Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

$NiFe_2O_4@SiO_2@PrNH_2$-DPA-$CeCl_3$: a cerium-based magnetic nano dual-acid catalyst with high efficacy and recyclability for domino sequential synthesis of lactam ring-fused 1,5-benzodiazepines

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Content

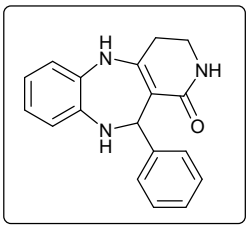
Table 1 Crystal data and structural refinement details for compound **4dad**.

Compound	4dad
Empirical formula	$C_{20}H_{21}Br_2N_3O_2$
Formula weight	495.22
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.7492(9)
b (Å)	21.4852(19)
c (Å)	8.9772(6)
α, *β*, *γ* (°)	90, 94.765(3), 90
Volume (Å^3)	2066.1(3)
Z	4
Density(calculated) (Mg·m^{-3})	1.592
Absorption coefficient (mm^{-1})	3.943
$F_{(000)}$	992
Crystal size (mm^3)	0.38 × 0.15 × 0.11
ϑ (°)	2.12 to 25.02
Reflections collected	9916
Independent reflections ($R_{(int)}$)	3630 [R_{int} = 0.0839, R_{sigma} = 0.0908]
Data / restraints / parameters	3630/0/246
Goodness-of-fit on F^2	1.056
Final *R* indices [$I>2\sigma(I)$][a]	R_1 = 0.0675, wR_2 = 0.1806
R indices (all data)	R_1 = 0.1239, wR_2 = 0.2001
CCDC	2212904

[a] $R_1 = \sum||F_0| - |F_c|| / \sum|F_0|$; $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_0^2)^2]\}^{1/2}$.

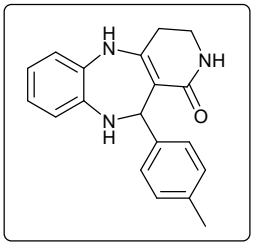
Spectral data of the synthesized compound **4aaa-4dae**

11-phenyl-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4aaa)



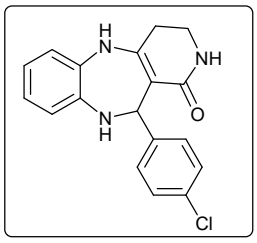
Creamy yellow solid; 95%; m.p.: 203-204 °C; IR (KBr): 3402, 3314, 3076, 1652, 1548, 1244 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.70 – 2.61 (2H, m, CH_2), 3.29 (2H, t, J = 6.0 Hz, CH_2), 5.65 (1H, d, J = 5.6 Hz, CH), 6.10 (1H, d, J = 5.8 Hz, NH), 6.56 – 6.50 (3H, m, Ph), 6.77 (1H, s, NH), 6.86 – 6.82 (1H, m, Ph), 7.01 (1H, t, J = 6.5 Hz, Ph), 7.16 – 7.10 (4H, m, Ph), 8.37 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 30.3, 38.6, 57.7, 102.4, 119.6, 120.1, 121.3, 122.0, 126.2, 127.9, 128.1, 132.5, 138.4, 145.7, 148.3, 168.4 ppm; MS calcd for $C_{18}H_{17}N_3O$ 291.14, found 292.10 (M + 1); Anal. calcd (%) for $C_{18}H_{17}N_3O$: C 74.20, H 5.88, N 14.42; found: C 74.21, H 5.86, N 14.43.

11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4aab)



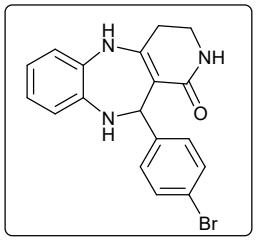
Brown solid; 93%; m.p.: 196-198 °C; IR (KBr): 3402, 3314, 3076, 1652, 1548, 1244 cm^{-1}; 3407, 3303, 3081, 1658, 1554, 1248 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.13 (3H, s, CH_3), 2.70 – 2.59 (2H, m, CH_2), 3.26 (2H, s, CH_2), 5.59 (1H, d, J = 5.2 Hz, CH), 6.03 (1H, d, J = 5.6 Hz, NH), 6.51 (3H, t, J = 7.2 Hz, Ph), 6.75 (1H, s, NH), 6.86 – 6.81 (1H, m, Ph), 6.95 (4H, dd, J = 44.1, 7.7 Hz, Ph), 8.40 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 21.0, 30.3, 38.6, 57.3, 102.6, 119.6, 120.0, 121.2, 122.0, 127.8, 128.7, 132.5, 134.9, 138.5, 142.6, 148.2, 168.4 ppm; MS calcd for $C_{19}H_{19}N_3O$ 305.15, found 306.10 (M + 1); Anal. calcd (%) for $C_{19}H_{19}N_3O$: C 74.73, H 6.27, N 13.76; found: C 74.72, H 6.25, N 13.76.

11-(4-chlorophenyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4aac)



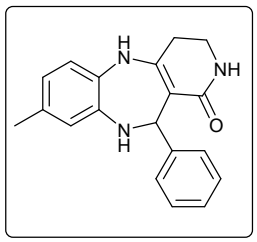
Apricot solid; 96%; m.p.: 213-215 °C; IR (KBr): 3407, 3308, 3077, 1652, 1559, 1249 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.67 (2H, dt, J = 14.7, 8.5 Hz, CH_2), 3.27 (2H, s, CH_2), 5.62 (1H, d, J = 5.3 Hz, CH), 6.12 (1H, d, J = 5.5 Hz, NH), 6.50 (1H, s, Ph), 6.58 – 6.53 (2H, m, Ph), 6.80 (1H, s, NH), 6.89 – 6.85 (1H, m, Ph), 7.18 – 7.12 (4H, m, Ph), 8.49 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 30.2, 38.5, 57.2, 101.8, 119.8, 120.3, 121.3, 122.2, 128.1, 129.7, 130.7, 132.6, 138.2, 144.6, 148.6, 168.3 ppm; MS calcd for $C_{18}H_{16}ClN_3O$ 325.10, found 326.10 (M + 1); Anal. calcd (%) for $C_{18}H_{16}ClN_3O$: C 66.36, H 4.95, N 12.90; found: C 66.34, H 4.96, N 12.92.

11-(4-bromophenyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4aad)



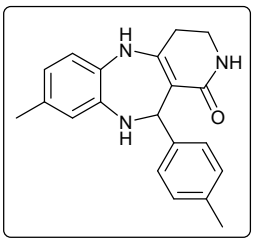
Milk white solid; 96%；m.p.: 234-235 °C; IR (KBr): 3408, 3306, 3082, 1652, 1553, 1243 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.69 – 2.58 (2H, m, CH_2), 3.26 (2H, t, J = 5.9 Hz, CH_2), 5.60 (1H, d, J = 5.7 Hz, CH), 6.11 (1H, d, J = 5.9 Hz, NH), 6.51 – 6.47 (1H, m, Ph), 6.55 (2H, dd, J = 8.8, 5.2 Hz, Ph), 6.79 (1H, s, NH), 6.86 – 6.82 (1H, m, Ph), 7.08 (2H, d, J = 8.3 Hz, Ph), 7.30 (2H, d, J = 8.2 Hz, Ph), 8.41 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 30.2, 38.5, 57.3, 101.8, 119.3, 119.73, 120.4, 121.3, 122.2, 130.1, 131.0, 132.6, 138.1, 145.0, 148.5, 168.2 ppm; MS calcd for $C_{18}H_{16}BrN_3O$ 369.05, found 370.10 (M + 1); Anal. calcd (%) for $C_{18}H_{16}BrN_3O$: C 58.39, H 4.36, N 11.35; found: C 58.43, H 4.34, N 11.32.

8-methyl-11-phenyl-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4baa)



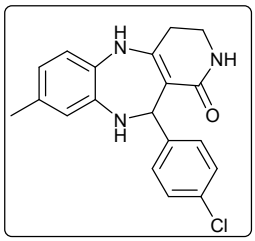
Milky solid; 94%；m.p.: 185-186 °C; IR (KBr): 3411, 3308, 3076, 1642, 1553, 1233 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 1.99 (3H, s, CH_3), 2.65 – 2.58 (2H, m, CH_2), 3.24 (2H, d, J = 5.9 H, CH_2), 5.62 (1H, d, J = 5.6 Hz, CH), 5.99 (1H, d, J = 5.7 Hz, NH), 6.30 (1H, s, Ph), 6.34 (1H, d, J = 8.0 Hz, Ph), 6.71 (2H, d, J = 8.1 Hz, Ph), 7.00 (1H, t, J = 6.3 Hz, NH), 7.12 (4H, d, J = 6.5 Hz, Ph), 8.28 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 20.5, 30.2, 38.4, 57.3, 101.7, 119.4, 120.6, 121.3, 126.0, 127.7, 128.0, 129.8, 130.5, 138.0, 145.5, 148.1, 168.2 ppm; MS calcd for $C_{19}H_{19}N_3O$ 305.15, found 306.10 (M + 1); Anal. calcd (%) for $C_{19}H_{19}N_3O$: C 74.73, H 6.27, N 13.76; found: C 74.72, H 6.23, N 13.76.

8-methyl-11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4bab)



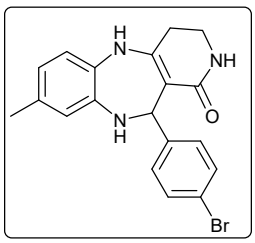
Apricot solid; 96%；m.p.: 185-186 °C; IR (KBr): 3614, 3308, 3076, 1657, 1554, 1243 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 1.99 (3H, s, CH_3), 2.14 (3H, s, CH_3), 2.63-2.57 (2H, m, CH_2), 3.24 (2H, t, J = 5.6 Hz, CH_2), 5.58 (1H, d, J = 1.5 Hz, CH), 5.97 (1H, d, J = 0.5 Hz, NH), 6.30 (1H, s, Ph), 6.34 (1H, d, J = 8.0 Hz, Ph), 6.69 (1H, s, Ph), 6.71 (1H, s, NH), 6.91 (2H, d, J = 7.8 Hz, Ph), 7.01 (2H, d, J = 7.8 Hz, Ph), 8.26 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 20.7, 21.0, 30.3, 38.6, 57.2, 102.1, 119.5, 120.7, 121.4, 127.8, 128.8, 130.0, 130.5, 135.0, 138.2, 142.7, 148.1, 168.3 ppm; MS calcd for $C_{20}H_{21}N_3O$ 319.17, found 320.10 (M + 1); Anal. calcd (%) for $C_{20}H_{21}N_3O$: C 75.21, H 6.62, N 13.16; found: C 75.20, H 6.58, N 13.16.

11-(4-chlorophenyl)-8-methyl-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4bac)



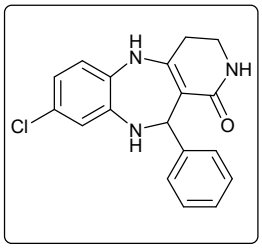
Apricot solid；97%；m.p.: 193-194 °C; IR (KBr): 3604, 3080, 1657, 1553, 1209 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.01 (3H, s, CH_3), 2.61 (2H, m, J = 14.7, 7.1 Hz, CH_2), 3.24 (2H, d, J = 6.2 Hz, CH_2), 5.59 (1H, d, J = 5.7 Hz, CH), 6.03 (1H, d, J = 5.8 Hz, NH), 6.29 (1H, s, Ph), 6.36 (1H, s, Ph), 6.74-6.71 (2H, m, NH, Ph), 7.17 (4H, t, J = 9.2 Hz, Ph), 8.33 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 20.7, 30.3, 38.5, 57.0, 101.4, 119.7, 121.0, 121.4, 128.1, 129.7, 130.0, 130.7, 130.9, 137.9, 144.7, 148.5, 168.2 ppm; MS calcd for $C_{19}H_{18}ClN_3O$ 339.11, found 340.10 (M + 1); Anal. calcd (%) for $C_{19}H_{18}ClN_3O$: C 67.16, H 5.34, N 12.37; found: C 67.20, H 5.33, N 12.39.

11-(4-bromophenyl)-8-methyl-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4bad)



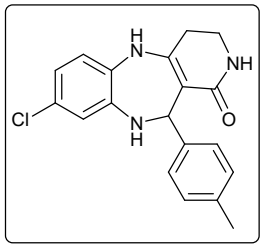
Powder white solid；98%；m.p.: 214-215°C; IR (KBr): 3623, 3407, 3062, 1658, 1558, 1214 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.01 (3H, s, CH_3), 2.65-2.56 (2H, m, CH_2), 3.25 (2H, s, CH_2), 5.57 (1H, d, J = 5.3 Hz, CH), 6.03 (1H, d, J = 5.4 Hz, NH), 6.29 (1H, s, Ph), 6.37 (1H, d, J = 6.6 Hz, Ph), 6.74 (2H, t, J = 8.5 Hz, NH, Ph), 7.07 (2H, d, J = 8.0 Hz, Ph), 7.31 (2H, d, J = 8.1 Hz, Ph), 8.34 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 20.7, 30.2, 38.5, 57.1, 101.3, 119.3, 119.8, 121.0, 121.4, 130.0, 130.2, 130.9, 131.0, 137.9, 145.1, 148.6, 168.3 ppm; MS calcd for $C_{19}H_{18}BrN_3O$ 383.06, found 384.10 (M + 1); Anal. calcd (%) for $C_{19}H_{18}BrN_3O$: C 59.39, H 4.72, N 10.94; found: C 59.42, H 4.70, N 10.96.

8-chloro-11-phenyl-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepin-1-one (4caa)



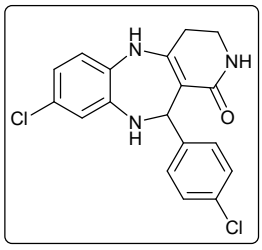
Milk white solid; 93%；m.p.: 246-248°C；IR (KBr): 3358, 3303, 3082, 1651, 1559, 1254 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.61 (2H, dd, J = 14.2, 7.1 Hz, CH_2), 3.26 (2H, d, J = 6.0 Hz, CH_2), 5.64 (1H, d, J = 5.7 Hz, CH), 6.37 (1H, d, J = 5.8 Hz, NH), 6.59-6.54 (2H, m, Ph), 6.82 (2H, d, J = 9.0 Hz, Ph), 7.03 (1H, t, J = 6.4 Hz, NH), 7.18-7.12 (4H, m, Ph), 8.49 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 30.1, 38.5, 57.5, 102.7, 119.6, 120.0, 120.8, 125.2, 126.5, 127.8, 128.4, 131.7, 139.9, 145.0, 148.0, 168.1 ppm; MS calcd for $C_{18}H_{16}ClN_3O$ 325.10, found 326.20 (M + 1); Anal. calcd (%) for $C_{18}H_{16}ClN_3O$: C 66.36, H 4.95, N 12.90; found: C 66.34, H 4.92, N 12.92.

8-chloro-11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4cab)



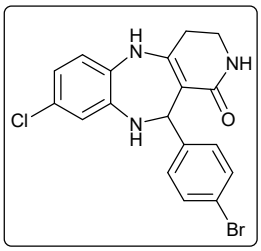
Cream yellow solid；91%；m.p.: 183-185°C；IR (KBr): 3618, 3313, 3018, 1652, 1548, 1259 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.16 (3H, s, CH_3), 2.62 (2H, d, J = 4.8 Hz, CH_2), 3.26 (2H, s, CH_2), 5.60 (1H, d, J = 3.9 Hz, CH), 6.34 (1H, d, J = 4.6 Hz, NH), 6.55 (2H, s, Ph), 6.82 (2H, s, NH, Ph), 6.98 (4H, dd, J = 26.0, 7.1 Hz, Ph), 8.47 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 21.0, 30.1, 38.5, 57.2, 102.9, 119.5, 120.0, 120.7, 125.1, 127.7, 129.0, 131.7, 135.3, 140.0, 142.1, 147.9, 168.1 ppm; MS calcd for $C_{19}H_{18}ClN_3O$ 339.11, found 340.20 (M + 1); Anal. calcd (%) for $C_{19}H_{18}ClN_3O$: C 67.16, H 5.34, N 12.37; found: C 67.21, H 5.31, N 12.39.

8-chloro-11-(4-chlorophenyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4cac)



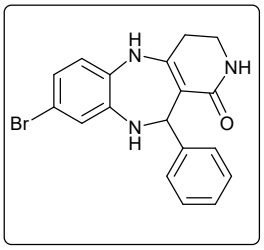
Milky solid；94%；m.p.: 184-185°C；IR (KBr): 3603, 3076, 1667, 1555, 1258 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.63 (2H, q, J = 15.9 Hz, CH_2), 3.28 (2H, s, CH_2), 5.62 (1H, d, J = 3.0 Hz, CH), 6.41 (1H, d, J = 3.7 Hz, NH), 6.56 (1H, s, Ph), 6.60 (1H, d, J = 8.4 Hz, Ph), 6.91 – 6.83 (2H, m, NH, Ph), 7.18 (4H, dd, J = 33.0, 7.7 Hz, Ph), 8.55 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 30.1, 38.4, 57.0, 102.17, 119.9, 120.0, 120.9, 125.4, 128.5, 129.6, 131.1, 131.7, 139.6, 144.1, 148.3, 168.0 ppm; MS calcd for $C_{18}H_{15}Cl_2N_3O$ 359.06, found 359.90 (M + 1); Anal. calcd (%) for $C_{18}H_{15}Cl_2N_3O$: C 60.02, H 4.20, N 11.66; found: C 60.06, H 4.18, N 11.70.

11-(4-bromophenyl)-8-chloro-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4cad)



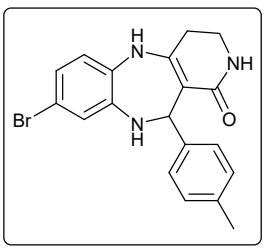
Off-white solid；94%；m.p.: 187-189°C；IR (KBr): 3608, 3087, 1672, 1554, 1258 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.65 (2H, dt, J = 15.6, 12.4 Hz, CH_2), 3.28 (2H, s, CH_2), 5.60 (1H, d, J = 3.7 Hz, CH), 6.44 (1H, d, J = 4.3 Hz, NH), 6.58 (1H, s, Ph), 6.61 (1H, s, NH), 6.90 (2H, s, Ph), 7.09 (2H, d, J = 7.5 Hz, Ph), 7.35 (2H, d, J = 7.5 Hz, Ph), 8.65 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 30.1, 38.4, 57.0, 102.1, 119.6, 119.9, 120.0, 121.0, 125.4, 130.0, 131.2, 131.7, 139.6, 144.5, 148.4, 168.1 ppm; MS calcd for $C_{18}H_{15}BrClN_3O$ 403.01, found 403.80 (M + 1); Anal. calcd (%) for $C_{18}H_{15}BrClN_3O$: C 53.42, H 3.74, N 10.38; found: C 53.45, H 3.72, N 10.42.

8-bromo-11-phenyl-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4daa)



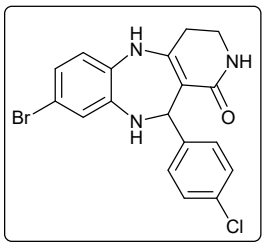
Yellow-green solid；93%；m.p.: 250-252°C；IR (KBr): 3609, 3308, 3076, 1657, 1539, 1254 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.63 (2H, dd, J = 12.4, 6.5 Hz, CH_2), 3.26 (2H, d, J = 6.2 Hz, CH_2), 5.63 (1H, d, J = 5.7 Hz, CH), 6.37 (1H, d, J = 5.9 Hz, NH), 6.68 (2H, d, J = 6.8 Hz, Ph), 6.77 (1H, d, J = 9.1 Hz, Ph), 6.83 (1H, s, Ph), 7.04 (1H, t, J = 6.8 Hz, NH), 7.17-7.12 (4H, m, Ph), 8.49 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 30.1, 38.5, 57.5, 102.8, 113.1, 121.2, 122.4, 122.8, 126.5, 127.8, 128.4, 132.1, 140.2, 145.0, 148.0, 168.0 ppm; MS calcd for $C_{18}H_{16}BrN_3O$ 369.05, found 370.1 (M + 1); Anal. calcd (%) for $C_{18}H_{16}BrN_3O$: C 58.39, H 4.36, N 11.35; found: C 58.43, H 4.34, N 11.38.

8-bromo-11-(p-tolyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4dab)



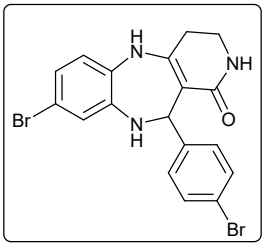
Milk white solid; 91%；m.p.: 192-194°C；IR (KBr): 3618, 3308, 3076, 1651, 1548, 1253 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.16 (3H, s, CH_3), 2.65-2.58 (2H, m, CH_2), 3.25 (2H, d, J = 6.2 Hz, CH_2), 5.59 (1H, d, J = 5.6 Hz, CH), 6.34 (1H, d, J = 5.9 Hz, NH), 6.70-6.66 (2H, m, NH, Ph), 6.76 (1H, d, J = 8.2 Hz, Ph), 6.83 (1H, s, Ph), 6.95 (2H, d, J = 7.9 Hz, Ph), 7.01 (2H, d, J = 8.0 Hz, Ph), 8.47 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 21.0, 30.1, 38.5, 57.2, 103.0, 113.1, 121.1, 122.4, 122.7, 127.7, 129.0, 132.0, 135.3, 140.3, 142.0, 147.9, 168.1 ppm; MS calcd for $C_{19}H_{18}BrN_3O$ 383.06, found 383.90 (M + 1); Anal. calcd (%) for $C_{19}H_{18}BrN_3O$: C 59.39, H 4.72, N 10.94; found: C 59.42, H 4.70, N 10.96.

