European Journal of Organic Chemistry

Supporting Information

ZnBr₂ Mediated C—N Bond Formation using Cinnamyl Alcohol and 2-Amino Pyridines

Ahwan Panigrahi, Mahadev Sharanappa Sherikar, and Kandikere Ramaiah Prabhu*

Table of contents

S.No	Title	Page No.
1	General experimental	S-3
2	Typical experimental procedure	S-3
3	Scale up experimental procedure	S-3
4	Characterization data for products	S-4
5	Crystal structure of product 3aa	S-10
6	Crystal data of Product 3aa	S-10
7	^1H and ^{13}C spectra of products	S-21

General experimental

NMR spectra were recorded on a 400 MHz spectrometer in CDCl₃. Tetramethylsilane (TMS; δ = 0.00 ppm) for ¹H NMR in CDCl₃ has served as an internal standard. The solvent signal (CDCl₃, δ = 77.00 ppm) was used as an internal standard for ¹³C NMR. IR spectra were measured using an FT-IR spectrometer. Mass spectra were obtained with a Q-TOF Mass Spectrometer (HRMS). Flash column chromatography was carried out by packing glass columns with commercial silica gel 230-400 mesh (commercial suppliers), and thin-layer chromatography was carried out using silica gel GF-254. All substituted cinnamyl alcohol derivatives were prepared using the reported literature procedure. Cinnamyl alcohol was purchased from Sigma. 2-Amino pyridine derivatives were purchased from local suppliers. 2-Amino pyrimidine and ZnBr₂ were purchased from Alfa Aesar. Other solvents used for workup and chromatographic procedures were purchased from commercial suppliers and used without further purification.

Typical experimental procedure:

Alcohol derivative **1** (0.33 mmol, as 1 equiv), 2-amino pyridine derivative **2** (0.39 mmol, 1.2 equiv) were added in DCE (1.5 mL) in an 8-mL screw-cap reaction vial, and the reaction mixture was stirred at rt for 5 min. or until the reaction mixture becomes homogeneous, followed by ZnBr₂ (0.33 mmol) addition and the reaction mixture was heated at 100 °C for 1-24h. The completion of the reaction has been monitored by TLC. After completion of the reaction, added water (5 mL) and extracted with DCM (3 x 10 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified on a silica gel column using EtOAc/petroleum ether to get pure products.

Scale-up reaction:

Alcohol derivative **1a** (1.050 gm, 7.09 mmol, as 1 equiv), 2-amino pyridine derivative **2a** (8.51 mmol, 1.2 equiv) were added in DCE (30 mL) into a 2-necked 100 mL round bottom flask, and the reaction mixture was stirred at rt for 10 min. or until the reaction mixture becomes homogeneous, followed by ZnBr₂ (7.09 mmol, 1 equiv) addition and the reaction was refluxed at 100 °C for 3h followed by TLC. After the completion of the reaction, added water (15 mL) and extracted with DCM (3 x 30 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified on a silica gel column using EtOAc/petroleum ether to get pure product **3aa** (1.580 gm, 99%).

Characterization data for the products:

- 1) **(E)-N-(4-Phenylbut-3-en-2-yl)pyridin-2-amine (3aa)**. Colorless solid; **Yield** – (73.5 mg, 99%); **mp**: 75-78 °C; **R_f** (30% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm⁻¹): 1601, 3249; **¹H NMR** (400 MHz, CDCl₃): δ 1.41 (d, *J* = 6.68 Hz, 3 H), 4.41 (q, *J* = 6.45 Hz, 1 H), 4.74 (d, *J* = 6.38 Hz, 1 H), 6.22 (dd, *J* = 15.99, 5.69 Hz, 1 H), 6.40 (d, *J* = 8.35 Hz, 1 H), 6.55 (m, 2 H), 7.20 (t, *J* = 7.17 Hz, 1 H), 7.28 (t, *J* = 7.55 Hz, 2 H), 7.34 (d, *J* = 7.42 Hz, 2 H), 7.39 (m, 1 H), 8.08 (d, *J* = 4.10 Hz, 1 H), **¹³C NMR** (100 MHz, CDCl₃): δ 21.8, 49.2, 107.0, 113.0, 126.4, 127.5, 128.6, 129.3, 132.5, 136.9, 137.6, 148.2, 158.2; **HRESI-MS** (m/z): Calculated for C₁₅H₁₇N₂ (M + H)⁺: 225.1392, found (M + H)⁺: 225.1394.

- 2) **(E)-N-(4-Phenylbut-3-en-2-yl)pyrimidin-2-amine (3ab)**. Colorless oily; **Yield** – (47 mg, 63%); **R_f** (10% EtOAc/petroleum ether) 0.2; Prepared as shown in typical experimental procedure. **IR** (Neat, cm⁻¹): 1590, 3258; **¹H NMR** (400 MHz, CDCl₃): δ 1.41 (d, *J* = 6.76 Hz, 3 H), 4.84 (m, 1 H), 5.58 (d, *J* = 8.08 Hz, 1 H), 6.28 (dd, *J* = 16.04, 5.43 Hz, 1 H), 6.50 (t, *J* = 4.79 Hz, 1 H), 6.57 (dd, *J* = 15.98, 0.99 Hz, 1 H), 7.20 (t, *J* = 7.14 Hz, 1 H), 7.28 (t, *J* = 7.71 Hz, 2 H), 7.34 (d, *J* = 7.33 Hz, 2 H), 8.27 (d, *J* = 4.63 Hz, 2 H), **¹³C NMR** (100 MHz, CDCl₃): δ 21.1, 48.0, 110.6, 126.3, 127.3, 128.4, 128.9, 131.8, 136.9, 158.0, 1.61.6; **HRESI-MS** (m/z): Calculated for C₁₄H₁₆N₃ (M + H)⁺: 226.1344, found (M + H)⁺: 226.1344.

