

# Ultrasound-Assisted Synthesis of Fluorescent Azatetracyclic Derivatives: An Energy-Efficient Approach

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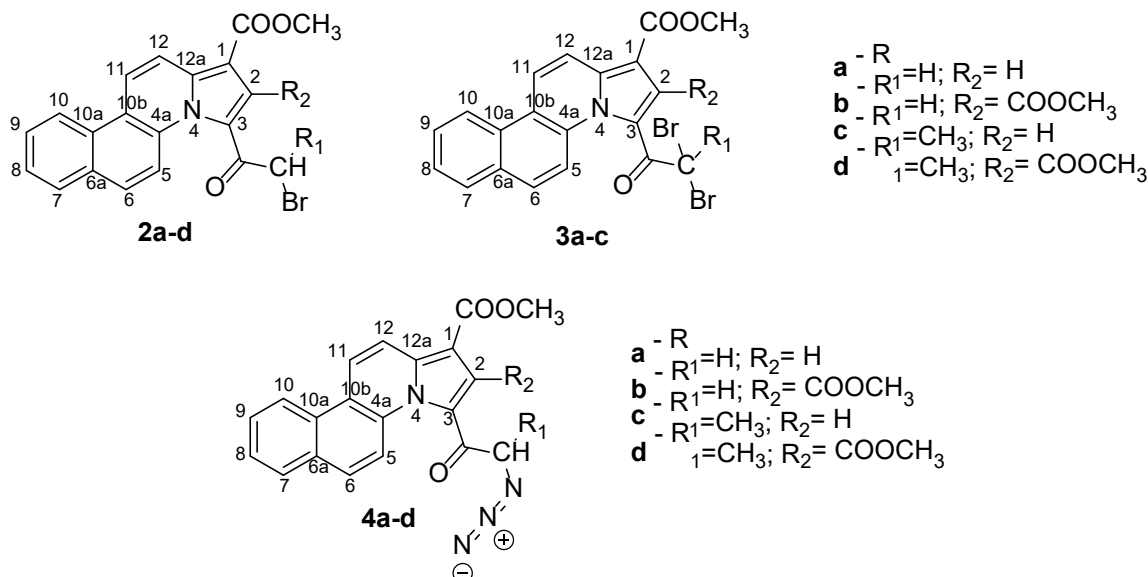
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### 1. Spectral characterization of the obtained compounds

The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet. Chemical shifts were reported in delta ( $\delta$ ) units, part per million (ppm) and coupling constants ( $J$ ) in Hz.



**Methyl 3-(2-bromoacetyl)benzo[f]pyrrolo[1,2-a]quinoline-1-carboxylate (2a).** (0.206 g, 52% (under conventional heating) and 0.345 g, 87% (under ultrasounds)) as a straw-yellow crystals, m.p. 194–195 °C;  $R_f$  (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.70; **IR** (cm<sup>-1</sup>): 3067, 3032 (C-H arom.), 2952 (C-H aliph.), 1696 (C=O, ester), 1650 (C=O, keto), 1611, 1547, 1499, 1445, 1406 (aromatic and heteroaromatic ring), 1241, 1194, 1178, 1154, 1088, 1028 (C–O–C, ester), 642 (C–Br); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.63 (1H, d,  $J$  = 9.5 Hz, H-11), 8.58 (1H, d,  $J$  = 8.0 Hz, H-10), 8.49 (1H, d,  $J$  = 9.5 Hz, H-12), 8.13 (1H, s, H-2), 8.01 (2H, m, overlapped peaks, H-5, H-6), 7.98 (1H, d,  $J$  = 8.0 Hz, H-7), 7.73 (1H, td,  $J$  = 7.0, 8.0 Hz, H-9), 7.65 (1H, t,  $J$  = 7.0, 8.0 Hz, H-8), 4.53 (2H, s, CH<sub>2</sub> of bromoacetyl group from 3<sup>rd</sup> position), 3.98 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  180.6 (CO keto group from 3<sup>rd</sup> position), 164.2 (CO keto ester from 1<sup>st</sup> position), 141.2 (C-12a), 132.4 (C-4a), 131.1 (C-6a), 129.8 (C-6), 129.6 (C-10a), 129.0 (C-7), 128.6 (C-2), 127.9 (C-9), 127.0 (C-8), 125.8 (C-3), 125.1 (C-11), 123.0 (C-10), 121.4 (C-10b), 119.7 (C-5), 117.4 (C-12), 107.4 (C-1), 51.7 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 32.3 (CH<sub>2</sub> of bromoacetyl group from 3<sup>rd</sup> position). Anal. calc. for C<sub>20</sub>H<sub>14</sub>BrNO<sub>3</sub> (396.24): C 60.62, H 3.56, N 3.53; found: C 60.56, H 3.51, N 3.50.

**Dimethyl 3-(2-bromoacetyl)benzo[f]pyrrolo[1,2-a]quinoline-1,2-dicarboxylate (2b).** (0.209 g, 46% (under conventional heating) and 0.336 g, 74% (under ultrasounds)) as a yellow crystals, m.p. 174–175 °C;  $R_f$  (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.53; **IR** (cm<sup>-1</sup>): 3104, 3024, 3000 (C-H arom.), 2949, 2928 (C-H aliph.), 1727, 1708 (C=O, ester), 1633 (C=O, keto), 1612, 1543, 1484, 1468, 1442, 1399, 1351, 1355 (aromatic and heteroaromatic ring), 1230, 1176, 1157, 1092 (C–O–C, ester), 629 (C–Br); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.46 (2H, m, overlapped peaks, H-10, H-11), 8.31 (1H, d,  $J$  = 9.5 Hz, H-12), 7.96 (1H, d,  $J$  = 9.0 Hz, H-6), 7.92 (1H, d,  $J$  = 8.0 Hz, H-7), 7.69 (1H, td,  $J$  = 7.0, 8.0 Hz, H-9), 7.61 (2H, m, overlapped peaks, H-5, H-8), 4.37 (2H, s, CH<sub>2</sub> of bromoacetyl group from 3<sup>rd</sup> position), 4.06 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 3.94 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  183.5 (CO keto group from 3<sup>rd</sup> position), 166.5 (CO keto ester from 1<sup>st</sup> position), 163.3 (CO keto ester from 2<sup>nd</sup> position), 138.2 (C-12a), 131.4 (C-4a), 130.9 (C-6a), 130.4 (C-6), 130.2 (C-10a), 129.6 (C-2), 128.9 (C-7), 128.2 (C-9), 127.2 (C-8), 124.3 (C-11), 123.8 (C-3), 122.9 (C-10), 121.5 (C-10b), 118.3 (C-5), 117.7 (C-12), 105.4 (C-1), 53.6 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 52.0 (CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position), 33.6 (CH<sub>2</sub> of bromoacetyl group

from 3<sup>rd</sup> position). Anal. calc. for C<sub>22</sub>H<sub>16</sub>BrNO<sub>5</sub> (454.28): C 58.17, H 3.55, N 3.08; found: C 58.12, H 3.50, N 3.04.

**Methyl 3-(2-bromopropanoyl)benzo[f]pyrrolo[1,2-a]quinoline-1-carboxylate (2c).** (0.217 g, 53% (under conventional heating) and 0.349 g, 85% (under ultrasounds)) as a straw-yellow crystals, m.p. 201–202 °C; R<sub>f</sub> (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.70; IR (cm<sup>-1</sup>): 3062, 3053, 3000 (C-H arom.), 2949, 2937 (C-H aliph.), 1709 (C=O, ester), 1641 (C=O, keto), 1609, 1545, 1505, 1447, 1413, 1355 (aromatic and heteroaromatic ring), 1237, 1231, 1158, 1122, 1086 (C–O–C, ester) 609 (C–Br); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.58 (2H, m, overlapped peaks, H-10, H-11), 8.46 (1H, d, J = 9.5 Hz, H-12), 8.08 (1H, s, H-2), 8.01 (1H, d, J = 9.5 Hz, H-6), 7.95 (2H, m, overlapped peaks, H-5, H-7), 7.71 (1H, t, J = 7.5 Hz, H-9), 7.63 (1H, t, J = 7.5 Hz, H-8), 5.48 (2H, q, J = 6.5 Hz, CHBr of bromopropanoyl group from 3<sup>rd</sup> position), 3.97 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 2.01 (3H, d, J = 6.5 Hz, CH<sub>3</sub> of bromopropanoyl group from 3<sup>rd</sup> position); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 183.0 (CO keto group from 3<sup>rd</sup> position), 164.3 (CO keto ester from 1<sup>st</sup> position), 141.2 (C-12a), 132.3 (C-4a), 131.0 (C-6a), 129.8 (C-6), 129.6 (C-10a), 128.9 (C-7), 127.9 (C-9), 127.1 (C-2), 126.9 (C-8), 125.9 (C-3), 124.8 (C-11), 123.0 (C-10), 121.3 (C-10b), 119.5 (C-5), 117.4 (C-12), 107.1 (C-1), 51.7 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 45.1 (CHBr of bromopropanoyl group from 3<sup>rd</sup> position), 20.7 (CH<sub>3</sub> of bromopropanoyl group from 3<sup>rd</sup> position). Anal. calc. for C<sub>21</sub>H<sub>16</sub>BrNO<sub>3</sub> (410.27): C 61.48, H 3.93, N 3.41; found: C 61.42, H 3.88, N 3.37.

**Dimethyl 3-(2-bromopropanoyl)benzo[f]pyrrolo[1,2-a]quinoline-1,2-dicarboxylate (2d).** (0.253 g, 54% (under conventional heating) and 0.328 g, 70% (under ultrasounds)) as a yellow crystals, m.p. 162–163 °C; R<sub>f</sub> (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.53; IR (cm<sup>-1</sup>): 3057, 3036, 3007 (C-H arom.), 2952, 2932 (C-H aliph.), 1741, 1708 (C=O, ester), 1659 (C=O, keto), 1604, 1541, 1498, 1470, 1400, 1341 (aromatic and heteroaromatic ring), 1260, 1213, 1180, 1133, 1100 (C–O–C, ester), 657 (C–Br); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.26 (1H, d, J = 8.5 Hz, H-10), 8.22 (1H, d, J = 10.0 Hz, H-11), 8.07 (1H, d, J = 10.0 Hz, H-12), 7.86 (1H, d, J = 9.5 Hz, H-6), 7.79 (1H, d, J = 7.5 Hz, H-7), 7.66 (1H, d, J = 9.5 Hz, H-5), 7.55 (1H, t, J = 7.0 Hz, H-9), 7.49 (1H, t, J = 7.0 Hz, H-8), 5.09 (1H, q, J = 7.0 Hz, CHBr of bromopropanoyl group from 3<sup>rd</sup> position), 4.05 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 3.91 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position), 1.95 (3H, d, J = 7.0 Hz, CH<sub>3</sub> of bromopropanoyl group from 3<sup>rd</sup> position); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 185.6 (CO keto group from 3<sup>rd</sup> position), 166.6 (CO keto ester from 1<sup>st</sup> position), 163.3 (CO keto ester from 2<sup>nd</sup> position), 138.1 (C-12a), 131.2 (C-4a), 130.6 (C-6a), 130.2 (C-6), 129.6 (C-10a), 129.3 (C-2), 128.6 (C-7), 127.9 (C-9), 126.9 (C-8), 123.9 (C-11), 123.6 (C-3), 122.6 (C-10), 121.1 (C-10b), 117.9 (C-5), 117.3 (C-12), 104.9 (C-1), 53.4 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 51.9 (CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position), 46.8 (CHBr of bromopropanoyl group from 3<sup>rd</sup> position), 20.4 (CH<sub>3</sub> of bromopropanoyl group from 3<sup>rd</sup> position). Anal. calc. for C<sub>23</sub>H<sub>18</sub>BrNO<sub>5</sub> (468.30): C 58.99, H 3.87, N 2.99; found: C 58.93, H 3.83, N 2.94.

**Methyl 3-(2,2-dibromoacetyl)benzo[f]pyrrolo[1,2-a]quinoline-1-carboxylate (3a).** (0.048 g, 10% (under conventional heating) and 0 g, 0% (under ultrasounds)) as a yellow crystals, m.p. 170–171 °C; R<sub>f</sub> (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.68; IR (cm<sup>-1</sup>): 3113, 3022, 2996 (C-H arom.), 2943 (C-H aliph.), 1693 (C=O, ester), 1652 (C=O, keto), 1543, 1504, 1467, 1450, 1334 (aromatic and heteroaromatic ring), 1284, 1256, 1233, 1188, 1163, 1115 (C–O–C, ester), 698, 648 (C–Br); <sup>1</sup>H NMR (500 MHz, DMSO): δ 9.06 (1H, d, J = 9.5 Hz, H-11), 8.88 (1H, d, J = 8.5 Hz, H-10), 8.66 (1H, s, H-2), 8.46 (1H, d, J = 9.5 Hz, H-12), 8.27 (1H, d, J = 9.5 Hz, H-6), 8.14 (1H, d, J = 7.5 Hz, H-7), 8.09 (1H, s, CH of dibromoacetyl group from 3<sup>rd</sup> position), 7.82 (2H, m, overlapped peaks, H-9, H-5), 7.76 (1H, t, J = 7.5 Hz, H-8), 3.92 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position); <sup>13</sup>C NMR (125 MHz, DMSO): δ 176.3 (CO keto group from 3<sup>rd</sup> position), 163.3 (CO keto ester from 1<sup>st</sup> position), 141.1 (C-12a), 131.3 (C-4a), 130.5 (C-6a), 130.2 (C-6), 129.1 (C-10a), 128.8 (C-7), 128.6 (C-2), 128.3 (C-9), 127.4 (C-8), 126.3 (C-11), 123.6 (C-10), 121.4 (C-10b), 120.9 (C-3), 118.5 (C-5), 117.0 (C-12), 106.8 (C-1), 51.6 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 44.4 (CH of dibromoacetyl group from 3<sup>rd</sup> position). Anal. calc. for C<sub>20</sub>H<sub>13</sub>Br<sub>2</sub>NO<sub>3</sub> (475.14): C 50.56, H 2.76, N 2.95; found: C 50.51, H 2.73, N 2.90.

**Dimethyl 3-(2,2-dibromoacetyl)benzo[f]pyrrolo[1,2-a]quinoline-1,2-dicarboxylate (3b).** (0.080 g, 15% (under conventional heating) and 0 g, 0% (under ultrasounds)) as a yellow-orange

crystals, *m.p.* 178–179 °C; *R<sub>f</sub>* (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.60; **IR** (cm<sup>−1</sup>): 3047, 3037, 3003, (C–H arom.), 2944, 2930 (C–H aliph.), 1733, 1717 (C=O, ester), 1669 (C=O, keto), 1610, 1542, 1468, 1441, 1401, 1356, 1338 (aromatic and heteroaromatic ring), 1251, 1219, 1184, 1123, 1097 (C–O–C, ester), 652, 639 (C–Br); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.56 (2H, *m*, overlapped peaks, H-10, H-11), 8.39 (1H, *d*, *J* = 9.5 Hz, H-12), 8.04 (1H, *d*, *J* = 9.5 Hz, H-6), 7.97 (1H, *d*, *J* = 7.5 Hz, H-7), 7.73 (2H, *m*, overlapped peaks, H-9, H-5), 7.66 (1H, *t*, *J* = 7.5 Hz, H-8), 6.70 (1H, *s*, CH of dibromoacetyl group from 3<sup>rd</sup> position), 4.07 (3H, *s*, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 3.96 (3H, *s*, CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 178.5 (CO keto group from 3<sup>rd</sup> position), 166.2 (CO keto ester from 1<sup>st</sup> position), 163.1 (CO keto ester from 2<sup>nd</sup> position), 139.1 (C-12a), 131.6 (C-4a), 131.1 (C-6a), 131.0 (C-6), 131.0 (C-10a), 129.7 (C-2), 129.1 (C-7), 128.4 (C-9), 127.4 (C-8), 125.0 (C-11), 123.0 (C-10), 121.7 (C-3), 119.6 (C-10b), 117.8 (C-12), 117.7 (C-5), 105.9 (C-1), 53.8 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 52.2 (CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position), 41.6 (CH of dibromoacetyl group from 3<sup>rd</sup> position). *Anal. calc.* for C<sub>22</sub>H<sub>15</sub>Br<sub>2</sub>NO<sub>5</sub> (533.17): C 49.56, H 2.84, N 2.63; *found*: C 49.50, H 2.80, N 2.60.

**Methyl 3-(2,2-dibromopropanoyl)benzo[f]pyrrolo[1,2-a]quinoline-1-carboxylate (3c).** (0.054 g, 11% (under conventional heating) and 0 g, 0% (under ultrasounds)) as a yellow crystals, *m.p.* 175–176 °C; *R<sub>f</sub>* (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.68; **IR** (cm<sup>−1</sup>): 3108, 3023 (C–H arom.), 2960, 2928 (C–H aliph.), 1712 (C=O, ester), 1633 (C=O, keto), 1594, 1546, 1495, 1440, 1408 (aromatic and heteroaromatic ring), 1262, 1237, 1150, 1083, 1032 (C–O–C, ester), 667 (C–Br); **<sup>1</sup>H NMR** (500 MHz, DMSO): δ 9.02 (1H, *d*, *J* = 9.5 Hz, H-11), 8.87 (1H, *d*, *J* = 8.0 Hz, H-10), 8.69 (1H, *s*, H-2), 8.45 (1H, *d*, *J* = 9.5 Hz, H-12), 8.17 (1H, *d*, *J* = 9.5 Hz, H-6), 8.14 (1H, *d*, *J* = 8.0 Hz, H-7), 7.83 (1H, *t*, *J* = 7.5 Hz, H-9), 7.75 (1H, *t*, *J* = 7.5 Hz, H-8), 7.69 (1H, *d*, *J* = 9.5 Hz, H-5) 3.93 (3H, *s*, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 2.89 (3H, *s*, CH<sub>3</sub> of dibromopropanoyl group from 3<sup>rd</sup> position); **<sup>13</sup>C NMR** (125 MHz, DMSO): δ 180.6 (CO keto group from 3<sup>rd</sup> position), 163.3 (CO keto ester from 1<sup>st</sup> position), 139.7 (C-12a), 131.4 (C-4a), 130.4 (C-6a), 130.0 (C-6), 129.2 (C-10a), 129.1 (C-2), 128.8 (C-7), 128.2 (C-9), 127.3 (C-8), 126.0 (C-11), 123.6 (C-10), 122.4 (C-3), 120.9 (C-10b), 119.6 (C-5), 116.7 (C-12), 106.1 (C-1), 58.6 (CBr<sub>2</sub> of dibromopropanoyl group from 3<sup>rd</sup> position), 51.7 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 37.4 (CH<sub>3</sub> of dibromopropanoyl group from 3<sup>rd</sup> position). *Anal. calc.* for C<sub>21</sub>H<sub>15</sub>Br<sub>2</sub>NO<sub>3</sub> (489.16): C 51.56, H 3.09, N 2.86; *found*: C 51.50, H 3.05, N 2.82.

**Methyl 3-(2-azidoacetyl)benzo[f]pyrrolo[1,2-a]quinoline-1-carboxylate (4a).** (0.147 g, 82% (under conventional heating) and 0.167 g, 93% (under ultrasounds)) as a yellow crystals, *m.p.* 189–190 °C; *R<sub>f</sub>* (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.65; **IR** (cm<sup>−1</sup>): 3121, 3017 (C–H arom.), 2955, 2924 (C–H aliph.), 2144, 2111 (N<sub>3</sub> azide), 1711 (C=O, ester), 1658 (C=O, keto), 1608, 1557, 1544, 1500, 1450, 1403, 1367 (aromatic and heteroaromatic ring), 1233, 1181, 1129, 1089 (C–O–C, ester); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.65 (1H, *d*, *J* = 9.5 Hz, H-11), 8.60 (1H, *d*, *J* = 8.5 Hz, H-10), 8.51 (1H, *d*, *J* = 9.5 Hz, H-12), 8.12 (1H, *d*, *J* = 9.0 Hz, H-6), 8.09 (1H, *s*, H-2), 8.01 (2H, *m*, overlapped peaks, H-5, H-7), 7.74 (1H, *t*, *J* = 8.0 Hz, H-9), 7.66 (1H, *t*, *J* = 8.0 Hz, H-8), 4.60 (2H, *s*, CH<sub>2</sub> of azidoacetyl group from 3<sup>rd</sup> position), 3.98 (3H, *s*, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 182.2 (CO keto group from 3<sup>rd</sup> position), 164.2 (CO keto ester from 1<sup>st</sup> position), 141.1 (C-12a), 132.5 (C-4a), 131.1 (C-6a), 129.8 (C-6), 129.6 (C-10a), 129.0 (C-7), 128.6 (C-2), 128.0 (C-9), 127.1 (C-8), 125.6 (C-3), 125.2 (C-11), 123.0 (C-10), 121.5 (C-10b), 120.0 (C-5), 117.4 (C-12), 107.6 (C-1), 55.5 (CH<sub>2</sub> of azidoacetyl group from 3<sup>rd</sup> position), 51.7 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position). *Anal. calc.* for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub> (358.36): C 67.03, H 3.94, N 15.63; *found*: C 66.96, H 3.90, N 15.56.

