Supporting Information

A Facile Synthesis of Tetrahydroimidazo[1,2-*a*]pyridines and Tetrahydrobenzo[*b*]imidazo[1,2,3-*ij*][1,8]naphthyridines through NHC-Catalyzed Cascade Annulations

Changsheng Yao,[*†] Weihui Jiao,[‡] Zhaoxin Xiao,[‡] Yuanwei Xie,[‡] Tuanjie Li,[‡] Xiangshan Wang,[‡] Rui Liu[‡] and Chenxia Yu[‡]

[†]*School of Chemistry and Engineering, Key Laboratory of Biotechnology for Medicinal Plant, Jiangsu Normal University, Xuzhou, 221116, P. R. China*

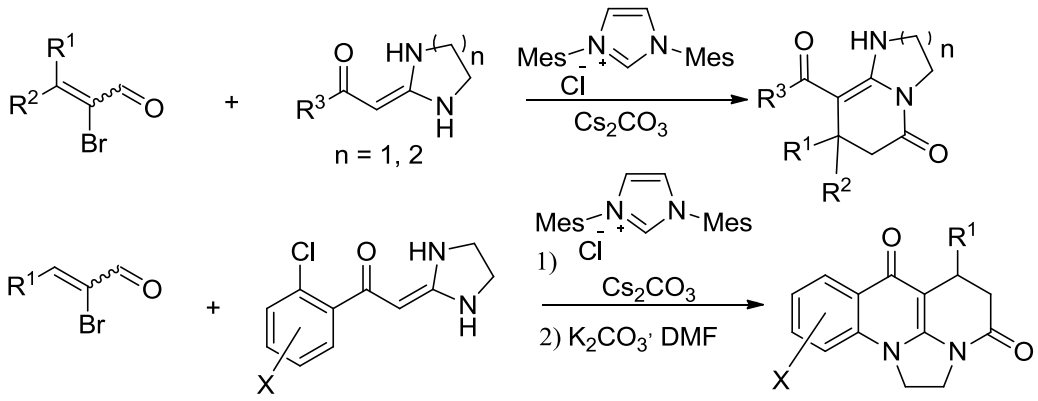
[‡]*School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China*

[*]*To whom correspondence should be addressed. Tel.: 0086-516-83500065; fax: 0086-516-83500065; E-mail: csyao@jsnu.edu.cn*.

1 General considerations

Common reagents and materials were purchased from commercial sources and purified by distillation or recrystalization. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^{1}H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d_6 (100 MHz, ^{13}C NMR) or $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard. High-resolution mass spectra (HRMS) were obtained on a micrOTOF-Q Ⅱ HRMS/MS instrument (Bruker) with the technique of electrospray ionization.

2. Experimental

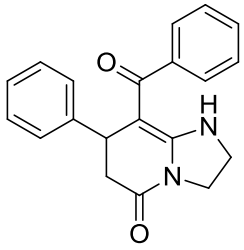


General Procedure for the Synthesis of **3**: Into an oven-dried 25 mL vial were weighed precatalyst **4d** (34 mg) and Cs_2CO_3 (520 mg). Toluene (7 mL) was added to the mixture. The resulting mixture was stirred at 25 ^oC for 5 min followed by the addition of α-bromo-α,β-unsaturated aldehyde(1.5 mmol) and HKA **2** (1 mmol) after the reaction mixture was stirred for about 7 min, the reaction system was kept at 65 ^oC with stirring until completion (monitored by TLC). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, mixtures of ethyl acetate / petroleum ether, 3:1, v/v).

General Procedure for the Synthesis of **5**: Into an oven-dried 25 mL vial were weighed catalyst **4d** (34 mg) and Cs_2CO_3 (520 mg). Toluene (7 mL) was added to the mixture. The resulting mixture was stirred at 25 ^oC for 5 min followed by the addition of α-bromo-α,β-unsaturated aldehyde(1.5 mmol) and HKA **2** (1 mmol) after the reaction mixture was stirred for about 7 min, the reaction system was kept at 65 ^oC with stirring until completion (monitored by TLC). After the removal of the solvent under reduced pressure, K_2CO_3 (138 mg, 1.0 mmol) and DMF (9 mL) was added and the mixture was heated to 100 ^oC. After the completion of the reaction as indicated by TLC, the mixture was cooled to room temperature. An amount of 50 mL water was added to precipitate the product, which was then filtered and washed with small amount of ethanol to give the pure product **5**.

3. Spectral data for all compounds

Compound 3a: 8-benzoyl-7-phenyl-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one

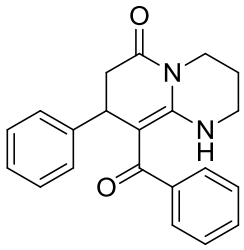


White solid; mp: 165-167 ^{o}C (reported 166-167 ^{o}C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.27 – 7.15 (m, 7H), 7.02 (d, J = 8.0 Hz, 2H), 4.14 – 4.07 (m, 2H), 3.96 – 3.83 (m, 3H), 2.97 (dd, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H), 2.78 (dd, J_1 = 2.0 Hz, J_2 = 16.4 Hz, 1H); IR (potassium bromide) (v, cm^{-1}): 3267, 2977, 2902, 1694, 1633, 1518, 1485, 1370, 1314, 1207, 1014, 721, 700; HRMS (ESI): m/z Calcd. for $C_{20}H_{17}N_2O_2$ [M-H]$^-$: 317.1290, found: 317.1290.

Compound 3b:
7-(4-chlorophenyl)-8-(2,4-dichlorobenzoyl)-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one

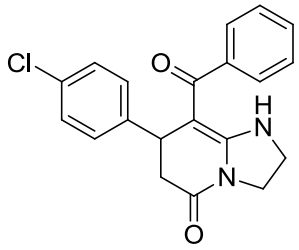
White solid; mp: 168-170 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.37 (s, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.07 (s, 1H), 6.82 (d, J = 7.6 Hz, 2H), 6.68 (s, 1H), 4.20 – 4.11 (m, 1H), 4.03-3.89 (m, 3H), 3.76 (d, J = 6.0 Hz, 1H), 3.04 (dd, J_1 = 7.2 Hz, J_2 = 16.8 Hz, 1H), 2.73 (d, J = 16.8 Hz, 1H); IR (potassium bromide) (v, cm^{-1}): 3230, 2987, 1685, 1635, 1535, 1486, 1372, 1319, 822, 789; HRMS (ESI): m/z Calcd. for $C_{20}H_{14}Cl_3N_2O_2$ [M-H]$^-$: 419.0121, found: 419.0108.

Compound 3c: 9-benzoyl-8-phenyl-3,4,7,8-tetrahydro-1*H*-pyrido[1,2-*a*]pyrimidin-6(2*H*)-one



Flaxen solid; mp: 168-170 ^{o}C (reported 167-168 ^{o}C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.99 (s, 1H), 7.26 – 7.19 (m, 6H), 7.10 (d, J = 7.2 Hz, 2H), 7.05 (d, J = 6.8 Hz, 2H), 4.04 – 3.95 (m, 2H), 3.58 – 3.48 (m, 3H), 2.98 – 2.93 (m, 1H), 2.82 (d, J = 15.6 Hz, 1H), 2.07 (s, 2H); IR (potassium bromide) (v, cm^{-1}): 3562, 3023, 1696, 1617, 1536, 1146, 722, 700; HRMS (ESI): m/z Calcd. for $C_{21}H_{19}N_2O_2$ [M-H]$^-$: 331.1447, found: 331.1448.

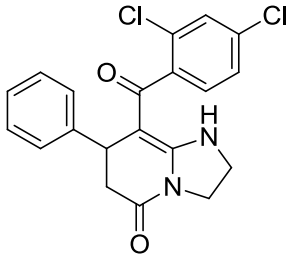
Compound 3d:
8-benzoyl-7-(4-chlorophenyl)-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one



Ash colored solid; mp: 170-172 ^{o}C (reported 190-191 ^{o}C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.36 – 7.23 (m, 5H), 7.16 (d, J = 7.2 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 4.17 – 4.10 (m, 2H, CH_2), 3.98 – 3.89 (m, 3H), 2.99 (dd, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H), 2.75 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 167.7, 157.3, 142.7, 141.2, 132.5, 129.3, 128.9, 128.1, 128.0, 126.3, 88.0, 42.8, 41.9, 40.7, 37.7; IR (potassium bromide) (v, cm^{-1}): 3297, 3051, 2916, 1695, 1629, 1517, 1482, 1367, 1313, 1014, 749, 701, 641; HRMS (ESI): m/z Calcd. for $C_{20}H_{16}ClN_2O_2$ [M-H]$^-$: 351.0900, found: 351.0901.

Compound 3e :

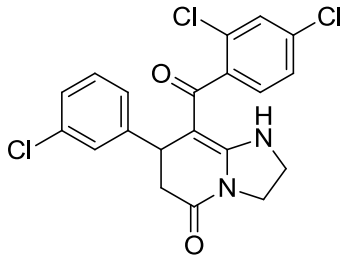
8-(2,4-dichlorobenzoyl)-7-phenyl-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one



White solid; mp: 209-210 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.42 – 7.35 (m, 1H), 7.16 (s, 3H), 7.01 (s, 1H), 6.86 (s, 2H), 6.65 (s, 1H), 4.21 – 4.07 (m, 1H), 4.00 – 3.89 (m, 3H), 3.75 (d, J = 4.0 Hz, 1H, CH), 3.03 (dd, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H), 2.75 (d, J = 16.4 Hz, 1H); IR (potassium bromide) (v, cm^{-1}): 3278, 3072, 1687, 1639, 1533, 1479, 1446, 1371, 1197, 1156, 1010, 843, 701, 182; HRMS (ESI): m/z Calcd. for $C_{20}H_{15}Cl_2N_2O_2$ [M-H]$^-$: 385.0511, found: 385.0494.

Compound 3f :

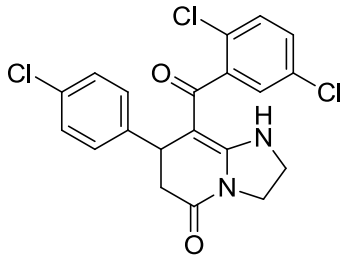
7-(3-chlorophenyl)-8-(2,4-dichlorobenzoyl)-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one



White solid; mp: 211-213 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.35 (s, 1H), 7.15 – 7.06 (m, 3H), 6.81 (s, 1H), 6.75 (d, J = 6.8 Hz, 1H), 6.68 (s, 1H), 4.18 – 4.09 (m, 1H), 4.02 – 3.90 (m, 3H), 3.75 (d, J = 6.4 Hz, 1H, CH), 3.03 (dd, J_1 = 7.6 Hz, J_2 = 16.8 Hz, 1H), 2.74 (dd, J_1 = 2.0 Hz, J_2 = 16.8 Hz, 1H); IR (potassium bromide) (v, cm^{-1}): 3318, 3045, 1691, 1631, 1586, 1518, 1487, 1368, 1316, 1204, 1021, 822, 777; HRMS (ESI) m/z: Calcd. for $C_{20}H_{14}Cl_3N_2O_2$ [M-H]$^-$: 419.0121, found: 419.0121.

Compound 3g:

7-(4-chlorophenyl)-8-(2,5-dichlorobenzoyl)-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one

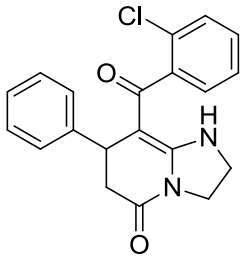


Ash colored solid; mp: 216-218 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.24 (s, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 6.64 (s, 1H), 4.18 – 4.07 (m, 1H), 4.01 – 3.87 (m, 3H), 3.74 (d, J = 4.0 Hz, 1H, CH), 3.03 (dd, J_1 = 7.6 Hz, J_2 = 16.8 Hz, 1H), 2.70 (dd, J_1 = 1.6 Hz, J_2 = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 157.2, 141.2,

132.7, 129.6, 128.8, 127.8, 88.6, 42.86, 42.03, 40.3, 37.6; IR (potassium bromide) (v, cm^{-1}): 3277, 2975, 2906, 1690, 1644, 1517, 1487, 1451, 1368, 1319, 1210, 1093, 1019, 892, 816; HRMS (ESI): m/z Calcd. for $C_{20}H_{14}Cl_3N_2O_2$ $[M-H]^-$: 419.0121, found: 419.0114.

Compound 3h:

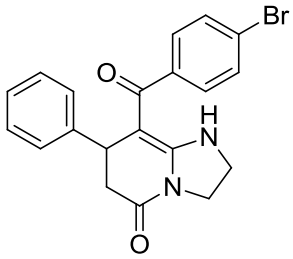
8-(2-chlorobenzoyl)-7-phenyl-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one



Yellow solid; mp: 175-176 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.33 (s, 1H), 7.24 – 7.16 (m, 4H), 7.04 (s, 1H), 6.84 (d, J = 6.0 Hz, 2H), 6.72 (s, 1H), 4.19 – 4.08 (m, 1H), 3.95 – 3.86 (m, 3H), 3.80 (d, J = 4.4 Hz, 1H, CH), 3.06 (dd, J_1 = 7.2 Hz, J_2 = 16.4 Hz, 1H), 2.76 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 156.9, 143.9, 140.1, 129.5, 128.5, 127.8, 126.7, 126.5, 126.5, 89.2, 42.8, 41.9, 40.5, 38.0; IR (potassium bromide) (v, cm^{-1}): 3298, 3058, 3027, 1687, 1636, 1531, 1485, 1449, 1372, 1318, 1208, 1163, 1072, 1017, 936, 762, 733, 691, 633; HRMS (ESI): m/z Calcd. for $C_{20}H_{16}ClN_2O_2$ $[M-H]^-$: 351.0900, found: 351.0891.

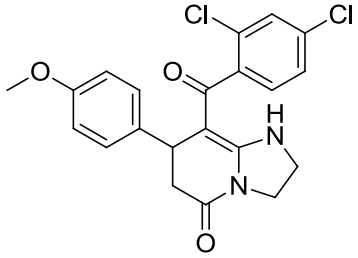
Compound 3i:

8-(4-bromobenzoyl)-7-phenyl-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one



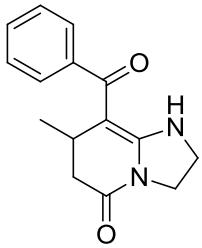
Yellow solid; mp: 189-190 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.38 (d, J = 7.6 Hz, 2H), 7.31 – 7.21 (m, 3H), 7.05 (d, J = 7.6 Hz, 4H), 4.18 – 4.10 (m, 1H), 4.07 (d, J = 6.8 Hz, 1H), 3.99 – 3.87 (m, 3H), 2.99 (dd, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H), 2.80 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 167.9, 157.7, 143.9, 140.1, 131.1, 128.9, 128.3, 126.9, 126.7, 123.4, 88.2, 42.9, 41.9, 40.9, 38.2; IR (potassium bromide) (v, cm^{-1}): 3282, 3061, 1687, 1637, 1530, 1443, 1366, 1316, 1202, 1153, 1006, 767; HRMS (ESI): m/z Calcd. for $C_{20}H_{16}BrN_2O_2$ $[M-H]^-$: 395.0395, found: 395.0406.

