Supporting Information

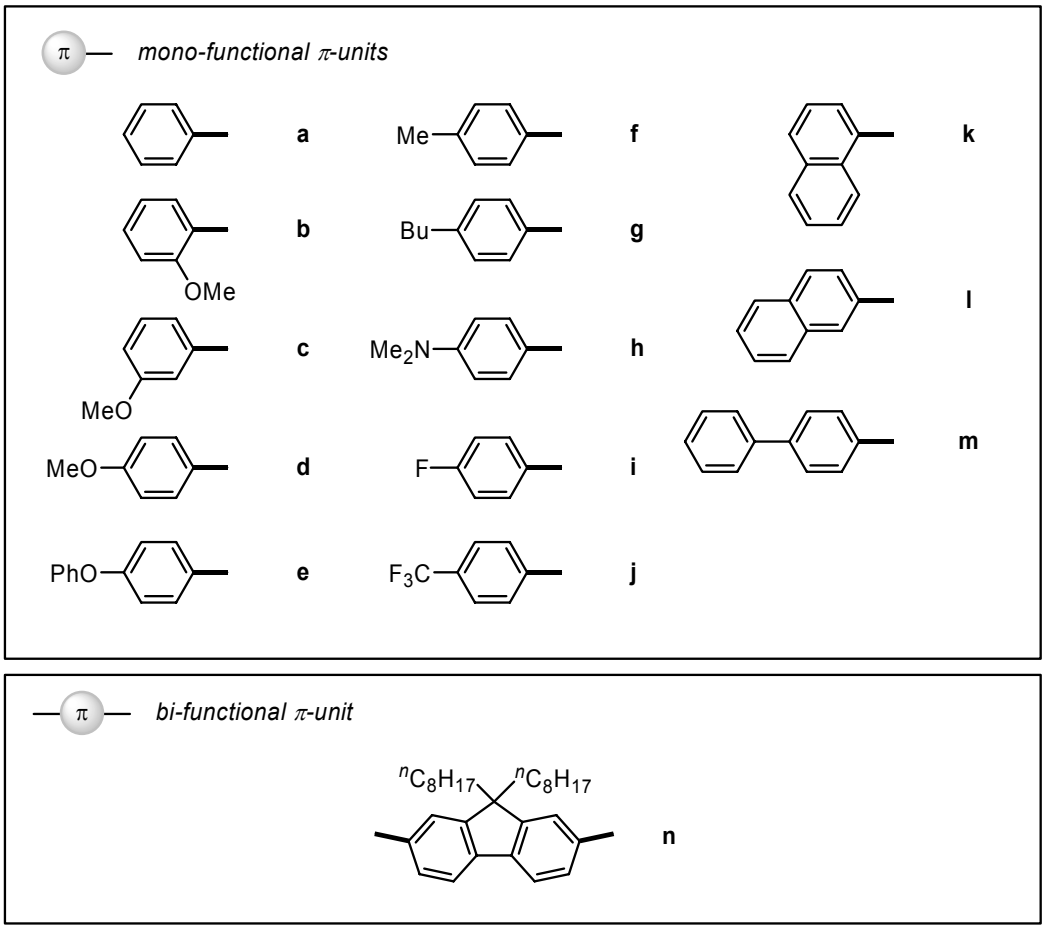
Pyrimidine-Cored Extended π-Systems: General Synthesis and Interesting Fluorescent Properties

Kenichiro Itami,* Daisuke Yamazaki, and Jun-ichi Yoshida*

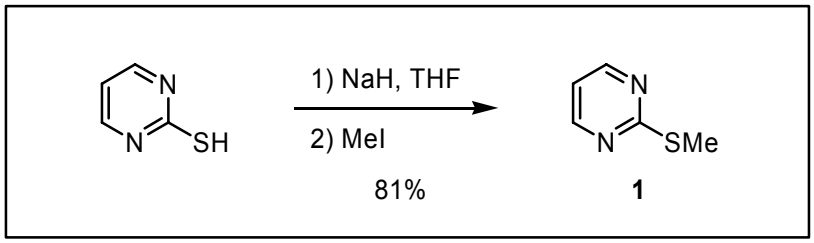
Department of Synthetic Chemistry & Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

General. ^{1}H and ^{13}C NMR spectra were recorded on Varian MERCURYplus-400 (^{1}H 400 MHz, ^{13}C 100 MHz), and JEOL A-500 (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometers in $CDCl_3$. UV/Vis spectra were recorded on Shimadzu UV-2500 spectrophotometer. Fluorescence spectra were recorded on Horiba Jobin Yvon SPEX FluoroMax-3 spectrofluorometer. EI and CI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMS-HX110A spectrometer. Gel permeation chromatography was carried out with Japan Analytical Industry LC-918. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification.

Assignment of π-Units. By following the synthetic methods described in this paper, we succeeded in installing the following 14 π-units onto the pyrimidine core in this study. For simplicity, we assigned them alphabetically as follows and used them in compound assignment.

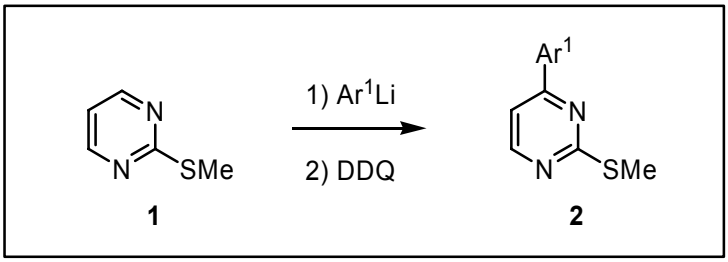


Synthesis of 2-Methylthiopyrimidine (1).

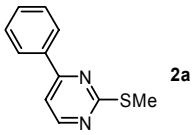


To a suspension of NaH (55wt% suspension in mineral oil, 6.01 g, 138 mmol) in THF (310 mL) was added 2-mercaptopyrimidine (11.8 g, 105 mmol) at 0 °C. After stirring the mixture at 0 °C for 30 min, a solution of MeI (19.5 g, 137 mmol) in THF (32 mL) was added to the mixture at 0 °C. After stirring the mixture at room temperature for 4 h, H_2O (200 mL) was added to the mixture. This mixture was extracted with $CHCl_3$ (150 mL × 3) and the combined organic phase was dried over $MgSO_4$. Removal of the solvent under reduced pressure, followed by distillation (50 °C, 0.1 mmHg) afforded **1** (10.8 g, 81%) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 6.96 (t, *J* = 6.8 Hz, 1H), 8.52 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 116.0, 156.8, 172.6. HRMS (EI) *m*/*z* calcd for $C_5H_6N_2S$: 126.0252, found: 126.0249.

Synthesis of 4-Aryl-2-methylthiopyrimidines 2.

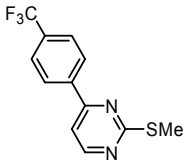


Typical Procedure: To a solution of **1** (63.6 mg, 0.50 mmol) in THF (1.5 mL) was added a solution of PhLi (0.53 mmol, 0.93 M) in THF at 0 °C. After stirring the mixture at 0 °C for 2 h, HOAc (23 μL), H_2O (1 mL), and a solution of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ; 116.3 mg, 0.51 mmol) in THF (1.5 mL) were added to the mixture. After stirring the mixture at room temperature for 45 min, 3M NaOH solution (0.2 mL) was added to the mixture. This mixture was extracted with EtOAc (1 mL × 3) and the combined organic phase was dried over $MgSO_4$. Removal of the solvent under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc = 5/1) **2a** (101.2 mg, >99%) as white solid.



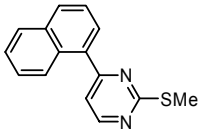
2a:[1] >99% yield from **1** and PhLi. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 3H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.45–7.50 (m, 3H), 8.05–8.10 (m, 2H), 8.53 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 111.8, 127.0, 128.8, 131.0, 136.2, 157.4, 163.6, 172.6.

(1) Fürstner, A.; Leiter, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856.



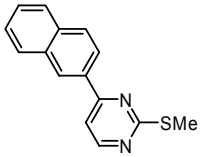
2j

2j: 93% yield from **1** and 4-$CF_3C_6H_4Li$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 3H), 7.38 (d, *J* = 5.2 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 2H), 8.59 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 112.0, 123.7 (q, $J_{C–F}$ = 269.8 Hz), 125.7 (q, $J_{C–F}$ = 3.8 Hz), 127.4, 132.6 (q, $J_{C–F}$ = 32.5 Hz), 139.6 (q, $J_{C–F}$ = 1.2 Hz), 157.8, 162.1, 173.1. HRMS (EI) *m*/*z* calcd for $C_{12}H_9N_2F_3S$: 270.0439, found: 270.0440.



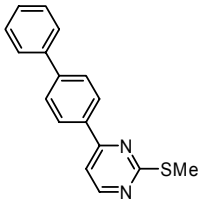
2k

2k: 68% yield from **1** and 1-naphthyllithium. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (s, 3H), 7.23 (d, *J* = 5.2 Hz, 1H), 7.48–7.58 (m, 3H), 7.65 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.88–7.92 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.17–8.22 (m, 1H), 8.61 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 116.8, 124.9, 125.0, 126.0, 126.7, 127.7, 128.4, 130.2, 130.3, 133.7, 135.5, 156.9, 166.3, 172.4. HRMS (EI) *m*/*z* calcd for $C_{15}H_{12}N_2S$: 252.0721, found 252.0721.



2l

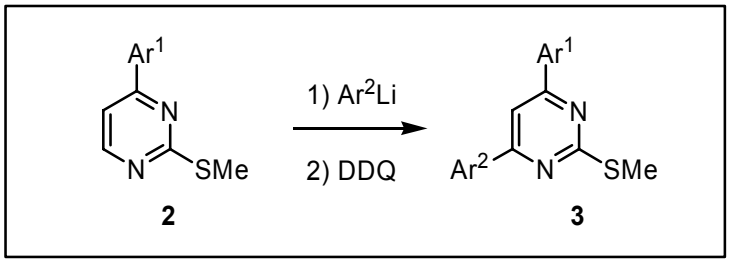
2l: 95% yield from **1** and 2-naphthyllithium. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 7.22 (d, *J* = 5.2 Hz, 1H), 7.31–7.50 (m, 2H), 7.78–7.87 (m, 3H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.42–8.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 112.1, 123.8, 126.6, 127.52, 127.55, 127.7, 128.7, 129.0, 133.1, 133.6, 134.7, 157.6, 163.8, 172.8. HRMS (EI) *m*/*z* calcd for $C_{15}H_{12}N_2S$: 252.0721, found: 252.0726.



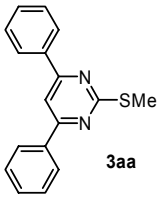
2m

2m: 85% yield from **1** and 4-biphenyllithium. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 7.36–7.38 (m, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.45–7.49 (m, 2H), 7.63–7.65 (m, 2H), 7.71 (dm, *J* = 8.8 Hz, 2H), 8.17 (dm, *J* = 8.8 Hz, 2H), 8.54 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 107.5, 127.0, 127.4, 127.6, 127.8, 128.8, 135.6, 140.1, 143.6, 154.0, 164.0, 172.6. HRMS (EI) *m*/*z* calcd for $C_{17}H_{14}N_2S$: 278.0878, found: 278.0879.

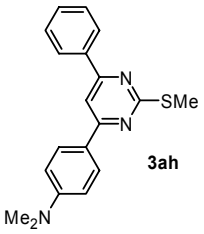
Synthesis of 4,6-Diaryl-2-methylthiopyrimidines 3.



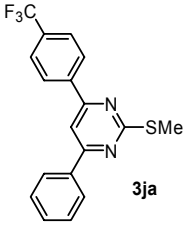
Typical Procedure: To a solution of **2a** (49.4 mg, 0.24 mmol) in THF (1.0 mL) was added a solution of PhLi (0.40 mmol, 0.87 M) in THF at 0 °C. After stirring the mixture at room temperature for 4 h, HOAc (23 μL), H_2O (1 mL), and a solution of DDQ (61.6 mg, 0.27 mmol) in THF (1 mL) were added to the mixture. After stirring the mixture at room temperature for 45 min, 3M NaOH solution (0.2 mL) was added to the mixture. This mixture was extracted with EtOAc (1 mL × 3) and the combined organic phase was dried over $MgSO_4$. Removal of the solvent under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc = 5/1) afforded **3aa** (67.9 mg, >99%) as white solid.



3aa: >99% yield from **2a** and PhLi. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (s, 3H), 7.48–7.52 (m, 6H), 7.76 (s, 1H), 8.10–8.16 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 107.8, 127.1, 128.7, 130.8, 136.8, 164.5, 172.6. HRMS (EI) *m*/*z* calcd for $C_{17}H_{14}N_2S$: 278.0878, found 278.0878.

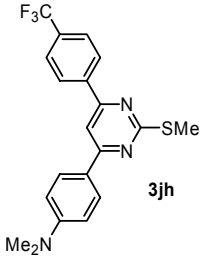


3ah: 64% yield from **2a** and 4-$Me_2NC_6H_4Li$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 2.97 (s, 6H), 6.69 (dm, *J* = 9.2 Hz, 2H), 7.42–7.48 (m, 3H), 7.59 (s, 1H), 8.03 (d, *J* = 9.2 Hz, 2H), 8.07–8.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 40.1, 105.9, 111.5, 123.6, 126.9, 128.2, 128.5, 130.2, 137.1, 152.0, 163.4, 164.0, 171.7. HRMS (EI) *m*/*z* calcd for $C_{19}H_{19}N_3S$: 321.1300, found 321.1295.



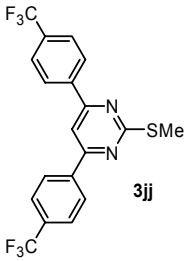
3ja: 64% yield from **2j** and PhLi. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H), 7.49–7.50 (m, 3H), 7.72–7.74 (m, 3H), 8.11–8.13 (m, 2H), 8.21 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 108.0, 123.8 (q, J_{C-F} = 269.7 Hz), 125.6 (q, J_{C-F} = 4.0 Hz), 127.1, 127.4, 128.8, 131.0, 132.4 (q, J_{C-F} = 32.1 Hz), 136.4, 140.1, 162.9,

164.8, 172.9. HRMS (EI) *m/z* calcd for $C_{18}H_{13}N_2F_3S$: 346.0752, found 346.0750.



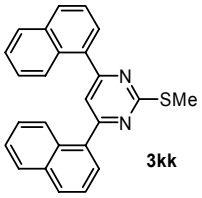
3jh

3jh: 92% yield from **2j** and 4-$Me_2NC_6H_4Li$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H), 3.05 (s, 6H), 6.37 (d, *J* = 9.2 Hz, 2H), 7.63 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 9.2 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 40.2, 106.3, 111.6, 123.4, 123.9 (q, J_{C-F} = 269.8 Hz), 125.5 (q, J_{C-F} = 4.0 Hz), 127.3, 128.4, 132.0 (q, J_{C-F} = 32.1 Hz), 140.7 (q, J_{C-F} = 1.2 Hz), 152.3, 162.1, 164.5, 172.2. HRMS (EI) *m/z* calcd for $C_{20}H_{18}N_3F_3S$: 389.1174, found 389.1175.



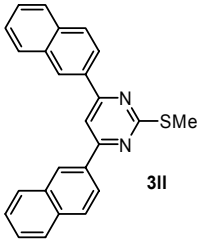
3jj

3jj: 92% yield from **2j** and 4-$CF_3C_6H_4Li$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 3H), 7.60 (d, *J* = 8.4 Hz, 4H), 7.77 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 108.2, 123.7 (q, J_{C-F} = 269.8 Hz), 125.7 (q, J_{C-F} = 3.9 Hz), 127.5, 132.7 (q, J_{C-F} = 32.2 Hz), 139.7, 163.3, 173.4. HRMS (EI) *m/z* calcd for $C_{19}H_{12}N_2F_6S$: 414.0625, found 414.0624.



3kk

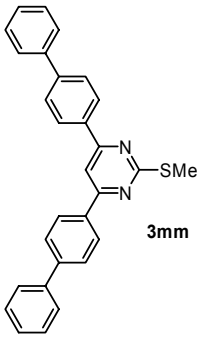
3kk: 59% yield from **2k** and 1-naphthyllithium. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (s, 3H), 7.51–7.59 (m, 7H), 7.75 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.90–7.93 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.32–8.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 117.9, 125.2, 125.3, 126.2, 127.0, 128.0, 128.6, 130.4, 130.6, 133.9, 135.9, 166.8, 172.6. HRMS (EI) *m/z* calcd for $C_{25}H_{18}N_2S$: 378.1191, found 378.1187.



3ll

3ll: 63% yield from **2l** and 2-naphthyllithium. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 7.52–7.56 (m, 4H), 7.87–7.89 (m, 2H), 7.94 (s, 1H), 7.97–8.00 (m, 4H), 8.25 (dm, *J* = 8.6 Hz, 2H), 8.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 108.2, 124.0, 126.5, 127.3, 127.4, 127.6, 128.5, 128.9, 133.1, 134.1, 134.5, 164.3,

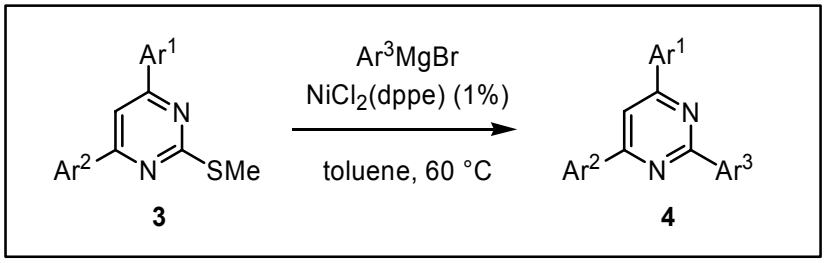
172.6. HRMS (EI) *m/z* calcd for $C_{25}H_{18}N_2S$: 378.1191, found 378.1190.



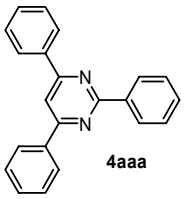
3mm

3mm: 56% yield from **2m** and 4-biphenyllithium. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 7.36–7.41 (m, 2H), 7.45–7.50 (m, 4H), 7.66 (dm, *J* = 8.0 Hz, 4H), 7.74 (dm, *J* = 6.4 Hz, 4H), 7.85 (s, 1H), 8.24 (dm, *J* = 8.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 107.5, 127.0, 127.4, 127.6, 127.77, 127.78, 135.6, 140.1, 143.6, 164.0, 172.6. HRMS (EI) *m/z* calcd for $C_{29}H_{22}N_2S$: 430.1504, found 430.1504.

Synthesis of 2,4,6-Triarylpyrimidines 4.



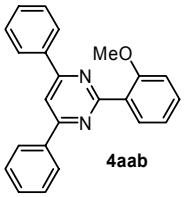
Typical Procedure: To a solution of **3aa** (53.8 mg, 0.19 mmol) and $NiCl_2$(dppe) (1.1 mg, 2.0 μmol) in toluene (1.0 mL) was added a solution of PhMgBr (0.30 mmol, 2.94 M) in THF at room temperature. This mixture was stirred at 60 °C for 4 h. After cooling the mixture to room temperature, the reaction was quenched with 1N HCl (1 mL) and the resulting solution was neutralized by adding $NaHCO_3$. This mixture was extracted with EtOAc (2 mL × 3) and the combined organic phase was dried over $MgSO_4$. Removal of the solvent under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc = 10/1) afforded **4aaa** (58.6 mg, >99%) as white solid.



4aaa

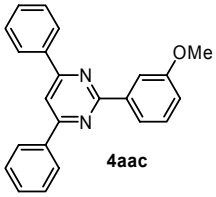
4aaa:[2] >99% yield from **3aa** and PhMgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.60 (m, 9H), 8.02 (s, 1H), 8.28–8.32 (m, 4H), 8.72–8.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.2, 127.1, 128.3, 128.4, 128.8, 130.5, 130.6, 137.4, 138.0, 164.3, 164.5.

(2) Schomaker, J. M.; Delia, T. J. *J. Org. Chem.* **2001**, *66*, 7125.



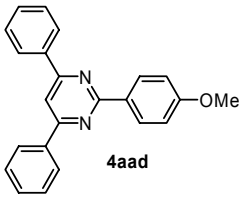
4aab

4aab: 92% yield from **3aa** and 2-$MeOC_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.10–7.14 (m, 2H), 7.46–7.51 (m, 1H), 7.52–7.57 (m, 6H), 7.99 (dt, *J* = 7.2, 1.8 Hz, 1H), 8.02 (s, 1H), 8.22–8.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 110.0, 112.5, 120.6, 127.2, 128.7, 129.1, 130.4, 130.6, 131.7, 137.5, 158.0, 164.5, 165.7. HRMS (EI) *m*/*z* calcd for $C_{23}H_{18}N_2O$: 338.1419, found 338.1413.



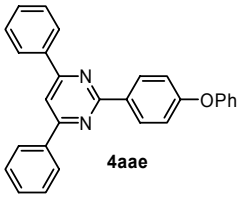
4aac

4aac: 85% yield from **3aa** and 3-$MeOC_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.06 (ddd, *J* = 8.2, 2.6, 0.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.49–7.58 (m, 6H), 7.99 (s, 1H), 8.24–8.28 (m, 5H), 8.32 (dd, *J* = 7.6, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 110.3, 113.6, 116.4, 121.0, 127.1, 128.8, 129.3, 130.6, 137.4, 139.5, 159.7, 164.1, 164.5. HRMS (EI) *m*/*z* calcd for $C_{23}H_{18}N_2O$: 338.1419, found 338.1422.



