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Selective Isomerization of Terminal Olefin Catalyzed by a Ruthenium Complex: A Novel Indole Synthesis *via* Ring-Closing Metathesis (RCM).

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Experimental Section

All melting points are uncorrected. Infrared (IR) absorption spectra (cm^{-1}) were recorded using a KBr pellet. ^{1}H NMR (and ^{13}C NMR) spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 400, 500 or 600 MHz, with TMS as an internal standard. Silica gel 60 N (Spherical, neutral, Kanto Chemical Co., Inc.) for column chromatography and E. Merck precoated TLC plates, silica gel $60F_{254}$, for preparative thin layer chromatography were used. The organic layers were dried over anhydrous $MgSO_4$ or Na_2SO_4. Ruthenium carbene catalyst (**A**), **2a** – **2e**, **5a** – **5c**, **5e**, and **5g** were obtained commercially. Compounds **1**,[1] **5d**[2] and **5f**[3] were prepared according to the reported procedures.

*Preparation of **4h-4k***

N-Allyl-*N*-*p*-toluenesulfonyl-2-ethenylaniline (**4h**): To a stirring solution of 2-vinylaniline (500 mg) in pyridine (12.6 mL), was added *p*-toluenesulfonyl chloride (1.2 eq) and the mixture was stirred at rt for 3 h. The reaction was quenched by sat.

$NaHCO_3$ and organic compounds were extracted with Et_2O. Eveporation of the dried solvent gave a crude residue which was subjected to column chromatography (*n*-hexane:AcOEt = 7:1) to give *N*-*p*-toluenesulfonyl-2-ethenylaniline (826 mg, 72%) as colorless needles. To a stirring solution of *N*-*p*-toluenesulfonyl-2-ethenylaniline (779 mg) in CH_3CN (63 mL), added K_2CO_3 (10 eq) and allyl bromide (3.0 eq) and the mixture was stirred at rt for 12h. The reaction was quenched by sat. $NaHCO_3$ and organic compounds were extracted with Et_2O. After evaporation of solvents, the obtaied crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 20:1) to give **4h** (849 mg, 95%) as colorless needles. mp = 65-66 °C (MeOH). ^{1}H-NMR (400 MHz) δ 7.65-7.57 (m, 3H), 7.30-7.25 (m, 3H), 7.15-7.00 (m, 2H), 6.68-6.65 (m, 1H), 5.78-5.65 (m, 2H), 5.31-5.27 (m, 1H), 5.00-4.94 (m, 2H), 4.26 (br s, 1H), 3.98 (br s, 1H), 2.42 (s, 3H). ^{13}C-NMR (100 MHz), δ 143.5, 138.6, 136.7, 136.1, 132.7, 132.4, 129.5, 129.0, 128.5, 127.9, 127.8, 126.0, 119.3, 115.8, 54.8, 21.6. IR (KBr) cm^{-1} 1340, 1157. LR-MS (EI) *m/z* 313 (M^++H). HRMS (FAB) calcd for $C_{18}H_{20}NSO_2$ 314.1215 (M^++1), found 314.1234.

N-Allyl-*N*-toluenesulfonyl-2-ethenyl-4-methoxyaniline (**4i**): To a solution of 5-methoxy-2-nitrobenzoic acid (5.05 g, 25.6 mmol) in EtOH (100 mL), was added 5% palladium on charcoal (105 mg) and the mixture was stirred under hydrogen atmosphere at room temperature for 12 h. After the starting material was disappeared on TLC, the solution was filtrated through a celite pad and the filtrate was concentrated to give 4.00 g (97%) of 3-methoxyanthranilic acid**.** To a solution of 3-methoxyanthranilic acid (15.0 g, 89.7 mmol) in dimethoxypropane (550 mL, 16 eq) was added 36% hydrochloric acid

