



Supporting Information

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Cycloisomerization Promoted by the Combination of a Ruthenium Carbene Catalyst and Vinyloxytrimethylsilane, and its Application to the Synthesis of Heterocyclic Compounds: 3-Methylene-2, 3-dihydroindoles and 3-Methylene-2, 3-dihydrobenzofurans

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Infrared absorption spectra were recorded using a JASCO FT/IR-230 spectrometer. ¹H NMR spectra were recorded in CDCl₃ at 25 °C unless otherwise noted, at 400 or 600 MHz, with TMS as an internal standard. ¹³C NMR spectra were recorded in CDCl₃ at 25 °C unless otherwise noted, at 100 MHz. Flash column chromatography were performed with silica gel 60 N (spherical, neutral, 40-50 μm, Kanto Chemical Co., Inc.). **2a**, **2b**, **9**, **A**, **B**, **C**, and **D** were obtained commercially. **1**¹, **10**², **11**³, **12**⁴, **23**⁵, **24**⁵, **26**¹, **28**⁶, **G**⁷, *N*-*tert*-butoxycarbonyl-*p*-toluenesulfonamide⁸ and *N*-*p*-toluenesulfonyl-2-vinylaniline¹ were prepared according to the reported procedures.

Preparation of Dienes.

N,N-Diallyl-*p*-toluenesulfonamide **5**

To a solution of *p*-toluenesulfonamide (684.9 mg, 4.0 mmol) and K₂CO₃ (1.38 g, 10.0 mmol) in CH₃CN (40 mL) was added allyl bromide (0.87 mL, 10.0 mmol), and the mixture was refluxed 4 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The crude residue was subjected to column chromatography (*n*-hexane : AcOEt = 5 : 1) on silica gel to give **5**⁹ (957.6 mg, 95%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.71 (d, 2H, *J* = 8.3 Hz), 7.30 (d, 2H, *J* = 8.1 Hz), 5.61 (tdd, 2H, *J* = 17.3, 9.8, 6.3 Hz), 5.15-5.67 (m, 2H), 5.12-5.13 (m, 2H), 3.80 (d, 4H, *J* = 6.4 Hz), 2.43 (t, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ 143.1, 137.2, 132.5, 129.5, 127.0, 118.8, 49.2, 21.3.

N,N-Diallylbenzylamine **13**

To a solution of benzylamine (214 mg, 2.0 mmol) and K₂CO₃ (1.38 g, 10.0 mmol) in CH₃CN (26 mL) was added allyl bromide (0.43 mL, 5.0 mmol), and the mixture was stirred for 10 hours at rt. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The crude residue was subjected to column chromatography (*n*-hexane : AcOEt = 10 : 1) on silica gel to give **13**¹⁰ (336.7 mg, 90%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.32-7.35 (m, 3H), 7.21-7.30 (m, 2H), 5.88 (ddt, 2H, *J* = 6.2, 10.3, 17.2 Hz), 5.19 (ddt, 2H, *J* = 1.5, 2.0, 17.2 Hz), 5.14 (ddt, 2H, *J* = 1.1, 2.0, 10.3 Hz), 3.57 (s, 2H), 3.08 (ddd, 4H, *J* = 1.3, 1.3, 6.4 Hz); IR (neat) cm⁻¹ 2794, 1643, 918, 698.

N-Allyl-*N*-(3-butenyl)-*p*-toluenesulfonamide **14**

To a solution of *N*-*tert*-butoxycarbonyl-*p*-toluenesulfonamide⁸ (400 mg, 1.47 mmol) and K₂CO₃ (406 mg, 2.94 mmol) in CH₃CN (15 mL) was added allyl bromide (0.25 mL, 2.94 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 to give *N*-allyl-*N*-*tert*-butoxycarbonyl-*p*-toluenesulfonamide quantitatively. To a solution of *N*-allyl-*N*-*tert*-butoxycarbonyl-*p*-toluenesulfonamide in CH₂Cl₂ (15 mL) was added trifluoroacetic acid (1.7 mL, 22.1 mmol), and the mixture was stirred for 40 hours at rt. The reaction was quenched by addition of K₂CO₃ and water. The organic compounds were extracted with CH₂Cl₂ and the combined organic layers were dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the crude residue was subjected to column chromatography (*n*-hexane : AcOEt = 2 : 1) on silica gel to give *N*-allyl-*p*-toluenesulfonamide¹¹ (306.2 mg, 98%) as a colorless solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.76 (d, 2H, *J* = 8.3 Hz), 7.32 (d, 2H, *J* = 8.5 Hz), 5.73 (ddt, 1H, *J* = 5.9, 10.2, 17.1 Hz), 5.17 (ddt, 1H, *J* = 1.5, 2.7, 17.1 Hz), 5.11 (ddt, 1H, *J* = 1.5, 2.9, 10.3 Hz), 4.38 (brs, 1H), 3.59 (m, 2H), 2.44 (s, 3H).