- 3) **(E)-N-(4-Phenylbut-3-en-2-yl)pyrazin-2-amine (3ac)**. Pale yellow oily; **Yield** – (25 mg, 33%); **R_f** (30% EtOAc/petroleum ether) 0.4; Prepared as shown in typical experimental procedure. **IR** (Neat, cm⁻¹): 1588, 3264; **¹H NMR** (400 MHz, CDCl₃): δ 1.43 (d, *J* = 6.73 Hz, 3 H), 4.58 (m, 1 H), 4.90 (d, *J* = 6.94 Hz, 1 H), 6.21 (dd, *J* = 15.99, 5.83 Hz, 1 H), 6.56 (d, *J* = 16.65 Hz, 1 H), 7.21 (t, *J* = 7.20 Hz, 1 H), 7.29 (t, *J* = 7.76 Hz, 2 H), 7.34 (d, *J* = 7.39 Hz, 2 H), 7.79 (d, *J* = 2.71 Hz, 1 H), 7.90 (s, 1 H), 7.98 (m, 1 H), **¹³C NMR** (100 MHz, CDCl₃): δ 21.2, 48.4, 126.2, 127.5, 128.4, 129.6, 131.3, 131.9, 132.8, 136.5, 141.9, 153.8. **HRESI-MS** (m/z): Calculated for C₁₄H₁₆N₃ (M + H)⁺: 226.1344, found (M + H)⁺: 226.1340.

- 4) **(E)-5-Chloro-N-(4-phenylbut-3-en-2-yl)pyridin-2-amine (3ad)**. Colorless solid; **Yield** – (80 mg, 94%); **mp**: 84-88 °C; **R_f** (10% EtOAc/petroleum ether) 0.4; Prepared as shown in typical experimental procedure. **IR** (Neat, cm⁻¹): 1595, 3690; **¹H NMR** (400 MHz, CDCl₃): δ 1.39 (d, *J* = 6.66 Hz, 3 H), 4.36 (m, 1 H), 4.85 (d, *J* = 6.83 Hz, 1 H), 6.17 (dd, *J* = 15.99, 5.79 Hz, 1 H), 6.33 (d, *J* = 8.81 Hz, 1 H), 6.52 (d, *J* = 15.99 Hz, 1 H), 7.20 (t, *J* = 7.18 Hz, 1 H), 7.28 (t, *J* = 7.88 Hz, 2 H), 7.32 (m, 3 H), 8.02 (d, *J*

= 2.44 Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 49.4, 107.7, 119.7, 126.3, 127.5, 128.5, 129.5, 131.8, 136.6, 137.2, 146.4, 156.4 **HRESI-MS** (mz): Calculated for $\text{C}_{15}\text{H}_{16}\text{ClN}_2$ ($\text{M} + \text{H}$) $^+$: 259.1002, found ($\text{M} + \text{H}$) $^+$: 259.1001.

5) **(E)-5-Bromo-4-methyl-N-(4-phenylbut-3-en-2-yl)pyridin-2-amine (3ae)** Colorless solid;

Yield – (97 mg, 93%); **mp**: 100-104 °C; **R_f** (10% EtOAc/petroleum ether) 0.4; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1599, 3692; ^1H NMR (400 MHz, CDCl_3): δ 1.38 (d, J = 6.68 Hz, 3 H), 2.23 (s, 3 H), 4.37 (m, 1 H), 4.76 (d, J = 7.25 Hz, 1 H), 6.19 (dd, J = 15.94, 5.50 Hz, 1 H), 6.27 (s, 1 H), 6.52 (d, J = 15.94 Hz, 1 H), 7.20 (t, J = 7.11 Hz, 1 H), 7.27 (t, J = 7.80 Hz, 2 H), 7.33 (d, J = 7.45 Hz, 2 H), 8.08 (s, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 22.5, 49.2, 108.6, 110.5, 126.3, 127.4, 128.5, 129.3, 132.0, 136.7, 147.6, 149.0, 157.2 **HRESI-MS** (mz): Calculated for $\text{C}_{16}\text{H}_{18}\text{BrN}_2$ ($\text{M} + \text{H}$) $^+$: 317.0653, found ($\text{M} + \text{H}$) $^+$: 317.0654.

6) **(E)-N-(4-(o-Tolyl)but-3-en-2-yl)pyridin-2-amine (4ba)** yellow oily; **Yield** – (67 mg,

85%); **R_f** (30% EtOAc/petroleum ether) 0.6; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1601, 3246; ^1H NMR (400 MHz, CDCl_3): δ 1.43 (d, J = 6.75 Hz, 3 H), 2.26 (s, 3 H), 4.41 (m, 1 H), 4.75 (d, J = 6.45 Hz, 1 H), 6.06 (dd, J = 15.86, 5.82 Hz, 1 H), 6.42 (d, J = 8.46 Hz, 1 H), 6.56 (m, 1 H), 6.76 (dd, J = 15.77, 0.91 Hz), 7.12 (m, 3 H), 7.40 (m, 2 H), 8.08 (dd, J = 5.01, 1.04 Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 19.7, 21.8, 49.5, 107.0, 113.0, 125.6, 126.0, 127.3, 130.2, 133.7, 135.3, 136.0, 137.5, 148.1, 158.1; **HRESI-MS** (mz): Calculated for $\text{C}_{16}\text{H}_{19}\text{N}_2$ ($\text{M} + \text{H}$) $^+$: 239.1548, found ($\text{M} + \text{H}$) $^+$: 239.1545.

