<Supporting Information>

**Development of Isomerization and Cycloisomerization with Use of a Ruthenium Hydride
with *N*-Heterocyclic Carbene and Its Application to the Synthesis of Heterocycles**

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All melting points are uncorrected. Infrared absorption spectra were recorded using a JASCO FT/IR-230 spectrometer. ^1H NMR spectra were recorded in CDCl_3 at 25 °C unless otherwise noted, at 400 MHz, with TMS as an internal standard. ^{13}C NMR spectra were recorded in CDCl_3 at 25 °C unless otherwise noted, at 100 MHz. ^{31}P NMR spectra were recorded at 25 °C unless otherwise noted at 161 MHz, with 80% H_3PO_4 ($\delta = 0$) as an external standard. All moisture-sensitive reactions were performed under an Ar atmosphere. Syntheses of ruthenium catalysts were carried out in a glovebox (Miwa, DBO-1NKP-TA) containing less than 1 ppm of oxygen and water. Flash column chromatographies were performed with silica gel 60 N (spherical, neutral, 40-50 μm , Kanto Chemical Co., Inc.). **11a-c**, and **11d** were obtained commercially. **1d**¹, **1f**¹, **1h**¹, **1i**¹, **7**², **11e**³, **11f**⁴, **14**⁵, and **18a**⁶ were prepared according to the reported procedures.

Preparation of dienes.

1a: To a stirring solution of *N*-*p*-toluenesulfonyl-2-ethenylaniline⁷ (779 mg, 2.85 mmol) in CH₃CN (63 mL) were added K₂CO₃ (3.94 g, 28.5 mmol) and allyl bromide (0.74 mL, 8.55 mmol), and the mixture was stirred for 12 hours at rt. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 20:1) to give **1a** (849 mg, 95%). Mp 65-66 °C (MeOH), colorless needles; ¹H NMR δ 7.64 (dd, 1H, *J* = 8.1, 1.5 Hz), 7.59 (d, 2H, *J* = 8.3 Hz), 7.26-7.30 (m, 3H), 7.13 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.04 (dd, 1H, *J* = 17.6, 11.0 Hz), 6.68 (dd, 1H, *J* = 7.8, 1.0 Hz), 5.73 (ddt, 1H, *J* = 16.8, 10.0, 6.8 Hz), 5.73 (dd, 1H, *J* = 17.6, 1.0 Hz), 5.30 (dd, 1H, *J* = 12.0, 1.0 Hz), 4.99 (dd, 1H, *J* = 10.0, 1.5 Hz), 4.97 (dd, 1H, *J* = 17.1, 1.5 Hz), 4.25 (m, 1H), 4.00 (m, 1H), 2.45 (s, 3H); ¹³C NMR δ 143.5, 138.6, 136.7, 136.1, 132.7, 132.4, 129.5, 129.0, 128.5, 127.9, 127.9, 126.0, 119.3, 115.8, 54.8, 21.6; IR (KBr) cm⁻¹ 1340, 1157; LRMS (EI) *m/z* 313 (M⁺+H); HRMS (FAB) calcd for C₁₈H₂₀NO₂S (M⁺+H) 314.1215, found 314.1234; Anal. Calcd for C₁₈H₁₉NO₂S: C 68.98 H 6.11 N 4.47, found: C 69.01 H 6.20 N 4.47.

1b: To a cooled (0 °C) solution of BrPh₃PMe (6.97 g, 19.5 mmol) in THF (120 mL) under an Ar atmosphere, NaN(TMS)₂ (1.0 M, THF solution, 19.5 mL, 19.5 mmol) was added. The solution was stirred for 1 hour at 0 °C. To the solution was added a solution of commercially available 3-methoxy-2-nitrobenzaldehyde (2.65 g, 14.6 mmol) in THF (20 + 10 mL), and the mixture was stirred for 11 hours at rt. The reaction was quenched by sat. aq. NH₄Cl. The organic compounds were extracted with AcOEt and the combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography

(*n*-hexane:AcOEt = 2:1) to give 2-ethenyl-6-methoxynitrobenzene (2.40 g, 92%). Mp 58-59 °C (MeOH), colorless needles; ^1H NMR δ 7.38 (dd, 1H, J = 8.1, 8.1 Hz), 7.19 (d, 1H, J = 8.1 Hz), 6.94 (d, 1H, J = 8.3 Hz), 6.59 (dd, 1H, J = 17.3, 11.0 Hz), 5.84 (d, 1H, J = 17.3 Hz), 5.47 (d, 1H, J = 11.2 Hz), 3.89 (s, 3H); ^{13}C NMR δ 150.7, 140.4, 130.8, 130.7, 129.3, 119.7, 117.8, 111.4, 56.4; IR (KBr) cm^{-1} 1528, 1372, 1065; LRMS (EI) m/z 179 (63%, M^+), 77 (100%, base peak); HRMS (FAB) calcd for $\text{C}_9\text{H}_{10}\text{NO}_3$ ($\text{M}^+\text{+H}$) 180.0661, found 180.0651; Anal. Calcd for $\text{C}_9\text{H}_9\text{NO}_3$: C 60.33 H 5.06 N 7.82, found: C 60.29 H 4.88 N 7.81.

To a solution of 2-ethenyl-6-methoxynitrobenzene (2.40 g, 13.4 mmol) in EtOH (77 mL) were added AcOH (77 mL) and iron powder (2.99 g, 53.6 mmol), and the mixture was refluxed for 6 hours, then cooled to rt. After addition of water, and K_2CO_3 to neutralize the aqueous layer, the organic compounds were extracted with Et_2O . The combined organic layers were washed with brine, and dried over Na_2SO_4 . After removal of the solvent, the residue was resolved in CH_2Cl_2 (23 mL). To the solution, *p*-toluenesulfonyl chloride (2.57 g, 13.6 mmol) and pyridine (2.74 mL, 33.9 mmol) were added, and the mixture was stirred for 20 hours at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with CH_2Cl_2 . The combined organic layers 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) to give *N*-*p*-toluenesulfonyl-2-ethenyl-6-methoxyaniline (1.56 g, 38%, 2 steps). Mp 146-147 °C (MeOH), colorless needles; ^1H NMR δ 7.49 (d, 2H, J = 8.3 Hz), 7.36 (dd, 1H, J = 17.8, 11.0 Hz), 7.28 (d, 1H, J = 8.1 Hz), 7.17 (d, 2H, J = 8.5 Hz), 7.16 (dd, 1H, J = 8.5, 7.6 Hz), 6.53 (d, 1H, J = 7.6 Hz), 6.24 (brs, 1H), 5.78 (dd, 1H, J = 17.6, 1.0 Hz), 5.35 (dd, 1H, J = 11.2, 1.0 Hz), 3.21 (s, 3H), 2.38 (s, 3H); ^{13}C NMR δ 154.1, 143.2, 137.5, 136.4, 133.2, 128.8, 128.0, 127.6,

122.2, 117.8, 115.1, 109.2, 54.9, 21.5; IR (KBr) cm^{-1} 3265, 2972, 1331, 1164; LRMS (EI) m/z 303 (18%, M^+), 148 (100%, base peak); Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$: C 63.34 H 5.65 N 4.62, found: C 63.48 H 5.61 N 4.53.

To a stirring solution of *N*-*p*-toluenesulfonyl-2-ethenyl-6-methoxyaniline (200 mg, 0.66 mmol) in CH_3CN (20 mL) were added K_2CO_3 (182 mg, 1.32 mmol) and allyl bromide (0.10 mL, 1.32 mmol), and the mixture was refluxed for 2 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 3:1) to give **1b** (212 mg, 93%). Mp 95-96 °C (AcOEt/*n*-hexane), colorless prisms; ^1H NMR δ 7.63 (d, 2H, J = 8.2 Hz), 7.23-7.27 (m, 4H), 7.21 (dd, 1H, J = 17.6, 11.0 Hz), 6.66 (dd, 1H, J = 7.1, 2.4 Hz), 5.74-5.81 (m, 1H), 5.77 (dd, 1H, J = 17.8, 1.1 Hz), 5.34 (dd, 1H, J = 11.0, 1.1 Hz), 4.93-4.98 (m, 2H), 4.39-4.44 (m, 1H), 3.91 (dd, 1H, J = 14.1, 8.1 Hz), 3.26 (s, 3H), 2.43 (s, 3H); ^{13}C NMR δ 156.8, 142.6, 140.8, 137.9, 133.6, 133.3, 129.2, 128.9, 127.8, 124.8, 118.5, 117.6, 115.9, 110.1, 54.6, 53.1, 21.4; IR (KBr) cm^{-1} 2924, 1574, 1339, 1158; LRMS (EI) m/z 188 (100%, base peak), 343 (0.6%, M^+); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) 344.1320, found 344.1317; Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$: C 66.45 H 6.16 N 4.08, found: C 66.53 H 6.14 N 4.03.

1c: To a solution of 2-bromo-5-methoxyaniline⁸ (200 mg, 0.99 mmol) in pyridine (0.90 mL) was added *p*-toluenesulfonyl chloride (226 mg, 1.19 mmol), and the mixture was stirred for 17.5 hours at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with AcOEt. The combined organic layers 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) to give *N*-*p*-toluenesulfonyl-2-bromo-5-methoxyaniline (353 mg, 100%). Mp 98-99 °C

(*n*-hexane/AcOEt), colorless prisms; ^1H NMR δ 7.67 (d, 2H, J = 8.0 Hz), 7.21-7.28 (m, 4H), 6.93 (brs, 1H), 6.53 (dd, 1H, J = 8.8, 3.2 Hz), 3.78 (s, 3H), 2.38 (s, 3H); ^{13}C NMR δ 159.7, 144.3, 135.8, 135.4, 132.7, 129.7, 127.3, 112.6, 107.5, 105.7, 55.6, 21.6; IR (neat) cm^{-1} 3789, 3253, 1591, 1484, 1336, 1163; LRMS (EI) m/z 355 (M^+); HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{14}\text{BrNO}_3\text{S}$ (M^+) 354.9878, found 354.9895; Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{BrNO}_3\text{S}$: C 47.20 H 3.96 N 3.93, found: C 47.29 H 4.03 N 3.85.

To a solution of *N*-*p*-toluenesulfonyl-2-bromo-5-methoxyaniline (100 mg, 0.28 mmol) in toluene (4 mL) were added $\text{Pd}(\text{dba})_2$ (8.1 mg, 5 mol%), triphenylphosphine (14.7 mg, 20 mol%) and tributylvinyltin (0.10 mL, 0.34 mmol), and then the mixture was refluxed for 16 hours. After removal of the solvent, the residue was redissolved in CH_2Cl_2 , filtered through a celite pad, and the pad was washed with CH_2Cl_2 . The organic solution was extracted with CH_2Cl_2 , after addition of sat. aq. NaHCO_3 . The combined organic layers 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 = 6:1) to give *N*-*p*-toluenesulfonyl-2-ethenyl-5-methoxyaniline (31.3 mg, 37%). Mp 97-99 °C (*n*-hexane/AcOEt), colorless prisms; ^1H NMR δ 7.63 (d, 2H, J = 7.6 Hz), 7.18-7.33 (m, 3H), 6.94 (d, 1H, J = 2.4 Hz), 6.70 (dd, 1H, J = 8.8, 2.8 Hz), 6.36-6.48 (m, 2H), 5.39 (d, 1H, J = 17.2 Hz), 5.17 (d, 1H, J = 11.2 Hz), 3.76 (s, 3H), 2.39 (s, 3H); ^{13}C NMR δ 159.7, 143.9, 136.4, 134.2, 130.9, 129.6, 127.8, 127.2, 124.5, 116.6, 112.7, 109.0, 55.4, 21.5; IR (neat) cm^{-1} 3702, 3587, 3249, 1965, 1322, 1160; LRMS (EI) m/z 303 (M^+); HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) 304.1007, found 304.1005; Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$: C 63.34 H 5.65 N 4.62, found: C 63.11 H 5.78 N 4.64.

To a stirring solution of *N*-*p*-toluenesulfonyl-2-ethenyl-5-methoxyaniline (300 mg, 0.99 mmol)

in CH₃CN (33 mL) were added K₂CO₃ (205 mg, 1.49 mmol) and allyl bromide (170 μ L, 1.98 mmol), and the mixture was refluxed for 3 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 8:1) to give **1c** (300 mg, 92%) as a colorless oil. ¹H NMR δ 7.62 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 1H, *J* = 8.8 Hz), 7.29 (d, 2H, *J* = 8.0 Hz), 6.90 (dd, 1H, *J* = 17.6, 10.8 Hz), 6.85 (dd, 1H, *J* = 8.8, 2.8 Hz), 6.22 (d, 1H, *J* = 2.8 Hz), 5.74 (dddd, 1H, *J* = 16.8, 10.0, 6.8, 6.8 Hz), 5.59 (dd, 1H, *J* = 17.6, 1.2 Hz), 5.17 (dd, 1H, *J* = 11.2, 0.8 Hz), 4.94-5.03 (m, 2H), 3.89-4.31 (m, 2H), 3.65 (s, 3H), 2.44 (s, 3H); ¹³C NMR δ 159.0, 143.5, 137.4, 136.0, 132.2, 132.1, 131.0, 129.4, 127.7, 126.6, 119.1, 114.6, 114.0, 113.4, 55.1, 54.6, 21.3; IR (neat) cm⁻¹ 3697, 2926, 1604, 1503, 1340, 1250, 1152, 988; LRMS (EI) *m/z* 343 (M⁺); HRMS (FAB) calcd for C₁₉H₂₂NO₃S (M⁺+H) 344.1320, found 344.1318.

1e: To a stirring solution of *N*-*p*-toluenesulfonyl-2-ethenyl-3-methoxyaniline⁹ (143 mg, 0.47 mmol) in CH₃CN (18 mL) were added K₂CO₃ (114 mg, 0.83 mmol) and allyl bromide (100 μ L, 1.10 mmol), and the mixture was refluxed for 1.5 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:CH₂Cl₂ = 1:2) to give **1e** (152.4 mg, 94%) as a colorless oil. ¹H NMR δ 7.63 (d, 2H, *J* = 8.4 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 7.06 (dd, 1H, *J* = 8.4, 8.0 Hz), 6.80-6.89 (m, 2H), 6.35 (d, 1H, *J* = 8.0 Hz), 6.09 (dd, 1H, *J* = 18.0, 2.4 Hz), 5.73 (dddd, 1H, *J* = 13.6, 10.0, 7.2, 6.8 Hz), 5.49 (dd, 1H, *J* = 12.4, 2.4 Hz), 4.94-5.00 (m, 2H), 4.11-4.31 (m, 1H), 3.91-4.09 (m, 1H), 3.86 (s, 3H), 2.44 (s, 3H); ¹³C NMR δ 158.9, 143.4, 138.3, 136.3, 132.4, 129.4, 129.2, 128.0, 127.3, 127.2, 121.2, 120.5, 119.2, 111.0, 55.5, 54.7, 21.5; IR (neat) cm⁻¹ 2934, 1736, 1572, 1469, 1345, 1264, 1160, 1090; LRMS (FAB) *m/z* 344

($M^+ + H$); HRMS (FAB) calcd for $C_{19}H_{22}NO_3S$ ($M^+ + H$) 344.1320, found 344.1322.

1g: To a solution of commercially available 3-chloroanthranilic acid (1.3 g, 7.58 mmol) in MeOH (19 mL) was added conc. H_2SO_4 (0.78 mL), and the mixture was refluxed for 28 hours. After addition of 1N NaOH, the organic compounds were extracted with AcOEt. The combined organic layers 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 = 5:1) to give 3-chloroanthranilic acid methyl ester (1.0 g, 72%) as a colorless oil. 1H NMR δ 7.81 (dd, 1H, J = 8.0, 1.6 Hz), 7.40 (dd, 1H, J = 8.0, 1.6 Hz), 6.58 (dd, 1H, J = 8.0, 7.6 Hz), 6.27 (brs, 2H), 3.88 (s, 3H).

