Palladium-Catalyzed Amidation of Enol Triflates- A New Synthesis of Enamides

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Supplementary Material

All reactions were carried out under a nitrogen atmosphere. Solvents and reagents were used as purchased without purification or drying. The Xanphos ligand was prepared in-house, but is commercially available from Strem Chemicals, both sources of ligand gave the same results. Thin layer chromatography was performed on Merck KGaA silica gel $60F_{254}$ glass precoated plates (250 μm thickness) and visualized by shortwave light.

Melting points were determined on a MEL-TEMPII apparatus fitted with a Fluke 50S thermocouple and are uncorrected. Infrared absorption spectra were recorded as thin films on polyethylene card using a Nicolet Magna-IR spectrometer 550 or as a solid on a Nicolet Nexus-670 FTIR operating in Attenuated Total Reflectance mode. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX400 NMR. Mass spectrometry was performed on a Hewlett Packard Series 1100 MSD. HRMS were run on a Micromass Ultima API US QTof mass spectrometer using electrospray ionization in the positive ion mode. Elemental analyses were carried out by Qualitative Technologies Inc., Whitehouse, NJ or in-house.

All new compounds were characterized by ^{1}H and ^{13}C NMR, IR, MS and/or combustion analysis/HRMS.

Preparation of enol triflates.

Enol triflates **3**,[1] **4**,[2] **6**[3] and **7**[4] were prepared according to literature procedures.

Enol Triflate **1**

To a stirred, cooled (0 °C) suspension of potassium hydride (1.85 g of 30 wt%, 13.8 mmol) in THF (15.0 mL) was added 3-trifluoromethylphenylacetone (1.40 g, 6.94 mmol) which resulted in vigorous hydrogen evolution. After 30 minutes N-phenyltrifluoromethanesulfonamide (2.97 g, 8.33 mmol) was added and the resulting mixture warmed to room temperature over two hours and followed by T.L.C. On complete reaction MeO*t*Bu (20 mL) was added and the reaction quenched **cautiously** with ethanol (1.0 mL), then water (20 mL) and the layers separated. The aqueous layer was further extracted with MeO*t*Bu (20 mL) and the combined organics washed with water (20 mL), 10% sodium chloride solution (20 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give a 93:7 ratio of enol triflates. The major isomer was isolated by column chromatography (10% EtOAc in hexanes) to give **1** as a colourless oil (1.56 g, 68%). IR (film) 1690, 1418, 1334, 1213, 1141 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 6.20 (s, 1H), 2.31 (s, 3H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 146.2, 132.6, 132.0, 131.0 (q, *J* = 30.2 Hz), 129.1, 125.7 (q, *J* = 5.0 Hz), 125.0 (q, *J* = 5.0 Hz), 124.0 (q, *J* = 271 Hz), 119.0, 118.0 (q, *J* = 311 Hz), 20.7: LCMS No mass ions: Anal. Calcd for $C_{11}H_8F_6O_3S$: C, 39.53; H, 2.41. Found C, 39.80; H, 2.28.

Enol triflate **5**

To a solution of diphenylacetone (2.06 g, 9.81 mmol) in THF (25 mL) at 0 °C was added sodium hydride (785 mg, 60 wt% in mineral oil, 19.6 mmol) and the mixture stirred for 2 hours at the same temperature. $NPhTf_2$ was added and stirring was continued as the mixture warmed to room temperature and was then quenched cautiously with water (30 mL). The mixture was extracted with MeO*t*Bu (30 mL), the organics concentrated in vacuo and the crude oil purified by flash column chromatography (2% EtOAc in hexanes) to afford the desired enol triflate (2.50 g, 75%) as a colorless oil. IR (film) 1416, 1246, 1209 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 6H), 7.26 – 7.24

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[2] Lishultz, B. H.; Reuter, D. C; Ellsworth, E. L. *J. Org. Chem*. **1989**, *54*, 4975.

[3] McMurray, J. E.; Scott, W. J. *Tetrahedron Lett*. **1983**, 979.

[4] Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem*. **1986**, *51*, 277.

