Supporting Information for:

Dimerization of Heteroaromatic *N*-Oxides under Metal-free Conditions

Hui Wang, Yu Pei, Jie Bai, Jinli Zhang, Yangjie Wu*, Xiuling Cui*

Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou, 450052, P.R. China

E-mail: cuixl@zzu.edu.cn; wyj@zzu.edu.cn

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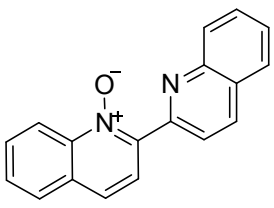
I. General experimental information

All reactions were carried out under an air atmosphere in a flame-dried tube (≈ 5mL volume) equipped with a dehumidifier and a magnetic stirring element. The solvents were purified and dried according to standard methods prior to use. Other reagents were obtained from the commercial suppliers and used without further purification. The ^{t}BuOLi (99% purity) and silica gel were purchased from Energy Chemical and Qing Dao Hai Yang Chemical Industry Co., respectively. All of the heteroaromatic *N*-oxides were prepared according to literature procedures.[1] The NMR spectra were recorded on a Bruker DPX-400 spectrometer. Chemical shifts were reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR (400 MHz), chloroform-*d* (δ 77.00) for ^{13}C NMR (100 MHz). High resolution mass spectra (HRMS) were recorded on a Agilent 6450 spectrometer. Melting points were recorded on a XT4A melting point apparatus and were uncorrected.

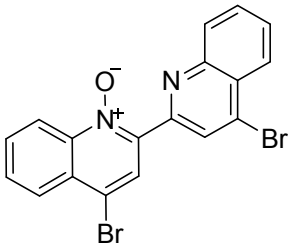
II. General synthesis procedure

A flame-dried tube equipped with a magnetic stir bar was charged with ^{t}BuOLi (60 mg, 0.75 mmol), heteroaromatic *N*-oxide (0.5 mmol) and toluene (2.5 ml). Stirring was continued for 3 h at 120 ^{o}C. The mixture was purified by column chromatography on silica gel (**2a**, **2e-2f**, **2h-2o**) or recrystallization from chloroform (**2b-2d, 2g**) afforded the desired products.

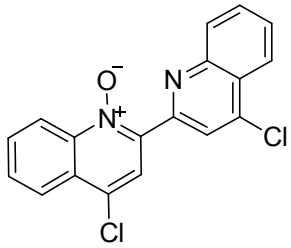
III. Experimental data for the described substances



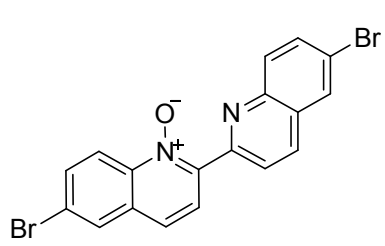
[2,2'-biquinoline] 1-oxide (**2a**)[2] Slight yellow solid (63mg, 93%): mp 170-171 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.59 (t, *J* = 7.4 Hz, 1 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.72-7.83 (m, 3 H), 7.87 (d, *J* = 8.1 Hz, 2 H), 8.18 (d, *J* = 8.5 Hz, 1 H), 8.26-8.31 (t, *J* = 8.0 Hz, 2 H), 8.88 (d, *J* = 8.5 Hz, 1 H), 8.94 (d, *J* = 8.6 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 120.2, 122.9, 123.7, 125.4, 127.4, 127.6, 128.1, 128.2, 129.0, 129.6, 129.8, 130.3, 130.5, 135.7, 142.3, 143.8, 148.1, 151.6 ppm. **HRMS** (EI^+): calculated for $C_{18}H_{12}N_2O$ [M+H$^+$]: 273.1022, found: 273.1026.



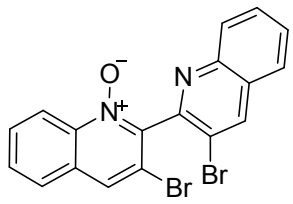
4,4'-dibromo-[2,2'-biquinoline] 1-oxide (**2b**) Slight yellow solid (91mg, 84%): mp 242-243 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71 (t, J = 7.3 Hz, 1 H), 7.77-7.89 (m, 3H), 8.19-8.28 (m, 3 H), 8.71 (s, 1 H), 8.92 (d, J = 8.6 Hz, 1 H), 9.5 (s, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 108.1, 119.5, 120.9, 126.6, 126.9, 127.9, 128.1, 128.9, 129.4, 130.2, 130.5, 130.6, 131.3, 134.0, 142.7, 143.4, 148.4, 150.0 ppm. **HRMS** (EI^+): calculated for $C_{18}H_{10}Br_2N_2O$ [M+H$^+$]: 428.9233, found: 428.9235.



4,4'-dichloro-[2,2'-biquinoline] 1-oxide (**2c**) Slight yellow solid (74mg, 87%): mp 225-226 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.70 (t, J = 7.9 Hz, 1 H), 7.76-7.89 (m, 3 H), 8.21-8.30 (m, 3 H), 8.53 (s, 1 H), 8.92 (d, J = 8.6 Hz, 1 H), 9.28 (s, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ =121.0, 122.9, 123.3, 124.2, 125.3, 126.7, 128.1, 128.6, 129.5, 130.0, 130.4, 130.6, 131.3, 142.7, 143.4, 148.7, 150.1 ppm. **HRMS** (EI^+): calculated for $C_{18}H_{10}Br_2N_2O$ [M+H$^+$]: 341.0243, found: 341.0244.

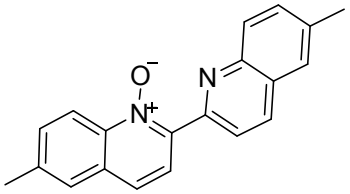


6,6'-dibromo-[2,2'-biquinoline] 1-oxide (**2d**) Yellow solid (93mg, 86%): mp 244-246 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.8, 1 H), 7.79-7.86 (m, 2 H), 8.02-8.05 (m, 3 H), 8.19 (d, J = 8.4 Hz, 1 H), 8.35 (d, J = 8.9 Hz, 1H), 8.74 (d, J = 9.0 Hz, 1H), 9.01 (d, J = 8.6 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 120.4, 121.8, 122.4, 123.6, 123.7, 125.0, 129.3, 129.7, 130.2, 131.7, 133.3, 133.8, 134.8, 141.5, 143.7, 146.8, 151.6 ppm. **HRMS** (EI^+): calculated for $C_{18}H_{10}Br_2N_2O$ [M+H$^+$]: 428.9233, found: 428.9231.

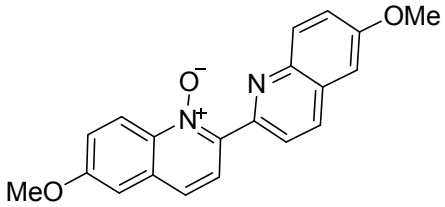


3,3'-dibromo-[2,2'-biquinoline] 1-oxide (**2e**) Pale slight yellow solid (81mg, 75%): mp 91-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.64-7.74 (m, 2 H), 7.76-7.82 (m, 2 H), 7.86 (d, J = 8.1 Hz, 2 H), 8.12-8.17 (t, J = 8.7 Hz, 2 H), 8.57 (s, 1 H), 8.71 (d, J = 8.7 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 115.6, 117.1, 120.2, 126.8, 127.2, 128.0, 128.4, 129.1,

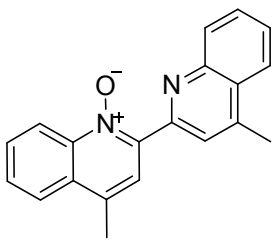
129.8, 129.9, 130.1, 130.5, 139.2, 140.9, 143.9, 146.7, 152.0 ppm. **HRMS** (EI^+): calculated for $C_{18}H_{10}Br_2N_2O$ [$M+H^+$]: 428.9233, found: 428.9235.



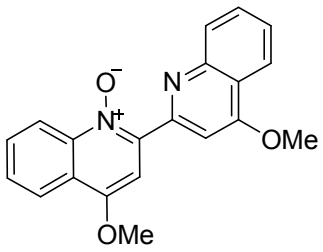
6,6'-dimethyl-[2,2'-biquinoline] 1-oxide (**2f**)[3] Slight yellow solid (49 mg, 65%): mp 172-173 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.57 (s, 6 H), 7.56-7.65 (m, 4 H), 7.74 (d, J = 8.8 Hz, 1 H), 8.06 (d, J =8.6 Hz, 1 H), 8.19 (d, J = 8.7 Hz, 1 H), 8.24 (d, J = 8.9 Hz, 1 H), 8.76 (d, J = 8.6 Hz, 1 H), 8.91 (d, J = 8.6 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.5, 21.8, 120.0, 123.0, 123.7, 125.0, 126.4, 127.1, 128.2, 129.5, 130.4, 131.9, 132.6, 134.9, 137.4, 139.2, 140.8, 143.3, 146.8, 150.8 ppm. **HRMS** (EI^+): calculated for $C_{20}H_{16}N_2O$ [$M+H^+$]: 301.1335, found: 301.1341.



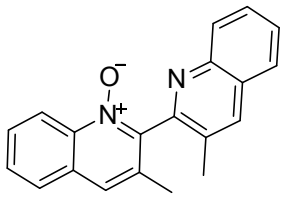
6,6'-dimethoxy-[2,2'-biquinoline] 1-oxide (**2g**) Slight yellow solid (36 mg, 53%): m.p. 223-224 °C. **^{1}H NMR**(400 MHz, $CDCl_3$): δ = 3.96 (s, 6 H), 7.13 (t, J = 2.8 Hz, 2 H), 7.37-7.42 (m, 2 H), 7.71 (d, J = 8.9Hz, 1 H), 8.06 (d, J = 9.2 Hz, 1 H), 8.17 (d, J = 8.7 Hz, 1 H), 8.27 (d, J = 8.8 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 55.6, 55.7, 104.8, 106.0, 121.9, 122.4, 122.5, 123.2, 124.2, 124.4, 129.2, 131.2, 131.6, 134.3, 137.8, 142.2, 144.2, 149.0, 158.4, 159.6 ppm. **HRMS** (EI^+): calculated for $C_{20}H_{16}N_2O_3$ [$M+H^+$]: 333.1234, found: 333.1236.



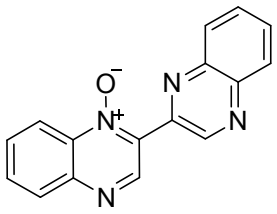
4,4'-dimethyl-[2,2'-biquinoline] 1-oxide (**2h**) Slight yellow solid (37 mg, 49%): mp 201-202 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.74 (s, 3 H), 2.81 (s, 3 H), 7.62 (td, J = 1.0, 6.9 Hz, 1 H), 7.69-7.77 (m, 2 H), 7.82 (td, J = 1.3, 6.9 Hz, 2 H), 8.00-8.08 (m, 3 H), 8.19 (d, J = 8.7 Hz, 1 H), 8.77 (s, 1 H), 8.95 (d, J = 8.8 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.5, 19.0, 120.7, 123.5, 123.8, 123.9, 124.8, 127.2, 128.3, 128.7, 129.3, 129.9, 130.2, 130.4, 133.9, 141.8, 143.3, 144.0, 147.9, 151.4 ppm. **HRMS** (EI^+): calculated for $C_{20}H_{16}N_2O$ [$M+H^+$]: 301.1335, found: 301.1341.



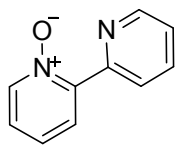
4,4'-dimethoxy-[2,2'-biquinoline] 1-oxide (**2i**) Slight yellow solid (23 mg, 28%): m.p. 202-203 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.19 (s, 6 H), 7.57 (t, J = 8.0 Hz, 1 H), 7.67-7.78 (m, 3 H), 7.83-7.88 (m, 1 H), 8.13 (d, J = 8.3 Hz, 1 H), 8.27 (t, J = 6.8 Hz, 2 H), 8.72 (s, 1 H), 8.91 (d, J = 8.7 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 55.1, 55.3, 100.9, 101.6, 119.3, 120.4, 120.9, 121.5, 121.9, 125.4, 127.2, 128.2, 128.8, 130.0, 141.2, 143.4, 147.6, 151.7, 125.5, 161.1 ppm. **HRMS** (EI^+): calculated for $C_{20}H_{16}N_2O_3$ [M+H$^+$]: 333.1234, found: 333.1236.



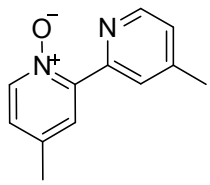
3,3'-dimethyl-[2,2'-biquinoline] 1-oxide (**2j**)[4] Slight yellow solid (26 mg, 34%): mp 232-234 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.19 (s, 3 H), 2.36 (s, 3 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.62-7.73 (m, 4 H), 7.84 (d, J = 6.6 Hz, 2 H), 8.10 (d, J = 6.7 Hz, 2 H), 8.73 (d, J = 8.6 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 17.6, 19.1, 119.9, 125.7, 127.0, 127.1, 127.3, 128.3, 128.6, 128.7, 129.3, 129.4, 129.7, 130.6, 131.2, 136.3, 140.2, 145.4, 146.8, 153.6 ppm. **HRMS** [ESI^+] calculated for $C_{20}H_{16}N_2O$ [M+H$^+$]: 301.1335, found: 301.1343.



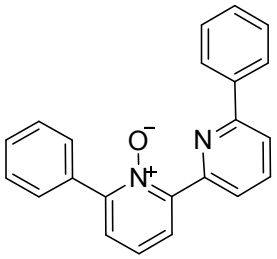
[2,2'-biquinoxaline] 1-oxide (**2k**)[5] Slight yellow solid (49 mg, 72%): mp 246-247 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.82-7.93 (m, 4 H), 8.21-8.26 (m, 3 H), 8.74 (dd, J =1.1, 8.6 Hz, 1 H), 9.68 (s, 1 H), 10.28 (s, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 119.3, 129.4, 129.9, 130.3, 130.6, 130.7, 131.3, 132.2, 135.9, 137.2, 142.29, 142.34, 144.6, 145.3, 146.1, 148.2 ppm. **HRMS** [ESI^+] calculated for $C_{16}H_{10}N_4O$ [M+H$^+$]: 275.0927, found: 275.0929.



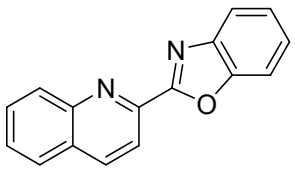
[2,2'-bipyridine] 1-oxide (**2l**)[6] White solid (31 mg, 72%): mp 58-59 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 (td, J = 3.2, 7.5 Hz, 1 H), 7.30-7.39 (m, 2 H), 7.82 (td, J =1.8, 7.9 Hz, 1 H), 8.16 (dd, J = 2.0, 6.0 Hz, 1 H), 8.31 (d, J = 6.3 Hz, 1 H), 8.72 (d, J = 4.1 Hz, 1 H), 8.88 (d, J = 8.0 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 124.2, 125.2, 125.3, 125.7, 127.7, 136.1, 140.5, 147.2, 149.3, 149.5 ppm. **HRMS** [ESI^+] calculated for $C_{10}H_8N_2O$ [M+H$^+$]: 173.0709, found: 173.0708.



4,4'-dimethyl-[2,2'-bipyridine] 1-oxide (**2m**)[7] Slight yellow solid (31 mg, 64%): mp 78-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.34 (s, 3 H), 2.28 (s, 3 H), 7.02 (dd, *J* = 2.5, 6.6 Hz, 1 H), 7.11 (d, *J* =4.2 Hz, 1 H), 7.87 (d, *J* =2.1 Hz, 1 H), 8.15 (d, *J* =6.6 Hz, 1 H), 8.51 (d, *J* = 5.0 Hz, 1 H), 8.65 (s, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 20.2, 21.2, 125.1, 125.9, 126.3, 128.1, 137.3, 139.8, 146.4, 147.4, 148.9, 149.4 ppm. **HRMS** [ESI$^+$] calculated for $C_{12}H_{12}N_2O$ [M+H$^+$]: 201.1022, found: 201.1025.



6,6'-diphenyl-[2,2'-bipyridine] 1-oxide (**2n**) Slight yellow solid (28 mg, 35%): mp 133-135 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53-7.42 (m, 8 H), 7.82-7.78 (m, 3 H), 7.87 (t, *J* =7.8 Hz, 1 H), 8.10 (d, *J* =7.2 Hz, 2 H), 8.31 (dd, *J* =3.4, 6.9 Hz, 1 H), 8.84 (d, *J* = 7.8 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 120.7, 124.1, 125.2, 126.8, 127.1, 128.2, 128.7, 129.0, 129.3, 129.4, 133.3, 136.8, 139.0, 148.1, 149.8, 150.1, 156.7 ppm. **HRMS** [ESI$^+$] calculated for $C_{22}H_{16}N_2O$ [M+H$^+$]: 325.1335, found: 325.1338.



