■ Supporting Information: om-2010-00646q

Catalytic Tail-to-tail Selective Dimerization of Methyl Methacrylate Promoted by Ruthenium(0) Complex

Masafumi Hirano,* Yuki Hiroi, Nobuyuki Komine, and Sanshiro Komiya

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-26 Nakacho, Koganei, Tokyo 184-8588, Japan.

Experimental

General procedures

All manipulations were carried out under dry nitrogen using standard Schlenk and vacuum line techniques. Benzene and pentane were dried over anhydrous calcium chloride and then distilled from sodium wire under nitrogen with benzophenone ketyl as an indicator. Acetonitrile was dried over calcium chloride and distilled over calcium hydride under nitrogen. Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**) was prepared according to the reported method.[1] Methyl methacrylate was dried over anhydrous $MgSO_4$ and purified by the valve-to-valve distillation under reduced pressure. Deuterated solvents for use in NMR experiments were purchased from Kanto Chemical and dried with sodium wire for C_6D_6, and was directly vacuum transferred into an NMR tube. NMR spectra were recorded on a JEOL LA-300 or ECX-400 spectrometers (300.4 MHz or 399.8 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 (TC-1 or TC-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-1, 0.25 mmf x 30 m).

Preparation and characterization of 2a. Methyl methacrylate (540 μL, 5.09 mmol) was added into **1** (16.5 mg, 0.0489 mmol) in Schlenk tube by the valve-to-valve distillation under reduced pressure. The mixture was stirred at 30 ˚C for 20 min and then all volatile matters were removed under reduced pressure. After quenching of the catalyst by exposure to air, a **2a** dominant product was obtained (**2a**/*Z*-**2b**/*E*-**2b** = 55/27/18). Since **2a** could not be separated form the mixture, **2a** was characterized spectroscopically as shown in Fig. S1. **2a**: ^{1}H NMR (300 MHz, r.t., C_6D_6): δ 1.02 (d, J = 7.2 Hz, 3H, C*Me*), 1.52 (dq, J = 13.2, 6.6 Hz, 1H, C*H*Me), 1.85 (m, 1H, CH_2CHMe), 2.23 (t, J = 6.9 Hz, 2H, CH_2), 2.23 (m, 1H, CH_2CHMe), 3.33 (s, 3H, O*Me*), 3.36 (s, 3H, O*Me*), 5.24 (s, 1H, =CH_2), 6.12 (s, 1H, =CH_2). GC-MS(EI): m/z = 200 (M^+), 169 (M^+–OMe), 141 (M^+–CO_2Me).

Preparation and characterization of *E*-2b, *Z*-2b and *E*-3a. Similar to **2a**, methyl methacrylate (1.08 mL, 10.2 mmol) was heated at 70 ˚C for 8 h in the presence of **1** (34.0 mg, 0.101 mmol) to give a mixture of products. After removal of all volatile matters, the products were obtained as an orange oil (375.6 mg). The mixture was separated by silicagel column chromatography (hexane/ethyl acetate = 5/1) to give the dimers (220.4 mg, 59%. **2a**/*Z*-**2b**/*E*-**2b** = 1/5/94) and the trimers (69.9 mg, 19%. **3z**/*Z*-**3a**/*E*-**3a** = 25/7/68). It is notable that isomerization the stereochemistry of **2b** was confirmed by the differential NOE (Fig. S2) and the isomerization from *Z*-**2b** to *E*-**2b** was confirmed by use of GLC analysis. *E*-**2b**: ^{1}H NMR (300 MHz, r.t., C_6D_6): δ 0.97 (d, *J* = 7.2 Hz, 3H, CH*Me*), 1.76 (s, 3H, C*Me*), 2.05 (m, 1H, =CHCH_2), 2.34 (m, 2H, =CHCH_2 and C*H*Me), 3.30 (s, 3H, O*Me*), 3.42 (s, 3H, O*Me*), 6.75 (t, *J* = 7.5 Hz, 1H, =C*H*). ^{13}C{^{1}H} NMR (74.5 MHz, r.t., C_6D_6): 12.6 (s, C*Me*), 16.8 (s, C*Me*), 32.5 (s, *C*H or *C*H_2), 38.9 (s, *C*H_2 or *C*H), 51.2 (s, O*Me*), 51.3 (s, O*Me*), 129.91 (s, =*C*Me), 138.8 (s, =*C*H), 167.8 (s, *C*O), 175.3 (s, *C*O). GC-MS(EI): *m*/*z* = 200 (M^+), 185 (M^+–Me), 169 (M^+–OMe), 141 (M^+–CO_2Me). *Z*-**2b**: ^{1}H NMR (300 MHz, r.t., C_6D_6): δ 1.06 (d, *J* = 7.2 Hz, 3H, CH*Me*), 1.76 (s, 3H, *Me*), 2.47 (sext, *J* = 7.2 Hz, 1H, C*H*Me), 2.76 (q, *J* = 7.5 Hz, 1H, =CHCH_2), 2.83 (q, *J* = 7.5 Hz, 1H, =CHCH_2), 3.33 (s, 3H, O*Me*), 3.38 (s, 3H, O*Me*), 5.76 (t, *J* = 7.5 Hz, 1H, =C*H*). GC-MS(EI): *m*/*z* = 200 (M^+), 185 (M^+–Me), 169 (M^+–OMe), 141 (M^+–CO_2Me).

E-**3a** was obtained by the preparative GLC with a TCD detector from the mixture of trimers (69.9 mg, 19%. **3z**/*Z*-**3a**/*E*-**3a** = 25/7/68) as a dominant product of the isomer (**3z**/*E*-**3a** = 27/73). Since further purification of **3a** was difficult, **3a** was characterized by the spectroscopic method. Although it was difficult to specify the stereochemistry by the spectroscopic data alone, this species was assigned as *E*-**3a** because thermal isomerization of the initial product (*Z*-**3a**) to this species (*E*-**3a**) was observed by the GLC analysis. *E*-**3a**: ^{1}H NMR (300 MHz, r.t., C_6D_6): δ 1.02 (d, *J* = 7.2 Hz, 3H, CH*Me*), 1.10 (d, *J* = 6.0 Hz, 3H, CH*Me*), 1.62 (m, 1H, CH_2CMe), 1.89 (m, 1H, CH_2CMe), 2.18 (m, 1H, =CHCH_2CMe), 2.31-2.53 (m, 5H, =CHCH_2CMe, =CHCH$_2$C*H*Me, CH$_2$CH$_2$C*H*CMe, =C(CO_2Me)CH_2), 3.28 (s, 3H, =C(CO_2*Me*)), 3.39 (s, 6H, CO_2*Me*), 6.68 (t, *J* = 7.5 Hz, 1H, =C*H*). ^{13}C{^{1}H} NMR (75.4 MHz, r.t., C_6D_6): δ 17.0 (1˚), 17.3 (1˚), 25.0 (2˚), 33.4 (2˚), 33.5 (2˚), 39.5 (3˚), 39.1 (3˚), 51.1 (1˚), 51.3 (1˚), 133.8 (4˚), 139.6 (3˚), 167.4 (4˚), 175.3 (4˚), 176.2 (4˚). GC-MS(EI): *m*/*z* = 300

(M^+), 269 (M^+–OMe), 241 (M^+–CO_2Me).

Preparation of 6. Complex **1** (98.8 mg, 0.293 mmol) was placed in a 25mL-Schlenk tube into which benzene (2 mL) was introduced by the valve-to-valve distillation. Into the solution, PMe_3 (65 μL, 0.63 mmol) and methyl methacrylate (66 μL, 0.62 mmol) were added by a hypodermic syringe to give a yellow solution. The solution was warmed at 50 ˚C for 20 h. After removal of all volatile materials, yellow oil was obtained (161.5 mg). Crystallization of the oil from cold penane (1 mL) gave yellow platelets of Ru(*cisoid*-κ^4-methyl methacrylate)(*cisoid*-η^2-methyl methacrylate)(PMe_3)$_2$ (**6**) in 32% yield (42.2 mmol, 0.093 mmol). ^{1}H NMR (300 MHz, r.t., C_6D_6): 0.82 (d, *J* = 9.3 Hz, 9H, P*Me*), 1.26-1.31 (overlapped, 1H, CH_2=), 1.29 (d, *J* = 7.8 Hz, 9H, P*Me*), 1.84 (partly overlapped, 1H, CH_2=), 1.89 (s, 3H, =C*Me*), 2.11 (overlapped, 1H, CH_2=), 2.15 (d, *J* = 4.2 Hz, 3H, =C*Me*), 3.33 (s, 3H, CO_2*Me*), 3.45-3.50 (overlapped, 1H, CH_2=), 3.51 (s, 3H, CO_2*Me*). ^{13}C{^{1}H} NMR (75.5 MHz, r.t., C_6D_6): 17.7 (s, *Me*), 18.9 (d, *J* = 30 Hz, P*Me*), 23.8 (s, *Me*), 40.5 (s, *C*H_2), 46.2 (s, *C*Me), 46.4 (s, CH_2), 50.2 (O*Me*), 50.5 (*s,* O*Me*), 52.8 (s, *C*Me=), 169.7 (s, *C*O_2), 179.8 (s, *C*O_2). ^{31}P{^{1}H} NMR (121.6 MHz, r.t., C_6D_6): 0.09 (d, *J* = 21.9 Hz, 1P, *P*Me_3), 30.82 (d, *J* = 21.9 Hz, 1P, *P*Me_3). IR (KBr, cm^{-1}): 3034(m), 2968(m), 1674(vs), 1537(m), 1459(s), 1430(s), 1354(vs), 1298(m), 1280(m), 1256(m), 1187(m), 1163(m), 1124(m), 1012(vs), 984(vs), 935(m), 851(m), 818(m), 800(m), 767(s), 714(s), 665(w), 569(w).

