Supporting Information
for DOI: 10.1055/s-0030-1260773
© Georg Thieme Verlag KG Stuttgart · New York 2011
Proline-catalytic Enantioselective Synthesis of aza-Quaternary Carbon derivatives

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, P. R. China

Liqi Li, Manyi Han, Mingxing Xiao, Zhixiang Xie*
xiezx@lzu.edu.cn

Supporting Information

List of contents

1. General Information ........................................................................................................2
2. Experimental Procedures and Data ..............................................................................2
3. References ..................................................................................................................10
4. $^1$H and $^{13}$C NMR and HPLC Spectra of Products ..............................................11
5. The crystal structure data and refinement for 3c and 3h ......................37
1. General information

The L-proline and the aldehydes are all commercially available from Aldrich or Alfa Aesar. DMF was pretreated with 4Å molecular sieves overnight and then distilled from 4Å molecular sieves below 70°C under vacuum prior to use. Other chemicals were used as received, and all reactions conducted under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) was used for column chromatography.

$^1$H NMR, $^{13}$C NMR spectra were recorded on Bruker AM-400 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. HRMS data were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEX II 47e mass spectrometer. HRMS were registered in the electro-spray ionization mode. The enantiomeric excess (ee) of the products were determined by HPLC using Daicel Chiralpak OD-H columns with $i$PrOH/hexane as eluent.

2. Preparation of Substrates Data:

General Procedure

To a stirred solution of imine (0.1mmol) in dry DMF or DMSO(3.0 mL) was added aldehyde (0.15mmol) and L-proline (0.02mmol). The reaction was warmed to 30°C and stirring is continued for several hours at this temperature. The reaction mixture was quenched with water, extracted with diethyl ether and dried over anhydrous Na$_2$SO$_4$. The solvent and the excess aldehyde were removed in vacuo. After flash chromatography (pentane / EtOAc) the corresponding Mannich product was obtained.
Preparation of Compound 3a and 4a

Propanal (8.7mg, 0.15mmol) and 1'-tosyl-1'H,3H-2,3'-biindol-3-one\(^{\text{i}}\) (40mg, 0.1mmol) were combined in DMSO catalyzed by L-proline according to the general procedure afforded compound \(3a\) as a yellow solid (43mg, 95% yield).  

\[\text{\(^{1}\text{H NMR}\)}\]

(400MHz, CDCl\(_3\)): \(\delta\) 9.56 (s, 1H), 7.93 (dd, 2H, J = 11.2Hz, J = 8.0Hz), 7.68 (d, 2H, J = 8.4Hz), 7.61 (d, 2H, J = 7.6Hz), 7.45-7.55 (m, 1H), 7.33 (t, 1H, J = 8.0Hz), 7.26 (m, 1H), 7.18 (d, 2H, J = 8.4Hz), 6.91 (dd, 2H, J = 7.6Hz, J = 16.0Hz), 5.23 (s, 1H), 3.67 (dd, 1H, J = 7.2Hz, J = 14.4Hz), 2.32 (s, 3H), 1.05 (d, 3H, J = 7.2Hz).

\[\text{\(^{13}\text{C NMR}\)}\]

(100MHz, CDCl\(_3\)): 200.8, 199.7, 159.9, 145.3, 137.9, 135.9, 134.6, 130.0, 129.9, 127.5, 126.8, 125.3, 125.2, 124.1, 123.7, 121.6, 120.2, 119.9, 114.0, 112.5, 69.9, 51.9, 21.6, 9.1.  

\[\text{IR (KBr)}\ v (\text{cm}^{-1})\]: 3387, 3145, 3051, 2956, 2923, 2729, 1722, 1698, 1617, 1371, 1173.