(79.0 mL). The mixture was stirred at room temperature for 12 h and quenched by addition of $NaHCO_3$. The product was extracted with AcOEt (3 x 1000 mL), and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane: AcOEt = 3:1) on silica gel 60 (120 g) to give 5.20 g (32%) of 3-methoxyanthranilic acid methylester. To a solution of 3-methoxyanthranilic acid methylester (100 mg, 0.55 mmol) in CH_2Cl_2 (4.00 mL) under Ar atmosphere, were added pyridine (0.13 mL, 1.65 mmol, 3 eq) and TsCl (1.30 mmol, 1.2 eq). The mixture was stirred at room temperature for 1 h. and quenched by the addition of water. The mixture was extracted with AcOEt (3 x 50 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 5:1) on silica gel 60 (6 g) to give 150 mg (82%) of *N*-toluenesulfonyl-3-methoxyanthranilic acid methylester**.** To a cooled (-78 °C) solution of *N*-toluenesulfonyl-3-methoxyanthranilic acid methylester (5.50 g, 16.4 mmol) in toluene (120 mL) under Ar atmosphere, was added DIBAL (1 M toluene solution, 54.1 mmol, 3.3 eq). The mixture was stirred at –78 °C for 1 h and the reaction was quenched by the addition of MeOH and Rochelle's salt. Then the solution was allowed to stir at room temperature until separation of organic and water layers. The mixture was extracted with AcOEt (3 x 100 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 5:1) on silica gel 60 (55 g) to give 4.57 g (91%) of *N*-toluenesulfonyl-2-hydroxy-4-methylmethoxyaniline**.** To a solution of *N*-toluenesulfonyl-2-hydroxy-4-methylmethoxyaniline (80.0 mg, 0.24 mmol) in benzene (10.0 mL), was added MnO_2 (0.51 g, 0.58 mmol, 2.4 eq). The mixture was

refluxed for 4 h and filtered through a celite pad. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 5:1) on silica gel 60 (4 g) to give 70.0 mg (91%) of *N*-toluenesulfonyl-2-formyl-4-methoxyaniline. To a mixture of *N*-toluenesulfonyl-2-formyl-4-methoxyaniline (100 mg, 0.33 mmol) and K_2CO_3 (70.0 mg, 0.50 mmol, 1.5 eq) in DMF (10.0 mL) under Ar atmosphere, was added allyl bromide (0.04 mL, 0.50 mmol, 1.5 eq). The mixture was stirred at 80 °C for 1 h and the reaction was quenched by addition of $NaHCO_3$. The mixture was extracted with Et_2O (3x30 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 3:1) on silica gel 60 (3 g) to give 110 mg (97%) of *N*-allyl-*N*-toluenesulfonyl-2-formyl-4-methoxyaniline**.** To a cooled (-78 °C) solution of $BrPh_3PMe$ (34.0 mg, 0.96 mmol, 3 eq) in THF (5.00 mL) under Ar atmosphere, was added $KN(TMS)_2$ (0.5 M in THF solutuion 1.91 mL, 0.96 mmol, 3 eq). The mixture was stirred at –78 °C for 15 min. To this mixture, was added *N*-allyl-*N*-toluenesulfonyl-2-formyl-4-methoxyaniline (110 mg, 0.32 mmol) and the solution was warmed to room temperature for 1 h. The reaction was quenched by addition of sat. NH_4Cl. The mixture was extracted with AcOEt (3x30 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 10:1) on silica gel 60 (3 g) to give 110 mg (98%) of **4i** as yellow oil. ^{1}H-NMR (400 MHz) : δ 7.36 (2H, d, *J* = 2.0 Hz), 7.20 (2H, d, *J* = 2.0 Hz), 7.16 (1H, d, *J* = 2.2 Hz), 7.14 (1H, d, *J* = 0.8 Hz), 6.67 (1H, dd, *J* = 0.8, 2.2 Hz), 5.79-5.81 (1H, m), 5.75-5.58 (1H, m), 5.16 (2H, d,*J* = 2.0 Hz), 5.02 (2H, d, J = 2.5 Hz), 4.93 (2H, d, *J* = 1.9 Hz), 3.80 (3H, s),

