

# Supporting Information

**Novel Synthesis of Benzalacetone Analogues of Naphth[*a*]azulenes by  
Intramolecular Tropylium Ion-mediated Furan Ring-opening Reaction and X-ray  
Investigation of a Naphth[1,2-*a*]azulene Derivative**

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## General Experimental

1,2-Dibromonaphthalene (**4**),<sup>1</sup> 2-bromo-1-iodonaphthalene (**9**),<sup>2</sup> 2,3-dibromonaphthalene (**14**),<sup>3</sup> tropylium tetrafluoroborate,<sup>4</sup> triphenylmethyl tetrafluoroborate,<sup>5</sup> and methoxycycloheptatriene<sup>6</sup> were prepared according to the reported procedures. 2-Methyl-5-trimethylstannylfuran was prepared by a procedure described earlier.<sup>7</sup> Tetrahydrofuran was freshly distilled from benzophenone ketyl radical under nitrogen prior to use. Toluene was dried over Na and freshly distilled before use. Other solvent and reagents were purchased from chemical suppliers and used without further purification. Column chromatography was performed with

silica-gel. Extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and solvents were removed under reduced pressure with a rotary evaporator. All melting points were determined on a hot-plate melting point apparatus and are uncorrected. All yields given refer to as isolated yields. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded at 400 MHz and 250 MHz in CD<sub>3</sub>Cl. The following abbreviations for stating the multiplicity of the signals have been used: s (singlet), d (doublet), dd (double doublet), t (triplet), m (multiplet). Chemical shifts refer to signals of tetramethylsilane in the case of <sup>1</sup>H and <sup>13</sup>C spectra. Mass spectra were recorded under electron impact (EI) at 70 eV.

#### **Preparation of 1-bromo-2-(5-methyl-2-furyl)naphthalene (5)**

A mixture of 1,2-dibromonaphthalene (**4**) (2.86 g, 10 mmol), 2-methyl-5-trimethylstannylfuran (3.68 g, 15 mmol), tetrakis(triphenylphosphine)palladium(0) (1.16g, 1.0 mmol), and dry toluene (75 mL) was refluxed for 12 h under a nitrogen atmosphere. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (Wako-gel FC40) using hexane as eluent to give **5** (1.38g, 48 %). Colorless prisms, mp 66 °C. <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) □ 2.39(s, 3H), 6.15(d, 1H, *J* = 3.4 Hz), 7.20(d, 1H, *J* = 3.4 Hz), 7.45-7.55(m, 2H), 7.73-7.75(m, 2H), 7.87(d, 1H, *J* = 8.9 Hz), 8.39(d, 1H, *J* = 8.5 Hz). *m/z* 289, 288, 287(M<sup>+</sup>), 286, 245, 243, 179, 178. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>OBr: C, 62.74;

H, 3.86. Found: C, 62.68, H, 3.90.

#### **Preparation of 2-bromo-1-(5-methyl-2-furyl)naphthalene (10)**

The procedure described above was used, **10** was prepared from 2-bromo-1-iodonaphthalene (**9**) and 2-methyl-5-trimethylstannylfuran. Yield: 48.2 %. Pale yellow oil.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ )  $\delta$  2.43(s, 3H), 6.21(d, 1H,  $J = 3.6$  Hz), 6.48(d, 1H,  $J = 3.6$  Hz), 7.45-7.48(m, 2H), 7.68-7.74(m, 3H), 7.82(dd, 1H,  $J = 7.7$  Hz, 1.7Hz).  $m/z$  289, 288, 287( $\text{M}^+$ ), 286, 245, 243, 164, 163. Anal. Calcd for  $\text{C}_{15}\text{H}_{11}\text{OBr}$ : C, 62.74; H, 3.86. Found: C, 62.63, H, 3.80.

#### **Preparation of 2-bromo-3-(5-methyl-2-furyl)naphthalene (15)**

The procedure described above was used, **15** was prepared from 2,3-dibromonaphthalene (**14**) and 2-methyl-5-trimethylstannylfuran. Yield: 51.0 %. Pale yellow prisms, mp 48-50 °C.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ )  $\delta$  2.43(s, 3H), 6.15(d, 1H,  $J = 3.4$  Hz), 7.13(d, 1H,  $J = 3.4$  Hz), 7.42-7.46(m, 2H), 7.71(dd, 2H,  $J = 9.0$  Hz, 2.1 Hz), 7.84(dd, 1H,  $J = 9.0$  Hz, 2.1 Hz), 8.15(s, 1H), 8.22(s, 1H).  $m/z$  289, 288, 287( $\text{M}^+$ ), 286, 245, 243, 179, 178, 164, 163. Anal. Calcd for  $\text{C}_{15}\text{H}_{11}\text{OBr}$ : C, 62.74; H, 3.86. Found: C, 62.82, H, 3.77.

#### **Preparation of 1-cycloheptatrienyl-2-(5-methyl-2-furyl)naphthalene (6)**

To a solution of 1-bromo-2-(5-methyl-2-furyl)naphthalene (**5**) (523 mg, 1.82 mmol) in

dry THF (10 mL), 1.25 mL of n-butyllithium (1.6 M solution in hexane, 2.0 mmol) was added slowly at  $-78\text{ }^{\circ}\text{C}$  under nitrogen atmosphere. The reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 3h. Then powdered **5**, (356 mg, 2.00 mmol) was added in limited amounts. The mixture was allowed to warm to room temperature and stirred overnight. Usual work-up gave **6** in 62.0 % yield (336 mg). Pale yellow oil.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ )  $\delta$  2.34(s, 3H), 4.12-4.24(m, 1H), 5.56-5.60(m, 2H), 6.02(d, 1H,  $J = 3.4\text{ Hz}$ ), 6.20-6.24(m, 3H), 6.62-6.63(m, 2H), 7.45-7.46(m, 2H), 7.70(d, 1H,  $J = 8.6\text{ Hz}$ ), 7.80(d, 1H,  $J = 8.6\text{ Hz}$ ), 7.88(dd, 1H,  $J = 7.3\text{ Hz}$ ,  $2.1\text{ Hz}$ ), 8.35(dd, 1H,  $J = 7.3\text{ Hz}$ ,  $2.6\text{ Hz}$ ).  $m/z$  298( $\text{M}^+$ ), 255, 253, 240, 239, 228. Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}$ : C, 88.56; H, 6.08. Found: C, 88.62, H, 6.20.

#### **Preparation of 2-cycloheptatrienyl-1-(5-methyl-2-furyl)naphthalene (11)**

The procedure described above was used, **11** was prepared from 2-bromo-1-(5-methyl-2-furyl)naphthalene (**10**). Yield: 61.6 %. Pale yellow oil.  $^1\text{H}$  NMR(400MHz,  $\text{CDCl}_3$ )  $\delta$  2.32(s, 3H), 3.02-3.03(m, 1H), 5.42-5.44(m, 2H), 6.06(d, 1H,  $J = 3.0\text{ Hz}$ ), 6.20-6.22(m, 2H), 6.24(d, 1H,  $J = 3.0\text{ Hz}$ ), 6.65-6.66(m, 2H), 7.45-7.46(m, 2H), 7.73(d, 1H,  $J = 8.5\text{ Hz}$ ), 7.77(d, 1H,  $J = 9.8\text{ Hz}$ ), 7.86(d, 1H,  $J = 9.4\text{ Hz}$ ), 7.97(d, 1H,  $J = 8.5\text{ Hz}$ ).  $m/z$  298( $\text{M}^+$ ), 255, 240, 239, 149. Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}$ : C, 88.56; H, 6.08. Found: C, 88.83, H, 6.18.

