Supplementary Material (ESI) for Green Chemistry

Ruthenium(II) catalyzed synthesis of un saturated oxazolines via arene C-H bond alkenylation

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Table of Contents

- S2 General remarks
- S2 General procedures for alkenylation reactions
- S3 Characterization data of alkenylated products
- S7 References
- S8 ¹H and ¹³C NMR Spectra

General remarks

All reagents were obtained from commercial sources and used as received. Methanol and ethanol (anhydrous, HPLC grade, Aldrich) were used as received. Technical grade petroleum ether (40-60 $^{\circ}$ C bp.) and ethyl acetate were used for chromatography column.

¹H NMR spectra were recorded in CDCl₃ at ambient temperature on AVANCE I 300, AVANCE III 400 spectrometers at 300.1 MHz and 400.1 MHz, respectively, using the solvent as internal standard (7.26 ppm). ¹³C NMR spectra were obtained at 75 or 100 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad.

GC analyses were performed with GC-2014 (Shimadzu) 2010 equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 M×0.25 mm×0.25 mm film thickness), was used with N₂/air as vector gas. GCMS were measured by GCMS-QP2010S (Shimadzu) with GC-2010 equipped with a 30-m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 M×0.25 mm×0,25 mm film thickness), was used with helium as vector gas.

The following GC conditions were used: initial temperature 100 °C, for 2 minutes, then rate 10 °C/min. until 250 °C and 250 °C for 12 minutes.

Melting points were performed on a LEICA VMHB Kofler system.

4,4-dimethyl-2-(o-tolyl)-ozaxoline and 2-(o-tolyl)-ozaxoline were synthesized by known method^{1,2}.

<u>General procedure for optimisation study for [RuCl₂(*p*-cymene)]₂ catalyzed alkenylation of 2-phenyloxazoline with methylacrylate</u>

 $[RuCl_2(p-cymene)]_2$ (0.0125 mmol, 7.7 mg), methylacrylate (0.65 mmol, 59 µL), 2-phenyloxazoline (0.5 mmol, 66 μL), Cu(OAc)₂.H₂O (0.8-1.0 equiv.), additive (0-0.05 mmol) and ethanol (2 mL) were introduced in Schlenck tube under air, equipped with magnetic stirring bar and was stirred at required temperature. After 3h, the conversion of reaction was analyzed by gas chromatography and the the monoalkenylated/dialkenylated product ratio was calculated by ¹H NMR of the crude mixture. The solvent was then evaporated under vacuum and the desired product was purified by silica gel chromatography column using a mixture of petrol ether/ethyl acetate as the eluent.

<u>General procedure for optimisation study for [RuCl₂(*p*-cymene)]₂ catalyzed alkenylation of 2-(*o*-tolyl)-4,4-dimethyloxazoline with styrene</u>

[RuCl₂(*p*-cymene)]₂ (0.025 mmol, 15.3 mg), styrene (0.65 mmol, 75 μ L), 2-(o-tolyl) -4,4-dimethyloxazoline (0.5 mmol, 94.5 mg), Cu(OAc)₂.H₂O (0.5-0.8 equiv.), additive (0-0.1 mmol) and ethanol (2 mL) were introduced in Schlenck tube under air, equipped with magnetic stirring bar and was stirred at required temperature. After 24h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by silica gel chromatography column using a mixture of petrol ether/ethyl acetate as the eluent.

General procedure for [RuCl₂(p-cymene)]₂ catalyzed alkenylation of oxazolines

 $[RuCl_2(p-cymene)]_2$ (0.025 mmol, 15.3 mg), alkene (0.65 mmol), oxazoline (0.5 mmol), $Cu(OAc)_2.H_2O$ (0.4 mmol, 80 mg), 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate (0.05 mmol, 17.4 mg) and ethanol (2 mL) were introduced in Schlenck tube under air, equipped with magnetic stirring bar and was stirred at 80°C. When the reaction was completed, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by silica gel chromatography column and a mixture of petrol ether/ethyl acetate as the eluent.