To a solution of *N*-allyl-*p*-toluenesulfonamide (100 mg, 0.47 mmol) and K₂CO₃ (196 mg, 1.42 mmol) in CH₃CN (5 mL) was added 4-bromo-1-butene (0.14 mL, 1.42 mmol), and the mixture was refluxed for 6 hours. The solution was filtrated through a celite pad and the filtrate was concentrated under reduced pressure. The crude residue was subjected to column chromatography (*n*-hexane : AcOEt = 10 : 1) on silica gel to give

14 (111.6 mg, 89%) as a colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, 2H, $J = 8.2$ Hz), 7.30 (d, 2H, $J = 8.1$ Hz), 5.70 (tdd, 1H, $J = 17.2, 10.3, 6.8$ Hz), 5.64 (tdd, 1H, $J = 17.0, 10.3, 6.4$ Hz), 5.18 (d, 1H, $J = 18.5$ Hz), 5.14 (d, 1H, $J = 11.0$ Hz), 5.04 (d, 1H, $J = 17.0$ Hz), 5.02 (d, 1H, $J = 10.3$ Hz), 3.81 (d, 2H, $J = 6.2$ Hz), 3.18 (t, 2H, $J = 7.5$ Hz), 2.42 (s, 3H), 2.28 (td, 2H, $J = 7.5, 7.0$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 143.1, 137.0, 134.6, 133.1, 129.6, 127.1, 118.7, 116.9, 50.6, 46.6, 32.8, 21.4; IR (neat) cm^{-1} 3079, 2979, 2925, 1344, 1159; LRMS (EI) m/z 265 (20%, M^+), 224 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2\text{S}$; 266.1215, found 266.1209.

N-Allyl-*N*-(2-butenyl)-*p*-toluenesulfonamide **15**

15 was prepared in a manner similar to that of **14** using *N*-allyl-*p*-toluenesulfonamide and crotyl bromide. **15** was obtained as a colorless oil ($E : Z = 4.8 : 1$, 89%). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.69 (d, 2H, $J = 8.1$ Hz), 7.29 (d, 2H, $J = 7.9$ Hz), 5.51-5.69 (m, 2H), 5.17-5.28 (m, 1H), 5.11-5.14 (m, 2H), 3.85 (d, 0.70H, $J = 7.0$ Hz), 3.79 (d, 2H, $J = 6.2$ Hz), 3.74 (d, 1.30H, $J = 1.7$ Hz), 2.43 (s, 3H), 1.63 (d, 2.48H, $J = 6.4$ Hz), 1.58 (d, 0.52H, $J = 6.2$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 143.1, 143.0, 137.5, 137.4, 133.0, 132.8, 132.6, 130.5, 129.6, 129.5, 128.5, 127.1, 125.1, 124.5, 118.9, 118.5, 49.3, 49.2, 48.9, 48.6, 43.0, 21.4, 17.5, 12.8; IR (neat) cm^{-1} 2920, 2856, 1341, 1159; LRMS (EI) m/z 265 (21%, M^+), 91 (100%, base peak); HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2\text{S}$; 266.1215, found 266.1190.