To a solution of 3-chloroanthranilic acid methyl ester (200 mg, 1.08 mmol) in pyridine (1 mL) was added *p*-toluenesulfonyl chloride (247 mg, 1.30 mmol), and the mixture was refluxed for 3 hours. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with CH_2Cl_2 . After the combined organic layers were washed with 1N HCl, the organic layers 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 = 5:1) to give *N-p*-toluenesulfonyl-3-chloroanthranilic acid methyl ester (143 mg, 40%). Mp 135-136 °C (*n*-hexane/AcOEt), colorless prisms; 1H NMR δ 8.27 (brs, 1H), 7.70 (dd, 1H, J = 7.6, 1.6 Hz), 7.63 (dd, 1H, J = 8.0, 1.2 Hz), 7.54 (d, 2H, J = 8.4 Hz), 7.17-7.28 (m, 3H), 3.66 (s, 3H), 2.41 (s, 3H).

To a stirring solution of *N-p*-toluenesulfonyl-3-chloroanthranilic acid methyl ester (500 mg, 1.47 mmol) in CH_3CN (50 mL) were added K_2CO_3 (305 mg, 2.21 mmol) and allyl bromide (0.26 mL, 2.94 mmol), and the mixture was refluxed for 4 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained

crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 5:1) to give *N*-allyl-*N*-*p*-toluenesulfonyl-3-chloroanthranilic acid methyl ester (512 mg, 92%). Mp 91-92 °C (*n*-hexane/AcOEt), colorless prisms; ¹H NMR δ 7.75 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.59 (d, 2H, *J* = 8.0 Hz), 7.49 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.32 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.25 (d, 2H, *J* = 8.8 Hz), 6.04 (dddd, 1H, *J* = 17.2, 10.0, 8.0, 6.0 Hz), 5.12 (dd, 1H, *J* = 17.2, 1.2 Hz), 5.01 (dd, 1H, *J* = 10.0, 0.8 Hz), 4.48 (dd, 1H, *J* = 14.0, 6.0 Hz), 4.30 (dd, 1H, *J* = 14.0, 8.0 Hz), 3.78 (s, 3H), 2.42 (s, 3H); ¹³C NMR δ 166.1, 143.2, 138.0, 136.7, 135.9, 135.2, 133.5, 132.9, 129.4, 129.4, 129.1, 127.3, 119.0, 53.8, 52.4, 21.5; IR (neat) cm⁻¹ 3744, 2953, 1739, 1598, 1495, 1442, 1338, 1155; LRMS (FAB) *m/z* 380 (M⁺+H); HRMS (FAB) calcd for C₁₈H₂₀ClNO₄S (M⁺+H) 380.0723, found 380.0722; Anal. Calcd for C₁₈H₁₉ClNO₄S: C 56.91 H 4.78 N 3.69, found: C 56.92 H 4.85 N 3.61.

To a cooled (-78 °C) solution of *N*-allyl-*N*-*p*-toluenesulfonyl-3-chloroanthranilic acid methyl ester (400 mg, 1.05 mmol) in toluene (12 mL), was added DIBAL (1.0 M, toluene solution, 3.47 mmol, 3 eq). The mixture was stirred at -78 °C for 3 hours. The reaction was quenched by MeOH and sat. aq. Rochelle's salt, and the solution was allowed to stir at rt 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 over Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography (*n*-hexane:AcOEt = 4:1) to give *N*-allyl-*N*-*p*-toluenesulfonyl-2-chloro-6-hydroxymethylaniline (378 mg, 100%) as a colorless solid. Mp 82-83 °C (*n*-hexane), colorless prisms; ¹H NMR δ 7.63-7.66 (m, 2H), 7.54 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.23-7.34 (m, 4H), 5.88 (dddd, 1H, *J* = 16.8, 10.0, 8.8, 5.2 Hz), 5.07 (d, 1H, *J* = 10.0 Hz), 5.01 (dd, 1H, *J* = 16.8, 1.2 Hz), 4.94 (dd, 1H, *J* = 12.8, 4.0 Hz), 4.51-4.57 (m, 2H),

3.88 (dd, 1H, $J = 14.4, 8.8$ Hz), 2.96 (dd, 1H, $J = 9.6, 4.0$ Hz), 2.44 (s, 3H); ^{13}C NMR δ 145.6, 143.7, 136.8, 133.9, 133.4, 132.3, 129.9, 129.7, 129.5, 128.9, 127.6, 120.0, 61.5, 53.1, 21.4; IR (neat) cm^{-1} 3436, 2925, 1734, 1597, 1494, 1443, 1338, 1157; LRMS (FAB) m/z 352 ($\text{M}^+ + \text{H}$); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{17}\text{ClNO}_3\text{S}$ ($\text{M}^+ - \text{H}$) 350.0618, found 350.0605; Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}_4\text{S}$: C 58.03 H 5.16 N 3.98, found: C 58.07 H 5.21 N 3.89.

To a solution of *N*-allyl-*N*-*p*-toluenesulfonyl-2-chloro-6-hydroxymethylaniline (314 mg, 0.89 mmol) in CH_3CN (25 mL) was added MnO_2 (263 mg, 3.02 mmol). The mixture was refluxed for 9 hours and filtered through celite pad. After removal of the solvent, the residue was subjected to column chromatography (*n*-hexane:AcOEt = 5:1) to give *N*-allyl-*N*-*p*-toluenesulfonyl-2-chloro-6-formylaniline (235 mg, 75%) as a yellow solid. Mp 61-63 °C; ^1H NMR δ 10.21 (d, 1H, $J = 0.8$ Hz), 7.92 (dd, 1H, $J = 8.0, 1.6$ Hz), 7.59-7.63 (m, 2H), 7.58 (dd, 1H, $J = 8.0, 1.6$ Hz), 7.42 (ddd, 1H, $J = 8.0, 8.0, 0.8$ Hz), 7.28 (d, 2H, $J = 8.0$ Hz), 5.87 (dddd, 1H, $J = 16.8, 10.0, 8.8, 5.6$ Hz), 5.10 (d, 1H, $J = 10.0$ Hz), 5.05 (d, 1H, $J = 16.8$ Hz), 4.64 (dd, 1H, $J = 14.4, 5.6$ Hz), 4.03 (dd, 1H, $J = 14.4, 8.8$ Hz), 2.44 (s, 3H); ^{13}C NMR δ 189.6, 144.1, 138.6, 137.8, 136.7, 135.7, 135.0, 131.6, 129.8, 129.7, 127.5, 126.9, 121.1, 53.3, 21.6; IR (neat) cm^{-1} 3902, 2926, 1691, 1582, 1445, 1342, 1160; LRMS (FAB) m/z 350 ($\text{M}^+ + \text{H}$); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{17}\text{ClNO}_3\text{S}$ ($\text{M}^+ + \text{H}$) 350.0618, found 350.0637.

To a cooled (0 °C) solution of BrPh_3PMe (35 mg, mmol) in THF (2 mL), $\text{KN}(\text{TMS})_2$ (0.5 M, toluene solution, 0.4 mL, 0.20 mmol) was added. The solution was stirred for 1 hour at 0 °C. To the solution was added a solution of *N*-allyl-*N*-*p*-toluenesulfonyl-2-chloro-6-formylaniline (35 mg, 0.10 mmol) in THF (1.5 mL), and the mixture was stirred for 2.5 hours at rt. The reaction was quenched by sat. aq. NH_4Cl . The organic compounds were extracted with AcOEt and the

combined organic layers 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 = 30:1) to give **1g** (32 mg, 92%) as a colorless oil. ^1H NMR δ 7.72 (d, 2H, J = 8.4 Hz), 7.55 (dd, 1H, J = 7.6, 2.0 Hz), 7.17-7.33 (m, 4H), 6.98 (dd, 1H, J = 17.6, 10.8 Hz), 5.83 (dddd, 1H, J = 18.0, 10.0, 7.6, 6.4 Hz), 5.74 (dd, 1H, J = 7.6, 1.2 Hz), 5.33 (dd, 1H, J = 11.2, 1.2 Hz), 4.93-5.04 (m, 2H), 4.37 (dddd, 1H, J = 14.4, 6.4, 1.2, 1.2 Hz), 4.07 (dddd, 1H, J = 14.4, 7.6, 1.2, 1.2 Hz), 2.44 (s, 3H); ^{13}C NMR δ 143.5, 141.7, 137.5, 135.5, 133.3, 132.3, 129.5, 129.4, 129.3, 127.8, 127.7, 124.4, 119.5, 117.0, 53.3, 21.51; IR (neat) cm^{-1} 3726, 2917, 1597, 1557, 1494, 1440, 1346, 1160; LRMS (FAB) m/z 348 ($\text{M}^+\text{+H}$); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{19}\text{ClNO}_2\text{S}$ ($\text{M}^+\text{+H}$) 348.0825, found 348.0827.

1j: To a cooled (0°C) solution of commercially available 2-chloro-6-nitrotoluene (25.0 mmol, 4.29 g) and HCHO (35% in water, 75.0 mmol, 6.43 mL) in DMSO (63 mL) was added a solution of KOH (62.5 mmol, 3.51 g) in water (4.4 mL), and the mixture was stirred for 1 hour at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with ether. The combined organic layers were washed with brine and dried over Na_2SO_4 . After removal of the solvent, the residue was subjected to column chromatography (*n*-hexane:AcOEt = 4:1) to give 3-chloro-2-(2-hydroxyethyl)nitrobenzene (4.12 g, 82%). Mp $60\text{--}61^\circ\text{C}$ (*n*-hexane/AcOEt), colorless plates; ^1H NMR δ 7.72 (dd, 1H, J = 8.1, 1.0 Hz), 7.64 (dd, 1H, J = 8.1, 1.2 Hz), 7.34 (dd, 1H, J = 8.1, 8.1 Hz), 3.96 (t, 2H, J = 6.6 Hz), 3.28 (t, 2H, J = 6.8 Hz), 1.69 (brs, 1H); ^{13}C NMR δ 152.0, 136.7, 133.8, 131.0, 127.9, 122.9, 61.2, 32.7; IR (KBr) cm^{-1} 3305, 1529, 1360, 1042; LRMS (FAB) m/z 202 (85%, $\text{M}^+\text{+H}$); HRMS (FAB) calcd for $\text{C}_8\text{H}_9\text{ClNO}_3$ ($\text{M}^+\text{+H}$) 202.0271, found 202.0276; Anal. Calcd for $\text{C}_8\text{H}_8\text{ClNO}_3$: C 47.66 H 4.00 N 6.95, found: C 47.63

H 4.08 N 6.86.

To a solution of 3-chloro-2-(2-hydroxyethyl)nitrobenzene (19.8 mmol, 4.00 g) and Et₃N (33.7 mmol, 4.70 mL) in CH₂Cl₂ (20 mL) was added dropwise methanesulfonyl chloride (21.8 mmol, 1.69 mL) at 0 °C, and the mixture was stirred for 2 hours at rt. After addition of sat. aq. NH₄Cl (15 mL), the organic compounds were extracted with CH₂Cl₂. The combined organic layers were washed with 1N HCl, sat. aq. NaHCO₃ and brine, and dried over Na₂SO₄. After removal of the solvent, the residue was resolved in CH₂Cl₂ (20 mL), and DBU (37.6 mmol, 5.62 mL) was added to the solution at 0 °C. The mixture was stirred for 12 hours at rt, and refluxed for 2 hours. After addition of sat. aq. NH₄Cl, the organic compounds were extracted with CH₂Cl₂. The combined organic layers were washed with 1N HCl and brine, and dried over Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography (*n*-hexane:AcOEt = 20:1) to give 3-chloro-2-ethenylnitrobenzene (3.00 g, 82%, 2 steps) as a yellow oil. ¹H NMR δ 7.63 (dd, 1H, *J* = 8.1, 1.2 Hz), 7.61 (dd, 1H, *J* = 8.1, 1.2 Hz), 7.34 (dd, 1H, *J* = 8.1, 8.1 Hz), 6.80 (dd, 1H, *J* = 17.8, 11.5 Hz), 5.63 (dd, 1H, *J* = 11.7, 0.5 Hz), 5.47 (dd, 1H, *J* = 17.8, 0.5 Hz); ¹³C NMR δ 150.6, 135.0, 133.1, 131.6, 129.3, 128.4, 122.3, 122.0; IR (KBr) cm⁻¹ 3087, 2875, 1526, 1360, 949; LRMS (EI) *m/z* 183 (26%, M⁺), 154 (100%, base peak).

To a solution of 3-chloro-2-ethenylnitrobenzene (0.56 mmol, 102 mg) in EtOH (3.2 mL) were added AcOH (3.2 mL) and iron powder (2.23 mmol, 125 mg), and the mixture was refluxed for 2.5 hours, then cooled to rt. After addition of water (5 mL), and K₂CO₃ to neutralize the aqueous layer, the organic compounds were extracted with Et₂O. The combined organic layers were washed with brine, and dried over Na₂SO₄. After removal of the solvent, the residue was resolved in CH₂Cl₂ (2 mL). To the solution, *p*-toluenesulfonyl chloride (0.67 mmol, 128 mg)

and pyridine (1.68 mmol, 0.14 mL) were added, and the mixture was stirred for 3 days at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with CH_2Cl_2 . The combined organic layers 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) to give *N*-*p*-toluenesulfonyl-3-chloro-2-ethenylaniline (120 mg, 70%). Mp 137-138 °C (*n*-hexane/AcOEt), colorless needles; ^1H NMR δ 7.64 (d, 2H, J = 8.5 Hz), 7.54 (dd, 1H, J = 7.8, 1.5 Hz), 7.24 (d, 2H, J = 8.1 Hz), 7.15 (dd, 1H, J = 8.1, 8.1 Hz), 7.11 (dd, 1H, J = 8.1, 1.5 Hz), 7.02 (brs, 1H), 6.34 (dd, 1H, J = 18.1, 11.5 Hz), 5.65 (dd, 1H, J = 11.5, 1.2 Hz), 5.20 (dd, 1H, J = 18.3, 1.5 Hz), 2.39 (s, 3H); ^{13}C NMR δ 144.3, 136.0, 135.2, 133.7, 130.8, 129.8, 128.8, 128.4, 127.2, 125.4, 123.1, 118.8, 21.6; IR (KBr) cm^{-1} 3264, 1566, 1337, 1166, 940; LRMS (EI) m/z 307 (17%, M^+), 252 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{15}\text{ClNO}_2\text{S}$ ($\text{M}^+\text{+H}$) 308.0512, found 308.0520; Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{ClNO}_2\text{S}$: C 58.53 H 4.58 N 4.55, found: C 58.68 H 4.70 N 4.52.

To a stirring solution of *N*-*p*-toluenesulfonyl-3-chloro-2-ethenylaniline (40.1 mg, 0.13 mmol) in CH_3CN (5 mL) were added K_2CO_3 (35.9 mg, 0.26 mmol) and allyl bromide (0.06 mL, 0.65 mmol), and the mixture was refluxed for 1 hour. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 10:1) to give **1j** (44.3 mg, 98%). Mp 80-81 °C (*n*-hexane/AcOEt), colorless plates; ^1H NMR δ 7.62 (d, 2H, J = 8.3 Hz), 7.37 (d, 1H, J = 8.1 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.05 (dd, 1H, J = 8.1, 8.1 Hz), 6.70 (dd, 1H, J = 18.1, 11.7 Hz), 6.67 (d, 1H, J = 8.1 Hz), 5.79 (dd, 1H, J = 17.8, 1.5 Hz), 5.70 (tdd, 1H, J = 17.1, 10.2, 6.6 Hz), 5.63 (dd, 1H, J = 12.0, 1.5 Hz), 5.00 (d, 1H, J = 10.5 Hz), 4.96 (d, 1H, J = 17.1 Hz), 4.09

(brs, 2H), 2.45 (s, 3H); ^{13}C NMR δ 143.7, 138.6, 138.2, 136.3, 134.1, 132.1, 130.7, 130.3, 129.6, 127.9, 127.8, 127.4, 122.4, 119.6, 54.6, 21.6; IR (KBr) cm^{-1} 3023, 2915, 1341, 1163, 663; LRMS (FAB) m/z 348 (41%, $\text{M}^+\text{+H}$), 192 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{19}\text{ClNO}_2\text{S}$ ($\text{M}^+\text{+H}$) 348.0825, found 348.0807; Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2\text{S}$: C 62.15 H 5.22 N 4.03, found: C 62.19 H 5.30 N 3.97.