Characterization data of products

Methyl (E)-3-[2-(2-oxazolinyl)-phenyl]acrylate (2a)



Light yellow solid, yield = 61%, 71 mg, M. p.: 130-132 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.57 (d, 1H, *J* = 16.0 Hz), 7.86 (m, 1H), 7.62 (d, 1H, *J* = 7.8 Hz), 7.48-7.42 (m, 2H), 6.37 (d, 1H, *J* = 16.0 Hz), 4.44 (t, 2H, *J* = 9.6 Hz), 4.14 (t, 2H, *J* = 9.6 Hz), 3.81 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =167.4, 163.9, 144.2, 135.1, 131.0, 130.2, 129.6, 127.7, 127.5, 119.8, 67.5, 55.8, 51.9. GC: t_R = 15.1 min. MS (EI): m/z: 200 (M⁺-OMe, 5), 172 (100), 128 (65), 115 (15).

Dimethyl (2*E*,2'*E*)-3,3'-[2-(2-oxazolinyl)-1,3-phenylene]diacrylate (3a)



Colorless solid, yield = 4%, 10 mg, M. p.: 144-145 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.85 (d, 2H, *J* = 15.9 Hz), 7.67 (d, 2H, *J* = 7.8 Hz), 7.49 (t, 1H, *J* = 7.8 Hz), 6.40 (d, 2H, *J* = 15.9 Hz), 4.54 (t, 2H, *J* = 9.6 Hz), 4.22 (t, 2H, *J* = 9.6 Hz), 3.81 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =167.0, 162.4, 141.9, 135.1, 130.5, 129.8, 128.0, 121.0, 68.3, 55.8, 52.0. GC: t_R = 21.8 min. MS (EI): m/z: 315 (M⁺, 2), 284 (5), 256 (100), 196 (20), 115 (8).

(E)-2-(2-methyl-6-styrylphenyl)-4,4-dimethyl-oxazoline³ (4a)



White solid, yield = 65%, 95 mg, M. p.: 85-87 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.57 (d, 1H, J = 7.8 Hz), 7.50 (d, 2H, J = 7.2 Hz), 7.40-7.26 (m, 5H), 7.15 (d, 1H, J = 7.5 Hz), 7.08 (d, 1H, J = 16.2 Hz), 4.17 (s, 2H), 2.41 (s, 3H), 1.51 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =161.9, 137.6, 137.4, 136.8, 130.8, 129.7, 129.2, 128.8, 128.3, 127.8, 126.7, 126.2, 122.9, 79.2, 68.3, 28.7, 19.7. GC: t_R = 19.3 min. MS (EI): m/z: 291 (M⁺, 10), 214 (100), 142 (10), 115 (10), 55 (15).

(E)-2-[2-methyl-6-(4-(tert-butyl)styryl)phenyl]-4,4-dimethyl-oxazoline (4b)



Yellow solid, yield = 59%, 102 mg, M. p.: 94-96 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.58 (d, 1H, *J* = 7.8 Hz), 7.48-7.41 (m, 4H), 7.35-7.30 (m, 2H), 7.15 (d, 1H, *J* = 7.5 Hz), 7.09 (d, 1H, *J* = 16.2 Hz), 4.18 (s, 2H), 2.42 (s, 3H), 1.53 (s, 6H), 1.38 (s, 9H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =162.0, 150.9, 137.3, 137.0, 134.8, 130.5, 129.6, 129.0, 128.1, 126.4, 125.7, 125.4, 122.7, 79.1, 68.3, 34.7, 31.4, 28.7, 19.7. GC: t_R = 25.6 min. MS (EI): m/z: 347 (M⁺, 15), 214 (100), 142 (7), 115 (5), 55 (10).

Methyl (E)-3-[2-(4,4-dimethyl-2-oxazolinyl)-3-methylphenyl]acrylate (4c)



Colorless oil, yield = 67%, 91 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.85 (d, 1H, *J* = 15.9 Hz), 7.46 (d, 1H, *J* = 7.8 Hz), 7.32-7.23 (m, 1H), 7.21 (d, 1H, *J* = 7.2 Hz), 6.37 (d, 1H, *J* = 15.9 Hz), 4.15 (s, 2H), 3.76 (s, 3H), 2.36 (s, 3H), 1.46 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =167.2, 161.2, 142.5, 137.8, 133.9, 131.6, 129.8, 129.7, 123.7, 119.7, 79.4, 68.5, 51.7, 28.5, 19.6. GC: t_R = 15.6 min. MS (EI): m/z: 258 (M⁺ - Me, 3), 242 (M⁺ - OMe, 10), 214 (100), 142 (25), 115 (30), 55 (25).

