Supporting Information

TFA promoted (hetero) arylation/hydroxylation of quinoxaline-2-one derivatives with electron-rich aromatic compounds

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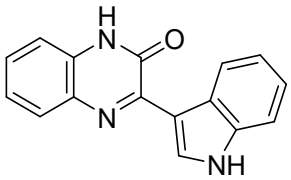
1. General methods: Unless stated otherwise, solvents and chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. With out purification to get the desired products. Melting points were recorded on a DBK digital melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 and 500 MHz Bruker Biospin A III FT-NMR spectrometer. ^{1}H and ^{13}C NMR spectra were determined in DMSO-d_6 solution by using 500/400 and 125/100 MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), dd (doublet of doublet), t (triplet) and m (multiplet). Coupling constants (*J*) are given in hertz. High-resolution mass spectra were recorded on a Bruker maxis-TOF mass spectrometer.

2,3-Dichloroquinoxaline (**1a**)[1] and 2,3-dichloro-6,7-dimethylquinoxaline (**1b**)[1] 1-allyl-1*H*-indole[2] (**2o**), 1-methyl-1*H*-indole[2] (**2j**) 1-benzyl-1*H*-indole (**2m**)[2,] 5-bromo-1-methyl-1H-indole (**2k**)[2], 1-ethyl-1*H*-indole (**2l**)[2] were synthesized using literature procedures. Commercially available 2,3-dichloropyrazine (**1c**), 4,6-dichloropyrimidine (**1d**), 2-methyl-1*H*-indole (**2l**), 2-phenyl-1*H*-indole (**2m**) were used without further purification.

2. General procedure for synthesis of hetero/aryl substituted quinoxalin-2-ones/ pyrazin -2(1*H*)-one/ pyrimidin-4(3*H*)-one (4/6):

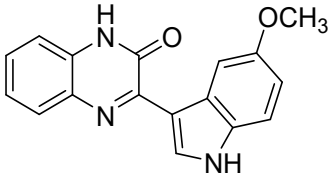
A mixture of quinoxaline (**1**, 1.0 equiv.), an appropriate aryl/hetero aryl substrate (**2**, 1.0 equiv.), and TFA (4 equiv.) was stirred at room temperature (25-27 ^{o}C) for 8 hours. In TFA, the reaction mixture initially appeared as a brown semi-solid. After 15 minutes of stirring, the appearance changed to dark brown slurry. This transition suggests that the reaction is progressing, forming products and altering the physical state of the mixture. The reaction progress was monitored by TLC. After the reaction was complete, the mixture was poured into 50 mL of ice-cold water with stirring. The aqueous layer was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate mixture to obtain the desired product (**4**).

3-(1*H*-Indol-3-yl)quinoxalin-2(1*H*)-one (4aa)



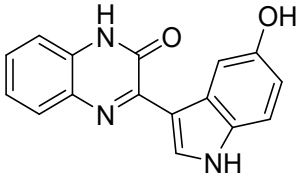
Brown solid; mp = 325 – 327 °C (Lit[3] 328.8 – 329.4 °C) °C; R_f= 0.3 (50% EA/PE) **^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.41 (s, 1H), 11.78 (s, 1H), 8.93 (d, J = 2.5 Hz, 1H), 8.87 (t, J = 4.3 Hz, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 3.7 Hz, 2H); **^{13}C NMR** (125 MHz, DMSO – d_6) δ 159.6, 157.2, 141.5, 138.3, 137.8, 135.3, 133.2, 132.8, 131.4, 128.4, 128.2, 127.8, 126.2, 120.1, 117.1, 116.5; **HR-MS: (ESI+) m/z** calculated for $[C_{16}H_{12}N_3O]^+$ = $[M + H]^+$ 262.0975, found 262.0974.

3-(5-Methoxy-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4ab)



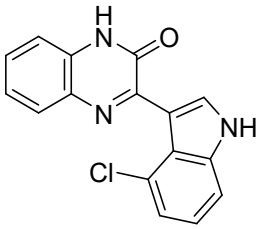
Brown solid; mp = 314.8 – 316.5 °C (Lit[3] 317.5 – 317.9 °C); R_f= 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.27 (s, 1H), 11.56 (s, 1H), 8.78 (s, 1H), 8.35 (s, 1H), 7.74 (s, 1H), 7.25 (d, J = 38.8 Hz, 2H), 7.00 (d, J = 12.4 Hz, 3H), 3.77 (s, 3H); **^{13}C NMR** (125 MHz, DMSO – d_6) δ 155.6, 155.3, 133.9, 133.1, 131.6, 130.5, 128.3, 128.0, 127.3, 126.0, 123.5, 115.6, 112.9, 112.5, 111.5, 105.5, 55.7.

3-(5-Hydroxy-1H-indol-3-yl)quinoxalin-2(1H)-one (4ac)



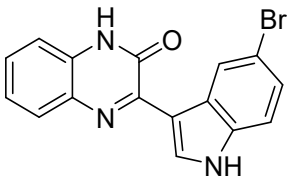
Brown solid; mp = 247 – 249 °C (Lit[3] 251.7 – 253.1 °C); R_f= 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.33 (s, 1H), 11.53 (s, 1H), 8.96 (s, 1H), 8.84 (s, 1H), 8.31 (s, 1H), 7.81 (d, J = 6.5 Hz, 1H), 7.40 (d, J = 6.5 Hz, 1H), 7.32 (s, 2H), 7.11 (d, J = 21.5 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 154.9, 152.9, 152.5, 133.7, 133.2, 130.9, 130.5, 128.1, 127.7, 126.0, 123.7, 115.4, 112.8, 112.6, 111.2, 108.2.

3-(4-Chloro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4ad)



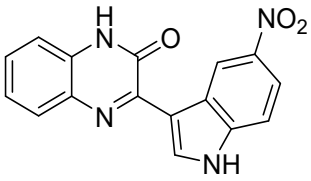
Yellow solid; mp = 268 – 270 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.41 (s, 1H), 11.89 (s, 1H), 7.97 (d, J = 2.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 8.8 Hz, 2H), 7.30 (dd, J = 15.2, 8.0 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 155.7, 153.9, 138.1, 132.5, 132.1, 130.3, 129.7, 128.7, 125.9, 124.3, 123.6, 123.0, 121.5, 115.5, 112.2, 111.5; **HR-MS:** (ESI+) m/z calculated for $[C_{16}H_{11}ClN_3O]^+$ = $[M + H]^+$ 296.0585, found 296.0584.

3-(5-Bromo-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4ae)



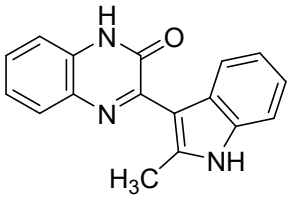
Yellow solid; mp = 268 – 270 °C (Lit[4] 265.4 – 266.7 °C); R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.46 (s, 1H), 11.96 (s, 1H), 8.98 (d, J = 20.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.35 (dd, J = 19.6, 9.2 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 158.4, 154.7, 140.2, 138.3, 136.4, 135.7, 134.6, 130.7, 128.8, 128.1, 125.5, 123.8, 116.1, 115.5, 114.4, 111.3; **HR-MS: (ESI+) m/z** calculated for $[C_{16}H_{11}BrN_3O]^+$ = $[M + H]^+$ 340.0080, found 340.0080.

3-(5-Nitro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4af)



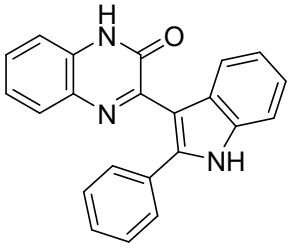
Orange solid; mp = 398 – 400 °C (Lit[4] 409.8 – 410.2 °C); R_f = 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 11.66 (s, 1H), 11.30 (s, 1H), 8.37 (s, 1H), 8.10 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.58 (s, 3H), 7.48 (d, J = 8.5 Hz, 1H); 13C NMR (100 MHz, DMSO – d6) δ 156.0, 155.6, 146.1, 140.6, 140.1, 140.0, 138.4, 128.4, 127.0, 126.1, 126.0, 122.3, 120.3, 116.9, 116.3, 112.4.

3-(2-Methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4ag)



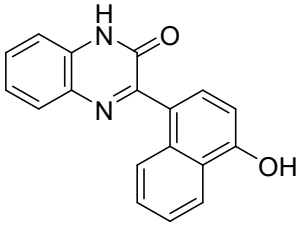
Brown solid; mp = 287 – 289 °C (Lit[3] 289.3 – 289.9 °C); R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.32 (s, 1H), 11.48 (s, 1H), 7.77 (dd, J = 13.6, 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.35– 7.27 (m, 3H), 7.09 – 7.00 (m, 2H), 2.56 (s, 3H).); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 155.1, 139.8, 135.6, 133.0, 131.7, 129.2, 128.4, 128.3, 123.6, 121.4, 121.3, 120.0, 115.4, 111.1 (2C), 109.67, 14.8; **HR-MS:** (ESI+) m/z calculated for $[C_{17}H_{14}N_3O]^+ = [M + H]^+$ 276.1132, found 276.1115.

3-(2-Phenyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4ah)



Brown solid; mp = 278 – 280 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.26 (s, 1H), 11.82 (s, 1H), 7.76 – 7.71 (m, 2H), 7.53 – 7.47 (m, 4H), 7.39 (t, J = 7.4 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.21 – 7.17 (m, 1H), 7.07 (d, J = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 155.7, 155.5, 154.5, 139.8, 136.5, 133.7, 132.9, 132.2, 129.9, 128.9, 128.7, 128.3, 128.1, 126.0, 123.6, 122.6, 120.6, 120.6, 115.6, 115.5, 112.0, 109.0; **HR-MS:** (ESI+) m/z calculated for $[C_{22}H_{16}N_3O]^+ = [M + H]^+$ 338.1288, found 338.1266.

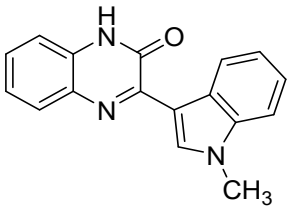
3-(4-Hydroxynaphthalen-1-yl)quinoxalin-2(1H)-one (4ai)



Off white solid; mp = 292 – 294 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.55 (s, 1H), 10.56 (s, 1H), 8.24 – 8.21 (m, 1H), 7.90 (dd, J = 7.2, 4.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H); 13C NMR (100 MHz, DMSO – d6) δ 158.5, 155.4, 155.1, 132.9, 132.6, 130.5, 129.6, 129.1, 126.9, 126.0, 125.0,

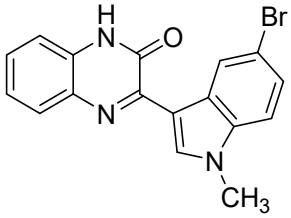
124.9, 124.7, 123.7, 123.5, 122.65 115.7, 107.5; **HR-MS:** (ESI+) m/z calculated for $[C_{18}H_{13}N_2O_2]^+ = [M + H]^+$ 289.0972, found 289.0968.

3-(1-Methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4aj)



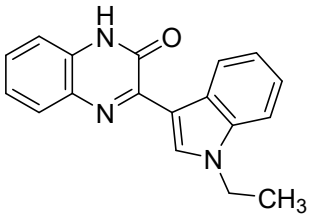
Yellow solid; mp = 287 – 289 °C (Lit[3] 290.1 – 292 °C); R_f = 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.45 (s, 1H), 8.94 (s, 1H), 8.90 (d, J = 7.5 Hz, 1H), 7.86 (dd, J = 9.0, 1.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.32 – 7.27 (m, 4H), 3.92 (s, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 154.8, 152.1, 137.3, 137.2, 133.1, 130.6, 128.4, 128.0, 127.1, 123.7, 123.6, 123.1, 121.7, 115.4, 110.7, 110.6, 33.4; **HR-MS**: **(ESI+) m/z** calculated for $[C_{17}H_{14}N_3O]^+ = [M + H]^+$ 276.1132, found 276.1131.

3-(5-Bromo-1-methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4ak)



Brown solid; mp = 320 – 322 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.51 (s, 1H), 8.98 (d, J = 28.4 Hz, 2H), 7.84 (d, J = 6.4 Hz, 1H), 7.57 – 7.32 (m, 5H), 3.92 (s, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 154.4, 151.5, 138.0, 135.8, 132.6, 130.4, 128.5, 128.4, 127.8, 125.3 (2C), 123.6, 115.2, 114.4, 112.6, 109.9, 33.4; **HR-MS:** (ESI+) m/z calculated for $[C_{17}H_{13}BrN_3O]^+ = [M + H]^+$ 354.0237, found 354.0236.

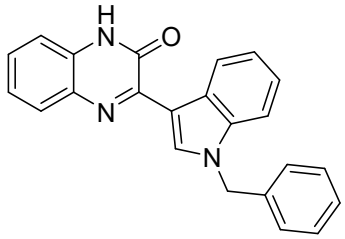
3-(1-Ethyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4al)



Yellow solid; mp = 280 – 282 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.45 (s, 1H), 8.98 (s, 1H), 8.91 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.41 – 7.31 (m, 4H), 4.35 (dd, J = 13.6, 6.4 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 154.8, 152.1, 136.2, 135.7, 133.1,

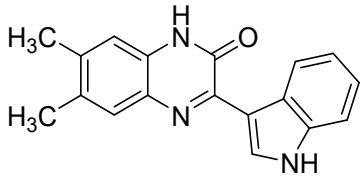
130.6, 128.4, 128.0, 127.3, 123.7, 123.6, 123.0, 121.7, 115.4, 110.9, 110.6, 41.4, 15.8; **HR-MS:** (ESI+) m/z calculated for $[C_{18}H_{16}N_3O]^+ = [M + H]^+$ 290.1288, found 290.1285.

3-(1-Benzyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4am)



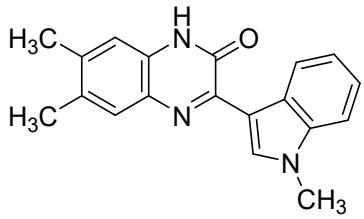
Off white solid[5]; mp = 290 – 292 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.46 (s, 1H), 9.09 (s, 1H), 8.93 (dd, J = 6.5, 1.5 Hz, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.45 – 7.41 (m, 1H), 7.34 – 7.24 (m, 9H), 5.57 (s, 2H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 154.8, 152.1, 138.0, 136.7, 136.6, 133.1, 130.7, 129.1 (2C), 128.6, 128.1, 128.1, 127.6 (3C), 127.4, 123.8, 123.3, 121.9, 115.5, 111.4, 111.1, 50.0.

3-(1*H*-Indol-3-yl)-6,7-dimethylquinoxalin-2(1*H*)-one (4ba)



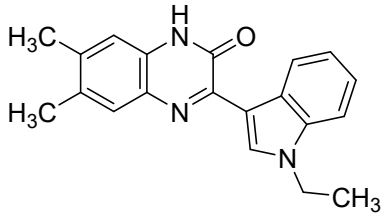
Brown solid; mp = 330 – 332 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.24 (s, 1H), 11.70 (s, 1H), 8.90 – 8.87 (m, 2H), 7.64 (s, 1H), 7.50 (d, J = 5.5 Hz, 1H), 7.23 – 7.21 (m, 2H), 7.06 (s, 1H), 2.30 (s, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 155.6, 154.9, 151.4, 137.7, 136.7, 132.9, 131.6, 128.6, 128.1, 126.6, 123.8, 122.9, 121.2, 116.1, 115.5, 112.2, 19.4 (2C).

6,7-Dimethyl-3-(1-methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (4bj)



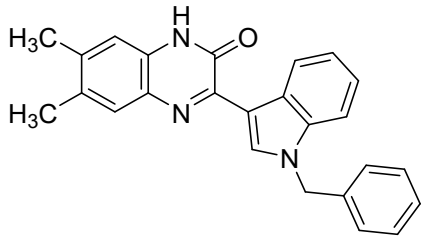
Brown solid; mp = 288 – 290 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 11.77 (s, 1H), 8.87 (s, 1H), 7.64 (s, 1H), 7.31 – 7.24 (m, 2H),7.07 (s, 1H), 6.88 (s, 2H), 3.90 (s, 3H), 2.16 (s, 6H); **^{13}C NMR** (125 MHz, DMSO – d_6) δ 155.6, 154.8, 137.2, 136.6, 132.2, 131.5, 128.5, 128.0, 127.1, 123.7, 123.5, 122.9, 121.5, 116.1, 115.4, 110.5, 33.4, 20.1, 19.4; **HR-MS:** (ESI+) m/z calculated for $[C_{19}H_{18}N_3O]^+ = [M + H]^+$ 304.1444, found 304.1441.

3-(1-Ethyl-1*H*-indol-3-yl)-6,7-dimethylquinoxalin-2(*1H*)-one (4bl)



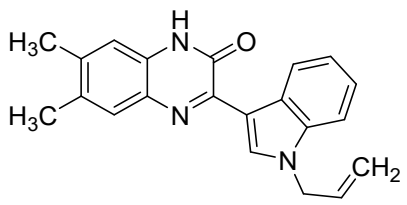
Brown solid; mp = 280 – 282 °C; R_f= 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.33 (s, 1H), 8.91 (d, J = 12.8 Hz, 2H), 7.63 (d, J = 22.4 Hz, 2H), 7.27 (s, 2H), 7.07 (s, 1H), 4.35 (s, 2H), 2.32 (s, 6H), 1.42 (s, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 154.9, 151.1, 137.8, 136.2, 135.2]2, 132.2, 131.6, 128.6, 128.1, 127.3, 123.8, 123.0, 121.5, 115.5, 111.1, 110.6, 41.3, 20.2, 19.5, 15.8; **HR-MS:** (ESI+) m/z calculated for $[C_{20}H_{20}N_3O]^+$ = $[M + H]^+$ 318.1601, found 318.1597.

3-(1-Benzyl-1*H*-indol-3-yl)-6,7-dimethylquinoxalin-2(1*H*)-one (4bm)



Yellow solid; mp = 295 – 297 °C; R_f= 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.33 (s, 1H), 9.04 (s, 1H), 8.92 – 8.90 (m, 1H), 7.67 (s, 1H), 7.57 – 7.54 (m, 1H), 7.35 – 7.31 (m, 2H), 7.27 – 7.23 (m, 5H), 7.08 (s, 1H), 5.58 (s, 2H), 2.32 (d, J = 3.2 Hz, 6H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 153.4, 150.6, 137.3, 136.4, 136.3, 136.2, 132.8, 132.5, 130.0, 129.1, 128.6 (2C), 128.3, 128.1, 127.6, 127.3, 127.0, 123.5, 123.2, 122.8, 121.5, 114.9, 111.0, 110.7, 49.5; **HR-MS:** (ESI+) m/z calculated for $[C_{25}H_{22}N_3O]^+$ = $[M + H]^+$ 380.1757, found 380.1751.

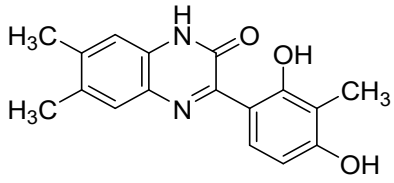
3-(1-Allyl-1*H*-indol-3-yl)-6,7-dimethylquinoxalin-2(1*H*)-one (4bp)



Brown solid; mp = 279 – 281 °C; R_f= 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.31 (s, 1H), 8.90 (s, 2H), 7.65 (s, 1H), 7.54 (d, J = 6.5 Hz, 1H), 7.27 (s, 2H), 7.08 (s, 1H),

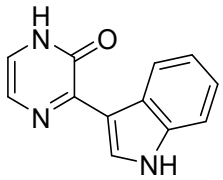
6.09 – 6.03 (m, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 5.13 (d, *J* = 16.5 Hz, 1H), 4.96 (s, 2H), 2.32 (s, 6H); **^{13}C NMR** (100 MHz, DMSO – d_6) 154.8, 151.0, 137.9, 136.6, 135.8, 134.4, 132.3, 131.5, 128.6, 128.1, 127.2, 123.7, 123.0, 121.6, 117.8, 115.5, 111.3, 110.9, 48.9, 20.1, 19.5;.**HR-MS:** (ESI+) m/z calculated for $[C_{21}H_{20}N_3O]^+$ = $[M + H]^+$ 330.1601, found 330.1597.

3-(2,4-Dihydroxy-3-methylphenyl)-6,7-dimethylquinoxalin-2(1*H*)-one (4bq)



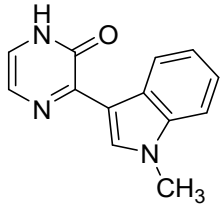
Yellow solid; mp = 283 – 285 ^{o}C; R_f= 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 14.74 (s, 1H), 12.53 (s, 1H), 10.00 (s, 1H), 8.92 (d, *J* = 9.2 Hz, 1H), 7.55 (s, 1H), 7.07 (s, 1H), 6.42 (d, *J* = 9.2 Hz, 1H), 2.29 (d, *J* = 6.4 Hz, 6H), 2.04 (s, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 161.0, 159.3, 154.9, 152.3, 138.9, 132.5, 129.3, 129.1, 127.4, 125.9, 115.0, 110.3, 110.1, 106.1, 19.7, 19.0, 8.3; **HR-MS:** (ESI+) m/z calculated for $[C_{17}H_{17}N_2O_3]^+$ = $[M + H]^+$ 297.1234, found 297.1231.

3-(1*H*-Indol-3-yl)pyrazin-2(1*H*)-one (4ca)



Brown solid; mp = 260 – 262 ^{o}C; R_f= 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.16 (s, 1H), 11.57 (s, 1H), 8.78 (d, *J* = 2.0 Hz, 1H), 8.60 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 16.8, 7.6 Hz, 2H), 7.20 – 7.13 (m, 3H); **^{13}C NMR** (125 MHz, DMSO – d_6) δ 155.2, 152.1, 136.6, 131.4, 126.4, 123.2, 123.1, 122.6, 121.8, 120.8, 112.1, 112.1; **HR-MS:** (ESI+) m/z calculated for $[C_{12}H_{10}N_3O]^+$ = $[M + H]^+$ 212.0819, found 212.0818.

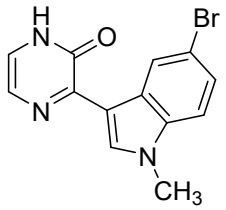
3-(1-Methyl-1*H*-indol-3-yl)pyrazin-2(1*H*)-one (4cj)



Off white solid; mp = 265 – 267 ^{o}C; R_f= 0.3 (50% EA/PE**); ^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.19 (s, 1H), 8.77 (s, 1H), 8.62 (d, *J* = 10.0 Hz, 1H), 7.51 (d, *J* = 10.5 Hz, 1H), 7.42 (d,

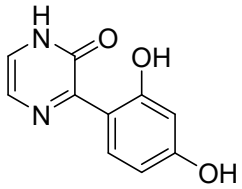
J = 5.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.20 – 7.16 (m, 2H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 155.1, 151.8, 137.2, 135.3, 126.8, 123.3 (2C), 122.8, 121.9, 121.2, 111.2, 110.4, 33.3; **HR-MS: (ESI+) m/z** calculated for $[C_{13}H_{12}N_3O]^+$ = $[M + H]^+$ 226.0975, found 226.0960.

3-(5-Bromo-1-methyl-1*H*-indol-3-yl)pyrazin-2(1*H*)-one (4ck)



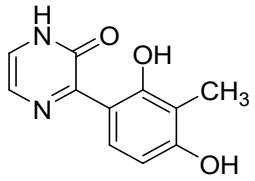
Brown solid; mp = 290 – 292 °C; R_f = 0.3 (50% EA/PE)**; ^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.27 (s, 1H), 8.78 (s, 2H), 7.52 (d, *J* = 10.5 Hz, 1H), 7.47 (d, *J* = 4.5 Hz, 1H), 7.39 (d, *J* = 10.5 Hz, 1H), 7.22 (d, *J* = 4.5 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 155.1, 151.3, 136.4, 136.0, 128.4, 125.2 (2C), 123.3, 122.5, 114.1, 112.7, 110.7, 33.5; **HR-MS:** (ESI+) m/z calculated for $[C_{13}H_{11}BrN_3O]^+$ = $[M + H]^+$ 304.0080, found 304.0057.

3-(2,4-Dihydroxyphenyl)pyrazin-2(1*H*)-one (4cr)



Yellow solid; mp = 275 – 277 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 13.91 (s, 1H), 12.59 (s, 1H), 9.96 (s, 1H), 8.88 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 11.2 Hz, 2H), 6.31 (d, J = 8.0 Hz, 1H), 6.26 (s, 1H); 13C NMR (100 MHz, DMSO – d6) δ 162.0, 160.9, 155.3, 152.3, 131.7, 125.0, 119.7, 110.9, 106.7, 103.0; HR-MS: (ESI+) m/z calculated for [C10H9N2O3]+ = [M + H]+ 205.0608, found 205.0612.

