Supporting Information

for

“Copper-Catalyzed Coupling of Amides and Carbamates with Vinyl Halides”

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General Considerations: Copper (I) iodide (98 %) was purchased from Strem Chemical Company and was a fine powder. Cesium carbonate was purchased from Aldrich. Potassium carbonate was purchased from Alfa Aesar. These materials should be free-flowing powder and should be protected from moisture. All other reagents are available commercially and were used without further purification. All reagents were weighed and handled in air. Flash column chromatography was performed with Silicycle ultra pure silica gel (230-400 mesh). Melting points were recorded on a Mel-Temp II, Laboratory Devices, Inc. IR spectra were recorded on an ASI ReactIR™ 1000 and were obtained by placing samples directly on the DiComp probe. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. ¹H and ¹³C NMR were obtained on a Varian 300 or 500 MHz instrument with chemical shifts reported in ppm relative to residual solvent signals or TMS as an internal standard. Gas chromatographic analyses were performed on a Hewlett Packard 5890 instrument with a FID detector and a Hewlett Packard 30 m x 0.25 mm i.d. HP-5 capillary column. Many of the products are only weakly UV active so that the stain of the TLC plates with I₂ was necessary in order to follow the reactions. Control reactions without ligand were performed for all compounds; in all cases the amount of product formed was much less than that formed in the presence of ligand. Control reactions without ligand for the reactions of vinyl bromides gave less than 20% product without ligand. The products from the vinyl-iodide reactions were difficult to assess by GC; however, the conversion of the vinyl iodide was less than 30%. Yields reported in Tables 1 and 2 are an average of two or more runs. The procedures described in this section are representative; thus, the yields may differ slightly from those given in Tables 1 and 2. Spectroscopic data of the known compounds matches with the data reported in the corresponding references. All new compounds were further characterized by elemental analysis except for 1-(1,2-dimethyl-propenyl)-azetidin-2-one, 1-(1,2-dimethyl-propenyl)-pyrrolidin-2-one, 1-(1,2-dimethyl-propenyl)-piperidin-2-one and 3-acetylamino-acrylic acid ethyl ester.

General procedure A: amidation of vinyl bromides.

A resealable Schlenk tube was charged with CuI (9.6 mg, 0.050 mmol, 5.0 mol%), K₂CO₃ (280 mg, 2.0 mmol) and amide (or carbamate) (1.2 mmol), evacuated and backfilled with argon. *N,N'*-Dimethylethylenediamine (11 μ L, 0.10 mmol, 10 mol%), vinyl bromide (1.00 mmol) and toluene (1.0 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve, immerse in a preheated oil bath; the reaction mixture was stirred at the indicated temperature until the complete consumption of starting material was observed as indicated by GC analysis. The reaction vessel was removed from the oil bath and the resulting pale tan suspension was allowed to reach room temperature, then, it was filtered through a plug silica gel (1 $\times$ 0.5 cm) eluting with ethyl acetate (50 mL). The filtrate was concentrated and the residue was purified by column chromatography on silica gel (2 $\times$ 10 cm, ethyl acetate) to provide the desired product.

Preparation of *N*-(2-methyl-1-propenyl)-2-pyrrolidinone. Using general procedure A, 2-pyrrolidinone (94 μ L, 1.2 mmol) and 1-bromo-2-methylpropene (102.5 μ L, 1.00 mmol) were allowed to react at 90 °C for 22 h. The desired product was isolated as a colorless oil (130 mg, 93% yield). The ¹H and ¹³C spectra matched those reported by Zezza.¹

Preparation of 1-(1,2-dimethyl-propenyl)-azetidin-2-one. Employing general procedure A, 2-azetidinone (85 mg, 1.2 mmol) and 2-bromo-3-methyl-2-butene (116 μ L, 1.0 mmol) were allowed to react at 110 °C for 25 h. Flash chromatography of the crude product (CH₂Cl₂: EtOAc, 90:10) provided 122.8 mg (88 %) of the title compound as a clear oil. ¹H NMR (500 MHz, CDCl₃): δ 1.70 (s, 6H), 1.79 (s, 3H), 2.94 (t, J = 4.3 Hz, 2H), 3.40 (t, J = 4.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 14.9, 19.6, 20.2, 35.4, 39.5, 123.8, 125.9, 165.1. IR (neat, cm⁻¹): 2962, 2912, 2863, 1740, 1673, 1447, 1364, 1239, 1129, 1030, 774.

