

Supporting information for

Metal-free oxidative acylation/cyclization of *N*-methacryloyl-2-phenylbenzimidazole with aryl aldehydes: An easy access to benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones

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1. General methods.....	S2
2. Characterization data of products.....	S2-S9
3. Copies of NMR spectra of 3a-v and 4a,4b.....	S10-S33

1. General methods

All the chemicals were purchased from commercial sources and used without further purification. Reactions were performed in oven-dried sealed tubes and the reactions were conducted under a nitrogen atmosphere. Glass syringes were used to transfer solvents. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Melting points (MP) were obtained on Buchi B-540. ¹H and ¹³C NMR (proton-decoupled) spectra were recorded in CDCl₃ solvent on 300, 400 or 500 MHz NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra and HRMS were recorded on mass

spectrometry by Electrospray ionization (ESI) or Atmospheric pressure chemical ionization (APCI) technique.

2. Characterization data of products

3a. 5-Methyl-5-(2-oxo-2-phenylethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 80%, mp 189-191 °C ¹H NMR (400 MHz, CDCl₃) δ 8.65 – 8.45 (m, 1H), 8.34 (d, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 6.9 Hz, 3H), 7.58 – 7.52 (m, 1H), 7.49 – 7.39 (m, 6H), 7.37 – 7.30 (m, 1H), 4.31 (d, *J* = 18.2 Hz, 1H), 4.15 (d, *J* = 18.2 Hz, 1H), 1.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 173.3, 150.1, 144.1, 141.9, 135.7, 133.6, 131.6, 128.6, 128.1, 127.6, 126.4, 125.6, 125.3, 124.4, 119.8, 115.6, 49.3, 46.2, 30.2. HRMS (*m/z*) calcd for C₂₄H₁₉O₂N₂ [M+H]⁺ 367.1441, found 367.1457.

3b. 5-(2-(3-Chlorophenyl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 75%, mp 209-211 °C ¹H NMR (500 MHz, CDCl₃) δ 8.60 – 8.53 (m, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.82 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.39 (m, 4H), 7.4 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.30 (m, 1H), 4.28 (d, *J* = 18.3 Hz, 1H), 4.09 (d, *J* = 18.3 Hz, 1H), 1.73 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 194.9, 173.1, 150.0, 144.0, 141.7, 137.1, 135.0, 133.6, 131.7, 130.0, 128.2, 127.7, 126.5, 126.1, 125.7, 125.4, 124.3, 123.0, 119.8, 115.6, 49.3, 46.1, 30.2. HRMS (*m/z*) calcd for C₂₅H₂₂ON₂Cl [M+H]⁺ 401.1415, found 401.1355.

3c. 5-(2-(Furan-2-yl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 77%, mp 166-168 °C ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, *J* = 7.3 Hz, 1H), 8.34 (d, *J* = 7.1 Hz, 1H), 7.85 (d, *J* = 7.1 Hz, 1H), 7.55 (s, 1H), 7.49 – 7.39 (m, 4H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 3.4 Hz, 1H), 6.52–6.43 (m, 1H), 4.15 (d, *J* = 18.3 Hz, 1H), 4.03 (d, *J* = 18.3 Hz, 1H), 1.72 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 185.4, 173.1, 152.0, 150.0, 146.4, 144.1, 141.6, 131.6, 129.1, 127.6, 126.4, 125.6, 125.3, 124.6, 123.1, 119.7, 117.2, 115.6, 112.5, 48.9, 45.8, 30.1. HRMS (*m/z*) calcd for C₂₂H₁₇O₃N₂ [M+H]⁺ 357.1233, found 357.1248.

3d. 5-Methyl-5-(2-(naphthalen-1-yl)-2-oxoethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 69%, mp 186-188 °C ¹H NMR (400 MHz, CDCl₃) δ 8.60 – 8.55 (m, 1H), 8.43 – 8.34 (m, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.91 – 7.87 (m, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.42 (m, 6H), 7.41 – 7.34 (m, 2H), 4.47 (d, *J* = 18.0 Hz, 1H), 4.18 (d, *J* = 18.0 Hz, 1H), 1.74 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 200.0, 173.3, 150.1, 144.1, 141.9, 134.2, 133.8, 133.3, 131.7, 131.6, 129.9, 128.2, 128.1, 127.9, 127.6, 126.5, 126.4, 125.6, 125.5, 125.4, 124.4, 124.1, 123.2, 119.8, 115.7, 52.3, 46.7, 30.1. HRMS (*m/z*) calcd for C₂₈H₂₁O₂N [M+H]⁺ 417.1597, found 417.1607.

3e. 5-(2-(2-Fluorophenyl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 68%, mp 159-160 °C ¹H NMR (500 MHz, CDCl₃) δ 8.58 – 8.52 (m, 1H), 8.37 – 8.30 (m, 1H), 7.91 – 7.83 (m, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 – 7.39 (m, 5H), 7.39 – 7.35 (m, 1H), 7.19 – 7.09 (m, 2H), 4.31 (dd, *J* = 19.0, 3.3 Hz, 1H), 4.16 (dd, *J* = 19.0, 3.4 Hz, 1H), 1.71 (s, 3H) ¹³C NMR (100 MHz, CDCl₃) δ 194.2, 194.1, 173.3, 163.6, 161.1, 150.1, 144.1, 142.0, 135.4, 135.3, 131.7, 131.6, 130.8, 127.6, 126.3, 125.6, 125.3, 124.5, 124.5, 124.0, 123.9, 123.0, 119.8, 116.8, 116.5, 115.6, 54.1, 54.0, 46.3, 30.2. HRMS (*m/z*) calcd for C₂₄H₁₈O₂N₂F [M+H]⁺ 385.1346, found 385.1358.

3f. 5-Methyl-5-(2-oxo-2-(thiophen-2-yl)ethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 79%, mp 192-194 °C ¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.50 (m, 1H), 8.38 – 8.30 (m, 1H), 7.90 – 7.81 (m, 1H), 7.76 (d, *J* = 3.1 Hz, 1H), 7.60 (d, *J* = 4.3 Hz, 1H), 7.51 – 7.34 (m, 5H), 7.15 – 7.08 (m, 1H), 4.27 (d, *J* = 17.9 Hz, 1H), 4.05 (d, *J* = 17.9 Hz, 1H), 1.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 188.9, 173.0, 149.9, 144.1, 142.6, 141.6, 134.2, 132.2, 131.6, 128.1, 127.6, 126.4, 125.6, 125.4, 124.5, 123.0, 119.8, 115.6, 49.6, 46.2, 30.2. HRMS (*m/z*) calcd for C₂₄H₂₁N₂O₂S [M+H]⁺ 401.1323, found 401.1345.

3g. 5-(2-(4-Bromophenyl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 67%, mp 230-232 °C ¹H NMR (400 MHz, CDCl₃) δ 8.58 – 8.51 (m, 1H), 8.36 – 8.30 (m, 1H), 7.75 – 7.69 (m, 1H), 7.75 – 7.69 (m, 2H), 7.59 – 7.55 (m, 2H), 7.49 – 7.39 (m, 4H), 7.34 – 7.30 (m, 1H), 4.27 (d, *J* = 18.2 Hz, 1H), 4.09 (d, *J* = 18.2 Hz, 1H), 1.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.2, 173.2, 150.0, 144.0, 141.7, 134.4, 132.0, 131.7, 131.6, 129.5, 129.0, 127.7, 126.4, 125.7, 125.4, 124.3, 123.0, 119.8, 115.6, 49.2, 46.1, 30.2. HRMS (*m/z*) calcd for C₂₄H₁₈O₂N₂Br [M+H]⁺ 445.0546, found 445.0560.

3h. 5-(2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one

White solid, Yield 68%, mp 120-122 °C ¹H NMR (500 MHz, CDCl₃) δ 8.58 – 8.54 (m, 1H), 8.38 – 8.32 (m, 1H), 8.00– 7.99 (m, 2H), 7.89 – 7.85 (m, 1H), 7.67 – 7.61 (m, 2H), 7.61 – 7.57 (m, 2H), 7.49 – 7.34 (m, 8H), 4.34 (d, *J* = 18.2 Hz, 1H), 4.18 (d, *J* = 18.2 Hz, 1H), 1.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 173.3, 150.1, 146.3, 145.3, 142.0, 139.6, 134.4, 131.6, 128.9, 128.7, 128.4, 127.6, 127.3, 126.4, 125.6, 125.3, 124.4, 123.1, 121.3, 119.8, 118.1, 115.6, 49.3, 46.2, 30.2. HRMS (*m/z*) calcd for C₃₀H₂₃O₂N₂ [M+H]⁺ 443.1754, found 443.1765.

3i. 5-(2-(4-Bromothiophen-2-yl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one

White solid, Yield 74%, mp 131-133 °C ¹H NMR (300 MHz, CDCl₃) δ 8.59 – 8.47 (m, 1H), 8.38 – 8.28 (m, 1H), 7.91 – 7.80 (m, 1H), 7.67 (s, 1H), 7.55 – 7.38 (m, 5H), 7.37 – 7.31 (d, 1H), 4.23 (d, *J* = 18.0 Hz, 1H), 3.99 (d, *J* = 18.0 Hz, 1H), 1.72 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 188.0, 172.8, 149.8, 144.1, 143.0, 141.3, 134.3, 131.7, 131.6, 131.5, 127.8, 126.5, 125.7, 125.4, 124.4, 123.0, 119.8, 115.6, 110.9, 49.3, 46.1, 30.2. HRMS (*m/z*) calcd for C₂₂H₁₆O₂N₂BrS[M+H]⁺ 451.0110, found 451.0128.

3j. 5-Methyl-5-(2-oxo-2-(*o*-tolyl)ethyl)benzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one

White solid, Yield 70%, mp 178-180 °C ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 5.8 Hz, 1H), 8.36 (d, *J* = 7.1 Hz, 1H), 7.86 (d, *J* = 6.8 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.53 – 7.30 (m, 7H), 7.14 (d, *J* = 7.0 Hz, 1H), 4.29 (d, *J* = 17.9 Hz, 1H), 4.01 (d, *J* = 18.0 Hz, 1H), 2.10 (s, 3H), 1.69 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 173.3, 150.1, 144.0, 142.0, 138.6, 136.4,

132.0, 131.7, 131.5, 131.3, 128.4, 127.5, 126.4, 125.6, 125.3, 124.3, 123.1, 119.7, 115.6, 51.9, 46.5, 30.1, 21.0. HRMS (*m/z*) calcd for C₂₅H₂₁O₂N₂ [M+H]⁺ 381.1597, found 381.1612.

3k. 5-(2-(6-Bromobenzo[d][1,3]dioxol-5-yl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 73%, mp 161-163 °C ¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.50 (m, 1H), 8.38 – 8.31 (m, 1H), 7.88 – 7.82 (m, 1H), 7.52 – 7.40 (m, 4H), 7.38 – 7.34 (m, 1H), 6.97 (s, 1H), 6.76 (s, 1H), 5.98 (s, 2H), 4.31 (d, *J* = 18.1 Hz, 1H), 4.09 (d, *J* = 18.1 Hz, 1H), 1.69 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 198.0, 172.9, 150.7, 149.9, 147.4, 144.1, 141.4, 132.9, 131.7, 131.5, 127.7, 126.4, 125.6, 125.4, 124.8, 123.1, 119.8, 115.6, 113.8, 111.9, 109.2, 102.5, 52.9, 46.8, 30.1. HRMS (*m/z*) calcd for C₂₅H₁₈BrN₂O₄ [M+H]⁺ 489.0449, found 489.0461.

3l. 5-(2-(3-Methoxyphenyl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 77%, mp 119-121 °C ¹H NMR (400 MHz, CDCl₃) δ 8.60 – 8.50 (m, 1H), 8.34 (d, *J* = 7.3 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.37 – 7.31 (m, 2H), 7.30 (s, 1H), 7.12 – 7.04 (m, 1H), 4.29 (d, *J* = 18.2 Hz, 1H), 4.13 (d, *J* = 18.2 Hz, 1H), 3.75 (s, 3H), 1.72 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.0, 173.3, 159.8, 150.1, 144.1, 141.9, 137.0, 131.7, 131.6, 129.6, 127.6, 126.4, 125.6, 125.3, 124.4, 123.0, 120.7, 120.5, 119.8, 115.6, 111.9, 55.4, 49.4, 46.2, 30.2. HRMS (*m/z*) calcd for C₂₅H₂₁O₃N₂ [M+H]⁺ 397.1546, found 397.1554.

3m. 3-Ethyl-5-methyl-5-(2-oxo-2-phenylethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 79%, mp 135-137 °C ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 7.4 Hz, 1H), 7.91 – 7.81 (m, 3H), 7.59 – 7.51 (m, 1H), 7.47 – 7.37 (m, 4H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.12 (s, 1H), δ 4.30 (d, *J* = 18.2 Hz, 1H), 4.14 (d, *J* = 18.2 Hz, 1H). 2.66 (q, *J* = 7.6 Hz, 2H), 1.72 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.2, 173.5, 150.3, 148.3, 144.1, 142.0, 135.8, 133.6, 131.6, 128.6, 128.1, 127.4, 126.5, 125.5, 125.1,

123.7, 120.6, 119.6, 115.6, 49.3, 46.2, 30.3, 29.1, 15.1. HRMS (m/z) calcd for $C_{26}H_{23}O_2N_2$ $[M+H]^+$ 395.1754, found 428.395.1765.

3n. 3-Bromo-5-(2-(4-bromophenyl)-2-oxoethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 67%, mp 131-133 °C 1H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.30 (m, 1H), 8.00 – 7.92 (m, 1H), 7.81 – 7.69 (m, 3H), 7.64 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 7.30 – 7.27 (m, 1H), 7.24 – 7.19 (m, 1H), 4.31 (d, $J = 18.3$ Hz, 1H), 4.07 (d, $J = 18.3$ Hz, 1H), 1.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 172.2, 144.8, 143.6, 135.1, 134.3, 132.0, 131.9, 131.6, 131.0, 129.5, 129.1, 126.1, 125.7, 123.6, 122.5, 122.0, 120.8, 115.6, 49.2, 46.6, 30.6. HRMS (m/z) calcd for $C_{24}H_{17}O_2N_2Br_2$ $[M+H]^+$ 522.9651, found 522.9692.

3o. 3-Bromo-5-methyl-5-(2-oxo-2-phenylethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 76%, mp 140-142 °C 1H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, $J = 8.3$ Hz, 1H), 8.31 (d, $J = 7.5$ Hz, 1H), 7.92 – 7.81 (m, 3H), 7.61 – 7.53 (m, 2H), 7.50 – 7.37 (m, 5H), 4.34 (d, $J = 18.4$ Hz, 1H), 4.06 (d, $J = 18.4$ Hz, 1H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 172.5, 149.2, 144.0, 143.8, 135.5, 133.8, 131.6, 131.0, 128.7, 128.1, 127.9, 127.7, 126.1, 125.8, 125.6, 122.2, 119.9, 115.6, 49.4, 46.1, 30.0. HRMS (m/z) calcd for $C_{24}H_{18}O_2N_2Br$ $[M+H]^+$ 445.0546, found 445.0558.

3p. 5-(2-(4-Chlorophenyl)-2-oxoethyl)-5,9,10-trimethylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 71%, mp 119-121 °C 1H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.46 (m, 1H), 8.11 (s, 1H), 7.81 – 7.75 (m, 2H), 7.62 (s, 1H), 7.45 – 7.41 (m, 2H), 7.40 – 7.36 (m, 2H), 7.32 – 7.27 (m, 1H), 4.25 (d, $J = 18.2$ Hz, 1H), 4.06 (d, $J = 18.2$ Hz, 1H), 2.41 (d, $J = 4.3$ Hz, 6H), 1.71 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 173.1, 149.2, 142.5, 141.5, 140.1, 134.7, 134.6, 134.0, 131.2, 129.9, 129.4, 129.0, 127.6, 126.2, 124.3, 123.3, 120.0, 115.9, 49.1, 46.1, 30.2, 20.5. HRMS (m/z) calcd for $C_{26}H_{22}O_2N_2Cl$ $[M+H]^+$ 429.1364, found 429.1371.

3q. 5,9,10-Trimethyl-5-(2-oxo-2-phenylethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 78%, mp 239-241 °C ¹H NMR (500 MHz, CDCl₃) δ 8.58 – 8.43 (m, 1H), 8.12 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.64 (s, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.35 (m, 4H), 7.34 – 7.28 (m, 1H), 4.29 (d, *J* = 18.2 Hz, 1H), 4.13 (d, *J* = 18.2 Hz, 1H), 2.41 (d, *J* = 5.2 Hz, 6H), 1.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 173.2, 149.3, 142.5, 141.7, 135.8, 134.6, 134.5, 133.5, 131.2, 130.0, 128.6, 128.0, 127.5, 126.2, 124.3, 123.3, 120.0, 115.9, 49.2, 46.1, 30.2, 20.5. HRMS (*m/z*) calcd for C₂₆H₂₃O₂N₂ [M+H]⁺ 395.1754, found 395.1762.

3r. 5,9,10-Trimethyl-5-(2-oxo-2-(thiophen-2-yl)ethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 73%, mp 219-221 °C ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 6.7 Hz, 1H), 8.12 (s, 1H), 7.75 (d, *J* = 3.0 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.48 – 7.38 (m, 2H), 7.37 – 7.31 (d, *J* = 6.9 Hz, 1H), 7.15 – 7.07 (m, 1H), 4.24 (d, *J* = 17.9 Hz, 1H), 4.02 (d, *J* = 17.9 Hz, 1H), 2.41 (s, 6H), 1.70 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 188.8, 182.4, 173.0, 149.2, 142.7, 142.5, 141.3, 134.6, 134.5, 134.1, 132.1, 131.2, 130.0, 128.1, 127.6, 126.2, 124.4, 123.3, 120.0, 115.9, 49.6, 46.1, 30.2, 20.5. HRMS (*m/z*) calcd for C₂₄H₂₁O₂N₂S [M+H]⁺ 401.1318, found 401.1312.

3s. 2-Chloro-5-methyl-5-(2-oxo-2-phenylethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 65%, mp 97-99 °C ¹H NMR (400 MHz, CDCl₃) δ 8.55 (d, *J* = 2.2 Hz, 1H), 8.36 – 8.30 (m, 1H), 8.15 – 8.09 (m, 1H), 7.85 (dd, *J* = 9.3, 2.0 Hz, 1H), 7.57 (dd, *J* = 14.6, 7.2 Hz, 1H), 7.50 – 7.38 (m, 1H), 7.27 (d, *J* = 5.4 Hz, 1H), 4.32 (d, *J* = 18.3 Hz, 1H), 4.09 (d, *J* = 18.3 Hz, 1H), 1.72 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 196.0, 172.7, 148.8, 143.9, 140.2, 135.5, 133.8, 131.6, 130.2, 129.3, 129.2, 128.7, 128.5, 128.1, 126.1, 125.9, 125.9, 125.8, 124.7, 120.0, 115.7, 49.4, 46.0, 30.0. HRMS (*m/z*) calcd for C₂₅H₂₂ON₂Cl [M+H]⁺ 401.1415, found 401.1070.

