Supporting Information

Synthesis of new representatives of 11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridines – structural analogues of integrastatins A, B

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Abstract:. The Claisen–Schmidt condensation reaction of 3,5-diacetyl-2,6-dimethylpyridine with salicylic aldehyde in the presence of an acid unexpectedly afforded 1-[(*5S*,*11S*)-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one as the product of intramolecular cyclization instead of α,β-unsaturated ketones (mono- or bis-azachalcones). The obtained 1-[(*5S*,*11S*)-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one is a close nitrogen-containing structural analogue of natural inhibitors of HIV-1 integrase, namely *integrastatins A* and *B*, *epicoccolide A* and *epicocconigrone A*, containing a tetracyclic epoxybenzooxocine fragment. Substrate scope and mechanistic insights into the cyclization reaction were investigated. A possibility of selective oxidation of the methylene group of the oxocine ring with selenous acid to the carbonyl group was shown to prove structural similarity of the synthesized pyridine-containing analogs with the integrastatin scaffold.

DOI:

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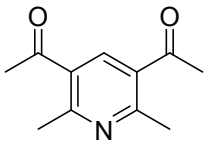
Experimental Procedures

1. Materials and Methods

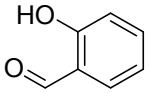
^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX400 (400 and 100 MHz, respectively) and Bruker AVANCE 500 (500 and 125 MHz, respectively) instruments using DMSO-d_6 (compounds **7e,g,p,t**) or $CDCl_3$ (remaining compounds) the internal standard was TMS or residual solvent signals (7.25 and 77.0 ppm in the case of $CDCl_3$ for ^{1}H and ^{13}C nuclei, respectively; 2.49 and 39.9 ppm ^{1}H and for ^{13}C nuclei in DMSO-d_6).

Gas chromatography–mass spectrometry (GC-MS) studies were carried out on a Trace GC Ultra chromatograph with a DSQ II mass-selective detector in the electron ionization mode (70 eV) on a Thermo TR-5 MS quartz capillary column, 15 m long, 0.25 mm inner diameter, with a film thickness of the stationary phase of 0.25 μm. Splitless input mode was used. Carrier gas discharge 20 ml / min. The velocity of the carrier gas (helium) is 1 ml / min. Evaporator temperature 200 °C, transition chamber temperature 200 °C, ion source temperature 200 °C. The temperature of the column thermostat was changed according to the program: from 15 (5 min delay) to 220 °C at a rate of 20 °C per minute, to 290 °C at a rate of 15 °C per minute. The total analysis time was 30 min. The volume of the injected sample is 1 μl. Chromatograms were recorded in TIC mode. The range of mass scanning is 30 - 450 amu. The MALDI TOF (matrix-assisted laser desorption/ionization) mass-spectra were obtained on a Ultraflex-II mass spectrometer (Bruker Daltonics) in a positive ion mode using reflection mode (20 mV target voltage) with 4-hydroxybenzoic acid (and sodium 4-hydroxybenzoate) matrix. Elemental analysis was performed on a Carlo Erba 1106CHN instrument. Melting points were determined using a Koffler hot bench. Monitoring of the reaction course and the purity of the products was carried out by TLC on Sorbfil plates and visualized using iodine vapor or UV light.

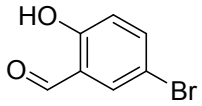
2. Starting Materials Preparation



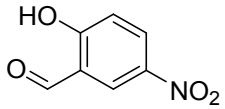
1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) was prepared by following a literature procedure [15]



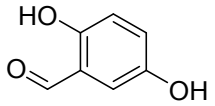
2-hydroxybenzaldehyde was commercially available (Sigma Aldrich).



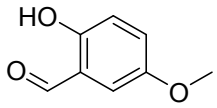
5-bromo-2-hydroxybenzaldehyde was commercially available (Sigma Aldrich).



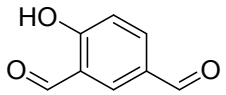
2-hydroxy-5-nitrobenzaldehyde was prepared by following a literature procedure [22]



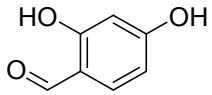
2,5-dihydroxybenzaldehyde was prepared by following a literature procedure [23]



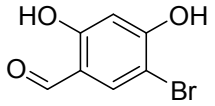
2-hydroxy-5-methoxybenzaldehyde was prepared by following a literature procedure [24]



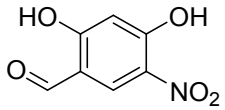
4-hydroxyisophthalaldehyde was prepared by following a literature procedure [25]



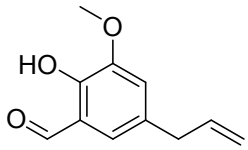
2,4-dihydroxybenzaldehyde was prepared by following a literature procedure [26]



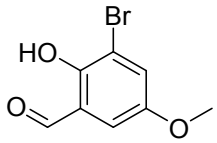
5-bromo-2,4-dihydroxybenzaldehyde was prepared by following a literature procedure [27]



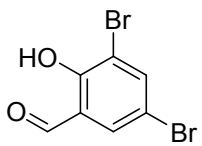
2,4-dihydroxy-5-nitrobenzaldehyde was prepared by following a literature procedure [28]



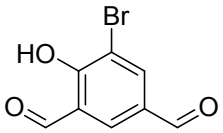
5-allyl-2-hydroxy-3-methoxybenzaldehyde was prepared by following a literature procedure [29]



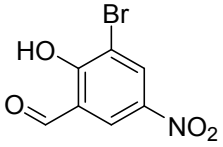
3-bromo-2-hydroxy-5-methoxybenzaldehyde was prepared by following a literature procedure [24]



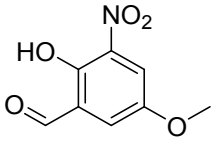
3,5-dibromo-2-hydroxybenzaldehyde was prepared by following a literature procedure [30]



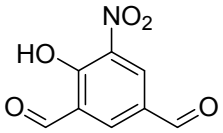
5-bromo-4-hydroxyisophthalaldehyde was prepared following a procedure adapted from the literature [27].
Bromine (0.120 mL, 2.0 mmol) was added dropwise to a solution of 4-hydroxyisophthalaldehyde (300 mg, 2.0 mmol) in acetic acid (5 mL). After stirring for 3 h at room temperature, the resulting mixture was poured into ice–water mixture (10 mL), then the precipitated product was filtered and washed with water, dried in vacuo, and the crude solids were recrystallized from a 2-propanol to yield 5-bromo-4-hydroxyisophthalaldehyde (yield: 76% 347 mg). M.p. 138–140 °C).



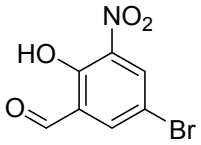
3-bromo-2-hydroxy-5-nitrobenzaldehyde was prepared by following a literature procedure [31]



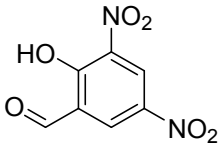
2-hydroxy-5-methoxy-3-nitrobenzaldehyde was prepared by following a literature procedure [32]



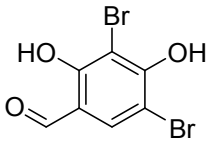
4-hydroxy-5-nitroisophthalaldehyde was prepared by following a literature procedure [33]



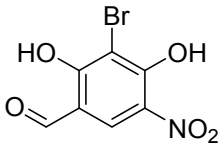
5-bromo-2-hydroxy-3-nitrobenzaldehyde was prepared by following a literature procedure [34]



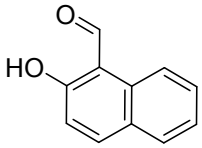
2-hydroxy-3,5-dinitrobenzaldehyde was prepared by following a literature procedure [22]



3,5-dibromo-2,4-dihydroxybenzaldehyde was prepared by following a literature procedure [35]



3-bromo-2,4-dihydroxy-5-nitrobenzaldehyde was prepared following a procedure adapted from the literature [27].
Bromine (0.065 mL, 1.25 mmol) was added dropwise to a solution of 2-hydroxy-5-nitrobenzaldehyde (167 mg, 1.25 mmol) in acetic acid (5 mL). After stirring for 4 h at room temperature, the resulting mixture was poured into ice–water mixture (10 mL), then the precipitated product was filtered and washed with water, dried in vacuo, and the crude solids were recrystallized from a 2-propanol to yield 3-bromo-2,4-dihydroxy-5-nitrobenzaldehyde (yield: 64% 209 mg). M.p. 175–176 °C).



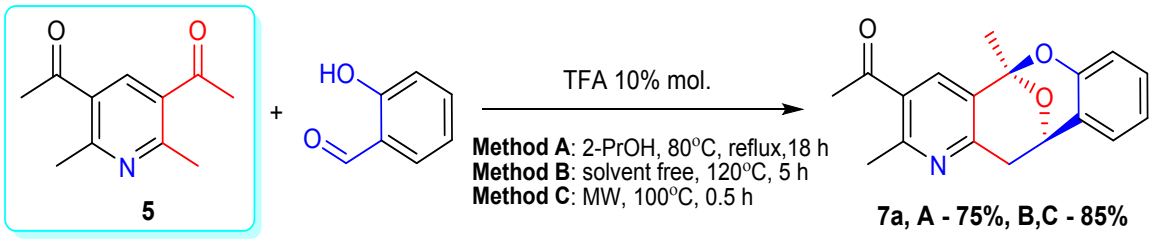
2-hydroxy-1-naphthaldehyde was prepared by following a literature procedure [36]

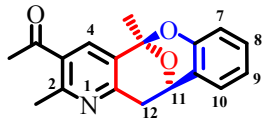
3.1 Synthesis of 11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridine 7a (solvent free)

Method B. 1.5 mmol of salicylic aldehyde and 10% (mol.) trifluoroacetic acid were added to 1.0 mmol of 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) **5**. The mixture without solvent was heated to 120 °C for 5 hours. After cooling up to 0 ^{0}C temperature, the formed precipitate was filtered, washed with cool 2-propanol and air-dried. The crude product was purified by recrystallization from 2-propanol.

Method C. 1.5 mmol of salicylic aldehyde and 10% (mol.) trifluoroacetic acid were added to 1.0 mmol of 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) **5**. The mixture was heated under microwave irradiation (in a Monowave 300 Anton Paar (Austria) apparatus) at 100°C for 30 min in a sealed 10-ml microwave vial. After cooling up to 0 ^{0}C temperature, the formed precipitate was filtered, washed with cool 2-propanol and air-dried. The crude product was purified by recrystallization from 2-propanol.

Scheme S1.





7a, 85%

Chemical Formula: $C_{18}H_{17}NO_3$
Molecular Weight: 295,338

1-(2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7a)

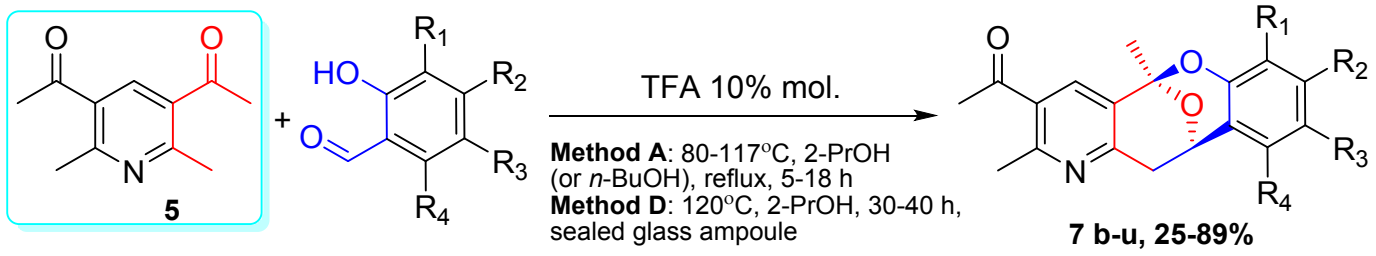
White crystals, 85% yield. M.p. 163-165 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.97 (s, 3H, 5-CH_3), 2.59 (s, 3H, C(O)CH_3), 2.66 (s, 3H, 2-CH_3), 3.05 (d, ^2J = 17.7 Hz, 1H, H-12a), 3.65 (dd, ^2J = 17.4 Hz, ^3J = 5.8 Hz, 1H, H-12b), 5.41 (d, ^3J = 5.5 Hz, 1H, H-11), 6.74 (d, ^3J = 7.3 Hz, 1H, H-7), 6.88 (td, ^3J = 7.6, ^4J = 1.2 Hz, 1H, H-9), 7.04 (dd, ^3J = 7.6, ^4J = 1.2 Hz, 1H, H-10), 7.10 (td, ^3J = 7.8, ^4J = 1.2 Hz, 1H, H-8), 7.98 (s, 1H, H-4). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.6, 26.1, 29.3, 39.4, 69.4, 96.3, 116.7, 121.2, 122.9, 125.6, 128.8, 129.3, 131.6, 134.4, 150.6, 154.8, 158.3, 199.7. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{18}NO_3^+$ $[M+H]^+$: 296.128; found: 296.354. MS (EI) m/z (I_{rel}, %): $[M]^+$ 295.15 (100), 280.13 (20), 252.08 (100), 210,14 (30), 135.10 (20). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74; found: C, 73.51; H, 5.37; N, 4.98.

3.2 Synthesis of 11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridines derivatives 7b-u

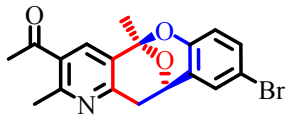
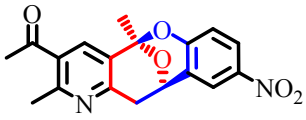
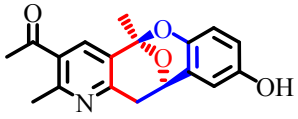
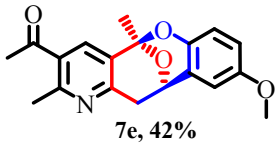
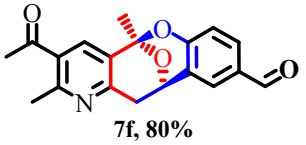
Method A. 1.0 mmol of the corresponding derivative of salicylic aldehyde and 10% (mol.) of TFA were added to 1.0 mmol of 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) **5**. The mixture was refluxed in 2-PrOH (or *n*-BuOH) for 5-18 hours (control by GC-MS). After cooling to room temperature, the precipitate was filtered, washed with cool 2-propanol and air-dried. The crude product was purified by recrystallization from 2-propanol.

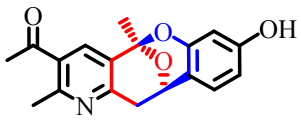
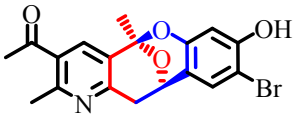
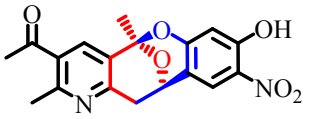
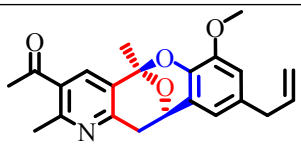
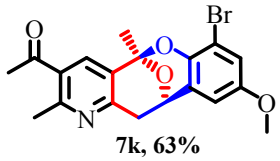
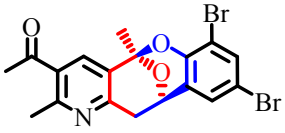
Method D. 1.0 mmol of the corresponding derivative of salicylic aldehyde and 10% (mol.) of TFA were added to 1.0 mmol of 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) **5**. The mixture in 1-5ml 2-PrOH was heated in a sealed glass ampoule to 120 ° C for 30-40 hours. After cooling up to 0 ^{0}C temperature, the ampoule was opened, the contents poured into ice–water mixture (50 ml), neutralized with NaOH (to pH 8-9). The resulting precipitate was filtered off, washed with cool 2-propanol, and dried. The crude product was purified by recrystallization from suitable solvent or column chromatography on silica gel.

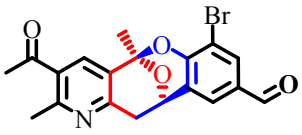
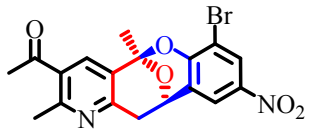
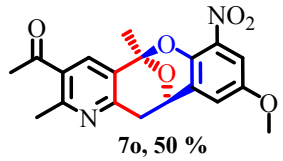
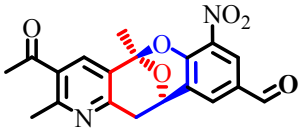
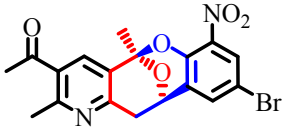
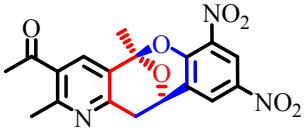
Scheme S2.

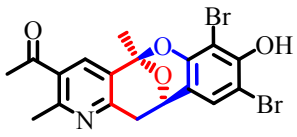
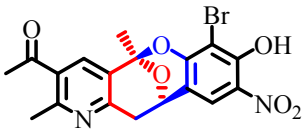
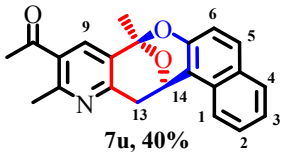


3.1 Characterization data of products 7b-u

 **7b, 63%** Chemical Formula: $C_{18}H_{16}BrNO_3$ Molecular Weight: 374,234	**1-(9-bromo-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7b)** Prepared from **5** and 5-bromo-2-hydroxybenzaldehyde following the method A. White crystals, 63% yield. M.p. 188-189 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.96 (s, 3H, 5-CH_3), 2.59 (s, 3H, C(O)CH_3), 2.67 (s, 3H, 2-CH_3), 3.03 (d, ^2J = 17.7 Hz, 1H, H-12a), 3.63 (dd, ^2J = 17.4 Hz, ^3J = 5.8 Hz, 1H, H-12b), 5.37 (d, ^3J = 5.5 Hz, 1H, H-11), 6.63 (d, ^3J = 7.9 Hz, 1H, H-7), 7.16-7.19 (m, 2H, H-8, H-10), 7.95 (s, 1H, H-4). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.6, 25.9, 29.4, 39.2, 69.0, 96.6, 113.3 (2C), 118.7, 124.9, 128.3, 128.9, 131.8, 134.3, 149.8, 154.4, 158.5, 199.6. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{17}NaBrNO_3^+$ [M+Na+H]$^+$: 397.028; found: 397.876. MS (EI) m/z (I_{rel}, %): [M]$^+$ 372.99 (64), [M+2]$^+$ 375.00 (58), 329.88 (58), 331.97 (44), 202.05 (46), 149.08 (36), 135.06 (65), 63.07 (36).
 **7c, 59%** Chemical Formula: $C_{18}H_{16}N_2O_5$ Molecular Weight: 340,335	**1-(2,5-dimethyl-9-nitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7c)** Prepared from **5** and 2-hydroxy-5-nitrobenzaldehyde following the method A. Beige crystals, 59% yield. M.p. 209-210 °C (2-PrOH-MeCN) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.99 (s, 3H, 5-CH_3), 2.58 (s, 3H, C(O)CH_3), 2.65 (s, 3H, 2-CH_3), 3.10 (d, ^2J = 18.3 Hz, 1H, H-12a), 3.68 (dd, ^2J = 18.3 Hz, ^3J = 4.6 Hz, 1H, H-12b), 5.48 (d, ^3J = 4.6 Hz, 1H, H-11), 6.82 (d, ^3J = 7.6 Hz, 1H, H-7), 7.95 (s, 1H, H-4), 7.98-8.01 (m, 1H, H-8), 8.01 (s, 1H, H-10). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.6, 25.7, 29.4, 38.9, 69.3, 97.7, 117.6, 122.1, 123.3, 124.8, 128.2, 132.0, 134.3, 141.5, 153.8, 156.2, 158.9, 199.5. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{17}N_2O_5^+$ [M+H]$^+$: 341.110; found: 341.395.
 **7d, 38%** Chemical Formula: $C_{18}H_{17}NO_4$ Molecular Weight: 311,337	**1-(9-hydroxy-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7d)** Prepared from **5** and 2,5-dihydroxybenzaldehyde following the method D. Beige crystals, 38% yield. M.p. 252-255 °C (2-PrOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.96 (s, 3H, 5-CH_3), 2.65 (s, 3H, C(O)CH_3), 2.86 (s, 3H, 2-CH_3), 3.23 (d, ^2J = 17.9 Hz, 1H, H-12a), 3.65 (dd, ^2J = 17.6 Hz, ^3J = 5.2 Hz, 1H, H-12b), 5.26 (d, ^3J = 5.2 Hz, 1H, H-11), 6.51 (d, ^4J = 2.2 Hz, 1H, H-10), 6.65 (d, ^3J = 8.8 Hz, 1H, H-7), 6.73 (dd, ^3J = 8.8, ^4J = 2.5 Hz, 1H, H-8), 8.23 (s, 1H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 25.3, 26.0, 29.3, 37.0, 68.2, 95.3, 111.6, 116.2, 117.4, 122.4, 128.6, 131.0, 133.5, 142.8, 151.7, 153.6, 156.5, 199.0. MS (EI) m/z (I_{rel}, %): [M]$^+$ 311.13 (58), 310.13 (17), 268.10 (43), 77.04 (18), 58.10 (20), 44.02 (86), 43.05 (98). Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50; found: C, 69.59; H, 5.33; N, 4.70.
 **7e, 42%** Chemical Formula: $C_{19}H_{19}NO_4$ Molecular Weight: 325,364	**1-(9-methoxy-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7e)** Prepared from **5** and 2-hydroxy-5-methoxybenzaldehyde following the method D. White crystals, 42% yield. M.p. 258-260 °C (SiO_2, acetone/hexane1:8). ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 1.92 (s, 3H, 5-CH_3), 2.50 (s, 3H, C(O)CH_3), 2.57 (s, 3H, 2-CH_3), 3.02 (d, ^2J = 17.4 Hz, 1H, H-12a), 3.50 (dd, ^2J = 17.6 Hz, ^3J = 5.7 Hz, 1H, H-12b), 3.64 (s, 3H, OCH_3), 5.41 (d, ^3J = 5.3 Hz, 1H, H-11), 6.63 (d, ^3J = 8.8 Hz, 1H, H-7), 6.65 (d, ^3J = 8.8 Hz, 1H, H-7), 6.67 (dd, ^3J = 8.8, ^4J = 2.8 Hz, 1H, H-8), 6.81 (d, J = 2.8 Hz, 1H, H-10), 8.25 (s, 1H, H-4). ^{13}C NMR (126 MHz, DMSO-d_6) δ ppm 23.8, 25.7, 29.7, 38.8, 55.3, 68.7, 96.3, 110.3, 115.0, 116.9, 123.8, 129.0, 131.8, 134.4, 144.0, 153.3, 154.3, 156.8, 200.6. MS (EI) m/z (I_{rel}, %): [M]$^+$ 325.09 (100), 310.06 (43), 282.07 (79), 42.96 (52). Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31; found: C, 70.39; H, 5.70; N, 4.16.
 **7f, 80%** Chemical Formula: $C_{19}H_{17}NO_4$ Molecular Weight: 323,348	**3-acetyl-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridine-9-carbaldehyde (7f)** Prepared from **5** and 4-hydroxyisophthalaldehyde following the method A. Yellow crystals, 80% yield. M.p. 185-187 °C (SiO_2, EtOAc/hexane 1:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.01 (s, 3H, 5-CH_3), 2.61 (s, 3H, C(O)CH_3), 2.69 (s, 3H, 2-CH_3), 3.16 (d, ^2J = 17.4 Hz, 1H, H-12a), 3.71 (dd, ^2J = 17.5 Hz, ^3J = 5.6 Hz, 1H, H-12b), 5.50 (d, ^3J = 5.5 Hz, 1H, H-11), 6.88 (d, ^3J = 8.8 Hz, 1H, H-7), 7.63 (d, ^4J = 2.0 Hz, 1H, H-10), 7.66 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1H, H-8), 8.00 (s, 1H, H-4), 9.82 (s, 1H, CHO). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 24.3, 25.8, 29.4, 38.8, 69.3, 97.2, 117.7, 123.4, 127.9, 128.9, 130.2, 130.9, 132.1, 134.6, 154.0, 156.0, 158.5, 190.4, 199.3. MS (EI) m/z (I_{rel}, %): [M]$^+$ 323.11 (100), 322.06 (23), 308.06 (20), 280.06 (54), 202.06 (15), 135.06 (14), 43.01 (69). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33; found: C, 70.74; H, 5.11; N, 4.15.

 **7g, 50%** Chemical Formula: $C_{18}H_{17}NO_4$ Molecular Weight: 311,337	**1-(8-hydroxy-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7g)** Prepared from **5** and 2,4-dihydroxybenzaldehyde following the method A. White crystals, 50% yield. M.p. 234-235 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.95 (s, 3H, 5-CH_3), 2.60 (s, 3H, C(O)CH_3), 2.67 (s, 3H, 2-CH_3), 3.00 (d, ^2J = 16.9 Hz, 1H, H-12a), 3.61 (dd, ^2J = 17.4 Hz, ^3J = 5.5 Hz, 1H, H-12b), 4.83 (s, 1H, OH), 5.36 (d, ^3J = 5.0 Hz, 1H, H-11), 6.23 (d, ^4J = 2.3 Hz, 1H, H-7), 6.38 (dd, ^3J = 8.2, ^4J= 2.3 Hz, 1H, H-9), 6.89 (d, ^3J = 8.2 Hz, 1H, H-10), 7.97 (s, 1H, H-4). ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 24.0, 25.8, 29.9, 38.9, 68.6, 96.4, 102.5, 109.1, 114.0, 126.9, 129.3, 131.9, 134.6, 151.3, 154.7, 157.1, 157.8, 200.9. MS (EI) m/z (I_{rel}, %): [M]$^+$ 311.56 (80), 310.55 (20), 296.50 (20), 268.40 (100), 226.30 (27), 135.06 (20), 42.91 (47). Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50; found: C, 69.27; H, 5.76; N, 4.29.
 **7h, 55%** Chemical Formula: $C_{18}H_{16}BrNO_4$ Molecular Weight: 390,233	**1-(9-bromo-8-hydroxy-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7h)** Prepared from **5** and 5-bromo-2,4-dihydroxybenzaldehyde following the method A. White crystals, 55% yield. M.p. 254-256 °C (2-PrOH/acetone). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.95 (s, 3H, 5-CH_3), 2.59 (s, 3H, C(O)CH_3), 2.68 (s, 3H, 2-CH_3), 2.99 (d, ^2J = 17.4 Hz, 1H, H-12a), 3.61 (dd, ^2J = 17.2 Hz, ^3J = 5.3 Hz, 1H, H-12b), 5.34 (d, ^3J = 5.1 Hz, 1H, H-11), 5.39 (s, 1H, OH), 6.43 (s, 1H, H-7), 7.13 (s, 1H, H-10), 7.95 (s, 1H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 24.6, 26.0, 29.4, 39.5, 68.9, 96.7, 102.2, 104.3, 117.1, 128.3, 129.0, 131.9, 134.3, 151.6, 152.4, 154.6, 158.5, 199.6. MS (EI) m/z (I_{rel}, %): [M]$^+$ 389.04 (40), [M+2]$^+$ 391.03 (40), 348.00 (33), 345.99 (36), 202.09 (18), 43.03 (100). Anal. Calcd for $C_{18}H_{16}BrNO_4$: C, 55.40; H, 4.13; N, 3.59; found: C, 55.67; H, 4.35; N, 3.37.
 **7i, 58%** Chemical Formula: $C_{18}H_{16}N_2O_6$ Molecular Weight: 356,334	**1-(8-hydroxy-2,5-dimethyl-9-nitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7i)** Prepared from **5** and 2,4-dihydroxy-5-nitrobenzaldehyde following the method A. Yellow crystals, 58% yield. M.p. 218-219 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.00 (s, 3H, 5-CH_3), 2.61 (s, 3H, C(O)CH_3), 2.68 (s, 3H, 2-CH_3), 3.06 (d, ^2J = 17.4 Hz, 1H, H-12a), 3.67 (dd, ^2J = 17.4 Hz, ^3J = 5.5 Hz, 1H, H-12b), 5.44 (d, ^3J = 5.5 Hz, 1H, H-11), 6.46 (s, 1H, H-7), 7.90 (s, 1H, H-10), 7.95 (s, 1H, H-4), 10.65 (s, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.7, 25.6, 29.4, 39.1, 69.0, 97.9, 105.9, 116.5, 123.3, 128.3 (2 C), 132.0, 134.3, 153.8, 156.2, 158.8, 159.0, 199.4. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{17}N_2O_6^+$ [M+H]$^+$: 357.330; found: 357.519.
 **7j, 25%** Chemical Formula: $C_{22}H_{23}NO_4$ Molecular Weight: 365,429	**1-(9-allyl-7-methoxy-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7j)** Prepared from **5** and 5-allyl-2-hydroxy-3-methoxybenzaldehyde following the method A. Yellow crystals, 25% yield. M.p. 164-167 °C (2-PrOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.04 (s, 3H, 5-CH_3), 2.61 (s, 3H, C(O)CH_3), 2.76 (s, 3H, 2-CH_3), 3.25 (br.d, ^2J = 6.6 Hz, 3H, H-12a, CH_2), 3.68 (dd, ^2J = 17.7 Hz, ^3J = 5.6 Hz, 1H, H-12b), 3.79 (s, 3H, OCH_3), 5.03-5.09 (m, 2H, =CH_2), 5.38 (d, ^3J = 5.5 Hz, 1H, H-11), 5.87 (ddt, J = 17.1, 10.3, 6.8 Hz, 1H, -C<u>H</u>=CH_aH_b), 6.48 (d, ^4J = 1.3 Hz, 1H, H-8), 6.53 (d, ^4J = 1.5 Hz, 1H, H-10), 8.17 (s, 1H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 23.4, 26.2, 29.3, 38.3, 39.8, 55.8, 68.9, 96.2, 111.1, 116.1, 116.9, 123.0, 130.4, 132.1, 133.1, 135.9, 137.0, 138.1, 147.7, 154.2, 157.8, 198.7. MS (EI) m/z (I_{rel}, %): [M]$^+$ 365.18 (100), 350.14 (19), 322.12 (51), 202.08 (14), 42.97 (61). Anal. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83; found: C, 72.13; H, 6.55; N, 3.99.
 **7k, 63%** Chemical Formula: $C_{19}H_{18}BrNO_4$ Molecular Weight: 404,260	**1-(7-bromo-9-methoxy-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7k)** Prepared from **5** and 3-bromo-2-hydroxy-5-methoxybenzaldehyde following the method A. Yellow crystals, 63% yield. M.p. 160-161 °C (2-PrOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.02 (s, 3H, 5-CH_3), 2.60 (s, 3H, C(O)CH_3), 2.70 (s, 3H, 2-CH_3), 3.10 (d, ^2J = 17.6 Hz, 1H, H-12a), 3.65 (dd, ^2J = 17.4 Hz, ^3J = 5.5 Hz, 1H, H-12b), 3.70 (s, 3H, OCH_3), 5.37 (d, ^3J = 5.3 Hz, 1H, H-11), 6.54 (d, ^4J = 2.8 Hz, 1H, H-10), 6.93 (d, ^4J = 2.8 Hz, 1H, H-8), 8.03 (s, 1H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 24.1, 26.0, 29.4, 39.0, 55.8, 69.3, 97.0, 109.9, 110.7, 118.4, 124.5, 129.6, 132.1, 134.9, 141.7, 153.9, 154.1, 158.3, 199.2. MS (EI) m/z (I_{rel}, %): [M]$^+$ 403.05 (35), [M+2]$^+$ 405.04 (33), 362.02 (27), 359.99 (30), 201.98 (18), 42.98 (100). Anal. Calcd for $C_{19}H_{18}BrNO_4$: C, 56.45; H, 4.49; N, 3.46; found: C, 56.28; H, 4.68; N, 3.66.
 **7l, 65%** Chemical Formula: $C_{18}H_{15}Br_2NO_3$ Molecular Weight: 453,130	**1-(7,9-dibromo-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7l)** Prepared from **5** and 3,5-dibromo-2-hydroxybenzaldehyde following the method A. Beige crystals, 65% yield. M.p. 210-211 °C (2-PrOH/$CHCl_3$ 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.01 (s, 3H, 5-CH_3), 2.58 (s, 3H, C(O)CH_3), 2.65 (s, 3H, 2-CH_3), 3.01 (d, ^2J = 16.8 Hz, 1H, H-12a), 3.63 (dd, ^2J = 16.8 Hz, ^3J = 6.1 Hz, 1H, H-12b), 5.36 (d, ^3J = 6.1 Hz, 1H, H-11), 7.11 (s, 1H, H-10), 7.45 (s, 1H, H-8), 7.96 (s, 1H, H-4). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.6, 25.8, 29.4, 39.1, 69.1, 97.7, 111.7, 113.2, 126.0, 127.4, 128.6, 131.9, 134.3, 134.6, 147.2, 154.0, 158.8, 199.5. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{16}Br_2NO_3^+$ [M+H]$^+$: 454.950; found: 454.548.

 **7m, 80%** Chemical Formula: $C_{19}H_{16}BrNO_4$ Molecular Weight: 402,244	**3-acetyl-7-bromo-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridine-9-carbaldehyde (7m)** Prepared from **5** and 5-bromo-4-hydroxyisophthalaldehyde following the method A. Yellow crystals, 80% yield. M.p. 185-187 °C (SiO_2, acetone/hexane 1:8). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.09 (s, 3H, 5-CH_3), 2.62 (s, 3H, C(O)CH_3), 2.70 (s, 3H, 2-CH_3), 3.16 (d, ^2J = 17.6 Hz, 1H, H-12a), 3.74 (dd, ^2J = 17.6 Hz, ^3J = 5.4 Hz, 1H, H-12b), 5.51 (d, ^3J = 5.4 Hz, 1H, H-11), 7.58 (s, 1H, H-10), 7.89 (s, 1H, H-8), 8.04 (s, 1H, H-4), 9.78 (s, 1H, CHO). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 24.2, 25.6, 29.4, 38.6, 69.3, 98.4, 111.9, 124.8, 126.5, 128.7, 130.7, 132.3, 134.0, 134.8, 152.9, 153.6, 158.8, 189.2, 199.1. MS (EI) m/z (I_{rel}, %): $[M]^+$ 401.03 (37), $[M+2]^+$ 403.03 (37), 360.01 (14), 358.01 (17), 202.08 (22), 135.05 (18), 42.99 (100). Anal. Calcd for $C_{19}H_{16}BrNO_4$: C, 56.73; H, 4.01; N, 3.48; found: C, 56.94; H, 4.29; N, 3.19.
 **7n, 80%** Chemical Formula: $C_{18}H_{15}BrN_2O_5$ Molecular Weight: 419,231	**1-(7-bromo-2,5-dimethyl-9-nitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7n)** Prepared from **5** and 3-bromo-2-hydroxy-5-nitrobenzaldehyde following the method A. White crystals, 80% yield. M.p. 225-230 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.10 (s, 3H, 5-CH_3), 2.62 (s, 3H, C(O)CH_3), 2.68 (s, 3H, 2-CH_3), 3.13 (d, ^2J = 16.8 Hz, 1H, H-12a), 3.74 (dd, ^2J = 16.8 Hz, ^3J = 6.1 Hz, 1H, H-12b), 5.53 (d, ^3J = 6.1 Hz, 1H, H-11), 8.00 (s, 2H, H-4, H-10), 8.29 (s, 1H, H-8). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.6, 25.6, 29.5, 38.8, 69.4, 98.9, 111.3, 120.7, 124.4, 127.9, 128.1, 132.2, 134.2, 141.3, 153.4, 153.5, 159.2, 199.4. MS (EI) m/z (I_{rel}, %): $[M]^+$ 417.91 (17), $[M+2]^+$ 420.04 (14), 207.00 (23), 135.05 (20), 79.01 (25), 73.09 (27), 44.04 (42), 43.08 (100). Anal. Calcd for $C_{18}H_{15}BrN_2O_5$: C, 51.57; H, 3.61; Br, 19.06; N, 6.68; found: C, 51.41; H, 3.74; Br, 19.17; N, 6.47.
 **7o, 50 %** Chemical Formula: $C_{19}H_{18}N_2O_6$ Molecular Weight: 370,361	**1-(9-methoxy-2,5-dimethyl-7-nitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]-oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7o)** Prepared from **5** and 2-hydroxy-5-methoxy-3-nitrobenzaldehyde following the method A. Yellow crystals, 50% yield. M.p. 208-210 °C (2-PrOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.03 (s, 3H, 5-CH_3), 2.60 (s, 3H, C(O)CH_3), 2.67 (s, 3H, 2-CH_3), 3.04 (d, ^2J = 17.4 Hz, 1H, H-12a), 3.68 (dd, ^2J = 17.4 Hz, ^3J = 5.5 Hz, 1H, H-12b), 3.76 (s, 3H, OCH_3), 5.45 (d, ^3J = 5.3 Hz, 1H, H-11), 6.87 (d, ^4J = 2.9 Hz, 1H, H-10), 7.29 (d, ^4J = 3.1 Hz, 1H, H-8), 8.00 (s, 1H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 24.6, 25.8, 29.3, 39.2, 56.0, 69.5, 97.6, 109.5, 117.4, 126.6, 128.4, 132.0, 134.6, 138.1, 139.6, 152.5, 153.9, 159.0, 199.5. MS (EI) m/z (I_{rel}, %): $[M]^+$ 370.16 (81), 353.18 (32), 352.17 (57), 323.16 (57), 322.14 (72), 280.13 (25), 251.13 (14), 238.13 (14), 43.01 (100). Anal. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.62; H, 4.90; N, 7.56; found: C, 61.88; H, 4.66; N, 7.81.
 **7p, 60%** Chemical Formula: $C_{19}H_{16}N_2O_6$ Molecular Weight: 368,345	**3-acetyl-2,5-dimethyl-7-nitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridine-9-carbaldehyde (7p)** Prepared from **5** and 4-hydroxy-5-nitroisophthalaldehyde following the method A. Yellow crystals, 60% yield. M.p. 215-218 °C (2-PrOH/acetone 5:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 2.09 (s, 3H, 5-CH_3), 2.51 (s, 3H, C(O)CH_3), 2.60 (s, 3H, 2-CH_3), 3.16 (d, ^2J = 17.9 Hz, 1H, H-12a), 3.65 (dd, ^2J = 17.9 Hz, ^3J = 5.5 Hz, 1H, H-12b), 5.82 (d, ^3J = 5.4 Hz, 1H, H-11), 8.21 (d, ^4J = 1.5 Hz, 1H, H-10), 8.34 (d, ^4J = 1.7 Hz, 1H, H-8), 8.36 (s, 1H, H-4), 9.88 (s, 1H, CHO). ^{13}C NMR (126 MHz, DMSO-d_6) δ ppm 23.8, 25.1, 29.8, 38.1, 68.8, 99.3, 126.4, 126.7, 127.1, 128.5, 131.4, 132.3, 134.7, 138.0, 148.8, 153.4, 157.8, 190.3, 200.6. MS (EI) m/z (I_{rel}, %): $[M]^+$ 368.10 (48), 351.06 (47), 350.05 (100), 321.09 (63), 320.08 (47), 207.01 (43), 202.09 (25), 178.07 (31), 152.09 (24), 135.06 (35), 77.02 (25), 63.06 (24). Anal. Calcd for $C_{19}H_{16}N_2O_6$: C, 61.96; H, 4.38; N, 7.61; found: C, 61.67; H, 4.54; N, 7.46.
 **7q, 56%** Chemical Formula: $C_{18}H_{15}BrN_2O_5$ Molecular Weight: 419,231	**1-(9-bromo-2,5-dimethyl-7-nitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7q)** Prepared from **5** and 5-bromo-2-hydroxy-3-nitrobenzaldehyde following the method A. White crystals, 56% yield. M.p. 218-220 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.07 (s, 3H, 5-CH_3), 2.59 (s, 3H, C(O)CH_3), 2.65 (s, 3H, 2-CH_3), 3.10 (d, ^2J = 18.3 Hz, 1H, H-12a), 3.71 (dd, ^2J = 17.5 Hz, ^3J = 5.3 Hz, 1H, H-12b), 5.50 (d, ^3J = 6.1 Hz, 1H, H-11), 7.98 (s, 2H, H-4, H-10), 8.26 (s, 1H, H-8). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.6, 25.5, 29.4, 38.8, 69.4, 98.9, 111.3, 120.7, 124.4, 127.9, 128.1, 132.2, 134.2, 141.3, 153.4, 153.5, 159.2, 199.4. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{16}BrN_2O_5^+$ $[M+H]^+$: 421.018; found: 421.572.
 **7r, 75%** Chemical Formula: $C_{18}H_{15}N_3O_7$ Molecular Weight: 385,332	**1-(2,5-dimethyl-7,9-dinitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7r)** Prepared from **5** and 2-hydroxy-3,5-dinitrobenzaldehyde following the method A. Yellow crystals, 75% yield. M.p. 196-198 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.08 (s, 3H, 5-CH_3), 2.48 (s, 3H, C(O)CH_3), 2.57 (s, 3H, 2-CH_3), 3.22 (d, ^2J = 16.8 Hz, 1H, H-12a), 3.65 (dd, ^2J = 16.8 Hz, ^3J = 6.1 Hz, 1H, H-12b), 5.82 (d, ^3J = 4.6 Hz, 1H, H-11), 8.38 (s, 1H, H-4), 8.58 (d, ^4J = 3.1 Hz, 1H, H-10), 8.64 (d, ^4J = 3.1 Hz, 1H, H-8). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 23.8, 25.0, 29.9, 37.8, 69.0, 99.9, 120.8, 126.6, 126.9, 126.9, 132.4, 135.1, 137.3, 139.6, 149.3, 153.3, 157.9, 200.7. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{16}N_3O_7^+$ $[M+H]^+$: 386.330; found: 386.576.

 **7s, 60%** Chemical Formula: $C_{18}H_{15}Br_2NO_4$ Molecular Weight: 469,129	**1-(7,9-dibromo-8-hydroxy-2,5-dimethyl-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7s)** Prepared from **5** and 3,5-dibromo-2,4-dihydroxybenzaldehyde following the method A. Yellow crystals, 60% yield. M.p. 235-240 °C (2-PrOH/dioxane 5:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.03 (s, 3H, 5-CH_3), 2.60 (s, 3H, C(O)CH_3), 2.68 (s, 3H, 2-CH_3), 3.01 (d, ^2J = 16.8 Hz, 1H, H-12a), 3.65 (dd, ^2J = 17.5 Hz, ^3J = 5.3 Hz, 1H, H-12b), 5.38 (d, ^3J = 4.6 Hz, 1H, H-11), 6.02 (br. s, 1H, OH), 7.17 (s, 1H, H-10), 7.98 (s, 1H, H-4). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.6, 25.8, 29.4, 39.2, 68.8, 97.7, 99.0, 101.2, 117.4, 127.5, 128.7, 131.9, 134.2, 148.1, 149.5, 154.2, 158.7, 199.6. MS (MALDI-TOF) m/z: calcd for $C_{18}H_{16}Br_2NO_4^+$ $[M+H]^+$: 469.942; found: 470.547.
 **7t, 89%** Chemical Formula: $C_{18}H_{15}BrN_2O_6$ Molecular Weight: 435,230	**1-(7-bromo-8-hydroxy-2,5-dimethyl-9-nitro-11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-3-yl)ethan-1-one (7t)** Prepared from **5** and 3-bromo-2,4-dihydroxy-5-nitrobenzaldehyde following the method A. Yellow crystals, 89% yield. M.p. 226-228 °C (2-PrOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 2.08 (s, 3H, 5-CH_3), 2.51 (s, 3H, C(O)CH_3), 2.60 (s, 3H, 2-CH_3), 3.11 (d, ^2J = 17.9 Hz, 1H, H-12a), 3.65 (dd, ^2J = 18.0 Hz, ^3J = 5.5 Hz, 1H, H-12b), 5.63 (d, ^3J = 5.4 Hz, 1H, H-11), 8.18 (s, 1H, H-10), 8.32 (s, 1H, H-4). ^{13}C NMR (126 MHz, DMSO-d_6) δ, ppm 23.5, 25.2, 29.8, 38.1, 68.1, 98.9, 100.2, 116.1, 122.7, 127.9, 130.3, 132.4, 134.6, 151.0, 153.2, 154.1, 157.4, 200.4. Anal. Calcd for $C_{18}H_{15}BrN_2O_6$: C, 49.67; H, 3.47; N, 6.44; found: C, 49.97; H, 3.73; N, 6.21.
 **7u, 40%** Chemical Formula: $C_{22}H_{19}NO_3$ Molecular Weight: 345,398	**1-(8,11-dimethyl-13,14-dihydro-8*H*-8,14-epoxynaphtho[1',2':7,8]oxocino[4,3-*b*]pyridin-10-yl)ethan-1-one (7u)** Prepared from **5** and 2-hydroxy-1-naphthaldehyde following the method A. White crystals, 40% yield. M.p. 176-178 °C (2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.03 (s, 3H, 5-CH_3), 2.57 (s, 3H, C(O)CH_3), 2.61 (s, 3H, 2-CH_3), 3.40 (d, ^2J = 17.4 Hz, 1H, H-13a), 3.75 (dd, ^2J = 17.4 Hz, ^3J = 5.8 Hz, 1H, H-13b), 5.89 (d, ^3J = 5.5 Hz, 1H, H-14), 6.94 (d, ^3J = 8.9 Hz, 1H, H-6), 7.34 (t, ^3J = 7.4 Hz, 1H, H-2), 7.51 (t, ^3J = 7.4 Hz, 1H, H-3), 7.61 (d, ^3J = 9.0 Hz, 1H, H-5), 7.65 (d, ^3J = 8.5 Hz, 1H, H-4), 7.72 (d, ^3J = 8.1 Hz, 1H, H-1), 8.01 (s, 1H, H-9). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 24.5, 26.0, 29.3, 37.7, 67.9, 96.4, 114.4, 118.1, 121.0, 123.8, 127.1, 128.9 (2C), 129.2, 129.5, 130.0, 131.8, 134.2, 148.3, 154.9, 158.2, 199.6. MS (MALDI-TOF) m/z: calcd for $C_{22}H_{20}NO_3^+$ $[M+H]^+$: 346.400; found: 346.494.