4aad

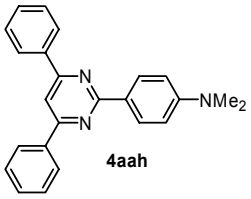
4aad:[3] 84% yield from **3aa** and 4-$MeOC_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.02 (d, *J* = 9.2 Hz, 2H), 7.48–7.52 (m, 6H), 7.90 (s, 1H), 8.22–8.25 (m, 4H), 8.65 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 109.5, 113.6, 127.1, 128.7, 129.9, 130.5, 130.8, 137.5, 161.6, 164.0, 164.3.



4aae

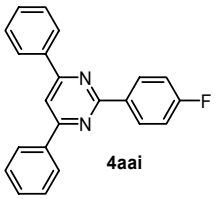
4aae: 90% yield from **3aa** and 4-$PhOC_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.20 (m, 5H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.55–7.59 (m, 6H), 7.98 (s, 1H), 8.28–8.30 (m, 4H), 8.73 (dd, *J* = 9.0, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.8, 118.2, 119.3, 123.5, 127.1, 128.7, 129.7, 130.1, 130.6, 133.0, 137.4, 156.5, 159.5, 163.8, 164.5. HRMS (EI) *m*/*z* calcd for $C_{28}H_{20}N_2O$: 400.1576, found 400.1574.

(3) Kakiya, H.; Yagi, K.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2002**, *124*, 9032.



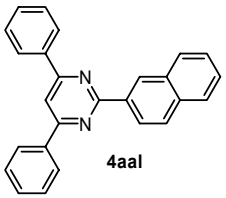
4aah

4aah: >99% yield from **3aa** and 4-$Me_2NC_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 6H), 6.80 (d, *J* = 8.8 Hz, 2H), 7.46–7.52 (m, 6H), 7.85 (s, 1H), 8.25 (dm, *J* = 7.6 Hz, 4H), 8.60 (dm, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4, 108.7, 111.5, 126.0, 127.1, 128.6, 129.6, 130.3, 137.9, 152.0, 164.2, 164.7. HRMS (EI) *m*/*z* calcd for $C_{24}H_{21}N_3$: 351.1735, found 351.1731.



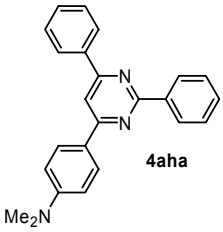
4aai

4aai: 75% yield from **3aa** and 4-FC_6H_4MgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.4 Hz, 2H), 7.55–7.61 (m, 6H), 8.02 (s, 1H), 8.27–8.29 (m, 4H), 8.72–8.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.1, 115.2 (d, $J_{C–F}$ = 21.5 Hz), 127.1, 128.8, 130.4 (d, $J_{C–F}$ = 8.7 Hz), 130.7, 134.2 (d, $J_{C–F}$ = 2.7 Hz), 137.3, 163.4, 164.5 (d, $J_{C–F}$ = 247.5 Hz), 164.6. HRMS (EI) *m*/*z* calcd for $C_{22}H_{15}N_2F$: 326.1217, found 326.1217.



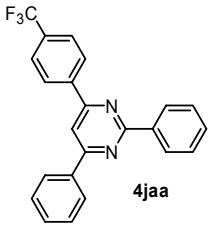
4aal

4aal: >99% yield from **3aa** and 2-naphthylmagnesium bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.63 (m, 8H), 7.91–7.94 (m, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 8.07–8.10 (m, 1H), 8.33–8.36 (m, 4H), 8.84 (dd, *J* = 8.8, 1.6 Hz, 1H), 9.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.3, 125.4, 126.0, 126.8, 127.2, 127.6, 127.9, 128.6, 128.8, 129.2, 130.6, 133.2, 134.6, 135.4, 137.5, 164.3, 164.6. HRMS (EI) *m*/*z* calcd for $C_{26}H_{18}N_2$: 358.1470, found 358.1476.



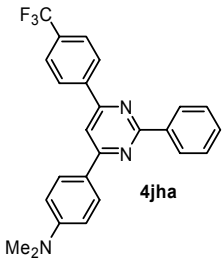
4aha

4aha: 96% yield from **3ah** and PhMgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (s, 6H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.50–7.58 (m, 6H), 7.92 (s, 1H), 8.23–8.29 (m, 4H), 8.73 (dm, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 108.5, 111.8, 124.6, 127.1, 128.2, 128.3, 128.7, 130.1, 130.2, 137.9, 138.5, 152.1, 163.8, 164.0, 164.3. HRMS (EI) *m*/*z* calcd for $C_{24}H_{21}N_3$: 351.1735, found 351.1733.



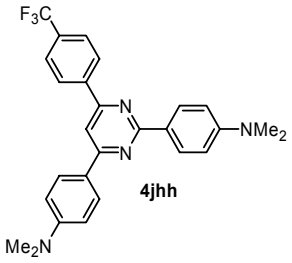
4jaa

4jaa: 97% yield from **3ja** and PhMgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.60 (m, 6H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.99 (s, 1H), 8.25–8.28 (m, 2H), 8.36 (d, *J* = 8.8 Hz, 2H), 8.66–8.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.3, 123.9 (q, $J_{C–F}$ = 269.8 Hz), 125.7 (q, $J_{C–F}$ = 3.6 Hz), 127.1, 127.4, 128.3, 128.8, 130.7, 130.9, 132.2 (q, $J_{C–F}$ = 32.3 Hz), 137.0, 137.6, 140.7, 162.9, 164.4, 164.9. HRMS (EI) *m*/*z* calcd for $C_{25}H_{15}N_2F_3$: 376.1187, found 376.1187.



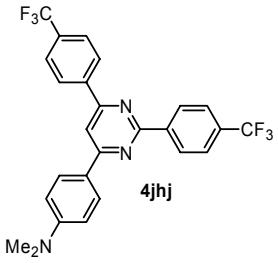
4jha

4jha: 96% yield from **3jh** and PhMgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 6H), 6.78 (d, *J* = 9.2 Hz, 2H), 7.48–7.54 (m, 3H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.83–7.87 (m, 1H), 8.19 (d, *J* = 9.2 Hz, 2H), 8.24 (d, *J* = 7.6 Hz, 2H), 8.66–8.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 108.8, 111.7, 124.2, 124.9 (q, $J_{C–F}$ = 269.8 Hz), 125.6 (q, $J_{C–F}$ = 3.6 Hz), 127.4, 128.26, 128.29, 128.4, 130.4, 132.4 (q, $J_{C–F}$ = 32.5 Hz), 138.2, 141.4, 152.2, 162.3, 164.2, 164.7. HRMS (EI) *m*/*z* calcd for $C_{25}H_{20}N_3F_3$: 419.1609, found 419.1613.



4jhh

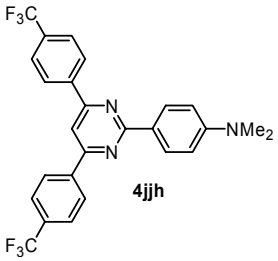
4jhh: >99% yield from **3jh** and 4-$Me_2NC_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.065 (s, 6H), 3.068 (s, 6H), 6.806 (d, *J* = 8.8 Hz, 2H), 6.811 (d, *J* = 8.8 Hz, 2H), 7.76 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.57 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.2, 40.4, 107.4, 111.5, 111.7, 124.7, 125.4, 126.1, 126.8 (q, $J_{C–F}$ = 272.5 Hz), 127.3, 128.2, 129.5, 131.5 (q, $J_{C–F}$ = 32.1 Hz), 141.8, 151.9, 152.0, 161.9, 164.3, 164.4. HRMS (EI) *m*/*z* calcd for $C_{27}H_{25}N_4F_3$: 462.2031, found 462.2032.



4jhj

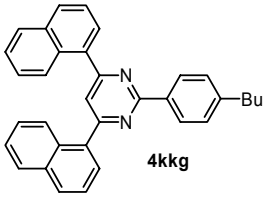
4jhj: 35% yield from **3jh** and 4-$CF_3C_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (s, 6H), 6.82 (d, *J* = 9.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.93 (s, 1H), 8.21 (d, *J* = 9.2 Hz, 2H), 8.33 (d, *J* =

8.0 Hz, 2H), 8.78 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.2, 109.3, 111.7, 123.7, 123.9 (q, $J_{C–F}$ = 269.7 Hz), 124.2 (q, $J_{C–F}$ = 269.7 Hz), 125.1 (q, $J_{C–F}$ = 3.5 Hz), 125.6 (q, $J_{C–F}$ = 3.5 Hz), 127.4, 128.4, 128.5, 131.9 (q, $J_{C–F}$ = 32.1 Hz), 132.1 (q, $J_{C–F}$ = 32.2 Hz), 140.9, 141.4, 152.4, 162.3, 162.8, 164.9. HRMS (EI) m/z calcd for $C_{26}H_{19}N_3F_6$: 487.1483, found 487.1482.



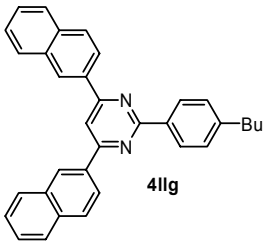
4jjh

4jjh: 95% yield from **3jj** and 4-$Me_2NC_6H_4MgBr$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (s, 6H), 6.81 (d, J = 9.2 Hz, 2H), 7.80 (d, J = 8.4 Hz, 4H), 7.86 (s, 1H), 8.34 (d, J = 8.4 Hz, 4H), 8.62 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 109.1, 111.5, 123.9 (q, $J_{C–F}$ = 269.8 Hz), 125.1, 125.7 (q, $J_{C–F}$ = 3.6 Hz), 127.5, 129.8, 132.2 (q, $J_{C–F}$ = 32.1 Hz), 140.9, 152.3, 163.2, 165.1. HRMS (EI) m/z calcd for $C_{26}H_{19}N_3F_6$: 487.1483, found 487.1482.



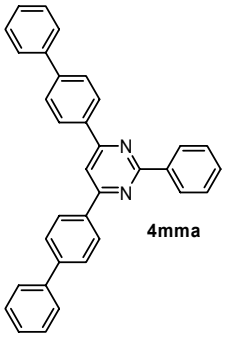
4kkg

4kkg: 95% yield from **3kk** and 4-BuC_6H_4MgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 1.32–1.42 (m, 2H), 1.60–1.70 (m, 2H), 2.68 (t, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.51–7.55 (m, 4H), 7.58 (d, J = 7.2 Hz, 2H), 7.73 (s, 1H), 7.79 (dm, J = 7.2 Hz, 2H), 7.90–7.93 (m, 2H), 7.95 (d, J = 8.4 Hz, 2H), 8.45–8.47 (m, 2H), 8.57 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 33.6, 35.7, 119.9, 125.2, 125.4, 126.0, 126.8, 127.9, 128.4, 128.50, 128.54, 130.1, 130.7, 133.9, 135.3, 136.5, 145.8, 164.1, 166.8. HRMS (EI) m/z calcd for $C_{34}H_{28}N_2$: 464.2252, found 464.2253.



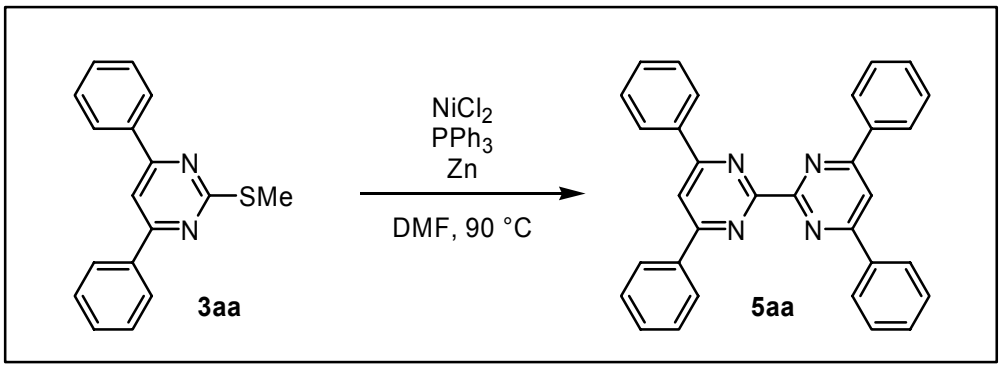
4llg

4llg: >99% yield from **3ll** and 4-BuC_6H_4MgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.2 Hz, 3H), 1.37–1.48 (m, 2H), 1.61–1.67 (m, 2H), 2.71 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.49–7.53 (m, 4H), 7.83–7.86 (m, 2H), 7.92–7.97 (m, 4H), 7.98 (s, 1H), 8.26 (dm, J = 8.4 Hz, 2H), 8.64 (d, J = 8.0 Hz, 2H), 8.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 33.6, 35.8, 110.1, 124.1, 126.3, 127.0, 127.2, 127.6, 128.38, 128.42, 128.9, 133.1, 134.4, 134.7, 135.6, 145.6, 164.12, 164.16, 164.4. HRMS (EI) m/z calcd for $C_{34}H_{28}N_2$: 464.2252, found 464.2252.



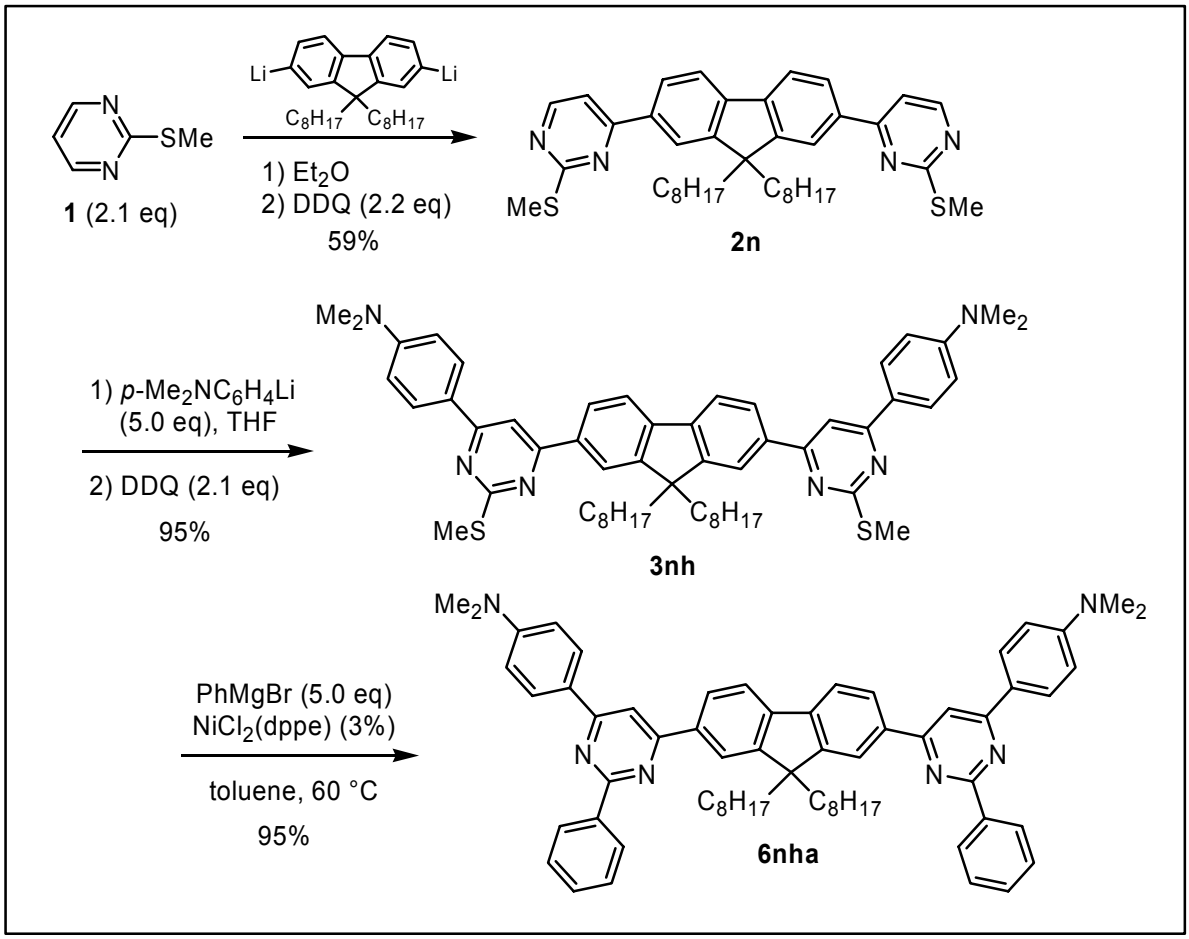
4mma: >99% yield from **3mm** and PhMgBr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.42 (m, 2H), 7.47–7.57 (m, 7H), 7.68 (d, *J* = 8.4 Hz, 4H), 7.79 (d, *J* = 8.8 Hz, 4H), 8.08 (s, 1H), 8.38 (d, *J* = 8.8 Hz, 4H), 8.75 (dm, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.9, 127.1, 127.5, 127.6, 127.7, 128.3, 128.4, 128.8, 130.5, 136.3, 138.1, 140.2, 143.4, 164.1, 164.4. HRMS (EI) *m*/*z* calcd for $C_{34}H_{24}N_2$: 460.1939, found 460.1939.

Synthesis of 5aa.



A mixture of $NiCl_2$ (19.5 mg, 0.15 mmol), PPh_3 (156.9 mg, 0.60 mmol), and Zn (14.6 mg, 0.23 mmol) in DMF (1.0 mL) was stirred at 50 °C for 0.5 h under argon. To this mixture was added **3aa** (40.7 mg, 0.15 mmol) and the resultant mixture was stirred at 90 °C for 24 h. After cooling the mixture to room temperature, *aq* NH_4OH (1 mL) and EDTA·2Na (150 mg) were added to the mixture. This mixture was extracted with $CHCl_3$ (2 mL × 3) and the combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc = 10/1) afforded **5aa** (46.9 mg, 68%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.60 (m, 12H), 8.23 (s, 2H), 8.33 (dd, *J* = 8.0, 2.0 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.4, 127.5, 128.8, 130.8, 137.1, 164.0, 165.4. HRMS (EI) *m*/*z* calcd for $C_{32}H_{22}N_4$: 462.1844, found 462.1845. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 264 (4.74) nm. FL ($CHCl_3$): λ_{max} = 410 nm; $\Phi_F = 4.6 \times 10^{-3}$ (reference to 9,10-diphenylanthracene; exited at 350 nm).

Synthesis of 6nha. Compound **6nha** was prepared by following the typical procedures for the preparation of triarylpyrimidines **4**.

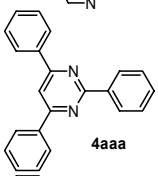
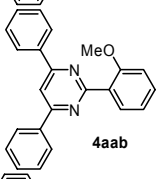
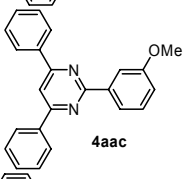
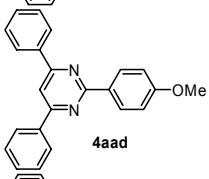
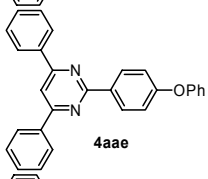
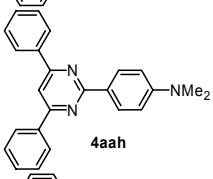
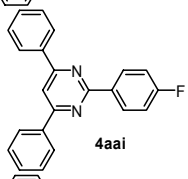
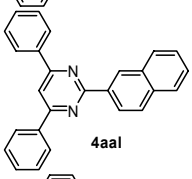
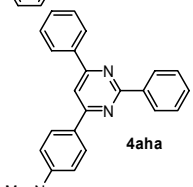
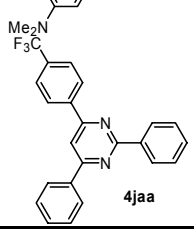


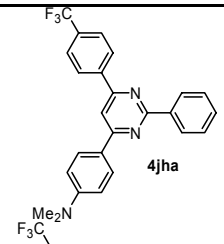
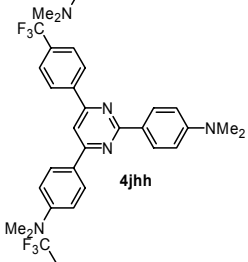
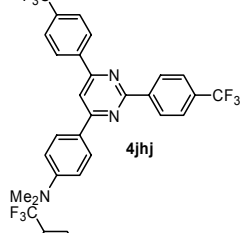
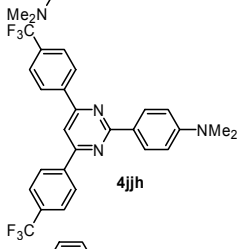
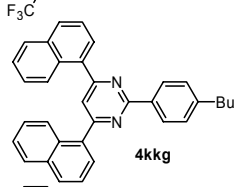
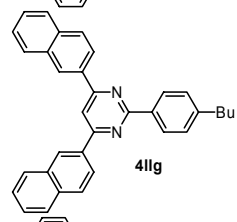
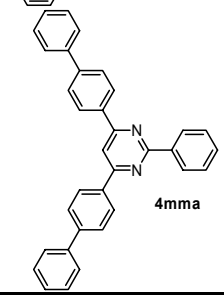
2n: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60–0.72 (m, 4H), 0.77 (t, J = 7.2 Hz, 6H), 1.00–1.20 (m, 20H), 2.05–2.12 (m, 4H), 2.68 (s, 6H), 7.44 (d, J = 5.2 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H), 8.11 (s, 2H), 8.12 (d, J = 8.8 Hz, 2H), 8.55 (d, J = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.3, 22.6, 23.9, 29.21, 29.22, 30.0, 31.8, 40.2, 55.5, 111.8, 120.5, 121.4, 126.3, 135.7, 143.0, 152.0, 157.3, 163.6, 172.5. HRMS (FAB) m/z calcd for $C_{39}H_{51}N_4S_2$ (MH^+): 639.3555, found 639.3554.