Compound 3j:
8-(2,4-dichlorobenzoyl)-7-(4-methoxyphenyl)-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one



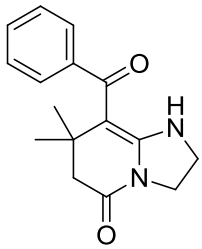
Yellow solid; mp: 127-129 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.34 (s, 1H), 7.03 (d, J = 5.2 Hz, 1H), 6.77 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 6.66 (s, 1H), 4.17 – 4.10 (m, 1H), 3.95 – 3.88 (m, 3H), 3.75(s, 3H), 3.70 (d, J = 6.8 Hz, 1H, CH), 2.99 (dd, J_1 = 7.2 Hz, J_2 = 16.4 Hz, 1H), 2.72 (dd, J_1 = 2.0 Hz, J_2 = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 167.9, 158.4, 157.2, 138.6, 135.7, 134.6, 129.2, 128.7, 127.5, 126.8, 113.9, 89.3, 55.2, 42.8, 41.9, 40.8, 37.2; IR (potassium bromide) (v, cm^{-1}): 3327, 3076, 2933, 1738, 1690, 1638, 1529, 1486, 1373, 1322, 1232, 1021, 826, 658, 564; HRMS (ESI): m/z Calcd. for $C_{21}H_{17}Cl_2N_2O_3$ [M-H]$^-$: 415.0616, found: 415.0600.

Compound 3k: 8-benzoyl-7-methyl-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one



Brown solid; mp: 148-150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.40 (s, 5H), 4.11 – 4.04 (m, 1H), 3.93 – 3.75 (m, 3H), 3.06 – 3.00 (m, 1H, CH), 2.72 (dd, J_1 = 6.4 Hz, J_2 = 16.4 Hz, 1H), 2.41 (dd, J_1 = 1.6 Hz, J_2 = 16.4 Hz, 1H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 163.7, 150.9, 136.4, 123.7, 122.9, 121.1, 86.2, 37.4, 36.6, 34.5, 22.2, 16.9; IR (potassium bromide) (v, cm^{-1}): 3288, 2958, 1693, 1624, 1524, 1491, 1377, 1205, 1019, 748, 700, 643; HRMS (ESI): m/z Calcd. for $C_{15}H_{15}N_2O_2$ [M-H]$^-$: 255.1134, found: 255.1142.

Compound 3l: 8-benzoyl-7,7-dimethyl-2,3,6,7-tetrahydroimidazo[1,2-*a*]pyridin-5(1*H*)-one

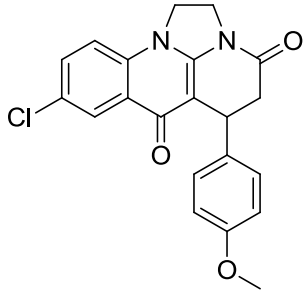


Yellow solid; mp: 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 4.59 (s, 1H), 3.99 – 3.79 (m, 4H), 3.05 (d, J = 17.2 Hz, 1H), 2.28 (t, J = 16.8 Hz, 1H), 1.16 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 162.4,

151.7, 131.9, 128.7, 123.7, 123.7, 48.2, 46.1, 37.5, 37.4, 28.9, 23.8, 21.0; IR (potassium bromide) (ν, cm^{-1}): 3070, 2964, 2882, 1675, 1636, 1406, 1372, 1272, 1218, 991, 755, 689, 628; HRMS (ESI): m/z Calcd. for $C_{16}H_{17}N_2O_2$ $[M-H]^-$: 269.1290, found: 269.1290.

Compound 5a:

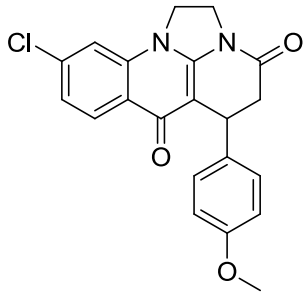
9-chloro-6-(4-methoxyphenyl)-1,2,5,6-tetrahydrobenzo[*b*]imidazo[1,2,3-*ij*][1,8]naphthyridine-4,7-dione



White solid; mp: 220-222 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 4.55 – 4.37 (m, 3H), 4.23 – 4.10 (m, 2H), 3.68 (s, 3H), 3.12 (dd, J_1 = 8.0 Hz, J_2 = 16.8 Hz, 1H), 2.69 (d, J = 16.4 Hz, 1H); IR (potassium bromide) (ν, cm^{-1}): 3061, 2907, 1709, 1635, 1546, 1514, 1381, 1251, 1175, 1035, 829, 793, 507; HRMS (ESI): m/z Calcd. for $C_{21}H_{17}ClN_2NaO_3$ $[M+Na]^+$: 403.0825, found: 403.0823.

Compound 5b:

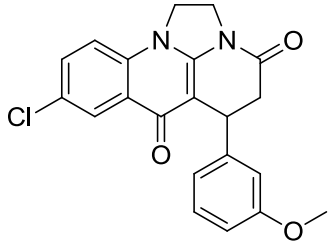
10-chloro-6-(4-methoxyphenyl)-1,2,5,6-tetrahydrobenzo[*b*]imidazo[1,2,3-*ij*][1,8]naphthyridine-4,7-dione



White solid; mp: 154-155 ^oC (reported 224-226 ^oC[2]); ^1H NMR (400 MHz, DMSO-d_6) δ 8.07 (d, J = 8.4 Hz, 1H), 7.64 (s, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 4.54 – 4.36 (m, 3H), 4.22 – 4.09 (m, 2H), 3.68 (s, 3H), 3.12 (dd, J_1 = 8.0 Hz, J_2 = 16.8 Hz, 1H), 2.68 (d, J = 16.4 Hz, 1H); IR (potassium bromide) (ν, cm^{-1}): 3059, 3036, 1706, 1638, 1613, 1573, 1540, 1513, 1434, 1372, 1247, 1029, 848, 783; HRMS (ESI): m/z Calcd. for $C_{21}H_{17}ClN_2NaO_3$ $[M+Na]^+$: 403.0825, found: 403.0829.

Compound 5c:

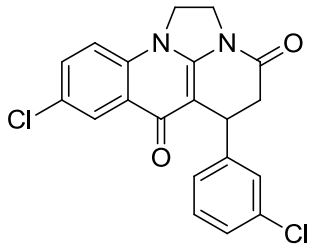
9-chloro-6-(3-methoxyphenyl)-1,2,5,6-tetrahydrobenzo[*b*]imidazo[1,2,3-*ij*][1,8]naphthyridine-4,7-dione



Straw-colored solid; mp: 288-290 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, J = 2.0 Hz, 1H), 7.73 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.82 – 6.75 (m, 3H), 4.55 – 4.47 (m, 2H), 4.42 – 4.35 (m, 1H, CH), 4.23 – 4.11 (m, 2H), 3.69 (s, 3H), 3.16 (dd, J_1 = 8.4 Hz, J_2 = 16.8 Hz, 1H), 2.73 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 167.6, 159.3, 147.9, 145.0, 135.5, 131.4, 129.5, 127.6, 126.0, 124.7, 118.5, 117.9, 113.0, 111.3, 99.2, 54.9, 45.4, 42.4, 38.8, 34.0; IR (potassium bromide) (v, cm^{-1}): 3054, 2909, 2838, 1703, 1640, 1614, 1599, 1580, 1519, 1470, 1378, 1278, 1157, 1035, 808; HRMS (ESI): m/z Calcd. for $C_{21}H_{17}ClN_2NaO_3$ $[M+Na]^+$: 403.0825, found: 403.0820.

Compound 5d:

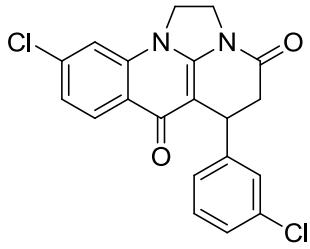
9-chloro-6-(3-chlorophenyl)-1,2,5,6-tetrahydrobenzo[*b*]imidazo[1,2,3-*ij*][1,8]naphthyridine-4,7-dione



Brown solid; mp: 262-264 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 4.0 Hz, 1H), 7.75 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.33 – 7.20 (m, 4H), 4.52 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 2H), 4.41 (dd, J_1 = 8.8 Hz, J_2 = 17.2 Hz, 1H), 4.23 – 4.13 (m, 2H), 3.18 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 1H), 2.74 (d, J = 16.0 Hz, 1H); IR (potassium bromide) (v, cm^{-1}): 3056, 2962, 2910, 1702, 1644, 1617, 1586, 1546, 1515, 1379, 1318, 1224, 1180, 808; HRMS (ESI): m/z Calcd. for $C_{20}H_{14}Cl_2N_2NaO_2$ $[M+Na]^+$: 407.0330, found: 407.0345.

Compound 5e:

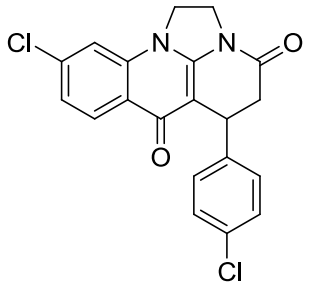
10-chloro-6-(3-chlorophenyl)-1,2,5,6-tetrahydrobenzo[*b*]imidazo[1,2,3-*ij*][1,8]naphthyridine-4,7-dione



Brown solid; mp: 156-158 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (d, J = 8.4 Hz, 1H), 7.65 (s, 1H), 7.37 – 7.19 (m, 5H), 4.50 (d, J = 7.2 Hz, 2H), 4.40 (dd, J_1 = 9.2 Hz, J_2 = 17.6 Hz, 1H), 4.23 – 4.12 (m, 2H), 3.18 (dd, J_1 = 8.4 Hz, J_2 = 16.4 Hz, 1H), 2.73 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 159.4, 151.5, 150.1, 140.9, 138.3, 138.1, 132.4, 129.7, 129.1, 128.3, 128.2, 127.3, 123.7, 123.2, 116.0, 115.4, 99.0, 45.9, 44.2; IR (potassium bromide) (v, cm^{-1}): 3060, 2967, 2909, 1691, 1648, 1616, 1583, 1538, 1519, 1373, 1228, 1092, 778, 684; HRMS (ESI): m/z Calcd. for $C_{20}H_{14}Cl_2N_2NaO_2$ $[M+Na]^+$: 407.0330, found: 407.0327.

Compound 5f:

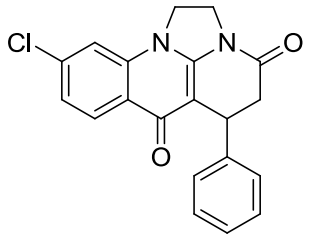
10-chloro-6-(4-chlorophenyl)-1,2,5,6-tetrahydrobenzo[*b*]imidazo[1,2,3-*ij*][1,8]naphthyridine-4,7-dione



Brown solid; mp: 151-153 ^{o}C (reported 223-225 ^{o}C[2]); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (d, J = 8.8 Hz, 1H), 7.65 (s, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.54 – 4.48 (m, 2H), 4.40 (dd, J_1 = 9.2 Hz, J_2 = 17.6 Hz, 1H), 4.23 – 4.10 (m, 2H), 3.17 (dd, J_1 = 8.0 Hz, J_2 = 16.8 Hz, 1H), 2.70 (d, J = 17.2 Hz, 1H); IR (potassium bromide) (v, cm^{-1}): 3057, 3036, 1712, 1640, 1614, 1577, 1520, 1420, 1369, 1315, 1231, 1093, 1013, 876, 842, 783, 648, 501; HRMS (ESI): m/z Calcd. for $C_{20}H_{14}Cl_2N_2NaO_2$ $[M+Na]^+$: 407.0330, found: 407.0342.

Compound 5g :

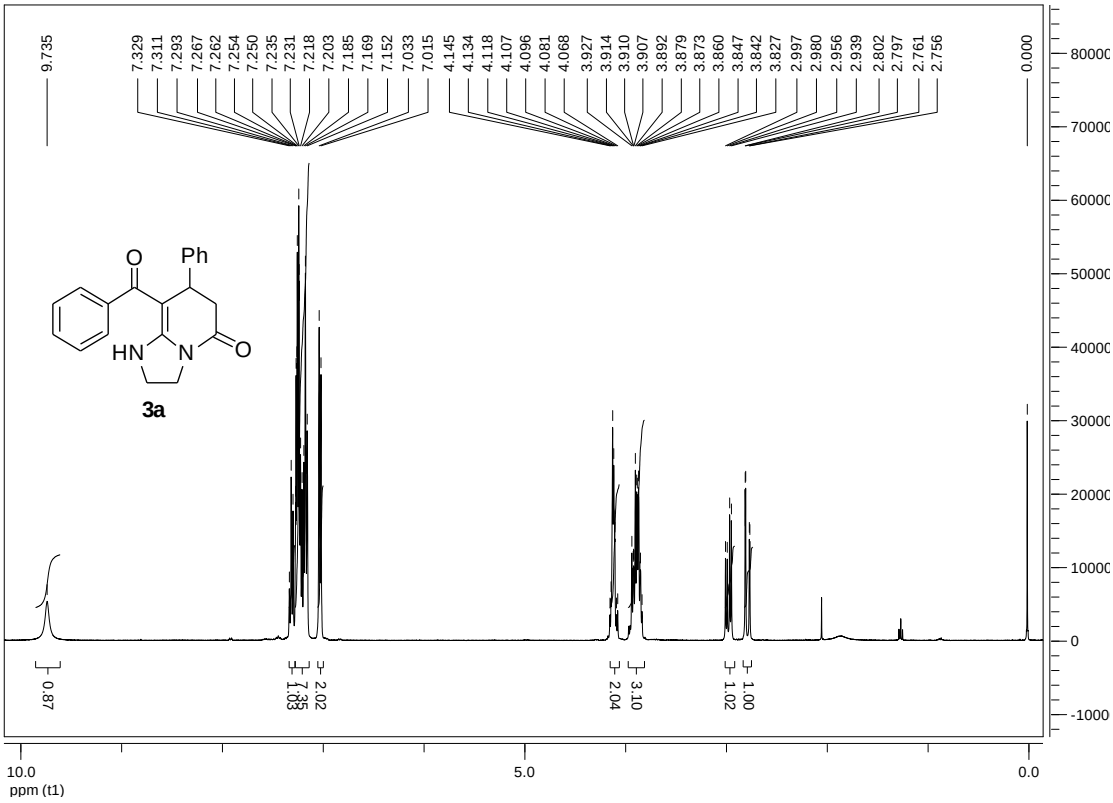
10-chloro-6-phenyl-1,2,5,6-tetrahydrobenzo[b]imidazo[1,2,3-*ij*][1,8]naphthyridine-4,7-dione



