Supporting Information for

Synthesis of dibromo- and tetrabromo-bipyrrrolines and their corresponding 2,6-diazasemibuvallene derivatives

Zhe Huang, Ming Zhan, Shaoguang Zhang, Qian Luo, Wen-Xiong Zhang* and Zhenfeng Xi*

†Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China
‡State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, China

zfxi@pku.edu.cn

Contents

1) General information S2
2) General procedure for the preparation of 2-6 S2-S7
3) X-ray crystallographic studies for 4a and 6 S7–S10
4) Reference S10
5) Copies 1H NMR and 13C NMR spectra of all new compounds S11-S52
1) General information

$^1$H (300 MHz) and $^{13}$C (75 MHz) NMR spectra were measured in CDCl$_3$ and $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were measured in CDCl$_3$ or C$_6$D$_6$. Chemical shifts ($\delta$) are reported in ppm downfield from tetramethylsilane. Single crystal X-ray data for 4a and 6 were collected at a temperatures of 180 K, respectively, using monochromated Mo K\(\alpha\) radiation. The structures were solved by direct method and refined by full-matrix least-squares on F2 for all data using Olex227 and SHELXTL software. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1056585 (4a) and CCDC 1056586 (6).

2) General procedure for the preparation of 2-6

**General Procedure for the Preparation of \(\alpha,\alpha'-\text{Dibromo-} \Delta^1\text{-bipyrrroles 2.}\)** NBS (4.4 mmol, 783 mg) was added to a solution of \(\Delta^1\text{-bipyrrroles 1 (2.0 mmol)}\) in 20 mL CCl$_4$ in a 50 mL Schlenk tube, the mixture was stirred at 80 $^\circ$C for 12 h. The reaction mixture was then quenched with water and extracted with acetic ether. The extract was washed with brine and dried over MgSO$_4$. The solvent was evaporated in vacuo to give yellow solid, which was purified by column chromatography (Petrol Ether: Ethyl Acetate = 50:1) to afford products \(\alpha,\alpha'-\text{dibromo-} \Delta^1\text{-bipyrrroles 2a-f.}\)

**2a**, colorless solid, yield: 48% (452 mg); $^1$H NMR (300MHz, CDCl$_3$, Me$_4$Si, 25 $^\circ$C): $\delta$ = 1.46-1.78 (m, 4H, CH$_2$), 2.01-2.07 (m, 2H, CH$_2$), 2.73-2.81 (m, 2H, CH$_2$), 5.56 (s, 2H, CH), 7.27-7.35 (m, 6H, CH), 7.74-7.77 (m, 4H, CH); $^{13}$C NMR (75 MHz, CDCl$_3$, Me$_4$Si, 25 $^\circ$C): $\delta$ = 22.36 (2 CH$_2$), 33.44 (2 CH$_2$), 56.03 (2 CH), 81.14 (2 quat. C), 128.45 (4 CH), 128.49 (4 CH), 131.27 (2 CH), 131.47 (2 quat. C), 168.09 (2 quat. C); HRMS calcd. for C$_{22}$H$_{21}$Br$_2$N$_2$ [M+H]$^+$: 471.0066, found 471.0058.

**2b**, yellow solid, yield: 55% (644 mg); $^1$H NMR (300MHz, CDCl$_3$, Me$_4$Si, 25 $^\circ$C): $\delta$ = 1.18-2.06 (m, 6H, CH; 30H, CH$_2$), 2.51-2.57 (m, 2H, CH$_2$), 4.94 (s, 2H, CH); $^{13}$C NMR (75 MHz, CDCl$_3$, Me$_4$Si, 25 $^\circ$C): $\delta$ = 22.60 (2 CH$_2$), 28.23 (6 CH), 32.48 (2 CH$_2$), 36.46 (6 CH$_2$), 37.66 (2 quat. C), 40.04 (6 CH$_2$), 56.22 (2 CH), 79.36 (2 quat. C), 179.26 (2 quat. C); HRMS calcd. for C$_{30}$H$_{41}$Br$_2$N$_2$ [M+H]$^+$: 587.1631, found 587.1630.