1k: To a stirring solution of *N-p*-toluenesulfonyl-2-ethenyl-3-methylaniline⁹ (125 mg, 0.44 mmol) in CH_3CN (14.5 mL) were added K_2CO_3 (89.8 mg, 0.65 mmol) and allyl bromide (750 μL , 0.87 mmol), and the mixture was refluxed for 5 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 10:1) to give **1k** (130 mg, 91%). Mp 88-89 °C (*n*-hexane/AcOEt), colorless prisms; ^1H NMR δ 7.62 (d, 2H, $J = 8.4$ Hz), 7.29 (d, 2H, $J = 8.0$ Hz), 7.16 (d, 1H, $J = 7.6$ Hz), 7.01 (dd, 1H, $J = 7.6, 7.6$ Hz), 6.82 (dd, 1H, $J = 18.0, 11.6$ Hz), 6.53 (d, 1H, $J = 7.6$ Hz), 5.72 (dddd, 1H, $J = 17.2, 10.4, 6.8, 6.8$ Hz), 5.56 (dd, 1H, $J = 12.0, 1.6$ Hz), 5.39 (dd, 1H, $J = 18.0, 1.6$ Hz), 4.85-5.05 (m, 2H), 3.87-4.32 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR δ 143.3, 139.4, 137.5, 137.2, 136.6, 133.3, 132.5, 130.7, 129.4, 127.8, 126.6, 126.3, 120.4, 118.9, 54.6, 21.5, 21.3; IR (neat) cm^{-1} 3869, 3702, 2982, 1595, 1338, 1163, 1086; LRMS (FAB) m/z 328 ($\text{M}^+\text{+H}$); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2\text{S}$ ($\text{M}^+\text{+H}$) 328.1371, found 328.1395.

1l: To a solution of commercially available 2-bromo-6-methylaniline (300 mg, 1.61 mmol) in pyridine (1.50 mL) was added *p*-toluenesulfonyl chloride (370 mg, 1.93 mmol), and the mixture was stirred for 8.5 hours at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with CH_2Cl_2 . After the combined organic layers were washed with 1N HCl, the

organic layers were washed brine, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by recrystallization from *n*-hexane and AcOEt to give *N*-*p*-toluenesulfonyl-2-bromo-6-methylaniline (456 mg, 83%). Mp 143-144 °C (*n*-hexane/AcOEt), colorless prisms; ¹H NMR δ 7.47-7.57 (m, 2H), 7.15-7.28 (m, 4H), 7.02 (dd, 1H, *J* = 8.0, 7.8 Hz), 6.21 (brs, 1H), 2.55 (s, 3H), 2.42 (s, 3H); ¹³C NMR δ 143.9, 140.7, 136.9, 132.9, 130.9, 130.3, 129.5, 128.5, 127.7, 123.4, 21.6, 20.3; IR (neat) cm⁻¹ 3854, 3750, 3255, 1595, 1458, 1398, 1335, 1159; LRMS (EI) *m/z* 339 (M⁺); HRMS (FAB) calcd for C₁₄H₁₅BrNO₂S (M⁺+H) 338.9929, found 338.9935; Anal. Calcd for C₁₄H₁₄BrNO₂S: C 49.42 H 4.15 N 4.12, found: C 49.31 H 4.23 N 4.02.

To a solution of *N*-*p*-toluenesulfonyl-2-bromo-6-methylaniline (286 mg, 0.84 mmol) in toluene (8.4 mL) were added Pd(PPh₃)₄ (29.1 mg, 3 mol%) and tributylvinyltin (0.25 mL, 0.84 mmol). The mixture was refluxed for 10 hours and filtered through a celite pad. After removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 7:1) to give *N*-*p*-toluenesulfonyl-2-ethenyl-6-methylaniline (149 mg, 62%) as a colorless solid. Mp 160-161 °C (*n*-hexane/AcOEt); ¹H NMR δ 7.57 (d, 2H, *J* = 8.0 Hz), 7.38 (d, 1H, *J* = 7.2 Hz), 7.23 (d, 2H, *J* = 8.0 Hz), 7.18 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.11 (d, 1H, *J* = 7.2 Hz), 6.64 (dd, 1H, *J* = 17.6, 10.8 Hz), 5.95 (brs, 1H), 5.51 (d, 1H, *J* = 16.8 Hz), 5.03 (d, 1H, *J* = 11.2 Hz), 2.42 (s, 3H), 2.09 (s, 3H); ¹³C NMR δ 143.7, 137.9, 137.3, 137.1, 132.8, 131.3, 130.4, 129.5, 127.9, 127.3, 123.9, 115.4, 21.5, 18.6; IR (neat) cm⁻¹ 3958, 3276, 1596, 1391, 1328, 1155, 1089, 792; LRMS (EI) *m/z* 287 (M⁺); HRMS (FAB) *m/z* calcd for C₁₆H₁₈NO₂S (M⁺+H) 288.1058, found 288.1036.

To a stirring solution of *N*-*p*-toluenesulfonyl-2-ethenyl-6-methylaniline (40.2 mg, 0.14 mmol) in

CH₃CN (4.6 mL) were added K₂CO₃ (29.0 mg, 0.21 mmol) and allyl bromide (240 μ L, 0.28 mmol), and the mixture was refluxed for 2.5 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure to give **1l** (43.1 mg, 94%) as a colorless oil. ¹H NMR δ 7.68 (d, 2H, J = 8.0 Hz), 7.41 (dd, 1H, J = 7.6, 1.2 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.20 (dd, 1H, J = 7.6, 7.6 Hz), 7.15 (dd, 1H, J = 7.6, 1.2 Hz), 6.38 (dd, 1H, J = 17.6, 11.2 Hz), 5.85 (dddd, 1H, J = 16.8, 10.0, 7.2, 6.8 Hz), 5.58 (d, 1H, J = 17.6 Hz), 5.03 (d, 1H, J = 11.2 Hz), 4.92-5.08 (m, 2H), 4.19 (dd, 1H, J = 14.4, 6.8 Hz), 4.01 (dd, 1H, J = 14.4, 7.2 Hz), 2.44 (s, 3H), 2.20 (s, 3H); ¹³C NMR δ 143.3, 139.9, 138.0, 137.7, 135.7, 133.5, 132.7, 130.7, 129.6, 128.3, 127.5, 123.7, 119.1, 115.5, 54.2, 21.5, 19.2; IR (neat) cm⁻¹ 3866, 3725, 1597, 1457, 1340, 1159, 1090; LRMS (EI) m/z 327 (M⁺); HRMS (FAB) m/z calcd for C₁₉H₂₂NO₂S (M⁺+H) 328.1371, found 328.1348.

1m: To a solution of *N*-acetyl-2-ethenylaniline¹⁰ (242 mg, 1.50 mmol) and NaH (60% in mineral oil, 120 mg, 3.00 mmol) in THF (5 mL) was added allyl bromide (0.26 mL, 3.00 mmol), and the mixture was stirred for 11 hours at rt. After addition of sat. aq. NH₄Cl, the organic compounds were extracted with AcOEt. The combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 3:1) to give **1m** (287 mg, 95%) as a colorless oil. ¹H NMR δ 7.65 (dd, 1H, J = 7.8, 2.0 Hz), 7.27-7.35 (m, 2H), 7.10 (dd, 1H, J = 7.6, 1.3 Hz), 6.73 (1H, dd, J = 17.5, 11.2 Hz), 5.82-5.92 (m, 1H), 5.79 (dd, 1H, J = 17.5, 1.1 Hz), 5.38 (dd, 1H, J = 11.3, 1.0 Hz), 5.03-5.11 (m, 2H), 4.63 (dd, 1H, J = 14.7, 6.1 Hz), 3.83 (dd, 1H, J = 14.4, 7.3 Hz), 1.77 (s, 3H); ¹³C NMR δ 170.5, 140.1, 135.5, 132.7, 131.7, 129.3, 128.8, 128.4, 126.3, 118.5, 117.1, 51.6, 22.5; IR (neat) cm⁻¹ 3488, 3068, 3016, 2924, 1666; LRMS (EI) m/z 118

(100%, base peak), 201 (M^+ , 7.9%); HRMS (EI) calcd for $C_{13}H_{16}NO$ ($M^+ + H$) 202.1232, found 202.1226.

1n: To a stirring solution of NaH (60% in mineral oil, 80.0 mg, 2.00 mmol) in THF (1 mL) were added *N*-benzoyl-2-ethenylaniline¹¹ (223 mg, 1.00 mmol) in THF (5 mL) and allyl bromide (0.17 mL, 2.00 mmol), and the mixture was stirred for 12 hours at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4 . After removal of the solvent, The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 10:1) to give **1n** (251.2 mg, 95%). Mp 66 °C (AcOEt/*n*-hexane), colorless prisms; 1H NMR δ 7.48 (d, 1H, J = 7.8 Hz), 7.26 (d, 2H, J = 7.1 Hz), 7.07-7.19 (m, 5H), 6.91 (d, 1H, J = 6.8 Hz), 6.86 (dd, 1H, J = 17.3, 11.0 Hz), 5.99 (dddd, 1H, J = 17.2, 10.0, 7.1, 5.9 Hz), 5.73 (d, 1H, J = 17.3 Hz), 5.37 (d, 1H, J = 11.0 Hz), 5.14 (d, 1H, J = 10.0 Hz), 5.12 (d, 1H, J = 17.2 Hz), 4.85 (dd, 1H, J = 14.4, 5.9 Hz), 3.97 (dd, 1H, J = 14.4, 7.1 Hz); ^{13}C NMR δ 170.4, 140.3, 135.7, 134.7, 132.2, 131.9, 130.0, 129.4, 128.1, 128.1, 127.6, 127.3, 126.1, 118.5, 116.7, 52.7; IR (KBr) cm^{-1} 3068, 2979, 1646, 1384; LRMS (EI) m/z 263 (100%, M^+ , base peak), 235 (100%); HRMS (FAB) calcd for $C_{18}H_{18}NO$ ($M^+ + H$) 264.1388, found 264.1377; Anal. Calcd for $C_{18}H_{17}NO$: C 82.10 H 6.51 N 5.32, found: C 82.14 H 6.52 N 5.19.

1o: To a solution of 2-ethenylaniline⁷ (300 mg, 2.52 mmol) in THF (6.3 mL) were added Boc_2O (1.1 mL, 5.04 mmol) and triethylamine (0.70 mL, 5.04 mmol), and the mixture was refluxed for 17 hours. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4 . After removal of

the solvent, The obtained crude residue was subjected to column chromatography (*n*-hexane:CH₂Cl₂ = 1:1) to give *N*-*tert*-butoxycarbonyl-2-ethenylaniline (544 mg, 98%) as a yellow oil. ¹H NMR δ 7.80 (d, 1H, *J* = 7.2 Hz), 7.38 (dd, 1H, *J* = 7.6, 1.2 Hz), 7.26 (ddd, 1H, *J* = 8.0, 7.6, 1.6 Hz), 7.07 (dd, 1H, *J* = 7.6, 7.2 Hz), 6.82 (dd, 1H, *J* = 17.6, 11.2 Hz), 6.41 (brs, 1H), 5.66 (dd, 1H, *J* = 17.6, 1.2 Hz), 5.41 (dd, 1H, *J* = 11.2, 1.2 Hz), 1.52 (s, 9H); ¹³C NMR δ 153.0, 135.0, 132.2, 129.2, 128.4, 126.8, 123.9, 121.7, 117.7, 80.5, 28.3; IR (neat) cm⁻¹ 3304, 2978, 1688, 1520, 1452, 1246, 1154; LRMS (EI) *m/z* 219 (M⁺); HRMS (FAB) calcd for C₁₃H₁₇NO₂ 219.1259, found 219.1254.

To a stirring solution of NaH (60% in mineral oil, 38.4 mg, 0.96 mmol) in THF (3 mL) were added *N*-*tert*-butoxycarbonyl-2-ethenylaniline (105 mg, 0.48 mmol) in THF (2 mL) and allyl bromide (83.1 μL, 0.96 mmol), and the mixture was stirred for 2 hours at 50 °C. After addition of sat. aq. NH₄Cl, the organic compounds were extracted with AcOEt. The combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 50:1) to give **1o** (118 mg, 95%) as a colorless oil. ¹H NMR δ 7.57 (brs, 1H), 7.22-7.24 (m, 2H), 7.07 (brs, 1H), 6.76 (dd, 1H, *J* = 17.6, 11.0 Hz), 5.83-5.93 (m, 1H), 5.72 (d, 1H, *J* = 17.5 Hz), 5.30 (d, 1H, *J* = 11.0 Hz), 5.07 (d, 2H, *J* = 13.9 Hz), 4.35 (m, 1H), 3.94 (m, 1H), 1.31 (s, 9H); ¹³C NMR δ 154.7, 139.9, 135.4, 133.6, 132.8, 128.6, 128.1, 127.1, 125.5, 117.6, 115.3, 80.0, 52.6, 28.1; IR (neat) cm⁻¹ 3069, 2978, 2929, 1697; LRMS (EI) *m/z* 57 (100% base peak), 259 (M⁺, 3.9%); HRMS (EI) calcd for C₁₆H₂₁NO₂ 259.1572, found 259.1584.

1p: To a solution of 2-ethenylaniline⁷ (100 mg, 0.84 mmol) in CH₂Cl₂ (10 mL) were added a solution of Na₂CO₃ (106 mg, 1.00 mmol) in water (2 mL) and

benzyloxycarbonyl chloride (0.14 mL, 1.00 mL), and the mixture was stirred for 12 hours at rt. After the organic compounds were extracted with CH_2Cl_2 , the combined organic layers were washed with brine and dried over Na_2SO_4 . After removal of the solvent, The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 5:1) to give *N*-benzyloxycarbonyl-2-ethenylaniline (156 mg, 73%). Mp 81-82 °C (*n*-hexane), colorless needles; ^1H NMR δ 7.82 (brs, 1H), 7.26-7.41 (m, 7H), 7.11 (dd, 1H, J = 7.5, 7.5 Hz), 6.79 (dd, 1H, J = 17.2, 11.0 Hz), 6.63 (brs, 1H), 5.65 (d, 1H, J = 17.4 Hz), 5.40 (d, 1H, J = 11.0 Hz), 5.21 (s, 2H); ^{13}C NMR δ 153.7, 136.0, 134.4, 131.9, 129.5, 128.5, 128.5, 128.4, 128.3, 126.8, 124.4, 121.9, 118.0, 67.0; IR (KBr) cm^{-1} 3276, 1690, 1523, 1239; LRMS (FAB) m/z 253 (M^+ , 32%), 91 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_2$ ($\text{M}^+\text{+H}$) 254.1181, found 254.1192; Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2$: C 75.87 H 5.97 N 5.53, found: C 75.68 H 6.02 N 5.49.

To a stirring solution of NaH (60% in mineral oil, 32.4 mg, 0.81 mmol) in THF (1 mL) were added *N*-benzyloxycarbonyl-2-ethenylaniline (88.7 mg, 0.35 mmol) in THF (1 mL) and allyl bromide (0.07 mL, 0.81 mmol), and the mixture was stirred for 12 hours at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4 . After removal of the solvent, The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 10:1) to give **1p** (94.3 mg, 92%) as a colorless oil. ^1H NMR ($\text{DMSO}-d_6$, 120 °C) δ 7.60-7.62 (m, 1H), 7.16-7.30 (m, 8H), 6.72 (dd, 1H, J = 17.6, 10.5 Hz), 5.87 (ddt, 1H, J = 16.8, 10.3, 6.4 Hz), 5.72 (dd, 1H, J = 17.6, 1.3 Hz), 5.29 (dd, 1H, J = 11.2, 1.3 Hz), 5.06-5.11 (m, 4H), 4.17 (brs, 2H); ^{13}C NMR ($\text{DMSO}-d_6$,

150 °C) δ 154.2, 138.9, 136.3, 134.9, 132.9, 132.0, 128.3, 127.6, 127.5, 126.9, 126.9, 126.6, 125.6, 116.9, 115.4, 66.1, 52.3; IR (neat) cm^{-1} 3066, 3033, 1704, 1398; LRMS (EI) m/z 158 (100%, base peak), 293 (17.5%, M^+); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_2$ ($M^+ + \text{H}$) 294.1494, found 294.1511.