Preparation of 1-(1,2-dimethyl-propenyl)-pyrrolidin-2-one. Employing general procedure A, 2-pyrrolidinone (91 μ L, 1.2 mmol) was allowed to react with 2-bromo-3-methyl-2-butene (116 μ L, 1.0 mmol) at 110 °C for 21 h. Flash chromatography of the crude product (EtOAc) provided 139.1

¹ Zezza, C. A.; Smith, M. B. *Synth. Commun.* **1987**, 17, 729.

mg (91 %) of the title compound as a clear oil. ^1H NMR (500 MHz, CDCl_3): δ 1.59 (s, 3H), 1.74 (s, 3H), 1.79 (s, 3H), 2.09 (m, 2H), 2.42 (t, $J = 8.2$ Hz, 2H), 3.42 (broad s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 15.0, 18.5, 19.4, 19.5, 30.9, 47.6, 125.2, 129.3, 173.6. IR (neat, cm^{-1}): 2983, 2916, 2873, 1671, 1410, 1295, 1258, 1146, 1011, 715.

Preparation of 1-(1,2-dimethyl-propenyl)-piperidin-2-one. Employing general procedure A, γ -valerolactam (119 mg, 1.2 mmol) was allowed to react with 2-bromo-3-methyl-2-butene (116 μL , 1.0 mmol) at 115 $^\circ\text{C}$ for 30 h. Flash chromatography of the crude product (EtOAc) provided 127.0 mg (76 %) of the title compound as a clear oil. ^1H NMR (500 MHz, CDCl_3): δ 1.57 (q, $J = 1.4$ Hz, 3H), 1.71 (d, $J = 0.6$ Hz, 3H), 1.81 (m, 7H), 2.41 (m, 2H), 3.17 (m, 1H), 3.33 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 15.0, 18.8, 19.3, 21.2, 23.1, 32.2, 47.7, 127.3, 130.2, 168.5. IR (neat, cm^{-1}): 2983, 2931, 2863, 1636, 1416, 1308, 1206, 1165, 828.

Preparation of cyclohexanecarboxylic acid (2-methyl-propenyl)-amide. Employing general procedure A, cyclohexylcarboxamide (151 mg, 1.2 mmol) was allowed to react with bromo-2-methylpropene (133mg, 116 μL , 1.0 mmol) at 110 $^\circ\text{C}$ for 24 h. Flash chromatography of the crude product (EtOAc) provided 155.0 mg (86 %) of the title compound as a white solid. Mp: 125.0-126.5. ^1H NMR (300 MHz, CDCl_3): δ 6.75 (br, 1H), 6.54 (dheptet, $J = 10.2, 1.5$ Hz, 1H), 2.14 (tt, $J = 11.7, 3.3$ Hz, 1H), 1.96-1.78 (m, 4H), 1.72 (d, $J = 1.5$ Hz, 3H), 1.64 (d, $J = 1.5$ Hz, 3H), 1.56-1.41 (m, 2H), 1.38-1.20 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 172.6, 116.9, 114.7, 45.6, 29.7, 25.8, 22.5, 16.6. IR (neat, cm^{-1}): 3294, 2933, 2921, 2856, 1648, 1528, 1447, 1376, 1252, 1218. Anal. Calcd. for $\text{C}_{11}\text{H}_{19}\text{NO}$: C, 72.88; H, 10.56. Found: C, 72.85; H, 10.56.