3nh: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64–0.74 (m, 4H), 0.77 (t, J = 6.8 Hz, 6H), 1.00–1.20 (m, 20H), 2.10–2.14 (m, 4H), 2.74 (s, 6H), 3.06 (s, 12H), 6.78 (d, J = 8.8 Hz, 4H), 7.72 (s, 2H), 7.84 (d, J = 8.4 Hz, 2H), 8.11–8.16 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.5, 22.7, 24.0, 29.32, 29.34, 30.1, 31.9, 40.2, 40.3, 55.6, 106.2, 111.6, 120.3, 121.5, 124.0, 126.3, 128.4, 136.7, 142.7, 151.9, 152.2, 163.8, 164.1, 171.8. HRMS (FAB) m/z calcd for $C_{55}H_{69}N_6S_2$ (MH^+): 877.5025, found 877.5029.

6nha: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73–0.81 (m, 4H), 0.74 (t, J = 6.4 Hz, 6H), 1.04–1.20 (m, 20H), 2.19–2.23 (m, 4H), 3.09 (s, 12H), 6.85 (d, J = 8.8 Hz, 4H), 7.48–7.58 (m, 6H), 7.92 (d, J = 7.8 Hz, 2H), 7.97 (s, 2H), 8.26–8.29 (m, 6H), 8.31 (d, J = 7.8 Hz, 2H), 8.75 (dm, J = 8.8 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 23.9, 29.23, 29.25, 30.0, 31.8, 40.2, 40.3, 55.6, 108.7, 111.9, 120.5, 121.6, 124.8, 126.5, 128.36, 128.43, 128.45, 130.3, 137.4, 138.7, 142.8, 152.2, 152.3, 164.16, 164.22, 164.5. HRMS (FAB) m/z calcd for $C_{65}H_{72}N_6$ (MH^+): 937.5897, found 937.5902. CV: E^1_{pc} = –2.65 V (determined with reference to Ag/AgCl using Bu_4NClO_4 (0.1 M in THF) as a supporting electrolyte). UV/Vis ($CHCl_3$): λ_{max} (log ε) = 377 (4.85) nm. FL ($CHCl_3$): λ_{max} = 461 nm; Φ_F = 0.52 (reference to 9,10-diphenylanthracene; exited at 350 nm).

Physical Properties of Pyrimidine-Cored π-Systems 4

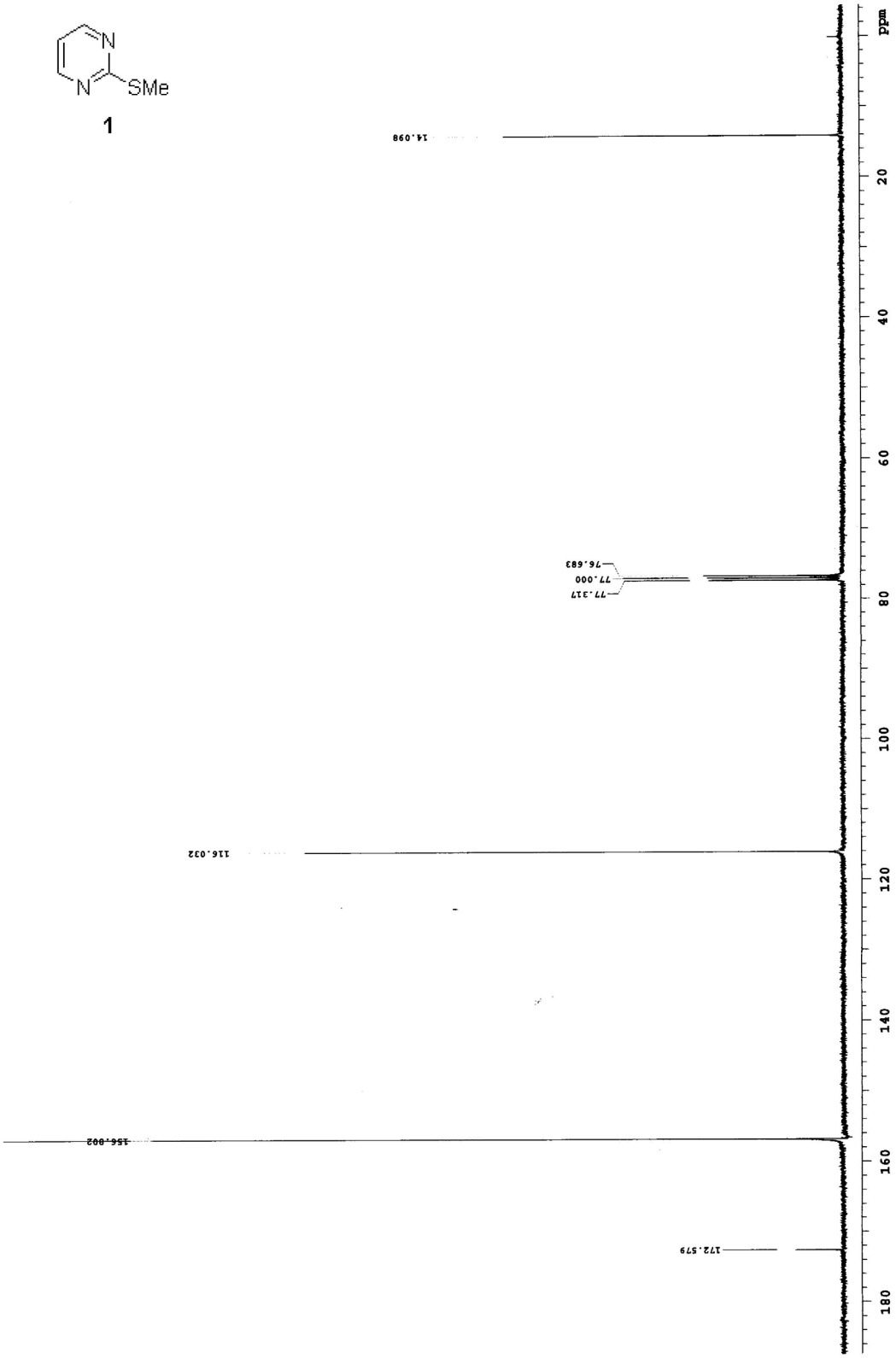
Compound	E^1_{pc} (V)[a]	UV/Vis[b]		Fluorescence[b]	
		λ_{max} (nm)	log ε	λ_{max} (nm)	Φ_F (x 10^{-2})[c]
	–2.56	278	2.60	379	nd
 **4aaa**	–2.23	265	4.90	381	0.14
 **4aab**	–2.28	267	4.89	381	nd
 **4aac**	–2.22	267	4.88	381	nd
 **4aad**	–2.24	281	4.85	381	nd
 **4aae**	–2.22	280	4.80	381	nd
 **4aah**	–2.27	344	4.42	495	4.60
 **4aai**	–2.20	270	4.92	352	nd
 **4aal**	–2.20	278	4.95	379	nd
 **4aha**	–2.34	363	4.45	444	63.0
 **4jaa**	–2.38	260 314	4.63 4.50	432	0.43

 4jha	–2.63	254 370	4.71 4.59	467	58.0
 4jhh	–2.58	246 352	4.32 4.61	479	13.0
 4jhj	–2.63	252 374	4.75 4.60	477	49.0
 4jjh	–2.60	240 280 354	4.54 4.41 4.50	539	8.70
 4kkg	–2.55	238	4.65	406	nd
 4llg	–2.56	265 328	4.88 4.29	384	nd
 4mma	–2.58	294 329	4.65 4.50	382	nd

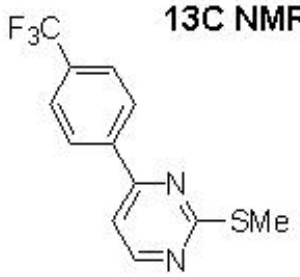
[a] Detemined by cyclic voltammetry under the following conditions: Sample, 0.1 mM; supporting electrolyte, 0.1 M Bu_4NClO_4 in THF; scan rate, 100 mV/s; reference, Ag/AgCl. [b] Measured in $CHCl_3$. [c] Quantum yields (Φ_F) were determined with reference to 9,10-diphenylanthracene (exited at 350 nm).[4]

(4) Hamal, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83.