3t. 1-Bromo-5-methyl-5-(2-oxo-2-phenylethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 68%, mp 194-196 °C ¹H NMR (400 MHz, CDCl₃) δ 8.39 – 8.31 (m, 1H), 8.01 – 7.94 (m, 1H), 7.91 – 7.83 (m, 2H), 7.76 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.49 – 7.39 (m, 4H), 7.33 – 7.28 (m, 1H), 7.24 – 7.18 (m, 1H), 4.35 (d, *J* = 18.3 Hz, 1H), 4.14 (d, *J* = 18.3 Hz, 1H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.9, 172.3, 147.5, 145.0, 135.6, 135.0, 133.7, 131.0, 130.9, 128.7, 128.1, 126.1, 125.6, 123.6, 122.5, 121.9, 120.7, 115.6, 49.3, 46.7, 30.6. HRMS (*m/z*) calcd for C₂₄H₁₈O₂N₂Br [M+H]⁺ 445.0546, found 445.0565.

3u. 6-methyl-6-(2-oxo-2-phenylethyl)imidazo[2,1-a]isoquinolin-5(6H)-one

Colourless oil, Yield 22%, ¹H NMR (400 MHz, CDCl₃) δ 8.34 – 8.29 (m, 1H), 7.88 – 7.85 (m, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.45 – 7.39 (m, 1H), 7.39 – 7.34 (m, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 4.22 (d, *J* = 18.2 Hz, 1H), 4.15 (d, *J* = 18.2 Hz, 1H), 1.66 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 196.0, 172.7, 135.6, 133.7, 131.9, 130.2, 128.9, 128.7, 128.1, 127.9, 127.5, 124.9, 124.1, 114.0, 49.5, 45.9, 29.9. HRMS (*m/z*) calcd for C₂₀H₁₆N₂O₂ [M+H]⁺ 317.1290, found 317.1283.

3v. 5-(2-oxo-2-phenylethyl)-5-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

Colourless oil, Yield 36%, ¹H NMR (400 MHz, CDCl₃) δ 8.56 – 8.53 (m, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.50 – 7.36 (m, 9H), 7.25 (s, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 4.89 (d, *J* = 17.8 Hz, 1H), 4.52 (d, *J* = 17.8 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 196.0, 171.0, 150.1, 144.1, 140.8, 135.9, 133.7, 133.3, 131.7, 130.1, 129.1, 128.7, 128.5, 128.4, 128.1, 128.0, 127.6, 127.2, 126.4, 126.2, 125.6, 125.4, 124.6, 119.8, 115.6, 54.2, 48.2. HRMS (*m/z*) calcd for C₂₉H₂₀N₂O₂ [M+H]⁺ found 429.1603, found 429.1609.

4a. 5-(2-Hydroxyethyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

White solid, Yield 55%, mp 159-161 °C ¹H NMR (400 MHz, CDCl₃) δ 8.42 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.39 – 8.33 (m, 1H), 7.80 – 7.72 (m, 1H), 7.60 – 7.51 (m, 1H), 7.48 – 7.36 (m, 4H), 3.62 – 3.49 (m, 1H), 3.32 – 3.18 (m, 1H), 3.00 – 2.84 (m, 1H), 2.30 – 2.18 (m, 1H), 1.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 149.7, 143.8, 140.8, 131.7, 131.5, 127.7, 126.1, 125.9, 125.7,

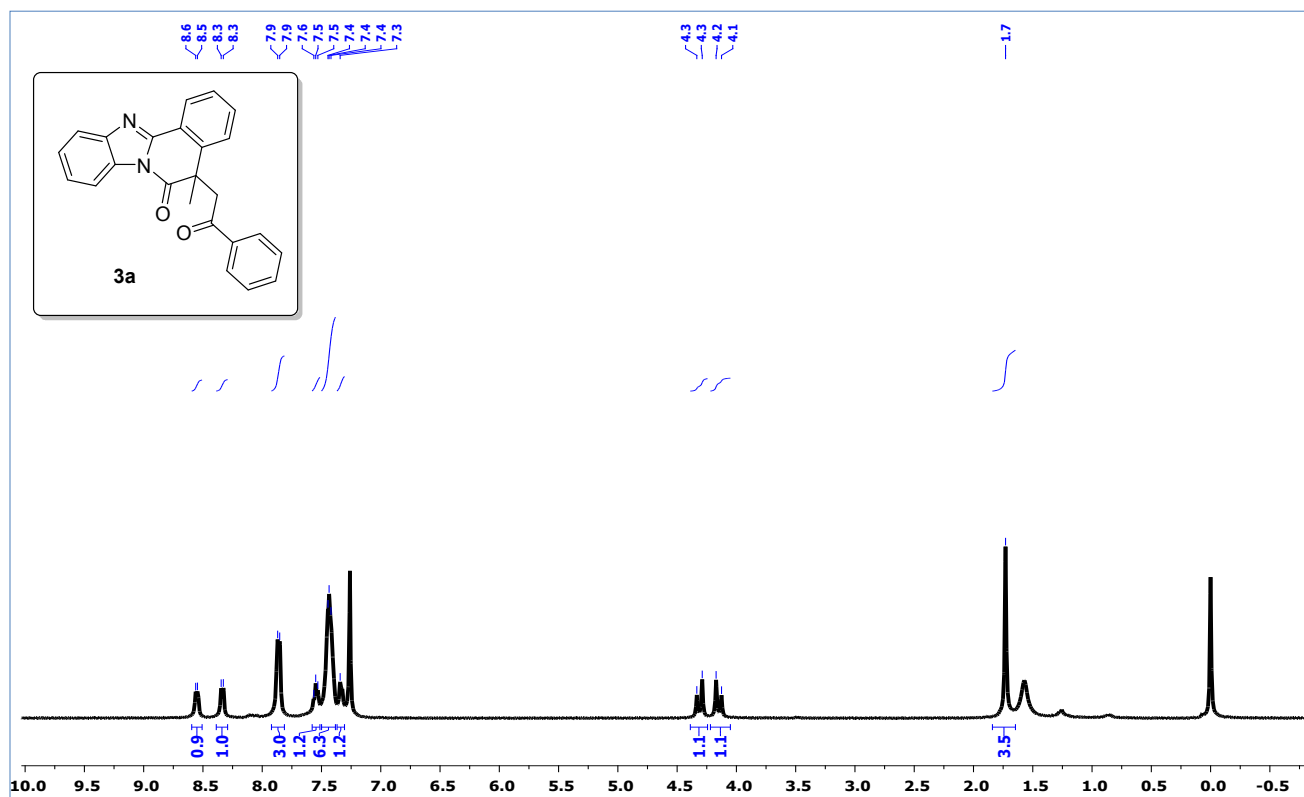
125.4, 123.0, 119.6, 115.7, 59.0, 47.0, 44.0, 29.9. HRMS (m/z) calcd for $C_{18}H_{17}N_2O_2$ $[M+H]^+$ 293.1290, found 293.1278.

4b. 5-(2-Hydroxypropyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one

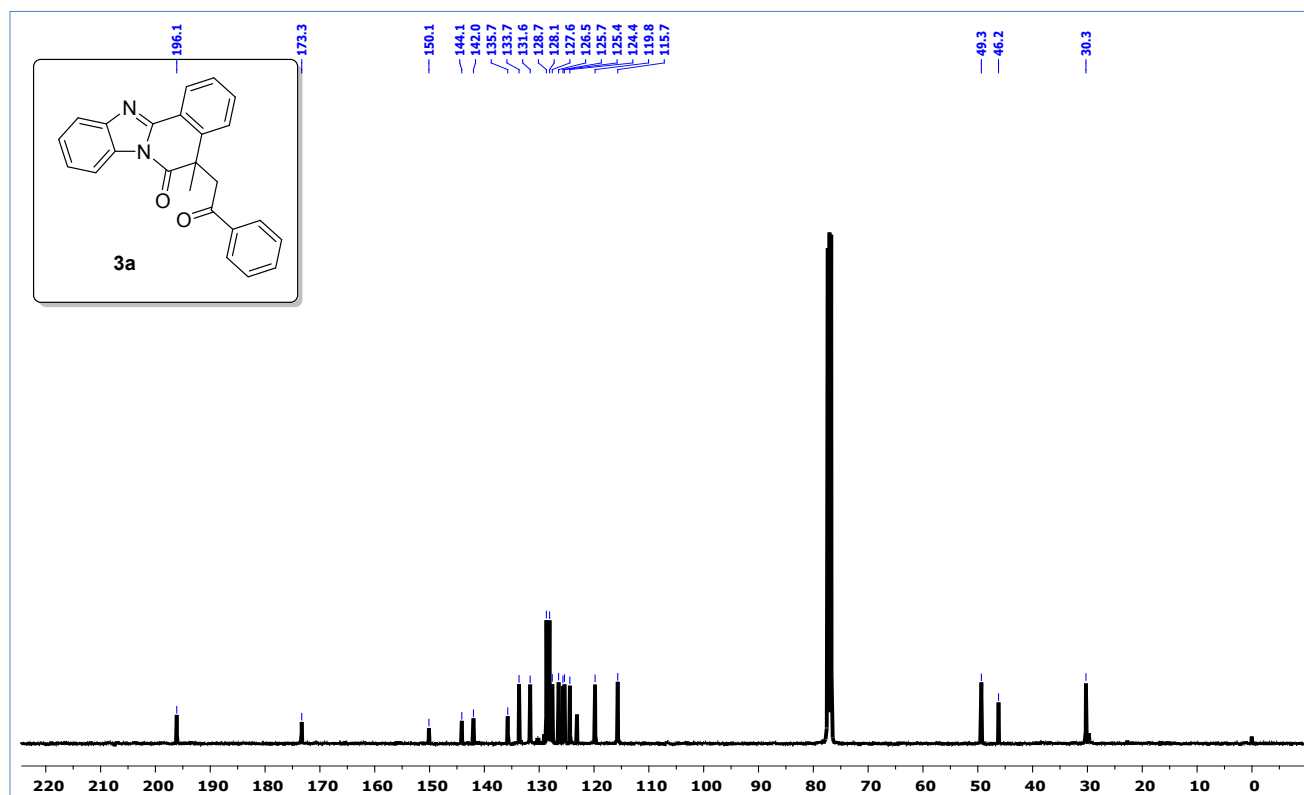
White solid, Yield 63%, mp 140-142 °C 1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, $J = 7.7$ Hz, 1H), 8.39 – 8.32 (m, 1H), 7.86 – 7.78 (m, 1H), 7.63 – 7.53 (m, 2H), 7.51 – 7.39 (m, 3H), 3.81 – 3.66 (m, 1H), 2.60 – 2.50 (m, 1H), 2.36 – 2.27 (m, 1H), 1.76 (s, 3H). 1.00 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 149.8, 144.1, 142.0, 131.7, 131.3, 127.7, 126.5, 126.1, 125.9, 125.6, 122.4, 119.8, 115.7, 65.7, 50.9, 47.8, 29.6, 24.3. HRMS (m/z) calcd for $C_{19}H_{19}N_2O_2$ $[M+H]^+$ 307.1446, found 307.1424.