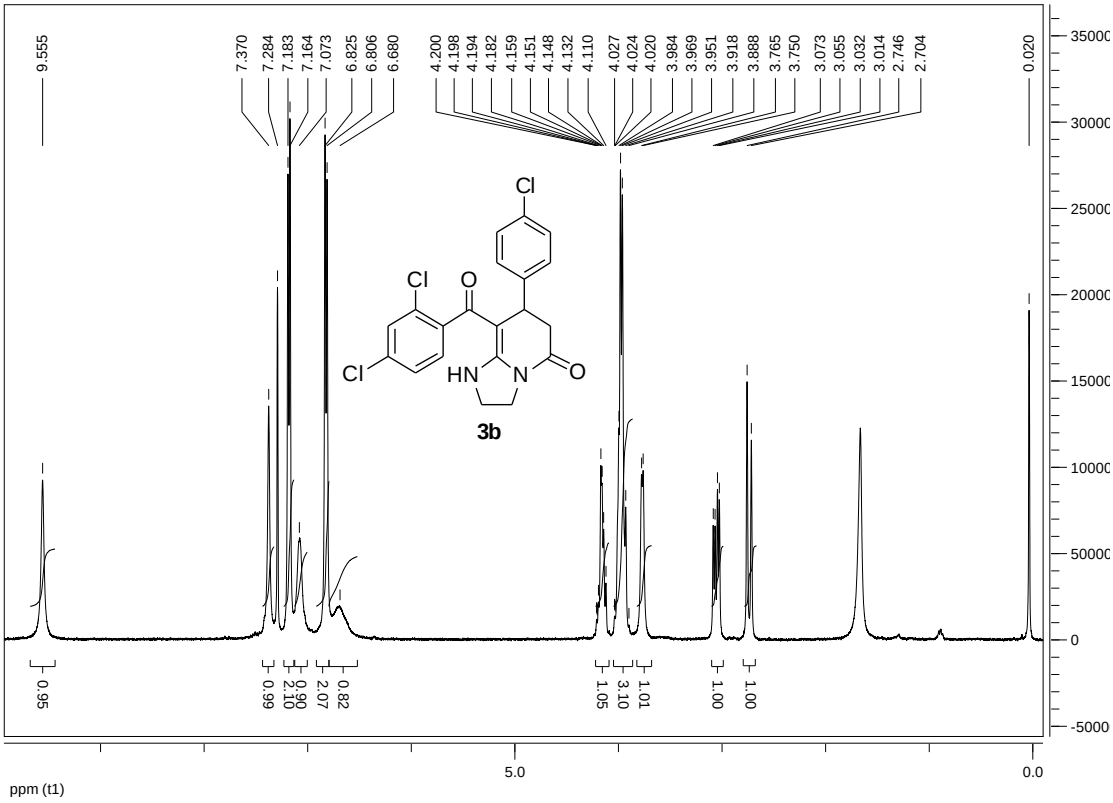
Brown solid; mp: 288-290 ^{o}C (reported 252-254 ^{o}C[2]); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (d, J = 8.8 Hz, 1H), 7.65 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.25 (s, 4H), 7.18 (d, J = 4.4 Hz, 1H), 4.55 – 4.48 (m, 2H), 4.40 (dd, J_1 = 8.8 Hz, J_2 = 17.6 Hz, 1H), 4.23 – 4.11 (m, 2H), 3.18 (dd, J_1 = 8.0 Hz, J_2 = 16.4 Hz, 1H), 2.71 (d, J = 16.8 Hz, 1H); IR (potassium bromide) (v, cm^{-1}): 3076, 2972, 2890, 1706, 1644, 1614, 1576, 1520, 1366, 1090, 950, 831, 740, 524; HRMS (ESI): m/z Calcd. for $C_{20}H_{15}ClN_2NaO_2$ $[M+Na]^+$: 373.0720, found: 373.0725.

(1) Yu, C.-Y.; Yang, P.-H.; Zhao, M.-X.; Huang, Z.-T. *Synlett*. **2006**, 1835–1840.

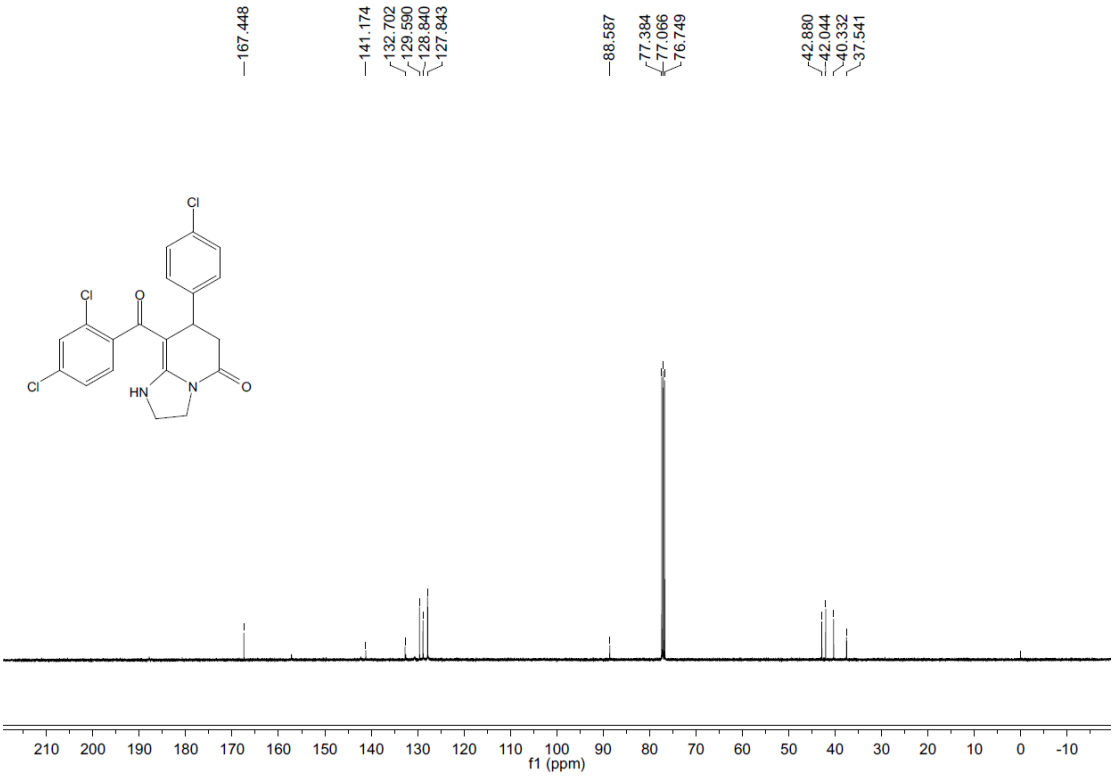
(2) Wen, L.-R.; Liu, C.; Li, M.; Wang, L.-J. *J. Org. Chem.* **2010**, *75*, 7605–7614.



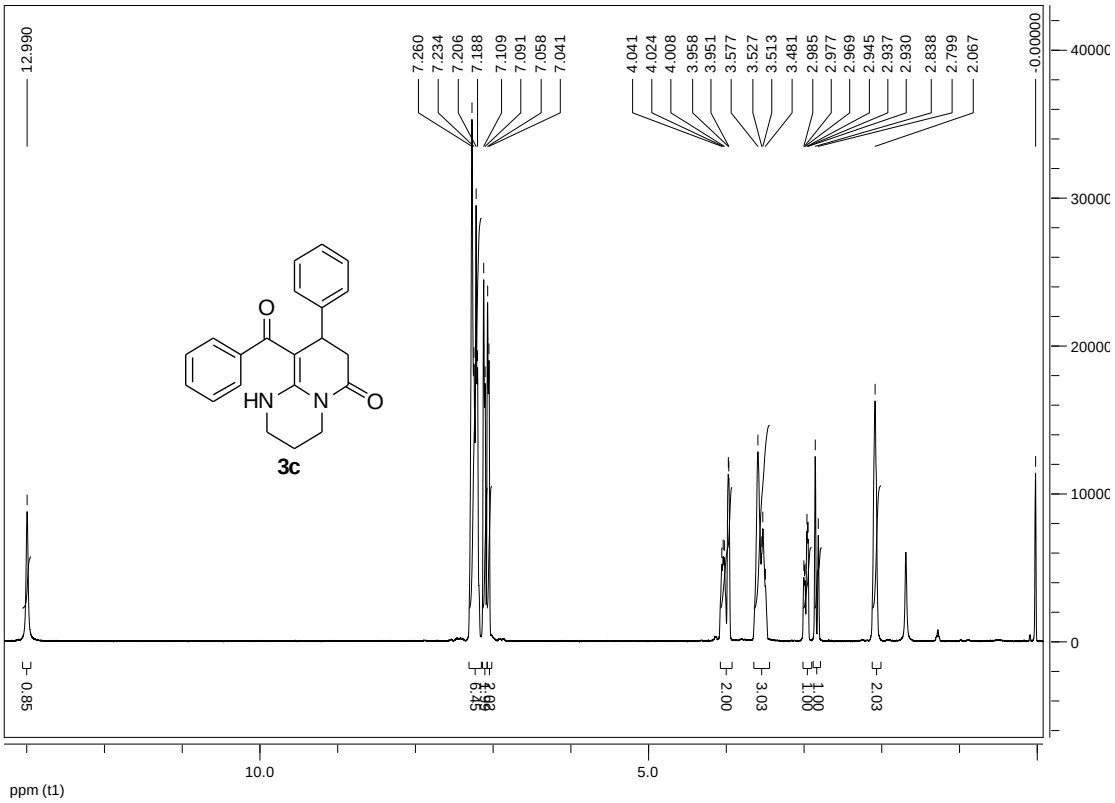
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3a**



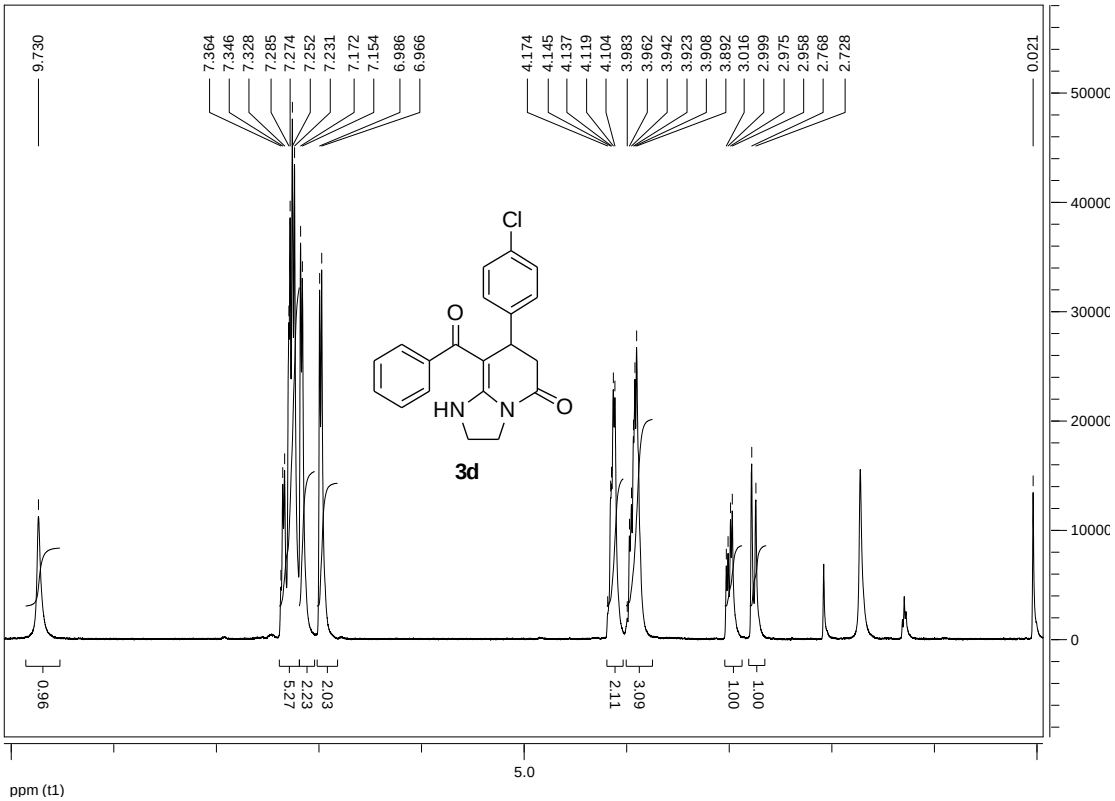
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3b**



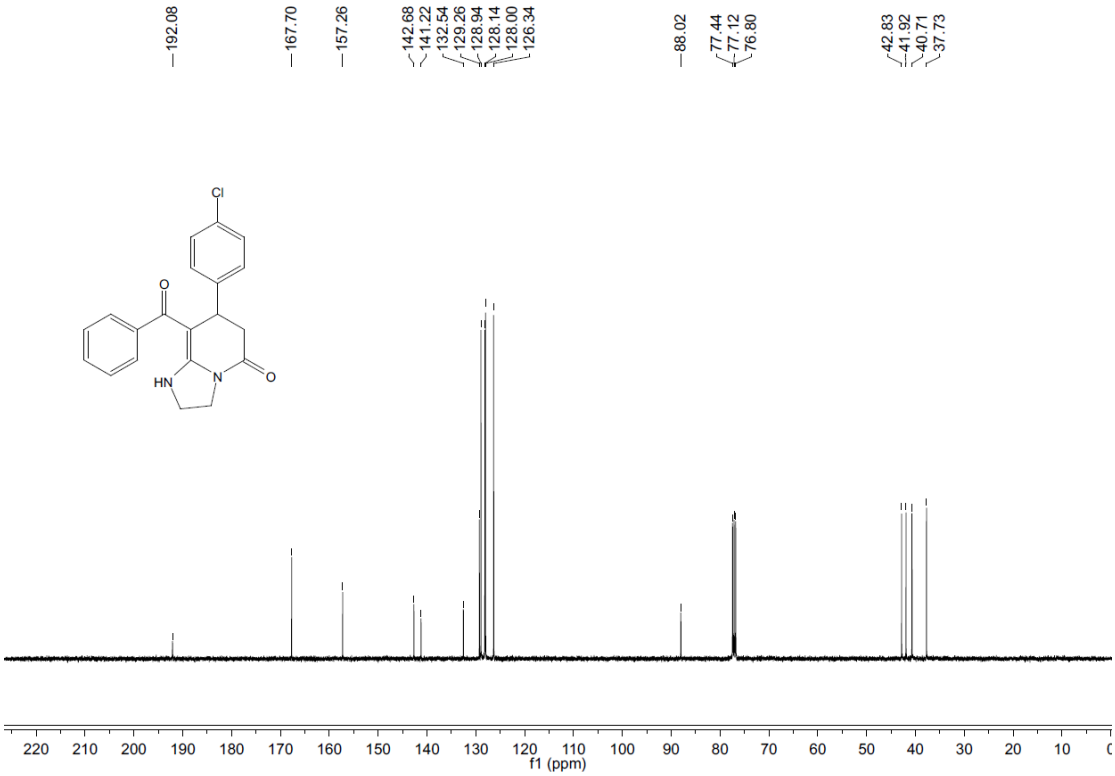
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3b**