Preparation of 1-{1-[2-(*tert*-butyl-dimethylsilyloxy)-ethyl]-vinyl}-pyrrolidin-2-one. Employing general procedure A, the reaction of 2-pyrrolidinone (91 μL , 1.2 mmol) and *t*-butyldimethylsilyl 3-bromo-but-3-enyl ether (265 mg, 1.0 mmol) was carried out at 110 $^\circ\text{C}$ for 14 h. Flash chromatography of the crude product (EtOAc) provided 244.0 mg (91 %) of 2:1

rotermeric mixture of the title compound as a clear oil. Spectra data for the major rotermer: ^1H NMR (300 MHz, CDCl_3): δ 4.54 (d, J = 10 Hz, 1H), 4.26 (dd, J = 6.0, 1.0 Hz, 2H), 3.59 (m, 3H), 2.42-2.52 (m, 2H) 2.12-1.98 (m, 4H), 0.91 (s, 9H), 0.09 (s, 6H). The ^1H NMR spectrum also displayed a minor set of signals corresponding to the amide rotermer δ 5.22 (t, J = 4.5 Hz, 2H), 3.74 (t, J = 7.0 Hz, 2H), 2.84 (dt J = 7.0 Hz, 2H), 2.42-2.52 (m, 2H) 2.12-1.98 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 174.0, 173.5, 143.1, 135.7, 117.0, 101.3, 61.7, 59.4, 49.2, 49.1, 36.8, 32.9, 32.7, 26.0, 25.7, 18.4, 18.2, 18.0, 15.2, -5.0, -5.2. IR (neat, cm^{-1}): 2954, 2929, 2887, 2858, 1698, 1623, 1463, 1387, 1254, 1094, 834, 776. Anal. Calcd. for $\text{C}_{14}\text{H}_{27}\text{NO}_2\text{Si}$: C, 62.04; H, 10.10. Found: C, 61.87; H, 10.10.

Preparation of 1-{1-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-vinyl}-piperidin-2-one.

Employing general procedure A, the coupling of γ -valerolactam (119 mg, 1.2 mmol), and 2-bromo-3-methyl-2-butene (265 mg, 1.0 mmol) was conducted at 110 $^{\circ}\text{C}$ for 15 h. Flash chromatography of the crude product (EtOAc) provided 232.0 mg (76 %) of the title compound as a clear oil. ^1H NMR (300 MHz, CDCl_3): δ 5.02 (t, J = 1.0 Hz, 1H), 4.95 (s, 2H), 3.708 (d, J = 6.5 Hz, 2H), 3.55-3.40 (m, 2H), 2.61 (dt, J = 6.5, 1.0 Hz, 2H), 2.50-2.38 (m, 2H), 1.90-1.80 (m, 2H) 0.90 (s, 9H), 0.07 (s, 6H). The ^1H NMR spectrum also displayed a minor set of signals corresponding to the amide rotermer δ 5.46 (t, J = 4.5 Hz, 1H), 4.28 (dd, J = 4.5, 0.5 Hz, 2H), 3.55-3.40 (m, 3H), 2.50-2.38 (m, 2H) 1.90-1.80 (m, 6H), 0.92 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 169.2, 169.0, 148.9, 139.5, 126.2, 111.0, 60.8, 59.7, 50.9, 50.1, 37.4, 32.8, 26.0, 25.9, 23.6, 23.5, 21.4, 18.4, 18.3, 15.5, -4.9, -5.1. IR (neat, cm^{-1}): 2950, 2931, 2858, 1648, 1414, 1306, 1254, 1094, 833, 775. Anal. Calcd. for $\text{C}_{15}\text{H}_{29}\text{NO}_2\text{Si}$: C, 63.55; H, 10.31. Found: C, 63.54; H, 10.40.