8-bromo-11-(4-chlorophenyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4dac)



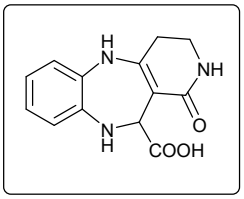
Powder white solid；92%；m.p.: 185-187°C；IR (KBr): 3607, 3323, 3086, 1677, 1553, 1259 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.70-2.58 (2H, m, CH_2), 3.27 (2H, s, CH_2), 5.61 (1H, d, J = 5.3 Hz, CH), 6.42 (1H, d, J = 5.6 Hz, NH), 6.71 (2H, d, J = 8.1 Hz, NH, Ph), 6.81 (1H, d, J = 8.2 Hz, Ph), 6.88 (1H, s, Ph), 7.14 (2H, d, J = 8.2 Hz, Ph), 7.22 (2H, d, J = 8.2 Hz, Ph), 8.60 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 30.1, 38.4, 57.0, 102.3, 113.3, 121.3, 122.7, 122.8, 128.3, 129.6, 131.1, 132.1, 139.9, 144.1, 148.3, 168.0 ppm; MS calcd for $C_{18}H_{15}BrClN_3O$ 403.01, found 403.80 (M + 1); Anal. calcd (%) for $C_{18}H_{15}BrClN_3O$: C 53.42, H 3.74, N 10.38; found: C 53.40, H 3.72, N 10.42.

8-bromo-11-(4-bromophenyl)-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-1-one (4dad)



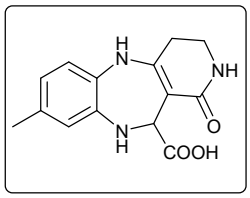
Milk white solid; 94%；m.p.: 175-176°C；IR (KBr): 3612, 3308, 3086, 1657, 1559, 1253 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.68-2.58 (2H, m, CH_2), 3.27 (2H, s, CH_2), 5.58 (1H, d, J = 5.6 Hz, CH), 6.40 (1H, d, J = 5.8 Hz, NH), 6.74–6.67 (2H, m, NH, Ph), 6.79 (1H, d, J = 8.4 Hz, Ph), 6.86 (1H, s, Ph), 7.07 (2H, d, J = 8.2 Hz, Ph), 7.36 (2H, d, J = 8.2 Hz, Ph), 8.54 (1H, s, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 30.1, 38.4, 57.0, 102.3, 113.3, 119.6, 121.3, 122.8, 130.0, 131.3, 132.0, 139.9, 144.5, 148.2, 167.9 ppm; MS calcd for $C_{18}H_{15}Br_2N_3O$ 446.96, found 447.80 (M + 1); Anal. calcd (%) for $C_{18}H_{15}Br_2N_3O$: C 48.14, H 3.37, N 9.36; found: C 48.13, H 3.36, N 9.40.

1-oxo-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-11-carboxylic acid (4aae)



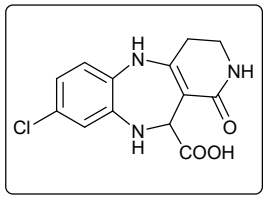
Brown-yellow solid; 87%; m.p.: 167-169°C；IR (KBr): 3455, 3323, 3096, 1722, 1658, 1553, 1233 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.55 (2H, t, J = 4.7 Hz, CH_2), 3.24 (2H, s, CH_2), 4.89 (1H, s, CH), 5.98 (1H, d, J = 1.1 Hz, NH), 6.69 (1H, t, J = 7.3 Hz, NH), 6.75 (1H, t, J = 7.3 Hz, Ph), 6.83 (1H, d, J = 7.6 Hz, Ph), 6.93 (1H, d, J = 7.6 Hz, Ph), 7.33 (1H, s, Ph), 8.69 (1H, s, NH), 13.11 (1H, s, COOH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 30.4, 38.2, 57.5, 96.9, 120.1, 120.1, 121.5, 122.6, 131.0, 138.6, 148.8, 170.1, 173.4 ppm; MS calcd for $C_{13}H_{13}N_3O_3$ 259.10, found 260.20 (M + 1); Anal. calcd (%) for $C_{13}H_{13}N_3O_3$: C 68.05, H 5.11, N 12.53; found: C 68.07, H 5.10, N 12.55.

8-methyl-1-oxo-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-11-carboxylic acid (4bae)



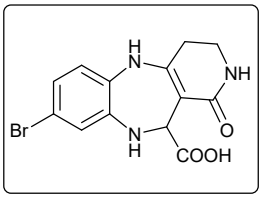
Brown-yellow solid; 89%; m.p.: 184-185°C；IR (KBr): 3446, 3347, 1736, 1638, 1568, 1238 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.15 (3H, s, CH_3), 2.75-2.54 (2H, m, CH_2), 3.23 (2H, s, CH_2), 4.86 (1H, d, J = 0.6 Hz, CH), 5.89 (1H, d, J = 0.6 Hz, NH), 6.50 (1H, d, J = 6.6 Hz, Ph), 6.63 (1H, s, NH), 6.81 (1H, d, J = 6.2 Hz, Ph), 7.31 (1H, s, Ph), 8.62 (1H, s, NH), 13.17 (1H, s, COOH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 20.7, 30.5, 38.2, 57.4, 96.2, 120.2, 120.9, 121.7, 128.5, 131.3, 138.4, 148.9, 170.2, 173.4 ppm; MS calcd for $C_{14}H_{15}N_3O_3$ 273.11, found 274.20 (M + 1); Anal. calcd (%) for $C_{14}H_{15}N_3O_3$: C 68.75, H 5.48, N 12.03; found: C 68.78, H 5.50, N 12.05.

8-chloro-1-oxo-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-11-carboxylic acid (4cae)



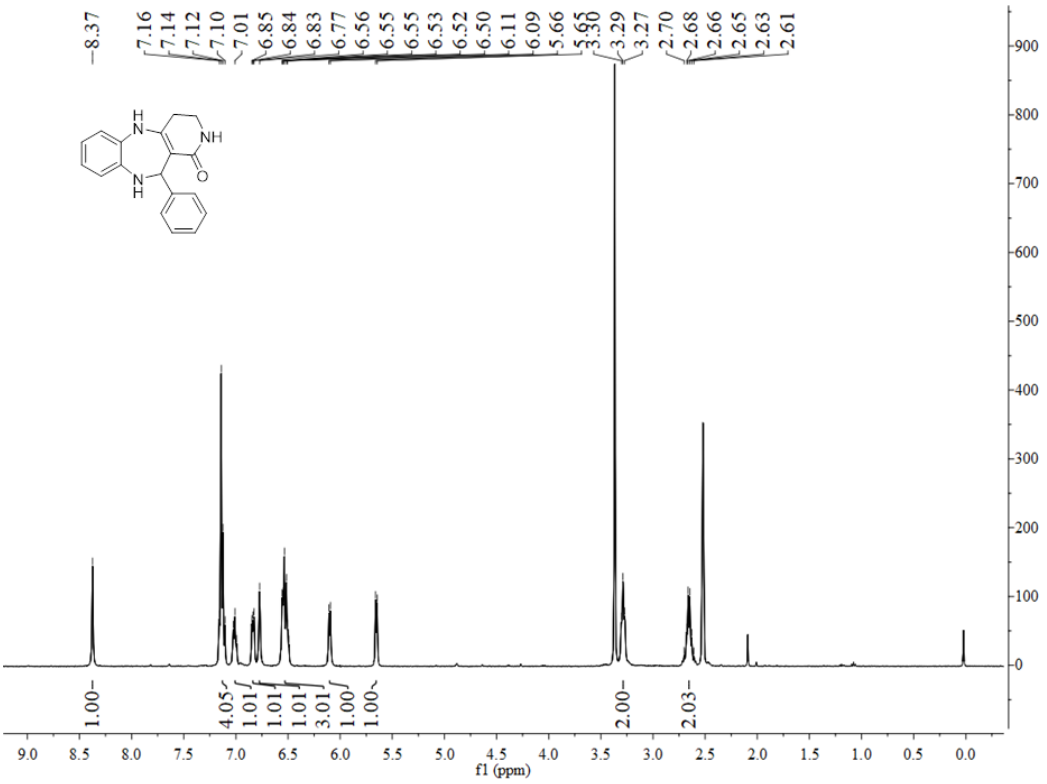
Yellow-green solid; 85%; m.p.: 204-205°C；IR (KBr): 3460, 3342, 1716, 1637, 1558, 1238 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.65 (2H, dt, J = 22.6, 7.7 Hz, CH_2), 3.24 (2H, s, CH_2), 4.92 (1H, d, J = 5.3 Hz, CH), 6.26 (1H, d, J = 5.5 Hz, NH), 6.72 (1H, dd, J = 8.5, 1.9 Hz, NH), 6.88 (1H, d, J = 1.9 Hz, Ph), 6.92 (1H, d, J = 8.5 Hz, Ph), 7.38 (1H, s, Ph), 8.76 (1H, s, NH), 13.15 (1H, s, COOH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 30.3, 38.2, 57.2, 97.3, 119.6, 120.3, 121.4, 125.9, 130.0, 140.1, 148.5, 169.8, 173.1 ppm; MS calcd for $C_{13}H_{12}ClN_3O_3$ 293.06, found 294.10 (M + 1); Anal. calcd (%) for $C_{13}H_{12}ClN_3O_3$: C 61.71, H 4.36, N 11.36; found: C 61.73, H 4.35, N 11.34.

8-bromo-1-oxo-2,3,4,5,10,11-hexahydro-1H-benzo[b]pyrido[4,3-e][1,4]diazepine-11-carboxylic acid (4dae)

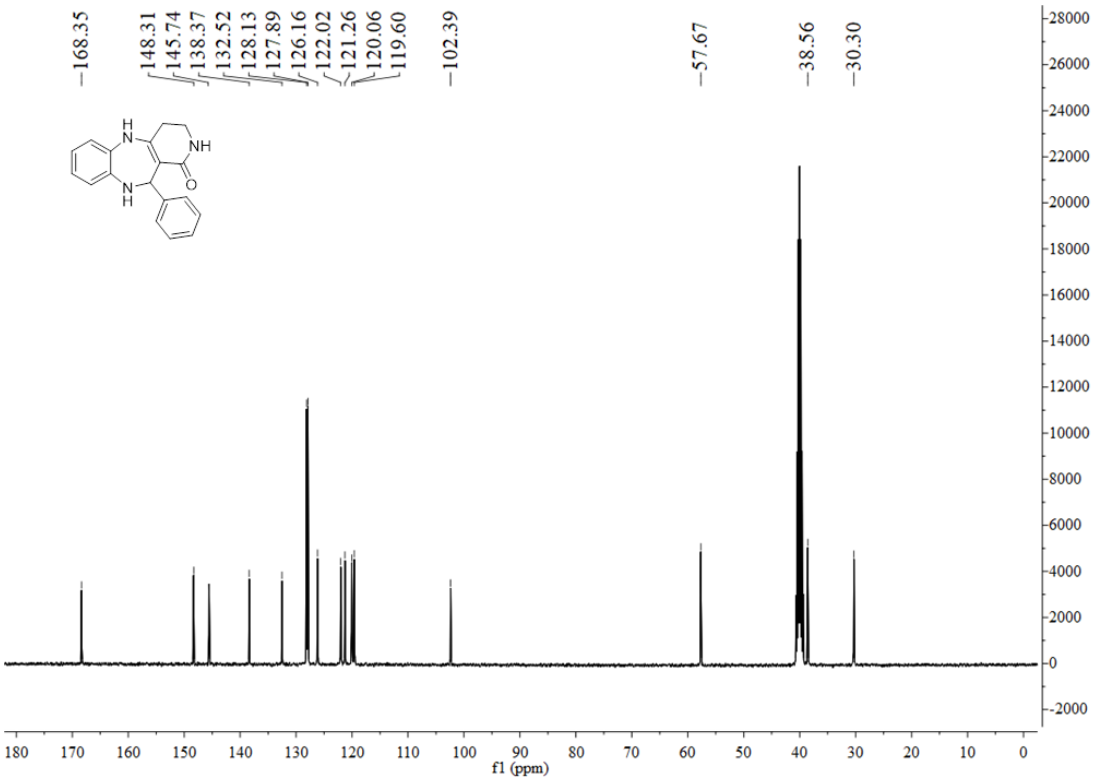


Creamy yellow solid; 85%; m.p.: 227-228°C；IR (KBr): 3455, 3337, 1711, 1638, 1564, 1249 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.3 (DMSO-d_6), δ 2.71-2.53 (2H, m, CH_2), 3.24 (2H, s, CH_2), 4.95 (1H, d, J = 1.6 Hz, CH), 6.28 (1H, d, J = 0.5 Hz, NH), 6.95-6.82 (2H, m, NH, Ph), 7.06-6.99 (1H, m, Ph), 7.38 (1H, s, Ph), 8.84 (1H, s, NH), 13.14 (1H, s, COOH) ppm; ^{13}C NMR (100 MHz, DMSO-*d*6, TMS): δ 30.3, 38.2, 57.3, 97.5, 113.8, 121.8, 122.4, 123.1, 130.5, 140.4, 148.5, 169.8, 173.2 ppm; MS calcd for $C_{13}H_{12}BrN_3O_3$ 337.01, found 338.10 (M + 1); Anal. calcd (%) for $C_{13}H_{12}BrN_3O_3$: C 55.09, H 3.89, N 10.14; found: C 55.11, H 3.90, N 10.12.

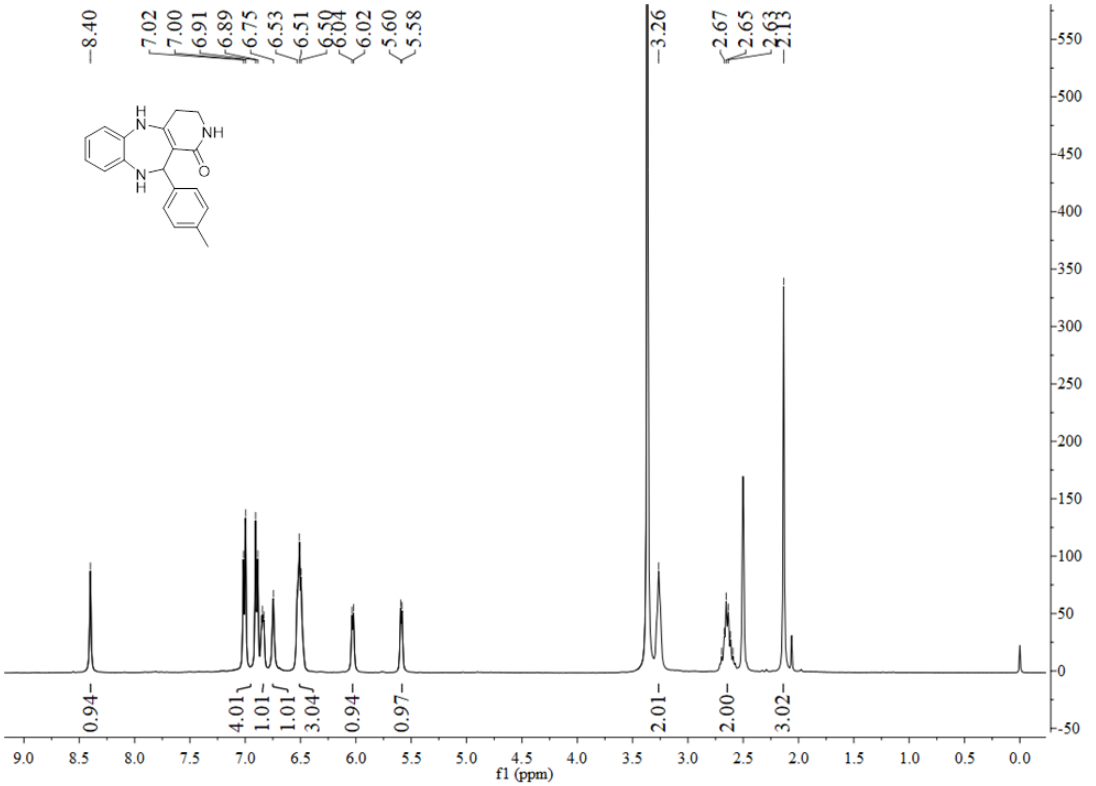
^{1}H NMR and ^{13}C NMR spectra of the synthesized compound **4aaa-4dae**