2.33 (3H, s); 13C-NMR (100 MHz, CDCl3) : δ 159.2, 152.0, 143.4, 139.7, 136.1, 132.8, 132.5, 130.1, 129.4, 127.8, 119.2, 115.8, 113.9, 110.3, 55.3, 54.9, 21.5; IR (neat) cm^{-1} : 3091, 3012, 2837, 1603, 1571; LRMS (FAB) : *m/z* 343 (M^++H, 10%), 188 (100%); HRMS (FAB) : calcd for $C_{19}H_{22}NO_3S$ (M^++H) ; 344.1242, found 344.1342; Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.45 ; H, 6.16; N, 4.08, found : C, 66.31; H,6.09; N , 3.93.

N-Allyl-*N*-toluenesulfonyl-2-ethenyl-4,5,6-trimethoxyaniline (**4j**): To a solution of ester 3,4,5-trimethoxyanthranilic acid methylester (724 mg, 3.00 mmol) in CH_2Cl_2 (3.00 mL) under Ar atmosphere, were added pyridine (0.485 mL, 6.00 mmol, 2 eq) and TsCl (3.60 mmol, 1.2 eq). The mixture was stirred at room temperature for 1 h. and quenched by the addition of water. The mixture was extracted with AcOEt (3 x 50 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 5:1) on silica gel 60 (5 g) to give 150 mg (80%) of *N*-toluenesulfonyl-3-methoxyanthranilic acid methylester**.** To a cooled (-78 °C) solution of *N*-toluenesulfonyl-3,4,5-trimethoxyanthranilic acid methylester (395 mg, 1.00 mmol) in toluene (5.00 mL) under Ar atmosphere, was added DIBAL (1 M toluene solution, 1.90 mmol, 1.9 eq). The mixture was stirred at ambient temperature for 1 h and the reaction was quenched by the addition of MeOH and Rochelle's salt. Then the solution was allowed to stir at room temperature until separation of organic and water layers. The mixture was extracted with AcOEt (3 x 10 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 5:1) on silica gel 60 (5 g) to give 193 mg (53%) of *N*-toluenesulfonyl-2-hydroxymethyl-4,5,6-trimethoxyaniline**.** To a solution of *N*-

toluenesulfonyl-2-hydroxymethyl-4,5,6-trimethoxyaniline (147 mg, 0.400 mmol) in benzene (5.00 mL), was added MnO_2 (83.9 g, 0.96 mmol, 2.4 eq). The mixture was refluxed for 4 h and filtered through a celite pad. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 5:1) on silica gel 60 (5 g) to give 120 mg (82%) of *N*-toluenesulfonyl-2-formyl-4,5,6-trimethoxyaniline. To a cooled (-78 °C) solution of $BrPh_3PMe$ (217 mg, 0.606 mmol, 2 eq) in THF (10.0 mL) under Ar atmosphere, was added $KN(TMS)_2$ (0.5 M in THF solutuion 1.21 mL, 0.606 mmol, 2 eq). The mixture was stirred at –78 °C for 15 min. To this mixture, was added *N*-toluenesulfonyl-2-formyl-4,5,6-trimethoxyaniline (111 mg, 0.303 mmol) and, the solution was warmed to room temperature for 1 h. The reaction was quenched by addition of sat. NH_4Cl. The mixture was extracted with AcOEt (3x30 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 2:1) on silica gel 60 (7.5 g) to give 12 mg (11%) of *N*-toluenesulfonyl-2-ethenyl-4,5,6-trimethoxyaniline. To a solution of *N*-toluenesulfonyl-2-ethenyl-4,5,6-trimethoxyaniline (12.0 mg, 0.0330 mmol) and K_2CO_3 (6.85 mg, 0.0495 mmol, 1.5 eq) in DMF (3.00 mL) under Ar atmosphere, was added allyl bromide (6.0 mg, 0.0495 mmol, 1.5 eq). The mixture was stirred at 80 °C for 1 h and the reaction was quenched by addition of $NaHCO_3$. The mixture was extracted with Et_2O (3x30 mL) and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 3:1) on silica gel 60 (3 g) to give 9.5 mg (71%) of **4j** as yellow oil. ^{1}H-NMR (400 MHz) : δ 7.72 (2H, d, *J* = 8.2 Hz), 7.28 (2H, d, *J* =

