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J. Serb. Chem. Soc. 81 (2) S59–S89 (2016) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Synthesis, cytotoxicity and computational study of novel protoberberine derivatives

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SPECTRAL DATA FOR SYNTHESISED COMPOUNDS

N-*(2-Bromoallyl)pyridinium bromide (4)*. Compound **4** was synthesised from pyridine and 2,3-dibromopropene as a light brown amorphous solid (720 mg, 85 %). Its melting point was not determined due to the hygroscopic properties of the compound.

N-*(2-Iodoallyl)isoquinolinium bromide (**14a**)*. Compound **14a** was synthesised from isoquinoline and 3-bromo-2-iodoprop-1-ene as a light brown amorphous solid (1.13 g, 92 %). Its melting point was not determined due to the hygroscopic properties of the compound.

*2-Iodoallyl-6,7-dimethoxy-2-isoquinolinium bromide (**14b**)*. Compound **14b** was synthesised from 6,7-dimethoxyisoquinoline and 3-bromo-2-iodoprop--1-ene as a white amorphous solid, m.p. > 270 °C (1.10 g, 96 %).

*4,9-Dihydro-2-(2-iodoallyl)-3*H*-pyrido[3,4,-*b*]indolium bromide (**22**)*. Compound **22** was synthesised from 3,4-dihydro-*β*-carboline and 3-bromo-2-iodoprop-1-ene as a dark orange amorphous solid, (1.04 g, 80 %). Melting point was not determined due to hygroscopic properties of the compound.

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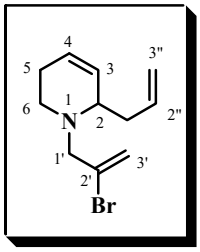
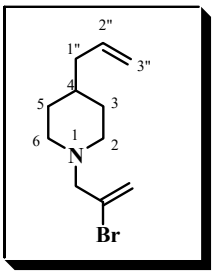
2-Allyl-1-(2-bromoallyl)-1,2,5,6-tetrahydropyridine (7)



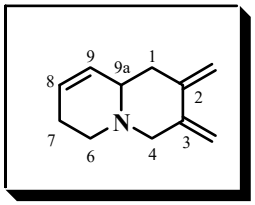
The products **7** and **8** were isolated after flash chromatography (SiO_2, 95:5 *V*/*V*, petroleum ether–diethyl ether) as a pale yellow oil, in ratio 1:1 (46 %). IR (ATR, ν / cm^{-1}): 2888, 1636, 1112, 961, 844; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 5.94–5.91 (*m*, 1H, H-3"), 5.84–5.76 (*m*, 2H, H-4, H-2"), 5.61 (*dd*, 1H, *J* = 4.4 and 1.6 Hz, H-3), 5.57 (*brs*, 1H, H-3'), 5.10 (*d*, 1H, *J* = 6.8 Hz, H-3"), 5.01 (*brs*, 1H, H-3'), 3.53 (*d*, 1H, *J* = 15.6 Hz, H-1'), 3.19 (*d*, 1H, *J* = 15.6 Hz, H-1'), 3.10–3.00 (*m*, 1H, H-2), 2.99–2.90 (*m,* 1H), 2.57–2.42 (*m*, 1H), 2.39–2.19 (*m*, 2H), 2.11–2.01 (*m*, 2H, H-5); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 135.6, 131.9, 129.2, 125.4, 117.6, 116.4 (=CH_2), 62.3 (**C**H_2CBr); 58.4 C(2), 46.3 C(6), 37.9 (**C**H_2CH=CH_2), 24.0 (C-5); MS (EI) *m*/*z*: 241.0, 200.0, 120.1, 80.1; HRMS (ESI): calculated for $C_{11}H_{17}BrN$ $[M+H]^+$ 242.05389, found 242.05474.

*4-Allyl-1-(2-bromoallyl) piperidine (**8**)*



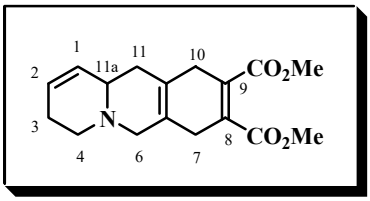
IR (ATR, ν / cm^{-1}): 2909, 1629, 1445, 980, 909, 892; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 5.84–5.82 (*m*, 1H), 5.81–5.67 (*m*, 1H), 5.56 (*s*, 1H), 5.05–4.99 (*m*, 1H), 4.95 (*s*, 1H), 3.16 (*s*, 2H), 2.93–2.86 (*m*, 2H), 2.03–1.92 (*m*, 4H), 1.69––1.65 (*m*, 3H), 1.33–1.24 (*m*, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$, δ / ppm): 137.0, 131.1, 118.2, 115.7, 66.8, 53.5, 40.9, 35.6, 31.9; MS (EI) *m*/*z*: 244.1, 202.0, 164.1, 138.1, 120.1; HRMS (ESI): calculated for $C_{11}H_{19}BrN$ $[M+H]^+$ 244.06954, found 244.06931.

*2,3,4,6,7,9a-Hexahydro-2,3-dimethylene-1*H*-quinolizine (**9**)*



The product was isolated after flash chromatography (SiO_2, 9:1 *V*/*V*, petroleum ether–diethyl ether) as a pale yellow oil (30 mg, 26 %). IR (ATR, ν / cm^{-1}): 2937, 2908, 2732, 1332, 1130, 891, 802; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 5.77–5.73 (*m*, 1H, H-9), 5.47 (*dd*, 1H, *J* = 10.0 and 1.5 Hz, H-8), 5.12 (*t*, 1H, *J* = = 1.5 Hz, =CH_2), 5.08 (*t*, 1H, *J* = 2.0 Hz, =CH_2), 4.81 (*t*, 1H, *J* = 2.0 Hz, =CH_2), 4,75 (*t*, 1H, *J* = 2.5 Hz, =CH_2), 3.36 (*d*, 1H, *J* = 12.5 Hz, H-4), 2.91 (*dt*, 1H, *J* = = 12.0 and 1.5 Hz, H-4), 2.88–2.85 (*m*, 1H, H-6), 2.67–2.64 (*m*, 1H, H-9a), 2.47– –2.42 (*m*, 1H, H-7), 2.39 (*dd*, 1H, *J* = 10.5 and 3.5 Hz, H-6), 2.35 (*dd*, 1H, *J* = = 13.5 and 3.5 Hz, H-1), 2.20–2.14 (*m*, 1H, H-1), 2.05–2.00 (*m*, 1H, H-7); ^{13}C- -NMR (125 MHz, $CDCl_3$ δ / ppm): 145.6 (C-2), 144.4 (C-3), 128.9 (C-8), 125.3 (C-9), 109.5 (H_2**C**=C-3), 109.4 5 (H_2**C**=C-2),, 61.7 (C-4), 60.5 (C-9a), 51.1 (C-6), 40.2 (C-1), 26.0 (C-7); MS (EI) *m*/*z*:160.1 $[M-H]^+$, 146.1, 80.1, 67.1; HRMS (ESI): calculated for $C_{11}H_{16}N$ $[M+H]^+$ 162.12773, found 162.12773.

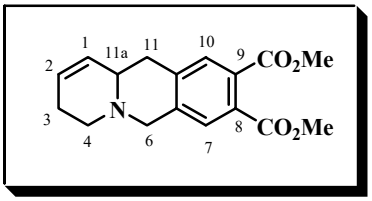
*Dimethyl-4,6,7,10,11,11a-hexahydro-3H-pyrido[1,2-b]isoquinoline-8,9-dicarboxylate (**10**)*



The product was isolated after flash chromatography (SiO_2, 9:1 *V*/*V*, diethyl ether–petroleum ether) as a creamy-white amorphous solid (38 mg, 72 %), m.p. 110–111 °C. IR (ATR, ν / cm^{-1}): 1712, 1273, 1071, 791, 757; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 5.78–5.75 (*m*, 1H, H-2), 5.51 (*d*, 1H, *J* = 10.0 Hz, H-1), 3.78 (*s*, 6H, $COOCH_3$), 3.10 (*d*, 1H, *J* = 20.0 Hz, H-11a), 2.95–2.82 (*m*, 7H, H-4, H-6, H-7, H-10), 2.43–2.40 (*m*, 2H, H-3, H-4), 2.05–2.03 (*m*, 2H, H-3, H-11), 1.94–1.90 (*m*, 1H, H-11); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.3 (C=O), 168.1 (C=O), 132.8 (C-7), 131.8 (C-8), 128.7 (C-1), 124.9 (C-2), 123.2 (C-6a), 122.9 (C-10a), 57.5 (C-11a), 56.9 (C-6), 52.2 (COO**C**H_3), 50.6 (C-4), 36.1 (C-11), 32.2 (C-10), 30.3 (C-7), 25.9 (C-3); MS (ESI) *m*/*z*: 304.0, 272.0, 243.1,

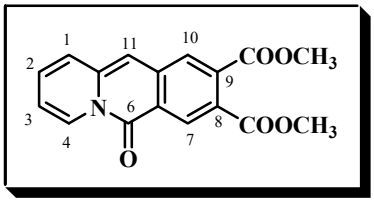
134.1, 115.2; HRMS (ESI) calculated for $C_{17}H_{22}NO_4$ $[M+H]^+$ 304.15433, found 304.15410.

*Dimethyl 3,6,11,11a-tetrahydro-4*H*-pyrido[1,2-*b*]isoquinoline-8,9-dicarboxylate (**11**)*



The product was isolated after flash chromatography (SiO_2, 9:1 *V*/*V*, diethyl ether–petroleum ether) as a yellow oil (10 mg, 80 %), which solidified upon standing, m.p. 75–78 °C. IR (ATR, ν / cm^{-1}): 1716, 1435, 1268, 1121, 776; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 7.46 (*s*, 1H, H-10), 7.43 (*s*, 1H, H-7), 5.86–5.83 (*m*, 1H, H-2), 5.89 (*d*, 1H, *J* = 10.0 Hz, H-1), 3.98 (*d*, 1H, *J* = 15.5 Hz, H-6), 3.89 (*s*, 3H, $COOCH_3$), 3.88 (*s*, 3H, $COOCH_3$), 3.56 (*d*, 1H, *J* = 15.5 Hz, H-6), 3.04–3.01 (*m*, 1H, H-4), 2.99–2.96 (*m*, 1H, H-11a), 2.85 (*dd*, 1H, *J* = 7.0 and 4.0 Hz, H-11), 2.78–2.72 (*m*, 1H, H-11), 2.52–2.47 (*m*, 2H, H-3, H-4), 2.10–2.06 (*m*, 1H, H-3); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.1 (C=O), 167.9 (C=O), 138.5, 138.2, 129.9, 129.2, 129.2 (C-10), 128.3 (C-1), 127.0 (C-7), 125.5 (C-2), 57.6 (C-6), 57.0 (C-11a), 52.5 (2×CH_3), 50.8 (C-4), 35.7 (C-11), 25.8 (C-3) ppm; MS (ESI) *m/z*: 302.1, 271.1, 201.1, 155.1, 142.1; HRMS (ESI): calculated for $C_{17}H_{20}NO_4$ $[M+H]^+$ 302.13868, found 302.13883.

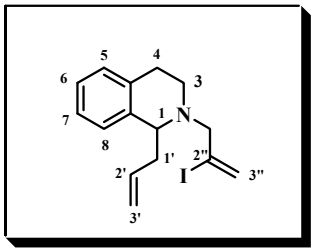
*Dimethyl 6-oxo-6*H*-pyrido[1,2-*b*]isoquinoline-8,9-dicarboxylate (**12**)*



The product was isolated after flash chromatography (SiO_2, 6:4 *V*/*V*, dichloromethane–diethyl ether) as orange needles (12 mg, 53 %), m.p. 171–174 °C. IR (ATR, ν / cm^{-1}): 1715, 1668, 1634, 1616, 1119, 737; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 9.11 (*s*, 1H, H-7), 8.88 (*d*, 1H, *J* = 7.6 Hz, H-4), 7.83 (*s*, 1H, H-10), 7.35 (*d*, 1H, *J* = 9.0 Hz, H-1), 7.14 (*dd*, 1H, *J* = 9.0 and 6.5 Hz, H-2), 6.85 (*s*, 1H, H-11), 6.75 (*t*, 1H, *J* = 6.5 Hz, H-3), 3.98 (*s*, 3H, $COOCH_3$), 3.96 (*s*, 3H, $COOCH_3$); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.8 ($C=O_{ester}$), 166.4 ($C=O_{ester}$), 158.7 ($C=O_{lactam}$), 139.8 (10a), 137.9 (C-11a), 136.3 (C-9), 131.7 (C-8), 128.4 (C-2), 126.7 (C-4), 126.2 (C-10), 125.7 (C-1), 125.1 (C-8), 119.2 (C-6a),

113.1 (C-3), 100.3 (C-11), 52.9 ($COO\underline{C}H_3$), 52,6 ($COO\underline{C}H_3$); MS (ESI) *m*/*z*: 312.1 $[M+H]^+$, 280.1, 265.1, 253.1, 222.1, 194.1, 166.1, 140.1; HRMS (ESI): calculated for $C_{17}H_{14}NO_5$ $[M+H]^+$ 312.08665, found 312.08524.

*1-Allyl-1,2,3,4-tetrahydro-2-(2-iodoallyl)isoquinoline (**16a**)*

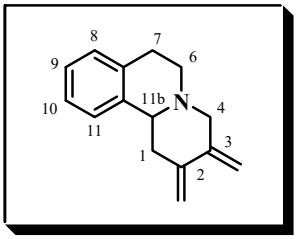


The product was isolated after flash chromatography (SiO_2, 98:2 *V*/*V*, petroleum ether–diethyl ether) as a pale yellow oil (610 mg, 70 %). IR (ATR, ν / cm^{-1}): 2907, 2803, 1637, 1615, 1498, 1427, 1123, 903, 742; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 7.26–7.03 (*m*, 4H, ArH), 6.36 (*dd*, 1H, *J* = 1.5 and 1.0 Hz, H-3"), 6.03–5.95 (*m*, 1H, H-2'), 5.86 (*d*, 1H, *J* = 1.0 Hz, H-3'), 5.04–4.99 (*m*, 2H, H-3", H-3'), 3.71 (*dd*, 1H, *J* = 7.5 and 5.5 Hz, H-1), 3.31 (*d*, 2H, *J* = 4.5 Hz, H-1'), 3.25–3.19 (*m*, 1H, H-3), 2.87–2.82 (*m*, 1H, H-4), 2.79–2.75 (*m*, 1H, H-3), 2.64 (*dt*, 1H, *J* = 16.5 and 4.5 Hz, H-4), 2.59–2.53 (*m*, 1H, H-1'), 2.47–2.42 (*m*, 1H, H-1'); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 137.9, 136.7, 134.5, 128.9, 127.7, 126.3, 126.0, 115.9 (CHC=**C**H_2), 111.6 (I**C**=), 65.4 (**C**H_2CI=CH_2), 61.1 (C-1), 43.3 (C-3), 40.7 (**C**H_2CH=CH_2), 25.2 (C-4); MS (EI) *m*/*z*: 338.0, 298.0, 170.1, 130.1; HRMS (ESI): calculated for $C_{15}H_{19}IN$ $[M+H]^+$ 340.05567, found 340.05547.

