Niobium-Catalyzed Coupling Reaction of α-Keto Acids with *ortho*-Phenylenediamines: Synthesis of 3-Arylquinoxalin-2(1*H*)-ones

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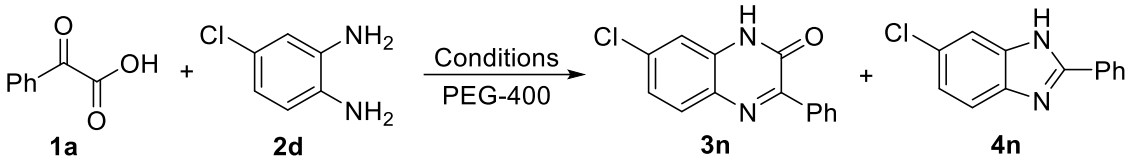
General information: The reactions were monitored by TLC carried out on pre-coated TLC sheets ALUGRAM® Xtra SIL G/UV_{254} by using UV light as visualization agent and the mixture of 5% vanillin in 10% H_2SO_4 under heating conditions as developing agent. Merck silica gel (particle size 63-200 μm) was used to flash chromatography. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400 MHz on a Bruker Avance III HD NMR 400 spectrometer. The spectra were recorded in DMSO-d_6. Coupling constants (*J*) are reported in Hertz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz on a Bruker Avance III HD NMR 400 spectrometer. The chemical shifts are reported in ppm, referenced to the solvent peak of DMSO-d_6. Mass spectra (MS) were measured on a Shimadzu GCMS-QP2010 mass spectrometer. High-resolution mass spectra were obtained on a Bruker Daltonics micrOTOF-Q II instrument equipped with an ESI and APCI source operating in both positive and negative modes. The samples were dissolved in HPLC-grade acetonitrile and injected into the APCI source by means of a syringe pump at a flow rate of 5.0 μL/min. The Compass 1.3 for micrOTOF-Q II software (Bruker daltonics, USA) was used for data acquisition, processing, and isotopic simulations. The ultrasound-promoted reactions were performed using a Cole Parmer-ultrasonic processor Model CPX 130, with a maxim power of 130 W, operating at amplitude of 20%-60% and a frequency of 20 kHz. Melting point (mp) values were measured in a Marte PFD III instrument with a 0.1 °C precision.

General procedure to prepare 3-aryl quinoxalin-2(1*H*)-ones 3a-r: In a test tube were added the α-keto acid **1** (0.3 mmol) followed by *o*-phenylenediamine **2** (0.3 mmol), ANO (5 mol%) and PEG-400 (0.5 mL). The resulting solution was sonicated for 10 minutes (20 KHz, 20% of ultrasonic amplitude). Thereafter, the reaction mixture was extracted with saturated sodium bicarbonate solution (20 mL) and ethyl acetate (3 x 10 mL). The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated under reduce

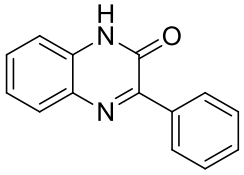
pressure. The crude material was then purified by silica gel column chromatography using hexane/ethyl acetate (85:15) mixture as eluent.

Table S1. Evaluation of the selectivity to quinoxalin-2(1*H*)-one **3k**.



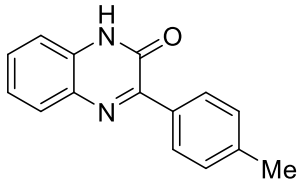
Entry	ANO (mol%)	Energy Source	**3n** Yield (%)[a]	**4n** Yield (%)[a]	(**3n** + **4n**) Overall yield (%)
1	5	US (20 %)[b]	40	35	75
2	5	US (60 %)[c]	27	40	67
3	5	oil bath[d]	25	21	46
4	none	US (20 %)[b]	28	30	58

[a] Isolated yields. [b] A mixture of **1a** (0.3 mmol) and **2d** (0.3 mmol) in PEG-400 (0.5 mL) was sonicated in an open flask for 10 min. [c] The US probe was adjusted to 60% of amplitude. [d] The reaction was performed under conventional heating (oil bath) at 70 ˚C in an open flask. [e] The US probe was adjusted to 20% of amplitude.



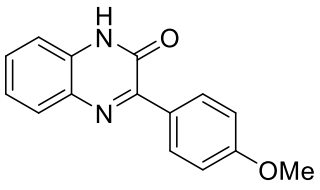
3-phenylquinoxalin-2(1*H*)-one (3a)

Yield: 64 mg (96%); white solid; mp 226 °C (dec.) (Lit.[1] 245-247 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.57 (s, 1H); 8.34–8.27 (m, 2H); 7.84 (d, J = 7.9 Hz, 1H); 7.59–7.45 (m, 4H); 7.37–7.29 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.6, 154.2, 135.6, 132.1, 132.0, 130.3, 130.2, 129.2, 128.8, 127.9, 123.4, 115.1. MS (relative intensity) *m/z*: 222 (74), 194 (100), 90 (22), 77 (21), 63 (28).



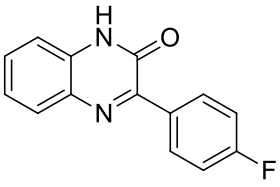
3-(*p*-tolyl)quinoxalin2-(1*H*)-one (3b)

53 mg (75%); white solid; mp 251 °C (dec.) (Lit.[2] > 250°C). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 12.53 (s, 1H); 8.26 (d, J = 8,2 Hz, 2H); 7.82 (d, J = 7,8 Hz, 1H); 7.52 (t, J = 7,7 Hz, 1H); 7.31 (dd, J = 11,4; 8,3 Hz, 4H); 3.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.6, 153.8, 140.1, 132.9, 132.0, 131.9, 130.1, 129.2, 128.6, 128.5, 123.4, 115.0, 21.1. MS (relative intensity) *m/z*: 236 (64), 208 (100), 149 (27), 117 (25), 103 (24), 97 (16), 91 (39), 83 (23).



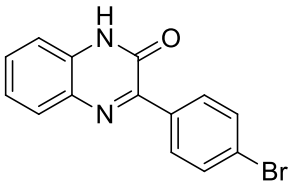
3-(4-methoxyphenyl)quinoxalin-2(1*H*)-one (3c)

Yield: 25 mg (34%); white solid; mp 270 °C (dec.) (Lit.[2] >250 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.50 (s, 1H); 8.40 (d, J = 8,9 Hz; 2H); 7.80 (d, J = 7,9 Hz; 1H); 7.54–7.45 (m, 1H); 7.37–7.25 (m, 2H); 7.04 (d, J = 8,9 Hz; 2H); 3.84 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 161.0, 154.7, 153.1, 132.1, 131.8, 131.0, 129.7, 128.5, 125.1, 123.3, 115.0, 113.3, 55.3. MS (relative intensity) *m/z*: 252 (50), 224 (32), 207 (100), 181 (27), 133 (17), 73 (52), 44 (99).



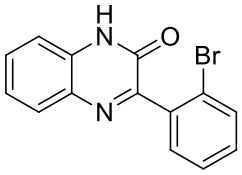
3-(4-fluorophenyl)quinoxalin-2(1*H*)-one (3d)

Yield: 60 mg (84%); yellow solid; mp 275 °C (dec.) (Lit.[2] 247-248 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.60 (s, 1H); 8.47–8.35 (m, 2H); 7.83 (d, J = 8,0 Hz; 1H); 7.59–7.49 (m, 1H); 7.38–7.26 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 163.4 (d, $^{1}J_{C\text{-}F}$ = 248,4 Hz), 154.6, 152.9, 132.1, 132.1, 132.1, 132.9, 131.7 (J = 8.6 Hz), 130.4, 128.7, 123.5, 115.1, 114.8 (J = 21.5 Hz). MS (relative intensity) *m/z*: 240 (70), 212 (100), 107 (10), 90 (18), 75 (10), 64 (31), 52 (10).



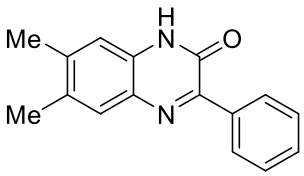
3-(4-bromophenyl)quinoxalin2-(1*H*)-one (3e)

Yield: 63 mg (70%); yellow solid; mp 275 °C (dec.) (Lit.[2] >250 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.63 (s, 1H); 8.30 (d, J = 8,6 Hz; 2H); 7.84 (d, J = 8,0 Hz; 1H); 7.70 (d, J = 8,6 Hz; 2H); 7.59–7.51 (m, 1H); 7.39–7.28 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.5, 152.8, 134.7, 132.1, 131.9, 131.2, 130.9, 130.6, 128.8, 124.0, 123.5, 115.2. MS (relative intensity) *m/z*: 300 (82), 272 (78), 193 (100), 111 (45), 90 (42), 63 (41), 44 (51).



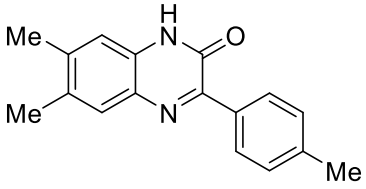
3-(2-bromophenyl)quinoxalin-2(1*H*)-one (3f)

Yield: 72 mg (82%); yellow solid; mp 248 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.64 (s, 1H); 7.81 (dd, J = 8.0, 1.0 Hz, 1H); 7.72 (d, J = 8.0 Hz, 1H); 7.63–7.56 (m, 1H); 7.55–7.47 (m, 2H); 7.45–7.30 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 158.4, 153.7, 137.6, 132.5, 132.2, 131.6, 130.9, 130.8, 130.7, 128.9, 127.4, 123.5, 121.7, 115.5. MS (relative intensity) *m/z*: 300 (1), 221 (100), 193 (21), 110 (10), 90 (16), 63 (11). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{10}BrN_2O$, 300.9898; found, 300.9895.



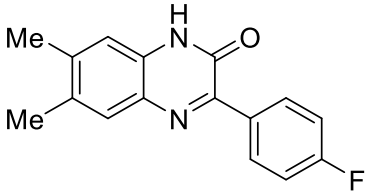
6,7-dimethyl-3-phenylquinoxalin-2(1*H*)-one (3g)

Yield: 63 mg (85%); yellow solid; mp 261 °C (dec.) (Lit.[3] >250 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.43 (s, 1H); 8.32–8.24 (m, 2H); 7.59 (s, 1H); 7.50–7.44 (m, 3H); 7.08 (s, 1H); 2.34–2.27 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.7, 152.8, 140.1, 135.9, 132.1, 130.6, 130.1, 129.9, 129.1, 128.6, 127.9, 115.1, 19.9, 18.9. MS (relative intensity) *m/z*: 250 (22), 221 (14), 207 (100), 191 (14), 133 (14), 73 (47), 44 (98).



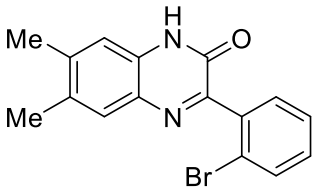
6,7-dimethyl-3-(*p*-tolyl)quinoxalin-2(1*H*)-one (3h)

Yield: 63 mg (80%); yellow solid; mp 223 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.38 (s, 1H); 8.25 (d, J = 8.2 Hz, 1H); 7.56 (s, 1H); 7.27 (d, J = 8.2 Hz, 2H); 7.06 (s, 1H); 2.36 (s, 3H); 2.32–2.25 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.7, 152.4, 139.6, 133.1, 132.0, 130.6, 129.9, 130.0, 129.0, 128.4, 126.1, 115.0, 21.0, 19.8, 19.0. MS (relative intensity) *m/z*: 264 (100), 236 (74), 118 (13), 91 (24), 65 (10). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O$, 265.1335; found, 265.1336.



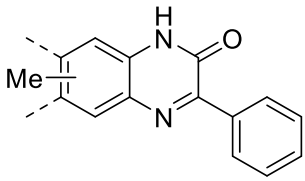
3-(4-fluorophenyl)-6,7-dimethylquinoxalin-2(1*H*)-one (3i)

Yield: 73 mg (91%); yellow solid; mp 291 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.47 (s, 1H); 8.44–8.36 (m, 2H); 7.59 (s, 1H); 7.34–7.26 (m, 2H); 7.08 (s, 1H); 2.31 (s, 3H); 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 163.2 (d, $^{1}J_{C\text{-}F}$ = 248.0 Hz), 154.6, 151.4, 140.1, 132.3 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 132.2, 131.5 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 130.5, 130.1, 128.5, 115.1, 114.8 (d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 19.8, 19.0. ^{19}F NMR (376 MHz, DMSO-d_6) δ (ppm) 110.90 (dt, $^{4}J_{C\text{-}F}$ = 5.6 Hz, $^{3}J_{C\text{-}F}$ = 8.6 Hz). MS (relative intensity) *m/z*: 268 (100), 240 (73), 225 (73), 118 (10), 91 (31), 65 (15). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{14}FN_2O$, 269.1090; found, 269.1086.



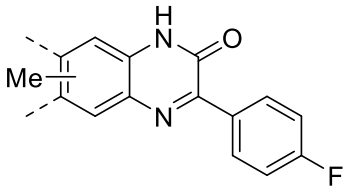
3-(2-bromophenyl)-6,7-dimethylquinoxalin-2(1*H*)-one (3j)

Yield: 49 mg (50%); white solid; mp 269 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.45 (s, 1H); 7.69 (d, J = 7.9 Hz; 1H); 7.55 (s, 1H); 7.49–7.45 (m, 2H); 7.43–7.35 (m, 1H); 7.12 (s, 1H); 2.31 (s, 3H); 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 157.2, 153.9, 140.9, 138.0, 132.5, 132.4, 131.0, 130.8, 130.6, 130.4, 128.8, 127.6, 122.1, 115.6, 20.0, 19.1. MS (relative intensity) *m/z*: 328 (2), 249 (100), 207 (24), 117 (10), 91 (9), 73 (11), 44 (19). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{14}BrN_2O$, 329.0284; found, 329.0287.



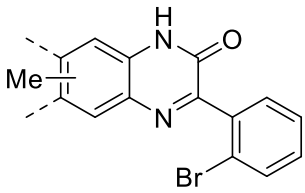
7-methyl-3-phenylquinoxalin-2(1H)-one and 6-methyl-3-phenylquinoxalin-2(1H)-one (3k:3k*)

After the column chromatography, it was obtained a yellow solid as an inseparable mixture of isomers **3k** and **3k*** (1.3:1) in 83% yield.[4] ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.51 (s, 1H); 8.33–8.26 (m, 2H); 7.72 (d, J = 8.2 Hz, 0.6H); 7.65 (s, 0.5H); 7.57–7.43 (m, 5H); 7.24 (d, J = 8.2 Hz, 0.5H); 7.19–7.07 (m, 1.2H); 2.44–2.85 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.7, 154.5, 153.9, 152.9, 140.6, 135.7, 132.7, 132.0, 131.5, 130.3, 130.1, 130.0, 129.2, 129.1, 128.9, 128.5, 128.3, 127.8, 126.3, 124.8, 114.8, 114.7, 21.3, 20.4.



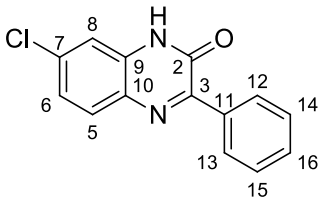
3-(4-fluorophenyl)-7-methylquinoxalin-2(1H)-one and 3-(4-fluorophenyl)-6-methylquinoxalin-2(1H)-one (3l:3l*)

After the column chromatography, it was obtained a white solid as an inseparable mixture of isomers **3l** and **3l*** (1.5:1) in 89% yield.[4] ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.51 (s, 1 H); 8.44–8.34 (m, 2 H); 7.68 (d, 8.0 Hz, 0.6H); 7.61 (s, 0.45H); 7.37–7.25 (m, 3H); 7.22 (d, J = 8.2 Hz, 0.45H); 7.16–7.06 (m, 1H) 2.42–2.34 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 165.5, 164.4, 154.7, 154.5, 152.5, 151.5, 140.6, 132.7, 132.2, 132.2, 132.1, 132.0, 131.9, 131.9, 131.6, 131.5, 131.5, 130.2, 129.8, 128.4, 128.2, 124.8, 115.7, 115.5, 114.9, 114.7, 21.3, 20.4.



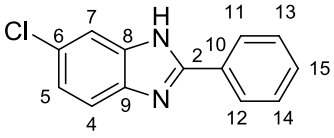
3-(2-bromophenyl)-7-methylquinoxalin-2(1H)-one and 3-(2-bromophenyl)-6-methylquinoxalin-2(1H)-one (3m:3m*)

After the column chromatography, it was obtained a white solid as an inseparable mixture of isomers **3m** and **3m*** (1.5:1) in 73% yield.[4] ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.57 (s, 1H); 7.77–7.65 (m, 2H); 7.61 (s, 0.4H); 7.56–7.34 (m, 4H); 7.27 (d, J = 8.2 Hz, 0.4 H); 7.19–7.10 (m, 1H); 2.42 (s, 1.8 H); 2.38 (s, 1.2H) . ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 158.3, 157.2, 153.8, 153.6, 141.3, 137.8, 132.8, 132.4, 132.2, 132.0, 131.6, 130.9, 130.8, 130.6, 130.6, 130.2, 129.9, 128.6, 128.5, 127.4, 124.8, 121.9, 121.8, 115.2, 115.0, 21.3, 20.4.



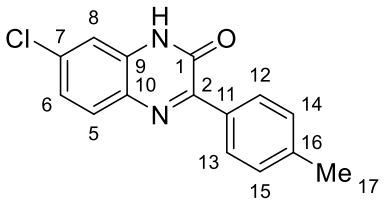
7-chloro-3-phenylquinoxalin-2(1*H*)-one (3n)

Yield: 32 mg (40%); white solid; mp 225 °C (dec.) (Lit.[5] 274- 275 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.70 (1H, br s, NH); 8.31–8.28 (2H, m, 12-H, 13-H); 7.89 (1H, d, J = 2.3 Hz, 8-H); 7.59 (1H, dd, J = 8.7, 2.4 Hz, 6-H); 7.52–7.46 (3H, m, 14-H,15-H,16-H); 7.35 (1H, d, J = 8.7 Hz, 5-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 155.3 (C=N), 154.3 (C=O), 135.2 (C-16), 132.5 (C-Cl), 131.0 (C-10), 130.5 (C-16), 130.1 (C-6), 129.3 (C-12, C-13), 127.9 (C-14, C-15), 127.6 (C-8), 126.9 (C-9), 116.7 (C-5). ^{15}N NMR (40 MHz, DMSO-d_6) δ (ppm) 226.7 (5-H). MS (relative intensity) *m/z*: 256 (74), 228 (100), 192 (12), 166 (10), 90 (15), 77(18), 63 (28), 51 (10).



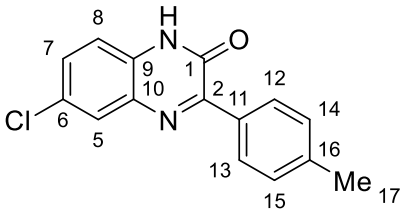
6-chloro-2-phenyl-1*H*-benzo[*d*]imidazole (4n)

Yield: 26 mg (35%); yellow solid; mp 215 °C (dec.) (Lit.[6] 285 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.60 (1H, br s, NH); 8.29–8.27 (2H, m, 11-H, 12-H); 7.82–7.80 (1H, m, 5-H); 7.53–7.46 (3H, m, 13-H, 14-H, 15-H); 7.33–7.30 (2H, m, 5-H, 7-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.3 (C=N), 135.3 (C-10), 134.3 (C-Cl), 133.1 (C-8), 130.8 (C-9), 130.4 (C-15), 130.4 (C-4), 129.2 (C-11, C-12), 127.9 (C-13, C-14), 123.5 (C-5), 114.3 (C-7). ^{15}N NMR (40 MHz, DMSO-d$_6$) δ (ppm) 326,5 (4-H), 153,4 (7-H). MS (relative intensity) *m/z*: 228 (100), 256 (73), 192 (11), 166 (10), 124 (9), 114 (9), 104 (11), 90 (19).



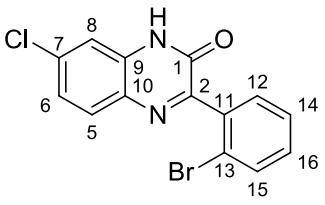
7-chloro-3-(*p*-tolyl)quinoxalin-2(1*H*)-one (3o)

Yield: 38 mg (47%); white solid; mp 270 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.50 (1H, br s, NH); 8.24 (2H, d, J = 8,0 Hz, 12-H,13-H); 7.81 (1H, d, J = 8,4 Hz, 5-H); 7.34–7.28 (4H, m, 6-H, 8-H, 14-H, 15-H); 2.38 (3H, s, 17-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 154.4, 154.0, 140.3, 134.0, 132.9, 132.6, 130.8, 130.3, 129.2, 128.5, 123.4, 114.3, 21.1. ^{15}N NMR (40 MHz, DMSO-d_6) δ (ppm) 324.2 (5-H), 153.4 (8-H). MS (relative intensity) *m/z*: 270 (84), 242 (100), 107 (19), 134 (18), 116 (10), 103 (13), 90 (14). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{12}ClN_2O$, 271.0633; found, 271.0629.



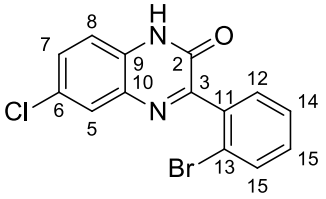
6-chloro-3-(*p*-tolyl)quinoxalin-2(1*H*)-one (3o*)

Yield: 30 mg (38%); yellow solid; mp 241 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.63 (1H, br s, NH); 8.25 (2H, d, J = 8.2 Hz, 12-H, 13-H); 7.86 (1H, d, J = 2.3 Hz, 5-H); 7.56 (1H, dd, J = 8.7, 2.4 Hz, 7-H); 7.31 (3H, t, J = 8.2 Hz, 8-H, 14-H, 15-H); 2.38 (3H, s, 17-H). ^{13}C RMN (100 MHz, DMSO-d_6) δ (ppm) 155.1, 154.4, 140.6, 132.6, 132.5, 130.9, 129.9, 129.3, 128.5, 127.5, 126.9, 116.7, 21.1. **^{15}N NMR (40 MHz, DMSO-d_6):** δ 323.6 (5-H), 153.1 (8-H). MS (intensidade relativa) *m/z*: 270 (84), 242 (100), 207 (18), 134 (19), 116 (9), 103 (17), 90 (18). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{12}ClN_2O$, 271.0633; found, 271.0630.



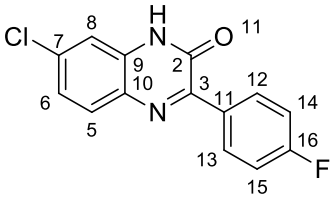
3-(2-bromophenyl)-7-chloroquinoxalin-2(1*H*)-one (3p)

Yield: 64 mg (64%); white solid; mp 243 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.72 (1H, br s, NH); 7.82 (1H, d, J = 9.2 Hz, 5-H); 7.72 (1H, d, J = 7.6 Hz, 12-H); 7.58–7.46 (2H, m, 15-H, 16-H); 7.42 (1H, td, J = 7.6, 2.1 Hz, 14-H); 7.38–7.33 (2H, m, 8-H, 6-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 158.7 (C=N), 153.4 (C=O), 137.3 (C-11), 135.0 (C-Cl), 133.5 (C-10), 132.3 (C-12), 132.2 (C-14), 130.9 (C-5), 130.6 (C-9), 130.4 (C-15), 127.4 (C-16), 123.6 (C-8), 121.6 (C-Br), 114.7 (C-6). ^{15}N NMR (40 MHz, DMSO-d_6) δ (ppm) 334.4 (5-H), 151.9 (8-H). MS (relative intensity) *m/z*: 336 (3), 255 (100), 192 (24), 127 (20), 124 (14), 96 (8). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_9BrClN_2O$, 336.9559; found, 336.9557.



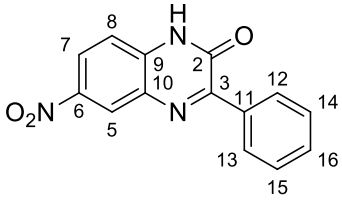
3-(2-bromophenyl)-6-chloroquinoxalin-2(1*H*)-one (3p*)

Yield: 26 mg (28%); yellow solid; mp 236.8 °C (dec.) ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.77 (1H, br s, NH); 7.89 (1H, d, J = 2.3 Hz, 5-H); 7.72 (1H, d, J = 7.9 Hz, 12-H); 7.65 (1H, dd, J = 8.8, 2.3 Hz, 7-H), 7.55 - 7.48 (2H, m, 15-H, 16-H); 7.47 - 7.38 (1H, m, 14-H), 7.38 (1H, d, J = 8.8 Hz, 8-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 159.86 (C=N), 153.51 (C=O), 137.31 (C-Br), 132.27 (C-Cl), 132.22 (C-9), 131.51 (C-11), 131.00 (C-7), 130.89 (C-15), 127.94 (C-8), 127.55 (C-5), 127.22 (C-12), 121.64 (C-10), 117.24 (C-14). ^{15}N NMR (40 MHz, DMSO-d_6) δ (ppm) 146.0 (8-H). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_9BrClN_2O$, 334.9587; found, 334.9588.



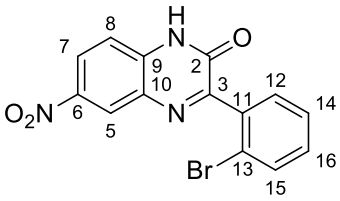
7-chloro-3-(4-fluorophenyl)quinoxalin-2(1*H*)-one (3q)

Yield: 48 mg (58%); white solid; mp 277 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.65 (1H, br s, NH); 8.41–8.38 (2H, m, 14-H, 15-H); 7.84 (1H, d, J = 8.5 Hz, 5-H); 7.37–7.31 (4H, m, 6-H, 8-H, 12-H, 13-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 163.45 (d, $^{1}J_{C\text{-}F}$ = 249.2 Hz, C-F), 154.36 (C=N), 153.16 (C=O), 134.33 (C-9), 133.07 C-Cl), 131.75 (d, $^{2}J_{C\text{-}F}$ = 8.7 Hz, C-12, C-13), 130.71 (C-10), 130.39 (C-5), 123.56 (C-8), 114.91 (d, $^{3}J_{C\text{-}F}$ = 21.5 Hz, C-14, C-15), 114.35 (C-6). ^{15}N NMR (40 MHz, DMSO-d$_6$) δ (ppm) 325,2 (5-H), 153.2 (8-H). ^{19}F NMR (376 MHz, DMSO-d_6) δ (ppm) 110.03 (dt, $^{4}J_{C\text{-}F}$ = 7.5 Hz; $^{3}J_{C\text{-}F}$ = 11.2 Hz). MS (relative intensity) m/z: 274 (68), 246 (100), 184 (11), 124 (12), 90 (16), 63 (33). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_9ClFN_2O$, 275.0388; found, 275.0386.



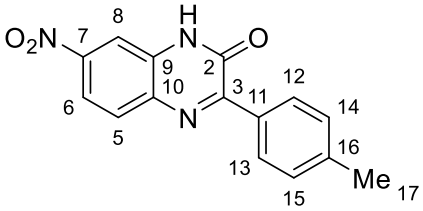
6-nitro-3-fenilquinoxalin-2(1*H*)-ona (3r*)

Yield: 30 mg (37%). yellow solid. mp: 279 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.86 (1H, br s, NH); 8.36–8.33 (2H, m, 12-H, 13-H); 8.13 (1H, d, J = 2.3 Hz, 5-H); 8.10–8.07 (1H, m,7-H); 8.04 (1H, d, J = 8.7 Hz, 5-H); 7.59–7.50 (3H, m, 14-H, 15-H, 16-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 158.1 (C=N), 155.0 (C=O), 147.6 (C-9), 136.1 (C-NO_2), 134.8 (C-10), 131.8 (C-11), 131.5 (C-16), 130.3 (C-8), 129.8 (C-12, C-13), 128.3 (C-14, C-15), 118.2 (C-7), 111.0 (C-5). ^{15}N NMR (40 MHz, DMSO-d$_6$) δ (ppm) 368.9 (5-H), 323.2, (7-H) 156.9 (8-H). MS (relative intensity) m/z: 267 (100), 239 (45), 209 (92), 193 (39), 166 (43), 104 (66), 90 (80).



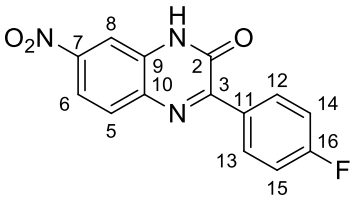
3-(2-bromophenyl)-6-nitroquinoxalin-2(1*H*)-one (3s*)

Yield: 29 mg (28%); white solid; mp 257 °C (dec.).^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 13.16 (1H, br s, NH); 8.60 (1H, d, J = 2.5 Hz, 5-H); 8.42 (1H, dd, J = 9.1, 2.5 Hz, 7-H); 7.74 (1H, d, J = 7.6 Hz, 16-H); 7.58–7.51 (3H, m, 14-H, 12-H, 8-H); 7.45 (1H, td, J = 7.7, 2.0 Hz, 15-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 160.8 (C=N), 153.6 (C=O), 142.7 (C-NO_2), 137.6 (C-9), 136.8 (C-11), 132.3 (C-12), 131.2 (C-14), 130.9 (C-16), 130.4 (C-10), 127.5 (C-15), 125.5 (C-7), 124.5 (C-5), 121.5 (C-Br), 116.6 (C-8). ^{15}N NMR (40 MHz, DMSO-d_6) δ (ppm) 369,1 (5-H, 7-H, 8-H), 333,4 (5-H), 160,6 (8-H). MS (relative intensity) *m/z*: 345 (3), 266 (100), 220 (31), 192 (11), 165 (6), 102 (7), 90 (18). HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{14}H_9BrN_3O_3$, 345.9822; found, 345.9810.



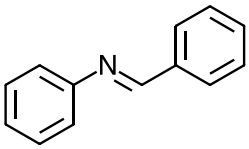
7-nitro-3-(*p*-tolyl)quinoxalin-2(1*H*)-one (3t)

Yield: 32 mg (38%); yellow solid; mp 274.2 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.83 (1H, br s, NH); 8.31 (2H, d, J = 8.2 Hz, 14-H, 15-H); 8.13–8.04 (2H, m, 6-H, 8-H); 8.00 (1H, d, J = 8.8 Hz; 5-H); 7.33 (2H, d, J = 8.1 Hz; 12-H, 13-H); 2.39 (3H, s, 17-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 157.1, 154.4, 146.8, 141.4, 135.6, 132.2, 132.2, 129.8, 129.7, 128.7, 117.6, 110.5, 21.1. MS *m/z* (relative intensity): 281 (100), 253 (39), 223 (32), 207 (26), 180 (16), 90 (19). ^{15}N NMR (40 MHz, DMSO-d_6) δ (ppm) 369,2 (8-H), 321,2 (6-H). HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{15}H_{12}N_3O_3$, 282.0873; found, 282.0870.



3-(4-fluorophenyl)-7-nitroquinoxalin-2(1*H*)-one (3u)

Yield: 30 mg (35%); yellow solid; mp 277 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.90 (1H, br s, NH); 8.48–8.44 (2H, m, 12-H); 8.13–8.08 (2H, m, 8-H, 6-H); 8.04 (1H, d, J = 8.8 Hz; 5-H); 7.39–7.34 (2H, m,13-H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 163.9 (d, $^{1}J_{C\text{-}F}$ = 250.1 Hz, C-F), 156.2 (C=N), 154.3 (C=O), 147.0 (C-NO_2), 135.4 (C-10), 132.3 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz, C-12), 131.4 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz, C-9), 129.9 (C-11), 117.6 (C-6), 115.1 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz, C-13), 110.6 (C-8). ^{19}F NMR (376 MHz, DMSO-d_6) δ (ppm) 108.77 (dt, $^{4}J_{C\text{-}F}$ = 5.9 Hz; $^{3}J_{C\text{-}F}$ = 8.7 Hz). ^{15}N NMR (40 MHz, DMSO-d_6) δ (ppm) 369 (6-H), 322,5 (5-H), 153 (8-H). MS (relative intensity) *m/z*: 285 (64), 253 (26), 227 (39), 207 (100), 184 (21), 73 (48), 44 (84). HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{14}H_9FN_3O_3$, 286.0628; found, 286.0622.



(*E*)-(Phenylmethylidene)aniline (6)

Yield: 42 mg (79%); yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.69 (1H, s); 8.04 (2H, d, J = 7.2 Hz); 7.58–7.60 (3H, m); 7.48–7.52 (2H, m); 7.32–7.35 (2H, m). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 161.0, 151.9, 136.5, 131.9, 129.7, 129.2, 129.1, 126.4, 121.4.

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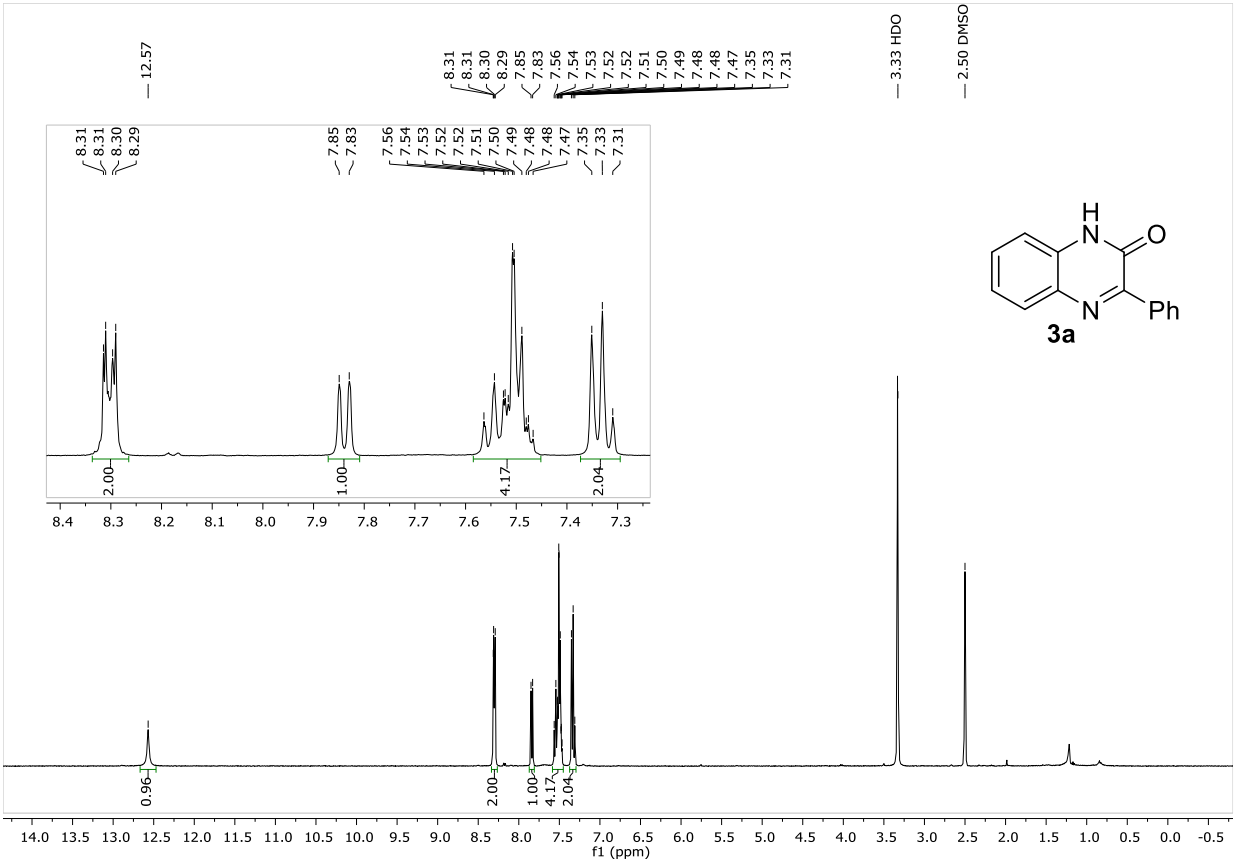
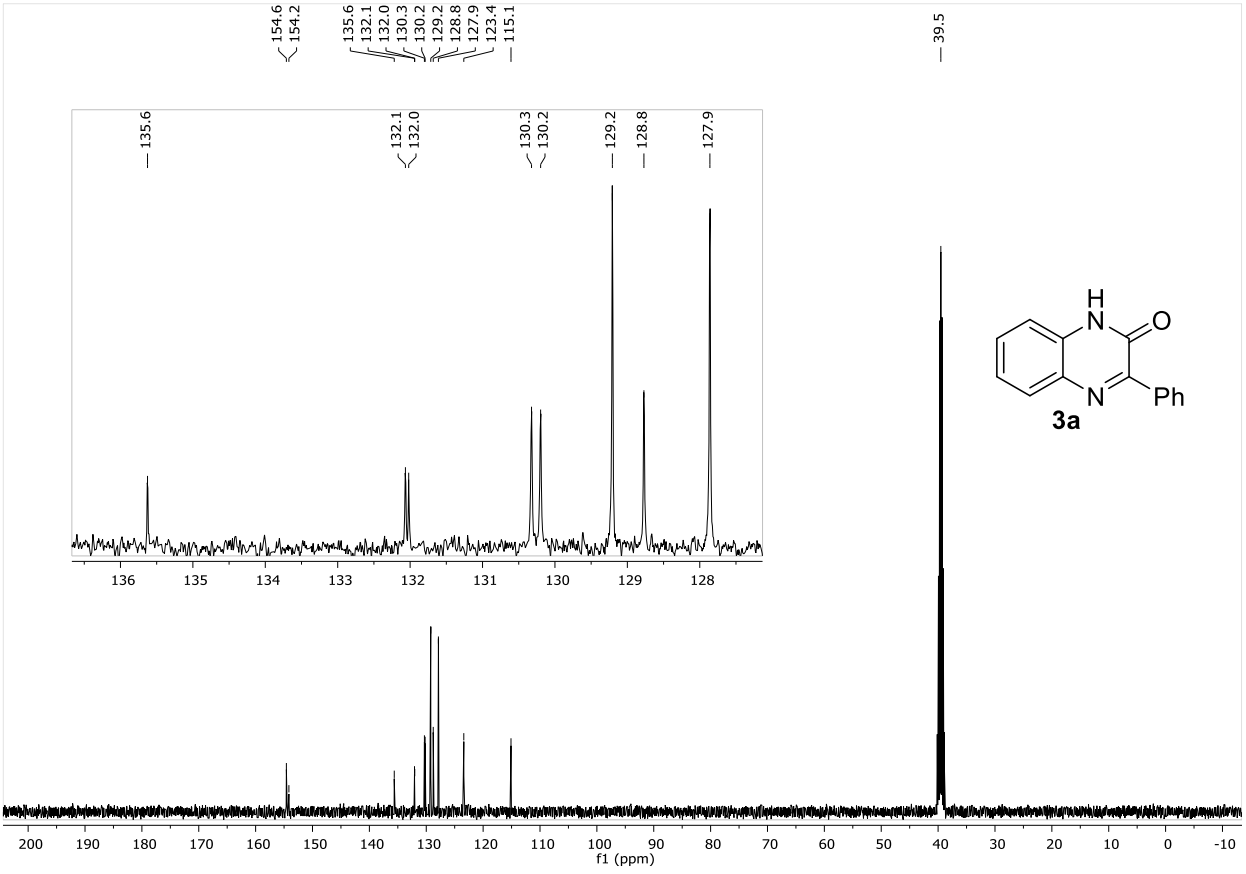
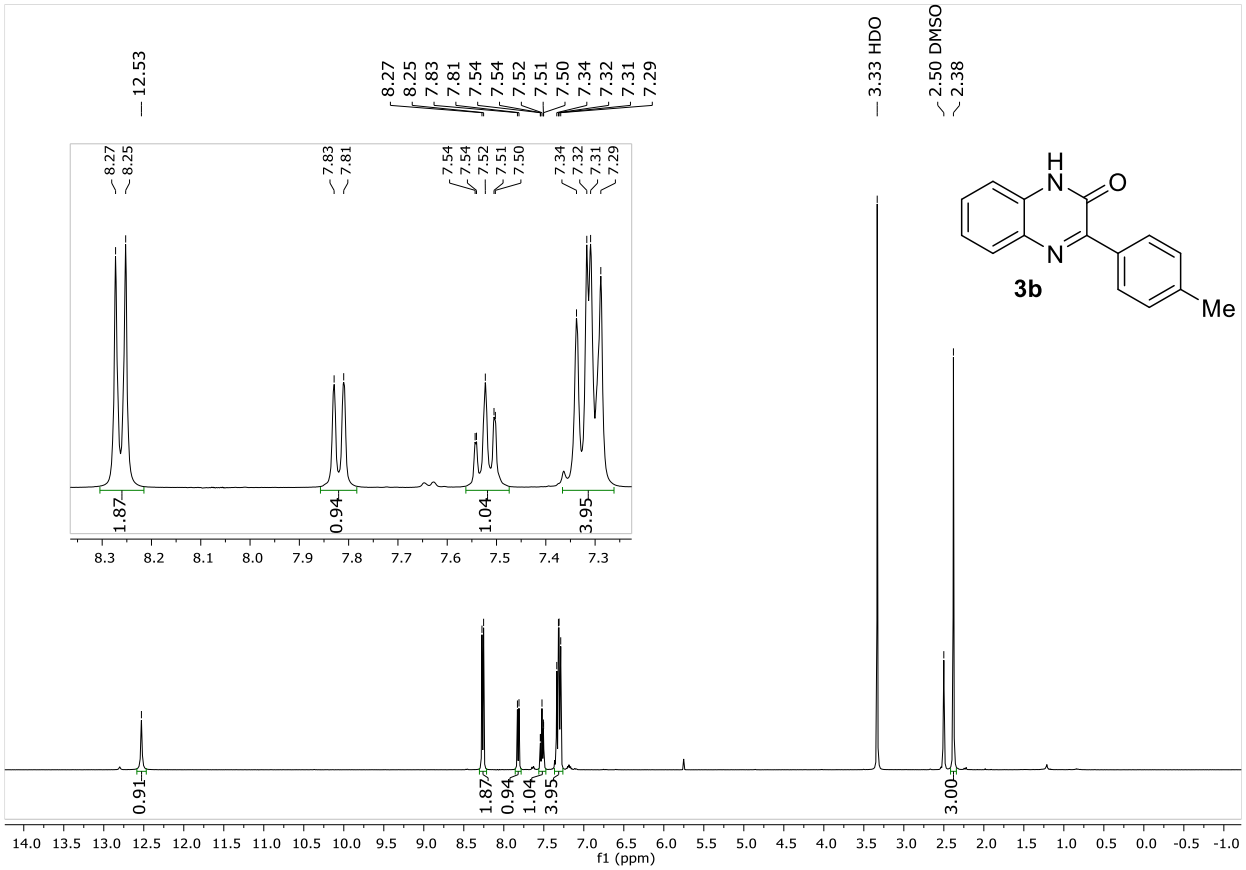


