

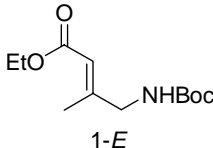
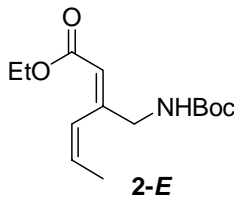
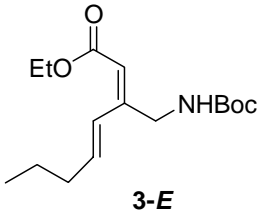
*Supporting Information***Enol Tosylates as Viable Partners in Pd-catalyzed Cross Coupling Reactions**

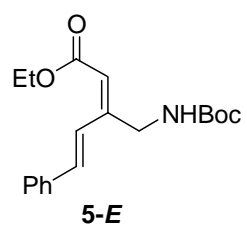
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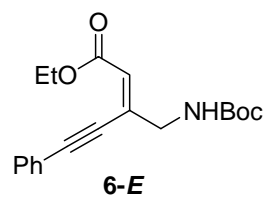
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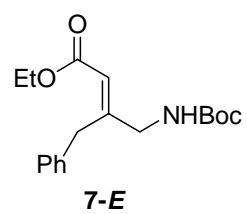
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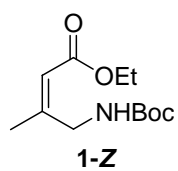
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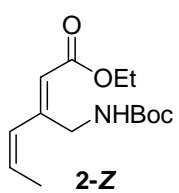
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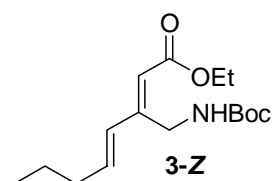
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General Methods: All reactions were run under an atmosphere of nitrogen using anhydrous solvents purchased from Aldrich. All reagents were purchased from commercial suppliers and used as received. Compounds **4b** and **5b** were prepared as previously reported in the literature.¹ All NMR spectra were recorded on a 400 MHz instrument in CDCl₃ unless otherwise noted.

General Procedure for Suzuki Coupling

A Schlenk flask was charged with enol tosylate (0.5 g, 1.25 mmol), *cis*-propenyl boronic acid (1.2 equiv., 1.50 mmol), and PdCl₂(dppf)-CH₂Cl₂ (10 mol%, 0.125 mmol). THF (13 mL) and deionized water (1.3 mL) were added followed by Cs₂CO₃ (3 equiv., 3.75 mmol) and the flask was evacuated and backfilled with N₂ three times. The resulting reaction was stirred overnight at 60 °C under N₂. HPLC of the reaction mixture indicated complete conversion. The mixture was cooled to room temperature and 15 mL of ethyl acetate was added followed by 15 mL of NaHCO₃ (saturated aqueous solution). After the phase cut, the organic layer was washed with 2 x 15mL of brine. The organic layer was dried over MgSO₄ and treated with KB-B Darco (50 mg),

and filtered through Solka Floc. Evaporation and chromatography on silica gel with the indicated solvent system afforded the product.

General Procedure for Sonogashira coupling

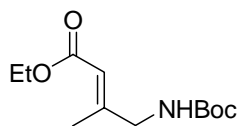
A Schlenk flask was charged with enol tosylate (0.5 g, 1.25 mmol), phenylacetylene (1.2 equiv., 1.50 mmol), [Pd(allyl)Cl]₂ (2.5 mol%, 0.031 mmol), di-*tert*-butylphosphinobiphenyl (10 mol%, 0.125 mmol), CuI (15 mol%, 0.188 mmol), and DABCO (2 equiv., 2.5 mmol). CH₃CN (5 mL) was added and the flask was evacuated and backfilled with N₂ three times. The resulting reaction was stirred overnight at ambient temperature under N₂. HPLC of the reaction mixture indicated complete conversion. The mixture was diluted with 15 mL of ethyl acetate and 15 mL of NaHCO₃ (saturated aqueous solution). After the phase cut, the organic layer was washed with 2 x 15mL of brine. The organic layer was dried over MgSO₄ and treated with KB-B Darco (50 mg), and filtered through Solka Floc. Evaporation and chromatography on silica gel with the indicated solvent system afforded the product.