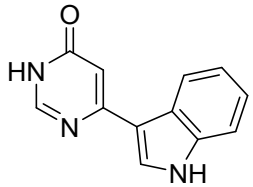
3-(2,4-Dihydroxy-3-methylphenyl)pyrazin-2(1*H*)-one (4cq)



Light yellow solid; mp = 272 – 274 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 14.32 (s, 1H), 12.54 (s, 1H), 9.87 (s, 1H), 8.80 (d, J = 9.2 Hz, 1H), 7.36 (dd, J = 11.2, 3.6 Hz, 2H), 6.38 (d, J = 9.2 Hz, 1H), 2.00 (s, 3H); 13C NMR (100 MHz, DMSO – d6) δ

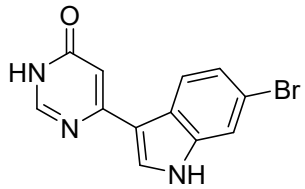
160.5, 159.2, 156.7, 155.9, 153.0, 128.8, 125.3, 119.8, 110.7, 106.2, 8.7; **HR-MS:** (ESI+) m/z calculated for $[C_{11}H_{11}N_2O_3]^+ = [M + H]^+$ 219.0764, found 219.0761.

6-(1*H*-Indol-3-yl)pyrimidin-4(3*H*)-one (6ca)



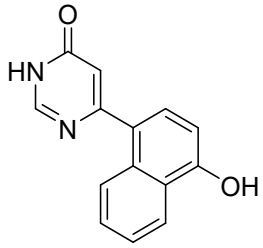
Black solid; mp = 254 – 256 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) δ 12.21 (s, 1H), 11.78 (s, 1H), 8.18 – 8.16 (m, 3H), 7.47 (s, 1H), 7.17 (s, 2H), 6.66 (s, 1H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 162.1, 160.0, 149.7, 137.7, 129.2, 125.2, 122.4, 121.3, 121.1, 113.3, 112.7, 106.1; **HR-MS:** (ESI+) m/z calculated for $[C_{12}H_{10}N_3O]^+ = [M + H]^+$ 212.0818, found 212.0817.

6-(6-Bromo-1*H*-indol-3-yl)pyrimidin-4(3*H*)-one (6ce)



Orange solid; mp = 277 – 279 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (500 MHz, DMSO – d_6) 12.24 (s, 1H), 11.87 (s, 1H), 8.20 – 8.18 (m, 3H), 7.65 (d, J = 2.0 Hz, 1H), 7.27 (dd, J = 8.5, 2.0 Hz, 1H), 6.67 (s, 1H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 162.0, 159.6, 149.9, 138.5, 129.8, 124.4, 123.8, 123.3, 115.1, 115.0, 113.5, 106.6; **HR-MS:** (ESI+) m/z calculated for $[C_{12}H_9BrN_3O]^+ = [M + H]^+$ 289.9924, found 289.9920.

6-(4-Hydroxynaphthalen-1-yl)pyrimidin-4(3H)-one (6ci)

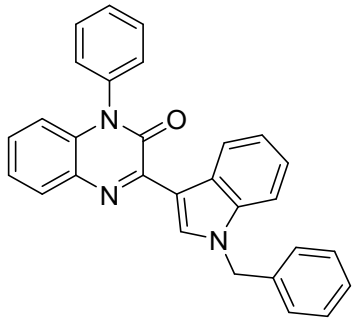


Brown solid; mp = 248 – 250 °C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 12.57 (s, 1H), 10.60 (s, 1H), 8.29 – 8.21 (m, 3H), 7.50 (s, 3H), 6.94 (s, 1H), 6.46 (s, 1H)**; ^{13}C NMR** (100 MHz, DMSO – d_6) δ 165.0, 162.0, 155.3, 149.7, 131.9, 129.0, 127.2, 126.9,

125.8, 125.3, 125.1, 122.8, 114.5, 107.9**; HR-MS:** (ESI+) m/z calculated for $[C_{14}H_{11}N_2O_2]^+$ = $[M + H]^+$ 239.0815, found 239.0812.

3. Procedure for the synthesis of 3-(1-Benzyl-1*H*-indol-3-yl)-1-phenylquinoxalin-2(1*H*)-one (8):

A mixture of the substituted 3-(1-Benzyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (**4am**) (0.284 mmol), aryl boronic acid (**7**) (0.426 mmol), anhydrous $Cu(OAc)_2$ (0.284 mmol) and Et_3N (0.568 mmol) in 1,2-dichloroethane (5 mL) was stirred at ambient temperature for 4 h. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered through celite. The filtrate was concentrated under vacuum, and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate to afford the desired product.



Brown solid; mp = 255 – 257 ˚C; R_f = 0.3 (50% EA/PE); **^{1}H NMR** (400 MHz, DMSO – d_6) δ 8.98 (s, 2H), 7.98 (d, J = 6.8 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.48 (d, J = 7.6 Hz, 2H), 7.37 – 7.28 (m, 9H), 6.54 (d, J = 8.4 Hz, 1H), 5.55 (s, 2H); **^{13}C NMR** (100 MHz, DMSO – d_6) δ 154.3, 150.6, 137.7, 137.5, 136.1, 135.6, 131.8, 131.0, 128.6 (2C), 128.2, 127.7, 127.5, 127.1 (2C), 126.9, 123.3, 122.6, 121.2, 115.0, 111.0, 110.6, 49.4, 19.7, 19.0; **HR-MS:** (ESI+) m/z calculated for $[C_{29}H_{22}N_3O]^+$ = $[M + H]^+$ 428.1757, found 428.1751.

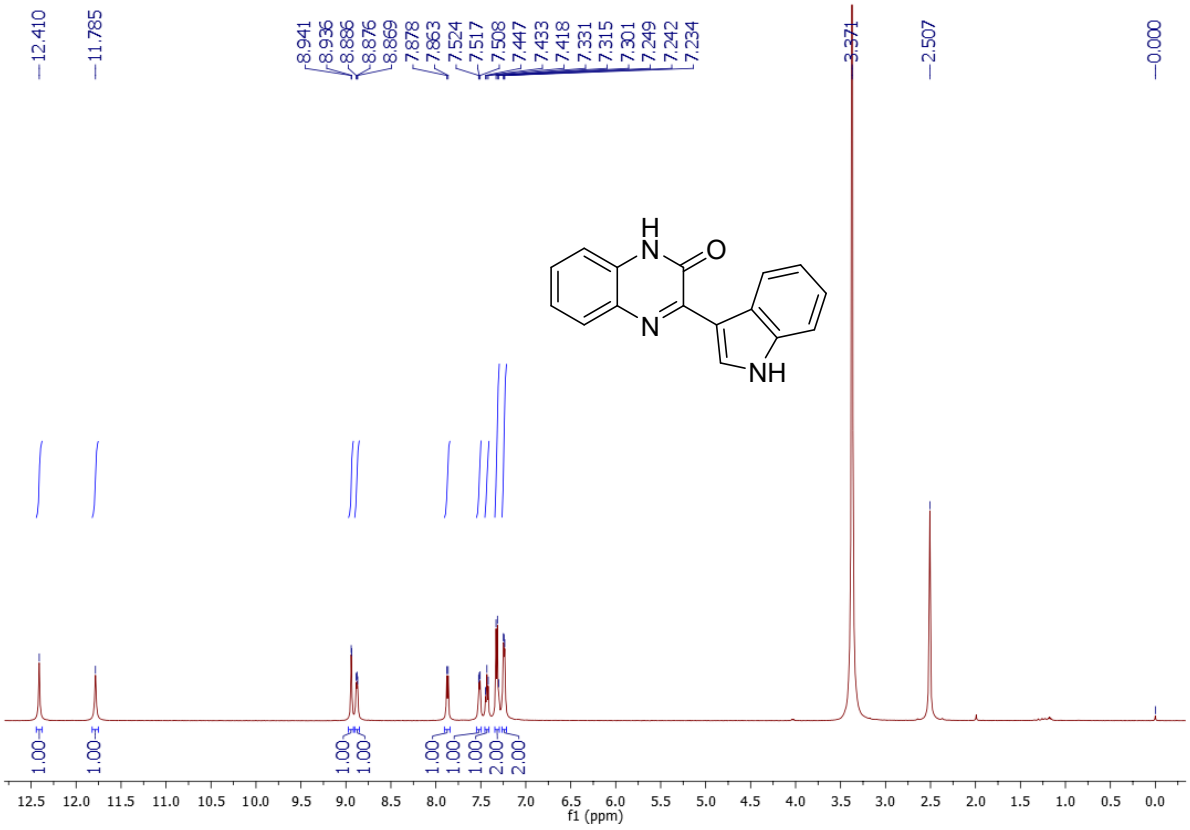
4. References:

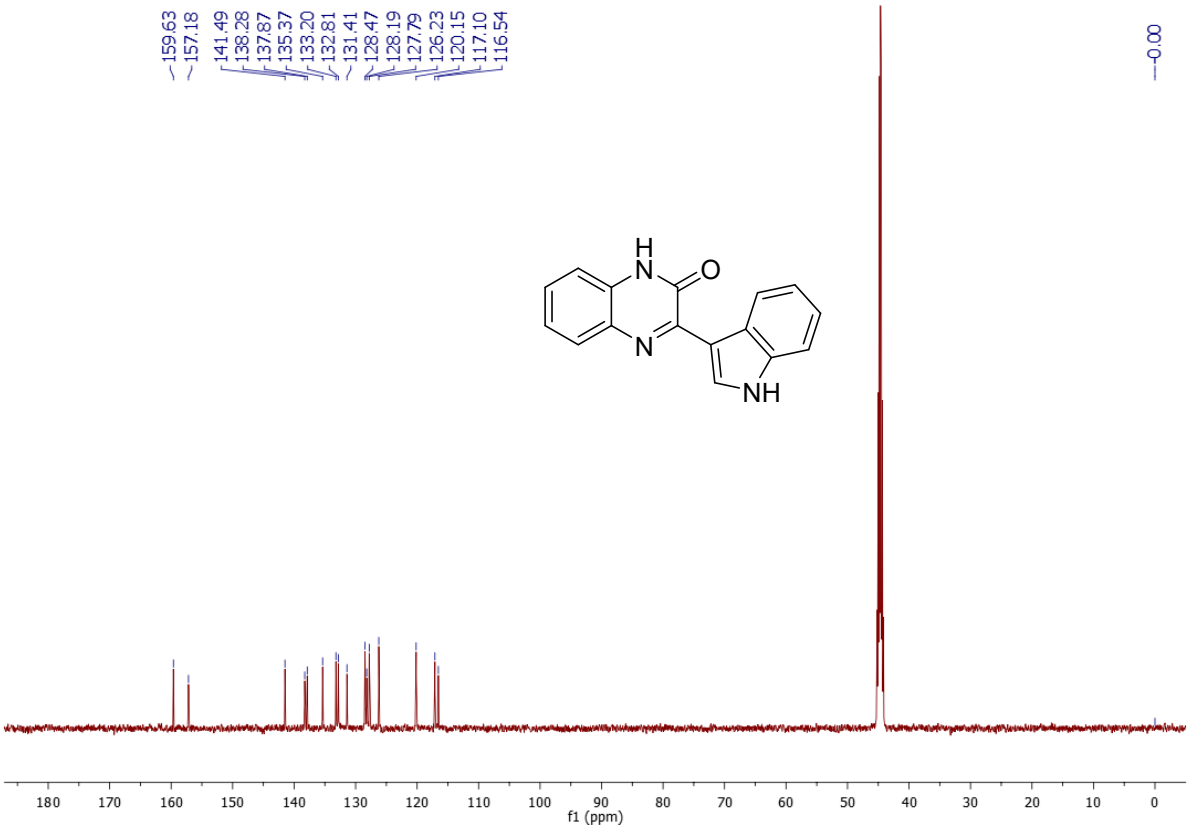
1. A. P. Komin and M. Carmack, *J. Heterocycl. Chem*. **1976**, *13*, 13-22.
2. Zhang, L.; Peng, C.; Zhao, D.; Wang, Y.; Fu, H. -J.; Shen ; Li, J. -X. *Chem. Commun*. **2012**, 4i8, 5928. (b) Su, Y. M.; Hou, Y.; Yin, F.; Xu, Y. M.; X. Y. Li,; Zheng, Q.; Wang. X. S. *Org. Lett*. **2014**, *16*, 2958. (c) Lajarín-Cuesta, R.; Nanclares, C.; ArranzTagarro, J. A.; González-Lafuente, L.; Arribas, R. L,; Araujo de Brito, M.; Gandía, L.; de los Ríos, C. Gramine. *J. Med. Chem*. **2016**, *59*, 6265. (d) Nguyen, T. B.; Corbin, M.; Retailleau, P.; Ermolenko, L.; Al-Mourabit, A. *Org. Lett.* **2015**, *17*,

4956. (e) Kannaboina, P.; Anilkumar, K.; Aravind, S.; Vishwakarma, R. A.; Das, P. *Org. Lett*., **2013**, 1i5, 5718.

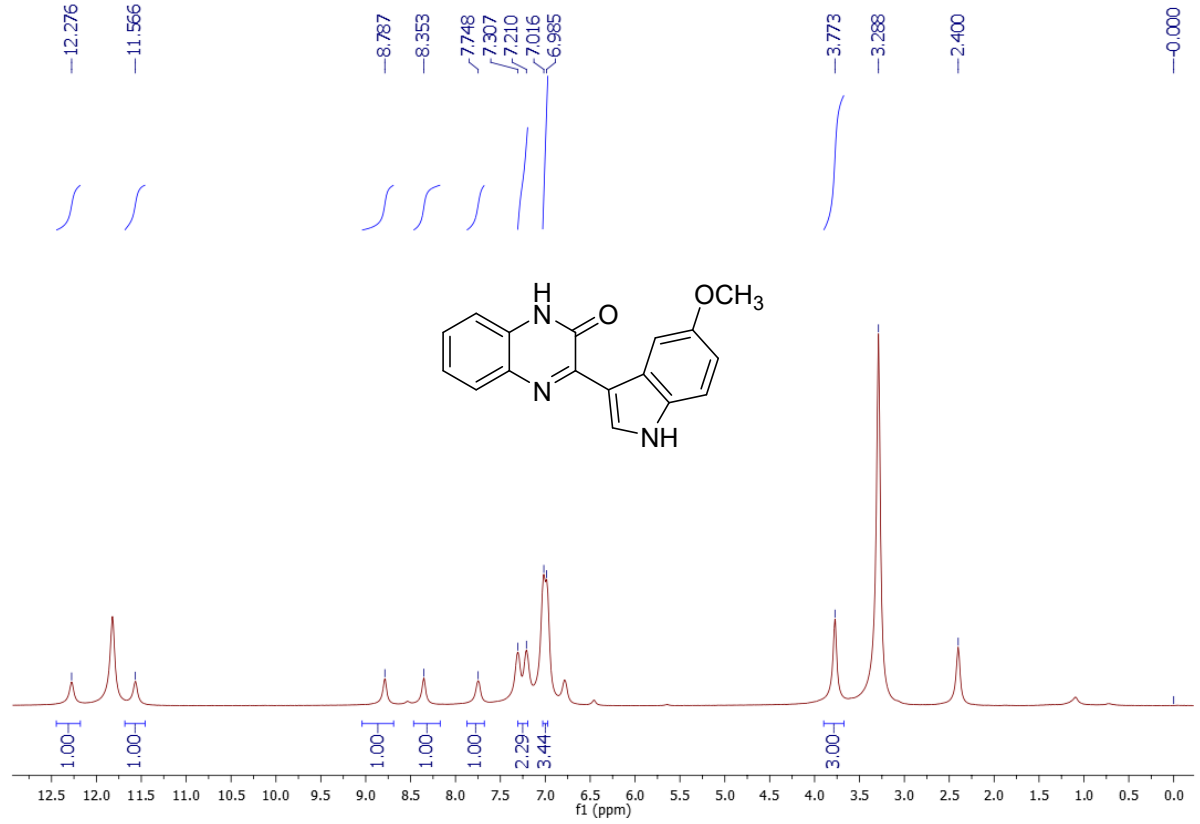
3. M. Noikham, T. Kittikool, S. Yotphan, *Synthesis.* **2018**, *50*, 2337-2346.
4. Y.-Y. Han, Z.-J. Wub, X.-M. Zhang, W.-C. Yuan, *Tetrahedron Lett.* **2010**, *51*, 2023.
5. E. R. El-Sawy, F. A. Bassyouni, S. H. Abu-Bakar, H. M. Rady, M. M. Abdlla. *Acta Pharm*. **2009,** *59***,** 55–71.

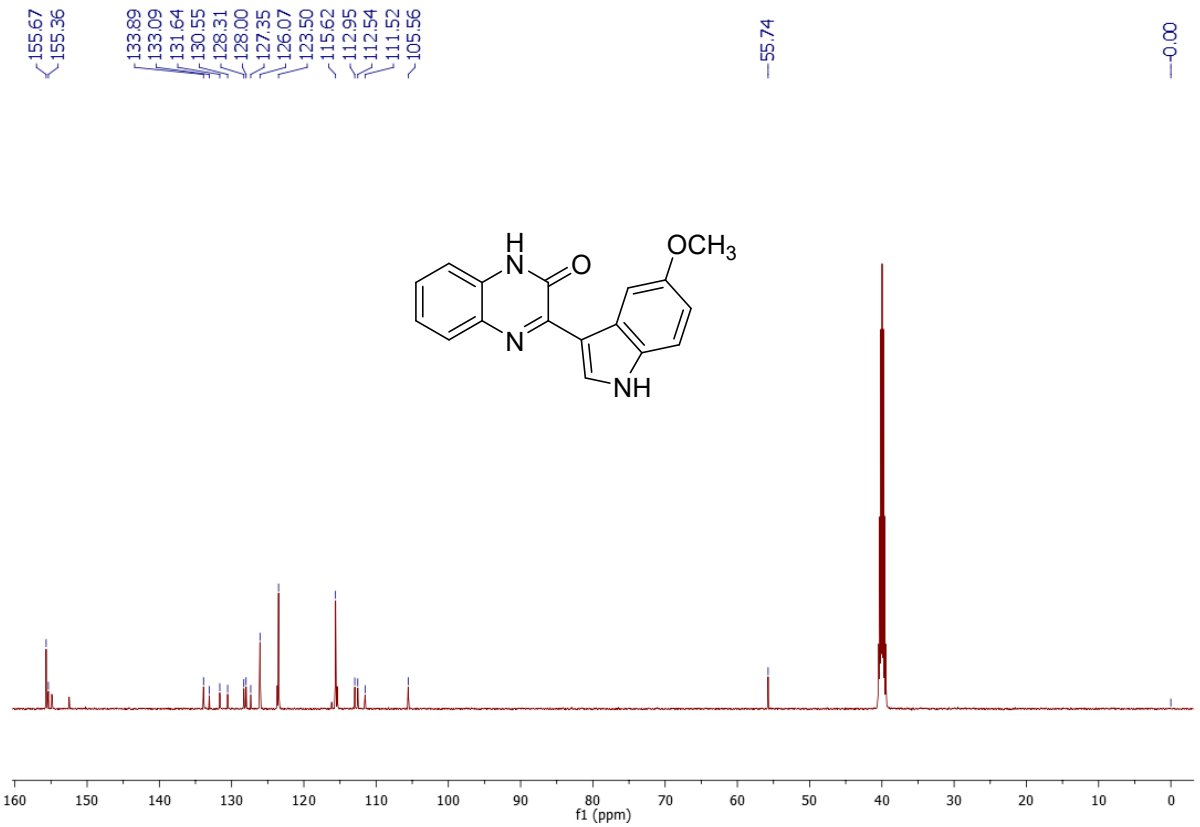
Copies of ^{1}H and ^{13}C NMR spectra
Compound 4aa



