Hz, 1H, =C*H*).

$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $C_6D_6$): δ 12.7 (s, *Me*), 32.9 (s, *C*H$_2$), 39.0 (s, *C*H), 51.3 (s, O*Me*), 67.9 (s, O*C*H$_2$CH$_2$), 72.4 (s, O*C*H$_2$CH), 128.4 (s, =*C*), 142.9 (s, =*C*H), 167.8 (s, *C*=O).

GC-MS(EI): *m*/*z* = 170 (M$^+$), 155 (M$^+$-Me), 140 (M$^+$-MeOH).

*Z*-**2d**: methyl (*Z*)-2-methyl-3-(tetrahydrofuran-3-yl)acrylate:



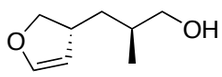

$^1$H NMR (400 MHz, r.t., $C_6D_6$): δ 1.32 (dq, *J* = 11.9, 7.8 Hz, 1H, C$H_2$), 1.78 (s, 3H, *Me*), 1.88 (m, 1H, C$H_2$), 3.36 (overlapped with **2c**, OC$H_2$CH), 3.42 (s, 3H, O*Me*), 3.60 (overlapped with *E*-**2d**, 1H, OC$H_2$CH$_2$), 3.71 (overlapped with *E*-**2d**, 1H, OC$H_2$CH$_2$), 3.84 (m, 1H, C*H*), 3.96 (t, *J* = 7.8 Hz, 1H, OC$H_2$CH), 5.55 (d, *J* = 9.6 Hz, 1H, =C*H*).

$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $C_6D_6$): δ 20.7 (s, *Me*), 33.8 (s, *C*H$_2$), 39.6 (s, *C*H), 51.3 (s, O*Me*), 68.4 (s, O*C*H$_2$CH$_2$), 73.2 (s, O*C*H$_2$CH), 128.7 (s, =*C*), 144.4 (s, =*C*H), 167.6 (s, *C*=O).

GC-MS(EI): *m*/*z* = 170 (M$^+$), 155 (M$^+$-Me), 140 (M$^+$-MeOH).

**Preparation of 2aa.** Into a 25mL-Schlenk tube were added the cross dimer **2a** (120.4 mg, 0.7074 mmol **2a**: 78% purity) and 10 mL THF. The solution was cooled to –78 ˚C and DIBAL (0.77 M in hexanes, 3.8 mL, 2.91 mmol) was added dropwise by a hypodermic syringe. The solution was stirred for 2.5 h and quenched by the dropwise addition of methanol (1 mL). After the solution was allowed to rise to the room temperature, 6mL of saturated $KNaC_4H_4O_6$ was added dropwisely by a pipette. After 30 min, the mixture was poured into ethyl acetate and brine. The layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers ware dried over $Na_2SO_4$. Evaporation of the solvent provided 3-(2,3-Dihydro-furan-3-yl)-2-methyl-propan-1-ol (**2a**) (97.7 mg, 0.687 mmol 100%(crude)) as a viscous colorless oil.

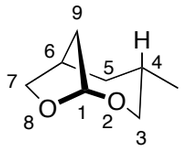
**2aa**: 3-(2,3-Dihydro-furan-3-yl)-2-methyl-propan-1-ol:




$^1$H NMR (400 MHz, r.t., $C_6D_6$): δ 0.72 (d, *J* = 6.4 Hz, 3H, C*Me*), 0.91 (m, 2H, C$H_2$, -O*H*), 1.36 (m, 2H, C$H_2$, C*H*), 2.76 (m, 1H, C*H*), 3.07 (dd, *J* = 6.0, 10.1 Hz, 1H, C$H_2$), 3.12 (dd, *J* = 6.0, 10.1 Hz, 1H, C$H_2$), 3.77 (dd, *J* = 6.4, 8.7 Hz, 1H, OC$H_2$), 4.17 (t, *J* = 9.6 Hz, 1H, OC$H_2$), 4.78 (t, *J* = 2.3 Hz, 1H, OCH=C*H*), 6.25 (t, *J* = 2.2 Hz, 1H, OC*H*=CH).
$^{13}$C{$^1$H} NMR (75.45 MHz, r.t., $C_6D_6$): δ 16.7 (s, *Me*), 34.1 (s, *C*H), 39.7 (s, *C*$H_2$), 40.1 (s, *C*H), 67.9 (s, O*C*$H_2$), 75.7 (s, O*C*$H_2$), 104.3 (s, =*C*H), 146.1 (s, O*C*H=).
GC-MS(EI): *m*/*z* = 142 ($M^+$), 127 ($M^+$-Me), 124 ($M^+$-$H_2O$).

**Preparation of 2ab.** Into a 25mL-Schlenk tube were added compound **2aa** (51.0 mg, 0.359 mmol), $[PtCl_2(H_2C{=}CH_2)]_2$ (5.0 mg, 0.0085 mmol), $PPh_3$ (4.7 mg, 0.018 mmol) and $C_2H_2Cl_4$ (200 μL). The solution was heated to 70 ˚C and stirred for 3.5 h. After quenching of the catalyst by exposure to air, silicagel column chromatography of the residue (Merck Kieselgel 60, pentane/diethyl ether = 10/1 then finally 1/1) gave *rac*-(1*R*,4*S*,6*R*)-4-methyl-2,8-dioxabicyclo[4.2.1]nonane (**2ab**) (8.4 mg, 0.059 mmol 16%) as a viscous colorless oil. Its stereochemistry was characterized by pNOESY and difference NOE NMR spectra. (See Fig. S6-S11.)

**2ab**: *rac*-(1*R*,4*S*,6*R*)-4-methyl-2,8-dioxa-bicyclo[4.2.1]nonane:

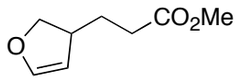



$^1$H NMR (400 MHz, r.t., $C_6D_6$): δ 0.57 (d, *J* = 6.9 Hz, 3H, *Me*), 0.69 (dd, *J* = 14.2, 11.0 Hz, 1H, 5-C$H_b$), 1.43 (ddd, *J* = 12.8, 7.3, 5.0 Hz, 1H, 9-C$H_a$), 1.50 (ddd, *J* = 14.2, 7.3, 6.0 Hz,1H, 5-C$H_a$), 1.70 (d, *J* = 12.8 Hz, 1H, 9-C$H_b$), 1.62-1.76 (m, overlapped, 1H, 4-C*H*),

1.85 (q, $J$ = 7.3 Hz, 1H, 6-C*H*), 3.45 (m, 2H, 3-C*H*), 3.61 (d, $J$ = 8.2 Hz, 1H, 7-C$H_b$), 3.76 (t, $J$ = 7.8 Hz, 1H, 7-C$H_a$), 5.58 (d, $J$ = 5.0 Hz, 1H, 1-C*H*).
$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $C_6D_6$): δ 19.08 (s, *Me*), 34.23 (s, 6-*C*H), 34.46 (s, 4-*C*H), 36.97 (s, 9-*C*$H_2$), 40.73 (s, 5-*C*$H_2$), 67.83 (3-*C*$H_2$), 79.52 (7-*C*$H_2$), 102.25 (1-*C*H).
GC-MS(EI): $m/z$ = 142 ($M^+$).

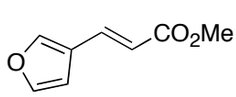
**Preparation and characterization of 3a and 3e.** Methyl acrylate (MA) (230 μL, 2.56 mmol) and 2,5-dihydrofuran (950 μL, 12.6 mmol) were added into **1** (42.5 mg, 0.126 mmol) in Schlenk tube by the valve-to-valve distillation under reduced pressure. The mixture was stirred at 30 ˚C for 24 hours. Products were determined quantity by GLC using $CHPh_3$ as an initial standard. Then, all volatile matters were removed under reduced pressure. After quenching of the catalyst by exposure to air, silicagel column chromatography of the residue (Merck, Kieselgel 60, hexane/ethyl acetate = 10/1 then finally 2/1) gave a mixture of methyl 3-(2,3-dihydrofuran-3-yl)propionate (**3a**) and methyl (*E*)-3-furan-3-yl-acrylate (**3e**) (**3a**/**3e** = 72/28, 36.7 mg, 9%) as a viscous colorless oil. Since **3a** and **3e** could not be separated each other, **3a** and **3e** were characterized by the spectroscopic method as shown in Fig. S12. In this reaction, dimethyl (*E*)-2-hexenedioate (**3f**), a tail-to-tail dimer of MA, was also obtained as a side product (16% yield).