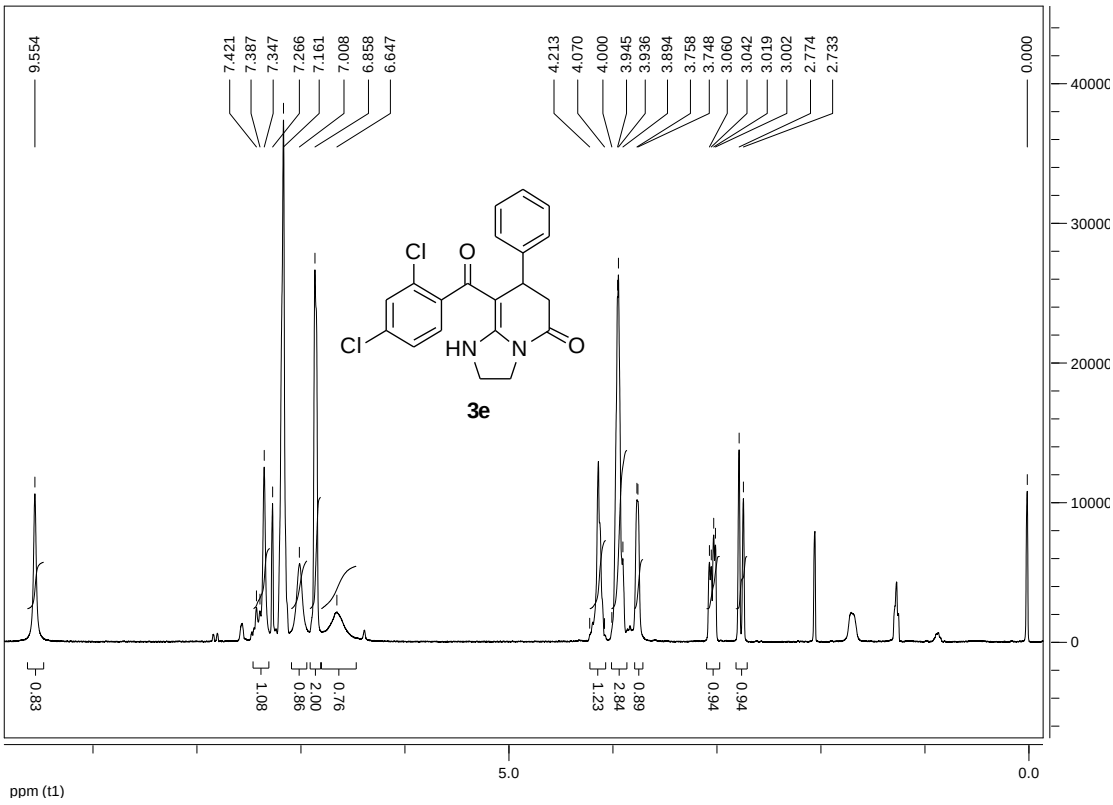
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3c**



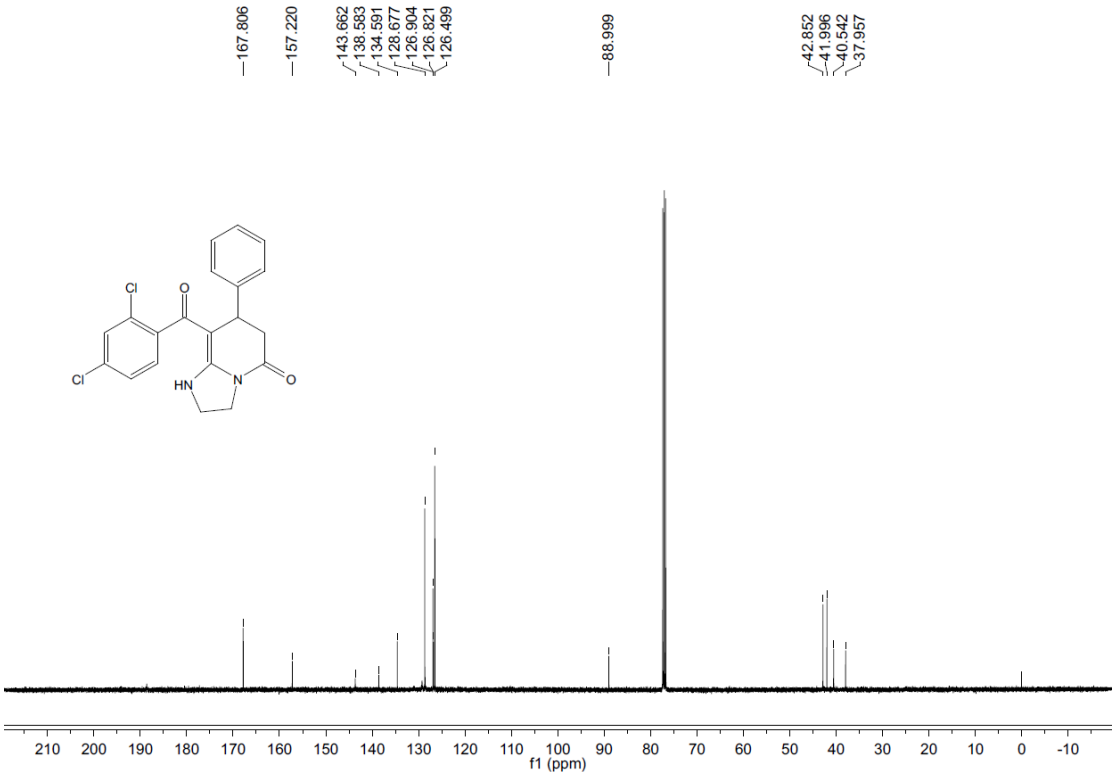
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3d**



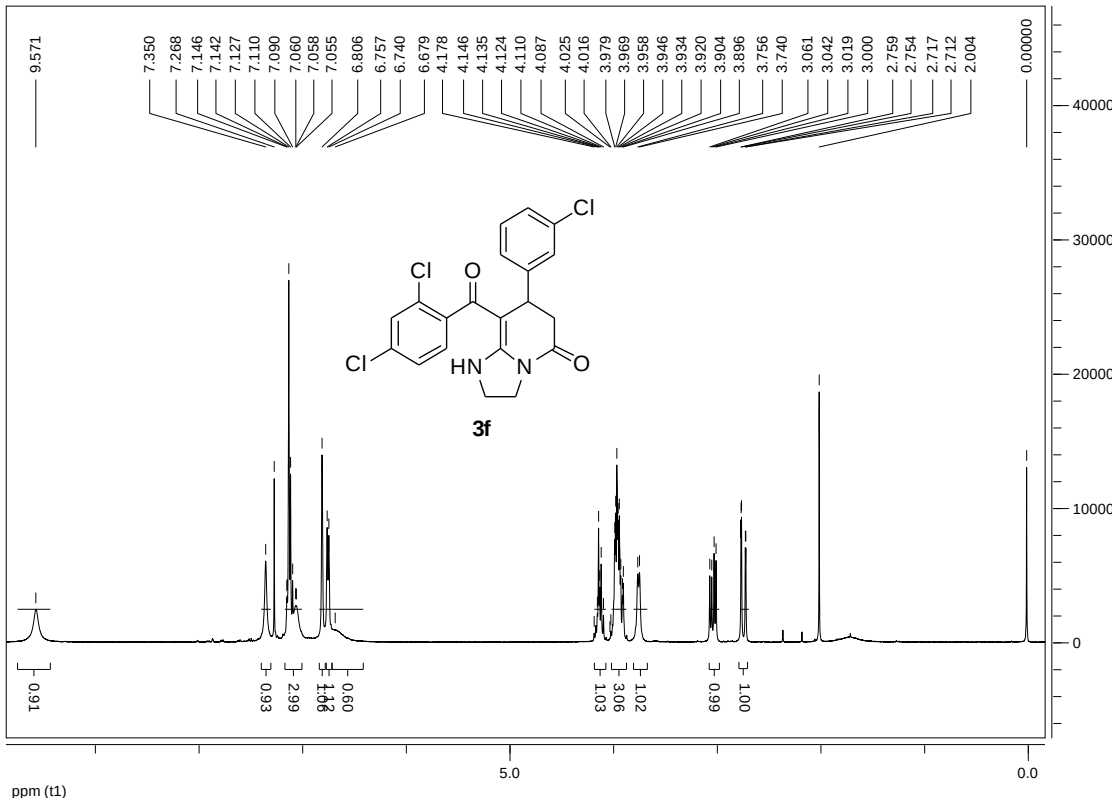
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3d**



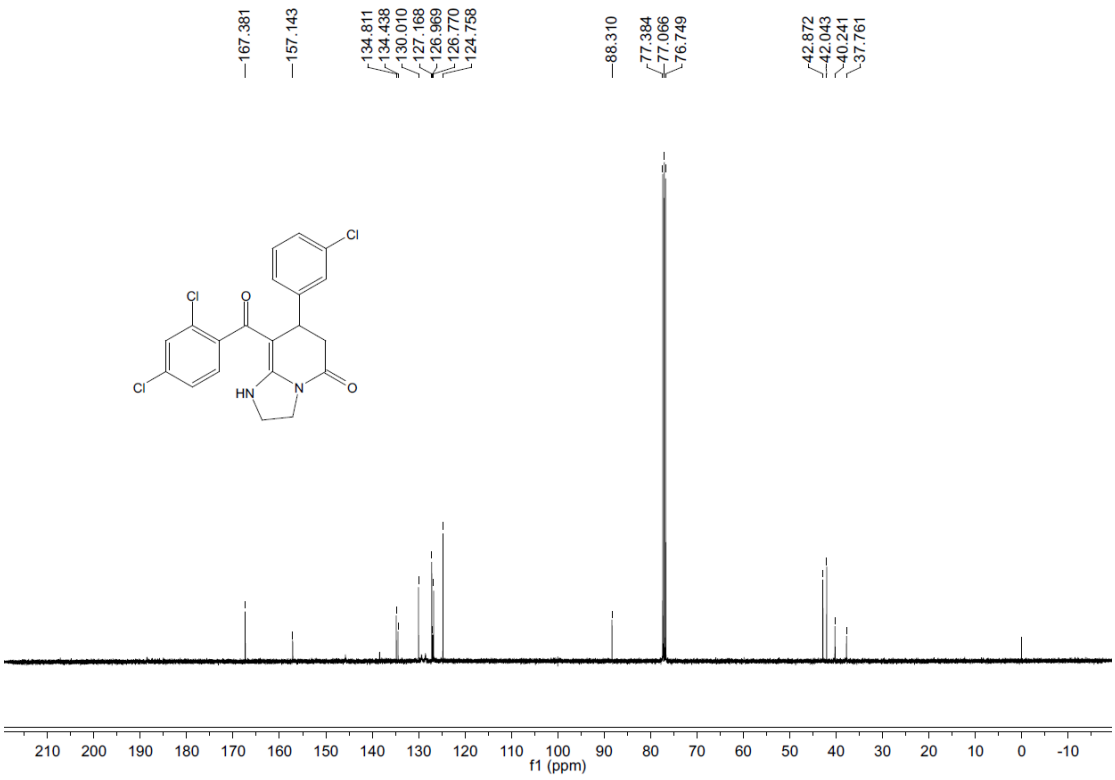
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3e**



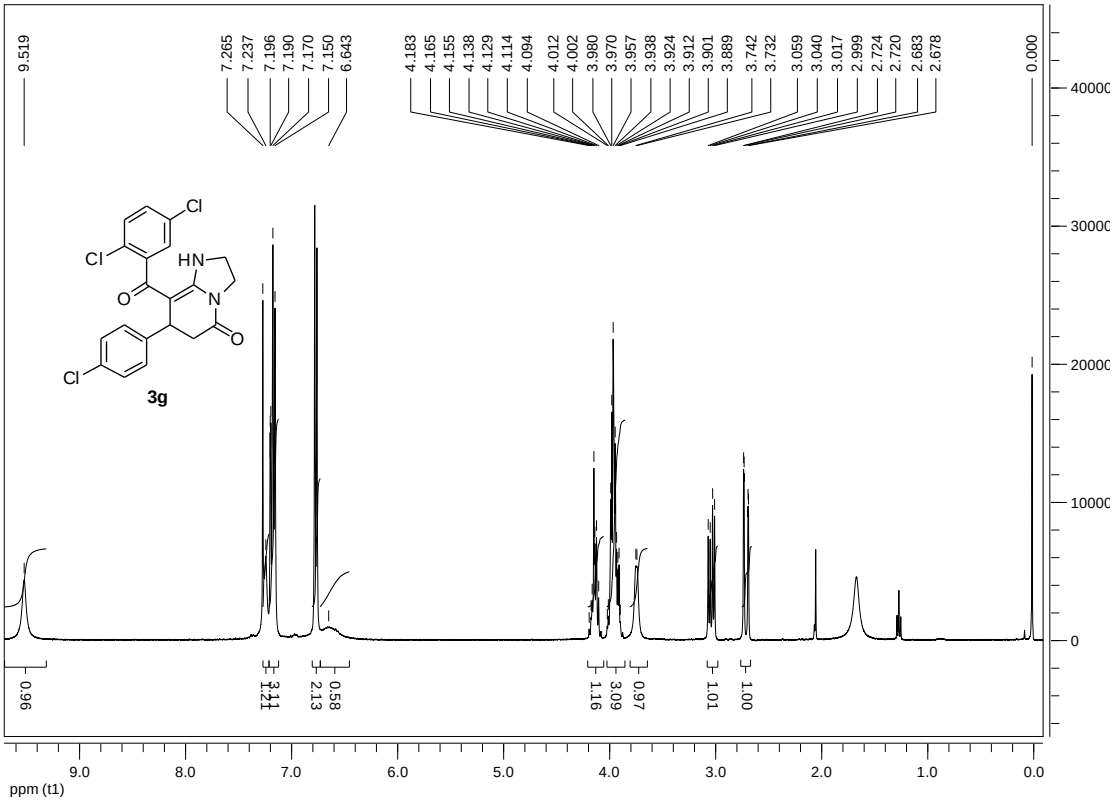
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3e**