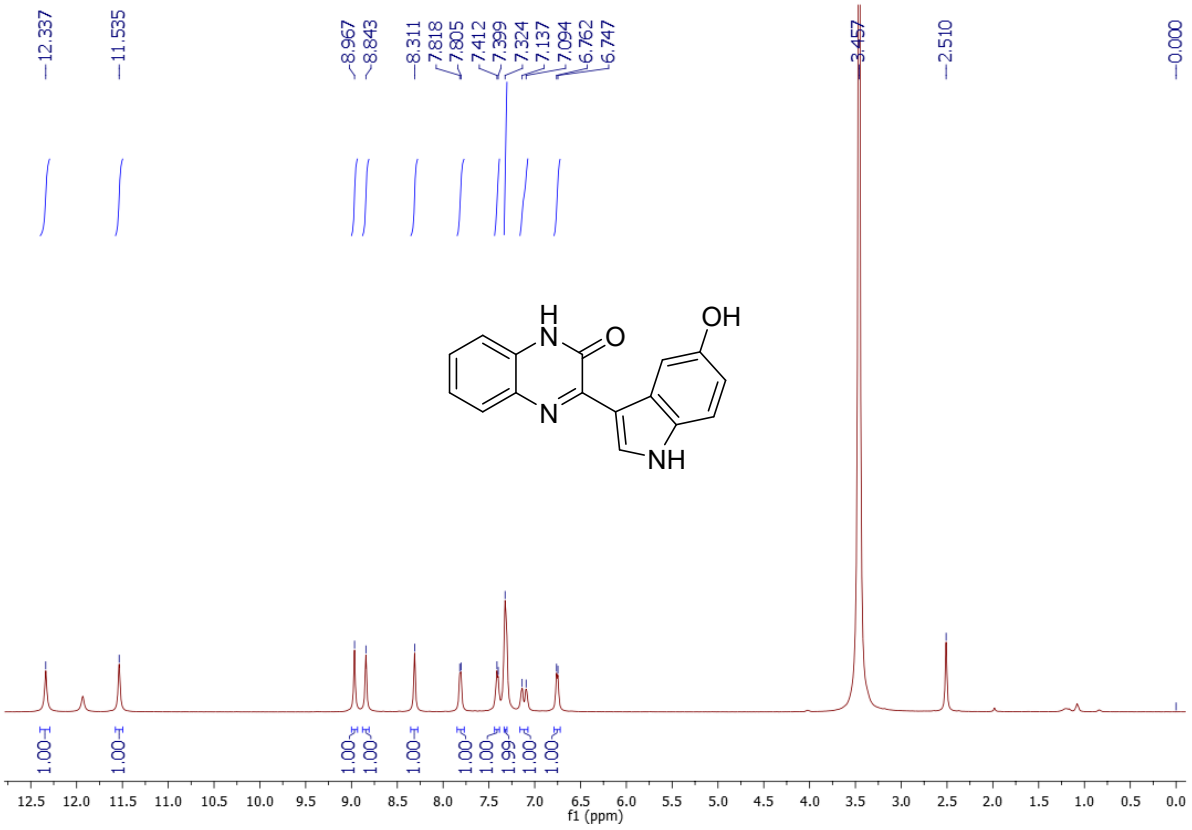


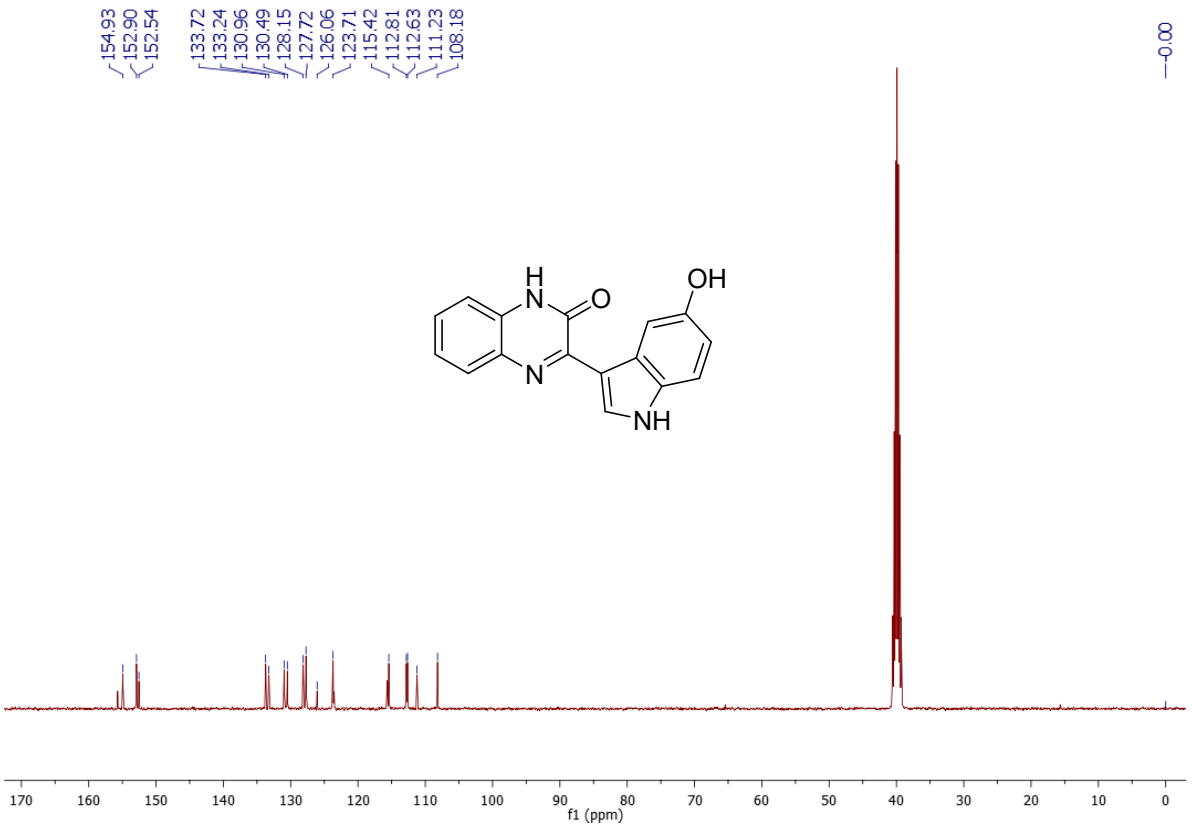
Compound 4ab



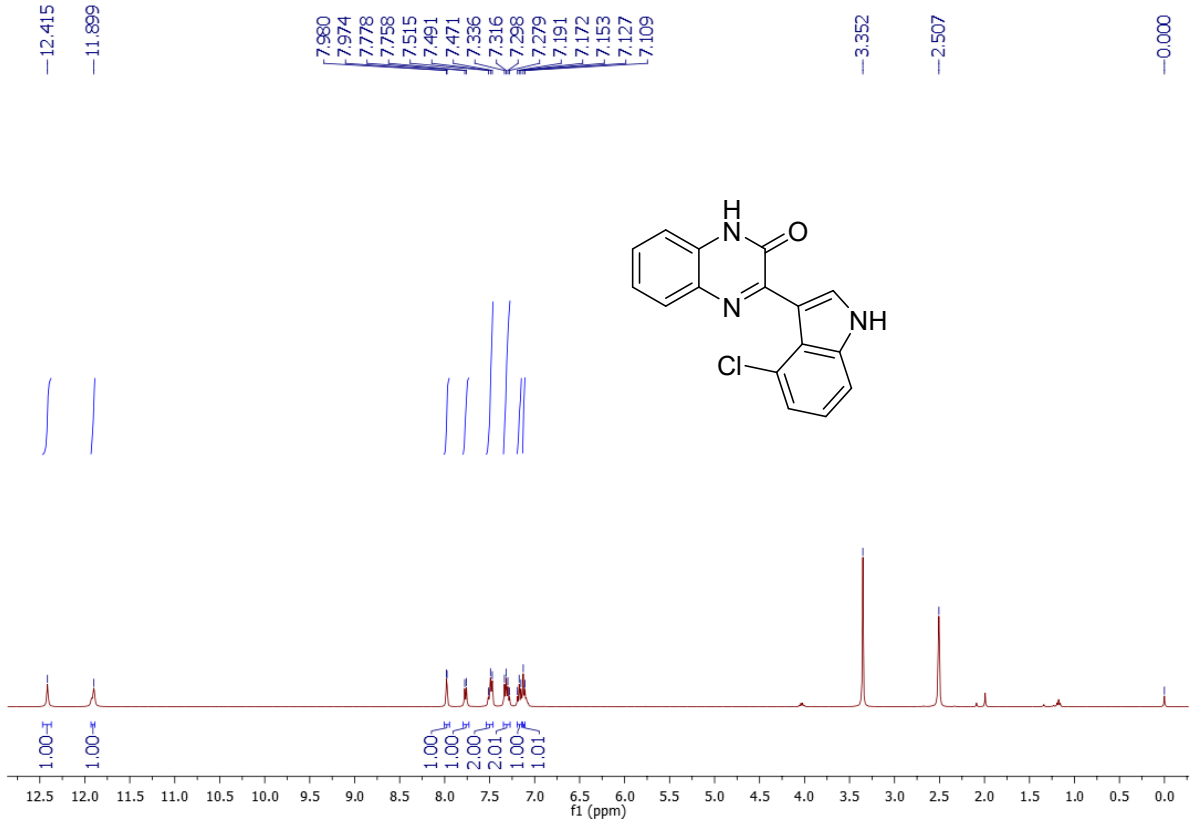


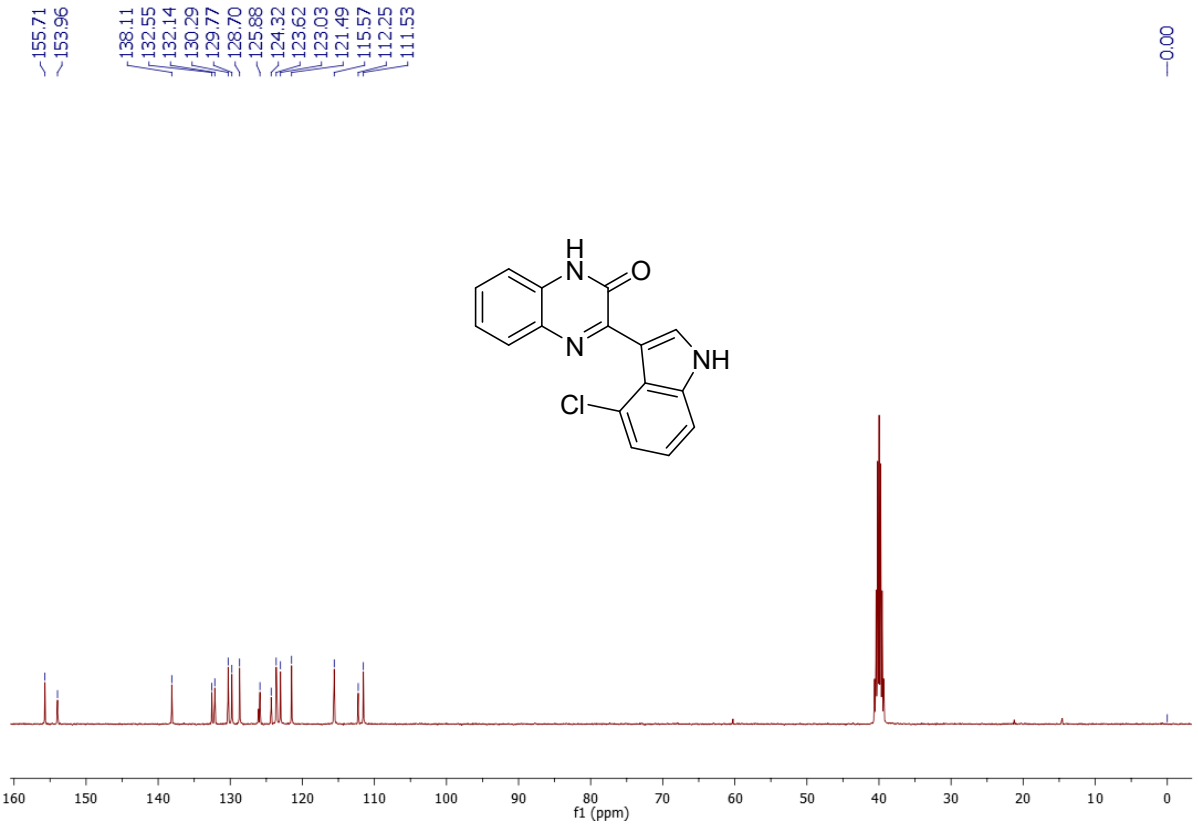
Compound 4ac



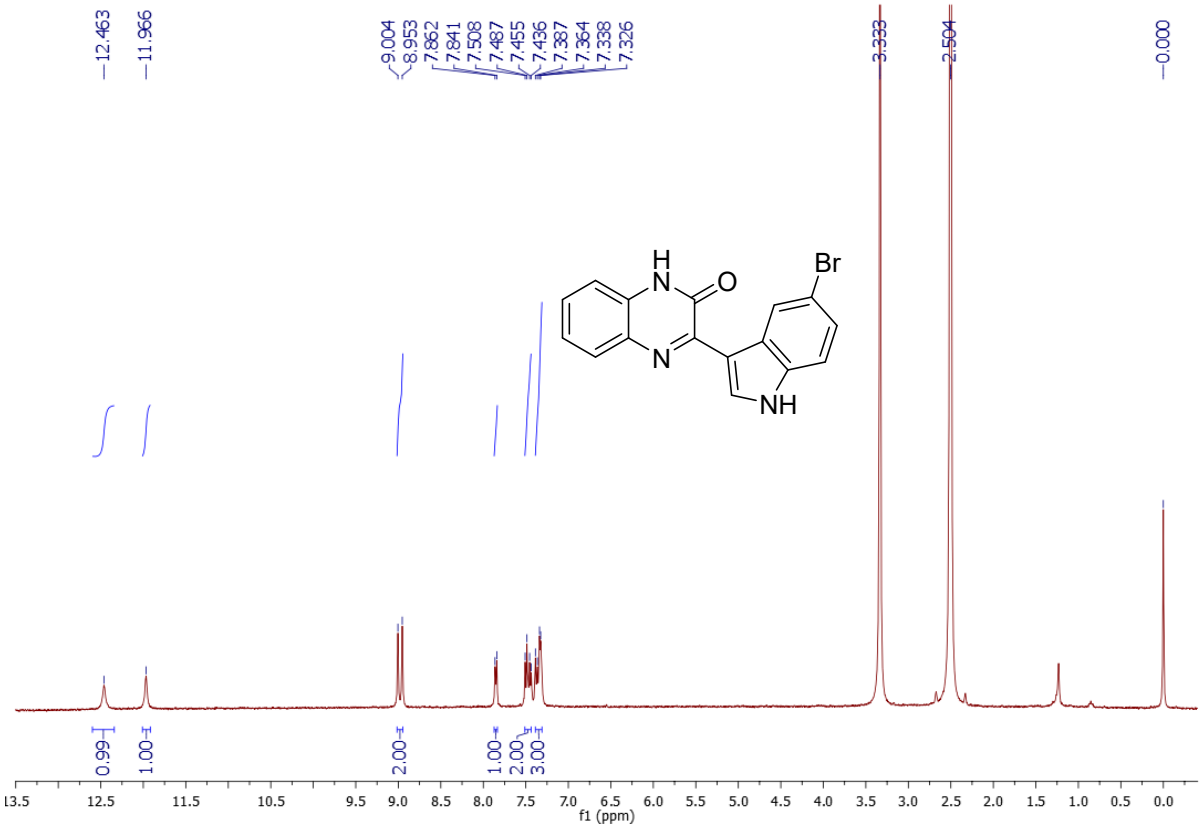


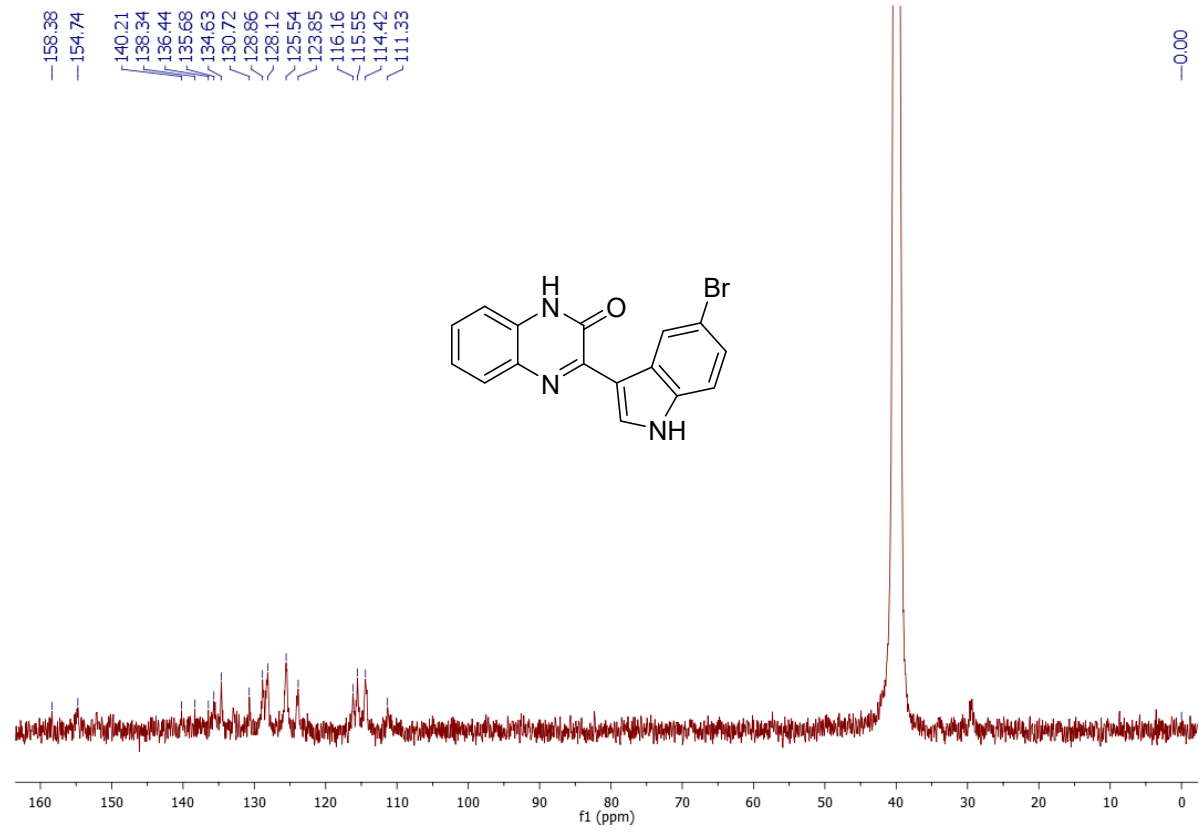
Compound 4ac



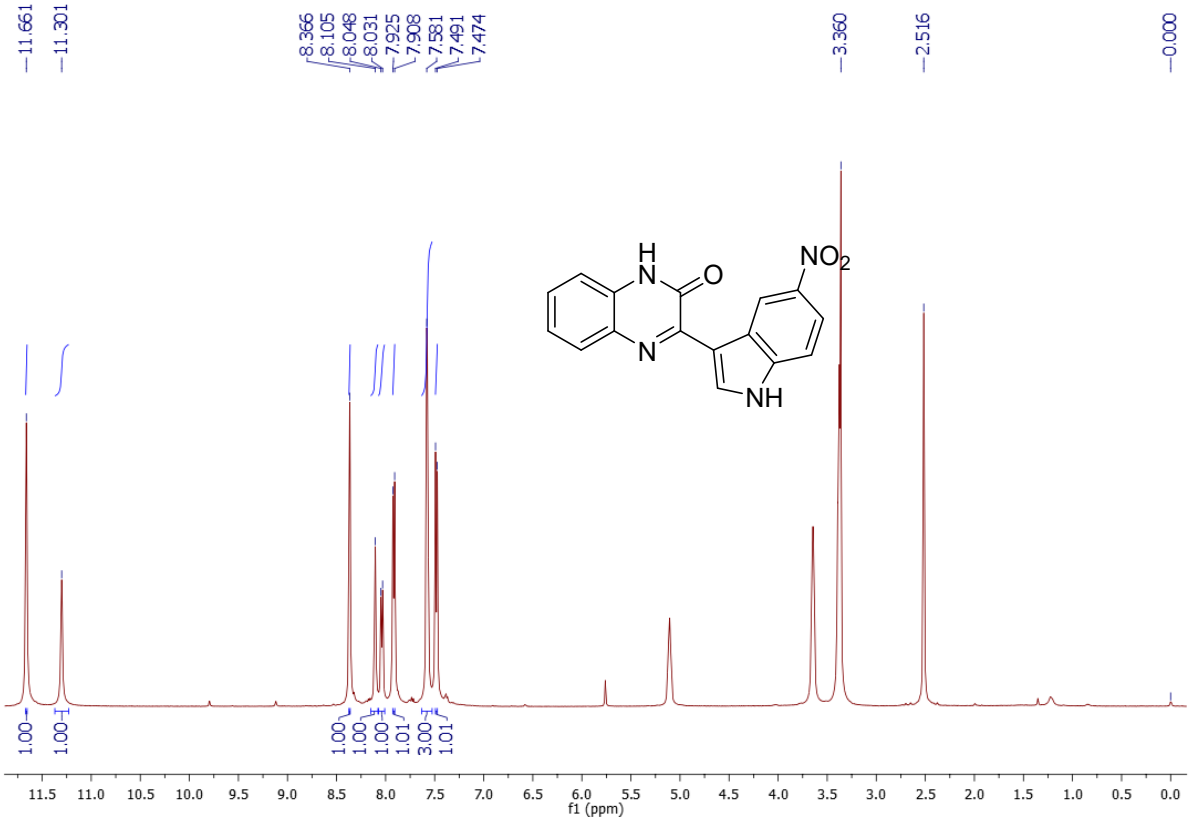


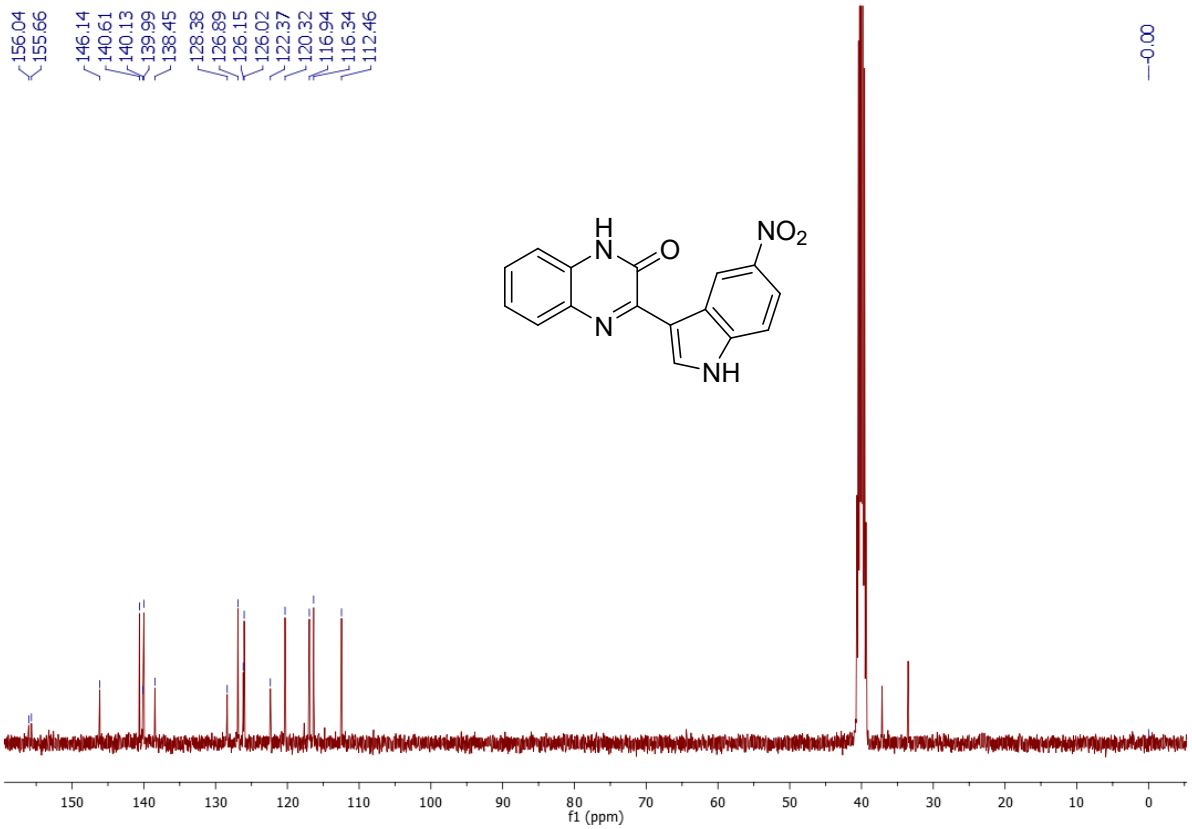
Compound 4ae



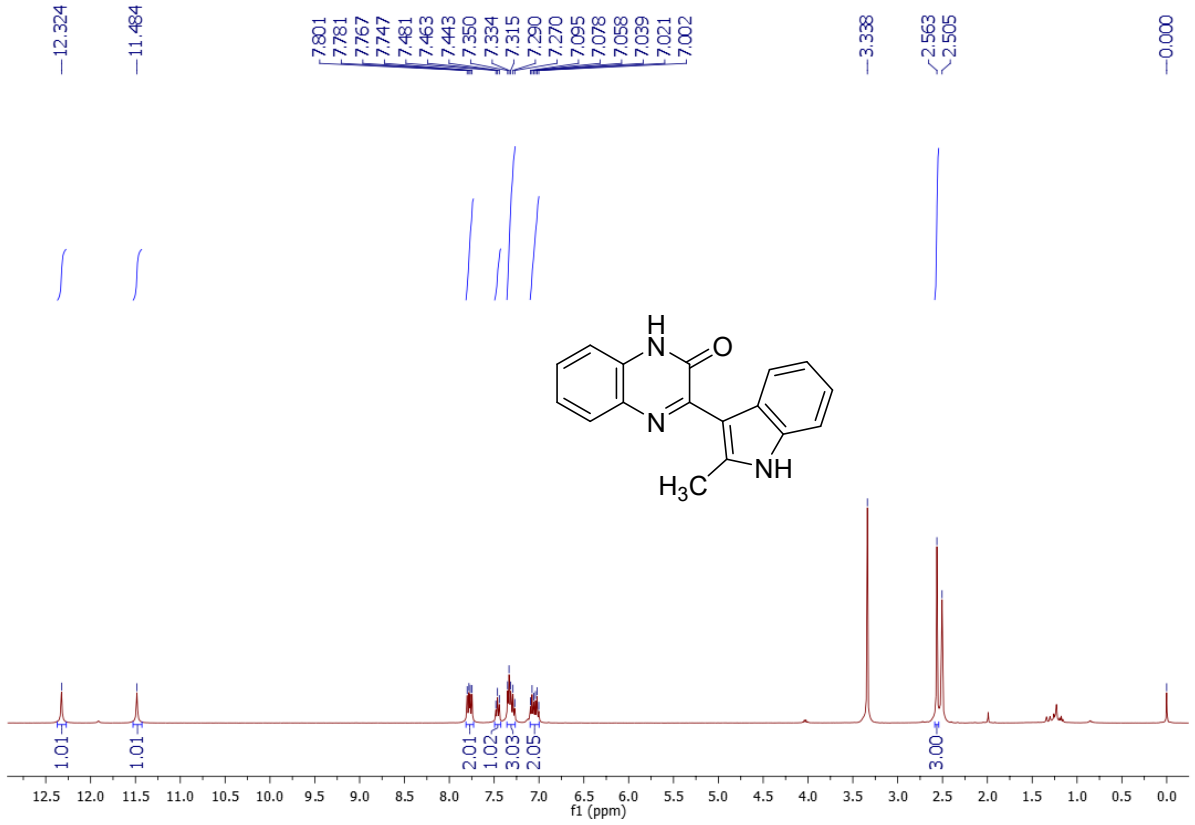


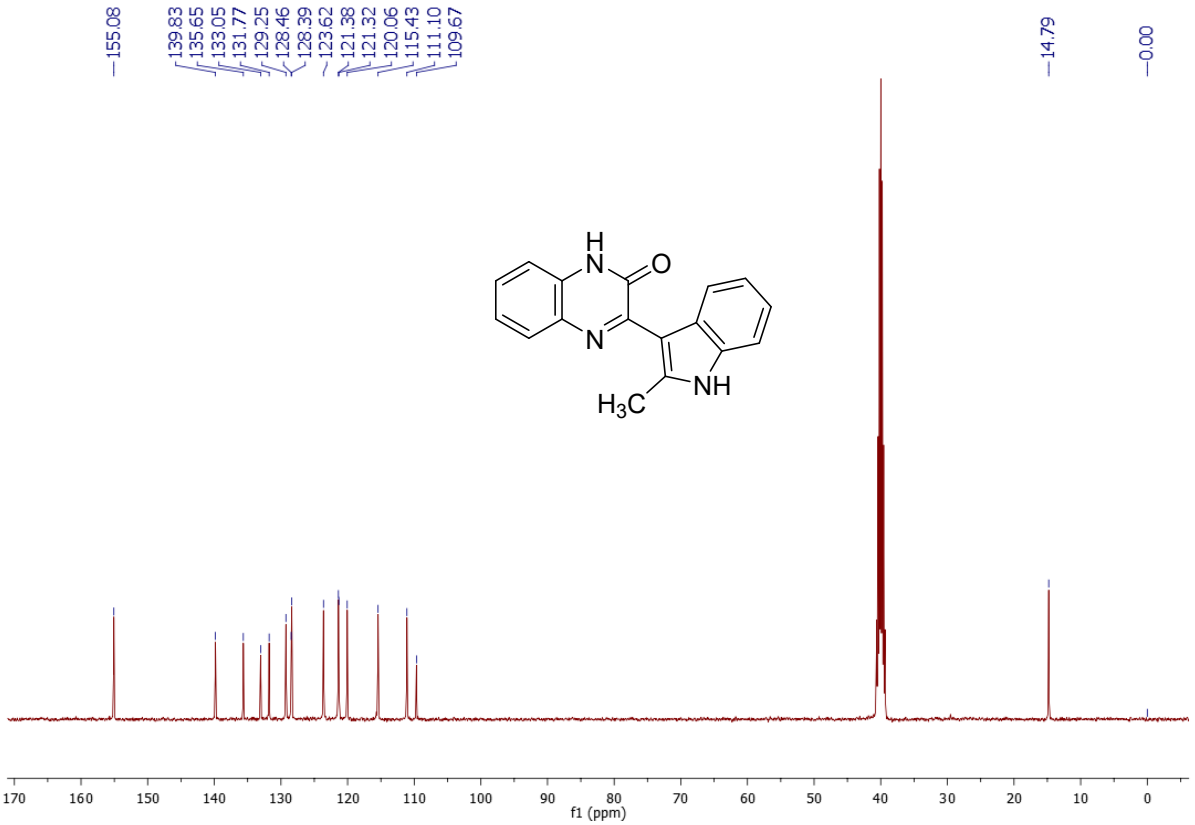
Compound 4af



