SUPPORTING INFORMATION

Synthesis of 3-Substituted Quinolines via Transition Metal-Catalyzed Reductive Cyclization of *o*-Nitro Baylis-Hillman Acetates

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General Experimental.

All reactions were conducted in oven dried glassware using freshly distilled solvents under an atmosphere of nitrogen with magnetic stirring, unless otherwise noted. High pressure reactions were carried out in stainless steel reaction vessels or in thick glass (Fisher-Porter) bottles. TLC was performed using silica gel with fluorescent indicator. Flash chromatography was performed with silica gel 230-400 mesh. ^1H and ^{13}C NMR spectra were recorded at 300 MHz. Compounds **2a**,¹ $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2$,² $[(\text{C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\text{Ru}_2(\text{CO})_4$,³ $(\text{Cp})_2\text{Fe}_2(\text{CO})_2(\text{dppe})$,⁴ and $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ ⁵ were prepared according to literature procedures and gave satisfactory spectroscopic data.

Methyl 2-[hydroxymethyl-(2-nitrophenyl)]acrylate (**1a**)

2-Nitrobenzaldehyde (2.00 g, 13.2 mmol) was dissolved in methyl acrylate (20 mL), DABCO (1.48 g, 13.2 mmol) was added slowly over 5 min upon which the mixture became a dark orange-red. The mixture was stirred at room temperature for 5 days. The methyl acrylate was removed in vacuo, and the residue was dissolved in Et_2O , washed with 1M HCl (3 x 20 mL), and then with water (2 x 10 mL). The ether extract was concentrated on a rotary evaporator and then chromatographed over silica gel (Et_2O /hexanes, 1:1) to give **1a** ($R_f = 0.28$) as a straw colored oil (3.1 g, 99%), which crystallized from cold ether. mp 28-29 °C; IR (film) 3445, 2946, 1699, 1537 cm^{-1} ; ^1H NMR (300 MHz; d_6 -acetone) 3.64 (s, 3 H), 5.1 (br s, 1 H), 5.81 (d, $J = 1.2$ Hz, 1 H), 6.26

¹ Mason, P. I. H.; Emslie, N. D. *Tetrahedron* **1994**, 50, 12001.

² King, R. B.; Iqbal, M. Z.; King, A. D., Jr. *J. Organomet. Chem.* **1979**, 171, 53.

³ Ovchinnikov, M. V.; Angelici, R. J. *J. Am. Chem. Soc.* **2000**, 122, 6130.

⁴ Haines, R. J.; Du Preez, A. L. *J. Organomet. Chem.* **1970**, 21, 181.

⁵ Astruc, D.; Catheline, D. *Organometallics* **1984**, 3, 1094.

(m, 2 H), 7.52 (td, $J = 8.1$ Hz, 1.8 Hz, 1 H), 7.69 (td, $J = 7.8$ Hz, $J = 1.2$ Hz, 1 H), 7.76 (dd, $J = 7.8$ Hz, 1.8 Hz, 1 H), 7.9 (dd, $J = 8.1$ Hz, $J = 1.2$ Hz, 1 H); ^{13}C NMR (75.45 MHz; d_6 -acetone) 51.7, 66.4, 124.4, 124.6, 128.9, 129.2, 133.2, 137.3, 143.1, 148.8, 165.8; MS (EI) 220 ($\text{M}^+ - \text{OH}$, 10), 191 ($\text{M}^+ - \text{NO}_2$, 100), 160 (40), 132 (146), 117 (38), 117 (38), 104 (40), 77 (42), 51 (28); HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_5\text{Na}$ ($\text{M} + \text{Na}$) 260.0535; found: 260.0463.

Methyl 2-[hydroxymethyl-(6-nitro-1,3-benzodioxol-5-yl)]acrylate (1b)

