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SUPPLEMENTARY MATERIAL TO

Synthesis and biological evaluation of some drug-like scaffolds of benzo- and pyrido-fused medium-sized *N*-heterocycles obtained *via* intramolecular Friedel–Crafts acylation reactions

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ANALYTICAL AND SPECTRAL DATA

(*E*)-*N*-(Pyridin-2-yl)cinnamamide (3a): Yellow plates; 85%; mp 148–150 ºC (ethanol); IR (KBr, ν, cm^{-1}): 3280, 3075, 2980, 1672, 1600, 1480, 1450, 1355, 1250, 1120, 765. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.25 (1H, s, NH), 6.74 (1H, d, J = 15.7 Hz, =CH), 7.10 (1H, ddd, J_1 = 7.4, J_2 = 4.8, J_3 = 1.2 Hz), 7.43 (2H, dddd, J_1 = 8.1, J_2 = 7.2, J_3 = 2.0, J_4 = 0.5 Hz), 7.44 (1H, tt, J_1 = 7.2, J_2 = 1.6 Hz), 7.51 (2H, dddd, J_1 = 8.1, J_2 = 2.3, J_3 = 1.6, J_4 = 0.5 Hz), 7.62 (1H, d, J = 15.7 Hz, =CH), 7.65 (1H, ddd, J_1 = 7.9, J_2 = 1.2, J_3 = 0.5 Hz), 7.75 (1H, ddd, J_1 = 7.9, J_2 = 7.4, J_3 = 1.9 Hz), 8.40 (1H, ddd, J_1 = 4.8, J_2 = 1.9, J_3 = 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 114.6 (1C, Ar., Py-C-6"), 117.6 (1C, Ar., Py-C-4"), 118.4 (1C, =C^{2}H-), 128.0 (2C, Ar., C-3', C-5'), 129.0 (2C, Ar., C-4', C-6'), 129.4 (1C, Ar.,C-2'), 135.8 (1C, Ar.,C-1'), 139.2 (1C, Ar., Py-C-5"), 141.0 (1C, =C^{3}H-), 148.1 (1C, Ar., Py-C-3"), 152.9 (1C, Ar., Py-C-1"), 164.9 (1C, C=O, C-1). MS (EI, 70 eV) m/z (%), 225 (M^++1, 32), 224 (M^+, 100), 216 (17), 203 (27), 188 (12), 175 (21), 147 (28), 134 (15), 119 (37), 106 (15), 91 (17), 90 (25), 67 (84), 54 (30). Anal. Calcd. for $C_{14}H_{12}N_2O$ (224); C, 75.00; H, 5.35; N, 12.50. Found: C, 75.12; H, 5.33; N, 12.47%.

(*E*)-*N*,3-di(pyridin-2-yl)acrylamide (3b): Yellow needles, 78%, mp 132-34 °C (AcOEt); IR (KBr, ν, cm^{-1}): 3247, 3077, 2973, 1670, 1600, 1480, 1384, 1275, 1182, 892. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.72 (1H, s, NH), 6.85 (1H, d, J = 15.5 Hz, =CH), 7.10 (1H, ddd, J_1 = 7.9, J_2 = 4.8, J_3 = 1.2 Hz), 7.43 (1H, d, J = 15.5 Hz, =CH), 7.54 (1H, ddd, J_1 = 7.4, J_2 = 4.7, J_3 = 1.4 Hz), 7.65 (1H, ddd, J_1 = 7.9, J_2 = 1.2, J_3 = 0.5 Hz), 7.71 (1H, ddd, J_1 = 7.7, J_2 = 1.4, J_3 = 0.5 Hz), 7.75 1H, (td, J_1 = 7.9, J_2 = 1.9 Hz), 7.89 (1H, ddd, J_1 = 7.7, J_2 = 7.4, J_3 = 1.9 Hz), 8.40 (1H, ddd, J_1 = 4.8, J_2 = 1.9, J_3 = 0.5 Hz), 8.73 (1H, ddd, J_1 = 4.7, J_2 = 1.9, J_3 = 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 115.2 (1C, Ar., C-6"), 118.4 (1C, Ar., C-4"), 122.8 (1C, Ar., C-6'), 123.3 (1C, =C^{2}H-), 127.2 (1C, Ar., C-4'), 139.2 (1C, Ar.,C-5'), 139.6 (1C, Ar.,C-5"), 139.8 (1C, =C^{3}H-), 148.1 (1C, Ar.,C-3'), 149.2 (1C, Ar.,C-3"), 152.9 (1C, Ar., C-1'), 155.3 (1C, Ar., C-1"), 168.4 (1C, C=O, C-1). MS (EI, 70 eV) m/z (%), 228 (M^++3, 3), 226 (M^++1, 32), 225 (M^+, 100), 190 (41), 188 (35), 176 (2), 166 (5), 153 (18), 141 (33), 118 (39), 106 (10), 94 (11), 90 (82), 71 (9), 47 (19). Anal. Calcd. for $C_{13}H_{11}N_3O$ (225); C, 69.33; H, 4.88; N, 18.66. Found: C, 69.30; H, 4.94; N, 18.58%.

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(*E*)-*N*-(Pyridin-2-ylmethyl)cinnamamide (3c): Pale pink plates; 90%; mp 104-6 ºC (Lit.[35] mp 100-101 (ethanol); IR (KBr, *v*, cm^{-1}): 3250, 2920, 1662, 1615, 1577, 1480, 1440, 1355, 1264, 1060, 779. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.65 (2H, s, CH_2), 5.43 (1H, s, NH), 6.61 (1H, d, J = 15.6 Hz, =CH), 7.11 (1H, ddd, J_1 = 7.4, J_2 = 4.6, J_3 = 1.2 Hz), 7.25 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.35 (m, 2H), 7.43 (1H, tt, J_1 = 7.2, J_2 = 1.3 Hz), 7.50 (m, 2H), 7.65 (1H, d, J = 15.6 Hz, =CH), 7.63 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 8.55 (1H, ddd, J_1 = 4.6, J_2 = 1.9, J_3 = 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 44.1 (1C, N-CH_2-), 120.0 (1C, =C^2H-), 120.5 (1C, Ar., Py-C-4"), 123.6 (1C, Ar., Py-C-6"), 128.0 (2C, Ar., C-2', C-6'), 129.0 (2C, Ar., C-3', C-5'), 129.4 (1C, Ar.,C-4'), 135.8 (1C, Ar.,C-1'), 139.1 (1C, Ar., Py-C-5"), 140.9 (1C, =C^3H-), 148.0 (1C, Ar., Py-C-3"), 157.3 (1C, Ar., Py-C-1"), 170.2 (1C, C=O, C-1). MS (EI, 70 eV) m/z (%), 239 (M^++1, 46), 238 (M^+, 71), 230 (12), 208 (7), 199 (16), 184 (5), 167 (11), 149 (11), 126 (13), 112 (32), 98 (100), 90 (53), 74 (55), 69 (27). Anal. Calcd. for $C_{15}H_{14}N_2O$ (238); C, 75.63; H, 5.88; N, 11.76. Found: C, 76.01; H, 5.80; N, 11.55%.

(*E*)-3-(Pyridin-2-yl)-*N*-((pyridin-2-yl)methyl)acrylamide (3d): Yellow crystals; 81%; mp 158–60 ºC (ethanol); IR (KBr, *v*, cm^{-1}): 3237, 3068, 2975, 1688, 1605, 1585, 1440, 1330, 1265, 1127, 790. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.66 (2H, s, CH_2), 5.62 (1H, s, NH), 6.78 (1H, d, J = 15.2 Hz, =CH), 7.16 (1H, ddd, J_1 = 7.4, J_2 = 4.6, J_3 = 1.2 Hz), 7.29 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.40 (1H, d, J = 15.2 Hz, =CH), 7.52 (1H, ddd, J_1 = 7.4, J_2 = 4.7, J_3 = 1.4 Hz), 7.63 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.75 (1H, ddd, J_1 = 7.7, J_2 = 1.4, J_3 = 0.5 Hz), 7.89 (1H, ddd, J_1 = 7.7, J_2 = 7.4, J_3 = 1.9 Hz), 8.54 (1H, ddd, J_1 = 4.6, J_2 = 1.9, J_3 = 0.5 Hz), 8.77 (1H, ddd, J_1 = 4.7, J_2 = 1.9, J_3 = 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 45.7 (1C, N-CH_2-), 120.4 (1C, Ar., C-4"), 122.8 (1C, Ar., C-6'), 123.3 (1C, Ar.,C-4'), 123.6 (1C, Ar., C-6"), 128.0 (1C, =C^2H-), 139.1 (1C, Ar.,C-5'), 139.8 (1C, Ar.,C-5"), 141.1 (1C, =C^3H-), 148.0 (1C, Ar., C-3"), 149.2 (1C, Ar., C-3'), 155.3 (1C, Ar.,C-1'), 157.3 (1C, Ar., C-1"), 175.2 (1C, C=O, C-1). MS (EI, 70 eV) m/z (%), 240 (M^++1, 4), 239 (M^+, 22), 238 (2), 208 (6), 199 (13), 184 (6), 167 (35), 149 (15), 126 (18), 112 (36), 106 (26), 98 (100), 93 (6), 84 (46), 74 (35), 69 (20), 55 (54). Anal. Calcd. for $C_{14}H_{13}N_3O$ (239); C, 70.29; H, 5.43; N, 17.57. Found: C, 70.24; H, 5.40; N, 17.63%.

3,4-Dihydro-4-phenyl-1,8-naphthyridin-2(1*H*)-one (4a): Yellowish brown plates; 80%; mp 170 ºC *dec.* (acetone); IR (KBr, *v*, cm^{-1}): 3345, 3047, 2945, 1677, 1600, 1585, 1480, 1480, 1474, 1340, 1255, 1140, 769. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.84 (2H, dd, J_1 = 16.3, J_2 = 3.0 Hz, C^3H_2), 5.08 (1H, dd, J_1 = 4.1, J_2 = 1.8 Hz, C^4H), 6.66 (1H, dd, J_1 = 8.1, J_2 = 4.6 Hz), 7.15 (1H, tdd, J_1 = 7.7, J_2 = 1.5, J_3 = 1.3 Hz), 7.21 (2H, dddd, J_1 = 7.8, J_2 = 7.7, J_3 = 1.9, J_4 = 0.5 Hz), 7.27 (2H, dddd, J_1 = 7.8, J_2 = 1.4, J_3 = 1.3, J_4 = 0.5 Hz), 8.05 (1H, dd, J_1 = 4.6, J_2 = 1.9 Hz), 8.36 (1H, dd, J_1 = 8.1, J_2 = 1.9 Hz), 9.78 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 38.1 (1C, -CH_2-, C-3), 40.6 (1C, -CH-, C-4), 114.0 (1C, Ar., Py-C-6), 121.0 (1C, Ar.,C-4'), 126.8 (1C, Ar., Py-C-4a), 128.7 (2C, Ar., C-2', C-6'), 129.3 (2C, Ar., C-3', C-5'), 131.7 (1C, Ar., Py-C-5), 143.2 (1C, Ar.,C-1'), 144.3 (1C, Ar., Py-C-7), 151.2 (1C, Ar., Py-C-8a), 169.4 (1C, C=O, C-2). MS (EI, 70 eV) m/z (%), 224 (M^+, 12), 223 (71), 209 (4), 192 (2), 180 (3), 165 (34), 134 (24), 119 (2), 112 (3), 106 (100), 91 (44), 90 (17), 79 (14), 65 (9). Anal. Calcd. for $C_{14}H_{12}N_2O$ (224); C, 75.00; H, 5.35; N, 12.50. Found: C, 75.06; H, 5.40; N, 12.46%.

3,4-Dihydro-4-(pyridin-2-yl)-1,8-naphthyridin-2(1*H*)-one (4b): White crystals; 88%, mp 135-37 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3405, 3030, 2965, 1678, 1600, 1490, 1450, 1260, 1145, 1080, 792. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.82 (2H, dd, J_1 = 16.3, J_2 = 3.0 Hz, C^3H_2), 5.32 (1H, dd, J_1 = 4.1, J_2 = 1.8 Hz, C^4H), 6.67 (1H, dd, J_1 = 8.1, J_2 = 4.6 Hz), 7.18 (1H, ddd, J_1 = 7.4, J_2 = 4.9, J_3 = 1.2 Hz), 7.27 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.68 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.95 (1H, dd, J_1 = 8.1, J_2 = 1.9 Hz), 8.11 (1H, dd, J_1 = 4.6,

J_2 = 1.9 Hz), 8.55 (1H, ddd, J_1 = 4.9, J_2 = 1.9, J_3 = 0.5 Hz), 9.34 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 37.1 (1C, -CH-, C-4), 42.1 (1C, -CH_2-, C-3), 113.3 (1C, Ar., C-6), 120.0 (1C, Ar., C-4'), 120.3 (1C, Ar., C-5'), 126.4 (1C, Ar., C-6'), 130.9 (1C, Ar., C-4a), 139.6 (1C, Ar., C-5), 144.4 (1C, Ar., C-7), 146.5 (1C, Ar., C-8a), 152.2 (1C, Ar.,C-3'), 165.4 (1C, Ar.,C-1'), 173.4 (1C, C=O, C-2). MS (EI, 70 eV) m/z (%), 226 (M^++1, 9), 225 (M^+, 66), 208 (2), 194 (2), 181 (3), 165 (37), 148 (16), 133 (12), 120 (100), 105 (28), 91 (24), 77 (51), 68 (3). Anal. Calcd. for $C_{13}H_{11}N_3O$ (225); C, 69.33; H, 4.88; N, 18.66. Found: C, 69.28; H, 4.91; N, 18.70%.

5,6,8,9-Tetrahydro-5-phenylpyrido[2,3-*c*]azepin-7-one (4c): Yellow needles; 79%, m.p. 172-75 °C (AcOEt); IR (KBr, *v*, cm^{-1}): 3410, 3040, 2950, 1700, 1590, 1480, 1440 1375, 1280, 1176, 796. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.08 (2H, dd, J_1 = 16.2, J_2 = 6.2 Hz, C^6H_2), 4.32 (1H, dd, J_1 = 10.2, J_2 = 2.3 Hz, C^5H), 4.89 (2H, d, J = 12.0 Hz, N-C^9H_2), 7.12 (1H, dd, J_1 = 7.4, J_2 = 4.6 Hz), 7.18 (1H, tdd, J_1 = 7.7, J_2 = 1.5, J_3 = 1.3 Hz), 7.25 (2H, dddd, J_1 = 7.8, J_2 = 7.7, J_3 = 1.9, J_4 = 0.5 Hz), 7.39 (2H, dddd, J_1 = 7.8, J_2 = 1.4, J_3 = 1.3, J_4 = 0.5 Hz), 7.66 (1H, dd, J_1 = 7.4, J_2 = 1.9 Hz), 8.49 (1H, dd, J_1 = 4.6, J_2 = 1.9 Hz), 9.63 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 42.7 (1C, -CH-, C-5), 46.6 (1C, -CH_2-, C-1), 50.7 (1C, -CH_2-, C-4), 122.0 (1C, Ar., Py-C-7), 127.0 (1C, Ar.,C-4'), 128.8 (2C, Ar., C-2', C-6'), 129.7 (2C, Ar., C-3', C-5'), 132.3 (1C, Ar., Py-C-6), 133.3 (1C, Ar., Py-C-5a), 143.4 (1C, Ar.,C-1'), 145.4 (1C, Ar., Py-C-8), 159.6 (1C, Ar., Py-C-9a), 175.8 (1C, C=O, C-3). MS (EI, 70 eV) m/z (%), 239 (M^++1, 6), 238 (M^+, 25), 203 (2), 194 (100), 180 (87), 165 (12), 151 (8), 137 (26), 109 (69), 95 (26), 90 (19), 67 (22). Anal. Calcd. for $C_{15}H_{14}N_2O$ (238); C, 75.63; H, 5.88; N, 11.76. Found: C, 75.58; H, 5.90; N, 11.79%.

5,6,8,9-Tetrahydro-5-(pyridin-2-yl)pyrido[2,3-*c*]azepin-7-one (4d): Yellow crystal; m.p. 180 ºC *dec.*, 75% (AcOEt); IR (KBr, *v*, cm^{-1}): 3180, 3040, 2975, 1677, 1600, 1590, 1447, 1375, 1240, 1160, 795. ^{1}H NMR: δ 3.15 (2H, dd, J_1 = 16.3, J_2 = 6.2 Hz, J_3 = C^6H_2), 4.65 (1H, dd, J_1 = 10.2, J_2 = 2.2 Hz, C^5H), 4.87 (2H, d, J = 12.0 Hz, N-C^9H_2), 7.14 (1H, dd, J_1 = 7.1, J_2 = 4.6 Hz), 7.20 (1H, ddd, J_1 = 7.4, J_2 = 4.9, J_3 = 1.2 Hz), 7.27 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.68 (2H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 8.51 (1H, ddd, J_1 = 4.9, J_2 = 1.9, J_3 = 0.5 Hz), 8.58 (1H, dd, J_1 = 4.6, J_2 = 1.9 Hz), 9.81 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 40.1 (1C, -CH-, C-5), 46.6 (1C, -CH_2-, C-1), 49.3 (1C, -CH_2-, C-4), 119.9 (1C, Ar., C-6), 121.1 (1C, Ar., C-4'), 127.0 (1C, Ar., C-6'), 132.5 (1C, Ar., C-5), 132.7 (1C, Ar., C-5'), 139.8 (1C, Ar., C-5a), 146.7 (1C, Ar., C-8), 147.2 (1C, Ar., C-3'), 156.3 (1C, Ar., C-9a), 165.6 (1C, Ar.,C-1'), 172.7 (1C, C=O, C-3). MS (EI, 70 eV) m/z (%), 239 (M^++1, 3), 238 (M^+, 11), 223 (60), 210 (15), 206 (4), 197 (18), 181 (100), 165 (20), 152 (25), 139 (4), 115 (3), 90 (30), 76 (5), 69 (7). Anal. Calcd. for $C_{14}H_{13}N_3O$ (**239**); C, 70.29; H, 5.43; N, 17.57. Found: C, 70.35; H, 5.45; N, 17.49%.

1,2,3,4-Tetrahydro-4-phenyl-1,8-naphthyridine (5a): Yellow crystals; 90%; mp 115-17 ºC (benzene); IR (KBr, *v*, cm^{-1}): 3430, 3050, 2975, 1698, 1600, 1590, 1470, 1440, 1361, 1270, 1121, 779. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.06 (2H, dddd, J_1 = 13.4, J_2 = 7.0, J_3 = 6.6, J_4 = 2.5 Hz, C^3H_2), 3.43 (2H, ddd, J_1 = 13.8, J_2 = 6.6, J_3 = 2.5 Hz, N-C^2H_2), 3.94 (1H, dd, J_1 = 10.1, J_2 = 3.9 Hz, C^4H), 7.12 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.16 (1H, tt, J_1 = 7.7, J_2 = 1.3 Hz), 7.20 (2H, dtd, J_1 = 7.8, J_2 = 1.2, J_3 = 0.5 Hz), 7.28 (2H, dddd, J_1 = 7.8, J_2 = 7.7, J_3 = 1.9, J_4 = 0.5 Hz), 8.07 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.23 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 9.57 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 30.8 (1C, -CH_2-, C-3), 36.9 (1C, -CH_2-, C-2), 39.9 (1C, -CH-, C-4), 111.2 (1C, Ar., Py-C-6), 117.7 (1C, Ar., Py-C-4a), 126.7 (1C, Ar., C-4'), 128.7 (2C, Ar., C-2', C-6'), 129.1 (2C, Ar., C-3', C-5'), 132.9 (1C, Ar., C-1'), 144.9 (1C, Ar., Py-C-5), 144.9 (1C, Ar., Py-C-7), 163.8 (1C, Ar., Py-C-8a). MS (EI, 70 eV) m/z (%), 212 (M^++2, 2), 211 (M^++1, 11), 210 (M^+, 64), 205 (2), 195 (100), 181 (32), 167 (12), 154 (8), 140 (5), 133 (21),

105 (8), 91 (15), 77 (29), 67 (2). Anal. Calcd. for $C_{14}H_{14}N_2$ (210); C, 80.00; H, 6.66; N, 13.33. Found: C, 80.11; H, 6.60; N, 13.27%.