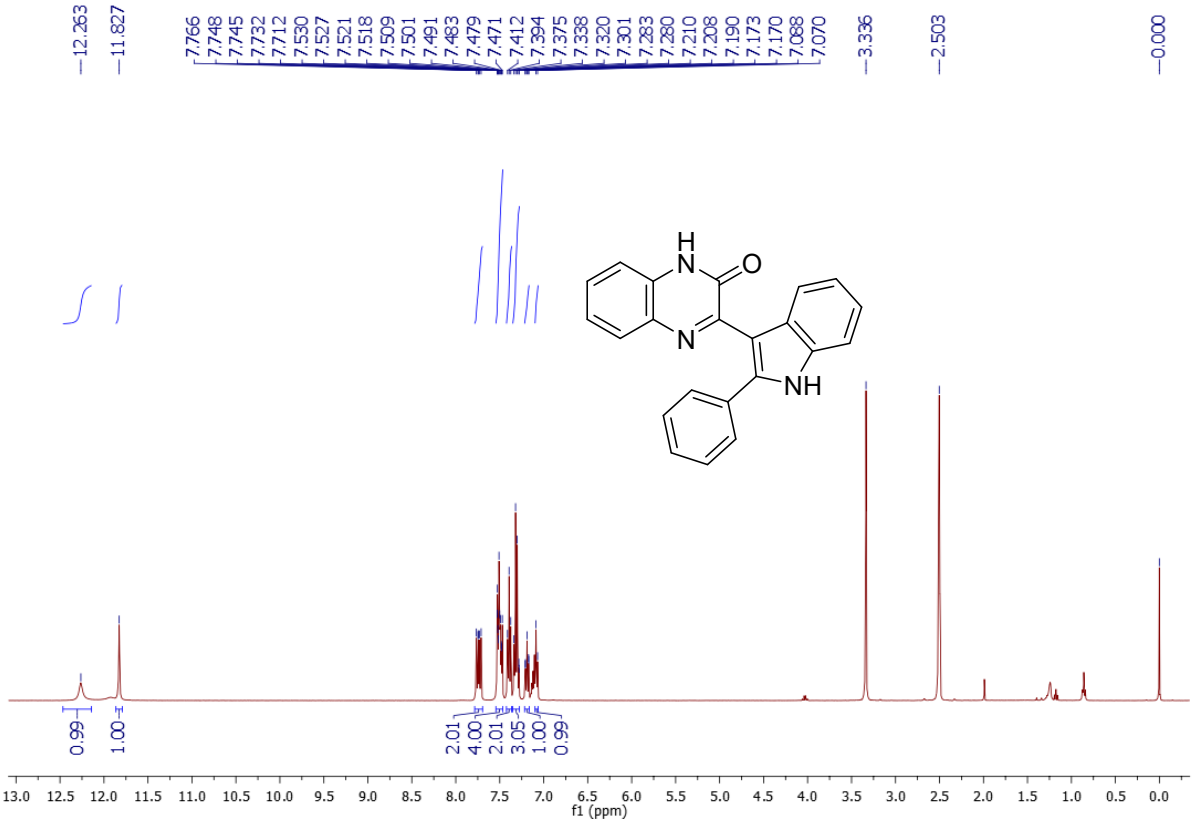


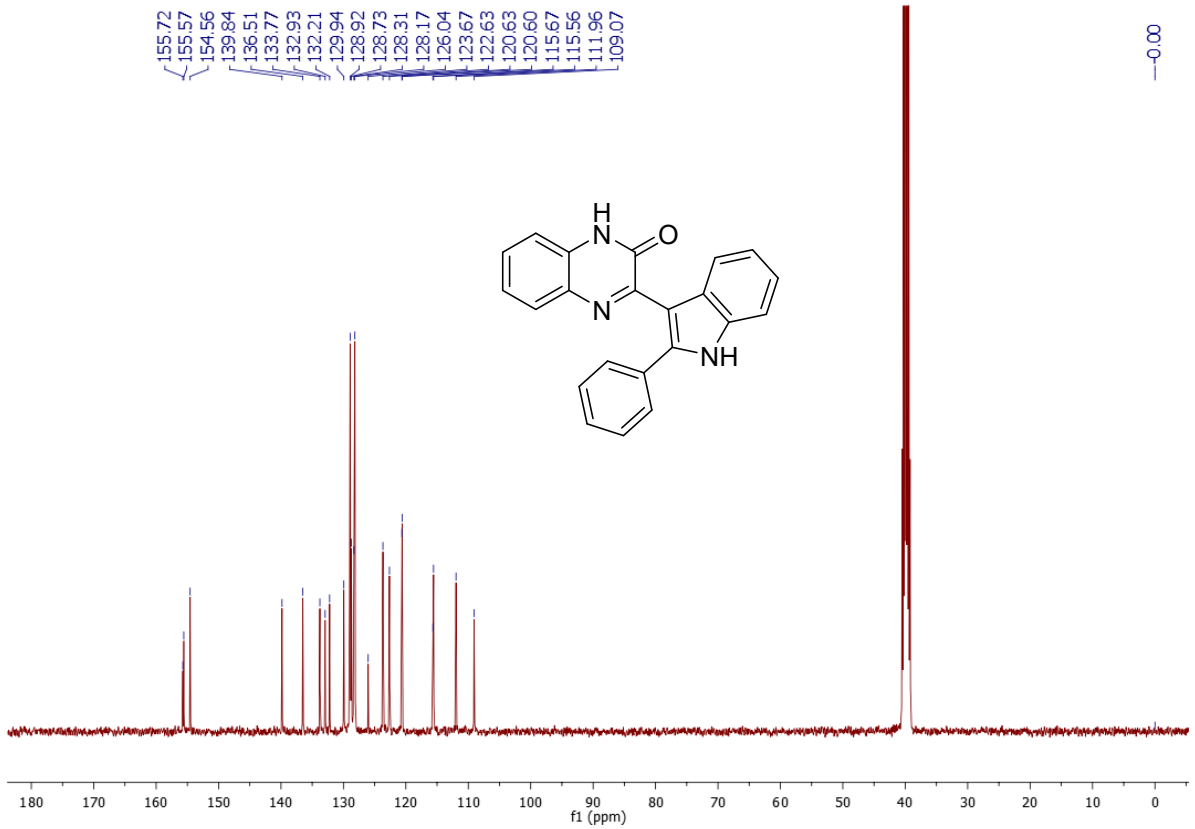
Compound 4ag



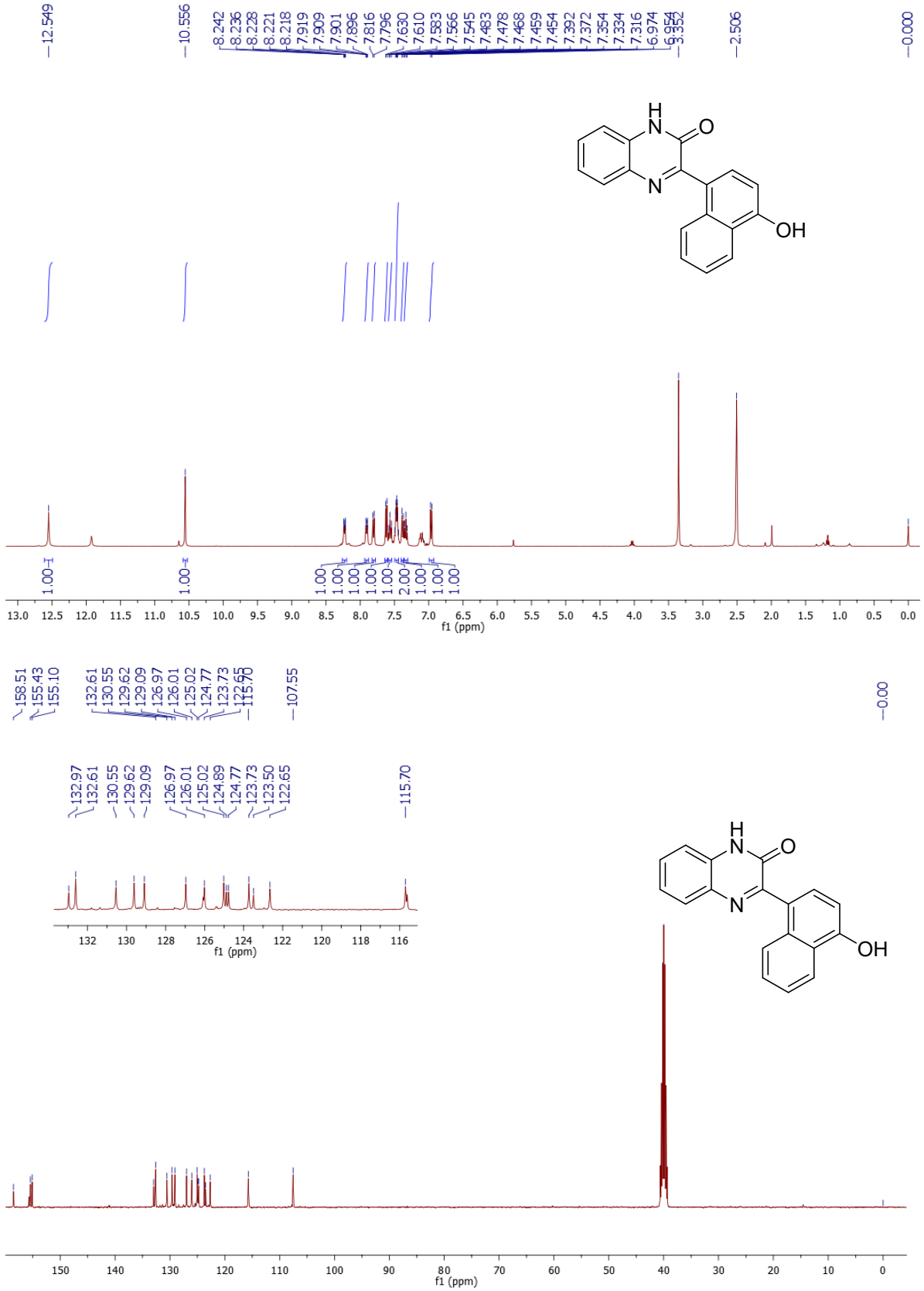


Compound 4ah

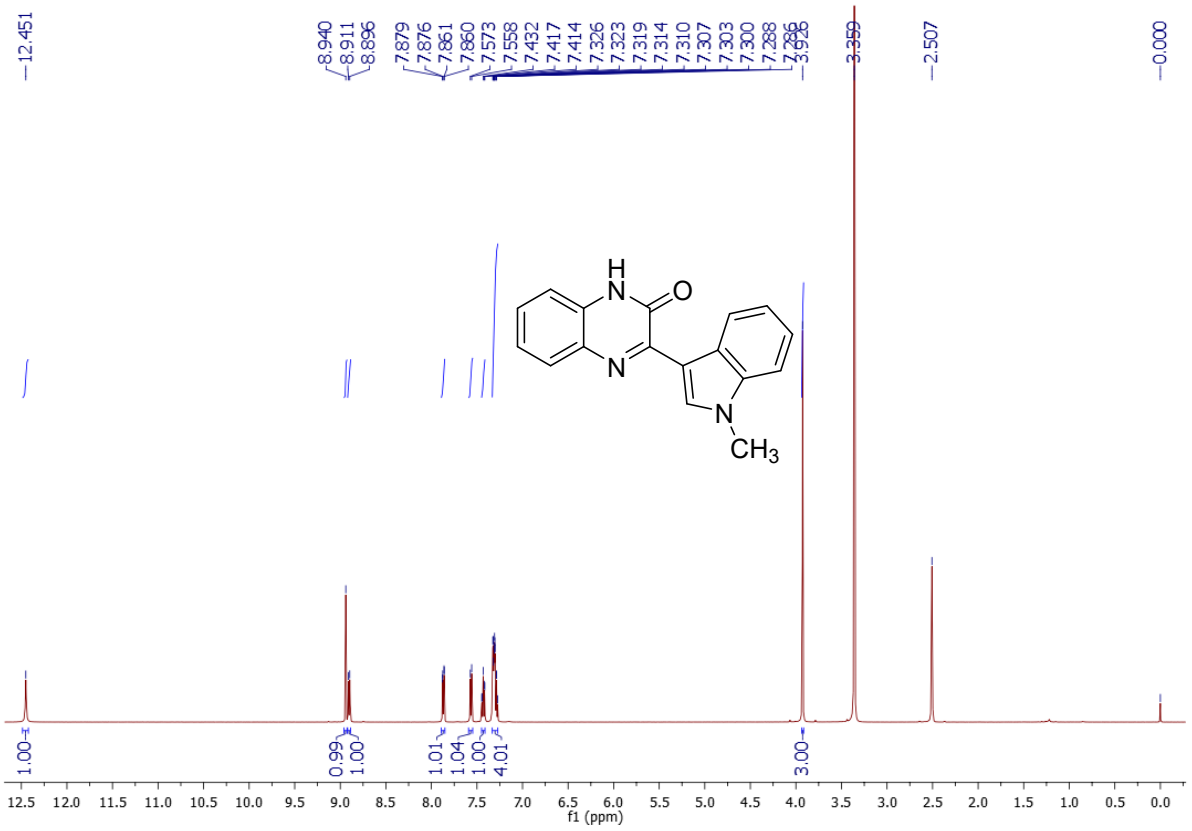


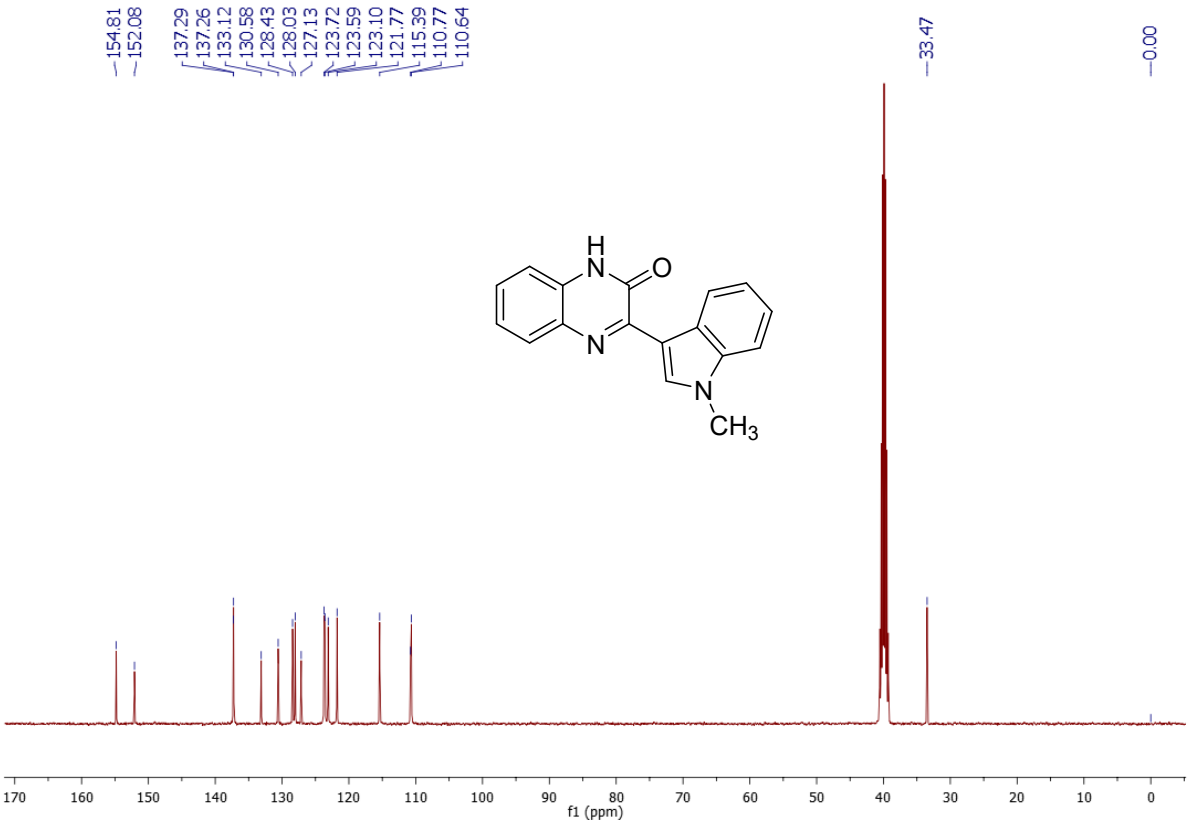


Compound 4ai



Compound 4aj





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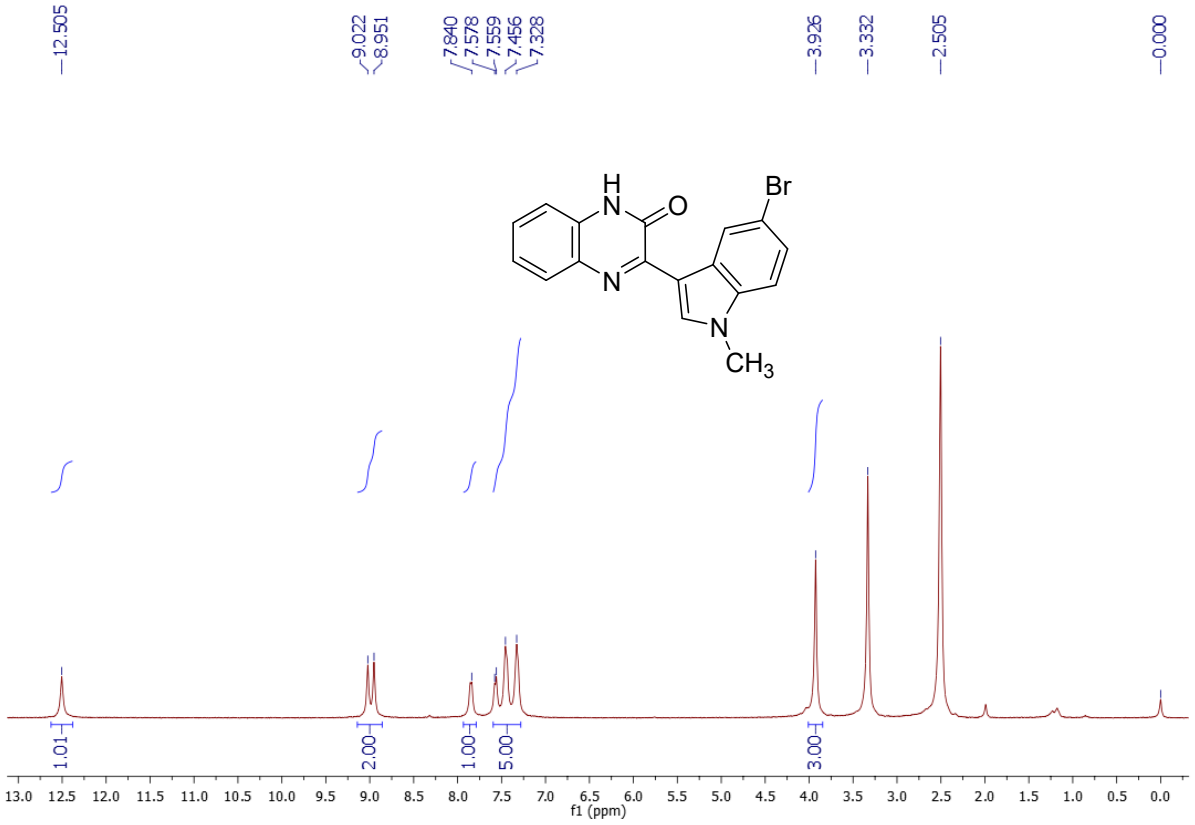

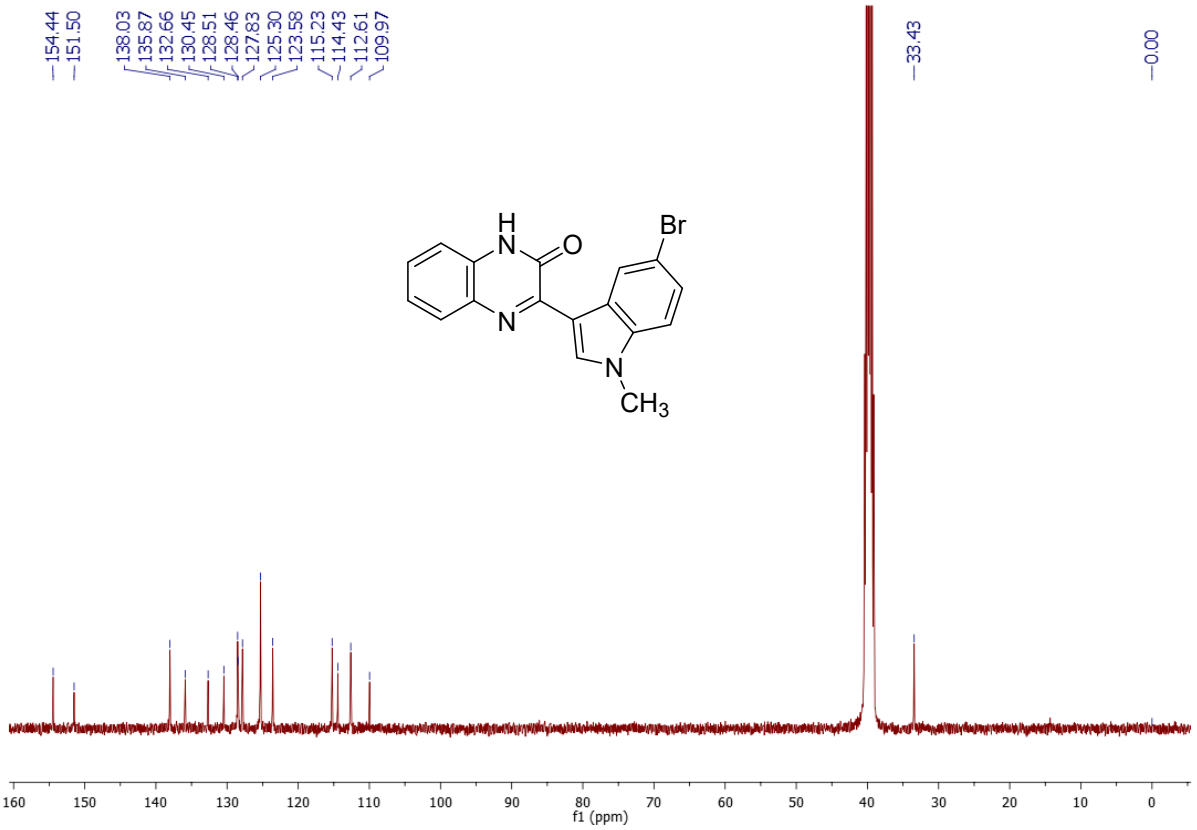

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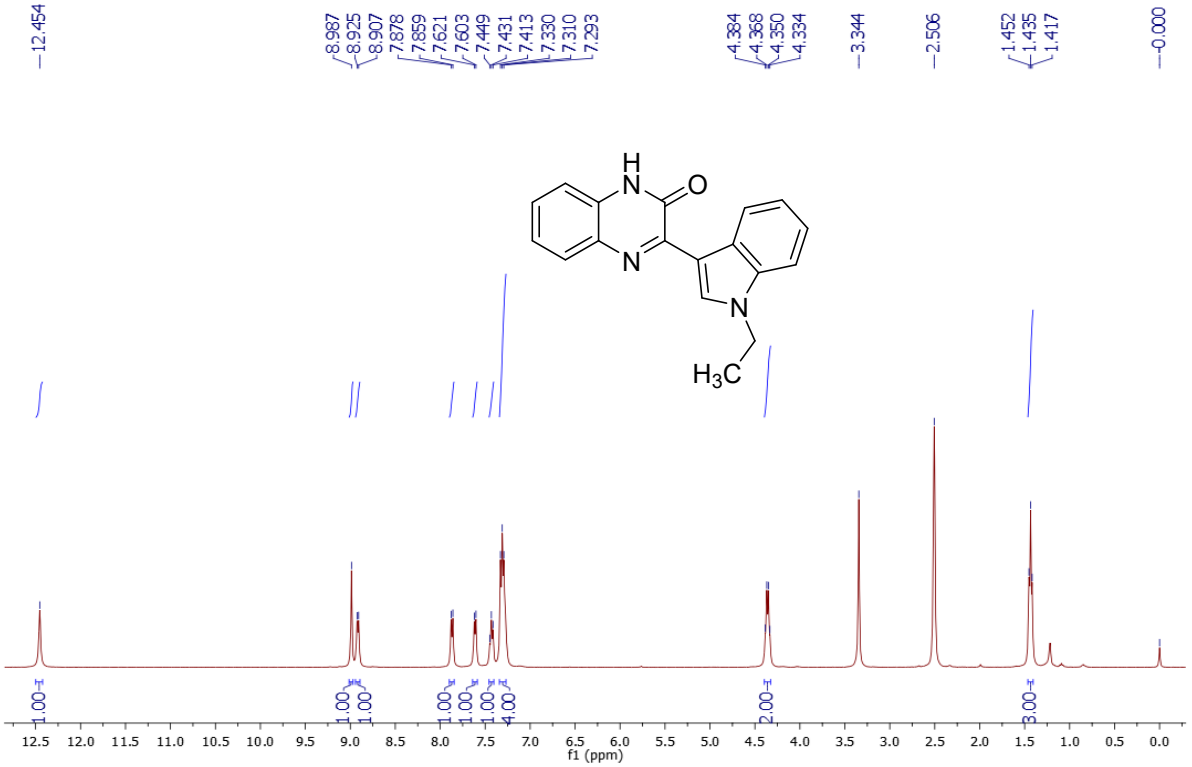