To a mixture of sodium borohydride (38mg, 0.1mmol) and dry methanol was added a solution of \(3a\) (46mg, 0.1mmol) in methanol at 0°C, and the reaction mixture was stirred for 10 minutes. Water was added, and the product was extracted with EtOAc, dried over anhydrous Na\(_2\)SO\(_4\). Removal of the solvent followed by purification of the residue by TLC (pentane / EtOAc = 2 : 1) gave compound \(4a\) (45mg, 98%) as yellow solid.  

\[\text{\(^{1}\text{H NMR}\)}\ (400 MHz, CDCl\(_3\), ppm): \delta\ 7.94 (d, 2H, J = 8.4), 7.66 (t, 2H, J =
8.4 Hz), 7.58 (d, 1H, J = 7.6 Hz), 7.46 (m, 1H), 7.30 (t, 1H, J = 8.0 Hz), 7.23 (t, 1H, J = 6.8 Hz), 7.15 (d, 2H, J = 8.0 Hz), 6.92 (d, 1H, J = 8.4 Hz), 6.84 (t, 1H, J = 7.2 Hz), 5.36 (s, 1H), 3.54 (d, 1H, J = 4.4 Hz), 2.88 (dd, 1H, J = 12 Hz, J = 5.2 Hz), 2.30 (s, 3H), 2.19 (s, 1H), 0.94 (d, 3H, J = 7.2 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$): 201.8, 160.5, 145.1, 137.6, 136.0, 134.8, 129.9, 128.3, 126.8, 125.1, 125.0, 124.1, 123.4, 121.8, 120.6, 120.5, 119.7, 114.0, 112.6, 72.3, 64.2, 41.2, 21.5, 11.8. IR (KBr) ν (cm$^{-1}$): 3358, 3149, 3052, 2928, 2880, 1701, 1617, 1367, 1173, 1050. HRMS (ESI): calcd for C$_{24}$H$_{27}$N$_2$O$_4$S$^+$ [M+H$^+$]: 461.1530; Found 461.1535. Enantiomeric excess: 99%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH = 80: 20, flow rate 1.00 mL/min, rt): $t_R$(major) = 16.3 min, $t_R$(minor) = 14.6 min.

Preparation of Compound 3b

![Compound 3b Diagram]

Isobutylaldehyde (11mg, 0.15mmol) and 1'-tosyl-1'H,3H-2,3'-biindol -3-one (40mg, 0.1mmol) were combined in DMSO catalyzed by L-proline according to the general procedure afforded compound 3b as a yellow solid (24mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 9.65 (s, 1H), 7.97 (d, 1H, J = 8.4 Hz), 7.89 (s, 1H), 7.74 (d, 2H, J=8.4 Hz), 7.63 (d, 2H, J=8.0 Hz), 7.43-7.48 (m, 1H), 7.23-7.30 (m, 2H), 7.18-7.22 (m, 2H), 6.83-6.91 (m, 2H), 5.66 (s, 1H), 2.32(s, 3H), 1.32(s, 3H), 1.16(s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 205.1, 200.5, 160.4, 145.2, 137.8, 135.3, 134.9, 129.9, 129.2, 126.9, 126.7, 124.9, 124.7, 123.4, 121.7, 120.9, 119.8, 116.4, 113.9, 112.6, 70.9, 52.6, 21.5, 18.5, 18.2. IR (KBr) ν (cm$^{-1}$): 3422, 3147, 3053, 2970, 2926, 1718, 1695, 1614, 1373, 1173. HRMS (ESI): calcd for C$_{27}$H$_{24}$N$_2$O$_4$SNa $[M+Na]^+$: 495.1349; Found 495.1355. Enantiomeric excess: 99%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH = 90: 10, flow rate 1.00 mL/min, rt): $t_R$(major) = 17.6 min, $t_R$(minor) = 15.9 min.
Preparation of Compound 3c