X-ray analysis of 6. Crystals of **6** was obtained from cold pentane. A selected crystal of **6** for X-ray analysis was mounted on the top of glass capillary with Paraton N-oil. The X-ray analysis was performed on a Rigaku AFC7R-Mercury II CCD system. The reflection data were collected at 200 K under cold nitrogen stream. The collected data were solved by direct methods (SIR92),[2] and refined by a full-matrix least-squre procedure using SHELXL97.[3] The crystal belonged to space group $P2_1/c$. All non-hydrogen atoms except incorporated THF were refined with anisotropic displacement parameters and hydrogen atoms were placed in theoretical positions and were refined using a riding model.

Appendix.

Attempt for Dimerization of MMA by Combination of $RuCl_3 \cdot 3H_2O$ with Zn.

This reaction was carried out to check whether in situ generated Ru(0) species was effective for dimerization of MMA or not.[4] $RuCl_3 \cdot 3H_2O$ (13.1 mg, 0.0501 mmol) and Zn powder (79.3 mg, 1.21 mmol) were added into a Schlenk tube. Into the Schlenk tube, degassed MMA (3.0 mL, 28.0 mmol) and methanol (100 μL) were transferred by vacuum distillation. The mixture was heated at 50 ˚C for 2 h. By the GLC analysis, the dimers and trimers of MMA were not observed.

Table S1. Crystallographic and Physical Data for 6.

formula	'C16 H34 O4 P2 Ru '
formula weight	453.46
crystal color	yellow
size (mm x mm x mm)	0.73 x 0.45 x 0.39
crystal system	*monoclinic*
space group	$P2_1/c$ (No.14)
a (Å)	8.8300(5)
b (Å)	27.2735(17)
c (Å)	17.7050(10)
β (deg)	94.314(4)
volume (Å^3)	4251.7(4)
Z	8
F(000)	1888.00
temp (K)	200.0
μ (mm-1)	0.902
radiation type	MoKα
diffractometer	Rigaku AFC7R-Mercury II
diffrn reflns number	25780
reflns number total	9526
reflns number gt	8678
reflns threshold expression	$F^2>2.0\sigma(F^2)$
refine ls structure factor coef	Fsqd
refine ls R factor gt	0.0446
refine ls wR factor ref	0.1318
refine ls goodness of fit ref	0.935

'$w = 1/[\sigma\text{^}(F_o^2)+(0.0830P)^2+10.1362P]$ where $P=(F_o^2+2F_c^2)/3$'

Table S2. Atomic Coordinates for 6.

atom	*x*	*y*	*z*	U_{ani}
Ru(1)	0.51350(3)	0.710458(9)	0.570568(15)	0.02631(8)
Ru(2)	0.90792(3)	0.466940(9)	0.738554(13)	0.02475(7)
P(1)	0.77309(10)	0.72938(4)	0.57767(6)	0.0363(2)
P(2)	0.48068(11)	0.71154(3)	0.44444(5)	0.03271(18)
P(3)	0.65283(10)	0.49136(3)	0.73640(6)	0.0352(2)
P(4)	0.92936(10)	0.44547(3)	0.86036(5)	0.03301(18)
O(1)	0.5117(3)	0.68693(10)	0.69721(16)	0.0440(6)
O(2)	0.2861(4)	0.64727(14)	0.7007(2)	0.0627(9
O(3)	0.3438(4)	0.82017(11)	0.47501(17)	0.0549(7)
O(4)	0.5188(3)	0.86007(11)	0.5489(2)	0.0544(7)
O(5)	0.9202(3)	0.46527(9)	0.60747(14)	0.0379(5)
O(6)	1.1469(3)	0.42709(11)	0.59740(16)	0.0463(6)
O(7)	1.0705(4)	0.55774(12)	0.87790(17)	0.0582(8)
O(8)	0.9162(4)	0.60918(11)	0.81197(19)	0.0558(7)
C(1)	0.5855(4)	0.63611(13)	0.5762(2)	0.0413(8)
C(2)	0.4281(4)	0.63783(13)	0.5936(2)	0.0370(7)
C(3)	0.4124(4)	0.65835(14)	0.6675(2)	0.0416(8)
C(4)	0.3010(5)	0.60950(16)	0.5535(2)	0.0514(10)
C(5)	0.2687(8)	0.6695(2)	0.7733(3)	0.085(2)
C(6)	0.3096(4)	0.74953(14)	0.5897(2)	0.0381(7)
C(7)	0.4307(4)	0.78529(12)	0.5948(2)	0.0355(7)
C(8)	0.4246(4)	0.82150(13)	0.5332(2)	0.0403(7)
C(9)	0.4913(5)	0.80309(15)	0.6728(2)	0.0470(9)
C(10)	0.5121(7)	0.89779(19)	0.4909(3)	0.0700(14)
C(11)	0.8544(5)	0.7222(2)	0.6751(3)	0.0614(12)
C(12)	0.8421(5)	0.79036(16)	0.5550(3)	0.0564(11)
C(13)	0.9010(4)	0.6910(2)	0.5264(3)	0.0623(13)
C(14)	0.5416(4)	0.65657(16)	0.3954(2)	0.0474(9)

Table S2. continued

atom	*x*	*y*	*z*	U_{ani}
C(15)	0.5811(5)	0.75715(16)	0.3906(2)	0.0476(9)
C(16)	0.2850(4)	0.71593(17)	0.4024(2)	0.0481(9)
C(17)	0.8219(4)	0.39747(13)	0.7007(2)	0.0397(7)
C(18)	0.9822(4)	0.39942(13)	0.6883(2)	0.0363(7)
C(19)	1.0139(4)	0.43199(13)	0.6281(2)	0.0361(7)
C(20)	1.0992(5)	0.36238(16)	0.7185(2)	0.0510(10)
C(21)	1.1787(5)	0.46178(17)	0.5391(2)	0.0521(10)
C(22)	1.1200(3)	0.50517(13)	0.7428(2)	0.0328(6)
C(23)	1.0058(3)	0.54223(11)	0.74565(19)	0.0302(6)
C(24)	1.0028(4)	0.56834(13)	0.8185(2)	0.0394(7)
C(25)	0.9602(4)	0.57222(14)	0.6757(2)	0.0410(8)
C(26)	0.9083(8)	0.6384(2)	0.8785(3)	0.0816(19)
C(27)	0.5155(4)	0.44768(17)	0.7700(3)	0.0551(11)
C(28)	0.5915(5)	0.54800(17)	0.7803(3)	0.0582(11)
C(29)	0.5771(5)	0.50040(19)	0.6387(2)	0.0564(11)
C(30)	0.8546(5)	0.38528(15)	0.8840(2)	0.0477(9)
C(31)	0.8346(5)	0.48147(18)	0.9303(2)	0.0501(9)
C(32)	1.1226(4)	0.43952(18)	0.9047(2)	0.0479(9)

Table S3. Anisotropic Parameters for 6.

atom	U11	U22	U33	U12	U13	U23
Ru(1)	0.02299(14)	0.02441(14)	0.03140(15)	-0.00091(8)	0.00126(10)	-0.00067(8)
Ru(2)	0.02223(13)	0.02449(14)	0.02729(14)	0.00225(8)	0.00022(9)	-0.00128(8)
P(1)	0.0258(4)	0.0352(4)	0.0473(5)	-0.0041(3)	-0.0003(3)	-0.0018(3)
P(2)	0.0317(4)	0.0349(4)	0.0314(4)	0.0001(3)	0.0015(3)	-0.0052(3)
P(3)	0.0240(3)	0.0335(4)	0.0481(5)	0.0037(3)	0.0022(3)	0.0023(3)
P(4)	0.0335(4)	0.0364(4)	0.0291(4)	0.0009(3)	0.0016(3)	0.0026(3)
O(1)	0.0454(15)	0.0439(15)	0.0418(14)	-0.0112(11)	-0.0025(11)	0.0069(11)
O(2)	0.060(2)	0.073(2)	0.0575(19)	-0.0342(17)	0.0179(15)	-0.0083(16)
O(3)	0.077(2)	0.0429(15)	0.0429(15)	0.0095(14)	-0.0073(14)	0.0006(12)
O(4)	0.0610(19)	0.0358(14)	0.0658(19)	-0.0032(13)	0.0005(15)	0.0086(13)
O(5)	0.0452(14)	0.0364(13)	0.0313(12)	0.0097(10)	-0.0011(10)	-0.0020(9)
O(6)	0.0530(16)	0.0442(15)	0.0435(14)	0.0184(12)	0.0149(12)	0.0023(11)
O(7)	0.087(2)	0.0471(17)	0.0398(15)	-0.0082(16)	-0.0034(15)	-0.0097(12)
O(8)	0.070(2)	0.0390(15)	0.0606(18)	0.0072(14)	0.0219(15)	-0.0112(13)
C(1)	0.0384(18)	0.0274(16)	0.058(2)	0.0041(13)	0.0014(16)	0.0043(14)
C(2)	0.0353(17)	0.0270(15)	0.0486(19)	-0.0060(13)	0.0023(14)	0.0053(13)
C(3)	0.0403(19)	0.0382(18)	0.046(2)	-0.0077(15)	0.0019(15)	0.0075(15)
C(4)	0.049(2)	0.041(2)	0.065(2)	-0.0159(17)	0.0042(19)	-0.0072(18)
C(5)	0.087(4)	0.112(5)	0.059(3)	-0.045(3)	0.028(2)	-0.018(3)
C(6)	0.0311(16)	0.0384(18)	0.0458(19)	0.0056(13)	0.0085(14)	-0.0037(14)
C(7)	0.0405(18)	0.0281(16)	0.0378(17)	0.0070(13)	0.0018(14)	-0.0049(12)
C(8)	0.045(2)	0.0314(17)	0.045(2)	0.0094(14)	0.0082(15)	-0.0028(14)
C(9)	0.060(2)	0.0379(19)	0.042(2)	0.0059(17)	-0.0008(17)	-0.0099(15)
C(10)	0.076(3)	0.048(2)	0.086(3)	-0.004(2)	0.012(2)	0.018(2)
C(11)	0.047(2)	0.070(3)	0.063(2)	-0.004(2)	-0.021(2)	0.002(2)
C(12)	0.045(2)	0.046(2)	0.078(3)	-0.0188(18)	0.005(2)	0.002(2)
C(13)	0.0275(18)	0.063(2)	0.098(3)	0.0019(18)	0.010(2)	-0.014(2)
C(14)	0.045(2)	0.050(2)	0.047(2)	0.0049(17)	0.0028(16)	-0.0175(17)