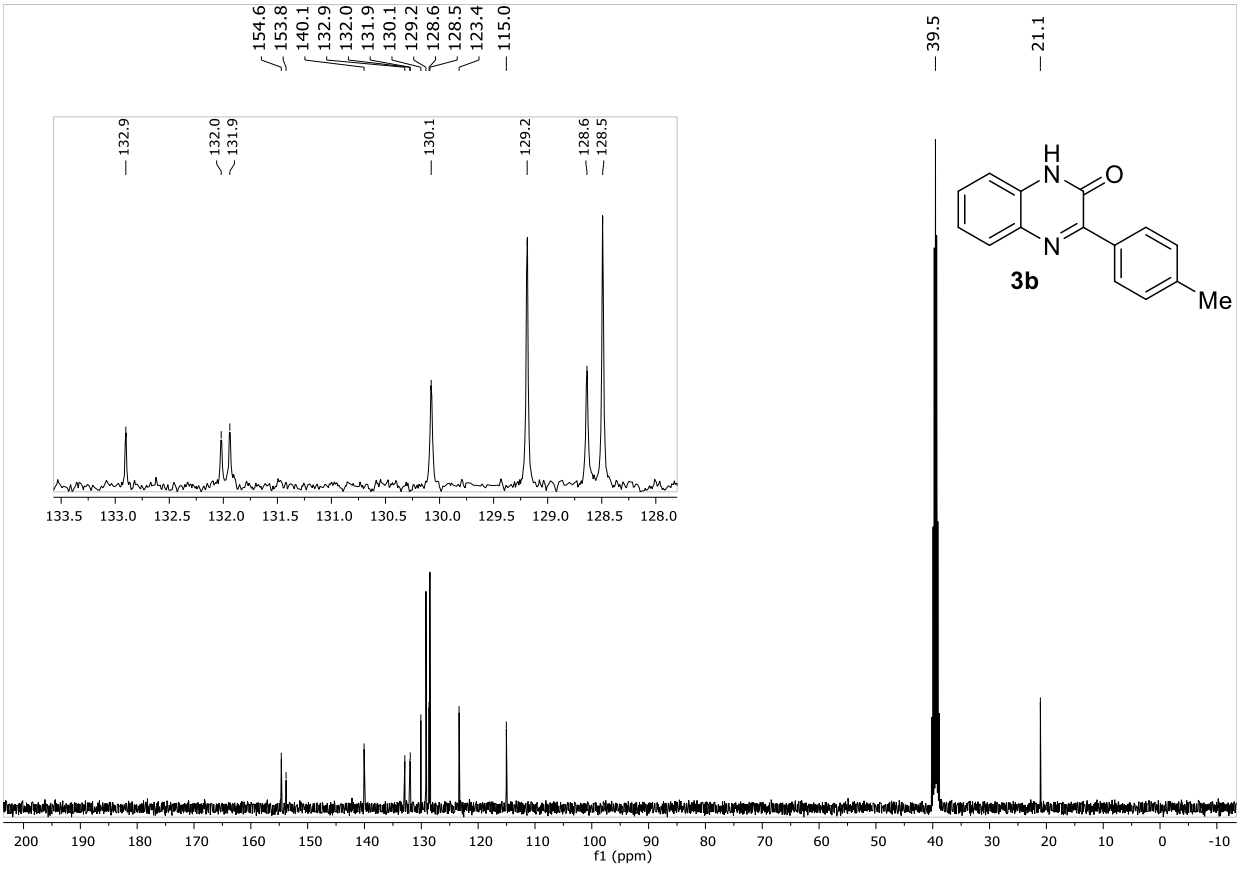
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3a**.



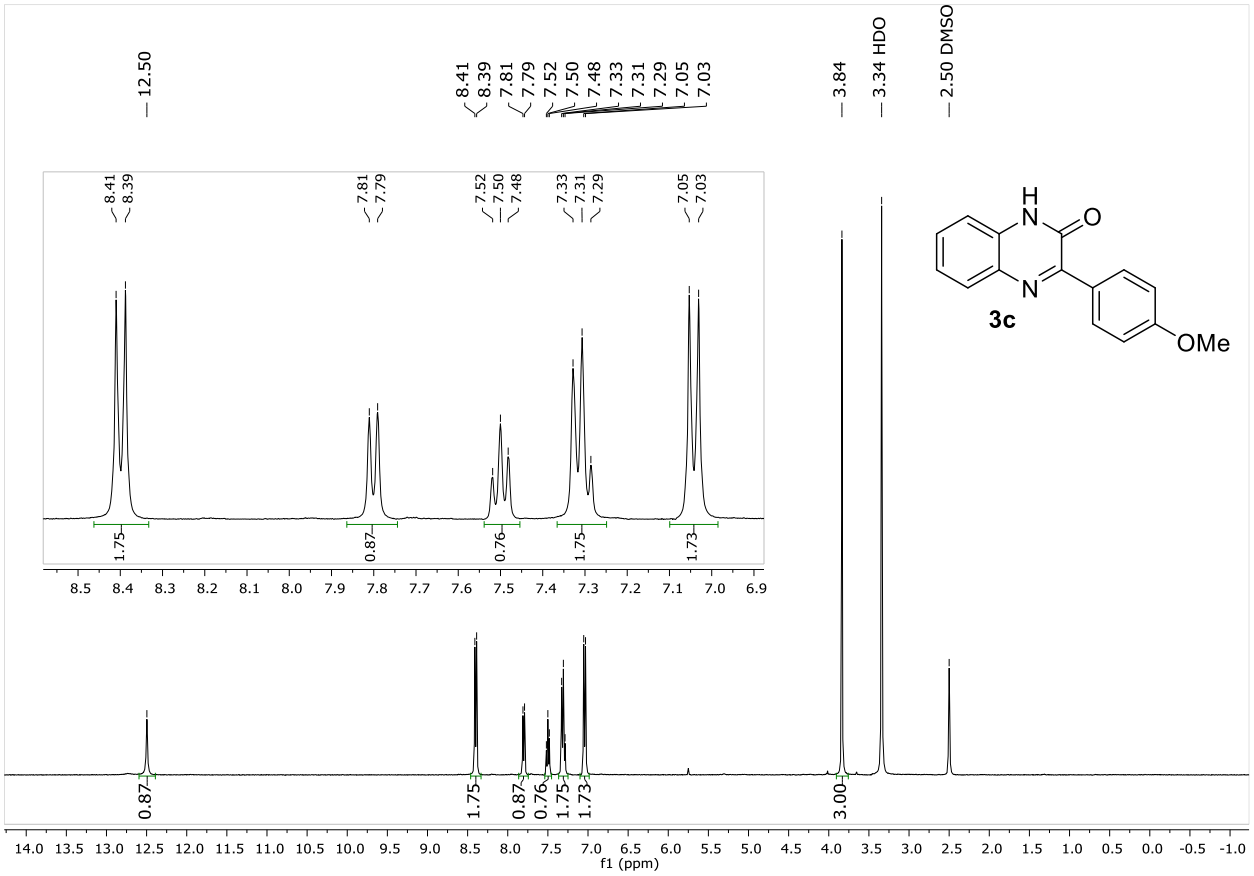
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3a**.



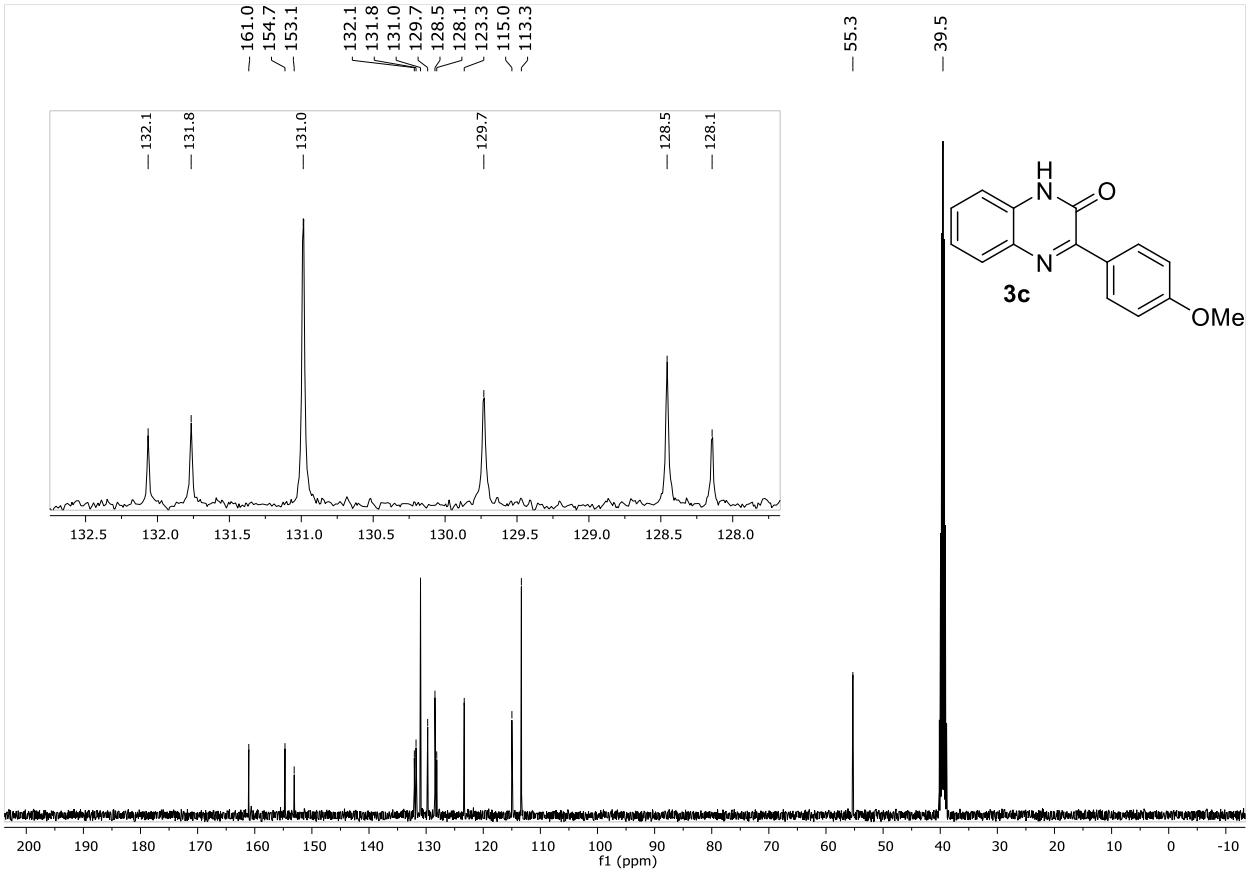
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3b**.



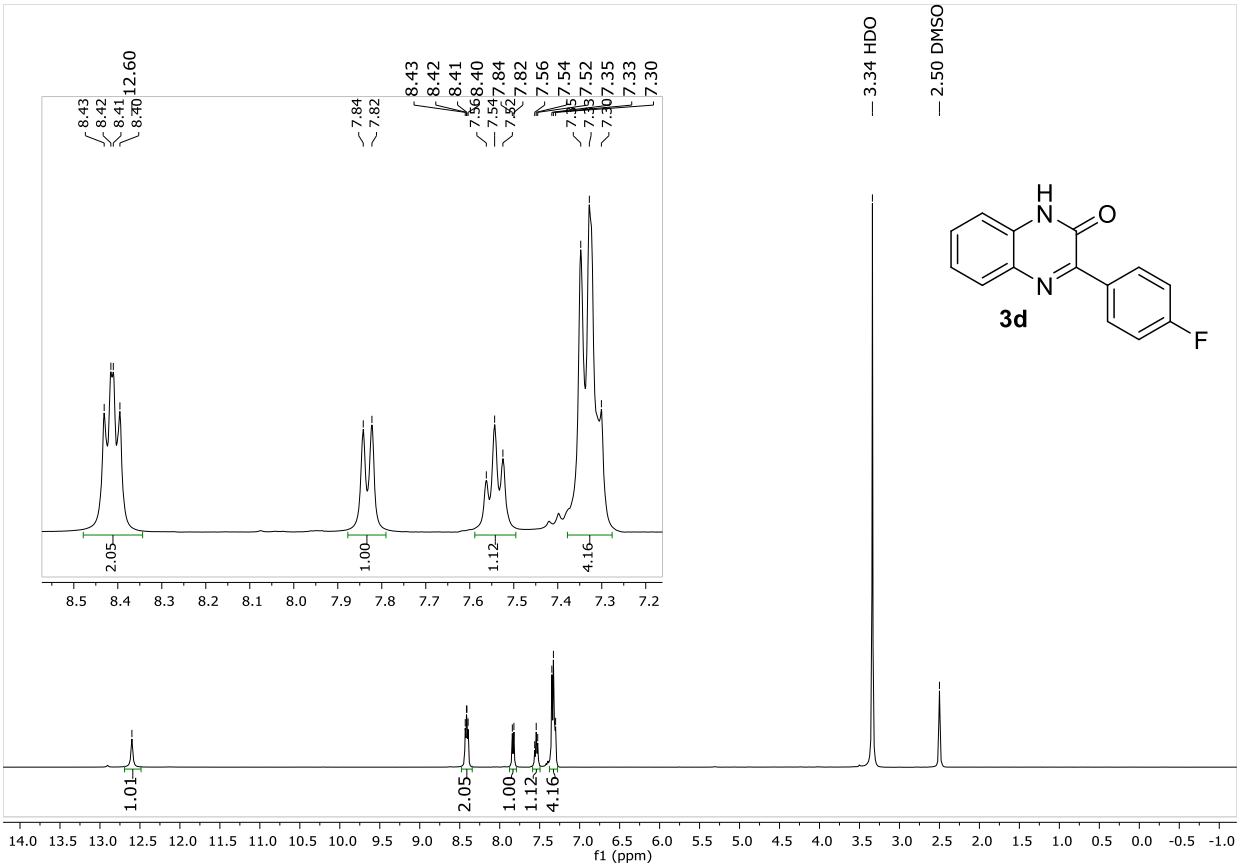
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3b**.



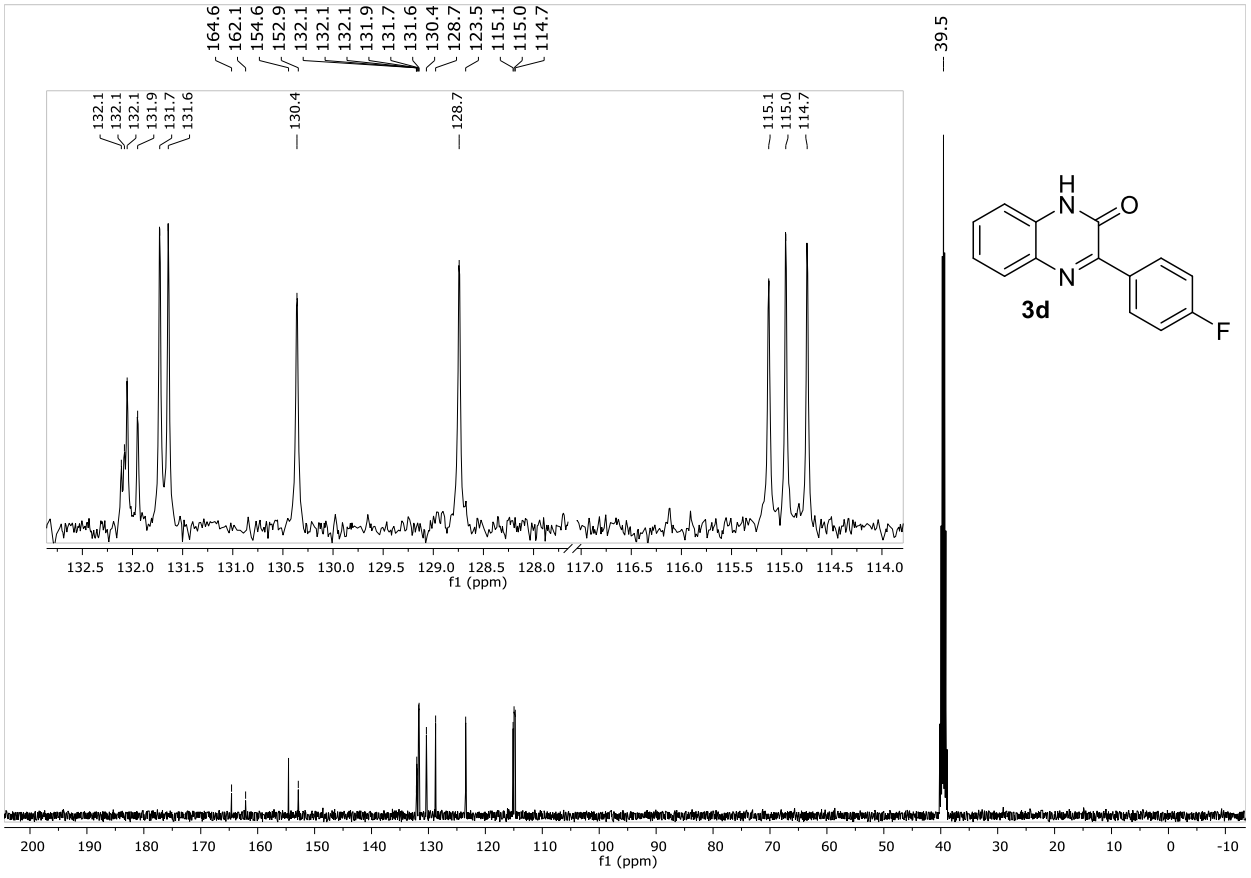
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3c**.



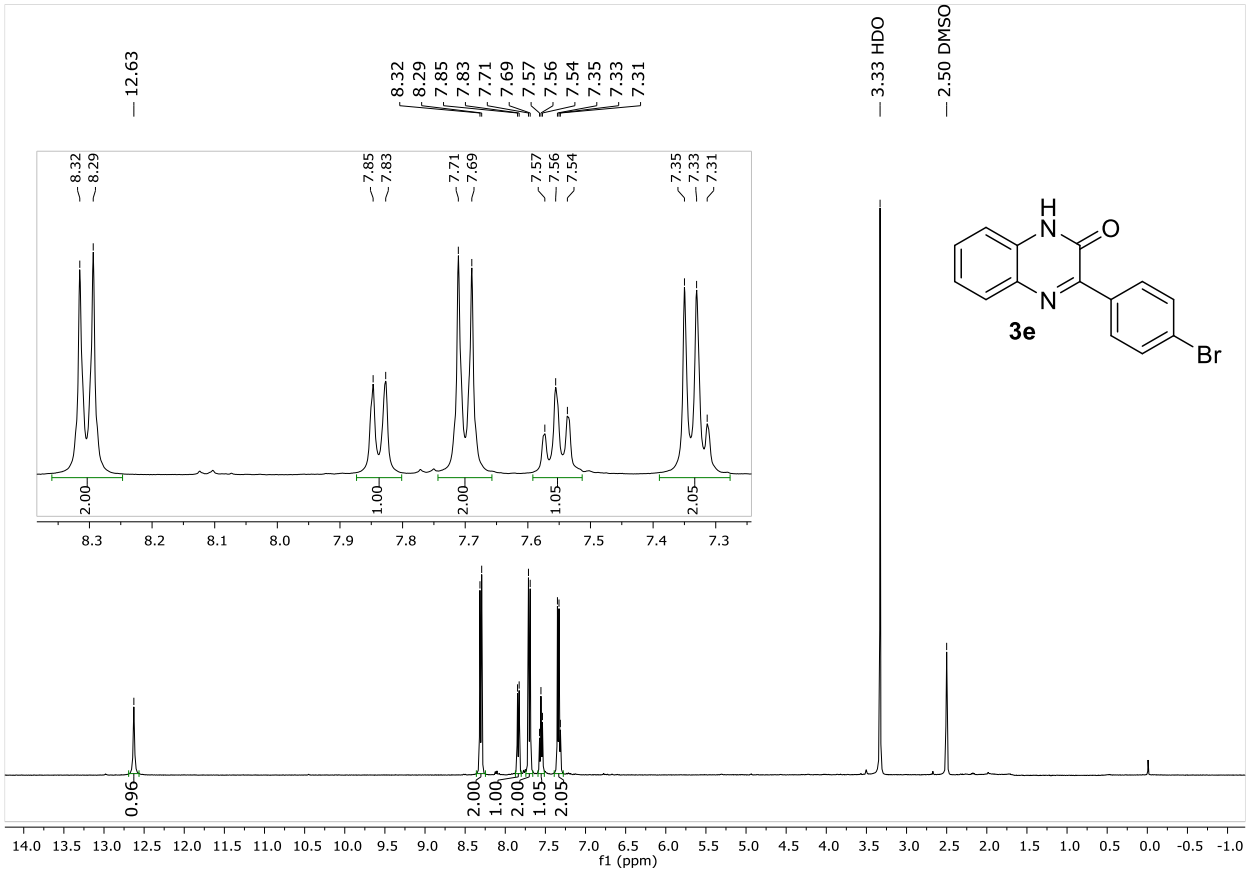
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3c**.



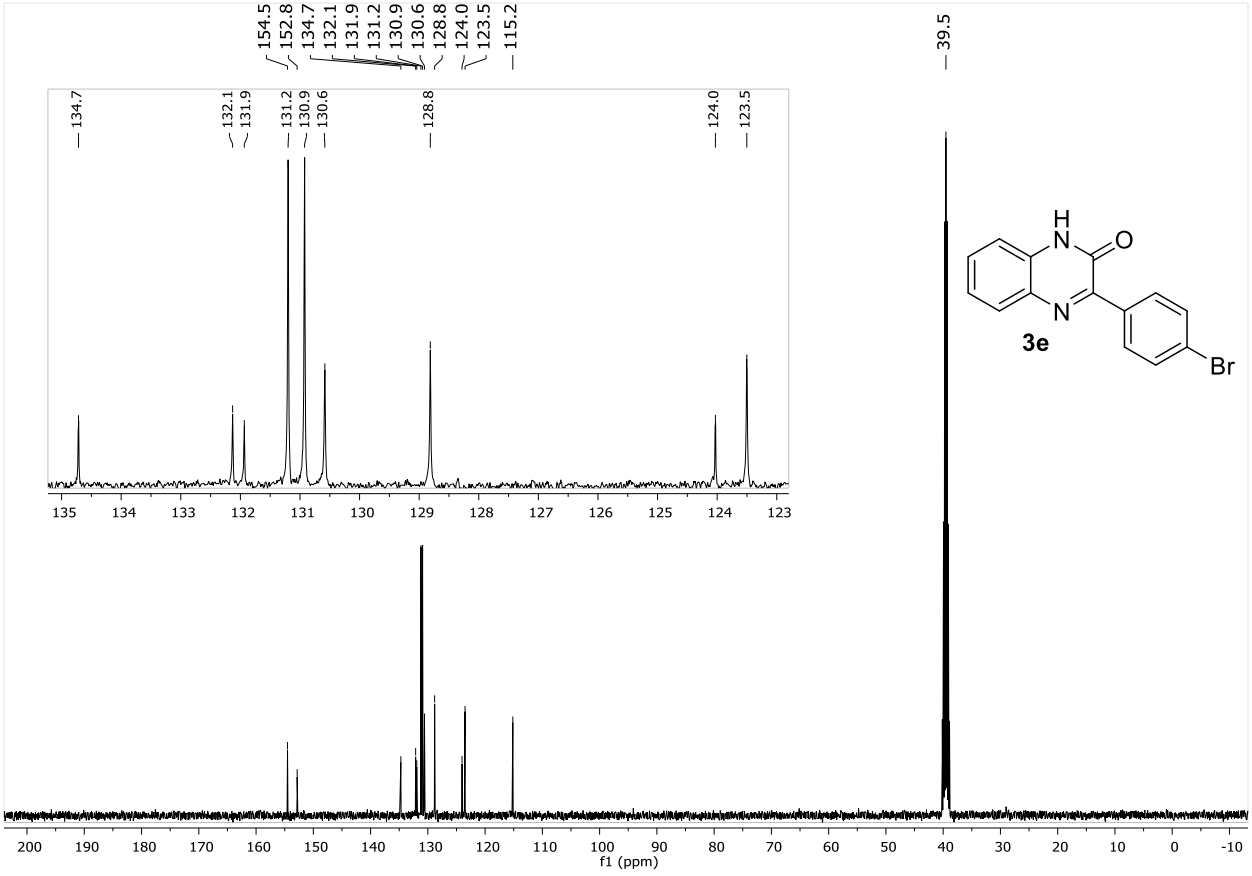
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3d**.



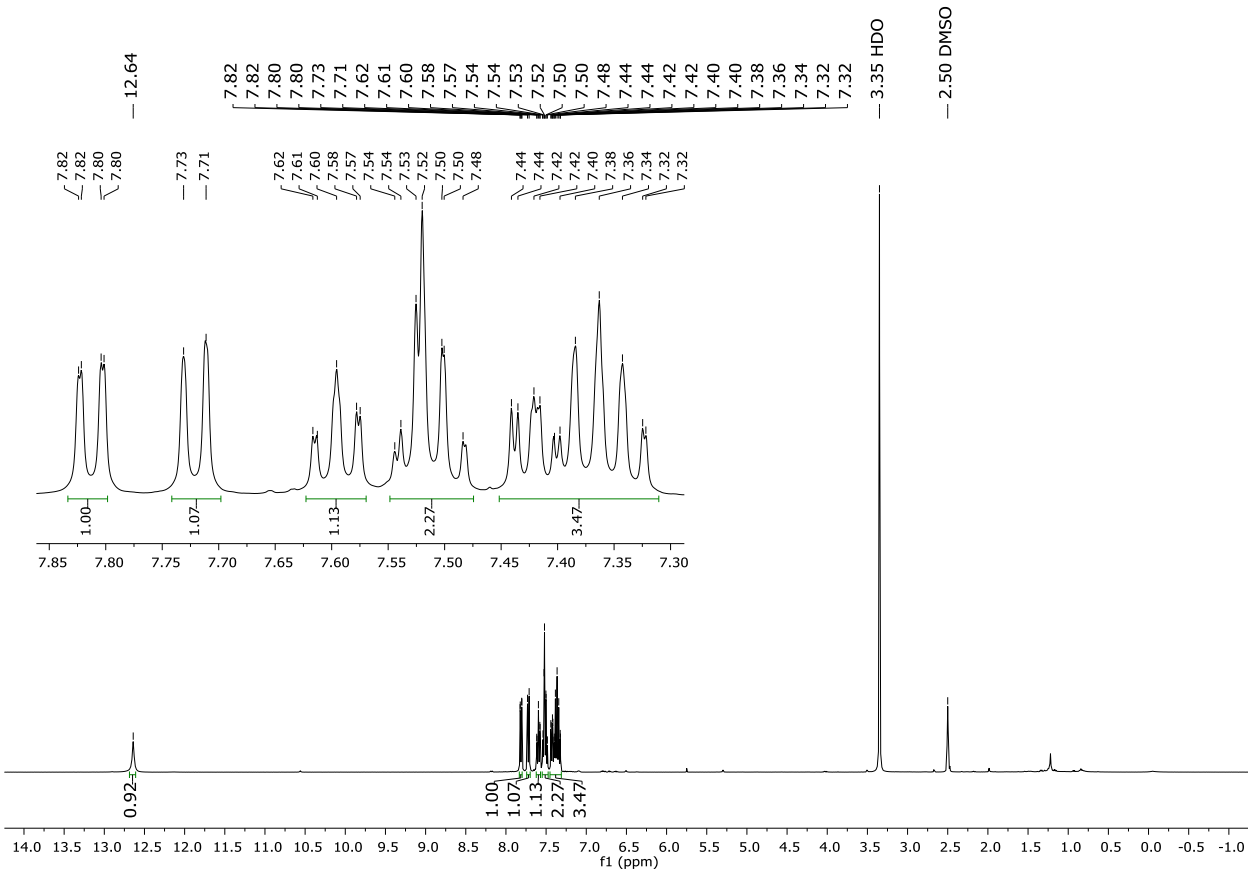
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3d**.



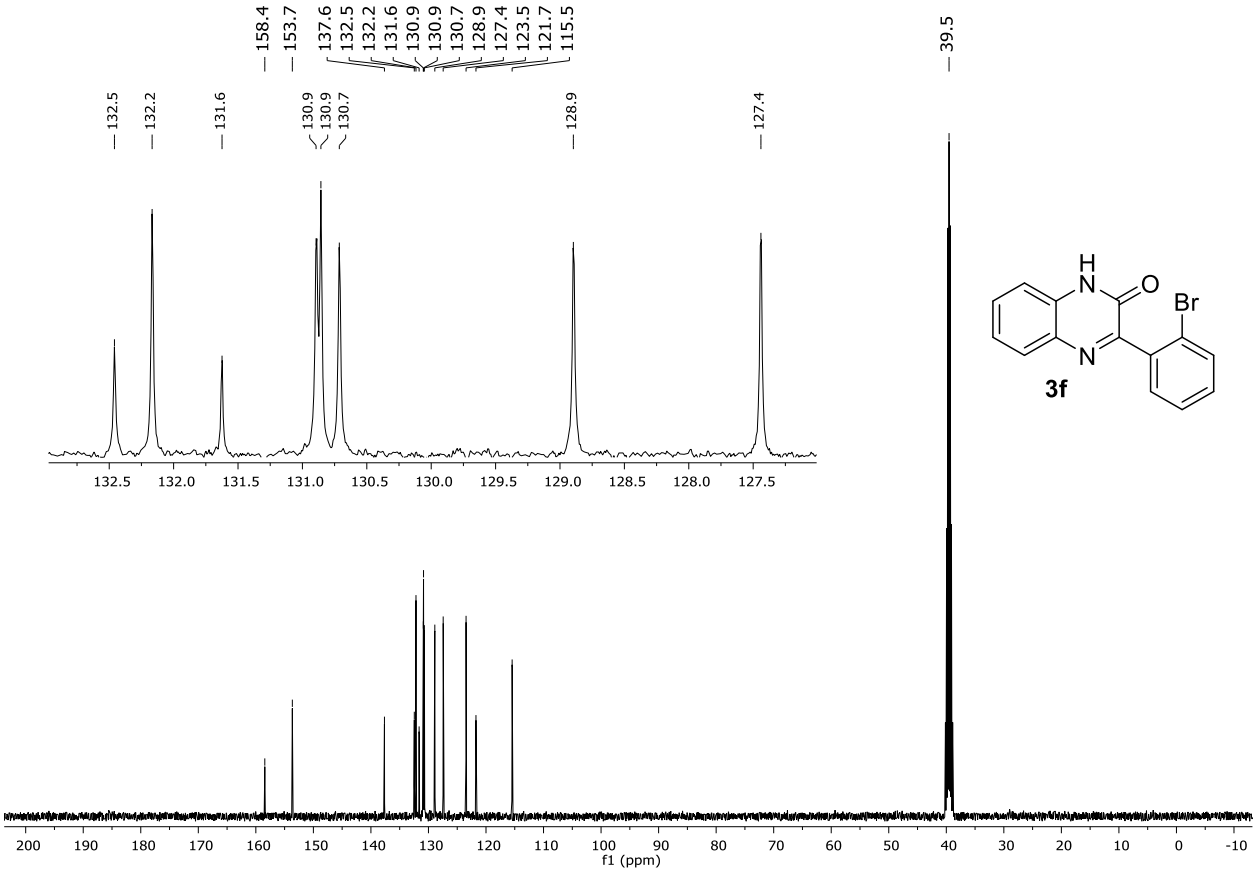
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3e**.



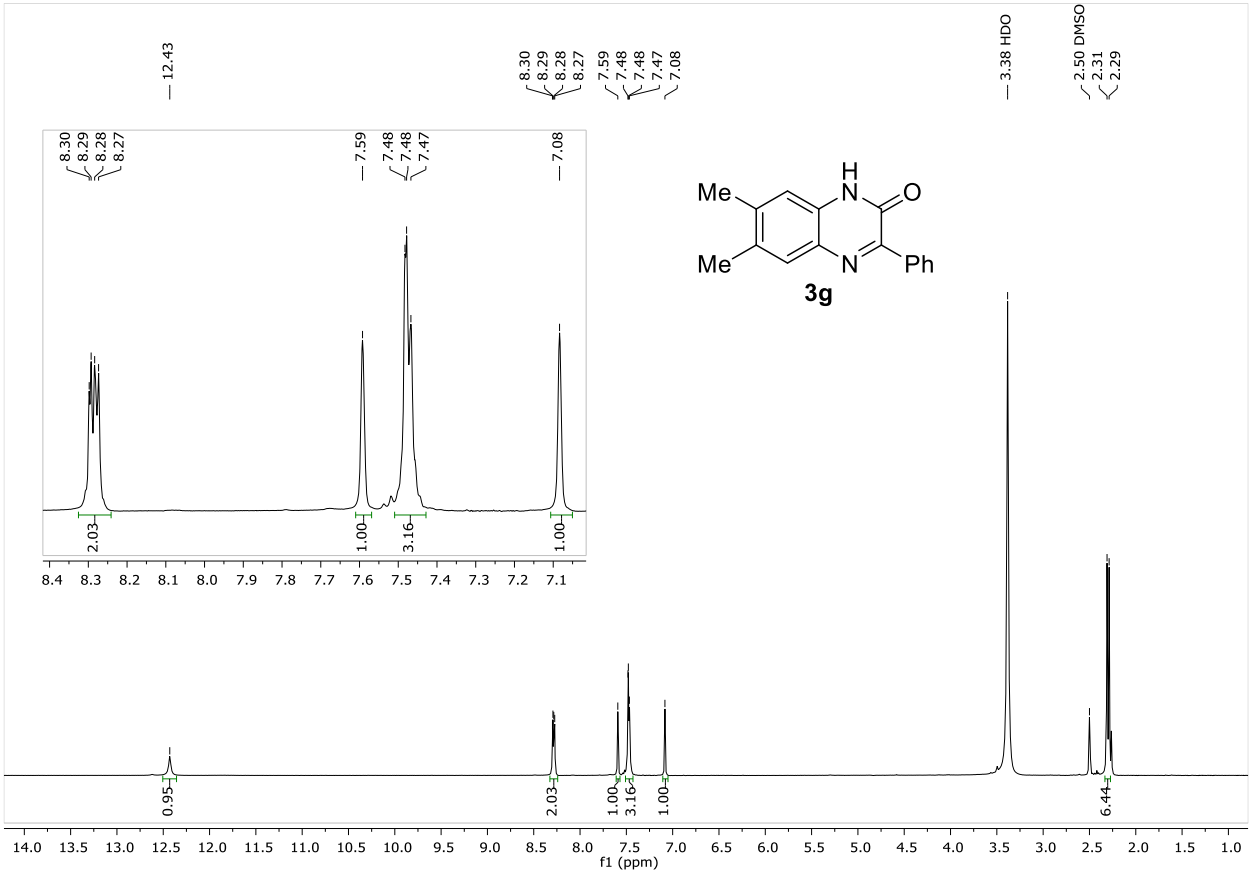
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3e**.