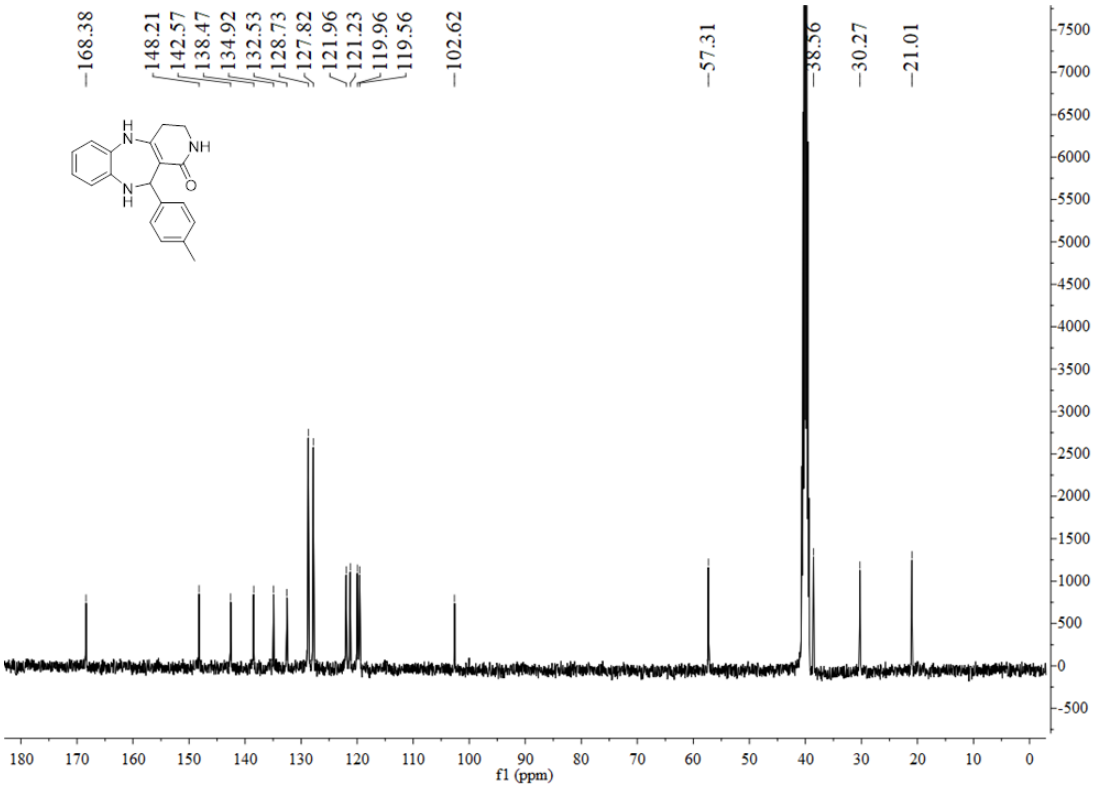
^{1}H NMR spectra of compound **4aaa**



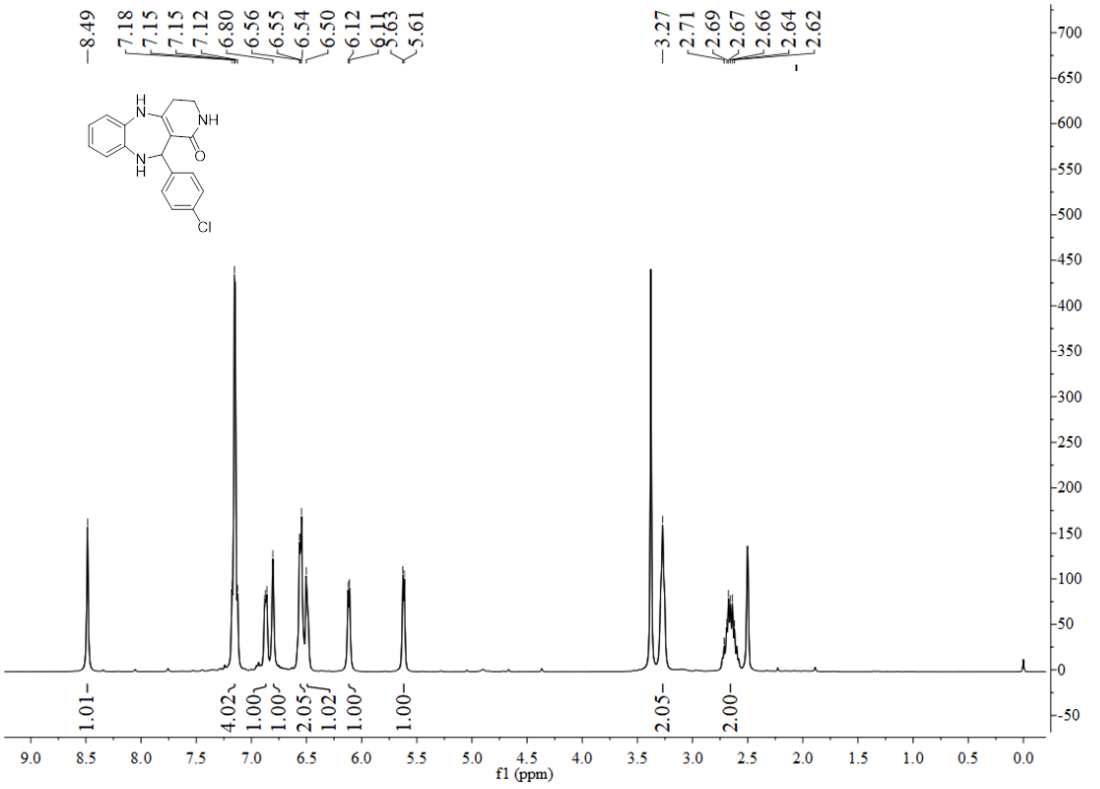
^{13}C NMR spectra of compound **4aaa**



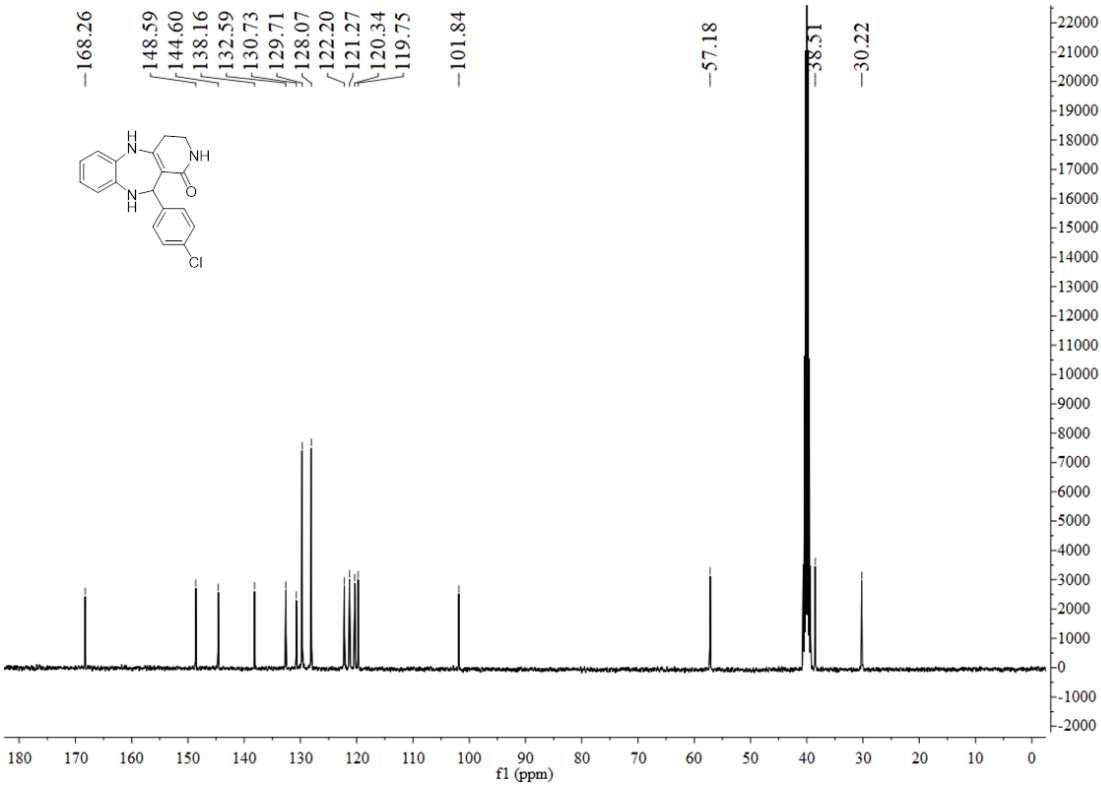
^{1}H NMR spectra of compound **4aab**



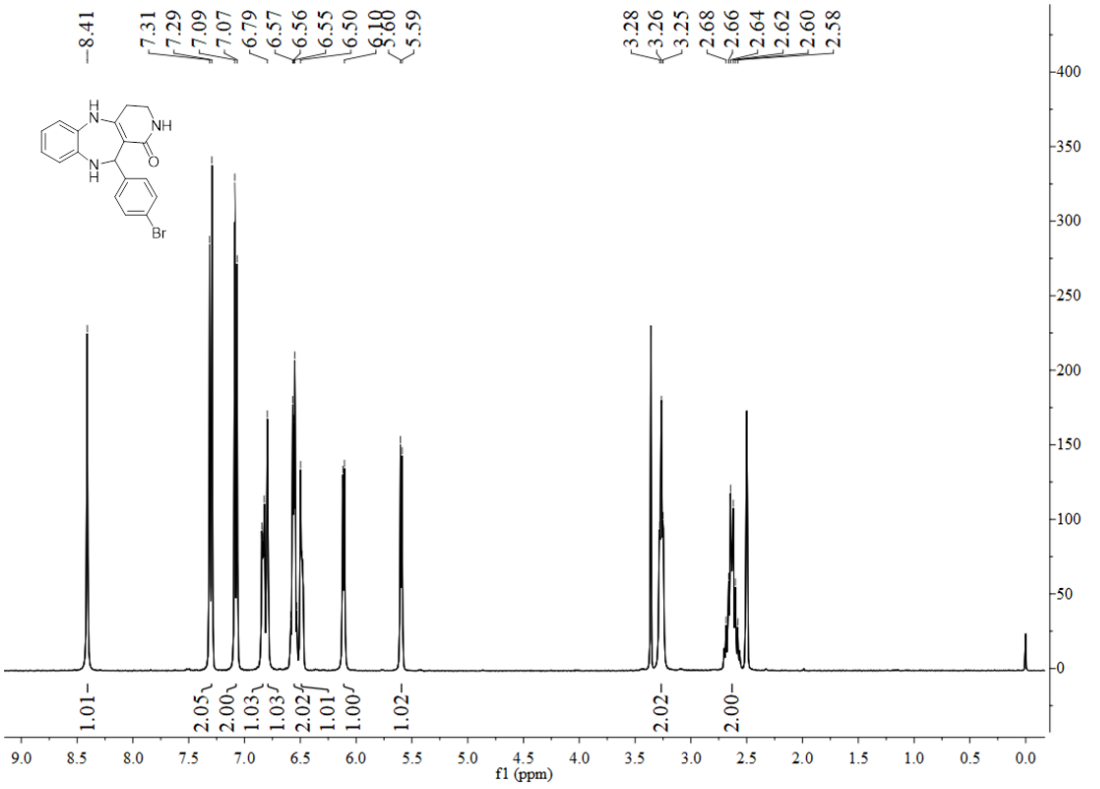
^{13}C NMR spectra of compound **4aab**



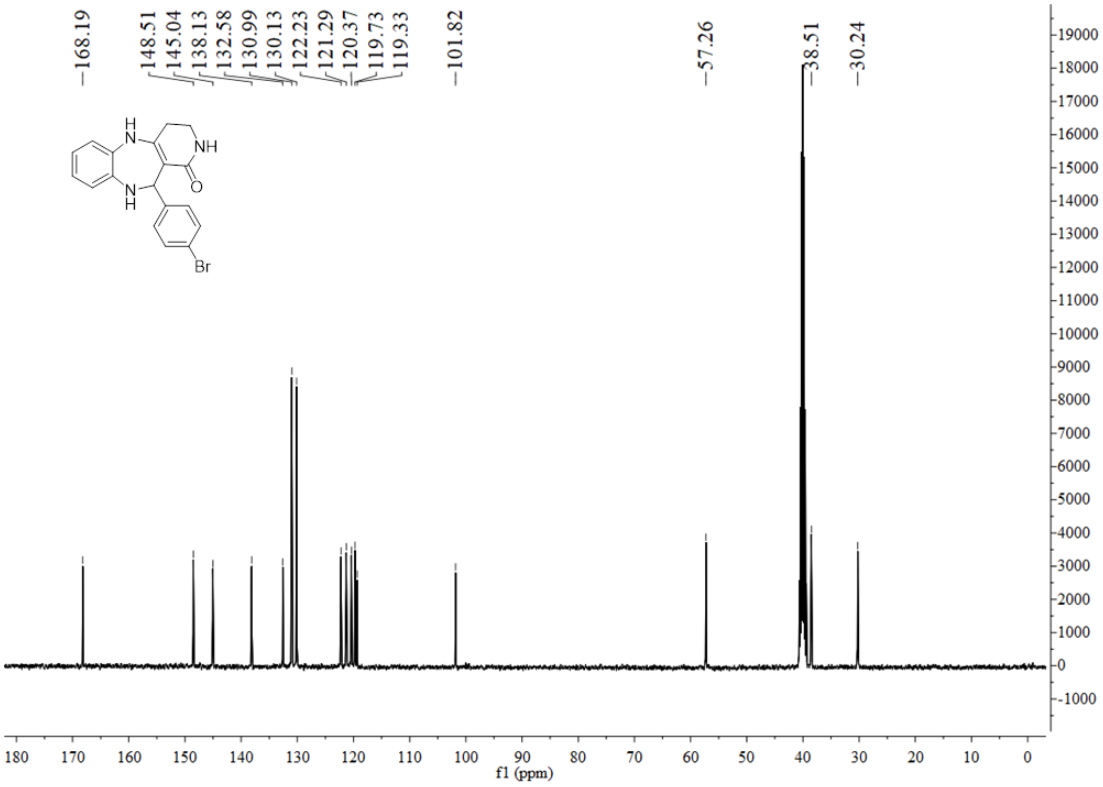
^{1}H NMR spectra of compound **4aac**



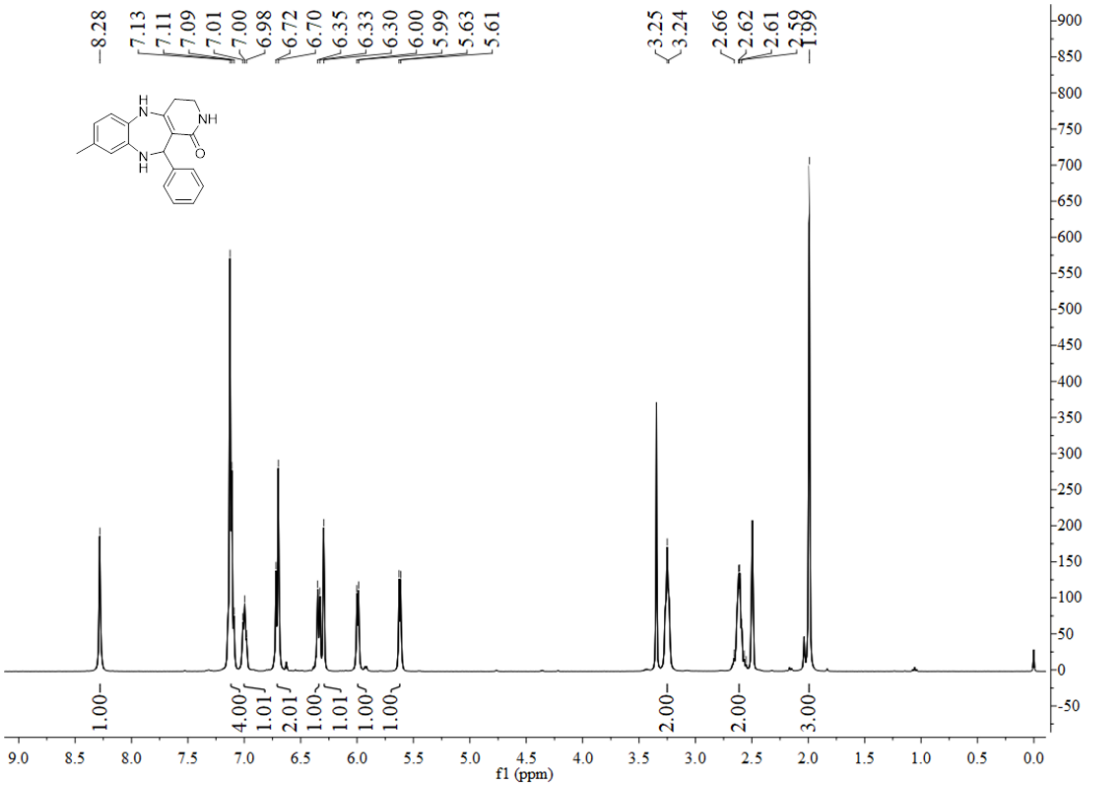
^{13}C NMR spectra of compound **4aac**



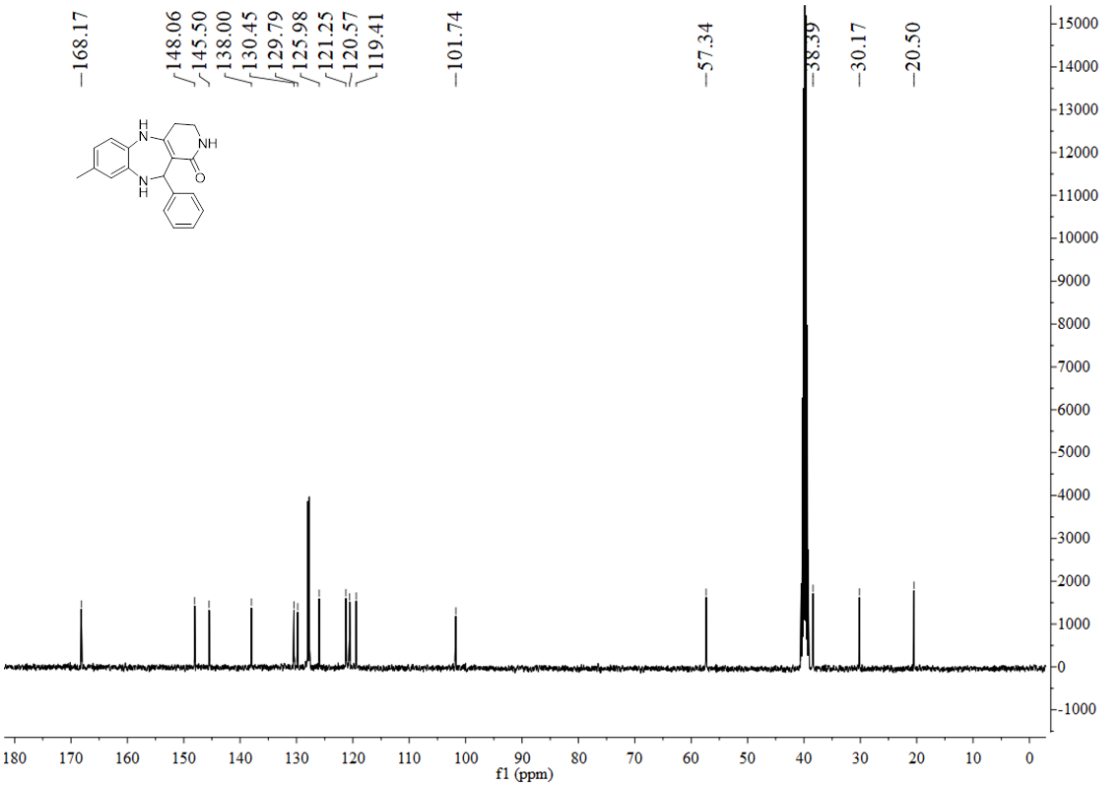
^{1}H NMR spectra of compound **4aad**



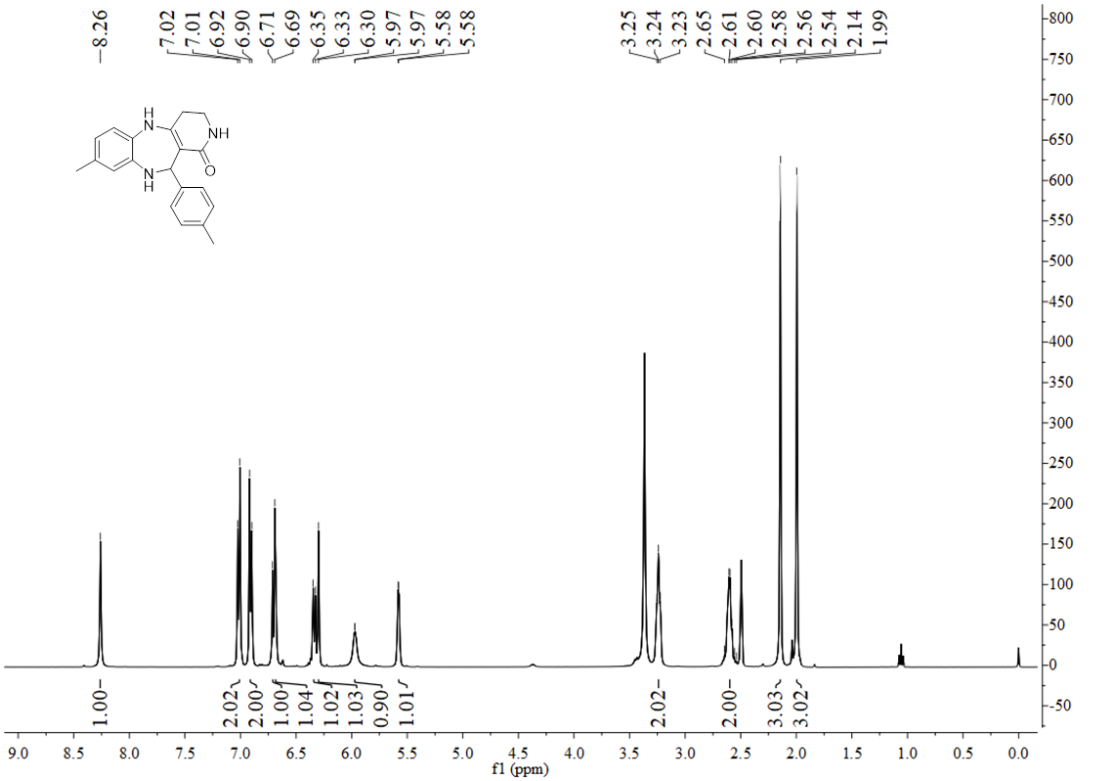
^{13}C NMR spectra of compound **4aad**