1,2,3,4-Tetrahydro-4-(pyridin-2-yl)-1,8-naphthyridine (5b): Yellow crystals; 84%; mp 122-24 ºC (ethanol); IR (KBr, *v*, cm^{-1}): 3440, 3075, 2980, 1695, 1600, 1580, 1470, 1440, 1385, 1252, 1170, 794. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.13 (2H, dddd, J_1 = 13.6, J_2 = 6.9, J_3 = 6.6, J_4 = 2.5 Hz, C^3H_2), 3.45 (2H, ddd, J_1 = 13.8, J_2 = 6.6, J_3 = 2.5 Hz, N-C^2H_2), 4.15 (1H, dd, J_1 = 10.1, J_2 = 3.8 Hz, C^4H), 7.17 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.20 (1H, ddd, J_1 = 7.4, J_2 = 4.5, J_3 = 1.2 Hz), 7.28 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.68 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.93 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.13 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.52 (1H, ddd, J_1 = 4.5, J_2 = 1.9, J_3 = 0.5 Hz), 9.48 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 28.3 (1C, -CH_2-, C-3), 36.9 (1C, -CH_2-, C-2), 39.6 (1C, -CH-, C-4), 110.3 (1C, Ar., C-6), 117.7 (1C, Ar., C-4a), 120.6 (1C, Ar., C-4'), 125.0 (1C, Ar., C-6'), 131.6 (1C, Ar., C-5'), 139.4 (1C, Ar., C-5), 145.5 (1C, Ar., C-3'), 146.0 (1C, Ar., C-7), 153.4 (1C, Ar., C-1'), 167.7 (1C, Ar., C-8a). MS (EI, 70 eV) m/z (%), 213 (M^++2, 2), 212 (M^++1, 13), 211 (M^+, 36), 195 (2), 183 (6), 170 (77), 153 (100), 141 (3), 135 (12), 125 (15), 107 (5), 90 (20), 79 (14), 68 (4). Anal. Calcd. for $C_{13}H_{13}N_3$ (211); C, 73.93; H, 6.16; N, 19.90. Found: C, 73.88; H, 6.21; N, 19.90%.

6,7,8,9-Tetrahydro-5-phenyl-5*H*-pyrido[2,3-*c*]azepine (5c): Yellow crystals; 92%; mp 138-140 ºC (ethanol); IR (KBr, *v*, cm^{-1}): 3390, 3020, 2956, 1690, 1600, 1590, 1470, 1440, 1375, 1240, 1122, 798. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.18 (2H, dddd, J_1 = 13.9, J_2 = 6.6, J_3 = 4.7, J_4 = 2.6 Hz, C^6H_2), 2.89 (2H, ddd, J_1 = 11.3, J_2 = 6.6, J_3 = 2.6 Hz, C^7H_2), 3.97 (2H, d, J = 15.0 Hz, N-C^9H_2), 4.17 (1H, dd, J_1 = 8.1, J_2 = 1.4 Hz, C^5H), 7.12 (1H, dd, J_1 = 8.0, J_2 = 4.7 Hz), 7.18 (1H, tt, J_1 = 7.7, J_2 = 1.3 Hz), 7.21 (2H, dddd, J_1 = 7.8, J_2 = 7.7, J_3 = 1.9, J_4 = 0.5 Hz), 7.27 (2H, dtd, J_1 = 7.8, J_2 = 1.2, J_3 = 0.5 Hz), 8.31 (1H, dd, J_1 = 8.0, J_2 = 1.9 Hz), 8.67 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 9.41 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 35.7 (1C, -CH-, C-5), 50.4 (1C, -CH_2-, C-4), 54.5 (1C, -CH_2-, C-1), 56.9 (1C, -CH_2-, C-3), 122.6 (1C, Ar., Py-C-7), 126.9 (1C, Ar., C-4'), 128.9 (2C, Ar., C-2', C-6'), 129.5 (2C, Ar., C-3', C-5'), 132.8 (1C, Ar., Py-C-6), 134.4 (1C, Ar., Py-C-5a), 145.0 (1C, Ar., C-1'), 145.9 (1C, Ar., Py-C-8), 169.3 (1C, Ar., Py-C-9a). MS (EI, 70 eV) m/z (%), 225 (M^++1, 7), 224 (M^+, 100), 222 (40), 191 (3), 177 (2), 156 (2), 145 (44), 128 (2), 109 (25), 91 (39), 74 (25), 61 (2), 50 (7). Anal. Calcd. for $C_{15}H_{16}N_2$ (224); C, 80.35; H, 7.14; N, 12.50. Found: C, 80.42; H, 7.17; N, 12.40%.

6,7,8,9-Tetrahydro-5-(pyridin-2-yl)-5*H*-pyrido[2,3-*c*]azepine (5d): Yellow crystals; 89%; mp 158-61 ºC (ethanol); IR (KBr, *v*, cm^{-1}): 3420, 3040, 2985, 1700, 1605, 1580, 1475, 1440, 1374, 1248, 1127, 770. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.17 (2H, dddd, J_1 = 13.9, J_2 = 6.6, J_3 = 4.7, J_4 = 2.6 Hz, C^6H_2), 2.95 (2H, ddd, J_1 = 10.1, J_2 = 6.6, J_3 = 2.6 Hz C^7H_2), 4.03 (2H, d, J = 15.0 Hz, N-C^9H_2), 4.41 (1H, dd, J_1 = 8.1, J_2 = 1.4 Hz, C^5H), 7.20 (2H, ddd, J_1 = 7.4, J_2 = 4.5, J_3 = 1.2 Hz), 7.25 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.60 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.95 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.58 (1H, ddd, J_1 = 4.5, J_2 = 1.9, J_3 = 0.5 Hz), 8.72 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 9.72 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 35.0 (1C, -CH-, C-5), 50.4 (1C, -CH_2-, C-4), 50.8 (1C, -CH_2-, C-1), 54.5 (1C, -CH_2-, C-3), 120.6 (1C, Ar., C-7), 121.5 (1C, Ar., C-4'), 125.6 (1C, Ar., C-6'), 133.3 (1C, Ar., C-5'), 133.5 (1C, Ar., C-6), 139.5 (1C, Ar., C-5a), 146.3 (1C, Ar., C-8), 147.6 (1C, Ar., C-3'), 155.4 (1C, Ar., C-9a), 168.1 (1C, Ar., C-1'). MS (EI, 70 eV) m/z (%), 226 (M^++1, 10), 224 (M^+, 53), 208 (2), 194 (2), 181 (12), 165 (2), 148 (30), 120 (100), 105 (31), 91 (17), 74 (52), 68 (3), 51 (16). Anal. Calcd. for $C_{14}H_{15}N_3$ (225); C, 74.66; H, 6.66; N, 18.66. Found: C, 74.64; H, 6.71; N, 18.64%.

Ethyl 2-(3,4-dihydro-4-phenyl-1,8-naphthyridin-1(2*H*)-yl)acetate (7a): Pale yellow needles; 74%, mp 115–17 ºC (ethanol); IR (KBr, *v*, cm^{-1}): 3060, 2975, 1730, 1600, 1580, 1470, 1445, 1354, 1271, 780. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.17 (3H, t, J = 7.1 Hz, CH_3), 2.05 (2H, dddd, J_1 = 13.7, J_2 = 7.2, J_3 = 6.9, J_4 = 1.9 Hz, C^3H_2), 3.36 (2H, ddd, J_1 = 13.8, J_2 = 6.9, J_3 = 1.9 Hz, N-C^2H_2), 3.66 (2H, s, $C^{\alpha}H_2$), 3.86 (1H, dd, J_1 = 9.7, J_2 = 4.6 Hz, C^4H), 4.14 (2H, q, J = 7.1 Hz, CH_2), 7.10 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.14 (1H, tt, J_1 = 7.7, J_2 = 1.3 Hz), 7.19 (2H, dtd, J_1 = 7.8, J_2 = 1.2, J_3 = 0.5 Hz), 7.31 (1H, dddd, J_1 = 7.8, J_2 = 7.7, J_3 = 1.9, J_4 = 0.5 Hz), 8.12-8.35 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.7 (1C, -OCH$_2$<u>*CH*$_3$</u>), 29.7 (1C, -CH_2-, C-3), 39.9 (1C, -$C^{\alpha}H_2$CO), 47.5 (1C, -CH-, C-4), 50.7 (1C, -O<u>*CH*$_2$</u>CH_3), 61.1 (1C, -CH_2-, C-2), 113.6 (1C, Ar., Py-C-6), 124.9 (1C, Ar., Py-C-4a), 126.7 (1C, Ar., C-4'), 128.7 (2C, Ar., C-2', C-6'), 129.1 (2C, Ar., C-3', C-5'), 134.3 (1C, Ar., Py-C-5), 144.9 (1C, Ar., C-1'), 145.1 (1C, Ar., Py-C-7), 156.7 (1C, Ar., Py-C-8a), 171.0 (1C, C=O). MS (EI, 70 eV) m/z (%), 297 (M^++1, 4), 296 (M^+, 31), 275 (27), 251 (M^+-COEt, 100), 218 (7), 189 (4), 143 (72), 115 (60), 91 (11), 77 (26). Anal. Calcd. for $C_{18}H_{20}N_2O_2$ (296); C, 72.97; H, 6.75; N, 9.45. Found: C, 73.05; H, 6.73; N, 9.38%.

Ethyl 3-(3,4-dihydro-4-phenyl-1,8-naphthyridin-1(2*H*)-yl)propanoate (7b): Buff crystals; 81%, mp 129–31 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3065, 2979, 1735, 1605, 1590, 1480, 1445, 1370, 1185, 789. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.14 (3H, t, J = 7.1 Hz, CH_3), 2.03 (2H, dddd, J_1 = 13.7, J_2 = 7.2, J_3 = 6.9, J_4 = 1.9 Hz, C^3H_2), 2.50 (2H, t, J = 6.7 Hz, $C^{\alpha}H_2$), 3.39 (t, J = 6.7 Hz, $C^{\beta}H_2$), 3.44 (ddd, J_1 = 13.7, J_2 = 6.9, J_3 = 1.9 Hz, N-C^2H_2), 3.86 (1H, dd, J_1 = 9.7, J_2 = 4.6 Hz, C^4H), 4.10 (2H, q, J = 7.1 Hz, CH_2), 7.18 (2H, m), 7.15 (2H, dtd, J_1 = 7.8, J_2 = 1.2, J_3 = 0.5 Hz), 7.28 (2H, dddd, J_1 = 7.8, J_2 = 7.7, J_3 = 1.9, J_4 = 0.5 Hz), 8.08 (dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.31 (dd, J_1 = 7.6, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.5 (1C, -OCH$_2$<u>*CH*$_3$</u>), 29.7 (1C, -CH_2-, C-3), 35.5 (1C, -$C^{\alpha}H_2$CO), 39.9 (1C, -CH-, C-4), 47.9 (1C, N-$C^{\beta}H_2$), 48.1 (1C, -O<u>*CH*$_2$</u>CH_3), 61.8 (1C, -CH_2-, C-2), 112.5 (1C, Ar., Py-C-6), 122.4 (1C, Ar., Py-C-4a), 126.7 (1C, Ar., C-4'), 128.7 (2C, Ar., C-2', C-6'), 129.1 (2C, Ar., C-3', C-5'), 134.4 (1C, Ar., Py-C-5), 144.9 (1C, Ar., C-1'), 145.9 (1C, Ar., Py-C-7), 156.2 (1C, Ar., Py-C-8a), 172.8 (1C, C=O). MS (EI, 70 eV) m/z (%), 310 (M^+, 33), 271 (6), 265 (M^+-OEt, 100), 224 (5), 186 (38), 170 (21), 153 (61), 117 (82), 106 (40), 89 (35), 90 (23), 77 (68). Anal. Calcd. for $C_{19}H_{22}N_2O_2$ (310); C, 73.54; H, 7.09; N, 9.03. Found: C, 73.50; H, 7.03; N, 9.12%.

Ethyl 2-(3,4-dihydro-4-(pyridin-2-yl)-1,8-naphthyridin-1(2*H*)-yl)acetate (7c): Pale yellow needles; 78%, mp 140–42 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3030, 2965, 1732, 1600, 1580, 1460, 1485, 1330, 1277, 770. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.16 (3H, t, J = 7.1 Hz, CH_3), 2.09 (2H, dddd, J_1 = 13.6, J_2 = 7.2, J_3 = 6.9, J_4 = 1.9 Hz, C^3H_2), 3.36 (2H, ddd, J_1 = 14.6, J_2 = 6.9, J_3 = 1.9 Hz, N-C^2H_2), 3.68 (2H, s, $C^{\alpha}H_2$), 3.99 (dd, J_1 = 9.7, J_2 = 4.6 Hz, C^4H), 4.19 (2H, q, J = 7.1 Hz, CH_2), 7.07 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.18 (1H, ddd, J_1 = 7.4, J_2 = 4.5, J_3 = 1.2 Hz), 7.28 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.61 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.95 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.20 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.58 (1H, ddd, J_1 = 4.5, J_2 = 1.9, J_3 = 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 15.0 (1C, -OCH$_2$<u>*CH*$_3$</u>), 27.9 (1C, -CH_2-, C-3), 39.9 (1C, -CH-, C-4), 47.5 (1C, -CH_2-, C-2), 50.7 (1C, -$C^{\alpha}H_2$CO), 61.9 (1C, -O<u>*CH*$_2$</u>CH_3), 113.0 (1C, Ar., C-6), 120.6 (1C, Ar., C-4'), 124.7 (1C, Ar., C-4a), 125.0 (1C, Ar., C-6'), 132.6 (1C, Ar., C-5'), 139.4 (1C, Ar., C-5), 146.0 (1C, Ar., C-7), 146.1 (1C, Ar., C-3'), 156.0 (1C, Ar., C-8a), 167.7 (1C, Ar., C-1'), 175.5 (1C, C=O). MS (EI, 70 eV) m/z (%), 298 (M^++1 7), 297 (M^+, 62), 274 (42), 252 (M^+-OEt, 100), 225 (88), 197 (37), 181 (50), 152 (24), 104 (17), 93 (13), 90 (8), 77 (17). Anal. Calcd. for $C_{17}H_{19}N_3O_2$ (297); C, 68.68; H, 6.39; N, 14.14. Found: C, 68.74; H, 6.42; N, 14.10%.

Ethyl 3-(3,4-dihydro-4-(pyridin-2-yl)-1,8-naphthyridin-1(2*H*)-yl)propanoate (7d): Brownish needles; 76%, mp 104–6 ºC (ethanol); IR (KBr, *v*, cm^{-1}): 3064, 2982, 1730, 1600, 1580, 1470, 1440, 1375, 1285, 1134, 789. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.18 (3H, t, J = 7.1 Hz, CH_3), 2.14 (2H, dddd, J_1 = 13.6, J_2 = 7.2, J_3 = 6.9, J_4 = 1.9 Hz, C^3H_2), 2.50 (2H, t, J = 6.7 Hz, $C^{\alpha}H_2$), 3.34 (2H, ddd, J_1 = 13.8, J_2 = 6.9, J_3 = 1.9 Hz, N-C^2H_2), 3.38 (2H, t, J = 6.7 Hz, $C^{\beta}H_2$), 4.02 (1H, dd, J_1 = 9.7, J_2 = 4.6 Hz C^4H), 4.15 (2H, q, J = 7.1 Hz, CH_2), 7.12 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.24 (1H, ddd, J_1 = 7.4, J_2 = 4.5, J_3 = 1.2 Hz), 7.30 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.61 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.85 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.19 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.50 (1H, ddd, J_1 = 4.5, J_2 = 1.9, J_3 = 0.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 15.8 (1C, -$OCH_2\underline{CH_3}$), 27.9 (1C, -CH_2-, C-3), 35.5 (1C, -$C^{\alpha}H_2CO$), 39.9 (1C, -CH-, C-4), 47.9 (1C, -CH_2-, C-2), 48.1 (1C, N-$C^{\beta}H_2$), 63.5 (1C, -$O\underline{CH_2}CH_3$), 111.8 (1C, Ar., C-6), 120.6 (1C, Ar., C-4'), 121.7 (1C, Ar., C-4a), 125.0 (1C, Ar., C-6'), 132.7 (1C, Ar., C-5'), 139.4 (1C, Ar., C-5), 146.0 (1C, Ar., C-7), 146.9 (1C, Ar., C-3'), 155.8 (1C, Ar., C-8a), 167.7 (1C, Ar., C-1'), 178.5 (1C, C=O). MS (EI, 70 eV) m/z (%), 312 (M^++1, 13), 311 (M^+, 34), 275 (20), 266 (M^+-OEt, 14), 265 (100), 249 (48), 187 (14), 165 (18), 148 (24), 121 (43), 105 (11), 92 (47), 77 (57). Anal. Calcd. for $C_{18}H_{21}N_3O_2$ (311); C, 69.45; H, 6.75; N, 13.50. Found: C, 69.42; H, 6.80; N, 13.45%.

Ethyl 2-(6,7-dihydro-5-phenyl-5*H*-pyrido[2,3-*c*]azepin-8(9*H*)-yl)acetate (7e): Yellow crystals; 84%, mp 134-36 ºC (AcOEt); IR (KBr, *v*, cm^{-1}): 3060, 2971, 1740, 1605, 1590, 1480, 1445, 1363, 1250, 1185, 790. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.24 (3H, t, J = 7.1 Hz, CH_3), 2.03 (2H, dddd, J_1 = 13.9, J_2 = 6.6, J_3 = 4.7, J_4 = 2.6 Hz, C^6H_2), 2.85 (2H, ddd, J_1 = 6.6, J_2 = 5.8, J_3 = 2.6 Hz, C^7H_2), 3.51 (2H, s, $C^{\alpha}H_2$), 4.02 (1H, dd, J_1 = 8.1, J_2 = 1.4 Hz, C^5H), 4.13 (2H, d, J = 12.6 Hz, N-C^9H_2), 4.17 (2H, q, J = 7.1 Hz, CH_2), 7.10-7.18 (2H, m), 7.24 (2H, dddd, J_1 = 7.8, J_2 = 7.7, J_3 = 1.9, J_4 = 0.5 Hz), 7.31 (2H, dtd, J_1 = 7.8, J_2 = 1.2, J_3 = 0.5 Hz), 8.38 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.64 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.7 (1C, -$OCH_2\underline{CH_3}$), 34.2 (1C, -CH-, C-5), 55.0 (1C, -CH_2-, C-4), 56.5 (1C, -CH_2-, C-1), 57.3 (1C, -CH_2-, C-3), 60.3 (1C, -$C^{\alpha}H_2CO$), 61.7 (1C, -$O\underline{CH_2}CH_3$), 121.9 (1C, Ar., Py-C-7), 126.9 (1C, Ar., C-4'), 128.9 (2C, Ar., C-2', C-6'), 129.5 (2C, Ar., C-3', C-5'), 133.6 (1C, Ar., Py-C-6), 136.1 (1C, Ar., Py-C-5a), 145.0 (1C, Ar., C-1'), 146.0 (1C, Ar., Py-C-8), 157.7 (1C, Ar., Py-C-9a), 171.4 (1C, C=O). MS (EI, 70 eV) m/z (%), 311 (M^++1, 12), 310 (M^+, 26), 275 (27), 265 (M^+-OEt, 100), 246 (10), 218 (5), 189 (41), 171 (23), 143 (54), 151 (76), 105 (9), 89 (13), 77 (38). Anal. Calcd. for $C_{19}H_{22}N_2O_2$ (310); C, 73.54; H, 7.09; N, 9.03. Found: C, 73.60; H, 7.12; N, 8.95%.

Ethyl 3-(6,7-dihydro-5-phenyl-5*H*-pyrido[2,3-*c*]azepin-8(9*H*)-yl)propanoate (7f): Pale yellow crystals; 81%, mp 172-75 ºC (benzene); IR (KBr, *v*, cm^{-1}): 3072, 2964, 1740, 1600, 1590, 1475, 1440, 1392, 1277, 1170, 795. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.18 (3H, t, J = 7.1 Hz, CH_3), 2.05 (2H, dddd, J_1 = 13.9, J_2 = 6.6, J_3 = 4.7, J_4 = 2.6 Hz, C^6H_2), 2.48 (2H, t, J = 3.9 Hz, $C^{\alpha}H_2$), 2.91 (2H, ddd, J_1 = 7.8, J_2 = 6.6, J_3 = 2.6 Hz, C^7H_2), 2.93 (2H, t, J = 3.9 Hz, $C^{\beta}H_2$), 4.01 (1H, d, J = 11.9 Hz, C^5H), 4.17 (2H, dd, J_1 = 8.1, J_2 = 1.4 Hz, N-C^9H_2), 4.28 (2H, q, J = 7.1 Hz, CH_2), 7.10 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.20 (1H, tt, J_1 = 7.7, J_2 = 1.3 Hz), 7.25 (m, 2H), 7.31 (2H, dtd, J_1 = 7.8, J_2 = 1.2, J_3 = 0.5 Hz), 8.32 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.60 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.2 (1C, -$OCH_2\underline{CH_3}$), 34.2 (1C, -CH-, C-5), 34.2 (1C, -$C^{\alpha}H_2CO$), 51.6 (1C, -CH_2-, C-4), 54.3 (1C, N-$C^{\beta}H_2$), 56.5 (1C, -CH_2-, C-3), 61.1 (1C, -CH_2-, C-1), 62.5 (1C, -$O\underline{CH_2}CH_3$), 121.9 (1C, Ar., Py-C-7), 126.9 (1C, Ar., C-4'), 128.9 (2C, Ar., C-2', C-6'), 129.5 (2C, Ar., C-3', C-5'), 133.6 (1C, Ar., Py-C-6), 136.1 (1C, Ar., Py-C-5a), 145.0 (1C, Ar., C-1'), 146.0 (1C, Ar., Py-C-8), 157.7 (1C, Ar., Py-C-9a), 175.4 (1C, C=O). MS (EI, 70 eV) m/z (%), 325 (M^++1, 6), 324 (M^+,

20), 287 (18), 279 (M^+-OEt, 100), 240 (11), 223 (18), 196 (54), 169 (64), 109 (12), 105 (9), 97 (75), 89 (11), 76 (8). Anal. Calcd. for $C_{20}H_{24}N_2O_2$ (324); C, 74.07; H, 7.40; N, 8.64. Found: C, 74.05; H, 7.45; N, 8.71%.