N-Allyl-*N*-(2-methyl-2-propenyl)-*p*-toluenesulfonamide **16**

16 was prepared in a manner similar to that of **14** using *N*-allyl-*p*-toluenesulfonamide and methallyl bromide. **16** was obtained as a colorless oil (89%). ¹H-NMR (400 MHz, CDCl₃) δ 7.71 (d, 2H, *J* = 8.2 Hz), 7.30 (d, 2H, *J* = 8.1 Hz), 5.52 (ddt, 1H, *J* = 17.6, 9.7, 6.6 Hz), 5.06-5.11 (m, 2H), 4.91 (d, 1H, *J* = 0.6 Hz), 4.85 (d, 1H, *J* = 0.7 Hz), 3.77 (d, 2H, *J* = 6.6 Hz), 3.70 (s, 2H), 2.43, (s, 3H), 1.69 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ 143.1, 140.0, 137.4, 132.2, 129.6, 127.1, 119.1, 114.4, 52.7, 49.3, 21.4, 19.8; IR (neat) cm⁻¹ 3080, 2979, 2920, 1345, 1161; LRMS (EI) *m/z* 265 (100%, M⁺, base peak); HRMS (FAB) calcd for C₁₄H₂₀NO₂S; 266.1215, found 266.1212.

N-Allyl-*N*-*p*-toluenesulfonyl-3-chloro-2-vinylaniline **25**

To a cooled (0°C) solution of 2-chloro-6-nitrotoluene (25 mmol, 4.3 g) and HCHO (35% in water, 75 mmol, 6.4 mL) in DMSO (63 mL) was added a solution of KOH (62.5 mmol, 3.5 g) in water (4.4 mL), and the mixture was stirred for 1 hour at rt. After addition of saturated NH₄Cl (30 mL), the organic compounds were extracted with ether (50 mL x 2) 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 = 4 : 1) to give 1-chloro-2-(2-hydroxyethyl)-3-nitrobenzene as a colorless solid (4.12 g, 82%). ¹H-NMR (400 MHz, CDCl₃) δ 7.72 (dd, 1H, *J* = 1.0, 8.1 Hz), 7.64 (dd, 1H, *J* = 1.2, 8.1 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); ¹³C-NMR (100 MHz, CDCl₃) δ 152.04, 136.68, 133.78, 131.04, 127.94, 122.94,

61.16, 32.66; 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.

To a solution of 1-chloro-2-(2-hydroxyethyl)-3-nitrobenzene (19.8 mmol, 4.0 g) and Et_3N (33.7 mmol, 4.70 mL) in dichloromethane (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 saturated NH_4Cl (15 mL), the organic compounds were extracted with dichloromethane. The combined organic layers were washed with 1N HCl, saturated NaHCO_3 and brine, and dried over Na_2SO_4 . After removal of the solvent, the residue was resolved in dichloromethane (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 saturated NH_4Cl (10 mL), the organic compounds were extracted with dichloromethane. The combined organic layers were washed with 1N HCl and 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 1-chloro-3-nitro-2-vinylbenzene as a colorless solid (3.0 g, 82%, 2 steps). ^1H -NMR (400 MHz, CDCl_3) δ 7.63 (dd, 1H, J = 1.2, 8.1 Hz), 7.61 (dd, 1H, J = 1.2, 8.1 Hz), 7.34 (dd, 1H, J = 8.1 Hz), 6.80 (dd, 1H, J = 11.5, 17.8), 5.63 (dd, 1H, J = 0.5, 11.7 Hz), 5.47 (dd, 1H, J = 0.5, 17.8 Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 150.58, 134.95, 133.13, 131.56, 129.28, 128.35, 122.29, 121.97; IR (KBr) cm^{-1} 3087, 2875, 1526, 1360, 949; LRMS (EI) m/z 183 (26%, M^+), 154 (100%, base peak).

To a solution of 1-chloro-3-nitro-2-vinylbenzene (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), the aqueous layer was neutralized by addition of K_2CO_3 . The combined organic layers were washed with brine, and dried over Na_2SO_4 . After removal of the solvent, the residue was resolved in dichloromethane (2 mL). To the solution, *p*-toluenesulfonamide (0.67 mmol, 128 mg) and pyridine (1.68 mmol, 0.1 mL) were added, and the mixture was stirred for 3 days at rt. After addition of saturated NH_4Cl , the organic compounds were extracted with dichloromethane. 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-vinylaniline (120 mg, 70%) as a colorless solid. 1H -NMR (400 MHz, $CDCl_3$) 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 (100 MHz, $CDCl_3$) δ 144.28, 135.99, 135.22, 133.65, 130.80, 129.76, 128.77, 128.44, 127.16, 125.37, 123.08, 118.81, 21.55; IR (KBr) cm^{-1} 3264, 1566, 1337, 1166, 940; LRMS (EI) m/z 307 (17%, M^+), 252 (100%, base peak); HRMS (FAB) calcd for $C_{15}H_{15}ClNO_2S$ ($M^+ + H$); 308.0512, found 308.0520.