2-(quinolin-2-yl)benzo[d]oxazole (**2o**)[8] Slight yellow solid (51 mg, 41%): mp 172-173 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35-7.43 (m, 2 H), 7.57 (t, *J* = 7.7 Hz, 1 H), 7.69 (d, *J* = 7.2 Hz, 1 H), 7.76 (t, *J* = 7.2 Hz, 1 H), 7.83 (t, *J* = 8.9 Hz, 2 H), 8.27 (d, *J* = 8.6 Hz, 1 H), 8.32 (d, *J* = 8.5 Hz, 1 H), 8.41 (d, *J* = 8.5 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 111.4, 120.1, 120.7, 124.9, 126.2, 127.6, 128.0, 128.6, 130.2, 130.3, 137.1, 141.7, 145.8, 147.9, 151.2 ppm. **HRMS** [ESI$^+$] calculated for $C_{16}H_{10}N_2O$ [M+H$^+$]: 247.0866, found: 247.0869.

IV. References

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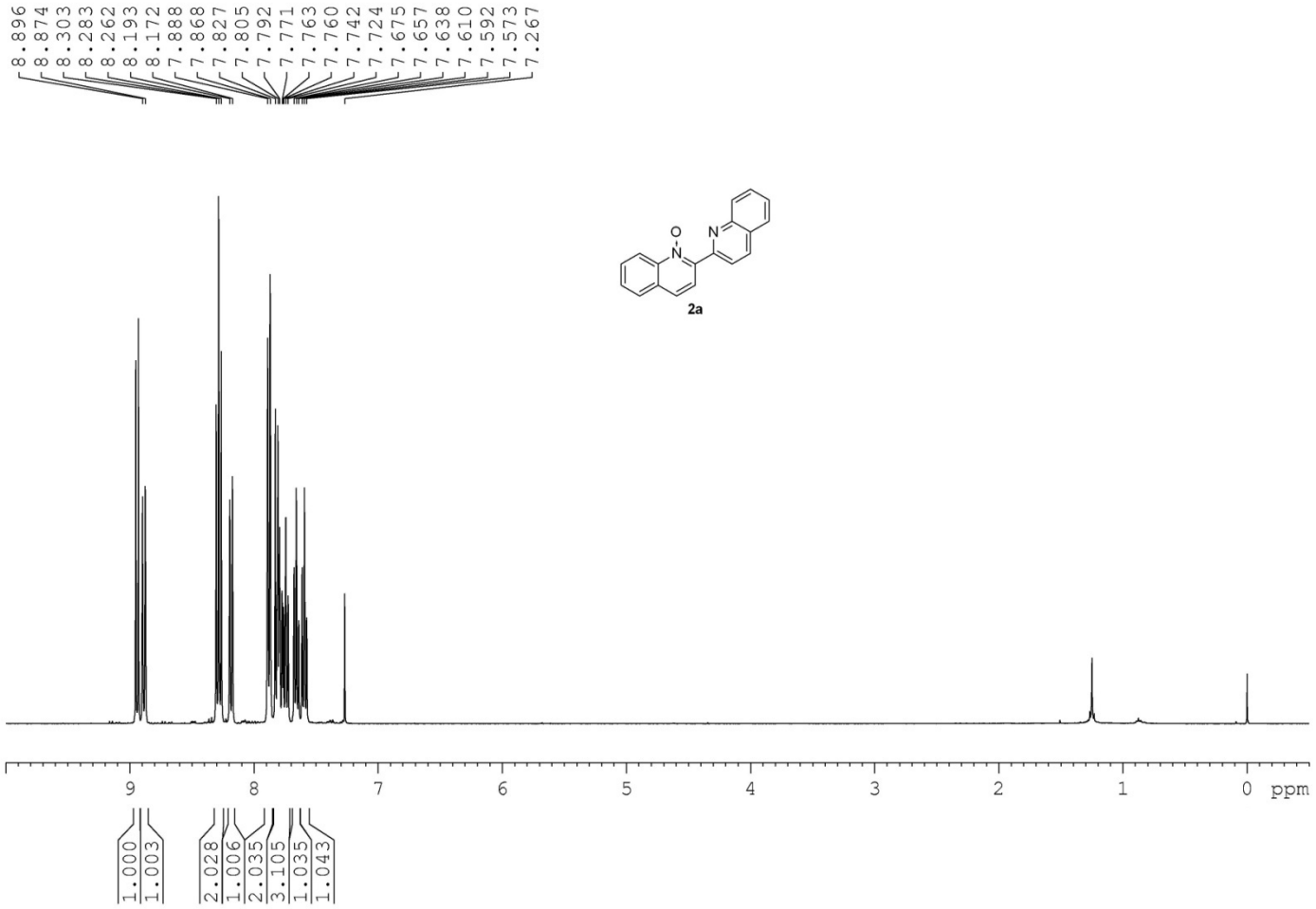
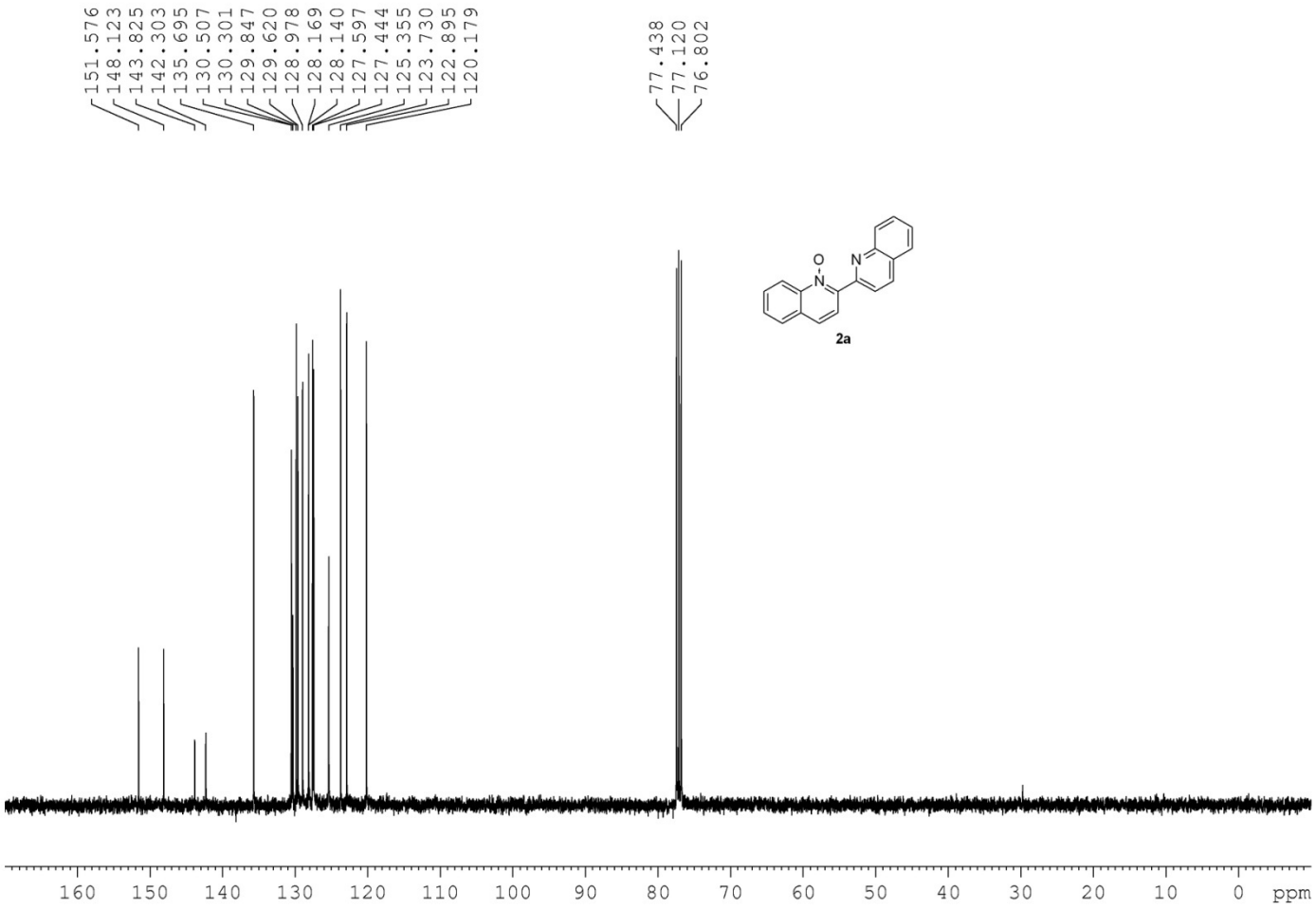
(8) K. Inamoto, Y. Araki, S. Kikkawa, M. Yonemoto, Y. Tanaka, Y. kondo, *Org. Biomol. Chem.* **2013**, *11*, 4438.

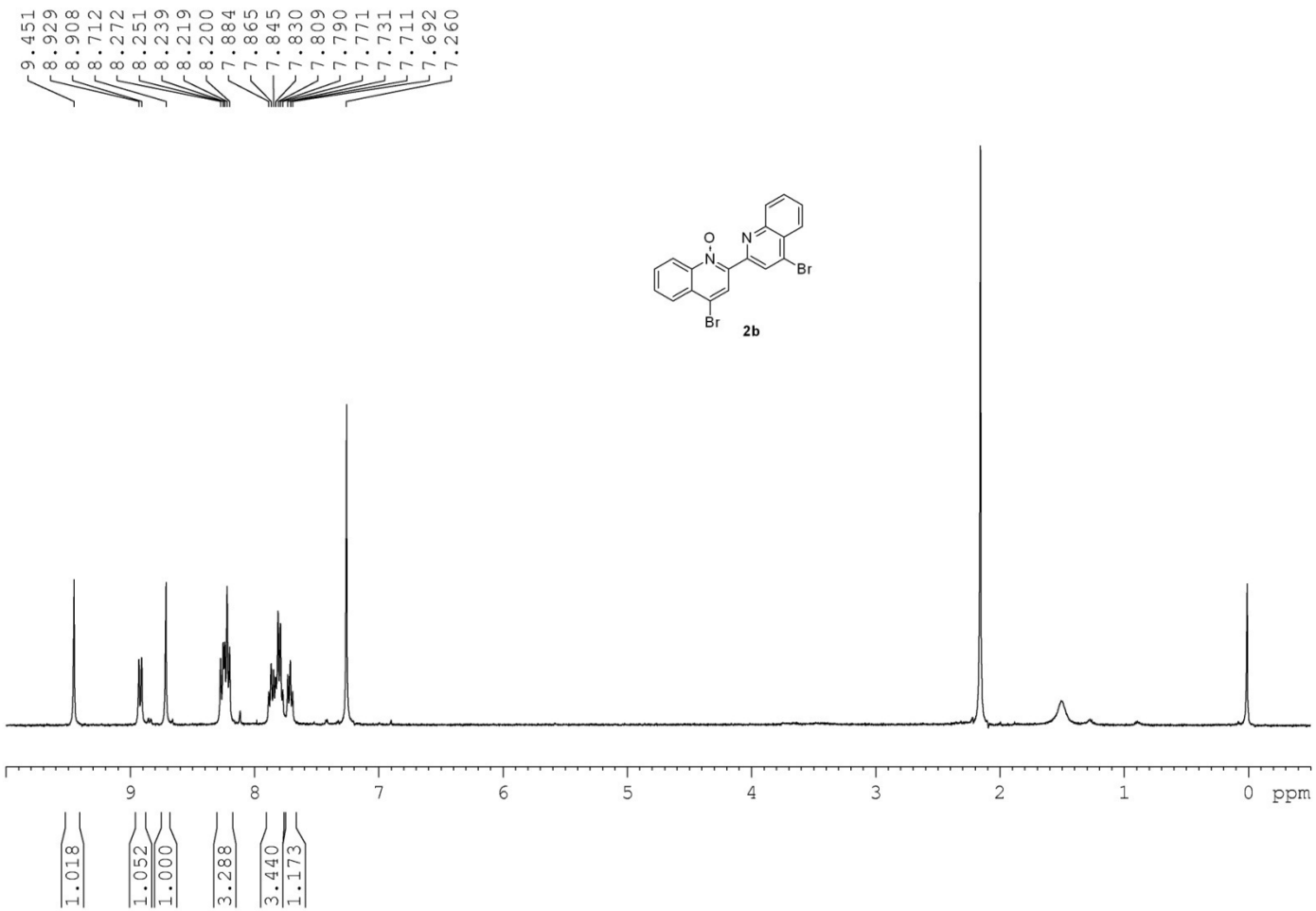
V. Copies of ^{1}H and ^{13}C NMR spectra