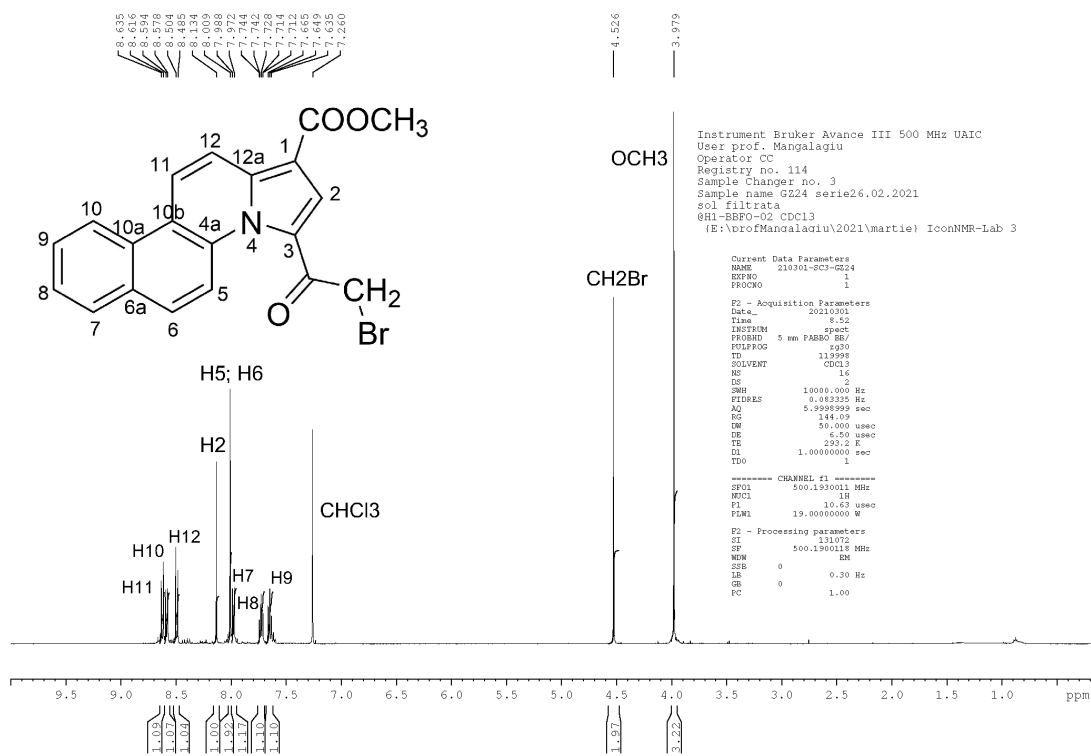
**Dimethyl 3-(2-azidoacetyl)benzo[f]pyrrolo[1,2-a]quinoline-1,2-dicarboxylate (4b).** (0.146 g, 70% (under conventional heating) and 0.179 g, 86% (under ultrasounds)) as a yellow-orange crystals, *m.p.* 137–138 °C; *R<sub>f</sub>* (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.45; **IR** (cm<sup>−1</sup>): 3004 (C–H arom.), 2962, 2929 (C–H aliph.), 2115, 2102 (N<sub>3</sub> azide), 1717, 1702 (C=O, ester), 1659 (C=O, keto), 1611, 1547, 1471, 1446, 1404, 1368 (aromatic and heteroaromatic ring), 1262, 1246, 1163, 1132, 1101, 1031 (C–O–C, ester); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.60 (2H, *m*, overlapped peaks, H-10, H-11), 8.47 (1H, *d*, *J* = 9.5 Hz, H-12), 8.05 (1H, *d*, *J* = 9.5 Hz, H-6), 8.00 (1H, *d*, *J* = 7.5 Hz, H-7), 7.78 (1H, *t*, *J* = 7.0 Hz, H-9), 7.69 (1H, *t*, *J* = 7.0 Hz, H-8), 7.63 (1H, *d*, *J* = 9.5 Hz, H-5), 4.33 (2H,

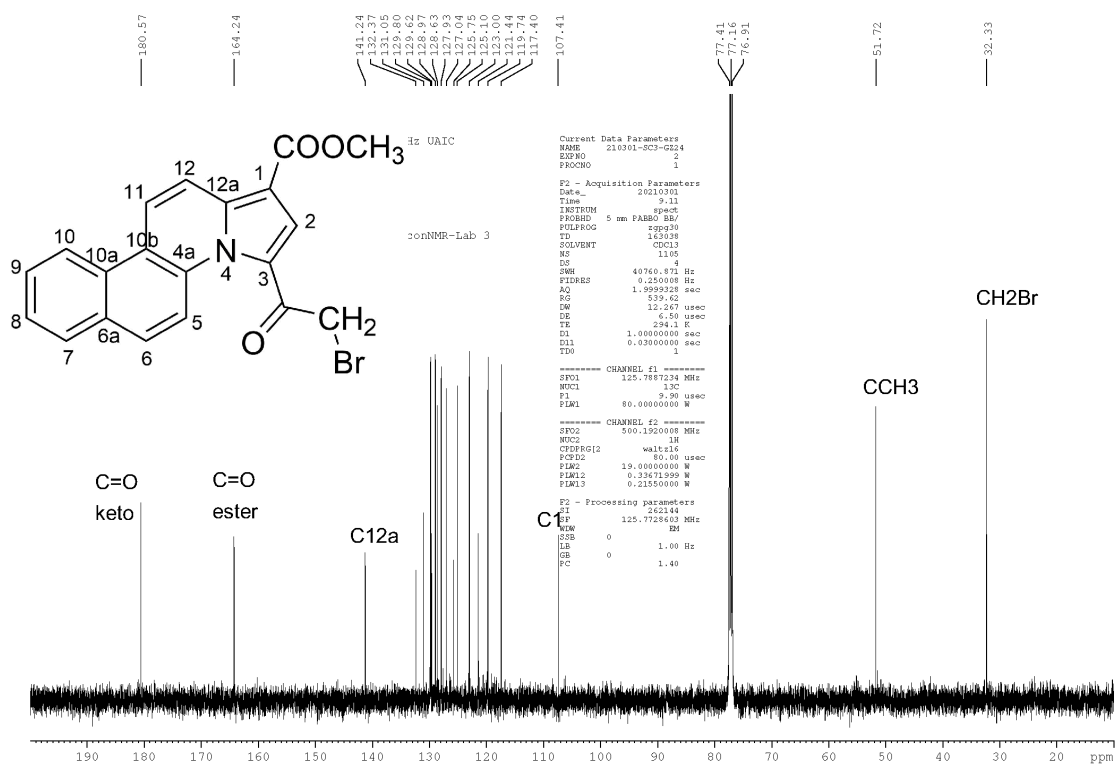
s, CH<sub>2</sub> of azidoacetyl group from 3<sup>rd</sup> position), 4.05 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 3.96 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 186.7 (CO keto group from 3<sup>rd</sup> position), 166.3 (CO keto ester from 1<sup>st</sup> position), 163.4 (CO keto ester from 2<sup>nd</sup> position), 138.1 (C-12a), 131.6 (C-4a), 131.0 (C-6a), 130.6 (C-6), 130.3 (C-10a), 129.8 (C-2), 129.1 (C-7), 128.4 (C-9), 127.4 (C-8), 124.3 (C-11), 124.0 (C-3), 123.1 (C-10), 121.7 (C-10b), 118.5 (C-5), 118.0 (C-12), 105.7 (C-1), 56.6 (CH<sub>2</sub> of azidoacetyl group from 3<sup>rd</sup> position), 53.6 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 52.1 (CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position). Anal. calc. for C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>O<sub>5</sub> (416.39): C 63.46, H 3.87, N 13.46; found: C 63.40, H 3.84, N 13.40.

**Methyl 3-(2-azidopropanoyl)benzo[f]pyrrolo[1,2-a]quinoline-1-carboxylate (4c).** (0.155 g, 83% (under conventional heating) and 0.177 g, 95% (under ultrasounds)) as a yellow crystals, m.p. 167–168 °C; R<sub>f</sub> (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.65; IR (cm<sup>-1</sup>): 3078, 3025 (C-H arom.), 2974, 2949, 2921 (C-H aliph.), 2110, 2088, 2063 (N<sub>3</sub> azide), 1693 (C=O, ester), 1645 (C=O, keto), 1609, 1544, 1507, 1494, 1439, 1414, 1404, 1322 (aromatic and heteroaromatic ring), 1238, 1176, 1085, 1051, 1031 (C–O–C, ester); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.44 (2H, m, overlapped peaks, H-10, H-11), 8.33 (1H, d, J = 9.5 Hz, H-12), 8.04 (1H, s, H-2), 7.92 (1H, d, J = 9.5 Hz, H-6), 7.89 (1H, d, J = 8.0 Hz, H-7), 7.84 (1H, d, J = 9.5 Hz, H-5), 7.63 (1H, t, J = 7.5 Hz, H-9), 7.57 (1H, t, J = 7.5 Hz, H-8), 4.71 (2H, q, J = 7.0 Hz, CHN<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position), 3.95 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 1.73 (3H, d, J = 7.0 Hz, CH<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 185.6 (CO keto group from 3<sup>rd</sup> position), 164.0 (CO keto ester from 1<sup>st</sup> position), 141.1 (C-12a), 132.1 (C-4a), 130.8 (C-6a), 129.6 (C-6), 129.4 (C-10a), 128.8 (C-7), 128.6 (C-9), 127.8 (C-2), 126.9 (C-8), 125.6 (C-3), 124.8 (C-11), 122.8 (C-10), 121.2 (C-10b), 119.6 (C-5), 117.2 (C-12), 107.4 (C-1), 59.6 (CHN<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position), 51.6 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 17.3 (CH<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position). Anal. calc. for C<sub>21</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub> (372.38): C 67.73, H 4.33, N 15.05; found: C 67.67, H 4.29, N 14.99.

**Dimethyl 3-(2-azidopropanoyl)benzo[f]pyrrolo[1,2-a]quinoline-1,2-dicarboxylate (4d).** (0.146 g, 68% (under conventional heating) and 0.179 g, 83% (under ultrasounds)) as a yellow-orange crystals, m.p. 160–161 °C; R<sub>f</sub> (99.5/0.5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) 0.45; IR (cm<sup>-1</sup>): 3034, 3014 (C-H arom.), 2950, 2930 (C-H aliph.), 2131, 2114, 2100 (N<sub>3</sub> azide), 1732, 1697 (C=O, ester), 1665 (C=O, keto), 1610, 1544, 1503, 1468, 1442, 1408 (aromatic and heteroaromatic ring), 1264, 1228, 1189, 1159, 1094, 1074 (C–O–C, ester); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.57 (1H, d, J = 8.0 Hz, H-10), 8.53 (1H, d, J = 9.5 Hz, H-11), 8.43 (1H, d, J = 9.5 Hz, H-12), 8.04 (1H, d, J = 9.0 Hz, H-6), 7.98 (1H, d, J = 8.0 Hz, H-7), 7.75 (1H, t, J = 7.5, 8.0 Hz, H-9), 7.66 (1H, t, J = 7.5, 8.0 Hz, H-8), 7.58 (1H, d, J = 9.0 Hz, H-5), 4.30 (1H, q, J = 7.0 Hz, CHN<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position), 4.03 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 3.95 (3H, s, CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position), 1.56 (3H, d, J = 7.0 Hz, CH<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 190.7 (CO keto group from 3<sup>rd</sup> position), 166.1 (CO keto ester from 1<sup>st</sup> position), 163.4 (CO keto ester from 2<sup>nd</sup> position), 137.7 (C-12a), 131.4 (C-4a), 130.9 (C-6a), 130.7 (C-6), 130.0 (C-10a), 129.7 (C-2), 129.1 (C-7), 128.4 (C-9), 127.3 (C-8), 123.9 (C-3), 123.8 (C-11), 123.0 (C-10), 121.5 (C-10b), 118.2 (C-5), 118.1 (C-12), 105.5 (C-1), 60.9 (CHN<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position), 53.4 (CH<sub>3</sub> of methoxycarbonyl group from 1<sup>st</sup> position), 52.1 (CH<sub>3</sub> of methoxycarbonyl group from 2<sup>nd</sup> position), 16.7 (CH<sub>3</sub> of azidopropanoyl group from 3<sup>rd</sup> position). Anal. calc. for C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O<sub>5</sub> (430.42): C 64.18, H 4.22, N 13.02; found: C 64.13, H 4.18, N 12.97.

## 2. NMR spectra of the obtained compounds

Figure S1a. <sup>1</sup>H NMR spectrum of the compound 2a.

Figure S1b. <sup>13</sup>C NMR spectrum of the compound 2a.

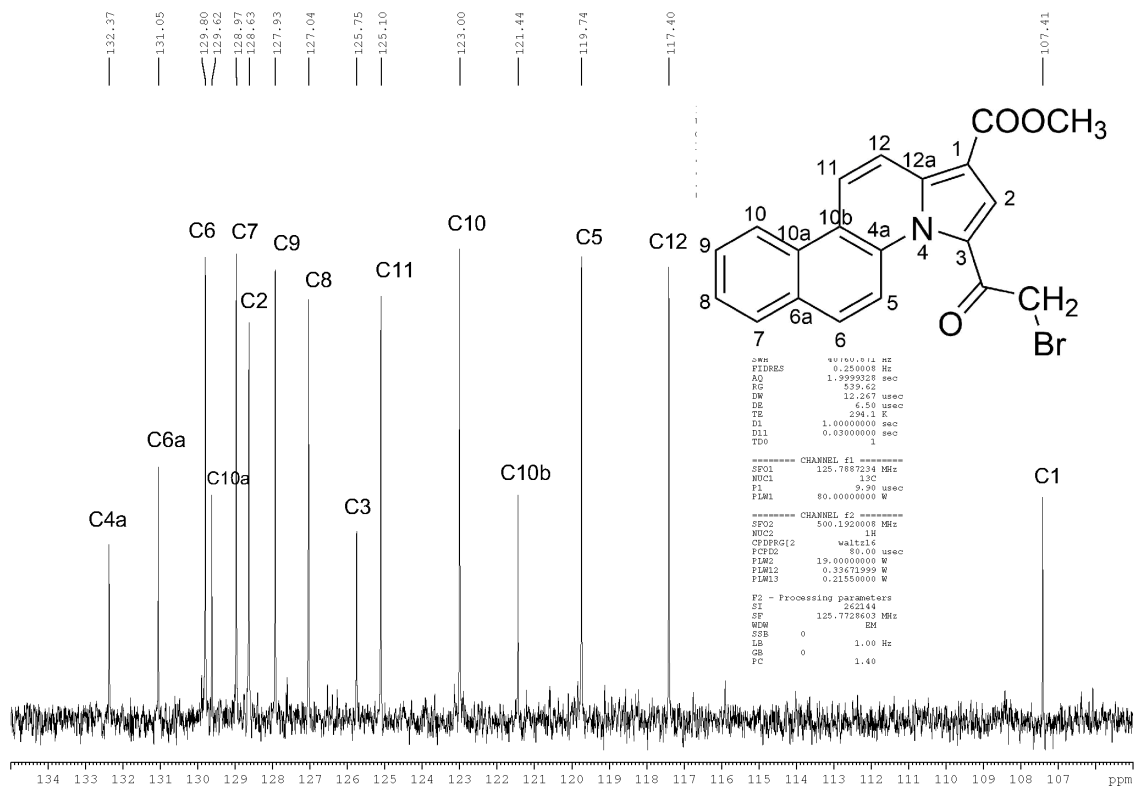
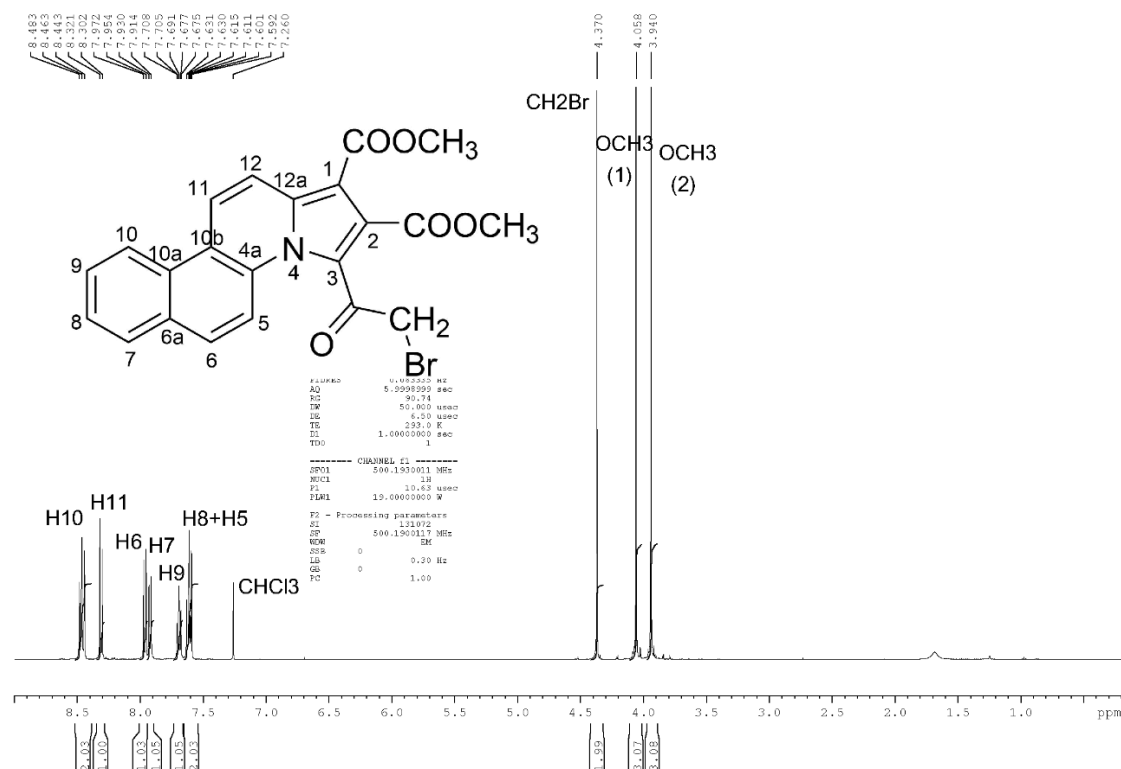
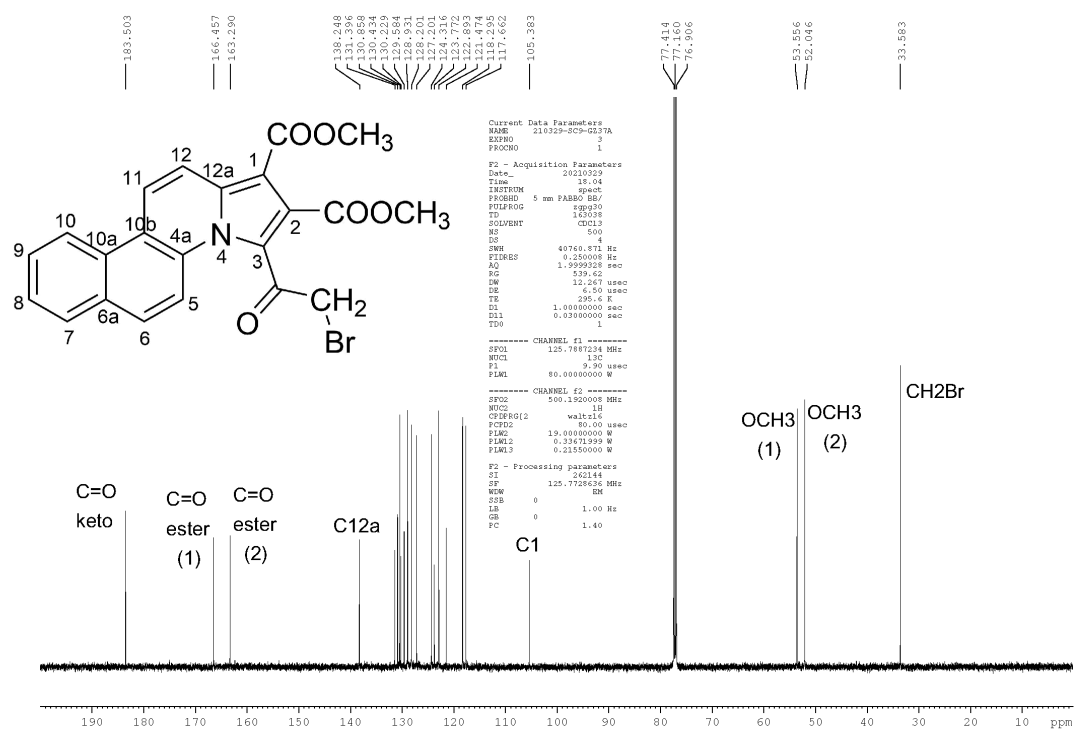
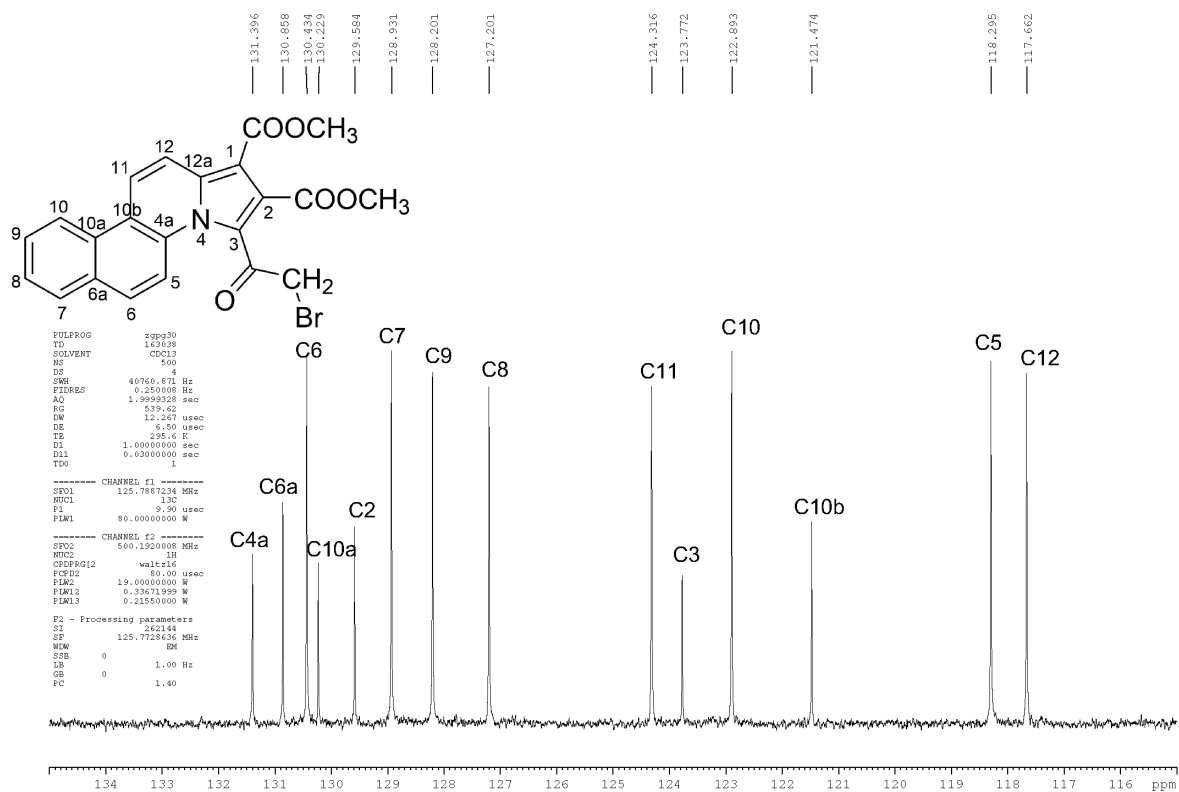


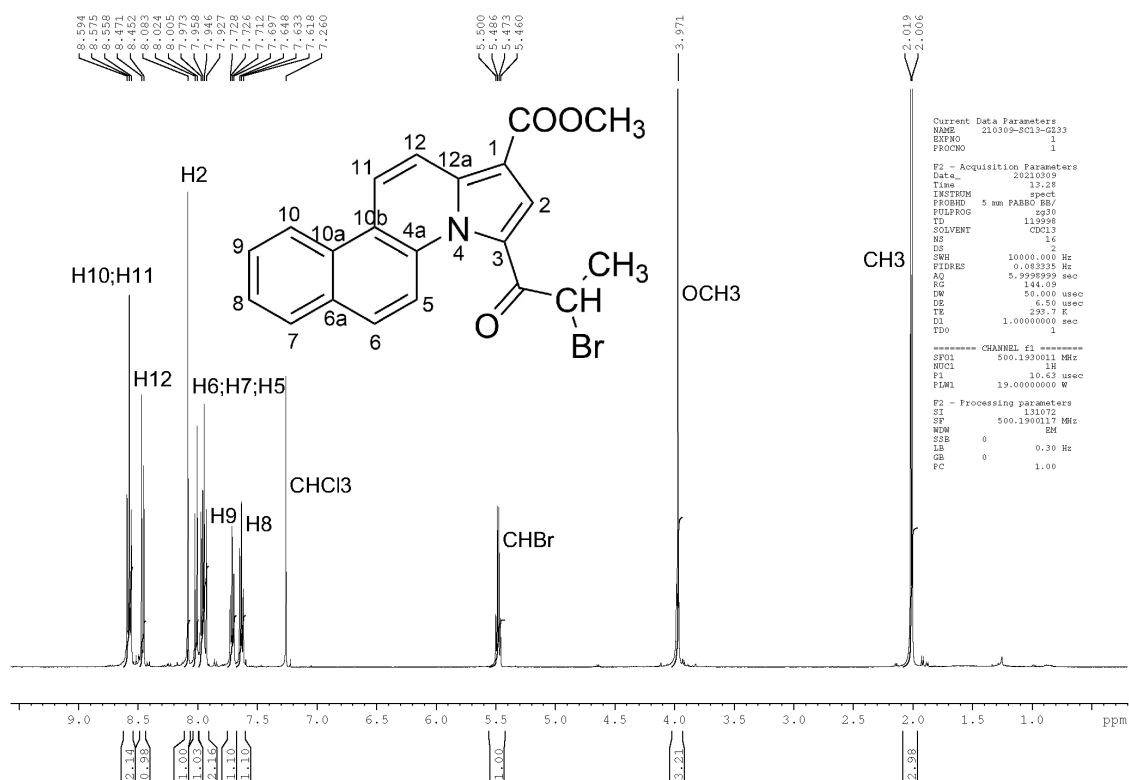
Figure S1c. Detail in the aromatic area of the  $^{13}\text{C}$  NMR spectrum of the compound 2a.

