The dicarbonylation of indoles via Friedel-Crafts reaction with dicarbonyl nitrile generated in situ and retro cyanohydrination

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Supporting Information

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1. General considerations

All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$, acetone-D_6 or DMSO-D_6 using a Bruker ASCEND 400 spectrometer. Chemical shifts are expressed in ppm and *J* values are given in Hz. High resolution mass spectra were recorded on bruker micrOTOF-QIII MS (ESI). IR spectra were recorded on a Bio-Rad FTS-40 spectrometer. Column chromatography was performed with 200-300 mesh silica gel using flash column techniques. Melting points (uncorrected) were determined on a yalixien X-4 melting point apparatus. All the solvents and reagents were used directly as obtained commercially unless otherwise noted.

Procedure for the synthesis of **3aa**. A solution of indole (**1a**) (58.6 mg, 0.5 mmol), benzoylacetonitrile (**2a**) (108.8 mg, 0.75 mmol), 4-oxo-TEMPO (255 mg, 1.5 mmol) and CuCl (5 mg, 0.05 mmol)in acetic acid (5.0 mL) under an air atmosphere was stirred at room tmperature for 2 h (complete consumption of indicated by TLC). The mixture was then concentrated in vacuo to give a residue that was dissolved in ethyl acetate (50 mL). Washing the ethyl acetate solution with aqueous $NaHCO_3$ (2×30 mL) followed by drying over sodium sulphate and concentration in vacuo gave a residue that was subjected to flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1 as an eluent) to afford **3aa** as a yellow solid (87%).

2. Reference for known compounds

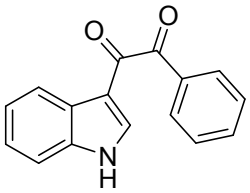
Some of the products are reported by other groups (**3aa**[1], **3ad**[1], **3ae**[1], **3af**[1], **3ag**[1], **3al**[2], **4ba**[1], **4ca**[3], **4da**[1], **4ea**[1], **4fa**[3], **4ma**[1], **4na**[1] and **4oa**[1]). The ^{1}H, ^{13}C NMR and HRMS of these products were provided.

1. J.-C. Wu, R.-J. Song, Z.-Q. Wang, X.-C. Huang, Y.-X. Xie, J.-H. Li, *Angewandte Chemie International Edition* **2012**, *51*, 3453-3457.

2. I. T. Hogan, M. Sainsbury, *Tetrahedron* **1984**, *40*, 681-682.

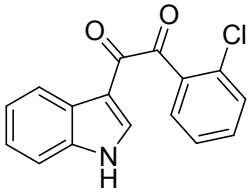
3. R.-Y. Tang, X.-K. Guo, J.-N. Xiang, J.-H. Li, *The Journal of Organic Chemistry* **2013**, *78*, 11163-11171.

3. Characterization data of compounds 3aa-3al, 4ba-4oa, and 5



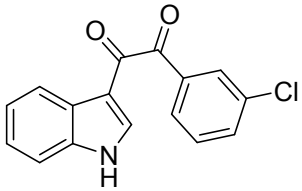
1-(1H-indol-3-yl)-2-phenylethane-1,2-dione (3aa)

^{1}H NMR (400 MHz, Acetone-D_6) δ 11.38 (s, 1H), 8.41 – 8.34 (m, 1H), 8.13 (d, *J* = 3.2 Hz, 1H), 8.06 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.75 – 7.68 (m, 1H), 7.64 – 7.54 (m, 3H), 7.37 – 7.30 (m, 2H); ^{13}C NMR (101 MHz, Acetone-D_6) δ 194.7, 189.5, 138.1, 137.8, 135.2, 134.5, 130.7, 129.8, 126.5, 124.8, 123.7, 122.6, 114.4, 113.3; HRMS calcd for $C_{16}H_{11}NO_2Na$ $(M+Na)^+$ 272.0682, found 272.0683.



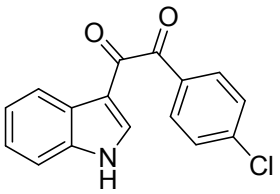
1-(2-chlorophenyl)-2-(1H-indol-3-yl)ethane-1,2-dione (3ab)

Yellow solid: m.p. 202-203 ºC; IR (cm^{-1}) 1698, 1666, 1602, 1581, 1517; ^{1}H NMR (400 MHz, DMSO-D_6) δ 12.45 (s, 1H), 8.36 (d, *J* = 3.2 Hz, 1H), 8.21 – 8.13 (m, 1H), 7.81 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.67 (td, *J* = 7.8, 1.6 Hz, 1H), 7.62 – 7.49 (m, 3H), 7.35 – 7.25 (m, 2H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 193.3, 185.8, 138.0, 136.9, 134.4, 134.3, 132.1, 132.0, 130.5, 127.7, 125.5, 123.8, 122.8, 121.2, 112.8, 111.8; HRMS calcd for $C_{16}H_{10}ClNO_2Na$ $(M+Na)^+$ 306.0292, found 306.0295.



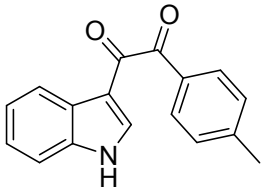
1-(3-chlorophenyl)-2-(1H-indol-3-yl)ethane-1,2-dione (3ac)

Yellow solid: m.p. 203-204 ºC; IR (cm^{-1}) 1671, 1603, 1584, 1516; ^{1}H NMR (400 MHz, DMSO-D_6) δ 12.48 (s, 1H), 8.24 (s, 2H), 7.95 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 4.7 Hz, 1H), 7.37 – 7.27 (m, 2H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 192.3, 187.3, 138.5, 137.0, 134.8, 134.3, 133.9, 131.2, 128.8, 128.76, 125.1, 124.0, 123.0, 121.2, 112.8, 112.4; HRMS calcd for $C_{16}H_{10}ClNO_2Na$ $(M+Na)^+$ 306.0292, found 306.0296.



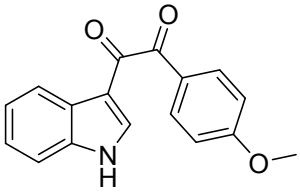
1-(4-chlorophenyl)-2-(1H-indol-3-yl)ethane-1,2-dione (3ad)

^{1}H NMR (400 MHz, DMSO-D_6) δ 12.45 (s, 1H), 8.22 (t, *J* = 4.9 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.36 – 7.27 (m, 2H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 192.6, 187.8, 139.6, 138.3, 137.0, 131.7, 131.6, 129.3, 125.0, 123.9, 122.9, 121.2, 112.8, 112.4; HRMS calcd for $C_{16}H_{10}NClNaO_2$ $(M+Na)^+$ 306.0292, found 306.0300.



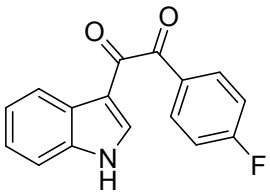
1-(1H-indol-3-yl)-2-(p-tolyl)ethane-1,2-dione (3ae)

^{1}H NMR (400 MHz, DMSO-D_6) δ 12.40 (s, 1H), 8.26 – 8.18 (m, 1H), 8.15 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 (p, *J* = 6.5 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 193.7, 188.9, 145.5, 137.8, 137.0, 130.5, 129.9, 129.7, 125.0, 123.8, 122.8, 121.2, 112.8, 112.6, 21.4; HRMS calcd for $C_{17}H_{13}NNaO_2$ $(M+Na)^+$ 286.0838, found 286.0843.



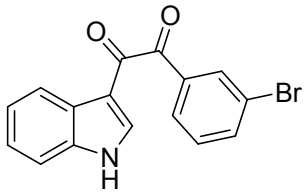
1-(1H-indol-3-yl)-2-(4-methoxyphenyl)ethane-1,2-dione (3af)

^{1}H NMR (400 MHz, DMSO-D_6) δ 12.36 (s, 1H), 8.25 – 8.16 (m, 1H), 8.12 (s, 1H), 7.97 – 7.88 (m, 2H), 7.59 – 7.50 (m, 1H), 7.30 (dt, *J* = 6.7, 3.6 Hz, 2H), 7.16 – 7.06 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 192.7, 189.2, 164.4, 137.7, 137.0, 132.3, 125.8, 125.1, 123.8, 122.8, 121.2, 114.6, 112.8, 55.8; HRMS calcd for $C_{17}H_{13}NNaO_3$ $(M+Na)^+$ 302.0788, found 302.0793.



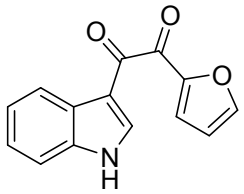
1-(4-fluorophenyl)-2-(1H-indol-3-yl)ethane-1,2-dione (3ag)

^{1}H NMR (400 MHz, Acetone-D_6) δ 11.41 (s, 1H), 8.42 – 8.33 (m, 1H), 8.22 – 8.07 (m, 3H), 7.66 – 7.56 (m, 1H), 7.43 – 7.25 (m, 4H); ^{13}C NMR (101 MHz, Acetone-D_6) δ 193.0, 189.0, 167.2 (d, *J* = 254.2 Hz), 138.0, 133.8 (d, *J* = 9.8 Hz), 131.2 (d, *J* = 2.9 Hz), 126.5, 124.9, 123.7, 122.6, 116.8 (d, *J* = 22.3 Hz), 114.3, 113.3; HRMS calcd for $C_{16}H_{10}FNO_2Na$ $(M+Na)^+$ 290.0588, found 290.0587.



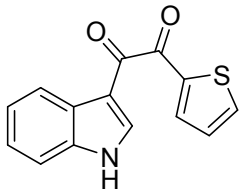
1-(3-bromophenyl)-2-(1H-indol-3-yl)ethane-1,2-dione (3ah)

Yellow solid: m.p. 187-188 ºC; IR (cm^{-1}) 1670, 1600, 1583, 1516; ^{1}H NMR (400 MHz, DMSO-D_6) δ 12.48 (s, 1H), 8.23 (dd, *J* = 8.6, 3.7 Hz, 2H), 8.09 (t, *J* = 1.7 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.35 – 7.30 (m, 2H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 192.2, 187.3, 138.5, 137.2, 137.9, 135.0, 131.7, 131.4, 129.0, 125.0, 123.9, 122.9, 122.3, 121.2, 112.8, 112.4; HRMS calcd for $C_{16}H_{10}BrNO_2Na$ $(M+Na)^+$ 349.9787, found 349.9792.



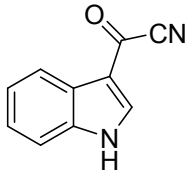
1-(furan-2-yl)-2-(1H-indol-3-yl)ethane-1,2-dione (3ai)

Yellow solid: m.p. 202-203 ºC; IR (cm^{-1}) 1670, 1655, 1599, 1516; ^{1}H NMR (400 MHz, DMSO-D_6) δ 12.42 (s, 1H), 8.29 (d, *J* = 3.2 Hz, 1H), 8.25 – 8.16 (m, 2H), 7.56 (ddd, *J* = 7.7, 6.1, 3.4 Hz, 2H), 7.36 – 7.25 (m, 2H), 6.81 (dd, *J* = 3.6, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 185.8, 180.6, 150.1, 149.5, 138.2, 136.9, 125.4, 123.9, 123.7, 122.8, 121.3, 113.3, 112.8, 112.0; HRMS calcd for $C_{14}H_9NO_3Na$ $(M+Na)^+$ 262.0475, found 262.0480.