3-Methyl butanal (13mg, 0.15mmol) and 1'-tosyl-1'H,3H-2,3'-biindol -3-one (40mg, 0.1mmol) were combined in DMSO catalyzed by L-proline according to the general procedure afforded compound 3c as a yellow solid (36mg, 74% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 9.69 (d, 1H, J = 1.2Hz), 7.95 (dd, 2H, J = 9.2Hz, J = 11.2Hz), 7.61-7.64 (m, 3H), 7.57 (d, 1H, J = 7.6Hz), 7.50 (m, 1H), 7.25-7.34 (m, 2H), 7.14 (d, 2H, J = 8.0Hz), 6.97 (d, 1H, J = 8.0Hz), 6.89 (t, 1H, J = 7.2Hz), 5.22 (s, 1H), 3.60 (dd, 1H, J = 1.6Hz, J = 3.2Hz), 2.31 (s, 3H), 1.95 (ddd, 1H, J = 3.6Hz, J = 7.2Hz, J = 10.4Hz), 1.04 (d, 3H, J = 7.2Hz), 1.00 (d, 3H, J = 7.2Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 201.0, 199.6, 159.8, 145.2, 137.6, 136.1, 134.6, 129.9, 127.6, 126.7, 125.3, 123.9, 123.8, 121.8, 120.2, 120.1, 119.5, 114.0, 112.5, 70.4, 60.7, 26.9, 22.7, 21.5, 19.1. IR (KBr) $\nu$ (cm$^{-1}$): 3364, 3141, 3051, 2959, 2922, 2852, 1707, 1615, 1370, 1173. HRMS (ESI): calecd for C$_{28}$H$_{26}$N$_2$O$_4$SNa $[M+Na]^+$: 509.1505; Found 509.1499. Enantiomeric excess: 99%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH = 90: 10, flow rate 1.00 mL/min, rt): $t_R$(major) = 29.1 min, $t_R$ (minor) = 21.7 min.

Preparation of Compound 3d

Acetone (9mg, 0.15mmol) and 1'-tosyl-1'H,3H-2,3'-biindol -3-one (40mg, 0.1mmol) were combined in DMF catalyzed by L-proline according to the general procedure afforded compound
3d as a yellow solid (38mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.90 (d, 1H, J = 8.4Hz), 7.75 (d, 1H, J = 8.0Hz), 7.68 (d, 2H, J = 8.0Hz), 7.63 (s, 1H), 7.58 (d, 1H, J = 8.0Hz), 7.47-7.51 (m, 1H), 7.23-7.27 (m, 1H), 7.14-7.18 (m, 1H), 6.92 (d, 1H, J = 8.4Hz), 6.83 (t, 1H, J = 7.2Hz), 6.14 (s, 1H), 3.72 (d, 1H, J = 17.2Hz), 2.79 (d, 1H, J = 17.2Hz), 2.29 (s, 3H), 2.13 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 206.3, 199.8, 159.9, 144.9, 137.9, 135.6, 134.8, 129.8, 127.9, 126.8, 125.3, 124.7, 123.4, 121.6, 120.1, 119.2, 118.7, 113.7, 112.4, 66.5, 48.1, 31.3, 21.5.

IR (KBr) $\nu$ (cm$^{-1}$): 3386, 3141, 3052, 2919, 2852, 1700, 1616, 1366, 1172. HRMS (ESI): calcd for C$_{26}$H$_{23}$N$_2$O$_4$S$^+$ [M+H$^+$]: 459.1373; Found 459.1367. Enantiomeric excess: 94%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH = 80: 20, flow rate 1.00 mL/min, rt): $t_R$(major) = 31.7 min, $t_R$(minor) = 18.7 min.

Preparation of Compound 3e

![3e](image_url)