**3a**: methyl 3-(2,3-dihydrofuran-3-yl)propionate:




$^1$H NMR (400 MHz, r.t., $CDCl_3$): δ 1.71 (dq, $J$ = 7.3, 3.2 Hz, 2H, C$H_2$), 2.30 (t, $J$ = 7,8 Hz, 2H, C$H_2$), 2.95 (m, 1H, C*H*), 3.64 (s, 3H, O*Me*), 3.94 (dd, $J$ = 8.7, 6.0 Hz, 1H, OC$H_2$), 4.32 (t, $J$ = 9.2 Hz, 1H, OC$H_2$), 4.91 (t, $J$ = 2.8 Hz, 1H, =C*H*), 6.31 (t, $J$ = 2.3 Hz, 1H, OC*H*=).
$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $CDCl_3$): δ 30.19 (s, *C*$H_2$), 31.32 (s, *C*$H_2$), 41.22 (s, *C*H), 51.54 (s, O*Me*), 74.59 (s, O*C*$H_2$), 103.30 (s, =*C*H), 146.13 (s, O*C*H=), 173.75 (s, *C*=O).
GC-MS(EI): $m/z$ = 156 ($M^+$), 141 ($M^+$-Me), 125 ($M^+$-OMe), 96 ($M^+$-$HCO_2Me$).

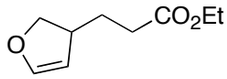
**3e**: methyl (*E*)-3-furan-3-yl-acrylate:




$^1$H NMR (400 MHz, r.t., $CDCl_3$): δ 3.75 (s, 3H, O*Me*), 6.14 (d, $J$ = 15.6 Hz, 1H, =C*H*), 6.57 (s, 1H, =C*H*), 7.41 (s, 1H, OC*H*=), 7.56 (d, $J$ = 16.0 Hz, 1H, =C*H*), 7.63 (s, 1H, OC*H*=).
$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $CDCl_3$): δ 51.54 (s, O*Me*), 107.31 (s, =*C*H), 117.40 (s, =*C*H), 122.48 (s, =*C*), 134.76 (s, =*C*H), 144.34 (s, O*C*H=), 144.60 (s, O*C*H=), 167.35 (s, *C*=O).
GC-MS(EI): $m/z$ = 152 ($M^+$), 121 ($M^+$-MeOH), 93 ($M^+$-$CO_2Me$).

**Preparation and characterization of 4a and 4e.** Ethyl acrylate (EA) (280 μL, 2.58 mmol) and 2,5-dihydrofuran (950 μL, 12.6 mmol) were added into **1** (42.2 mg, 0.125 mmol) in a Schlenk tube by the valve-to-valve distillation under reduced pressure. The mixture was stirred at 30 ˚C for 24 hours. The formation of the products was monitored by GLC using $CHPh_3$ as an initial standard. Then, all volatile matters were removed under reduced pressure. After quenching of the catalyst by exposure to air, silicagel column chromatography of the residue (Merck Kieselgel 60, hexane/ethyl acetate = 10/1 then finally 2/1) gave mixture of ethyl 3-(2,3-dihydrofuran-3-yl)propionate (**4a**) and ethyl (*E*)-3-furan-3-yl-acrylate (**4e**) (**4a**/**4e** = 81/19, 51.8 mg, 12%) as a viscous colorless oil. Since **4a** and **4e** could not be separated each other, **4a** and **4e** were characterized spectroscopically as shown in Fig. S13. In this reaction, diethyl (*E*)-2-hexenedioate (**4f**), a tail-to-tail dimer of EA was also formed as a side product (20% yield).

**4a**: ethyl 3-(2,3-dihydrofuran-3-yl)propionate:

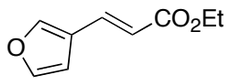



$^1$H NMR (400 MHz, r.t., $CDCl_3$): δ 1.24 (t, *J* = 6.9 Hz, 3H, *Me*), 1.72 (q, *J* = 7,8 Hz, 1H, C*H*$_2$), 1.73(q, *J* = 7.8 Hz, 1H, C*H*$_2$), 2.29 (t, *J* = 8.2 Hz, 2H, C*H*$_2$), 2.97 (m, 1H, C*H*), 3.95 (dd, *J* = 9.2, 7.6 Hz, 1H, OC*H*$_2$), 4.11(q, *J* = 7.3 Hz, 2H, OC*H*$_2$), 4.33 (t, *J* = 9.6 Hz, 1H, OC*H*$_2$), 4.92 (t, *J* = 2.3 Hz, 1H, =C*H*), 6.32 (t, *J* = 2.3 Hz, 1H, OC*H*=).

$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $CDCl_3$): δ 14.2 (s, *Me*), 30.3 (s, *C*H$_2$), 31.7 (s, *C*H$_2$), 41.3 (s, *C*H), 60.4 (s, O*C*H$_2$), 74.7 (s, O*C*H$_2$), 103.4 (s, =*C*H), 146.1 (s, O*C*H=), 173.4 (s, *C*=O).

GC-MS(EI): *m*/*z* = 170 ($M^+$), 125 ($M^+$-OEt), 96 ($M^+$-$HCO_2Et$).

**4e**: ethyl (*E*)-3-furan-3-yl-acrylate:




$^1$H NMR (400 MHz, r.t., $CDCl_3$): δ 1.30 (t, *J* = 6.9 Hz, 3H), 4.22 (q, *J* = 7.3 Hz, 2H), 6.14 (d, *J* = 16.0 Hz, 1H), 6.58 (brs, 1H), 7.41 (brs, 1H), 7.56 (d, *J* = 16.0 Hz, 1H), 7.64 (brs, 1H)

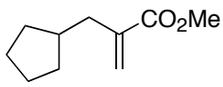
$^{13}$C{$^1$H} NMR (100.53 MHz, r.t., $CDCl_3$): δ 14.3, 60.4, 107.4, 117.9, 122.6, 134.5, 144.3, 144.4, 167.0.

GC-MS(EI): *m*/*z* = 166 ($M^+$), 151 ($M^+$-Me), 121 ($M^+$-OEt), 93 ($M^+$-$CO_2Et$)

**Preparation and characterization of 5c and 5d.** MMA (270 μL, 2.54 mmol) and cyclopentene (1110 μL, 12.58 mmol) were added into **1** (42.4 mg, 0.126 mmol) in a Schlenk tube by the valve-to-valve distillation under reduced pressure. The mixture was stirred at 30 ˚C for 4 hours. Then all volatile matters were removed under reduced pressure. After quenching of the catalyst by exposure to air, silicagel column chromatography of the residue (Meck, Kieselgel60, pentane/diethyl ether = 1:0 then finally

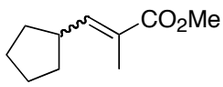
2:1) gave an *E* and *Z* mixture of methyl 2-cyclopentylmethylacrylate (**5c**) and methyl 3-cyclopentyl-2-methylacrylate (**5d**) (**5c**/**5d** = 93/7, 25.0 mg, 6%) as a viscous colorless oil. Since **5c** and **5d** could not be separated each other, **5c** and **5d** were characterized spectroscopically as shown in Fig. S14. In this reaction, the tail-to-tail dimer of MMA was produced as a dominant side product (50% yield).

**5c**: methyl 2-cyclopentylmethylacrylate:



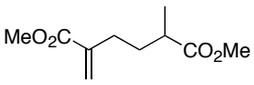

$^{1}$H NMR (400 MHz, r.t., $CDCl_3$): δ 1.11 (m, 2H, C*H*$_2$), 1.50 (m, 2H, C*H*$_2$), 1.59(m, 2H, C*H*$_2$), 1.70(m, 2H, C*H*$_2$), 2.01 (septet, *J* = 7.8 Hz, 1H, C*H*), 2.29 (d, *J* = 7.3 Hz, 2H, C*H*$_2$), 3.73 (s, 3H, OMe), 5.51 (d, *J* = 1.4 Hz, 1H, =C*H*$_2$), 6.1 (d, *J* = 1.4 Hz, 1H, =C*H*$_2$).
$^{13}$C{$^{1}$H} NMR (100.53 MHz, r.t., $CDCl_3$): δ 24.9 (s, *C*H$_2$), 32.3 (s, *C*H$_2$), 38.1 (s, *C*H$_2$), 38.5 (s, *C*H), 51.7 (s, O*Me*), 125.1 (s, =*C*H$_2$), 140.2 (s, *C*=), 168.0 (s, *C*=O).
GC-MS(EI): *m*/*z* = 168 ($M^+$), 153 ($M^+$-Me), 137 ($M^+$-OMe), 100 ($M^+$-$C_5H_8$(cyclopentene)).

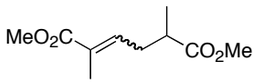
*E*- or *Z*-**5d**: methyl 3-cyclopentylmethacrylate:

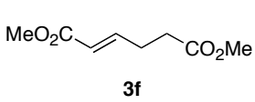



$^{1}$H NMR (400 MHz, r.t., $CDCl_3$): δ 1.85 (s, 3H, *Me*), 3.72 (s, 3H, O*Me*) , 6.68 (d, *J* = 9.6 Hz 1H, =C*H*) other peaks were overlapped with **5c**.
GC-MS(EI): *m*/*z* = 168 ($M^+$), 153 ($M^+$-Me), 137 ($M^+$-OMe), 108 ($M^+$-$HCO_2Me$), 101 ($M^+$-$C_5H_7$(cyclopentene-H)).