7) **(E)-N-(4-(3-Methoxyphenyl)but-3-en-2-yl)pyridin-2-amine (4ca)** Colorless liquid; **Yield**

– (50 mg, 60%); **R_f** (20% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1601; ^1H NMR (400 MHz, CDCl_3): δ 1.42 (d, J = 6.77 Hz, 3 H), 3.79 (s, 3 H), 4.42 (m, 1 H), 4.71 (d, J = 6.90 Hz, 1 H), 6.22 (dd, J = 15.90, 5.61 Hz, 1 H), 6.41 (d, J = 8.40 Hz, 1 H), 6.56 (m, 2 H), 6.77 (dd, J = 8.19, 2.01 Hz, 1 H), 6.88 (d, J = 2.03 Hz, 1 H), 6.94 (d, J = 7.68 Hz, 1 H), 7.20 (t, J = 7.89 Hz, 1 H), 7.40 (m, 1 H), 8.08 (dd, J = 4.98, 1.04 Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.7, 49.2, 55.2, 106.9, 111.6, 113.0, 113.1, 119.0, 129.1, 129.5, 132.7, 137.5, 138.3, 148.1, 158.0, 159.8, **HRESI-MS** (mz): Calculated for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}$ ($\text{M} + \text{H}$) $^+$: 255.1497, found ($\text{M} + \text{H}$) $^+$: 255.1495.

8) **(E)-N-(4-(p-Tolyl)but-3-en-2-yl)pyridin-2-amine (4da)**

Yellow oily; **Yield** – (70 mg, 89%); **R_f** (30% EtOAc/petroleum ether) 0.8; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1600, 3295; ^1H NMR (400 MHz, CDCl_3): δ 1.40 (d, J = 6.68 Hz, 3 H), 2.30 (s, 3 H), 4.39 (q, J = 6.26 Hz, 1 H), 4.74 (d, J = 5.63 Hz, 1

H), 6.16 (dd, $J = 15.96, 5.74$ Hz, 1 H), 6.39 (d, $J = 8.57$ Hz, 1 H), 6.54 (m, 2 H), 7.09 (d, $J = 7.95$ Hz, 2 H), 7.23 (d, $J = 7.83$ Hz, 2 H), 7.38 (m, 1 H), 8.08 (dd, $J = 4.78, 0.79$ Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.1, 21.8, 49.2, 106.9, 112.9, 126.2, 129.1, 129.2, 131.3, 134.1, 137.2, 137.5, 148.1, 158.1, **HRESI-MS** (m/z): Calculated for $\text{C}_{16}\text{H}_{19}\text{N}_2$ ($\text{M} + \text{H}$) $^+$: 239.1548, found ($\text{M} + \text{H}$) $^+$: 239.1548.

- 9) ***N*-Cinnamylpyridin-2-amine (4ea)** Light yellow solid; **Yield** – (42 mg, 60%); **mp**: 76-80 °C; **R_f** (30% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1601, 3311; ^1H NMR (400 MHz, CDCl_3): δ 4.09 (t, $J = 5.32$ Hz, 3 H), 4.79 (s, 1 H), 6.30 (dt, $J = 15.87, 5.73$ Hz, 1 H), 6.42 (d, $J = 8.38$ Hz, 1 H), 6.58 (m, 2 H), 7.21 (t, $J = 7.27$ Hz, 1 H), 7.27 (t, $J = 7.94$ Hz, 2 H), 7.35 (d, $J = 7.50$ Hz, 2 H), 7.41 (m, 1 H), 8.10 (d, $J = 4.94$ Hz, 0.92 H), ^{13}C NMR (100 MHz, CDCl_3): δ 44.2, 106.9, 113.1, 126.3, 126.6, 127.5, 128.5, 131.3, 136.8, 137.5, 148.1, 158.6; **HRESI-MS** (m/z): Calculated for $\text{C}_{14}\text{H}_{15}\text{N}_2$ ($\text{M} + \text{H}$) $^+$: 211.1235, found ($\text{M} + \text{H}$) $^+$: 211.1232.

- 10) ***(E)*-N-(4-(Naphthalen-2-yl)but-3-en-2-yl)pyridin-2-amine (4fa)** Colourless liquid; **Yield** – (54mg, 60%); **R_f** (20% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1600; ^1H NMR (400 MHz, CDCl_3): δ 1.51 (d, $J = 6.72$ Hz, 3 H), 4.54 (q, $J = 5.93$ Hz, 1 H), 4.88 (s, 1 H), 6.25 (dd, $J = 15.70, 5.70$ Hz, 1 H), 6.50 (d, $J = 8.42$ Hz, 1 H), 6.60 (m, 1 H), 7.33 (d, $J = 15.70$ Hz, 1 H), 7.40-7.48 (m, 4 H), 7.55 (d, $J = 7.06$ Hz, 1 H), 7.76 (d, $J = 8.12$ Hz, 1 H), 7.83 (m, 1 H), 8.02 (m, 1 H), 8.13 (d, $J = 4.18$ Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.8, 49.5, 107.1, 113.1, 123.80, 123.84, 125.5, 125.7, 125.9, 126.7, 127.7, 128.4, 131.2, 133.6, 134.7, 135.6, 137.6, 148.1, 158.1 **HRESI-MS** (m/z): Calculated for $\text{C}_{19}\text{H}_{19}\text{N}_2$ ($\text{M} + \text{H}$) $^+$: 275.1548, found ($\text{M} + \text{H}$) $^+$: 275.1548.