2-Nitropiperonal (3.00 g, 15.4 mmol) was dissolved in methyl acrylate (20 mL), DABCO (1.72 g, 15.4 mmol) was added slowly over 5 min upon which the mixture became a dark orange-red. The mixture was stirred at room temperature for 7 days; after one day a yellow precipitate formed. After the above described workup, chromatography on silica gel using a gradient elution with Et_2O /hexanes (20% to 50% Et_2O) gave (4.10 g, 95 %) of compound **1b**. $R_f = 0.20$ (1:1, Et_2O /hexanes); mp 122-123.5 °C; IR (KBr) 3494, 1712, 1637, 1531, 1482, 1343, 1256, 1030, 879, 822 cm^{-1} ; ^1H NMR (300 MHz; CD_3CN) 3.71 (s, 3 H), 4.02 (br s, 1 H), 5.67 (d, $J = 0.9$ Hz, 1 H), 6.15 (m, 3 H), 7.17 (s, 1 H), 7.49 (s, 1 H); ^{13}C NMR (75.45 MHz; CD_3CN) 52.6, 67.3, 104.5, 105.7, 108.2, 125.5, 135.2, 142.2, 143.4, 148.2, 153.0, 166.8; MS (EI) 235 ($\text{M}^+ - \text{NO}_2$, 20), 221 (32), 204 (76), 188 (64), 176 (100), 160 (26), 148 (18), 135 (9), 120 (7), 104 (4), 77 (3), 53 (8); HRMS (ESI) calc. for $\text{C}_{12}\text{H}_{11}\text{NO}_7\text{Na}$ ($\text{M} + \text{Na}$) 304.0433; found: 304.0412; Anal. calcd for: C 51.25, H 3.94, N 4.98; found: C 51.25, H 3.99, N 4.86.

Methyl 2-[hydroxymethyl-(5-chloro-2-nitrophenyl)]acrylate (1c)

5-Chloro-2-nitrobenzaldehyde (1.00 g, 5.3 mmol), sold as a mixture from Aldrich of at least 77 % purity, was dissolved in 15 mL of methyl acrylate. DABCO (0.60 g, 5.4 mmol) was then added over 5 minutes after which the mixture darkened. The mixture was stirred at room temperature for 4 days, followed by the workup described for compound **1a**. Chromatography on silica gel with Et₂O/hexanes (gradient elution: 1:5 to 1:1) gave 1.0 g (93% yield based upon the purity of the starting material) of the Baylis-Hillman adduct **1c** as a yellow solid. *R*_f = 0.40 (1:1, Et₂O/hexanes); mp 63-65°C; IR (KBr) 3475, 1722, 1529, 1367, 1297 cm⁻¹; ¹H NMR (300 MHz; d₆-acetone) 3.69 (s, 3 H), 5.38 (d, *J* = 5.1 Hz, 1 H), 5.81 (d, *J* = 0.9 Hz, 1 H), 6.29 (m, 2 H), 7.59 (dd, *J* = 8.7 Hz, *J* = 2.4 Hz, 1 H), 7.79 (d, *J* = 2.4 Hz, 1 H), 8.0 (d, *J* = 8.7 Hz, 1 H); ¹³C NMR (75.45 MHz; d₆-acetone) 52.2, 66.8, 125.7, 127.0, 129.3, 129.6, 139.5, 140.5, 143.2, 147.5, 166.1; MS (EI) 254 (M⁺ -OH, 1), 227 (30), 225 (M⁺ -NO₂, 100), 194 (20), 166 (15), 138 (6); HRMS (ESI) calcd. for C₁₁H₁₀NO₅Na (M⁺ Na) 294.0145; found: 294.0103.

Methyl 2-[hydroxymethyl-(4,5-dimethoxy-2-nitrophenyl)]acrylate (1d)

DABCO (1.78 g, 11.8 mmol) was added to a stirred solution of technical grade (80%) 6-nitro veratraldehyde (2.5 g, 11.8 mmol) in methyl acrylate (15 mL). After stirring for 10 days at room temperature, methyl acrylate was removed *in vacuo* and the straw colored oil taken up in Et₂O (40 mL). The ethereal solution was washed sequentially with 1M HCl (3 x 20 mL) and water (2 x 10 mL). The ether extract was dried with MgSO₄ and concentrated. The residue was dissolved in a minimal amount of hot toluene and allowed to stand at -10°C over night. The solution containing a white solid was filtered and washed with cold hexanes to give (1.85 g, 66%) of the Baylis-

Hillman adduct **1d**. mp 80-81 °C; IR (KBr) 3336 (br), 1720 (s), 1521, 1267, 1066 cm⁻¹; ¹H NMR (300 MHz; d₆-acetone) 3.69 (s, 3 H), 3.91 (s, 3 H), 3.92 (s, 3 H), 5.09 (br s, 1 H), 5.58 (s, 1 H), 6.15 (s, 1 H), 6.34 (s, 1 H), 7.35 (s, 1 H), 7.58 (s, 1 H); ¹³C NMR (75.45 MHz; d₆-acetone) 52.0, 56.4, 67.1, 108.4, 110.9, 124.5, 133.0, 140.7, 144.0, 148.7, 153.9, 166.4; MS (EI) 297 (M⁺, 10), 280 (98), 270 (40), 220 (45), 192 (100), 176 (60), 164 (42), 136 (36); Anal. calcd for C₁₃N₁₅NO₇: C 52.53; H 5.09; N 4.71; found C 52.77; H 5.10; N 4.64.