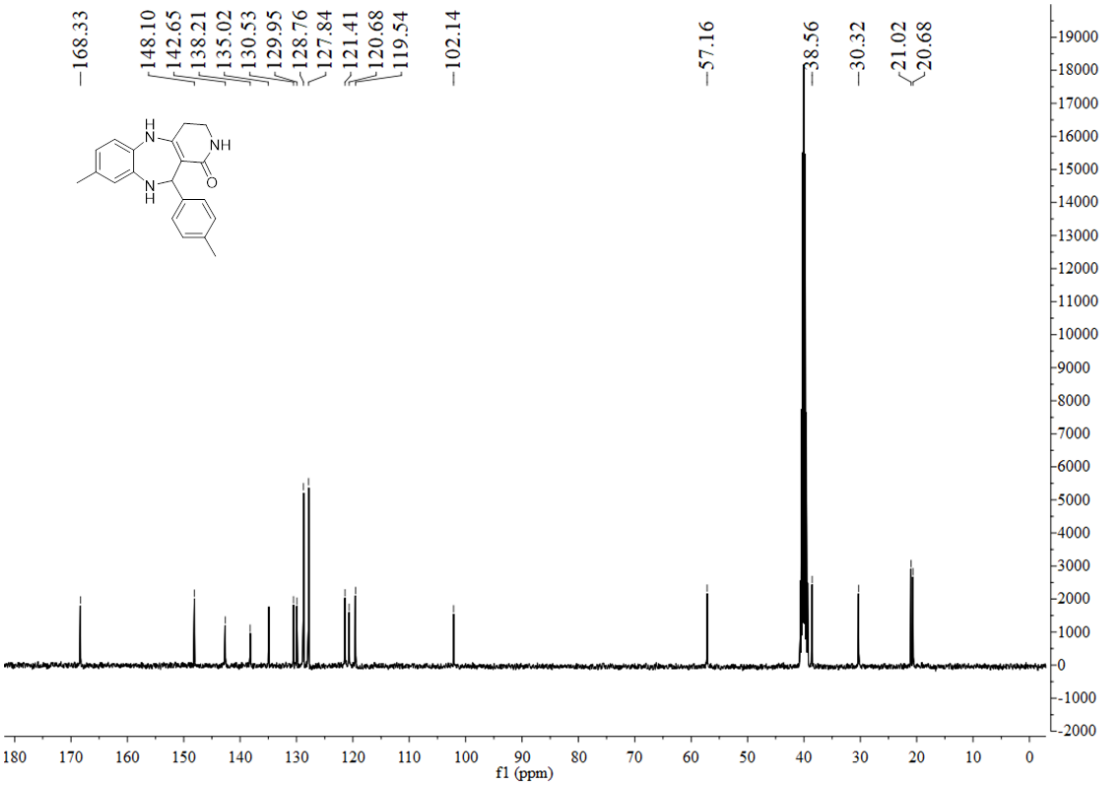
^{1}H NMR spectra of compound **4baa**



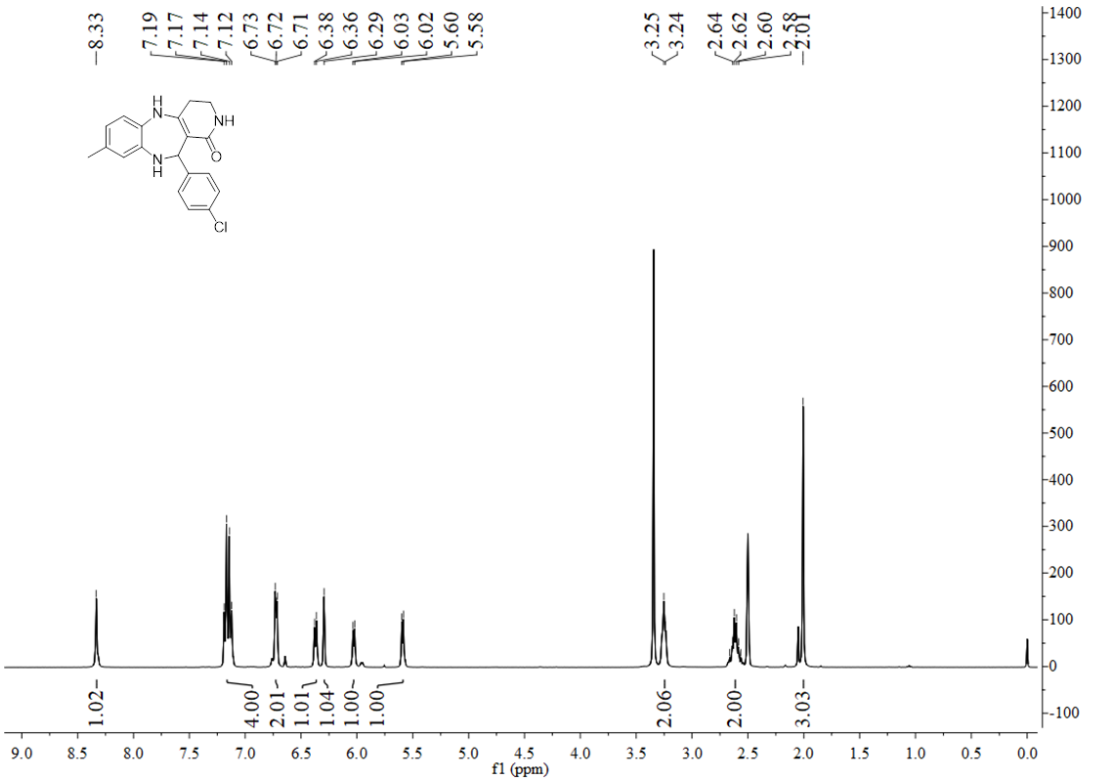
^{13}C NMR spectra of compound **4baa**



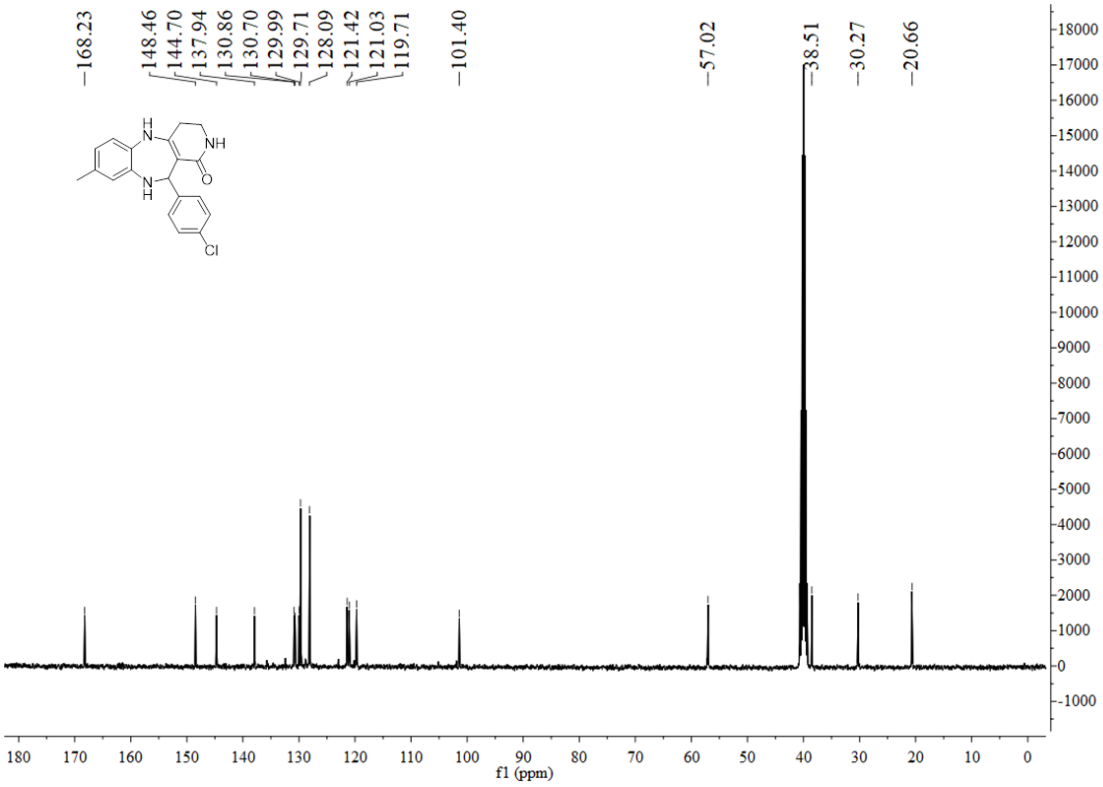
^{1}H NMR spectra of compound **4bab**



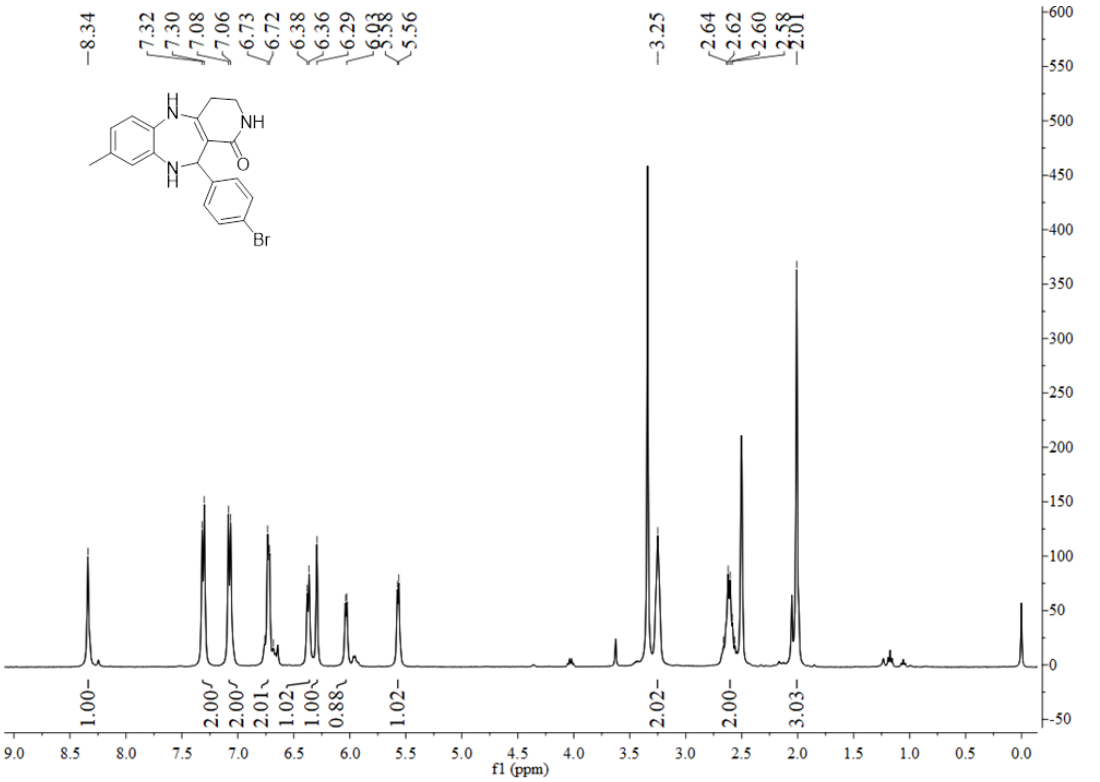
^{13}C NMR spectra of compound **4bab**



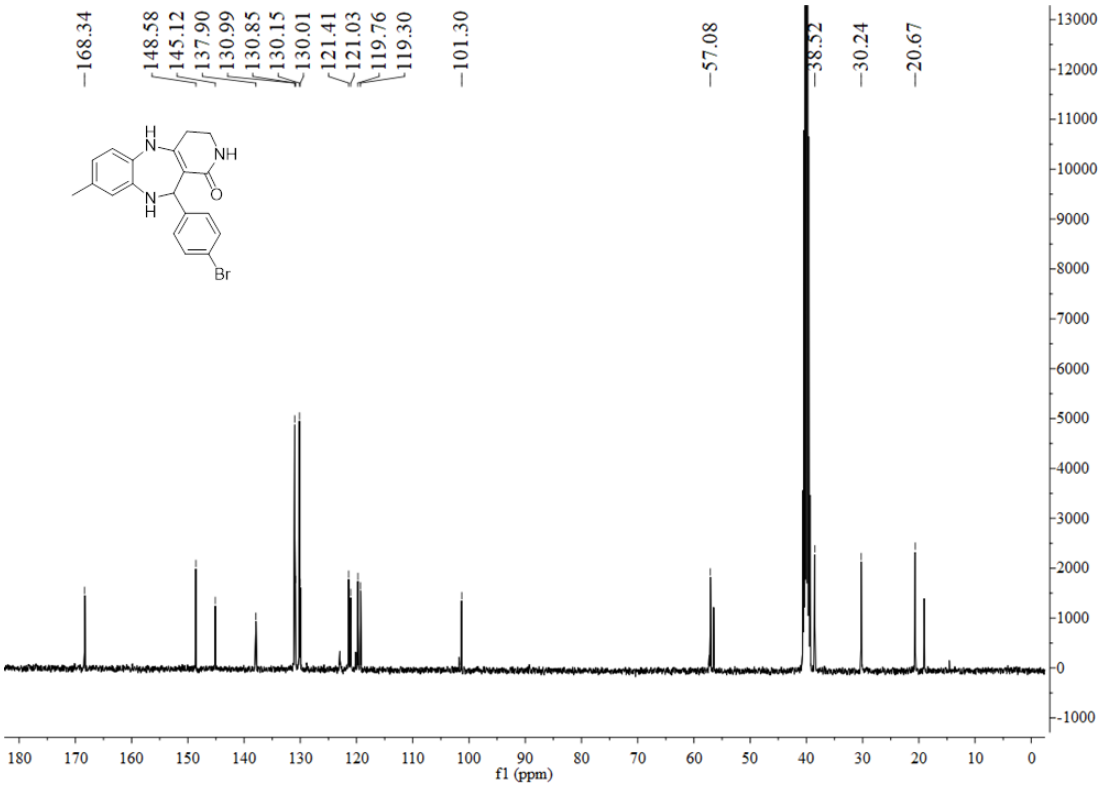
^{1}H NMR spectra of compound **4bac**



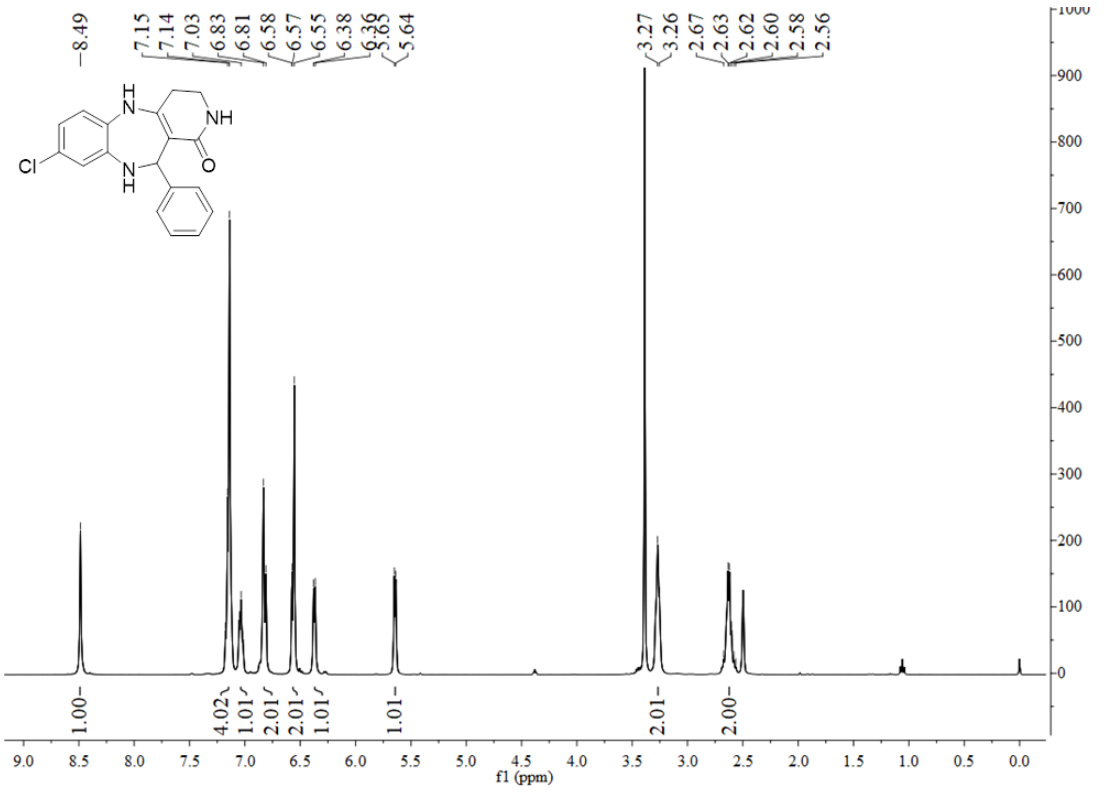
^{13}C NMR spectra of compound **4bac**



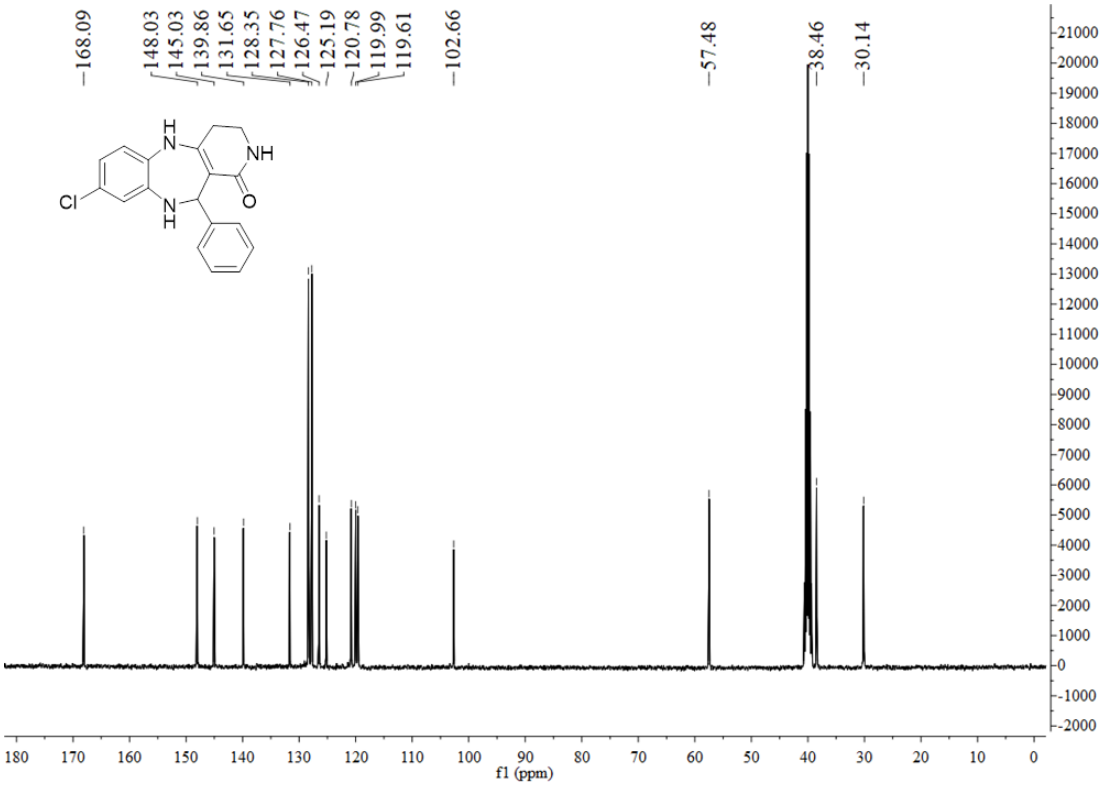
^{1}H NMR spectra of compound **4bad**



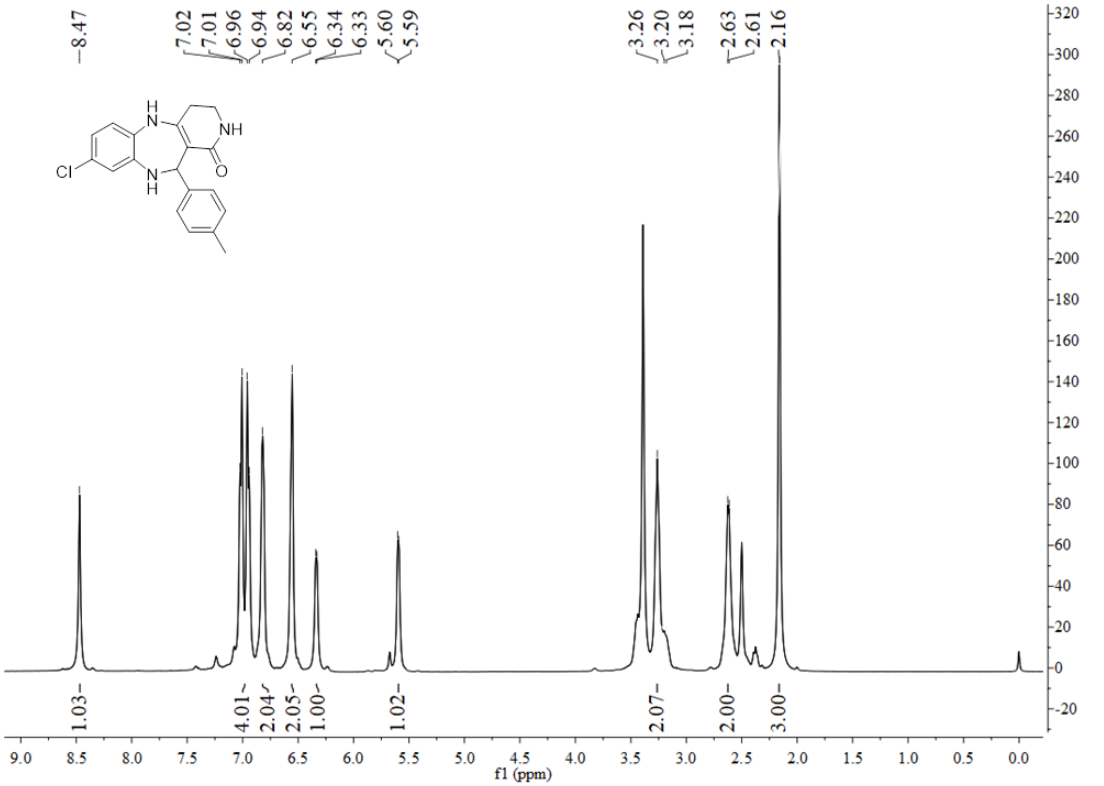
^{13}C NMR spectra of compound **4bad**



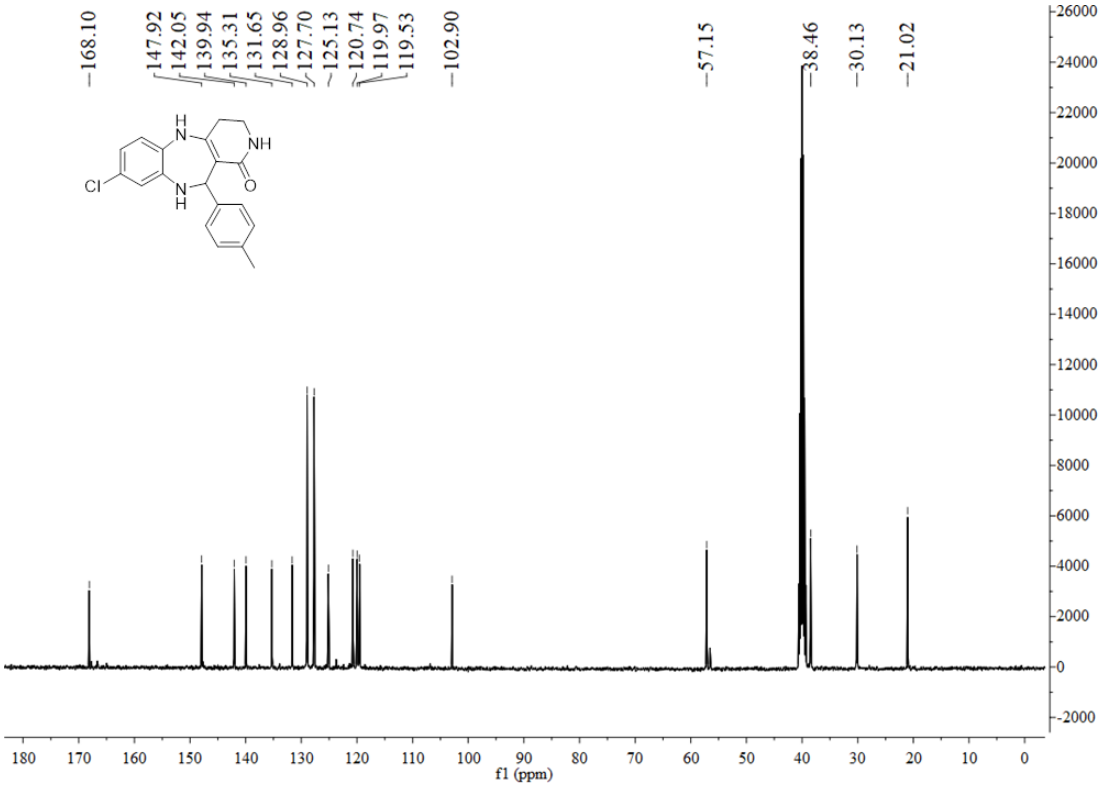