### **Preparation of 2-cycloheptatrienyl-3-(5-methy-2-furyl)naphthalene (16)**

To a mixture of Mg (150 mg, 6mmol), a crystal of I<sub>2</sub>, and 10 mL of dry THF, a mixture of **15** (1.44 g, 5 mmol) and 5mL of dry THF was added over half an hour. When the addition was complete, the whole was refluxed for 1 hr. After the flask was cooled to room temperature, a mixture of methoxycycloheptatriene (1.50 g, 12.5 mmol) and 5 mL of dry THF was added. The reaction mixture was refluxed for 1 h. Usual work-up gave **16** in 52.0 % yield (775mg). Colorless powder, mp 98-100 °C. <sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) δ 2.34(s, 3H), 3.36(t, 1H, *J* = 5.6 Hz), 5.51-5.52(m, 2H), 6.01(d, 1H, *J* = 3.0 Hz), 6.26(d, 1H, *J* = 3.0 Hz), 6.28-6.29(m, 2H), 6.72-6.74(m, 2H), 7.45-7.46(m, 2H), 7.83-7.87(m, 2H), 8.07(s, 1H), 8.10(s, 1H). *m/z* 298(M<sup>+</sup>), 255, 254, 253, 252, 241, 240, 239, 228. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O: C, 88.56; H, 6.08. Found: C, 88.78, H, 6.22.

### **Thermal isomerization of 6, 11, and 16 to 6', 11', and 16', respectively.**

A xylene solution of **6** was refluxed for 5 h. After evaporation of the solvent, the residue was subjected to short column chromatography over silica gel (Wako-gel C200) to give **6'** in almost quantitative yield. In a similar manner, **11** and **16** gave **11'** and **16'**, respectively.

### **Preparation of 2-(5-methyl-2-furyl)-1-tropylnaphthalene (7)**

A solution of **6'** (330 mg, 1.10 mmol) in 3 mL of dry dichloromethane was added to a

solution of triphenylmethyl tetrafluoroborate (369 mg, 1.10 mmol) at ambient temperature and was stirred for 5 min. After addition of 100 mL of dry ether, the resulting precipitates were collected, washed with dry ether, and dried *in vacuo* to yield **7** (355 mg, yield: 86 %). Dark red powder. Mp > 200 °C.

#### **The spectral data of **8****

$^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.59 (s, 3H), 6.85(d, 1H,  $J$  = 15.8 Hz), 7.33(dd, 1H,  $J$  = 9.5, 9.8 Hz), 7.44(t, 1H,  $J$  = 9.4 Hz), 7.65(d, 1H,  $J$  = 9.1 Hz), 7.70(m, 2H), 7.88(d, 1H,  $J$  = 9.0 Hz), 8.08(m, 1H), 8.41(d, 1H,  $J$  = 9.0 Hz), 8.68(d, 1H,  $J$  = 15.8 Hz), 8.71(d, 1H,  $J$  = 8.5 Hz), 8.75(d, 1H,  $J$  = 8.5 Hz), 8.84(d, 1H,  $J$  = 9.0 Hz).  $^{13}\text{C}$  NMR(75 MHz,  $\text{CDCl}_3$ )  $\delta$  28.0, 118.6, 119.6, 123.6, 123.4, 124.5, 125.2, 126.3, 126.3, 127.5, 127.9, 129.9, 130.0, 131.2, 131.7, 133.6, 134.6, 135.1, 137.1, 140.9, 141.4, 198.4.  $m/z$  296( $\text{M}^+$ ), 295, 281, 253, 252, 126, 125, 113, 112.

#### **The spectral data of **13****

$^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.52 (s, 3H), 7.11(d, 1H,  $J$  = 15.8 Hz), 7.42(dd, 1H,  $J$  = 9.4, 9.8 Hz), 7.54(t, 1H,  $J$  = 9.8 Hz), 7.62(d, 1H,  $J$  = 8.1 Hz), 7.70(m, 1H), 7.80(m, 1H), 8.10(m, 2H), 8.33(d, 1H,  $J$  = 9.0 Hz), 8.48(d, 1H,  $J$  = 15.8 Hz), 8.75(d, 1H,  $J$  = 10.7 Hz), 9.01(d, 1H,  $J$  = 8.5 Hz), 9.41(d, 1H,  $J$  = 9.4 Hz).  $^{13}\text{C}$  NMR(75 MHz,  $\text{CDCl}_3$ )  $\delta$  27.7, 118.7, 121.6, 124.0, 125.6, 125.9, 126.1, 126.3, 126.6, 127.1, 128.0, 128.9, 129.9, 131.4,



134.6, 134.8, 137.3, 138.2, 138.9, 139.4, 198.1.  $m/z$  296(M<sup>+</sup>), 295, 253, 252, 149, 128, 127.

### **The spectral data of 18**

<sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  2.48 (s, 3H), 6.92(m, 1H), 7.01(m, 2H), 7.13(d, 1H,  $J$  = 15.8 Hz), 7.23(d, 1H,  $J$  = 2.6 Hz), 7.35(d, 1H,  $J$  = 2.6 Hz), 7.55-7.62(m, 2H), 7.95-8.10(m, 2H), 8.18(d, 1H,  $J$  = 15.8 Hz), 8.46(s, 1H), 8.67(s, 1H). <sup>13</sup>C NMR(75 MHz, CDCl<sub>3</sub>)  $\delta$  30.1, 116.1, 117.7, 119.8, 120.8, 124.5, 124.7, 126.3, 126.8, 128.1, 128.5, 128.6, 129.6, 129.8, 131.8, 134.0, 134.4, 134.6, 137.1, 144.0, 167.3, 198.5.  $m/z$  296(M<sup>+</sup>), 295, 281, 253, 252, 126, 125, 113, 112.

### **X-ray crystallography**

A SMART 1000/CCD diffractometer was employed for the diffraction measurements of az3 at room temperature using graphite monochromated Mo-K $\alpha$  radiations ( $\lambda$  = 0.71073 Å,  $2\theta < 55^\circ$ ). The structure was solved by a direct method and refined by full-matrix least-squares calculations against  $F_o^2$  with absorption corrections (SADABS) using a program package SHELXL-97.<sup>8</sup> Non-hydrogen atoms were included in the structure refinements applying anisotropic displacement parameters. The positions of all

hydrogen atoms were found in the difference Fourier maps and they were included in the refinement with isotropic displacement parameters.

Crystal data and details of the data collection and processing for **8**: C<sub>22</sub>H<sub>17</sub>O,  $M = 297$ , monoclinic, space group C2/c (no.15),  $a = 22.229(9)$   $b = 5.344(2)$ ,  $c = 27.376(11)$  Å,  $\beta = 111.999(7)^\circ$ ,  $U = 3015(2)$  Å<sup>3</sup>,  $Z = 8$ .  $T = 297$  K.  $D_c = 1.310$  g cm<sup>-3</sup>.  $F(000) = 1256$ .

Crystal dimensions: 0.1 x 0.1 x 0.1 mm,  $\mu(\text{Mo-K}\alpha) = 0.079$  mm<sup>-1</sup>, 8017 reflections measured (index range  $h$  -27 to 12,  $k$  -6 to 6,  $l$  -30 to 33), 3073 unique ( $R_{\text{int}} = 0.0608$ ).