**2c**, yellow solid, yield: 49% (488 mg); $^1$H NMR (300MHz, CDCl$_3$, Me$_4$Si, 25 $^\circ$C): $\delta$ = 1.55-1.79 (m, 4H, CH$_2$), 2.08-2.15 (m, 2H, CH$_2$), 2.36 (s, 6H, CH$_3$), 2.82-2.86 (m, 2H, CH$_2$), 5.62 (s, 2H,
CH), 7.20 (d, J = 8.4 Hz, 4H, CH), 7.73 (d, J = 8.4 Hz, 4H, CH); 13C NMR (75 MHz, CDCl3, Me4Si, 25 °C): δ = 21.38 (2 CH₃), 22.29 (2 CH₂), 33.41 (2 CH₂), 56.21 (2 CH), 80.99 (2 quat. C), 128.54 (4 CH), 128.85 (2 quat. C), 129.26 (4 CH), 141.84 (2 quat. C), 168.15 (2 quat. C); HRMS calcd. for C₂₄H₂₅Br₂N₂ [M+H]⁺: 499.0379, found 499.0379.

2d, yellow solid, yield: 42% (360 mg); ¹H NMR (300MHz, CDCl3, Me₄Si, 25 °C): δ = 1.15 (s, 18H, CH₃), 1.32-1.39 (m, 4H, CH₂), 2.00-2.07 (m, 2H, CH₂), 2.52-2.56 (m, 2H, CH₂), 4.97 (s, 2H, CH); 13C NMR (75 MHz, CDCl3, Me4Si, 25 °C): δ = 22.54 (2 CH₂), 29.48 (6 CH₃), 32.33 (2 CH), 35.58 (2 quat. C), 56.68 (2 CH), 80.12 (2quat. C), 179.55 (2 quat. C); HRMS calcd. for C₁₈H₂₉Br₂N₂ [M+H]⁺: 431.0692, found 431.0688.

2e, yellow solid, yield: 75%(606 mg); ¹H NMR (300MHz, CDCl3, Me4Si, 25 °C): δ = 1.22 (s, 18H, CH₃), 1.54 (s, 6H, CH₃), 4.95 (s, 2H, CH); 13C NMR (75 MHz, CDCl3, Me4Si, 25 °C): δ = 19.24 (2 CH₃), 29.43 (6 CH₃), 35.78 (2quat. C), 56.10 (2CH), 83.01 (2quat. C), 181.13 (2quat. C); HRMS calcd. for C₁₆H₂₇Br₂N₂ [M+H]⁺: 405.0463, found 405.0470.

2f, yellow solid, yield: 73%(712 mg); ¹H NMR (400MHz, CDCl3, Me₄Si, 25 °C): δ = 0.93 (t, J = 7.2 Hz, 6H, CH₃), 1.21 (s, 18H, CH₃), 1.32-1.37 (m, 2H, CH₂), 1.52-1.60 (m, 2H, CH₂), 1.67-1.74 (m, 2H, CH₂), 1.90-1.98 (m, 2H, CH₂); 13C NMR (100 MHz, CDCl3, Me₄Si, 25 °C): δ = 14.03 (2 CH₃), 23.37 (2 CH₂), 26.97 (2 CH₂), 29.48 (6 CH₃), 32.33 (2 CH₂), 35.88 (2quat. C), 54.51 (2 CH), 86.00 (2quat. C), 180.41 (2quat. C); HRMS calcd. for C₂₂H₃₉Br₂N₂ [M+H]⁺: 489.1402, found 489.1497.