3.3 Reaction Optimization

Table S1. Reaction conditions and conversion of pyridine **5** to oxocine **7a** in various solvents using 1.2 equiv. salicylic aldehyde

Entry	Solvent	Catalyst, 10 mol. %	T (°C)	t (h)	Conversion, %*
1	2-propanol / or ethanol	TFA	80	0.5	1.0
2	2-propanol	TFA	80	0.75	2.0
3	2-propanol	TFA	80	2	35.0
4	2-propanol	TFA	80	7	59.2
5	2-propanol	TFA	80	14	73.8
6	2-propanol	TFA	80	19	82
7	2-propanol	HCl	80	11	79
8	2-propanol	HCl	80	18	85
9	DMF	TFA	100	5	22.5
10	DMF	TFA	100	10	36
11	DMF	TFA	100	20	61
12	dioxane	TFA	100	5	3.2
13	dioxane	TFA	100	10	8
14	dioxane	TFA	100	20	27.7
15	toluene	TFA	110	5	17
16	toluene	TFA	110	10	29.5
17	toluene	TFA	110	20	58
18	acetonitrile	TFA	82	5	0.5
19	acetonitrile	TFA	82	10	1.7
20	acetonitrile	TFA	82	30	7
21	THF	TFA	66	5	0.8
22	THF	TFA	66	10	2.5
23	THF	TFA	66	30	51
24	chloroform	TFA	61	5	3
25	chloroform	TFA	61	10	5.1
26	chloroform	TFA	61	30	11.1
27	hexane	TFA	68	5	2
28	hexane	TFA	68	10	5.5
29	hexane	TFA	68	30	46.4
30	2-propanol	-	80	25	5.4 (+ 3.7% of

					chalcone)
31	ethanol	1.5 eq NaOH	25	2	1.5
32	ethanol	3.0 eq NaOH	25	2	40

* Determined by Gas chromatography–mass spectrometry (GC-MS) of the reaction mixture

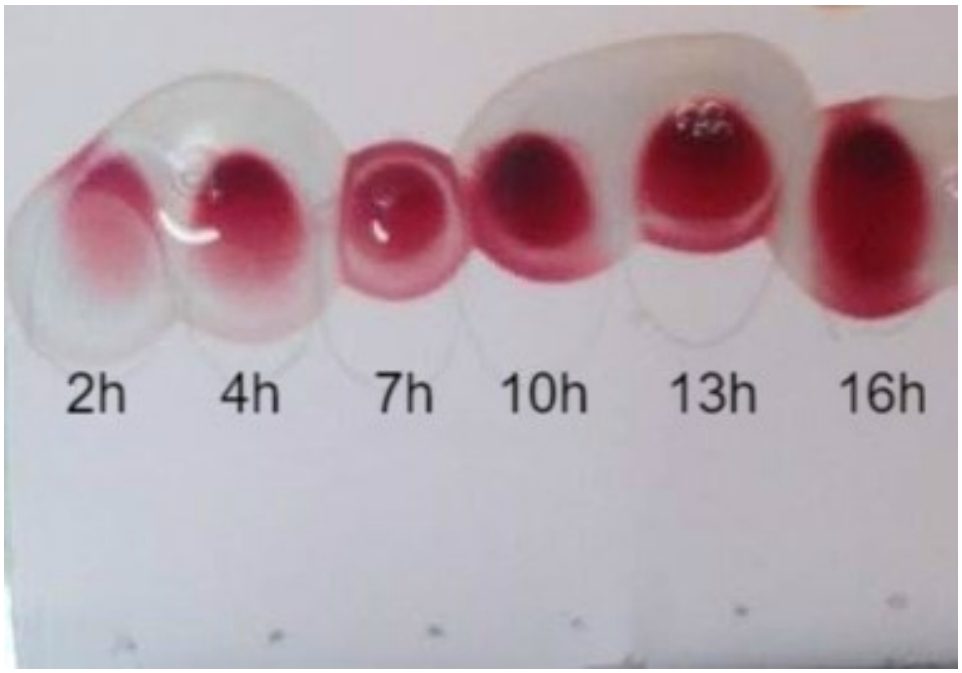


Figure S1. Control of the reaction by TLC using Marquis reagent*[a]

* conc. H_2SO_4 with addition of formalin in a ratio of 10:1.
[a] Reaction condition: EtOH, HCl (catalyst), 16-20 hours

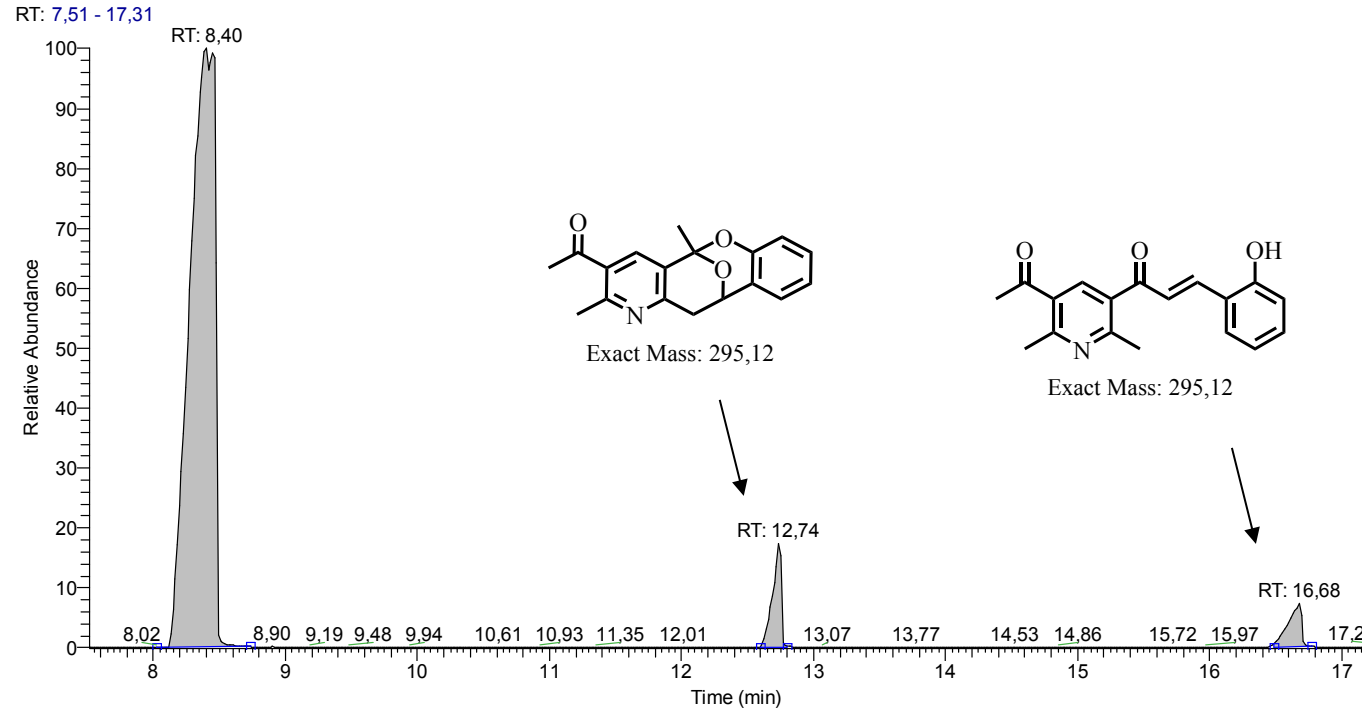


Figure S2. Fragment of the chromatogram of the reaction mixture (in the absence of a catalyst)

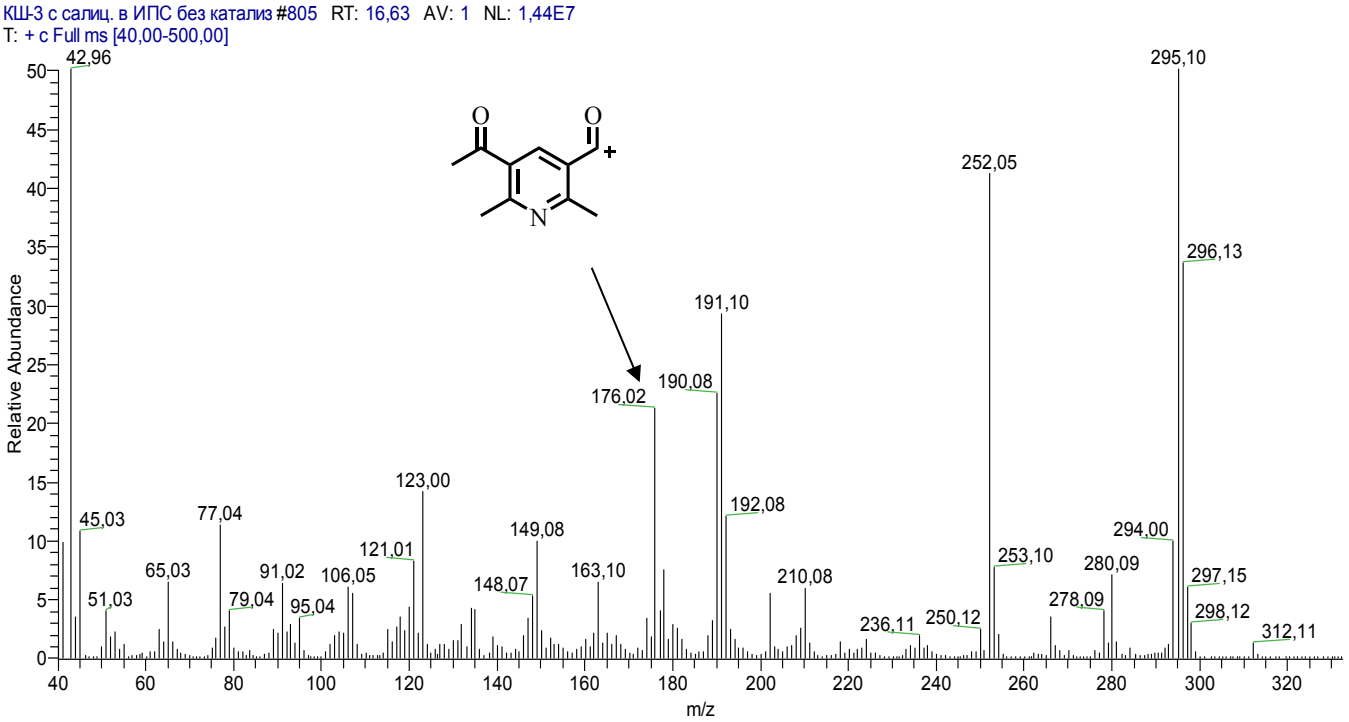


Figure S3. Mass Spectrum of the reaction mixture (t_R = 16,63 min)

Table S2. Solvent-free reaction of pyridine **5** with salicylic aldehyde [a]

entry	temp (˚C)	t (h)	Conversion, % [b]
1	90	0,75	14.5
2	90	4	70.8
3	90	6	74.6
4	90	10	87.5
5	110	2.5	87.1
6	110	4.0	88.8
7	120	0.5	11.8
8	120	2.0	82.1
9	120	4.0	97.2
10	120	5.0	100
11	100 (MW)[c]	0.5	99

[a] Reaction conditions: **5** (1.0 equiv.), salicylic aldehyde (1.5 equiv.), trifluoroacetic acid (10 mol%).
[b] Conversion of pyridine **5** by GC-MS data.
[c] was heated under microwave irradiation (in a Monowave 300 Anton Paar (Austria) apparatus) at 100°C for 30 min in a sealed 10-ml microwave vial.

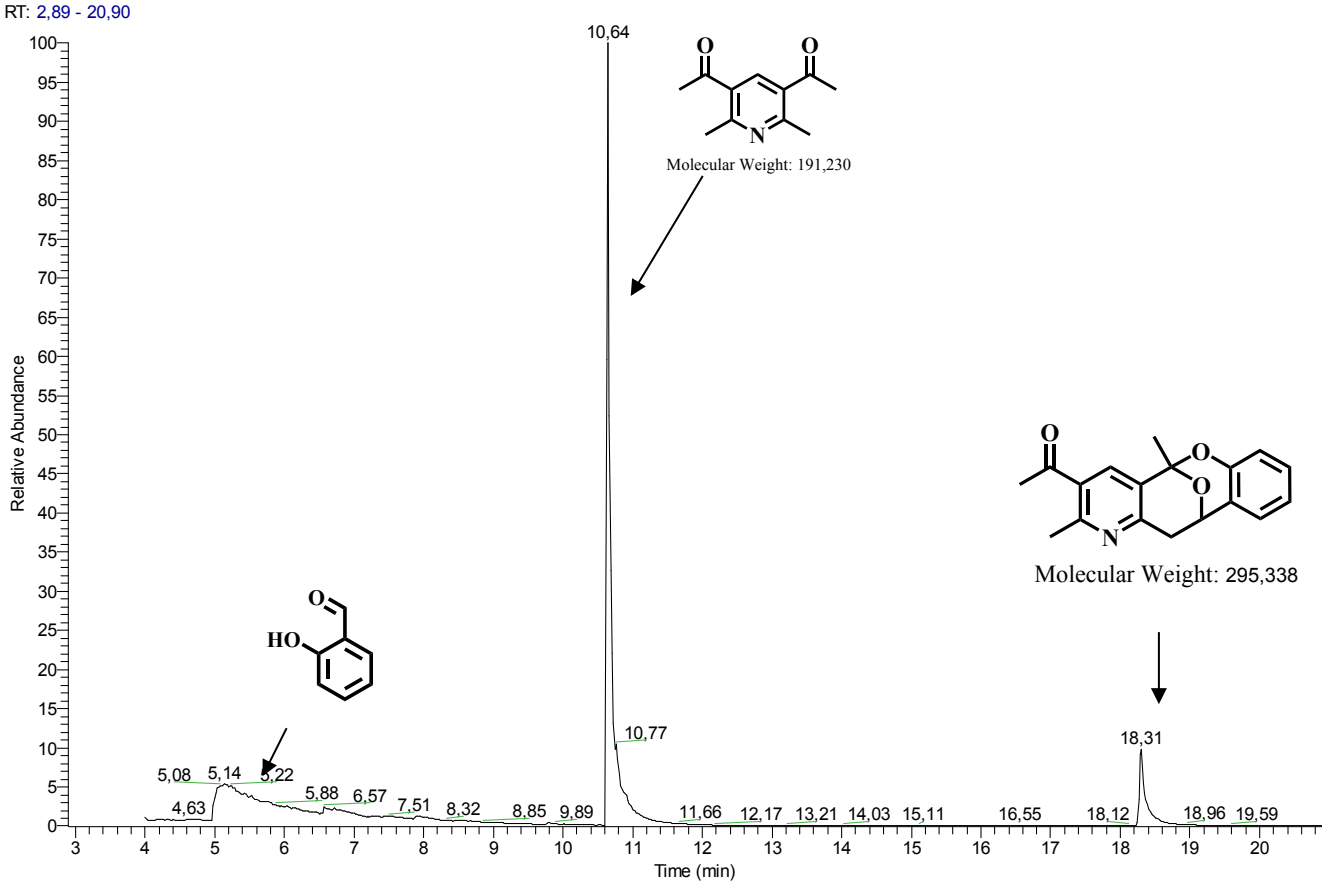


Figure S4. Chromatogram of the reaction mixture after 30 min (solvent free, TFA (10 mol. %), 120°C)

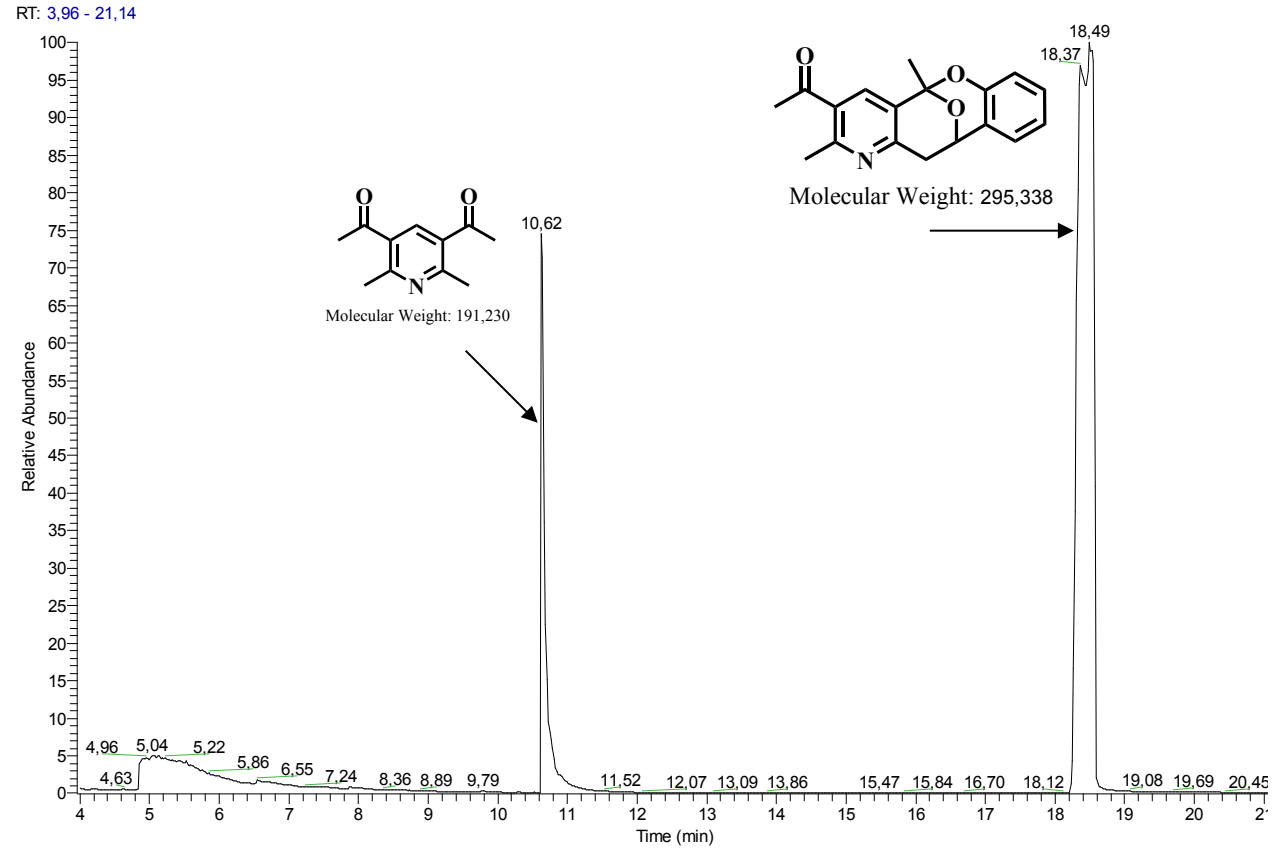


Figure S5. Chromatogram of the reaction mixture after 2 hours (solvent free, TFA (10 mol. %), 120°C)

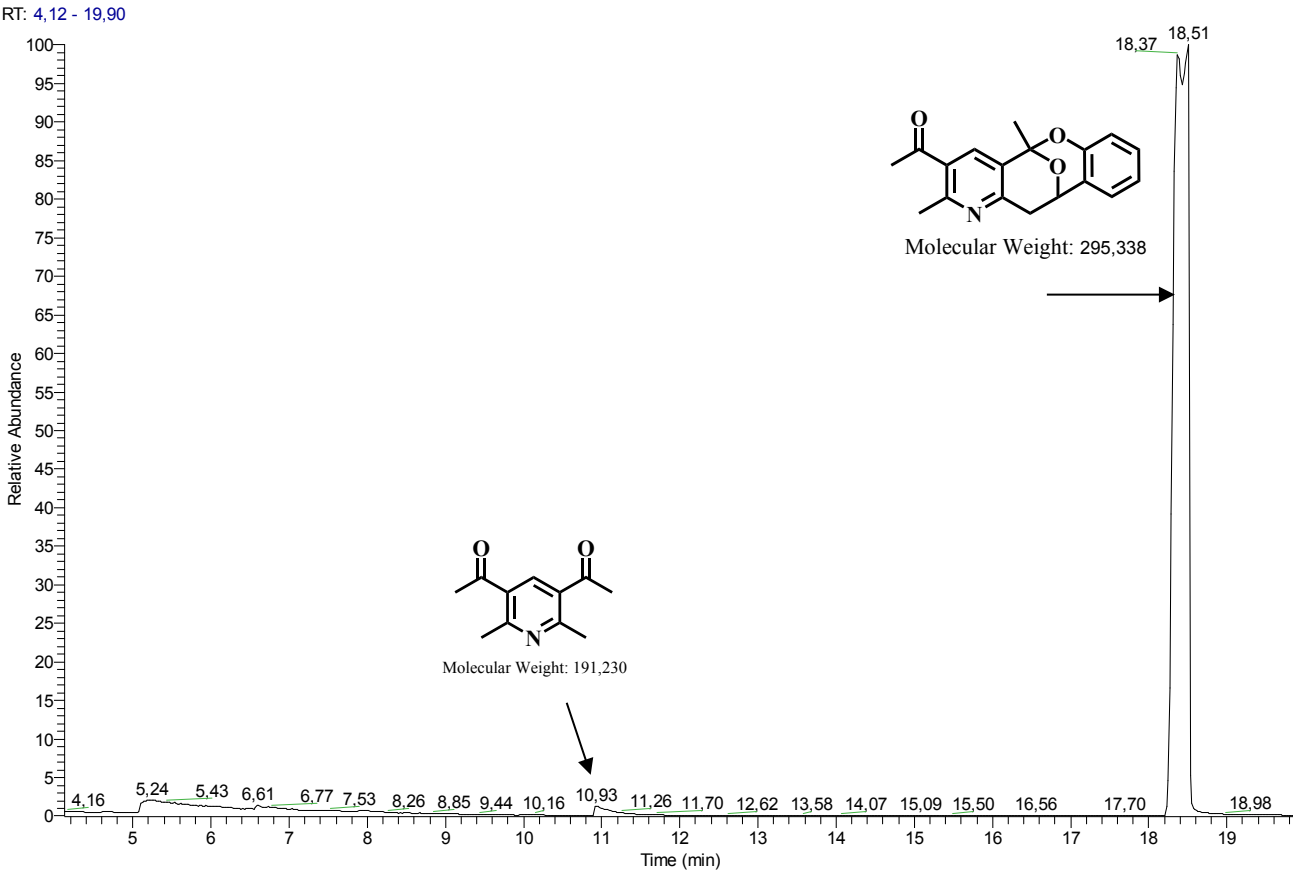
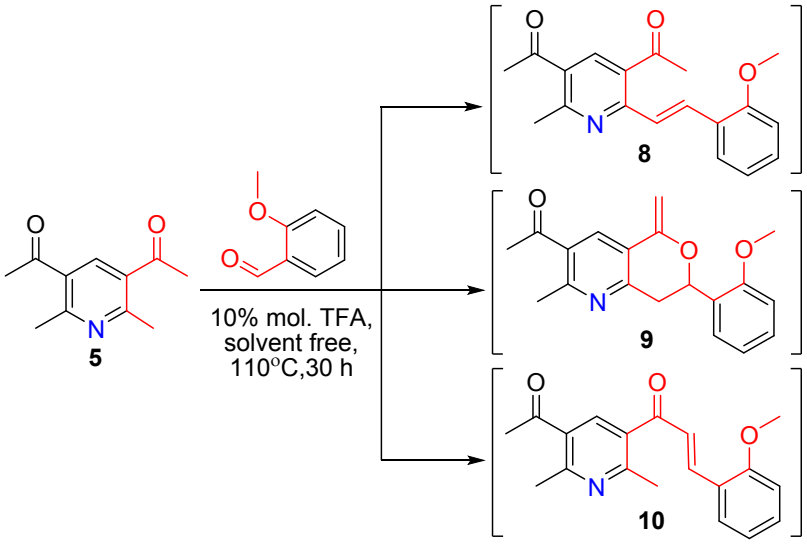


Figure S6. Chromatogram of the reaction mixture after 4 hours (solvent free, TFA (10 mol. %), 120°C)

3.4 Mechanistic Investigation



Exact Mass: 309,136

Scheme S3. Mechanistic investigation by the example of the interaction of pyridine **5** with 2-methoxybenzaldehyde

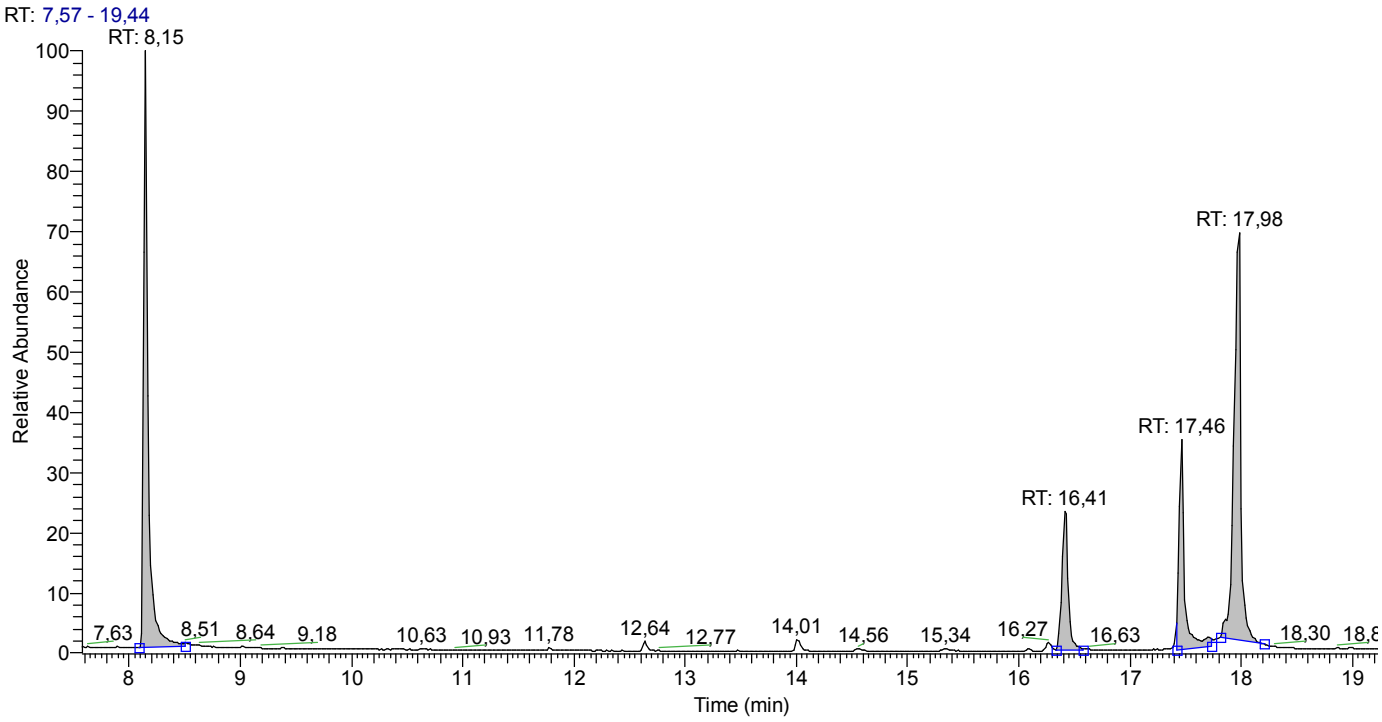


Figure S7. Fragment of the chromatogram of the reaction mixture (30h)

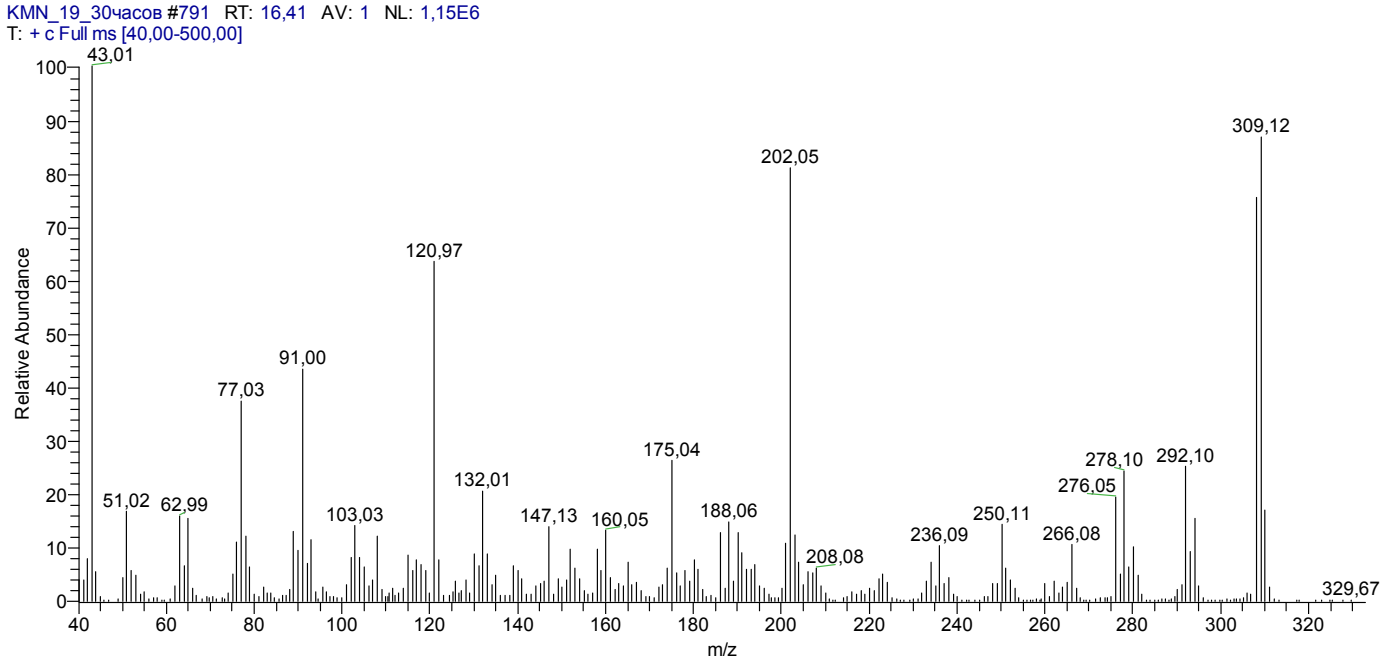


Figure S8. Mass Spectrum: one of the reaction products **8-10** (t_R = 16,41 min)

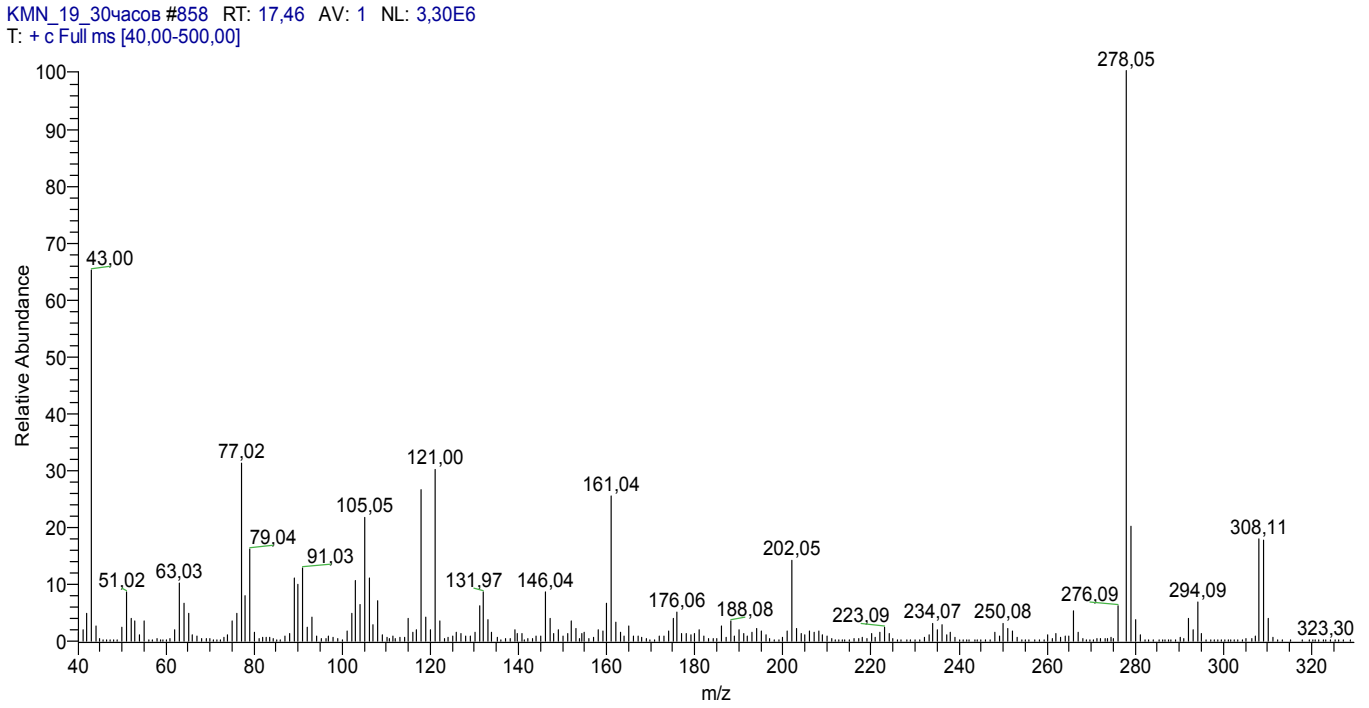


Figure S9. Mass Spectrum: one of the reaction products **8-10** (t_R = 17,46 min)

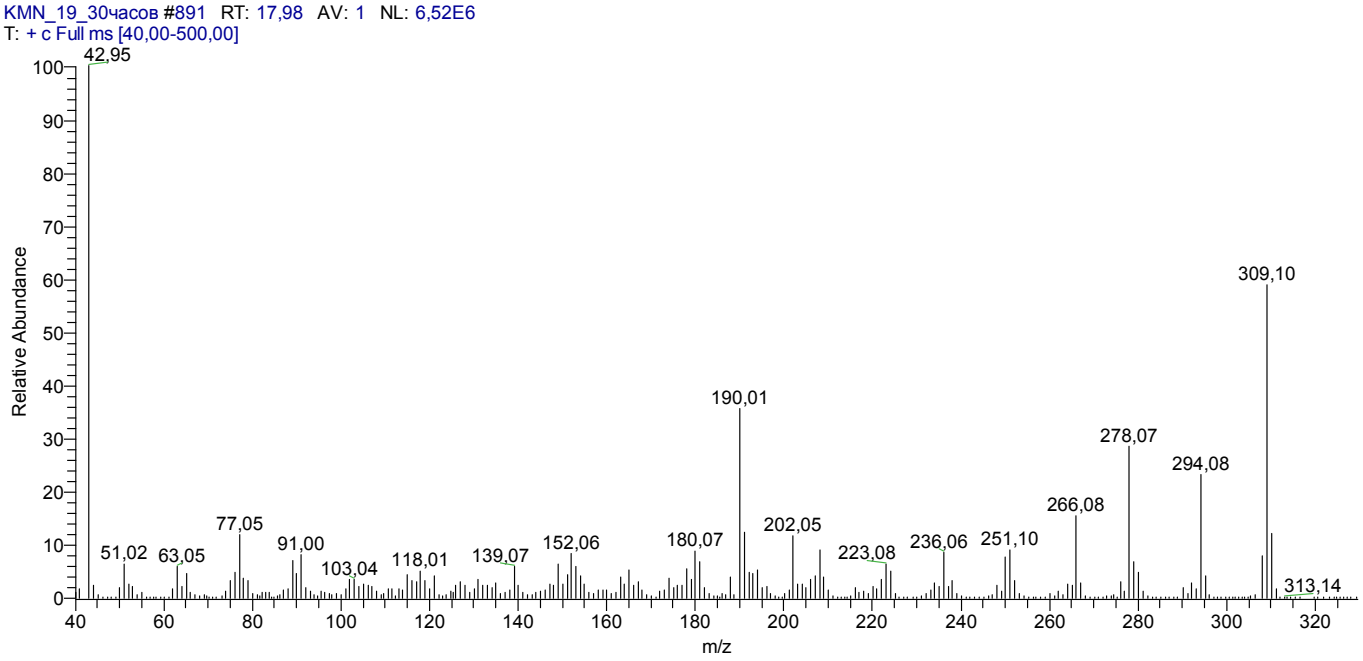
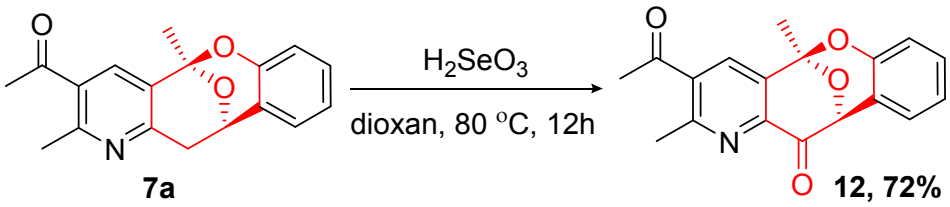


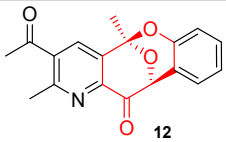
Figure S10. Mass Spectrum: one of the reaction products **8-10** (t_R = 17,98 min)

4. Procedure of oxidation 11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridine 7a

Solution of 1.5 mmol H_2SeO_3 in dioxane (7 ml) was added to 1.0 mmol of 5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (**7a**). The mixture was heated to 80°C for 12 hours. After cooling to room temperature, the mixture was purified to remove the precipitated elemental selenium by flash column chromatography on silica gel (eluted with acetone). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with EtOAc/hexane 1:5).

Scheme S4.





12

Chemical Formula: $C_{18}H_{15}NO_4$
Molecular Weight: 309,321

3-acetyl-2,5-dimethyl-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridin-12(11*H*)-one (12)
Yellow crystals, 72% yield. M.p. 198-200 °C (EtOAc/hexane 1:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.06 (s, 3H, 5-CH_3), 2.65 (s, 3H, C(O)CH_3), 2.77 (s, 3H, 2-CH_3), 5.49 (s, 1H, H-11), 6.80 (d, ^3J = 7.9 Hz, 1H, H-7), 6.65 (td, ^3J = 7.5, ^4J = 0.9 Hz, 1H, H-8), 7.19-7.23 (m, 2H, H-9, H-10), 8.03 (s, 1H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 24.4, 26.4, 29.8, 76.5, 97.1, 115.6, 117.2; 122.3, 126.4, 130.4, 134.1, 134.9, 137.7, 143.8, 150.0, 159.5, 190.2, 199.7. MS (EI) m/z (I_{rel}, %): [M^+] 309.14 (96), 281.16 (40), 280.14 (38), 266.14 (39), 252.14 (45), 238.16 (73), 77.09 (24), 44.06 (40), 43.07 (100). Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53; found: C, 69.61; H, 4.63; N, 4.70.

5. X-Ray Structural Study of compound 7a

Single crystals of compound **7a** are obtained from slow evaporation of 2-PrOH solution at room temperature. Crystallographic details are shown in the table **S3**. CCDC-2035579 contain supplementary crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Experimental details

compound **7a**	
Crystal data	
Chemical formula	$C_{18}H_{17}NO_3$
M_r	295.32
Crystal system, space group	Triclinic, $P\ \bar{1}$
Temperature (K)	296
a, b, c (Å)	8.7769 (10), 9.1976 (12), 10.1697 (12)
α, β, γ (°)	74.462 (5), 81.905 (5), 69.130 (5)
V (Å^3)	738.13 (16)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.54 × 0.42 × 0.19
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan *SADABS2008*/1
T_{min}, T_{max}	0.895, 0.926
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25930, 3979, 3416
R_{int}	0.025
$(\sin\theta/\lambda)_{max}$ (Å^{-1}), θ_{max} (°)	0.686, 29.188
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.130, 0.94
No. of reflections	3979
No. of parameters	202
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, -0.21
CCDC	2035579

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2018), Bruker *SHELXTL*.

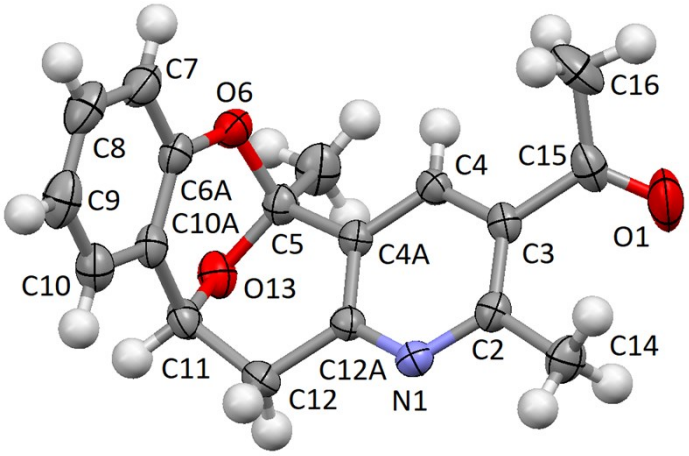


Figure S11. Molecular structure of compound **1** (50% thermal ellipsoids are shown).

Table S4. Selected bond lengths (Å)

N1 - C2	1.3411(14)	N1 - C12A	1.3447(13)	C2 - C3	1.4058(15)
C3 - C15	1.5042(15)	O1 - C15	1.2101(18)	C15 - C16	1.493(2)
C5 - O6	1.4472(14)	C5 - O13	1.4075(14)	C4A - C5	1.5272(14)
O6 - C6A	1.3798(14)	C11 - O13	1.4406(15)	C4A - C12A	1.3939(14)

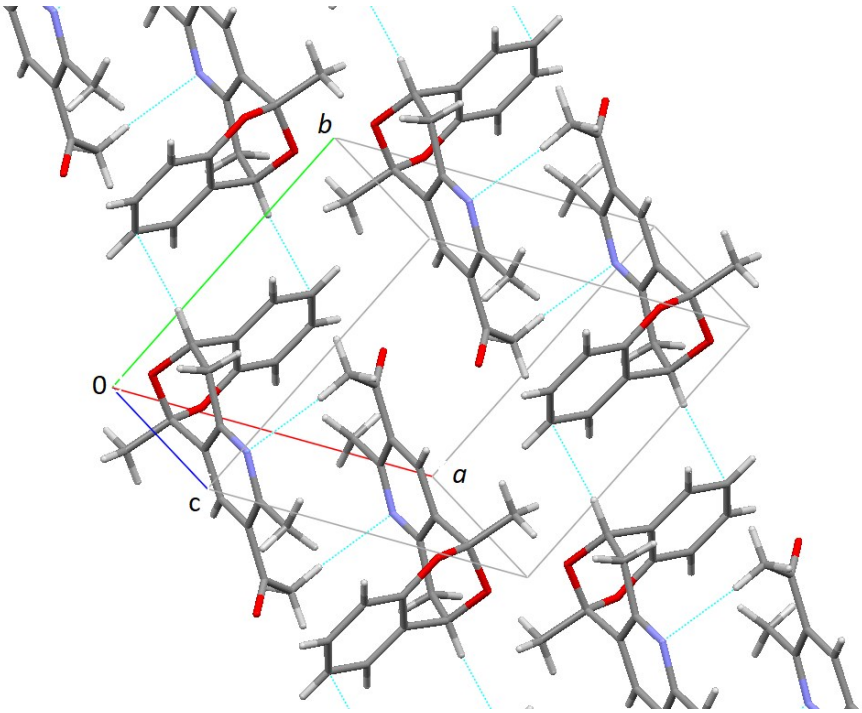


Figure S12. Molecular packing in the crystal of compound **7a** with short intermolecular contacts.

6. Author Contributions

The reported study was funded by RFBR according to the research project [No. 19-03-00376].

Spectrophotometric studies were performed on the basis of the Research Resource Center “Natural Resource Management and Physico-Chemical Research” Institute of Chemistry, Tyumen State University (with the financial support of the Ministry of Science and Higher Education of the Russian Federation (contract no. 05.594.21.0019, unique identification number RFMEFI59420X0019).