Table S3. continued

atom	U11	U22	U33	U12	U13	U23
C(15)	0.057(2)	0.050(2)	0.0370(18)	-0.0038(18)	0.0111(17)	0.0016(16)
C(16)	0.040(2)	0.057(2)	0.045(2)	0.0058(17)	-0.0090(16)	-0.0103(17)
C(17)	0.045(2)	0.0320(17)	0.0417(18)	-0.0041(14)	-0.0007(15)	-0.0076(13)
C(18)	0.0435(19)	0.0281(15)	0.0376(17)	0.0083(13)	0.0050(14)	-0.0034(12)
C(19)	0.0424(19)	0.0326(16)	0.0328(16)	0.0062(14)	0.0001(13)	-0.0066(12)
C(20)	0.062(2)	0.040(2)	0.052(2)	0.0217(18)	0.0131(19)	0.0069(16)
C(21)	0.060(2)	0.056(2)	0.042(2)	0.009(2)	0.0160(18)	0.0018(17)
C(22)	0.0247(14)	0.0349(16)	0.0389(16)	-0.0027(12)	0.0023(12)	-0.0029(13)
C(23)	0.0289(15)	0.0263(15)	0.0355(16)	-0.0041(12)	0.0037(12)	-0.0032(12)
C(24)	0.045(2)	0.0315(16)	0.0424(19)	-0.0089(14)	0.0092(15)	-0.0053(14)
C(25)	0.045(2)	0.0330(17)	0.0452(19)	-0.0035(14)	0.0023(15)	0.0063(14)
C(26)	0.127(5)	0.049(2)	0.074(3)	0.007(3)	0.044(3)	-0.018(2)
C(27)	0.0276(18)	0.050(2)	0.089(3)	-0.0018(16)	0.0111(19)	0.010(2)
C(28)	0.043(2)	0.044(2)	0.089(3)	0.0129(18)	0.017(2)	-0.006(2)
C(29)	0.043(2)	0.059(2)	0.065(2)	0.0097(19)	-0.0119(19)	0.009(2)
C(30)	0.050(2)	0.044(2)	0.049(2)	-0.0054(17)	0.0066(17)	0.0115(16)
C(31)	0.054(2)	0.062(2)	0.0351(18)	0.002(2)	0.0125(16)	-0.0046(17)
C(32)	0.045(2)	0.060(2)	0.0371(19)	0.0045(18)	-0.0073(15)	0.0069(17)

Table S4. Bond Distances (Å) for 6.

Ru(1) P(1) 2.3437(9)	Ru(1) P(2) 2.2303(9)
Ru(1) O(1) 2.333(2)	Ru(1) C(1) 2.125(3)
Ru(1) C(2) 2.169(3)	Ru(1) C(6) 2.141(3)
Ru(1) C(7) 2.221(3)	Ru(2) P(3) 2.3464(9)
Ru(2) P(4) 2.2289(9)	Ru(2) O(5) 2.332(2)
Ru(2) C(17) 2.130(3)	Ru(2) C(18) 2.168(3)
Ru(2) C(22) 2.140(3)	Ru(2) C(23) 2.228(3)
P(1) C(11) 1.828(5)	P(1) C(12) 1.826(4)
P(1) C(13) 1.830(5)	P(2) C(14) 1.833(4)
P(2) C(15) 1.836(4)	P(2) C(16) 1.834(4)
P(3) C(27) 1.831(4)	P(3) C(28) 1.829(5)
P(3) C(29) 1.824(5)	P(4) C(30) 1.829(4)
P(4) C(31) 1.831(4)	P(4) C(32) 1.831(4)
O(1) C(3) 1.259(4)	O(2) C(3) 1.333(5)
O(2) C(5) 1.440(7)	O(3) C(8) 1.208(5)
O(4) C(8) 1.357(4)	O(4) C(10) 1.452(6)
O(5) C(19) 1.263(4)	O(6) C(19) 1.337(5)
O(6) C(21) 1.444(5)	O(7) C(24) 1.206(4)
O(8) C(24) 1.351(4)	O(8) C(26) 1.429(6)
C(1) C(2) 1.447(5)	C(2) C(3) 1.441(5)
C(2) C(4) 1.496(5)	C(6) C(7) 1.445(5)
C(7) C(8) 1.470(5)	C(7) C(9) 1.523(5)
C(17) C(18) 1.450(5)	C(18) C(19) 1.432(5)
C(18) C(20) 1.513(5)	C(22) C(23) 1.431(4)
C(23) C(24) 1.475(5)	C(23) C(25) 1.514(5)

Table S5. Bond Angles (deg) for 6.

P(1) Ru(1) P(2) 95.95(3)	P(1) Ru(1) O(1) 94.95(7)
P(1) Ru(1) C(1) 85.39(10)	P(1) Ru(1) C(2) 122.91(10)
P(1) Ru(1) C(6) 135.44(10)	P(1) Ru(1) C(7) 97.02(10)
P(2) Ru(1) O(1) 162.94(7)	P(2) Ru(1) C(1) 94.31(12)
P(2) Ru(1) C(2) 100.32(10)	P(2) Ru(1) C(6) 96.00(10)
P(2) Ru(1) C(7) 99.30(9)	O(1) Ru(1) C(1) 73.53(13)
O(1) Ru(1) C(2) 62.68(12)	O(1) Ru(1) C(6) 85.30(12)
O(1) Ru(1) C(7) 92.34(11)	C(1) Ru(1) C(2) 39.36(14)
C(1) Ru(1) C(6) 136.04(14)	C(1) Ru(1) C(7) 165.84(15)
C(2) Ru(1) C(6) 96.70(14)	C(2) Ru(1) C(7) 132.76(14)
C(6) Ru(1) C(7) 38.64(14)	P(3) Ru(2) P(4) 95.85(3)
P(3) Ru(2) O(5) 96.07(7)	P(3) Ru(2) C(17) 85.89(10)
P(3) Ru(2) C(18) 123.65(10)	P(3) Ru(2) C(22) 134.33(9)
P(3) Ru(2) C(23) 96.16(8)	P(4) Ru(2) O(5) 161.97(6)
P(4) Ru(2) C(17) 94.18(10)	P(4) Ru(2) C(18) 99.64(9)
P(4) Ru(2) C(22) 94.80(9)	P(4) Ru(2) C(23) 100.56(8)
O(5) Ru(2) C(17) 73.25(12)	O(5) Ru(2) C(18) 62.42(11)
O(5) Ru(2) C(22) 86.46(11)	O(5) Ru(2) C(23) 91.56(10)
C(17) Ru(2) C(18) 39.40(14)	C(17) Ru(2) C(22) 137.28(14)
C(17) Ru(2) C(23) 164.81(13)	C(18) Ru(2) C(22) 97.89(13)
C(18) Ru(2) C(23) 132.68(13)	C(22) Ru(2) C(23) 38.19(12)
Ru(1) P(1) C(11) 109.87(17)	Ru(1) P(1) C(12) 122.01(15)
Ru(1) P(1) C(13) 119.01(15)	C(11) P(1) C(12) 101.0(2)
C(11) P(1) C(13) 101.2(2)	C(12) P(1) C(13) 100.6(2)
Ru(1) P(2) C(14) 116.26(14)	Ru(1) P(2) C(15) 119.84(13)
Ru(1) P(2) C(16) 117.07(14)	C(14) P(2) C(15) 97.9(2)
C(14) P(2) C(16) 99.35(19)	C(15) P(2) C(16) 102.8(2)
Ru(2) P(3) C(27) 117.93(14)	Ru(2) P(3) C(28) 123.17(15)
Ru(2) P(3) C(29) 109.68(16)	C(27) P(3) C(28) 100.8(2)