25 was prepared in a manner similar to that of **14** using *N*-*p*-toluenesulfonyl-3-chloro-2-vinylaniline and allyl bromide. **25** was obtained as a colorless solid (90%). 1H -NMR (400 MHz, $CDCl_3$) 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 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 (100 MHz, CDCl_3) δ 143.70, 138.61, 138.21, 136.29, 134.05, 132.06, 130.73, 130.30, 129.56, 127.90, 127.84, 127.43, 122.38, 119.59, 54.59, 21.56; IR (KBr) cm^{-1} 3023, 2915, 1341, 1163, 663; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{19}\text{ClNO}_2\text{S}$ ($\text{M}^+ + \text{H}$); 348.0825, found 348.0807.

N-(3-Butenyl)-*N*-*p*-toluenesulfonyl-2-vinylaniline **27**

27 was prepared in a manner similar to that of **14** using *N*-*p*-toluenesulfonyl-2-vinylaniline and 4-bromo-1-butene. **27** was obtained as a colorless solid (91%). ^1H -NMR (400 MHz, CDCl_3) 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, $J = 14.6$ Hz), 4.99 (d, 1H, $J = 11.5$ Hz), 3.76 (brs, 1H), 3.33 (brs, 1H), 2.44 (s, 3H), 2.22 (brs, 1H), 2.12 (brs, 1H); ^{13}C -NMR (100 MHz, CDCl_3) 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.

2-Allyloxy-5-methoxystyrene **29**

2-Allyloxy-5-methoxybenzaldehyde was prepared in a manner similar to that of **14** using 2-hydroxy-5-methoxybenzaldehyde and allyl bromide.

2-Allyloxy-5-methoxybenzaldehyde was obtained as a yellow oil (99%). ¹H-NMR (400 MHz, CDCl₃) δ 10.5 (s, 1H), 7.34 (d, 1H, *J* = 3.2 Hz), 7.12 (d, 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); ¹³C-NMR (100 MHz, CDCl₃) 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 C₁₁H₁₂O₃; 192.0786, found 192.0799.

To a cooled (0 °C) solution of BrPh₃PMe (1.1 g, 3.1 mmol) in THF (20 mL) under an Ar atmosphere, KN(TMS)₂ (20w/v% toluene solution, 3.5 mL, 3.1 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, 2.6 mmol) in THF (2 mL x 3), and the mixture was stirred for 12 hours at rt. The reaction was quenched by addition of saturated 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 = 30 : 1) to give **29** as a colorless oil (87%). ¹H-NMR (400 MHz, CDCl₃) 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 (100 MHz, CDCl_3) 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.

2-(3-Butenyloxy)-5-methoxystyrene **30**

2-(3-Butenyloxy)-5-methoxybenzaldehyde was prepared in a manner similar to that of **14** using 2-hydroxy-5-methoxybenzaldehyde and 4-bromo-1-butene.

2-(3-Butenyloxy)-5-methoxybenzaldehyde was obtained as a yellow oil (65%).

^1H -NMR (400 MHz, CDCl_3) δ 10.5 (s, 1H), 7.22 (dd, 1H, $J = 3.1$ Hz), 7.11 (d, 1H, $J = 3.3, 9.0$ Hz), 6.94 (d, 1H, $J = 9.0$ Hz), 5.90 (ddt, 1H, $J = 6.8, 10.3, 17.0$ Hz), 5.18 (ddt, 1H, $J = 1.7, 3.3, 17.2$ Hz), 5.13 (ddt, 1H, $J = 1.1, 1.6, 10.3$ Hz), 4.10 (t, 2H, $J = 6.6$ Hz), 3.80 (s, 3H), 2.58 (dtdd, 2H, $J = 1.3, 1.3, 6.6, 6.8$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) 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.