7. References

[1] S. B. Singh, D. L. Zink, D. S. Quamina, F. Pelaez, A. Teran, P. Felock, D. J. Hazuda, *Tetrahedron Lett.* **2002**, *43*, 2351−2354.
[2] F. M. Talontsi, B. Dittrich, A. Schuffler, H. Sun, H. Laatsch, *Eur. J. Org. Chem.* **2013**, *15*, 3174−3180.
[3] M. El Amrani, D. Lai, A. Debbab, A. H. Aly, K. Siems, C. Seidel, M. Schnekenburger, A. Gaigneaux, M. Diederich, D. Feger, W. Lin, P. Proksch, *J. Nat. Prod.* **2014**, *77*, 49−56.
[4] H. Oumzil, S. Ghoulami, M. Rhajaoui, A. Ilidrissi, S. Fkih-Tetouani, M. Faid, A. Benjouad, *Phytotherapy Research,* **2002**, *16*(8), 727−731.
[5] Y. Pommier, A. A. Johnson, C. Marchand, *Nature Reviews Drug Discovery* **2005**, *4*(3), 236.
[6] B. Wang, *HIV-1 integrase: mechanism and inhibitor design, Vol. 9* (Ed.: N. Neamati), John Wiley & Sons, **2011**.
[7] J. S. Foot, G. M. Giblin, R. J. Taylor, *Org. Lett.* **2003**, *5*, 4441−4444.
[8] J. S. Foot, G. M. Giblin, A. C. Whitwood, R. J. Taylor, *Organic & Biomolecular Chemistry* **2005**, *3*, 756 – 763.
[9] C. V. Ramana, Nageswara Reddy, C.; Gonnade, R. G. *Chem. Commun.* **2008**, 3151−3153.
[10] A. More, C. V. Ramana, *Org. Lett.* **2016**, *18*, 612−615.
[11] A. A. More, C. V. Ramana, *Org. Lett.* **2016**, *18*, 1458−1461.
[12] P. M. Tadross, P. Bugga, B. M. Stoltz, *Org. Biomol. Chem.* **2011**, *9*, 5354−5357.
[13] J. Y. Jeong, J. Sperry, M. A. Brimble, *J. Org. Chem.* **2019**, *84*, 11935−11944.
[14] Y. Yamagiwa, N. Haruna, H. Kawakami, K. Matsumoto, *Bull. Chem. Soc. Jpn.* **2020**, *93*(8), 1036-1042.
[15] I. V. Kulakov, A. A. Karbainova, Z. T. Shulgau, T. M. Seilkhanov, Y. V. Gatilov, A. S. Fisyuk/ *Chem. Heterocycl. Compd.* **2017**, *53*(10), 1094-1097.
[16] A. L. Oleshchuk, A. A. Karbainova, T. N. Krivoruchko, Z. T. Shulgau, T. M. Seilkhanov, I. V. Kulakov, *Chem. Heterocycl. Compd.* **2019**, *55*(1), 47-51.
[17] N. Kumar, A. Bhatnagar, R. Dudhe, *Arabian Journal of Chemistry* **2017**, *10*(2), S2443-S2452.
[18] a) R. Rajeev, A. C. Shan, *Ind. J. Chem.* **1994**, *33*(8), 775; b) I. V. Kulakov, S. A. Talipov, Z. T. Shulgau, T. M. Seilkhanov, *Chem. Heterocycl. Compd.* **2014**, *50*(10), 1478-1486.
[19] Mao D., Hong, G., Wu, Sh., Liu, X. Yu, Ji., and Wang, L. Lewis-Acid-Catalyzed Benzylic Reactions of 2-Methylazaarenes with Aldehydes. *Eur. J. Org. Chem*. 2014, 14, 3009-3019.
[20] A. A. Altaf, A. Shahzad, Z. Gul, N. Rasool, A. Badshah, B. Lal, E. Khan, *Journal of Drug Design and Medicinal Chemistry* **2015**, *1*(1), 1-11.
[21] P. Prathima, S. P. Sethy, T. Sameena, K. Shailaja, *Asian J. Research Chem.* **2013**, *6*(10), 888-899.
[22] M. Kunduracı, E. Özkaramete, N. Yılmaz, S. Öz, I. Svoboda, E. K. Inal, O. J. Atakol, *Therm. Anal. Calorim.* **2013**, *112*(3), 1587–1599.
[23] J. Song, H. Zhao, Y. Liu, H. Han, Z. Li, W. Chu, Z. Sun, *New J. Chem.* **2017**, *41*(1), 372–376.
[24] E. M. McGarrigle, D. M. Murphy, D. G. Gilheany, *Tetrahedron: Asymmetry* **2004**, *15*(8), 1343–1354.
[25] F. M. Mei, L. J. Chen, G. X. Li, *Appl. Organomet. Chem.* **2010**, *24*, 86–91.
[26] W. L. Mendelson, S. Hayden, *Synth. Commun.* **1996**, *26*(3), 603–610.
[27] Z. Liu, G. Yoon, S. H. Cheon, *Tetrahedron* **2010**, *66*(17), 3165–3172.
[28] R. P. Burman, S. Gupta, J. Bhatti, K. Verma, D. Rajak, M. S. Gill, *Natural Product Research,* **2019**, *33*(8), 1147-1157.
[29] G. A. Brancaglion, A. E. Toyota, J. V. C. Machado, A. Á. F. Júnior, A. T. Silveira, D. F. V. Boas, E. G. Santos, I. S. Caldas, D. T. Carvalho, *Chemical Biology & Drug Design* **2018**, *92*(5), 1888-1898.
[30] R. Córdoba, N. S. Tormo, A. F. Medarde, J. Plumet, *Bioorg. Med. Chem.* **2007**, *15*(15), 5300–5315.
[31] K. Rajesh, M. Somasundaram, R. Saiganesh, K. K. Balasubramanian, *JOC* **2007**, *72*(15), 5867–5869.
[32] L. Rubenstein, J. Chem. Soc., *Trans.* **1925**, *127*, 1998-2004.
[33] E. V. Braude, M. A. Gal'bershtam, *Chem. Heterocycl. Compd.* **1979**, *15*(2), 173–179.
[34] M. R. Heinrich, W. Steglich, M. G. Banwell, Y. Kashman, *Tetrahedron* **2003**, *59*(46), 9239–9247.
[35] A. C. Silva, H. Benelkebir, R. S. C. Lopes, C. C. Lopes, A. Ganesan, *J. Braz. Chem. Soc.* **2018**, *29*(5), 1157-1161.
[36] S. Vojacek, K. Beese, Z. Alhalabi, S. Swyter, A. Bodtke, C. Schulzke, M. Jung, W. Sippl, A. Link, *Arch. Pharm.* **2017**, *350*(7), e1700097.
[37] E. L. Trump, M. X. Zhou, *Transactions of the Kansas Academy of Science* **1993**, *1903*, 167-180.

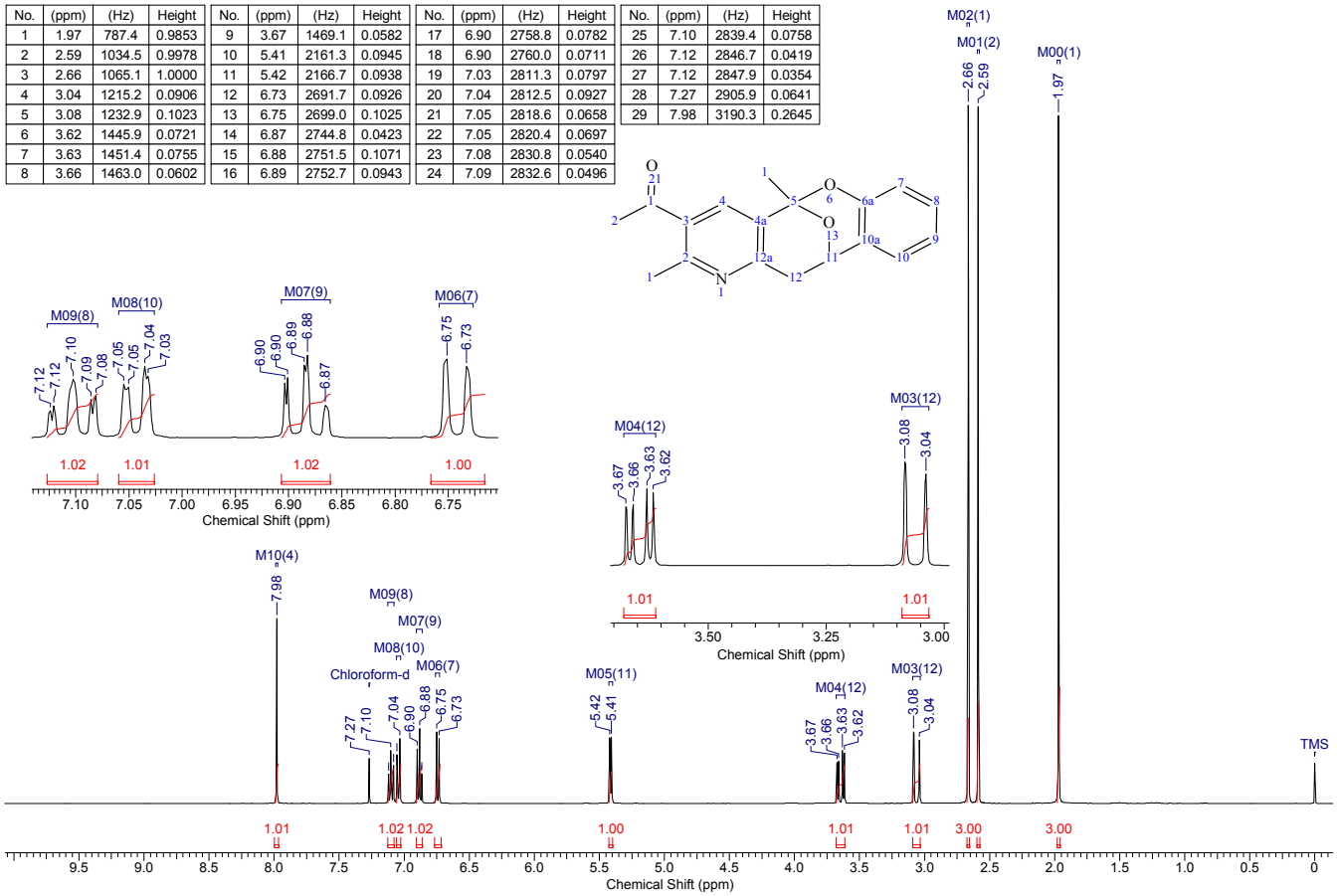
8. Copies of NMR Spectra of Products

No.	(ppm)	(Hz)	Height
1	1.97	787.4	0.9853
2	2.59	1034.5	0.9978
3	2.66	1065.1	1.0000
4	3.04	1215.2	0.0906
5	3.08	1232.9	0.1023
6	3.62	1445.9	0.0721
7	3.63	1451.4	0.0755
8	3.66	1463.0	0.0602

No.	(ppm)	(Hz)	Height
9	3.67	1469.1	0.0582
10	5.41	2161.3	0.0945
11	5.42	2166.7	0.0938
12	6.73	2691.7	0.0926
13	6.75	2699.0	0.1025
14	6.87	2744.8	0.0423
15	6.88	2751.5	0.1071
16	6.89	2752.7	0.0943

No.	(ppm)	(Hz)	Height
17	6.90	2758.8	0.0782
18	6.90	2760.0	0.0711
19	7.03	2811.3	0.0797
20	7.04	2812.5	0.0927
21	7.05	2818.6	0.0658
22	7.05	2820.4	0.0697
23	7.08	2830.8	0.0540
24	7.09	2832.6	0.0496

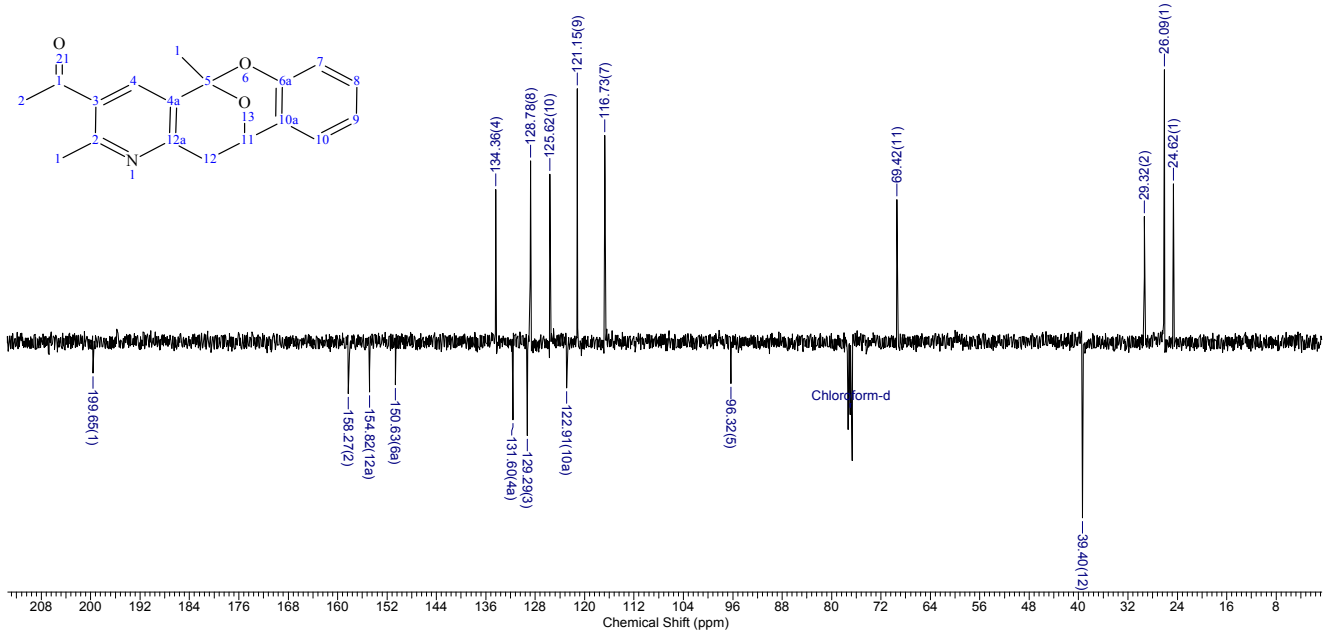
No.	(ppm)	(Hz)	Height
25	7.10	2839.4	0.0758
26	7.12	2846.7	0.0419
27	7.12	2847.9	0.0354
28	7.27	2905.9	0.0641
29	7.98	3190.3	0.2645



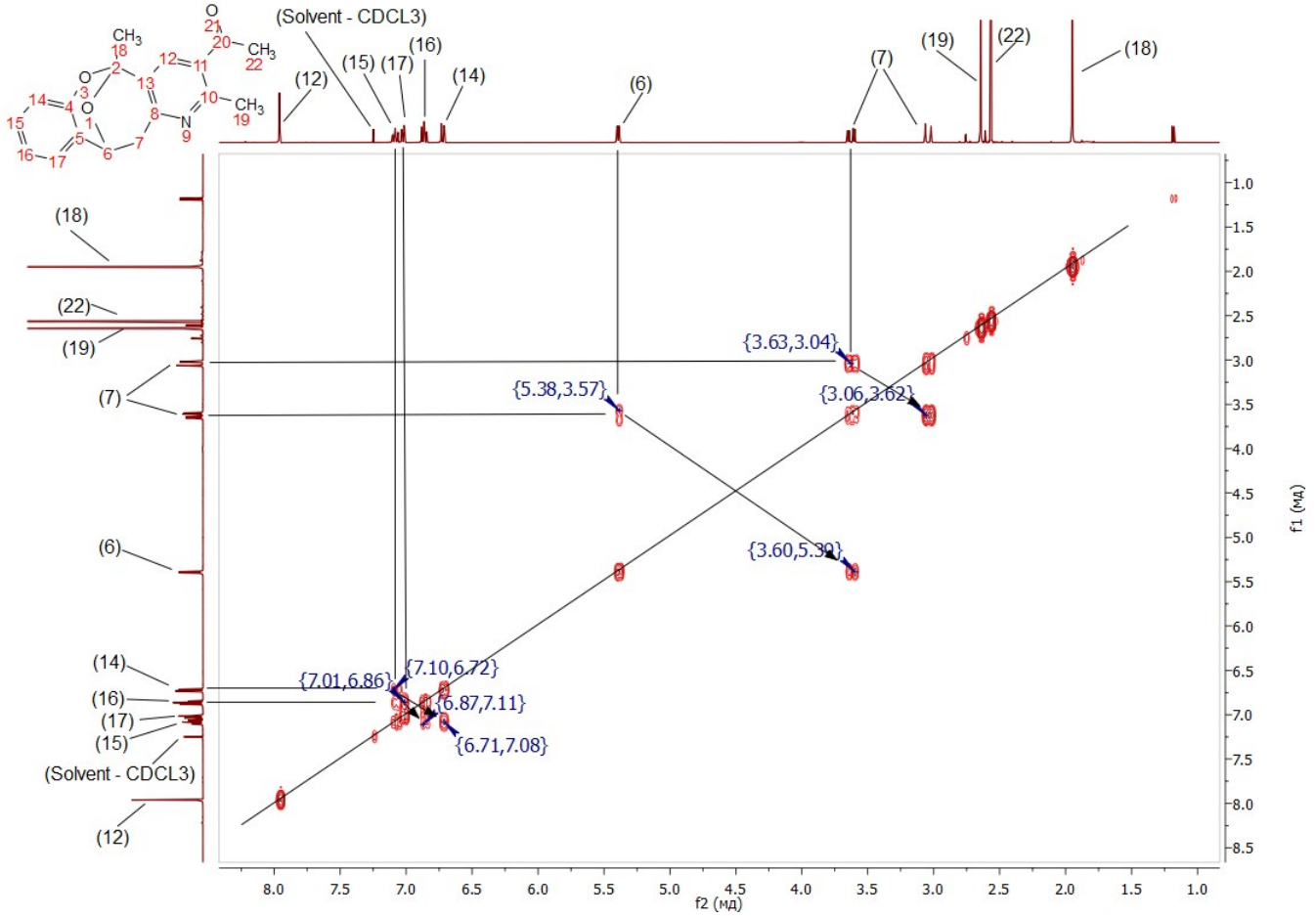
No.	Atom	Exp. Shift (ppm)
1	1	24.62
2	1	26.09
3	2	29.32
4	12	39.40
5	11	69.42
6	5	96.32

No.	Atom	Exp. Shift (ppm)
7	7	116.73
8	9	121.15
9	10a	122.91
10	10	125.62
11	8	128.78
12	3	129.29

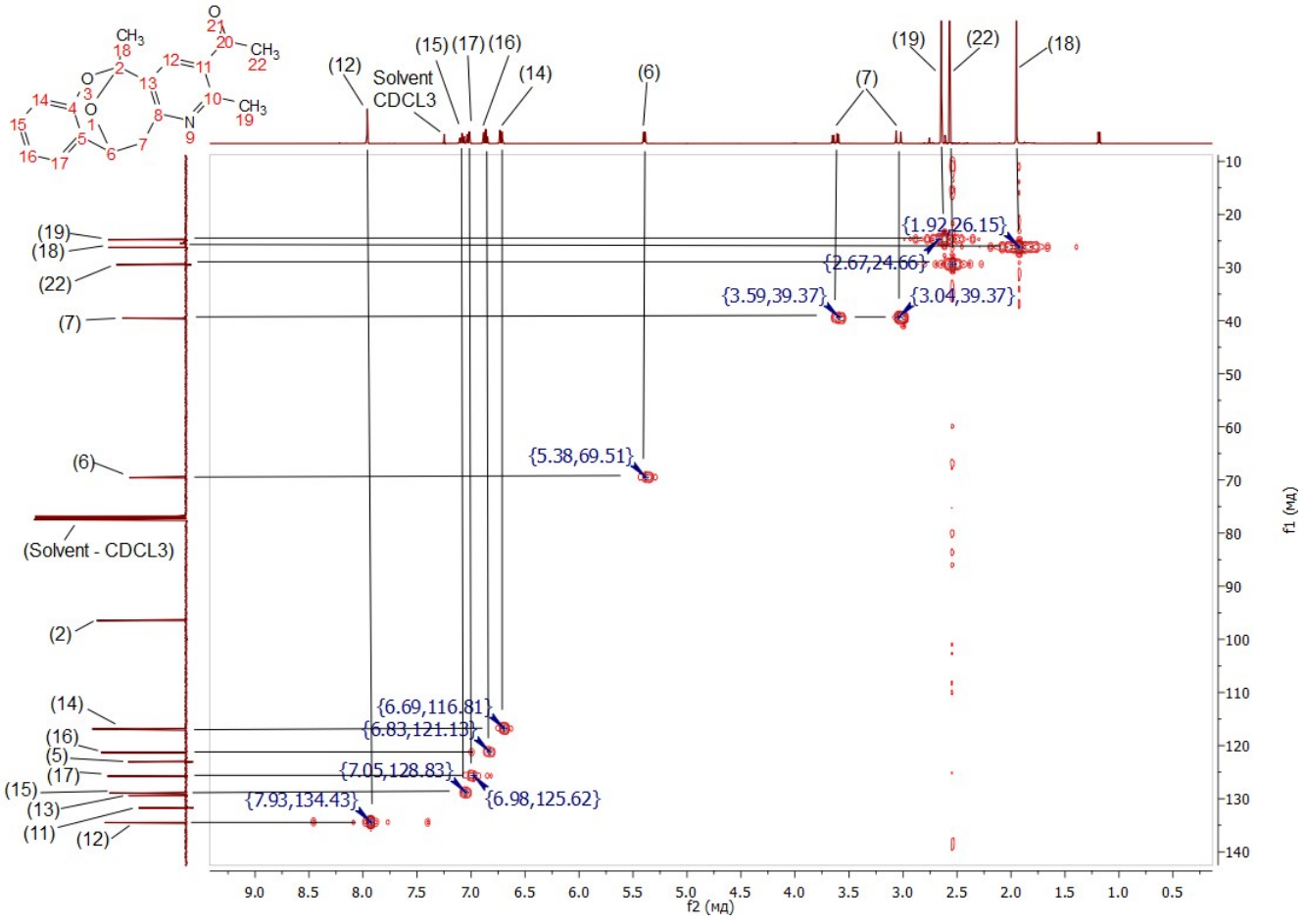
No.	Atom	Exp. Shift (ppm)
13	4a	131.60
14	4	134.36
15	6a	150.63
16	12a	154.82
17	2	158.27
18	1	199.65



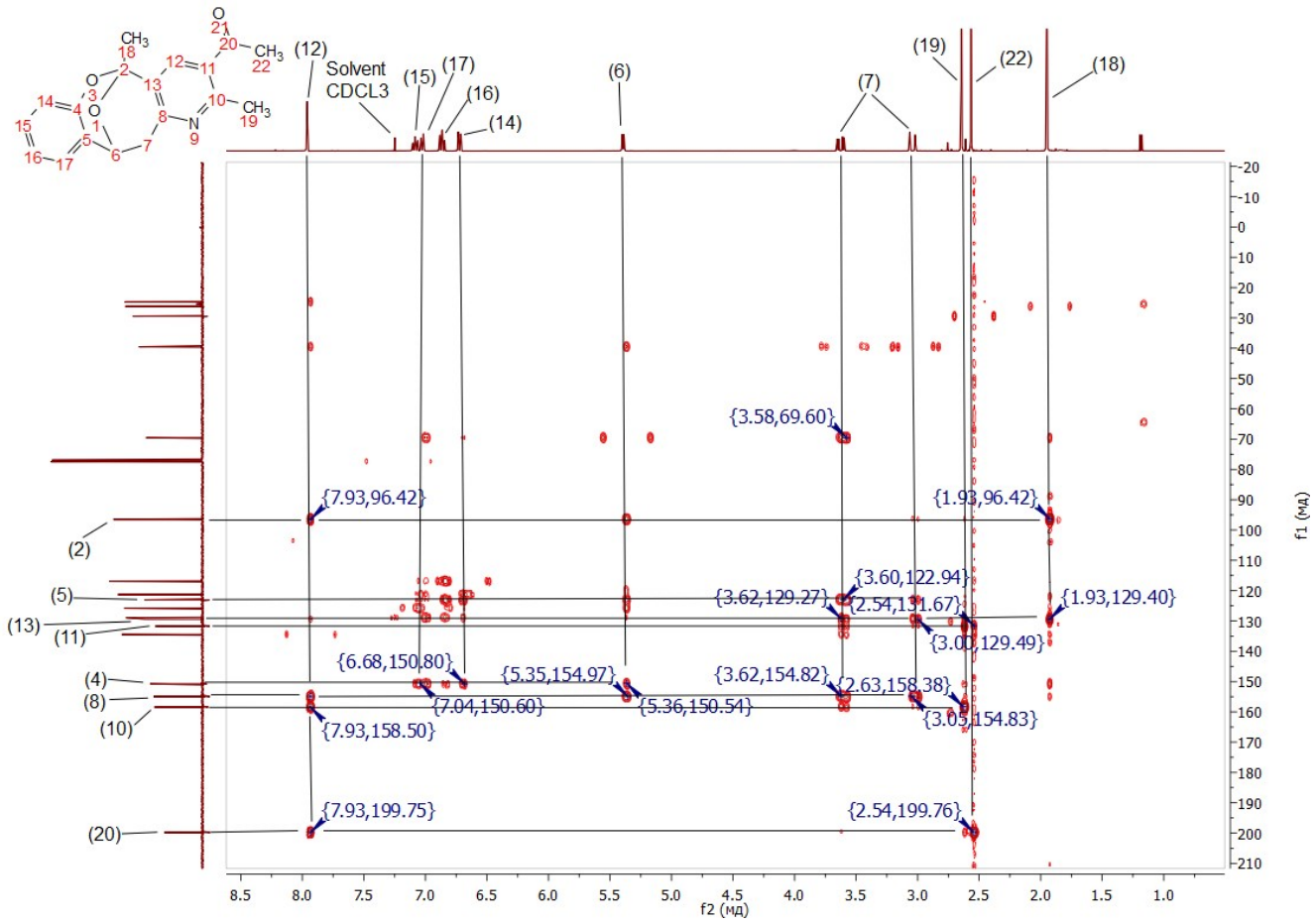
^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7a**



COSY (400 MHz, $CDCl_3$) NMR Spectra of **7a**



HMQC (400 MHz, $CDCl_3$) NMR Spectra of **7a**

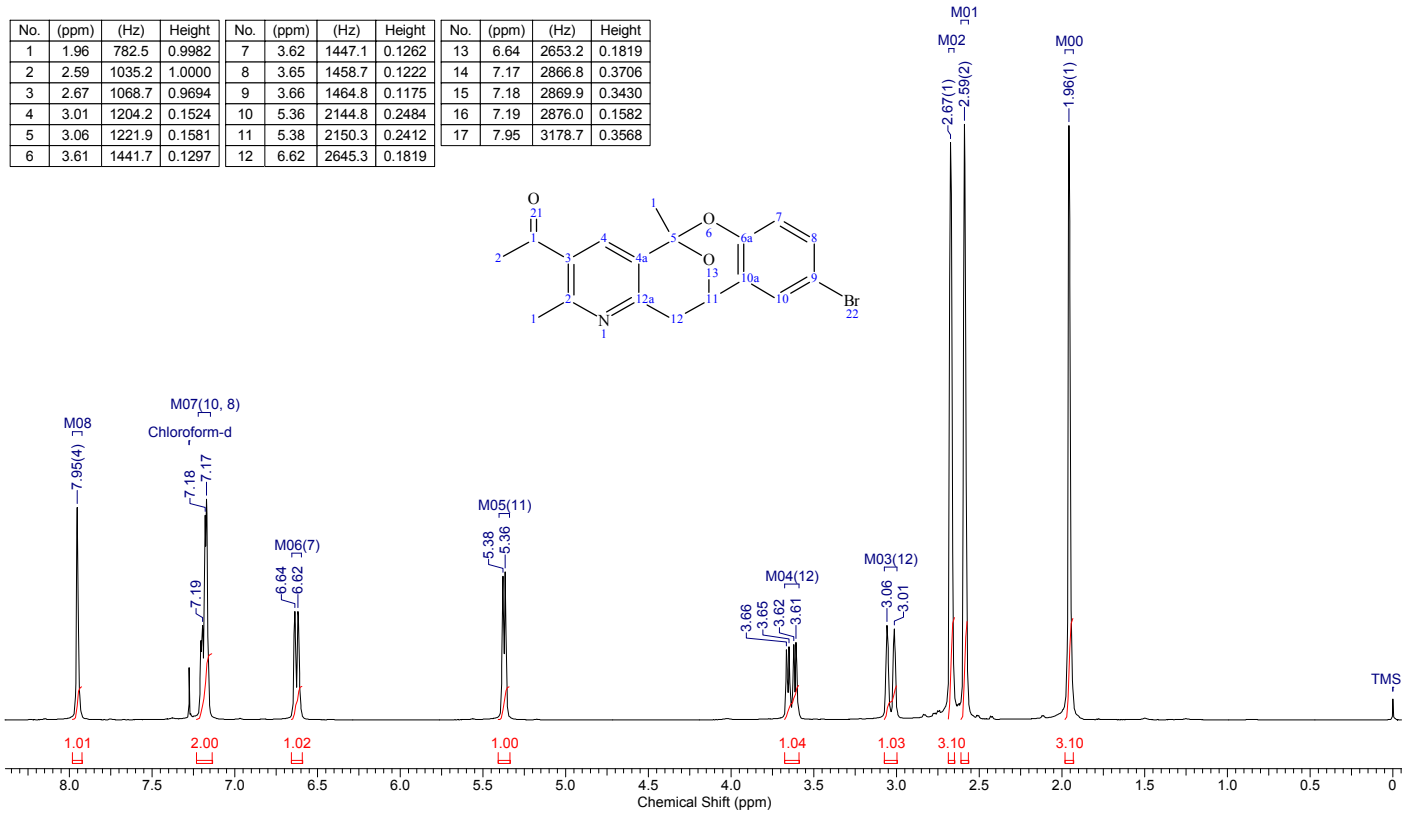


HMBC (400 MHz, $CDCl_3$) NMR Spectra of **7a**

No.	(ppm)	(Hz)	Height
1	1.96	782.5	0.9982
2	2.59	1035.2	1.0000
3	2.67	1068.7	0.9694
4	3.01	1204.2	0.1524
5	3.06	1221.9	0.1581
6	3.61	1441.7	0.1297

No.	(ppm)	(Hz)	Height
7	3.62	1447.1	0.1262
8	3.65	1458.7	0.1222
9	3.66	1464.8	0.1175
10	5.36	2144.8	0.2484
11	5.38	2150.3	0.2412
12	6.62	2645.3	0.1819

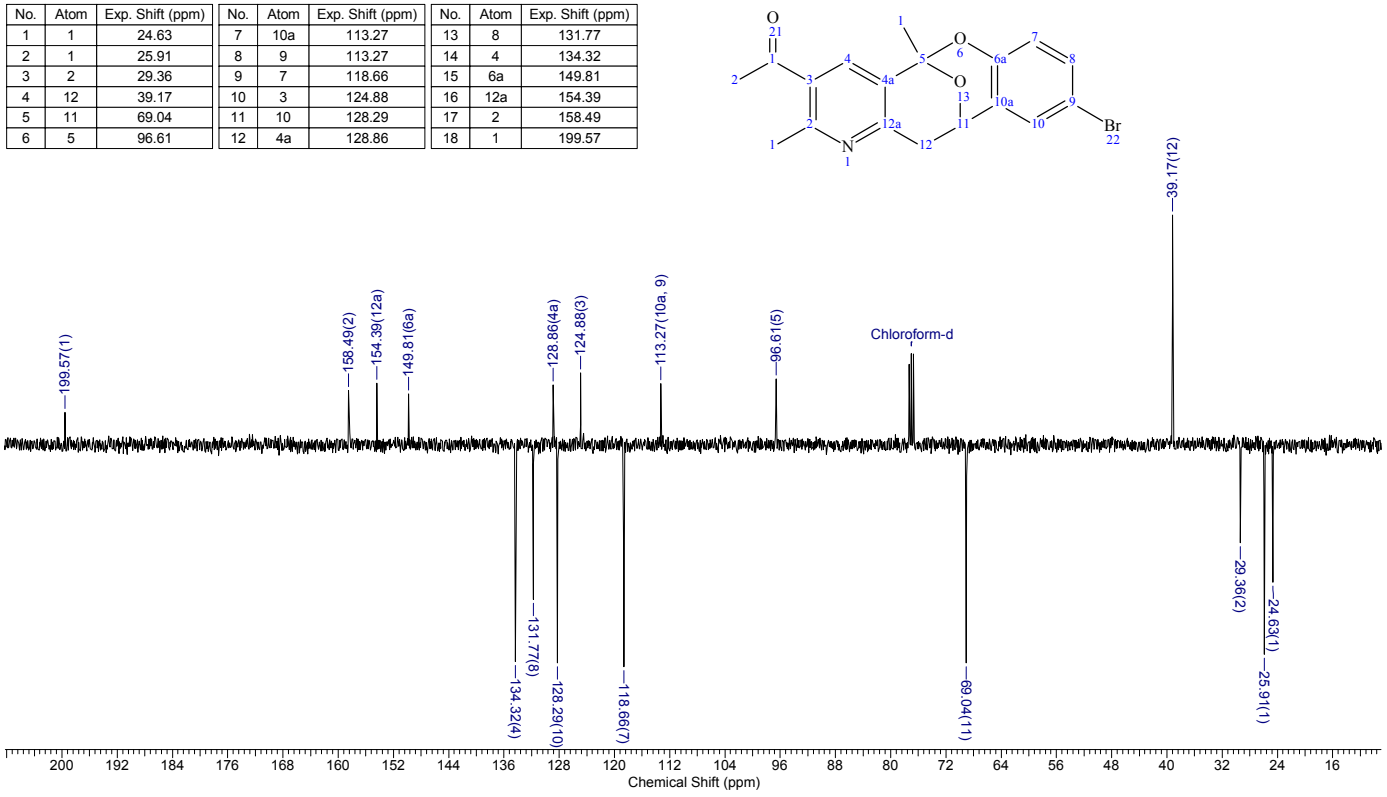
No.	(ppm)	(Hz)	Height
13	6.64	2653.2	0.1819
14	7.17	2866.8	0.3706
15	7.18	2869.9	0.3430
16	7.19	2876.0	0.1582
17	7.95	3178.7	0.3568



No.	Atom	Exp. Shift (ppm)
1	1	24.63
2	1	25.91
3	2	29.36
4	12	39.17
5	11	69.04
6	5	96.61

No.	Atom	Exp. Shift (ppm)
7	10a	113.27
8	9	113.27
9	7	118.66
10	3	124.88
11	10	128.29
12	4a	128.86

No.	Atom	Exp. Shift (ppm)
13	8	131.77
14	4	134.32
15	6a	149.81
16	12a	154.39
17	2	158.49
18	1	199.57

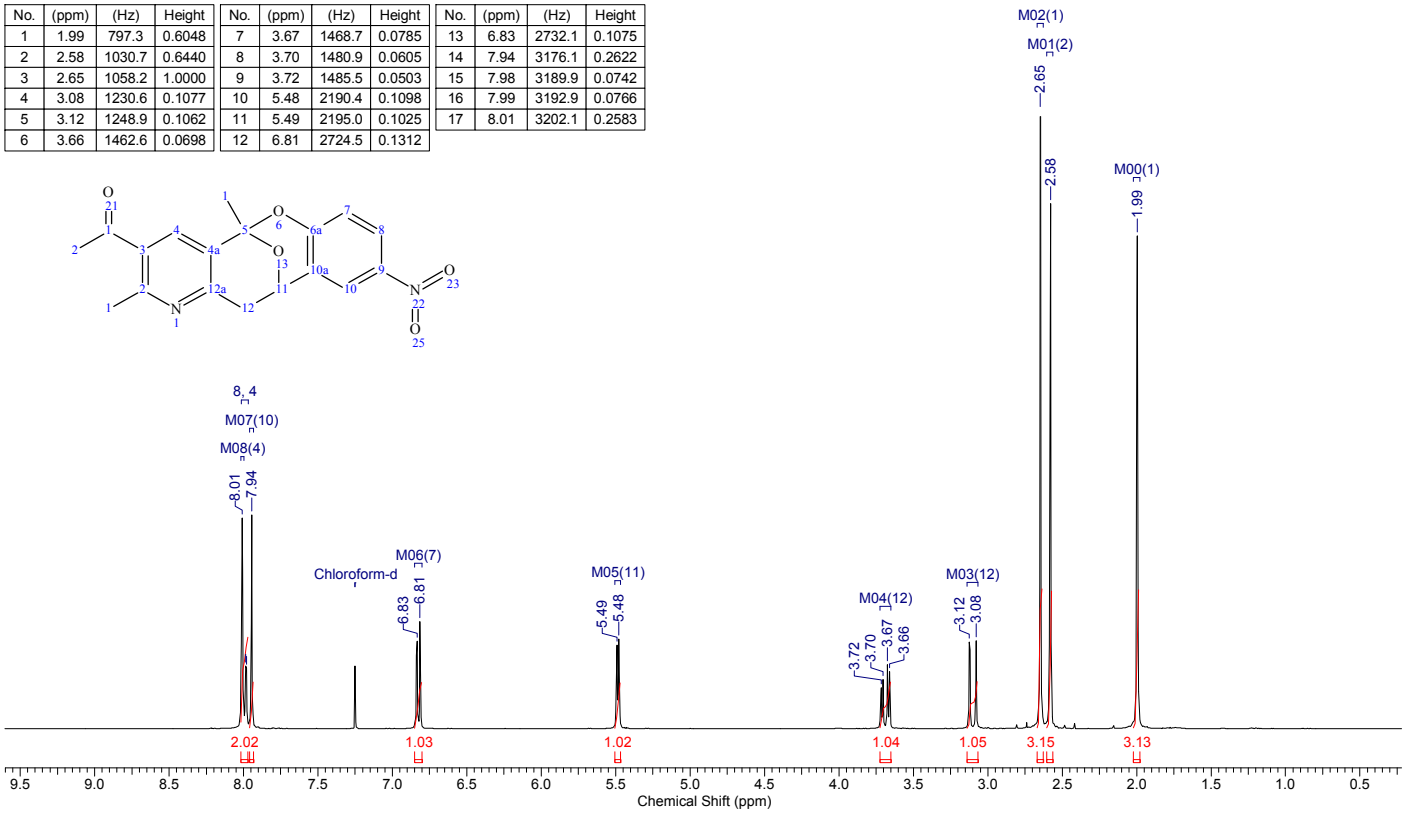


^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7b**

No.	(ppm)	(Hz)	Height
1	1.99	797.3	0.6048
2	2.58	1030.7	0.6440
3	2.65	1058.2	1.0000
4	3.08	1230.6	0.1077
5	3.12	1248.9	0.1062
6	3.66	1462.6	0.0698

No.	(ppm)	(Hz)	Height
7	3.67	1468.7	0.0785
8	3.70	1480.9	0.0605
9	3.72	1485.5	0.0503
10	5.48	2190.4	0.1098
11	5.49	2195.0	0.1025
12	6.81	2724.5	0.1312

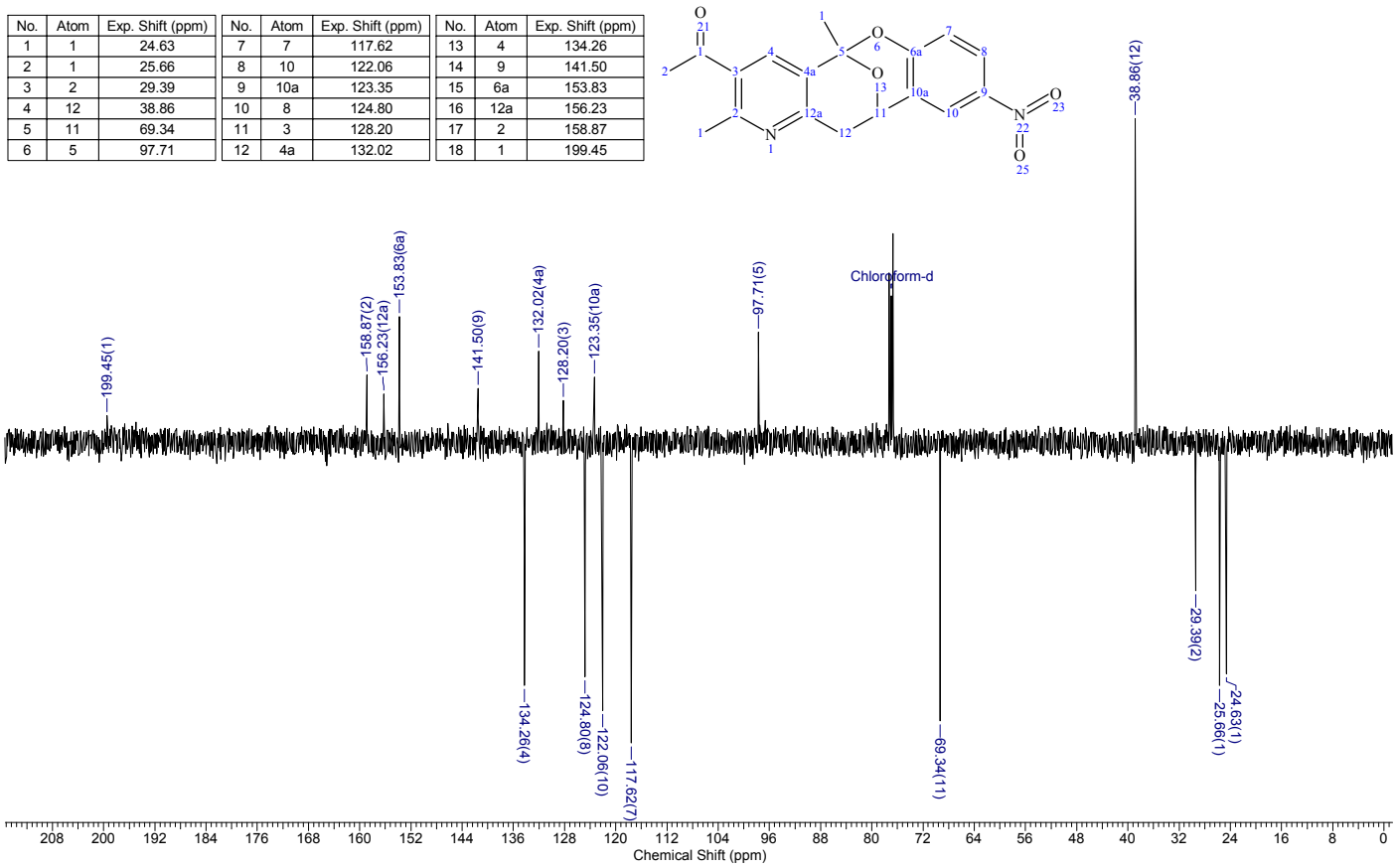
No.	(ppm)	(Hz)	Height
13	6.83	2732.1	0.1075
14	7.94	3176.1	0.2622
15	7.98	3189.9	0.0742
16	7.99	3192.9	0.0766
17	8.01	3202.1	0.2583



No.	Atom	Exp. Shift (ppm)
1	1	24.63
2	1	25.66
3	2	29.39
4	12	38.86
5	11	69.34
6	5	97.71

No.	Atom	Exp. Shift (ppm)
7	7	117.62
8	10	122.06
9	10a	123.35
10	8	124.80
11	3	128.20
12	4a	132.02

No.	Atom	Exp. Shift (ppm)
13	4	134.26
14	9	141.50
15	6a	153.83
16	12a	156.23
17	2	158.87
18	1	199.45

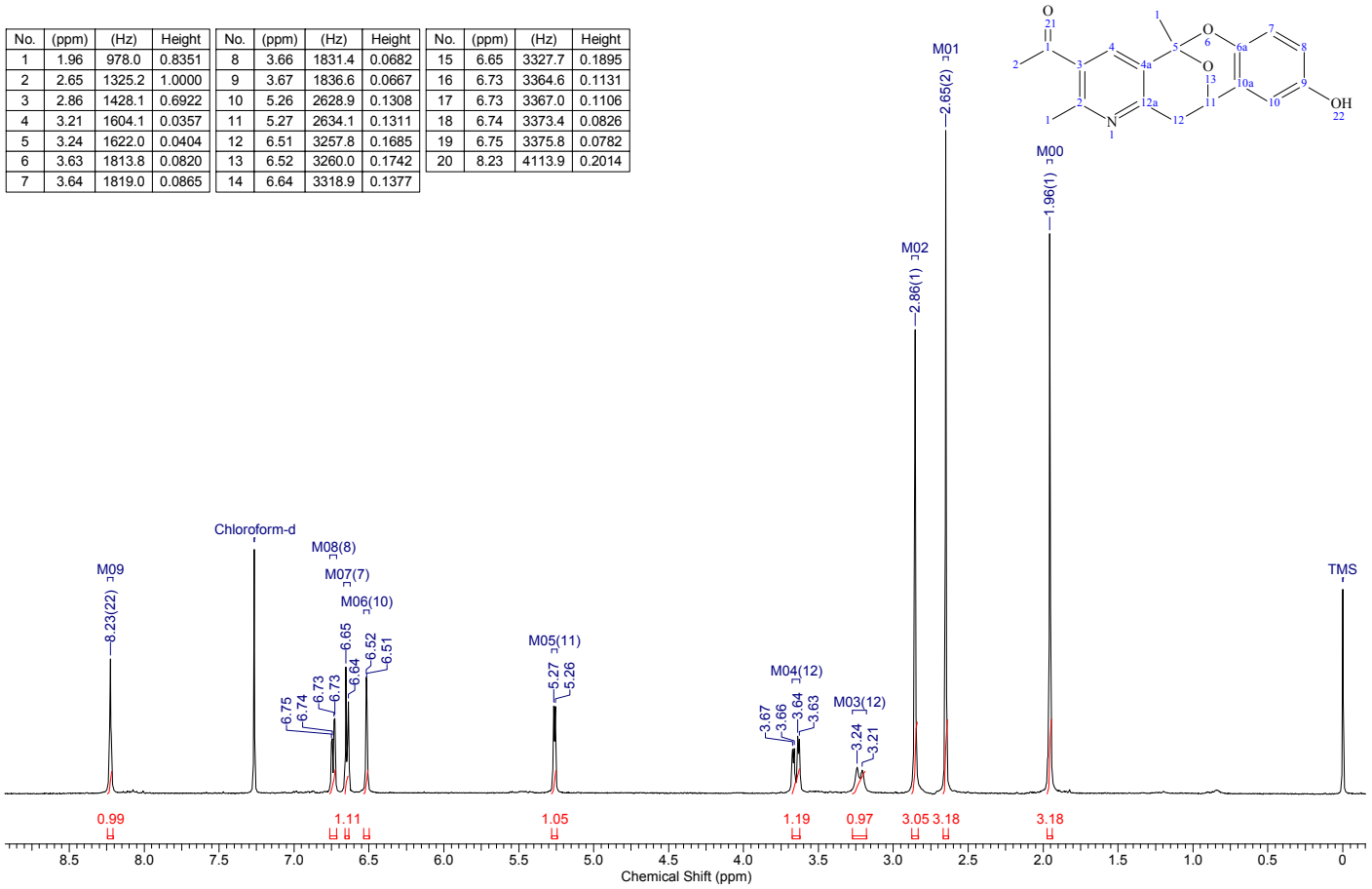


^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7c**

No.	(ppm)	(Hz)	Height
1	1.96	978.0	0.8351
2	2.65	1325.2	1.0000
3	2.86	1428.1	0.6922
4	3.21	1604.1	0.0357
5	3.24	1622.0	0.0404
6	3.63	1813.8	0.0820
7	3.64	1819.0	0.0865