- 11) ***N*-((3*E*,5*E*)-6-Phenylhexa-3,5-dien-2-yl)pyridin-2-amine (4ga)** Yellow oily; **Yield** – (57 mg, 69%); **R_f** (10% EtOAc/petroleum ether) 0.1; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1600, 3252; ^1H NMR (400 MHz, CDCl_3): δ 1.38 (d, $J = 6.75$ Hz, 3 H), 4.36 (q, $J = 6.43$ Hz, 1 H), 4.70 (d, $J = 5.69$ Hz, 1 H), 5.84 (dd, $J = 15.27, 5.74$ Hz, 1 H), 6.34-6.41 (m, 1 H), 6.50 (d, $J = 15.65$ Hz, 1 H), 6.55-6.58 (m, 1 H), 6.75 (dd, $J = 10.60, 15.66$ Hz, 1 H), 7.20 (t, $J = 7.20$ Hz, 1 H), 7.29 (t, $J = 7.92$ Hz, 2 H), 7.35-7.43 (m, 3 H), 8.08 (d, $J = 4.69$ Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 48.9, 107.6, 112.9, 126.9, 127.4, 128.4, 128.5, 129.7, 132.0, 136.6, 137.2, 137.6, 148.0, 158.0; **HRESI-MS** (m/z): Calculated for $\text{C}_{17}\text{H}_{19}\text{N}_2$ ($\text{M} + \text{H}$) $^+$: 251.1548, found ($\text{M} + \text{H}$) $^+$: 251.1546.

- 12) ***(E)*-N-(4-(2-Chlorophenyl)but-3-en-2-yl)pyridin-2-amine (4ha)** Yellow oily; **Yield** – (76 mg, 89%); **R_f** (20% EtOAc/petroleum ether) 0.4; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1600; ^1H NMR (400 MHz, CDCl_3): δ 1.44 (d, $J = 6.71$ Hz, 3 H), 4.43-4.51 (m, 1 H),

4.72 (d, $J = 7.12$ Hz, 1 H), 6.19 (dd, $J = 15.94, 6.91$ Hz, 1 H), 6.44 (d, $J = 8.47$ Hz, 1 H), 6.57 (ddd, $J = 7.30, 5.09, 0.78$ Hz, 1 H), 6.95 (dd, $J = 16.01, 0.97$ Hz, 1 H), 7.12-7.20 (m, 2 H), 7.32 (dd, $J = 7.65, 1.53$ Hz, 1 H), 7.39-7.43 (m, 1 H), 7.48 (dd, $J = 7.57, 1.89$ Hz, 1 H), 8.08 (dd, $J = 5.03, 1.07$ Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 49.3, 107.0, 113.1, 125.8, 126.7, 126.8, 128.4, 129.6, 133.0, 135.0, 135.4, 137.5, 148.1, 157.9. **HRESI-MS** (m/z): Calculated for $\text{C}_{15}\text{H}_{16}\text{ClN}_2$ ($M + H$) $^+$: 259.1002, found ($M + H$) $^+$: 259.1000.

- 13) (E)-N-(4-(3-Bromophenyl)but-3-en-2-yl)pyridin-2-amine (4ia)** Yellow oily; **Yield** – (80 mg, 80%); **R_f** (30% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1599, 3252; ^1H NMR (400 MHz, CDCl_3): δ 1.41 (d, $J = 6.73$ Hz, 3 H), 3.79, 4.40-4.48 (m, 1 H), 4.69 (d, $J = 6.78$ Hz, 1 H), 6.23 (dd, $J = 15.93, 5.57$ Hz, 1 H), 6.38 (d, $J = 8.44$ Hz, 1 H), 6.48 (d, $J = 16.03$ Hz, 1 H), 6.55-6.58 (m, 1 H), 7.13 (t, $J = 7.83$ Hz, 1 H), 7.24 (d, $J = 7.83$ Hz, 1 H), 7.31-7.33 (m, 1 H), 7.38-7.42 (m, 1 H), 7.49 (s, 1 H), 8.08 (dd, $J = 4.93, 0.91$ Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 49.0, 107.0, 113.1, 122.7, 125.0, 127.8, 129.2, 130.0, 130.2, 134.1, 137.5, 139.1, 148.1, 157.9. **HRESI-MS** (m/z): Calculated for $\text{C}_{15}\text{H}_{16}\text{BrN}_2$ ($M + H$) $^+$: 303.0497, found ($M + H$) $^+$: 303.0493.

- 14) (E)-N-(4-(4-Chlorophenyl)but-3-en-2-yl)pyridin-2-amine (4ja)** Yellow oily; **Yield** – (80 mg, 94%); **R_f** (20% EtOAc/petroleum ether) 0.3; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1600; ^1H NMR (400 MHz, CDCl_3): δ 1.40 (d, $J = 6.75$ Hz, 3 H), 4.38-4.47 (m, 1 H), 4.71 (d, $J = 6.46$ Hz, 1 H), 6.20 (dd, $J = 15.91, 5.55$ Hz, 1 H), 6.38 (d, $J = 8.31$ Hz, 1 H), 6.50 (d, $J = 15.96$ Hz, 1 H), 6.54-6.57 (m, 1 H), 7.24 (s, 4 H), 7.37-7.41 (m, 1 H), 8.07 (d, $J = 4.65$ Hz, 1 H), ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 49.0, 107.0, 113.1, 127.5, 127.9, 128.6, 133.0, 133.1, 135.4, 137.5, 148.1, 158.0. **HRESI-MS** (m/z): Calculated for $\text{C}_{15}\text{H}_{16}\text{ClN}_2$ ($M + H$) $^+$: 259.1002, found ($M + H$) $^+$: 259.1004.

- 15) (E)-4-(3-(Pyridin-2-ylamino)but-1-en-1-yl)benzonitrile (4ka)** Colorless oily; **Yield** – (27.5 mg, 33%); **R_f** (30% EtOAc/petroleum ether) 0.4; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1618, 2225, 3300; ^1H NMR (400 MHz, CDCl_3): δ 1.47 (d, $J = 6.74$ Hz, 3 H), 4.32 (q, $J = 6.41$ Hz, 1 H), 6.31 (dd, $J = 15.93, 5.62$ Hz, 2 H), 6.49 (d, $J = 8.56$ Hz, 1 H), 6.57 (d, $J = 15.94$ Hz, 1 H), 6.62 (t, $J = 6.33$ Hz, 1 H), 7.39 (d, $J = 8.36$ Hz, 2 H), 7.50-7.55 (m, 3 H), 8.08-8.08 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 21.4, 49.9, 108.0, 110.8, 113.2, 118.8, 126.9, 128.2, 132.3, 135.3, 139.7, 141.0, 147.0, 157.7. **HRESI-MS** (m/z): Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_3$ ($M + H$) $^+$: 250.1344, found ($M + H$) $^+$: 250.1345.