1q: To a solution of 2-ethenylaniline⁷ (396 mg, 3.33 mmol) in CH_2Cl_2 (8.4 mL) were added methanesulfonyl chloride (3.66 mmol, 0.28 mL) and pyridine (3.66 mmol, 0.30 mL), and the mixture was stirred for 8 hours at rt. After addition of sat. aq. NH_4Cl , the organic compounds were extracted with CH_2Cl_2 . After the combined organic layers were washed with 1N HCl, the organic layers were washed brine, and dried over Na_2SO_4 . The solvent was removed by evaporator to give *N*-methanesulfonyl-2-ethenylaniline (644 mg, 98%). Mp 102-103 °C (*n*-hexane/AcOEt), colorless needles; ^1H NMR δ 7.42-7.53 (m, 2H), 7.17-7.37 (m, 2H), 6.91 (dd, 1H, J = 17.6, 11.2 Hz), 6.40 (brs, 1H), 5.72 (d, 1H, J = 17.6 Hz), 5.48 (d, 1H, J = 11.2 Hz), 3.00 (s, 3H); ^{13}C NMR δ 133.2, 132.2, 131.6, 129.0, 127.3, 126.6, 124.2, 118.8, 40.0; IR (neat) cm^{-1} 3918, 3229, 3024, 1630, 1456, 1399, 1312, 1149; LRMS (EI) m/z 197 (M^+); HRMS (FAB) calcd for $\text{C}_9\text{H}_{12}\text{NO}_2\text{S}$ ($M^+ + \text{H}$) 198.0589, found 198.0592; Anal. Calcd for $\text{C}_9\text{H}_{11}\text{NO}_2\text{S}$: C 54.80 H 5.62 N 7.10, found: C 54.82 H 5.80 N 7.15.

To a stirring solution of *N*-methanesulfonyl-2-ethenylaniline (200 mg, 1.01 mmol) in CH_3CN (34 mL) were added K_2CO_3 (210 mg, 1.52 mmol) and allyl bromide (130 μL , 1.52 mmol), and the mixture was refluxed for 4 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure to give **1q** (234 mg, 98%) as a colorless oil. ^1H NMR δ 7.67 (dd, 1H, J = 7.6, 2.0 Hz), 7.24-7.38 (m, 3H), 7.08 (dd, 1H, J = 17.6, 11.2 Hz), 5.86

(ddt, 1H, $J = 15.2, 10.4, 6.8$ Hz), 5.79 (dd, 1H, $J = 17.6, 0.8$ Hz), 5.39 (dd, 1H, $J = 11.2, 0.8$ Hz), 5.08-5.14 (m, 2H), 4.06-4.30 (m, 2H), 2.98 (s, 3H); ^{13}C NMR δ 138.0, 136.6, 132.5, 132.4, 129.6, 128.9, 128.5, 126.4, 119.7, 116.5, 54.5, 39.4; IR (neat) cm^{-1} 3735, 3065, 1483, 1333, 1152, 1063, 774; LRMS (FAB) m/z 238 ($\text{M}^+\text{+H}$); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_2\text{S}$ ($\text{M}^+\text{+H}$) 238.0902, found 238.0902.

1r: To a stirring solution of *N-p*-toluenesulfonyl-2-ethenylaniline⁷ (300 mg, 1.10 mmol) in CH_3CN (22 mL) were added K_2CO_3 (304 mg, 2.20 mmol) and 4-bromo-1-butene (0.22 mL, 2.20 mmol), and the mixture was refluxed for 4 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 20:1) to give **1r** (279 mg, 77%) as a colorless oil. ^1H NMR δ 7.67 (d, 1H, $J = 7.9$ Hz), 7.57 (d, 2H, $J = 8.2$ Hz), 7.31 (dd, 1H, $J = 7.7, 7.7$ Hz), 7.27 (d, 2H, $J = 8.2$ Hz), 7.15 (dd, 1H, $J = 7.7, 7.7$ Hz), 7.06 (dd, 1H, $J = 17.6, 11.0$ Hz), 6.68 (d, 1H, $J = 7.7$ Hz), 5.73 (d, 1H, $J = 17.8$ Hz), 5.68 (ddt, 1H, $J = 17.4, 10.1, 7.0$ Hz), 5.29 (d, 1H, $J = 11.2$ Hz), 5.00 (d, 1H, $J = 17.4$ Hz), 4.99 (d, 1H, $J = 10.1$ Hz), 3.76 (brs, 1H), 3.33 (brs, 1H), 2.44 (s, 3H), 2.22 (brs, 1H), 2.12 (brs, 1H); ^{13}C NMR δ 143.4, 138.8, 136.8, 135.7, 134.4, 132.8, 129.4, 128.5, 128.5, 128.1, 127.8, 126.0, 117.1, 115.6, 51.4, 32.7, 21.5; IR (KBr) cm^{-1} 3067, 2865, 1638, 1596, 1484, 1346, 1163; LRMS (EI) m/z 327 (2%, M^+), 130 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2\text{S}$ ($\text{M}^+\text{+H}$) 328.1371, found 328.1360.

1s: To a stirring solution of *N-p*-toluenesulfonyl-2-ethenylaniline⁷ (200 mg, 0.73 mmol) in CH_3CN (15 mL) were added K_2CO_3 (131 mg, 0.95 mmol) and methyl 4-bromocrotonate (0.17 mL, 1.46 mmol), and the mixture was refluxed for 40 minutes. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained

crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 5:1) to give **1s** (255 mg, 94%). (*E*)-Isomer, mp 97-98 °C (*n*-hexane/AcOEt), colorless plates; ¹H NMR δ 7.62 (dd, 1H, *J* = 7.9, 1.5 Hz), 7.58 (d, 2H, *J* = 8.2 Hz), 7.31 (ddd, 1H, *J* = 8.0, 8.0, 1.0 Hz), 7.29 (d, 2H, *J* = 8.1 Hz), 7.15 (ddd, 1H, *J* = 7.7, 7.7, 1.5 Hz), 6.93 (dd, 1H, *J* = 17.6, 11.0 Hz), 6.79 (dt, 1H, *J* = 15.7, 6.4 Hz), 6.75 (dd, 1H, *J* = 7.9, 1.1 Hz), 5.80 (dt, 1H, *J* = 15.7, 1.3 Hz), 5.71 (dd, 1H, *J* = 17.6, 1.1 Hz), 5.30 (dd, 1H, *J* = 11.2, 1.1 Hz), 4.26 (m, 2H), 3.67 (s, 3H), 2.44 (s, 3H); ¹³C NMR δ 165.9, 143.9, 141.9, 138.3, 136.5, 135.8, 132.4, 129.6, 129.2, 128.9, 128.2, 127.8, 126.5, 123.9, 116.5, 52.7, 51.6, 21.6; IR (neat) cm⁻¹ 1724, 1340, 1260, 1155; LRMS (EI) *m/z* 216 (100%, base peak), 340 (35%), 371 (4%, M⁺); HRMS (FAB) calcd for C₂₀H₂₂NO₄S (M⁺+H) 372.1270, found 372.1286.

1t: To a solution of *N*-*p*-toluenesulfonyl-2-ethenylaniline⁷ (8.80 mmol, 2.40 g), methyl *trans*-5-hydroxy-2-pentenoate (26.3 mmol, 3.42 g), and triphenylphosphine (26.3 mmol, 6.90 g) in THF (88 mL) were added diethyl azodicarboxylate (40%, toluene solution, 26.3 mmol, 13.2 mL) dropwise, and the mixture was stirred for 4 hours at rt. After removal of the solvent, the residue was subjected to column chromatography (*n*-hexane:AcOEt = 5:1) to give **1t** (3.30 g, 99%) as a colorless oil. ¹H NMR δ 7.66 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.56 (d, 2H, *J* = 8.3 Hz), 7.31 (ddd, 1H, *J* = 7.3, 7.3, 0.7 Hz), 7.28 (d, 2H, *J* = 7.8 Hz), 7.16 (ddd, 1H, *J* = 8.1, 8.1, 1.7 Hz), 7.02 (dd, 1H, *J* = 17.6, 11.0 Hz), 6.78 (ddd, 1H, *J* = 15.9, 6.8, 6.8 Hz), 6.67 (dd, 1H, *J* = 7.8, 1.2 Hz), 5.77 (ddd, 1H, *J* = 15.9, 1.5, 1.5 Hz), 5.71 (dd, 1H, *J* = 17.6, 1.0 Hz), 5.30 (dd, 1H, *J* = 11.0, 1.0 Hz), 3.83 (m, 1H), 3.70 (s, 3H), 3.40 (m, 1H), 2.44 (s, 3H), 2.30-2.37 (m, 2H); ¹³C NMR δ 166.4, 144.6, 143.7, 138.8, 136.5, 135.5, 132.6, 129.5, 128.7, 128.5, 128.2, 127.8, 126.2, 123.0, 116.0, 51.4, 50.3, 31.2, 21.5; IR (neat) cm⁻¹ 2950, 1722, 1346, 1158; LRMS (EI) *m/z* 131

(100%, base peak), 385 (3%, M^+); HRMS (FAB) calcd for $C_{21}H_{24}NO_4S$ ($M^+ + H$) 386.1426, found 386.1411.

18b: To a stirring solution of commercially available 2-hydroxy-5-methoxybenzaldehyde (1.00 g, 6.57 mmol) in CH_3CN (66 mL) were added K_2CO_3 (1.82 g, 13.1 mmol) and allyl bromide (1.14 mL, 13.1 mmol), and the mixture was refluxed for 1 hour. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 30:1) to give 2-allyloxy-5-methoxybenzaldehyde (1.25 g, 99%) as a yellow oil. 1H NMR δ 10.5 (s, 1H), 7.34 (d, 1H, J = 3.2 Hz), 7.12 (dd, 1H, J = 9.0, 3.2 Hz), 6.94 (d, 1H, J = 9.0 Hz), 6.07 (tdd, 1H, J = 17.1, 10.5, 5.1 Hz), 5.43 (dd, 1H, J = 17.3, 1.5 Hz), 5.32 (dd, 1H, J = 10.5, 1.2 Hz), 4.62 (d, 2H, J = 5.1 Hz), 3.81 (s, 3H); ^{13}C NMR δ 189.5, 155.7, 153.7, 132.6, 125.3, 123.4, 117.9, 114.8, 110.2, 69.9, 55.7; IR (neat) cm^{-1} 2864, 1683, 1495; LRMS (EI) m/z 192 (51%, M^+), 151 (100%, base peak); HRMS (FAB) calcd for $C_{11}H_{12}O_3$; 192.0786, found 192.0799.

To a cooled (0 °C) solution of $BrPh_3PMe$ (1.10 g, 3.10 mmol) in THF (20 mL), $KN(TMS)_2$ (20w/v%, toluene solution, 3.57 mL, 3.10 mmol) was added. The solution was stirred for 1 hour at 0 °C. To the solution was added a solution of 2-allyloxy-5-methoxybenzaldehyde (500 mg, 2.60 mmol) in THF (2 mL x 3), and the mixture was stirred for 12 hours at rt. The reaction was quenched by sat. aq. NH_4Cl . The organic compounds were extracted with AcOEt and the combined organic layers 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 = 30 : 1) to give **18b** (430 mg, 87%) as a colorless oil. 1H NMR δ 7.07 (dd, 1H, J = 17.8, 11.2 Hz), 7.04 (dd, 1H, J = 2.9, 2.9 Hz), 6.81 (d, 1H, J = 9.0 Hz), 6.76 (dd, 1H, J = 9.0, 2.9 Hz), 6.07 (tdd, 1H, J =

17.2, 10.6, 5.1 Hz), 5.73 (dd, 1H, $J = 17.6, 1.3$ Hz), 5.40 (ddd, 1H, $J = 17.2, 3.3, 1.7$ Hz), 5.27 (dd, 1H, $J = 11.0, 1.3$ Hz), 5.26 (ddd, 1H, $J = 10.4, 2.3, 1.5$ Hz), 4.50 (ddd, 2H, $J = 5.1, 1.7, 1.7$ Hz), 3.79 (s, 3H); ^{13}C NMR δ 153.9, 150.1, 133.6, 131.5, 128.1, 117.1, 114.6, 114.2, 113.8, 111.6, 70.1, 55.6; IR (neat) cm^{-1} 3085, 2939, 1493, 1215; LRMS (FAB) m/z 190 (M^+ , 53%); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$ 190.0994, found 190.1006.

18c: To a stirring solution of commercially available 2-hydroxy-5-methoxybenzaldehyde (365 mg, 2.40 mmol) in CH_3CN (24 mL) were added K_2CO_3 (663 mg, 4.80 mmol) and 4-bromo-1-butene (0.49 mL, 4.80 mmol), and the mixture was refluxed for 23 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The obtained crude residue was subjected to column chromatography (n -hexane:AcOEt = 7:1) to give 2-(3-butenyloxy)-5-methoxybenzaldehyde (323 mg, 65%) as a yellow oil. ^1H NMR δ 10.5 (s, 1H), 7.22 (d, 1H, $J = 3.1$ Hz), 7.11 (dd, 1H, $J = 9.0, 3.3$ Hz), 6.94 (d, 1H, $J = 9.0$ Hz), 5.90 (ddt, 1H, $J = 17.0, 10.3, 6.8$ Hz), 5.18 (ddt, 1H, $J = 17.2, 3.3, 1.7$ Hz), 5.13 (ddt, 1H, $J = 10.3, 1.6, 1.1$ Hz), 4.10 (t, 2H, $J = 6.6$ Hz), 3.80 (s, 3H), 2.58 (dtdd, 2H, $J = 6.8, 6.6, 1.3, 1.3$ Hz); ^{13}C NMR δ 189.6, 156.1, 153.6, 134.0, 125.2, 123.5, 117.4, 114.5, 110.0, 68.3, 55.7, 33.6; IR (neat) cm^{-1} 3077, 2941, 2866, 1683, 1495, 1278, 1219; LRMS (EI) m/z 206 (35%, M^+), 152 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$ 206.0943, found 206.0931.

To a cooled (0 °C) solution of BrPh_3PMe (722 mg, 2.00 mmol) in THF (5 mL), $\text{KN}(\text{TMS})_2$ (0.5 M, toluene solution, 4.00 mL, 2.00 mmol) was added. The solution was stirred for 30 minutes at 0 °C. To the solution was added a solution of 2-(3-butenyloxy)-5-methoxybenzaldehyde (209 mg, 1.00 mmol) in THF (2 mL x 3), and the mixture was stirred for 1 hour at rt. The reaction

was quenched by sat. aq. NH_4Cl . The organic compounds were extracted with AcOEt and the combined organic layers 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 = 15 : 1) to give **18c** (201 mg, 97%) as a colorless oil. ^1H NMR δ 7.03 (dd, 1H, J = 17.6, 11.2 Hz), 7.03 (d, 1H, J = 2.7 Hz), 6.79 (d, 1H, J = 8.8 Hz), 6.75 (dd, 1H, J = 9.0, 2.9 Hz), 5.91 (ddt, 1H, J = 17.1, 10.2, 6.8 Hz), 5.73 (dd, 1H, J = 17.6, 1.2 Hz), 5.25 (dd, 1H, J = 11.0, 1.2 Hz), 5.16 (ddt, 1H, J = 17.3, 1.7, 1.5 Hz), 5.10 (ddt, 1H, J = 10.3, 1.7, 1.2 Hz), 3.97 (t, 2H, J = 6.6 Hz), 3.77 (s, 3H), 2.54 (dddt, 2H, J = 6.8, 6.6, 1.5, 1.2 Hz); ^{13}C NMR δ 153.8, 150.5, 134.7, 131.5, 127.9, 116.9, 114.5, 113.8 (2C), 111.6, 68.6, 55.6, 33.9; IR (neat) cm^{-1} 3082, 2937, 1495, 1215; LRMS (EI) m/z 204 (73%, M^+), 150 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ 204.1150, found 204.1146.