Ethyl (E)-3-[2-(4,4-dimethyl-2-oxazolinyl)-3-methylphenyl]acrylate (4d)



Colorless oil, yield = 81%, 116 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.84 (d, 1H, *J* = 15.9 Hz), 7.47 (d, 1H, *J* = 7.8 Hz), 7.31-7.27 (m, 1H), 7.21 (d, 1H, *J* = 7.5 Hz), 6.36 (d, 1H, *J* = 15.9 Hz), 4.24 (t, 2H, *J* = 7.2 Hz), 4.14 (s, 2H), 2.36 (s, 3H), 1.46 (s, 6H), 1.30 (t, 3H, *J* = 7.2 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =166.7, 161.1, 142.1, 137.8, 134.0, 131.6, 129.8, 129.7, 123.6, 120.2, 79.3, 68.5, 60.5, 28.5, 19.5, 13.4. GC: t_R = 16.5 min. MS (EI): m/z: 258 (M⁺ - Et, 5), 242 (M⁺ - OEt, 10), 214 (100), 142 (20), 115 (25), 55 (25).

(E)-2-(2-methyl-6-styrylphenyl)oxazoline (4e)



Colorless oil, yield = 54%, 71 mg, ¹H NMR (400 MHz, CDCl₃): δ = 7.47 (d, 1H, *J* = 8.0 Hz), 7.39 (d, 2H, *J* = 7.2 Hz), 7.29-7.05 (m, 6 H) 6.97 (d, 1H, *J* = 16.4 Hz), 4.38 (t, 2H, *J* = 9.6 Hz), 4.07 (t, 2H, *J* = 9.6 Hz), 2.29 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ =164.5, 137.7, 137.6, 137.1, 131.0, 129.8, 129.3, 128.8, 128.3, 127.9, 126.9, 126.5, 123.0, 67.6, 55.5, 19.9. GC: t_R = 19.4 min. MS (EI): m/z: 263 (M⁺, 10), 186 (100), 142 (30), 115 (15).

(E)-2-[2-methyl-6-(4-methylstyryl)phenyl]oxazoline (4f)



Colorless oil, yield = 46%, 64 mg, ¹H NMR (400 MHz, CDCl₃): δ = 7.55 (d, 1H, *J* = 8.0 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 7.32 (t, 1H, *J* = 7.6 Hz), 7.19-7.14 (m, 4H), 7.04 (d, 1H, *J* = 16.4 Hz), 4.47 (t, 2H, *J* = 9.6 Hz), 4.17 (t, 2H, *J* = 9.6 Hz), 2.38 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ =164.5, 137.8, 137.6, 137.2, 134.9, 130.9, 129.7, 129.5, 129.1, 128.2, 126.8, 125.5, 122.9, 67.5, 55.6, 21.4, 19.9. GC: t_R = 21.2 min. MS (EI): m/z: 277 (M⁺, 15), 186 (100), 142 (25), 115 (10).

(E)-2-[2-methyl-6-(4-(tert-butyl)styryl)phenyl]oxazoline (4g)



Light yellow oil, yield = 46%, 73 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.56 (d, 1H, *J* = 7.8 Hz), 7.47-7.13 (m, 7H), 7.06 (d, 1H, *J* = 16.2 Hz), 4.47 (t, 2H, *J* = 9.6 Hz), 4.17 (t, 2H, *J* = 9.6 Hz), 2.39 (s, 3H), 1.36 (s, 9H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 164.6, 151.1, 137.6, 137.2, 134.9, 130.8, 129.7, 129.1, 128.1, 126.6, 125.8, 125.7, 123.0, 67.5, 55.5, 34.8, 31.5, 19.9. GC: t_R = 26.4 min. MS (EI): m/z: 319 (20, M⁺), 186 (100), 142 (15), 115 (10).