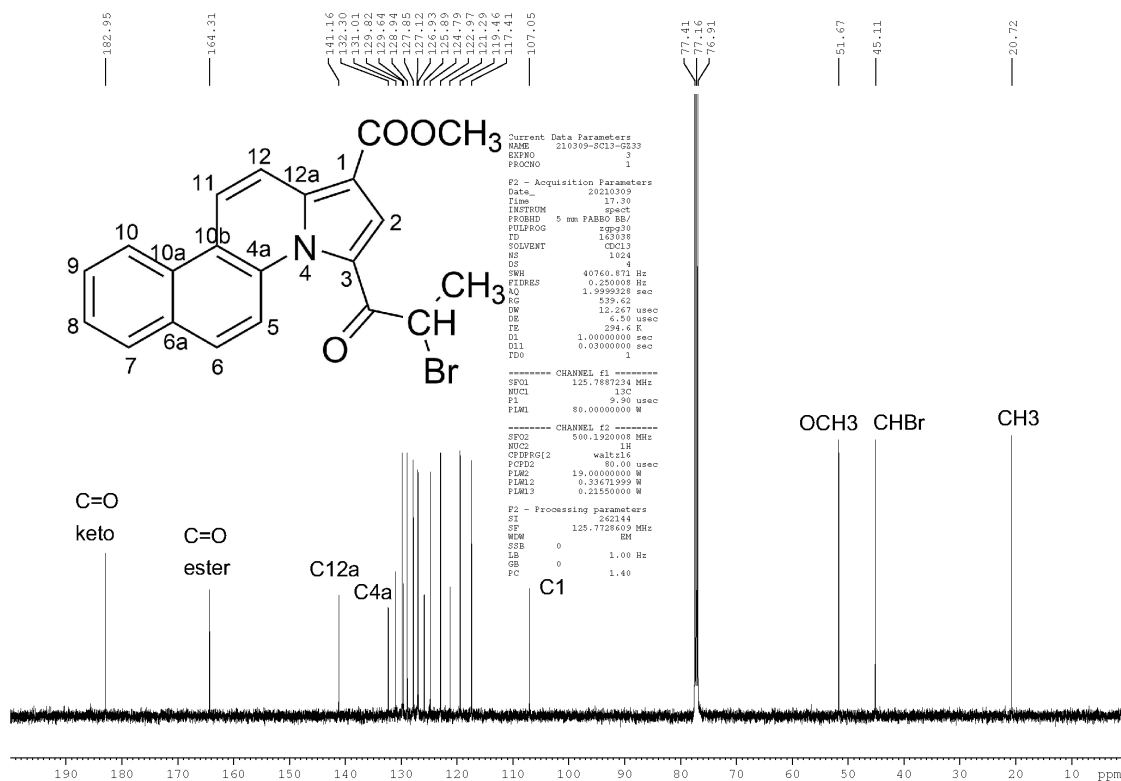


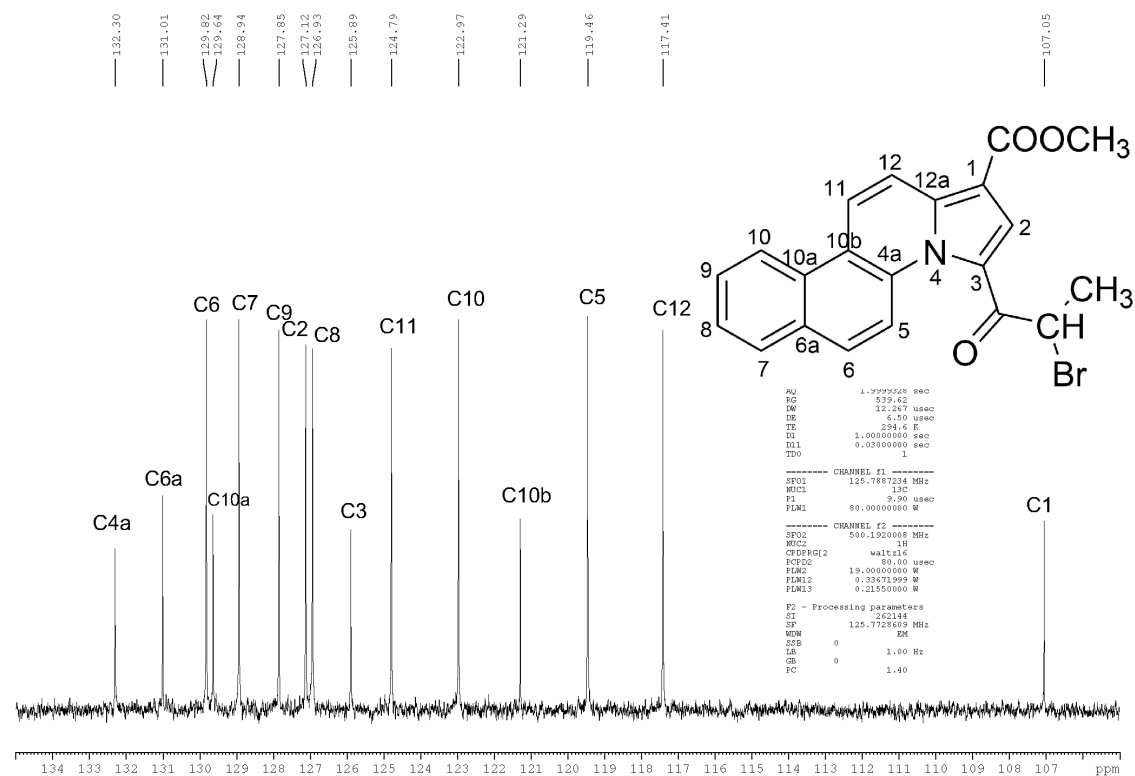
Figure S2a. <sup>1</sup>H NMR spectrum of the compound 2b.Figure S2b. <sup>13</sup>C NMR spectrum of the compound 2b.



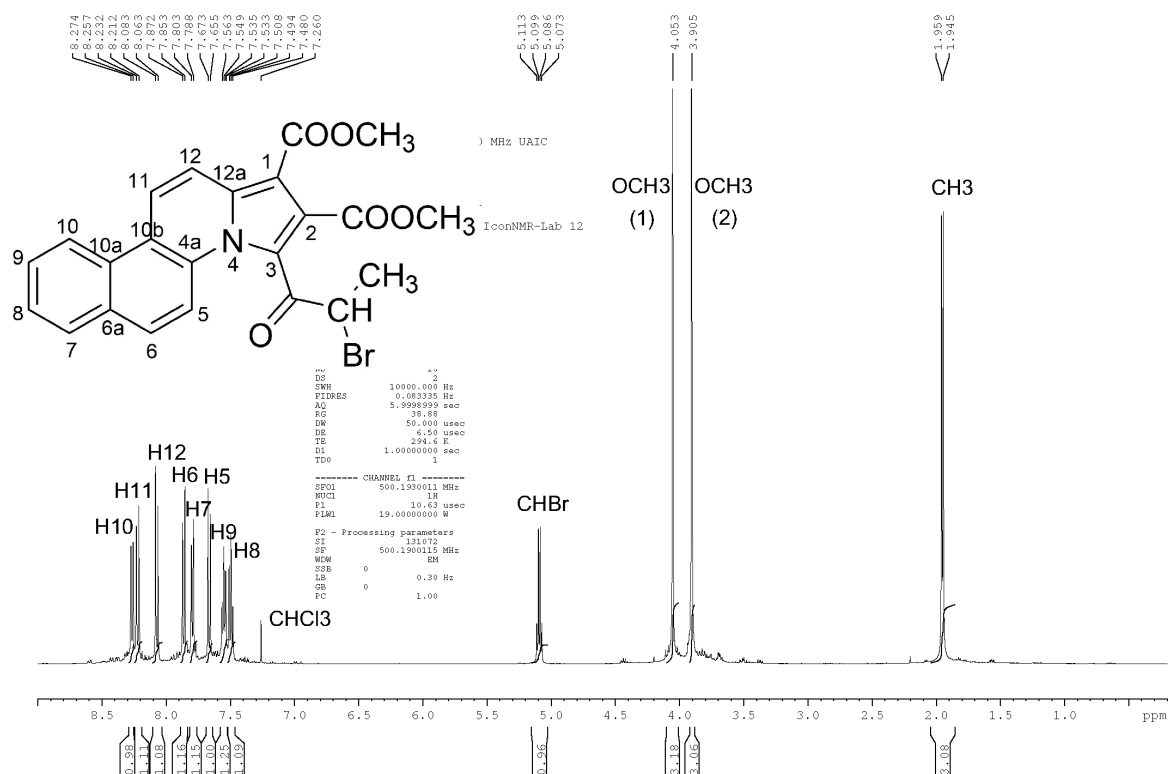
**Figure.S2c** Detail in the aromatic area of the  $^{13}\text{C}$  NMR spectrum of the compound **2b**.

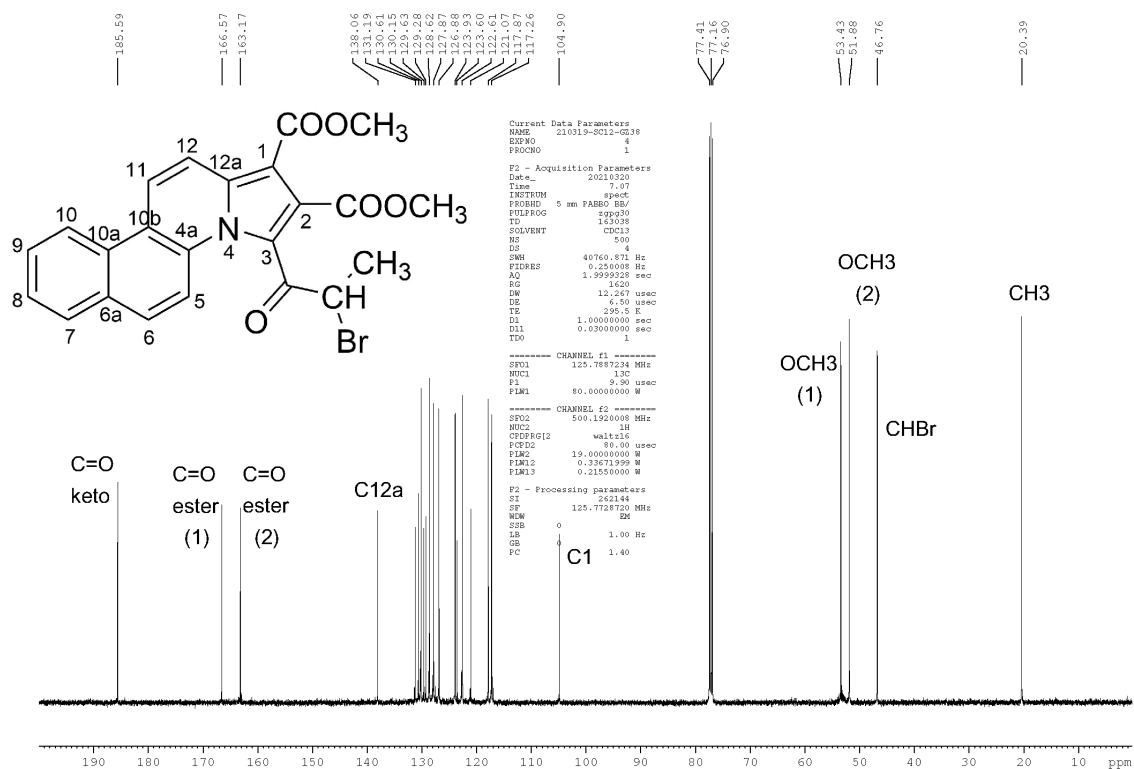
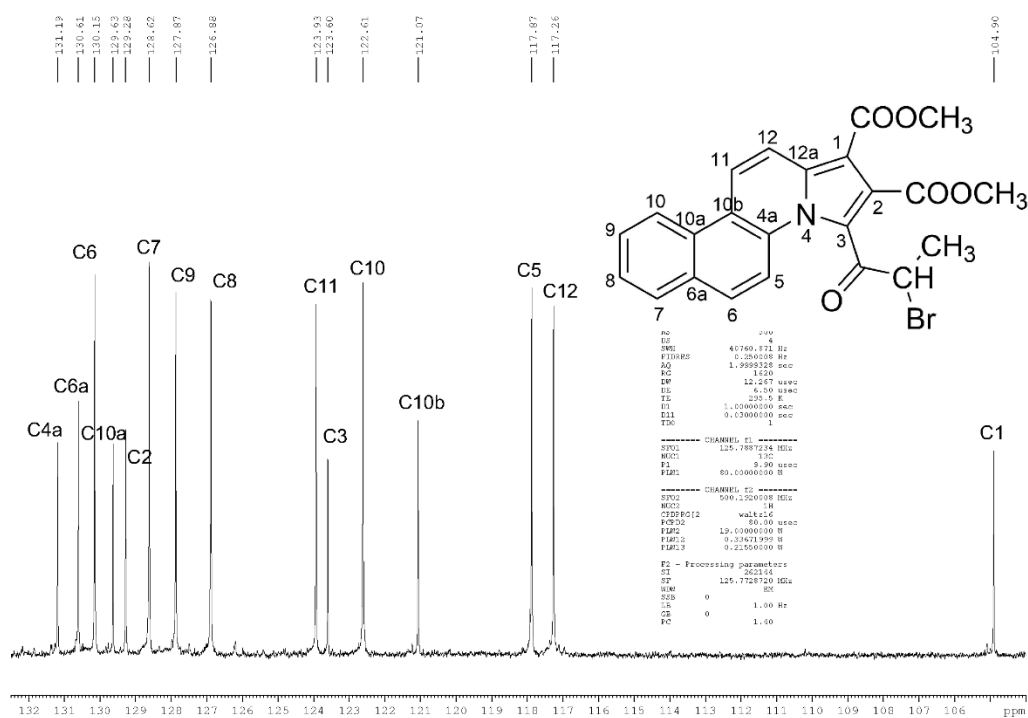
Figure S3a. <sup>1</sup>H NMR spectrum of the compound 2c.

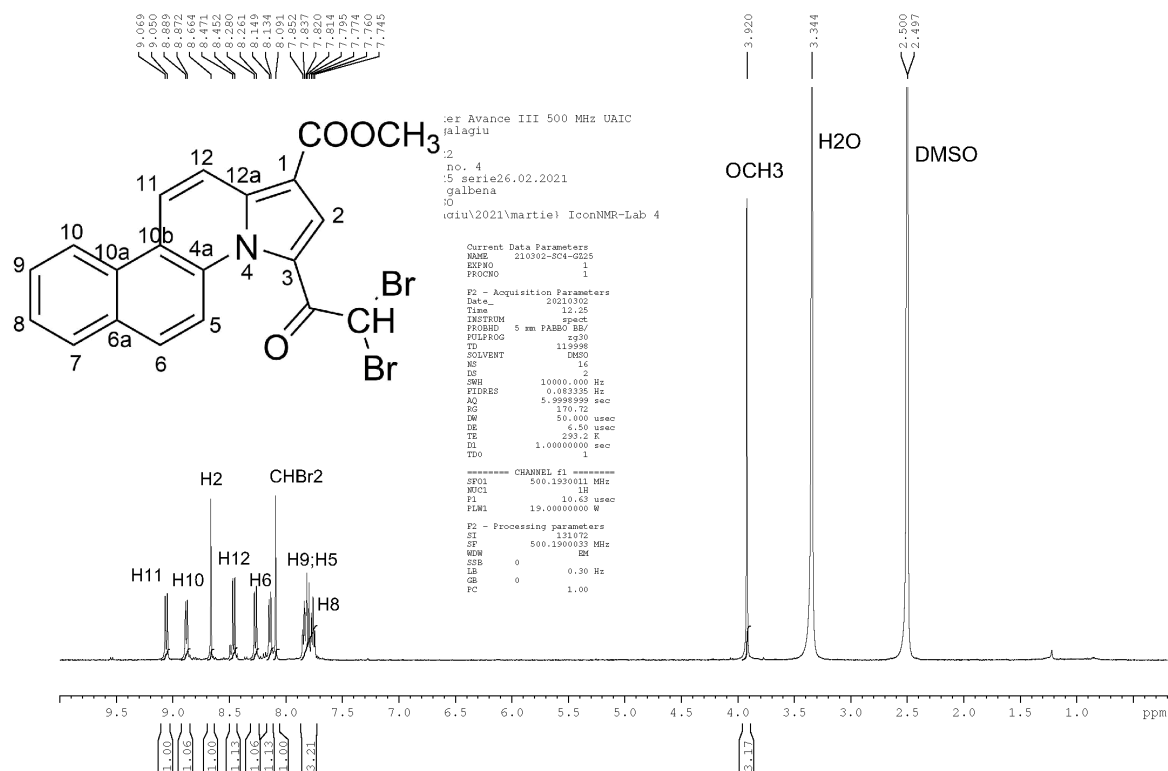
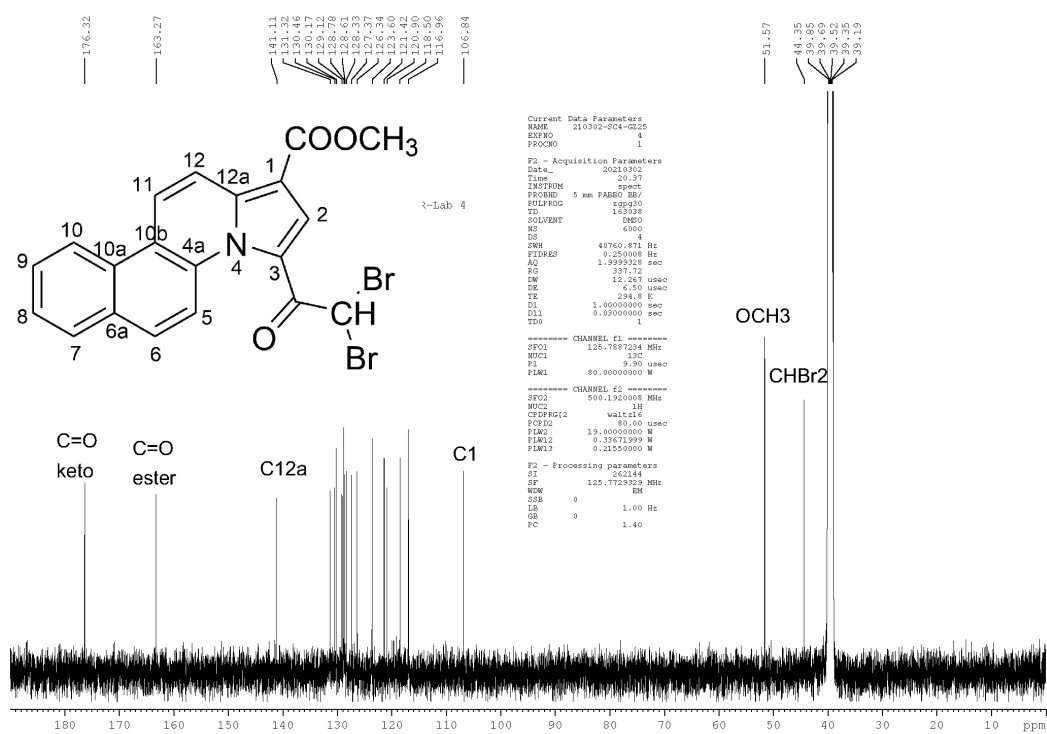
Figure S3b. <sup>13</sup>C NMR spectrum of the compound 2c.



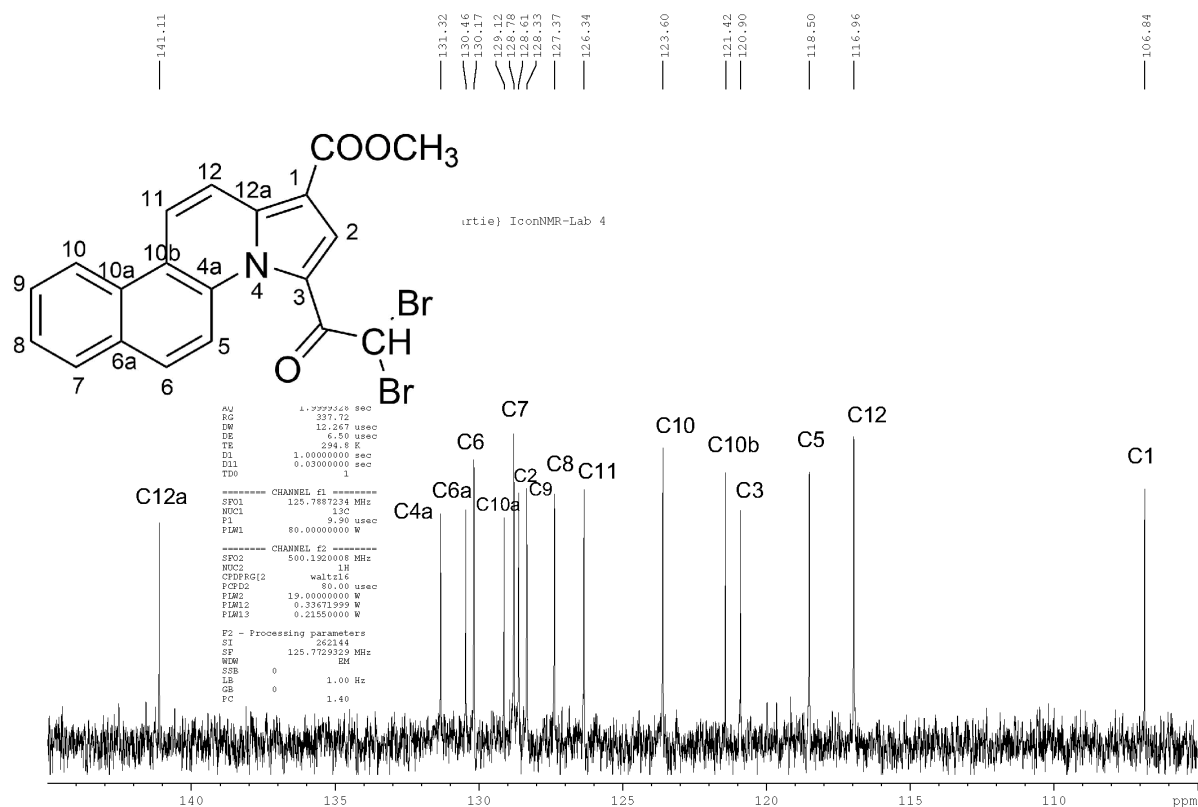
**Figure S3c.** Detail in the aromatic area of the <sup>13</sup>C NMR spectrum of the compound 2c.