No.	(ppm)	(Hz)	Height
8	3.66	1831.4	0.0682
9	3.67	1836.6	0.0667
10	5.26	2628.9	0.1308
11	5.27	2634.1	0.1311
12	6.51	3257.8	0.1685
13	6.52	3260.0	0.1742
14	6.64	3318.9	0.1377

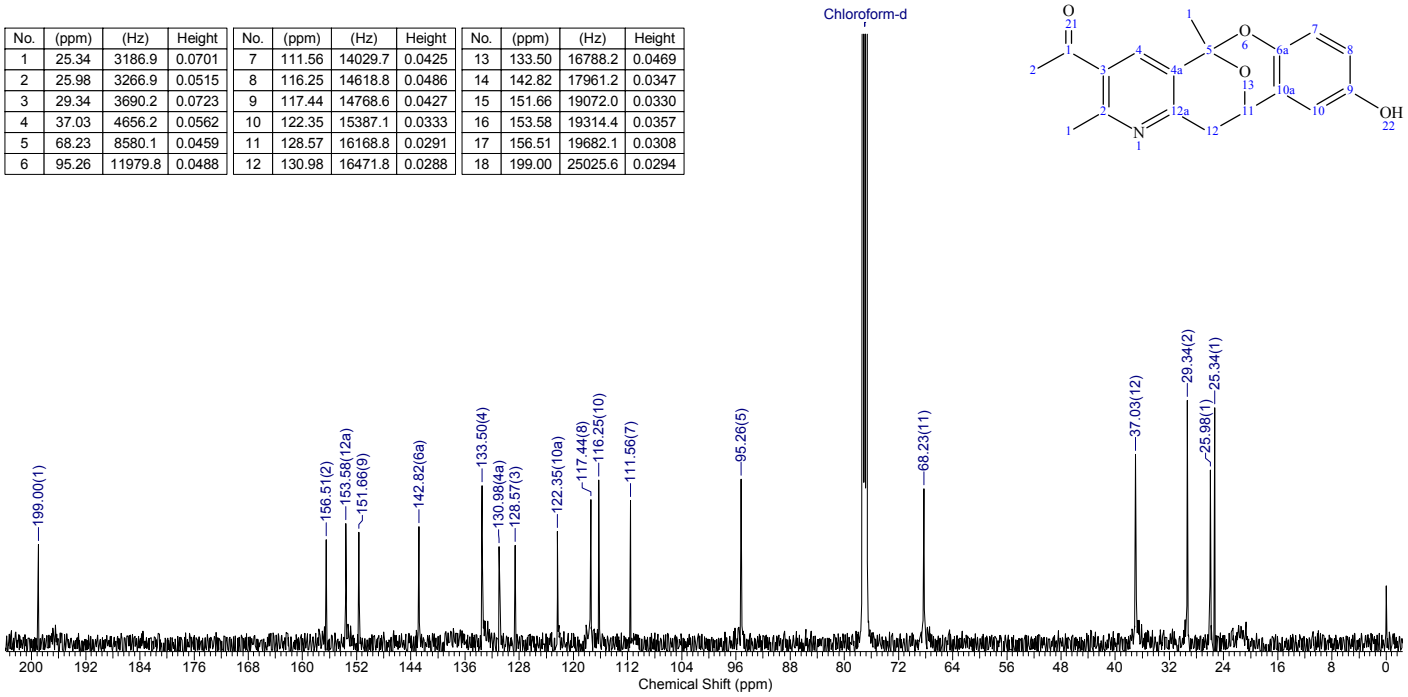
No.	(ppm)	(Hz)	Height
15	6.65	3327.7	0.1895
16	6.73	3364.6	0.1131
17	6.73	3367.0	0.1106
18	6.74	3373.4	0.0826
19	6.75	3375.8	0.0782
20	8.23	4113.9	0.2014



No.	(ppm)	(Hz)	Height
1	25.34	3186.9	0.0701
2	25.98	3266.9	0.0515
3	29.34	3690.2	0.0723
4	37.03	4656.2	0.0562
5	68.23	8580.1	0.0459
6	95.26	11979.8	0.0488

No.	(ppm)	(Hz)	Height
7	111.56	14029.7	0.0425
8	116.25	14618.8	0.0486
9	117.44	14768.6	0.0427
10	122.35	15387.1	0.0333
11	128.57	16168.8	0.0291
12	130.98	16471.8	0.0288

No.	(ppm)	(Hz)	Height
13	133.50	16788.2	0.0469
14	142.82	17961.2	0.0347
15	151.66	19072.0	0.0330
16	153.58	19314.4	0.0357
17	156.51	19682.1	0.0308
18	199.00	25025.6	0.0294

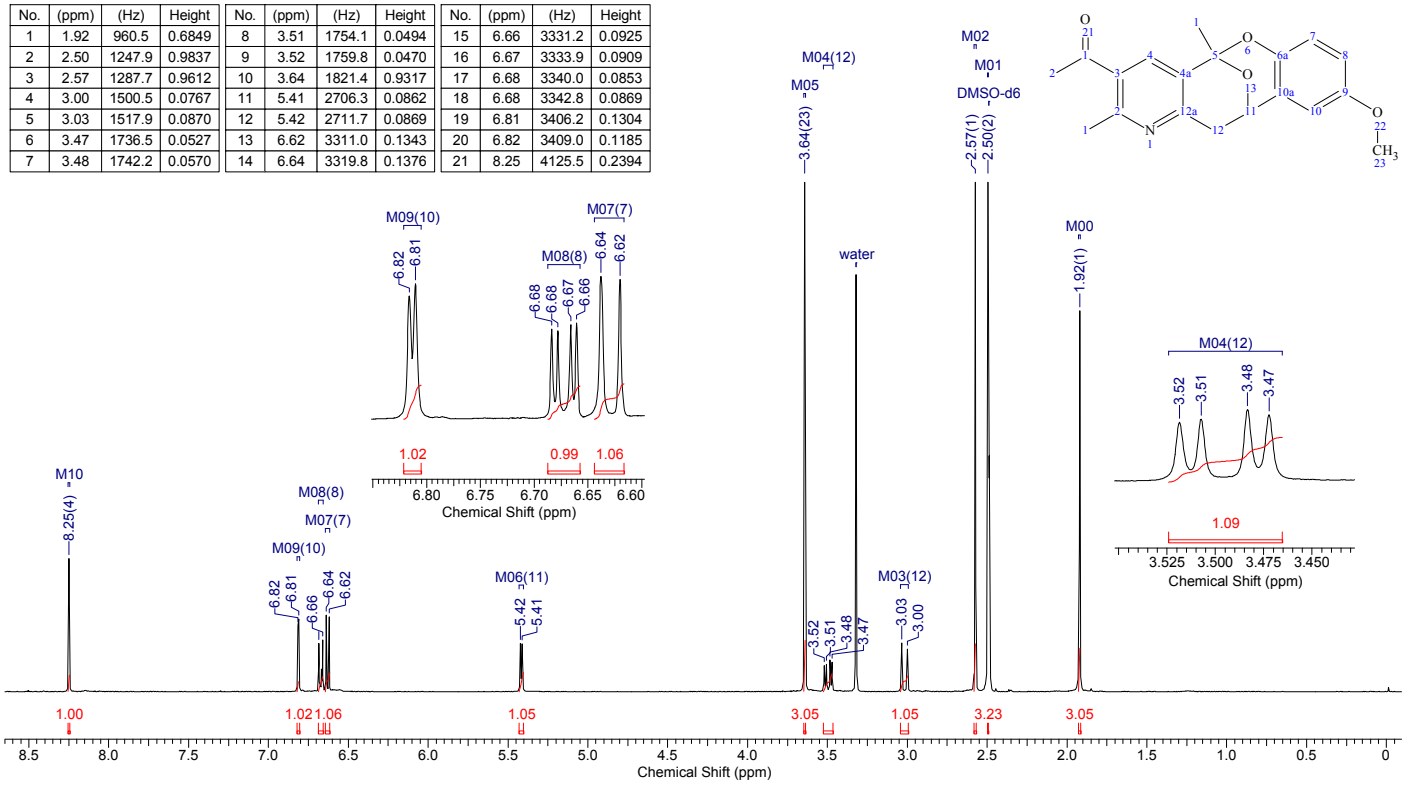


^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7d**

No.	(ppm)	(Hz)	Height
1	1.92	960.5	0.6849
2	2.50	1247.9	0.9837
3	2.57	1287.7	0.9612
4	3.00	1500.5	0.0767
5	3.03	1517.9	0.0870
6	3.47	1736.5	0.0527
7	3.48	1742.2	0.0570

No.	(ppm)	(Hz)	Height
8	3.51	1754.1	0.0494
9	3.52	1759.8	0.0470
10	3.64	1821.4	0.9317
11	5.41	2706.3	0.0862
12	5.42	2711.7	0.0869
13	6.62	3311.0	0.1343
14	6.64	3319.8	0.1376

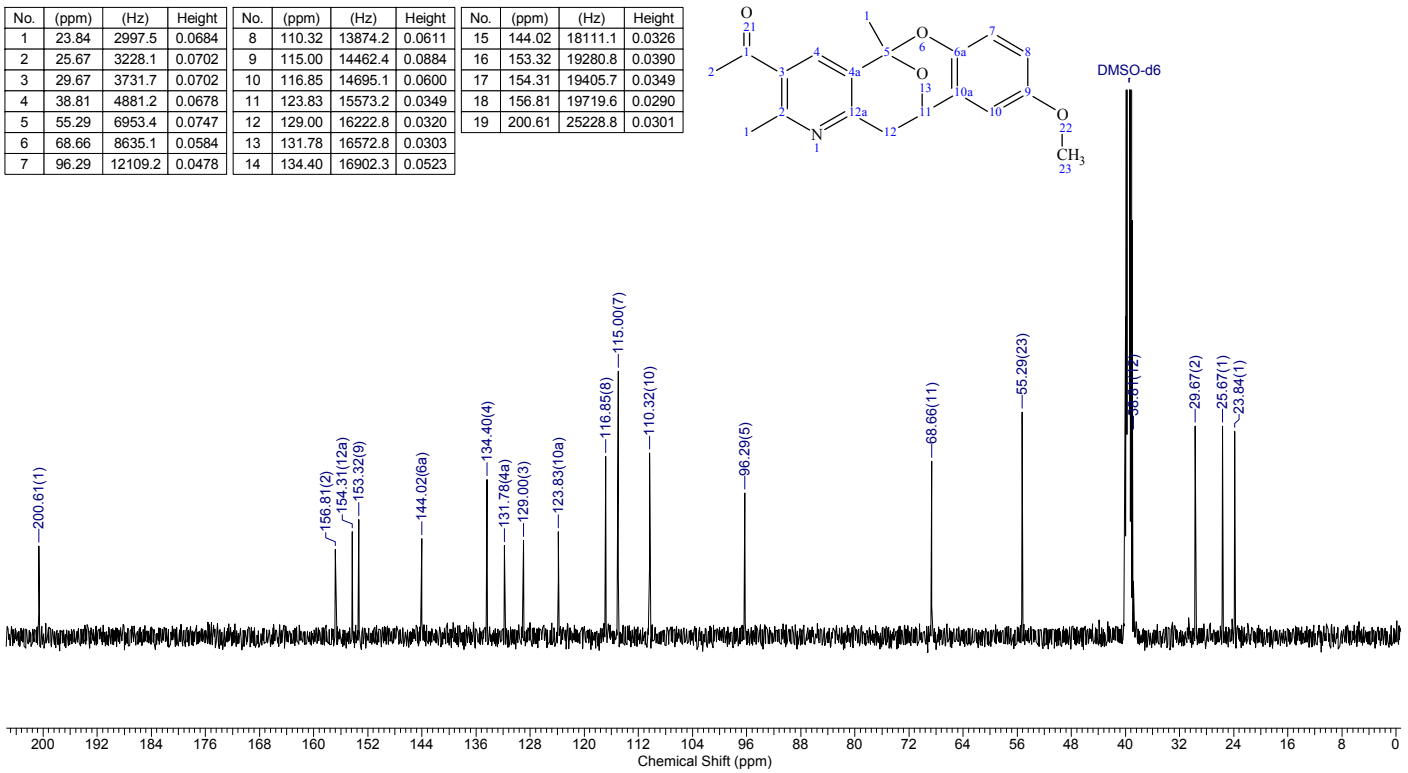
No.	(ppm)	(Hz)	Height
15	6.66	3331.2	0.0925
16	6.67	3333.9	0.0909
17	6.68	3340.0	0.0853
18	6.68	3342.8	0.0869
19	6.81	3406.2	0.1304
20	6.82	3409.0	0.1185
21	8.25	4125.5	0.2394



No.	(ppm)	(Hz)	Height
1	23.84	2997.5	0.0684
2	25.67	3228.1	0.0702
3	29.67	3731.7	0.0702
4	38.81	4881.2	0.0678
5	55.29	6953.4	0.0747
6	68.66	8635.1	0.0584
7	96.29	12109.2	0.0478

No.	(ppm)	(Hz)	Height
8	110.32	13874.2	0.0611
9	115.00	14462.4	0.0884
10	116.85	14695.1	0.0600
11	123.83	15573.2	0.0349
12	129.00	16222.8	0.0320
13	131.78	16572.8	0.0303
14	134.40	16902.3	0.0523

No.	(ppm)	(Hz)	Height
15	144.02	18111.1	0.0326
16	153.32	19280.8	0.0390
17	154.31	19405.7	0.0349
18	156.81	19719.6	0.0290
19	200.61	25228.8	0.0301

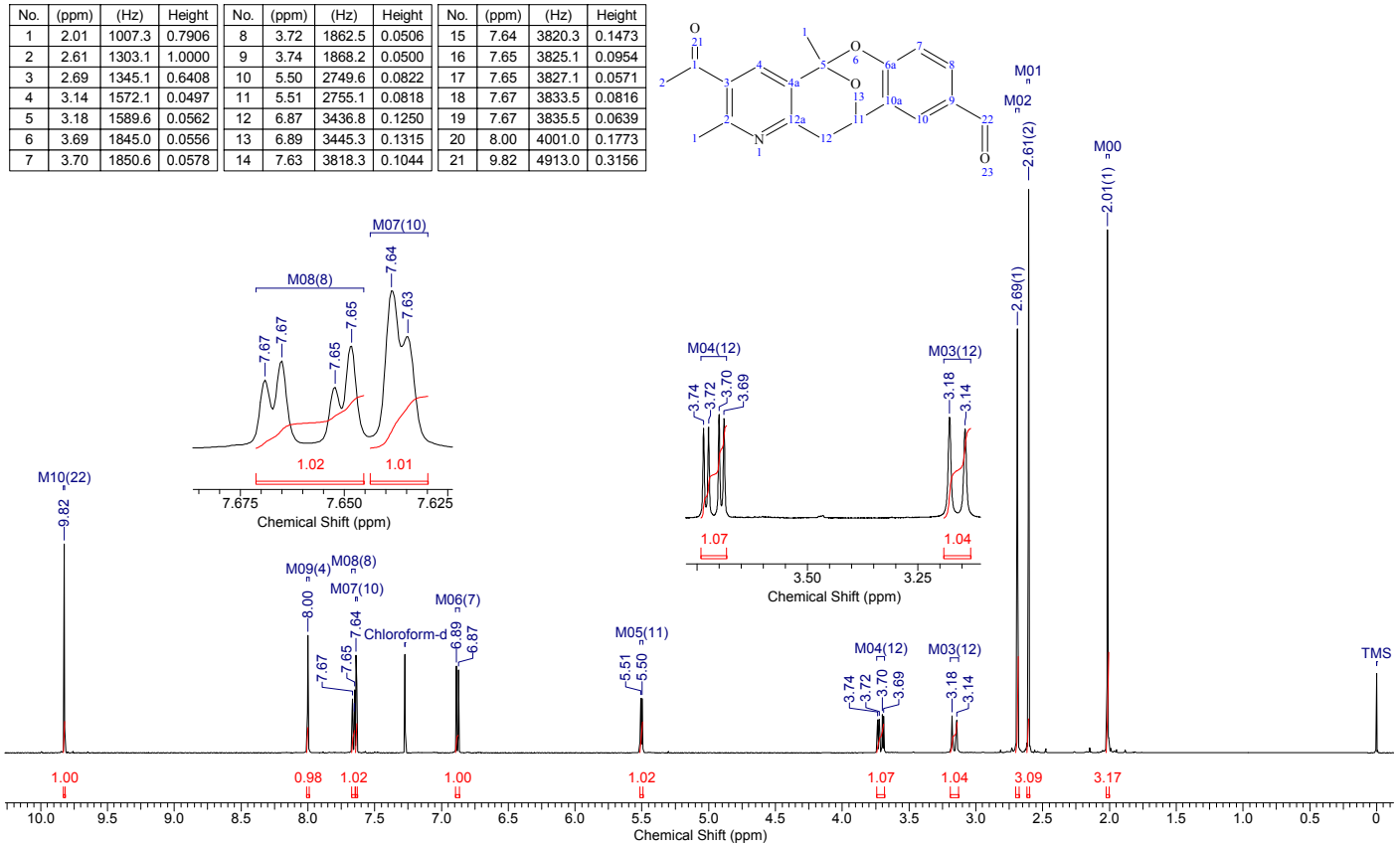


^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7e**

No.	(ppm)	(Hz)	Height
1	2.01	1007.3	0.7906
2	2.61	1303.1	1.0000
3	2.69	1345.1	0.6408
4	3.14	1572.1	0.0497
5	3.18	1589.6	0.0562
6	3.69	1845.0	0.0556
7	3.70	1850.6	0.0578

No.	(ppm)	(Hz)	Height
8	3.72	1862.5	0.0506
9	3.74	1868.2	0.0500
10	5.50	2749.6	0.0822
11	5.51	2755.1	0.0818
12	6.87	3436.8	0.1250
13	6.89	3445.3	0.1315
14	7.63	3818.3	0.1044

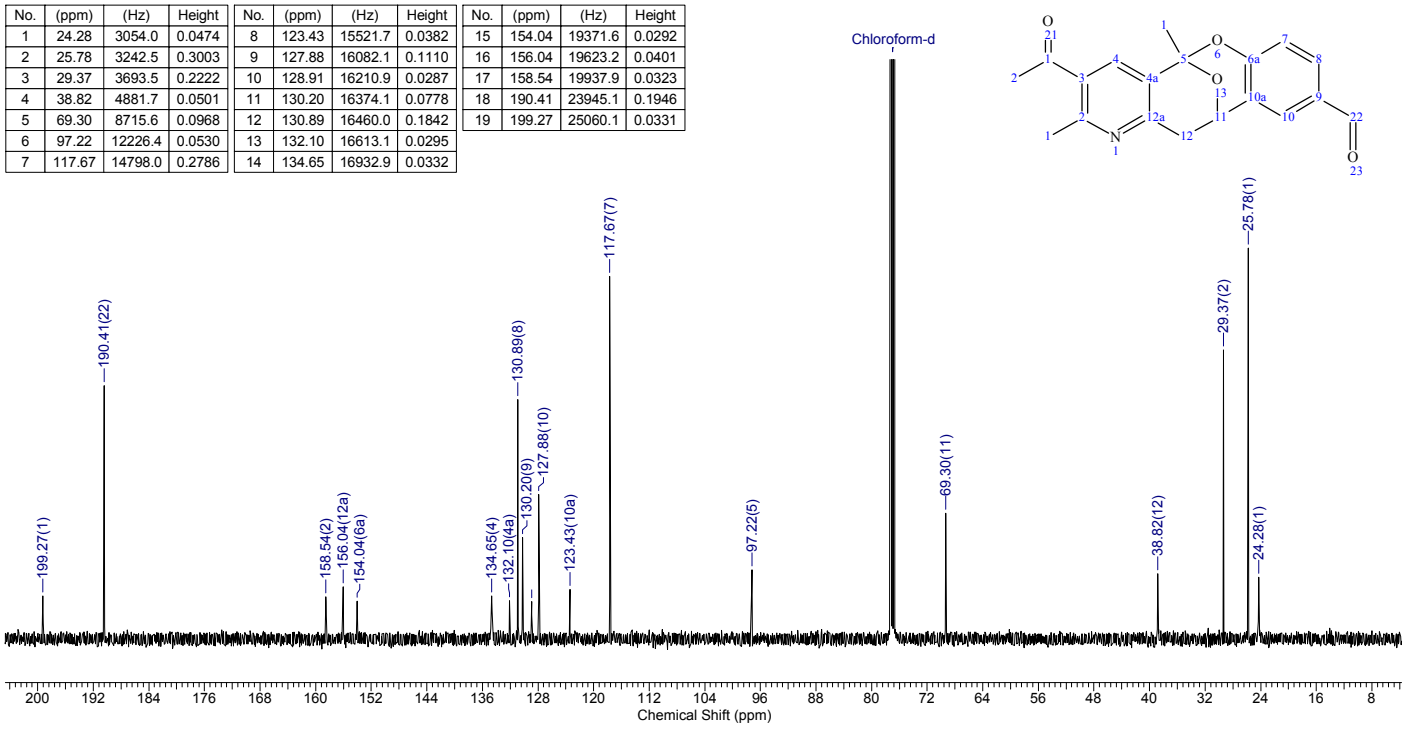
No.	(ppm)	(Hz)	Height
15	7.64	3820.3	0.1473
16	7.65	3825.1	0.0954
17	7.65	3827.1	0.0571
18	7.67	3833.5	0.0816
19	7.67	3835.5	0.0639
20	8.00	4001.0	0.1773
21	9.82	4913.0	0.3156



No.	(ppm)	(Hz)	Height
1	24.28	3054.0	0.0474
2	25.78	3242.5	0.3003
3	29.37	3693.5	0.2222
4	38.82	4881.7	0.0501
5	69.30	8715.6	0.0968
6	97.22	12226.4	0.0530
7	117.67	14798.0	0.2786

No.	(ppm)	(Hz)	Height
8	123.43	15521.7	0.0382
9	127.88	16082.1	0.1110
10	128.91	16210.9	0.0287
11	130.20	16374.1	0.0778
12	130.89	16460.0	0.1842
13	132.10	16613.1	0.0295
14	134.65	16932.9	0.0332

No.	(ppm)	(Hz)	Height
15	154.04	19371.6	0.0292
16	156.04	19623.2	0.0401
17	158.54	19937.9	0.0323
18	190.41	23945.1	0.1946
19	199.27	25060.1	0.0331

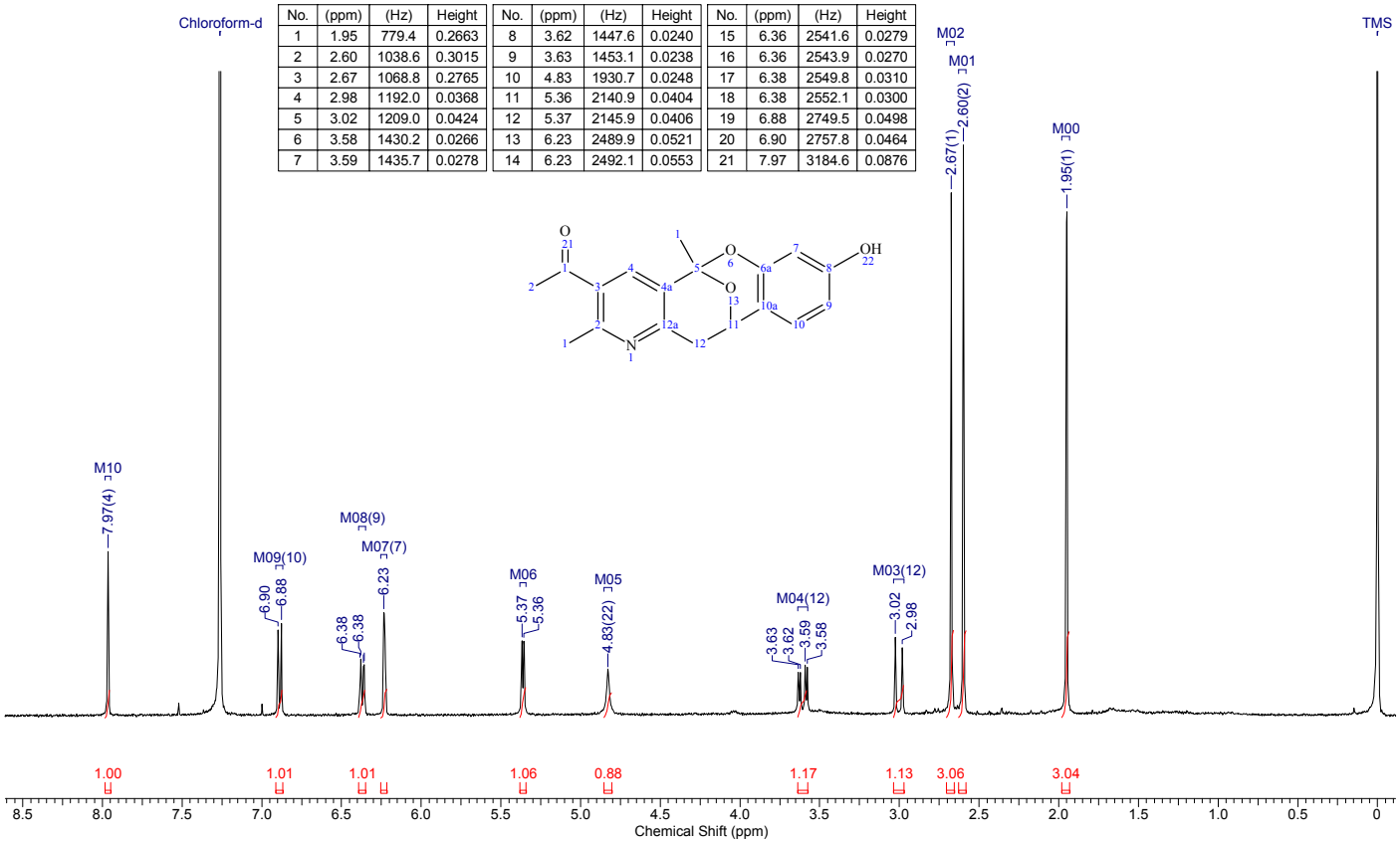


^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7f**

No.	(ppm)	(Hz)	Height
1	1.95	779.4	0.2663
2	2.60	1038.6	0.3015
3	2.67	1068.8	0.2765
4	2.98	1192.0	0.0368
5	3.02	1209.0	0.0424
6	3.58	1430.2	0.0266
7	3.59	1435.7	0.0278

No.	(ppm)	(Hz)	Height
8	3.62	1447.6	0.0240
9	3.63	1453.1	0.0238
10	4.83	1930.7	0.0248
11	5.36	2140.9	0.0404
12	5.37	2145.9	0.0406
13	6.23	2489.9	0.0521
14	6.23	2492.1	0.0553

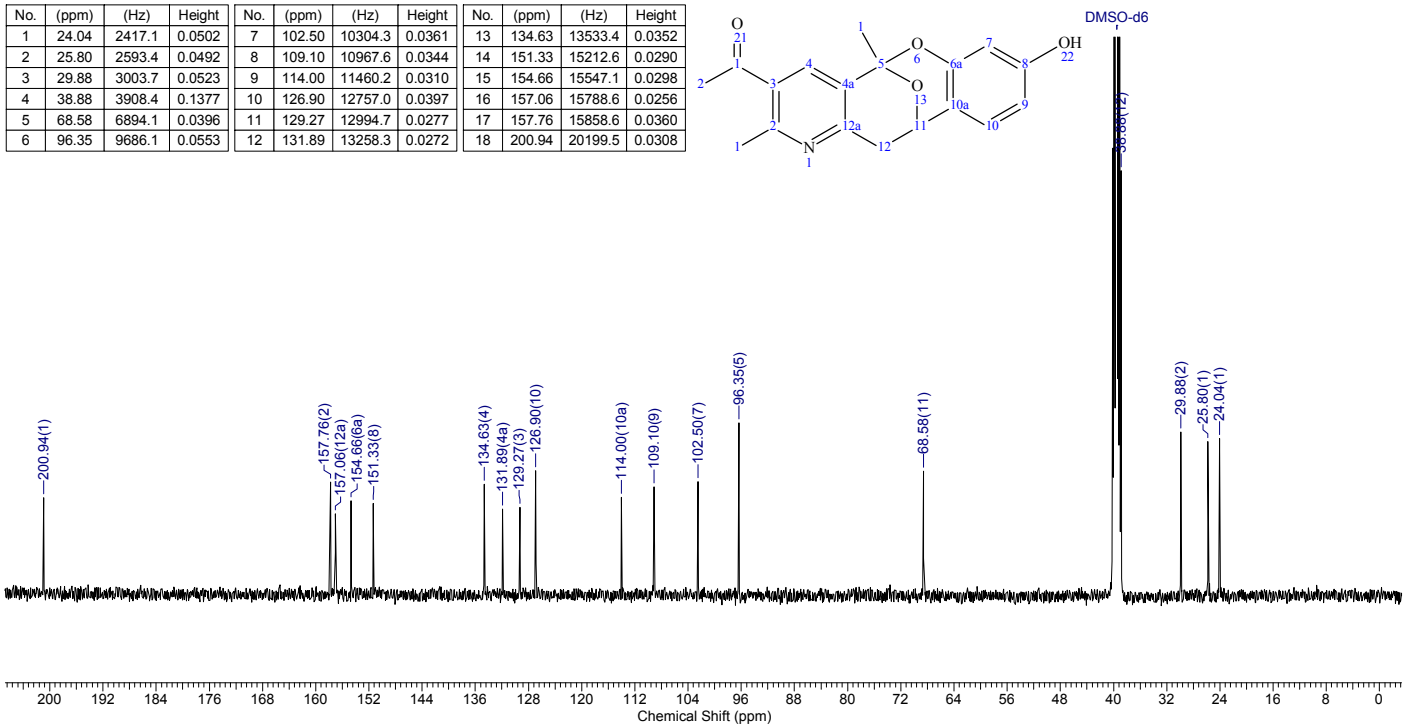
No.	(ppm)	(Hz)	Height
15	6.36	2541.6	0.0279
16	6.36	2543.9	0.0270
17	6.38	2549.8	0.0310
18	6.38	2552.1	0.0300
19	6.88	2749.5	0.0498
20	6.90	2757.8	0.0464
21	7.97	3184.6	0.0876



No.	(ppm)	(Hz)	Height
1	24.04	2417.1	0.0502
2	25.80	2593.4	0.0492
3	29.88	3003.7	0.0523
4	38.88	3908.4	0.1377
5	68.58	6894.1	0.0396
6	96.35	9686.1	0.0553

No.	(ppm)	(Hz)	Height
7	102.50	10304.3	0.0361
8	109.10	10967.6	0.0344
9	114.00	11460.2	0.0310
10	126.90	12757.0	0.0397
11	129.27	12994.7	0.0277
12	131.89	13258.3	0.0272

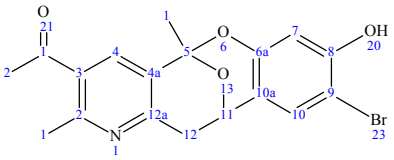
No.	(ppm)	(Hz)	Height
13	134.63	13533.4	0.0352
14	151.33	15212.6	0.0290
15	154.66	15547.1	0.0298
16	157.06	15788.6	0.0256
17	157.76	15858.6	0.0360
18	200.94	20199.5	0.0308

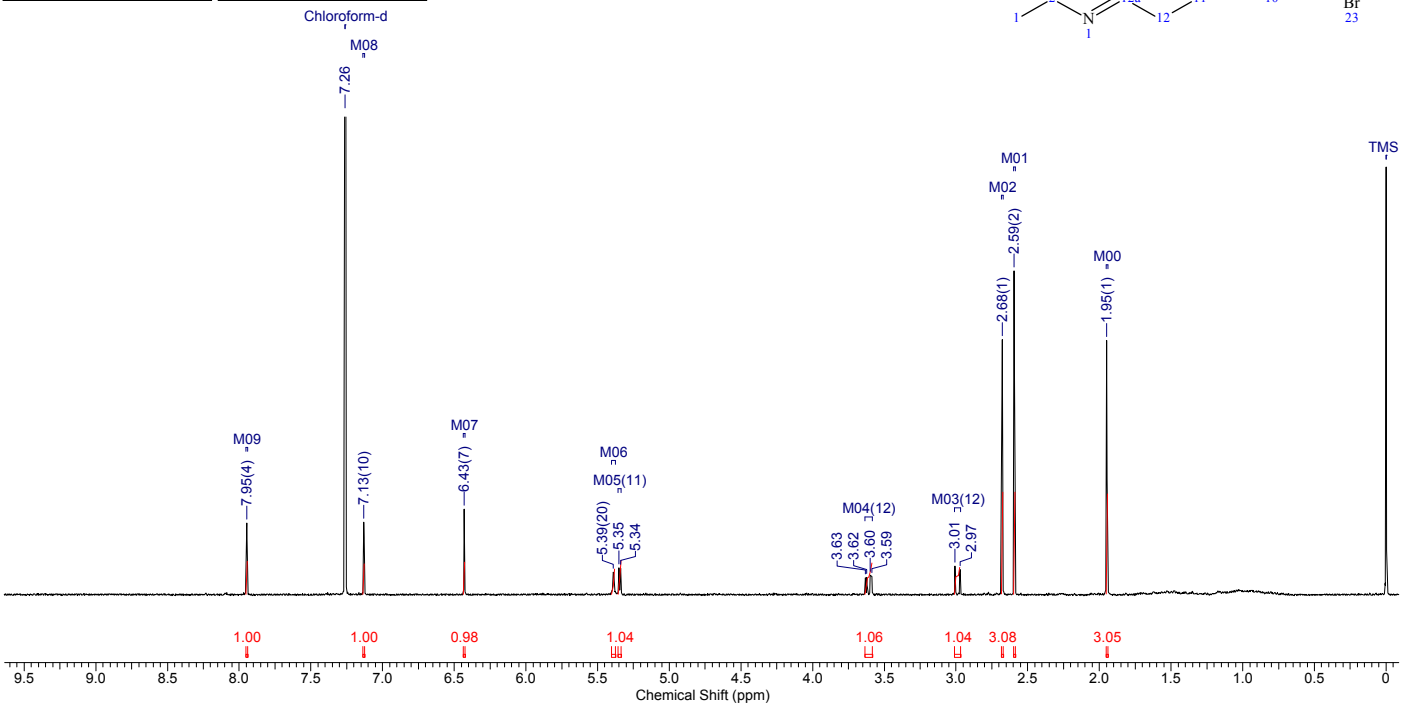


^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7g**

No.	(ppm)	(Hz)	Height
1	1.95	974.2	0.1905
2	2.59	1297.3	0.2427
3	2.68	1339.3	0.1912
4	2.97	1486.6	0.0188
5	3.01	1503.9	0.0213
6	3.59	1793.9	0.0134
7	3.60	1799.3	0.0145
8	3.62	1811.3	0.0127

No.	(ppm)	(Hz)	Height
9	3.63	1816.4	0.0124
10	5.34	2670.6	0.0197
11	5.35	2675.7	0.0200
12	5.39	2695.6	0.0167
13	6.43	3216.7	0.0640
14	7.13	3565.9	0.0542
15	7.26	3631.7	1.0000
16	7.95	3974.7	0.0536

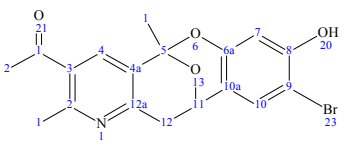




No.	(ppm)	(Hz)	Height
1	24.64	3099.3	0.0123
2	25.96	3264.2	0.0129
3	29.38	3694.2	0.0121
4	39.51	4969.1	0.0114
5	68.95	8670.8	0.0118
6	96.72	12163.1	0.0084

No.	(ppm)	(Hz)	Height
7	102.23	12856.5	0.0056
8	104.27	13113.1	0.0094
9	117.13	14730.5	0.0062
10	128.30	16134.1	0.0092
11	129.04	16227.5	0.0040
12	131.88	16584.3	0.0053

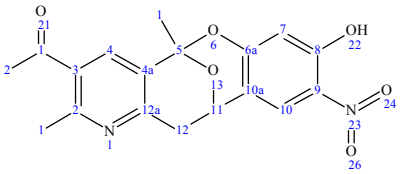
No.	(ppm)	(Hz)	Height
13	134.31	16890.6	0.0084
14	151.59	19063.4	0.0053
15	152.44	19170.3	0.0046
16	154.55	19436.2	0.0035
17	158.55	19938.6	0.0068
18	199.59	25099.5	0.0043



^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7h**

No.	(ppm)	(Hz)	Height
1	2.00	799.6	0.8260
2	2.61	1042.3	1.0000
3	2.68	1072.5	0.8532
4	3.04	1214.0	0.0805
5	3.08	1231.4	0.0926
6	3.65	1458.1	0.0602
7	3.66	1463.6	0.0634
8	3.69	1475.5	0.0529

No.	(ppm)	(Hz)	Height
9	3.70	1481.0	0.0528
10	5.44	2175.2	0.0900
11	5.45	2180.7	0.0881
12	6.46	2581.0	0.2740
13	7.90	3158.9	0.2280
14	7.95	3179.5	0.2386
15	10.65	4256.2	0.3251



No.	(ppm)	(Hz)	Height
1	24.67	2480.4	0.0461
2	25.65	2578.1	0.0461
3	29.42	2957.7	0.0406
4	39.13	3933.4	0.0477
5	68.99	6935.3	0.0430
6	97.93	9844.3	0.0361

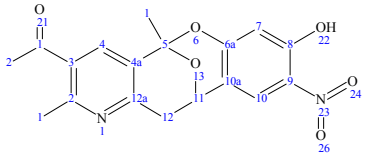
No.	(ppm)	(Hz)	Height
7	105.91	10646.5	0.0407
8	116.46	11707.5	0.0236
9	123.32	12396.7	0.0497
10	128.27	12894.1	0.0340
11	132.04	13273.7	0.0204
12	134.27	13498.0	0.0417

No.	(ppm)	(Hz)	Height
13	153.75	15456.1	0.0272
14	156.23	15705.3	0.0308
15	158.79	15962.2	0.0217
16	159.03	15986.1	0.0240
17	199.41	20046.2	0.0249

No.	Atom	Exp. Shift (ppm)
1	1	24.67
2	1	25.65
3	2	29.42
4	12	39.13
5	11	68.99
6	5	97.93

No.	Atom	Exp. Shift (ppm)
7	7	105.91
8	10a	116.46
9	10	123.32
10	3	128.27
11	9	128.27
12	4a	132.04

No.	Atom	Exp. Shift (ppm)
13	4	134.27
14	6a	153.75
15	8	156.23
16	12a	158.79
17	2	159.03
18	1	199.41



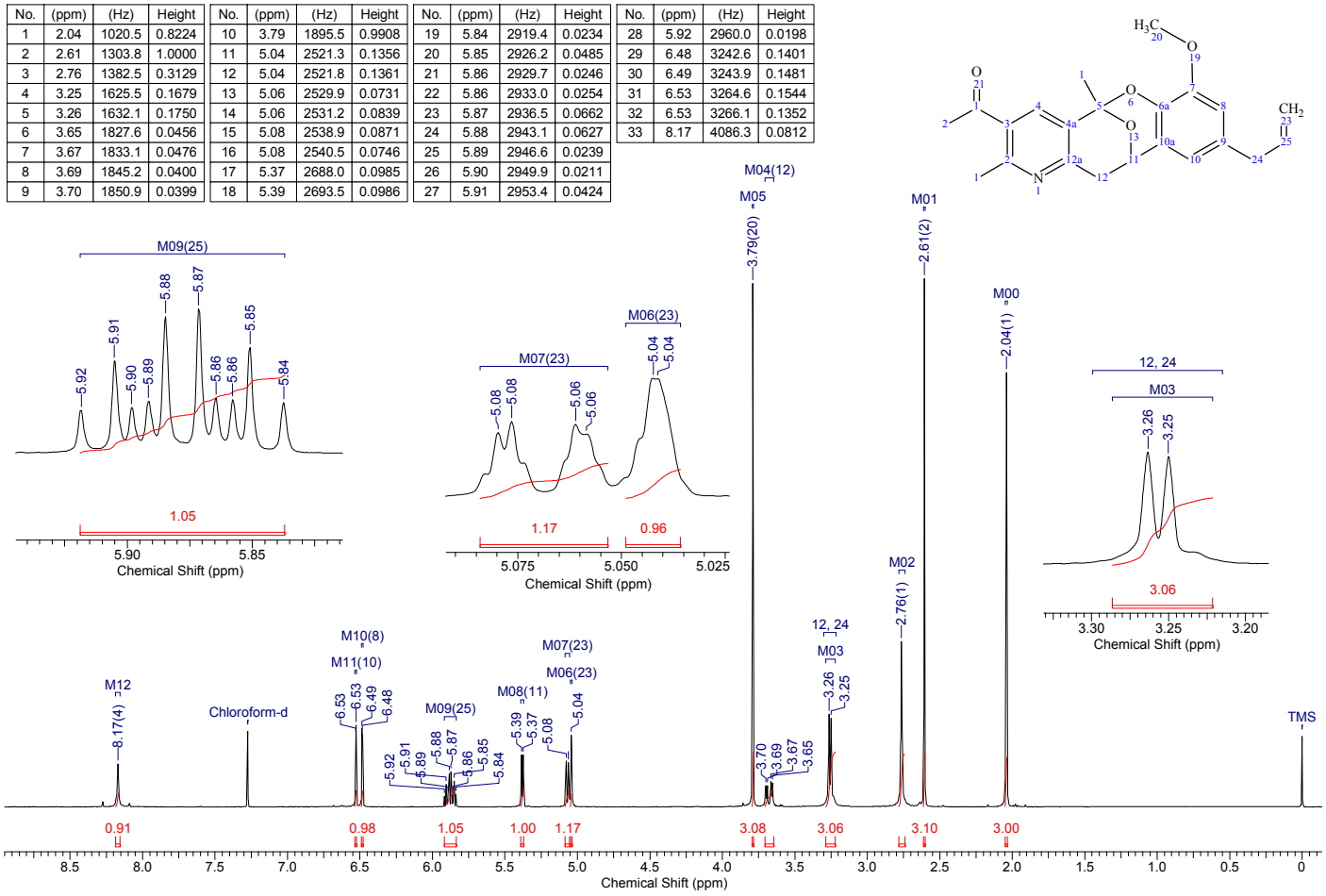
^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7i**

No.	(ppm)	(Hz)	Height
1	2.04	1020.5	0.8224
2	2.61	1303.8	1.0000
3	2.76	1382.5	0.3129
4	3.25	1625.5	0.1679
5	3.26	1632.1	0.1750
6	3.65	1827.6	0.0456
7	3.67	1833.1	0.0476
8	3.69	1845.2	0.0400
9	3.70	1850.9	0.0399

No.	(ppm)	(Hz)	Height
10	3.79	1895.5	0.9908
11	5.04	2521.3	0.1356
12	5.04	2521.8	0.1361
13	5.06	2529.9	0.0731
14	5.06	2531.2	0.0839
15	5.08	2538.9	0.0871
16	5.08	2540.5	0.0746
17	5.37	2688.0	0.0985
18	5.39	2693.5	0.0986

No.	(ppm)	(Hz)	Height
19	5.84	2919.4	0.0234
20	5.85	2926.2	0.0485
21	5.86	2929.7	0.0246
22	5.86	2933.0	0.0254
23	5.87	2936.5	0.0662
24	5.88	2943.1	0.0627
25	5.89	2946.6	0.0239
26	5.90	2949.9	0.0211
27	5.91	2953.4	0.0424

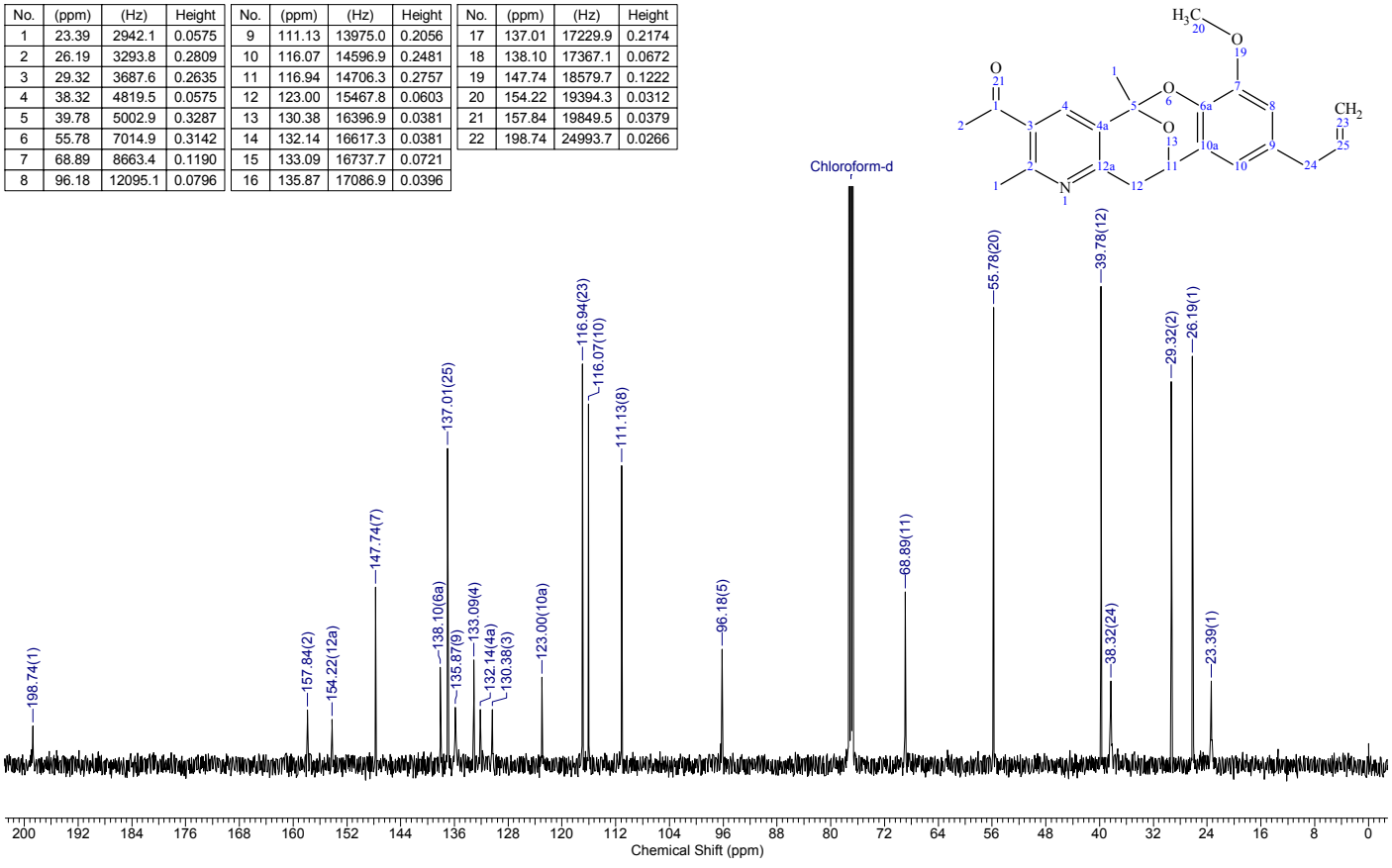
No.	(ppm)	(Hz)	Height
28	5.92	2960.0	0.0198
29	6.48	3242.6	0.1401
30	6.49	3243.9	0.1481
31	6.53	3264.6	0.1544
32	6.53	3266.1	0.1352
33	8.17	4086.3	0.0812



