Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Synthesis of dibromo- and tetrabromo-bipyrrolines 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

^{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_6D_6. Chemical shifts (δ) 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 Kα 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 α,α'-Dibromo-Δ^1-bipyrrolines 2. NBS (4.4 mmol, 783 mg) was added to a solution of Δ^1-bipyrrolines **1** (2.0 mmol) in 20 ml CCl_4 in a 50 ml Schlenk tube, the mixture was stirred at 80 ^{o}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 α,α'-dibromo-Δ^1-bipyrrolines **2a-f**.

2a, colorless solid, yield: 48% (452 mg); ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 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_4Si, 25 ^{o}C): δ = 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 $C_{22}H_{21}Br_2N_2$ $[M+H]^+$: 471.0066, found 471.0058.

2b, yellow solid, yield: 55% (644 mg); ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 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_4Si, 25 ^{o}C): δ = 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 $C_{30}H_{41}Br_2N_2$ $[M+H]^+$: 587.1631, found 587.1630.

2c, yellow solid, yield: 49% (488 mg); ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 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); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 21.38 (2 CH_3), 22.29 (2 CH_2), 33.41 (2 CH_2), 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 $C_{24}H_{25}Br_2N_2$ $[M+H]^+$: 499.0379, found 499.0379.

2d, yellow solid, yield: 42% (360 mg); ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 1.15 (s, 18H, CH_3), 1.32-1.39 (m, 4H, CH_2), 2.00-2.07 (m, 2H, CH_2), 2.52-2.56 (m, 2H, CH_2), 4.97 (s, 2H, CH);^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 22.54 (2 CH_2), 29.48 (6 CH_3), 32.33 (2 CH), 35.58 (2 quat. C), 56.68 (2 CH), 80.12 (2 quat. C), 179.55 (2 quat. C); HRMS calcd. for $C_{18}H_{29}Br_2N_2$ $[M+H]^+$: 431.0692, found 431.0688.

2e, yellow solid, yield: 75%(606 mg); ^{1}H NMR (300MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 1.22 (s, 18H, CH_3), 1.54 (s, 6H, CH_3), 4.95 (s, 2H, CH);^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 19.24 (2 CH_3), 29.43 (6 CH_3), 35.78 (2 quat. C), 56.10(2 CH), 83.01 (2 quat. C), 181.13 (2 quat. C); HRMS calcd. for $C_{16}H_{27}Br_2N_2$ $[M+H]^+$: 405.0463, found 405.0470.

2f, yellow solid, yield: 73%(712 mg); ^{1}H NMR (400MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 0.93 (t, *J* = 7.2 Hz, 6H, CH_3), 1.21 (s, 18H, CH_3), 1.32-1,37 (m, 2H, CH_2), 1.52-1.60 (m, 2H, CH_2), 1.67-1.74 (m, 2H, CH_2), 1.90-1.98 (m, 2H, CH_2);^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, 25 ^{o}C): δ = 14.03 (2 CH_3), 23.37 (2 CH_2), 26.97 (2 CH_2), 29.48 (6 CH_3), 32.33 (2 CH_2), 35.88 (2 quat. C), 54.51 (2 CH), 86.00 (2 quat. C), 180.41 (2 quat. C);HRMS calcd. for $C_{22}H_{39}Br_2N_2$ $[M+H]^+$: 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-Δ^1-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-d_8 and monitored by NMR to comfirm α,α'-dibromo-Δ^1-bipyrroline was totally disappeared. The THF and THF-d_8 was evaporated in vacuo to give brown solid again. Then the 2,6-Diazasemibuvallene **3** was extracted by mixture solvent (Hexane:Et_2O = 3:1) diethyl ether from brown solid, and the salt (LiBr) was removed.

3a, yellow solid, yield: 81%(126mg); ^{1}H NMR (300MHz, THF-d_8, 25 ^{o}C): δ = 1.29-1.36 (m, 4H, CH_2), 1.68-1.78 (m, 2H, CH_2), 2.16-2.23 (m, 2H, CH_2), 5.55 (s, 2H, CH), 7.19-7.26 (m, 6H, CH), 7.71-7.74 (m, 4H, CH);^{13}C NMR (75 MHz, THF-d_8, Me_4Si, 25 ^{o}C): δ = 22.49 (2 CH_2), 28.94 (2

CH_2), 79.47 (2 quat. C), 100.74 (2 CH), 127.56 (4 CH), 128.88 (4 CH), 129.51 (2 CH), 135.81 (2 quat. C), 153.14 (2 quat. C). Elemental Analysis Calcd (%) for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97; Found: C, 83.94; H, 6.28; N, 8.38.

3b *(CAS 1387574-71-1),* yellow solid, yield: 75%(160 mg); ^{1}H NMR (300MHz, THF-d_8, 25 ^{o}C): δ = 1.12-2.01 (m, 6H, CH; 32H, CH_2), 4.73 (s, 2H, CH);^{13}C NMR (75 MHz, THF-d_8, 25 ^{o}C): δ = 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 ^{o}C): δ = 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 ^{o}C): δ = 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 ^{o}C): δ = 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 ^{o}C): δ = 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 ^{o}C): δ = 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 ^{o}C): δ = 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 ^{o}C): δ = 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 ^{o}C): δ = 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 α,α'-Dibromo-Δ^1-bipyrrolines 4. NBS (20.0 mmol, 3.56 g) was added to a solution of Δ^1-bipyrrolines **1** (2.0 mmol) in 20 ml CCl_4 in a 50 ml Schlenk tube, the mixture was stirred at 80 ^{o}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

$MgSO_4$. 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 α,α,α',α'-tetrabromo-Δ^1-bipyrrolines **4**.

4a, yellow solid, yield: 81% (1.012 g). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.61-1.69 (m, 2H, CH_2), 1.78-1.81 (m, 2H, CH_2), 2.53-2.57 (m, 2H, CH_2), 2.87-2.91 (m, 2H, CH_2), 7.37-7.46 (m, 6H, C_6H_5), 8.29-8.31 (m, 4H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, TMS, 25 ^{o}C): δ = 23.1 (2 CH_2), 32.1 (2 CH_2), 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 $C_{22}H_{19}Br_4N_2$ $[M+H]^+$: 626.8202, found: 626.8199.

4b, yellow solid, yield: 78% (1.068g). ^{1}H NMR (400MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 1.64-1.72 (m, 2H, CH_2), 1.79-1.81 (m, 2H, CH_2), 2.49-2.54 (m, 2H, CH_2), 2.90-2.93 (m, 2H, CH_2), 3.83 (s, 6H, CH_3), 6.90 (d, *J* = 8 Hz, 4H, C_6H_5), 8.22 (d, *J* = 8 Hz, 4H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 22.2 (2 CH_2), 31.1 (2 CH_2), 55.5 (2 CH_3O), 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 $C_{24}H_{23}Br_4O_2N_2$ $[M+H]^+$: 686.8416, found: 686.8419.

4c, yellow solid, yield: 63% (823 mg). ^{1}H NMR (400MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 1.68-1.71 (m, 2H, CH_2), 1.81-1.83 (m, 2H, CH_2), 2.37 (s, 6H, CH_3), 2.54-2.58 (m, 2H, CH_2), 2.92-2.95 (m, 2H, CH_2), 7.25-7.33 (m, 4H, C_6H_5), 7.97 (s, 2H, C_6H_5), 8.10-8.12 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 21.5 (2 CH_2), 22.1 (2 CH_2), 30.8 (2 CH_3), 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 $C_{24}H_{23}Br_4N_2$ $[M+H]^+$: 654.8518, found: 654.8522.

4d, yellow solid, yield: 83% (971 mg). ^{1}H NMR (400MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 1.40-1.43 (m, 2H, CH_2), 1.44 (s, 18H, CH_3), 1.71-1.74 (m, 2H, CH_2), 2.45-2.52 (m, 2H, CH_2), 2.65-2.69 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 22.3 (2 CH_2), 29.7 (2 CH_2), 29.9 (6 CH_3), 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 $C_{18}H_{27}Br_4N_2$ $[M+H]^+$: 586.8829, found: 586.8825.

4e, yellow solid, yield: 76% (977 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 0.93 (t, *J* = 8Hz, 6H, CH_3), 1.29-1.37 (m, 8H, CH_2), 1.48 (s, 18H, CH_3), 1.90-1.94 (m, 2H, CH_2), 2.24-2.31 (m, 2H, CH_2); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 14.3 (2 CH_3), 24.4 (2 CH_2), 26.9 (2

CH_2), 30.7 (6 CH_3), 35.2 (2 CH_2), 39.1 (2 quat. C), 68.9 (2 quat. C), 84.5 (2 quat. C), 176.4 (2 C=N). HRMS: *m/z*: calcd for $C_{22}H_{37}N_2$ $[M+H]^+$: 644.9614, found: 644.9617.

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',α'-dibromo-Δ^1-bipyrrolines **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-d_8 and monitored by NMR to comfirm α,α,α',α'-dibromo-Δ^1-bipyrroline was totally disappeared. The THF and THF-d_8 was evaporated in vacuo to give brown solid again. Then the 4,8-dibromo-2,6-diazasemibuvallenes were extracted by mixture solvent (Hexane:Et_2O = 4:1) diethyl ether from brown solid, and the salt (LiBr) was removed.

5a, yellow solid, yield: 83% (195 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.27-1.36 (m, 2H, CH_2), 1.76-1.78 (m, 4H, CH_2), 2.39-2.42 (m, 2H, CH_2), 7.32-7.33 (m, 6H, C_6H_5), 7.78-7.80 (m, 4H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 22.0 (2 CH_2), 26.9 (2 CH_2), 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 $C_{22}H_{18}Br_2N_2$: 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). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 0.86-0.88 (m, 2H, CH_2), 1.27-1.36 (m, 4H, CH_2), 1.73-1.77 (m, 2H, CH_2), 3.76 (s, 6H, OCH_3), 6.85 (d, *J* = 8 Hz, 4H, C_6H_5), 7.75 (d, *J* = 8 Hz, 4H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 22.2 (2 CH_2), 27.1 (2 CH_2), 55.8 (2 CH_3O), 79.0 (2 quat. C), 114.4 (4 CH), 126.6 (2 quat. C), 130.7 (4 CH), 151.1 (2 quat. C), 162.0 (2 C=N). Elemental Analysis Calcd (%) for $C_{24}H_{22}Br_2N_2O_2$: 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). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.22 (s, 18H, CH_3), 1.29-1.31 (m, 2H, CH_2), 1.37-1.41 (m, 4H, CH_2), 2.16-2.20 (m, 2H, CH_2); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 21.9 (2 CH_2), 26.7 (2 CH_2), 28.7 (6 CH_3), 35.8 (2 quat. C), 78.5 (2 quat. C), 98.8 (2 quat. C), 159.4 (2 C=N). Elemental Analysis Calcd (%) for $C_{18}H_{26}Br_2N_2$: 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-d_8 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 transfored 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-d_8, 25 ^{o}C): δ = 1.23 (brs, 1H, CH_2), 1.29 (brs, 1H, CH_2), 1.33 (s, 9H, CH_3), 1.45 (s, 9H, CH_3), 1.55-1.68 (m, 4H, CH_2), 2.38-2.45 (m, 1H, CH_2), 2.79-2.84 (m, 1H, CH_2); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 22.8 (1 CH_2), 25.8 (1 CH_2), 27.8 (3 CH_3), 28.6 (3 CH_3), 34.7 (1 CH_2), 36.5 (1 quat. C), 37.7 (1 quat. C), 41.6 (1 CH_2), 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*: calcd for $C_{18}H_{27}Br_2N_2$ $[M+H]^+$: 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 (λ = 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

www.ccdc.cam.ac.uk/data_request/cif. [2,3]

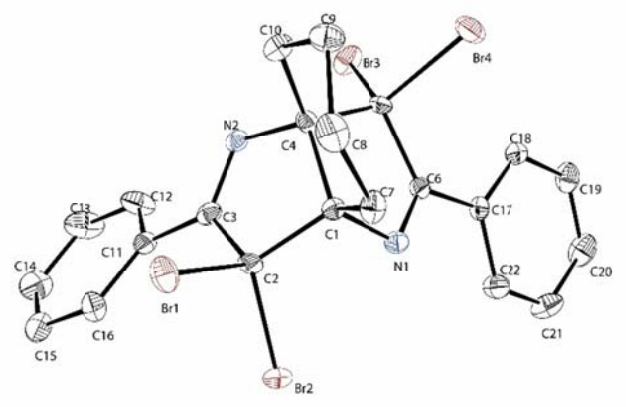


Figure S1. ORTEP drawing of **4a** with 30% probability thermal ellipsoids.

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

Identification code	**4a**
Empirical formula	$C_{22}H_{18}Br_4N_2$
Formula weight	630.02
Temperature/K	180.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.7971(8)
b/Å	15.2395(13)
c/Å	26.1285(19)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4299.2(6)
Z	8
ρ_{calc}g/cm^3	1.947
μ/mm^{-1}	7.500
F(000)	2432.0

Crystal size/mm^3	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 [R_{int} = 0.0564, R_{sigma} = 0.0792]
Data/restraints/parameters	4215/0/253
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.0992
Final R indexes [all data]	R_1 = 0.0826, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	1.81/-0.62

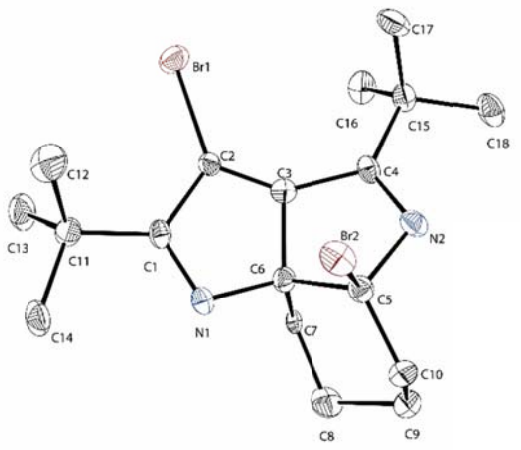


Figure S2. ORTEP drawing of **6** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

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

Identification code	**6**
Empirical formula	$C_{18}H_{26}Br_2N_2$
Formula weight	430.23
Temperature/K	180.01(10)
Crystal system	monoclinic

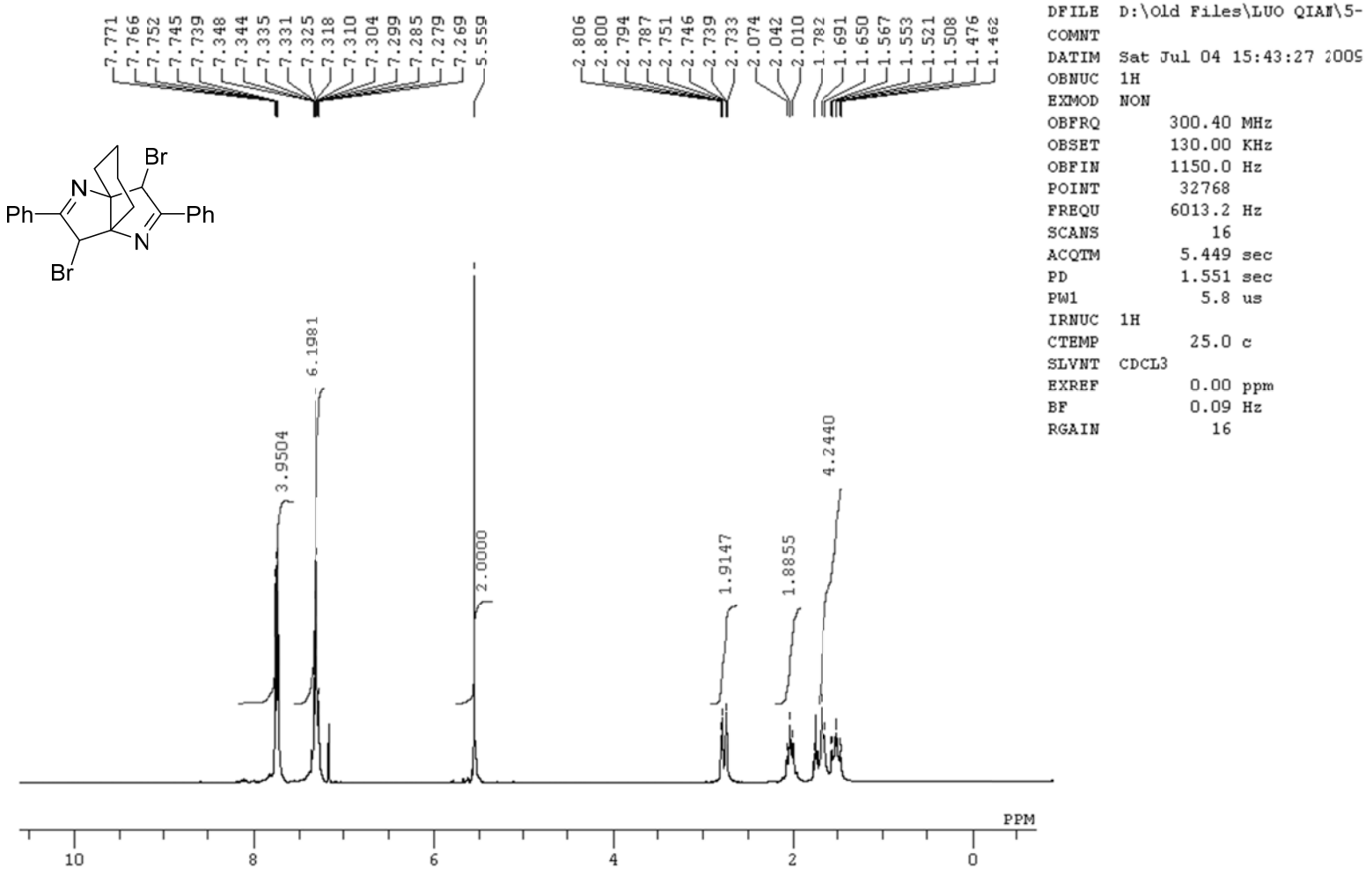
Space group	$P2_1/c$
a/Å	6.6642(4)
b/Å	19.8278(16)
c/Å	14.8224(10)
α/°	90
β/°	101.924(7)
γ/°	90
Volume/$Å^3$	1916.3(2)
Z	4
$\rho_{calc}g/cm^3$	1.491
μ/mm^{-1}	4.229
F(000)	872.0
Crystal size/mm^3	0.1 × 0.03 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.618 to 52.042
Index ranges	$-8 \leq h \leq 8$, $-22 \leq k \leq 24$, $-18 \leq l \leq 18$
Reflections collected	11160
Independent reflections	3773 [R_{int} = 0.0696, R_{sigma} = 0.0903]
Data/restraints/parameters	3773/0/205
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1172
Final R indexes [all data]	R_1 = 0.0978, wR_2 = 0.1320
Largest diff. peak/hole / e $Å^{-3}$	0.97/-0.63

4) References

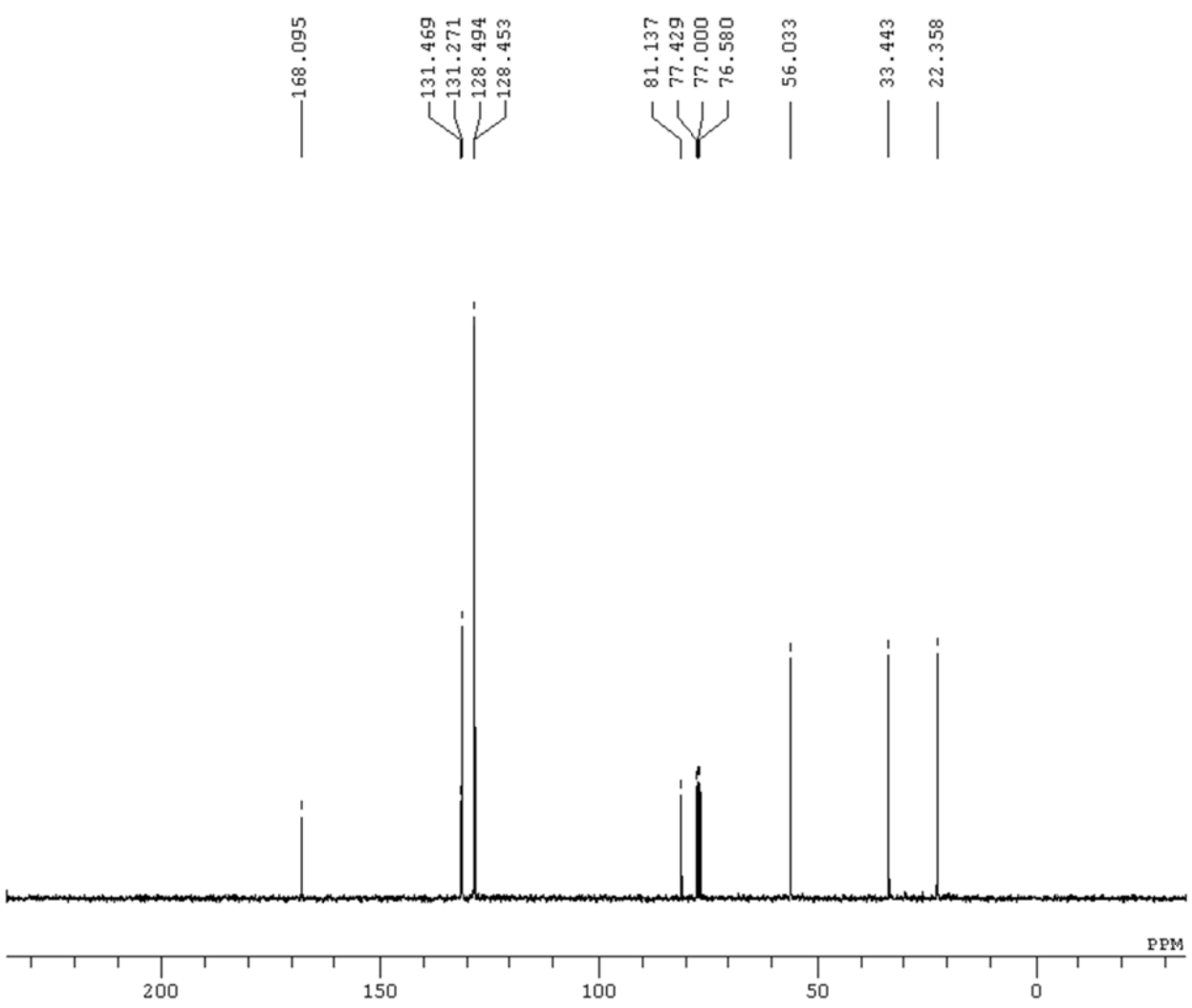
Sheldrick, G. M. SHELXTL 5.10 for Windows NT: *Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.: (Madison, WI, 1997).

3) Copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds

2a-^{1}H NMR

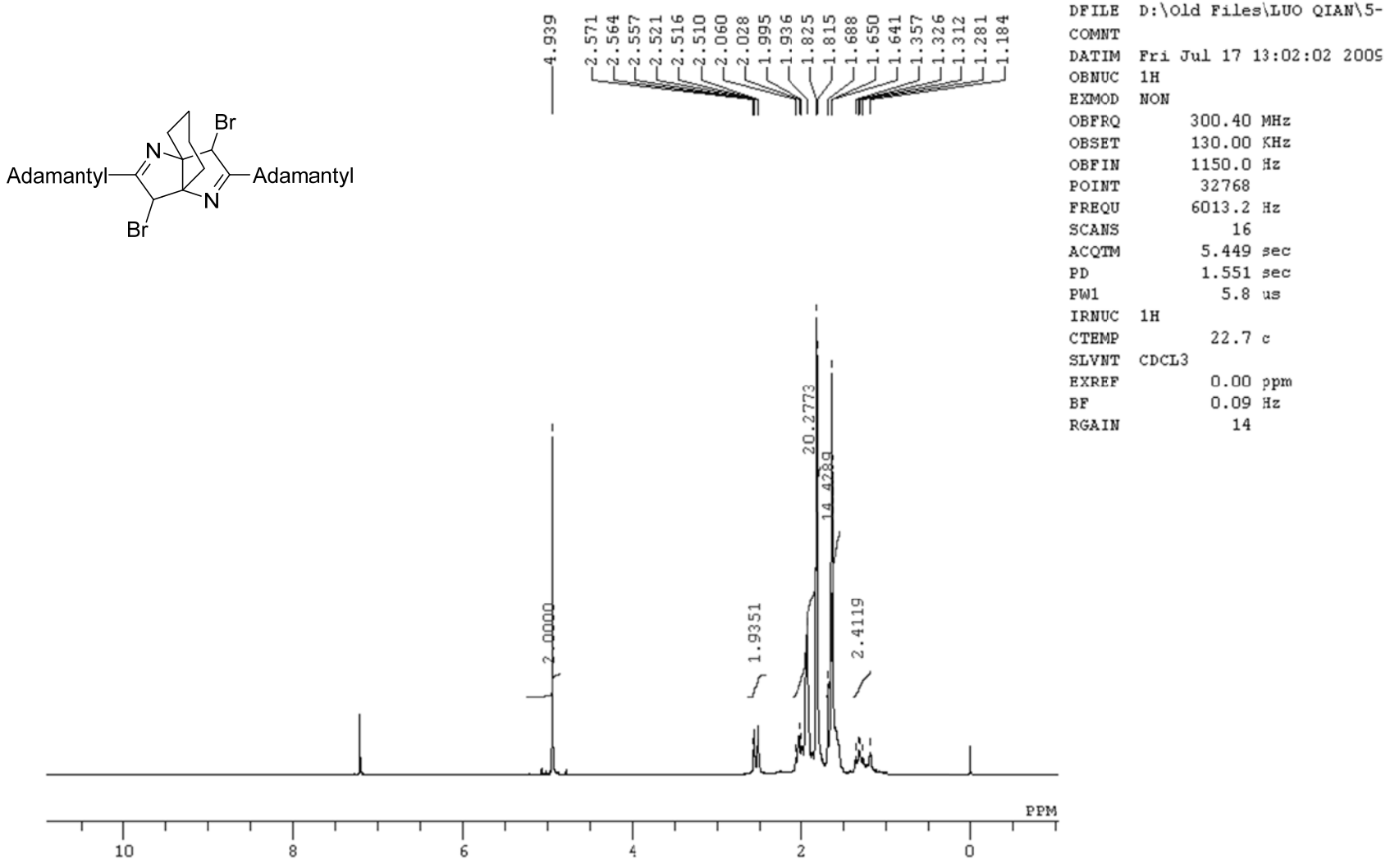


2a-^{13}C NMR

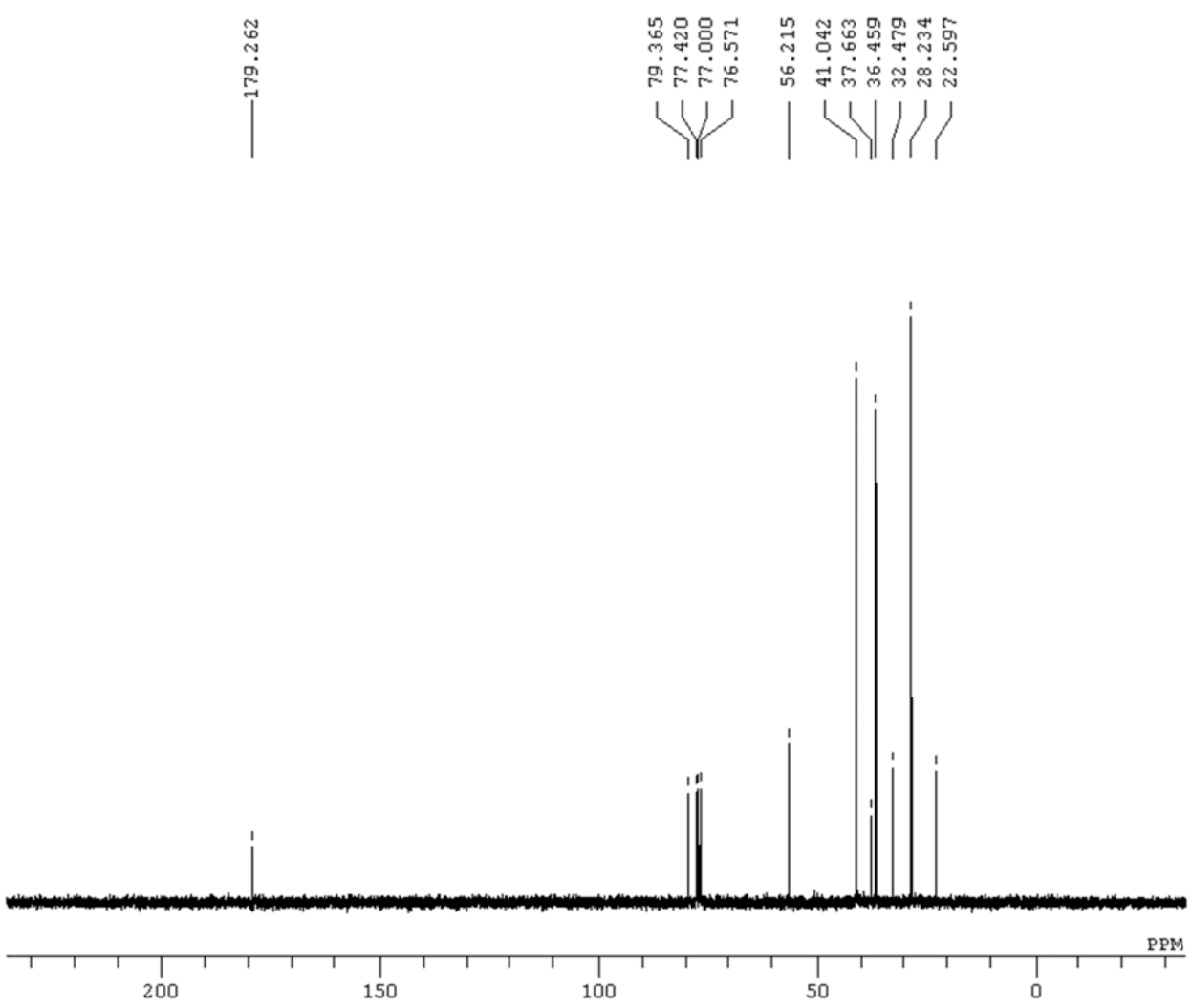



```
DFILE  D:\Old Files\LUO QIAN\5-
COMNT
DATIM  Sat Jul 04 15:35:58 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS           48
ACQTM         1.606 sec
PD            1.394 sec
PW1             5.0 us
IRNUC  1H
CTEMP          25.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.62 Hz
RGAIN            27
```

2b-^{1}H NMR

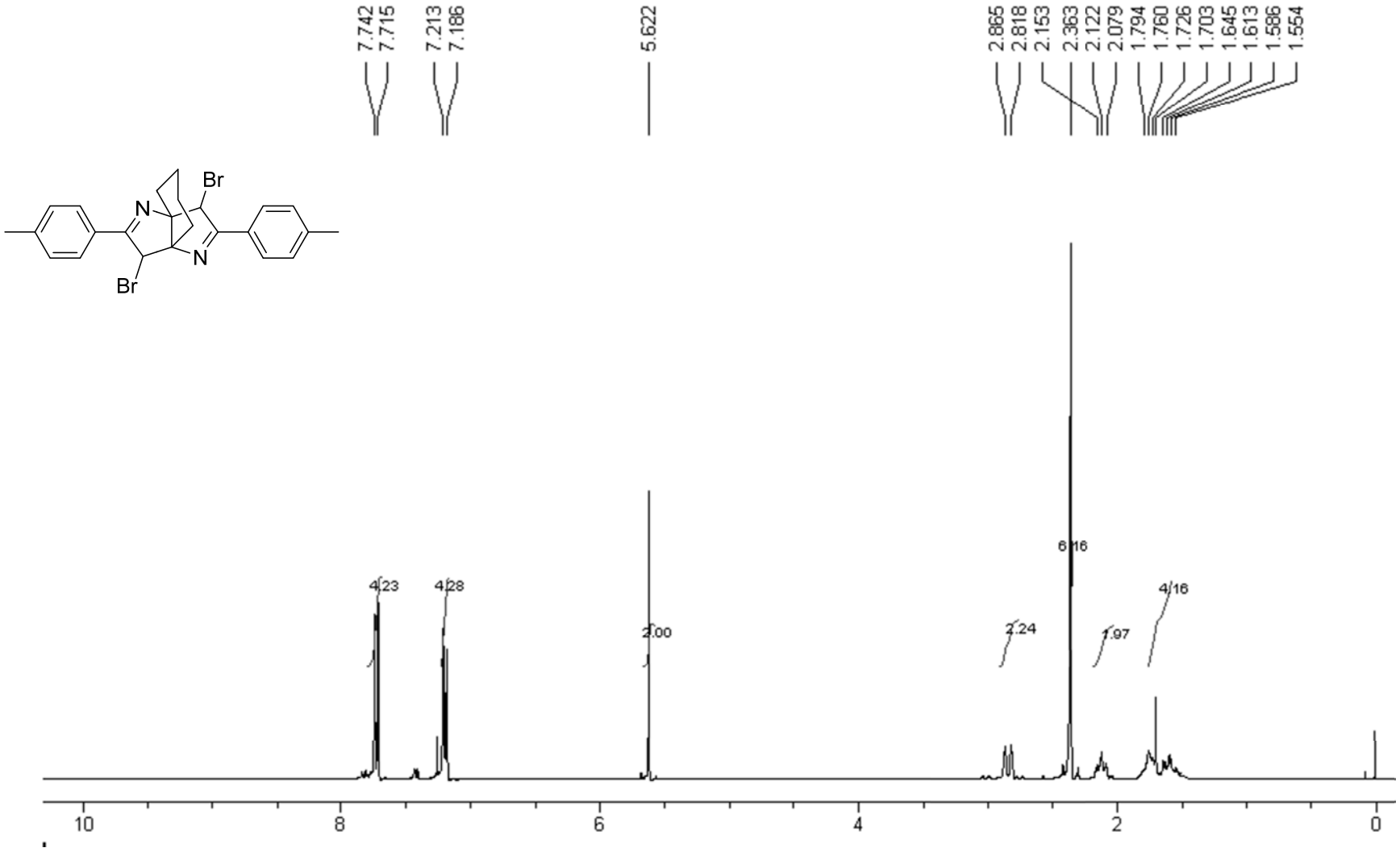

Br
N
Adamantyl
Adamantyl
N
Br
4.939
2.571
2.564
2.557
2.521
2.516
2.510
2.060
2.028
1.995
1.936
1.825
1.815
1.688
1.650
1.641
1.357
1.326
1.312
1.281
1.184
DFILE D:\Old Files\LUO QIAN\5-
COMNT
DATIM Fri Jul 17 13:02:02 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 14
2.0000
1.9351
20.2773
14.4289
2.4119
PPM
10
8
6
4
2
0

2b-^{13}C NMR

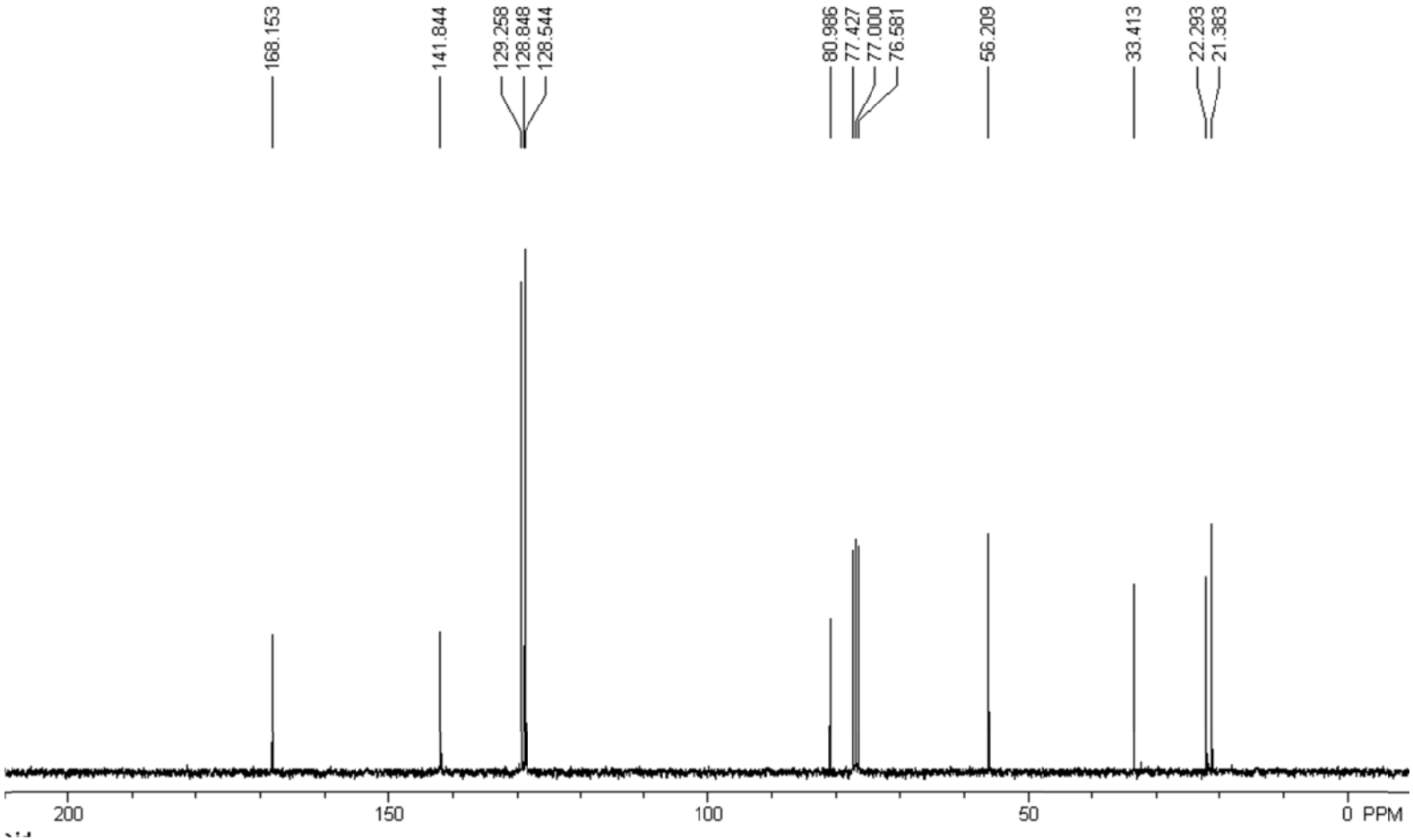



```
DFILE  D:\Old Files\LUO QIAN\5-
COMNT
DATIM  Fri Jul 17 12:54:39 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS           80
ACQTM         1.606 sec
PD            1.394 sec
PW1             5.0 us
IRNUC  1H
CTEMP          23.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.62 Hz
RGAIN            26
```

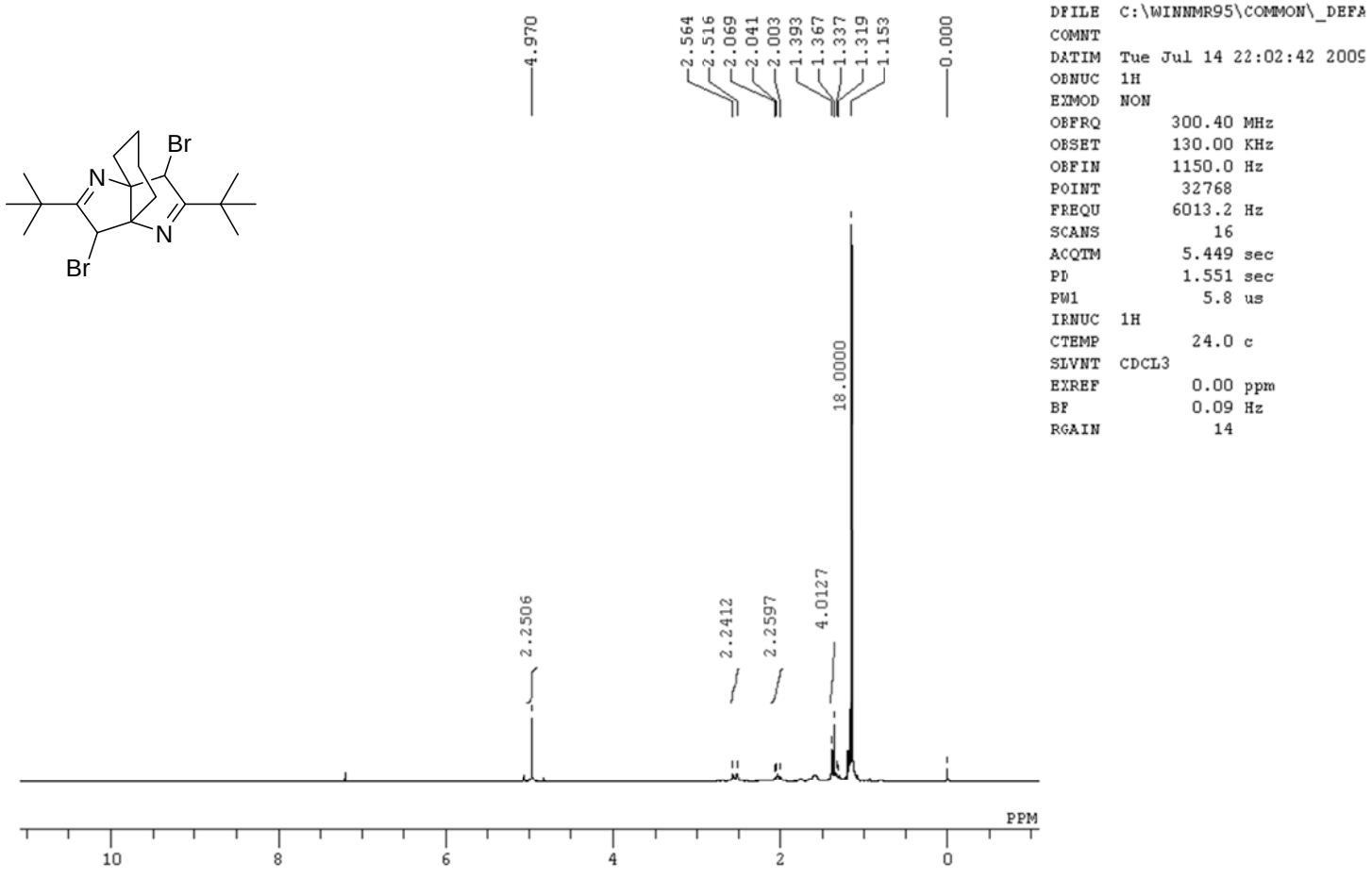
2c-^{1}H NMR


7.742
7.715
7.213
7.186
5.622
2.865
2.818
2.153
2.363
2.122
2.079
1.794
1.760
1.726
1.703
1.645
1.613
1.586
1.554
Br
N
N
Br
4.23
4.28
2.00
2.24
6.16
1.97
4.16
10
8
6
4
2
0