*1-Allyl-1,2,3,4-tetrahydro-2-(2-iodoallyl)-6,7-dimethoxyisoquinoline (**16b**)*

The product was isolated after flash chromatography (SiO_2, 9:1 *V*/*V*, petroleum ether–ethyl acetate) as a pale yellow oil (500 mg, 60 %). IR (ATR, cm^{-1} ν / cm^{-1}): 2932, 1511, 1225, 1105, 900; ^{1}H-NMR (300 MHz, $CDCl_3$ δ / ppm): 7.38 (*s*, 1H, ArH), 6.67 (*s*, 1H, ArH), 6.51–6.48 (*m*, 2H, H-3', H-3"), 5.81–5.84 (*m*, 1H, H-2"), 5.21–5.16 (*m*, 2H, H-3', H-3"), 4.43 (*s*, 1H, H-1), 4.07–3.96 (*m*, 2H), 3.87 (*s*, 6H, OCH_3), 3.90–3.80 (*m*, 1H), 3.57–3.49 (*m*, 2H), 3.12 (*s*, 2H), 2.66 (*s*, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$ δ / ppm): 149.4, 148.0, 139.6, 131.9, 121.1, 120.7, 120.6, 111.1, 111.0, 61.7, 60.9, 43.5, 39.6, 21.9; MS (EI) *m*/*z*: 399.1, 359.0, 321.1, 273.1; HRMS (ESI): calculated for $C_{17}H_{23}INO_2$ $[M+H]^+$ 400.07680, found 400.07774.

*1,3,4,6,7,11b-Hexahydro-2,3-dimethylene-2*H*-pyrido[2,1-*a*]isoquinoline (**17a**)*

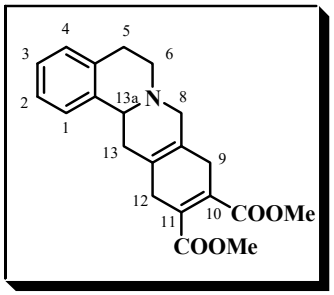


The product was isolated after flash chromatography (SiO_2, 8:2 *V*/*V*, petroleum ether–diethyl ether) as a pale yellow amorphous solid (210 mg, 70 %), m.p. 80-81 °C. IR (ATR, ν / cm^{-1}): 2926, 2735, 1617, 1492, 1450, 1136, 1137, 732; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 7.21–7.10 (*m*, 4H, ArH), 5.16–5.15 (*m*, 2H, =CH_2), 4.87 (*t*, 1H, *J* = 2.0 Hz, =CH_2), 4.84 (*brs*, 1H, =CH_2), 3.49 (*d*, 1H, *J* = 13.0 Hz, H-4), 3.44 (*d*, 1H, *J* = 10.5 Hz, H-11b), 3.19–3.13 (*m*, 2H, H-4, H-7), 3.06–3.02 (*m*, 1H, H-6), 2.92 (*dd*, 1H, *J* = 14.0 and 3.0 Hz, H-1), 2.77 (*dt*, 1H, *J* = 6.0 and 3.0 Hz, H-7), 2.57 (*td*, 1H, *J* = 4.0 and 11.0 Hz, H-6), 2.40–2.34 (*m*, 1H, H-1); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 145.5, 144.1, 137.5, 134.4, 128.9, 126.2, 125.8, 125.3, 109.7 (**C**H_2=), 109.4 (**C**H_2=), 62.3 (C-11b), 62.1 (C-4), 50.7 (C-6), 40.0 (C-1), 29.6 (C-7); MS (EI) *m*/*z*: 211.1, 196.1, 182.1, 130.0, 115.0; HRMS (ESI): calculated for $C_{15}H_{18}N$ $[M+H]^+$ 212.14338, found 212.14299.

*1,3,4,6,7,11b-Hexahydro-9,10-dimethoxy-2,3-dimethylene-2*H*-pyrido[2,1-*a*]isoquinoline (**17b**)*

The product was isolated after flash chromatography (SiO_2, 65:35 *V*/*V*, petroleum ether–ethyl acetate) as a pale yellow amorphous solid (370 mg, 61 %), m.p. 65–67 °C. IR (ATR, ν / cm^{-1}): 1510, 1257, 1227, 1130, 1021; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 6.67 (*s*, 1H, H-11), 6.59 (*s*, 1H, H-8), 5.16–5.15 (*m*, 2H, =CH_2), 4.87 (*t*, 1H, *J* = 2.0 Hz, =CH_2), 4.84 (*s*, 1H, =CH_2), 3.87 (*s*, 3H, OCH_3), 3.85 (*s*, 3H, OCH_3), 3.48 (*d*, 1H, *J* = 13.0 Hz, H-4), 3.36 (*d*, 1H, *J* = 10.5 Hz, H-11b), 3.16–3.00 (*m*, 3H, H-4, H-7, H-6), 2.86 (*dd*, 1H, *J* = 13.5 and 3.0 Hz, H-1), 2.67 (*dt*, 1H, *J* = 15.5 and 3.5 Hz, H-7), 2.55 (*td*, 1H, *J* = 10.5 and 4.0 Hz, H-6), 2.39–2.35 (*m*, 1H, H-1); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 147.5, 147.2, 145.4, 144.1, 129.4, 126.6, 111.4 (C-8), 109.7 (C-2'), 109.4 (C-3'), 108.5 (C-11), 62.0 (C-11b), 61.9 (C-4), 56.0 (O**C**H_3), 55.8 (O**C**H_3), 50.8 (C-6), 40.1 (C-1), 29.2 (C-7); MS (EI) *m*/*z*: 270.1, 256.1, 240.1, 190.0; HRMS (ESI): calculated for $C_{17}H_{22}NO_2$ $[M^+$+H] 272.16451, found 272.16501.

*Dimethyl 5,8,9,12,13,13a-hexahydro-6*H-*isoquino[2,1*-b*]isoquinoline-10,11--dicarboxylate (**18a**)*



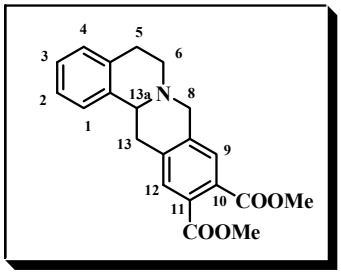
The product was isolated after flash chromatography (SiO_2, 95:5 *V*/*V*, diethyl ether–petroleum ether) as a pale yellow amorphous solid (70 mg, 90 %), m.p. 121–124 °C. IR (ATR, ν / cm^{-1}): 2950, 1716, 1433, 1267, 1196, 1068, 736; ^{1}H--NMR (500 MHz, $CDCl_3$ δ / ppm): 7.17–7.10 (*m*, 4H, ArH), 3.79 (*s*, 3H, $COOCH_3$), 3.78 (*s*, 3H, $COOCH_3$), 3.58 (*dd*, 1H, *J*=10.5 and 3.0 Hz, H-13b), 3.22 (*brd*, 1H, *J*=16.0 Hz, H-8), 3.17–3.14 (*m*, 1H, H-5), 3.09 (*dd*, 1H, *J*=11.0 and 4.0 Hz, H-6), 3.01–2.91 (*m*, 5H, H-8, H-9, H-12), 2.73 (*brd*, 1H, *J*=16.0 Hz, H-5), 2.59–2.49 (*m*, 2H, H-6, H-13), 2.22–2.16 (*m*, 1H, H-13); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.3 ($C{=}O_{ester}$); 168.1 ($C{=}O_{ester}$), 137.6, 134.2, 132.8, 131.8, 128.8, 126.1, 125.9, 125.2, 123.2, 122.9, 59.2 (C-11b), 58.0 (C-8), 52.2 (2C, $COOH_3$), 50.8 (C-6), 36.7 (C-13), 32.2 (C-12), 30.1 (C-9), 29.3 (C-5); MS (ESI) *m*/*z*: 354.0, 322.0, 184.1, 132.0, 117.0; HRMS (ESI): calculated for $C_{21}H_{24}NO_4$ $[M+H]^+$ 354.16998, found 354.16918.

*Methyl 5,8,9,12,13,13a-hexahydro-6*H-*isoquino[2,1-b]isoquinoline-11-carboxylate (**18b'**)*. Compounds **18b** and **18b'** were synthesised from **17a** and methylpropiolate following the general procedure for the synthesis of cycloadducts by Diels–Alder reaction. Two products, separated by flash chromategraphy (SiO_2, 7:3 *V*/*V*, ethyl acetate–petroleum ether), were isolated in 1:1 ratio (30 mg, 72 % combined yield). Compound **18b'** was isolated as yellow oil which solidified upon standing, m.p. 63–65 °C. IR (ATR, ν / cm^{-1}): 2948, 1717, 1434, 1255, 726; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 7.19–7.10 (*m*, 4H, ArH), 6.99––6.98 (*m*, 1H, H-10), 3.76 (*s*, 3H, $COOCH_3$), 3.59 (*dd*, 1H, *J* = 11.0 and *J* = 3.5 Hz, H-13a), 3.22—3.16 (*m*, 2H, H-8, H-5), 3.10 (*ddd*, 1H, *J* = 11.0, 5.5 and 1.5 Hz, H-6), 3.00 (*brd*, 1H, *J* = 15.0 Hz, H-8), 2.86–2.81 (*m*, 4H, H-12, H-9), 2.73 (*brd*, 1H, *J* = 15.0 Hz, H-5), 2.59–2.54 (*m*, 2H, H-13, H-6), 2.24–2.19 (*m*, 1H, H-13); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 167.3 (C=O), 137.8, 135.8 (C-10), 134.3, 128.8, 127.7, 126.1, 126.0, 125.3, 124.9, 122.5, 59.4 (C-13a), 58.4 (C-8), 51.6 ($COO\mathbf{C}H_3$), 50.9 (C-6), 37.2 (C-13), 29.9 (C-9), 29.8 (C-12), 29.4 (C-5); MS (ESI) *m*/*z*: 296.1, 264.1, 236.1, 220.1, 217.1, 144.1; HRMS (ESI): calculated for $C_{19}H_{21}NO_2$ $[M+H]^+$ 296.16451, found 296.16488.

*Methyl 5,8,9,12,13,13a-hexahydro-6*H-*isoquino[2,1*-b*]isoquinoline-10-carboxylate (**18b**)*. Compound was isolated as a yellow oil which solidified upon standing, m.p. 110–116 °C. IR (ATR, ν / cm^{-1}): 2950, 1717, 1653, 1435, 1253, 724; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 7.37–7.36 (*m*, 1H, ArH), 7.18–7.10 (*m*, 3H, ArH), 7.01–6.99 (*m*, 1H, H-11), 3.76 (*s*, 3H, $COOCH_3$), 3.58 (*dd*, 1H, *J* = = 11.0 and 3.5 Hz, H-13a), 3.23 (*d*, 1H, *J* = 15.0 Hz, H-8), 3.21-3.15 (*m*, 1H, H-5), 3.09 (*ddd*, 1H, *J* = 11.0, 5.6 Hz and 2.0 Hz, H-6), 3.02 (*brd*, 1H, *J* = 16.5 Hz, H-8), 2.91–2.77 (*m*, 4H, H-9, H-12), 2.73 (*brd*, 1H, *J* = 16.5 Hz, H-5), 2.57 (*td*, 1H, *J* = 11.5 Hz and 3.5 Hz, H-6), 2.51 (*brd*, 1H, *J*=16.5 Hz, H-13), 2.21–2.15 (*m*, 1H, H-13); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 167.3 (C=O), 137.9, 136.4, (C-11), 134.4, 128.8, 127.3, 126.0, 125.9, 125.2, 124.5, 122.9, 59.4 (C-13a), 58.7 (C-8), 51.6 (COO**C**H_3), 50.9 (C-6), 36.9 (C-13), 31.9 (C-12), 29.4 (C-5), 27.9 (C-9); MS (ESI) *m*/*z*: 296.1; 184.1; 132.1; 117.1; HRMS (ESI): calculated for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.16451, found 296.16451.

*Dimethyl 5,8,9,12,13,13a-hexahydro-2,3-dimethoxy-6*H-*isoquino[2,1*-b*]isoquinoline-10,11-dicarboxylate (**18c**)*. The product was isolated after flash chromatography (SiO_2, 7:3 *V*/*V*, ethyl acetate–petroleum ether) as a white amorphous solid (50 mg, 80 %), m.p. 170 °C. IR (ATR, ν / cm^{-1}): 1711, 1517, 1280, 1256, 1070, 781;^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 6.63 (*s*, 1H, H-4), 6.59 (*s*, 1H, H-5), 3.86 (*s*, 6H, $COOCH_3$), 3.79 (*s*, 6H, OCH_3), 3.52 (*dd*, *J* = 10.5 and 3.5 Hz, H-13a), 3.22 (*d*, 1H, *J* = 15.0 Hz, H-8), 3.11–2.95 (*m*, 7H, H-5, H-6, H-9, H-12, H-8), 2.65–2.61 (*m*, 1H, H-5), 2.58–2.52 (*m*, 1H, H-6), 2.46 (*brd*, 1H, *J* = 16.0 Hz, H-13), 2.21–2.15 (*m*, 1H, H-13); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.3 ($C=O_{ester}$), 168.2 ($C=O_{ester}$), 147.5, 147.4, 132.7, 132.0, 129.5, 126.5, 123.1, 122.9, 111.3, 108.3, 58.9 (C-13a), 58.0 (C-8), 56.0 (OCH_3), 55.8 (OCH_3), 52.2 (2C, COO**C**H_3), 51.0 (C-6), 36.9 (C-13), 32.3 (C-12), 30.2 (C-9), 28.9 (C-5); MS (EI) *m*/*z:* 268.1, 210.1, 136.1; HRMS (ESI): calculated for $C_{23}H_{28}NO_6$ $[M+H]^+$ 414.19111, found 414.19005.

*Dimethyl 5,8,13,13a-tetrahydro-6*H-*isoquino[2,1*-b*]isoquinoline-10,11-dicarboxylate (**19a**)*



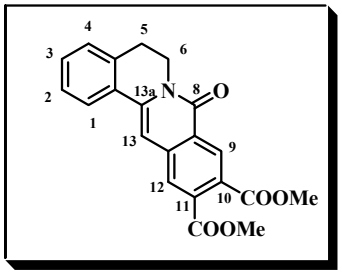
The product was isolated after flash chromatography (SiO_2, 4:1 *V*/*V*, diethyl ether–petroleum ether) as a yellow oil (15 mg, 63 %), which solidified upon

standing, m.p. 108–110 °C. IR (ATR, ν / cm^{-1}): 3283, 2922, 1699, 1621, 1606, 1439, 1299, 1284, 1148, 1231, 737; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 7.53 (*s*, 1H, H-12), 7.48 (*s*, 1H, H-9), 7.25–7.14 (*m*, 4H, ArH), 4.08 (*d*, 1H, *J* = 15.5 Hz, H-8), 3.90 (*s*, 6H, $COOCH_3$), 3,75 (*d*, 1H, *J* = 15.5 Hz, H-8), 3.70 (*dd*, 1H, *J* = 11.5 and 4.0 Hz, H-13a), 3.41 (*dd*, 1H, *J* = 16.5 and 4.0 Hz, H-13), 3.23–3.16 (*m*, 2H, H-5, H-6), 2.95 (*dd*, 1H, *J* = 16.5 and 11.0 Hz, H-13), 2.80–2.76 (*m*, 1H, H-5), 2.69–2.64 (*m*, 1H, H-6); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.1 (C=O), 167.9 (C=O), 138.4, 138.0, 137.1, 134.4, 130.0, 129.4, 129.3, 128.9, 126.9, 126.4, 126.2, 125.4, 59.3 (C-13a), 58.0 (C-8), 52.6 (2×CH_3), 50.9 (C-6), 36.5 (C-13), 29.4 (C-5); MS (ESI) *m*/*z*: 352.1, 130.1, 117.1, 103.1; HRMS (ESI) calculated for $C_{21}H_{22}NO_4$ $[M+H]^+$ 352.15433, found 352.15493.