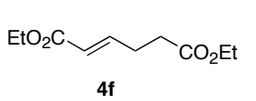
**Characterization of acrylate dimers**




**3f**




**4f**

The tail-to-tail dimers of MMA and MA were characterized by comparison with previous data.[3] The EA dimer (diethyl (*E*)-2-hexenedioate (**4f**)) was characterized by GC-MS and $^{1}$H NMR spectra.
**4f**: $^{1}$H NMR (400 MHz, r.t., $CDCl_3$): δ 1.24 (t, *J* = 6.8 Hz, 3H), 1.26 (t, *J* = 6.8 Hz, 3H), 2.43-2.55(m, 4H), 4.13(q, *J* = 7.3 Hz, 2H) , 4.16(q, *J* = 7.3 Hz, 2H), 5.83(dt, *J* = 15.6, 1.4 Hz, 1H) , 6.93(dt, *J* = 15.6, 6.4 Hz, 1H).
GC-MS(EI): *m*/*z* = 201 (M+$H^+$), 171 ($M^+$-Et), 154 ($M^+$-EtOH), 171 ($M^+$-Et), 126 ($M^+$-$HCO_2Et$).

**Appendix.**

**Cross dimerization between MMA and 2,5-dihydrofuran catalyzed by Ru(1,5-COD)(1,3,5-COT).** MMA (270 μL, 2.54 mmol) and 2,5-dihydrofuran (950 μL, 12.6 mmol) were added into Ru(1,5-COD)(1,3,5-COT) (39.8 mg, 0.126 mmol) in a Schlenk tube by the valve-to-valve distillation under reduced pressure. The mixture was stirred at 30 ˚C for 24 hour. Products were determined quantity by GLC using biphenyl at initial standard.

**The reaction of 2,5-dihydrofuran catalyzed by 1**

2,5-dihydrofuran (760 μL, 10.1 mmol) was added into **1** (34.2 mg, 0.101 mmol) in Schlenk tube by the valve-to-valve distillation under reduced pressure. The mixture was stirred at 30 ˚C for 24 hour. 2,5-dihydrofuran was isomerized to 2,3-dihydrofuran(96%). By the GLC analysis, a dimer of 2,5-dihydrofuran was not observed.

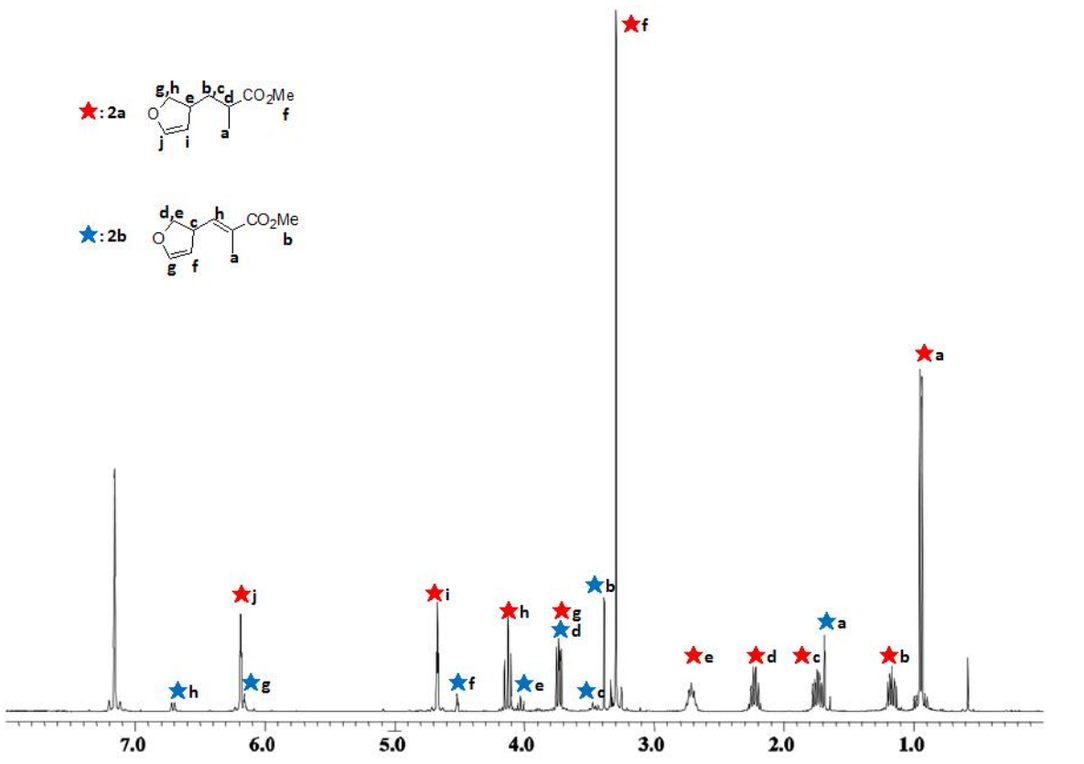



**Figure S1.** $^{1}$H NMR spectrum for a mixture of **2a** and **2b** (**2a**/**2b** = 88/12) (400 MHz, benzene-$d_6$).

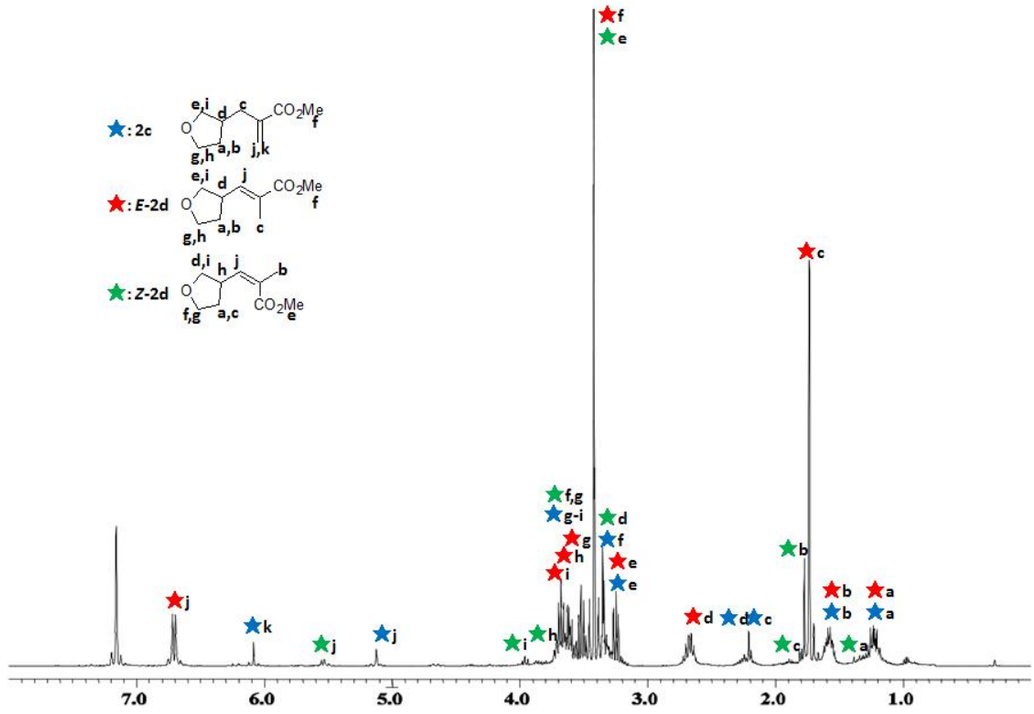



**Figure S2.** $^{1}$H NMR spectrum for a mixture of **2c** and **2d** (**2c**/*E*-**2d**/*Z*-**2d** = 14/78/8) (400 MHz, benzene-$d_6$).

