Electronic Supplementary Information (ESI) 1

Synthesis of Ru complex (B)[7, 66]

Preparation of $H_2NCH_2CH_2NHSO_2C_8H_7$

A CH_2Cl_2 solution (15 mL) of 4-vinylbenzensulfonyl chloride (5 mL) was dropped into 5 mL of ethylene diamine dissolved in 10 mL of CH_2Cl_2, and the mixture was stirred for 3 h. CH_2Cl_2 (200 mL), H_2O (100 mL), and HCl/ H_2O (2 M, 200 mL) were added to the solution, and the water layer was washed with CH_2Cl_2 twice. After filtration, the water layer was neutralized by KOH solution (2 M, pH 9-10) and extracted with 150 mL of CH_2Cl_2 three times. The organic layers were dried with Na_2SO_4, and filtrated, and the solvents were evaporated. ^{1}H NHR (400 MHz, $CDCl_3$, 298 K): δ in ppm = 2.80 (m, 2H; CH_2), 2.97 (m, 2H; CH_2), 5.43 (d, 1H; CH=CH_2), 5.87 (d, 1H; CH=CH_2), 6.75 (dd, 2H; CH=CH_2), 7.52 (d, 2H; C_6H_4), 7.82 (d, 2H; C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ in ppm = 40.92, 45.40 (NCH_2), 117.33, 126.76, 127.38, 135.36, 138.76, 141.74 (C_6H_4-CH=CH_2).

Synthesis of Ru precursor [(*p*-cymene)Ru{$H_2NCH_2CH_2NSO_2C_8H_7$}Cl]

$H_2NCH_2CH_2NHSO_2C_8H_7$ (226 mg, 1 mmol) dissolved in CH_2Cl_2/CH_3OH (1/1, 15 mL) and $NaOCH_3$ (1 mmol) in CH_3OH (0.5 mL) were slowly added to a CH_2Cl_2 solution (20 mL) of Ru_2(*p*-cymene)$_2Cl_4$ (306 mg, 0.5 mmol). The mixture was stirred for 3 h under N_2 atmosphere, and then the solvent was evaporated. The residue was dissolved in CH_2Cl_2/Et_2O (2/1, 30 mL), and after filtration the solution was reduced to 2 mL under vacuum. *n*-Hexane (15 mL) was added, and the precipitate was dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD, 4:1, 298 K): δ in ppm = 1.26 (d, 6H; CH(CH_3)$_2$), 2.15 (s, 3H; CH_3, (*p*-cymene)), 2.30 (brd, 4H; NCH_2), 2.83 (sept, 1H; CH(CH_3)$_2$), 5.29 (d, 1H; CH=CH_2), 5.47 (brd, 2H; CH (*p*-cymene)), 5.62 (d, 2H; CH (*p*-cymene)), 5.79 (d, 1H; CH=CH_2), 6.70 (dd, 1H; CH=CH_2), 7.40 (d, 2H; C_6H_4), 7.81 (d, 2H; C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$/CD_3OD, 4:1, 298 K): δ in ppm = 18.56, 22.53 (CH_3, *p*-cymene), 30.76 (CH, *p*-cymene), 47.11, 47.37 (NCH_2), 81.29 (CH, *p*-cymene), 96.66, 102.46 (C, *p*-cymene), 115.57, 126.08, 127.75, 136.24, 139.88, 142.46 (C_6H_4-CH=CH_2).

Synthesis of sulfoxides and sulfones

General procedure for the synthesis of sulfoxides and sulfones

To a solution of 2 g of organic sulfide in CH_2Cl_2 (20 mL), *m*-CPBA (1 and 2 equivalent for the synthesis of sulfoxide and sulfone, respectively) in CH_2Cl_2 (20 mL and 30 mL, respectively) was added slowly at 273 K. After stirring for 3 h at 273 K, an aqueous saturated $NaHCO_3$

solution (10 mL) was added to quench the reaction mixture. It was stirred for another 1 h at room temperature. The aqueous part was separated and extracted with CH_2Cl_2 (20 mL) two times. The combined organic parts were washed with water (50 mL), brine (20 mL × 2) and dried over $MgSO_4$. The crude compound was purified by silica gel column chromatography.

4-Chlorophenyl methyl sulfoxide Eluent: EtOAc; **y**ield: 73 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ in ppm = 2.72 (s, 3H; CH_3), 7.50 (dd, 2H; C_6H_4), 7.59 (dd, 2H; C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ in ppm = 44.04, 124.96, 129.62, 137.17, 144.26.

4-Fluorophenyl methyl sulfoxide Eluent: EtOAc; **y**ield: 76 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ in ppm = 2.72 (d, 3H; CH_3), 7.23 (m, 2H; C_6H_4), 7.66 (m, 2H; C_6H_4). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ in ppm = 44.17, 116.57, 116.80, 125.80, 125.89, 141.16, 141.20, 163.05, 165.55.

Phenyl *p*-tolyl sulfoxide Eluent: hexane/EtOAc (6/4); yield: 86 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ in ppm = 2.36 (s, 3H; CH_3), 7.25 (d, 2H; Ar), 7.44 (m, 3H; Ar), 7.53 (d, 2H; Ar), 7.62 (m, 2H; Ar). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ in ppm = 21.40, 124.69, 124.99, 129.25, 130.02, 130.86, 141.63, 142.49, 145.82.