^{1}H NMR spectrum of compound **2a**



^{13}C NMR spectrum of compound **2a**



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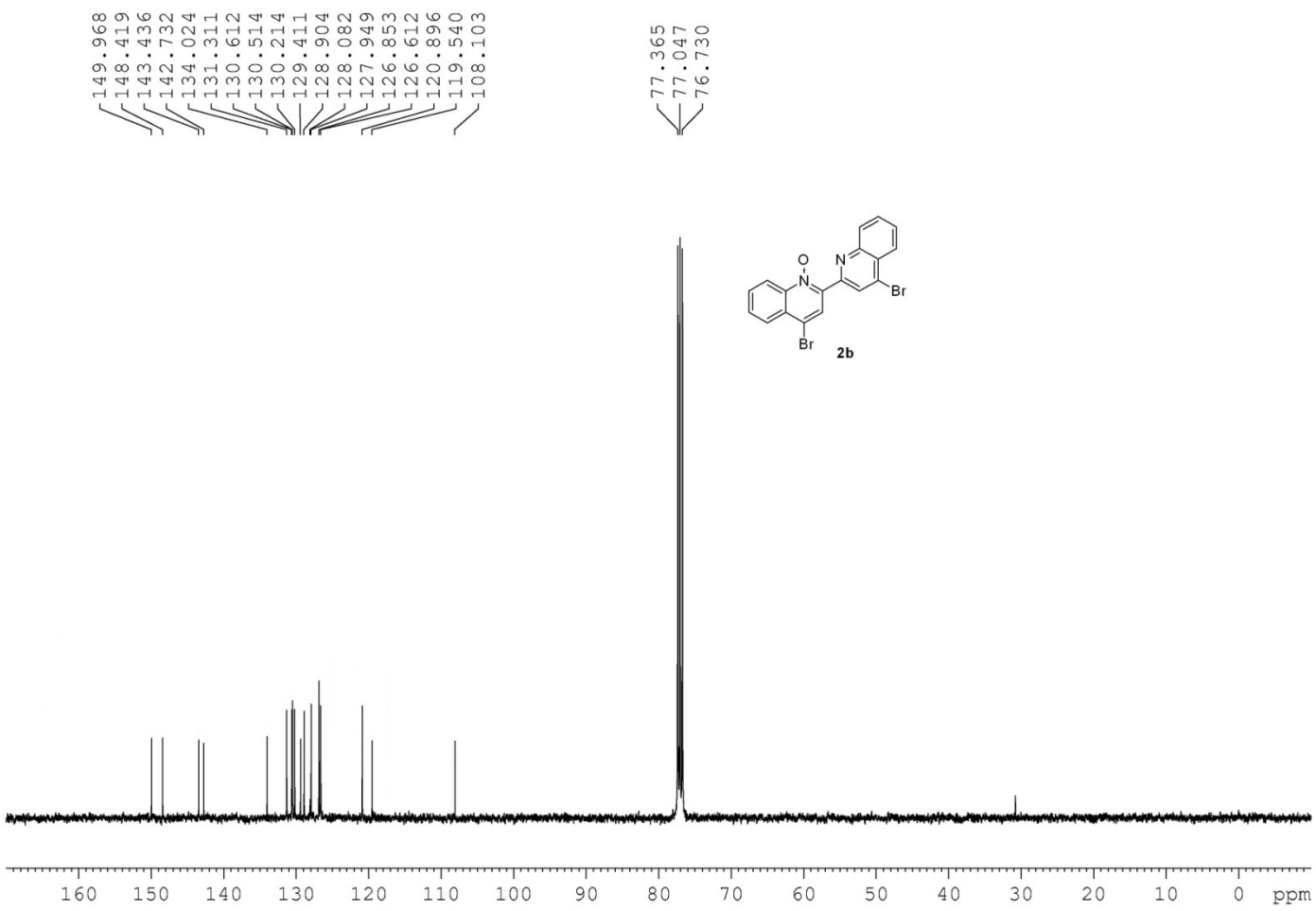
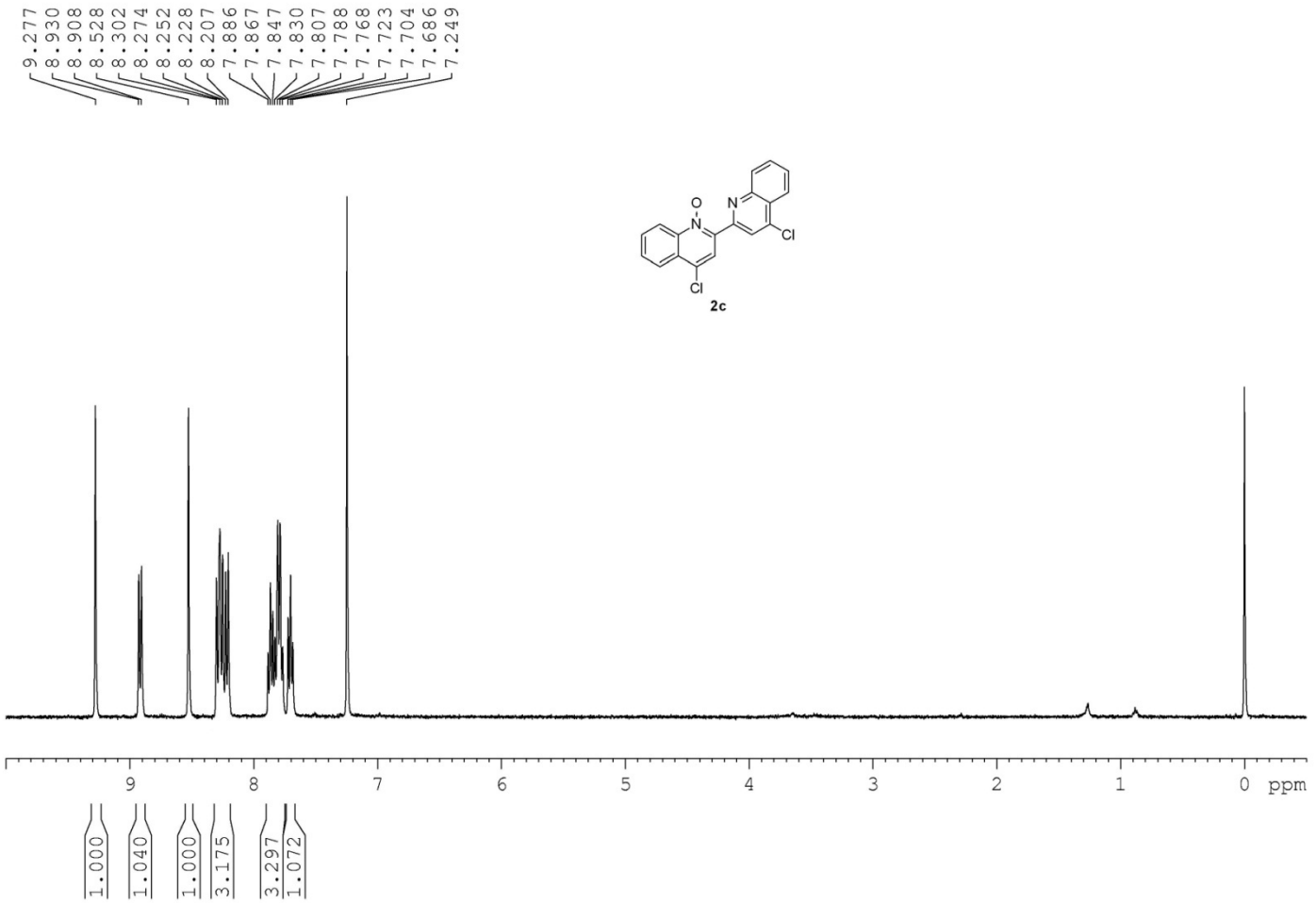
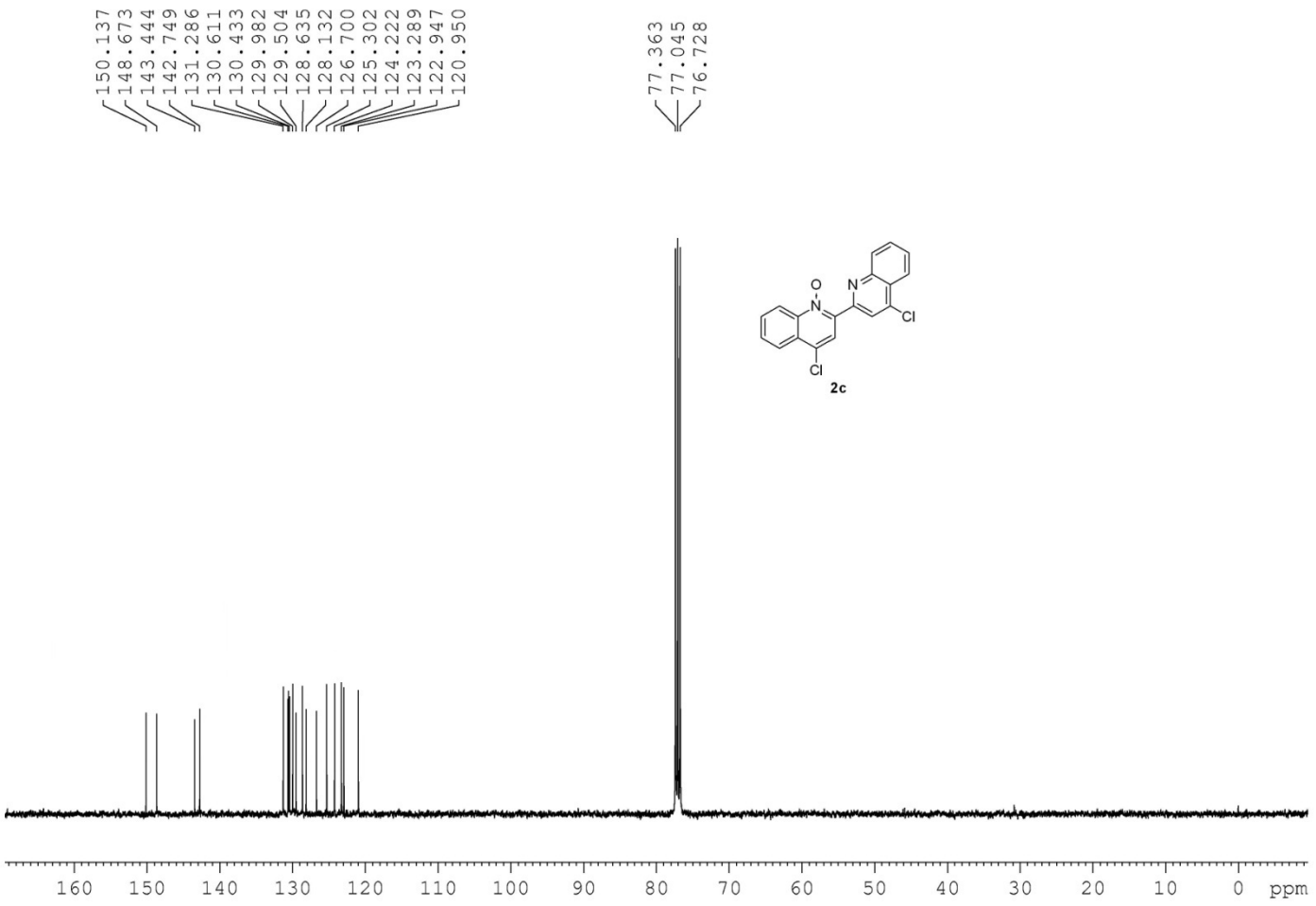