Preparation of 3-(2-methyl-propenyl)-oxazolidin-2-one. Employing general procedure A, the coupling of oxazolidin-2-one (104 mg, 1.2 mmol) and bromo-2-methylpropene (133mg, 116 μL , 1.0 mmol) was carried out at 110 $^{\circ}\text{C}$ for 16 h. Flash chromatography of the crude product (EtOAc) provided 134.0 mg (95 %) of the title compound as a clear oil. ^1H NMR (300 MHz, CDCl_3): δ

5.85-5.82 (m, 1H), 4.42-4.35 (m, 2H), 3.81-3.74 (m, 2H), 1.76 (d, $J = 1.2$ Hz, 3H), 1.73 (d, $J = 1.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 157.2, 129.1, 118.6, 62.2, 46.6, 22.9, 18.0. IR (neat, cm^{-1}): 2962, 2923, 2856, 1729, 1684, 1410, 1250, 1098, 1250, 1048. Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{NO}_2$: C, 59.56; H, 7.85. Found: C, 59.61; H, 7.81.

Preparation of 4-benzyl-3-(2-methyl-propenyl)-oxazolidin-2-one. Employing general procedure A, the cross-coupling of 4-benzyl-oxazolidin-2-one (177 mg, 1 mmol) and bromo-2-methylpropene (160mg, 139 μL , 1.2 mmol) was carried out at 110 $^\circ\text{C}$ for 16 h. Flash chromatography of the crude product (EtOAc) provided 221 mg (96 %) of the title compound as a white solide. Mp. = 59-60 $^\circ\text{C}$ ^1H NMR (300 MHz, CDCl_3): δ 7.38-7.12 (m, 5H), 5.69 (heptet, $J = 1.2$ Hz, 1H), 4.28-4.03 (m, 3H), 3.10 (dd, $J = 14, 4$ Hz, 2h), 2.66 (dd, $J = 14, 10.5$ Hz, 2H), 1.80 (d, $J = 1.2$ Hz, 3H), 1.75 (d, $J = 1.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 156.6, 135.6, 134.1, 129.1, 128.8, 127.1, 116.9, 66.7, 58.6, 38.4, 22.6, 18.3. IR (neat, cm^{-1}): 3062, 3029, 2971, 2916, 1748, 1681, 1497, 1409, 1239, 1100, 1044, 1030, 754, 700. Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ C, 72.70; H, 7.41 Found: C, 72.65; H, 7.36.

Preparation of 4-phenyl-5-methyl-3-(2-methyl-propenyl)-oxazolidin-2-one. Employing general procedure A, the coupling of 4-phenyl-5-methyl-oxazolidin-2-one (177 mg, 1 mmol) and bromo-2-methylpropene (160mg, 139 μL , 1.2 mmol) was carried out at 110 $^\circ\text{C}$ for 16 h. Flash chromatography of the crude product (EtOAc) provided 215 mg (93 %) of the title compound as a clear oil. ^1H NMR (300 MHz, CDCl_3): δ 7.42-7.26 (m, 5H), 5.70 (heptet, $J = 1.5$ Hz, 1H), 5.66 (d, $J = 7.8$ Hz, 1H), 4.23 (dq, $J = 7.8, 6.6$ Hz, 1H), 1.78 (d, $J = 1.5$ Hz, 3H), 1.73 (d, $J = 1.5$ Hz, 3H), 0.75 (d, $J = 6.6$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 156.5, 135.0, 134.1, 128.4, 128.2, 125.2,

116.8, 78.5, 57.5, 22.5, 18.1, 14.6. IR (neat, cm^{-1}): 3068, 3035, 2977, 2935, 2917, 1750, 1679, 1455, 1397, 1378, 1262, 1229, 1191, 1111, 1046, 980, 756. Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ C, 72.7; H, 7.41. Found: C, 72.38; H, 7.58.