Ethyl 2-(6,7-dihydro-5-(pyridin-2-yl)-5*H*-pyrido[2,3-*c*]azepin-8(9*H*)-yl)acetate (7g): Yellow needles; 85%, mp 158–60 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3040, 2975, 1737, 1600, 1580, 1470, 1440, 1376, 1273, 1145, 768. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.17 (3H, t, J = 7.1 Hz, CH_3), 2.06 (2H, dddd, J_1 = 13.6, J_2 = 6.6, J_3 = 4.7, J_4 = 2.6 Hz, C^6H_2), 2.83 (2H, ddd, J_1 = 7.4, J_2 = 6.6, J_3 = 2.6 Hz C^7H_2), 3.51 (2H, s, $C^{\alpha}H_2$), 4.15 (2H, d, J = 12.6 Hz, N-C^9H_2), 4.18 (2H, q, J = 7.1 Hz, CH_2), 4.48 (1H, dd, J_1 = 8.1, J_2 = 1.4 Hz, C^5H), 7.11 (1H, dd, J_1 = 7.5, J_2 = 4.7 Hz), 7.20 (1H, ddd, J_1 = 7.4, J_2 = 4.5, J_3 = 1.2 Hz), 7.31 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.62 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.80 (1H, dd, J_1 = 7.5, J_2 = 1.9 Hz), 8.52 (1H, ddd, J_1 = 4.5, J_2 = 1.9, J_3 = 0.5 Hz), 8.65 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 15.7 (1C, -$OCH_2\underline{CH_3}$), 33.7 (1C, -CH-, C-5), 49.7 (1C, -CH_2-, C-4), 55.0 (1C, -CH_2-, C-1), 57.3 (1C, -CH_2-, C-3), 60.3 (1C, -$C^{\alpha}H_2CO$), 62.2 (1C, -$O\underline{CH_2}CH_3$), 120.2 (1C, Ar., C-7), 121.5 (1C, Ar., C-4'), 125.6 (1C, Ar., C-6'), 133.5 (1C, Ar., C-5'), 135.2 (1C, Ar., C-6), 139.5 (1C, Ar., C-5a), 146.3 (1C, Ar., C-8), 147.5 (1C, Ar., C-3'), 153.0 (1C, Ar., Py-C-9a), 167.8 (1C, Ar., C-1'), 171.4 (1C, C=O). MS (EI, 70 eV) m/z (%), 312 (M^++1, 12), 311 (M^+, 100), 290 (11), 275 (19), 266 (M^+-OEt, 29), 265 (55), 249 (38), 187 (12), 165 (14), 115 (24), 92 (45), 77 (18). Anal. Calcd. for $C_{18}H_{21}N_3O_2$ (311); C, 69.45; H, 6.75; N, 13.50. Found: C, 69.52; H, 6.71; N, 13.47%.

Ethyl 3-(6,7-dihydro-5-(pyridin-2-yl)-5*H*-pyrido[2,3-*c*]azepin-8(9*H*)-yl)propanoate (7h): Greenish crystals; 72%, mp 151-53 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3074, 2967, 1740, 1600, 1590, 1480, 1440, 1378, 1280, 1195, 788. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.13 (3H, t, J = 7.1 Hz, CH_3), 2.10 (2H, dddd, J_1 = 13.6, J_2 = 6.6, J_3 = 4.7, J_4 = 2.6 Hz, C^6H_2), 2.48 (2H, t, J = 3.9 Hz, $C^{\alpha}H_2$), 2.88 (2H, ddd, J_1 = 7.6, J_2 = 6.6, J_3 = 2.6 Hz, C^7H_2), 2.90 (2H, t, J = 3.9 Hz, $C^{\beta}H_2$), 4.04 (2H, d, J = 11.9 Hz, N-C^9H_2), 4.15 (2H, q, J = 7.1 Hz, CH_2), 4.48 (1H, dd, J_1 = 8.1, J_2 = 1.4 Hz, C^5H), 7.11 (1H, dd, J_1 = 7.5, J_2 = 4.7 Hz), 7.22 (1H, ddd, J_1 = 7.4, J_2 = 4.5, J_3 = 1.2 Hz), 7.29 (1H, ddd, J_1 = 7.6, J_2 = 1.2, J_3 = 0.5 Hz), 7.61 (1H, ddd, J_1 = 7.6, J_2 = 7.4, J_3 = 1.9 Hz), 7.90 (1H, dd, J_1 = 7.5, J_2 = 1.9 Hz), 8.55 (1H, ddd, J_1 = 4.5, J_2 = 1.9, J_3 = 0.5 Hz), 8.68 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 16.1 (1C, -$OCH_2\underline{CH_3}$), 33.7 (1C, -CH-, C-5), 34.2 (1C, -$C^{\alpha}H_2CO$), 49.7 (1C, -CH_2-, C-4), 51.6 (1C, -CH_2-, C-3), 54.3 (1C, -CH_2-, C-1), 61.3 (1C, N-$C^{\beta}H_2$), 62.4 (1C, -$O\underline{CH_2}CH_3$), 120.2 (1C, Ar., C-7), 121.5 (1C, Ar., C-4'), 125.6 (1C, Ar., C-6'), 133.5 (1C, Ar., C-5'), 135.2 (1C, Ar., C-6), 139.5 (1C, Ar., C-5a), 146.3 (1C, Ar., C-8), 147.5 (1C, Ar., C-3'), 153.0 (1C, Ar., Py-C-9a), 167.8 (1C, Ar., C-1'), 180.6 (1C, C=O). MS (EI, 70 eV) m/z (%), 326 (M^++1, 7), 325 (M^+, 36), 303 (46), 280 (M^+-OEt, 100), 267 (36), 230 (39), 196 (18), 184 (22), 145 (14), 91 (20), 77 (21). Anal. Calcd. for $C_{19}H_{23}N_3O_2$ (325); C, 70.15; H, 7.07; N, 12.92. Found: C, 70.20; H, 7.11; N, 12.95%.

5,12-Ethano-6*H*-benzo[*e*]pyrido[2,3-*b*]azocin-7(12*H*)-one (8a): Yield 0.61 g (81%, method I), 0.56 g (75%, method II), 0.53 g (71%, method III), Pale yellow crystals; mp 137-40 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3030, 2975, 1693, 1600, 1580, 1480, 1440, 1376, 1255, 1184, 792. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.03 (2H, dddd, J_1 = 13.3, J_2 = 8.0, J_3 = 4.1, J_4 = 3.6 Hz, *bridged-*CH_2), 3.51 (2H, ddd, J_1 = 11.9, J_2 = 8.0, J_3 = 3.6 Hz, *bridged-*NCH_2), 4.30 (1H, dd, J_1 = 6.7, J_2 = 1.4 Hz $C^{12}H$), 4.92 (2H, d, J = 16.1 Hz, N-C^6H_2CO), 7.14 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.28 (1H, ddd, J_1 = 8.0, J_2 = 1.4, J_3 = 0.4 Hz), 7.30-7.42 (2H, m), 7.94 (1H, ddd, J_1 = 7.9, J_2 = 1.3, J_3 = 0.4 Hz), 8.02 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.17 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 28.4 (1C, bridged-CH_2-, C-13), 32.9 (1C,

-CH-, C-12), 40.0 (1C, bridged-CH_2-, C-14), 50.0 (1C, -CH_2CO, C-6), 121.2 (1C, Ar., Py-C-2), 122.7 (1C, Ar., Py-C-12a), 124.6 (1C, Ar., C-9), 126.1 (1C, Ar., C-11a), 126.7 (2C, Ar., C-8, C-11), 127.8 (2C, Ar., C-10, C-7a), 128.7 (1C, Ar., Py-C-1), 151.7 (1C, Ar., Py-C-3), 156.4 (1C, Ar., Py-C-4a), 203.5 (1C, C=O, C-7). MS (EI, 70 eV) m/z (%), 252 (M^++2, 5), 251 (M^++1, 31), 250 (M^+, 100), 222 (36), 209 (15), 197 (6), 185 (66), 165 (33), 147 (18), 108 (17), 92 (28), 77 (26). Anal. Calcd. for $C_{16}H_{14}N_2O$ (250); C, 76.80; H, 5.60; N, 11.20. Found: C, 76.85; H, 5.57; N, 11.24%.

6,7-Dihydro-5,13-ethanobenzo[*e*]pyrido[2,3-*b*]azonin-8(13*H*)-one (8b): Yield 0.63 g (80%, method I), 0.57 g (73%, method II), 0.55 g (70%, method III), Yellow solid; mp 168-71 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3060, 2974, 1700, 1600, 1585, 1480, 1440, 1393, 1284, 1178, 782. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.11 (2H, dddd, J_1 = 14.4, J_2 = 7.2, J_3 = 3.3, J_4 = 3.1 Hz, *bridged-*CH_2), 2.84 (2H, ddd, J_1 = 15.7, J_2 = 6.4, J_3 = 2.8 Hz, C^7H_2), 3.57 (2H, ddd, J_1 = 14.4, J_2 = 6.9, J_3 = 3.6 Hz, *bridged-*NCH_2), 3.85 (2H, ddd, J_1 = 14.4, J_2 = 6.6, J_3 = 2.5 Hz, C^6H_2), 4.50 (1H, dd, J_1 = 4.5, J_2 = 1.7 Hz, C^{13}H), 7.09 (1H, dd, J_1 = 7.5, J_2 = 4.7 Hz), 7.31 (1H, ddd, J_1 = 11.5, J_2 = 1.8, J_3 = 0.5 Hz), 7.33 (1H, ddd, J_1 = 7.8, J_2 = 7.5, J_3 = 1.8 Hz), 7.45 (1H, ddd, J_1 = 11.5, J_2 = 7.5, J_3 = 1.2 Hz), 7.98 (1H, ddd, J_1 = 7.8, J_2 = 1.2, J_3 = 0.5 Hz), 8.09 (1H, dd, J_1 = 7.5, J_2 = 1.9 Hz), 8.18 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 26.4 (1C, bridged-CH_2-, C-14), 35.9 (1C, -CH_2CO, C-7), 40.0 (1C, -CH-, C-13), 50.9 (1C, bridged-CH_2-, C-15), 51.7 (1C, N-CH_2-, C-6), 121.2 (1C, Ar., Py-C-2), 122.7 (1C, Ar., Py-C-13a), 124.6 (1C, Ar., C-10), 126.1 (1C, Ar., C-12a), 126.7 (2C, Ar., C-9, C-12), 127.8 (2C, Ar., C-11, C-8a), 128.7 (1C, Ar., Py-C-1), 151.7 (1C, Ar., Py-C-3), 156.4 (1C, Ar., Py-C-4a), 210.8 (1C, C=O, C-8). MS (EI, 70 eV) m/z (%), 265 (M^++1, 12), 264 (M^+, 60), 246 (53), 236 (100), 219 (6), 207 (31), 193 (10), 178 (3), 165 (45), 152 (63), 134 (33), 92 (20), 77 (32). Anal. Calcd. for $C_{17}H_{16}N_2O$ (264); C, 77.27; H, 6.06; N, 10.60. Found: C, 77.32; H, 6.09; N, 10.55%.

6,12-Dihydro-5*H*-7,12-ethanodipyrido[2,3-*b*:2',3'-*e*]azocin-5-one (8c): Yield 0.63 g (84%, method I), 0.57 g (77%, method II), 0.55 g (74%, method III), Yellow crystals, mp 184-86 °C (benzene); IR (KBr, ν, cm^{-1}): 3034, 2979, 1692, 1600, 1580, 1500, 1440, 1322, 1275, 1153, 794. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.14 (2H, dddd, J_1 = 13.4, J_2 = 7.9, J_3 = 4.1, J_4 = 3.6 Hz, *bridged-*CH_2), 3.49 (2H, ddd, J_1 = 12.4, J_2 = 7.9, J_3 = 3.6 Hz, *bridged-*NCH_2), 4.83 (2H, dd, J_1 = 6.7, J_2 = 1.4 Hz, N-C^6H_2CO), 4.95 (1H, d, J = 16.2 Hz, C^{12}H), 7.11 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.25 (1H, dd, J_1 = 7.8, J_2 = 4.5 Hz), 7.80 (1H, dd, J_1 = 7.8, J_2 = 1.9 Hz), 7.97 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.12 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.70 (1H, dd, J_1 = 4.5, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 27.4 (1C, bridged-CH_2-, C-13), 32.9 (1C, -CH-, C-12), 45.4 (1C, bridged-CH_2-, C-14), 56.2 (1C, -$\underline{CH_2}$CO, C-6), 121.1 (1C, Ar., C-10), 121.2 (1C, Ar., C-11a), 124.6 (1C, Ar., C-3), 126.7 (1C, Ar., C-4a), 127.8 (1C, Ar., C-4), 128.7 (1C, Ar., C-11), 149.2 (1C, Ar., C-9), 151.7 (1C, Ar., C-2), 154.6 (1C, Ar., C-7a), 156.4 (1C, Ar., C-12a), 206.4 (1C, C=O, C-5). MS (EI, 70 eV) m/z (%), 252 (M^++1, 11), 251 (M^+, 100), 223 (30), 192 (2), 162 (12), 145 (39), 135 (55), 117 (20), 108 (19), 92 (46), 77 (24). Anal. Calcd. for $C_{15}H_{13}N_3O$ (251); C, 71.71; H, 5.17; N, 16.73. Found: C, 71.68; H, 5.22; N, 16.71%.

6,7-Dihydro-8,13-ethanodipyrido[2,3-*b*:2',3'-*e*]azonin-5(13*H*)-one (8d): Yield 0.69 g (88%, method I), 0.63 g (81%, method II), 0.56 g (71%, method III), Yellow needles, mp 154-56 °C (AcOEt); IR (KBr, *v*, cm^{-1}): 3018, 2945, 1700, 1605, 1585, 1470, 1440, 1394, 1241, 1179, 794. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.19 (2H, dddd, J_1 = 14.3, J_2 = 7.2, J_3 = 3.3, J_4 = 3.1 Hz, *bridged-*CH_2), 2.82 (2H, ddd, J_1 = 15.7, J_2 = 6.4, J_3 = 2.8 Hz, C^6H_2), 3.47 (2H, ddd, J_1 = 14.5, J_2 = 6.9, J_3 = 3.5 Hz, *bridged-*NCH_2), 3.83 (2H, ddd, J_1 = 14.4, J_2 = 6.6, J_3 = 2.5 Hz C^7H_2), 4.76 (1H, dd, J_1 = 4.4, J_2 = 1.7 Hz, C^{13}H), 6.95 (1H, dd, J_1 = 7.9, J_2 = 4.5 Hz), 7.14 (1H,

dd, J_1 = 7.5, J_2 = 4.7 Hz), 7.85 (1H, dd, J_1 = 7.9, J_2 = 1.9 Hz), 7.92 (1H, dd, J_1 = 7.5, J_2 = 1.9 Hz), 8.15 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.92 (1H, dd, J_1 = 4.5, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 31.2 (1C, bridged-CH_2-, C-14), 35.9 (1C, $\underline{CH_2}$CO, C-6), 45.4 (1C, -CH-, C-13), 49.1 (1C, bridged-CH_2-, C-15), 50.44 (1C,N-$\underline{CH_2}$, C-7), 121.1 (1C, Ar., C-11), 121.2 (1C, Ar., C-12a), 124.6 (1C, Ar., C-3), 126.7 (1C, Ar., C-4a), 127.8 (1C, Ar., C-4), 128.7 (1C, Ar., C-12), 149.2 (1C, Ar., C-10), 151.7 (1C, Ar., C-2), 154.6 (1C, Ar., C-8a), 156.4 (1C, Ar., C-13a), 215.8 (1C, C=O, C-5). MS (EI, 70 eV) m/z (%), 267 (M^++2, 15), 266 (M^++1, 20), 265 (M^+, 57), 237 (47), 230 (100), 195 (25), 167 (10), 154 (29), 139 (22), 126 (13), 111 (15), 90 (36), 75 (17). Anal. Calcd. for $C_{16}H_{15}N_3O$ (265); C, 72.45; H, 5.66; N, 15.84. Found: C, 72.50; H, 5.71; N, 15.79%.

7,13-Dihydro-6,13-ethanobenzo[*f*]pyrido[2,3-*c*]azonin-8(5*H*)-one (8e): Yield 0.66 g (84%, method I), 0.63 g (80%, method II), 0.56 g (72%, method III), Creamy powder; mp 139-41 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3052, 2973, 1695, 1600, 1480, 1440, 1392, 1240, 1186, 775. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.17 (2H, dddd, J_1 = 13.3, J_2 = 7.0, J_3 = 3.4, J_4 = 1.7 Hz, *bridged-*CH_2), 2.86 (2H, ddd, J_1 = 7.0, J_2 = 6.5, J_3 = 1.7 Hz, *bridged-*NCH_2), 4.03 (2H, d, J = 11.9 Hz, C^5H_2), 4.27-4.41 (3H, dd, J_1 = 5.5, J_2 = 1.4 Hz, N-C^7H_2CO), 4.35 (d, J = 12.9 Hz, C^{13}H), 7.08 (1H, dd, J_1 = 7.6, J_2 = 4.7 Hz), 7.24 (1H, ddd, J_1 = 10.3, J_2 = 1.8, J_3 = 0.4 Hz), 7.34 (1H, ddd, J_1 = 7.9, J_2 = 7.3, J_3 = 1.8 Hz), 7.46 (1H, ddd, J_1 = 10.3, J_2 = 7.3, J_3 = 1.3 Hz), 7.85 (1H, ddd, J_1 = 7.9, J_2 = 1.3, J_3 = 0.4 Hz), 8.35 (1H, dd, J_1 = 7.6, J_2 = 1.9 Hz), 8.72 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 31.7 (1C, -CH-, C-13), 32.9 (1C, bridged-CH_2-, C-14), 51.4 (1C, -CH_2-, C-5), 53.4 (1C, bridged-CH_2-, C-15), 59.2 (1C, N-CH_2CO, C-7), 123.4 (1C, Ar., Py-C-2), 124.6 (1C, Ar., C-10), 124.9 (1C, Ar., C-11), 128.0 (1C, Ar., C-8a), 128.7 (1C, Ar., Py-C-13a), 128.9 (2C, Ar., C-9, C-12), 135.6 (2C, Ar., Py-C-1, C-12a), 149.2 (1C, Ar., Py-C-3), 149.9 (1C, Ar., Py-C-4a), 202.2 (1C, C=O, C-8). MS (EI, 70 eV) m/z (%), 264 (M^+, 19), 263 (100), 262 (43), 236 (32), 221 (20), 200 (68), 184 (3), 170 (2), 165 (12), 147 (20), 108 (16), 92 (31), 77 (24). Anal. Calcd. for $C_{17}H_{16}N_2O$ (264); C, 77.27; H, 6.06; N, 10.60. Found: C, 77.29; H, 5.98; N, 10.67%.

7,8-Dihydro-5*H*-6,14-ethanobenzo[*f*]pyrido[2,3-*c*]azecin-9(14*H*)-one (8f): Yield 0.75 g (91%, method I), 0.64 g (78%, method II), 0.56 g (68%, method III), Yellow solid; mp 164-66 ºC (acetone); IR (KBr, *v*, cm^{-1}): 3060, 2935, 1700, 1600, 1575, 1470, 1440, 1359, 1235, 1170, 798. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.66 (2H, dddd, J_1 = 11.1, J_2 = 7.7, J_3 = 6.3, J_4 = 2.2 Hz, *bridged-*$C^{15}H_2$), 3.09 (2H, ddd, J_1 = 10.1, J_2 = 6.3, J_3 = 2.2 Hz, C^8H_2), 3.34 (2H, ddd, J_1 = 10.6, J_2 = 7.5, J_3 = 2.5 Hz, *bridged-*$NC^{16}H_2$), 3.50 (2H, ddd, J_1 = 11.1, J_2 = 7.5, J_3 = 2.5 Hz, C^7H_2), 4.37-4.48 (2H, dd, J_1 = 8.6, J_2 = 6.9 Hz, C^5H_2), 4.45 (1H, d, J = 15.8 Hz, C^{14}H), 7.06 (1H, dd, J_1 = 7.6, J_2 = 4.6 Hz), 7.19 (1H, ddd, J_1 = 11.5, J_2 = 1.1, J_3 = 0.5 Hz), 7.41 (1H, ddd, J_1 = 11.5, J_2 = 10.2, J_3 = 1.3 Hz), 7.57 (1H, ddd, J_1 = 10.2, J_2 = 8.9, J_3 = 1.1 Hz), 7.77 (1H, ddd, J_1 = 8.9, J_2 = 1.3, J_3 = 0.5 Hz), 8.05 (1H, dd, J_1 = 4.6, J_2 = 2.0 Hz), 8.37 (1H, dd, J_1 = 7.6, J_2 = 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 31.2 (1C, -CH-, C-14), 32.9 (1C, bridged-CH_2-, C-15), 35.9 (1C, CH_2CO, C-8), 51.4 (1C, -CH_2-, C-7), 53.4 (1C, -CH_2-, C-5), 59.5 (1C, bridged-CH_2-, C-16), 123.4 (1C, Ar., Py-C-2), 124.6 (1C, Ar., C-11), 124.9 (1C, Ar., C-12), 128.0 (1C, Ar., C-9a), 128.7 (1C, Ar., Py-C-14a), 128.9 (2C, Ar., C-10, C-13), 135.6 (2C, Ar., Py-C-1, C-13a), 149.2 (1C, Ar., Py-C-3), 149.9 (1C, Ar., Py-C-4a), 200.8 (1C, C=O, C-8). MS (EI, 70 eV) m/z (%), 280 (M^++2, 7), 279 (M^++1, 16), 278 (M^+, 100), 250 (19), 244 (9), 214 (3), 196 (9), 184 (13), 167 (5), 154 (27), 140 (18), 108 (76), 92 (48), 77 (25). Anal. Calcd. for $C_{18}H_{18}N_2O$ (278); C, 77.69; H, 6.47; N, 10.07. Found: C, 77.74; H, 6.50; N, 9.99%.