3. Copies of NMR spectra of products

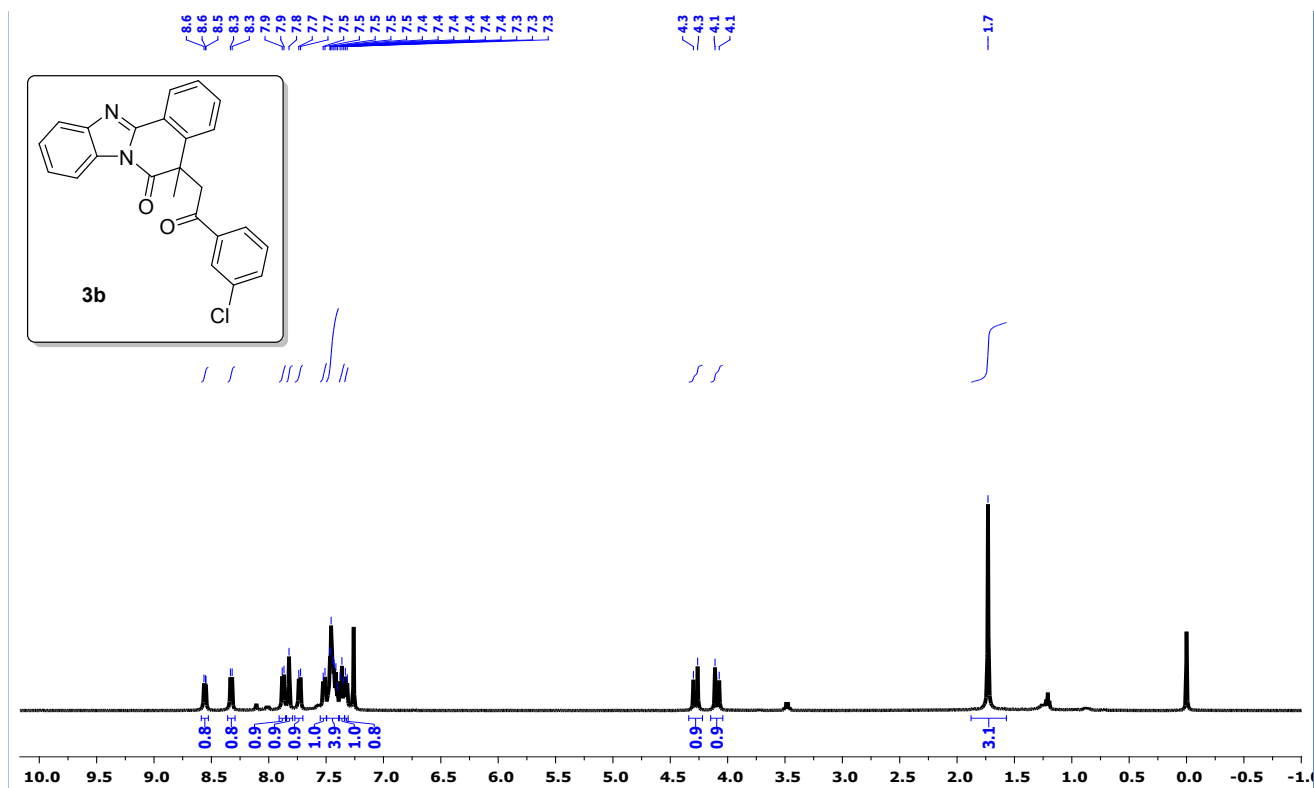
¹H NMR (400 MHz, CDCl₃) of compound 3a



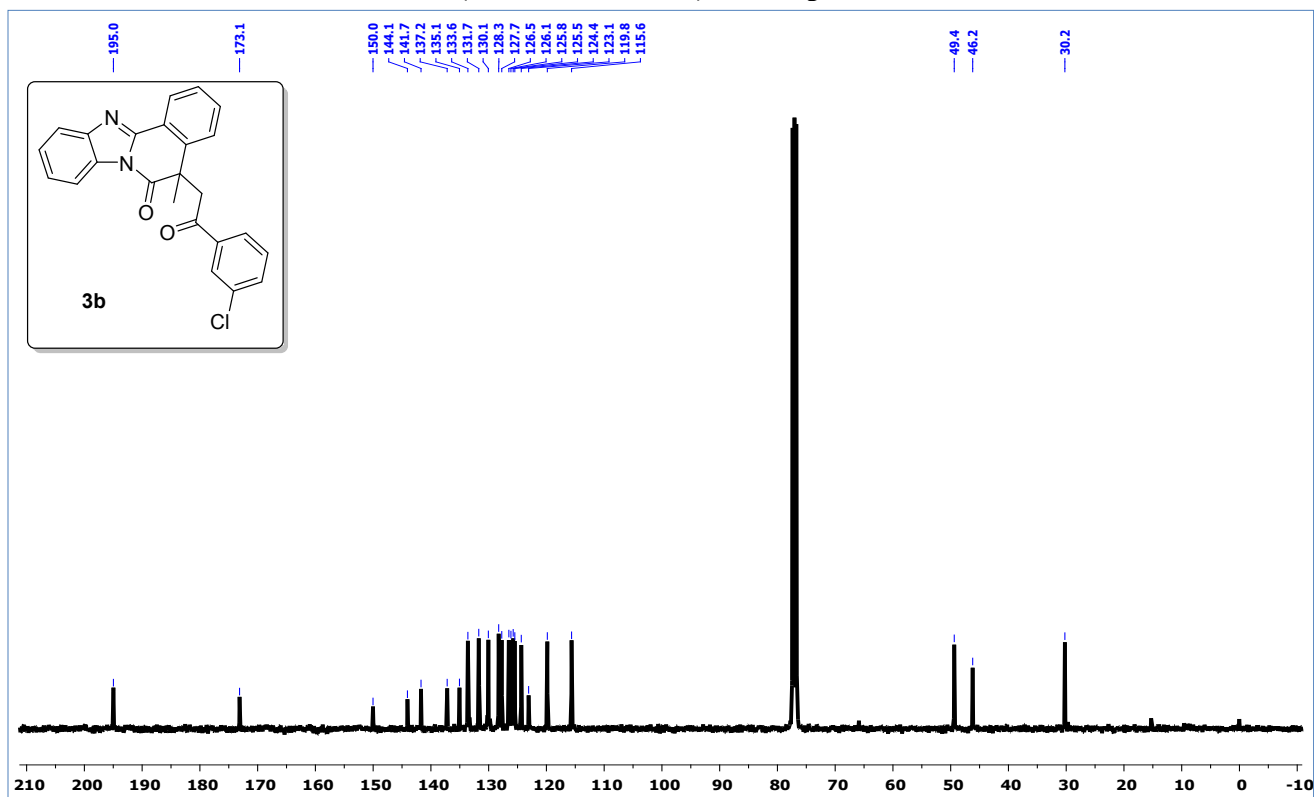
¹³C NMR (100 MHz, CDCl₃) of compound 3a



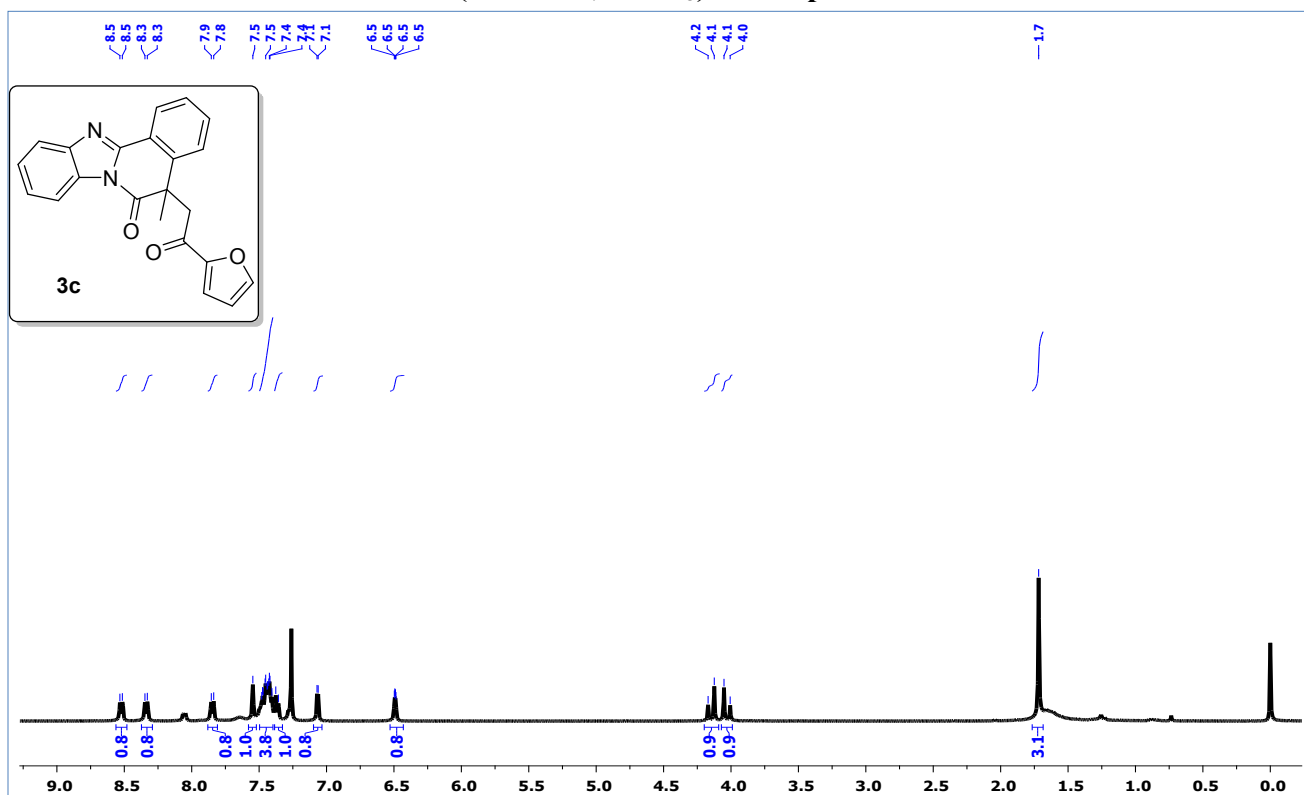
¹H NMR (500 MHz, CDCl₃) of compound 3b



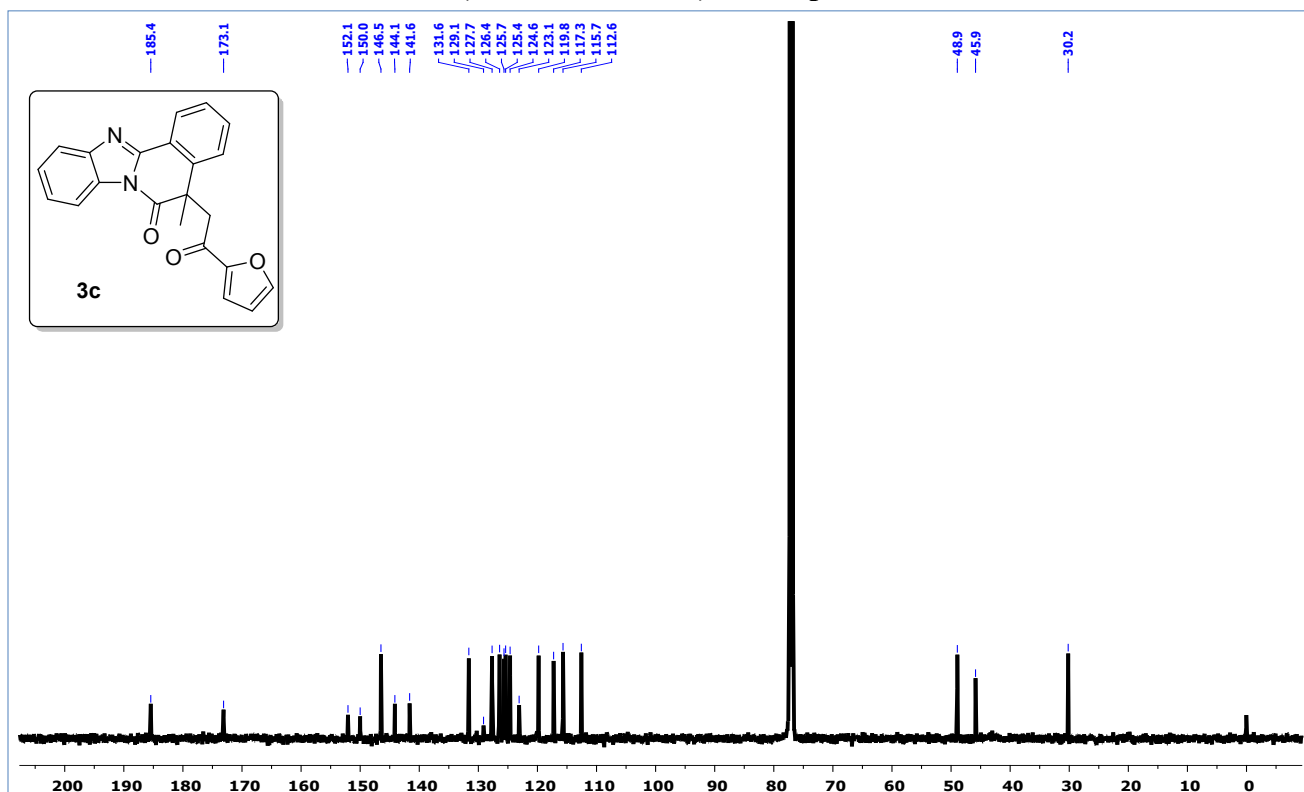
¹³C NMR (100 MHz, CDCl₃) of compound 3b



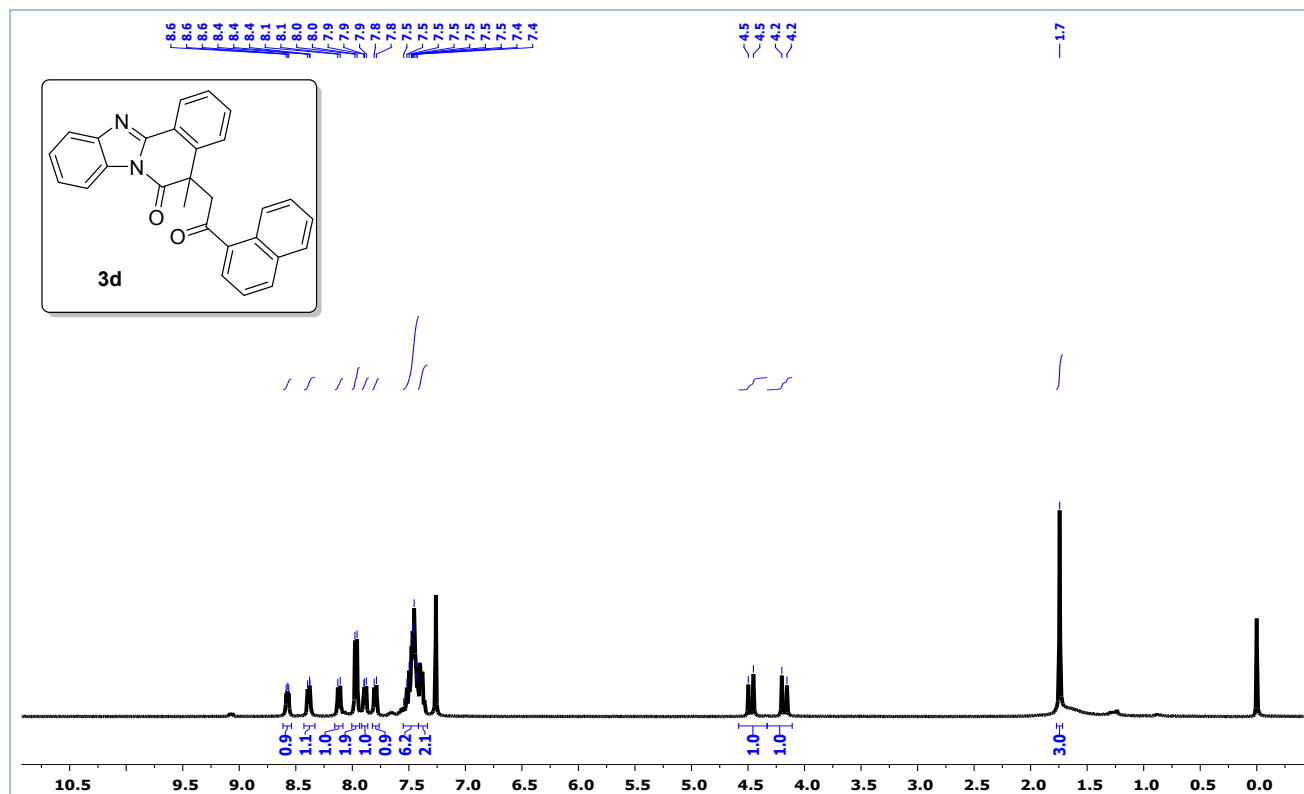
¹H NMR (400 MHz, CDCl₃) of compound 3c



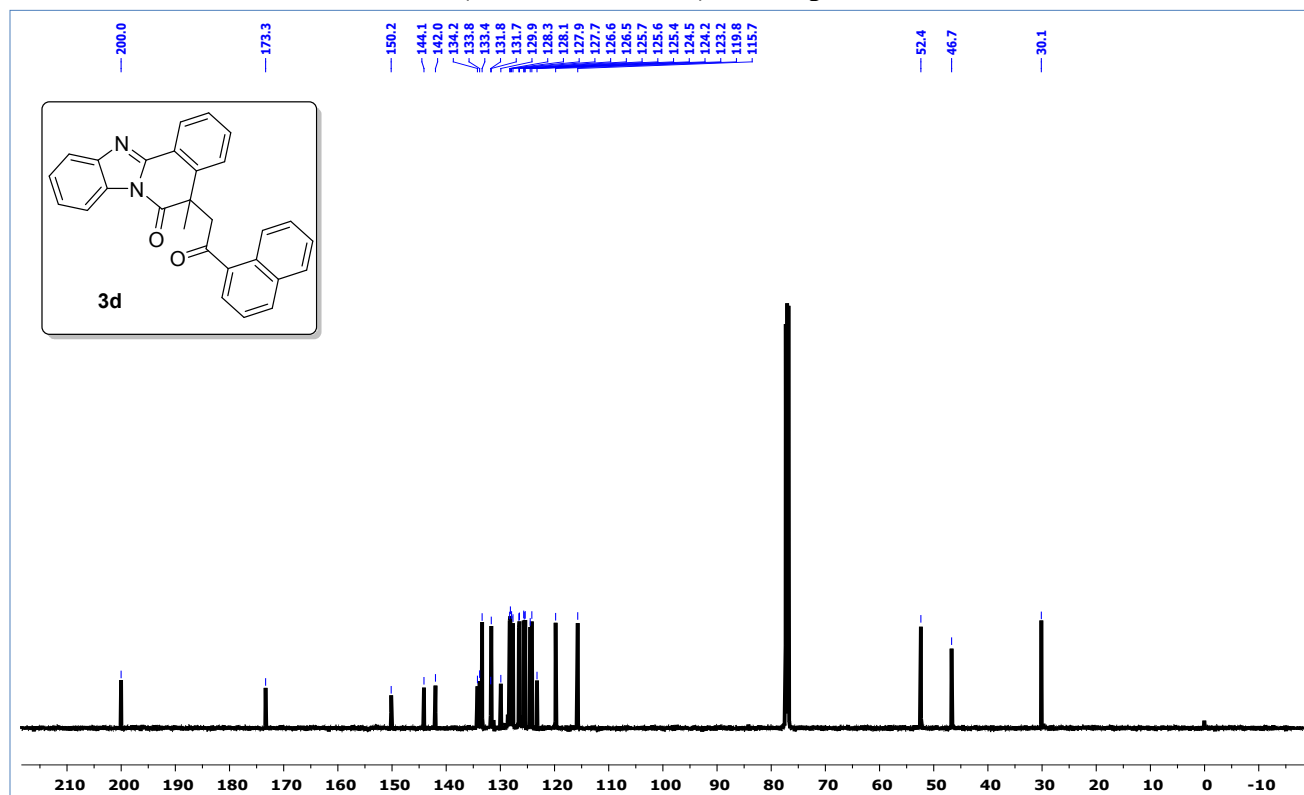
¹³C NMR (126 MHz, CDCl₃) of compound 3c