*Methyl 5,8,13,13a-tetrahydro-6*H*-isoquino[2,1-*b*]isoquinoline-10-carboxylate (**19b**)*. The product was isolated after flash chromatography (SiO_2, 1:1 *V*/*V*, diethyl ether–petroleum ether) as yellow plates (10 mg, 72 %), m.p. 133–136 °C. IR (ATR, ν / cm^{-1}): 2953, 2929, 1713, 1441, 1289, 1198, 745; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 7.82 (*d*, 1H, *J* = 8.0 Hz, H-11), 7.79 (*s*, 1H, H-9), 7.27––7.26 (*m*, 1H, ArH), 7.23–7.14 (*m*, 4H, ArH), 4.08 (*d*, 1H, *J* = 15.0 Hz, H-8), 3.90 (*s*, 3H, CH_3), 3.75 (*d*, 1H, *J* = 15.5 Hz, H-8), 3.70 (*dd*, 1H, *J* = 11.0 and 3.5 Hz, H-13a), 3.42 (*dd*, 1H, *J* = 17.0 and 4.0 Hz, H-13), 3.24–3.16 (*m*, 2H, H-5, H-6), 2.95 (*dd*, 1H, *J* = 16.5 and 11.5 Hz, H-13), 2.79–2.75 (*m*, 1H, H-5), 2.67–2.63 (*m*, 1H, H-6); ^{13}C-NMR (125 MHz, $CDCl_3$ *c*): 167.1 (C=O), 140.1, 137.4, 134.7, 134.4, 128.9, 128.8, 127.7, 127.5, 127.3, 126.2, 126.1, 125.4, 59.5 (C-13a), 58.3 (C-8), 51.9 (**C**H_3), 51.1 (C-6), 36.8 (C-13), 29.4 (C-5); MS (EI) *m*/*z*: 293.1 [M^+], 278.1, 232.0, 163.0, 130.1, 103.0; HRMS (ESI) calculated for $C_{19}H_{20}NO_2$ $[M+H]^+$ 294.14886, found 294.14906.

*Dimethyl 5,8,13,13a-tetrahydro-2,3-dimethoxy-6*H*-isoquino[2,1-*b*]isoquinoline-10,11-dicarboxylate (**19c**)*. The product was isolated after flash chromategraphy (SiO_2, 95:5 *V*/*V*, diethyl ether–petroleum ether) as yellow needles (12 mg, 78 %), m.p. 173–175 °C. IR (ATR, ν / cm^{-1}): 1721, 1513, 1258, 1100, 728; ^{1}H--NMR (500 MHz, $CDCl_3$ δ / ppm): 7.55 (*s*, 1H, H-12), 7.47 (*s*, 1H, H-9), 6.1 (*s*, 1H, H-1), 6.23 (*s*, 1H, H-4), 4.08 (*d*, 1H, *J* = 15.5 Hz, H-8), 3.90 (*s*, 3H, $COCH_3$), 3.89 (*s*, 6H, $COCH_3$, OCH_3), 3.87 (*s*, 3H, OCH_3), 3.74 (*d*, 1H, *J* = 15.5 Hz, H-8), 3.63 (*dd*, 1H, *J* = 11.0 and 3.5 Hz, H-13a), 3.37 (*dd*, 1H, *J* = 16.5 and 3.5 Hz, H-13), 3.17–3.11 (*m*, 2H, H-5, H-6), 2.93 (*dd*, 1H, *J* = 16.5 and 11.0 Hz, H-13), 2.71–2.61 (*m*, 2H, H-6, H-5); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.1 (C=O), 168.0 (C=O), 147.7 (C-2), 147.5 (C-3), 138.3, 138.1, 129.9, 129.5, 129.4 (C-12), 128.9, 126.9 (C-9), 126.6, 111.4, 108.4, 59.0 (C-13a), 58.0 (C-8), 56.0 (O**C**H_3), 55.8 (O**C**H_3), 52.5 (2C, CO**C**H_3), 51.1 (C-6), 36.7 (C-13), 28.9 (C-5); MS (ESI) *m*/*z*: 412.1 $[M+H]^+$; 380.1, 348.1, 322.1, 277.9, 250.1; HRMS (ESI): calculated for $C_{23}H_{26}NO_6$ $[M+H]^+$ 412.17646, found 412.17642.

*Dimethyl 5,6-dihydro-8-oxo-8*H-*isoquino[2,1*-b*]isoquinoline-10,11-dicarboxylate (**20a**)*



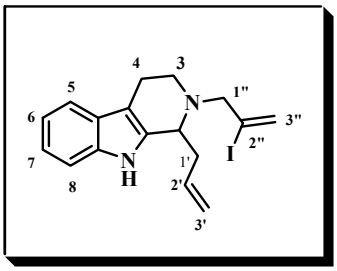
The product was isolated after flash chromatography (SiO_2, 4:1 *V*/*V*, diethyl ether–petroleum ether) as yellow needles (5 mg, 70 %), m.p. 178–180 °C. This derivative gave specific azure colour with Dragendorff reagent. IR (ATR, ν / cm^{-1}): 1729, 1712, 1645, 1620, 1293, 1161, 772; ^{1}H-NMR (200 MHz, $CDCl_3$ δ / ppm): 8.88 (*s*, 1H), 7.84–7.78 (*m*, 3H), 7.42–7.27 (*m*, 2H), 7.00 (*s*, 1H), 4.37 (*t*, 2H, *J* = = 6.0 Hz), 3.97 (*s*, 3H, $COOCH_3$), 3.94 (*s*, 3H, $COOCH_3$), 3.04 (*t*, 2H, *J* = 6.0 Hz, H-5); ^{13}C-NMR (50 MHz, $CDCl_3$ δ / ppm) 168.5 ($C{=}O_{ester}$), 166.6 ($C{=}O_{ester}$), 161.3 ($C{=}O_{lactam}$), 140.6, 138.7, 136.4, 135.7, 130.6, 130.2, 129.5, 128.2, 127.7, 127.3, 126.7, 125.4, 125.1, 101.8, 52.9, 52.7, 39.8, 28.3; MS (ESI) *m*/*z*: 364.1, 332.1, 317.1, 290.1, 230.1; HRMS (ESI): calculated for $C_{21}H_{18}NO_5$ $[M+H]^+$ 364.11795, found 364.11783.

*Methyl 5,6-dihydro-8-oxo-8*H-*isoquino[2,1*-b*]isoquinoline-10-carboxylate (**20b**)*. The product was isolated after flash chromatography (SiO_2, 7:3 *V*/*V*, diethyl ether–petroleum ether) as yellow rombs (8 mg, 45 %), m.p. 202–204 °C. Compound gave specific purple-brown colour with Dragendorff reagent. IR (ATR, ν / cm^{-1}): 1703, 1651, 1614, 1600, 1288, 766; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 9.11 (*d*, 1H, *J* = 1.5 Hz, H-9), 8.24 (*dd*, 1H, *J* = 8.4 and 1.6 Hz, H-11), 7.86–7.84 (*m*, 1H, H-1), 7.62 (*d*, 1H, *J* = 8.2 Hz, H-12), 7.40–7.38 (*m*, 2H, H-2, H-3), 7.34–7.30 (*m*, 1H, H-4), 7.04 (*s*, 1H, H-13), 4.39 (*t*, 2H, *J* = 6.1 Hz, H-6), 3.97 (*s*, 3H, $COOCH_3$), 3.04 (*t*, 2H, *J* = 6.1 Hz, H-5); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 166.6 ($C{=}O_{ester}$), 161.9 ($C{=}O_{lactam}$), 139.9, 139.8, 135.7, 132.5, 130.5, 129.9, 129.8, 128.1, 127.6, 126.4, 125.3, 102.2 (C-13), 52.2 (CH_3), 39.7 (C-6), 28.4 (C-5) ppm; MS (ESI) *m*/*z*: 306.0, 276.0, 247.1, 232.0, 176.1; 203.0; HRMS (ESI): calculated for $C_{19}H_{16}NO_3$ $[M+H]^+$ 306.11247, found 306.11202.

*Dimethyl 5,6-dihydro-2,3-dimethoxy-8-oxo-8*H-*isoquino[2,1*-b*]isoquinoline--10,11-dicarboxylate (**20c**)*. The product was isolated after flash chromatography (SiO_2, 1:1 *V*/*V*, diethyl ether–petroleum ether) as yellow needles (12 mg, 50 %), m.p. 220–221 °C. Compound gave specific blue colour with Dragendorff reagent. IR (ATR, ν / cm^{-1}): 1709, 1563, 1514, 1241, 1046, 787; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 8.88 (*s*, 1H, H-9), 7.78 (*s*, 1H, H-12), 7.25 (*s*, 1H, H-1), 6.88 (*s*,

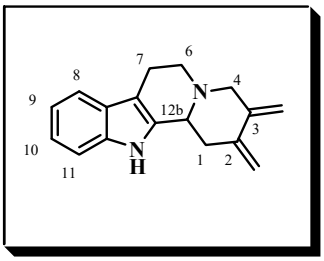
1H, H-13), 6.76 (*s*, 1H, H-4), 4.36 (*t*, 2H, *J* = 6.0 Hz, H-6), 3.99 (*s*, 3H, OCH_3), 3.96 (*s*, 3H, $COOCH_3$), 3.95(*s*, 3H, OCH_3), 3.94 (*s*, 3H, $COOCH_3$), 2.97 (*t*, 2H, *J* = 6.0 Hz, H-5); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 168.5 ($C{=}O_{ester}$), 166.6 ($C{=}O_{ester}$), 161.4 ($C{=}O_{lactam}$), 151.1 (C-2), 148.7 (C-3), 140.6, 138.9, 136.4, 130.6 (C-9), 129.3, 126.8, 126.4 (C-12), 124.6, 121.5, 110.5 (C-4), 108.1 (C-1), 100.4 (C-13), 56.3 (OCH_3), 56.1 (OCH_3), 52.9 ($COO\mathbf{C}H_3$), 52.6 ($COO\mathbf{C}H_3$), 39.9 (C-6), 27.8 (C-5); MS (EI) *m*/*z*: 355.1, 298.9, 281.1, 263.1, 207.0; HRMS (ESI): calculated for $C_{23}H_{22}NO_7$ $[M+H]^+$ 424.13908, found 424.13949.

*1-Allyl-2,3,4,9-tetrahydro-2-(2-iodoallyl)-1*H*-pyrido[3,4-*b*]indole (**23**)*



The product was isolated after flash chromatography (SiO_2, 9:1 *V*/*V*, petroleum ether–diethyl ether) as a pale yellow oil (173 mg, 42 %). IR (ATR, ν / cm^{-1}): 3230, 3070, 2916, 1615, 1451, 741; ^{1}H-NMR (200 MHz, $CDCl_3$ δ / ppm): 7.76 (*brs*, 1H, N-H), 7.55–7.05 (*m*, 4H, ArH), 6.37 (*d*, 1H, *J* = 1.2 Hz, H-3"), 5.90–6.09 (*m*, 1H, H-2'), 5.89 (*d*, 1H, *J* = 1.0 Hz, H-3"), 5.16 (*d*, 2H, *J* = = 12.0 Hz, H-3'), 3.74 (*t*, 1H, *J* = 6.6 Hz, H-1), 3.33 (*s*, 2H, H-1'), 3.25–3.00 (*m*, 1H), 2.86–2.45 (*m*, 4H); ^{13}C-NMR (50 MHz, $CDCl_3$ δ / ppm): 136.2, 135.7, 134.8, 127.0, 126.6, 121.6, 119.4, 118.1, 117.5, 111.8, 110.7, 108.1, 64.8, 56.7, 44.7, 39.4, 18.7; MS (EI) *m*/*z*: 378$[M]^+$, 337 $[M\text{-allyl}]^+$, 209.1, 169.1; HRMS (ESI): calculated for $C_{17}H_{20}IN_2$ $[M+H]^+$ 379.06657, found 379.06643.

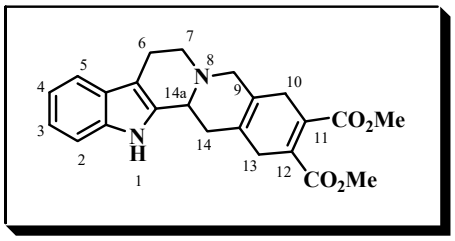
*1,2,3,4,6,7,12,12b-Octahydro-2,3-dimethylene-indolo[2,3-*a*]quinolizine (**24**)*



The product was isolated after flash chromatography (SiO_2, 7:3 *V*/*V*, petroleum ether–diethyl ether) as a pale yellow amorphous solid (126 mg, 50 %), m.p. 153–156 °C. IR (ATR, ν / cm^{-1}): 3418, 3049, 2949, 1643, 1314, 743; ^{1}H-NMR

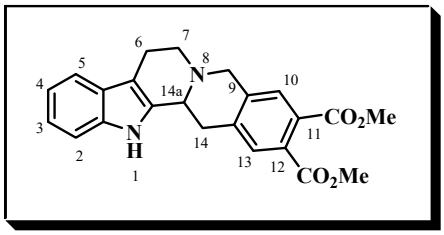
(500 MHz, $CDCl_3$ δ / ppm): 7.74 (*brs*, 1H, N-H), 7.48 (*d*, 1H, J = 8.0 Hz, H-8), 7.31 (*dt*, 1H, J = 8.0 and 0.5 Hz, H-11), 7.16–7.08 (*m*, 2H, H-9, H-10), 5.19–5.18 (*m*, 2H, $=CH_2$), 4.88 (*s*, 2H, $=CH_2$), 3.56 (*d*, 1H, J = 12.5 Hz, H-4), 3.47–3.44 (*m*, 1H, H-12b), 3.18–3.13 (*m*, 2H, H-4, H-6), 3.07–2.99 (*m*, 1H, H-7), 2.79-2.74 (*m*, 2H; H-1, H-7), 2,66 (*td*, J = 11.0 and 4.5 Hz, H-6), 2.50–2.44 (*m*, 1H, H-1); ^{13}C--NMR (125 MHz, $CDCl_3$ δ / ppm): 144.4, 143.9, 136.1, 134.1, 127.2, 121.6, 119.5, 118.2, 110.8 (C-11), 110.3 (C_2=**C**H_2), 110.1 (C_3=**C**H_2), 108.7 (C-7a), 61.4 (C-4), 59.2 (C-12b), 52.3 (C-6), 38.6 (C-1), 21.6 (C-7); MS (EI) *m*/*z*: 259.2 $[M]^+$, 235.1, 220.1, 206.1, 169.1; HRMS (ESI): calculated for $C_{17}H_{19}N_2$ $[M+H]^+$ 251.15428, found 251.15374.