Table S5. continued

C(27) P(3) C(29) 101.1(2)	C(28) P(3) C(29) 100.9(2)
Ru(2) P(4) C(30) 116.81(14)	Ru(2) P(4) C(31) 120.22(14)
Ru(2) P(4) C(32) 116.55(14)	C(30) P(4) C(31) 97.8(2)
C(30) P(4) C(32) 99.4(2)	C(31) P(4) C(32) 102.46(19)
Ru(1) O(1) C(3) 79.9(2)	C(3) O(2) C(5) 116.5(4)
C(8) O(4) C(10) 114.3(3)	Ru(2) O(5) C(19) 78.8(2)
C(19) O(6) C(21) 116.6(3)	C(24) O(8) C(26) 116.9(3)
Ru(1) C(1) C(2) 71.9(2)	Ru(1) C(2) C(1) 68.7(2)
Ru(1) C(2) C(3) 82.8(2)	Ru(1) C(2) C(4) 129.9(2)
C(1) C(2) C(3) 111.5(3)	C(1) C(2) C(4) 125.5(3)
C(3) C(2) C(4) 120.7(3)	O(1) C(3) O(2) 122.4(3)
O(1) C(3) C(2) 120.6(3)	O(2) C(3) C(2) 117.0(3)
Ru(1) C(6) C(7) 73.7(2)	Ru(1) C(7) C(6) 67.69(19)
Ru(1) C(7) C(8) 117.9(2)	Ru(1) C(7) C(9) 111.7(2)
C(6) C(7) C(8) 114.9(3)	C(6) C(7) C(9) 118.7(3)
C(8) C(7) C(9) 116.8(3)	O(3) C(8) O(4) 120.8(3)
O(3) C(8) C(7) 126.8(3)	O(4) C(8) C(7) 112.3(3)
Ru(2) C(17) C(18) 71.7(2)	Ru(2) C(18) C(17) 68.9(2)
Ru(2) C(18) C(19) 82.0(2)	Ru(2) C(18) C(20) 129.9(2)
C(17) C(18) C(19) 112.5(3)	C(17) C(18) C(20) 124.8(3)
C(19) C(18) C(20) 120.7(3)	O(5) C(19) O(6) 122.1(3)
O(5) C(19) C(18) 120.0(3)	O(6) C(19) C(18) 117.9(3)
Ru(2) C(22) C(23) 74.24(18)	Ru(2) C(23) C(22) 67.57(17)
Ru(2) C(23) C(24) 117.5(2)	Ru(2) C(23) C(25) 111.9(2)
C(22) C(23) C(24) 115.6(2)	C(22) C(23) C(25) 119.8(3)
C(24) C(23) C(25) 115.7(2)	O(7) C(24) O(8) 120.8(3)
O(7) C(24) C(23) 127.3(3)	O(8) C(24) C(23) 111.8(3)

Table S6. Torsion Angles (deg) for 6.

P(1) Ru(1) P(2) C(14) 79.60(16)	P(1) Ru(1) P(2) C(15) -37.80(17)
P(1) Ru(1) P(2) C(16) -163.31(16)	P(2) Ru(1) P(1) C(11) -170.72(19)
P(2) Ru(1) P(1) C(12) 71.6(2)	P(2) Ru(1) P(1) C(13) -54.8(2)
P(1) Ru(1) O(1) C(3) -147.0(2)	O(1) Ru(1) P(1) C(11) -3.9(2)
O(1) Ru(1) P(1) C(12) -121.6(2)	O(1) Ru(1) P(1) C(13) 112.0(2)
P(1) Ru(1) C(1) C(2) 163.3(2)	C(1) Ru(1) P(1) C(11) -76.9(2)
C(1) Ru(1) P(1) C(12) 165.4(2)	C(1) Ru(1) P(1) C(13) 39.0(2)
P(1) Ru(1) C(2) C(1) -19.9(2)	P(1) Ru(1) C(2) C(3) 96.5(2)
P(1) Ru(1) C(2) C(4) -139.0(3)	C(2) Ru(1) P(1) C(11) -64.3(2)
C(2) Ru(1) P(1) C(12) 178.0(2)	C(2) Ru(1) P(1) C(13) 51.5(2)
P(1) Ru(1) C(6) C(7) 7.4(2)	C(6) Ru(1) P(1) C(11) 84.5(2)
C(6) Ru(1) P(1) C(12) -33.2(2)	C(6) Ru(1) P(1) C(13) -159.7(2)
P(1) Ru(1) C(7) C(6) -174.77(19)	P(1) Ru(1) C(7) C(8) 77.9(2)
P(1) Ru(1) C(7) C(9) -61.5(2)	C(7) Ru(1) P(1) C(11) 89.1(2)
C(7) Ru(1) P(1) C(12) -28.6(2)	C(7) Ru(1) P(1) C(13) -155.0(2)
P(2) Ru(1) O(1) C(3) -17.4(4)	O(1) Ru(1) P(2) C(14) -49.8(3)
O(1) Ru(1) P(2) C(15) -167.2(2)	O(1) Ru(1) P(2) C(16) 67.2(3)
P(2) Ru(1) C(1) C(2) -101.0(2)	C(1) Ru(1) P(2) C(14) -6.21(19)
C(1) Ru(1) P(2) C(15) -123.6(2)	C(1) Ru(1) P(2) C(16) 110.89(19)
P(2) Ru(1) C(2) C(1) 84.2(2)	P(2) Ru(1) C(2) C(3) -159.37(19)
P(2) Ru(1) C(2) C(4) -34.9(3)	C(2) Ru(1) P(2) C(14) -45.45(18)
C(2) Ru(1) P(2) C(15) -162.85(19)	C(2) Ru(1) P(2) C(16) 71.64(19)
P(2) Ru(1) C(6) C(7) -97.39(19)	C(6) Ru(1) P(2) C(14) -143.41(18)
C(6) Ru(1) P(2) C(15) 99.19(19)	C(6) Ru(1) P(2) C(16) -26.31(19)
P(2) Ru(1) C(7) C(6) 88.0(2)	P(2) Ru(1) C(7) C(8) -19.4(2)
P(2) Ru(1) C(7) C(9) -158.8(2)	C(7) Ru(1) P(2) C(14) 177.73(18)
C(7) Ru(1) P(2) C(15) 60.33(19)	C(7) Ru(1) P(2) C(16) -65.17(19)
O(1) Ru(1) C(1) C(2) 66.8(2)	C(1) Ru(1) O(1) C(3) -63.3(2)
O(1) Ru(1) C(2) C(1) -97.3(2)	O(1) Ru(1) C(2) C(3) 19.18(19)

Table S6. continued

O(1) Ru(1) C(2) C(4) 143.6(4)	C(2) Ru(1) O(1) C(3) -22.3(2)
O(1) Ru(1) C(6) C(7) 99.7(2)	C(6) Ru(1) O(1) C(3) 77.8(2)
O(1) Ru(1) C(7) C(6) -79.5(2)	O(1) Ru(1) C(7) C(8) 173.2(2)
O(1) Ru(1) C(7) C(9) 33.8(2)	C(7) Ru(1) O(1) C(3) 115.8(2)
C(1) Ru(1) C(2) C(3) 116.5(3)	C(1) Ru(1) C(2) C(4) -119.1(4)
C(1) Ru(1) C(6) C(7) 160.0(2)	C(6) Ru(1) C(1) C(2) 2.2(3)
C(1) Ru(1) C(7) C(6) -75.7(6)	C(1) Ru(1) C(7) C(8) 176.9(4)
C(1) Ru(1) C(7) C(9) 37.5(7)	C(7) Ru(1) C(1) C(2) 62.9(6)
C(2) Ru(1) C(6) C(7) 161.4(2)	C(6) Ru(1) C(2) C(1) -178.5(2)
C(6) Ru(1) C(2) C(3) -62.0(2)	C(6) Ru(1) C(2) C(4) 62.5(3)
C(2) Ru(1) C(7) C(6) -25.5(2)	C(2) Ru(1) C(7) C(8) -132.8(2)
C(2) Ru(1) C(7) C(9) 87.7(3)	C(7) Ru(1) C(2) C(1) -162.8(2)
C(7) Ru(1) C(2) C(3) -46.3(2)	C(7) Ru(1) C(2) C(4) 78.2(4)
C(6) Ru(1) C(7) C(8) -107.3(3)	C(6) Ru(1) C(7) C(9) 113.2(3)
P(3) Ru(2) P(4) C(30) 80.28(16)	P(3) Ru(2) P(4) C(31) -37.78(17)
P(3) Ru(2) P(4) C(32) -162.55(17)	P(4) Ru(2) P(3) C(27) -53.5(2)
P(4) Ru(2) P(3) C(28) 73.4(2)	P(4) Ru(2) P(3) C(29) -168.33(17)
P(3) Ru(2) O(5) C(19) -149.0(2)	O(5) Ru(2) P(3) C(27) 113.0(2)
O(5) Ru(2) P(3) C(28) -120.2(2)	O(5) Ru(2) P(3) C(29) -1.88(18)
P(3) Ru(2) C(17) C(18) 164.3(2)	C(17) Ru(2) P(3) C(27) 40.3(2)
C(17) Ru(2) P(3) C(28) 167.1(2)	C(17) Ru(2) P(3) C(29) -74.5(2)
P(3) Ru(2) C(18) C(17) -18.9(2)	P(3) Ru(2) C(18) C(19) 99.1(2)
P(3) Ru(2) C(18) C(20) -137.2(3)	C(18) Ru(2) P(3) C(27) 52.2(2)
C(18) Ru(2) P(3) C(28) 179.0(2)	C(18) Ru(2) P(3) C(29) -62.6(2)
P(3) Ru(2) C(22) C(23) 2.0(2)	C(22) Ru(2) P(3) C(27) -156.0(2)
C(22) Ru(2) P(3) C(28) -29.2(2)	C(22) Ru(2) P(3) C(29) 89.1(2)
P(3) Ru(2) C(23) C(22) -178.55(18)	P(3) Ru(2) C(23) C(24) 73.3(2)
P(3) Ru(2) C(23) C(25) -64.1(2)	C(23) Ru(2) P(3) C(27) -154.8(2)
C(23) Ru(2) P(3) C(28) -28.0(2)	C(23) Ru(2) P(3) C(29) 90.35(19)