2c-^{13}C NMR

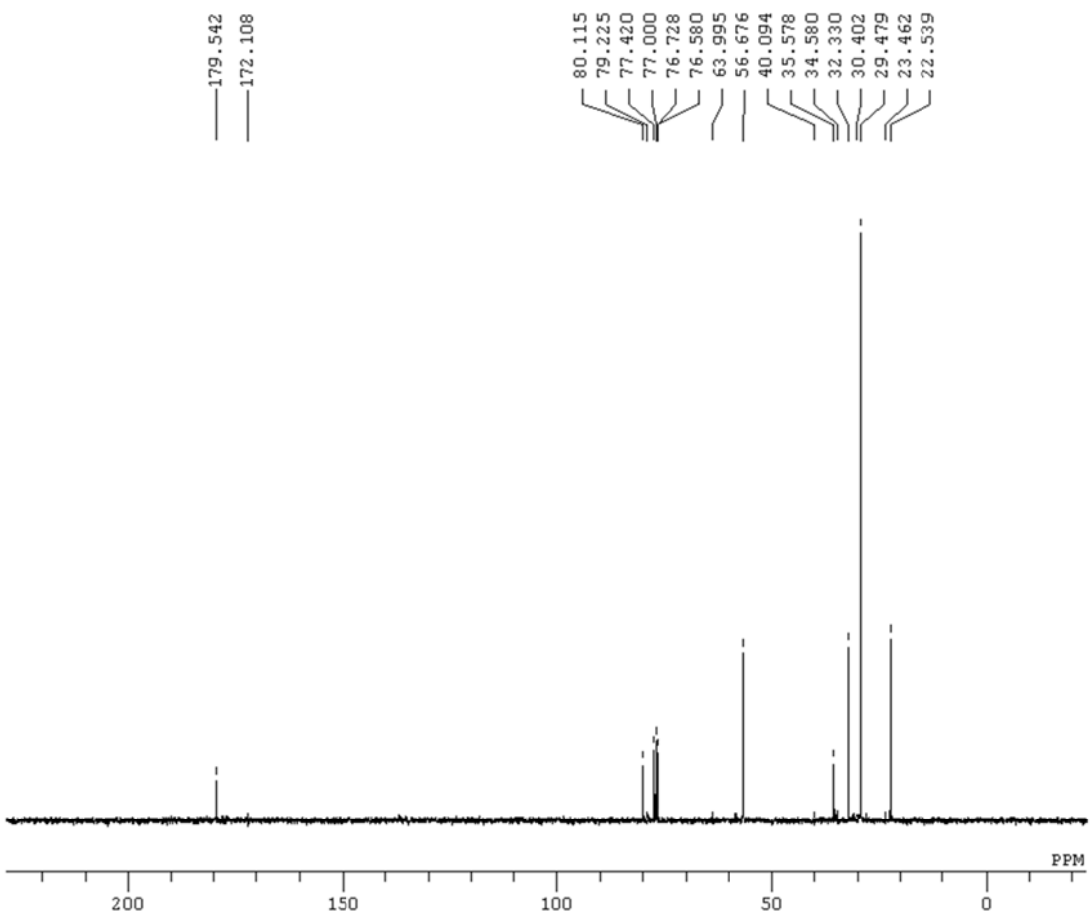

168.153
141.844
129.258
128.848
128.544
80.986
77.427
77.000
76.581
56.209
33.413
22.293
21.383
200
150
100
50
0 PPM

2d-^{1}H NMR



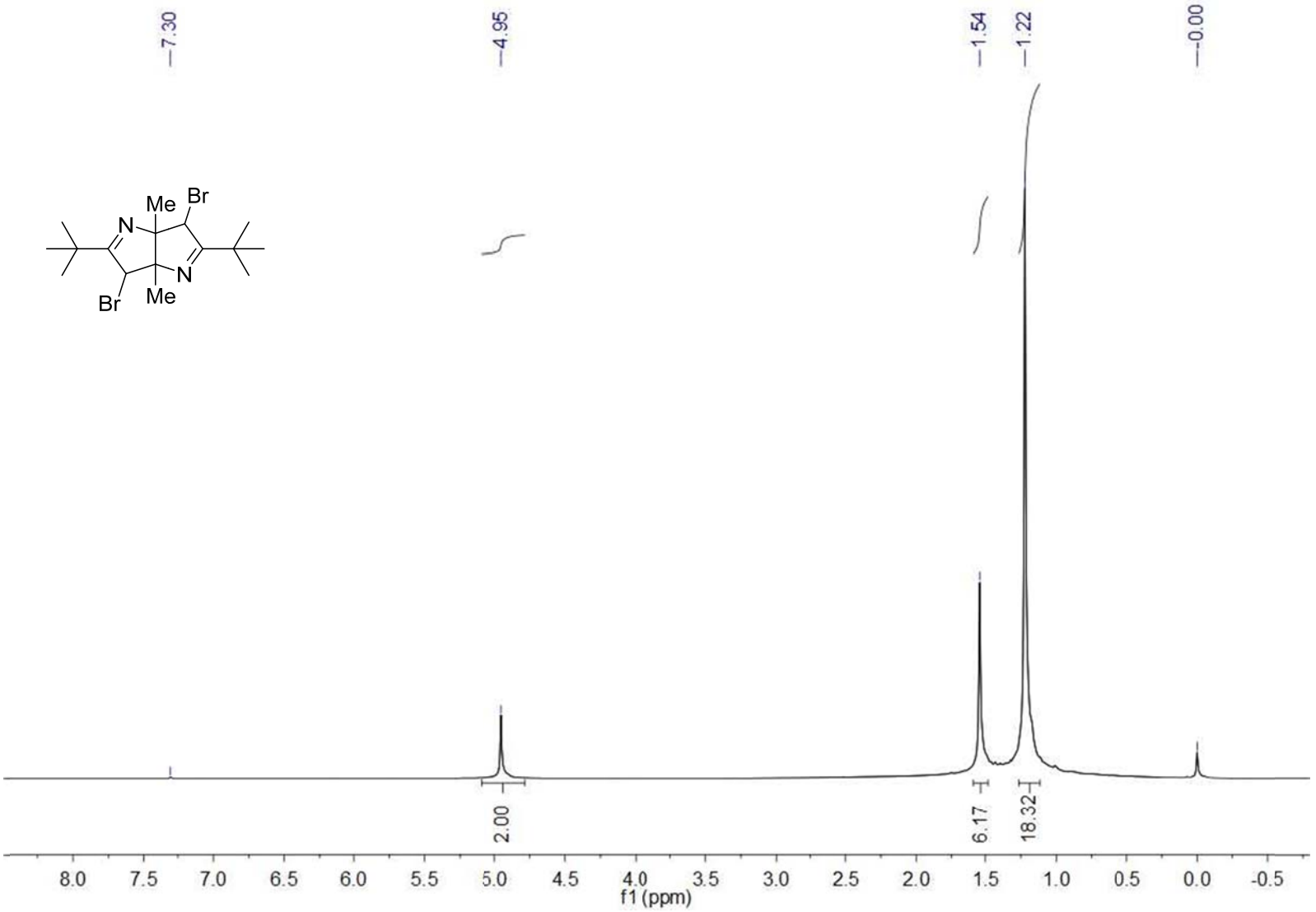

```
DFILE  C:\WINNMR95\COMMON\_DEFA
COMNT
DATIM  Tue Jul 14 22:02:42 2009
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN       1150.0 Hz
POINT        32768
FREQU       6013.2 Hz
SCANS           16
ACQTM        5.449 sec
PD           1.551 sec
PW1            5.8 us
IRNUC  1H
CTEMP         24.0 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.09 Hz
RGAIN           14
```

2d-^{13}C NMR

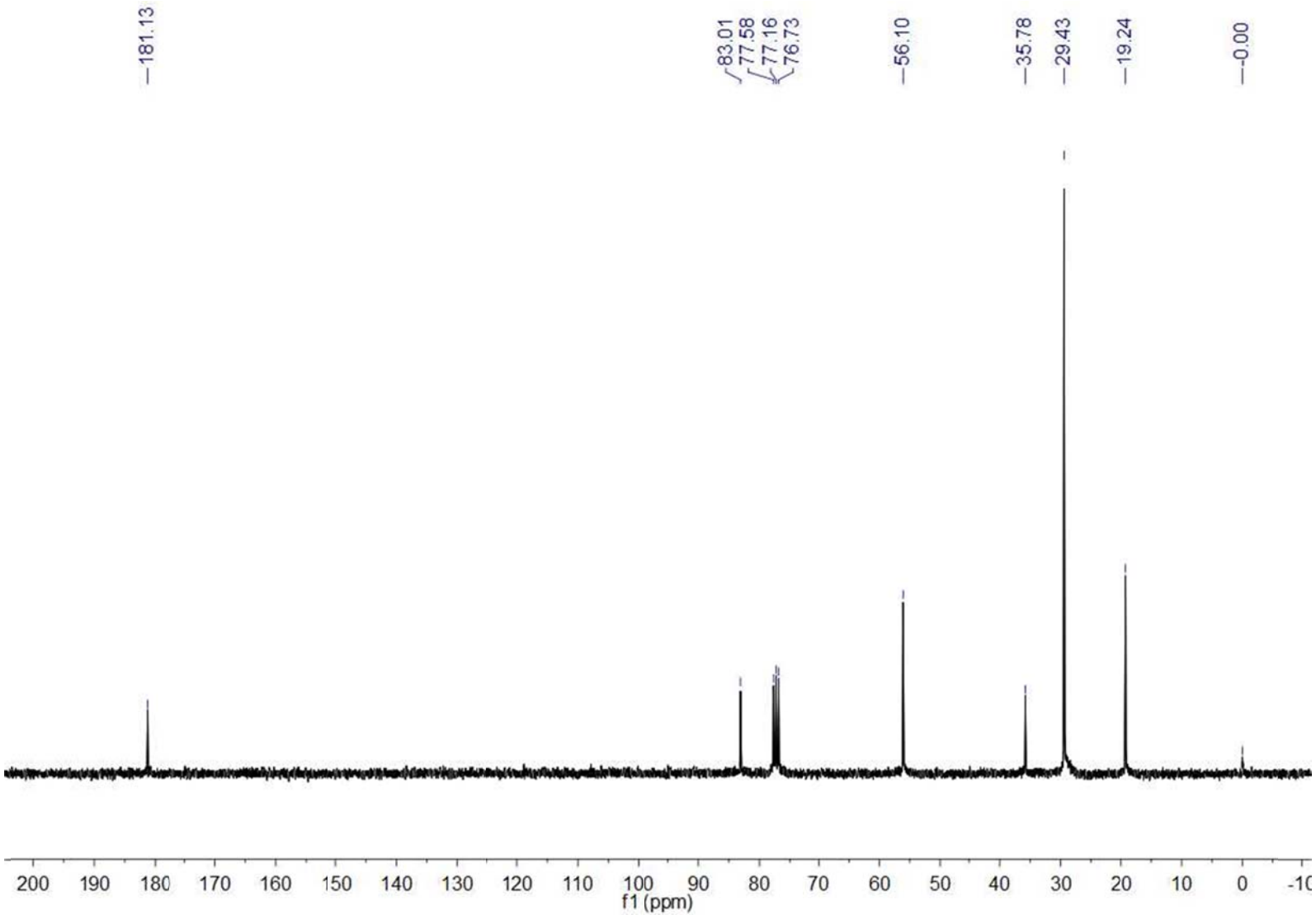



```
DFILE  D:\Old Files\LUO QIAN\5-
COMNT
DATIM  Tue Jul 14 21:55:28 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS           24
ACQTM         1.606 sec
PD            1.394 sec
PW1             5.0 us
IRNUC  1H
CTEMP          24.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.62 Hz
RGAIN            26
```

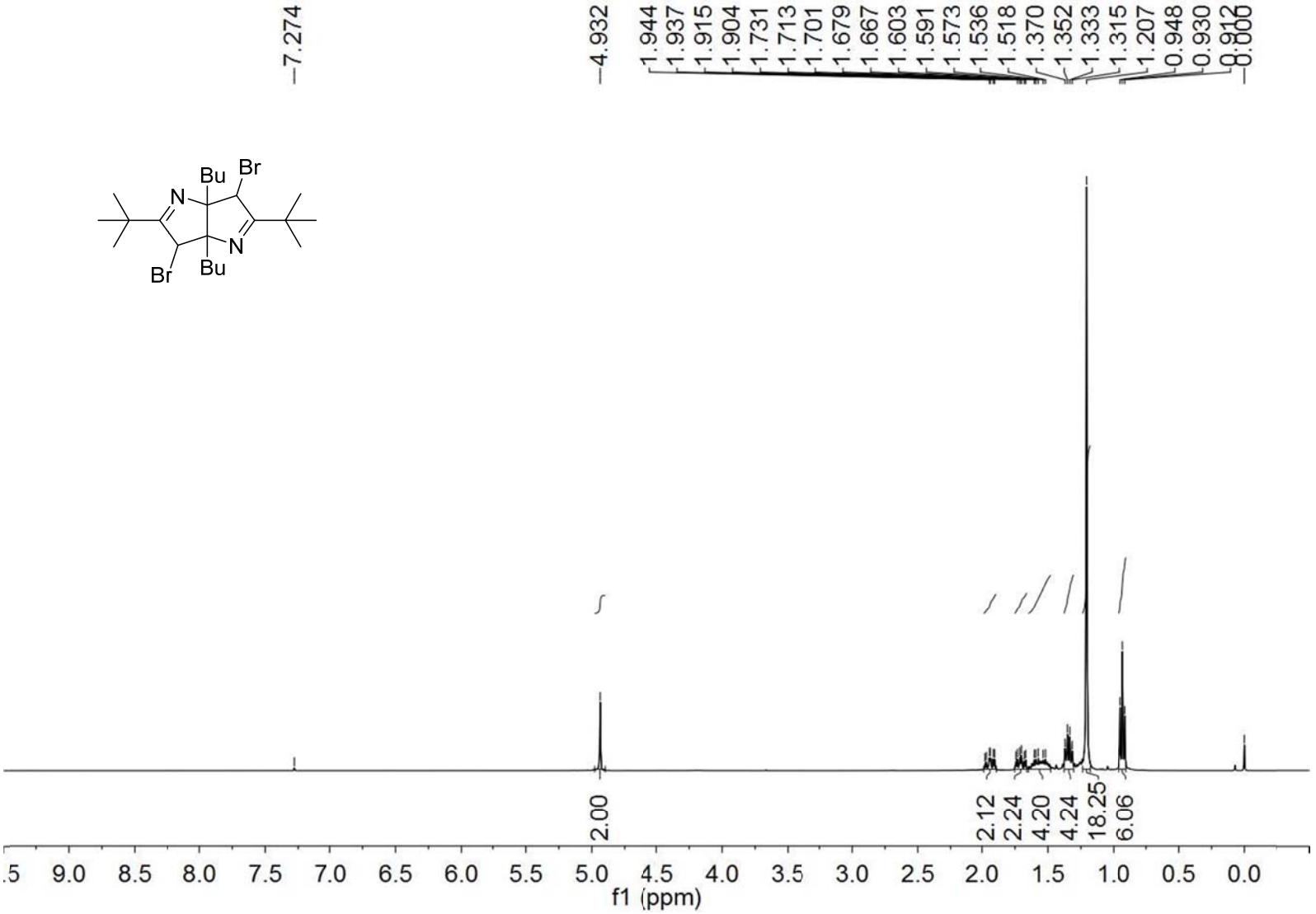
2e-^{1}H NMR


7.30
4.95
1.54
1.22
0.00
Me
Br
N
N
Br
Me
2.00
6.17
18.32
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

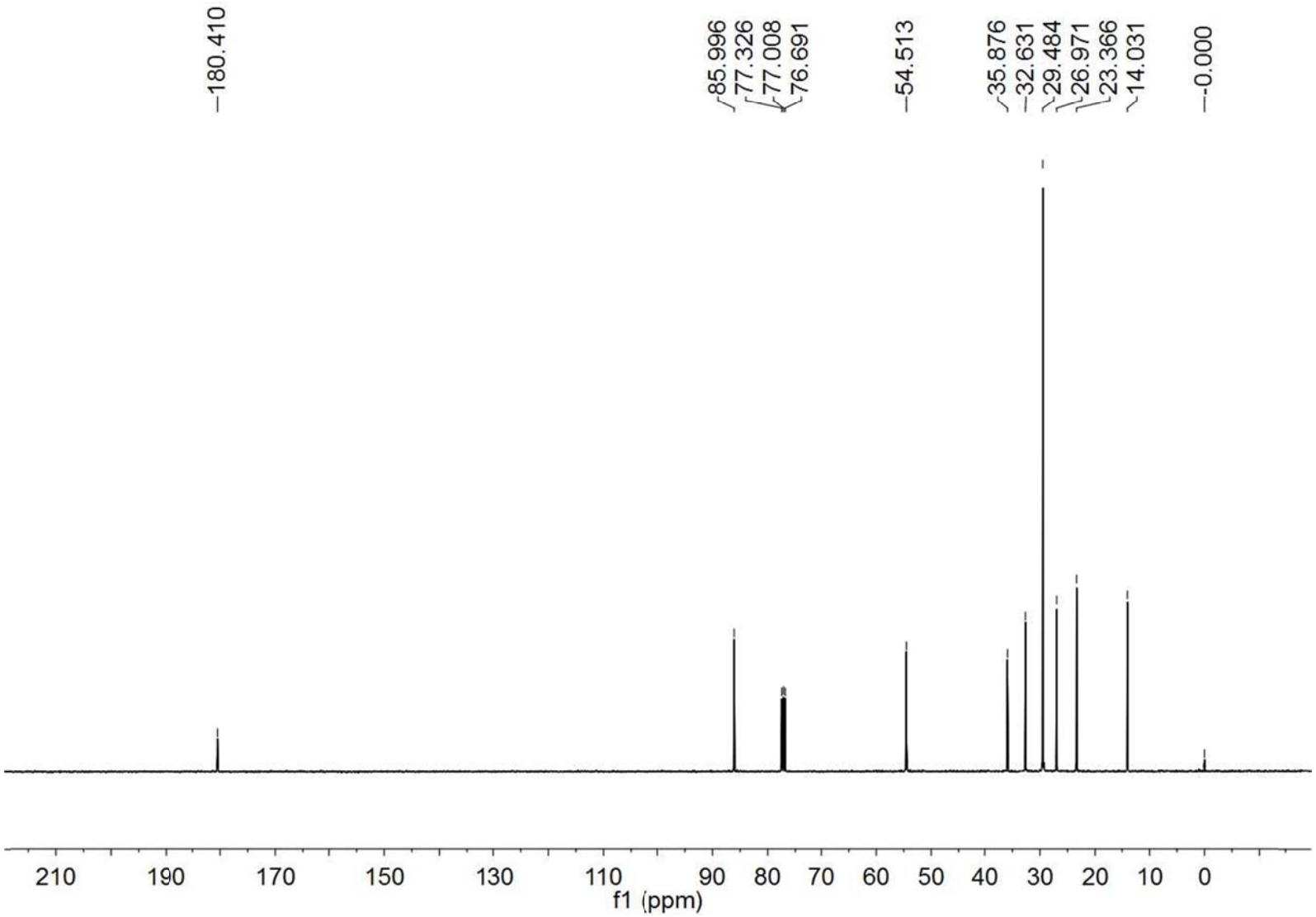
2e-^{13}C NMR


181.13
83.01
77.58
77.16
76.73
56.10
35.78
29.43
19.24
0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

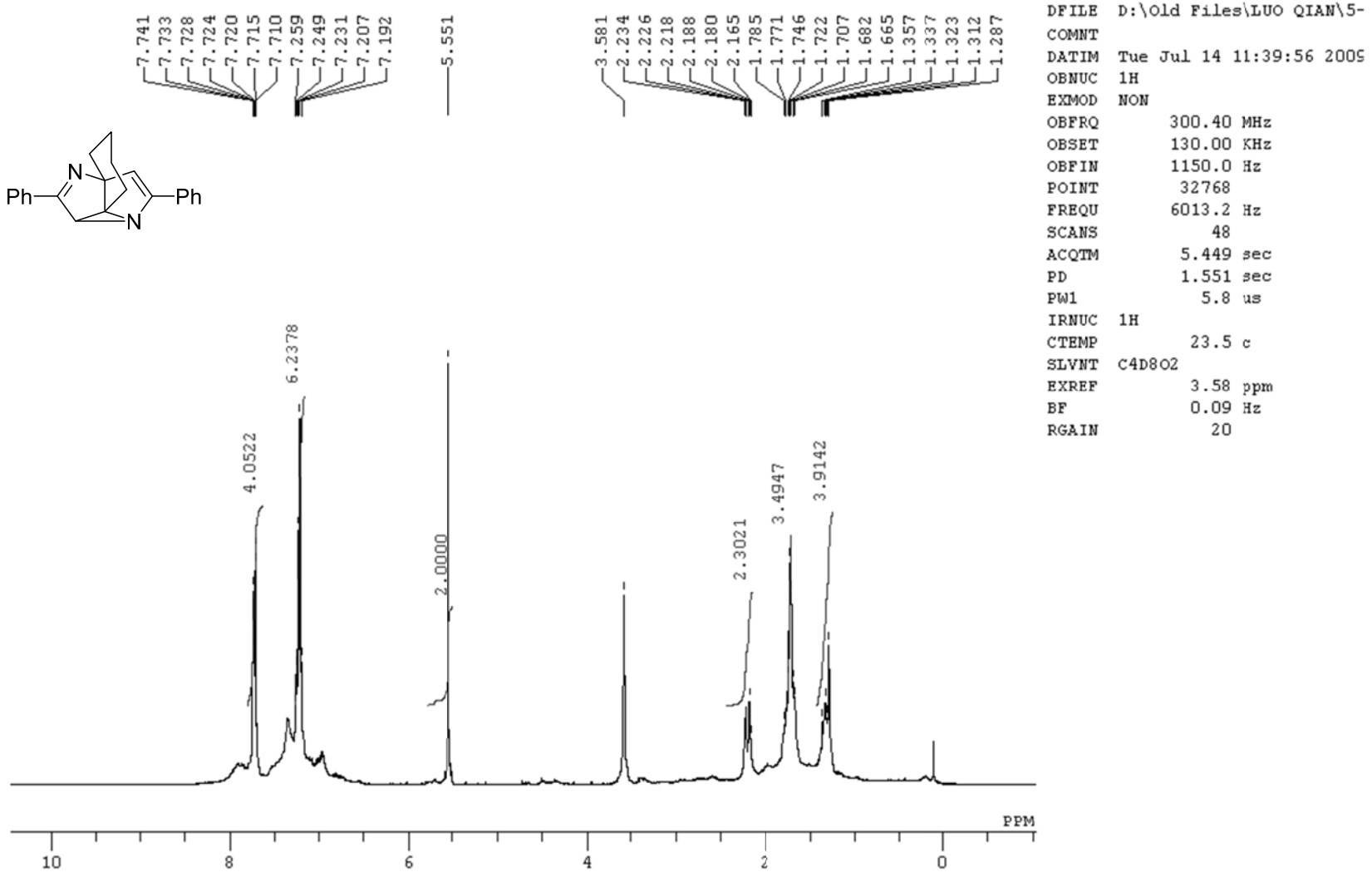
2f-^{1}H NMR


7.274
4.932
1.944
1.937
1.915
1.904
1.731
1.713
1.701
1.679
1.667
1.603
1.591
1.573
1.536
1.518
1.370
1.352
1.333
1.315
1.207
0.948
0.930
0.912
0.900
Bu
Br
N
N
Br
Bu
2.00
2.12
2.24
4.20
4.24
18.25
6.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

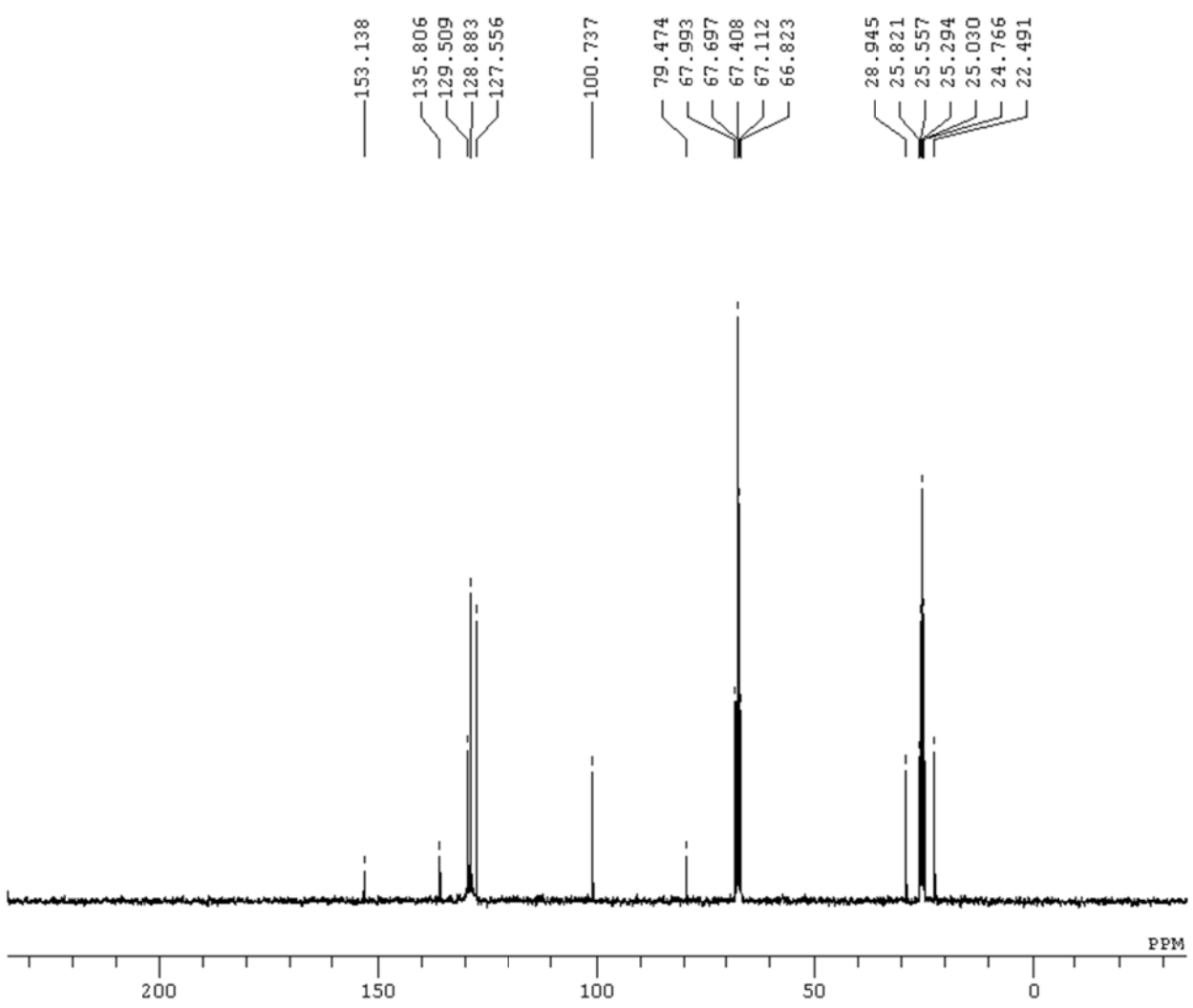
2f-^{13}C NMR


180.410
85.996
77.326
77.008
76.691
54.513
35.876
32.631
29.484
26.971
23.366
14.031
0.000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3a-^{1}H NMR