Phenyl *p*-tolyl sulfone Eluent: hexane/EtOAc (6/4); yield: 82 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ in ppm = 2.39 (s, 3H; CH_3), 7.29 (d, 2H; Ar), 7.51 (m, 3H; Ar), 7.82 (d, 2H; Ar), 7.93 (d, 2H; Ar). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ in ppm = 21.56, 127.50, 127.72, 129.21, 129.91, 132.99, 138.65, 141.99, 144.15.

Benzyl methyl sulfoxide Eluent: EtOAc; yield: 84 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ in ppm = 2.45 (s, 3H; CH_3), 3.92 (d, 1H; CH_2), 4.05 (d, 1H; CH_2), 7.28-7.40 (m, 5H; C_6H_5). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ in ppm = 37.28, 60.30, 128.44, 128.98, 129.66, 130.02.

Allyl phenyl sulfoxide Eluent: hexane/EtOAc (4/6); yield: 96 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ in ppm = 3.55 (m, 2H; CH_2), 5.20 (d, 1H; CH=CH_2), 5.33 (d, 1H; CH=CH_2), 5.65 (m, 1H; CH=CH_2), 7.48-7.62 (m, 5H; C_6H_5). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ in ppm = 60.83, 123.92, 124.36, 125.21, 129.05, 131.13, 142.83.