Table S6. continued

P(4) Ru(2) O(5) C(19) -17.9(3)	O(5) Ru(2) P(4) C(30) -50.9(2)
O(5) Ru(2) P(4) C(31) -168.9(2)	O(5) Ru(2) P(4) C(32) 66.3(2
P(4) Ru(2) C(17) C(18) -100.11(19)	C(17) Ru(2) P(4) C(30) -6.00(19)
C(17) Ru(2) P(4) C(31) -124.1(2)	C(17) Ru(2) P(4) C(32) 111.2(2)
P(4) Ru(2) C(18) C(17) 84.8(2)	P(4) Ru(2) C(18) C(19) -157.20(19)
P(4) Ru(2) C(18) C(20) -33.5(3)	C(18) Ru(2) P(4) C(30) -45.34(19)
C(18) Ru(2) P(4) C(31) -163.4(2)	C(18) Ru(2) P(4) C(32) 71.8(2)
P(4) Ru(2) C(22) C(23) -100.98(18)	C(22) Ru(2) P(4) C(30) -144.20(18)
C(22) Ru(2) P(4) C(31) 97.7(2)	C(22) Ru(2) P(4) C(32) -27.03(19)
P(4) Ru(2) C(23) C(22) 84.31(19)	P(4) Ru(2) C(23) C(24) -23.8(2)
P(4) Ru(2) C(23) C(25) -161.2(2)	C(23) Ru(2) P(4) C(30) 177.68(18)
C(23) Ru(2) P(4) C(31) 59.63(19)	C(23) Ru(2) P(4) C(32) -65.15(19)
O(5) Ru(2) C(17) C(18) 66.7(2)	C(17) Ru(2) O(5) C(19) -65.2(2)
O(5) Ru(2) C(18) C(17) -97.1(2)	O(5) Ru(2) C(18) C(19) 20.87(19)
O(5) Ru(2) C(18) C(20) 144.6(4)	C(18) Ru(2) O(5) C(19) -24.1(2)
O(5) Ru(2) C(22) C(23) 97.05(19)	C(22) Ru(2) O(5) C(19) 76.7(2)
O(5) Ru(2) C(23) C(22) -82.3(2)	O(5) Ru(2) C(23) C(24) 169.6(2)
O(5) Ru(2) C(23) C(25) 32.2(2)	C(23) Ru(2) O(5) C(19) 114.6(2)
C(17) Ru(2) C(18) C(19) 118.0(3)	C(17) Ru(2) C(18) C(20) -118.3(4)
C(17) Ru(2) C(22) C(23) 157.5(2)	C(22) Ru(2) C(17) C(18) 1.6(3)
C(17) Ru(2) C(23) C(22) -81.5(5)	C(17) Ru(2) C(23) C(24) 170.3(4)
C(17) Ru(2) C(23) C(25) 32.9(6)	C(23) Ru(2) C(17) C(18) 65.9(5)
C(18) Ru(2) C(22) C(23) 158.6(2)	C(22) Ru(2) C(18) C(17) -178.9(2)
C(22) Ru(2) C(18) C(19) -60.9(2)	C(22) Ru(2) C(18) C(20) 62.8(3)
C(18) Ru(2) C(23) C(22) -29.5(2)	C(18) Ru(2) C(23) C(24) -137.6(2)
C(18) Ru(2) C(23) C(25) 85.0(2)	C(23) Ru(2) C(18) C(17) -161.0(2)
C(23) Ru(2) C(18) C(19) -43.0(2)	C(23) Ru(2) C(18) C(20) 80.7(4)
C(22) Ru(2) C(23) C(24) -108.1(3)	C(22) Ru(2) C(23) C(25) 114.4(3)
Ru(1) O(1) C(3) O(2) -141.1(3)	Ru(1) O(1) C(3) C(2) 36.1(3)

Table S6. continued

C(5) O(2) C(3) O(1) -0.3(6)	C(5) O(2) C(3) C(2) -177.6(4)
C(10) O(4) C(8) O(3) -0.0(5)	C(10) O(4) C(8) C(7) -177.7(3)
Ru(2) O(5) C(19) O(6) -138.0(3)	Ru(2) O(5) C(19) C(18) 39.2(3)
C(21) O(6) C(19) O(5) -0.2(4)	C(21) O(6) C(19) C(18) -177.4(3)
C(26) O(8) C(24) O(7) -0.6(6)	C(26) O(8) C(24) C(23) -178.1(4)
Ru(1) C(1) C(2) C(3) -72.6(2)	Ru(1) C(1) C(2) C(4) 124.6(3)
Ru(1) C(2) C(3) O(1) -38.9(3)	Ru(1) C(2) C(3) O(2) 138.4(3)
C(1) C(2) C(3) O(1) 24.7(5)	C(1) C(2) C(3) O(2) -158.0(3)
C(4) C(2) C(3) O(1) -171.6(3)	C(4) C(2) C(3) O(2) 5.7(5)
Ru(1) C(6) C(7) C(8) 111.5(3)	Ru(1) C(6) C(7) C(9) -103.4(3)
Ru(1) C(7) C(8) O(3) 65.7(5)	Ru(1) C(7) C(8) O(4) -116.8(3)
C(6) C(7) C(8) O(3) -11.1(6)	C(6) C(7) C(8) O(4) 166.3(3)
C(9) C(7) C(8) O(3) -156.9(4)	C(9) C(7) C(8) O(4) 20.6(5)
Ru(2) C(17) C(18) C(19) -71.2(2)	Ru(2) C(17) C(18) C(20) 124.7(3)
Ru(2) C(18) C(19) O(5) -42.3(3)	Ru(2) C(18) C(19) O(6) 134.9(3)
C(17) C(18) C(19) O(5) 20.8(4)	C(17) C(18) C(19) O(6) -161.9(3)
C(20) C(18) C(19) O(5) -174.4(3)	C(20) C(18) C(19) O(6) 2.9(5)
Ru(2) C(22) C(23) C(24) 110.9(2)	Ru(2) C(22) C(23) C(25) -103.3(2)
Ru(2) C(23) C(24) O(7) 66.0(5)	Ru(2) C(23) C(24) O(8) -116.6(2)
C(22) C(23) C(24) O(7) -10.8(5)	C(22) C(23) C(24) O(8) 166.5(3)
C(25) C(23) C(24) O(7) -158.1(4)	C(25) C(23) C(24) O(8) 19.2(4)

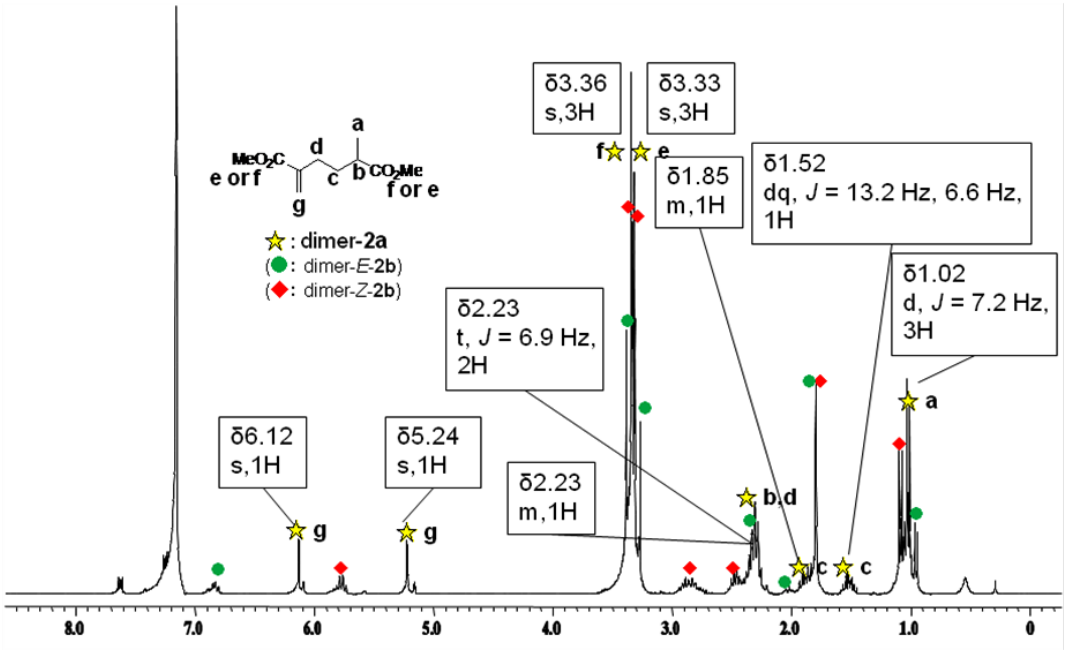


Figure S1. ^{1}H NMR spectrum for a mixture of **2a**, *Z*-**2b** and *E*-**2b** (**2a**/*Z*-**2b**/*E*-**2b** = 55/27/18) (300 MHz, benzene-d_6).

