

Supplementary Data

Reversal of Regioselectivity (Straight vs. Cross Ring Closure) in the Intramolecular [2+2] Photocycloaddition of Phenanthrene Derivatives

Shigeo Kohmoto,[†] Shugo Hisamatsu,[†] Hakuei Mitsuhashi,[†] Masahiro Takahashi,[†] Hyuma Masu,[‡]
Isao Azumaya,[‡] Kentaro Yamaguchi[‡] and Keiki Kishikawa[†]*

[†]Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba
University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

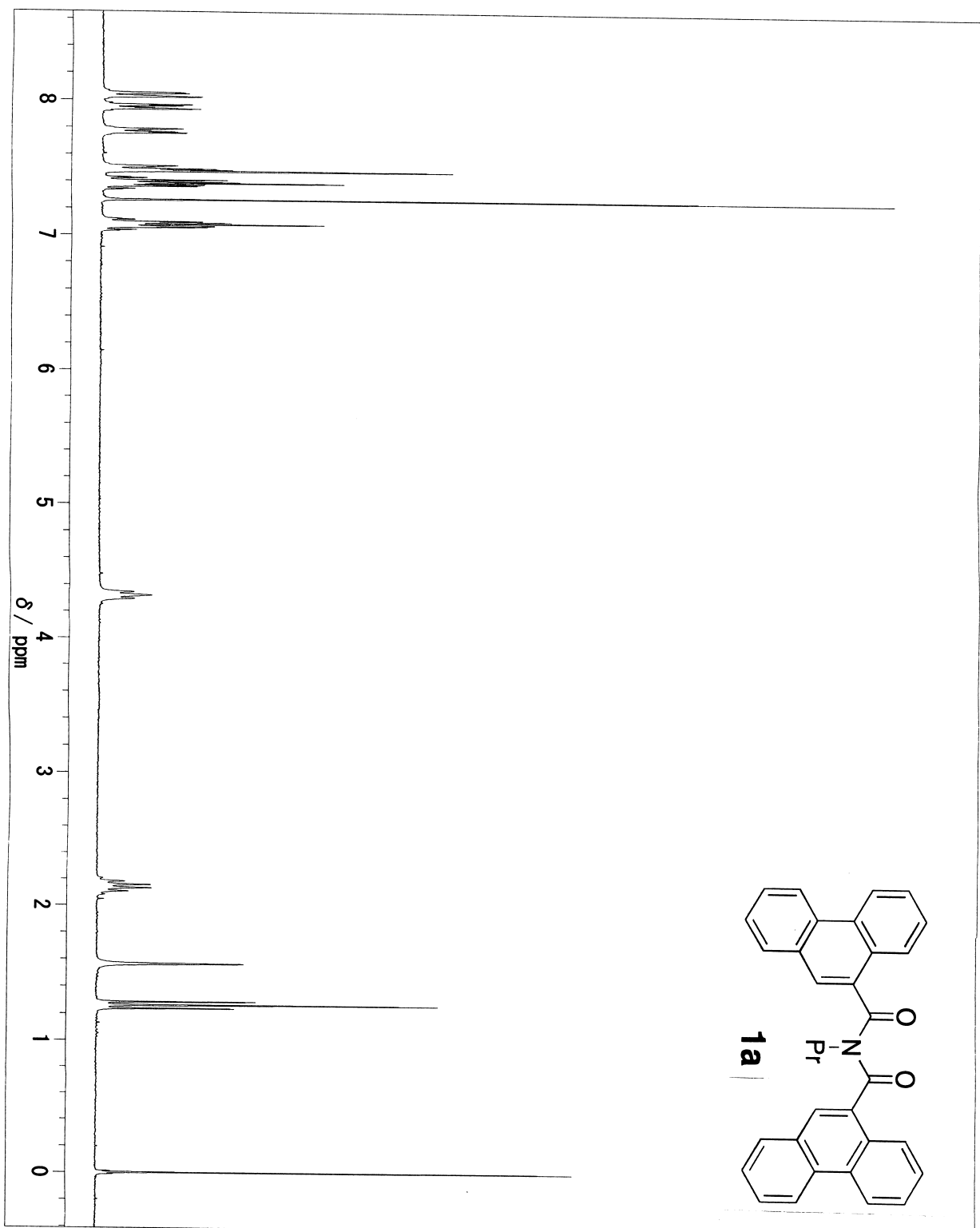
[‡]Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido,
Sanuki, Kagawa 769-2193, Japan