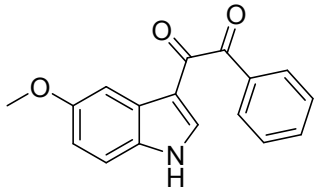
1-(1H-indol-3-yl)-2-(thiophen-2-yl)ethane-1,2-dione (3aj)

Yellow solid: m.p. 207-208 ºC; IR (cm^{-1}) 1670, 1645, 1599, 1516; ^1H NMR (400 MHz, DMSO-D_6) δ 12.44 (s, 1H), 8.33 (s, 1H), 8.23 (dd, *J* = 10.6, 5.1 Hz, 2H), 7.96 (d, *J* = 3.3 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.36 – 7.25 (m, 3H); ^{13}C NMR (101 MHz, DMSO) δ 185.9, 185.4, 139.0, 138.4, 137.9, 136.9, 136.9, 129.2, 125.5, 123.9, 122.9, 121.3, 112.8, 111.9; HRMS calcd for $C_{14}H_9NO_2SNa$ $(M+Na)^+$ 278.0246, found 278.0250.



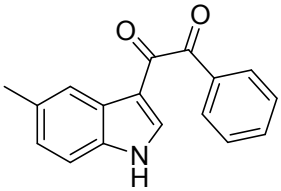
1H-indole-3-carbonyl cyanide (3am)

^1H NMR (400 MHz, DMSO-D_6) δ 12.91 (s, 1H), 8.63 (s, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.41 – 7.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 141.4, 137.6, 124.9, 124.2, 123.8, 121.0, 116.2, 114.4, 113.3; HRMS calcd for $C_{10}H_6N_2NaO$ $(M+Na)^+$ 193.0372, found 193.0381.



1-(5-methoxy-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ba)

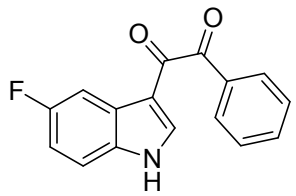
^1H NMR (400 MHz, DMSO-D_6) δ 12.31 (s, 1H), 8.09 (d, *J* = 2.6 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.78 – 7.70 (m, 2H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 194.0, 188.4, 156.2, 137.9, 134.7, 133.0, 131.7, 129.7, 129.1, 126.0, 113.6, 113.6, 112.5, 103.0, 55.4; HRMS calcd for $C_{17}H_{13}NNaO_3$ $(M+Na)^+$ 302.0788, found 302.0796.



1-(5-methyl-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ca)

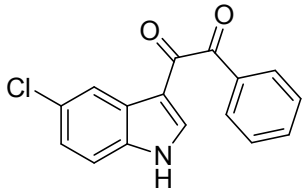
^1H NMR (400 MHz, DMSO-D_6) δ 12.31 (s, 1H), 8.10 (d, *J* = 3.3 Hz, 1H), 8.05 (s, 1H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 194.0, 188.5, 137.9, 135.3, 134.6, 133.0, 131.9, 129.7, 129.1, 125.3,

121.0, 112.4, 112.2, 21.3; HRMS calcd for $C_{17}H_{13}NNaO_2$ $(M+Na)^+$ 286.0838, found 286.0846.



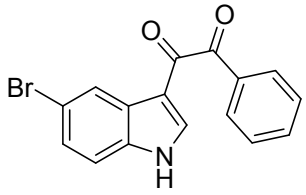
1-(5-fluoro-1H-indol-3-yl)-2-phenylethane-1,2-dione (4da)

^{1}H NMR (400 MHz, Acetone-D_6) δ 11.46 (s, 1H), 8.20 (s, 1H), 8.07 – 8.01 (m, 3H), 7.75 – 7.70 (m, 1H), 7.65 – 7.56 (m, 3H), 7.14 (td, *J* = 9.1, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, Acetone-D_6) δ 194.4, 189.2, 160.6 (d, *J* = 236.5 Hz), 139.1, 139.0 (d, *J* = 17.6 Hz), 135.3, 134.5 (d, *J* = 18.5 Hz), 130.8, 129.8, 127.3 (d, *J* = 11.2 Hz), 114.6 (d, *J* = 9.8 Hz), 114.5 (d, *J* = 4.4 Hz), 113.0 (d, *J* = 26.2 Hz), 107.6 (d, *J* = 25.1 Hz); HRMS calcd for $C_{16}H_{10}FNO_2Na$ $(M+Na)^+$ 290.0588, found 290.0590.



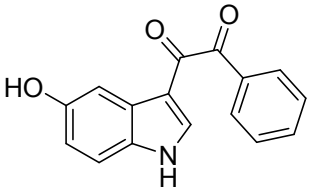
1-(5-chloro-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ea)

^{1}H NMR (400 MHz, Acetone-D_6) δ 11.51 (s, 1H), 8.37 (d, *J* = 2.0 Hz, 1H), 8.20 (s, 1H), 8.09 – 8.03 (m, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.34 (dd, *J* = 8.7, 2.1 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 193.6, 188.4, 139.2, 135.5, 134.8, 132.8, 129.8, 129.2, 127.5, 126.2, 123.9, 120.3, 114.5, 112.1; HRMS calcd for $C_{16}H_{10}ClNO_2Na$ $(M+Na)^+$ 306.0292, found 306.0285.



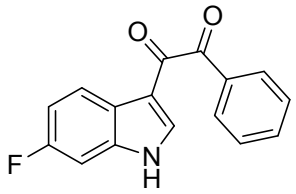
1-(5-bromo-1H-indol-3-yl)-2-phenylethane-1,2-dione (4fa)

^{1}H NMR (400 MHz, DMSO-D_6) δ 12.59 (s, 1H), 8.36 (d, *J* = 1.6 Hz, 1H), 8.25 (s, 1H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.46 (dd, *J* = 8.6, 1.9 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 193.6, 188.4, 139.0, 135.8, 134.8, 132.8, 129.8, 129.2, 126.8, 126.5, 123.3, 115.6, 114.9, 112.0; HRMS calcd for $C_{16}H_{10}BrNO_2Na$ $(M+Na)^+$ 349.9787, found 349.9795.



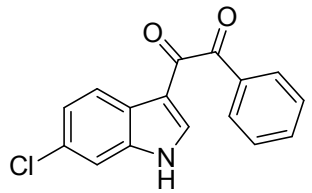
1-(5-hydroxy-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ga)

Brown solid: m.p. 214-215 ºC; IR (cm^{-1}) 3239, 1653, 1626, 1593, 1517; ^1H NMR (400 MHz, DMSO-D_6) δ 12.18 (s, 1H), 9.22 (s, 1H), 8.01 (d, *J* = 3.3 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.77 – 7.70 (m, 1H), 7.59 (dd, *J* = 10.7, 4.8 Hz, 3H), 7.34 (d, *J* = 8.7 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.4 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 194.2, 188.2, 154.0, 137.5, 134.6, 133.1, 131.0, 129.7, 129.1, 126.2, 113.5, 113.2, 112.1, 105.6; HRMS calcd for $C_{16}H_{11}NO_3Na$ $(M+Na)^+$ 288.0631, found 288.0634.



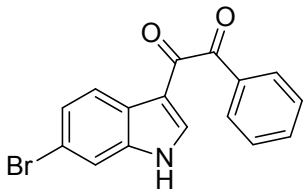
1-(6-fluoro-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ia)

Yellow solid: m.p. 209-210 ºC; IR (cm^{-1}) 1660, 1608, 1593, 1519; ^1H NMR (400 MHz, DMSO-D_6) δ 12.46 (s, 1H), 8.25 – 8.17 (m, 2H), 7.97 (d, *J* = 7.5 Hz, 2H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 9.5, 2.1 Hz, 1H), 7.23 – 7.14 (m, 1H); ^{13}C NMR (101 MHz, DMSO-D_6)_δ 193.7, 188.5, 159.7 (d, *J* = 239.1 Hz), 138.7 (d, *J* = 1.7 Hz), 137.2 (d, *J* = 13.2 Hz), 134.7, 132.9, 129.8, 129.1, 122.4 (d, *J* = 10.6 Hz), 121.7, 112.5, 111.2 (d, *J* = 24.0 Hz), 99.2 (d, *J* = 26.0 Hz); HRMS calcd for $C_{16}H_{10}FNO_2Na$ $(M+Na)^+$ 290.0588, found 290.0595.



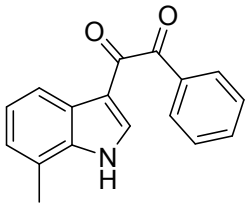
1-(6-chloro-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ja)

Yellow solid: m.p. 232-233 ºC; IR (cm^{-1}) 1663, 1605, 1598, 1518; ^1H NMR (400 MHz, DMSO-D_6) δ 12.50 (s, 1H), 8.28 – 8.16 (m, 2H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.75 (t, *J* = 7.1 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 193.7, 188.4, 138.9, 137.5, 134.8, 132.8, 129.8, 129.2, 128.3, 123.8, 123.1, 122.5, 112.5, 112.5; HRMS calcd for $C_{16}H_{10}ClNO_2Na$ $(M+Na)^+$ 306.0292, found 306.0295.



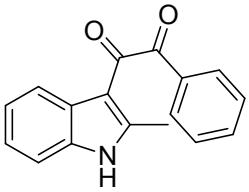
1-(6-bromo-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ka)

Brown solid: m.p. 241-242 ºC; IR (cm^{-1}) 1664, 1605, 1574, 1516; ^1H NMR (400 MHz, DMSO-D_6) δ 12.52 (s, 1H), 8.23 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.46 (dd, *J* = 8.4, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 193.7, 188.5, 138.8, 137.9, 134.8, 132.8, 129.8, 129.2, 125.8, 124.1, 122.8, 116.4, 115.5, 112.5; HRMS calcd for $C_{16}H_{10}BrNO_2Na$ $(M+Na)^+$ 349.9787, found 349.9794.



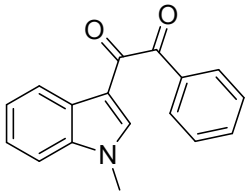
1-(7-methyl-1H-indol-3-yl)-2-phenylethane-1,2-dione (4la)

Orange solid: m.p. 186-187 ºC; IR (cm^{-1}) 1664, 1608, 1593, 1561; ^1H NMR (400 MHz, DMSO-D_6) δ 12.47 (s, 1H), 8.17 (d, *J* = 3.3 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.01 – 7.93 (m, 2H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.1 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 194.0, 188.6, 137.5, 136.4, 134.6, 133.0, 129.7, 129.1, 124.9, 124.4, 123.0, 122.2, 118.7, 113.0, 16.7; HRMS calcd for $C_{17}H_{13}NO_2Na$ $(M+Na)^+$ 286.0838, found 286.0844.