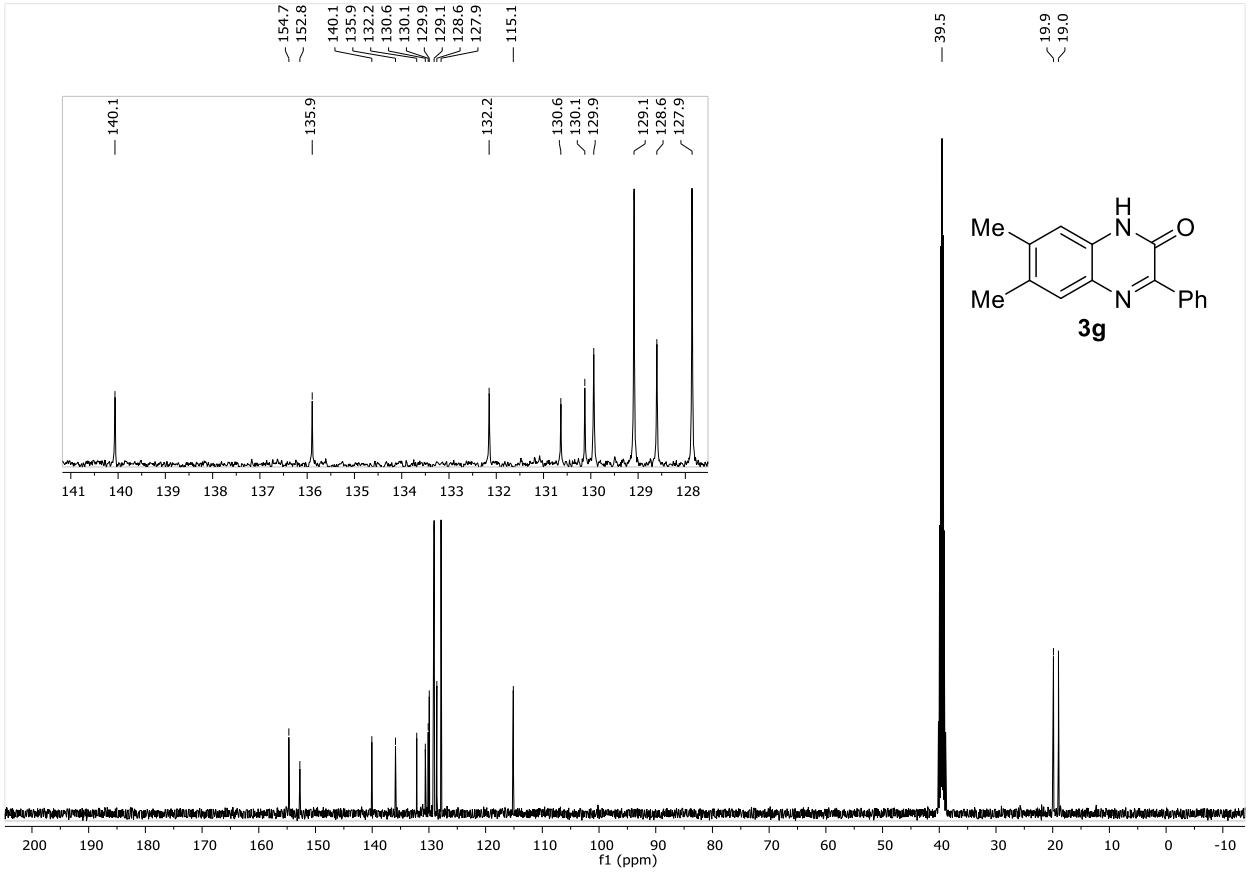
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3f**.



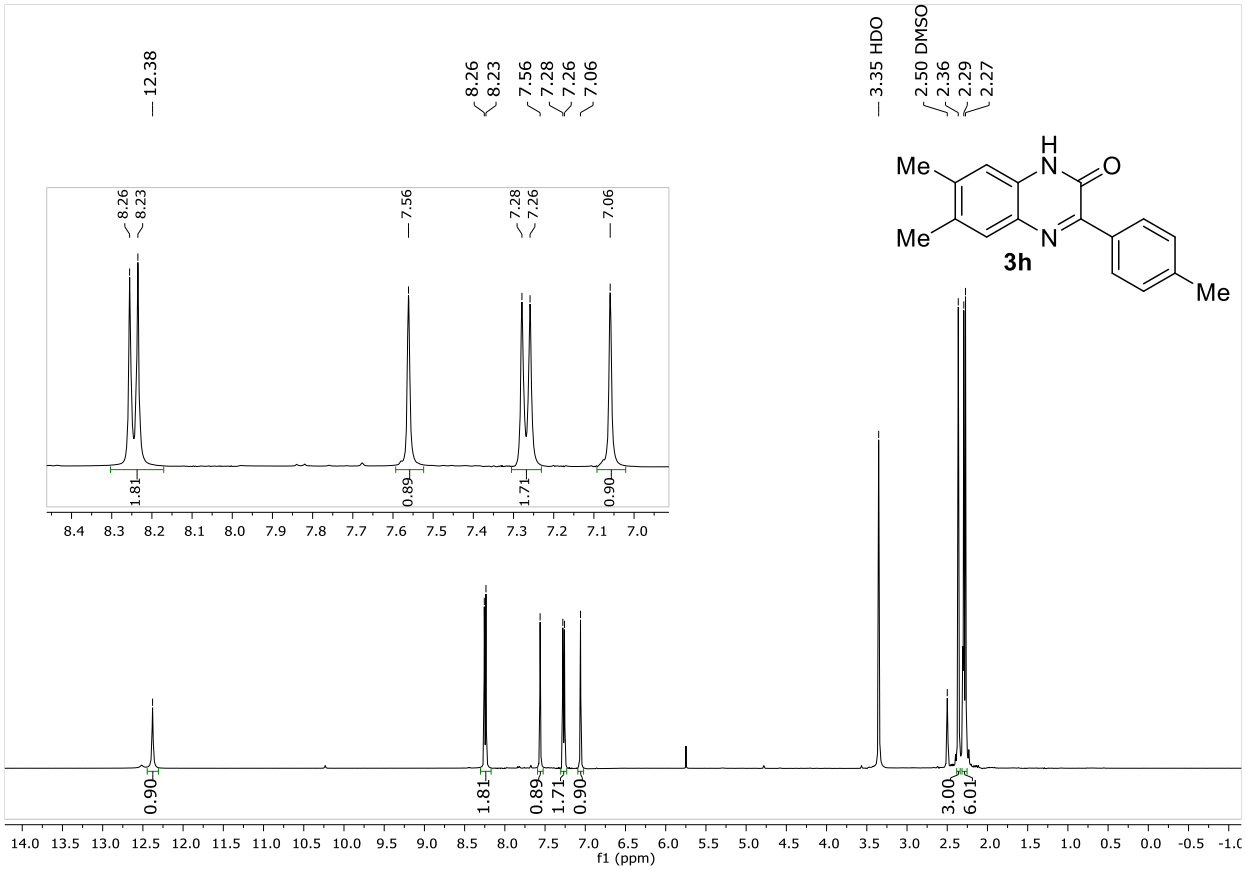
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3f**.



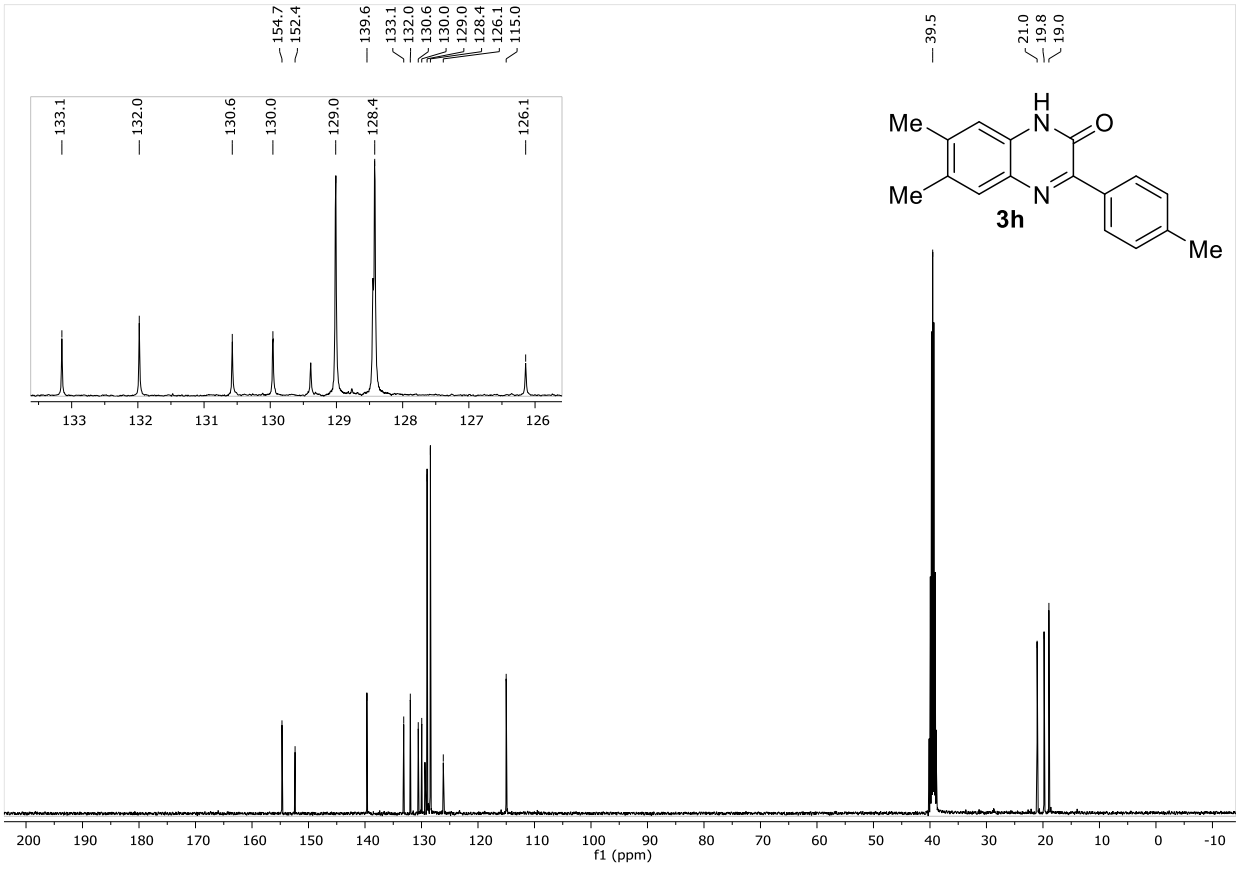
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3g**.



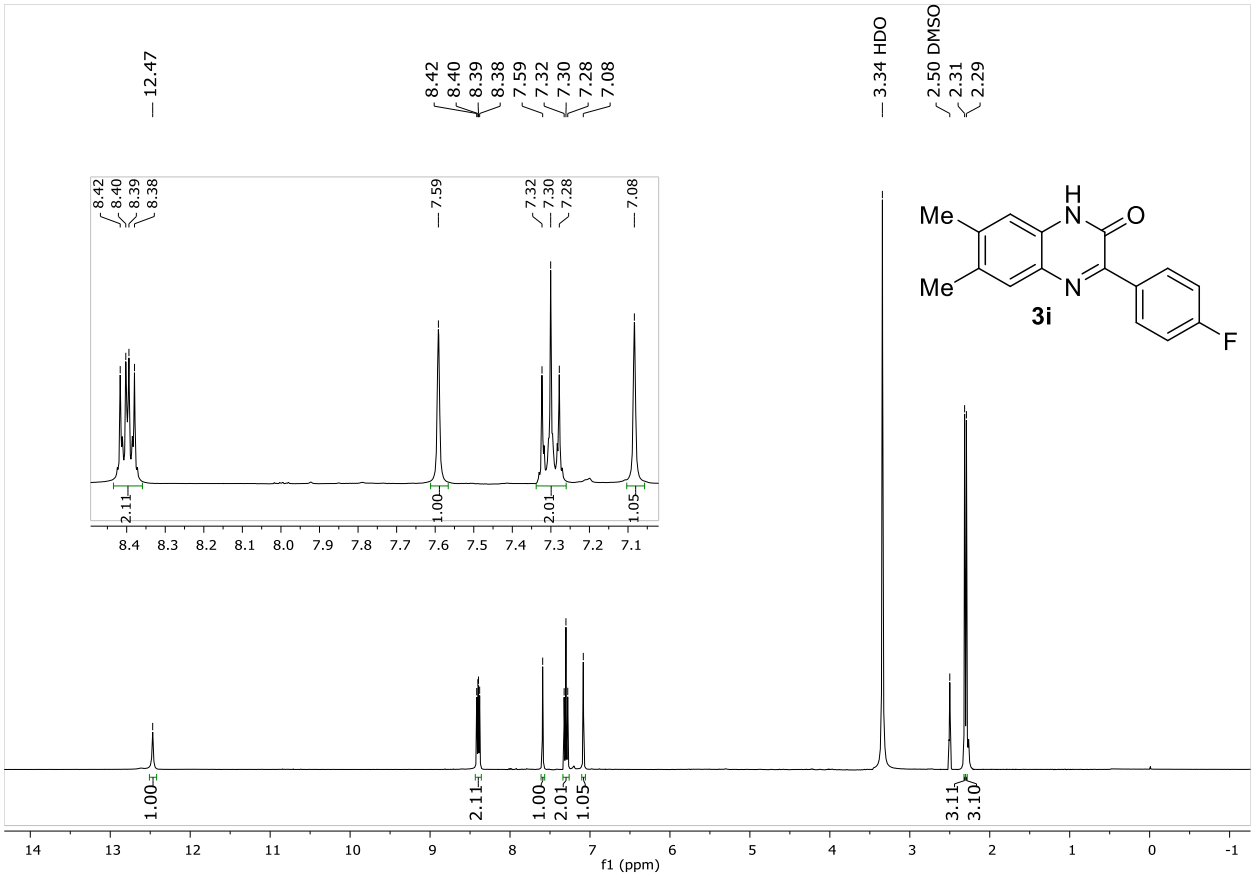
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3g**.



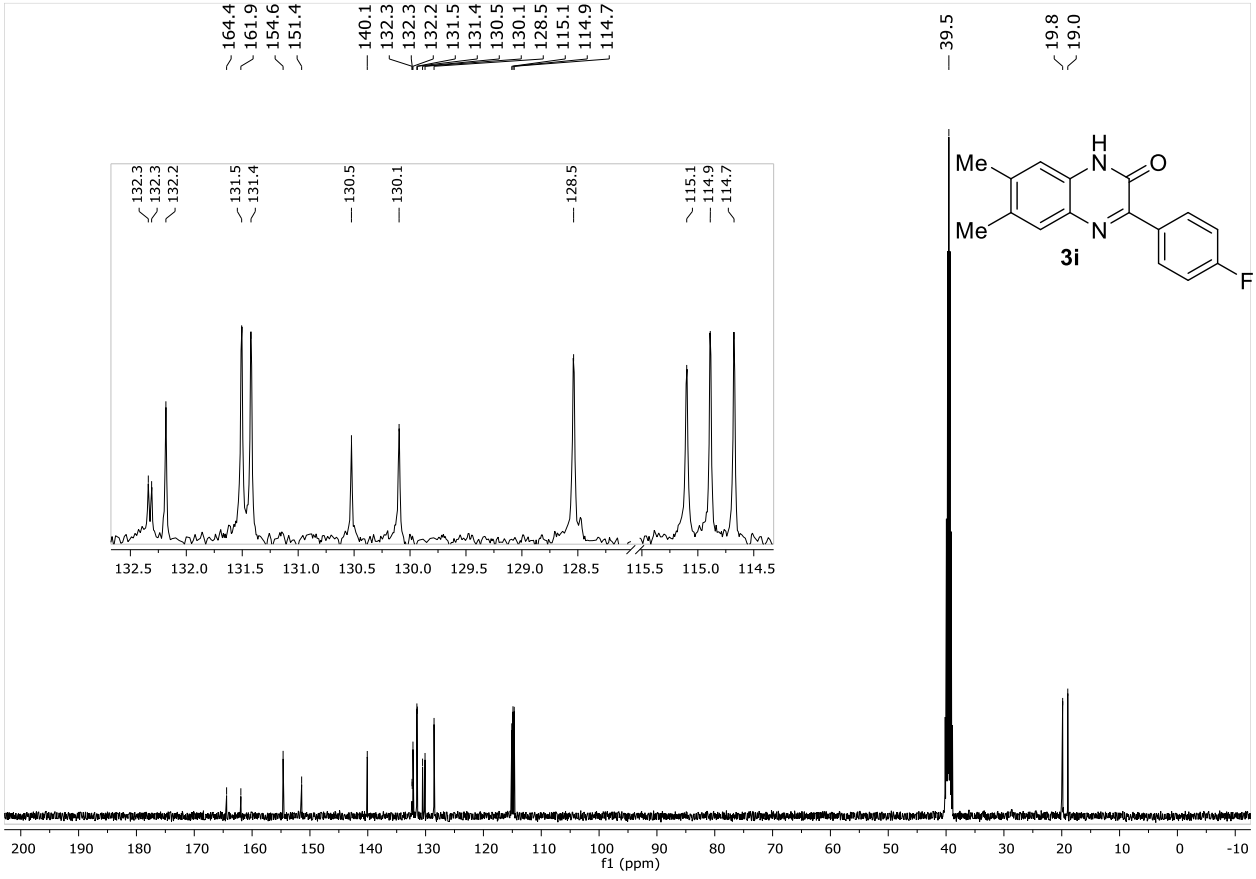
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3h**.



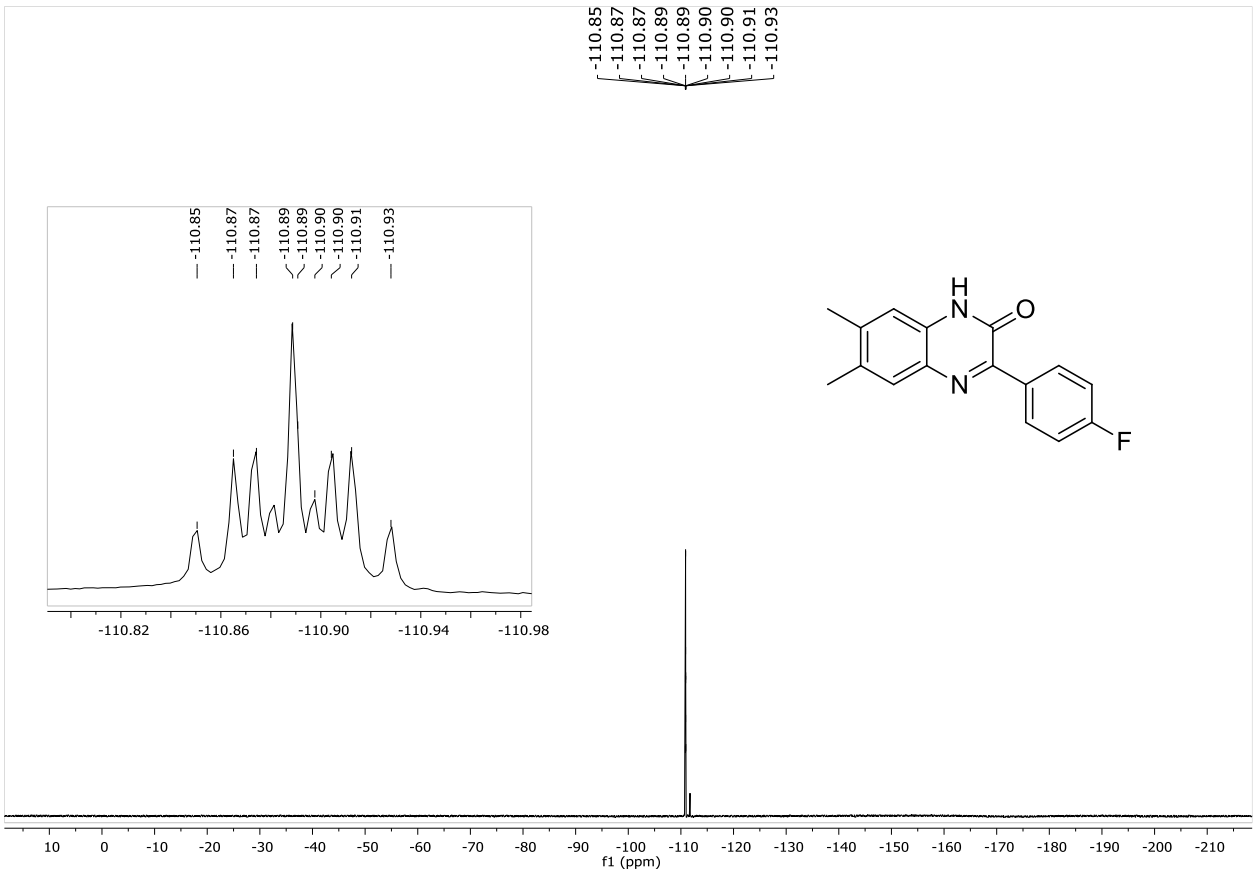
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3h**.



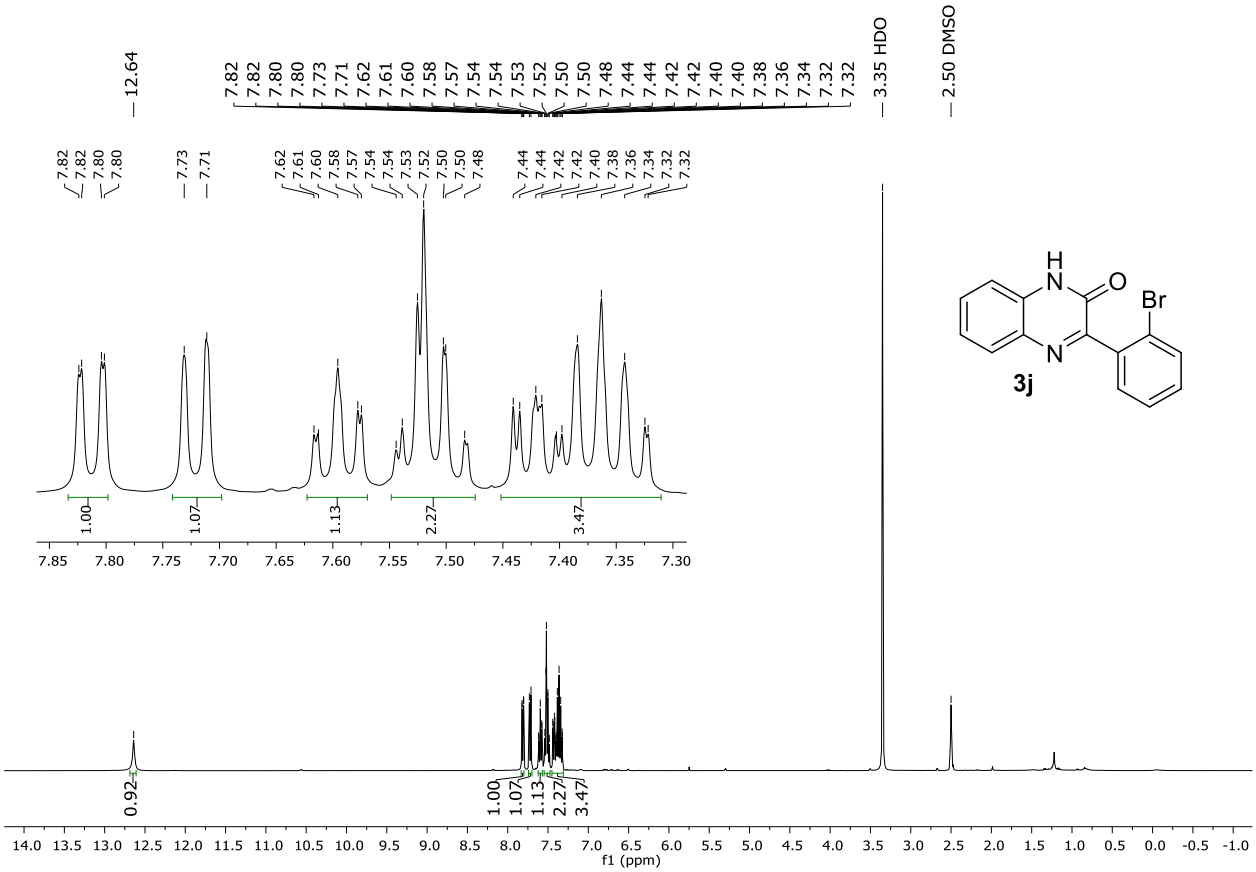
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3i**.



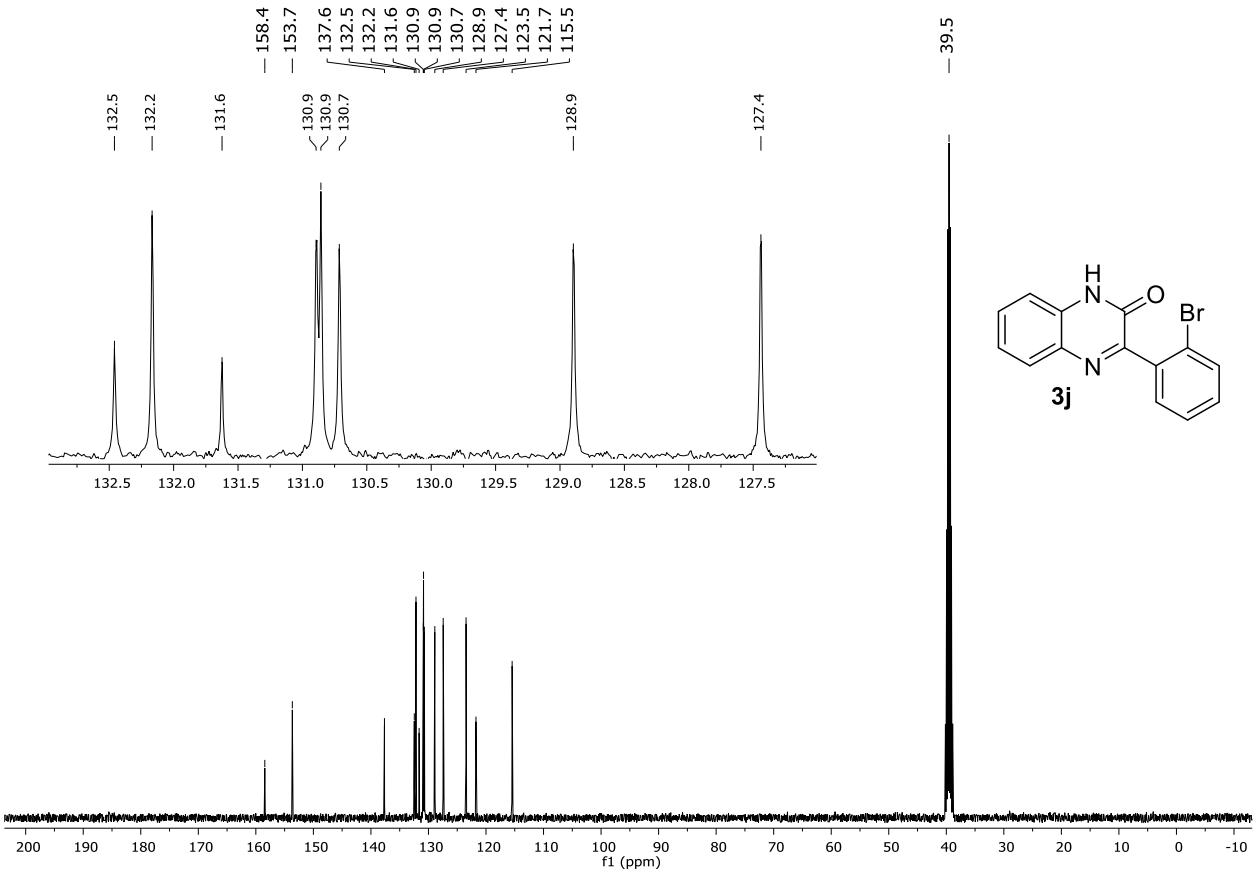
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3i**.



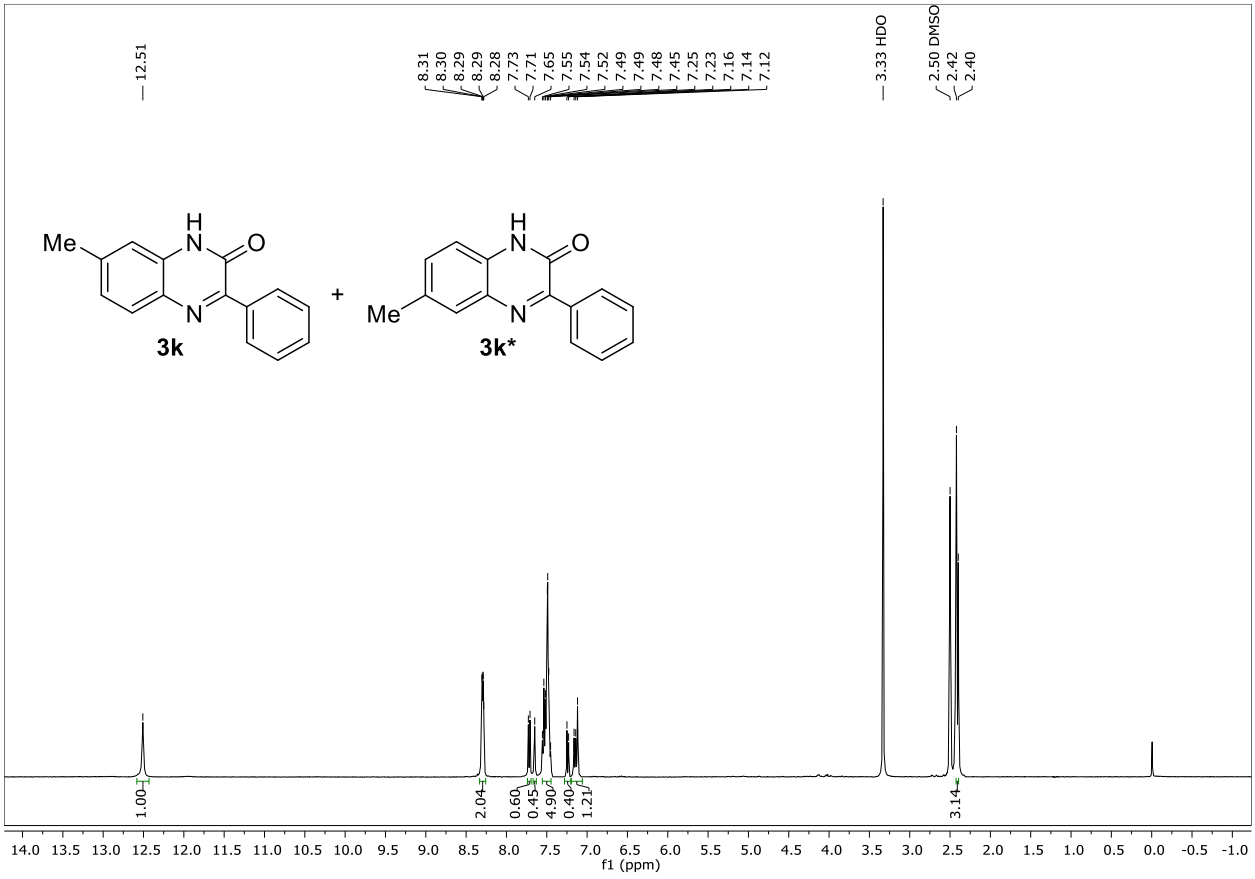
^{19}F NMR (376 MHz, DMSO-d_6) spectrum of **3i**.



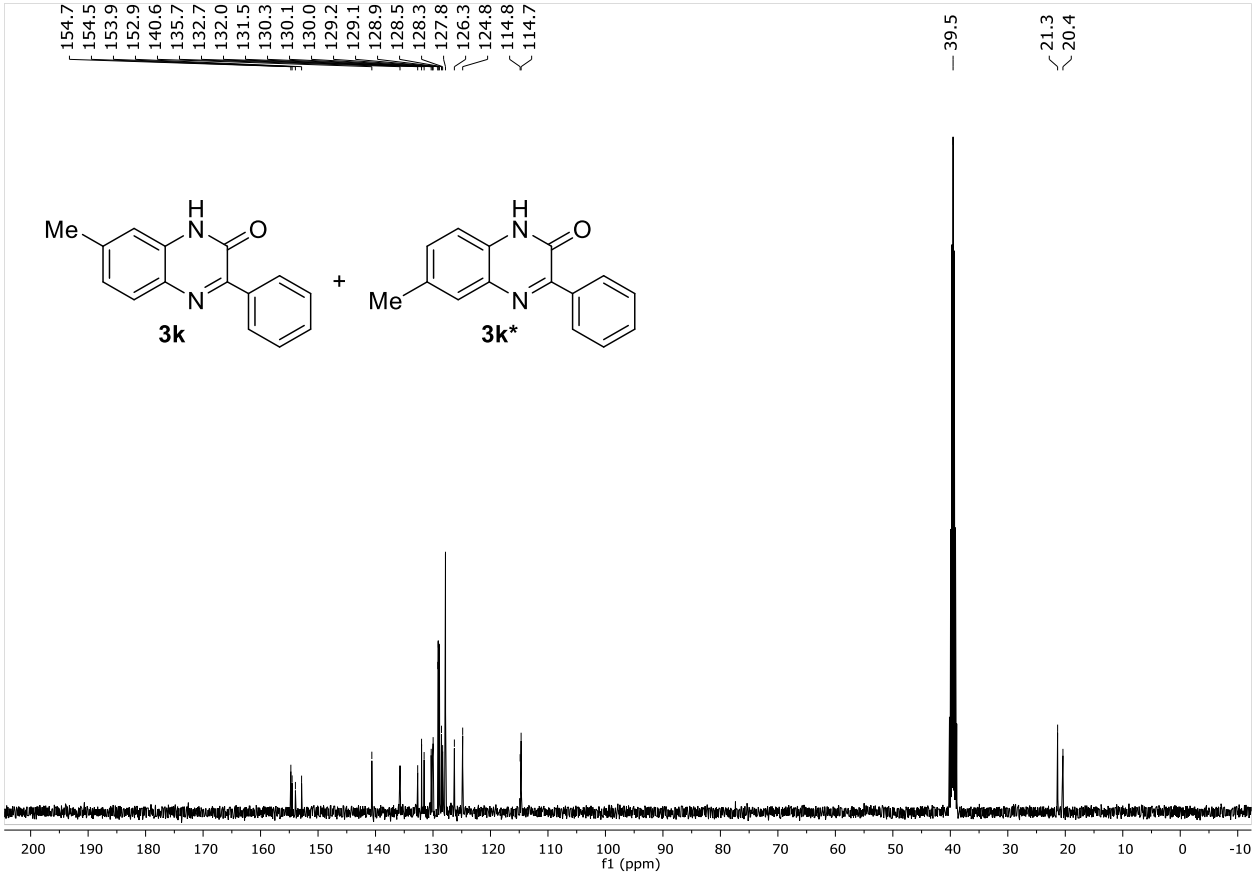
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3j**.



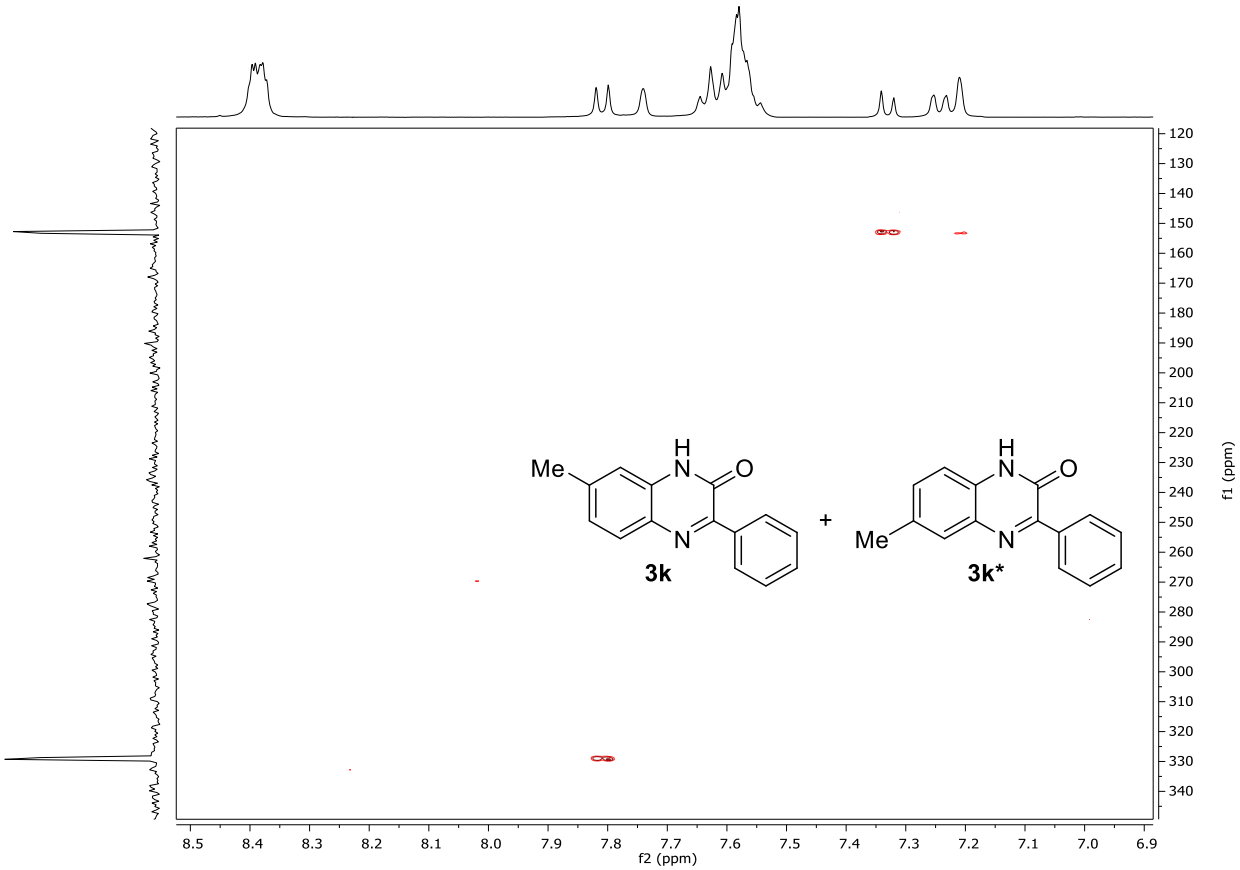
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3j**.