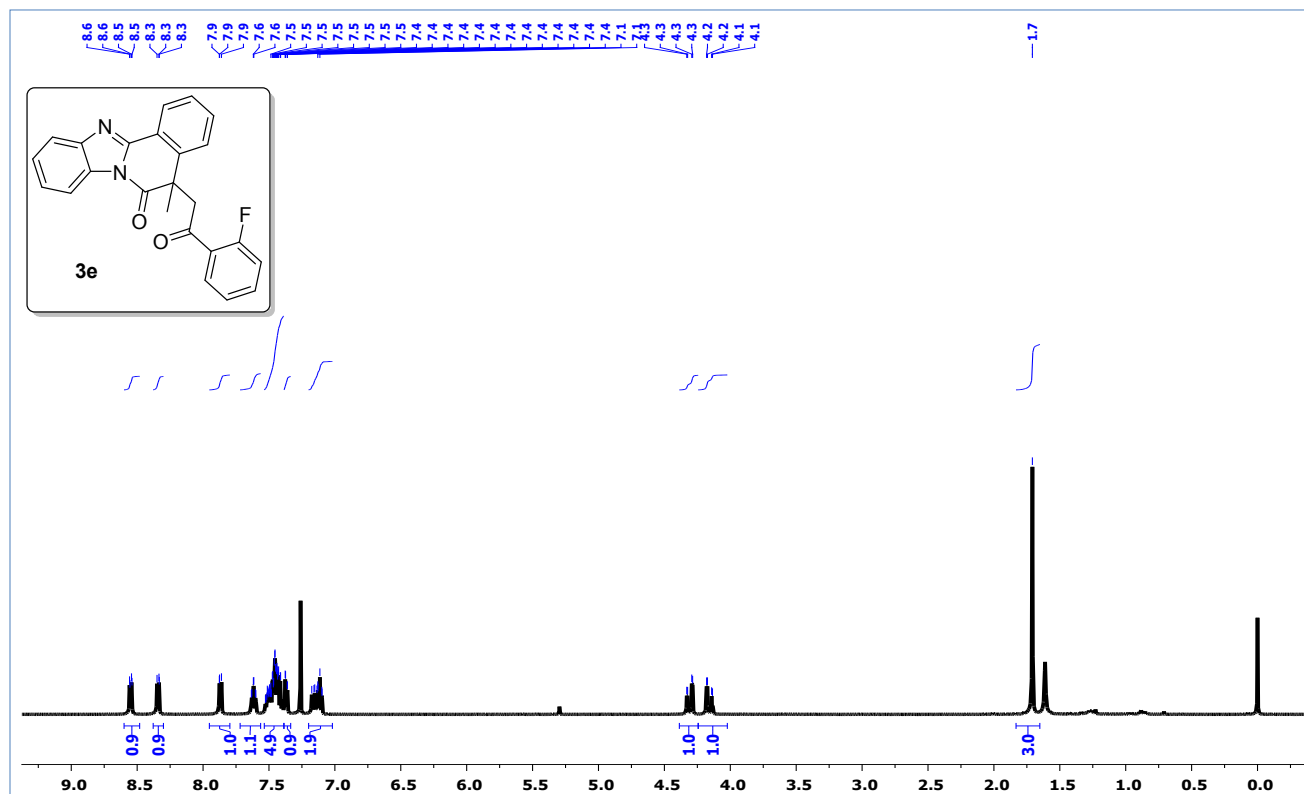
¹H NMR (400 MHz, CDCl₃) of compound 3d



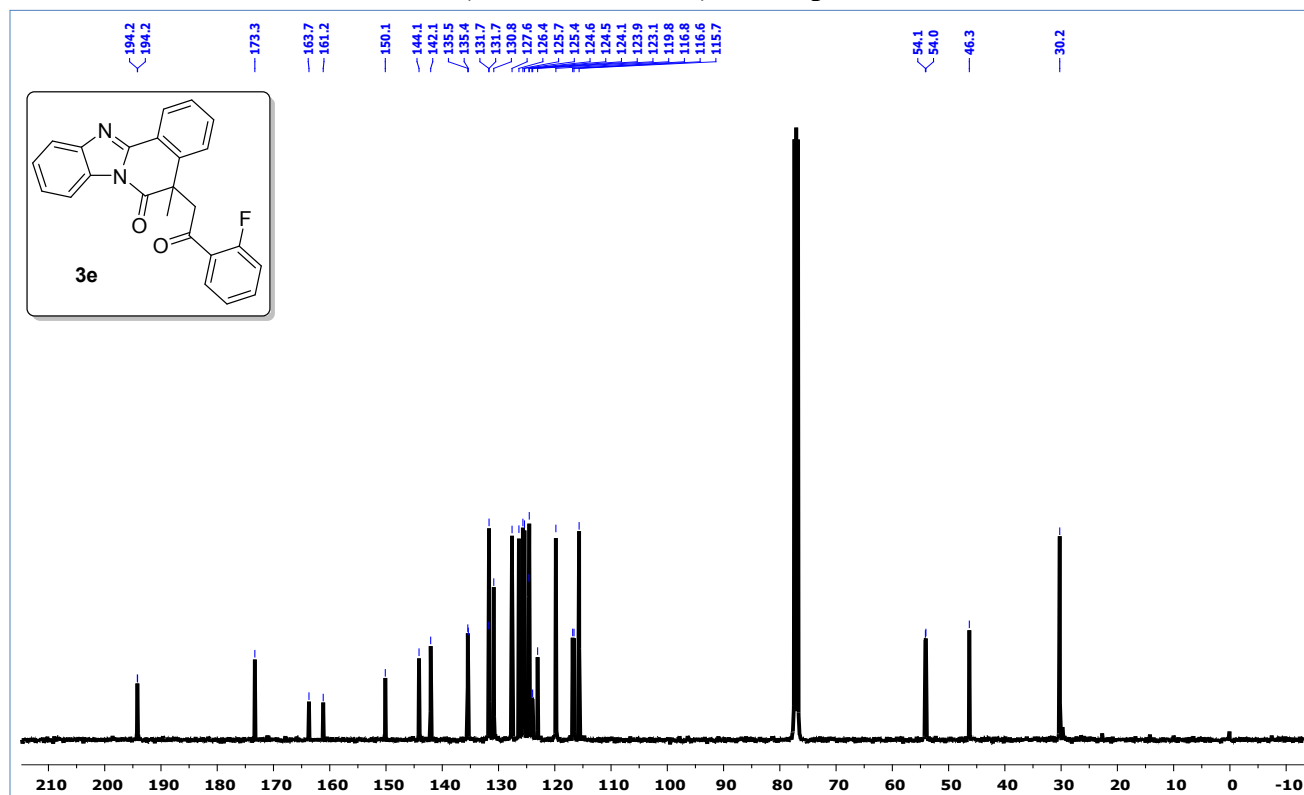
¹³C NMR (126 MHz, CDCl₃) of compound 3d



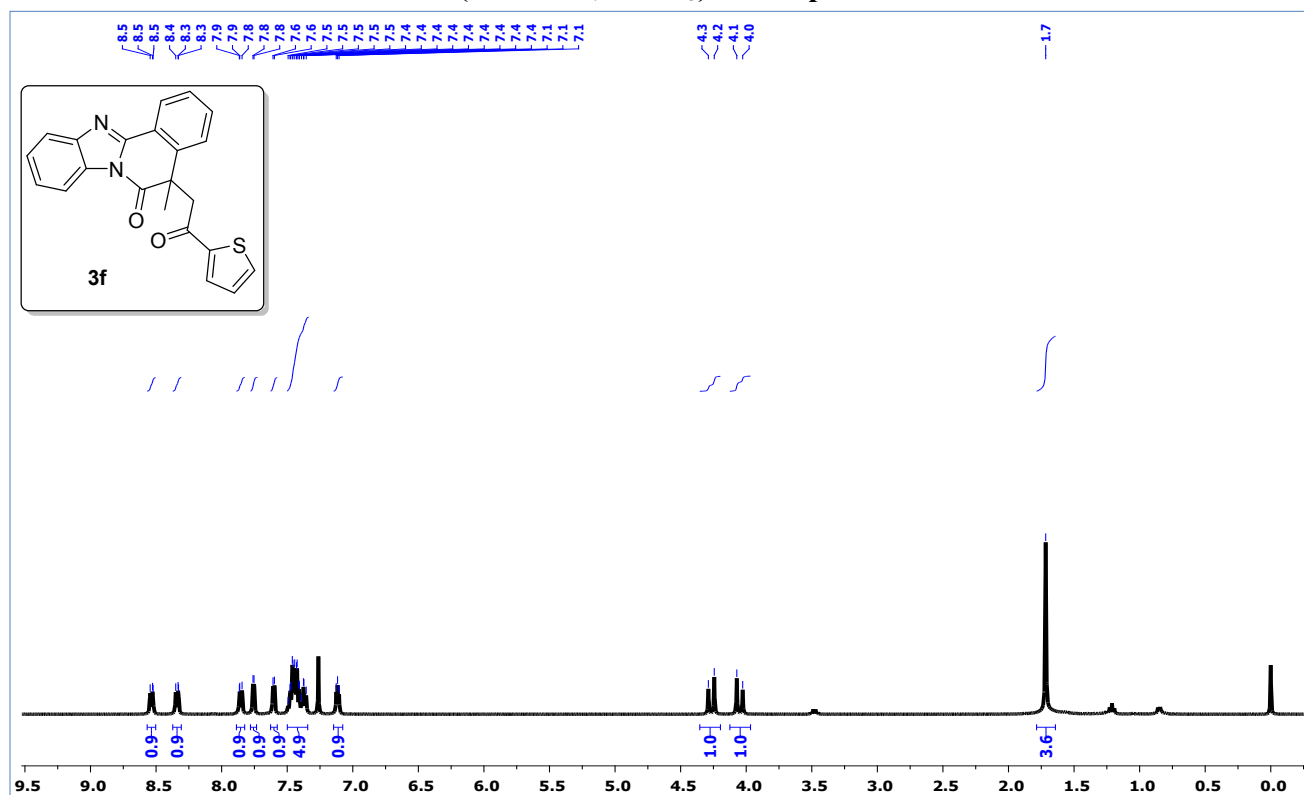
¹H NMR (500 MHz, CDCl₃) of compound 3e



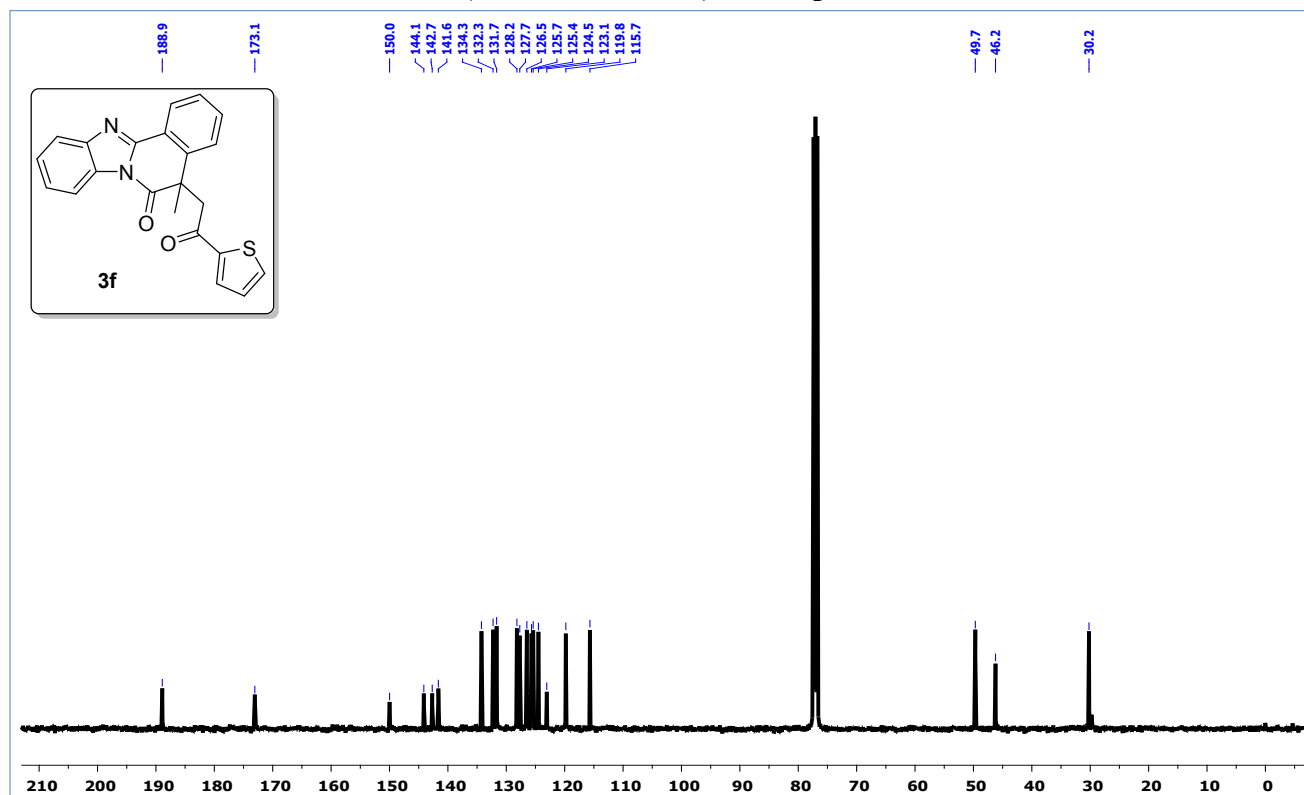
¹³C NMR (100 MHz, CDCl₃) of compound 3e



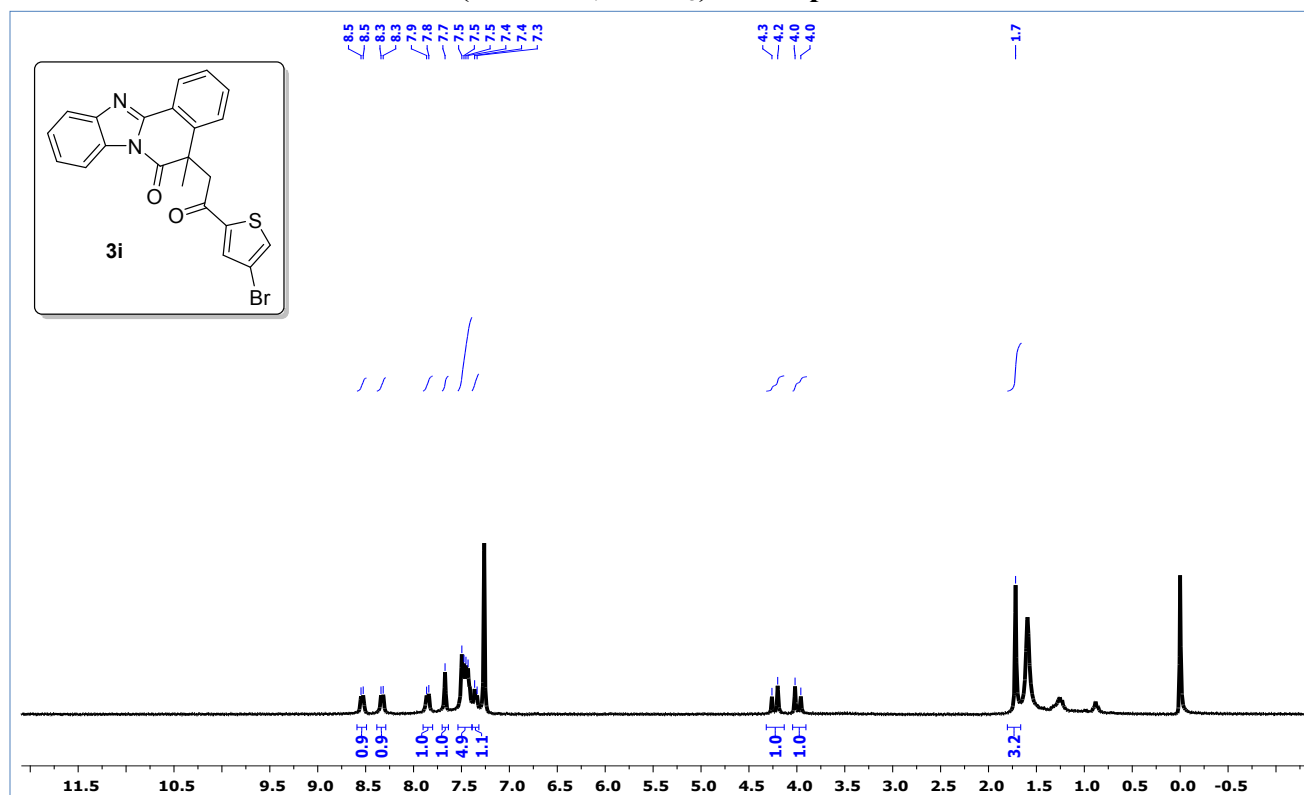
¹H NMR (400 MHz, CDCl₃) of compound 3f



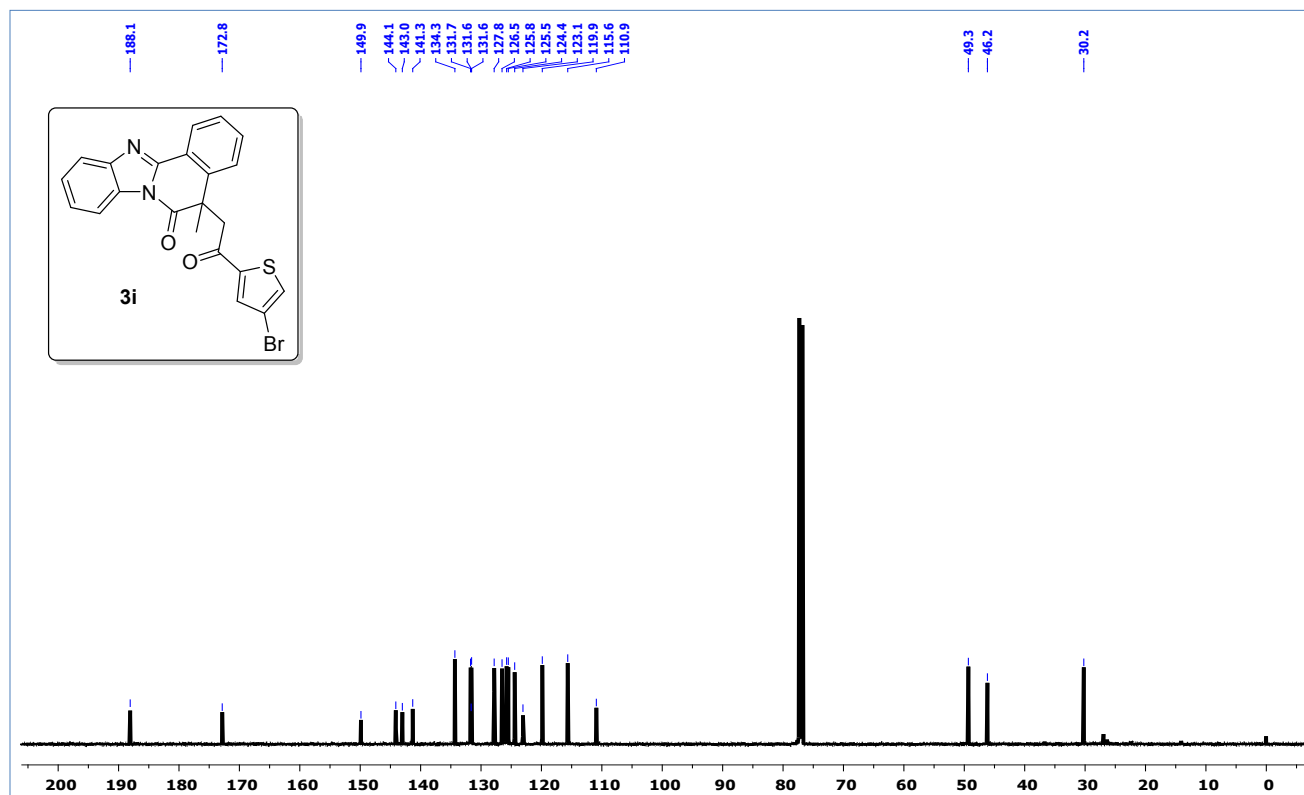
¹³C NMR (100 MHz, CDCl₃) of compound 3f



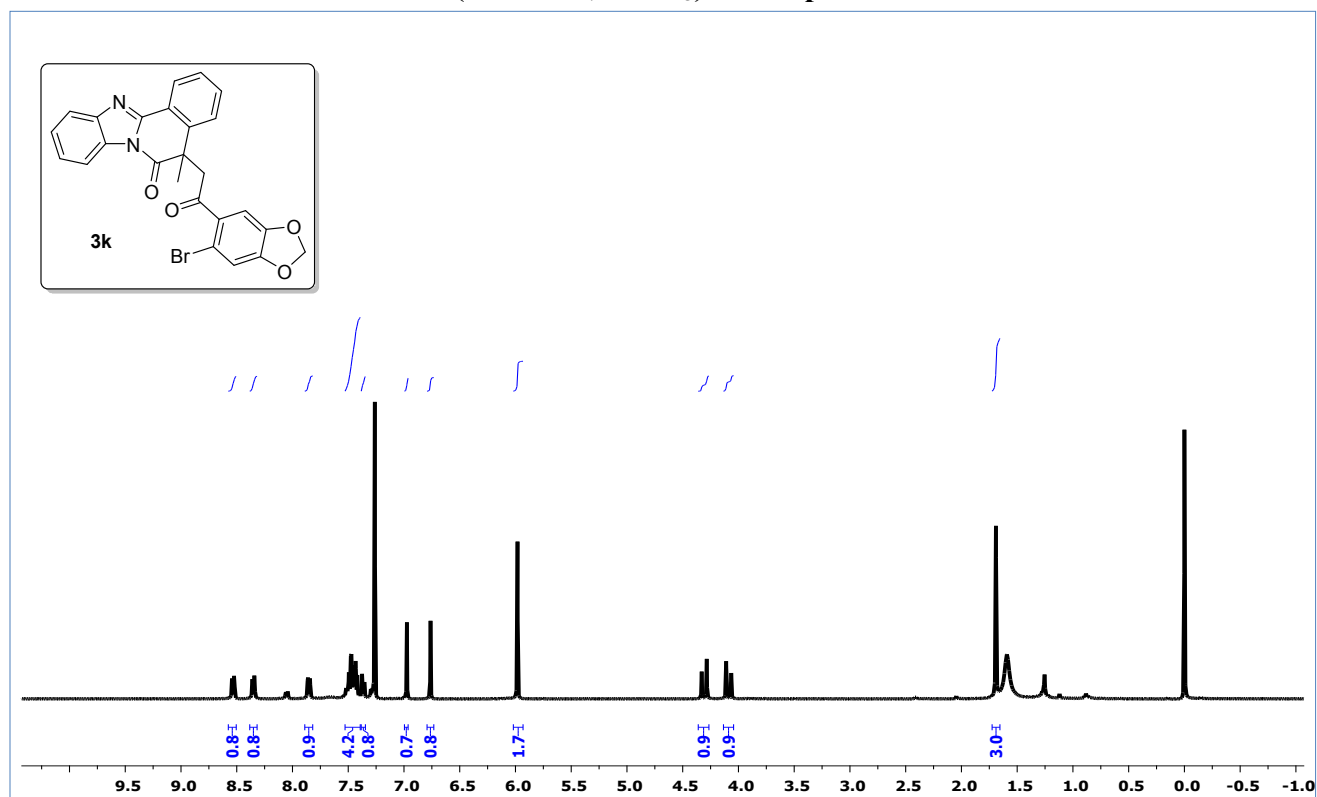