e-mail: kohmoto@faculty.chiba-u.jp

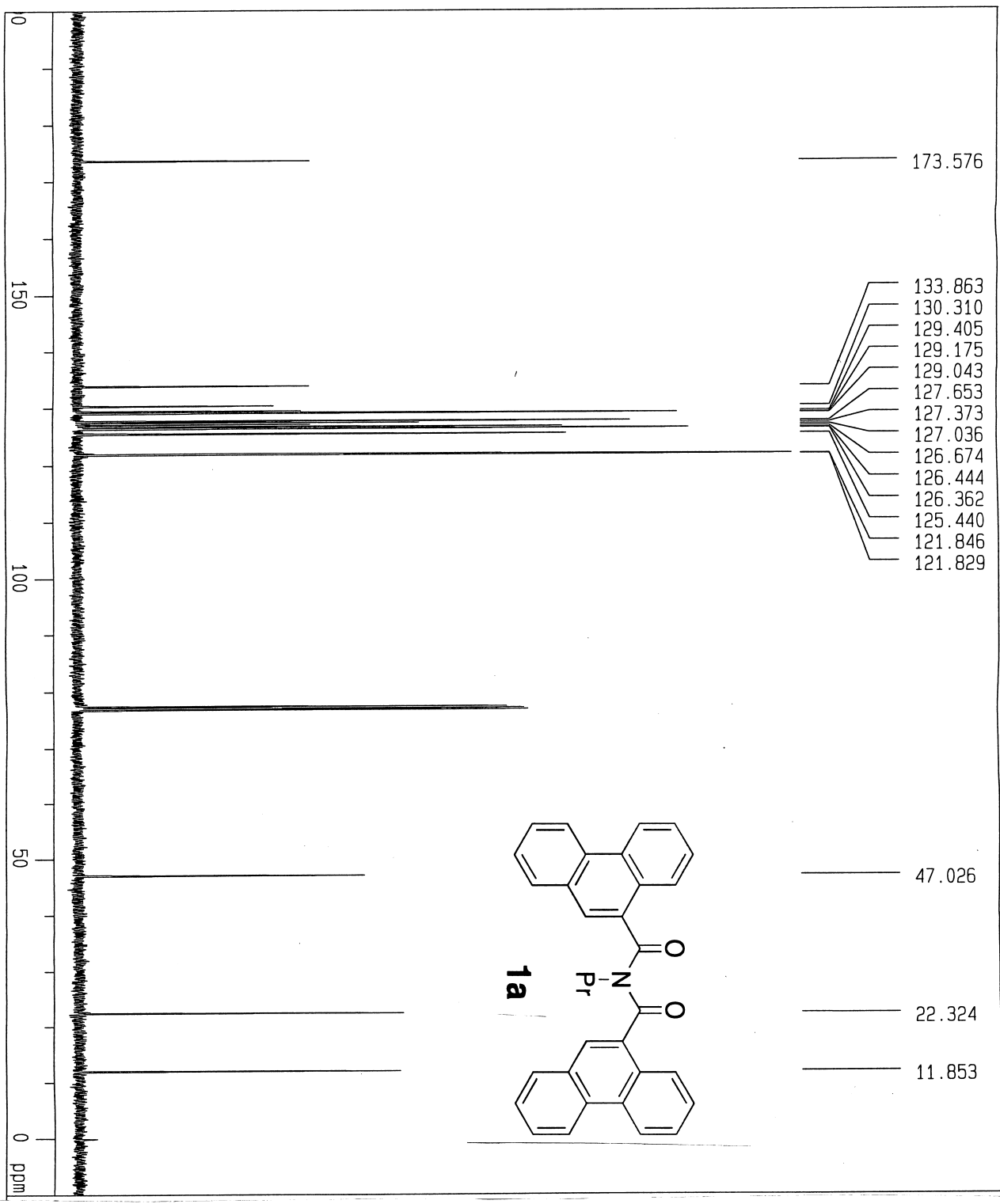
Contents

● ¹ H NMR spectrum of 1a	S2
● ¹³ C NMR spectrum of 1a	S3
● ¹ H NMR spectrum of 2a	S4
● ¹³ C NMR spectrum of 2a	S5
● ¹ H NMR spectrum of 3a	S6
● ¹³ C NMR spectrum of 3a	S7
● ¹ H NMR spectrum of 1b	S8
● ¹³ C NMR spectrum of 1b	S9
● ¹ H NMR spectrum of 2b	S10
● ¹ H NMR spectrum of 3b	S11
● ¹ H NMR spectrum of 4	S12
● ¹³ C NMR spectrum of 4	S13
● ¹ H NMR spectrum of 5	S14
● ¹³ C NMR spectrum of 5	S15
● Spectral data of 1b , 2b , 3b , 4 and 5	S16-17