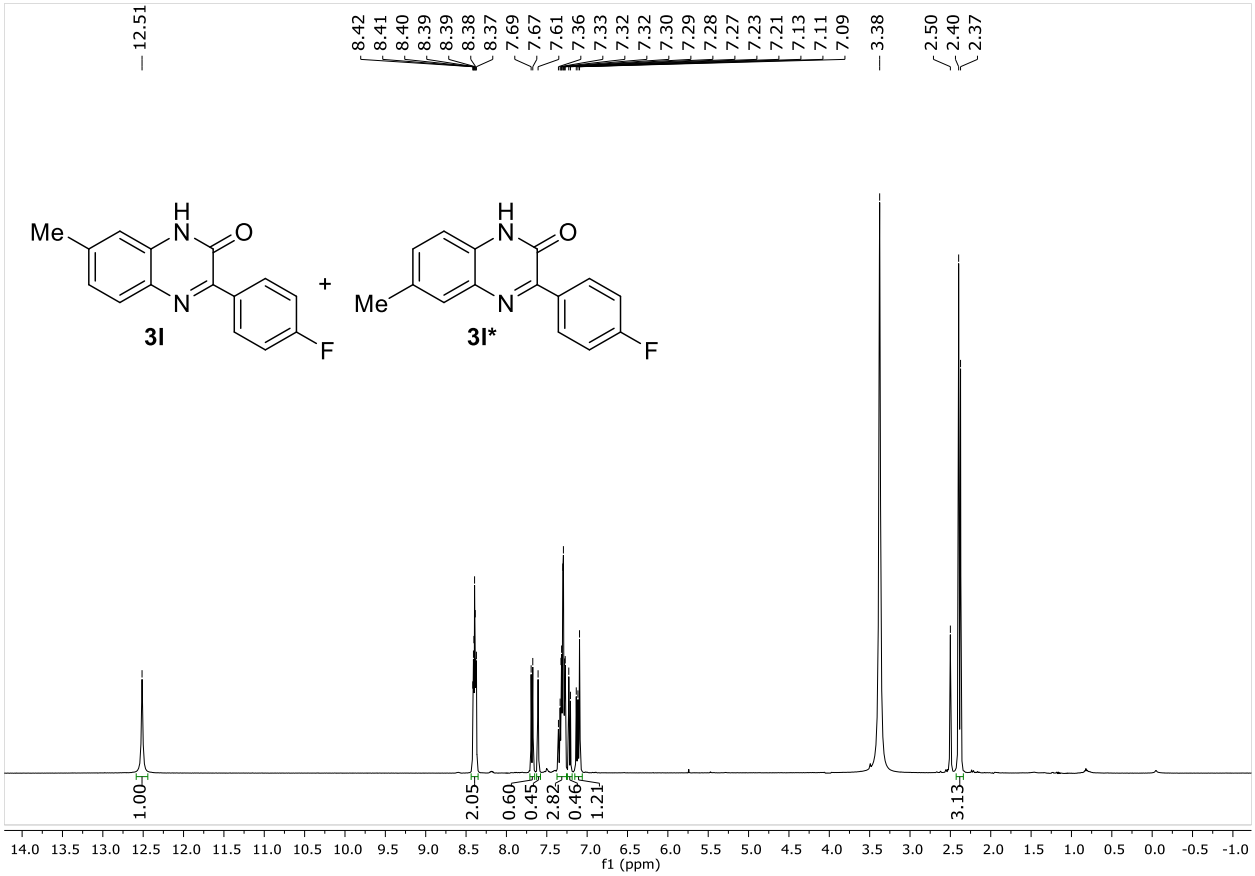
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3k**:**3k***.



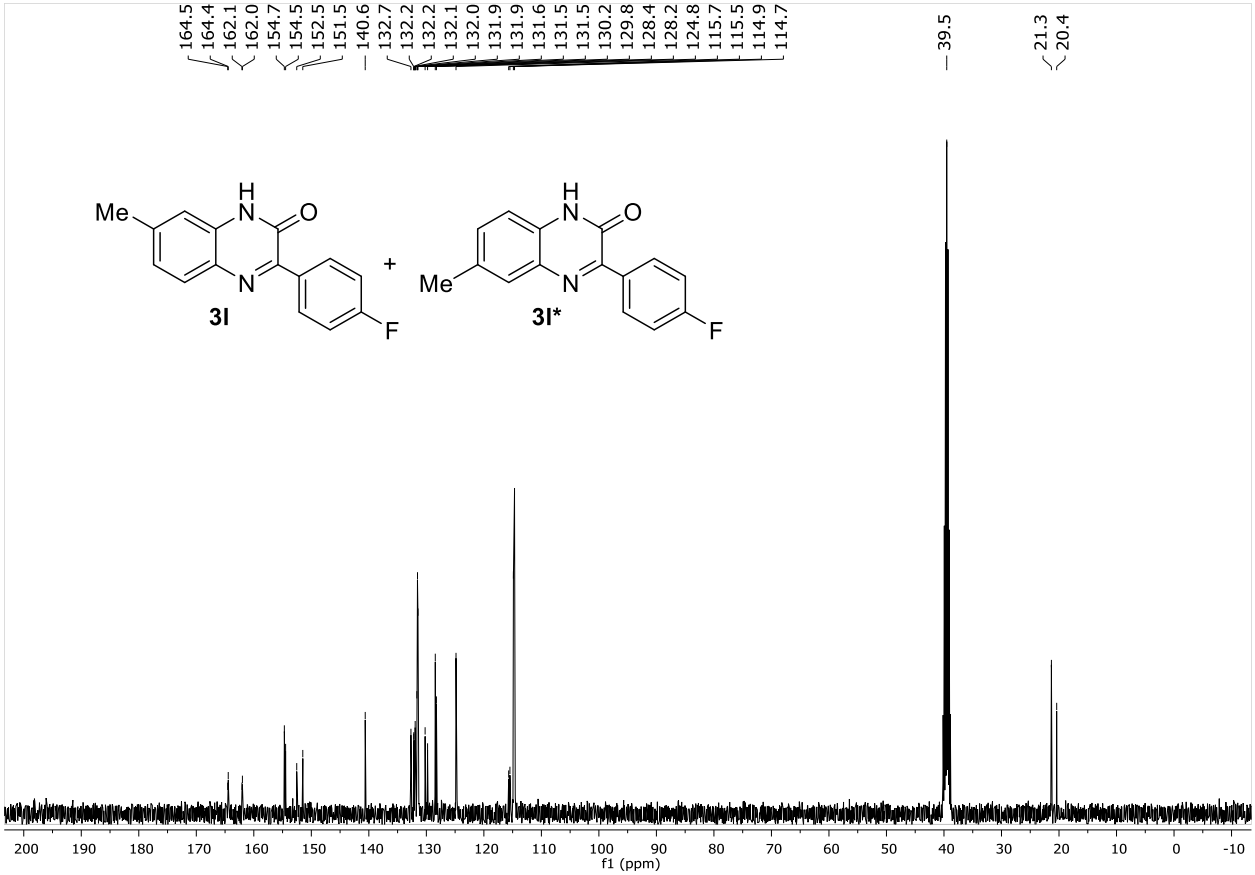
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3k** + **3k***.



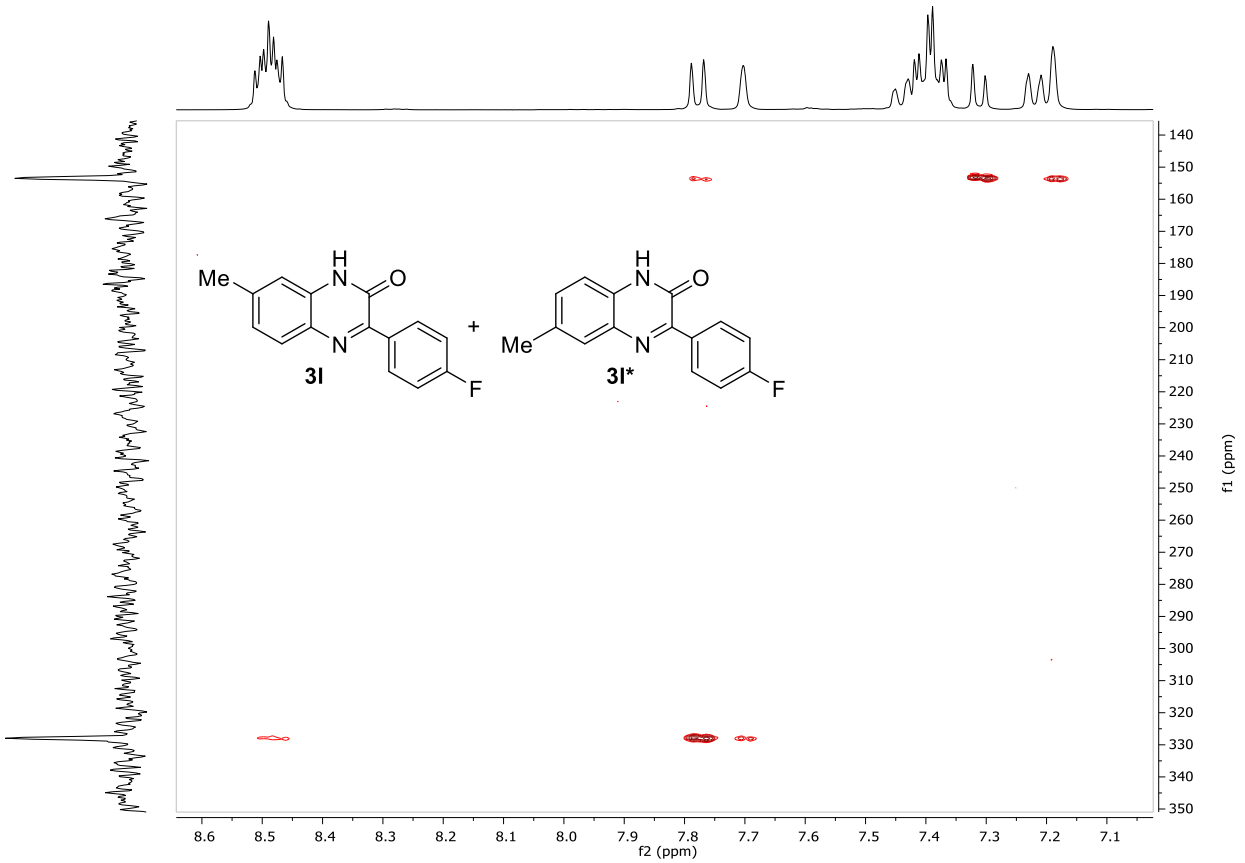
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3k** + **3k***.



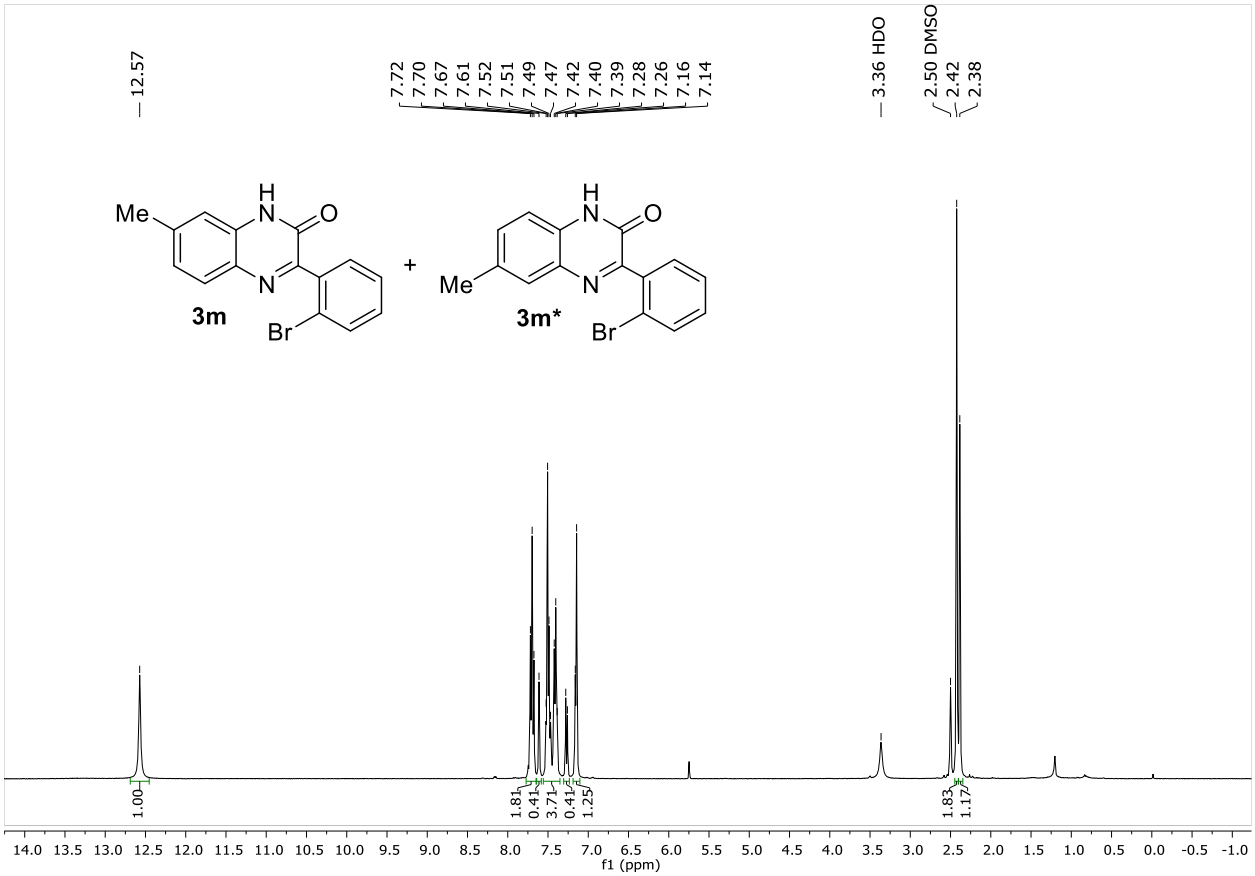
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3l** + **3l***.



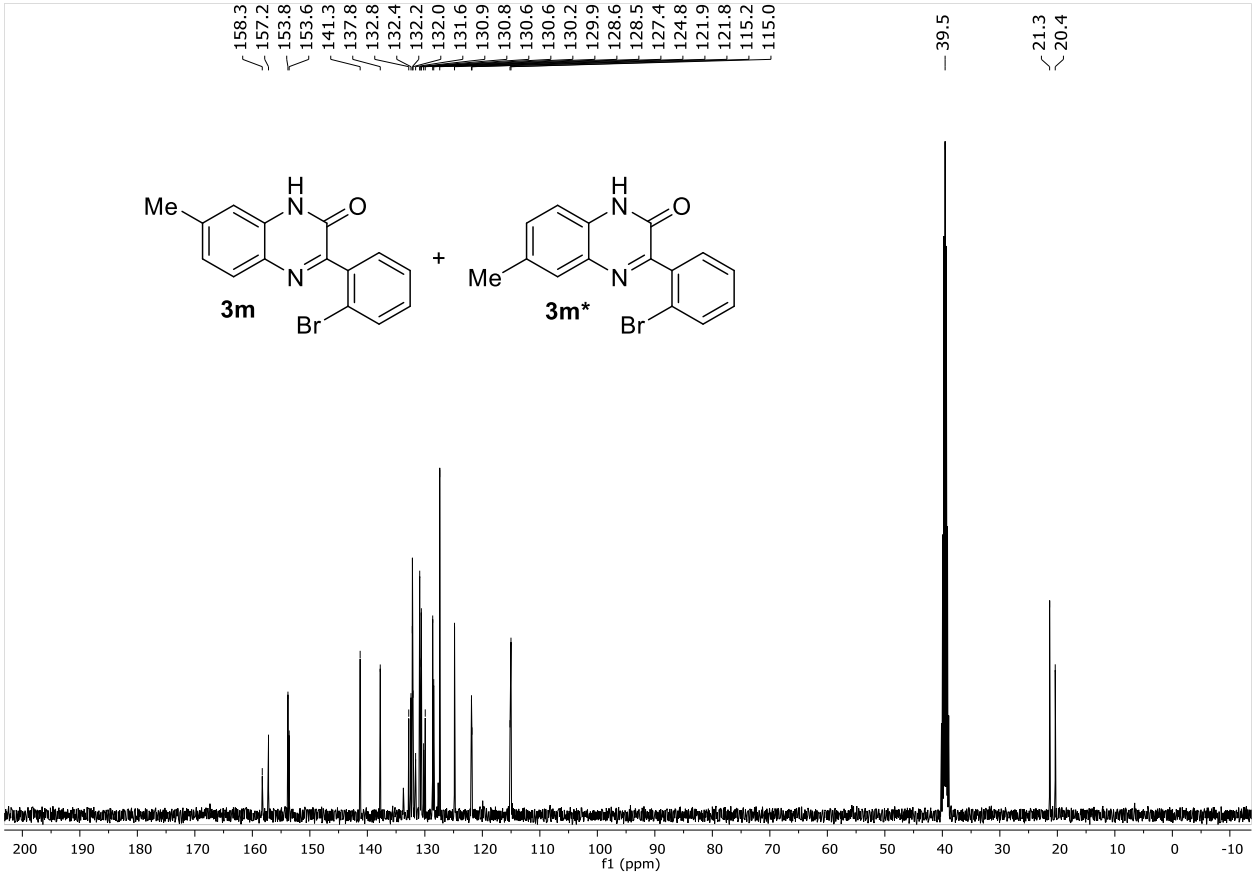
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3l** + **3l***.



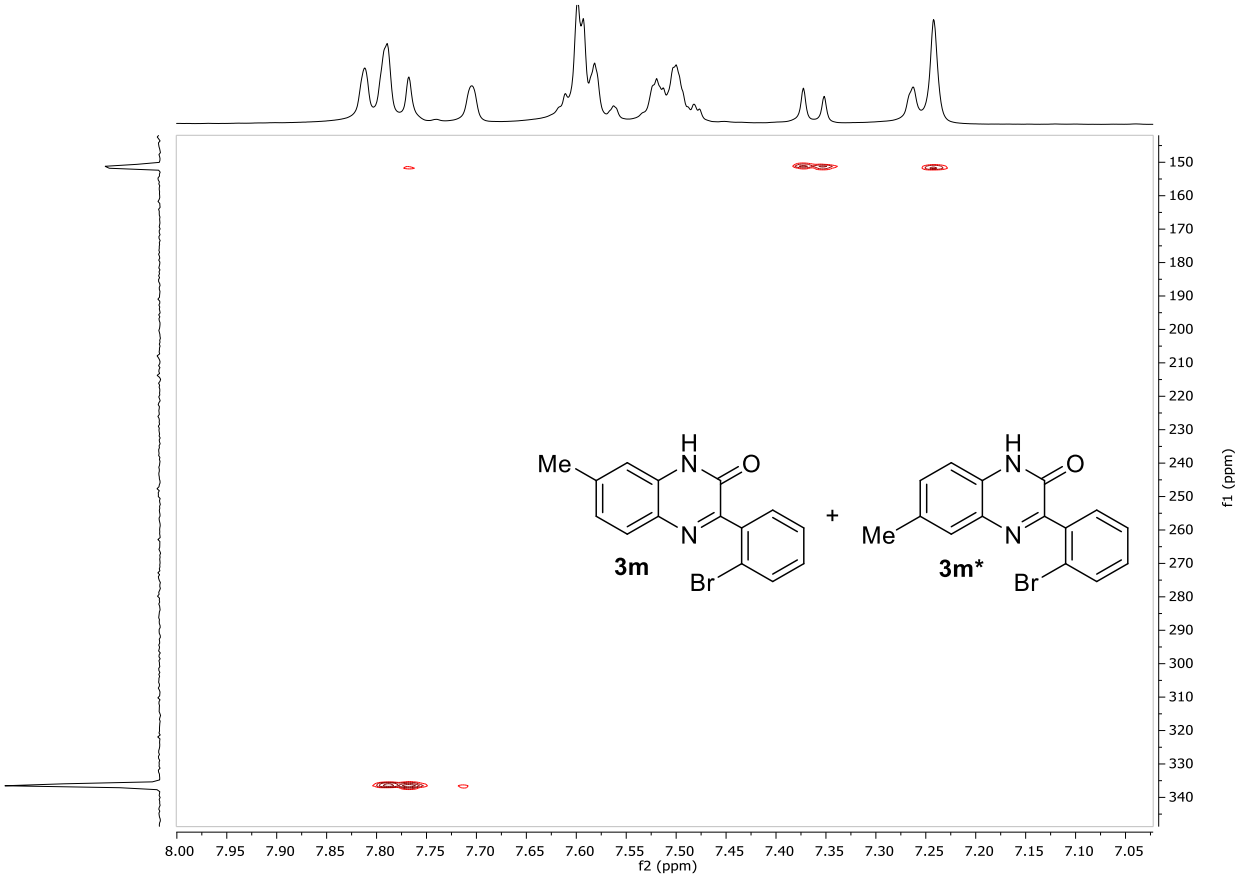
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3l** + **3l***.



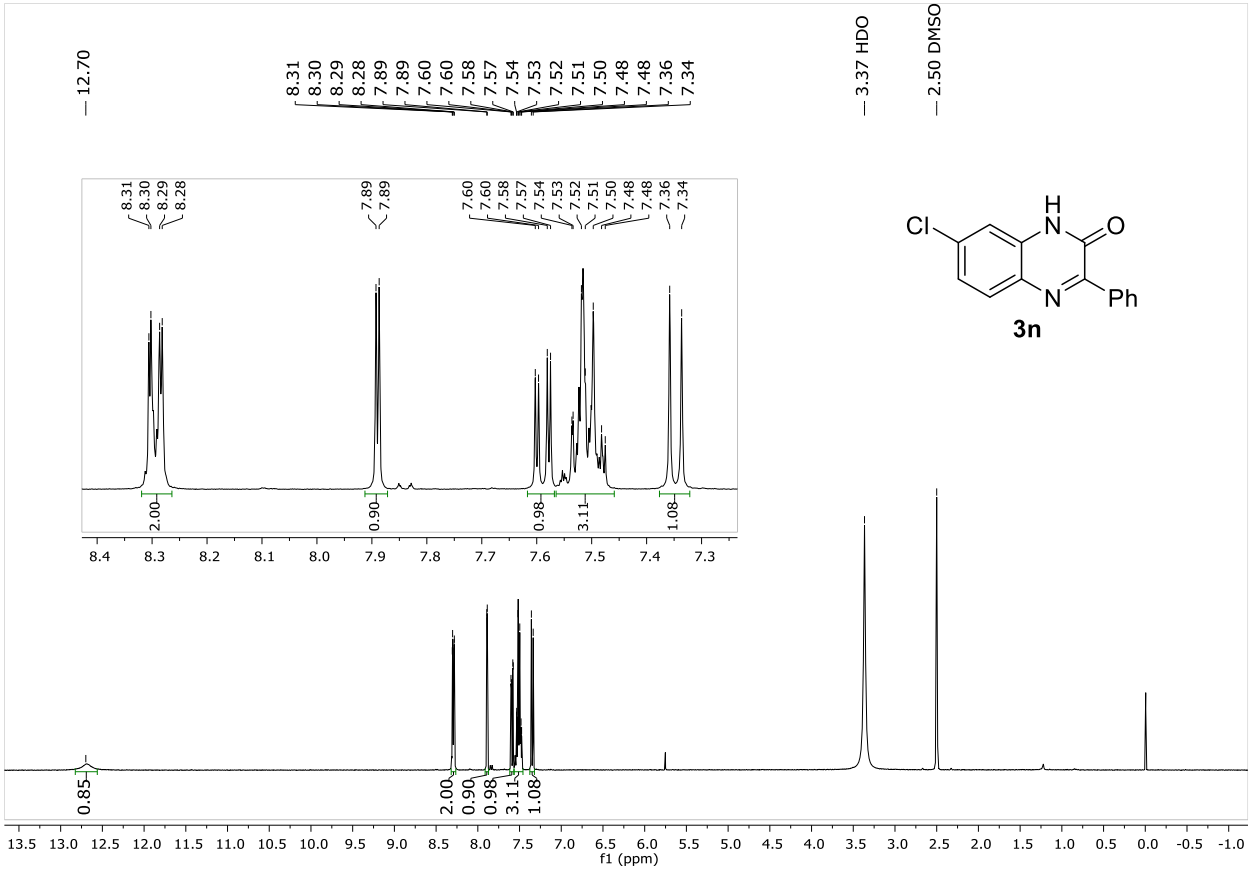
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3m** + **3m***.



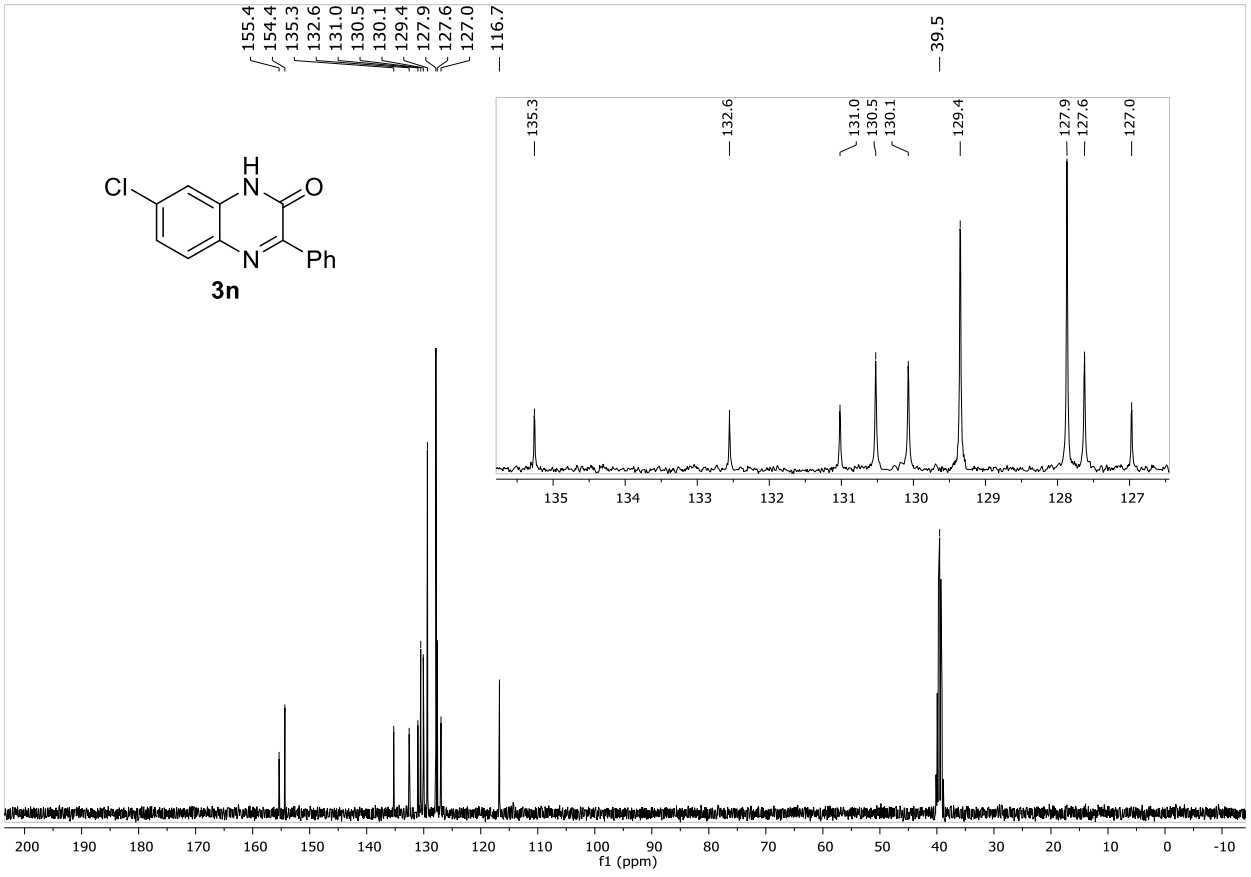
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of **3m** + **3m***.



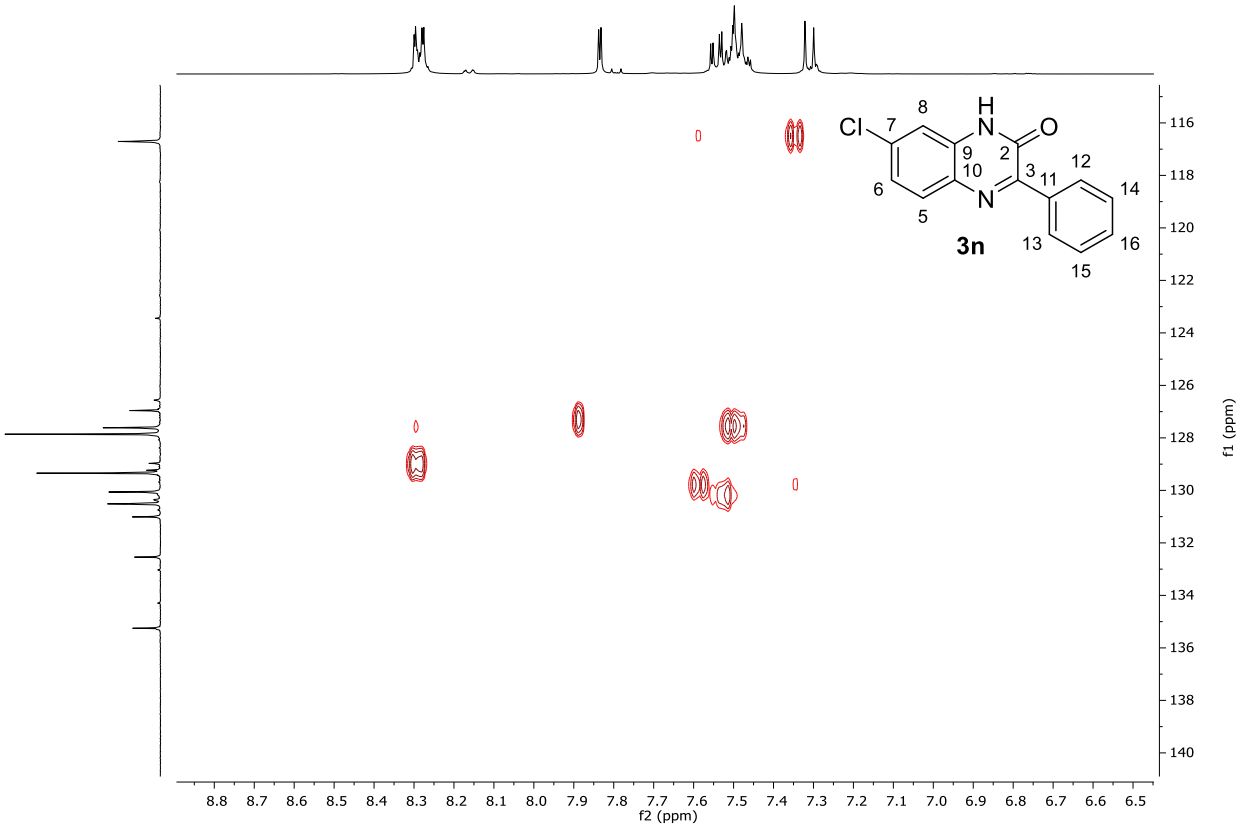
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d$_6$) spectrum of **3m** + **3m***.



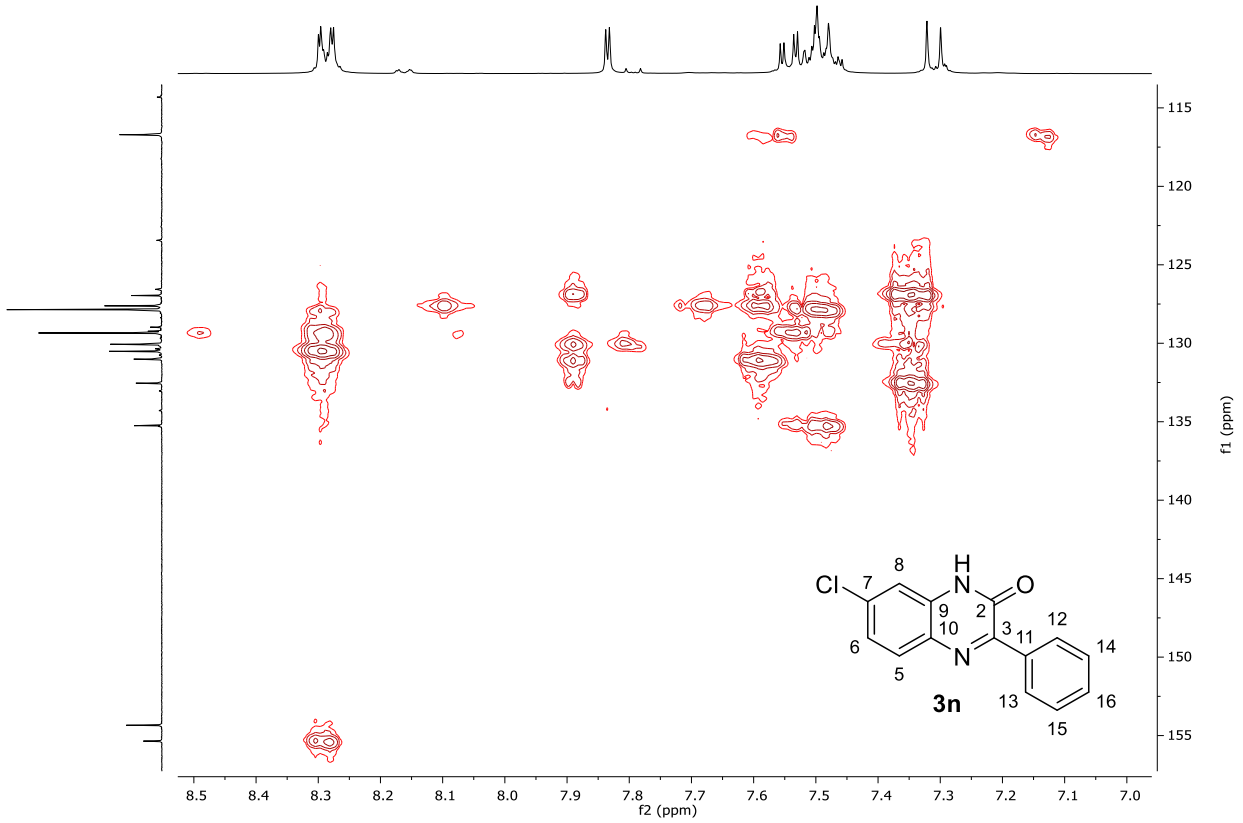
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3n**.



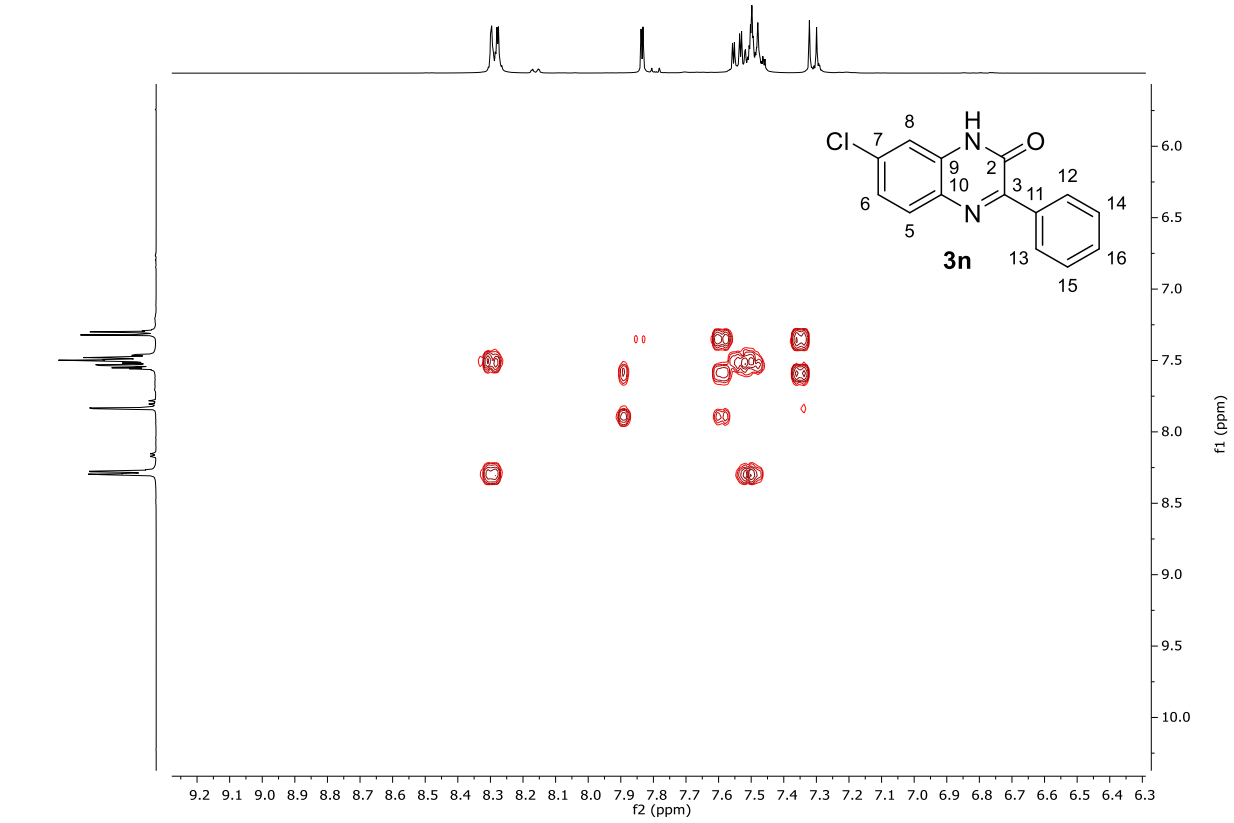
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3n**.



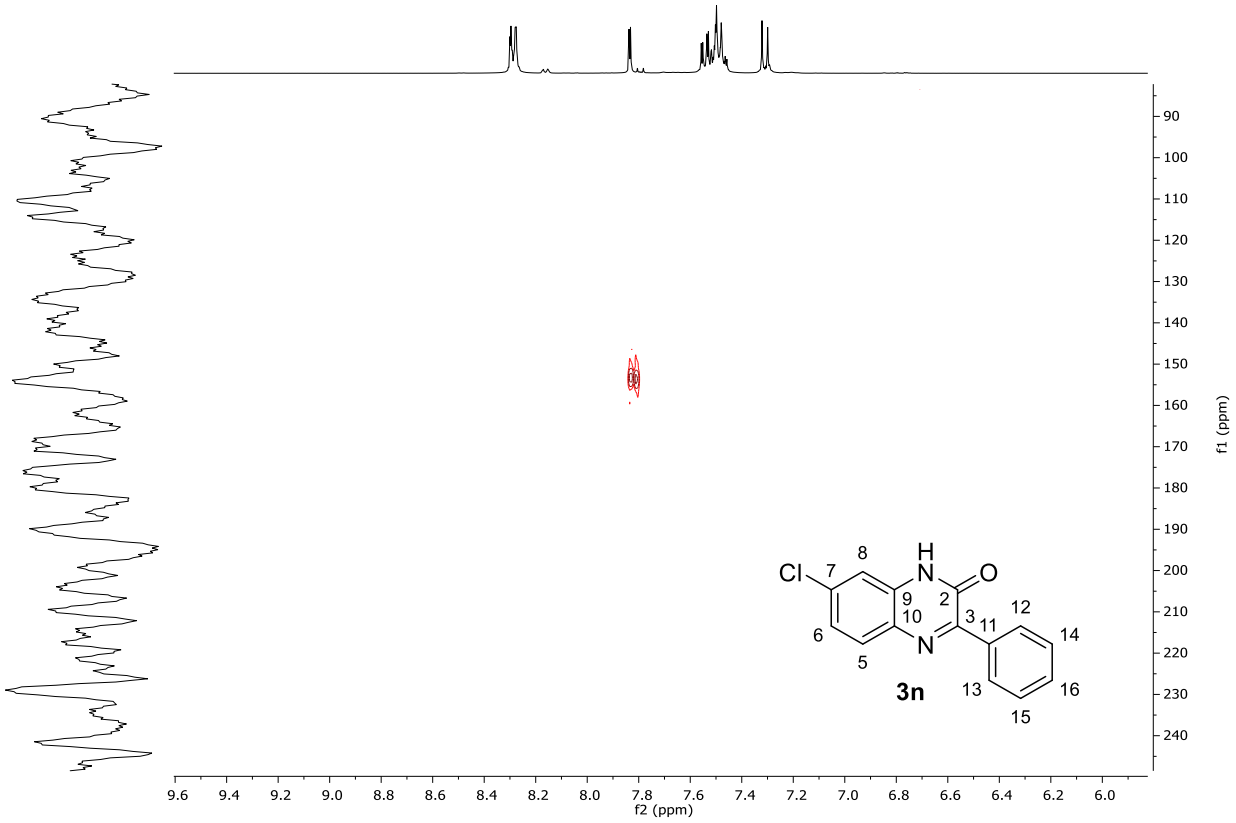
^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d_6) spectrum of **3n**.