Electronic Supplementary Information (ESI) 2

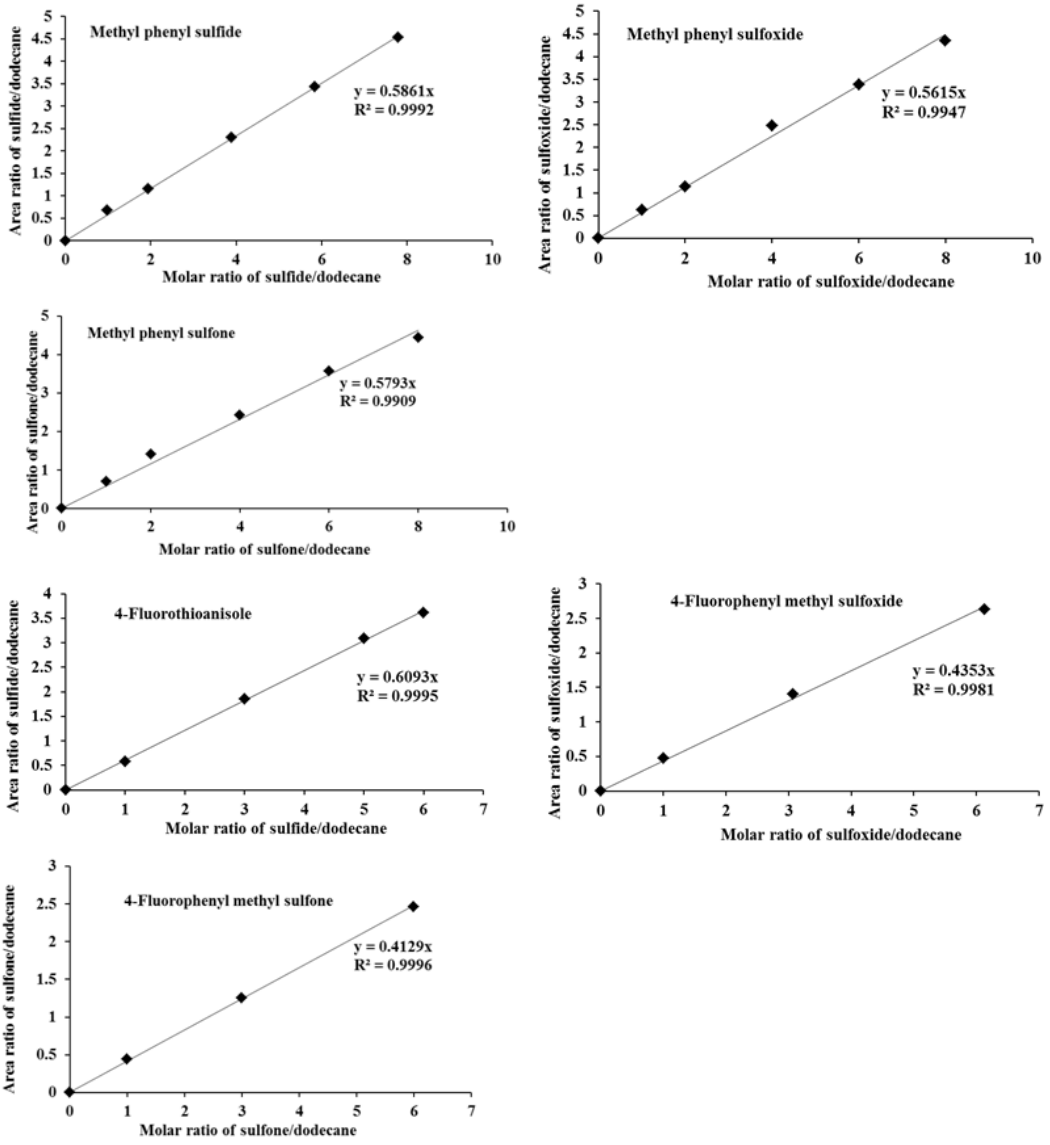
GC analysis

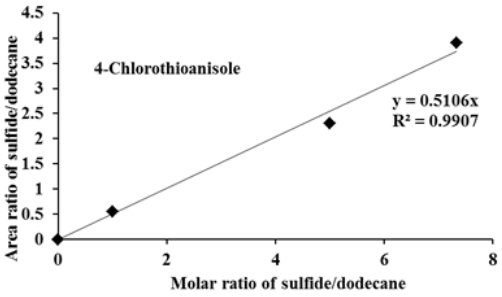
Table SI 1 Detail of GC analysis

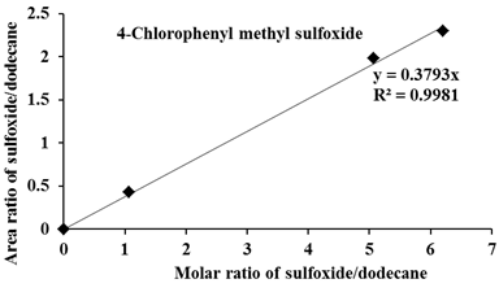
Column temperature programming	Carrier gas	Compound	Retention time /min
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 15 K/min Final temp.: 473 K Final holding time: 5 min Injection temp.: 523 K Detector temp.: 523 K	He Inlet press.: 100 kPa	Methyl phenyl sulfide (MPS) Methyl phenyl sulfoxide (MPSO) Methyl phenyl sulfone ($MPSO_2$) Dodecane EtOAc IBA Propanal 1-hexanal *n*-butanal Benzaldehyde	10.6 13.5 14.2 11.8 3.3 2.7 2.4 6.4 3.3 9.2
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 10 K/min Final temp.: 503 K Final holding time: 3 min Injection temp.: 573 K Detector temp.: 573 K	He Inlet press.: 100 kPa	4-Fluorothioanisole 4-Fluorophenyl methyl sulfoxide 4-Fluorophenyl methyl sulfone IBA Dodecane EtOAc	12.1 16.2 17.0 2.7 14.2 3.3
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 10 K/min Final temp.: 503 K Final holding time: 5 min Injection temp.: 523 K Detector temp.: 523 K	He Inlet press.: 130 kPa	4-Chlorothioanisole 4-Chlorophenyl methyl sulfoxide 4-Chlorophenyl methyl sulfone IBA Dodecane EtOAc	14.7 18.1 18.7 2.2 13.3 2.9
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 10 K/min Final temp.: 503 K Final holding time: 5 min Injection temp.: 523 K Detector temp.: 523 K	He Inlet press.: 130 kPa	Allyl phenyl sulfide Allyl phenyl sulfoxide Allyl phenyl sulfone IBA Dodecane EtOAc	13.6 17.5 18.2 2.1 13.2 2.5

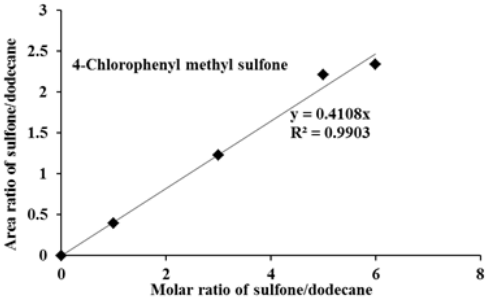
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 10 K/min Final temp.: 473 K Final holding time: 10 min Injection temp.: 523 K Detector temp.: 523 K	He Inlet press.: 130 kPa	Benzyl methyl sulfide Benzyl methyl sulfoxide Benzyl methyl sulfone IBA Dodecane EtOAc	12.8 17.6 18.2 1.9 13.2 2.1
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 15 K/min Final temp.: 473 K Final holding time: 5 min Injection temp.: 523 K Detector temp.: 523 K	He Inlet press.: 100 kPa	Dibutyl sulfide Dibutyl sulfoxide Dibutyl sulfone IBA Dodecane EtOAc	10.5 14.2 14.8 2.7 11.8 3.3
Column initial temp.: 323 K Holding time: 8 min Rate of heating: 10 K/min Final temp.: 503 K Final holding time: 5 min Injection temp.: 523 K Detector temp.: 523 K	He Inlet press.: 130 kPa	Tetrahydrothiophene Tetrahydrothiophene 1-oxide Sulfolane IBA Dodecane EtOAc	7.0 17.2 18.5 2.1 18.2 2.9
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 10 K/min Final temp.: 503 K Final holding time: 5 min Injection temp.: 523 K Detector temp.: 523 K	He Inlet press.: 130 kPa	Diphenyl sulfide Diphenyl sulfoxide Diphenyl sulfone IBA Dodecane EtOAc	19.1 22.9 23.6 2.1 13.1 2.5
Column initial temp.: 323 K Holding time: 3 min Rate of heating: 15 K/min Final temp.: 523 K Final holding time: 5 min Injection temp.: 573 K Detector temp.: 573 K	He Inlet press.: 130 kPa	Phenyl *p*-tolyl sulfide Phenyl *p*-tolyl sulfoxide Phenyl *p*-tolyl sulfone IBA Dodecane EtOAc	16.1 18.8 19.4 2.1 10.9 2.5

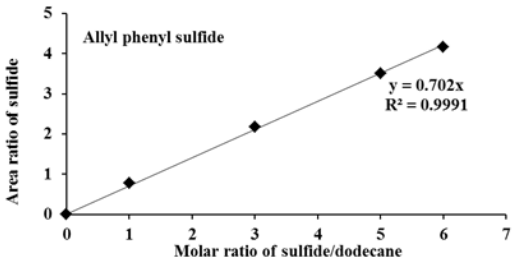
Figure SI 1 Calibration curves of the standard compounds.