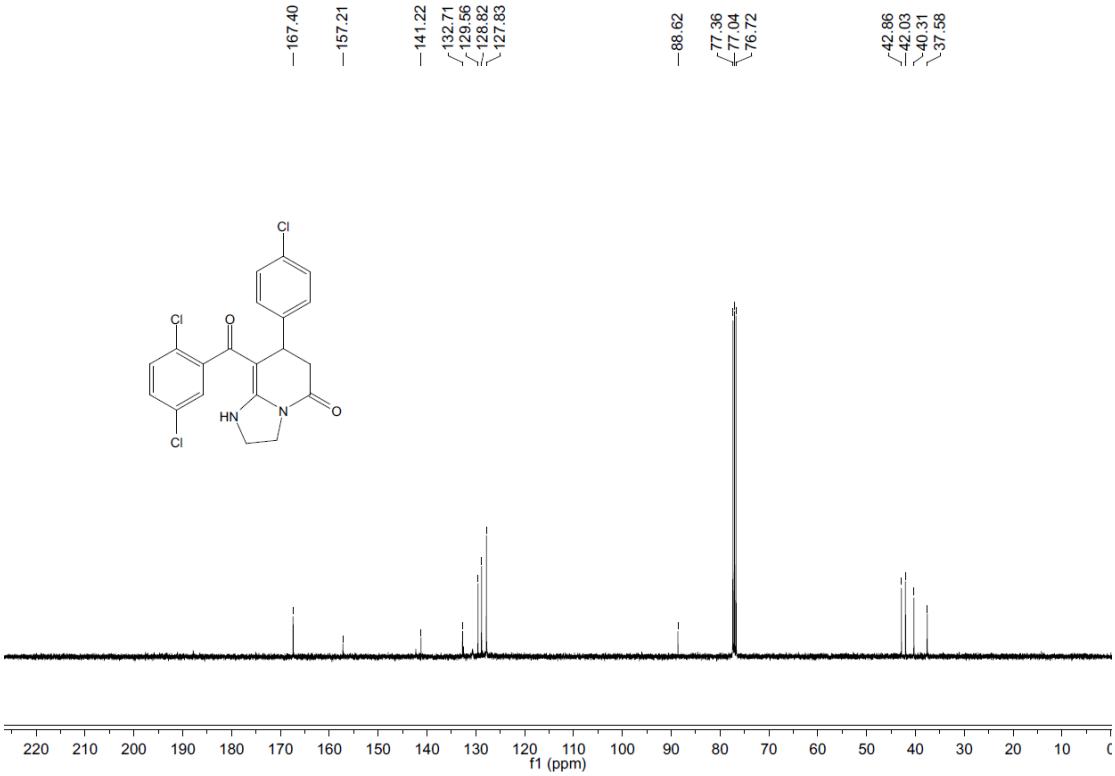
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3f**



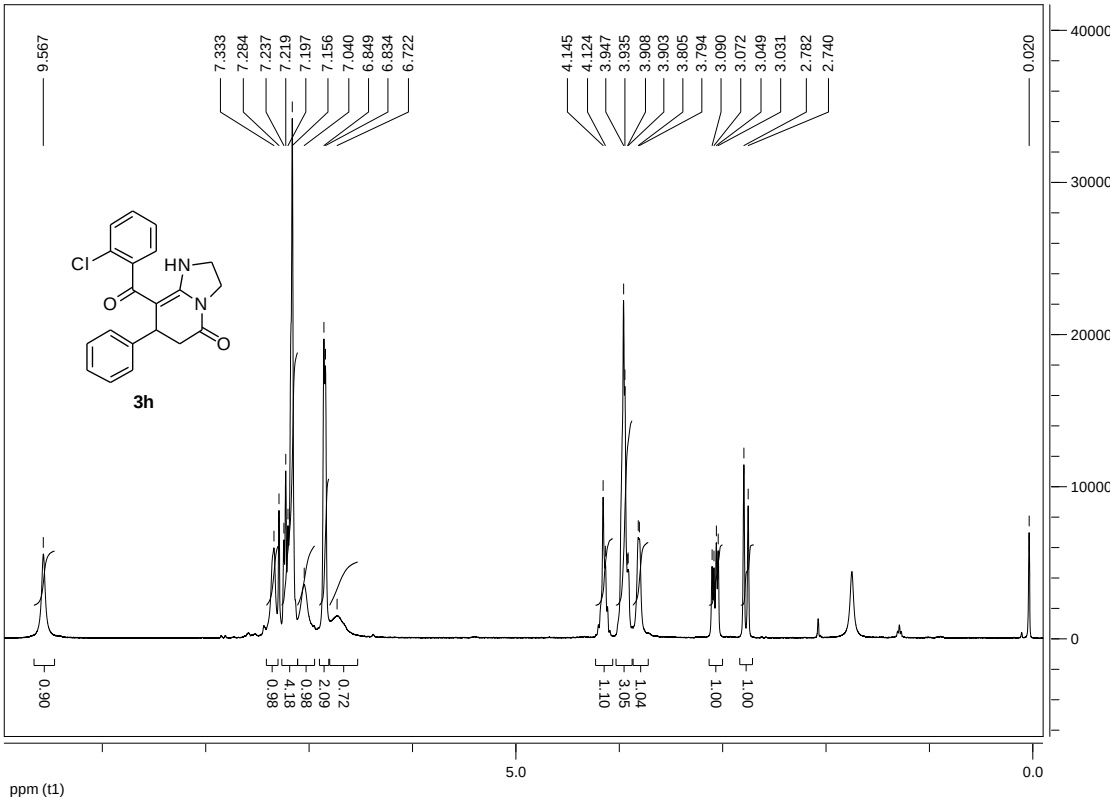
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3f**



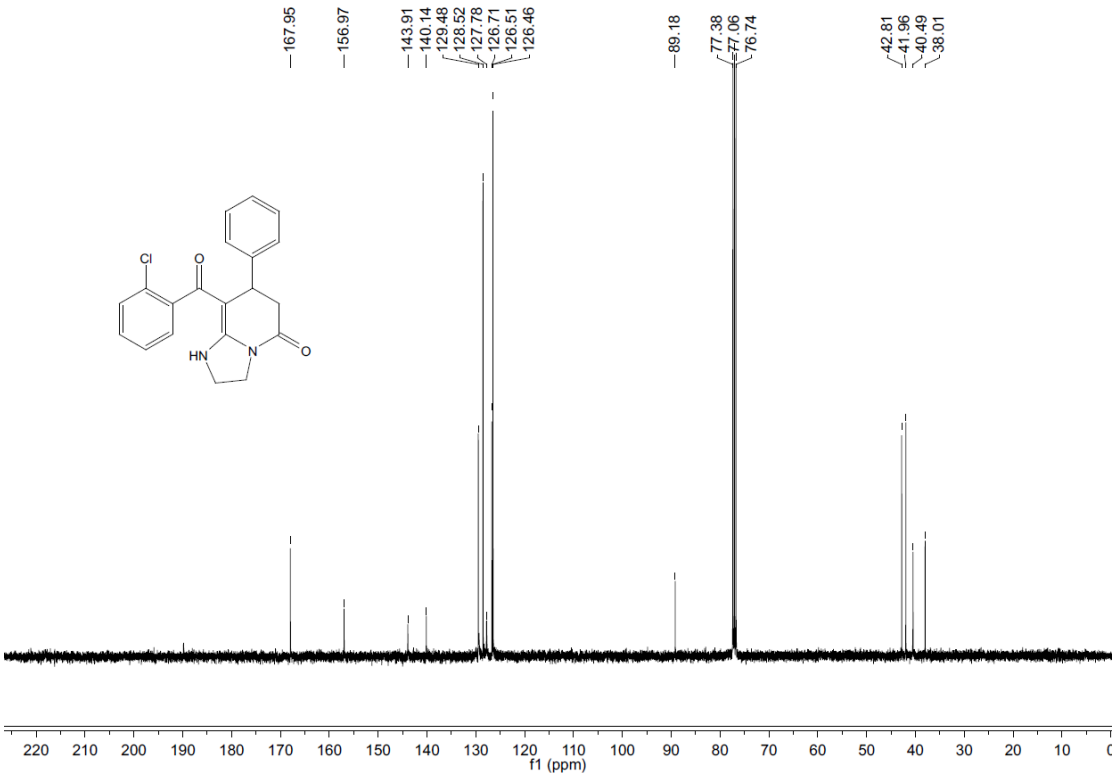
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3g**



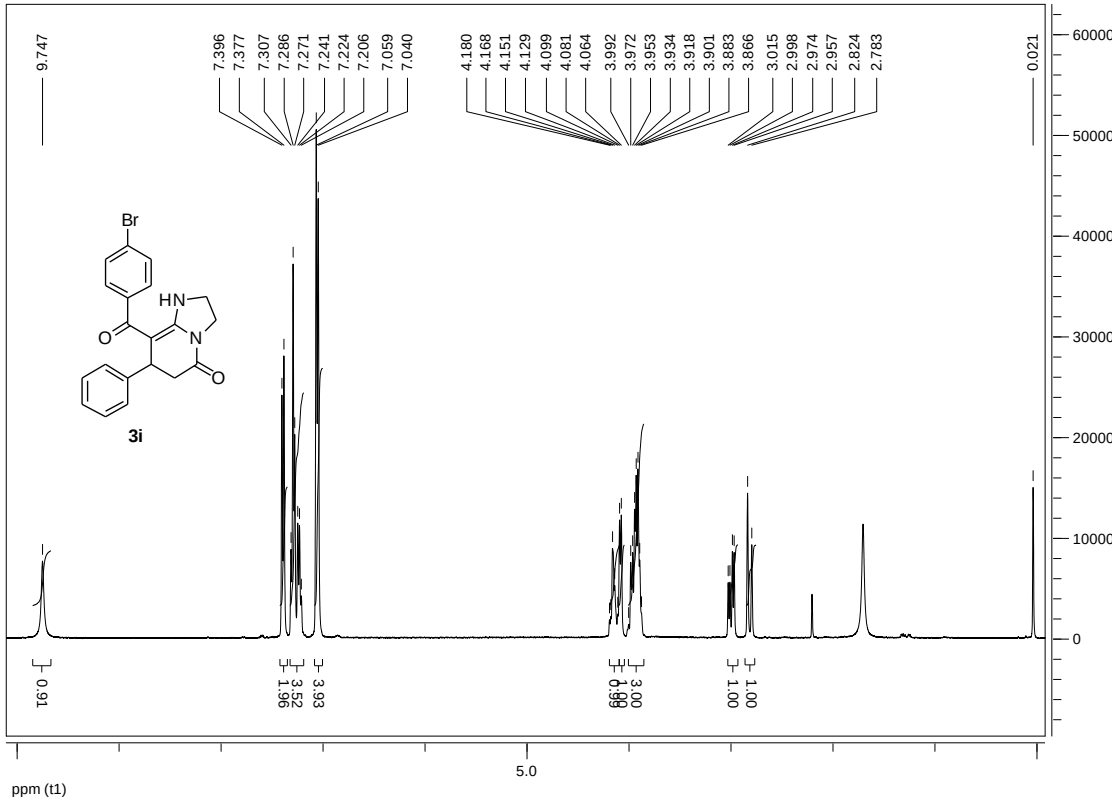
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3g**



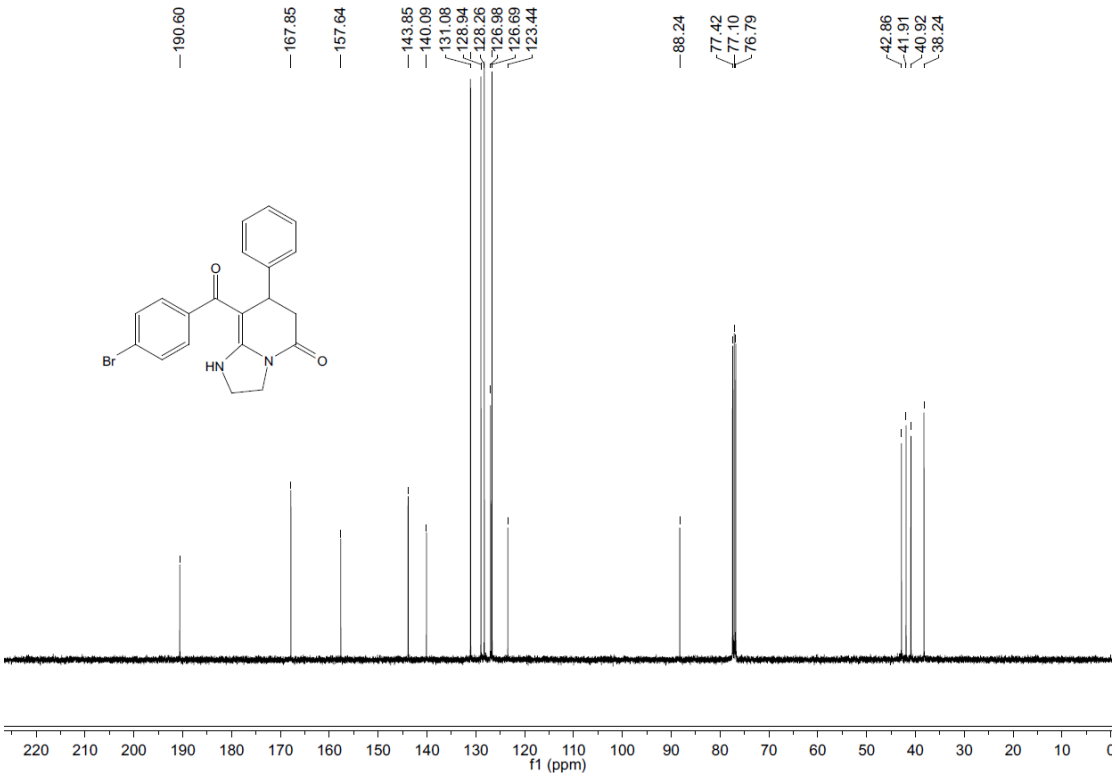
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3h**



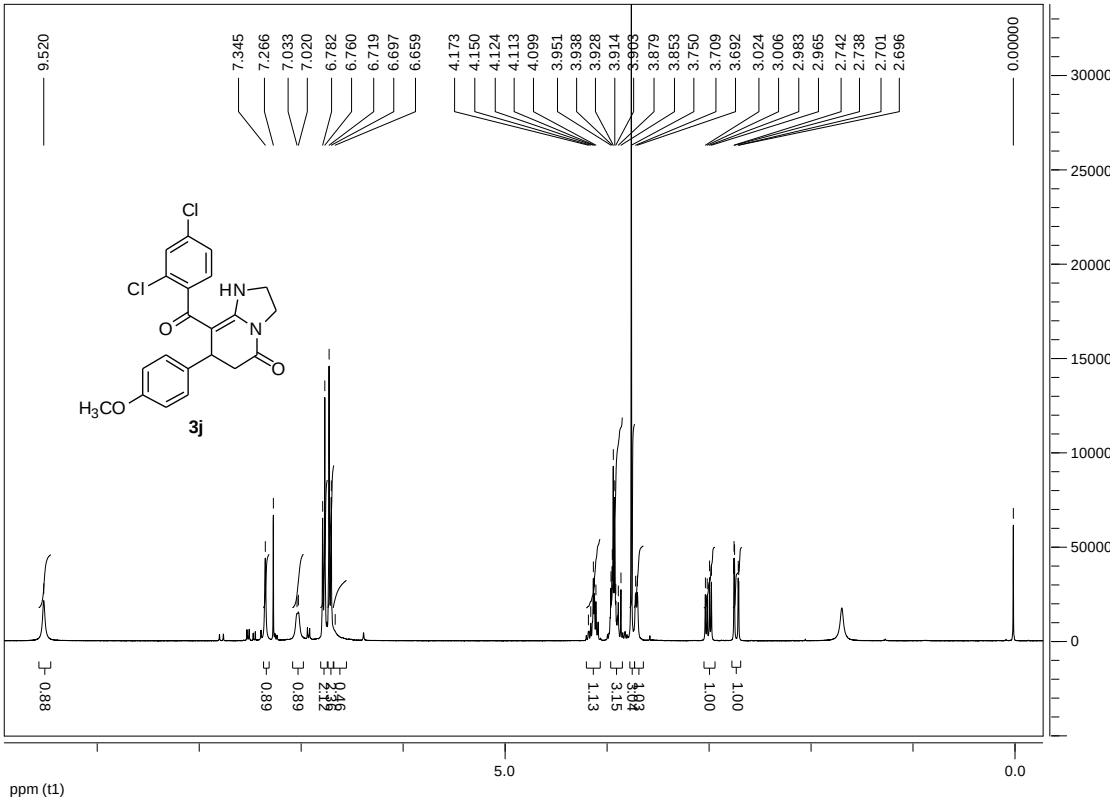
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3h**