¹H NMR (300 MHz, CDCl₃) of compound 3i



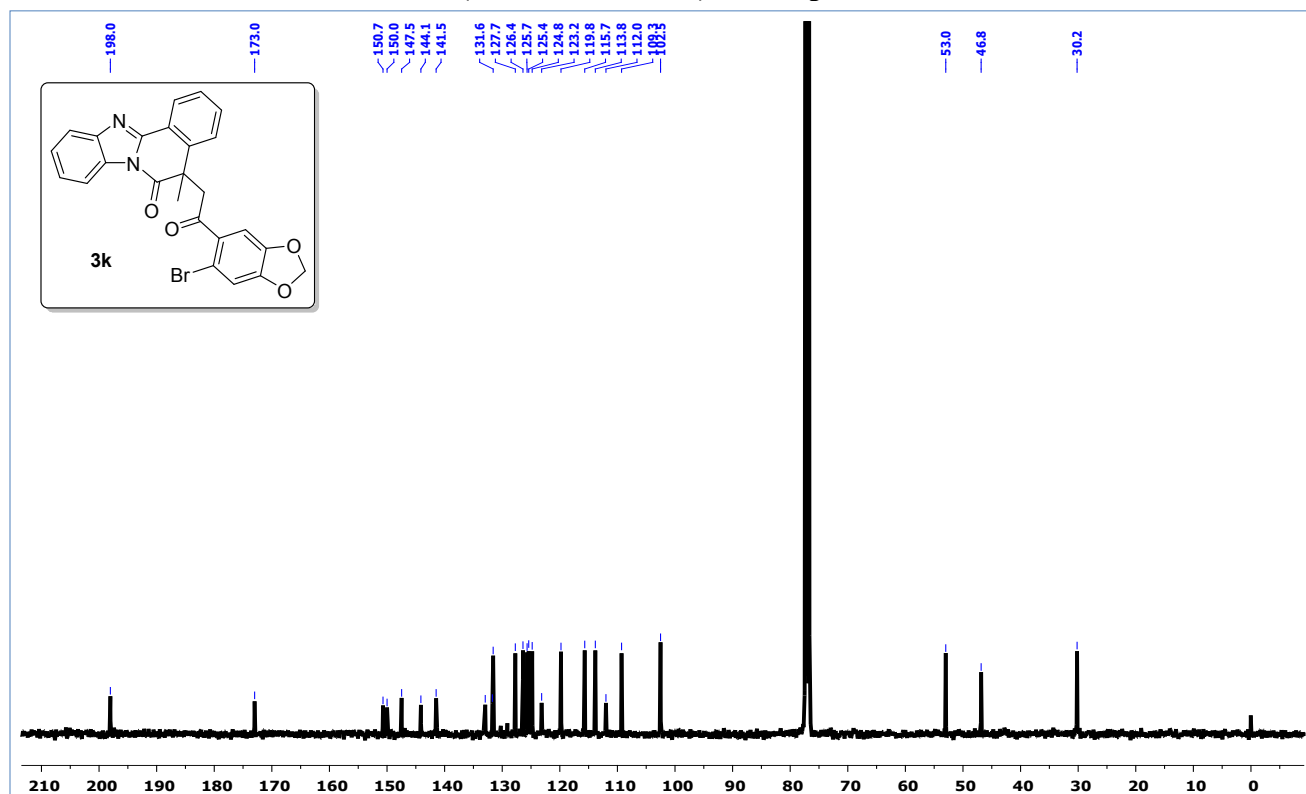
¹³C NMR (126 MHz, CDCl₃) of compound 3i



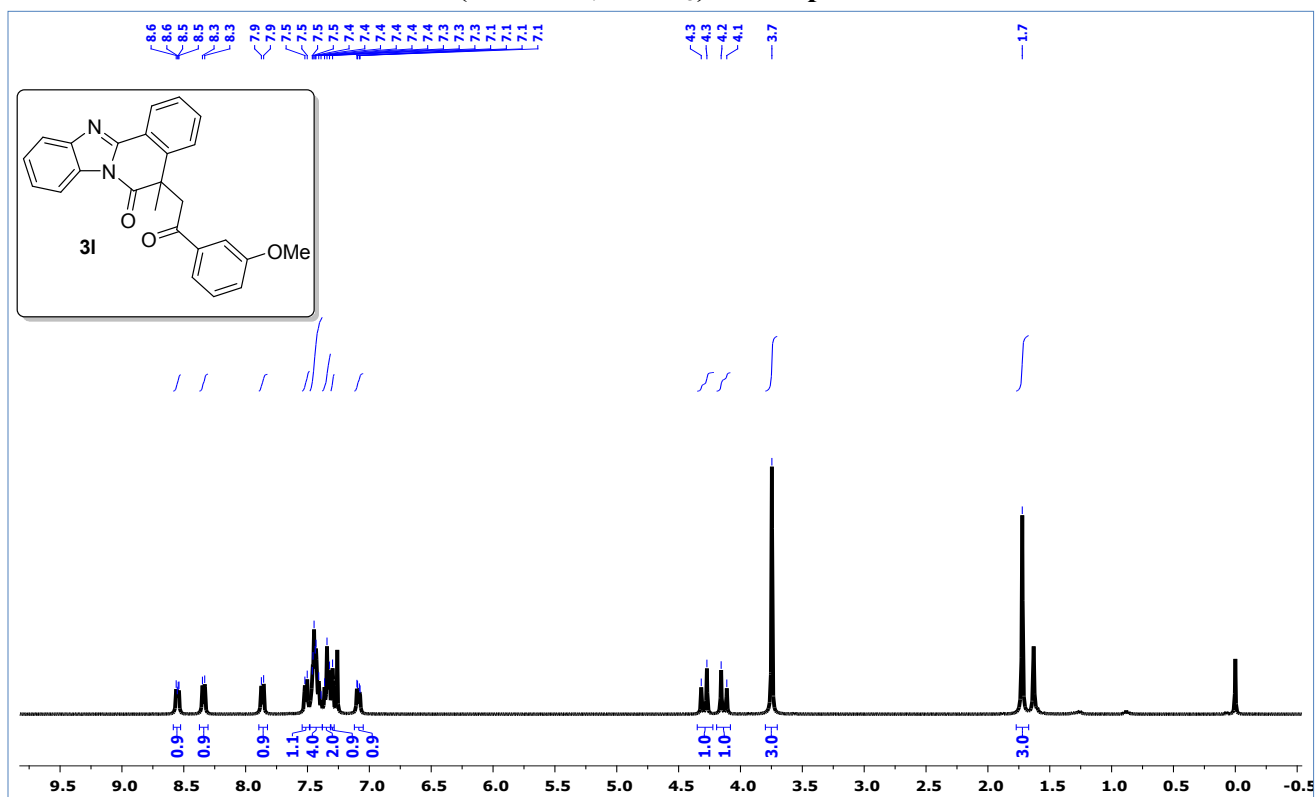
¹H NMR (400 MHz, CDCl₃) of compound 3k



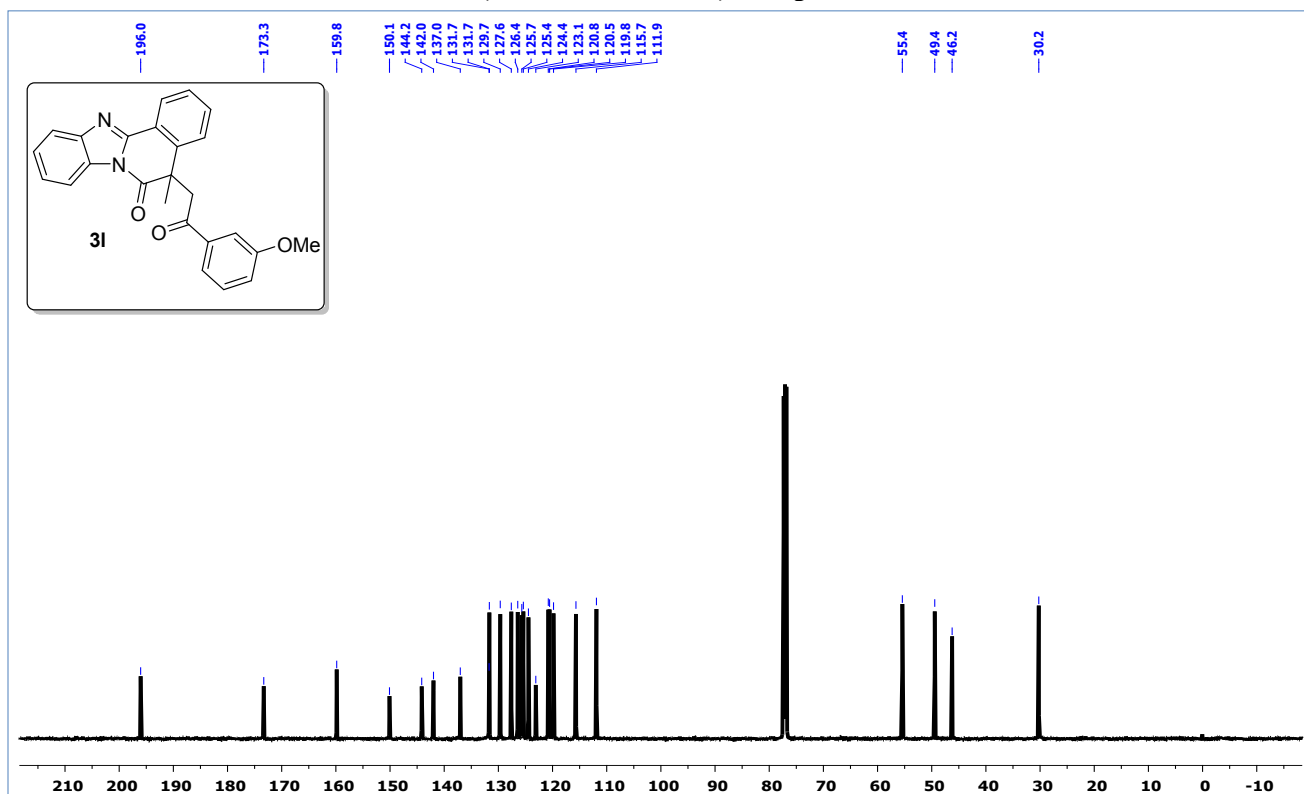
¹³C NMR (100 MHz, CDCl₃) of compound 3k



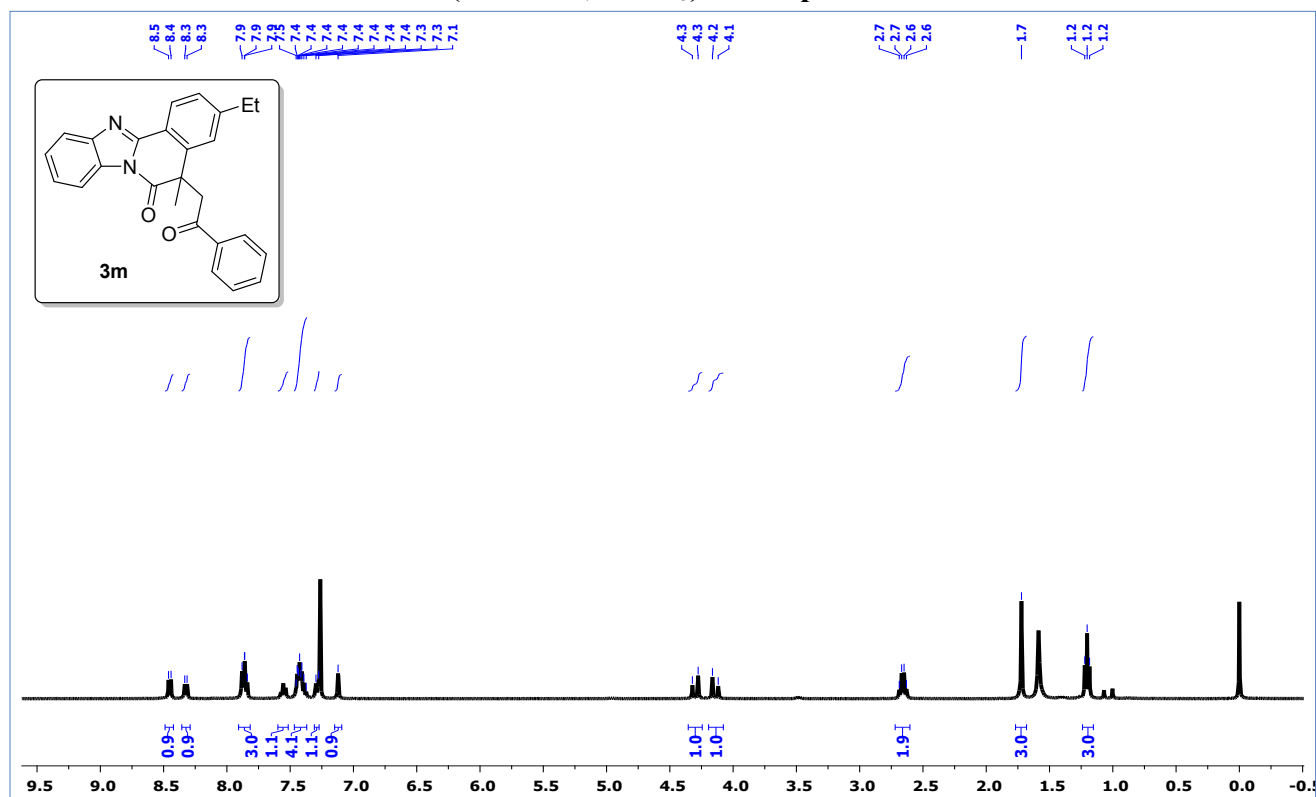
¹H NMR (400 MHz, CDCl₃) of compound 3I



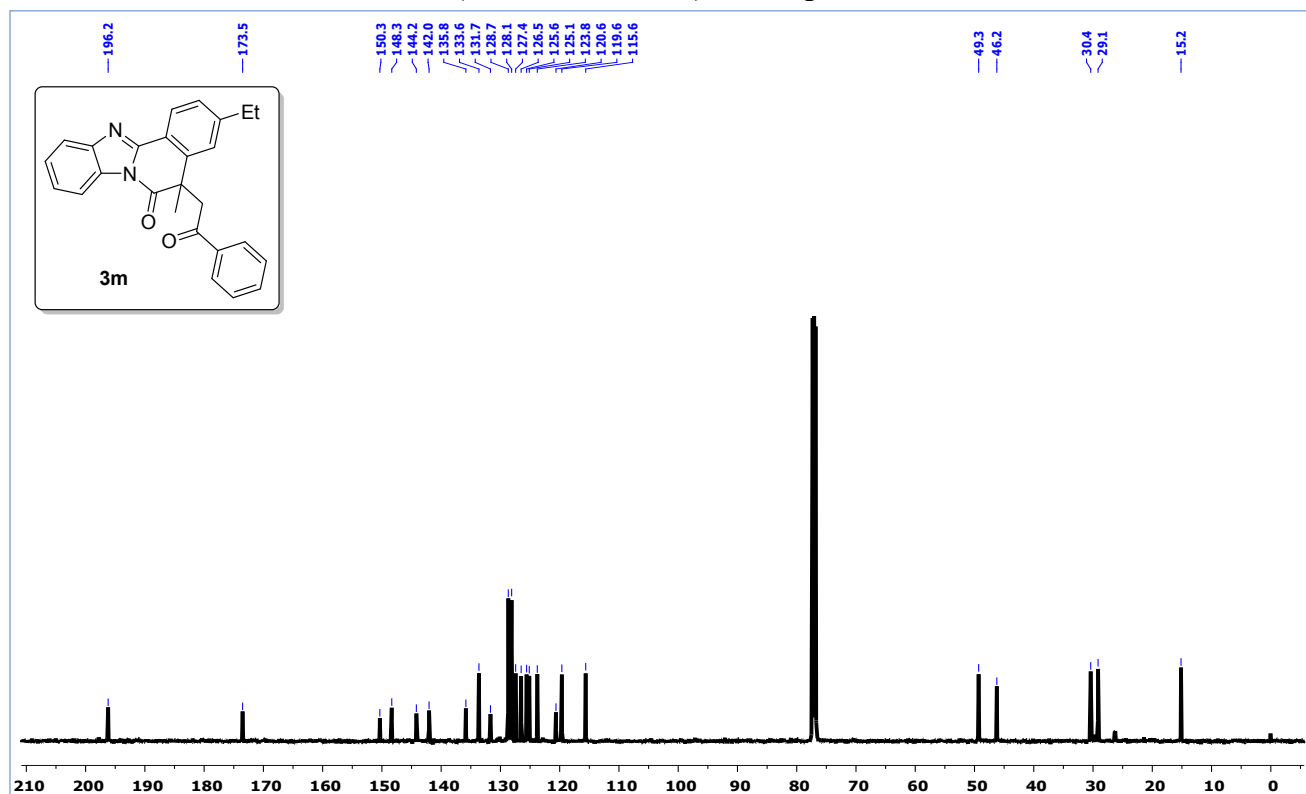
¹³C NMR (126 MHz, CDCl₃) compound 3I



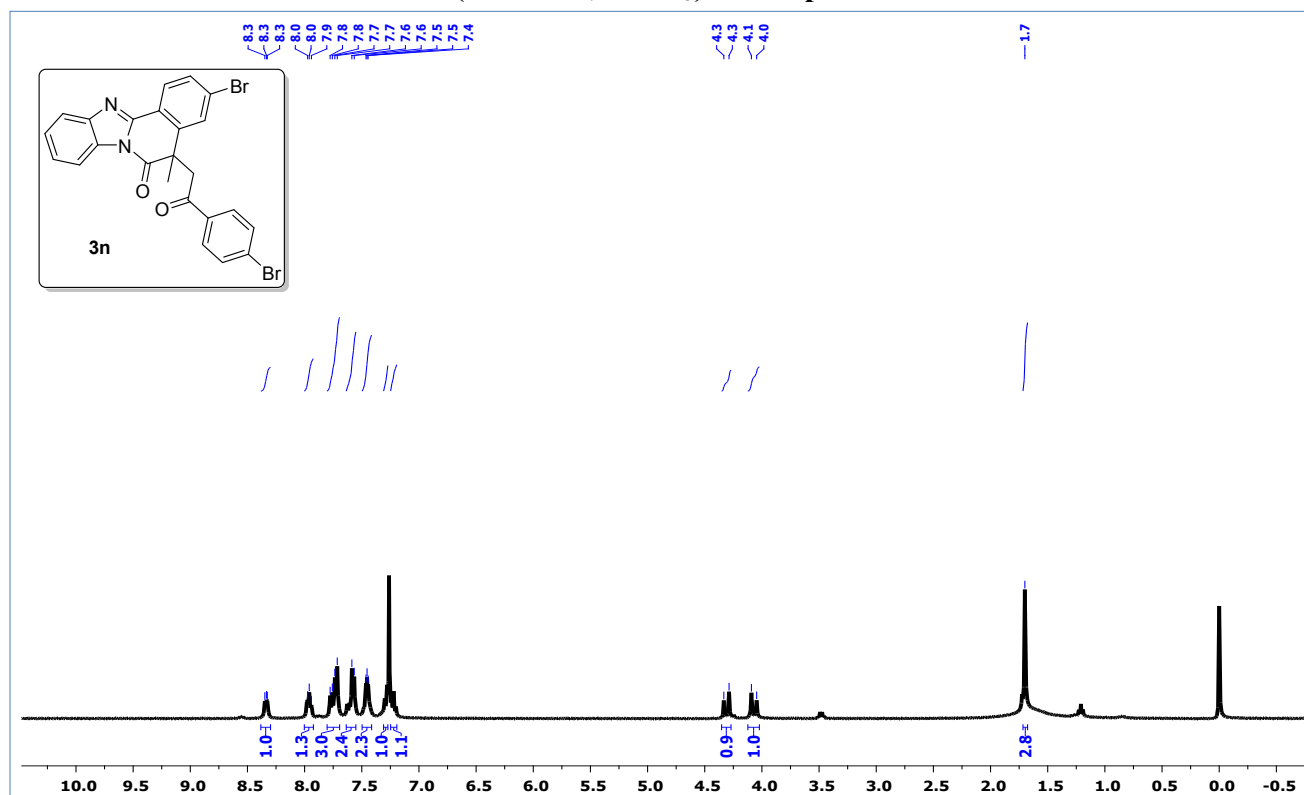
¹H NMR (400 MHz, CDCl₃) of compound 3m