Cyclohexanone (15mg, 0.15mmol) and 1'-tosyl-1'H,3H-2,3'-biindol -3-one (40mg, 0.1mmol) were combined in DMF catalyzed by L-proline according to the general procedure afforded compound 3e as a yellow solid (48mg, 96% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 8.04 (d, 1 H, J = 8.0Hz), 7.91 (d, 1H, J = 8.4Hz), 7.71 (m, 1H), 7.61 (d, 2H, J = 8.4Hz), 7.53 (d, 2H, J = 7.6Hz), 7.32-7.37 (m, 1H), 7.20-7.30 (m, 2H), 7.08 (d, 2H, J = 8.0Hz), 6.81 (t, 2H, J = 7.6Hz), 5.40 (s, 1H), 3.67 (dd, 1H, J = 5.2Hz, J = 12.4Hz), 2.28-2.35 (m, 2H), 2.26 (s, 3H), 2.00 (t, 1H, J = 6.4Hz), 1.78(d, 2H, J = 4.4Hz), 1.50-1.60 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 207.7, 200.3, 159.4, 145.1, 136.3, 136.1, 134.5, 129.8, 127.9, 126.7, 124.9, 124.8, 124.3, 123.5, 122.4, 120.7, 120.4, 119.2, 113.8, 119.9, 69.4, 56.2, 42.0, 28.5, 26.5, 25.0, 21.4.

IR (KBr) $\nu$ (cm$^{-1}$): 3400, 3145, 3049, 2931, 2862, 1710, 1619, 1370, 1173. HRMS (ESI): calcd for C$_{26}$H$_{26}$N$_2$O$_4$SNa [M+Na]$^+$: 521.1505; Found 521.1503.
Enantiomeric excess: 99%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH = 90:10, flow rate 1.00 mL/min, rt): $t_R$(major) = 60.8 min, $t_R$ (minor) = 51.4 min.

Preparation of Compound 3f

Propanal (8.7mg, 0.15mmol) and 2-(2-bromophenyl)-3H-indol-3-one$^2$ (28.5mg, 0.1mmol) were combined in DMF catalyzed by L-proline according to the general procedure afforded compound 3f as a yellow solid (27mg, 79% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 9.63 (s, 1H), 7.71-7.73 (m, 1H), 7.62-7.66 (m, 1H), 7.57-7.61 (m, 1H), 7.13-7.32 (m, 2H), 6.80-6.89 (m, 2H), 6.32 (s, 1H), 3.73 (dd, 1H, $J$ = 6.8Hz, $J$ = 13.6Hz), 1.05 (d, 3H, $J$ = 6.8Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 201.7, 201.2, 160.4, 138.3, 137.9, 135.7, 129.6, 129.0, 128.2, 127.9, 124.8, 122.2, 120.1, 112.3, 73.4, 51.2, 8.3. IR (KBr) $\nu$ (cm$^{-1}$): 3393, 3065, 2978, 2936, 2740, 1718, 1691, 1616, 1619, 1488, 1466, 1326, 755. HRMS (ESI): calcd for C$_{17}$H$_{15}$BrNO$_2^+$ [M+H]$^+$: 344.0281; Found 344.0284. Enantiomeric excess: 64%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH = 91:9, flow rate 1.00 mL/min, rt): $t_R$(major) = 13.4 min, $t_R$ (minor) = 12.0 min.

Preparation of Compound 3g

3-Methyl butanal (13mg, 0.15mmol) and 2-(2-bromophenyl)-3H-indol-3-one (28.5mg, 0.1mmol) were combined in DMF catalyzed by L-proline according to the general procedure afforded compound 3g as a yellow solid (32mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm):
\[ \delta \ 9.58 (d, 1H, J = 3.6Hz), 7.55-7.72 (m, 3H), 7.42-7.49 (m, 1H), 7.24-7.30 (m, 1H), 7.10-7.18 (m, 1H), 6.79-6.88 (m, 2H), 6.40 (s, 1H), 3.89 (dd, 3H, J = 3.6Hz, J = 5.4Hz), 2.30-2.36 (m, 1H), 1.00 \ (d, 1.2H, J = 6.8Hz), 0.93 (dd, 1H, J = 3.6Hz, J = 6.8Hz), 0.84 (d, 1.8H, J = 6.8Hz). \]

**\[\text{\textsuperscript{13}C NMR}\]** (100 MHz, CDCl\textsubscript{3}, ppm): \[ \delta \ 202.4, 201.7, 159.2, 138.0, 137.8, 135.9, 130.2, 129.5, 127.8, 124.9, 121.9, 120.6, 119.2, 112.0, 71.8, 63.5, 26.2, 23.7, 20.7. \]