2-(3-Butenyloxy)-5-methoxystyrene **30** was prepared in a manner similar to that of **29** using 2-(3-butenyloxy)-5-methoxybenzaldehyde. **30** was obtained as a colorless oil (97%). ^1H -NMR (400 MHz, CDCl_3) δ 7.03 (dd, 1H, $J = 11.2, 17.6$ Hz), 7.03 (d, 1H, $J = 2.7$ Hz), 6.79 (d, 1H, $J = 8.8$ Hz), 6.75 (dd, 1H, $J = 2.9, 9.0$ Hz), 5.91 (ddt, 1H, $J = 6.8, 10.2, 17.1$ Hz), 5.73 (dd, 1H, $J = 1.2, 17.6$ Hz), 5.25 (dd, 1H, $J = 1.2, 11.0$ Hz), 5.16 (ddt, 1H, $J = 1.5, 1.7, 17.3$ Hz), 5.10 (ddt, 1H, $J = 1.2, 1.7, 10.3$ Hz), 3.97 (t, 2H, $J = 6.6$

Hz), 3.77 (s, 3H), 2.54 (dddt, 2H, $J = 6.6, 6.8, 1.2, 1.5$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 153.8, 150.5, 134.6, 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.

Typical Procedure for Cycloisomerization.

To a solution of **5** (37.7 mg, 0.15 mmol) and vinyloxytrimethylsilane **2a** (17.4 mg, 0.15 mmol) in dichloromethane (12 mL, 0.0125 M) was added ruthenium carbene catalyst **B** (6.3 mg, 0.0075 mmol) under an Ar atmosphere and the mixture was refluxed for 2 hours. The solvent was removed under vacuum and obtained crude residue was subjected to column chromatography of silica gel (*n*-pentane : ether = 10 : 1) to give **6** (32.5 mg, 86%) as a colorless solid.

3-Methyl-4-methylene-1-*p*-toluenesulfonylpyrrolidine **6**¹² : mp 60-61 °C (AcOEt / *n*-hexane), a colorless prism. ^1H -NMR (400 MHz, CDCl_3) 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); ^{13}C -NMR (100 MHz, CDCl_3) δ 149.29, 143.56, 132.90, 129.64, 127.76, 105.96, 55.03, 52.14, 37.43, 21.51, 16.04.

3, 4-Dimethyl-1-*p*-toluenesulfonyl-2, 5-dihydropyrrole **7**¹³ : mp 153-154 °C (AcOEt / *n*-hexane), a colorless plate. ^1H -NMR (400 MHz, CDCl_3) 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); ^{13}C -NMR (100 MHz, CDCl_3) δ 143.23, 134.25, 129.66, 127.45, 126.17, 58.78, 21.48, 11.08.

1-*p*-Toluenesulfonyl-2, 5-dihydropyrrole **8**¹⁴ : mp 131-132 °C (AcOEt / *n*-hexane), a colorless needle. ^1H -NMR (400 MHz, CDCl_3) δ 7.72 (d, 2H, $J = 8.3$ Hz), 7.32 (d, 2H, $J = 8.3$ Hz), 5.65 (s, 2H), 4.12 (s, 4H), 2.43 (s, 3H).

4, 4-Bis(ethoxycarbonyl)-1-methyl-2-methylenecyclopentane **17**¹⁵ : a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 4.91 (d, 1H, $J = 2.0$ Hz), 4.80 (d, 1H, $J = 2.2$ Hz), 4.19 (q, 2H, $J = 7.1$ Hz), 4.18 (q, 2H, $J = 7.1$ Hz) 2.91-3.07 (m, 2H), 2.52-2.58 (m, 2H), 1.72-1.79 (m, 1H), 1.25 (t, 3H, $J = 7.1$ Hz), 1.24 (t, 3H, $J = 7.1$ Hz), 1.11 (d, 3H, $J = 6.3$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 171.9, 171.8, 153.4, 105.4, 61.4 (2C), 58.1, 42.1, 40.4, 37.2, 17.9, 14.0 (2C).