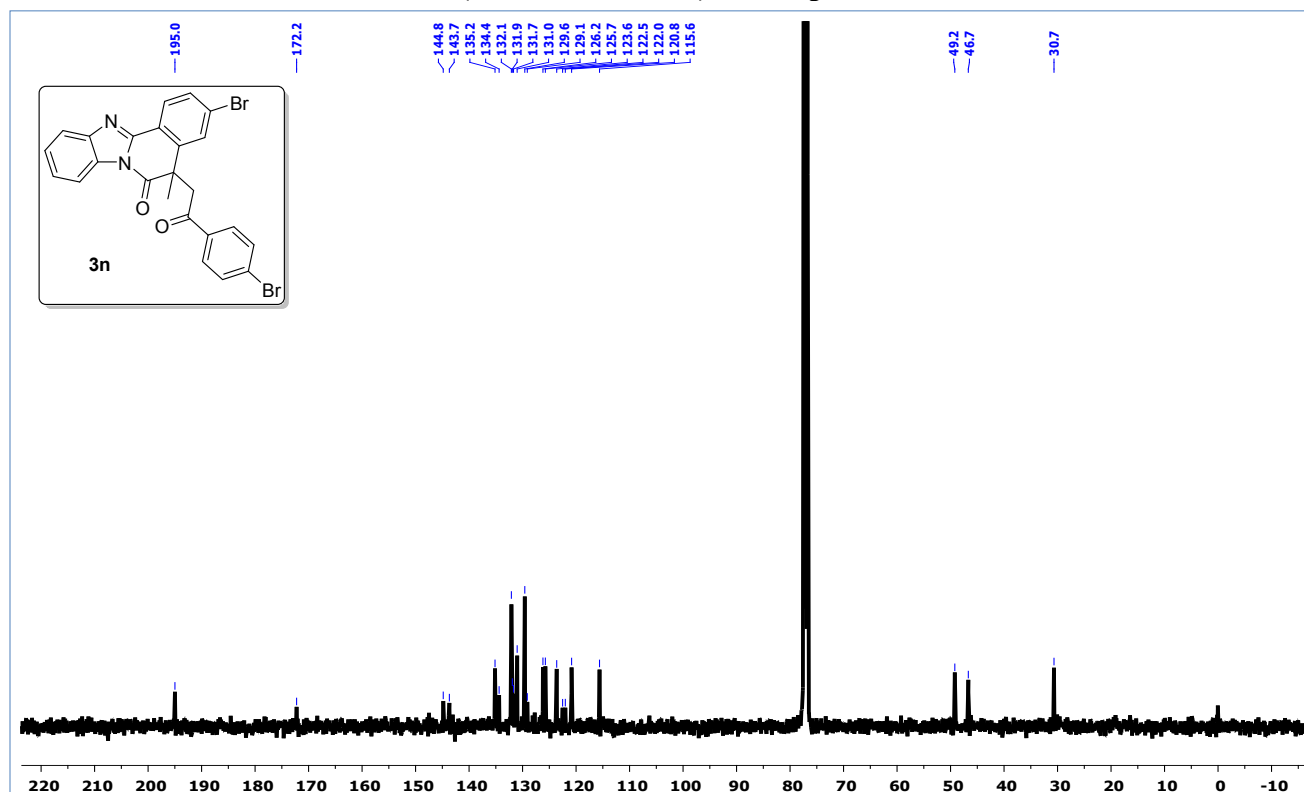
¹³C NMR (126 MHz, CDCl₃) of compound 3m



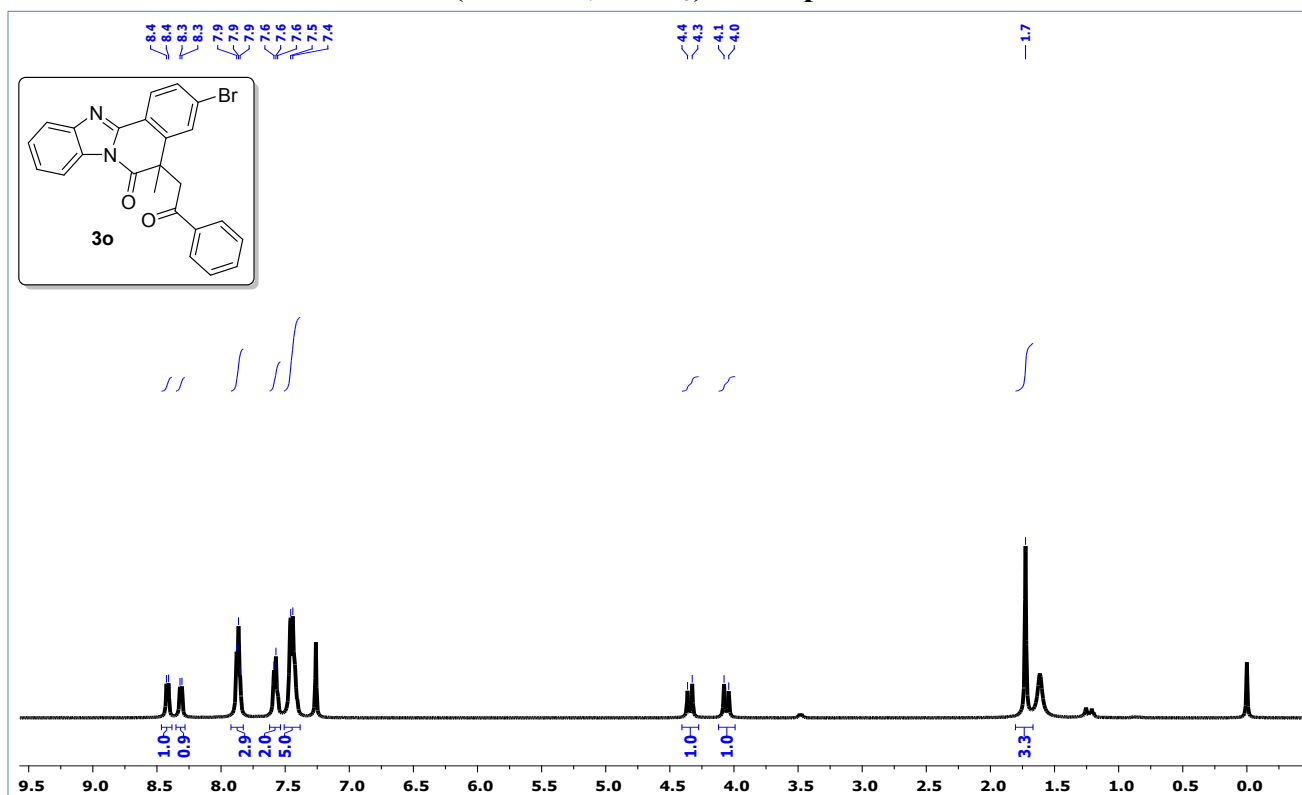
¹H NMR (400 MHz, CDCl₃) of compound 3n



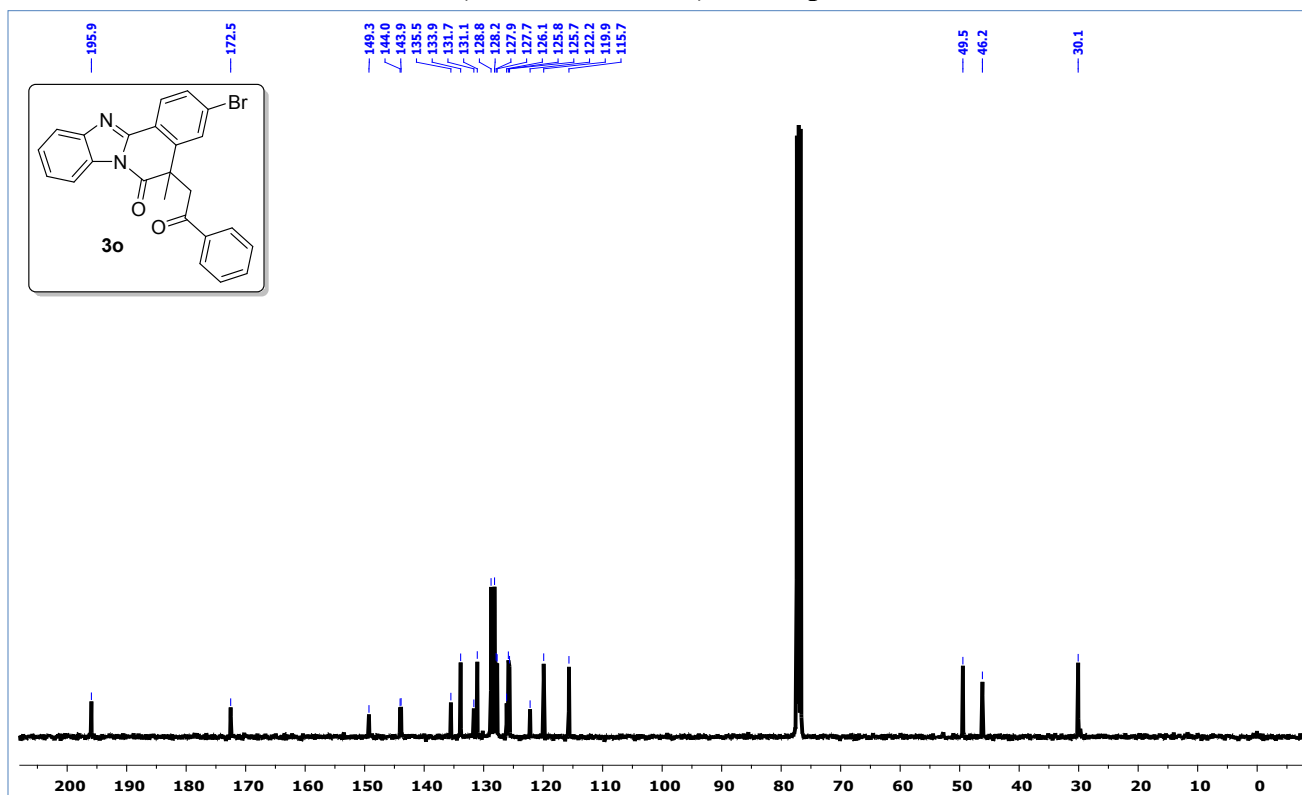
¹³C NMR (100 MHz, CDCl₃) of compound 3n



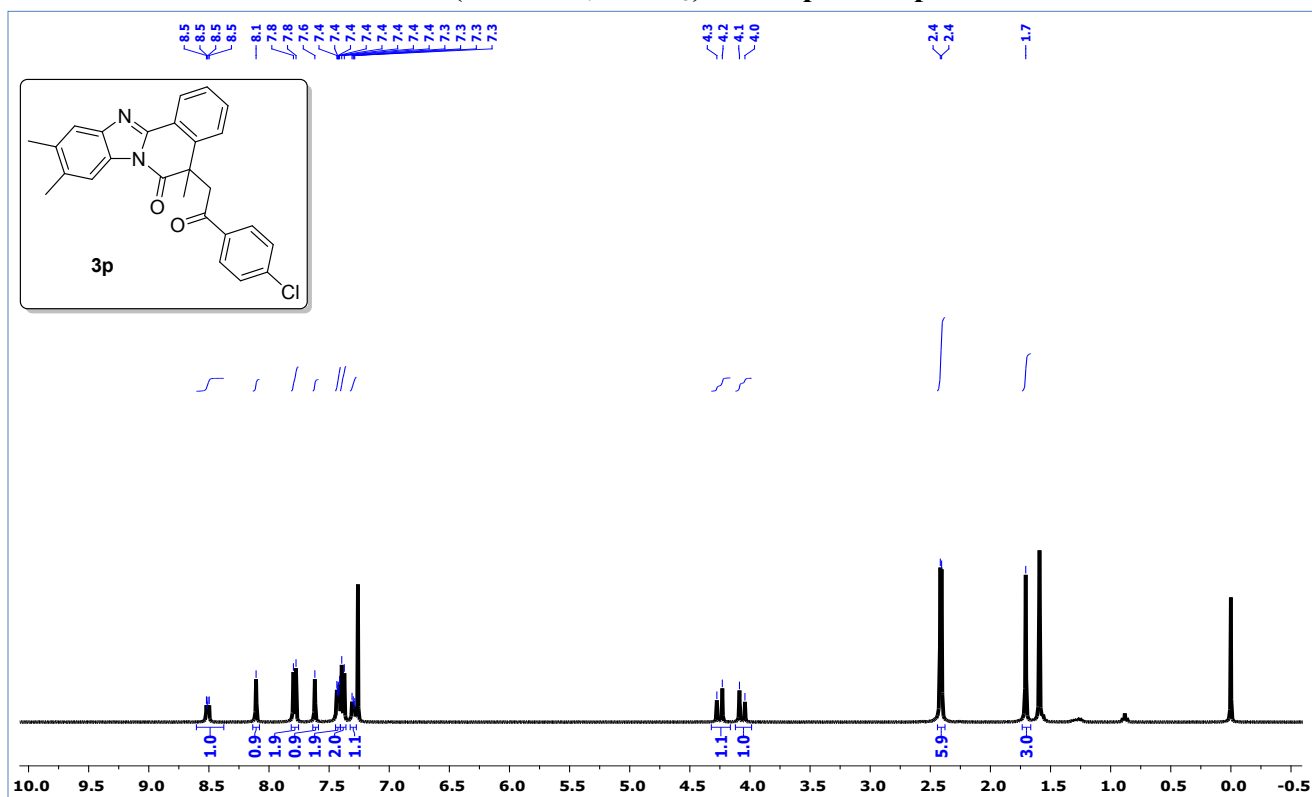
¹H NMR (400 MHz, CDCl₃) of compound 3o



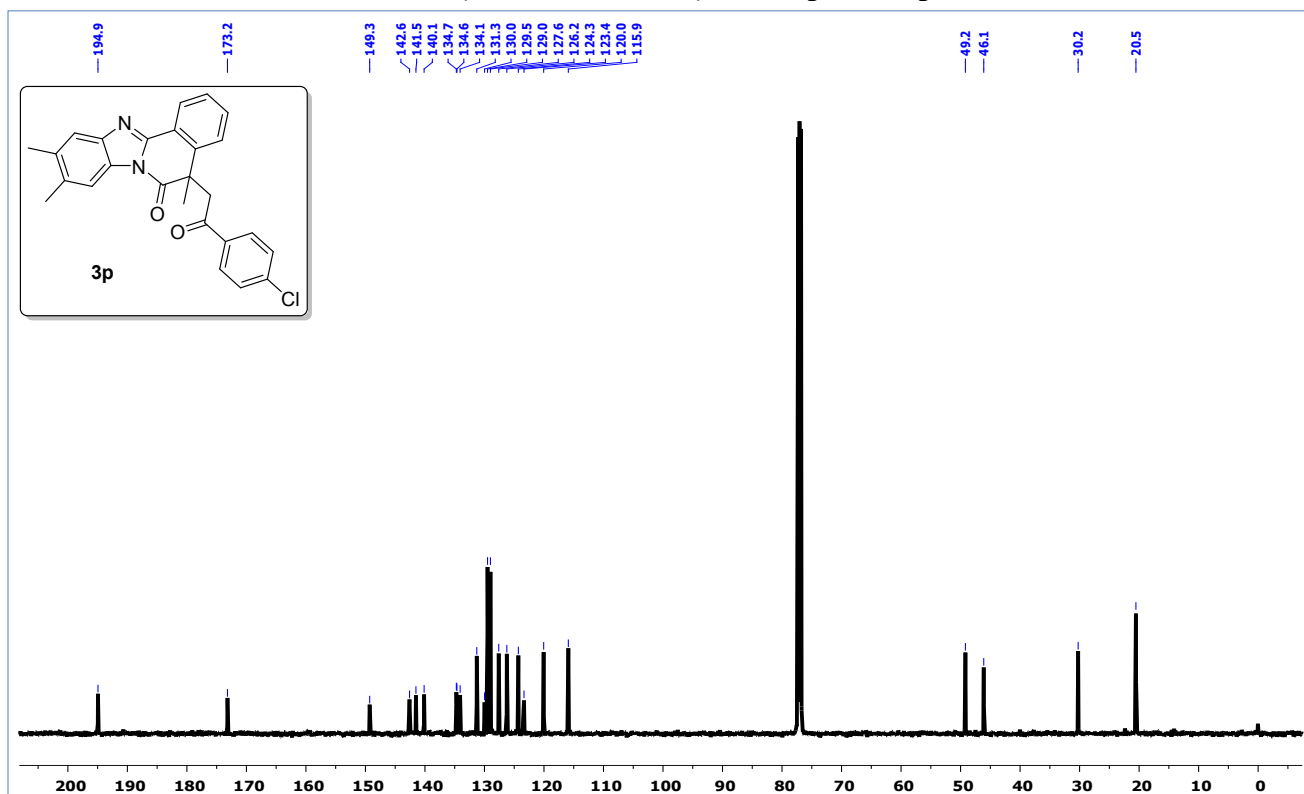
¹³C NMR (100 MHz, CDCl₃) of compound 3o



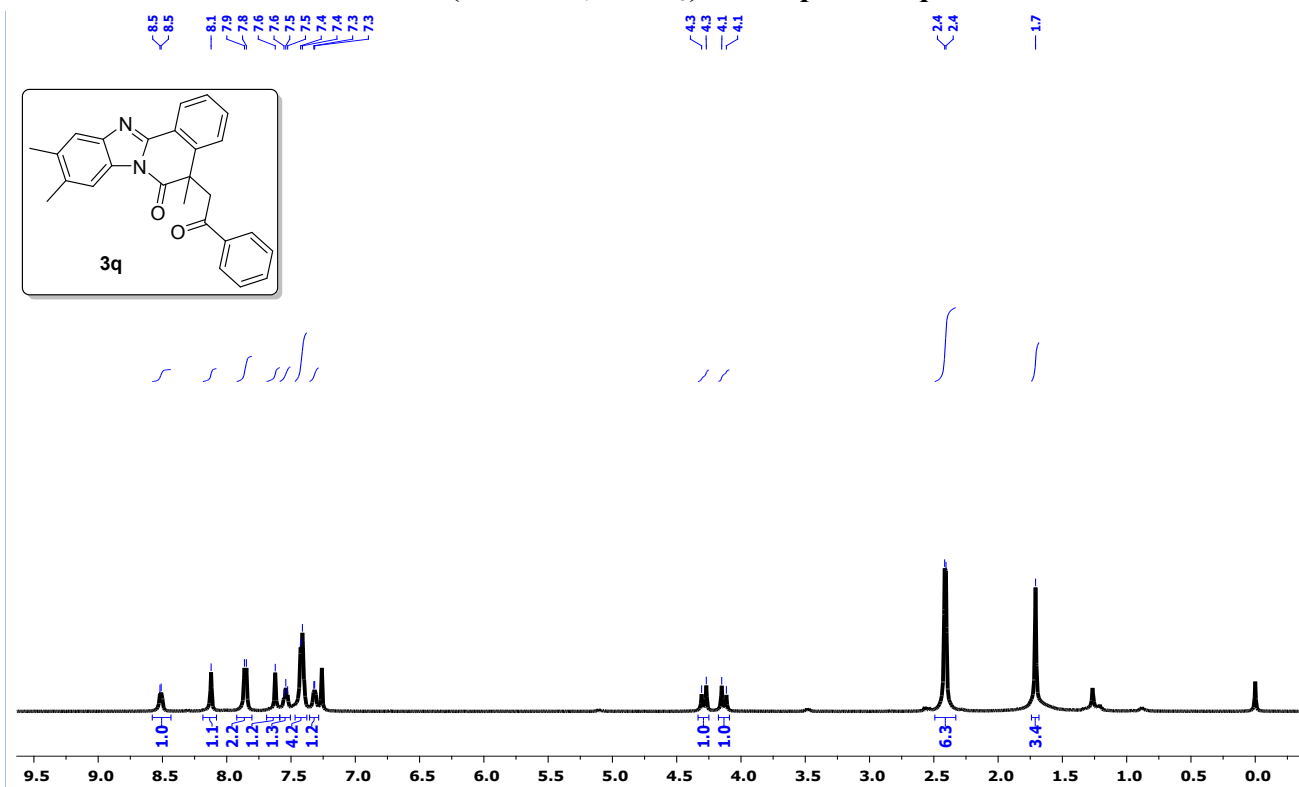
¹H NMR (400 MHz, CDCl₃) of compound 3p



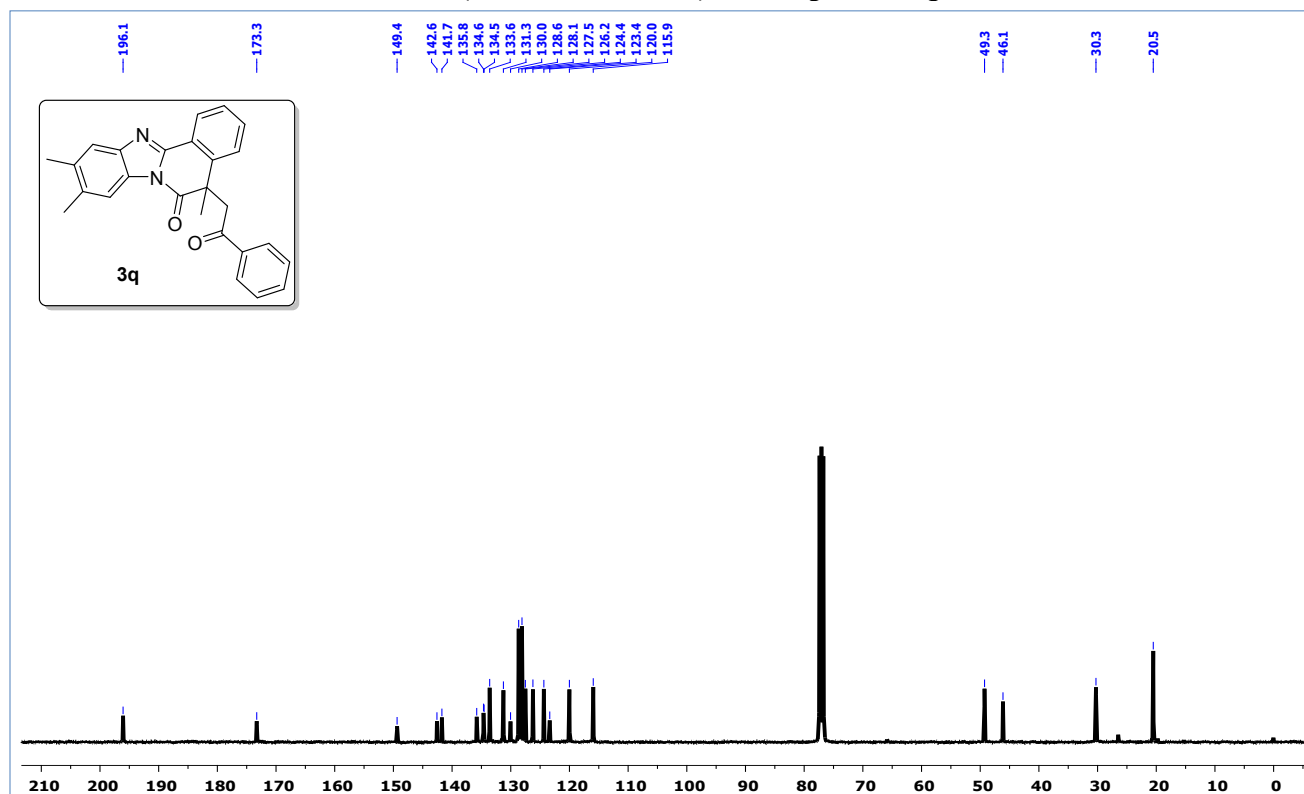