Figure S4a. <sup>1</sup>H NMR spectrum of the compound 2d.

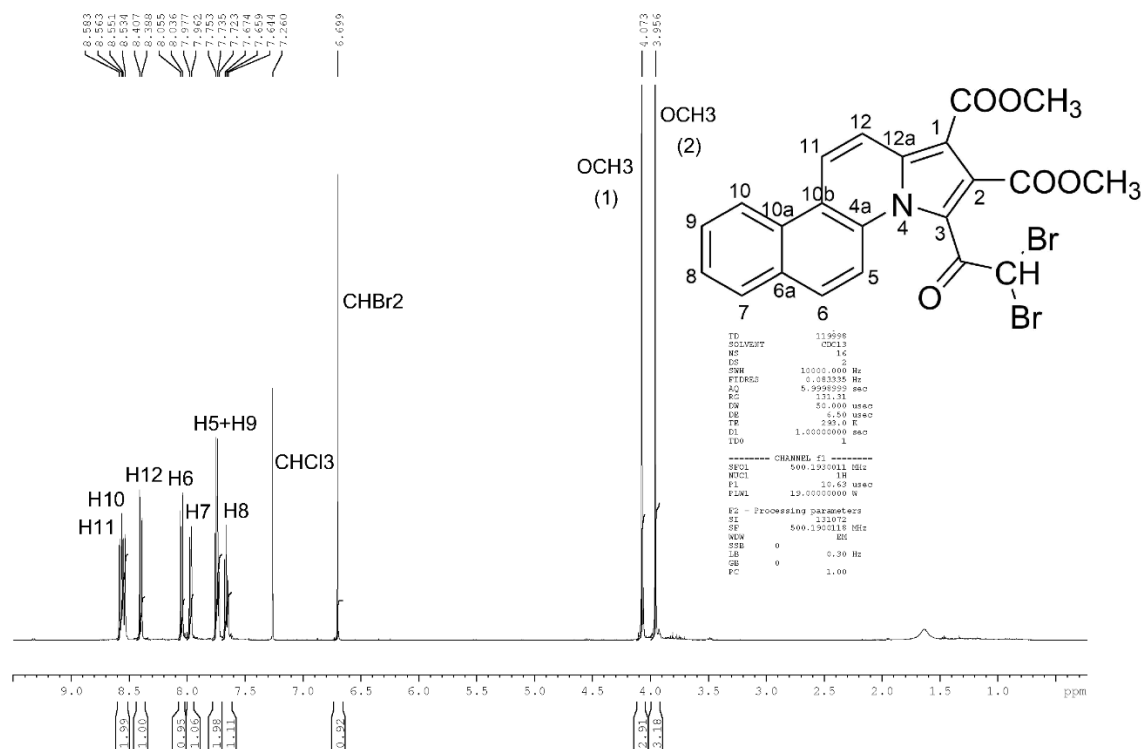
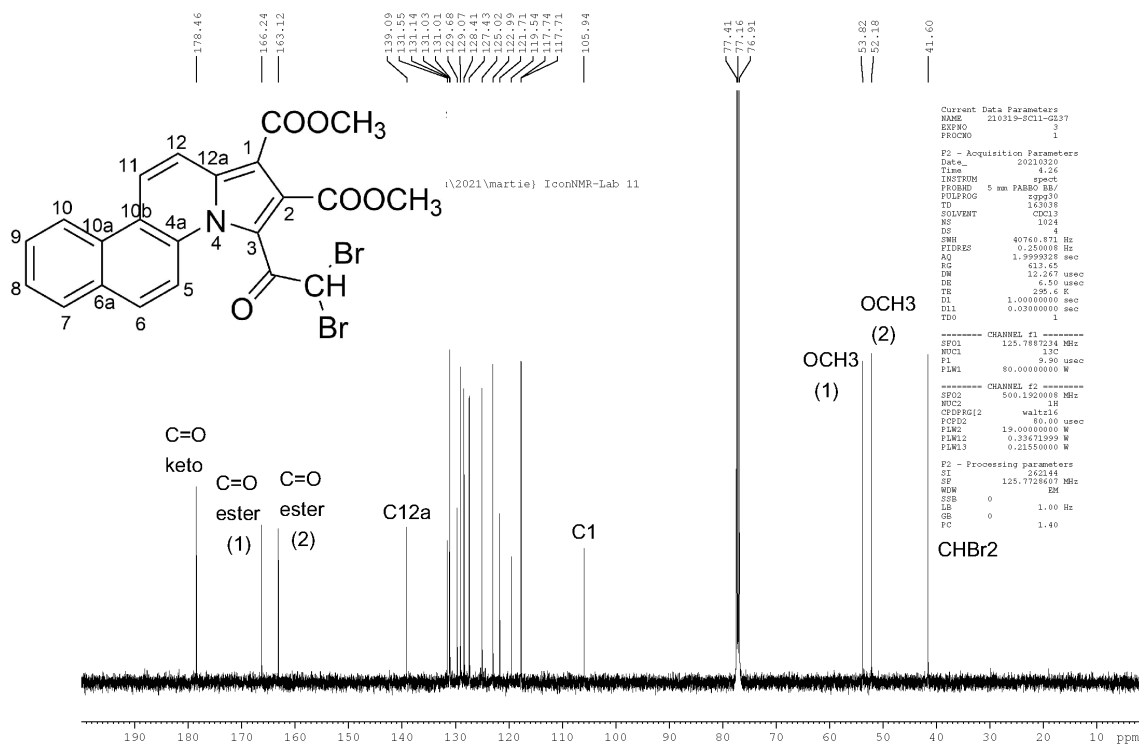
Figure S4b.  $^{13}\text{C}$  NMR spectrum of the compound 2d.Figure S4c. Detail in the aromatic area of the  $^{13}\text{C}$  NMR spectrum of the compound 2d.

Figure S5a.  $^1\text{H}$  NMR spectrum of the compound 3a.Figure S5b.  $^{13}\text{C}$  NMR spectrum of the compound 3a.





**Figure S5c.** Detail in the aromatic area of the <sup>13</sup>C NMR spectrum of the compound 3a.

Figure S6a. <sup>1</sup>H NMR spectrum of the compound 3b.Figure S6b. <sup>13</sup>C NMR spectrum of the compound 3b.

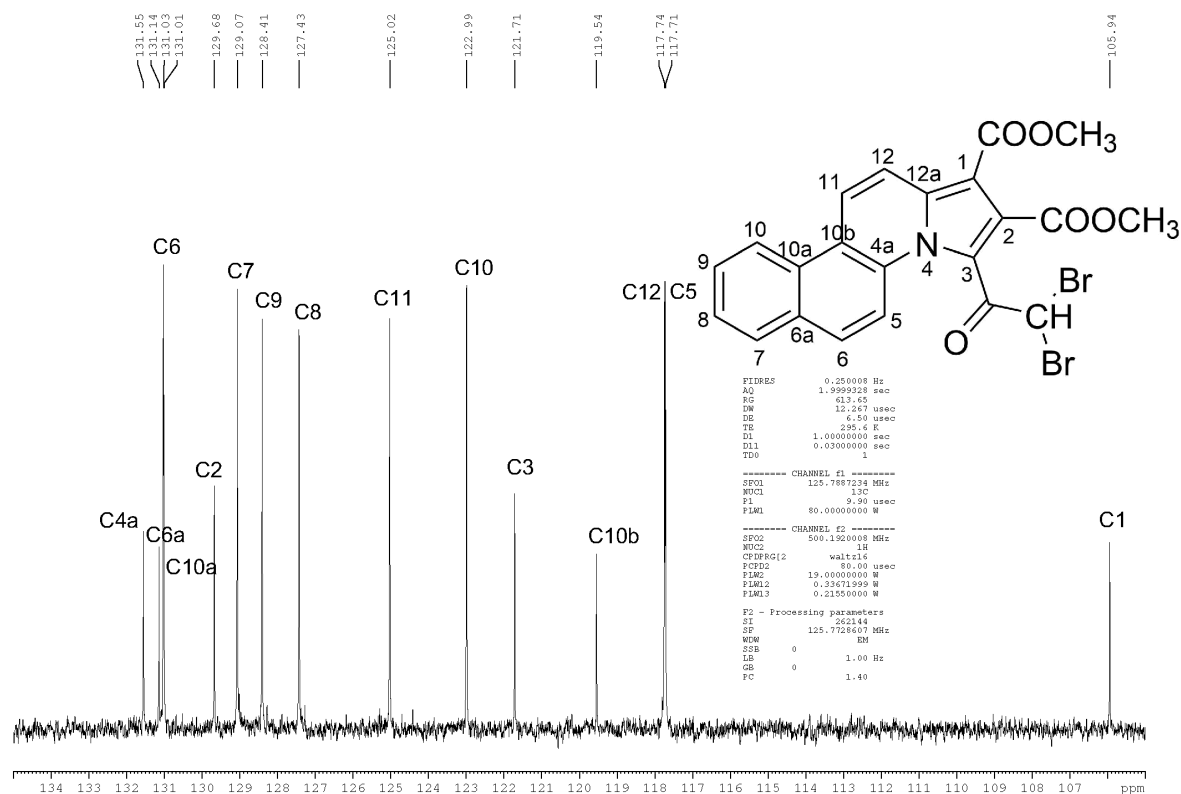
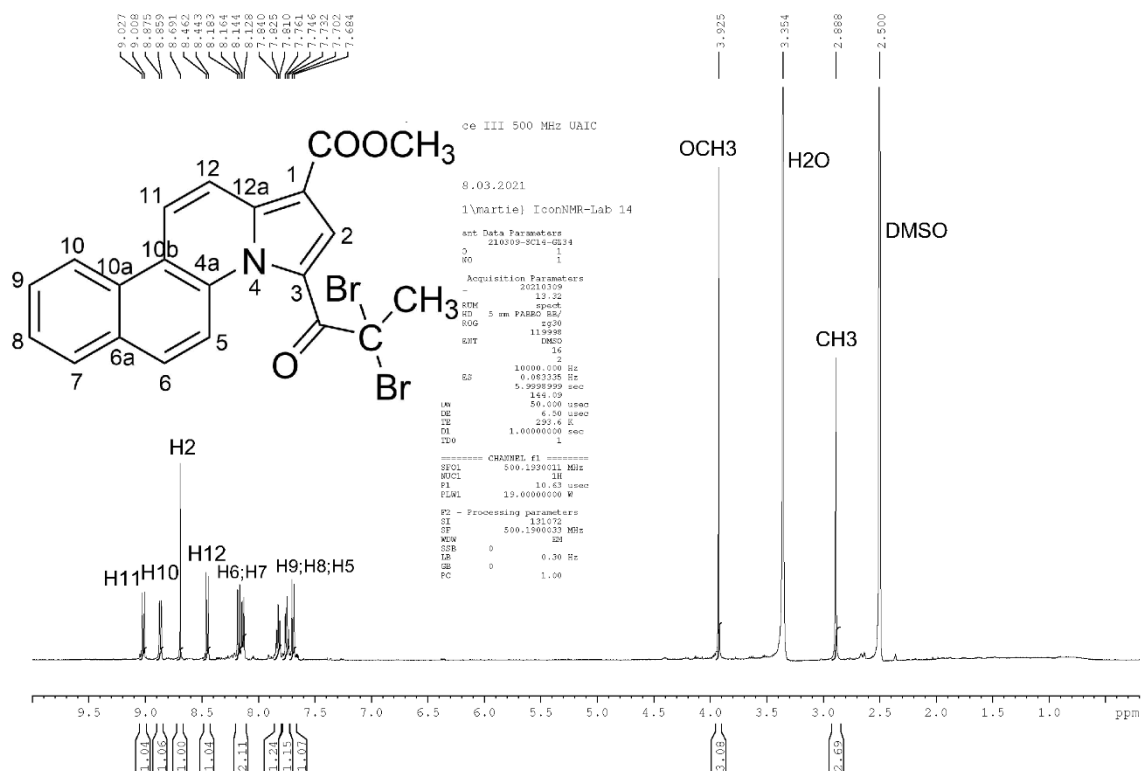
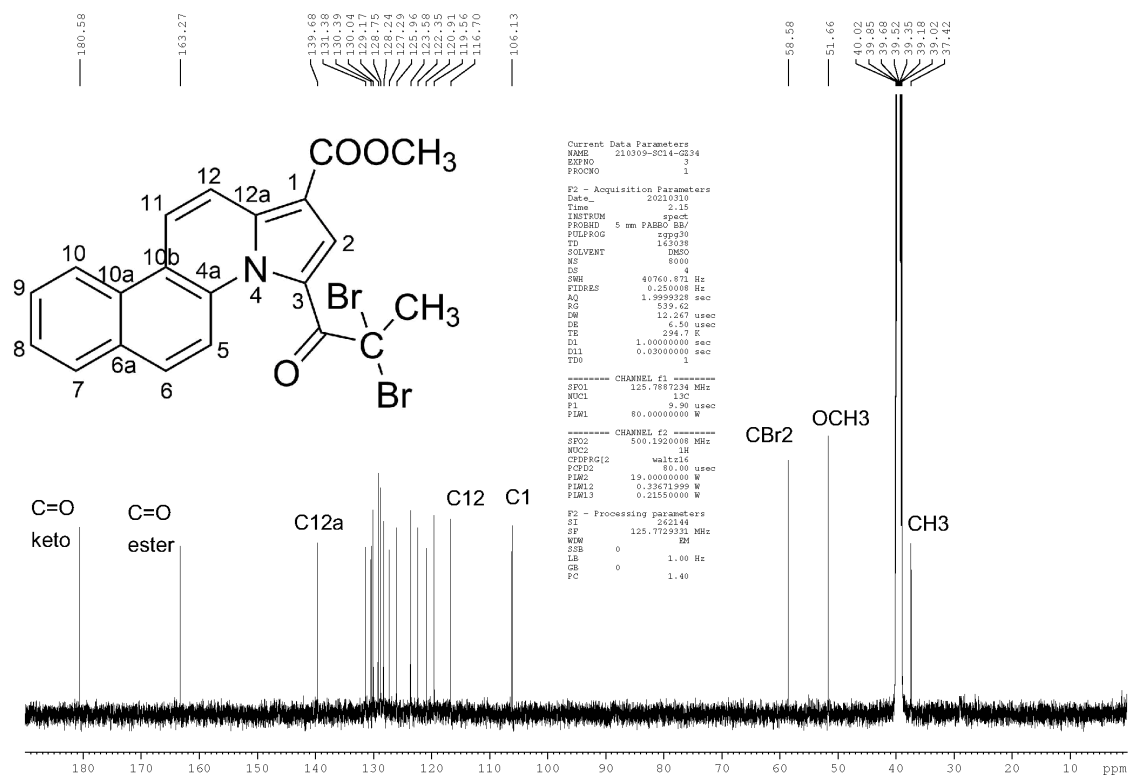


Figure S6c. Detail in the aromatic area of the <sup>13</sup>C NMR spectrum of the compound 3b.

Figure S7a.  $^1\text{H}$  NMR spectrum of the compound 3c.

Figure S7b. <sup>13</sup>C NMR spectrum of the compound 3c.

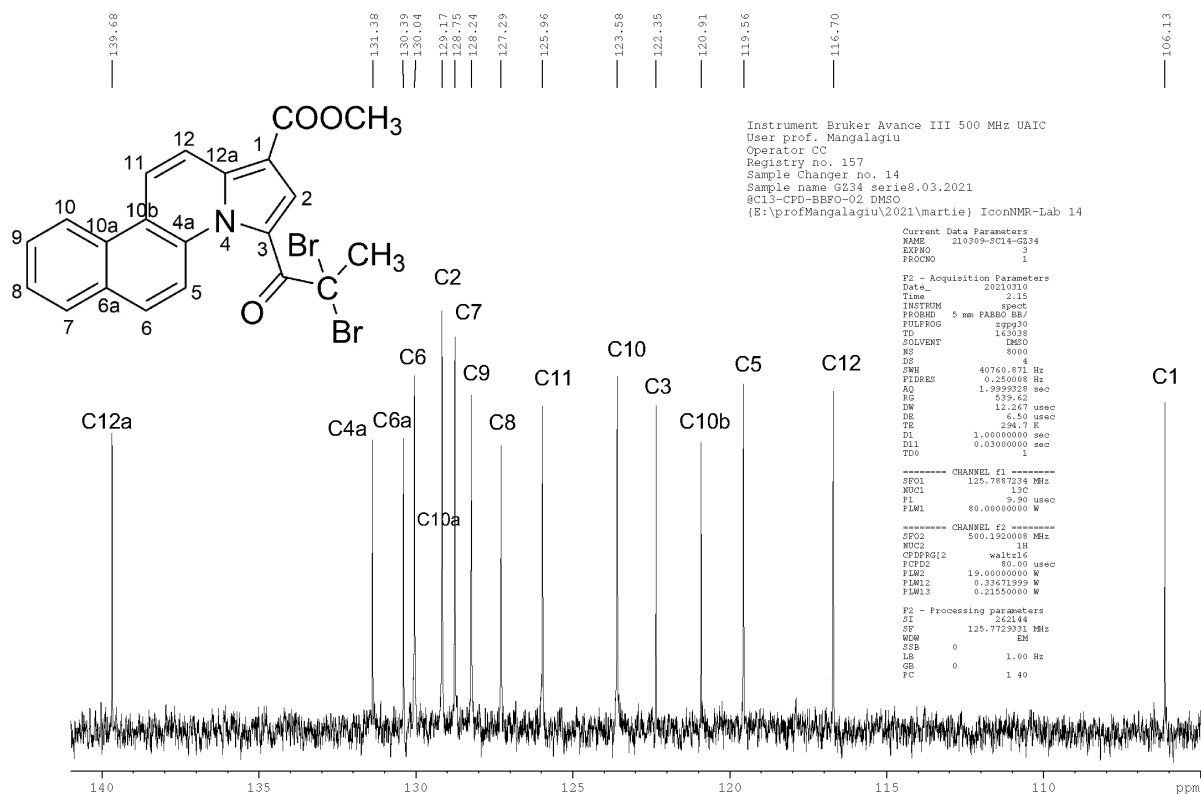
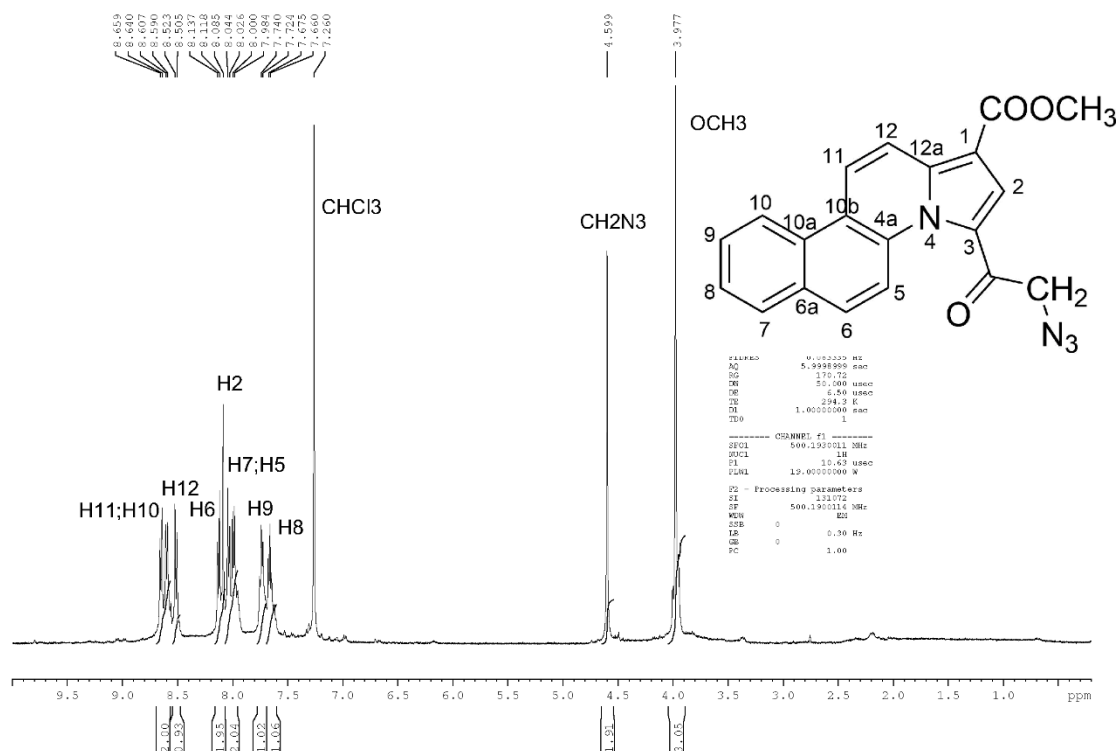
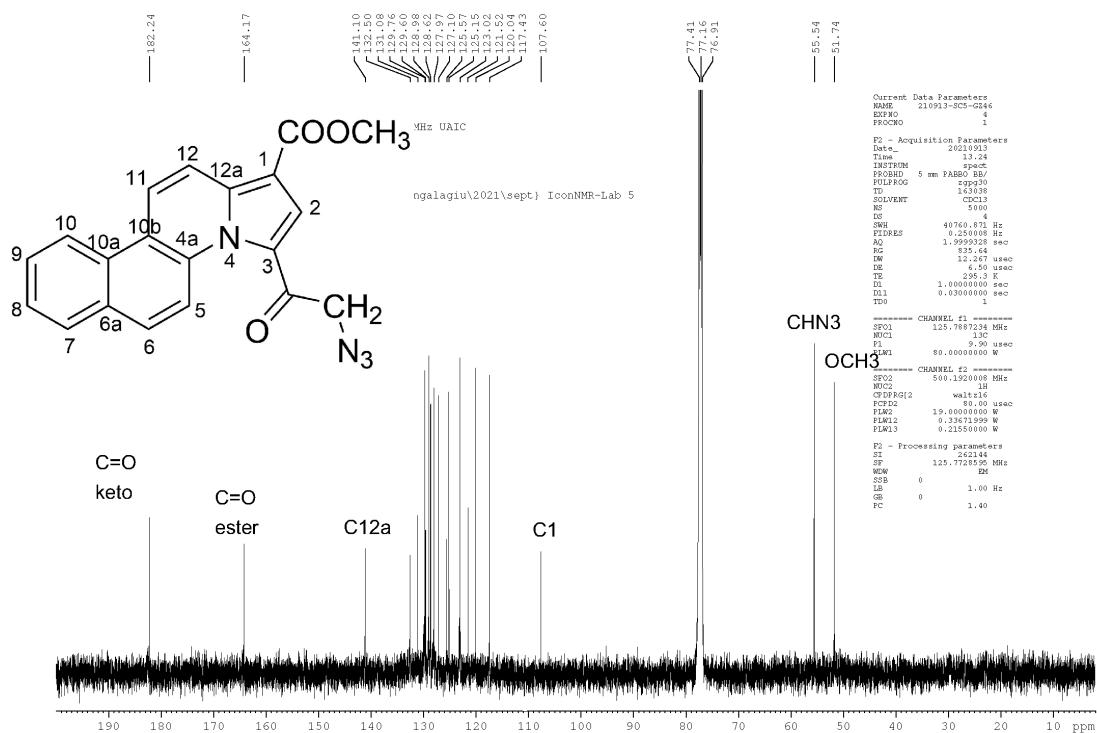


Figure S7c. Detail in the aromatic area of the  $^{13}\text{C}$  NMR spectrum of the compound 3c.