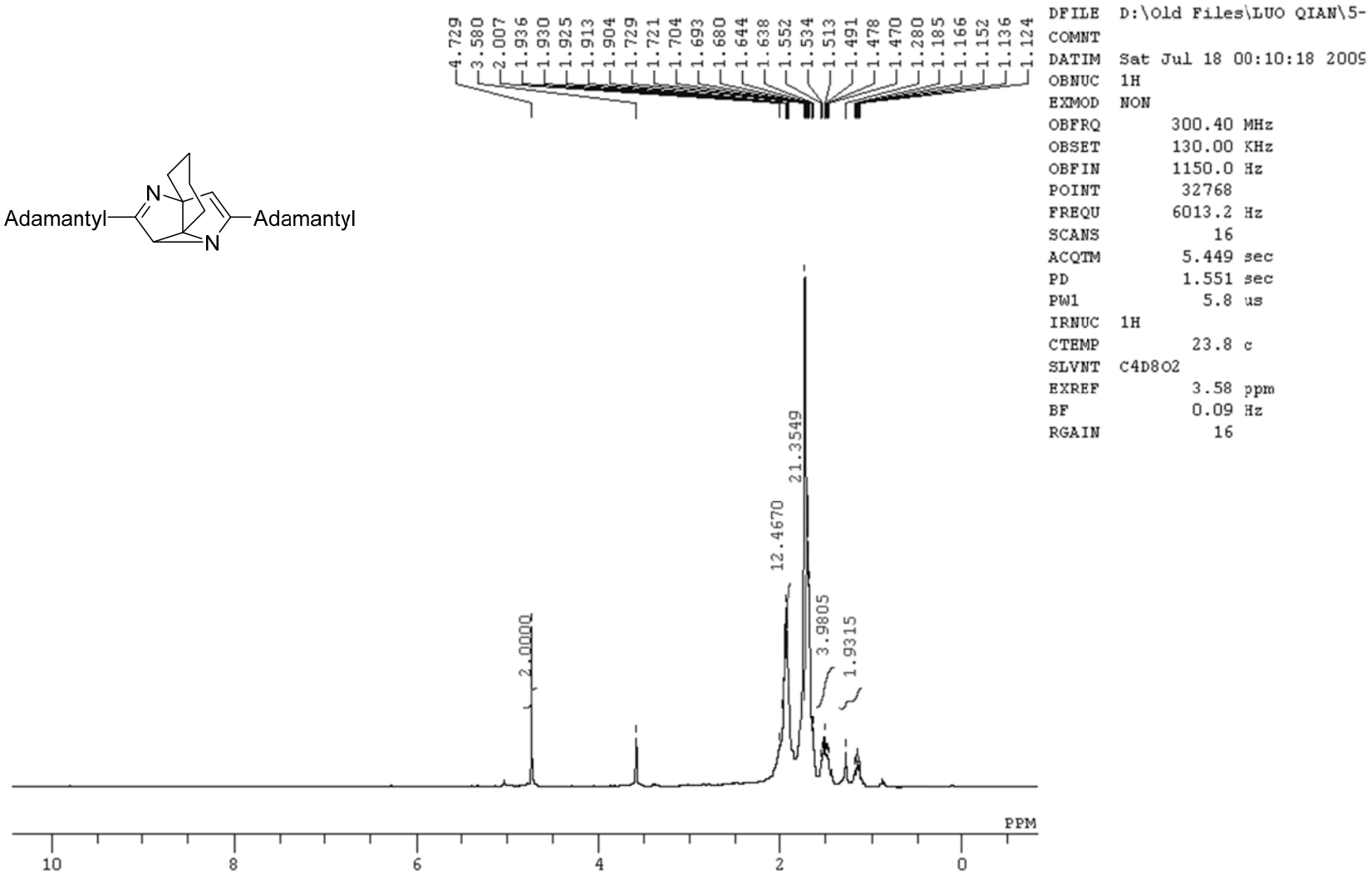

7.741
7.733
7.728
7.724
7.720
7.715
7.710
7.259
7.249
7.231
7.207
7.192
5.551
3.581
2.234
2.226
2.218
2.188
2.180
2.165
1.785
1.771
1.746
1.722
1.707
1.682
1.665
1.357
1.337
1.323
1.312
1.287
Ph
N
N
Ph
DFILE D:\Old Files\LUO QIAN\5-
COMNT
DATIM Tue Jul 14 11:39:56 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 48
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 23.5 c
SLVNT C4D8O2
EXREF 3.58 ppm
BF 0.09 Hz
RGAIN 20
4.0522
6.2378
2.0000
2.3021
3.4947
3.9142
PPM
10
8
6
4
2
0

3a-^{13}C NMR

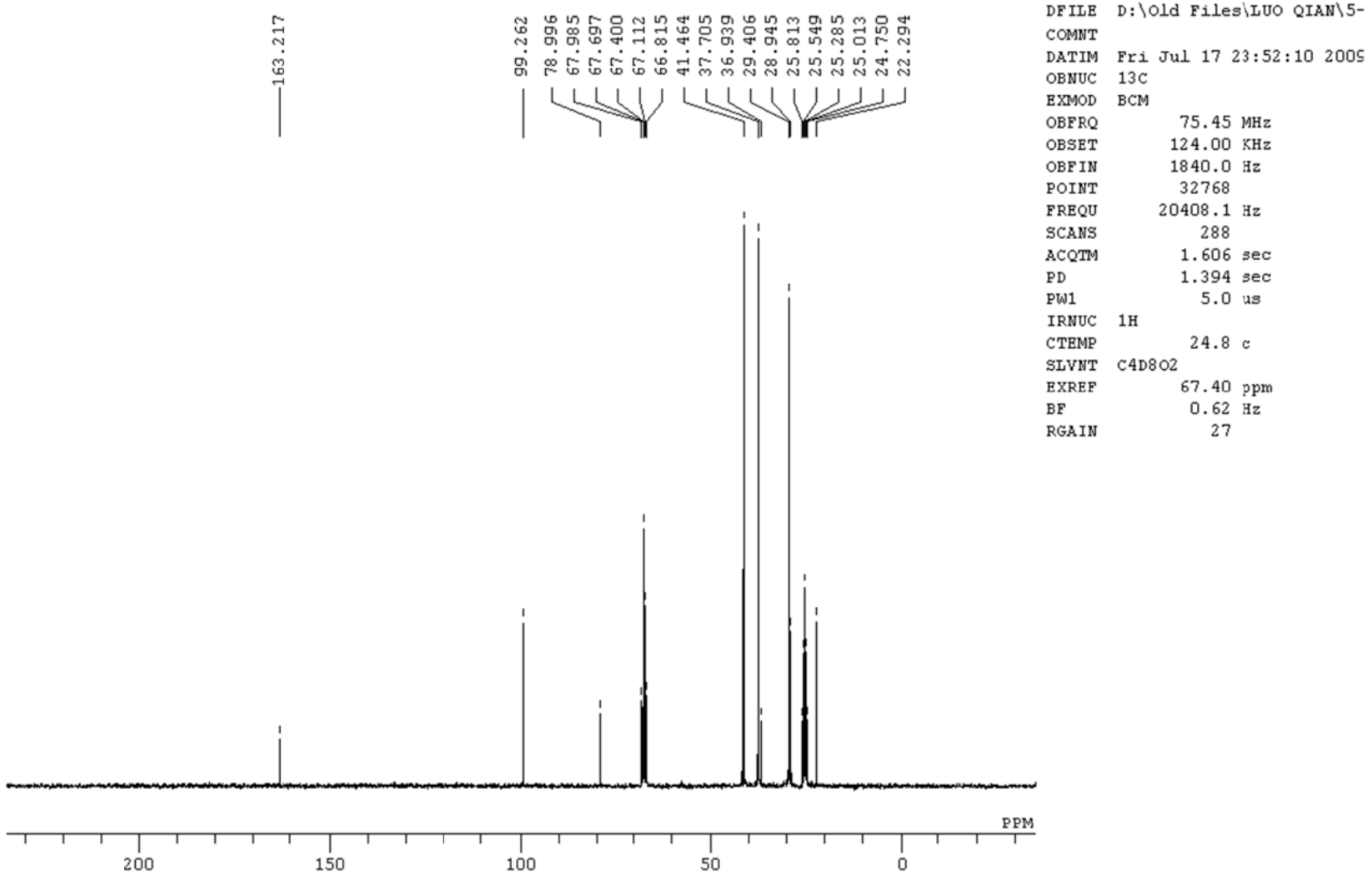



```
DFILE  D:\Old Files\LUO QIAN\5-
COMNT
DATIM  Tue Jul 14 11:54:36 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS          216
ACQTM        1.606 sec
PD           1.394 sec
PW1            5.0 us
IRNUC  1H
CTEMP         23.9 c
SLVNT  C4D8O2
EXREF        67.40 ppm
BF            1.20 Hz
RGAIN           26
```

3b-^{1}H NMR

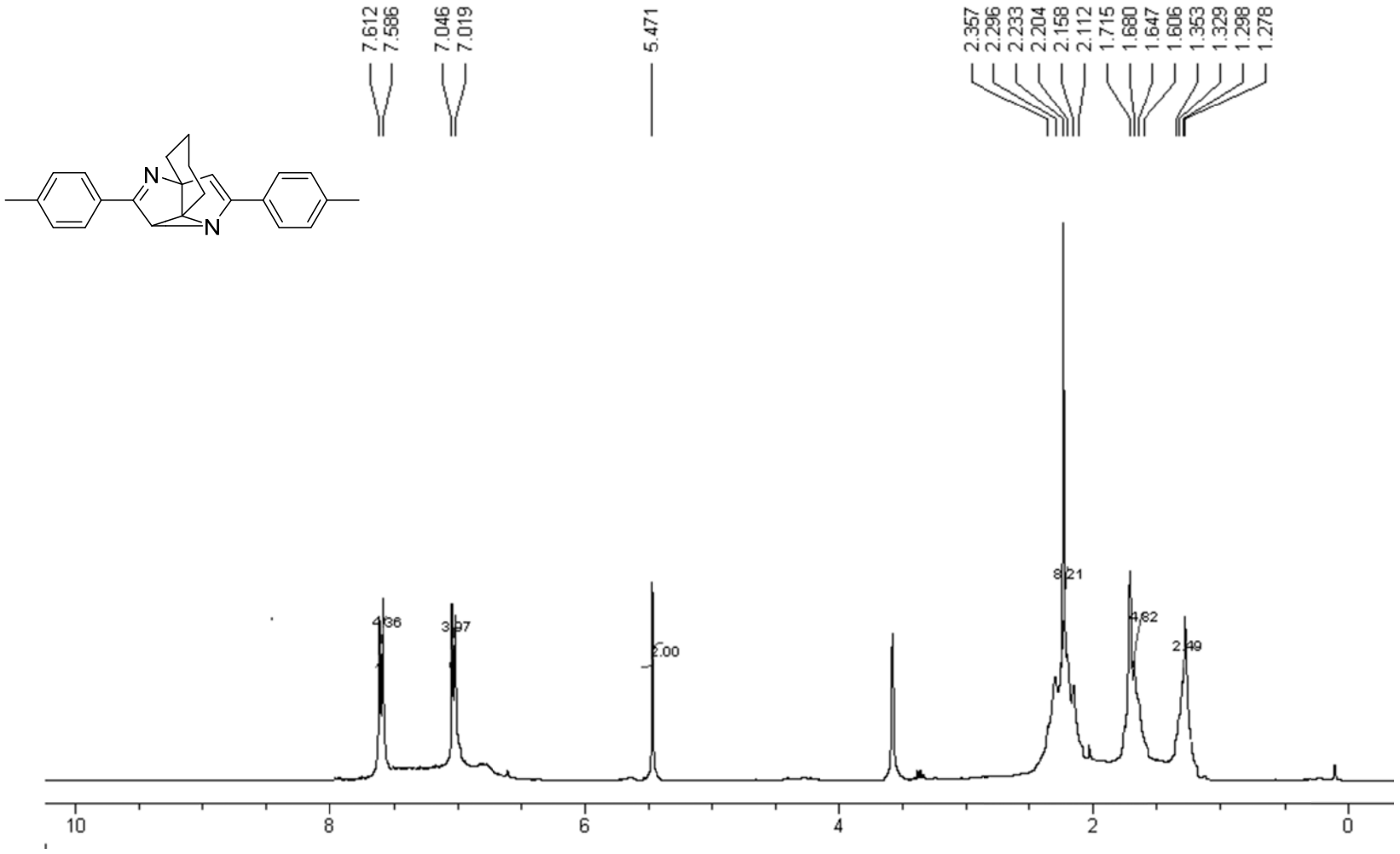

Adamantyl
N
N
Adamantyl
4.729
3.580
2.007
1.936
1.930
1.925
1.913
1.904
1.729
1.721
1.704
1.693
1.680
1.644
1.638
1.552
1.534
1.513
1.491
1.478
1.470
1.280
1.185
1.166
1.152
1.136
1.124
DFILE D:\Old Files\LUO QIAN\5-
COMNT
DATIM Sat Jul 18 00:10:18 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 23.8 c
SLVNT C4D8O2
EXREF 3.58 ppm
BF 0.09 Hz
RGAIN 16
21.3549
12.4670
3.9805
1.9315
2.0000
PPM
10
8
6
4
2
0

3b-^{13}C NMR

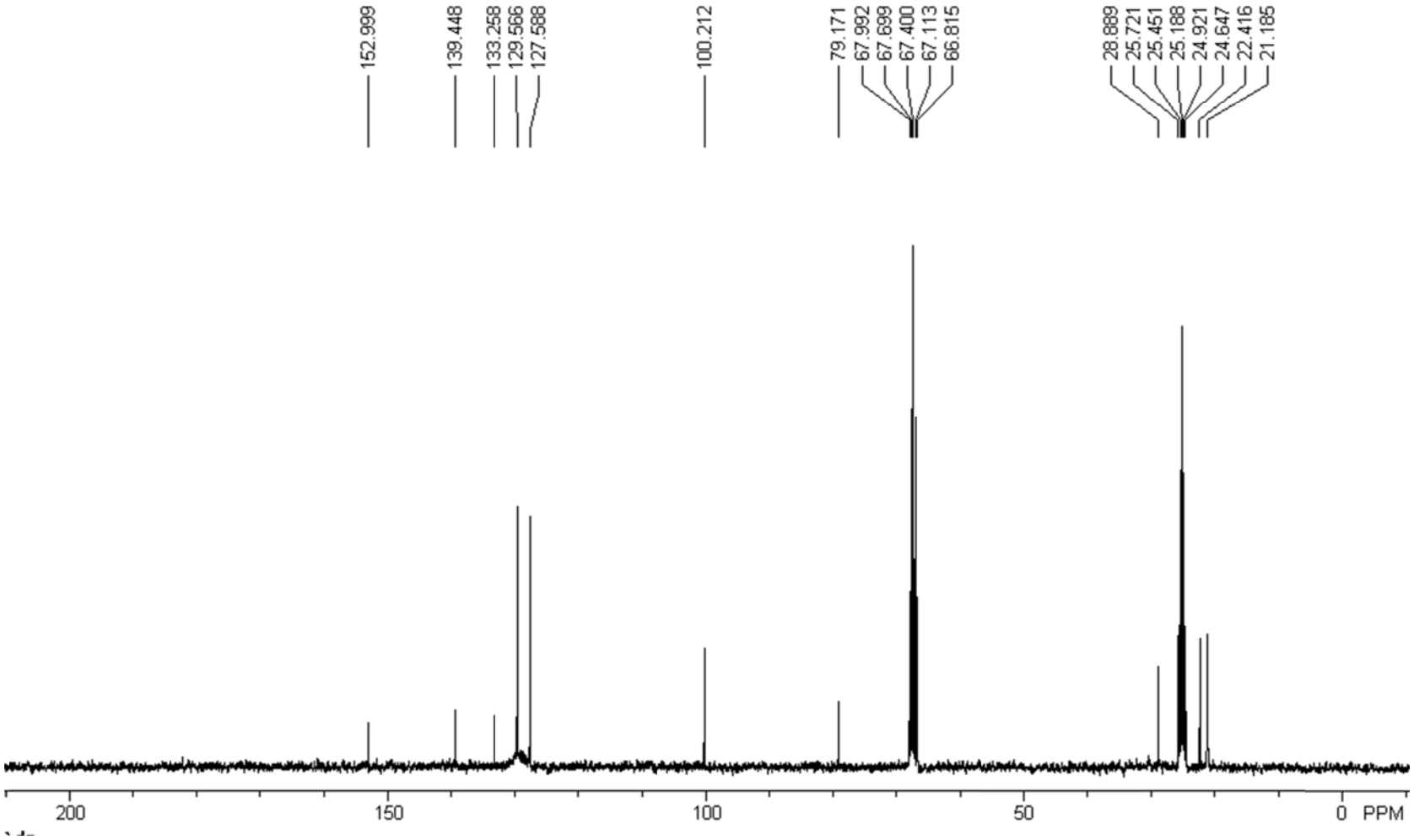



```
DFILE  D:\Old Files\LUO QIAN\5-
COMNT
DATIM  Fri Jul 17 23:52:10 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS          288
ACQTM        1.606 sec
PD           1.394 sec
PW1            5.0 us
IRNUC  1H
CTEMP         24.8 c
SLVNT  C4D8O2
EXREF        67.40 ppm
BF            0.62 Hz
RGAIN           27
```

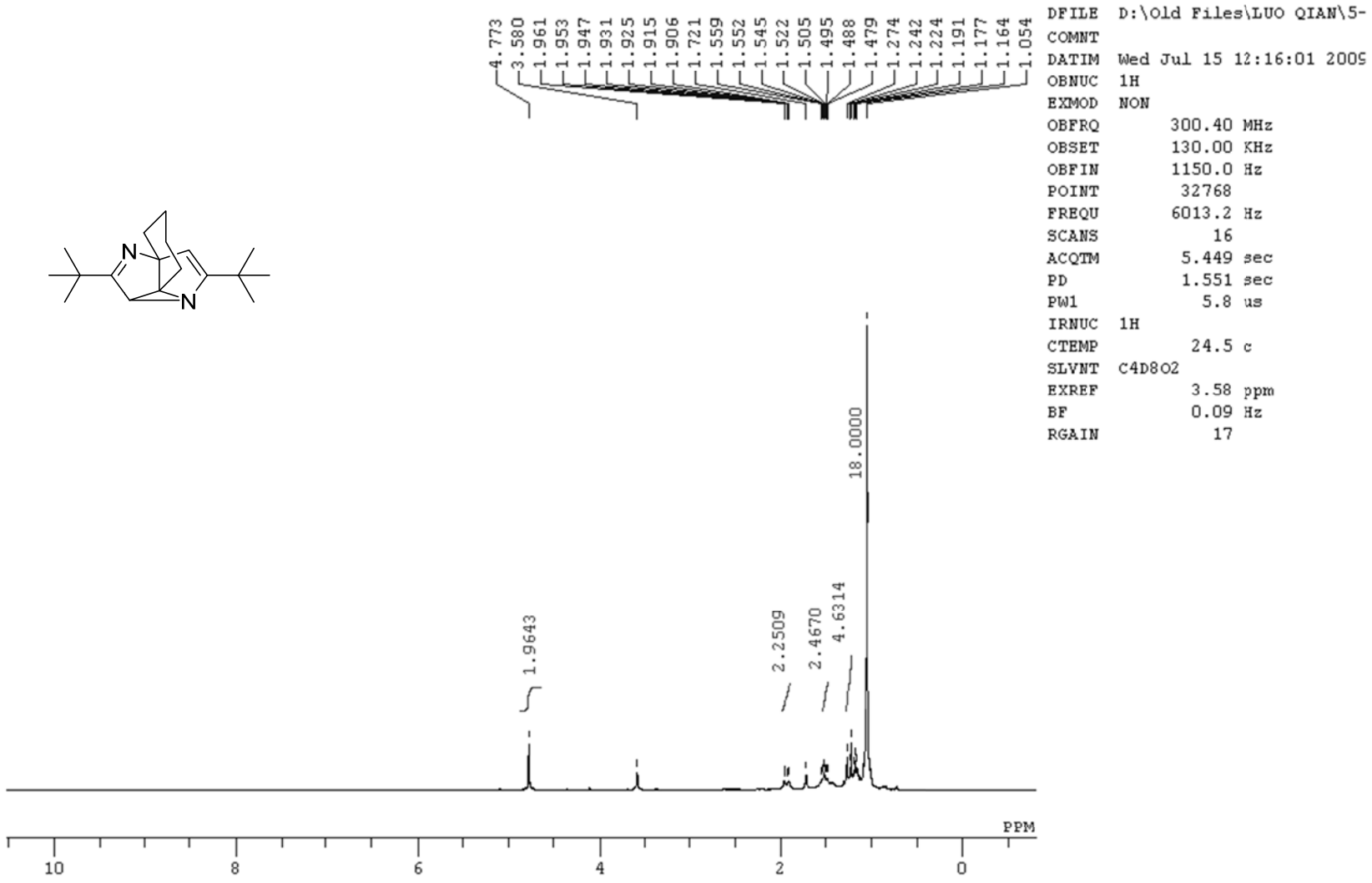
3c-^{1}H NMR


7.612
7.586
7.046
7.019
5.471
2.357
2.296
2.233
2.204
2.158
2.112
1.715
1.680
1.647
1.606
1.353
1.329
1.298
1.278
N
N
4.36
3.97
2.00
8.21
4.62
2.49
10
8
6
4
2
0