**\[\text{IR}\]** (KBr) \[ \nu \ (\text{cm}^{-1}): \ 3400, 3064, 2961, 2931, 2872, 1708, 1695, 1616, 1488, 1467, 1325, 754. \]

**HRMS** (ESI): calcd for C\textsubscript{19}H\textsubscript{19}BrNO\textsubscript{2} \[ [\text{M+H}]^+: \ 372.0594; \text{Found} \ 372.0588. \]

**Enantiomeric excess**: 66\%, determined by HPLC (Chiralpak OD-H, hexane/\textit{i}-PrOH = 91:9, flow rate 1.00 mL/min, rt): \[ t_R (major) = 9.0 \text{ min}, t_R (minor) = 8.6 \text{ min}. \]

---

**Preparation of Compound 3h**

![Chemical Structure](image)

Acetaldehyde (17mg, 40% in water, 0.15mmol) and 2-(2-bromophenyl)-3H-indol-3-one (28.5mg, 0.1mmol) were combined in DMF catalyzed by L-proline according to the general procedure afforded compound 3h as a yellow solid (32mg, 98\% yield).  

**\[\text{\textsuperscript{1}H NMR}\]** (300 MHz, CDCl\textsubscript{3}, ppm): \[ \delta \ 9.57 (d, 1H, J = 2.4Hz), 7.72 (d, 1H, J = 8.4Hz), 7.64 (dd, 1H, J = 1.2Hz, J = 8.4Hz), 7.42-7.51 (m, 2H), 7.25-7.31 (m, 1H), 7.16-7.20 (m, 1H), 6.23-6.89 (m, 2H), 6.24 (s, 1H), 3.60 (dd, 1H, J = 3.0Hz, J = 16.2Hz), 3.15 (d, 1H, J = 17.1Hz). \]

**\[\text{\textsuperscript{13}C NMR}\]** (75 MHz, CDCl\textsubscript{3}, ppm): \[ \delta \ 194.1, 192.6, 153.4, 131.7, 129.6, 129.2, 123.7, 123.2, 121.5, 118.7, 71.8, 63.5, 106.4, 63.7, 42.9. \]

**\[\text{IR}\]** (KBr) \[ \nu \ (\text{cm}^{-1}): \ 3386, 3066, 2839, 2738, 1698, 1616, 1487, 1468, 1326, 755. \]

**HRMS** (ESI): calcd for C\textsubscript{16}H\textsubscript{13}BrNO\textsubscript{2} \[ [\text{M+H}]^+: \ 330.0214; \text{Found} \ 330.0210. \]

**Enantiomeric excess**: 82\%, determined by HPLC (Chiralpak OD-H, hexane/\textit{i}-PrOH = 80:20, flow rate 1.00 mL/min, rt): \[ t_R (major) = 32.8 \text{ min}, t_R (minor) = 29.8 \text{ min}. \]
Preparation of Compound 5

