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 60F₂₅₄ glass precoated plates (250 μ m thickness) and visualized by shortwave light.

Melting points were determined on a MEL-TEMP II 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. ¹H and ¹³C 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 ¹H and ¹³C 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 MeOtBu (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 MeOtBu (20 mL) and the combined organics washed with water (20 mL), 10% sodium chloride solution (20 mL), dried over MgSO₄ 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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.6 MHz, CDCl₃) 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 C₁₁H₈F₆O₃S: 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. NPhTf₂ 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 MeOtBu (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: ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.33 (m, 6H), 7.26 – 7.24

¹ Rigby, J. H.; Qabar, M. *J. Am. Chem. Soc.* **1991**, *113*, 8975.

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 $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}_3\text{S}$: 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} : ^1H 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 $\text{Pd}_2(\text{dba})_3$ (23.0 mg, 0.025 mmol). The mixture was de-gassed and stirred at 50 $^\circ\text{C}$ 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 $^\circ\text{C}$: IR (solid) 2900, 1649, 1623, 1509 cm^{-1} : ^1H 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 $\text{C}_{17}\text{H}_{23}\text{NO}$ (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 $\text{Pd}_2(\text{dba})_3$ (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 (CHCl₃ soln) 3270, 1663, 1329, cm⁻¹: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.6 MHz, CDCl₃) 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 C₁₂H₁₂F₃ON: 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 (CHCl₃ soln) 3293, 1672, 1340, 1329, 1125, cm⁻¹: ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.32 (m, 5H), 7.13 (s, 1H), 2.11 (s, 3H), 2.05 (s, 3H): ¹³C NMR (100.6 MHz, CDCl₃) 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 (CHCl₃ soln) 3270, 2920, 1640 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.6 MHz, CDCl₃) 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 C₁₇H₁₄F₃ON: 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, CDCl₃) 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), 6.53 (s, 1H), 2.60 (m, 2H), 2.33 (m, 2H), 1.80 (s, 3H), 1.74 (m, 4H): ¹³C NMR (100.6 MHz, CDCl₃) 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 C₁₄H₁₇NO: 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 ¹H NMR (400 MHz, CDCl₃) 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: ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100.5 MHz, CDCl₃) 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 C₂₄H₂₉NO (MH⁺) theory 336.2327, measured 336.2330: Anal. Calcd for C₂₃H₂₉NO: 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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.5 MHz, CDCl₃) 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 C₁₁H₁₈NO₄ (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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.5 MHz, CDCl₃) 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 C₁₆H₁₉N (MH⁺) theory 242.1545, measured 242.1551.

⁵ (a) Bochu, C.; Couture, A.; Lablache-Combier, A. *Tetrahedron*, **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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.5 MHz, CDCl₃) 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 C₁₆H₁₇NO: 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 (1.0M in THF) as base in place of Cs₂CO₃ at 80 °C to afford a 47% yield of the known enamide⁶ along with keto-ester resulting from hydrolysis of the enol triflate. ¹H NMR (400 MHz, CDCl₃) 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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.5 MHz, CDCl₃) 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 C₁₇H₂₃NO₂ (MH⁺) theory 274.1807, measured 274.1818.

Enamide 19

The general procedure was followed with enol triflate **3** (179 mg) and benzylcarbamate to afford a 95 % yield of the desired enamide. MP = 82 - 84 °C: IR (solid) 1692, 1664, 1505, 1488, 1452: ¹H (400 MHz, CDCl₃) δ ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR

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, CDCl₃) 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 C₂₀H₂₂NO₂ (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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.5 MHz, CDCl₃) 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 C₁₅H₁₉NO₄S (MH⁺) theory 310.1113, measured 310.1109: Anal. Calcd for C₁₅H₁₉NO₄S: 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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.5 MHz, CDCl₃) 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 C₁₉H₁₈NOBr⁷⁹ (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: ¹H NMR (400 MHz, CDCl₃) 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): ¹³C NMR (100.5 MHz, CDCl₃) 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: ^1H 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 $\text{C}_{11}\text{H}_{13}\text{NOBr}^{79}$ (MH^+) theory 254.0181, measured 254.0190.