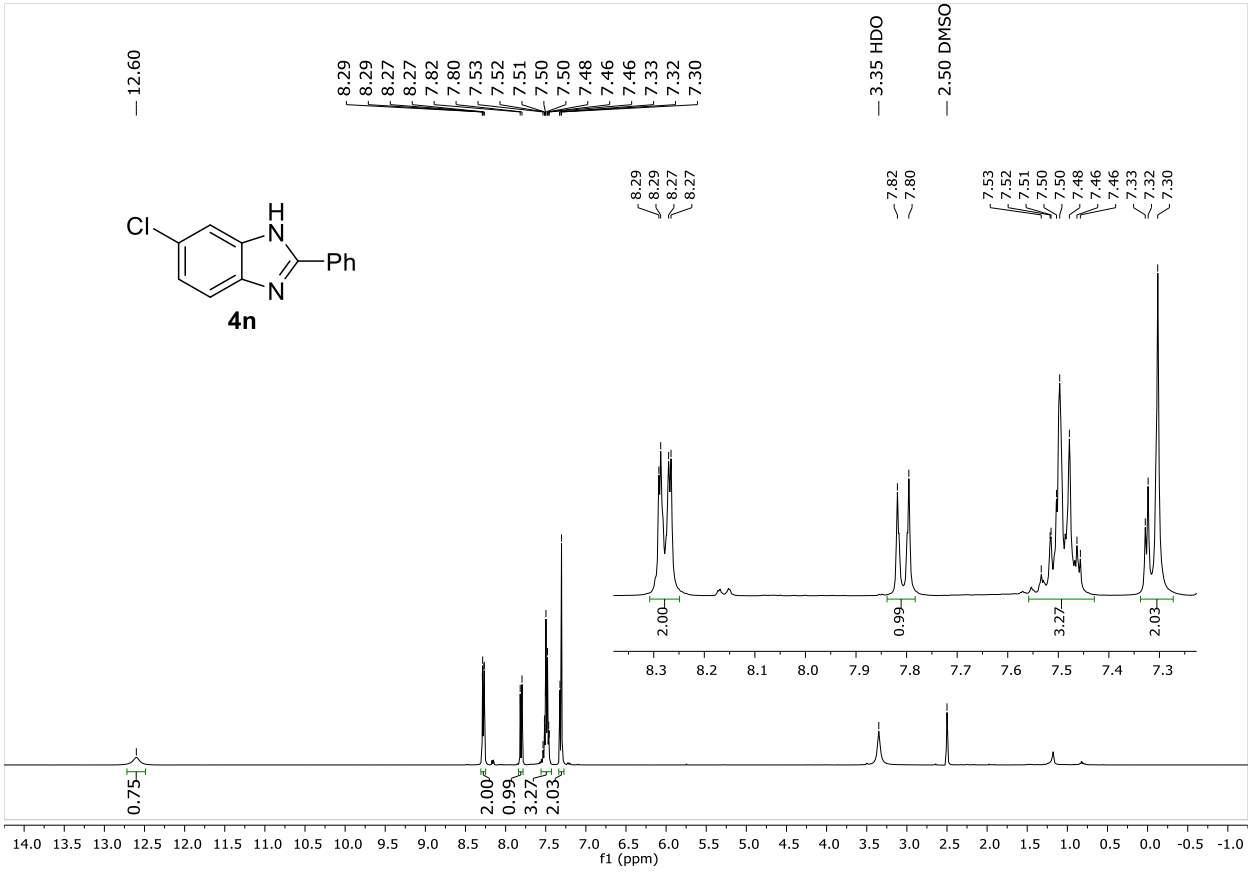
^{1}H-^{13}C HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3n**.



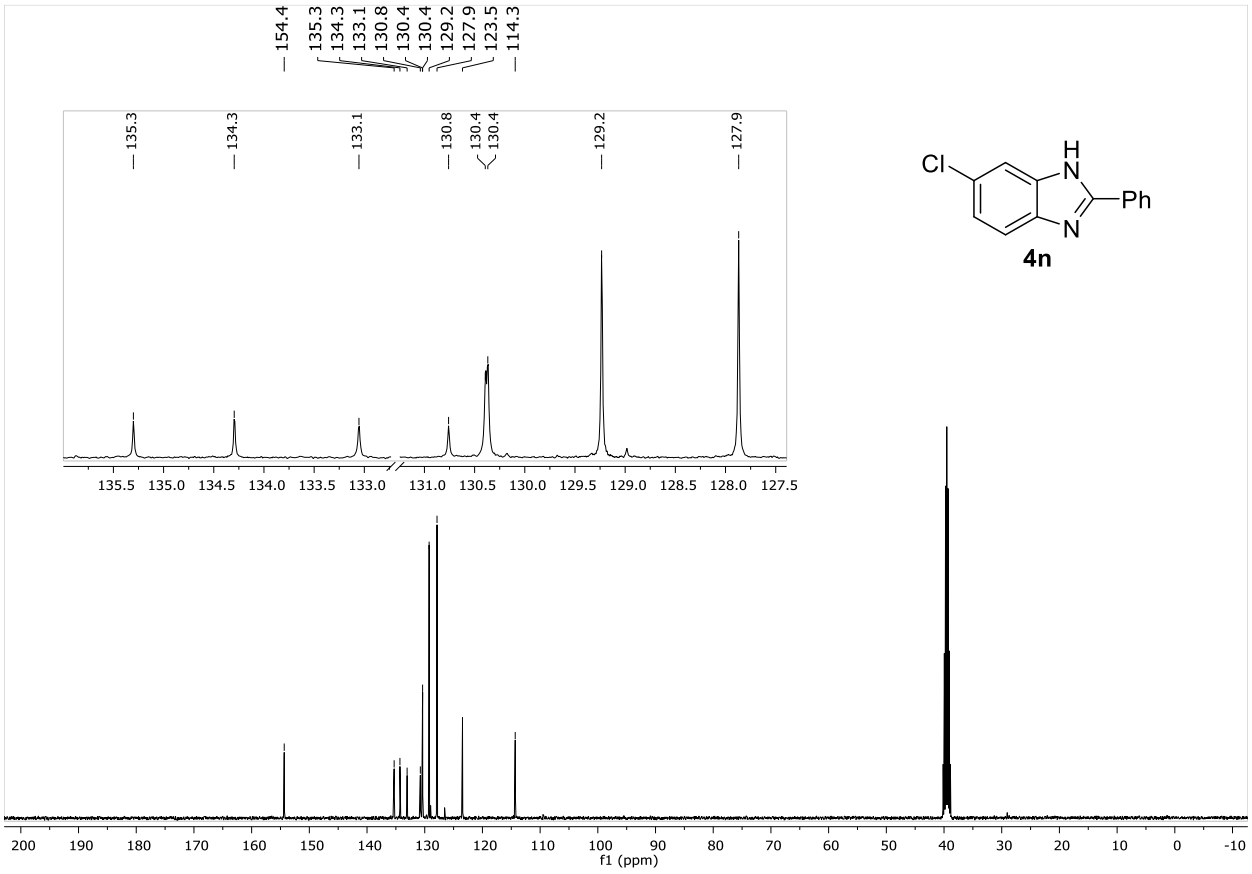
^{1}H COSY NMR (400 MHz, DMSO-d$_6$) spectrum of **3n**.



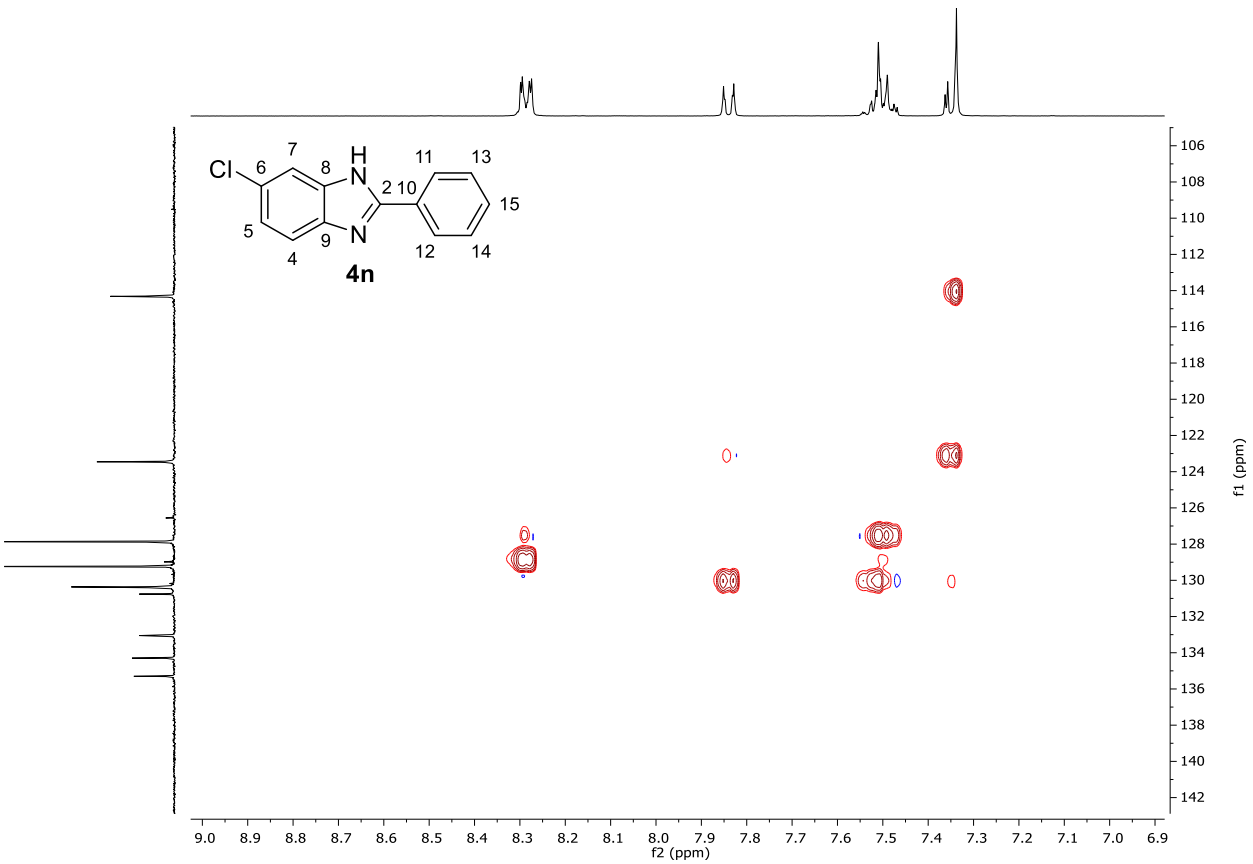
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d$_6$) spectrum of **3n**.



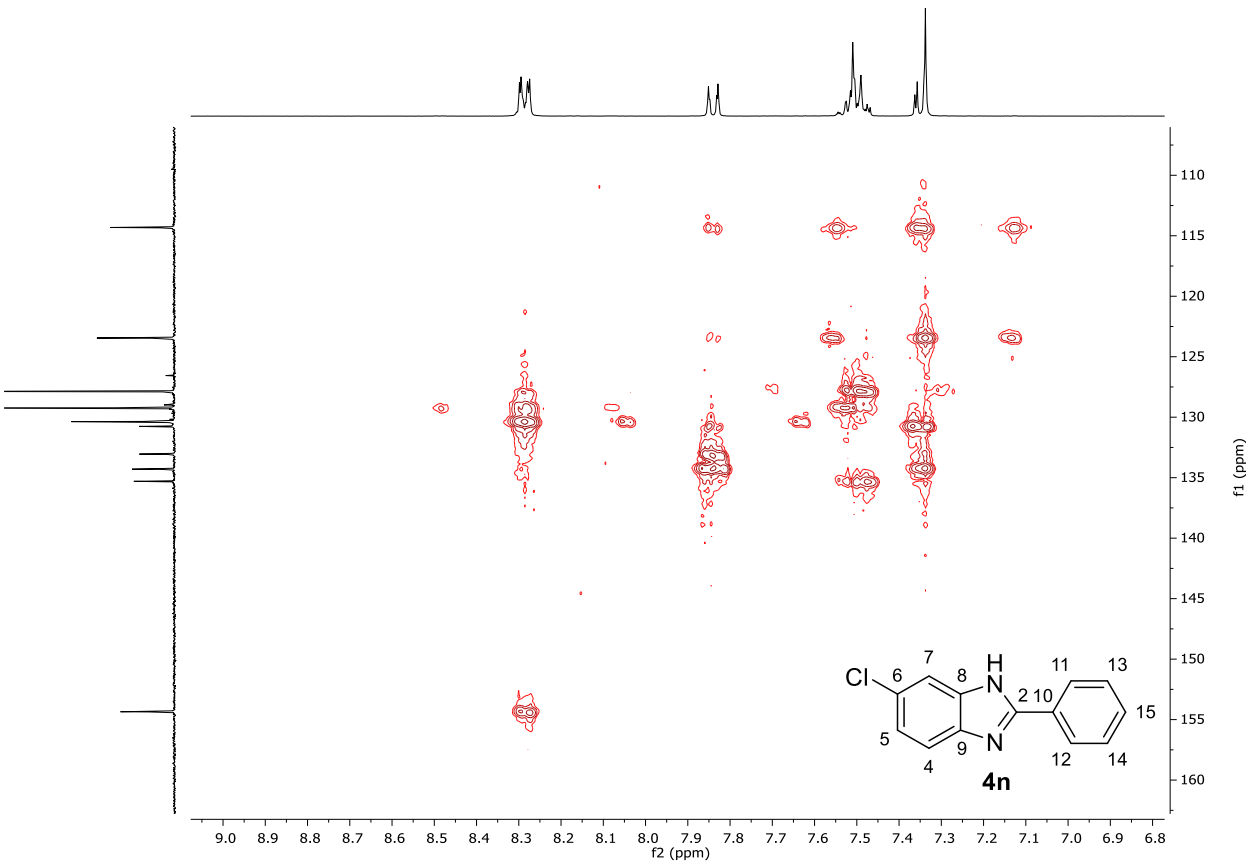
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **4n**.



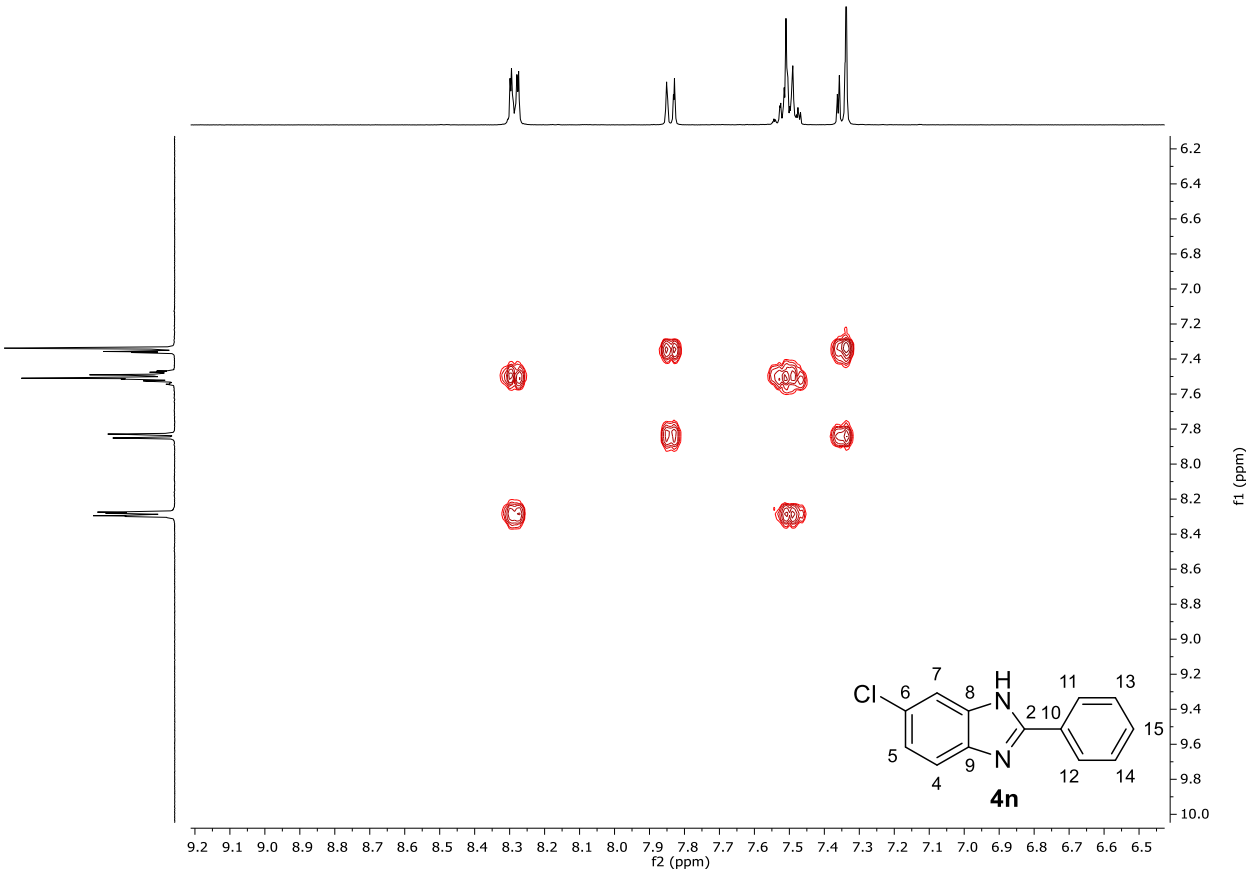
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **4n**.



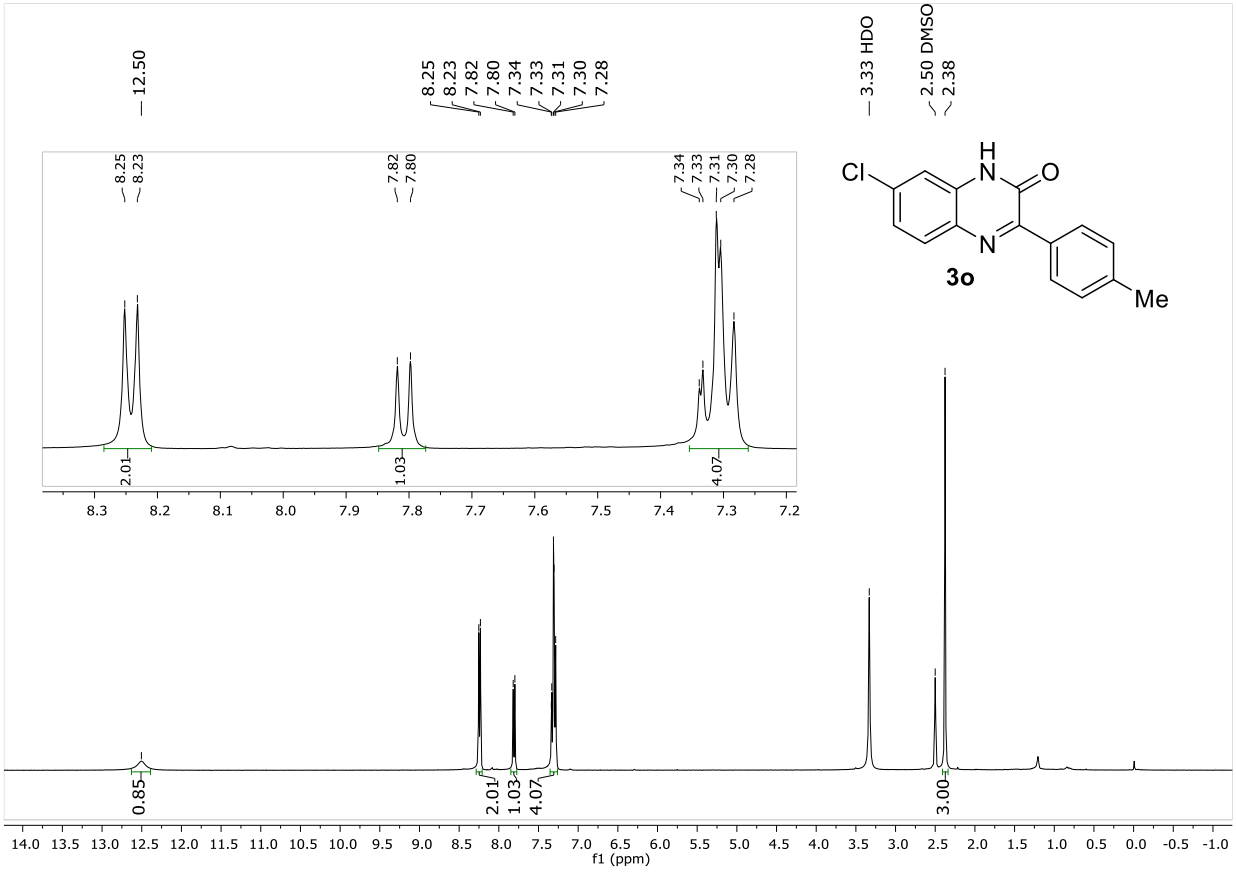
^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d$_6$) spectrum of **4n**.



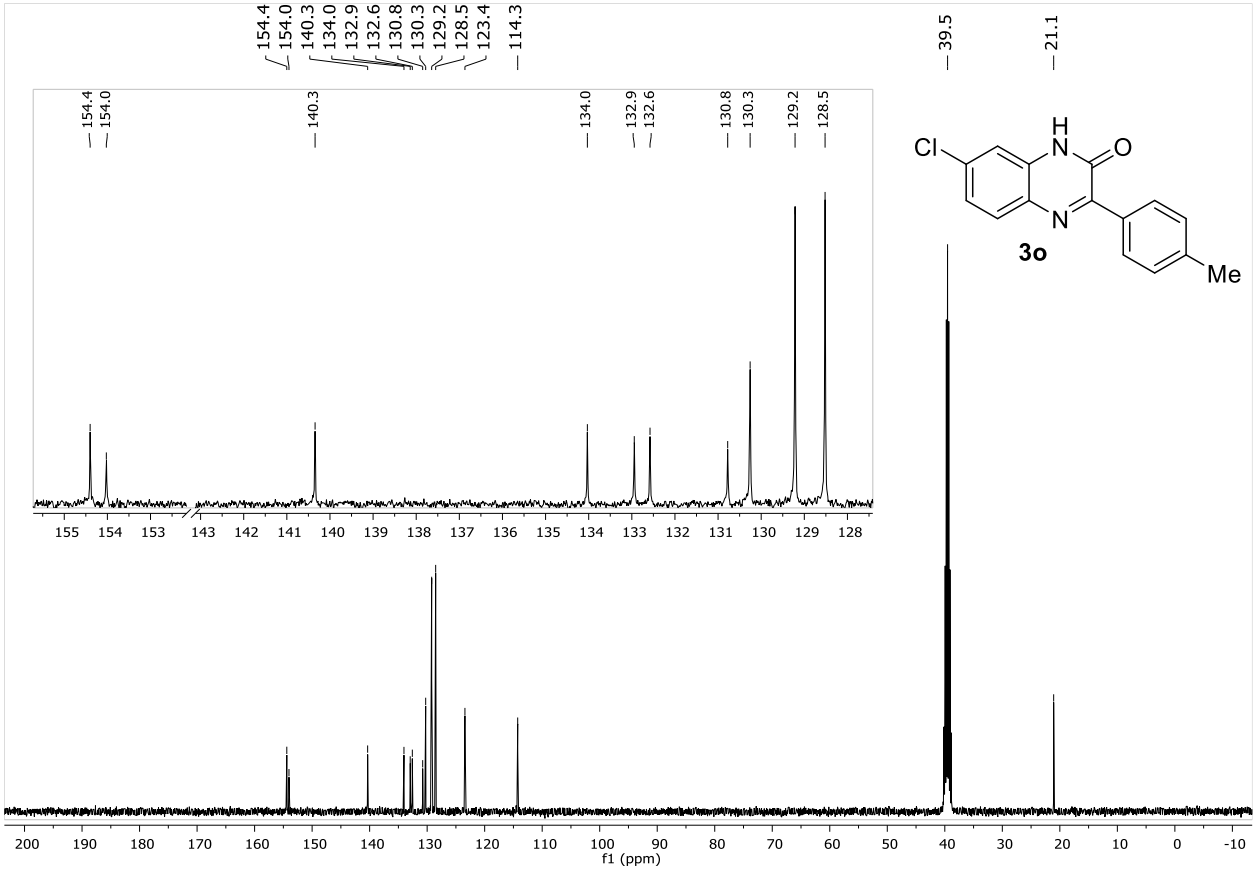
^{1}H-^{13}C HMBC NMR (400 MHz, DMSO-d$_6$) spectrum of **4n**.



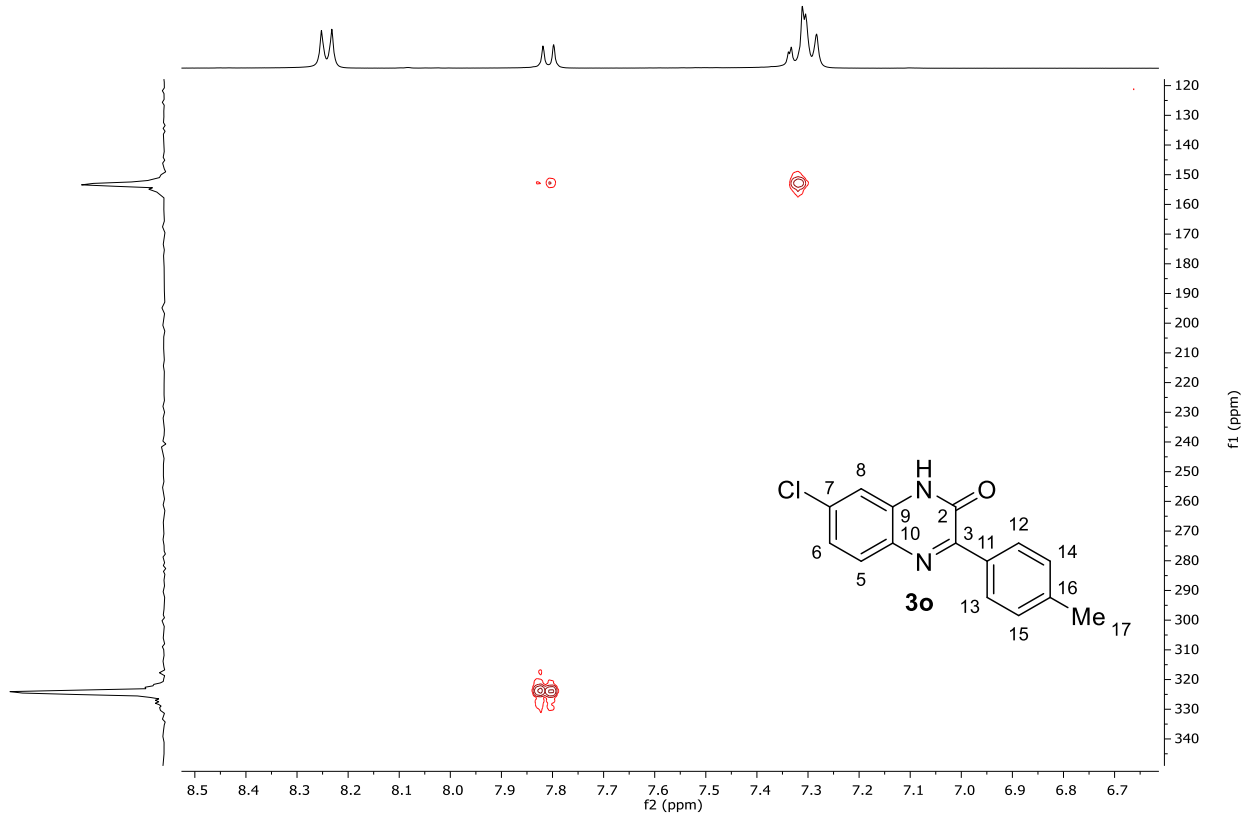
^{1}H COSY NMR (400 MHz, DMSO-d_6) spectrum of **4n**.



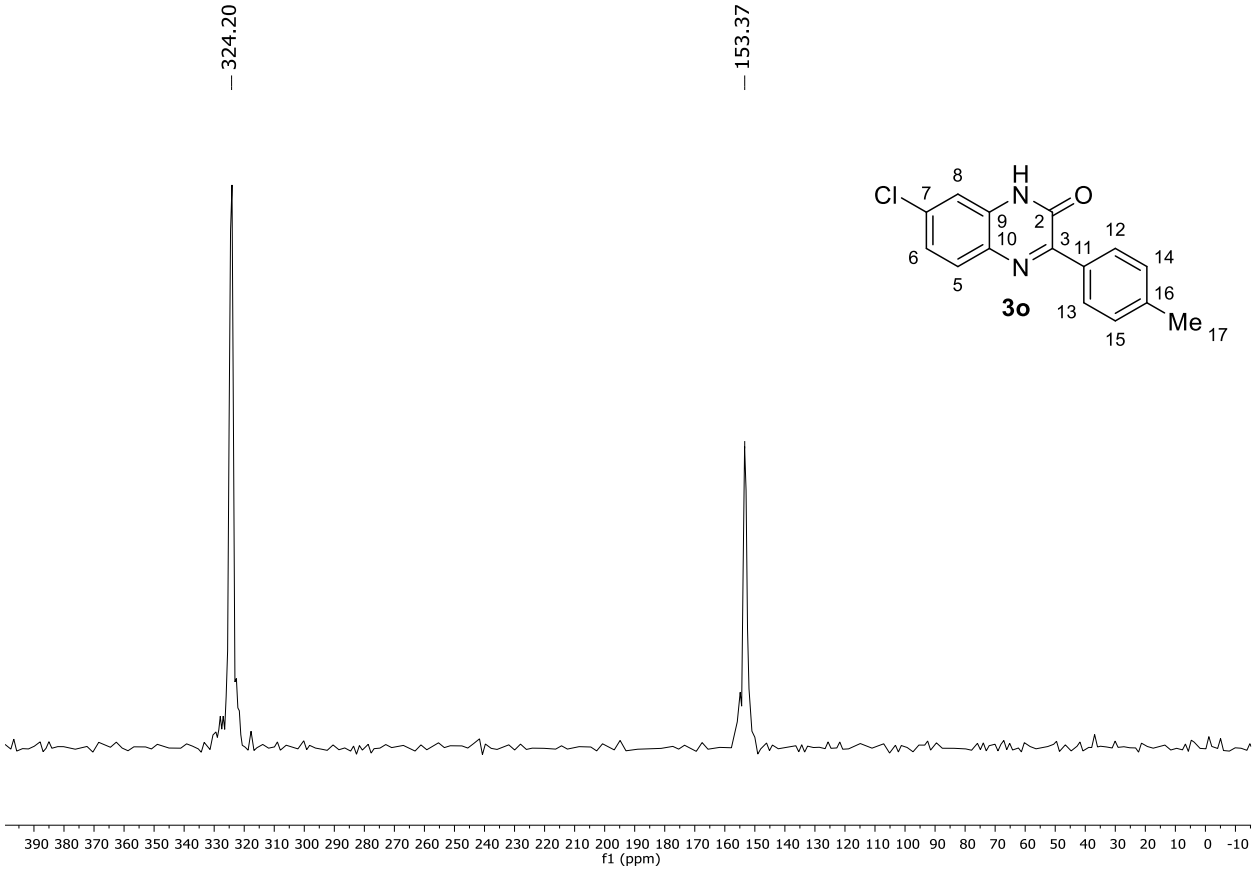
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3o**.



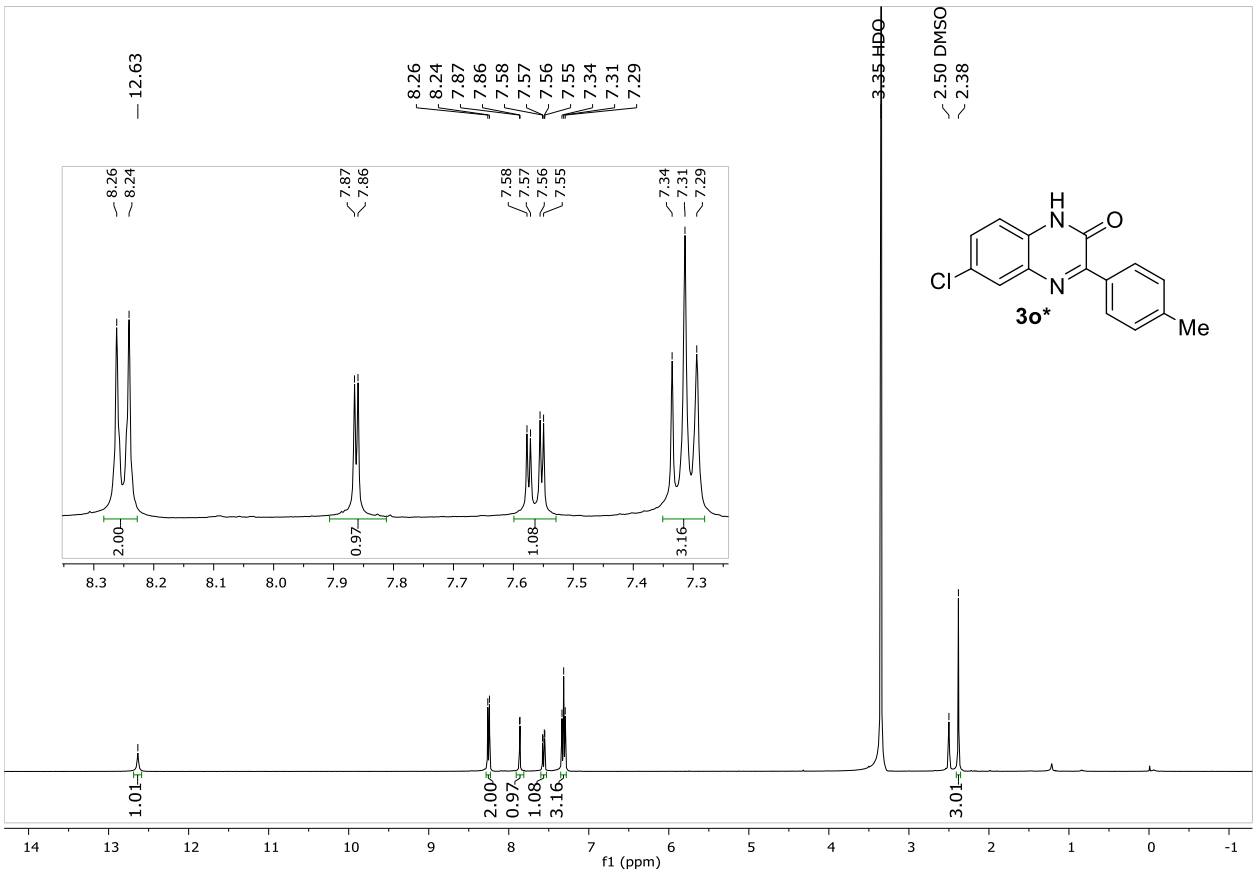
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3o**.



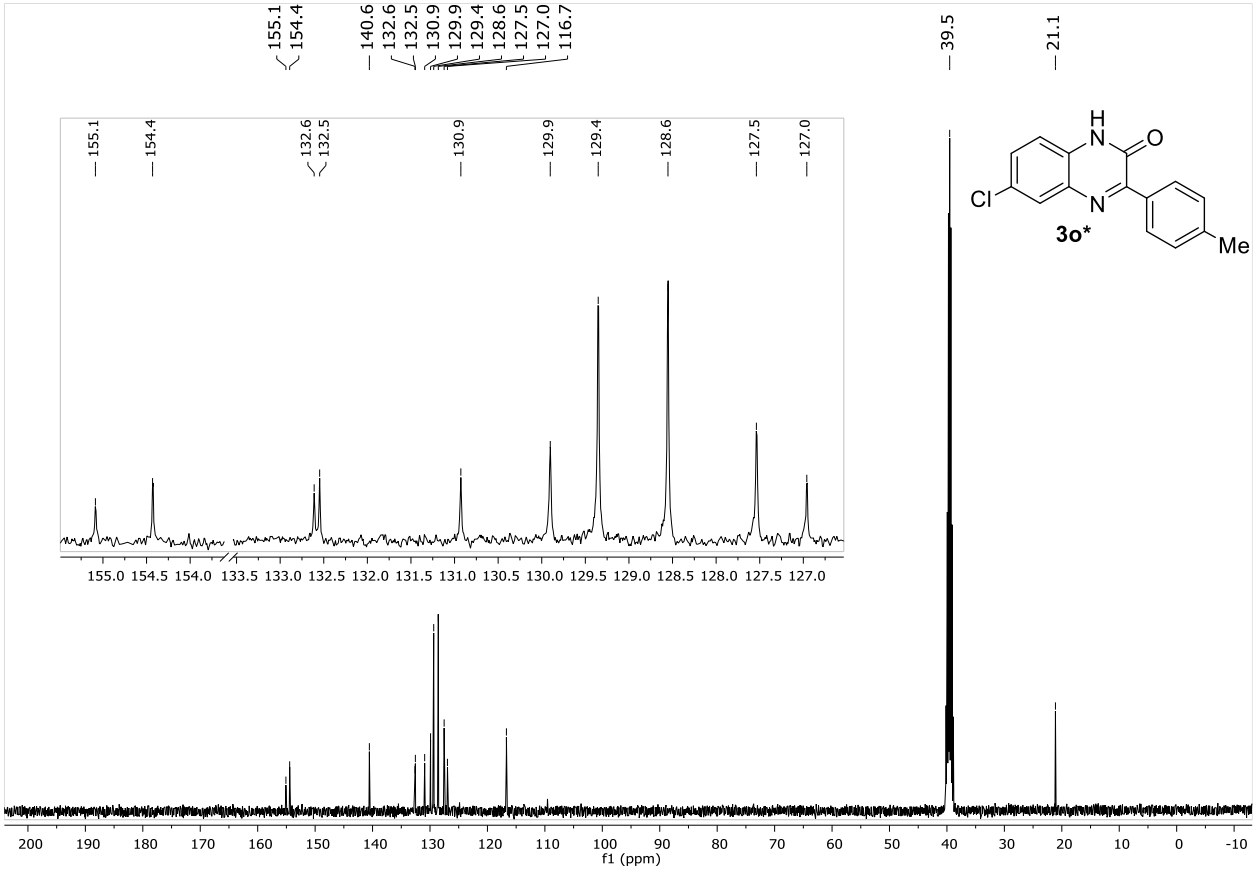
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3o**.