Compound 3h (100mg, 0.3mmol) was dissolved in methanol/THF (1:1), and cooled to 0°C under N₂, 2,4-Dimethoxybenzylamine (250mg, 1.5mmol) followed by acetic acid (220mg, 3mmol) was added to the reaction mixture, which was stirred at 0 °C for 30 min. NaCNBH₃ (38mg, 0.6mmol) was added to the reaction mixture, the reaction mixture was allowed to warm to room temperature and was stirred for 10 h. The reaction mixture was diluted with water after 1h, and extracted with EtOAc. The combined extracts were washed with saturated Na₂CO₃ solution, dried over Na₂SO₄, and concentrated. The crude product was purified by chromatography (30:1 Chloroform / Methanol) to afford compound 5 (125mg, 87% yield). ¹H NMR (400 MHz, CDCl₃, ppm): 7.91 (s, 1H), 7.59-7.63 (m, 2H), 7.47-7.52 (m, 1H), 7.32 (q, 1H, J = 1.6Hz, J = 7.6Hz), 7.18-7.23 (m, 1H), 7.09-7.16 (m, 2H), 6.97 (d, 1H, J = 8.4Hz), 6.85 (t, 1H, J = 7.6Hz), 6.44 (s, 1H), 6.34 (2H), 4.07 (d, 1H, J = 9.6Hz), 3.84 (d, 1H, J = 13.2Hz), 3.81 (s, 3H), 3.76 (s, 3H), 2.98 (dd, 1H, J = 4.8Hz, J = 11.2Hz), 2.73-2.89 (3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 202.4, 162.4, 160.6, 158.6, 139.0, 135.7, 135.0, 132.6, 130.0, 129.0, 127.9, 125.1, 122.4, 120.2, 119.7, 113.4, 109.8, 104.7, 98.6, 72.2, 55.7, 55.4, 47.7, 43.5, 31.2. IR (KBr) ν (cm⁻¹): 3365, 3068, 2968, 2939, 2839, 1676, 1616, 1589, 1510, 1490, 1465, 1397, 1377, 1328, 1292, 1209, 1158, 1135, 1030, 757, 731. HRMS (ESI): calcd for C₂₅H₂₆BrN₂O₃⁺ [M+H]⁺: 481.1121; Found 481.1128.

Preparation of Compound 6
Compound 5 (48mg, 0.1mmol) was dissolved in dry pyridine, and cooled to 0°C, the acetic anhydride (50mg, 0.5mmol) was added. After being stirred at 0°C for 1 h, the reaction mixture was poured into saturated NH₄Cl, and extracted with EtOAc. The combined extracts were washed with saturated Na₂CO₃, dried over Na₂SO₄, and concentrated. The crude product was purified by chromatography (1:1 hexane/EtOAc) to afford compound 6 (37mg, 71% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.58-7.72 (m, 3H), 7.42-7.51 (m, 1H), 7.26 (t, 1H, J = 7.6Hz), 7.10-7.18 (m, 1H), 6.76-8.90 (m, 3H), 6.37-6.43 (m, 2H), 6.38 (s, 1H), 4.54 (d, 0.4H, J = 14.8Hz), 4.42 (d, 0.6H, J = 14.4Hz), 4.45 (d, 0.4H, J = 16.4Hz), 4.24 (d, 0.6H, J = 16.4Hz), 3.69-3.74 (6H), 3.55 (m, 1H), 2.96 (m, 1H), 2.68 (m, 1H), 2.31 (m, 1H), 2.04 (s, 1.4H), 2.14 (s, 1.6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 201.4, 200.6, 171.3, 160.5, 160.3, 158.1, 137.5, 135.2, 130.9, 129.2, 128.9, 127.8, 124.4, 122.9, 120.5, 118.6, 116.6, 112.5, 103.7, 98.5, 71.2, 55.2, 55.1, 47.7, 40.9, 34.4, 21.5. HRMS (ESI): calcd for C₂₇H₂₈BrN₂O₄⁺ [M+H]⁺: 523.1227; Found 523.1215.

3. References


4. $^1$H and $^{13}$C NMR and HPLC Spectra of Products
Mixture of 4a and ent-4a
<table>
<thead>
<tr>
<th>Time (分鍾)</th>
<th>Height</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.563</td>
<td>118923</td>
<td>8243817</td>
</tr>
</tbody>
</table>
### Mixture of 3c and ent-3c

<table>
<thead>
<tr>
<th>Time (分钟)</th>
<th>Height</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.076</td>
<td>131513</td>
<td>16142899</td>
</tr>
</tbody>
</table>

### Mixture of 3c and ent-3c

<table>
<thead>
<tr>
<th>Time (分钟)</th>
<th>Height</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.702</td>
<td>73955</td>
<td>9990432</td>
</tr>
<tr>
<td>2</td>
<td>30.244</td>
<td>67463</td>
<td>8690940</td>
</tr>
</tbody>
</table>
### Mixture of 3d and ent-3d