(E)-2-[2-methyl-6-(4-bromostyryl)phenyl]oxazoline (4h)



White solid, yield = 40%, 68 mg, M. p.: 82-84 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.54 (d, 1H, J = 7.8 Hz), 7.47 (d, 2H, J = 8.4 Hz), 7.35-7.16 (m, 5H), 6.99 (d, 1H, J = 16.2 Hz), 4.47 (t, 2H, J = 9.6 Hz), 4.17 (t, 2H, J = 9.6 Hz), 2.39 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 164.3, 137.7, 136.7, 136.5, 131.9, 129.8, 129.7,129.6, 128.31, 128.29, 127.2, 123.0, 121.6, 67.6, 55.5, 20.0. GC: t_R = 25.3 min. MS (EI): m/z: 342 (M⁺, 10), 341 (10), 186 (100), 142 (25), 115 (10).

Methyl (E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylate (4i)



Yellow oil, yield = 71%, 87 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.80 (d, 1H, *J* = 15.9 Hz), 7.48 (d, 1H, *J* = 7.8 Hz), 7.35-7.23 (m, 2H), 6.39 (d, 1H, *J* = 15.9 Hz), 4.46 (t, 2H, *J* = 9.6 Hz), 4.15 (t, 2H, *J* = 9.6 Hz), 3.78 (s, 3H), 2.37 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =167.3, 163.6, 142.6, 138.1, 134.1, 131.8, 129.9, 129.6, 123.9, 119.8, 67.7, 55.5, 51.8, 19.9. GC: t_R = 15.7 min. MS (EI): m/z: 230 (M⁺ - Me, 2), 214 (M⁺ - OMe, 5), 186 (100), 142 (40), 115 (25), 77 (10).

Ethyl (E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylate (4j)



Yellow oil, yield = 80%, 104 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.79 (d, 1H, *J* = 15.9 Hz), 7.48 (d, 1H, *J* = 7.5 Hz), 7.33-7.21 (m, 2H), 6.37 (d, 1H, *J* = 15.9 Hz), 4.45 (t, 2H, *J* = 9.6 Hz), 4.22 (q, 2H, *J* = 7.1 Hz), 4.13 (t, 2H, *J* = 9.6 Hz), 2.35 (s, 3H), 1.30 (t, 3H, *J* = 7.1 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =166.7, 163.5, 142.3, 138.0, 134.1, 131.6, 129.8, 129.6, 123.8, 120.2, 67.7, 60.5, 55.4, 19.8, 14.3. GC: t_R = 16.4 min. MS (EI): m/z: 230 (M⁺ - Et, 2), 214 (M⁺ - OEt, 10), 186 (100), 142 (35), 115 (20), 77 (10).

Butyl (E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylate (4k)



Orange oil, yield = 70%, 101 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.79 (d, 1H, *J* = 15.9 Hz), 7.49 (d, 1H, *J* = 7.5 Hz), 7.34-7.22 (m, 2H), 6.37 (d, 1H, *J* = 15.9 Hz), 4.45 (t, 2H, *J* = 9.6 Hz), 4.20-4.10 (m, 4H), 2.36 (s, 3H), 1.69-1.62 (m, 2H), 1.46-1.39 (m, 2H), 0.95 (t, 3H, *J* = 7.5 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =166.8, 163.6, 142.3, 138.0, 134.1, 131.7, 129.8, 129.6, 123.8, 120.2, 67.7, 64.4, 55.4, 30.8, 19.8, 19.3, 13.8. GC: t_R = 16.4 min. MS (EI): m/z: 287 (M⁺, 2), 230 (M⁺ - Bu, 2), 214 (M⁺ - OBu, 10), 186 (100), 142 (25), 115 (20).

Benzyl (E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylate (4l)



Orange oil, yield = 69%, 111 mg, ¹H NMR (300 MHz, CDCl₃): δ = 7.88 (d, 1H, *J* = 15.9 Hz), 7.50 (d, 1H, *J* = 7.8 Hz), 7.41-7.24 (m, 7H), 6.45 (d, 1H, *J* = 15.9 Hz), 5.25 (s, 2H), 4.44 (t, 2H, *J* = 9.5 Hz), 4.13 (t, 2H, *J* = 9.5 Hz), 2.38 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =166.5, 163.6, 142.9, 138.0, 136.1, 134.0, 131.8, 129.9, 129.7, 128.6, 128.3, 128.2, 123.8, 119.8, 67.7, 66.4, 55.4, 19.8. GC: t_R = 16.4 min. MS (EI): m/z: 321 (M⁺, 2), 230 (M⁺ - Bn, 2), 214 (M⁺ - OBn, 2), 186 (100), 142 (20), 115 (15), 91 (35), 65 (10).