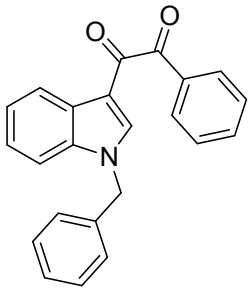
1-(2-methyl-1H-indol-3-yl)-2-phenylethane-1,2-dione (4ma)

^1H NMR (400 MHz, Acetone-D6) δ 11.22 (s, 1H), 8.03 (d, *J* = 7.4 Hz, 2H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.22 – 7.15 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 196.0, 190.0, 148.3, 135.8, 135.4, 133.2, 130.0, 126.8, 123.4, 123.0, 120.4, 118.6, 112.3, 14.8; IR (cm^{-1}): 1667, 1596; HRMS calcd for $C_{17}H_{13}NO_2Na$ $(M+Na)^+$ 286.0838, found 286.0842.



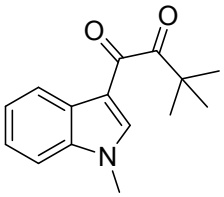
1-(1-methyl-1H-indol-3-yl)-2-phenylethane-1,2-dione (4na)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.1 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 2H), 7.88 (s, 1H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.48 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 187.3, 139.3, 137.4, 134.0, 133.1, 130.0, 128.4, 126.0, 123.9, 123.2, 122.4, 112.5, 109.7, 33.5; HRMS calcd for $C_{17}H_{13}NO_2Na$ $(M+Na)^+$ 286.0838, found 286.0843.



1-(1-benzyl-1H-indol-3-yl)-2-phenylethane-1,2-dione (4oa)

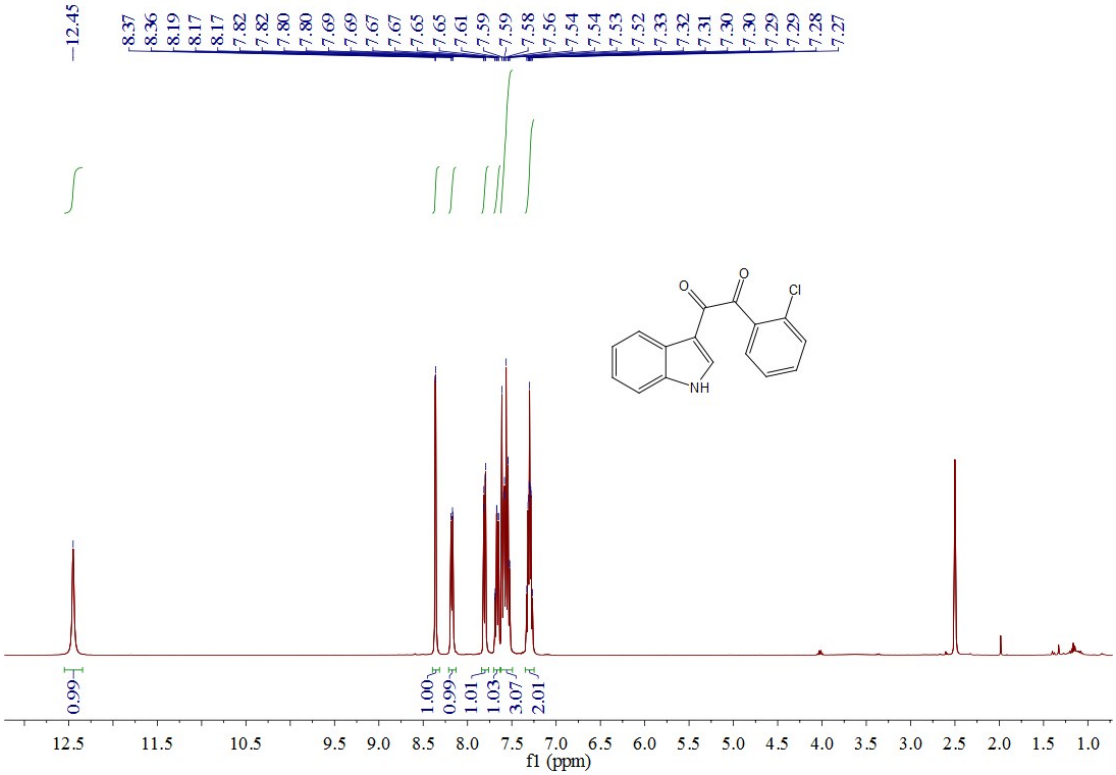
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.8 Hz, 1H), 8.14 – 8.06 (m, 2H), 7.91 (s, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.38 (ddd, *J* = 8.0, 5.8, 2.5 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.19 – 7.11 (m, 2H), 5.33 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 187.7, 139.0, 137.3, 135.2, 134.4, 133.5, 130.4, 129.1, 128.8, 128.4, 127.1, 126.7, 124.4, 123.6, 122.8, 113.4, 110.7, 51.2; HRMS calcd for $C_{23}H_{17}NO_2Na$ $(M+Na)^+$ 362.1151, found 362.1160.



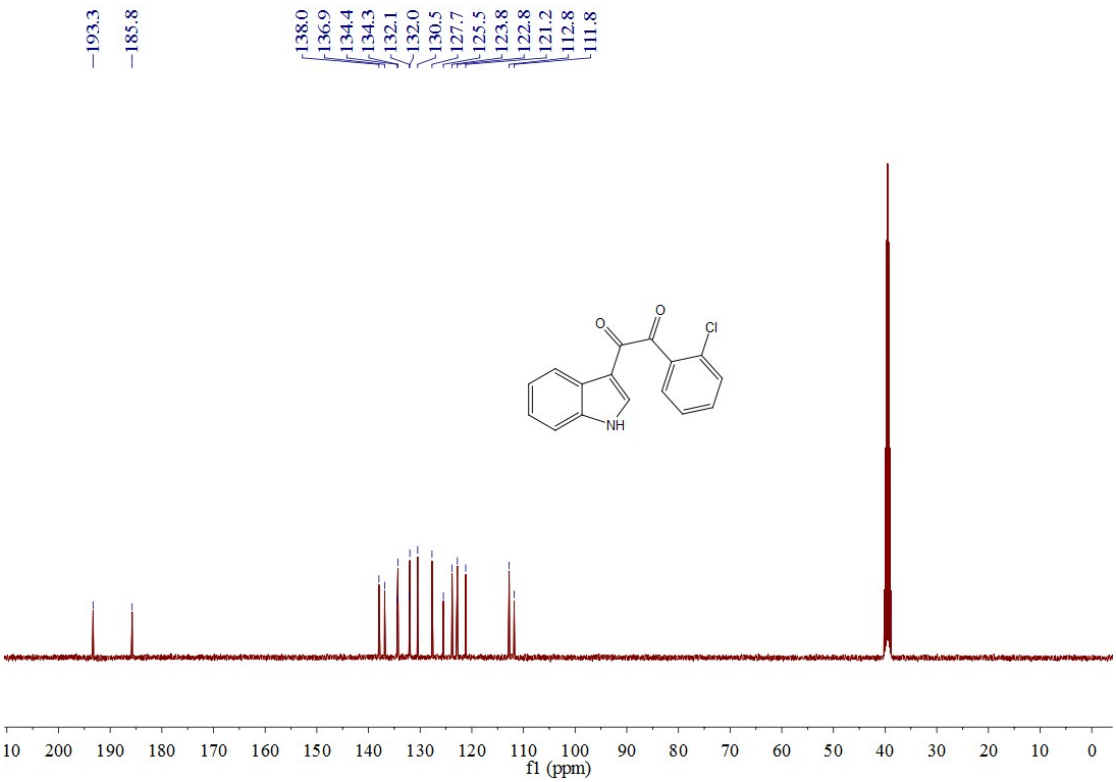
3,3-dimethyl-1-(1-methyl-1H-indol-3-yl)butane-1,2-dione (5)

Light yellow solid: m.p. 116-117 ºC; IR (cm^{-1}) 1698, 1666, 1601, 1581; ^{1}H NMR (400 MHz, DMSO-D_6) δ 8.16 (d, *J* = 7.2 Hz, 1H), 8.08 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.28 (m, 2H), 3.89 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, DMSO) δ 209.9, 189.5, 140.7, 137.6, 125.4, 123.7, 123.0, 121.2, 111.1, 111.1, 42.0, 33.4, 26.2; HRMS calcd for $C_{15}H_{17}NO_2Na$ $(M+Na)^+$ 266.1151, found 266.1149.

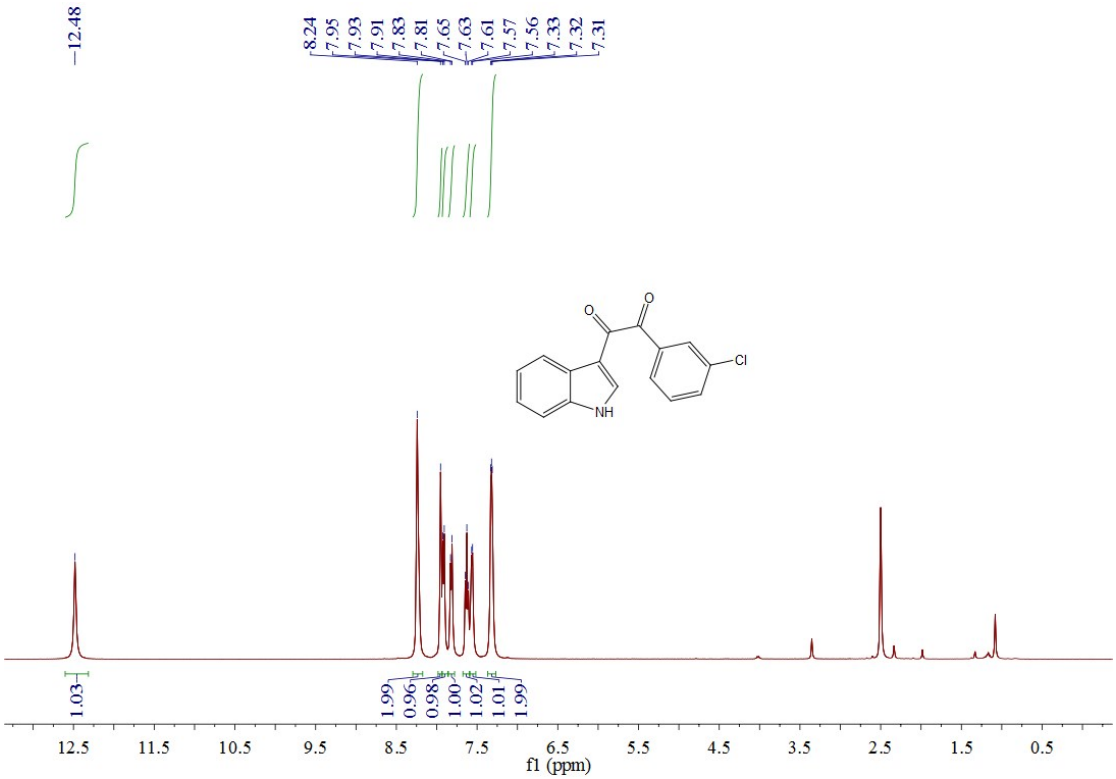
4. ^{1}H and ^{13}C NMR Spectra of all new compounds