*11,12-Dicarbmethoxy-1,6,7,9,10,13,14,14a-octahydroindolo[2,3-*a*]benzo[*e*]-quinolizine (**25**)*



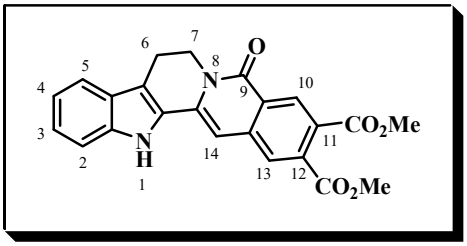
The product was isolated after flash chromatography (SiO_2, 8:2 *V*/*V*, diethyl ether–petroleum ether) as a creamy-white amorphous solid (50 mg, 80 %), m.p. 161–163 °C. IR (ATR, ν / cm^{-1}): 2949, 1716, 1659, 1434, 1260, 1069, 738; ^{1}H--NMR (500 MHz, $CDCl_3$ δ / ppm): 7.74 (*s*, 1H, ArH), 7.50 (*d*, 1H, J = 8.0 Hz, ArH), 7.32 (*d*, 1H, J = 8.0 Hz, ArH), 7.16 (*t*, 1H, J = 7.2 Hz, ArH), 7.11 (*t*, 1H, J = 7.0 Hz, ArH), 3.80 (*s*, 3H, $COOCH_3$), 3.79 (*s*, 3H, $COOCH_3$), 3.64–3.61 (*m*, 1H, H-3), 3.28 (*brd*, 1H, J = 15.5 Hz, H-9), 3.20 (*dd*, 1H, J = 11.5 and 4.5 Hz, H-7), 3.06–2.89 (*m*, 6H, H-6, H-9, H-10, H-13), 2.80–2.75 (*m*, 1H, H-6), 2.67 (*td*, 1H, J = 11.0 and 4.0 Hz, H-7), 2.31–2.33 (*m*, 2H, H-14); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.3 (C=O), 168.1 (C=O), 136.3, 134.1, 132.7, 131.9, 127.2, 123.7, 122.1, 121.6, 119.5, 118.3, 110.8, 108.7, 57.3 (C-9), 55.8 (C-14a), 52.3 (2C, COO**C**H_3), 51.9 (C-7), 34.9 (C-14), 32.3 (C-10), 30.3 (C-13), 21.5 (C-6); MS (ESI) *m*/*z*: 393.1, 171.1, 144.1, 117.1; HRMS (ESI): calculated for $C_{23}H_{25}N_2O_4$ $[M+H]^+$ 393.18088, found 393.17969.

*11,12-dicarbmethoxy-1,6,7,9,14,14a-hexahydroindolo[2,3-*a*]benzo[*e*]quinolizine (**26**)*



The product was isolated after flash chromatography (SiO_2, 9:1 *V*/*V*, diethyl ether–petroleum ether) as a pale yellow amorphous solid (17 mg, 72 %), m.p. 167–168 °C. IR (ATR, ν / cm^{-1}): 1720, 1434, 1271, 1125, 741; ^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm) 8.17 (*s*, 1H, N-H), 7.51 (*d*, 1H, *J* = 8.0 Hz, H-2), 7.45 (*s*, 2H, H-13, H-10), 7.35 (*d*, 1H, *J* = 8.0 Hz, H-5), 7.17 (*td*, 1H, *J* = 7.0 and 1.0 Hz, H-4), 7.10 (*td*, 1H, *J* = 7.0 and 1.0 Hz, H-3), 4.09 (*d*, 1H, *J* = 15.5 Hz, H-9), 3.91 (*s*, 3H, $COOCH_3$), 3.87 (*s*, 3H, $COOCH_3$), 3.70 (*d*, 1H, *J* = 15.5 Hz, H-9), 3.55––3.53 (*m*, 1H, H-14a), 3.27–3.24 (*m*, 1H, H-7), 3.11 (*dd*, 1H, *J* = 16.0 and 3.0 Hz, H-14), 3.06–2.99 (*m*, 1H, H-6), 2.94 (*dd*, 1H, *J* = 16.0 and 11.5 Hz, H-14), 2.82––2.79 (*m*, 1H, H-6), 2.71 (*td*, 1H, *J* = 11.5 and 3.5 Hz, H-7); ^{13}C-NMR (125 MHz, $CDCl_3$ δ / ppm): 168.3 (C=O), 168.0 (C=O), 138.2, 137.3, 136.4, 133.6, 130.0, 129.4, 129.3, 127.1, 127.0, 121.7 (C-10), 119.5 (C-11), 118.2 (C-12), 110.9, 108.7, 57.3 (C-21), 55.8 (C-3), 52.7 ($COO\mathbf{C}H_3$), 52.6 ($COO\mathbf{C}H_3$), 52.2 (C-7), 34.6 (C-14), 21.4 (C-6); MS (ESI) *m*/*z*: 391.1, 374.1, 359.1, 144.1, 117.1; HRMS (ESI): calculated for $C_{23}H_{23}N_2O_4$ $[M+H]^+$ 391.16523, found 391.16563.

*11,12-dicarbmethoxy-1,6,7-trihydroindolo[2,3-*a*]benzo[*e*]quinolizine-9-on (**27**)*

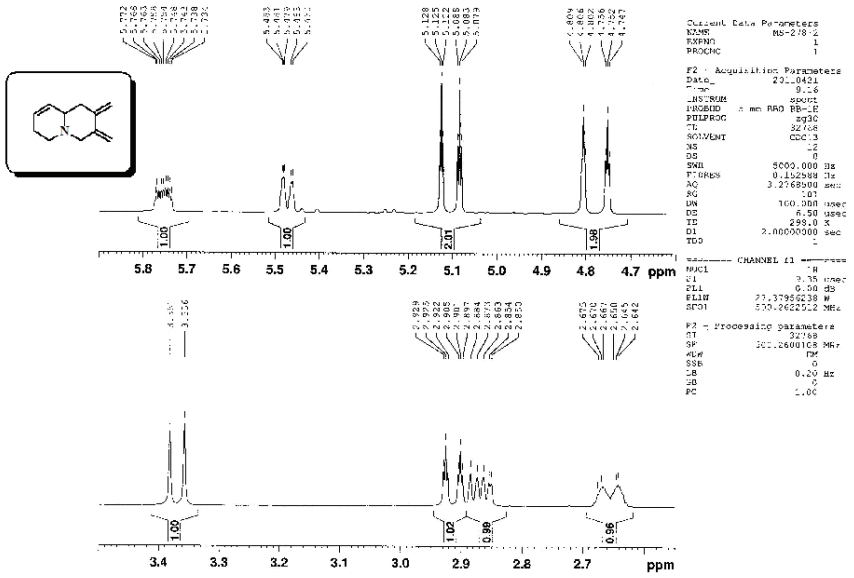


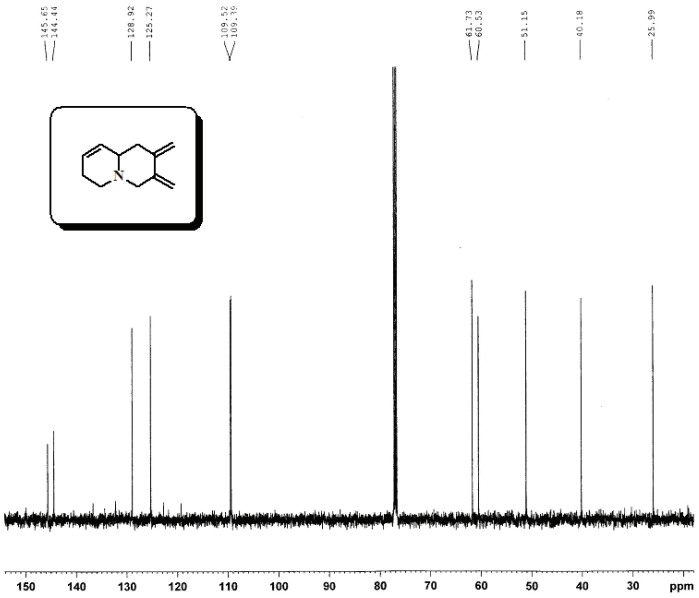
The product was isolated after flash chromatography (SiO_2, diethyl ether) as a yellow amorphous solid (5 mg, 45 %), m.p. 220–225 °C. Compound gave specific gray-blue colour with Dragendorff reagent. IR (ATR, ν / cm^{-1}): 3283, 2922, 1699, 1621, 1606, 1439, 1299, 1284, 1148, 1231, 737;^{1}H-NMR (500 MHz, $CDCl_3$ δ / ppm): 8.77 (*s*, 1H, H-10), 8.74 (*s*, 1H, N-H), 7.60 (*d*, 1H, *J* = 7.5 Hz, H-5), 7.56 (*s*, 1H, H-13), 7.45 (*d*, 1H, *J* = 8.0 Hz, H-2), 7.32 (*t*, 1H, *J* = 7.5 Hz, H-3), 7.18 (*t*, 1H, *J* = 7.5 Hz, H-4), 6.41 (*s*, 1H, H-14), 4.51 (*t*, 2H, *J* = 7.0 Hz,

H-7), 4.03 (*s*, 3H, $COOCH_3$), 3.63 (*s*, 3H, $COOCH_3$), 3.15 (*t*, 2H, J = 7.0 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$ δ / ppm): 169.5 ($C{=}O_{ester}$), 165.9 ($C{=}O_{ester}$), 161.2 ($C{=}O_{lactam}$), 138.7, 138.4, 136.9, 134.9, 130.7, 127.4, 126.1, 125.9, 125.5, 125.0, 124.9, 120.7, 119.6, 115.6, 111.8, 97.7, 53.2 ($COO\mathbf{C}H_3$), 52.2 ($COO\mathbf{C}H_3$), 41.0 (C-7), 19.7 (C-6); MS (ESI) *m*/*z*: 403.1, 371.1, 355.1, 343.1, 283.1; HRMS (ESI): calculated for $C_{23}H_{19}N_2O_5$ $[M+H]^+$ 403.12885, found 403.12910.

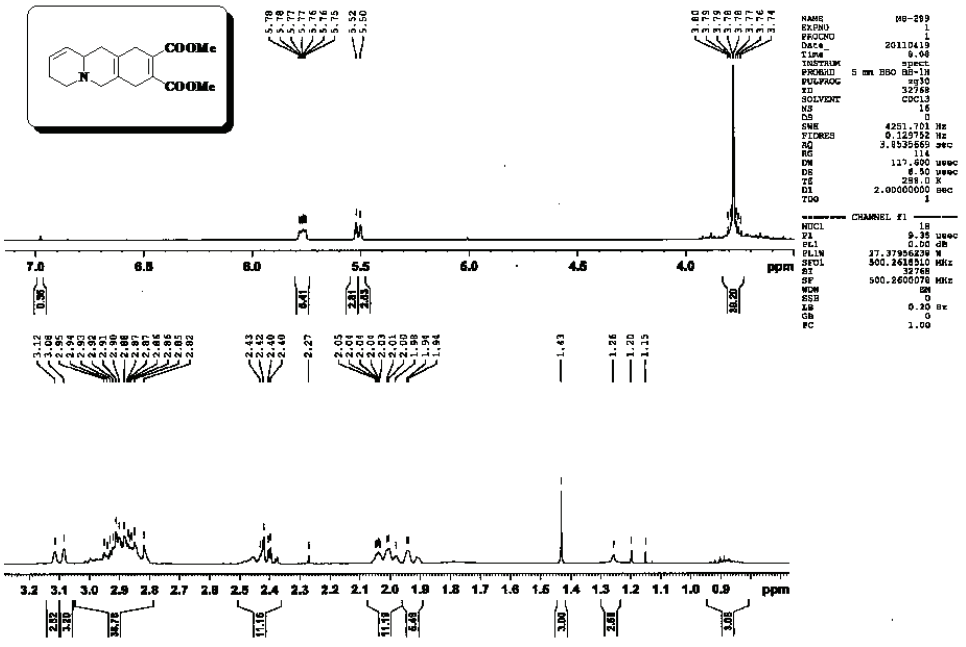
COPIES OF SELECTED ^{1}H- AND ^{13}C-NMR SPECTRA

