

SUPPORTING INFORMATION

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-[(5*S*,11*S*)-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-[(5*S*,11*S*)-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.

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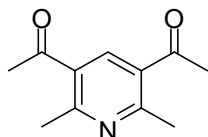
Experimental Procedures

1. Materials and Methods

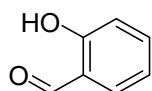
^1H and ^{13}C NMR spectra were recorded on a Bruker DRX400 (400 and 100 MHz, respectively) and Bruker AVANCE 500 (500 and 125 MHz, respectively) instruments using $\text{DMSO-}d_6$ (compounds **7e,g,p,t**) or CDCl_3 (remaining compounds) the internal standard was TMS or residual solvent signals (7.25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

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.

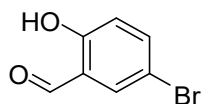
2. Starting Materials Preparation



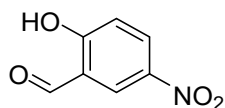
1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) was prepared by following a literature procedure [15]



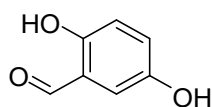
2-hydroxybenzaldehyde was commercially available (Sigma Aldrich).



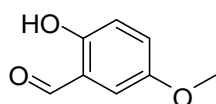
5-bromo-2-hydroxybenzaldehyde was commercially available (Sigma Aldrich).



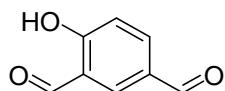
2-hydroxy-5-nitrobenzaldehyde was prepared by following a literature procedure [22]



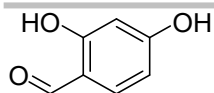
2,5-dihydroxybenzaldehyde was prepared by following a literature procedure [23]



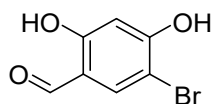
2-hydroxy-5-methoxybenzaldehyde was prepared by following a literature procedure [24]



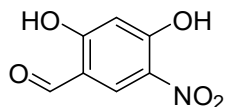
4-hydroxyisophthalaldehyde was prepared by following a literature procedure [25]



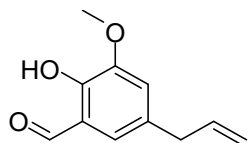
2,4-dihydroxybenzaldehyde was prepared by following a literature procedure [26]



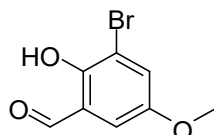
5-bromo-2,4-dihydroxybenzaldehyde was prepared by following a literature procedure [27]



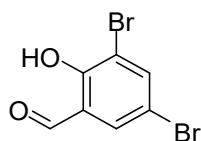
2,4-dihydroxy-5-nitrobenzaldehyde was prepared by following a literature procedure [28]



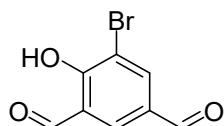
5-allyl-2-hydroxy-3-methoxybenzaldehyde was prepared by following a literature procedure [29]



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

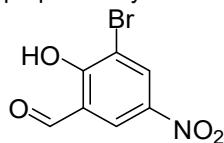


3,5-dibromo-2-hydroxybenzaldehyde was prepared by following a literature procedure [30]

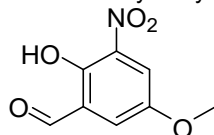


5-bromo-4-hydroxyisophthalaldehyde was prepared following a procedure adapted from the literature [27].

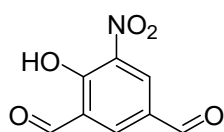
Bromine (0.120 mL, 2.0 mmol) was added dropwise to a solution of 4-hydroxyisophthalaldehyde (300 mg, 2.0 mmol) in acetic acid (5 mL). After stirring for 3 h at room temperature, the resulting mixture was poured into ice-water mixture (10 mL), then the precipitated product was filtered and washed with 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).



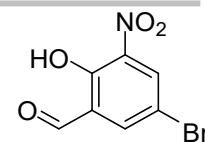
3-bromo-2-hydroxy-5-nitrobenzaldehyde was prepared by following a literature procedure [31]



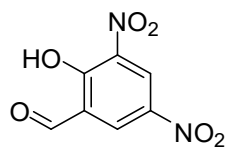
2-hydroxy-5-methoxy-3-nitrobenzaldehyde was prepared by following a literature procedure [32]



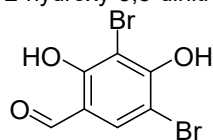
4-hydroxy-5-nitroisophthalaldehyde was prepared by following a literature procedure [33]



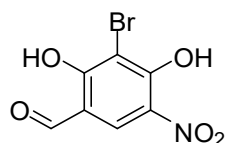
5-bromo-2-hydroxy-3-nitrobenzaldehyde was prepared by following a literature procedure [34]



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

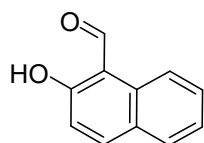


3,5-dibromo-2,4-dihydroxybenzaldehyde was prepared by following a literature procedure [35]



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).



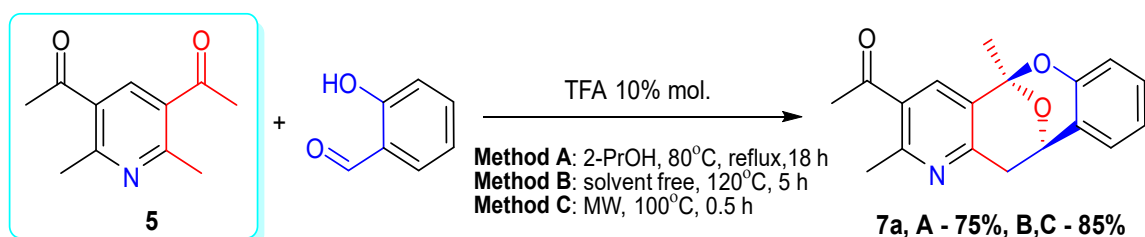
2-hydroxy-1-naphthaldehyde was prepared by following a literature procedure [36]

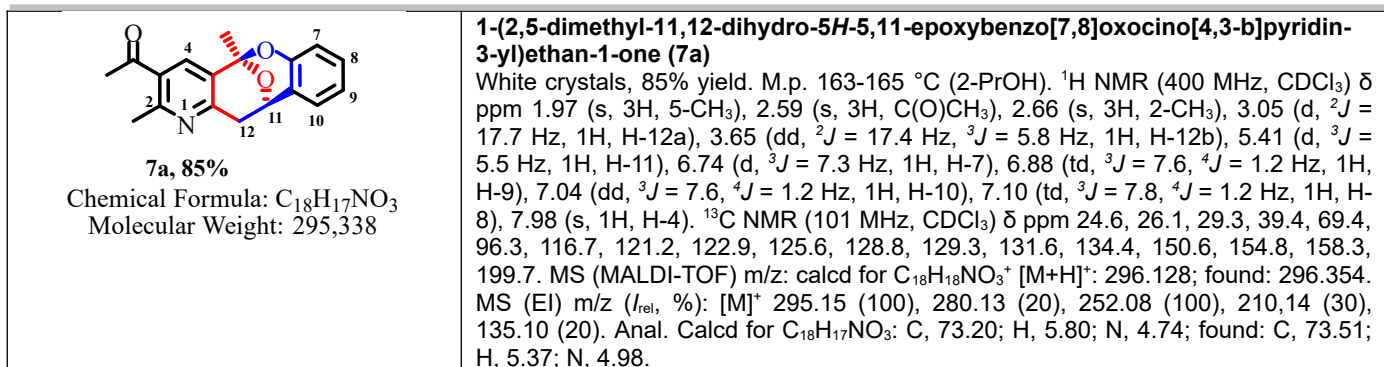
3.1 Synthesis of 11,12-dihydro-5*H*-5,11-epoxybenzo[7,8]oxocino[4,3-*b*]pyridine 7a (solvent free)

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 °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 °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.



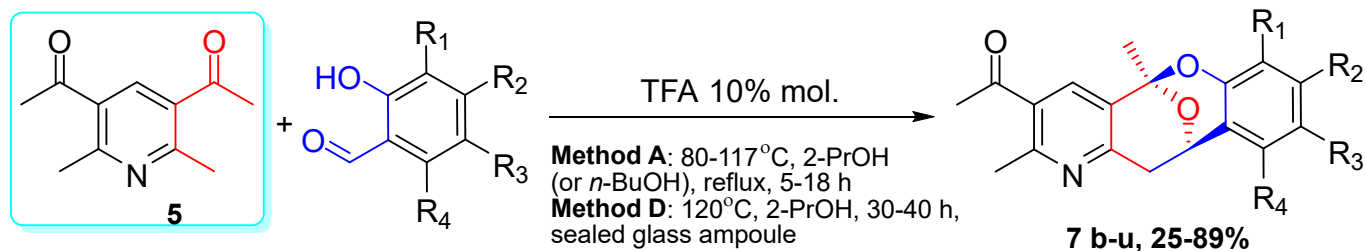


3.2 Synthesis of 11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridines derivatives 7b-u

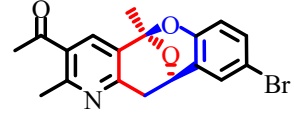

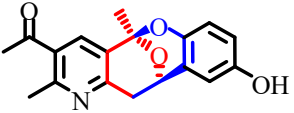
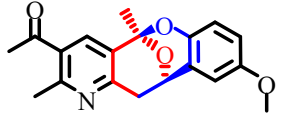
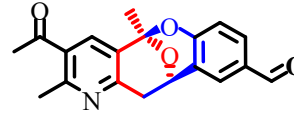
Method A. 1.0 mmol of the corresponding derivative of salicylic aldehyde and 10% (mol.) of TFA were added to 1.0 mmol of 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) **5**. The mixture was refluxed in 2-PrOH (or *n*-BuOH) for 5-18 hours (control by GC-MS). After cooling to room temperature, the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

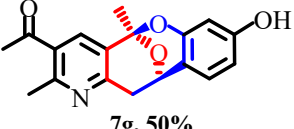
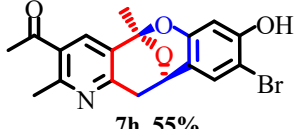
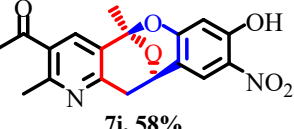
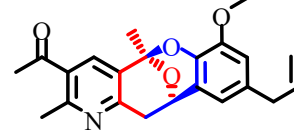
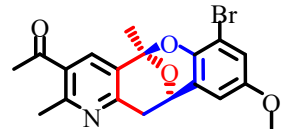
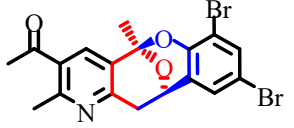
Method D. 1.0 mmol of the corresponding derivative of salicylic aldehyde and 10% (mol.) of TFA were added to 1.0 mmol of 1,1'-(2,6-dimethylpyridine-3,5-diyl)bis(ethan-1-one) **5**. The mixture in 1-5ml 2-PrOH was heated in a sealed glass ampoule to 120 °C for 30-40 hours. After cooling up to 0 °C temperature, 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.

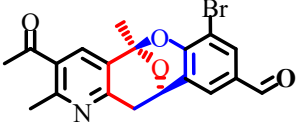
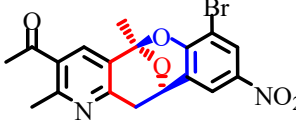
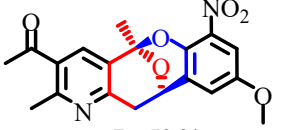
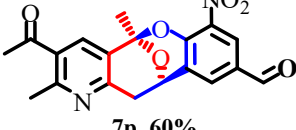
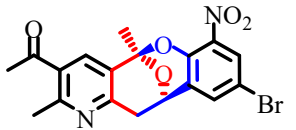
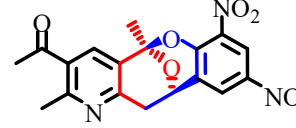
Scheme S2.



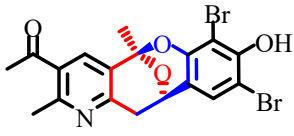
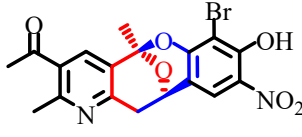
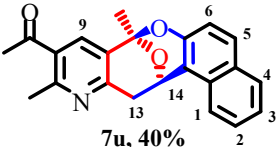
3.1 Characterization data of products 7b-u

 <p>7b, 63%</p> <p>Chemical Formula: C₁₈H₁₆BrNO₃ Molecular Weight: 374,234</p>	<p>1-(9-bromo-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7b)</p> <p>Prepared from 5 and 5-bromo-2-hydroxybenzaldehyde following the method A. White crystals, 63% yield. M.p. 188-189 °C (2-PrOH). ¹H NMR (400 MHz, CDCl₃) δ ppm 1.96 (s, 3H, 5-CH₃), 2.59 (s, 3H, C(O)CH₃), 2.67 (s, 3H, 2-CH₃), 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₇NaBrNO₃⁺ [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).</p>
 <p>7c, 59%</p> <p>Chemical Formula: C₁₈H₁₆N₂O₅ Molecular Weight: 340,335</p>	<p>1-(2,5-dimethyl-9-nitro-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7c)</p> <p>Prepared from 5 and 2-hydroxy-5-nitrobenzaldehyde following the method A. Beige crystals, 59% yield. M.p. 209-210 °C (2-PrOH-MeCN). ¹H NMR (400 MHz, CDCl₃) δ ppm 1.99 (s, 3H, 5-CH₃), 2.58 (s, 3H, C(O)CH₃), 2.65 (s, 3H, 2-CH₃), 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₇N₂O₅⁺ [M+H]⁺: 341.110; found: 341.395.</p>
 <p>7d, 38%</p> <p>Chemical Formula: C₁₈H₁₇NO₄ Molecular Weight: 311,337</p>	<p>1-(9-hydroxy-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7d)</p> <p>Prepared from 5 and 2,5-dihydroxybenzaldehyde following the method D. Beige crystals, 38% yield. M.p. 252-255 °C (2-PrOH). ¹H NMR (500 MHz, CDCl₃) δ ppm 1.96 (s, 3H, 5-CH₃), 2.65 (s, 3H, C(O)CH₃), 2.86 (s, 3H, 2-CH₃), 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). ¹³C NMR (126 MHz, CDCl₃) 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 C₁₈H₁₇NO₄: C, 69.44; H, 5.50; N, 4.50; found: C, 69.59; H, 5.33; N, 4.70.</p>
 <p>7e, 42%</p> <p>Chemical Formula: C₁₉H₁₉NO₄ Molecular Weight: 325,364</p>	<p>1-(9-methoxy-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7e)</p> <p>Prepared from 5 and 2-hydroxy-5-methoxybenzaldehyde following the method D. White crystals, 42% yield. M.p. 258-260 °C (SiO₂, acetone/hexane 1:8). ¹H NMR (500 MHz, DMSO-d₆) δ ppm 1.92 (s, 3H, 5-CH₃), 2.50 (s, 3H, C(O)CH₃), 2.57 (s, 3H, 2-CH₃), 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, OCH₃), 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, ⁴J = 2.8 Hz, 1H, H-10), 8.25 (s, 1H, H-4). ¹³C NMR (126 MHz, DMSO-d₆) 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 C₁₉H₁₉NO₄: C, 70.14; H, 5.89; N, 4.31; found: C, 70.39; H, 5.70; N, 4.16.</p>
 <p>7f, 80%</p> <p>Chemical Formula: C₁₉H₁₇NO₄ Molecular Weight: 323,348</p>	<p>3-acetyl-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridine-9-carbaldehyde (7f)</p> <p>Prepared from 5 and 4-hydroxyisophthalaldehyde following the method A. Yellow crystals, 80% yield. M.p. 185-187 °C (SiO₂, EtOAc/hexane 1:5). ¹H NMR (500 MHz, CDCl₃) δ ppm 2.01 (s, 3H, 5-CH₃), 2.61 (s, 3H, C(O)CH₃), 2.69 (s, 3H, 2-CH₃), 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). ¹³C NMR (126 MHz, CDCl₃) 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 C₁₉H₁₇NO₄: C, 70.58; H, 5.30; N, 4.33; found: C, 70.74; H, 5.11; N, 4.15.</p>

 <p>7g, 50%</p> <p>Chemical Formula: $C_{18}H_{17}NO_4$ Molecular Weight: 311,337</p>	<p>1-(8-hydroxy-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7g)</p> <p>Prepared from 5 and 2,4-dihydroxybenzaldehyde following the method A. White crystals, 50% yield. M.p. 234-235 °C (2-PrOH). 1H 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.</p>
 <p>7h, 55%</p> <p>Chemical Formula: $C_{18}H_{16}BrNO_4$ Molecular Weight: 390,233</p>	<p>1-(9-bromo-8-hydroxy-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7h)</p> <p>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). 1H 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.</p>
 <p>7i, 58%</p> <p>Chemical Formula: $C_{18}H_{16}N_2O_6$ Molecular Weight: 356,334</p>	<p>1-(8-hydroxy-2,5-dimethyl-9-nitro-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7i)</p> <p>Prepared from 5 and 2,4-dihydroxy-5-nitrobenzaldehyde following the method A. Yellow crystals, 58% yield. M.p. 218-219 °C (2-PrOH). 1H 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 $C_{18}H_{16}N_2O_6$: $[M+H]^+$: 357.330; found: 357.519.</p>
 <p>7j, 25%</p> <p>Chemical Formula: $C_{22}H_{23}NO_4$ Molecular Weight: 365,429</p>	<p>1-(9-allyl-7-methoxy-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7j)</p> <p>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). 1H 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, $-CH=CH_2$), 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.</p>
 <p>7k, 63%</p> <p>Chemical Formula: $C_{19}H_{18}BrNO_4$ Molecular Weight: 404,260</p>	<p>1-(7-bromo-9-methoxy-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7k)</p> <p>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). 1H 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.</p>
 <p>7l, 65%</p> <p>Chemical Formula: $C_{18}H_{15}Br_2NO_3$ Molecular Weight: 453,130</p>	<p>1-(7,9-dibromo-2,5-dimethyl-11,12-dihydro-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-3-yl)ethan-1-one (7l)</p> <p>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). 1H 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.</p>

 <p>7m, 80%</p> <p>Chemical Formula: C₁₉H₁₆BrNO₄ Molecular Weight: 402,244</p>	<p>3-acetyl-7-bromo-2,5-dimethyl-11,12-dihydro-5H-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 (SiO₂, acetone/hexane 1:8). ¹H NMR (500 MHz, CDCl₃) δ ppm 2.09 (s, 3H, 5-CH₃), 2.62 (s, 3H, C(O)CH₃), 2.70 (s, 3H, 2-CH₃), 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). ¹³C NMR (126 MHz, CDCl₃) 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>I</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 C₁₉H₁₆BrNO₄: C, 56.73; H, 4.01; N, 3.48; found: C, 56.94; H, 4.29; N, 3.19.</p>
 <p>7n, 80%</p> <p>Chemical Formula: C₁₈H₁₅BrN₂O₅ Molecular Weight: 419,231</p>	<p>1-(7-bromo-2,5-dimethyl-9-nitro-11,12-dihydro-5H-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). ¹H NMR (400 MHz, CDCl₃) δ ppm 2.10 (s, 3H, 5-CH₃), 2.62 (s, 3H, C(O)CH₃), 2.68 (s, 3H, 2-CH₃), 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). ¹³C NMR (101 MHz, CDCl₃) 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>I</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 C₁₈H₁₅BrN₂O₅: 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.</p>
 <p>7o, 50 %</p> <p>Chemical Formula: C₁₉H₁₈N₂O₆ Molecular Weight: 370,361</p>	<p>1-(9-methoxy-2,5-dimethyl-7-nitro-11,12-dihydro-5H-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). ¹H NMR (500 MHz, CDCl₃) δ ppm 2.03 (s, 3H, 5-CH₃), 2.60 (s, 3H, C(O)CH₃), 2.67 (s, 3H, 2-CH₃), 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, OCH₃), 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). ¹³C NMR (126 MHz, CDCl₃) 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>I</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 C₁₉H₁₈N₂O₆: C, 61.62; H, 4.90; N, 7.56; found: C, 61.88; H, 4.66; N, 7.81.</p>
 <p>7p, 60%</p> <p>Chemical Formula: C₁₉H₁₆N₂O₆ Molecular Weight: 368,345</p>	<p>3-acetyl-2,5-dimethyl-7-nitro-11,12-dihydro-5H-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). ¹H NMR (500 MHz, DMSO-d₆) δ ppm 2.09 (s, 3H, 5-CH₃), 2.51 (s, 3H, C(O)CH₃), 2.60 (s, 3H, 2-CH₃), 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). ¹³C NMR (126 MHz, DMSO-d₆) 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>I</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 C₁₉H₁₆N₂O₆: C, 61.96; H, 4.38; N, 7.61; found: C, 61.67; H, 4.54; N, 7.46.</p>
 <p>7q, 56%</p> <p>Chemical Formula: C₁₈H₁₅BrN₂O₅ Molecular Weight: 419,231</p>	<p>1-(9-bromo-2,5-dimethyl-7-nitro-11,12-dihydro-5H-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). ¹H NMR (400 MHz, CDCl₃) δ ppm 2.07 (s, 3H, 5-CH₃), 2.59 (s, 3H, C(O)CH₃), 2.65 (s, 3H, 2-CH₃), 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₆BrN₂O₅⁺ [M+H]⁺: 421.018; found: 421.572.</p>
 <p>7r, 75%</p> <p>Chemical Formula: C₁₈H₁₅N₃O₇ Molecular Weight: 385,332</p>	<p>1-(2,5-dimethyl-7,9-dinitro-11,12-dihydro-5H-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). ¹H NMR (400 MHz, CDCl₃) δ ppm 2.08 (s, 3H, 5-CH₃), 2.48 (s, 3H, C(O)CH₃), 2.57 (s, 3H, 2-CH₃), 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₆N₃O₇⁺ [M+H]⁺: 386.330; found: 386.576.</p>

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 <p>7s, 60%</p> <p>Chemical Formula: C₁₈H₁₅Br₂NO₄ Molecular Weight: 469,129</p>	<p>1-(7,9-dibromo-8-hydroxy-2,5-dimethyl-11,12-dihydro-5H-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). ¹H NMR (400 MHz, CDCl₃) δ ppm 2.03 (s, 3H, 5-CH₃), 2.60 (s, 3H, C(O)CH₃), 2.68 (s, 3H, 2-CH₃), 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₅Br₂NO₄⁺ [M+H]⁺: 469.942; found: 470.547.</p>
 <p>7t, 89%</p> <p>Chemical Formula: C₁₈H₁₅BrN₂O₆ Molecular Weight: 435,230</p>	<p>1-(7-bromo-8-hydroxy-2,5-dimethyl-9-nitro-11,12-dihydro-5H-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). ¹H NMR (500 MHz, DMSO-d₆) δ ppm 2.08 (s, 3H, 5-CH₃), 2.51 (s, 3H, C(O)CH₃), 2.60 (s, 3H, 2-CH₃), 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). ¹³C NMR (126 MHz, DMSO-d₆) 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 C₁₈H₁₅BrN₂O₆: C, 49.67; H, 3.47; N, 6.44; found: C, 49.97; H, 3.73; N, 6.21.</p>
 <p>7u, 40%</p> <p>Chemical Formula: C₂₂H₁₉NO₃ Molecular Weight: 345,398</p>	<p>1-(8,11-dimethyl-13,14-dihydro-8H-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). ¹H NMR (400 MHz, CDCl₃) δ ppm 2.03 (s, 3H, 5-CH₃), 2.57 (s, 3H, C(O)CH₃), 2.61 (s, 3H, 2-CH₃), 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). ¹³C NMR (101 MHz, CDCl₃) 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 C₂₂H₂₀NO₃⁺ [M+H]⁺: 346.400; found: 346.494.</p>

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)

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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

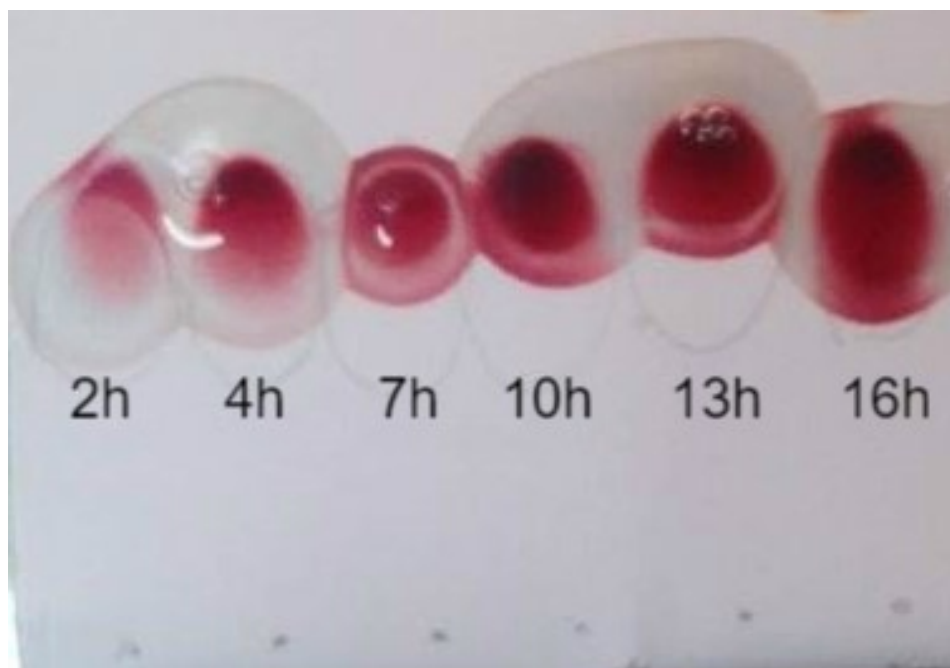


Figure S1. Control of the reaction by TLC using Marquis reagent^{*[a]}

* conc. H₂SO₄ with addition of formalin in a ratio of 10:1.

[a] Reaction condition: EtOH, HCl (catalyst), 16-20 hours

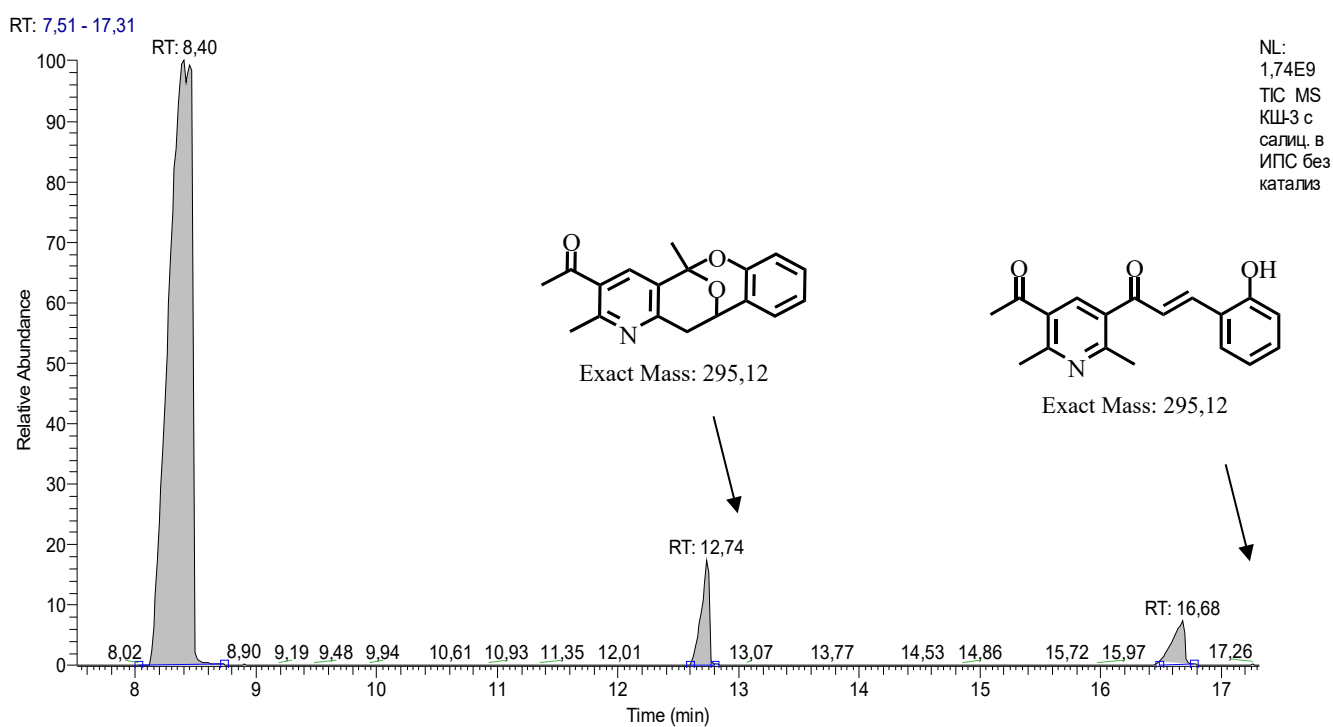


Figure S2. Fragment of the chromatogram of the reaction mixture (in the absence of a catalyst)

КШ-3 с солици, в ИПС без катализ #805 RT: 16,63 AV: 1 NL: 1,44E7

T: + c Full ms [40,00-500,00]

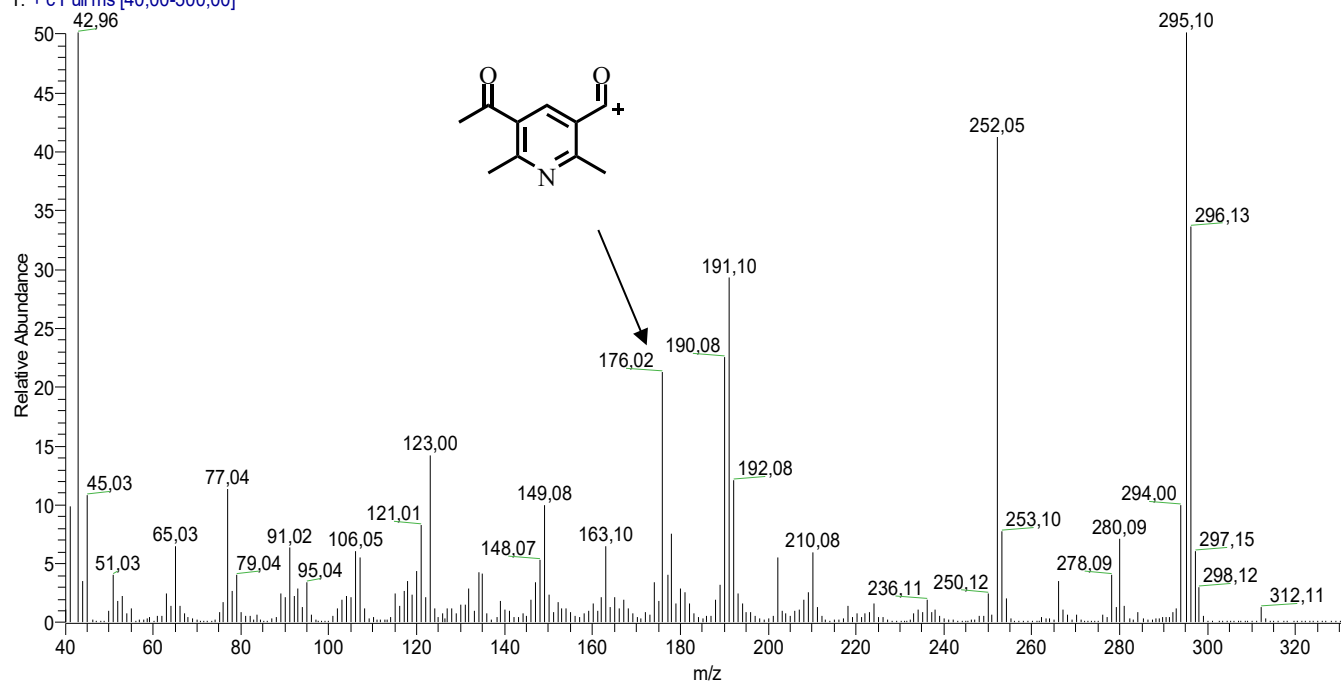
**Figure S3.** Mass Spectrum of the reaction mixture ($t_R = 16,63$ min)

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.

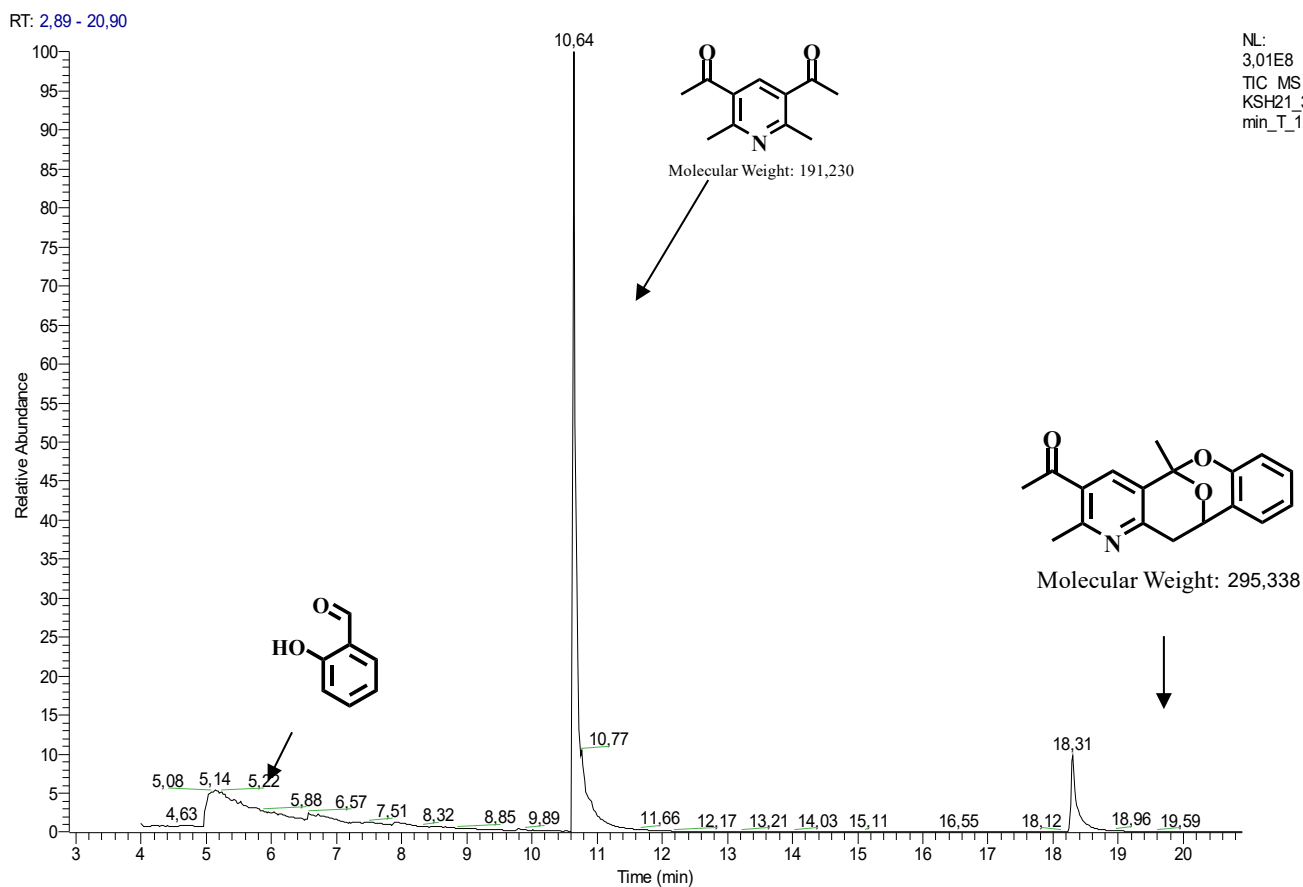
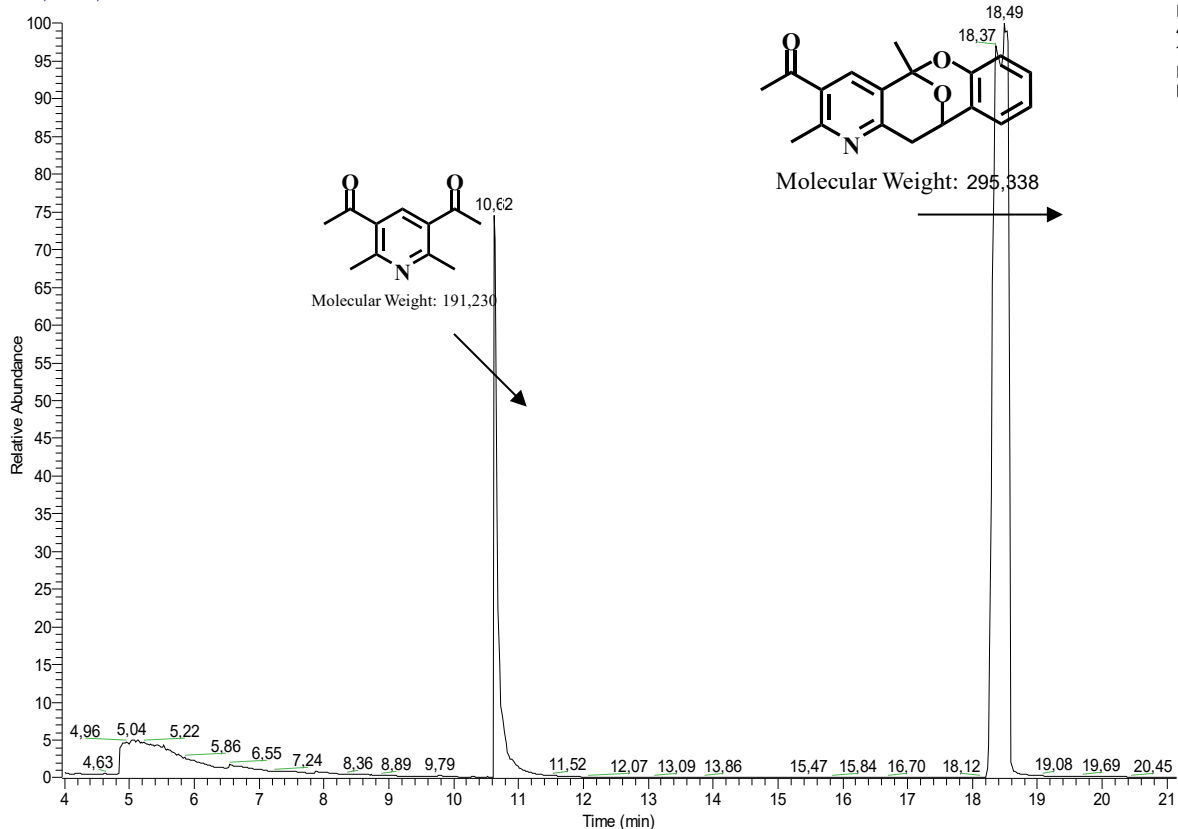
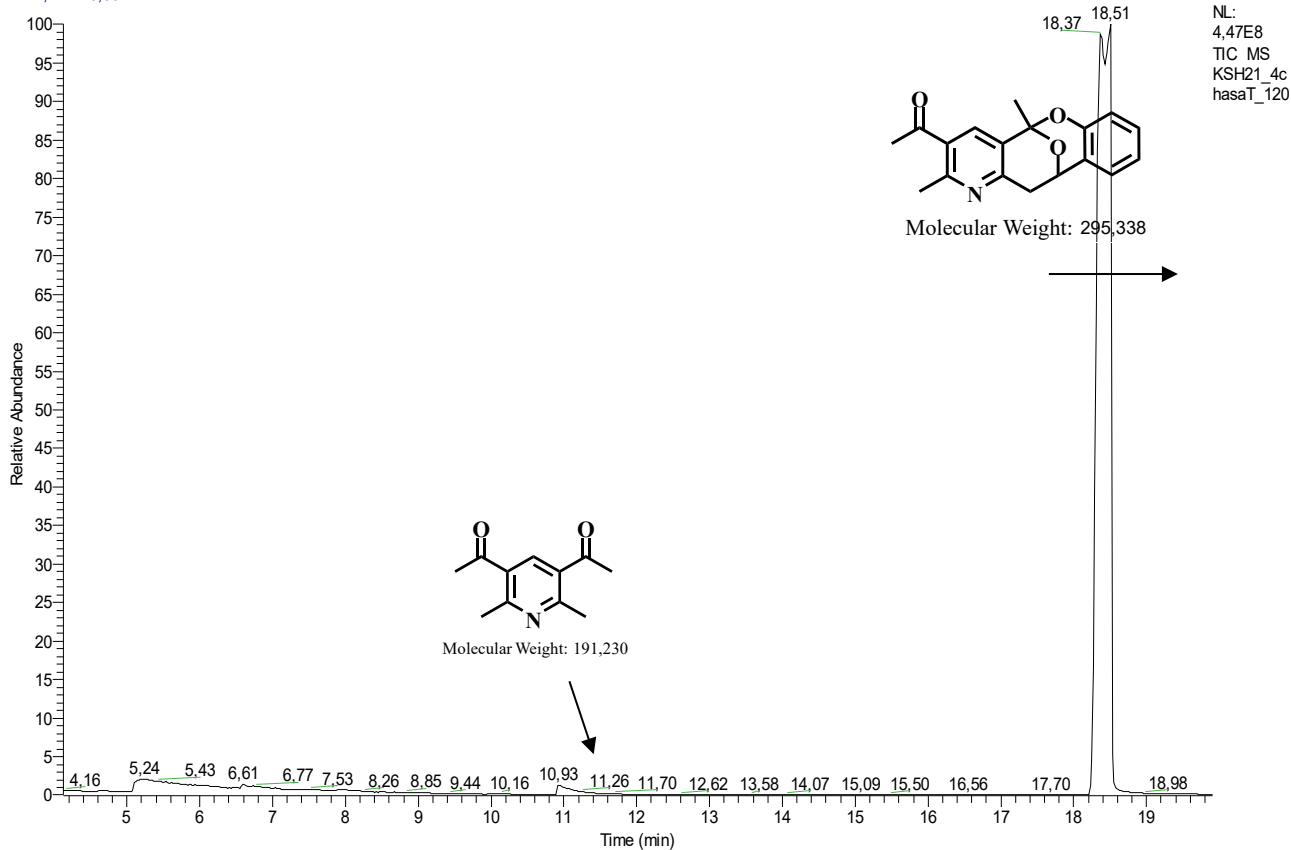