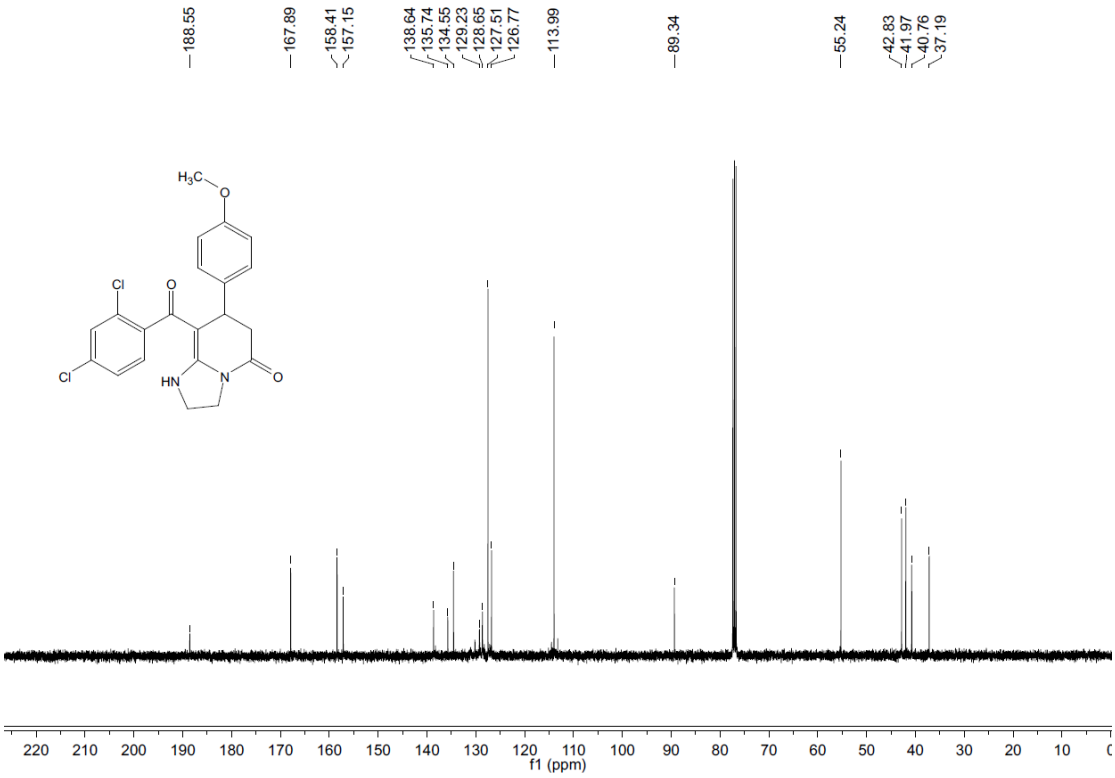
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3i**



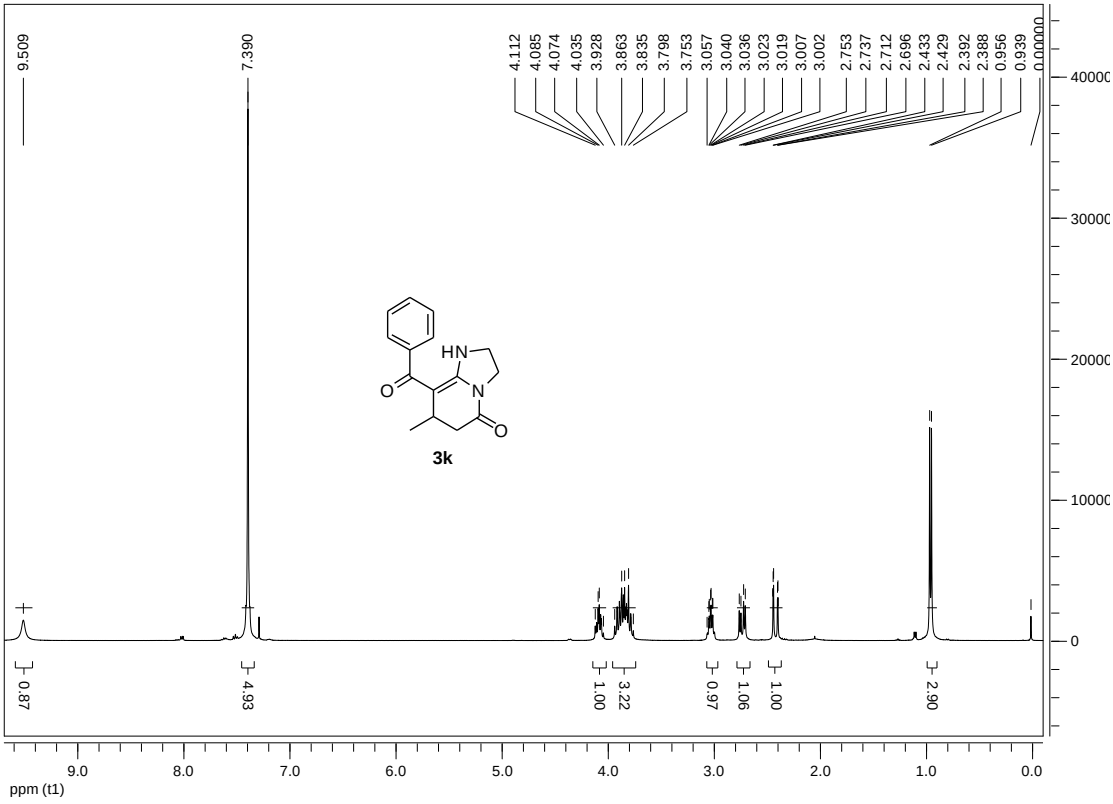
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3i**



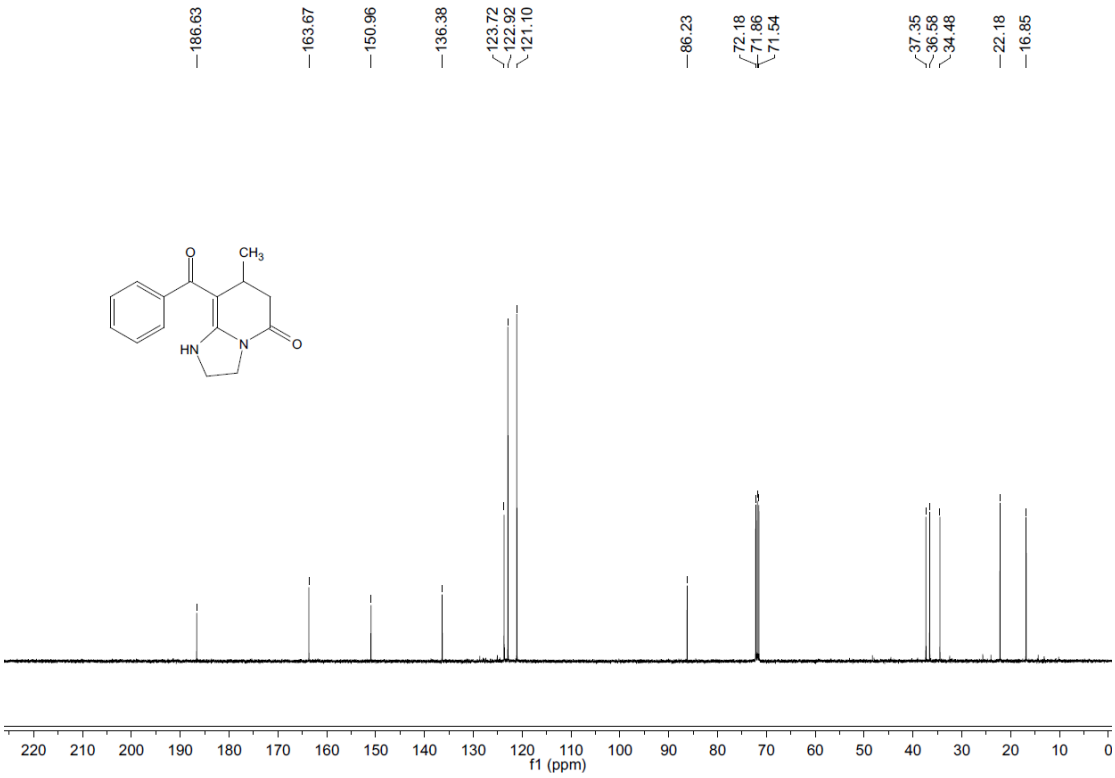
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3j**



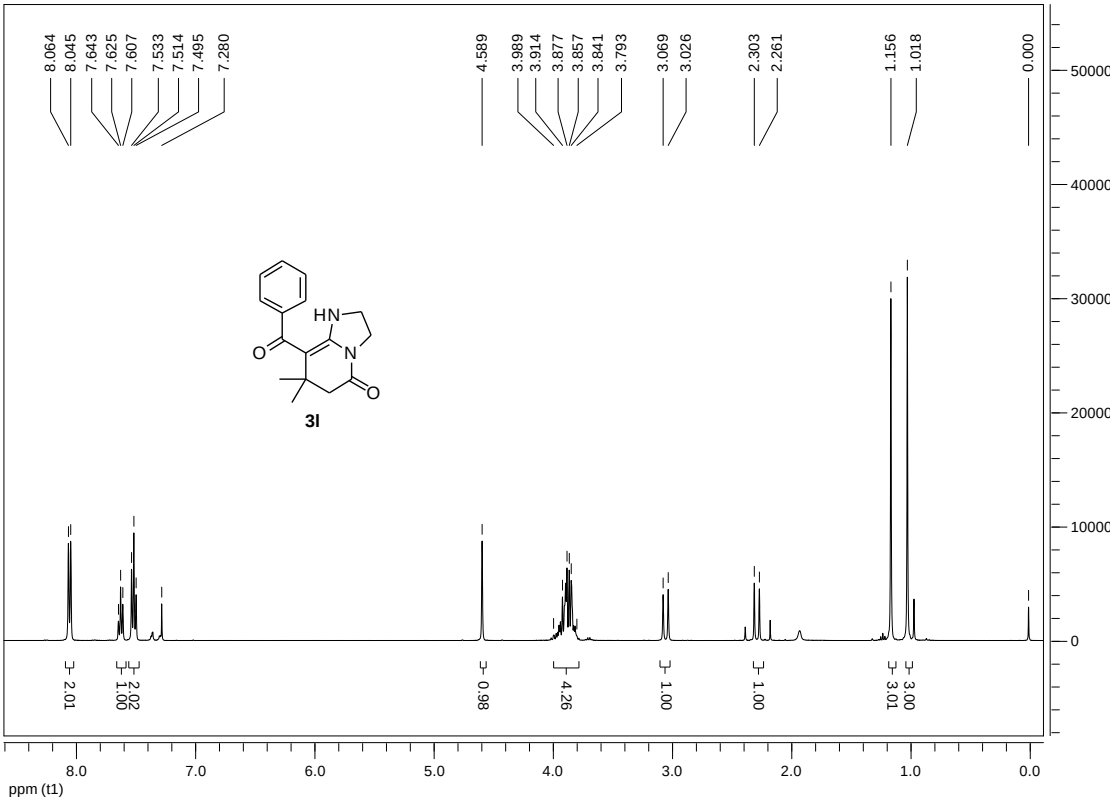
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3j**



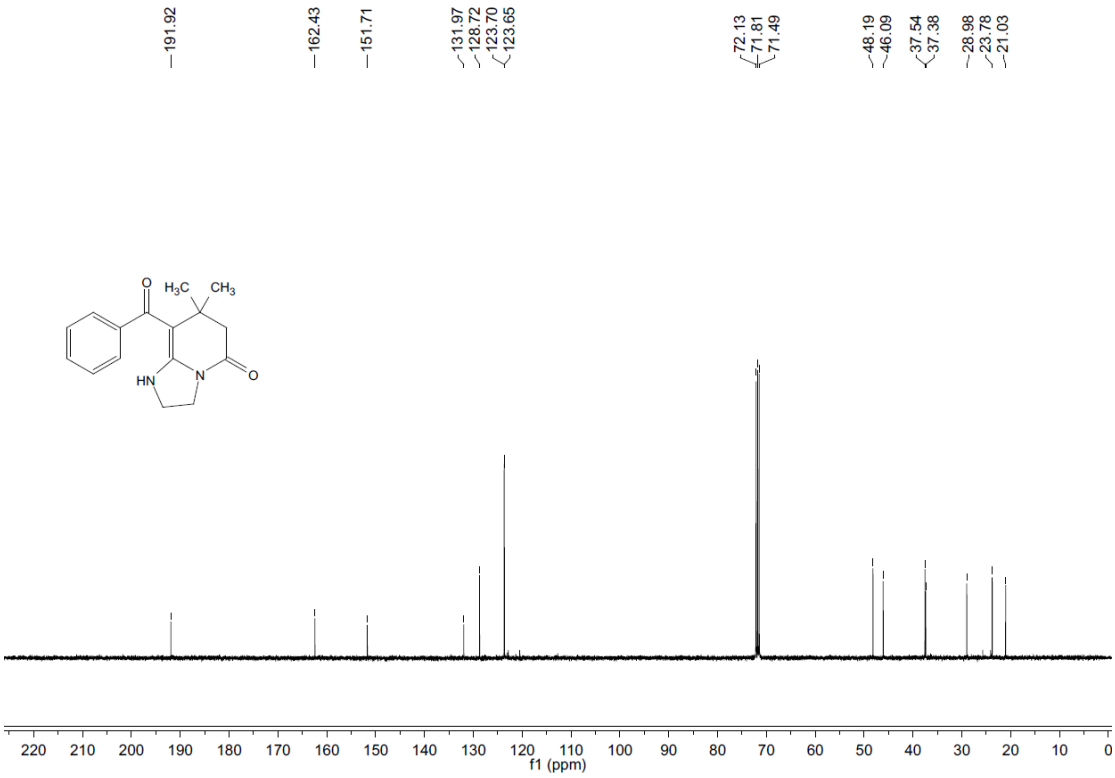
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3k**