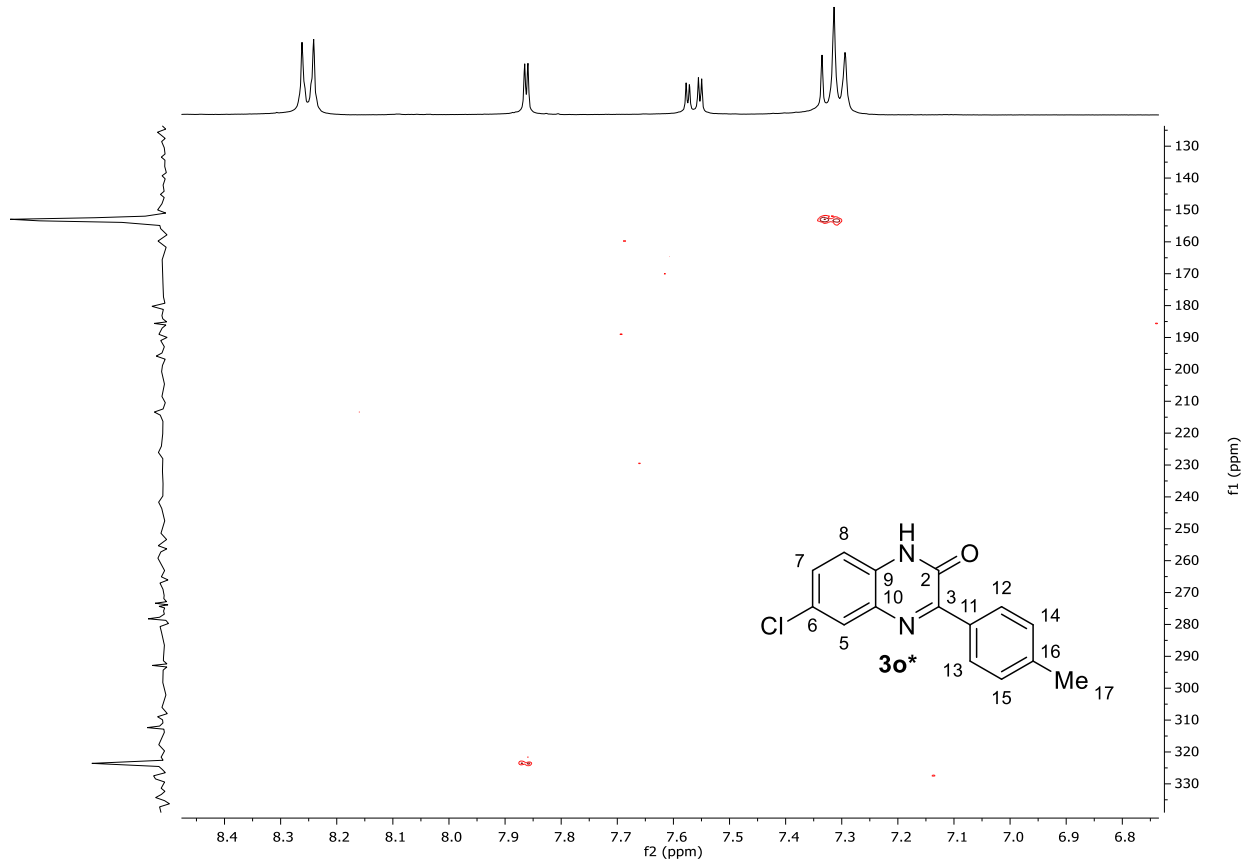
^{15}N NMR (40 MHz, DMSO-d_6) spectrum of **3o**.



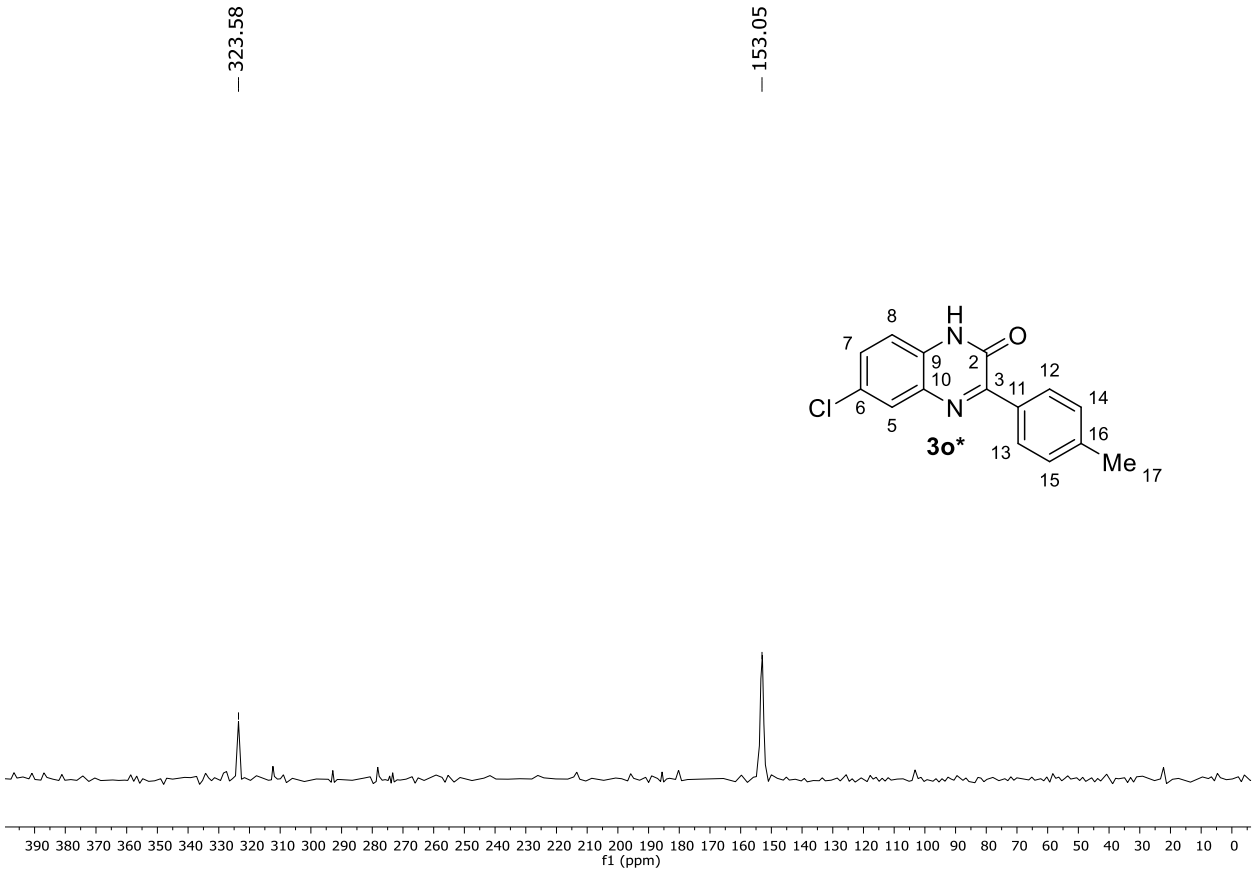
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3o***



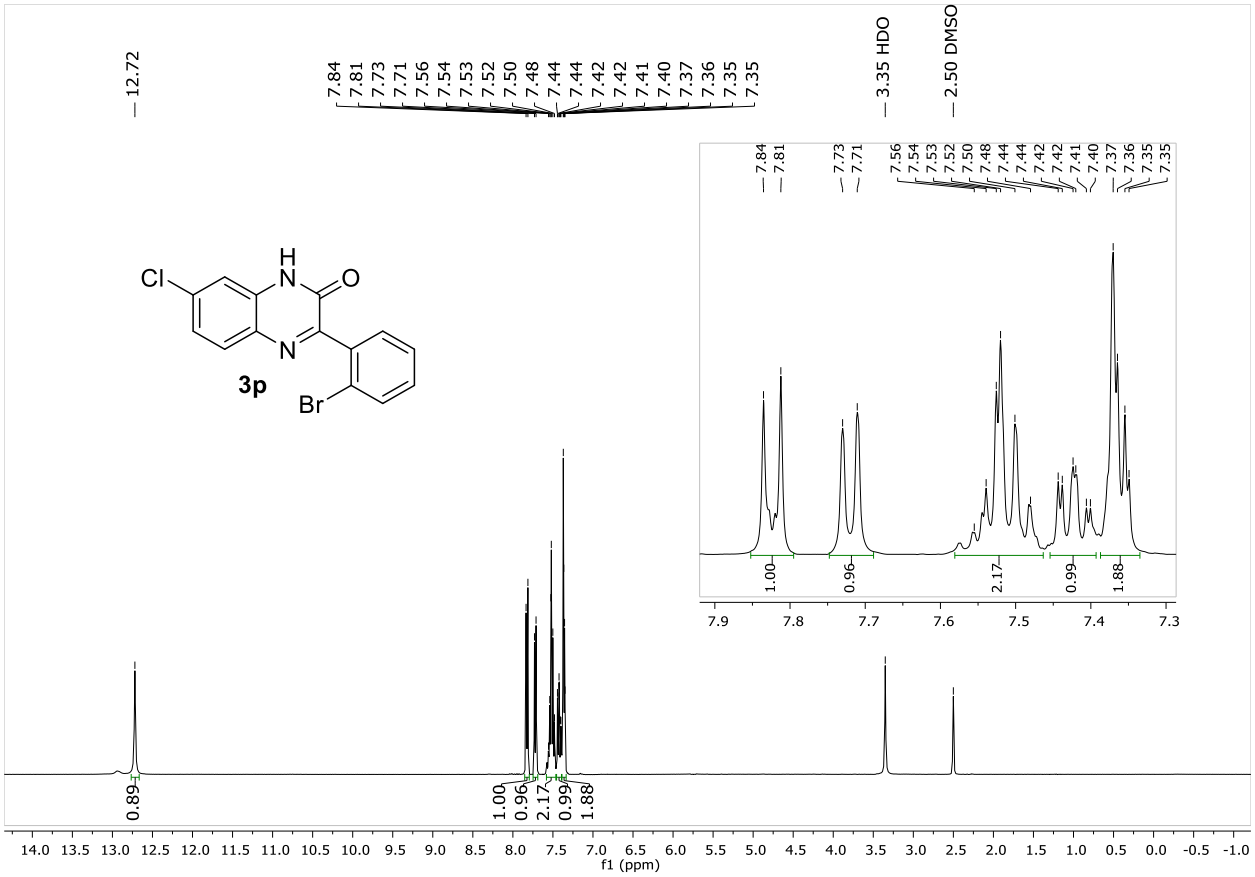
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3o***



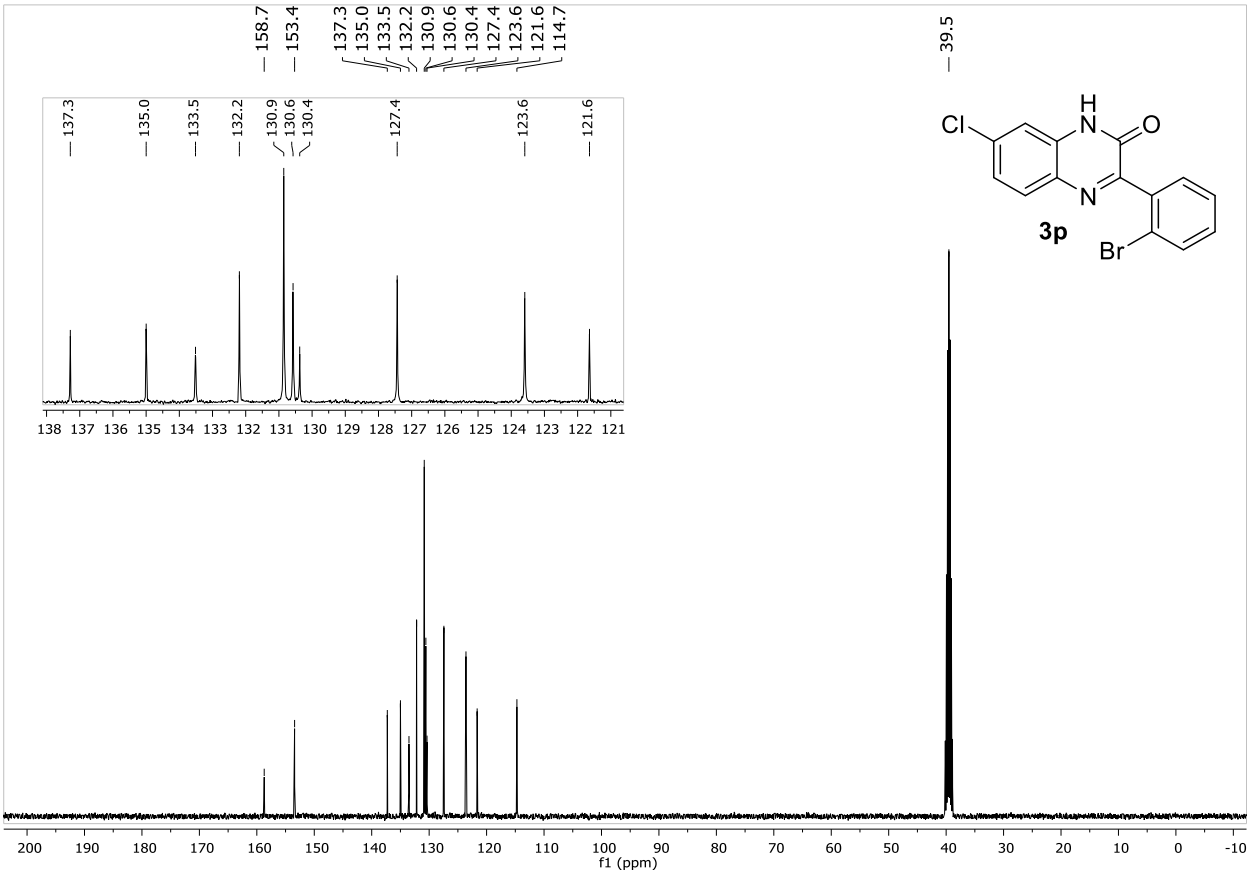
$^{1}H,^{15}N$ HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3o***



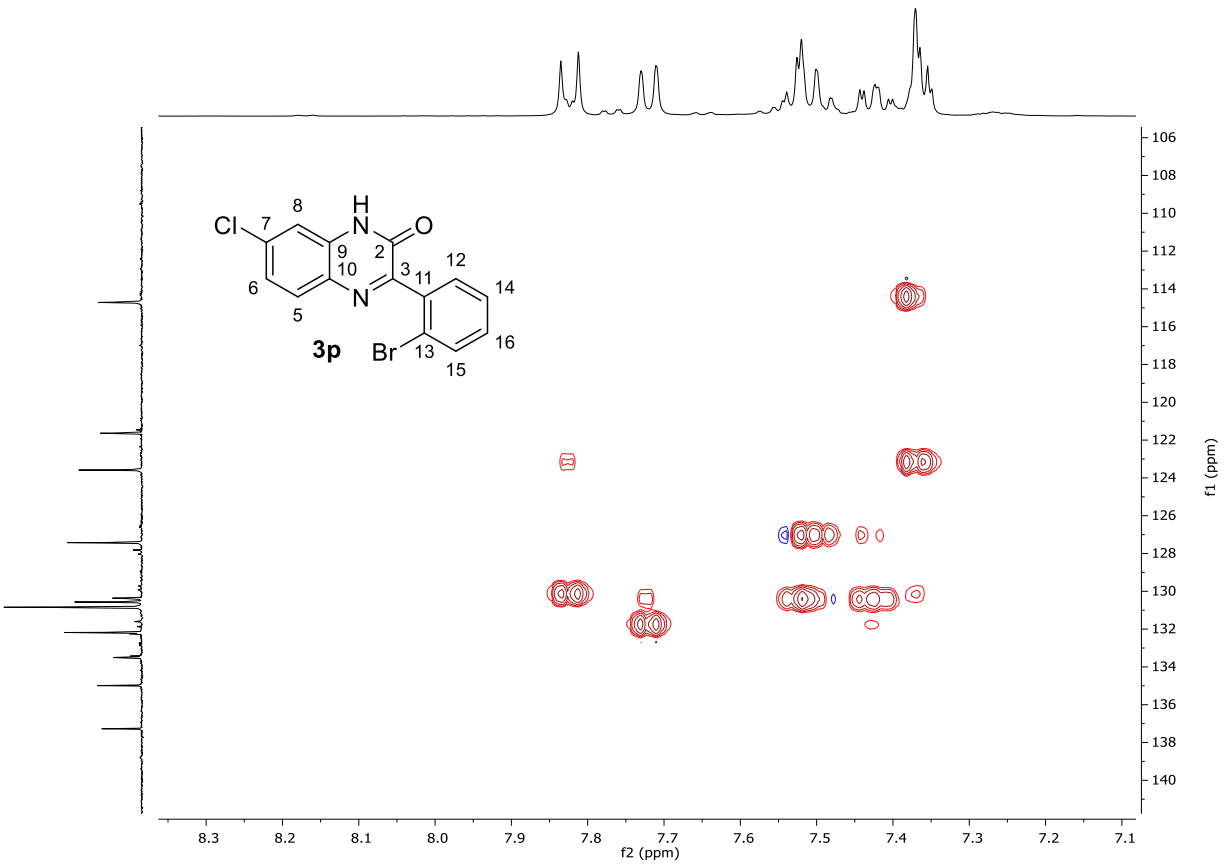
^{15}N NMR (40 MHz, DMSO-d_6) spectrum of **3o***



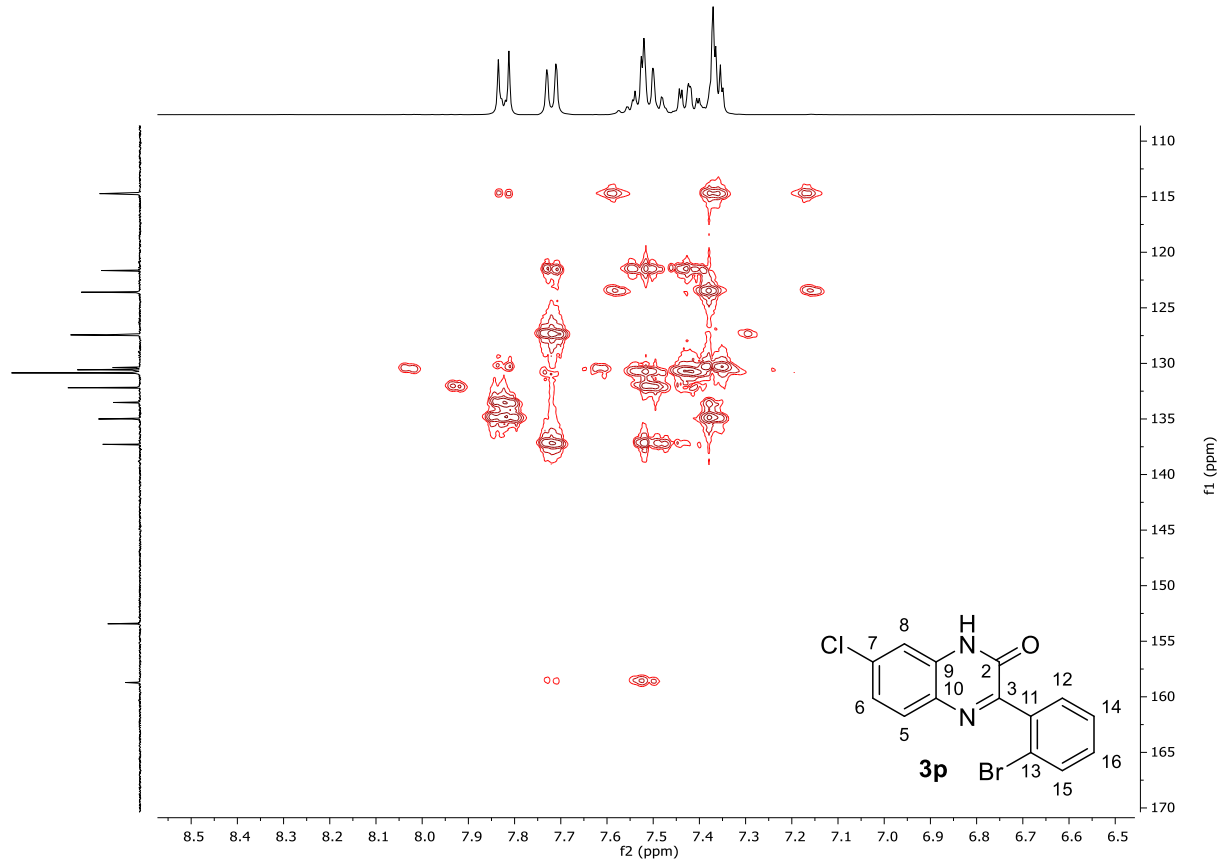
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3p**.



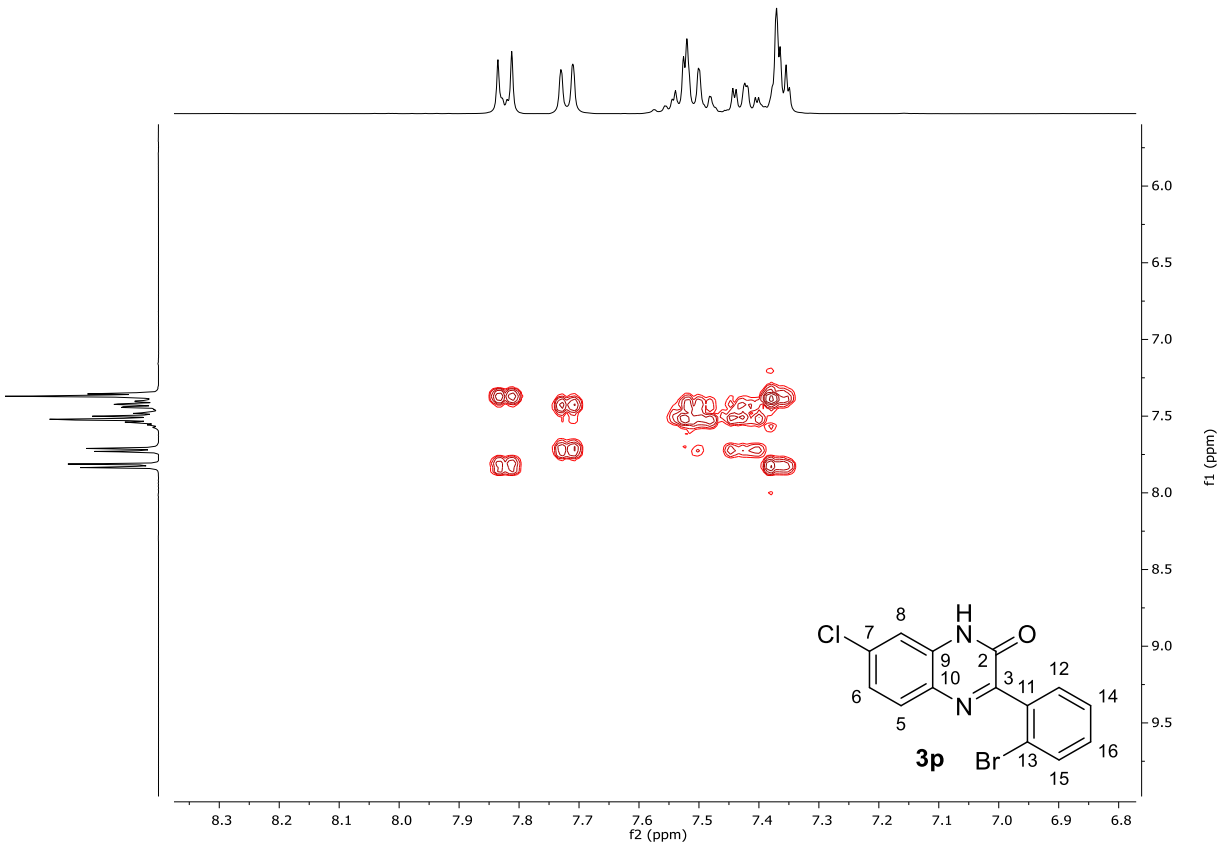
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3p**.



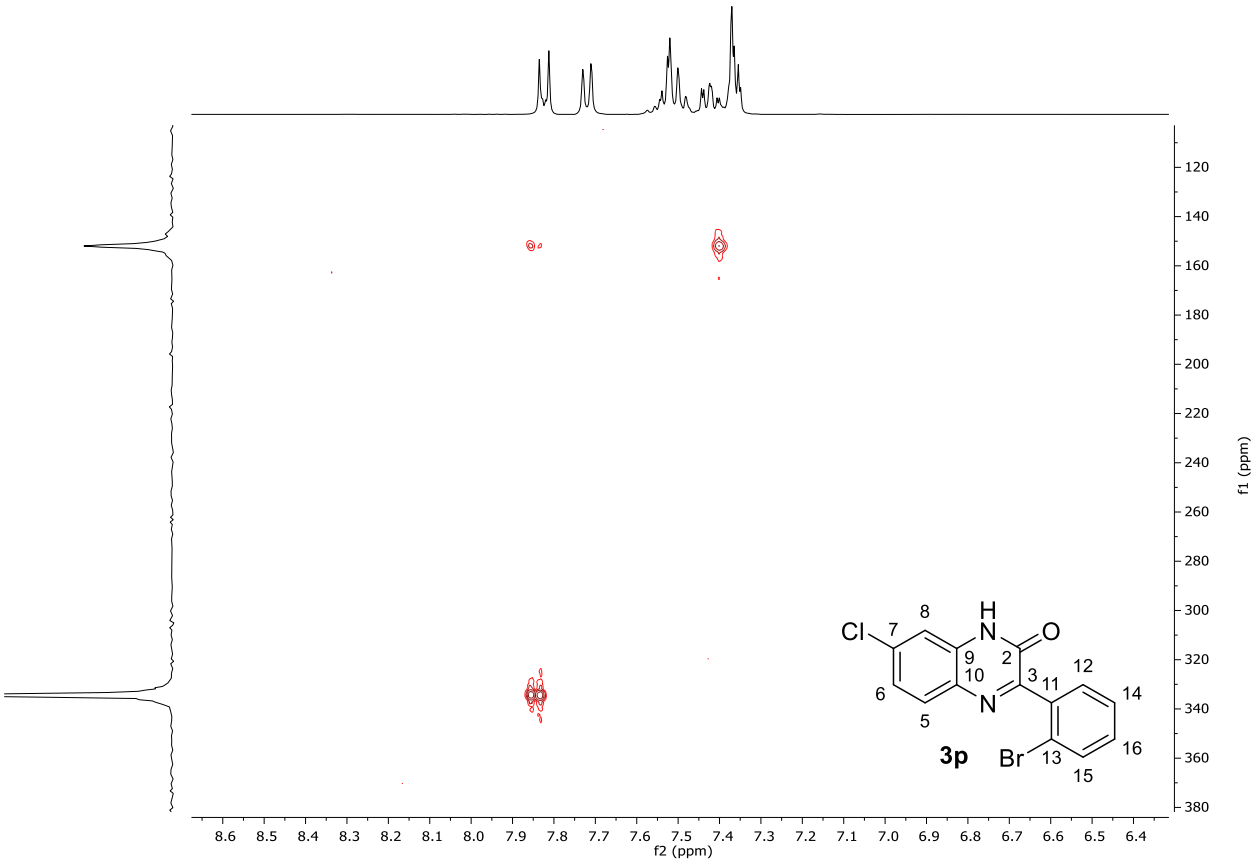
^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d$_6$) spectrum of **3p**.



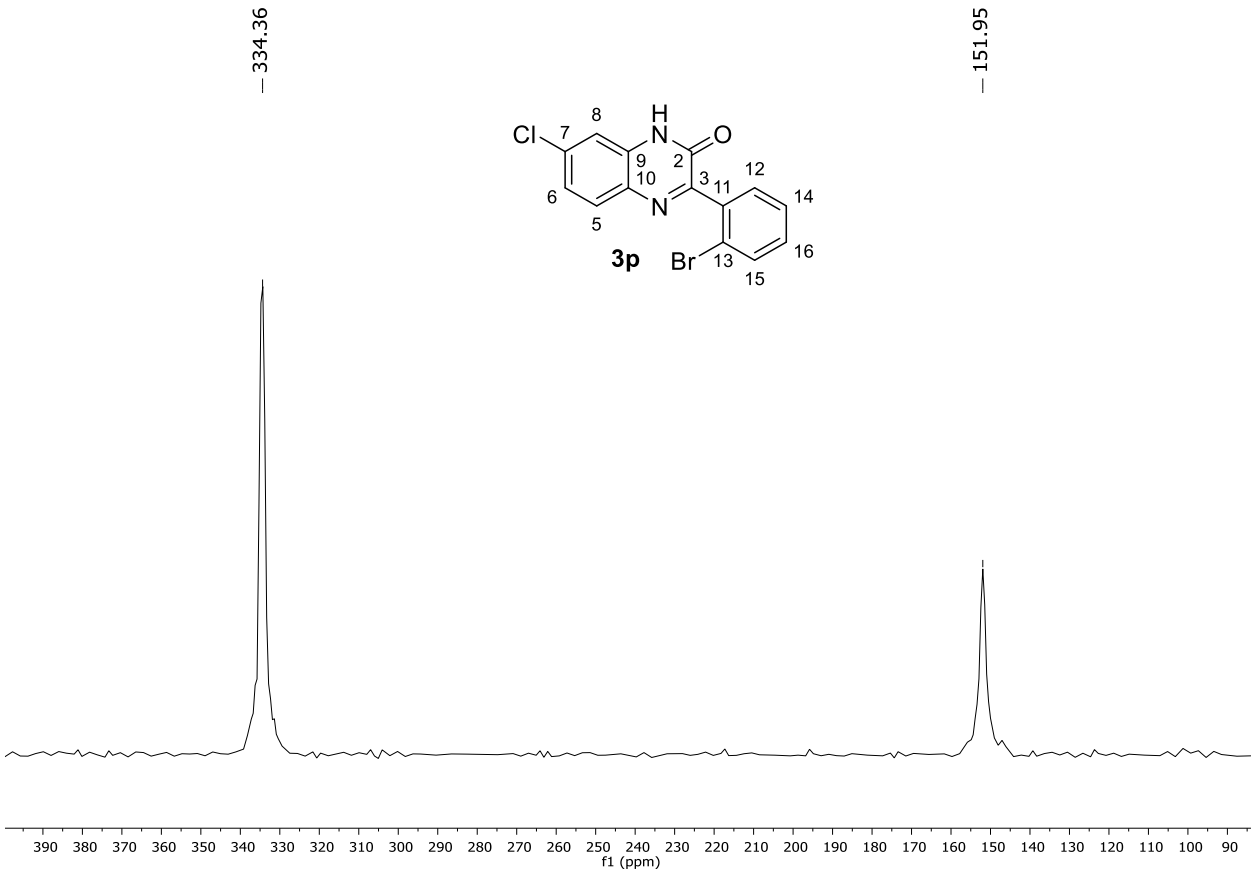
^{1}H-^{13}C HMBC NMR (400 MHz, DMSO-d$_6$) spectrum of **3p**.



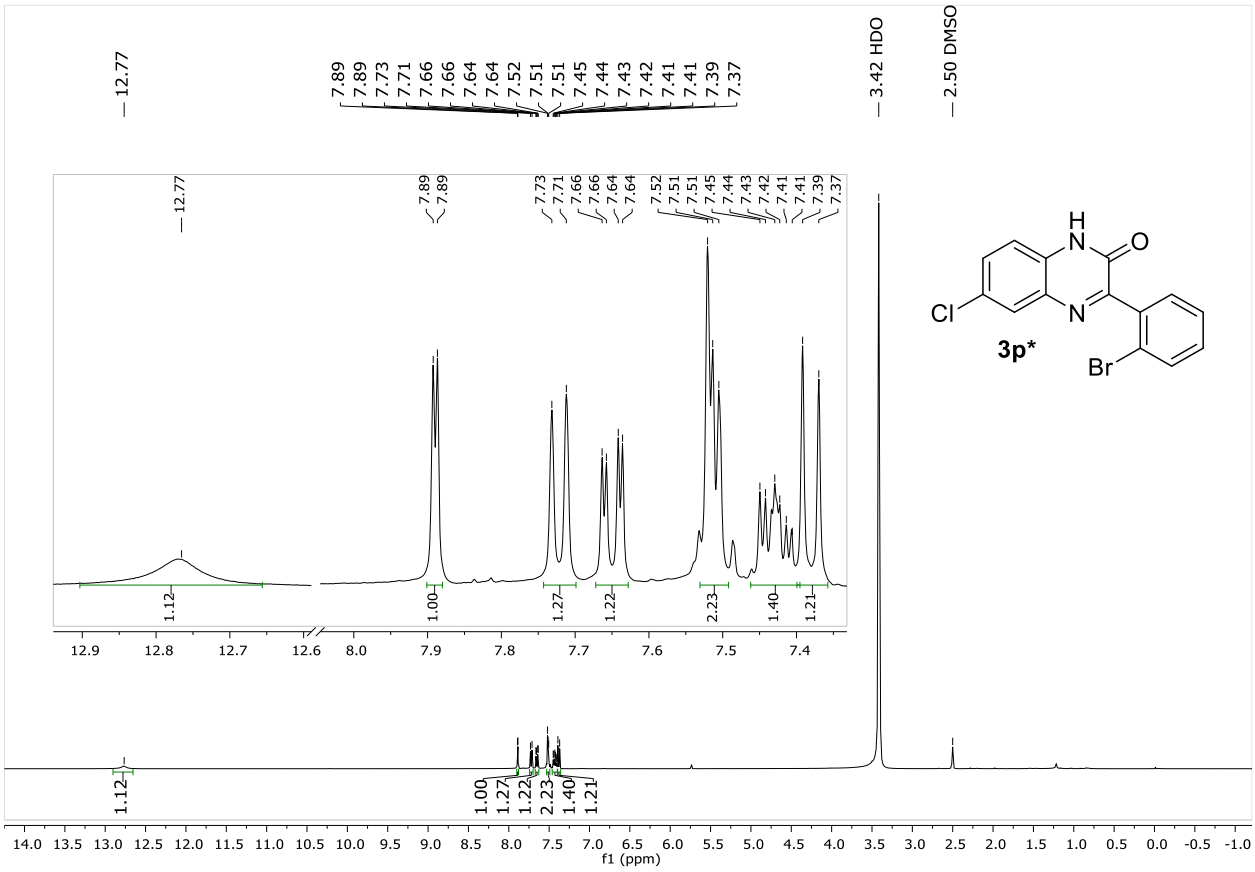
^{1}H COSY NMR (400 MHz, DMSO-d$_6$) spectrum of **3p**.



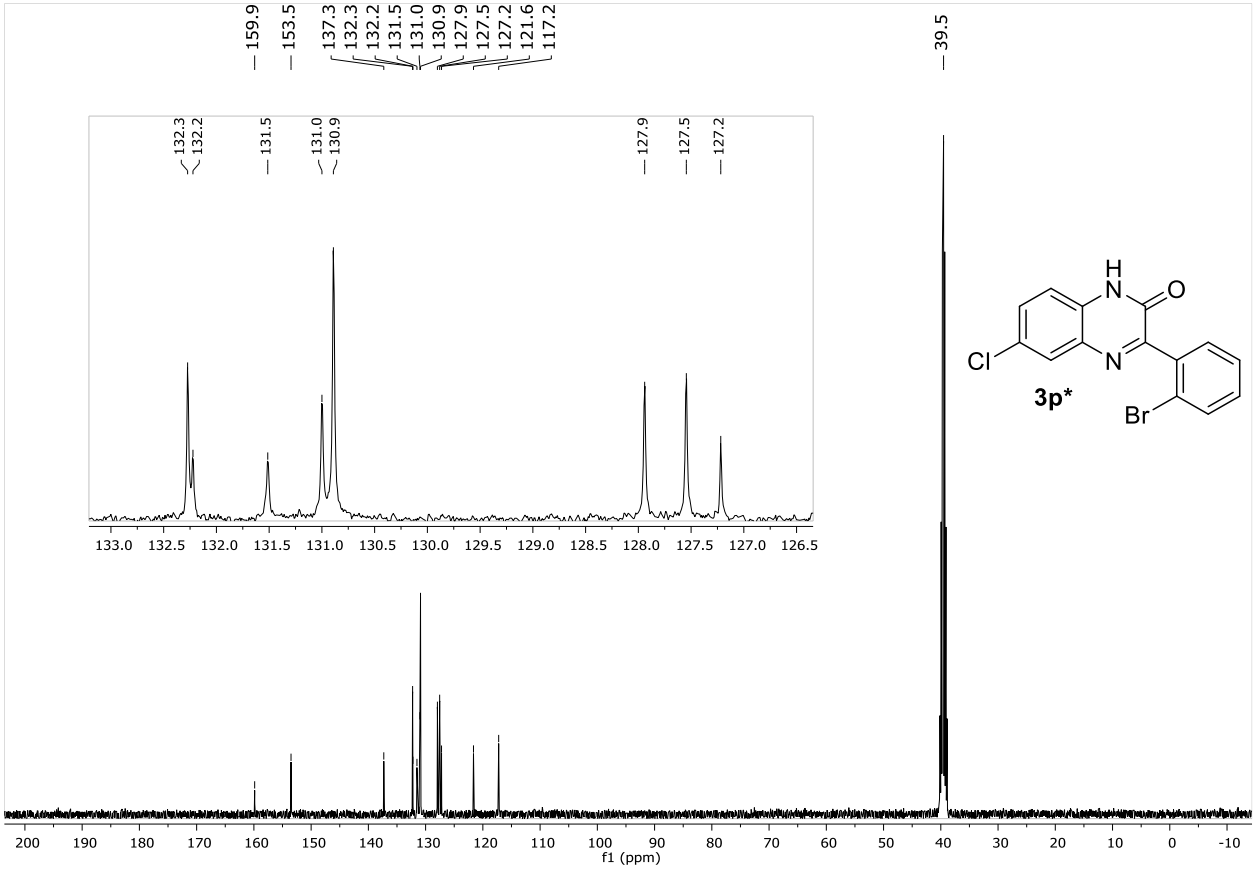
^{1}H-^{15}N HBMC (400 MHz, DMSO-d$_6$) spectrum of **3p**.