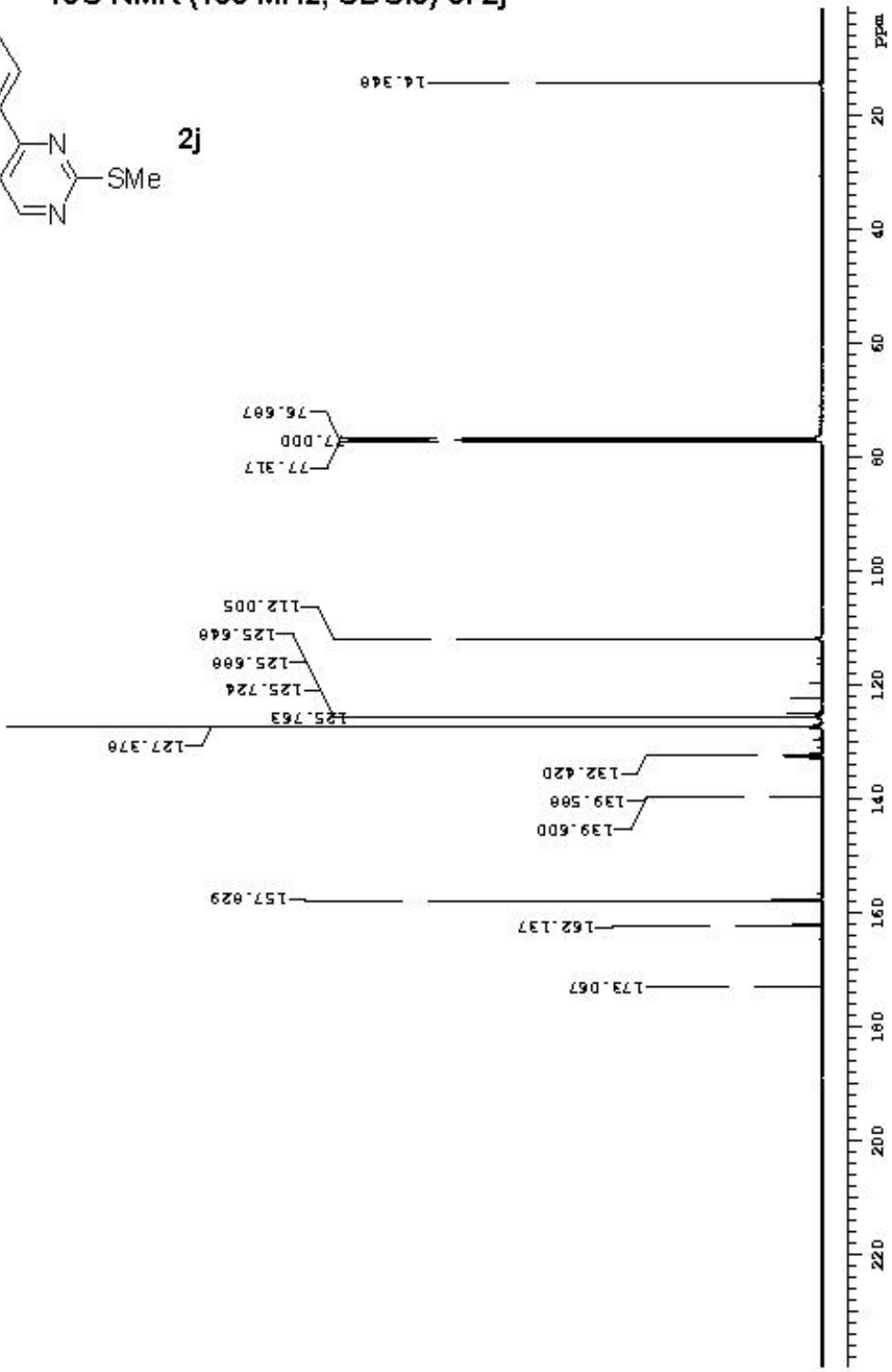
13C NMR (100 MHz, CDCl3) of 1



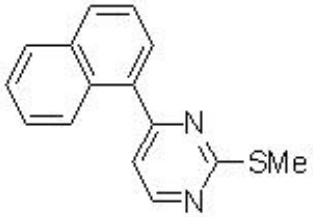
13C NMR (100 MHz, CDCl3) of 2j



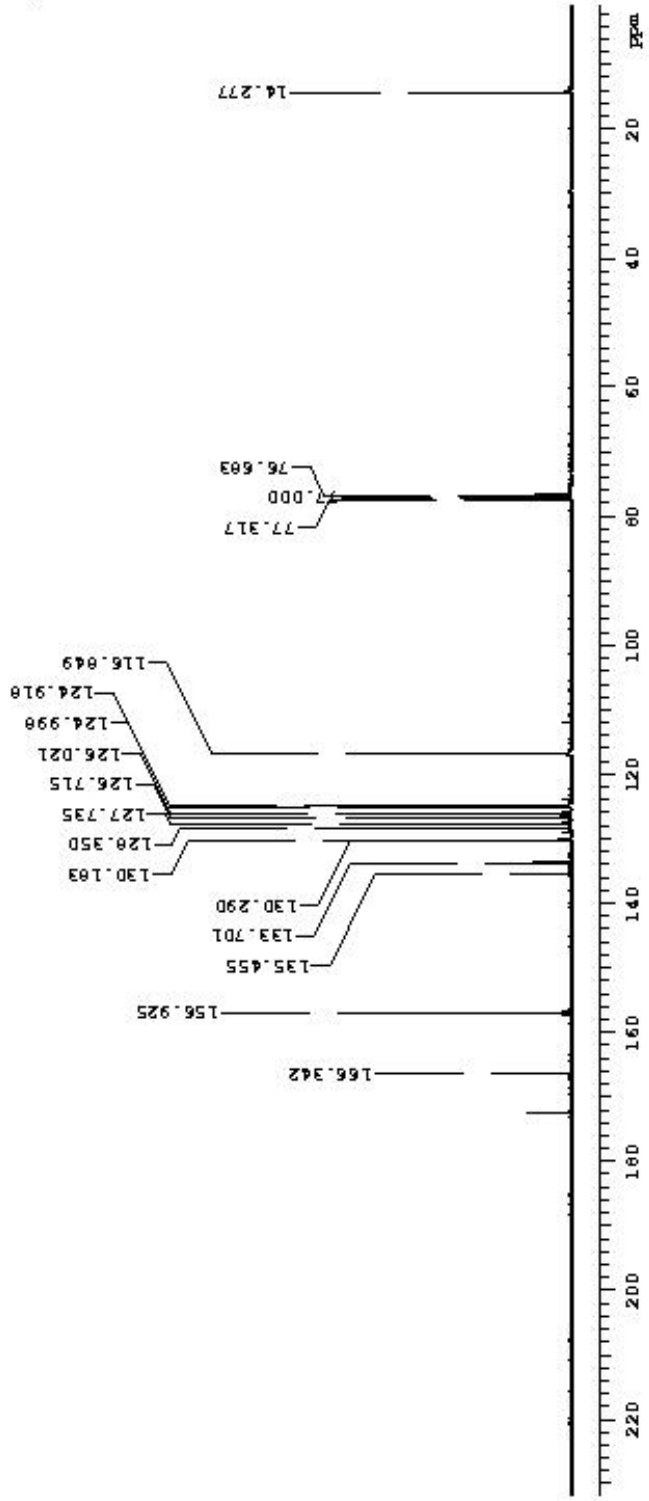
2j



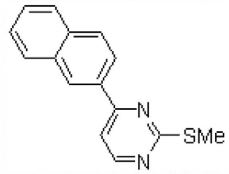
13C NMR (100 MHz, CDCl3) of 2k



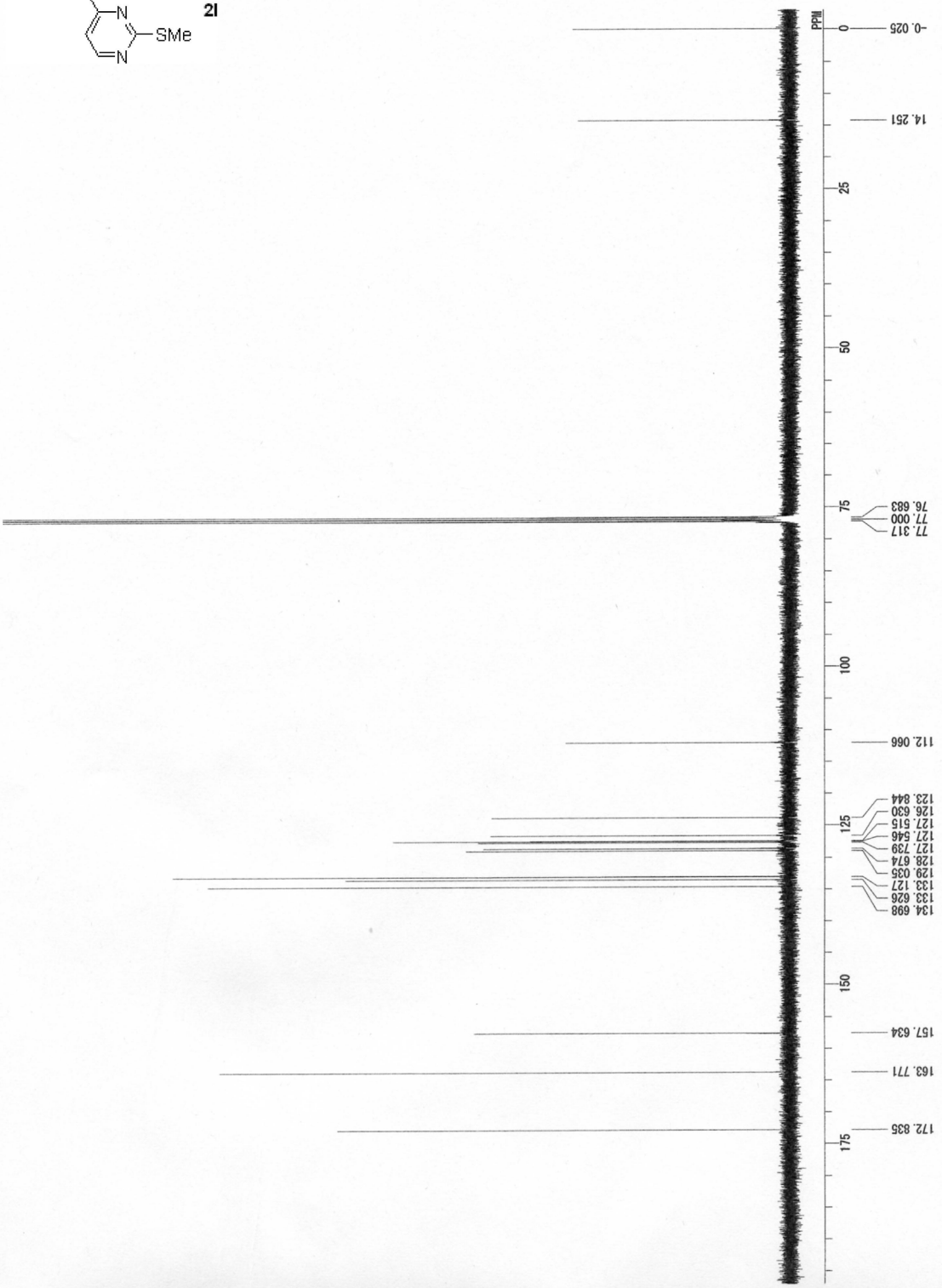
2k



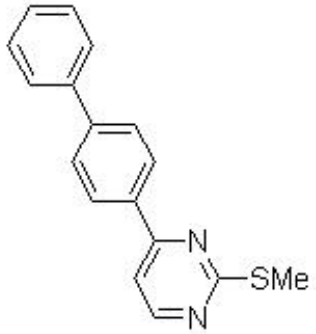
13C NMR (125 MHz, CDCl3) of 2l



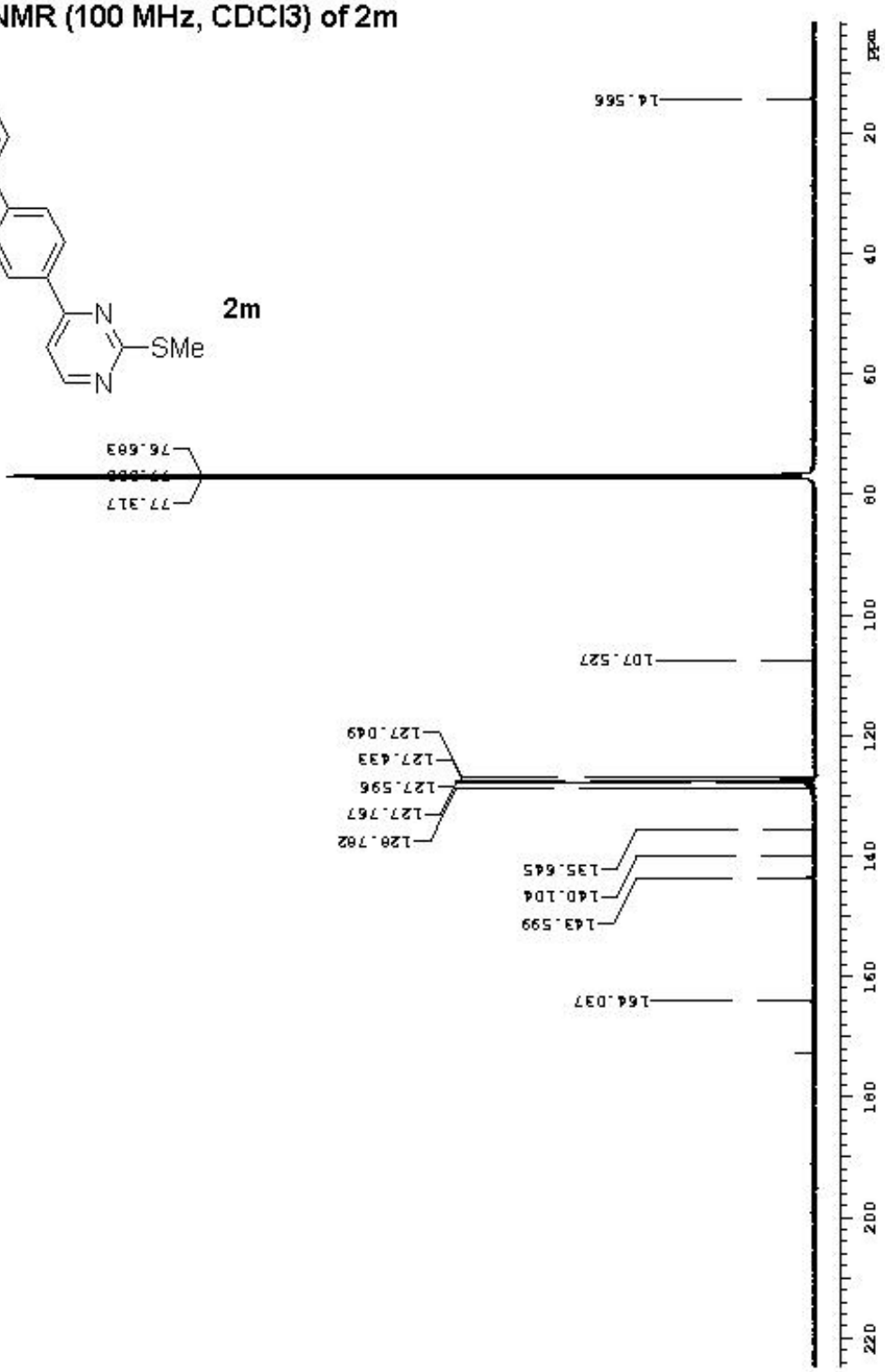
2l



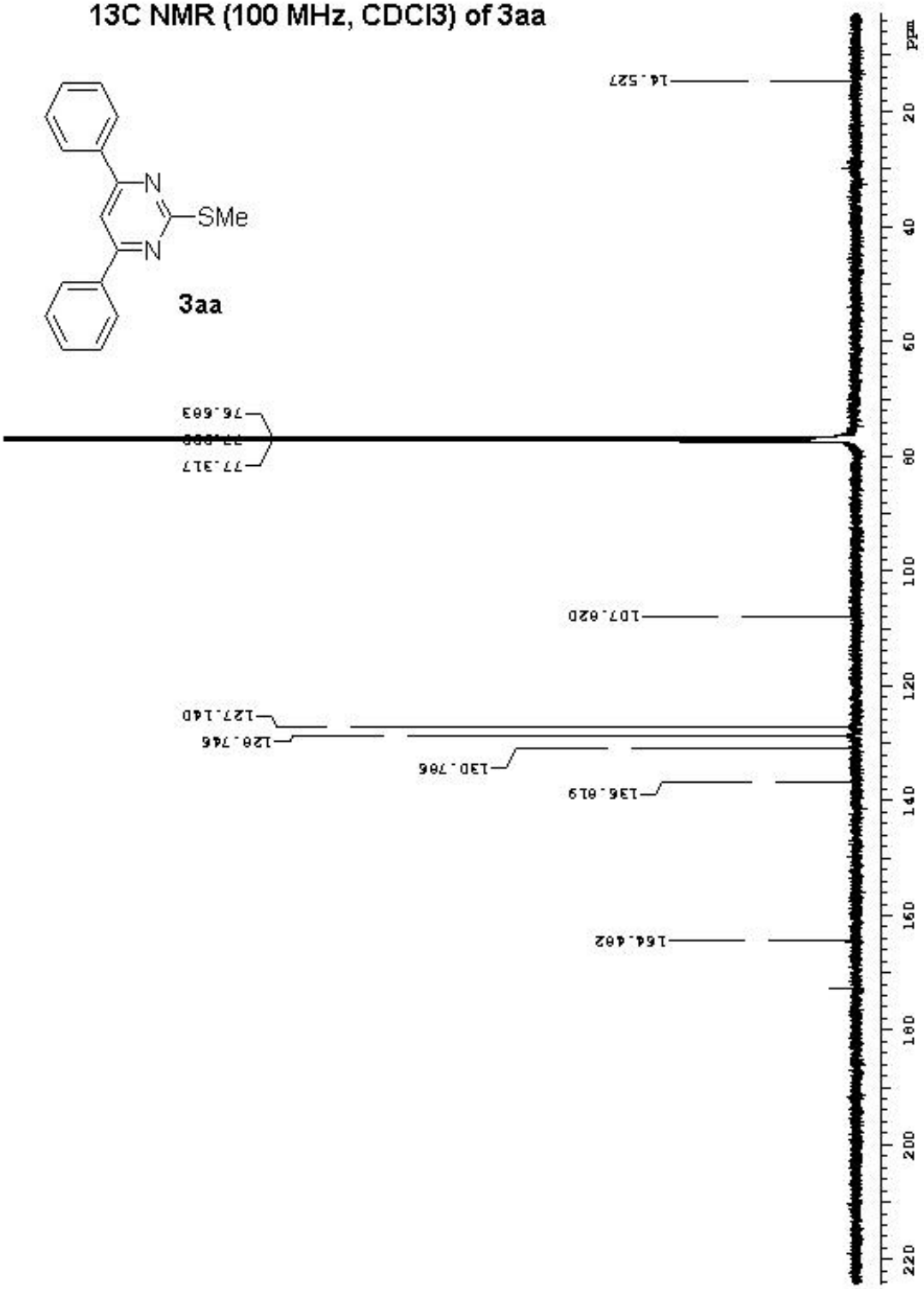
13C NMR (100 MHz, CDCl3) of 2m



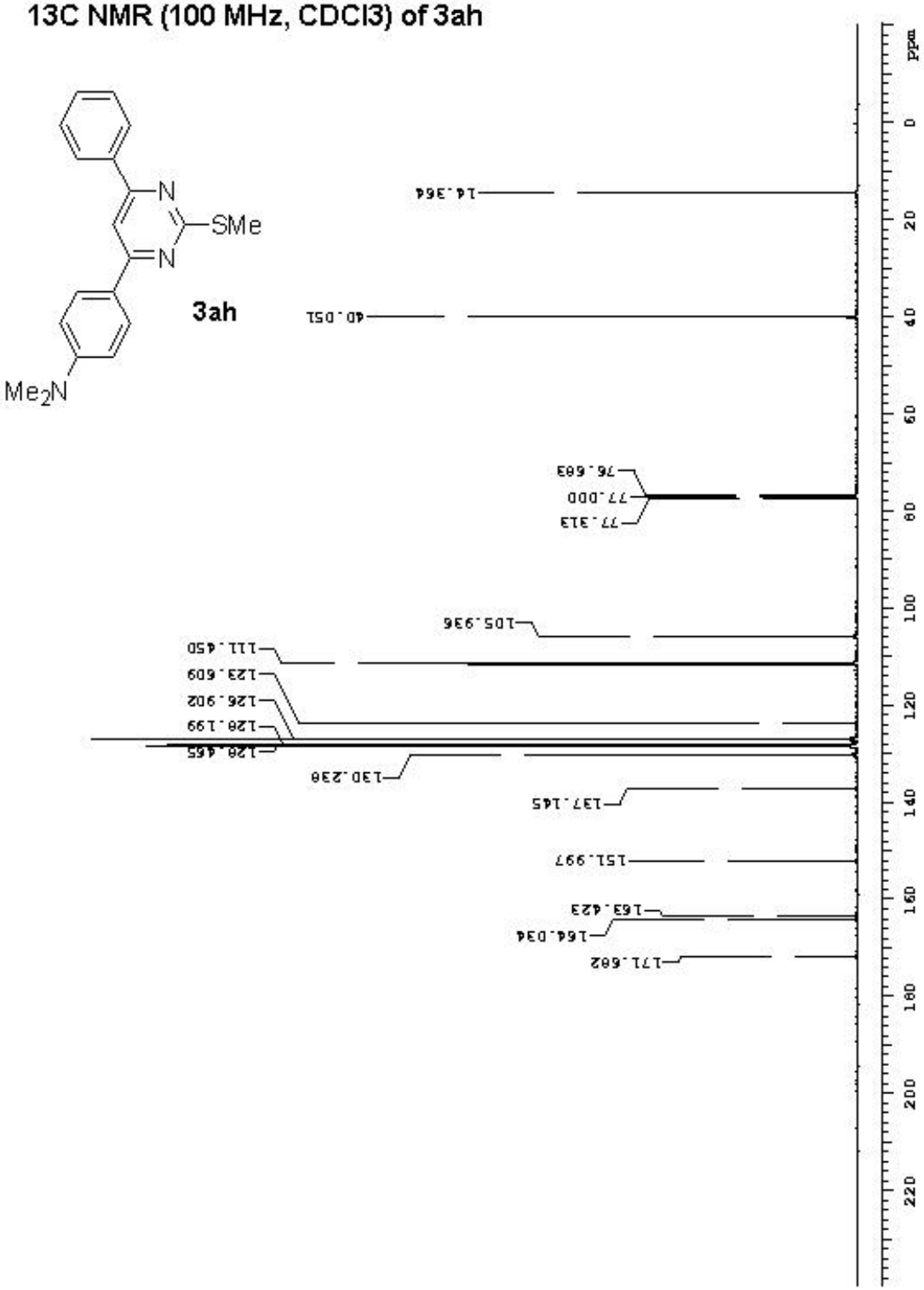
2m



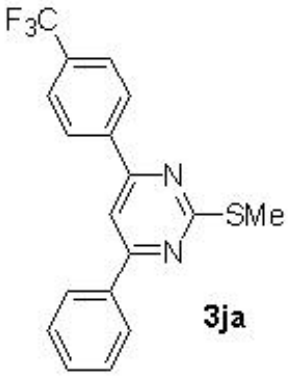