8,13-Dihydro-7,13-ethanodipyrido[2,3-*c*:2',3'-*f*]azonin-5(6*H*)-one (8g): Yield 0.71 g (90%, method I), 0.68 g (87%, method II), 0.56 g (72%, method III), Brownish crystals; mp

170-173 ºC (ethanol); IR (KBr, *v*, cm^{-1}): 3070, 2985, 1694, 1600, 1590, 1470, 1440, 1360, 1284, 1132, 774. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.09 (2H, dddd, J_1 = 13.5, J_2 = 7.0, J_3 = 3.5, J_4 = 1.7 Hz, *bridged-*CH_2), 2.89 (2H, ddd, J_1 = 7.0, J_2 = 5.9, J_3 = 1.7 Hz, *bridged-*NCH_2), 4.05 (2H, d, J = 11.9 Hz, C^6H_2), 4.36 (2H, d, J = 13.1 Hz, C^8H_2), 4.54 (1H, dd, J_1 = 5.5, J_2 = 1.4 Hz, $C^{13}H$), 7.12 (1H, dd, J_1 = 7.5, J_2 = 4.7 Hz), 7.29 (1H, dd, J_1 = 7.8, J_2 = 4.5 Hz), 7.71 (1H, dd, J_1 = 7.5, J_2 = 1.9 Hz), 7.91 (1H, dd, J_1 = 7.8, J_2 = 1.9 Hz), 8.64 (1H, dd, J_1 = 4.7, J_2 = 1.9 Hz), 8.76 (1H, dd, J_1 = 4.5, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 31.2 (1C, -CH-, C-13), 32.9 (1C, bridged-CH_2-, C-14), 51.4 (1C, -$\underline{CH_2}$, C-8), 53.4 (1C, bridged-CH_2-, C-15), 60.2 (1C, -$\underline{CH_2}$CO, C-6), 123.6 (1C, Ar., C-11), 124.6 (1C, Ar., C-3), 124.9 (1C, Ar., C-4a), 128.7 (1C, Ar., C-12a), 128.9 (1C, Ar., C-4), 135.6 (1C, Ar., C-12), 149.2 (2C, Ar., C-2, C-10), 149.9 (1C, Ar., C-8a), 151.6 (1C, Ar., C-13a), 212.5 (1C, C=O, C-5). MS (EI, 70 eV) m/z (%), 266 (M^++1, 6), 248 (5), 230 (49), 201 (4), 195 (25), 184 (2), 167 (10), 154 (29), 139 (23), 111 (16), 90 (8), 77 (18). Anal. Calcd. for $C_{16}H_{15}N_3O$ (265); C, 72.45; H, 5.66; N, 15.84. Found: C, 72.44; H, 5.70; N, 15.77%.

6,7,9,14-Tetrahydro-5*H*-8,14-ethanodipyrido[2,3-*c*:2',3'-*f*]azecin-5-one (8h): Yield 0.73 g (89%, method I), 0.71 g (86%, method II), 0.61 g (74%, method III), Gray crystals; mp 180 *dec.*°C (EtOAc); IR (KBr, *v*, cm^{-1}): 3046, 2972, 1705, 1600, 1580, 1480, 1440, 1362, 1235, 1170, 789. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.68 (2H, dddd, J_1 = 11.2, J_2 = 7.7, J_3 = 6.3, J_4 = 2.2 Hz, *bridged-*CH_2), 3.09 (2H, ddd, J_1 = 6.8, J_2 = 6.3, J_3 = 2.2 Hz, C^6H_2), 3.36 (2H, ddd, J_1 = 10.6, J_2 = 7.5, J_3 = 2.6 Hz, *bridged-*NCH_2), 3.49 (2H, ddd, J_1 = 11.1, J_2 = 7.5, J_3 = 2.6 Hz, C^7H_2), 4.42 (2H, d, J = 15.8 Hz, C^9H_2), 4.64 (1H, dd, J_1 = 8.7, J_2 = 6.8 Hz, $C^{14}H$), 7.02 (1H, dd, J_1 = 7.6, J_2 = 4.6 Hz), 7.28 (1H, dd, J_1 = 7.8, J_2 = 4.6 Hz), 7.71 (1H, dd, J_1 = 7.6, J_2 = 2.0 Hz), 7.93 (1H, dd, J_1 = 7.8, J_2 = 1.9 Hz), 8.12 (1H, dd, J_1 = 4.6, J_2 = 2.0 Hz), 8.49 (1H, dd, J_1 = 4.6, J_2 = 1.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 30.7 (1C, -CH-, C-14), 32.6 (1C, bridged-CH_2-, C-15), 35.9 (1C, -$\underline{CH_2}$CO, C-6), 51.4 (1C, -$\underline{CH_2}$, C-7), 53.4 (1C, -$\underline{CH_2}$, C-9), 63.3 (1C, bridged-CH_2-, C-16), 123.7 (1C, Ar., C-12), 124.6 (1C, Ar., C-3), 124.9 (1C, Ar., C-4a), 128.7 (1C, Ar., C-13a), 128.9 (1C, Ar., C-4), 135.6(1C, Ar., C-13), 149.2 (2C, Ar., C-2, C-11), 149.9 (1C, Ar., C-9a), 151.6 (1C, Ar., C-14a), 214.6 (1C, C=O, C-5). MS (EI, 70 eV) m/z (%), 280 (M^++1, 18), 279 (M^+, 100), 268 (12), 253 (25), 225 (23), 211 (17), 197 (4), 165 (5), 159 (38), 134 (45), 119 (62), 107 (42), 91 (47), 77 (20). Anal. Calcd. for $C_{17}H_{17}N_3O$ (279); C, 73.11; H, 6.09; N, 15.05. Found: C, 73.14; H, 6.15; N, 15.02%.