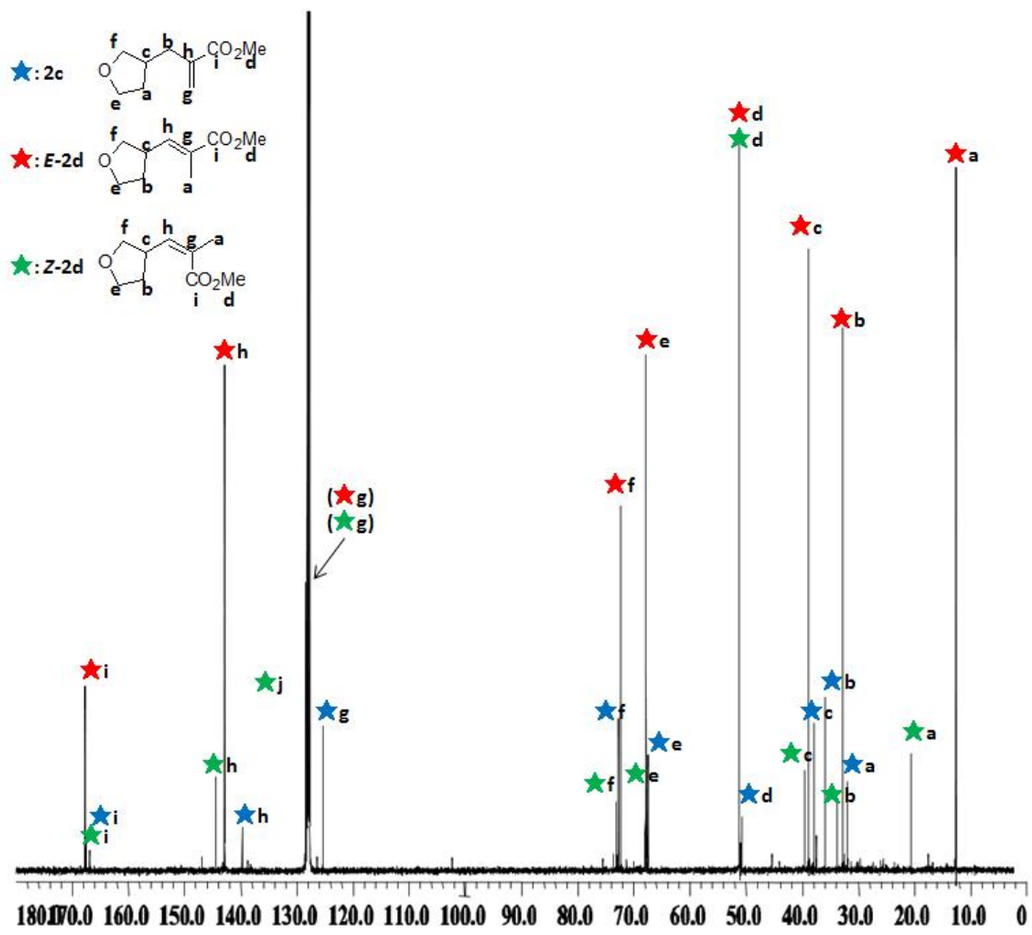



**Figure S3.** $^{13}C\{^{1}H\}$ NMR spectrum for a mixture of **2c** and **2d** (**2c**/*E*-**2d**/*Z*-**2d** = 14/78/8) (100.53 MHz, benzene-$d_6$).

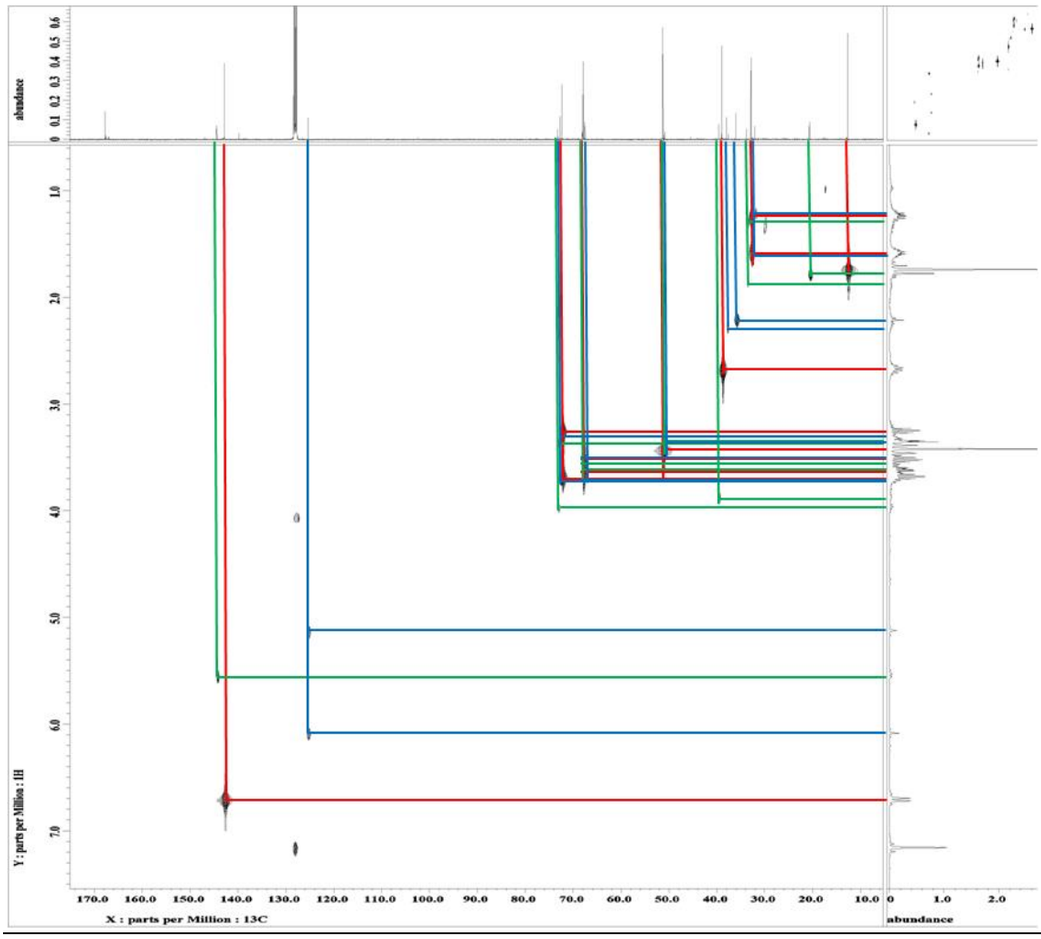



**Figure S4.** C–H Hetero-correlation spectrum for a mixture of **2c** and **2d** (**2c**/*E*-**2d**/*Z*-**2d** = 14/78/8) (100.53 MHz, benzene-$d_6$).

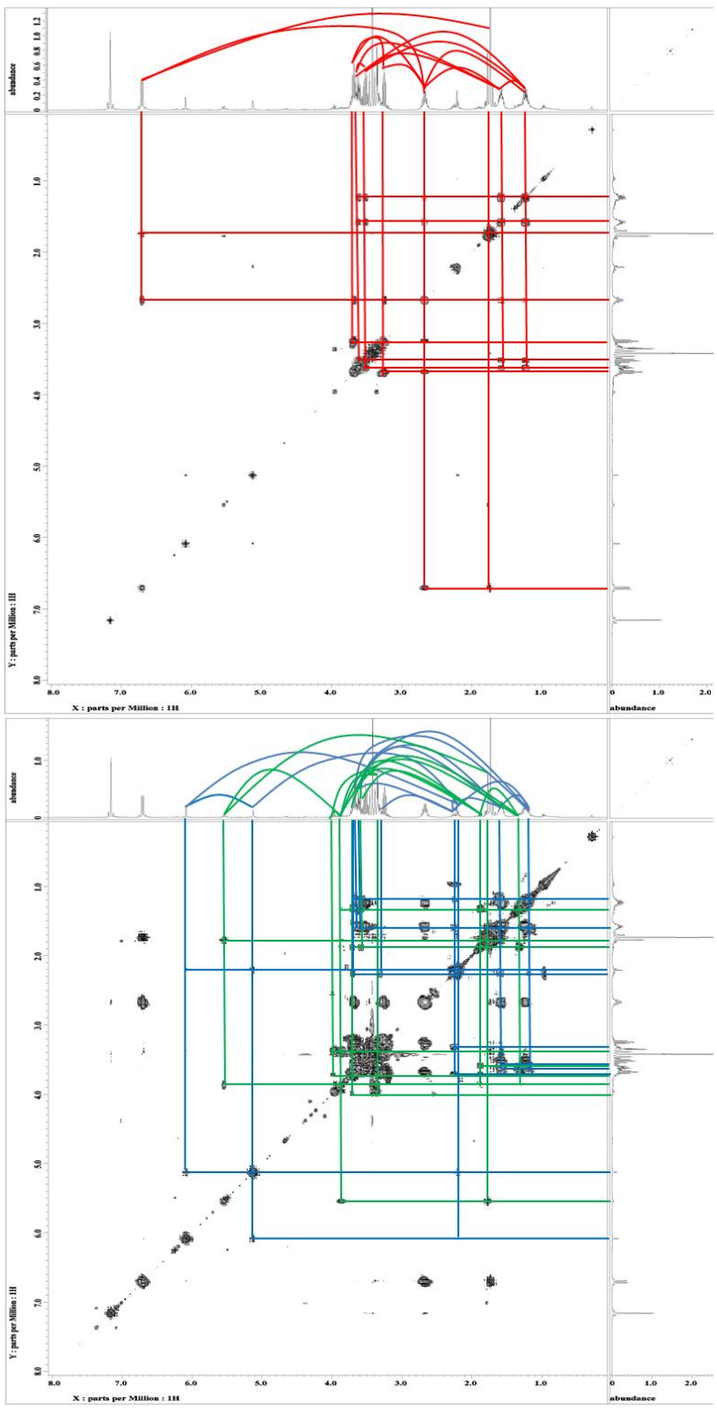



**Figure S5.** H-H COSY for a mixture of **2c** and **2d** (**2c**/*E*-**2d**/*Z*-**2d** = 14/78/8) (400 MHz, benzene-$d_6$).