General procedure for RCM.

To a solution of diene (20-100 mg) was added ruthenium catalyst (**A** or **B**) under an Ar atmosphere. The mixture was stirred under the conditions indicated in the tables. After removal of the solvent, the residue was purified by column chromatography on silica gel to give the corresponding cyclized product.

Spectral data of **2d**, **2f**, **2h**, and **2i** have been already reported in reference 1.

2a¹²: a colorless needle. Mp 85-87 °C (MeOH), lit.¹² Mp 85-86 °C; ^1H NMR δ 7.70 (d, 1H, J = 8.1 Hz), 7.25-7.30 (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 δ 143.3, 136.3, 134.9, 129.5, 129.0, 127.9, 127.2, 126.8, 126.6, 126.4,

125.8, 123.9, 45.3, 21.5; IR (KBr) cm^{-1} 1337, 1166; LRMS (EI) m/z 285 ($\text{M}^+ + \text{H}$).

2b: a colorless prism. Mp 102-103 °C (*n*-hexane/AcOEt); ^1H NMR δ 7.52 (d, 2H, $J = 8.3$ Hz), 7.19 (dd, 1H, $J = 8.3, 7.6$ Hz), 7.18 (d, 2H, $J = 8.3$ Hz), 6.91 (d, 1H, $J = 8.3$ Hz), 6.62 (d, 1H, $J = 7.3$ Hz), 6.09 (dt, 1H, $J = 9.5, 1.5$ Hz), 5.62 (dt, 1H, $J = 9.5, 4.2$ Hz), 4.23 (m, 2H), 3.88 (s, 3H), 2.40 (s, 3H); ^{13}C NMR δ 155.5, 143.3, 137.3, 131.9, 129.0, 127.9, 127.8, 126.2, 125.9, 123.8, 118.7, 112.3, 56.0, 45.7, 21.5; IR (neat) cm^{-1} 1568, 1473, 1347, 1159, 1083, 808; LRMS (EI) m/z 315 (100%, M^+ , base peak); Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3\text{S}$: C 64.74 H 5.43 N 4.44, found: C 64.46 H 5.51 N 4.31.

2c: a colorless oil; ^1H NMR δ 7.33 (d, 2H, $J = 8.4$ Hz), 7.30 (d, 1H, $J = 2.4$ Hz), 7.07 (d, 2H, $J = 8.4$ Hz), 6.84 (d, 1H, $J = 8.4$ Hz), 6.73 (dd, 1H, $J = 8.4, 2.4$ Hz), 5.98 (d, 1H, $J = 9.6$ Hz), 5.44 (dt, 1H, $J = 9.6, 4.0$ Hz), 4.41 (dd, 2H, $J = 4.0, 1.2$ Hz), 3.86 (s, 3H), 2.34 (s, 3H); ^{13}C NMR δ 159.2, 143.3, 136.4, 136.2, 1289.0, 127.3, 127.2, 125.5, 122.6, 120.8, 113.0, 111.8, 55.5, 45.3, 21.5; IR (neat) cm^{-1} 3866, 2930, 1607, 1493, 1349, 1163; LRMS (EI) m/z 315 (M^+).

2e¹³: a colorless oil; ^1H NMR δ 7.27-7.39 (m, 3H), 7.21 (dd, 1H, $J = 8.4, 8.0$ Hz), 7.08 (d, 2H, $J = 8.0$ Hz), 6.73 (d, 1H, $J = 8.0$ Hz), 6.39 (d, 1H, $J = 9.6$ Hz), 5.55 (dt, 1H, $J = 9.2, 4.0$ Hz), 4.40 (d, 2H, $J = 4.0$ Hz), 3.79 (s, 3H), 2.35 (s, 3H); LRMS (EI) m/z 315 (35%, M^+), 160 (100%, base peak).

2g: a yellow oil; ^1H NMR δ 7.47 (d, 2H, $J = 8.4$ Hz), 7.39 (d, 1H, $J = 8.0$ Hz), 7.18 (dd, 1H, $J = 8.0, 7.6$ Hz), 7.17 (d, 2H, $J = 8.0$ Hz), 6.89 (d, 1H, $J = 7.6$ Hz), 5.98 (d, 1H, $J = 9.2$ Hz), 5.54 (ddd, 1H, $J = 9.2, 4.0, 4.0$ Hz), 4.57-4.69 (m, 1H), 3.92-4.03 (m, 1H), 2.40 (s, 3H); ^{13}C NMR δ 143.8, 136.4, 133.5, 132.8, 132.4, 130.0, 129.2, 128.2, 128.0, 126.4, 125.6, 124.7, 45.8, 21.6; IR (neat) cm^{-1} 3735, 2922, 1732, 1596, 1448, 1353, 1159; LRMS (EI) m/z 319 (M^+); HRMS (FAB)

calcd for $C_{16}H_{15}ClNO_2S$ ($M^+ + H$) 320.0512, found 320.0492.

2j: a colorless oil; 1H NMR δ 7.64 (dd, 1H, $J = 7.6, 1.5$ Hz), 7.31 (d, 2H, $J = 8.3$ Hz), 7.24 (dd, 1H, $J = 7.8, 1.5$ Hz), 7.20 (dd, 1H, $J = 8.1, 7.8$ Hz), 7.11 (d, 2H, $J = 8.1$ Hz), 6.41 (d, 1H, $J = 9.8$ Hz), 5.70 (dt, 1H, $J = 9.8, 4.4$ Hz), 4.42 (dd, 2H, $J = 4.1, 1.7$ Hz), 2.36 (s, 3H); ^{13}C NMR (C_6D_6) δ 143.4, 137.3, 137.3, 131.1, 129.2, 128.3, 127.9, 127.5, 127.3, 126.1, 126.0, 122.1, 44.9, 21.0; IR (neat) cm^{-1} 1593, 1448, 1351, 1159; LRMS (EI) m/z 319 (100%, M^+ , base peak); HRMS (FAB) calcd for $C_{16}H_{14}ClNO_2S$ (M^+) 319.0434, found 319.0414.

2k: a colorless oil. 1H NMR δ 7.55 (d, 1H, $J = 8.0$ Hz), 7.30 (d, 2H, $J = 8.0$ Hz), 7.17 (dd, 1H, $J = 8.0, 7.6$ Hz), 7.07 (d, 2H, $J = 8.0$ Hz), 7.02 (d, 1H, $J = 7.6$ Hz), 6.20 (d, 1H, $J = 10.0$ Hz), 5.62 (dt, 1H, $J = 10.0, 4.0$ Hz), 4.39 (d, 2H, $J = 4.0$ Hz), 2.35 (s, 3H), 2.19 (s, 3H); ^{13}C NMR δ 143.2, 136.5, 135.1, 133.8, 128.9, 128.2, 127.9, 127.4, 127.3, 124.7, 123.7, 122.9, 44.8, 21.5, 18.8; IR (neat) cm^{-1} 3853, 3672, 2918, 1596, 1465, 1338, 1157, 1089; LRMS (EI) m/z 299 (M^+).

2l: a colorless oil. 1H NMR δ 7.29 (d, 2H, $J = 8.0$ Hz), 7.21 (d, 1H, $J = 7.6$ Hz), 7.15 (dd, 1H, $J = 7.6, 7.6$ Hz), 7.10 (d, 2H, $J = 8.4$ Hz), 6.76 (d, 1H, $J = 7.6$ Hz), 5.85 (dd, 1H, $J = 9.6, 2.8$ Hz), 5.40 (ddd, 1H, $J = 9.2, 5.2, 2.4$ Hz), 4.68 (dd, 1H, $J = 18.4, 5.6$ Hz), 3.92 (ddd, 1H, $J = 18.4, 2.4, 2.4$ Hz), 2.57 (s, 3H), 2.38 (s, 3H); ^{13}C NMR δ 143.4, 138.0, 136.3, 133.6, 131.1, 130.9, 128.9, 127.9, 127.1, 126.3, 124.5, 123.9, 46.0, 21.5, 19.48; IR (neat) cm^{-1} 3964, 3866, 2930, 1597, 1458, 1348, 1161, 1090; LRMS (EI) m/z 299 (M^+).

General procedure for the isomerization of terminal olefin.

To a stirred solution of terminal olefin (substrate) and **6a** (10 eq) in CH_2Cl_2 was added ruthenium carbene catalyst (**B**) (0.05 eq) under an Ar atmosphere and the mixture was refluxed

for 1.5 – 3 hours. The solvent was removed under vacuum and the resulting crude residue was subjected to column chromatography to give the corresponding isomerized product.

8¹⁴ (a mixture of *E*- and *Z*-isomers): a colorless oil. ¹H NMR δ 5.23-5.52 (m, 2H), 4.14-4.08 (m, 2H), 2.55-2.41 (m, 4.2H), 2.27-2.22 (m, 0.8H), 1.97-2.01 (m, 1H), 1.74-1.57 (m, 6H), 1.47-1.39 (m, 1H), 1.21-1.26 (m, 3H); ¹³C NMR δ 207.8, 207.7, 171.6, 128.8, 127.1, 125.6, 124.5, 61.2, 61.1, 61.1, 60.9, 41.1, 38.1, 35.7, 35.5, 31.9, 27.5, 22.5, 22.4, 17.9, 14.2, 14.1, 12.8; IR (neat) cm⁻¹ 2937, 2859, 1713, 1438, 1197.

12a¹⁵ (a mixture of *E*- and *Z*-isomers): a colorless oil. ¹H NMR δ 7.09-7.31 (m, 5H), 6.31-6.38 (m, 1H), 6.17 (qd, 0.93H, *J* = 15.6, 6.4 Hz), 5.68-5.77 (m, 0.07H), 1.84-1.80 (m, 3H).

12b¹⁶ (a mixture of *E*- and *Z*-isomers): a colorless oil. ¹H NMR δ 7.10-7.28 (m, 5H), 5.40-5.56 (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).

12c¹⁵ (a mixture of *E*- and *Z*-isomers): a colorless oil. ¹H NMR δ 7.23-7.28 (m, 2H), 6.81-6.85 (m, 2H), 6.32-6.36 (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), 1.85-1.90 (m, 3H).

12d¹⁷ (a mixture of *E*- and *Z*-isomers), a colorless oil. ¹H NMR δ 5.40-5.48 (m, 2H), 3.62 (t, 1.73H, *J* = 6.6 Hz), 3.55 (t, 0.27H, *J* = 6.6 Hz), 2.02-2.14 (m, 4H), 1.62-1.69 (m, 3H).

12e¹⁸ (a mixture of *E*- and *Z*-isomers), a colorless oil. ¹H NMR δ 7.25-7.37 (m, 5H), 5.35-5.57 (m, 2H), 4.52 (s, 0.26H), 4.50 (s, 1.74H), 3.45-3.50 (m, 2H), 2.29-2.40 (m, 0.26H), 1.98-2.17 (m, 1.74H), 1.61-1.71 (m, 5H).

12f¹⁹ (a mixture of *E*- and *Z*-isomers), a colorless oil. ¹H NMR δ 7.27-7.38 (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 δ 146.3, 145.2, 137.8, 137.4, 128.5, 128.4, 127.8, 127.8, 127.5, 127.6, 101.9, 99.5, 73.5, 71.1, 12.6, 9.3.

General procedure for isomerization of terminal olefin and subsequent RCM.

To a stirred solution of *N*-allyl-2-ethenylaniline (substrate) and **6a** (1 eq) in CH_2Cl_2 was added ruthenium carbene catalyst (**B**) (0.05 eq) under an argon atmosphere and the mixture was refluxed for 1.5 – 4 hours. After the removal of solvent, the obtained enamide was subjected to RCM under the conditions indicated in the tables. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to give the corresponding indoles.

4a¹²: a colorless needle. Mp 87-88 °C (MeOH), lit.¹² Mp 78.5-79.5 °C; ^1H NMR 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), 7.19-7.32 (m, 4H), 6.64 (d, 1H, $J = 3.4$ Hz), 2.31 (s, 3H); ^{13}C NMR δ 143.9, 135.3, 134.8, 130.7, 129.8, 126.8, 126.3, 124.5, 123.2, 121.3, 113.5, 109.0, 21.5; LRMS (EI) m/z 271 (100%, base peak, M^+).

4b²⁰: a colorless solid. Mp 50-52 °C, lit.²⁰ Mp 50-52 °C; ^1H NMR δ 7.83 (d, 1H, $J = 3.7$ Hz), 7.73 (d, 2H, $J = 8.3$ Hz), 7.25 (d, 2H, $J = 8.1$ Hz), 7.16 (dd, 1H, $J = 7.8, 1.2$ Hz), 7.11 (dd, 1H, $J = 7.6, 7.6$ Hz), 6.67 (dd, 1H, $J = 7.8, 1.2$ Hz), 6.63 (d, 1H, $J = 3.7$ Hz), 3.68 (s, 3H), 2.39 (s, 3H); ^{13}C NMR δ 147.3, 144.1, 137.3, 133.6, 129.3, 128.6, 127.3, 124.5, 124.0, 113.9, 106.9, 106.8, 55.4, 21.6.

4c²¹: a yellow solid. Mp 126-128 °C, lit.²¹ Mp 125-126 °C; ^1H NMR δ 7.74 (d, 2H, $J = 8.4$ Hz), 7.52 (d, 1H, $J = 2.4$ Hz), 7.43 (d, 1H, $J = 3.6$ Hz), 7.38 (d, 1H, $J = 8.8$ Hz), 7.22 (d, 2H, $J = 8.0$

Hz), 6.85 (dd, 1H, $J = 2.4, 8.4$ Hz), 6.57 (d, 1H, $J = 4.0$ Hz), 3.87 (s, 3H), 2.34 (s, 3H); ^{13}C NMR δ 157.9, 114.9, 135.9, 135.3, 129.8, 126.7, 125.1, 124.5, 121.7, 112.5, 109.0, 97.9, 55.8, 21.5; LRMS (EI) m/z 301 (53%, M^+), 146 (100%, base peak).

4d²⁰: a colorless needle. Mp 112-113 °C (MeOH), lit.²⁰ Mp 92.5-93.5 °C; ^1H NMR 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, 2H, $J = 8.2$ 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 δ 156.4, 144.8, 135.3, 131.7, 129.8, 129.6, 127.1, 126.7, 114.4, 113.7, 109.1, 103.6, 55.6, 21.5; LRMS (EI) m/z 301 (93%, M^+), 146 (100%, base peak).

4e⁹: a colorless oil. ^1H NMR δ 7.75 (d, 2H, $J = 8.4$ Hz), 7.59 (d, 1H, $J = 8.4$ Hz), 7.46 (d, 1H, $J = 3.6$ Hz), 7.23 (dd, 1H, $J = 8.4, 8.0$ Hz), 7.21 (d, 2H, $J = 8.4$ Hz), 6.76 (d, 1H, $J = 4.0$ Hz), 6.64 (d, 1H, $J = 8.0$ Hz), 3.90 (s, 3H), 2.33 (s, 3H).

4f: a colorless oil. ^1H NMR 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, 3H), 3.79 (s, 3H), 2.37 (s, 3H); ^{13}C NMR 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; IR (neat) cm^{-1} 2938, 1581; LRMS (EI) m/z 361 (100%, base peak, M^+); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_5\text{S}$ 361.0984, found 361.0961.