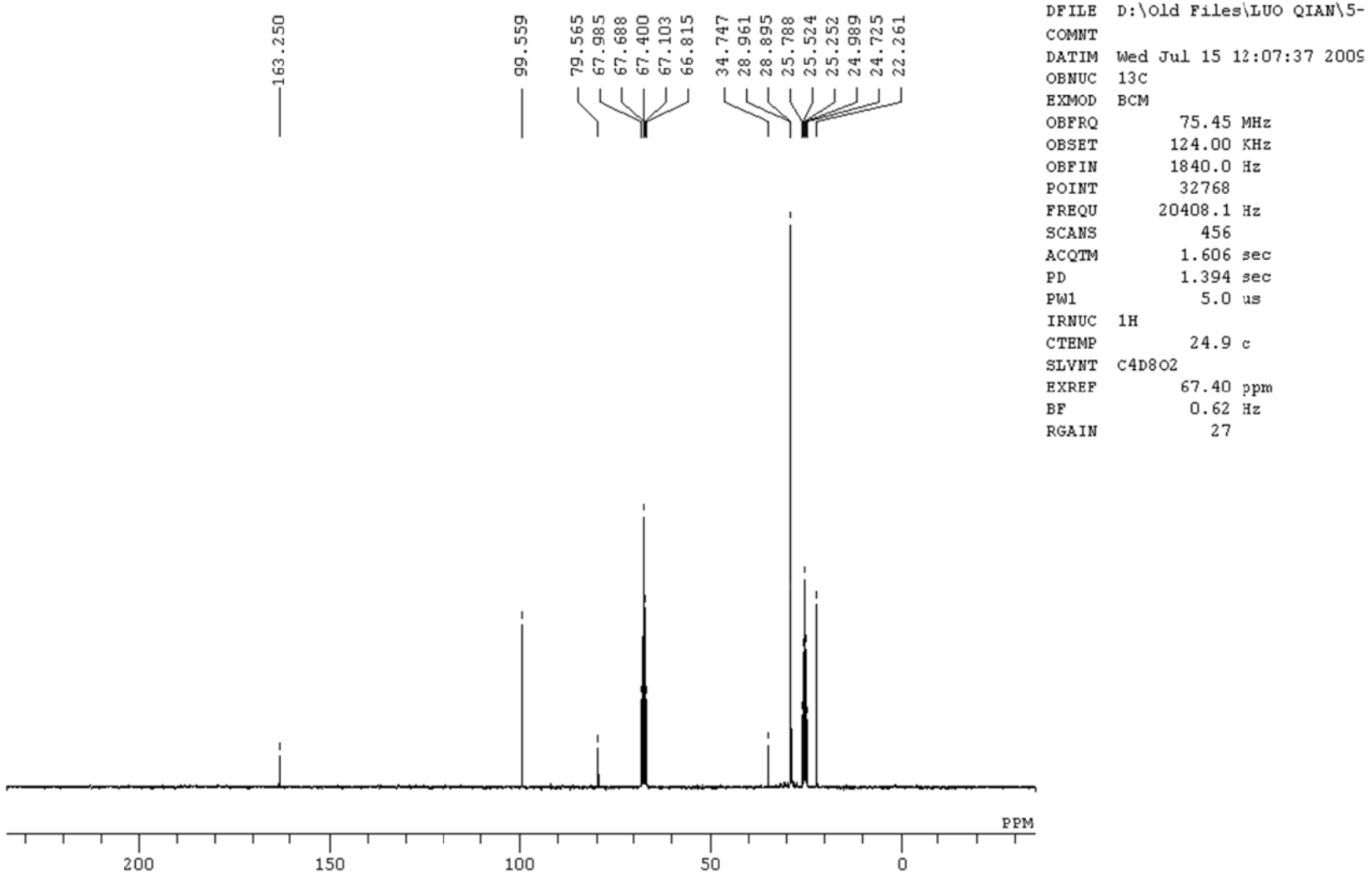
3c-^{13}C NMR


152.999
139.448
133.258
129.566
127.588
100.212
79.171
67.992
67.699
67.400
67.113
66.815
28.889
25.721
25.451
25.188
24.921
24.647
22.416
21.185
200
150
100
50
0 PPM

3d-^{1}H NMR

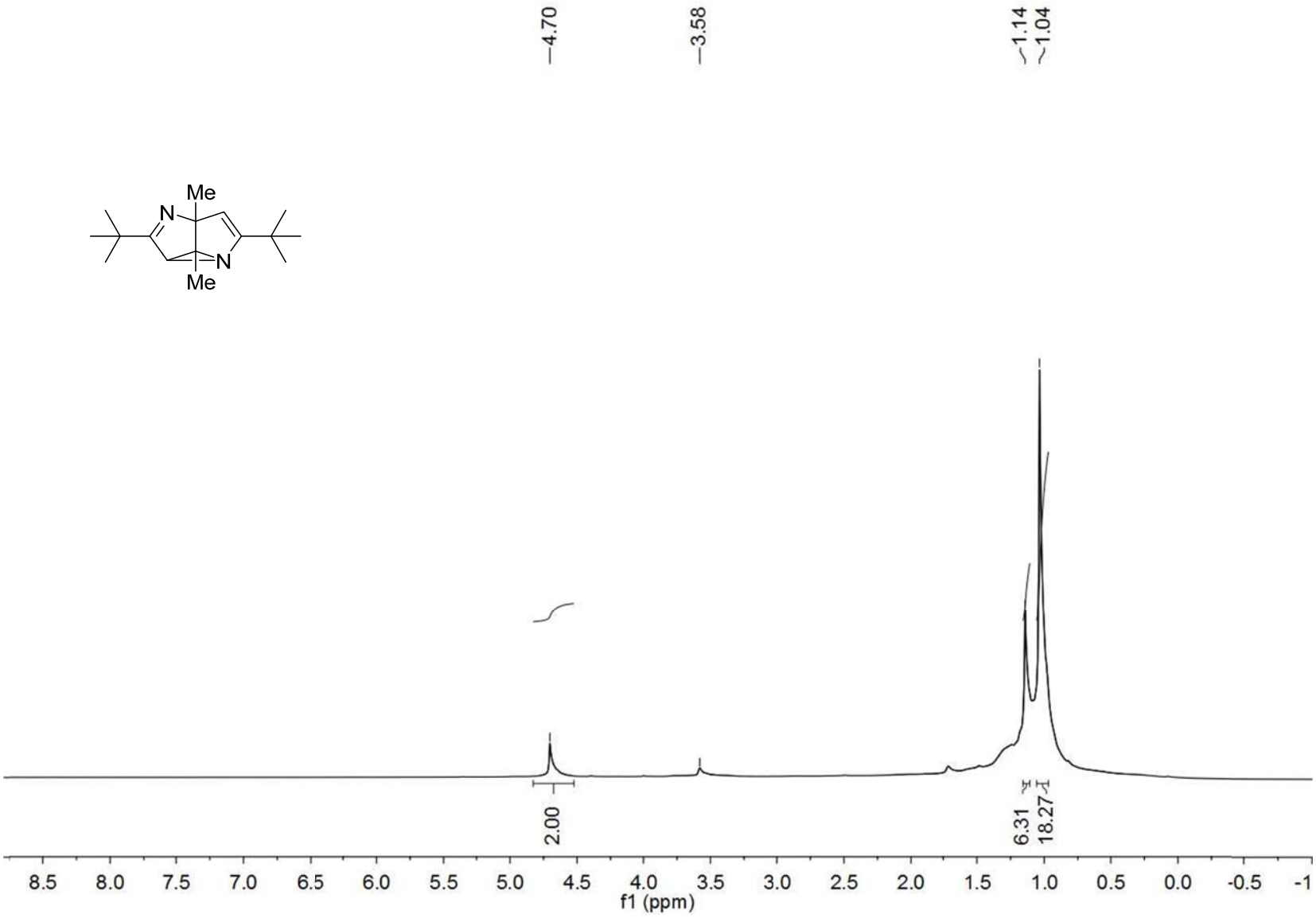

4.773
3.580
1.961
1.953
1.947
1.931
1.925
1.915
1.906
1.721
1.559
1.552
1.545
1.522
1.505
1.495
1.488
1.479
1.274
1.242
1.224
1.191
1.177
1.164
1.054
DFILE D:\Old Files\LUO QIAN\5-
COMNT
DATIM Wed Jul 15 12:16:01 2009
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 24.5 c
SLVNT C4D8O2
EXREF 3.58 ppm
BF 0.09 Hz
RGAIN 17
18.0000
1.9643
2.2509
2.4670
4.6314
PPM
10
8
6
4
2
0

3d-^{13}C NMR

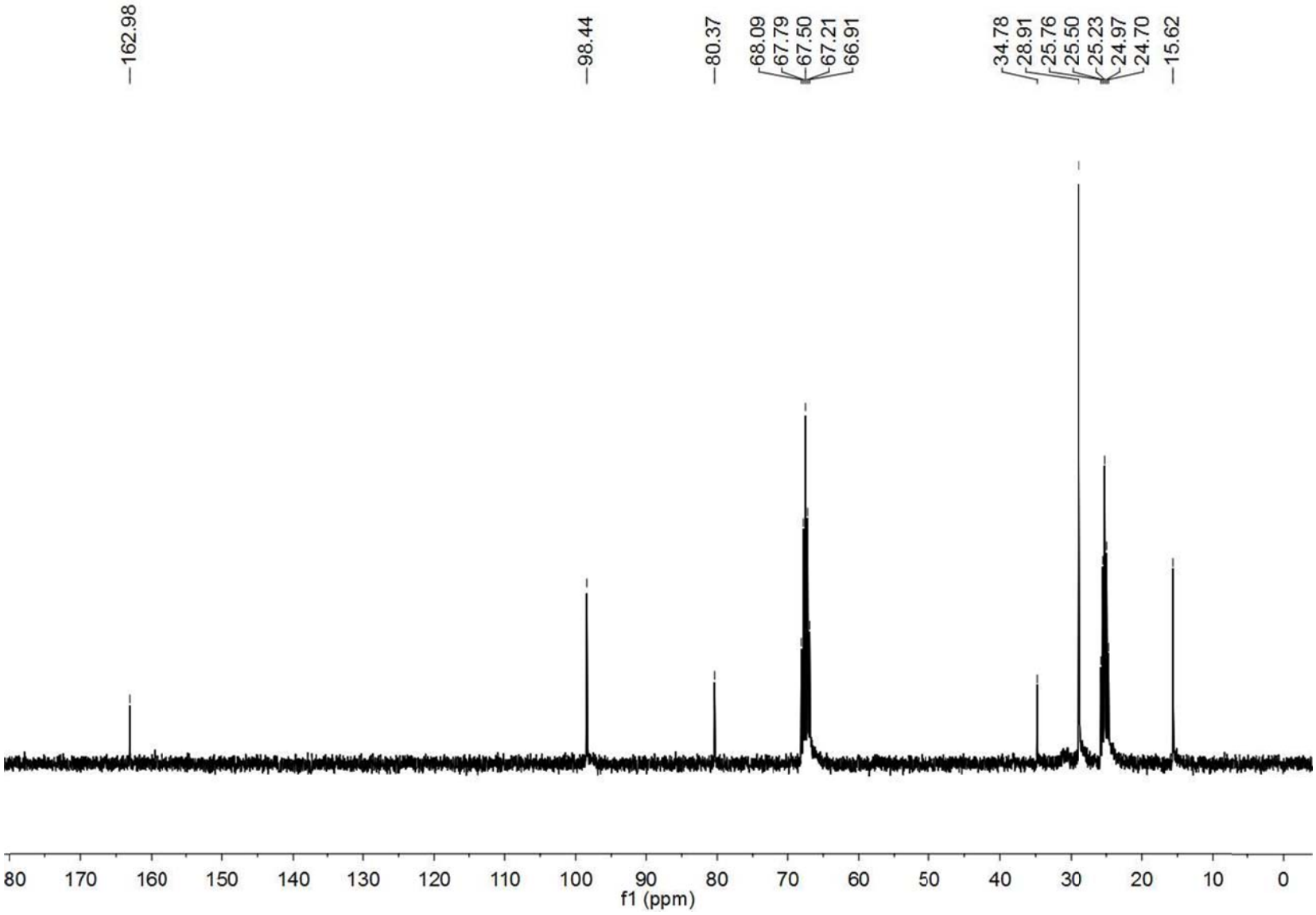



```
DFILE  D:\Old Files\LUO QIAN\5-
COMNT
DATIM  Wed Jul 15 12:07:37 2009
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS          456
ACQTM        1.606 sec
PD           1.394 sec
PW1            5.0 us
IRNUC  1H
CTEMP         24.9 c
SLVNT  C4D8O2
EXREF        67.40 ppm
BF            0.62 Hz
RGAIN           27
```

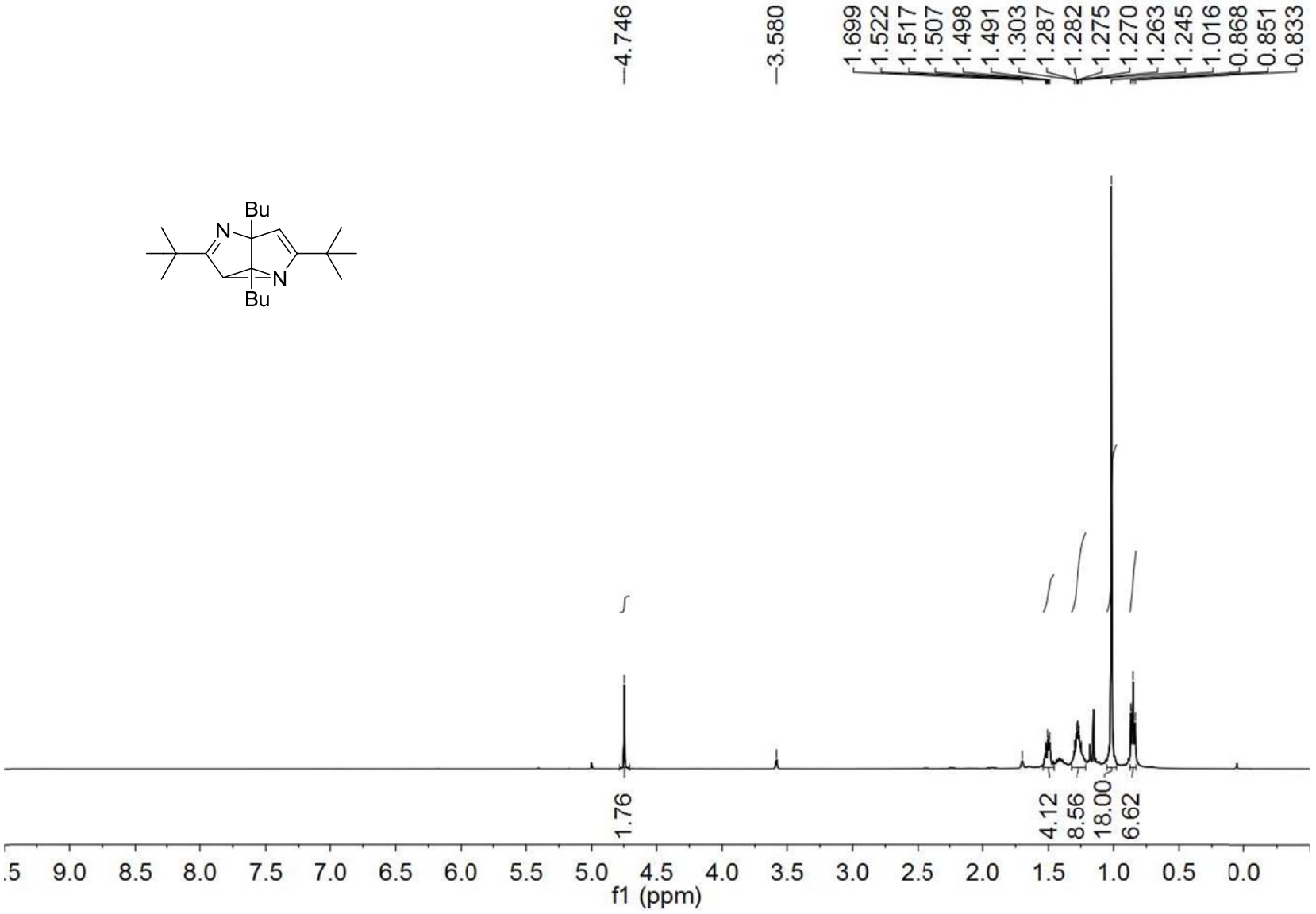
3e-^{1}H NMR


4.70
3.58
1.14
1.04
Me
N
N
Me
2.00
6.31
18.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

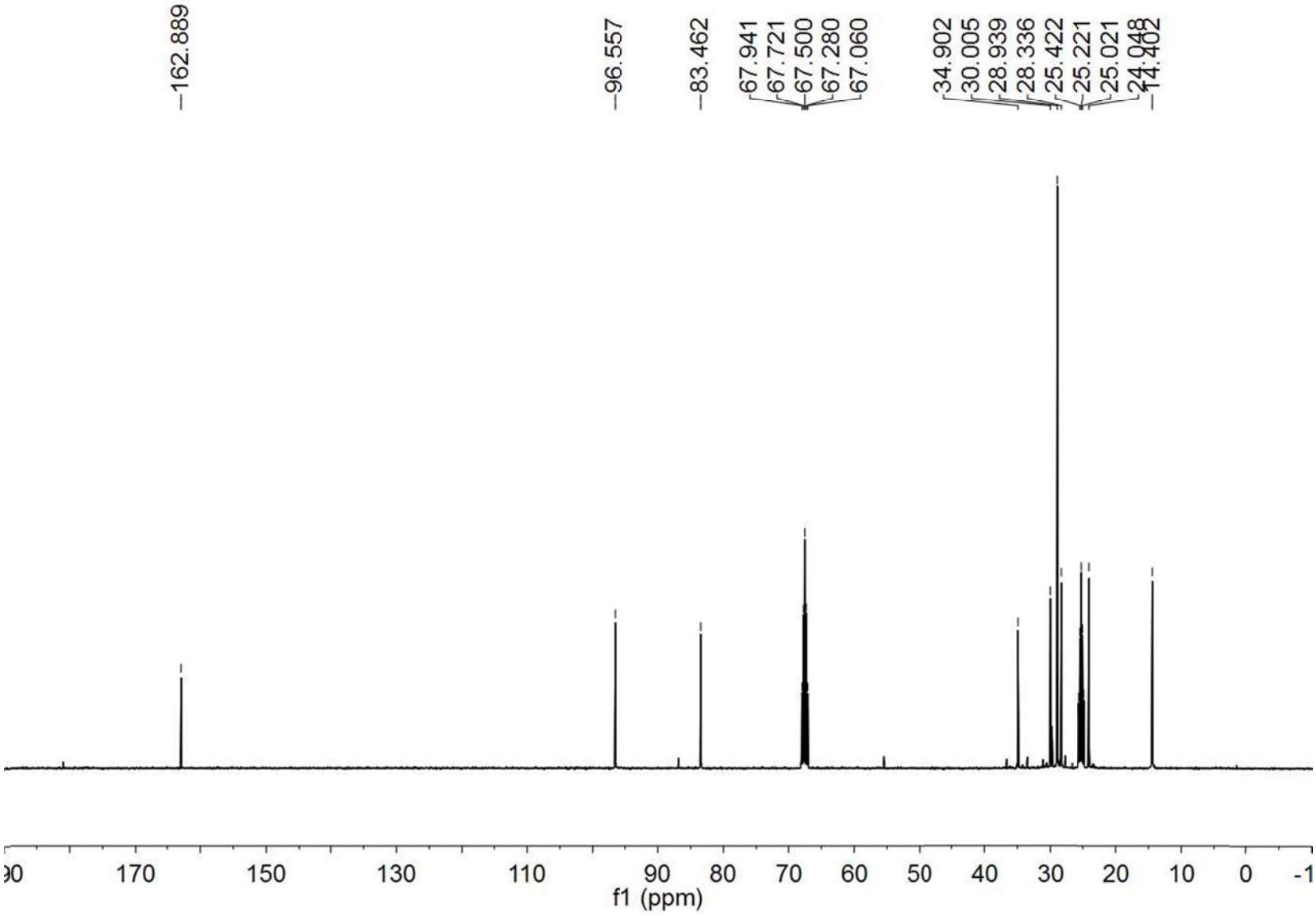
3e-^{13}C NMR


162.98
98.44
80.37
68.09
67.79
67.50
67.21
66.91
34.78
28.91
25.76
25.50
25.23
24.97
24.70
15.62
f1 (ppm)

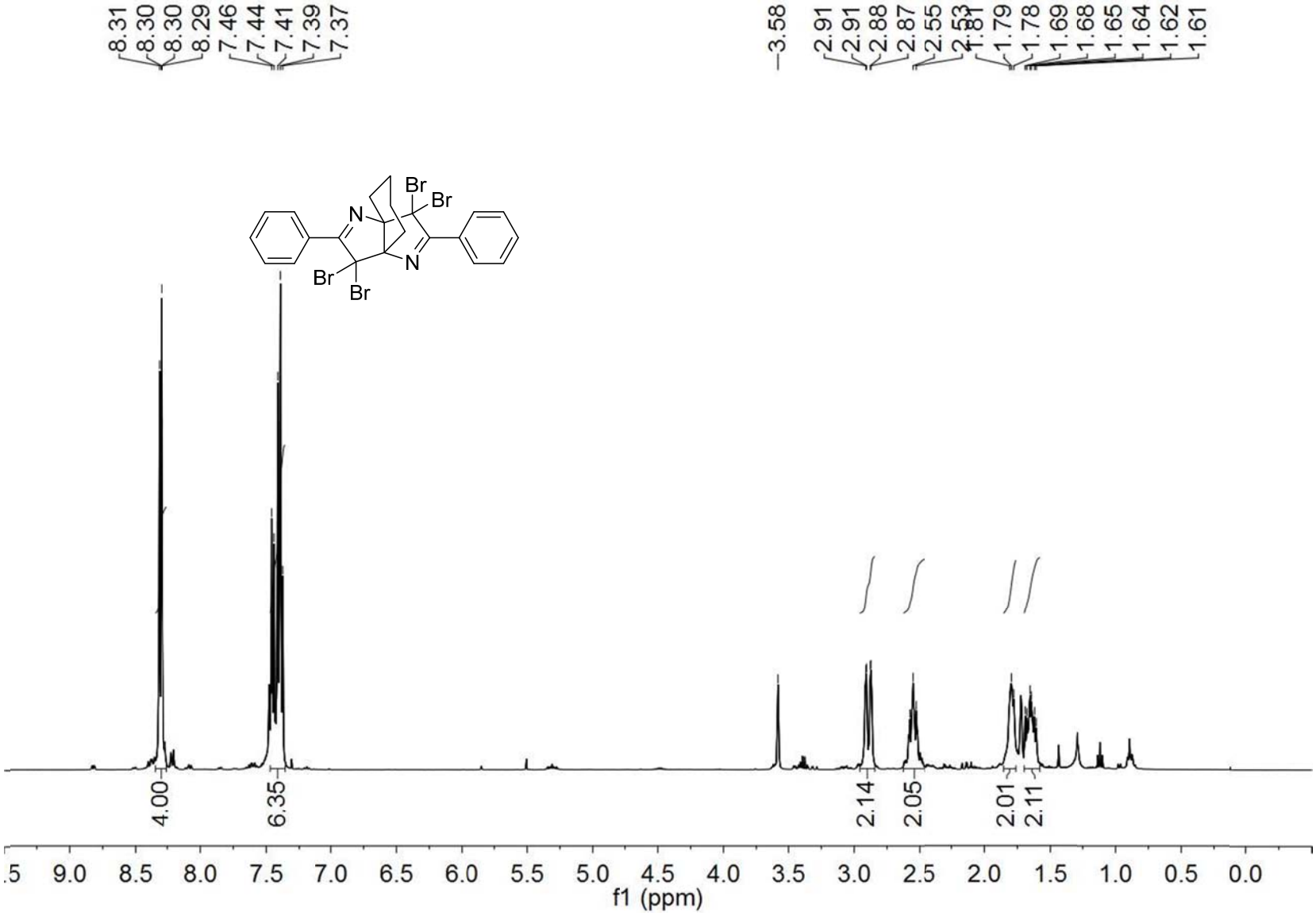
3f-^{1}H NMR


4.746
3.580
1.699
1.522
1.517
1.507
1.498
1.491
1.303
1.287
1.282
1.275
1.270
1.263
1.245
1.016
0.868
0.851
0.833
Bu
N
N
Bu
1.76
4.12
8.56
18.00
6.62
f1 (ppm)