The final  $R_1(F) = 0.0717$  for 3073 ( $>2\sigma(I)$ ) and  $wR_2(F^2) = 0.1848$  and GOF = 0.971 for all reflections,  $w^{-1} = [\sigma^2(F_o^2) + (0.0964p)^2 + 0.0000p]$  where  $p = (F_o^2 + 2F_c^2)/3$ , 272 parameters. Max. shift/esd = 0.000,  $\rho_{\text{max}} = 0.195$ ,  $\rho_{\text{min}} = -0.242$  eÅ<sup>-3</sup> on final difference map.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free from charge, by quoting the publication citation and deposition number: CCDC262360.

**Figure S1**

$^1\text{H}$  NMR spectrum for **5**

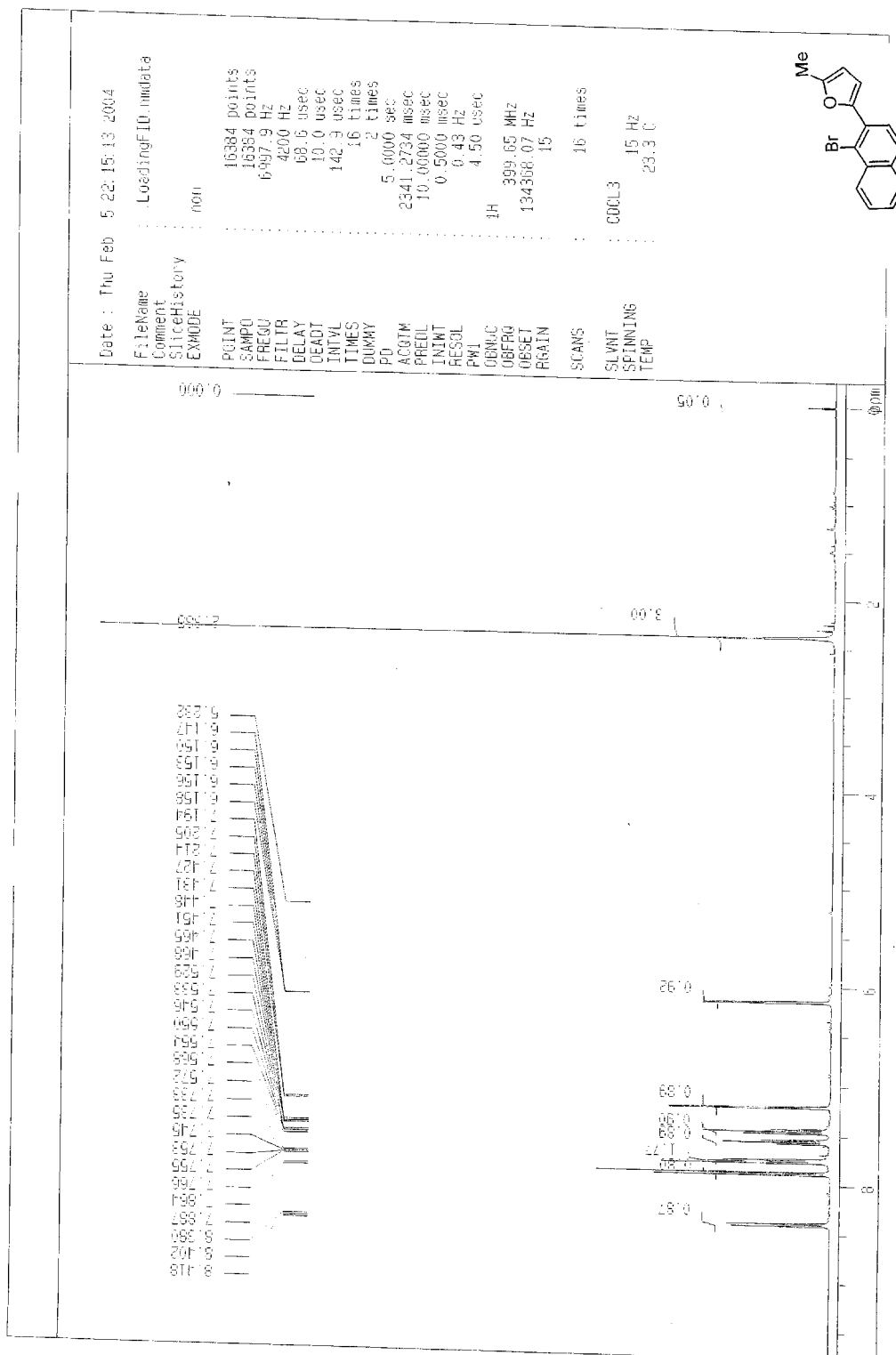
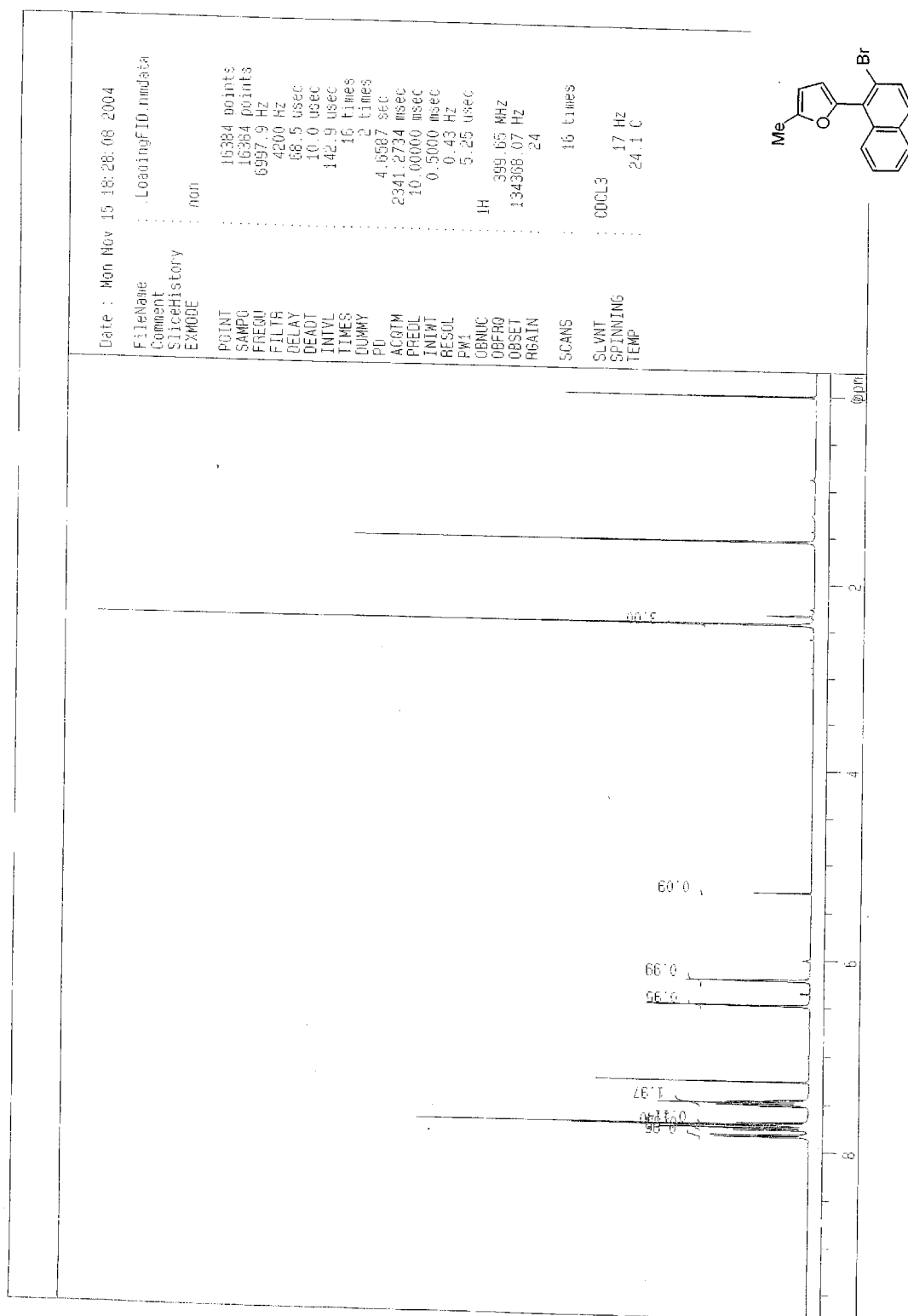