- 16) (E)-N-(4-(4-Nitrophenyl)but-3-en-2-yl)pyridin-2-amine (4la)** Yellow oily; **Yield** – (50 mg, 56%); **R_f** (30% EtOAc/petroleum ether) 0.2; Prepared as shown in typical

experimental procedure. **IR** (Neat, cm^{-1}): 1599, 1515, 1342; **^1H NMR** (400 MHz, CDCl_3): δ 1.45 (d, $J = 6.75$ Hz, 3 H), 4.49-4.57 (m, 1 H), 4.66 (d, $J = 6.94$ Hz, 1 H), 6.39-6.47 (m, 2 H), 6.58-6.65 (m, 2 H), 7.40-7.44 (m, 1 H), 7.46 (d, $J = 8.78$ Hz, 2 H), 8.09 (dd, $J = 4.96, 0.91$ Hz, 1 H), 8.13-8.15 (m, 2 H). **^{13}C NMR** (100 MHz, CDCl_3): δ 21.4, 48.9, 107.1, 113.3, 123.9, 126.8, 127.1, 137.62, 137.64, 143.4, 146.8, 148.1, 157.7. **HRESI-MS** (m/z): Calculated for $\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2$ ($\text{M} + \text{H}^+$): 270.1243, found ($\text{M} + \text{H}^+$): 270.1240.

- 17) (E)-N-(1-Phenylpent-1-en-3-yl)pyridin-2-amine (4ma)** Yellow oily; **Yield** – (65 mg, 83%); **R_f** (10% EtOAc/petroleum ether) 0.2; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1600; **^1H NMR** (400 MHz, CDCl_3): δ 1.02 (t, $J = 7.45$ Hz, 3 H), 1.74 (quartet, $J = 7.19$ Hz, 2 H), 4.14 (t, $J = 6.08$ Hz, 1 H), 4.97 (s, 1 H), 6.14 (dd, $J = 15.91, 6.30$ Hz, 1 H), 6.40 (d, $J = 8.41$ Hz, 1 H), 6.53-6.58 (m, 2 H), 7.18-7.21 (m, 1 H), 7.24-7.30 (m, 2 H), 7.33-7.41 (m, 3 H), 8.05 (d, $J = 4.88$ Hz, 1 H). **^{13}C NMR** (100 MHz, CDCl_3): δ 10.4, 28.9, 55.8, 106.8, 112.8, 126.3, 127.4, 128.5, 130.2, 131.1, 136.9, 137.7, 147.8, 158.3; **HRESI-MS** (m/z): Calculated for $\text{C}_{16}\text{H}_{19}\text{N}_2$ ($\text{M} + \text{H}^+$): 239.1548, found ($\text{M} + \text{H}^+$): 239.1552.

- 18) (E)-N-(1-Phenyloct-1-en-3-yl)pyridin-2-amine (4na)** Colorless liquid; **Yield** – (60 mg, 65%); **R_f** (20% EtOAc/petroleum ether) 0.6; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1601; **^1H NMR** (400 MHz, CDCl_3): δ 0.86-0.89 (m, 3 H), 1.28-1.33 (m, 4 H), 1.41-1.49 (m, 2 H), 1.68-1.75 (m, 2 H), 4.16 (s, 1 H), 5.67 (s, 1 H), 6.14 (dd, $J = 16.01, 6.54$ Hz, 1 H), 6.47 (d, $J = 8.57$ Hz, 1 H), 6.53-6.58 (m, 2 H), 7.18-7.22 (m, 1 H), 7.26-7.30 (m, 2 H), 7.33-7.35 (m, 2 H), 7.42-7.46 (m, 1 H), 8.00 (d, $J = 3.98$ Hz, 1 H). **^{13}C NMR** (100 MHz, CDCl_3): δ 14.0, 22.5, 25.6, 31.6, 35.8, 54.4, 107.3, 112.6, 126.3, 127.5, 128.5, 130.3, 130.9, 136.7, 138.7, 145.9, 157.5; **HRESI-MS** (m/z): Calculated for $\text{C}_{19}\text{H}_{25}\text{N}_2$ ($\text{M} + \text{H}^+$): 281.2018, found ($\text{M} + \text{H}^+$): 281.2018.

- 19) (E)-N-(1,3-Diphenylallyl)pyridin-2-amine (4oa)** Colorless solid; **Yield** – (90 mg, 95%); **mp**: 96-100 °C; **R_f** (20% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1599; **^1H NMR** (400 MHz, CDCl_3): δ 5.19 (d, $J = 4.95$ Hz, 1 H), 5.44 (t, $J = 5.77$ Hz, 1 H), 6.38-6.43 (m, 2 H), 6.57-6.63 (m, 2 H), 7.20-7.23 (m, 1 H), 7.26-7.30 (m, 3 H), 7.33-7.43 (m, 7 H), 8.08 (d, $J = 4.99, 1.00$ Hz, 1 H). **^{13}C NMR** (100 MHz, CDCl_3): δ 58.3, 107.2, 113.4, 126.5, 127.2, 127.6, 127.7, 128.5, 128.8, 130.0, 131.0, 136.5, 137.7, 141.5, 147.9, 157.7. **HRESI-MS** (m/z): Calculated for $\text{C}_{20}\text{H}_{19}\text{N}_2$ ($\text{M} + \text{H}^+$): 287.1548, found ($\text{M} + \text{H}^+$): 287.1548.