Preparation of 2-amino-N-(2-methyl-propenyl)-benzamide. Employing general procedure A, the cross-coupling of 4-Benzyl-5-methyl-oxazolidin-2-one (177 mg, 1 mmol) and bromo-2-methylpropene (160mg, 139 μL , 1.2 mmol) was carried out at 110 $^{\circ}\text{C}$ for 16 h. Flash chromatography of the crude product (EtOAc) provided 215 mg (93 %) of the title compound as a pale yellow solid. ^1H NMR (300 MHz, CDCl_3): δ 7.4 (br, 1H), 7.39-7.33 (m, 1H), 7.27-7.18 (m, 1H), 6.74-6.62 (m, 3H), 5.51 (br, 2H), 1.77 (d, $J = 1.0$ Hz, 3H), 1.703 (d, $J = 1.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.7, 148.9, 132.5, 126.8, 117.4, 116.9, 116.7, 115.9, 115.6, 22.6, 16.6. IR (neat, cm^{-1}): 3471, 3298, 1636, 1621, 1586, 1509, 1260, 744, 683. Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ C, 69.45; H, 7.42. Found: C, 69.73; H, 7.41.

Preparation of *trans*-N-(1-decenyl)acetamide. A resealable Schlenk tube was charged with CuI (9.6 mg, 0.050 mmol, 5.0 mol%), acetamide (118 mg, 2.00 mmol), Cs_2CO_3 (500 mg, 1.5 mmol). The tube was evacuated and backfilled with argon. *N,N'*-Dimethylethylenediamine (11 μL , 0.10 mmol, 10 mol%), *trans*-1-iodo-1-decene (202 μL , 1.00 mmol) and THF (1.0 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 25 $^{\circ}\text{C}$ for 15 h. After the resulting pale blue suspension was allowed to reach room temperature, ethyl acetate (2 mL) and dodecane (230 μL , internal GC standard) were added. A 50 μL sample of the supernatant solution was diluted with ethyl acetate (1 mL) and then analyzed by GC to indicate >99% conversion of *trans*-1-iodo-1-decene. The reaction mixture was filtered through a silica plug (1 $\times$ 0.5 cm) eluting with ethyl acetate (50 mL). The filtrate was concentrated and the residue was purified by column chromatography on silica gel (hexane-ethyl acetate 1:1) to provide the desired product as a white solid (161 mg, 82% yield). Mp: 56-57 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.15 (br d, 1H), 6.73 (ddt, $J = 14.4, 10.6, 1.4$ Hz, 1H), 5.13 (dt, $J = 14.4, 7.2$ Hz, 1H), 2.04-1.96 (m,

5H), 1.40-1.20 (m, 12H), 0.88 (t, $J = 6.7$ Hz, 3H). The ^1H NMR spectrum also displayed a minor set of signals corresponding to the amide rotamer (ca. 20:1 ratio of rotamers). ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 122.3, 113.1, 31.8, 29.8, 29.6, 29.4, 29.2, 29.1, 23.2, 22.6, 14.1. IR (neat, cm^{-1}): 3289, 3211, 1686, 1652, 1540, 1373, 944. Anal. Calcd. for $\text{C}_{12}\text{H}_{23}\text{NO}$: C, 73.04; H, 11.75. Found: C, 73.11; H, 11.84.

General procedure B: amidation of vinyl iodides.

A resealable Schlenk tube was charged with CuI (9.6 mg, 0.050 mmol, 5.0 mol%), amide (72 mg, 1.2 mmol), Cs_2CO_3 (500 mg, 1.5 mmol). The tube was evacuated and backfilled with argon. N,N' -Dimethylethylenediamine (11 μL , 0.10 mmol, 10 mol%), vinyl iodide (202 μL , 1.00 mmol) and THF (1.0 mL) or toluene (1.0 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve, immersed in a preheated oil bath and the reaction mixture was stirred for the time indicated. After the resulting pale blue suspension was allowed to reach room temperature, ethyl acetate (2 mL) and dodecane (230 μL , internal GC standard) were added. A 50 μL sample of the supernatant solution was diluted with ethyl acetate (1 mL) and then analyzed by GC to indicate >99% conversion of *cis*-1-iodo-1-decene. The reaction mixture was filtered through a silica plug (1 $\times$ 0.5 cm) eluting with ethyl acetate (50 mL). The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product.