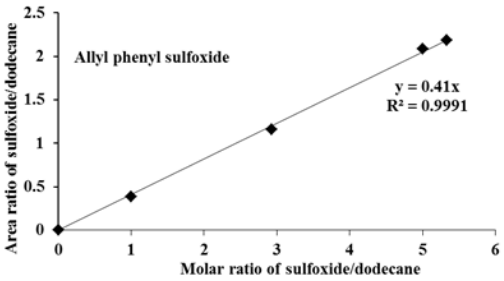


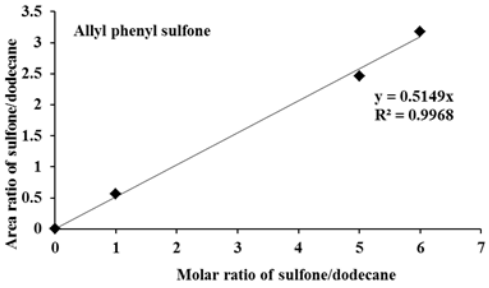


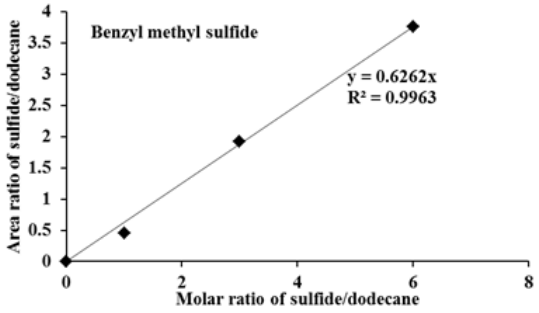


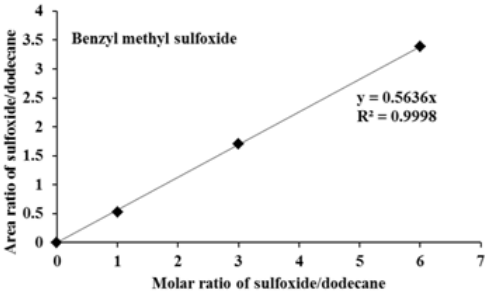


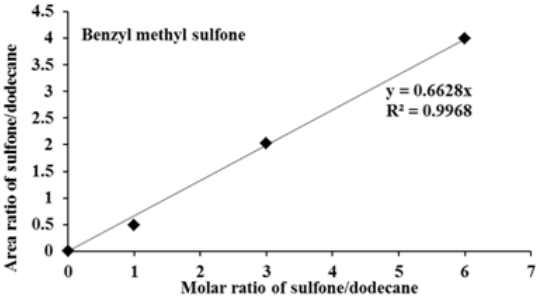


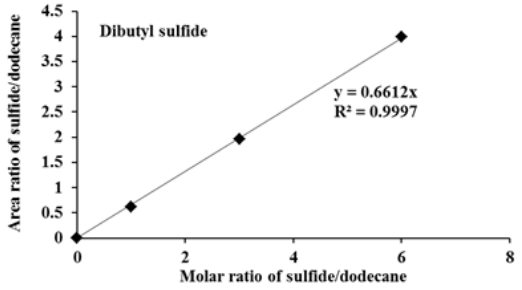


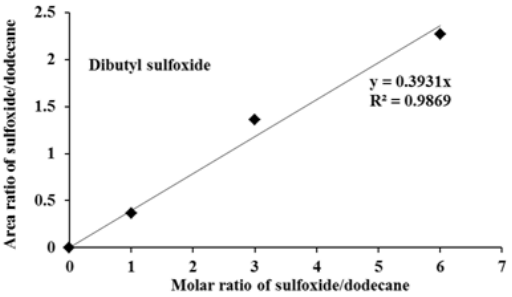


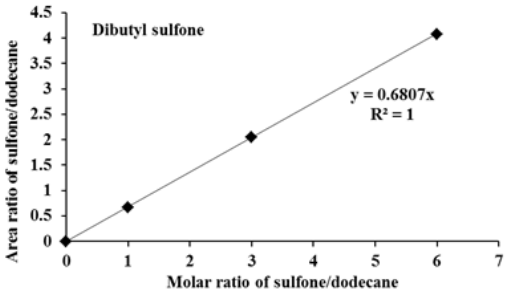


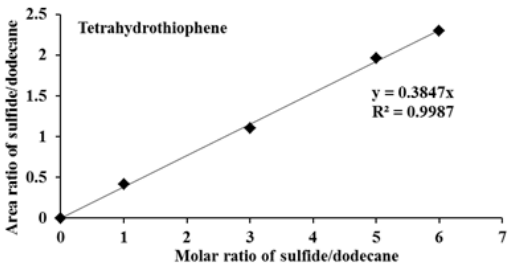


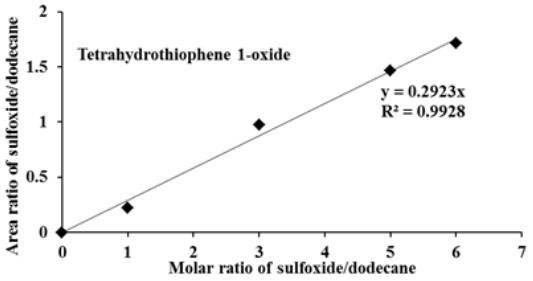


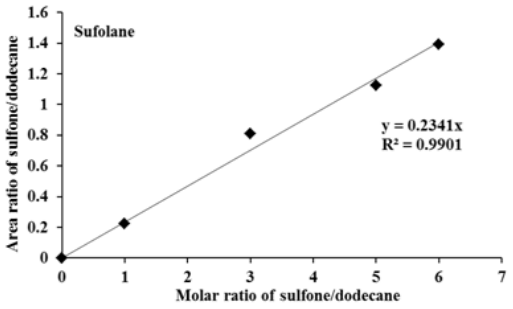


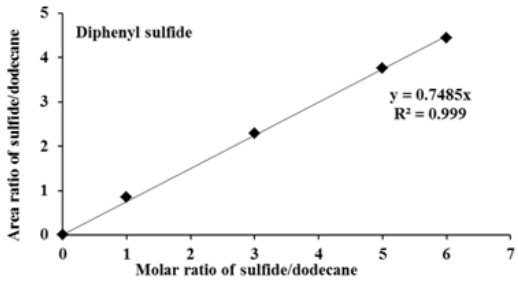