General Procedure for the Preparation of 2,6-Diazasemibuvallenes 3. Li (1.1 mmol, 8.4 mg) was added to a solution of α,α'-dibromo-Δ¹-bipyrrolines 2 (0.5 mmol) in 5 ml THF in a 25 ml round-bottom flask in glove box, the mixture was stirred at room temperature for 2-4 h. The solvent was evaporated in vacuo to give brown solid. This solid was dissolved in THF-d₈ and monitored by NMR to confirm α,α'-dibromo-Δ¹-bipyrroline was totally disappeared. The THF and THF-d₈ was evaporated in vacuo to give brown solid again. Then the 2,6-Diazasemibuvallene 3 was extracted by mixture solvent (Hexane:Et₂O = 3:1) diethyl ether from brown solid, and the salt (LiBr) was removed. 3a, yellow solid, yield: 81%(126mg); ¹H NMR (300MHz, THF-d₈, 25 °C): δ = 1.29-1.36 (m, 4H, CH₂), 1.68-1.78 (m, 2H, CH₂), 2.16-2.23 (m, 2H, CH₂), 5.55 (s, 2H, CH), 7.19-7.26 (m, 6H, CH), 7.71-7.74 (m, 4H, CH); 13C NMR (75 MHz, THF-d₈, Me₄Si, 25 °C): δ = 22.49 (2 CH₂), 28.94 (2
3b (CAS 1387574-71-1), yellow solid, yield: 75%(160 mg); $^1$H NMR (300MHz, THF-d$_8$, 25 °C): $\delta$ = 1.12-2.01 (m, 6H, CH; 32H, CH$_2$), 4.73 (s, 2H, CH); $^{13}$C NMR (75 MHz, THF-d$_8$, 25 °C): $\delta$ = 22.29 (2 CH$_2$), 28.94 (2 CH$_2$), 29.41 (6 CH), 36.94 (2 quat. C), 37.71 (6 CH$_2$), 41.46 (6 CH$_2$), 79.00 (2 quat. C), 99.26 (2 CH), 163.22 (2 quat. C).

3c, yellow solid, yield: 79%(134mg); $^1$H NMR (300MHz, THF-d$_8$, 25 °C): $\delta$ = 1.28-1.35 (m, 2H, CH$_2$), 1.61-1.72 (m, 4H, CH$_2$), 2.11-2.36 (m, 2H, CH$_2$), 2.23 (s, 6H, CH$_3$), 5.47 (s, 2H, CH), 7.03 (d, J = 8.1 Hz, 4H, CH), 7.60 (d, J = 8.1 Hz, 4H, CH); $^{13}$C NMR (75 MHz, THF-d$_8$, 25 °C): $\delta$ = 21.18 (2 CH$_3$), 22.42 (2 CH$_2$), 28.89 (2 CH$_2$), 79.17 (2 quat. C), 100.21 (2 CH), 127.59 (4 CH), 129.57 (4 CH), 133.26 (2 quat. C), 139.45 (2 quat. C), 153.00 (2 quat. C). Elemental Analysis Calcd (%) for C$_{24}$H$_{24}$N$_2$: C, 84.67; H, 7.11; N, 8.23; Found: C, 83.84; H, 6.78; N, 7.95.

3d (CAS 1387574-88-0), yellow solid, yield: 92%(125 mg); $^1$H NMR (300MHz, THF-d$_8$, 25 °C): $\delta$ = 1.05 (s, 18H, CH$_3$), 1.16-1.27 (m, 4H, CH$_2$), 1.48-1.56 (m, 2H, CH$_2$), 1.91-1.96 (m, 2H, CH$_2$), 4.77 (s, 2H, CH); $^{13}$C NMR (75 MHz, THF-d$_8$, 25 °C): $\delta$ = 22.26 (2 CH$_2$), 28.90 (2 CH$_2$), 28.96 (6 CH$_3$), 34.75 (2 quat. C), 79.56 (2 quat. C), 99.56 (2 CH), 163.25 (2 quat. C).

3e (CAS 1387574-76-6), yellow solid, yield: 88%(106 mg); $^1$H NMR (300MHz, THF-d$_8$, 25 °C): $\delta$ = 1.04 (s, 18H, CH$_3$), 1.14 (s, 6H, CH$_3$), 4.70 (s, 2H, CH); $^{13}$C NMR (75 MHz, THF-d$_8$, 25 °C): $\delta$ = 15.62 (2 CH$_3$), 28.91 (6 CH$_3$), 34.78 (2 quat. C), 80.37 (2 quat. C), 98.44 (2 CH), 162.98 (2 quat. C).