Preparation of *cis*-N-(1-decenyl)acetamide. Employing general procedure B, the coupling of *cis*-1-iodo-1-decene (202 μL , 1.00 mmol) and acetamide (72 mg, 1.2 mmol) was conducted at 50 $^\circ\text{C}$ for 12 h. Flash column chromatography (hexane-ethyl acetate 1:1) provided the desired product as a colorless oil (161 mg, 82% yield). Mp: 56-57 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.08 (br, 1H), 6.68 (ddt, $J = 10.5, 9.5, 1.0$ Hz, 1H), 4.72 (dt, $J = 10.5, 8.2$ Hz, 1H), 2.09 (s, 3H), 2.01 (qd, $J = 8.2, 1.0$ Hz, 2H), 1.48-1.23 (m, 12H), 0.90 (t, $J = 6.6$ Hz, 3H). The ^1H NMR spectrum also displayed a minor set of signals corresponding to the amide rotamer (ca. 20:1 ratio of rotamers). ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 120.6, 111.1, 31.9, 29.5, 29.4, 29.3, 25.8, 23.5, 22.7, 14.2. IR (neat, cm^{-1}): 3298, 3186, 2956, 2923, 2854, 1656, 1519, 1466, 1370, 1275. Anal. Calcd. for $\text{C}_{12}\text{H}_{23}\text{NO}$: C, 73.04; H, 11.75. Found: C, 72.98; H, 11.85.

Preparation of *N-trans*-dec-1-enyl-*trans*-3-phenyl-acrylamide. Employing general procedure B, the coupling of cinnamamide (177 mg, 1.2 mmol) and *trans*-1-iodo-dec-1-ene (266 mg, 1.0 mmol. Note: it contains 5 % *cis* isomer) was conducted at 70 °C for 13.5 h (note: potassium carbonate (276 mg, 2.0 mmol) was used as a base instead of Cs₂CO₃). Flash chromatography of the crude product (CH₂Cl₂) provided 245.1 mg (86 %) of the title compound as a white solid. Mp: 95-99°C; ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, J = 6.6 Hz, 3H), 1.23 (m, 12H), 2.02 (dt, J = 6.9, 6.6 Hz, 2H), 5.34 (dt, J = 14.0, 7.2 Hz, 1H), 6.56 (d, J = 15.3 Hz, 1H), 6.92 (dd, J = 14.3, 10.7 Hz, 1H), 7.26 (m, 3H), 7.43 (m, 2H), 7.67 (d, J = 15.7 Hz, 1H), 8.38 (d, J = 10.5 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 14.2, 22.7, 29.2, 29.3, 29.5, 30.0, 30.1, 31.9, 114.7, 120.1, 122.5, 127.7, 128.6, 129.6, 134.5, 141.6, 162.9. IR (CDCl₃, cm⁻¹): 3280, 3070, 2956, 2927, 2856, 1656, 1625, 1505, 1343, 1212, 976, 766. (Sample contains ~5 % of the *cis* isomer). Anal. Calcd. for C₁₆H₁₉NO: C, 79.95; H, 9.53. Found: C, 79.94; H, 9.59.