- 20) (E)-N-(3-Methyl-4-phenylbut-3-en-2-yl)pyridin-2-amine (4pa)** Colorless liquid; **Yield** – (63 mg, 80%); **R_f** (30% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm^{-1}): 1601; **^1H NMR** (400

MHz, CDCl₃): δ 1.44 (d, J = 6.70 Hz, 3 H), 2.27 (s, 3 H), 4.41 (m, 1 H), 4.77 (d, J = 5.66 Hz, 1 H), 6.06 (dd, J = 15.81, 5.94 Hz, 1 H), 6.43 (d, J = 8.45 Hz, 1 H), 6.57 (dd, J = 5.10, 6.37 Hz, 1 H), 6.76 (d, J = 15.73 Hz, 1 H), 7.10-7.14 (m, 3 H), 7.38-7.43 (m, 2 H), 8.06-8.08 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 19.7, 21.8, 49.6, 107.0, 113.0, 125.6, 126.0, 127.3, 130.2, 133.6, 135.3, 137.6, 147.9, 158.0. **HRESI-MS** (m/z): Calculated for C₁₆H₁₉N₂ (M + H)⁺: 239.1548, found (M + H)⁺: 239.1545.

- 21) *N*-(4-Methoxybenzyl)pyridin-2-amine (6qa)** Colorless solid; **Yield** – (55 mg, 78%); **mp**: 120-123 °C; **R_f** (30% EtOAc/petroleum ether) 0.7; Prepared as shown in typical experimental procedure. **IR** (Neat, cm⁻¹): 1602, 3229; **¹H NMR** (400 MHz, CDCl₃): δ 3.79 (s, 3 H), 4.42 (d, J = 5.56 Hz, 2 H), 4.91 (s, 1 H), 6.37 (d, J = 8.47 Hz, 1 H), 6.58 (dd, J = 6.90, 5.96 Hz, 1 H), 6.87 (d, J = 8.63 Hz, 2 H), 7.28 (d, J = 8.57 Hz, 2 H), 7.38-7.42 (m, 1 H), 8.09 (d, J = 4.04 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 45.8, 55.3, 106.8, 113.0, 114.0, 128.7, 131.0, 137.5, 148.0, 158.5, 158.8. **HRESI-MS** (m/z): Calculated for C₁₃H₁₅N₂O (M + H)⁺: 215.1184, found (M + H)⁺: 215.1187.

- 22) *N*-(1-Phenylethyl)pyridin-2-amine (6ra)** Yellow solid; **Yield** – (34 mg, 52%); **mp**: 83-86 °C; **R_f** (20% EtOAc/petroleum ether) 0.3; Prepared as shown in typical experimental procedure. **IR** (Neat, cm⁻¹): 1599, 3247; **¹H NMR** (400 MHz, CDCl₃): δ 1.56 (d, J = 6.71 Hz, 3 H), 4.65-4.71 (m, 1 H), 5.41 (s, 1 H), 6.20 (d, J = 8.42 Hz, 1 H), 6.55 (t, J = 6.34 Hz, 1 H), 7.21-7.25 (m, 1 H), 7.29-7.36 (m, 5 H), 8.06 (d, J = 3.62 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 24.4, 52.1, 107.0, 113.0, 125.8, 127.0, 128.7, 138.0, 144.4, 147.6, 157.8. **HRESI-MS** (m/z): Calculated for C₁₃H₁₅N₂ (M + H)⁺: 199.1235, found (M + H)⁺: 199.1237.

- 23) *N*-(1-(*o*-Tolyl)but-3-en-1-yl)pyridin-2-amine (6sa)** Brown oily; **Yield** – (56 mg, 71%); **R_f** (20% EtOAc/petroleum ether) 0.5; Prepared as shown in typical experimental procedure. **IR** (Neat, cm⁻¹): 1600; **¹H NMR** (400 MHz, CDCl₃): δ 2.46 (s, 3 H), 2.50 (t, J = 7.62 Hz, 1 H), 2.56-2.62 (m, 1 H), 4.78-4.83 (m, 1 H), 5.13-5.23 (m, 3 H), 5.73-5.84 (m, 1 H), 6.02 (d, J = 8.48 Hz, 1 H), 6.52 (ddd, J = 7.48, 5.04, 0.71 Hz, 1 H), 7.13-7.17 (m, 3 H), 7.25-7.30 (m, 1 H), 7.34-7.38 (m, 1 H), 8.04 (dd, J = 4.97, 1.06 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 19.1, 40.9, 52.1, 106.3, 113.0, 118.5, 125.4, 126.4, 126.9, 130.6, 134.2, 134.7, 137.6, 140.6, 148.0, 157.9. **HRESI-MS** (m/z): Calculated for C₁₆H₁₉N₂ (M + H)⁺: 239.1548, found (M + H)⁺: 239.1548.

Figure 1: Asymmetric Unit of the compound 3aa, ellipsoids are drawn with 50% probability

Bond precision: C-C = 0.0012 Å Wavelength=0.71073
 Cell: a=7.9925(3) b=5.4290(2) c=27.9143(10)
 alpha=90 beta=94.067(2) gamma=90
 Temperature: 100 K

Table 1. Crystal data and structure refinement for apzn.

Identification code 3aa
 Empirical formula $C_{15}H_{16}N_2$
 Formula weight 224.30
 Temperature 100(2) K
 Wavelength 0.71073 Å
 Crystal system Monoclinic
 Space group $P 2_1/c$
 Unit cell dimensions $a = 7.9925(3)$ Å $a = 90^\circ$.