13C NMR (100 MHz, CDCl3) of 3aa



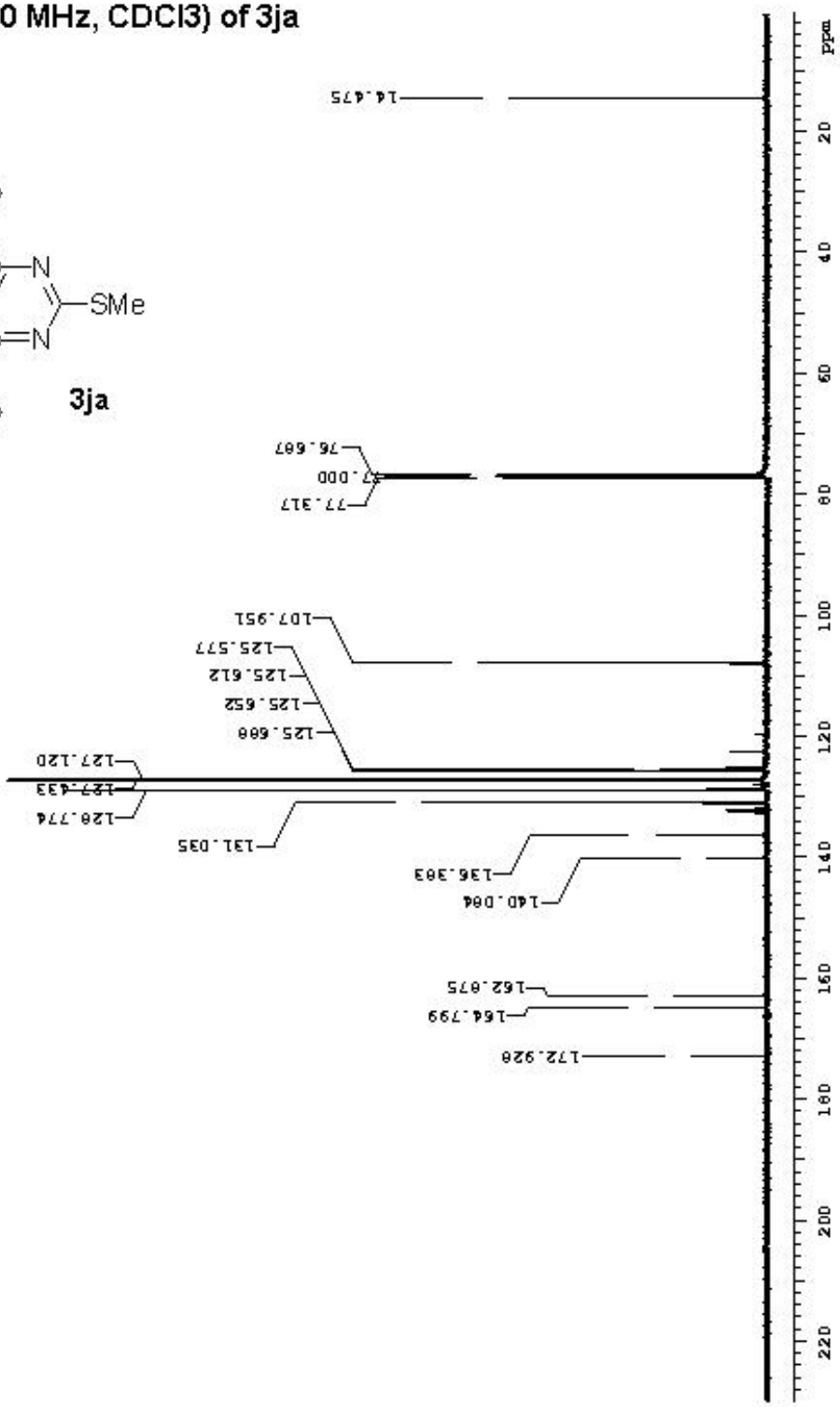
13C NMR (100 MHz, CDCl3) of 3ah



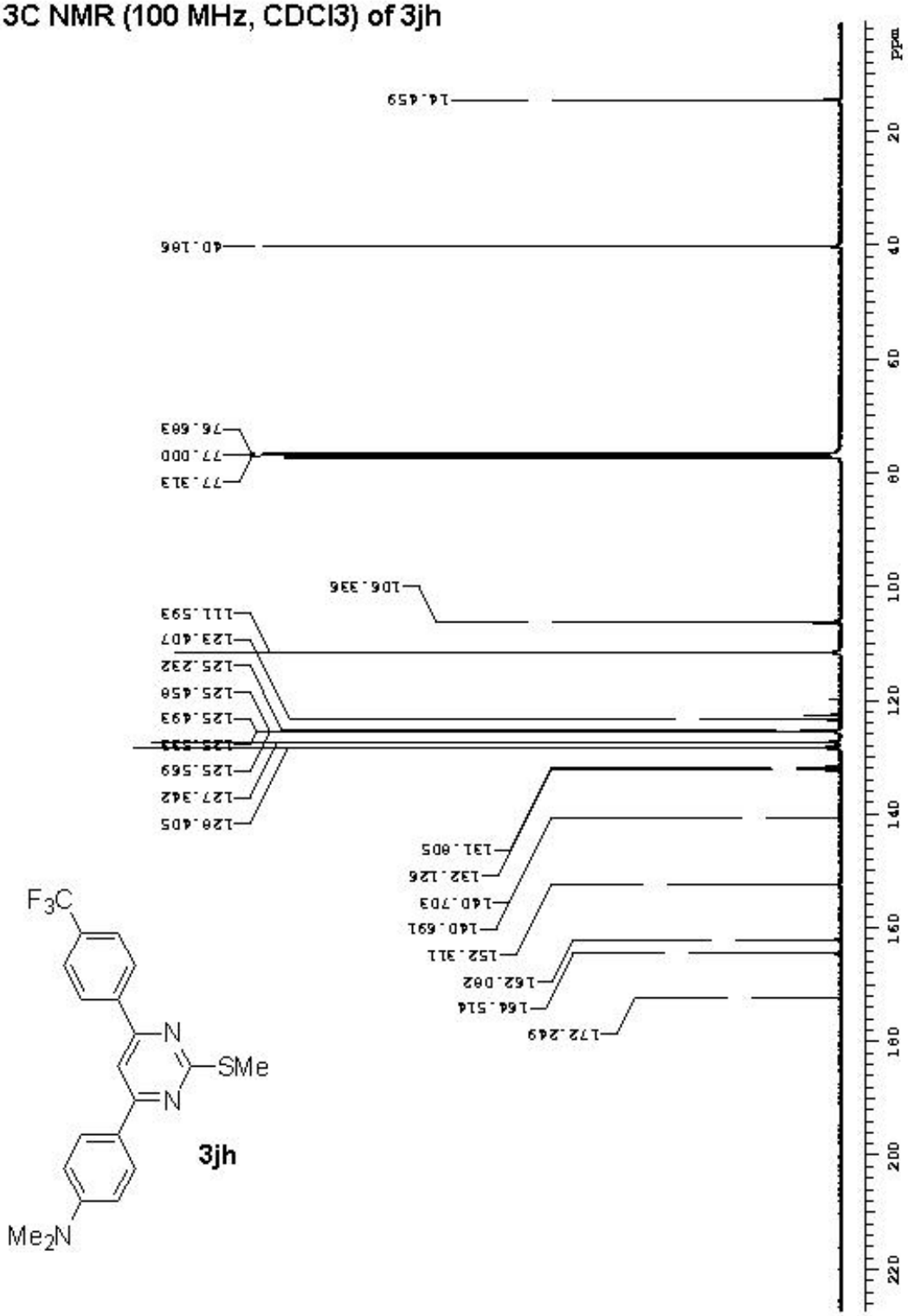
13C NMR (100 MHz, CDCl3) of 3ja



3ja

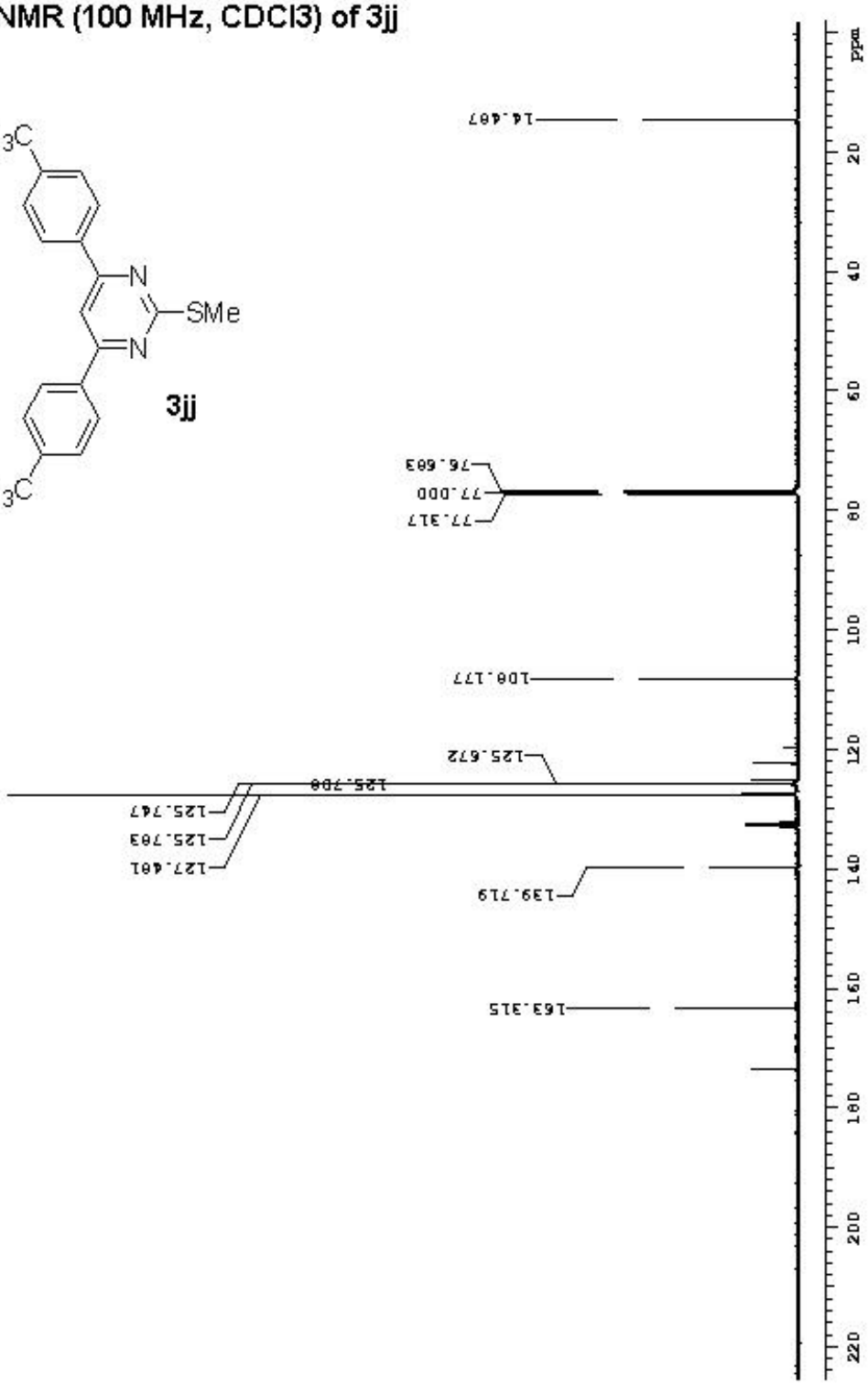


13C NMR (100 MHz, CDCl3) of 3jh

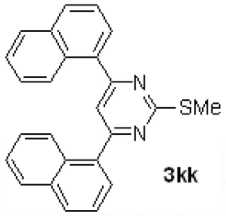


13C NMR (100 MHz, CDCl3) of 3jj

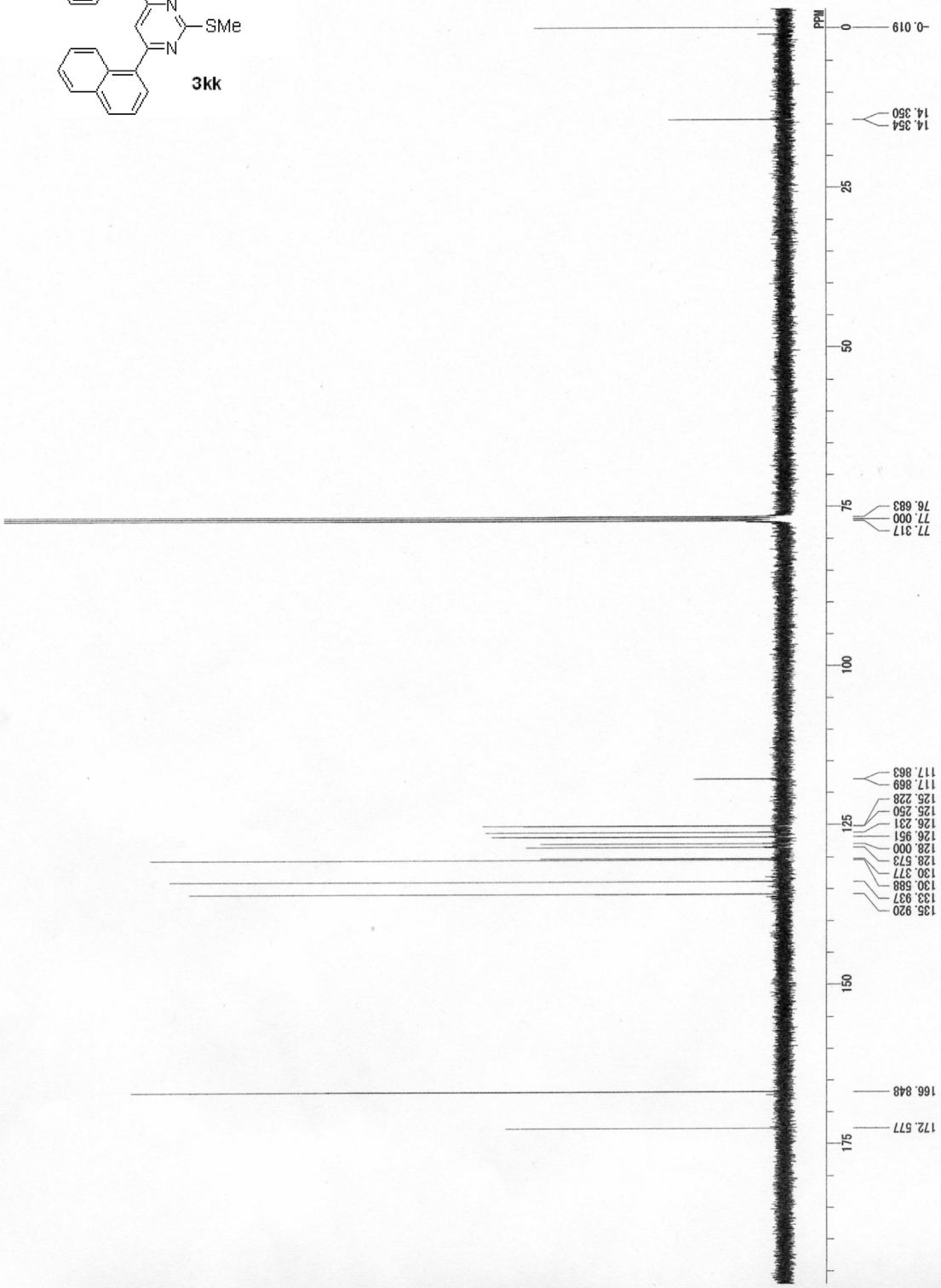
3jj



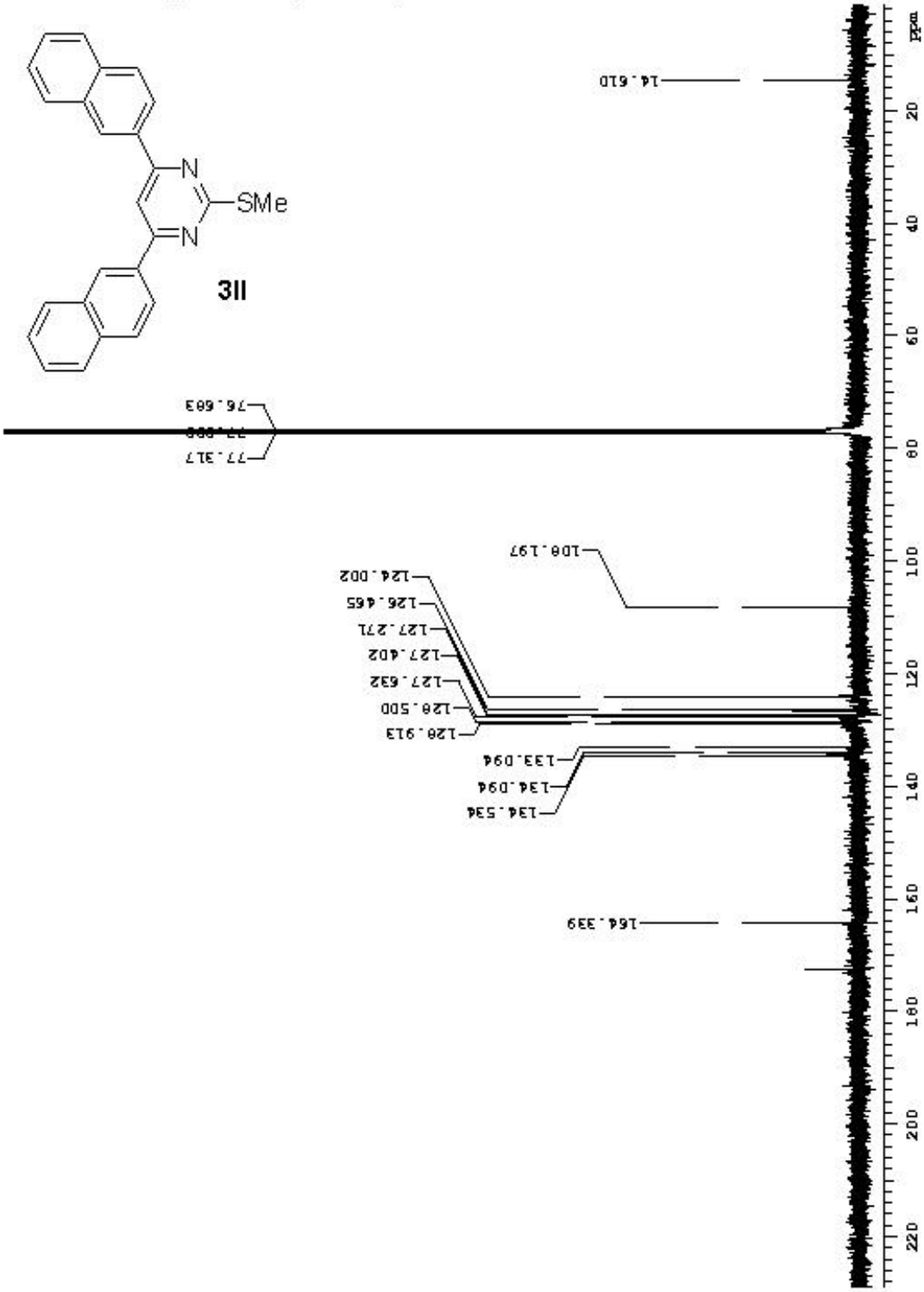
13C NMR (125 MHz, CDCl3) of 3kk



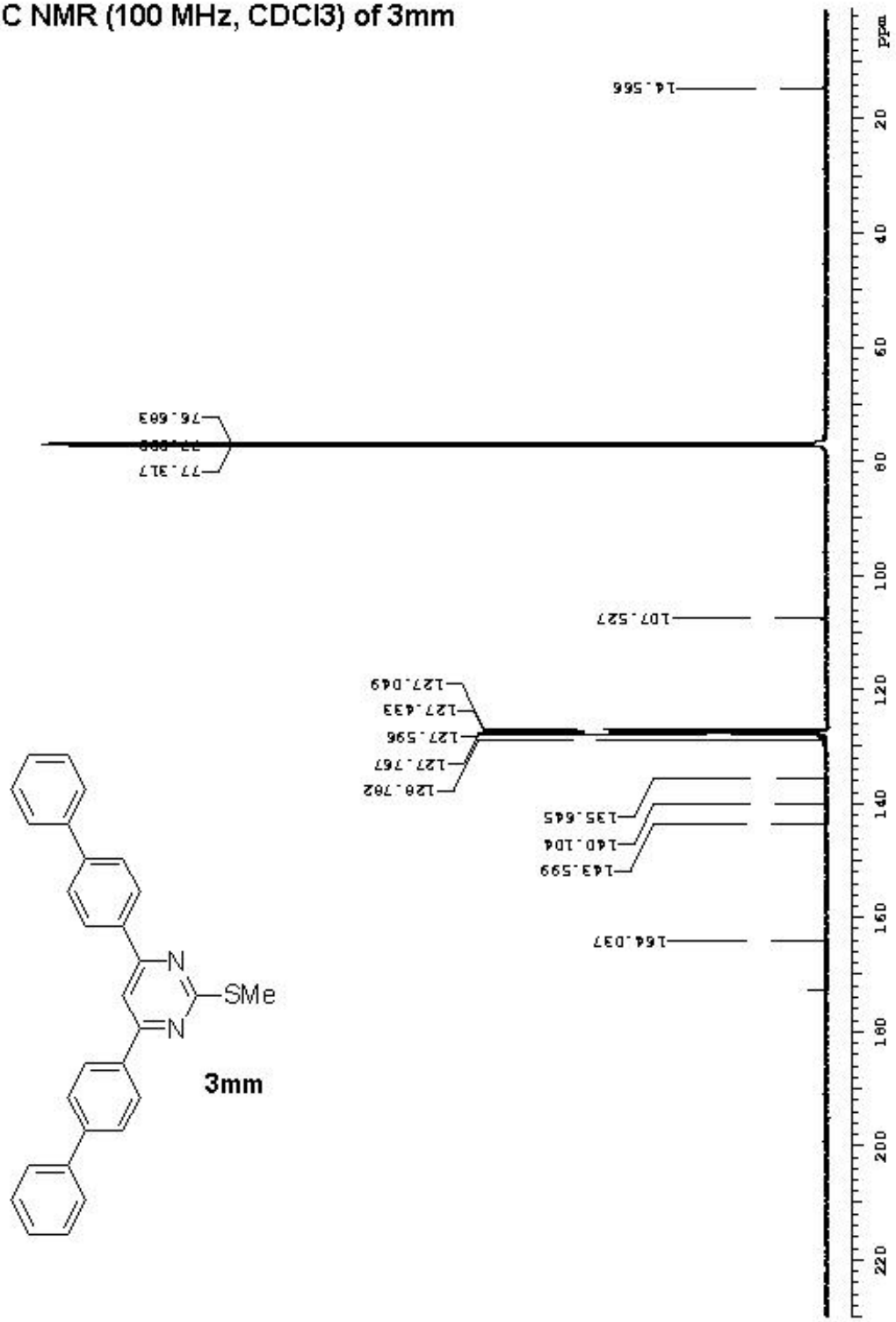
3kk



13C NMR (100 MHz, CDCl3) of 3ll

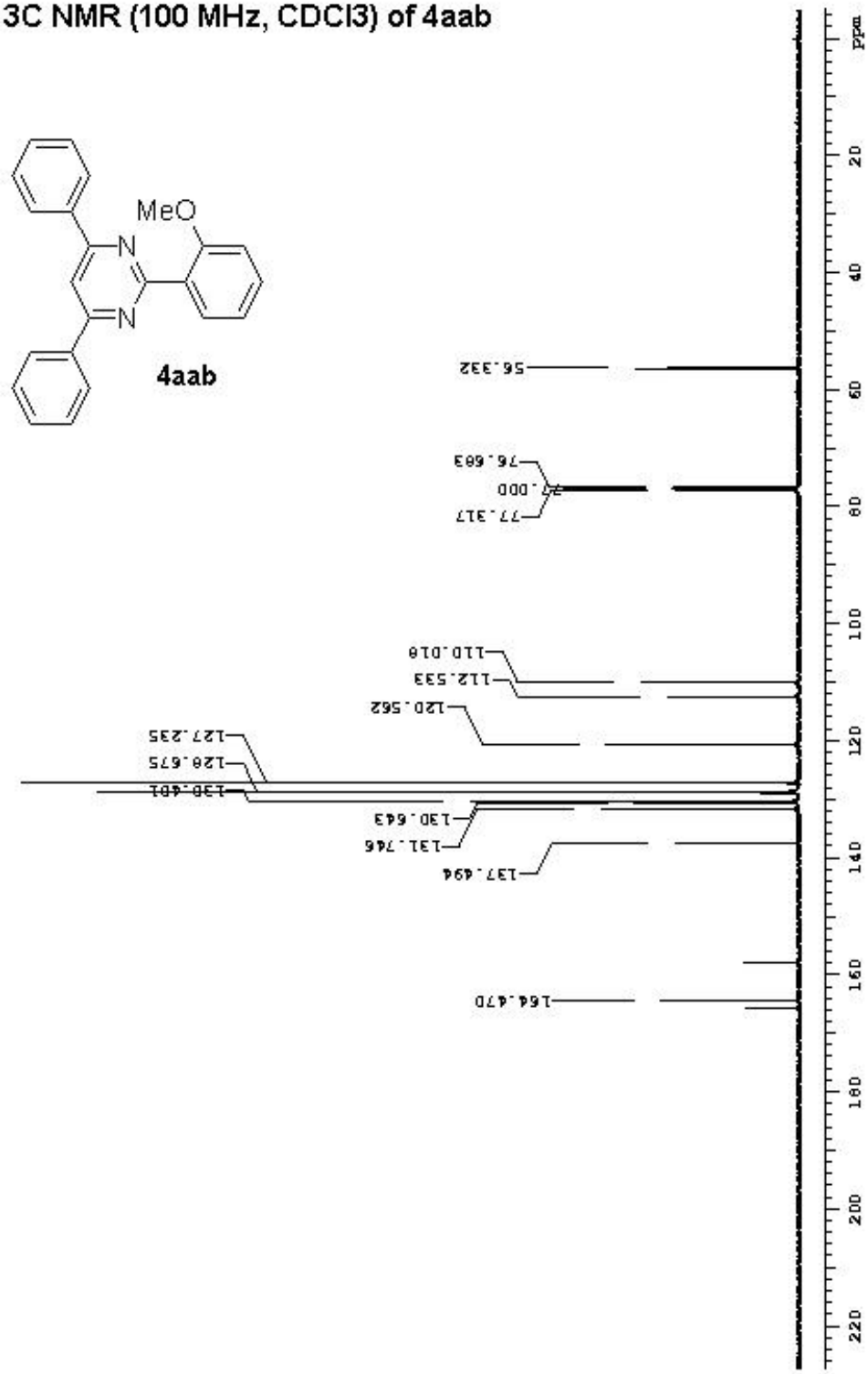