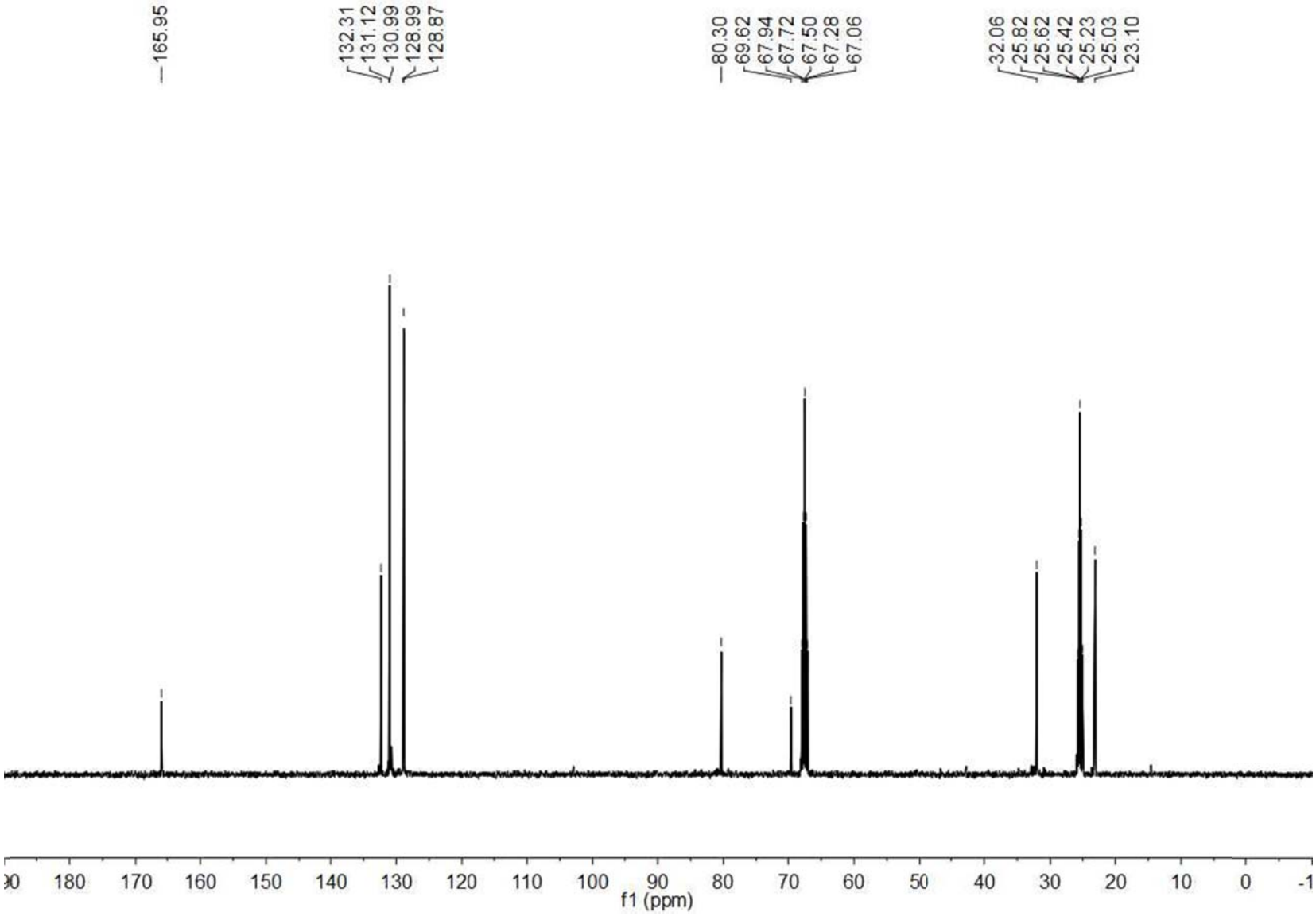
3f-^{13}C NMR


162.889
96.557
83.462
67.941
67.721
67.500
67.280
67.060
34.902
30.005
28.939
28.336
25.422
25.221
25.021
24.048
14.402
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

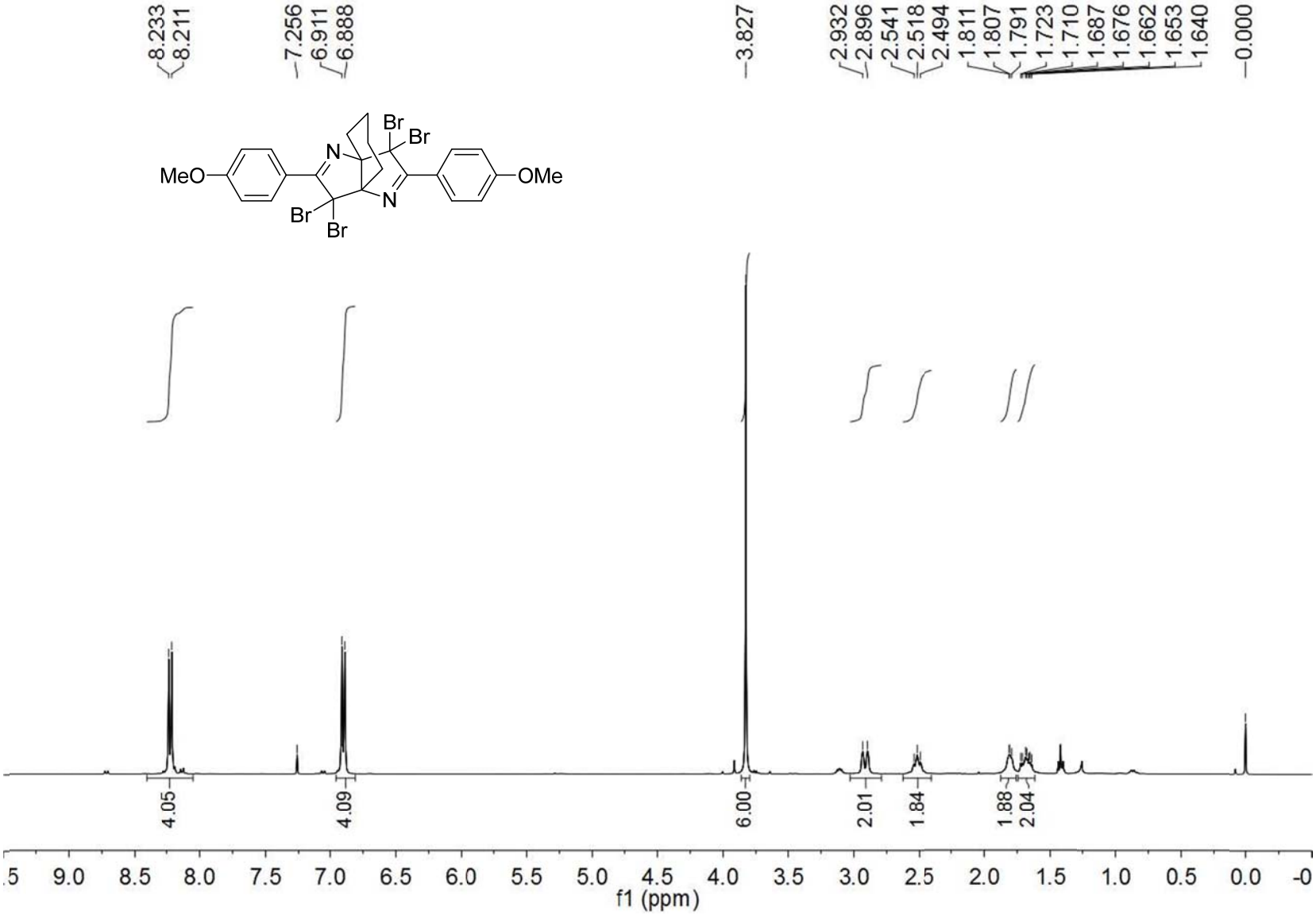
4a-^{1}H NMR


8.31
8.30
8.30
8.29
7.46
7.44
7.41
7.39
7.37
3.58
2.91
2.91
2.88
2.87
2.55
2.53
1.81
1.79
1.78
1.69
1.68
1.65
1.64
1.62
1.61
Br
Br
N
N
Br
Br
4.00
6.35
2.14
2.05
2.01
2.11
f1 (ppm)

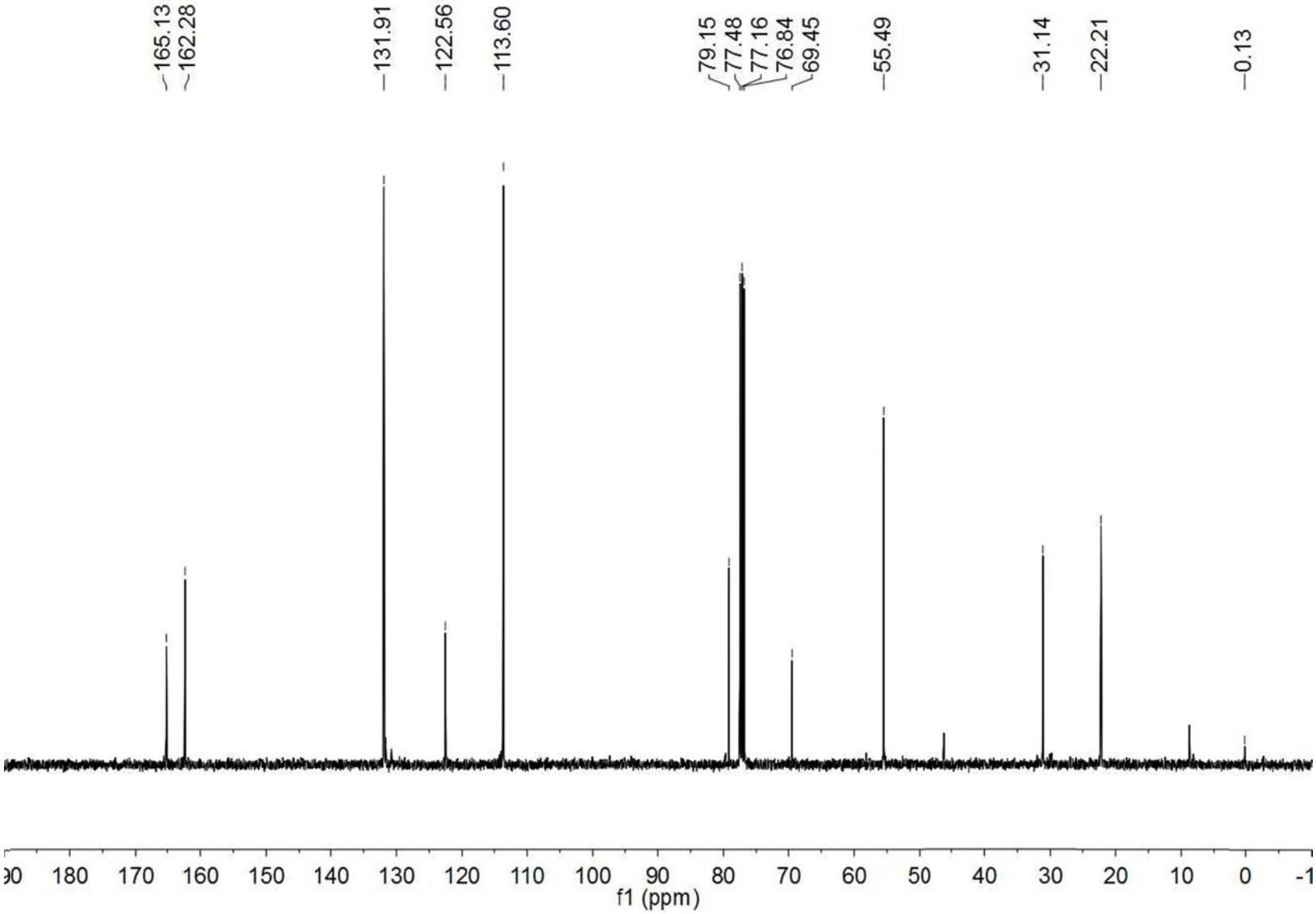
4a-^{13}C NMR


165.95
132.31
131.12
130.99
128.99
128.87
80.30
69.62
67.94
67.72
67.50
67.28
67.06
32.06
25.82
25.62
25.42
25.23
25.03
23.10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

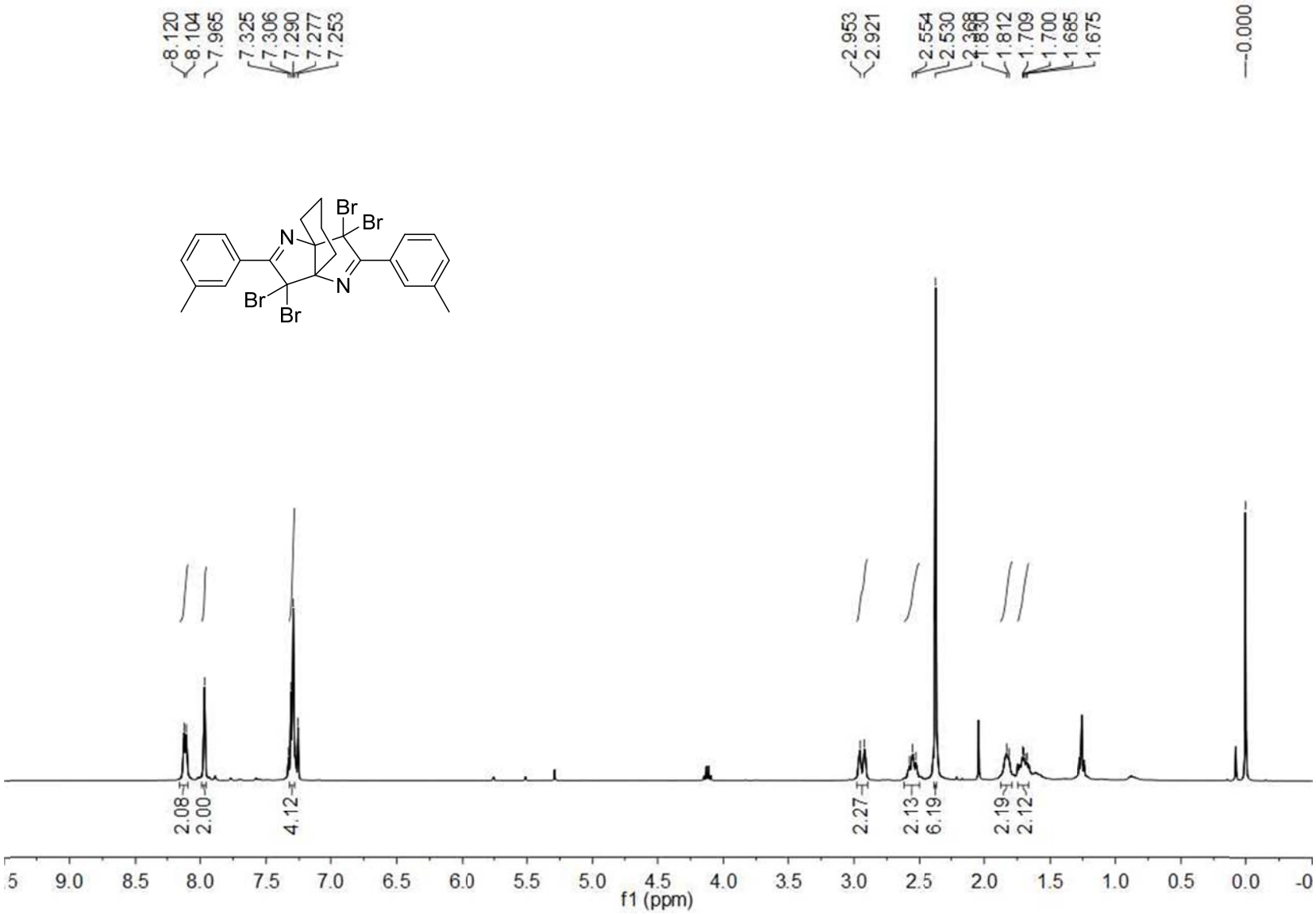
4b-^{1}H NMR


8.233
8.211
7.256
6.911
6.888
3.827
2.932
2.896
2.541
2.518
2.494
1.811
1.807
1.791
1.723
1.710
1.687
1.676
1.662
1.653
1.640
0.000
MeO
OMe
Br
Br
Br
Br
N
N
4.05
4.09
6.00
2.01
1.84
1.88
2.04
f1 (ppm)

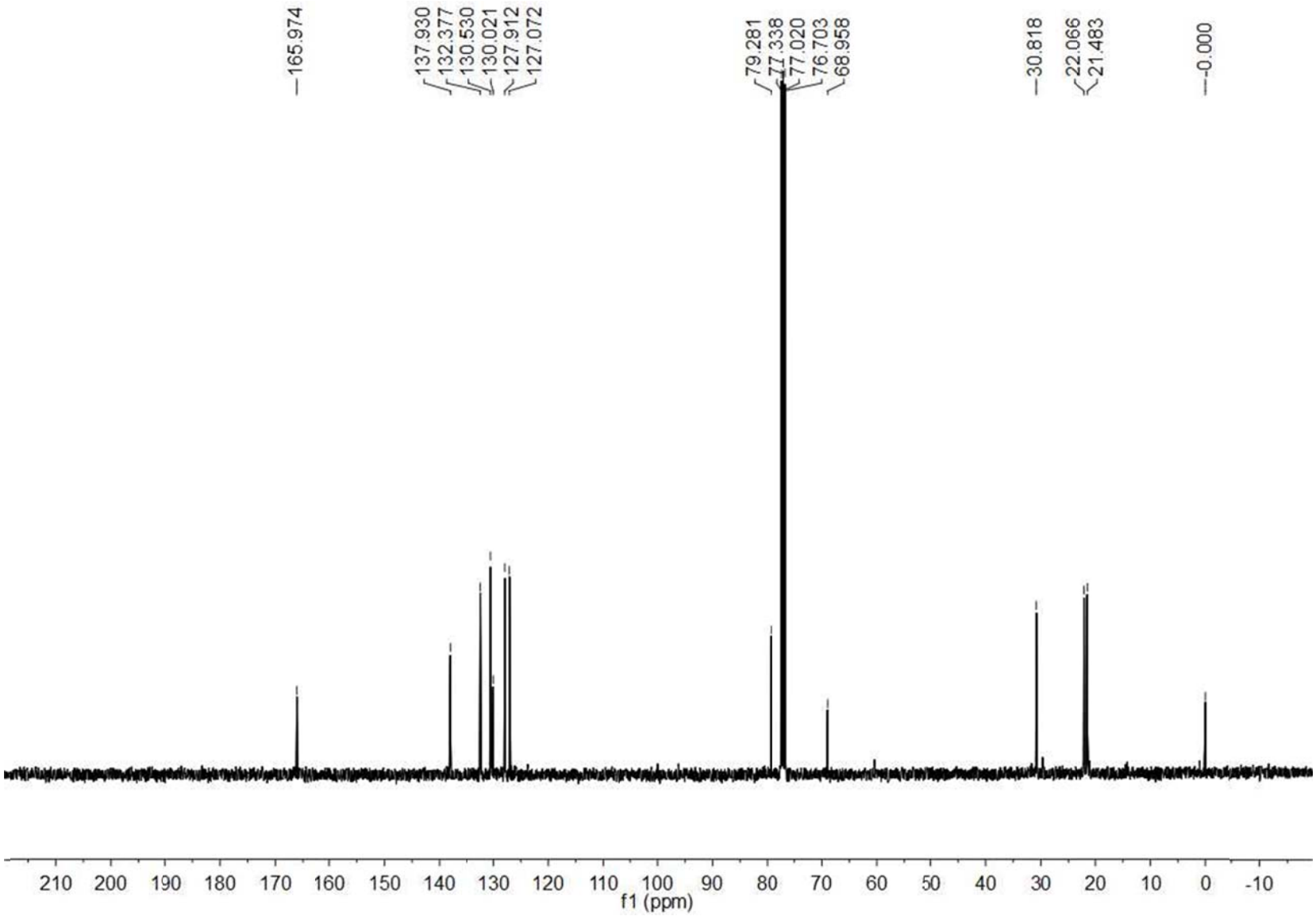
4b-^{13}C NMR


165.13
162.28
131.91
122.56
113.60
79.15
77.48
77.16
76.84
69.45
55.49
31.14
22.21
0.13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

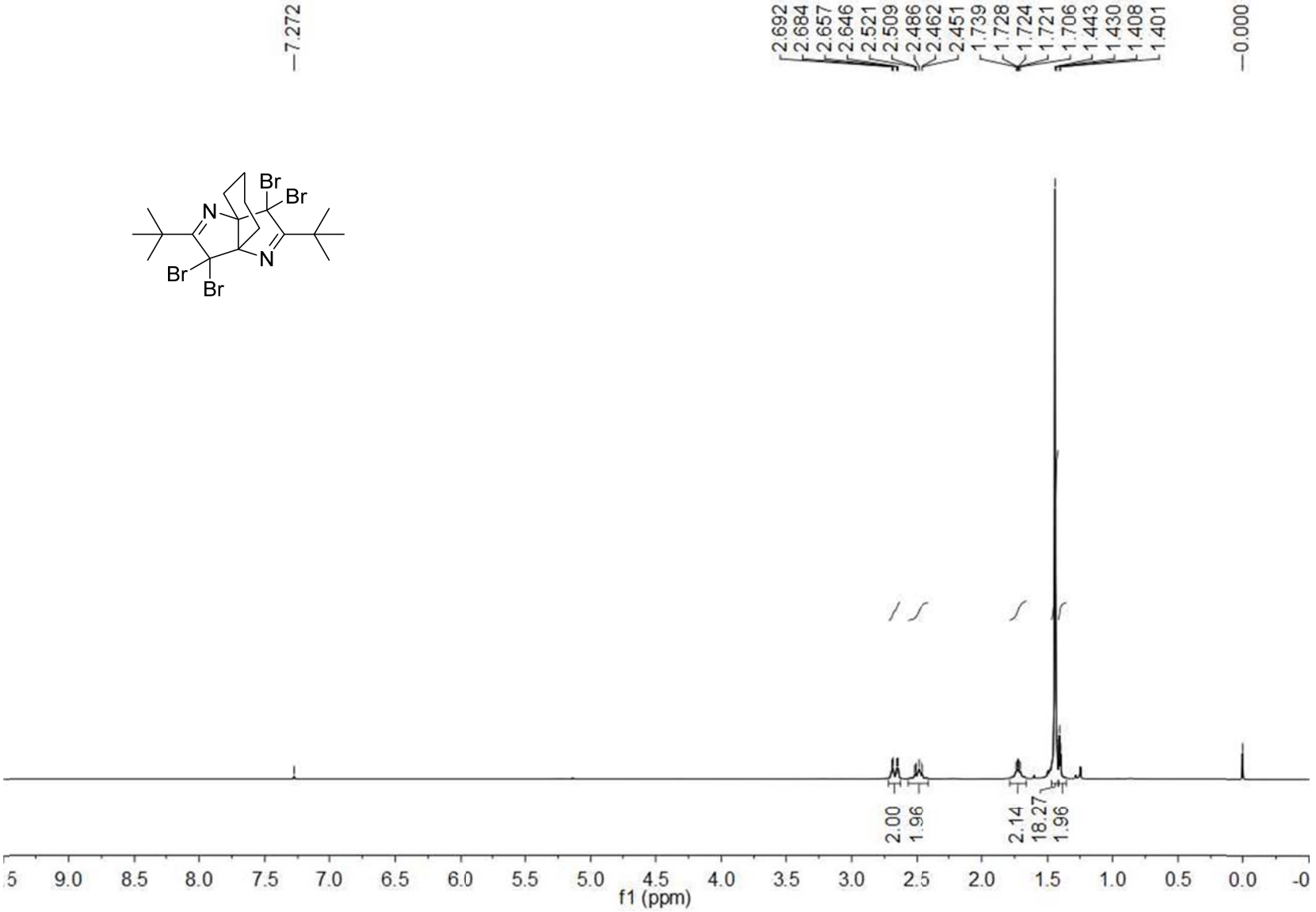
4c-^{1}H NMR


8.120
8.104
7.965
7.325
7.306
7.290
7.277
7.253
2.953
2.921
2.554
2.530
1.812
1.709
1.700
1.685
1.675
0.000
Br
Br
N
N
Br
Br
2.08
2.00
4.12
2.27
2.13
6.19
2.19
2.12
f1 (ppm)