(m, 4H), 2.24 (s, 3H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.0, 138.3, 137.0, 135.6, 129.7, 129.6, 128.5, 128.2, 128.1, 119.7, 116.5: LCMS no peaks: Anal. Calcd for $C_{16}H_{13}F_3O_3S$: C, 56.14; H, 3.83. Found C, 56.53; H, 3.43.

Enol triflate **21**

Starting from 3-bromophenylacetone a similar procedure to that used for enol triflate **1** (NaH as base, THF, DMPU solvent) afforded a 97:3 mixture of isomers which were purified by column chromatography (hexanes to 5% EtOAc in hexanes) to give a 63% yield of enol triflate as a single isomer and 25% yield of the corresponding alkyne. IR (film) 1417, 1242, 1215 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 7.0 Hz, 1H), 6.10 (s, 1H), 2.29 (s, 3H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 145.9, 133.8, 131.8, 131.4, 130.1, 127.4, 122.6, 119.0, 117.5 (q, *J* = 322 Hz), 20.7: LCMS no peaks.

Coupling reaction: General Procedure

Preparation of Enamide 11

To a solution of enol triflate **3** (255 mg, 0.832 mmol) in dioxane (5.0 mL) at room temperature was added Cs_2CO_3 (379 mg, 1.16 mmol), trimethylacetamide (109 mg, 1.08 mmol), Xantphos (43.6 mg, 0.075 mmol) and $Pd_2(dba)_3$ (23.0 mg, 0.025 mmol). The mixture was de-gassed and stirred at 50 °C for nine hours after which time complete conversion was obtained. The mixture was filtered, concentrated and purified by flash column chromatography (toluene) to give the desired enamide (214 mg, 96%). MP = 92-94 °C: IR (solid) 2900, 1649, 1623, 1509 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.27 (tt, *J* = 7.9, 1.4 Hz, 1H) 7.19 (dd, *J* = 7.9, 1.4 Hz, 2H), 6.73 (s, 1H), 2.64 (m, 2H), 2.35 (m, 2H), 1.76 (m, 4H), 1.00 (s, 9H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.3, 140.8, 130.9, 128.6, 128.1, 127.0, 125.6, 39.0, 30.7, 27.6, 27.3, 22.8, 22.7: LCMS 258 (MH^+, 80), 174 (80), 157 (100): HRMS $C_{17}H_{23}NO$ (MH^+) theory 258.1858, measured 258.1851.

Coupling reaction: General Procedure for room temperature couplings

Preparation of Enamides 2a and 2b

To a solution of enol triflate **1** (110 mg, 0.329 mmol) in dioxane (2.0 mL) at room temperature was added Cs_2CO_3 (150 mg, 0.461 mmol), acetamide (23.0 mg, 0.395 mmol), Xantphos (17.0 mg, 0.0296 mmol) and $Pd_2(dba)_3$ (9.0 mg, 0.0099 mmol). The mixture was de-gassed stirred at room temperature for nine hours after which time 85% conversion to a 92:8 mixture of isomers was obtained. The mixture was filtered, concentrated and purified by flash column chromatography (EtOAc) to give the

desired enamide (59.8 mg, 75%) and minor isomer (6.0 mg, 7%). For characterization purposes, larger amounts of the minor isomer were obtained with a longer reaction time.

Major isomer **2a**

MP 93 -94 °C: IR ($CHCl_3$ soln) 3270, 1663, 1329, cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.47 – 7.44 (m, 3H), 6.98 (s, 1H), 5.78 (s, 1H), 2.28 (s, 3H), 2.00 (s, 3H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 168.6, 136.7, 135.7, 131.4, 131.1 (q, *J* = 30 Hz), 129.2, 125.0 (q, *J* = 10 Hz), 124.1(q, *J* = 272 Hz), 123.4 (q, *J* = 10 Hz), 114.0, 24.0, 21.7: LCMS 202 (100), 182 (20): Anal. Calcd for $C_{12}H_{12}F_3ON$: C, 59.26; H, 4.97; N, 5.76. Found: C, 59.30; H, 4.85; N, 5.61.