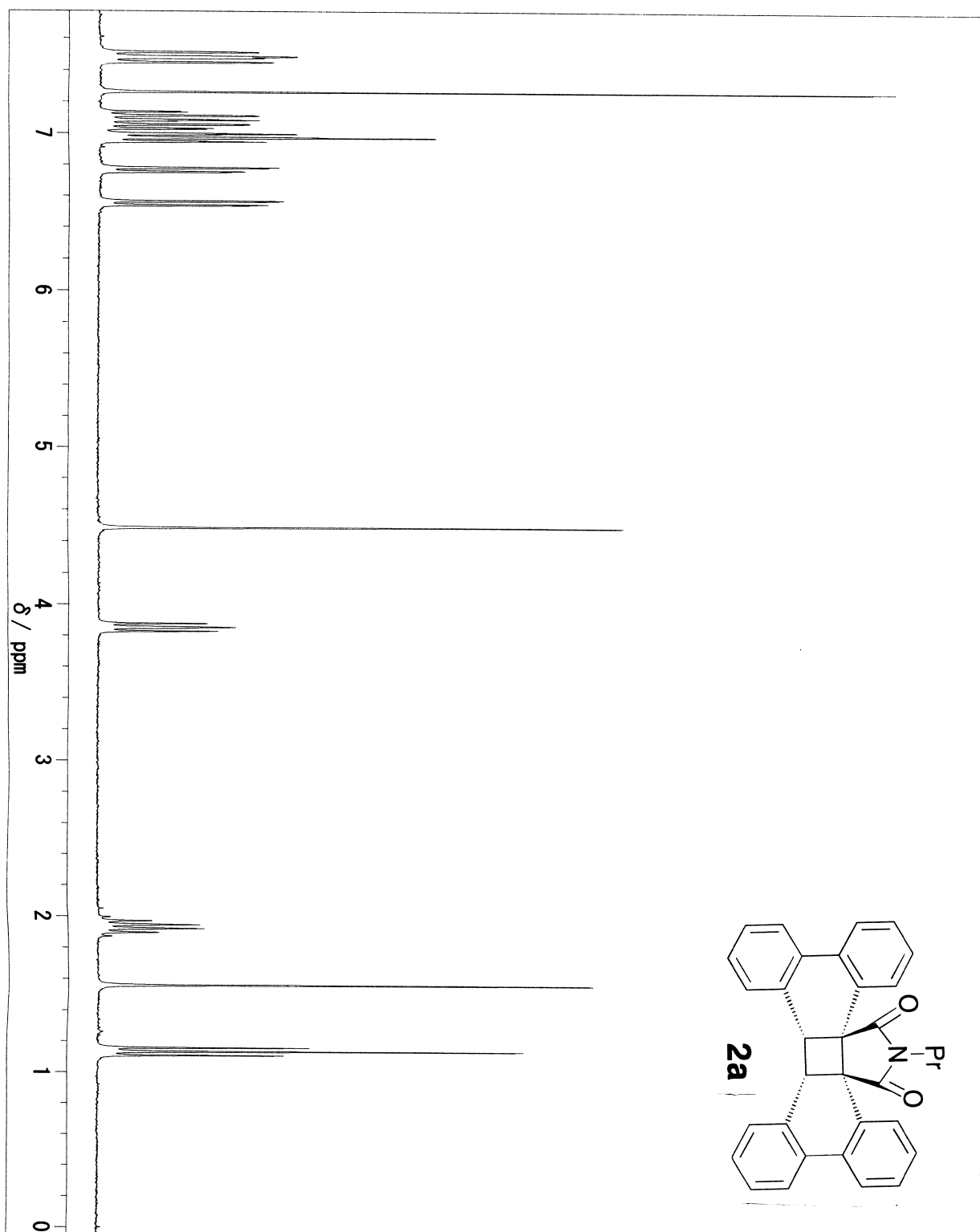
¹H NMR (300 MHz, CDCl₃) of **1a**



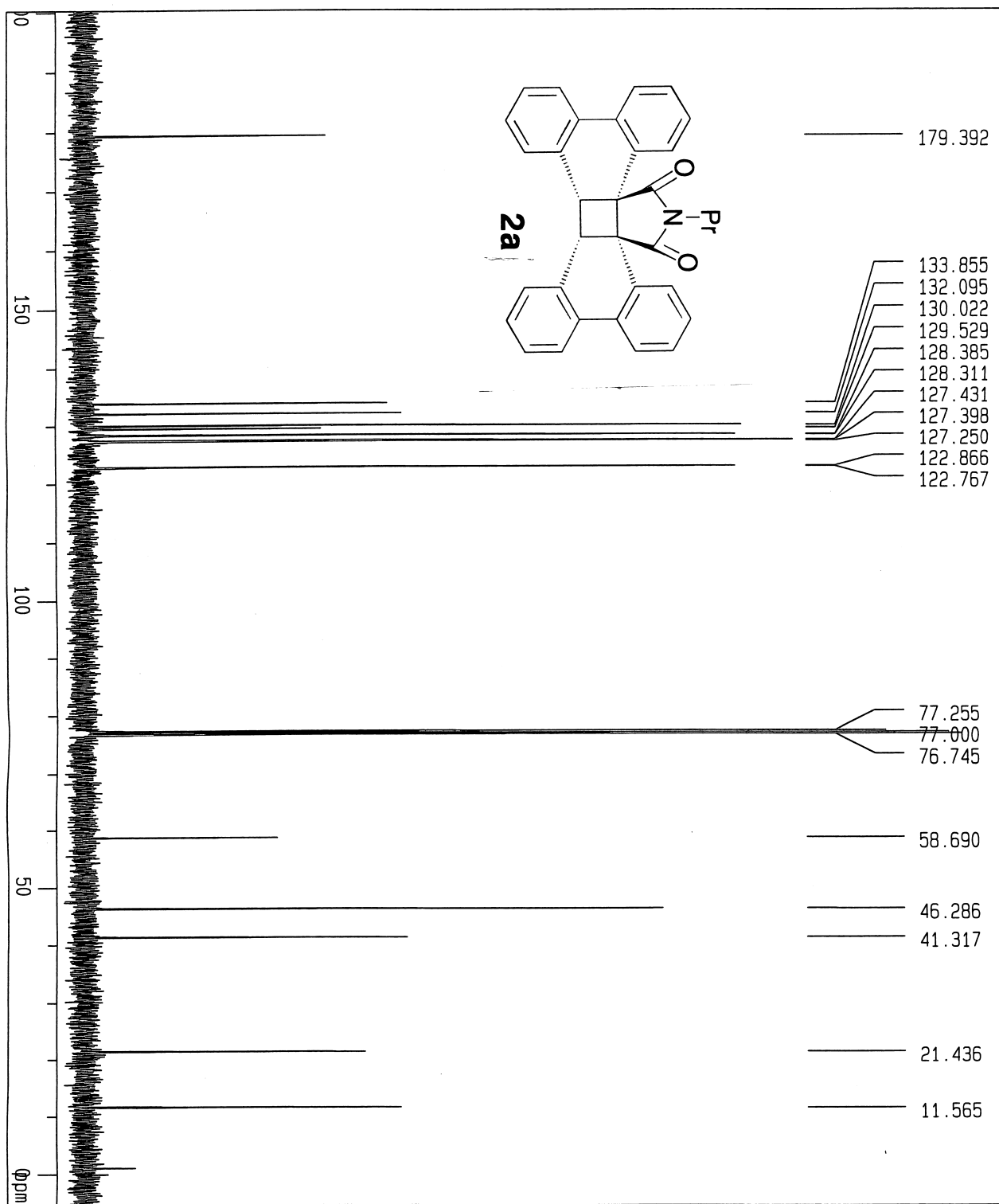
¹³C NMR (125 MHz, CDCl₃) of **1a**



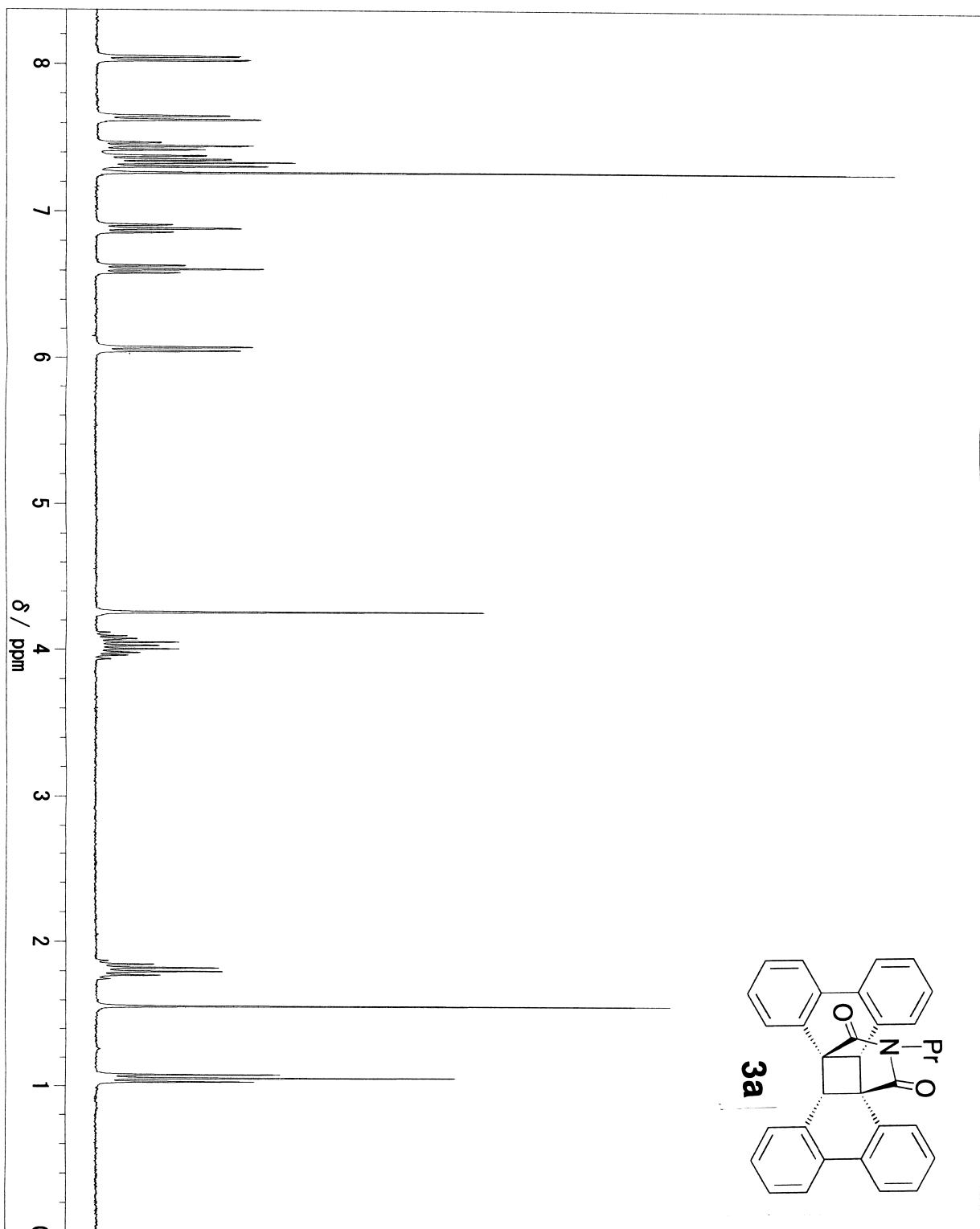