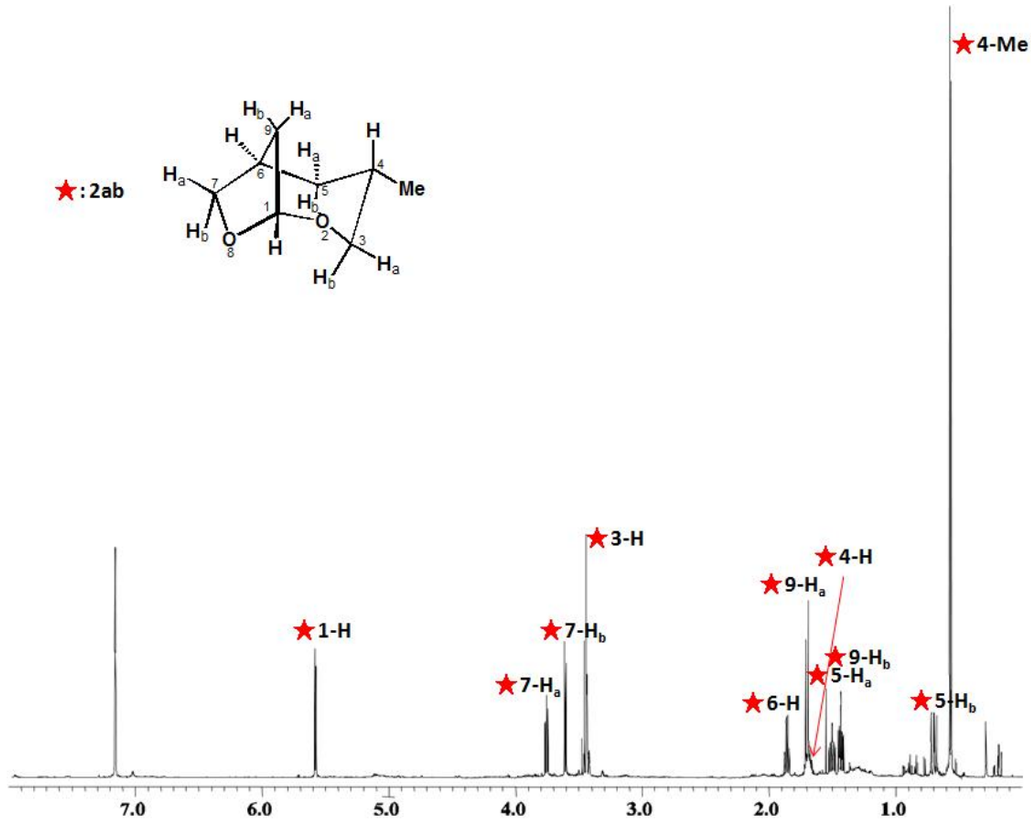



**Figure S6.** $^{1}$H NMR spectrum of **2ab** (600 MHz, benzene-$d_6$).

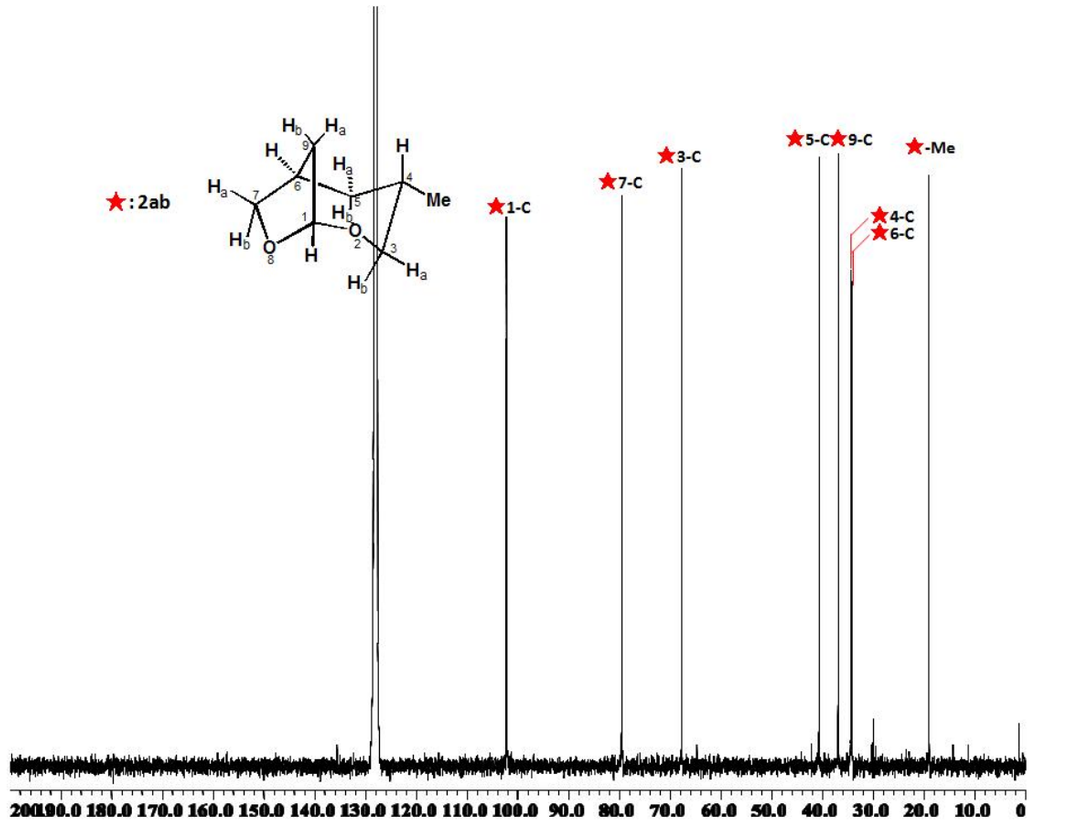



**Figure S7.** $^{13}C\{^{1}H\}$ NMR spectrum of **2ab** (100.53 MHz, benzene-$d_6$).

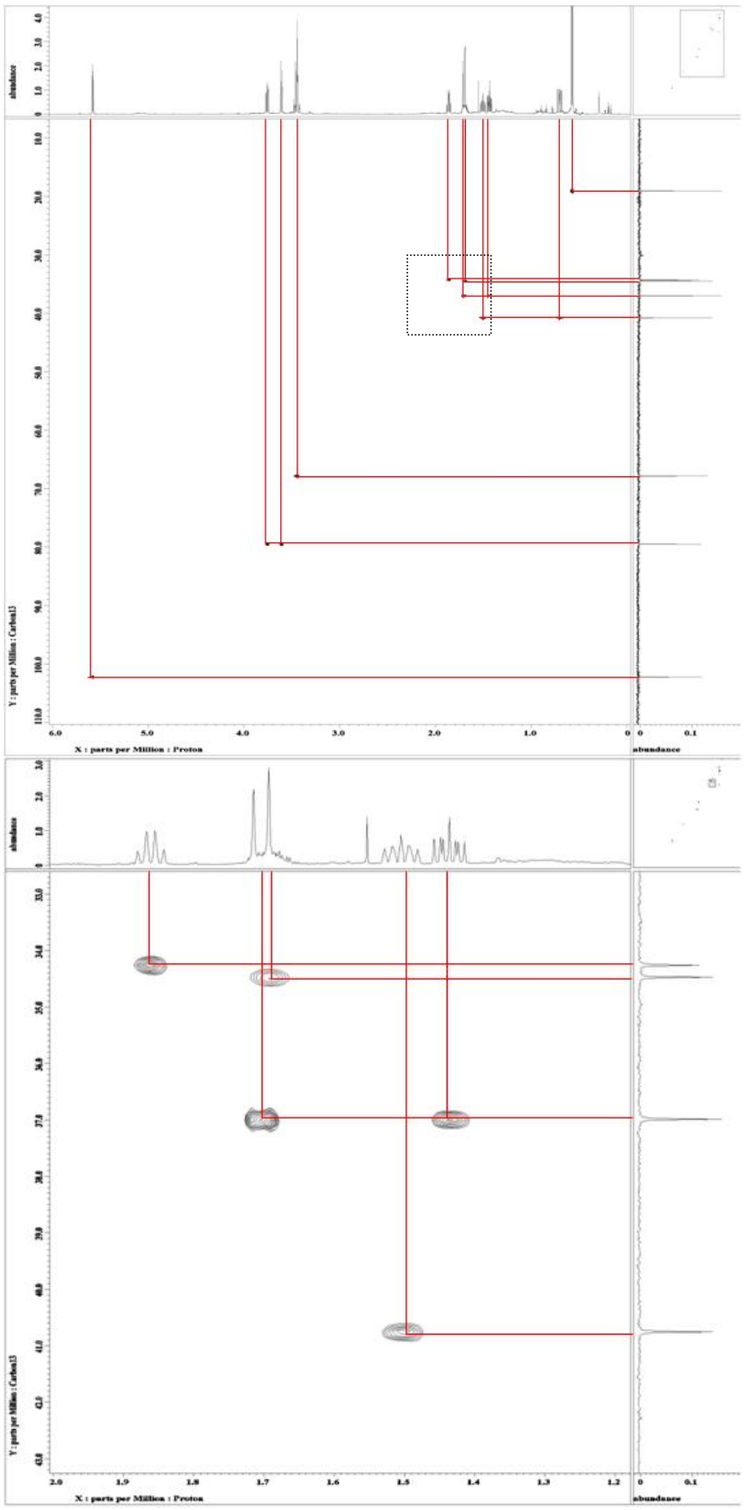


**Figure S8.** C–H Hetero-correlation spectrum of **2ab** (600 MHz, benzene-$d_6$).

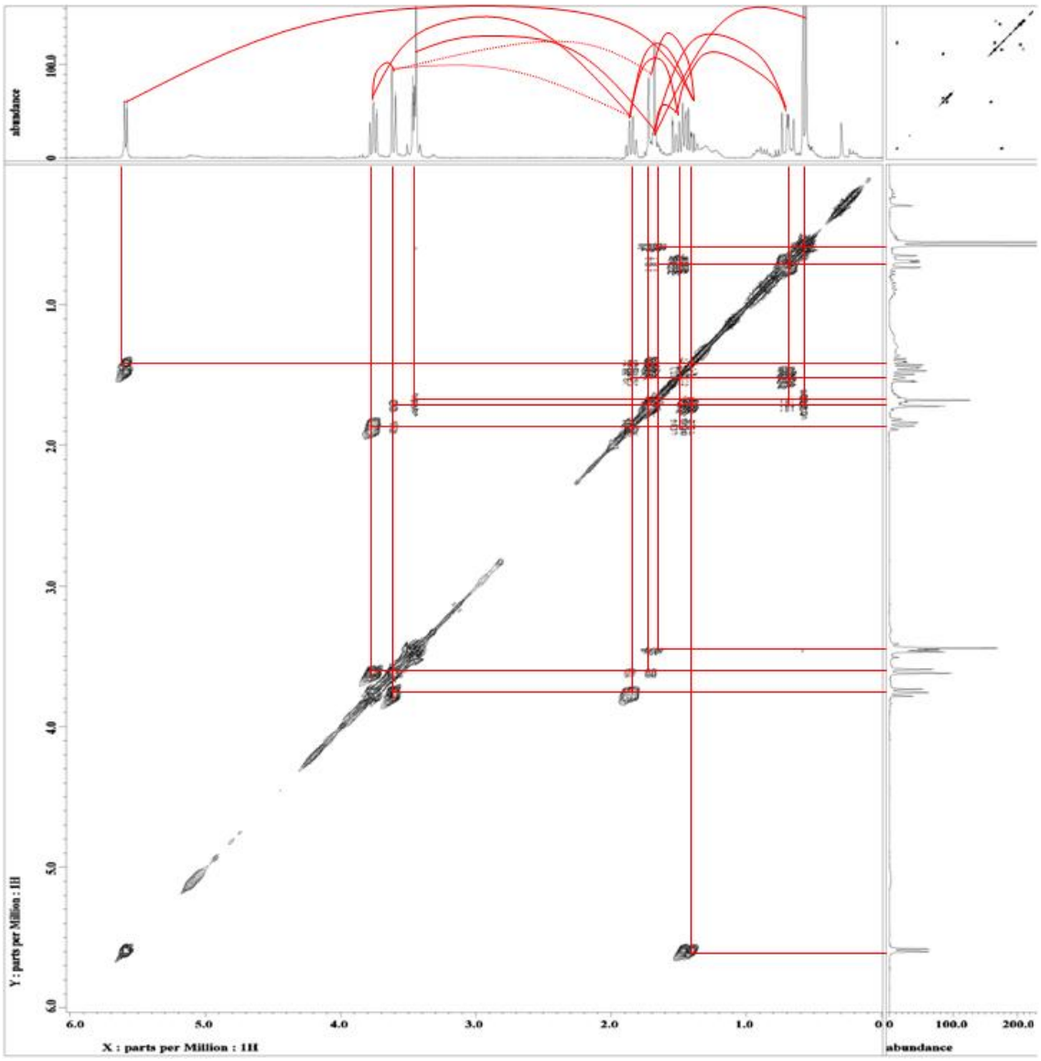