^{1}H NMR spectra of compound **4caa**



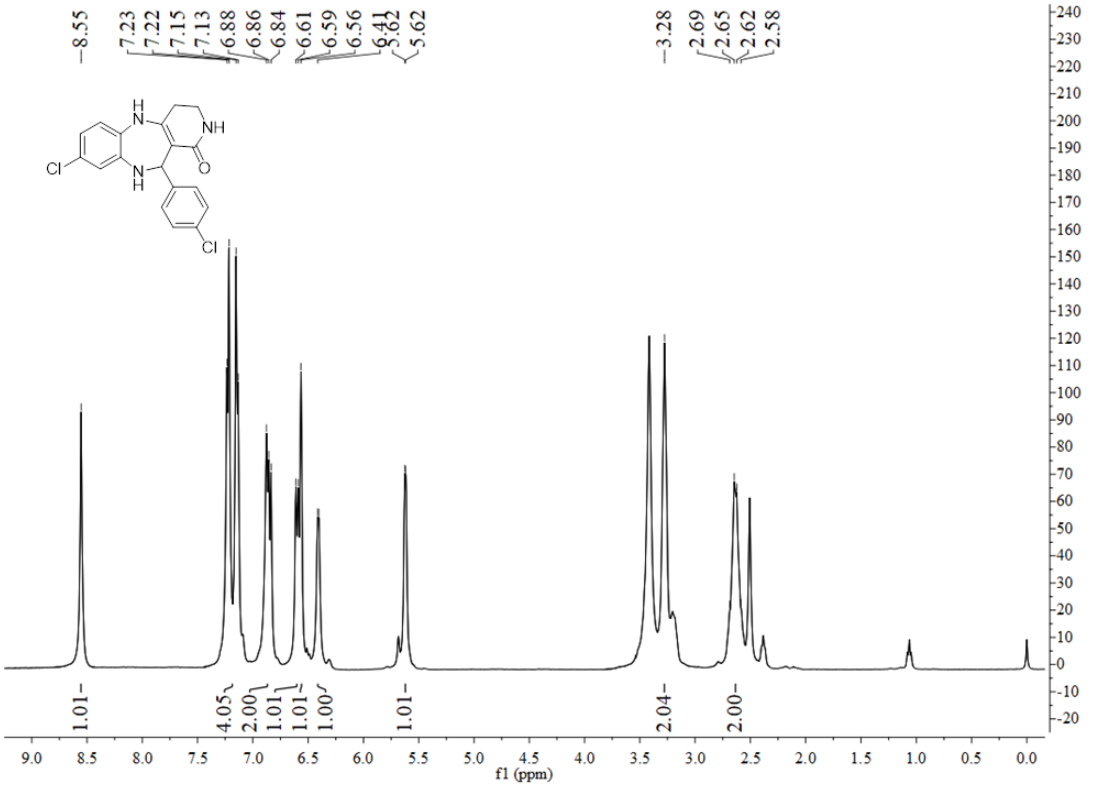
^{13}C NMR spectra of compound **4caa**



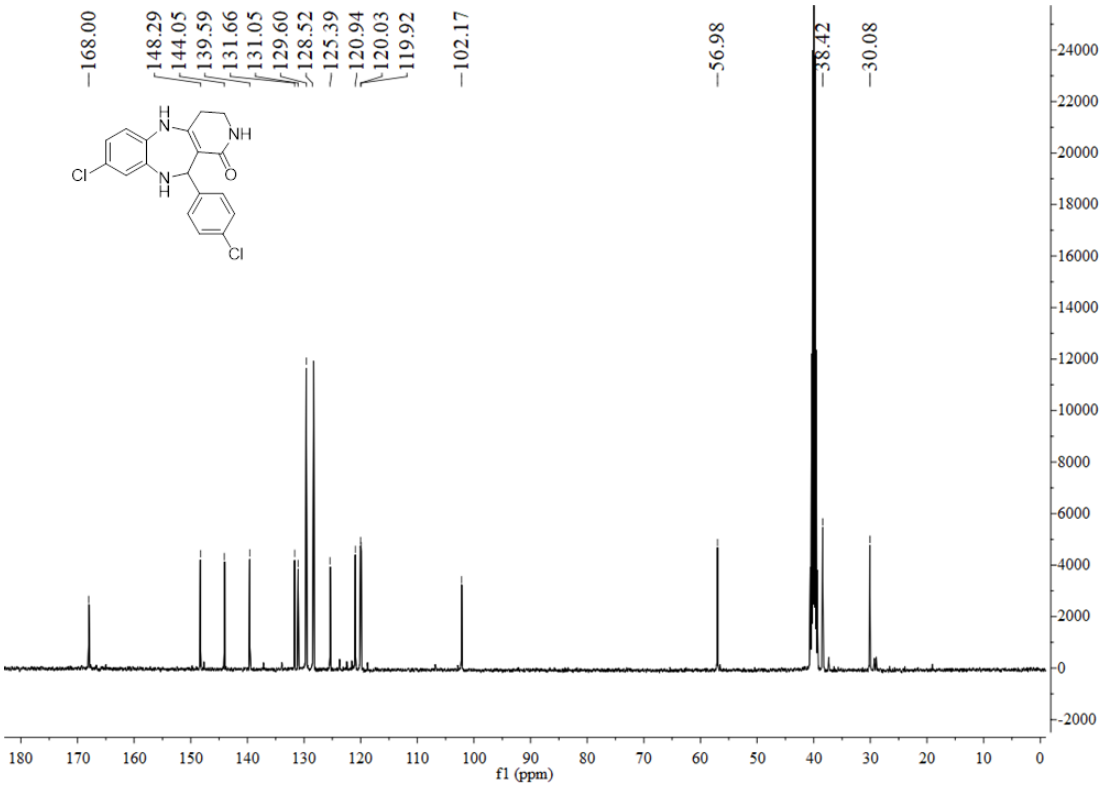
^{1}H NMR spectra of compound **4cab**



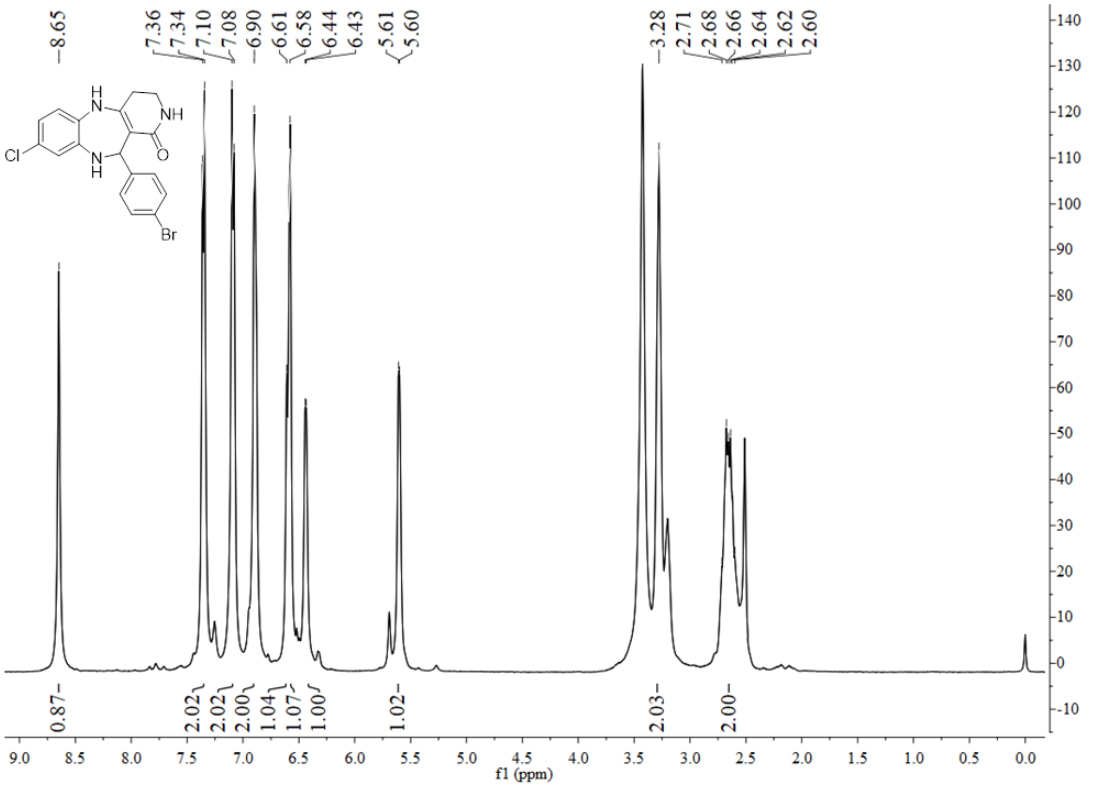
^{13}C NMR spectra of compound **4cab**



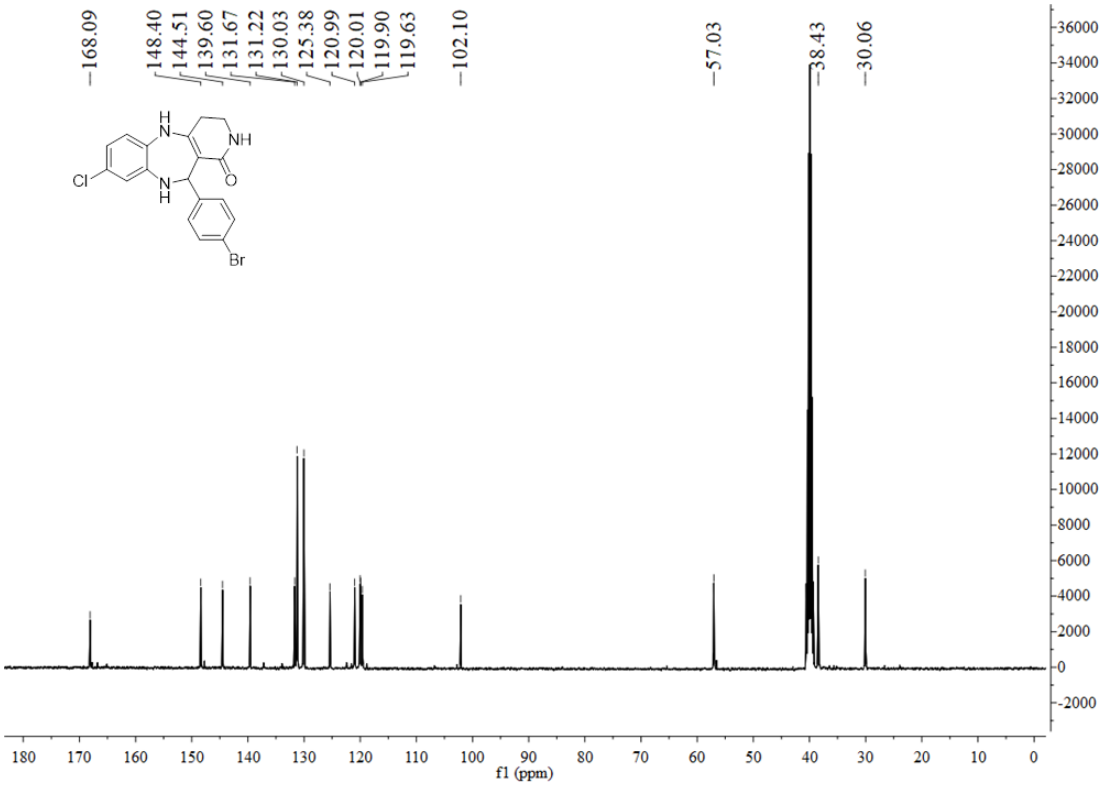
^{1}H NMR spectra of compound **4cac**



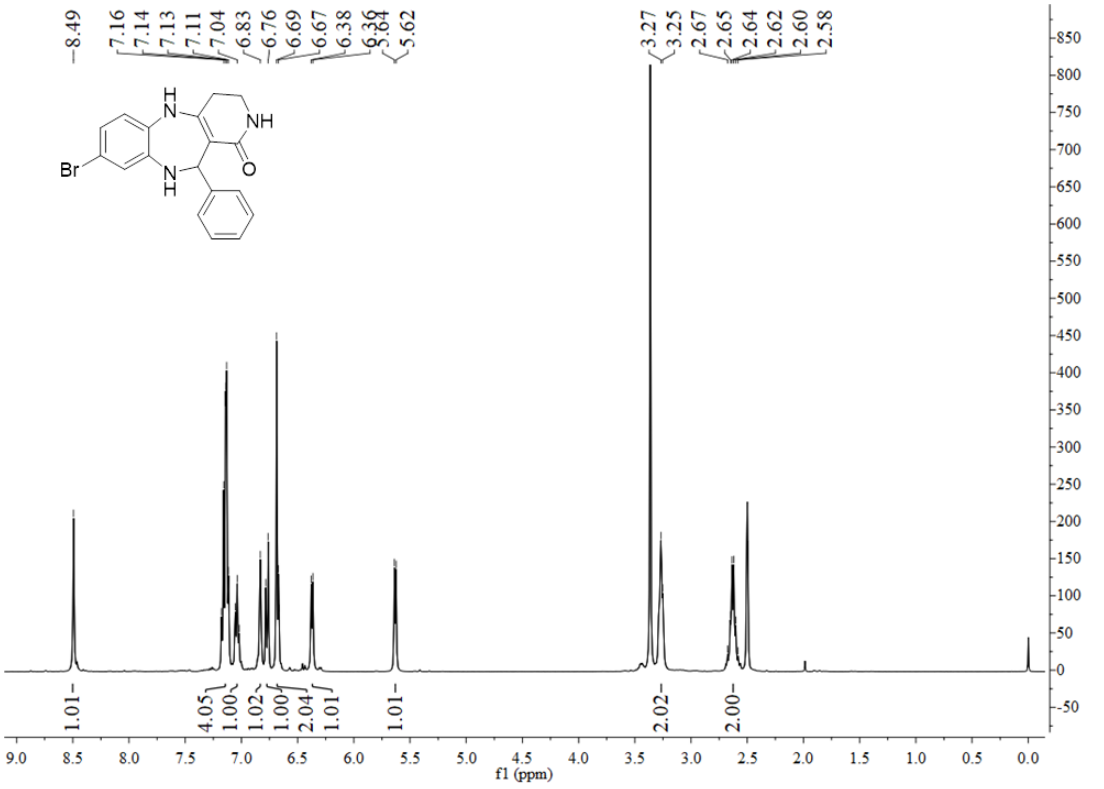
^{13}C NMR spectra of compound **4cac**



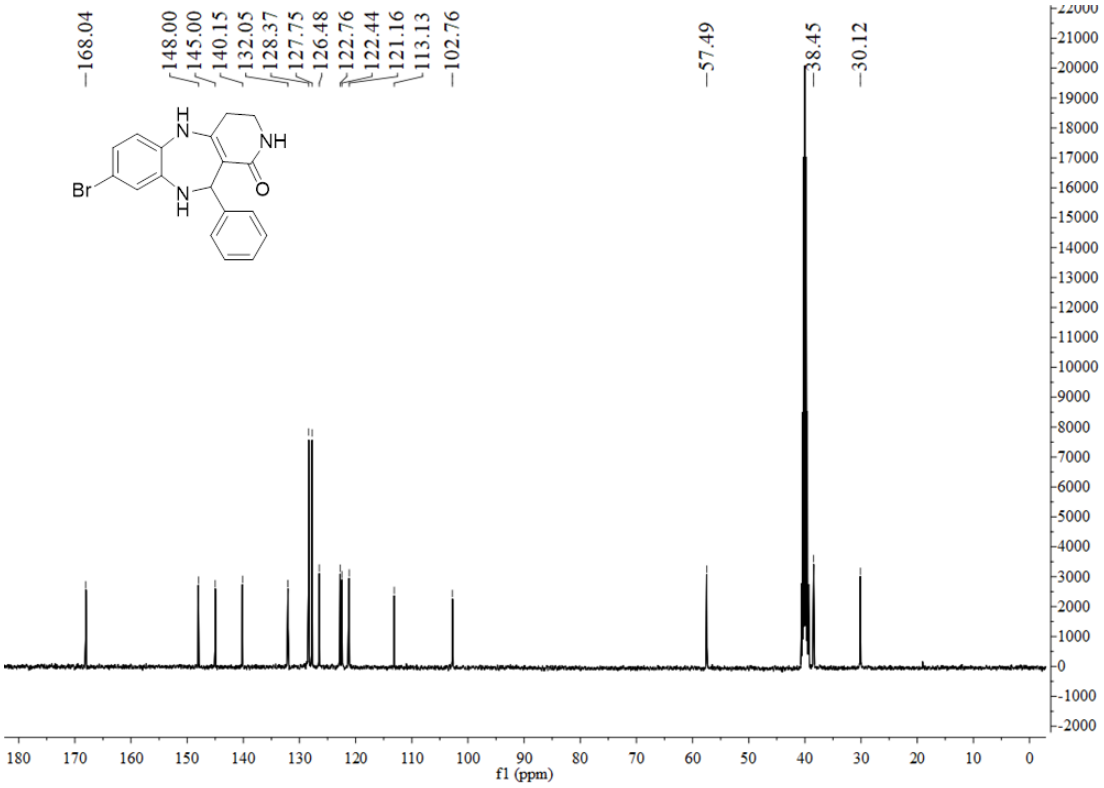
^{1}H NMR spectra of compound **4cad**



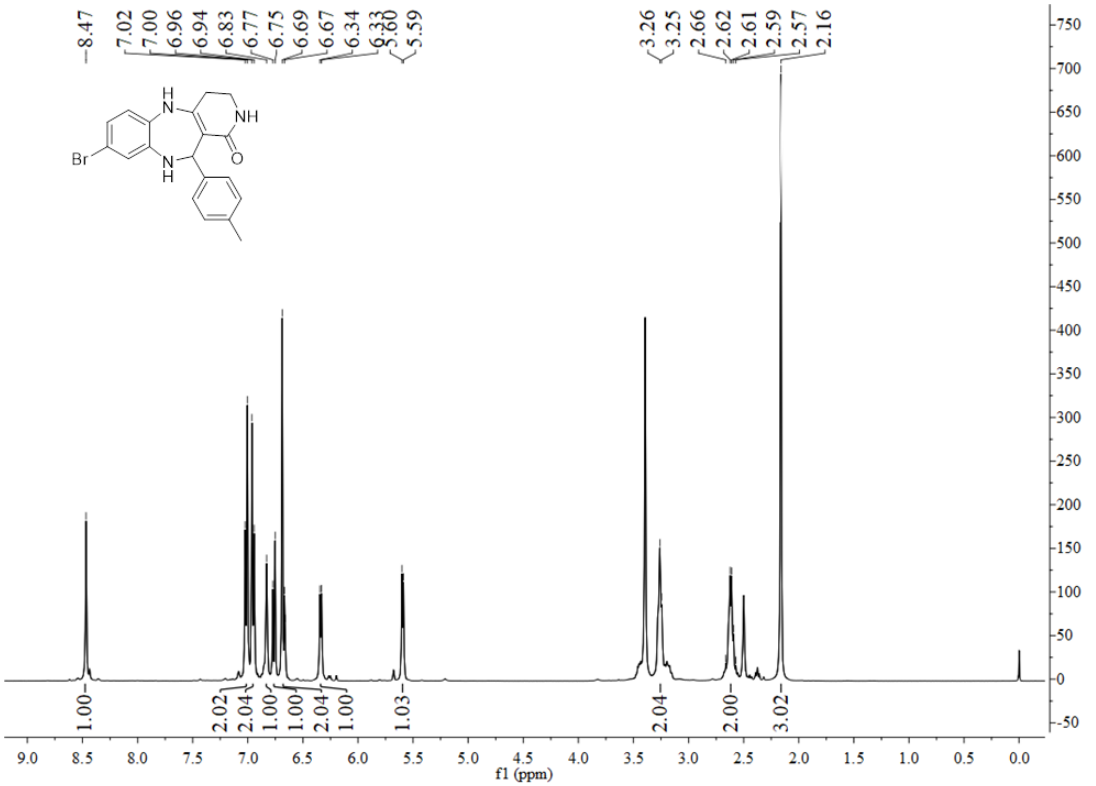
^{13}C NMR spectra of compound **4cad**



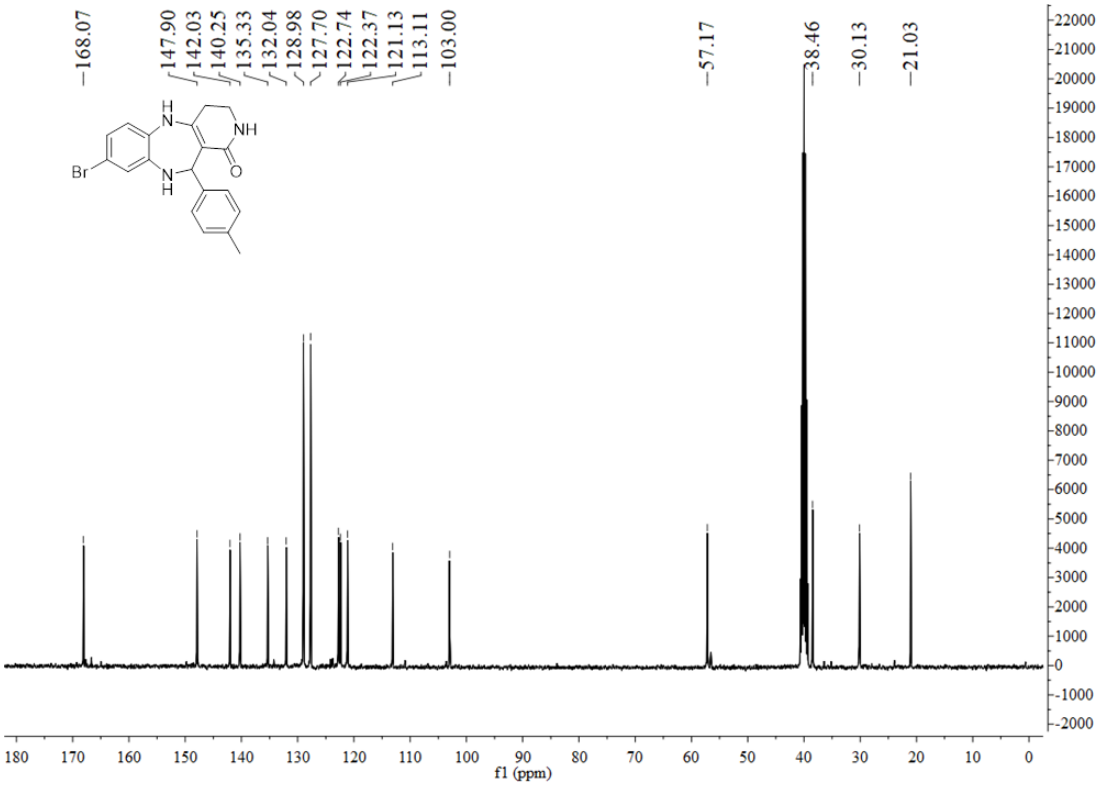