Minor Isomer **2b**

MP 79 - 80 °C: IR ($CHCl_3$ soln) 3293, 1672, 1340, 1329, 1125, cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 5H), 7.13 (s, 1H), 2.11 (s, 3H), 2.05 (s, 3H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 169.1, 138.0, 134.2, 132.1, 130.4 (q, *J* = 30 Hz), 128.5, 125.5 (q, *J* = 10 Hz), 124.0 (q, *J* = 272 Hz), 122.6 (q, *J* = 10 Hz), 114.5, 24.6, 17.8: LCMS 202 (100), 182 (10).

Enamide **8**

The general procedure for room temperature couplings was followed using enol triflate **1** (107 mg) and benzamide at room temperature for 8 hours, after which time the reaction had reached 85% conversion and gave a 89:11 ratio of enamide isomers. Major isomer: MP 137 - 138 °C: IR ($CHCl_3$ soln) 3270, 2920, 1640 cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.60 (s, 1H), 7.52 – 7.44 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 2H), 5.87 (s, 1H), 2.45 (s, 3H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.3, 136.7, 136.0, 134.3, 132.0, 131.5, 131.3 (q, *J* = 30 Hz), 129.4, 129.0, 127.0, 125.0 (q, *J* = 10 Hz), 124.1 (q, *J* = 272 Hz), 123.5 (q, *J* = 10 Hz), 113.8: LCMS 105 (100): Anal. Calcd for $C_{17}H_{14}F_3ON$: C, 66.90; H, 4.62; N, 4.59. Found: C, 66.74; H, 4.52; N, 4.50.

Enamide **9**

The general procedure was followed with enol triflate **3** (153 mg) and acetamide to afford a 88% yield of the enamide. MP add °C IR (film) add: ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 2H) 1H), 6.53 (s, 1H), 2.60 (m, 2H, 2.33 (m, 2H), 1.80 (s, 3H), 1.74 (m, 4H): ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 168.5, 140.9, 130.7, 128.7, 128.1, 127.0, 126.3, 30.9, 27.8, 23.8, 22.9, 22.8: LCMS 174 (100): Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.75; H, 7.96; N, 6.43.

Enamide **10**

The general procedure was followed with enol triflate **3** (255 mg) and benzamide to afford a 84% yield of the known enamide.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.43 (m, 1H), 7.41 – 7.29 (m, 5H), 7.28 – 7.25 (m, 3H), 2.81 (m, 2H), 2.40 (m, 2H), 1.82 – 1.79 (m, 4H).

Enamide **12**

The general procedure was followed with enol triflate **3** (255 mg) and 1-adamantancarboxamide to afford a 97% yield of the enamide. MP = 138 – 139 °C: IR (solid) 1638, 1514, 1489: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.3 Hz, 2H), 7.27 (tt, *J* = 7.3, 1.0 Hz, 1H), 7.19 (dd, *J* = 7.3, 1.0 Hz),2.64 (m, 2H), 2.36 (m, 2H), 1.94 (m, 4H), 1.72 (m, 3H), 1.70 -1.50 (m, 12H).^{13}C NMR (100.5 MHz, $CDCl_3$) δ 175.9, 140.9, 131.1, 128.7, 128.3, 127.1, 125.4, 41.2, 39.1, 36.5, 30.8, 28.1, 27.8, 22.9, 22.9: LCMS: 358 ($M + Na^+$)(30), 336 (MH^+)(100), 308 (15). HRMS $C_{24}H_{29}NO$ (MH^+) theory 336.2327, measured 336.2330: Anal. Calcd for $C_{23}H_{29}NO$: C, 82.34; H, 8.71; N, 4.18. Found: C, 82.16; H, 8.90; N, 4.18.