**Figure S9.** H–H COSY of **2ab** (300 MHz, benzene-$d_6$).

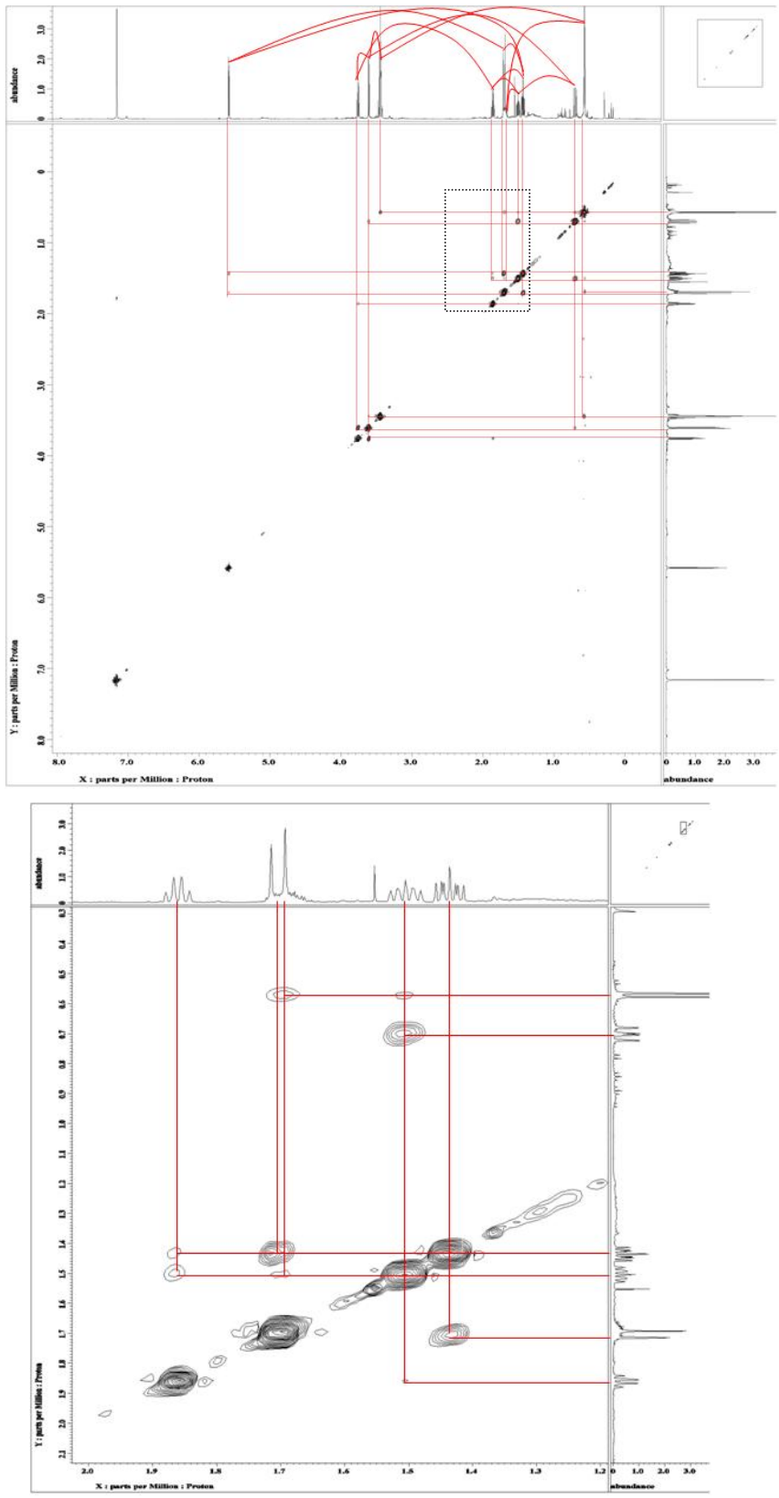



**Figure S10.** pNOESY NMR spectrum of **2ab** (600 MHz, benzene-$d_6$).

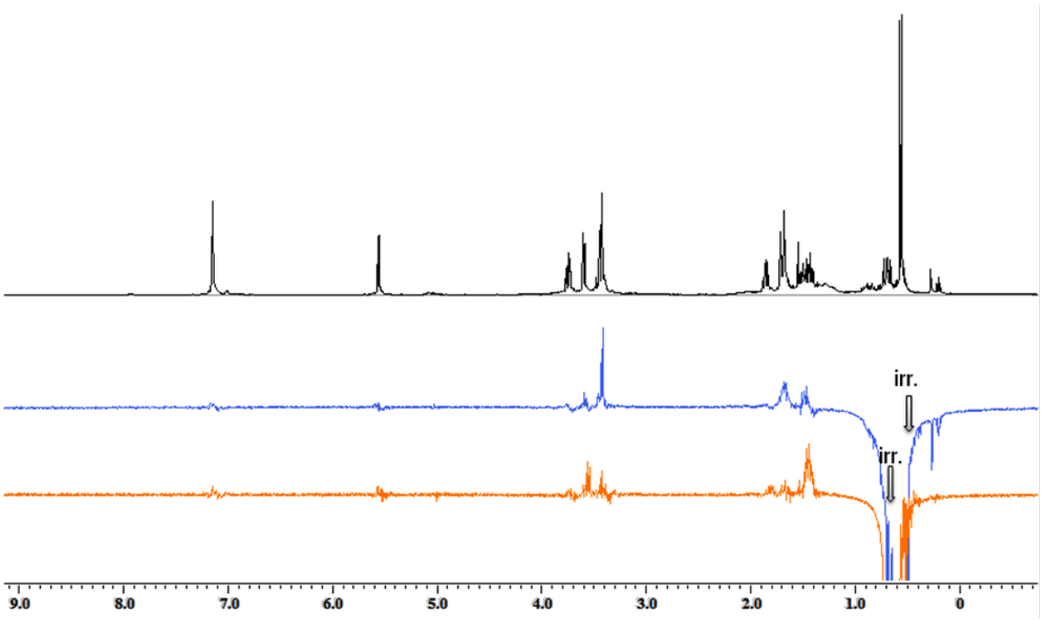
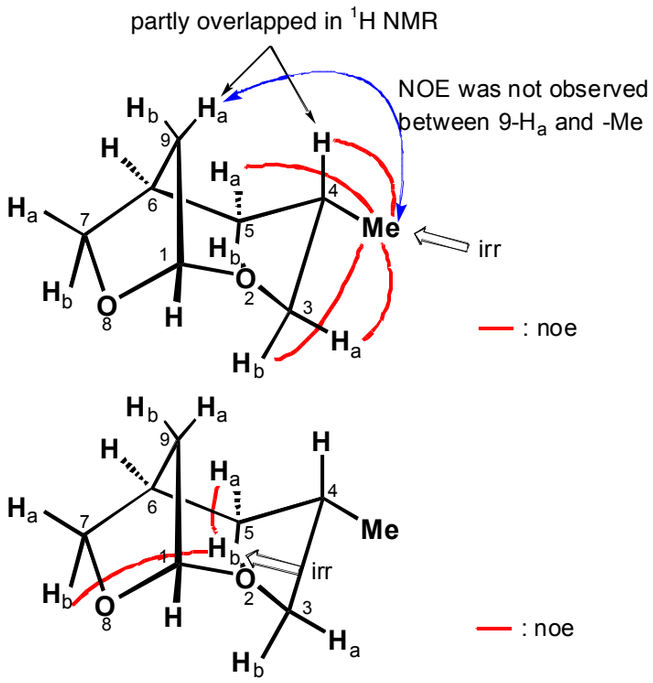