Figure S8a. <sup>1</sup>H NMR spectrum of the compound 4a.Figure S8b. <sup>13</sup>C NMR spectrum of the compound 4a.

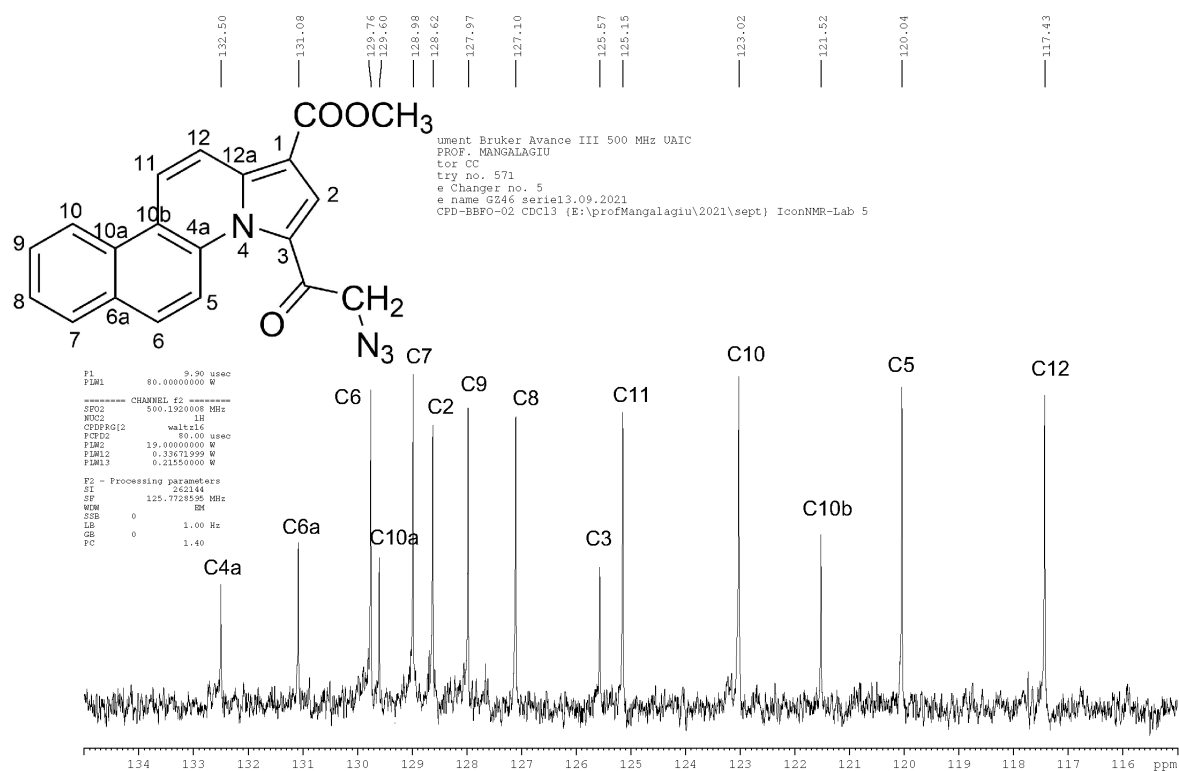
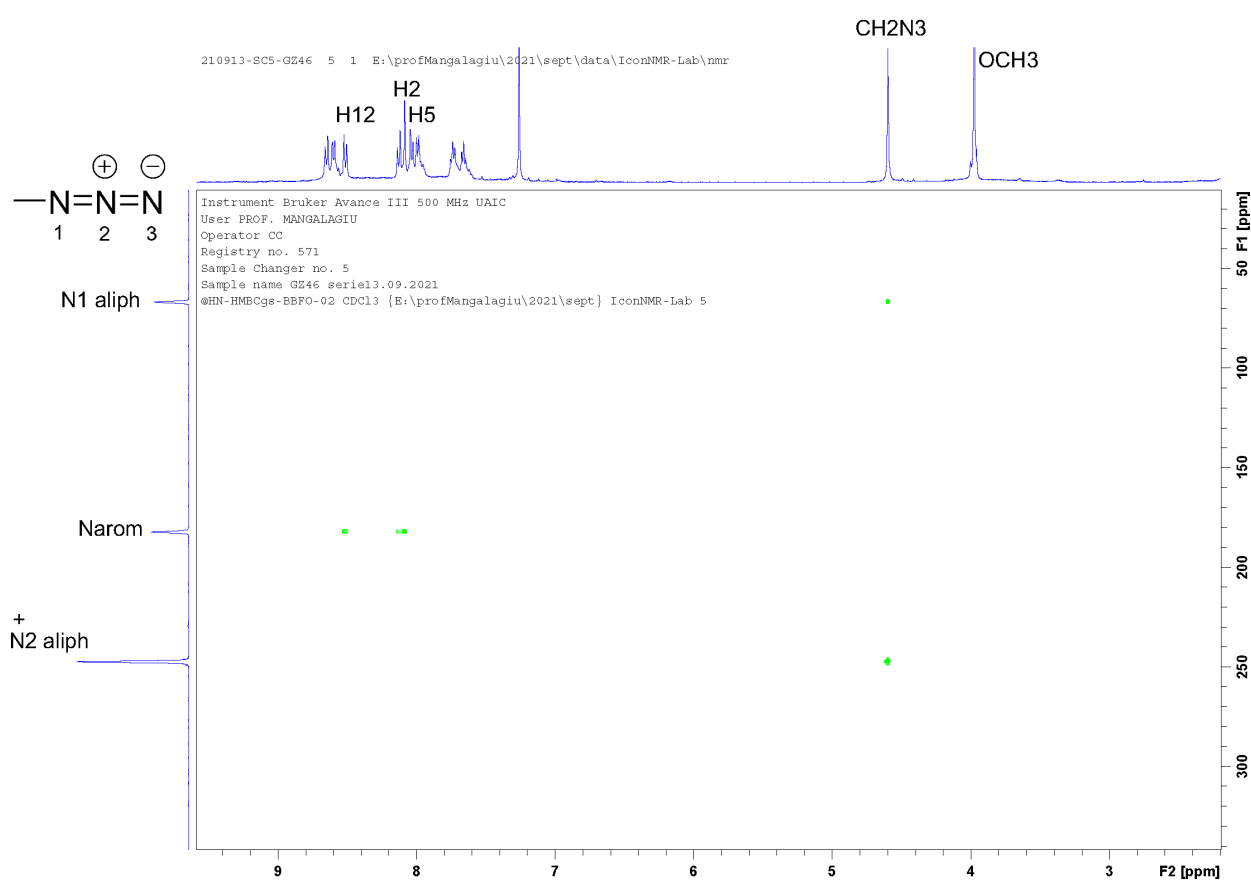
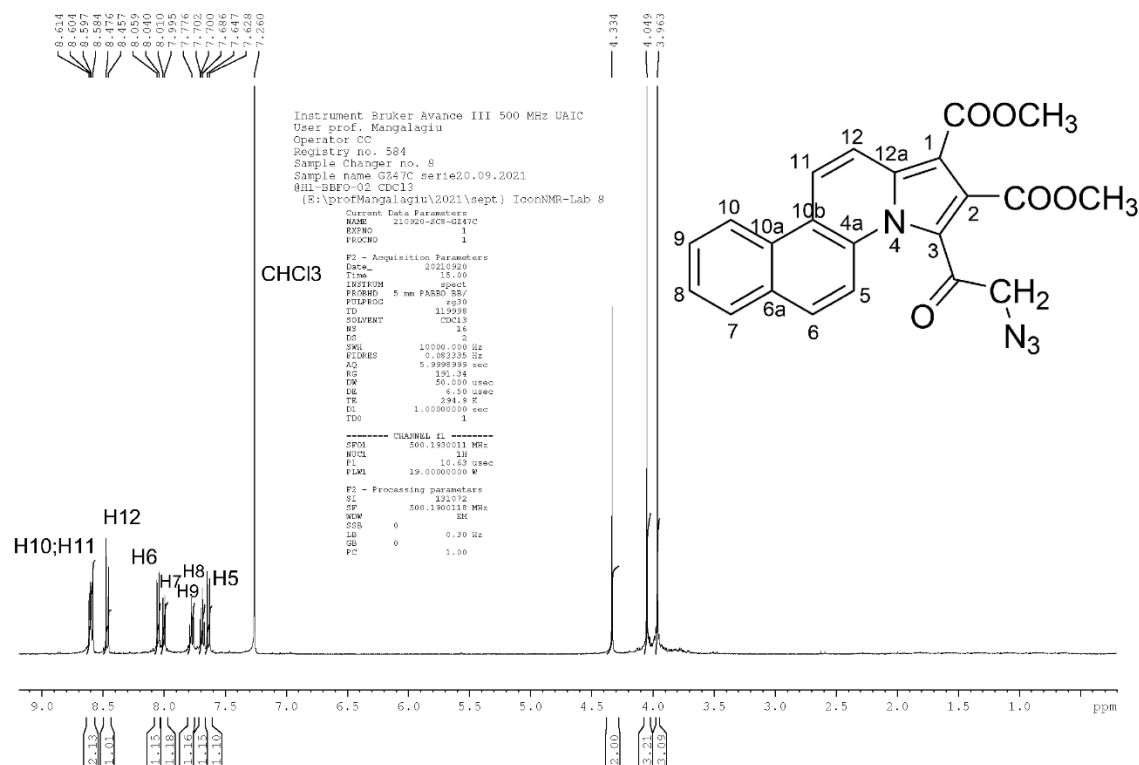
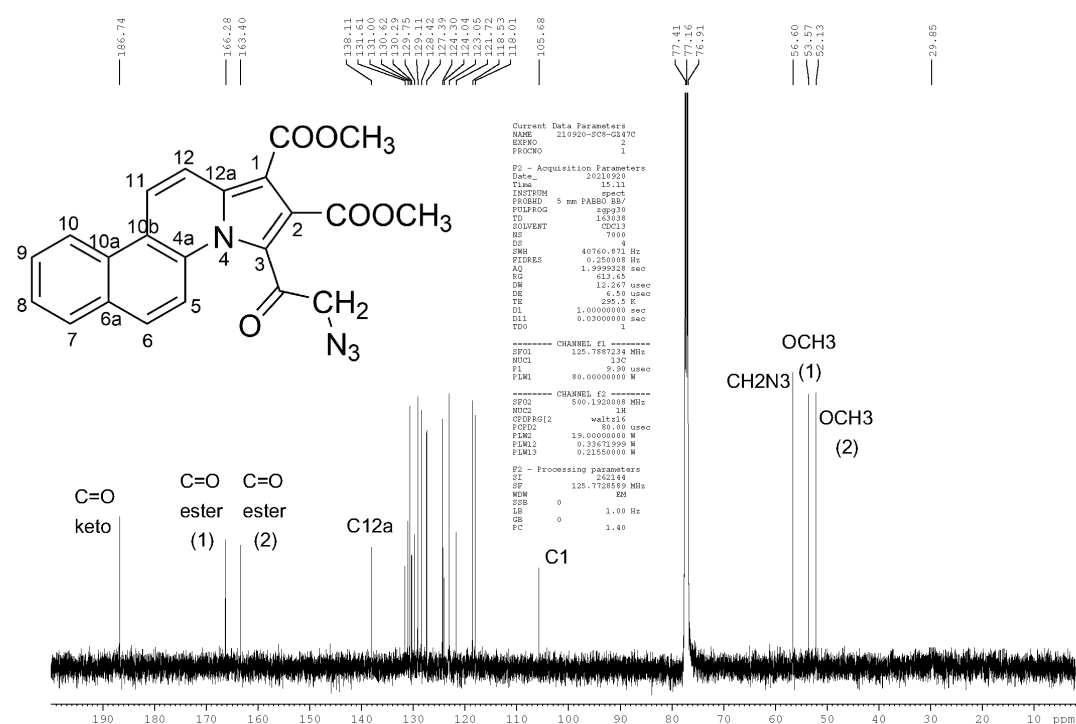


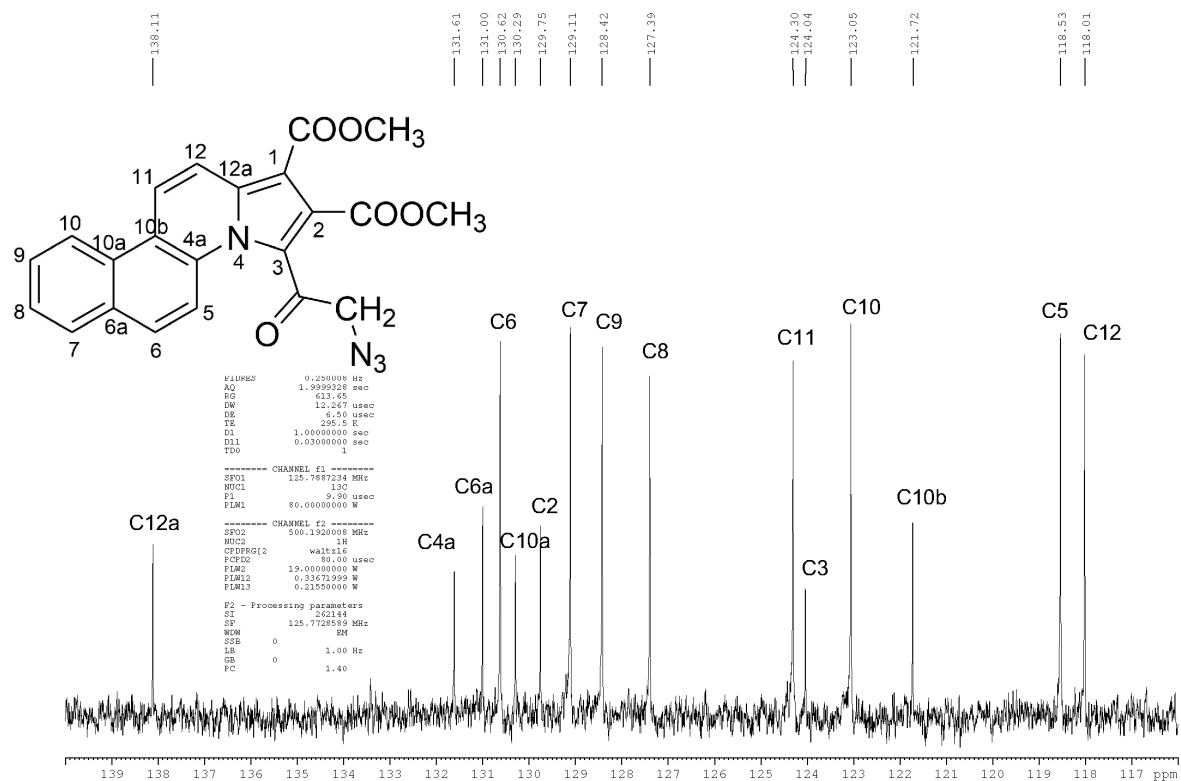
Figure S8c. Detail in the aromatic area of the <sup>13</sup>C NMR spectrum of the compound 4a.





**Figure S8d.** Long range  $^1\text{H}$ - $^{15}\text{N}$  correlation HMBC spectrum of the compound **4a**.

Figure S9a. <sup>1</sup>H NMR spectrum of the compound 4b.Figure S9b. <sup>13</sup>C NMR spectrum of the compound 4b.



**Figure S9c.** Detail in the aromatic area of the <sup>13</sup>C NMR spectrum of the compound **4b**.

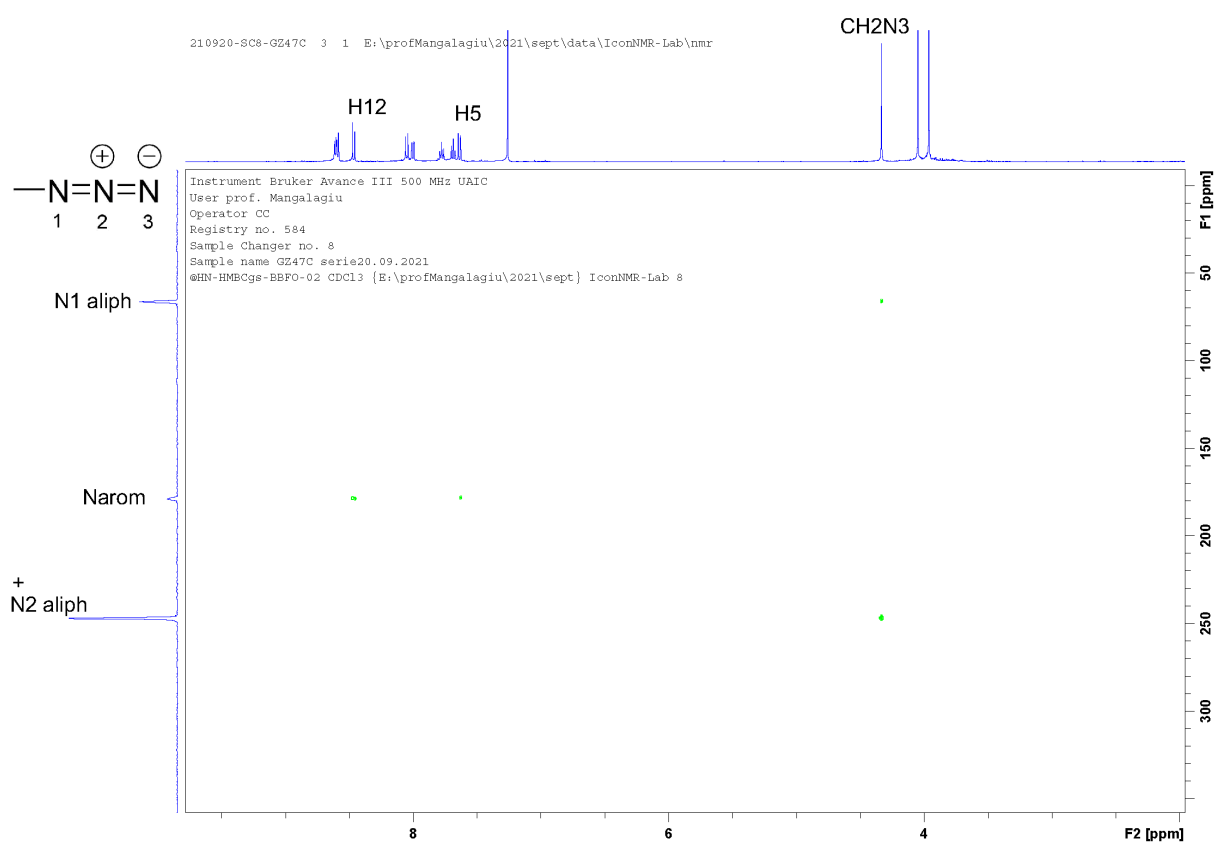
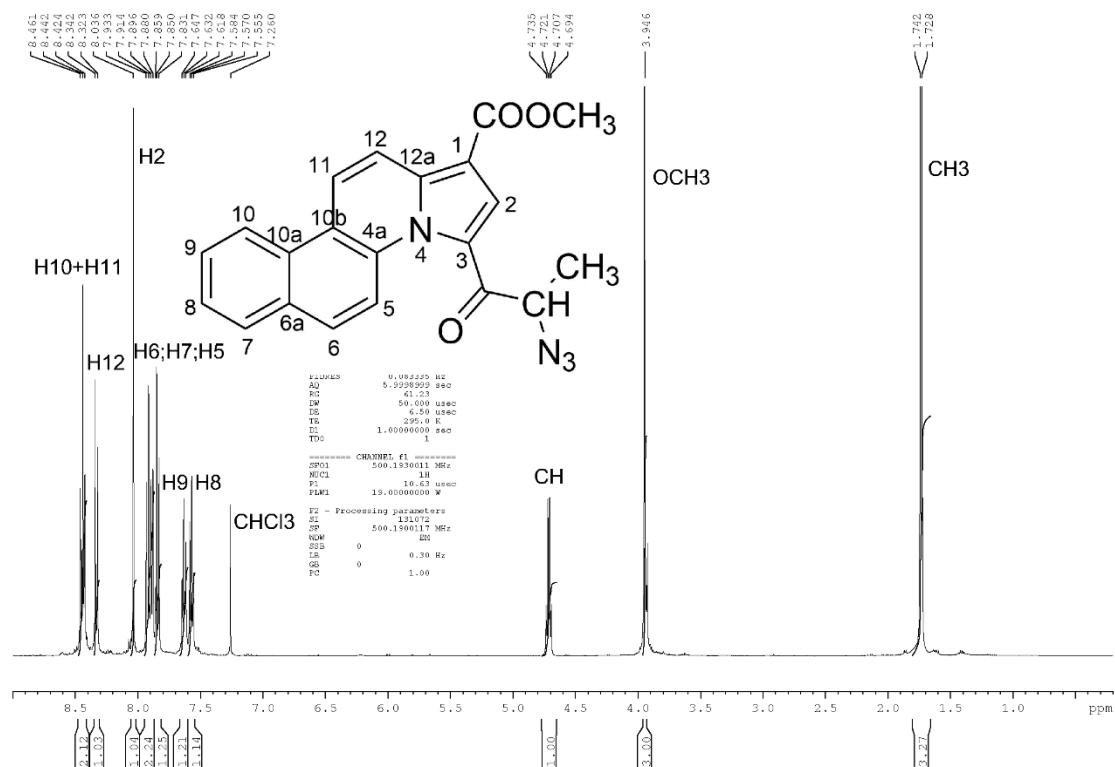
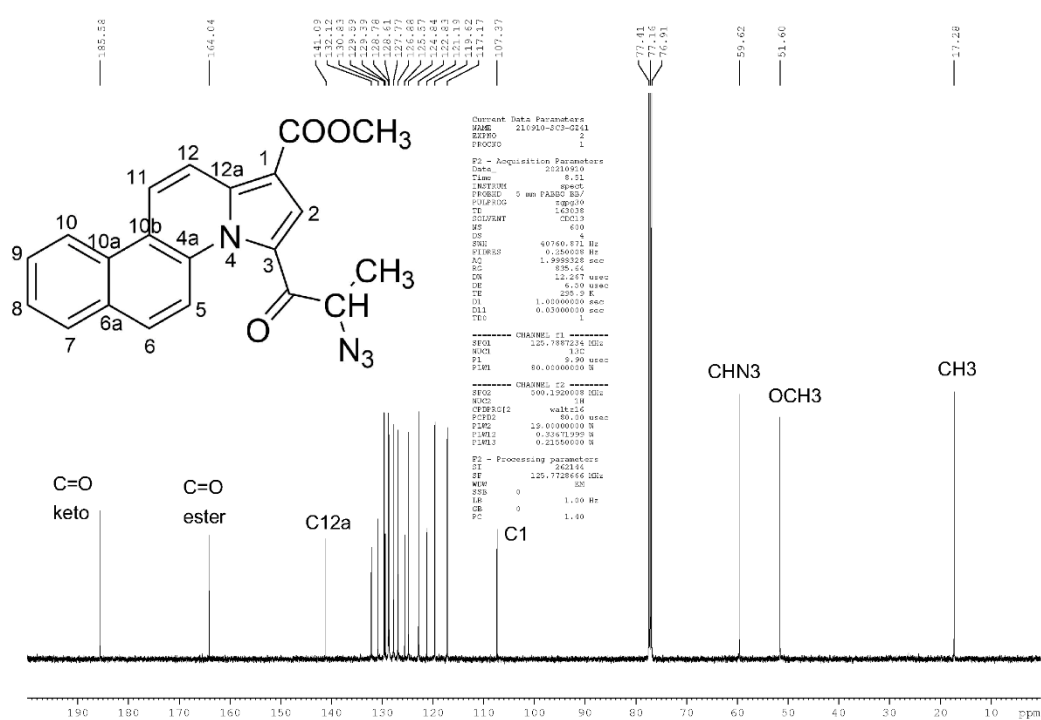
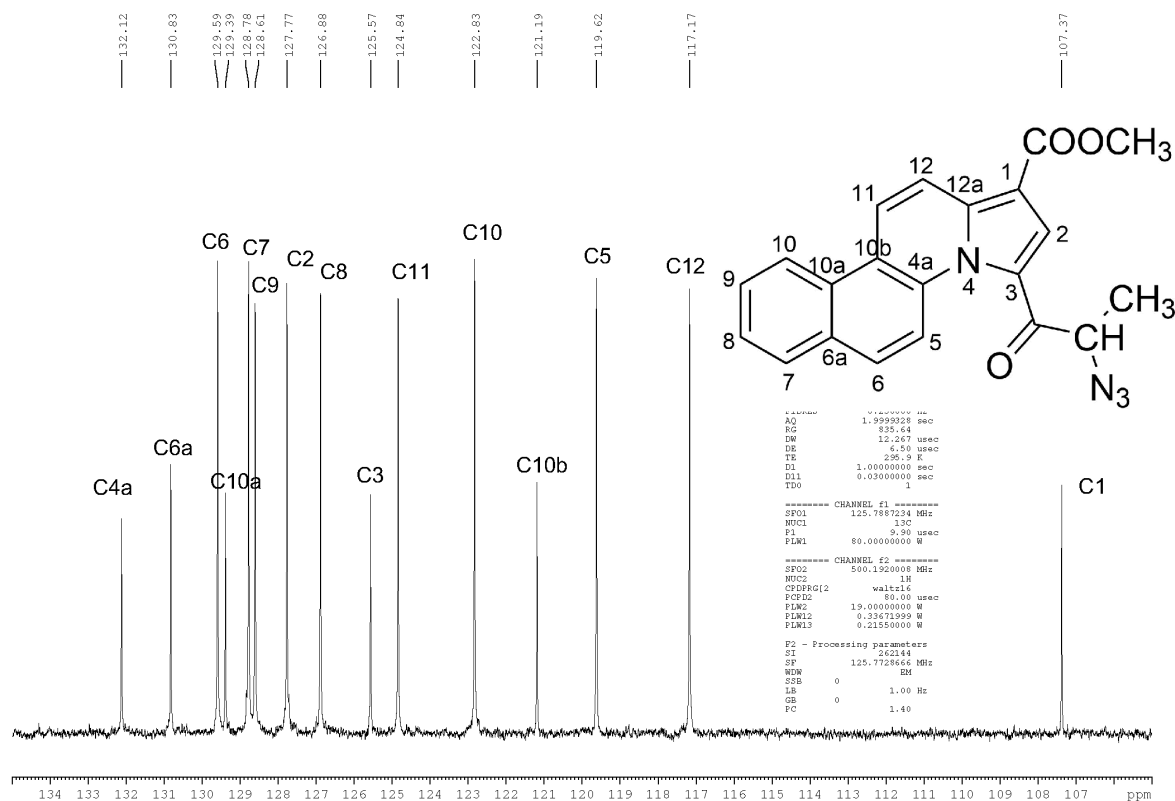