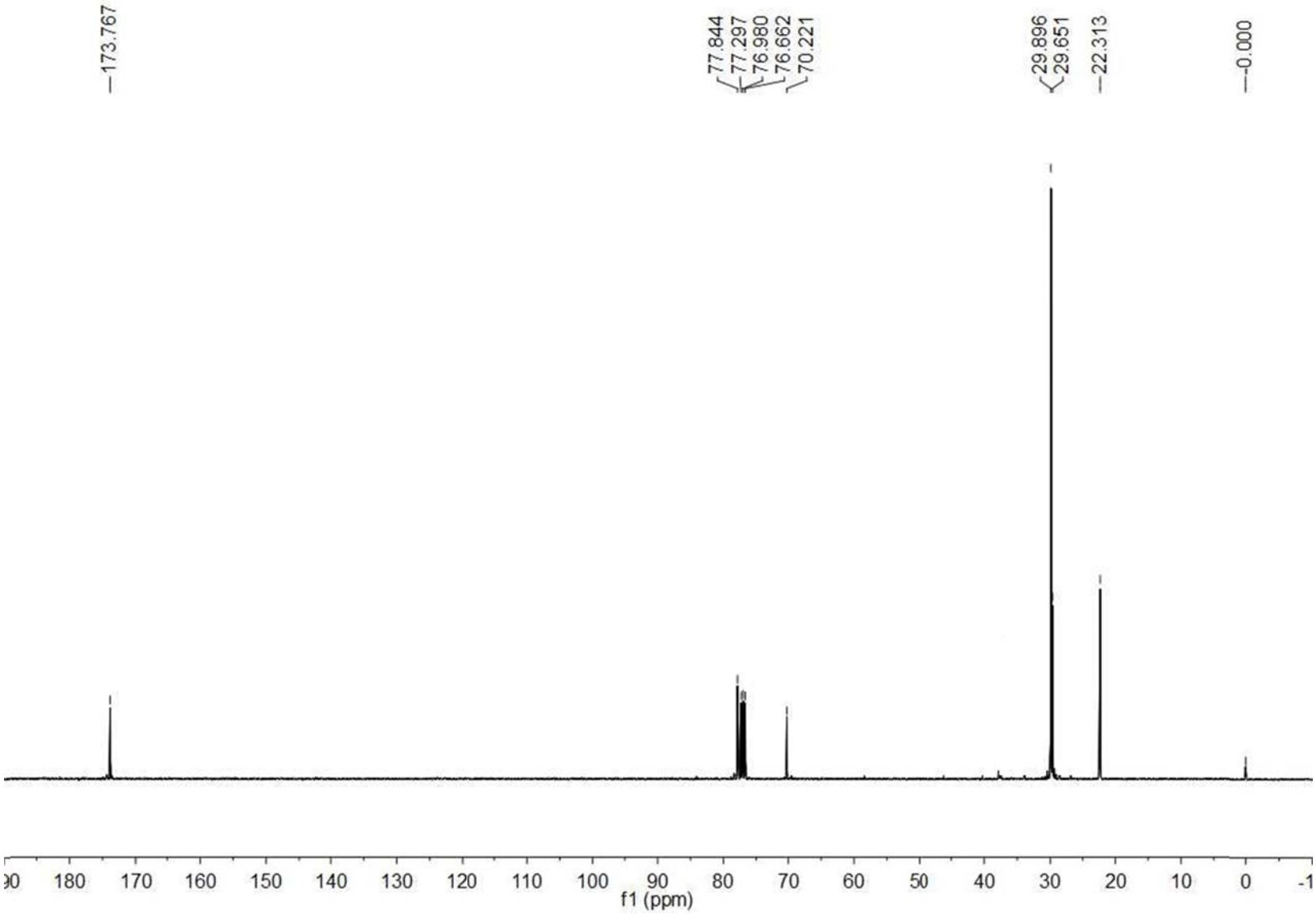
4c-^{13}C NMR


165.974
137.930
132.377
130.530
130.021
127.912
127.072
79.281
77.338
77.020
76.703
68.958
30.818
22.066
21.483
0.000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

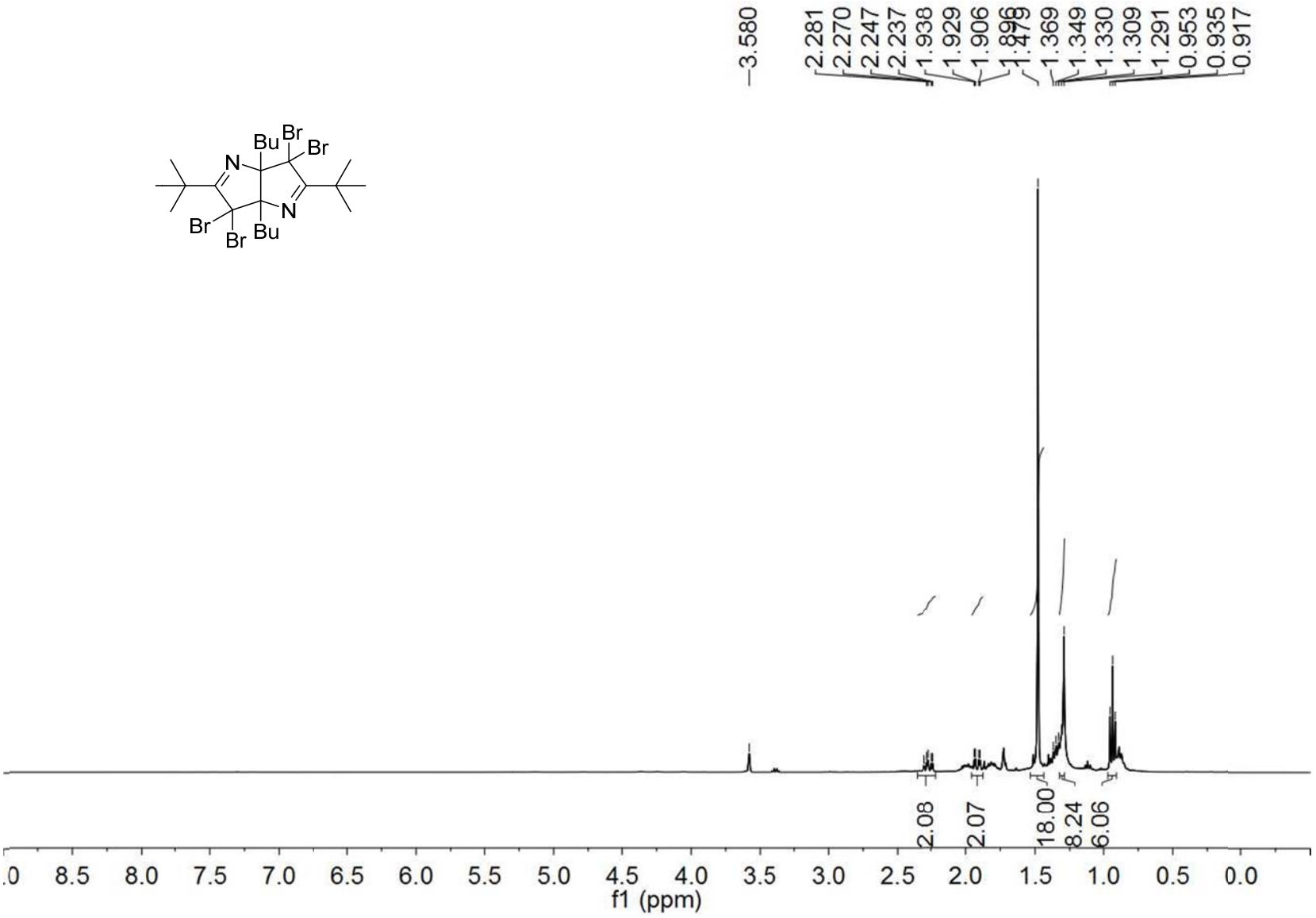
4d-^{1}H NMR


7.272
2.692
2.684
2.657
2.646
2.521
2.509
2.486
2.462
2.451
1.739
1.728
1.724
1.721
1.706
1.443
1.430
1.408
1.401
0.000
Br
Br
N
N
Br
Br
2.00
1.96
2.14
18.27
1.96
f1 (ppm)

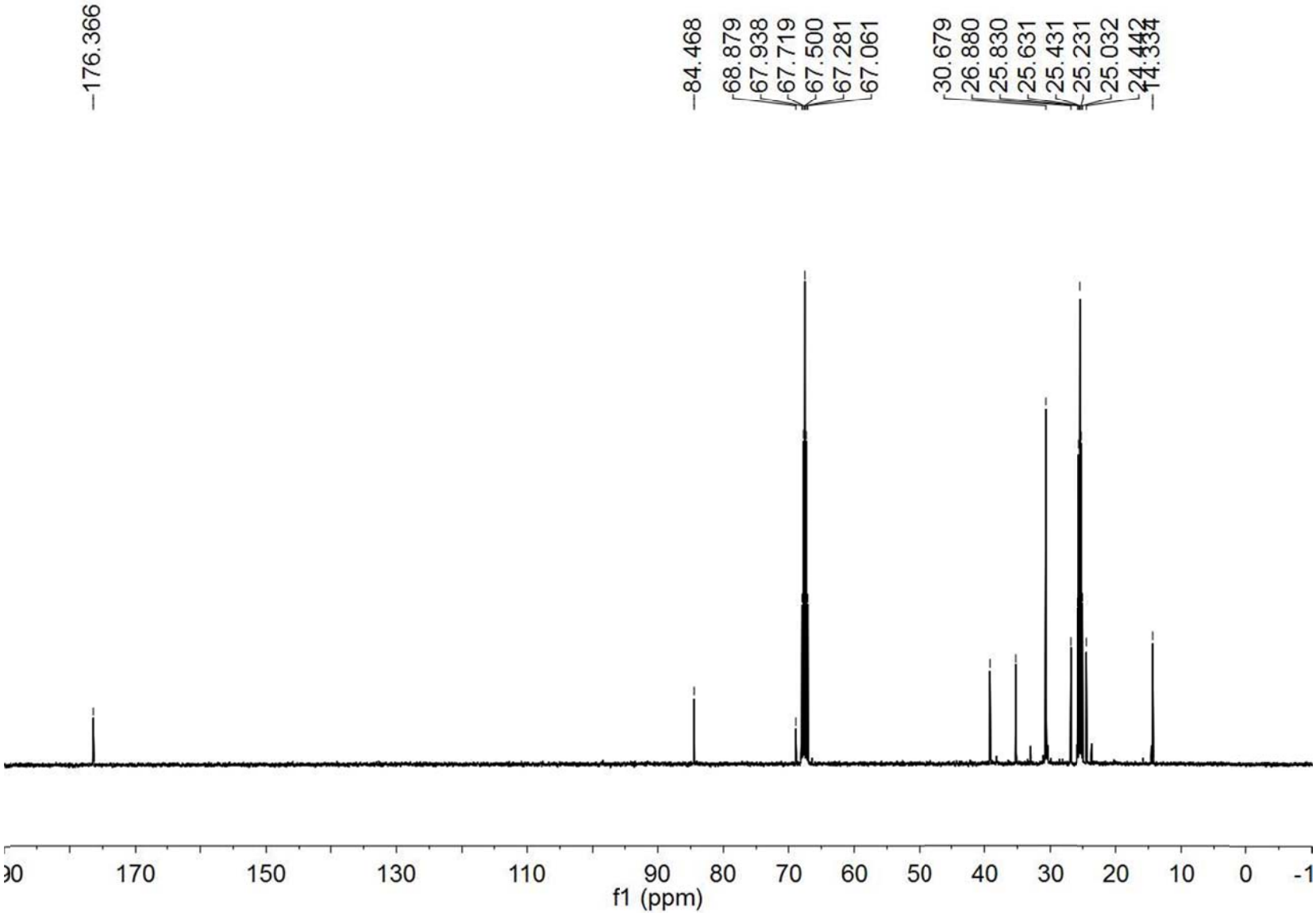
4d-^{13}C NMR


173.767
77.844
77.297
76.980
76.662
70.221
29.896
29.651
22.313
0.000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

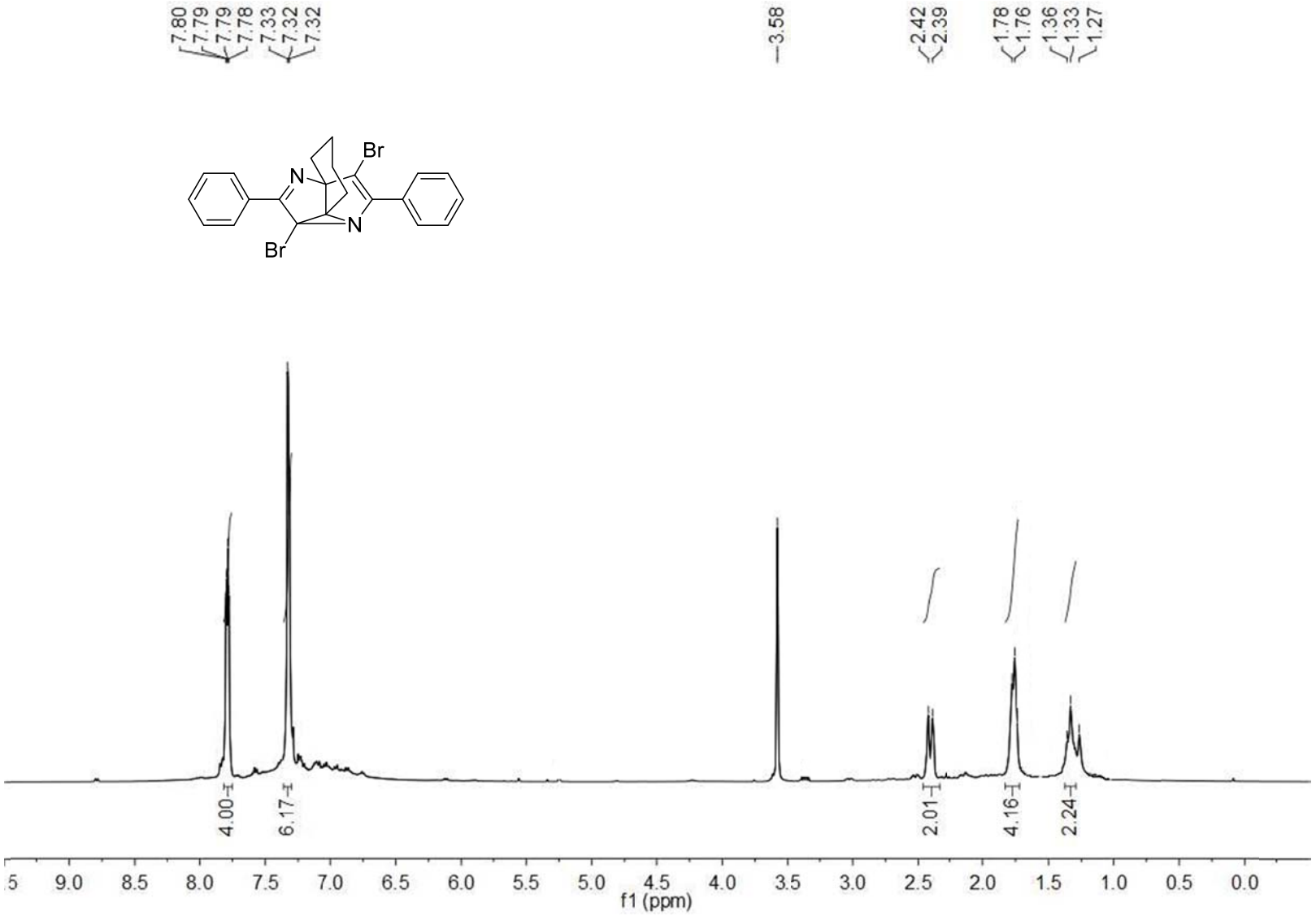
4e-^{1}H NMR


3.580
2.281
2.270
2.247
2.237
1.938
1.929
1.906
1.369
1.349
1.330
1.309
1.291
0.953
0.935
0.917
Bu
Br
Br
N
N
Br
Br
Bu
2.08
2.07
18.00
8.24
6.06
f1 (ppm)

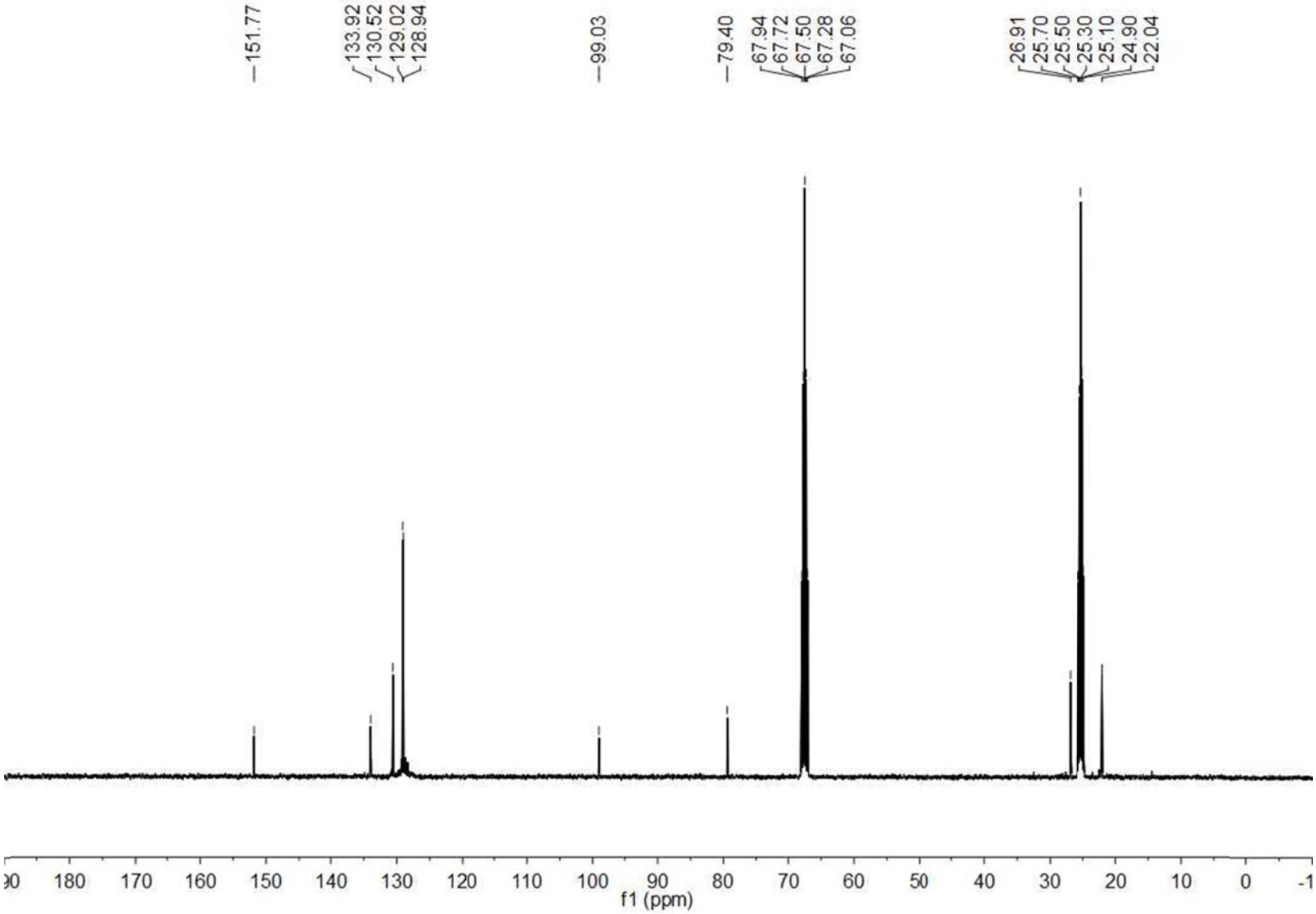
4e-^{13}C NMR


176.366
84.468
68.879
67.938
67.719
67.500
67.281
67.061
30.679
26.880
25.830
25.631
25.431
25.231
25.032
24.442
14.334
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