Figure S4. Chromatogram of the reaction mixture after 30 min (solvent free, TFA (10 mol. %), 120°C)

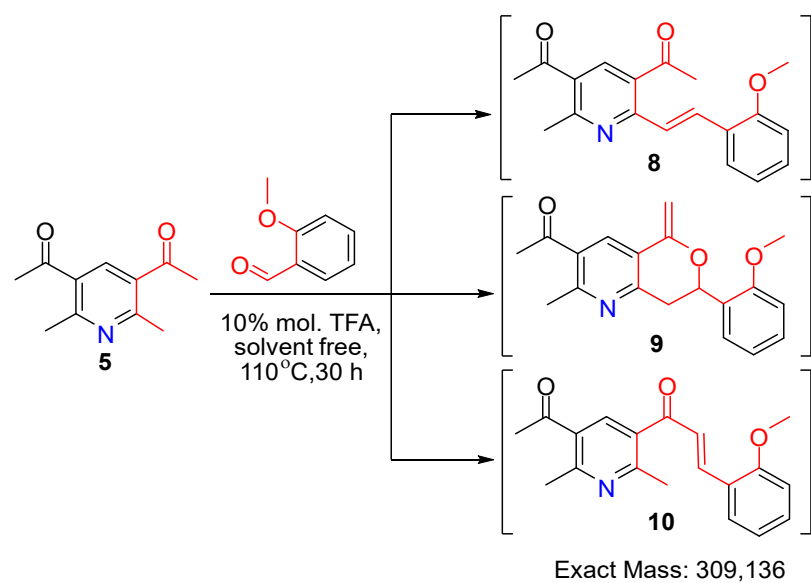
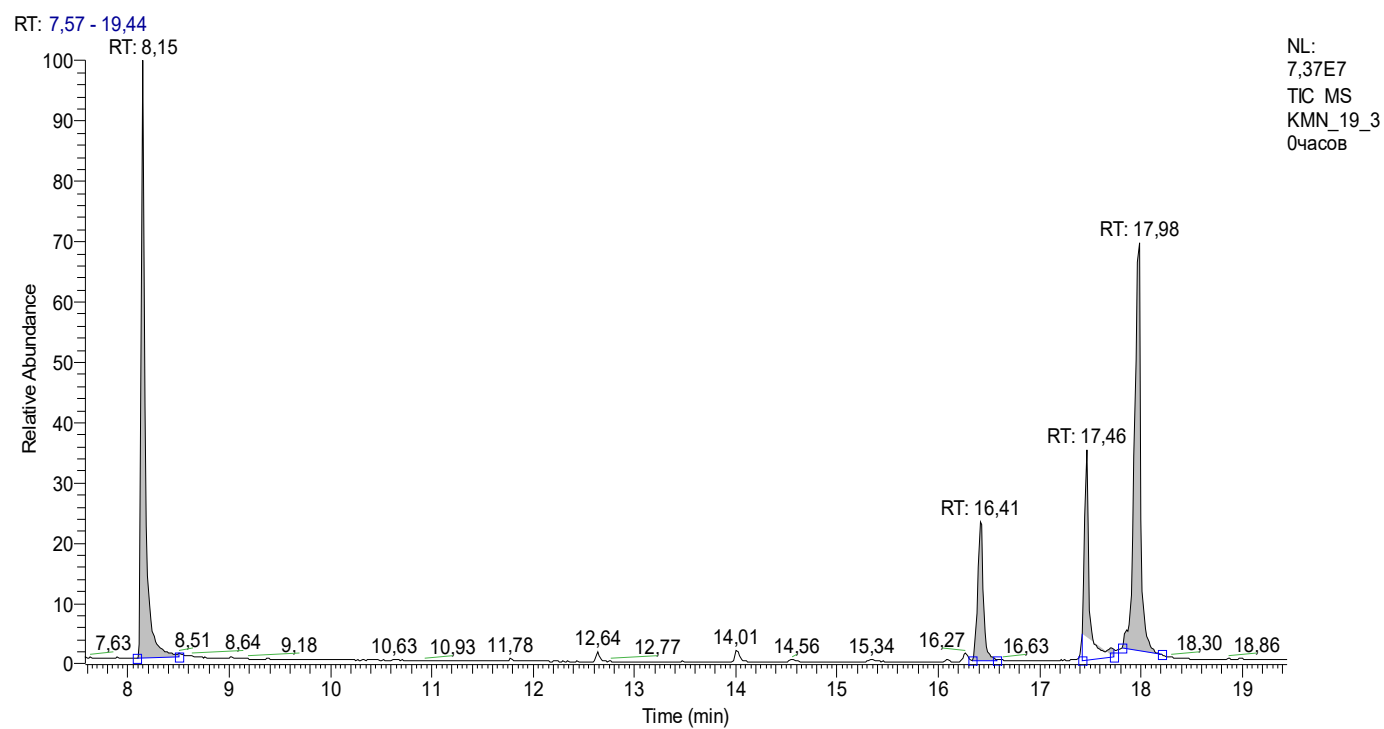
RT: 3.96 - 21.14

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

RT: 4.12 - 19.90

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

3.4 Mechanistic Investigation

**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)

SUPPORTING INFORMATION

KMN_19_30часов #791 RT: 16,41 AV: 1 NL: 1,15E6
T: + c Full ms [40,00-500,00]

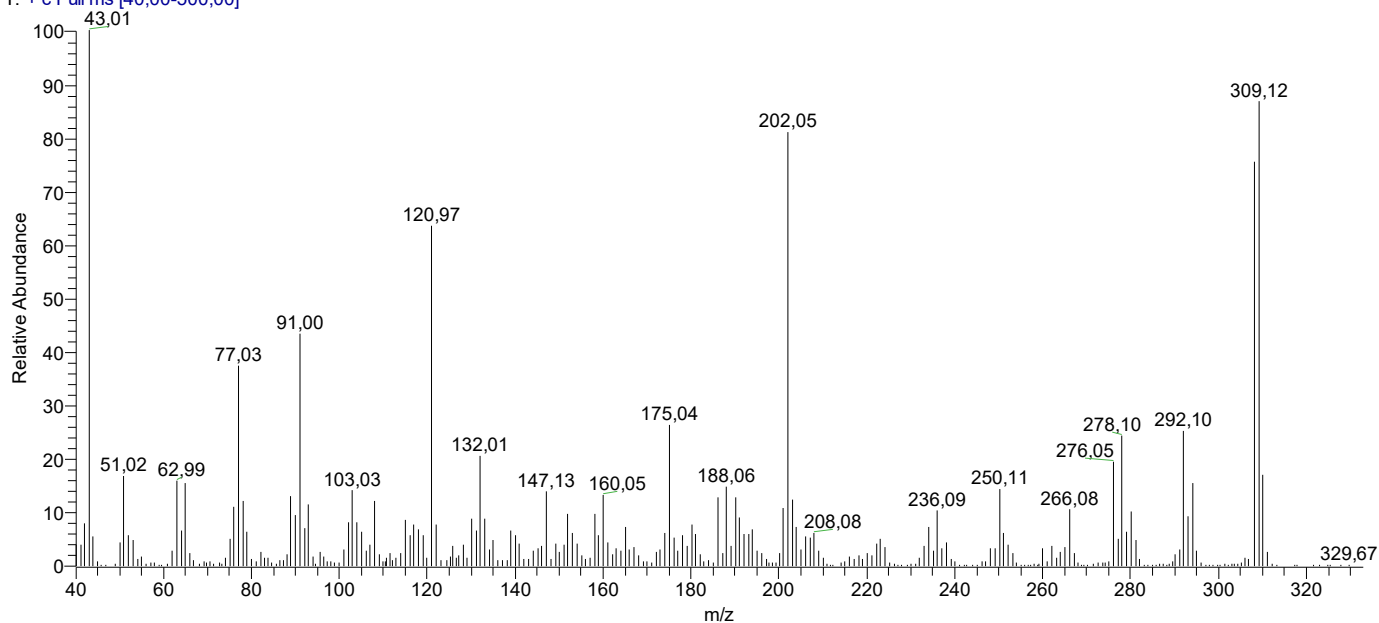


Figure S8. Mass Spectrum: one of the reaction products 8-10 ($t_R = 16,41$ min)

KMN_19_30часов #858 RT: 17,46 AV: 1 NL: 3,30E6
T: + c Full ms [40,00-500,00]

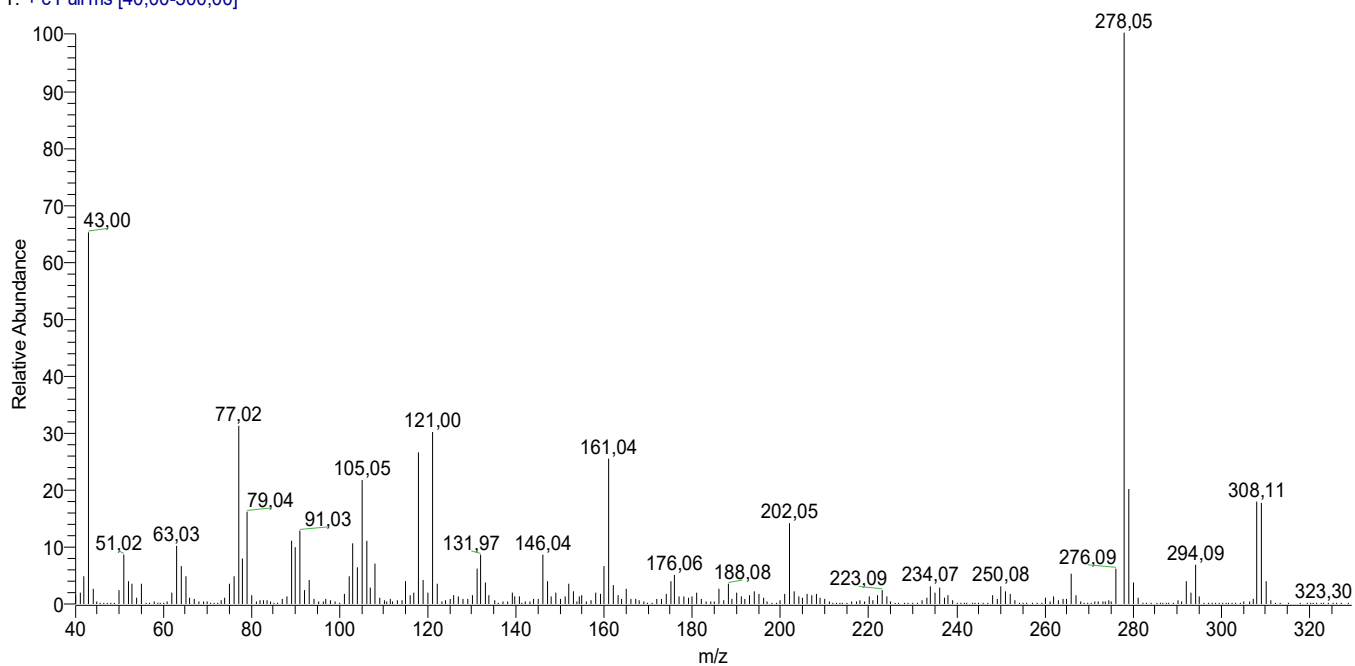


Figure S9. Mass Spectrum: one of the reaction products 8-10 ($t_R = 17,46$ min)

KMN_19_30часов #891 RT: 17,98 AV: 1 NL: 6,52E6
 T: + c Full ms [40,00-500,00]

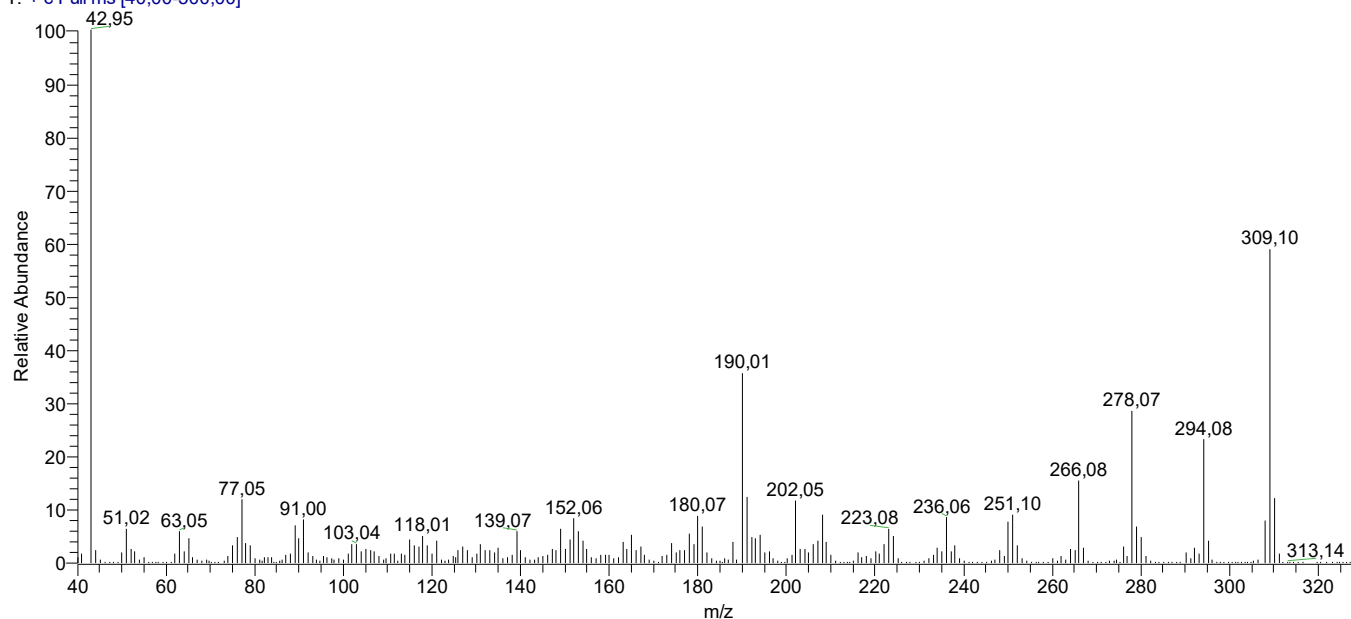
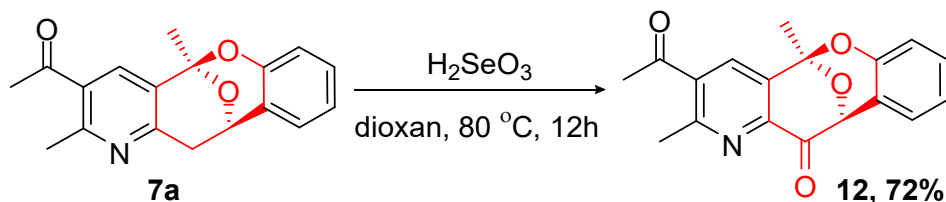


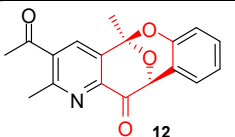
Figure S10. Mass Spectrum: one of the reaction products **8-10** ($t_R = 17,98$ min)

4. Procedure of oxidation 11,12-dihydro-5H-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	<p>3-acetyl-2,5-dimethyl-5H-5,11-epoxybenzo[7,8]oxocino[4,3-b]pyridin-12(11H)-one (12) Yellow crystals, 72% yield. M.p. 198-200 °C (EtOAc/hexane 1:5). 1H 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.</p>
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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
<i>M</i> _r	295.32
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.7769 (10), 9.1976 (12), 10.1697 (12)
α , β , γ (°)	74.462 (5), 81.905 (5), 69.130 (5)
<i>V</i> (Å ³)	738.13 (16)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.54 × 0.42 × 0.19
Data collection	
Diffractometer	Bruker <i>APEX</i> -II CCD
Absorption correction	Multi-scan <i>SADABS</i> 2008/1
<i>T</i> _{min} , <i>T</i> _{max}	0.895, 0.926
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	25930, 3979, 3416
<i>R</i> _{int}	0.025
(sin θ/λ) _{max} (Å ⁻¹), θ _{max} (°)	0.686, 29.188
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 0.130, 0.94
No. of reflections	3979
No. of parameters	202
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.34, -0.21
CCDC	2035579

Computer programs: Bruker *APEX*2, Bruker *SAINT*, *SHELXS*97 (Sheldrick, 2008), *SHELXL*2018/3 (Sheldrick, 2018), Bruker *SHELXTL*.

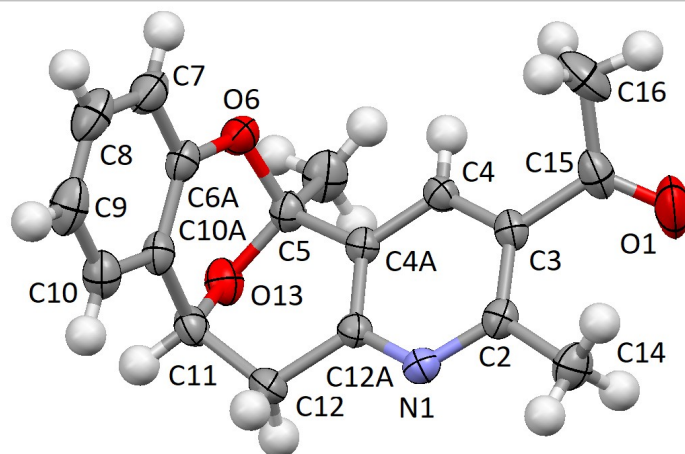


Figure S11. Molecular structure of compound **1** (50% thermal ellipsoids are shown).

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)

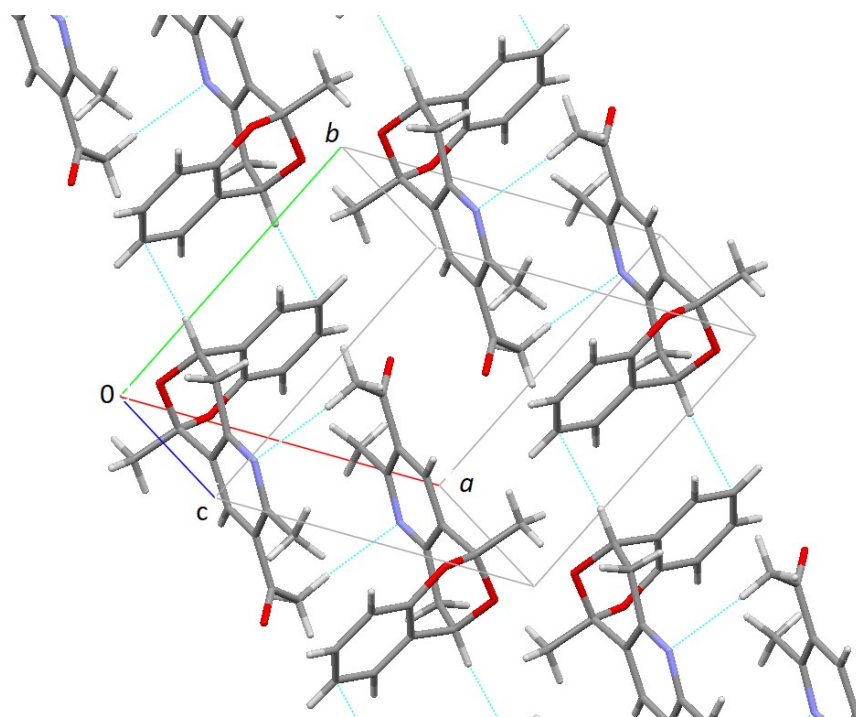


Figure S12. Molecular packing in the crystal of compound **7a** with short intermolecular contacts.

6. Author Contributions

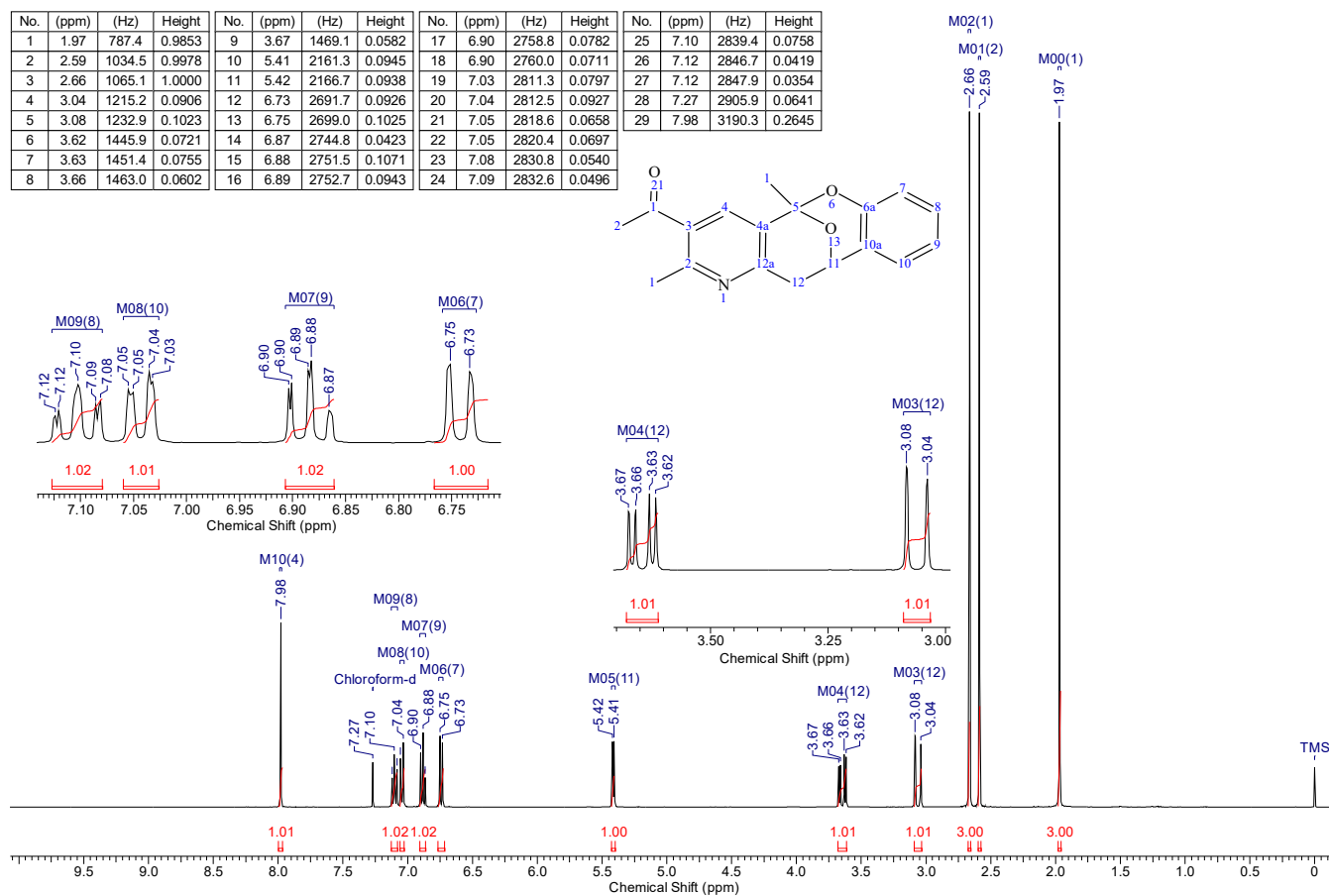
The reported study was funded by RFBR according to the research project [No. 19-03-00376].

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).

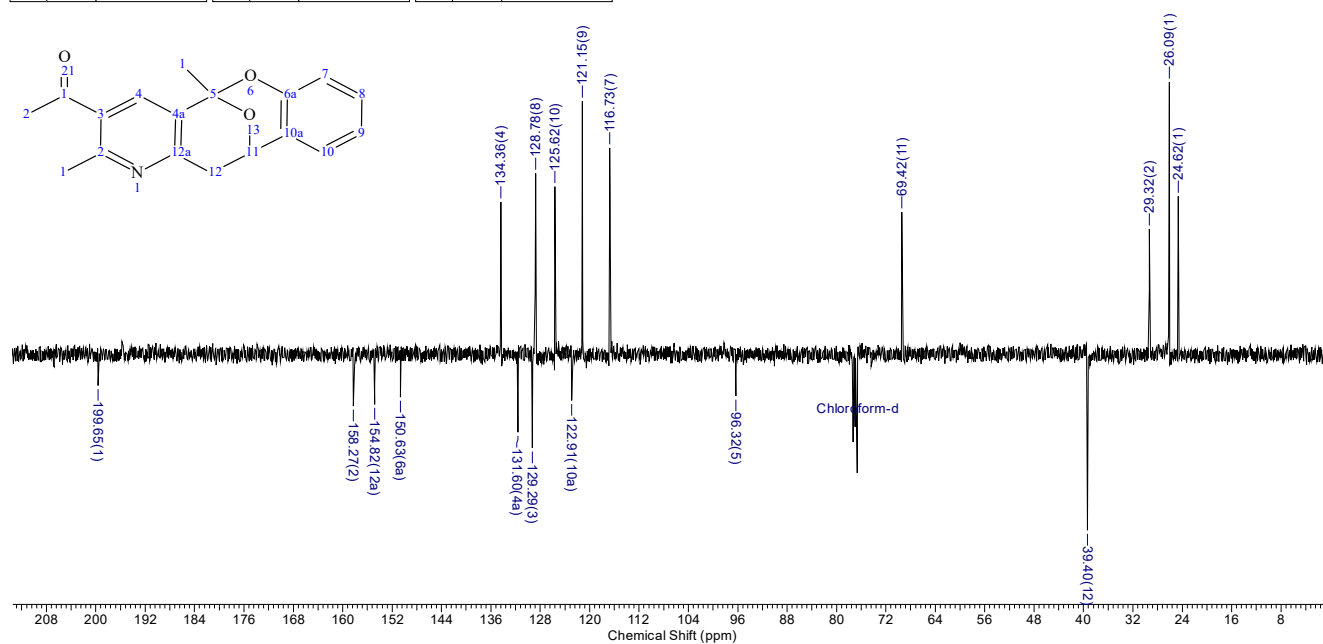
7. References

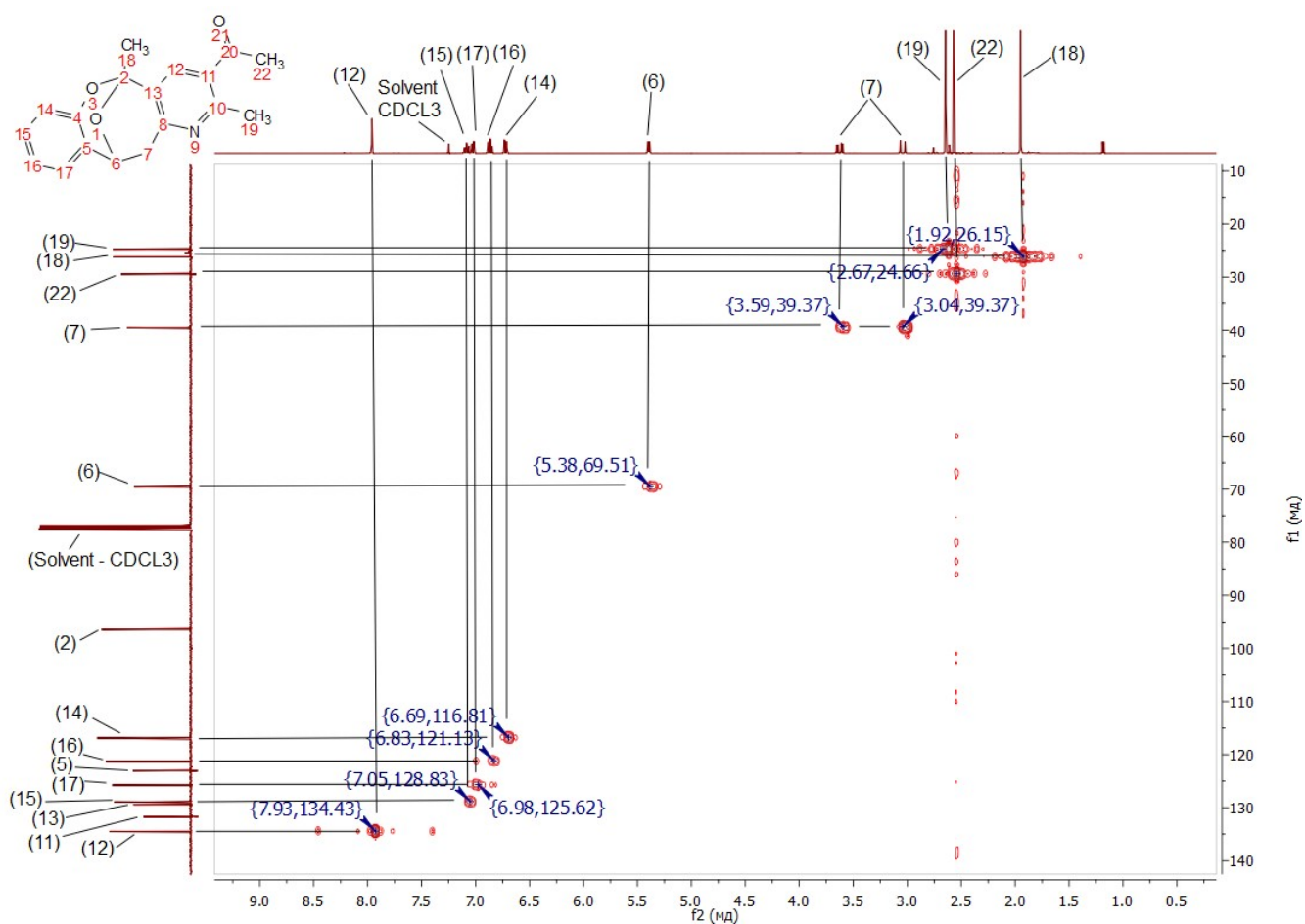
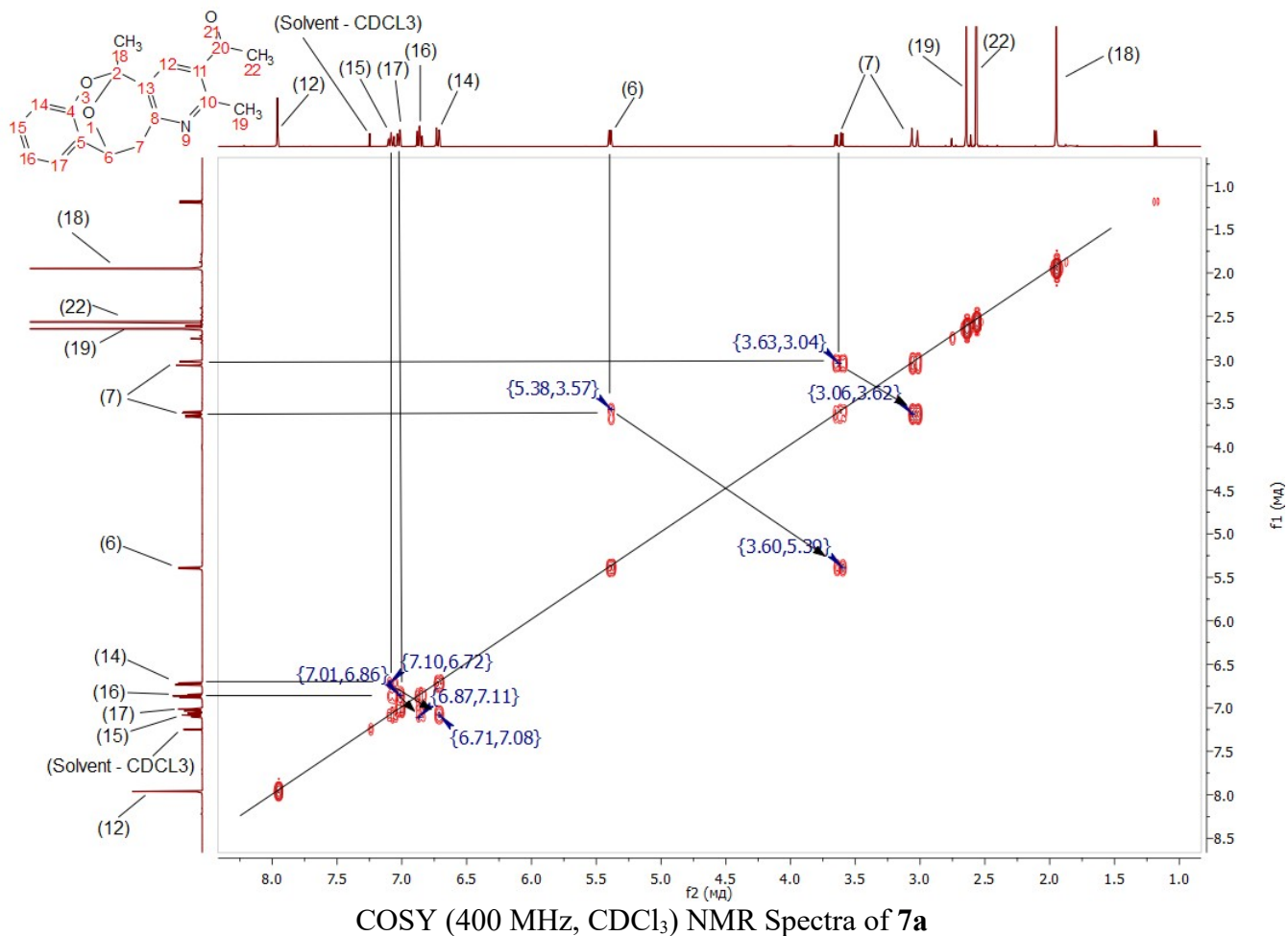
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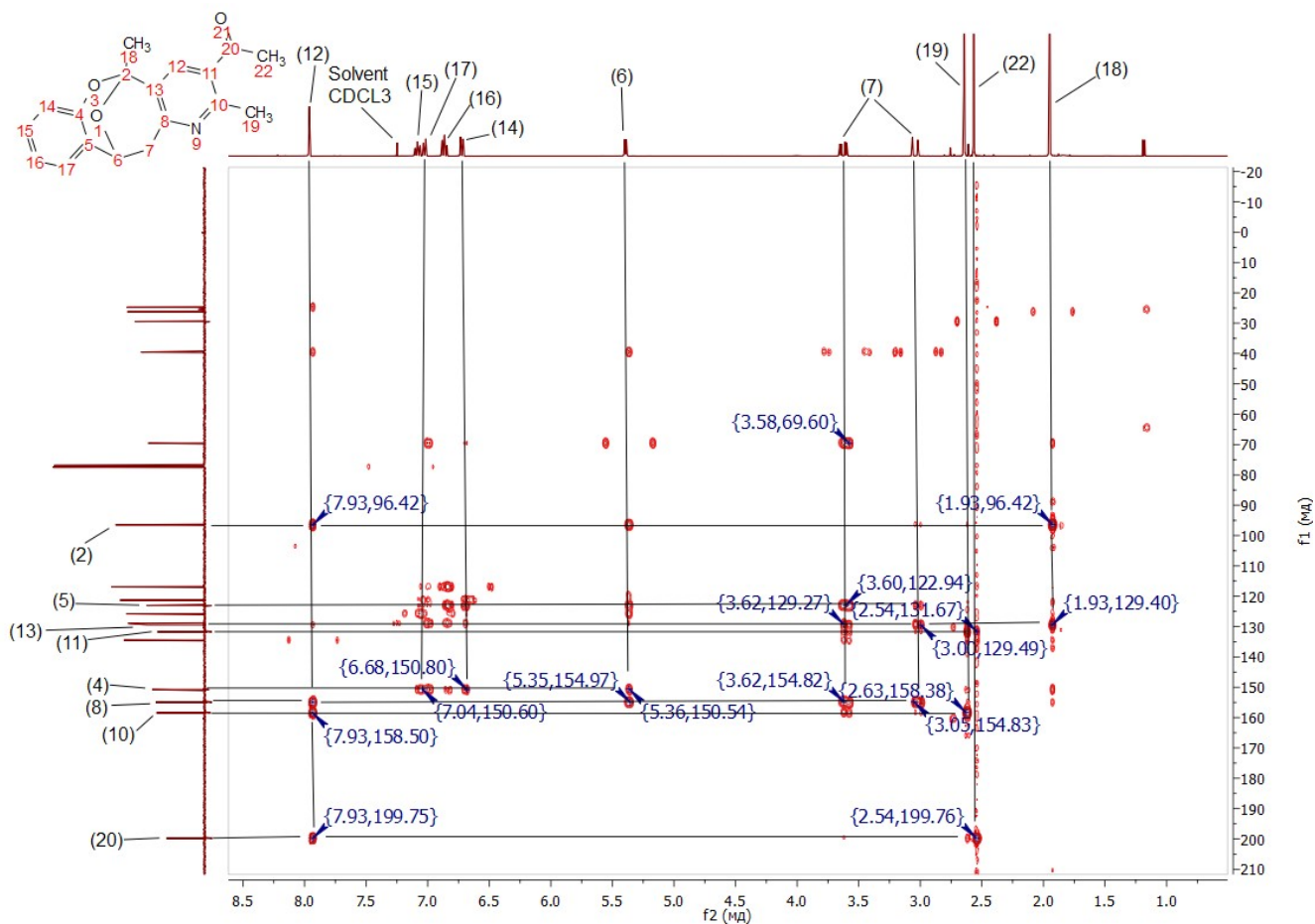
8. Copies of NMR Spectra of Products