13C NMR (100 MHz, CDCl3) of 3mm

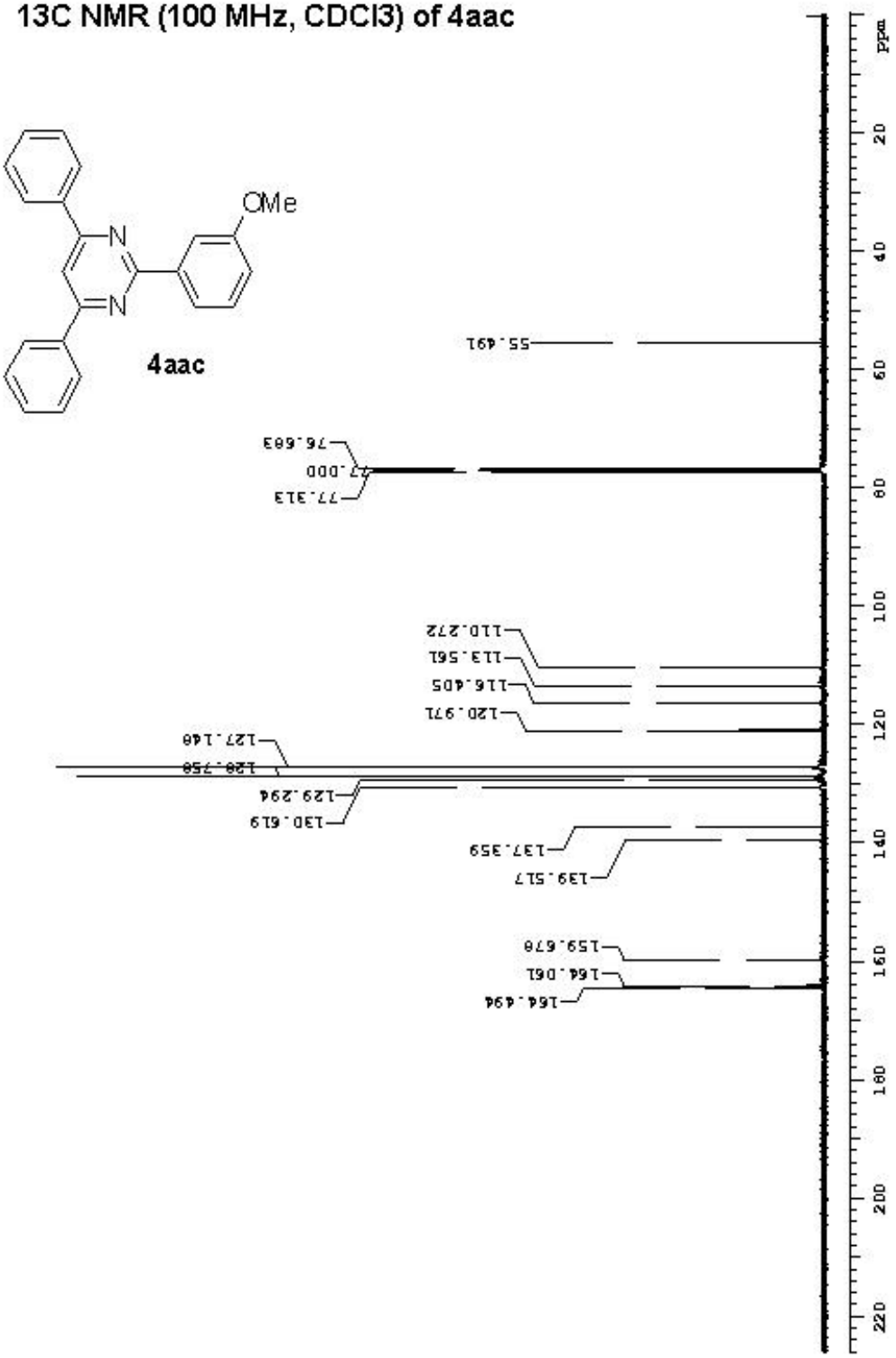


13C NMR (100 MHz, CDCl3) of 4aab

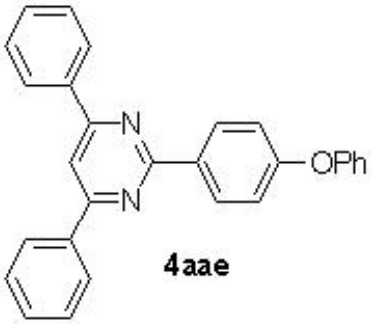
4aab



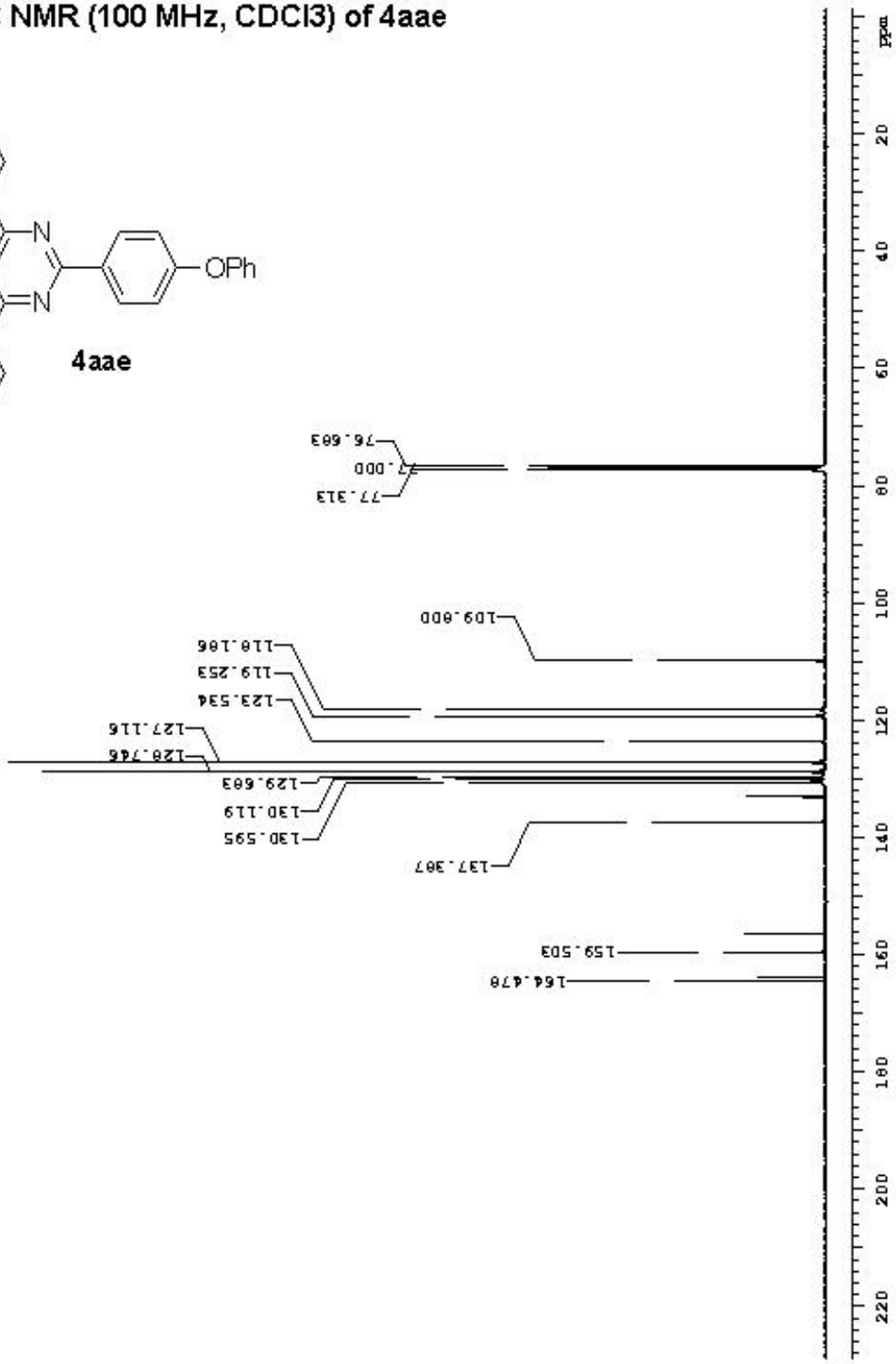
13C NMR (100 MHz, CDCl3) of 4aac



13C NMR (100 MHz, CDCl3) of 4aae

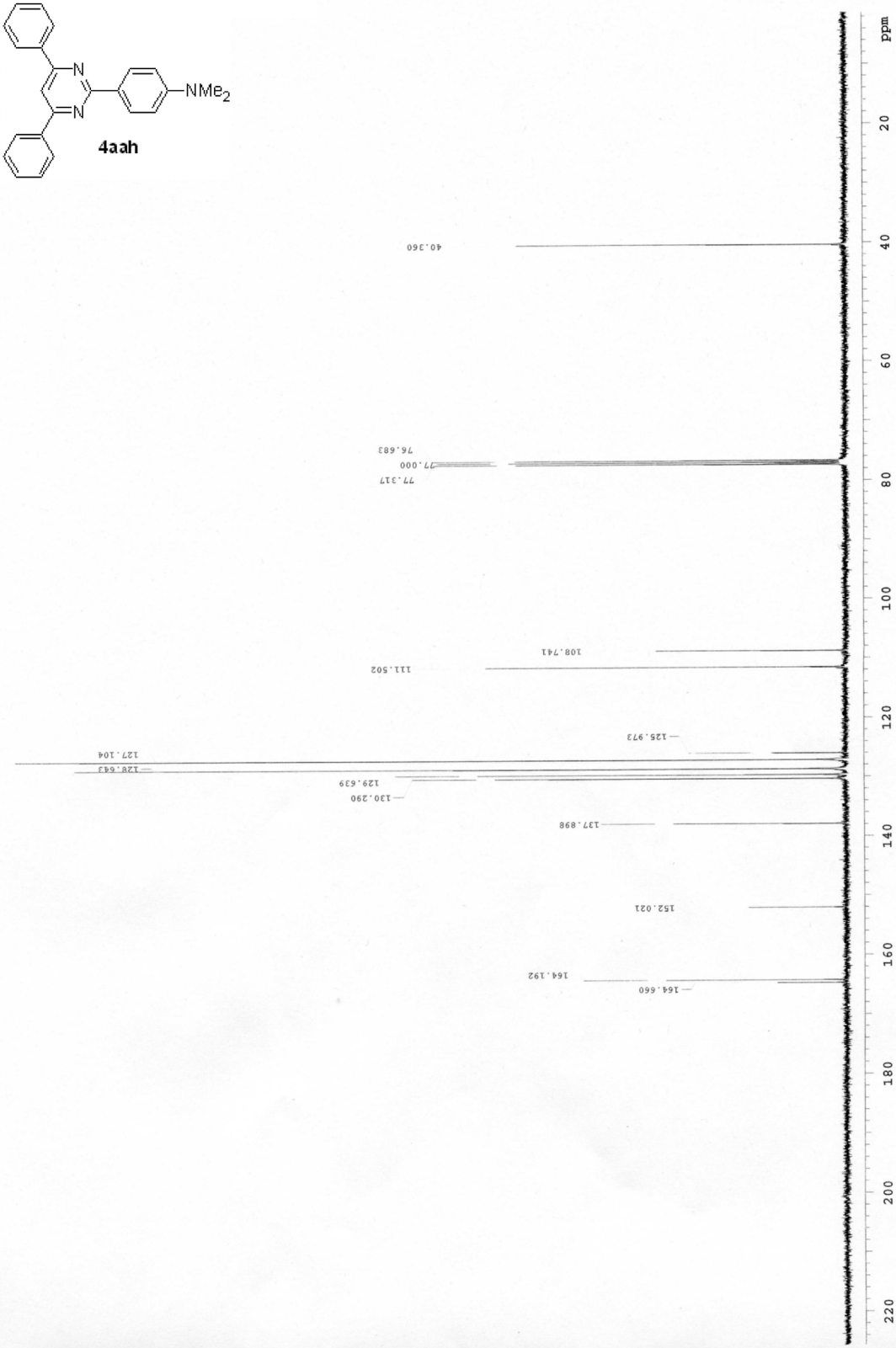


4aae

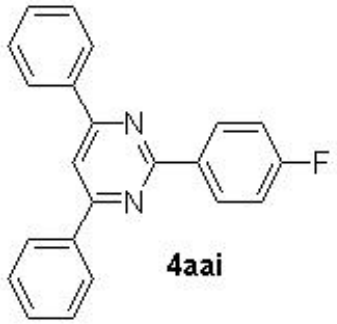


13C NMR (100 MHz, CDCl3) of 4aah

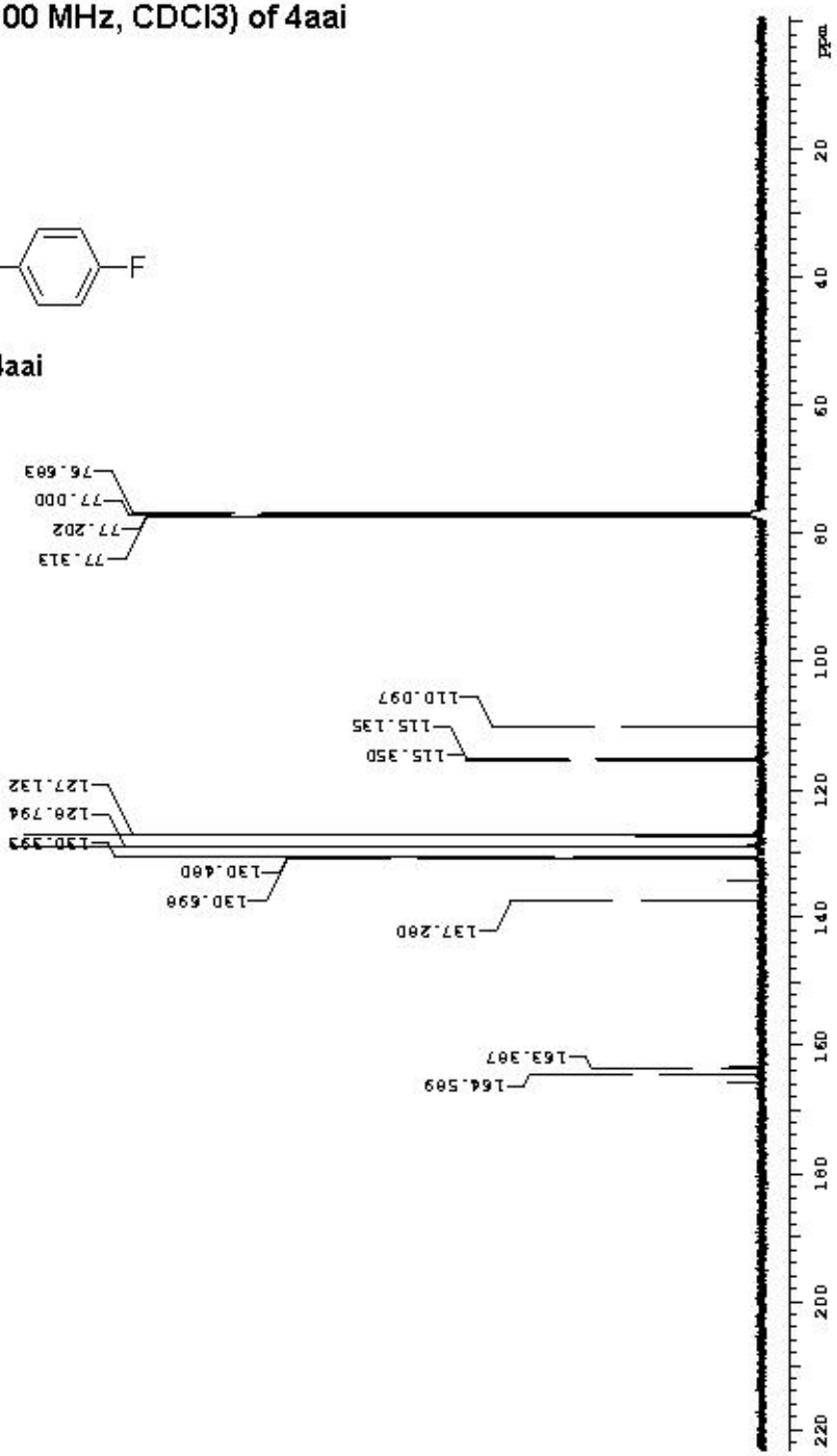
4aah



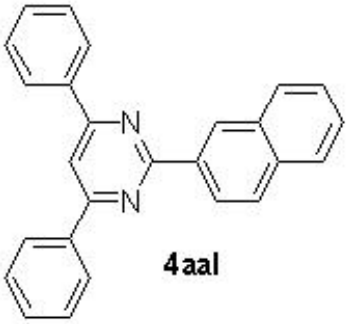
13C NMR (100 MHz, CDCl3) of 4aai



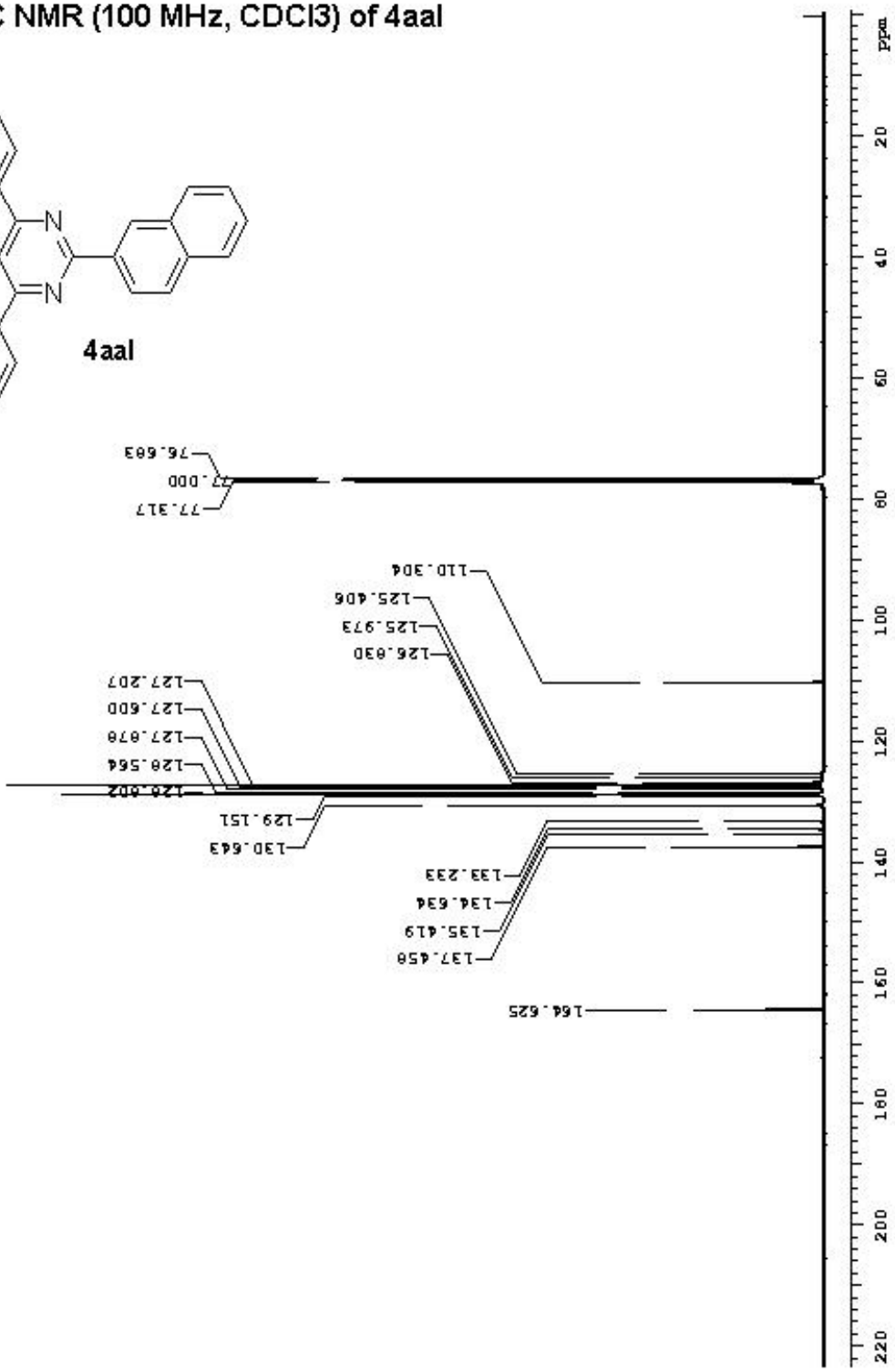
4aai



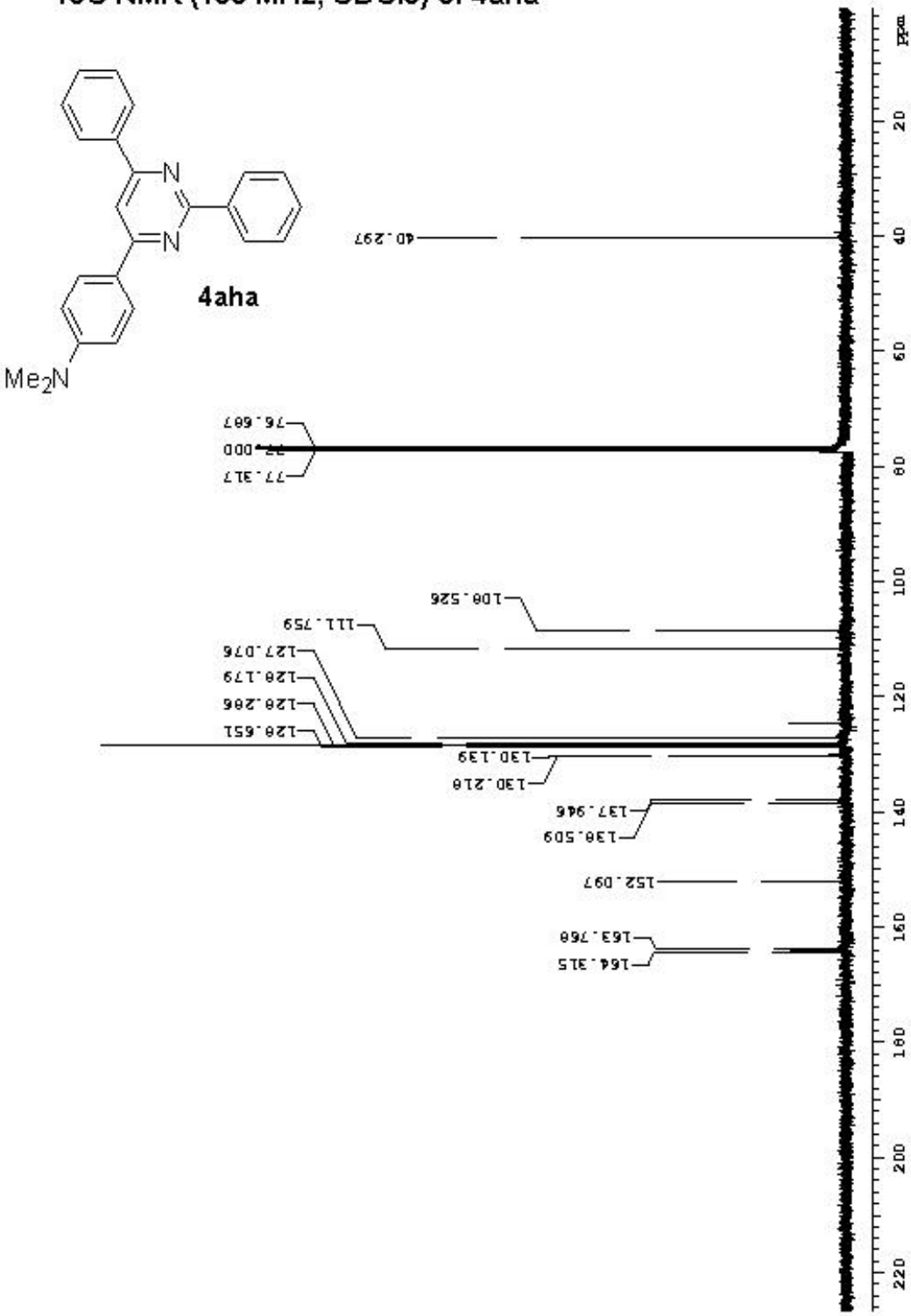