8.2 Hz), 6.88 (1H, dd, *J* = 17.8, 11.0 Hz), 6.83 (1H, s), 5.70-5.77 (1H, m), 5.63 (1H, d, *J* = 17.6 Hz), 5.22 (1H, d, J = 12.0 Hz), 4.5-4.99 (m, 2H), 4.29 (1H, dd, *J* = 14.2, 6.1 Hz), 3.97 (1H, dd, *J* = 14.4, 7.8 Hz), 3.90 (3H, s), 3.77 (3H, s), 3.63 (3H, s) 2.43 (3H, s); LRMS (FAB) : *m/z* 403 (M^++H).

N-Allyl-*N*-toluenesulfonyl-5-chloro-2-ethenylaniline (**4k**): To solution of purified 2-amino-4-chloro-benzoic acid (5.00 g, 29.1 mmol) in DMP (291 mL, 16 eq) was added 36% hydrochloric acid (58.2 mL). The solution mixture was stirred at room temperature for 12 h. and quenched by addition of $NaHCO_3$. The product was extracted with AcOEt (3x30mL), and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (*n*-Hexane:AcOEt = 3:1) on silica gel 60 (20 g) to give 3.59 g (67%) of 4-chloro-anthranilic acid methylester as white needles. To a solution of 4-chloro-anthranilic acid methylester (1.80 g, 9.70 mmol) in CH_2Cl_2 (20.0 mL) under Ar atmosphere, pyridine (12.3 mL, 29.1 mmol, 3 eq) and TsCl (2.22 g, 11.6 mmol, 1.2 eq) were added. The solution mixture was stirred at room temperature for 1 h. and quenched by the addition of water. The mixture was extracted with AcOEt (3x30 mL) and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (*n*-Hexane:AcOEt = 3:1) on silica gel 60 (100 g) to give 2.37 g (72%) of *N*-toluenesulfonyl-4-chloro-anthranilic acid methylester as colorless needles. To a cooled (-78 °C) solution of *N*-toluenesulfonyl-4-chloro-anthranilic acid methylester (0.16 g, 0.47 mmol) in toluene (3.00mL) under Ar atmosphere, DIBAL 1M in toluene solution (1.55 mmol, 3.3 eq) was added. The solution mixture was stirred at –78 °C for 1 h. and quenched by the addition of MeOH and Rochelle's salt, then the solution was allowed to stir at room temperature