^1H NMR (300 MHz, CDCl_3) of **2a**



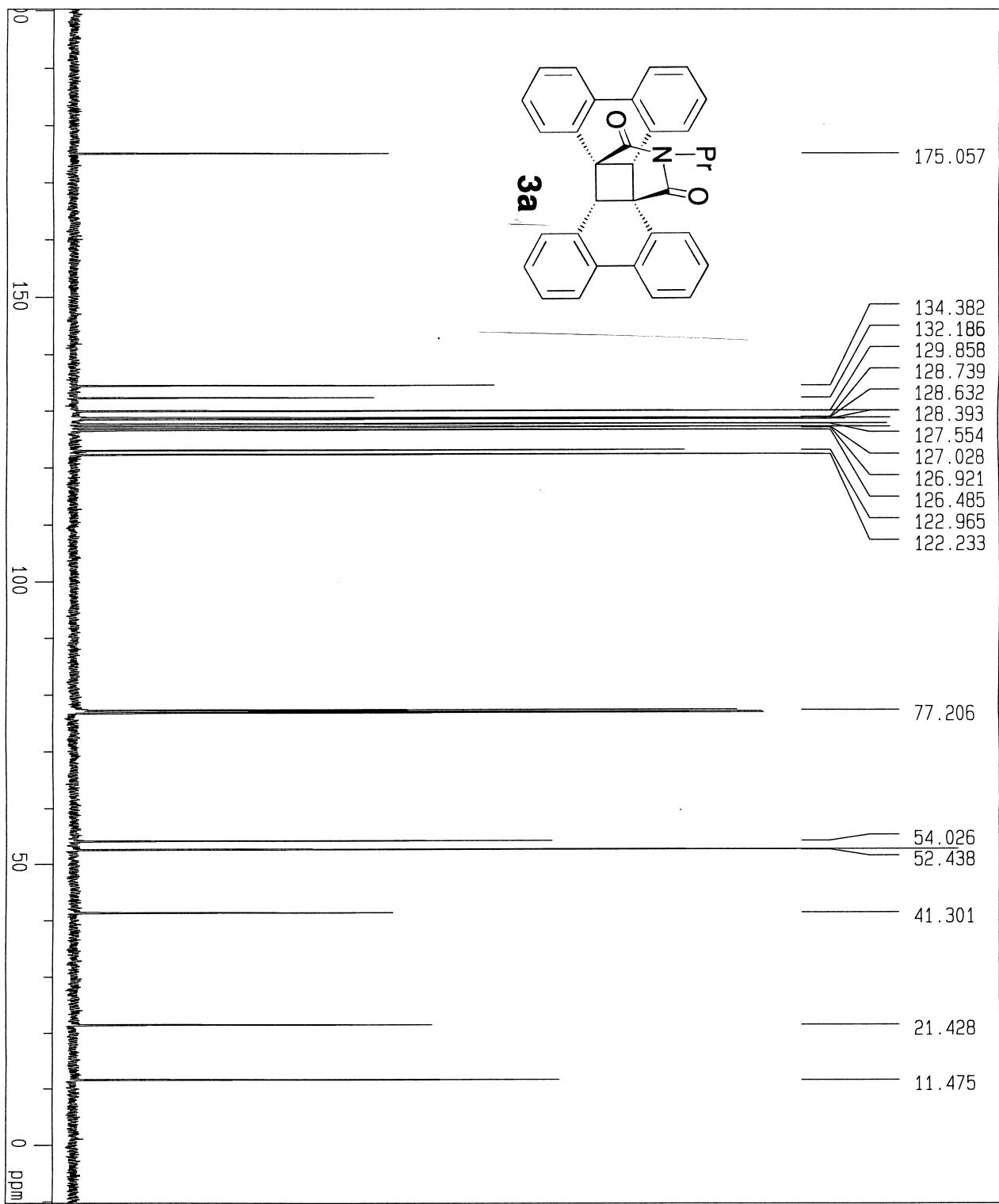
^{13}C NMR (125 MHz, CDCl_3) of **2a**



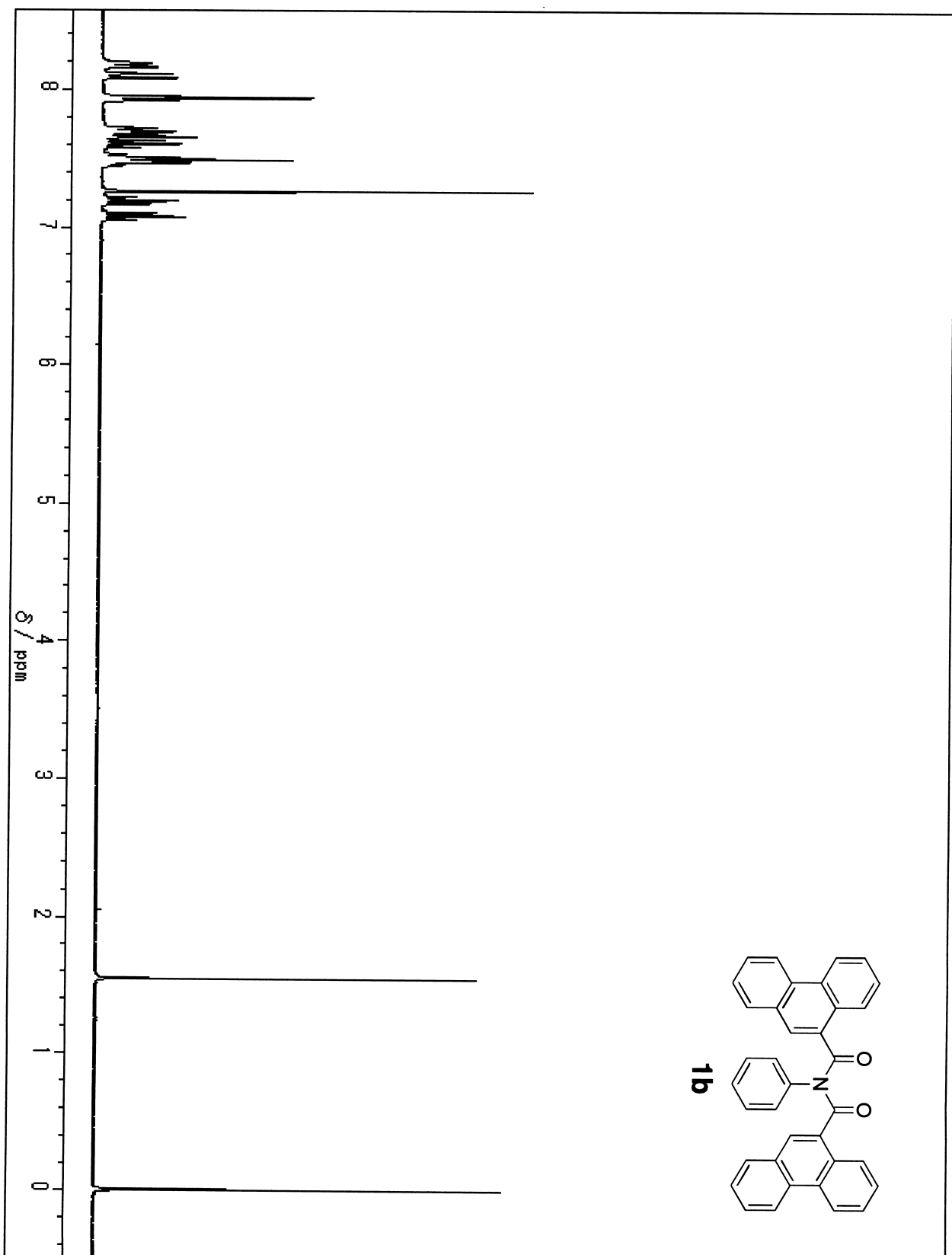
$^1\text{H NMR}$ (300 MHz, CDCl_3) of **3a**