13C NMR (100 MHz, CDCl3) of 4aal



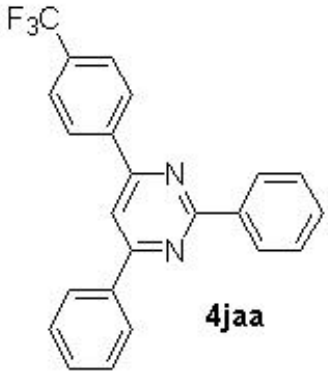
4aal



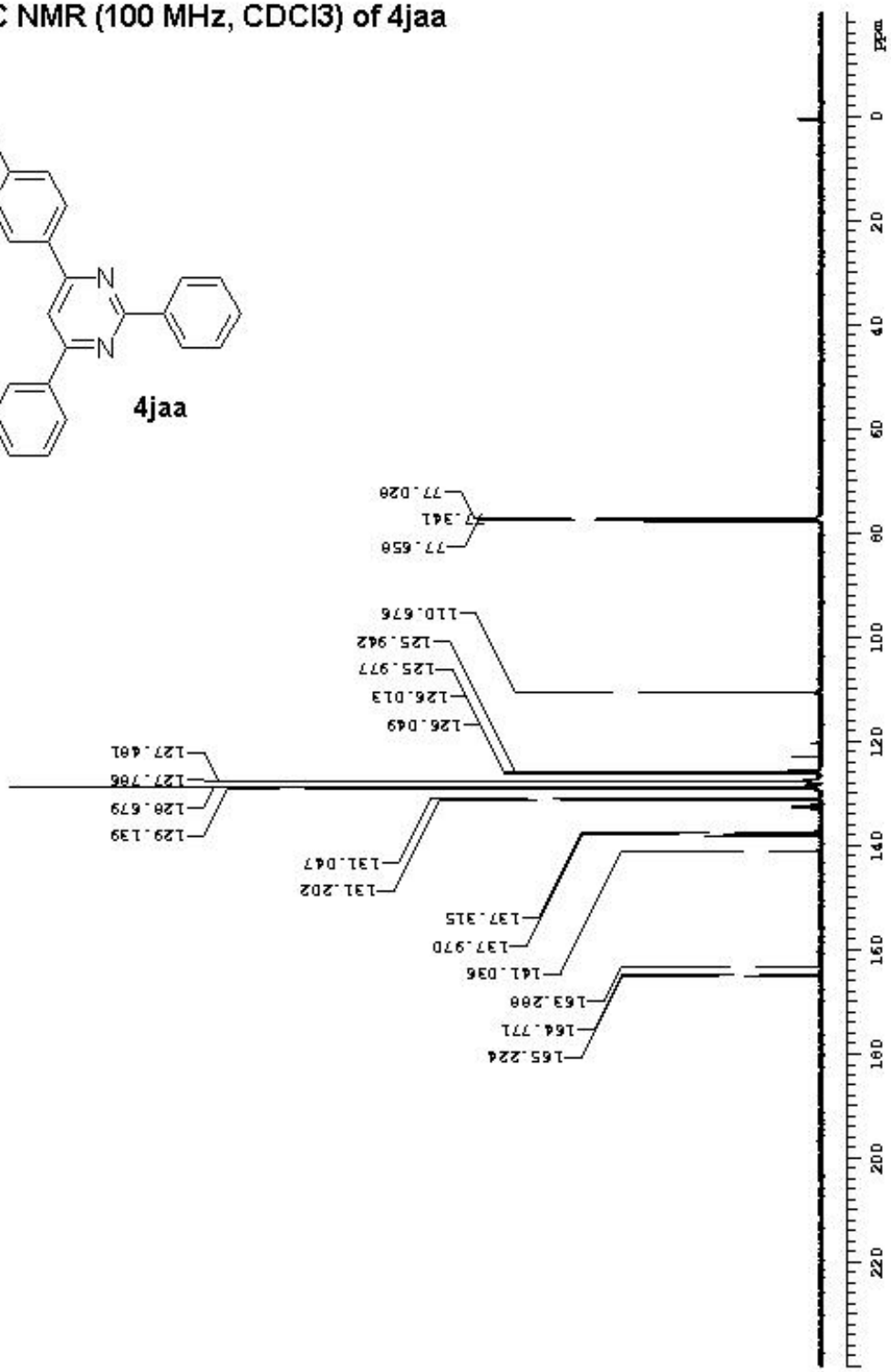
13C NMR (100 MHz, CDCl3) of 4aha



13C NMR (100 MHz, CDCl3) of 4jaa

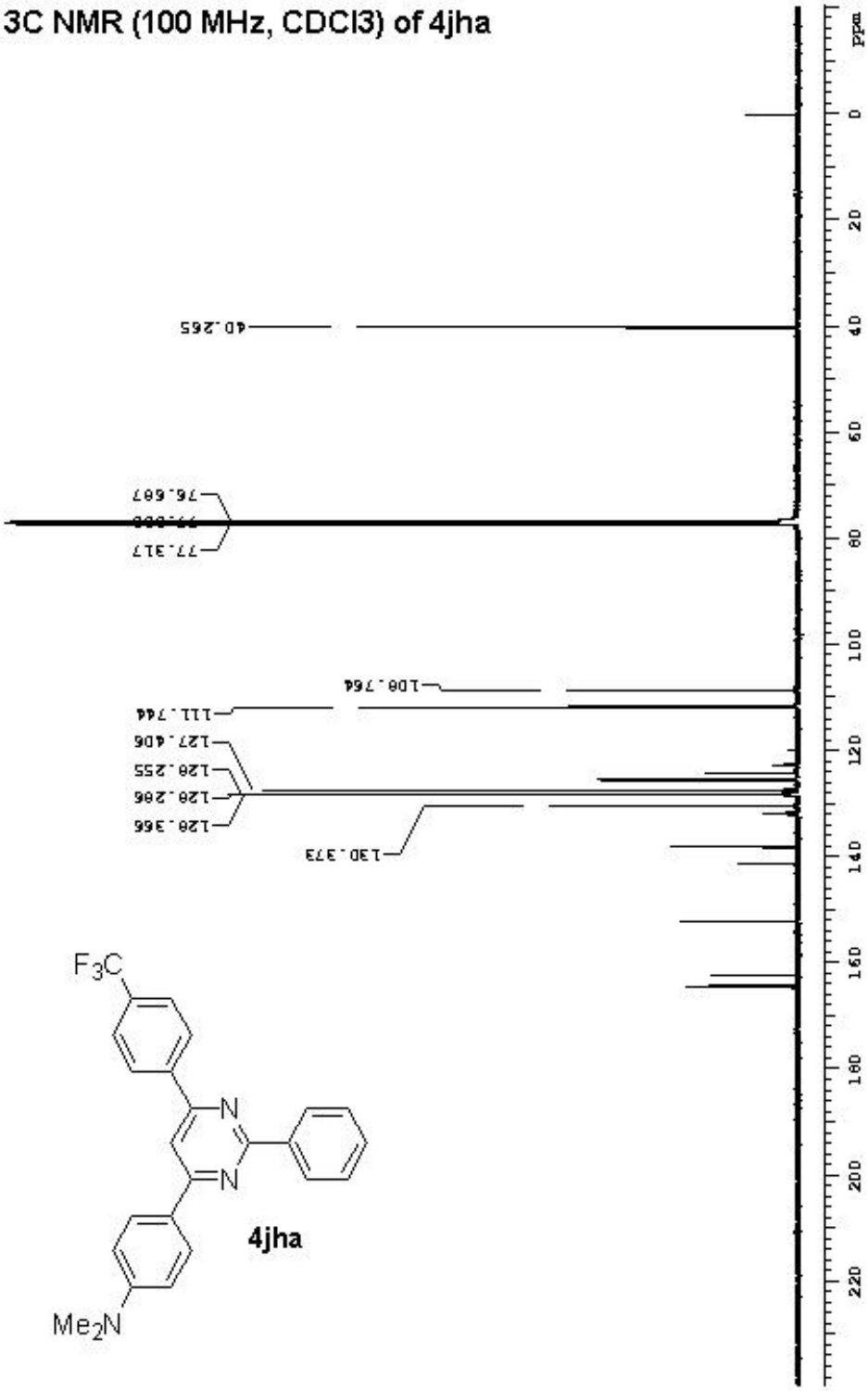


4jaa



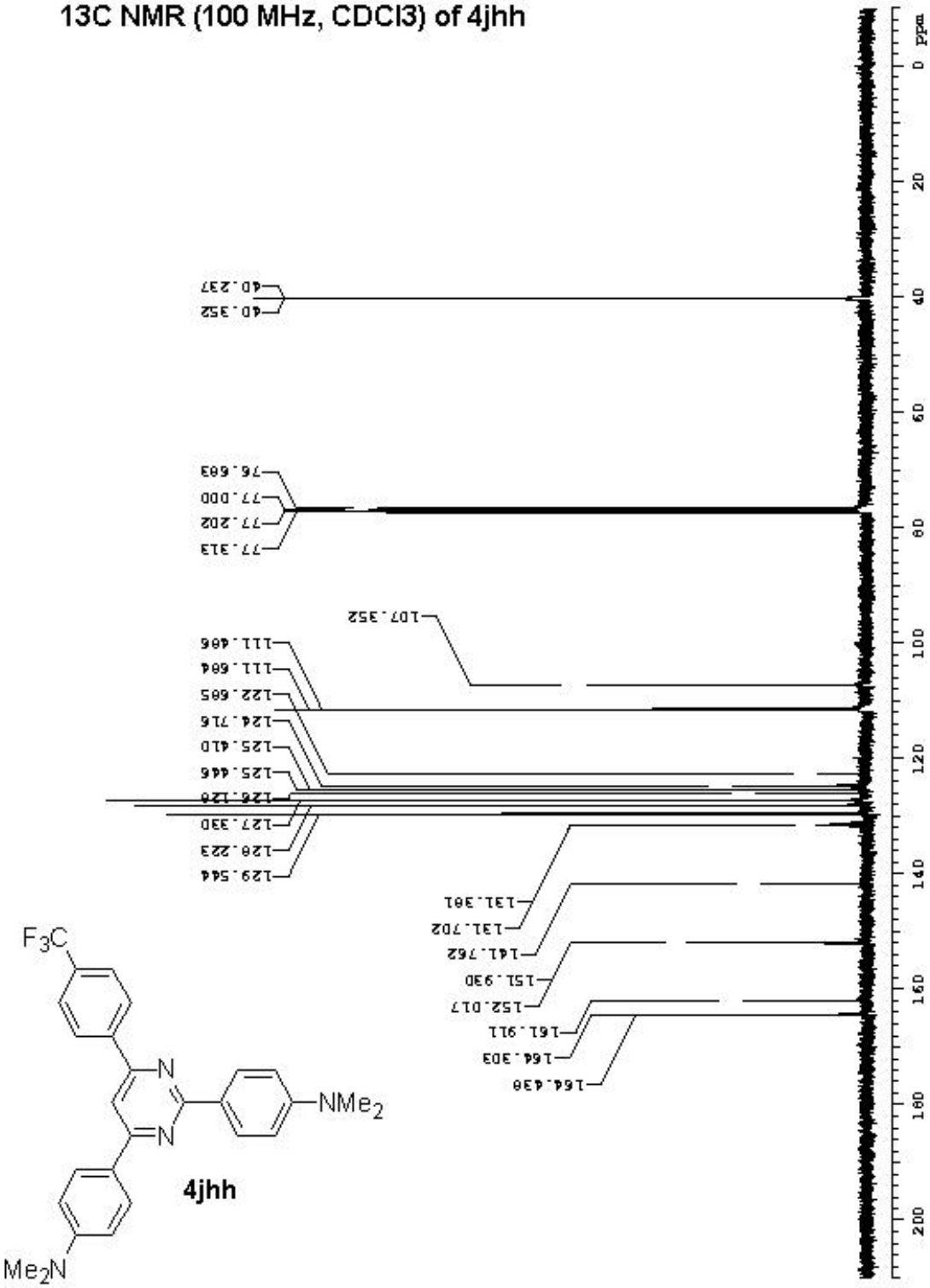
[

13C NMR (100 MHz, CDCl3) of 4jha

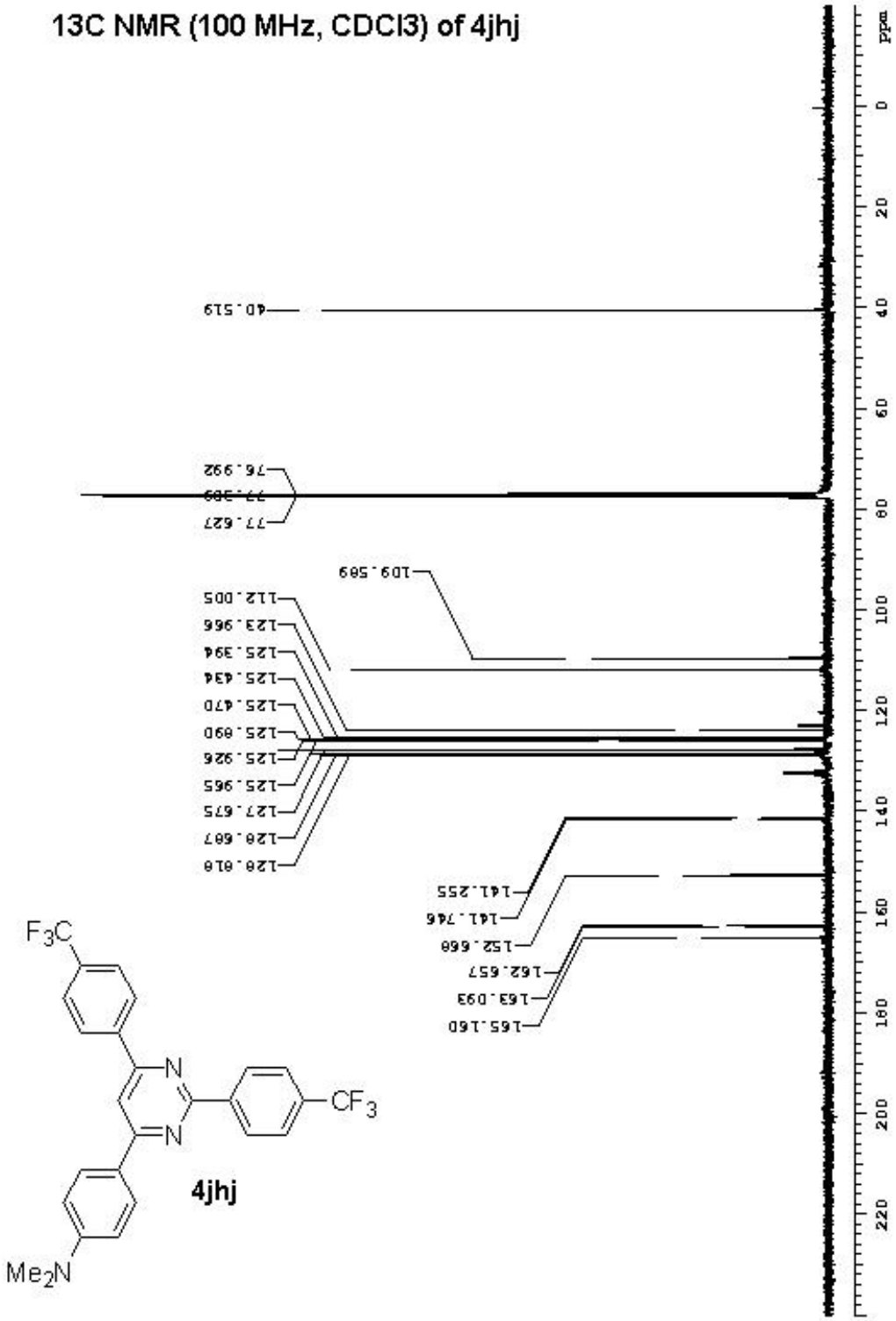


4jha

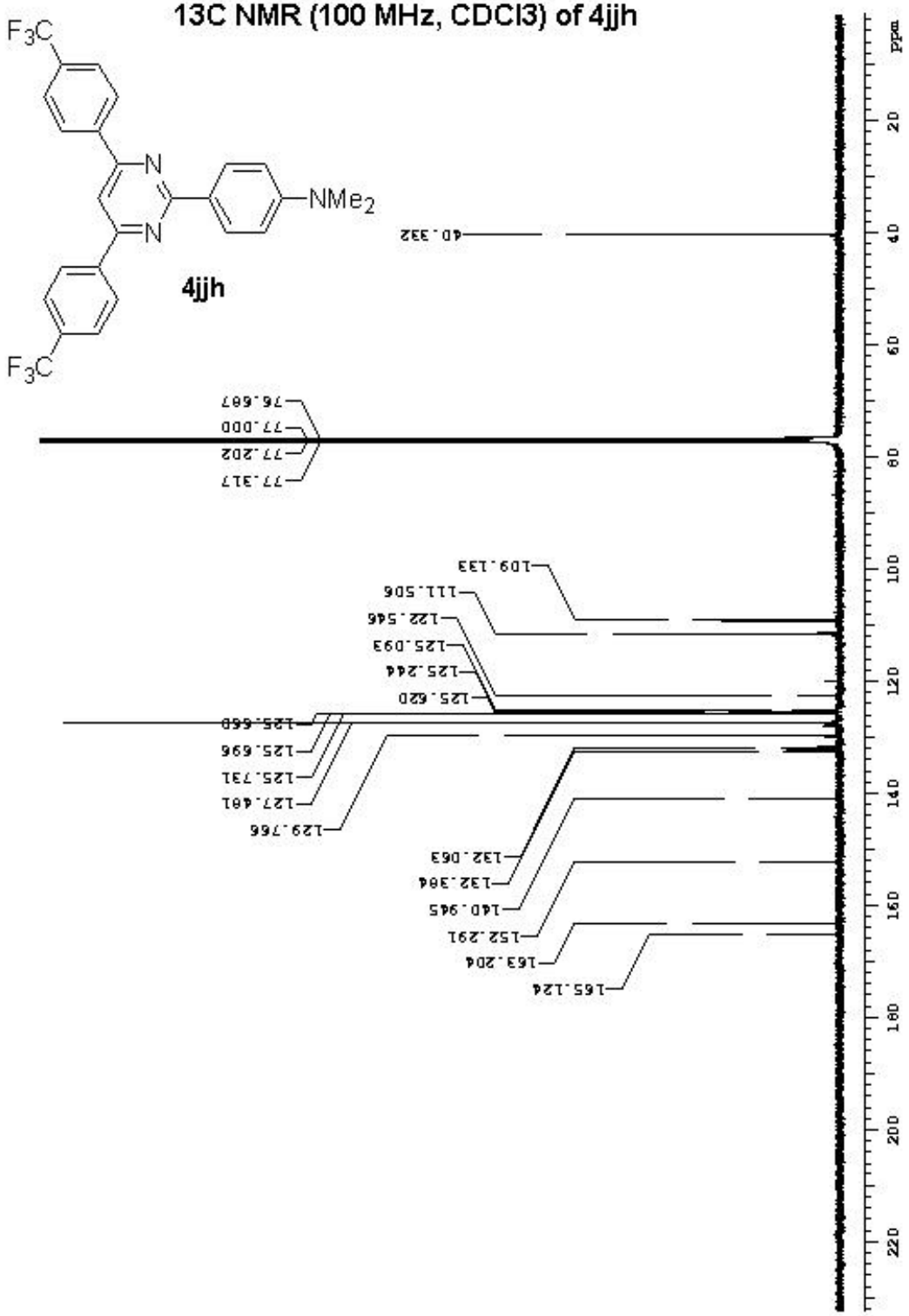
13C NMR (100 MHz, CDCl3) of 4jhh



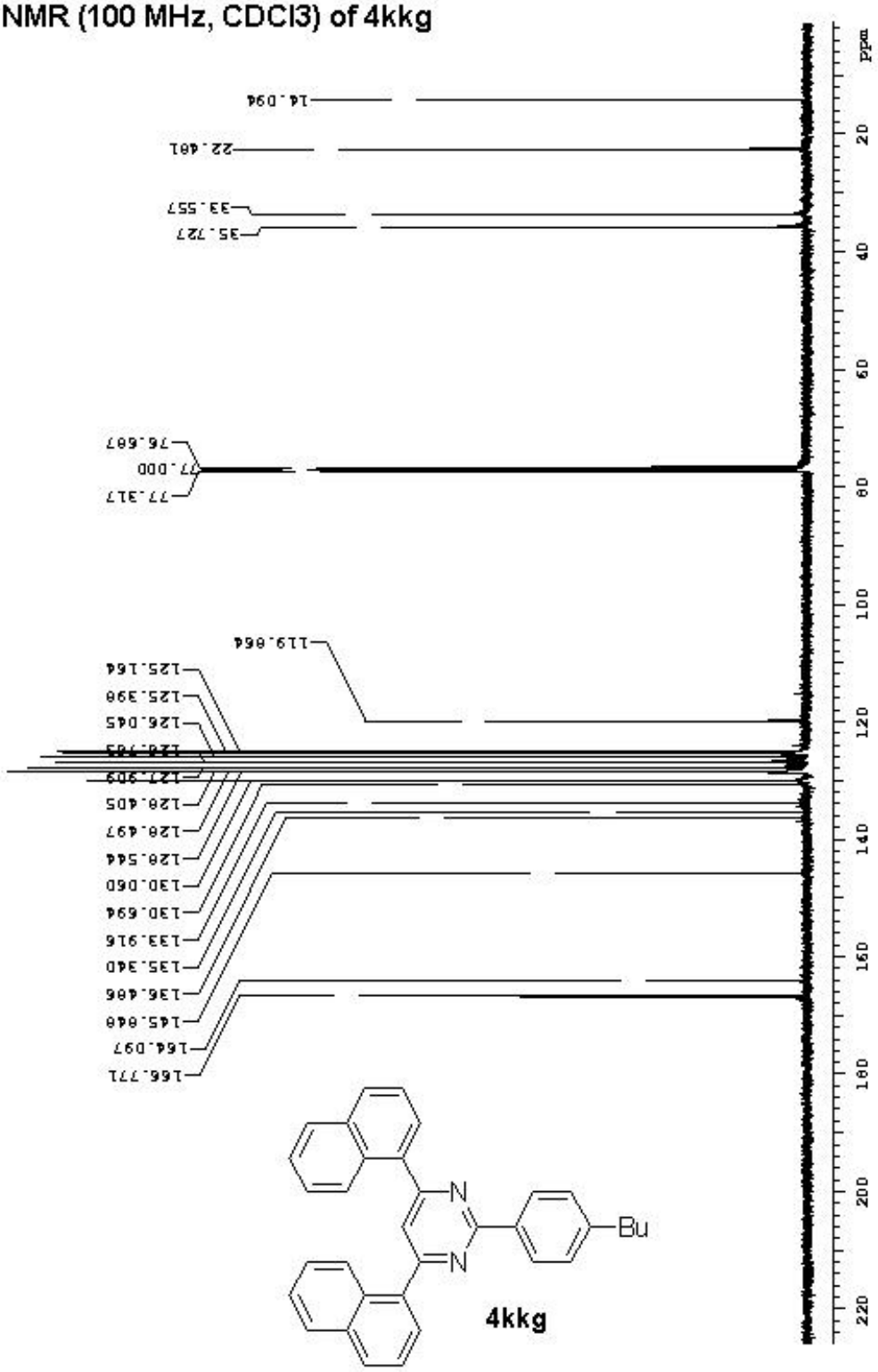
13C NMR (100 MHz, CDCl3) of 4jhj



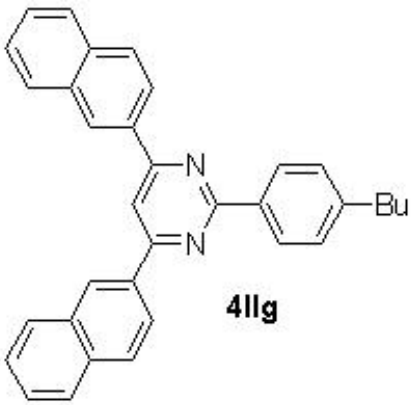
13C NMR (100 MHz, CDCl3) of 4jjh