until it was separtated into 2 layers. The mixture was extracted with AcOEt (3x30 mL) and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (*n*-Hexane : AcOEt = 3:2) on silica gel 60 (5 g) to give 100 mg (70%) of *N*-toluenesulfonyl-5-chloro-2-hydroxymethylaniline as colorless prisms. To a solution of alcohol *N*-toluenesulfonyl-5-chloro-2-hydroxymethylaniline (0.59 g, 1.89 mmol) in benzene (100 mL), MnO_2 (0.40 g, 4.54 mmol, 2.40 eq) and was added. The mixture was refluxed for 4 h and filtrated through a celite pad. After removal of the solvent, the residue was purified by column chromatography (*n*-Hexane: AcOEt = 2:1) on silica gel 60 (20 g) to give 420 mg (71%) of *N*-toluenesulfonyl-5-chloro-2-formylaniline as colorless needles. To a solution of *N*-toluenesulfonyl-5-chloro-2-formylaniline (1.11 g, 3.58 mmol) and K_2CO_3 (0.74 g, 5.37 mmol, 1.50 eq) in DMF (100.0 mL) under Ar atmosphere, allyl bromide (0.47 mL, 5.37 mmol, 1.5 eq) was added. The solution mixture was stirred at 80°C for 1 h. and quenched by the addition of $NaHCO_3$. The mixture was extracted with Et_2O (3x30 mL) and the combined organic phases were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (*n*-Hexane:AcOEt = 4:1) on silica gel 60 (45 g) to give 1.15 g (92%) of *N*-allyl-*N*-toluenesulfonyl-5-chloro-2-formylaniline as colorless prisms. To a cooled(-78 °C) solution of $BrPh_3PMe$ (61.3 mg, 1.71 mmol, 3 eq) in THF (50.0 mL) under Ar atmosphere, $KN(TMS)_2$(0.5 M THF solution, 3.43 mL, 1.71 mmol, 3 eq) was added. The solution mixture was stirred at –78 °C for 15 min. Then, to the solution mixture, *N*-allyl-*N*-toluenesulfonyl-5-chloro-2-formylaniline (200 mg, 0.57 mmol) was added and, warmed to room temperature for 1 h. The solution was quenched by the addition of Rochelle's salt. The mixture was extracted with AcOEt (3x30 mL) and the combined

organic phases were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (*n*-Hexane:AcOEt = 10:1) on silica gel 60 (8 g) to give 190 mg (98%) of **4k** as yellow oil; 1H-NMR (400 MHz, $CDCl_3$) : δ 7.54-7.60 (3H, m), 7.30 (3H, d, *J* = 7.9 Hz), 7.24 (1H, dd, *J* = 0.6, 5.1 Hz), 6.93-7.00 (1H, m), 6.65 (1H, s), 5.66-5.73 (2H, m), 5.30 (1H, dd, *J* = 0.9, 1.2 Hz), 4.99-5.02 (1H, m), 4.95 (1H, d, *J* = 1.3 Hz), 2.44 (3H, s), 1.43 (1H, s); 13C-NMR (100 MHz, CDCl3) : δ 143.9, 137.5, 137.3, 135.5, 132.9, 131.8, 131.7, 129.6, 129.1, 128.7, 127.8, 127.0, 119.6, 116.3, 54.6, 30.0, 21.7; IR (neat) cm^{-1} : 3448, 3074, 2925, 2867, 1699, 1595, 1352; LRMS (FAB) : *m/z* 348 (M^++H, 45%), 192 (100%); HRMS (FAB) : calcd for $C_{18}H_{19}ClNO_2S$; 348.0747, found 348.0816; Anal. Calcd for $C_{18}H_{18}ClNO_2S$: C, 61.15 ; H, 5.22; N, 4.03, found : C, 61.03; H,5.35; N , 3.75.

Typical procedure for isomerization

To a stirred solution of terminal olefin (substrate) and vinyloxytrimethylsilane (10 eq) in dichloromethane (0.0125 M), was added ruthenium carbene catalyst (0.05 eq) under argon atmosphere and the mixture was stirred at 50 °C for 3 h. The solvent was removed under vacuum and obtained crude residue was subjected to column chromatography to give isomerized product.

3[4]: a mixture of *E*- and *Z*-isomers. Colorless oil. ^{1}H-NMR (400 MHz) δ 5.52-5.23 (m, 2H), 4.08-4.14 (m, 2H), 2.41-2.55 (m, 4.2H), 2.22-2.27 (m, 0.8H), 2.01-1.97 (m, 1H), 1.57-1.74 (m, 6H), 1.39-1.47 (m, 1H), 1.21-1.26 (m, 3H). ^{13}C-NMR (100 Mz), δ 207.81, 207.69 171.59, 128.81, 127.05, 125.60, 124.51, 61.17, 61.12, 61.06, 60.90, 41.14, 38.06, 35.70, 35.51, 31.89, 27.53, 22.47, 22.44, 17.88, 14.17, 14.08, 12.79. IR (neat) cm^{-1} 2937, 2859, 1713, 1438, 1197.