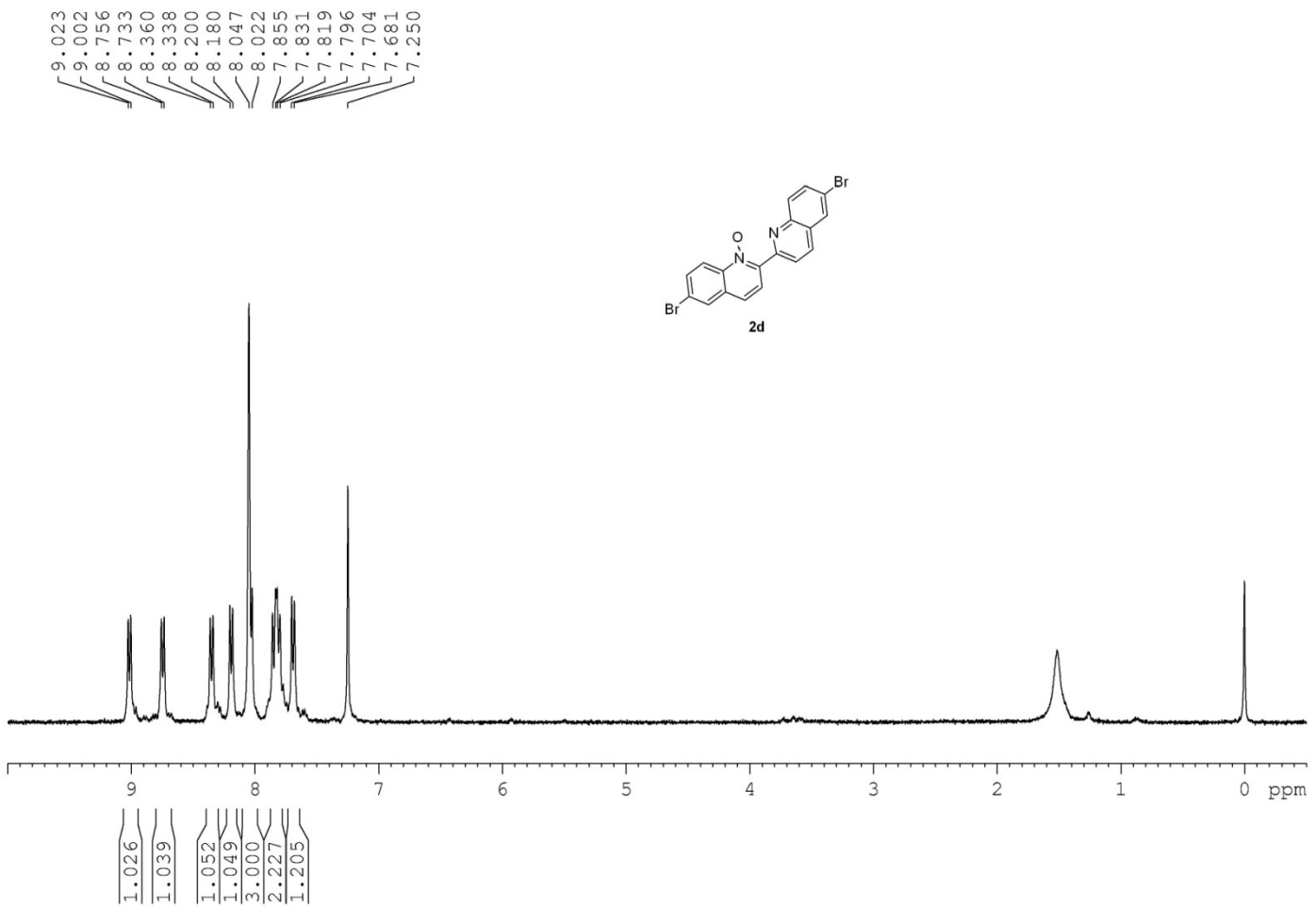
^{13}C NMR spectrum of compound **2b**



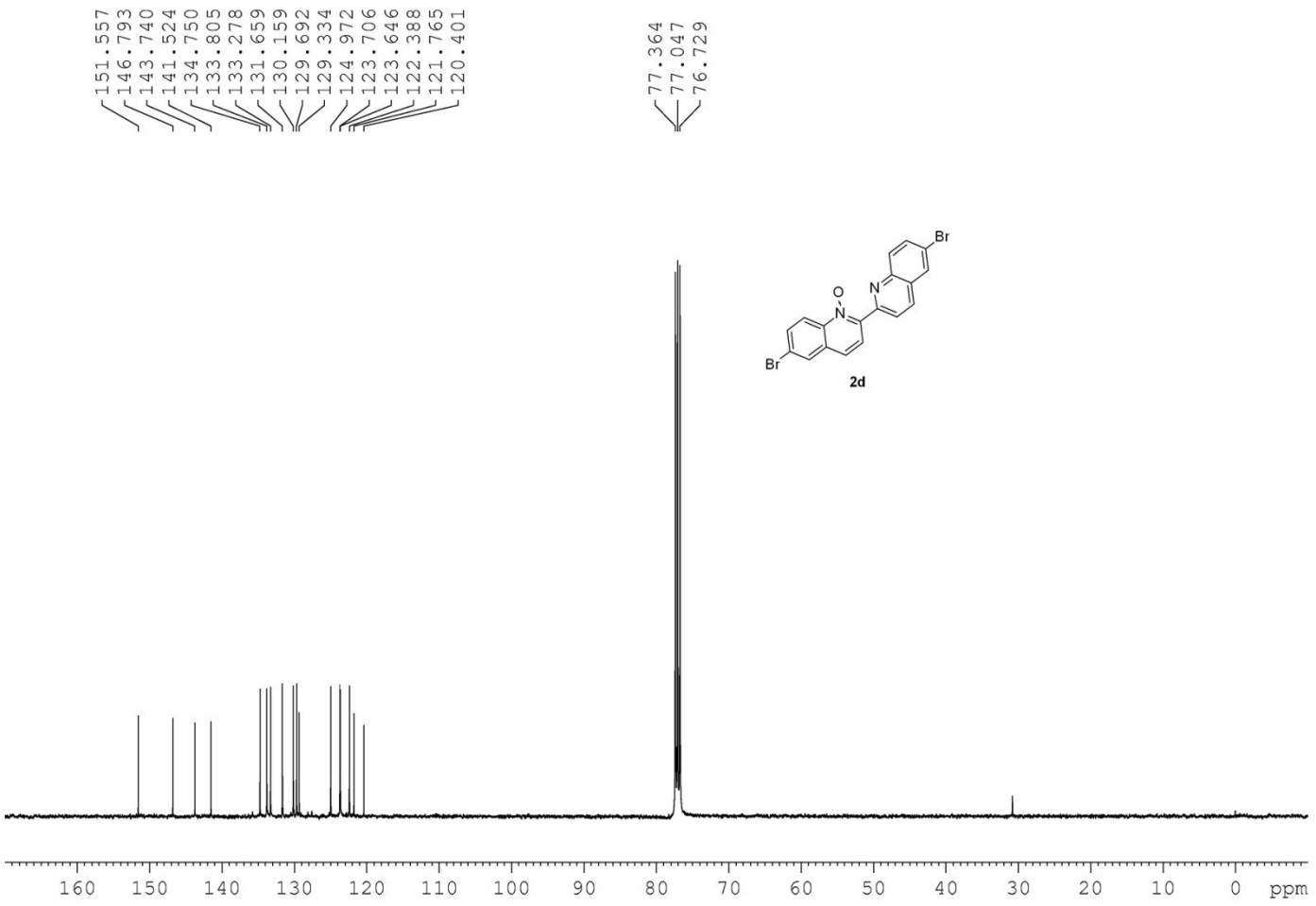
^{1}H NMR spectrum of compound **2c**



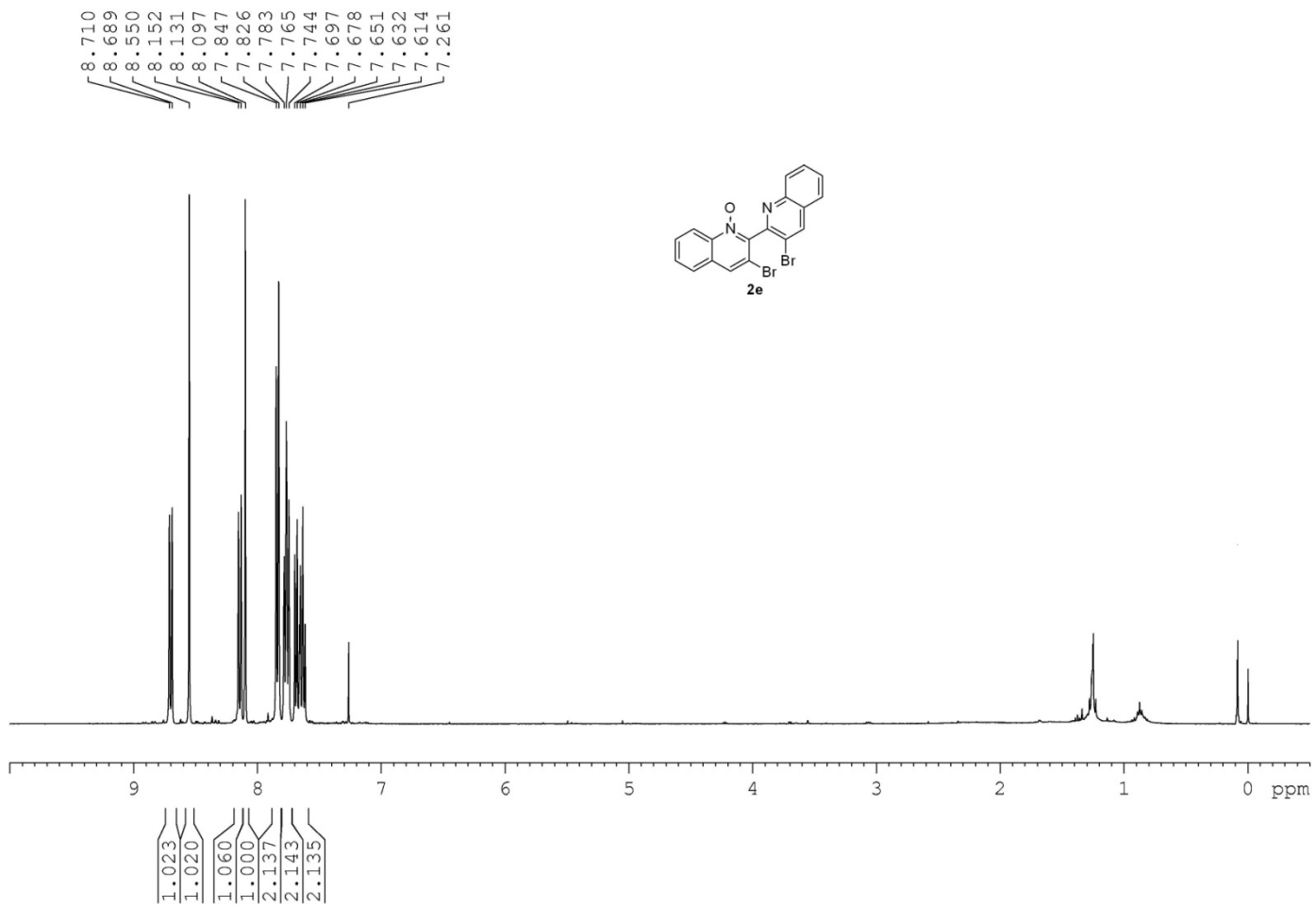
^{13}C NMR spectrum of compound **2c**



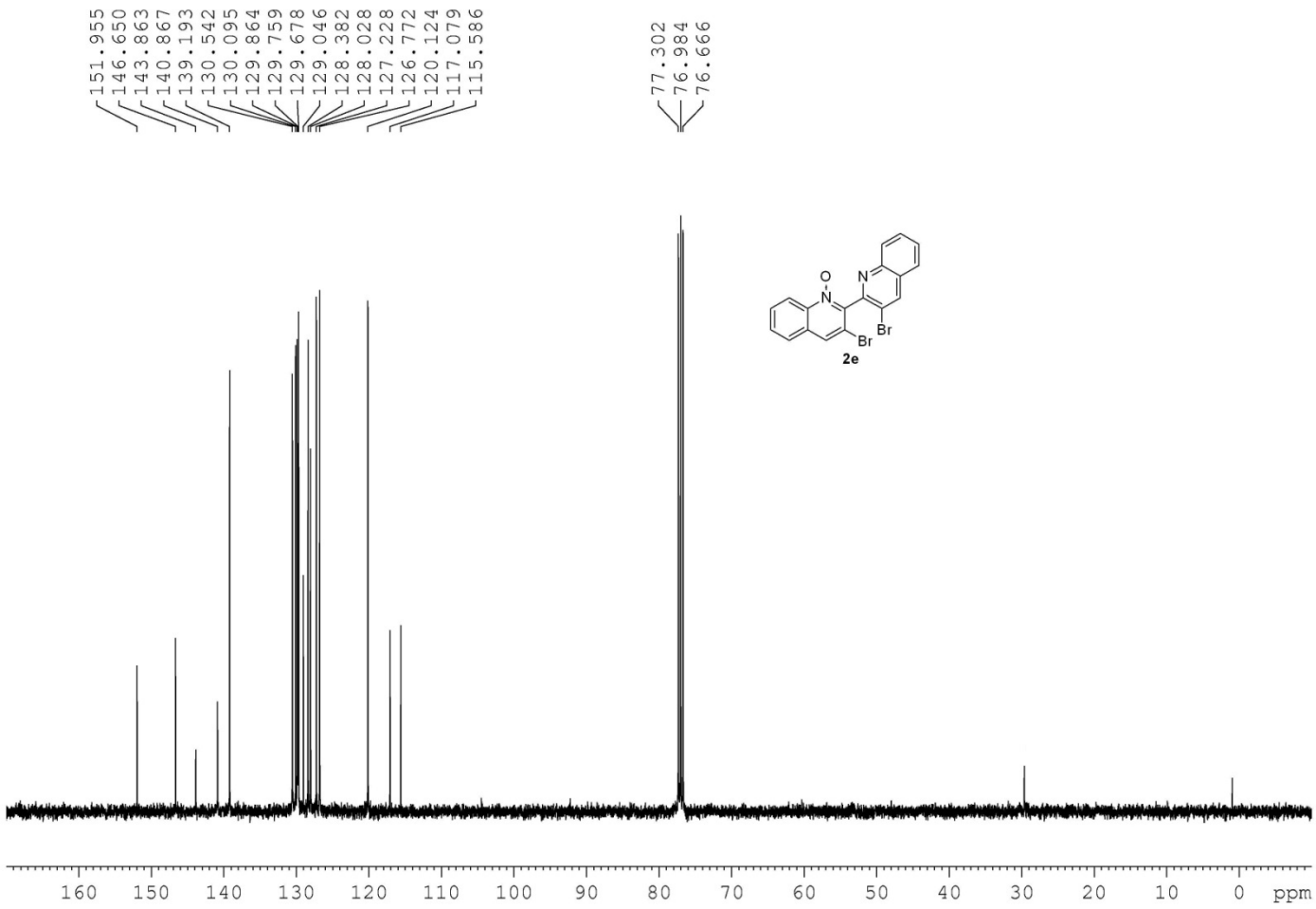
^{1}H NMR spectrum of compound **2d**



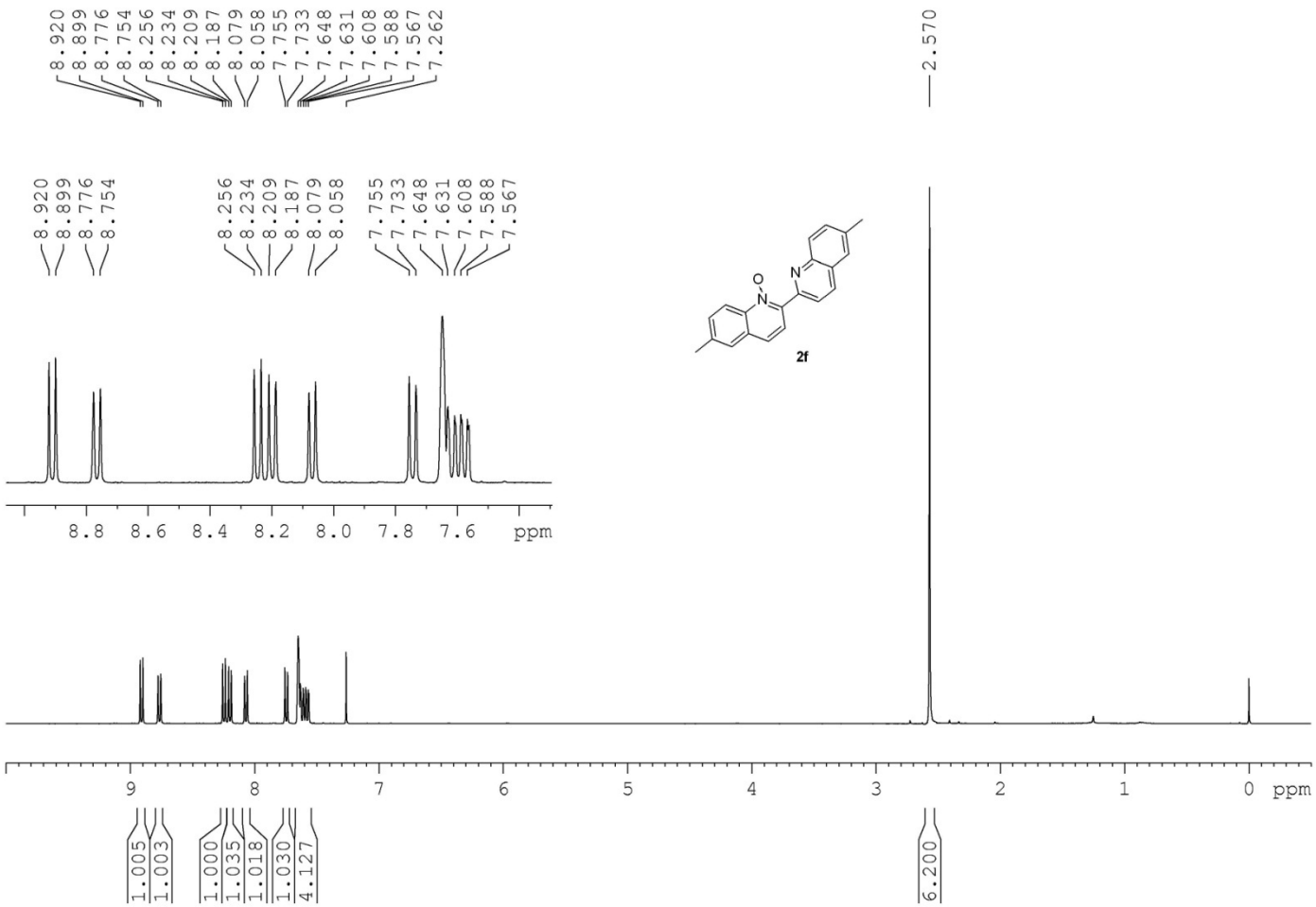
^{13}C NMR spectrum of compound **2d**