No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)
1	1	24.62	7	7	116.73	13	4a	131.60
2	1	26.09	8	9	121.15	14	4	134.36
3	2	29.32	9	10a	122.91	15	6a	150.63
4	12	39.40	10	10	125.62	16	12a	154.82
5	11	69.42	11	8	128.78	17	2	158.27
6	5	96.32	12	3	129.29	18	1	199.65

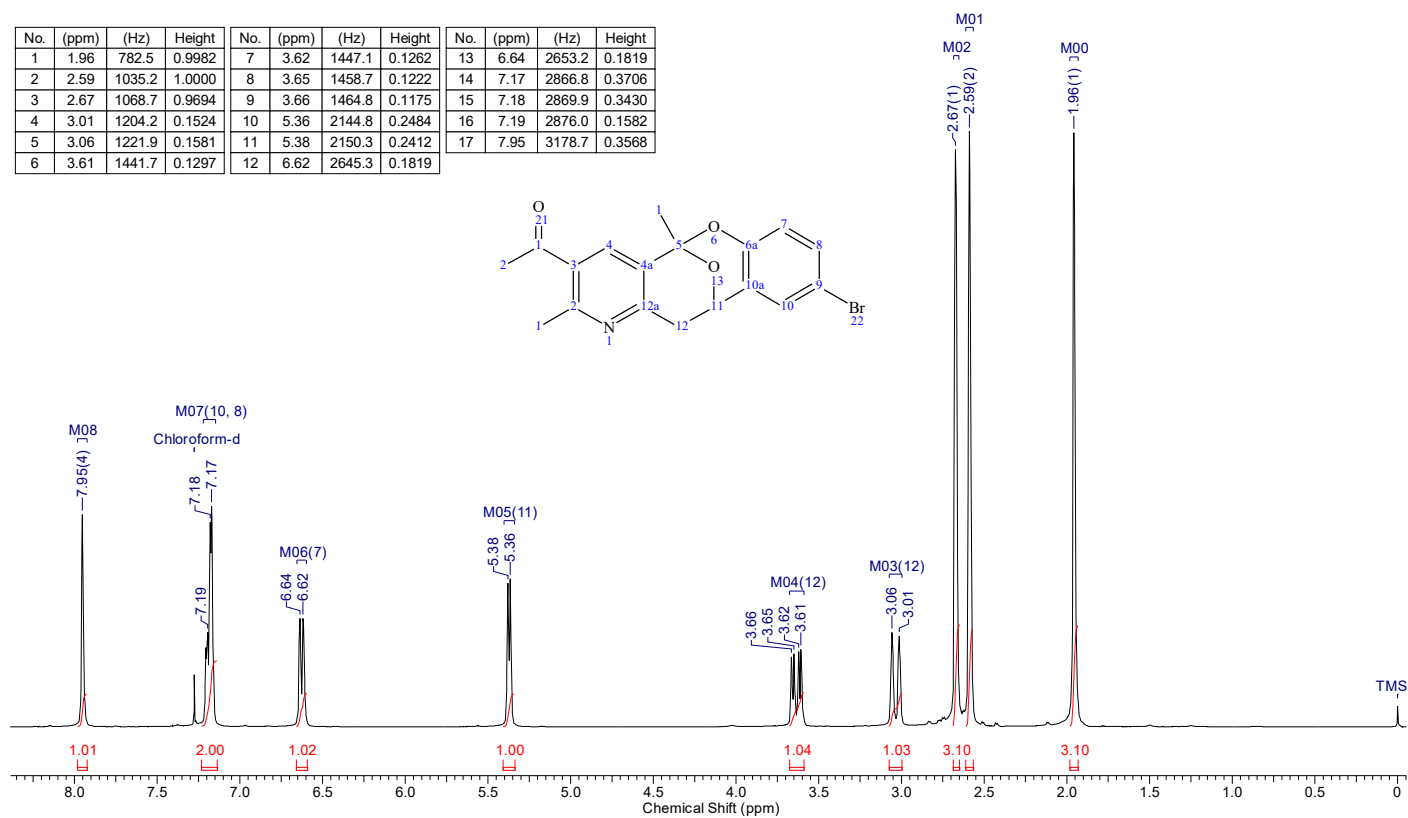

 ^1H (400 MHz, CDCl_3) and ^{13}C (100 MHz, CDCl_3) NMR Spectra of **7a**



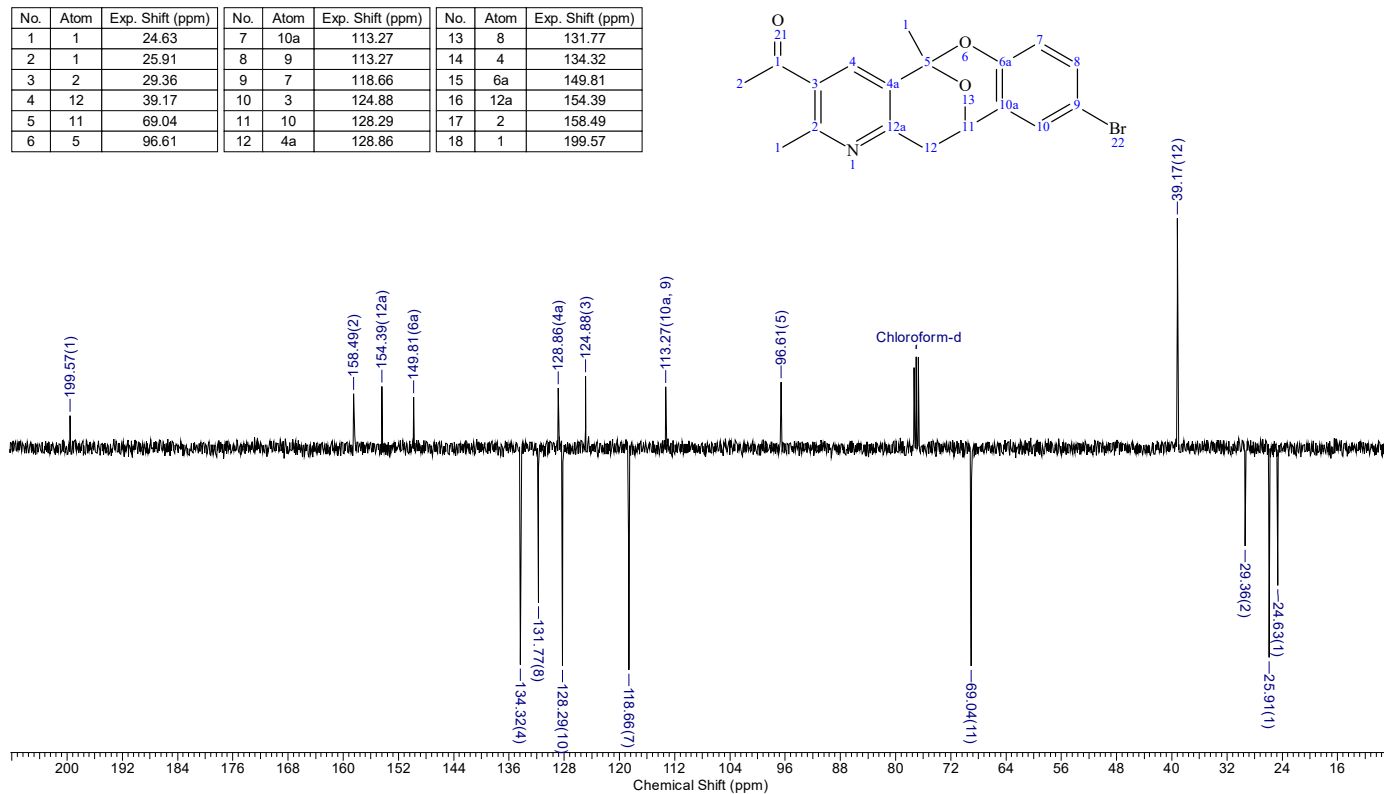


HMBC (400 MHz, CDCl₃) NMR Spectra of **7a**

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	1.96	782.5	0.9982	7	3.62	1447.1	0.1262	13	6.64	2653.2	0.1819
2	2.59	1035.2	1.0000	8	3.65	1458.7	0.1222	14	7.17	2866.8	0.3706
3	2.67	1068.7	0.9694	9	3.66	1464.8	0.1175	15	7.18	2869.9	0.3430
4	3.01	1204.2	0.1524	10	5.36	2144.8	0.2484	16	7.19	2876.0	0.1582
5	3.06	1221.9	0.1581	11	5.38	2150.3	0.2412	17	7.95	3178.7	0.3568
6	3.61	1441.7	0.1297	12	6.62	2645.3	0.1819				

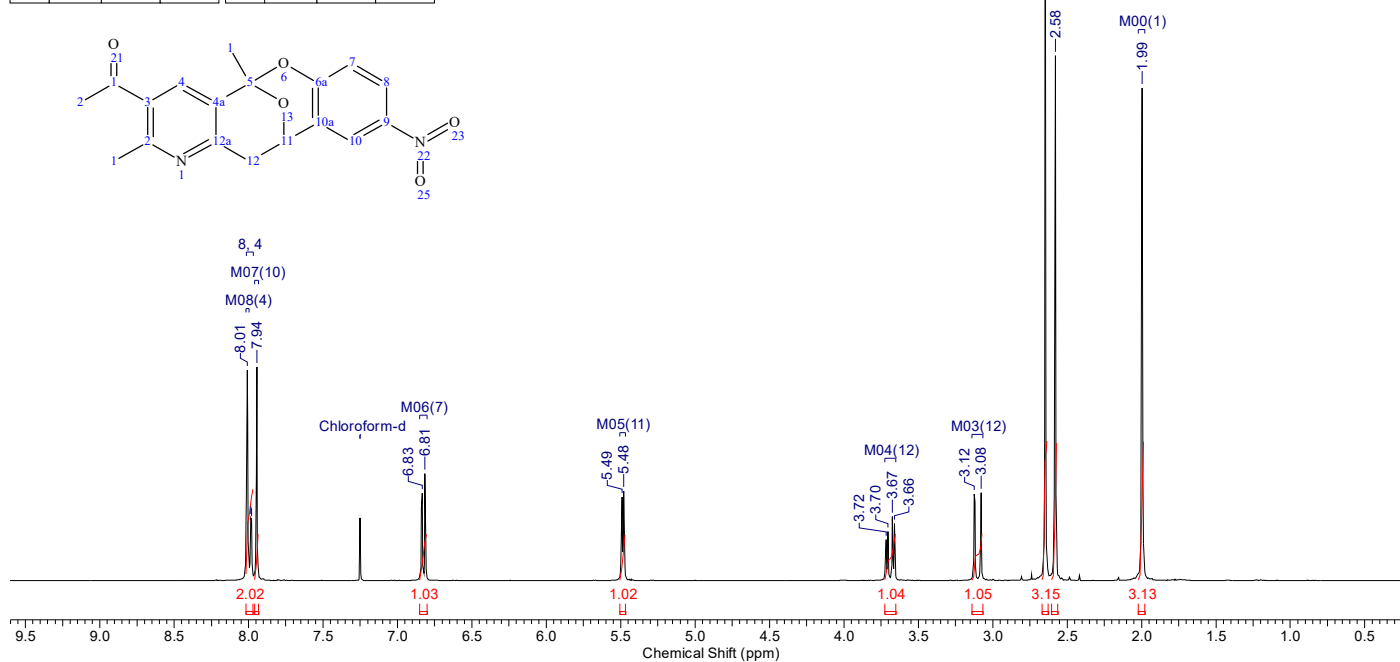


No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)
1	1	24.63	7	10a	113.27	13	8	131.77
2	1	25.91	8	9	113.27	14	4	134.32
3	2	29.36	9	7	118.66	15	6a	149.81
4	12	39.17	10	3	124.88	16	12a	154.39
5	11	69.04	11	10	128.29	17	2	158.49
6	5	96.61	12	4a	128.86	18	1	199.57

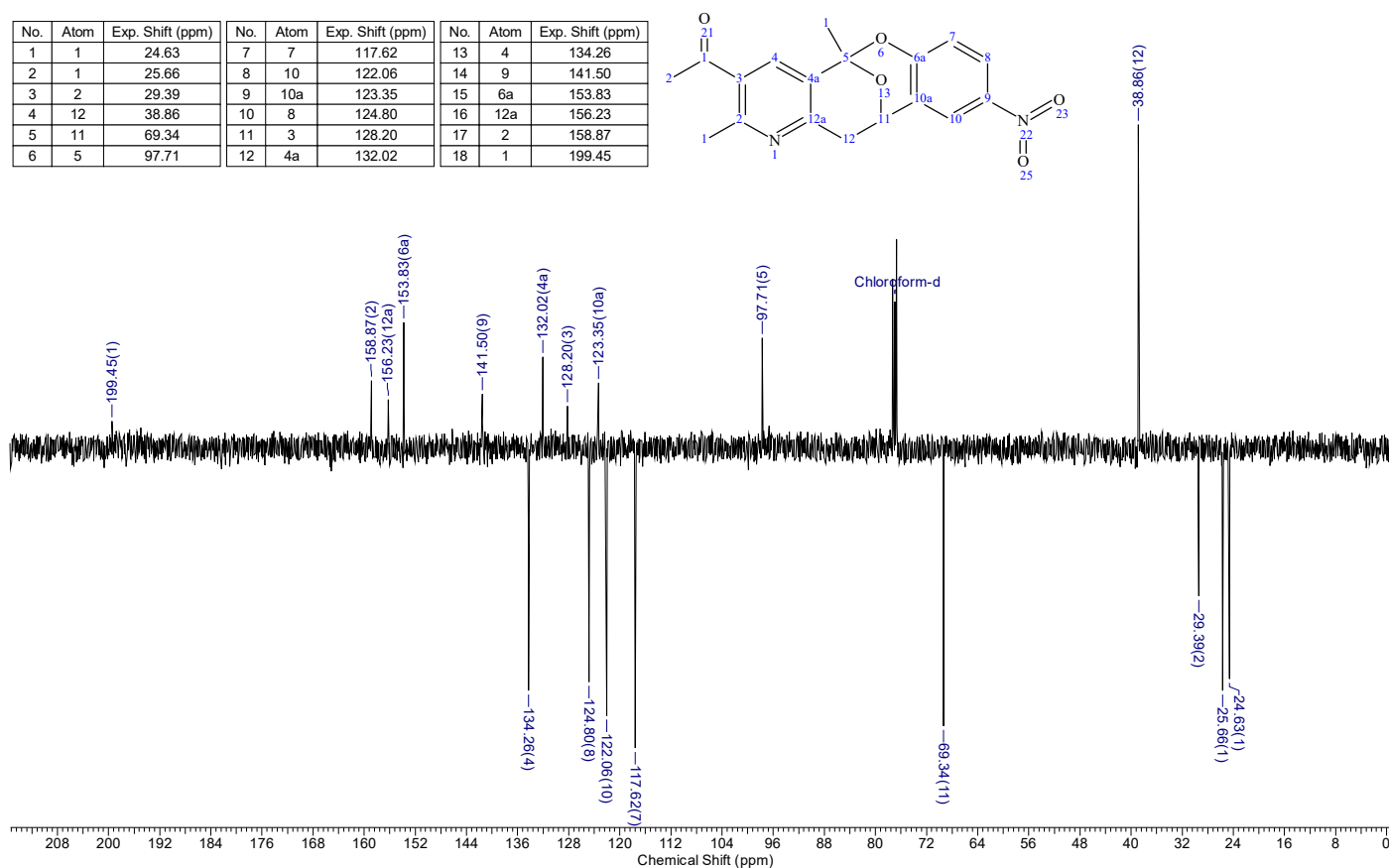


¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of 7b

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	1.99	797.3	0.6048	7	3.67	1468.7	0.0785	13	6.83	2732.1	0.1075
2	2.58	1030.7	0.6440	8	3.70	1480.9	0.0605	14	7.94	3176.1	0.2622
3	2.65	1058.2	1.0000	9	3.72	1485.5	0.0503	15	7.98	3189.9	0.0742
4	3.08	1230.6	0.1077	10	5.48	2190.4	0.1098	16	7.99	3192.9	0.0766
5	3.12	1248.9	0.1062	11	5.49	2195.0	0.1025	17	8.01	3202.1	0.2583
6	3.66	1462.6	0.0698	12	6.81	2724.5	0.1312				

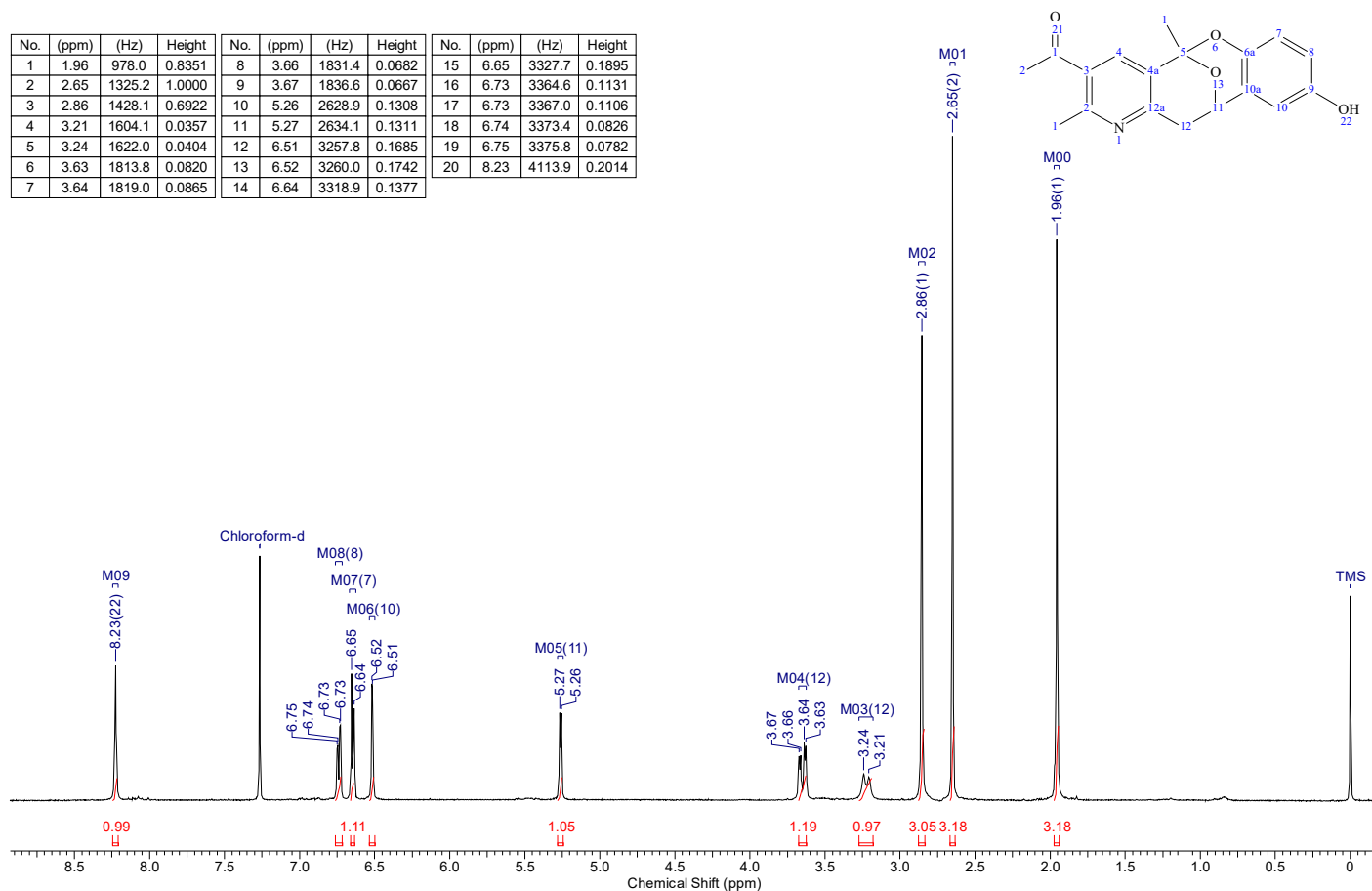


No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)
1	1	24.63	7	7	117.62	13	4	134.26
2	1	25.66	8	10	122.06	14	9	141.50
3	2	29.39	9	10a	123.35	15	6a	153.83
4	12	38.86	10	8	124.80	16	12a	156.23
5	11	69.34	11	3	128.20	17	2	158.87
6	5	97.71	12	4a	132.02	18	1	199.45

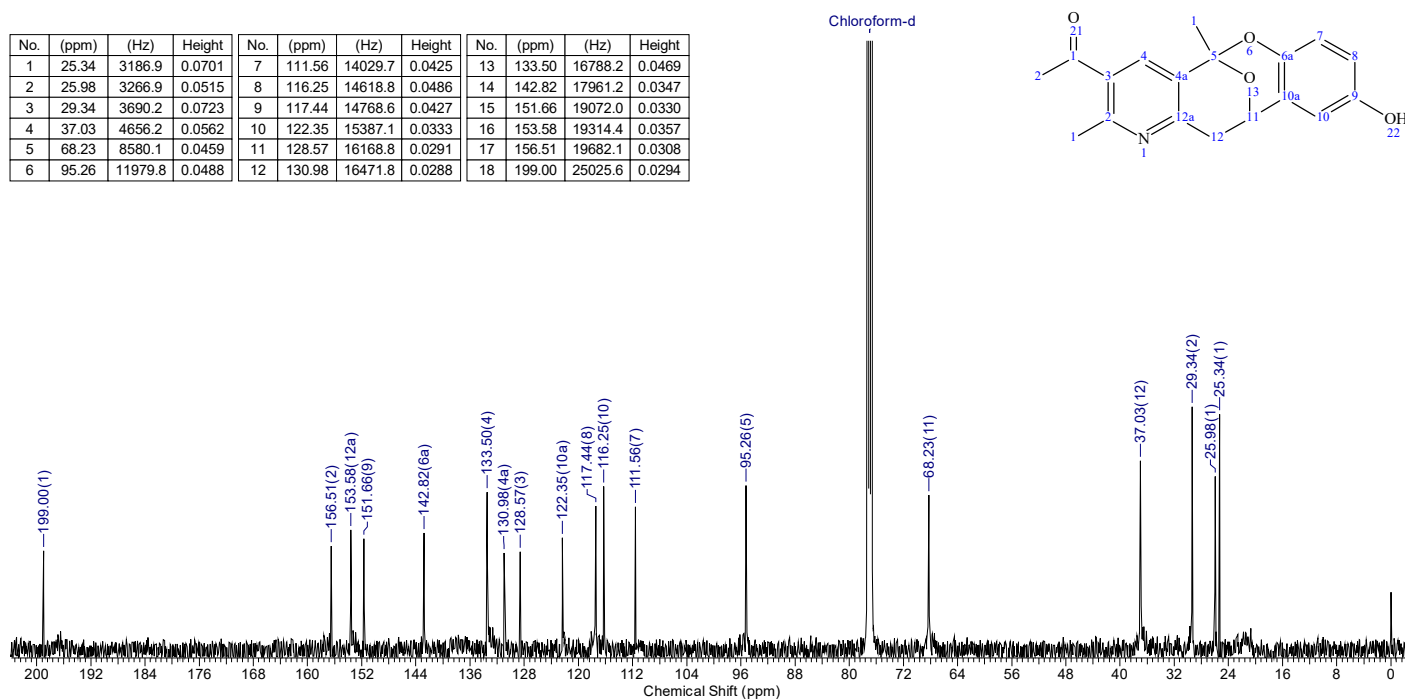


¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of 7c

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	1.96	978.0	0.8351	8	3.66	1831.4	0.0682	15	6.65	3327.7	0.1895
2	2.65	1325.2	1.0000	9	3.67	1836.6	0.0667	16	6.73	3364.6	0.1131
3	2.86	1428.1	0.6922	10	5.26	2628.9	0.1308	17	6.73	3367.0	0.1106
4	3.21	1604.1	0.0357	11	5.27	2634.1	0.1311	18	6.74	3373.4	0.0826
5	3.24	1622.0	0.0404	12	6.51	3257.8	0.1685	19	6.75	3375.8	0.0782
6	3.63	1813.8	0.0820	13	6.52	3260.0	0.1742	20	8.23	4113.9	0.2014
7	3.64	1819.0	0.0865	14	6.64	3318.9	0.1377				

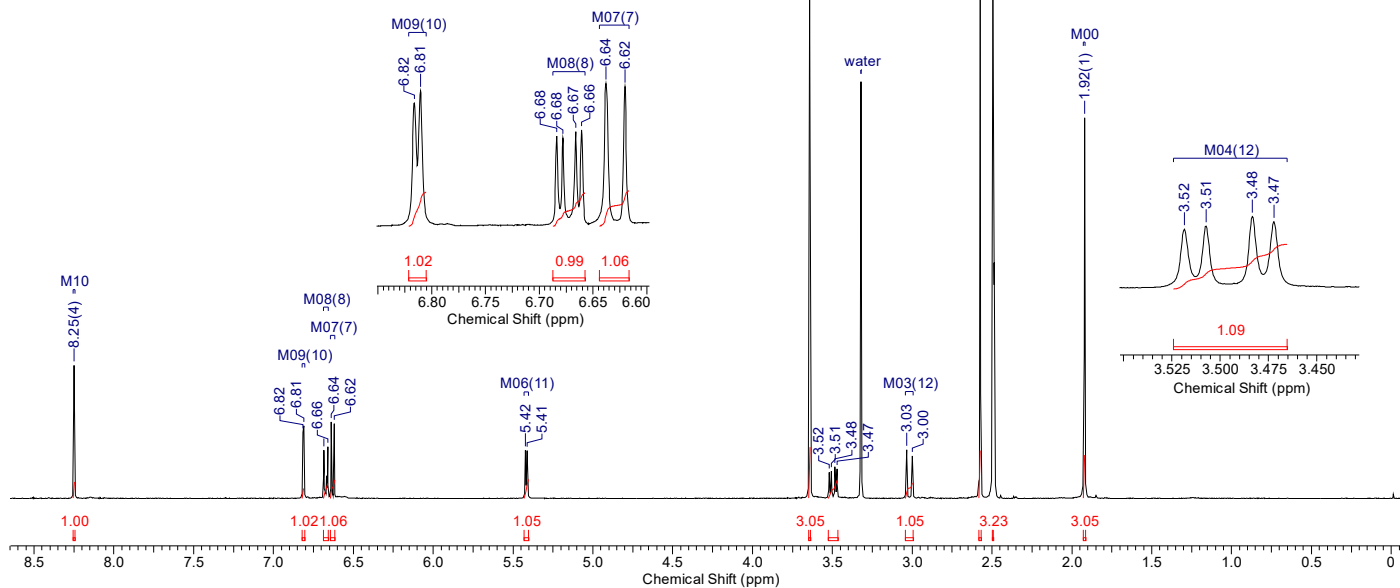


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	25.34	3186.9	0.0701	7	111.56	14029.7	0.0425	13	133.50	16788.2	0.0469
2	25.98	3266.9	0.0515	8	116.25	14618.8	0.0486	14	142.82	17961.2	0.0347
3	29.34	3690.2	0.0723	9	117.44	14768.6	0.0427	15	151.66	19072.0	0.0330
4	37.03	4656.2	0.0562	10	122.35	15387.1	0.0333	16	153.58	19314.4	0.0357
5	68.23	8580.1	0.0459	11	128.57	16168.8	0.0291	17	156.51	19682.1	0.0308
6	95.26	11979.8	0.0488	12	130.98	16471.8	0.0288	18	199.00	25025.6	0.0294

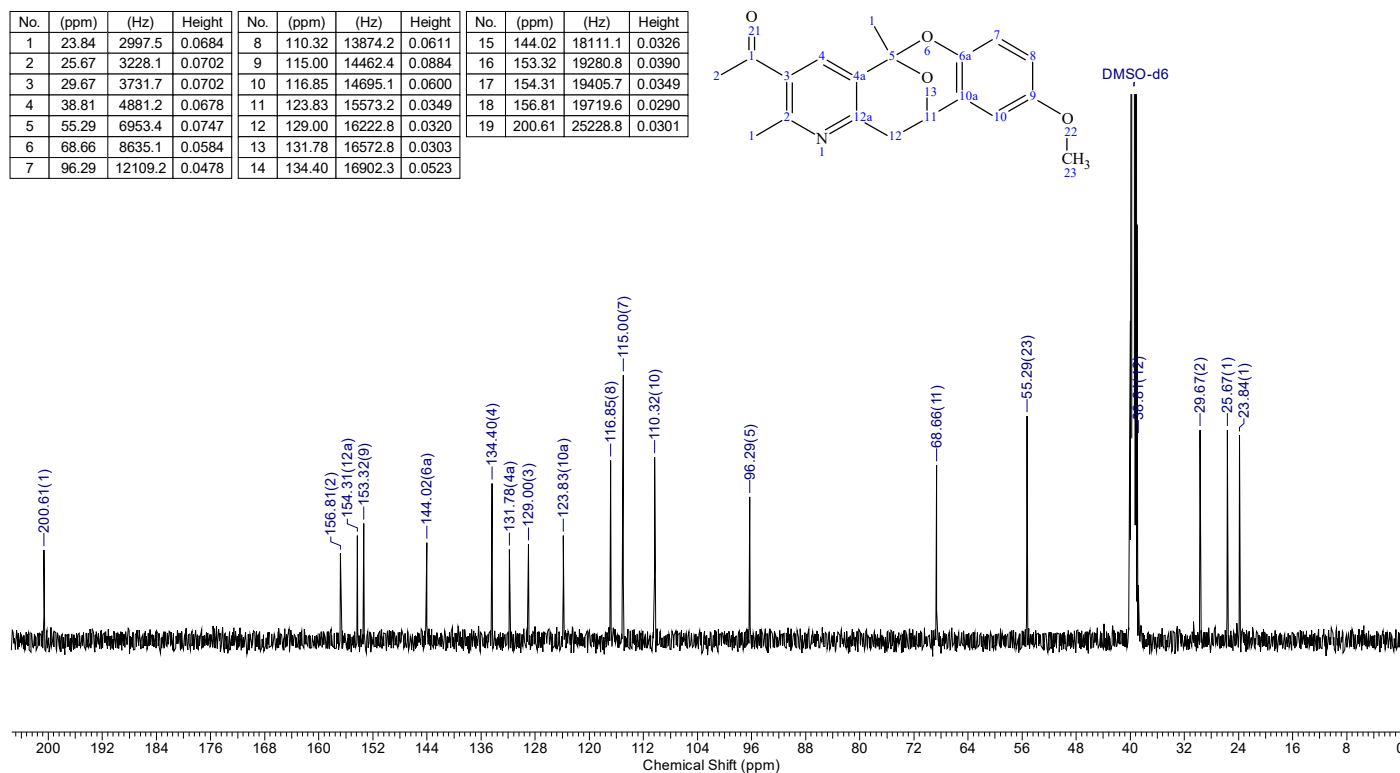


^1H (500 MHz, CDCl_3) and ^{13}C (126 MHz, CDCl_3) NMR Spectra of **7d**

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	1.92	960.5	0.6849	8	3.51	1754.1	0.0494	15	6.66	3331.2	0.0925
2	2.50	1247.9	0.9837	9	3.52	1759.8	0.0470	16	6.67	3333.9	0.0909
3	2.57	1287.7	0.9612	10	3.64	1821.4	0.9317	17	6.68	3340.0	0.0853
4	3.00	1500.5	0.0767	11	5.41	2706.3	0.0862	18	6.68	3342.8	0.0869
5	3.03	1517.9	0.0870	12	5.42	2711.7	0.0869	19	6.81	3406.2	0.1304
6	3.47	1736.5	0.0527	13	6.62	3311.0	0.1343	20	6.82	3409.0	0.1185
7	3.48	1742.2	0.0570	14	6.64	3319.8	0.1376	21	8.25	4125.5	0.2394

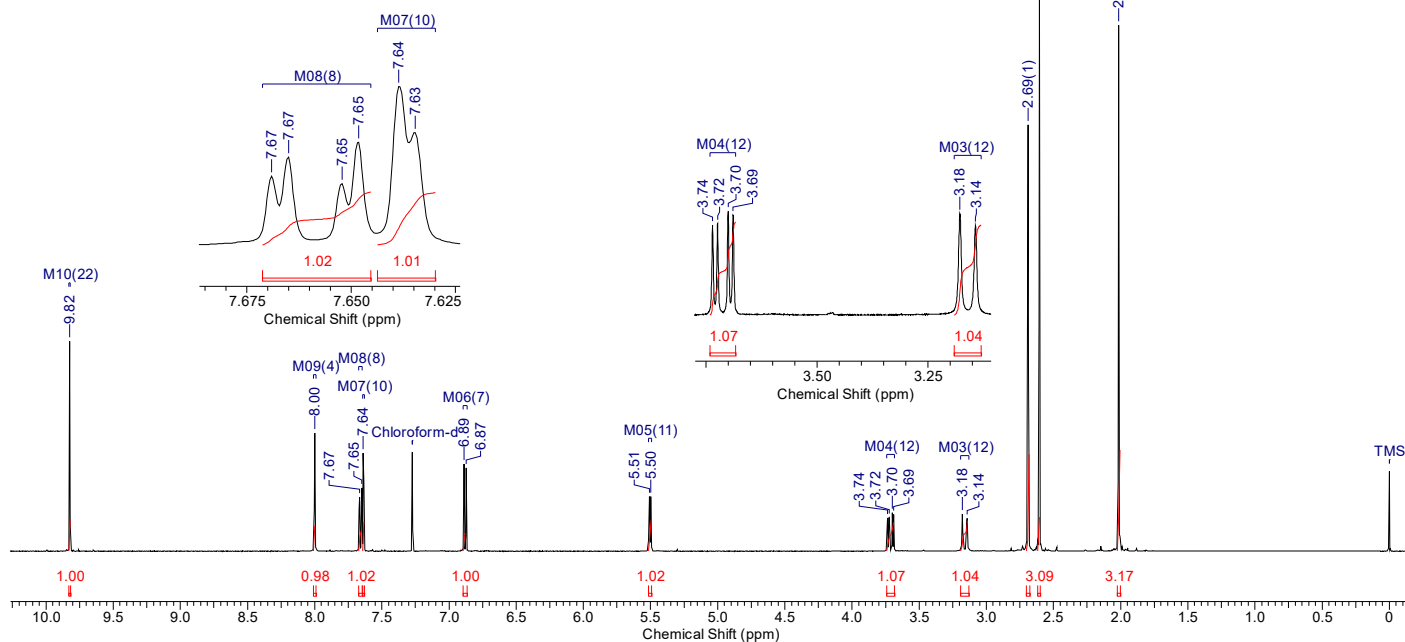
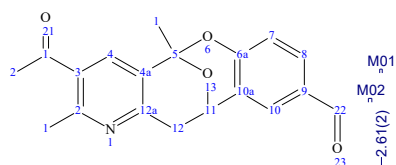


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	23.84	2997.5	0.0684	8	110.32	13874.2	0.0611	15	144.02	18111.1	0.0326
2	25.67	3228.1	0.0702	9	115.00	14462.4	0.0884	16	153.32	19280.8	0.0390
3	29.67	3731.7	0.0702	10	116.85	14695.1	0.0600	17	154.31	19405.7	0.0349
4	38.81	4881.2	0.0678	11	123.83	15573.2	0.0349	18	156.81	19719.6	0.0290
5	55.29	6953.4	0.0747	12	129.00	16222.8	0.0320	19	200.61	25228.8	0.0301
6	68.66	8635.1	0.0584	13	131.78	16572.8	0.0303				
7	96.29	12109.2	0.0478	14	134.40	16902.3	0.0523				