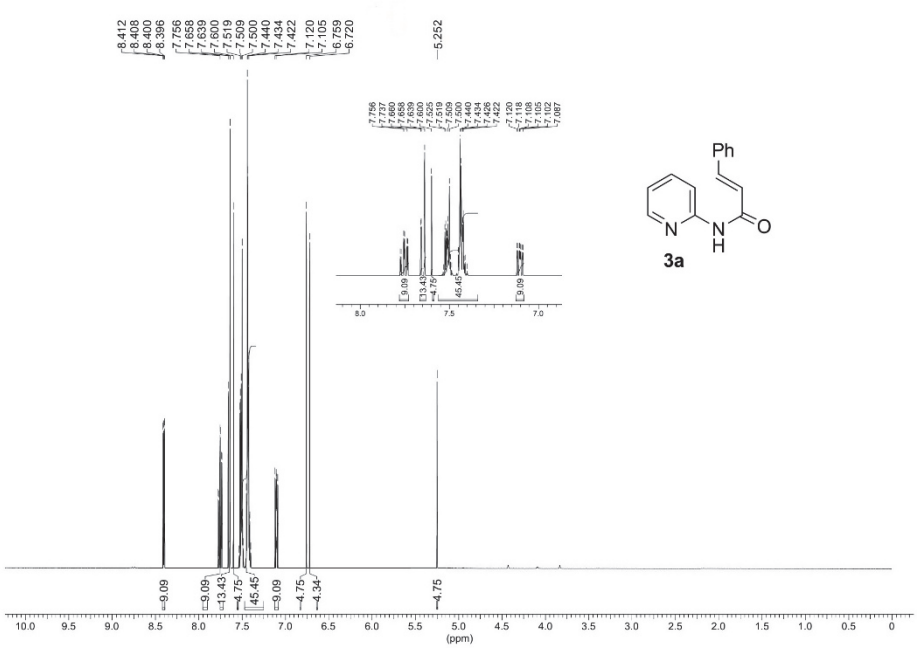

Fig. S-1. ^{1}H-NMR spectrum of compound **3a**

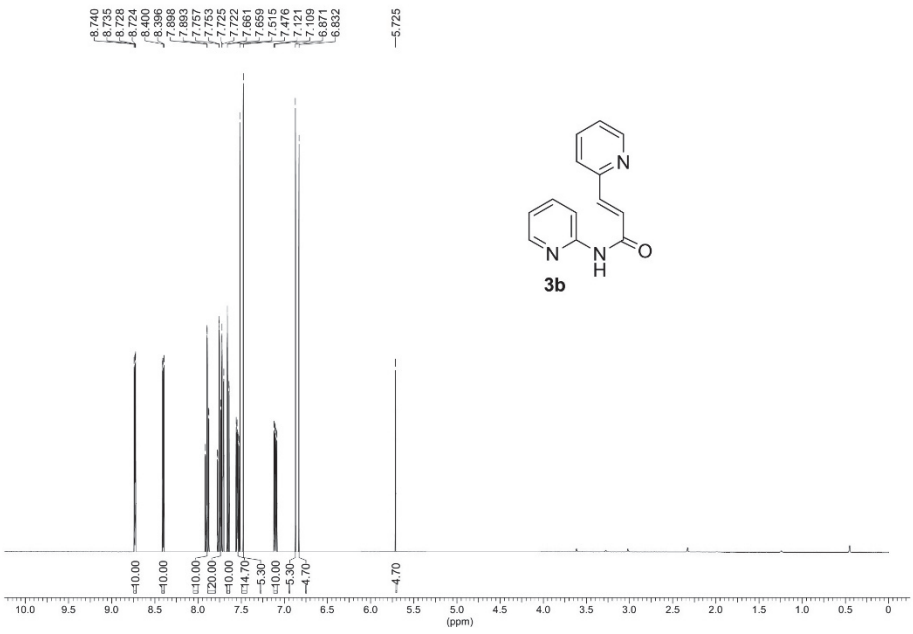

Fig. S-2. ^{1}H-NMR spectrum of compound **3b**

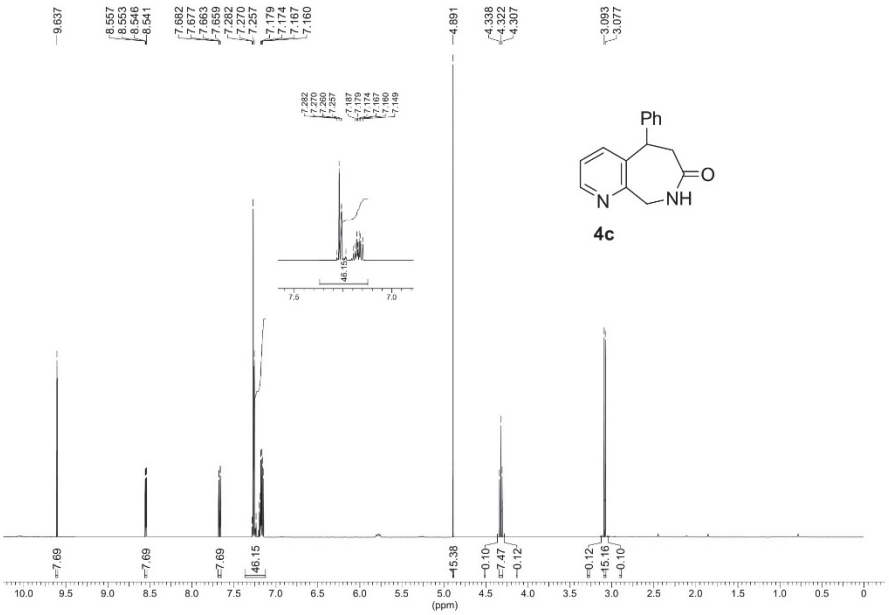

Fig. S-3. ^{1}H-NMR spectrum of compound **4c**

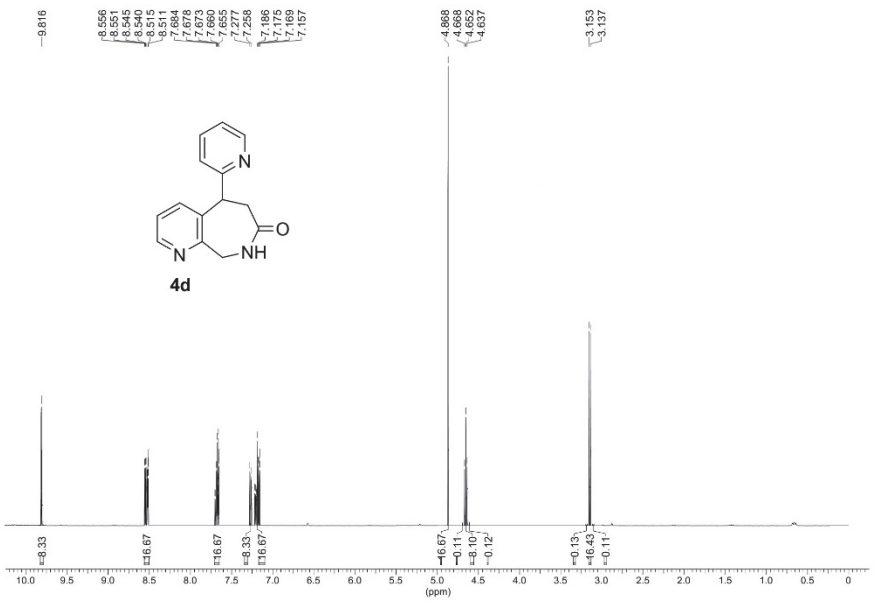

Fig. S-4. ^{1}H-NMR spectrum of compound **4d**

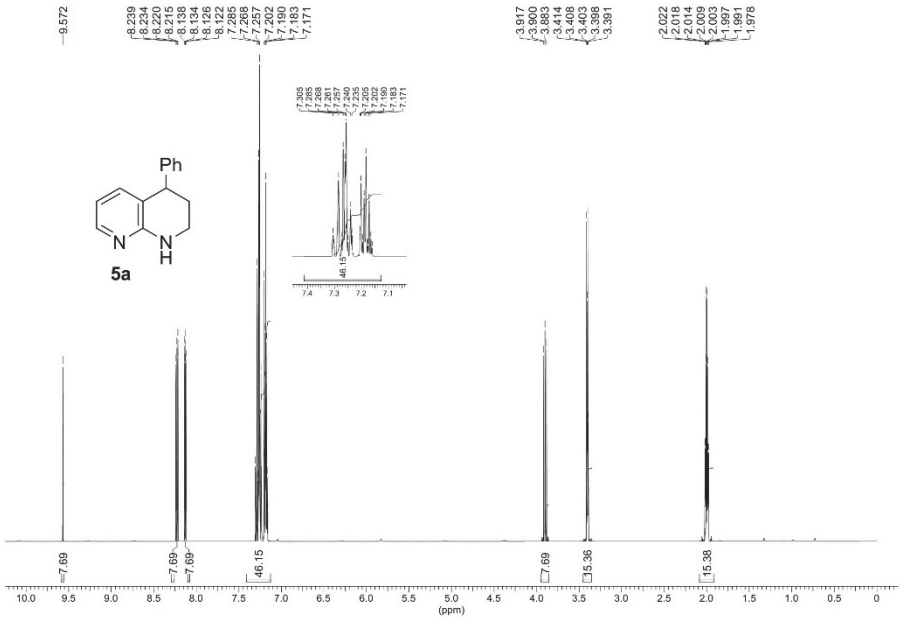

Fig. S-5. ^{1}H-NMR spectrum of compound 5a

Fig. S-6. ^{1}H-NMR spectrum of compound 5b

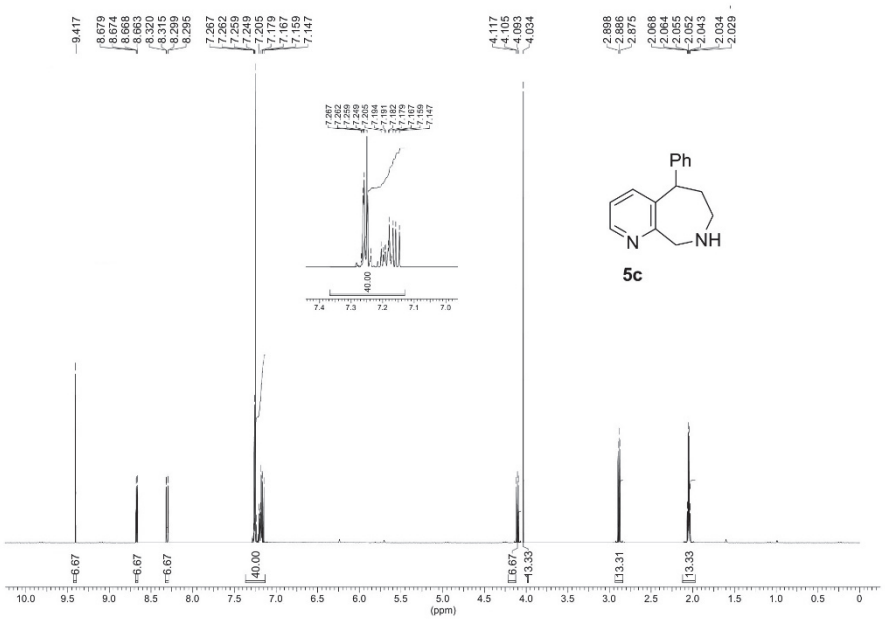

Fig. S-7. ^{1}H-NMR spectrum of compound **5c**

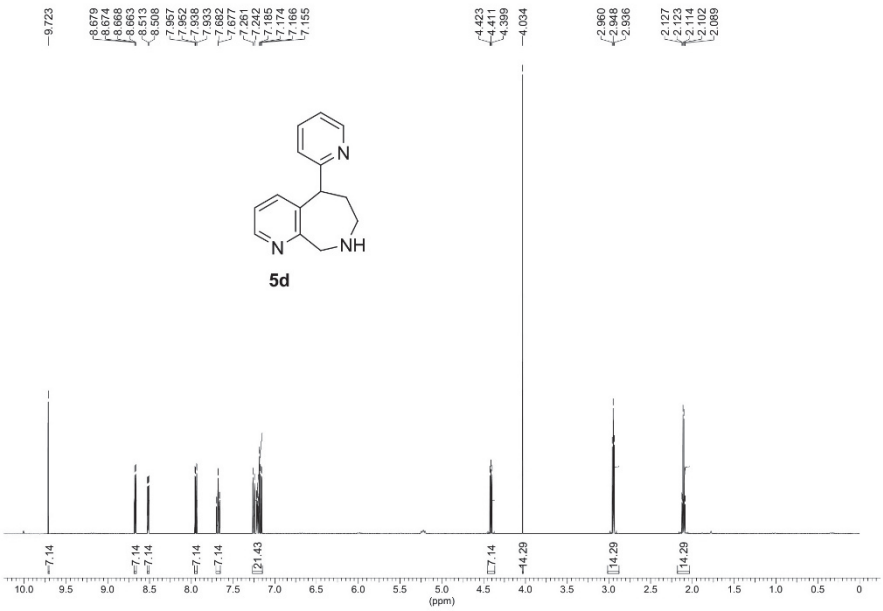

Fig. S-8. ^{1}H-NMR spectrum of compound **5d**

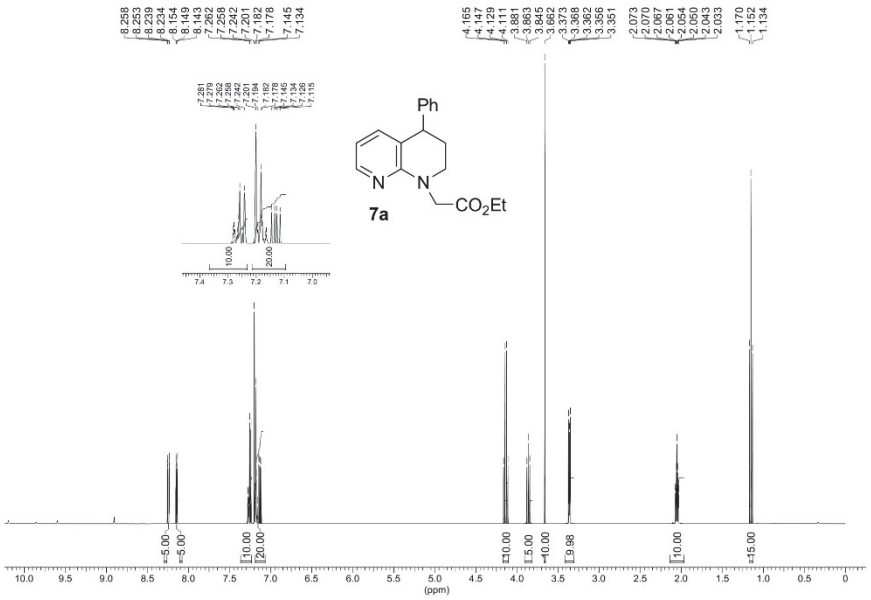

Fig. S-9. ^{1}H-NMR spectrum of compound **7a**

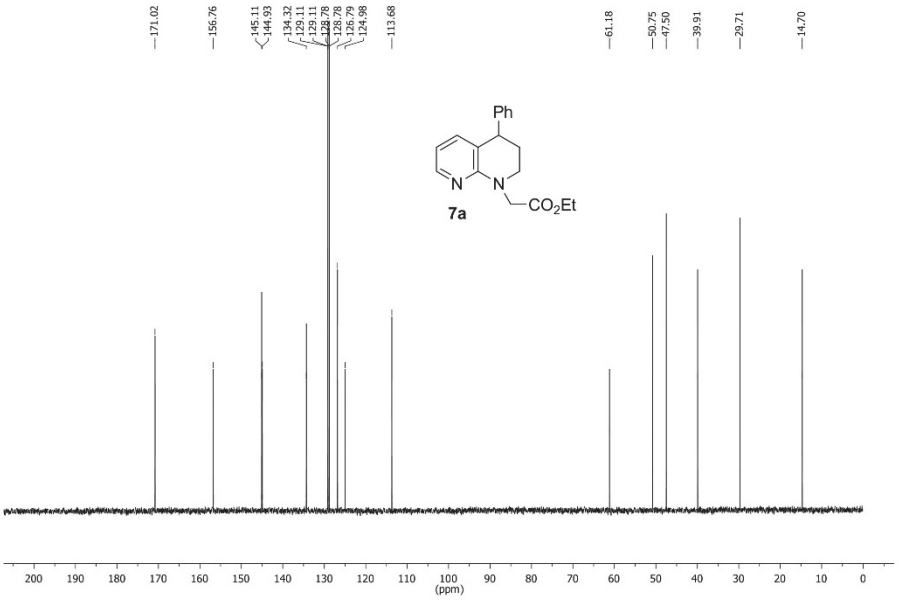

Fig. S-10. ^{13}C-NMR spectrum of compound **7a**

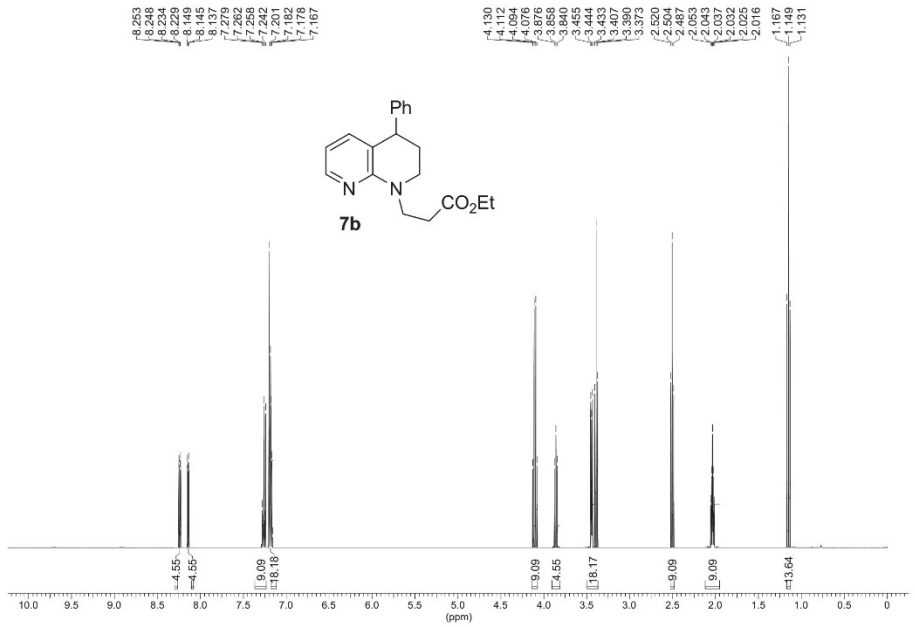

Fig. S-11. ^{1}H-NMR spectrum of compound **7b**

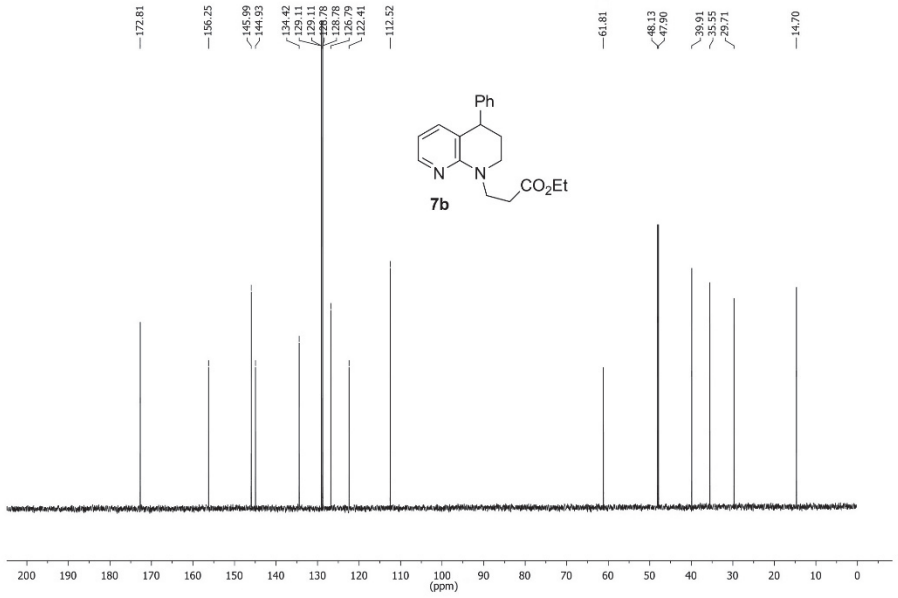

Fig. S-12. ^{13}C-NMR spectrum of compound **7b**

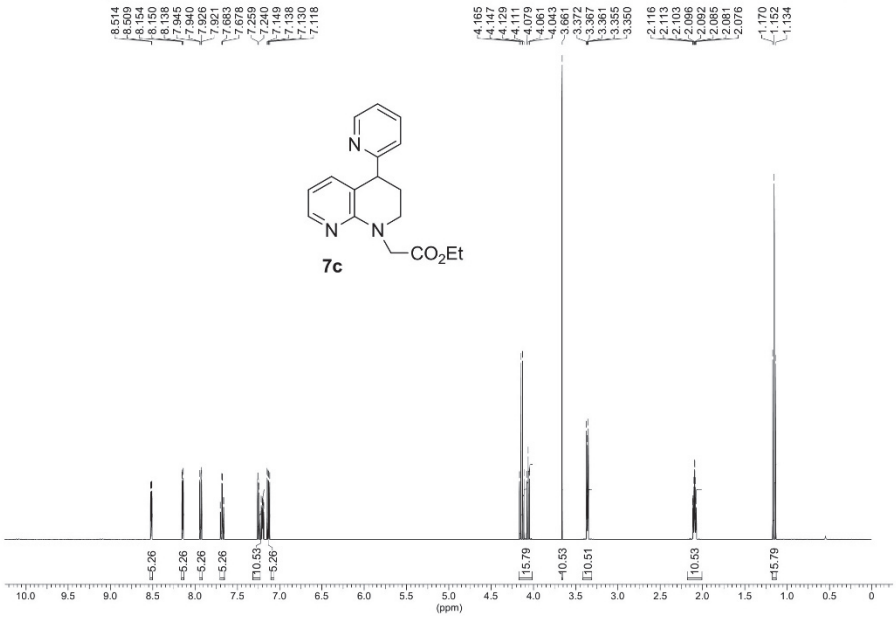

Fig. S-13. ^{1}H-NMR spectrum of compound **7c**

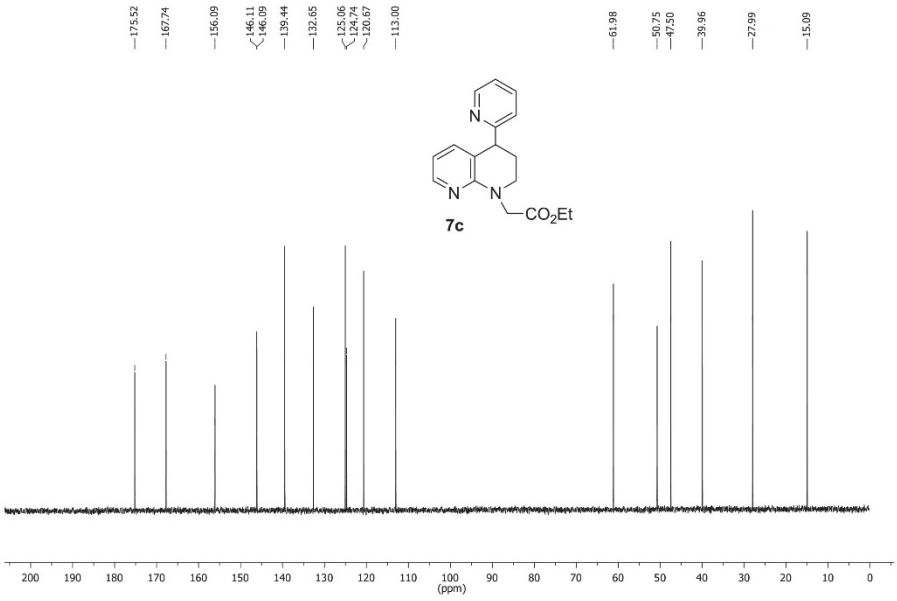

Fig. S-14. ^{13}C-NMR spectrum of compound **7c**

Fig. S-15. ^{1}H-NMR spectrum of compound **7d**

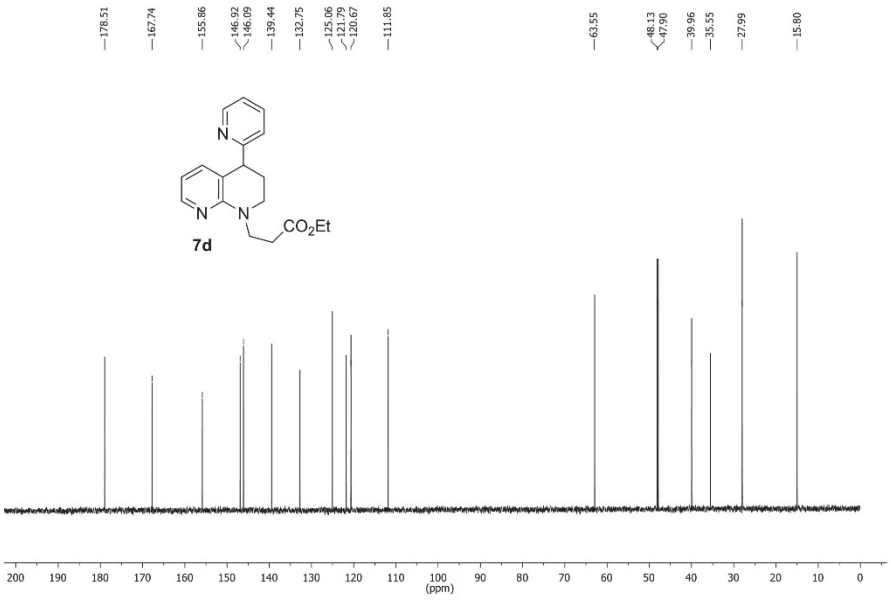

Fig. S-16. ^{13}C-NMR spectrum of compound **7d**

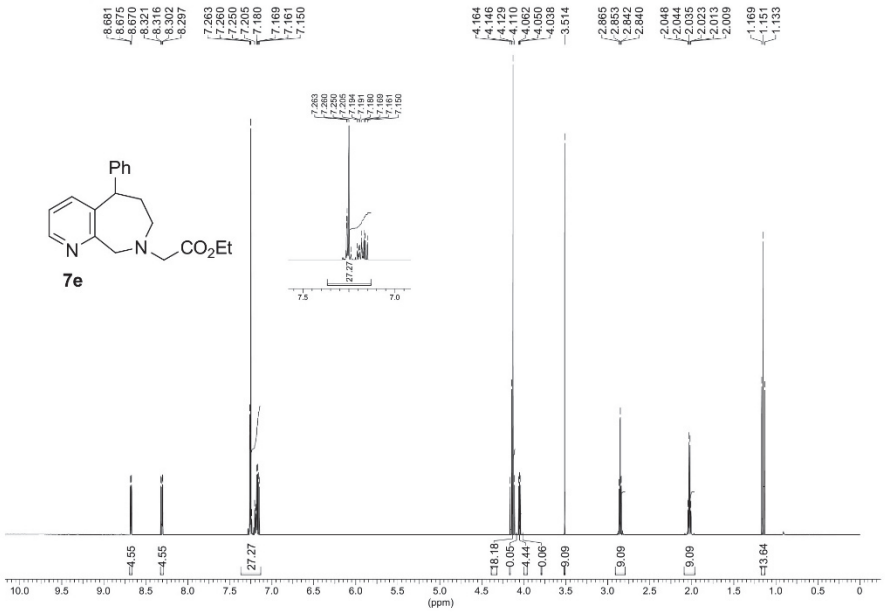

Fig. S-17. ^{1}H-NMR spectrum of compound **7e**

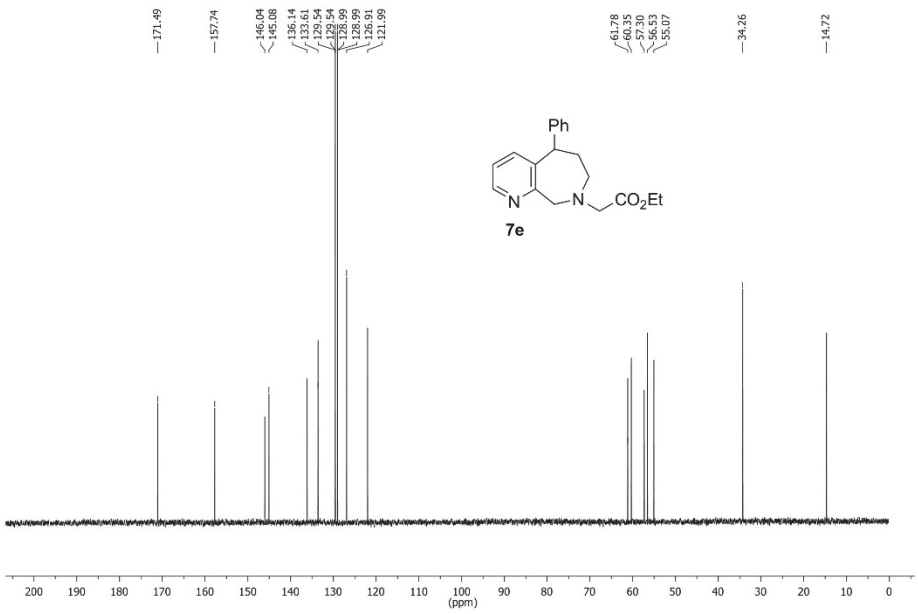