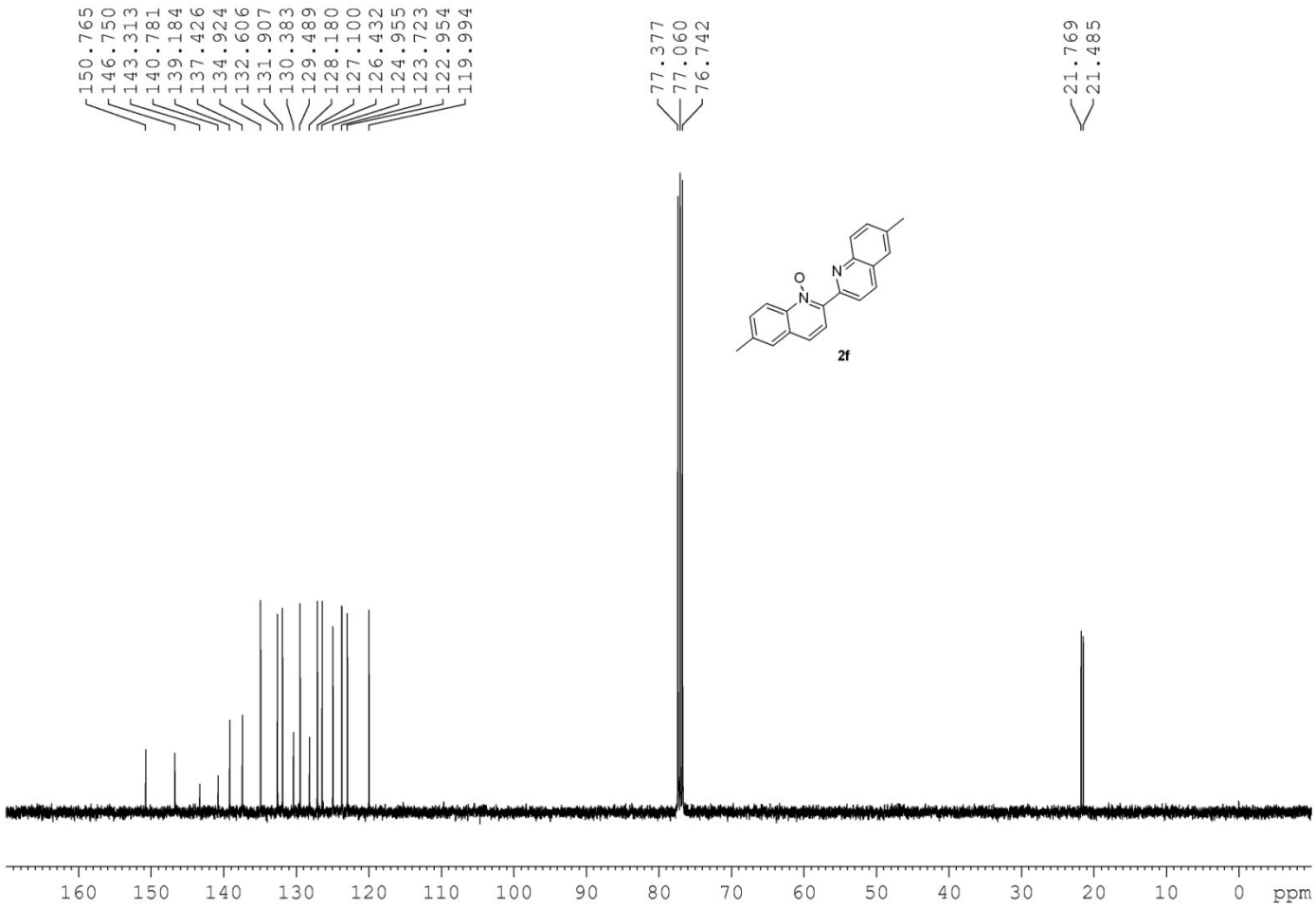
^{1}H NMR spectrum of compound **2e**



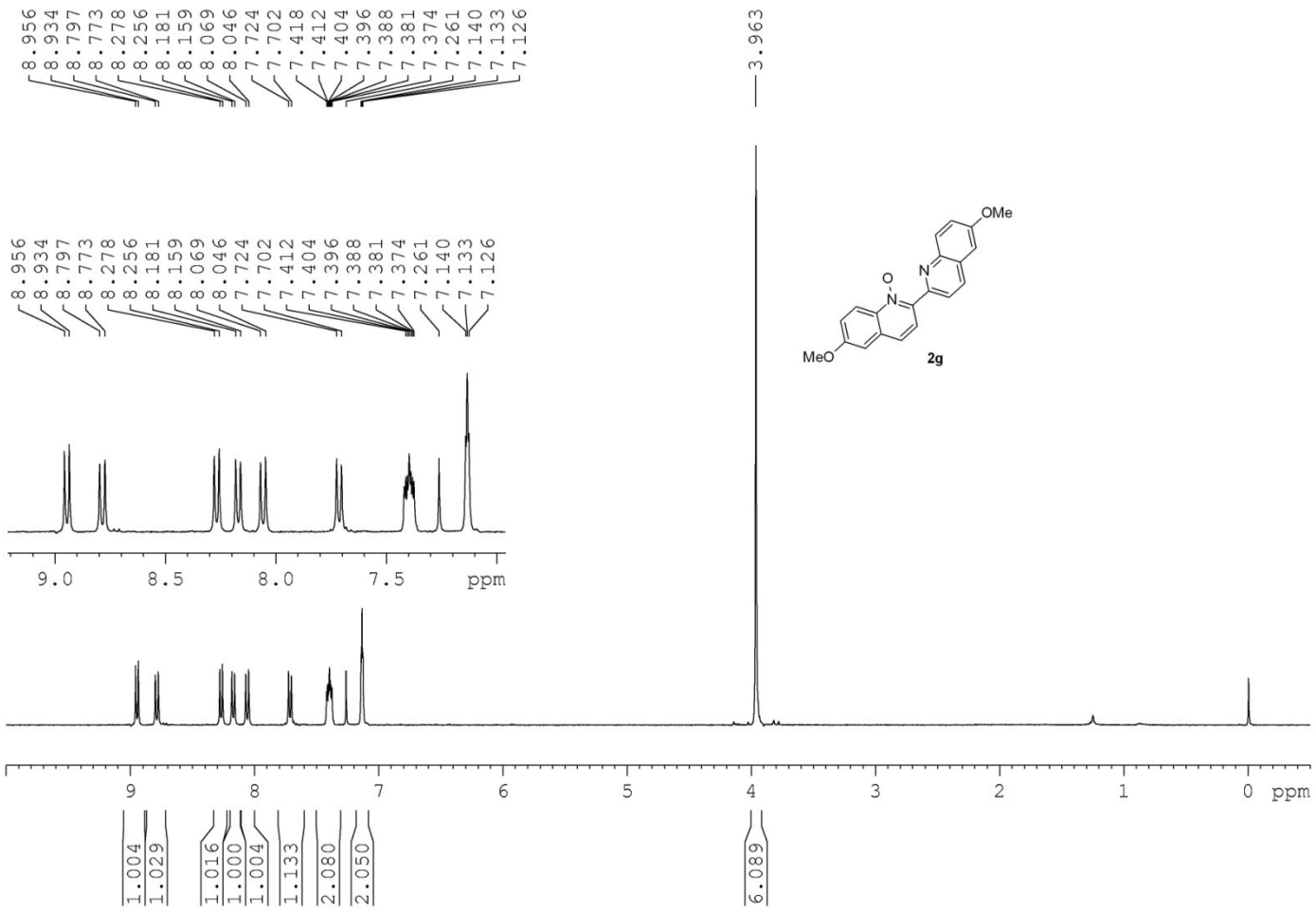
^{13}C NMR spectrum of compound **2e**



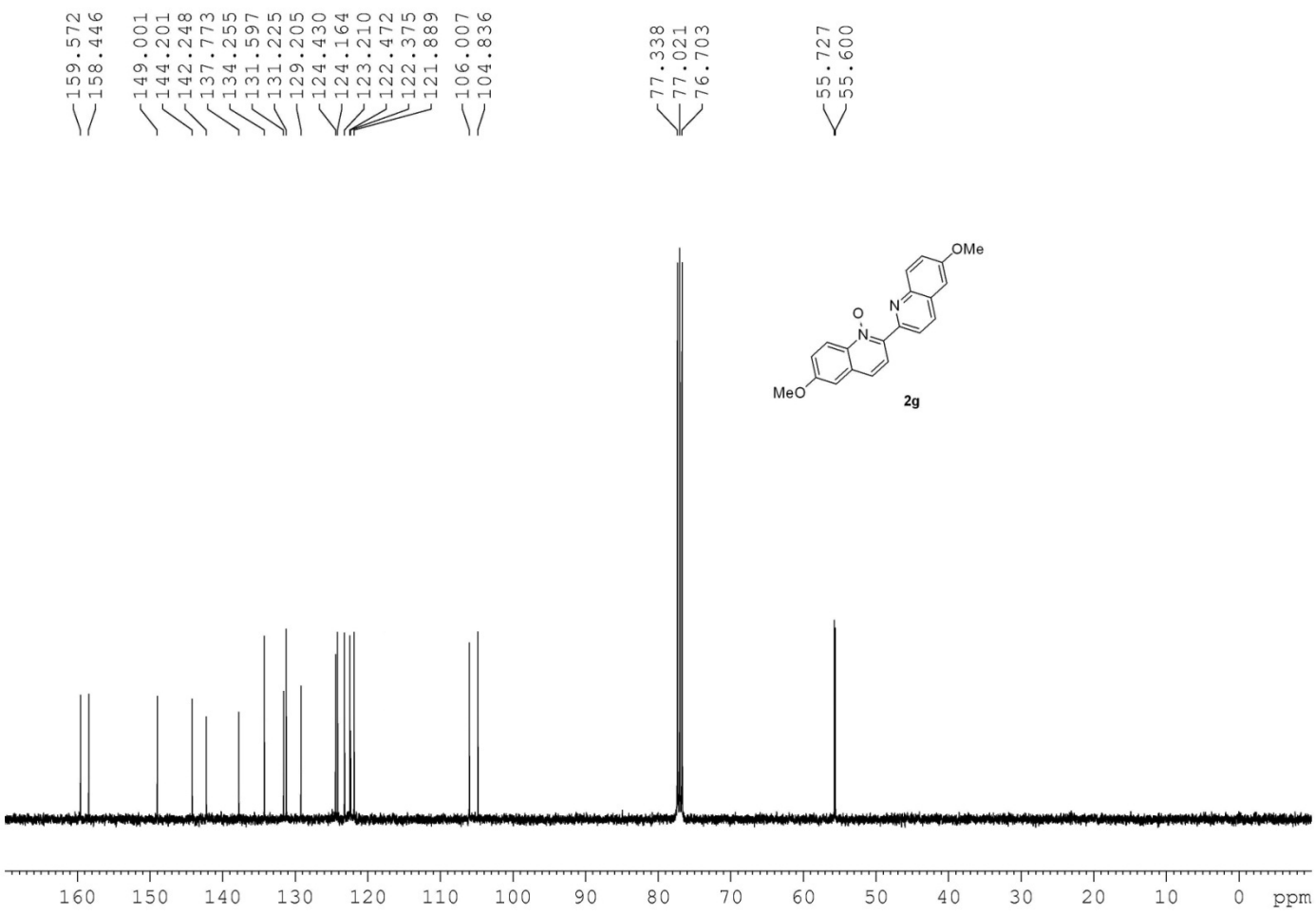
^{1}H NMR spectrum of compound **2f**



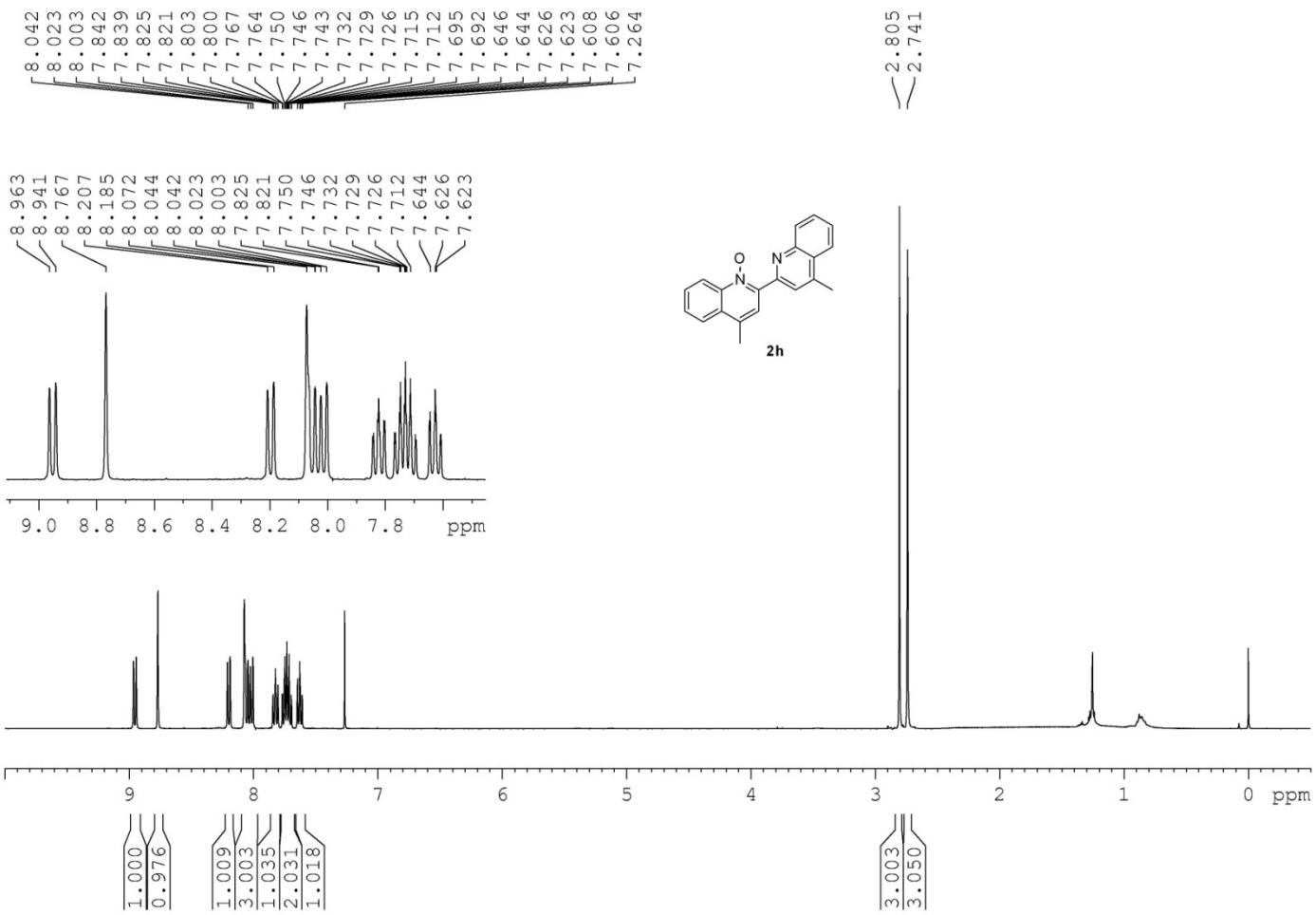
^{13}C NMR spectrum of compound **2f**



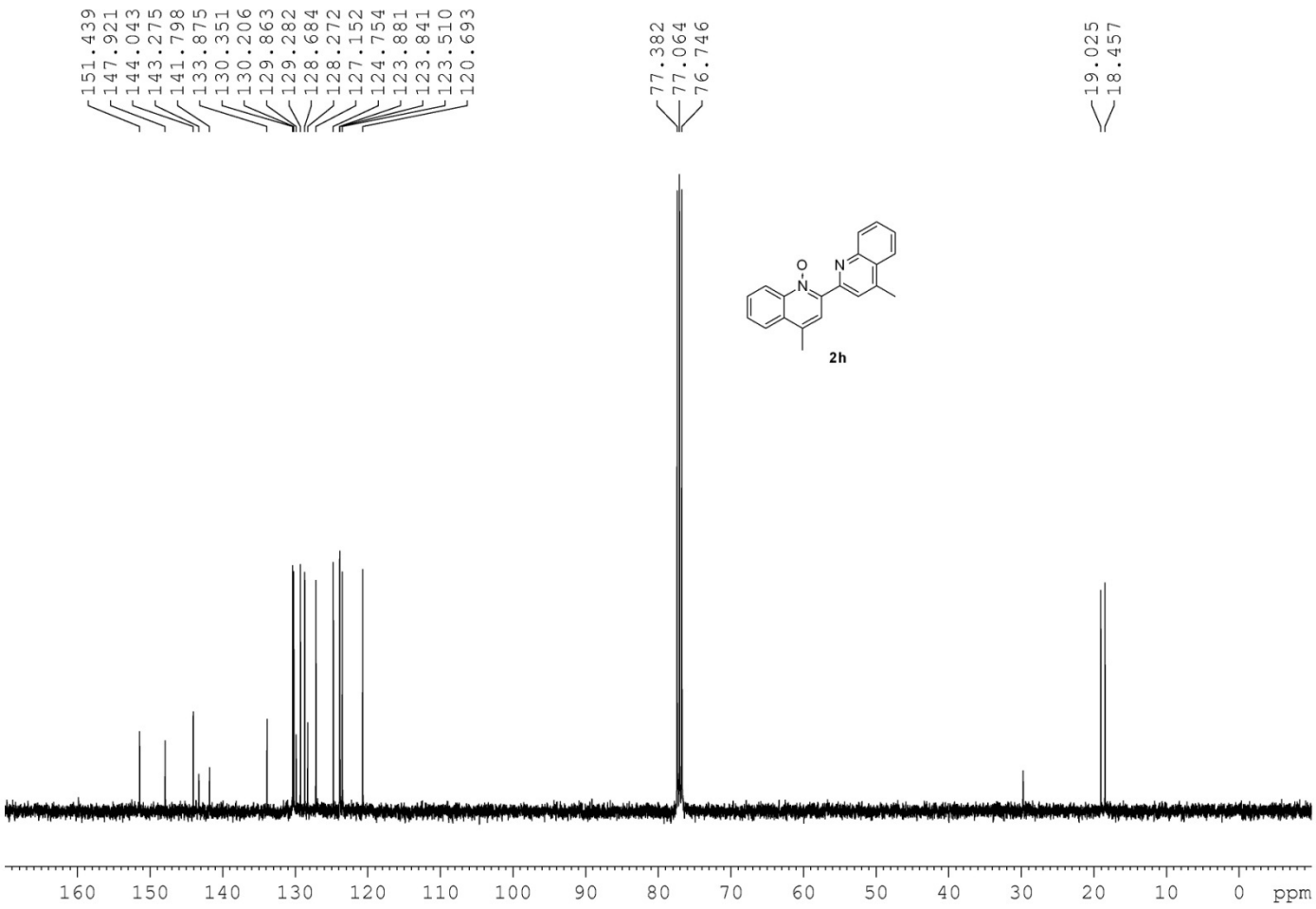
^{1}H NMR spectrum of compound **2g**