1, 1-Diacetyl-3-methyl-4-methylenecyclopentane **18**¹⁶ : a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 4.91 (d, 1H, $J = 2.2$ Hz), 4.78 (d, 1H, $J = 2.2$ Hz), 2.96 (d, 1H, $J = 17.0$ Hz), 2.88 (dd, 1H, $J = 2.0, 16.8$ Hz), 2.58 (dd, 1H, $J = 7.7, 12.6$ Hz), 2.42 (brm, 1H), 2.13 (s, 3H), 2.11 (s, 3H), 1.59 (dd, 1H, $J = 11.0, 12.6$ Hz), 1.08 (d, 3H, $J = 6.6$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 153.0, 105.7, 72.9, 39.6, 37.5, 37.2, 26.6, 26.2, 17.8; IR (neat) cm^{-1} 2981, 2934, 1732 1252, 1177.

3-Methyl-4-methylene-1-benzoylpyrrolidine **19**¹⁷ : a colorless oil. major and minor rotamers; ¹H-NMR (400 MHz, CDCl₃) δ 7.27-7.52 (major and minor, m, 5H), 5.08 (major, d, 0.62H, *J* = 1.5 Hz), 4.98 (major, d, 0.62H, *J* = 2.0 Hz), 4.92 (minor, s, 0.38H), 4.89 (minor, s, 0.38H), 4.44 (major, d, 0.62H, *J* = 16.6 Hz), 4.30 (major, d, 0.62H, *J* = 16.6 Hz), 4.15 (minor, dd, 0.38H, *J* = 8.1, 11.2 Hz), 4.13 (minor, d, 0.38H, *J* = 12.0 Hz), 4.04 (minor, d, 0.38H, *J* = 14.4 Hz), 3.72 (major, dd, 0.62H, *J* = 8.1, 10.0 Hz), 3.21 (minor, dd, 0.38H, *J* = 9.0, 9.0 Hz), 3.13 (major, dd, 0.62H, *J* = 9.5, 9.5 Hz), 2.72-2.87 (major and minor, m, 1H), 1.20 (minor, d, 1.14H, *J* = 7.1 Hz), 1.10 (major, d, 1.86H, *J* = 6.6 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 169.9 (minor), 169.4 (major), 150.0 (minor), 149.1 (major), 136.7 (minor), 136.4 (major), 129.9 (major and minor), 128.3 (major and minor), 127.2 (major), 126.9 (minor), 105.8 (major), 105.6 (minor), 56.5 (major), 53.8 (minor), 52.9 (minor), 50.8 (major), 38.0 (major), 36.2 (minor), 15.9 (minor), 15.2 (major); IR (neat) cm⁻¹ 3059, 2963, 2931, 2869, 1633, 1417.

N-tert-Butoxycarbonyl-3-methyl-4-methylenepyrrolidine **20** : a colorless oil. ¹H-NMR (400 MHz, CDCl₃, 55 °C) δ 4.94 (d, 1H, *J* = 1.2 Hz), 4.89 (dd, 1H, *J* = 2.2, 4.6 Hz), 4.02 (d, 1H, *J* = 15.1 Hz), 3.94 (d, 1H, *J* = 15.4 Hz), 3.71 (dd, 1H, *J* = 8.8, 8.8 Hz), 2.92 (dd, 1H, *J* = 8.5, 8.5 Hz), 2.69-2.75 (brm, 1H), 1.46 (s, 9H), 1.12 (d, 3H, *J* = 6.6 Hz); IR (neat) cm⁻¹ 3082, 2973, 2931, 2870, 1703, 1407, 1365, 1173, 1110; LRMS (EI) *m/z* 197 (60%, M⁺), 140 (100%, base peak); HRMS (FAB) calcd for C₁₁H₁₈NO₂ (M⁺-H); 196.1338, found 196.1331.