(E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylamide (4m)



White solid, yield = 55%, 63 mg (EtOAc/EtOH=10/90), M. p.: 137-139 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.72 (d, 1H, *J* = 15.6 Hz), 7.42 (d, 1H, *J* = 7.5 Hz), 7.32-7.21 (m, 2H), 6.39 (d, 1H, *J* = 15.6 Hz), 5.95 (brs, 2H), 4.47 (t, 2H, *J* = 9.6 Hz), 4.14 (t, 2H, *J* = 9.6 Hz), 2.37 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =167.8, 163.8, 140.0, 138.1, 134.5, 131.4, 129.9, 129.5, 123.9, 122.2, 67.8, 55.4, 19.9. GC: t_R = 17.7 min. MS (EI): m/z: 230 (M⁺, 2), 186 (100), 142 (65), 115 (45).

(E)-3-[2-(4,4-dimethyl-2-oxazolinyl)phenyl]acrylamide (40)



Yellow solid, yield = 57%, 70 mg (EtOAc/EtOH=5/90), M. p.: 154-156 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.04 (d, 1H, *J* = 15.6 Hz), 7.82 (d, 1H, *J* = 6.9 Hz), 7.51 (d, 1H, *J* = 6.9 Hz), 7.45-7.35 (m, 2H), 6.19 (d, 1H, *J* = 15.6 Hz), 6.12 (brs, 2H), 4.16 (s, 2H), 1.43 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ =168.3, 162.4, 135.5, 131.3, 130.4, 130.1, 129.2, 127.7, 127.6, 127.5, 79.5, 68.5, 28.5. GC: t_R = 17.7 min. MS (EI): m/z: 244 (M⁺, 2), 200 (100), 146 (40), 128 (45), 55 (60).

Methyl (E)-3-[2-(4,4-dimethyl-2-oxazolinyl)phenyl]acrylate (4p)



Light yellow solid, yield = 32%, 42 mg, M. p.: 78-80 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.49 (d, 1H, *J* = 16.0 Hz), 7.83 (d, 1H, *J* = 7.5 Hz), 7.65 (d, 1H, *J* = 7.2 Hz), 7.50-7.40 (m, 2H), 6.39 (d, 1H, *J* = 16.0 Hz), 4.15 (s, 2H), 3.82 (s, 3H), 1.44 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ =167.5, 161.6, 143.9, 134.9, 130.9, 130.3, 129.6, 128.4, 127.3, 119.8, 79.4, 68.5, 51.9, 28.6. GC: t_R = 15.1 min. MS (EI): m/z: 244 (M⁺ - Me, 2), 228 (M⁺ - OMe, 5), 200 (100), 146 (30), 128 (35), 55 (45).

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(E) 2-(2-methyl-6-styrylphenyl)-4,4-dimethyl-oxazoline (4a)





(E)-2-[2-methyl -6-(4-(*tert*-butyl)styryl)phenyl]-4,4-dimethyl-oxazoline (4b)







Methyl (*E*)-3-[2-(4,4-dimethyl-2-oxazolinyl)-3-methylphenyl]acrylate (4c)





(E)-2-(2-methyl-6-styrylphenyl)oxazoline (4e)





(E)-2-[2-methyl-6-(4-methylstyryl)phenyl]oxazoline (4f)





(E)-2-[2-methyl -6-(4-(*tert*-butyl)styryl)phenyl]oxazoline (4g)





(E)-2-[2-methyl -6-(4-bromostyryl)phenyl]oxazoline (4h)











100

50

150

200 ppm (f1) _ ___-500

0

Ethyl (E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylate (4j)





Butyl (E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylate (4k)











(E)-3-[2-(2-oxazolinyl)-3-methylphenyl]acrylamide (4m)





ppm (f1)





(E)-3-[2-(4,4-dimethyl-2-oxazolinyl)phenyl]acrylamide (40)