No.	(ppm)	(Hz)	Height
1	23.39	2942.1	0.0575
2	26.19	3293.8	0.2809
3	29.32	3687.6	0.2635
4	38.32	4819.5	0.0575
5	39.78	5002.9	0.3287
6	55.78	7014.9	0.3142
7	68.89	8663.4	0.1190
8	96.18	12095.1	0.0796

No.	(ppm)	(Hz)	Height
9	111.13	13975.0	0.2056
10	116.07	14596.9	0.2481
11	116.94	14706.3	0.2757
12	123.00	15467.8	0.0603
13	130.38	16396.9	0.0381
14	132.14	16617.3	0.0381
15	133.09	16737.7	0.0721
16	135.87	17086.9	0.0396

No.	(ppm)	(Hz)	Height
17	137.01	17229.9	0.2174
18	138.10	17367.1	0.0672
19	147.74	18579.7	0.1222
20	154.22	19394.3	0.0312
21	157.84	19849.5	0.0379
22	198.74	24993.7	0.0266

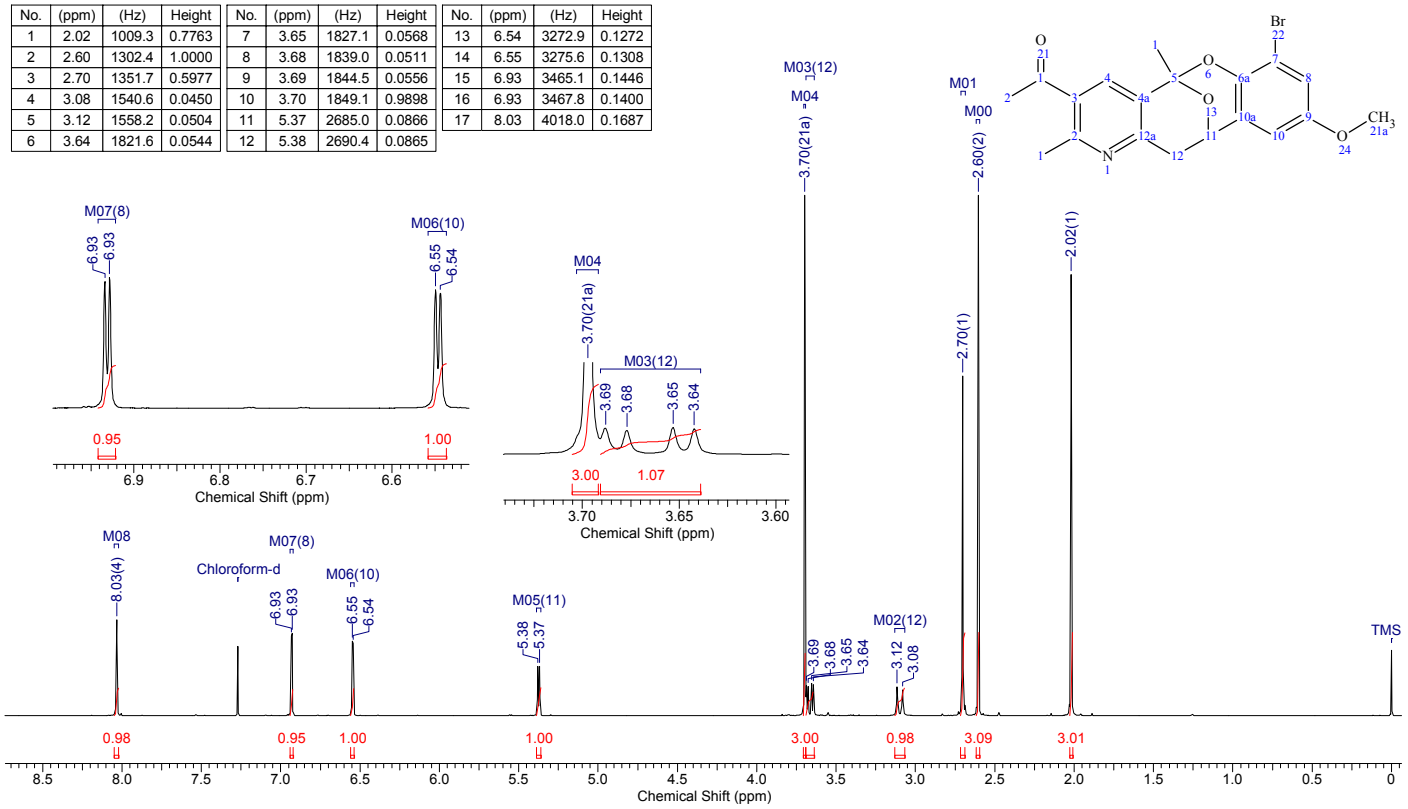


^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7j**

No.	(ppm)	(Hz)	Height
1	2.02	1009.3	0.7763
2	2.60	1302.4	1.0000
3	2.70	1351.7	0.5977
4	3.08	1540.6	0.0450
5	3.12	1558.2	0.0504
6	3.64	1821.6	0.0544

No.	(ppm)	(Hz)	Height
7	3.65	1827.1	0.0568
8	3.68	1839.0	0.0511
9	3.69	1844.5	0.0556
10	3.70	1849.1	0.9898
11	5.37	2685.0	0.0866
12	5.38	2690.4	0.0865

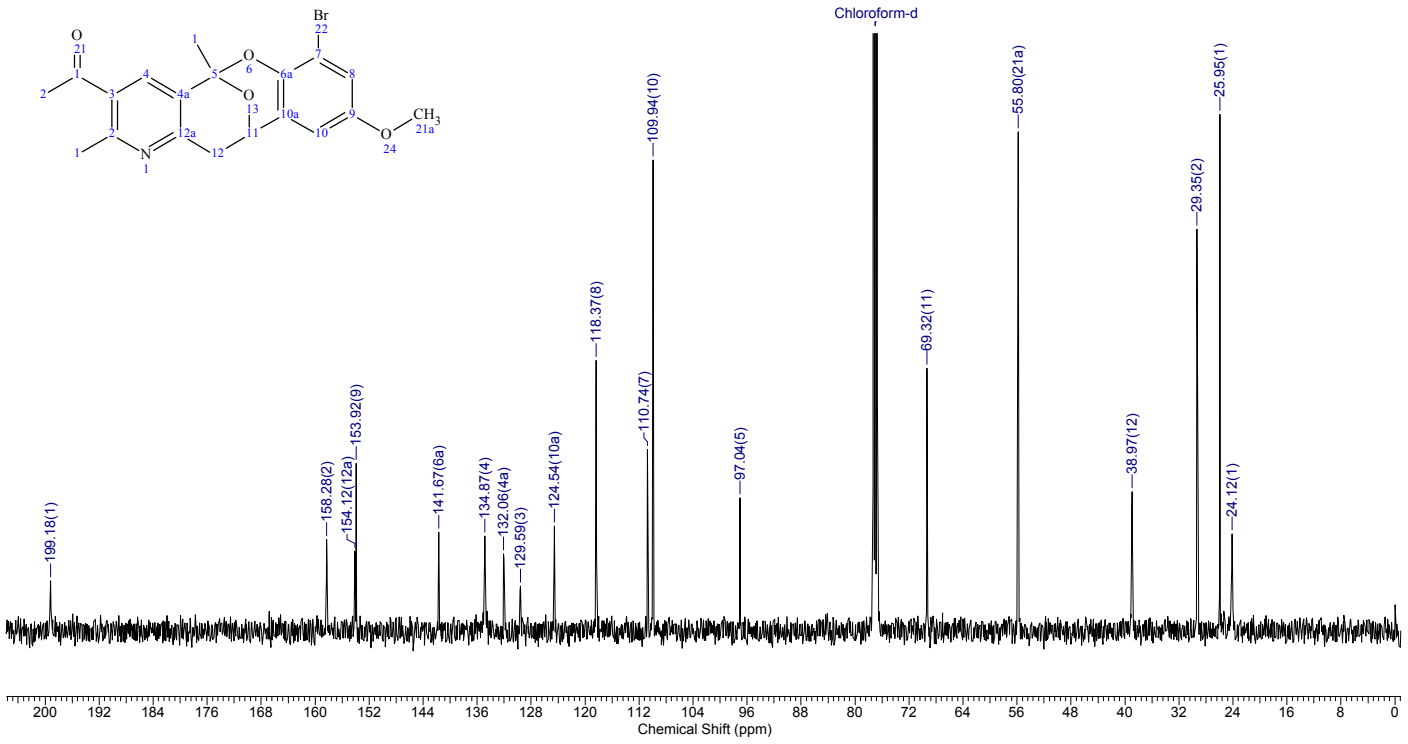
No.	(ppm)	(Hz)	Height
13	6.54	3272.9	0.1272
14	6.55	3275.6	0.1308
15	6.93	3465.1	0.1446
16	6.93	3467.8	0.1400
17	8.03	4018.0	0.1687



No.	(ppm)	(Hz)	Height
1	24.12	3033.8	0.0538
2	25.95	3263.5	0.2877
3	29.35	3691.0	0.2236
4	38.97	4901.1	0.0773
5	55.80	7017.5	0.2779
6	69.32	8718.1	0.1462
7	97.04	12203.7	0.0741

No.	(ppm)	(Hz)	Height
8	109.94	13825.2	0.2623
9	110.74	13926.2	0.1009
10	118.37	14885.5	0.1505
11	124.54	15662.2	0.0583
12	129.59	16296.7	0.0248
13	132.06	16608.1	0.0427
14	134.87	16960.7	0.0527

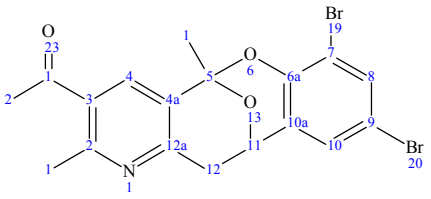
No.	(ppm)	(Hz)	Height
15	141.67	17815.6	0.0549
16	153.92	19356.4	0.0931
17	154.12	19381.7	0.0442
18	158.28	19905.1	0.0507
19	199.18	25048.4	0.0276



^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7k**

No.	(ppm)	(Hz)	Height
1	2.01	803.4	0.5749
2	2.58	1030.7	1.0000
3	2.65	1061.3	0.4278
4	2.99	1194.0	0.0742
5	3.03	1210.8	0.0963
6	3.61	1442.7	0.0609
7	3.62	1447.3	0.0402

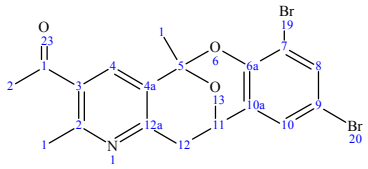
No.	(ppm)	(Hz)	Height
8	3.65	1459.5	0.0468
9	3.67	1465.6	0.0567
10	5.35	2140.1	0.0845
11	5.37	2146.2	0.0859
12	7.11	2843.5	0.1381
13	7.45	2979.3	0.1499
14	7.96	3183.8	0.1941

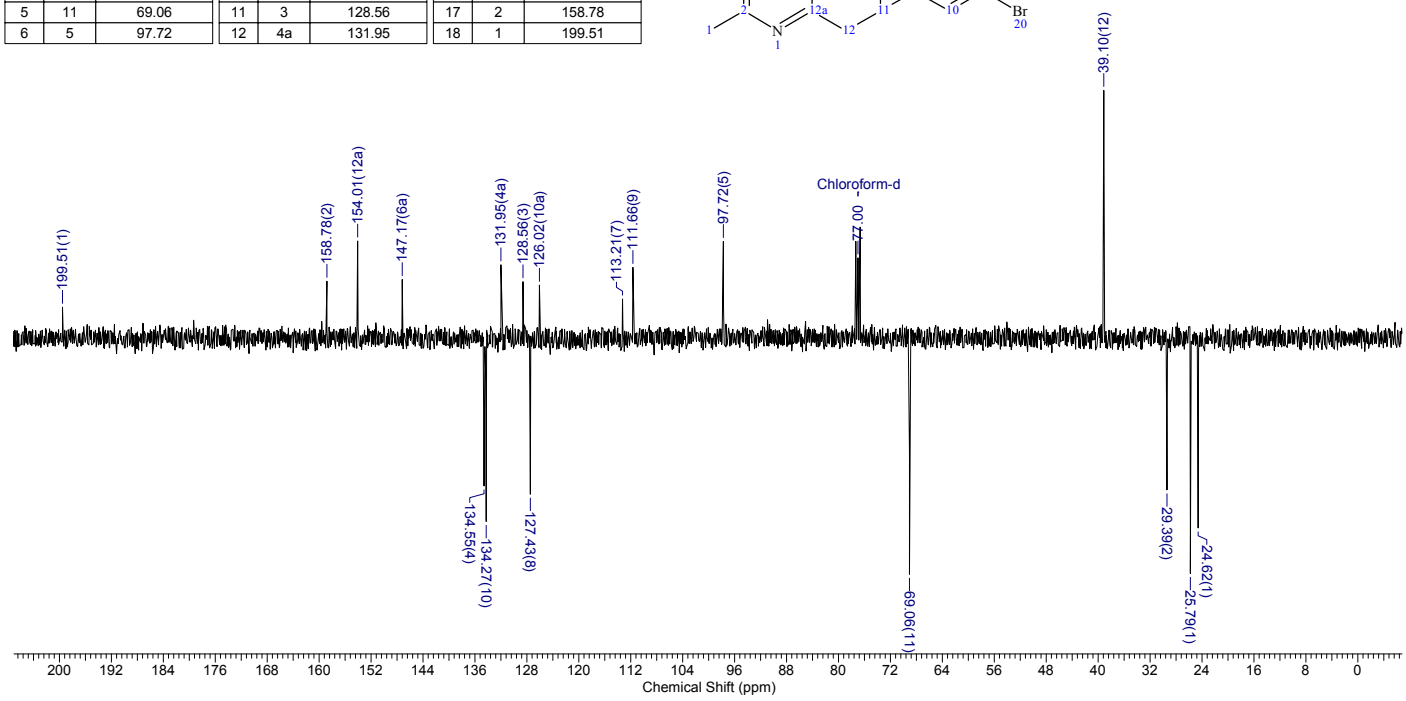


No.	Atom	Exp. Shift (ppm)
1	1	24.62
2	1	25.79
3	2	29.39
4	12	39.10
5	11	69.06
6	5	97.72

No.	Atom	Exp. Shift (ppm)
7	9	111.66
8	7	113.21
9	10a	126.02
10	8	127.43
11	3	128.56
12	4a	131.95

No.	Atom	Exp. Shift (ppm)
13	10	134.27
14	4	134.55
15	6a	147.17
16	12a	154.01
17	2	158.78
18	1	199.51



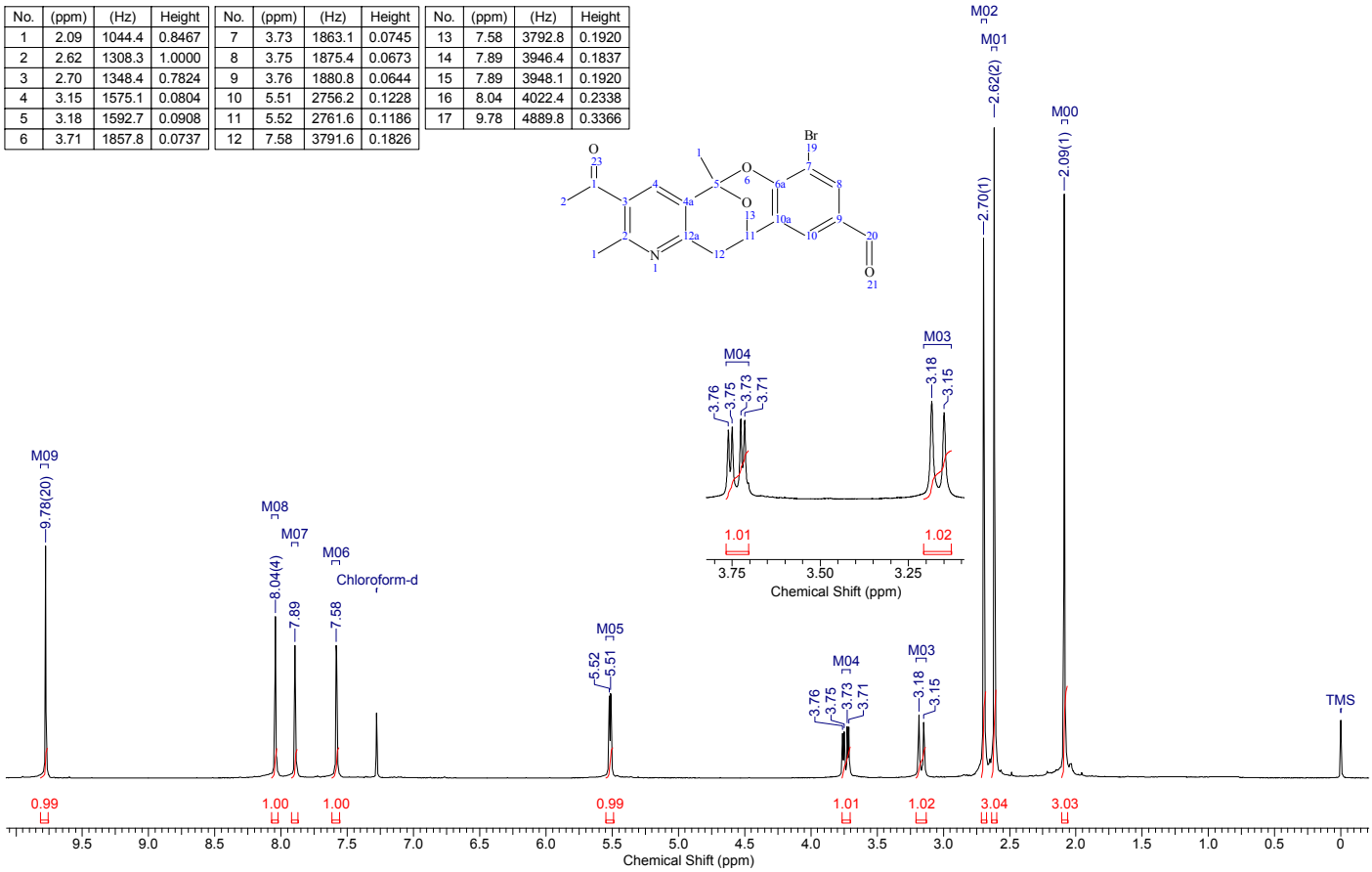


^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of ***7l***

No.	(ppm)	(Hz)	Height
1	2.09	1044.4	0.8467
2	2.62	1308.3	1.0000
3	2.70	1348.4	0.7824
4	3.15	1575.1	0.0804
5	3.18	1592.7	0.0908
6	3.71	1857.8	0.0737

No.	(ppm)	(Hz)	Height
7	3.73	1863.1	0.0745
8	3.75	1875.4	0.0673
9	3.76	1880.8	0.0644
10	5.51	2756.2	0.1228
11	5.52	2761.6	0.1186
12	7.58	3791.6	0.1826

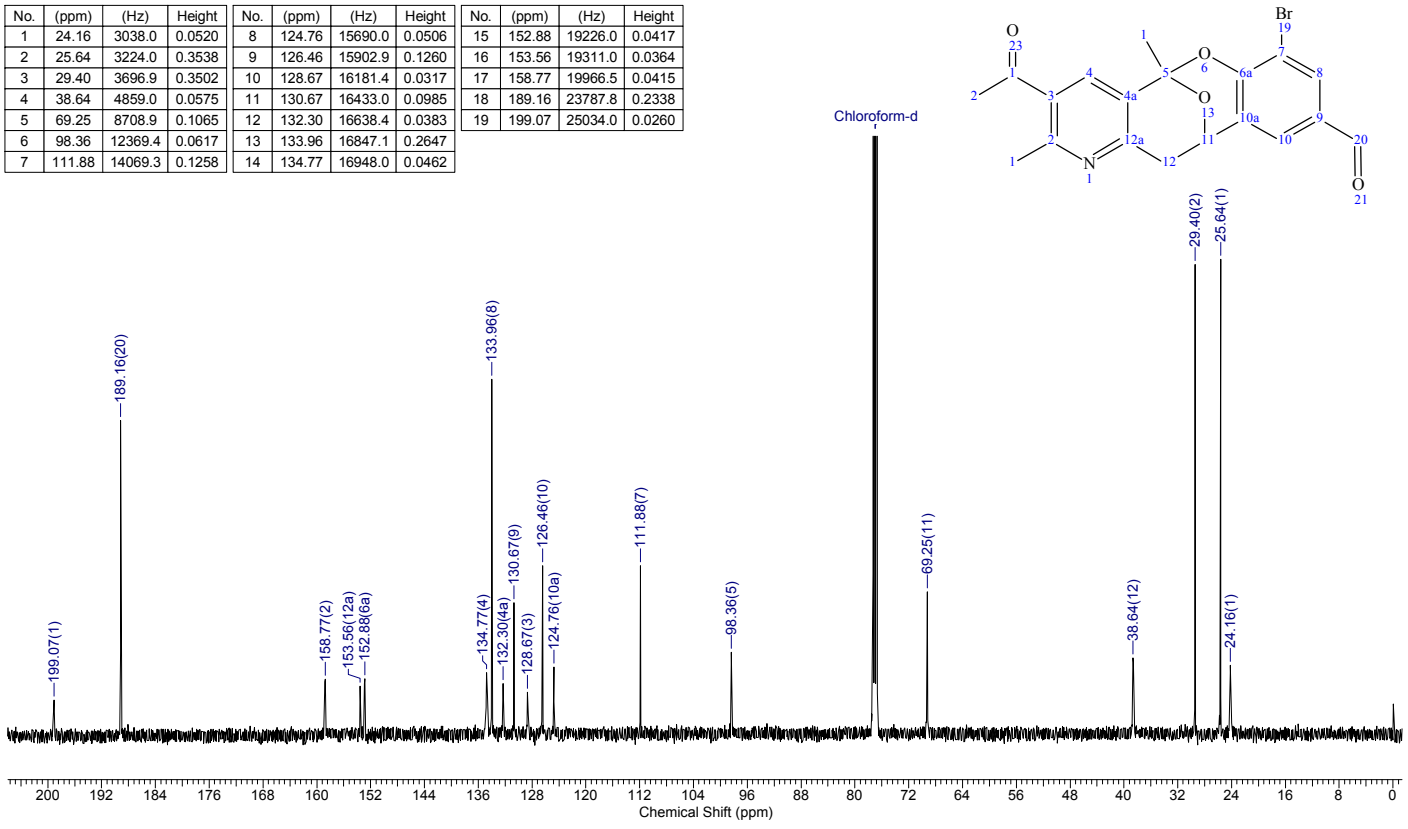
No.	(ppm)	(Hz)	Height
13	7.58	3792.8	0.1920
14	7.89	3946.4	0.1837
15	7.89	3948.1	0.1920
16	8.04	4022.4	0.2338
17	9.78	4889.8	0.3366



No.	(ppm)	(Hz)	Height
1	24.16	3038.0	0.0520
2	25.64	3224.0	0.3538
3	29.40	3696.9	0.3502
4	38.64	4859.0	0.0575
5	69.25	8708.9	0.1065
6	98.36	12369.4	0.0617
7	111.88	14069.3	0.1258

No.	(ppm)	(Hz)	Height
8	124.76	15690.0	0.0506
9	126.46	15902.9	0.1260
10	128.67	16181.4	0.0317
11	130.67	16433.0	0.0985
12	132.30	16638.4	0.0383
13	133.96	16847.1	0.2647
14	134.77	16948.0	0.0462

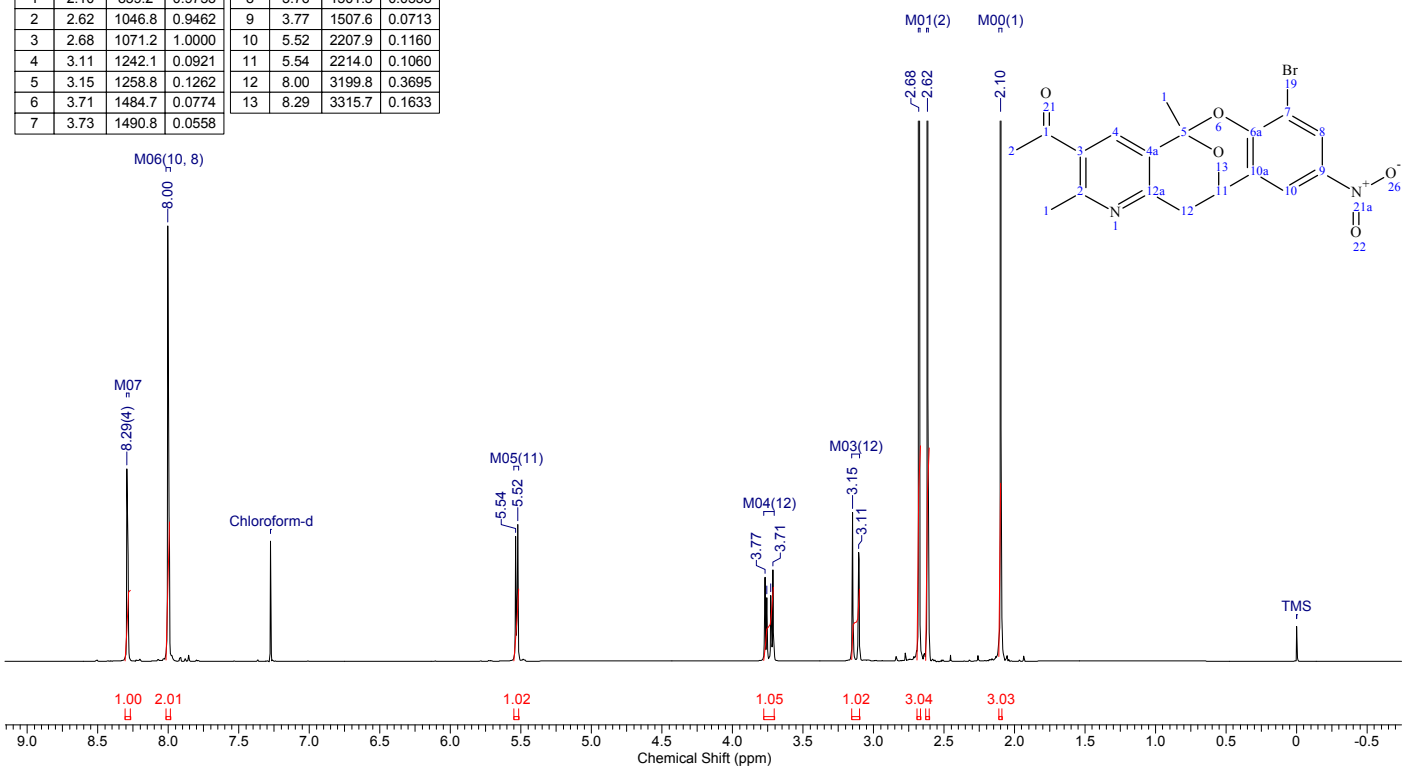
No.	(ppm)	(Hz)	Height
15	152.88	19226.0	0.0417
16	153.56	19311.0	0.0364
17	158.77	19966.5	0.0415
18	189.16	23787.8	0.2338
19	199.07	25034.0	0.0260



^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7m**

No.	(ppm)	(Hz)	Height
1	2.10	839.2	0.9753
2	2.62	1046.8	0.9462
3	2.68	1071.2	1.0000
4	3.11	1242.1	0.0921
5	3.15	1258.8	0.1262
6	3.71	1484.7	0.0774
7	3.73	1490.8	0.0558

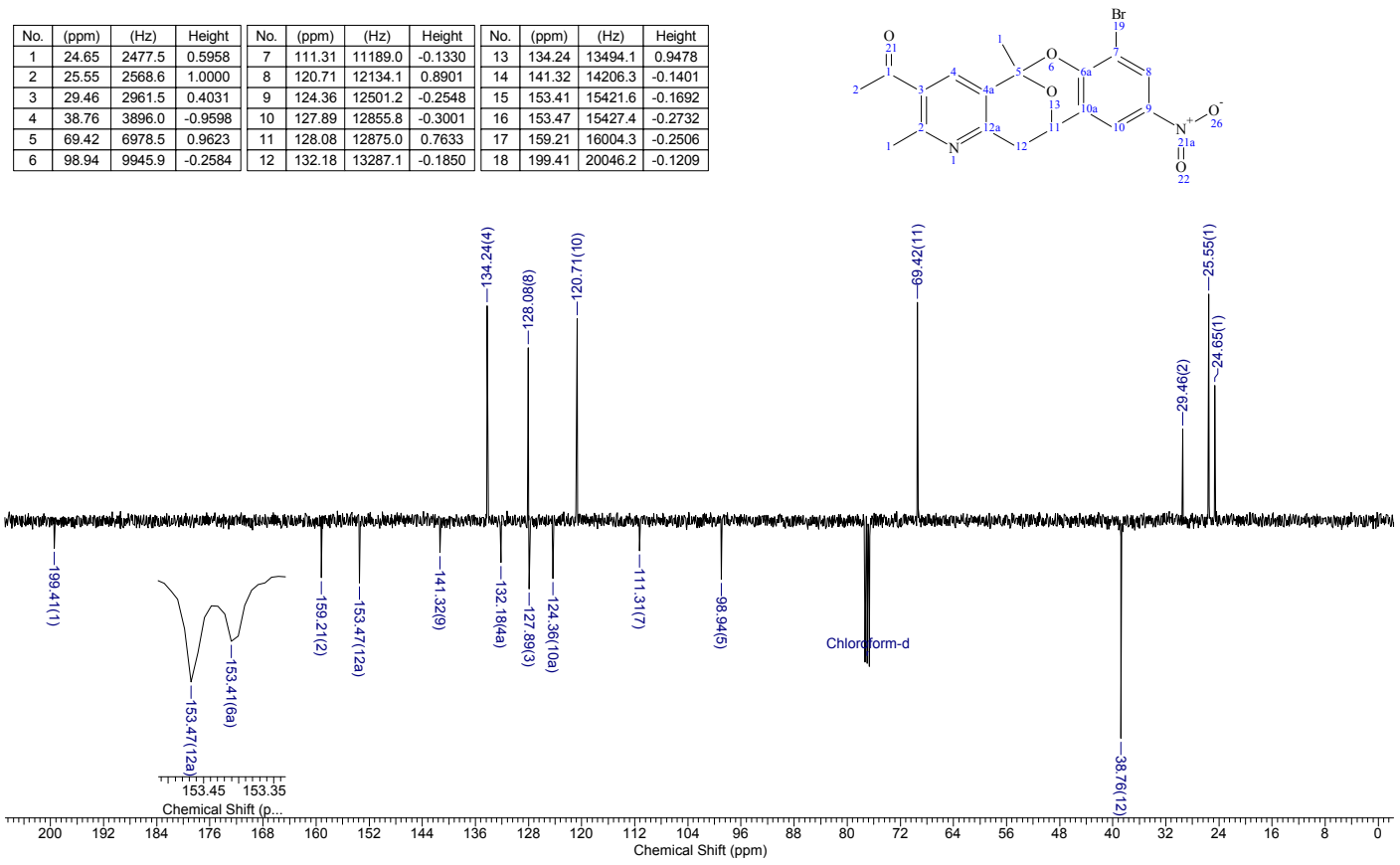
No.	(ppm)	(Hz)	Height
8	3.76	1501.5	0.0538
9	3.77	1507.6	0.0713
10	5.52	2207.9	0.1160
11	5.54	2214.0	0.1060
12	8.00	3199.8	0.3695
13	8.29	3315.7	0.1633



No.	(ppm)	(Hz)	Height
1	24.65	2477.5	0.5958
2	25.55	2568.6	1.0000
3	29.46	2961.5	0.4031
4	38.76	3896.0	-0.9598
5	69.42	6978.5	0.9623
6	98.94	9945.9	-0.2584

No.	(ppm)	(Hz)	Height
7	111.31	11189.0	-0.1330
8	120.71	12134.1	0.8901
9	124.36	12501.2	-0.2548
10	127.89	12855.8	-0.3001
11	128.08	12875.0	0.7633
12	132.18	13287.1	-0.1850

No.	(ppm)	(Hz)	Height
13	134.24	13494.1	0.9478
14	141.32	14206.3	-0.1401
15	153.41	15421.6	-0.1692
16	153.47	15427.4	-0.2732
17	159.21	16004.3	-0.2506
18	199.41	20046.2	-0.1209

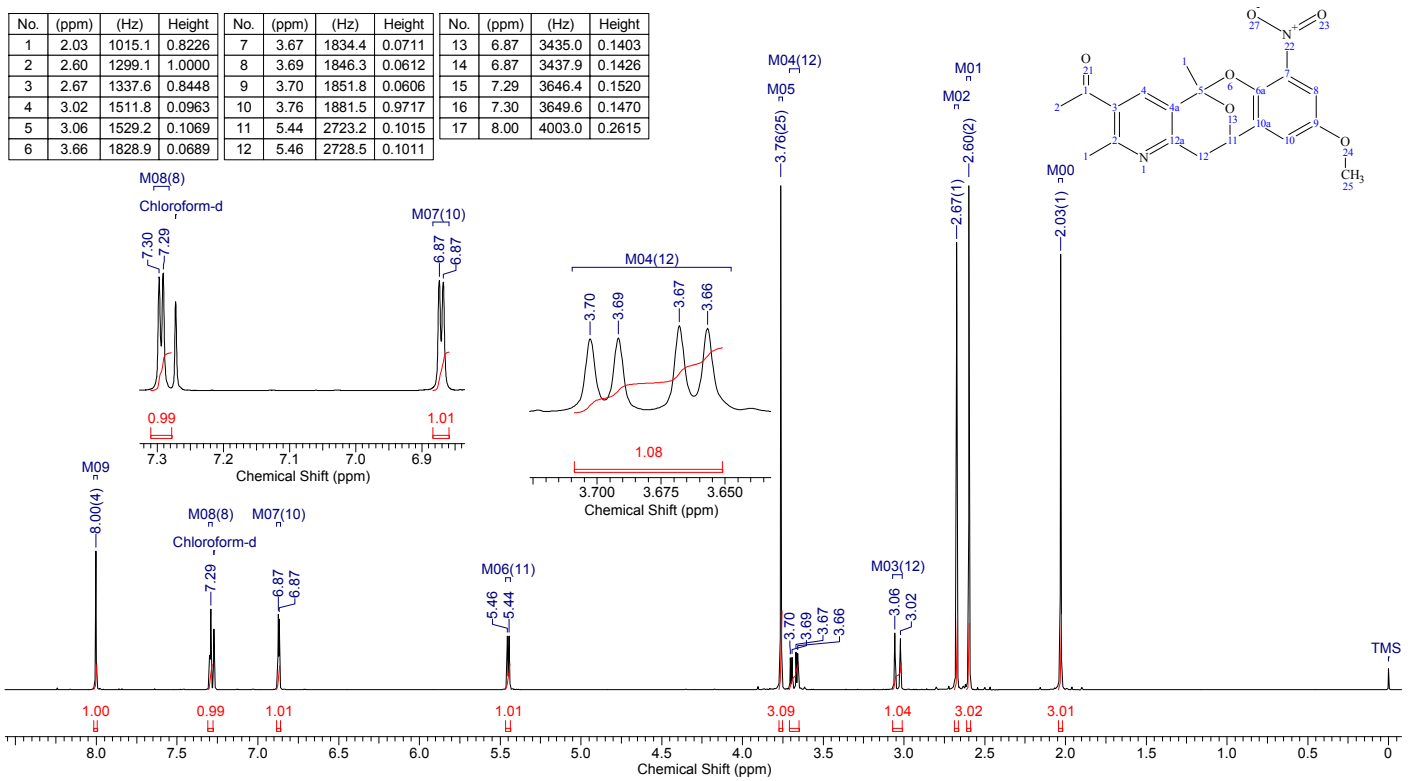


^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7n**

No.	(ppm)	(Hz)	Height
1	2.03	1015.1	0.8226
2	2.60	1299.1	1.0000
3	2.67	1337.6	0.8448
4	3.02	1511.8	0.0963
5	3.06	1529.2	0.1069
6	3.66	1828.9	0.0689

No.	(ppm)	(Hz)	Height
7	3.67	1834.4	0.0711
8	3.69	1846.3	0.0612
9	3.70	1851.8	0.0606
10	3.76	1881.5	0.9717
11	5.44	2723.2	0.1015
12	5.46	2728.5	0.1011

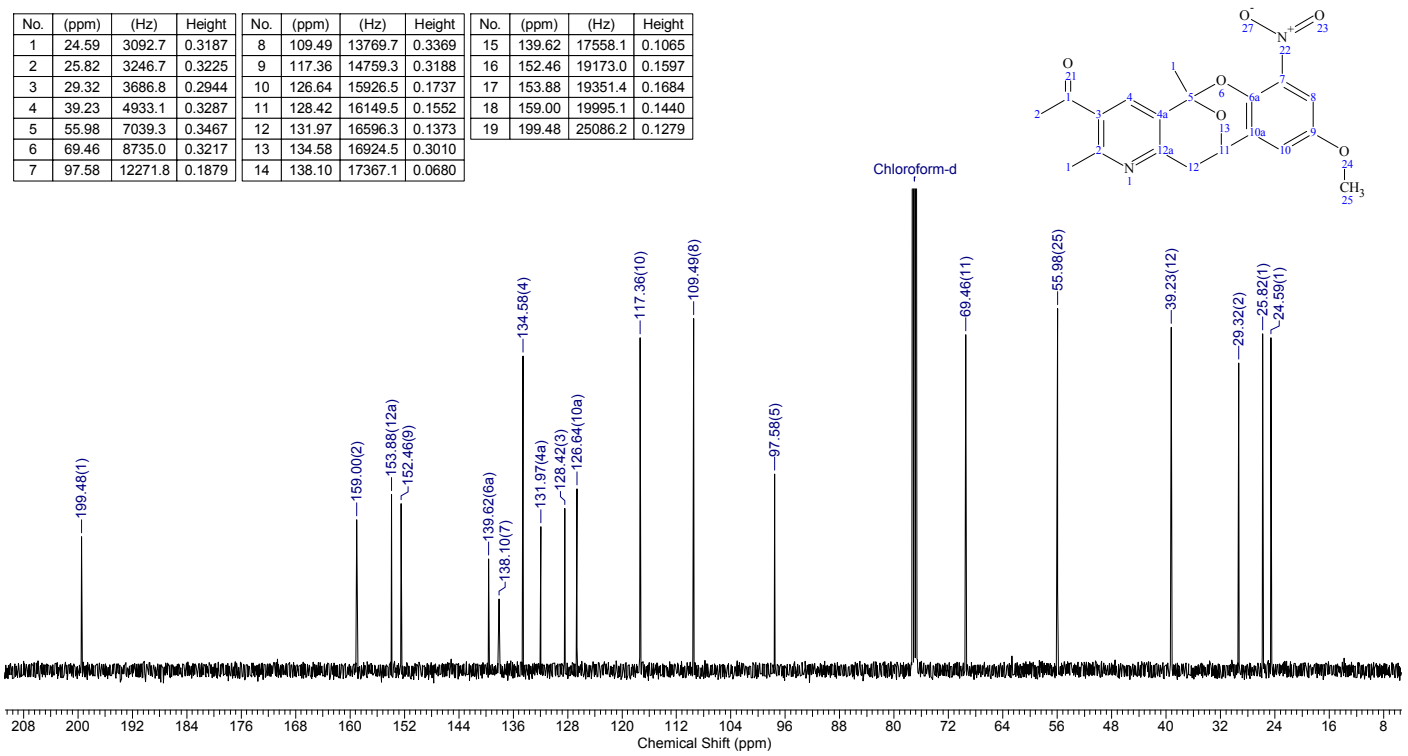
No.	(ppm)	(Hz)	Height
13	6.87	3435.0	0.1403
14	6.87	3437.9	0.1426
15	7.29	3646.4	0.1520
16	7.30	3649.6	0.1470
17	8.00	4003.0	0.2615



No.	(ppm)	(Hz)	Height
1	24.59	3092.7	0.3187
2	25.82	3246.7	0.3225
3	29.32	3686.8	0.2944
4	39.23	4933.1	0.3287
5	55.98	7039.3	0.3467
6	69.46	8735.0	0.3217
7	97.58	12271.8	0.1879

No.	(ppm)	(Hz)	Height
8	109.49	13769.7	0.3369
9	117.36	14759.3	0.3188
10	126.64	15926.5	0.1737
11	128.42	16149.5	0.1552
12	131.97	16596.3	0.1373
13	134.58	16924.5	0.3010
14	138.10	17367.1	0.0680

No.	(ppm)	(Hz)	Height
15	139.62	17558.1	0.1065
16	152.46	19173.0	0.1597
17	153.88	19351.4	0.1684
18	159.00	19995.1	0.1440
19	199.48	25086.2	0.1279

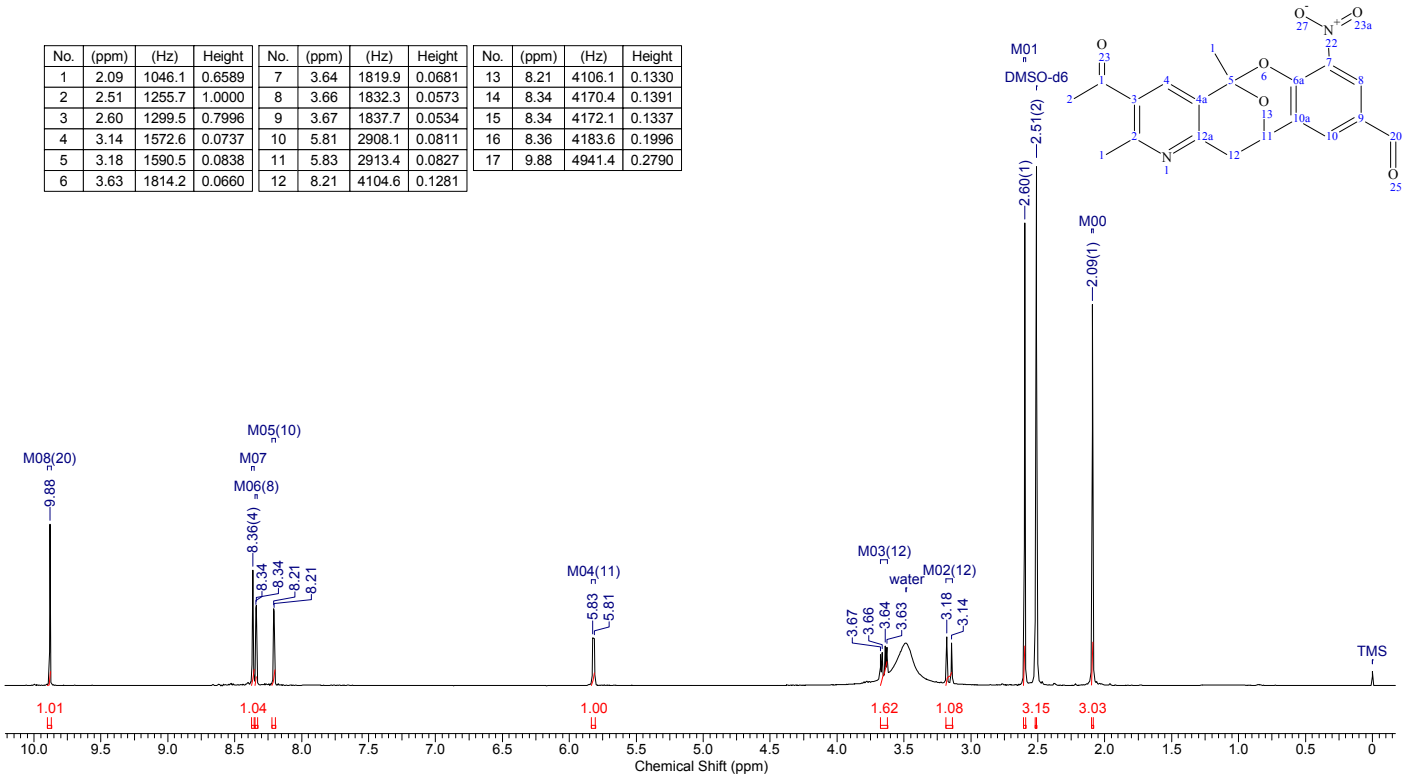


^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7o**

No.	(ppm)	(Hz)	Height
1	2.09	1046.1	0.6589
2	2.51	1255.7	1.0000
3	2.60	1299.5	0.7996
4	3.14	1572.6	0.0737
5	3.18	1590.5	0.0838
6	3.63	1814.2	0.0660