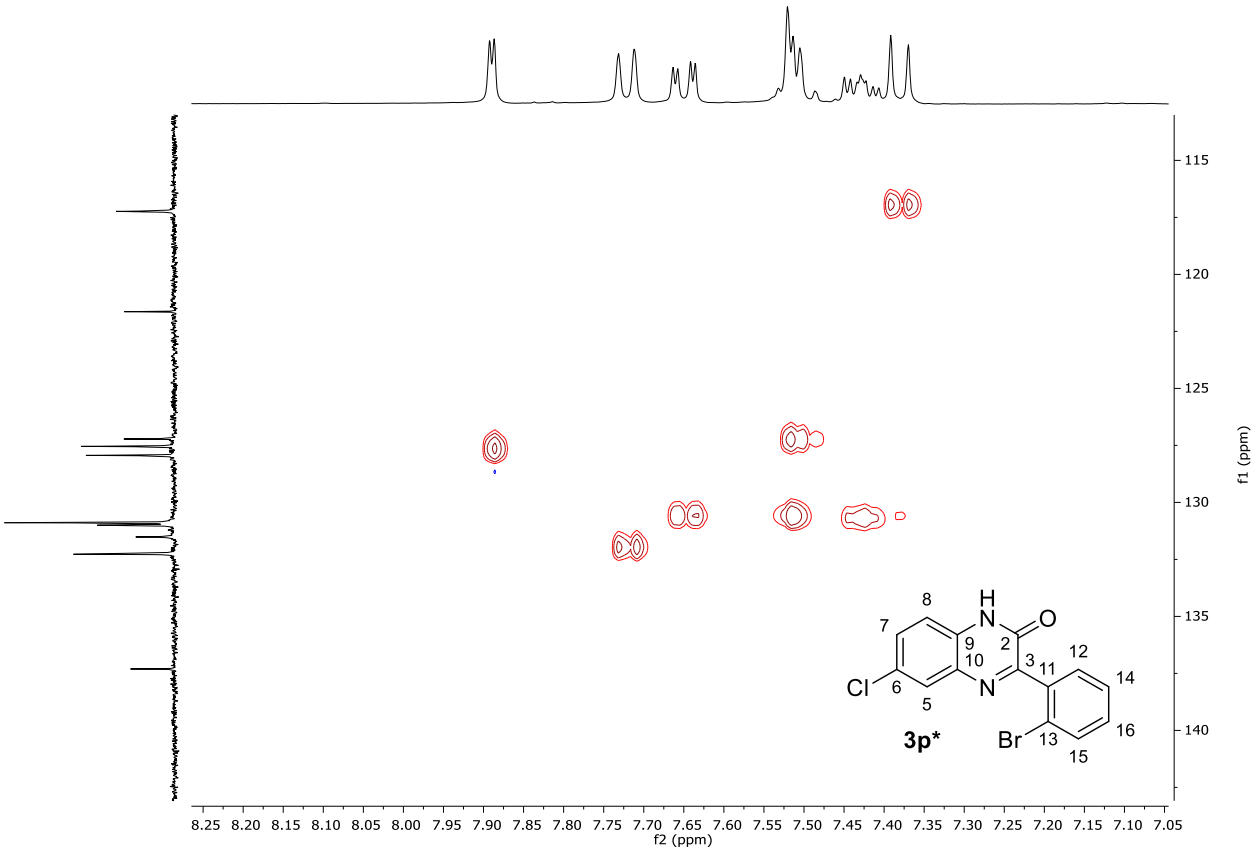
^{15}N NMR (40 MHz, DMSO-d_6) spectrum of **3p**.



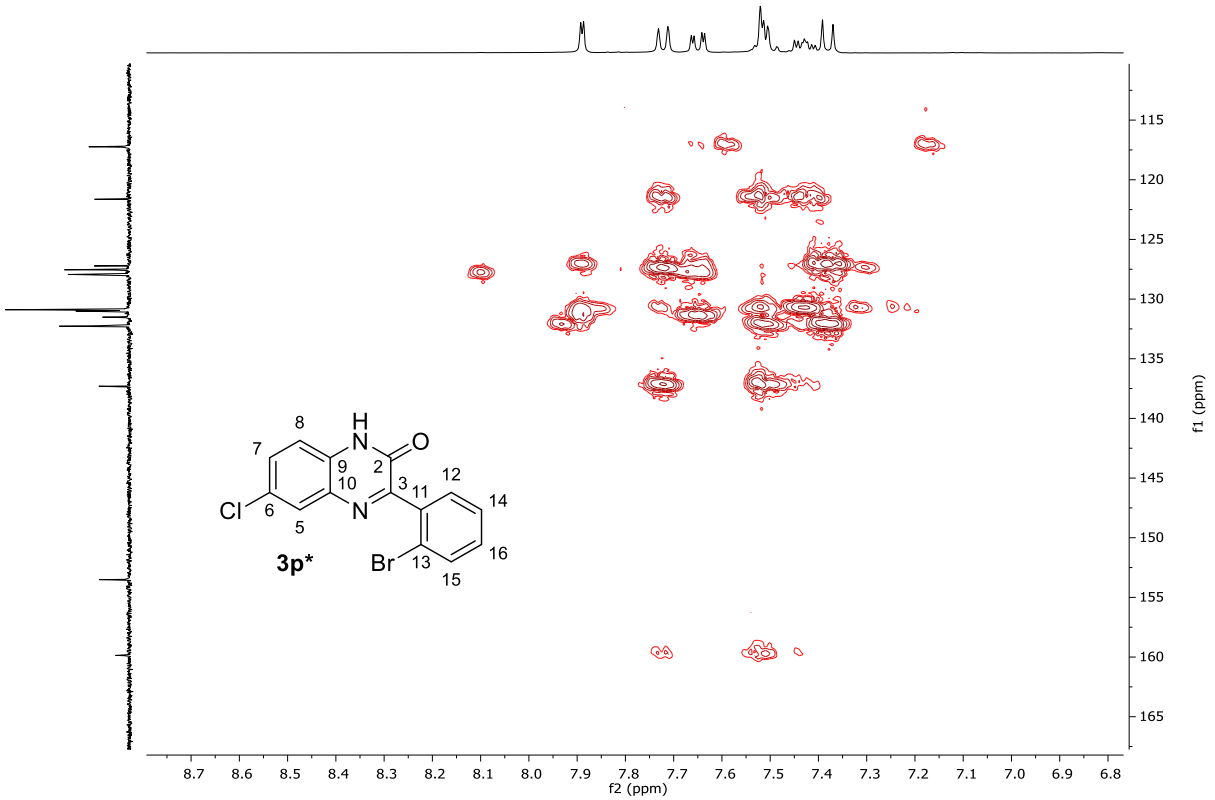
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3p***.



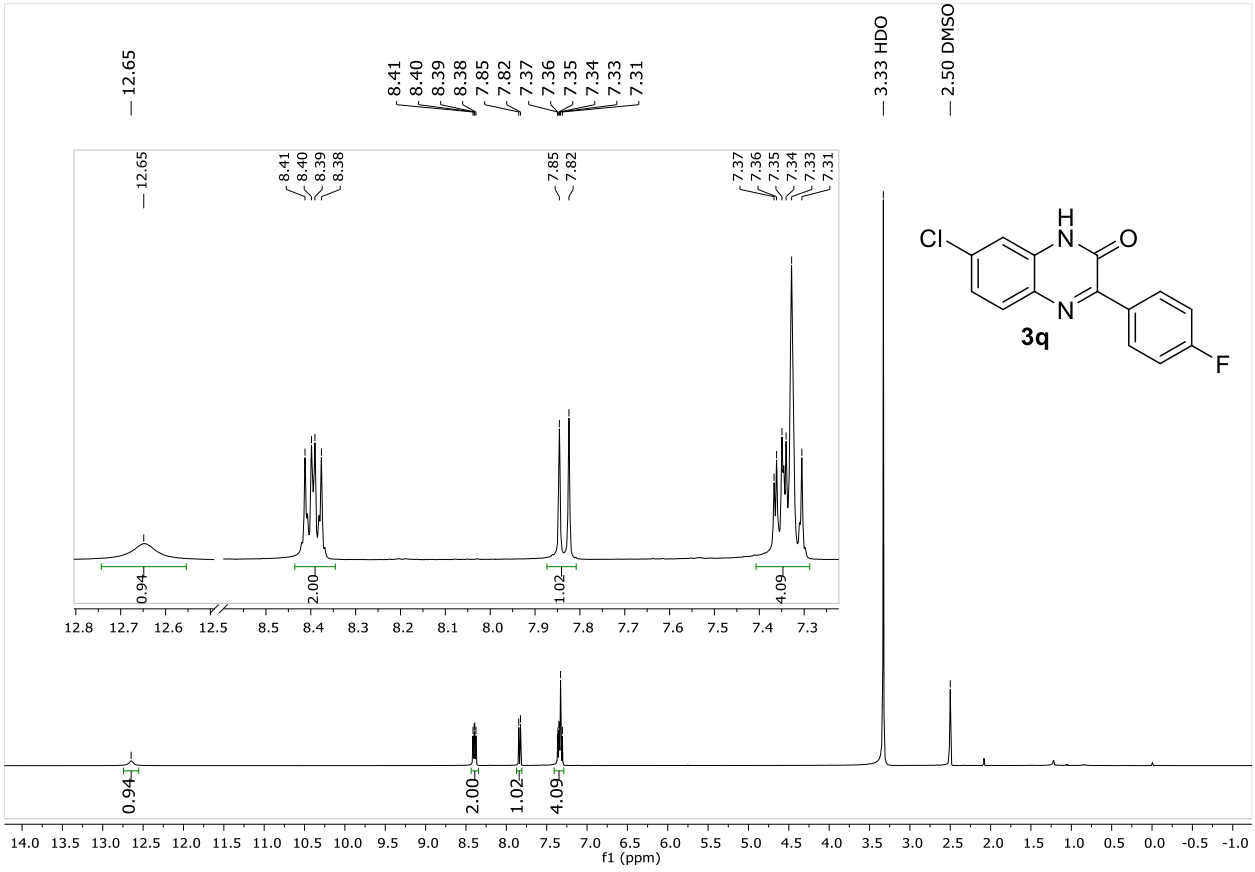
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3p***.



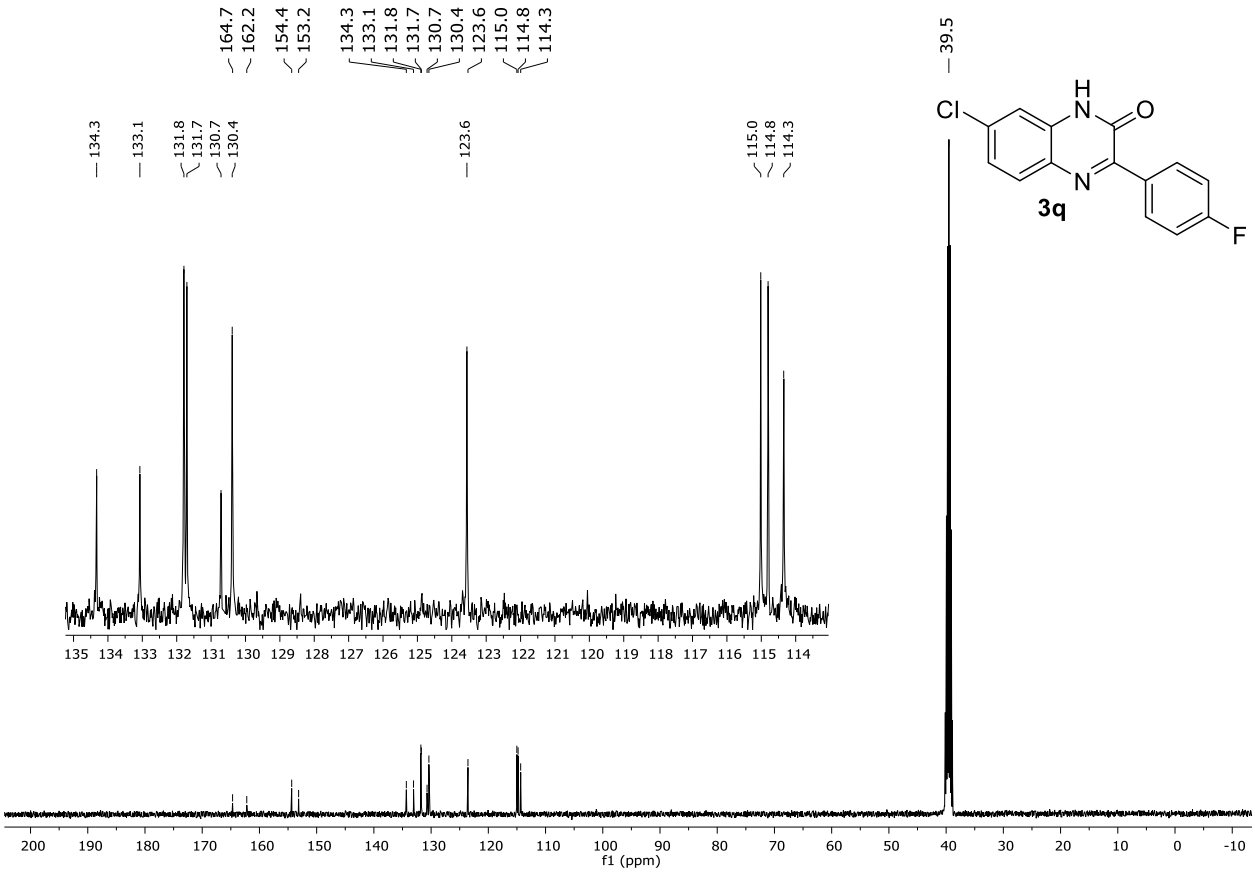
^{1}H-^{13}C HSQC (400 MHz, DMSO-d_6) spectrum of **3p***.



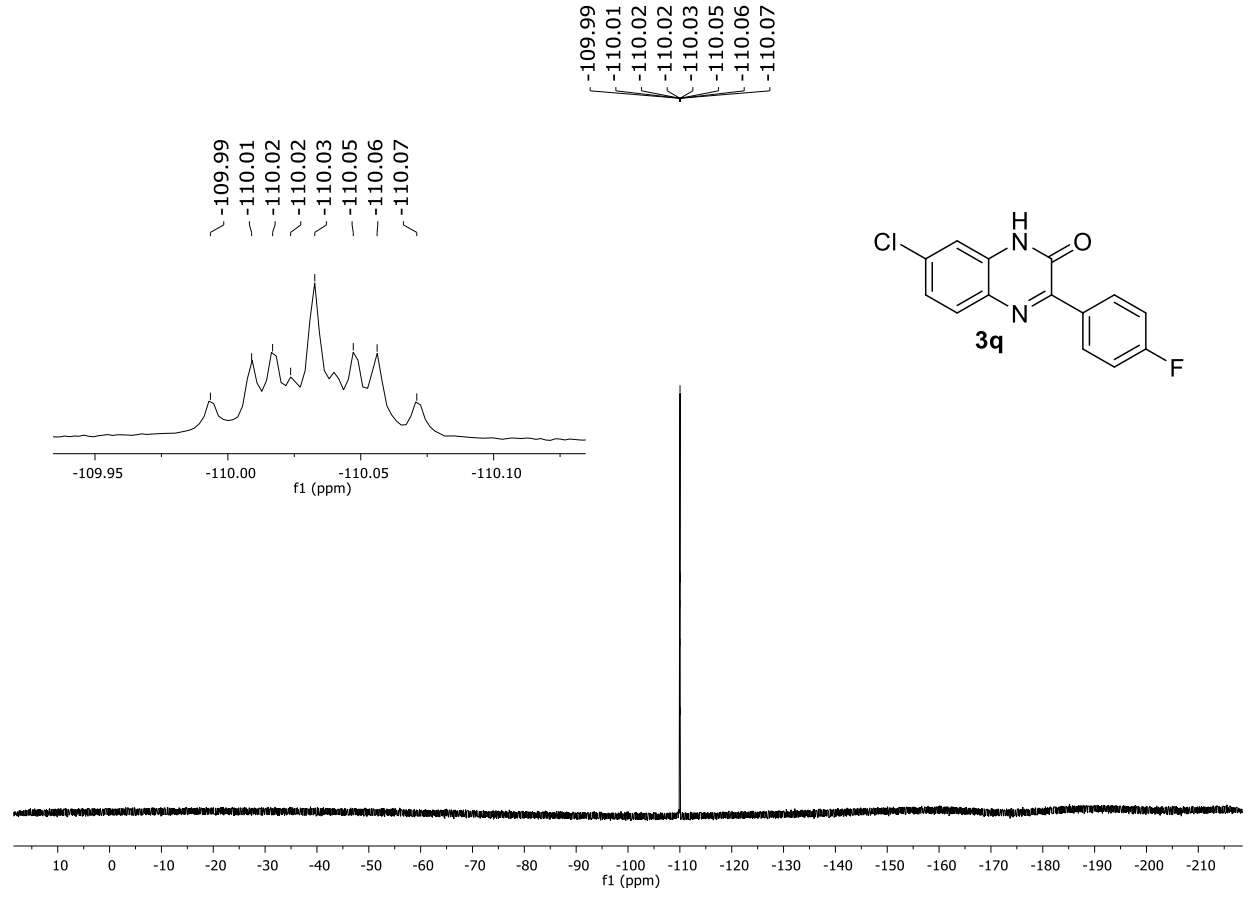
^{1}H-^{13}C HMBC (400 MHz, DMSO-d$_6$) spectrum of **3p***.



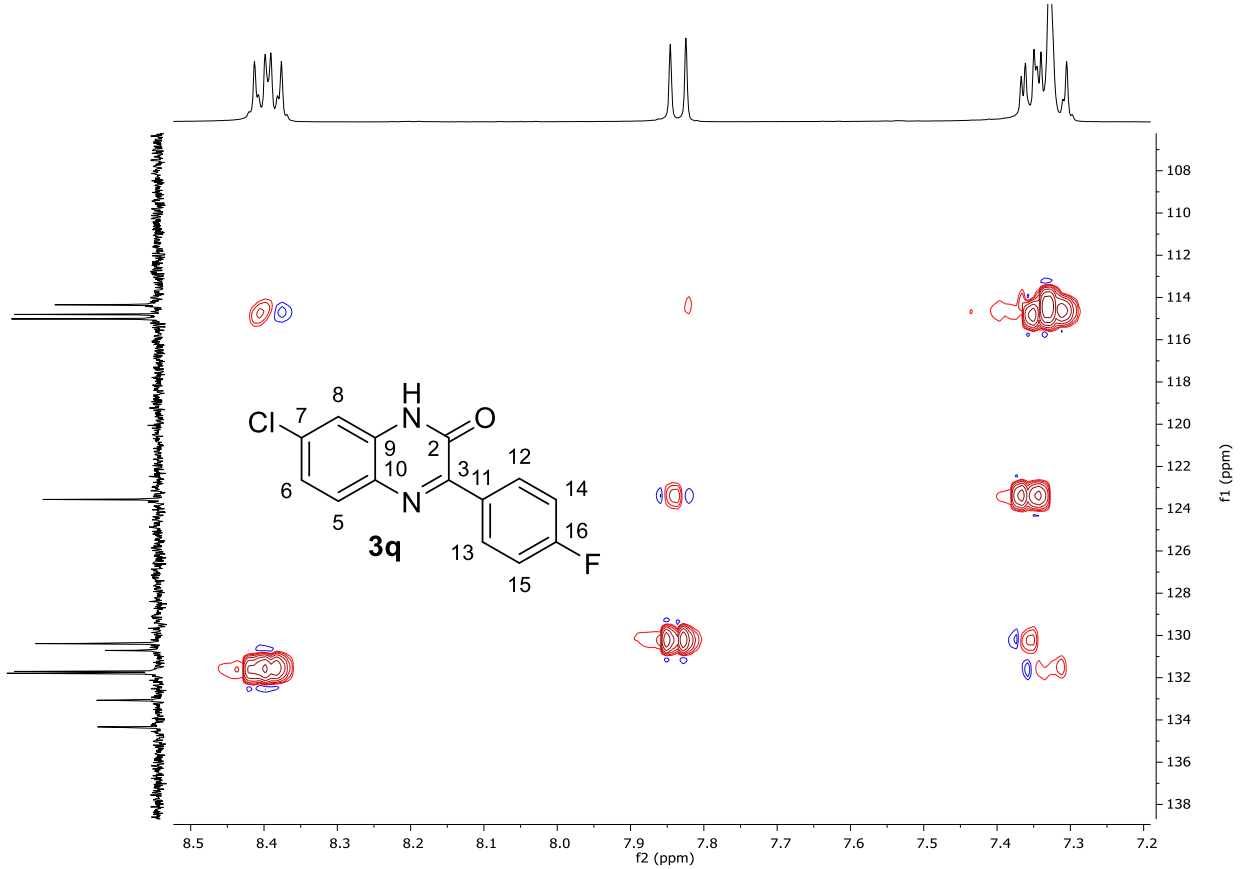
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of **3q**.



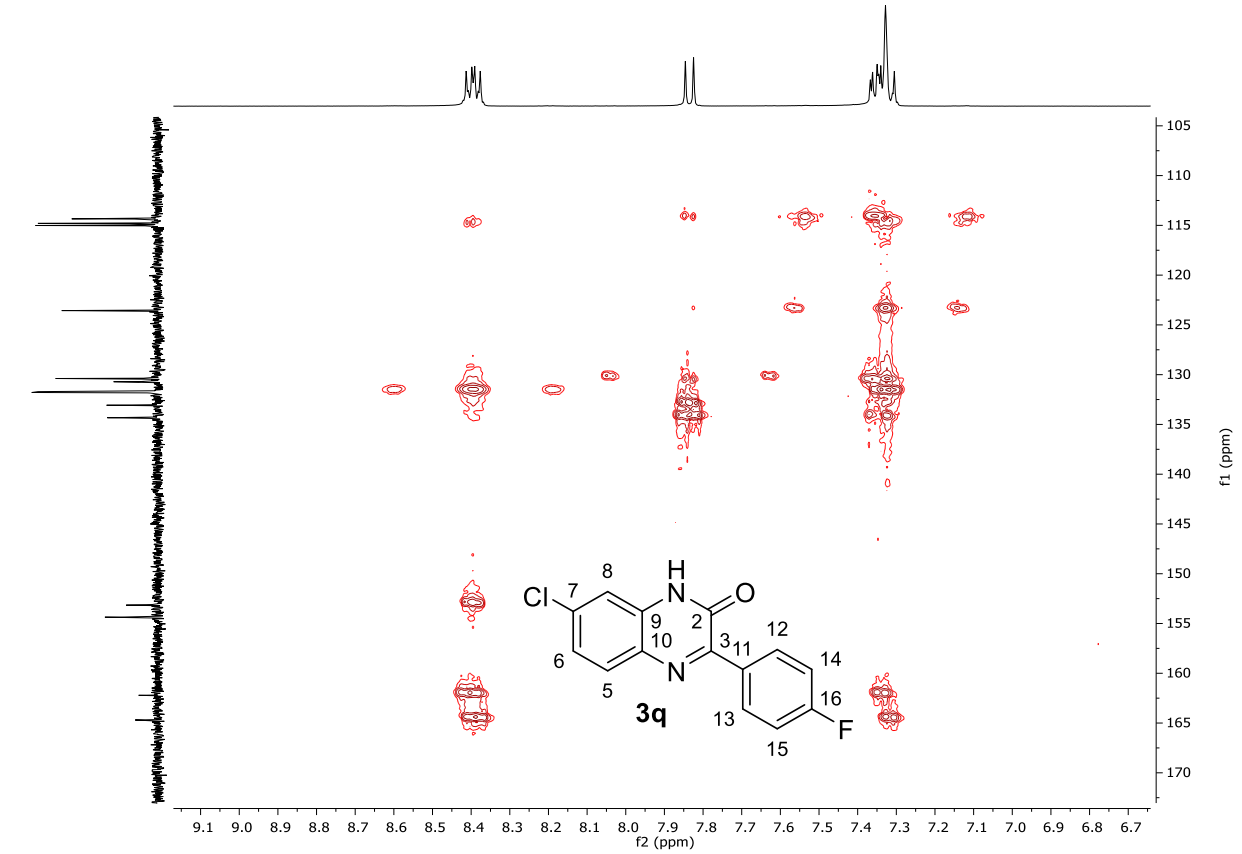
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3q.**



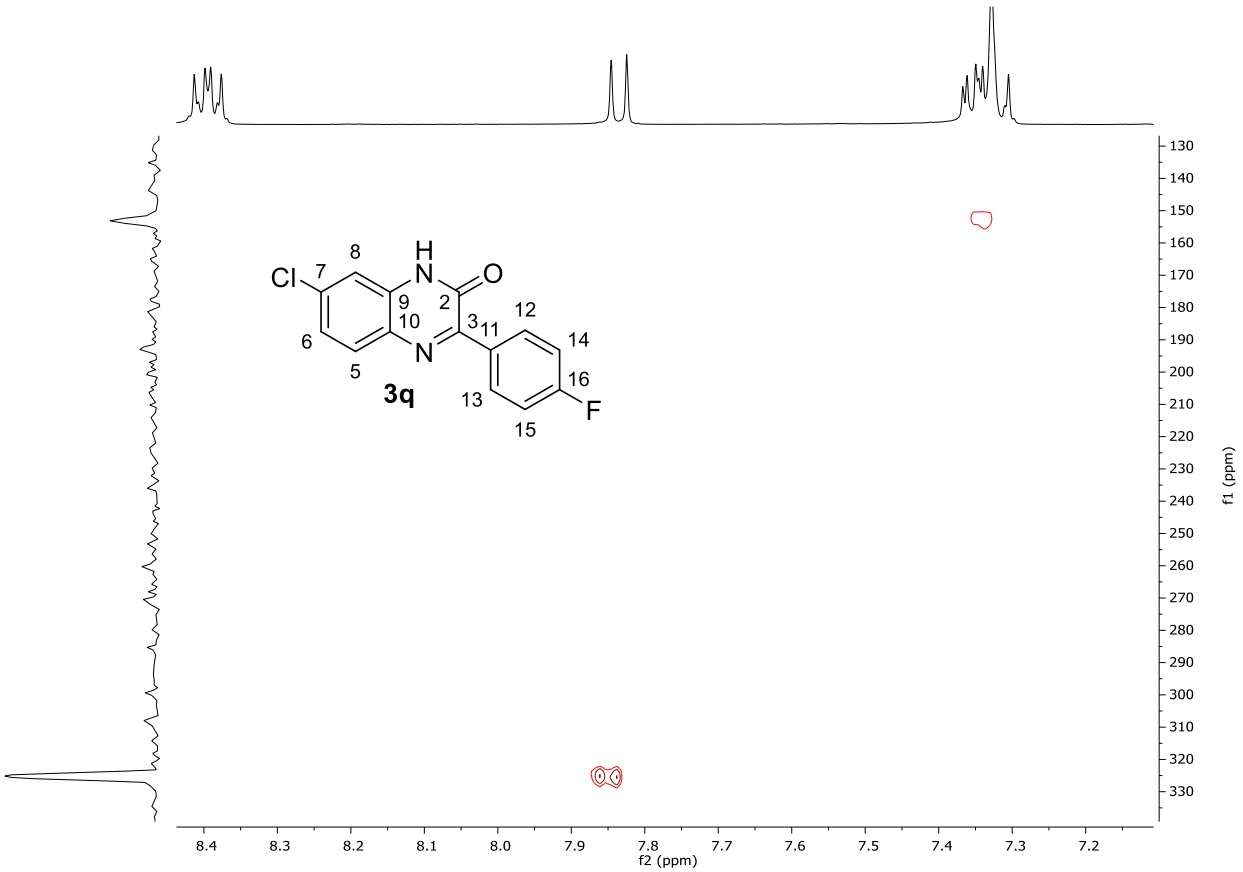
^{19}F NMR (376 MHz, DMSO-d_6) spectrum of **3q**.



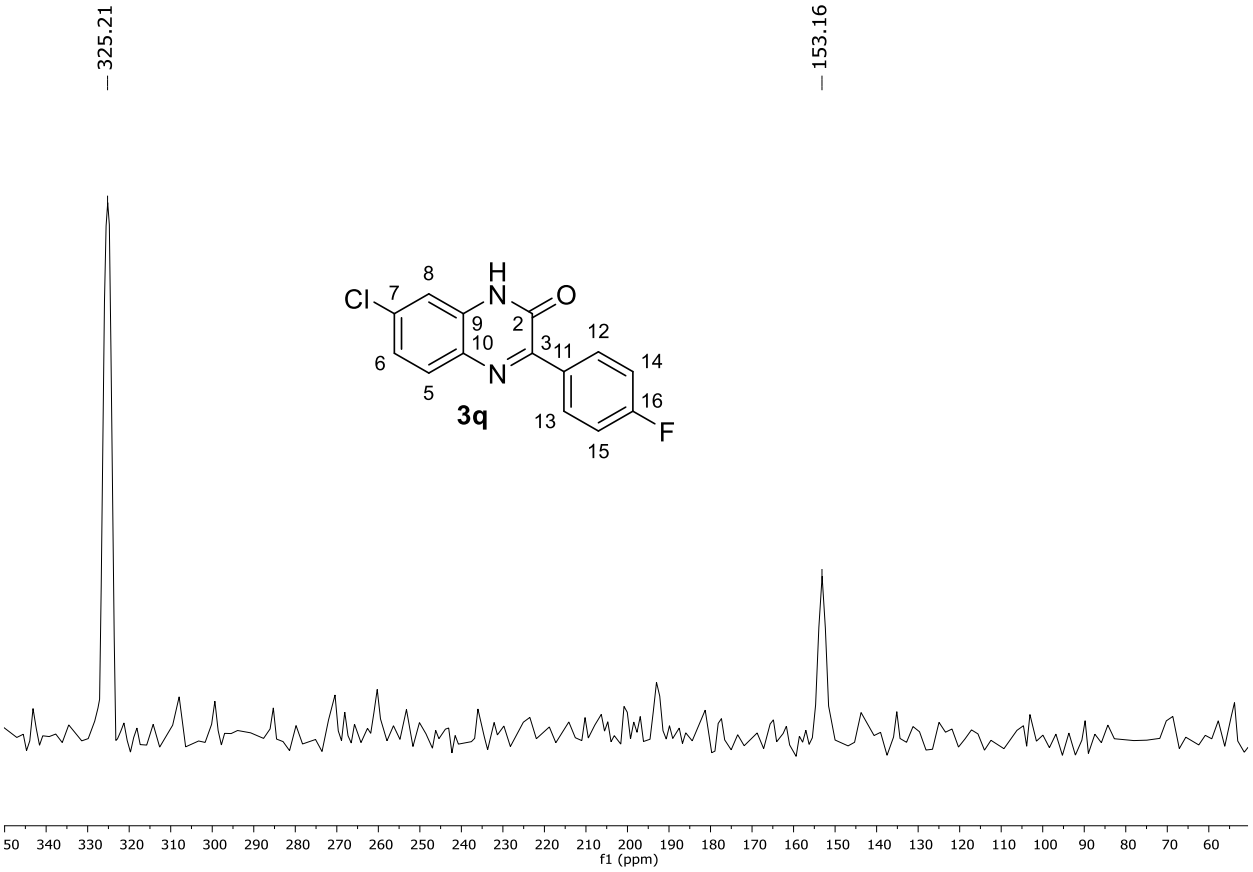
^{1}H-^{13}C HSQC (400 MHz, DMSO-d_6) spectrum of **3q.**



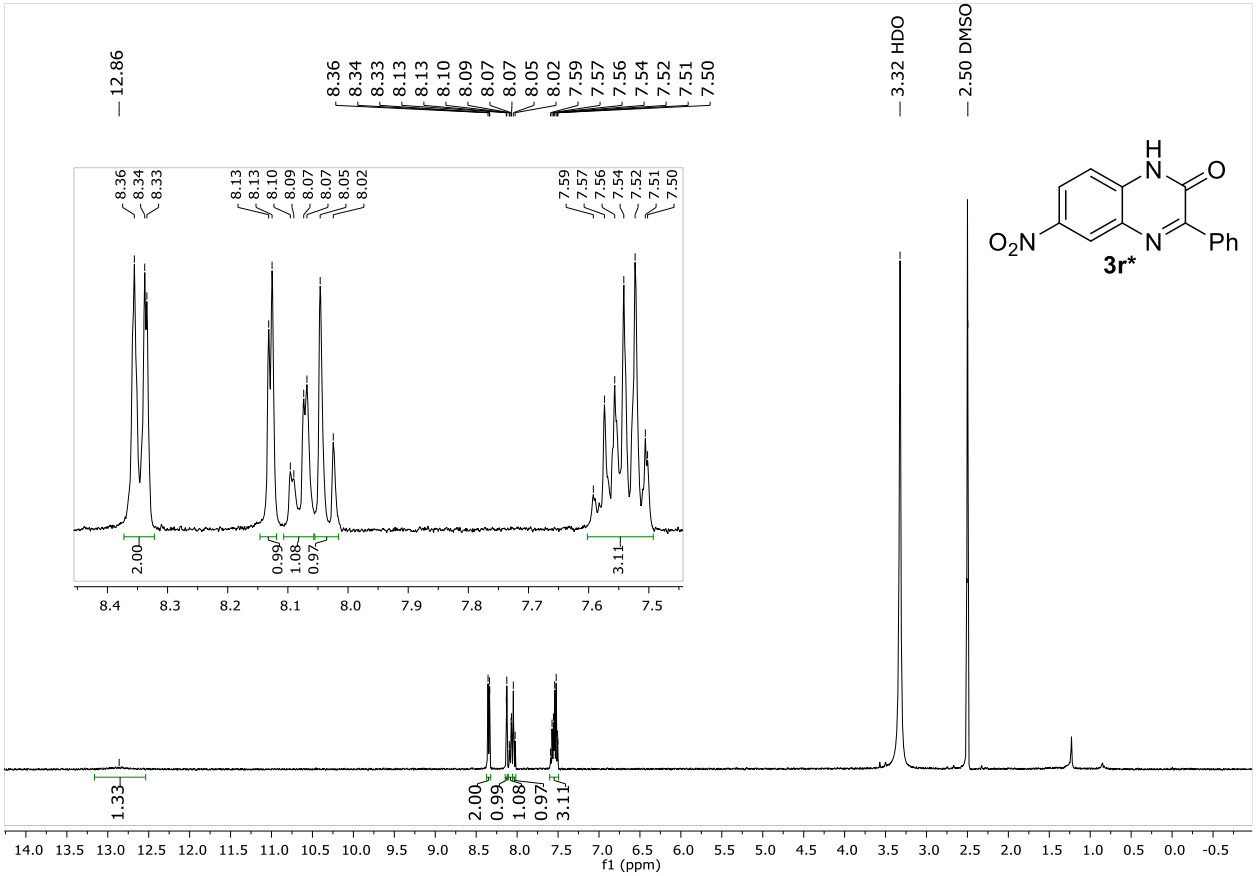
^{1}H-^{13}C HMBC (400 MHz, DMSO-d_6) spectrum of **3q**.



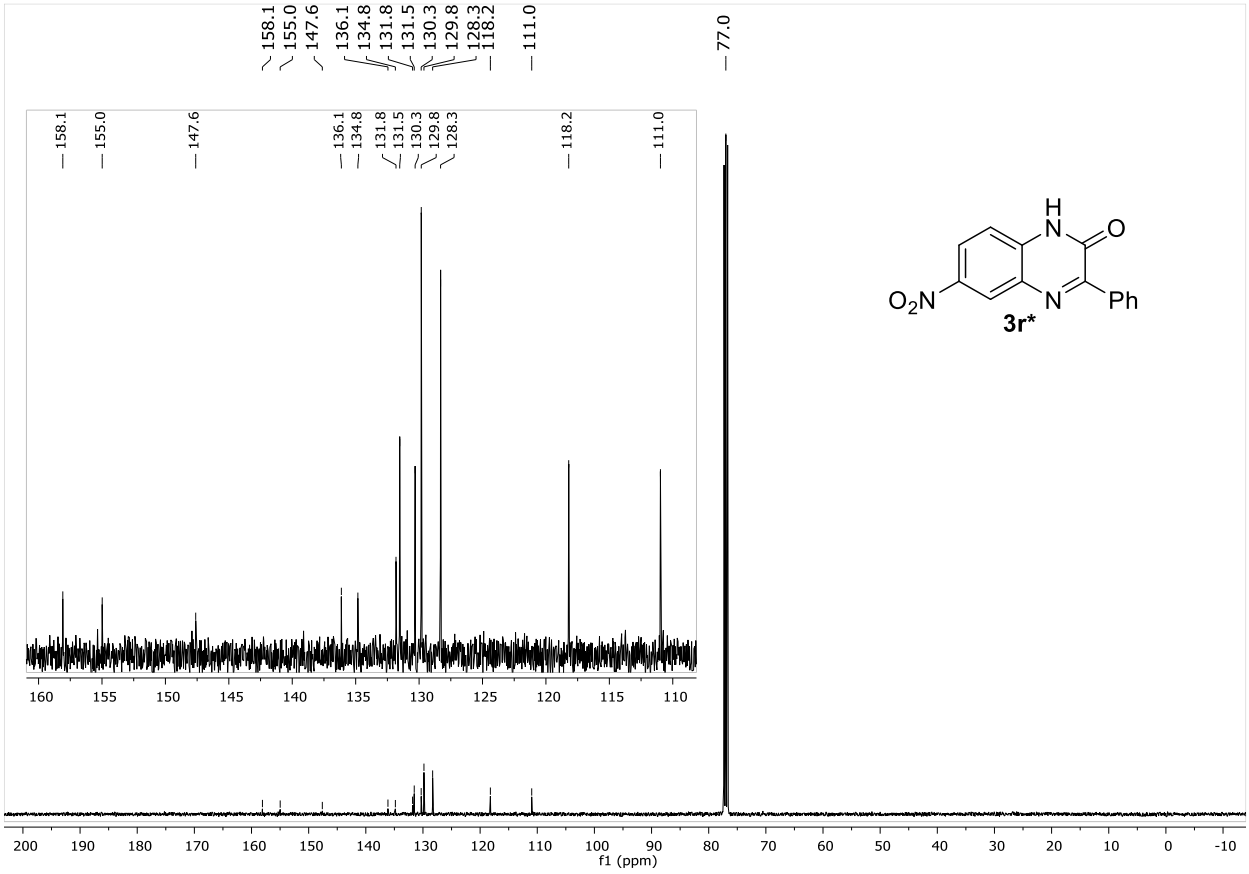
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d$_6$) spectrum of **3q**.



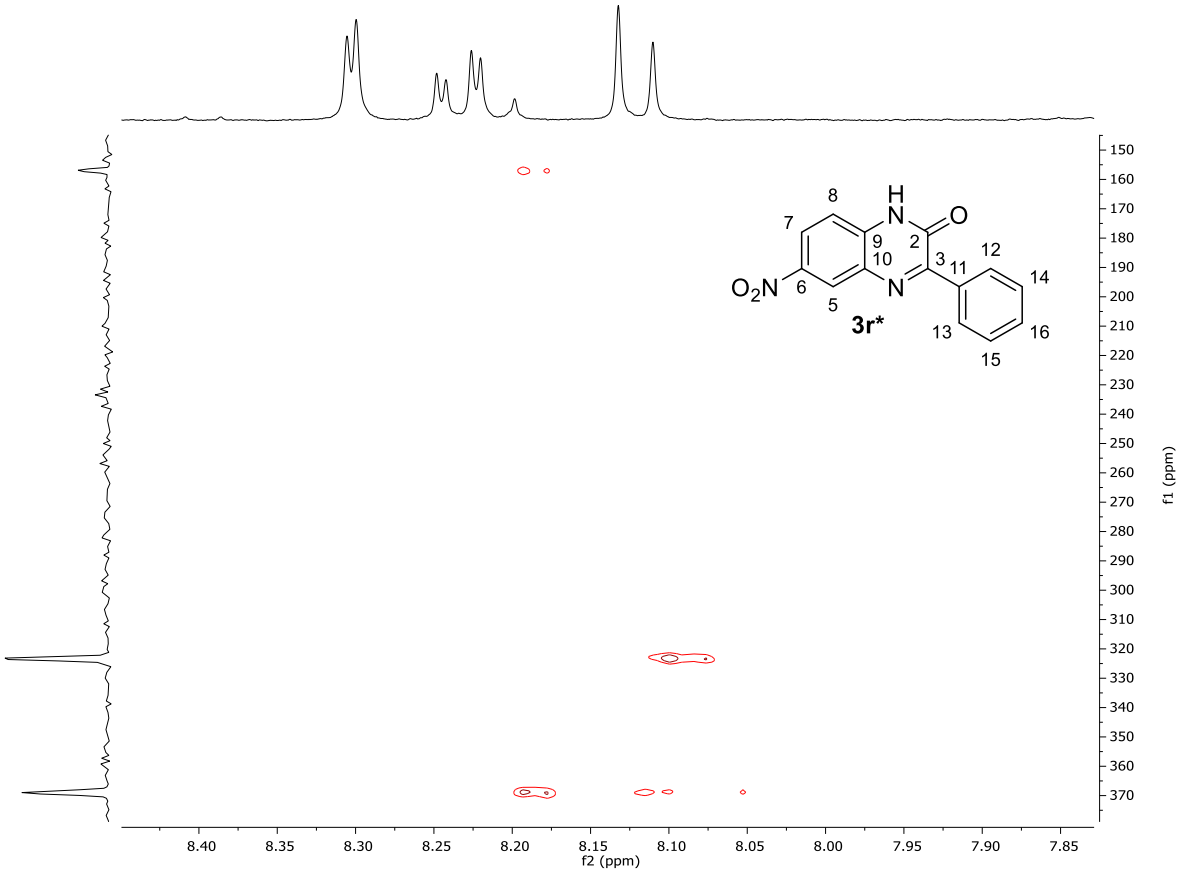
^{15}N NMR (40 MHz, DMSO-d$_6$) spectrum of **3q**.