4g²⁰: a yellow oil. ^1H NMR δ 7.90 (d, 1H, $J = 3.6$ Hz), 7.69 (d, 2H, $J = 8.4$ Hz), 7.46 (d, 1H, $J = 7.6$ Hz), 7.22-7.30 (m, 2H), 7.20 (d, 1H, $J = 8.0$ Hz), 7.11 (dd, 1H, $J = 7.6, 7.6$ Hz), 6.70 (d, 1H, $J = 3.6$ Hz), 2.39 (s, 3H); ^{13}C NMR δ 144.7, 137.1, 134.7, 130.4, 129.7, 127.7, 127.1, 126.8, 124.1, 120.1, 119.0, 107.4, 21.6.

4h: a colorless needle. Mp 153-153 °C (MeOH); ^1H NMR δ 8.01 (brs, 1H), 7.76 (d, 2H, $J = 8.5$ Hz), 7.54 (d, 1H, $J = 3.7$ Hz), 7.42 (d, 1H, $J = 8.3$ 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 δ 145.3, 135.1, 135.0, 130.6, 130.0, 129.2, 126.9, 126.8, 124.0, 122.1, 113.7, 108.7, 21.6; IR (KBr) cm^{-1} 1424, 1364, 1172; LRMS (EI) m/z 305 (100%, base peak, M^+), 152 (100%); HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{12}\text{ClNO}_2\text{S}$ 305.0277, found 305.0295.

4i⁹: a pale yellow solid. ^1H NMR δ 7.90 (d, 1H, J = 8.8 Hz), 7.74 (d, 2H, J = 8.4 Hz), 7.57 (d, 1H, J = 3.6 Hz), 7.49 (d, 1H, J = 2.4 Hz), 7.26 (dd, 1H, J = 8.8, 2.4 Hz), 7.23 (d, 2H, J = 8.0 Hz), 6.59 (d, 1H, J = 3.6 Hz), 2.35 (s, 3H); ^{13}C NMR δ 145.2, 135.0, 133.1, 131.9, 129.9, 129.1, 127.7, 126.8, 124.9, 120.9, 114.5, 108.4, 21.6; LRMS (EI) m/z 305 (73%, M^+), 91 (100%, base peak).

4j: a colorless solid. Mp 118-119 °C; ^1H NMR δ 7.89 (ddd, 1H, J = 6.0, 2.9, 0.7 Hz), 7.75 (d, 2H, J = 8.4 Hz), 7.60 (d, 1H, J = 3.7 Hz), 7.20-7.25 (m, 4H), 6.77 (dd, 1H, J = 3.7, 0.7 Hz), 2.33 (s, 3H); ^{13}C NMR δ 145.3, 135.4, 134.9, 130.0, 129.5, 126.8, 126.8, 126.5, 125.2, 123.0, 112.0, 107.1, 21.5; IR (neat) cm^{-1} 2925, 1355, 1165, 751; LRMS (EI) m/z 305 (63%, M^+), 91 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{12}\text{ClNO}_2\text{S}$ (M^+) 305.0277, found 305.0256.

4l²⁰: a red oil. ^1H NMR δ 7.78 (d, 1H, J = 3.6 Hz), 7.54 (d, 2H, J = 8.0 Hz), 7.39 (d, 1H, J = 7.6 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.12 (dd, 1H, J = 7.6, 7.6 Hz), 7.01 (d, 1H, J = 7.2 Hz), 6.69 (d, 1H, J = 3.6 Hz), 2.54 (s, 3H), 2.36 (s, 3H); ^{13}C NMR δ 144.5, 137.0, 134.8, 132.9, 129.8, 129.8, 128.2, 126.4, 124.9, 123.7, 119.2, 108.7, 21.8, 21.6.; LRMS (EI) m/z 285 (54%, M^+), 18 (100%, base peak).

4m²²: a colorless oil. ^1H NMR δ 8.44 (d, 1H, J = 7.8 Hz), 7.56 (d, 1H, J = 7.8 Hz), 7.33-7.44 (m, 2H), 7.27 (dd, 1H, J = 7.6, 7.6 Hz), 6.63 (d, 1H, J = 3.9 Hz), 2.63 (s, 3H); ^{13}C NMR δ 168.6, 135.6, 130.4, 125.2, 125.1, 123.7, 120.8, 116.5, 109.2, 24.0; LRMS (EI) m/z 159 (34%, M^+),

117 (100%, base peak).

4n²³: a colorless prism. Mp 59 °C (*n*-hexane/AcOEt), lit.²³ Mp 41-43 °C; ¹H NMR δ 8.41 (d, 1H, *J* = 8.3 Hz), 7.74 (dd, 2H, *J* = 8.1, 1.2 Hz), 7.59-7.63 (m, 2H), 7.54 (d, 1H, *J* = 6.3 Hz), 7.51 (d, 1H, *J* = 7.1 Hz), 7.39 (ddd, 1H, *J* = 7.3, 7.3, 1.2 Hz), 7.33 (dd, 1H, *J* = 7.3, 1.2 Hz), 7.30 (d, 1H, *J* = 3.7 Hz), 6.62 (d, 1H, *J* = 3.7 Hz); ¹³C NMR δ 168.7, 136.0, 134.6, 131.9, 130.8, 129.2, 128.6, 127.6, 124.9, 123.9, 120.9, 116.4, 108.5; LRMS (EI) *m/z* 221 (100%, base peak, M⁺), 105 (100%).

4o²⁴: a colorless oil. ¹H NMR δ 8.13 (brs, 1H), 7.55-7.60 (m, 2H), 7.20-7.31 (m, 2H), 6.57 (d, 1H, *J* = 3.7 Hz), 1.66 (s, 9H); ¹³C NMR δ 149.8, 135.1, 130.5, 125.9, 124.1, 122.6, 120.9, 115.1, 107.2, 83.6, 28.2.

4p: a colorless solid. Mp 42-44 °C; ¹H NMR δ 8.18 (d, 1H, *J* = 7.6 Hz), 7.62 (d, 1H, *J* = 3.7 Hz), 7.56 (d, 1H, *J* = 7.6 Hz), 7.48 (d-like, 2H, *J* = 6.3 Hz), 7.29-7.43 (m, 3H), 7.22-7.26 (m, 2H), 6.59 (d, 1H, *J* = 3.4 Hz), 5.46 (s, 2H); ¹³C NMR δ 150.8, 135.2, 135.1, 130.5, 128.7, 128.7, 128.4, 125.5, 124.5, 123.0, 121.0, 115.1, 108.2, 68.6; IR (KBr) cm⁻¹ 3152, 3034, 2962, 1736; LRMS (EI) *m/z* 251 (100%, base peak, M⁺), 207 (100%); HRMS (FAB) calcd for C₁₆H₁₃NO₂ 251.0946, found 251.0938.

4q²⁵: a red oil. ¹H NMR δ 7.92 (d, 1H, *J* = 8.0 Hz), 7.63 (d, 1H, *J* = 7.6 Hz), 7.44 (d, 1H, *J* = 3.2 Hz), 7.37 (dd, 1H, *J* = 8.0, 7.2 Hz), 7.30 (dd, 1H, *J* = 7.6, 7.2 Hz), 6.71 (d, 1H, *J* = 3.6 Hz), 3.09 (s, 3H); ¹³C NMR δ 134.9, 130.7, 126.1, 124.9, 123.6, 121.6, 113.0, 108.9, 40.7.

General procedure for cycloisomerization.

To a solution of diene and **6a** was added ruthenium carbene catalyst (**B**) (5-10 mol%) under an

Ar atmosphere and the mixture was refluxed. The solvent was removed under vacuum and the resulting crude residue was subjected to column chromatography to give the corresponding cycloisomerized product.

15²⁶: a colorless prism. Mp 60-61 °C (AcOEt/*n*-hexane), ¹H NMR δ 7.71 (d, 2H, *J* = 8.2 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 4.90 (d, 1H, *J* = 2.2 Hz), 4.85 (d, 1H, *J* = 2.2 Hz), 3.95 (d, 1H, *J* = 14.1 Hz), 3.74 (dd, 1H, *J* = 14.1, 1.8 Hz), 3.58 (qt, 1H, *J* = 6.4, 5.1 Hz), 2.67-2.71 (m, 2H), 2.44 (s, 3H), 1.04 (d, 3H, *J* = 6.4 Hz); ¹³C NMR δ 149.3, 143.6, 132.9, 129.6, 127.8, 106.0, 55.0, 52.1, 37.4, 21.5, 16.0; LRMS (EI) *m/z* 251 (65%, M⁺), 91 (100%, base peak).

16²⁷: a colorless plate. Mp 153-154 °C (AcOEt/*n*-hexane), ¹H NMR δ 7.72 (d, 2H, *J* = 8.0 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 3.97 (s, 4H), 2.43 (s, 3H), 1.54 (s, 6H); ¹³C NMR δ 143.2, 134.3, 129.7, 127.5, 126.2, 58.8, 21.5, 11.1; LRMS (EI) *m/z* 251 (58%, M⁺), 236 (100%, base peak).

5a: a colorless oil. ¹H NMR δ 7.75 (d, 1H, *J* = 8.1 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 1H, *J* = 7.5 Hz), 7.27 (dd, 1H, *J* = 7.3, 7.3 Hz), 7.15 (d, 2H, *J* = 8.2 Hz), 7.04 (dd, 1H, *J* = 7.5, 7.5 Hz), 5.37 (d, 1H, *J* = 2.4 Hz), 4.86 (d, 1H, *J* = 2.1 Hz), 4.60 (dddd, 1H, *J* = 4.2, 4.2, 2.2, 2.2 Hz), 2.33 (s, 3H), 2.17 (dq, 1H, *J* = 7.3, 4.2 Hz), 1.80 (dq, 1H, *J* = 7.3, 4.2 Hz), 0.87 (t, 3H, *J* = 7.3 Hz); ¹³C NMR δ 144.7, 144.1, 143.9, 134.4, 130.4, 130.0, 129.5, 127.2, 124.3, 120.2, 116.8, 102.7, 67.3, 30.0, 21.5, 7.2; IR (neat) cm⁻¹ 3065, 3031, 2967, 2926, 1599, 1462, 1358, 1170; LRMS (EI) *m/z* 313 (55%, M⁺), 158 (100%, base peak); HRMS (FAB) calcd for C₁₈H₁₉NO₂S 313.1137, found 313.1112.

5c: a colorless oil. ¹H NMR δ 7.56 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 1H, *J* = 2.4 Hz), 7.20 (d, 1H, *J* = 8.8 Hz), 7.16 (d, 2H, *J* = 8.0 Hz), 6.60 (dd, 1H, *J* = 8.8, 2.4 Hz), 5.19 (d, 1H, *J* = 2.4 Hz), 4.71 (d, 1H, *J* = 2.0 Hz), 4.56-4.64 (m, 1H), 3.86 (s, 3H), 2.34 (s, 3H), 2.17 (ddq, 1H, *J* = 14.8, 7.2,

5.2 Hz), 1.79 (ddq, 1H J = 14.8, 7.6, 4.0 Hz), 0.87 (dd, 3H, J = 7.6, 7.2 Hz); ^{13}C NMR δ 161.6, 145.6, 144.2, 143.9, 134.6, 129.6, 127.2, 123.3, 121.5, 111.6, 101.6, 99.9, 68.1, 55.7, 30.0, 21.5, 7.1; IR (neat) cm^{-1} 3455, 3087, 2966, 1736, 1610, 1494, 1356, 1165; LRMS (EI) m/z 343 (M^+).

5d: a colorless oil. ^1H NMR δ 7.67 (d, 1H, J = 8.8 Hz), 7.49 (d, 2H, J = 8.2 Hz), 7.14 (d, 2H, J = 7.3 Hz), 6.85 (dd, 1H, J = 7.0, 2.2 Hz), 6.78 (d, 1H, J = 2.4 Hz), 5.31 (d, 1H, J = 2.2 Hz), 4.84 (d, 1H, J = 1.8 Hz), 4.55 (m, 1H), 3.78 (s, 3H), 2.33 (s, 3H), 2.02-2.14 (m, 1H), 1.75-1.81 (m, 1H), 0.88 (t, 3H, J = 7.5 Hz); ^{13}C NMR δ 157.2, 145.0, 143.7, 137.8, 134.1, 131.8, 129.5, 127.3, 118.3, 116.5, 104.9, 102.9, 67.7, 55.6, 30.1, 21.5, 7.4; IR (neat) cm^{-1} 2961, 2924, 2854, 1482, 1355, 1167, 668; LRMS (EI) m/z 343 (18%, M^+), 188 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$, 343.1242, found 343.1247.

5e: a colorless oil. ^1H NMR δ 7.56 (d, 2H, J = 8.4 Hz), 7.38 (d, 1H, J = 8.0 Hz), 7.19 (dd, 1H, J = 8.0, 8.0 Hz), 7.14 (d, 2H, J = 8.4 Hz), 6.60 (d, 1H, J = 8.0 Hz), 5.77 (d, 1H, J = 2.4 Hz), 4.95 (d, 1H, J = 2.0 Hz), 4.56-4.61 (m, 1H), 3.84 (s, 3H), 2.33 (s, 3H), 2.18 (ddq, 1H, J = 14.4, 7.2, 5.2 Hz), 1.80 (ddq, 1H, J = 14.8, 7.2, 3.6 Hz), 0.88 (dd, 3H, J = 7.2, 7.2 Hz); ^{13}C NMR δ 156.9, 145.7, 143.8, 143.2, 134.5, 130.5, 129.5, 127.2, 118.0, 109.1, 106.6, 106.3, 67.5, 55.3, 30.3, 21.50, 7.02; IR (neat) cm^{-1} 2968, 2936, 1594, 1489, 1353, 1274, 1089; LRMS (EI) m/z 343 (M^+).

5h: a colorless oil. ^1H NMR δ 7.77 (d, 1H, J = 1.7 Hz), 7.57 (d, 2H, J = 8.3 Hz), 7.21 (d, 1H, J = 8.1 Hz), 7.19 (d, 2H, J = 8.1 Hz), 7.00 (dd, 1H, J = 8.3, 2.0 Hz), 5.36 (d, 1H, J = 2.0 Hz), 4.88 (d, 1H, J = 1.5 Hz), 4.62 (dddd, 1H, J = 5.1, 3.9, 2.0, 1.5 Hz), 2.35 (s, 3H), 2.18 (ddq, 1H, J = 14.2, 7.3, 5.4 Hz), 1.79 (ddq, 1H, J = 13.9, 7.6, 4.2 Hz), 0.85 (t, 3H, J = 7.3 Hz); ^{13}C NMR δ 145.0, 144.2, 143.6, 135.6, 134.3, 129.7, 128.9, 127.1, 124.6, 121.5, 116.8, 103.2, 67.7, 29.9,

21.5, 7.0; IR (neat) cm^{-1} 2968, 2925, 2854, 1597, 1361, 1170, 667; LRMS (EI) m/z 347 (6.4%, M^+), 314 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2\text{S}$ 347.0747, found 347.0746.

5i: a colorless oil. ^1H NMR δ 7.68 (d, 1H, $J = 8.5$ Hz), 7.53 (d, 2H, $J = 8.3$ Hz), 7.25 (d, 1H, $J = 2.0$ Hz), 7.22 (dd, 1H, $J = 8.8, 2.2$ Hz), 7.18 (d, 2H, $J = 8.1$ Hz), 5.37 (d, 1H, $J = 2.0$ Hz), 4.91 (d, 1H, $J = 1.5$ Hz), 4.61 (dddd, 1H, $J = 4.9, 4.4, 2.0, 1.5$ Hz), 2.35 (s, 3H), 2.16 (ddq, 1H, $J = 13.8, 7.3, 5.4$ Hz), 1.79 (ddq, 1H, $J = 13.9, 7.3, 4.2$ Hz), 0.86 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR δ 144.2, 143.7, 142.7, 134.1, 132.1, 129.9, 129.9, 129.7, 127.1, 120.9, 117.9, 104.2, 67.7, 30.0, 21.5, 7.1; IR (neat) cm^{-1} 2969, 2924, 1591, 1360, 1168, 667; LRMS (EI) m/z 347 (100%, M^+ , base peak); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2\text{S}$ 347.0747, found 347.0756.