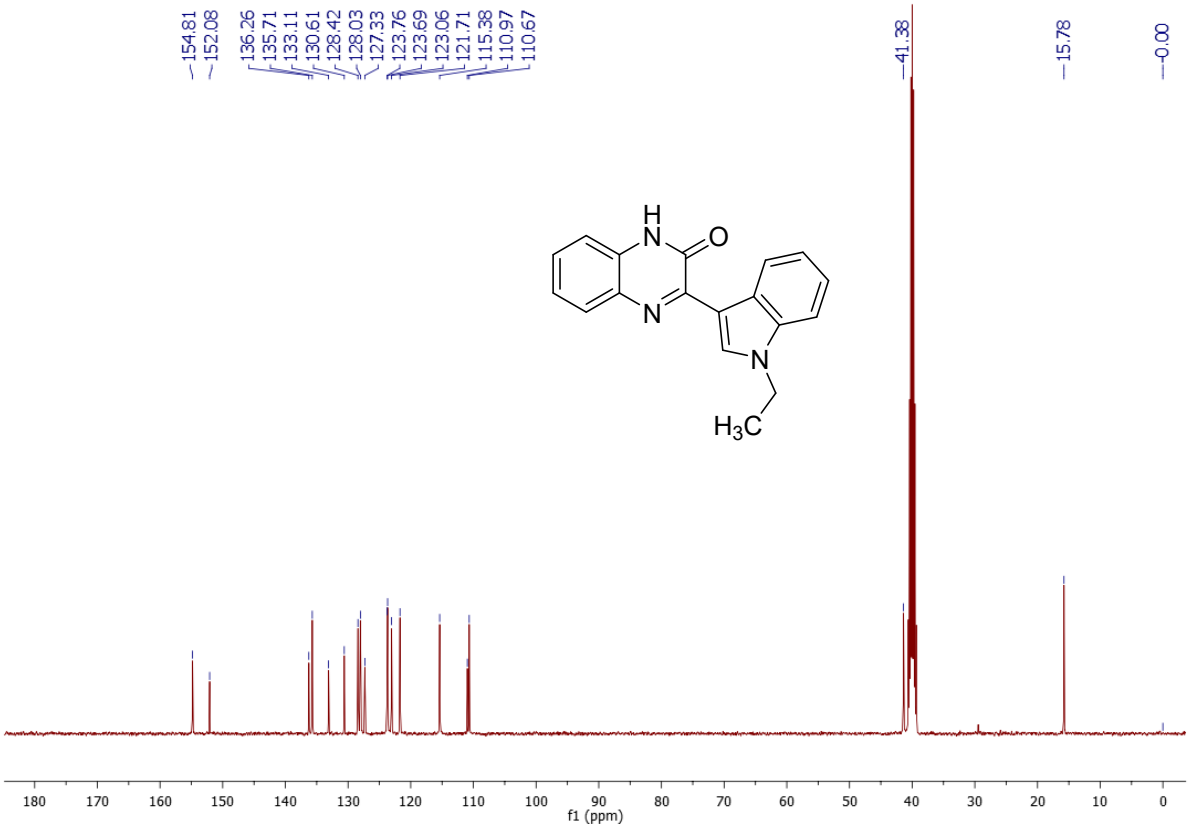

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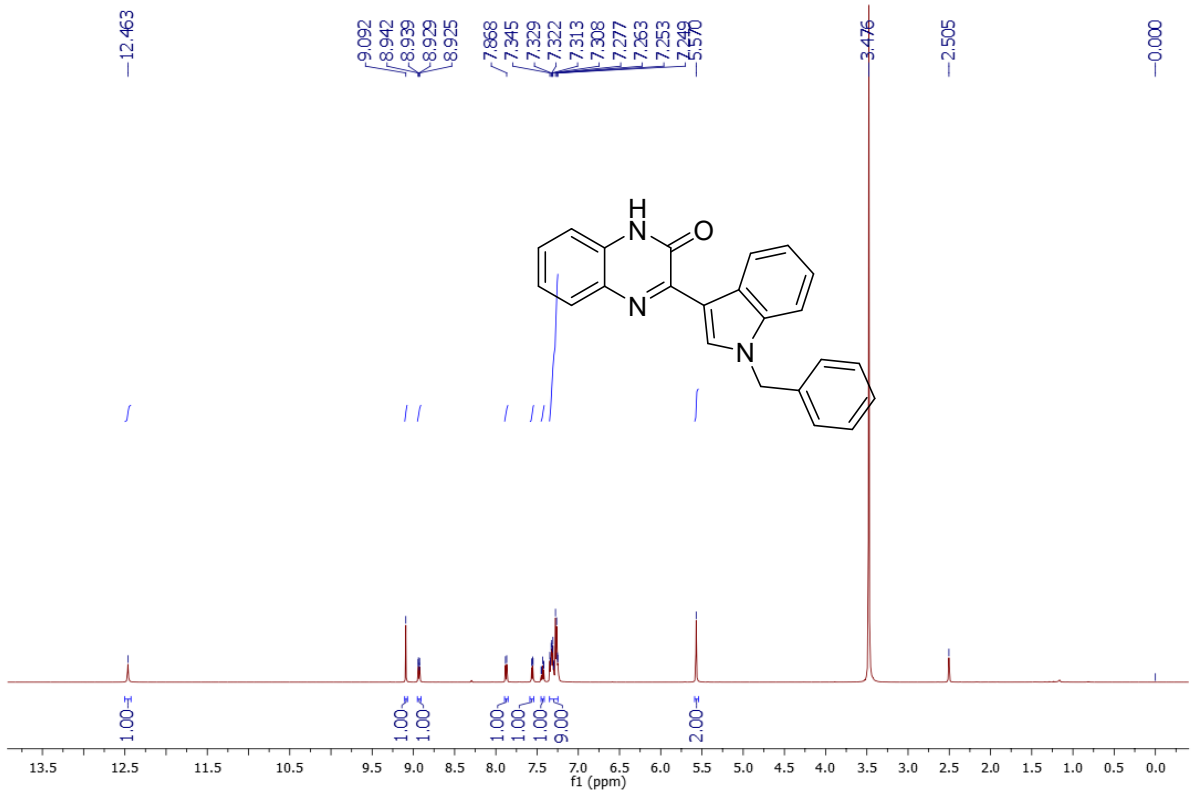

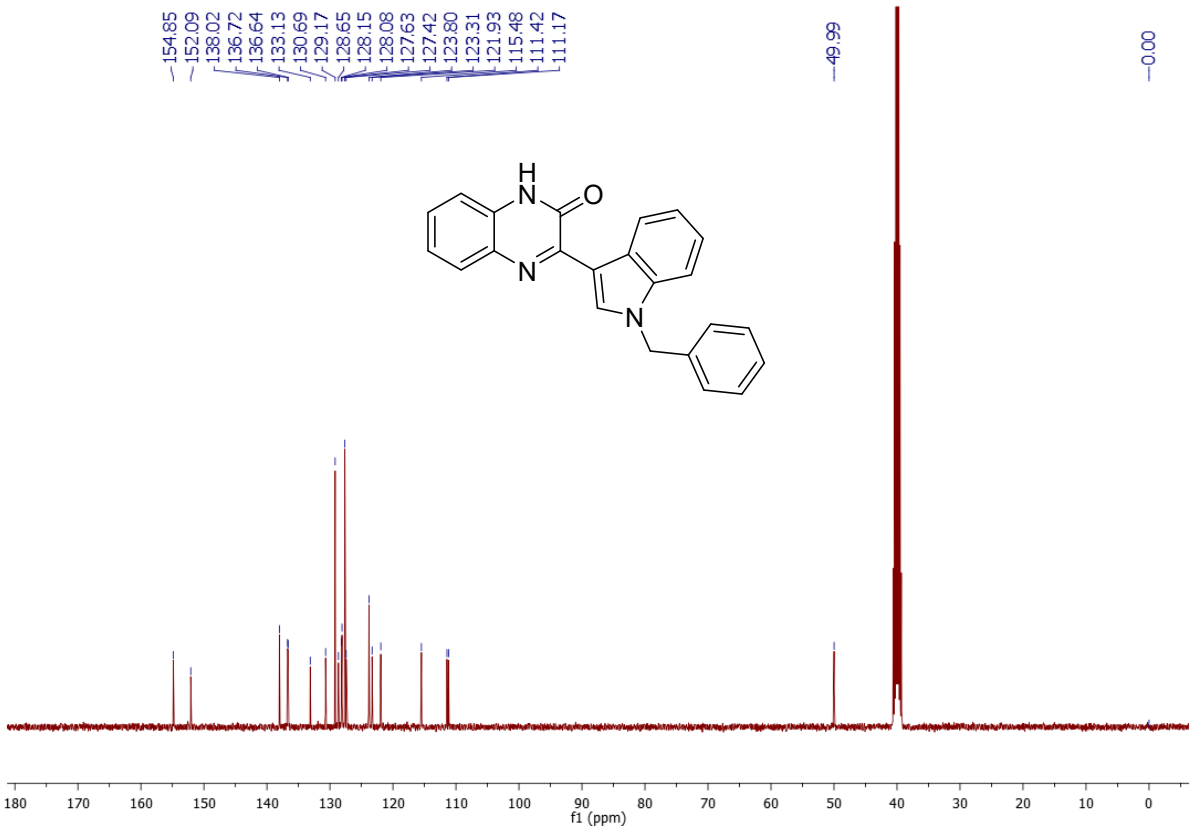

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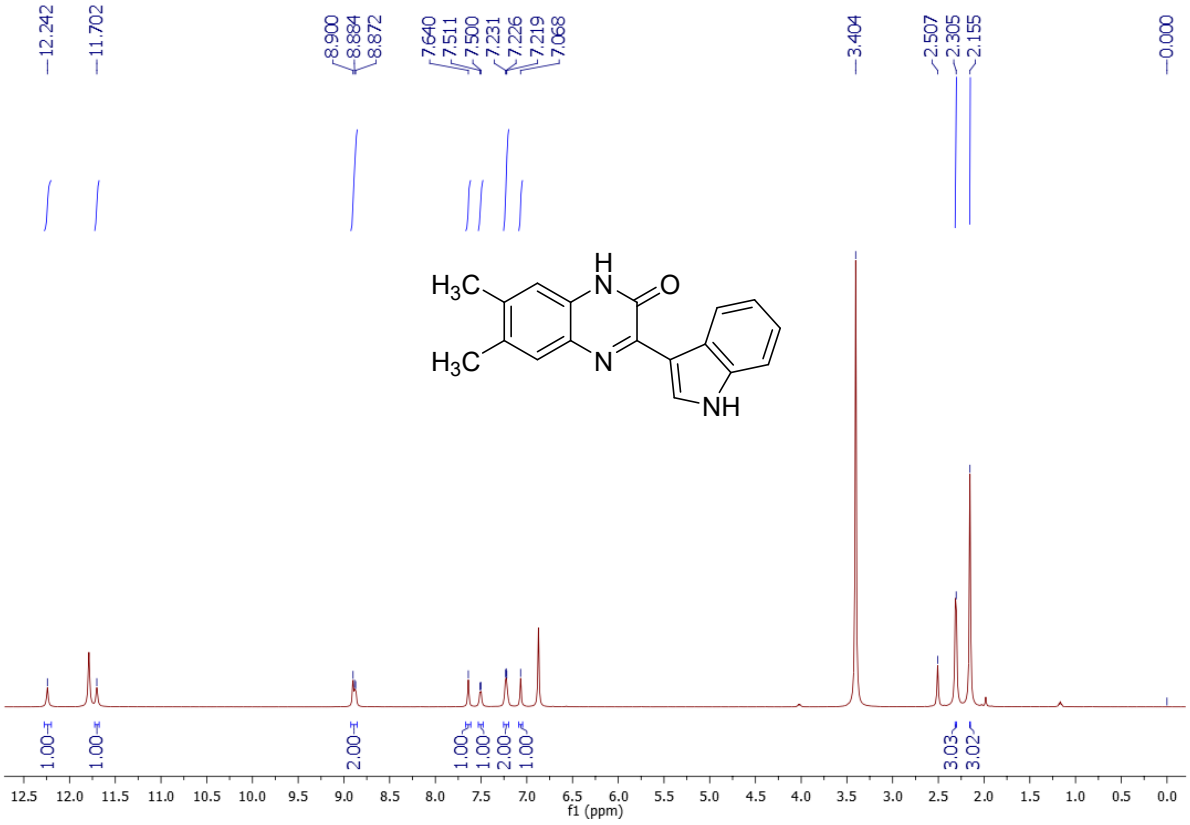

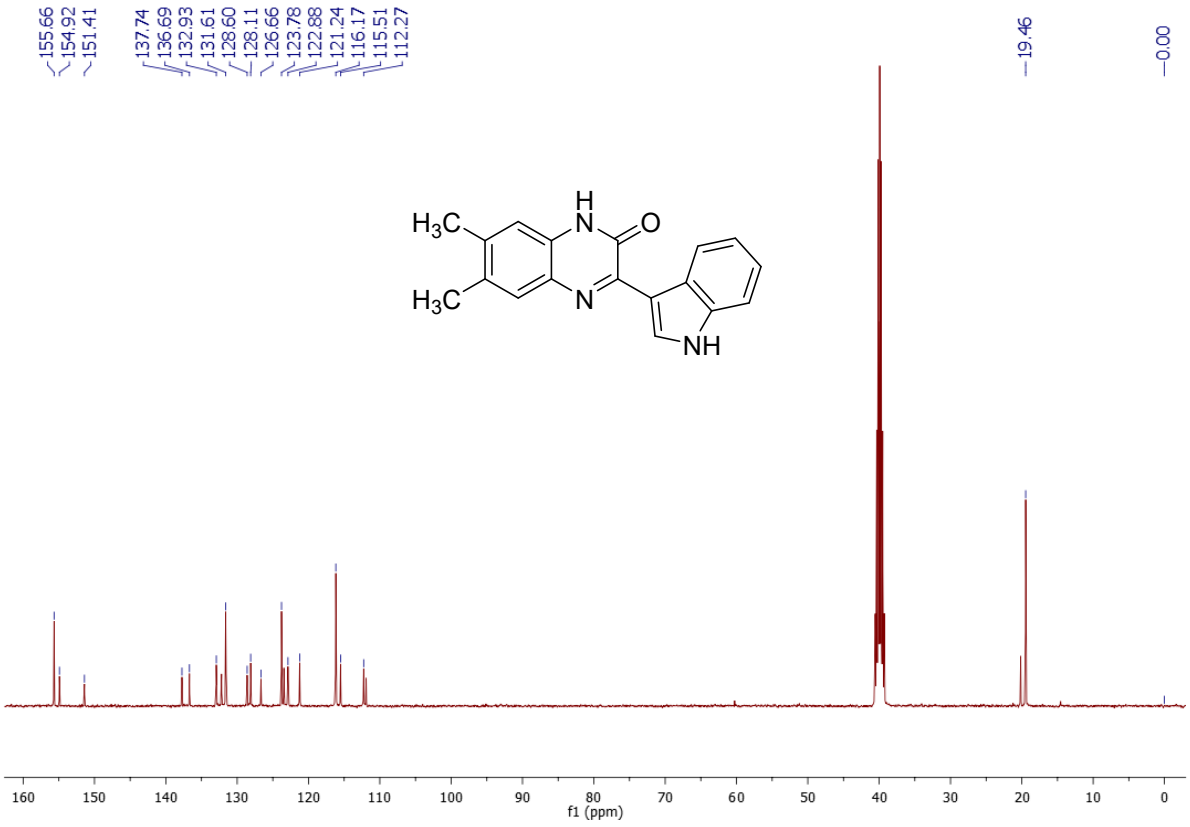

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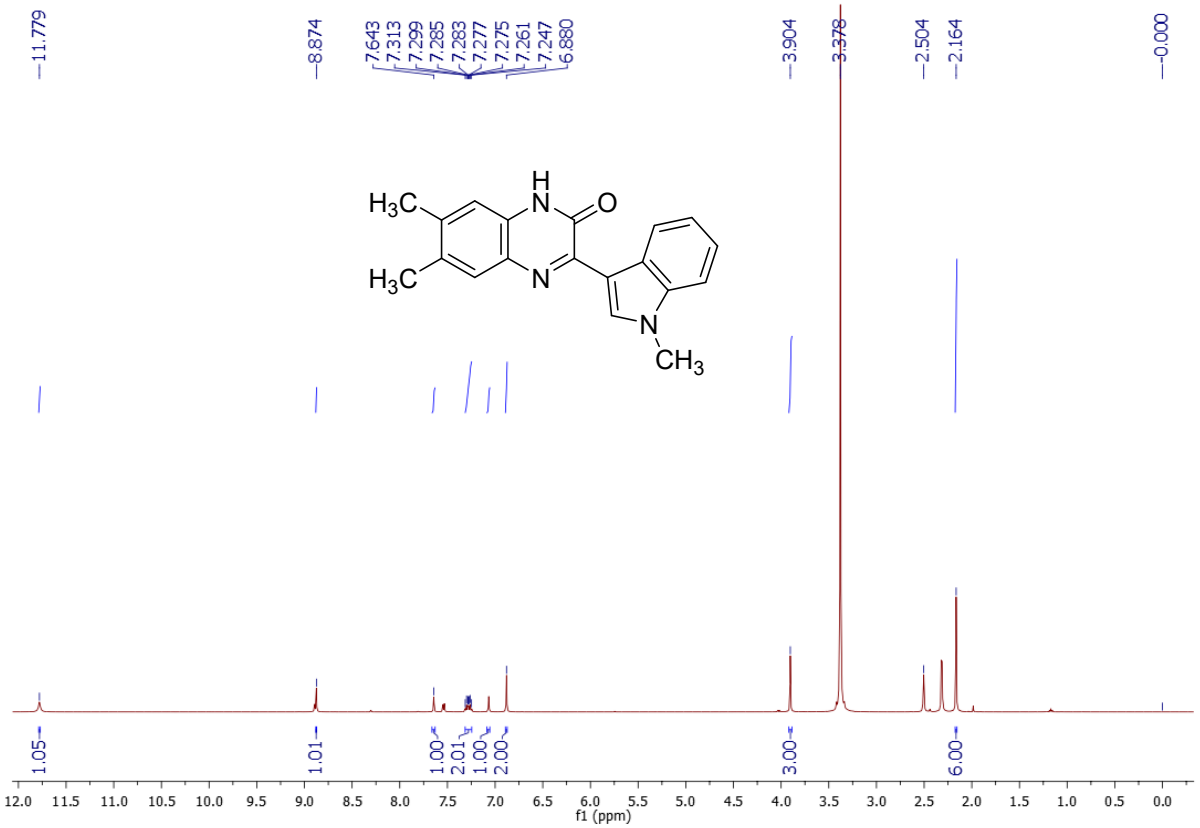

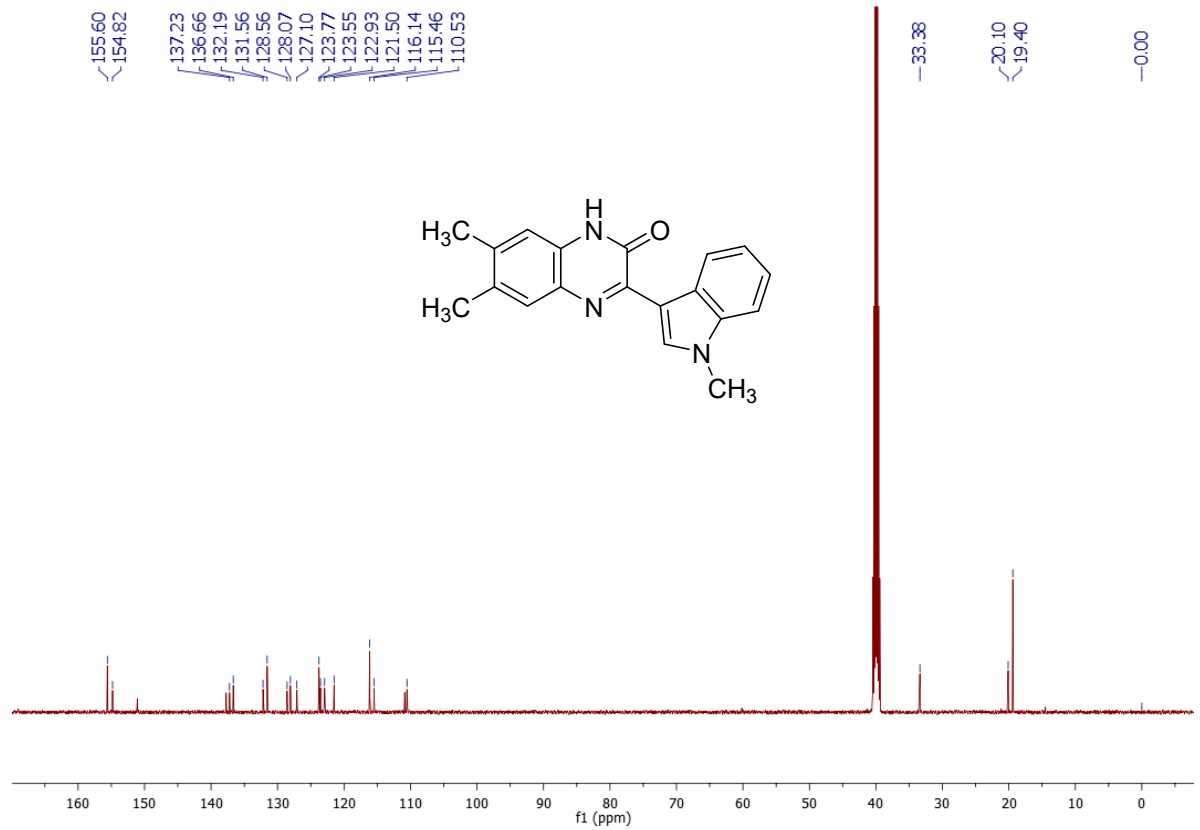

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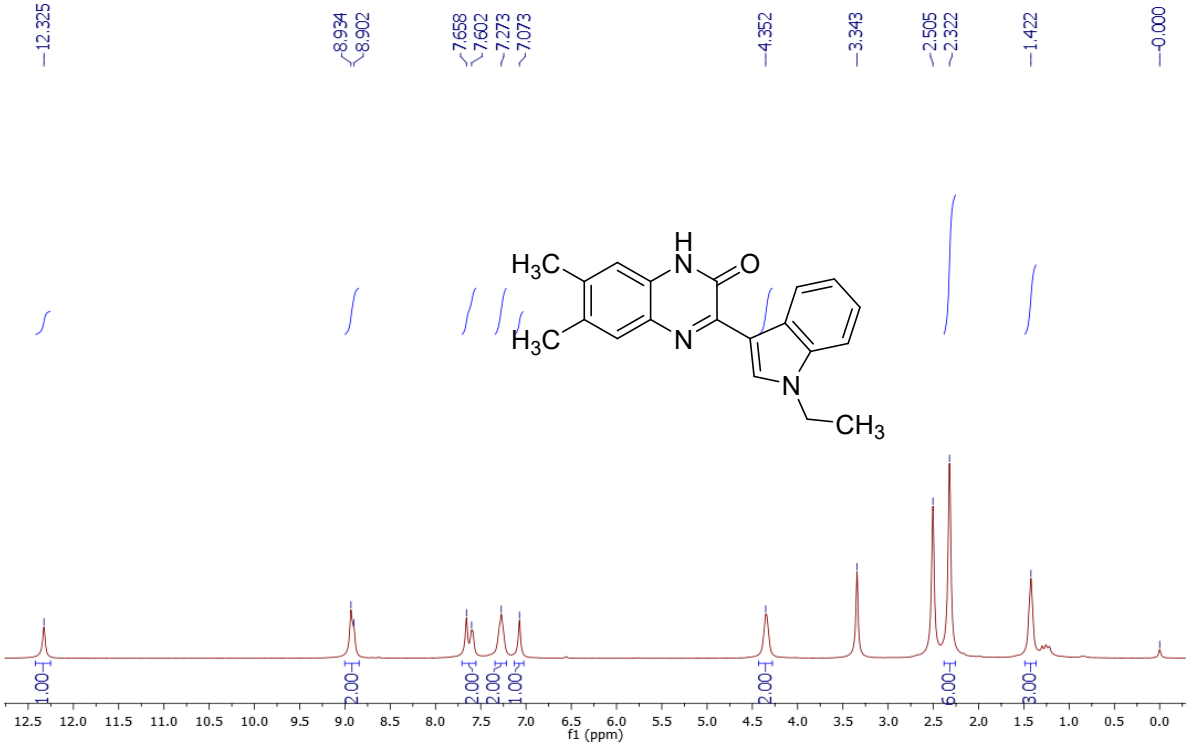