General Procedure for Stille coupling

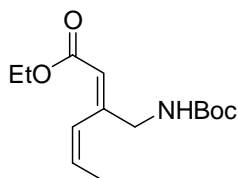
A Schlenk flask was charged with enol tosylate (0.3 g, 0.75 mmol), tributyl(phenyl)tin (1.2 equiv., 0.90 mmol), Pd(PPh₃)₄ (5 mol%, 0.038 mmol), and KF (3 equiv., 2.25 mmol). THF (2 mL) was added and the flask was evacuated and backfilled with N₂ three times. The resulting reaction was stirred overnight at 60 °C under N₂. HPLC of the reaction mixture indicated complete conversion. The mixture was cooled to room temperature and 15 mL of ethyl acetate was added followed by 15 mL of NaHCO₃ (saturated aqueous solution). After the phase cut, the organic layer was washed with 2 x 15mL of brine. The organic layer was dried over MgSO₄ and treated with KB-B Darco (50 mg), and filtered through Solka Floc. Evaporation and chromatography on silica gel with the indicated solvent system afforded the product. No spectra for product of Stille coupling are reported since they have been previously reported in the literature.¹ The isolated materials were compared spectroscopically and by reverse phase HPLC to samples of the authentic products.

References

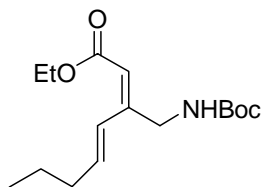
1. Baxter, J.M.; Steinhuebel, D.; Palucki, M.; Davies, I.W. *Org. Lett.* **2005**, 7, 215-218.



Compound 1-*E*: Isolated in 90% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 5.78 (s, 1H), 4.75 (s, 1H), 4.16 (q, 2H, *J* = 7.2 Hz), 2.13 (s, 3H), 1.46 (s, 9H), 1.28 (t, 3H, *J* = 7.1 Hz) ppm; ¹³C NMR δ 14.2, 16.6, 28.2, 47.5, 59.6, 79.8, 114.6, 155.3, 166.4. Anal. Calcd for C₁₂H₂₁NO₄: C, 59.24; H, 8.70; N, 5.76. Found: C, 59.02; H, 8.94; N, 5.68.
nOe (CDCl₃): 1.5% nOe from vinyl CH to CH₂.

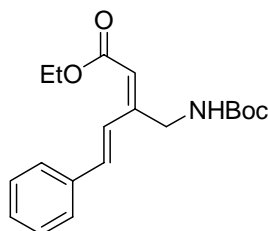


Compound 2-*E*: Isolated in 70% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 6.30 (d, 1H, *J* = 11.8 Hz), 5.87 (s, 1H), 5.79 (m, 1H), 4.74 (s, 1H), 4.15 (q, 2H, *J* = 7.1 Hz), 3.92 (d, 2H), 1.69 (dd, 3H, *J* = 1.2 Hz, *J* = 7.0 Hz), 1.46 (s, 9H), 1.26 (t, 3H, *J* = 7.1 Hz) ppm; ¹³C NMR δ 14.1, 15.1, 28.3, 45.6, 59.9, 79.7, 116.4, 125.6, 129.9, 152.3, 155.5, 165.7. Anal. Calcd for C₁₄H₂₃NO₄: C, 62.43; H, 8.61; N, 5.20. Found: C, 62.24; H, 8.73; N, 5.17.
nOe (CDCl₃): 1.3% nOe from vinyl CH to CH₂; 0.88% nOe from CH₂ to vinyl CH.



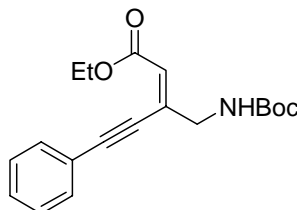
Compound 3-*E*: Isolated in 81% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 7.41 (d, 1H, *J* = 16.3 Hz), 6.15 (dt, 1H, *J* = 6.9 Hz, *J* = 16.3 Hz), 5.69 (s, 1H), 4.71 (s, 1H), 4.15 (q, 2H, *J* = 7.1 Hz), 4.04 (d, 2H, *J* = 5.5 Hz), 2.16 (q, 2H, *J* = 7.2 Hz), 1.44 (m, 11H), 1.27 (t, 3H, *J* = 7.2 Hz), 0.9 (t, 3H, *J* = 7.4 Hz) ppm; ¹³C NMR δ 13.6, 14.1, 22.0, 28.2, 35.4, 42.8, 59.8, 79.6, 114.4, 125.4, 138.3, 150.5, 155.4, 166.2. Anal. Calcd for C₁₆H₂₇NO₄: C, 64.62; H, 9.15; N, 4.71. Found:

C, 64.79; H, 9.37; N, 4.55. nOe (CDCl₃): 2.0% nOe from vinyl CH (5.69 ppm) to CH₂ (4.04 ppm); 3.8% nOe from CH₂ (4.04 ppm) to vinyl CH (6.15 ppm); 1.5% nOe from CH₂ (4.04 ppm) to vinyl CH (5.69 ppm)



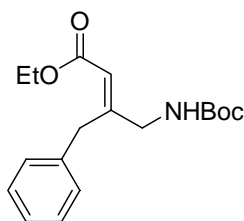
Compound 5-*E*: Isolated in 68% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 8.27 (d, 1H, *J* = 16.8 Hz), 7.52 (d, 2H, *J* = 7.2 Hz), 7.31 (m, 3H), 6.98 (d, 1H, *J* = 16.8 Hz), 5.87 (s, 1H), 4.77 (s, 1H), 4.21 (m, 4H), 1.47 (s, 9H), 1.32 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C NMR δ 14.2, 28.3, 42.8, 60.0, 79.8, 116.6, 123.5, 127.3, 128.6, 128.7, 134.8, 136.4, 150.2, 155.5, 166.2. Anal. Calcd for C₁₉H₂₅NO₄: C, 68.86; H, 7.60; N, 4.23. Found: C, 68.47; H, 7.66; N, 4.24.

nOe (CDCl₃): 2.8% nOe from vinyl CH to CH₂.



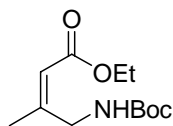
Compound 6-*E*: Isolated in 78% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 7.52 (m, 2H), 7.32 (m, 3H), 6.14 (s, 1H), 5.06 (s, 1H), 4.22 (q, 2H, *J* = 7.1 Hz), 4.00 (d, 2H, *J* = 5.8 Hz), 1.44 (s, 9H), 1.29 (t, 3H, *J* = 7.1 Hz) ppm; ¹³C NMR δ 14.2, 28.2, 46.0, 60.3, 79.9, 85.7, 101.5, 122.3, 123.0, 128.3, 129.2, 132.0, 135.8, 155.4, 164.8. Anal. Calcd for C₁₉H₂₃NO₄: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.25; H, 7.01; N, 4.04.

nOe (CDCl₃): 1.9% nOe from vinyl CH to CH₂; 0.6% nOe from CH₂ to vinyl CH.



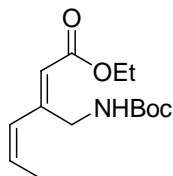
Compound 7-*E*: Isolated in 50% yield after SiO₂ chromatography from 5:2 (hexanes:EtOAc). ¹H NMR δ 7.22 (m, 5H), 5.91 (s, 1H), 4.69 (s, 1H), 4.20 (q, 2H, *J* = 7.1 Hz), 4.02 (s, 2H), 3.74 (d, 2H, *J* = 5.8 Hz), 1.44 (s, 9H), 1.30 (t, 3H, *J* = 7.1 Hz) ppm; ¹³C NMR δ 14.2, 28.2, 35.7, 45.4, 59.9, 79.7, 115.5, 126.4, 128.5, 128.7, 138.1, 155.6, 156.8, 166.3. Anal. Calcd for C₁₈H₂₅NO₄: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.52; H, 8.17; N, 4.34.

nOe (CDCl₃): 1.7% nOe from vinyl CH to CH₂ (3.74 ppm); 1.5% nOe from CH₂ (3.74 ppm) to vinyl CH; 1.2% nOe from CH₂ (3.74 ppm) to CH₂ (4.02 ppm); 0.91% from CH₂ (3.74 ppm) to aromatic CH.