3f (CAS 1387574-77-7), yellow solid, yield: 94%(155 mg); $^1$H NMR (400MHz, THF-d$_8$, 25 °C): $\delta$ = 0.85 (t, J = 7.2 Hz, 6H, CH$_3$), 1.02 (s, 18H, CH$_3$), 1.25-1.30 (m, 8H, CH$_2$), 1.49-1.52 (m, 4H, CH$_2$), 4.75 (s, 2H, CH); $^{13}$C NMR (100 MHz, THF-d$_8$, 25 °C): $\delta$ = 14.40 (2 CH$_3$), 24.05 (2 CH$_2$), 28.34 (2 CH$_2$), 28.94 (6 CH$_3$), 30.01 (2 CH$_2$), 34.90 (2 quat. C), 83.48 (2 quat. C), 96.56 (2 CH), 162.89 (2 quat. C).

General Procedure for the Preparation of $\alpha,\alpha'$-Dibromo-$\Delta^1$-bipyrrroles 4. NBS (20.0 mmol, 3.56 g) was added to a solution of $\Delta^1$-bipyrrroles 1 (2.0 mmol) in 20 ml CCl$_4$ in a 50 ml Schlenk tube, the mixture was stirred at 80 °C for 48 h. The reaction mixture was then quenched with water and extracted with acetic ether. The extract was washed with brine and dried over
MgSO₄. The solvent was evaporated in vacuo to give yellow solid, which was purified by column chromatography (Petrol Ether: Ethyl Acetate = 50:1) to afford products α,α,α’,α’-tetrabromo-Δ¹-bipyrrolines 4.

4a, yellow solid, yield: 81% (1.012 g). ¹H NMR (400MHz, THF-d₈, 25 °C): δ = 1.61-1.69 (m, 2H, CH₂), 1.78-1.81 (m, 2H, CH₂), 2.53-2.57 (m, 2H, CH₂), 2.87-2.91 (m, 2H, CH₂), 7.37-7.46 (m, 6H, C₆H₅); ¹³C NMR (100 MHz, THF-d₈, TMS, 25 °C): δ = 23.1 (2 CH₂), 32.1 (2 CH₂), 69.6 (2 quat. C), 80.3 (2 quat. C), 128.9 (4 CH), 131.0 (2 CH), 131.1 (4 CH), 132.3 (2 quat. C), 166.0 (2 C=N). HRMS: m/z: calcd for C₂₂H₁₉Br₄N₂ [M+H]⁺: 626.8202, found: 626.8199.

4b, yellow solid, yield: 78% (1.068g). ¹H NMR (400MHz, CDCl₃, TMS, 25 °C): δ = 1.67-1.72 (m, 2H, CH₂), 1.79-1.81 (m, 2H, CH₂), 2.49-2.54 (m, 2H, CH₂), 2.90-2.93 (m, 2H, CH₂), 3.83 (s, 6H, CH₃), 6.90 (d, J = 8 Hz, 4H, C₆H₅); ¹³C NMR (100 MHz, CDCl₃, TMS, 25 °C): δ = 22.2 (2 CH₂), 31.1 (2 CH₂), 55.5 (2 CH₃O), 69.5 (2 quat. C), 79.2 (2 quat. C), 113.6 (4 CH), 122.6 (2 quat. C), 131.9 (4 CH), 162.3 (2 quat. C), 165.1 (2 C=N). HRMS: m/z: calcd for C₂₄H₂₃Br₄O₂N₂ [M+H]⁺: 686.8416, found: 686.8419.