Figure S9d. Long range  $^1\text{H}$ - $^{15}\text{N}$  correlation HMBC spectrum of the compound **4b**.

Figure S10a. <sup>1</sup>H NMR spectrum of the compound 4c.Figure S10b. <sup>13</sup>C NMR spectrum of the compound 4c.



**Figure S10c.** Detail in the aromatic area of the  $^{13}\text{C}$  NMR spectrum of the compound 4c.

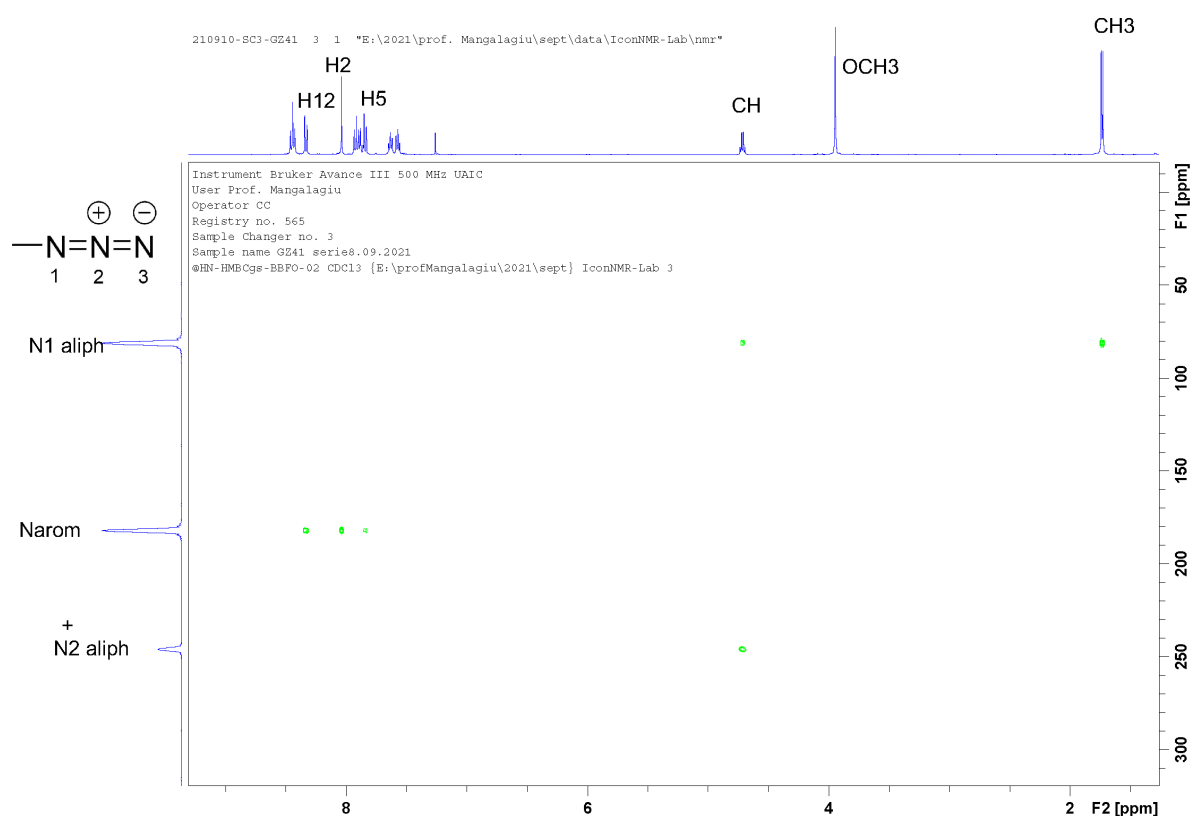
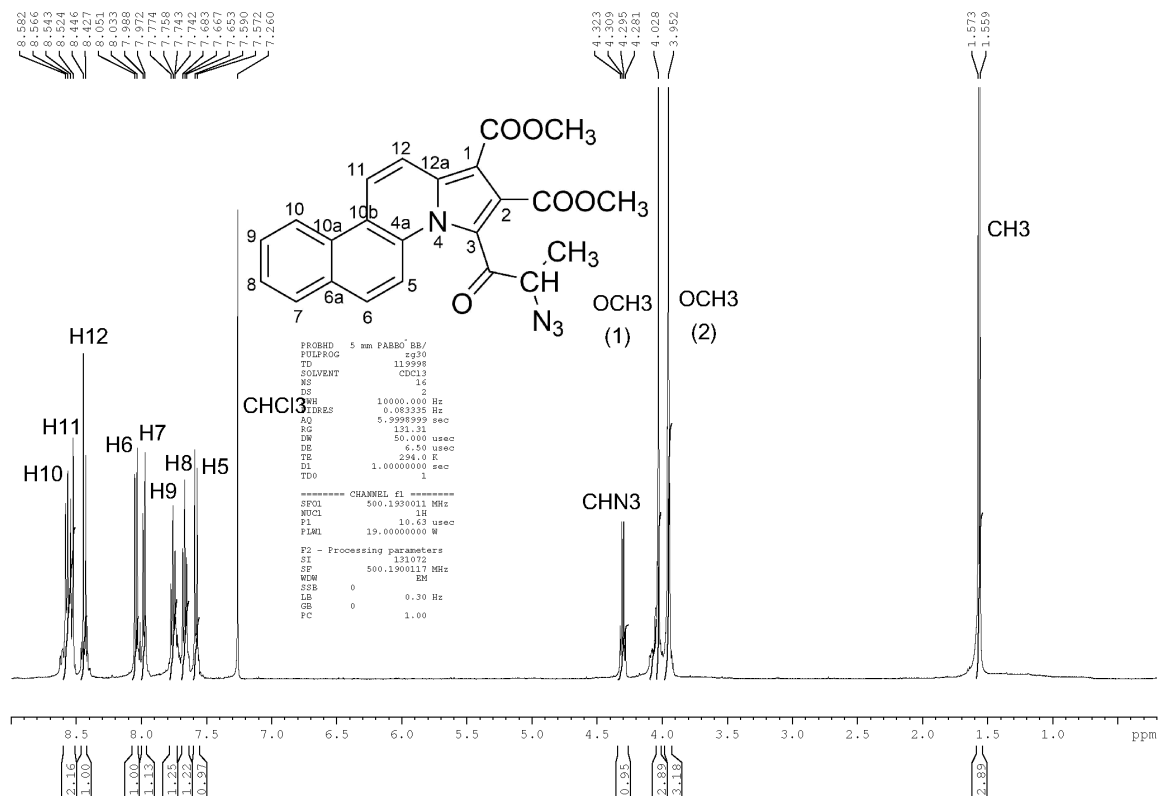
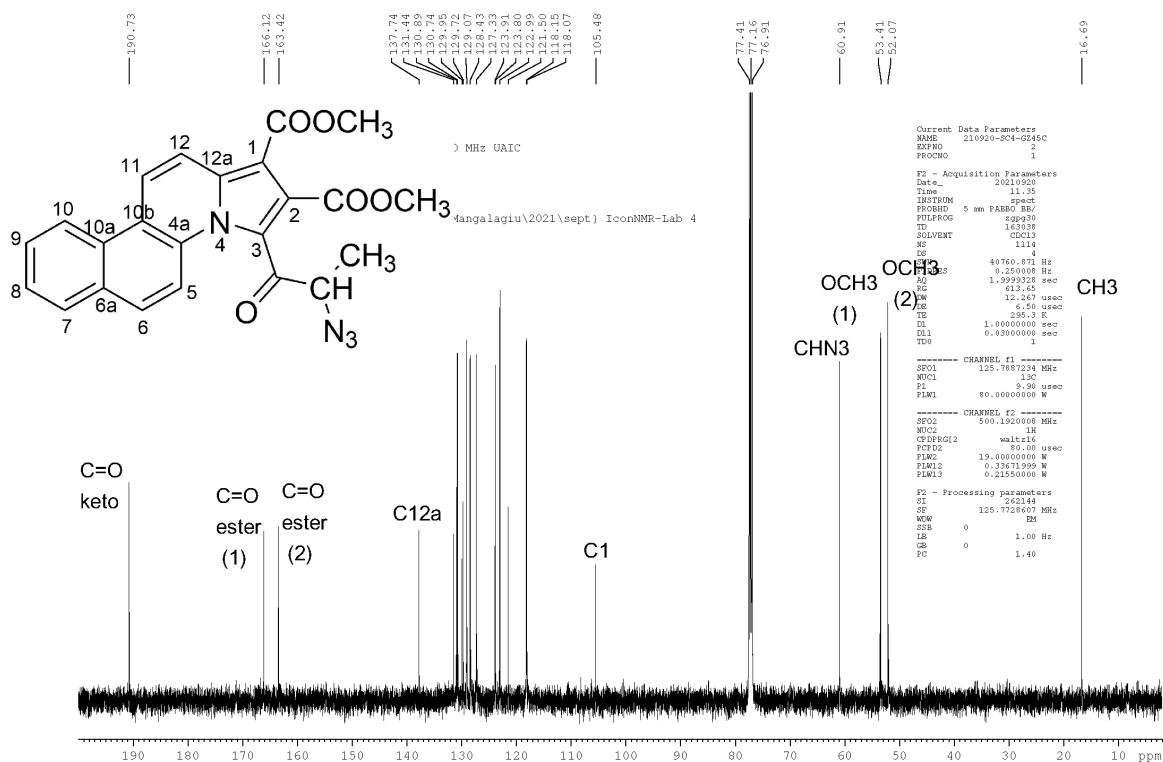
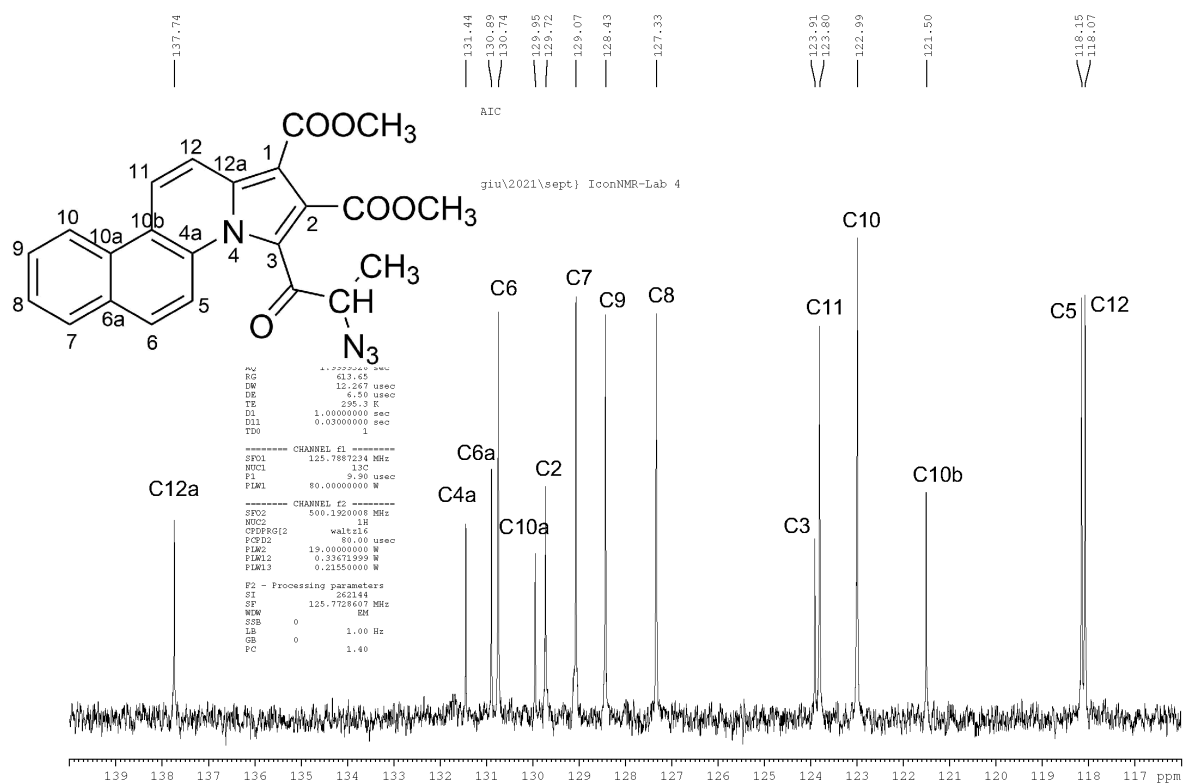
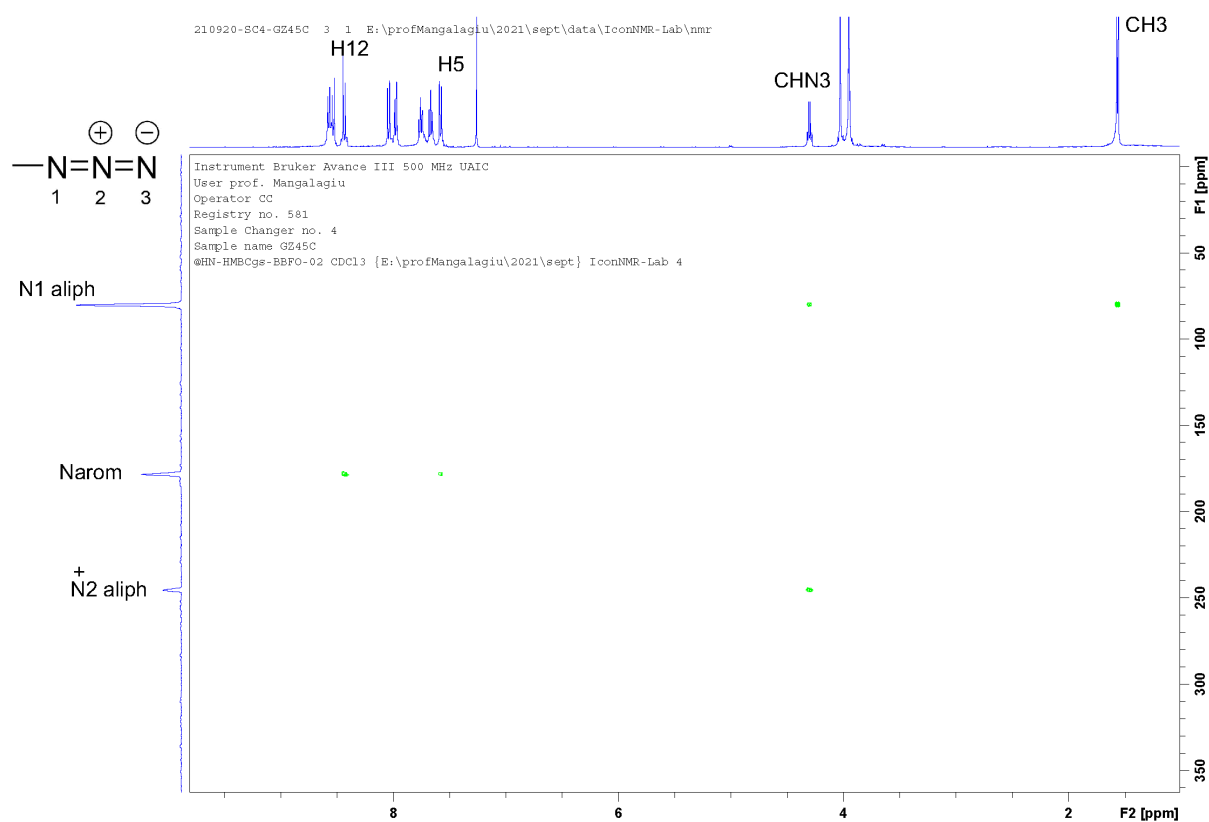


Figure S10d . Long range  $^1\text{H}$ - $^{15}\text{N}$  correlation HMBC spectrum of the compound **4c**.

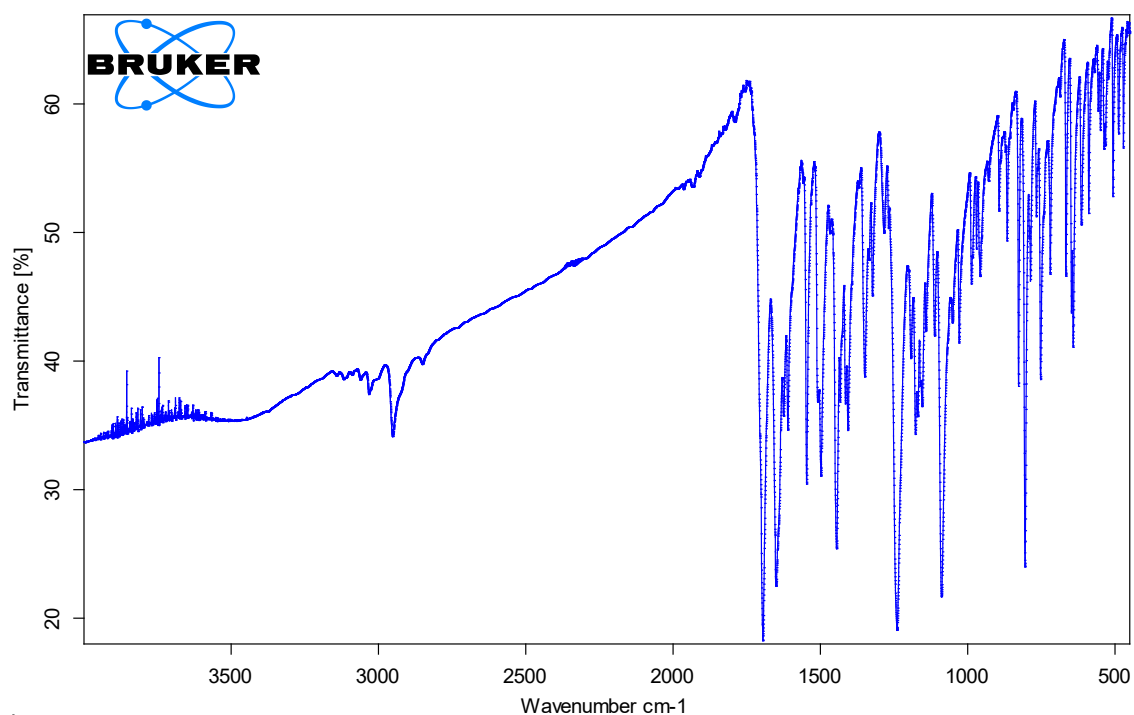
Figure S11a. <sup>1</sup>H NMR spectrum of the compound 4d.