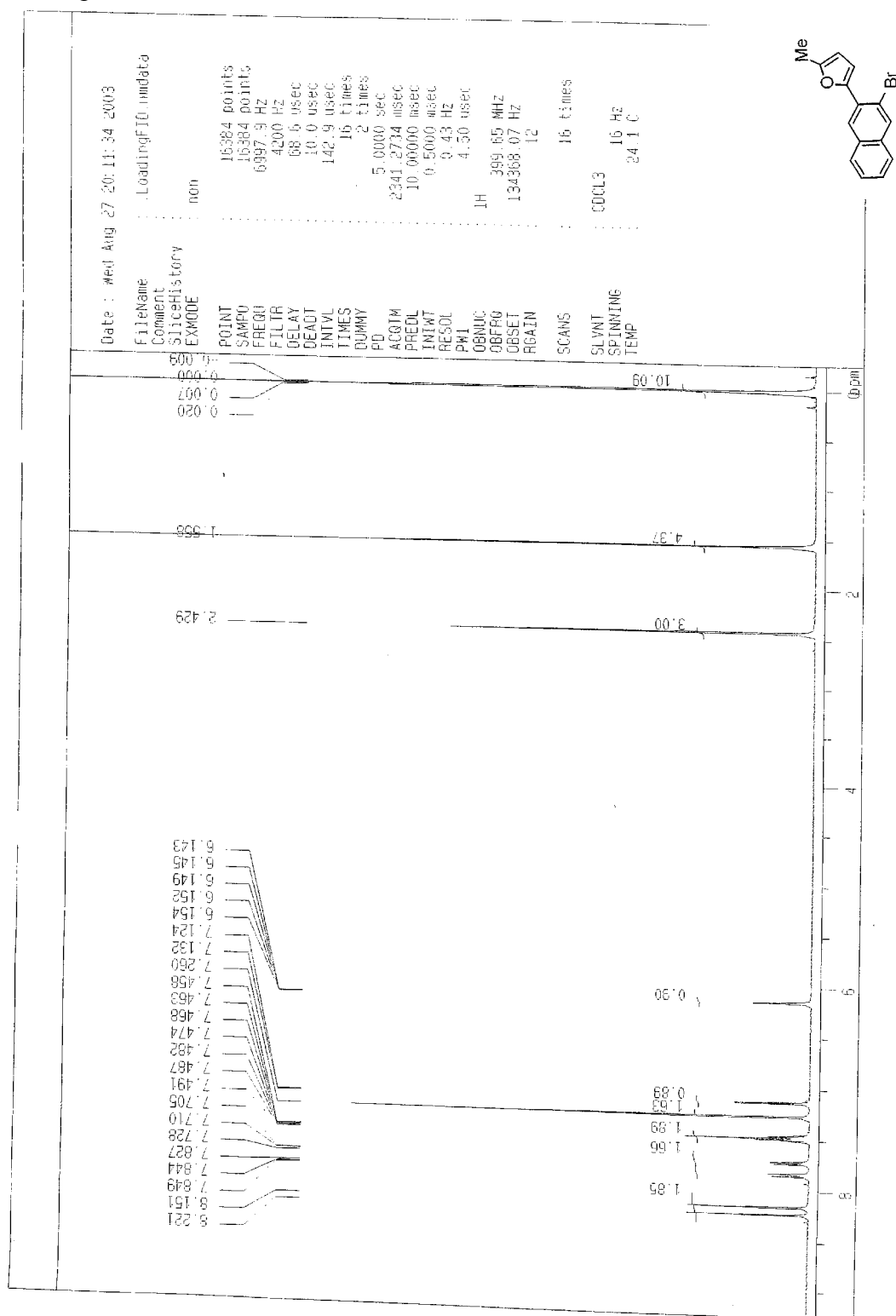
Figure S2

$^1\text{H}$  NMR spectrum for **10**



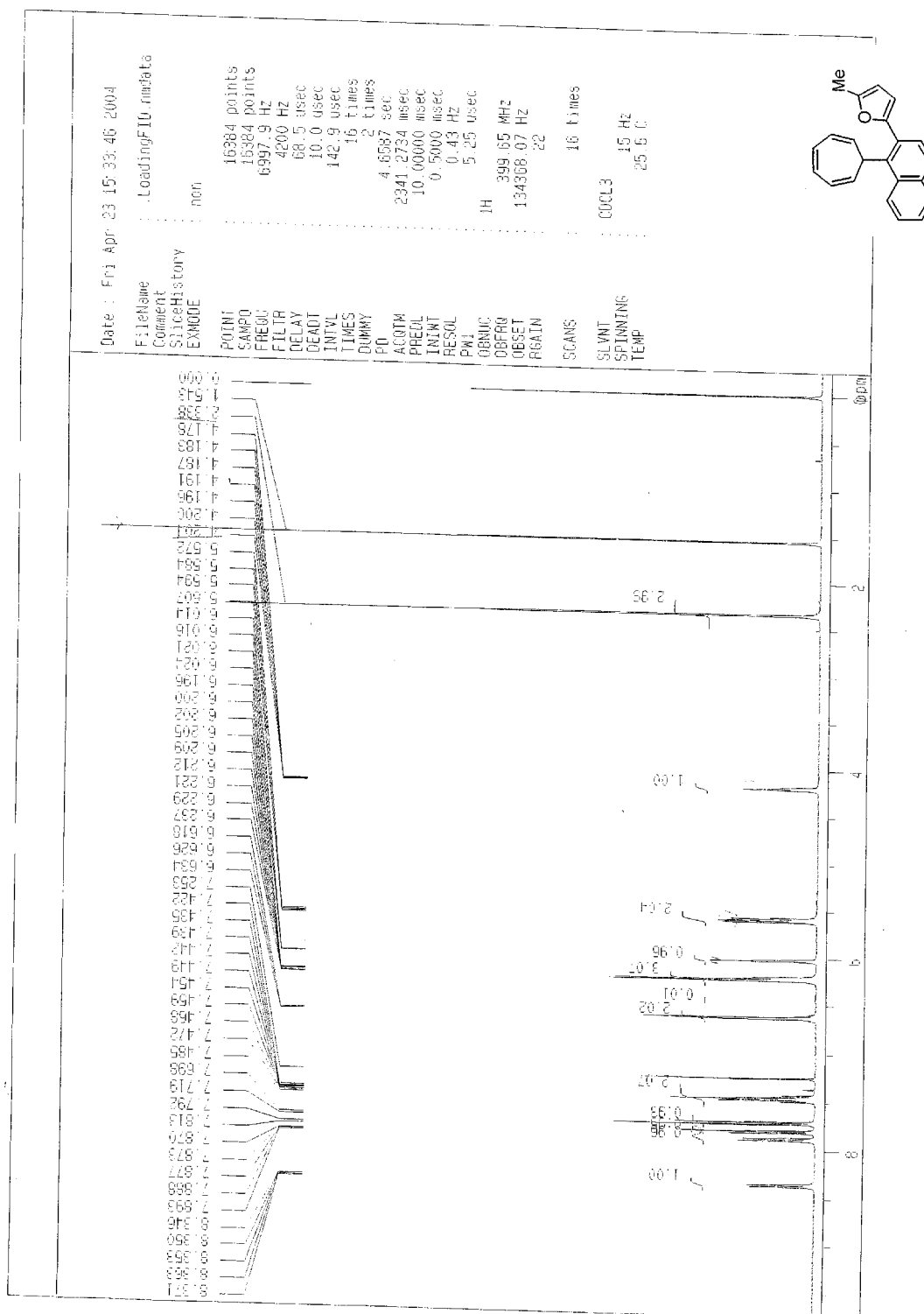
**Figure S3**

$^1\text{H}$  NMR spectrum for **15**



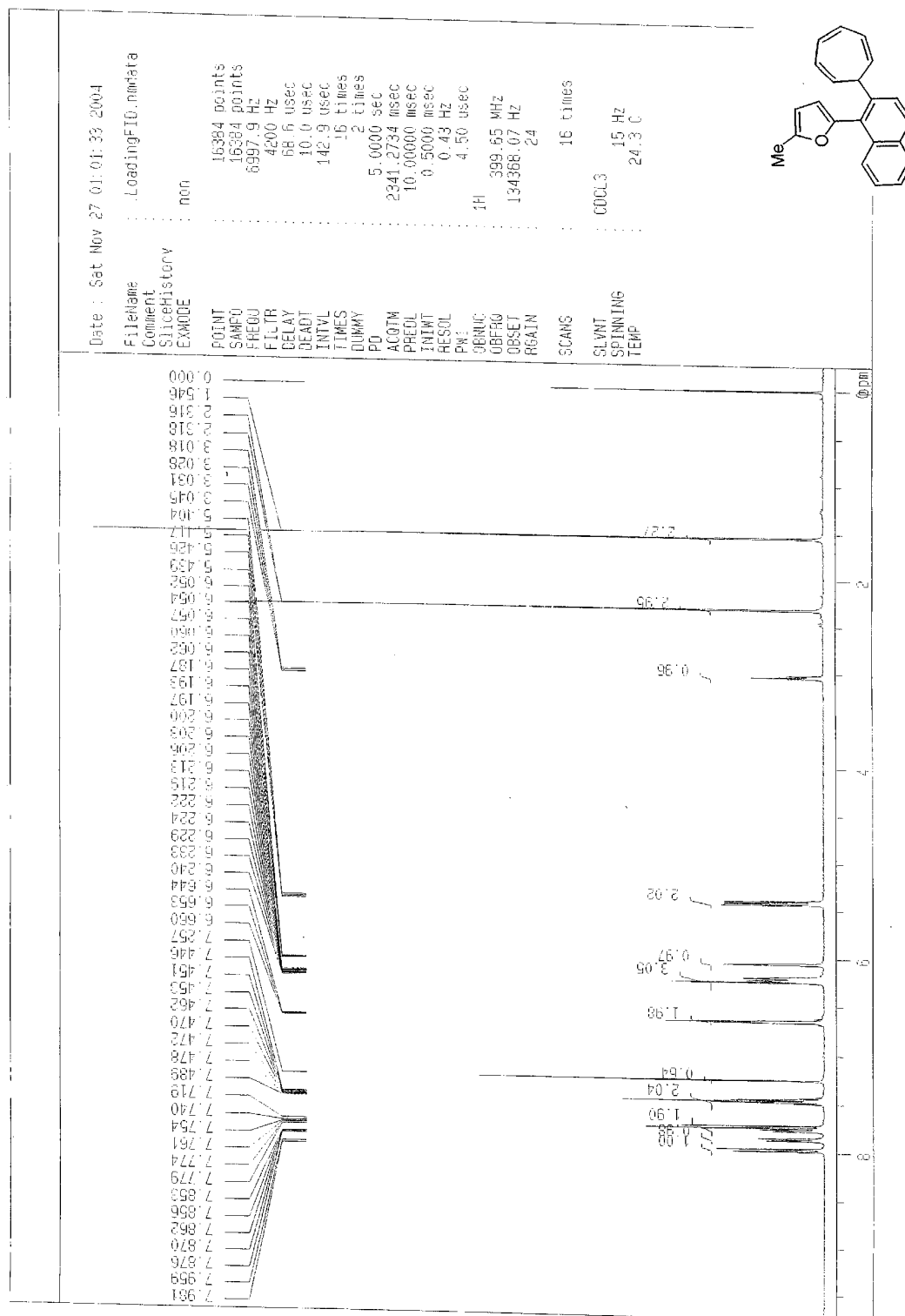
**Figure S4**

$^1\text{H}$  NMR spectrum for **6**



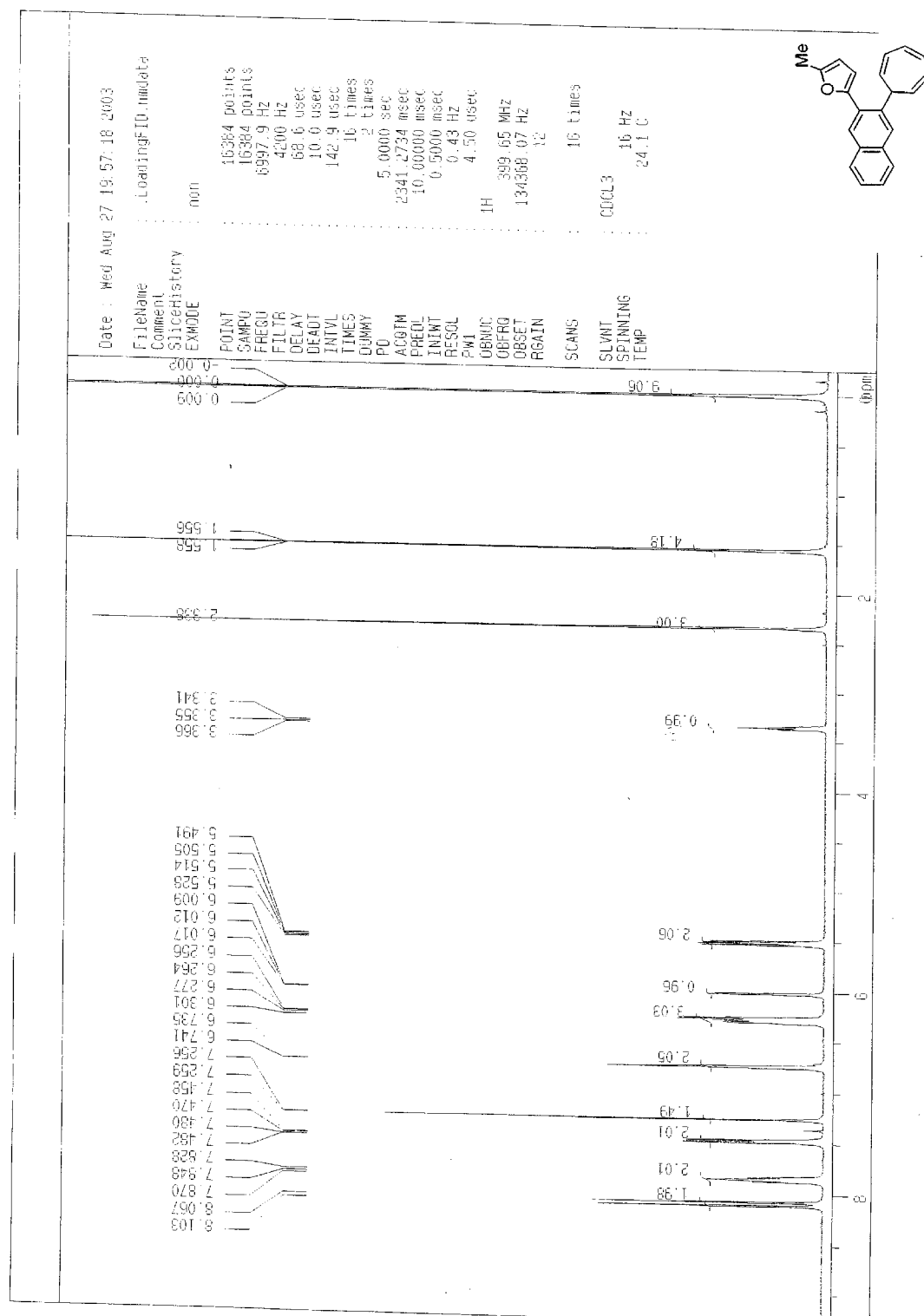