N-p-Toluenesulfonyl-3-ethyl-4-methylenepyrrolidine **21** : a colorless solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.71 (d, 2H, $J = 8.1$ Hz), 7.33 (d, 2H, $J = 8.5$ Hz), 4.91 (dd, 1H, $J = 4.2, 2.2$ Hz), 4.87 (dd, 1H, $J = 4.3, 2.2$ Hz), 3.87 (d, 1H, $J = 14.1$ Hz), 3.75 (dd, 1H, $J = 13.9, 2.0$ Hz), 3.50 (dd, 1H, $J = 9.3, 7.3$ Hz), 2.86 (dd, 1H, $J = 9.3, 7.1$ Hz), 2.50 (brm, 1H), 2.44 (s, 3H), 1.53-1.62 (m, 1H), 1.22-1.32 (m, 1H), 0.89 (t, 3H, $J = 7.6$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 147.9, 143.6, 132.8, 129.6, 127.8, 106.6, 53.2, 52.2, 44.5, 25.1, 21.5, 11.8; IR (KBr) cm^{-1} 2958, 2925, 2856, 1341, 1164, 1096, 664, 550; LRMS (EI) m/z 265 (98%, M^+), 266 (100%, base peak, $\text{M}^+ + \text{H}$); HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2\text{S}$ ($\text{M}^+ + \text{H}$); 266.1215, found 266.1211.

N-(1-Propenyl)-*N-p*-toluenesulfonyl-2-vinylaniline **3¹** : a colorless oil (mixture of *E*- and *Z*-isomers)

Z-isomer; $^1\text{H-NMR}$ (400 MHz, CDCl_3) 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); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 143.7, 138.1, 136.5, 134.3, 131.9, 130.1, 129.6, 129.2, 128.8, 128.3, 127.5, 126.2, 115.9, 107.3, 21.6, 14.9; IR (neat) cm^{-1} 3068, 3030, 2920, 2857, 1658, 1360, 1167; LRMS (EI) m/z 313 (87%, M^+), 271 (100%, base peak).

N-p-Toluenesulfonyl-2-ethyl-3-methylene-2, 3-dihydroindole **22** : a colorless oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) 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 (ddd, 1H, $J = 7.5, 7.5, 0.7$ Hz), 5.37 (d, 1H, $J = 2.4$ Hz), 4.86 (d, 1H, $J = 2.1$ Hz), 4.60 (ddt, 1H, $J = 2.2, 2.2, 4.4$ 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); ^{13}C -NMR (100 MHz, CDCl_3) δ 144.8, 144.1, 143.9, 134.5, 130.4, 130.0, 129.5, 127.2, 124.3, 120.7, 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 $\text{C}_{18}\text{H}_{19}\text{NO}_2\text{S}$; 313.1137, found 313.1112.

N-*p*-Toluenesulfonyl-5-chloro-2-ethyl-3-methylene-2, 3-dihydroindole **31** : a colorless oil. ^1H -NMR (400 MHz, CDCl_3) 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, $J = 2.2, 8.8$ 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, $J = 1.5, 2.0, 4.4, 4.9$ Hz), 2.35 (s, 3H), 2.16 (ddq, 1H, $J = 5.4, 7.3, 13.8$ Hz), 1.79 (ddq, 1H, $J = 4.2, 7.3, 13.9$ Hz), 0.86 (t, 3H, $J = 7.3$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 144.2, 143.6, 142.7, 134.1, 132.0, 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.

N-*p*-Toluenesulfonyl-6-chloro-2-ethyl-3-methylene-2, 3-dihydroindole **32** : a colorless oil. ^1H -NMR (400 MHz, CDCl_3) 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, $J = 2.0, 8.3$ Hz), 5.36 (d,

1H, $J = 2.0$ Hz), 4.88 (d, 1H, $J = 1.5$ Hz), 4.62 (dddd, 1H, $J = 1.5, 2.0, 3.9, 5.1$ Hz), 2.35 (s, 3H), 2.18 (ddq, 1H, $J = 5.4, 7.3, 14.2$ Hz), 1.79 (ddq, 1H, $J = 4.2, 7.6, 13.9$ Hz), 0.85 (t, 3H, $J = 7.3$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) 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).

N-*p*-Toluenesulfonyl-4-chloro-2-ethyl-3-methylene-2, 3-dihydroindole **33** : a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.68 (dd, 1H, $J = 0.7, 8.1$ 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, $J = 1.0, 8.1$ Hz), 6.10 (d, 1H, $J = 2.4$ Hz), 5.08 (d, 1H, $J = 2.0$ Hz), 4.62 (dddd, 1H, $J = 2.0, 2.4, 4.4, 4.9$ Hz), 2.35 (s, 3H), 2.13 (ddq, 1H, $J = 5.1, 7.3, 13.9$ Hz), 1.80 (ddq, 1H, $J = 4.6, 7.3, 14.6$ Hz), 0.88 (t, 3H, $J = 7.3$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) 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.