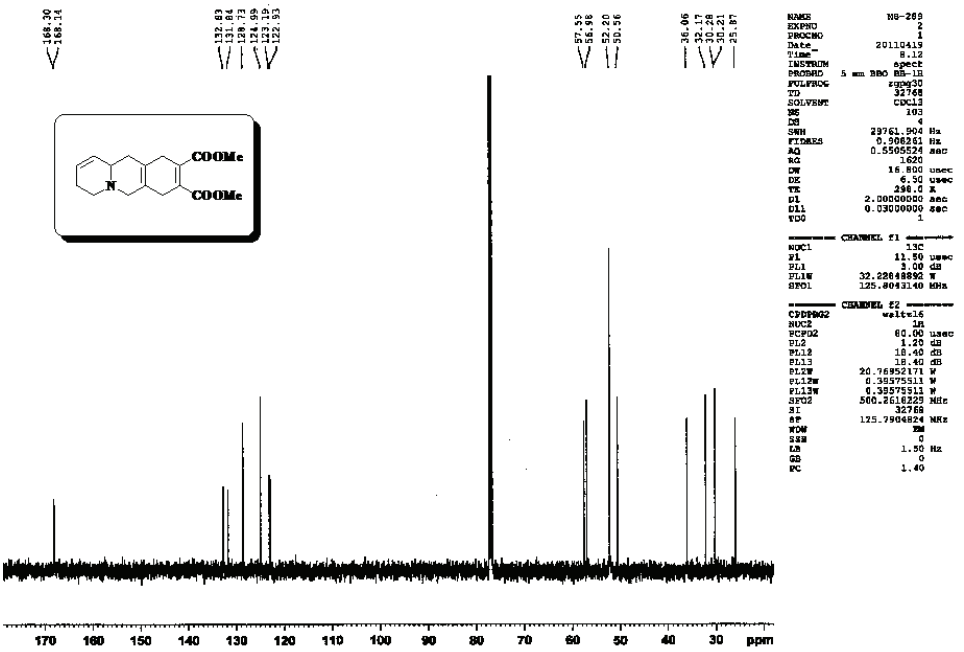
Compound ***9***



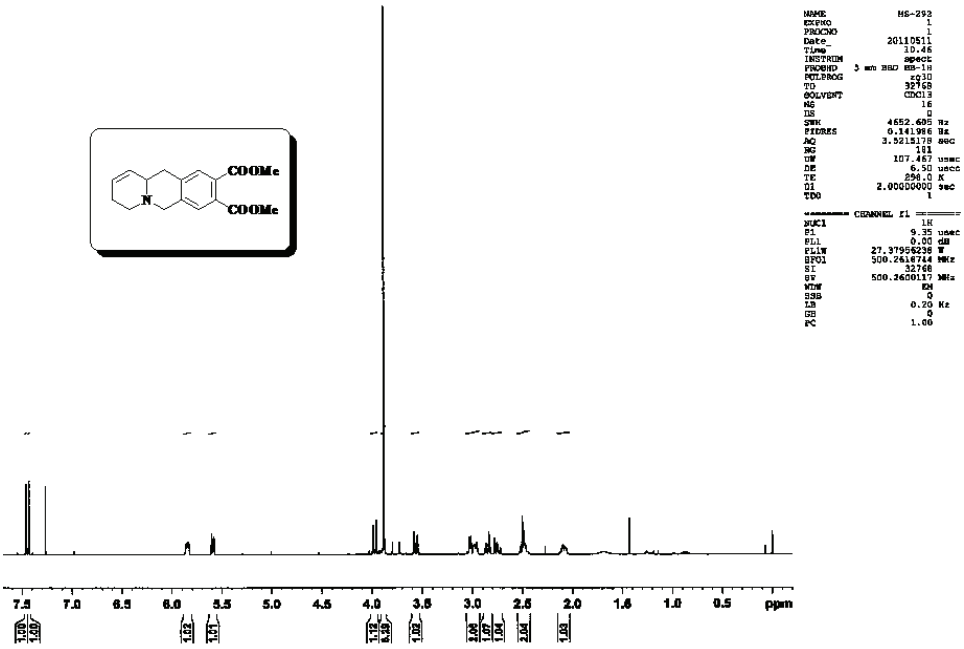


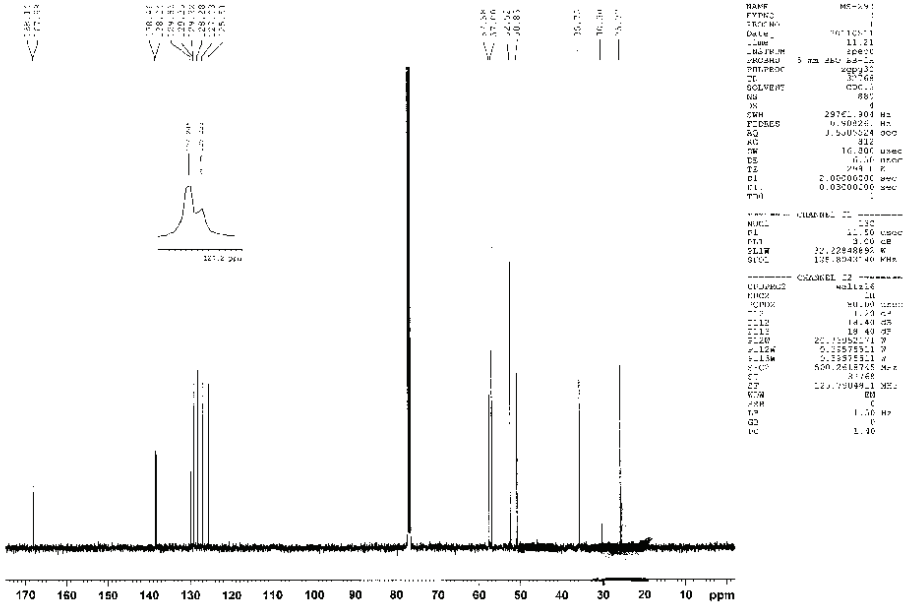
*Compound **10***



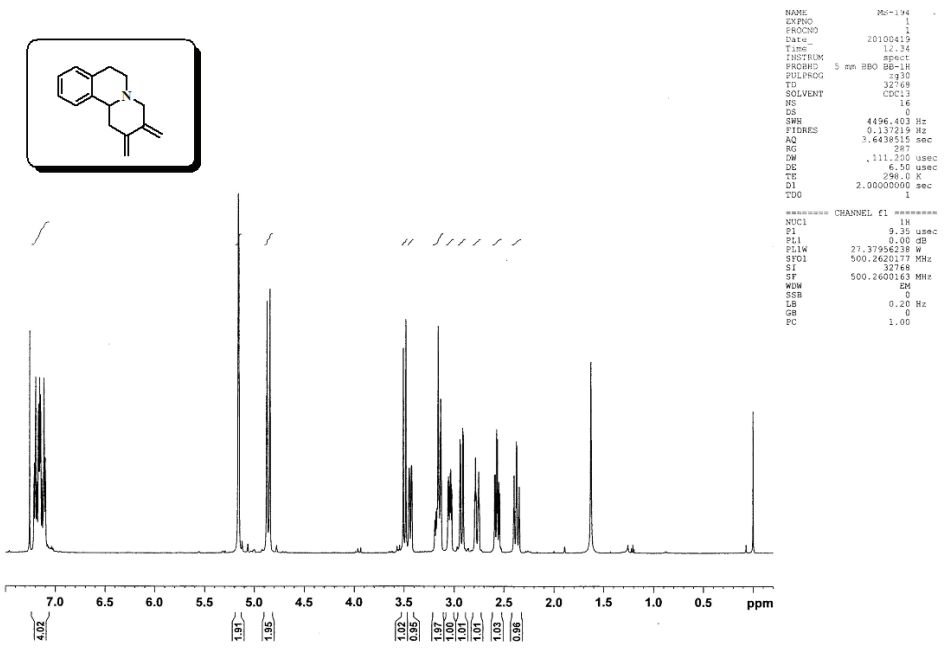


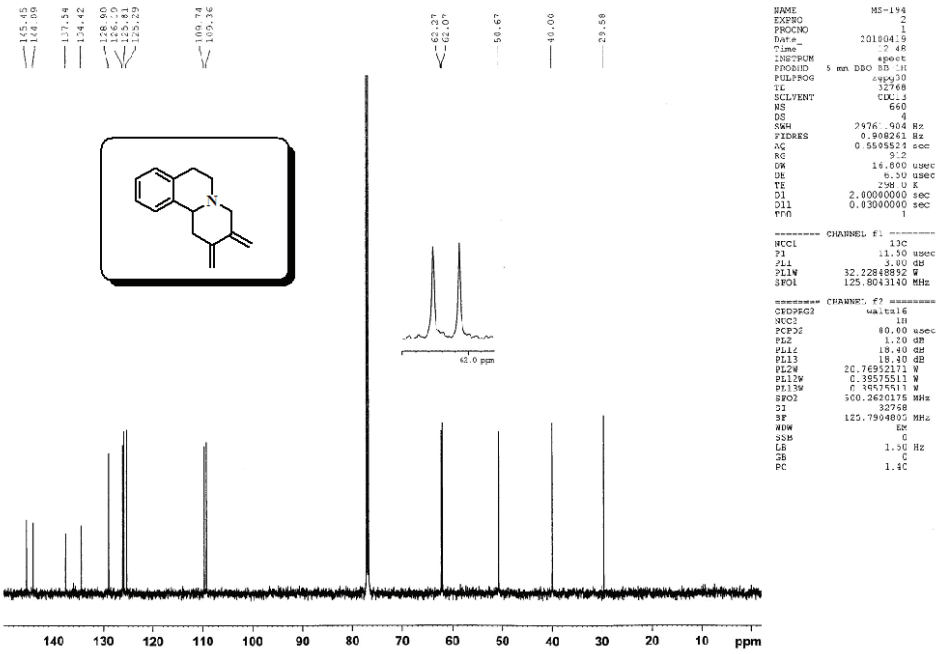
Compound ***11***



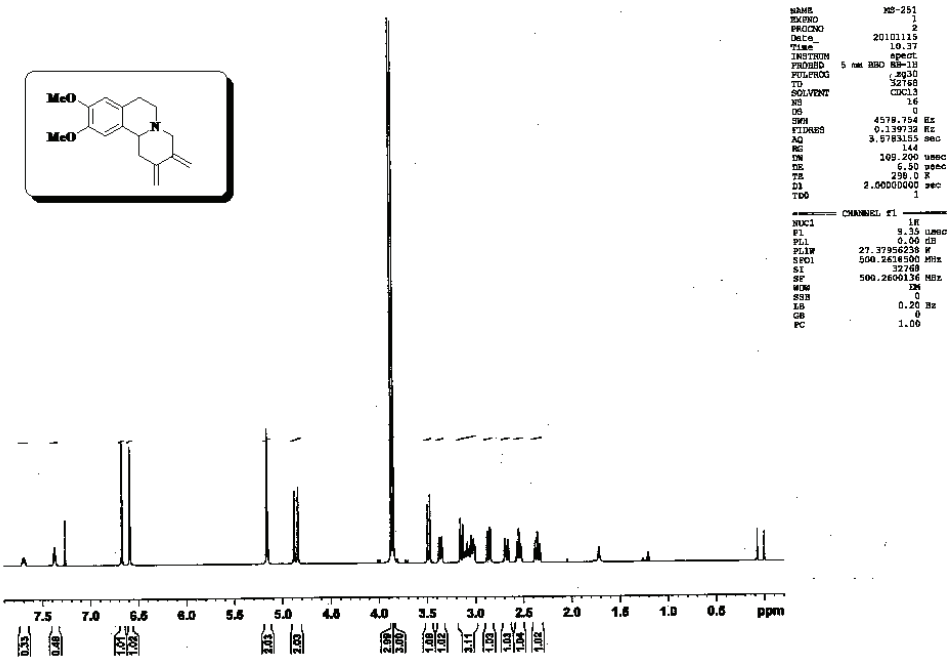


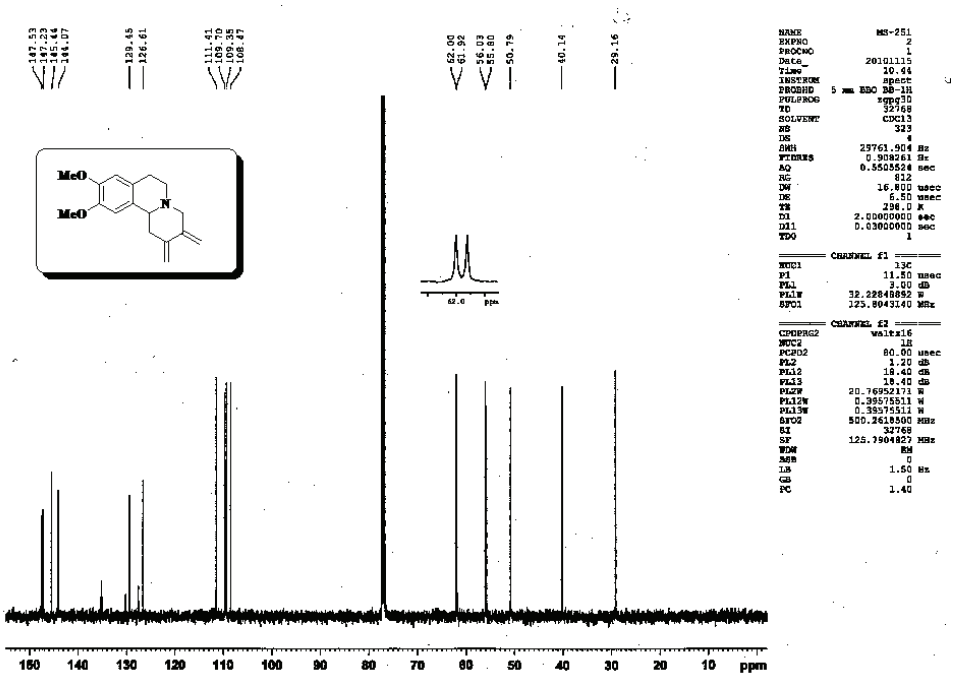
Compound ***17a***



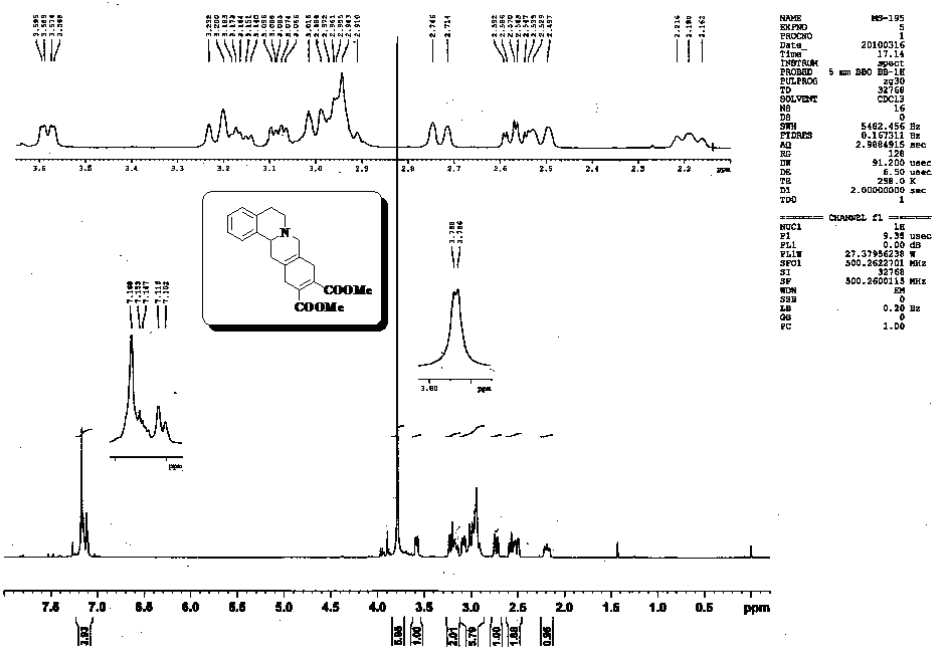


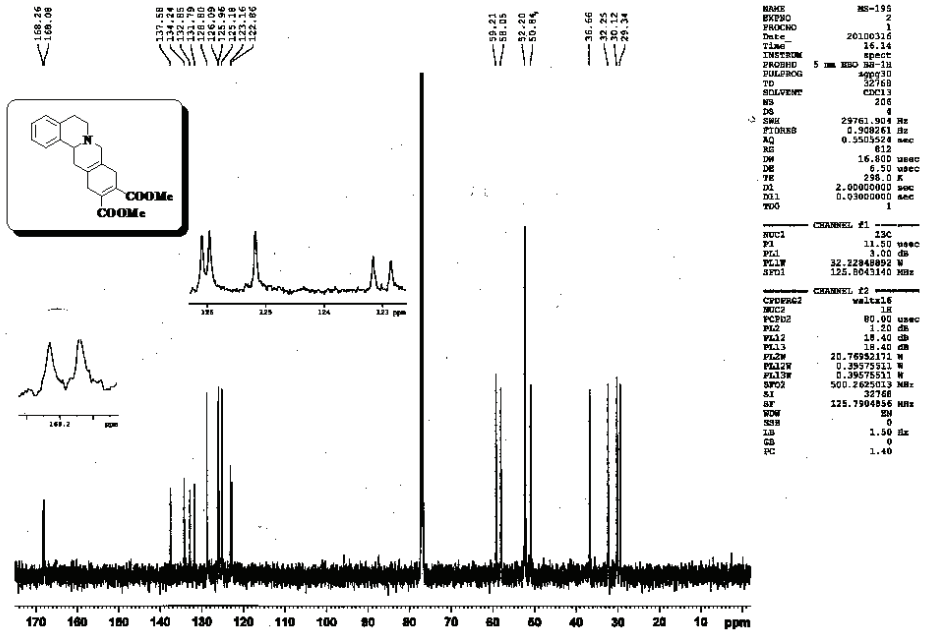
Compound ***17b***



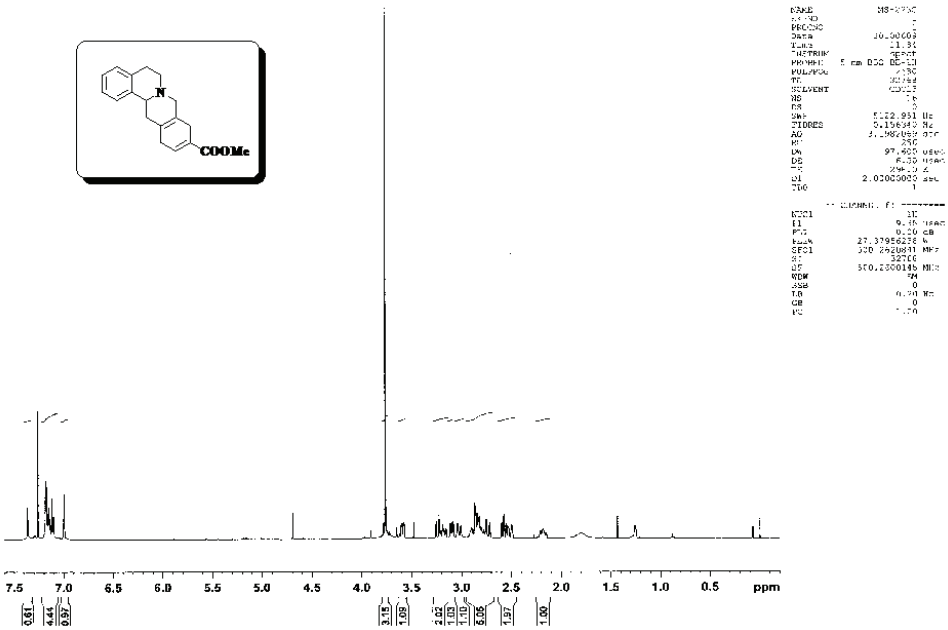


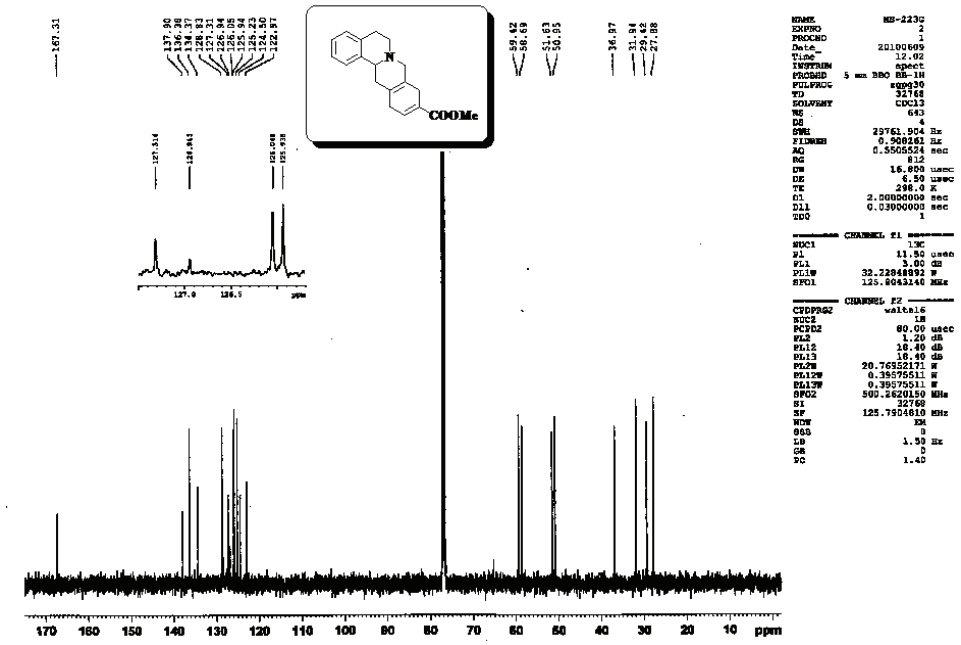
*Compound **18a***



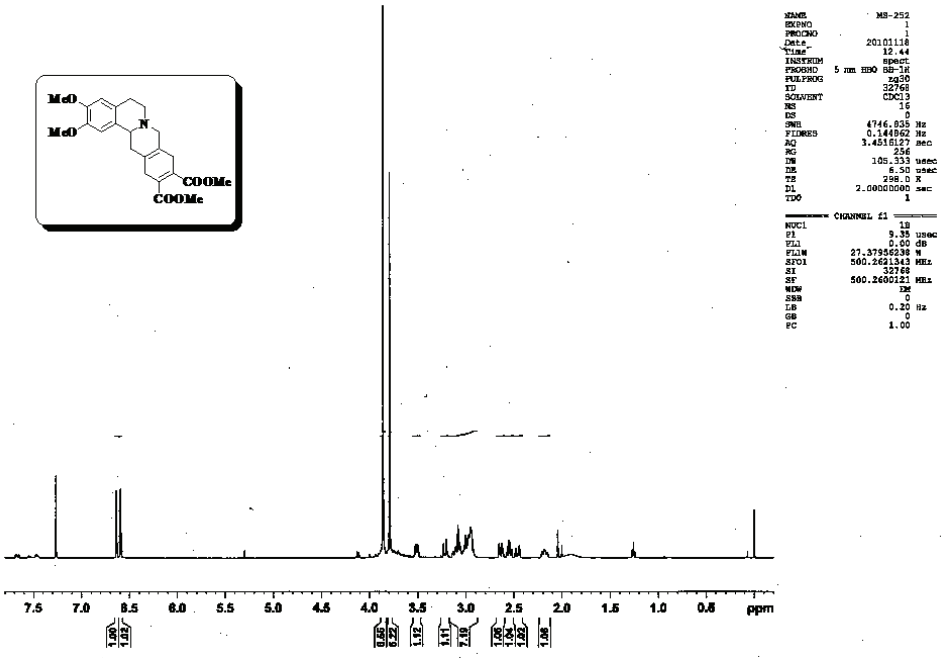


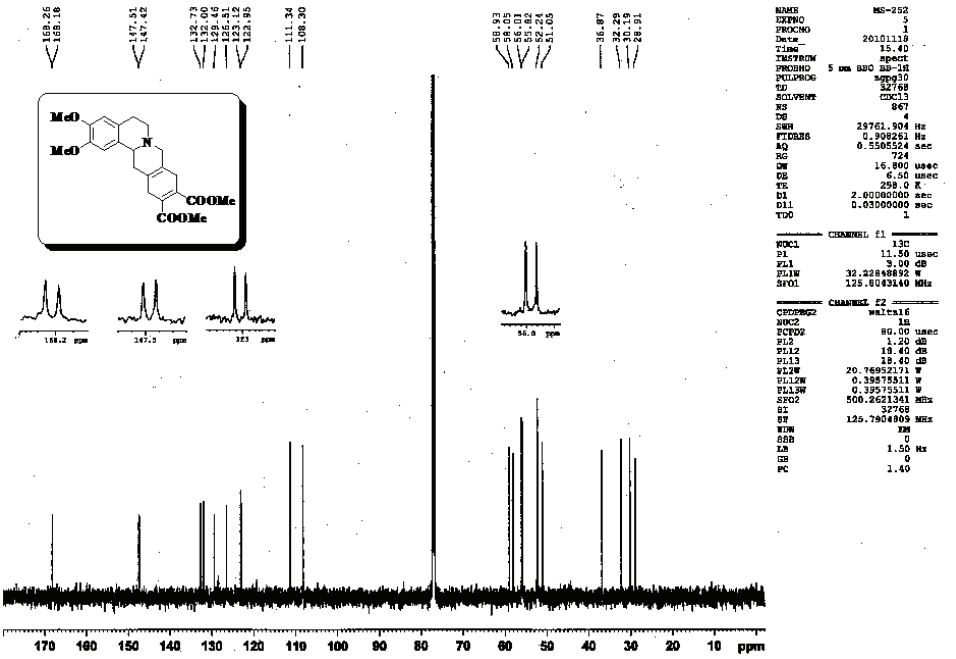
Compound ***18b***



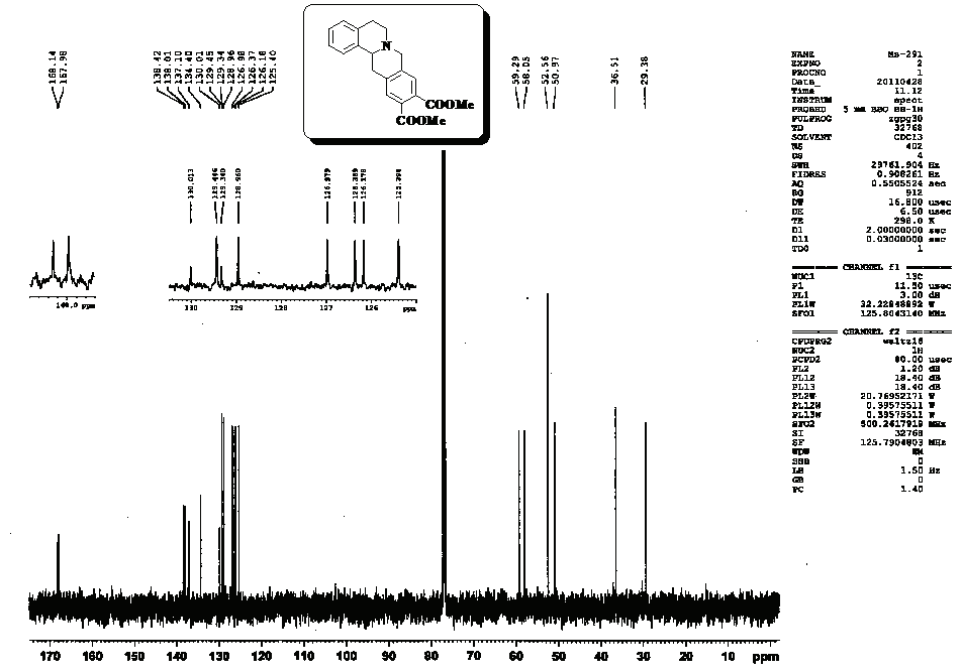


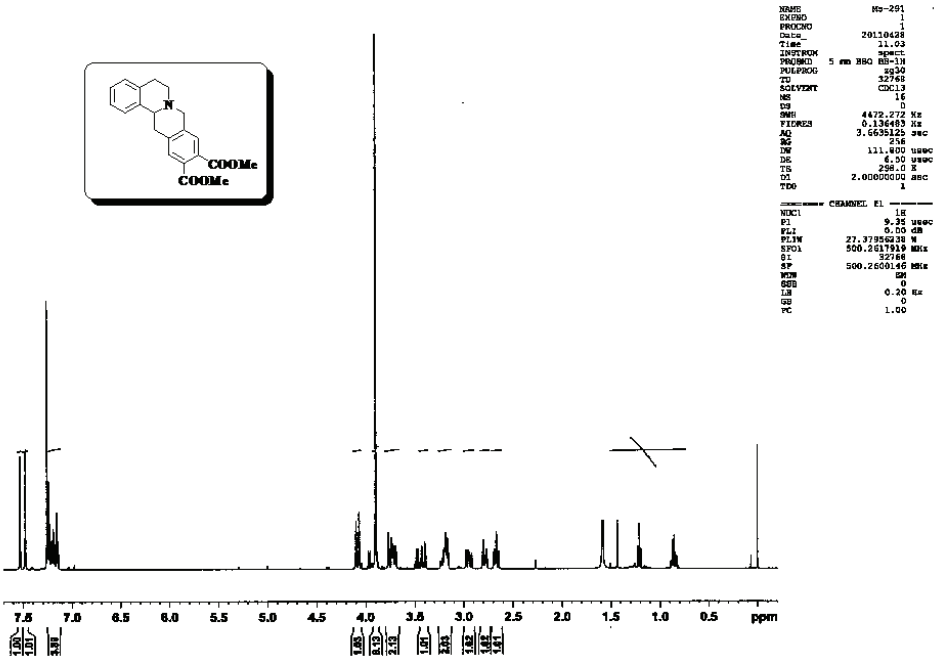
*Compound **18c***



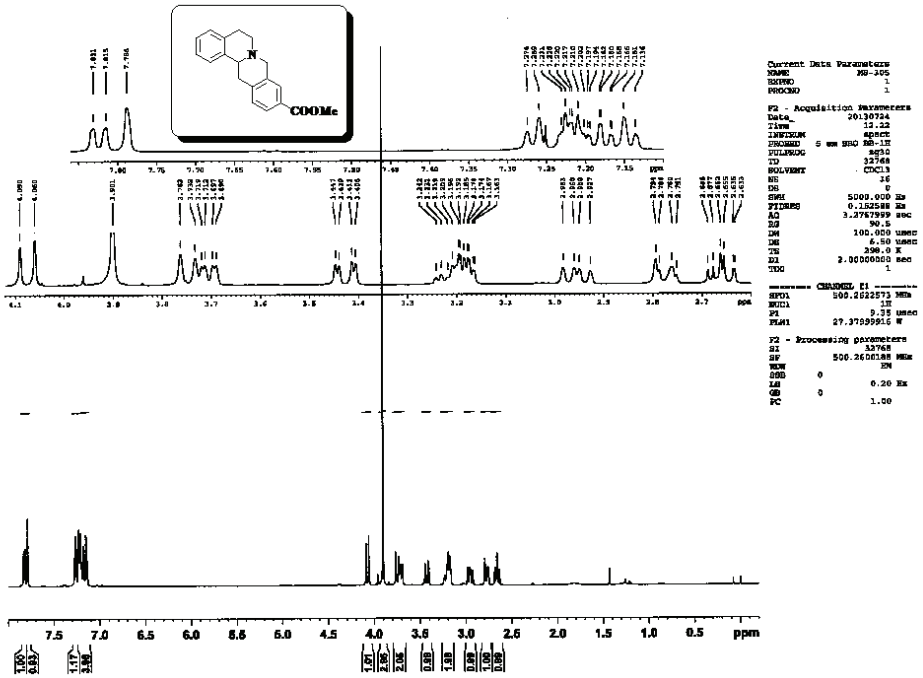


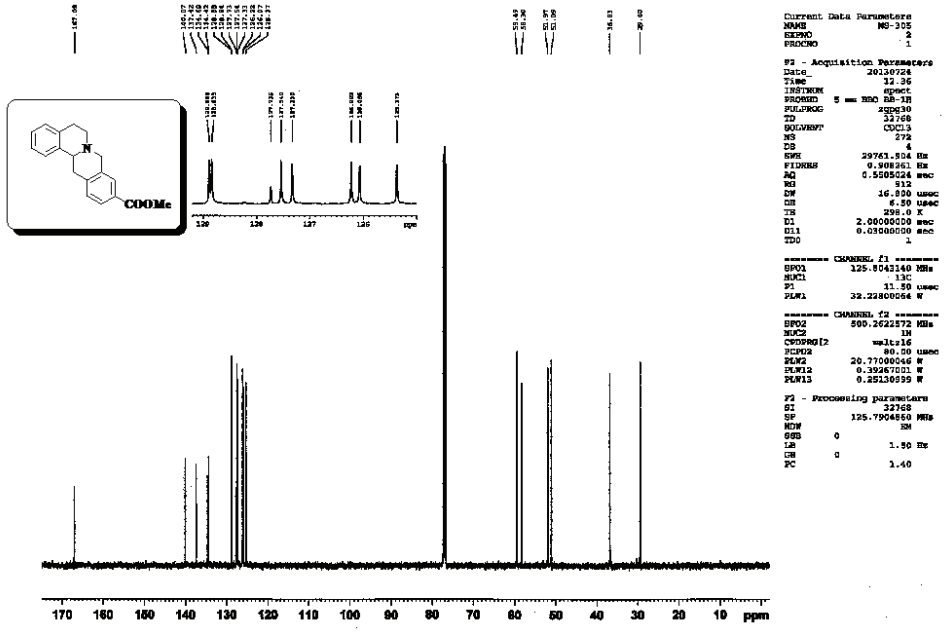
Compound ***19a***



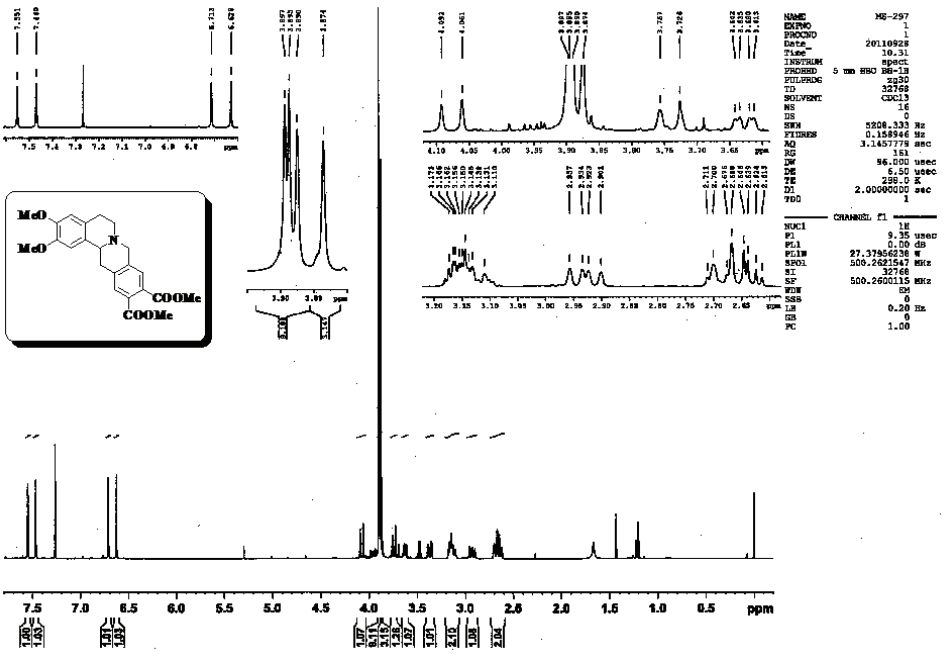


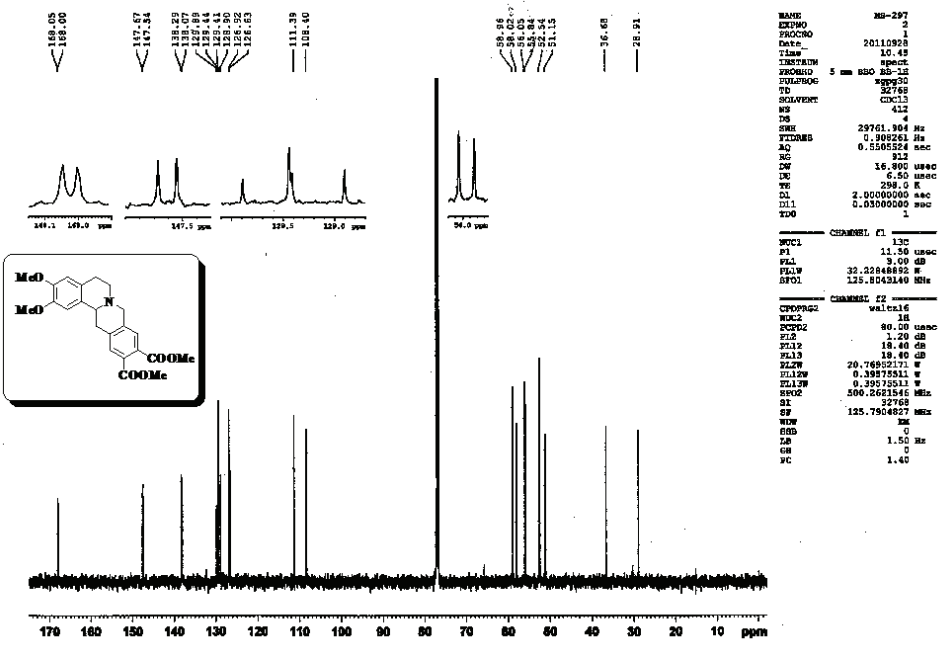