Preparation of *N-cis*-dec-1-enyl-*trans*-3-phenyl-acrylamide. Employing general procedure B, the coupling of cinnamamide (177 mg, 1.2 mmol) and *cis*-1-iodo-dec-1-ene (266 mg, 1.0 mmol) was conducted at 70 °C for 13.5 h (note: potassium carbonate (276 mg, 2.0 mmol) was used as a base instead of Cs₂CO₃). Flash chromatography of the crude product (CH₂Cl₂) provided 245.1 mg (86 %) of the title compound as a white solid. Mp: 95-99°C; ¹H NMR (300 MHz, CDCl₃): δ 0.87 (t, J = 6.6 Hz, 3H), 1.23 (m, 12H), 2.02 (dt, J = 6.9, 6.6 Hz, 2H), 5.34 (dt, J = 14.0, 7.2 Hz, 1H), 6.56 (d, J = 15.3 Hz, 1H), 6.92 (dd, J = 14.3, 10.7 Hz, 1H), 7.26 (m, 3H), 7.43 (m, 2H), 7.67 (d, J = 15.7 Hz, 1H), 8.38 (d, J = 10.5 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 14.2, 22.7, 29.2, 29.3, 29.5, 30.0, 30.1, 31.9, 114.7, 120.1, 122.5, 127.7, 128.6, 129.6, 134.5, 141.6, 162.9. IR (CDCl₃, cm⁻¹): 3280, 3070, 2956, 2927, 2856, 1656, 1625, 1505, 1343, 1212, 976, 766. Anal. Calcd. for C₁₆H₁₉NO: C, 79.95; H, 9.53. Found: C, 79.94; H, 9.59.

Preparation of 3-acetylamino-acrylic acid ethyl ester. Employing general procedure B, the coupling of acetamide (67 mg, 1.2 mmol) and ethyl *cis*-iodo-acrylate (226 mg, 1.0 mmol) was carried out at 70 °C for 5 h. Flash chromatography of the crude product (CH₂Cl₂) provided 108 mg (68 %) of the title compound as a viscous, clear oil. ¹H NMR (300 MHz, CDCl₃): δ 10.45 (br, 1H), 7.48 (dd, J = 10, 9 Hz, 1H), 5.12 (d, J = 10 Hz, 1H), 4.18 (q, J = 7.5 Hz, 2H), 2.16 (s, 3H),

1.30 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 169.2, 168.3, 138.0, 96.2, 60.2, 23.6, 14.2. IR (CDCl_3 , cm^{-1}): 3232, 2968, 2923, 2854, 1713, 1673, 1632, 1260, 1173, 1028.

Preparation of 3-acetylamino-but-2-enoic acid ethyl ester.² Employing general procedure B, the coupling of acetamide (67 mg, 1.2 mmol) and ethyl *cis*-iodo-acrylate (240 mg, 1.0 mmol) was conducted at 70 °C for 6 h. Flash chromatography of the crude product (CH_2Cl_2) provided 112 mg (65 %) of the title compound as white crystals. Mp. 62.0-63.0 °C (lit. Mp. 63.0-64.0 °C³). ^1H NMR (300 MHz, CDCl_3): δ 11.17 (br, 1H), 4.90 (s, 1H), 4.16 (q, J = 7.0 Hz, 2H), 2.38 (s, 3H), 2.15 (s, 3H), 1.29 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 169.2, 169.0, 155.0, 96.4, 59.8, 25.2, 21.9, 14.2. The spectral data matched the ones reported by Zhang.²

² Zhu, G.; Chen, Z.; Zhang, X. *J. Org. Chem.* **1999**, 64, 6907.

³ Yakimovich, S. I.; Kayukova, L. A.; Khrustalev, V. A.; Tsatsenkina, L. A. *Zhur. Org. Khim.* **1977**, 13, 1161.

STANDARD PROTON PARAMETERS

Solvent: CDCl₃
 Ambient temperature
 INOVA-500 "rocky"
 PULSE SEQUENCE
 Pulse 90.0 degrees
 Acq. time 3.200 sec
 Width 10000.0 Hz
 28 repetitions
 OBSERVE H1, 500.2312354 MHz
 DATA PROCESSING
 FI size 131072
 Total time 1 minutes