5a[5]: a mixture of *E*- and *Z*-isomers. Colorless oil. ^{1}H-NMR (400 MHz) δ 7.31-7.09 (m, 5H), 6.38-6.31 (m, 1H), 6.17 (qd, 0.93H, *J* = 15.6, 6.4 Hz), 5.77-5.68 (m, 0.07H), 1.80-1.84 (m, 3H).

5b[6]: a mixture of *E*- and *Z*-isomers. Colorless oil. ^{1}H-NMR (400 MHz) δ 7.28-7.10 (m, 5H), 5.56-5.40 (m, 2H), 3.34 (d, 0.53H, *J* = 5.1 Hz), 3.24 (d, 1.47H, J = 6.2 Hz), 1.66-1.61 (m, 3H).

5c[5]: a mixture of *E*- and *Z*-isomers. Colorless oil. ^{1}H-NMR (400 MHz) δ 7.28-7.23 (m, 2H), 6.85-6.81 (m, 2H), 6.36-6.32 (m, 1H), 6.09 (dq, 0.9H, *J* = 15.7, 6.6 Hz), 5.70 (dq, 0.1H, *J* = 11.6, 7.2 Hz), 3.82 (0.3H, s), 3.80 (2.7H, s), 1.90-1.85 (m, 3H). ^{13}C-NMR (100 Mz), δ 158.53, 130.78, 130.29, 129.97, 126.84, 125.10, 123.48, 113.87, 113.51, 55.26, 18.41, 14.11.

5d[7]: a mixture of *E*- and *Z*-isomers. Colorless oil. ^{1}H-NMR (400 MHz) δ 5.48-5.40 (m, 2H), 3.62 (t, 1.73H,m *J* = 6.6 Hz), 3.55 (t, 0.27H, *J* = 6.6 Hz), 2.14-2.02 (m, 4H), 1.69-1.62 (m, 3H).

5e[8]: a mixture of *E*- and *Z*-isomers. Colorless oil. ^{1}H-NMR (400 MHz) δ 7.37-7.25 (m, 5H), 5.57-5.35 (m, 2H), 4.52 (s, 0.26H), 4.50 (s, 1.74H), 2.40-2.29 (m, 0.26H), 2.17-1.98 (m, 1.74H), 1.71-1.61 (m, 5H).

5f[9]: a mixture of *E*- and *Z*-isomers. Colorless oil. ^{1}H-NMR (400 MHz) δ 7.38-7.27 (m, 5H), 6.31 (qd, 0.44H, *J* = 12.4, 1.5 Hz), 6.30 (qd, 0.56H, *J* = 6.10, 1.7), 4.87 (qd, 0.44H, *J* = 12.4, 6.7 Hz), 4.80 (s, 1.12H), 4.70 (s, 0.88H), 4.44 (qd, 0.56H, *J* = 6.8, 6.1 Hz), 1.63 (dd, 1.68H, *J* = 6.8, 1.7 Hz), 1.57 (dd, 1.32H, *J* = 6.7, 1.5 Hz), ^{13}C-NMR (100 Mz), δ = 146.26, 145.17, 137.82, 137.36, 128.45, 128.44, 127.79, 127.77, 127.52, 127.56, 101.85, 99.47, 73.49, 71.10, 12.59, 9.32.

5h: *Z*-isomer. Colorless oil. ^{1}H-NMR (400 MHz) δ 7.69-7.15 (m, 7H), 6.92 (dd, 1H, *J* = 13.9, 1.5 Hz), 6.76 (dd, 1H, *J* = 17.8, 11.2 Hz), 6.64 (d, 1H, *J* = 7.8 Hz), 5.71 (d, 1H, *J* = 17.8 Hz), 5.21 (d, 1H, *J* = 11.2 Hz), 4.20 (dq, 1H, *J* = 7.8, 6.8 Hz), 2.43 (s, 3H), 1.57 (dd, 3H, *J* = 6.8, 1.5 Hz).