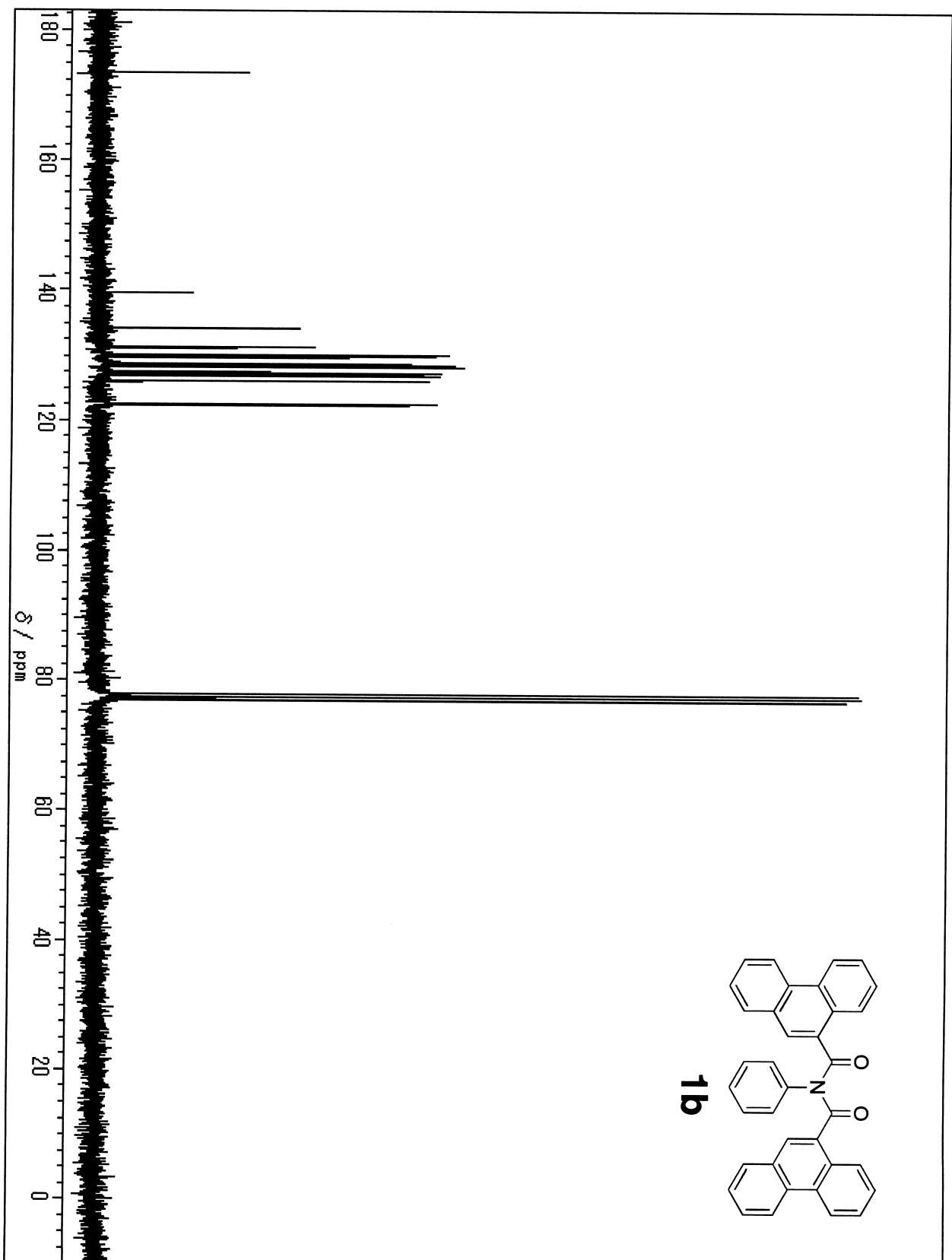
^{13}C NMR (125 MHz, CDCl_3) of **3a**



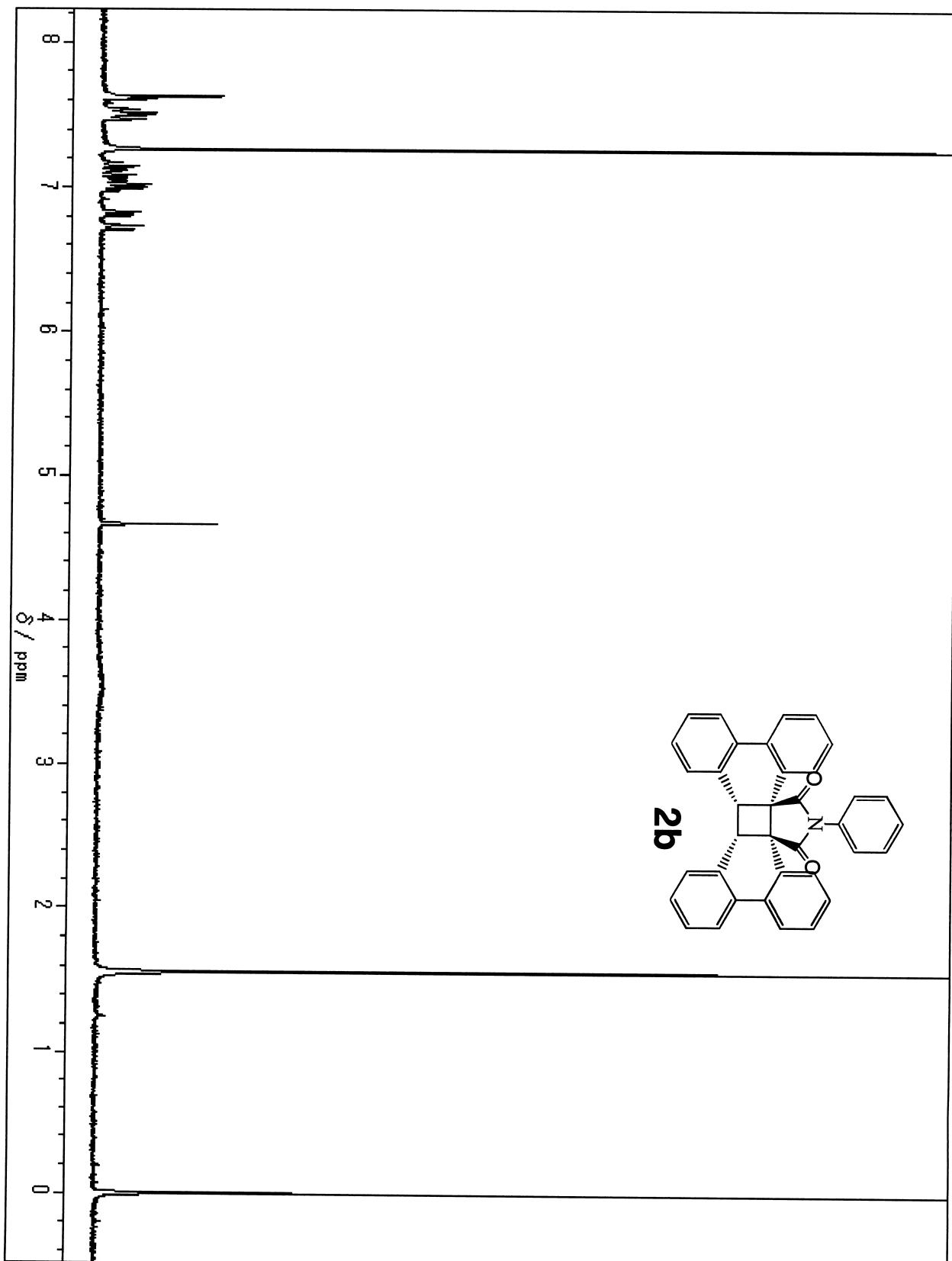
$^1\text{H NMR}$ (300MHz, CDCl_3) of **1b**