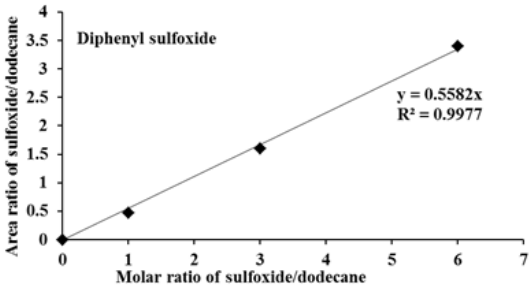


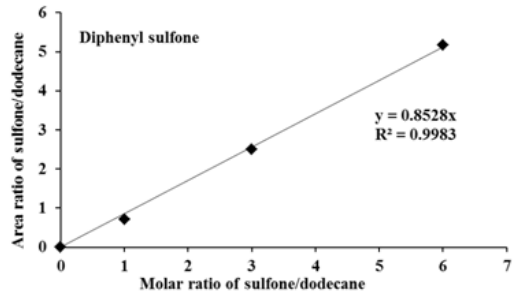


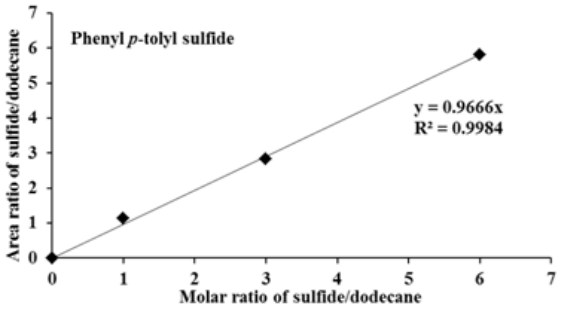


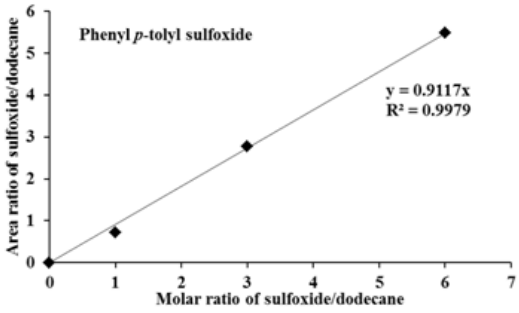


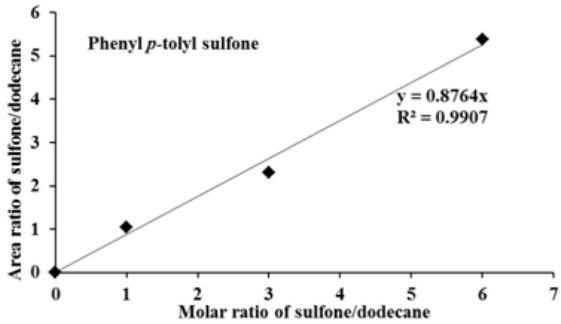


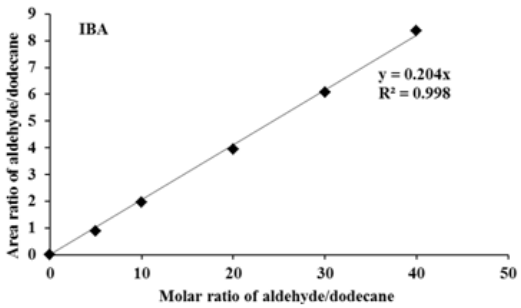


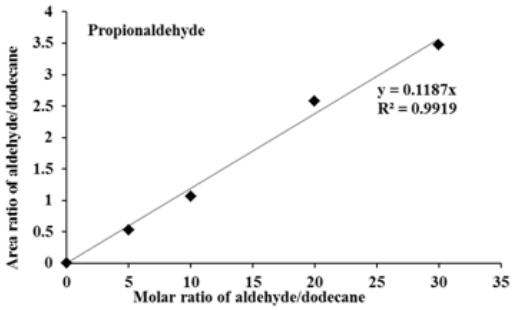


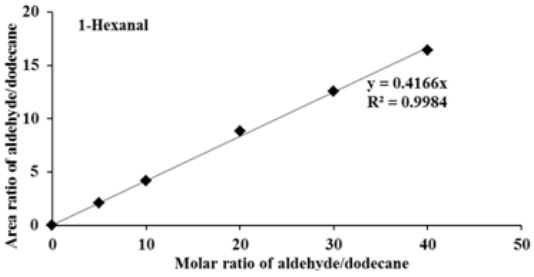












Electronic Supplementary Information (ESI) 3

Characterization

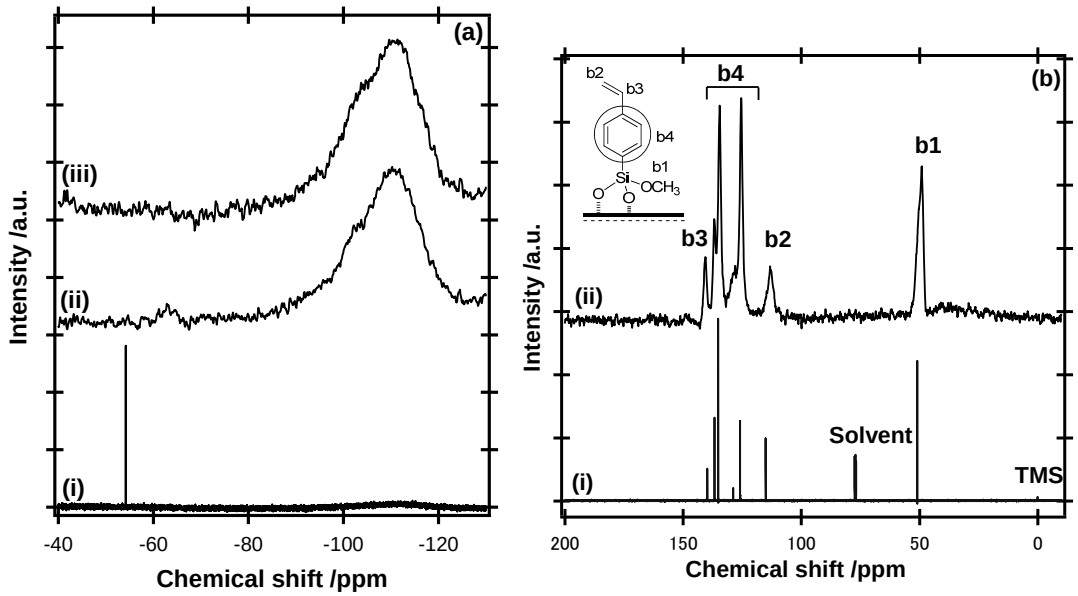