**Figure S11.** Difference NOE spectrum of **2ab** (400 MHz, benzene-$d_6$).



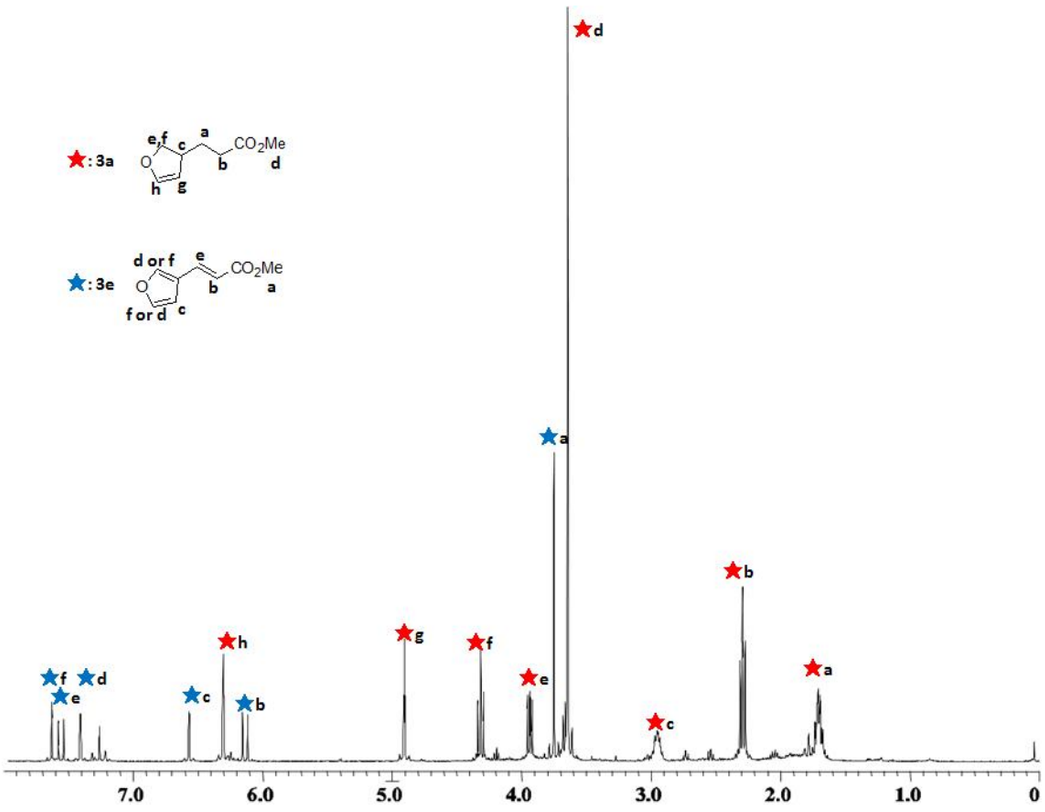



**Figure S12.** $^{1}$H NMR spectrum for a mixture of **3a** and **3e** (**3a**/**3e** = 76/24) (400 MHz, chloroform-*d*).

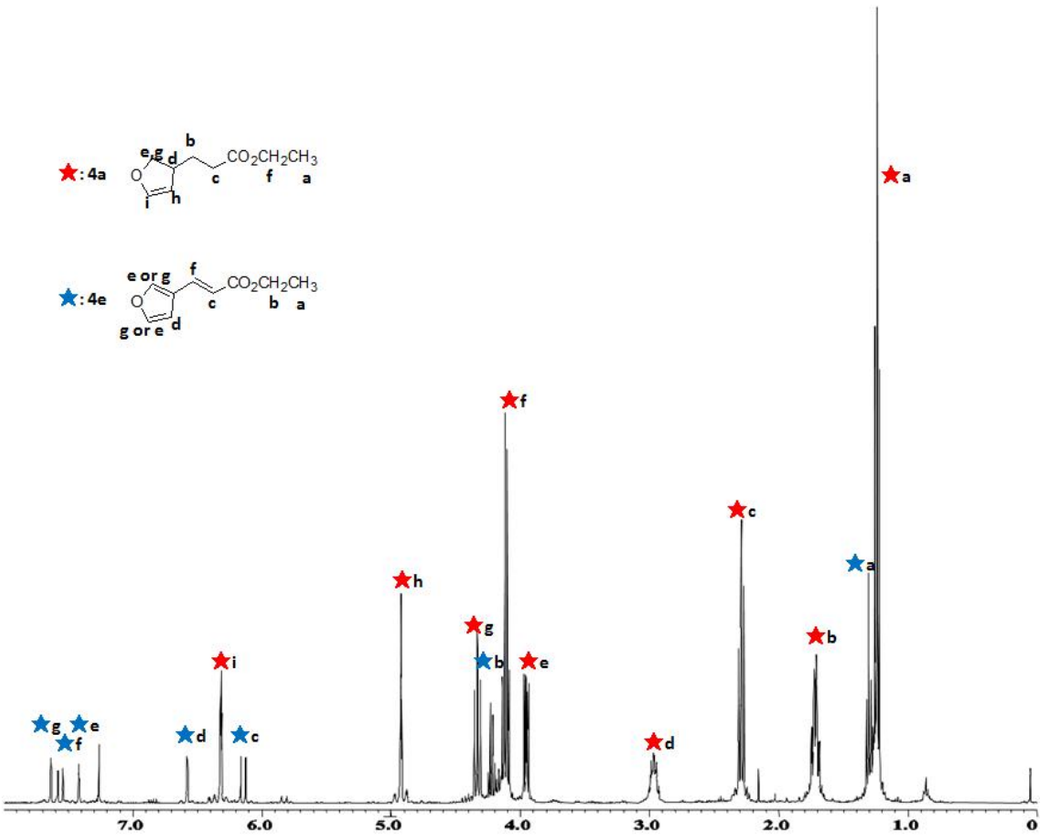



**Figure S13.** $^{1}$H NMR spectrum for a mixture of **4a** and **4e** (**4a**/**4e** = 81/19) (400 MHz, chloroform-*d*).