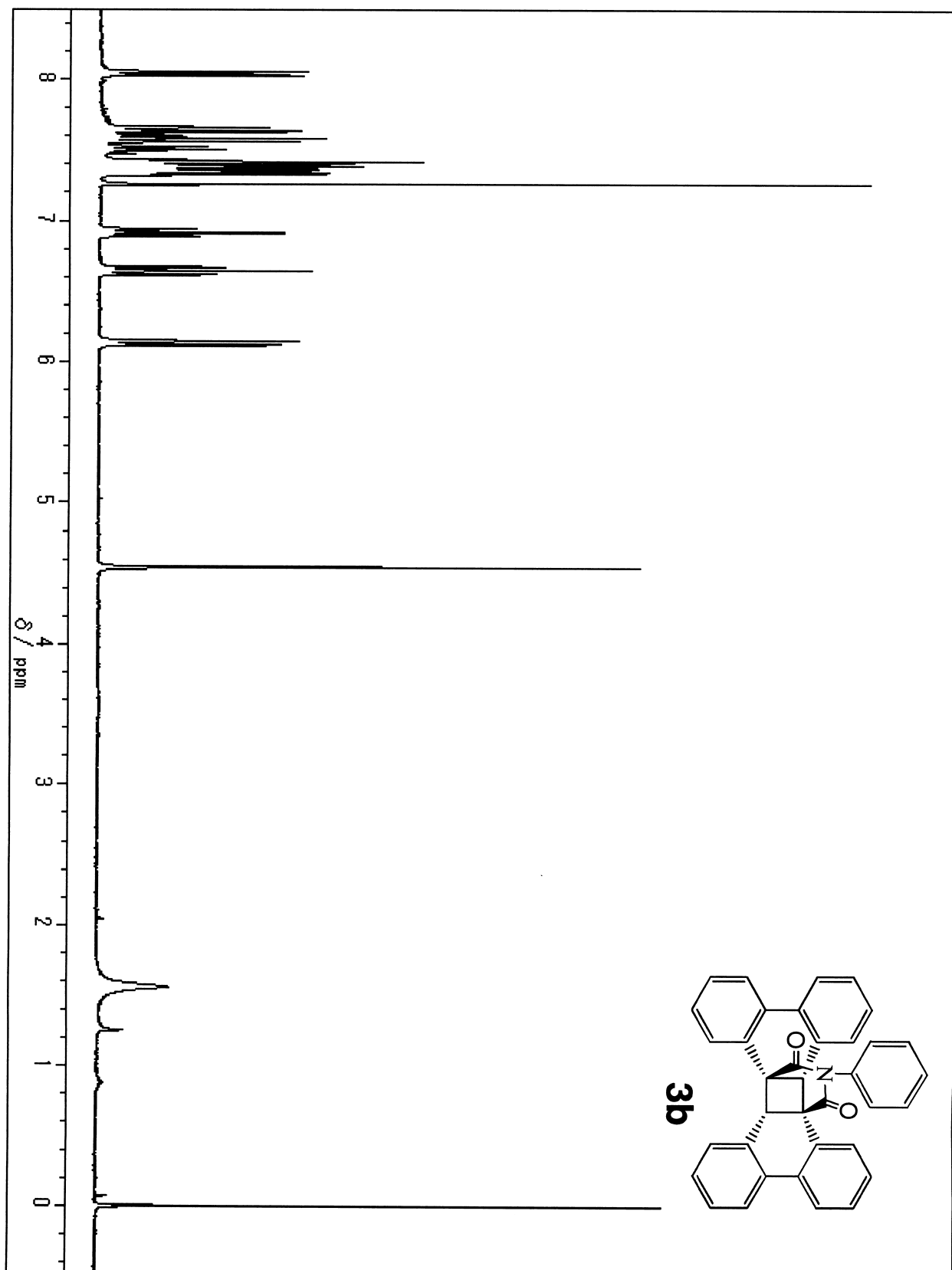
^{13}C NMR (75.5 MHz, CDCl_3) of **1b**



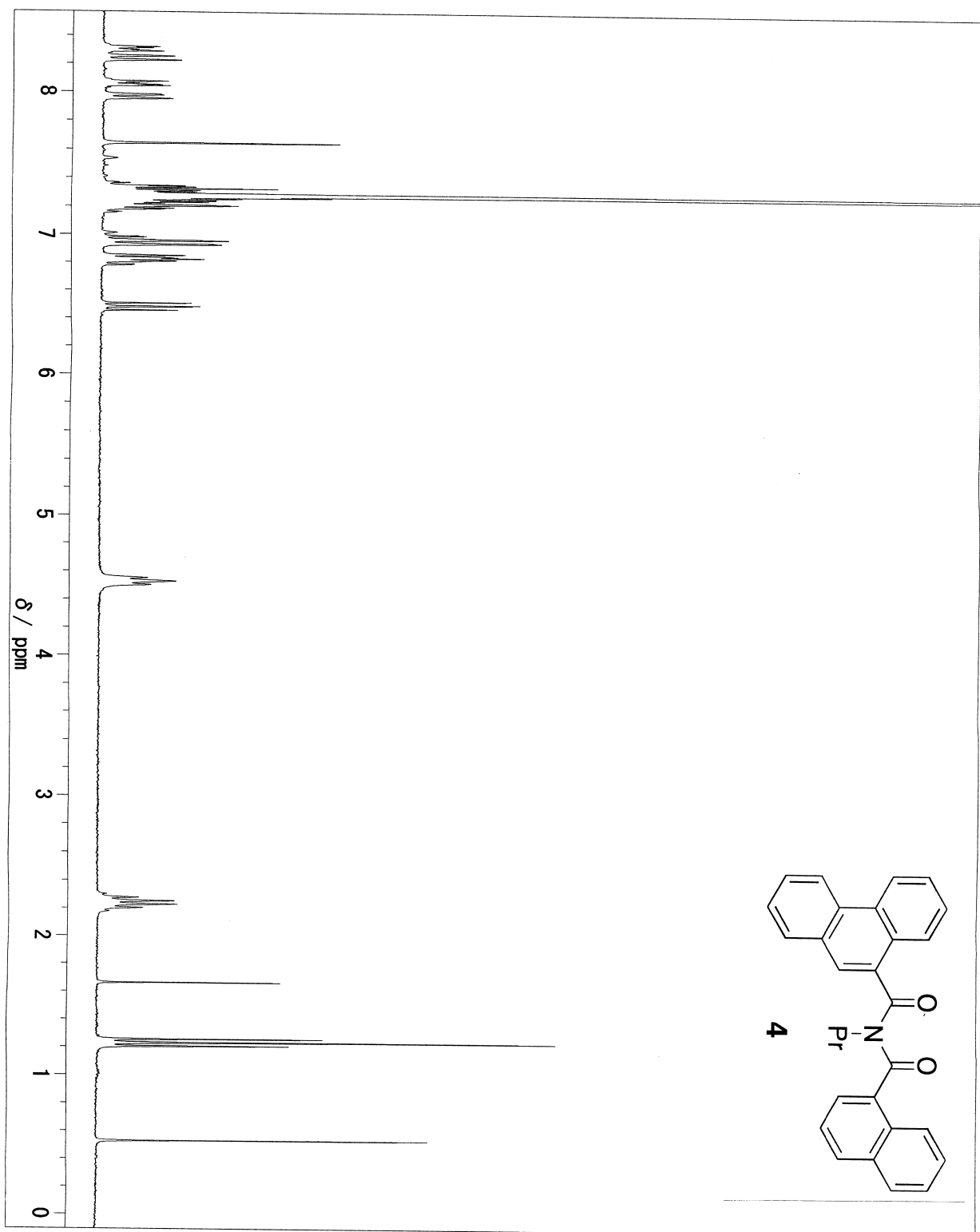
^1H NMR (300MHz, CDCl_3) of **2b**

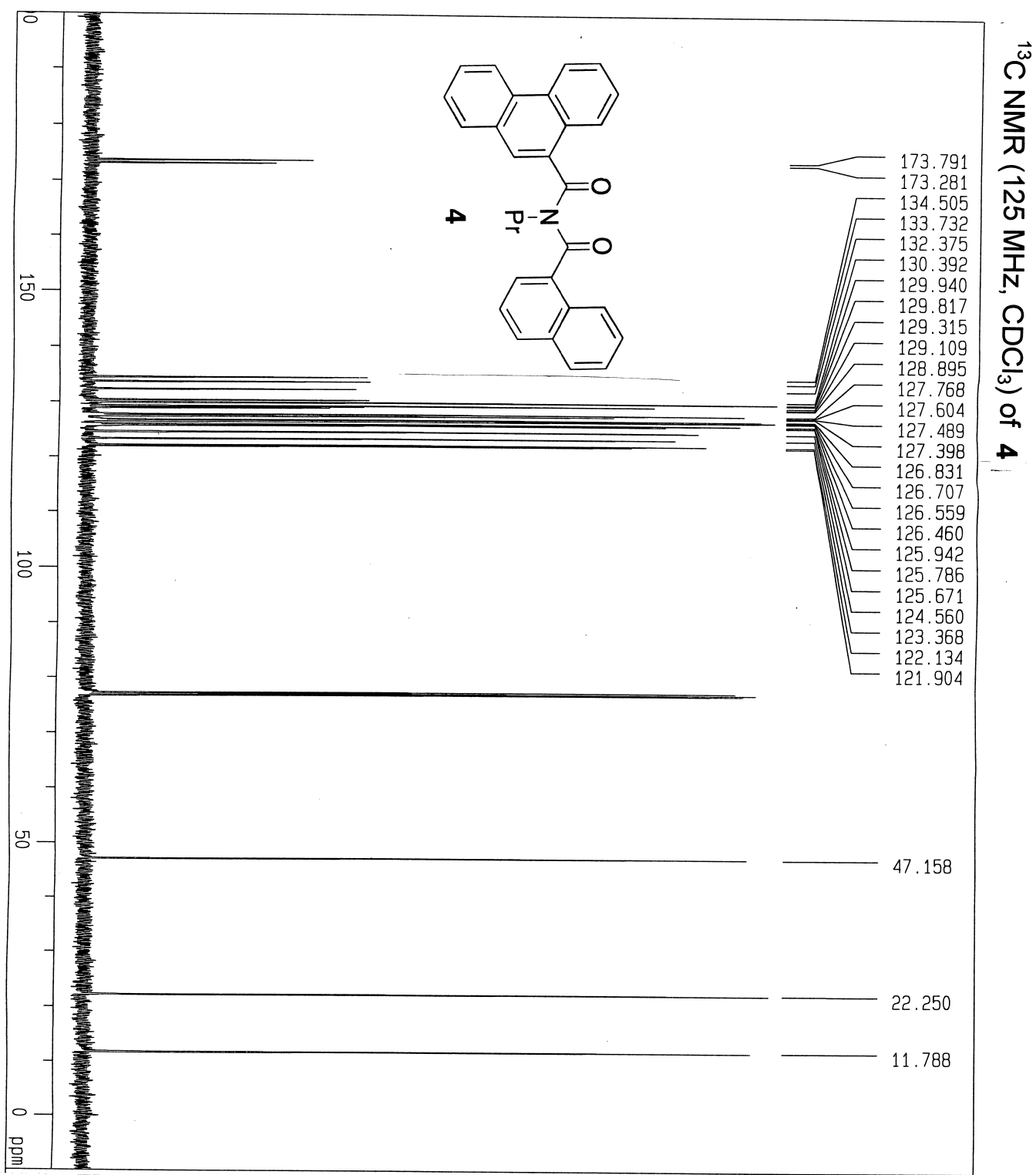


^1H NMR (300MHz, CDCl_3) of **3b**

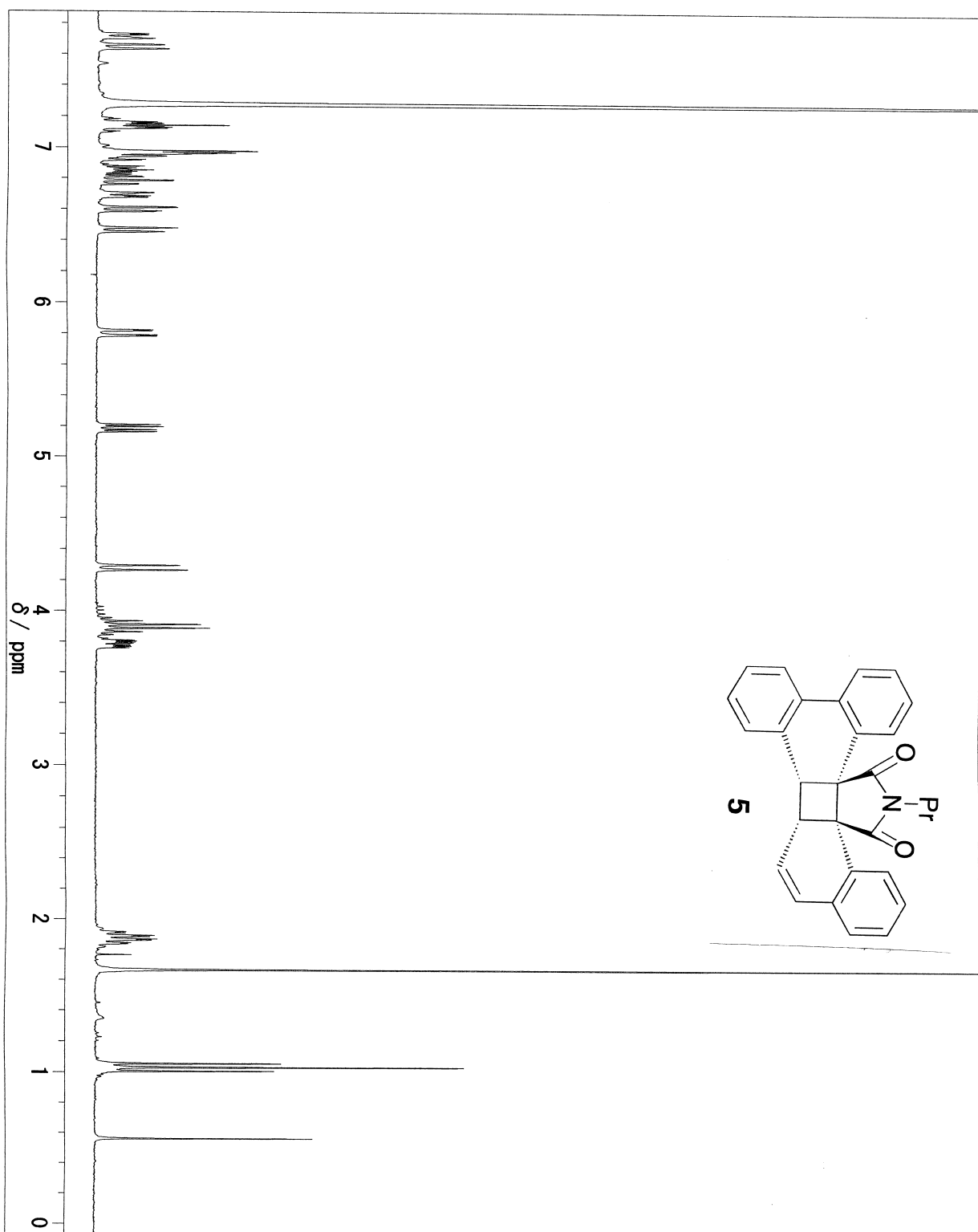


^1H NMR (300 MHz, C_6D_6) of **4**

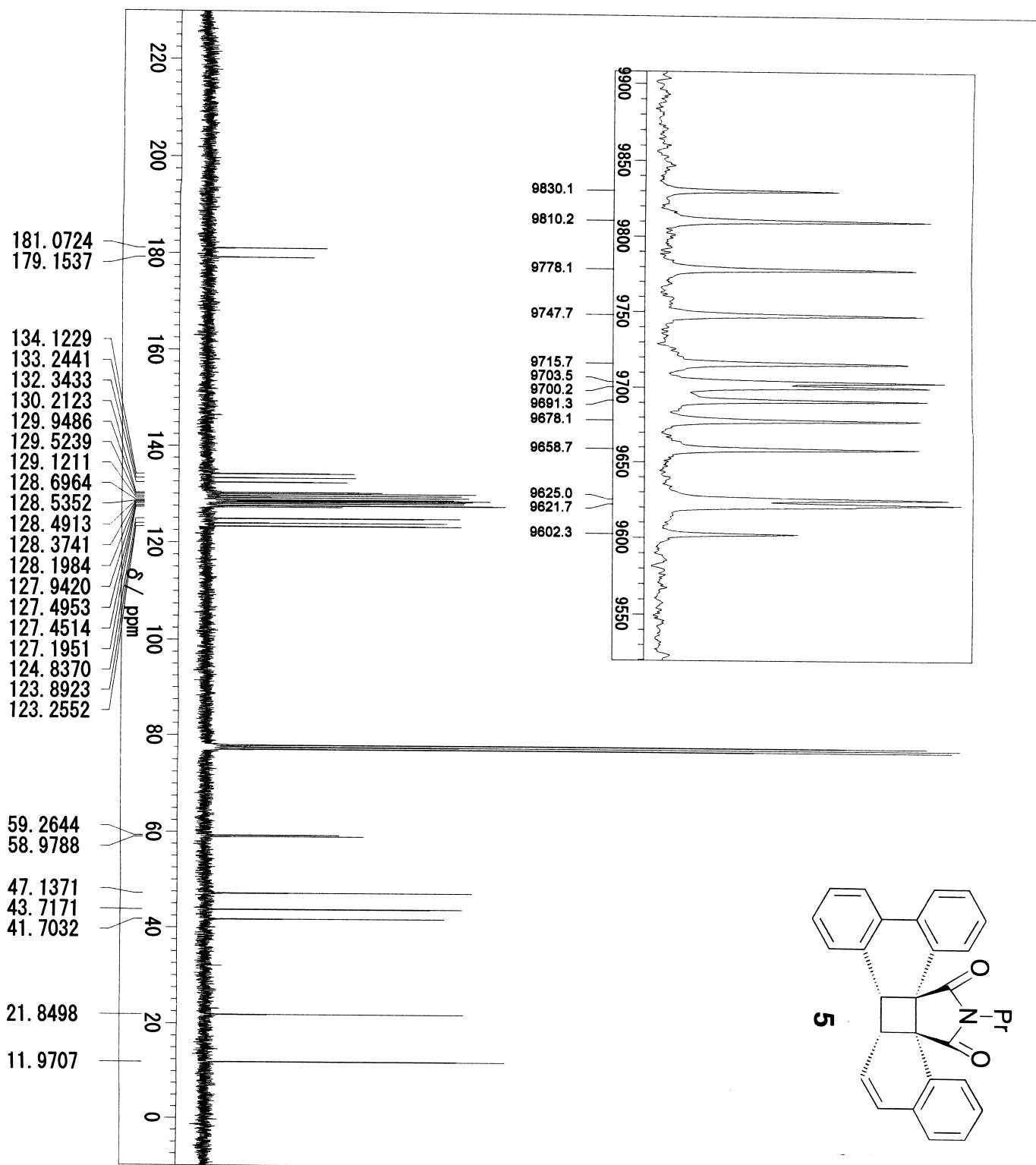




^1H NMR (300 MHz, C_6D_6) of **5**



¹³C NMR (75.5 MHz, CDCl₃) of **5**



Synthesis of *N*-(phenanthrene-9-carbonyl)-*N*-phenyl-phenanthrene-9-carboxamide (**1b**).

In a similar manner as for the synthesis of **1a**, **1b** was prepared from *N*-phenyl-9-phenanthrylcarboxamide and phenantroyl chloride in a yield of 26% as a colourless crystal after recrystallisation from ethyl acetate/hexane. Mp: 226.5–228°C; UV-vis (CH₃CN) 247 (99800), 314 (sh) nm (14600); IR (KBr) 3061 (w), 2923 (w), 1704 (m), 1666(s), 1449 (m), 1327 (m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.07 (m, 2H), 7.19 (m, 2H), 7.49 (m, 5H), 7.64 (m, 6H), 7.93 (m, 4H), 8.09 (d, *J* = 7.9 Hz, 2H), 8.17 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 122.3, 122.5, 126.0, 126.9, 127.1, 127.3, 127.5, 128.3, 128.5, 128.6, 128.7, 129.7, 129.8, 130.1, 130.1, 131.2, 134.0, 139.6, 173.6; HRMS (FAB) calcd for C₃₆H₂₃O₂NNa ([M+Na]⁺) 524.1621, found 524.1619.

Synthesis of *N*-(1-naphthoyl)-*N*-propylphenanthrene-9-carboxamide (**4**).

In a similar manner as for the preparation of **1**, imide **4** was prepared from *N*-propyl-9-phenanthrylcarboxamide and 1-naphthoyl chloride in 70 % yield. Mp: 146–148°C (colourless crystals from ethyl acetate/hexane); UV-vis (CH₃CN) 243 (50800), 297(sh) nm (13300); IR (KBr) 3052 (w), 2962 (w), 1693 (m), 1650 (s), 1329 