4c, yellow solid, yield: 63% (823 mg). ¹H NMR (400MHz, CDCl₃, TMS, 25 °C): δ = 1.68-1.71 (m, 2H, CH₂), 1.81-1.83 (m, 2H, CH₂), 2.37 (s, 6H, CH₃), 2.54-2.58 (m, 2H, CH₂), 2.92-2.95 (m, 2H, CH₂), 7.25-7.33 (m, 4H, C₆H₅), 7.97 (s, 2H, C₆H₅); ¹³C NMR (100 MHz, CDCl₃, TMS, 25 °C): δ = 21.5 (2 CH₂), 22.1 (2 CH₂), 30.8 (2 CH₃), 69.0 (2 quat. C), 79.3 (2 quat. C), 127.1 (2 CH), 127.9 (2 CH), 130.0 (2 quat. C), 130.5 (2 CH), 132.4 (2 CH), 137.9 (2 quat. C), 166.0 (2 C=N). HRMS: m/z: calcd for C₂₄H₂₃Br₄O₂N₂ [M+H]⁺: 654.8518, found: 654.8522.

4d, yellow solid, yield: 83% (971 mg). ¹H NMR (400MHz, CDCl₃, TMS, 25 °C): δ = 1.40-1.43 (m, 2H, CH₂), 1.44 (s, 18H, CH₃), 1.71-1.74 (m, 2H, CH₂), 2.45-2.52 (m, 2H, CH₂), 2.65-2.69 (m, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃, TMS, 25 °C): δ = 22.3 (2 CH₂), 29.7 (2 CH₂), 29.9 (6 CH₃), 37.8 (2 quat. C), 70.2 (2 quat. C), 77.8 (2 quat. C) 173.8 (2 C=N). HRMS: m/z: calcd for C₁₈H₂₃Br₄N₂ [M+H]⁺: 586.8829, found: 586.8825.

4e, yellow solid, yield: 76% (977 mg). ¹H NMR (400MHz, THF-d₈, 25 °C): δ = 0.93 (t, J = 8Hz, 6H, CH₃), 1.29-1.37 (m, 8H, CH₂), 1.48 (s, 18H, CH₃), 1.90-1.94 (m, 2H, CH₂), 2.24-2.31 (m, 2H, CH₂); ¹³C NMR (100 MHz, THF-d₈, 25 °C): δ = 14.3 (2 CH₃), 24.4 (2 CH₂), 26.9 (2
CH₂), 30.7 (2 CH₂), 35.2 (2 CH₂), 39.1 (2 quat. C), 68.9 (2 quat. C), 84.5 (2 quat. C), 176.4 (2 C=N).


**General Procedure for the Preparation of 2,6-Diazasemibuvallenes 5.** Li (1.1 mmol, 8.4 mg) was added to a solution of α,α′,α′-dibromo-Δ¹-bipyrrrolines 4 (0.5 mmol) in 5 ml THF in a 25 ml round-bottom flask in glove box, the mixture was stirred at room temperature for 2-4 h. The solvent was evaporated in vacuo to give brown solid. This solid was dissolved in THF-d₈ and monitored by NMR to confirm α,α,α′,α′-dibromo-Δ¹-bipyrrrole was totally disappeared. The THF and THF-d₈ was evaporated in vacuo to give brown solid again. Then the 4,8-dibromo-2,6-diazasemibuvallenes were extracted by mixture solvent (Hexane:Et₂O = 4:1) diethyl ether from brown solid, and the salt (LiBr) was removed.

5a, yellow solid, yield: 83% (195 mg). ¹H NMR (400MHz, THF-d₈, 25 °C): δ = 1.27-1.36 (m, 2H, CH₂), 1.76-1.78 (m, 4H, CH₂), 2.39-2.42 (m, 2H, CH₂), 7.32-7.33 (m, 6H, C₆H₅), 7.78-7.80 (m, 4H, C₆H₅); ¹³C NMR (100 MHz, THF-d₈, 25 °C): δ = 22.0 (2 CH₂), 26.9 (2 CH₂), 79.4 (2 quat. C), 99.0 (2 quat. C), 128.9 (4 CH), 129.0 (4 CH), 130.5 (2 CH), 133.9 (2 quat. C), 151.8 (2 C=N). Elemental Analysis Calcd (%) for C₂₂H₁₈Br₂N₂: C, 56.20; H, 3.86; N, 5.96; Found: C, 56.09; H, 3.71; N, 5.85.