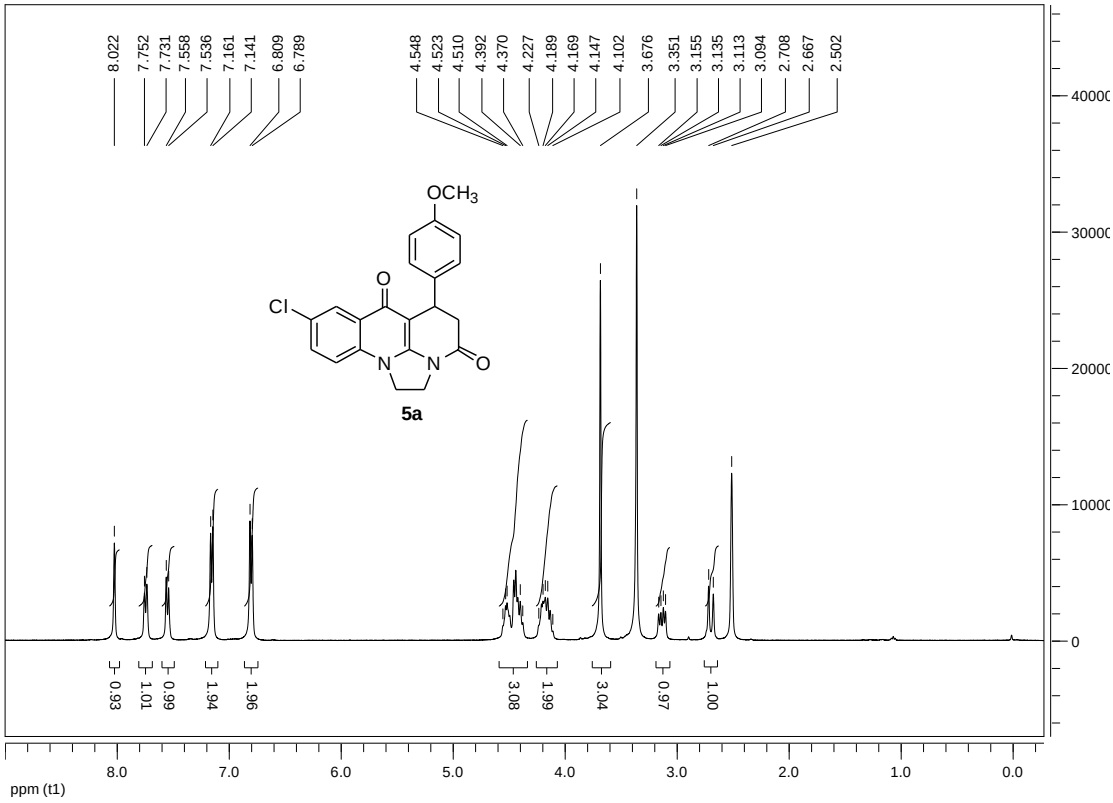
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3k**



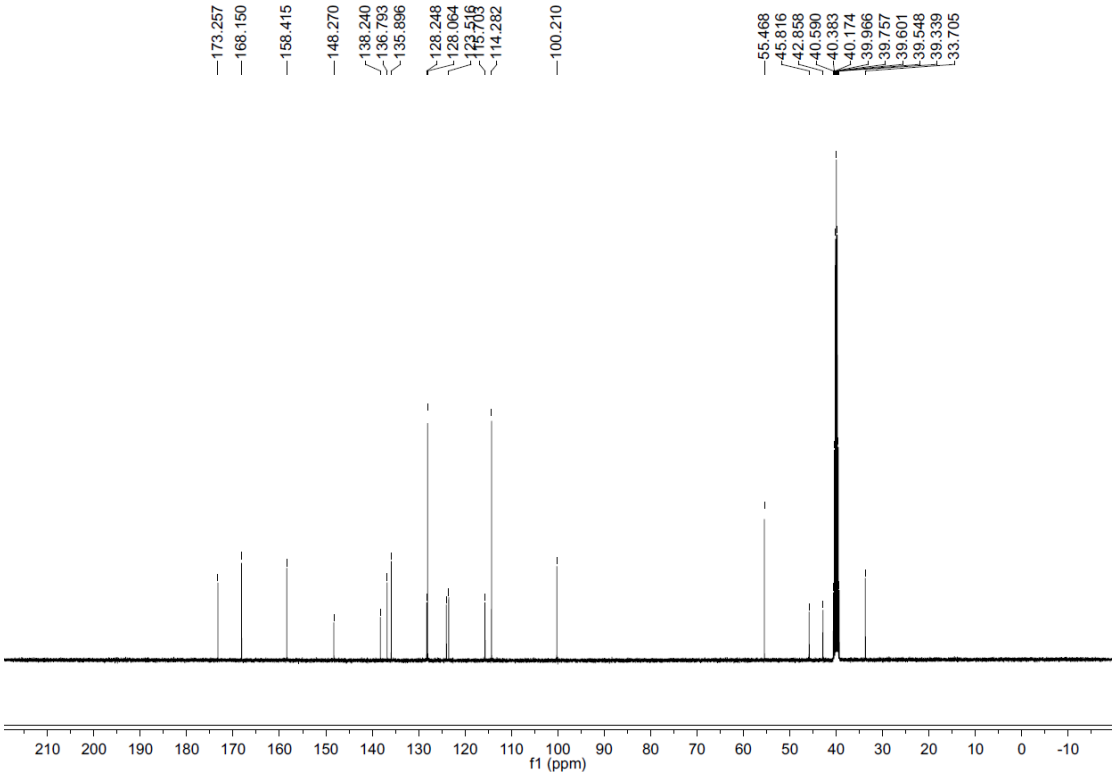
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3l**



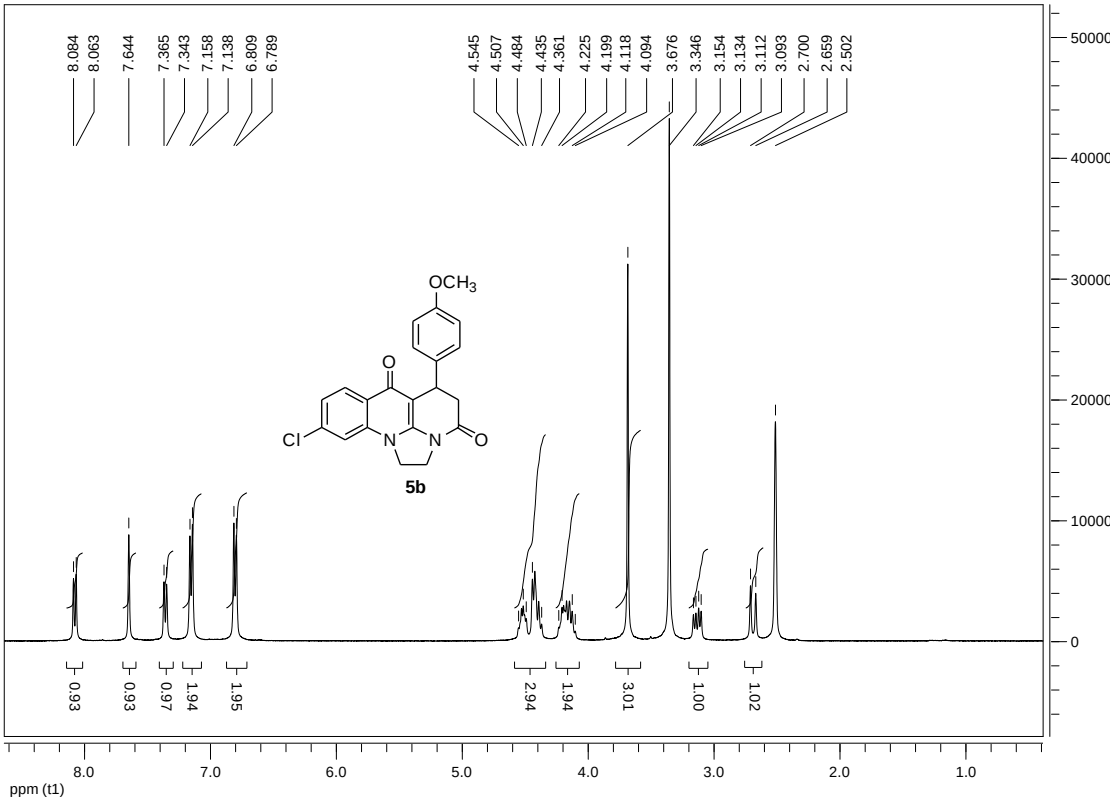
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3l**



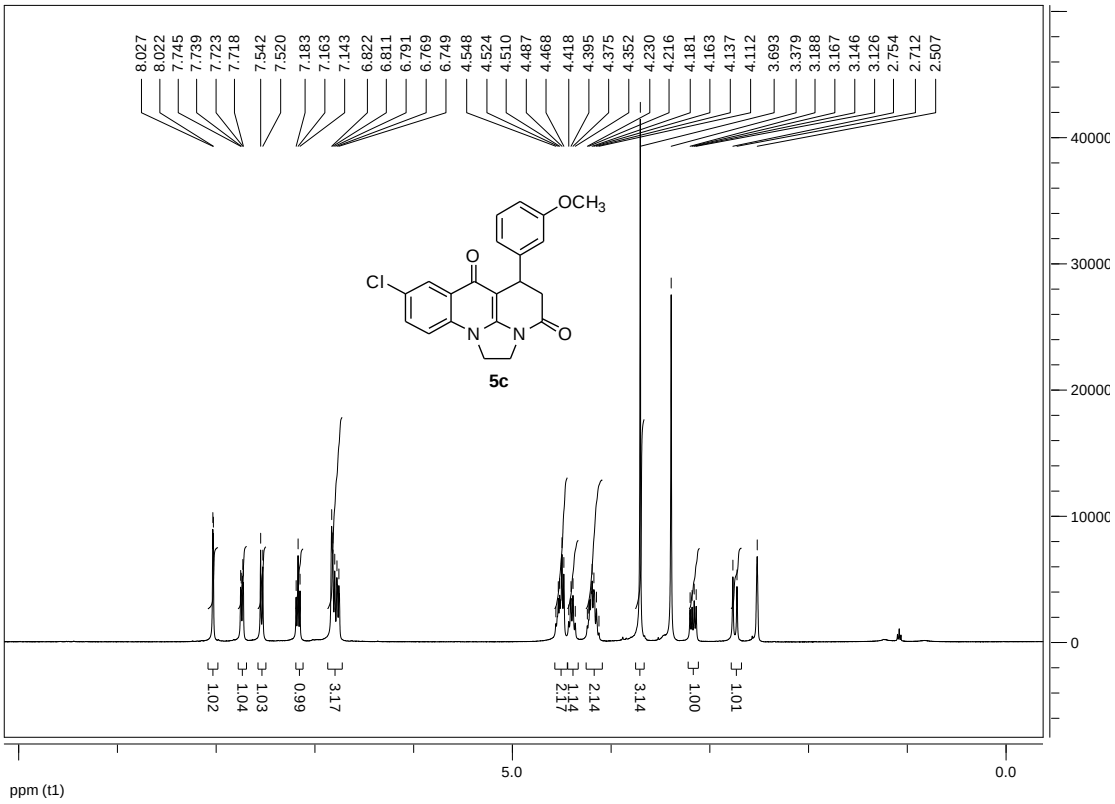
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **5a**



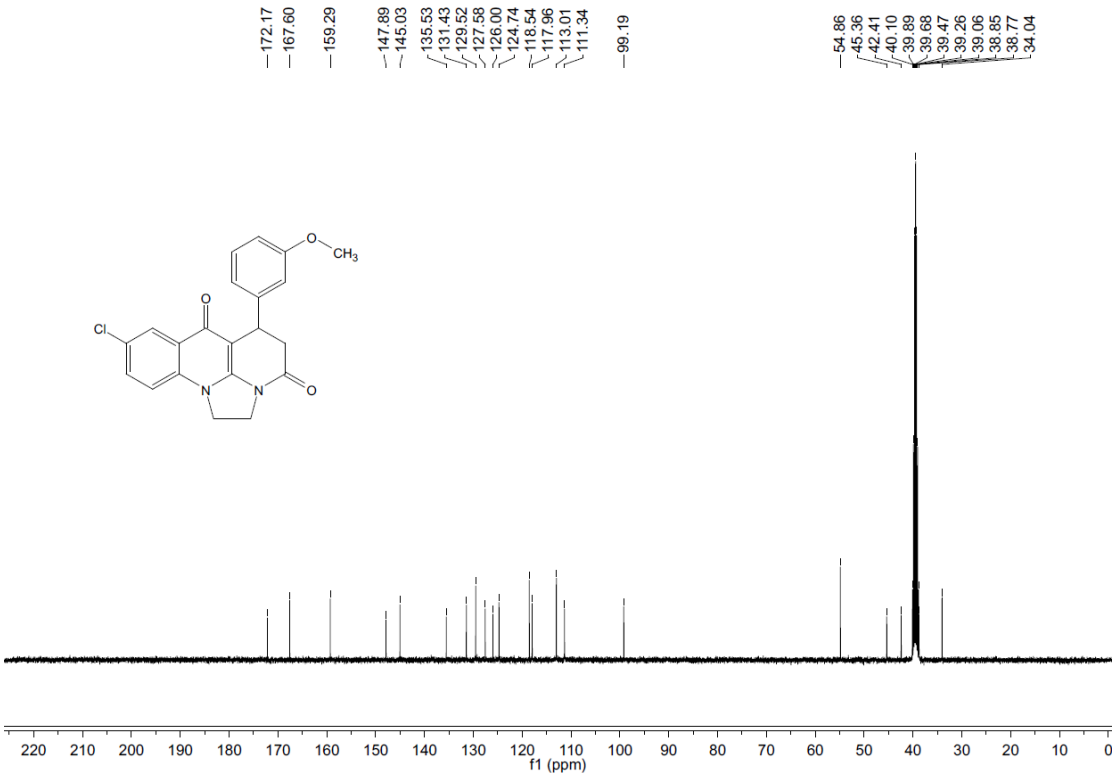
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **5a**



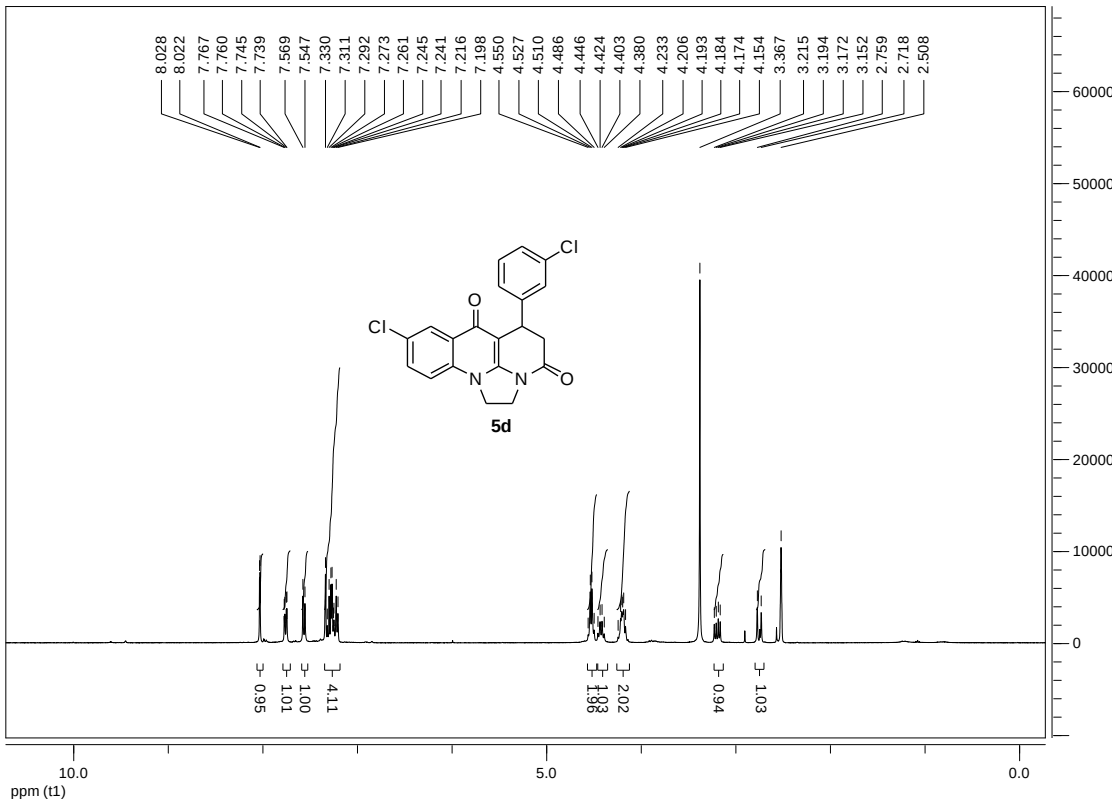
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **5b**