5i: *Z* -isomer. Colorless oil. ^{1}H-NMR (400 MHz) δ 7.61-7.66 (m, 8H), 6.54 (d, 1H, *J* = 8.8 Hz), 5.69 (d, 1H, *J* = 17.6 Hz), 5.21 (d, 1H, *J* = 11.0 Hz), 4.21 (dq, 1H, *J* = 7.8, 6.8 Hz), 3.82 (s, 3H), 2.43 (s, 3H), 1.57 (dd, 3H, *J* = 6.8, 1.5 Hz).

Typical procedure for RCM

To a stirring solution of diene (**4** or **5**) in solvent (0.0125 M), was added ruthenium carbene catalyst (0.05 eq) under argon atmosphere and the mixture was stirred. The solvent was removed under reduced pressure and obtained crude residue was subjected to column chromatography to give cyclized product.

6h[10]: Colorless needle. mp = 85-87 °C (MeOH). ^{1}H-NMR (400 MHz) δ 7.70 (d, 1H, *J* = 8.1 Hz), 7.30-7.25 (m, 3H), 7.18 (dd, 1H, *J* = 7.5, 7.3 Hz), 7.12 (d, 2H, *J* = 7.9 Hz), 6.93 (d, 1H, *J* = 7.3 Hz), 6.02 (d, 1H, *J* = 9.5 Hz), 5.58 (dt, 1H, *J* = 9.5, 3.6 Hz), 4.44 (d, 2H, *J* = 3.6 Hz), 2.34 (s, 3H). ^{13}C-NMR (100 MHz) δ 143.33, 136.25, 134.90, 129.49, 129.00, 127.92, 127.24, 126.80, 126.62, 126.41, 125.83, 123.92, 45.32, 21.48. IR (KBr) cm^{-1} = 1337.39, 1165.76. LR-MS (EI) *m/z* 285 (M^{+}+H).

6i: colorless needle (*n*-hexane/AcOEt), mp 152 °C; ^{1}H-NMR (400 MHz,) : δ 7.61 (2H, d, *J* = 1.7 Hz), 7.21 (2H, d, *J* = 1.7 Hz), 7.07 (1H, d, *J* = 2.2 Hz), 6.81 (1H, dd, *J* = 0.8, 2.2 Hz), 6.45 (1H, d, *J* = 0.8 Hz), 5.93 (1H, d, *J* = 2.4 Hz), 5.53-5.58 (1H, m), 4.40 (2H, d, *J* = 0.6 Hz), 3.80 (3H, s), 2.34 (3H, s); ^{13}C-NMR (100 MHz) : δ 158.1, 143.2,

136.1, 130.6, 129.0, 128.3, 127.7, 127.3, 125.8, 124.5, 112.9, 111.5, 55.4, 45.5, 21.5; IR (KBr) cm-1 : 3383, 2962, 1574, 1485; LRMS (FAB) : *m/z* 315 (M+, 25%), 154 (100%).

6k: colorless needles (*n*-Hexane/AcOEt), mp 113°C; ^{1}H-NMR (400 MHz, $CDCl_3$) : δ 7.73 (1H, d, *J* = 2.0 Hz), 7.35 (2H, d, *J* = 12 Hz), 7.14(1H, dd, *J* = 2.0, 2.2 Hz), 7.13 (2H, d, *J* = 12 Hz), 6.86 (1H, d, *J* = 8.0 Hz), 6.01 (1H, d, *J* = 9.5 Hz), 5.58-5.62 (1H, m), 4.43 (2H, dd, *J* = 2.6, 5.7), 2.35 (3H,s); ^{13}C-NMR (100 MHz, $CDCl_3$) : δ 143.8, 136.2, 136.1, 133.2, 129.3, 127.4, 126.8, 125.2, 124.2, 45.3, 29.8, 21.6; IR (KBr) cm^{-1} : 3448, 3065, 2926, 2989, 1593. LRMS (EI) : 319 (M^+, 40%), 164 (100%); HRMS (FAB) : calcd for $C_{16}H_{15}ClNO_2S$ (M^++H) ; 320.0434, found 320.0457; Anal. Calcd for $C_{16}H_{14}ClNO_2S$: C, 60.09 ; H, 4.41; N, 4.38, found : C, 59.97; H,4.51; N , 4.28