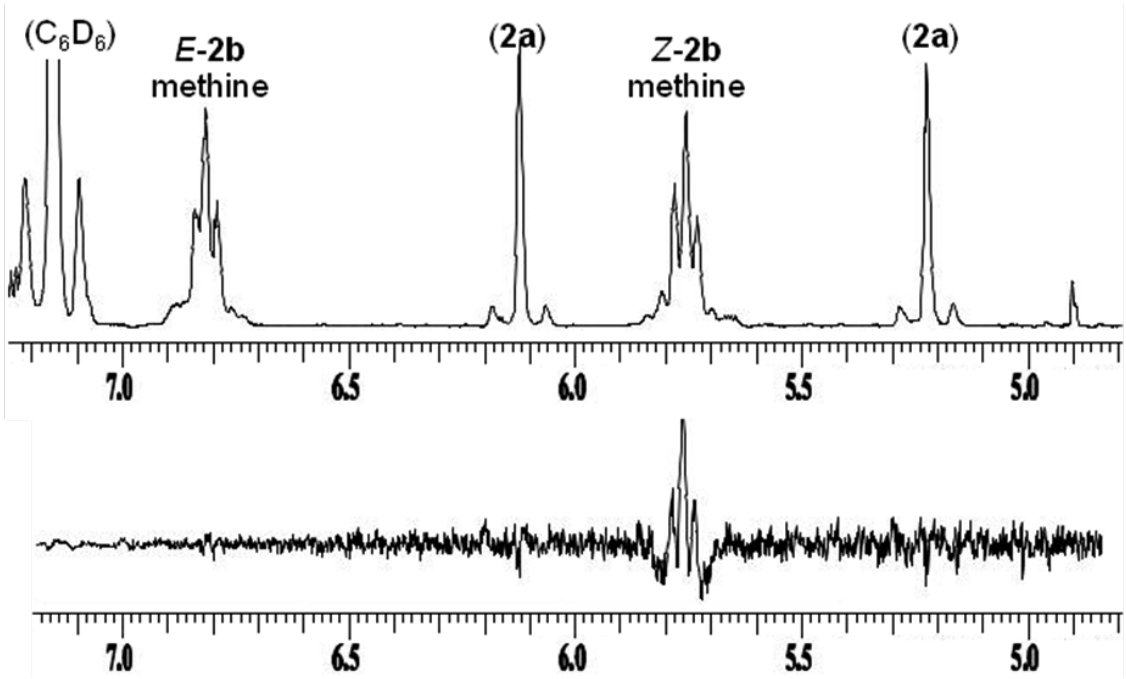


Figure S2. ^{1}H NMR and differential NOE (irradiated frequency 130181.67 Hz (δ1.76, -Me group)) spectrum of a mixture of **2a**, *Z*-**2b** and *E*-**2b** (**2a**/*Z*-**2b**/*E*-**2b** = 21/39/40) (300 MHz, benzene-d_6).

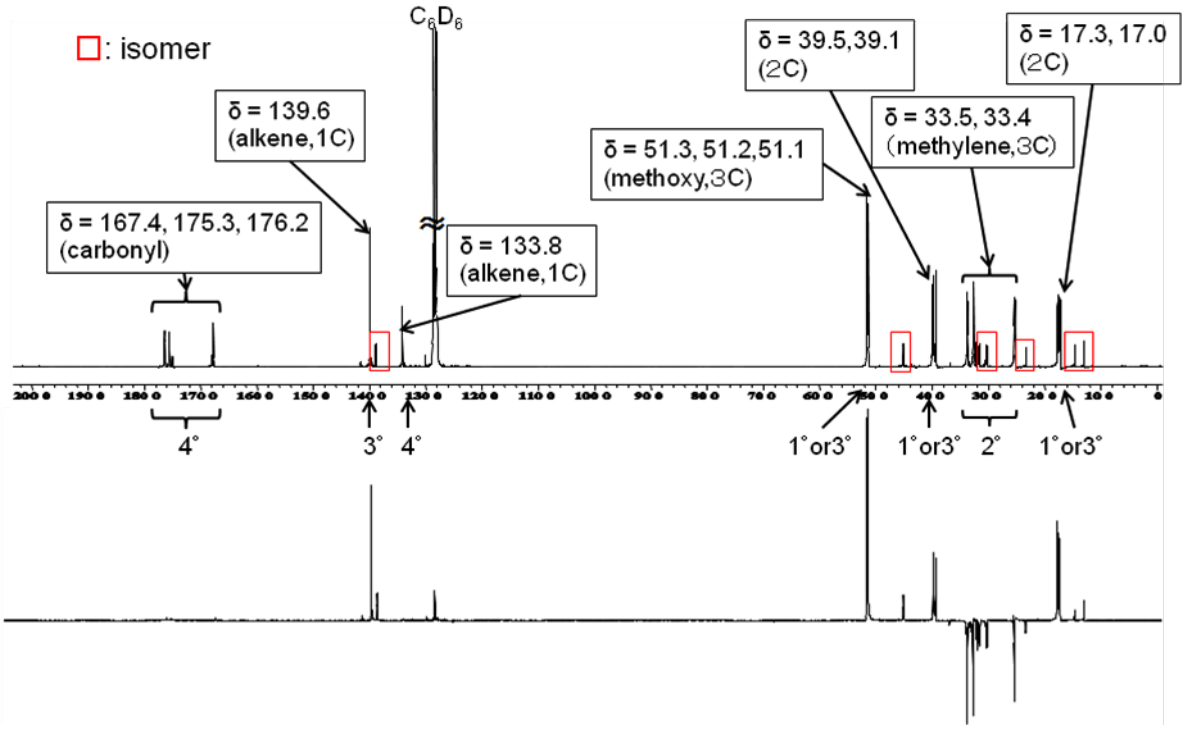


Figure S3. DEPT135 NMR spectrum of *E*-**3a** in benzene-d_6. The signals in red square are due to the unidentified trimers.