Fig. S-18. ^{13}C-NMR spectrum of compound **7e**

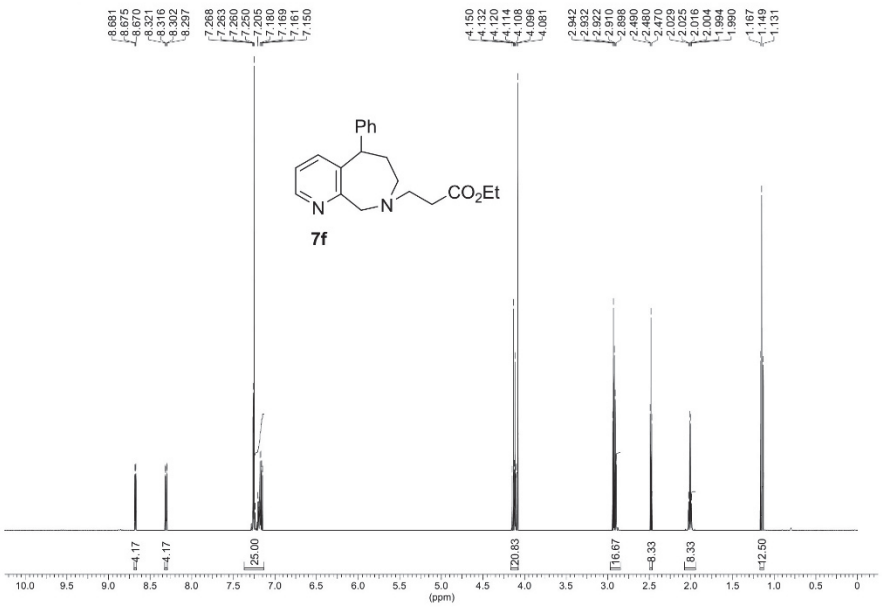

Fig. S-19. ^{1}H-NMR spectrum of compound **7f**

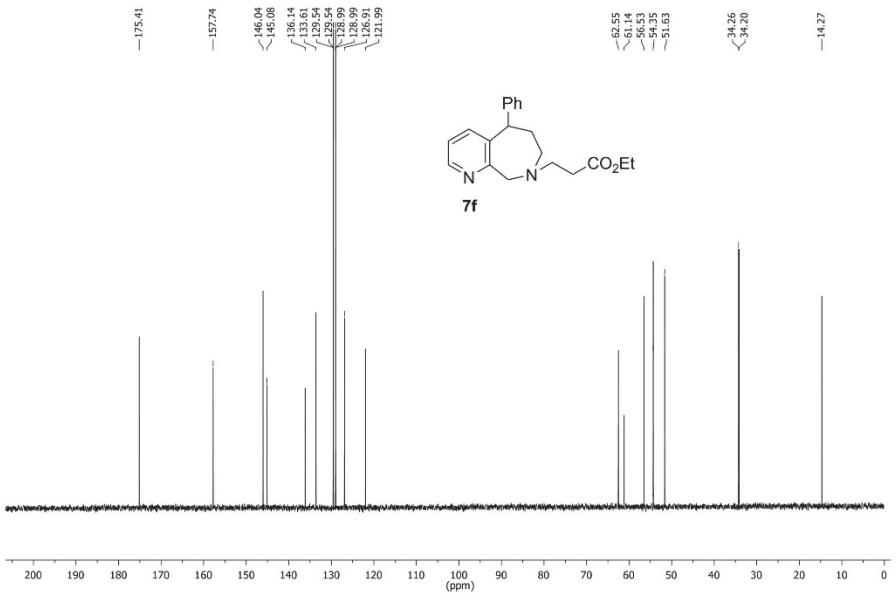

Fig. S-20. ^{13}C-NMR spectrum of compound **7f**

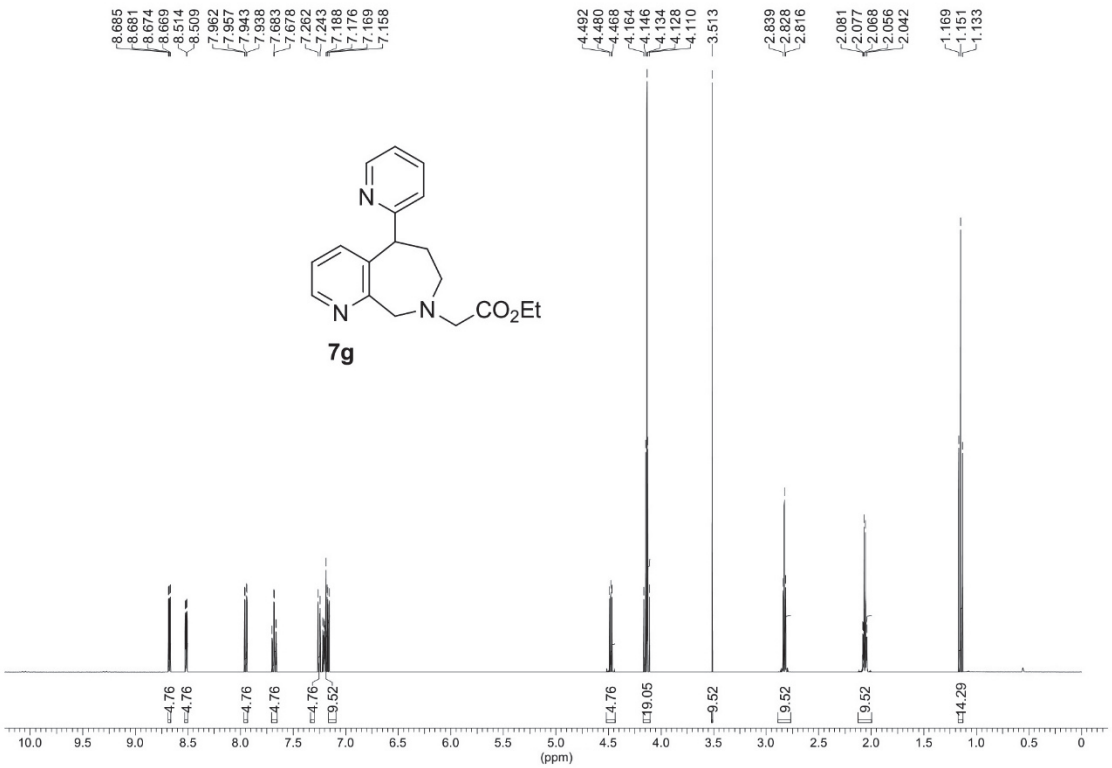

Fig. S-21. ^{1}H-NMR spectrum of compound **7g**

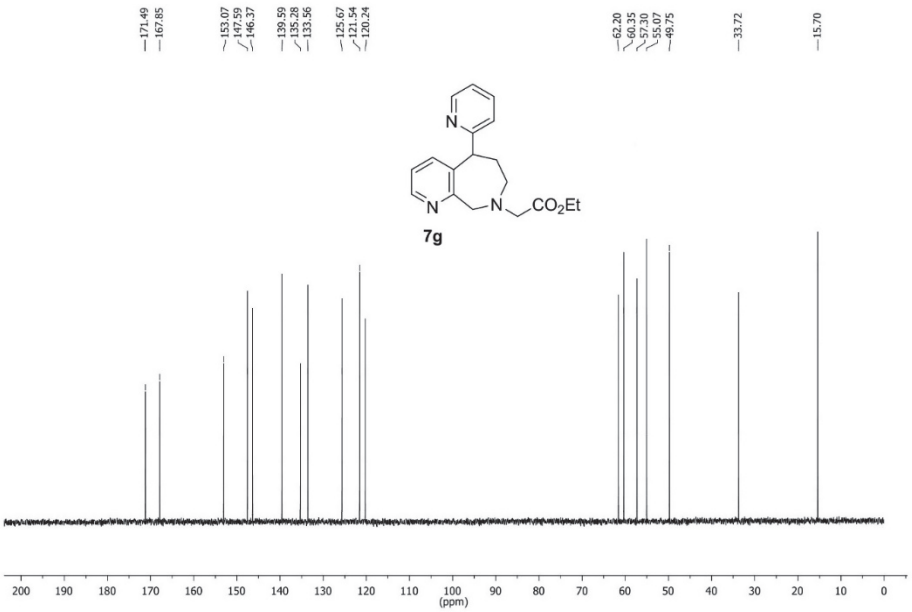

Fig. S-22. ^{13}C-NMR spectrum of compound **7g**

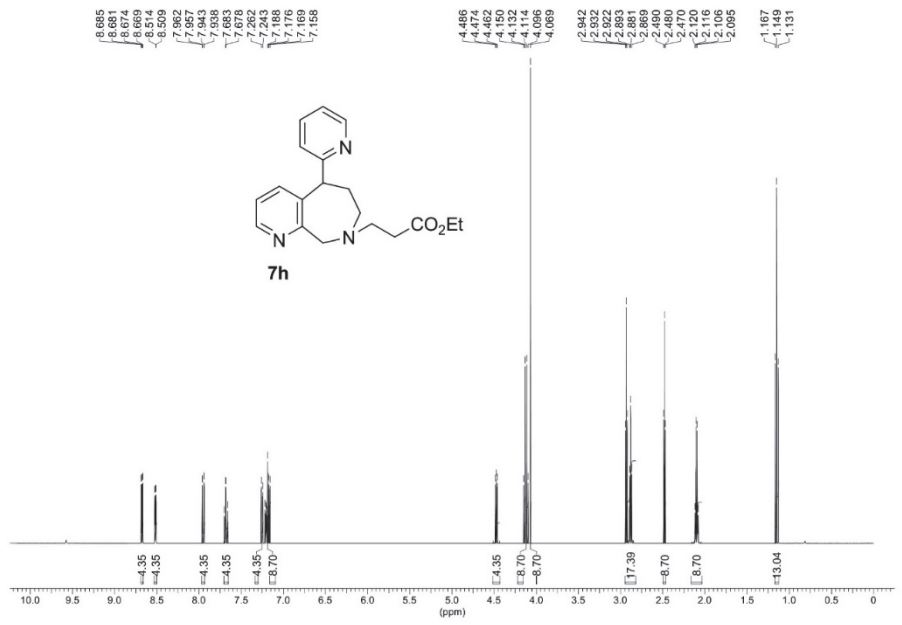

Fig. S-23. ^{1}H-NMR spectrum of compound **7h**

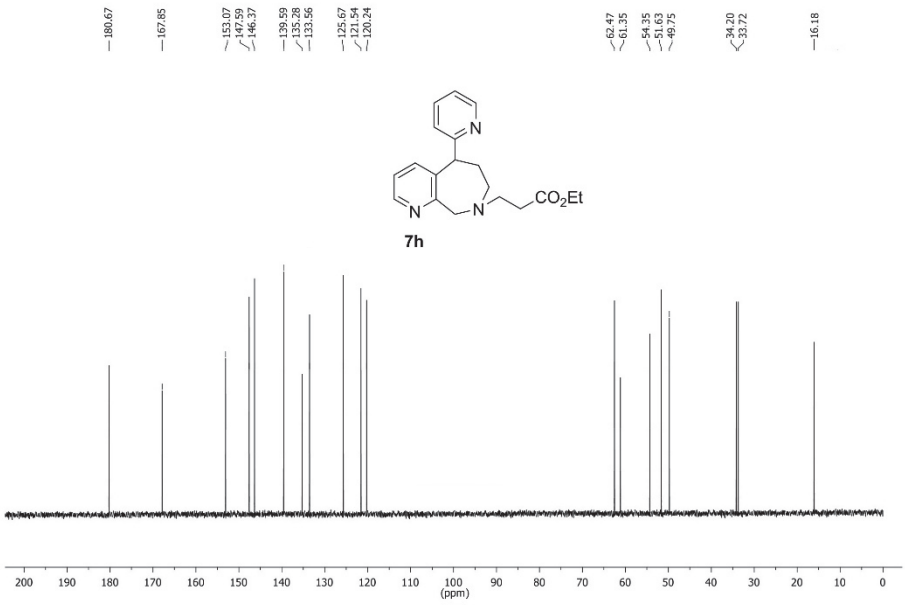

Fig. S-24. ^{13}C-NMR spectrum of compound **7h**

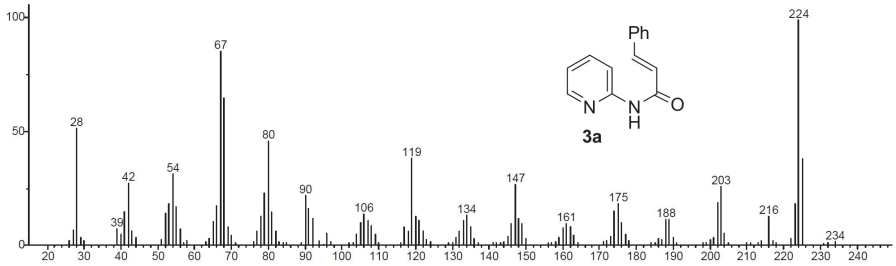

Fig. S-25. Mass spectrum of compound **3a**

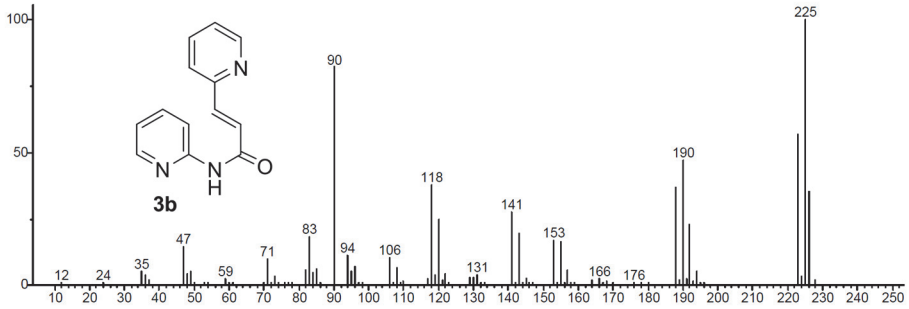

Fig. S-26. Mass spectrum of compound **3b**

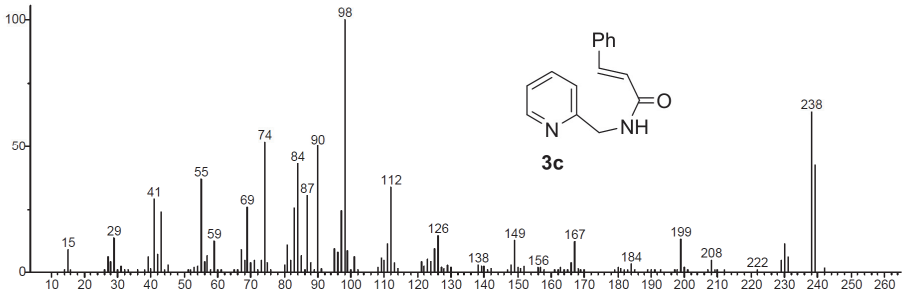

Fig. S-27. Mass spectrum of compound **3c**

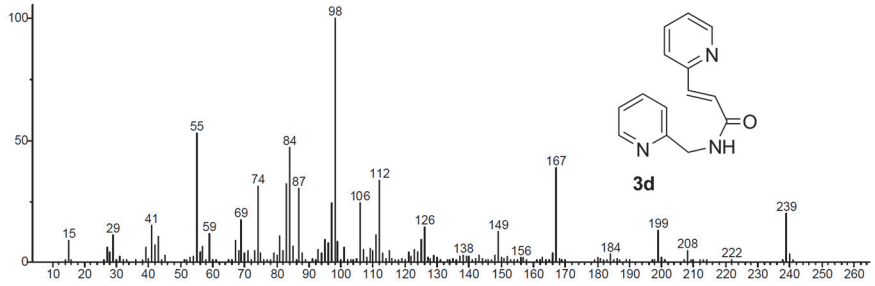

Fig. S-28. Mass spectrum of compound **3d**

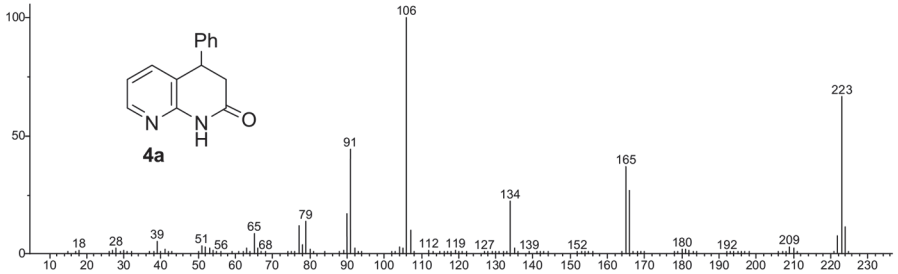

Fig. S-29. Mass spectrum of compound **4a**

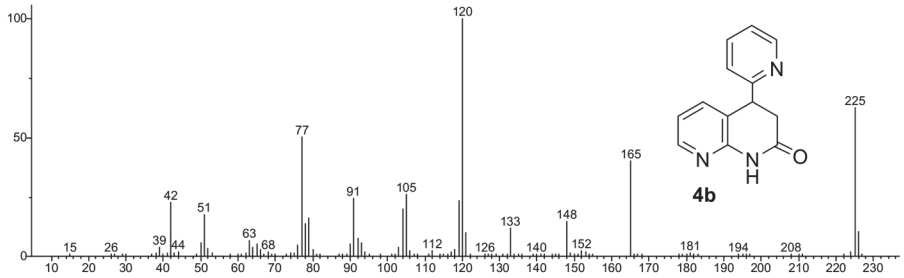

Fig. S-30. Mass spectrum of compound **4b**

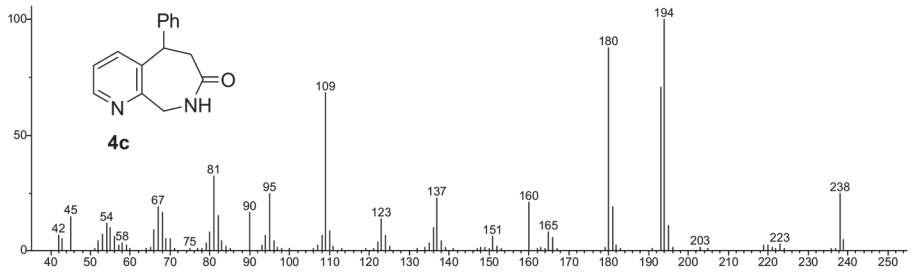

Fig. S-31. Mass spectrum of compound **4c**

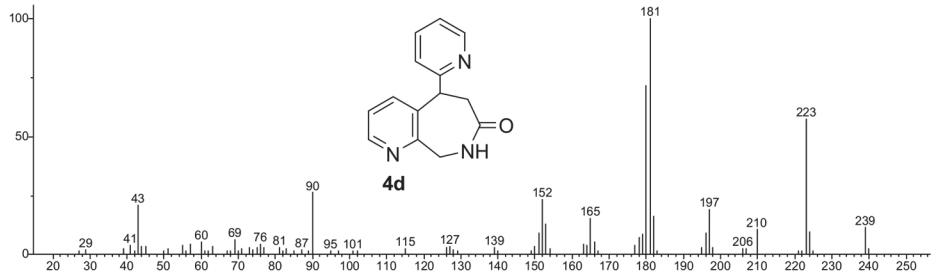

Fig. S-32. Mass spectrum of compound **4d**

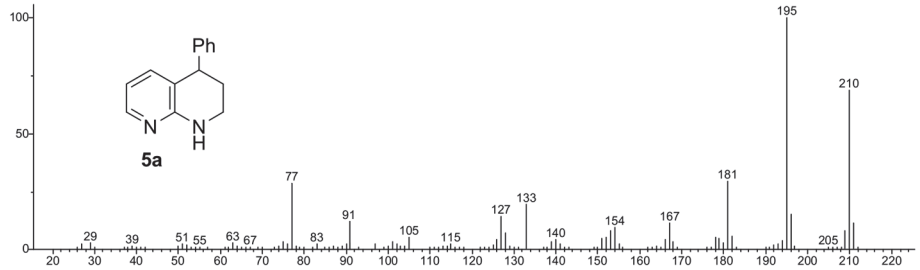

Fig. S-33. Mass spectrum of compound **5a**

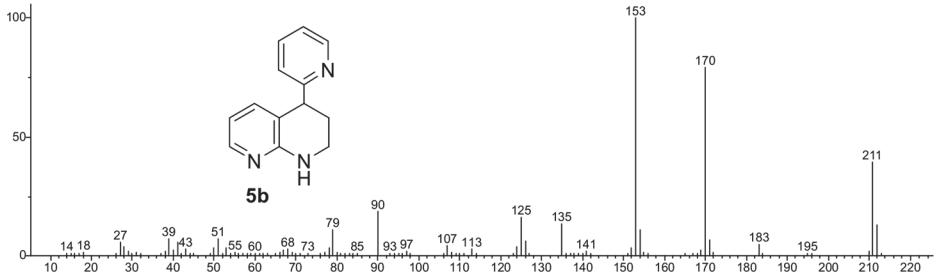

Fig. S-34. Mass spectrum of compound **5b**

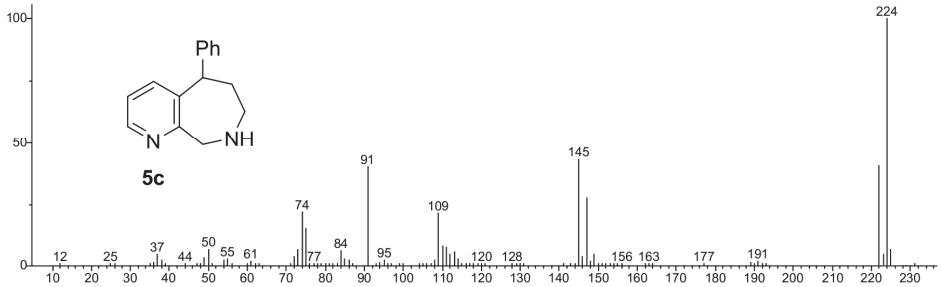