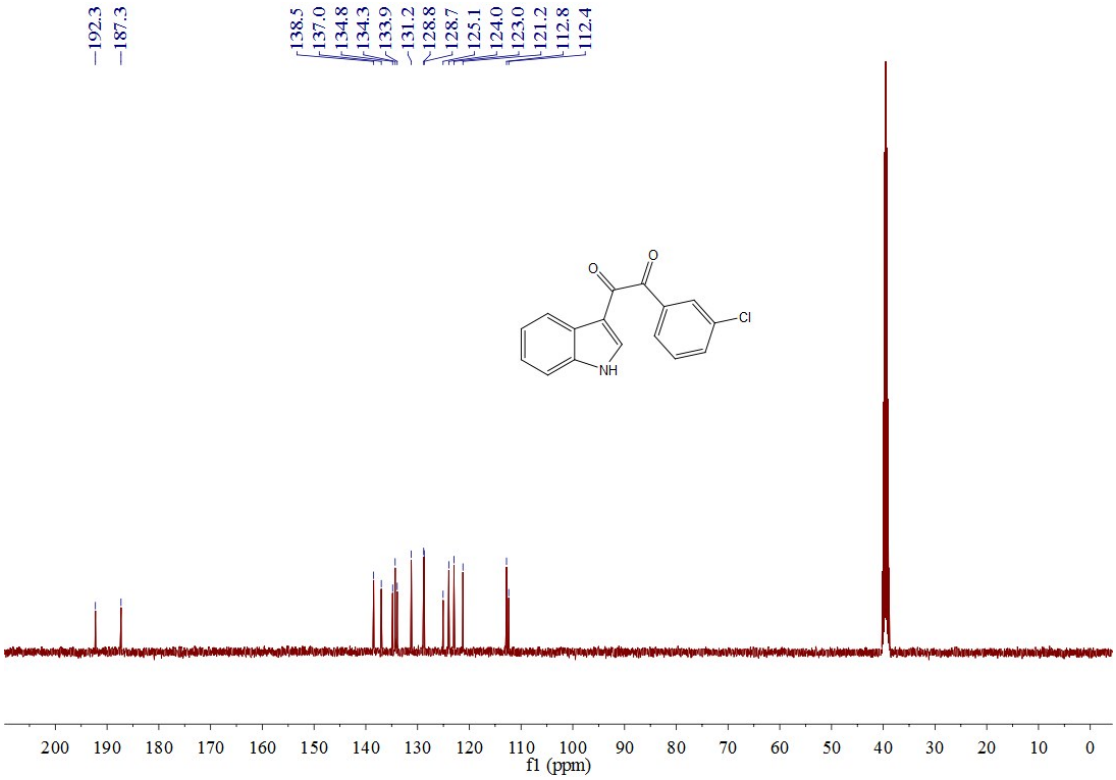
^{1}H NMR spectrum of **3ab** in DMSO at 297 K (δ in ppm).



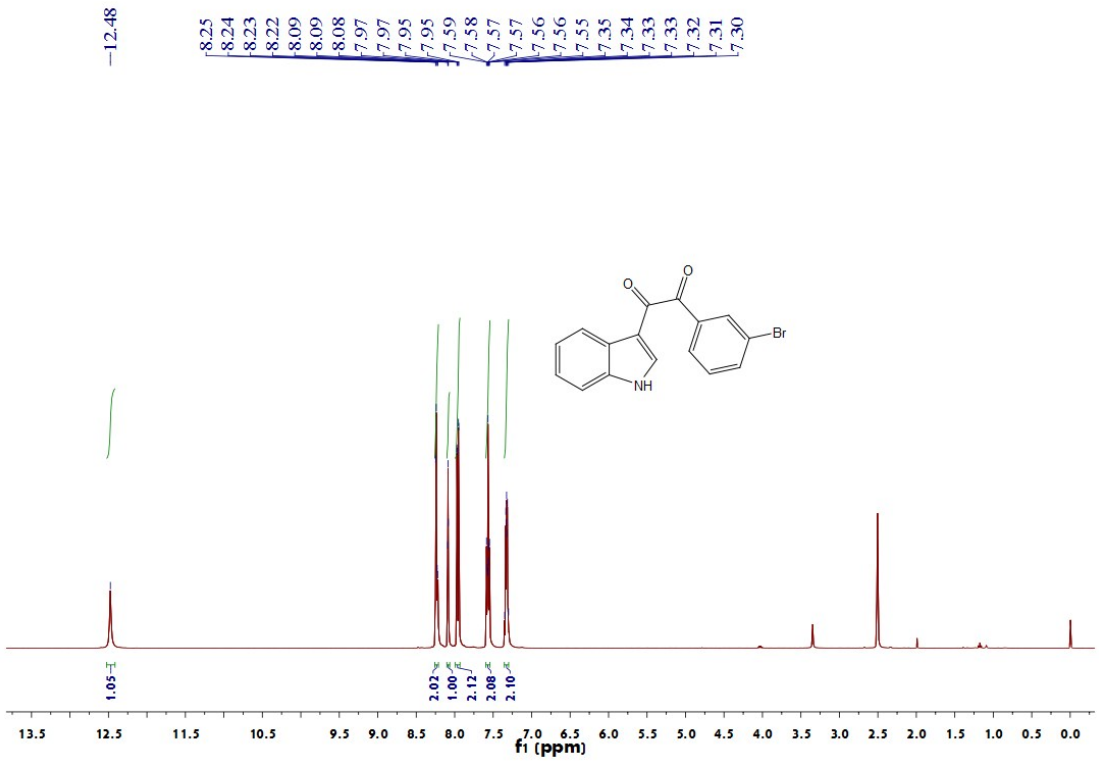
^{13}C NMR spectrum of **3ab** in DMSO at 297 K (δ in ppm).



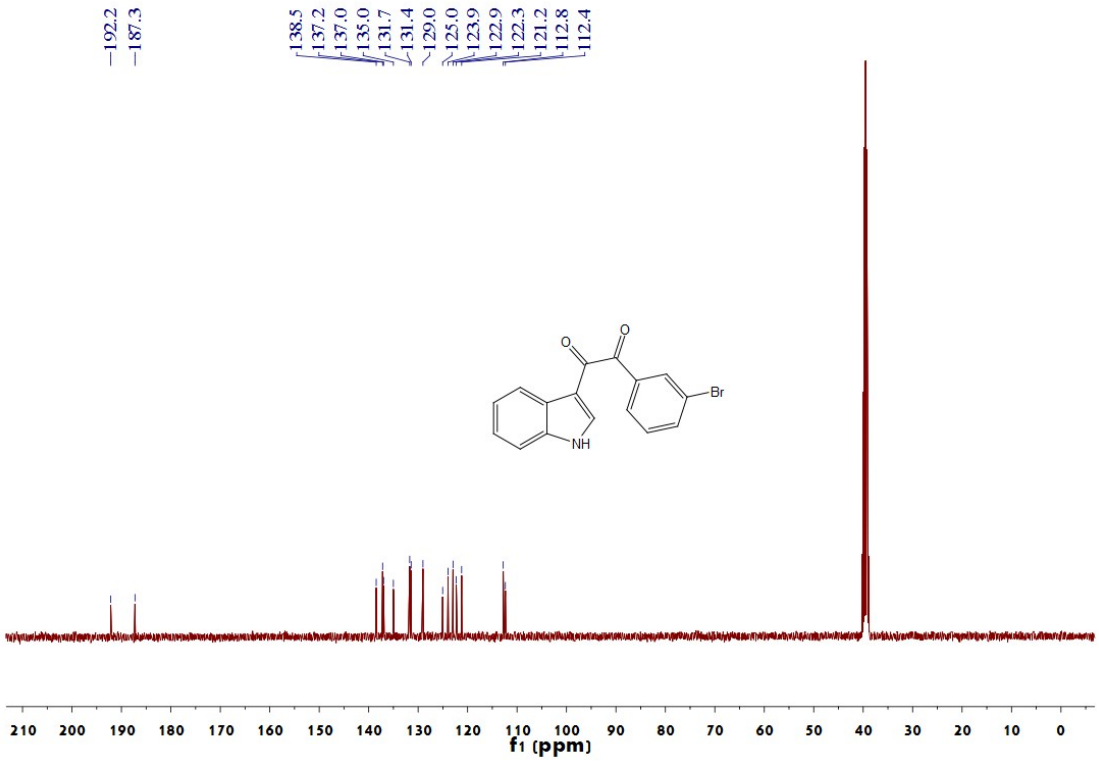
^{1}H NMR spectrum of **3ac** in DMSO at 297 K (δ in ppm).



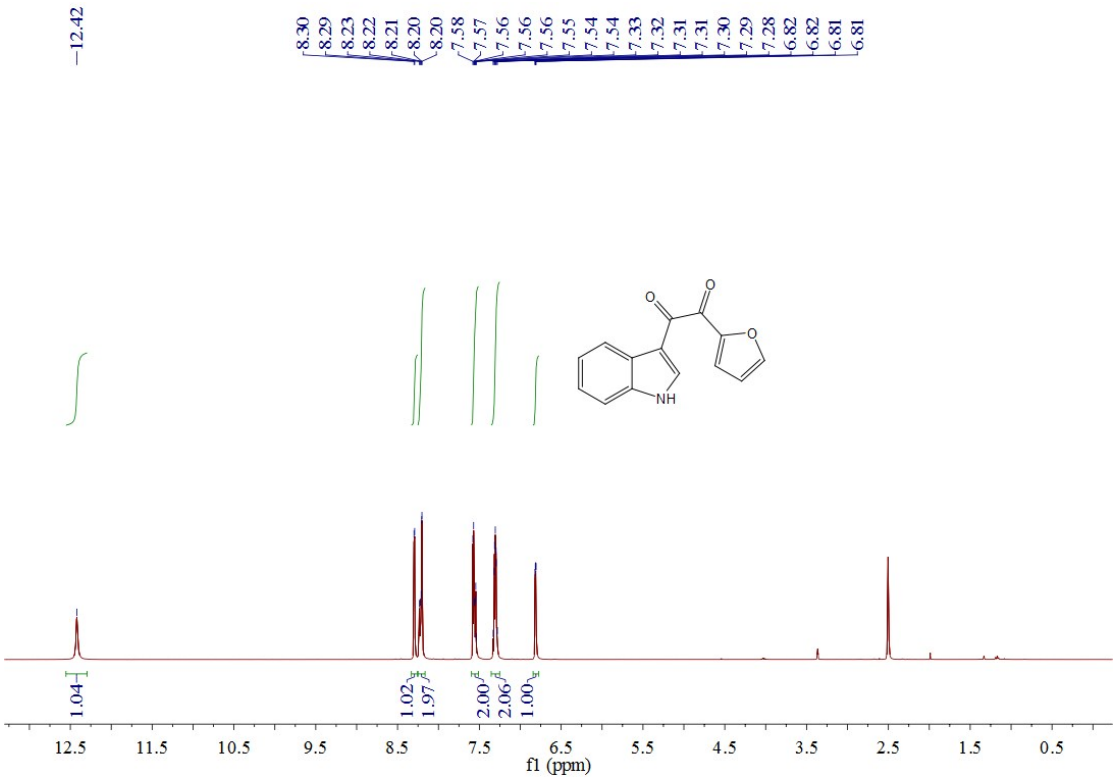
^{13}C NMR spectrum of **3ac** in DMSO at 297 K (δ in ppm).