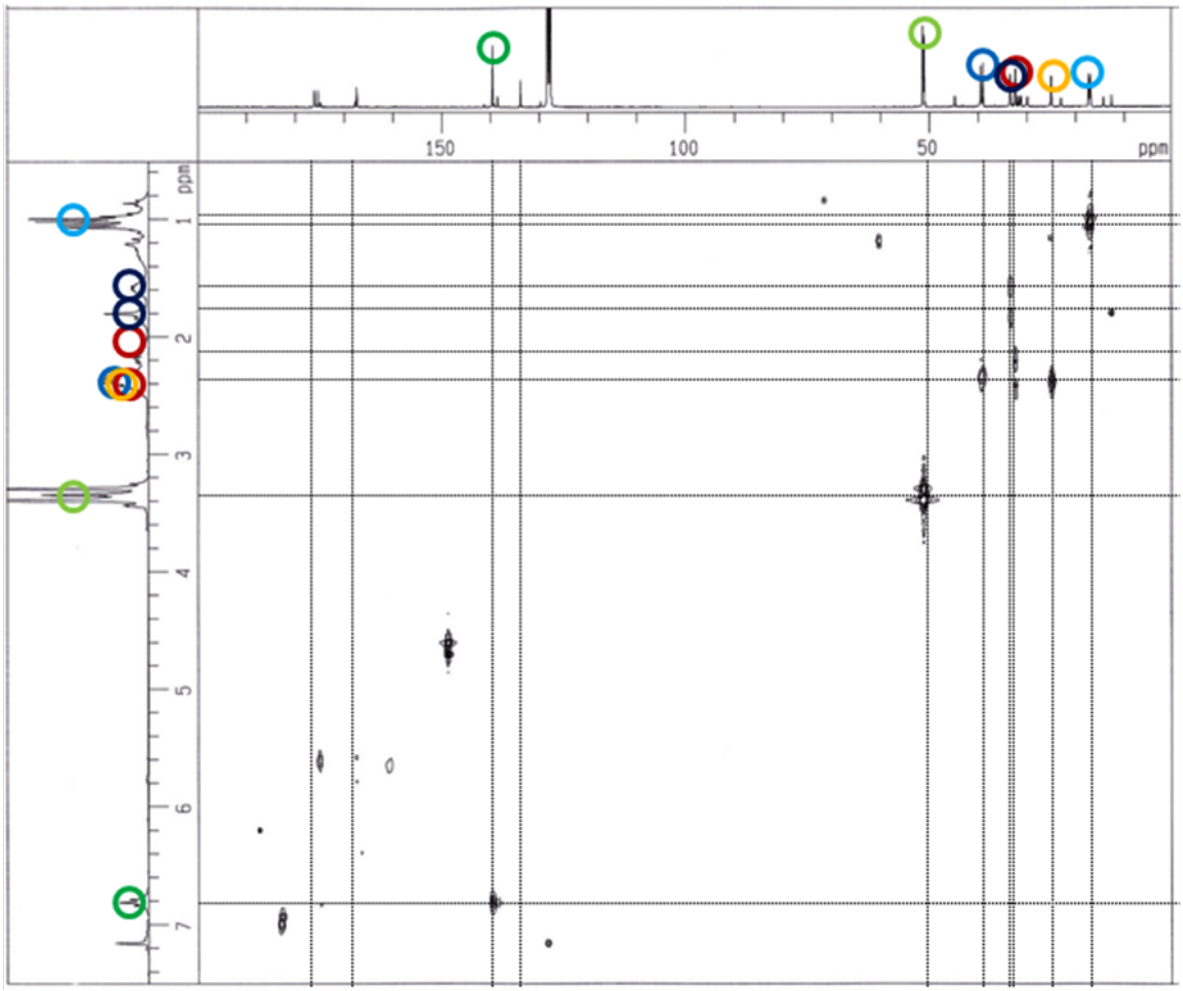


Figure S4. C-H hetero-correlation spectrum of *E*-**3a** in benzene-d_6.

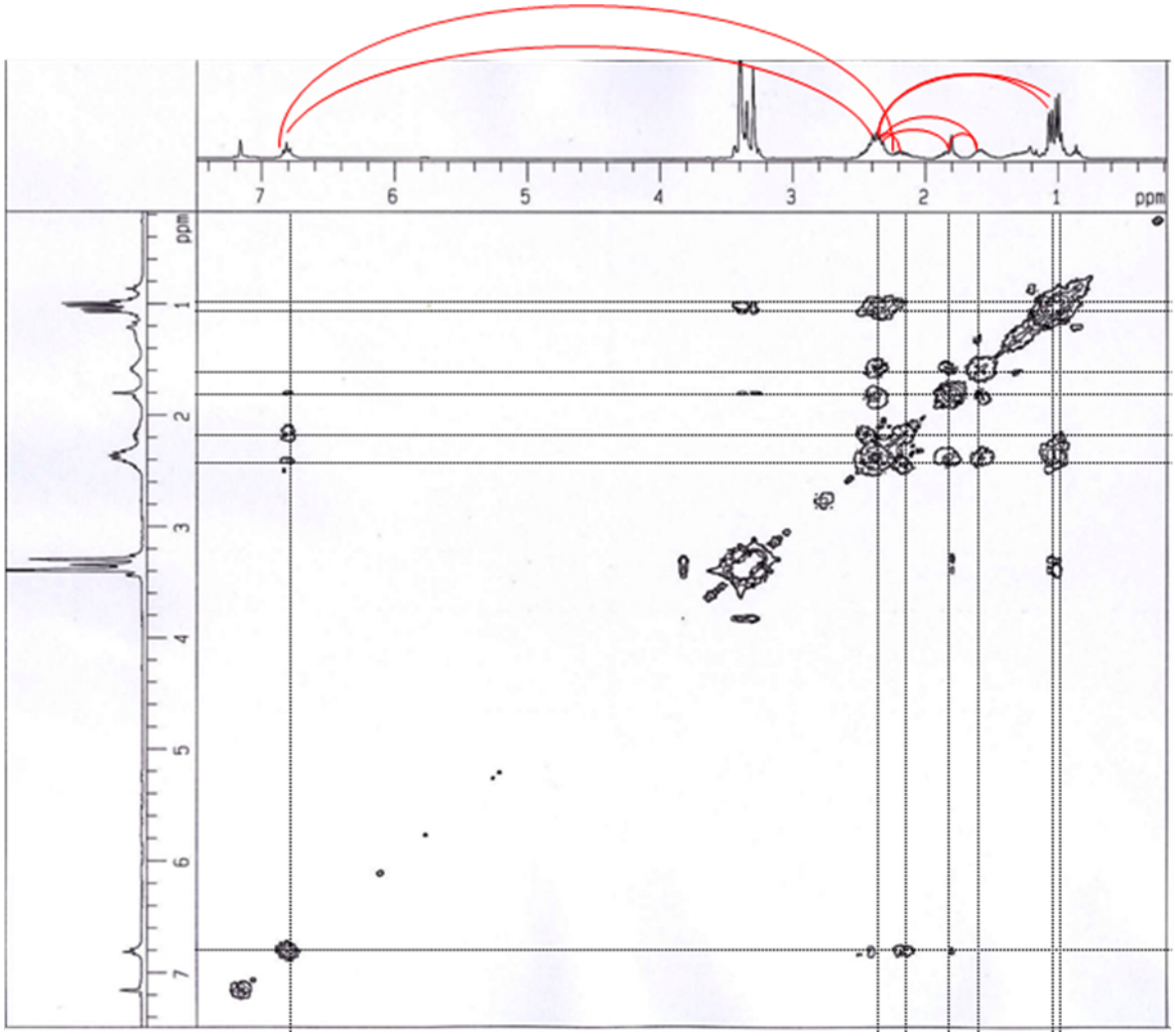


Figure S5. H-H COSY of *E*-**3a** in benzene-d_6.

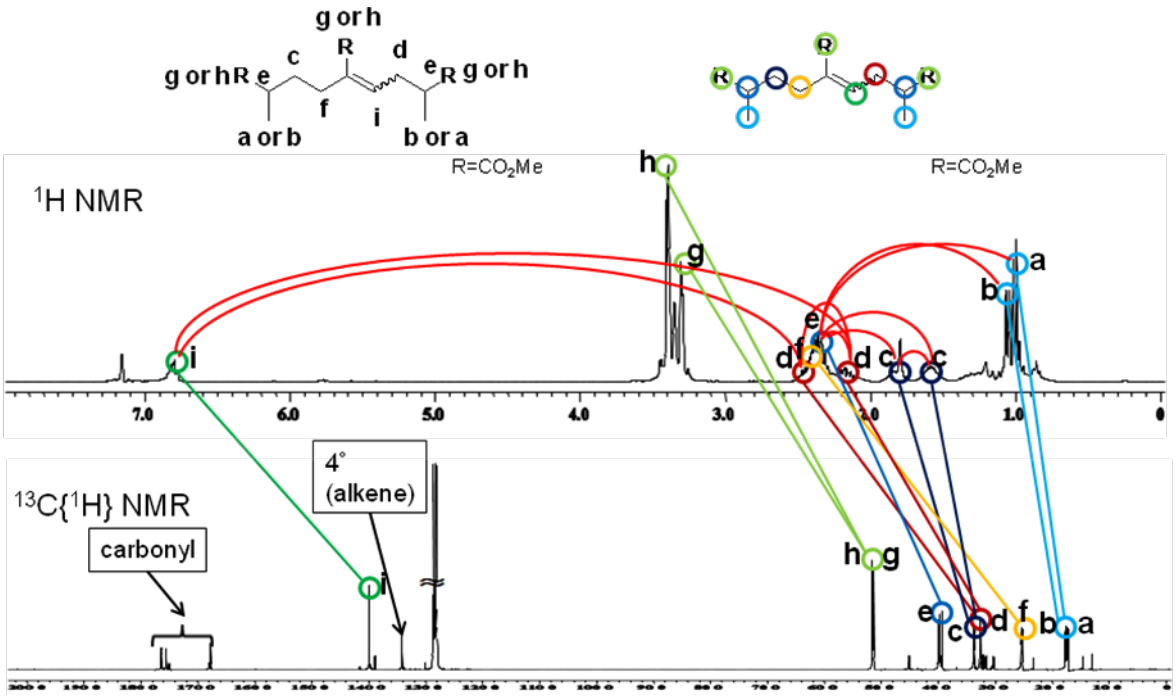


Figure S6. Assignment of signals in the ^{1}H and ^{13}C NMR spectra for *E*-**3a**.