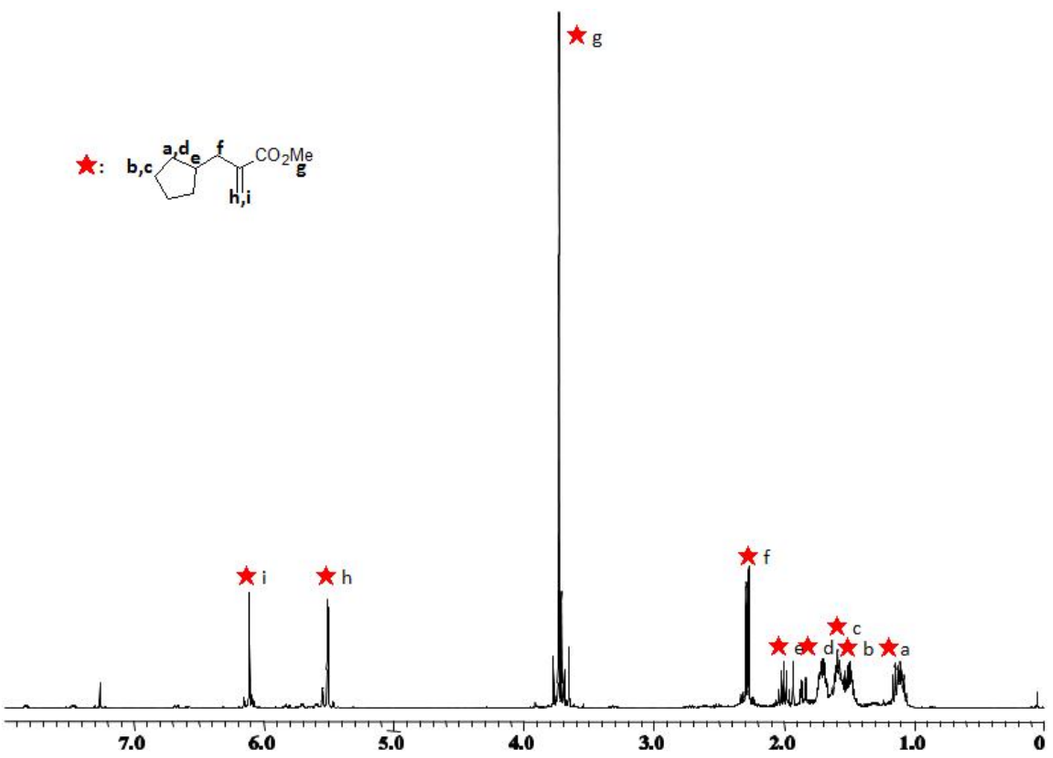



**Figure S14.** $^{1}$H NMR spectrum for a mixture of **5c** (400 MHz, benzene-$d_6$).

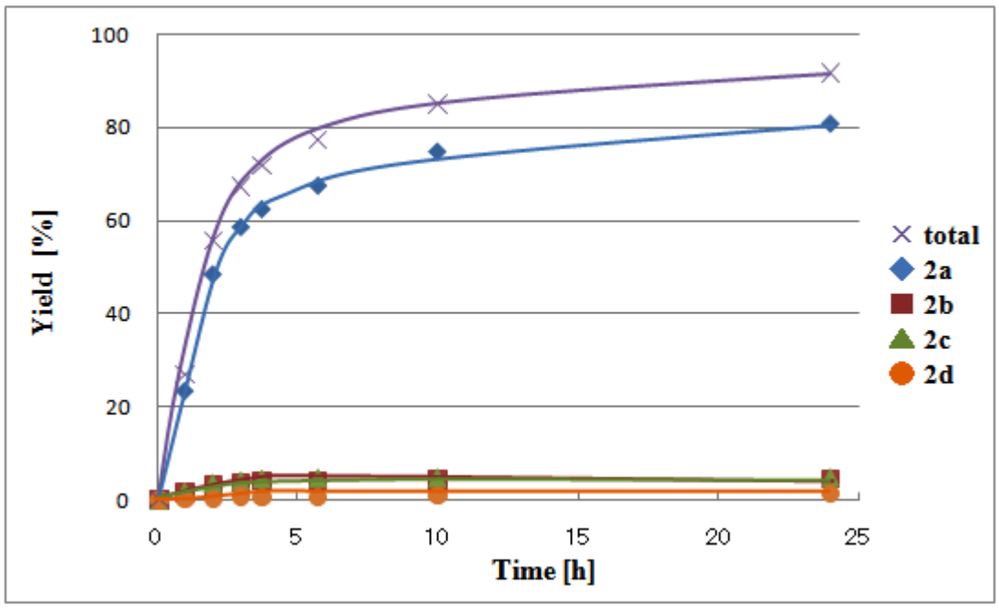



**Figure S15.** Time-yield curves for the cross dimerization between methyl methacrylate and 2,5-dihydrofuran promoted **1** (5 mol%) at 0 °C without use of solvent.

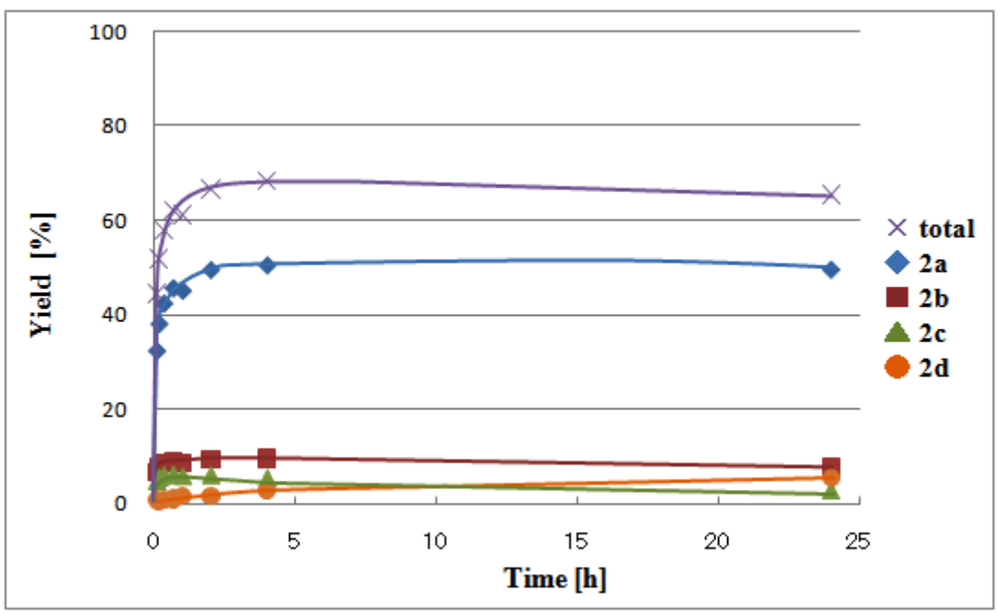



**Figure S16.** Time-yield curves for the cross dimerization between methyl methacrylate and 2,5-dihydrofuran promoted **1** (5 mol%) at 50 °C without use of solvent.

**References**

(1) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X. *Organometallics* **1991**, *10*, 3237.

(2) (a) Billington, D. C.; Kerr, W. J.; Pauson, P. L. *J. Organomet. Chem.* **1987**, 328, 223.
(b) Kilroy, T. G.; Hennessy, A. J.; Connolly, D. J.; Malone, Y. M.; Farrell, A.; Guiry, P. J. *J. Mol. Catal. A Chem.* **2003**, 196, 65.

(3) Hirano, M.; Hiroi, Y.; Komine, N.; Komiya, S. *Organometallics* **2010**, *29*, 3690.