5b, yellow solid, yield: 73% (193 mg). ¹H NMR (400MHz, THF-d₈, 25 °C): δ = 0.86-0.88 (m, 2H, CH₂), 1.27-1.36 (m, 4H, CH₂), 1.73-1.77 (m, 2H, CH₂), 3.76 (s, 6H, OCH₃), 6.85 (d, J = 8 Hz, 4H, C₆H₅), 7.75 (d, J = 8 Hz, 4H, C₆H₅); ¹³C NMR (100 MHz, THF-d₈, 25 °C): δ = 22.2 (2 CH₂), 27.1 (2 CH₂), 55.8 (2 CH₃O), 79.0 (2 quat. C), 114.4 (4 CH), 126.6 (2quat. C), 130.7 (4 CH), 151.1 (2quat. C), 162.0 (2 C=N). Elemental Analysis Calcd (%) for C₂₄H₂₂Br₂N₂O₂: C, 54.36; H, 4.18; N, 5.28; Found: C, 54.09; H, 4.03; N, 5.11.

5c, yellow solid, yield: 89% (190 mg). ¹H NMR (400MHz, THF-d₈, 25 °C): δ = 1.22 (s, 18H, CH₃), 1.29-1.31 (m, 2H, CH₂), 1.37-1.41 (m, 4H, CH₂), 2.16-2.20 (m, 2H, CH₂); ¹³C NMR (100 MHz, THF-d₈, 25 °C): δ = 21.9 (2 CH₂), 26.7 (2 CH₂), 28.7 (6 CH₃), 35.8 (2quat. C), 78.5 (2quat. C), 98.8 (2quat. C), 159.4 (2 C=N). Elemental Analysis Calcd (%) for C₁₈H₂₆Br₂N₂: C, 50.25; H, 6.09; 14; N, 6.51; Found: C, 50.04; H, 5.98; N, 6.38.
Procedure for the Preparation of Compound 6. 4,8-dibromo-2,6-diazasemibuvallene 5e (0.3 mmol) was dissolved in THF-d8 at room temperature in glove box. This solution was monitored by NMR. Almost 30 days later, 4,8-dibromo-2,6-diazasemibuvallene 5e was totally transformed to compound 6. At the same time, another part of this THF-d8 solution of 5e was shined by light, and compound 6 was formed in 3 days. The solvent was evaporated in vacuo to give yellow solid, which was purified by column chromatography (Petrol Ether: Ethyl Acetate = 100:1) to afford pure product 6 (105 mg) in 82% yield. Single crystals of 6 suitable for X-ray structural analysis were grown in hexane at room temperature.

6, yellow solid, yield: 82% (105 mg). \(^1\)H NMR (400MHz, THF-d8, 25 °C): \(\delta = 1.23\) (brs, 1H, CH2), 1.29 (brs, 1H, CH2), 1.33 (s, 9H, CH3), 1.45 (s, 9H, CH3), 1.55-1.68 (m, 4H, CH2), 2.38-2.45 (m, 1H, CH2), 2.79-2.84 (m, 1H, CH2); \(^1^3\)C NMR (100 MHz, THF-d8, 25 °C): \(\delta = 22.8\) (1 CH2), 25.8 (1 CH2), 27.8 (3 CH3), 28.6 (3 CH3), 34.7 (1 CH2), 36.5 (1 quat. C), 37.7 (1 quat. C), 41.6 (1 CH2), 86.0 (1 quat. C), 95.3 (1 quat. C), 107.9 (1 quat. C), 178.9 (1 quat. C), 181.0 (1 C=N), 181.3 (1 C=N). HRMS: \(m/z\) calced for C18H27Br2N2 [M+H]^+: 429.0464, found: 429.0473.