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.22 (t, *J* = 7.6 Hz, 3H), 2.09 (sext, *J* = 7.6 Hz, 2H), 4.28 (t, *J* = 7.6 Hz, 2H), 6.67 (dd, *J* = 8.3, 7.0 Hz, 1H), 6.99 (t, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 7.06 (td, *J* = 8.3, 1.2 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.22 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.50 - 7.38 (m, 4H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.0, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H); ¹³C NMR (125 MHz) δ 11.8, 22.3, 47.2, 121.9, 122.1, 123.4, 124.6, 125.7, 125.8, 125.9, 126.5, 126.6, 126.7, 126.8, 127.4, 127.5, 127.6, 127.8, 128.9, 129.1, 129.3, 129.8, 129.9, 130.4, 132.4, 133.7, 134.5, 173.3, 173.8; HRMS (FAB), calcd for C₂₉H₂₃NO₂ (M⁺) 417.1729, found 417.1723.

Photocycloaddition of **1b**.

Acetone solution (10 mL) of **1b** (60 mg, 0.12 mmol) was irradiated with a 450 W high-pressure Hg lamp under argon atmosphere through Pyrex filter for 1 h at 50°C. Due to the difficulty with separation by column chromatography, cycloadducts were purified by preparative HPLC (column: Merk Si60) eluted with hexane/ethyl acetate (8/1). Cycloadduct **2b**: Mp: 256–259°C (white powder); UV-vis (CH₃CN) 266.5 nm (19000); IR (KBr) 3061 (w), 2920 (w), 1773 (m), 1713(s), 1490(m), 1365 (m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.66 (s, 2H), 6.72 (dd, *J* = 7.5, 1.5 Hz, 2H), 6.81 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.17 - 6.97 (m, 9H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.62(d, *J* = 3.3 Hz, 2H), 7.63(s, 2H); HRMS (FAB) calcd for C₃₆H₂₃O₂NNa ([M+Na]⁺) 524.1621, found 524.1620. Cycloadduct **3b**: Mp: 220–225°C (white powder); UV-vis (CH₃CN) 265.5 nm (1.4900); IR (KBr) 3064 (w), 2922 (w), 1748 (m), 1703(s), 1488(m), 1366 (m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.13 (d, *J* = 7.9 Hz, 2H), 6.64 (td, *J* = 7.9, 1.1 Hz, 2H), 6.91 (td, *J* = 3.2, 1.5 Hz, 2H), 7.61 - 7.32 (m, 11H), 7.61(dd, *J* = 7.5 Hz, 1.5 Hz, 2H), 8.04 (dd, *J* = 7.9, 1.5 Hz, 2H); HRMS (FAB) calcd for C₃₆H₂₃O₂NNa ([M+Na]⁺) 524.1621, found 524.1619.

Photocycloaddition of **4**.

Acetone solution (25 mL) of **4** (118 mg, mmol) was irradiated with a 450 W high pressure Hg lamp through Pyrex filter for 1.5 h at 50 °C. After evaporation of solvent, the residue was chromatographed on silica gel eluted with hexane/ethyl acetate (5/1) to give **5** (87 mg, 74%) as a colourless crystal together with the recovery of **4** (24 mg, 20%). Cycloadduct **5**: Mp: 98–100°C (colourless crystals from ethyl acetate/hexane); UV-vis (CH₃CN) 265 nm (16600); IR (KBr) 3043 (w), 2955 (w), 1770 (w), 1699 (s), 1394 (m) cm⁻¹; ¹H NMR (396 MHz, CDCl₃) δ 1.10 (t, *J* = 7.4 Hz, 3H), 1.88 (sext, *J* = 7.4 Hz, 2H), 3.78 (dt, *J* = 14.7, 7.4 Hz, 1H), 3.83 (dt, *J* = 14.7, 7.4 Hz, 1H), 3.92 (ddd, *J* = 8.9, 3.8, 1.9 Hz, 1H), 4.37 (d, *J* = 8.9 Hz, 1H), 5.26 (dd, *J* = 10.0, 3.8 Hz, 1H), 5.93 (dd, *J* = 10.0, 1.9 Hz, 1H), 6.29 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.67 (dd, *J* = 7.2, 1.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.81 (td, *J* = 7.6, 1.2 Hz, 1H), 7.15 - 7.01 (m, 4H), 7.31 - 7.23 (m, 2H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 12.0, 21.8, 41.7, 43.7, 47.1, 59.0, 59.3, 123.3, 123.9, 124.8, 127.2, 127.5, 127.5, 127.9, 128.2, 128.4, 128.5, 128.5, 128.7, 129.1, 129.5, 130.2, 132.3, 133.2, 134.1, 179.2, 181.1; HRMS (FAB), calcd for C₂₉H₂₃NO₂ (M⁺) 417.1729, found 417.1723.