Enamide **13**

The general procedure was followed with enol triflate **4** (255 mg) and lactamide to afford an 89% yield of the enamide as a white solid. MP = 77 - 78 °C: IR (solid) 3220, 1633, 1589, 1489, 1464: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.05 (s, 1H), 4.24 (q, *J* = 6.8 Hz), 4.13 (q, *J* = 7.1 Hz, 2H), 3.08 (dd, *J* = 8.2, 7.2 Hz, 2H), 2.43 (m, 2H), 1.83 (qn, *J* = 7.8 Hz, 2H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 173.8, 167.3, 153.3, 109.0, 68.7, 60.5, 60.0, 33.9, 28.5, 21.0, 20.8, 14.3, 14.1: LCMS: 358 ($M + Na^+$)(30), 336 (MH^+)(100), 308 (15). HRMS $C_{11}H_{18}NO_4$ (MH^+) theory 228.1236, measured 228.1237.

Enamide **14**

The general procedure was followed with enol triflate **3** (250mg) and 2-pyrrolidinone to afford a 97% yield of the enamide as an oil. IR (film) 2930, 1687, 1409: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.25 (m, 2H), 7.19 – 7.17 (m, 3H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.37 (m, 2H), 2.27 (m, 2H), 2.19 (t, *J* = 7.8 Hz, 2H), 1.82 – 1.74 (m, 4H), 1.71 – 1.67 (m, 2H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 174.9, 141.0, 135.9, 131.7, 128.2, 127.3, 127.1, 48.3, 31.2, 30.9, 26.6, 22.7, 22.6, 19.0: LCMS 264 (M + Na)(20), 242 (MH+)(90), 157 (100). HRMS $C_{16}H_{19}N$ (MH^+) theory 242.1545, measured 242.1551.

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[5] (a) Bochu, C.; Couture, A.; Lablache-Combier, A. *Tetrahedon*, **1988**, *44*, 1959. (b) Jefford, C. W.; Jaber, A.; Boukouvalas, J. *Synthesis* **1988**, 391.

Enamide **15**

The general procedure was followed with enol triflate **5** (220 mg) and acetamide at 80 °C to afford a 76% yield of the enamide as an oil. IR (film) 3258, 3054, 3020, 2915, 2847, 1657, 1518, 1491: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.21 – 7.16 (m, 6H), 6.80 (s, 1H),2.26 (s, 3H), 1.90 (s, 3H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 168.7, 140.6, 140.2, 130.1, 130.0, 129.5, 128.8, 128.3, 128.1, 127.2, 126.7, 24.1, 17.8: LCMS 210 (100): Anal. Calcd for $C_{16}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 80.94; H, 6.84; N, 5.51.

Enamide **17**

The general procedure was followed with enol triflate **4** (253 mg) and benzamide using 1.4eq of KOtBu (1.0*M* in THF) as base in place of Cs_2CO_3 at 80 °C to afford a 47% yield of the known enamide[6] along with keto-ester resulting from hydrolysis of the enol triflate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.52 (t, *J* = 6.8 Hz, 1H), 7.45 (dd, *J* = 8.1, 6.8 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.31 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.93 (qn, *J* = 7.6 Hz, 2H),1.30 (t, *J* = 7.1 Hz, 3H).

Enamide **18**

The general procedure was followed with enol triflate **3** (256 mg) and *tert*-butylcarbamate to afford an 80% yield of the desired enamide. IR (film) 1731, 1483: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.25 (m, 1H), 7.20 (m, 2H), 5.90 (s, 1H), 2.61 – 2.59 (m, 2H), 2.35 – 2.32 (m, 2H), 1.79 – 1.64 (m, 4H), 1.38 (s, 9H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 153.5, 141.2, 130.0, 128.7, 128.3, 126.7, 123.4, 79.5, 31.0, 28.4, 27.6, 23.0, 22.9: LCMS 174 (20), 157 (100), 129 (20): HRMS $C_{17}H_{23}NO_2$ (MH^+) theory 274.1807, measured 274.1818.