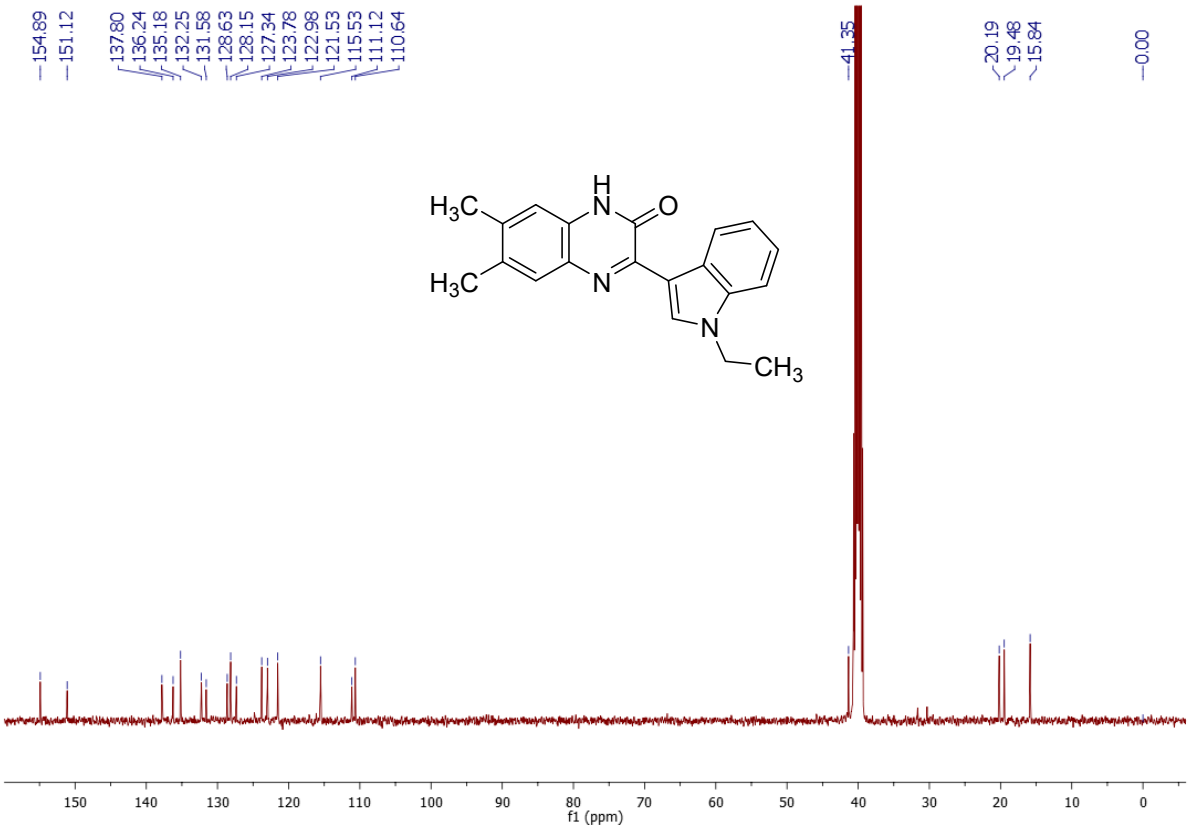

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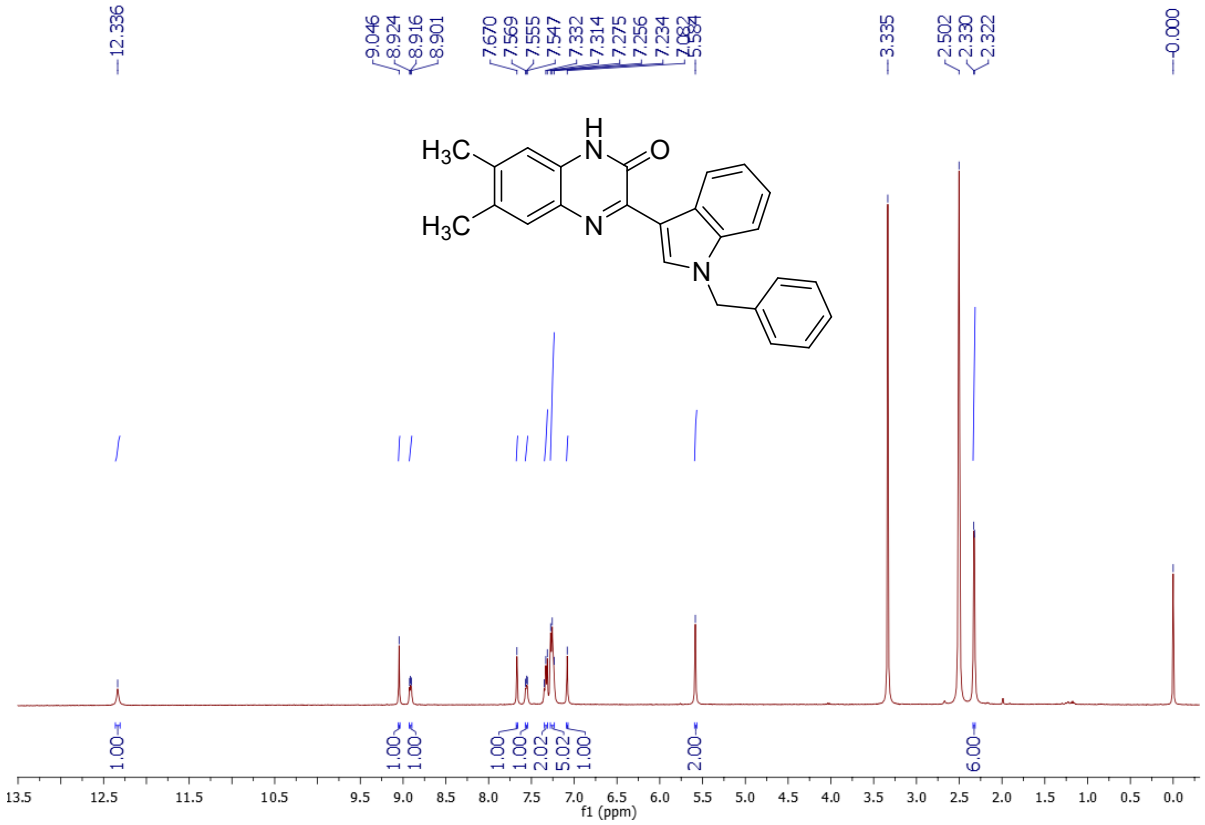

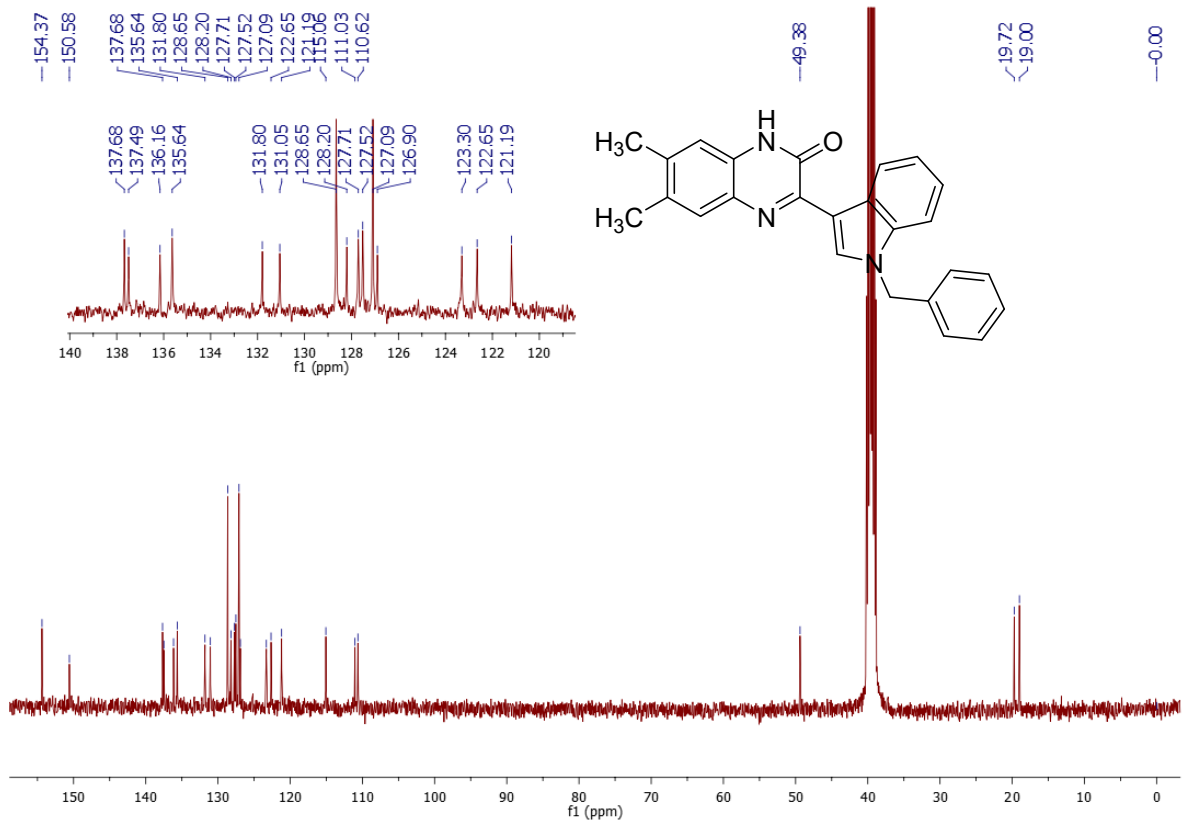

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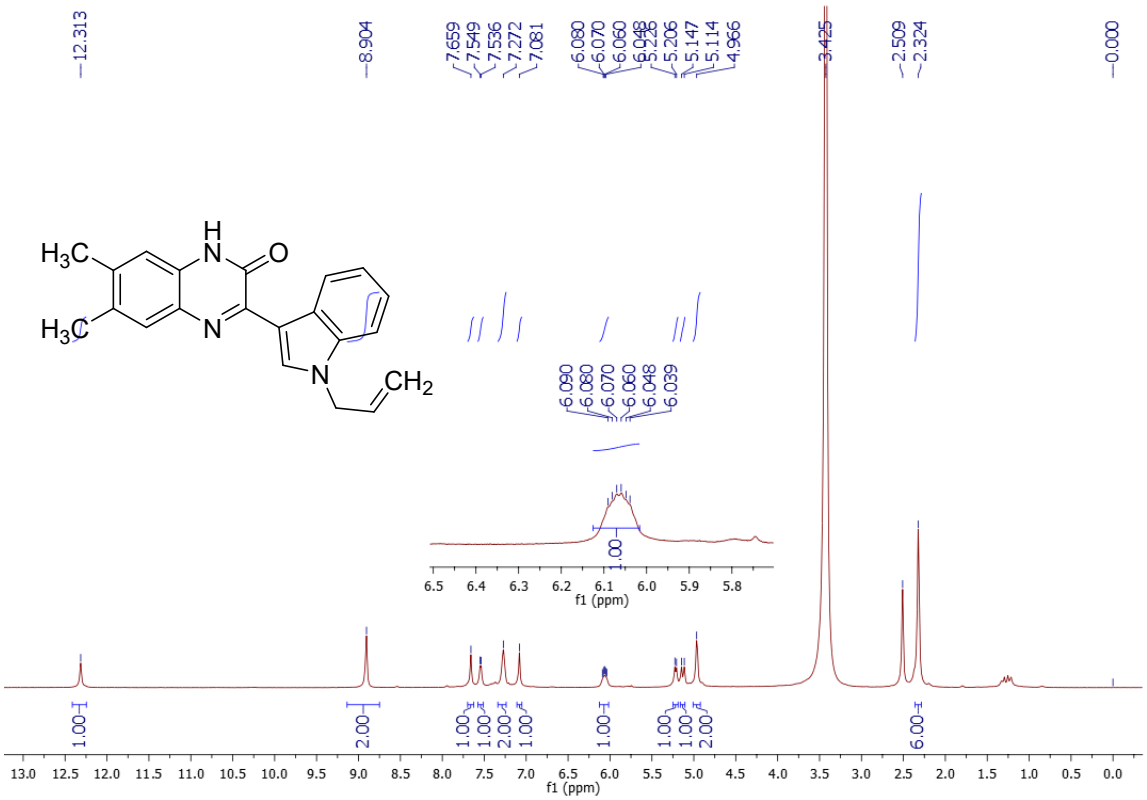

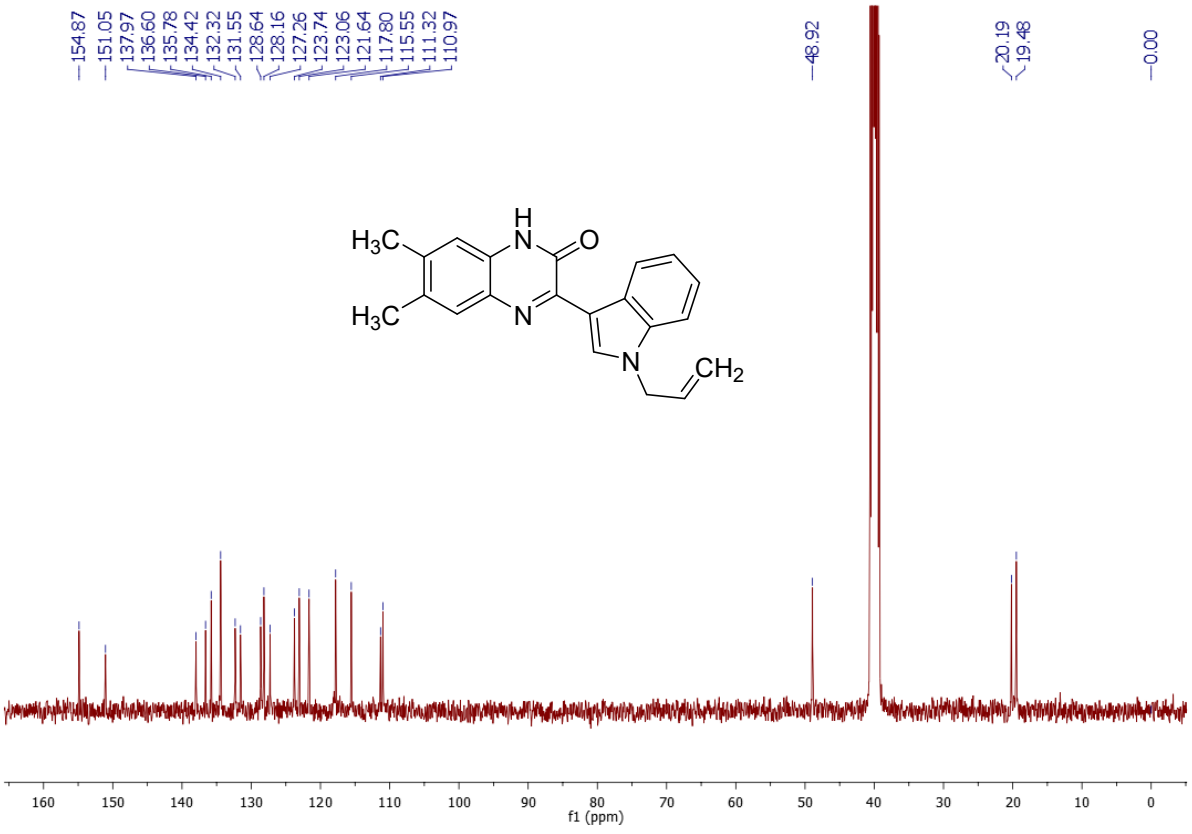

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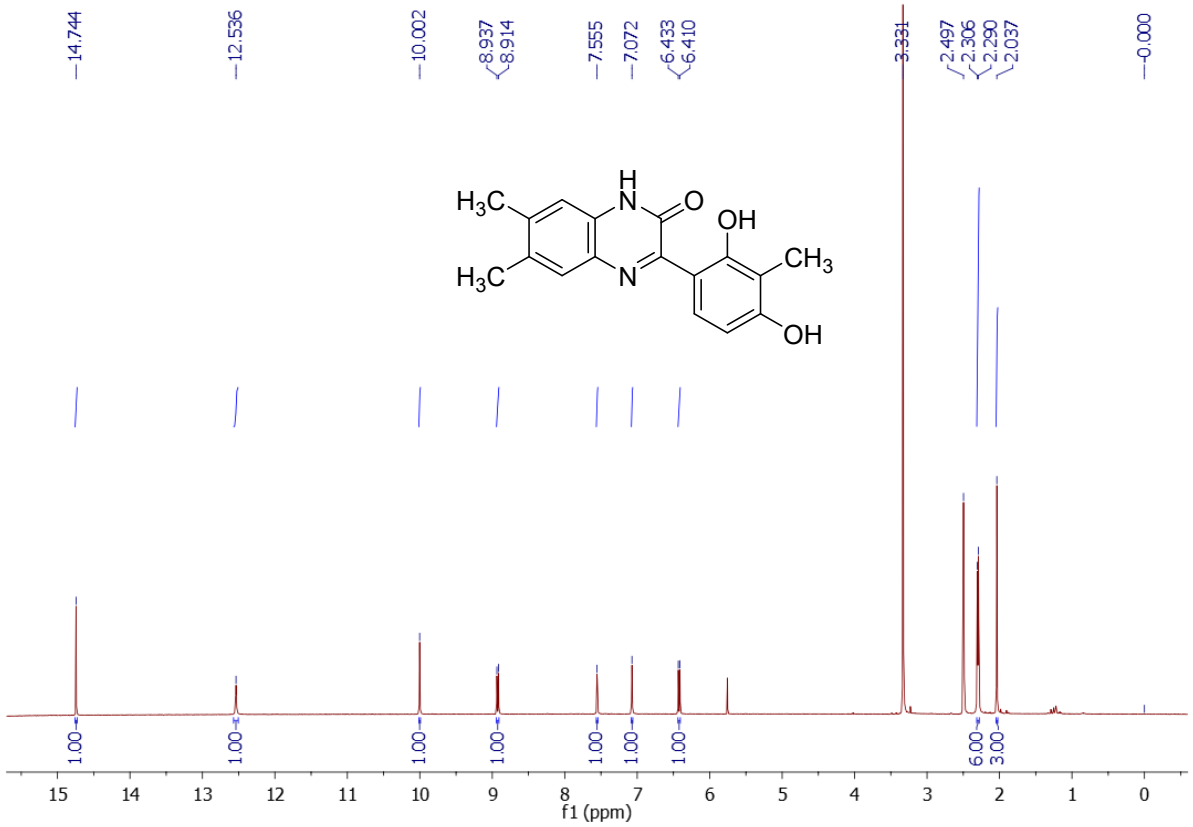

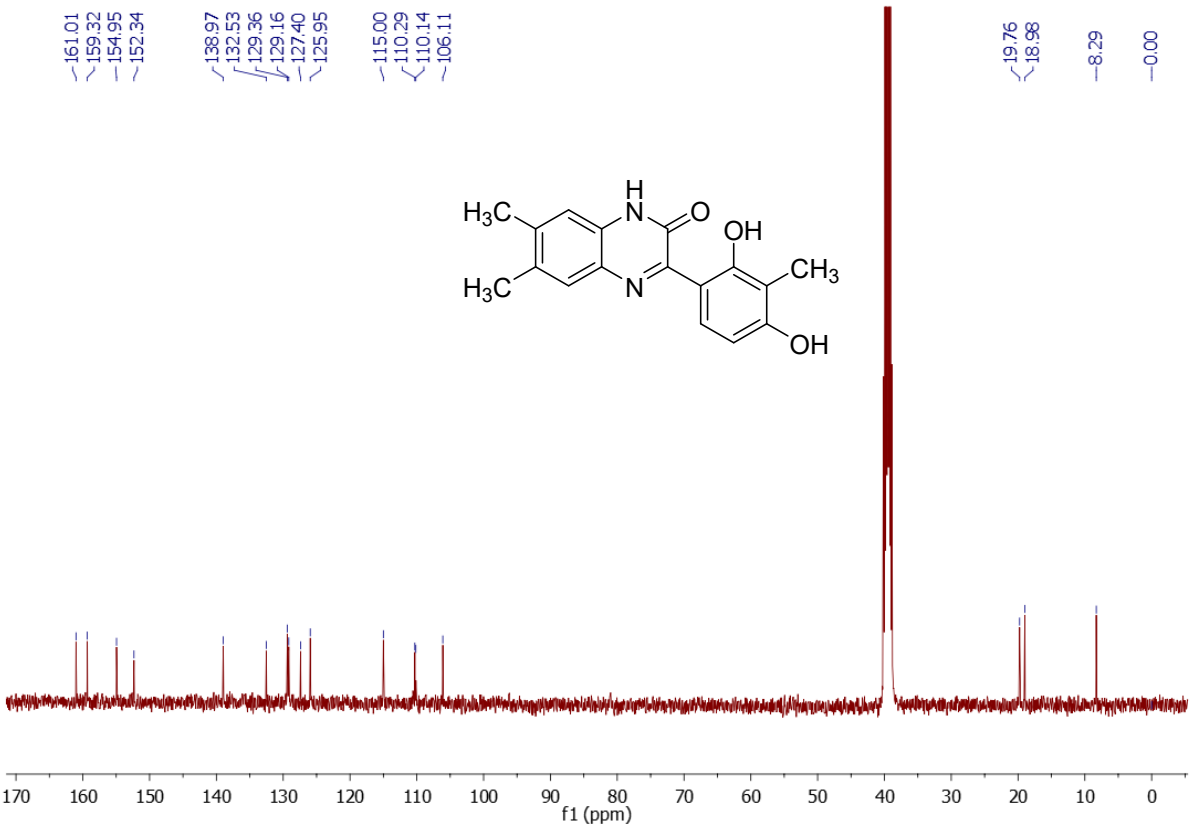

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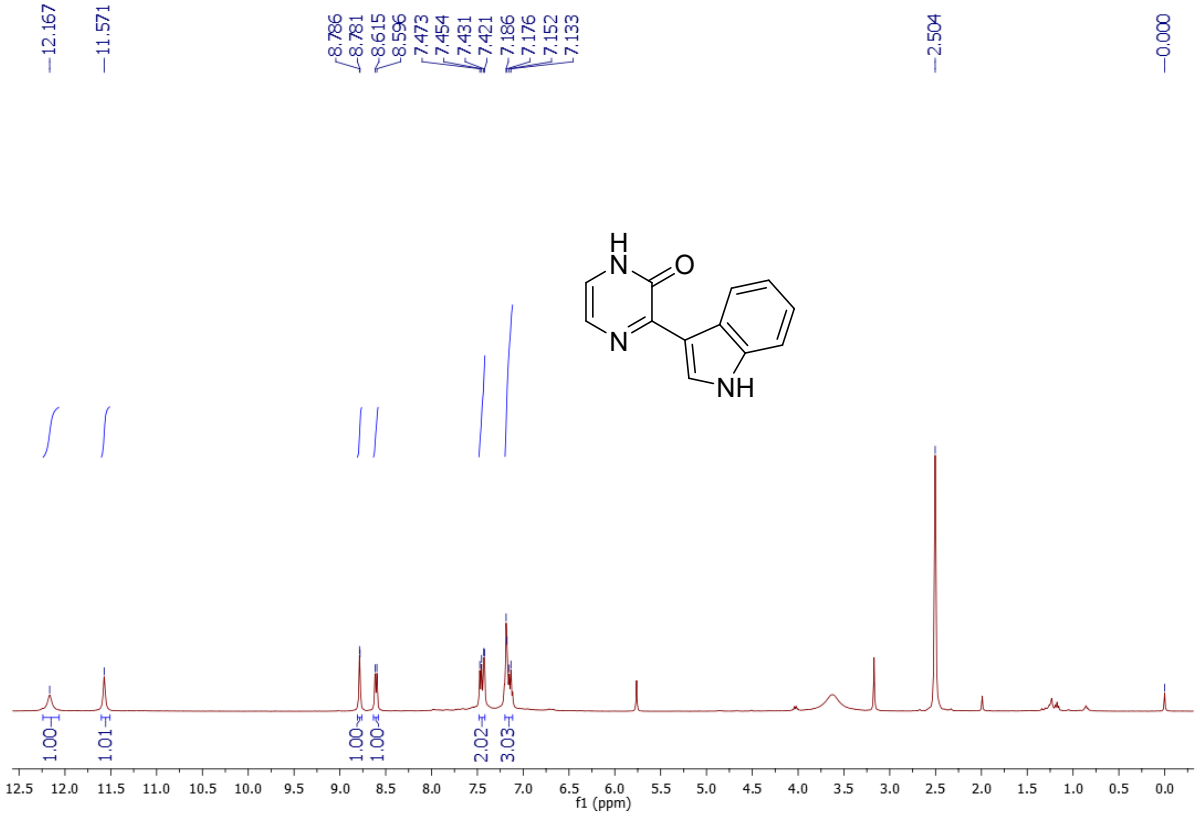