**Figure S5**

<sup>1</sup>H NMR spectrum for **11**



**Figure S6**

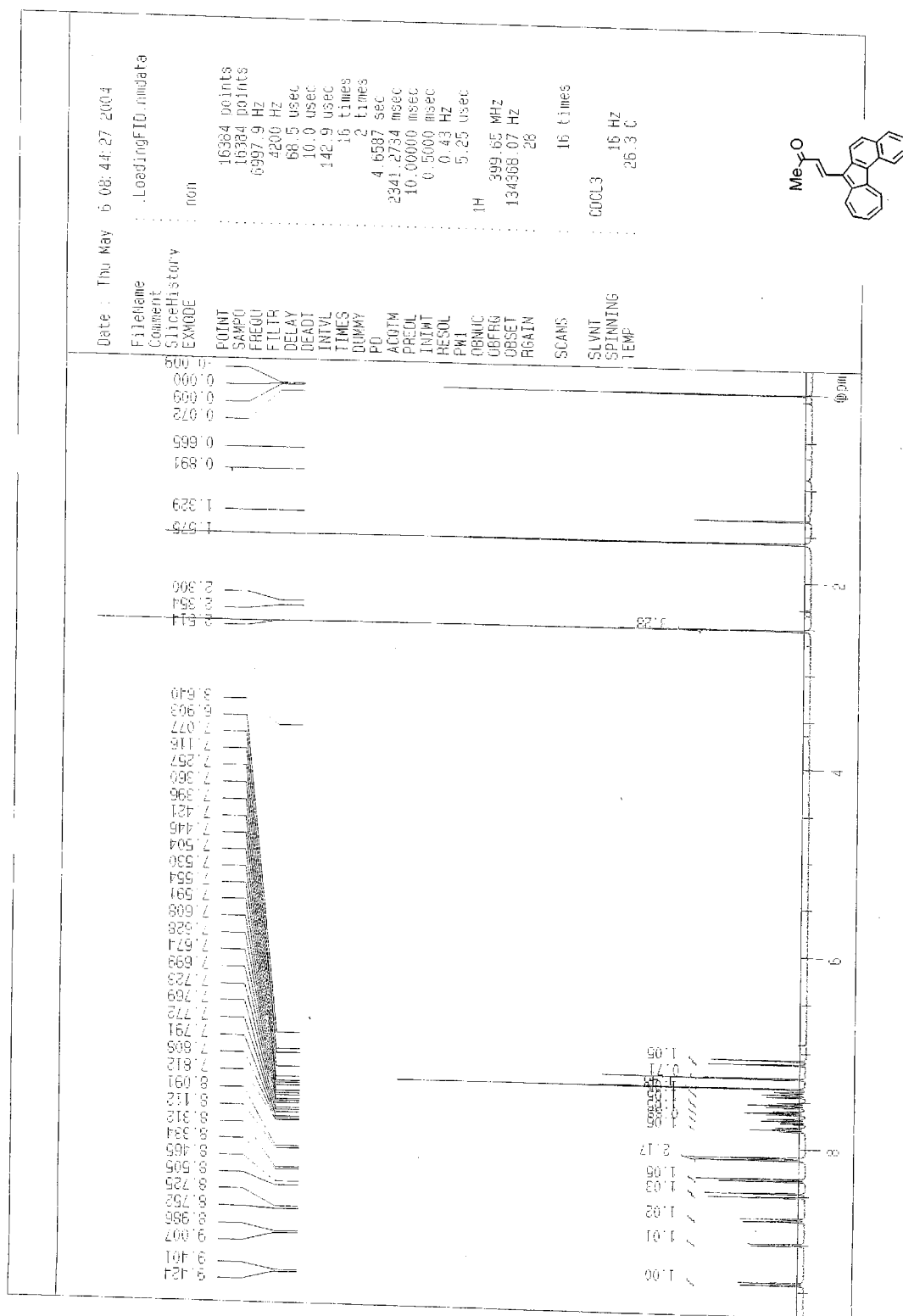
$^1\text{H}$  NMR spectrum for **16**





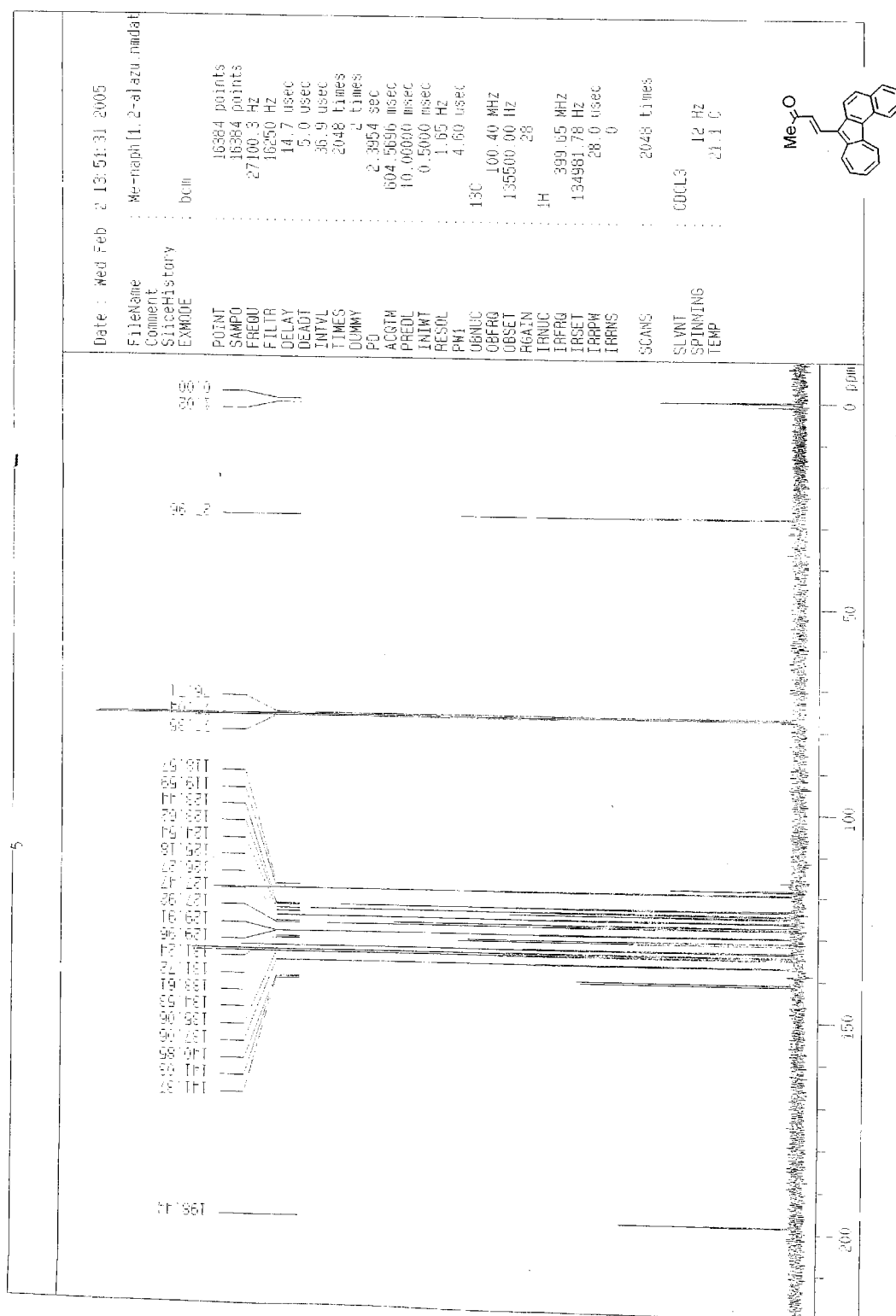
**Figure S7**

$^1\text{H}$  NMR spectrum for **8**



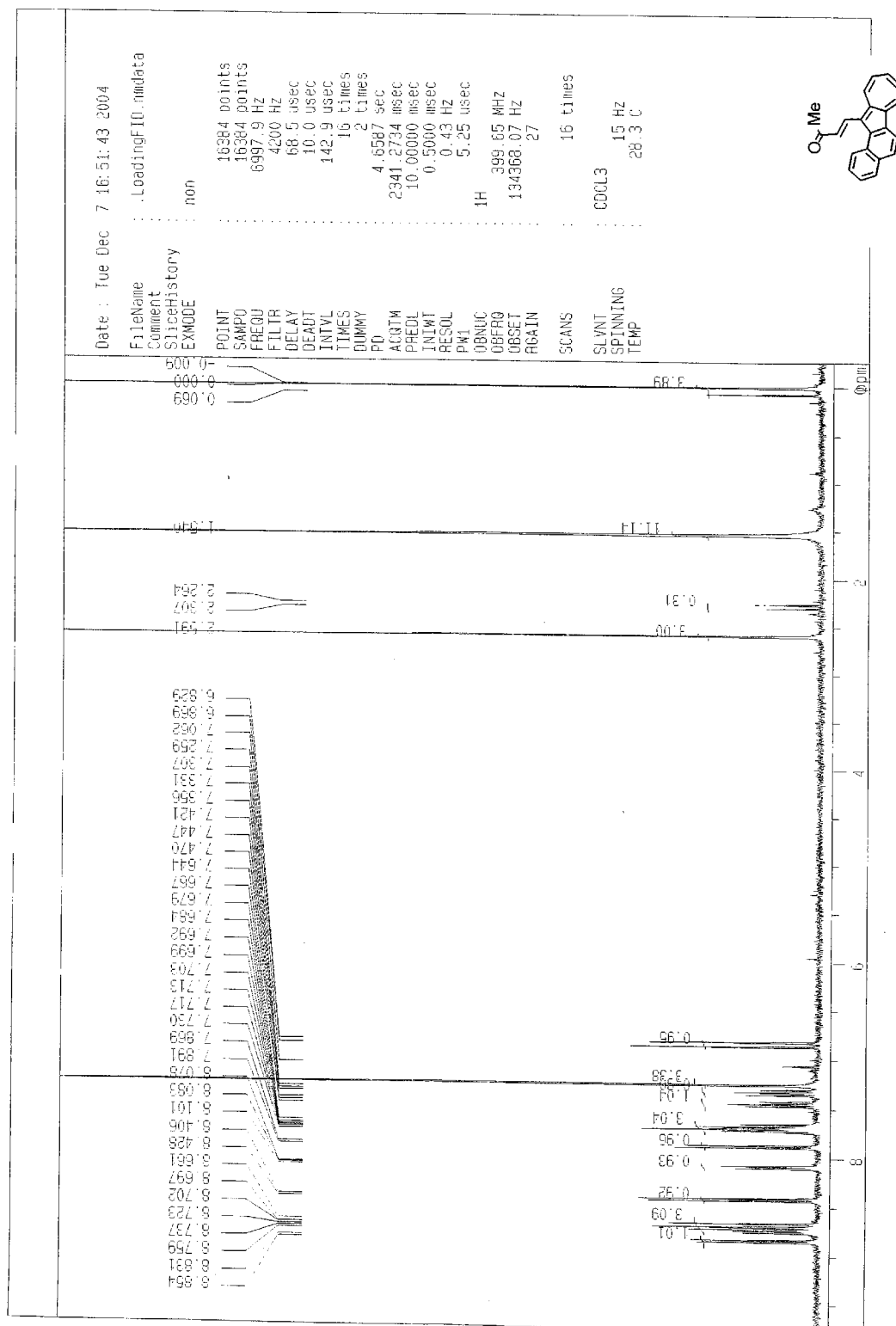
**Figure S8**

<sup>13</sup>C NMR spectrum for **8**

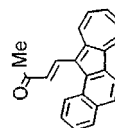