Enamide **19**

The general procedure was followed with enol triflate **3** (179 mg) and benzycarbamate to afford a 95 % yield of the desired enamide. MP = 82 - 84 °C: IR (solid) 1692, 1664, 1505, 1488, 1452: ^{1}H (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 7H), 7.27 (t, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 7.1 Hz, 2H), 6.10 (s, 1H), 5.06 (s, 2H), 2.64(m, 2H), 2.33 (m, 2H), 1.81 – 1.73 (m, 4H): ^{13}C NMR

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[6] (a) Connors, T. A.; Ross, W. C. J. *Journal of the Chemical Society, Abstracts*, **1960**, 2119. (b) Takao, T.; Yoshimoto, H.; Imoto, E. *Bull. Chem. Soc. Jpn*. **1967**, *40*, 2844.

(100.5 MHz, $CDCl_3$) δ 153.7, 140.7, 136.5, 129.5, 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 126.9, 66.5, 31.0, 27.2, 22.8, 22.7: LCMS 264 (100), 147 (60), 169 (50): HRMS $C_{20}H_{22}NO_2$ (MH^+) theory 308.1650, measured 308.1655.

Enamide **20**.

The general procedure was followed with enol triflate **4** (251 mg) and p-toluenesulfonamide to afford an 87 % yield of the desired enamide. MP = 72 – 74 °C. IR (solid) 1658, 1619, 1596: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.79 (qn, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 167.5, 152.6, 144.1, 137.8, 129.9, 127.1, 107.6, 60.1, 32.5, 28.7, 21.6, 20.6, 14.4: LCMS 264 (MH^+ - EtOH, 30), 236 (20), 155 (100), 119(30): HRMS $C_{15}H_{19}NO_4S$ (MH^+) theory 310.1113, measured 310.1109: Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.23; H, 6.19; N, 4.53.

Coupling of enol triflate 3 with 2-bromobenzamide

The general procedure was followed with enol triflate **3** (256 mg) and 2-bromobenzamide to afford an 88 % yield of the desired enamide.

MP = 109 - 111 °C. IR (solid) 1637, 1512, 1489: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.20 (m, 8H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.99 (s, 1H), 2.88 (m, 2H), 2.39 (m, 2H), 1.84 – 1.78 (m, 4H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 165.6, 140.6, 138.1, 133.3, 131.0, 130.2, 129.1, 128.7, 128.2, 128.1, 127.4, 127.2, 119.2, 32.9, 27.7, 22.8, 22.7: LCMS 378, 380 ($M + Na^+$)(10), 356, 358 (MH^+)(10), 200, 202 (80), 182, 184 (90), 157 (100): HRMS $C_{19}H_{18}NOBr^{79}$ (MH^+) theory 356.0650, measured 356.0641.

Coupling of enol triflate 4 with 2-bromobenzamide

The general procedure was followed with enol triflate **4** (254 mg) and 2-bromobenzamide to afford a 95 % yield of the desired enamide as a viscous oil.

IR (film) 1664, 1620, 1588, 1477: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (s, 1H), 7.63 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.38 (td, *J* = 7.8, 1.1 Hz, 1H), 7.31 (td, *J* = 7.8, 1.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.33 (br t, *J* = 7.6 Hz, 2H), 2.56 (m, 2H), 1.96 (qn, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 167.6, 165.4, 154.1, 137.4, 133.8, 131.7, 129.2, 127.6, 119.7, 109.3, 60.0, 34.2, 28.5, 21.1, 14.3: LCMS 297, 295 (MH^+ - EtOH)(20), 183, 185 (100).

Coupling of enol triflate 21 with acetamide

The general procedure was followed with enol triflate **21** (210 mg) and acetamide at room temperature to afford an 83 % yield of the desired enamide as a viscous oil.

IR (film) 1638, 1589, 1514, 1490: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.33 (dt, *J* = 6.8, 1.9 Hz, 1H), 7.18 – 7.10 (m, 3H), 5.65 (s, 1H), 2.27 (s, 3H), 2.02 (s, 3H): ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 168.7, 138.0, 135.4, 131.2, 129.7, 126.7, 122.9, 113.8, 24.1, 22.7: LCMS 212, 214 (100): HRMS $C_{11}H_{13}NOBr^{79}$ (MH^+) theory 254.0181, measured 254.0190.