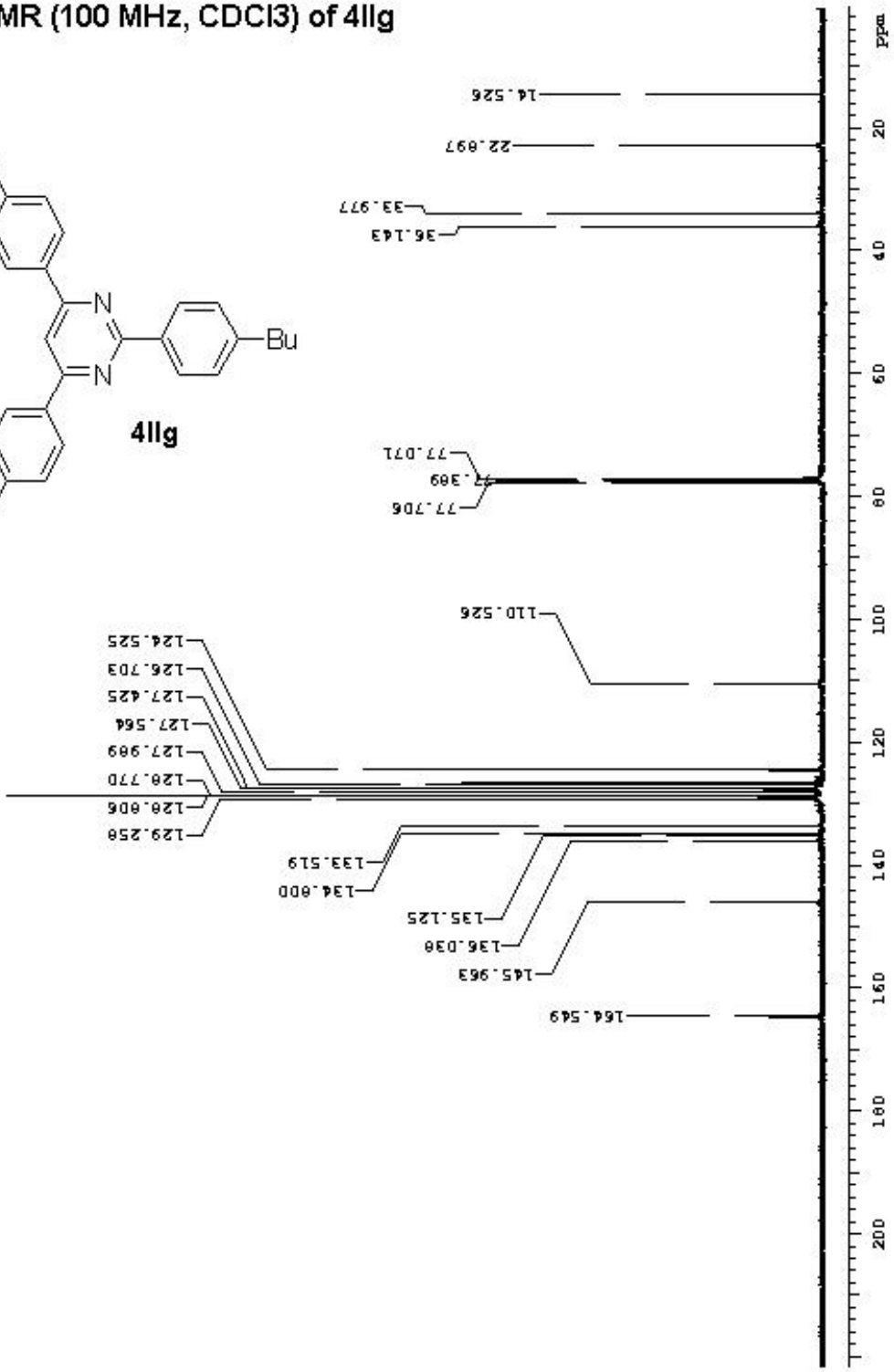
13C NMR (100 MHz, CDCl3) of 4kkg



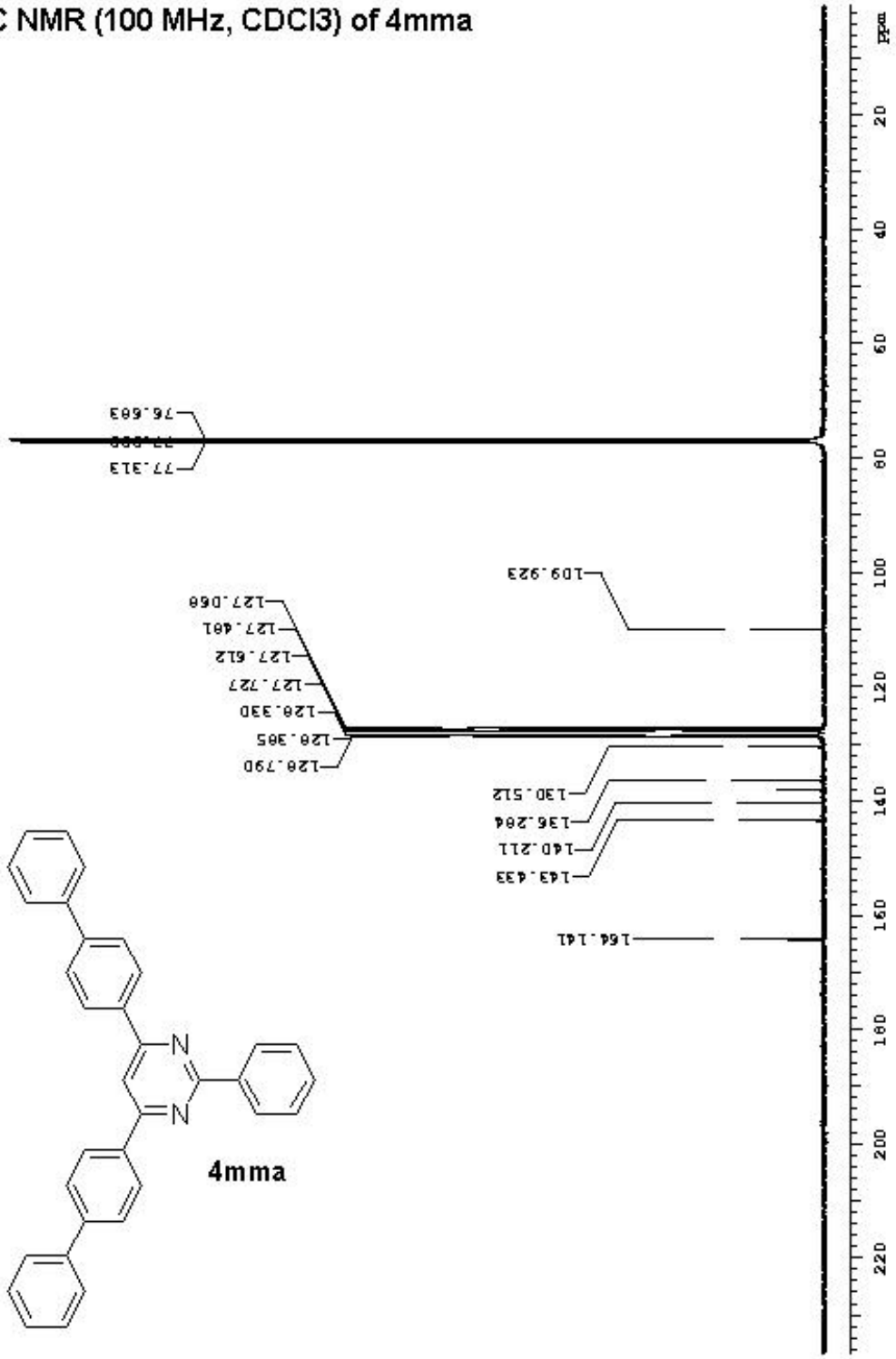
13C NMR (100 MHz, CDCl3) of 4llg



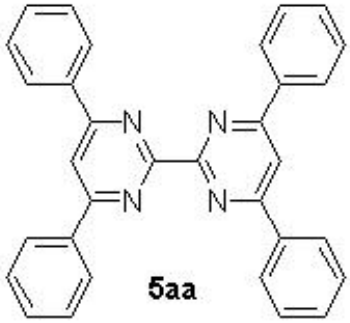
4llg



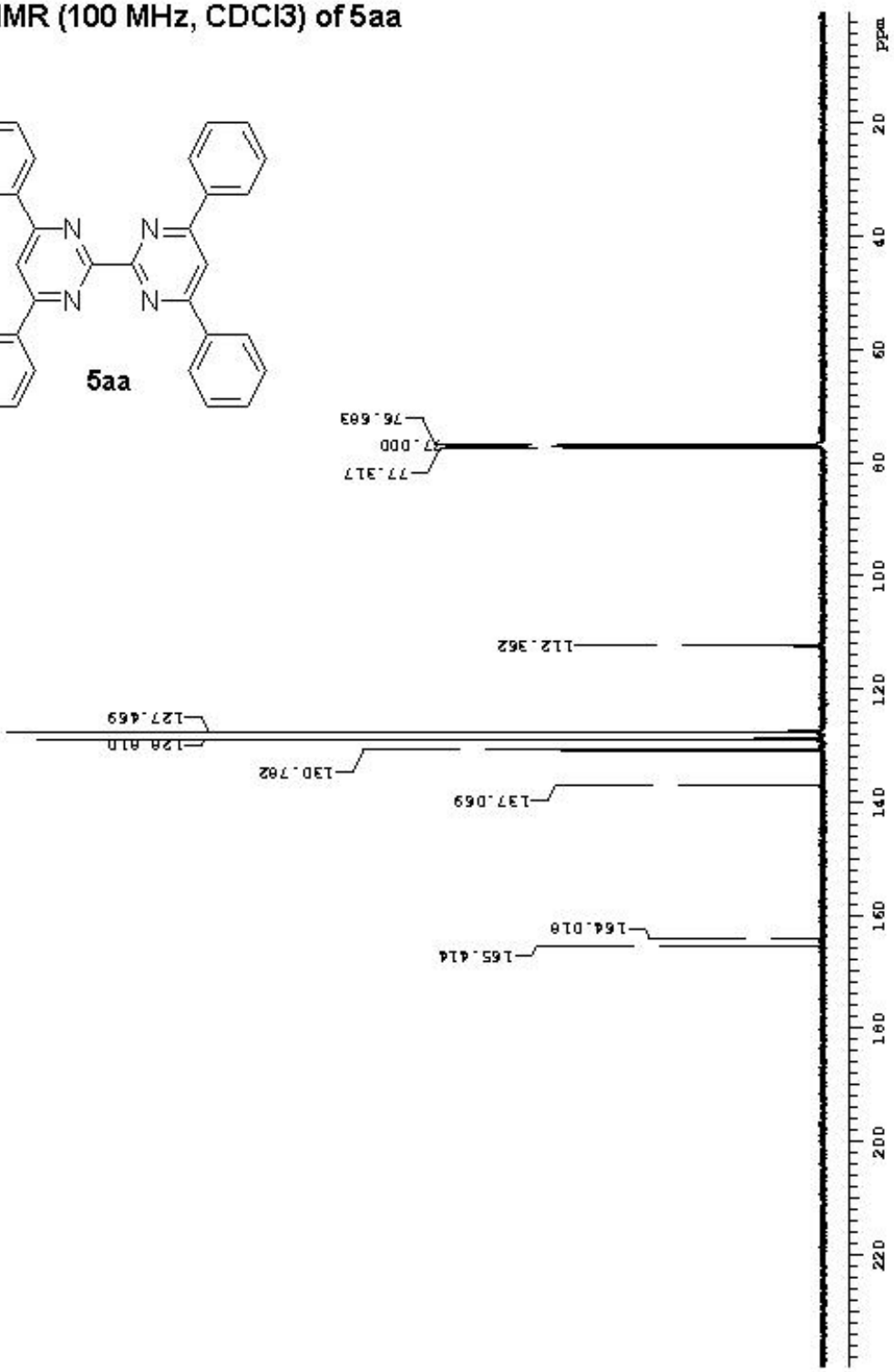
13C NMR (100 MHz, CDCl3) of 4mma



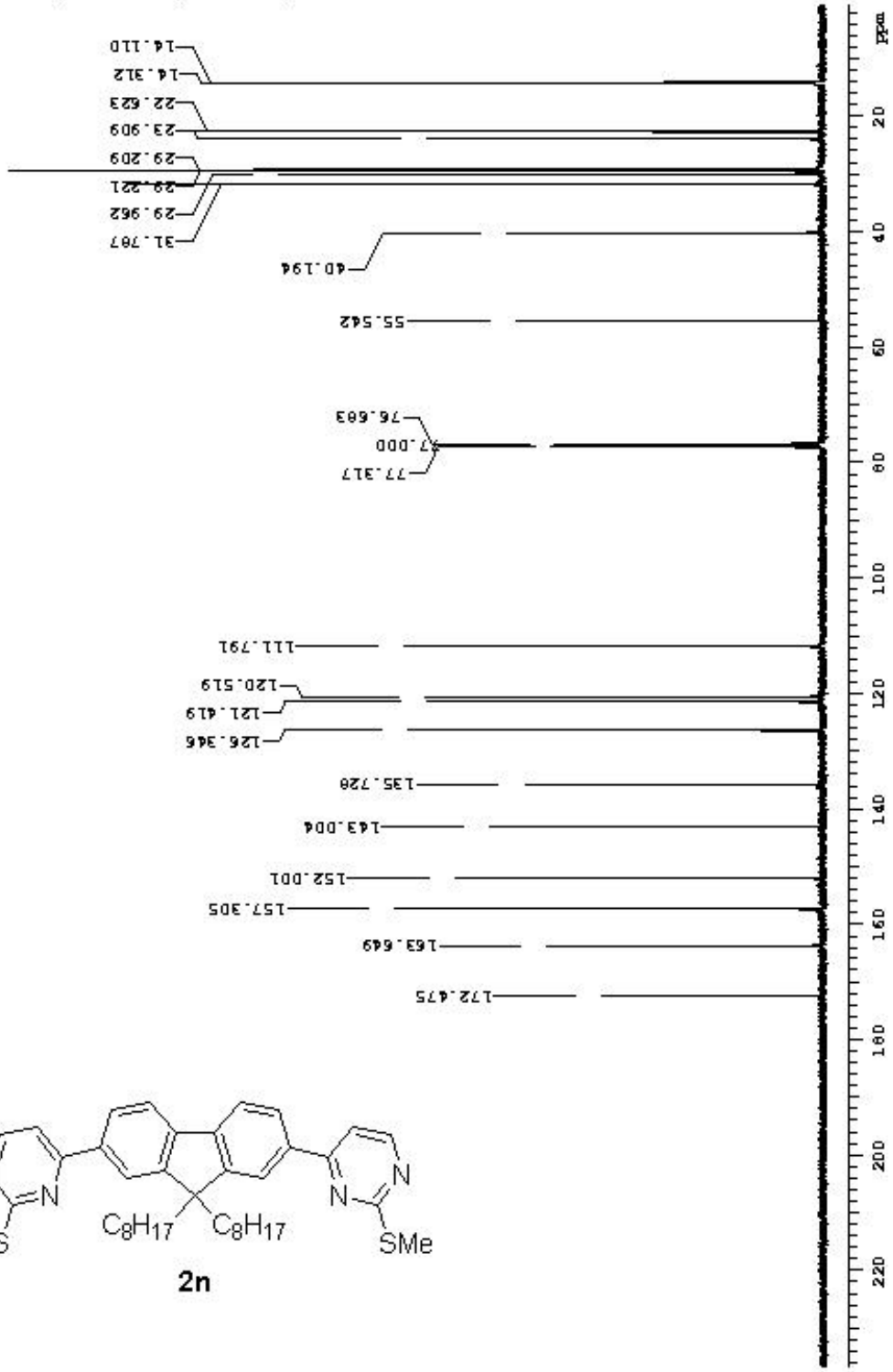
13C NMR (100 MHz, CDCl3) of 5aa

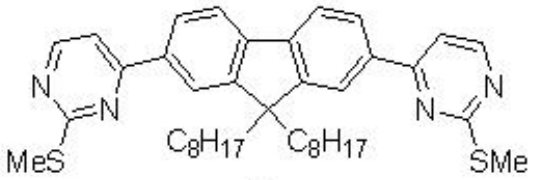


5aa



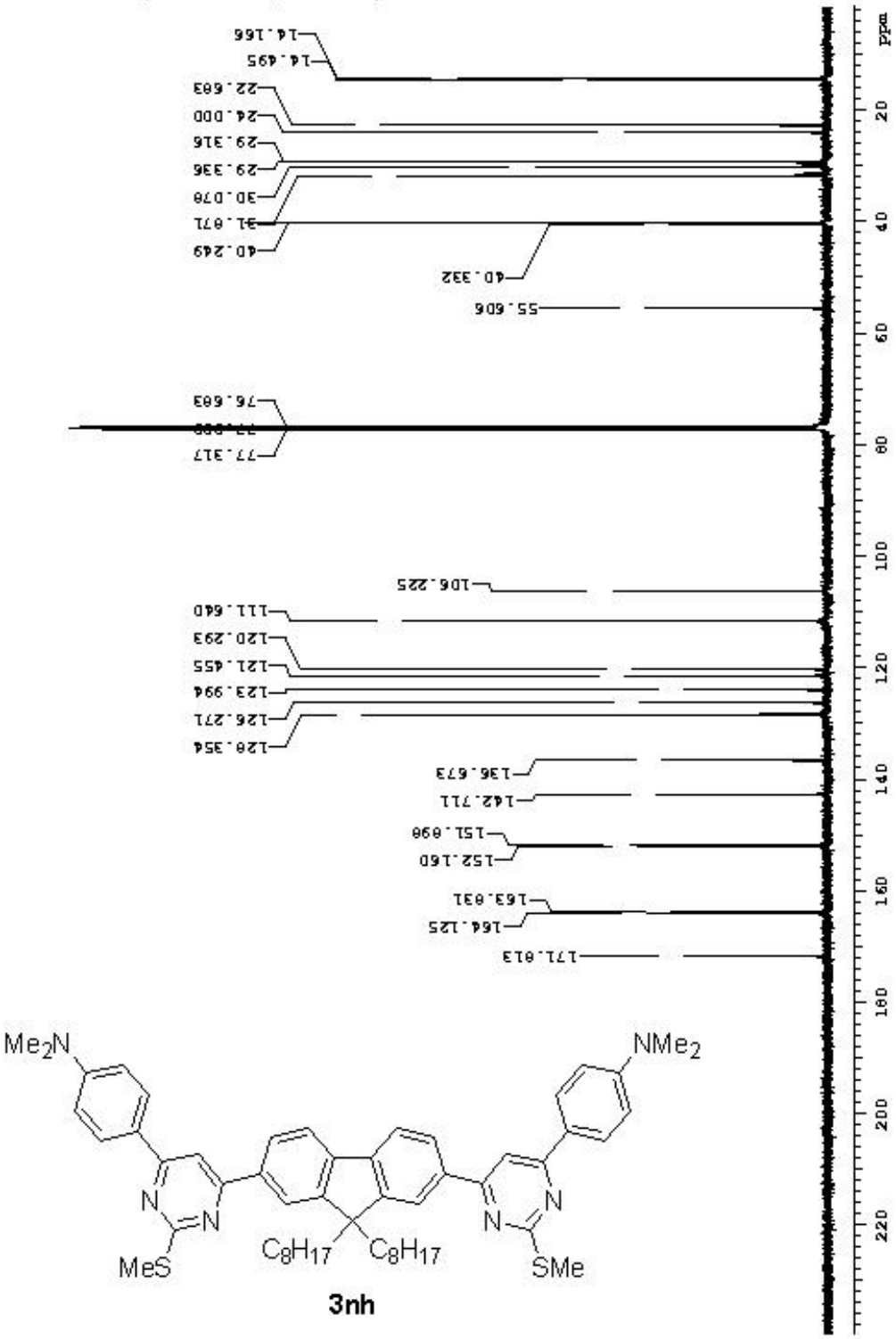
13C NMR (100 MHz, CDCl3) of 2n

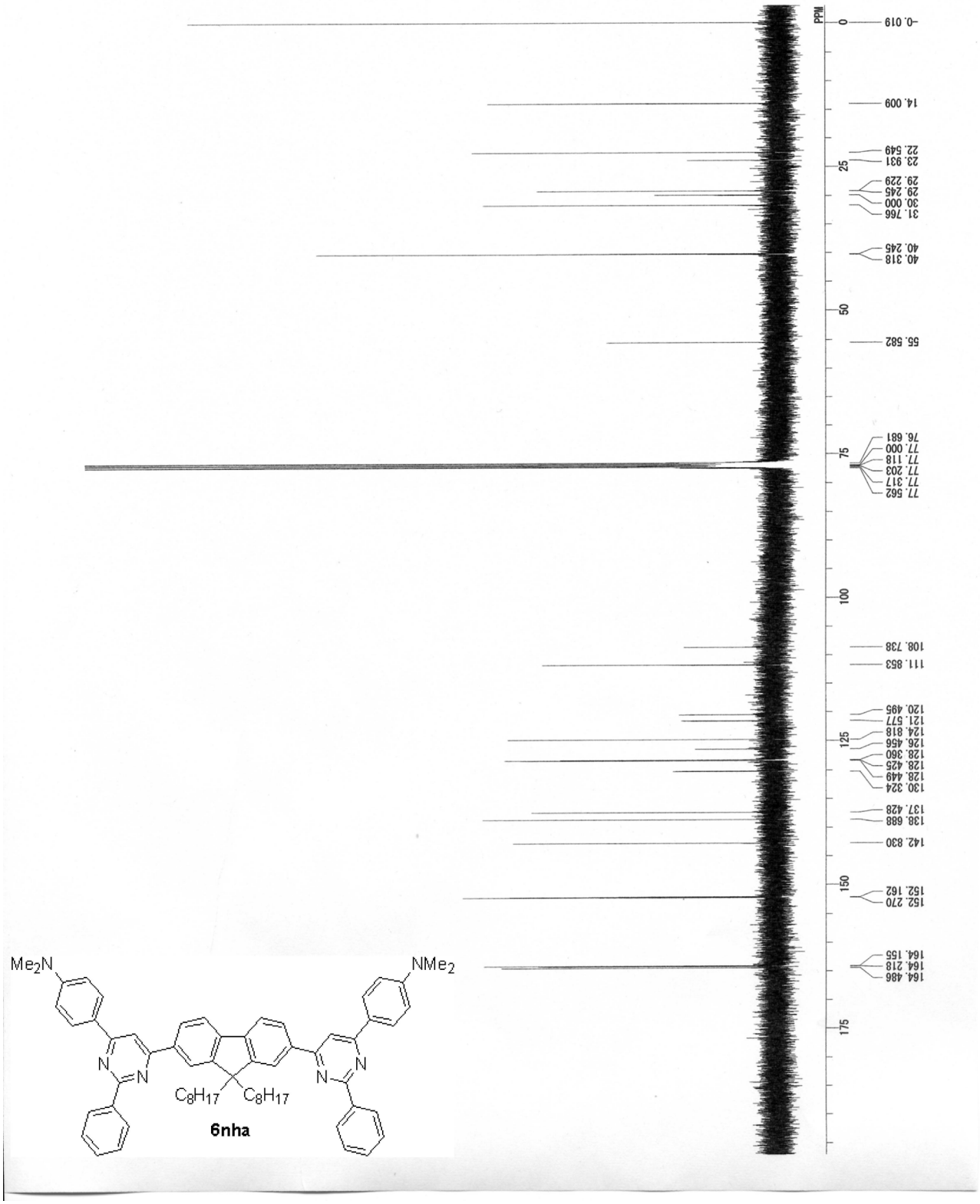




2n

13C NMR (100 MHz, CDCl3) of 3nh



3nh

13C NMR (125 MHz, CDCl3) of 6nha