¹³C NMR (126 MHz, CDCl₃) of compound 3p



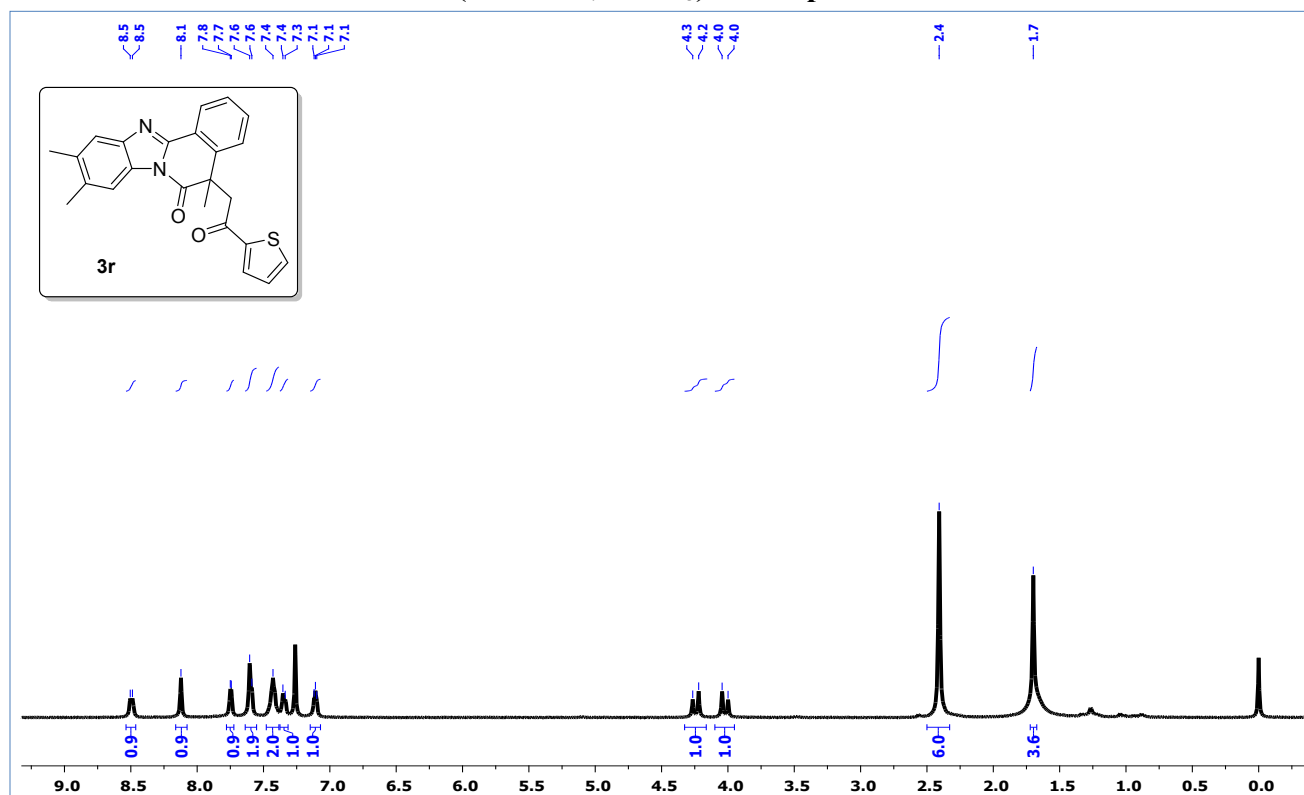
¹H NMR (500 MHz, CDCl₃) of compound 3q



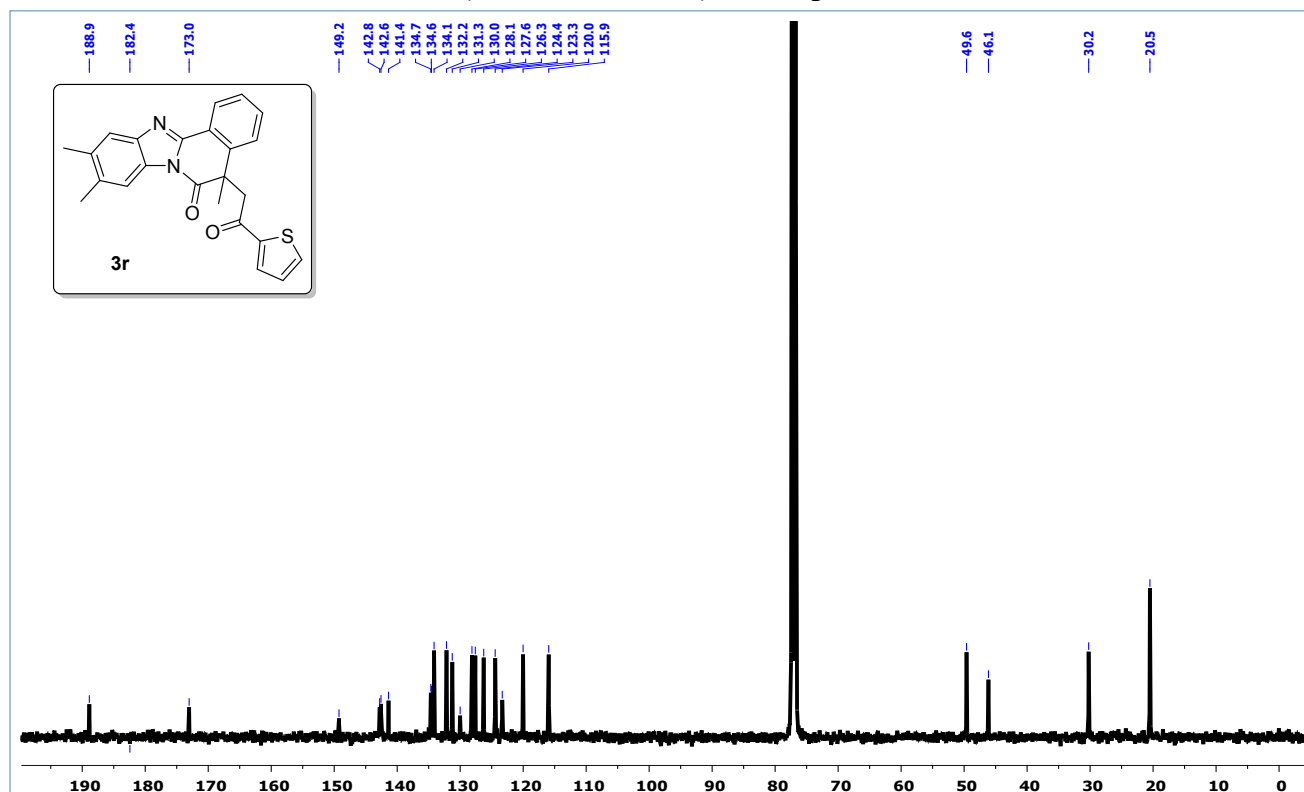
¹³C NMR (100 MHz, CDCl₃) of compound 3q



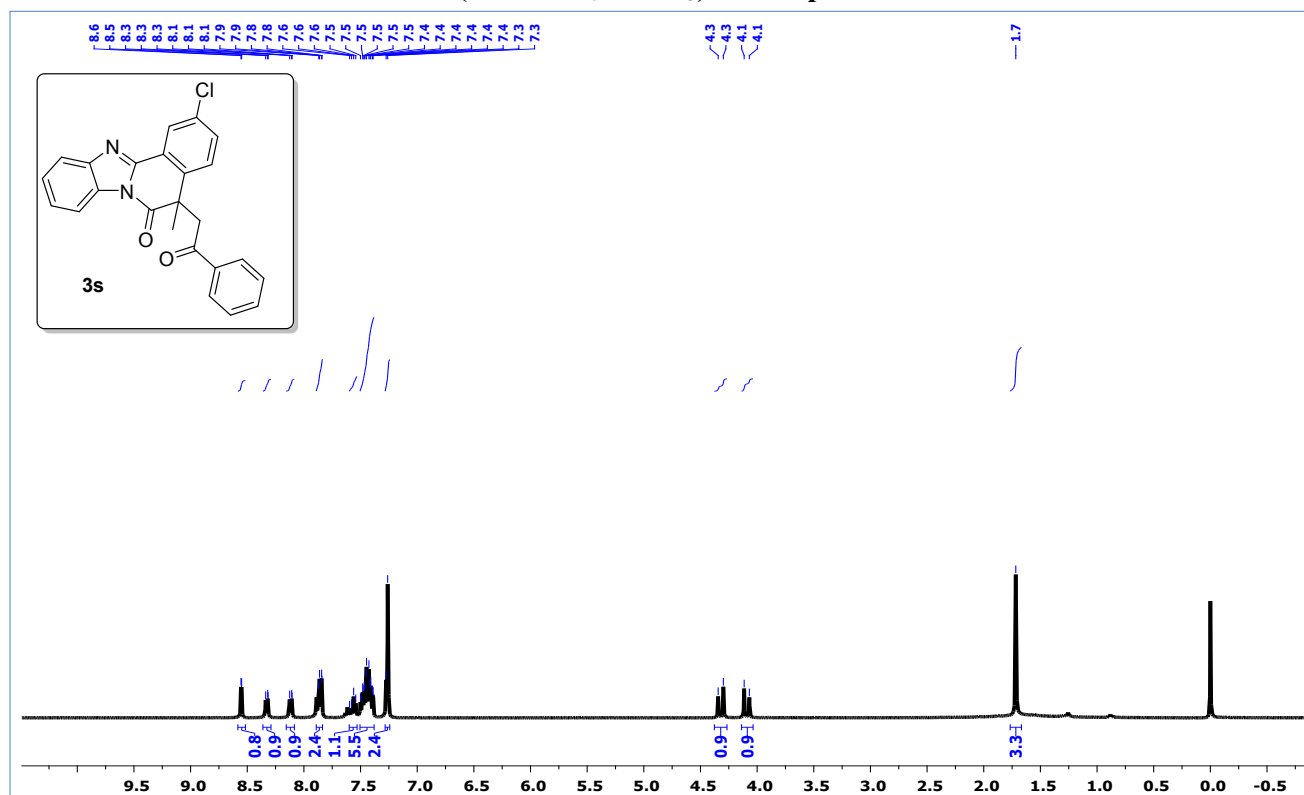
¹H NMR (400 MHz, CDCl₃) of compound 3r



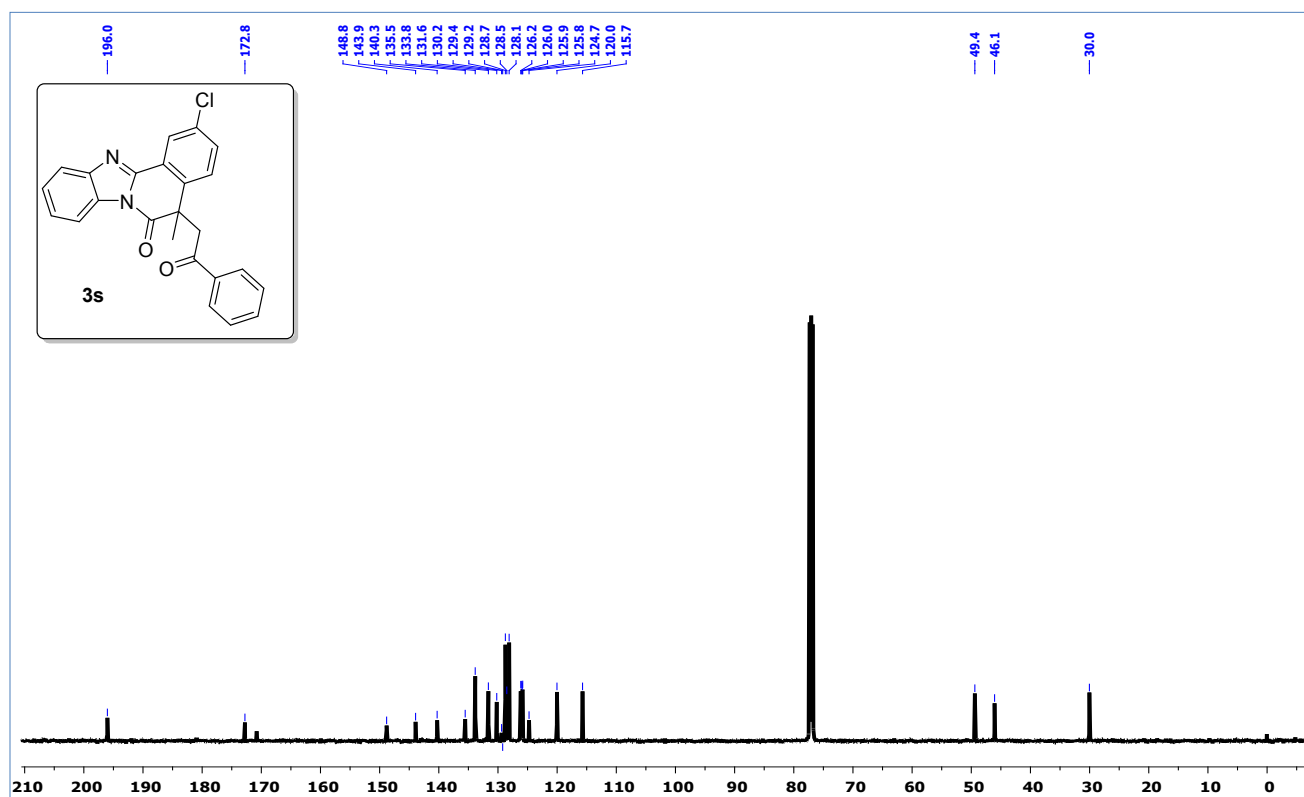
¹³C NMR (100 MHz, CDCl₃) of compound 3r



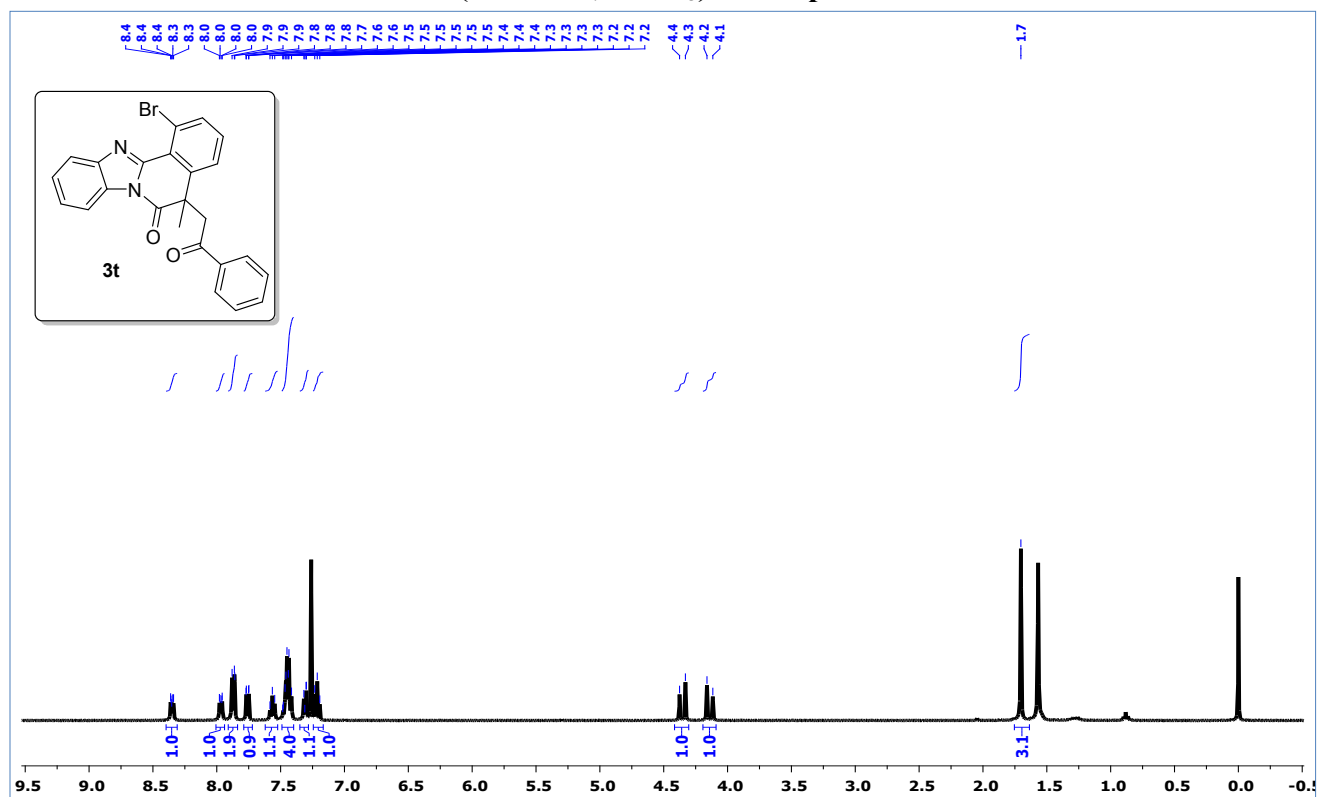
¹H NMR (400 MHz, CDCl₃) of compound 3s



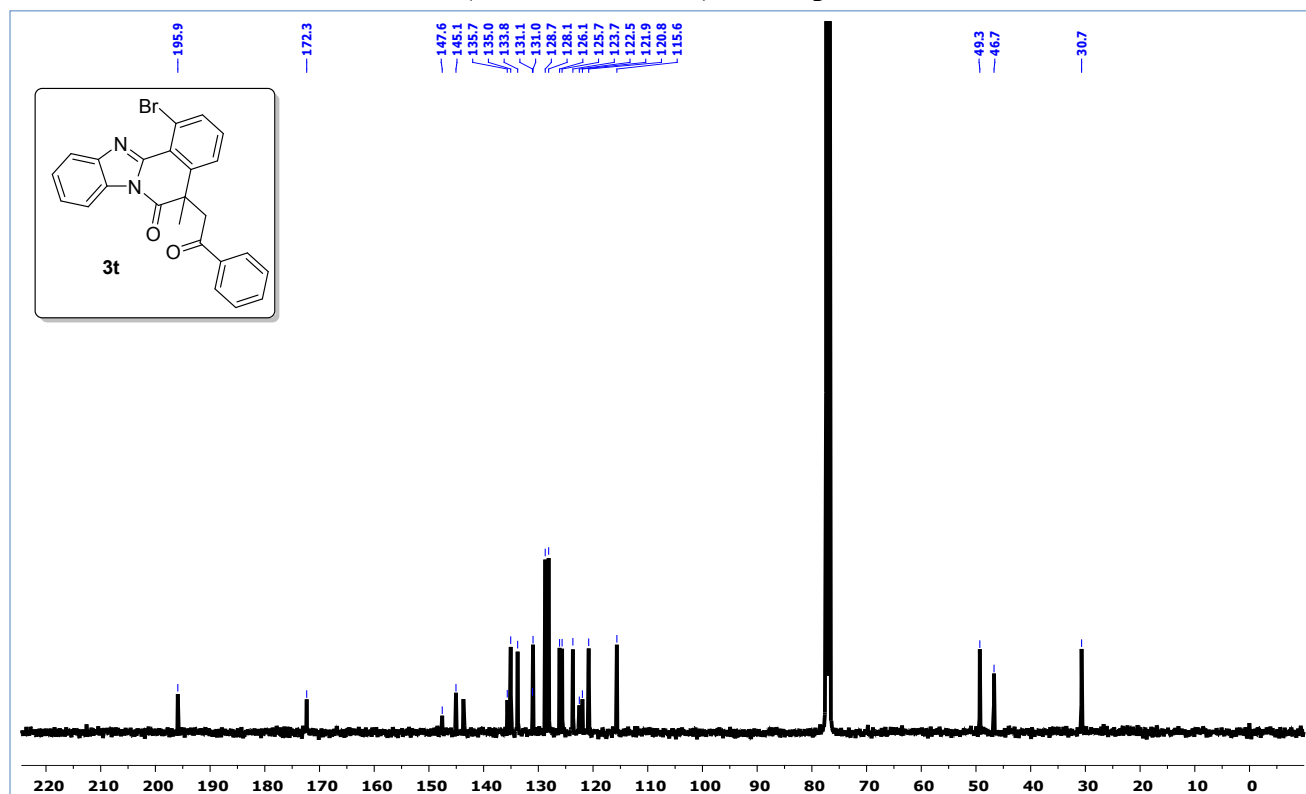
¹³C NMR (126 MHz, CDCl₃) of compound 3s