No.	(ppm)	(Hz)	Height
7	3.64	1819.9	0.0681
8	3.66	1832.3	0.0573
9	3.67	1837.7	0.0534
10	5.81	2908.1	0.0811
11	5.83	2913.4	0.0827
12	8.21	4104.6	0.1281

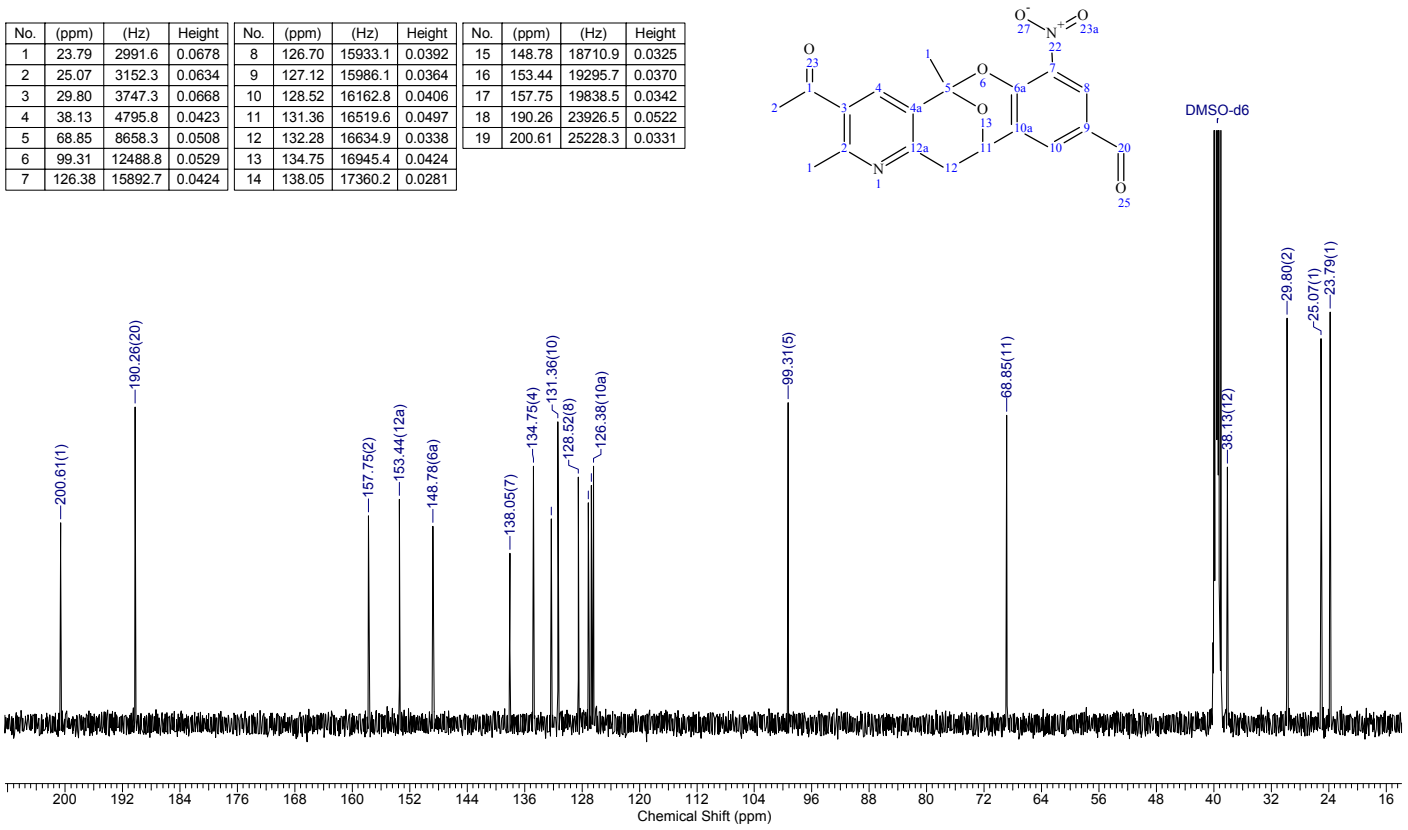
No.	(ppm)	(Hz)	Height
13	8.21	4106.1	0.1330
14	8.34	4170.4	0.1391
15	8.34	4172.1	0.1337
16	8.36	4183.6	0.1996
17	9.88	4941.4	0.2790



No.	(ppm)	(Hz)	Height
1	23.79	2991.6	0.0678
2	25.07	3152.3	0.0634
3	29.80	3747.3	0.0668
4	38.13	4795.8	0.0423
5	68.85	8658.3	0.0508
6	99.31	12488.8	0.0529
7	126.38	15892.7	0.0424

No.	(ppm)	(Hz)	Height
8	126.70	15933.1	0.0392
9	127.12	15986.1	0.0364
10	128.52	16162.8	0.0406
11	131.36	16519.6	0.0497
12	132.28	16634.9	0.0338
13	134.75	16945.4	0.0424
14	138.05	17360.2	0.0281

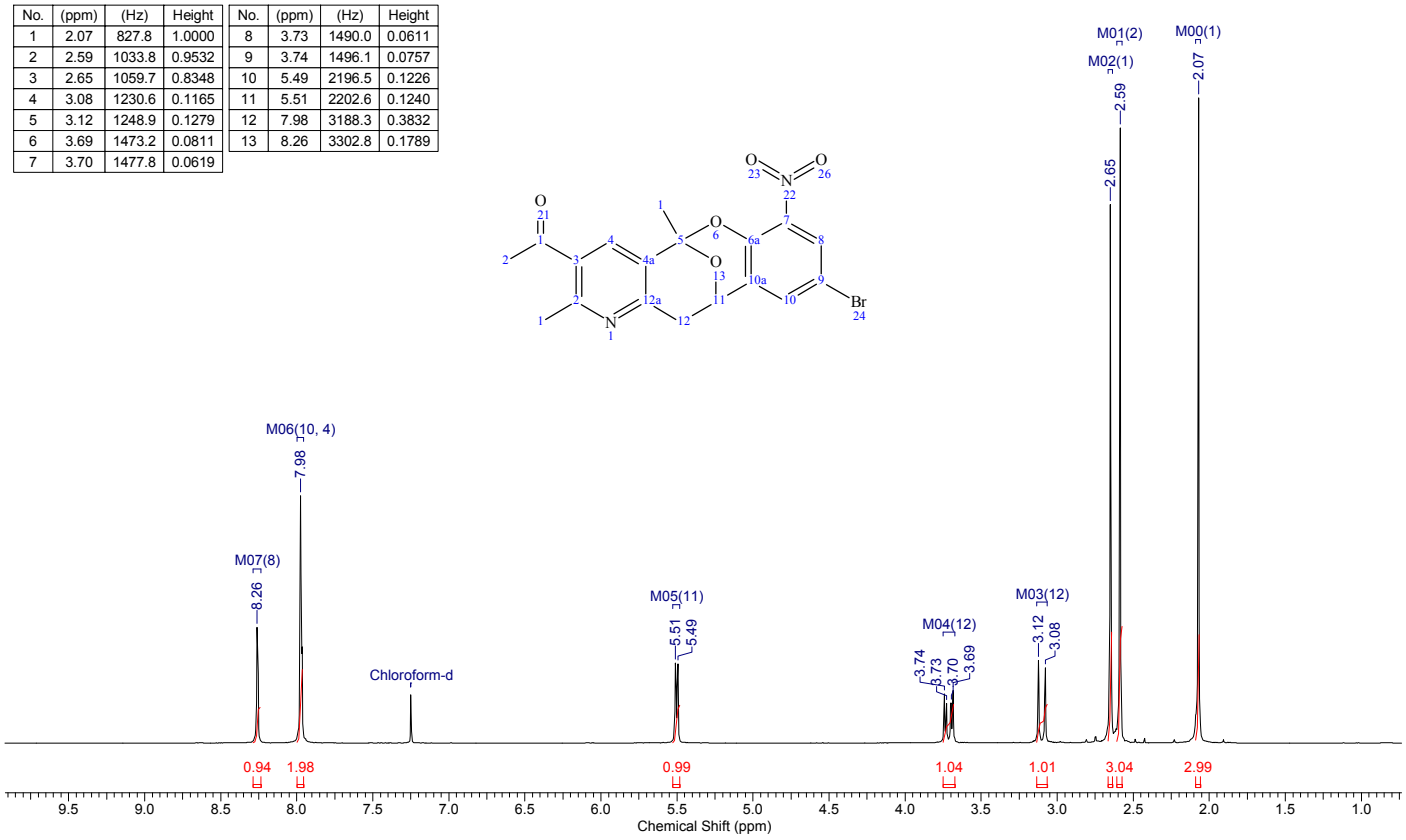
No.	(ppm)	(Hz)	Height
15	148.78	18710.9	0.0325
16	153.44	19295.7	0.0370
17	157.75	19838.5	0.0342
18	190.26	23926.5	0.0522
19	200.61	25228.3	0.0331



^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7p**

No.	(ppm)	(Hz)	Height
1	2.07	827.8	1.0000
2	2.59	1033.8	0.9532
3	2.65	1059.7	0.8348
4	3.08	1230.6	0.1165
5	3.12	1248.9	0.1279
6	3.69	1473.2	0.0811
7	3.70	1477.8	0.0619

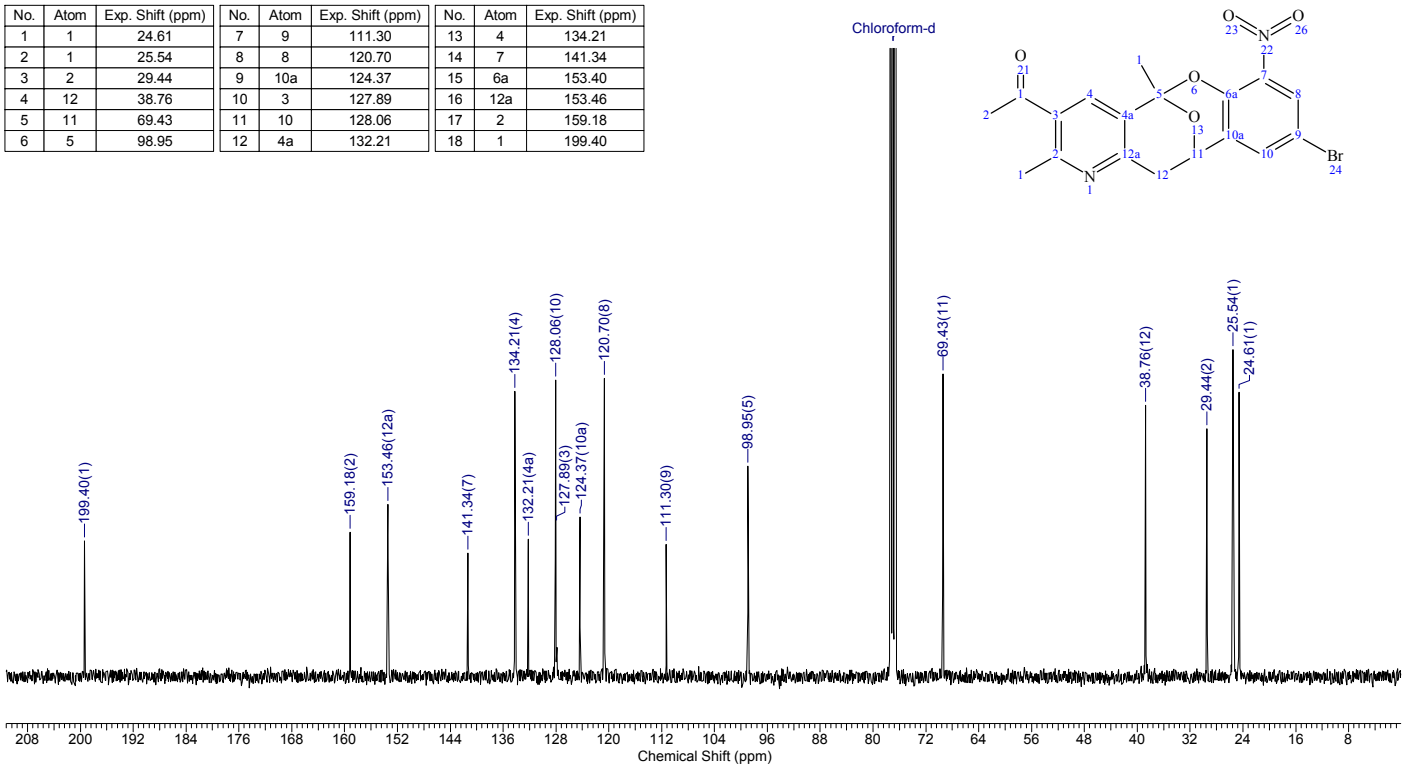
No.	(ppm)	(Hz)	Height
8	3.73	1490.0	0.0611
9	3.74	1496.1	0.0757
10	5.49	2196.5	0.1226
11	5.51	2202.6	0.1240
12	7.98	3188.3	0.3832
13	8.26	3302.8	0.1789



No.	Atom	Exp. Shift (ppm)
1	1	24.61
2	1	25.54
3	2	29.44
4	12	38.76
5	11	69.43
6	5	98.95

No.	Atom	Exp. Shift (ppm)
7	9	111.30
8	8	120.70
9	10a	124.37
10	3	127.89
11	10	128.06
12	4a	132.21

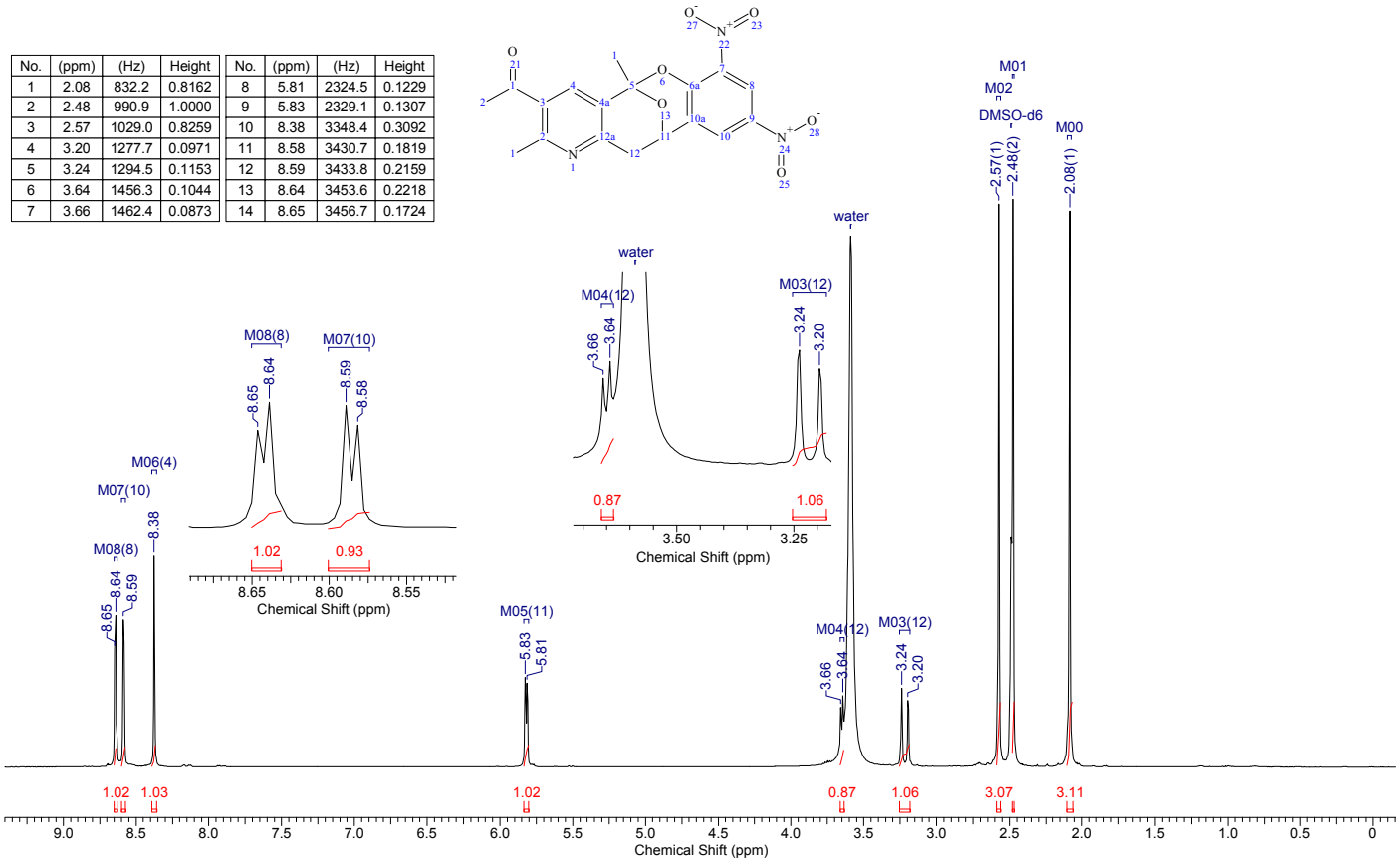
No.	Atom	Exp. Shift (ppm)
13	4	134.21
14	7	141.34
15	6a	153.40
16	12a	153.46
17	2	159.18
18	1	199.40



^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7q**

No.	(ppm)	(Hz)	Height
1	2.08	832.2	0.8162
2	2.48	990.9	1.0000
3	2.57	1029.0	0.8259
4	3.20	1277.7	0.0971
5	3.24	1294.5	0.1153
6	3.64	1456.3	0.1044
7	3.66	1462.4	0.0873

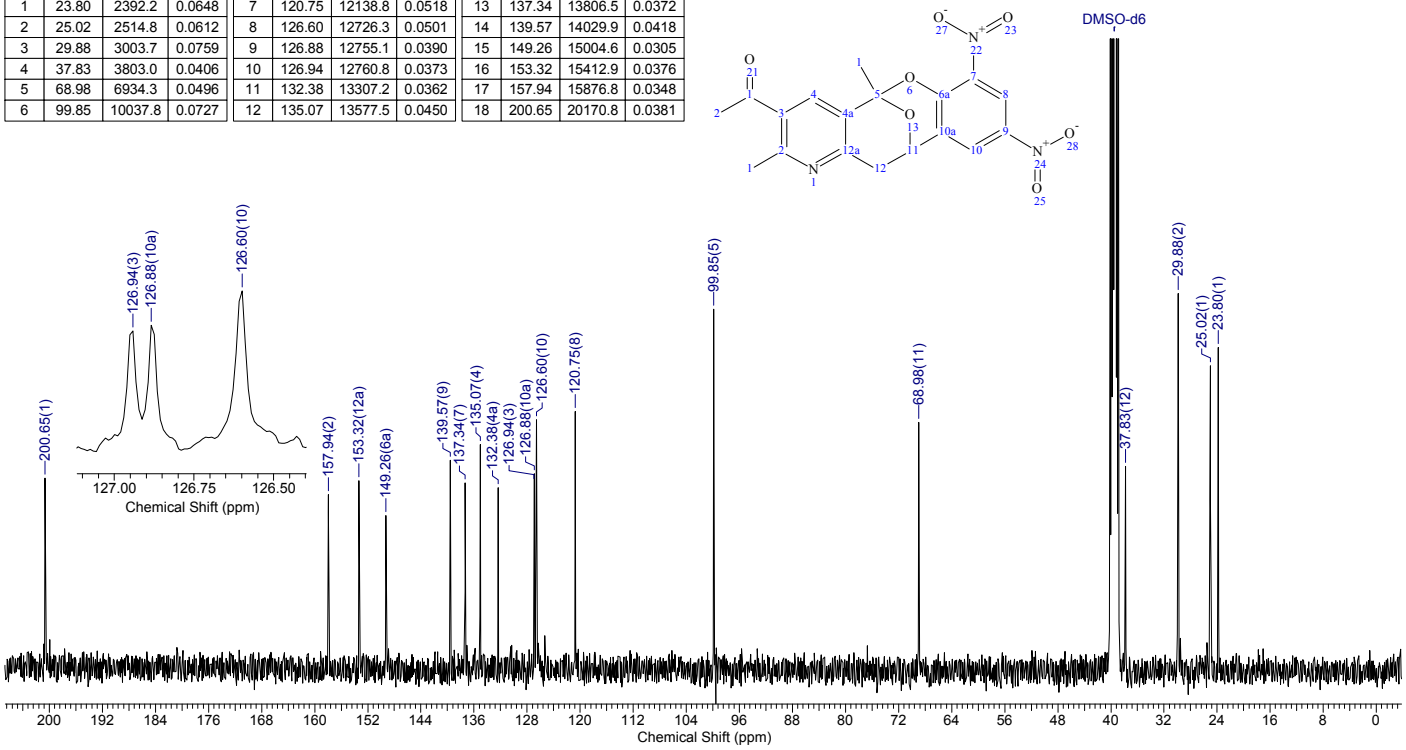
No.	(ppm)	(Hz)	Height
8	5.81	2324.5	0.1229
9	5.83	2329.1	0.1307
10	8.38	3348.4	0.3092
11	8.58	3430.7	0.1819
12	8.59	3433.8	0.2159
13	8.64	3453.6	0.2218
14	8.65	3456.7	0.1724



No.	(ppm)	(Hz)	Height
1	23.80	2392.2	0.0648
2	25.02	2514.8	0.0612
3	29.88	3003.7	0.0759
4	37.83	3803.0	0.0406
5	68.98	6934.3	0.0496
6	99.85	10037.8	0.0727

No.	(ppm)	(Hz)	Height
7	120.75	12138.8	0.0518
8	126.60	12726.3	0.0501
9	126.88	12755.1	0.0390
10	126.94	12760.8	0.0373
11	132.38	13307.2	0.0362
12	135.07	13577.5	0.0450

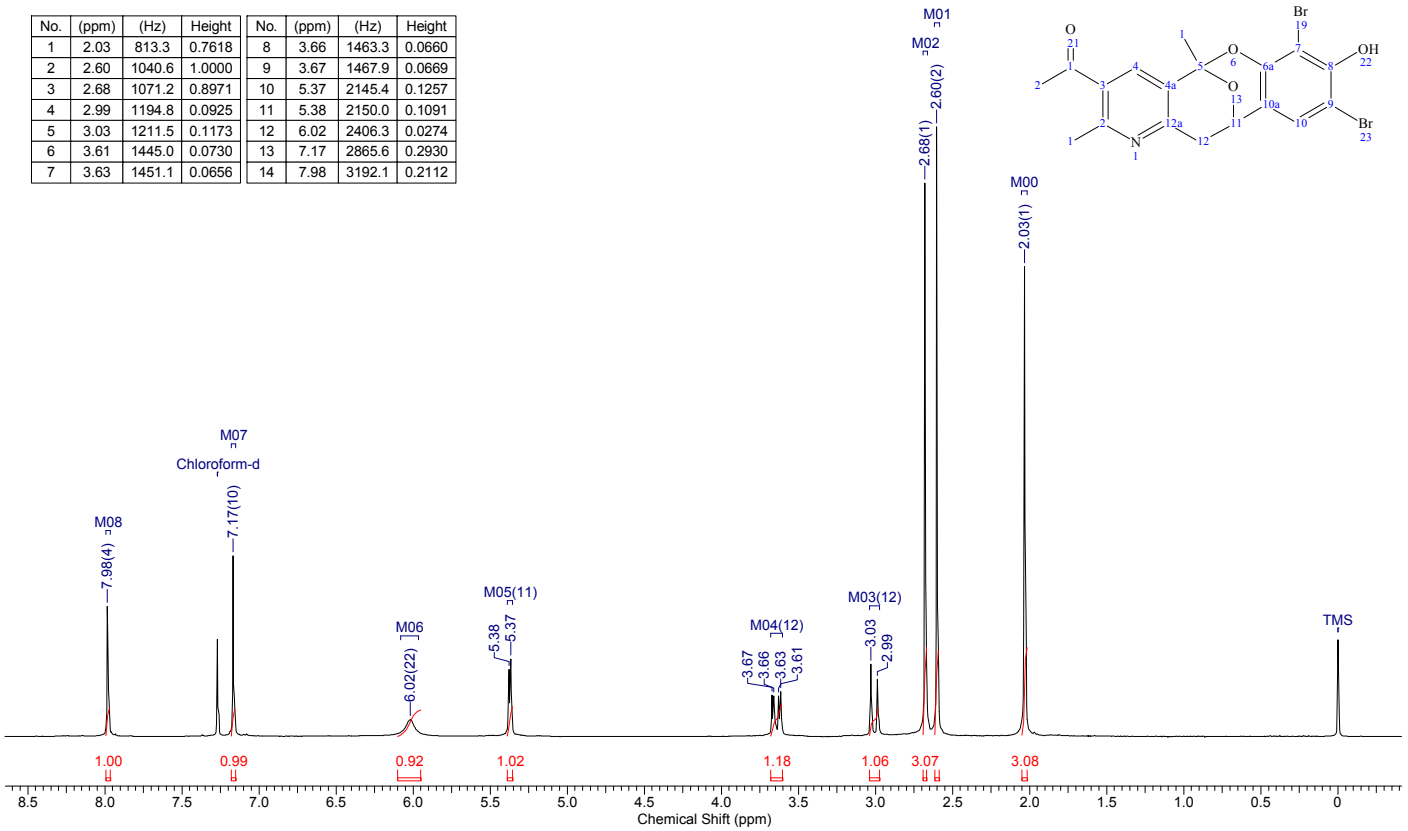
No.	(ppm)	(Hz)	Height
13	137.34	13806.5	0.0372
14	139.57	14029.9	0.0418
15	149.26	15004.6	0.0305
16	153.32	15412.9	0.0376
17	157.94	15876.8	0.0348
18	200.65	20170.8	0.0381



^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7r**

No.	(ppm)	(Hz)	Height
1	2.03	813.3	0.7618
2	2.60	1040.6	1.0000
3	2.68	1071.2	0.8971
4	2.99	1194.8	0.0925
5	3.03	1211.5	0.1173
6	3.61	1445.0	0.0730
7	3.63	1451.1	0.0656

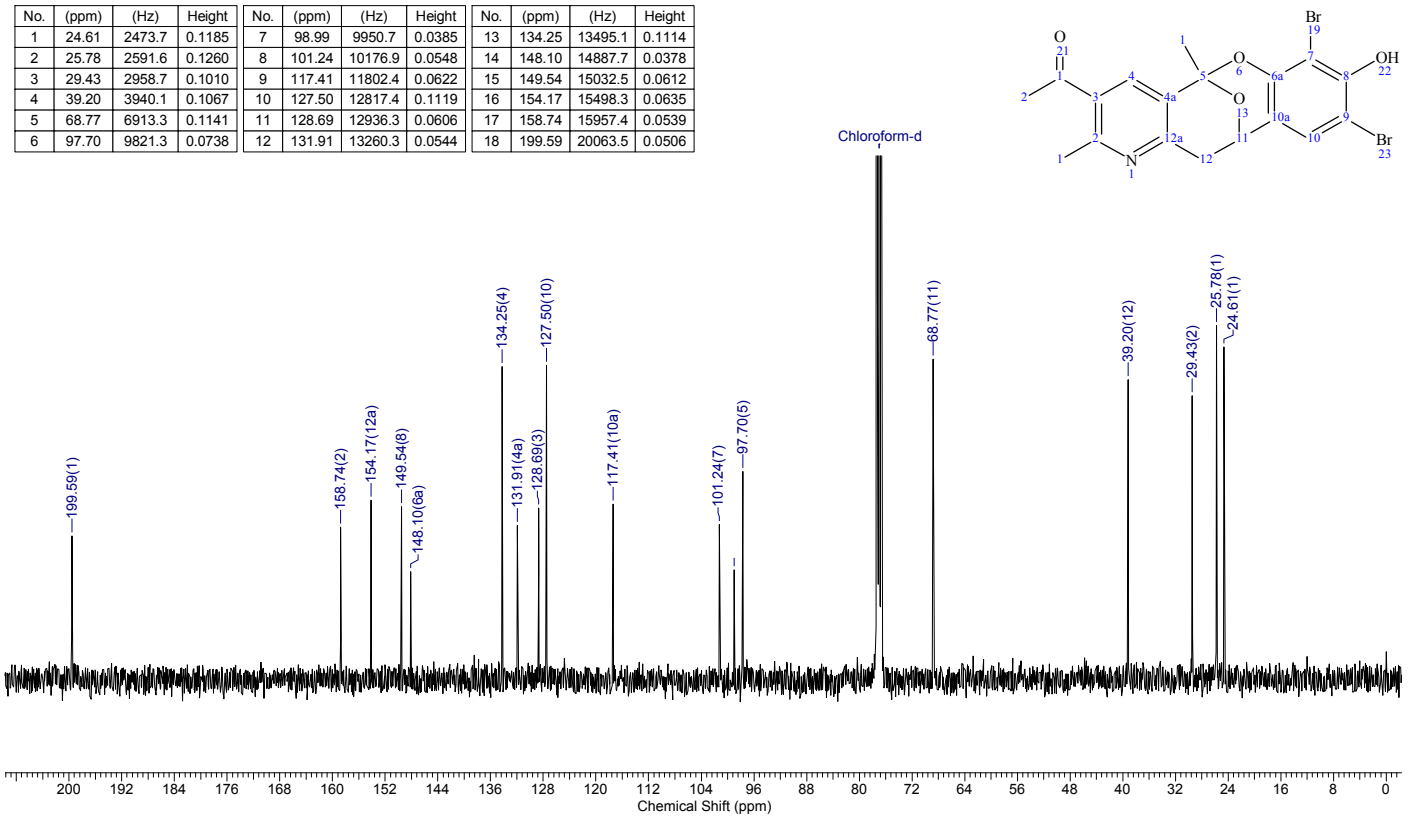
No.	(ppm)	(Hz)	Height
8	3.66	1463.3	0.0660
9	3.67	1467.9	0.0669
10	5.37	2145.4	0.1257
11	5.38	2150.0	0.1091
12	6.02	2406.3	0.0274
13	7.17	2865.6	0.2930
14	7.98	3192.1	0.2112



No.	(ppm)	(Hz)	Height
1	24.61	2473.7	0.1185
2	25.78	2591.6	0.1260
3	29.43	2958.7	0.1010
4	39.20	3940.1	0.1067
5	68.77	6913.3	0.1141
6	97.70	9821.3	0.0738

No.	(ppm)	(Hz)	Height
7	98.99	9950.7	0.0385
8	101.24	10176.9	0.0548
9	117.41	11802.4	0.0622
10	127.50	12817.4	0.1119
11	128.69	12936.3	0.0606
12	131.91	13260.3	0.0544

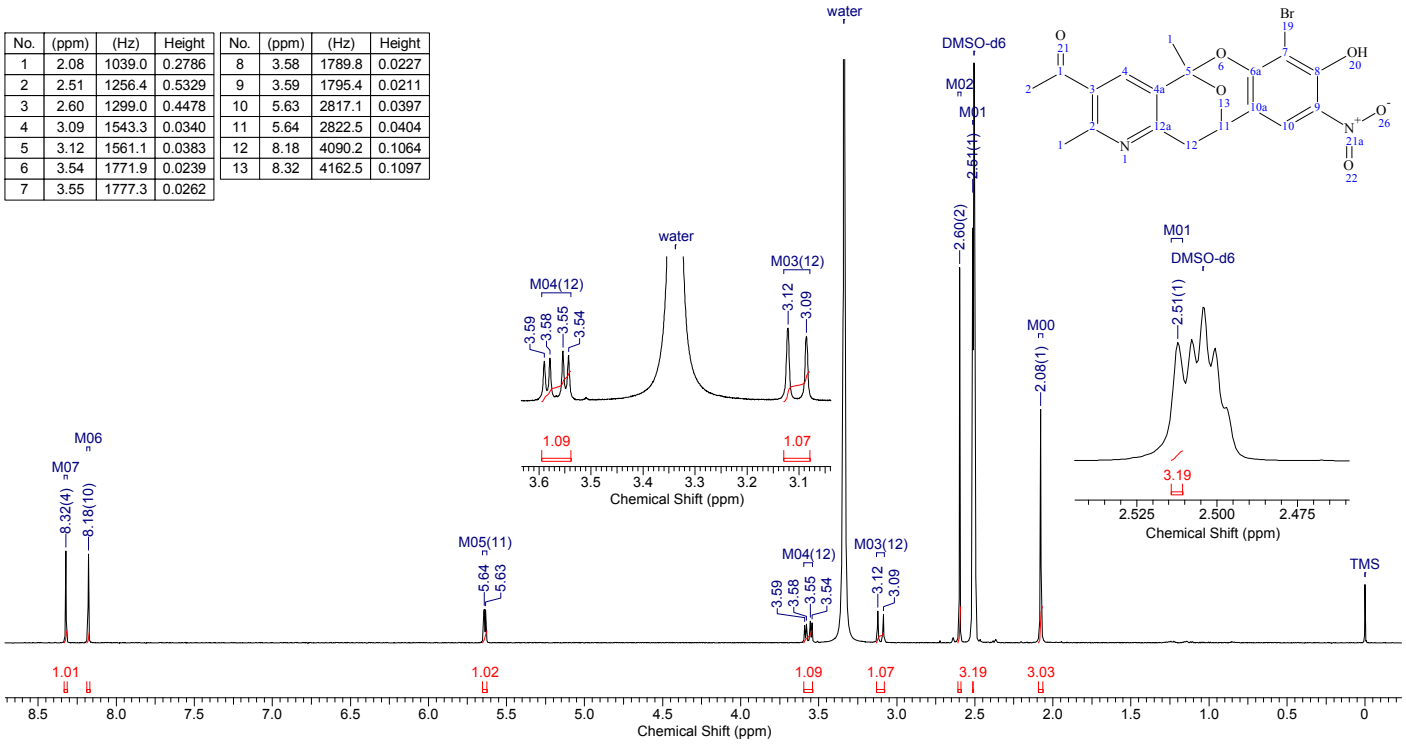
No.	(ppm)	(Hz)	Height
13	134.25	13495.1	0.1114
14	148.10	14887.7	0.0378
15	149.54	15032.5	0.0612
16	154.17	15498.3	0.0635
17	158.74	15957.4	0.0539
18	199.59	20063.5	0.0506



^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7s**

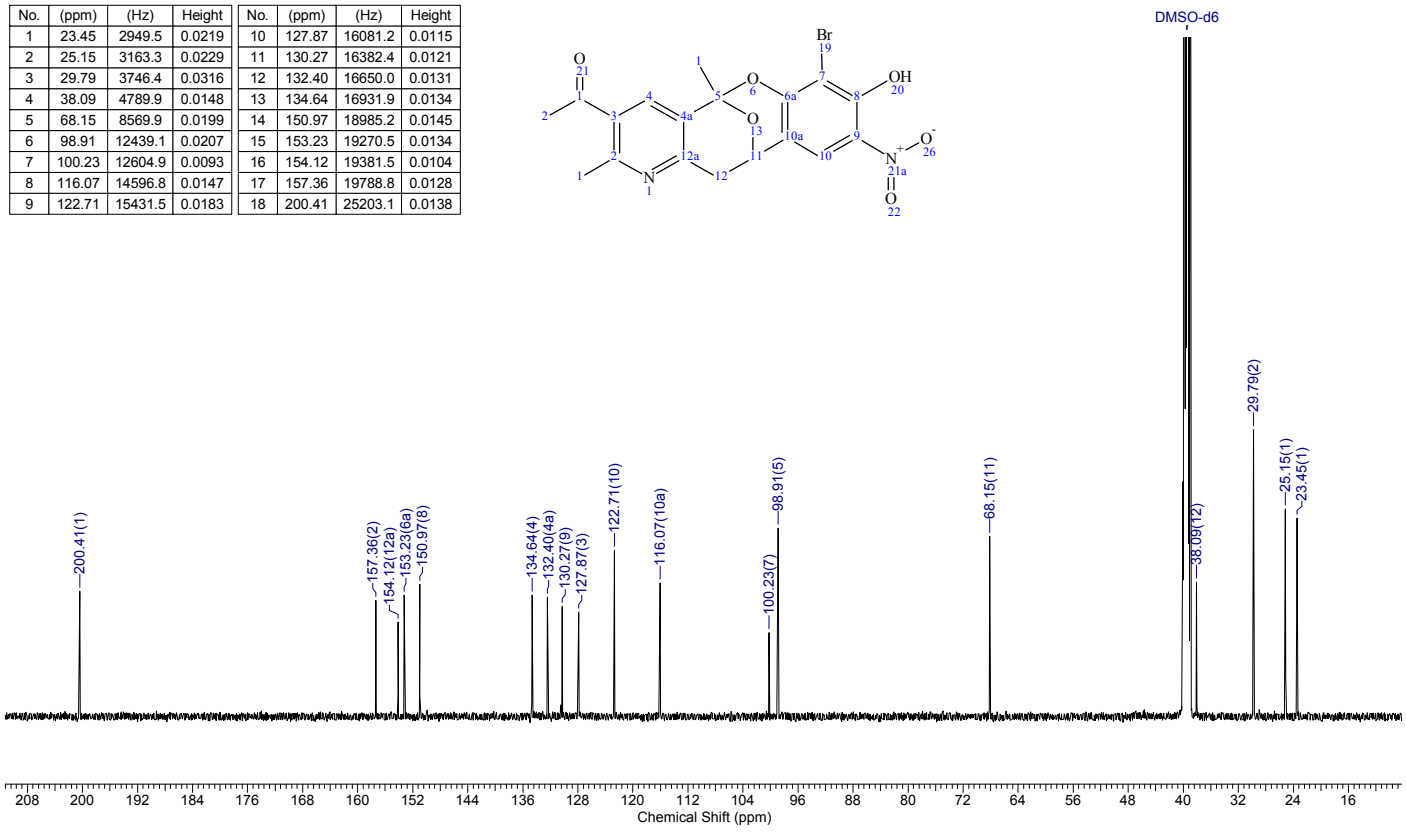
No.	(ppm)	(Hz)	Height
1	2.08	1039.0	0.2786
2	2.51	1256.4	0.5329
3	2.60	1299.0	0.4478
4	3.09	1543.3	0.0340
5	3.12	1561.1	0.0383
6	3.54	1771.9	0.0239
7	3.55	1777.3	0.0262

No.	(ppm)	(Hz)	Height
8	3.58	1789.8	0.0227
9	3.59	1795.4	0.0211
10	5.63	2817.1	0.0397
11	5.64	2822.5	0.0404
12	8.18	4090.2	0.1064
13	8.32	4162.5	0.1097



No.	(ppm)	(Hz)	Height
1	23.45	2949.5	0.0219
2	25.15	3163.3	0.0229
3	29.79	3746.4	0.0316
4	38.09	4789.9	0.0148
5	68.15	8569.9	0.0199
6	98.91	12439.1	0.0207
7	100.23	12604.9	0.0093
8	116.07	14596.8	0.0147
9	122.71	15431.5	0.0183

No.	(ppm)	(Hz)	Height
10	127.87	16081.2	0.0115
11	130.27	16382.4	0.0121
12	132.40	16650.0	0.0131
13	134.64	16931.9	0.0134
14	150.97	18985.2	0.0145
15	153.23	19270.5	0.0134
16	154.12	19381.5	0.0104
17	157.36	19788.8	0.0128
18	200.41	25203.1	0.0138



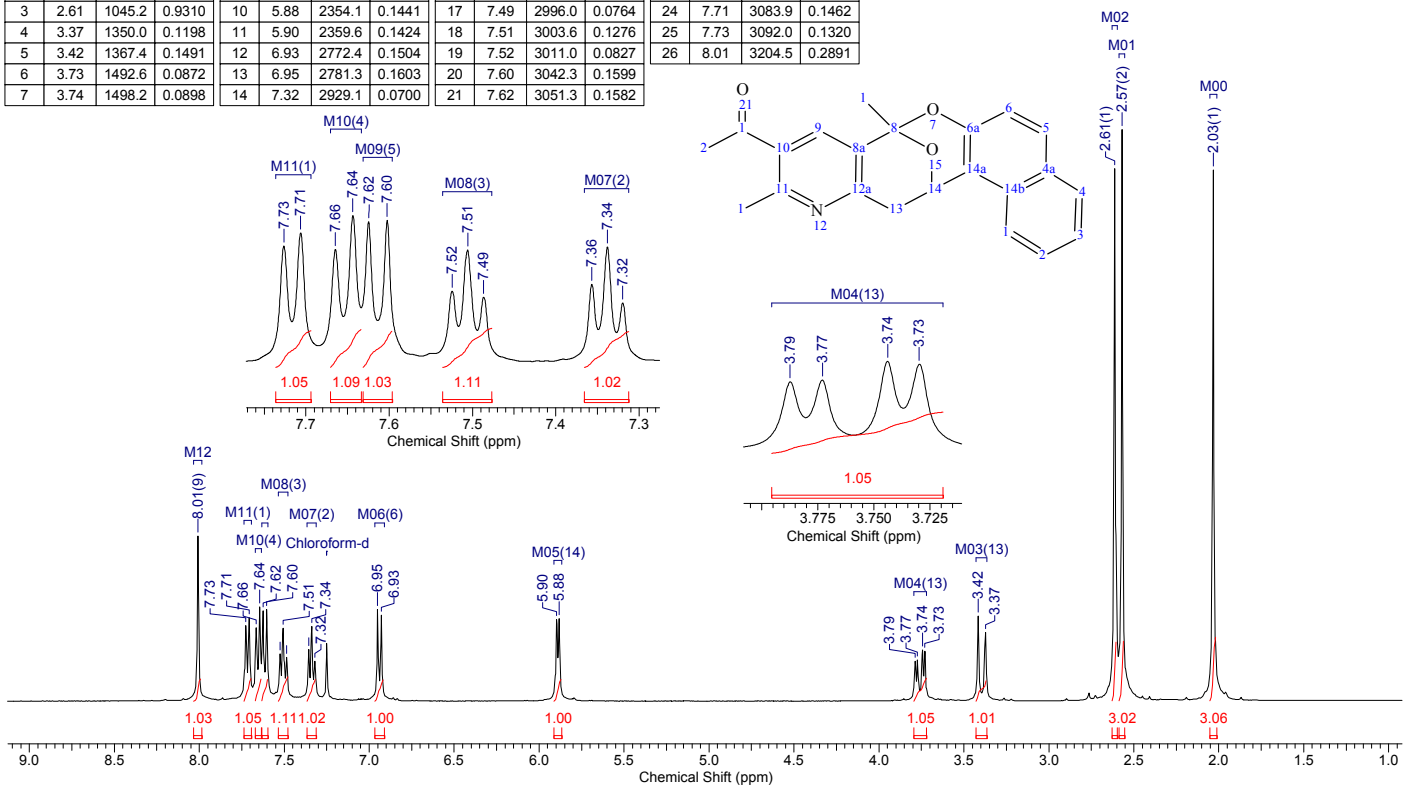
^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **7t**

No.	(ppm)	(Hz)	Height
1	2.03	813.4	0.9288
2	2.57	1028.0	1.0000
3	2.61	1045.2	0.9310
4	3.37	1350.0	0.1198
5	3.42	1367.4	0.1491
6	3.73	1492.6	0.0872
7	3.74	1498.2	0.0898

No.	(ppm)	(Hz)	Height
8	3.77	1509.8	0.0717
9	3.79	1515.6	0.0698
10	5.88	2354.1	0.1441
11	5.90	2359.6	0.1424
12	6.93	2772.4	0.1504
13	6.95	2781.3	0.1603
14	7.32	2929.1	0.0700

No.	(ppm)	(Hz)	Height
15	7.34	2936.4	0.1309
16	7.36	2943.9	0.0903
17	7.49	2996.0	0.0764
18	7.51	3003.6	0.1276
19	7.52	3011.0	0.0827
20	7.60	3042.3	0.1599
21	7.62	3051.3	0.1582

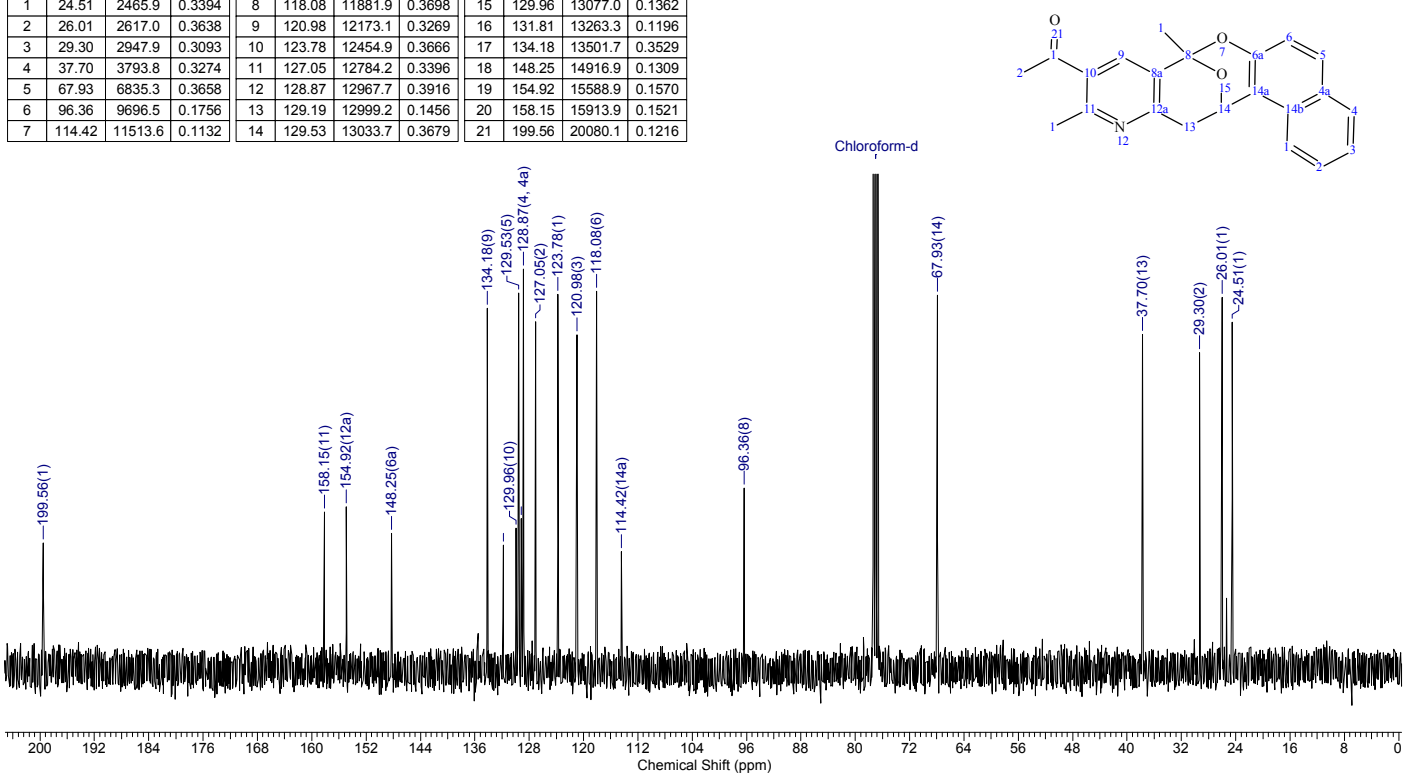
No.	(ppm)	(Hz)	Height
22	7.64	3058.8	0.1651
23	7.66	3067.3	0.1281
24	7.71	3083.9	0.1462
25	7.73	3092.0	0.1320
26	8.01	3204.5	0.2891