N-*p*-Toluenesulfonyl-2-ethyl-5-methoxy-3-methylene-2, 3-dihydroindole **34** : a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.67 (d, 1H, $J = 9.0$ Hz), 7.49 (d, 2H, $J = 8.2$ Hz), 7.14 (d, 2H, $J = 7.3$ Hz), 6.85 (dd, 1H, $J = 2.2, 7.0$ 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 (brm, 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 (100 MHz, CDCl_3) 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.

N-*p*-Toluenesulfonyl-3-methylene-2-propyl-2, 3-dihydroindole **35** : a colorless oil.

^1H -NMR (400 MHz, CDCl_3) 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, $J = 2.0, 2.4, 5.1$ 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 (100 MHz, CDCl_3) δ 145.2, 143.9, 143.8, 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.

2-Ethyl-3-methylene-2,3-dihydrobenzofuran **36** : a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.38 (dd, 1H, $J = 7.6, 0.7$ Hz), 7.20 (ddd, 1H, $J = 8.3, 8.3, 1.5$ Hz), 6.87 (ddd, 1H, $J = 7.6, 7.6, 1.0$ Hz), 6.84 (d, 1H, $J = 8.1$ Hz), 5.41 (d, 1H, $J = 2.9$ Hz), 5.12 (dddd, 1H, $J = 7.1, 4.1, 2.9, 2.4$ Hz), 4.89 (d, 1H, $J = 2.4$ Hz), 1.91 (ddq, 1H, $J = 14.6, 7.3, 4.0$ Hz), 1.75 (ddq, 1H, $J = 14.6, 7.3, 7.1$ Hz), 1.02 (t, 3H, $J = 7.3$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) 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 C₁₁H₁₁O (M⁺-H); 159.0810, found 159.0802.

2-Ethyl-5-methoxy-3-methylene-2,3-dihydrobenzofuran **37** : a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 6.90 (d, 1H, *J* = 2.7 Hz), 6.79 (dd, 1H, *J* = 2.4, 8.5 Hz), 6.75 (d, 1H, *J* = 8.8 Hz), 5.37 (d, 1H, *J* = 2.9 Hz), 5.11 (dddd, 1H, *J* = 2.4, 2.9, 3.9, 6.8), 4.88 (d, 1H, *J* = 2.4 Hz), 3.78 (s, 3H), 1.89 (ddq, 1H, *J* = 4.2, 7.3, 14.6 Hz), 1.74 (ddq, 1H, *J* = 7.1, 7.3, 14.4 Hz), 1.01 (t, 3H, *J* = 7.3 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 157.0, 154.1, 147.9, 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 C₁₂H₁₃O₂ (M⁺-H); 189.0916, found 189.0915.

3-Methylene-5-methoxy-2-propyl-2, 3-dihydrobenzofuran **38** : a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 6.90 (d, 1H, *J* = 2.6 Hz), 6.79 (dd, 1H, *J* = 2.6, 8.8 Hz), 6.74 (d, 1H, *J* = 8.6 Hz), 5.36 (d, 1H, *J* = 3.1 Hz), 5.15 (dddd, 1H, *J* = 2.6, 3.1, 4.0, 7.3 Hz), 4.88 (d, 1H, *J* = 2.6 Hz), 3.78 (s, 3H), 1.66-1.81 (m, 2H), 1.46-1.61 (m, 2H), 0.97 (t, 3H, *J* = 7.3 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 156.8, 154.1, 148.3, 126.3, 117.3, 110.7, 105.3, 99.7, 86.0, 56.0, 38.5, 17.8, 14.0; IR (neat) cm⁻¹ 2958, 2934, 1636, 1485, 1198; LRMS (EI) *m/z* 204 (100%, M⁺, base peak); HRMS (FAB) calcd for C₁₃H₁₅O₂ (M⁺-H); 203.1072, found 203.1078.

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