Figure S11b. <sup>13</sup>C NMR spectrum of the compound 4d.

**Figure S11c.** Detail in the aromatic area of the  $^{13}\text{C}$  NMR spectrum of the compound **4d**.**Figure S11d.** Long range  $^1\text{H}$ - $^{15}\text{N}$  correlation HMBC spectrum of the compound **4d**.

## 3. IR spectra of the obtained compounds



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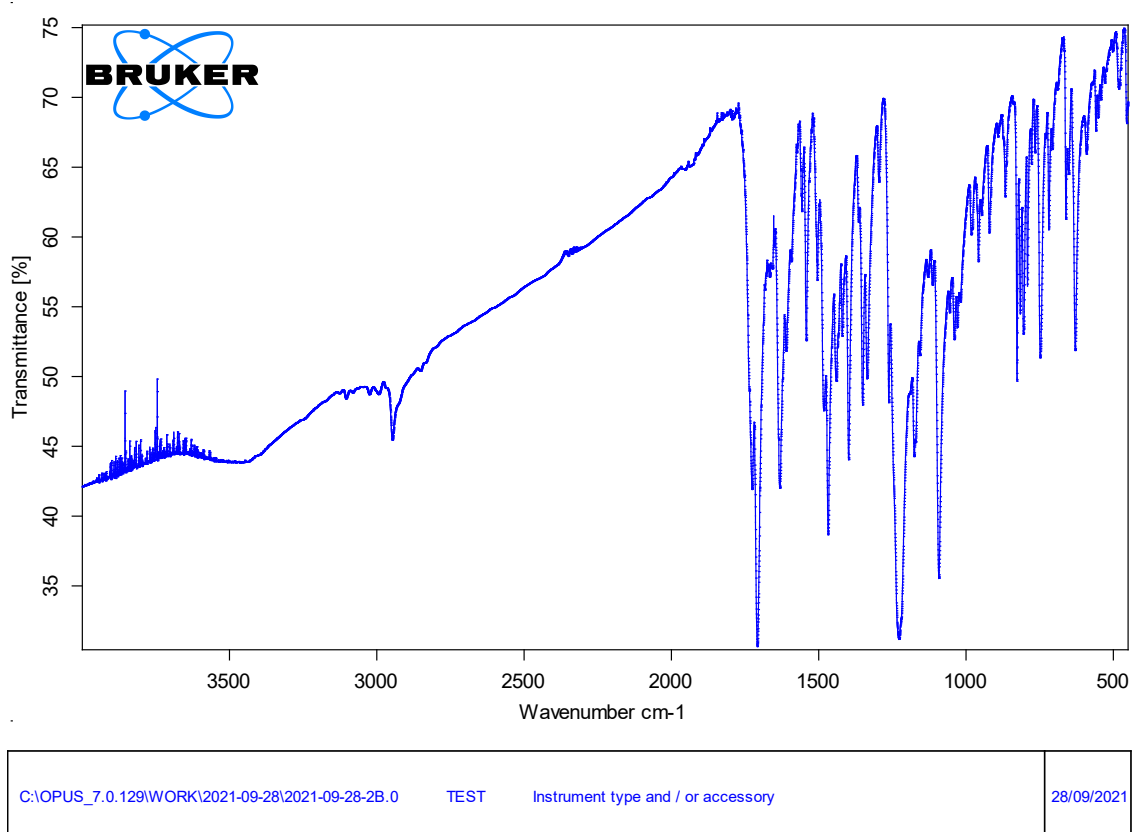
TEST

Instrument type and / or accessory

28/09/2021

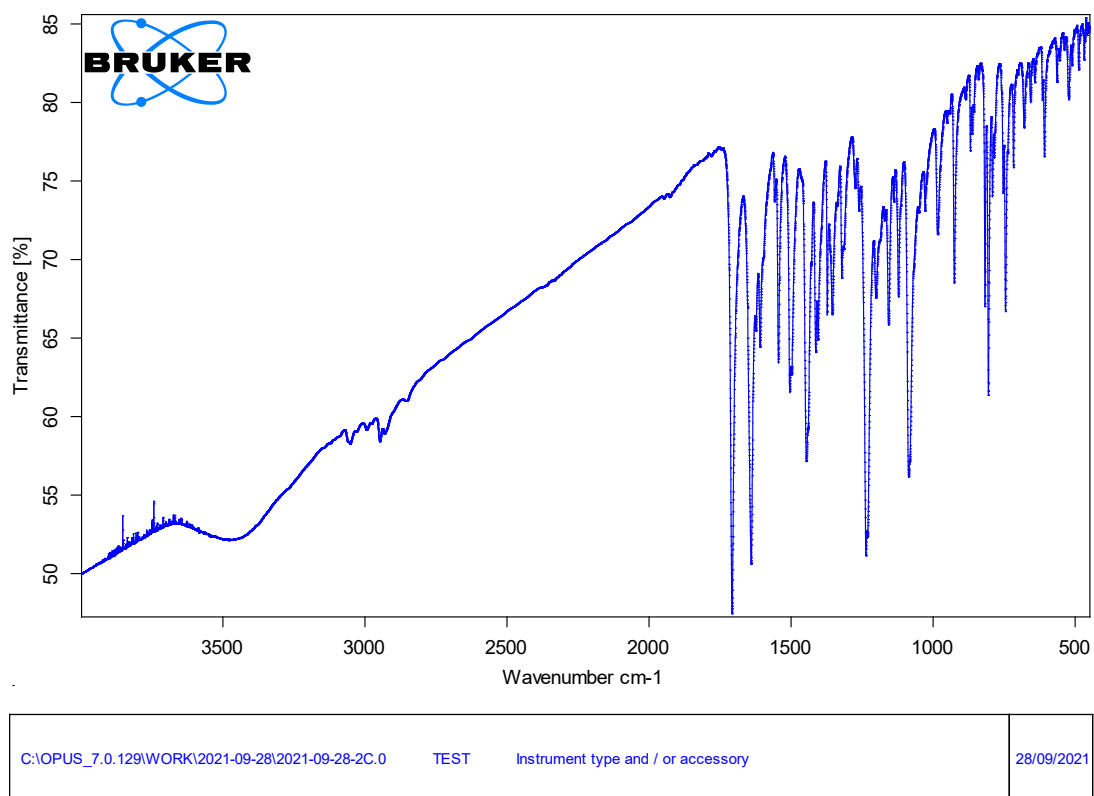
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Figure S12. IR spectrum of the compound 2a.



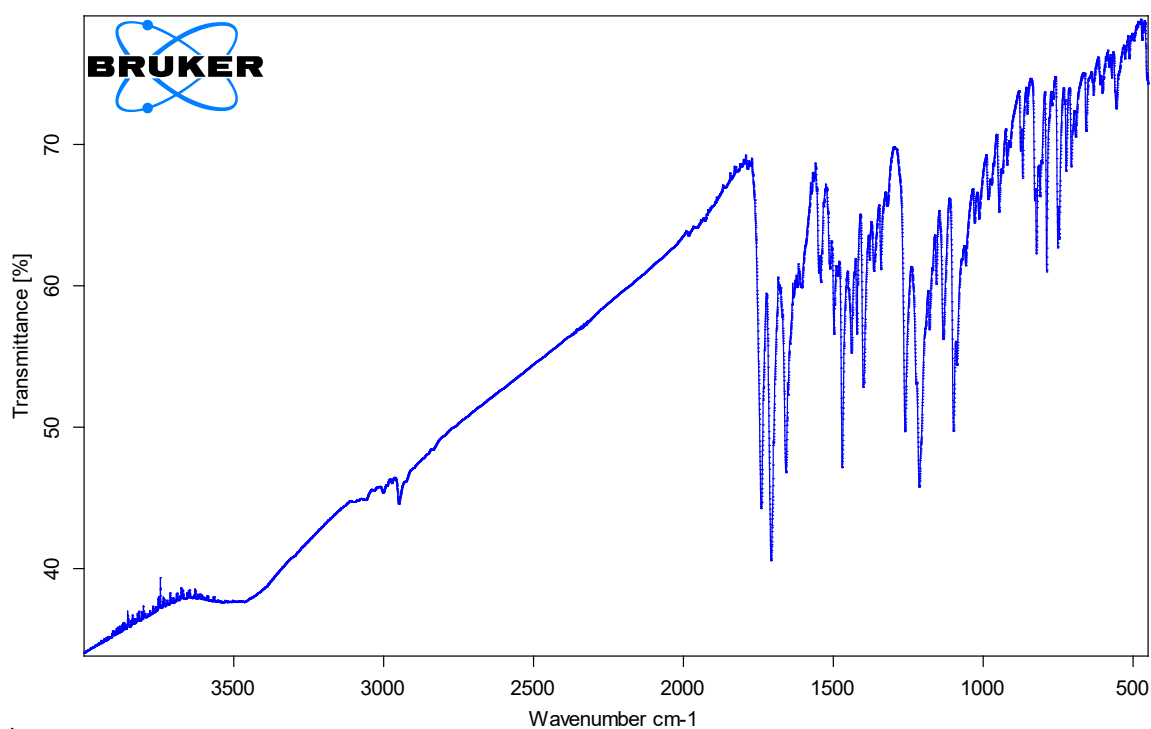
Page 1/1

Figure S13. IR spectrum of the compound 2b.



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Figure S14. IR spectrum of the compound 2c.



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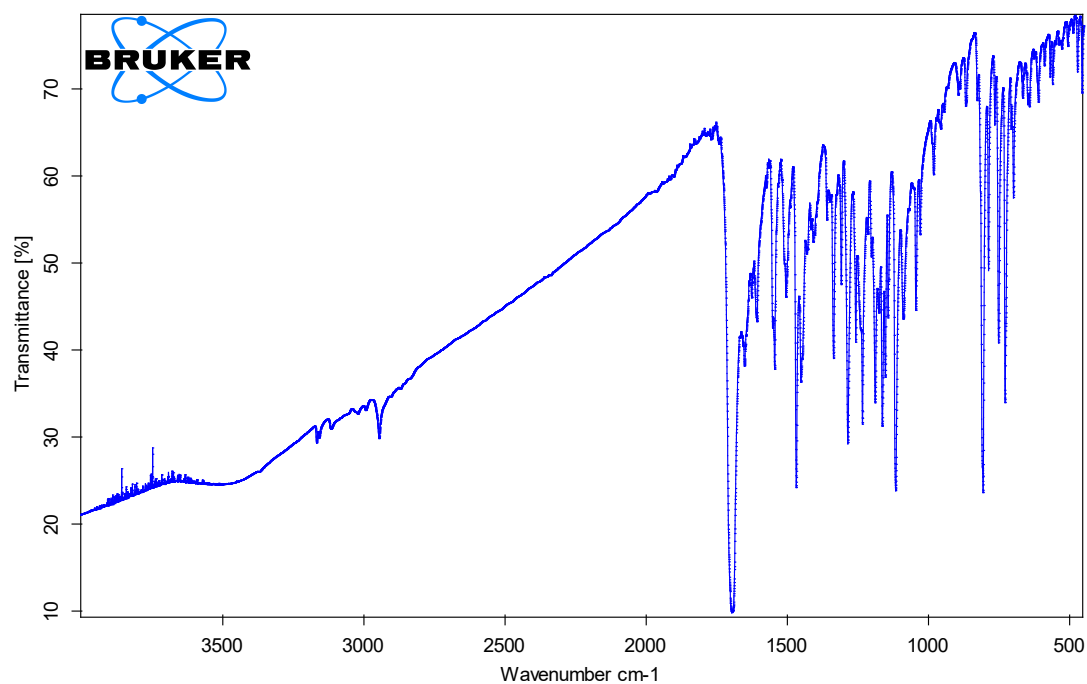
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Instrument type and / or accessory

28/09/2021

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Figure S15. IR spectrum of the compound 2d.



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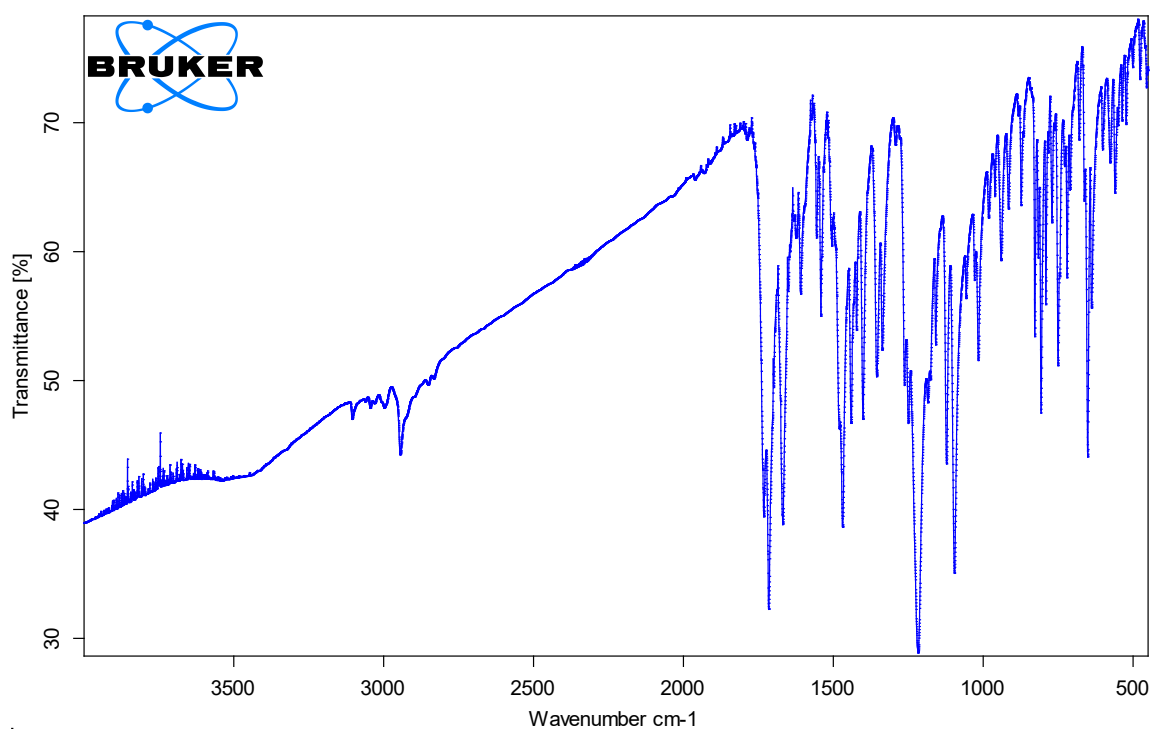
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Instrument type and / or accessory

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Figure S16. IR spectrum of the compound 3a.



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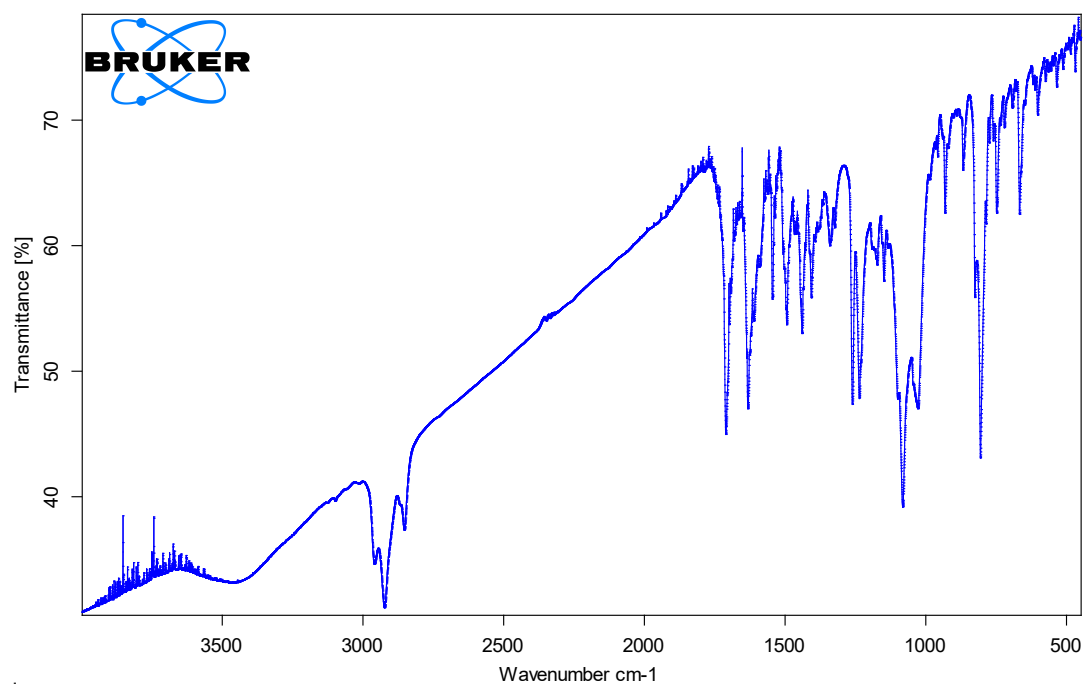
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Instrument type and / or accessory

28/09/2021

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Figure S17. IR spectrum of the compound 3b.



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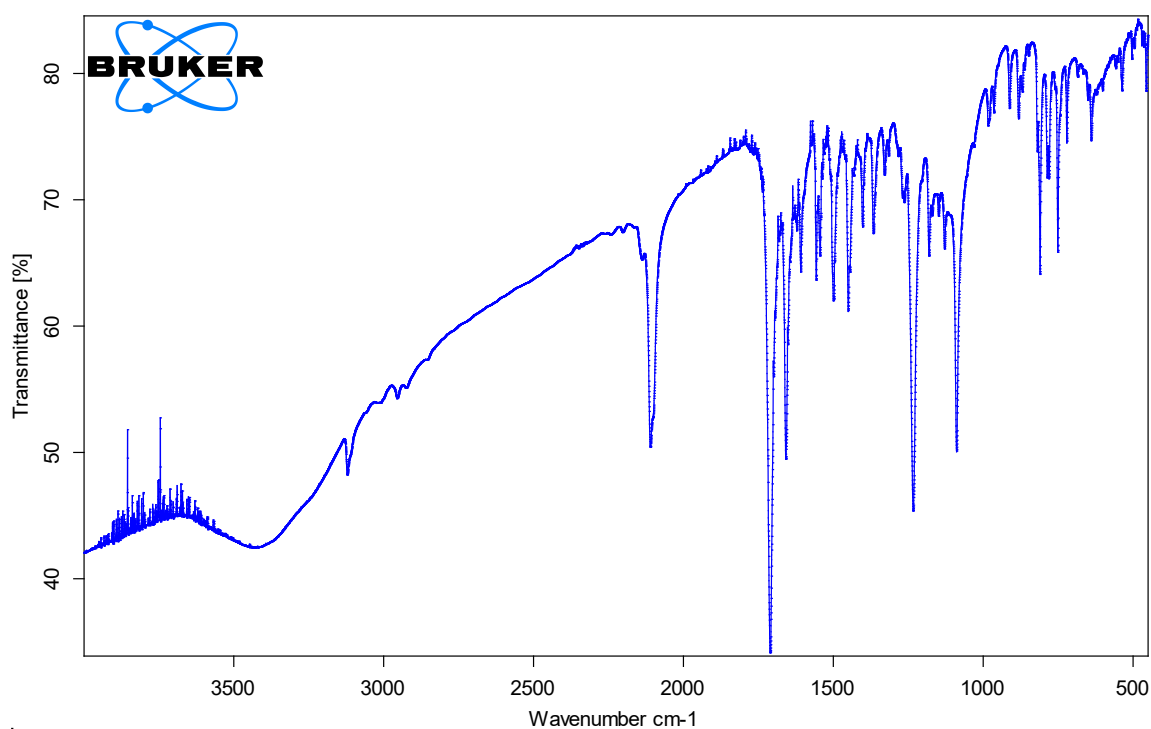
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Instrument type and / or accessory

28/09/2021

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Figure S18. IR spectrum of the compound 3c.



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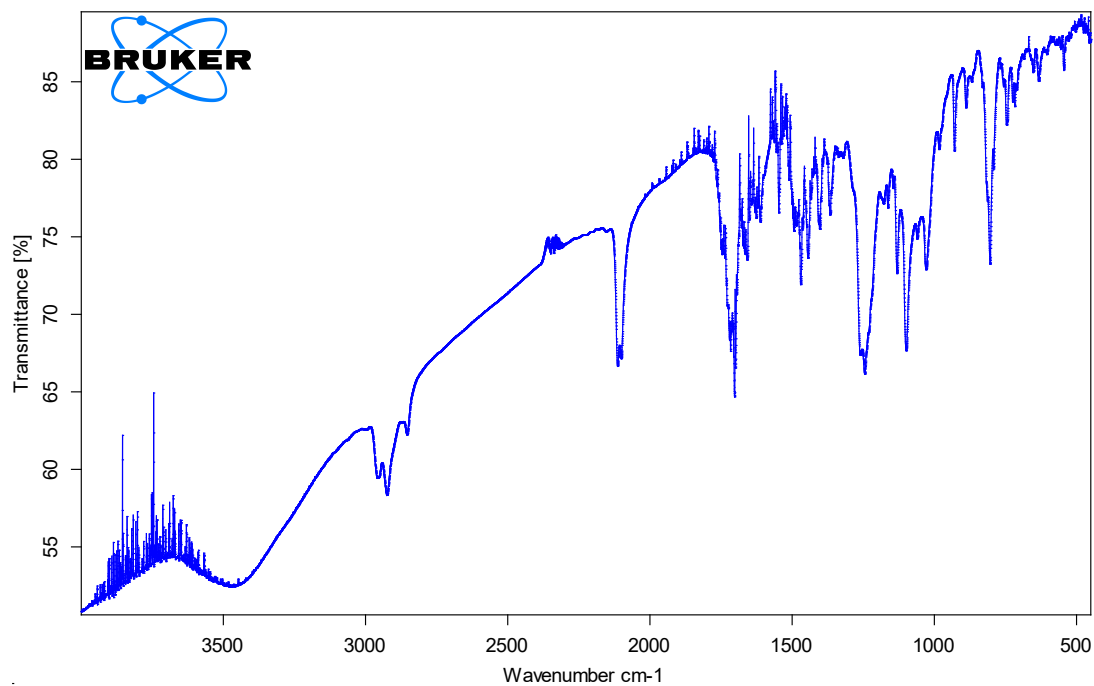
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Instrument type and / or accessory

28/09/2021

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Figure S19. IR spectrum of the compound 4a.