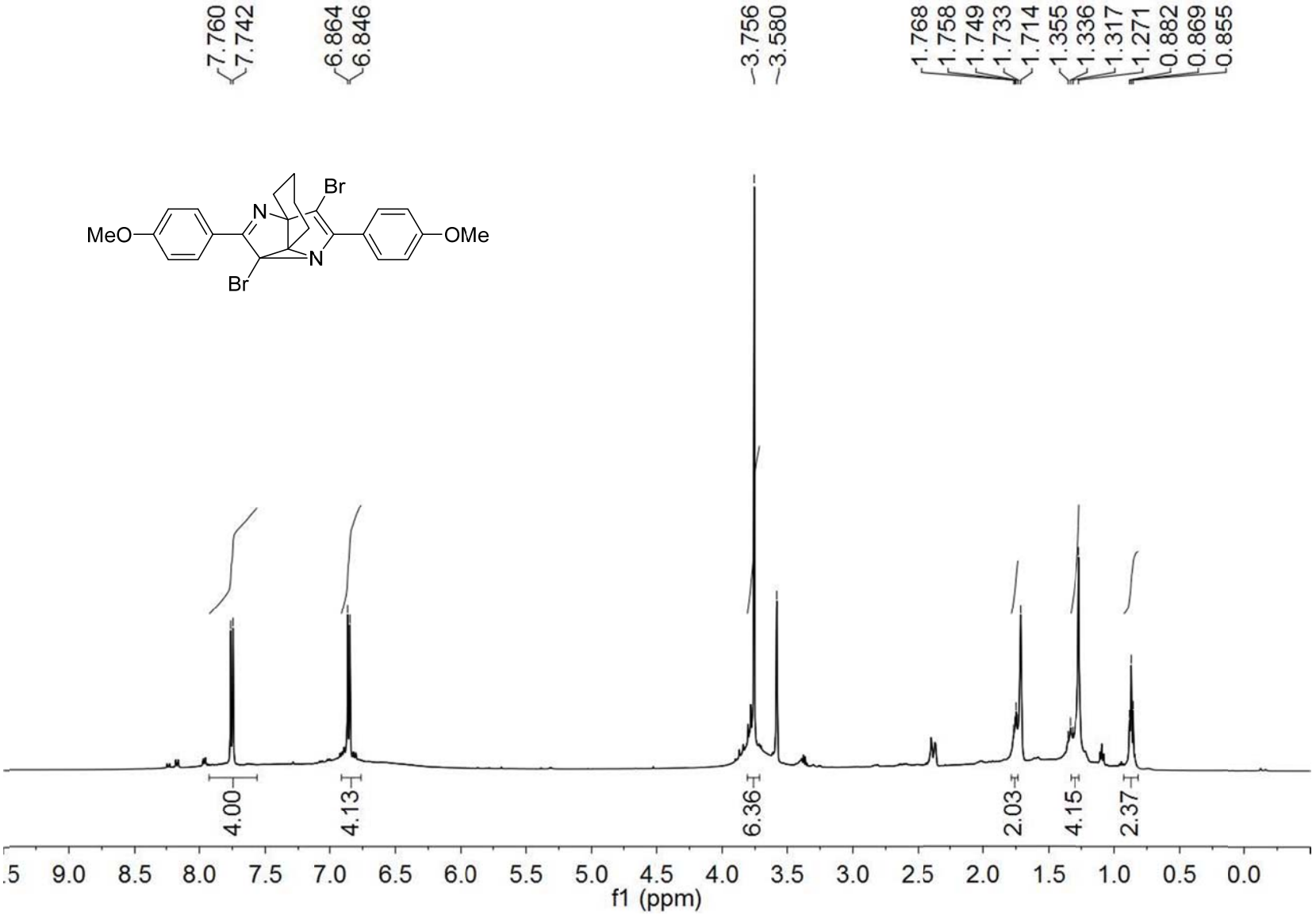
5a-^{1}H NMR


7.80
7.79
7.79
7.78
7.33
7.32
7.32
3.58
2.42
2.39
1.78
1.76
1.36
1.33
1.27
Br
N
N
Br
4.00
6.17
2.01
4.16
2.24
f1 (ppm)

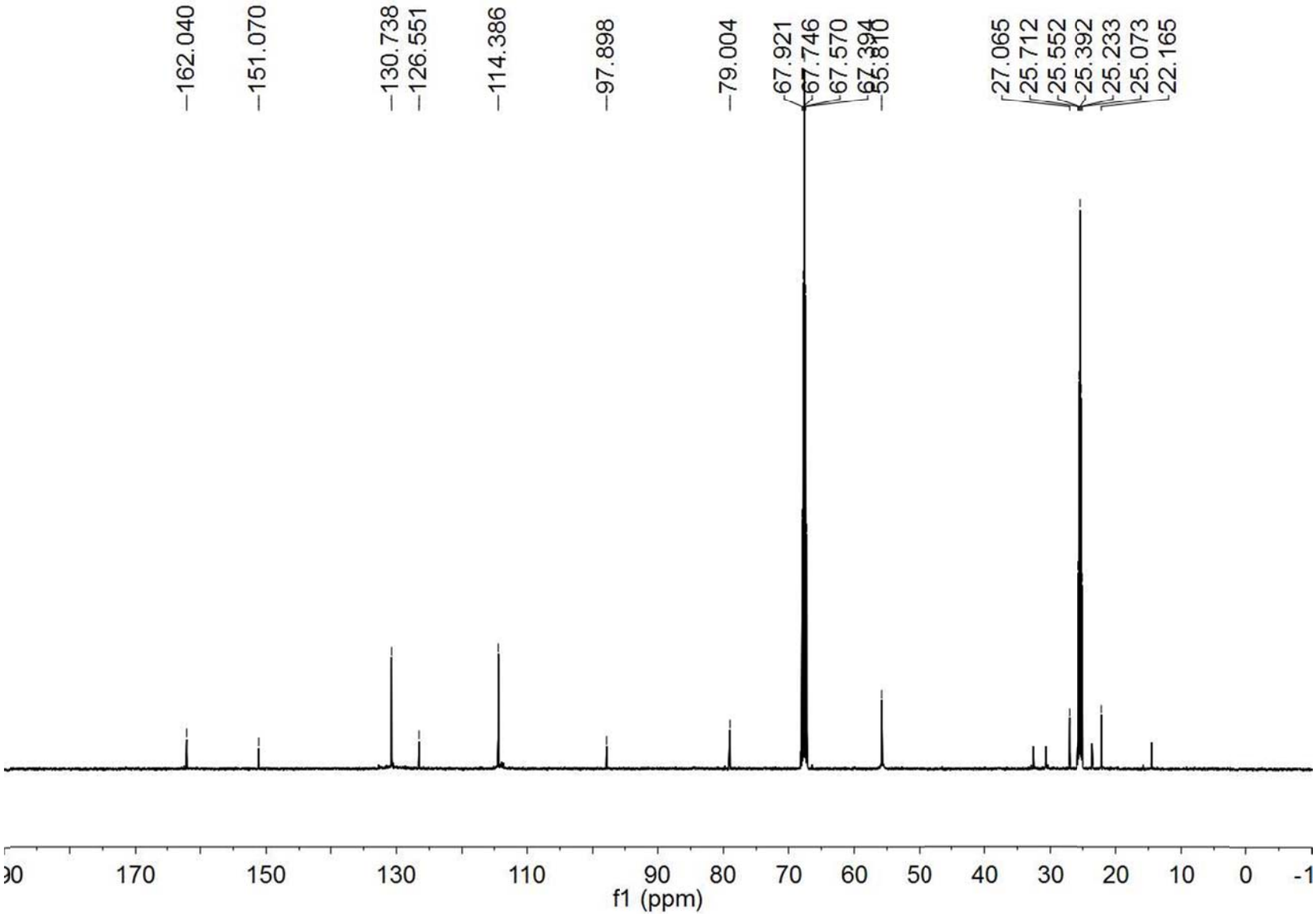
5a-^{13}C NMR


151.77
133.92
130.52
129.02
128.94
99.03
79.40
67.94
67.72
67.50
67.28
67.06
26.91
25.70
25.50
25.30
25.10
24.90
22.04
f1 (ppm)

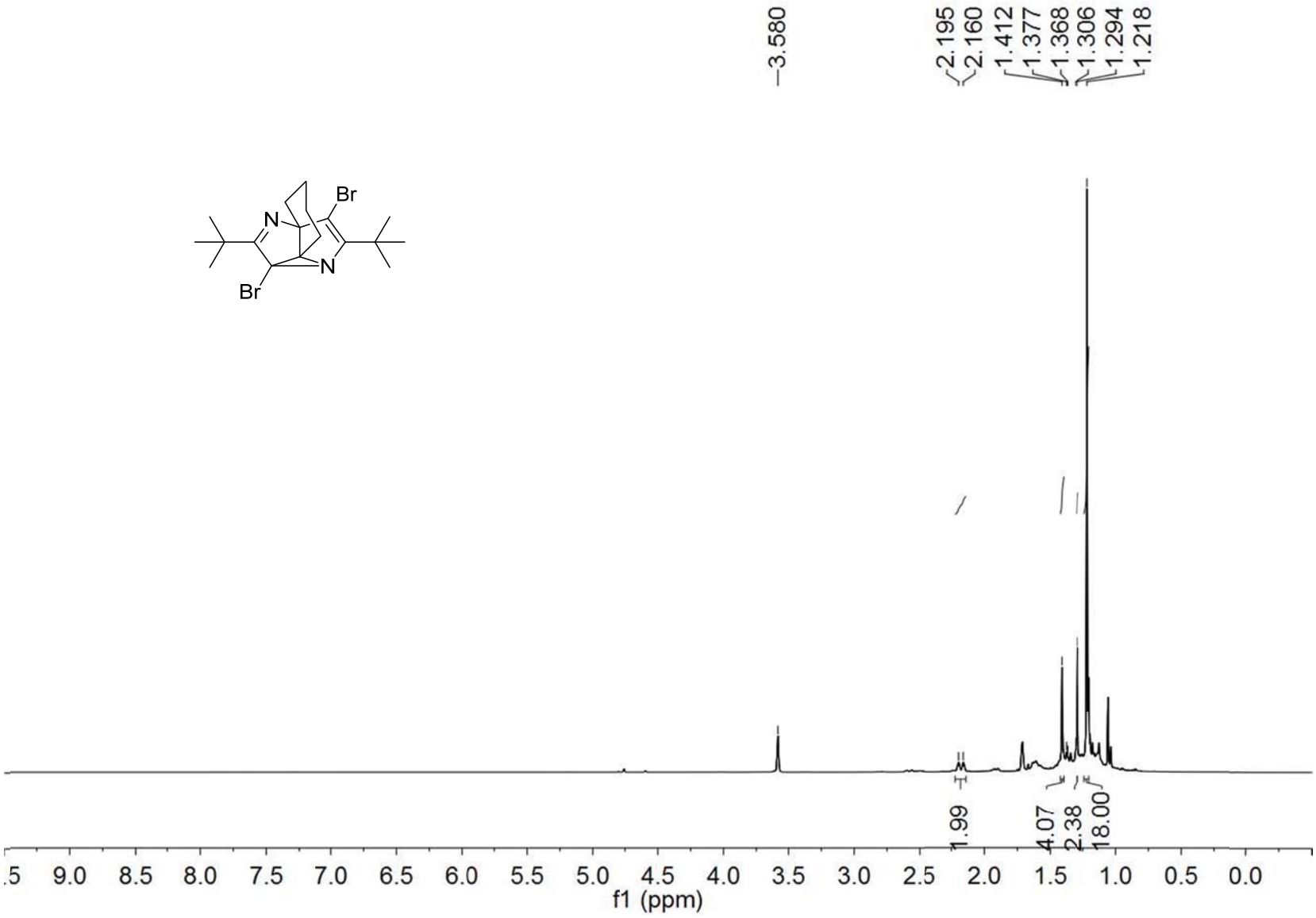
5b-^{1}H NMR


7.760
7.742
6.864
6.846
3.756
3.580
1.768
1.758
1.749
1.733
1.714
1.355
1.336
1.317
1.271
0.882
0.869
0.855
Br
N
MeO
OMe
N
Br
4.00
4.13
6.36
2.03
4.15
2.37
f1 (ppm)

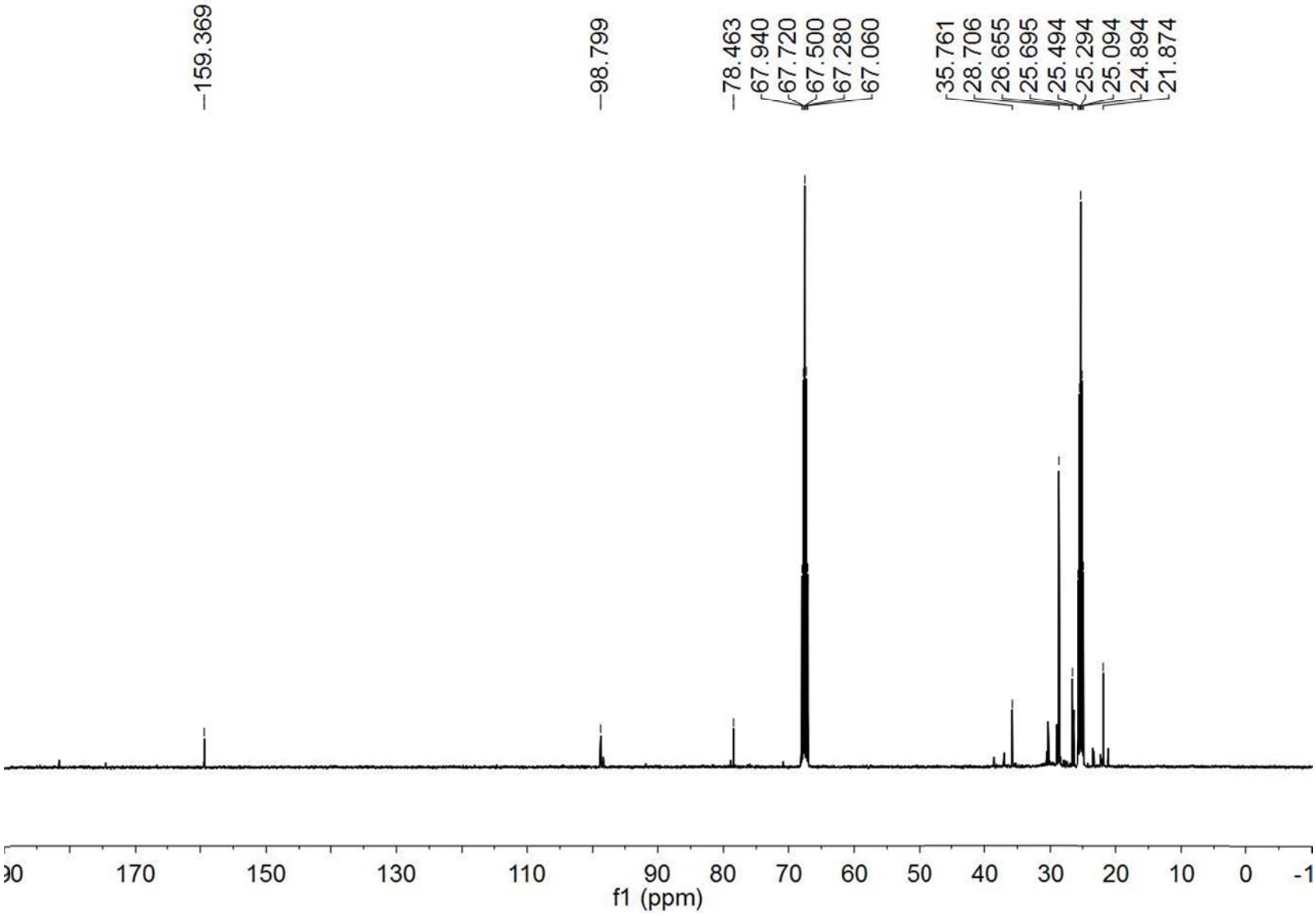
5b-^{13}C NMR


162.040
151.070
130.738
126.551
114.386
97.898
79.004
67.921
67.746
67.570
67.394
55.810
27.065
25.712
25.552
25.392
25.233
25.073
22.165
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

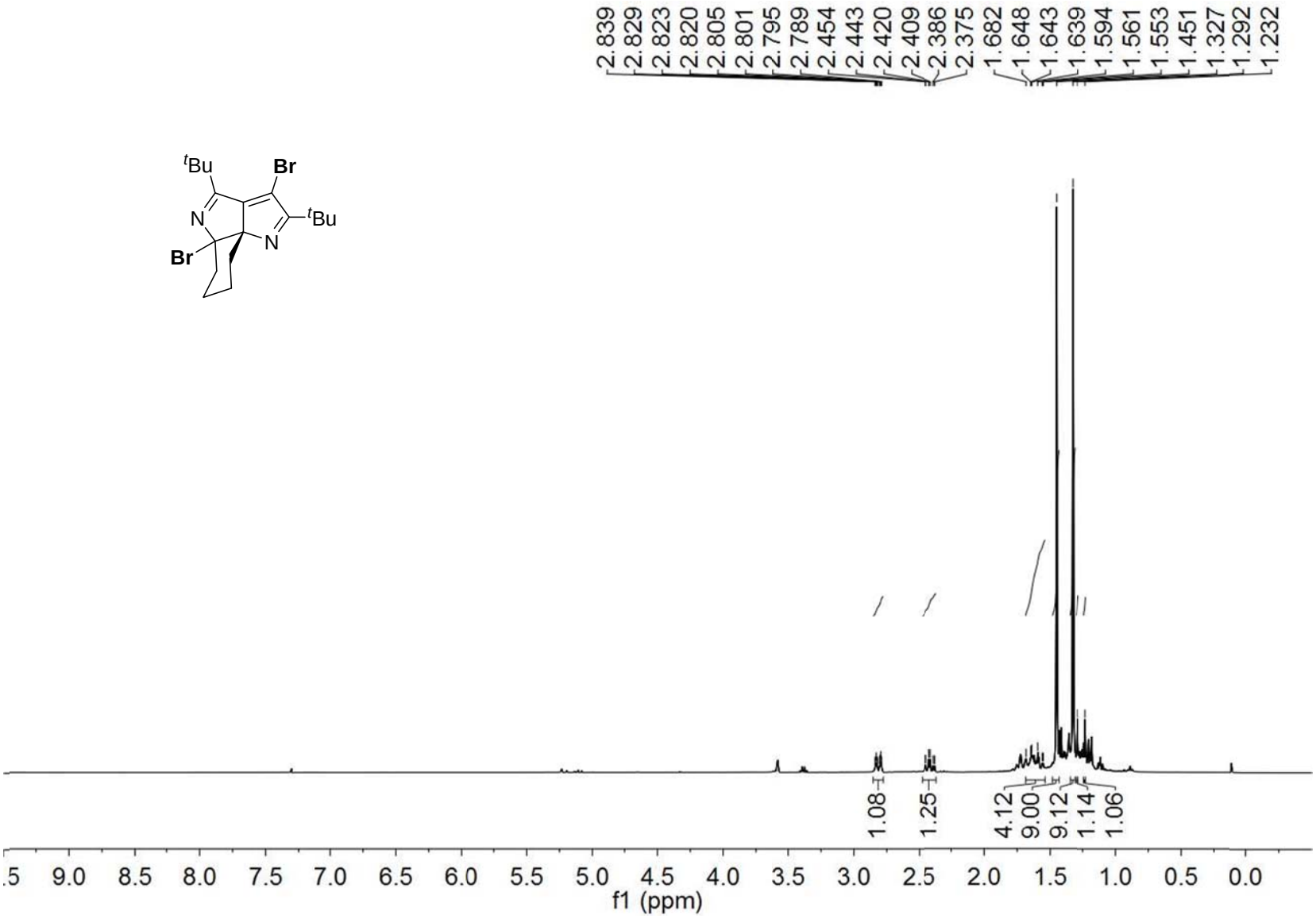
5c-^{1}H NMR


3.580
2.195
2.160
1.412
1.377
1.368
1.306
1.294
1.218
Br
N
N
Br
1.99
4.07
2.38
18.00
f1 (ppm)

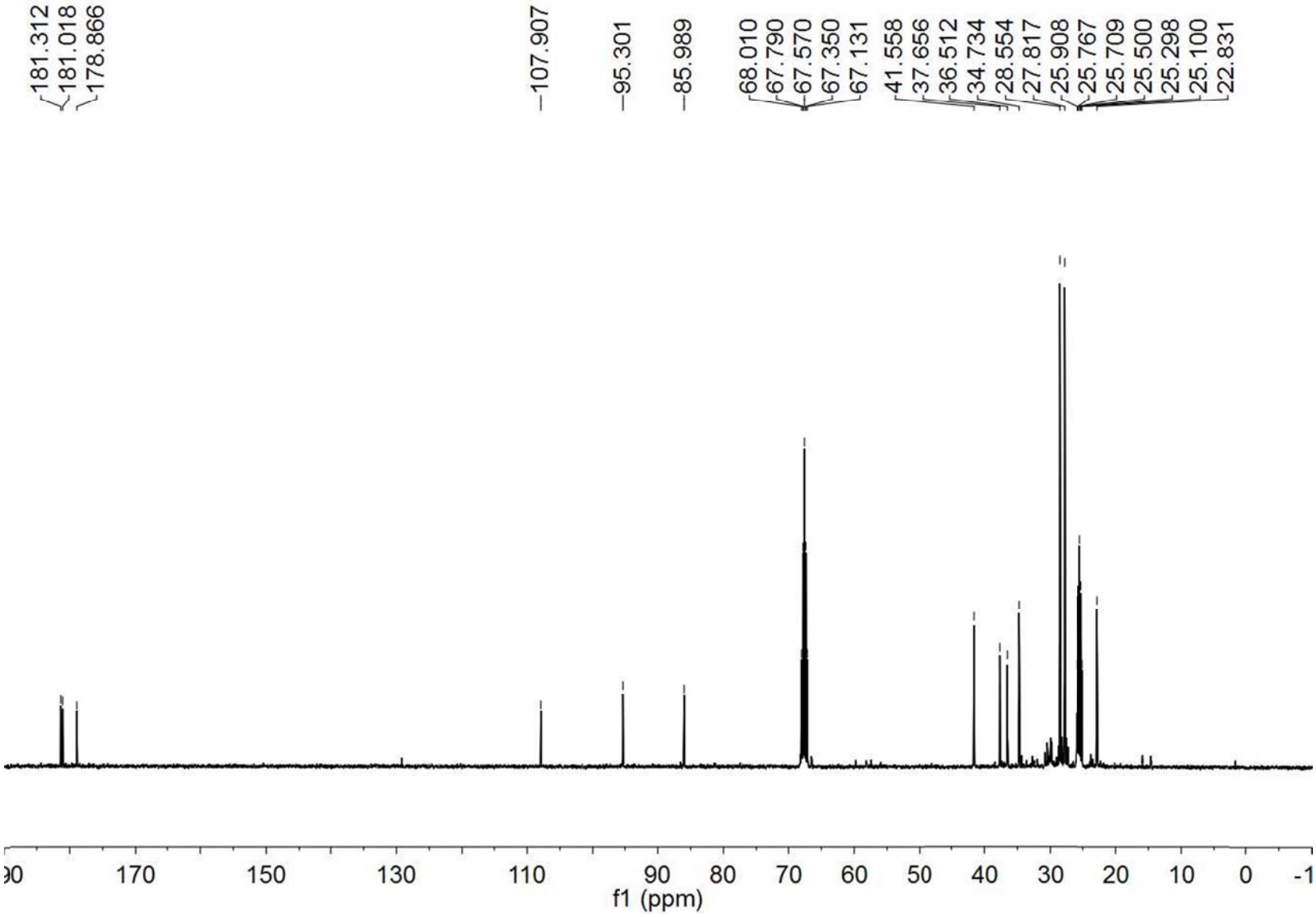
5c-^{13}C NMR


159.369
98.799
78.463
67.940
67.720
67.500
67.280
67.060
35.761
28.706
26.655
25.695
25.494
25.294
25.094
24.894
21.874
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6-^{1}H NMR


2.839
2.829
2.823
2.820
2.805
2.801
2.795
2.789
2.454
2.443
2.420
2.409
2.386
2.375
1.682
1.648
1.643
1.639
1.594
1.561
1.553
1.451
1.327
1.292
1.232
tBu
Br
N
tBu
N
Br
1.08
1.25
4.12
9.00
9.12
1.14
1.06
f1 (ppm)

6-^{13}C NMR


181.312
181.018
178.866
107.907
95.301
85.989
68.010
67.790
67.570
67.350
67.131
41.558
37.656
36.512
34.734
28.554
27.817
25.908
25.767
25.709
25.500
25.298
25.100
22.831
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)