^{1}H NMR spectra of compound **4daa**



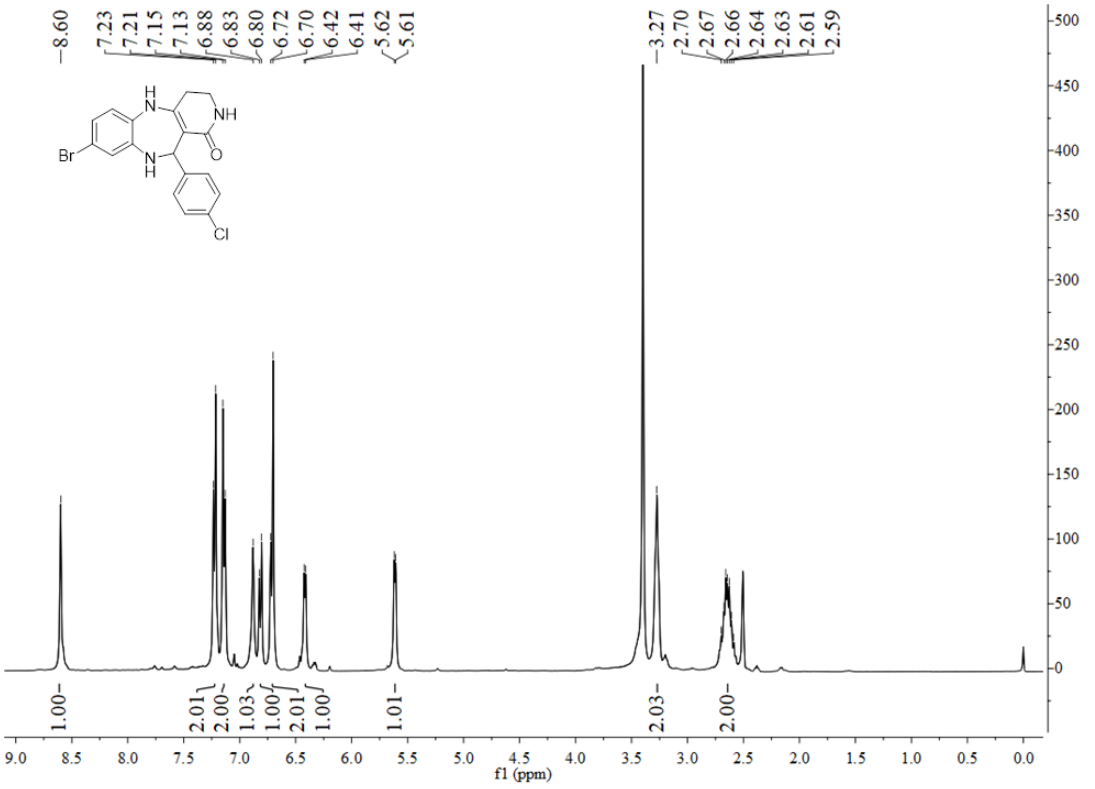
^{13}C NMR spectra of compound **4daa**



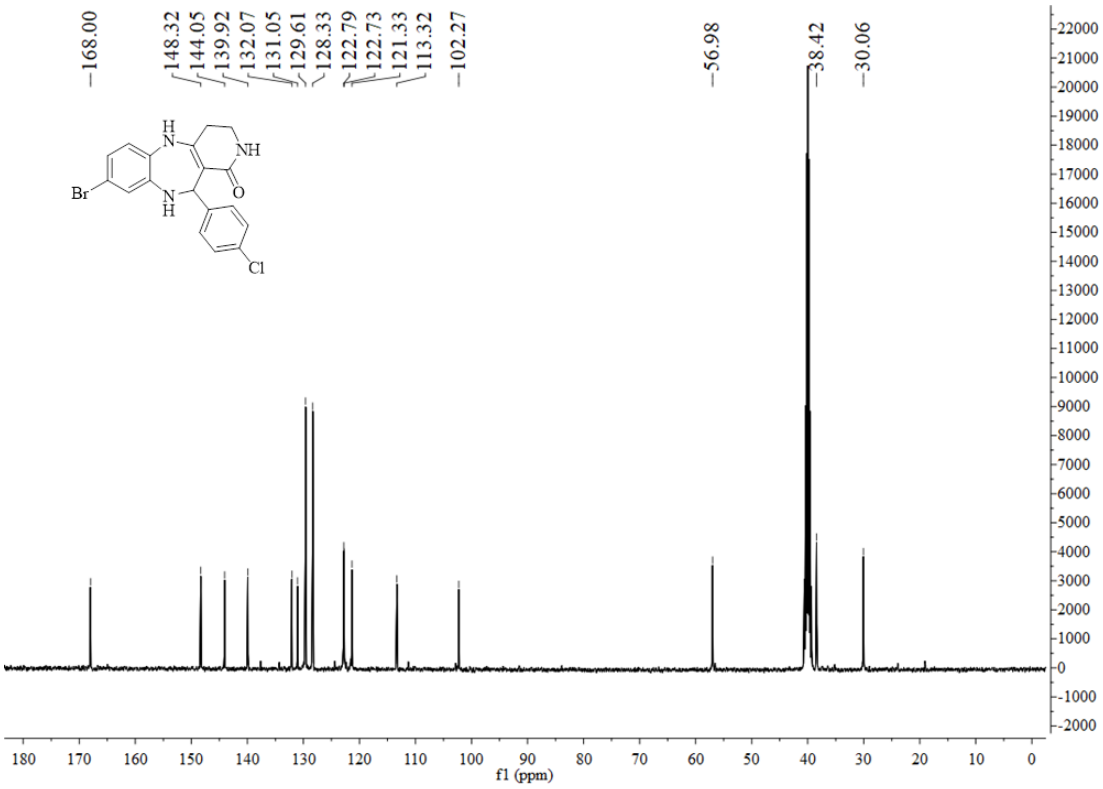
^{1}H NMR spectra of compound **4dab**



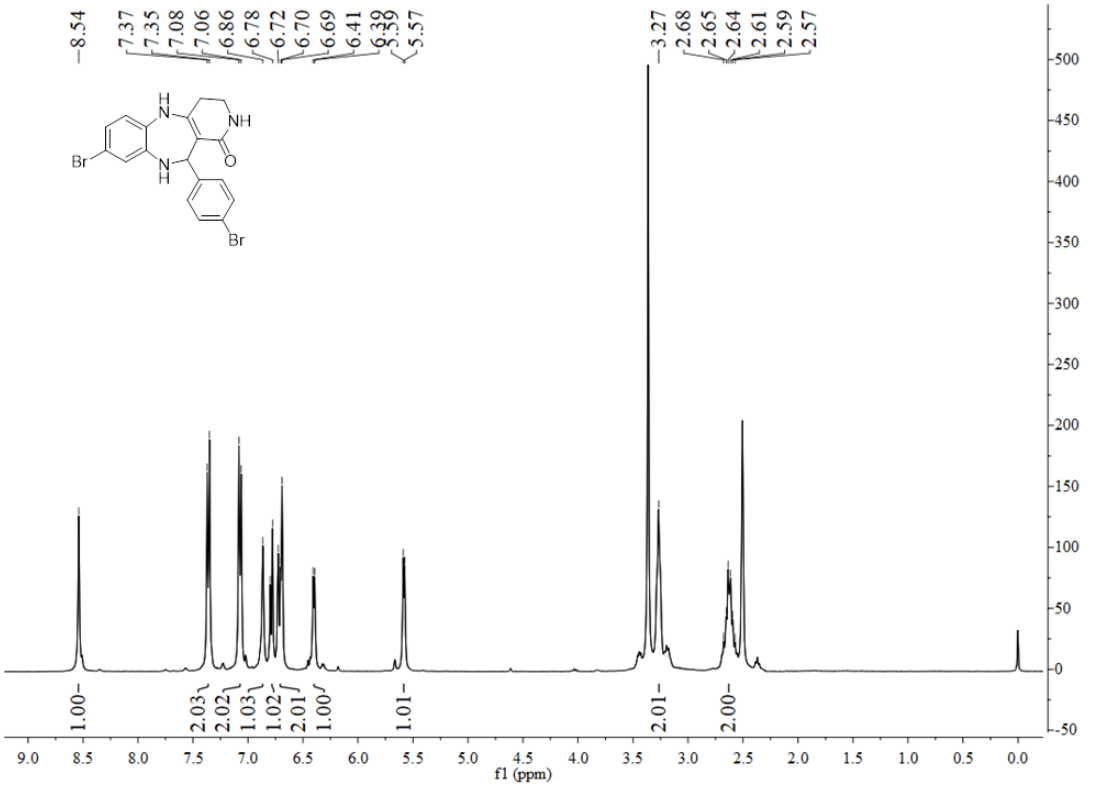
^{13}C NMR spectra of compound **4dab**



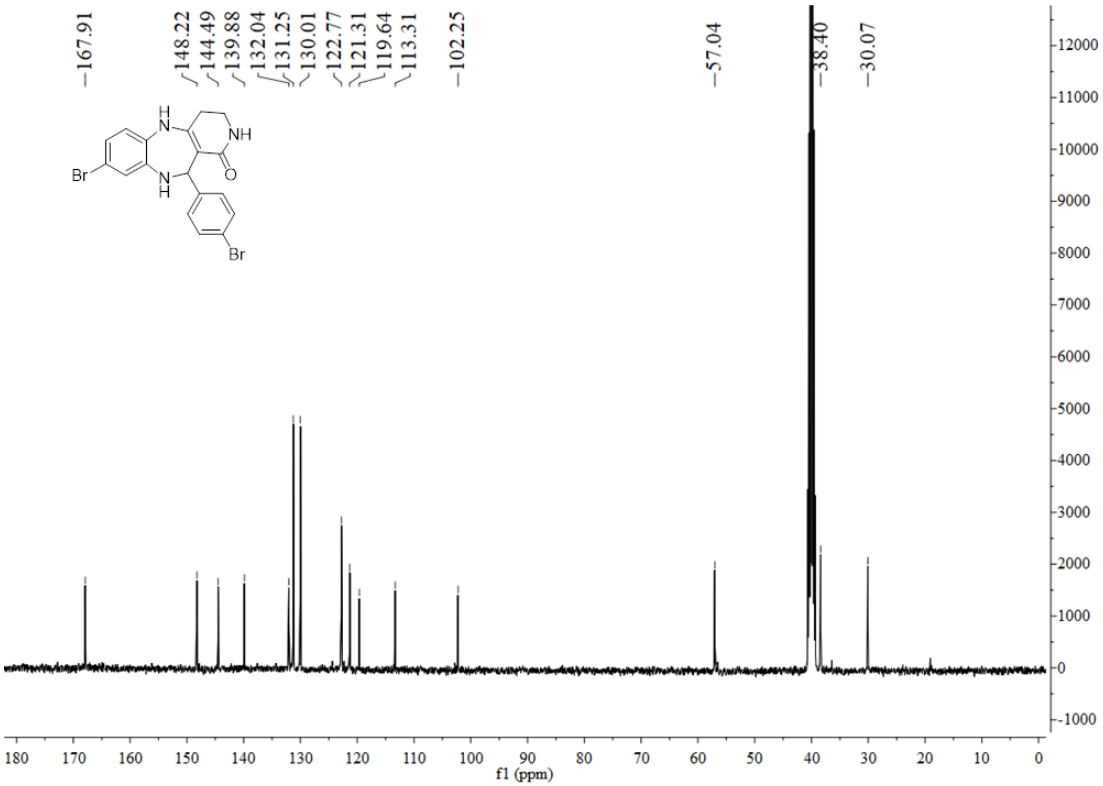
^{1}H NMR spectra of compound **4dac**



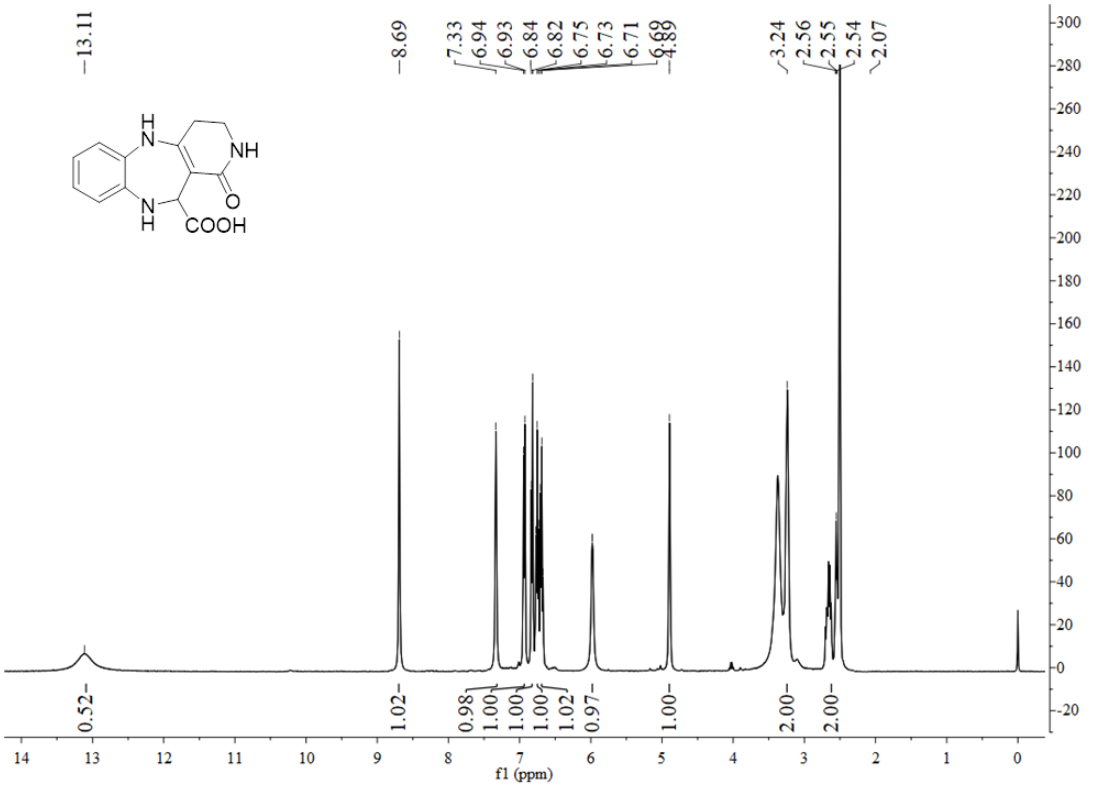
^{13}C NMR spectra of compound **4dac**



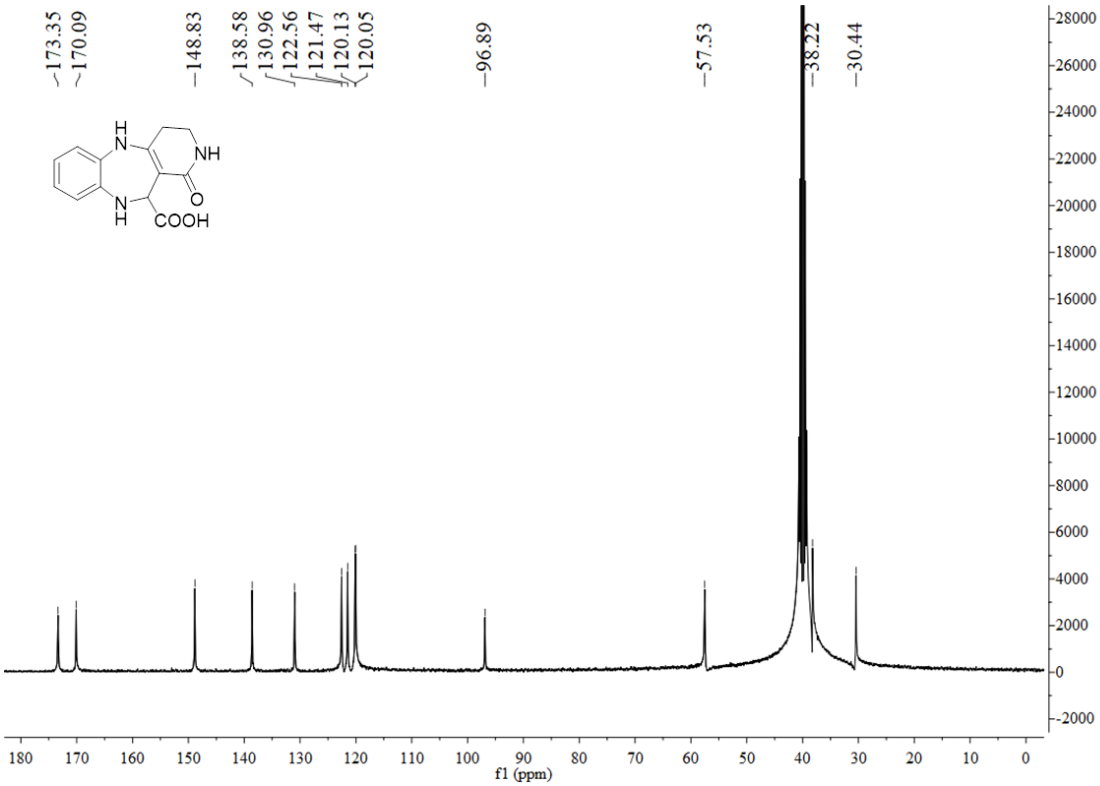
^{1}H NMR spectra of compound **4dad**



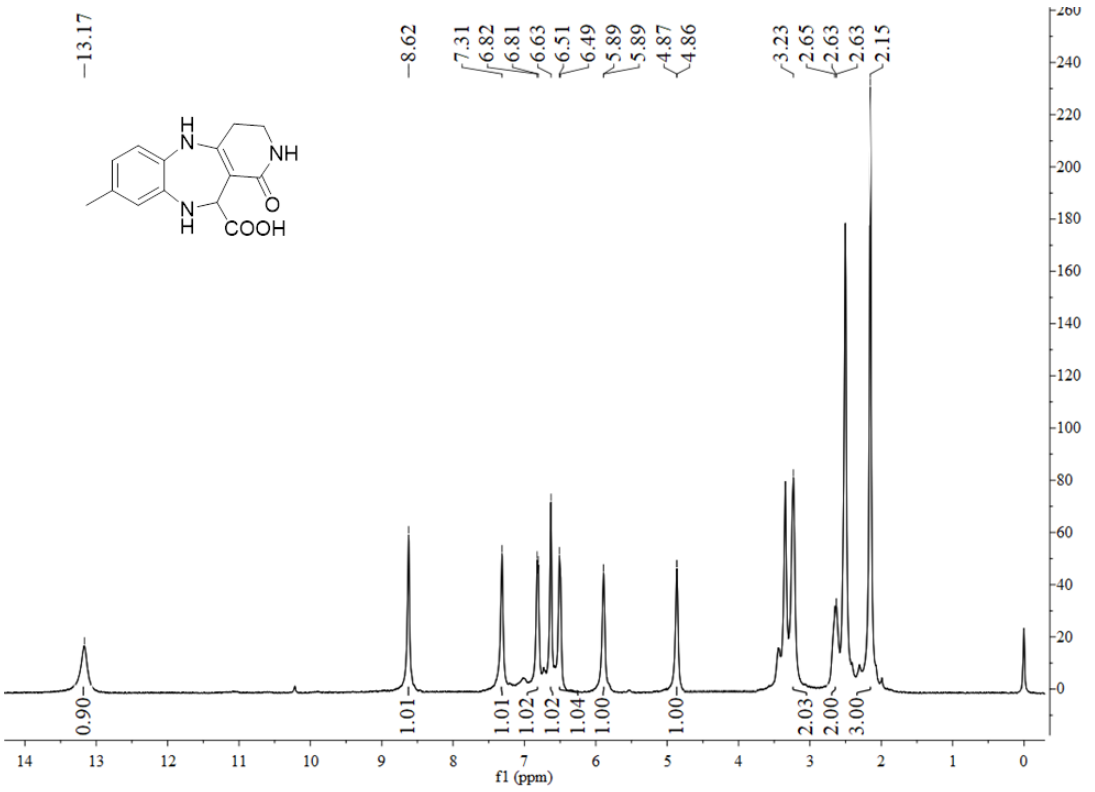
^{13}C NMR spectra of compound **4dad**



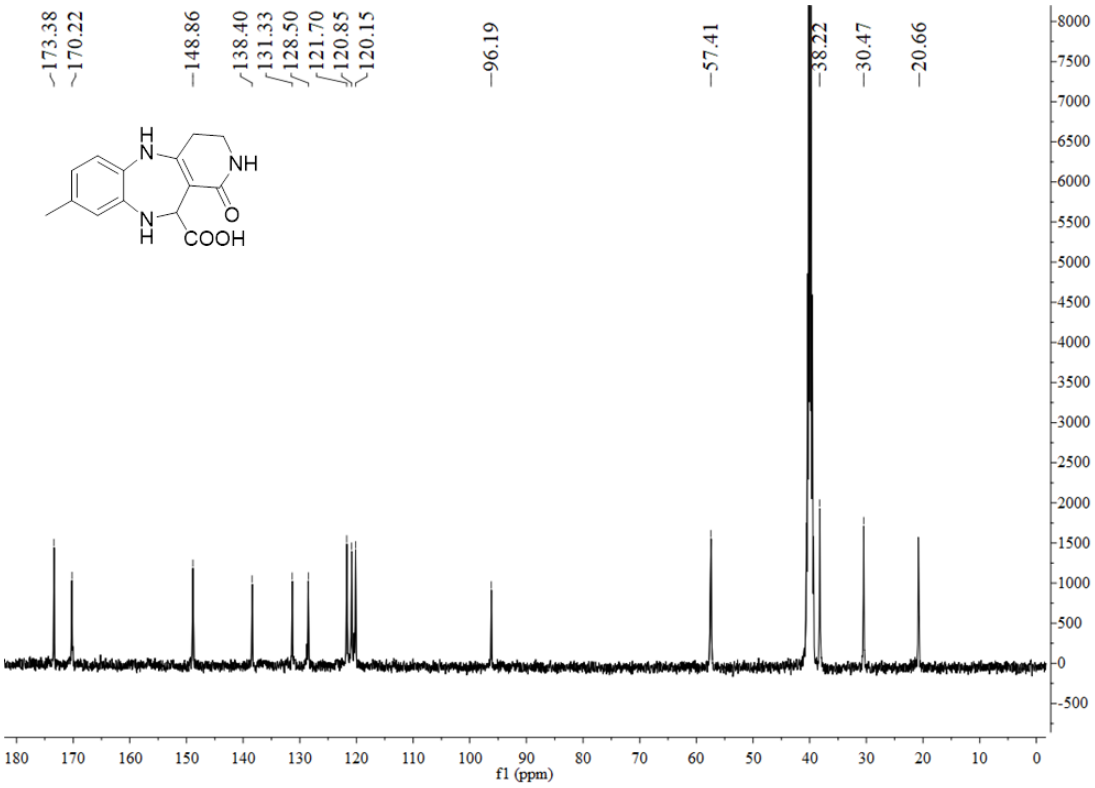