3) X-ray crystallographic studies

The single crystals of 4a, and 6 suitable for X-ray analysis were grown as shown in the experimental section. Data collections for 4a and 6 were performed at 180 K on SuperNova diffractometer, using monochromated Mo Kα radiation (\(\lambda = 0.71073 \) Å). The determination of crystal class and unit cell parameters was carried out by the CrystalClear (Rigaku Inc. 2007) program package for 4a and 6. The raw frame data were processed using CrystalClear (Rigaku Inc. 2007) for 4a and 6 to yield the reflection data file. The structures of 4a and 6 were solved by use of SHELXTL program. Refinement was performed on \(F^2\) anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds 4a and 6 are summarized in Table S1 - Table S4. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1056585 (4a), CCDC 1056586 (6). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via
Figure S1. ORTEP drawing of 4a with 30% probability thermal ellipsoids.

Table S1. Crystal data and structure refinement for 4a.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>4a</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{23}H_{18}Br_{4}N_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>630.02</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>180.00(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbca</td>
</tr>
<tr>
<td>a/Å</td>
<td>10.7971(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.2395(13)</td>
</tr>
<tr>
<td>c/Å</td>
<td>26.1285(19)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>4299.2(6)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>ρ_{calc} g/cm³</td>
<td>1.947</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>7.500</td>
</tr>
<tr>
<td>F(000)</td>
<td>2432.0</td>
</tr>
</tbody>
</table>
Crystal size/mm³: 0.2 × 0.2 × 0.2
Radiation: Mo Kα (λ = 0.7107)
2θ range for data collection/°: 6.728 to 52.044
Index ranges: -13 ≤ h ≤ 9, -18 ≤ k ≤ 11, -24 ≤ l ≤ 32
Reflections collected: 10810
Independent reflections: 4215 [Rint = 0.0564, Rsigma = 0.0792]
Data/restraints/parameters: 4215/0/253
Goodness-of-fit on F²: 1.065
Final R indexes [I>=2σ (I)]: R₁ = 0.0529, wR₂ = 0.0992
Final R indexes [all data]: R₁ = 0.0826, wR₂ = 0.1106
Largest diff. peak/hole / e Å⁻³: 1.81/-0.62

**Figure S2.** ORTEP drawing of 6 with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

**Table S2. Crystal data and structure refinement for 6.**

<table>
<thead>
<tr>
<th>Identification code</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₈H₂₆Br₂N₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>430.23</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>180.01(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
</tbody>
</table>
Space group
P2₁/c

a/Å 6.6642(4)
b/Å 19.8278(16)
c/Å 14.8224(10)
α/° 90
β/° 101.924(7)
γ/° 90
Volume/Å³ 1916.3(2)
Z 4
ρ calc g/cm³ 1.491
μ/mm⁻¹ 4.229
F(000) 872.0
Crystal size/mm³ 0.1 × 0.03 × 0.02
Radiation MoKα (λ = 0.71073)
2Θ range for data collection/° 5.618 to 52.042
Index ranges -8 ≤ h ≤ 8, -22 ≤ k ≤ 24, -18 ≤ l ≤ 18
Reflections collected 11160
Independent reflections 3773 [R int = 0.0696, R σ = 0.0903]
Data/restraints/parameters 3773/0/205
Goodness-of-fit on F² 1.028
Final R indexes [I>2σ(I)] R₁ = 0.0537, wR₂ = 0.1172
Final R indexes [all data] R₁ = 0.0978, wR₂ = 0.1320
Largest diff. peak/hole / e Å⁻³ 0.97/-0.63

4) References
Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: (Madison, WI, 1997).
3) Copies of $^1$H NMR and $^{13}$C NMR spectra of all new compounds

2a-$^1$H NMR

![NMR Spectra Diagram]