Fig. S-35. Mass spectrum of compound **5c**

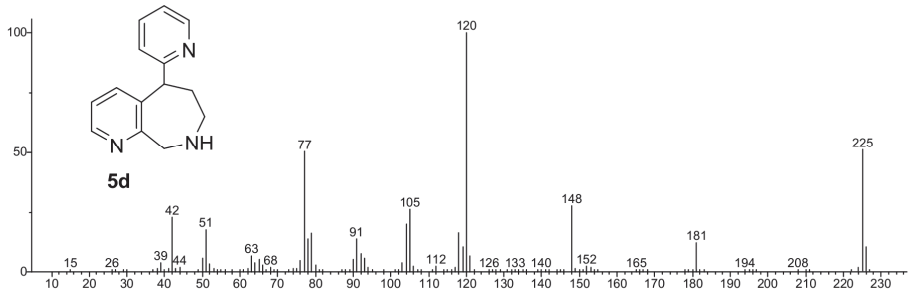

Fig. S-36. Mass spectrum of compound **5d**

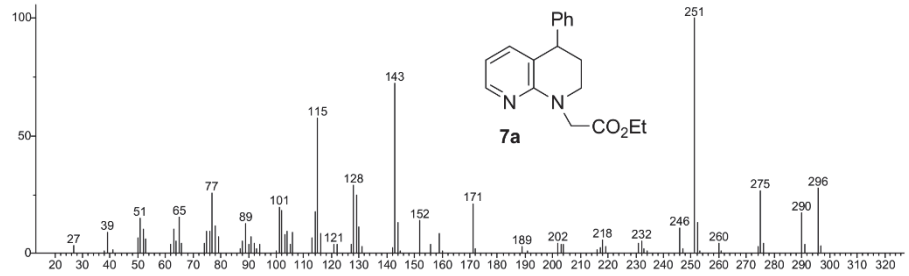

Fig. S-37. Mass spectrum of compound **7a**

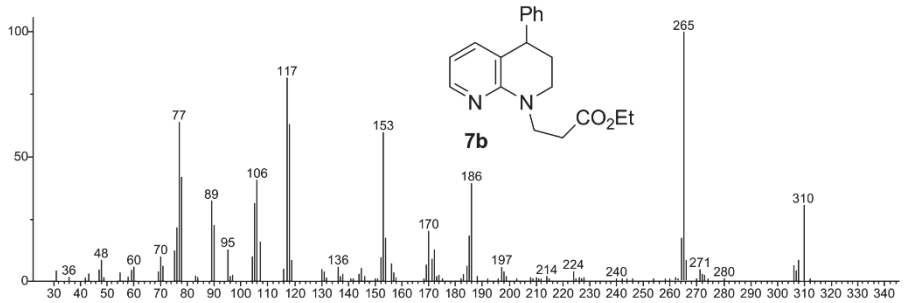

Fig. S-38. Mass spectrum of compound **7b**

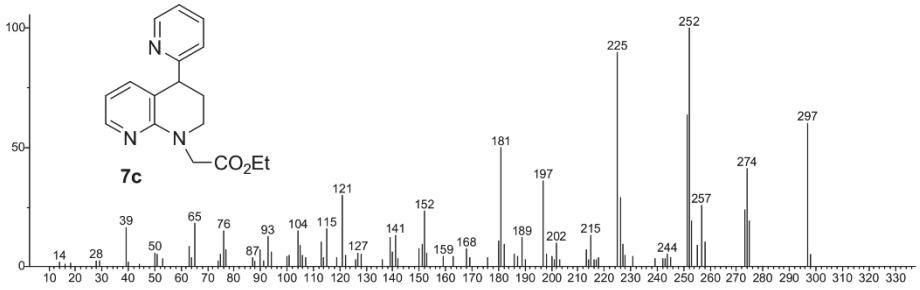

Fig. S-39. Mass spectrum of compound **7c**

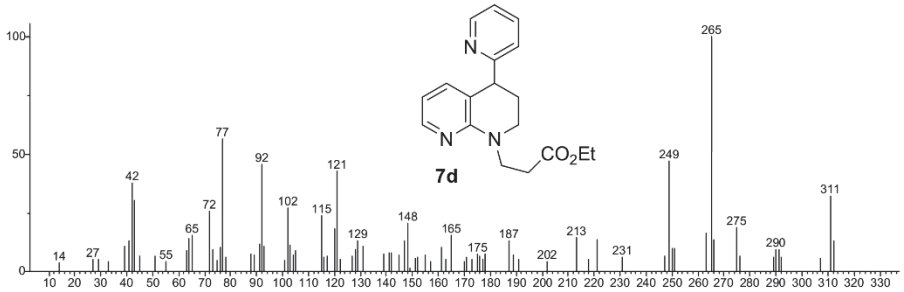

Fig. S-40. Mass spectrum of compound **7d**

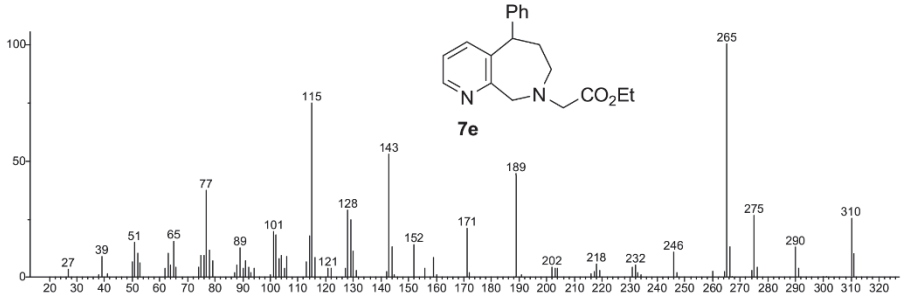

Fig. S-41. Mass spectrum of compound **7e**

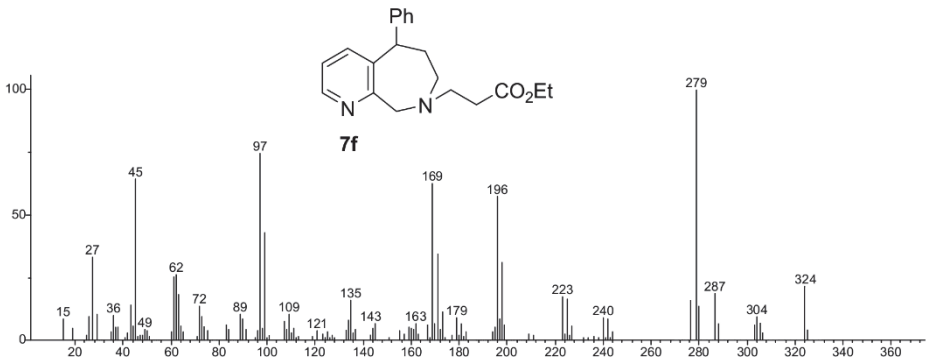

Fig. S-42. Mass spectrum of compound **7f**

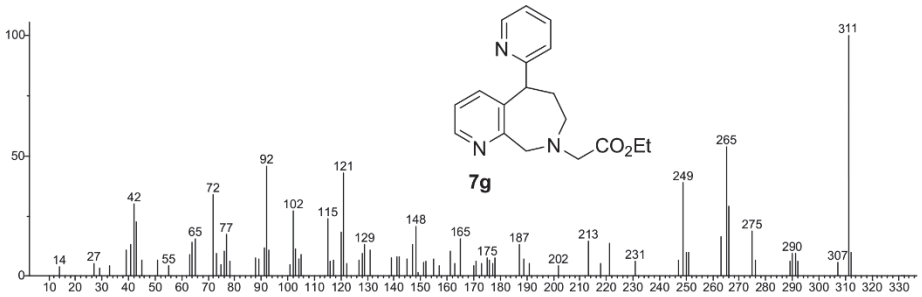

Fig. S-43. Mass spectrum of compound **7g**

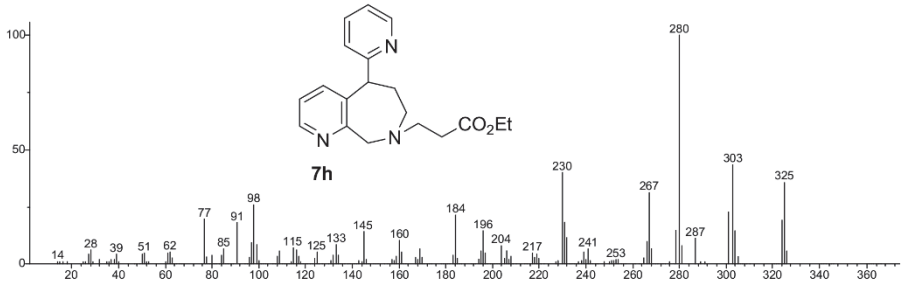

Fig. S-44. Mass spectrum of compound **7h**

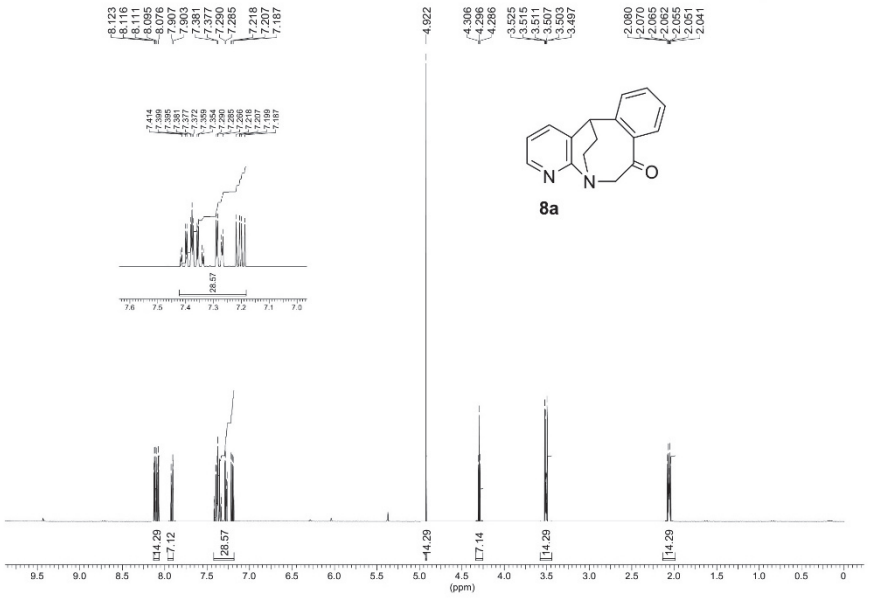

Fig. S-45. ^{1}H-NMR spectrum of compound **8a**

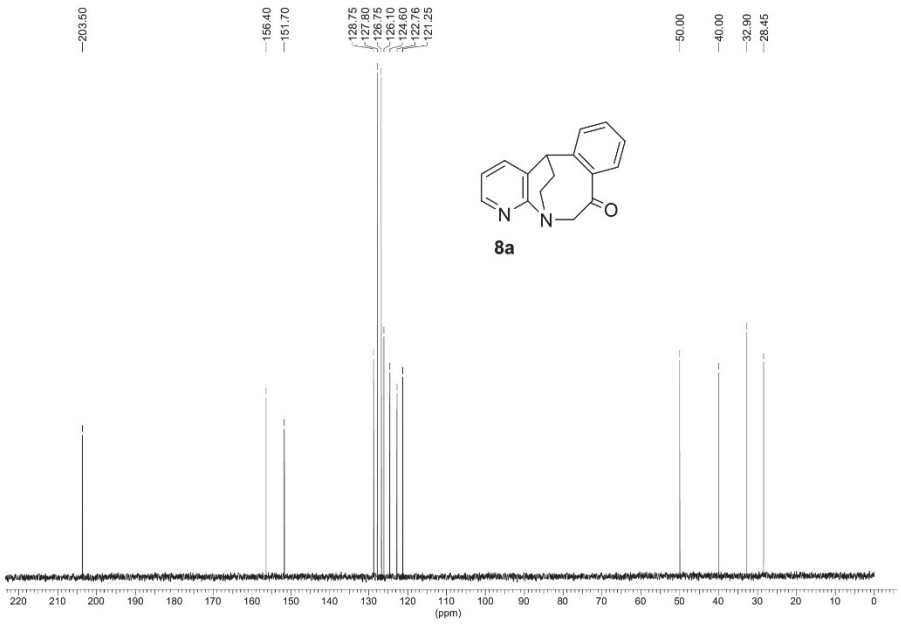

Fig. S-46. ^{13}C-NMR spectrum of compound **8a**

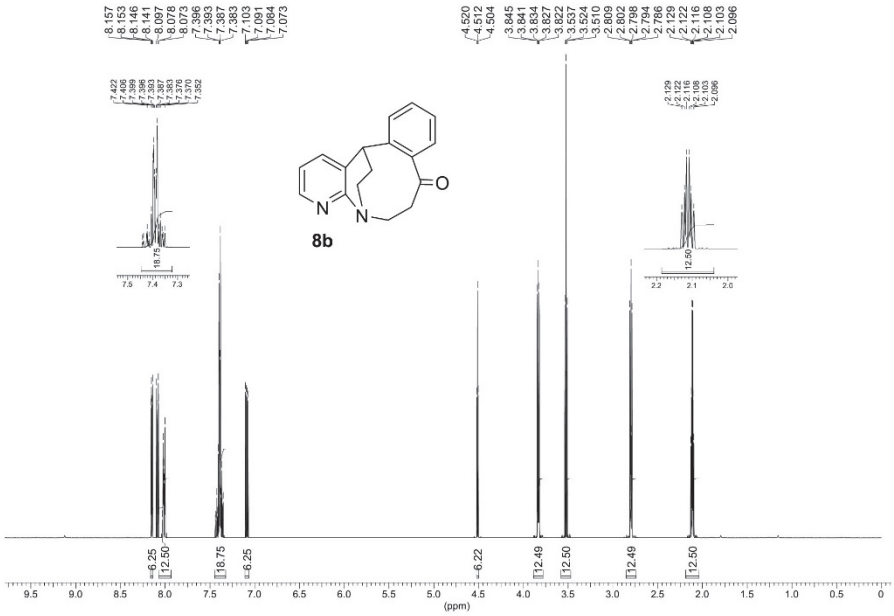

Fig. S-47. ^{1}H-NMR spectrum of compound **8b**

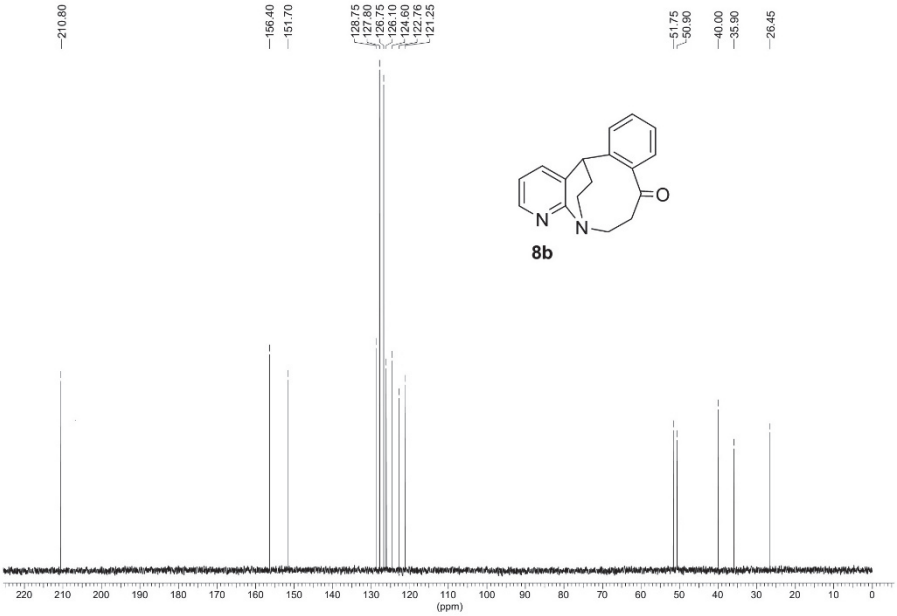

Fig. S-48. ^{13}C-NMR spectrum of compound **8b**

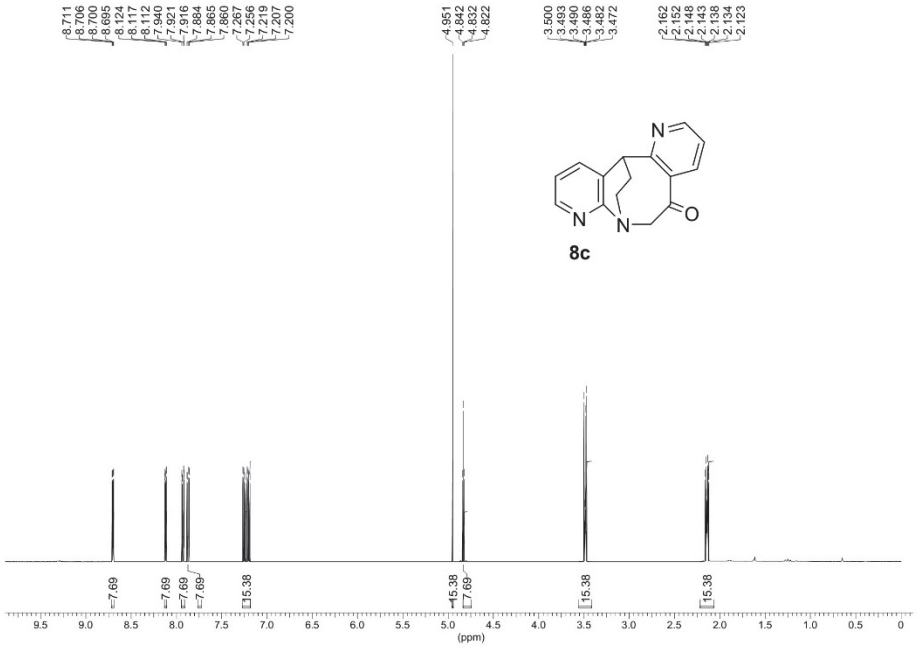

Fig. S-49. ^{1}H-NMR spectrum of compound **8c**

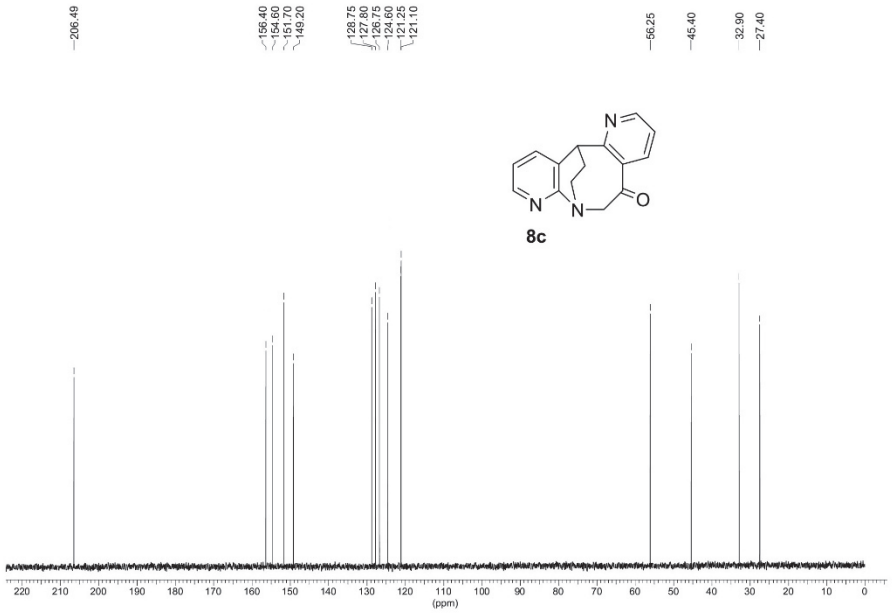

Fig. S-50. ^{13}C-NMR spectrum of compound **8c**

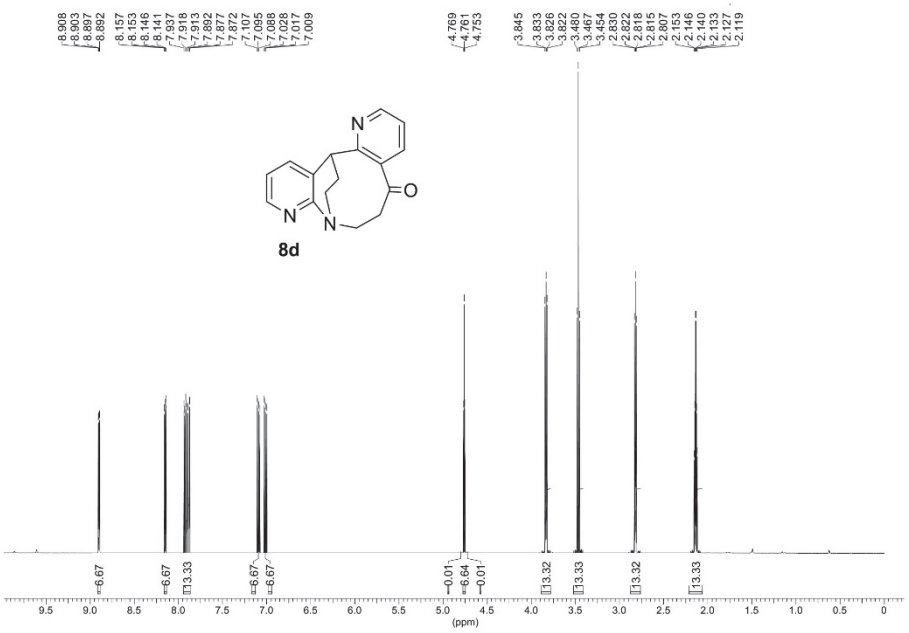

Fig. S-51. ^{1}H-NMR spectrum of compound **8d**