5j: a colorless oil. ^1H NMR δ 7.68 (dd, 1H, $J = 8.1, 0.7$ Hz), 7.54 (d, 2H, $J = 8.3$ Hz), 7.17 (d, 2H, $J = 8.5$ Hz), 7.16 (dd, 1H, $J = 8.1, 8.1$ Hz), 7.01 (dd, 1H, $J = 8.1, 1.0$ Hz), 6.10 (d, 1H, $J = 2.4$ Hz), 5.08 (d, 1H, $J = 2.0$ Hz), 4.62 (dddd, 1H, $J = 4.9, 4.4, 2.4, 2.0$ Hz), 2.35 (s, 3H), 2.13 (ddq, 1H, $J = 13.9, 7.3, 5.1$ Hz), 1.80 (ddq, 1H, $J = 14.6, 7.3, 4.6$ Hz), 0.88 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR δ 146.1, 144.2, 143.1, 134.4, 130.2, 130.0, 129.7, 127.1, 126.6, 126.1, 115.1, 109.3, 67.8, 30.6, 21.5, 7.2; IR (neat) cm^{-1} 2970, 2926, 2875, 1736, 1591, 1435, 1360, 1168, 667; LRMS (EI) m/z 347 (100%, M^+ , base peak); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2\text{S}$ 347.0747, found 347.0718.

5k: a colorless oil. ^1H NMR δ 7.61 (d, 1H, $J = 8.0$ Hz), 7.54 (d, 2H, $J = 8.4$ Hz), 7.15 (dd, 1H, $J = 8.0, 7.2$ Hz), 7.14 (d, 2H, $J = 8.0$ Hz), 6.82 (d, 1H, $J = 7.6$ Hz), 5.34 (d, 1H, $J = 1.6$ Hz), 4.97 (d, 1H, $J = 1.6$ Hz), 4.55-4.63 (m, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 2.05-2.20 (m, 1H), 1.72-1.85 (m, 1H), 0.87 (dd, 3H, $J = 7.6, 7.2$ Hz); ^{13}C NMR δ 146.0, 144.8, 143.7, 135.2, 134.7, 129.5, 129.2, 127.9, 127.2, 126.9, 114.5, 106.8, 67.7, 30.6, 21.5, 20.9, 7.3; IR (neat) cm^{-1} 3961, 3869,

3726, 2972, 1736, 1581, 1459, 1353, 1164; LRMS (EI) m/z 327 (M^+).

5m: a colorless oil. ^1H NMR δ 8.27 (d, 1H, $J = 7.2$ Hz), 7.45 (d, 1H, $J = 7.6$ Hz), 7.27 (dd, 1H, $J = 8.0, 7.6$ Hz), 7.06 (dd, 1H, $J = 7.6, 7.2$ Hz), 5.54 (d, 1H, $J = 2.0$ Hz), 5.02 (d, 1H, $J = 1.6$ Hz), 4.67-4.78 (m, 1H), 2.29 (s, 3H), 1.89-2.07 (m, 1H), 1.71-1.87 (m, 1H), 0.81 (dd, 3H, $J = 7.2, 6.8$ Hz); ^{13}C NMR δ 168.2, 145.2, 144.9, 129.9, 129.3, 123.9, 120.1, 118.0, 102.3, 65.5, 29.4, 23.4, 7.0; IR (neat) cm^{-1} 2934, 1704, 1658, 1600, 1462, 1387; LRMS (EI) m/z 130 (100%, base peak), 201 (23%, M^+); HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$ ($M^+ + \text{H}$) 202.1232, found 202.1231.

5n: a colorless oil. ^1H NMR δ 7.35-7.77 (m, 7H), 7.10 (dd, 1H, $J = 8.0, 7.6$ Hz), 7.01 (dd, 1H, $J = 8.0, 7.6$ Hz), 5.54 (d, 1H, $J = 2.0$ Hz), 5.02-5.11 (m, 1H), 4.99 (d, 1H, $J = 2.0$ Hz), 1.78-1.93 (m, 1H), 1.57-1.74 (m, 1H), 0.74 (dd, 3H, $J = 7.6, 7.2$ Hz); ^{13}C NMR δ 168.6, 145.0, 144.7, 137.4, 130.3, 130.0, 129.5, 128.7, 127.1, 123.8, 120.5, 116.6, 102.0, 65.8, 28.1, 6.9; IR (neat) cm^{-1} 3751, 2968, 1640, 1597, 1462, 1377; LRMS (EI) m/z 105 (100%, base peak), 263 (15%, M^+); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{18}\text{NO}$ ($M^+ + \text{H}$) 264.1388, found 264.1375.

5o: a colorless oil. ^1H NMR δ 7.53-8.10 (m, 1H), 7.41 (d, 1H, $J = 7.6$ Hz), 7.23 (dd, 1H, $J = 8.0, 8.0$ Hz), 6.97 (ddd, 1H, $J = 7.6, 7.6, 0.8$ Hz), 5.49 (d, 1H, $J = 2.4$ Hz), 4.97 (d, 1H, $J = 2.0$ Hz), 4.72-4.84 (m, 1H), 2.03-2.17 (m, 1H), 1.67-1.80 (m, 1H), 1.57 (s, 9H), 0.78 (dd, 3H, $J = 7.6, 7.2$ Hz); ^{13}C NMR δ (CD_2Cl_2 , 150 MHz) 152.0, 146.0, 130.0, 129.4, 122.6, 120.5, 115.9, 101.7, 101.6, 65.1, 65.0, 28.5, 28.4, 7.1; IR (neat) cm^{-1} 2978, 2931, 1723, 1455, 1330, 1135; LRMS (EI) m/z 259 (M^+).

5p: a colorless oil. ^1H NMR ($\text{DMSO}-d_6$, 120 $^\circ\text{C}$) δ 7.70-7.76 (m, 1H), 7.49-7.55 (m, 1H), 7.28-7.46 (m, 5H), 7.24 (ddd, 1H, $J = 8.0, 8.0, 1.2$ Hz), 7.00 (ddd, 1H, $J = 7.6, 7.6, 1.2$ Hz), 5.59 (d, 1H, $J = 2.4$ Hz), 5.29 (d, 1H, $J = 12.3$ Hz), 5.25 (d, 1H, $J = 12.3$ Hz), 5.06 (d, 1H, $J = 2.0$

Hz), 4.81-4.88 (m, 1H), 1.95-2.10 (m, 1H), 1.67-1.79 (m, 1H), 0.69 (dd, 3H, $J = 7.6, 7.2$ Hz); ^{13}C NMR (DMSO- d_6 , 150 °C) δ 151.2, 144.3, 143.2, 135.7, 129.0, 128.2, 127.6, 127.2, 127.0, 122.1, 119.6, 114.5, 101.5, 66.2, 63.8, 26.9, 5.9; IR (neat) cm^{-1} 3735, 2966, 1695, 1465, 1401, 1295, 1146, 1045; LRMS (EI) m/z 91 (100%, base peak), 293 (60%, M^+); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2$ (M^+) 293.1416, found 293.1411.

5q: a colorless oil. ^1H NMR δ 7.54 (d, 1H, $J = 8.0$ Hz), 7.47 (d, 1H, $J = 7.6$ Hz), 7.29 (dd, 1H, $J = 8.4, 7.6$ Hz), 7.12 (dd, 1H, $J = 7.6, 7.6$ Hz), 5.58 (d, 1H, $J = 2.0$ Hz), 5.05 (d, 1H, $J = 2.0$ Hz), 4.71 (dddd, 1H, $J = 5.2, 4.4, 2.0, 2.0$ Hz), 2.76 (s, 3H), 2.10 (ddq, 1H, $J = 14.4, 7.6, 5.2$ Hz), 1.82 (ddq, 1H, $J = 14.4, 7.2, 4.0$ Hz), 0.87 (dd, 3H, $J = 7.6, 7.2$ Hz); ^{13}C NMR δ 144.7, 143.9, 130.3, 130.1, 124.6, 121.0, 116.0, 103.3, 67.8, 35.4, 30.0, 7.1; IR (neat) cm^{-1} 2973, 2934, 1733, 1641, 1600, 1461, 1346, 1159; LRMS (EI) m/z 208 (100%, base peak), 237 (40%, M^+); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2\text{S}$ (M^+) 237.0824, found 237.0812.

5r: a colorless oil. ^1H NMR δ 7.74 (d, 1H, $J = 8.1$ Hz), 7.52 (d, 2H, $J = 8.2$ Hz), 7.30 (d, 1H, $J = 7.5$ Hz), 7.26 (d, 1H, $J = 7.5$ Hz), 7.14 (d, 2H, $J = 8.6$ Hz), 7.04 (dd, 1H, $J = 7.5, 7.5$ Hz), 5.34 (d, 1H, $J = 2.4$ Hz), 4.86 (d, 1H, $J = 2.0$ Hz), 4.62 (ddt, 1H, $J = 5.1, 2.4, 2.0$ Hz), 2.33 (s, 3H), 2.00-2.07 (m, 1H), 1.71-1.78 (m, 1H), 1.21-1.49 (m, 2H), 0.90 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR δ 145.2, 143.9, 143.9, 134.5, 130.4, 129.9, 129.5, 127.2, 124.4, 120.8, 117.1, 102.7, 66.6, 39.5, 21.5, 16.3, 14.0; IR (neat) cm^{-1} 2959, 2930, 2872, 1599, 1463, 1356, 1170; LRMS (EI) m/z 327 (100%, M^+ , base peak); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{S}$ 327.1293, found 327.1322.

3s (mixture of *E*- and *Z*-isomers): To a stirred solution of **1s** (51.2 mg, 0.14 mmol) in toluene (2.8 mL), was added $\text{RuClH}(\text{CO})(\text{PPh}_3)_3$ (26.3 mg, 27.5 μmol) under argon atmosphere. The solution was degassed three times by the freeze-pump-thaw (FTP) method and the mixture was

refluxed for 5 hours. The solvent was removed under reduced pressure and obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 5:1) to give **3s** (35.3 mg, 69%) as a colorless oil. For *E*-isomer; ^1H NMR δ 7.68 (d, 1H, J = 7.9 Hz), 7.59 (d, 2H, J = 8.2 Hz), 7.36 (dd, 1H, J = 7.9, 7.9 Hz), 7.28 (d, 2H, J = 8.4 Hz), 7.19 (dd, 1H, J = 7.7, 7.7 Hz), 7.08 (d, 1H, J = 14.1 Hz), 6.69 (d, 1H, J = 7.7 Hz), 6.68 (dd, 1H, J = 17.6, 11.0 Hz), 5.69 (d, 1H, J = 17.6 Hz), 5.19 (d, 1H, J = 11.0 Hz), 4.27 (dt, 1H, J = 13.9, 7.3 Hz), 3.60 (s, 3H), 2.98 (d, 2H, J = 7.5 Hz), 2.44 (s, 3H); ^{13}C NMR δ 172.2, 144.0, 138.0, 136.1, 133.5, 131.7, 131.2, 130.2, 129.7, 129.5, 128.6, 127.6, 126.4, 116.1, 103.1, 51.8, 35.0, 21.6; IR (neat) cm^{-1} 1735, 1360, 1162, 1131, 662; LRMS (EI) m/z 371 (19%, M^+), 216 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_4\text{S}$ ($\text{M}^+\text{+H}$) 372.1270, found 372.1289.

5s: a colorless oil. ^1H NMR δ 7.75 (d, 1H, J = 8.8 Hz), 7.50 (d, 2H, J = 8.4 Hz), 7.29 (d, 1H, J = 7.9 Hz), 7.28 (dd, 1H, J = 7.7, 7.7 Hz), 7.13 (d, 2H, J = 8.2 Hz), 7.06 (dd, 1H, J = 7.5, 7.5 Hz), 5.37 (d, 1H, J = 2.2 Hz), 4.92 (d, 1H, J = 1.8 Hz), 4.70 (m, 1H), 3.67 (s, 3H), 2.54-2.62 (m, 1H), 2.32 (s, 3H), 2.29-2.46 (m, 2H), 1.97-2.06 (m, 1H); ^{13}C NMR δ 173.8, 144.5, 144.1, 143.7, 133.9, 130.2, 130.1, 129.6, 127.3, 124.8, 120.9, 117.5, 103.4, 65.4, 51.6, 32.4, 28.2, 21.5; IR (neat) cm^{-1} 1733, 1354, 1163, 661; LRMS (EI) 371 (M^+ , 8%), 18 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_4\text{S}$ ($\text{M}^+\text{+H}$) 372.1270, found 372.1256.

3t (mixture of *E*- and *Z*- isomer): To a stirred solution of **1t** (332 mg, 0.86 mmol) in toluene (17 mL), was added $\text{RuClH}(\text{CO})(\text{PPh}_3)_3$ (81.9 mg, 86.0 μmol) under argon atmosphere. The solution was degassed three times by the freeze-pump-thaw (FTP) method and the mixture was refluxed for 15 hours. The solvent was removed under reduced pressure and obtained crude residue was subjected to column chromatography (*n*-hexane:AcOEt = 7:1) to give **3t** (*E*- and

Z-mixture, 274 mg, 83%) as a colorless solid. (*E*)-**3t** was obtained by recrystallization from *n*-hexane/AcOEt. For *E*-isomer; Mp 80-81 °C (*n*-hexane/AcOEt), colorless needles; ¹H NMR δ 7.66 (d, 1H, *J* = 7.8 Hz), 7.59 (d, 2H, *J* = 8.3 Hz), 7.35 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 7.18 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.00 (d, 1H, *J* = 13.7 Hz), 6.67 (dd, 1H, *J* = 17.6, 11.0 Hz), 6.64 (d, 1H, *J* = 7.8 Hz), 5.68 (d, 1H, *J* = 17.6 Hz), 5.19 (d, 1H, *J* = 11.0 Hz), 4.11-4.20 (m, 1H), 3.61 (s, 3H), 2.44 (s, 3H), 2.25 (m, 4H); ¹³C NMR δ 173.1, 143.9, 138.0, 136.3, 133.9, 131.8, 130.1, 129.6, 129.4, 129.3, 128.4, 127.5, 126.3, 116.0, 109.8, 51.4, 34.6, 25.3, 21.5; IR (neat) cm⁻¹ 1732, 1344, 1156, 1131, 664; LRMS (EI) *m/z* 385 (19%, M⁺), 230 (100%, base peak); HRMS (FAB) calcd for C₂₁H₂₄NO₄S (M⁺+H) 386.1426, found 386.1424; Anal. Calcd for C₂₁H₂₃NO₄S: C 65.43 H 6.01 N 3.63, found: C 65.43 H 6.22 N 3.62.

5t: a colorless prism. Mp 140-141 °C (*n*-hexane/AcOEt); ¹H NMR δ 7.75 (d, 1H, *J* = 8.1 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 7.26-7.31 (m, 2H), 7.14 (d, 2H, *J* = 8.6 Hz), 7.05 (dd, 1H, *J* = 7.7, 7.7 Hz), 5.37 (d, 1H, *J* = 2.6 Hz), 4.88 (d, 1H, *J* = 2.0 Hz), 4.61 (m, 1H), 3.63 (s, 3H), 2.25-2.44 (m, 2H), 2.33 (s, 3H), 2.09-2.17 (m, 1H), 1.71-1.86 (m, 2H), 1.61-1.68 (m, 1H); ¹³C NMR δ 173.8, 144.6, 144.0, 143.8, 134.1, 130.1, 130.0, 129.5, 127.2, 124.5, 120.9, 117.0, 103.0, 66.1, 51.5, 36.4, 33.8, 21.5, 18.6; IR (neat) cm⁻¹ 2947, 1732, 1460, 1352, 1163, 662; LRMS (EI) 385 (M⁺, 41%), 230 (100%, base peak); HRMS (FAB) calcd for C₂₁H₂₄NO₄S (M⁺+H) 386.1426, found 386.1420; Anal. Calcd for C₂₁H₂₃NO₄S: C 65.43 H 6.01 N 3.63, found: C 65.48 H 6.09 N 3.62.