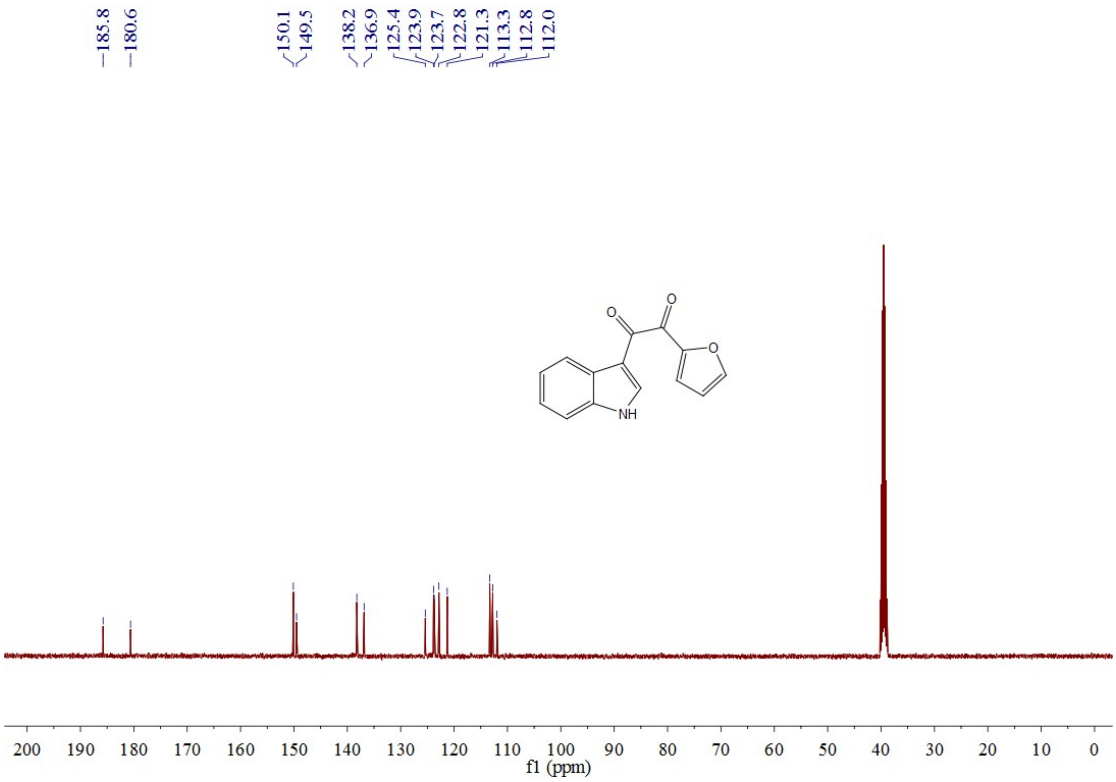
^{1}H NMR spectrum of **3ah** in DMSO at 297 K (δ in ppm).



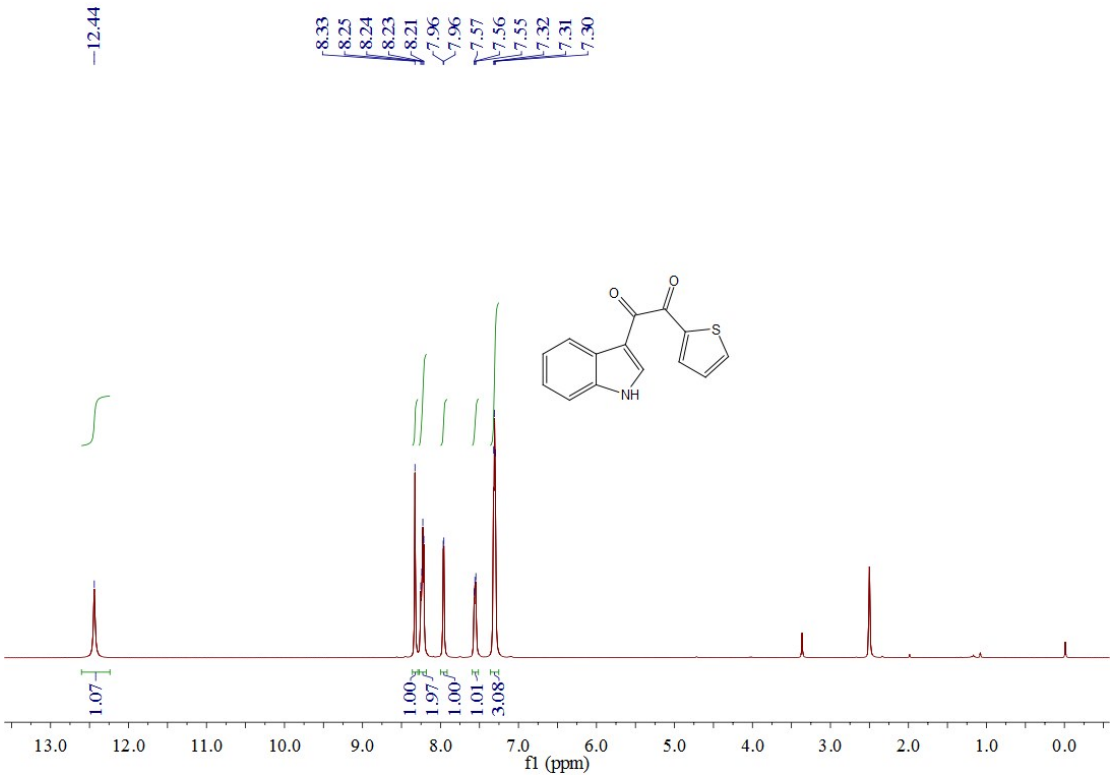
^{13}C NMR spectrum of **3ah** in DMSO at 297 K (δ in ppm).



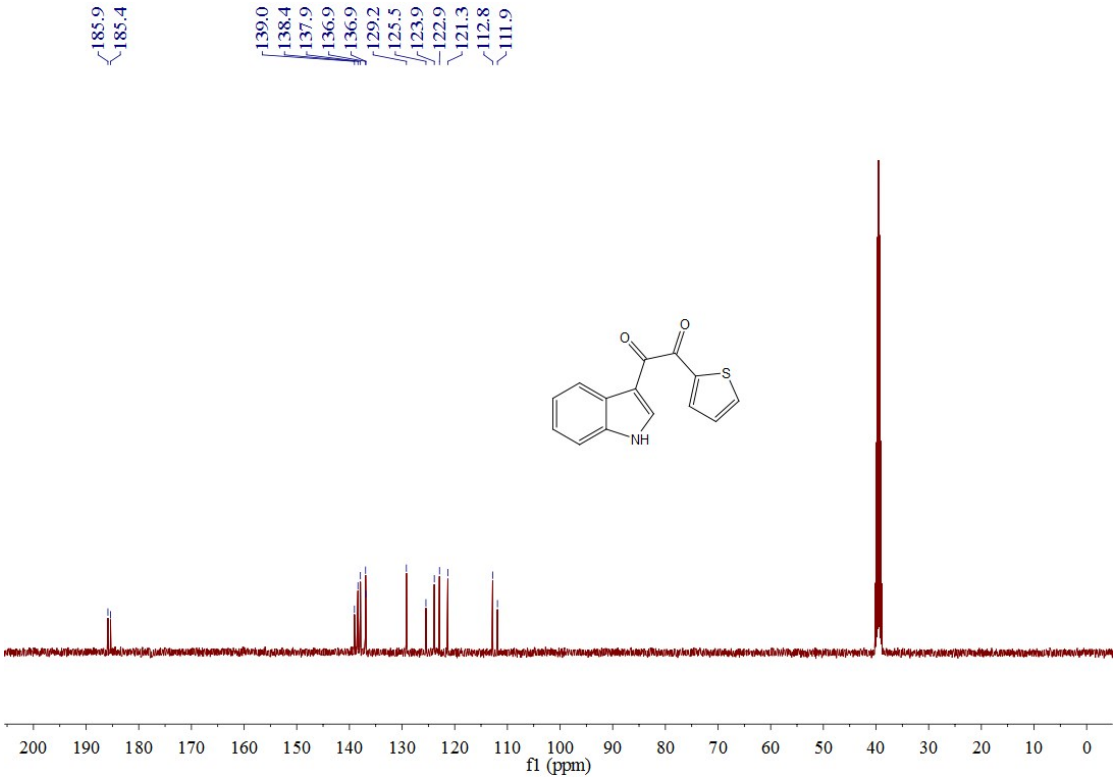
^{1}H NMR spectrum of **3ai** in DMSO at 297 K (δ in ppm).



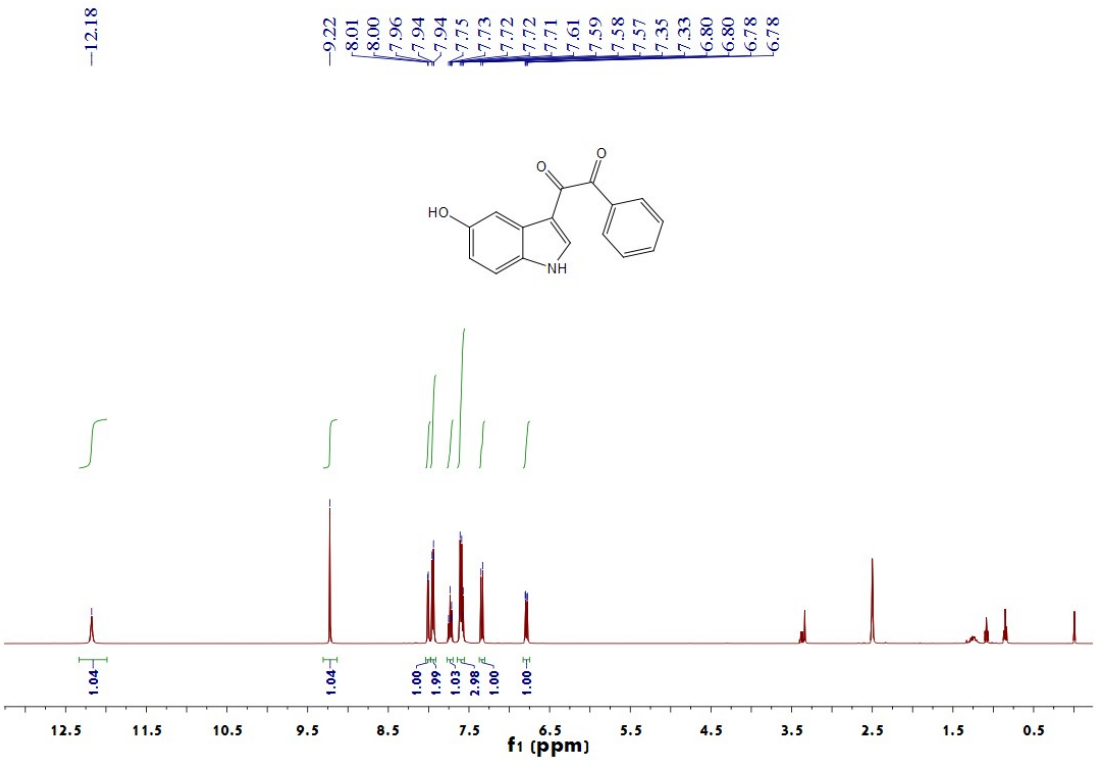
^{13}C NMR spectrum of **3ai** in DMSO at 297 K (δ in ppm).