Methyl 2-[hydroxymethyl-(1-nitro-2-naphthyl)]acrylate (1e**)**

1-Nitro-2-naphthaldehyde (1.23 g, 6.1 mmol) was dissolved in methyl acrylate (15 mL), DABCO (523 mg, 4.97 mmol) was added and the mixture was stirred for 5 days at room temperature. The methyl acrylate was removed *in vacuo*, and the residue was taken up in Et₂O (35 mL) and washed with 1M HCl (3 x 20 mL) and water (2 x 10 mL). The solution was dried with MgSO₄ concentrated and the residue was redissolved in a minimal amount of hot Et₂O and placed in a -10°C freezer overnight. The beige crystals were filtered to give (1.38g, 78%) of the Baylis Hillman adduct **1e**. mp 135-137 °C; IR (KBr) 3475, 1707, 1529, 1297 cm⁻¹; ¹H NMR (300 MHz; CD₃CN) 3.59 (s, 3 H), 4.20 (d, J = 4.5 Hz, 1 H), 5.78 (d, J = 3.9 Hz, 1 H), 6.05 (dd, J = 1.5 Hz, J = 0.9 Hz, 1 H), 7.56 (d, J = 8.7 Hz, 1 H), 7.61-7.77 (m, 3 H), 7.99 (dd, J = 2.1 Hz, J = 7.2 Hz, 1 H), 8.06 (d, J = 8.7 Hz, 1 H); ¹³C NMR (75.45 MHz; CD₃CN) 52.5, 67.9, 122.3, 124.8, 125.2, 126.7, 128.6, 129.0, 129.8, 131.9, 132.0, 134.1, 142.3, 166.3. MS (EI) 270 (M⁺-OH, 35), 241 (100), 209 (20), 181 (18), 152 (10); HRMS (ESI) Calcd for C₁₅H₁₃NO₅Na (M + Na) 310.0691, found 310.0637.

2-[Hydroxymethyl-(2-nitrophenyl)]acrylonitrile (**1f**)

2-nitrobenzaldehyde (2.0 g, 13.2 mmol) was dissolved in acrylonitrile (15 mL) and DABCO (1.48 g, 13.2 mmol) was added. After stirring at room temperature for 3 days, the acrylonitrile was removed *in vacuo*. The dark residue was dissolved in Et₂O (40 mL) and washed with 1M HCl (3 x 20 mL) and water (2 x 10 mL). The Et₂O extract was concentrated and chromatographed on SiO₂ with Et₂O/Hexanes (2 : 3) to give one main product of R_f = 0.20 as a yellow oil (693 mg, 26%) which was the Baylis-Hillman adduct **1f**. IR (CH₂Cl₂) 3054, 2986, 2306, 1530, 1422, 1263 cm⁻¹; ¹H NMR (300 MHz; d₆-acetone) 5.8 (br s, 1 H), 6.07 (s, 1 H), 6.09 (d, J = 0.9 Hz, 1 H), 6.15 (d, J = 0.9 Hz), 7.61 – 7.68 (m, 1 H), 7.84 (m, 1 H), 7.98 (dd, J = 1.2 Hz, J = 8.1 Hz, 1 H), 8.03 (dd, J = 1.2 Hz, J = 8.1 Hz); ¹³C NMR (75.45 MHz; d₆-acetone) 69.2, 117.4, 125.1, 126.3, 129.4, 130.1, 131.8, 134.3, 135.7, 148.7; HRMS (ESI) Anal. Calcd for C₁₀H₈N₂O₃Na (M + Na) 227.0433, found 227.0456.

Cmpd 1e

Cmpd 2d

STANDARD 1H OBSERVE

Data Collected on: cmmr3.chem.ou.edu-mercury300
 Archive directory: /export/home/knn/vnmr3sys/data
 Sample directory:
 File: PROTON

Pulse Sequence: zgpg30
 Solvent: Acetone

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 4.000 sec
 Width 4803.1 Hz

8 repetitions
 OBSERVE F1, 300.0701287 MHz
 DATA PROCESSING
 FT size 65536
 Total time 0 min

Cmpd 2e

Cmpd 2f