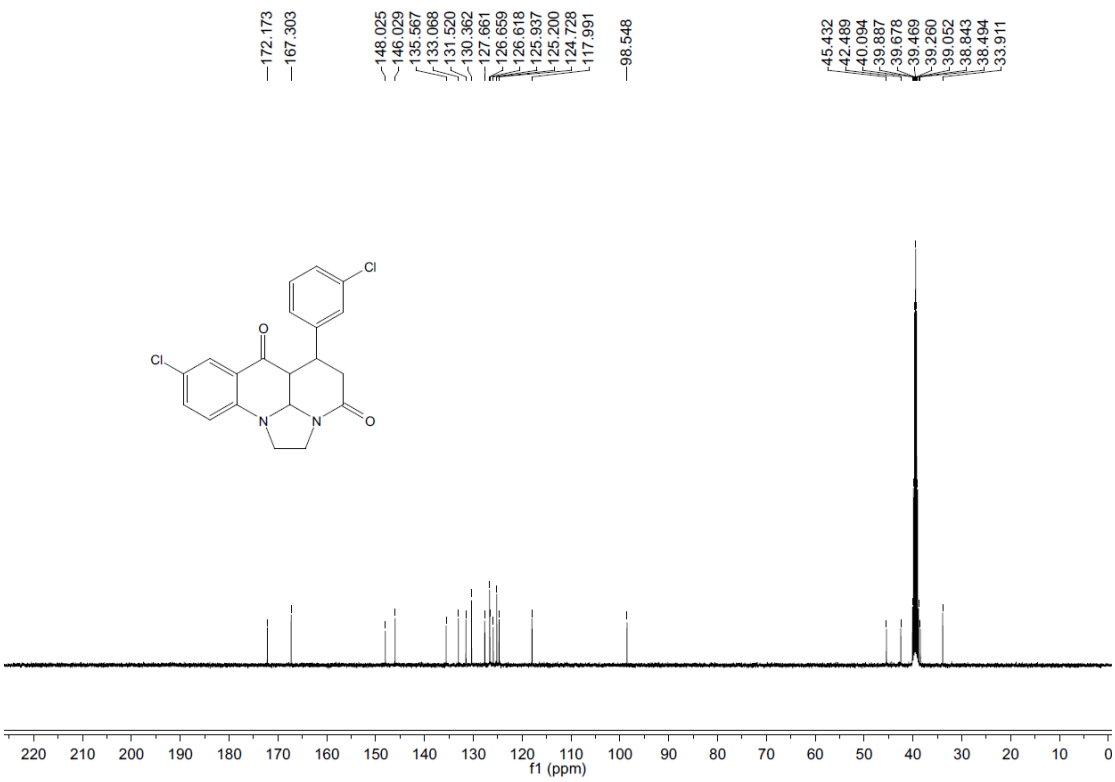
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **5c**



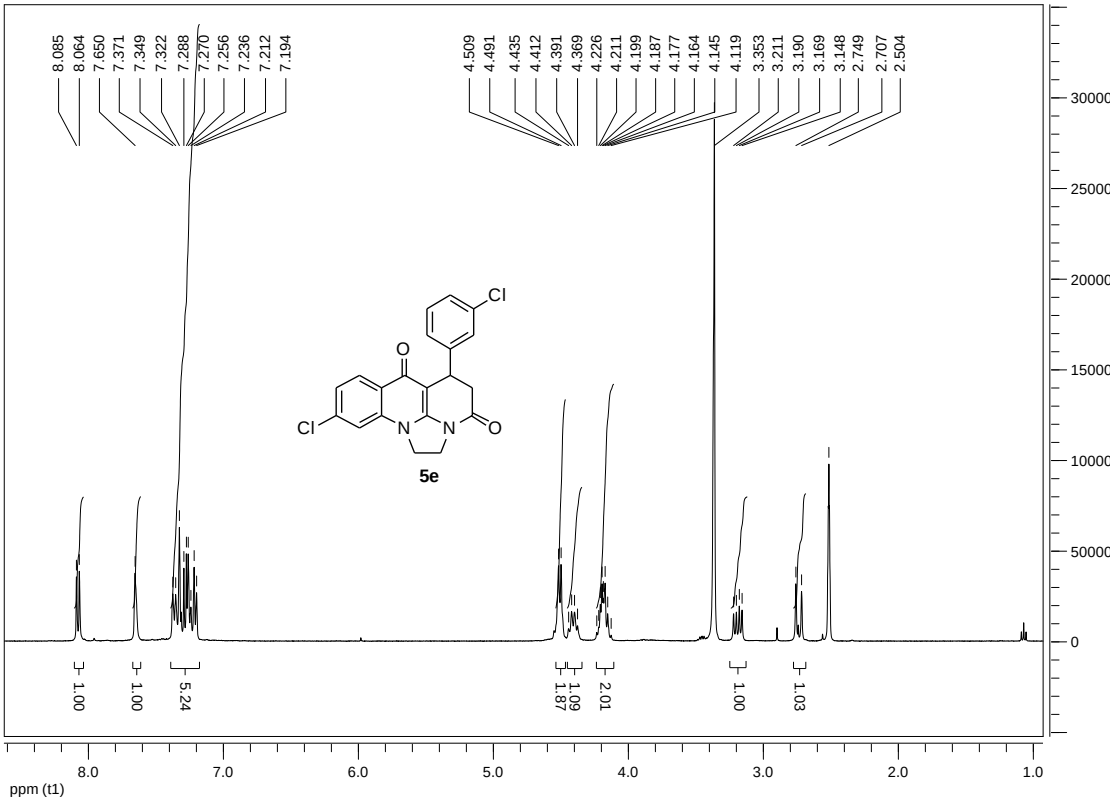
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **5c**



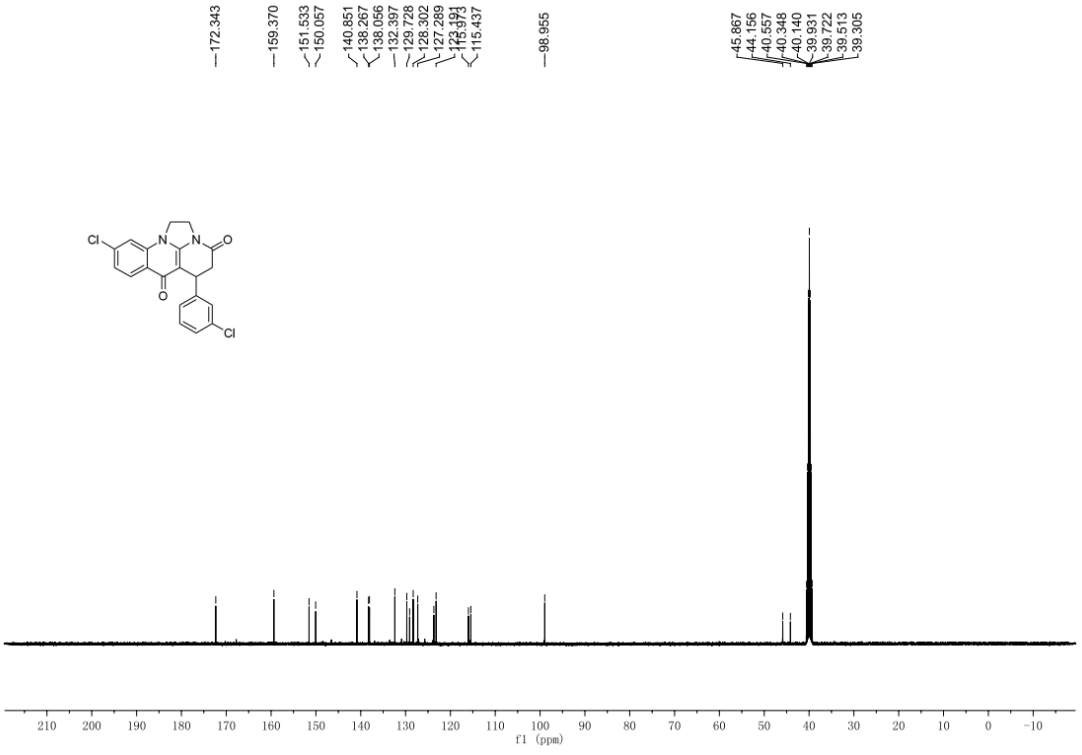
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **5d**



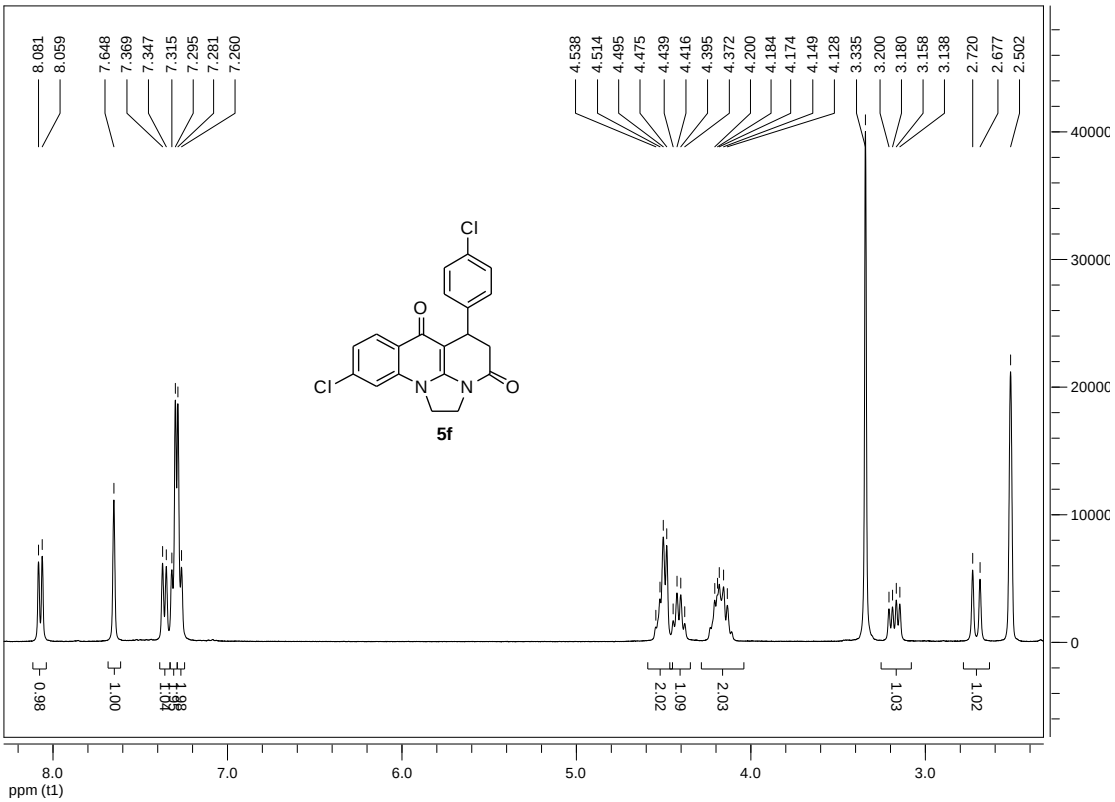
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **5d**



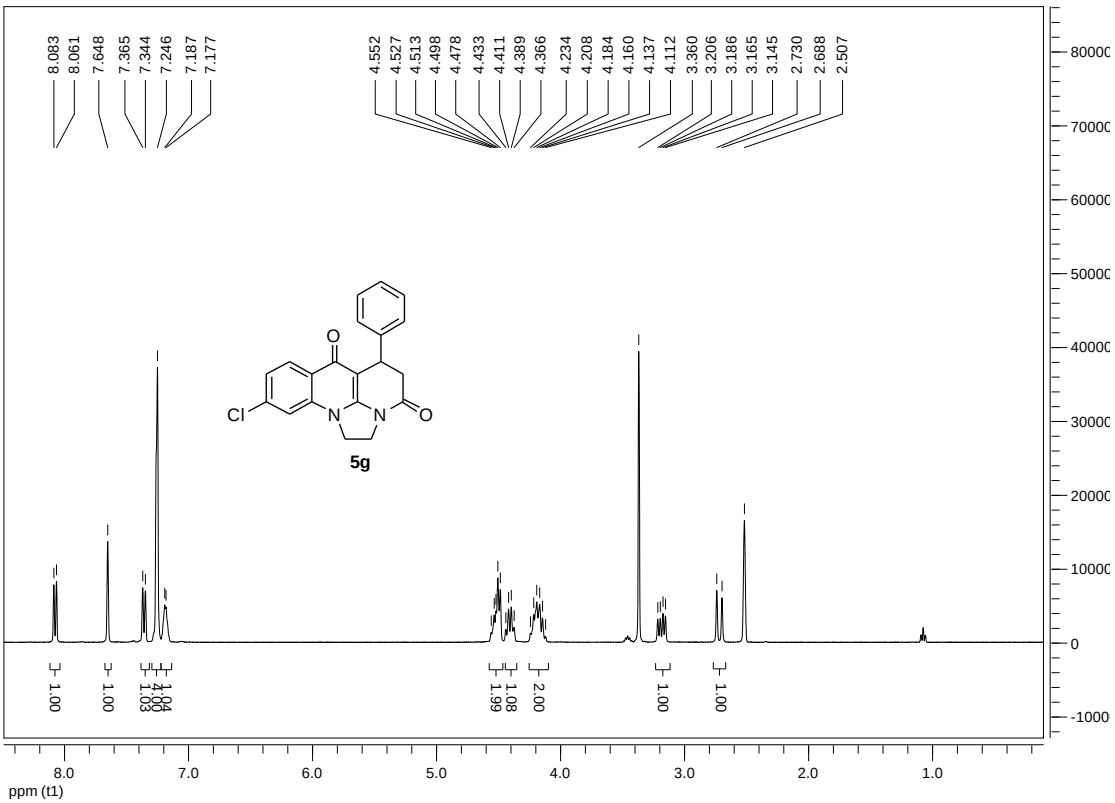
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **5e**



^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **5e**



^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **5f**



^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **5g**

Electronic Supplementary Material (ESI) for RSC Advances