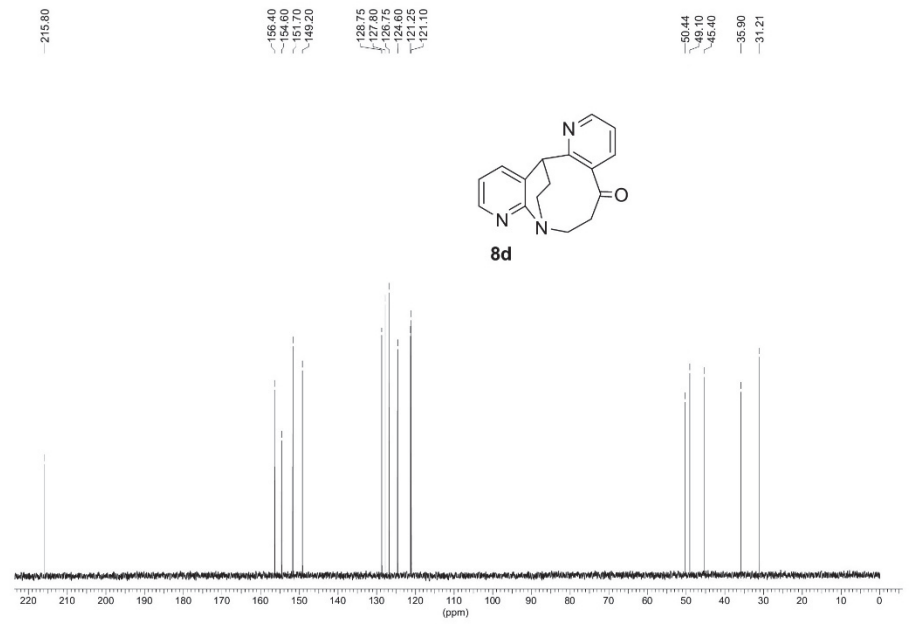

Fig. S-52. ^{13}C-NMR spectrum of compound **8d**

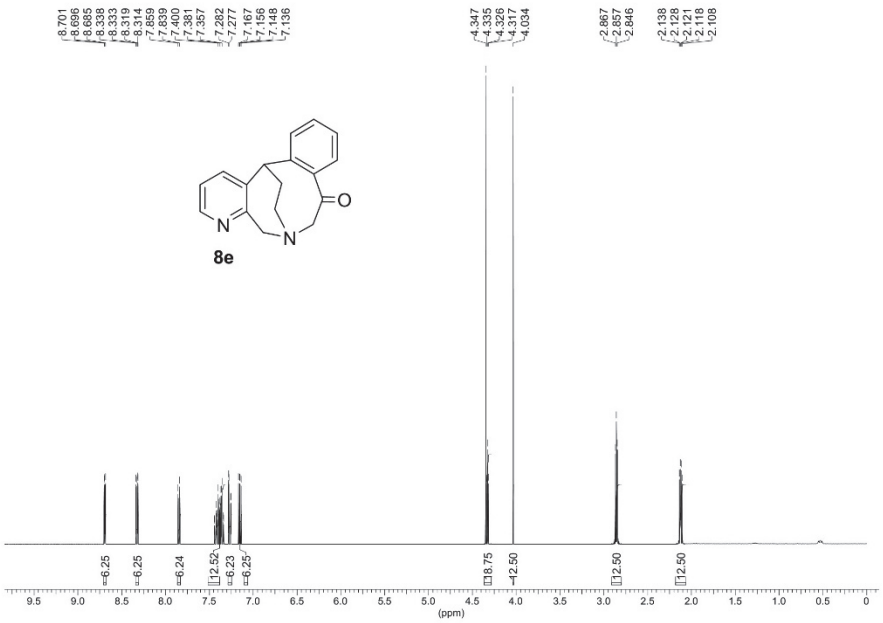

Fig. S-53. ^{1}H-NMR spectrum of compound **8e**

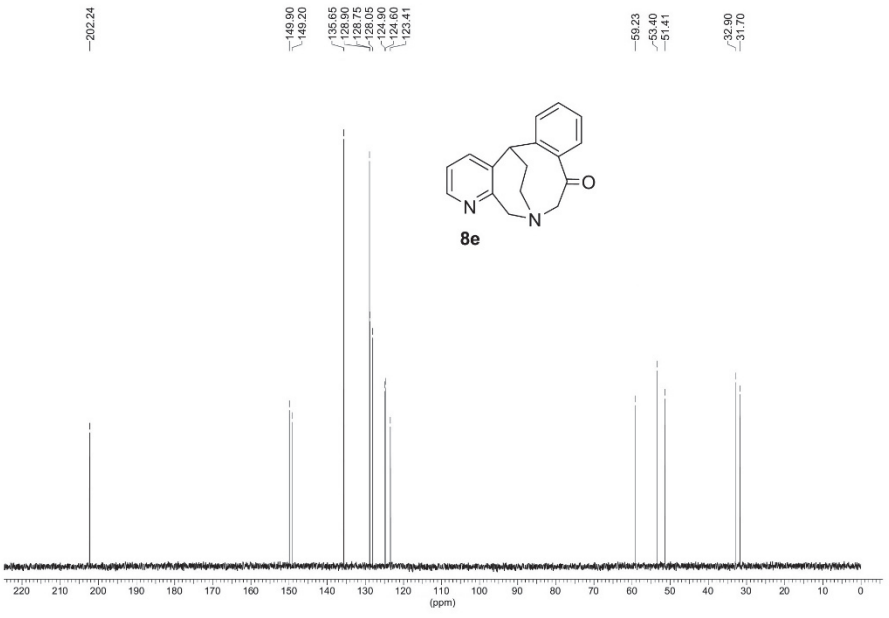

Fig. S-54. ^{13}C-NMR spectrum of compound **8e**

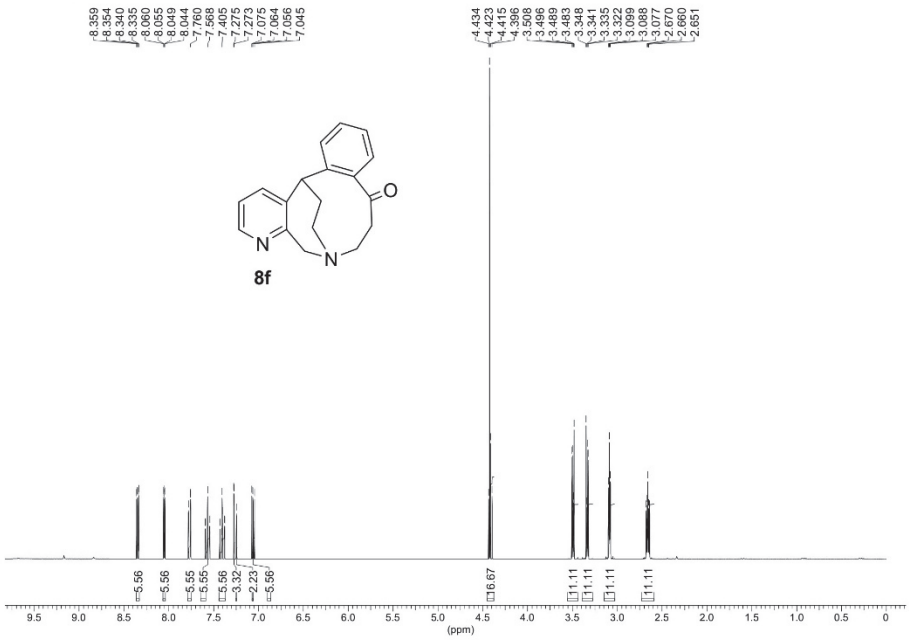

Fig. S-55. ^{1}H-NMR spectrum of compound **8f**

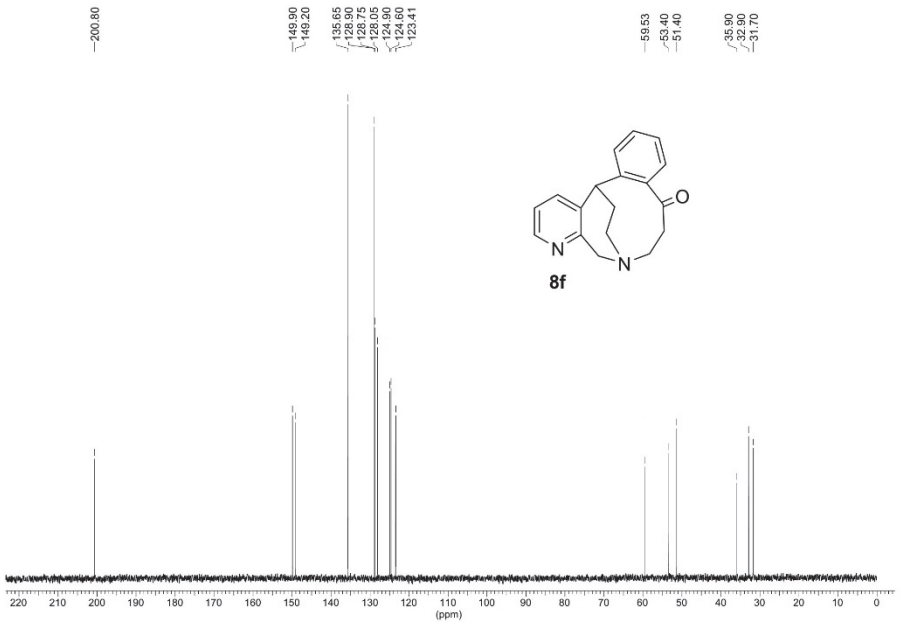

Fig. S-56. ^{13}C-NMR spectrum of compound **8f**

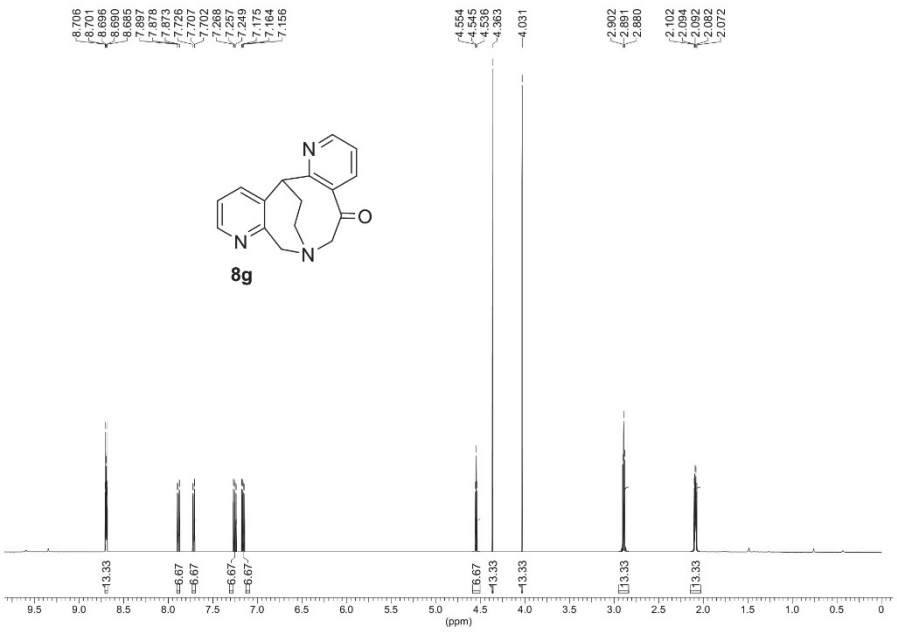

Fig. S-57. ^{1}H-NMR spectrum of compound **8g**

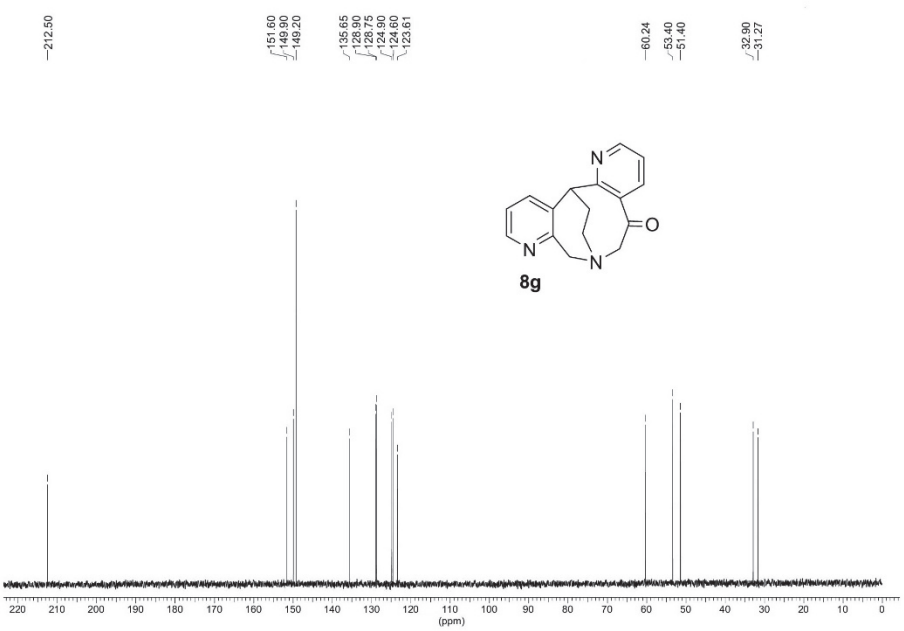

Fig. S-58. ^{13}C-NMR spectrum of compound **8g**

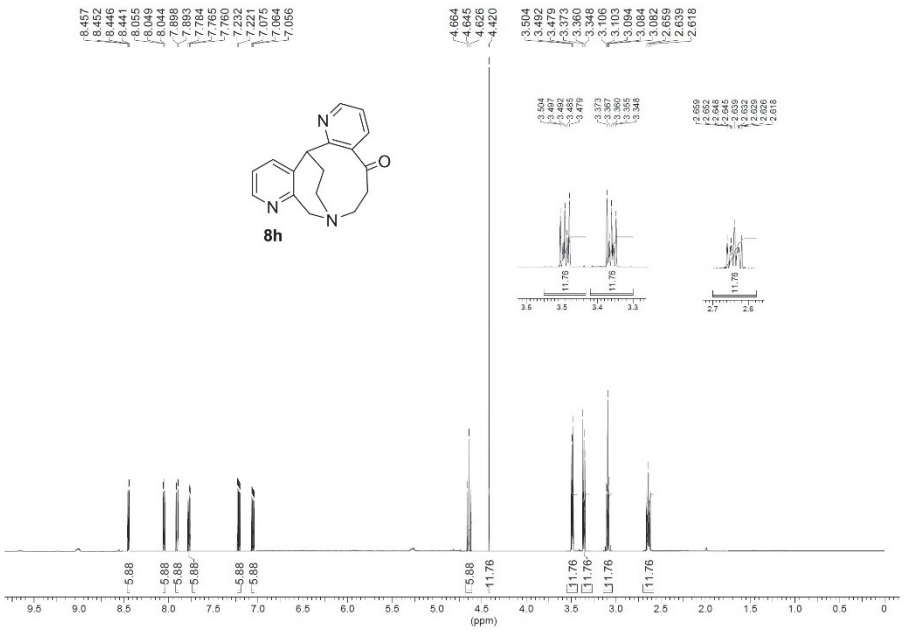

Fig. S-59. ^{1}H-NMR spectrum of compound **8h**

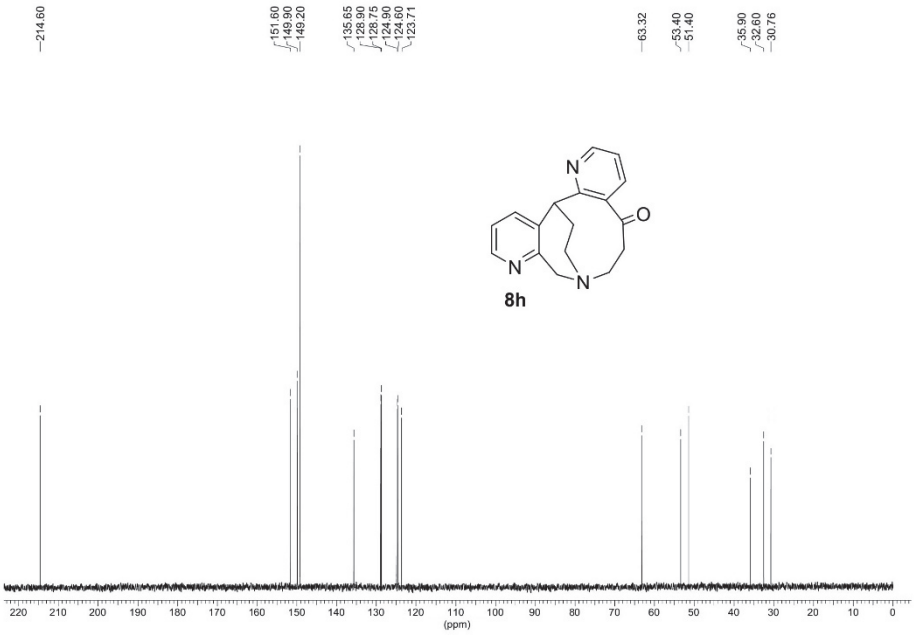

Fig. S-60. ^{13}C-NMR spectrum of compound **8h**

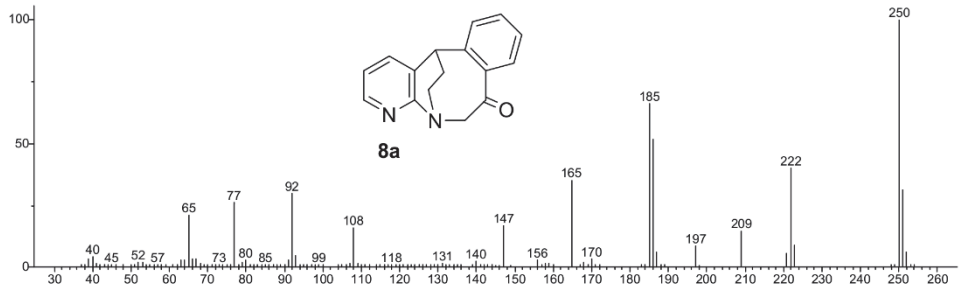

Fig. S-61. Mass spectrum of compound **8a**

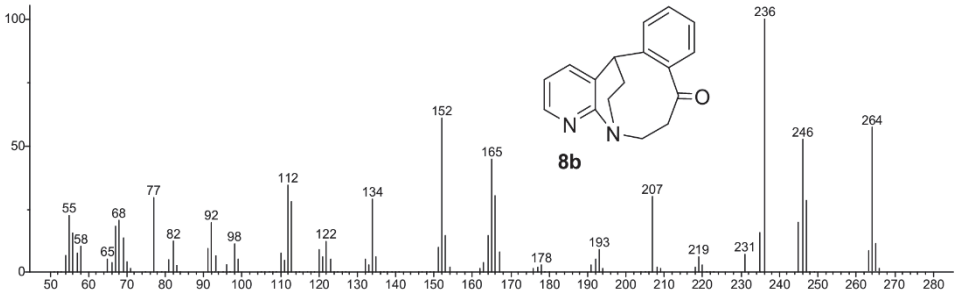

Fig. S-62. Mass spectrum of compound **8b**

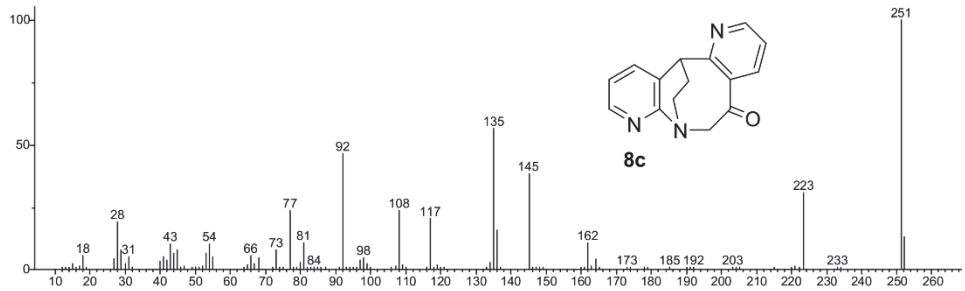

Fig. S-63. Mass spectrum of compound **8c**

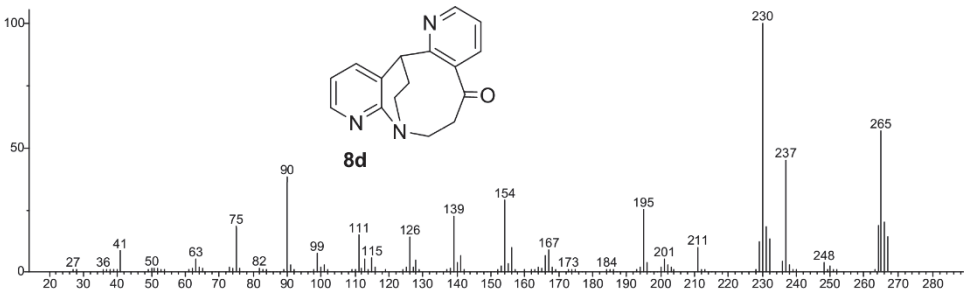

Fig. S-64. Mass spectrum of compound **8d**

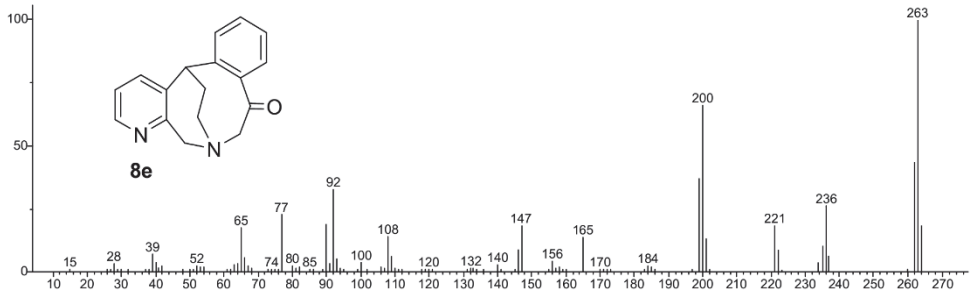

Fig. S-65. Mass spectrum of compound **8e**

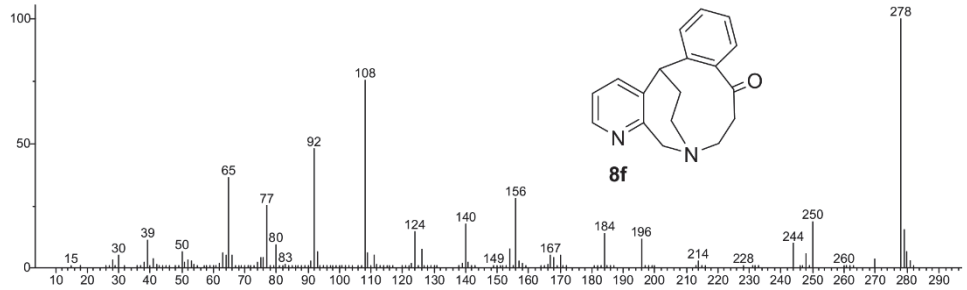

Fig. S-66. Mass spectrum of compound **8f**

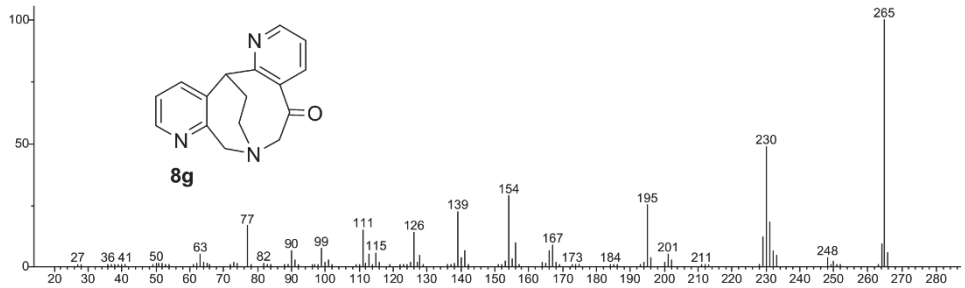

Fig. S-67. Mass spectrum of compound **8g**

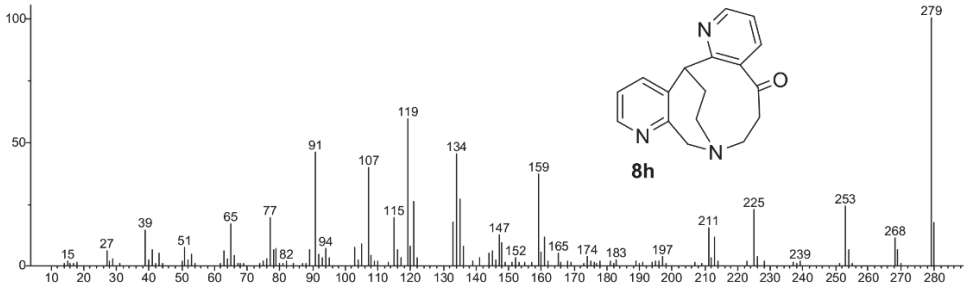

Fig. S-68. Mass spectrum of compound **8h**.