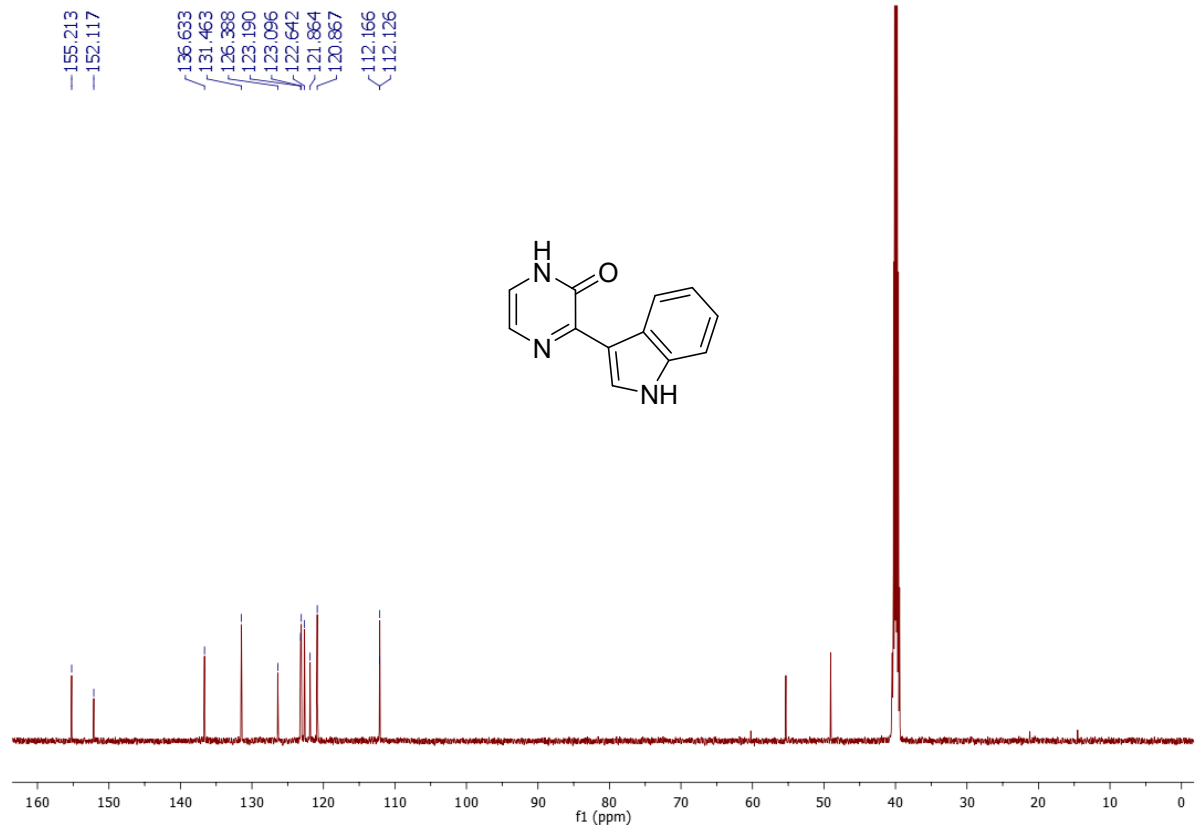

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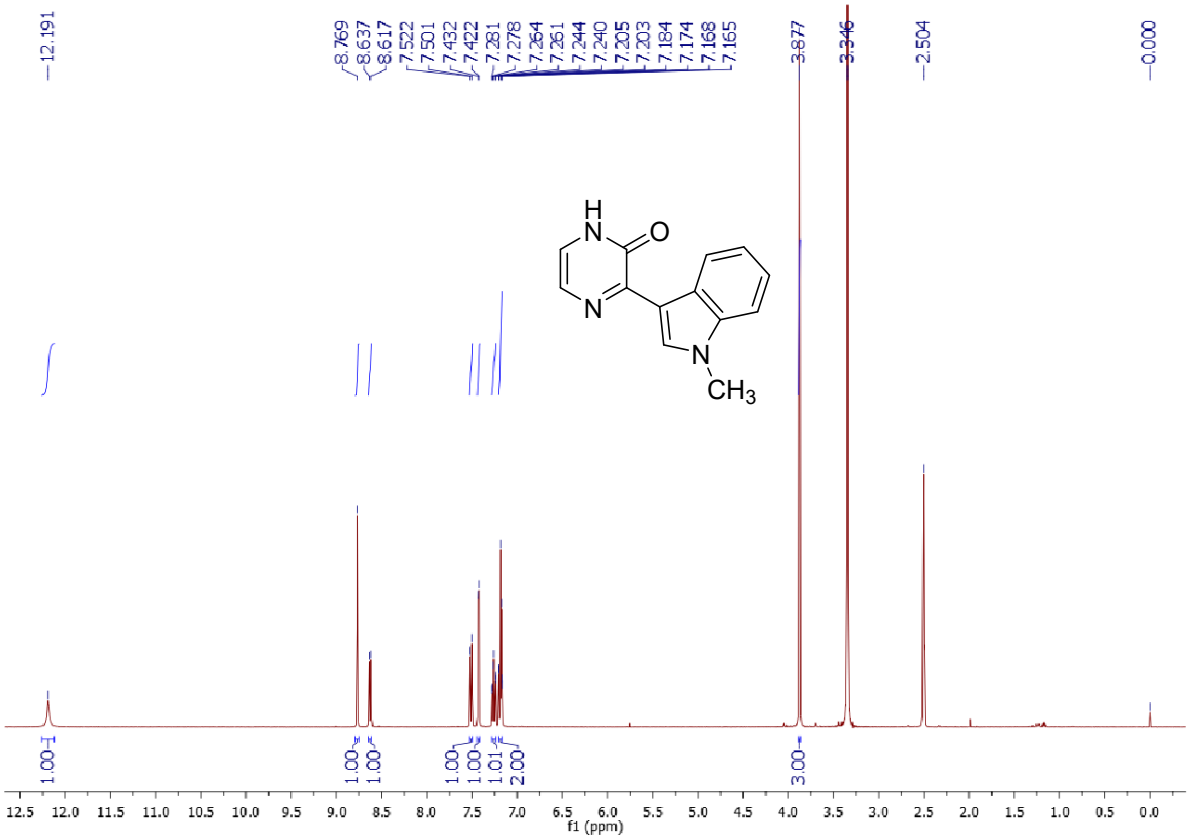

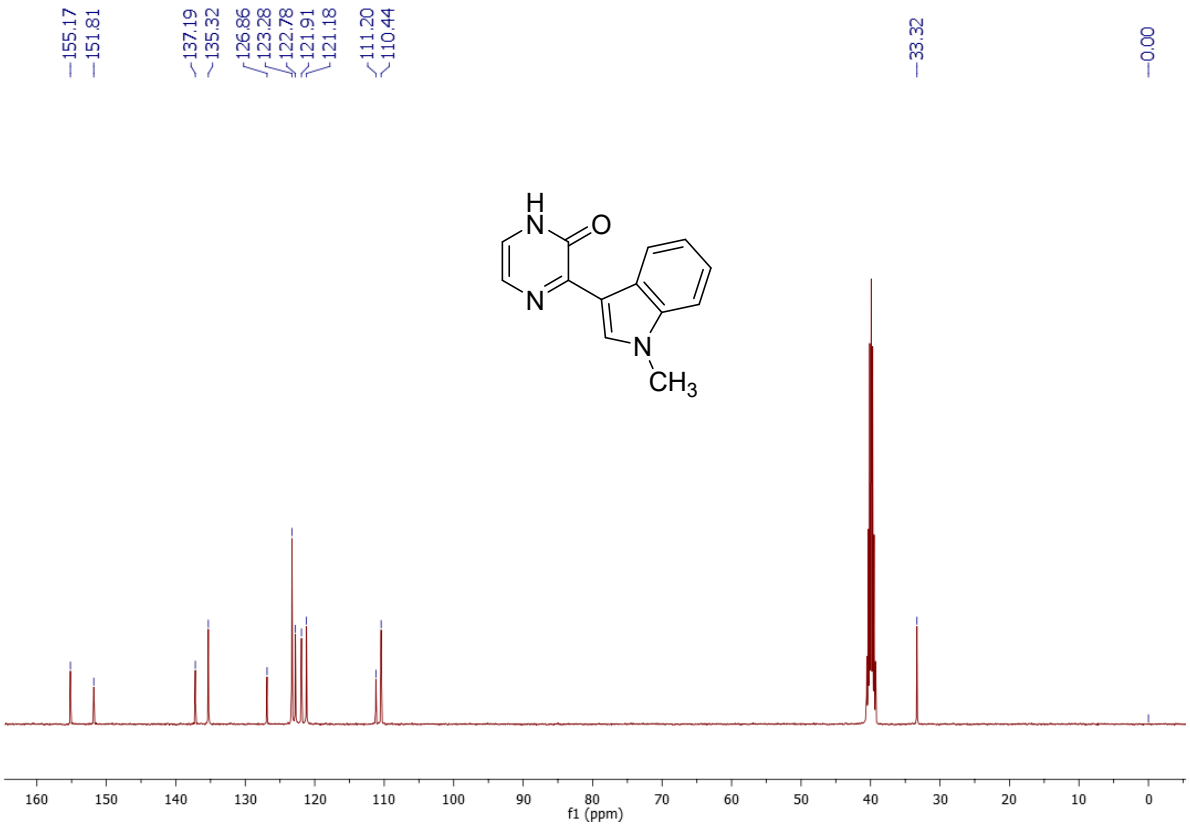

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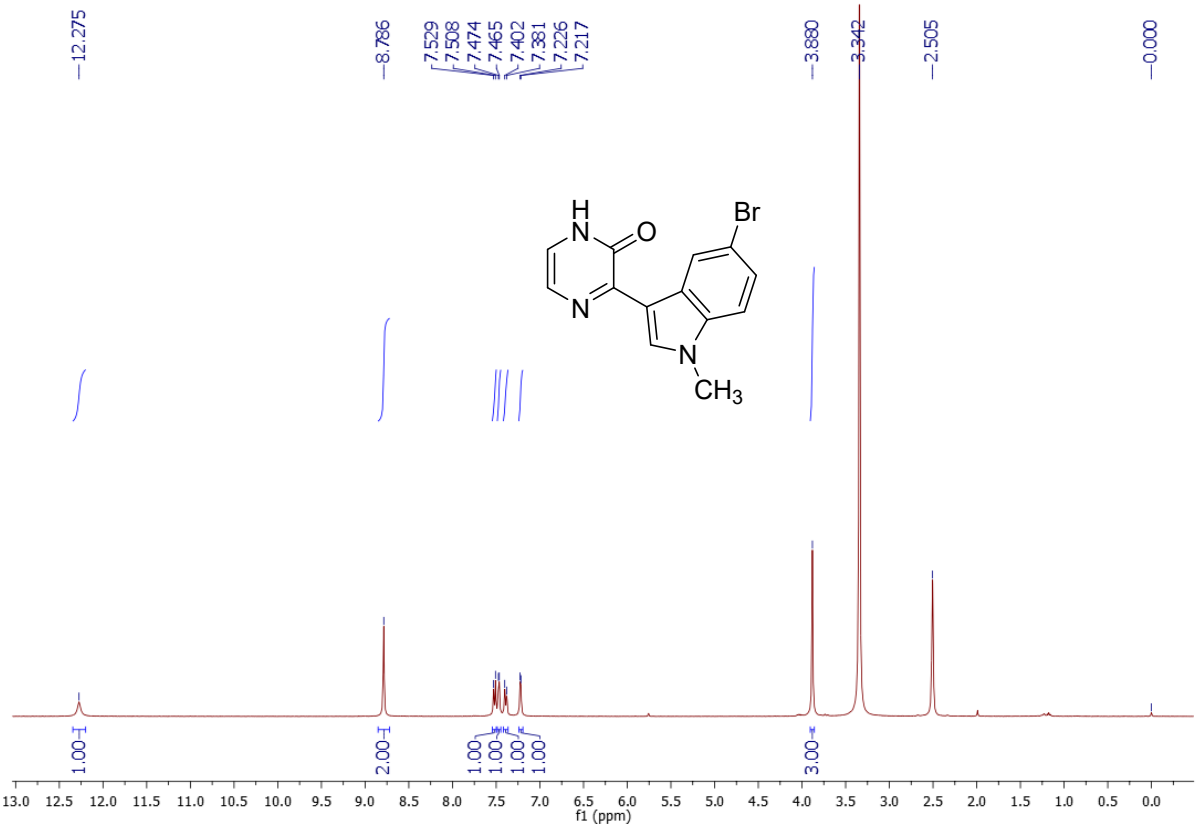

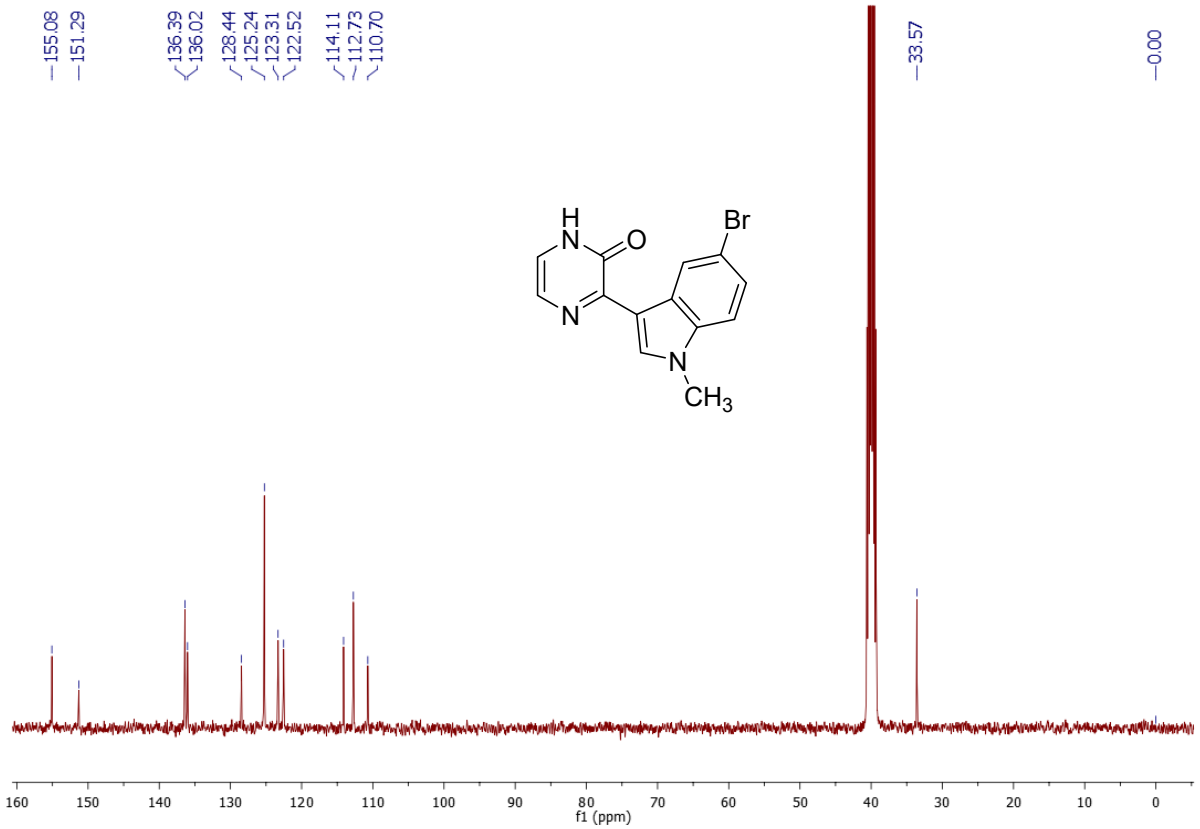

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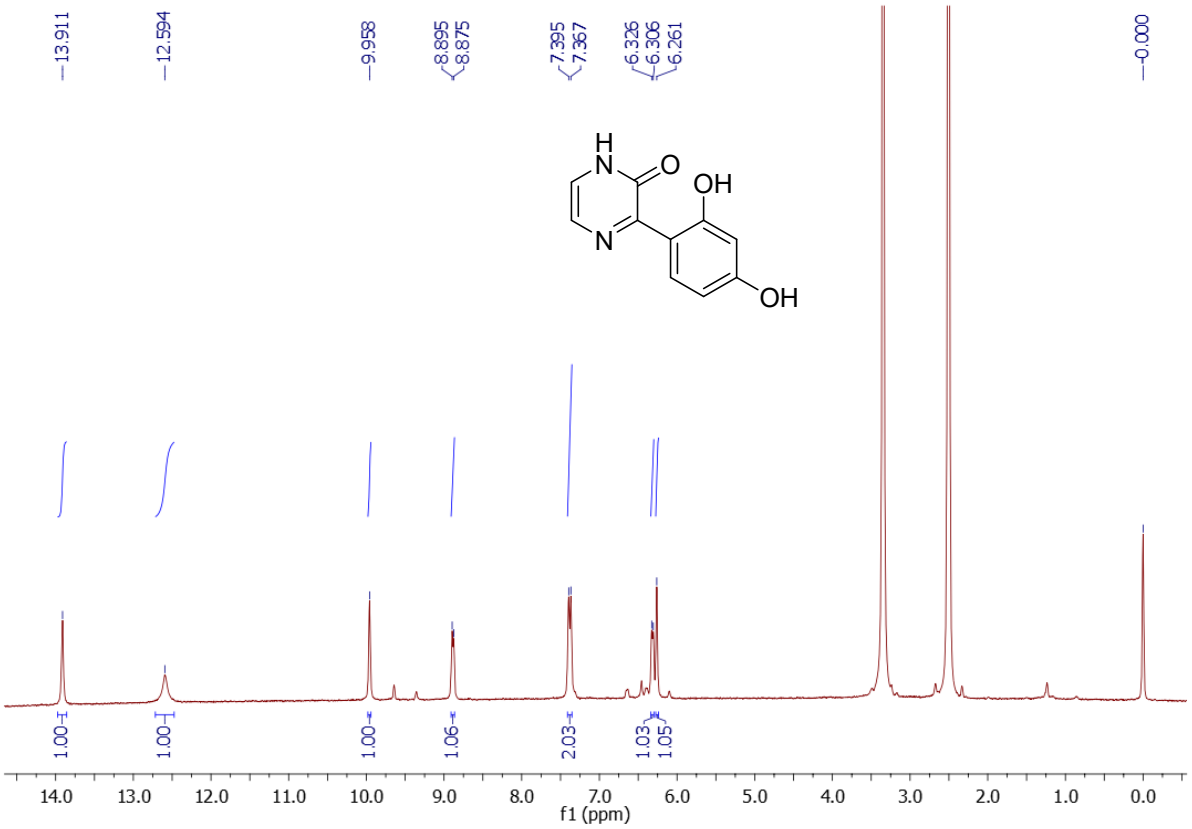

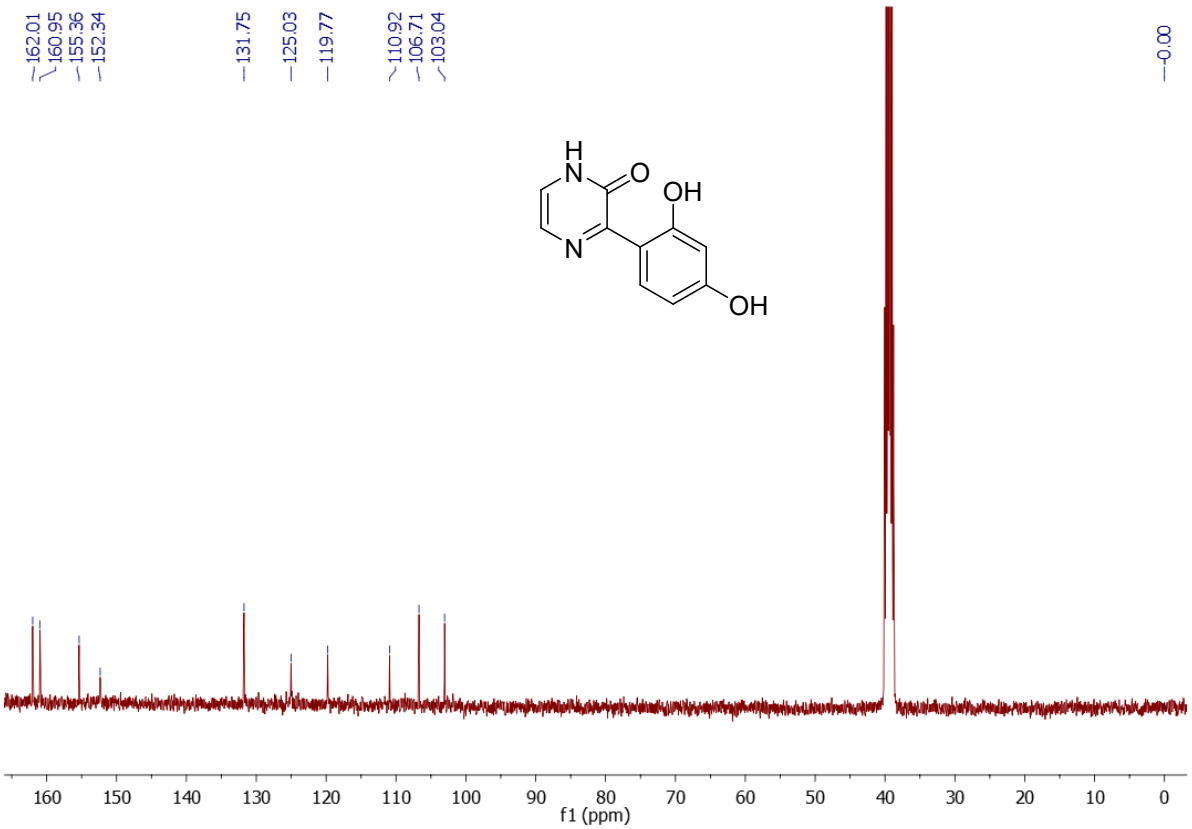

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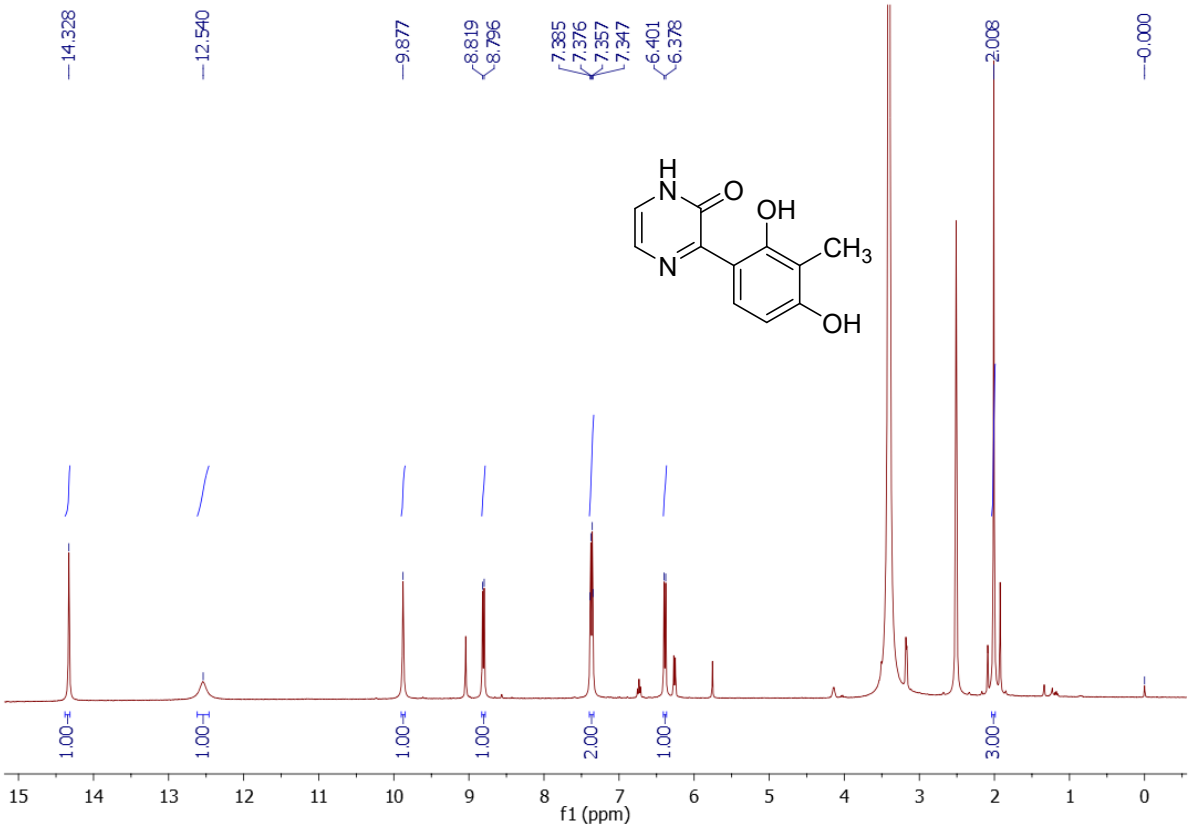