^{1}H NMR spectra of compound **4aae**



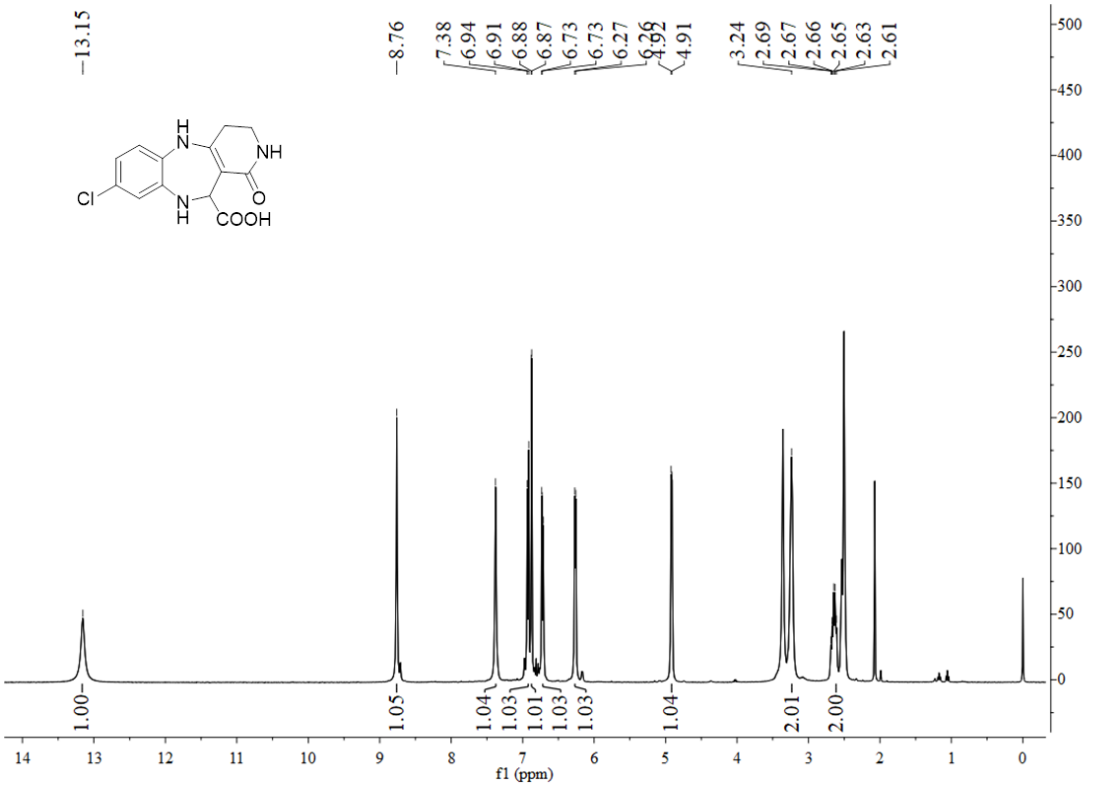
^{13}C NMR spectra of compound **4aae**



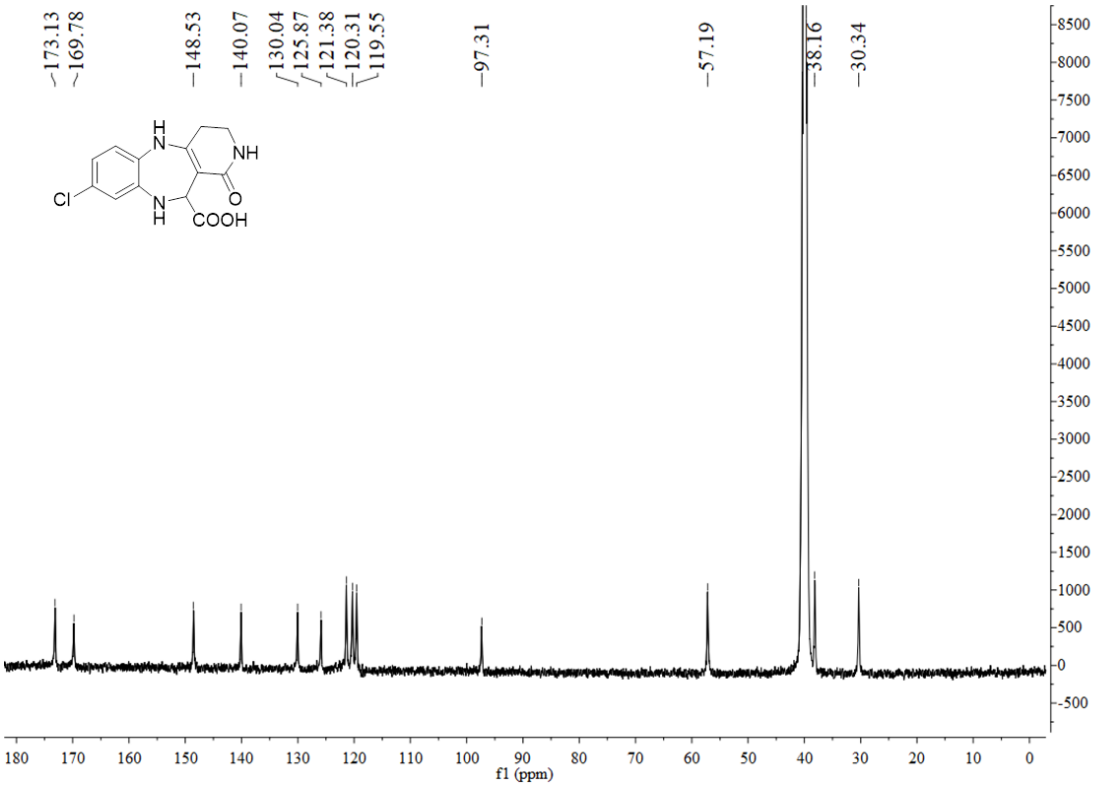
^{1}H NMR spectra of compound **4bae**



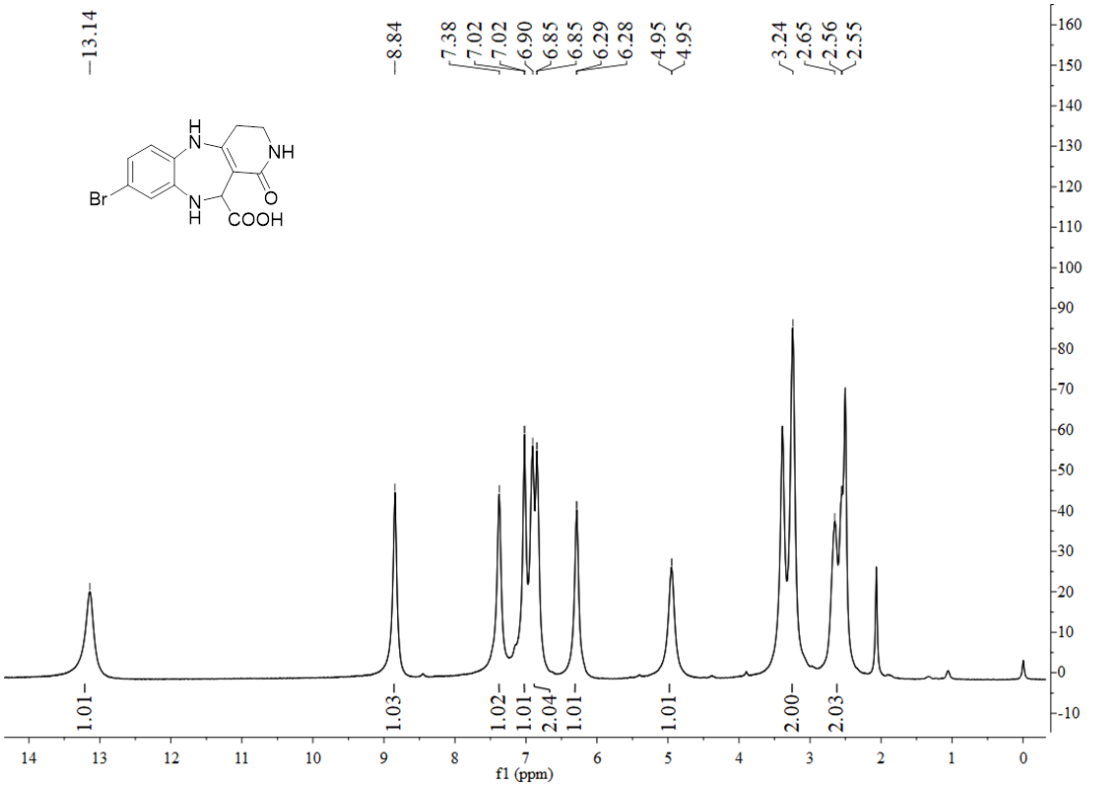
^{13}C NMR spectra of compound **4bae**



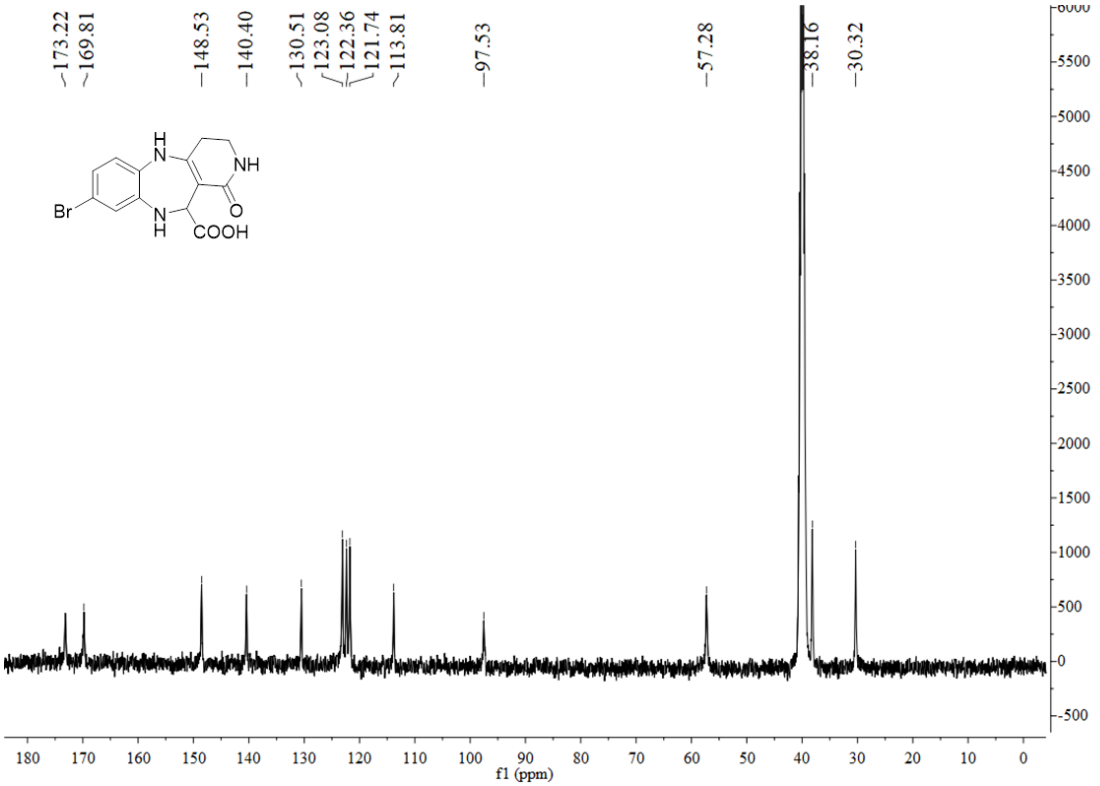
^{1}H NMR spectra of compound **4cae**



^{13}C NMR spectra of compound **4cae**

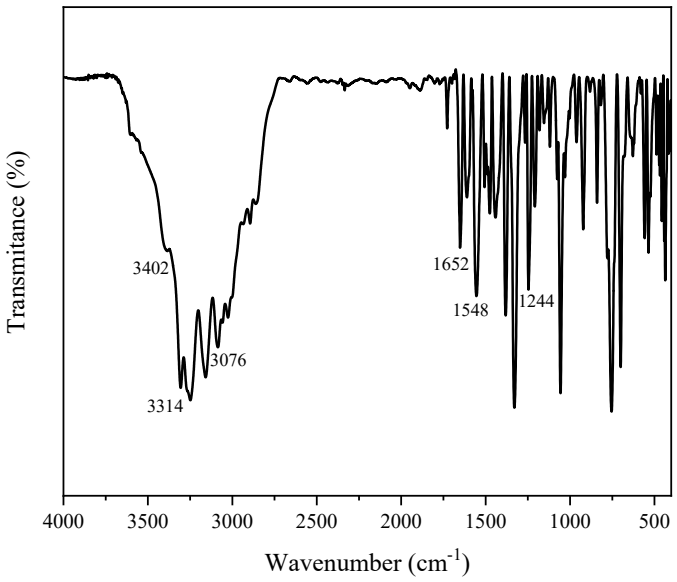


^{1}H NMR spectra of compound **4dae**

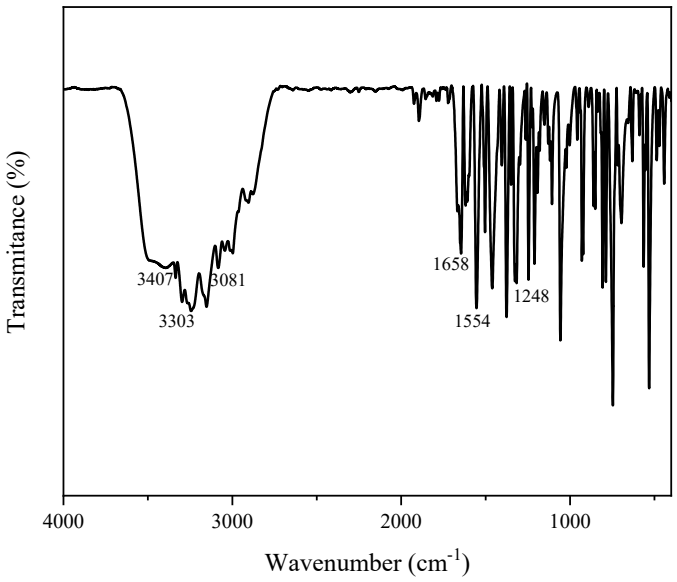


^{13}C NMR spectra of compound **4dae**

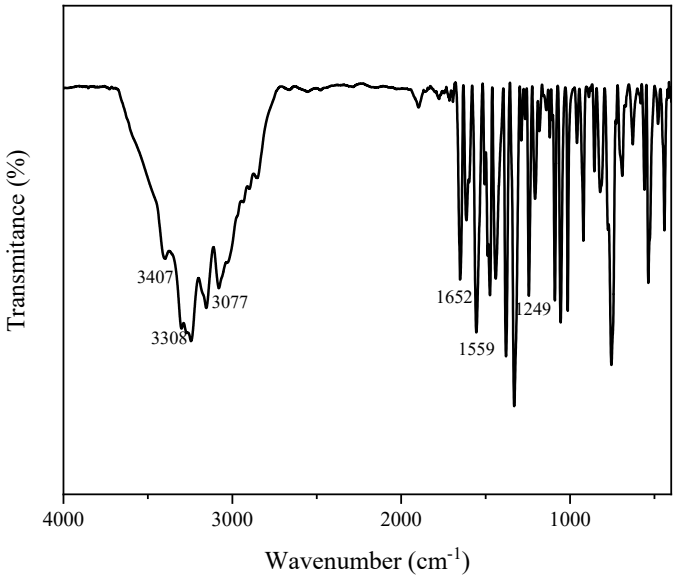
IR spectra of the synthesized compound **4aaa**-**4dae**