STANDARD CARBON PARAMETER

Solvent CDCl₃
 Ambient temperature
 User: j14-87
 INOVA-50 "rock"
 PULSE SEQUENCE
 Relax. delay 0.63 sec
 Pulse 6.4 degrees
 Acq. time 1.736 sec
 Width 3735.8 Hz
 80 repetitions
 OBSERVE C13, 12.7632713 MHz
 DECOUPLE H1, 50.2332753 MHz
 Power 3 dB
 continuously on
 WALTZ-5 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 31072
 Total time 3 minutes

STANDARD PROTON PARAMETERS

Solvent: CDCl₃
 Ambient temperature
 INOVA-500 "Rocky"
 PULSE SEQUENCE
 Pulse 90.0 degrees
 Acq. time 3.200 sec
 Width 10000.0 Hz
 8 repetitions
 OBSERVE H1, 500.2312418 MHz
 DATA PROCESSING
 FT size 131072
 Total time 1 minute

STANDARD CARBON PARAMETERS

Solvent: CDCl₃
 Ambient temperature
 User: 1-1487
 INVA-500 "rocky"
 PULSE SEQUENCE
 Relax. delay 0.763sec
 Pulse 65.4degrees
 Acq. time .736 sec
 Width 3773.8 Hz
 15 repetitions
 OBSERVE CH, 125.782579 MH
 DECOUPLE H, 500.232753 MH
 Power 37 dB
 continuously on
 VLTZ-16 modulated
 DAA PROCESSING
 Line broadening 0.1 Hz
 FTSIZE 13172
 Total time: minute

STANDARD PROTON PARAMETERS

Solvent: CDCl₃
 Ambient temperature
 INOVA-500 "Rocky"
 PULSE SEQUENCE
 Pulse 90.0 degrees
 Acq. time 3.200 sec
 Width 10000.0 Hz
 16 repetitions
 OBSERVE H1, 500.2311974 MHz
 DATA PROCESSING
 FT size 131072
 Total time 1 minute

STANDARD CARBON PARAMETERS

Solvent: CDCl₃
 Ambient temperature
 User: 1-14-87
 INOVA-500 "rocky"

PULSE SEQUENCE
 Relax. delay 0.763 sec
 Pulse 65.4 degrees
 Acq. time 1.736 sec
 Width 37735.8 Hz
 91 repetitions
 OBSERVE C13, 125.7832788 MHz
 DECOUPLE H1, 500.2332753 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 131072
 Total time 3 minutes

STANDARD 1H OBSERVE

exp7 std1h

SAMPLE DEC. & VT
date Jun 17 2003 dfrq 300.100
solvent CDC13 dn H1
file exp 39
ACQUISITION
sfrq 300.100 dm 0
tn H1 dnm nn
at 1.995 dmf 11300
np 17984
sw 4506.5 wfile
fb not used proc ft
bs 54 fn not used
tpwr 7.0 weff
pw 1.000 wexp
tof 0 wbs
nt 16 wnt
ct 0
alock not used
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -716.7
wp 4506.5
vs 200
sc 0
wc 250
hzmm 18.03
ls 98.60
rfl 2898.5
rfp 2181.7
th 20
ins 1.000
nm cdc ph

13C OBSERVE

expl std13c

SAMPLE DEC. 8 VT
 date Jun 17 2003 dfrq 300.100
 solvent CDCl3 dn H1
 file exp 39
 ACQUISITION
 sfrq 75.467 dm 0
 ln C13 dnm VVY
 at 2.501 dmf W
 np 113148 11000
 sw 22624.4 lb PROCESSING 0.50
 fb 12400 wlf1le ft
 bs 16 proc 262144
 tpwr 55 fn
 pw 7.0
 dl 0 warr
 tof -26.0 wexp
 nt 512 wps
 ct 0 wnt
 alock
 gain not used
 FLAGS
 il n
 in n
 dp y
 DISPLAY
 sp -3786.3
 wp 22624.4
 vs 97
 sc 0
 wc 250
 hzmm 90.50
 is 500.00
 rfi 9536.7
 rfp 5810.4
 th 6
 ins 100.000
 nm no ph