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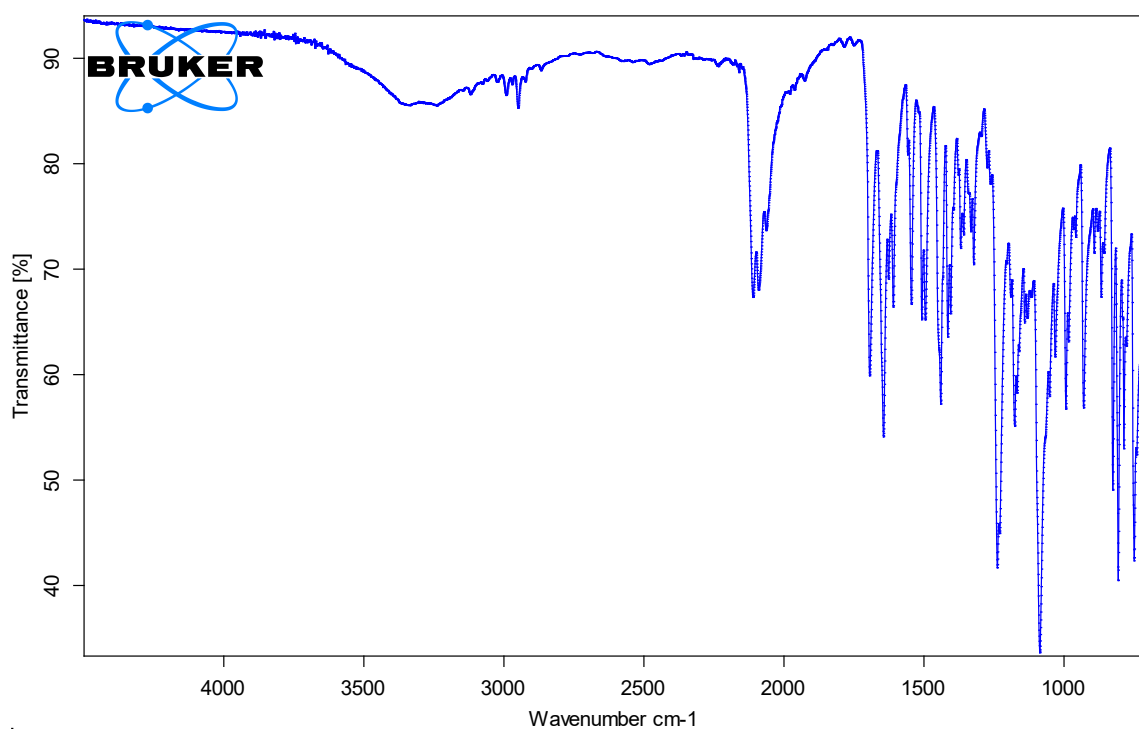
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Instrument type and / or accessory

28/09/2021

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Figure S20. IR spectrum of the compound 4b.



C:\OPUS\_7.0.129\WORK\2021-09-28-ATR\2021-09-28-4C.1

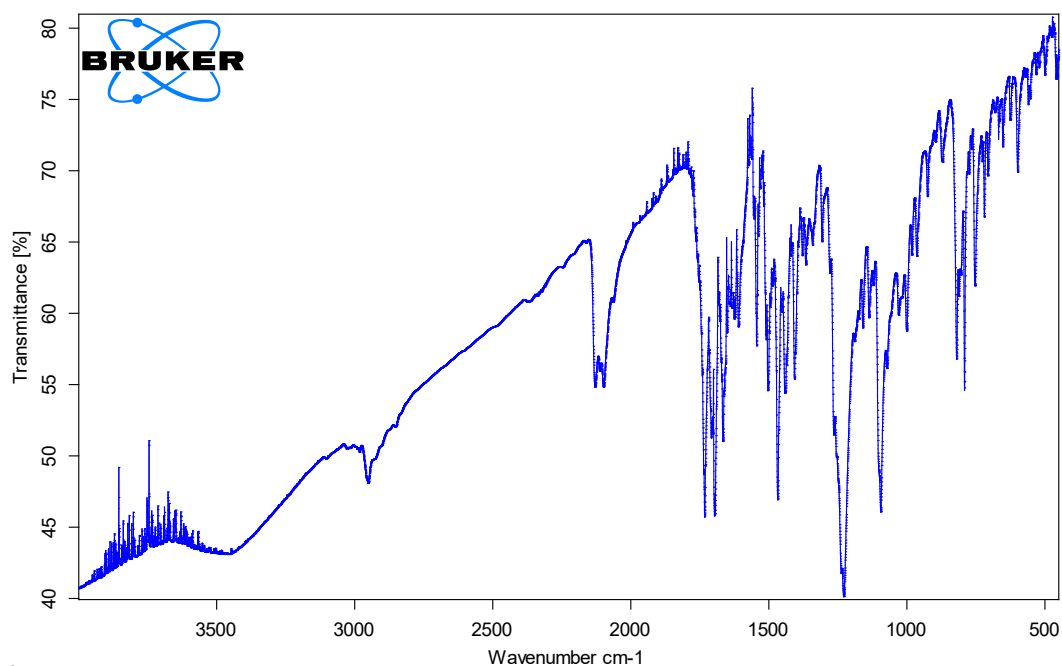
Sample description

Instrument type and / or accessory

28/09/2021

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Figure S21. IR spectrum of the compound 4c.



C:\OPUS\_7.0.129\WORK\2021-09-28\2021-09-28-4D.0

TEST

Instrument type and / or accessory

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Figure S22. IR spectrum of the compound 4d.



#### 4. UV spectra of the obtained compounds

##### Overlay Spectrum Graph Report

09/27/2021 10:51:14 AM

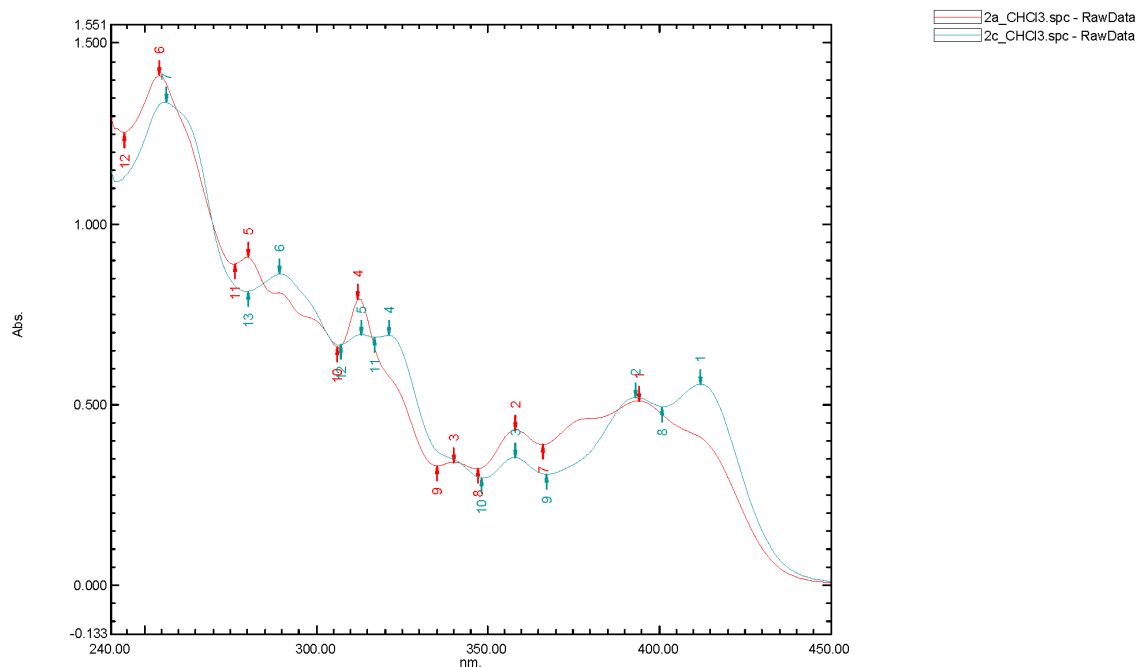


Figure S23. Overlaid UV-Vis spectra of the compounds **2a** and **2c** in chloroform.

##### Overlay Spectrum Graph Report

09/27/2021 10:51:59 AM

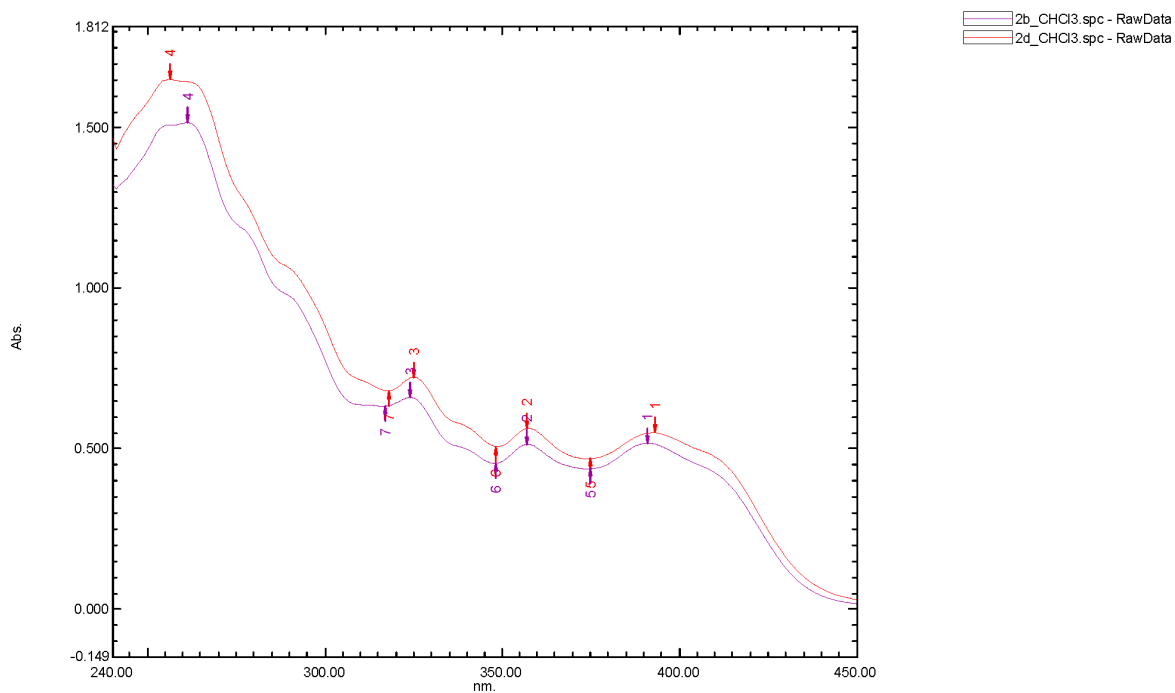


Figure S24. Overlaid UV-Vis spectra of the compounds **2b** and **2d** in chloroform.

## Overlay Spectrum Graph Report

09/27/2021 10:53:15 AM

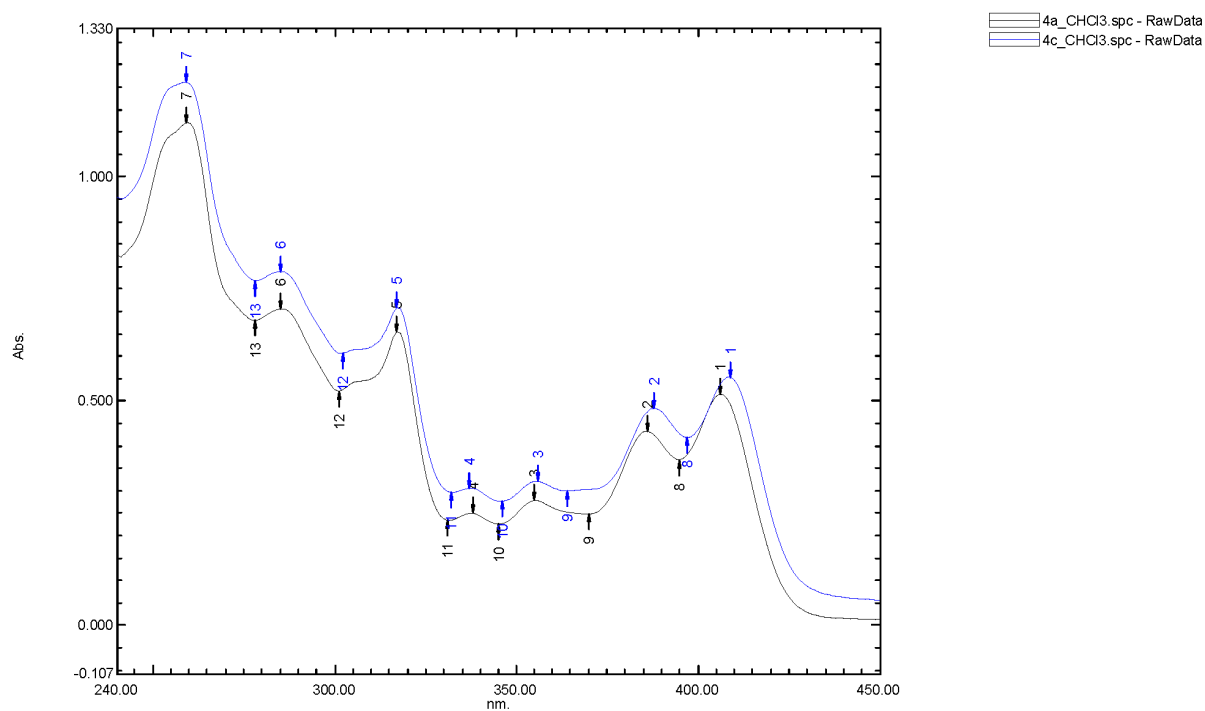


Figure S25. Overlaid UV-Vis spectra of the compounds 4a and 4c in chloroform.

## Overlay Spectrum Graph Report

09/27/2021 10:53:53 AM

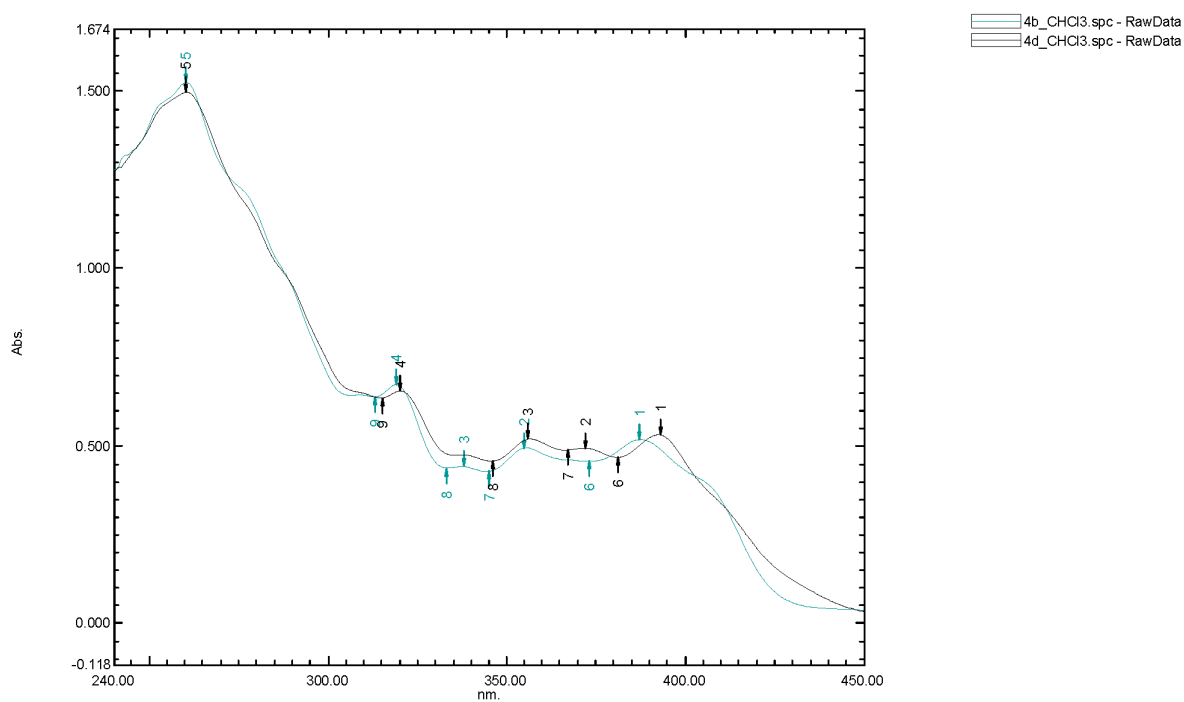
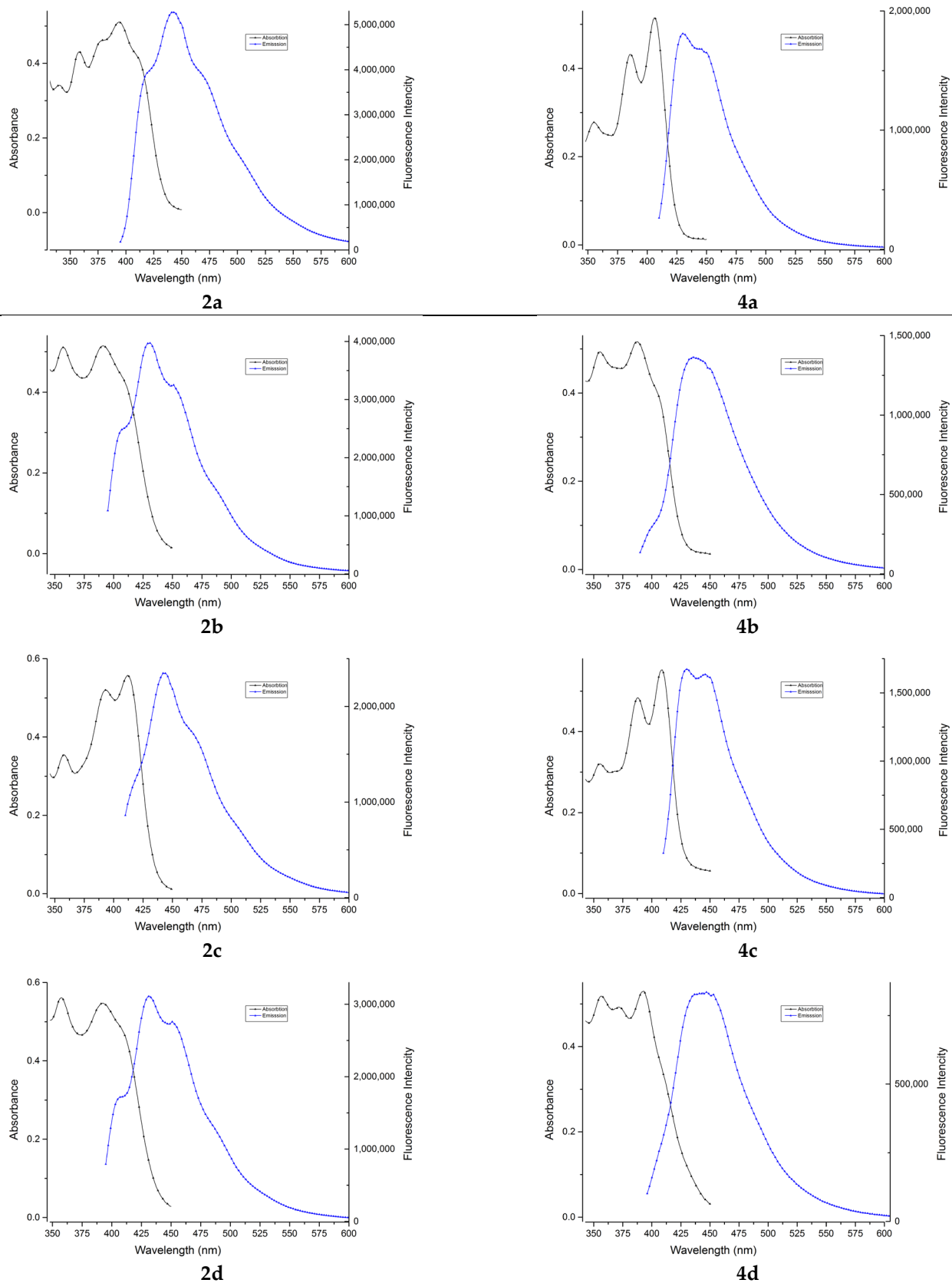


Figure S26. Overlaid UV-Vis spectra of the compounds 4b and 4c in chloroform.

In the case of the samples **2a-d** the profile of the third absorption region and the absorption maxima are similar for the samples **2a**, **2b** and **2d** (394 nm for **2a**, 391 nm for **2b** and 393 nm for **2d**), while for the sample **2c** the maximum of the absorption is situated on 412 nm. Sample **2c** present the same absorption bands like **2a**, **2b** and **2d** with a small bathochromic shift.

In the case of the samples **4a** and **4c** the profile of the third absorption region and the absorption maxima are similar (406 nm for **4a** and 409 nm for **4c**), while the samples **4b** and **4d** have similar profile of the third absorption region and the absorption maxima (387 nm for **4b** and 393 nm for **4d**). Samples **4a** and **4c** present the same absorption bands like **4b** and **4d** with a small bathochromic shift. The similar absorption behaviour of the samples **4a** with **4c** and of the samples **4b** with **4d** can be explained by their similar structure (samples **b** and **d** having a supplementary carbomethoxy group in the 2<sup>nd</sup> position of the azatetracyclic skeleton in comparison with the samples **a** and **c**).

### 5. Absorption vs emission spectra of the obtained compounds



**Figure S27.** The absorption (black line) and emission (blue line) spectra of functionalized derivatives: bromides **2a-d** (left column) and azides **4a-d** (right column). Excitation wavelength was: 380 nm for sample **4b**; 385 nm for samples **2a**, **2b**, **2d** and **4d**; and 400 nm for samples **2c**, **4a** and **4c**.

In the case of the bromides **2a-d**, the samples **2a** and **2c** have similar peak profile with  $\lambda_{\max} = 443$  nm for sample **2a** and respectively  $\lambda_{\max} = 444$  nm for sample **2c**. The fluorescence intensity of the sample **2a** is higher than the fluorescence intensity of the sample **2c**. The samples **2b** and **2d** have similar peak profile having  $\lambda_{\max} = 431$  nm for sample **2b** and respectively  $\lambda_{\max} = 433$  nm for sample **2d**. The fluorescence intensity of the sample **2b** is higher than the fluorescence intensity of the sample **2d**, but lower than the fluorescence intensity of the sample **2c**. The fluorescence intensity of all bromides **2a-d** is higher than the fluorescence of the corresponding azides **4a-d**.

In the case of the azides **4a-d**, the samples **4a** and **4c** have structured band with similar peak profile ( $\lambda_{\max} = 430$  nm for both sample **4a** and **4c**) and intensity. The azides **4b** and **4d** have similar peak profile ( $\lambda_{\max} = 435$  nm for sample **4b** and respectively  $\lambda_{\max} = 445$  nm for sample **4d**) with unstructured band. The fluorescence intensity of the sample **4d** is lower (almost a half) than the intensity of the sample **4b**. Sample **4a** have the highest fluorescence intensity from all the azides.