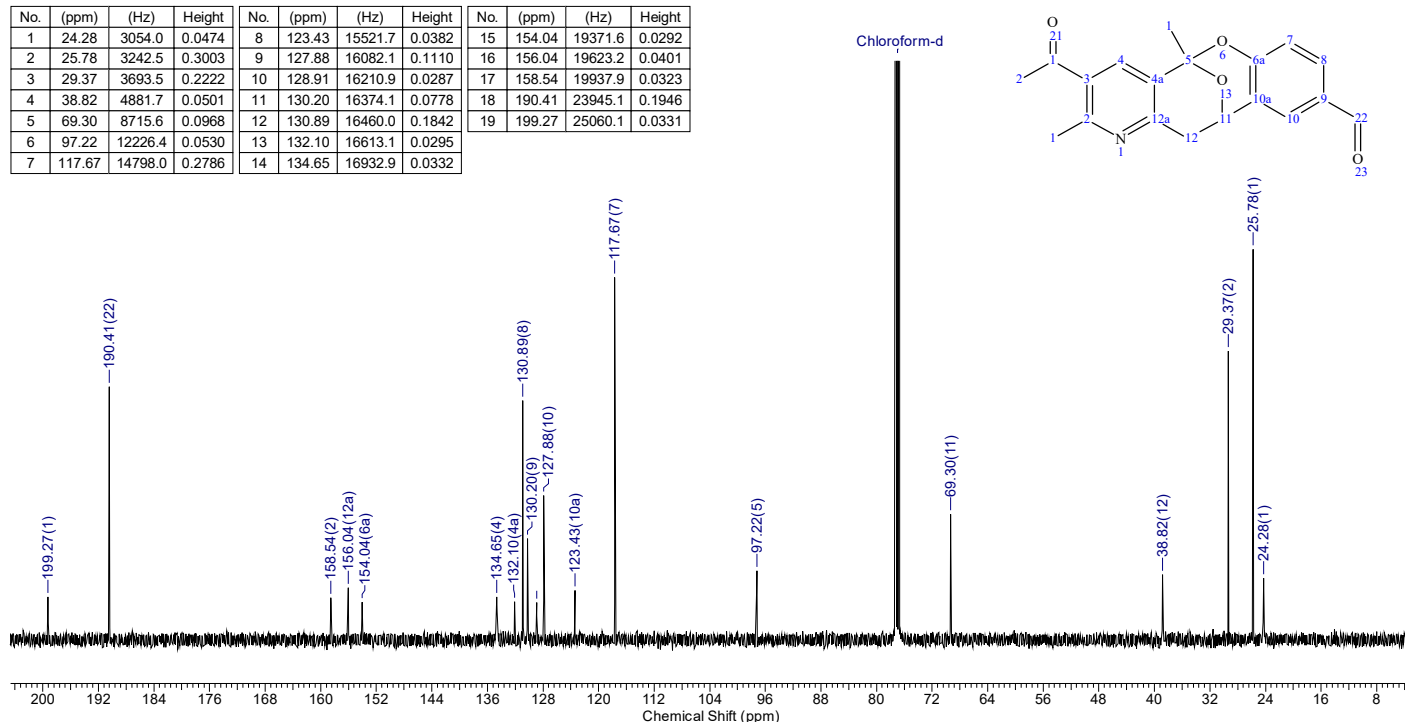


¹H (500 MHz, CDCl₃) and ¹³C (126 MHz, CDCl₃) NMR Spectra of 7e

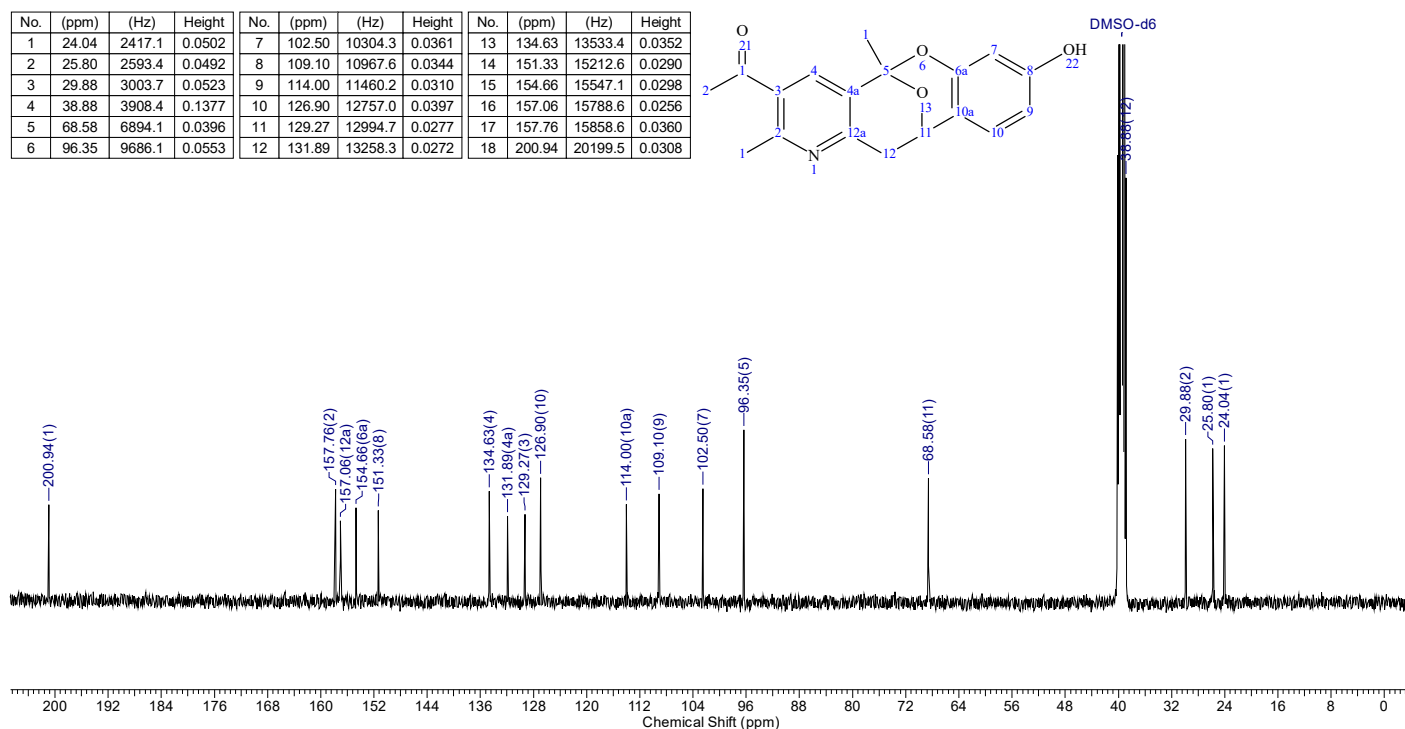
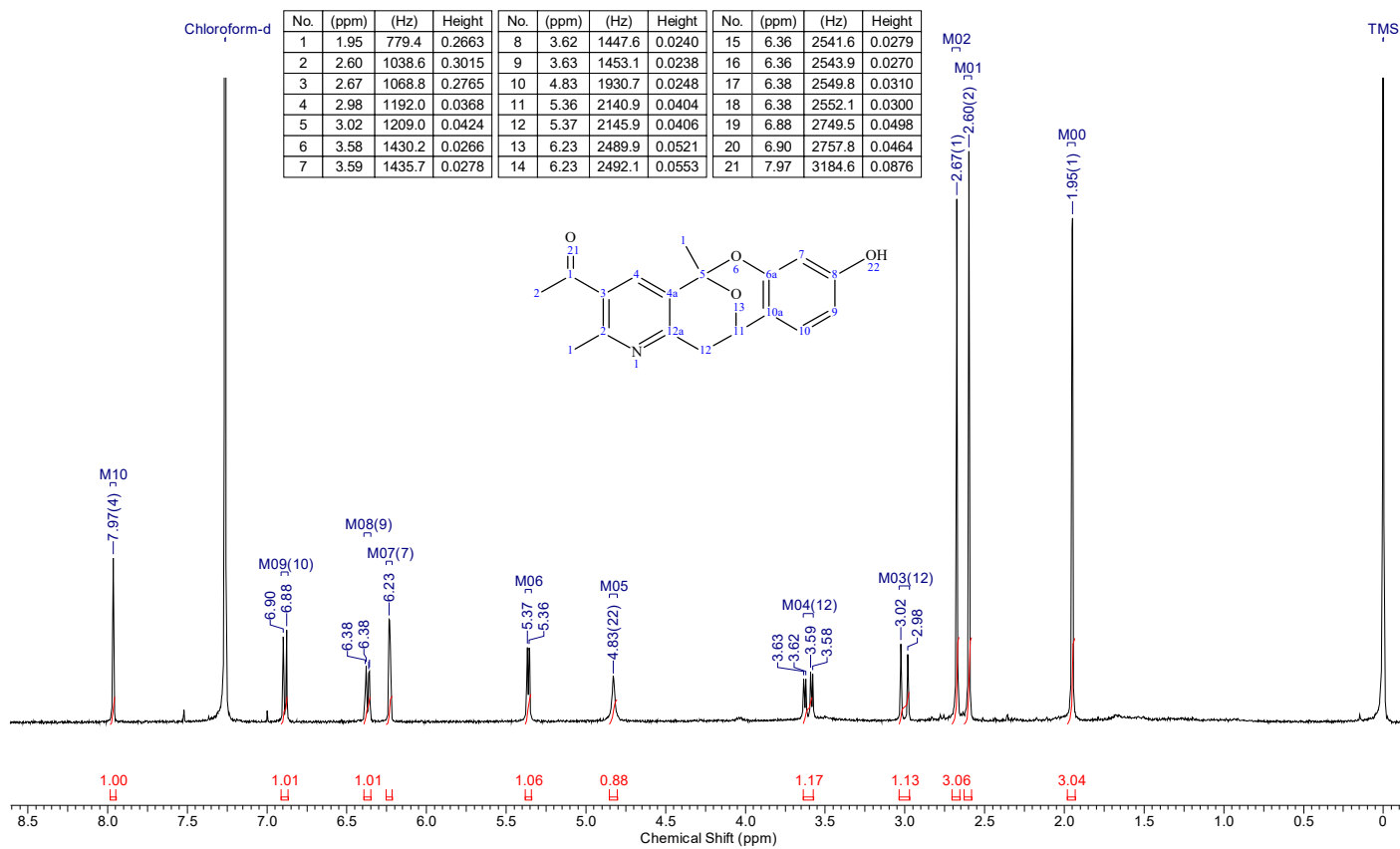
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.01	1007.3	0.7906	8	3.72	1862.5	0.0506	15	7.64	3820.3	0.1473
2	2.61	1303.1	1.0000	9	3.74	1868.2	0.0500	16	7.65	3825.1	0.0954
3	2.69	1345.1	0.6408	10	5.50	2749.6	0.0822	17	7.65	3827.1	0.0571
4	3.14	1572.1	0.0497	11	5.51	2755.1	0.0818	18	7.67	3833.5	0.0816
5	3.18	1589.6	0.0562	12	6.87	3436.8	0.1250	19	7.67	3835.5	0.0639
6	3.69	1845.0	0.0556	13	6.89	3445.3	0.1315	20	8.00	4001.0	0.1773
7	3.70	1850.6	0.0578	14	7.63	3818.3	0.1044	21	9.82	4913.0	0.3156



No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.28	3054.0	0.0474	8	123.43	15521.7	0.0382	15	154.04	19371.6	0.0292
2	25.78	3242.5	0.3003	9	127.88	16082.1	0.1110	16	156.04	19623.2	0.0401
3	29.37	3693.5	0.2222	10	128.91	16210.9	0.0287	17	158.54	19937.9	0.0323
4	38.82	4881.7	0.0501	11	130.20	16374.1	0.0778	18	190.41	23945.1	0.1946
5	69.30	8715.6	0.0968	12	130.89	16460.0	0.1842	19	199.27	25060.1	0.0331
6	97.22	12226.4	0.0530	13	132.10	16613.1	0.0295				
7	117.67	14798.0	0.2786	14	134.65	16932.9	0.0332				

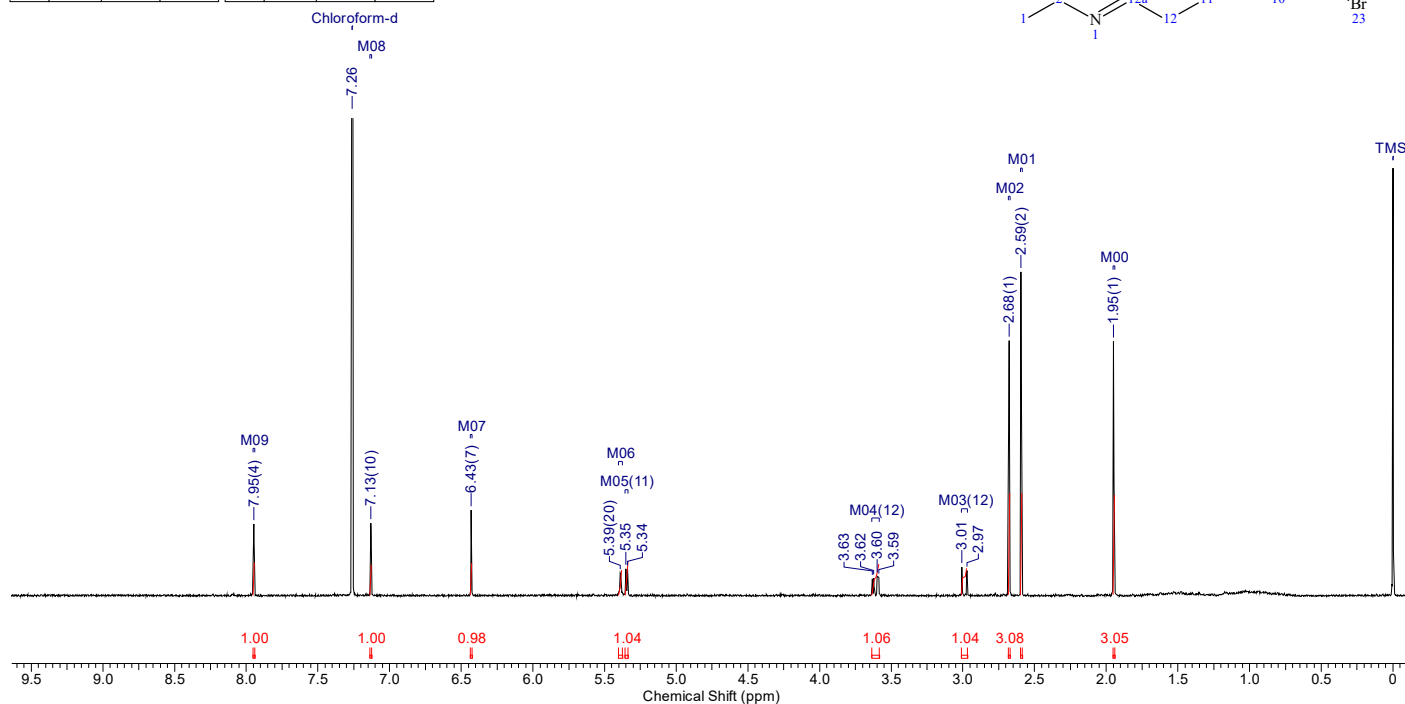
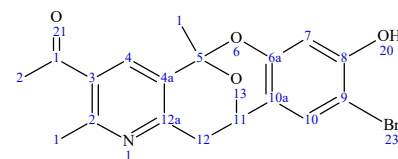


¹H (500 MHz, CDCl₃) and ¹³C (126 MHz, CDCl₃) NMR Spectra of 7f



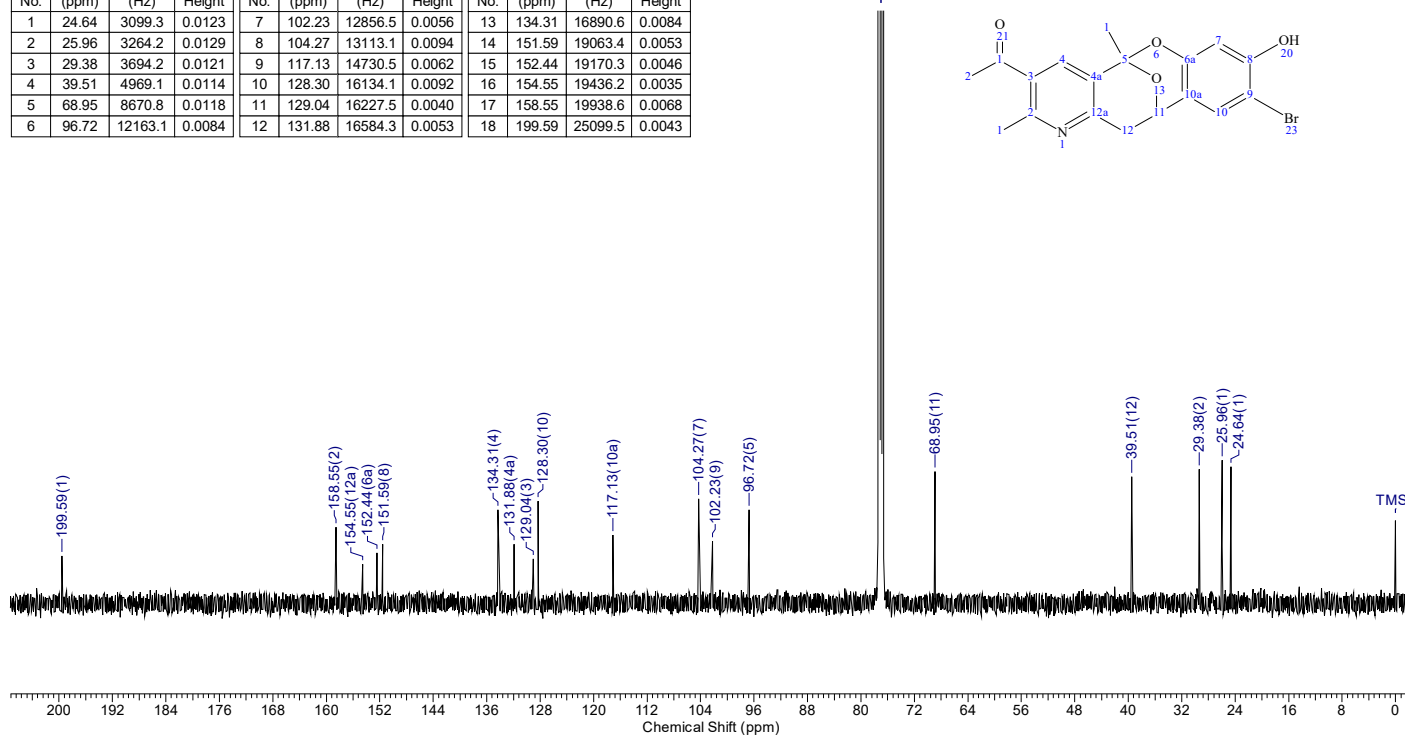
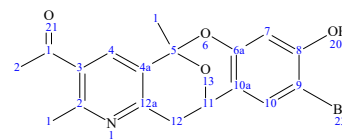
¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of **7g**

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	1.95	974.2	0.1905	9	3.63	1816.4	0.0124
2	2.59	1297.3	0.2427	10	5.34	2670.6	0.0197
3	2.68	1339.3	0.1912	11	5.35	2675.7	0.0200
4	2.97	1486.6	0.0188	12	5.39	2695.6	0.0167
5	3.01	1503.9	0.0213	13	6.43	3216.7	0.0640
6	3.59	1793.9	0.0134	14	7.13	3565.9	0.0542
7	3.60	1799.3	0.0145	15	7.26	3631.7	1.0000
8	3.62	1811.3	0.0127	16	7.95	3974.7	0.0536



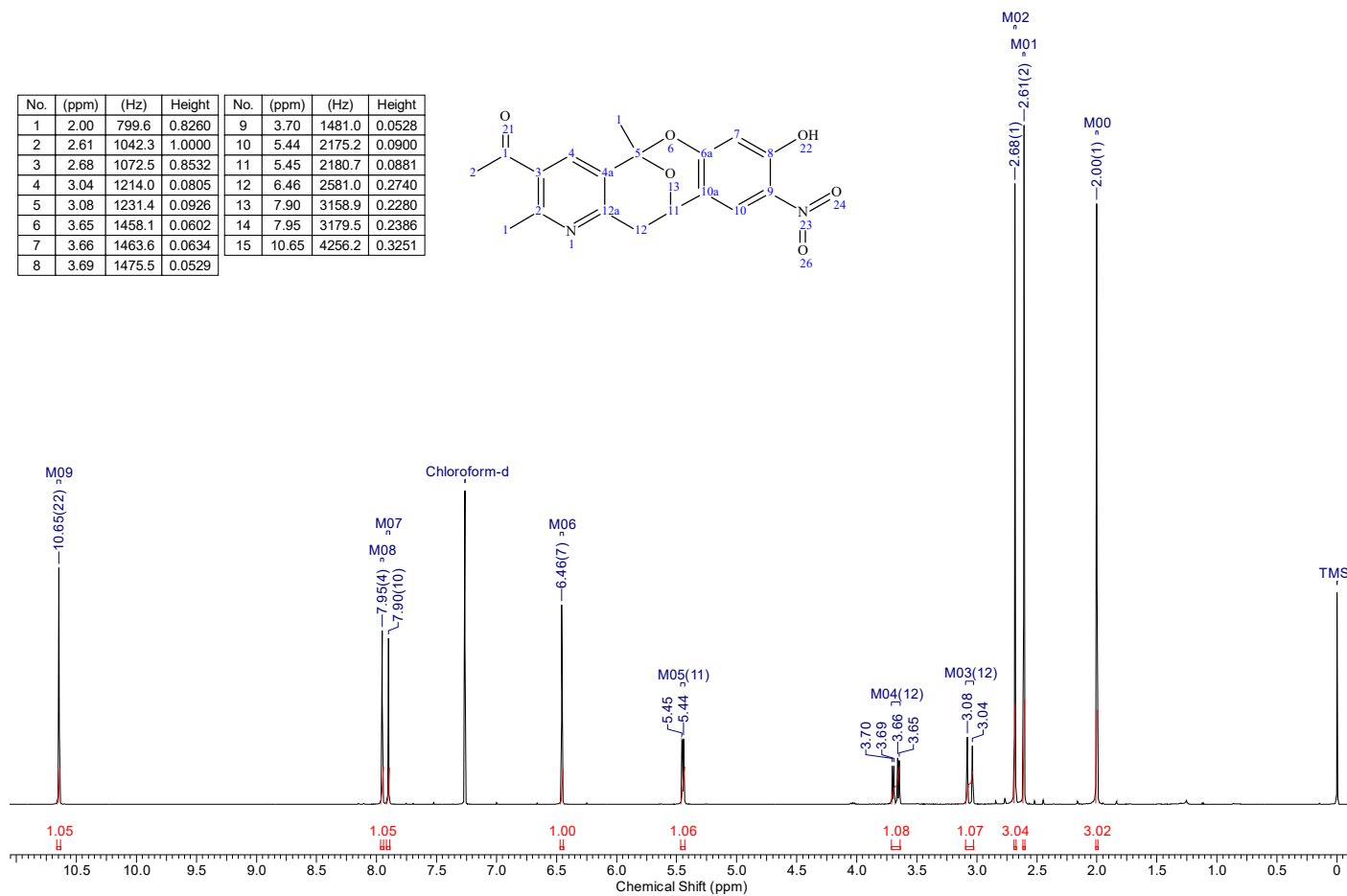
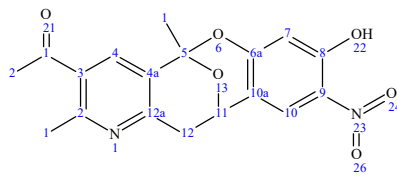
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.64	3099.3	0.0123	7	102.23	12856.5	0.0056	13	134.31	16890.6	0.0084
2	25.96	3264.2	0.0129	8	104.27	13113.1	0.0094	14	151.59	19063.4	0.0053
3	29.38	3694.2	0.0121	9	117.13	14730.5	0.0062	15	152.44	19170.3	0.0046
4	39.51	4969.1	0.0114	10	128.30	16134.1	0.0092	16	154.55	19436.2	0.0035
5	68.95	8670.8	0.0118	11	129.04	16227.5	0.0040	17	158.55	19938.6	0.0068
6	96.72	12163.1	0.0084	12	131.88	16584.3	0.0053	18	199.59	25099.5	0.0043

Chloroform-d



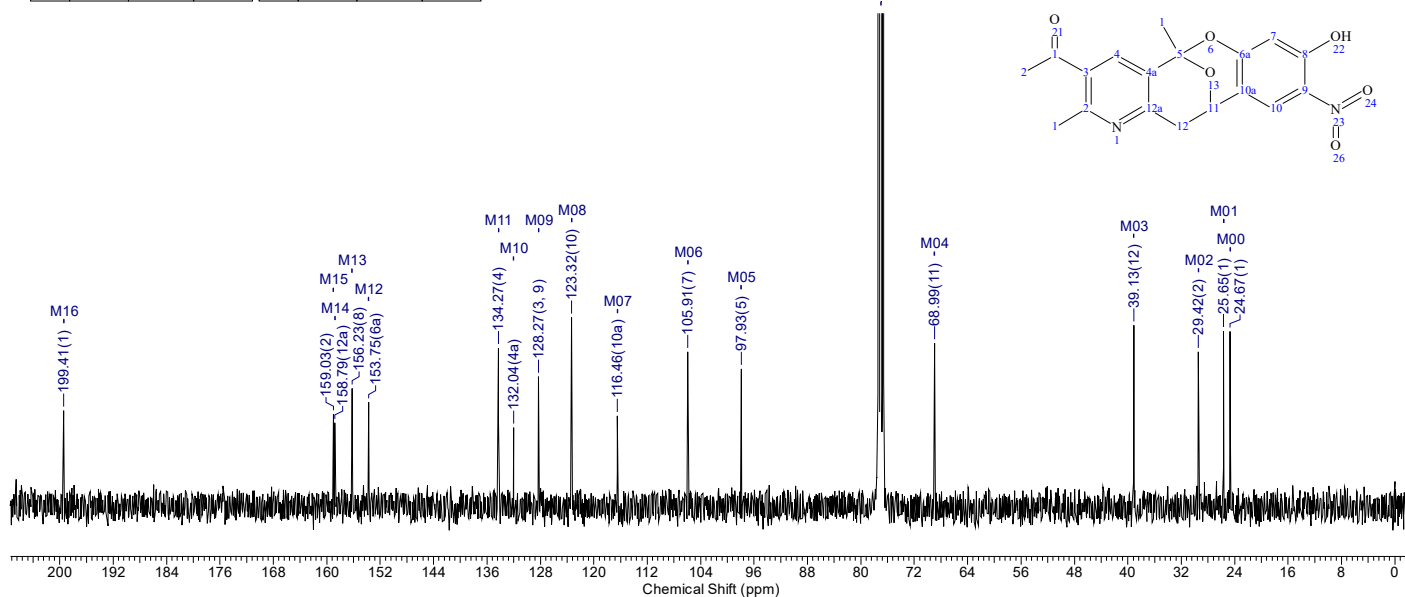
¹H (500 MHz, CDCl₃) and ¹³C (126 MHz, CDCl₃) NMR Spectra of **7h**

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.00	799.6	0.8260	9	3.70	1481.0	0.0528
2	2.61	1042.3	1.0000	10	5.44	2175.2	0.0900
3	2.68	1072.5	0.8532	11	5.45	2180.7	0.0881
4	3.04	1214.0	0.0805	12	6.46	2581.0	0.2740
5	3.08	1231.4	0.0926	13	7.90	3158.9	0.2280
6	3.65	1458.1	0.0602	14	7.95	3179.5	0.2386
7	3.66	1463.6	0.0634	15	10.65	4256.2	0.3251
8	3.69	1475.5	0.0529				



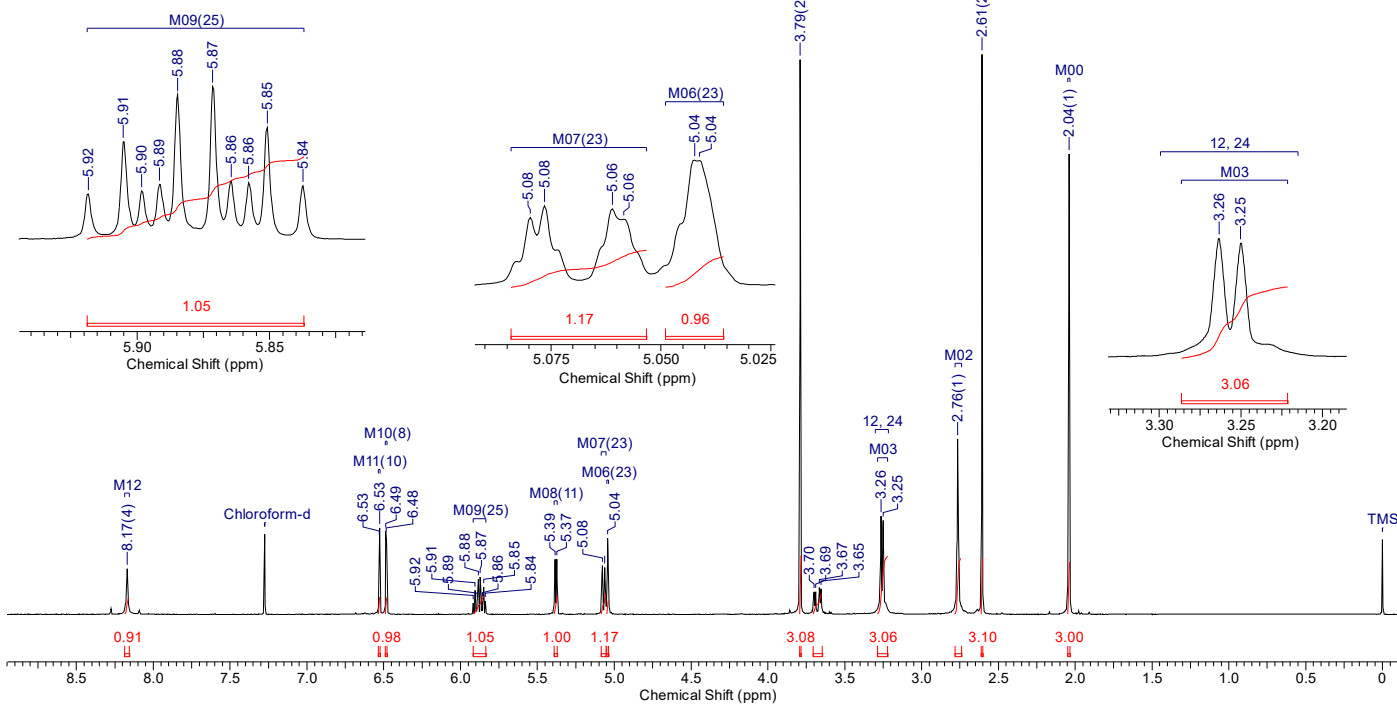
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)
1	24.67	2480.4	0.0461	7	105.91	10646.5	0.0407	13	153.75	15456.1	0.0272	1	1	24.67	7	7	105.91	13	4	134.27
2	25.65	2578.1	0.0461	8	116.46	11707.5	0.0236	14	156.23	15705.3	0.0308	2	1	25.65	8	10a	116.46	14	6a	153.75
3	29.42	2957.7	0.0406	9	123.32	12396.7	0.0497	15	158.79	15962.2	0.0217	3	2	29.42	9	10	123.32	15	8	156.23
4	39.13	3933.4	0.0477	10	128.27	12894.1	0.0340	16	159.03	15986.1	0.0240	4	12	39.13	10	3	128.27	16	12a	158.79
5	68.99	6935.3	0.0430	11	132.04	13273.7	0.0204	17	199.41	20046.2	0.0249	5	11	68.99	11	9	128.27	17	2	159.03
6	97.93	9844.3	0.0361	12	134.27	13498.0	0.0417					6	5	97.93	12	4a	132.04	18	1	199.41

Chloroform-d

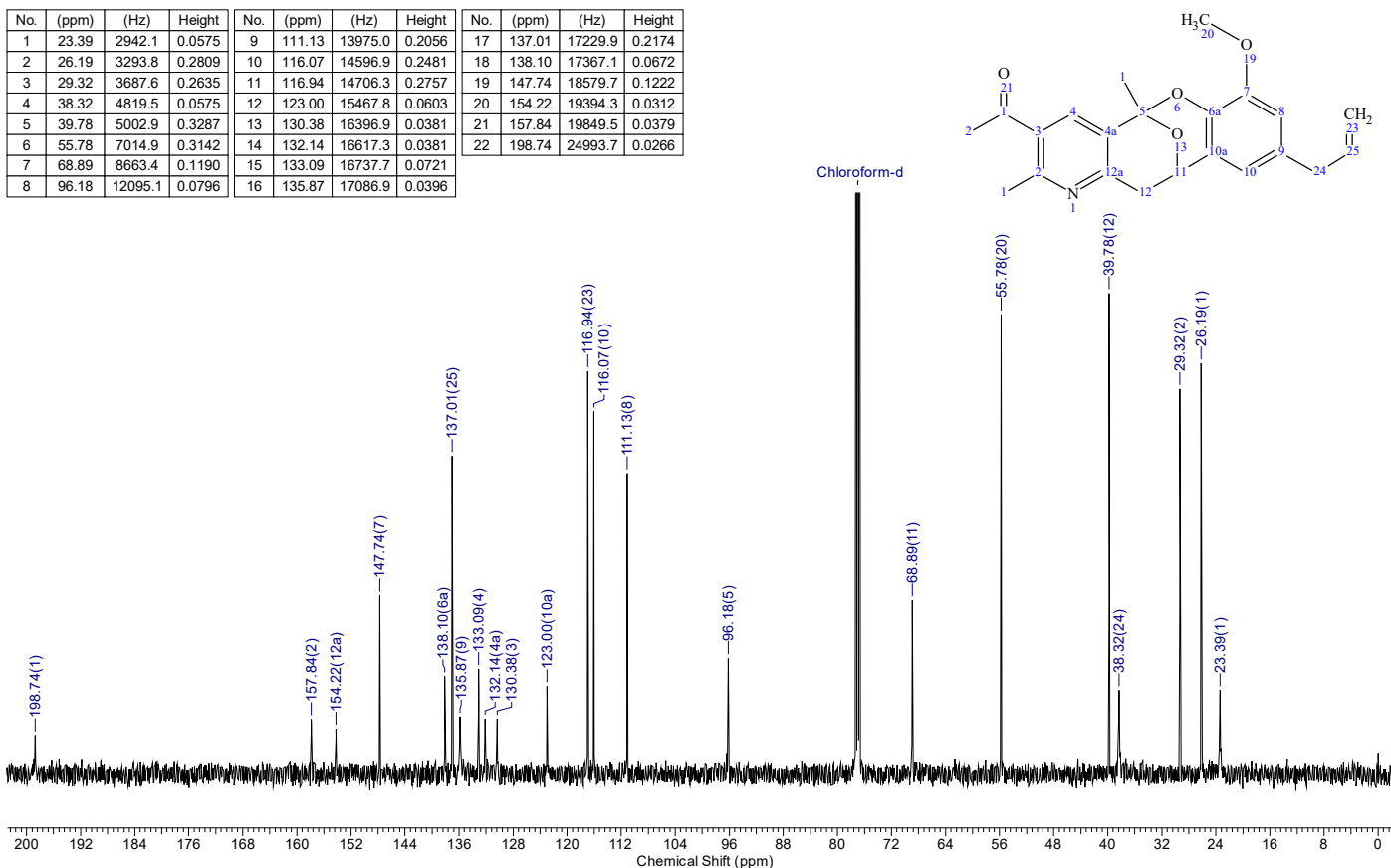


¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of 7i

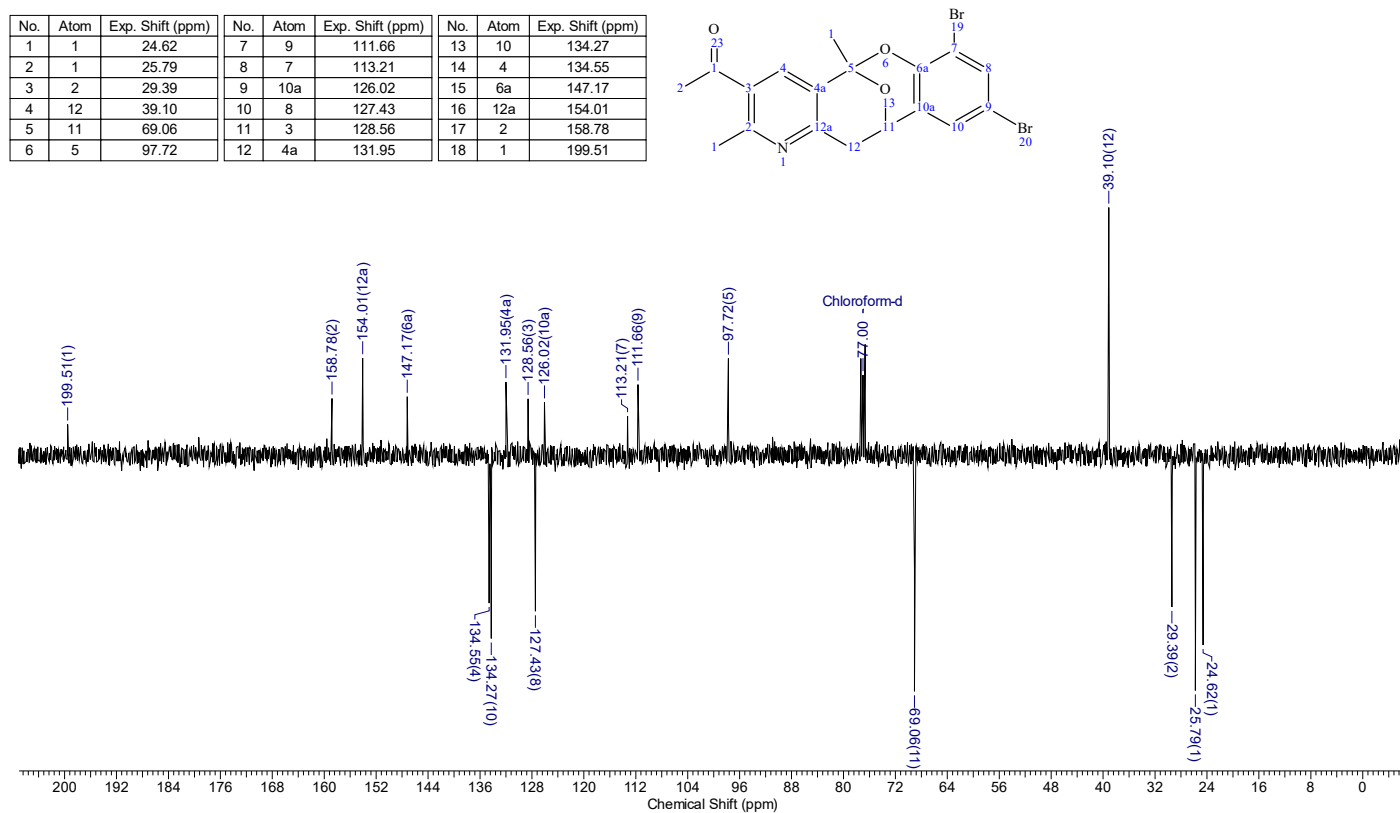
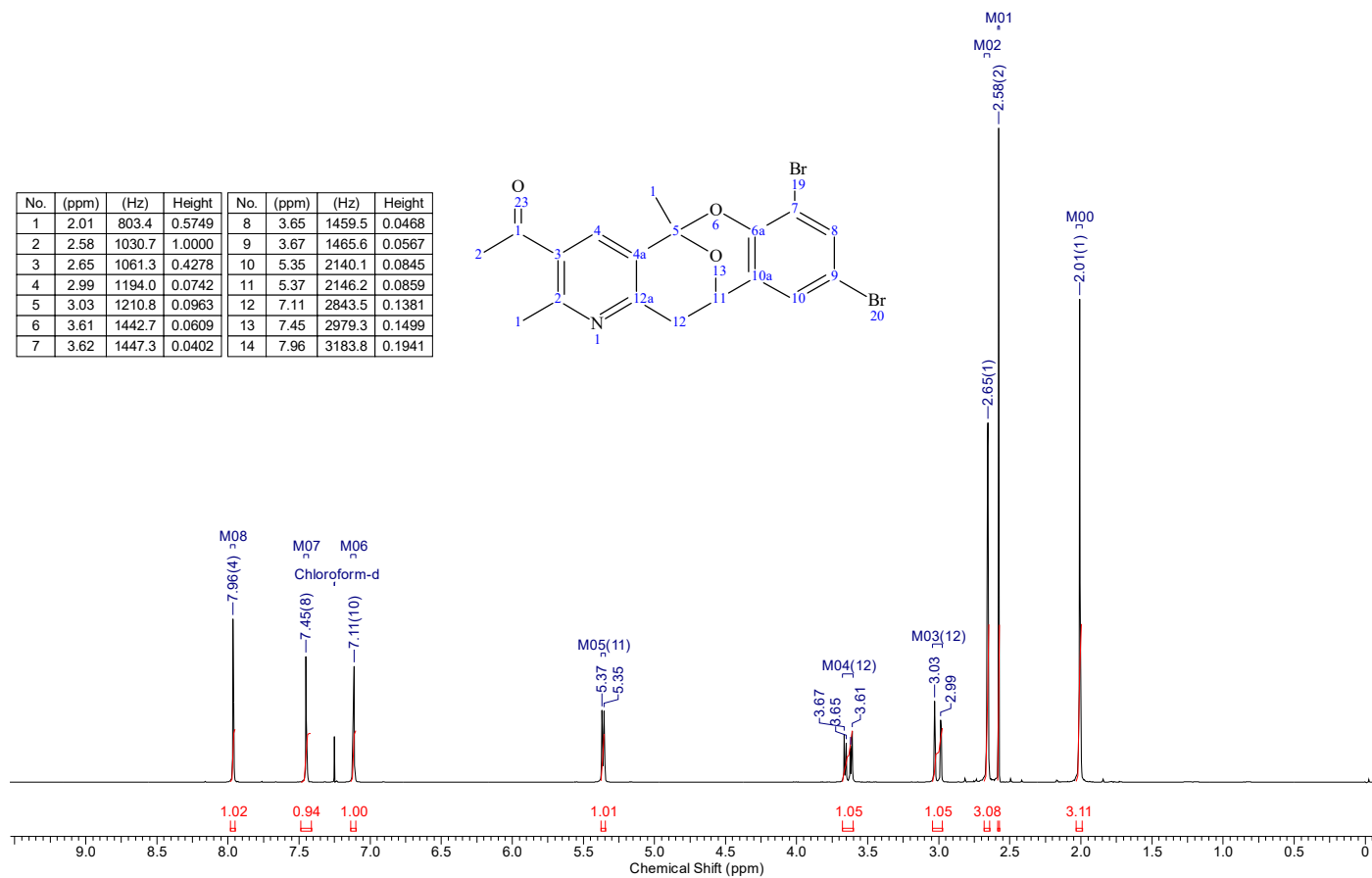
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.04	1020.5	0.8224	10	3.79	1895.5	0.9908	19	5.84	2919.4	0.0234	28	5.92	2960.0	0.0198
2	2.61	1303.8	1.0000	11	5.04	2521.3	0.1356	20	5.85	2926.2	0.0485	29	6.48	3242.6	0.1401
3	2.76	1382.5	0.3129	12	5.04	2521.8	0.1361	21	5.86	2929.7	0.0246	30	6.49	3243.9	0.1481
4	3.25	1625.5	0.1679	13	5.06	2529.9	0.0731	22	5.86	2933.0	0.0254	31	6.53	3264.6	0.1544
5	3.26	1632.1	0.1750	14	5.06	2531.2	0.0839	23	5.87	2936.5	0.0662	32	6.53	3266.1	0.1352
6	3.65	1827.6	0.0456	15	5.08	2538.9	0.0871	24	5.88	2943.1	0.0627	33	8.17	4086.3	0.0812
7	3.67	1833.1	0.0476	16	5.08	2540.5	0.0746	25	5.89	2946.6	0.0239				
8	3.69	1845.2	0.0400	17	5.37	2688.0	0.0985	26	5.90	2949.9	0.0211				
9	3.70	1850.9	0.0399	18	5.39	2693.5	0.0986	27	5.91	2953.4	0.0424				