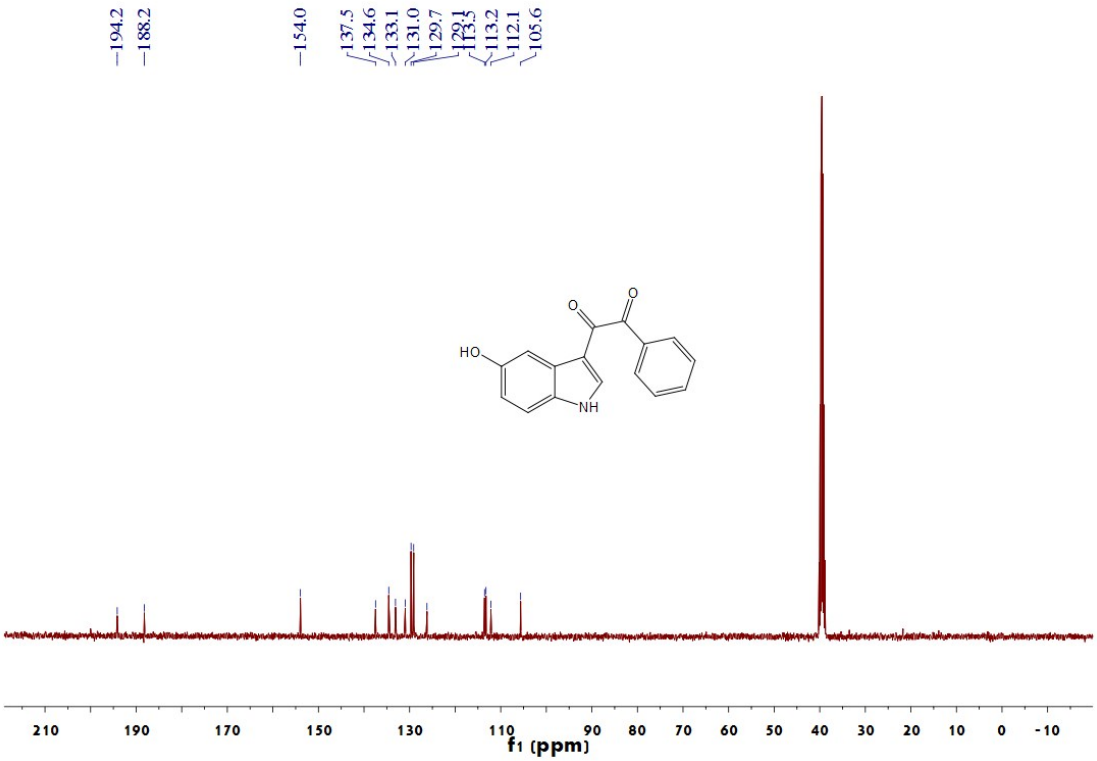
^{1}H NMR spectrum of **3aj** in DMSO at 297 K (δ in ppm).



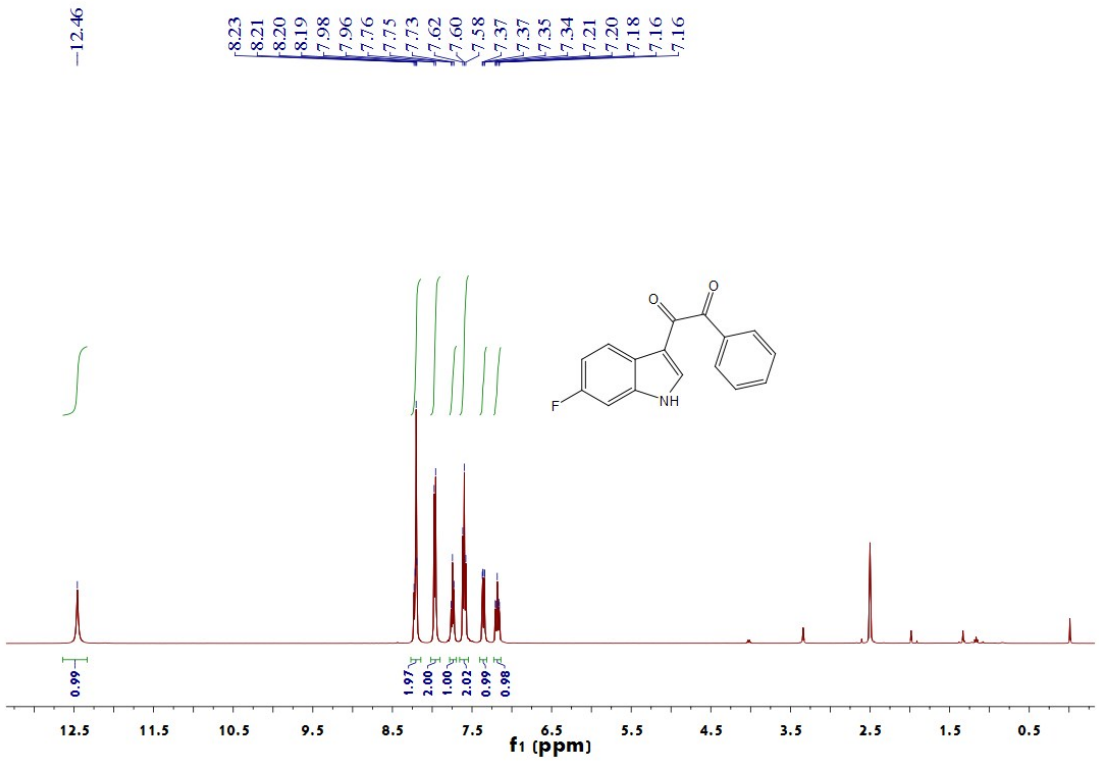
^{13}C NMR spectrum of **3aj** in DMSO at 297 K (δ in ppm).



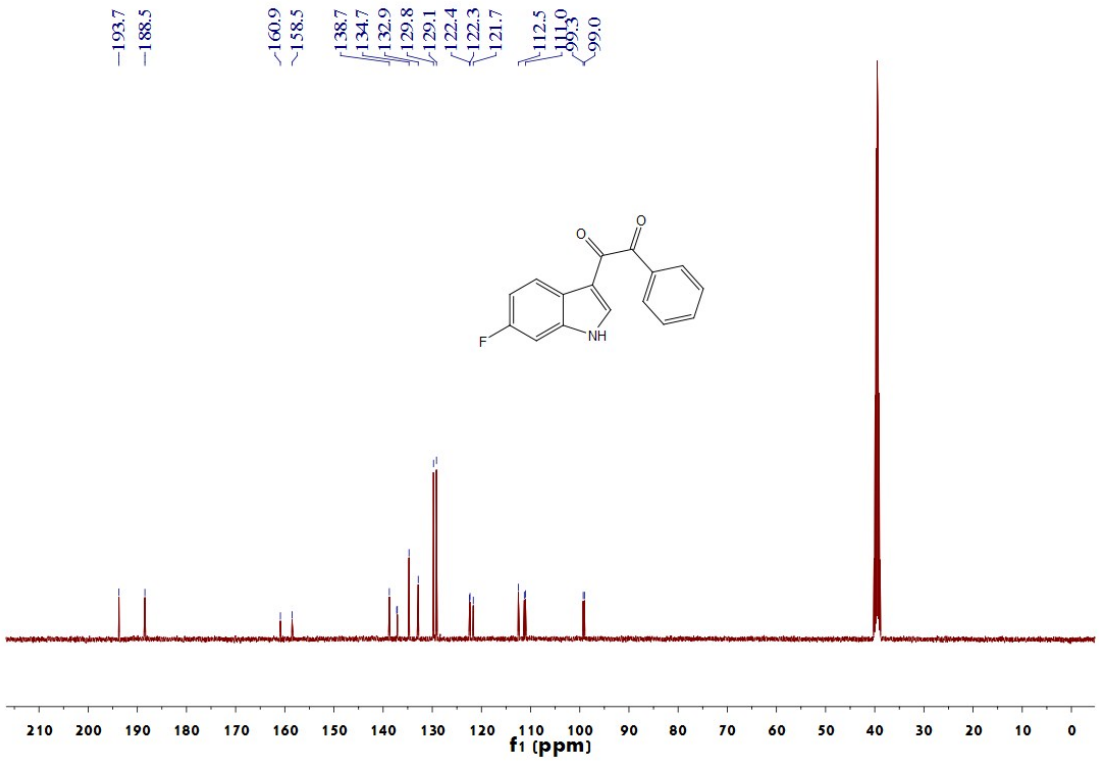
^{1}H NMR spectrum of **4ga** in DMSO at 297 K (δ in ppm).