**Figure S9**

$^1\text{H}$  NMR spectrum for **13**

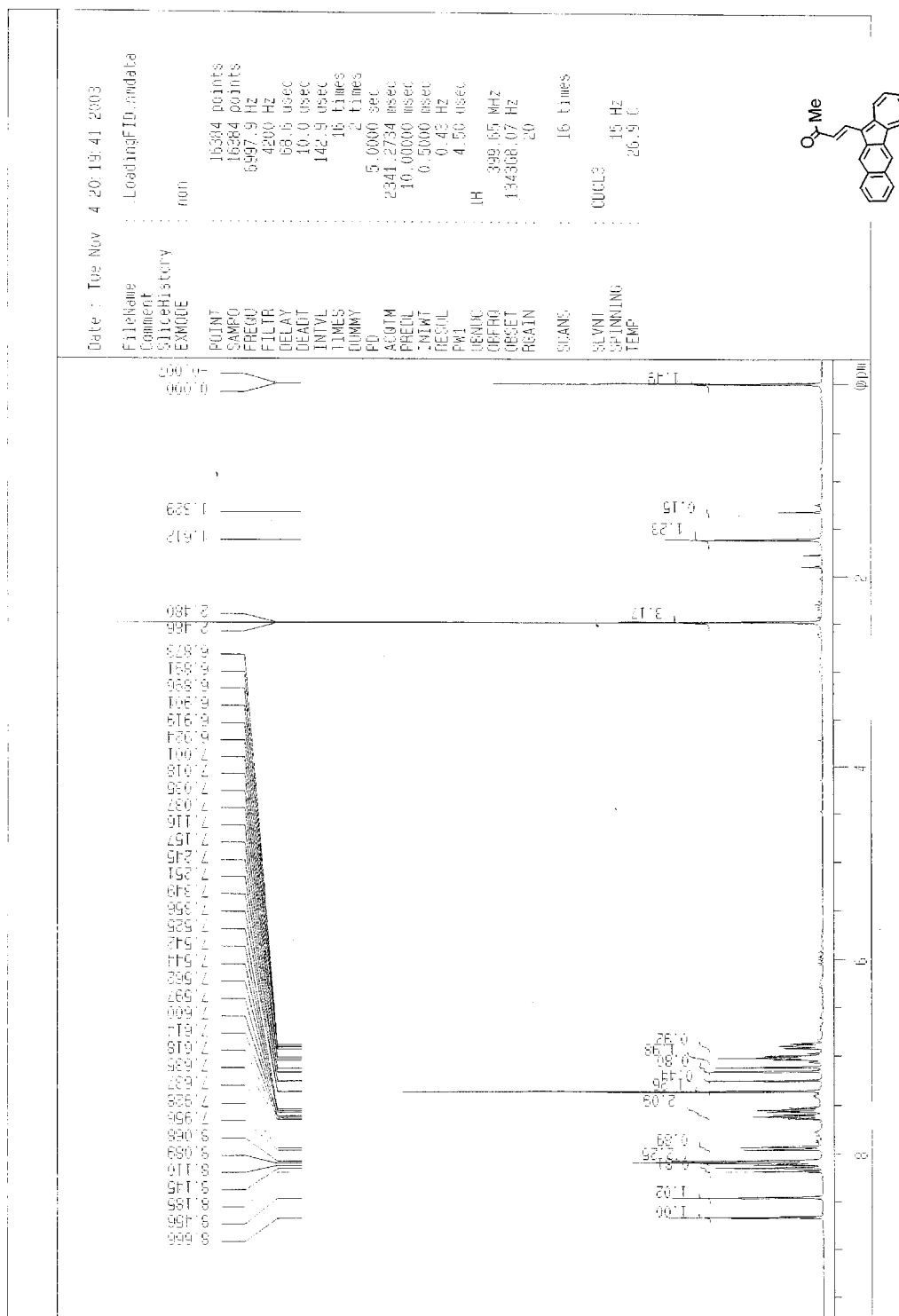


<sup>13</sup>C NMR spectrum for **13**



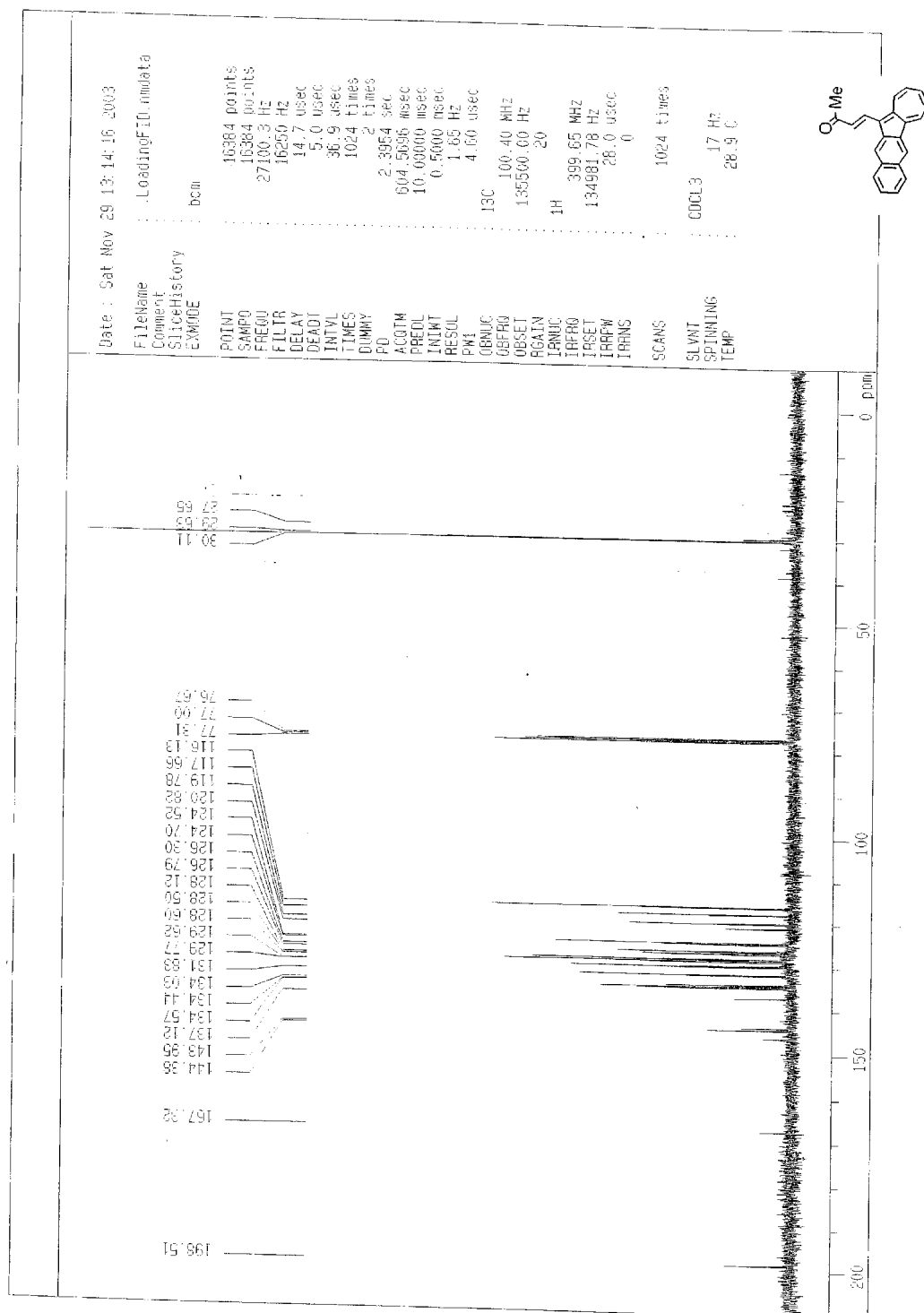
**Figure S11**

$^1\text{H}$  NMR spectrum for **18**



**Figure S12**

$^1\text{H}$  NMR spectrum for **18**



## References

- 1) Miller, J. J.; Meek, J. S.; Strickler, S. J. *J. Am. Chem. Soc.*, **1977**, *99*, 8175.
- 2) Geen, G. R.; Mann, I. S.; Mullane, M. V. *Tetrahedron*, **1998**, *54*, 9875.
- 3) Brooks, P.; Dontai, D.; Pelter, A.; Poticelli, F. *Synthesis*, **1999**, 1305.
- 4) Dauben, H. J. Jr.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.*, **1957**, *79*, 4557.
- 5) Dauben, H. J. Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.*, **1960**, *25*, 1442.
- 6) Jutz, C.; Voithenleitner, F. *Chem. Ber.*, **1964**, *97*, 29.
- 7) Sasabe, M.; Houda, Y.; Takagi, H.; Sugane, T.; Bo, X.; Yamamura, K. *J. Chem. Soc., Perkin 1*, **2000**, 3786.
- 8) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Goettingen, Germany, 1997.