No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	23.39	2942.1	0.0575	9	111.13	13975.0	0.2056	17	137.01	17229.9	0.2174
2	26.19	3293.8	0.2809	10	116.07	14596.9	0.2481	18	138.10	17367.1	0.0672
3	29.32	3687.6	0.2635	11	116.94	14706.3	0.2757	19	147.74	18579.7	0.1222
4	38.32	4819.5	0.0575	12	123.00	15467.8	0.0603	20	154.22	19394.3	0.0312
5	39.78	5002.9	0.3287	13	130.38	16396.9	0.0381	21	157.84	19849.5	0.0379
6	55.78	7014.9	0.3142	14	132.14	16617.3	0.0381	22	198.74	24993.7	0.0266
7	68.89	8663.4	0.1190	15	133.09	16737.7	0.0721				
8	96.18	12095.1	0.0796	16	135.87	17086.9	0.0396				



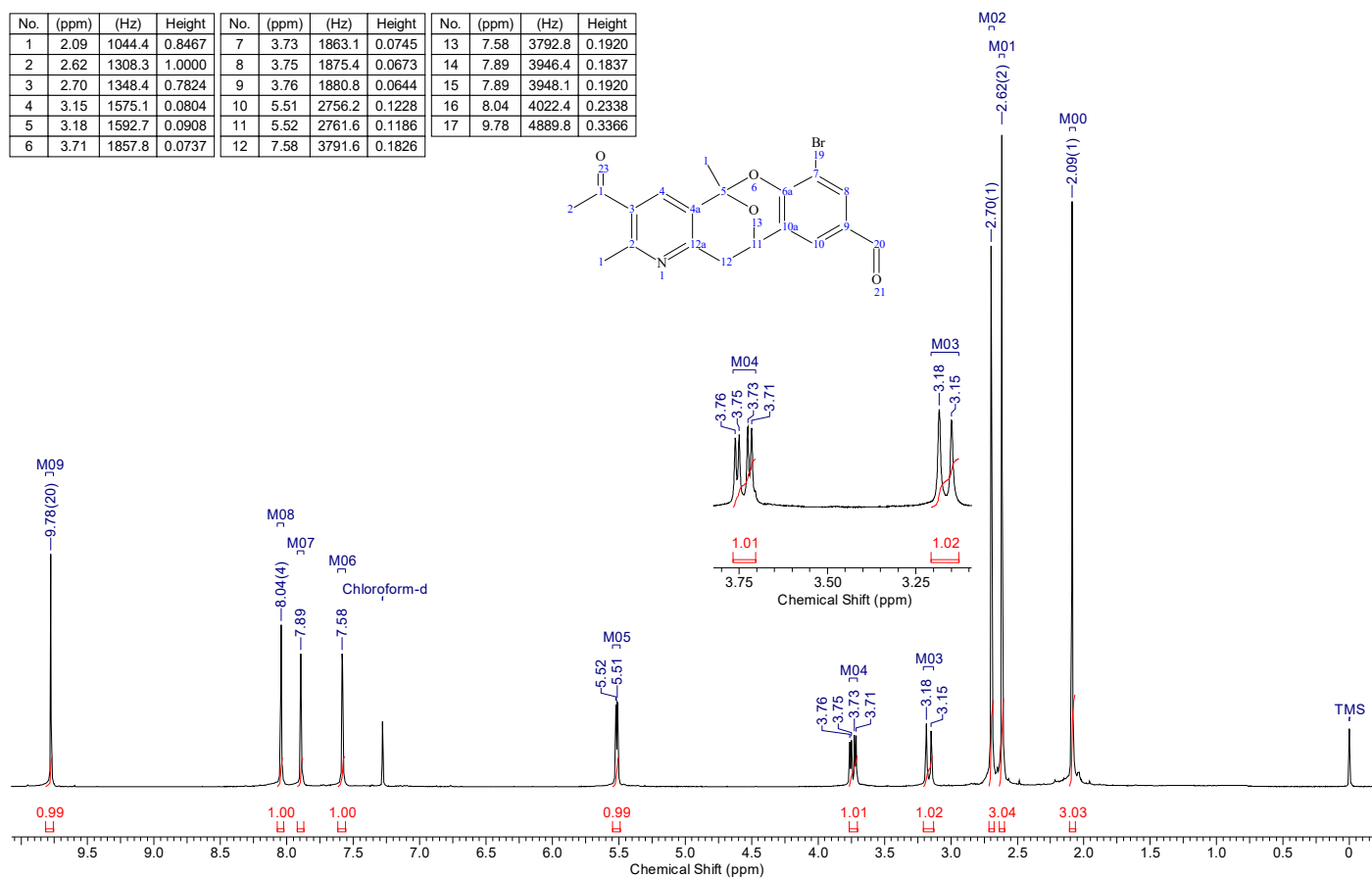
¹H (500 MHz, CDCl₃) and ¹³C (126 MHz, CDCl₃) NMR Spectra of 7j



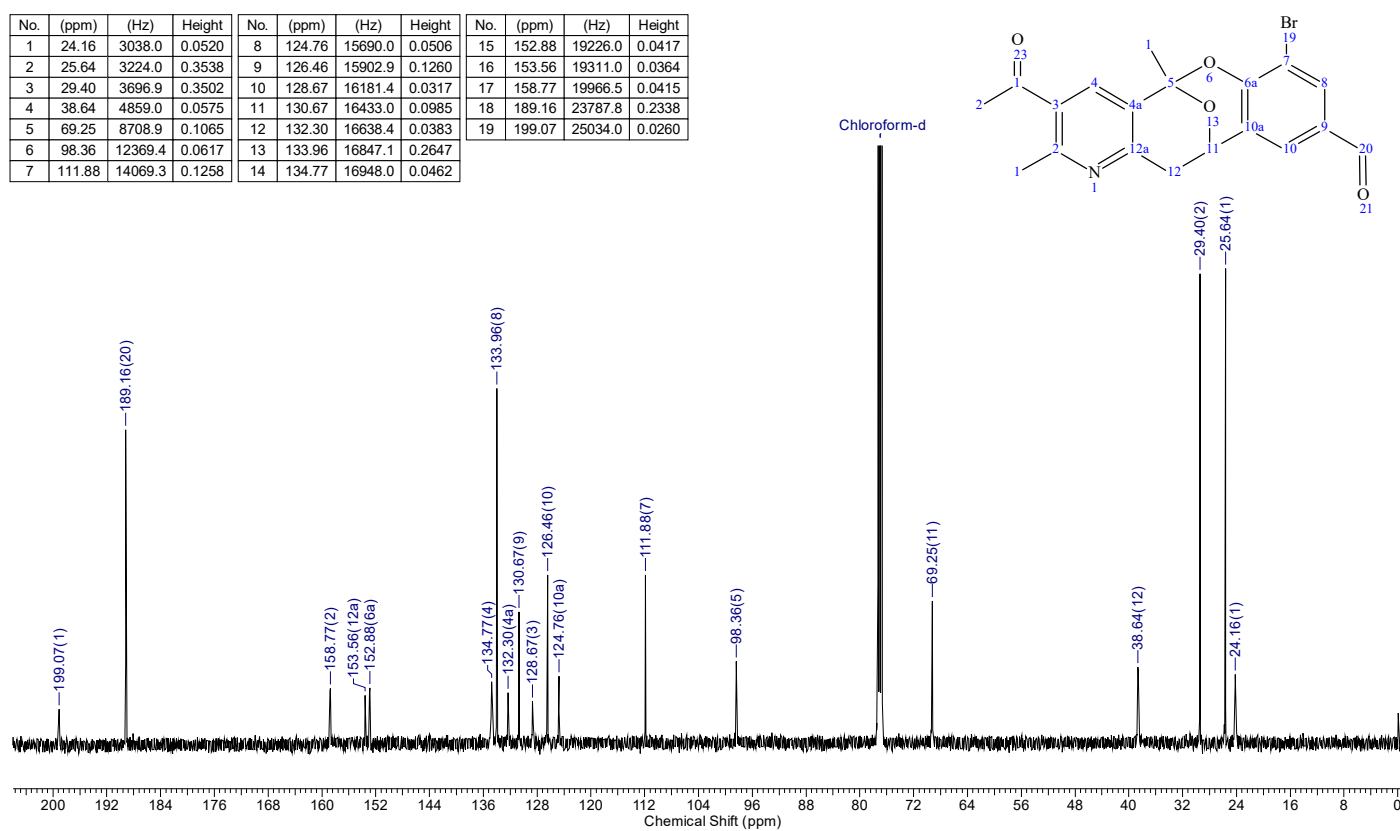
^1H (400 MHz, CDCl_3) and ^{13}C (100 MHz, CDCl_3) NMR Spectra of **7I**

SUPPORTING INFORMATION

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.09	1044.4	0.8467	7	3.73	1863.1	0.0745	13	7.58	3792.8	0.1920
2	2.62	1308.3	1.0000	8	3.75	1875.4	0.0673	14	7.89	3946.4	0.1837
3	2.70	1348.4	0.7824	9	3.76	1880.8	0.0644	15	7.89	3948.1	0.1920
4	3.15	1575.1	0.0804	10	5.51	2756.2	0.1228	16	8.04	4022.4	0.2338
5	3.18	1592.7	0.0908	11	5.52	2761.6	0.1186	17	9.78	4889.8	0.3366
6	3.71	1857.8	0.0737	12	7.58	3791.6	0.1826				



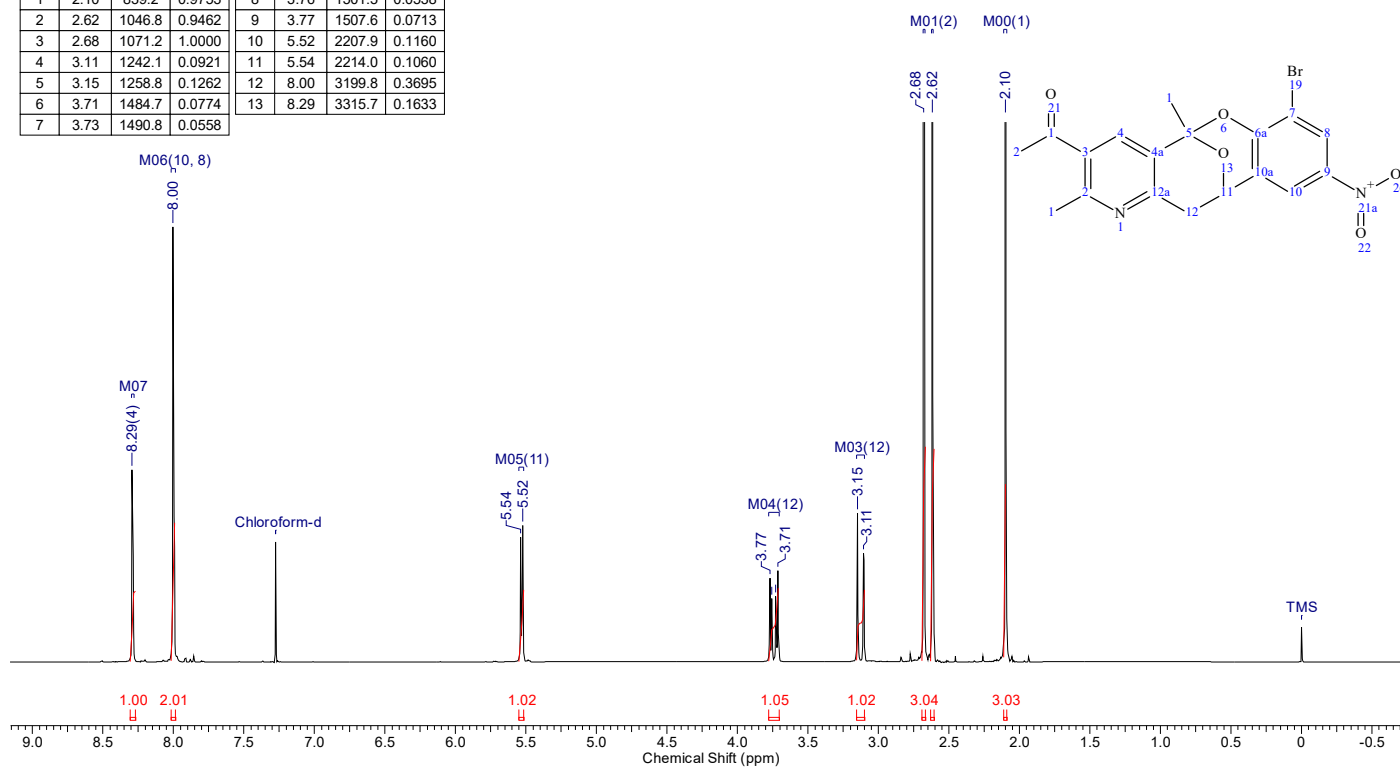
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.16	3038.0	0.0520	8	124.76	15690.0	0.0506	15	152.88	19226.0	0.0417
2	25.64	3224.0	0.3538	9	126.46	15902.9	0.1260	16	153.56	19311.0	0.0364
3	29.40	3696.9	0.3502	10	128.67	16181.4	0.0317	17	158.77	19966.5	0.0415
4	38.64	4859.0	0.0575	11	130.67	16433.0	0.0985	18	189.16	23787.8	0.2338
5	69.25	8708.9	0.1065	12	132.30	16638.4	0.0383	19	199.07	25034.0	0.0260
6	98.36	12369.4	0.0617	13	133.96	16847.1	0.2647				
7	111.88	14069.3	0.1258	14	134.77	16948.0	0.0462				



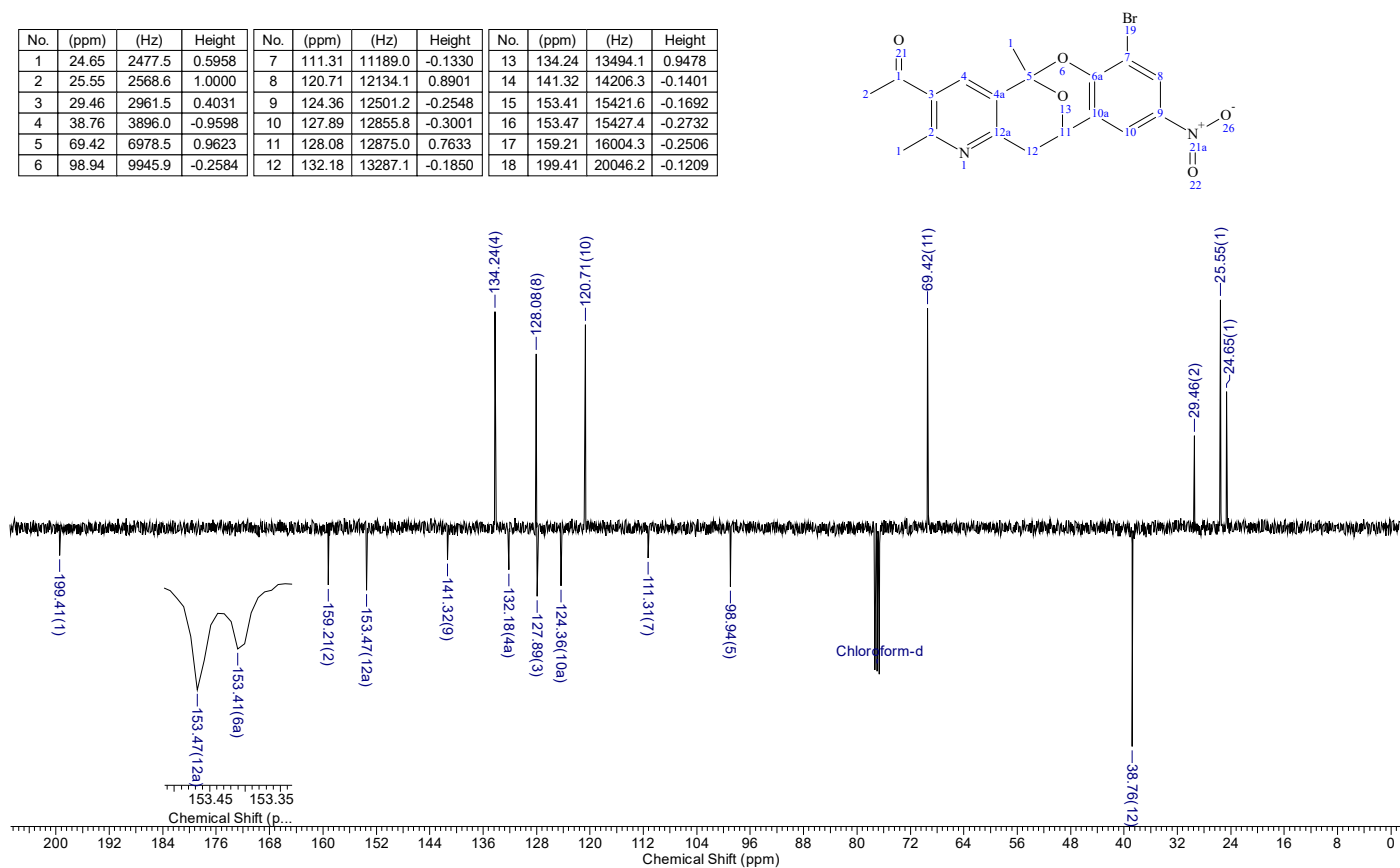
¹H (500 MHz, CDCl₃) and ¹³C (126 MHz, CDCl₃) NMR Spectra of **7m**

SUPPORTING INFORMATION

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.10	839.2	0.9753	8	3.76	1501.5	0.0538
2	2.62	1046.8	0.9462	9	3.77	1507.6	0.0713
3	2.68	1071.2	1.0000	10	5.52	2207.9	0.1160
4	3.11	1242.1	0.0921	11	5.54	2214.0	0.1060
5	3.15	1258.8	0.1262	12	8.00	3199.8	0.3695
6	3.71	1484.7	0.0774	13	8.29	3315.7	0.1633
7	3.73	1490.8	0.0558				



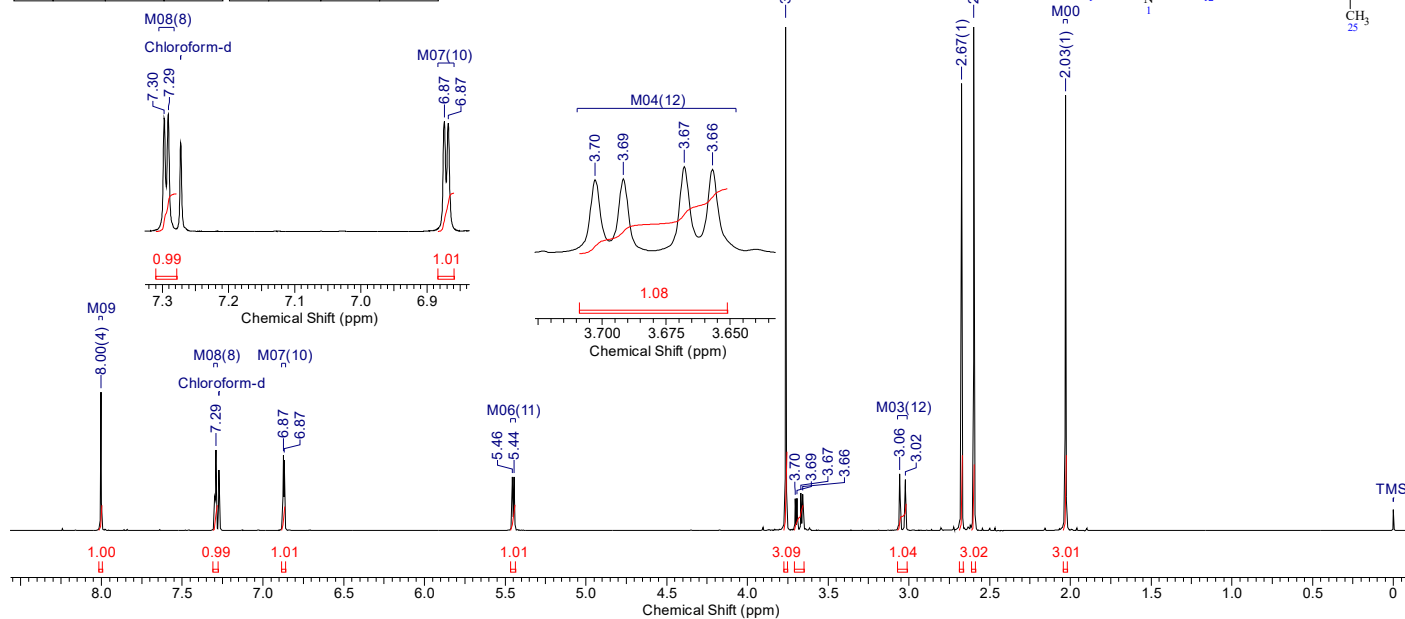
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.65	2477.5	0.5958	7	111.31	11189.0	-0.1330	13	134.24	13494.1	0.9478
2	25.55	2568.6	1.0000	8	120.71	12134.1	0.8901	14	141.32	14206.3	-0.1401
3	29.46	2961.5	0.4031	9	124.36	12501.2	-0.2548	15	153.41	15421.6	-0.1692
4	38.76	3896.0	-0.9598	10	127.89	12855.8	-0.3001	16	153.47	15427.4	-0.2732
5	69.42	6978.5	0.9623	11	128.08	12875.0	0.7633	17	159.21	16004.3	-0.2506
6	98.94	9945.9	-0.2584	12	132.18	13287.1	-0.1850	18	199.41	20046.2	-0.1209



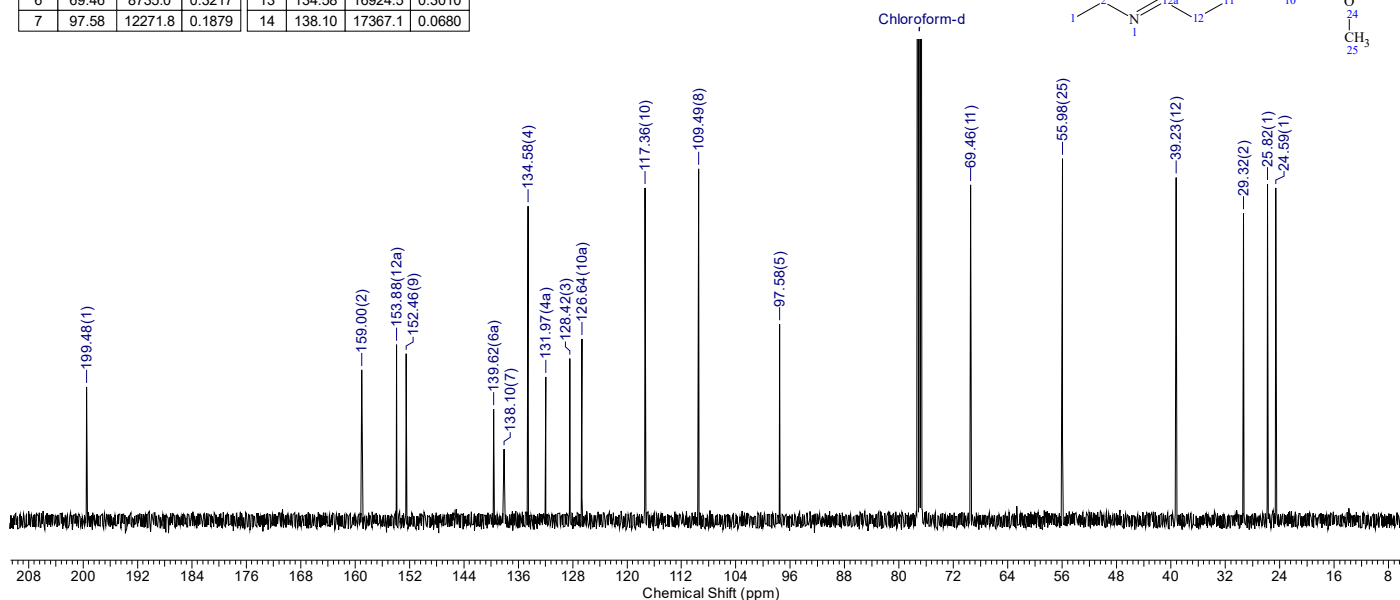
¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of **7n**

SUPPORTING INFORMATION

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.03	1015.1	0.8226	7	3.67	1834.4	0.0711	13	6.87	3435.0	0.1403
2	2.60	1299.1	1.0000	8	3.69	1846.3	0.0612	14	6.87	3437.9	0.1426
3	2.67	1337.6	0.8448	9	3.70	1851.8	0.0606	15	7.29	3646.4	0.1520
4	3.02	1511.8	0.0963	10	3.76	1881.5	0.9717	16	7.30	3649.6	0.1470
5	3.06	1529.2	0.1069	11	5.44	2723.2	0.1015	17	8.00	4003.0	0.2615
6	3.66	1828.9	0.0689	12	5.46	2728.5	0.1011				



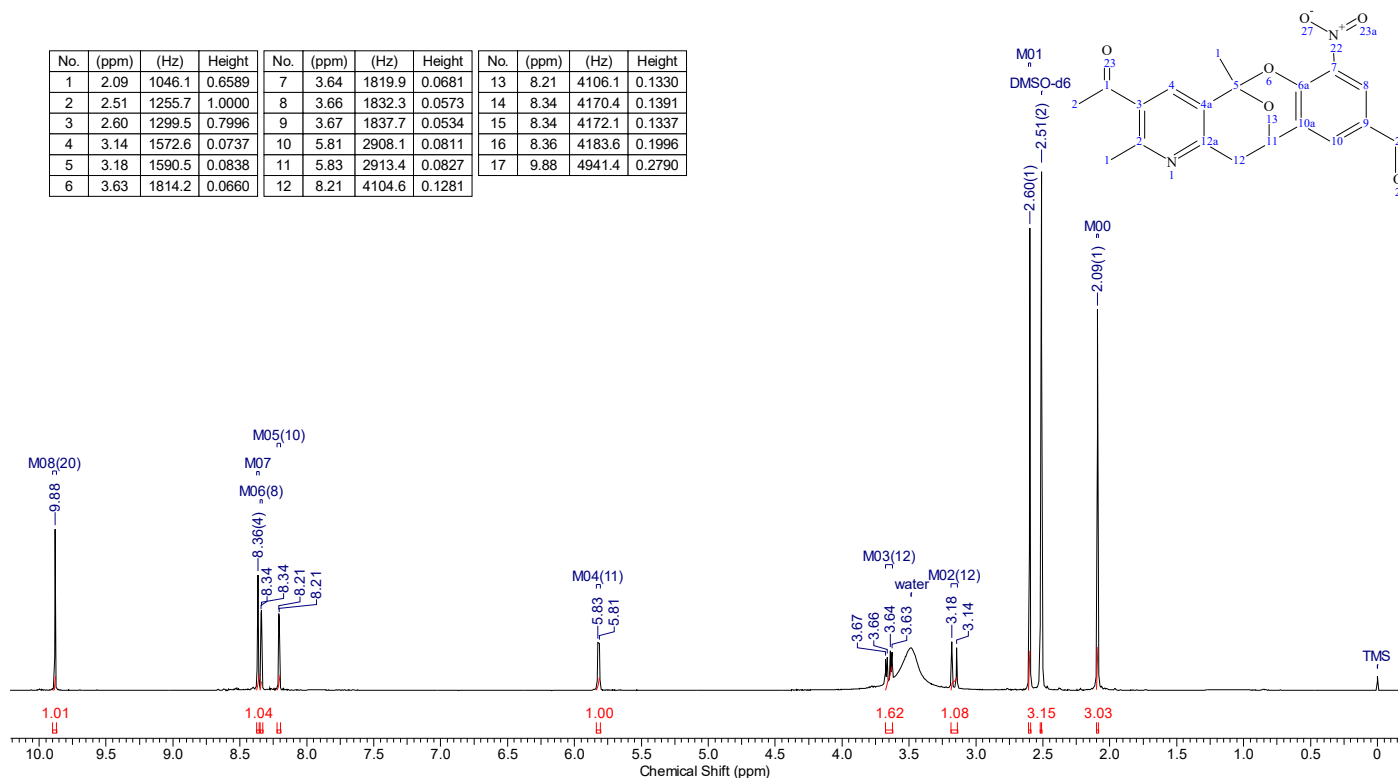
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.59	3092.7	0.3187	8	109.49	13769.7	0.3369	15	139.62	17558.1	0.1065
2	25.82	3246.7	0.3225	9	117.36	14759.3	0.3188	16	152.46	19173.0	0.1597
3	29.32	3686.8	0.2944	10	126.64	15926.5	0.1737	17	153.88	19351.4	0.1684
4	39.23	4933.1	0.3287	11	128.42	16149.5	0.1552	18	159.00	19995.1	0.1440
5	55.98	7039.3	0.3467	12	131.97	16596.3	0.1373	19	199.48	25086.2	0.1279
6	69.46	8735.0	0.3217	13	134.58	16924.5	0.3010				
7	97.58	12271.8	0.1879	14	138.10	17367.1	0.0680				



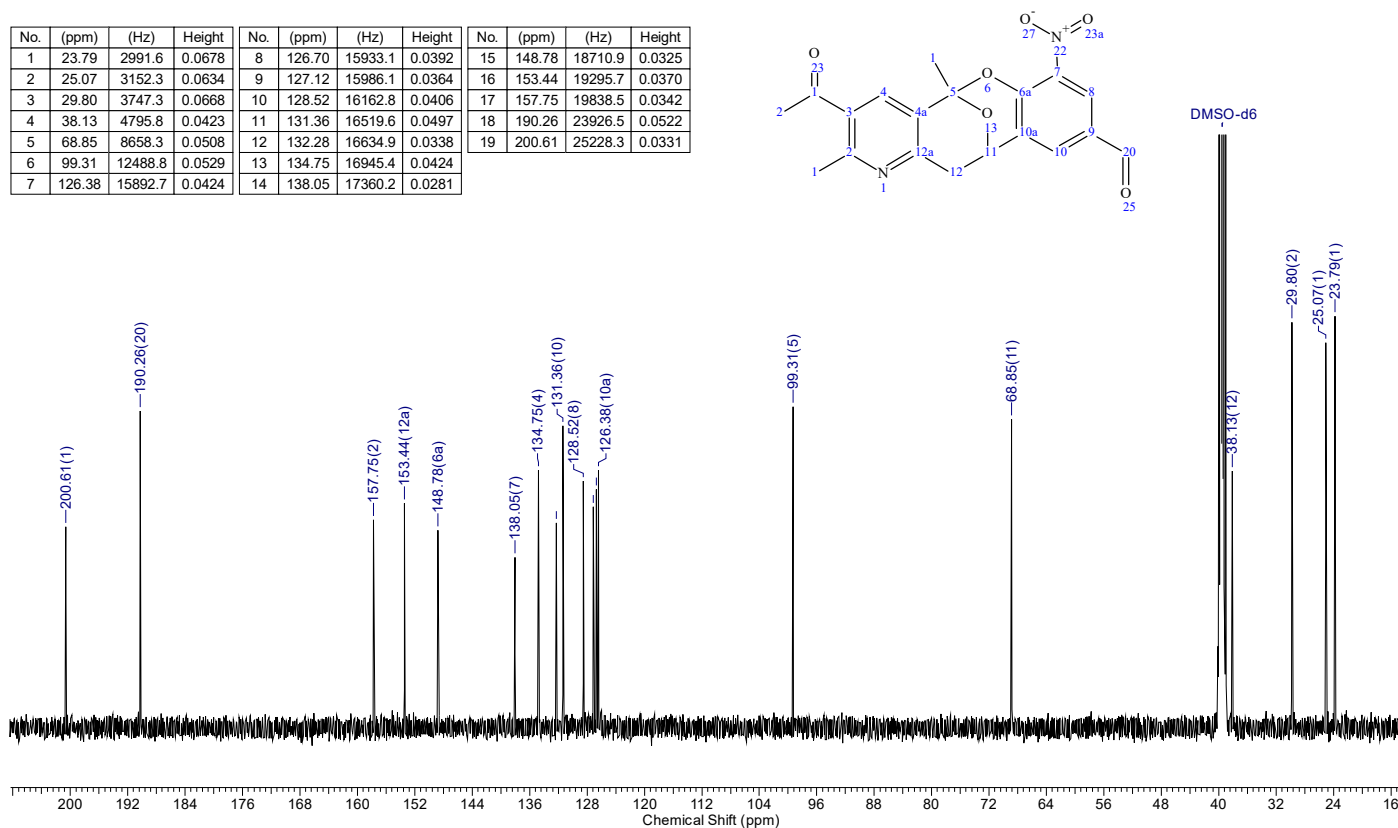
^1H (500 MHz, CDCl_3) and ^{13}C (126 MHz, CDCl_3) NMR Spectra of **70**

SUPPORTING INFORMATION

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.09	1046.1	0.6589	7	3.64	1819.9	0.0681	13	8.21	4106.1	0.1330
2	2.51	1255.7	1.0000	8	3.66	1832.3	0.0573	14	8.34	4170.4	0.1391
3	2.60	1299.5	0.7996	9	3.67	1837.7	0.0534	15	8.34	4172.1	0.1337
4	3.14	1572.6	0.0737	10	5.81	2908.1	0.0811	16	8.36	4183.6	0.1996
5	3.18	1590.5	0.0838	11	5.83	2913.4	0.0827	17	9.88	4941.4	0.2790
6	3.63	1814.2	0.0660	12	8.21	4104.6	0.1281				

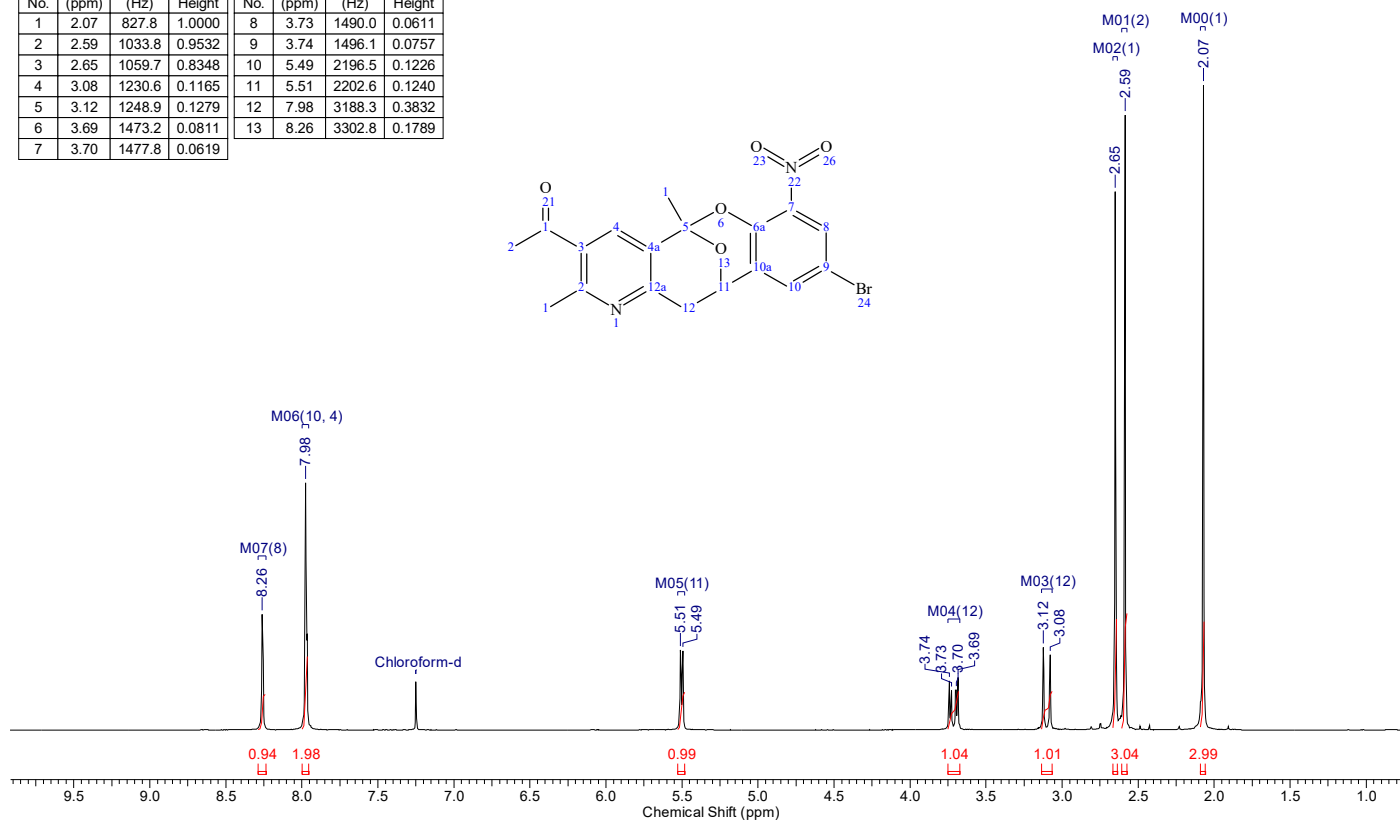


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	23.79	2991.6	0.0678	8	126.70	15933.1	0.0392	15	148.78	18710.9	0.0325
2	25.07	3152.3	0.0634	9	127.12	15986.1	0.0364	16	153.44	19295.7	0.0370
3	29.80	3747.3	0.0668	10	128.52	16162.8	0.0406	17	157.75	19838.5	0.0342
4	38.13	4795.8	0.0423	11	131.36	16519.6	0.0497	18	190.26	23926.5	0.0522
5	68.85	8658.3	0.0508	12	132.28	16634.9	0.0338	19	200.61	25228.3	0.0331
6	99.31	12488.8	0.0529	13	134.75	16945.4	0.0424				
7	126.38	15892.7	0.0424	14	138.05	17360.2	0.0281				