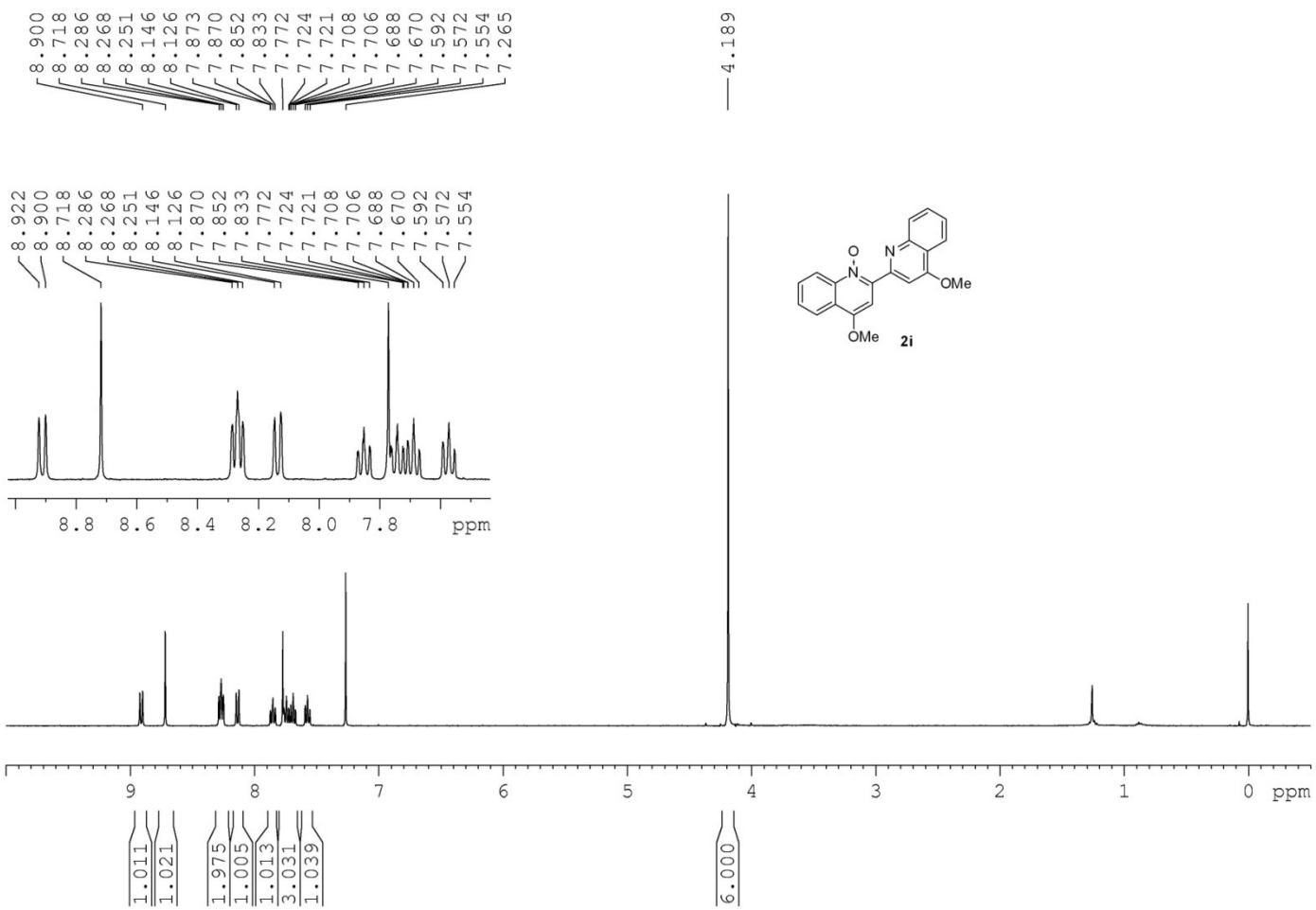
^{13}C NMR spectrum of compound **2g**



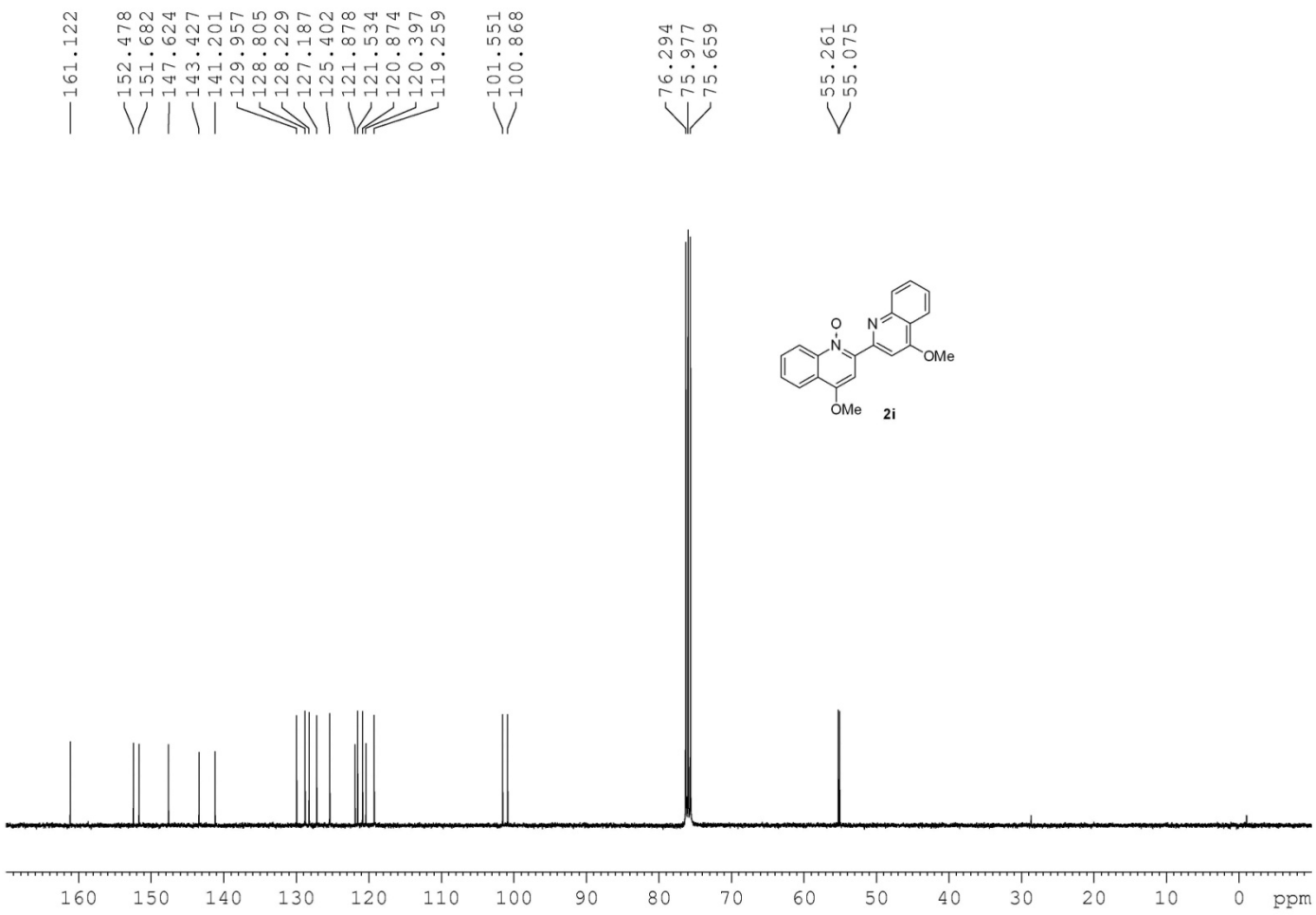
^{1}H NMR spectrum of compound **2h**



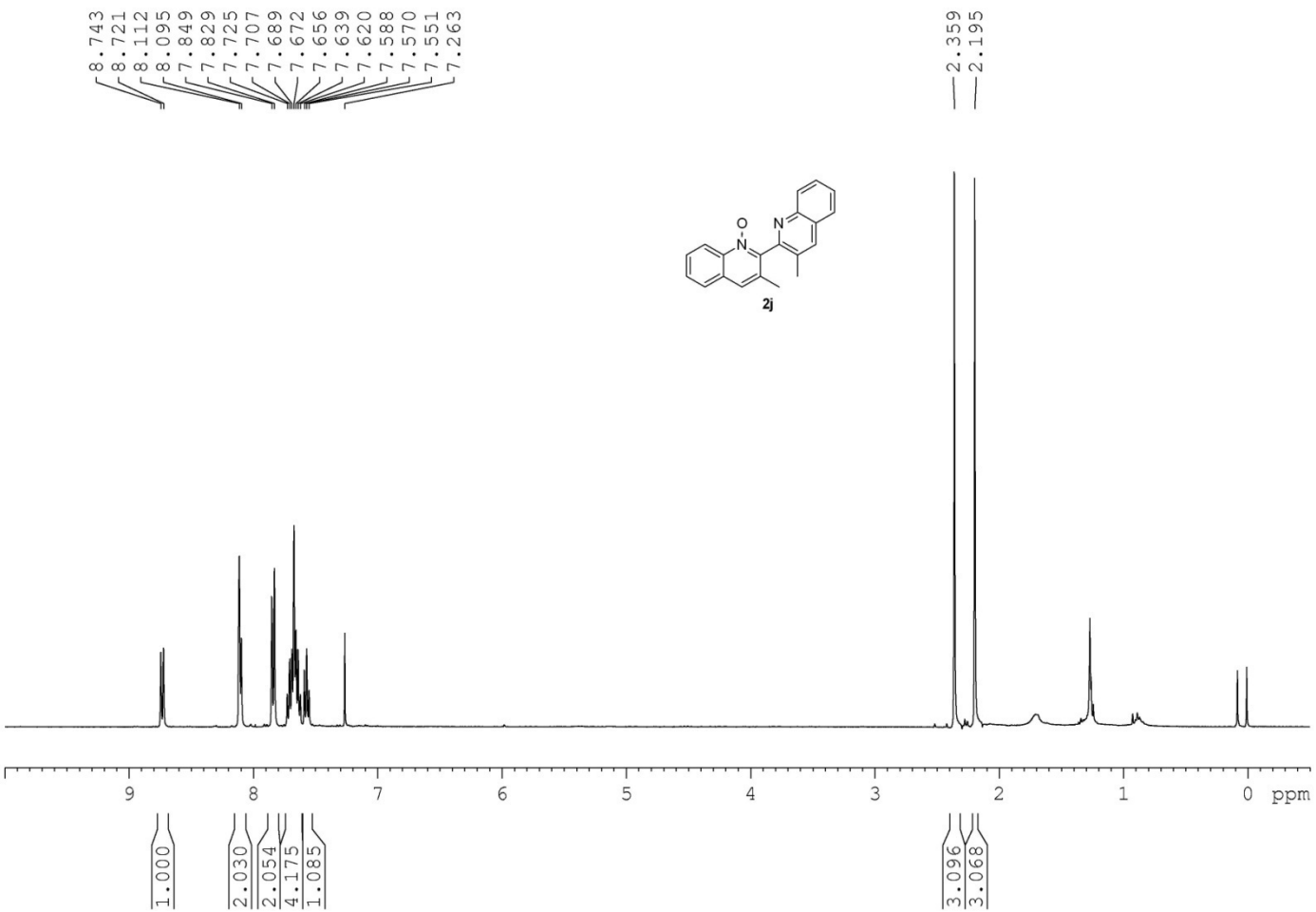
^{13}C NMR spectrum of compound **2h**



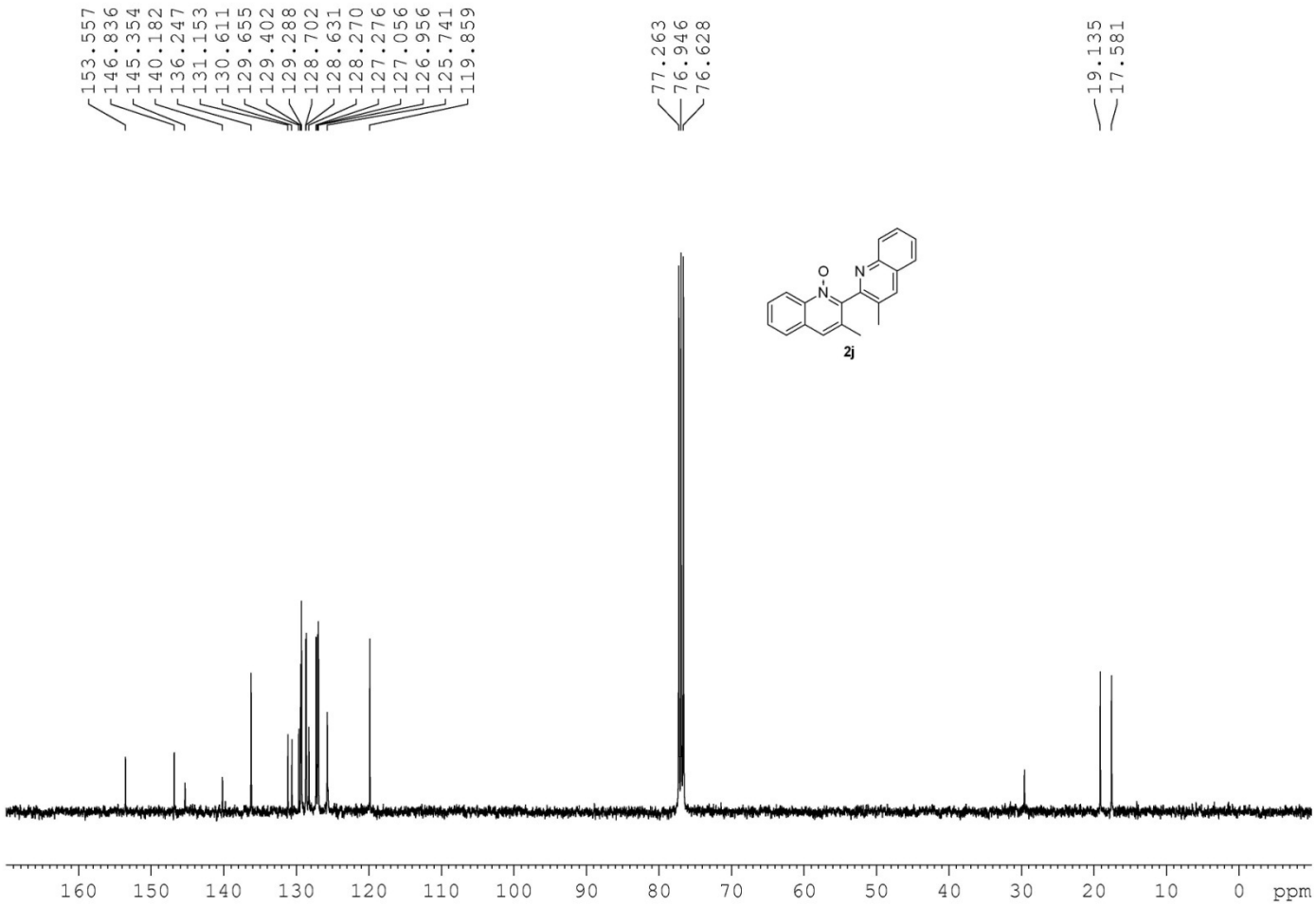
^{1}H NMR spectrum of compound **2i**



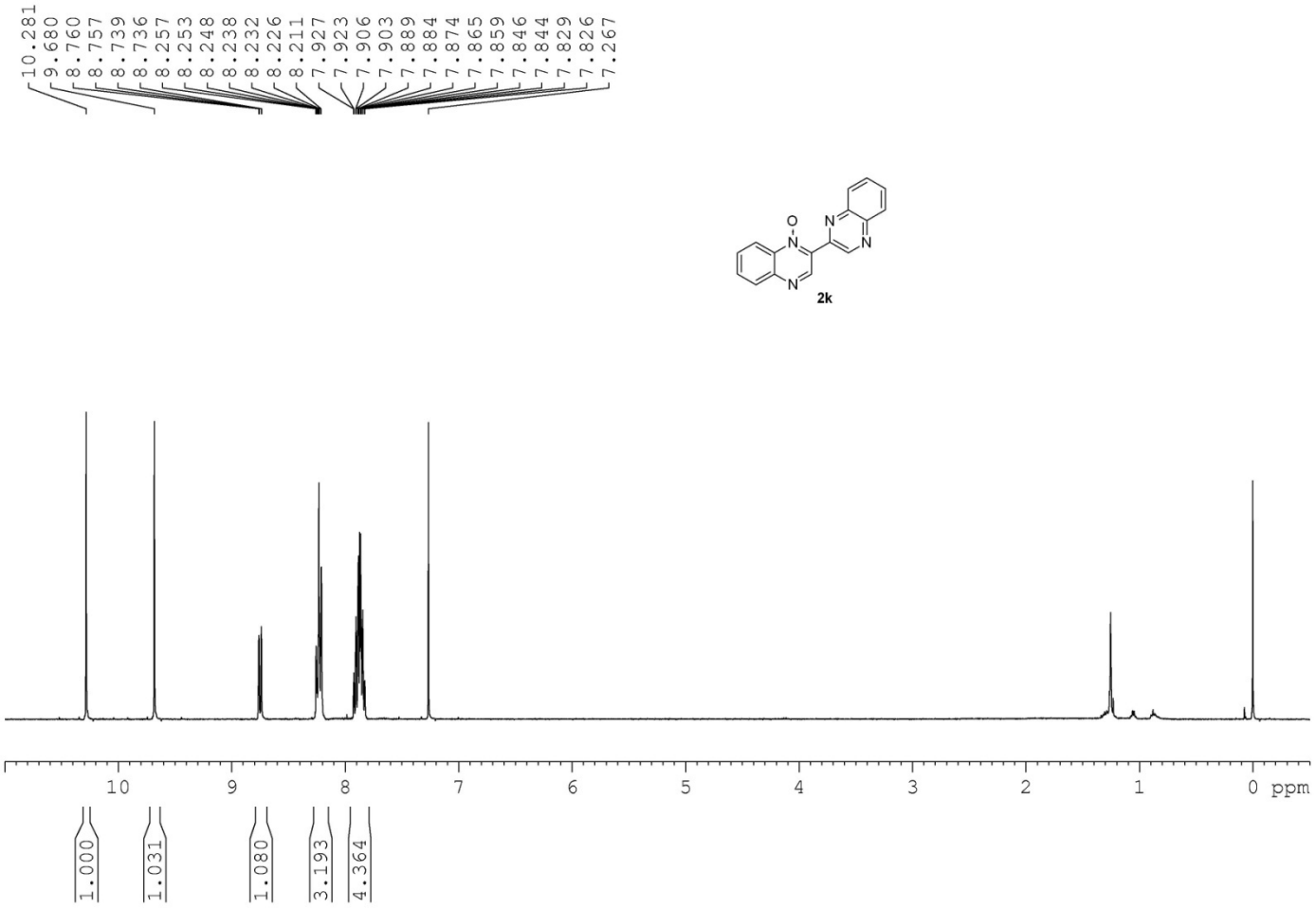
^{13}C NMR spectrum of compound **2i**



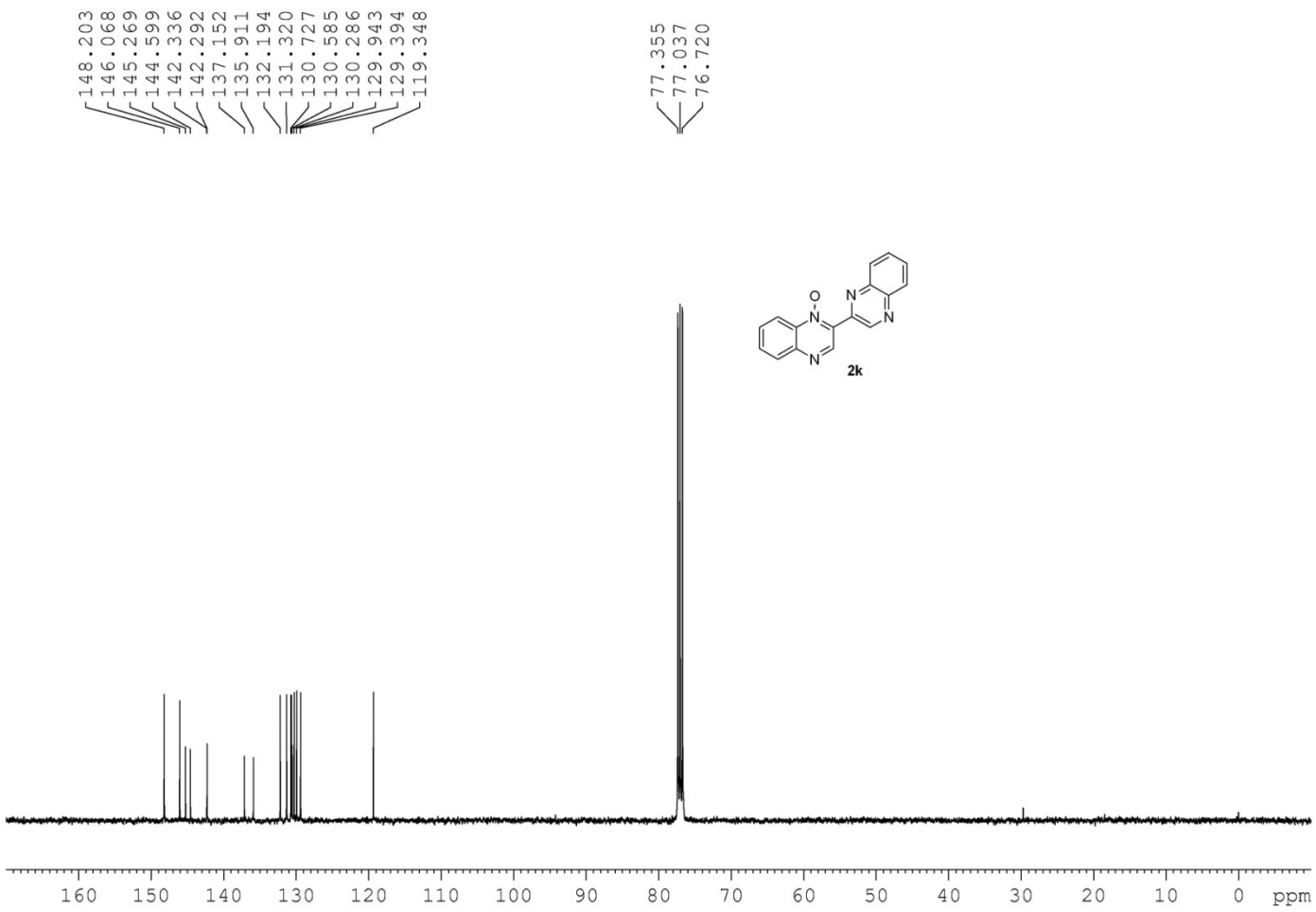