$b = 5.4290(2) \text{ \AA}$ $\beta = 94.067(2)^\circ$.
 $c = 27.9143(10) \text{ \AA}$ $\gamma = 90^\circ$.
Volume $1208.19(8) \text{ \AA}^3$
 Z 4
Density (calculated) 1.233 mg/m^3
Absorption coefficient 0.073 mm^{-1}
 $F(000)$ 480
Crystal size $0.190 \times 0.130 \times 0.070 \text{ mm}^3$
Theta range for data collection 1.463 to 30.565° .
Index ranges $-11 \leq h \leq 11$, $-7 \leq k \leq 7$, $-39 \leq l \leq 39$
Reflections collected 26394
Independent reflections 3690 [$R(\text{int}) = 0.0360$]
Completeness to $\theta = 25.242^\circ$ 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7461 and 0.6755
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 3690 / 0 / 159
Goodness-of-fit on F^2 1.051
Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0403$, $wR_2 = 0.1125$
 R indices (all data) $R_1 = 0.0438$, $wR_2 = 0.1162$
Extinction coefficient n/a
Largest diff. peak and hole 0.412 and $-0.191 \text{ e.\AA}^{-3}$

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³)

for apzn. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	393(1)	2602(1)	4461(1)	19(1)
N(2)	-1872(1)	5166(1)	4540(1)	19(1)
C(1)	3025(1)	228(2)	2827(1)	18(1)
C(2)	3418(1)	270(2)	2351(1)	20(1)
C(3)	2850(1)	2187(2)	2049(1)	20(1)
C(4)	1909(1)	4080(2)	2230(1)	20(1)
C(5)	1516(1)	4039(2)	2708(1)	19(1)
C(6)	2053(1)	2105(2)	3013(1)	16(1)
C(7)	1556(1)	2117(2)	3511(1)	17(1)
C(8)	1630(1)	216(2)	3816(1)	18(1)
C(9)	1134(1)	263(2)	4327(1)	18(1)
C(10)	2669(1)	-276(2)	4669(1)	22(1)
C(11)	-1241(1)	3179(2)	4326(1)	17(1)
C(12)	-3473(1)	5772(2)	4413(1)	22(1)
C(13)	-4513(1)	4489(2)	4084(1)	23(1)
C(14)	-3851(1)	2434(2)	3868(1)	21(1)
C(15)	-2209(1)	1763(2)	3985(1)	19(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for apzn.

N(1)-C(11)	1.3688(10)
N(1)-C(9)	1.4610(11)
N(1)-H(1N)	0.880(14)
N(2)-C(12)	1.3437(11)
N(2)-C(11)	1.3473(11)
C(1)-C(2)	1.3887(12)
C(1)-C(6)	1.4031(11)
C(1)-H(1)	0.9500
C(2)-C(3)	1.3937(12)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3894(12)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3921(12)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3997(11)
C(5)-H(5)	0.9500
C(6)-C(7)	1.4727(11)
C(7)-C(8)	1.3357(12)
C(7)-H(7)	0.9500
C(8)-C(9)	1.5101(12)
C(8)-H(8)	0.9500
C(9)-C(10)	1.5272(12)
C(9)-H(9)	1.0000
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800

C(11)-C(15) 1.4125(11)

C(12)-C(13) 1.3835(13)

C(12)-H(12) 0.9500

C(13)-C(14) 1.3901(13)

C(13)-H(13) 0.9500

C(14)-C(15) 1.3783(12)

C(14)-H(14) 0.9500

C(15)-H(15) 0.9500

C(11)-N(1)-C(9) 121.68(7)

C(11)-N(1)-H(1N) 114.2(9)

C(9)-N(1)-H(1N) 119.0(9)

C(12)-N(2)-C(11) 117.36(8)

C(2)-C(1)-C(6) 120.73(8)

C(2)-C(1)-H(1) 119.6

C(6)-C(1)-H(1) 119.6

C(1)-C(2)-C(3) 120.26(8)

C(1)-C(2)-H(2) 119.9

C(3)-C(2)-H(2) 119.9

C(4)-C(3)-C(2) 119.67(8)

C(4)-C(3)-H(3) 120.2

C(2)-C(3)-H(3) 120.2

C(3)-C(4)-C(5) 120.07(8)

C(3)-C(4)-H(4) 120.0

C(5)-C(4)-H(4) 120.0

C(4)-C(5)-C(6) 120.95(8)

C(4)-C(5)-H(5) 119.5

C(6)-C(5)-H(5) 119.5

C(5)-C(6)-C(1)	118.30(8)
C(5)-C(6)-C(7)	118.63(7)
C(1)-C(6)-C(7)	123.07(7)
C(8)-C(7)-C(6)	126.47(8)
C(8)-C(7)-H(7)	116.8
C(6)-C(7)-H(7)	116.8
C(7)-C(8)-C(9)	125.90(8)
C(7)-C(8)-H(8)	117.0
C(9)-C(8)-H(8)	117.0
N(1)-C(9)-C(8)	113.24(7)
N(1)-C(9)-C(10)	109.26(7)
C(8)-C(9)-C(10)	109.54(7)
N(1)-C(9)-H(9)	108.2
C(8)-C(9)-H(9)	108.2
C(10)-C(9)-H(9)	108.2
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(2)-C(11)-N(1)	116.20(7)
N(2)-C(11)-C(15)	121.99(8)
N(1)-C(11)-C(15)	121.81(8)
N(2)-C(12)-C(13)	124.54(9)
N(2)-C(12)-H(12)	117.7
C(13)-C(12)-H(12)	117.7
C(12)-C(13)-C(14)	117.60(8)