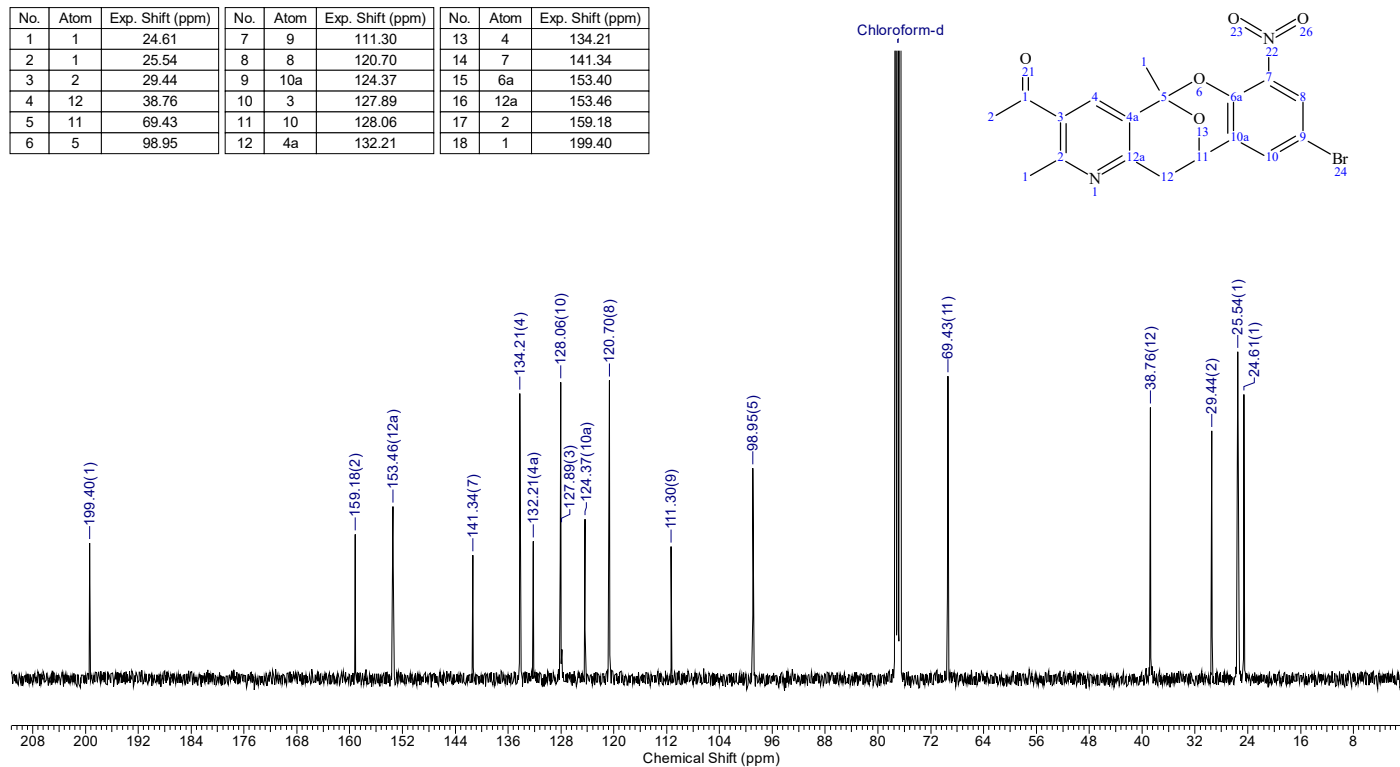


^1H (500 MHz, CDCl_3) and ^{13}C (126 MHz, CDCl_3) NMR Spectra of **7p**

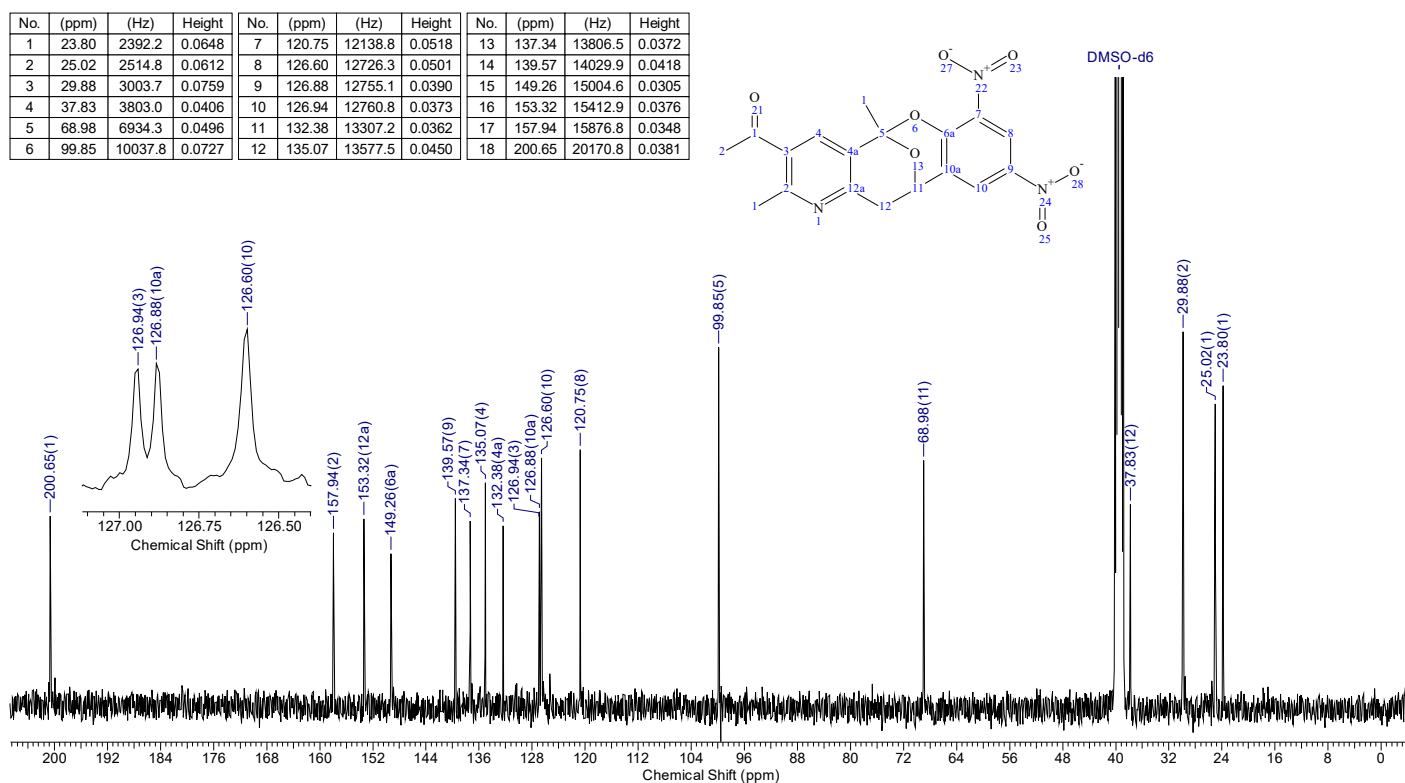
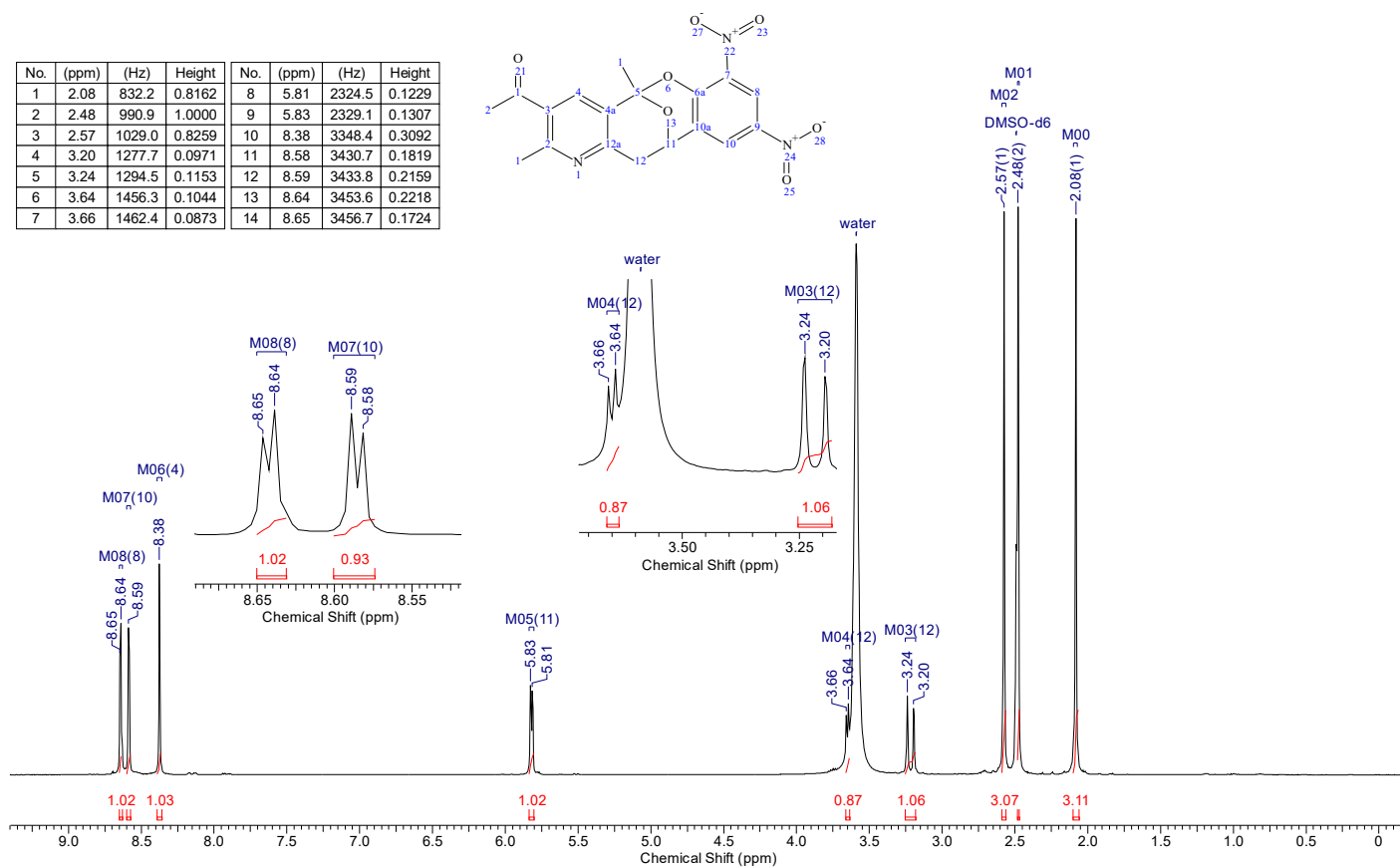
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.07	827.8	1.0000	8	3.73	1490.0	0.0611
2	2.59	1033.8	0.9532	9	3.74	1496.1	0.0757
3	2.65	1059.7	0.8348	10	5.49	2196.5	0.1226
4	3.08	1230.6	0.1165	11	5.51	2202.6	0.1240
5	3.12	1248.9	0.1279	12	7.98	3188.3	0.3832
6	3.69	1473.2	0.0811	13	8.26	3302.8	0.1789
7	3.70	1477.8	0.0619				



No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)
1	1	24.61	7	9	111.30	13	4	134.21
2	1	25.54	8	8	120.70	14	7	141.34
3	2	29.44	9	10a	124.37	15	6a	153.40
4	12	38.76	10	3	127.89	16	12a	153.46
5	11	69.43	11	10	128.06	17	2	159.18
6	5	98.95	12	4a	132.21	18	1	199.40

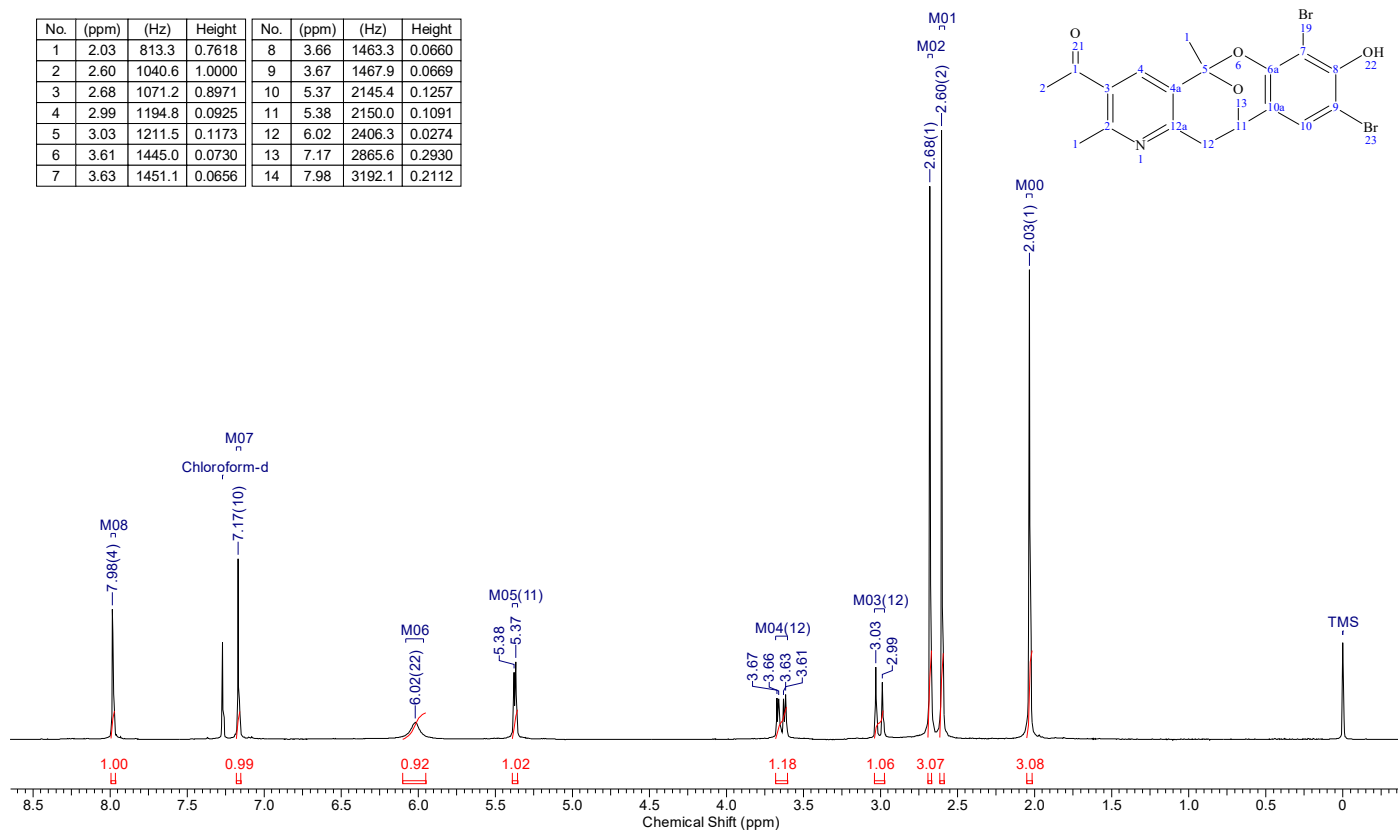


¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of 7q

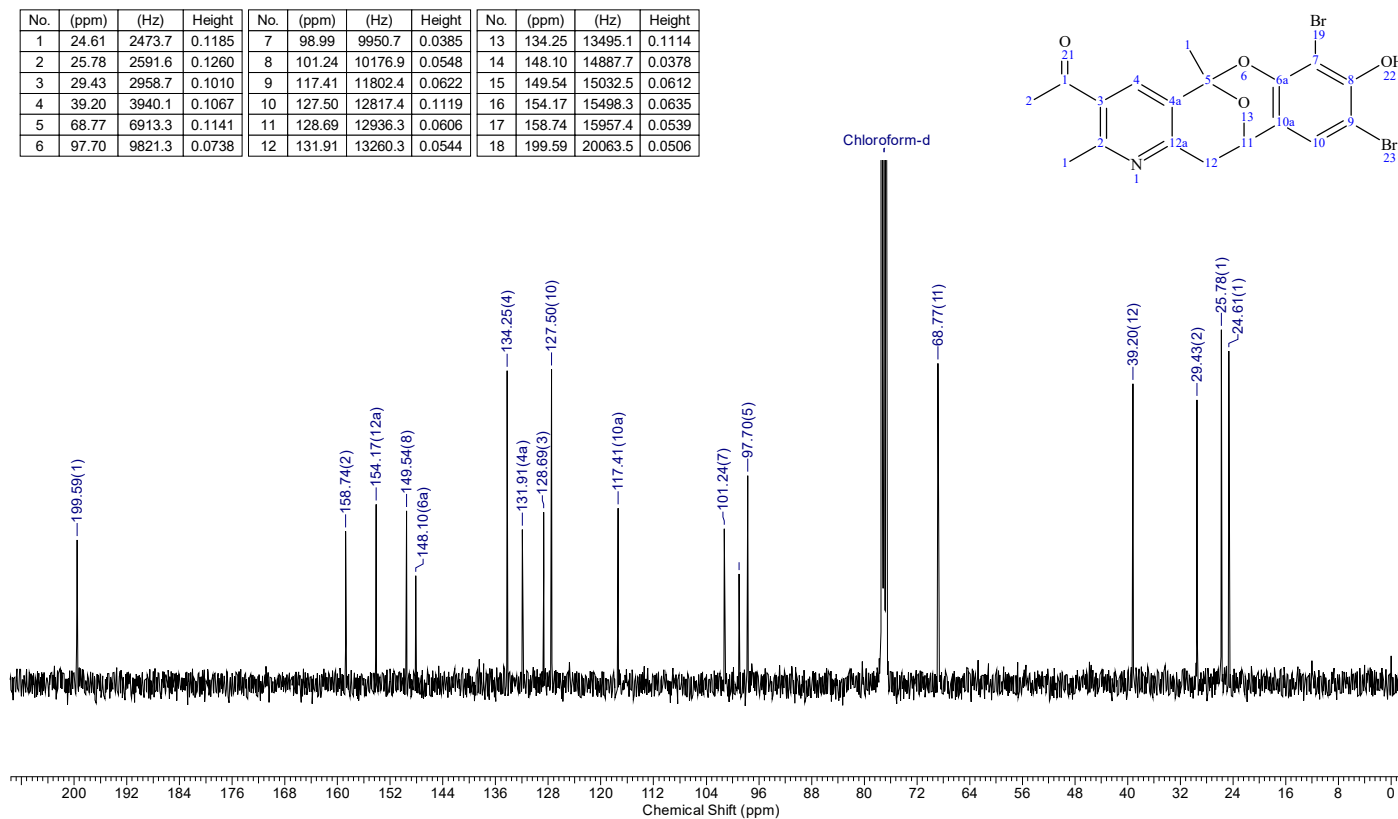


¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of 7r

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.03	813.3	0.7618	8	3.66	1463.3	0.0660
2	2.60	1040.6	1.0000	9	3.67	1467.9	0.0669
3	2.68	1071.2	0.8971	10	5.37	2145.4	0.1257
4	2.99	1194.8	0.0925	11	5.38	2150.0	0.1091
5	3.03	1211.5	0.1173	12	6.02	2406.3	0.0274
6	3.61	1445.0	0.0730	13	7.17	2865.6	0.2930
7	3.63	1451.1	0.0656	14	7.98	3192.1	0.2112

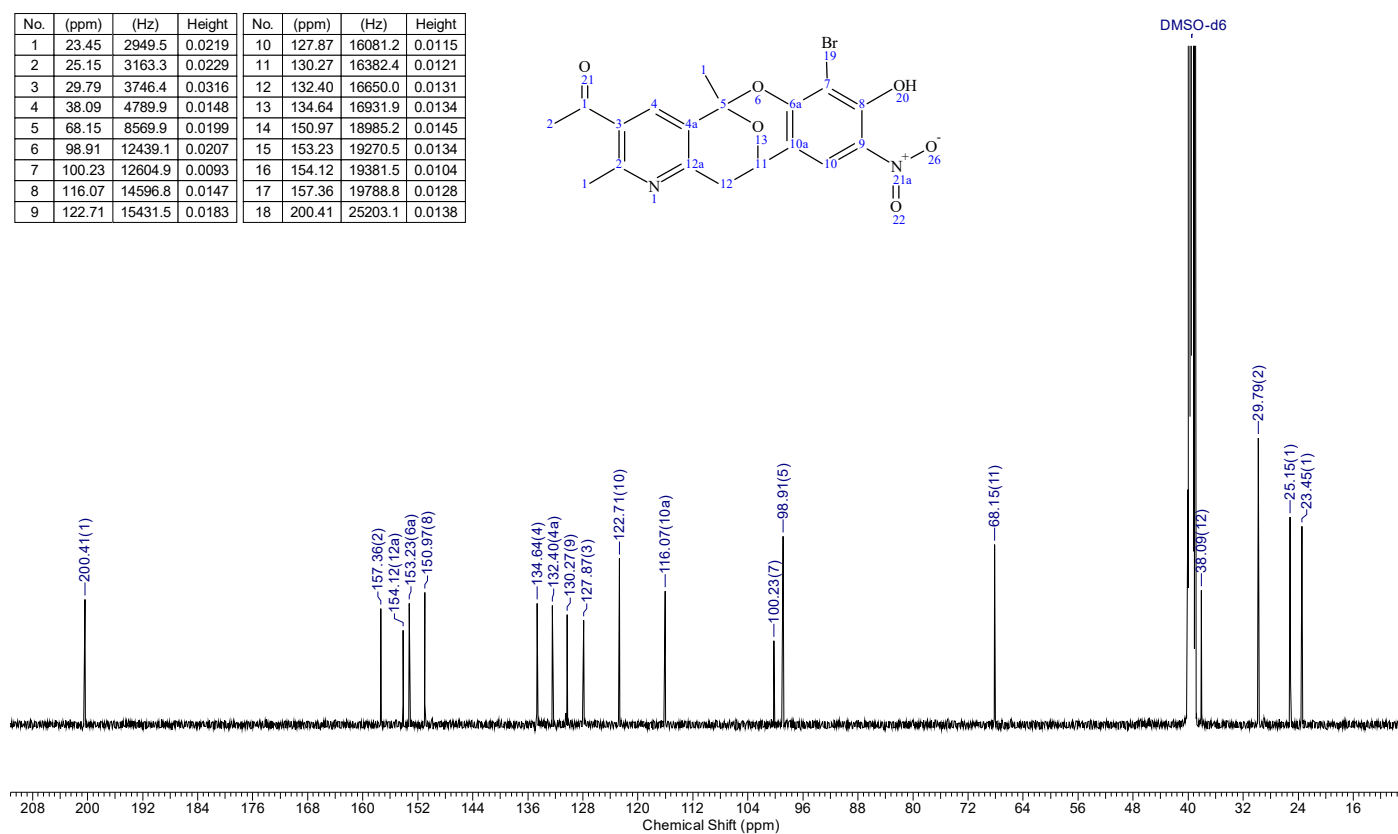
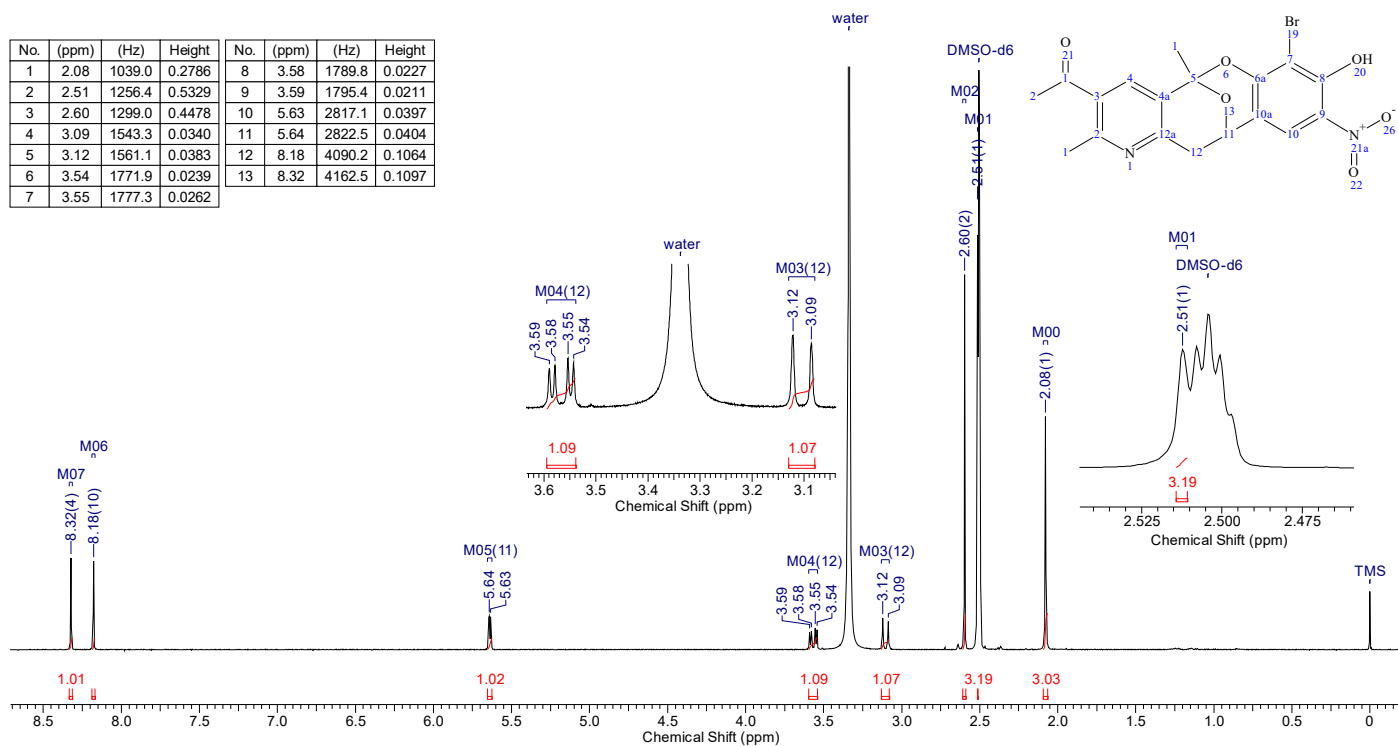


No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.61	2473.7	0.1185	7	98.99	9950.7	0.0385	13	134.25	13495.1	0.1114
2	25.78	2591.6	0.1260	8	101.24	10176.9	0.0548	14	148.10	14887.7	0.0378
3	29.43	2958.7	0.1010	9	117.41	11802.4	0.0622	15	149.54	15032.5	0.0612
4	39.20	3940.1	0.1067	10	127.50	12817.4	0.1119	16	154.17	15498.3	0.0635
5	68.77	6913.3	0.1141	11	128.69	12936.3	0.0606	17	158.74	15957.4	0.0539
6	97.70	9821.3	0.0738	12	131.91	13260.3	0.0544	18	199.59	20063.5	0.0506



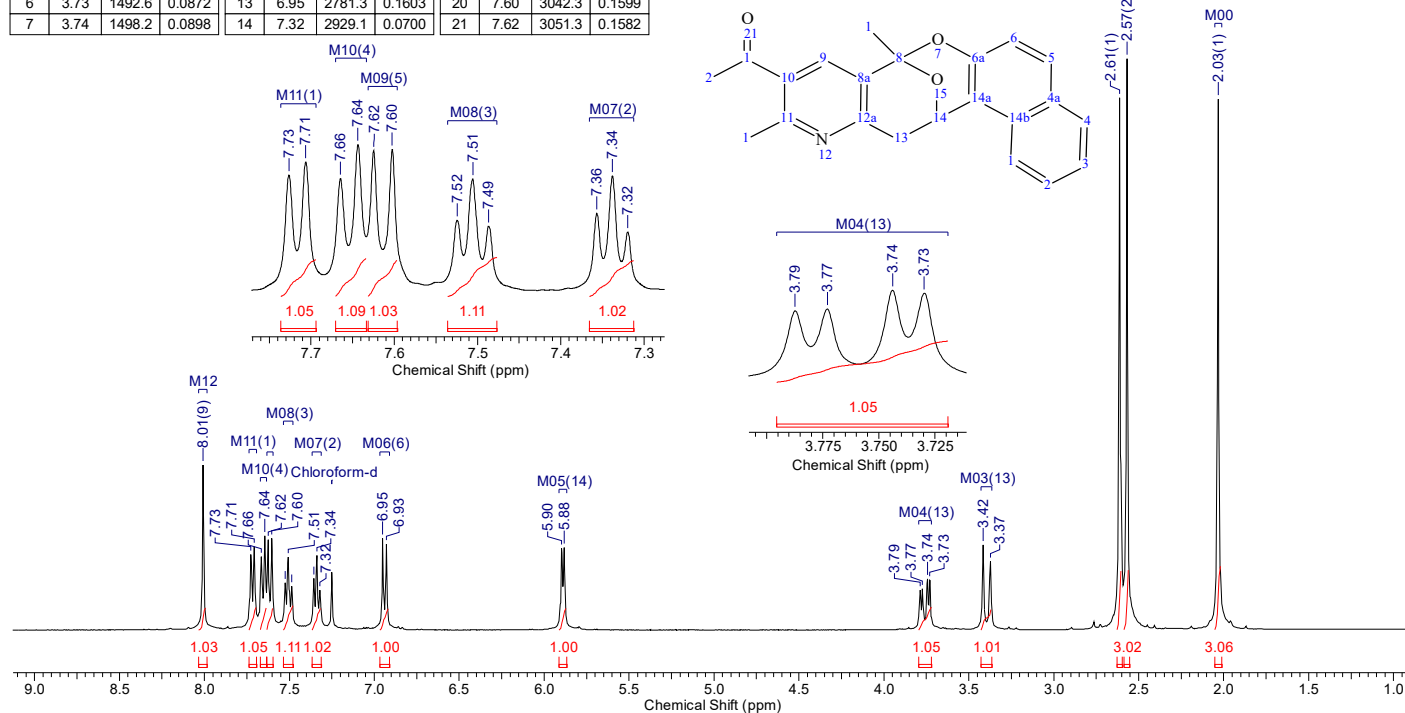
¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of 7s

SUPPORTING INFORMATION

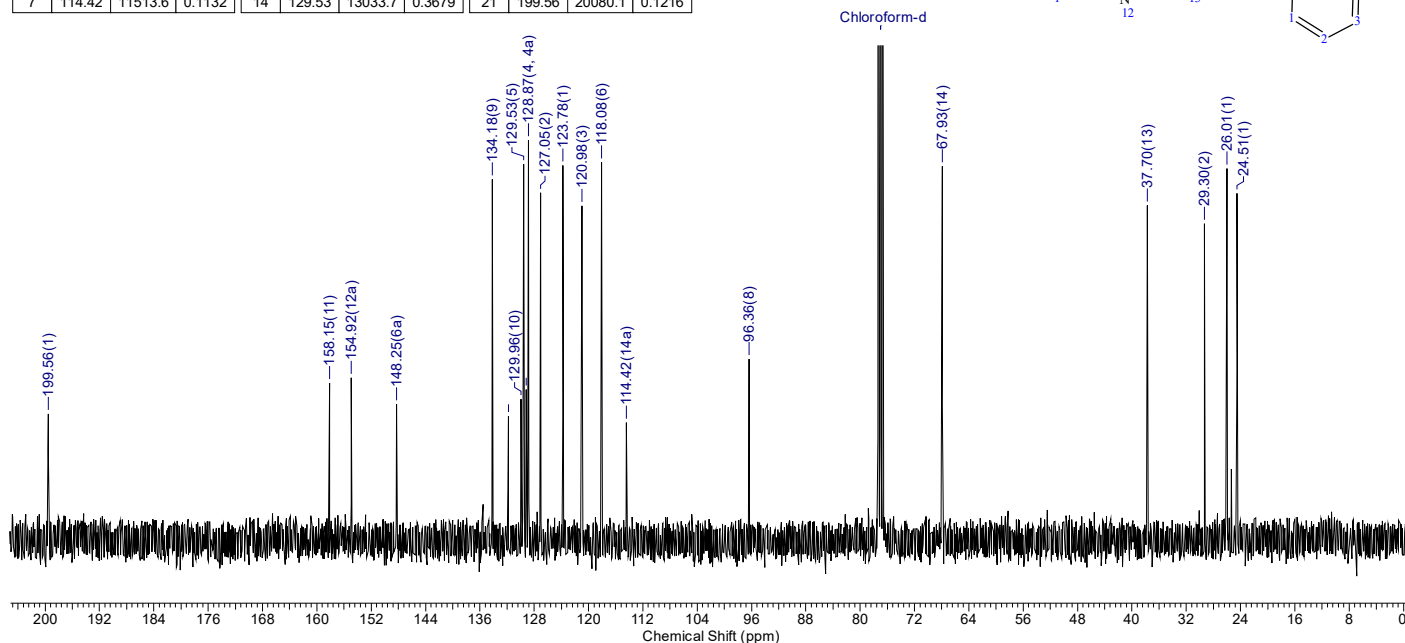


^1H (500 MHz, CDCl_3) and ^{13}C (126 MHz, CDCl_3) NMR Spectra of **7t**

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.03	813.4	0.9288	8	3.77	1509.8	0.0717	15	7.34	2936.4	0.1309	22	7.64	3058.8	0.1651
2	2.57	1028.0	1.0000	9	3.79	1515.6	0.0698	16	7.36	2943.9	0.0903	23	7.66	3067.3	0.1281
3	2.61	1045.2	0.9310	10	5.88	2354.1	0.1441	17	7.49	2996.0	0.0764	24	7.71	3083.9	0.1462
4	3.37	1350.0	0.1198	11	5.90	2359.6	0.1424	18	7.51	3003.6	0.1276	25	7.73	3092.0	0.1320
5	3.42	1367.4	0.1491	12	6.93	2772.4	0.1504	19	7.52	3011.0	0.0827	26	8.01	3204.5	0.2891
6	3.73	1492.6	0.0872	13	6.95	2781.3	0.1603	20	7.60	3042.3	0.1599				
7	3.74	1498.2	0.0898	14	7.32	2929.1	0.0700	21	7.62	3051.3	0.1582				



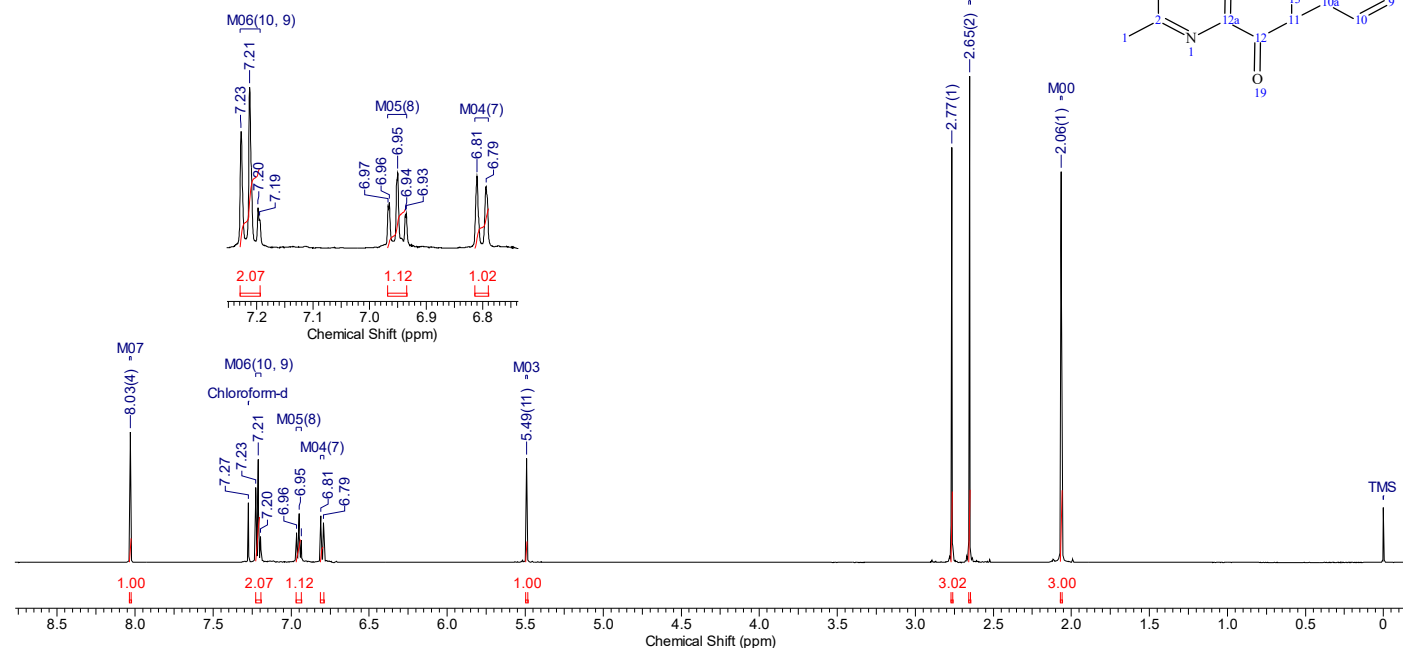
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.51	2465.9	0.3394	8	118.08	11881.9	0.3698	15	129.96	13077.0	0.1362
2	26.01	2617.0	0.3638	9	120.98	12173.1	0.3269	16	131.81	13263.3	0.1196
3	29.30	2947.9	0.3093	10	123.78	12454.9	0.3666	17	134.18	13501.7	0.3529
4	37.70	3793.8	0.3274	11	127.05	12784.2	0.3396	18	148.25	14916.9	0.1309
5	67.93	6835.3	0.3658	12	128.87	12967.7	0.3916	19	154.92	15588.9	0.1570
6	96.36	9696.5	0.1756	13	129.19	12999.2	0.1456	20	158.15	15913.9	0.1521
7	114.42	11513.6	0.1132	14	129.53	13033.7	0.3679	21	199.56	20080.1	0.1216



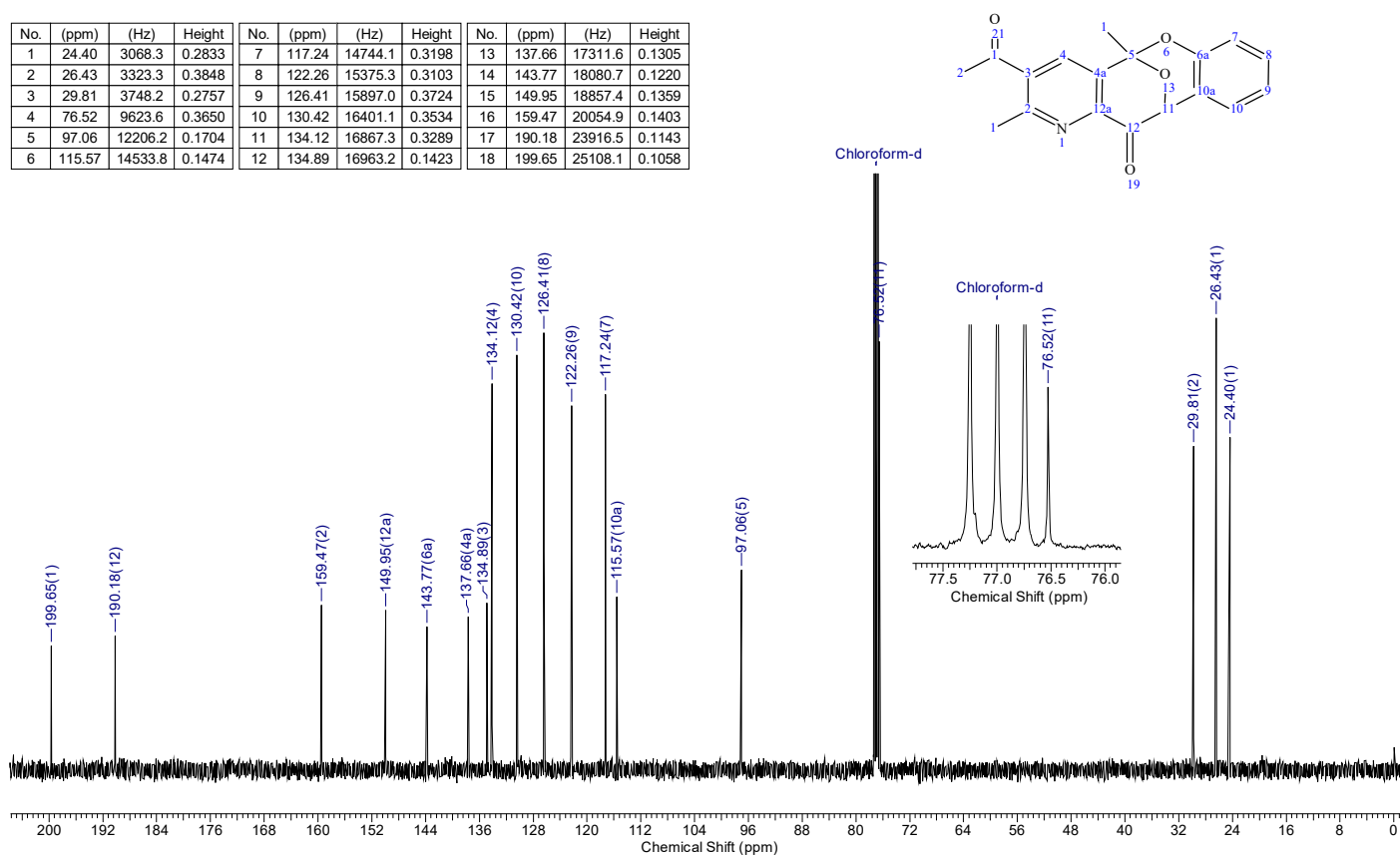
¹H (400 MHz, CDCl₃) and ¹³C (100 MHz, CDCl₃) NMR Spectra of **7u**