^{1}H NMR spectrum of compound **2j**



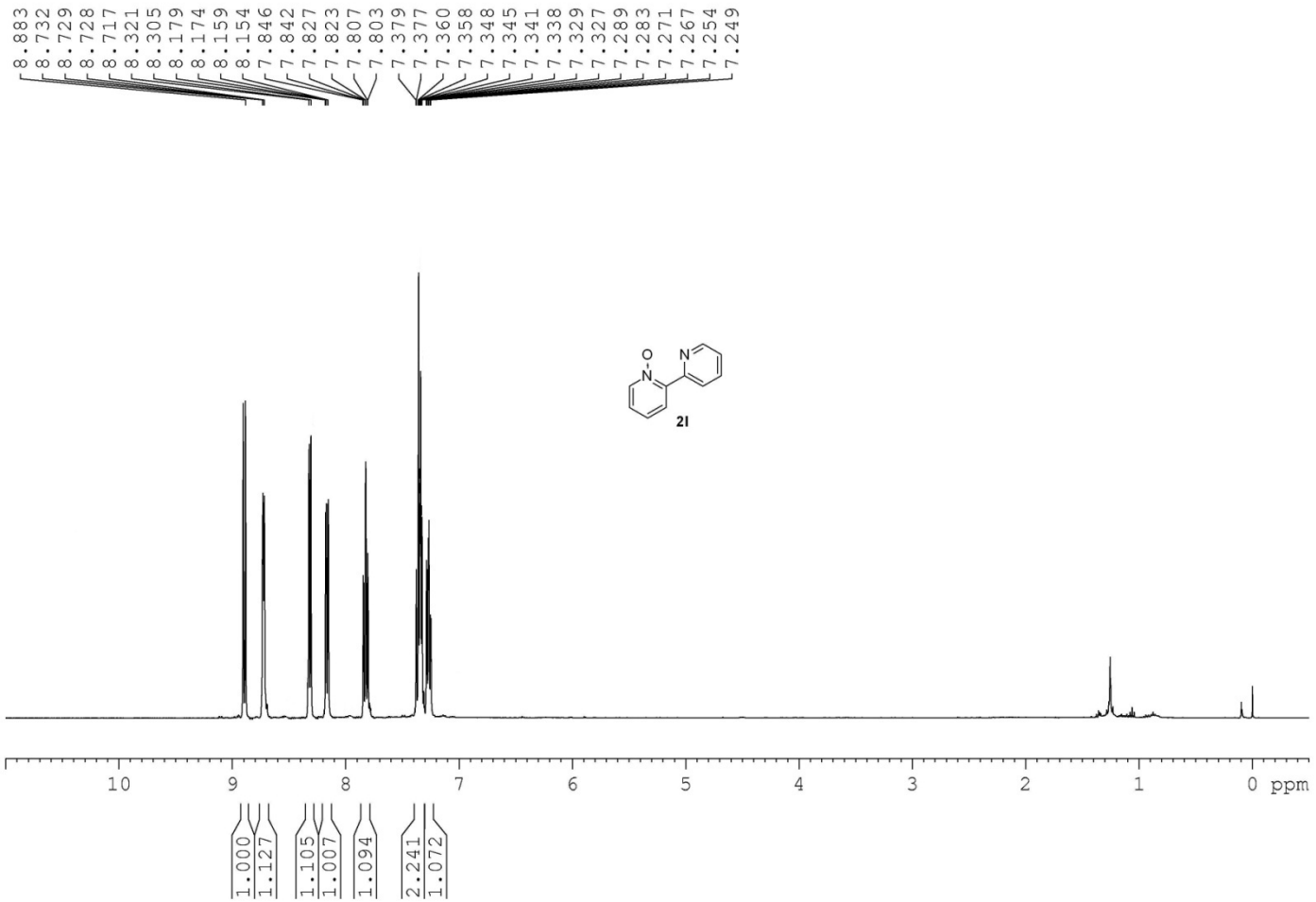
^{13}C NMR spectrum of compound **2j**



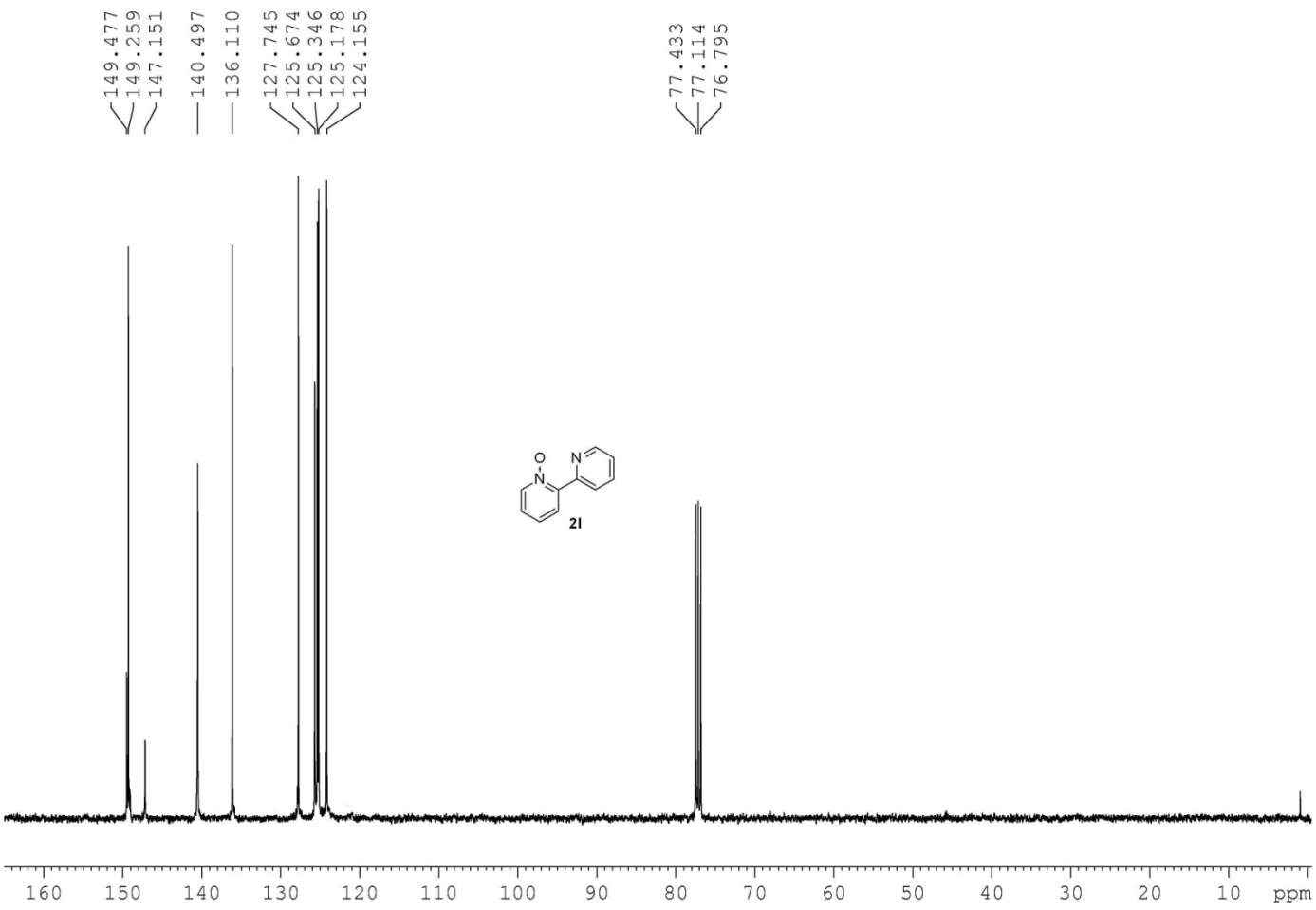
^{1}H NMR spectrum of compound **2k**



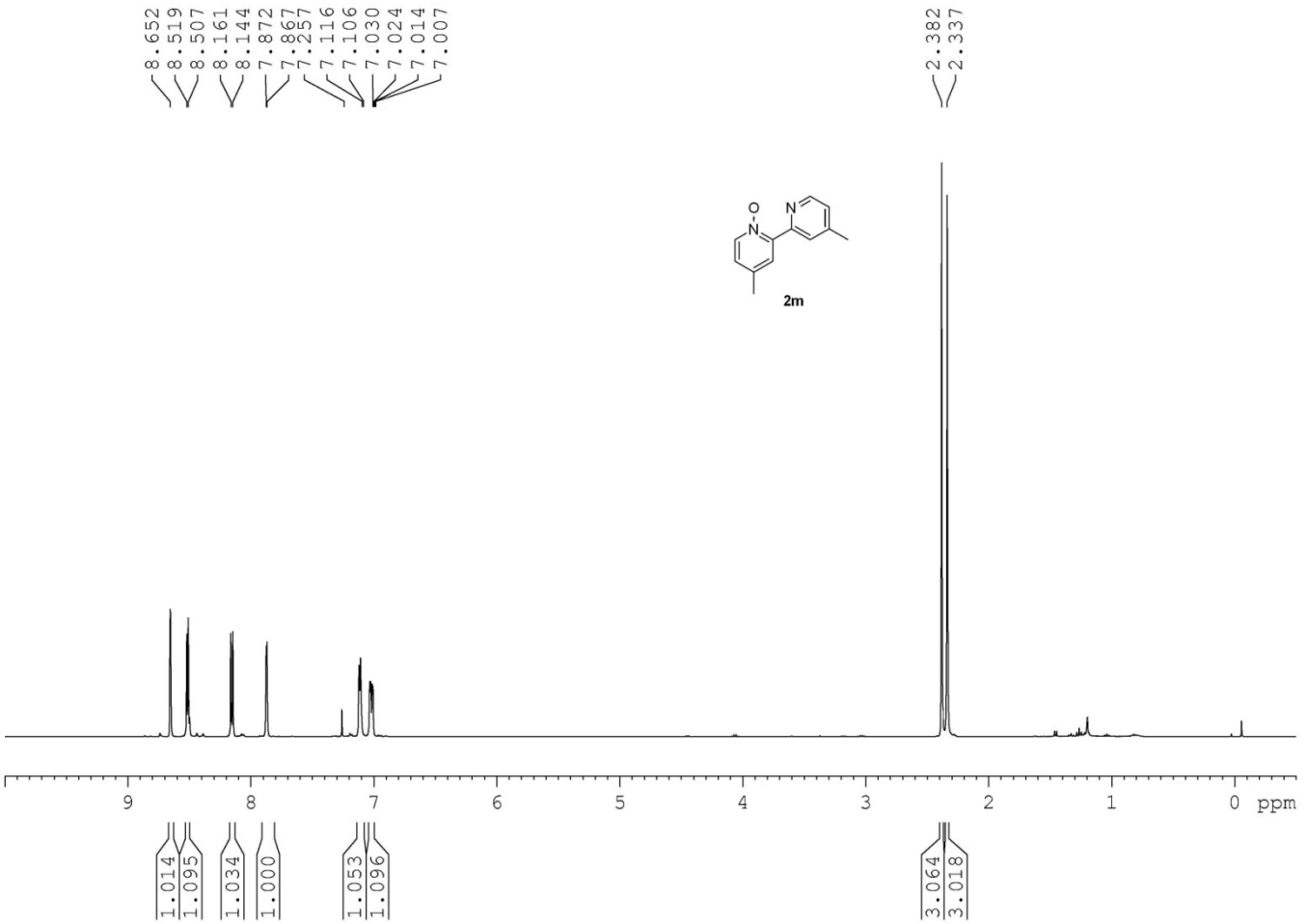
^{13}C NMR spectrum of compound **2k**



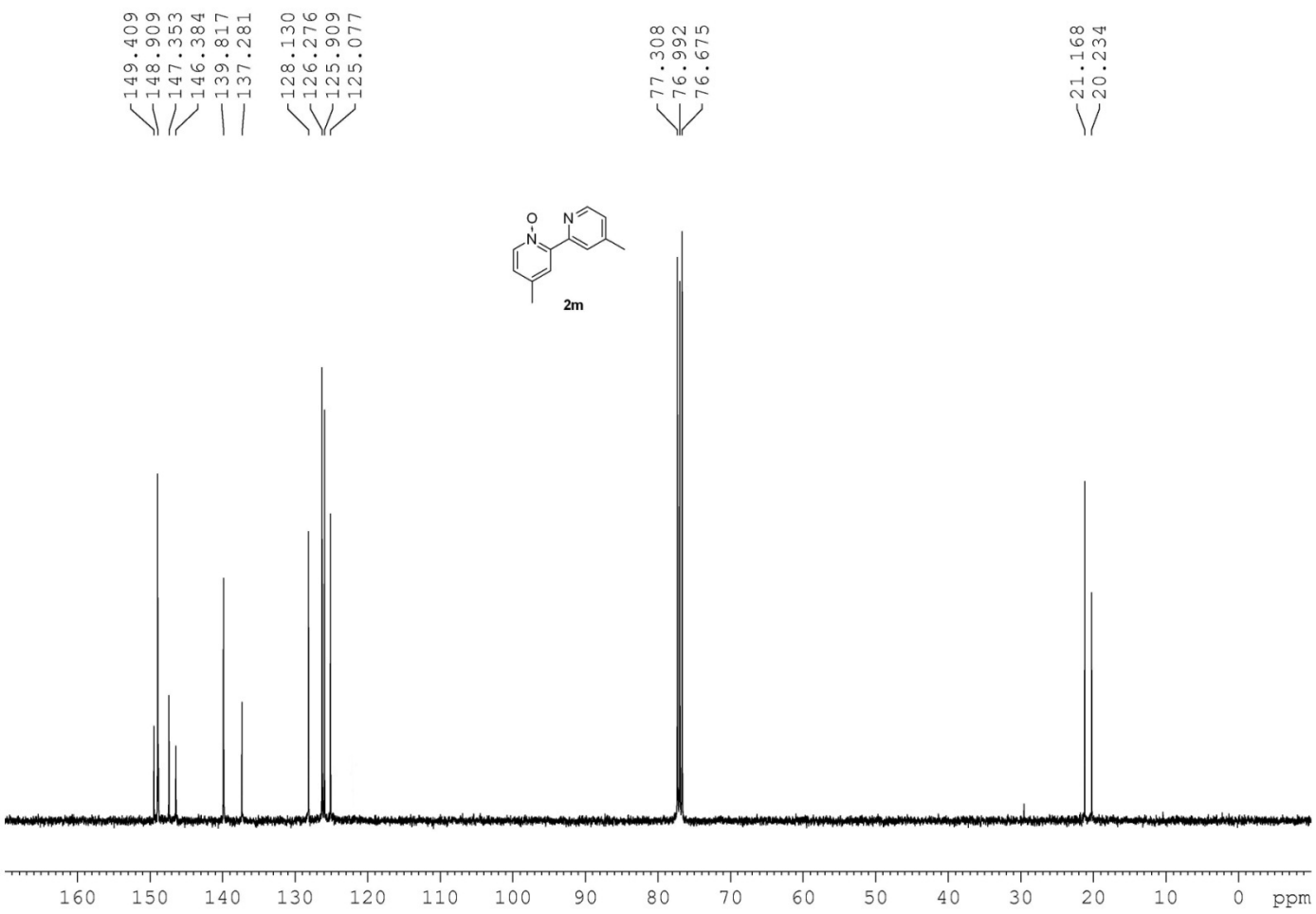
^{1}H NMR spectrum of compound **2l**



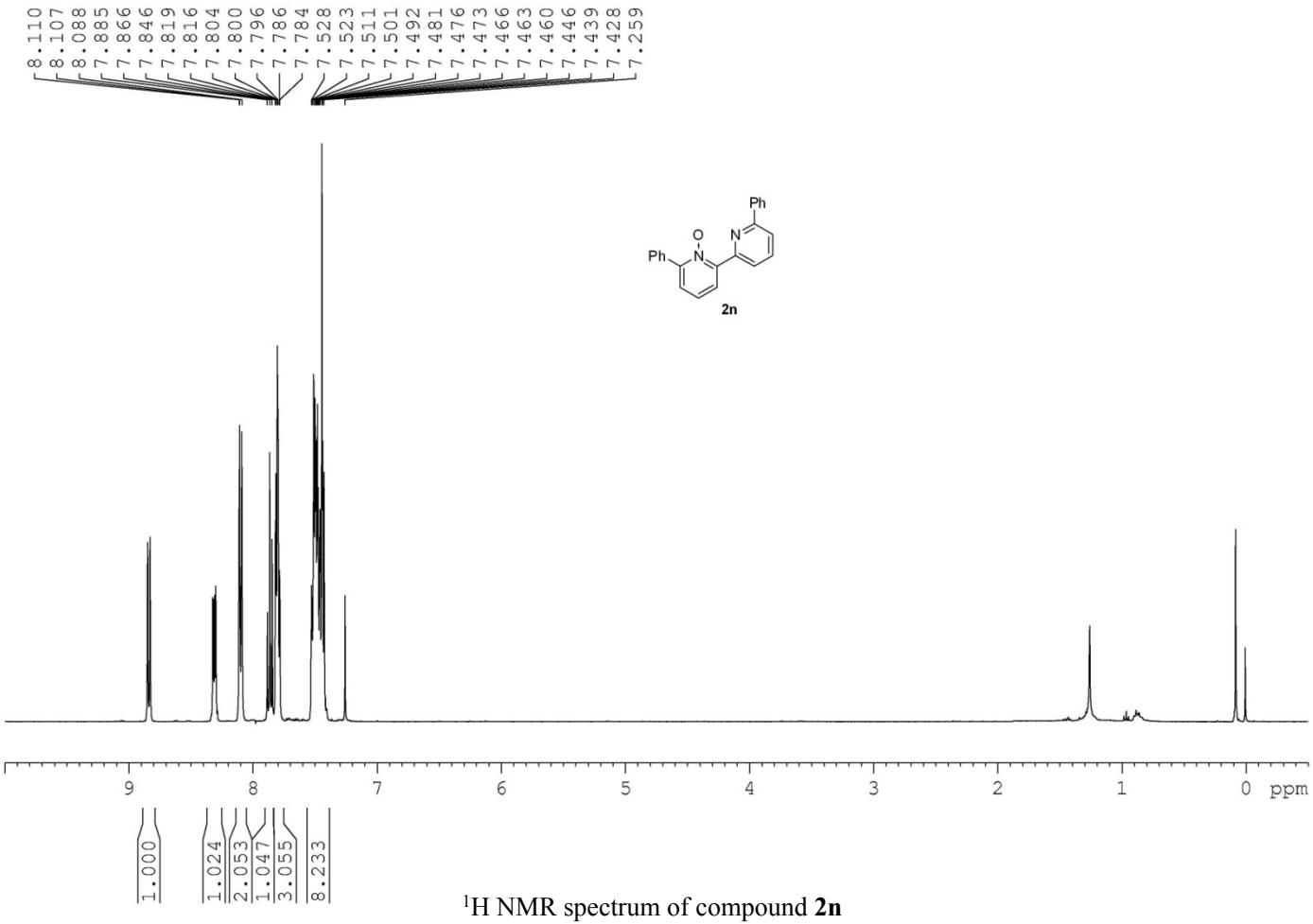