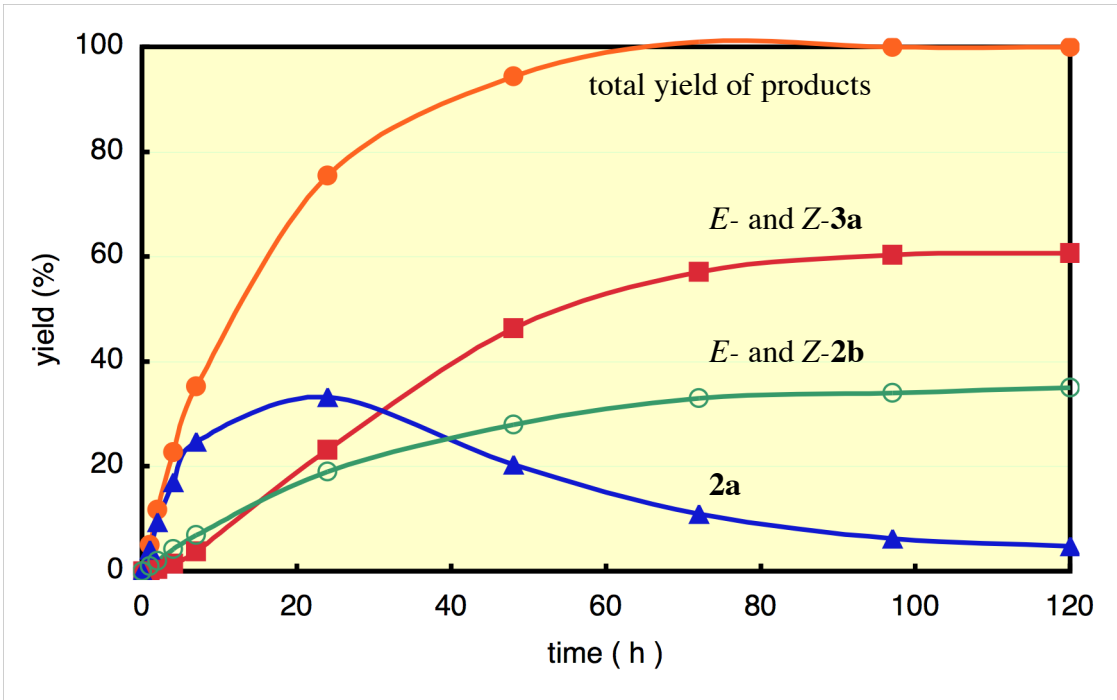


Figure S7. Time-yield curves for the dimerization and trimerization of methyl methacrylate promoted **1** in the presence of **1** (1 mol%) at 0 ˚C without use of solvent in the absence of MeCN.

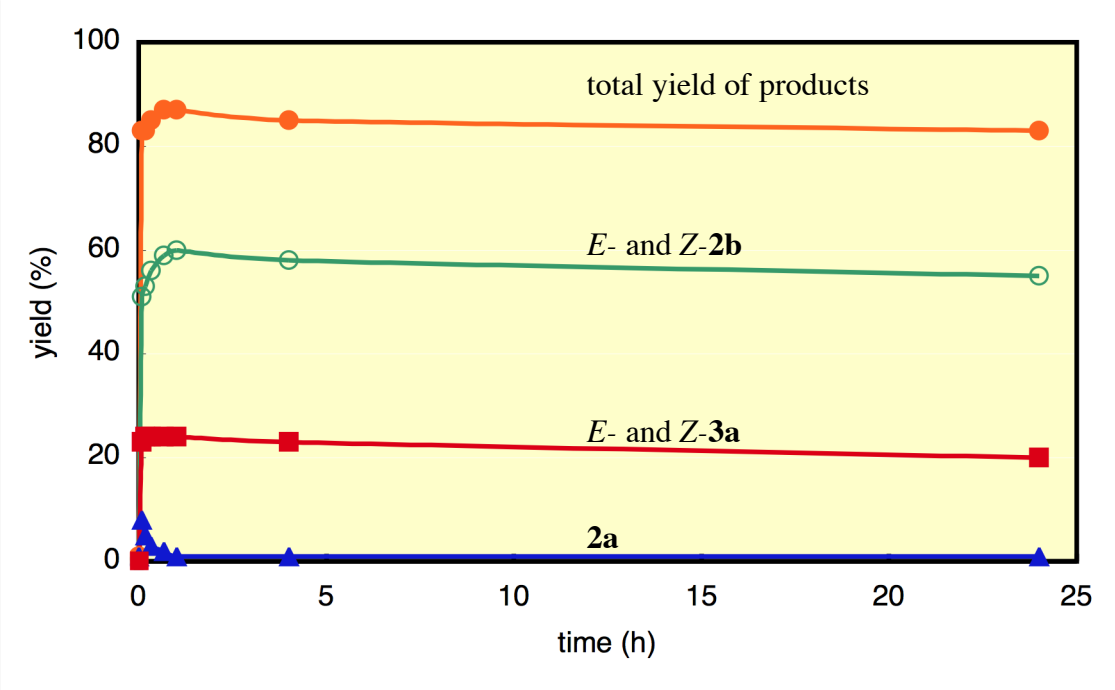
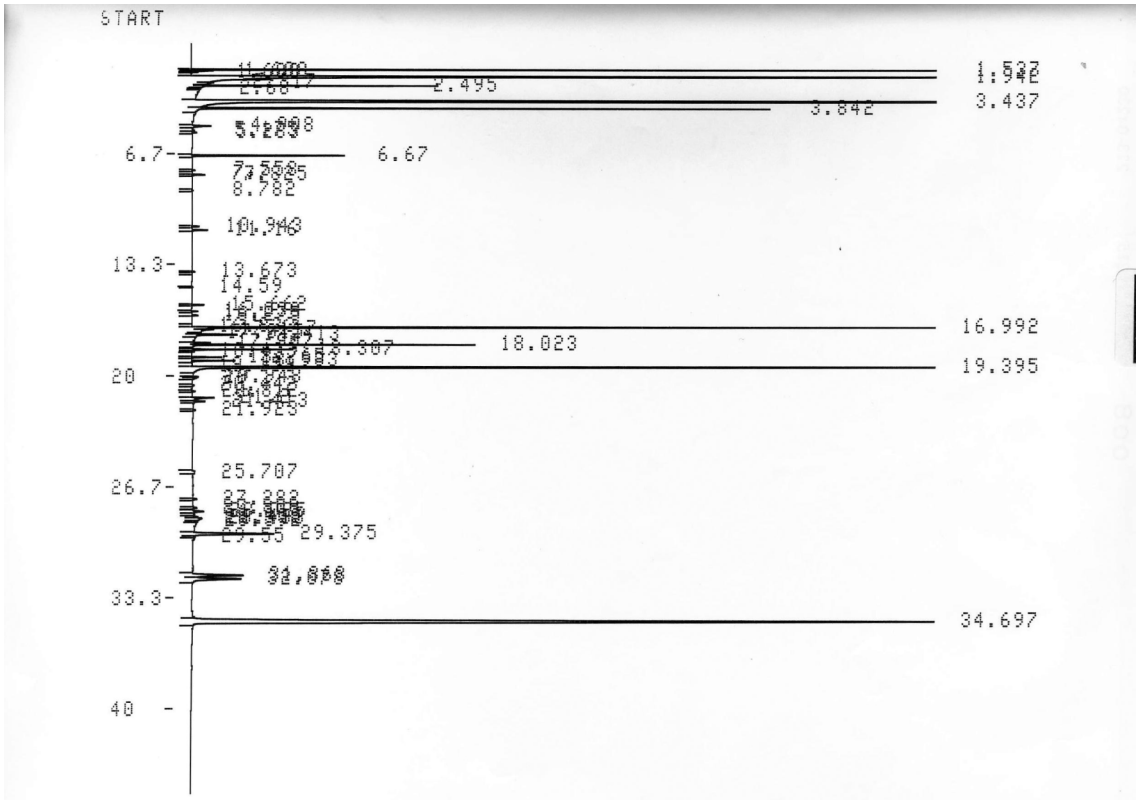


Figure S8. Time-yield curves for the dimerization and trimerization of methyl methacrylate promoted **1** in the presence of **1** (1 mol%) at 70 ˚C without use of solvent in the absence of MeCN.



CHROMATOPAC C-R6A FILE 6
SAMPLE NO 0 METHOD 461
REPORT NO 11114

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.537	2696			0.6982	
2	1.942	343902	S		89.059	
3	2.495	428	T		0.1108	
4	3.437	8945			2.3165	
5	3.842	1624	V		0.4205	
6	4.908	87			0.0225	
7	6.67	481			0.1245	
8	16.992	6191			1.6033	
9	17.117	186	V		0.0481	
10	17.413	211	V		0.0545	
11	17.907	98			0.0254	
12	18.023	672	V		0.1741	
13	18.307	247			0.0639	
14	18.765	85			0.0219	
15	18.983	115	V		0.0298	
16	19.395	10856			2.8114	
17	21.2	102			0.0265	
18	28.025	59			0.0153	
19	28.433	71	V		0.0183	
20	29.375	604			0.1564	
21	31.868	409			0.1059	
22	32.078	416	V		0.1077	
23	34.697	7667			1.9855	
	TOTAL	386151			100	

Figure S9. Typical GLC chart for the dimerization of MMA by **1** (10 mol%) at 70 ˚C for 4 h in the presence of MeCN (100 mol%). 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.

Table S7. Retention time and the assignment for **Figure S9**..

retention time (min)	assignment
1.537	hexane
1.942	acetone as solvent for GLC injection
2.495	methyl isobutyrate
3.437	MMA and MeCN
3.842	unknown compound
6.67	1,5-COD
16.992	naphthalene
18.023	*Z*-**2b**
18.307	**2a**
19.395	*E*-**2b**
28.025	*Z*-**3a**
29.375	*E*-**3a**
31.868	**3x** (unidentified trimer)
32.078	**3x** (unidentified trimer)
34.697	triphenylmethane as an internal standard

References

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

(2) Rigaku Amricas and Rigaku Corporation (2007). CrystalStructure (verion 3.8). Single Crystal Structure Analysis Software. Rigaku Americas, 9009 TX, USA 77381-5209. Rigaku, Tokyo 196-8666, Japan.

(3) G. M. Sheldrick, SHELXL97, A program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

(4) McKinney and Colton reported dimerization of methyl acrylate by this system: McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080.