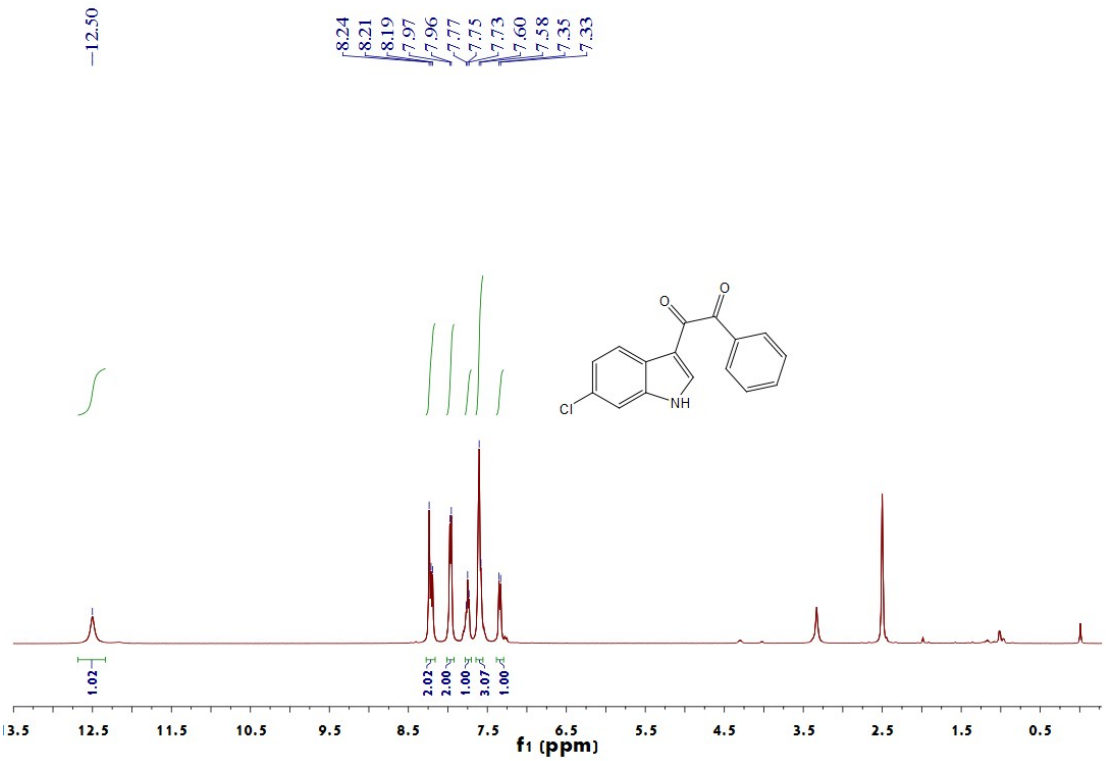
^{13}C NMR spectrum of **4ga** in DMSO at 297 K (δ in ppm).



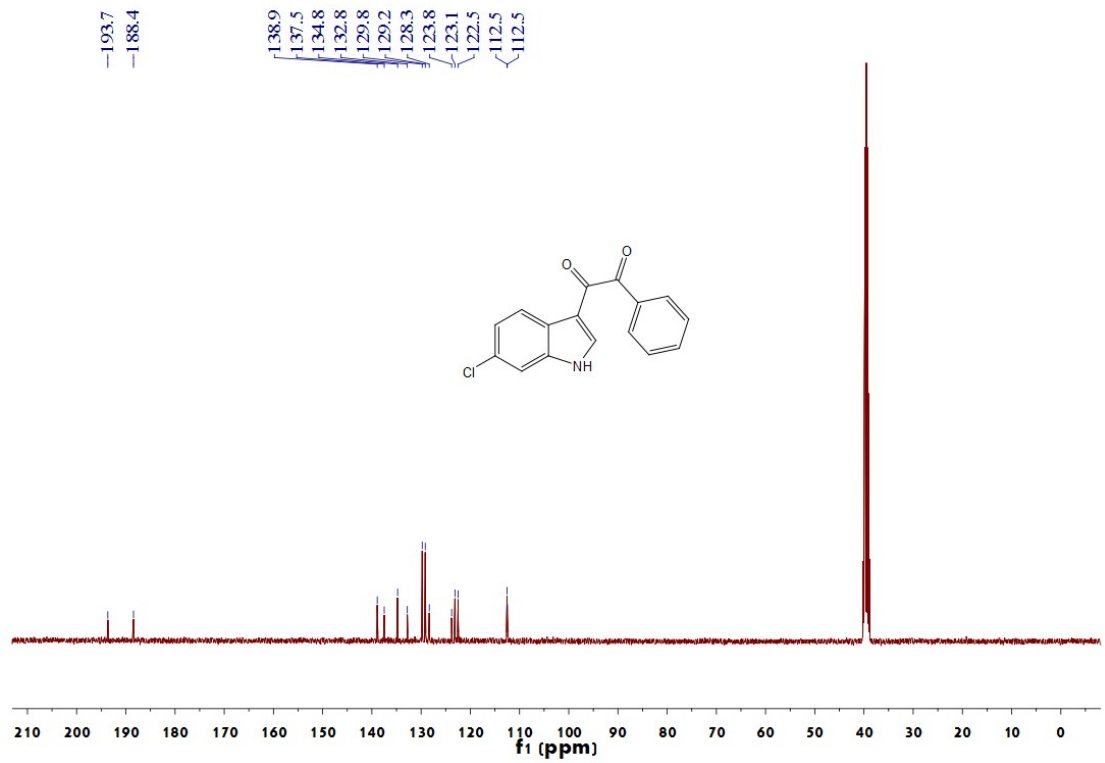
^{1}H NMR spectrum of **4ia** in DMSO at 297 K (δ in ppm).



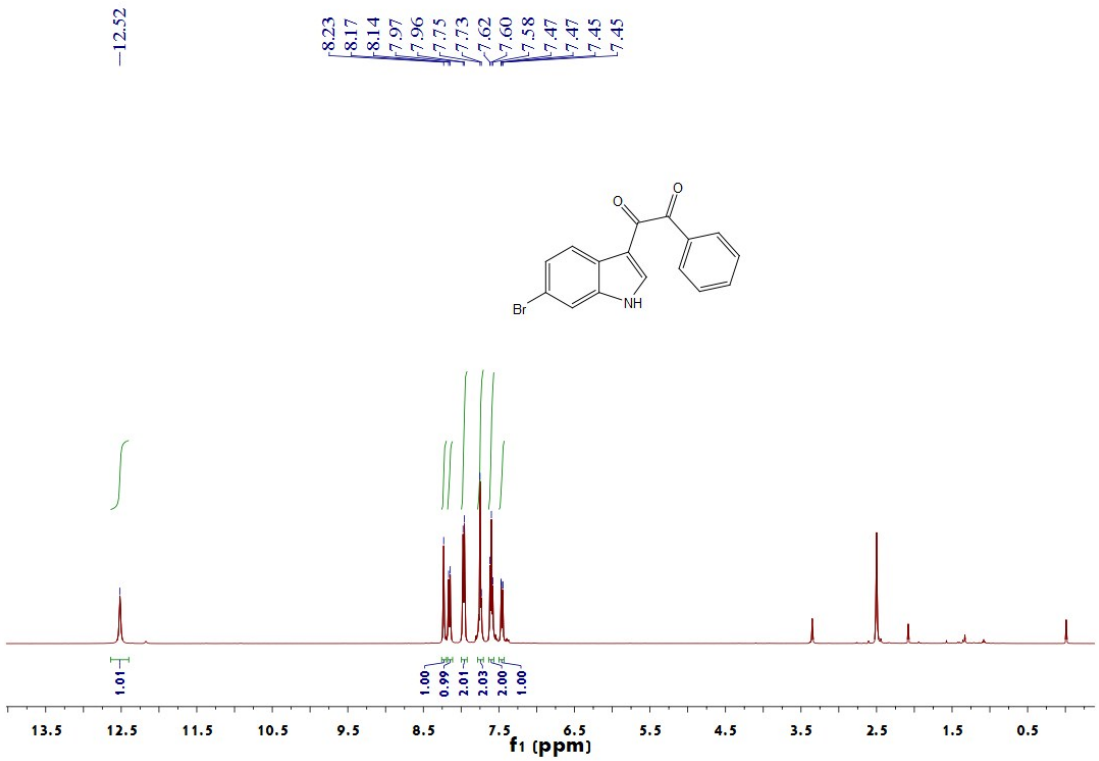
^{13}C NMR spectrum of **4ia** in DMSO at 297 K (δ in ppm).



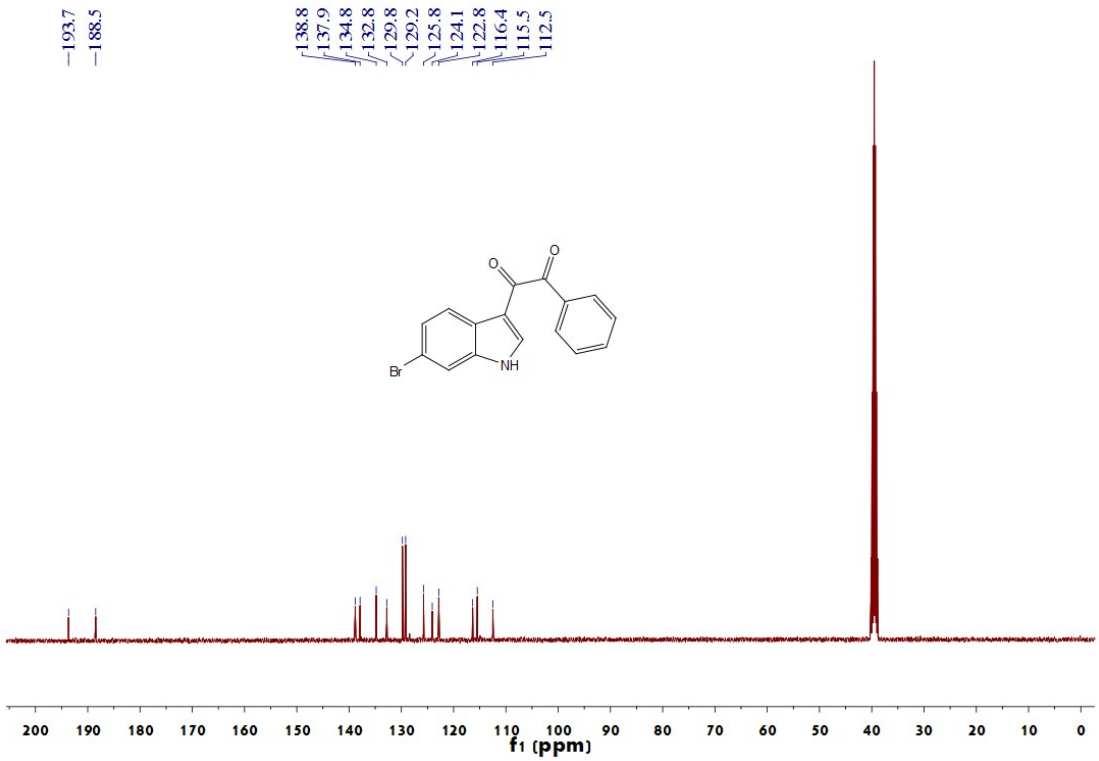
^{1}H NMR spectrum of **4ja** in DMSO at 297 K (δ in ppm).