^{13}C NMR spectrum of compound **2l**



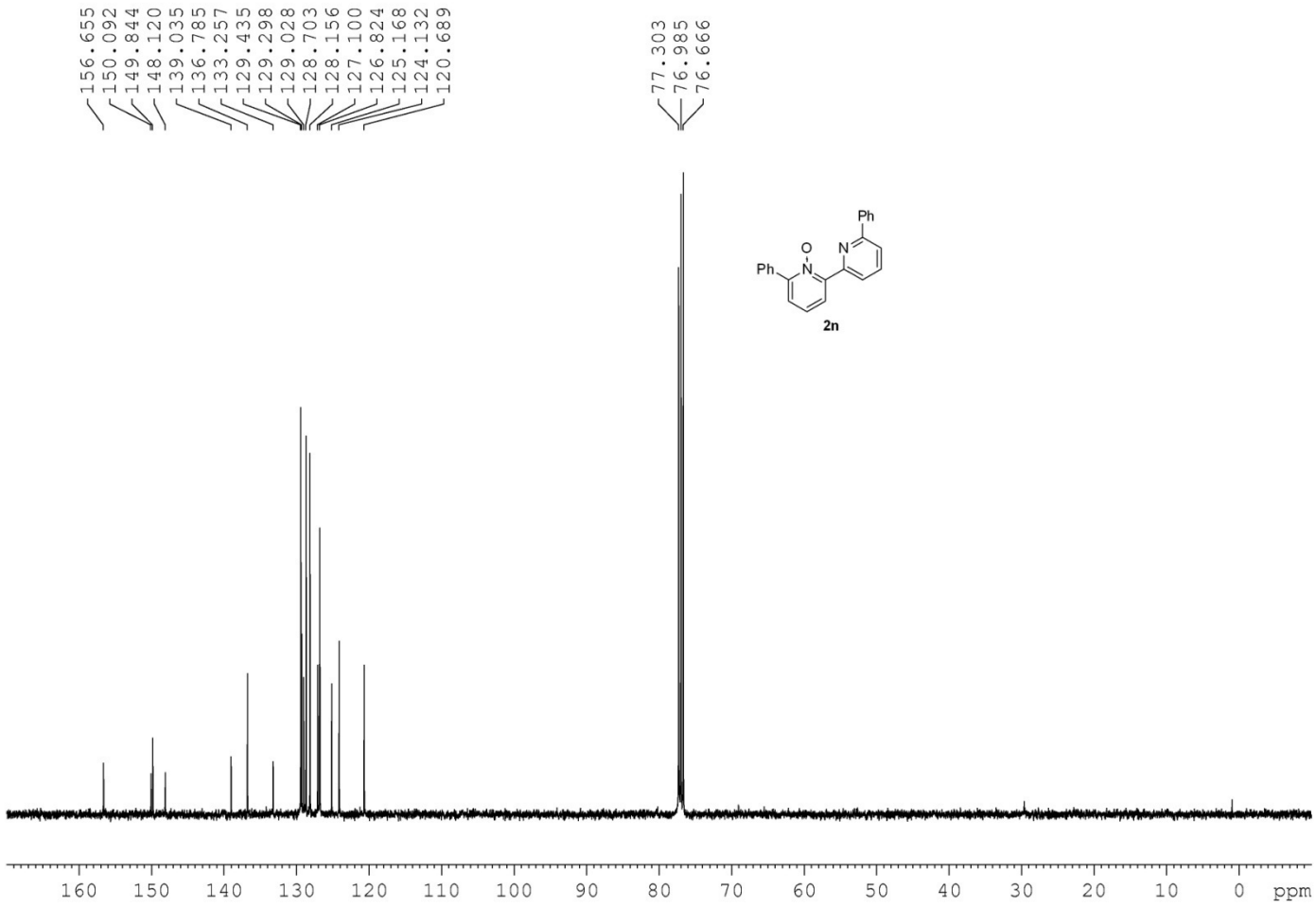
^{1}H NMR spectrum of compound **2m**



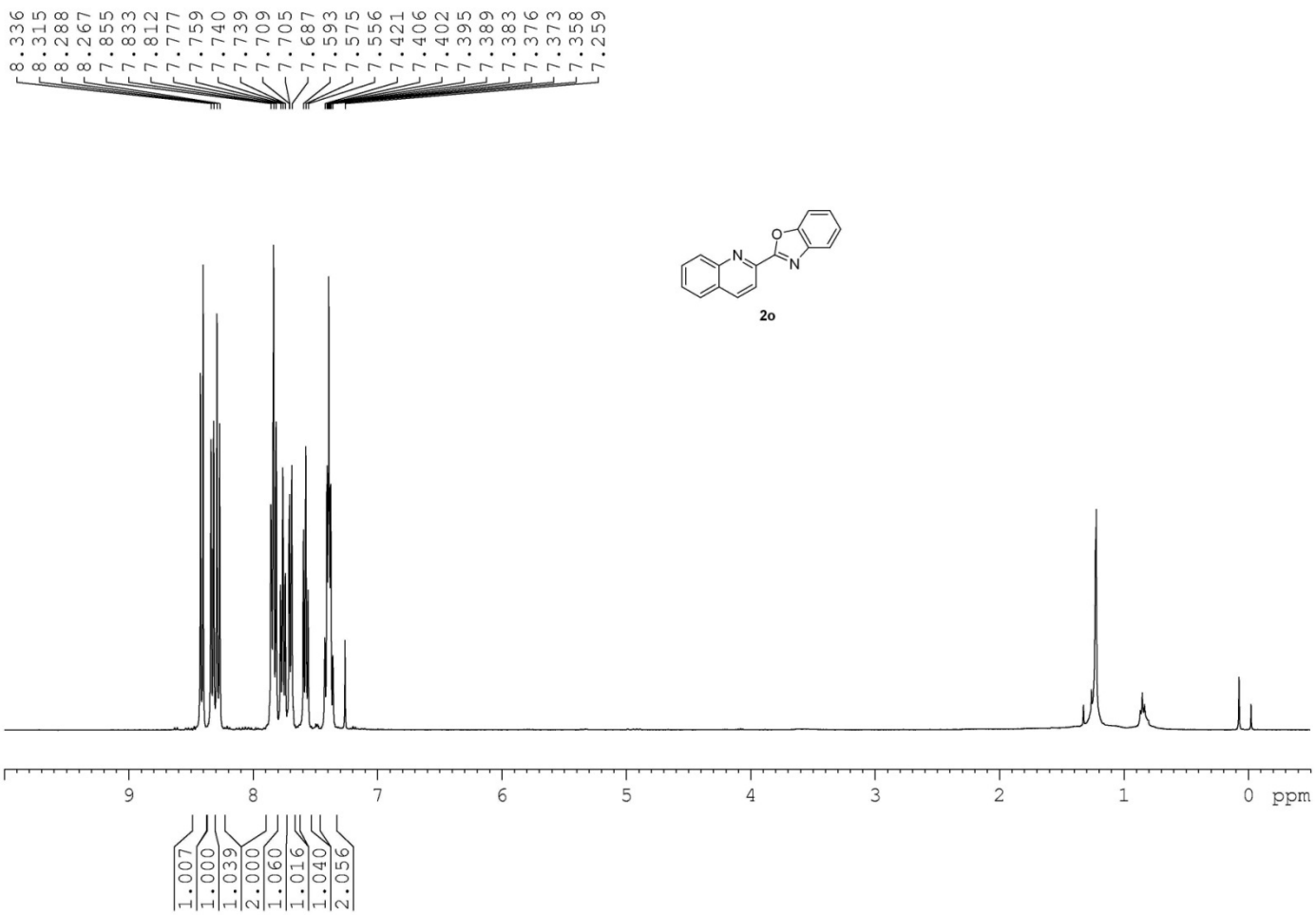
^{13}C NMR spectrum of compound **2m**



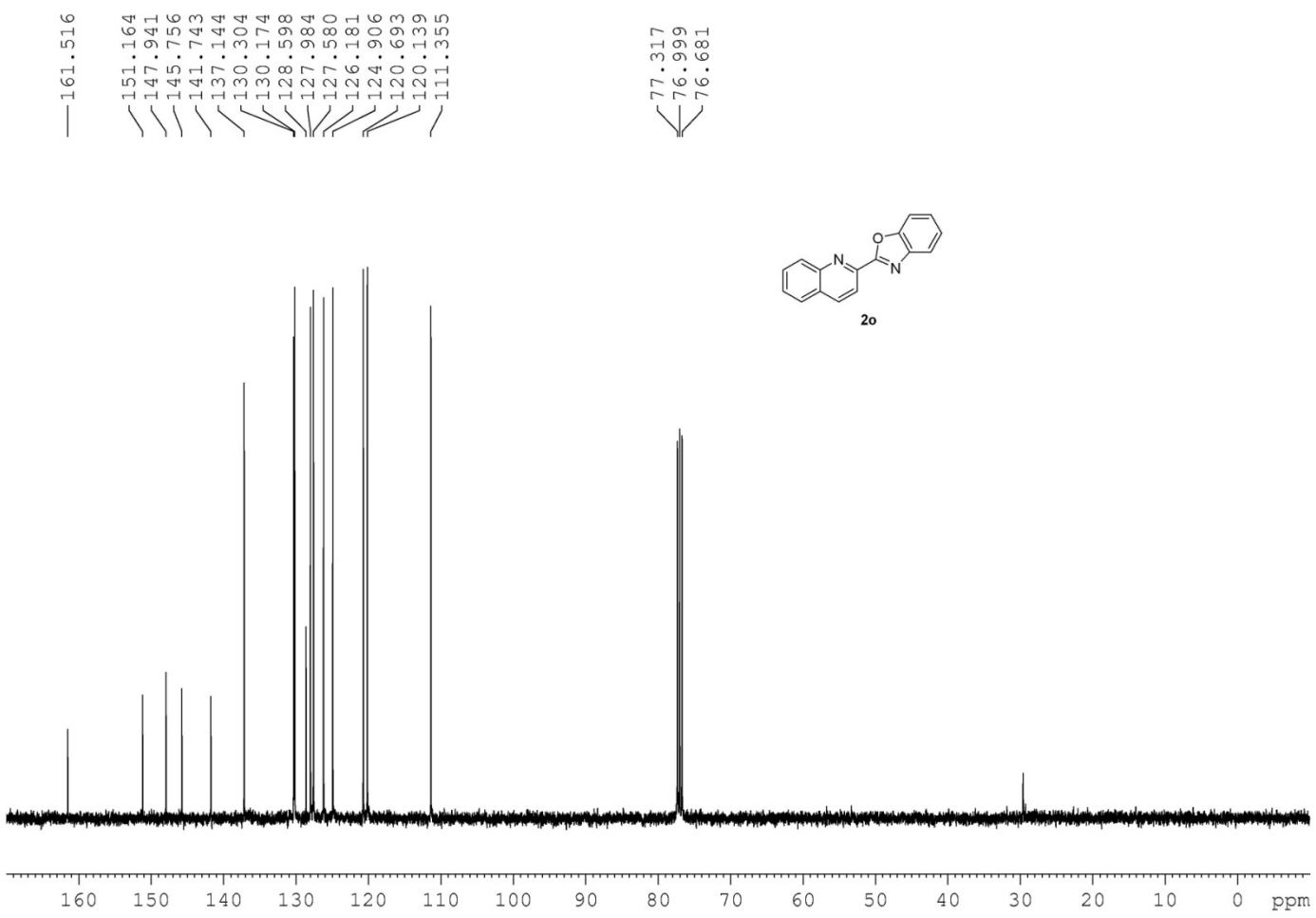
^{1}H NMR spectrum of compound **2n**



^{13}C NMR spectrum of compound **2n**



^{1}H NMR spectrum of compound **2o**



^{13}C NMR spectrum of compound **2o**