No.	(ppm)	(Hz)	Height
1	24.51	2465.9	0.3394
2	26.01	2617.0	0.3638
3	29.30	2947.9	0.3093
4	37.70	3793.8	0.3274
5	67.93	6835.3	0.3658
6	96.36	9696.5	0.1756
7	114.42	11513.6	0.1132

No.	(ppm)	(Hz)	Height
8	118.08	11881.9	0.3698
9	120.98	12173.1	0.3269
10	123.78	12454.9	0.3666
11	127.05	12784.2	0.3396
12	128.87	12967.7	0.3916
13	129.19	12999.2	0.1456
14	129.53	13033.7	0.3679

No.	(ppm)	(Hz)	Height
15	129.96	13077.0	0.1362
16	131.81	13263.3	0.1196
17	134.18	13501.7	0.3529
18	148.25	14916.9	0.1309
19	154.92	15588.9	0.1570
20	158.15	15913.9	0.1521
21	199.56	20080.1	0.1216

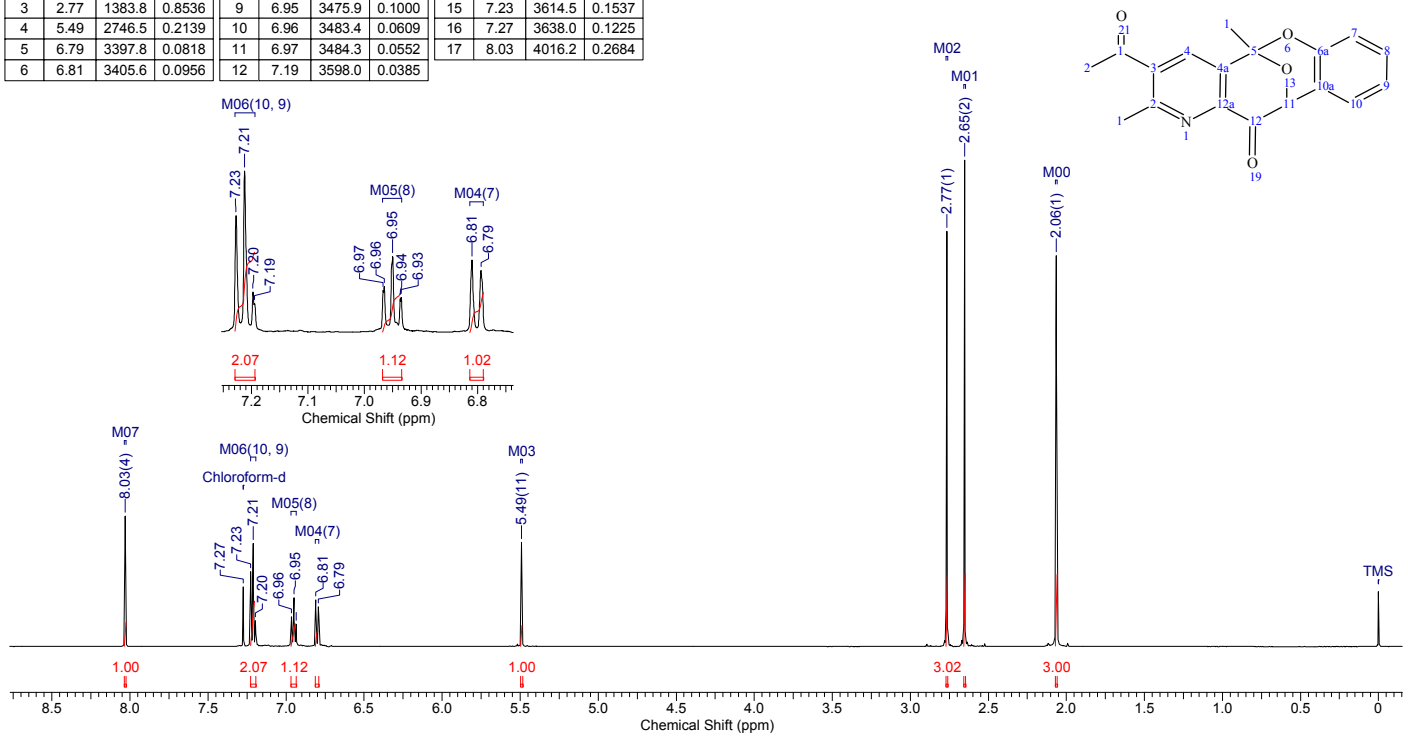


^{1}H (400 MHz, $CDCl_3$) and ^{13}C (100 MHz, $CDCl_3$) NMR Spectra of **7u**

No.	(ppm)	(Hz)	Height
1	2.06	1032.4	0.8035
2	2.65	1326.7	1.0000
3	2.77	1383.8	0.8536
4	5.49	2746.5	0.2139
5	6.79	3397.8	0.0818
6	6.81	3405.6	0.0956

No.	(ppm)	(Hz)	Height
7	6.93	3468.4	0.0463
8	6.94	3469.3	0.0451
9	6.95	3475.9	0.1000
10	6.96	3483.4	0.0609
11	6.97	3484.3	0.0552
12	7.19	3598.0	0.0385

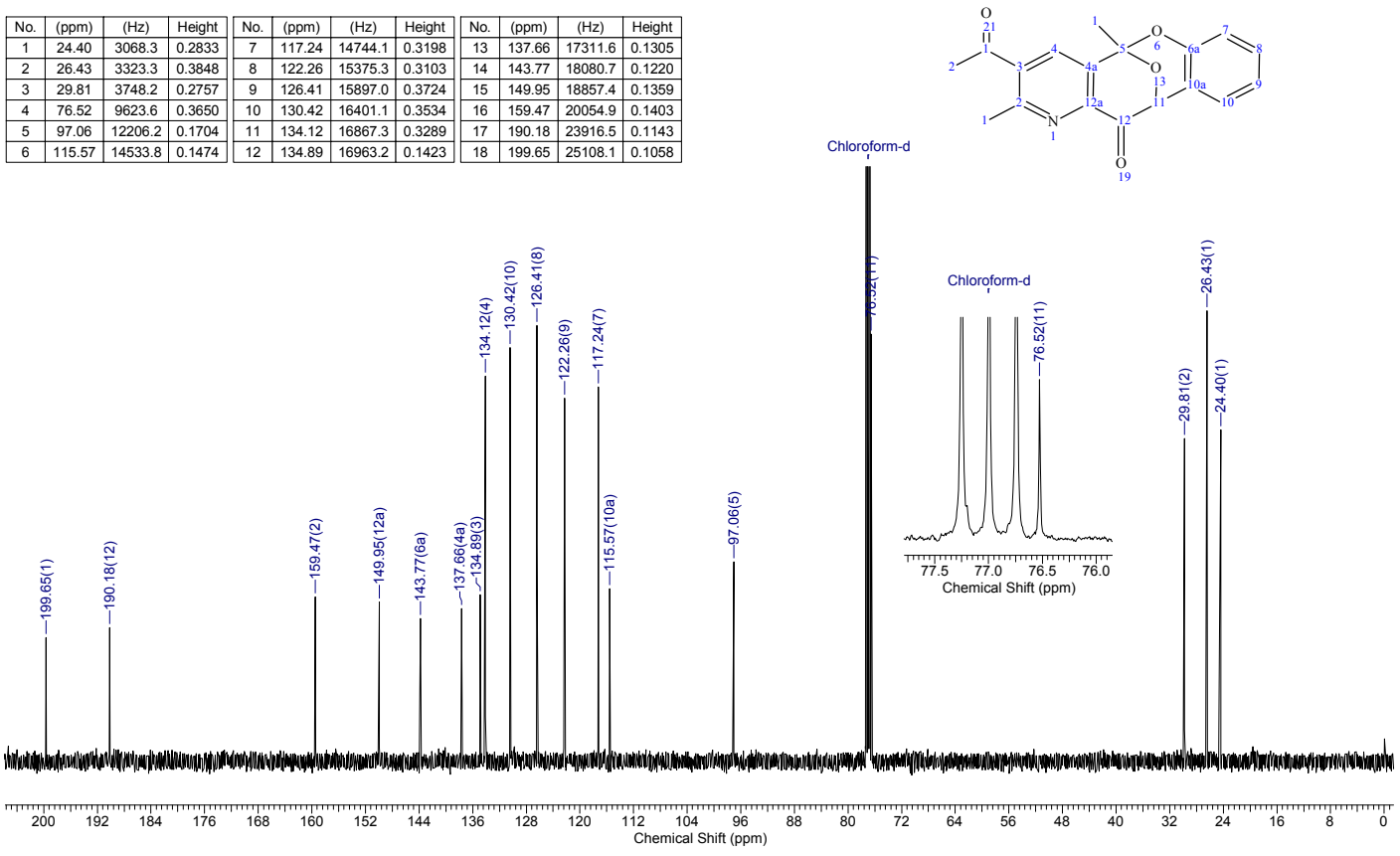
No.	(ppm)	(Hz)	Height
13	7.20	3599.5	0.0533
14	7.21	3606.8	0.2119
15	7.23	3614.5	0.1537
16	7.27	3638.0	0.1225
17	8.03	4016.2	0.2684



No.	(ppm)	(Hz)	Height
1	24.40	3068.3	0.2833
2	26.43	3323.3	0.3848
3	29.81	3748.2	0.2757
4	76.52	9623.6	0.3650
5	97.06	12206.2	0.1704
6	115.57	14533.8	0.1474

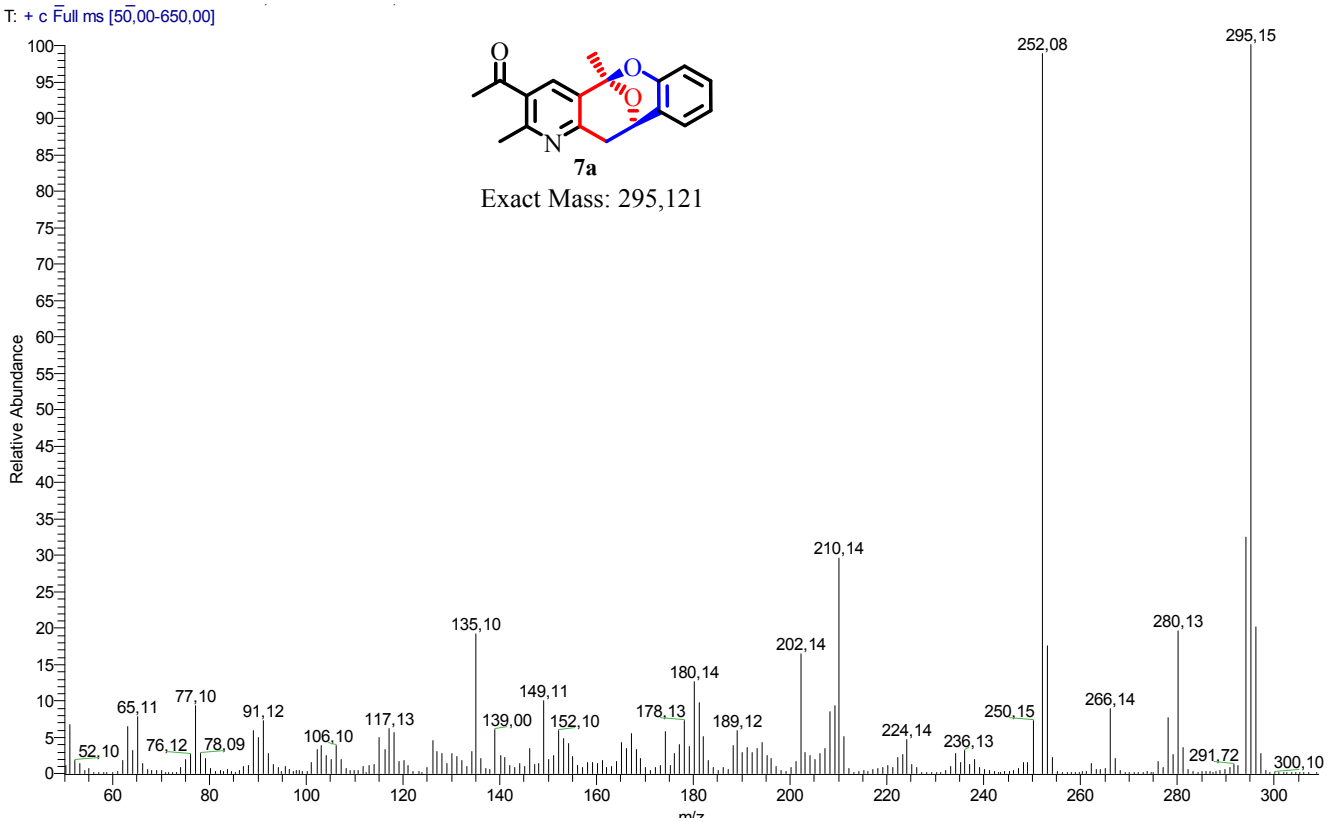
No.	(ppm)	(Hz)	Height
7	117.24	14744.1	0.3198
8	122.26	15375.3	0.3103
9	126.41	15897.0	0.3724
10	130.42	16401.1	0.3534
11	134.12	16867.3	0.3289
12	134.89	16963.2	0.1423

No.	(ppm)	(Hz)	Height
13	137.66	17311.6	0.1305
14	143.77	18080.7	0.1220
15	149.95	18857.4	0.1359
16	159.47	20054.9	0.1403
17	190.18	23916.5	0.1143
18	199.65	25108.1	0.1058

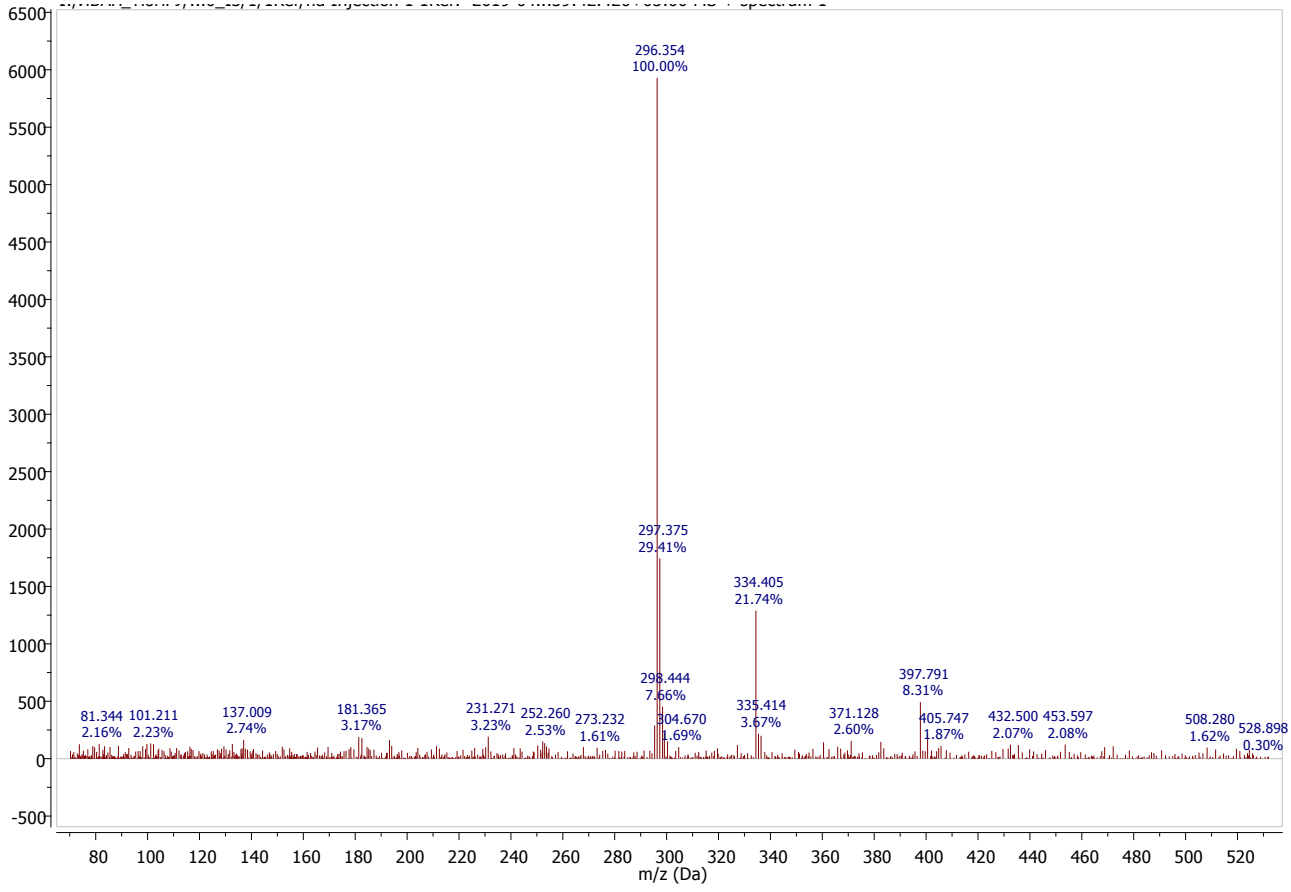


^{1}H (500 MHz, $CDCl_3$) and ^{13}C (126 MHz, $CDCl_3$) NMR Spectra of **11**

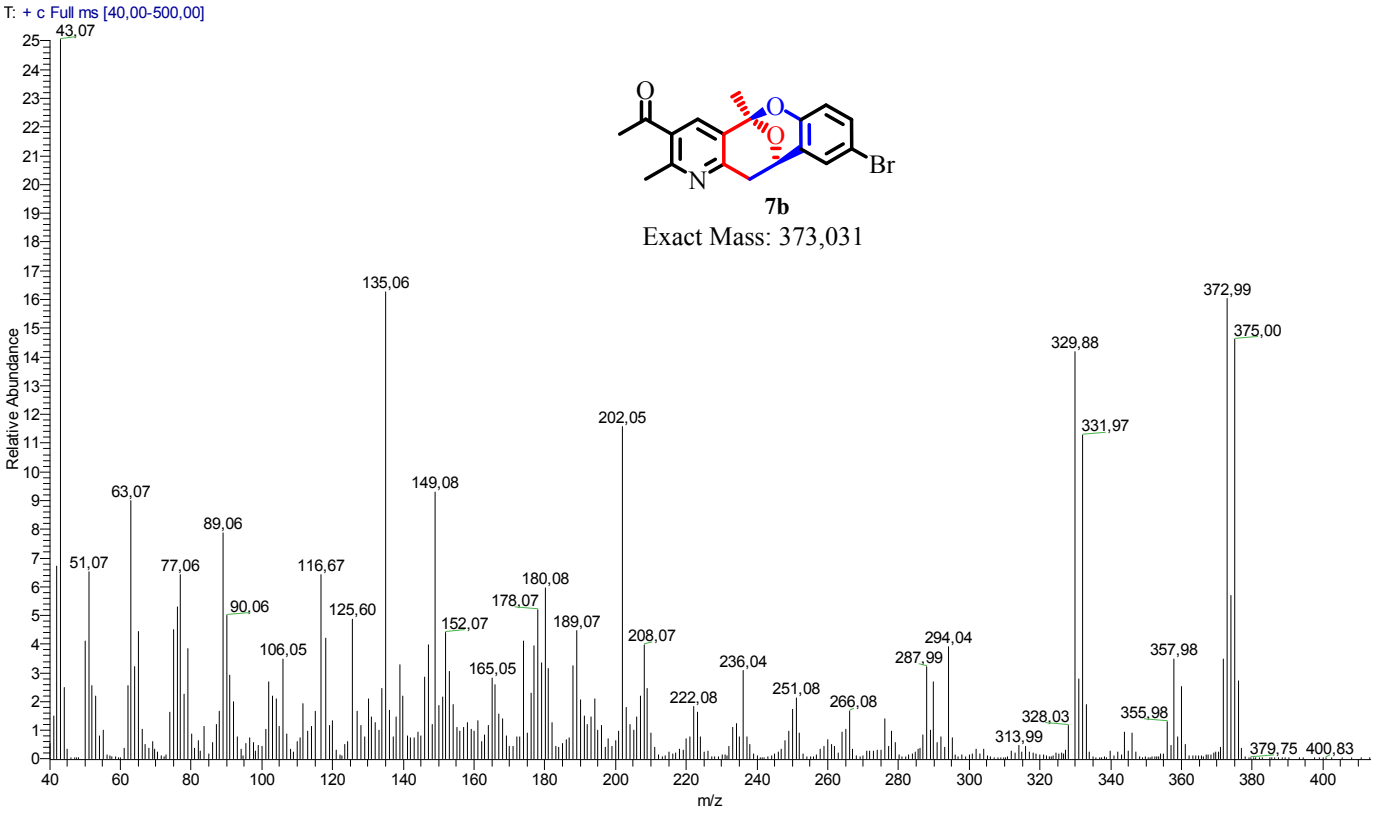
9. Copies of MS Spectra of Products



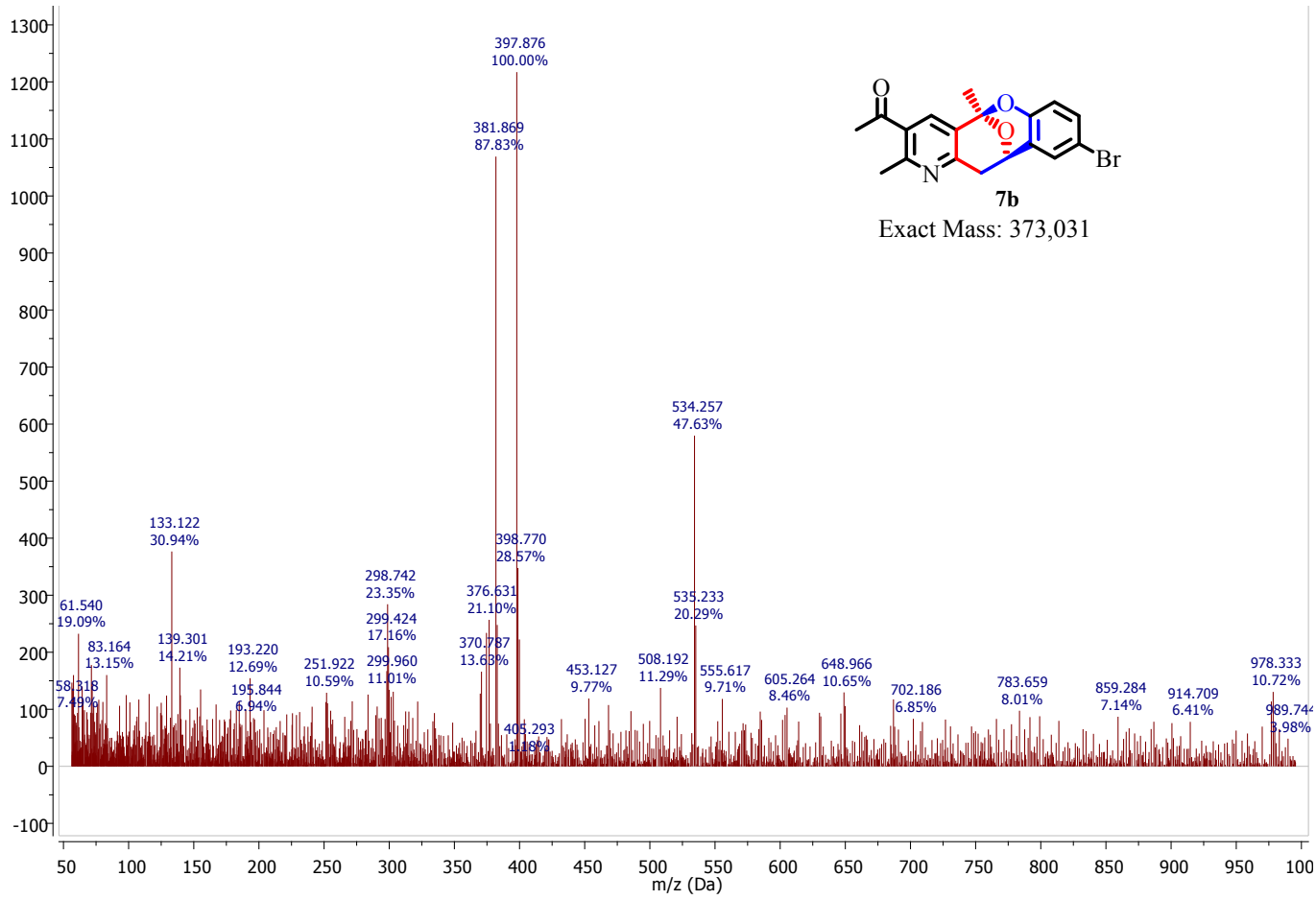
Mass spectrum (EI 70 eV) of (7a)



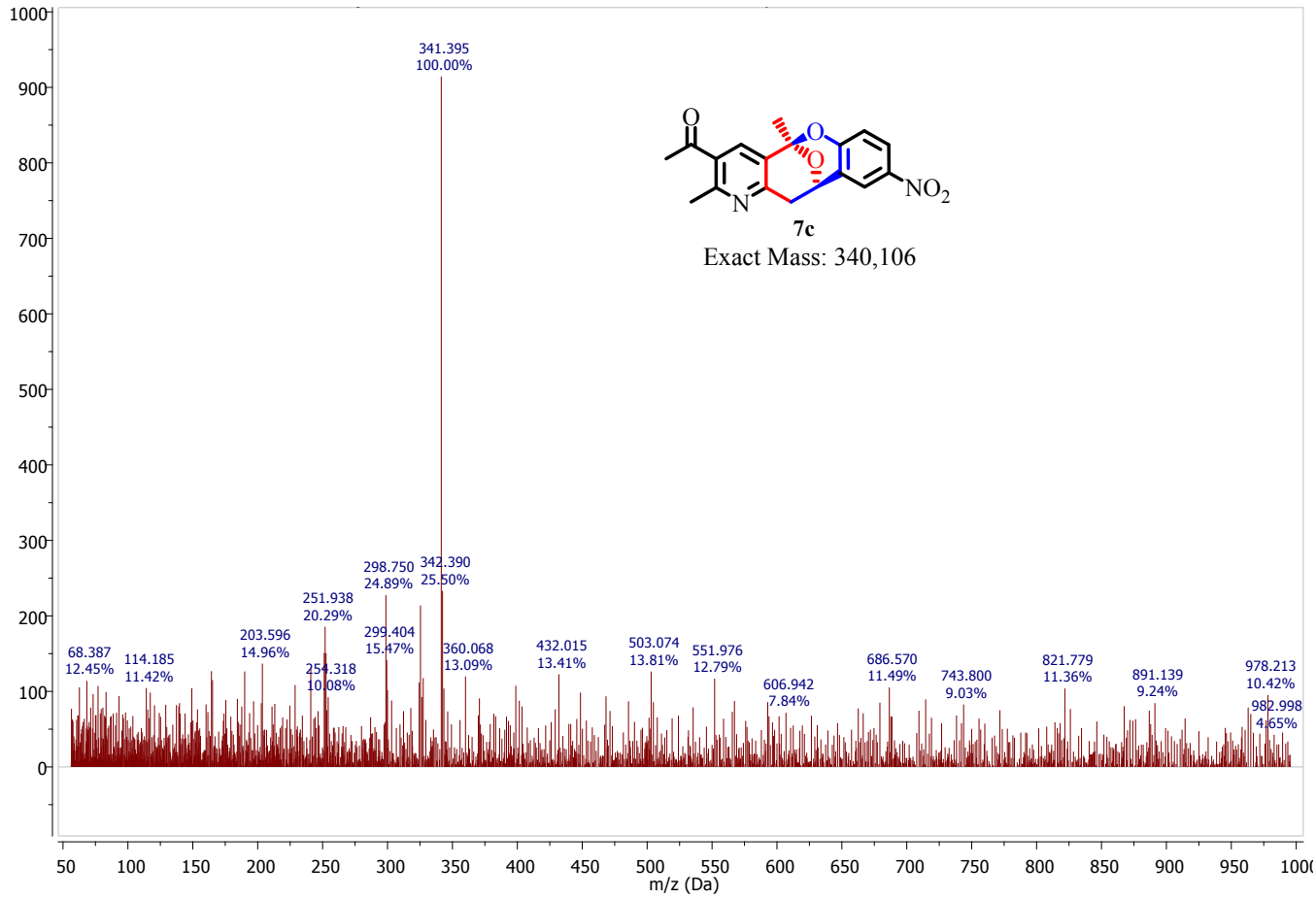
Mass spectrum (MALDI-TOF) of (7a)



Mass spectrum (EI 70 eV) of (7b)



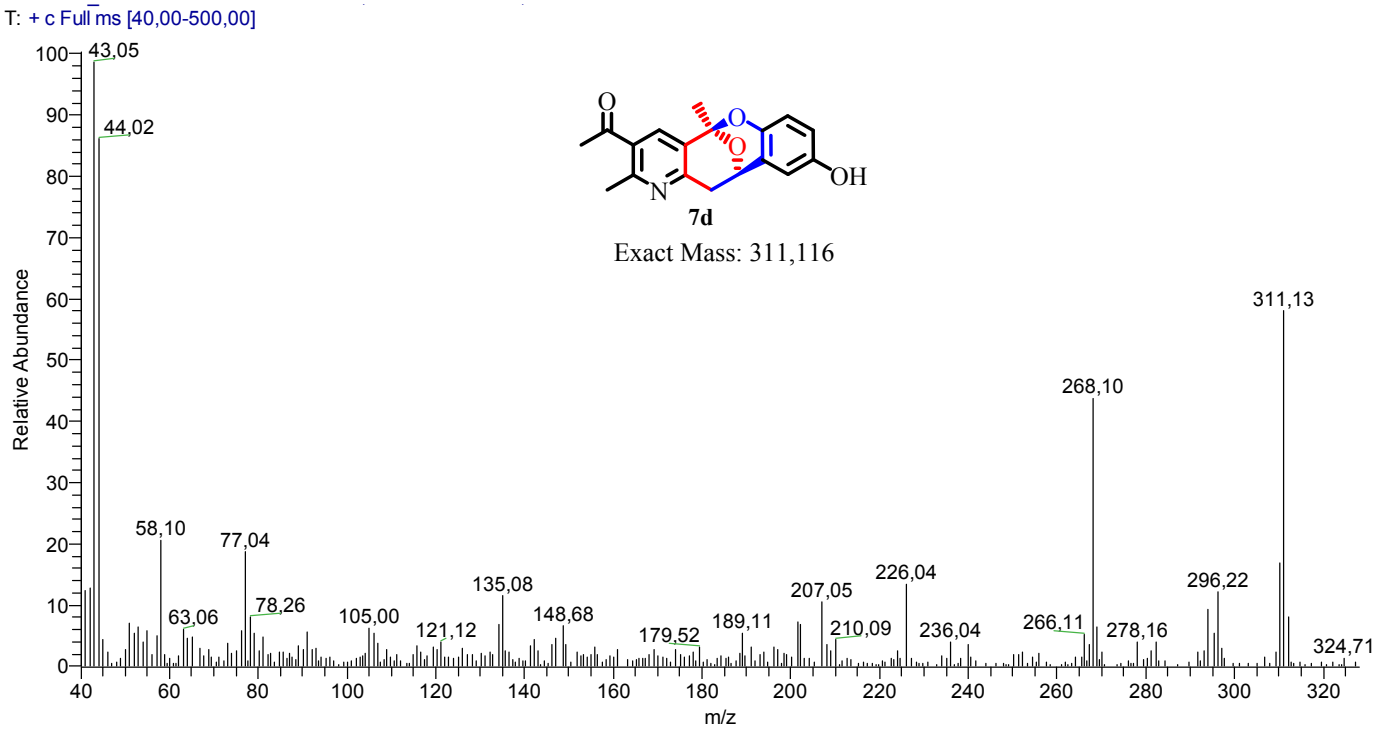
Mass spectrum (MALDI-TOF) of (7b)



7c

Exact Mass: 340,106

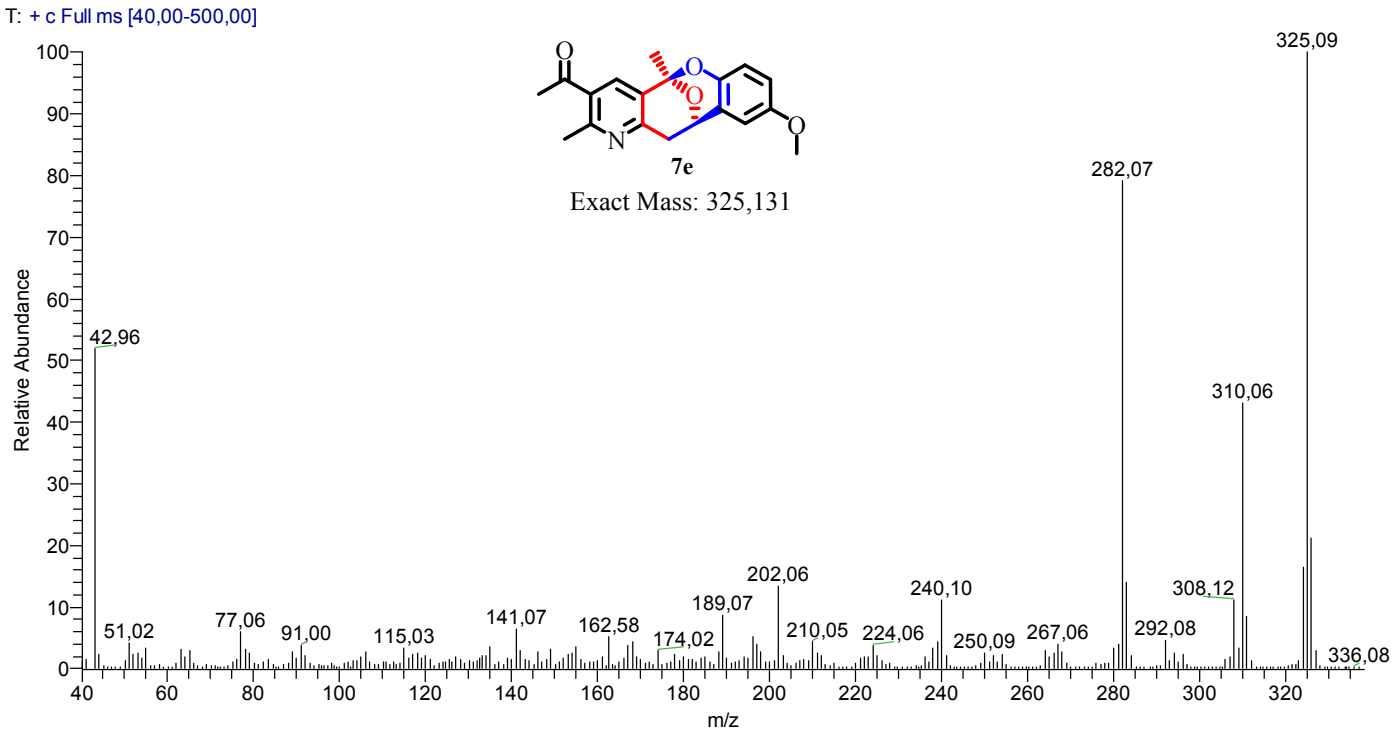
Mass spectrum (MALDI-TOF) of (7c)



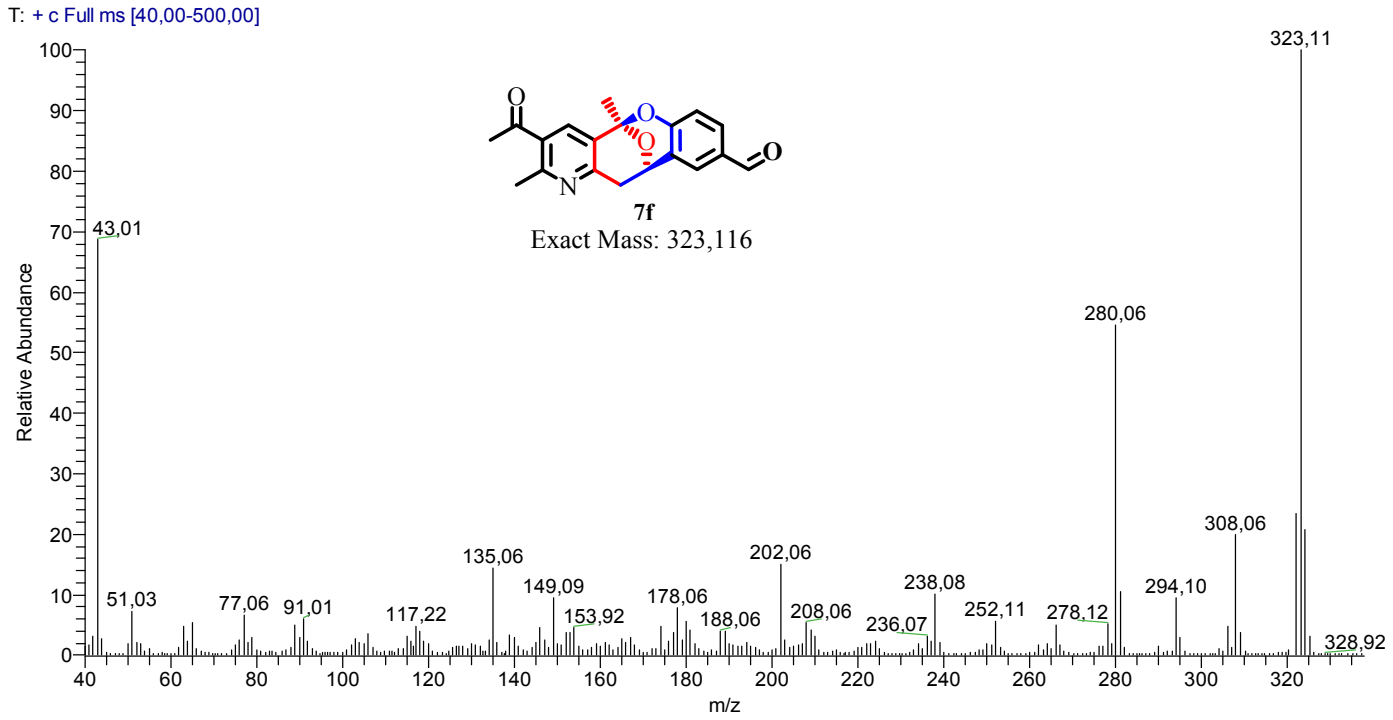
7d

Exact Mass: 311,116

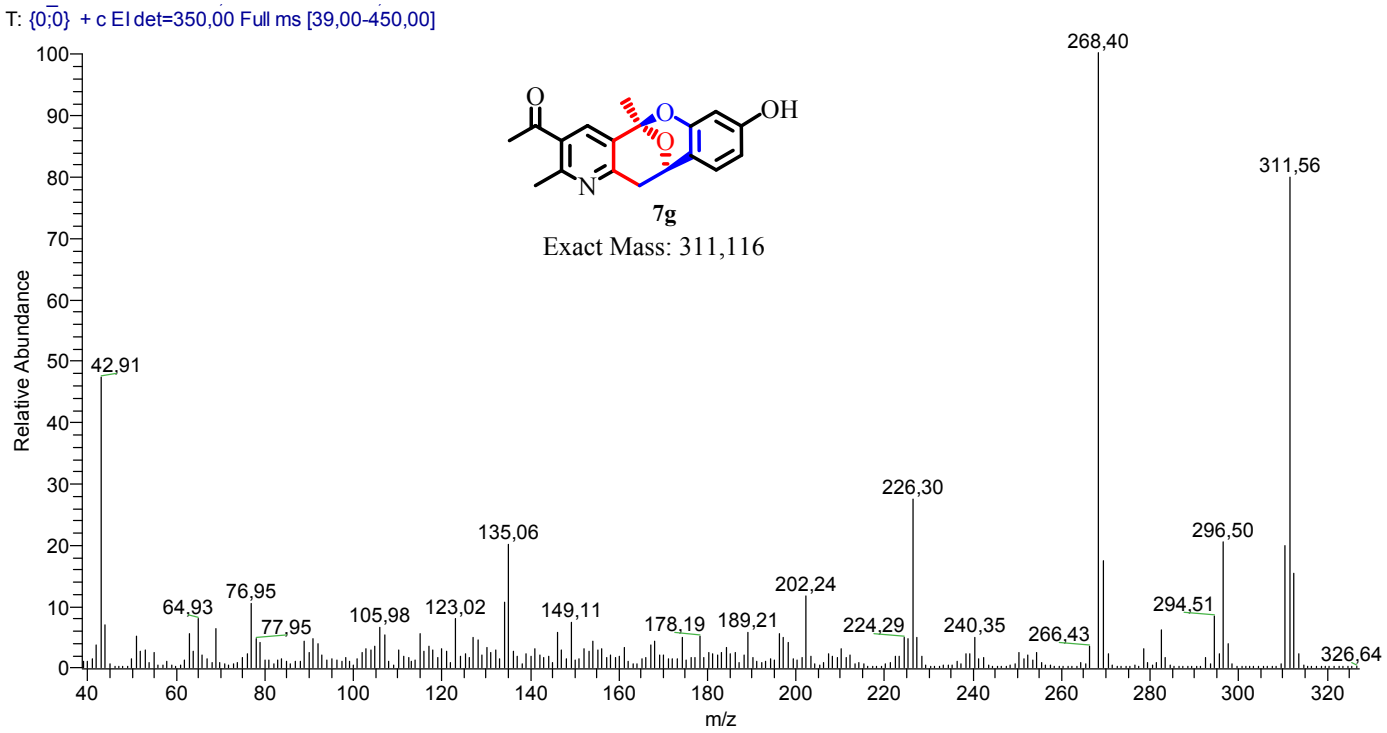
Mass spectrum (EI 70 eV) of (7d)



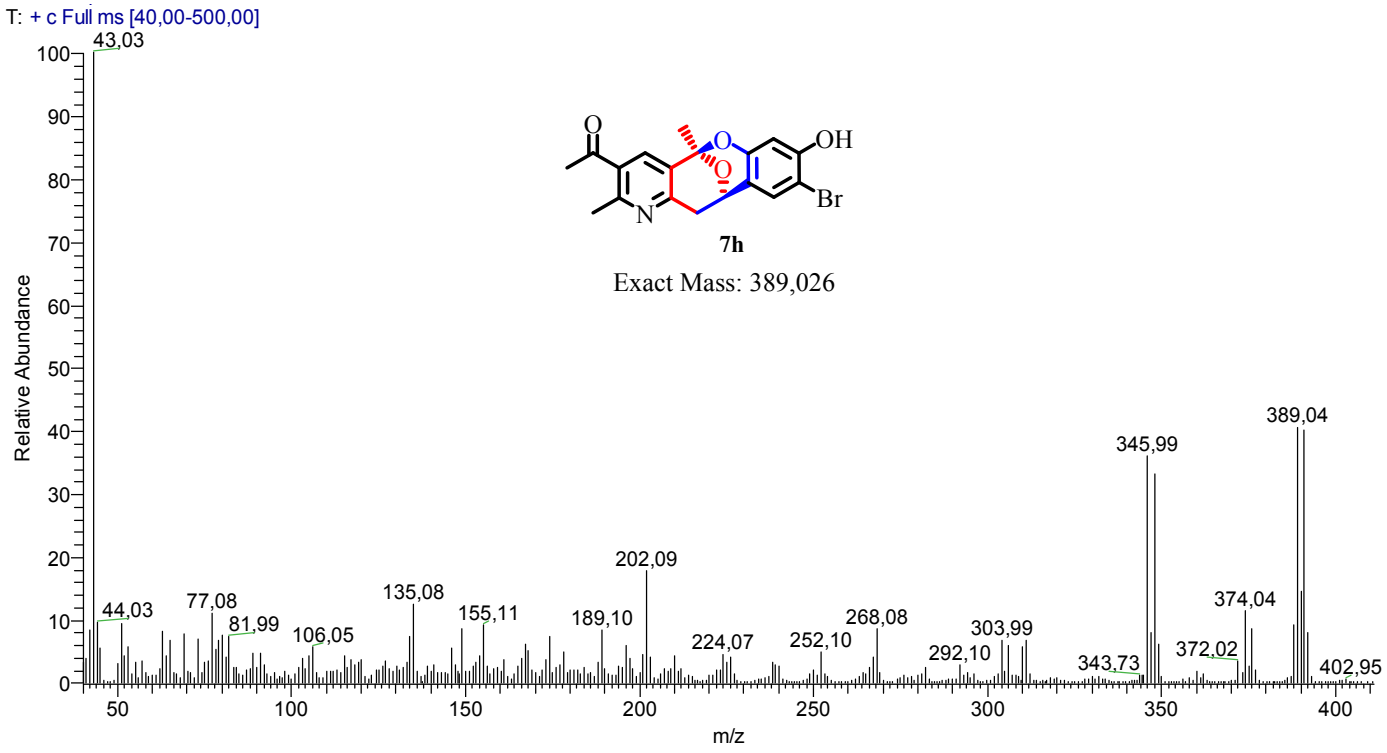
Mass spectrum (EI 70 eV) of (7e)