SUPPORTING INFORMATION

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	2.06	1032.4	0.8035	7	6.93	3468.4	0.0463	13	7.20	3599.5	0.0533
2	2.65	1326.7	1.0000	8	6.94	3469.3	0.0451	14	7.21	3606.8	0.2119
3	2.77	1383.8	0.8536	9	6.95	3475.9	0.1000	15	7.23	3614.5	0.1537
4	5.49	2746.5	0.2139	10	6.96	3483.4	0.0609	16	7.27	3638.0	0.1225
5	6.79	3397.8	0.0818	11	6.97	3484.3	0.0552	17	8.03	4016.2	0.2684
6	6.81	3405.6	0.0956	12	7.19	3598.0	0.0385				



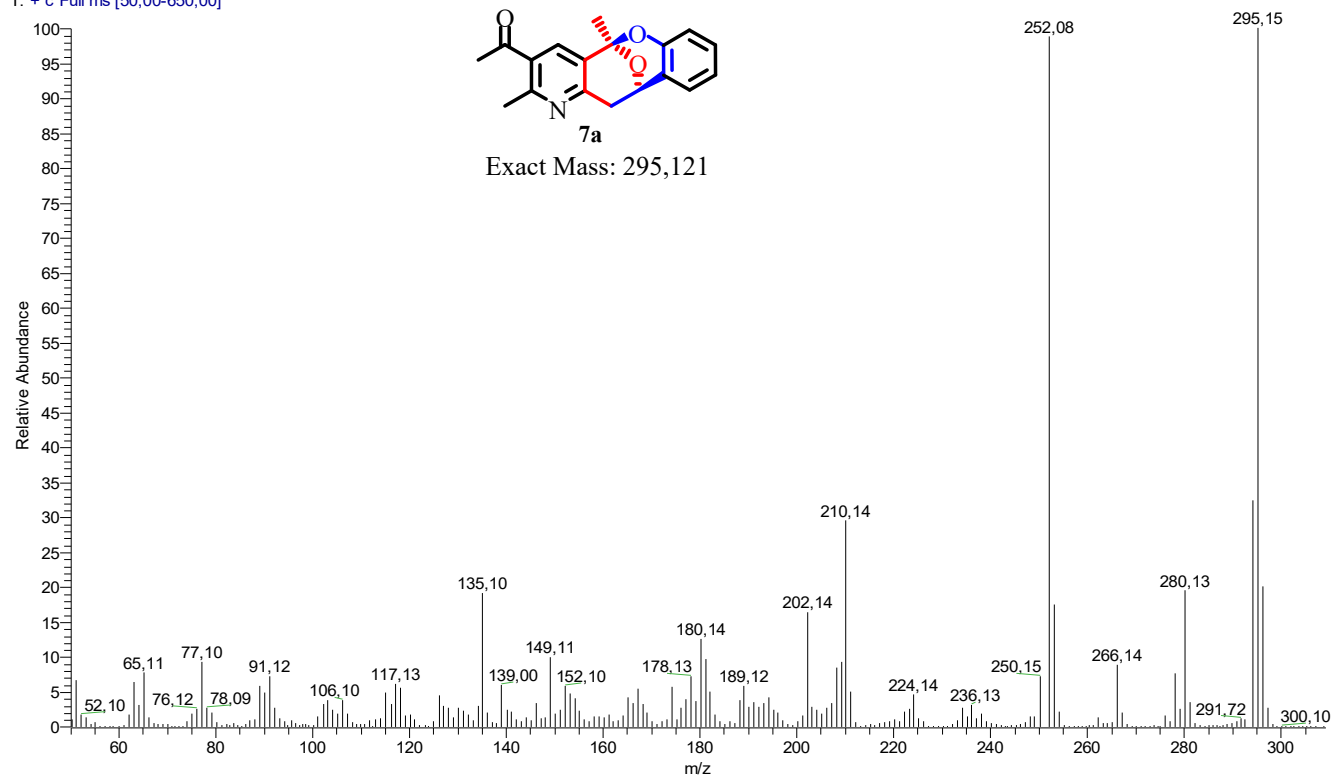
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	24.40	3068.3	0.2833	7	117.24	14744.1	0.3198	13	137.66	17311.6	0.1305
2	26.43	3323.3	0.3848	8	122.26	15375.3	0.3103	14	143.77	18080.7	0.1220
3	29.81	3748.2	0.2757	9	126.41	15897.0	0.3724	15	149.95	18857.4	0.1359
4	76.52	9623.6	0.3650	10	130.42	16401.1	0.3534	16	159.47	20054.9	0.1403
5	97.06	12206.2	0.1704	11	134.12	16867.3	0.3289	17	190.18	23916.5	0.1143
6	115.57	14533.8	0.1474	12	134.89	16963.2	0.1423	18	199.65	25108.1	0.1058



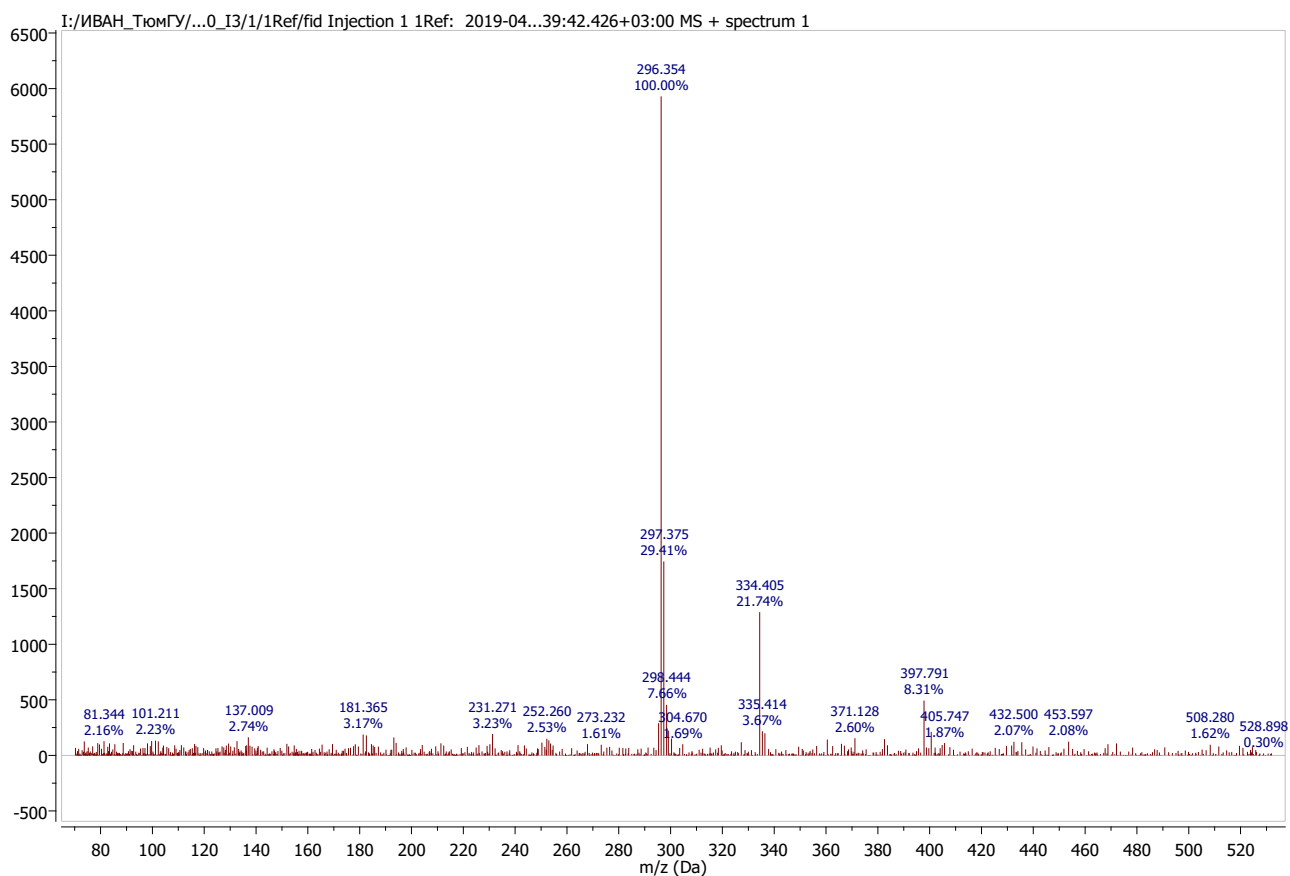
¹H (500 MHz, CDCl₃) and ¹³C (126 MHz, CDCl₃) NMR Spectra of 11

9. Copies of MS Spectra of Products

KSH21_4chasaT_120 #705 RT: 18,35 AV: 1 NL: 5,27E7
T: + c Full ms [50,00-650,00]

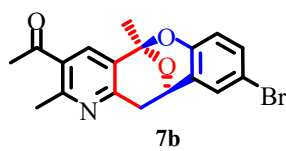
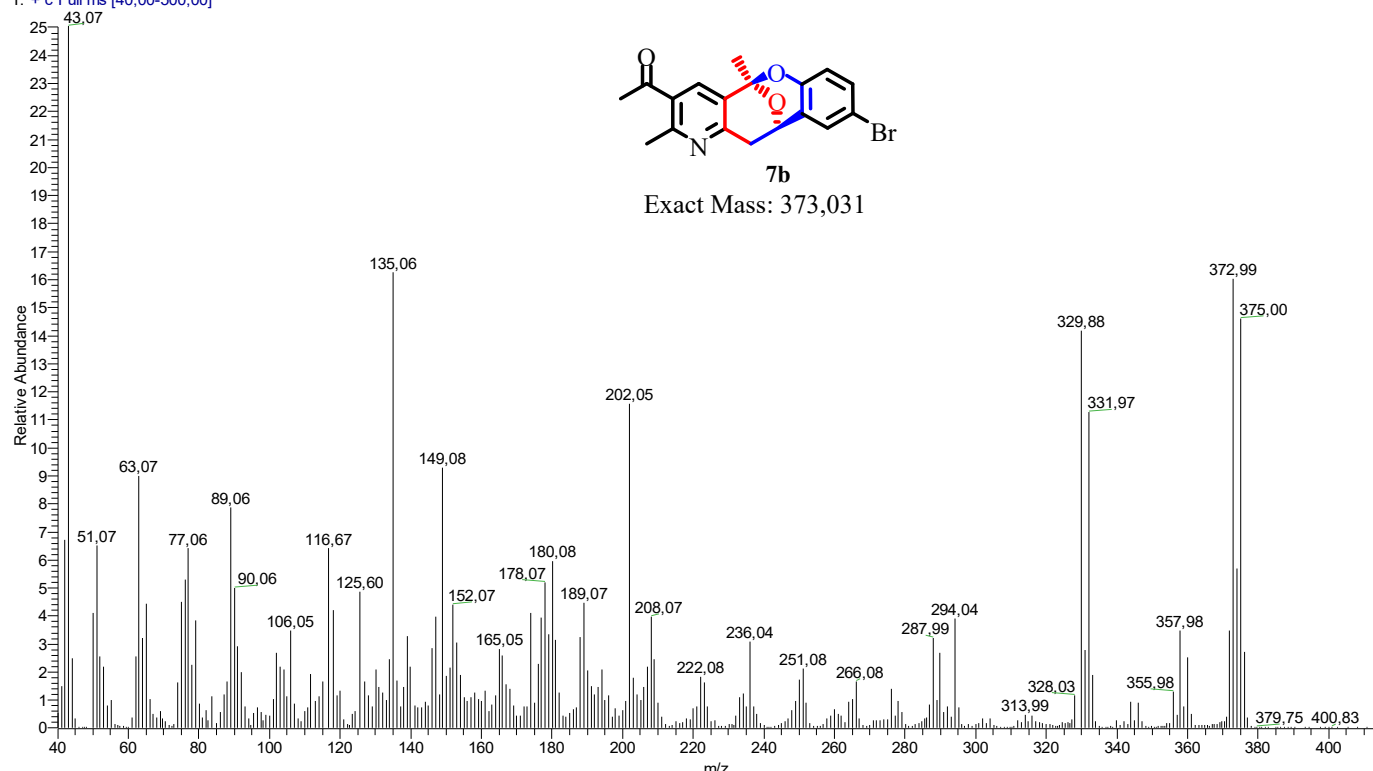


Mass spectrum (EI 70 eV) of (7a)

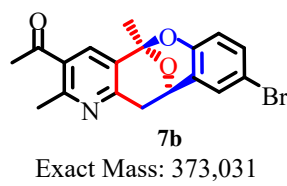
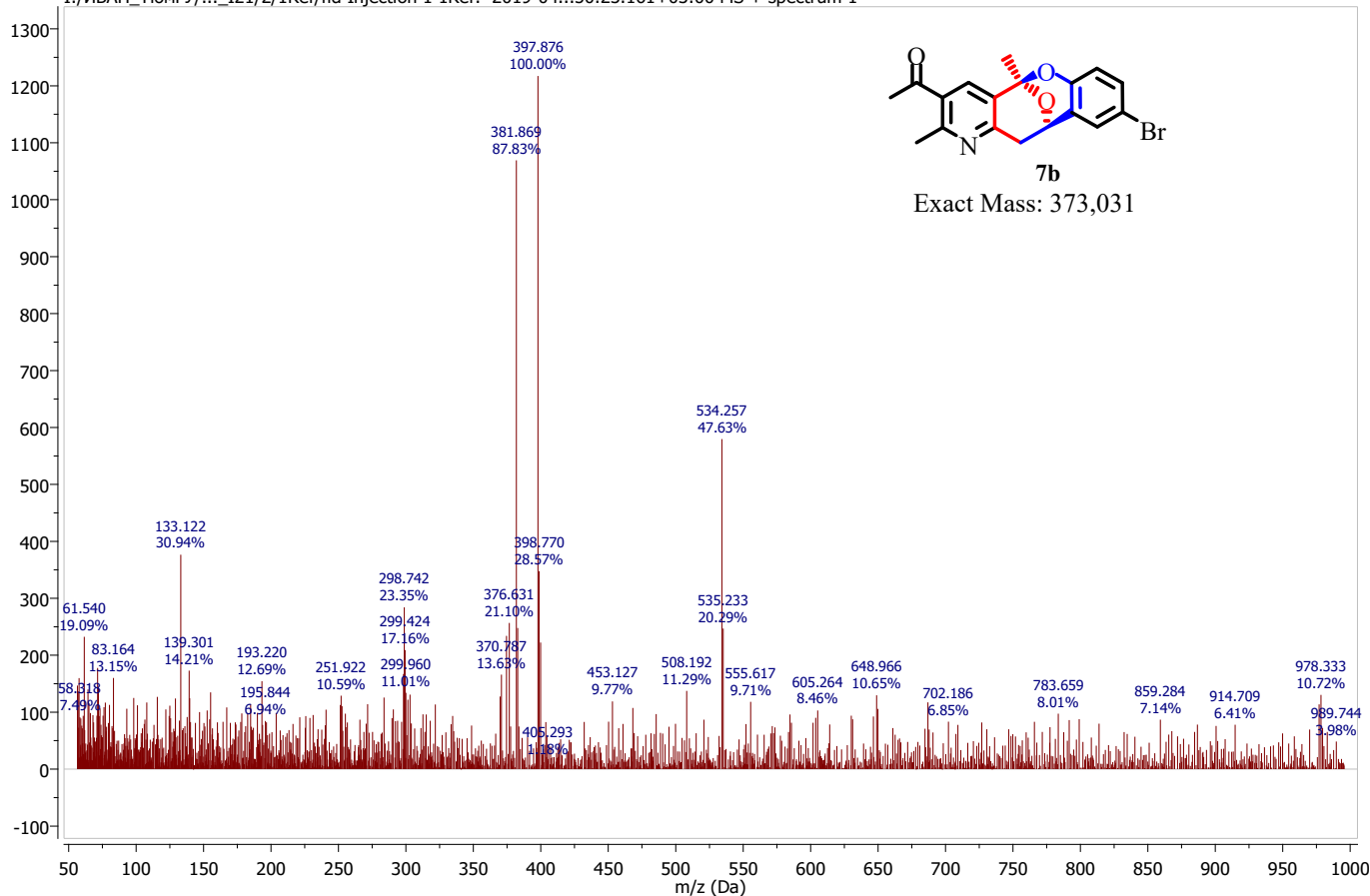


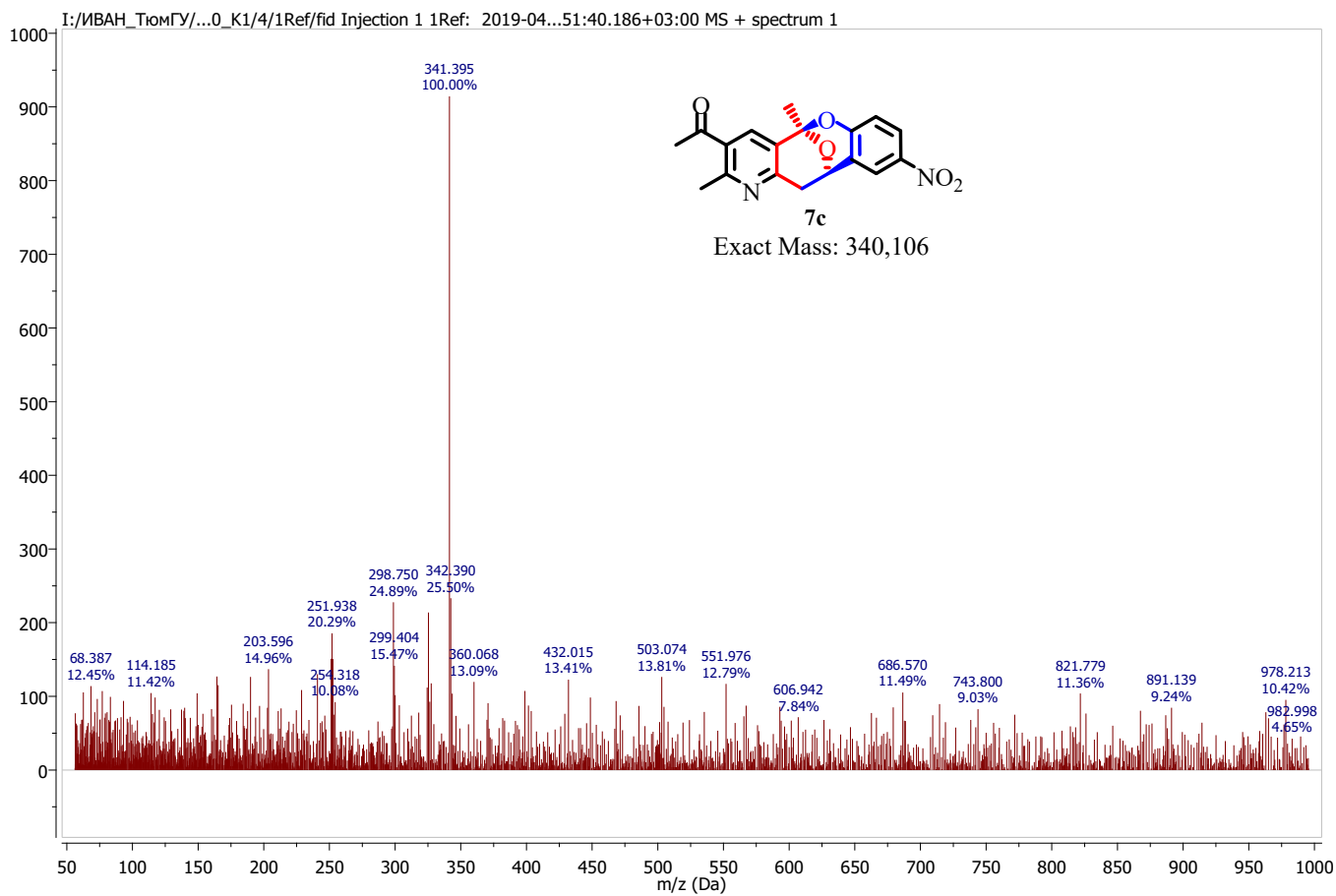
Mass spectrum (MALDI-TOF) of (7a)

KSH_73 #815 RT: 16.79 AV: 1 NL: 4.80E7
 T: + c Full ms [40,00-500,00]



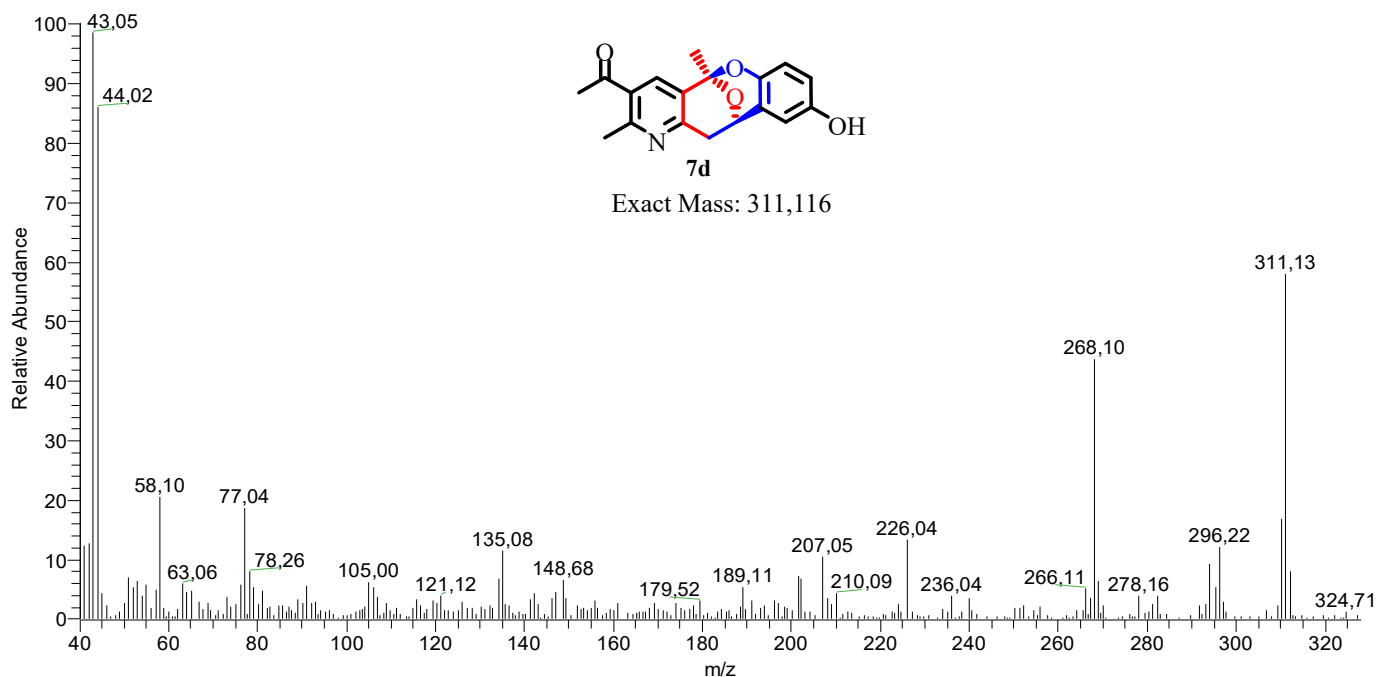
I:/ИВАН_ТюмГУ/..._I21/2/1Ref/fid Injection 1 1Ref: 2019-04...50:23.161+03:00 MS + spectrum 1





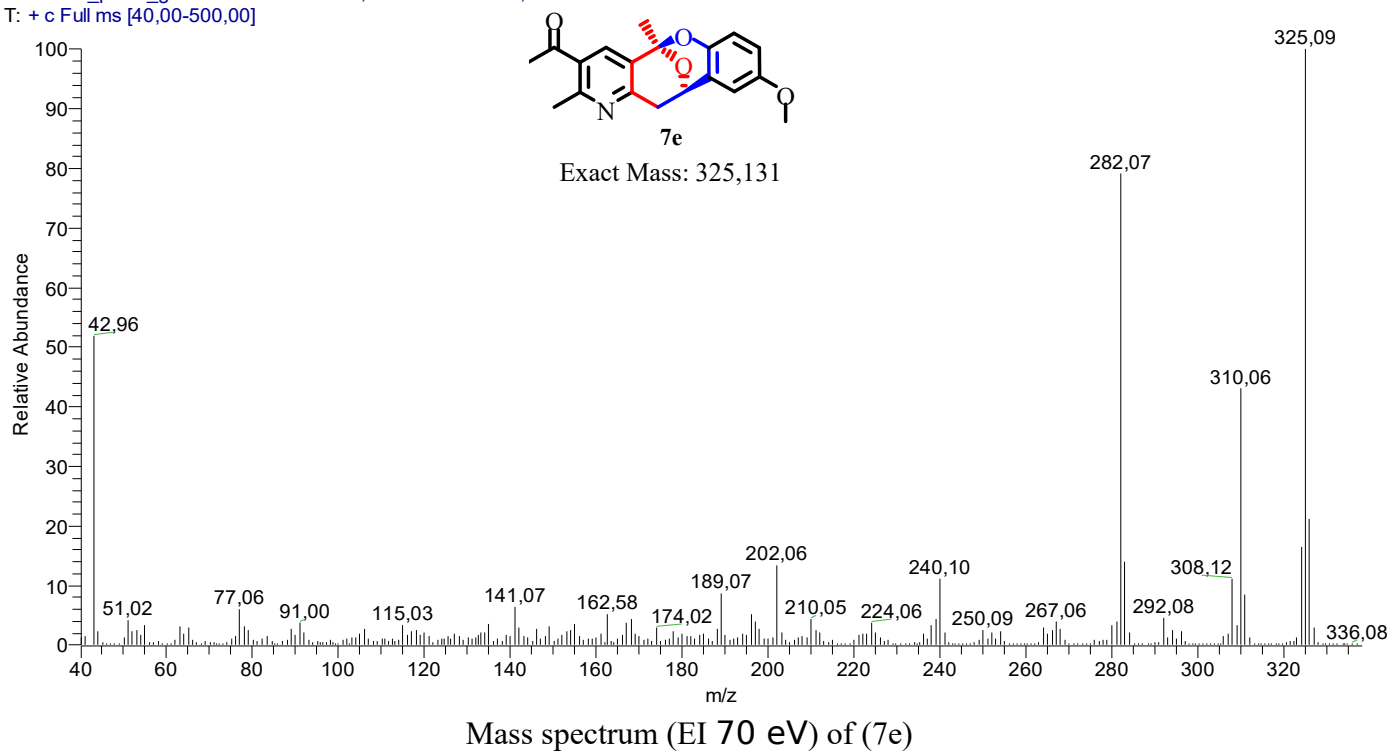
Mass spectrum (MALDI-TOF) of (7c)

KAO-120_200302123917 #850 RT: 17,34 AV: 1 NL: 9,85E4
T: + c Full ms [40,00-500,00]

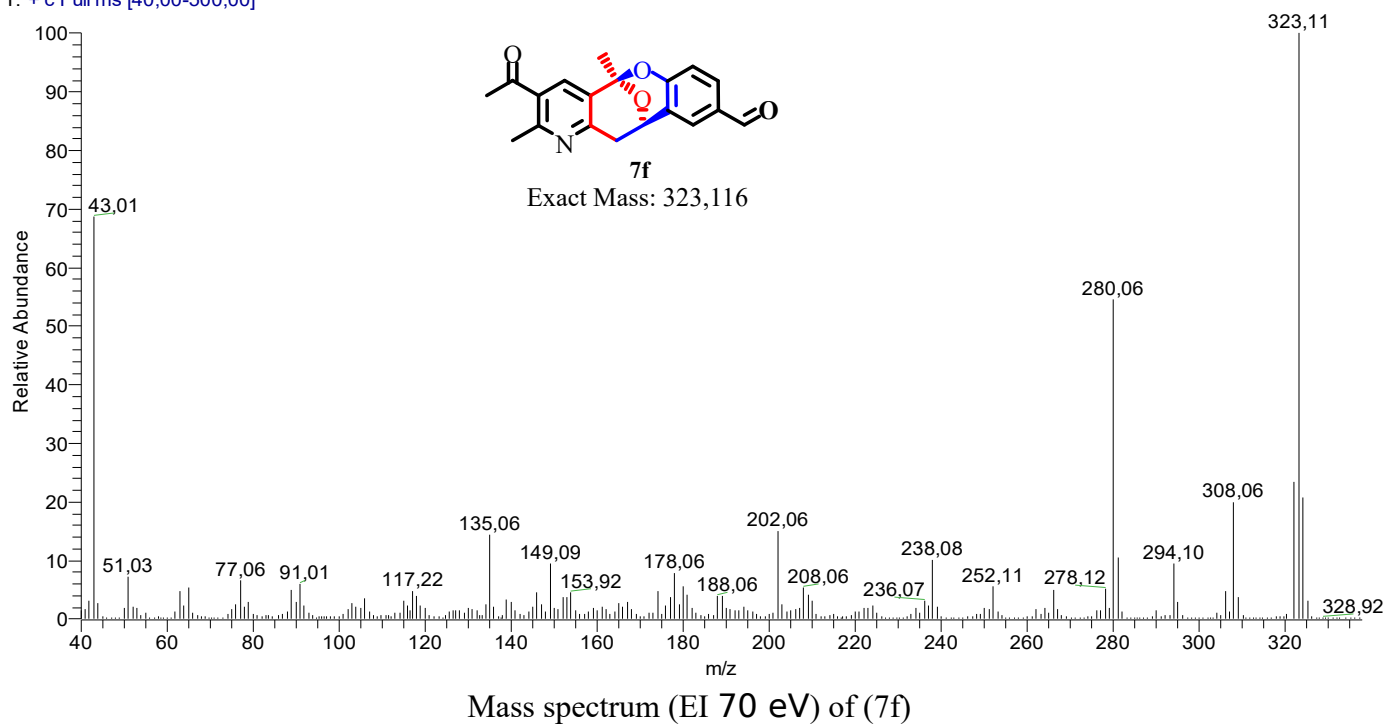


Mass spectrum (EI 70 eV) of (7d)

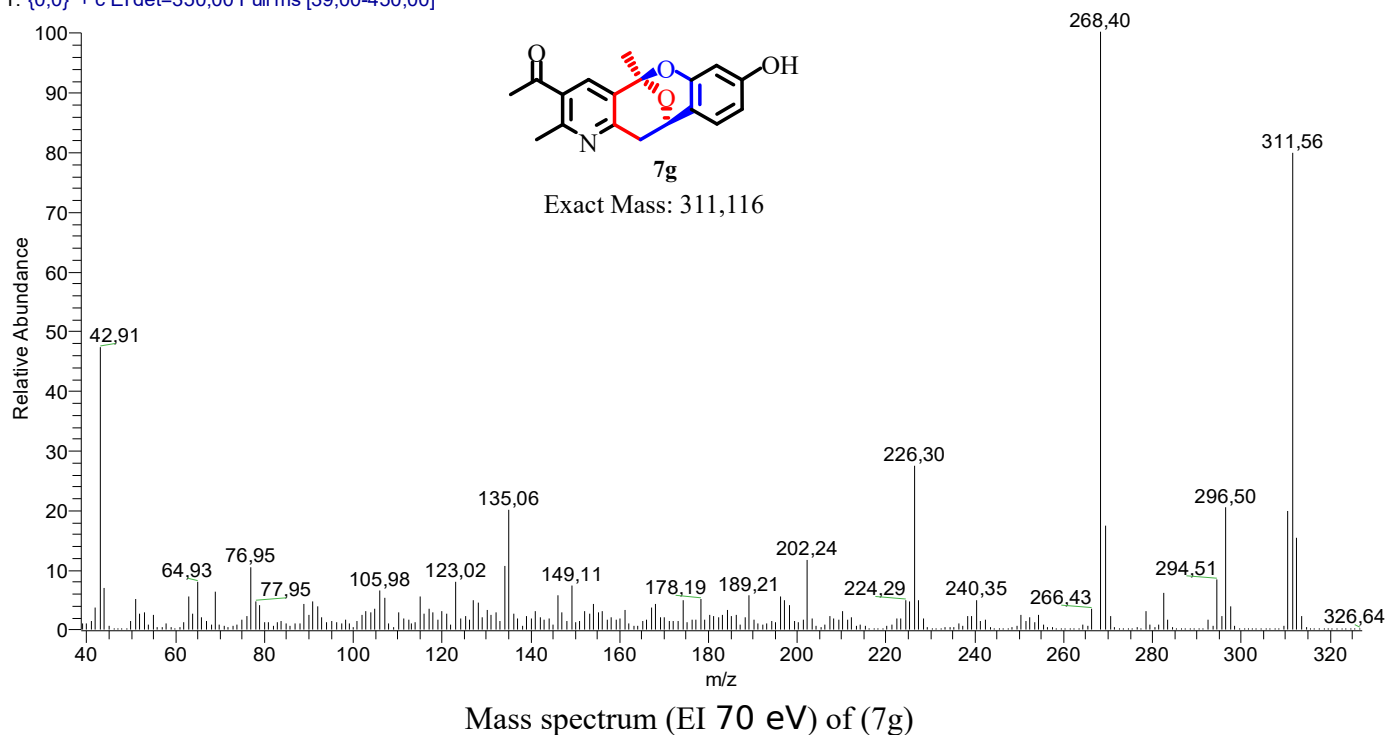
KAO-125_posle_geksana #766 RT: 16,02 AV: 1 NL: 9,51E6
T: + c Full ms [40,00-500,00]



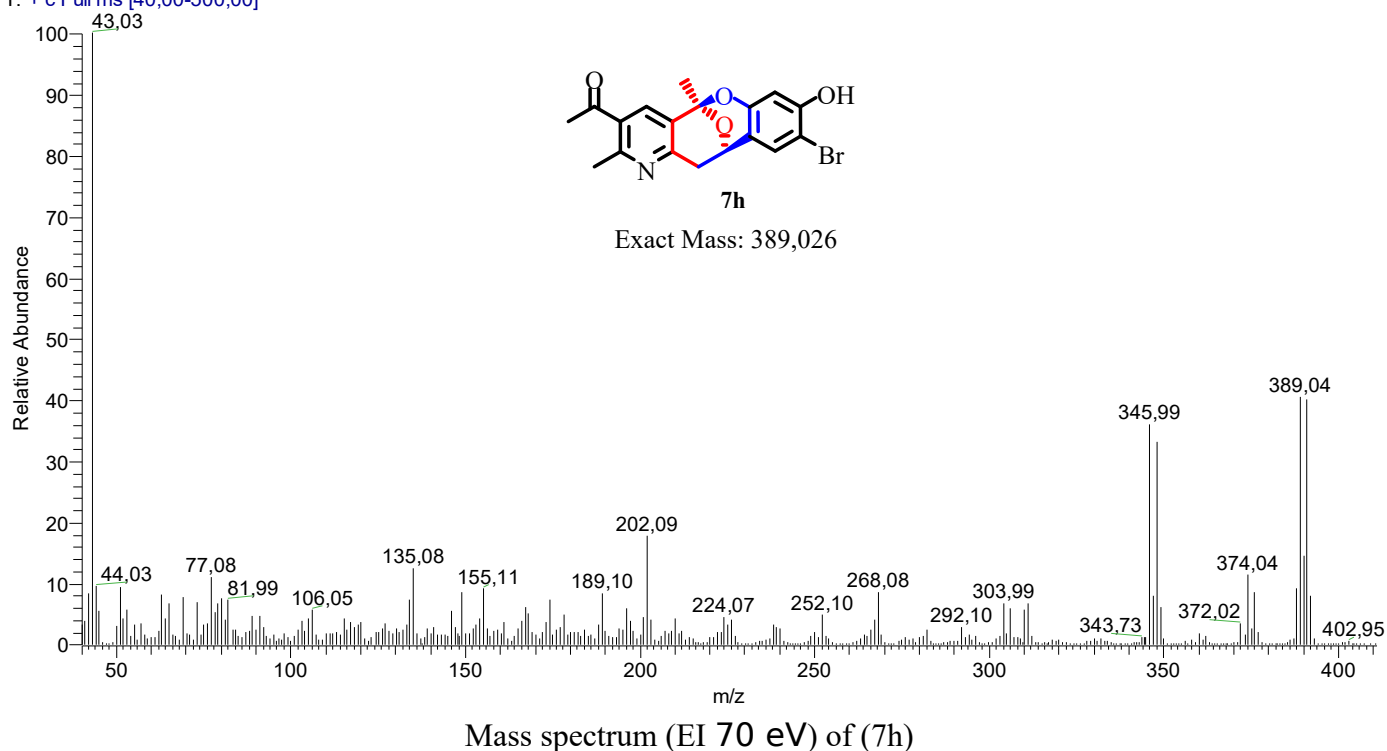
KAO-122krs #858 RT: 17,46 AV: 1 NL: 1,01E7
T: + c Full ms [40,00-500,00]



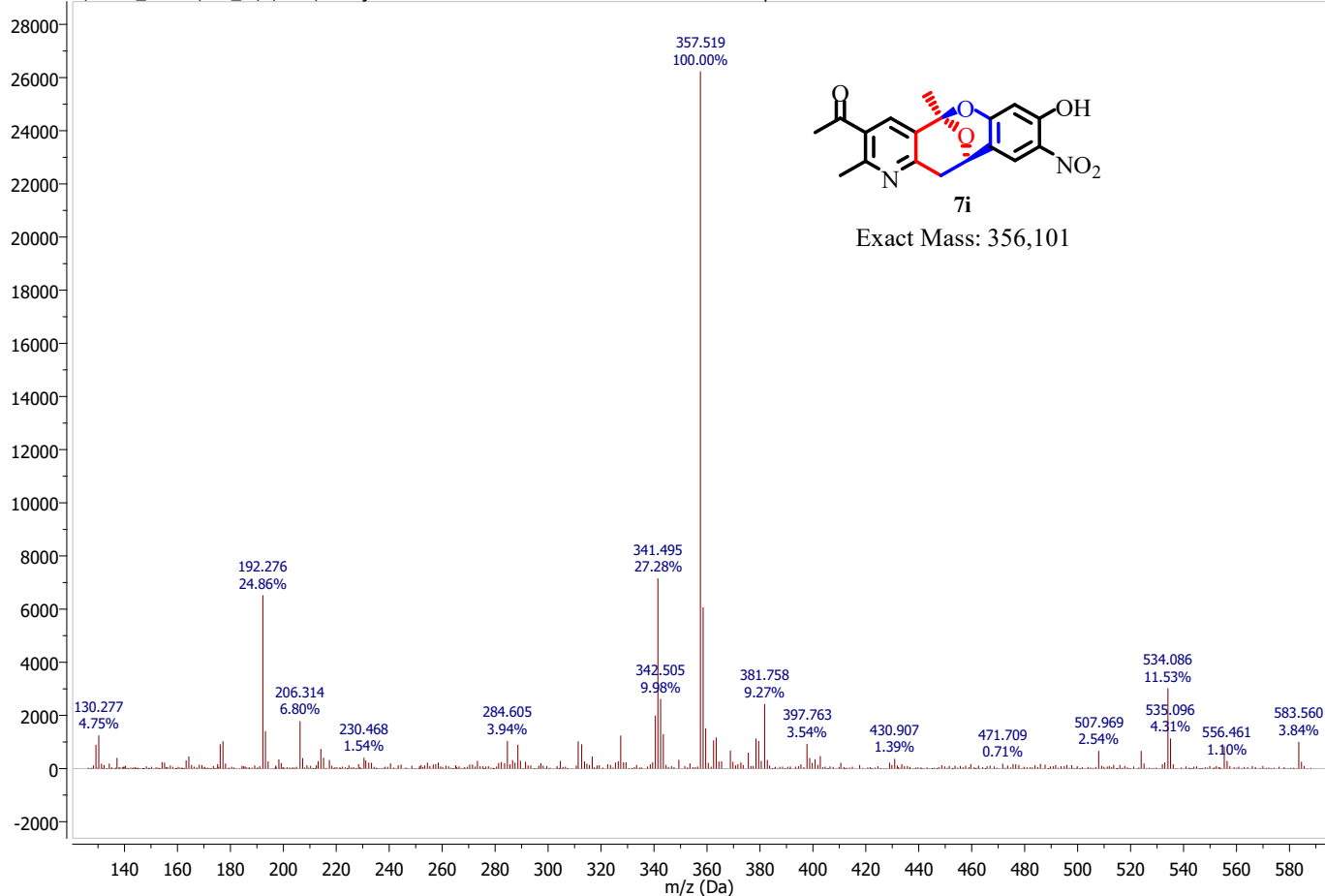
KVK_30 #2310 RT: 20,14 AV: 1 NL: 4,13E5
 T: {0;0} + c EI det=350,00 Full ms [39,00-450,00]