**File Information**
- **DFILE**: D:\\Gd Files\LUO QIAN\5-COMMT
- **DATIM**: Sat Jul 04 15:43:27 2005
- **OBMNIC**: 1H
- **OBFPQ**: 300.40 MHz
- **OBSET**: 130.00 KHz
- **OBFIN**: 1150.0 Hz
- **POINT**: 32768
- **FREQ**: 6013.2 Hz
- **SCANS**: 16
- **ACQTM**: 5.449 sec
- **PD**: 1.551 sec
- **FM1**: 5.0 us
- **IRBUC**: 1M
- **CTEMP**: 25.0 c
- **SLWNT**: CDCl3
- **HYPPF**: 0.00 ppm
- **BF**: 0.09 Hz
- **RGAIN**: 16
2a-$^{13}$C NMR

---

**S12**

---

**S12**
2b-\textsuperscript{1}H NMR
2b-$^{13}$C NMR
2c-1H NMR
$^{2c}$-$^{13}$C NMR
2d-\textsuperscript{1}H NMR
2d-\textsuperscript{13}C NMR
$^{2e}\text{-}^1\text{H NMR}$

![NMR spectrum diagram with peaks at various ppm values]
2e\textsuperscript{13}C NMR
2f-\textsuperscript{1}H NMR
$^{2f}$-$^{13}$C NMR
3a-^1^H NMR

Ph

Ph

S23
3a-\textsuperscript{13}C NMR

PFILE D:\Old Files\LUO QIAN\5-
COMMT
DATIM Tue Jul 14 11:54:36 2005
OBNUC 13C
EXPDM BCM
OFREQ 75.45 MHz
OBST 124.00 KHz
OBPIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 216
ACQTM 1.606 sec
PD 1.394 sec
PMI 5.0 us
IRNUC 1H
CTEMP 23.9 C
SLEVET C4D802
REF 67.40 ppm
e 1.20 Hz
RGAIN 26

S24
3b-$^1$H NMR

![NMR Spectrogram](image.png)
3b-$^{13}$C NMR
$3c$-$^1$H NMR

![NMR Spectrum Image]
$3c^{13}$C NMR
3d-^1H NMR

PFILE D:\Old Files\LUO QIAN5-COMET
DATIM Wed Jul 15 12:16:01 2005
OBNUC 1H
EXPFO NON
OFREQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PB 1.551 sec
PW1 5.0 us
IRNUC 1H
CTEMP 24.5 C
SLVET C4D8O2
EXRFF 3.58 ppm
BF 0.09 Hz
R:GAIN 17
3d-^{13}C NMR
$^{3e}$-$^1$H NMR

![NMR spectrum diagram with chemical shifts and peaks labeled: -4.70, -3.68, ~1.14, ~1.04, 2.00, 6.31%, 18.27%]
$3e^{13}C$ NMR
$3f^1H$ NMR
4a-$^1$H NMR

NMR spectrum showing chemical shifts and peaks for the compound 4a. The spectrum includes peaks at various ppm values, indicating the presence of different functional groups and atoms in the molecule. The compound structure is also shown, highlighting the presence of bromine (Br) atoms and other functional groups.

The spectrum has peaks at:
- 8.31, 8.30, 8.29, 7.46, 7.44, 7.39, 7.37 ppm
- 3.58, 2.91, 2.88, 2.87, 2.81, 1.79, 1.78, 1.68, 1.66, 1.64, 1.62, 1.61 ppm

The integration of these peaks provides information about the relative abundance and types of protons in the molecule.
4b-$^1$H NMR

[Chemical structure image]

[Spectroscopic data]
$^{13}$C NMR
$4c^{1}\text{H NMR}$
4c\textsuperscript{13}C NMR
4d-$^1$H NMR
$^{4d}$-$^{13}$C NMR
$^{1}H$ NMR
5a-^1^H NMR

[Diagram of a chemical structure with peaks labeled in ppm]

S45
5a-^{13}C NMR
$5b^{-1}H$ NMR
$^5\text{c}^{\text{13}}\text{C NMR}$

![NMR spectrum graph]

6-¹H NMR
6-$^{13}$C NMR