Fig. SI 2 (a) ^{29}Si NMR of (i) *p*-styryltrimethoxysilane (liquid-state NMR in $CDCl_3$), (ii) functionalized SiO_2 (Aerosil 300) with *p*-styryltrimethoxysilane (**A**) (solid-state MAS) and (iii) SiO_2 (Aerosil 300) (solid-state MAS). (b) ^{13}C NMR of (i) *p*-styryltrimethoxysilane (liquid-state NMR in $CDCl_3$) and (ii) functionalized SiO_2 (**A**) (solid-state MAS).

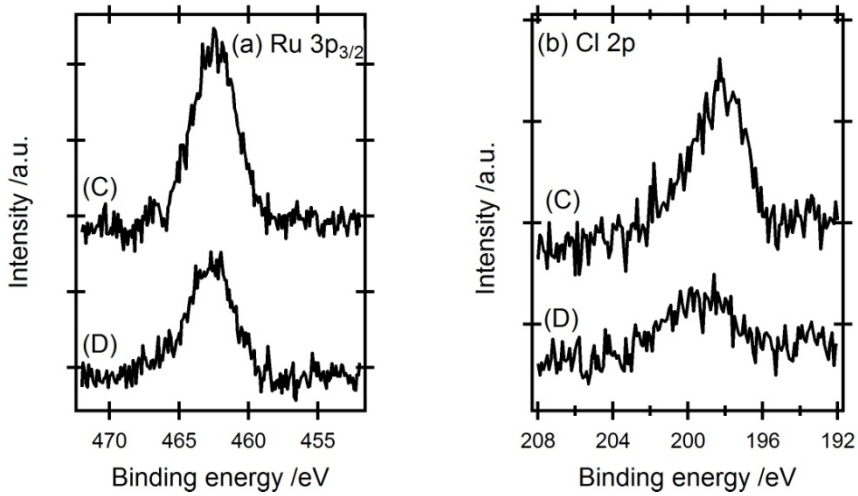


Fig. SI 3 XPS spectra of fresh **C** and **D** (Ru 1.6 wt%). (a) Ru $3p_{3/2}$ and (b) Cl 2p.