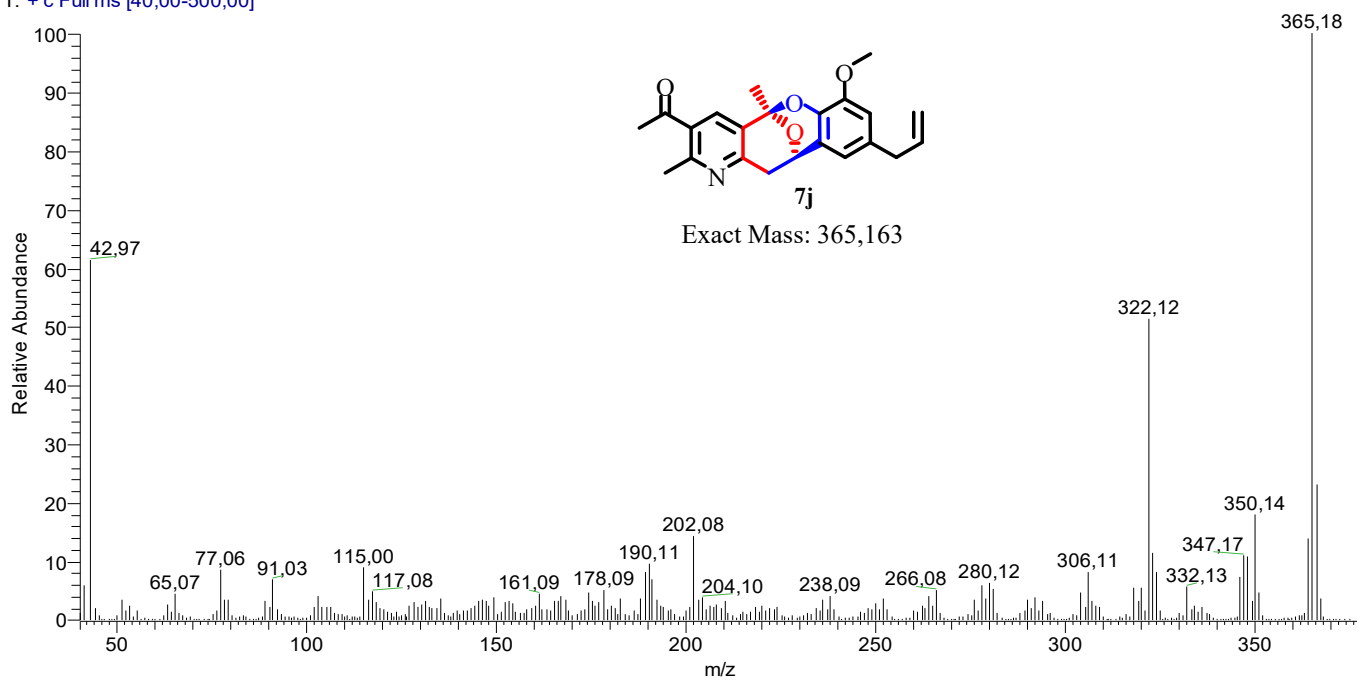
KVK-104povtor2 #907 RT: 19,23 AV: 1 NL: 4,25E6
 T: + c Full ms [40,00-500,00]



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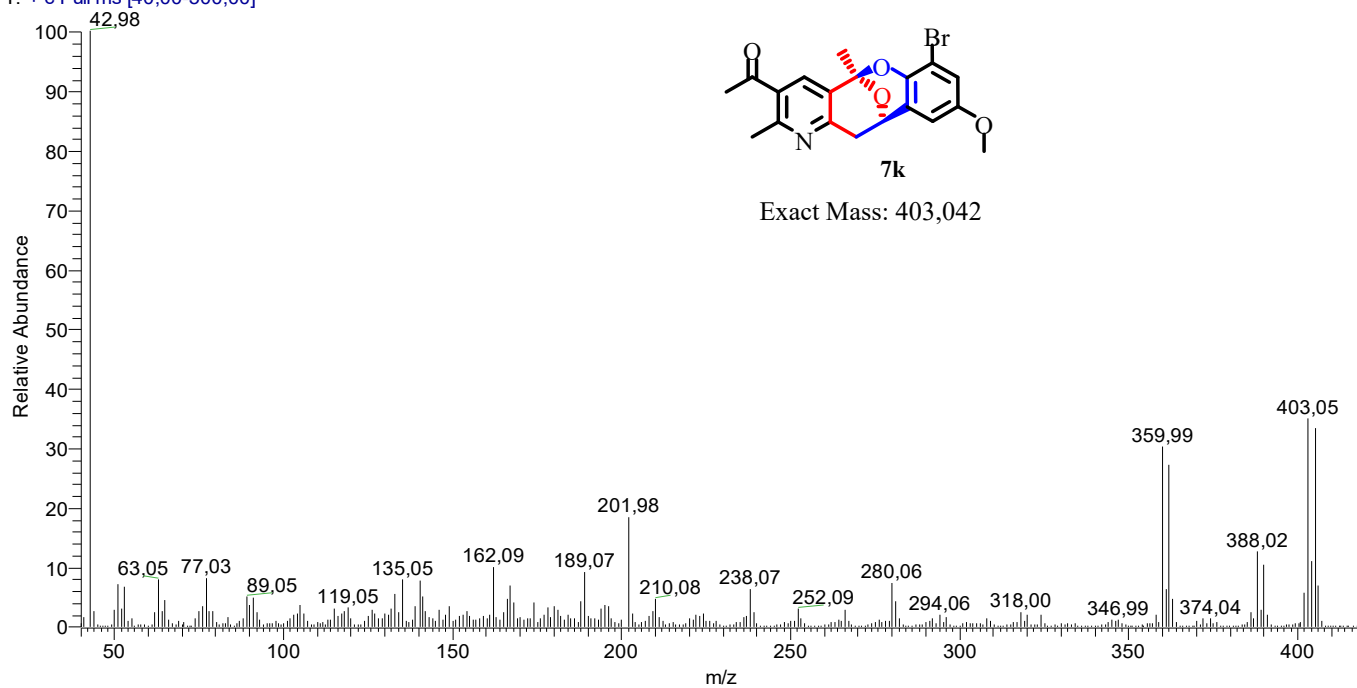
Mass spectrum (MALDI-TOF) of (7i)

КАО-126_чист #873 RT: 17,70 AV: 1 NL: 1,07E7
T: + c Full ms [40,00-500,00]

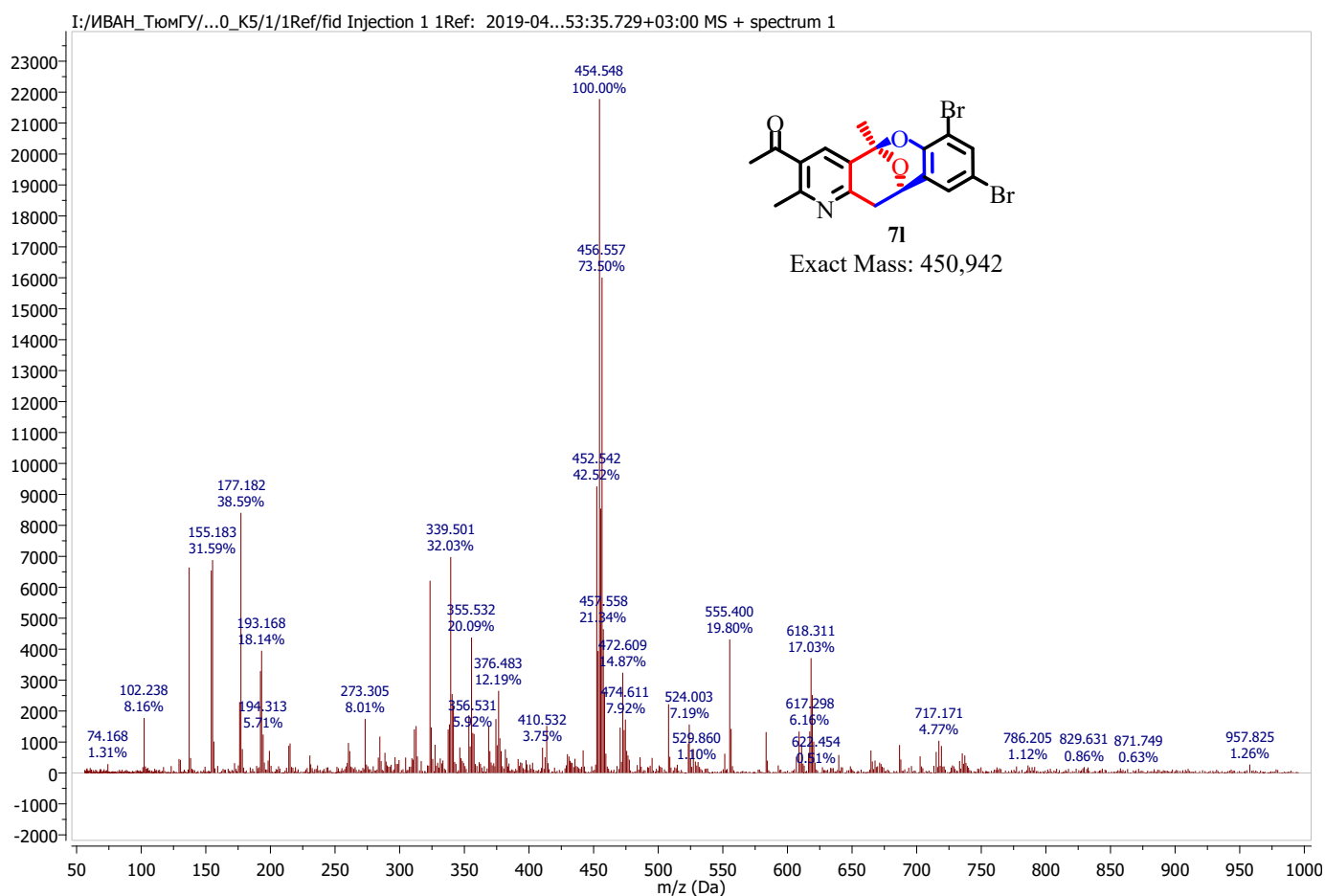
Mass spectrum (EI 70 eV) of (7j)

SUPPORTING INFORMATION

КАО-127_чист #922 RT: 18,47 AV: 1 NL: 3,27E7
 T: + c Full ms [40,00-500,00]

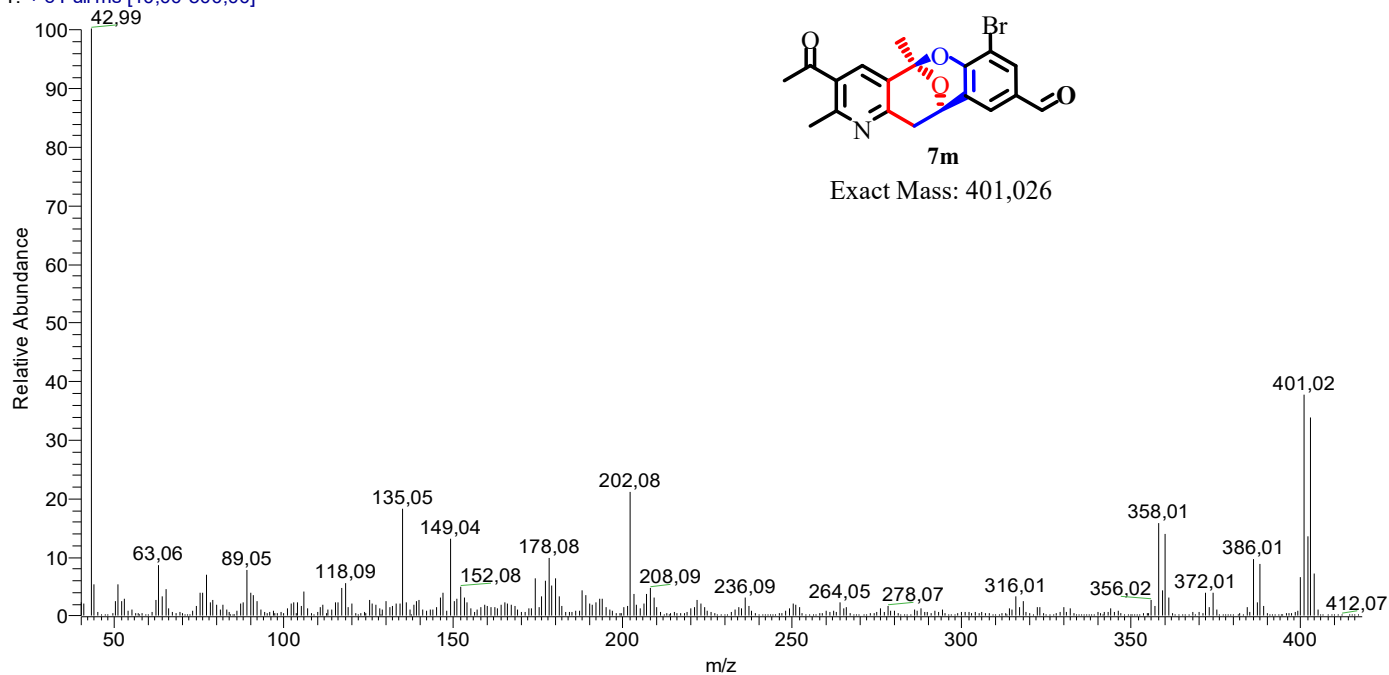


Mass spectrum (EI 70 eV) of (7k)



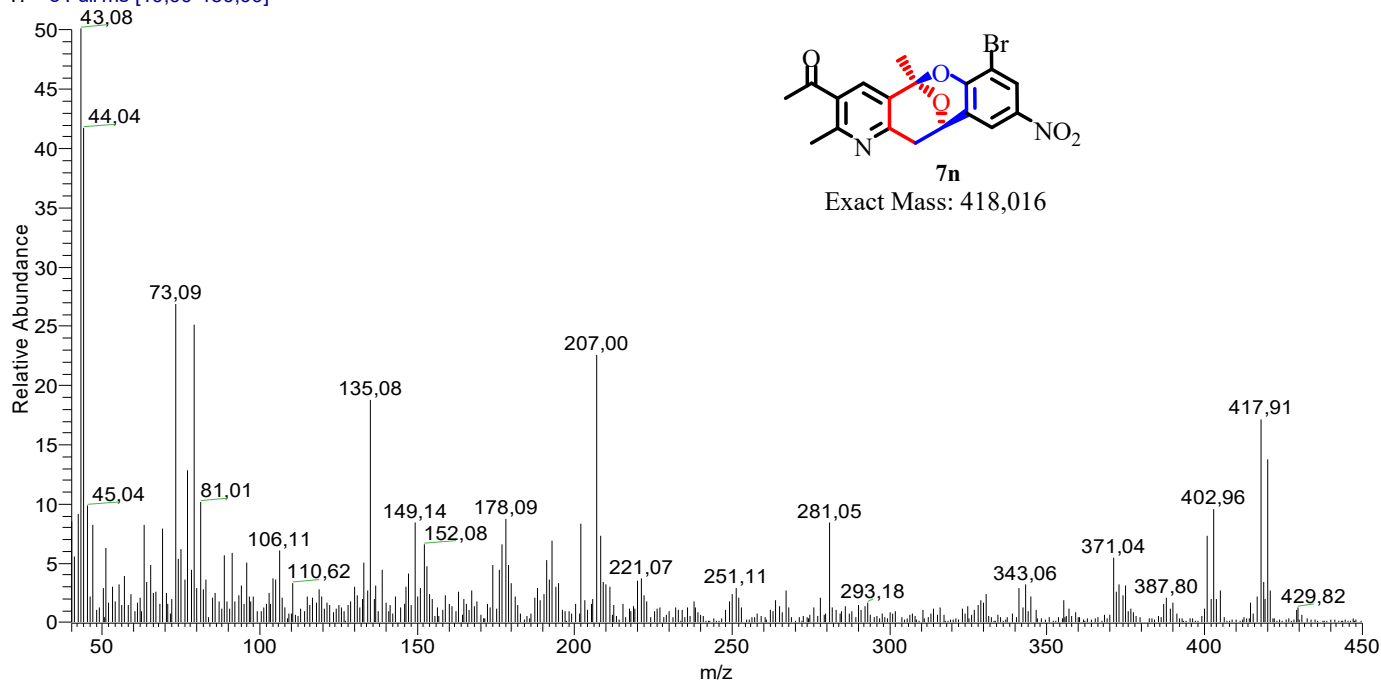
Mass spectrum (MALDI-TOF) of (7l)

KAO-131_tpl_165-170 #1019 RT: 20,99 AV: 1 NL: 6,47E6
 T: + c Full ms [40,00-500,00]



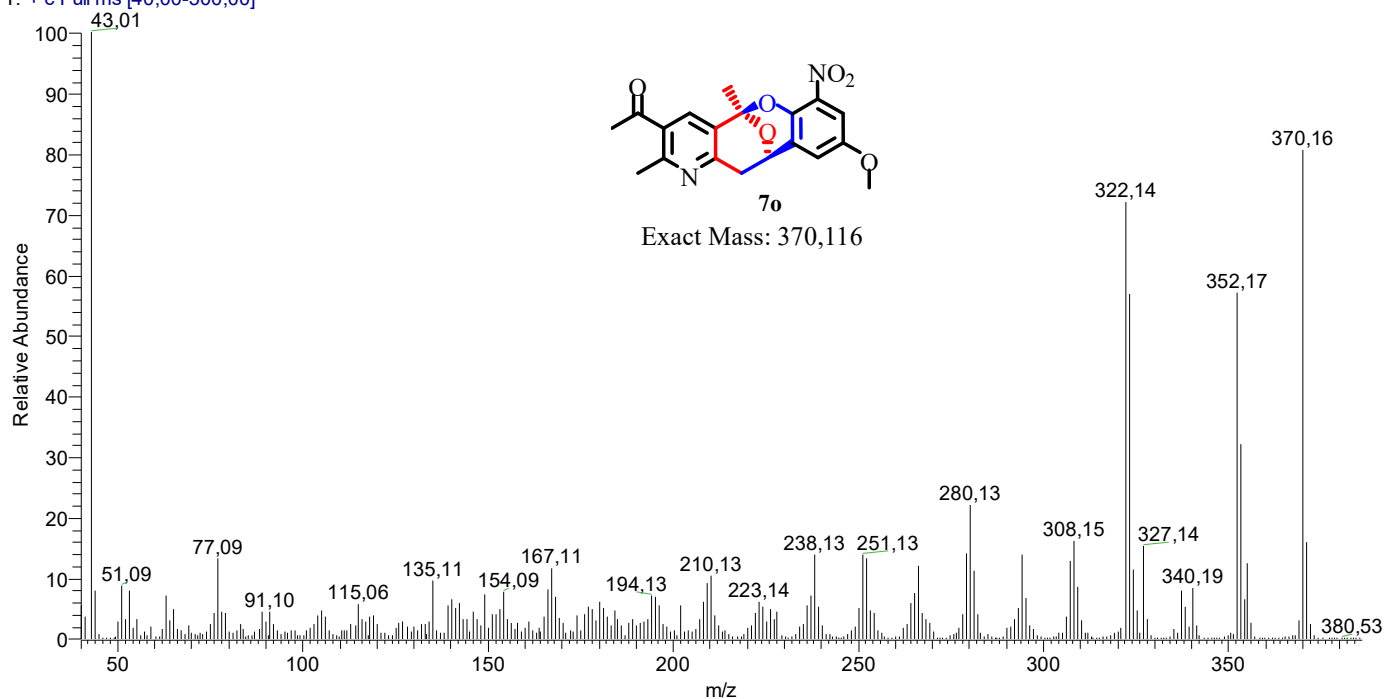
Mass spectrum (EI 70 eV) of (7m)

KCh_32_sir #1910 RT: 29,30 AV: 1 NL: 3,53E5
 T: + c Full ms [40,00-450,00]

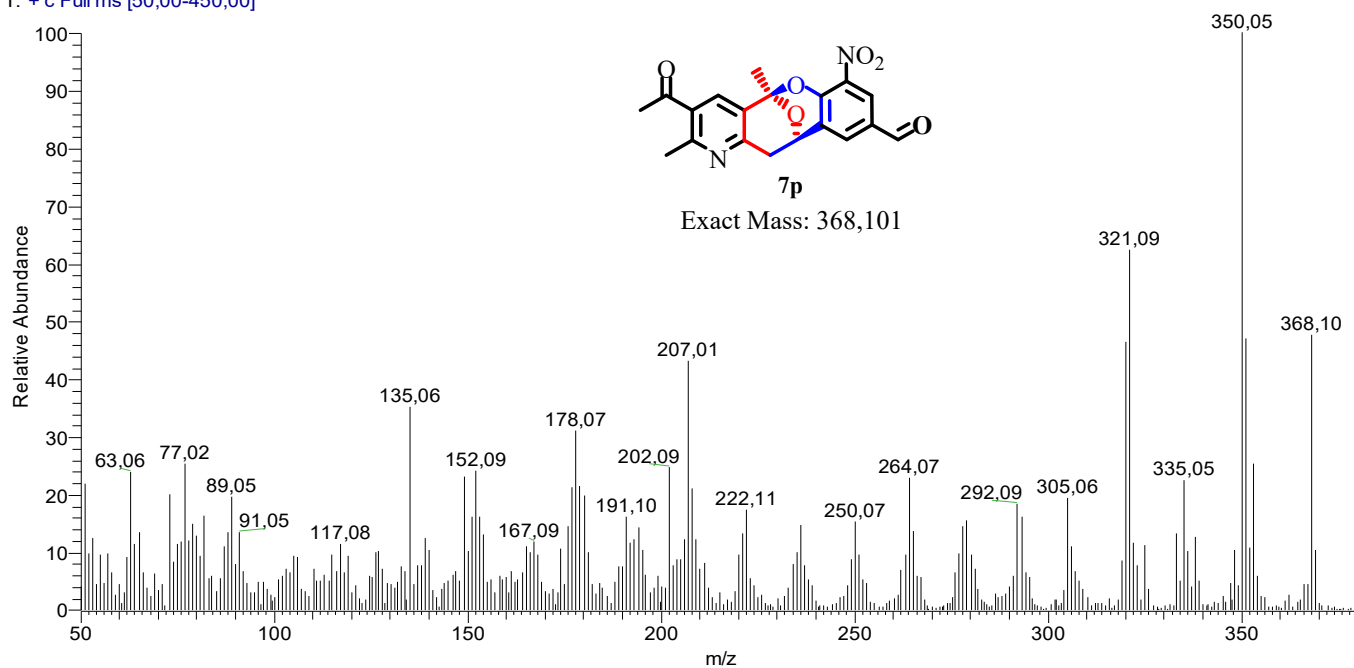


Mass spectrum (EI 70 eV) of (7n)

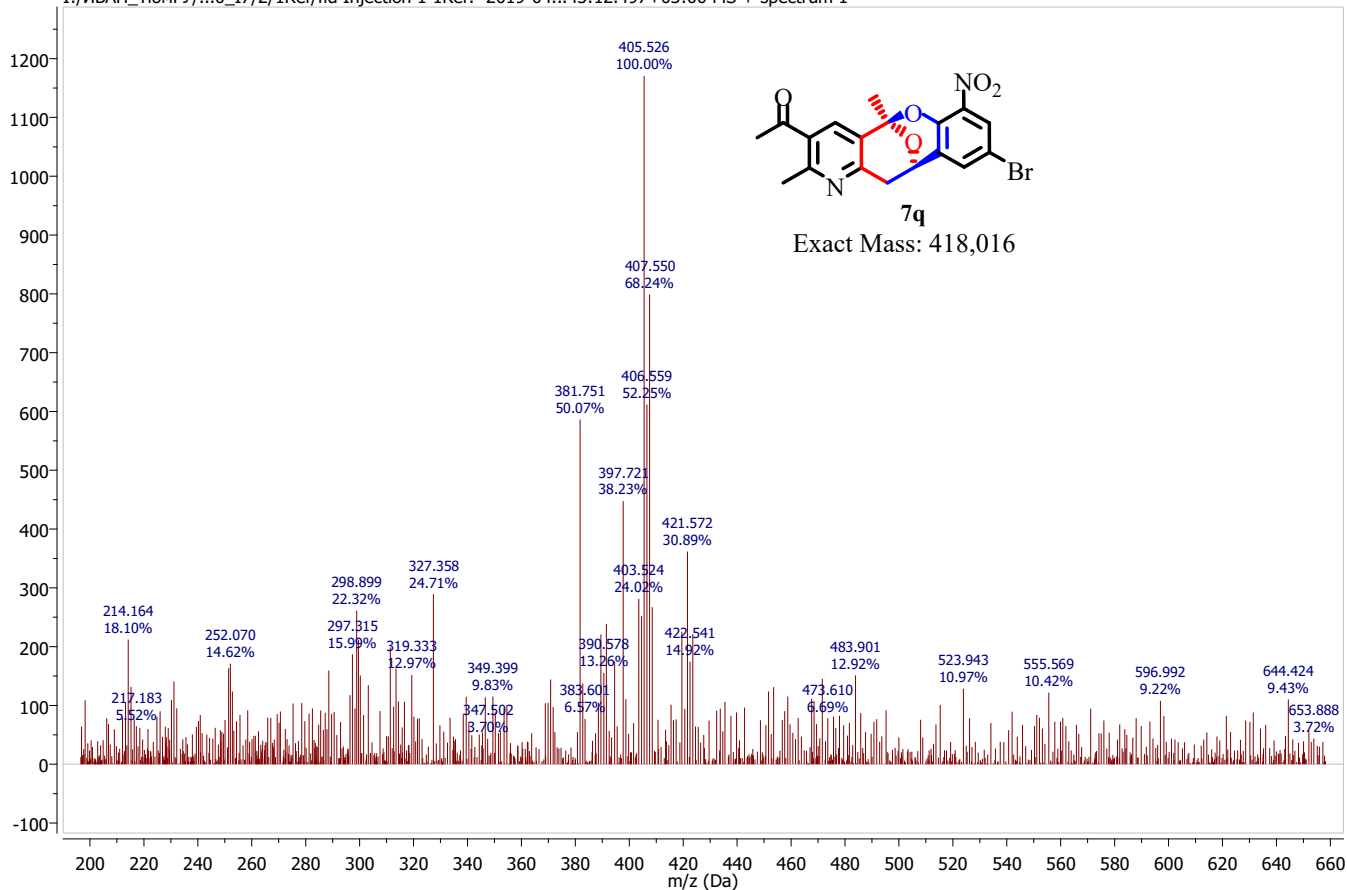
KAO-121_200302131409 #972 RT: 19,25 AV: 1 NL: 2,39E6
 T: + c Full ms [40,00-500,00]



KAO-135 #613 RT: 12,39 AV: 1 NL: 7,65E5
 T: + c Full ms [50,00-450,00]

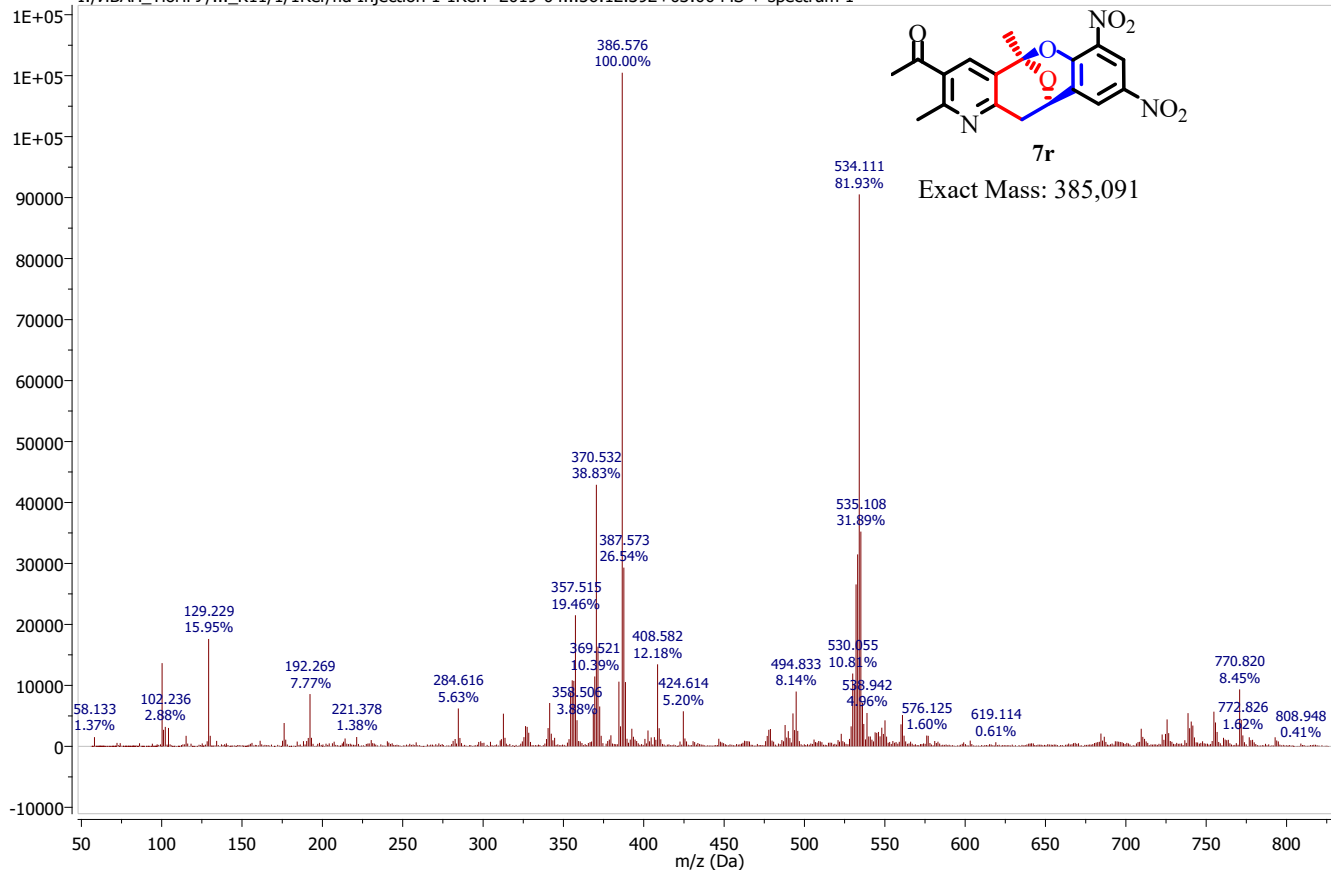


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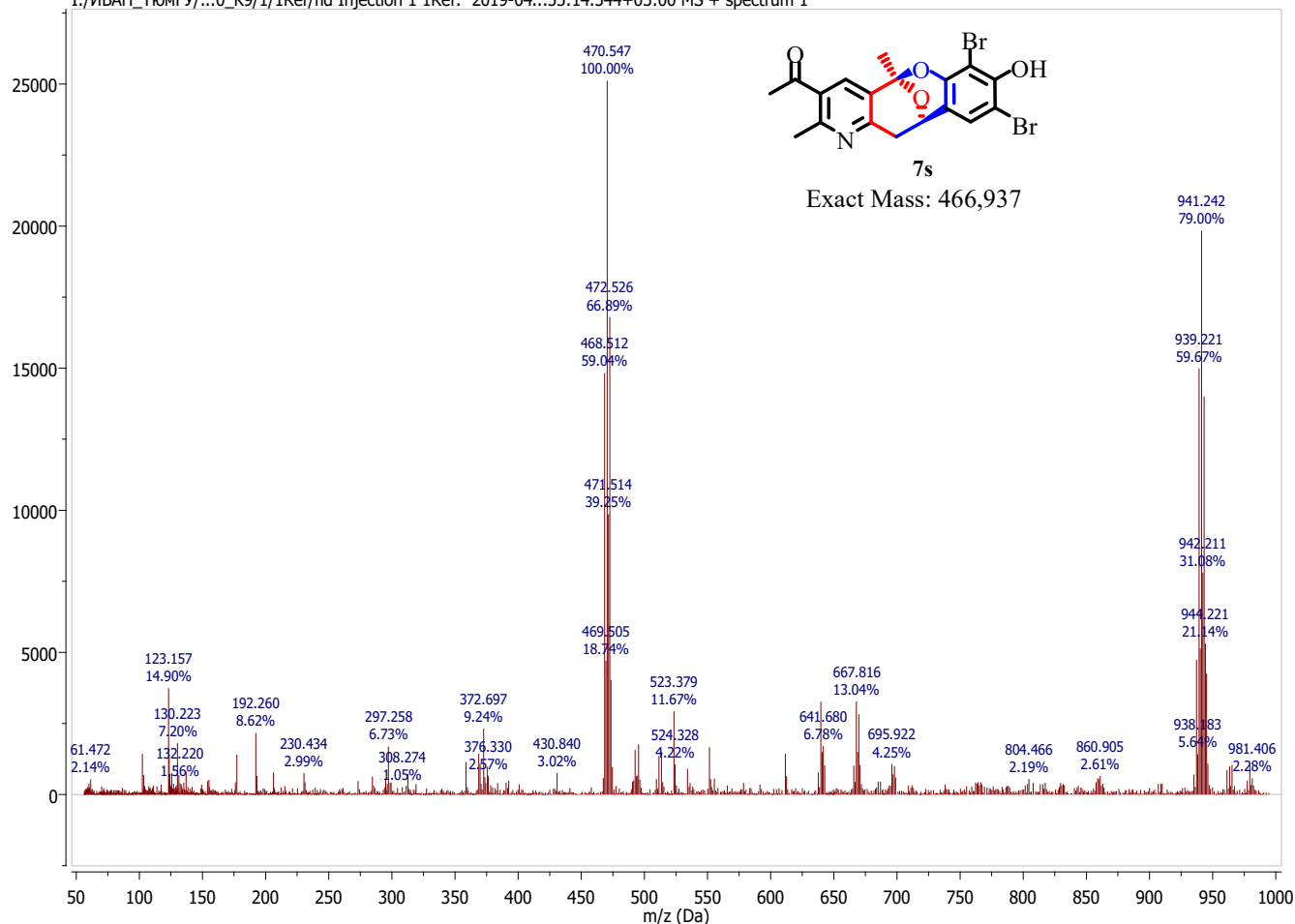
Mass spectrum (MALDI-TOF) of (7q)

I:/ИВАН_ТюмГУ/..._K11/1/1Ref/fid Injection 1 1Ref: 2019-04...56:12.392+03:00 MS + spectrum 1



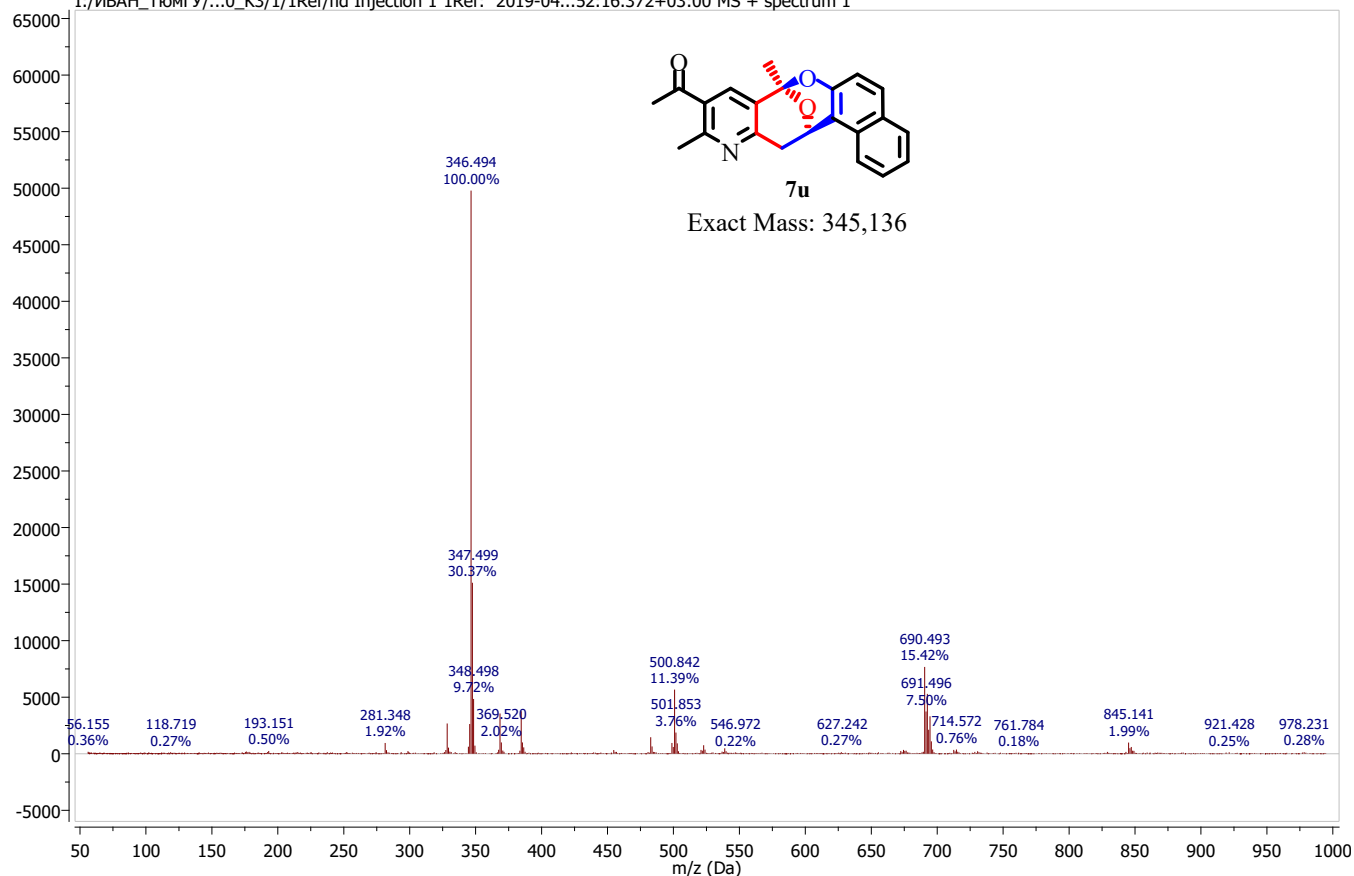
Mass spectrum (MALDI-TOF) of (7r)

I:/ИВАН_ТюмГУ/...0_K9/1/1Ref/fid Injection 1 1Ref: 2019-04...55:14.544+03:00 MS + spectrum 1



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

I:/ИВАН_ТюмГУ/...0_K3/1/1Ref/fid Injection 1 1Ref: 2019-04...52:16.372+03:00 MS + spectrum 1



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

KVE_15_200_kolonka #702 RT: 15,01 AV: 1 NL: 4,96E5
T: + c Full ms [40,00-500,00]