Compound ***19b***



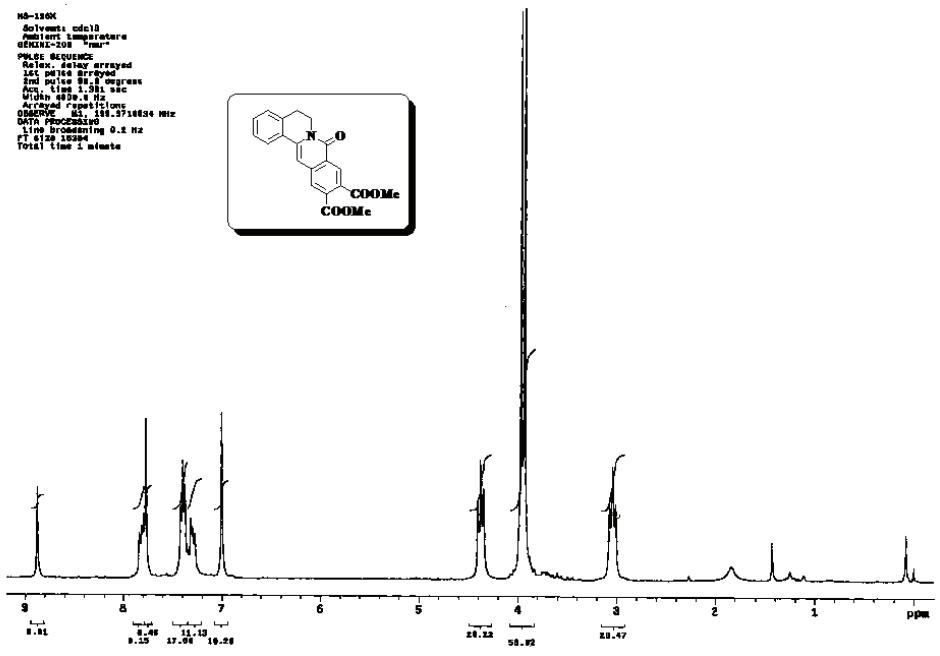


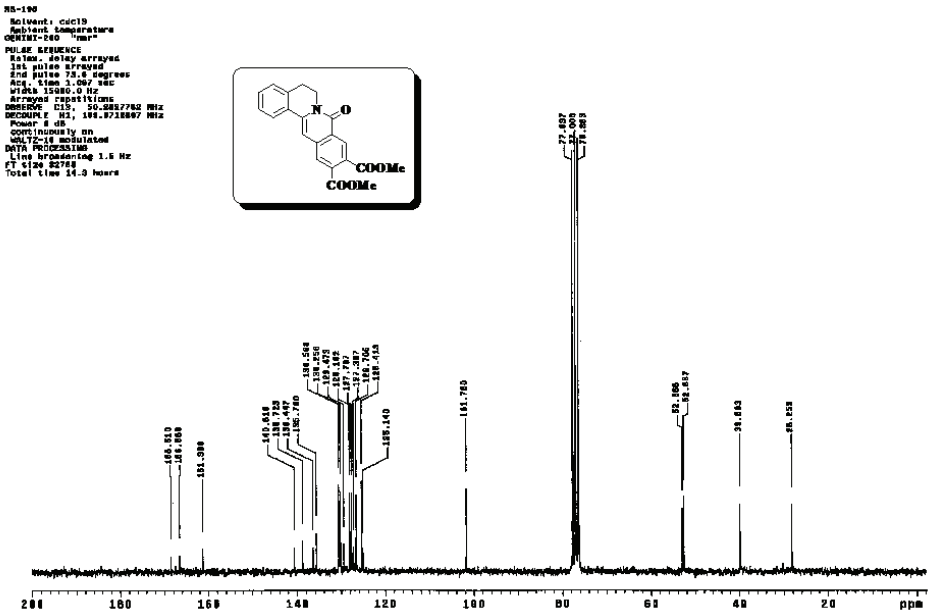
Compound ***19c***



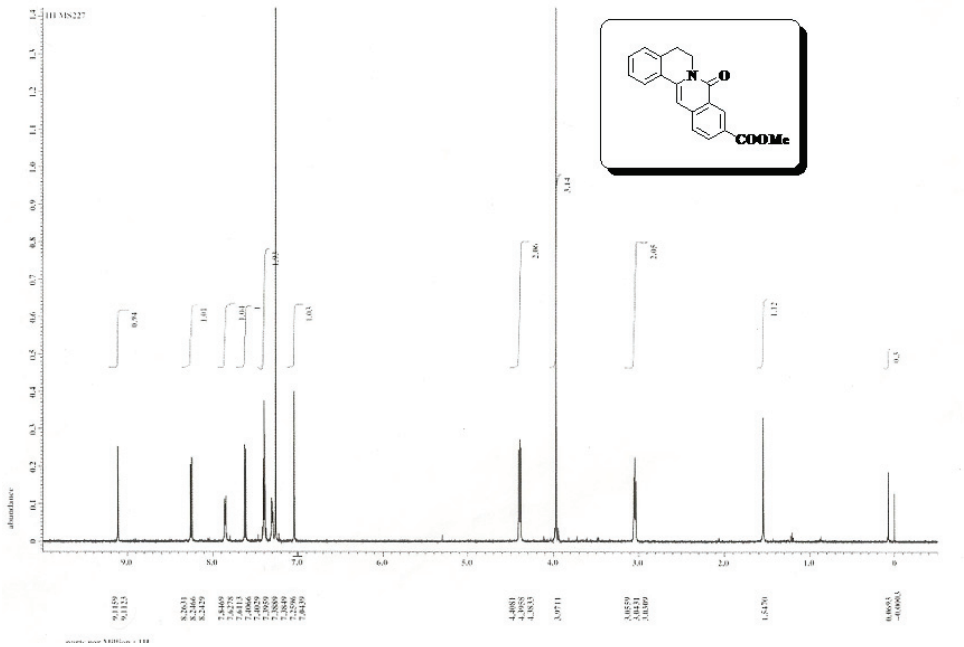


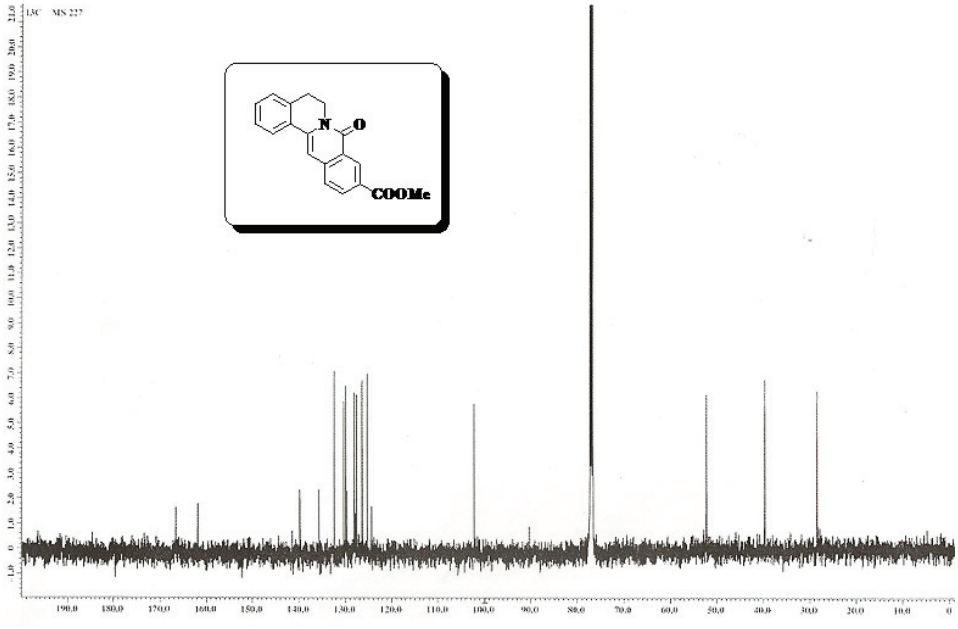
*Compound **20a***



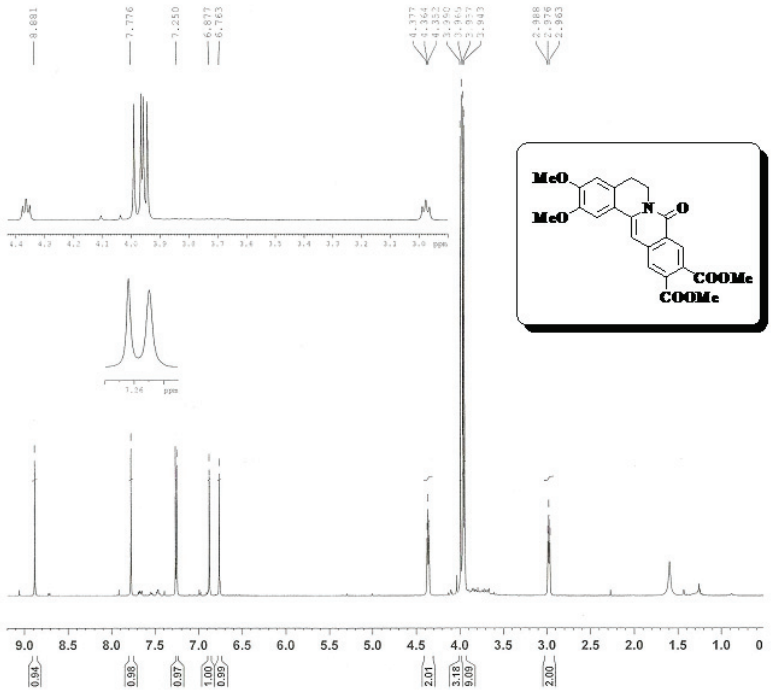


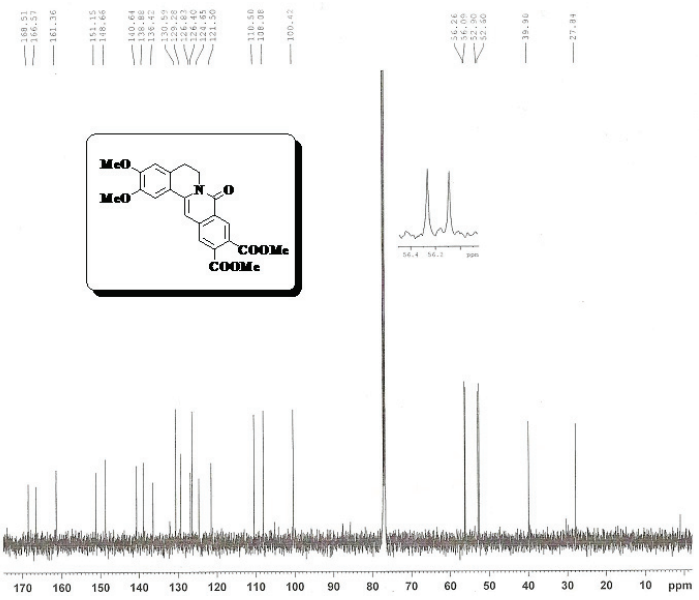
*Compound **20b***



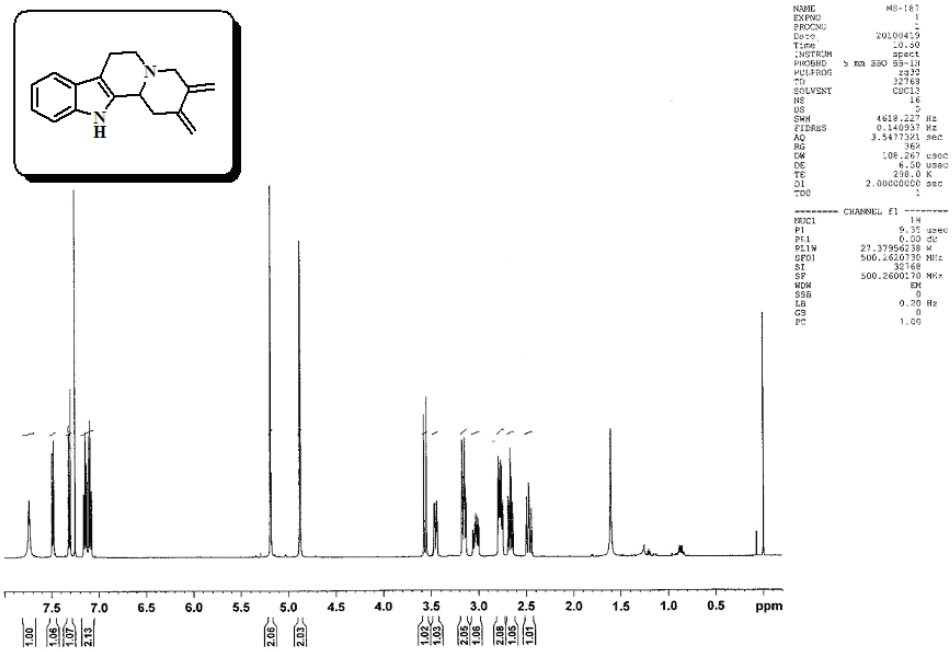


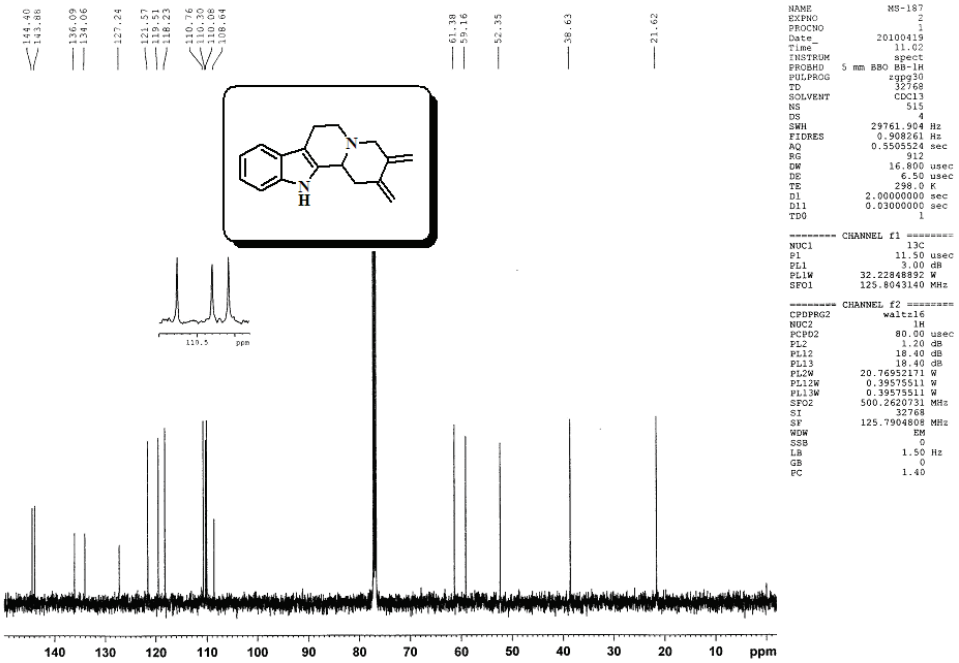
Compound ***20c***





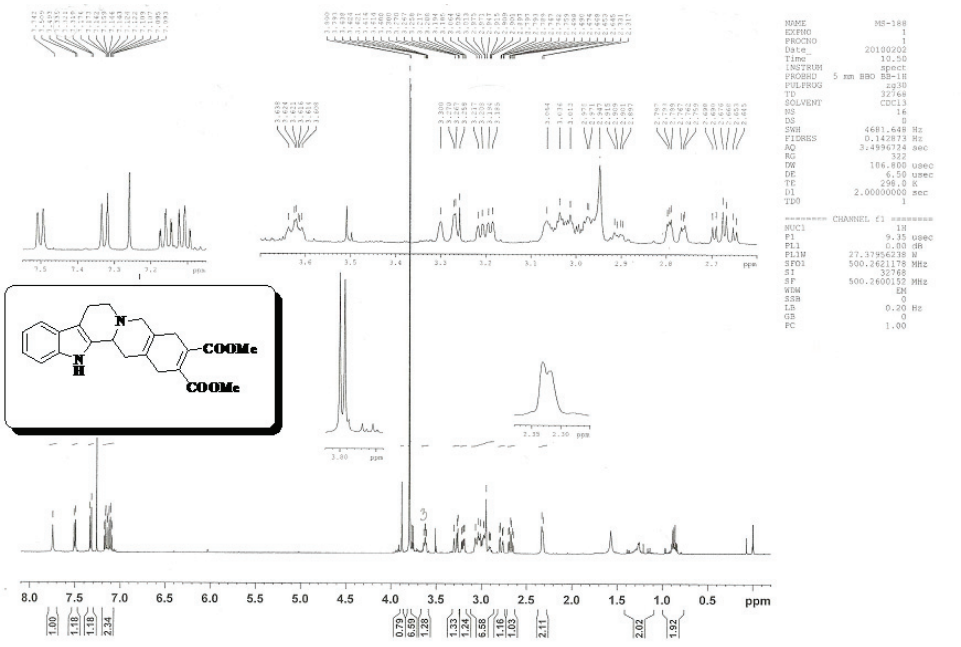
Compound ***24***





NAME	MS-187
EXPNO	2
PROCNO	1
Date_	20100419
Time_	11.02
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	515
DS	4
SWH	29761.904 Hz
FIDRES	0.908261 Hz
AQ	0.5505524 sec
RG	912
DW	16.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	11.50 usec
PL1	3.00 dB
PL1W	32.22848892 W
SFO1	125.8043140 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.20 dB
PL12	18.40 dB
PL13	18.40 dB
PL2W	20.76952171 W
PL12W	0.39575511 W
PL13W	0.39575511 W
SFO2	500.2620731 MHz