**Name:**

<table>
<thead>
<tr>
<th>Time (分钟)</th>
<th>Height</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.600</td>
<td>8103</td>
<td>642949</td>
</tr>
<tr>
<td>2</td>
<td>31.656</td>
<td>145952</td>
<td>21128008</td>
</tr>
</tbody>
</table>

**Mixture of 3d and ent-3d**
Mixture of 3e and ent-3e
Mixture of 3f and ent-3f
### Mixture of 3h and ent-3h

<table>
<thead>
<tr>
<th>Time (分钟)</th>
<th>Height</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.812</td>
<td>1072420</td>
<td>8.88</td>
</tr>
<tr>
<td>2</td>
<td>32.865</td>
<td>11004987</td>
<td>91.12</td>
</tr>
</tbody>
</table>

### Mixture of 3h and ent-3h

<table>
<thead>
<tr>
<th>Time (分钟)</th>
<th>Height</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.950</td>
<td>6860164</td>
<td>45.37</td>
</tr>
<tr>
<td>2</td>
<td>33.279</td>
<td>828993</td>
<td>54.63</td>
</tr>
</tbody>
</table>
5. The crystal structure data and refinement for 3c and 3i:

**3c**

Identification code  
cc

Empirical formula  
C32.50 H36 N2 O5.50 S

Formula weight  
574.69

Temperature  
293(2) K

Wavelength  
0.71073 Å

Crystal system, space group  
Monoclinic, Cc

Unit cell dimensions  
a = 30.281(15) Å  alpha = 90 deg.
b = 8.091(4) Å  beta = 92.748(6) deg.
c = 25.143(13) Å  gamma = 90 deg.

Volume  
6153(5) Å^3
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.241 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.149 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>2440</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.32 x 0.30 x 0.26 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.06 to 25.20 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-36&lt;=h&lt;=32, -9&lt;=k&lt;=9, -30&lt;=l&lt;=29</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>21321 / 5543 [R(int) = 0.0929]</td>
</tr>
<tr>
<td>Completeness to theta = 25.20</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9623 and 0.9539</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5543 / 0 / 377</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.997</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0662, wR2 = 0.1291</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1493, wR2 = 0.1576</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.184 and -0.368 e.A⁻³</td>
</tr>
</tbody>
</table>
3h

Identification code p212121

Empirical formula C16 H12 Br N O2

Formula weight 330.18

Temperature 296(2) K

Wavelength 0.71073 Å

Crystal system, space group Orthorhombic, P2(1)2(1)2(1)

Unit cell dimensions
\[
\begin{align*}
a &= 10.423(5) \text{ Å} & \alpha &= 90 \text{ deg.} \\
b &= 11.280(6) \text{ Å} & \beta &= 90 \text{ deg.} \\
c &= 11.618(6) \text{ Å} & \gamma &= 90 \text{ deg.}
\end{align*}
\]

Volume 1365.9(12) Å^3

Z, Calculated density 4, 1.606 Mg/m^3

Absorption coefficient 3.009 mm^-1
F(000)                             664
Crystal size                         0.32 x 0.25 x 0.21 mm
Theta range for data collection         2.52 to 25.20 deg.
Limiting indices                    -11<=h<=12, -13<=k<=13, -8<=l<=13
Reflections collected / unique       6443 / 2474 [R(int) = 0.0645]
Completeness to theta = 25.20         100.0 %
Absorption correction                None
Max. and min. transmission           0.5706 and 0.4460
Refinement method                   Full-matrix least-squares on F^2
Data / restraints / parameters       2474 / 0 / 185
Goodness-of-fit on F^2               0.947
Final R indices [I>2sigma(I)]        R1 = 0.0421, wR2 = 0.0829
R indices (all data)                 R1 = 0.0762, wR2 = 0.0975
Absolute structure parameter        0.009(16)
Largest diff. peak and hole          0.286 and -0.297 e.A^-3