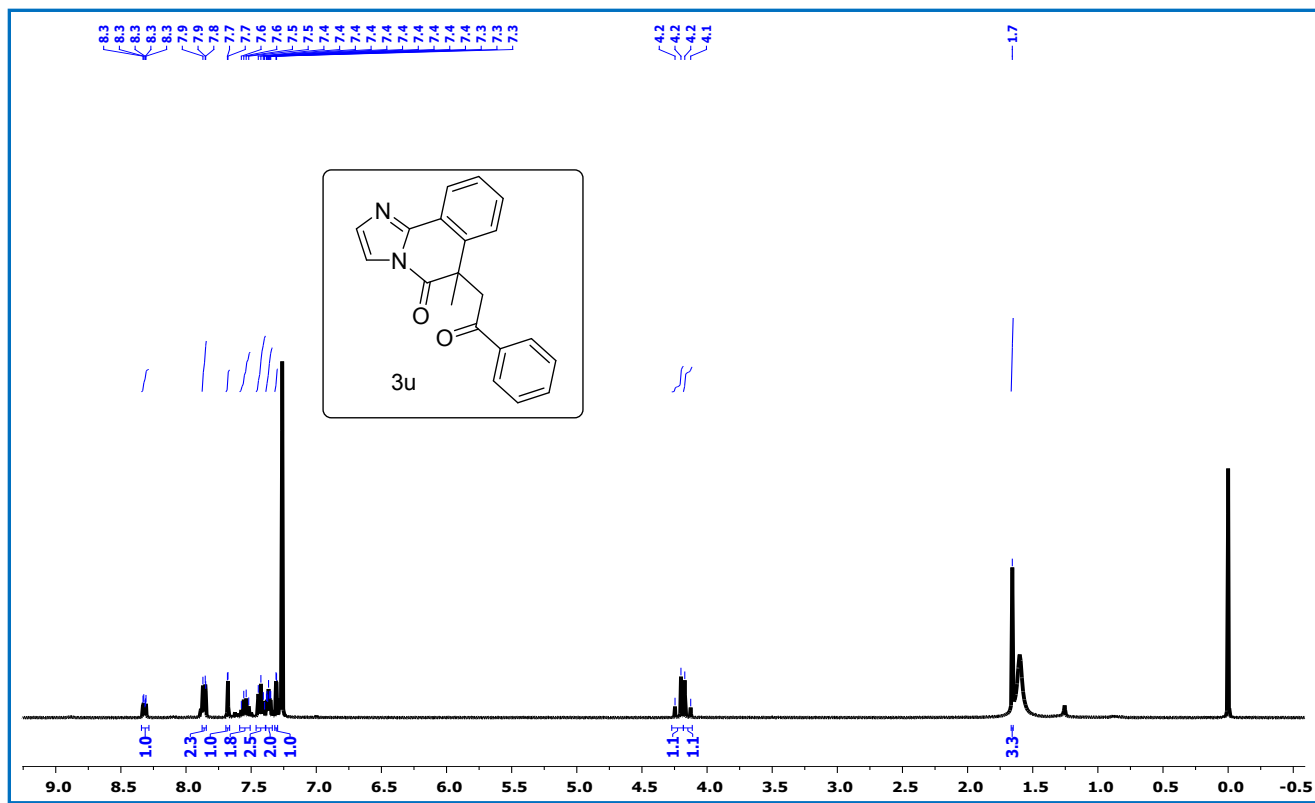
¹H NMR (400 MHz, CDCl₃) of compound 3t



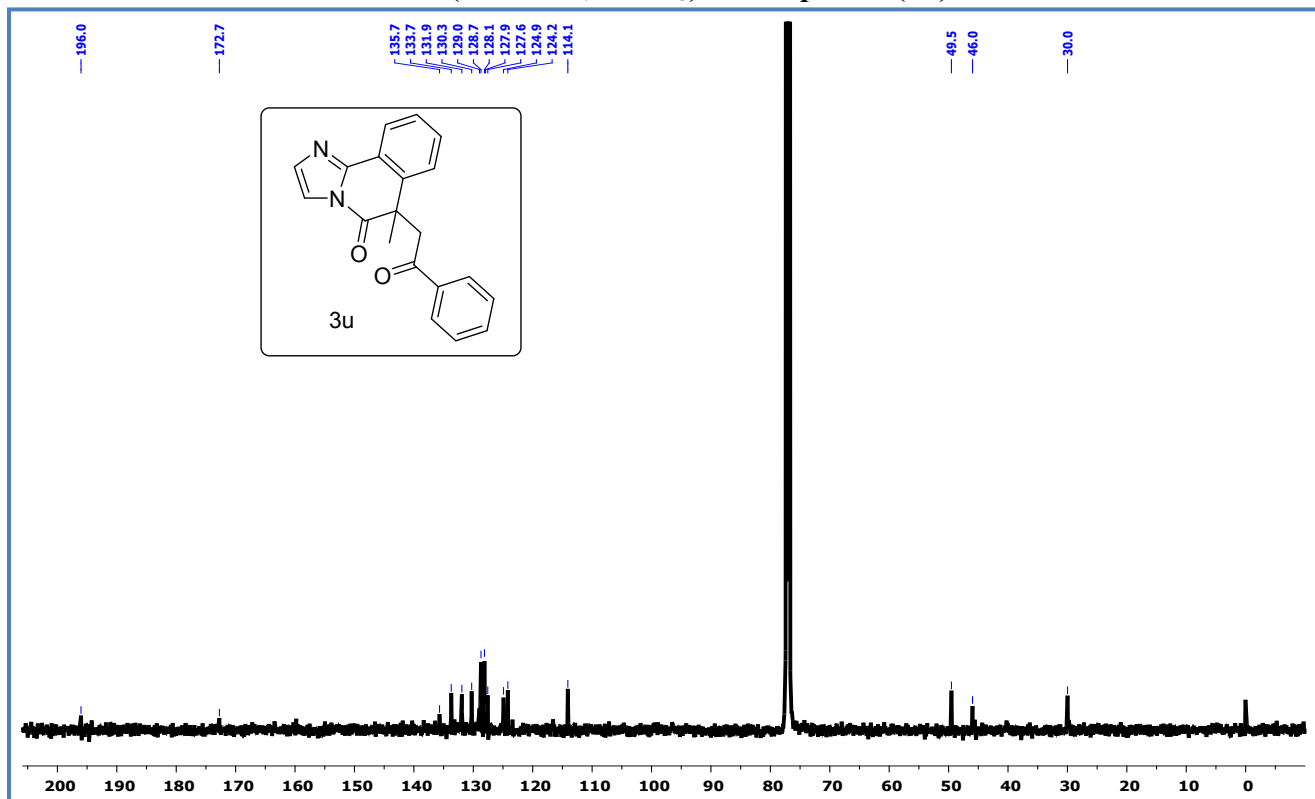
¹³C NMR (100 MHz, CDCl₃) of compound 3t



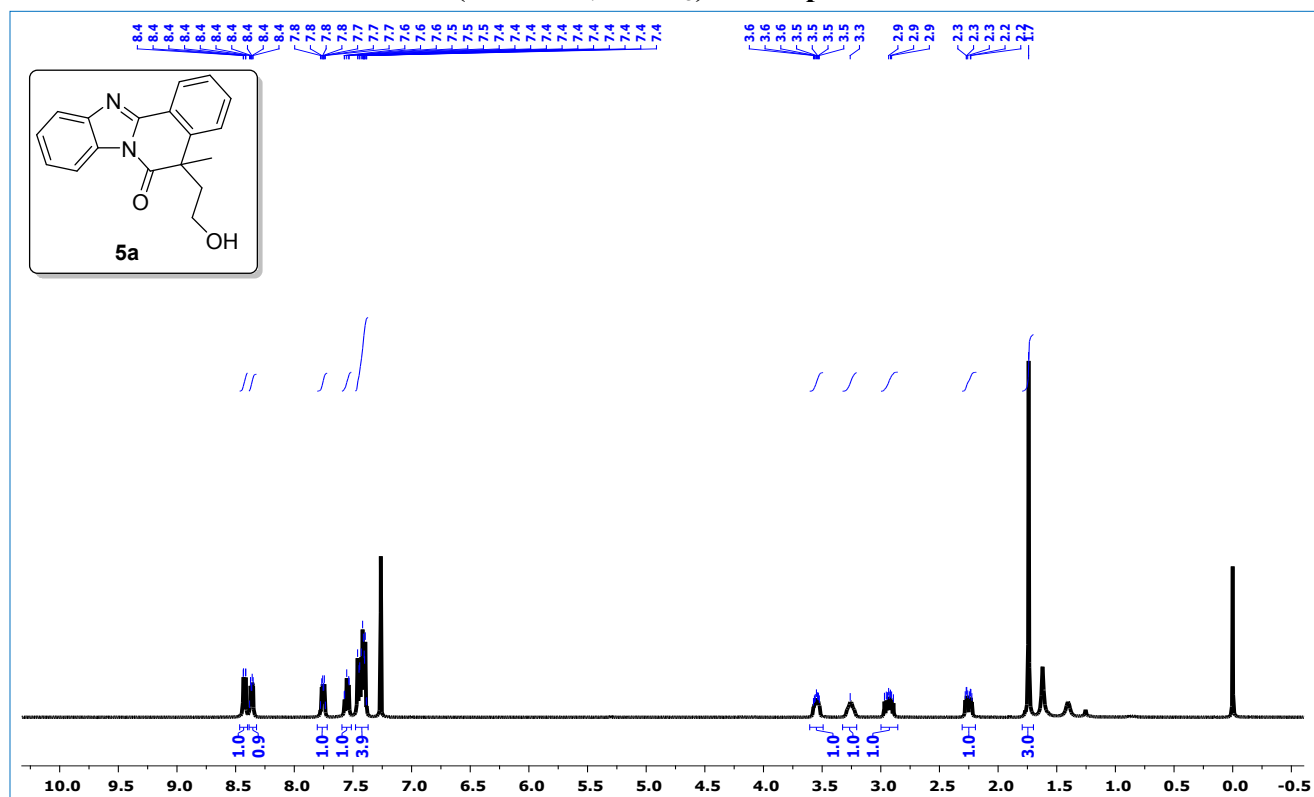
¹H NMR (400 MHz, CDCl₃) of compound 3u



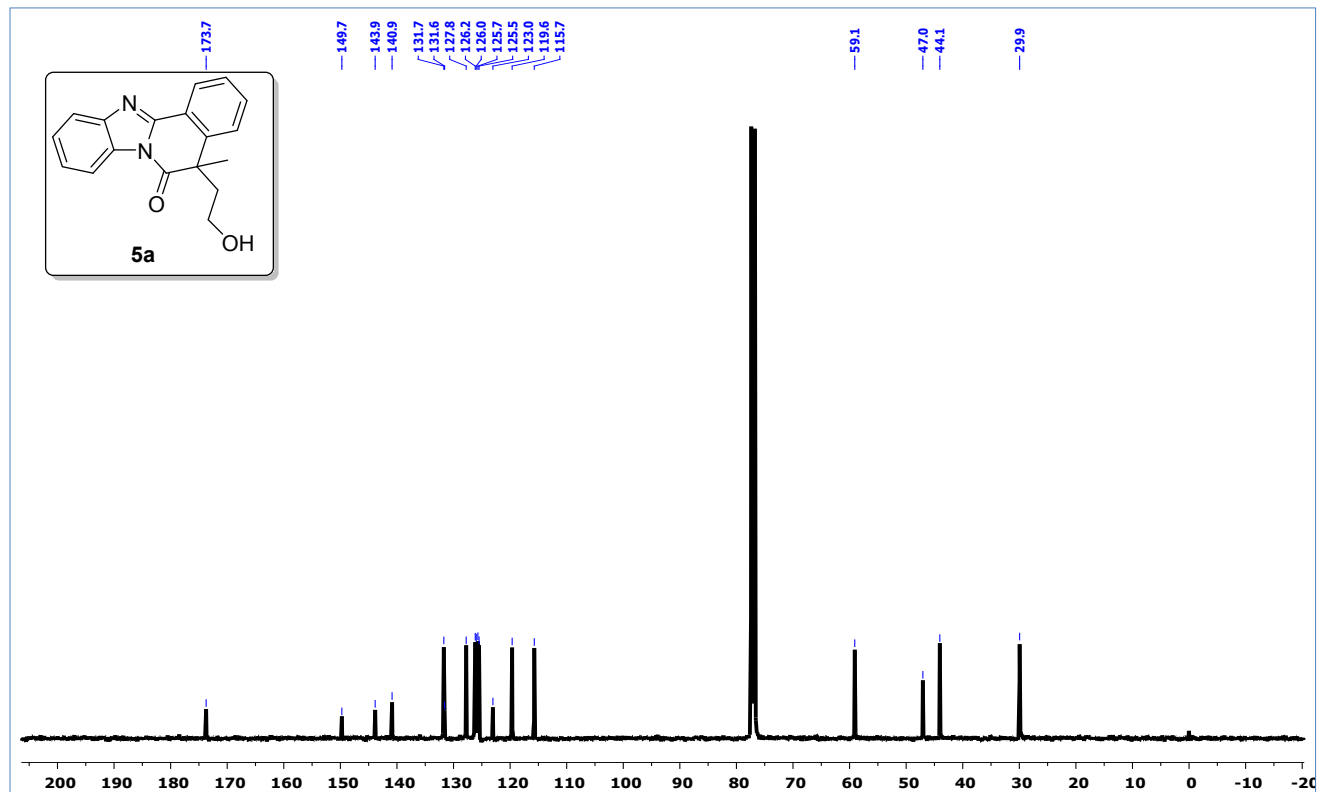
¹³C NMR (126 MHz, CDCl₃) of compound (3u)



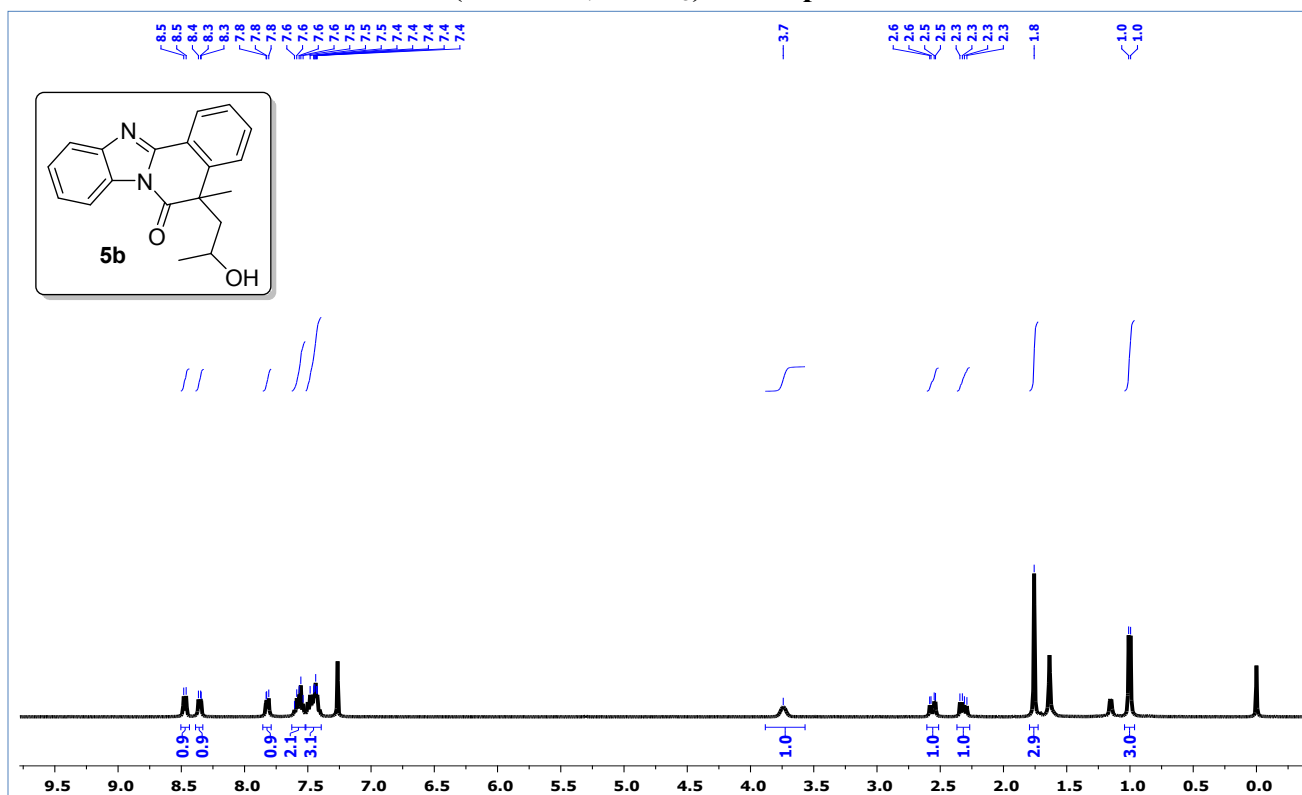
¹H NMR (400 MHz, CDCl₃) of compound 4a



¹³C NMR (100 MHz, CDCl₃) of compound 4a



¹H NMR (400 MHz, CDCl₃) of compound 4b



¹³C NMR (100 MHz, CDCl₃) of compound 4b