5u: To a cooled (-78 °C) solution of **5t** (159 mg, 0.41 mmol) in toluene (25 mL), was added DIBAL (1.01 M, toluene solution, 0.49 mL, 0.49 mmol). The mixture was stirred at -78 °C for 20 min. and the reaction was quenched by the addition of MeOH and sat. aq. Rochelle's salt. Then the solution was allowed to stir at rt until separation of organic and water layers. The

mixture was extracted with AcOEt and the combined organic layers were washed with brine and dried. After removal of the solvent, the residue was subjected to column chromatography (AcOEt:*n*-hexane = 1:4) to give 4-(*N*-*p*-toluenesulfonyl-3-methylene-2,3-dihydroindolyl)butanal (126 mg, 87%) as a colorless oil. ^1H NMR δ 9.72 (dd, 1H, $J = 1.5, 1.5$ Hz), 7.75 (d, 1H, $J = 8.1$ Hz), 7.52 (d, 2H, $J = 8.3$ Hz), 7.26-7.31 (m, 2H), 7.14 (d, 2H, $J = 8.5$ Hz), 7.05 (dd, 1H, $J = 7.6, 7.6$ Hz), 5.38 (d, 1H, $J = 2.4$ Hz), 4.89 (d, 1H, $J = 2.0$ Hz), 4.62 (m, 1H), 2.40-2.48 (m, 2H), 2.33 (s, 3H), 2.10-2.16 (m, 1H), 1.75-1.85 (m, 2H), 1.60-1.70 (m, 1H); ^{13}C NMR δ 202.4, 144.6, 144.1, 143.8, 134.0, 130.1, 130.1, 129.56, 127.2, 124.6, 120.9, 117.1, 103.0, 66.1, 43.6, 36.5, 21.5, 15.8; IR (neat) cm^{-1} 1720, 1460, 1351, 1163, 661; LRMS (EI) 355 (M^+ , 36%), 200 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) 356.1320, found 356.1309.

To a cooled (0 °C) solution of BrPh_3PMe (321 mg, 0.90 mmol) in THF (7 mL), KHMDS (0.7 M, toluene solution, 1.29 mL, 0.90 mmol) was added. The solution was stirred for 30 min. at 0 °C, then to the solution was added a solution of 4-(*N*-*p*-toluenesulfonyl-3-methylene-2,3-dihydroindolyl)butanal (106 mg, 0.30 mmol) in THF (2 + 0.5 + 0.5 mL), and the mixture was stirred for 20 min. at rt. The reaction was quenched by addition of sat. aq. NH_4Cl . The organic compounds were extracted with AcOEt and the combined organic layers 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 = 20:1) to give **5u** (84.2 mg, 79%) as a colorless oil. ^1H NMR δ 7.74 (d, 1H, $J = 8.3$ Hz), 7.53 (d, 2H, $J = 8.3$ Hz), 7.29 (dd, 1H, $J = 6.3, 1.0$ Hz), 7.27 (dd, 1H, $J = 6.8, 6.1$ Hz), 7.14 (d, 2H, $J = 7.8$ Hz), 7.04 (ddd, 1H, $J = 7.6, 7.6, 0.7$ Hz), 5.75 (ddt, 1H, $J = 17.1, 10.2, 6.6$ Hz), 5.35 (d, 1H, $J = 2.4$ Hz),

4.97 (dd, 1H, $J = 17.1, 2.0$ Hz), 4.92 (dd, 1H, $J = 10.2, 2.0$ Hz), 4.86 (d, 1H, $J = 2.0$ Hz), 4.62 (m, 1H), 2.32 (s, 3H), 2.00-2.13 (m, 4H), 1.42-1.57 (m, 1H), 1.26-1.31 (m, 1H); ^{13}C NMR δ 145.1, 143.9, 143.9, 138.6, 134.4, 130.3, 130.0, 129.5, 127.2, 124.4, 120.8, 117.0, 114.7, 102.7, 66.5, 36.7, 33.6, 22.2, 21.5; IR (neat) cm^{-1} 2927, 1460, 1353, 1164, 750; LRMS (EI) 353 (M^+ , 51%), 198 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_2\text{S}$ ($\text{M}^+ + \text{H}$) 354.1528, found 354.1533.

19a: a colorless oil. ^1H NMR (C_6D_6) δ 7.32 (dd, 1H, $J = 7.6, 1.2$ Hz), 7.09 (ddd, 1H, $J = 8.3, 8.3, 1.5$ Hz), 6.96 (d, 1H, $J = 8.1$ Hz), 6.82 (ddd, 1H, $J = 7.3, 7.3, 0.7$ Hz), 5.36 (d, 1H, $J = 2.9$ Hz), 4.99 (ddd, 1H, $J = 4.2, 3.9, 2.7$ Hz), 4.71 (d, 1H, $J = 3.4$ Hz), 1.74 (ddq, 1H, $J = 14.9, 7.6, 4.2$ Hz), 1.63 (dq, 1H, $J = 7.3, 14.6$ Hz), 1.03 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR δ 162.5, 147.4, 130.5, 126.0, 120.9, 120.4, 110.4, 99.8, 86.8, 29.0, 8.6; IR (neat) cm^{-1} 2970, 2936, 2878, 1608, 1465, 1229, 939, 747; LRMS (EI) m/z 160 (31%, M^+), 131 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{11}\text{O}$ ($\text{M}^+ - \text{H}$) 159.0810, found 159.0802.

19b: a colorless oil. ^1H NMR δ 6.90 (d, 1H, $J = 2.7$ Hz), 6.79 (dd, 1H, $J = 8.5, 2.4$ Hz), 6.75 (d, 1H, $J = 8.8$ Hz), 5.37 (d, 1H, $J = 2.9$ Hz), 5.11 (dddd, 1H, $J = 6.8, 3.9, 2.9, 2.4$ Hz), 4.88 (d, 1H, $J = 2.4$ Hz), 3.78 (s, 3H), 1.89 (ddq, 1H, $J = 14.6, 7.3, 4.2$ Hz), 1.74 (ddq, 1H, $J = 14.4, 7.3, 7.1$ Hz), 1.01 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR δ 157.0, 154.1, 147.89, 126.4, 117.3, 110.7, 105.2, 99.8, 87.1, 56.0, 29.1, 8.6; IR (neat) cm^{-1} 2970, 2936, 1639, 1485, 1198; LRMS (EI) m/z 190 (83%, M^+), 175 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{13}\text{O}_2$ ($\text{M}^+ - \text{H}$); 189.0916, found 189.0915.

19c: a colorless oil. ^1H NMR (C_6D_6) δ 7.04 (d, 1H, $J = 2.7$ Hz), 6.87 (d, 1H, $J = 8.8$ Hz), 6.81 (dd, 1H, $J = 8.8, 2.7$ Hz), 5.34 (d, 1H, $J = 3.2$ Hz), 5.12 (m, 1H), 4.75 (d, 1H, $J = 2.7$ Hz), 3.43

(s, 3H), 1.51-1.73 (m, 4H), 0.94 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR δ 156.8, 154.1, 148.3, 126.3, 117.3, 110.7, 105.3, 99.7, 86.0, 56.0, 38.5, 17.9, 14.0; IR (neat) cm^{-1} 2958, 2934, 1636, 1485, 1198; LRMS (EI) m/z 204 (100%, M^+ , base peak); HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2$ ($\text{M}^+ - \text{H}$) 203.1072, found 203.1078.

20: To a cooled (0 °C) solution of **5a** (65.4 mg, 0.21 mmol) in THF (4 mL), was added a solution of borane-dimethyl sulfide complex (1.05 mmol, 0.11 mL). The mixture was stirred at rt for 1.5 hours. After being cooled to 0 °C, it was treated sequentially with H_2O (1 mL), 1*N* aq. NaOH (1 mL) and 30% aq. H_2O_2 (0.34 mL). Then the solution was stirred at rt for 12 hours. The mixture was diluted with brine and extracted with AcOEt, and the combined organic layers were dried over Na_2SO_4 . After removal of the solvent, the residue was subjected to column chromatography (AcOEt/ *n*-hexane = 1:3) to give **20** (55.2 mg, 79%) as a colorless oil. ^1H NMR δ 7.66 (d, 1H, $J = 7.9$ Hz), 7.47 (d, 2H, $J = 8.4$ Hz), 7.25 (m, 1H), 7.12 (d, 2H, $J = 8.1$ Hz), 7.03-7.09 (m, 2H), 4.33 (ddd, 1H, $J = 10.4, 8.2, 3.7$ Hz), 3.94 (dd, 1H, $J = 10.6, 6.4$ Hz), 3.80 (dd, 1H, $J = 10.6, 8.6$ Hz), 2.92 (ddd, 1H, $J = 8.1, 8.1, 6.8$ Hz), 2.34 (s, 3H), 1.62-1.70 (m, 1H), 1.43-1.47 (m, 1H), 1.10 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR δ 143.7, 141.6, 135.8, 135.0, 129.5, 128.1, 126.9, 125.4, 123.7, 119.5, 67.0, 60.6, 46.1, 22.2, 21.5, 10.7; IR (neat) cm^{-1} 3298, 2930, 1461, 1343, 1160, 769; LRMS (EI) 331 (M^+ , 100%, base peak), 300 (100%), 272 (100%); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_3\text{S}$ ($\text{M}^+ + \text{H}$) 332.1320, found 332.1301.

21: To a cooled (-78 °C) solution of **5a** (46.5 mg, 0.15 mmol) in CH_2Cl_2 (1.5 mL), O_3 gas was bubbled until the color of the solution turned to blue. After the addition of dimethyl sulfide (0.75 mL, 0.75 mmol), it was stirred at rt for 3 hours. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (*n*-hexane:AcOEt = 10:1) to

give **21** (35.4 mg, 75%). Mp 146-147 °C (AcOEt / *n*-hexane), colorless needles; ^1H NMR δ 8.09 (d, 1H, $J = 8.0$ Hz), 7.68 (ddd, 1H, $J = 8.8, 7.6, 1.6$ Hz), 7.62 (d, 2H, $J = 8.4$ Hz), 7.60-7.63 (m, 1H), 7.21 (d, 2H, $J = 8.8$ Hz), 7.19 (ddd, 1H, $J = 7.6, 7.6, 0.8$ Hz), 3.97 (dd, 1H, $J = 5.6, 3.2$ Hz), 2.35 (s, 3H), 2.32 (ddq, 1H, $J = 14.8, 7.6, 6.0$ Hz), 2.19 (ddq, 1H, $J = 14.8, 7.6, 3.6$ Hz), 0.85 (dd, 3H, $J = 7.2, 7.2$ Hz); ^{13}C NMR δ 198.7, 153.7, 144.9, 137.1, 133.4, 129.9, 127.2, 125.3, 124.5, 124.2, 117.1, 68.0, 25.2, 21.5, 7.4; IR (neat) cm^{-1} 2922, 2849, 1715, 1602, 1460, 1351, 1168; LRMS (EI) 315 (M^+ , 46%), 160 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{S}$ ($\text{M}^+\text{+H}$) 316.1007, found 316.1005; Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3\text{S}$: C 64.74 H 5.43 N 4.44, found: C 64.77 H 5.69 N 4.44.

22: To a solution of **5u** (15.8 mg, 45.0 μmol) in toluene (4.5 mL), the 2nd-generation Grubbs catalyst (**B**) (1.9 mg, 5 mol%) was added and the solution was refluxed for 1 hour. After the removal of solvent, the residue was subjected to column chromatography (AcOEt/ *n*-hexane = 1:10) to give **22** (13.7 mg, 94%) as a colorless solid. ^1H NMR δ 7.76 (d, 1H, $J = 8.2$ Hz), 7.70 (d, 2H, $J = 8.4$ Hz), 7.23 (d, 1H, $J = 7.1$ Hz), 7.22 (d, 2H, $J = 8.6$ Hz), 7.19 (dd, 1H, $J = 7.3, 7.3$ Hz), 6.97 (ddd, 1H, $J = 7.5, 7.5, 0.9$ Hz), 5.84 (ddd, 1H, $J = 3.7, 3.7, 3.5$ Hz), 4.17 (ddd, 1H, $J = 7.9, 7.9, 3.7$ Hz), 2.78-2.82 (m, 1H), 2.36 (s, 3H), 2.25-2.36 (m, 2H), 1.97 (m, 1H), 1.63-1.71 (m, 2H); ^{13}C NMR δ 144.2, 143.4, 135.7, 133.4, 129.6, 129.4, 128.9, 127.7, 123.9, 120.0, 118.0, 115.4, 64.1, 29.1, 24.5, 21.5, 20.2; IR (neat) cm^{-1} 2923, 1458, 1351, 1167, 764, 660; LRMS (EI) 325 (M^+ , 31%), 170 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$ 325.1137, found 325.1137.

(H₂IMes)(PCy₃)(CO)ClRuH (E)

To a solution of vinyloxytrimethylsilane (**6a**) (34.9 mg, 0.30 mmol) in toluene (3 mL), the 2nd-generation Grubbs catalyst (**B**) (25.5 mg, 0.03 mmol) was added and the solution was stirred at 50 °C for 1 hour, upon which the solution changed color from dark red to bright orange. Removal of solvent under vacuum gave **E**²⁸ (22.6 mg, 100%) as an orange amorphous. ¹H NMR (C₆D₆) δ 6.97 (s, 2H), 6.92 (s, 2H), 3.42 (brs, 4H), 1.23-2.78 (m, 51H), -24.79 (d, 1H, *J* = 22.0 Hz); ¹³C NMR (C₆D₆) δ 217.9 (d, *J* = 89.0 Hz), 202.0 (d, *J* = 13.0 Hz), 137.5, 129.5, 128.9, 128.5, 126.9, 50.9 (d, *J* = 3.8 Hz), 34.3 (d, *J* = 17.7 Hz), 30.8, 29.9, 28.1, 28.0, 26.9, 21.1, 19.3; ³¹P NMR (C₆D₆) δ 46.66 (s); ¹H NMR (CD₂Cl₂) δ 6.91 (s, 2H), 6.88 (s, 2H), 3.96 (brs, 4H), 2.50 (s, 6H), 2.39 (s, 6H), 2.25 (s, 6H), 1.07-1.98 (brm, 33H), -25.43 (d, 1H, *J* = 21.6 Hz); ³¹P NMR (CD₂Cl₂) δ 46.23 (s); IR (toluene) cm⁻¹ 2935, 1897 (vs), 1585, 1265.

(H₂IMes)(PCy₃)Cl₂Ru=C(H)OEt (F**)**

According the procedure reported by Grubbs, to a solution of ethyl vinyl ether (**6f**) (2.30 mL, 24.0 mmol) in toluene (24 mL), the 2nd-generation Grubbs catalyst (**B**) (204 mg, 0.24 mmol) was added and the solution was stirred at 50 °C for 1 hour upon which the solution changed color from dark red to bright red. Removal of solvent under vacuum gave **F**²⁹ (195 mg, 100%) as a red powder. ¹H NMR (CD₂Cl₂) δ 13.64 (s, 1H), 6.96 (s, 2H), 6.94 (s, 2H), 3.89 (m, 4H), 3.24 (q, 2H, *J* = 7.3 Hz), 2.59 (s, 6H), 2.48 (s, 6H), 2.26 (s, 6H), 1.61 (m, 16H), 1.12 (t, 3H, *J* = 7.3 Hz), 1.01-1.13 (brm, 17H); ¹³C NMR (CD₂Cl₂) δ 277.4 (d, *J* = 9.2 Hz), 221.1 (d, *J* = 83.6 Hz), 139.0, 138.5, 138.3, 137.9, 137.8, 135.2, 130.0, 129.5, 75.0, 52.1 (d, *J* = 3.9 Hz), 51.9 (d, *J* = 2.3 Hz), 31.4 (d, *J* = 16.1 Hz), 29.3, 28.2 (d, *J* = 9.9 Hz), 26.6, 21.1, 20.9, 19.9, 18.9, 14.7; ³¹P NMR (CD₂Cl₂) δ 30.14 (s); LRMS (FAB) 816 (M⁺, 10%), 307 (80%), 538 (9%), 281 (100%),

base peak).

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