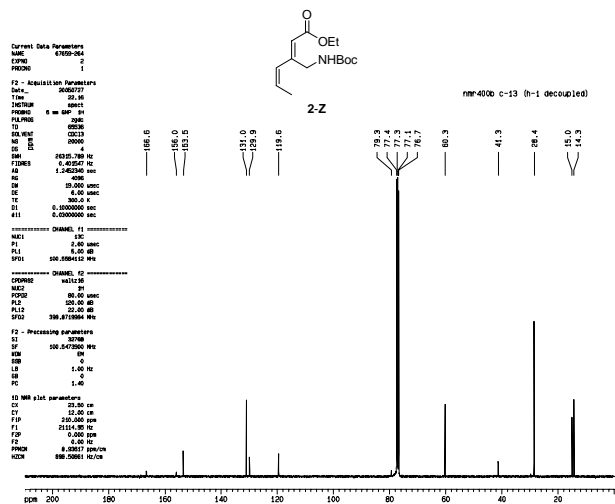
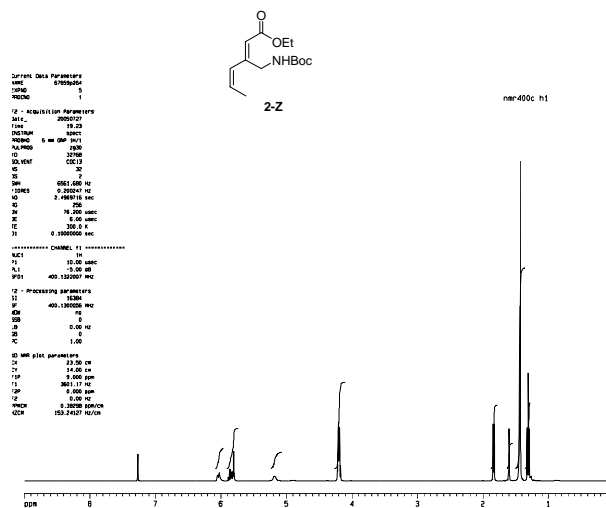
Compound 1-*Z*: Isolated in 45% yield after SiO₂ chromatography from 5:2 (hexanes:EtOAc). ¹H NMR δ 5.69 (d, 1H, *J* = 1.1 Hz), 5.19 (s, 1H), 4.09 (m, 4H), 1.92 (d, 3H, *J* = 1.3 Hz), 1.40 (s, 9H), 1.23 (t, 3H, *J* = 7.0 Hz) ppm; ¹³C NMR δ 14.1, 23.8, 28.3, 41.5, 59.8, 79.2, 117.8, 156.1, 157.1, 166.2. Anal. Calcd for C₁₂H₂₁NO₄: C, 59.24; H, 8.70; N, 5.76. Found: C, 59.08; H, 8.58; N, 5.68.

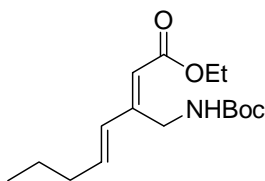
nOe (CDCl₃): 1.8% nOe from vinyl CH to CH₃; 0.76% nOe from CH₃ to CH₂; 0.96% nOe from CH₃ to vinyl CH



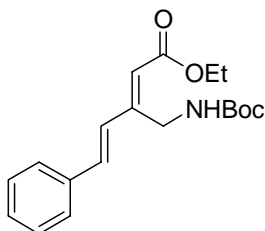
Compound 2-*Z*: Isolated in 54% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 5.99 (d, 1H, *J* = 11.7 Hz), 5.80 (m, 1H), 5.75 (s, 1H), 5.19 (s, 1H), 4.15 (m, 4H), 1.79 (dd, 3H, *J* = 1.9, *J* = 7.2 Hz), 1.38 (s, 9H), 1.26 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C NMR δ 14.1, 14.8, 28.2, 41.1, 60.0, 79.0, 119.3, 129.7, 130.8,

153.3, 155.8, 166.4. nOe (CDCl₃): 1.1% nOe from CH₃ to vinyl CH (5.75 ppm), 1.4% nOe from CH₃ to vinyl CH (5.80 ppm).