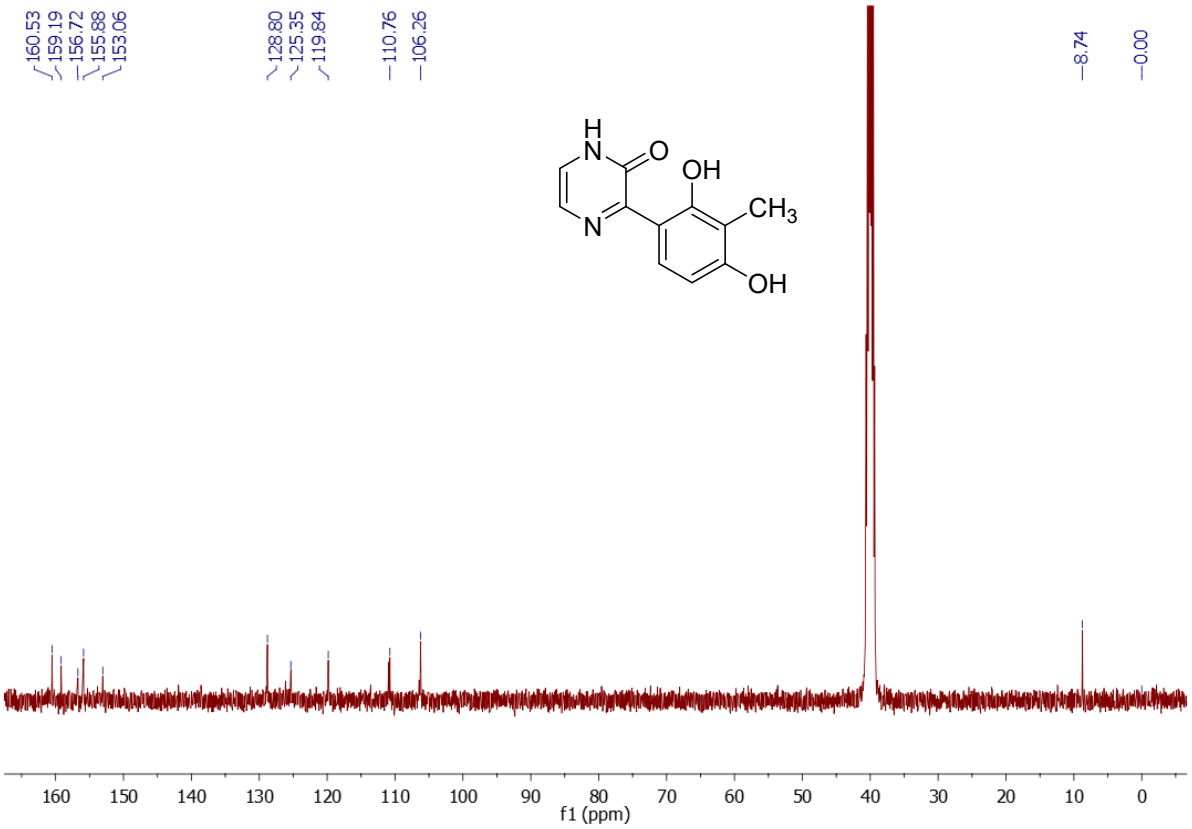

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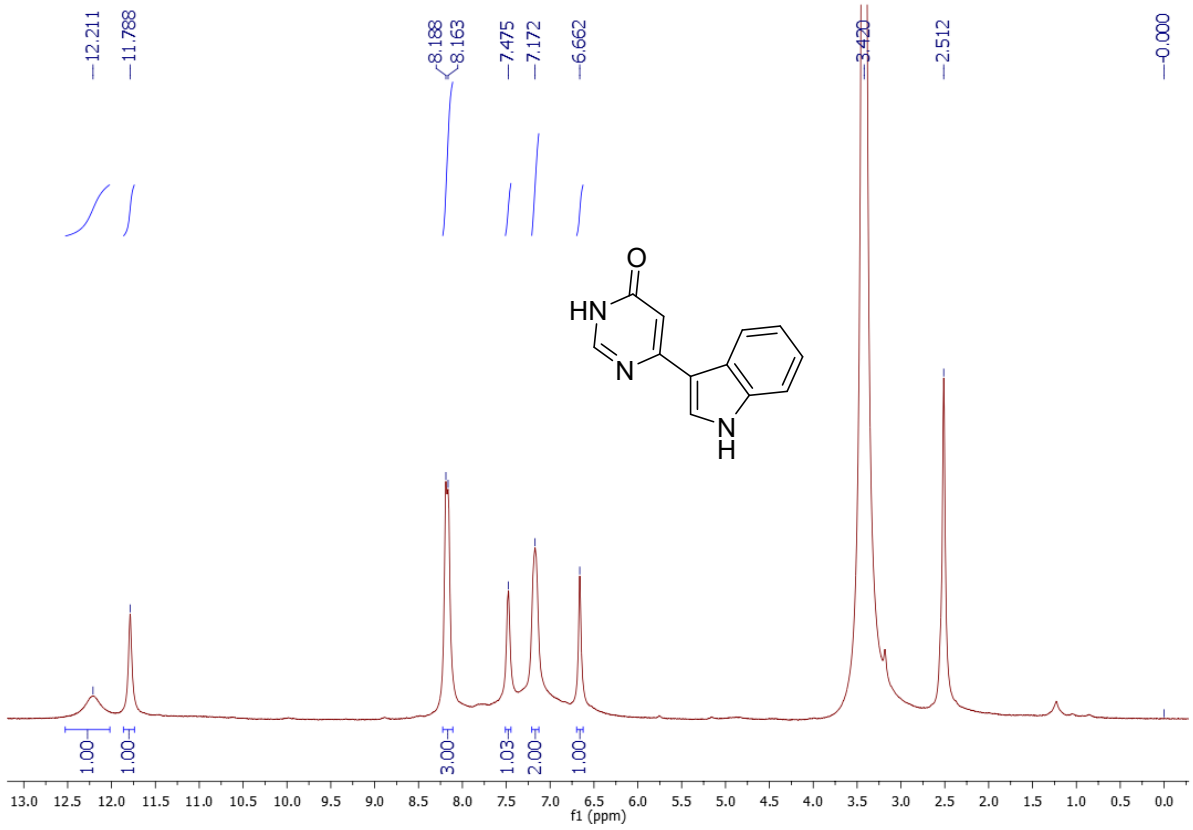

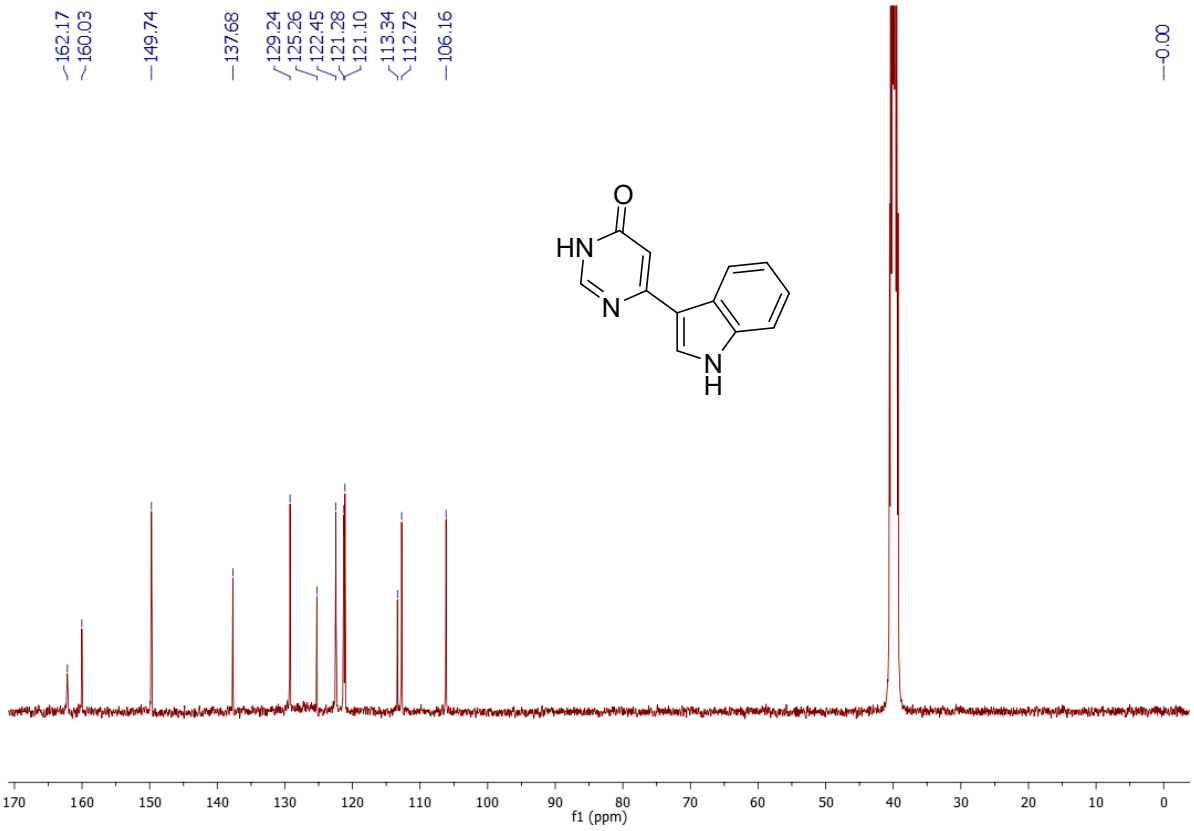

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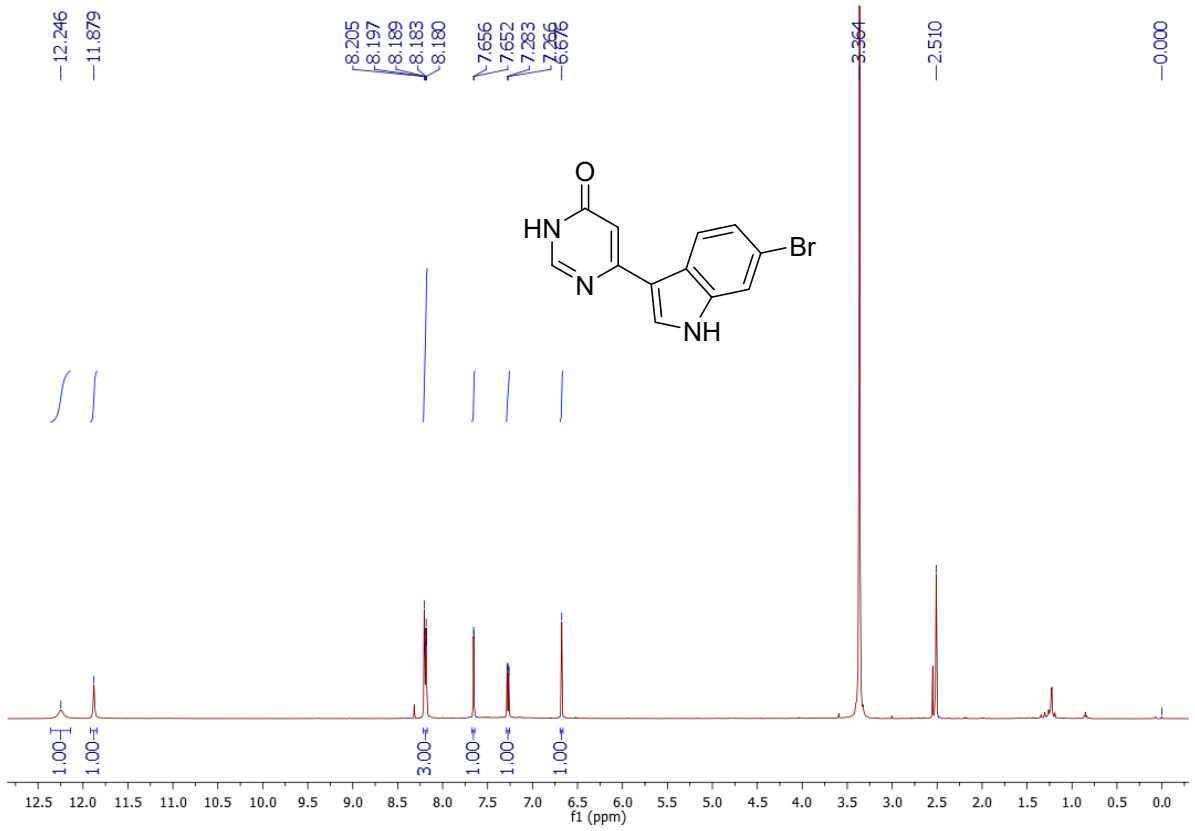

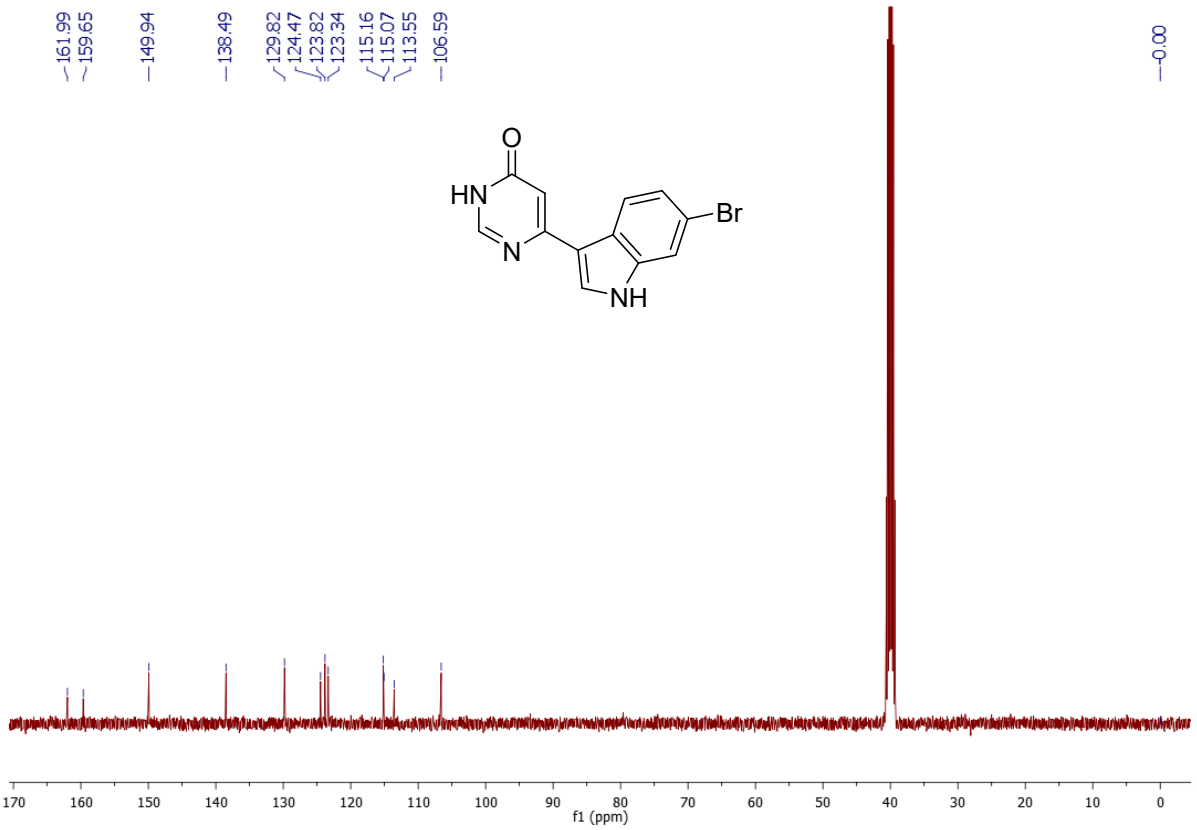

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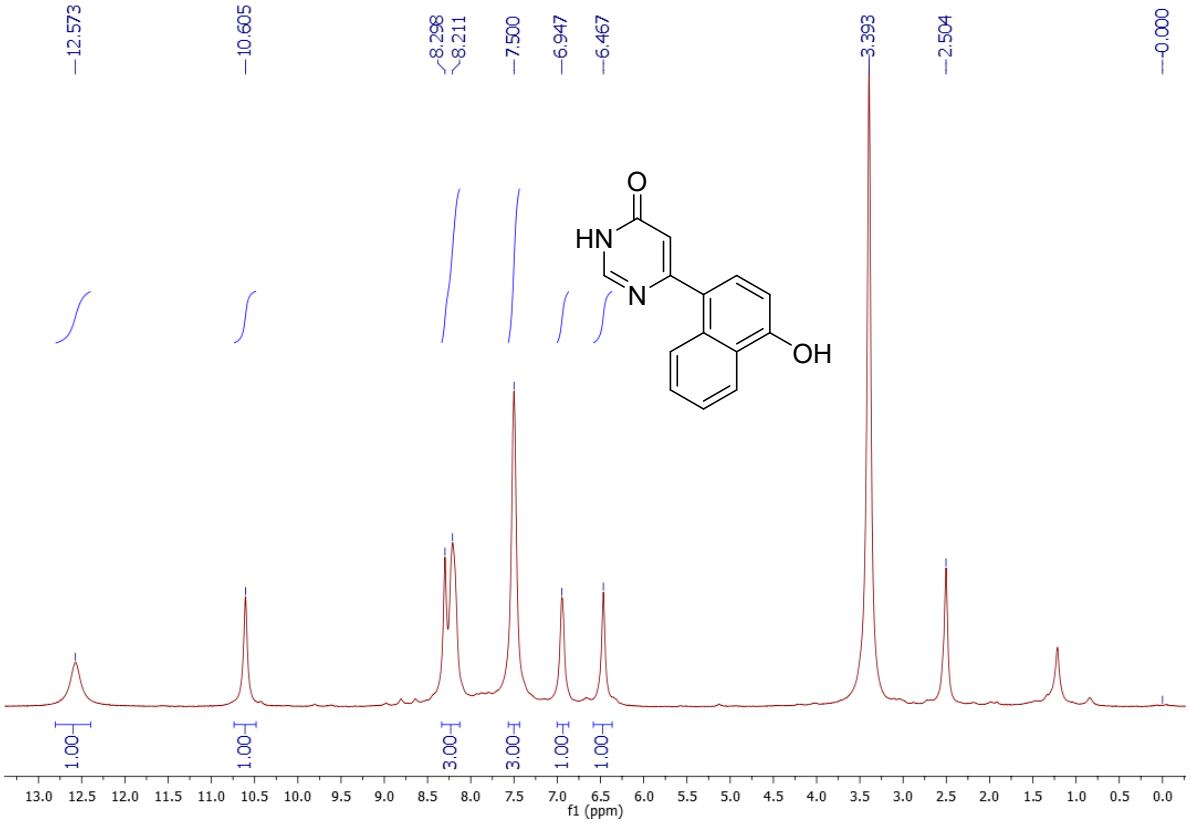

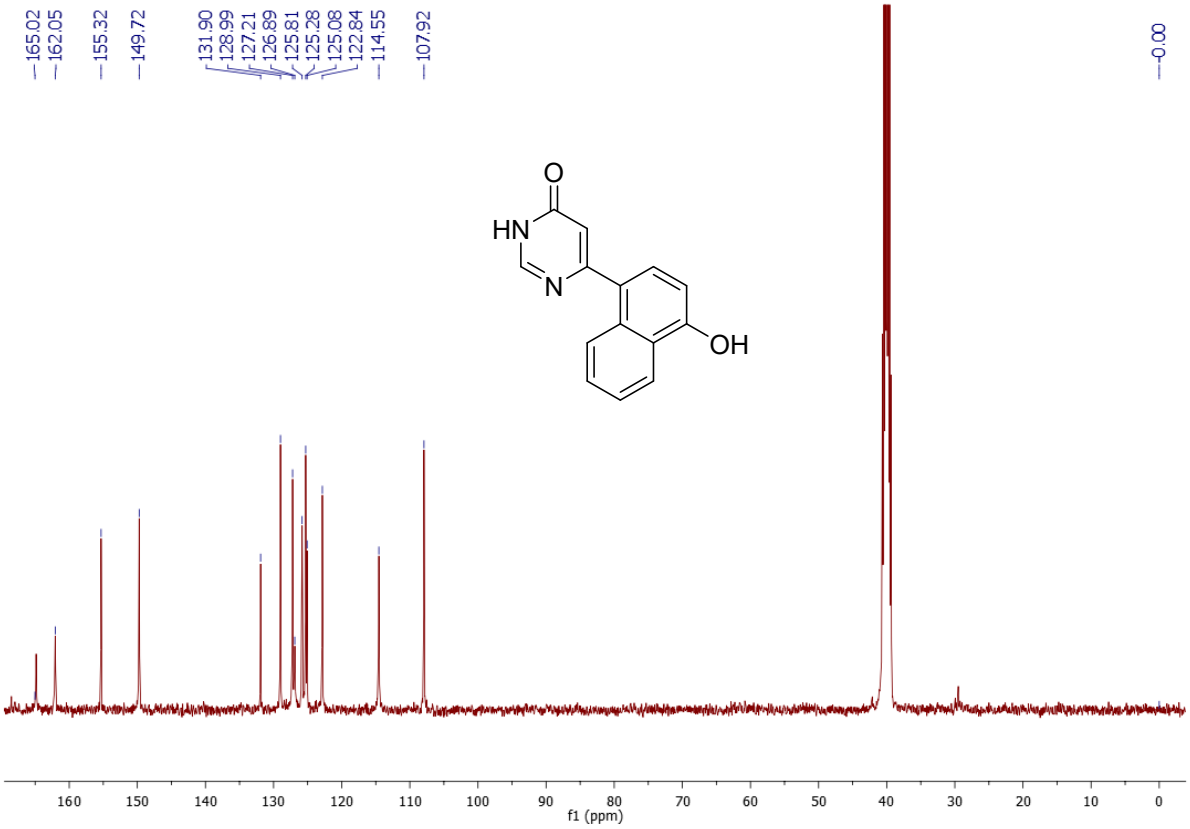

Compound 8

Compound 8