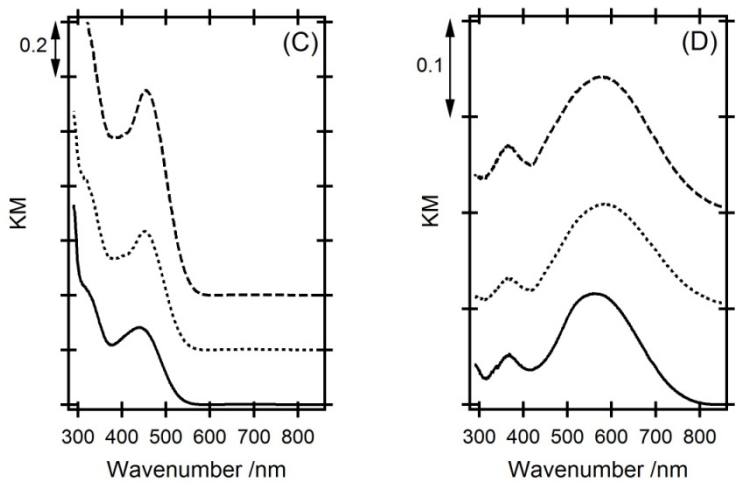
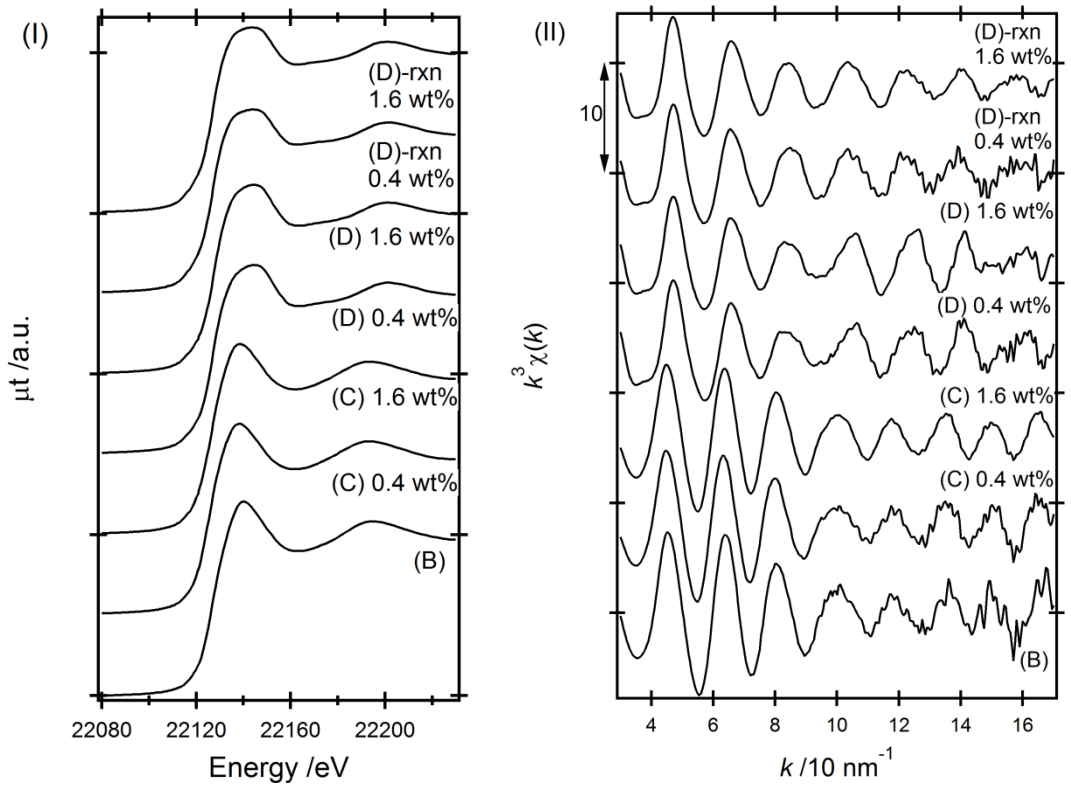


Fig. SI 4 DR-UV/vis spectra of fresh **C** and **D**. Solid line: Ru 0.4 wt%, dotted line: Ru 1.0 wt%, and dashed line: Ru 1.6 wt%.



(III)