7h[5]: Colorless needle. mp = 87-88 °C (MeOH). ^{1}H-NMR (400 MHz) δ 7.99 (d, 1H, *J* = 8.3 Hz), 7.75 (d, 2H, *J* = 8.3 Hz), 7.56 (d, 1H, *J* = 3.7 Hz), 7.51 (d, 1H, *J* = 7.8 Hz), 7.32-7.19 (m, 4H), 6.64 (d, 1H, *J* = 3.4 Hz), 2.31 (s, 3H). ^{13}C-NMR (100 MHz) δ 143.87, 135.27, 134.78, 130.71, 129.82, 126.77, 126.29, 124.50, 123.22, 121.32, 113.50, 108.98, 21.50. LR-MS (EI) *m/z* 271 (M^++H).

7i[11]: Colorless needle. mp = 112-113 °C (MeOH). ^{1}H-NMR (400 MHz) δ 7.87 (d, 1H, *J* = 8.8 Hz), 7.72 (d, 2H, *J* = 8.2 Hz), 7.51 (d, 1H, *J* = 3.8 Hz), 7.20 (d, 1H, *J* = 8.2 Hz), 6.96 (d, 1H, *J* = 2.2 Hz), 6.92 (dd, 1H, *J* = 8.8, 2.2 Hz), 6.57 (d, 1H, *J* = 3.8 Hz), 3.80 (s, 3H), 2.33 (s, 3H). ^{13}C-NMR (100 MHz) δ 156.38, 144.78, 135.27, 131.74, 129.79, 129.58, 127.11, 126.72, 114.40, 113.66, 109.14, 103.61, 55.61, 21.52. LR-MS (EI) *m/z* 301 (M^++H).

7j:colorless oil. ^{1}H-NMR (400 MHz) δ 7.75 (d, 2H, *J* = 8.3 Hz), 7.72 (d, 1H, *J* = 3.7

Hz), 7.24 (d, 2H, *J* = 8.5 Hz), 6.96 (s, 1H), 6.53 (d, 1H, *J* = 3.7 Hz), 3.85 (s, 3H), 3.79 (s, 3H9, 3.79 (s, 3H), 2.37 (s, 3H). ^{13}C-NMR (100 MHz) δ 151.2, 144.1, 141.5, 140.6, 136.8, 129.5, 128.8, 128.0, 127.2, 122.5, 107.2, 98.1, 61.1, 60.9, 56.1, 21.5. LR-MS (EI) *m/z* 361 (M^+).

7k: colorless needles. mp = 153-153 °C (MeOH). ^{1}H-NMR (400 MHz) δ 8.01 (s, 1H), 7.76 (d, 2H, *J* = 8.5 Hz), 7.54 (d, 1H, *J* = 3.7 Hz), 7.42 (d, 2H, *J* = 8.3 Hz), 7.25 (d, 2H, *J* = 8.8 Hz), 7.19 (dd, 1H, *J* = 8.3, 1.7 Hz), 6.61 (d, 1H, *J* = 3.7 Hz), 2.33 (s, 3H). ^{13}C-NMR (100 MHz) δ 145.2, 135.2, 135.0, 130.6, 130.0, 129.2, 126.9, 126.8, 124.0, 122.1, 113.7, 108.7, 21.6. LR-MS (EI) *m/z* 307 (M^+).

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