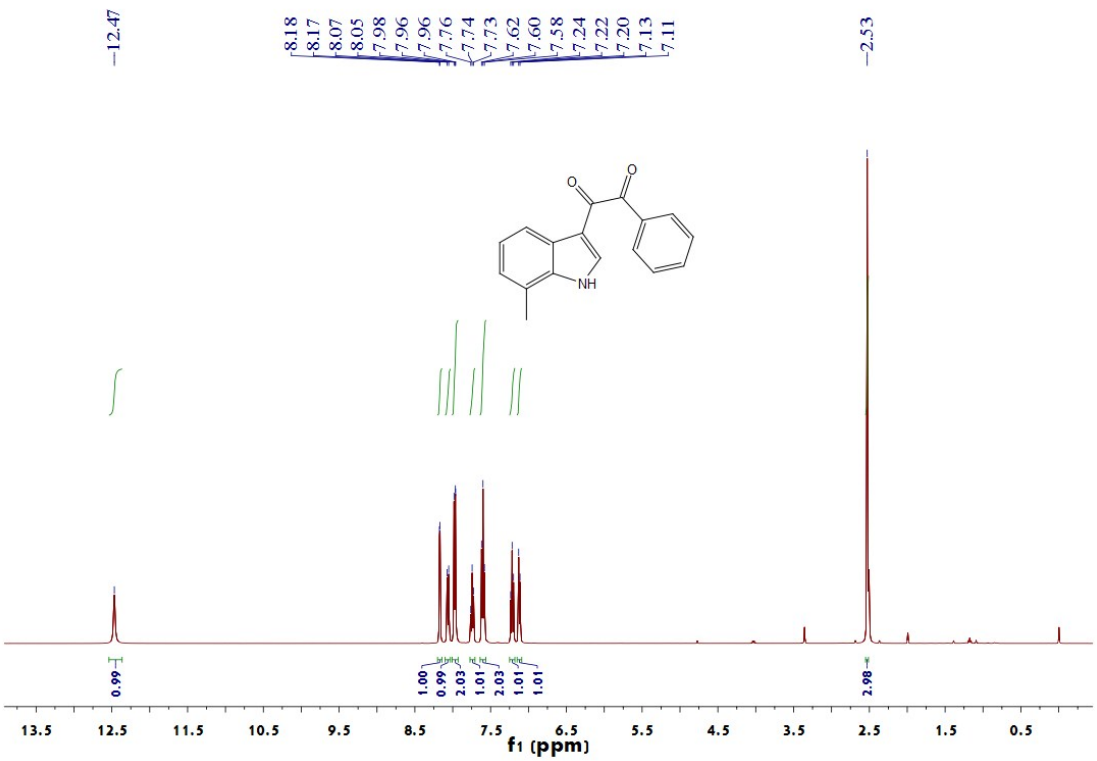
^{13}C NMR spectrum of **4ja** in DMSO at 297 K (δ in ppm).



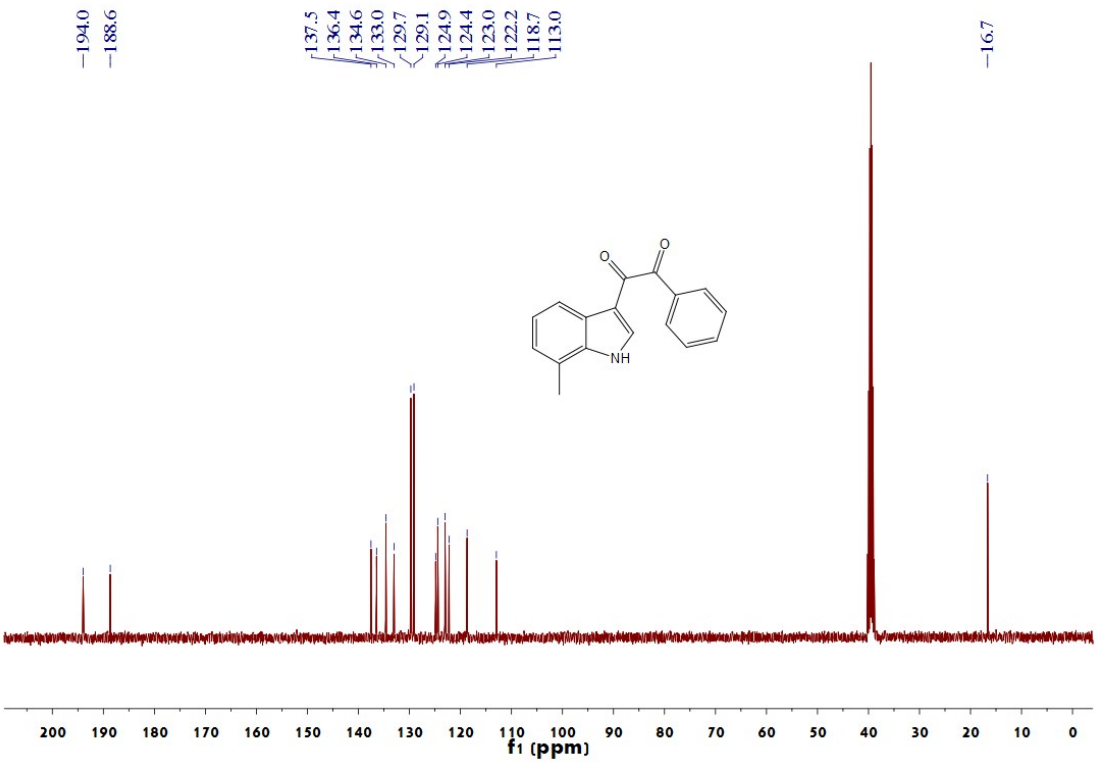
^{1}H NMR spectrum of **4ka** in DMSO at 297 K (δ in ppm).



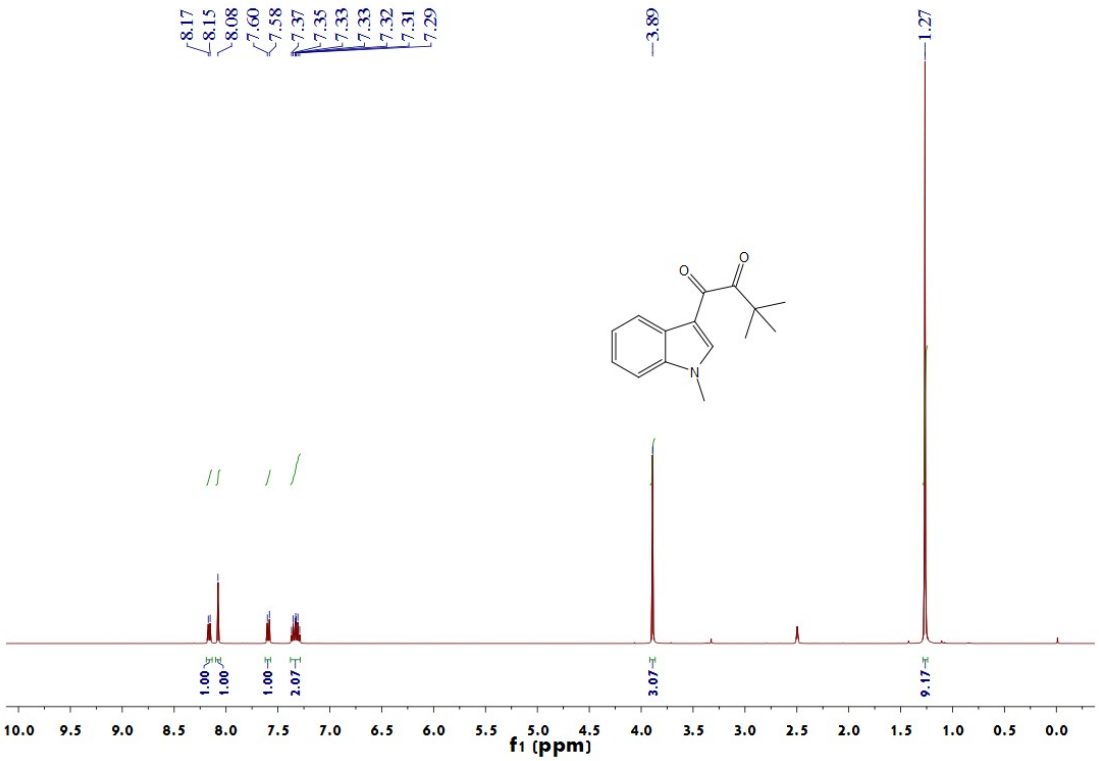
^{13}C NMR spectrum of **4ka** in DMSO at 297 K (δ in ppm).



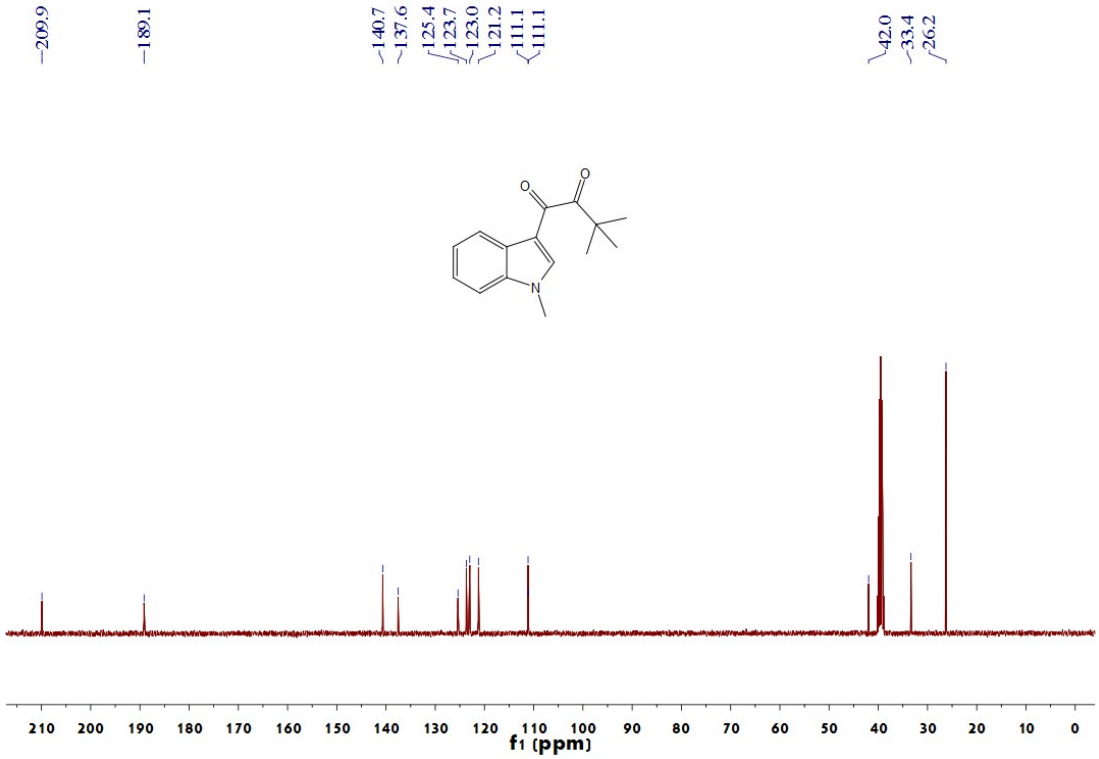
^{1}H NMR spectrum of **4la** in DMSO at 297 K (δ in ppm).



^{13}C NMR spectrum of **4la** in DMSO at 297 K (δ in ppm).



^{1}H NMR spectrum of **5** in DMSO at 297 K (δ in ppm).



^{13}C NMR spectrum of **5** in DMSO at 297 K (δ in ppm).