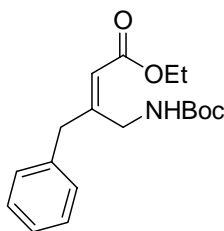




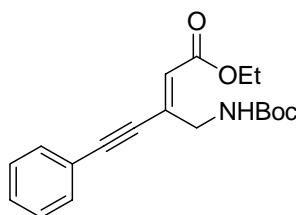
Compound 3-Z: Isolated in 56% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 6.53 (m, 1H), 5.99 (d, 1H, *J* = 15.7 Hz), 5.74 (s, 1H), 5.30 (s, 1H), 4.24 (d, 2H, *J* = 6.5 Hz), 4.15 (q, 2H, *J* = 7.1 Hz), 2.13 (q, 2H, *J* = 7.1 Hz), 1.43 (m, 11H), 1.26 (t, 3H, *J* = 7.1 Hz), 0.88 (t, 3H, *J* = 7.3 Hz) ppm; ¹³C NMR δ 13.5, 14.1, 21.9, 28.2, 35.2, 36.5, 60.0, 78.9, 118.6, 130.4, 139.7, 153.6, 155.4, 167.0. Anal. Calcd for C₁₆H₂₇NO₄: C, 64.62; H, 9.15; N, 4.71. Found: C, 64.45; H, 9.04; N, 4.72. nOe (CDCl₃): 3.6% nOe from vinyl CH (5.74 ppm) to vinyl CH (5.99 ppm); 3.6% nOe from vinyl CH (5.99 ppm) to vinyl CH (5.74 ppm); and 2.6% nOe from vinyl CH (5.99 ppm) to CH₂ (2.13 ppm).



Compound 5-Z: Isolated in 67% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 7.50 (d, 2H, *J* = 7.3 Hz), 7.42 (s, 1H), 7.33 (m, 3H), 6.74 (d, 1H, *J* = 16.2 Hz), 5.98 (s, 1H), 5.37 (s, 1H), 4.42 (d, 2H, *J* = 6.4 Hz), 4.21 (q, 2H, *J* = 7.1 Hz), 1.44 (s, 9H), 1.32 (t, 3H, *J* = 7.1 Hz) ppm; ¹³C NMR δ 14.2, 28.3, 36.6, 60.2, 79.2, 120.6, 127.2, 128.5, 128.6, 128.7, 136.1, 136.3, 153.3, 155.6, 166.8. Anal. Calcd for C₁₂H₂₁NO₄: C, 68.86; H, 7.60; N, 4.23. Found: C, 68.90; H, 7.72; N, 4.17. nOe (CDCl₃): 4.7% nOe from vinyl CH (5.98 ppm) to vinyl CH doublet (6.74 ppm); 4.8% nOe from vinyl CH (6.74 ppm) doublet to vinyl CH (5.98 ppm) singlet; 4.8% nOe from vinyl CH (6.74 ppm) doublet to aromatic CH (7.50 ppm).



Compound 6-Z: Isolated in 67% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 7.28 (m, 5H), 5.64 (s, 1H), 5.27 (s, 1H), 4.14 (m, 4H), 3.59 (s, 2H), 1.46 (s, 9H), 1.27 (t, 3H *J* = 7.1 Hz) ppm; ¹³C NMR δ 14.1, 28.3, 40.5, 43.4, 60.0, 79.2, 119.0, 126.7, 128.5, 129.3, 137.1, 156.0, 159.3, 166.3. Anal. Calcd for C₁₂H₂₁NO₄: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.68; H, 8.11; N, 4.27. nOe (CDCl₃): 0.9% nOe from vinyl CH to aromatic CH; 2.4% nOe from vinyl CH to CH₂ (3.59 ppm); 1.3% nOe from CH₂ (3.59 ppm) to CH₂ doublet (4.14 ppm); 1.7% nOe from CH₂ (3.59 ppm) to vinyl CH; 1.9% noe from CH₂ singlet to aromatic CH.



Compound 7-Z: Isolated in 57% yield after SiO₂ chromatography from 5:1 (hexanes:EtOAc). ¹H NMR δ 7.48 (m, 2H), 7.34 (m, 3H), 6.21 (s, 1H), 5.2 (s, 1H), 4.42 (d, 2H, *J* = 5.2), 4.19 (q, 2H, *J* = 7.1 Hz), 1.43 (s, 9H), 1.30 (t, 3H, *J* = 7.1 Hz) ppm; ¹³C NMR δ 14.1, 28.3, 41.1, 60.4, 79.4, 88.1, 96.8, 122.0, 124.4, 128.3, 129.2, 132.0, 140.3, 155.7, 165.5. Anal. Calcd for C₁₉H₂₃NO₄: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.12; H, 7.17; N, 4.15.