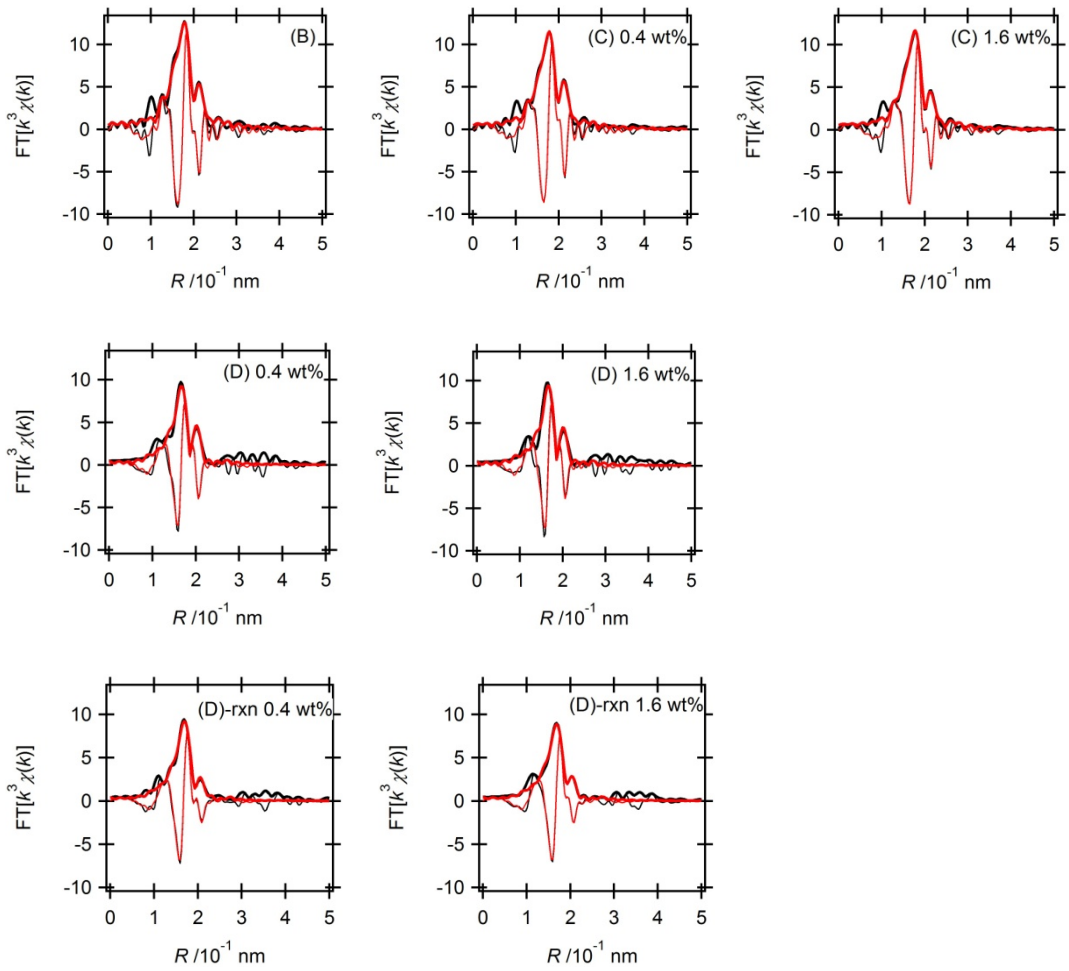


Fig. SI 5 Ru K-edge XANES spectra (I), EXAFS oscillations (II), and their EXAFS Fourier transforms (III) of **B**, **C**, **D**, and **D**-rxn measured at 20 K.

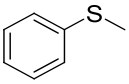
Table SI 2 Curve-fitting results of Ru K-edge EXAFS Fourier transforms of **C** and **D** (Ru 0.4 wt% and 1.6 wt%)

Shell	CN	Distance /nm	ΔE_0 /eV	σ^2 /nm^2
B k = 30-170 nm^{-1}, R = 0.115-0.25 nm, R_f = 1.0%				
Ru-N	2.0	0.208 ± 0.002	8 ± 5	(0.7 ± 2.3)×10^{-6}
Ru-C	6.0	0.219 ± 0.002	-1 ± 3	(1 ± 1)×10^{-5}
Ru-Cl	1.0	0.242 ± 0.003	8 ± 8	(2 ± 1)×10^{-5}
B k = 30-170 nm^{-1}, R = 0.115-0.25 nm, R_f = 1.0%				
Ru-N	1.9 ± 1.0	0.208 ± 0.003	8 ± 10	0.7×10^{-6}
Ru-C	5.9 ± 2.4	0.219 ± 0.002	-1 ± 6	1×10^{-5}
Ru-Cl	1.0 ± 0.2	0.242 ± 0.003	8 ± 10	2×10^{-5}
C 1.6 wt% k = 30-170 nm^{-1}, R = 0.115-0.25 nm, R_f = 0.5%				
Ru-N	2.0 ± 0.8	0.210 ± 0.002	4 ± 12	0.7×10^{-6}
Ru-C	4.5 ± 1.5	0.221 ± 0.002	2 ± 9	1×10^{-5}
Ru-Cl	0.8 ± 0.1	0.245 ± 0.002	10 ± 5	2×10^{-5}
C 0.4 wt% k = 30-170 nm^{-1}, R = 0.115-0.25 nm, R_f = 0.6%				
Ru-N	1.9 ± 0.7	0.210 ± 0.002	5 ± 9	0.7×10^{-6}
Ru-C	4.8 ± 1.7	0.221 ± 0.002	0 ± 6	1×10^{-5}
Ru-Cl	1.1 ± 0.2	0.244 ± 0.002	7 ± 6	2×10^{-5}
D 1.6 wt% k = 30-170 nm^{-1}, R = 0.13-0.24 nm, R_f = 1.1%				
Ru-N	2.7 ± 1.2	0.206 ± 0.002	0 ± 4	(2 ± 2)×10^{-5}
Ru-Cl	1.4 ± 1.4	0.235 ± 0.006	5 ± 9	(8 ± 8)×10^{-5}
D 0.4 wt% k = 30-170 nm^{-1}, R = 0.13-0.24 nm, R_f = 1.2%				
Ru-N	3.0 ± 1.1	0.206 ± 0.002	2 ± 4	(2 ± 2)×10^{-5}
Ru-Cl	1.3 ± 1.2	0.236 ± 0.005	6 ± 8	(7 ± 8)×10^{-5}
D-rxn 1.6 wt% k = 30-170 nm^{-1}, R = 0.13-0.24 nm, R_f = 0.3%				
Ru-N	3.4 ± 1.1	0.208 ± 0.002	2 ± 3	(3 ± 1)×10^{-5}
Ru-Cl	1.3 ± 1.2	0.235 ± 0.007	6 ± 9	(10 ± 7)×10^{-5}
D-rxn 0.4 wt% k = 30-170 nm^{-1}, R = 0.13-0.24 nm, R_f = 0.3%				
Ru-N	3.7 ± 0.7	0.208 ± 0.001	2 ± 3	(3 ± 1)×10^{-5}
Ru-Cl	1.4 ± 1.2	0.238 ± 0.007	10 ± 9	(13 ± 8)×10^{-5}

Electronic Supplementary Information (ESI) 4

Sulfoxidation

Table SI 3 MPS oxidation with peracetic acid[a]

Reactant	No catalyst			Catalyst **D**		
	Time /min	Conv. %[b]	MPSO Selectivity %[c]	Time /min	Conv. %[b]	MPSO Selectivity %[c]
	0	0	-	0	0	-
	1	39	97	1	61	>99
	3	52	>99	3	67	98
	5	57	>99	5	70	98

[a] Ru = 1.5×10^{-6} mol, MPS = 1.5×10^{-4} mol, CH_3CO_3H = 1.5×10^{-4} mol, dodecane = 1.5×10^{-4} mol, EtOAc 20 ml, 278 K. [b] MPS conversion % = (initial MPS – final MPS)/(initial MPS)×100. [c] MPSO selectivity % = produced MPSO/(produced MPSO + produced $MPSO_2$)×100.