C(12)-C(13)-H(13)	121.2
C(14)-C(13)-H(13)	121.2
C(15)-C(14)-C(13)	119.65(8)
C(15)-C(14)-H(14)	120.2
C(13)-C(14)-H(14)	120.2
C(14)-C(15)-C(11)	118.86(8)
C(14)-C(15)-H(15)	120.6
C(11)-C(15)-H(15)	120.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for apzn. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
N(1)	16(1)	22(1)	17(1)	-4(1)	0(1)	1(1)
N(2)	17(1)	20(1)	21(1)	-2(1)	0(1)	0(1)
C(1)	18(1)	18(1)	19(1)	0(1)	1(1)	1(1)
C(2)	21(1)	20(1)	20(1)	-2(1)	4(1)	1(1)
C(3)	21(1)	23(1)	18(1)	0(1)	3(1)	-1(1)
C(4)	20(1)	21(1)	19(1)	4(1)	1(1)	0(1)
C(5)	18(1)	18(1)	20(1)	0(1)	2(1)	1(1)
C(6)	14(1)	18(1)	17(1)	-1(1)	1(1)	-1(1)
C(7)	16(1)	19(1)	17(1)	-1(1)	1(1)	0(1)
C(8)	19(1)	20(1)	17(1)	-1(1)	2(1)	1(1)
C(9)	19(1)	19(1)	17(1)	0(1)	3(1)	1(1)
C(10)	22(1)	26(1)	18(1)	3(1)	1(1)	3(1)
C(11)	16(1)	20(1)	15(1)	1(1)	2(1)	-2(1)
C(12)	19(1)	22(1)	25(1)	-2(1)	1(1)	1(1)
C(13)	17(1)	26(1)	25(1)	-1(1)	-1(1)	0(1)
C(14)	19(1)	26(1)	19(1)	-2(1)	0(1)	-4(1)
C(15)	19(1)	22(1)	17(1)	-3(1)	2(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for apzn.

	x	y	z	U(eq)
H(1N)	801(17)		3360(30)	4722(5) 32(3)
H(1)	3419	-1086	3030	22
H(2)	4077	-1014	2229	24
H(3)	3105	2199	1722	25
H(4)	1533	5404	2028	24
H(5)	874	5343	2829	22
H(7)	1142	3628	3627	21
H(8)	2031	-1303	3699	22
H(9)	290	-1070	4366	22
H(10A)		3117	-1904	4597 33
H(10B)		2345	-250	5001 33
H(10C)		3529	979	4628 33
H(12)	-3922	7179	4561	26
H(13)	-5638	4993	4008	28
H(14)	-4527	1497	3641	26
H(15)	-1737	373	3837	23

Table 6. Torsion angles [$^{\circ}$] for apzn.

C(6)-C(1)-C(2)-C(3)	0.05(13)
C(1)-C(2)-C(3)-C(4)	1.00(13)
C(2)-C(3)-C(4)-C(5)	-0.96(13)
C(3)-C(4)-C(5)-C(6)	-0.13(13)
C(4)-C(5)-C(6)-C(1)	1.17(12)
C(4)-C(5)-C(6)-C(7)	-178.13(8)
C(2)-C(1)-C(6)-C(5)	-1.13(12)
C(2)-C(1)-C(6)-C(7)	178.13(8)
C(5)-C(6)-C(7)-C(8)	164.34(8)
C(1)-C(6)-C(7)-C(8)	-14.92(13)
C(6)-C(7)-C(8)-C(9)	179.27(8)
C(11)-N(1)-C(9)-C(8)	78.62(10)
C(11)-N(1)-C(9)-C(10)	-158.99(8)
C(7)-C(8)-C(9)-N(1)	5.24(12)
C(7)-C(8)-C(9)-C(10)	-116.99(10)
C(12)-N(2)-C(11)-N(1)	179.96(8)
C(12)-N(2)-C(11)-C(15)	-0.29(13)
C(9)-N(1)-C(11)-N(2)	168.51(7)
C(9)-N(1)-C(11)-C(15)	-11.24(12)
C(11)-N(2)-C(12)-C(13)	0.53(14)
N(2)-C(12)-C(13)-C(14)	-0.18(15)
C(12)-C(13)-C(14)-C(15)	-0.41(14)
C(13)-C(14)-C(15)-C(11)	0.62(13)
N(2)-C(11)-C(15)-C(14)	-0.27(13)
N(1)-C(11)-C(15)-C(14)	179.46(8)

Table 7. Hydrogen bonds for ap zn [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)d(H...A)	d(D...A)	<(DHA)	
N(1)-H(1N)...N(2)#1	0.880(14)	2.316(14)	3.1907(11)	172.1(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Data completeness= 0.995

Theta(max)= 30.565

R(reflections)= 0.0403(3369)

wR2(reflections)= 0.1162(3690)

S = 1.051

N par= 159

The ORTEP diagram and Crystal Parameters of **3aa** in thermal ellipsoids are drawn at 50% probability level. The crystal of suitable quality was obtained from slow evaporation of solution of **3aa** in ethyl acetate, and was analyzed by single crystal diffractometer. Atomic coordinates, bond lengths, bond angles, and thermal parameters for this compound have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2053449 contains supplementary crystallographic data.

158.145
148.102
137.537
136.092
135.376
133.716
130.227
127.365
126.068
125.672
113.044
107.060

77.391
77.073
76.756

49.586

21.862
19.784

157.973
148.164
139.123
137.572
134.113
130.242
130.018
129.228
127.814
125.045
122.735
113.156
107.011

77.372
77.055
76.738

49.025

21.651

157.765
148.181
146.803
143.485
137.644
137.620
127.186
126.885
123.963
113.352
107.131

77.355
77.038
76.720

48.949

21.473

158.877
158.557
148.012
137.587
131.078
128.718
114.044
113.087
106.873
77.356
77.038
76.720
55.308
45.841

157.921
148.069
140.621
137.659
134.793
134.245
130.645
126.922
126.436
125.423
118.565
113.097
106.359

77.357
77.039
76.722

52.117

40.965

19.185