SI	32768
SF	125.7904808 MHz
WDW	EM
SSB	0
LB	1.50 Hz
GB	0
PC	1.40

Compound ***25***



NAME	MS-188
EXPNO	1
PROCNO	1
Date_	20100202
Time_	10.50
INSTRUM	spect
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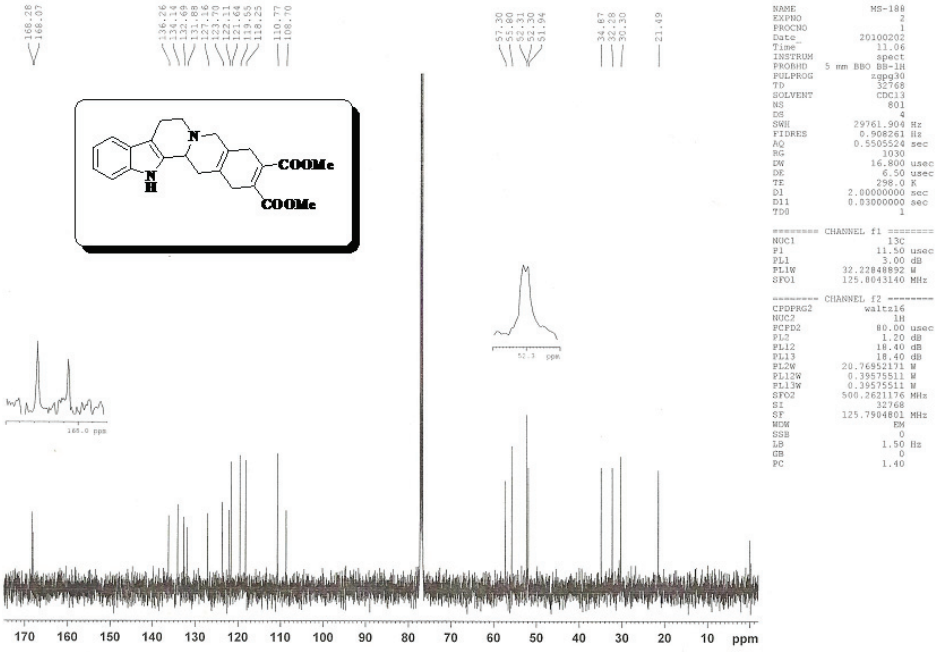
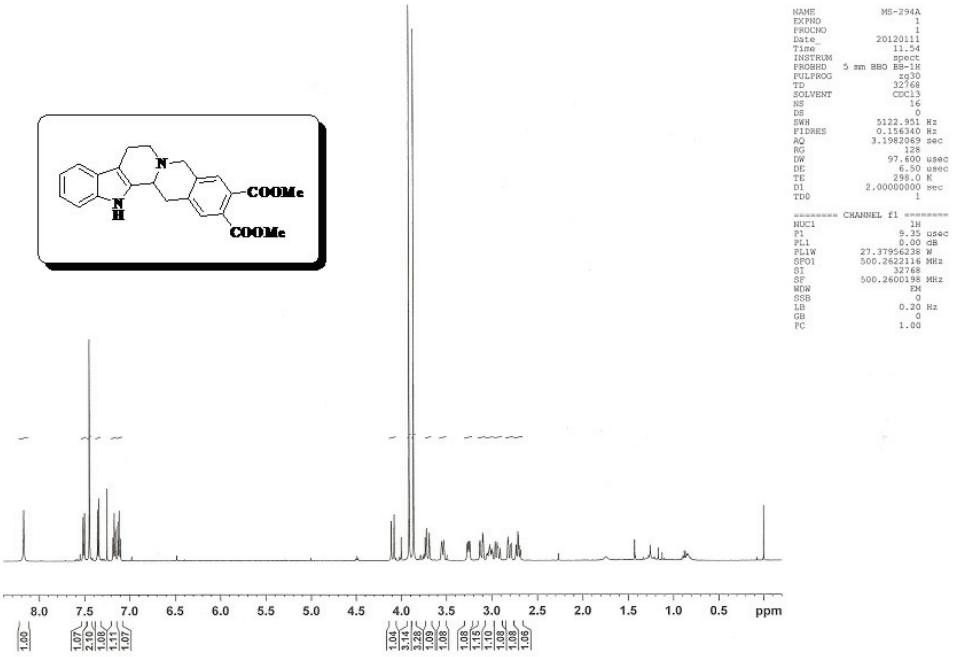
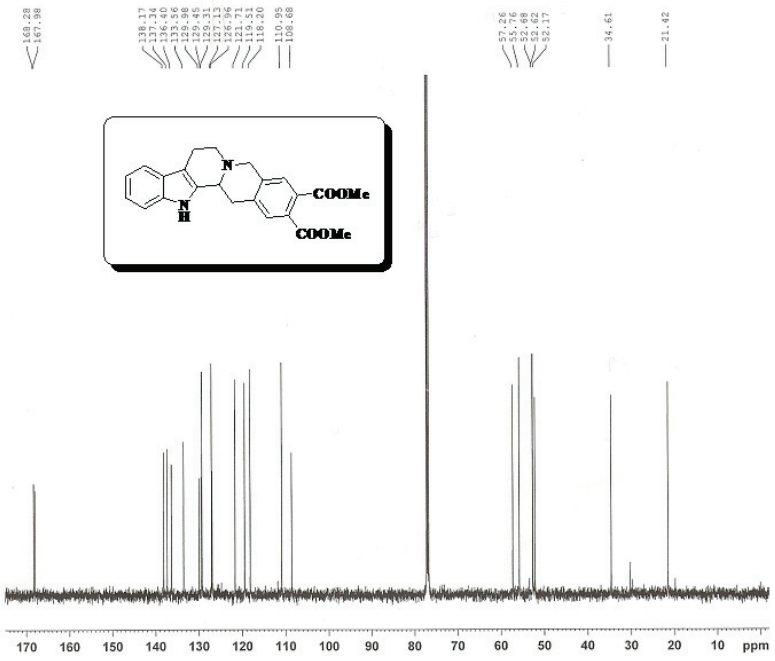
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	4681.648 Hz
FIDRES	0.142873 Hz
AQ	3.4996724 sec
RG	322
DW	106.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.35 usec
PL1	0.00 dB
PL1W	27.37956238 W
SFO1	500.2621178 MHz
SI	32768
SF	500.2600152 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



Compound ***26***



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EXPNO                     2
PROCNO                    1
Date_              20120111
Time                  12.18
INSTRUM               spect
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PULPROG               zgpg30
TD                     32768
SOLVENT                CDCl3
NS                       339
DS                         4
SWH               29761.904 Hz
FIDRES            0.908261 Hz
AQ                0.5505524 sec
RG                       912
DW                  16.800 usec
DE                   6.50 usec
TE                  298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                   11.50 usec
PL1                   3.00 dB
PL1W             32.22848892 W
SFO1             125.8043140 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                   1.20 dB
PL12                 18.40 dB
PL13                 18.40 dB
PL2W             20.76952171 W
PL12W             0.39575511 W
PL13W             0.39575511 W
SFO2             500.2622116 MHz
SI                     32768
SF               125.7904848 MHz
WDW                       EM
SSB                        0
LB                    1.50 Hz
GB                         0
PC                    1.40
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