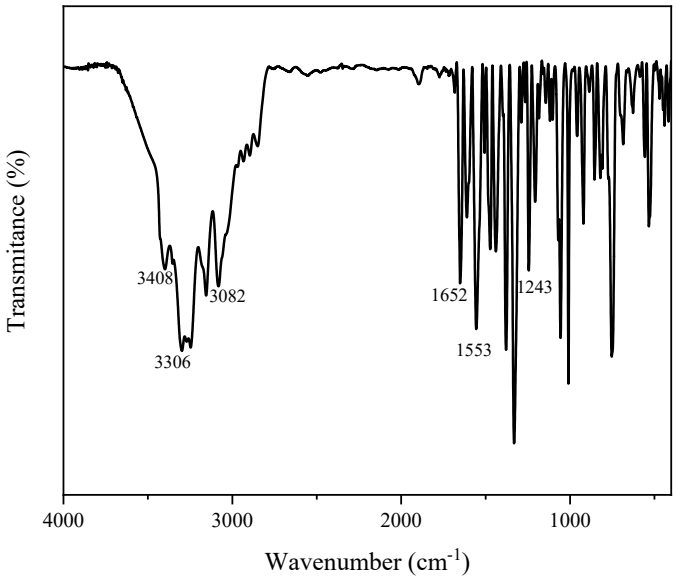
IR spectra of compound **4aaa**



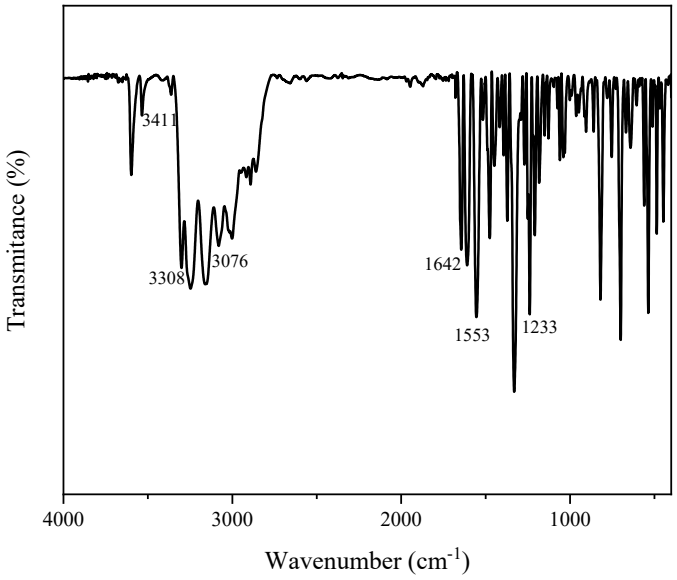
IR spectra of compound **4aab**



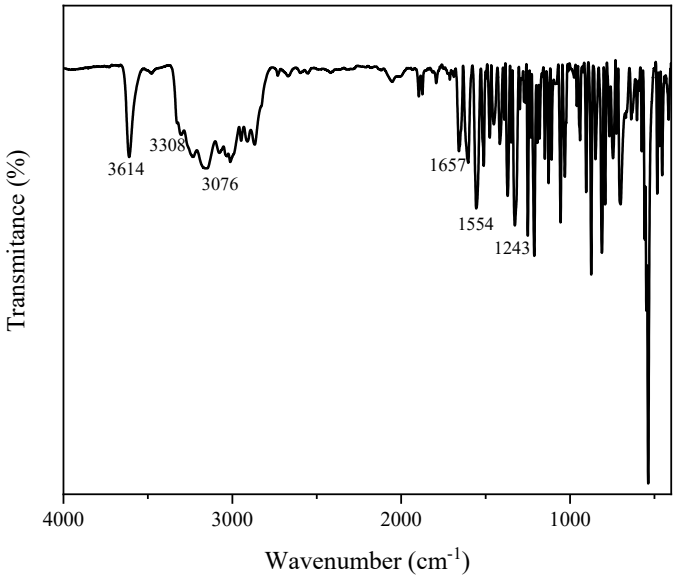
IR spectra of compound **4aac**



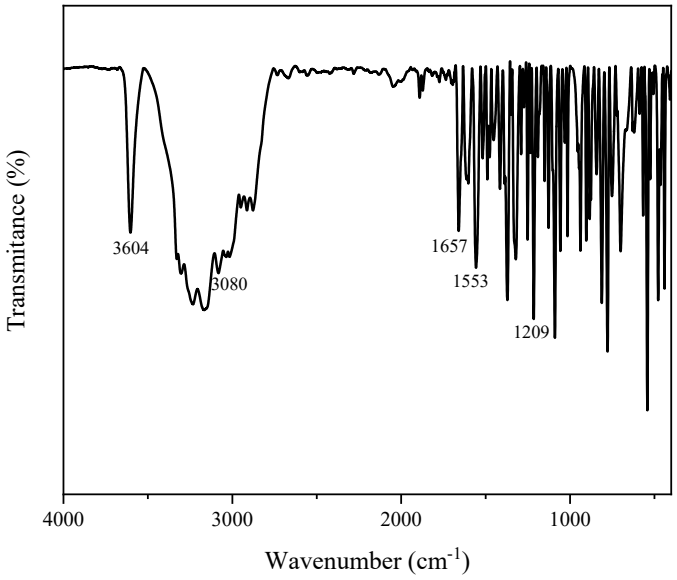
IR spectra of compound **4aad**



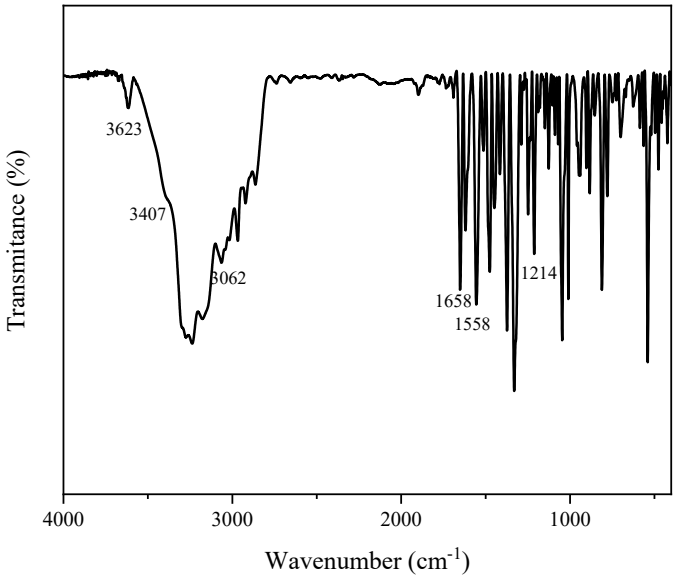
IR spectra of compound **4baa**



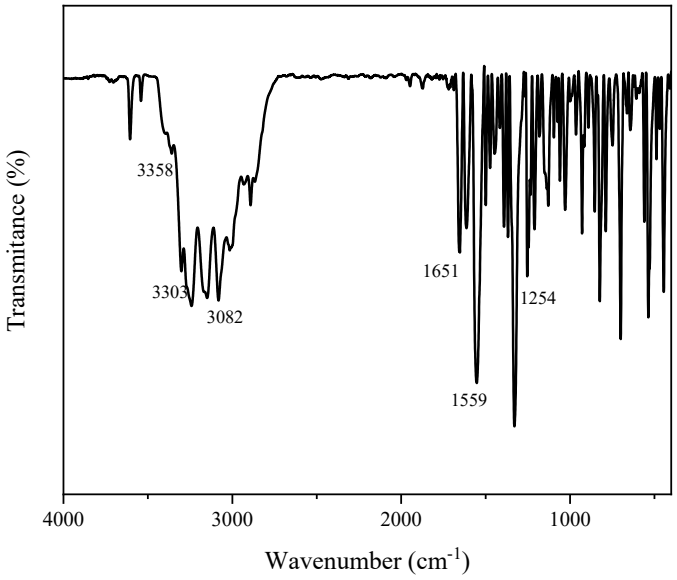
IR spectra of compound **4bab**



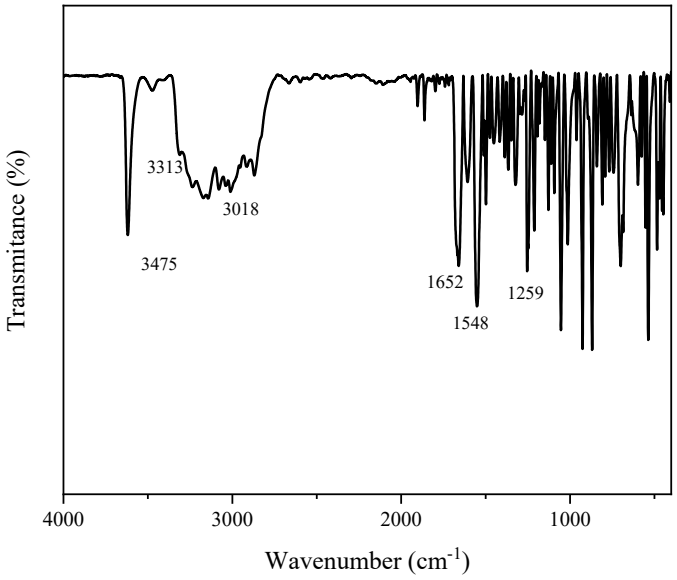
IR spectra of compound **4bac**



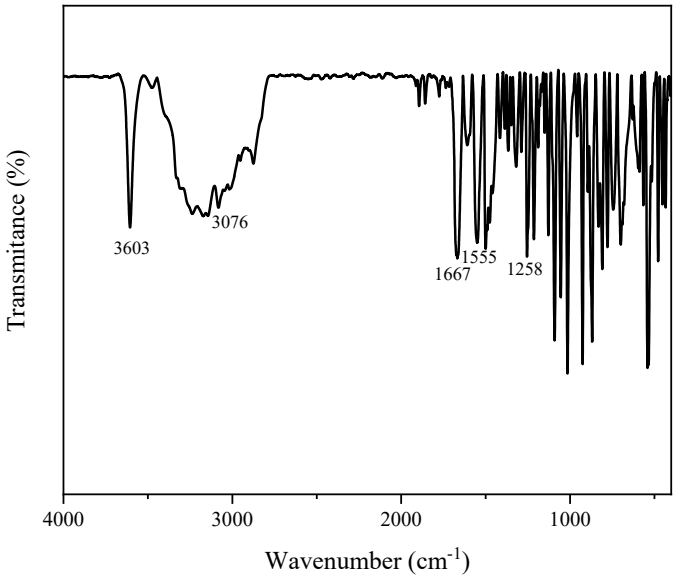
IR spectra of compound **4bad**



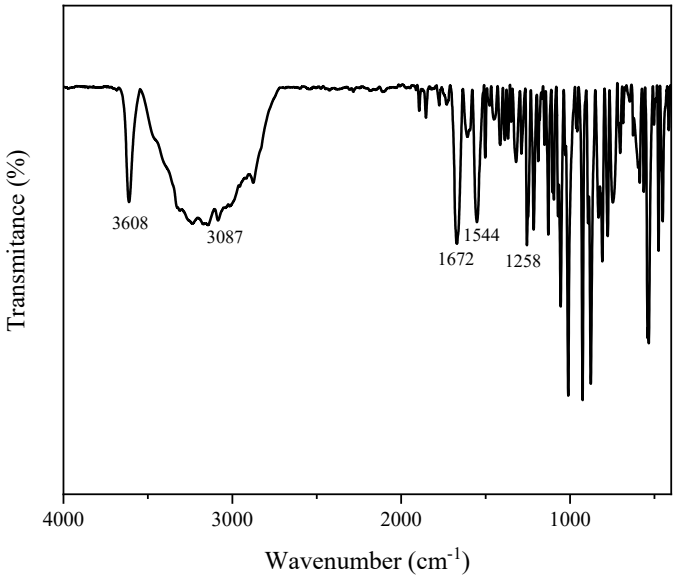
IR spectra of compound **4caa**



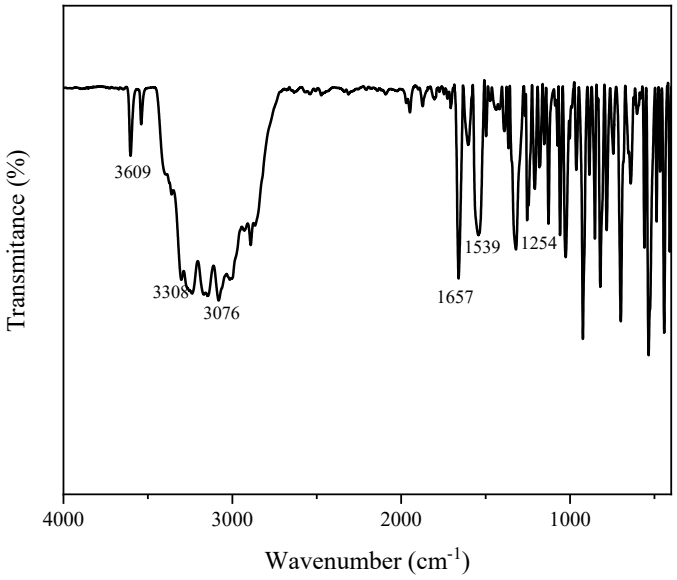
IR spectra of compound **4cab**



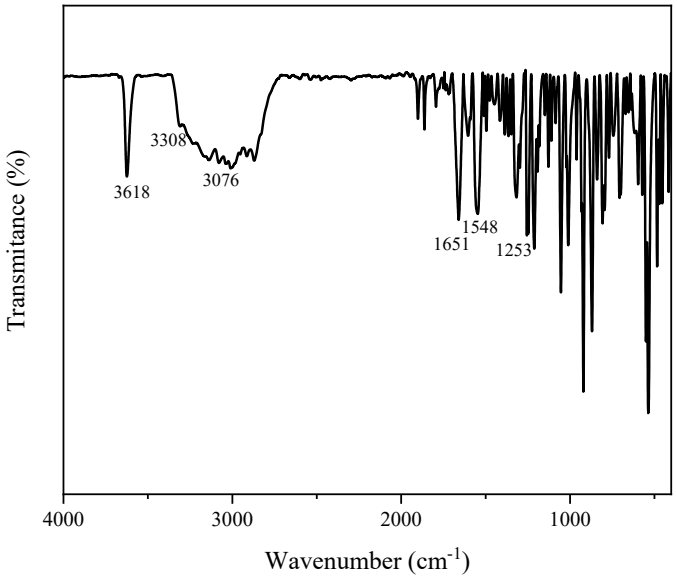
IR spectra of compound **4cac**



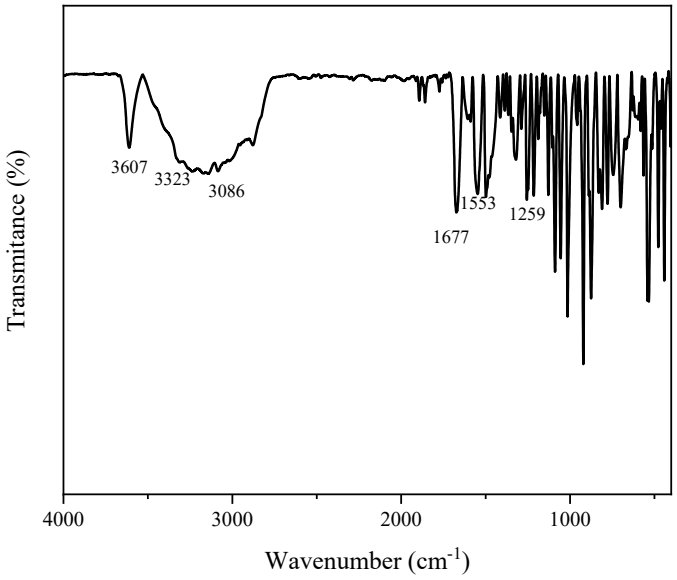
IR spectra of compound **4cad**



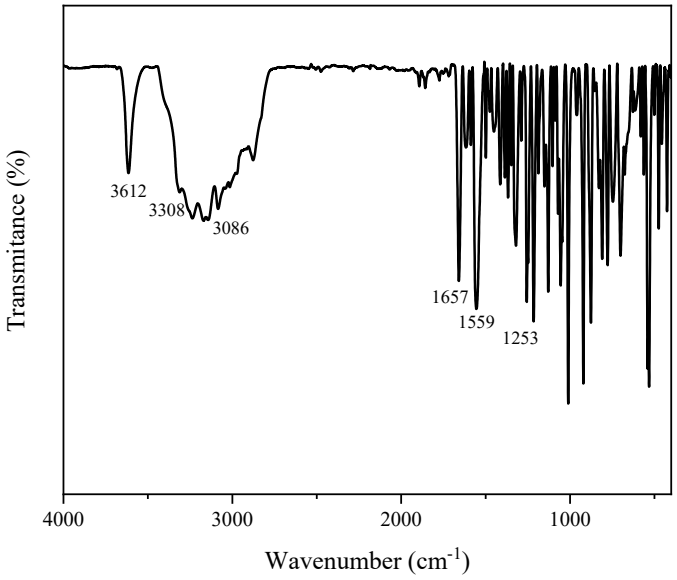
IR spectra of compound **4daa**



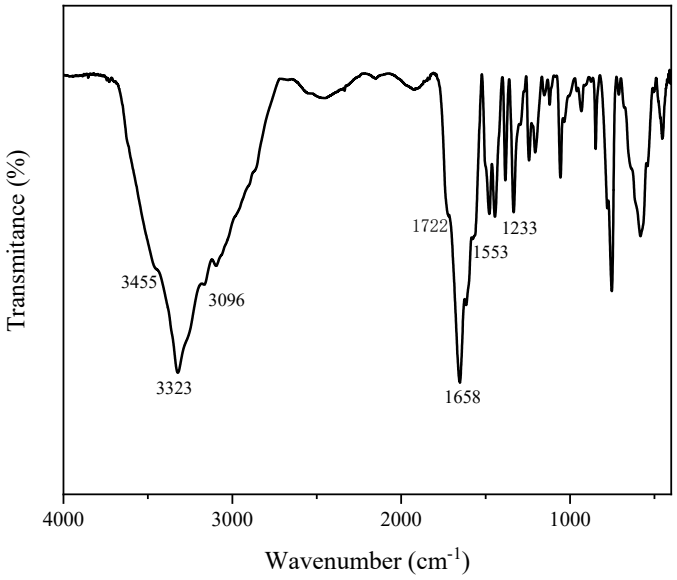
IR spectra of compound **4dab**



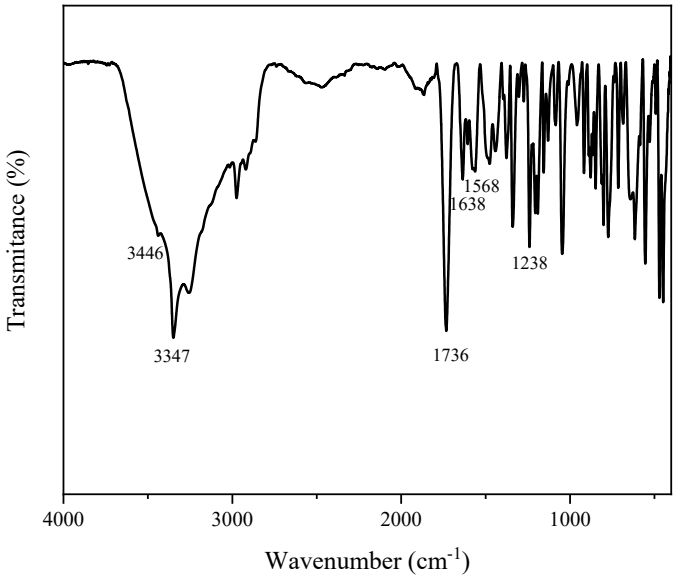
IR spectra of compound **4dac**



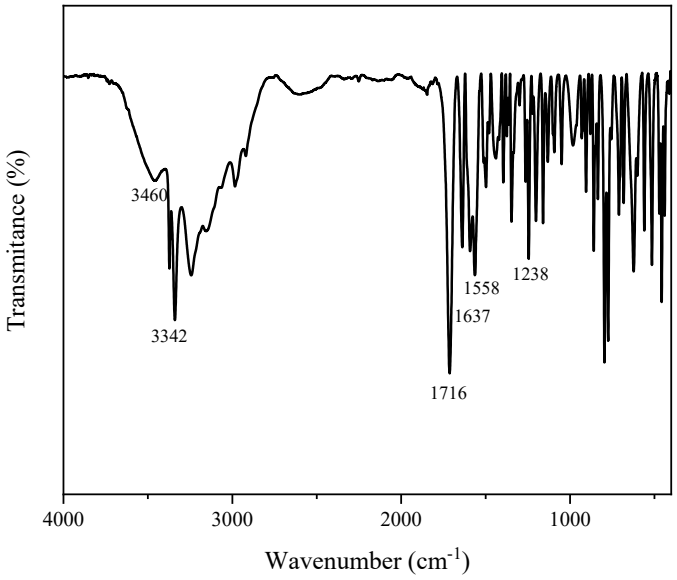
IR spectra of compound **4dad**



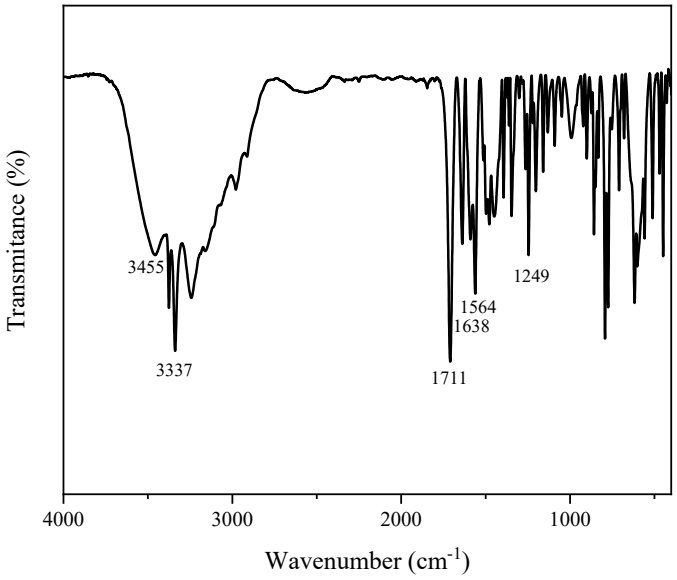
IR spectra of compound **4aae**



IR spectra of compound **4bae**



IR spectra of compound **4cae**



IR spectra of compound **4dae**

MS spectra of the synthesized compound **4aaa**-**4dae**

MS of compound **4aaa**

MS of compound **4aab**

MS of compound **4aac**

MS of compound **4aad**

MS of compound **4baa**

MS of compound **4bab**

MS of compound **4bac**

MS of compound **4bad**

MS of compound **4caa**

MS of compound **4cab**

MS of compound **4cac**

MS of compound **4cad**

MS of compound **4daa**

MS of compound **4dab**

MS of compound **4dac**

MS of compound **4dad**

MS of compound **4aae**

MS of compound **4bae**

MS of compound **4cae**

MS of compound **4dae**