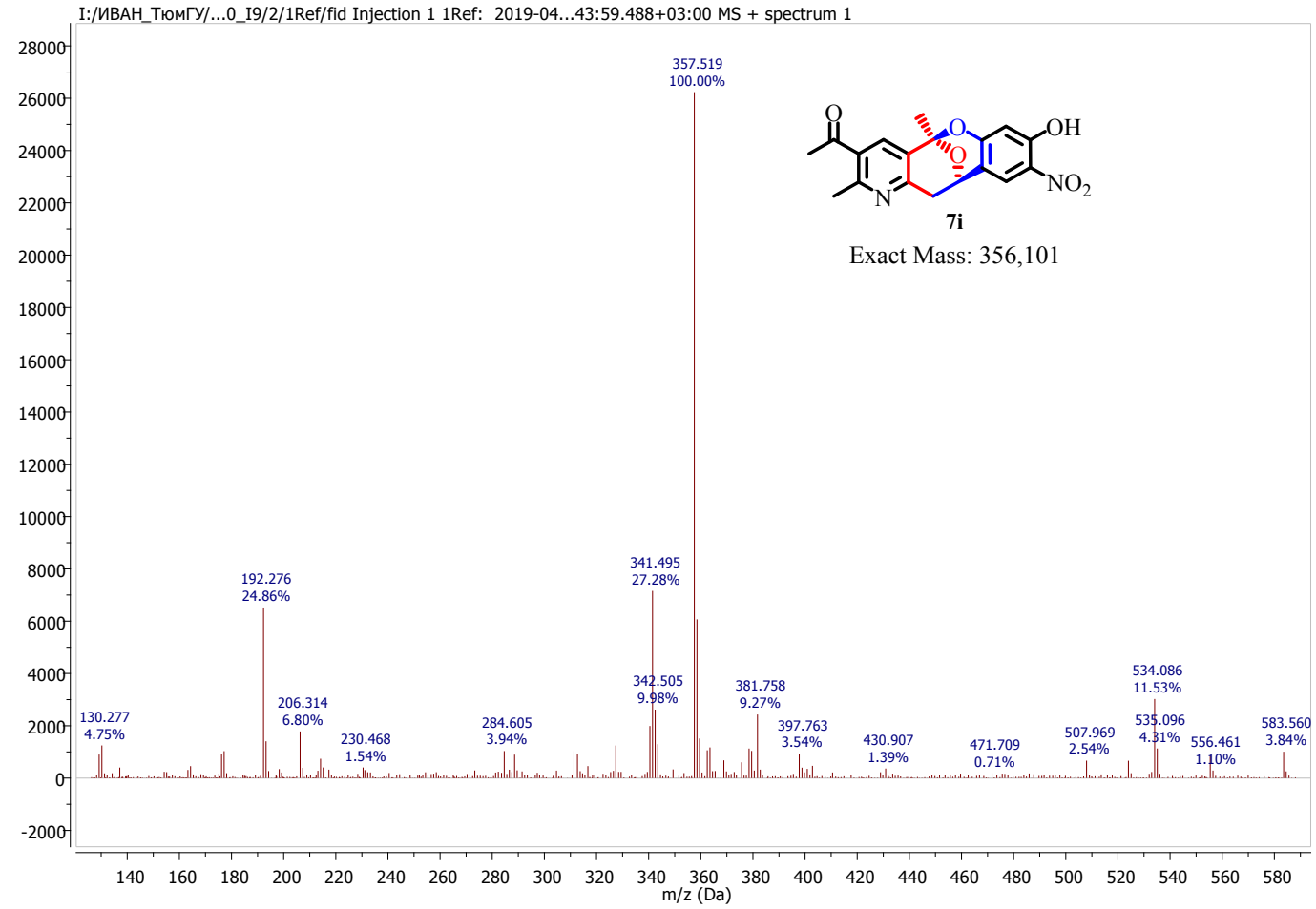
Mass spectrum (EI 70 eV) of (7f)



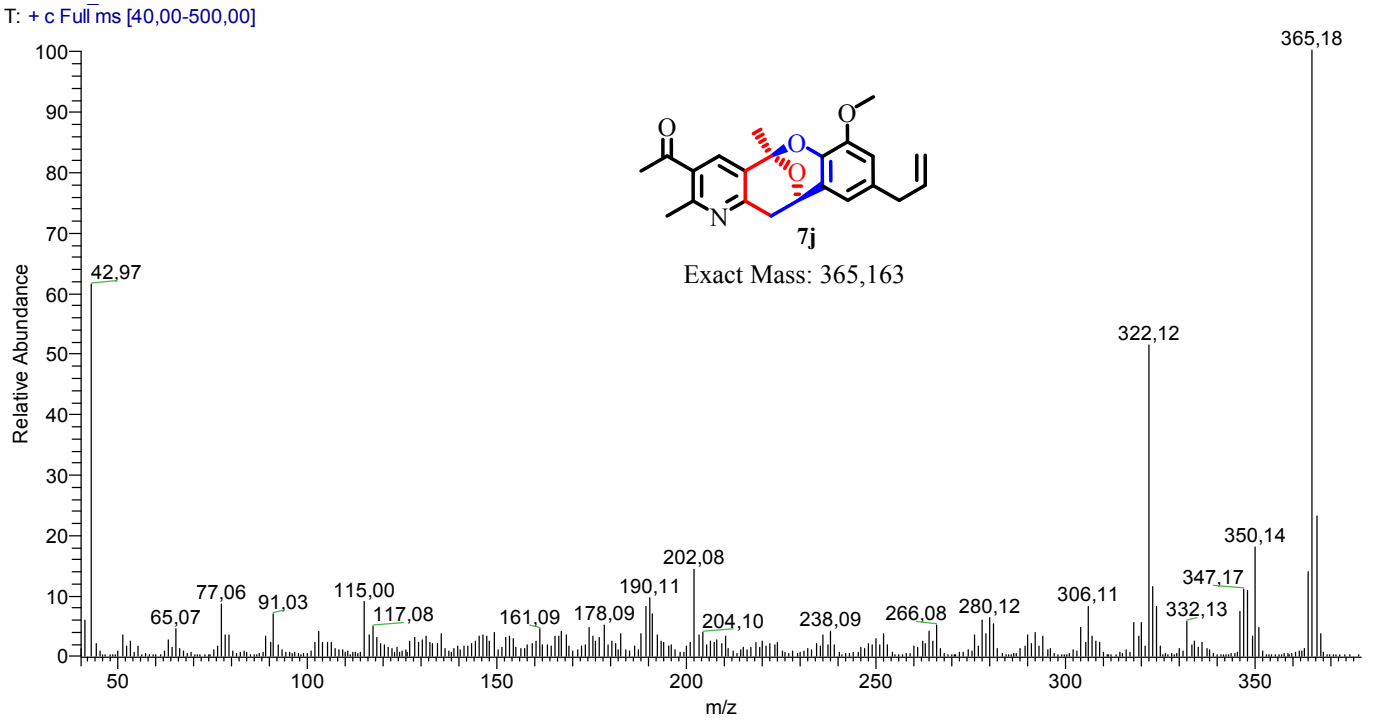
Mass spectrum (EI 70 eV) of (7g)



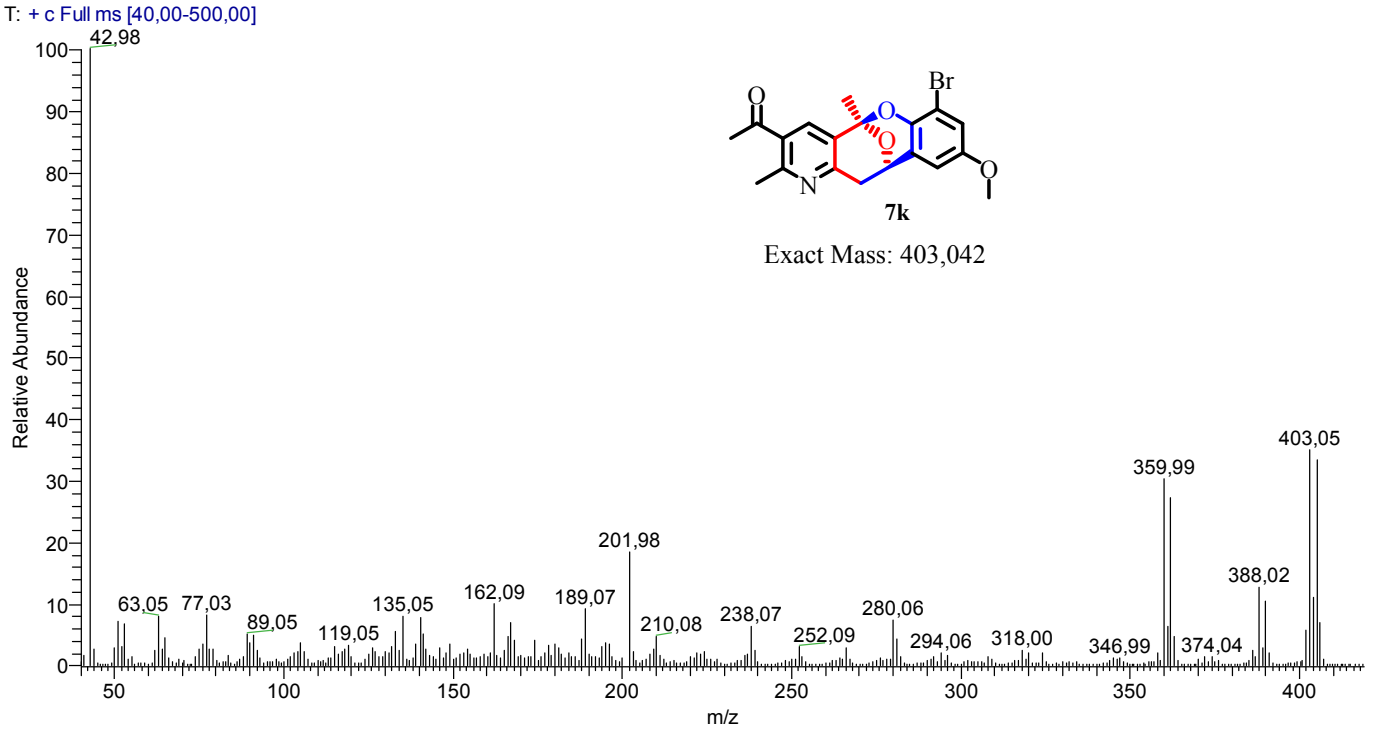
Mass spectrum (EI 70 eV) of (7h)



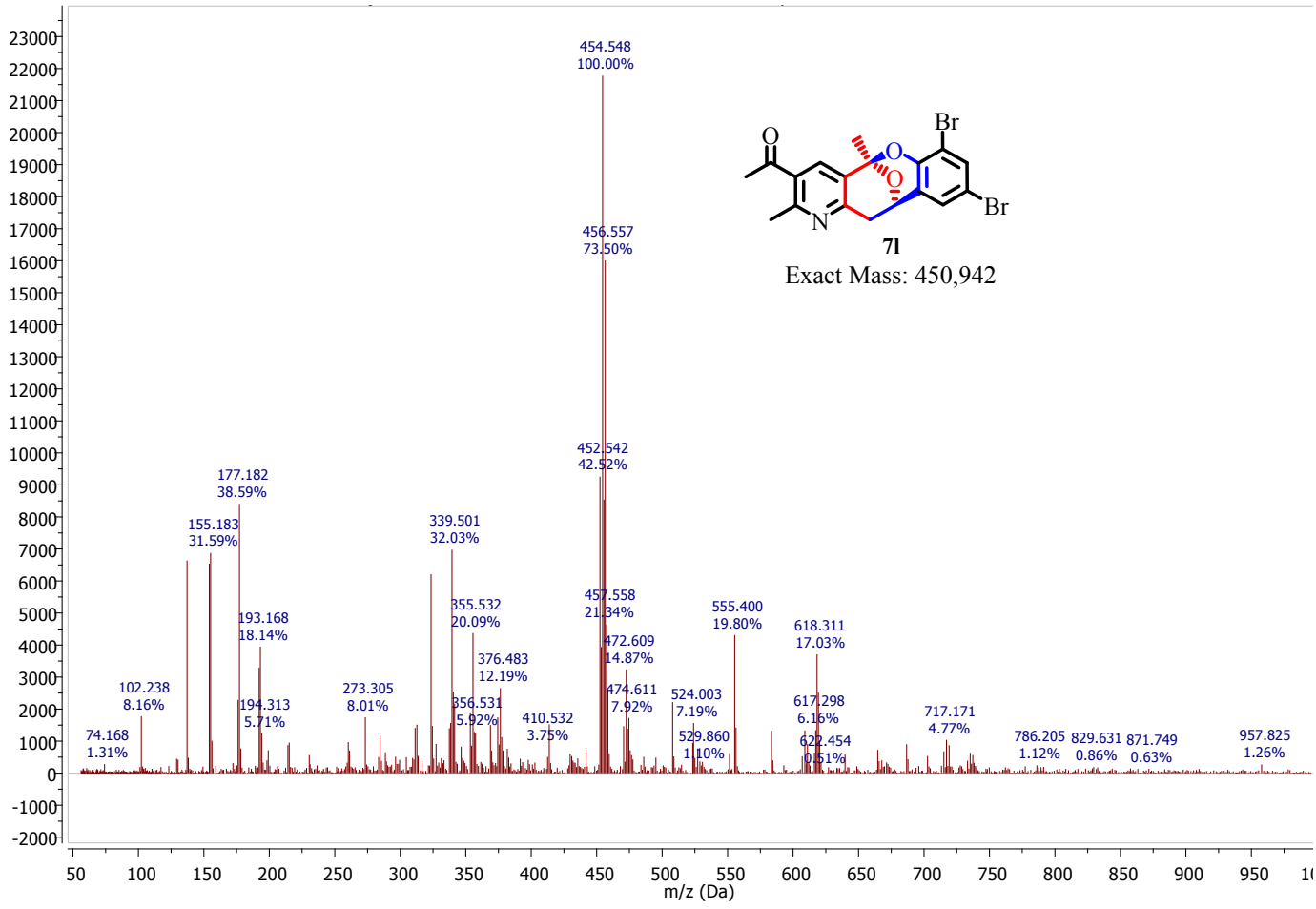
Mass spectrum (MALDI-TOF) of (7i)



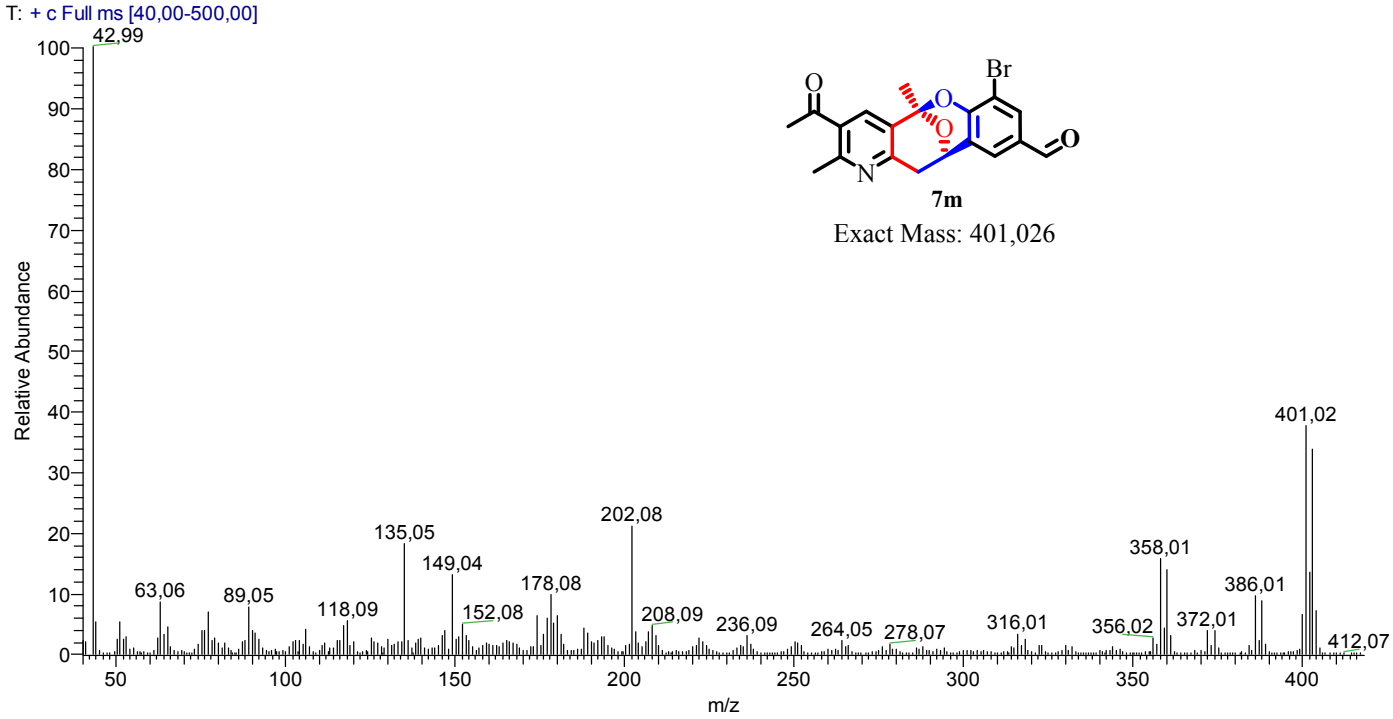
Mass spectrum (EI 70 eV) of (7j)



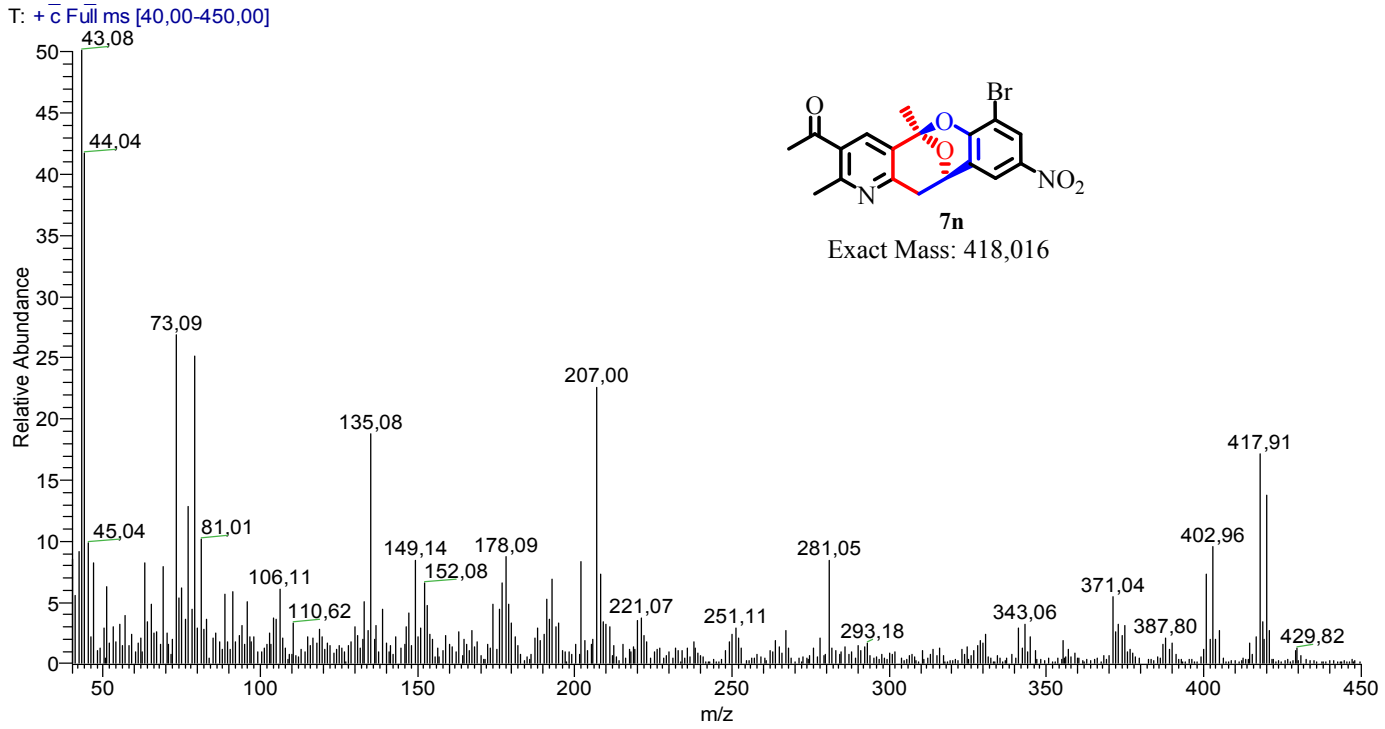
Mass spectrum (EI 70 eV) of (7k)



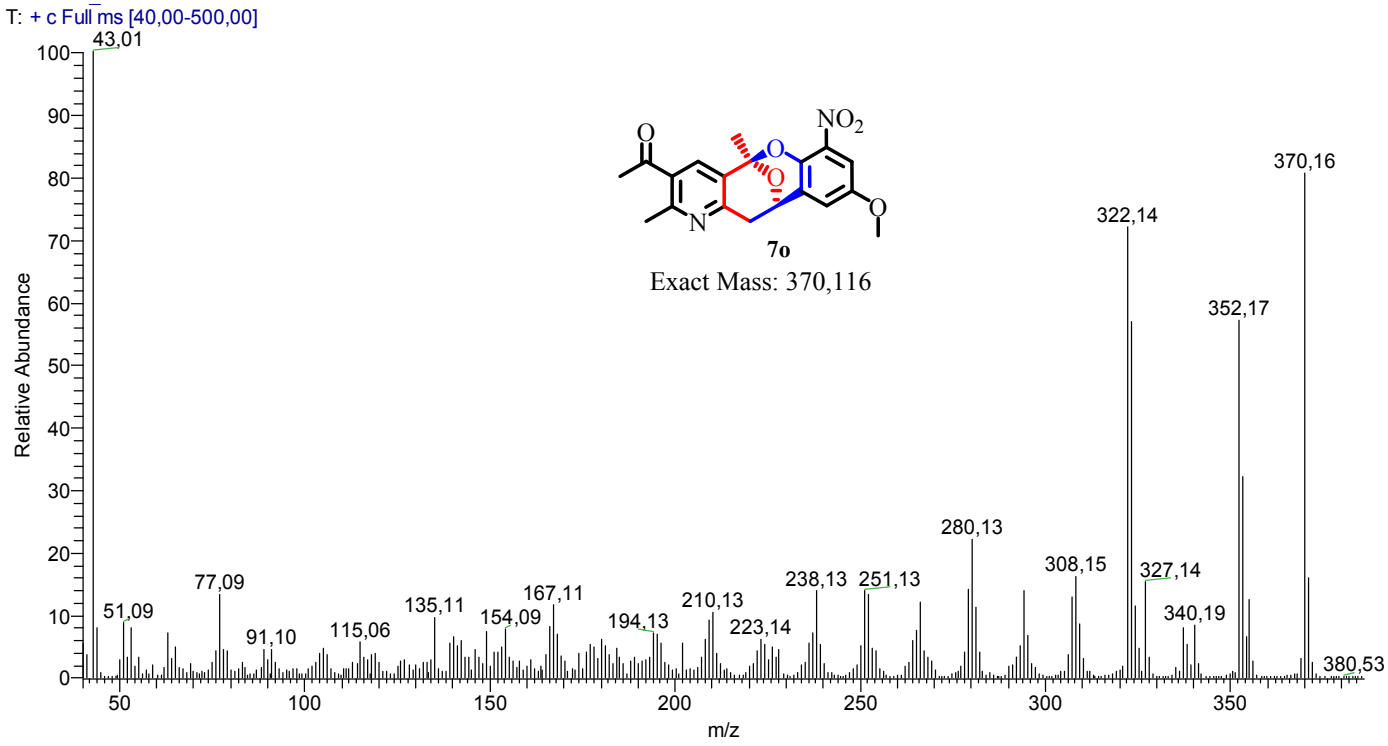
Mass spectrum (MALDI-TOF) of (7l)



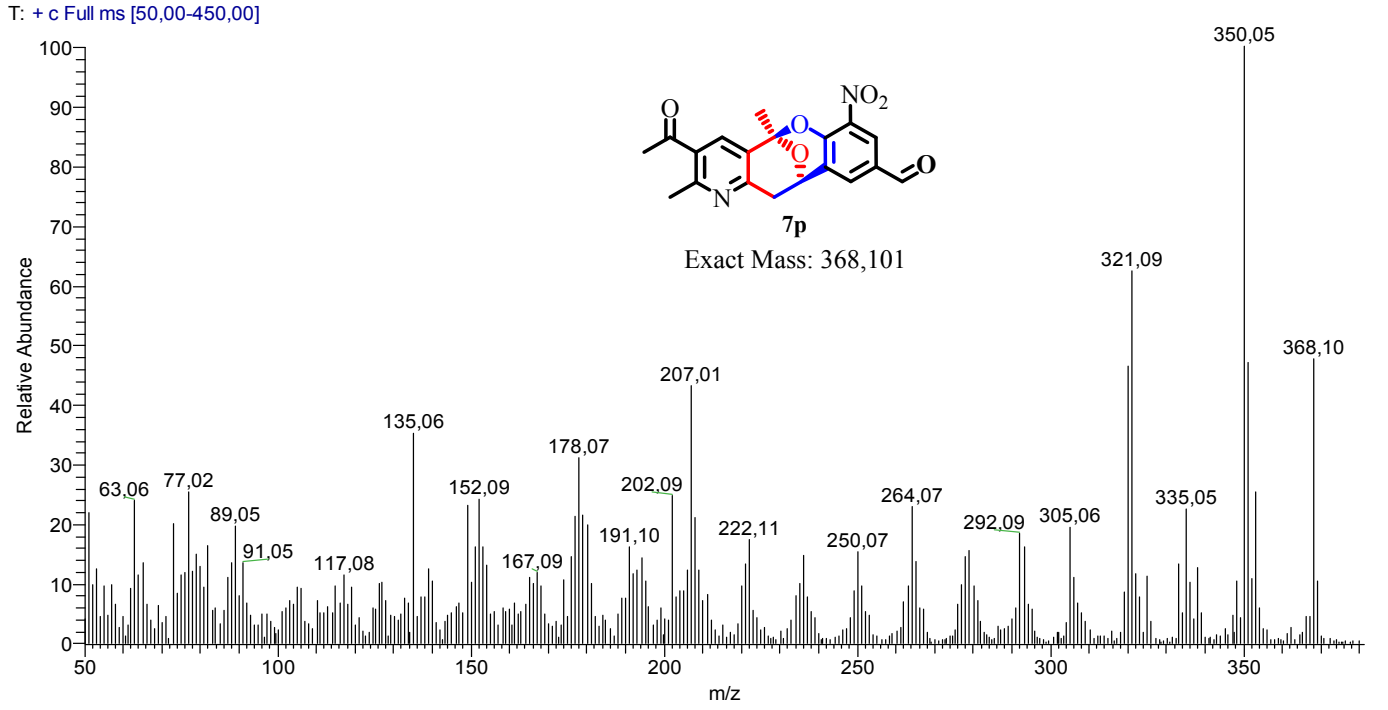
Mass spectrum (EI 70 eV) of (7m)



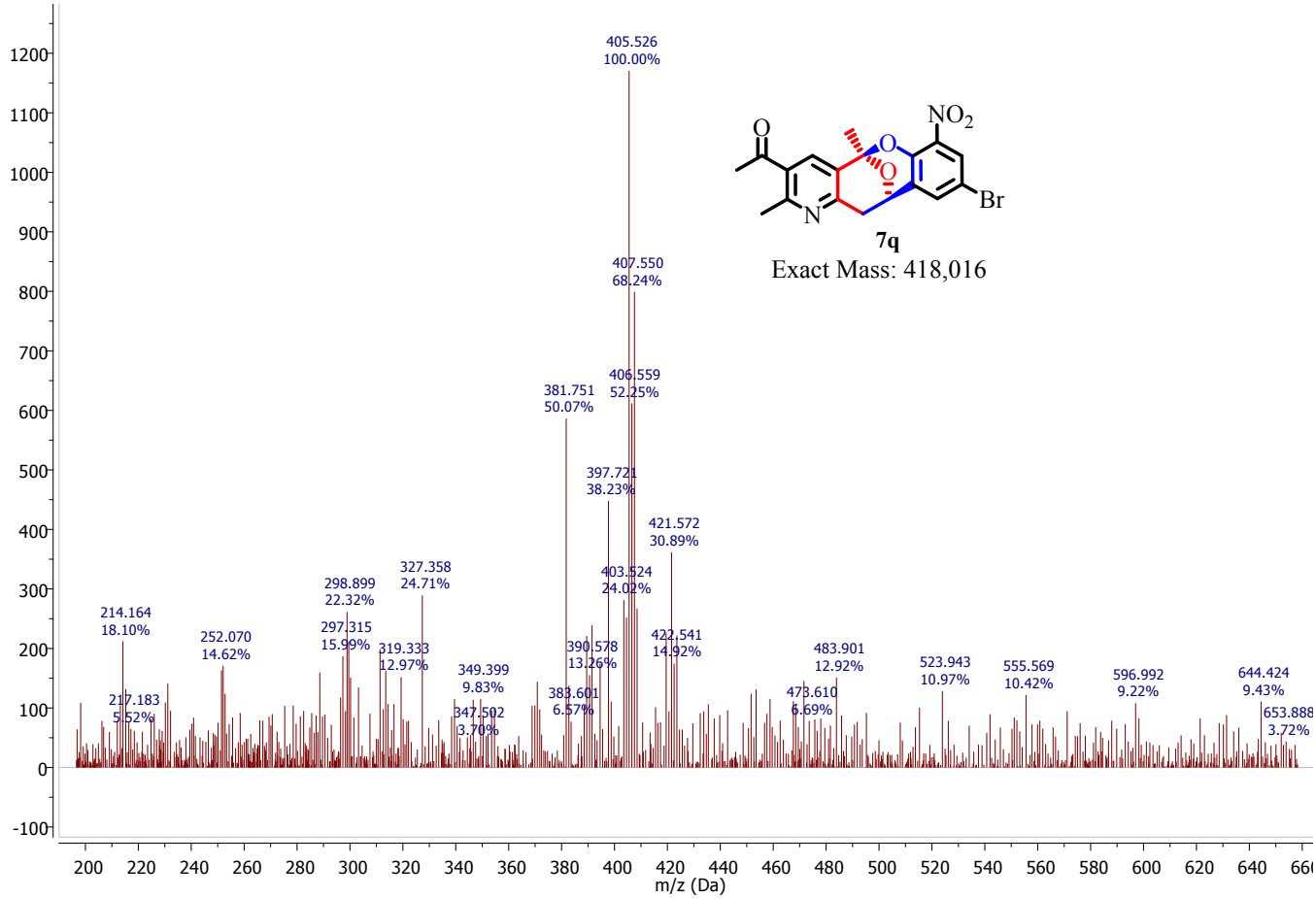
Mass spectrum (EI 70 eV) of (7n)



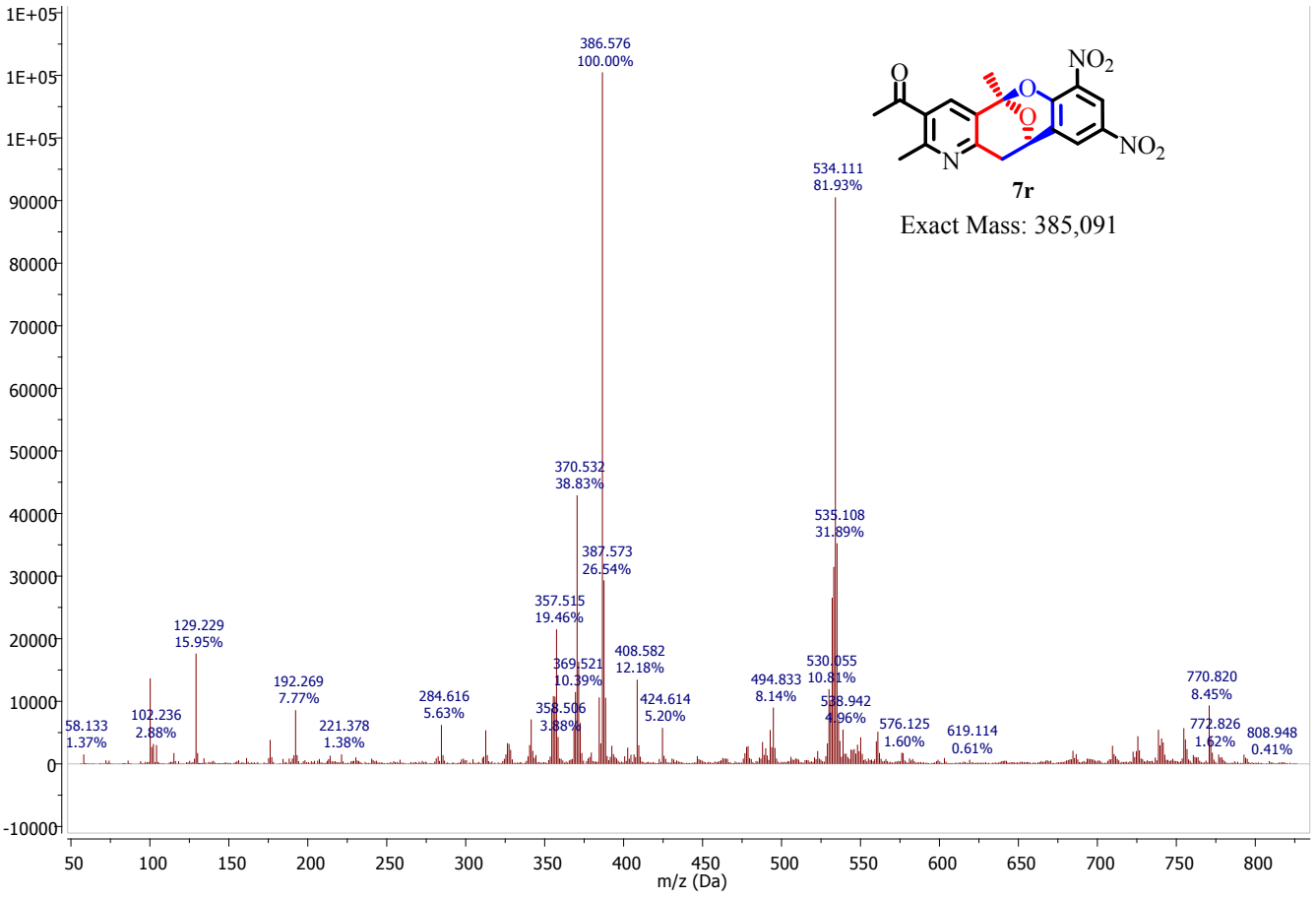
Mass spectrum (EI 70 eV) of (7o)



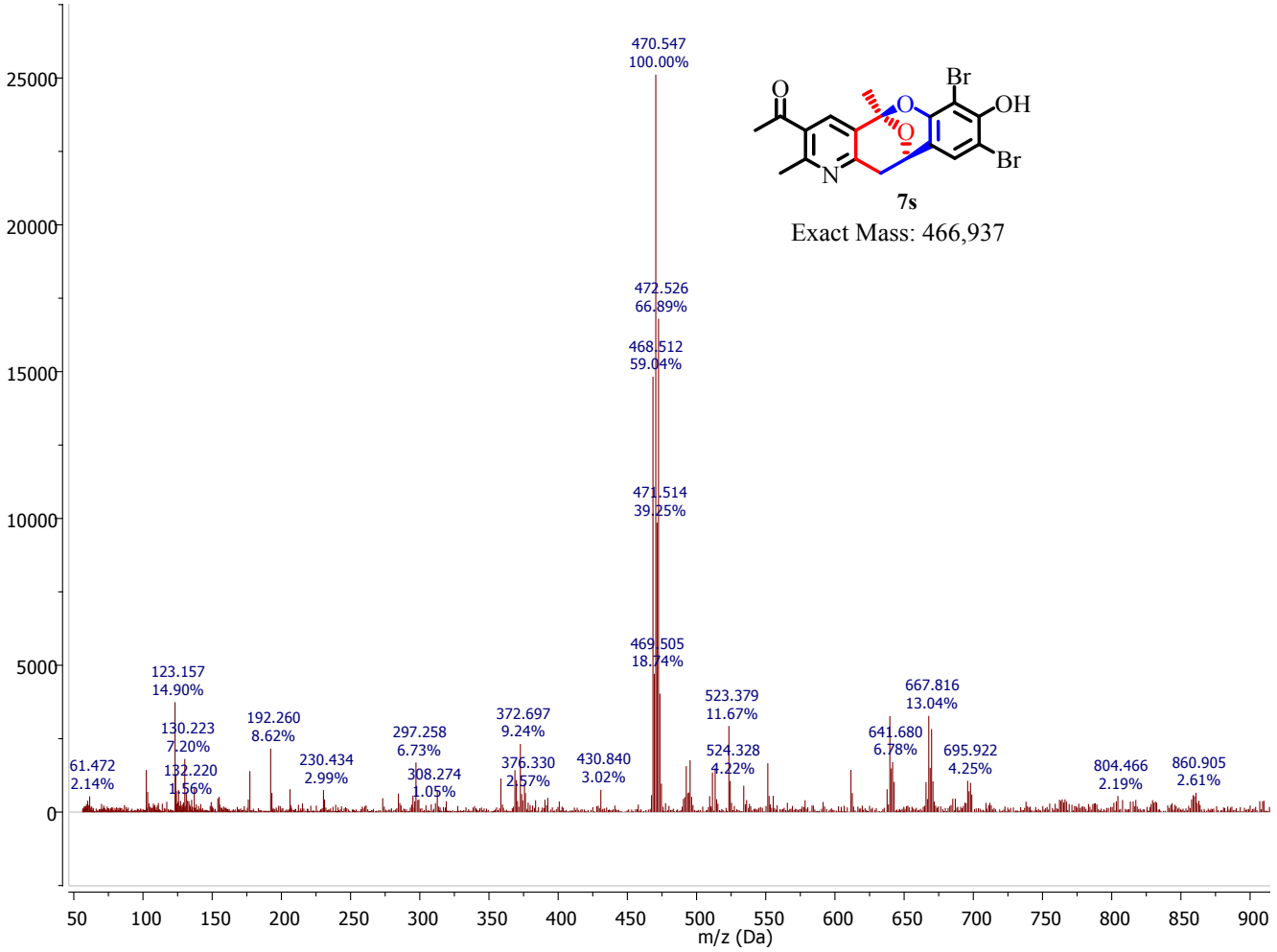
Mass spectrum (EI 70 eV) of (7p)



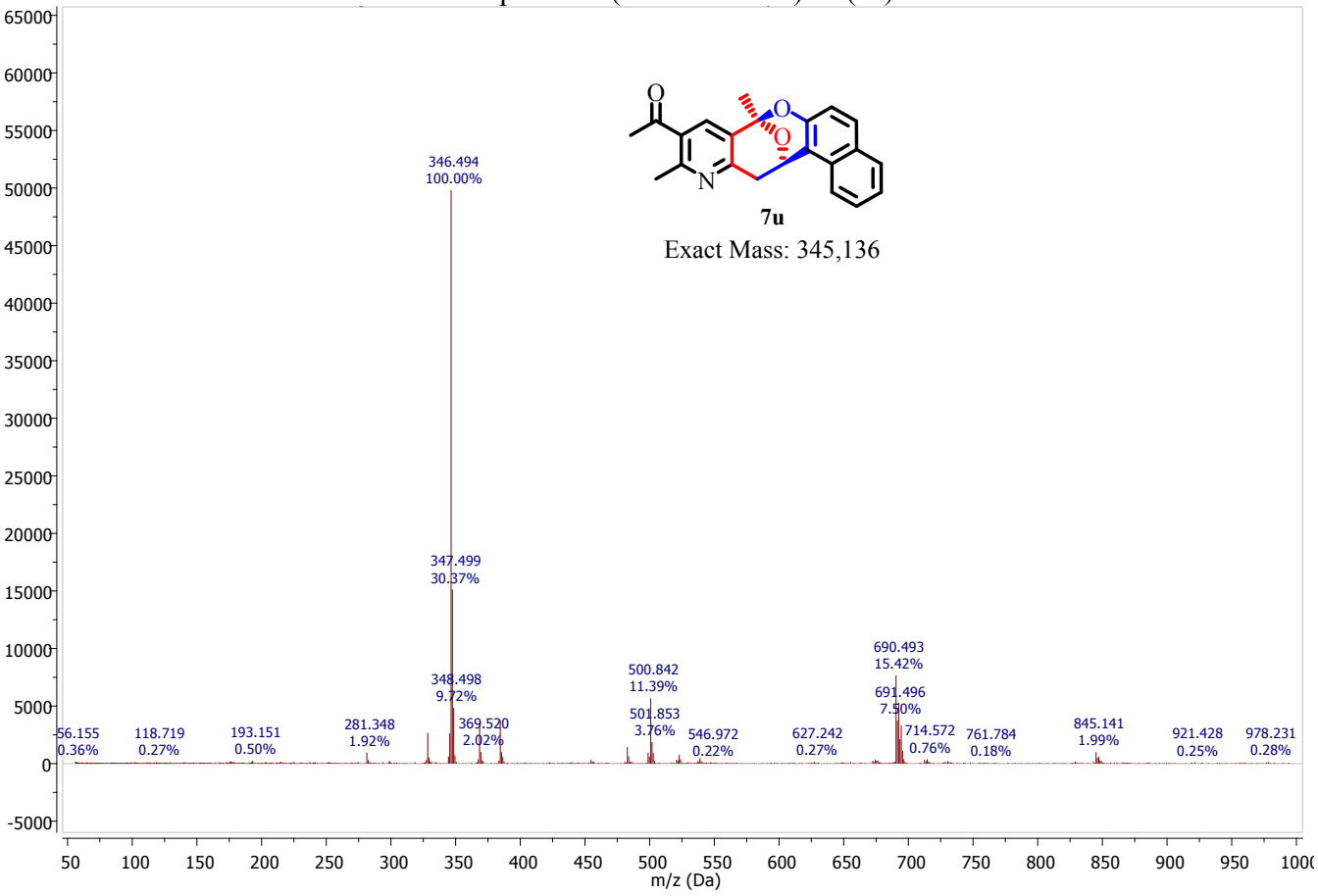
Mass spectrum (MALDI-TOF) of (7q)



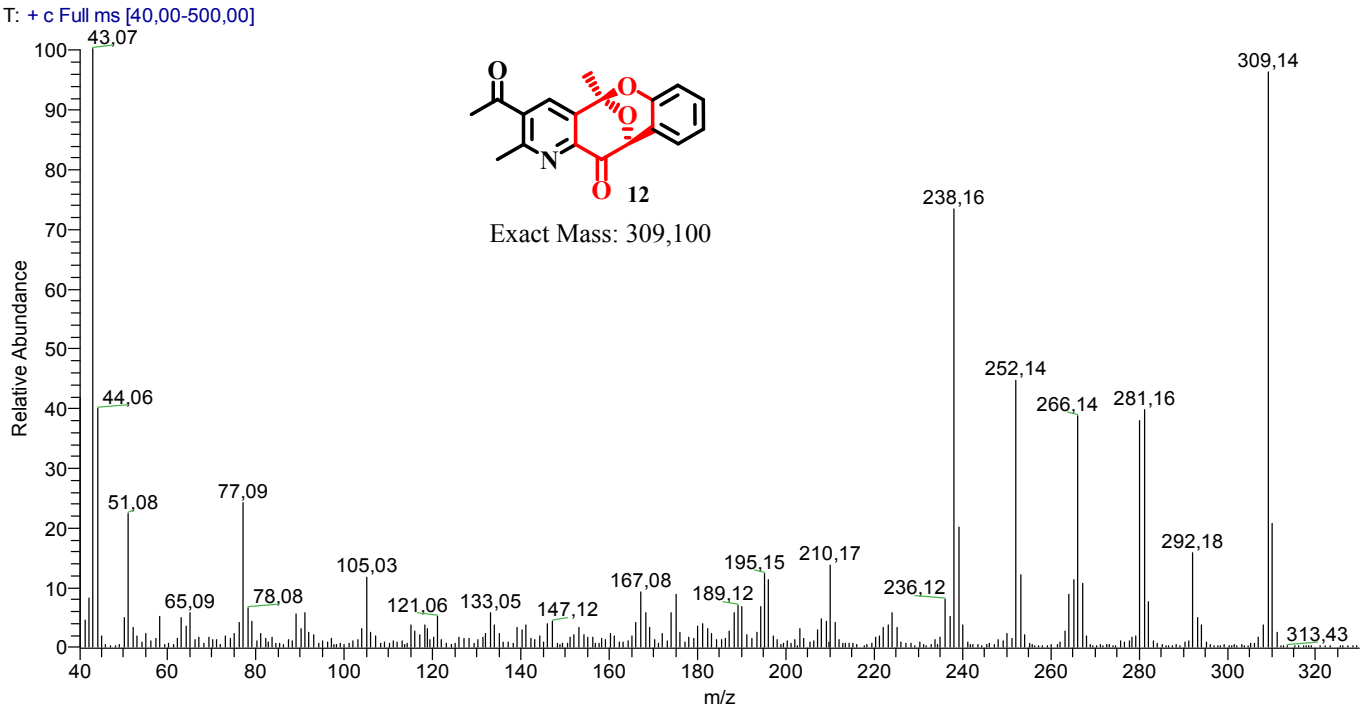
Mass spectrum (MALDI-TOF) of (7r)



Mass spectrum (MALDI-TOF) of (7s)



Mass spectrum (MALDI-TOF) of (7u)



Exact Mass: 309,100

Mass spectrum (EI 70 eV) of (12)