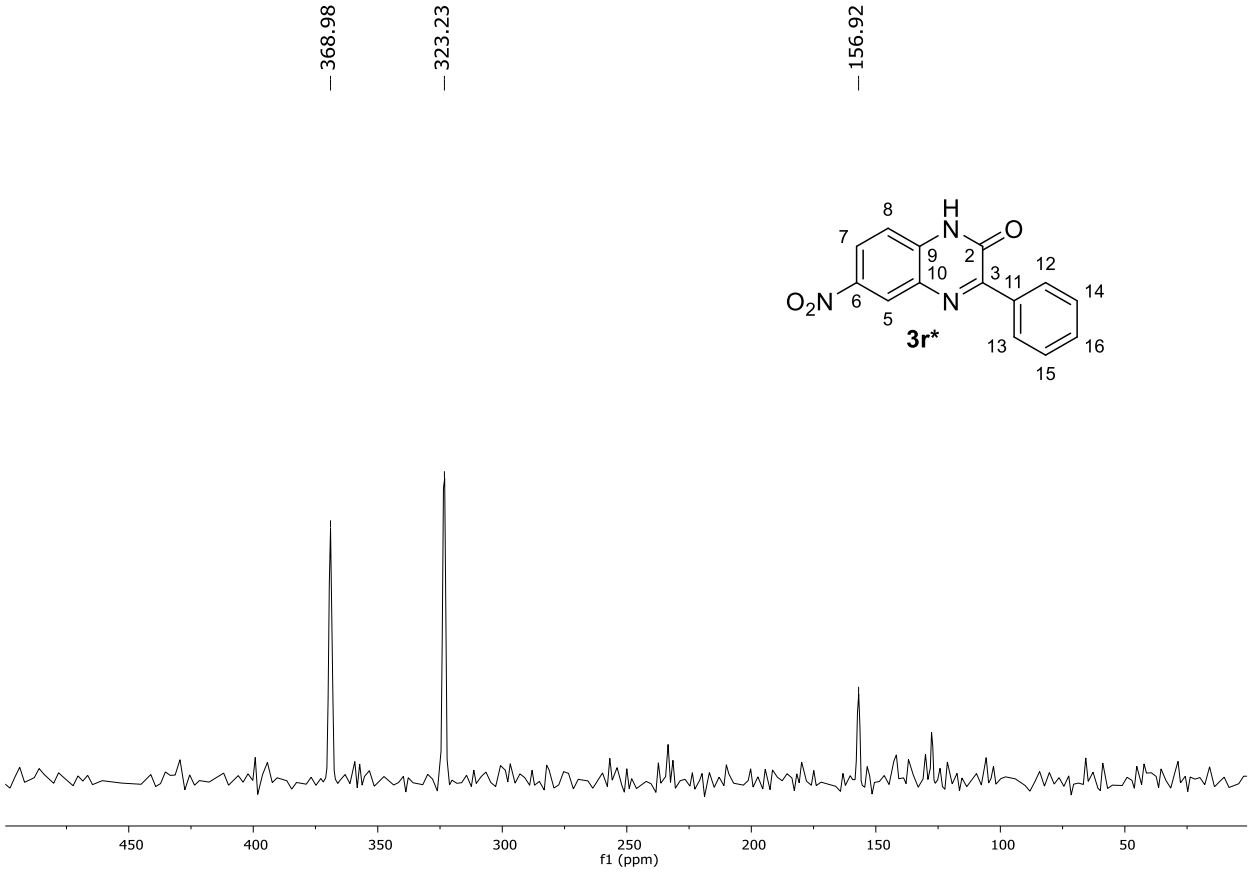
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3r***.



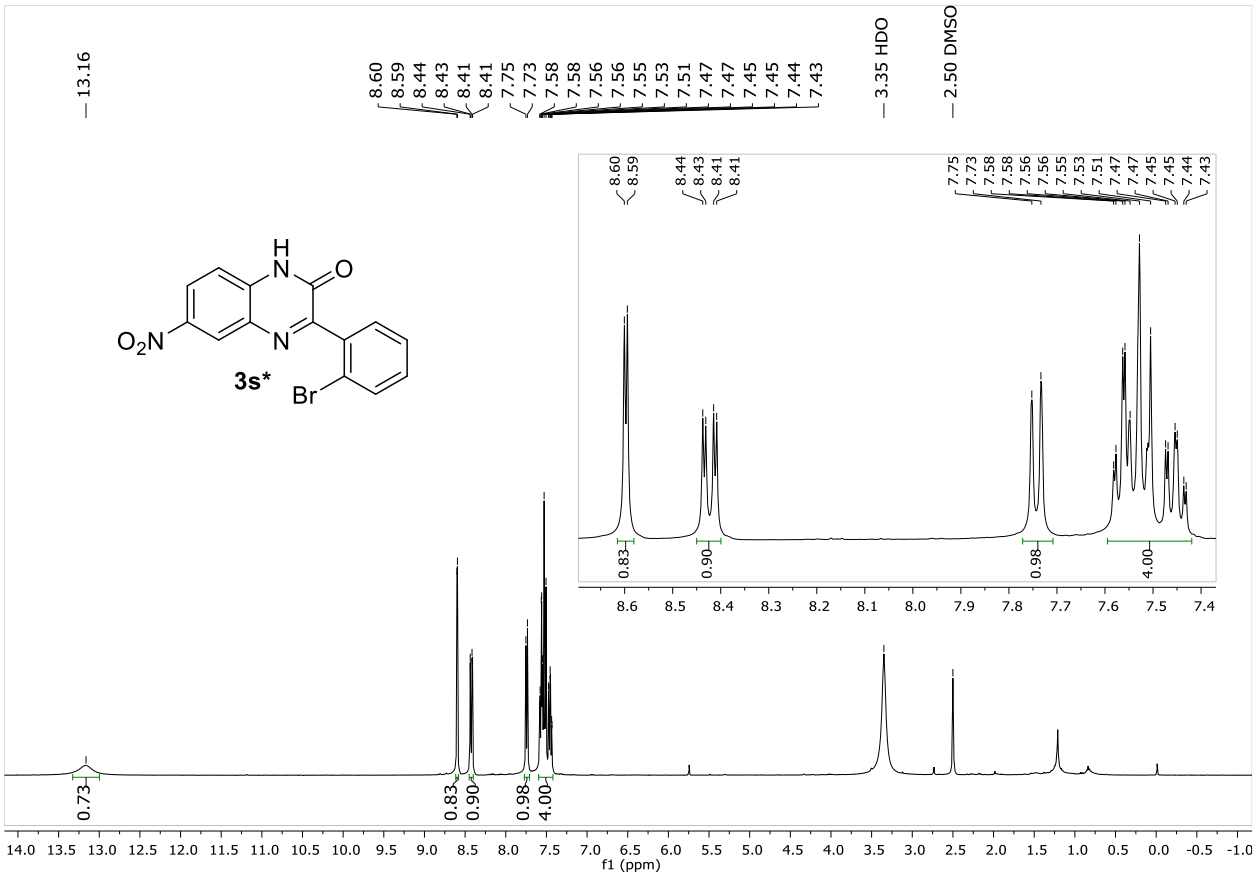
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3r***.



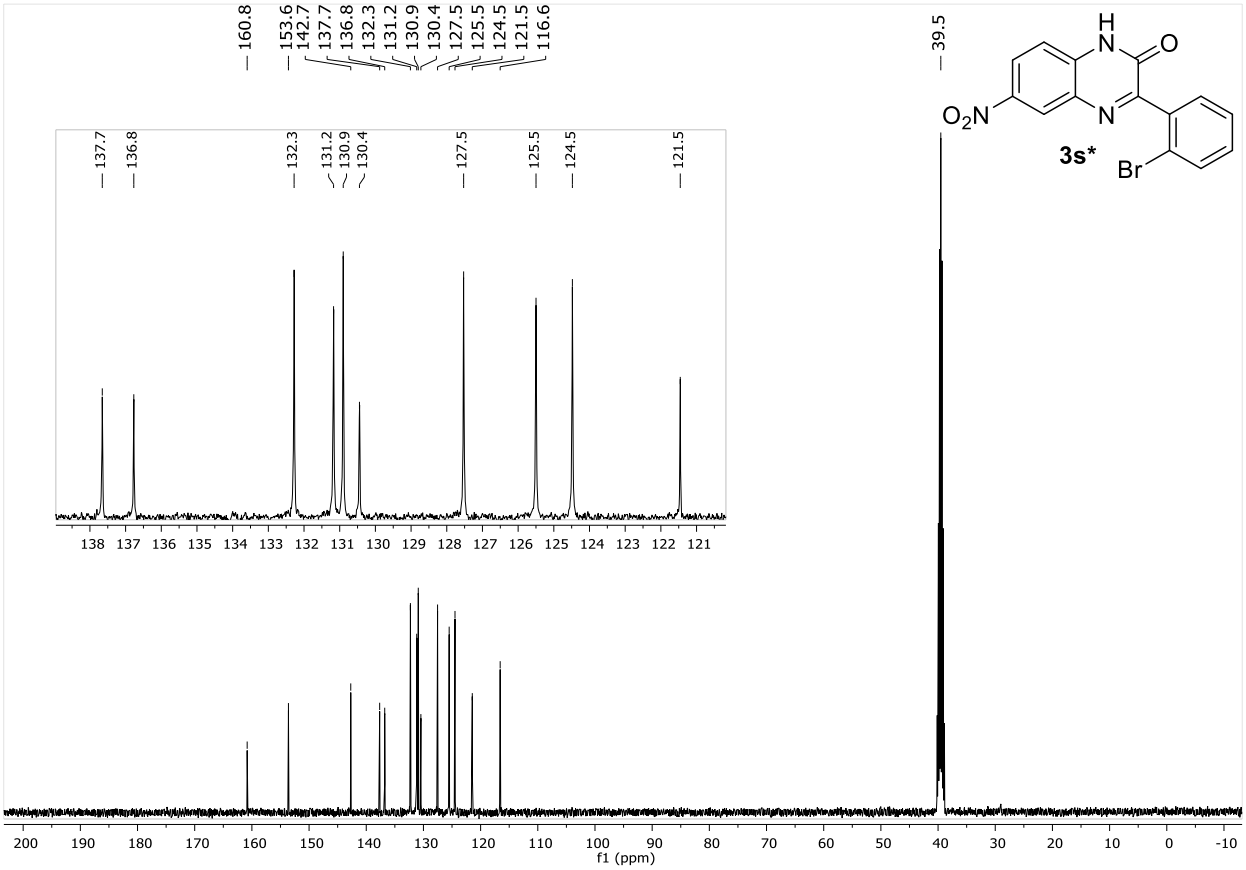
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3r***.



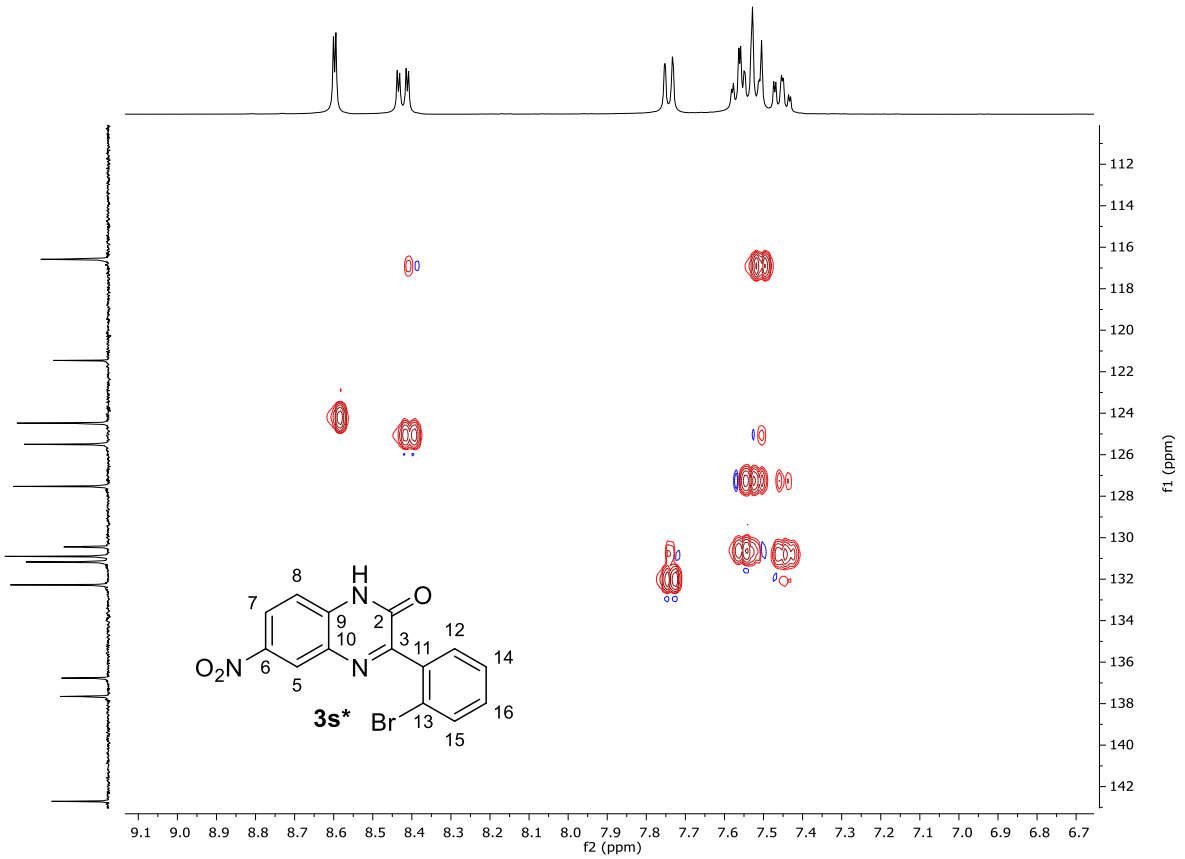
^{15}N NMR (40 MHz, DMSO-d_6) spectrum of **3r***.



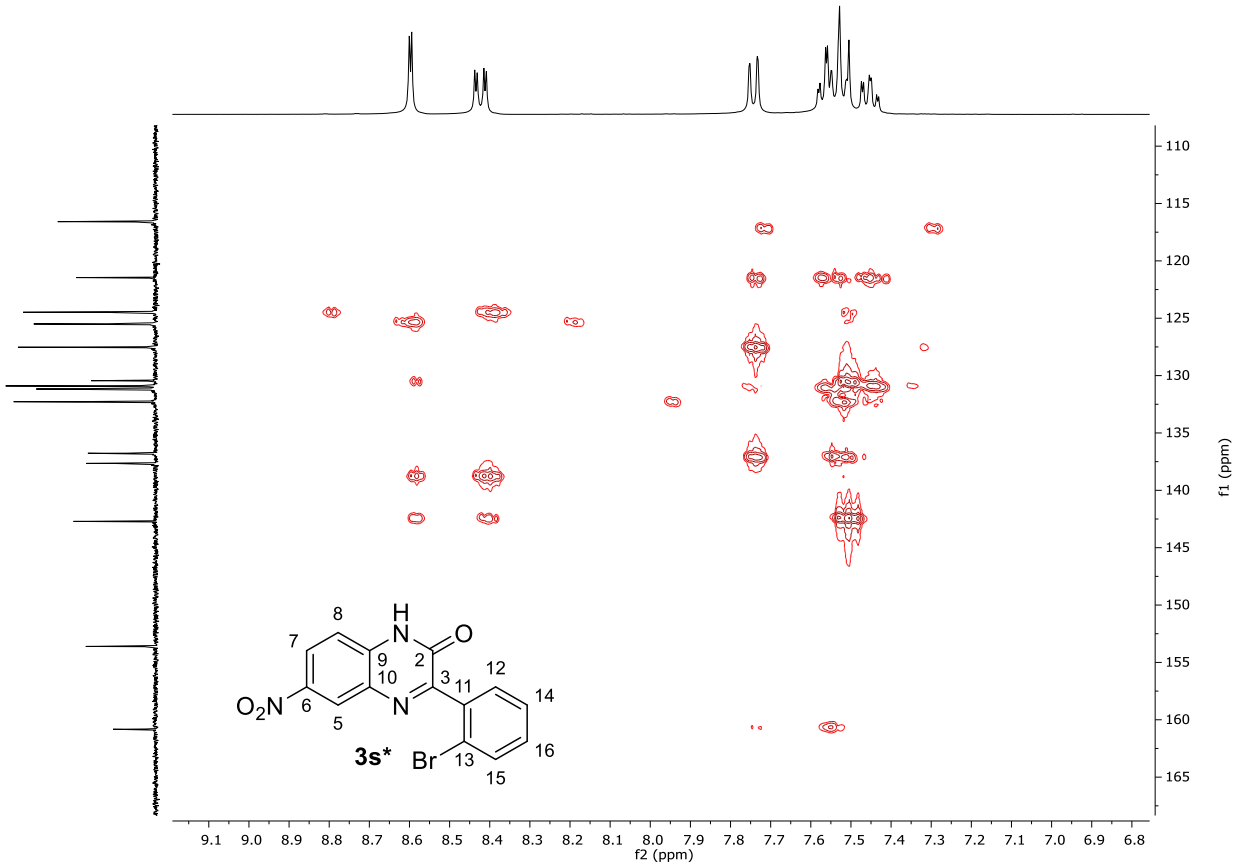
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3s***.



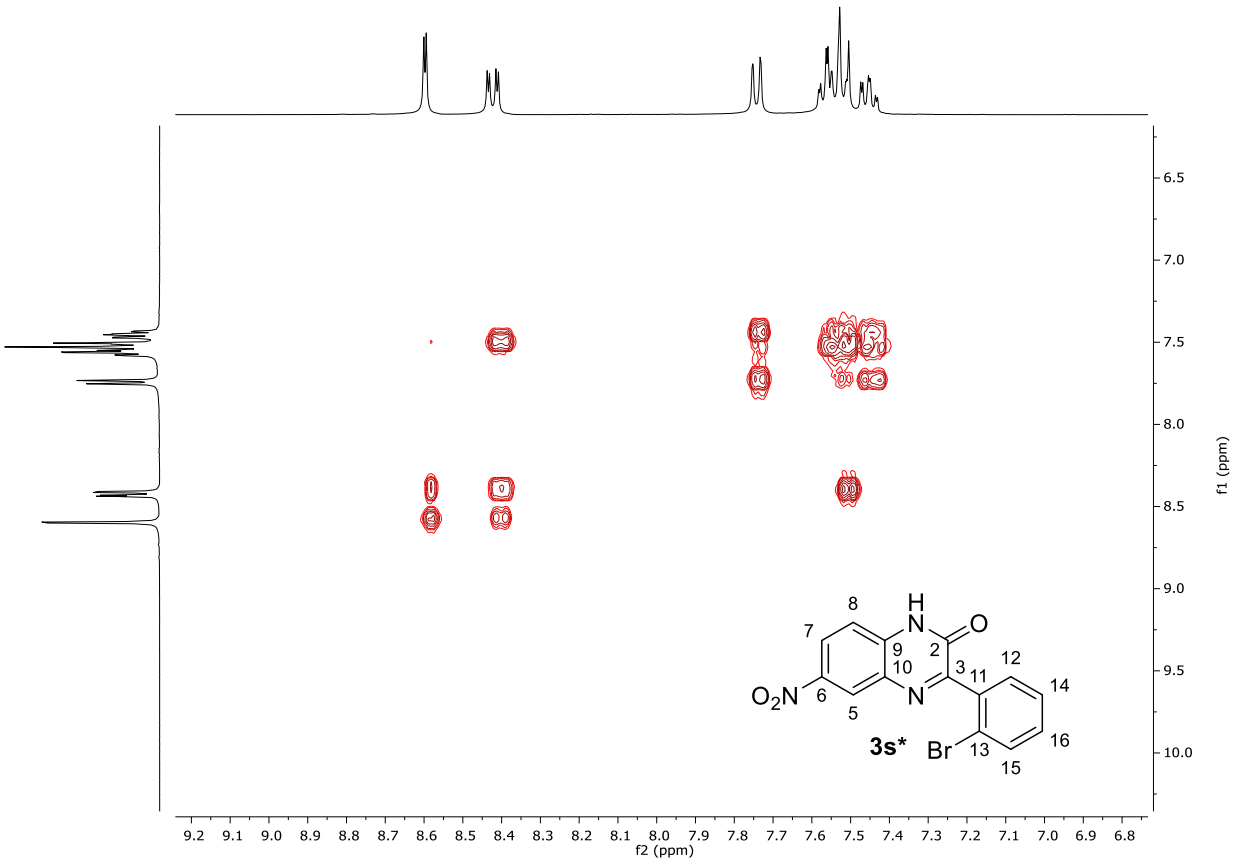
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3s***.



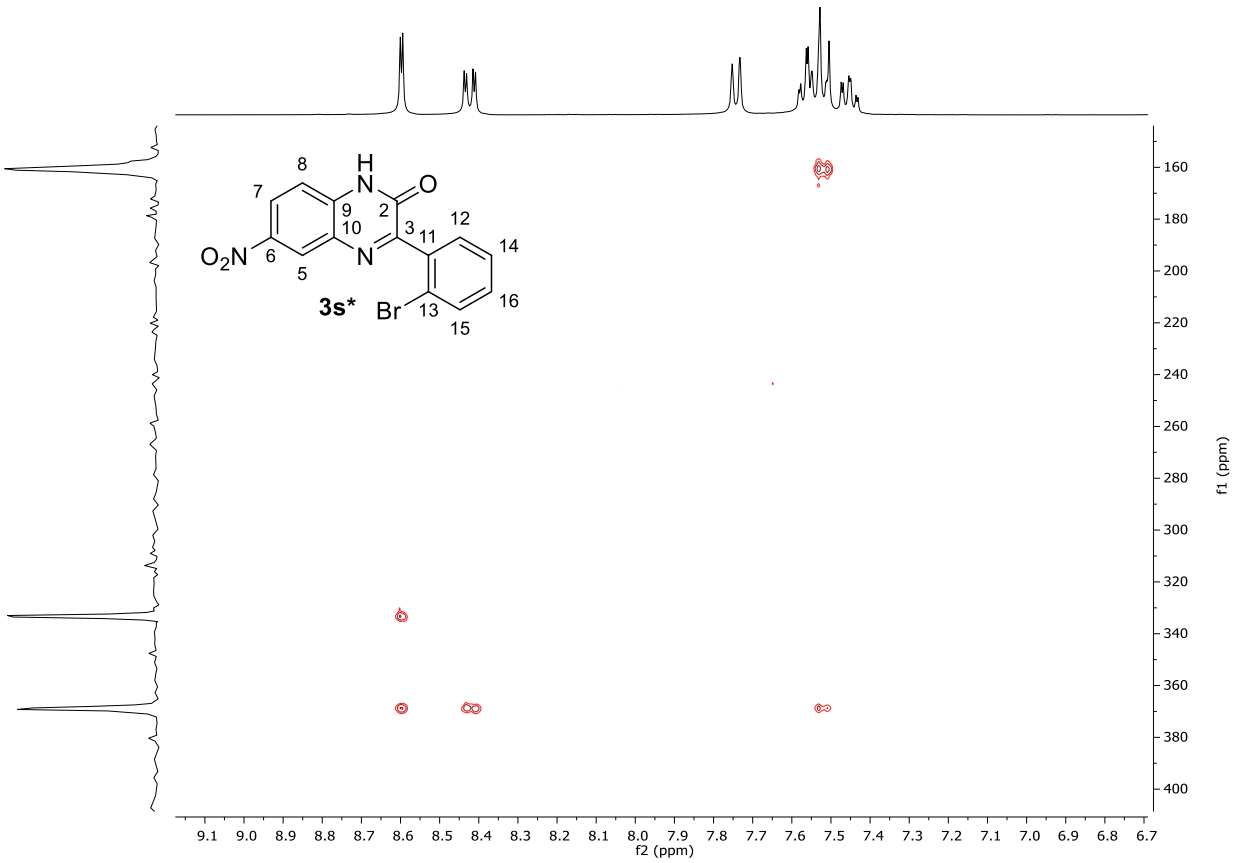
^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d_6) spectrum of **3s***.



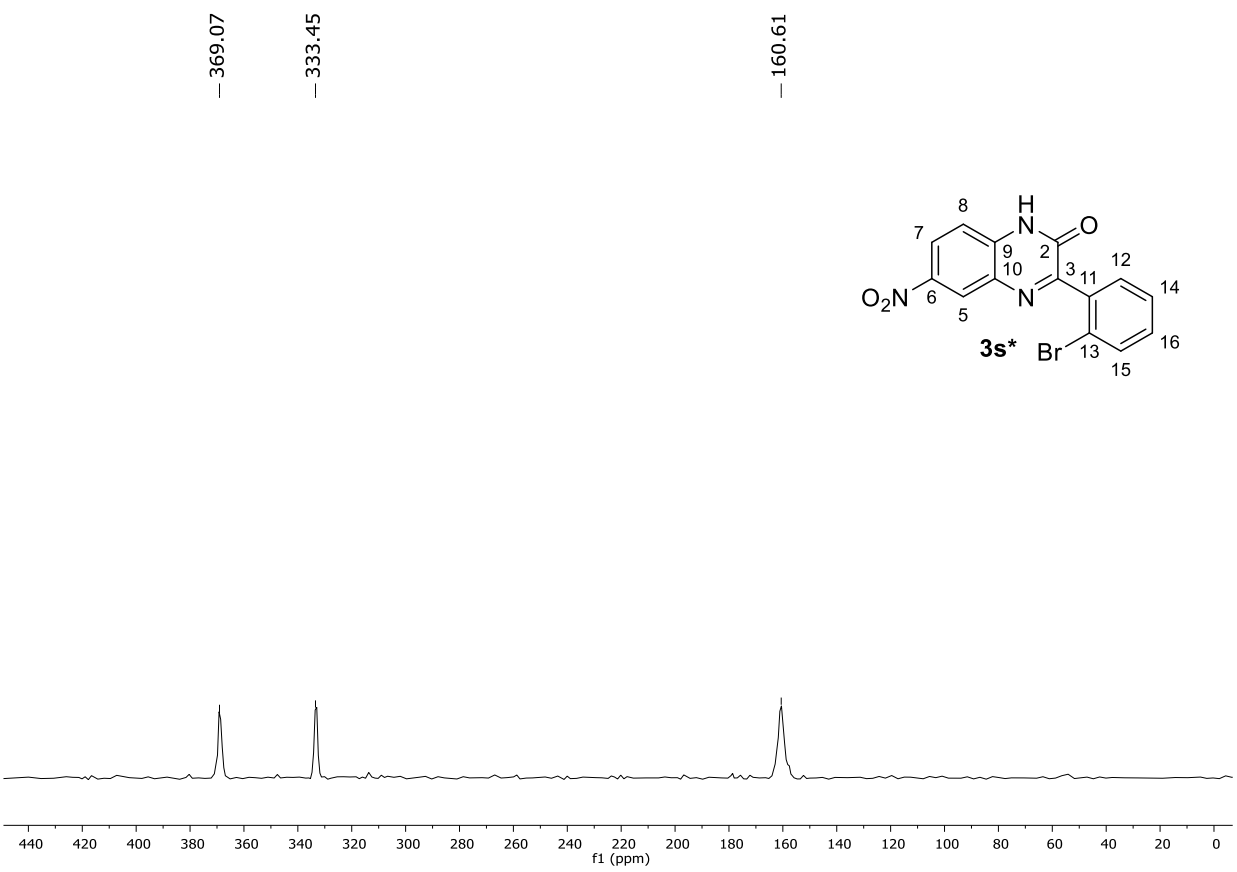
^{1}H-^{13}C HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3s***.



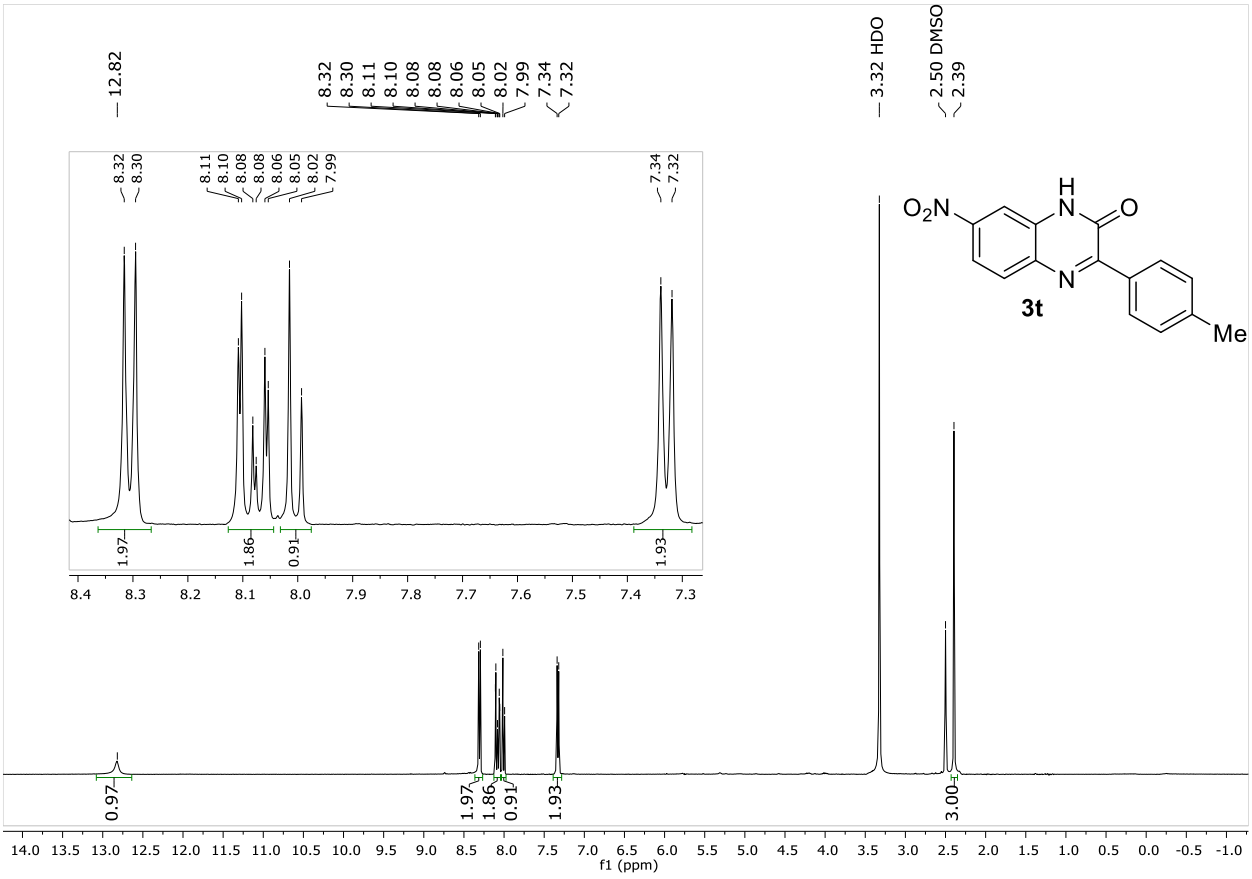
^{1}H COSY NMR (400 MHz, DMSO-d_6) spectrum of **3s***.



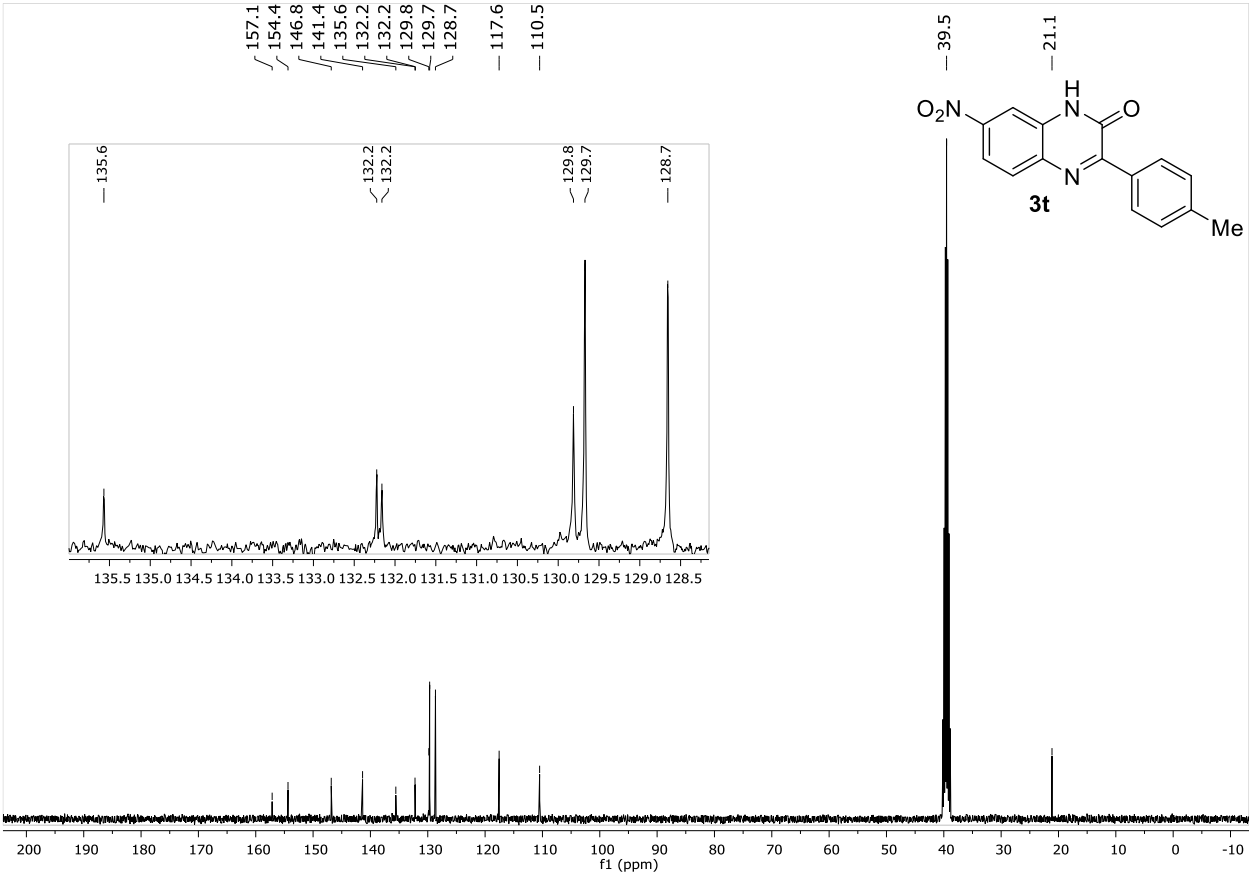
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d_6) spectrum of **3s***.



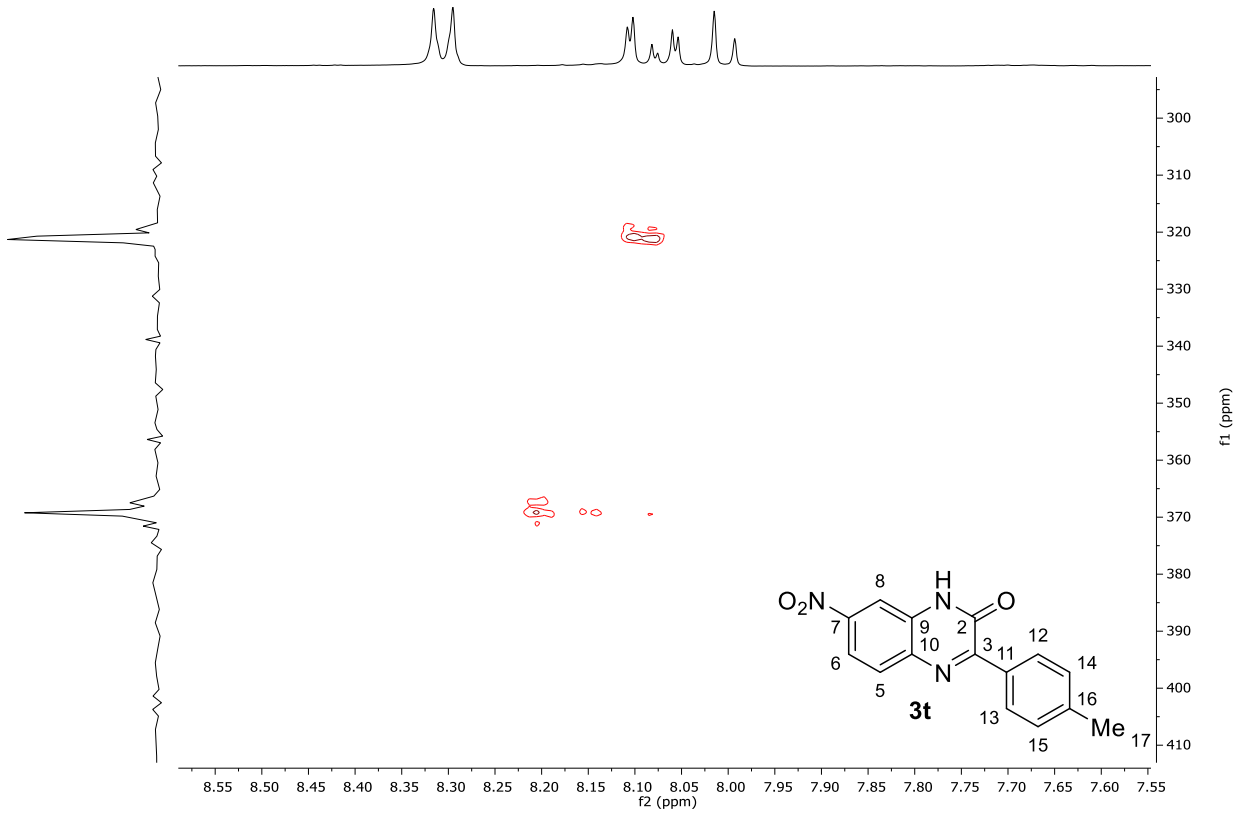
^{15}N NMR (40 MHz, DMSO-d_6) spectrum of **3s***.



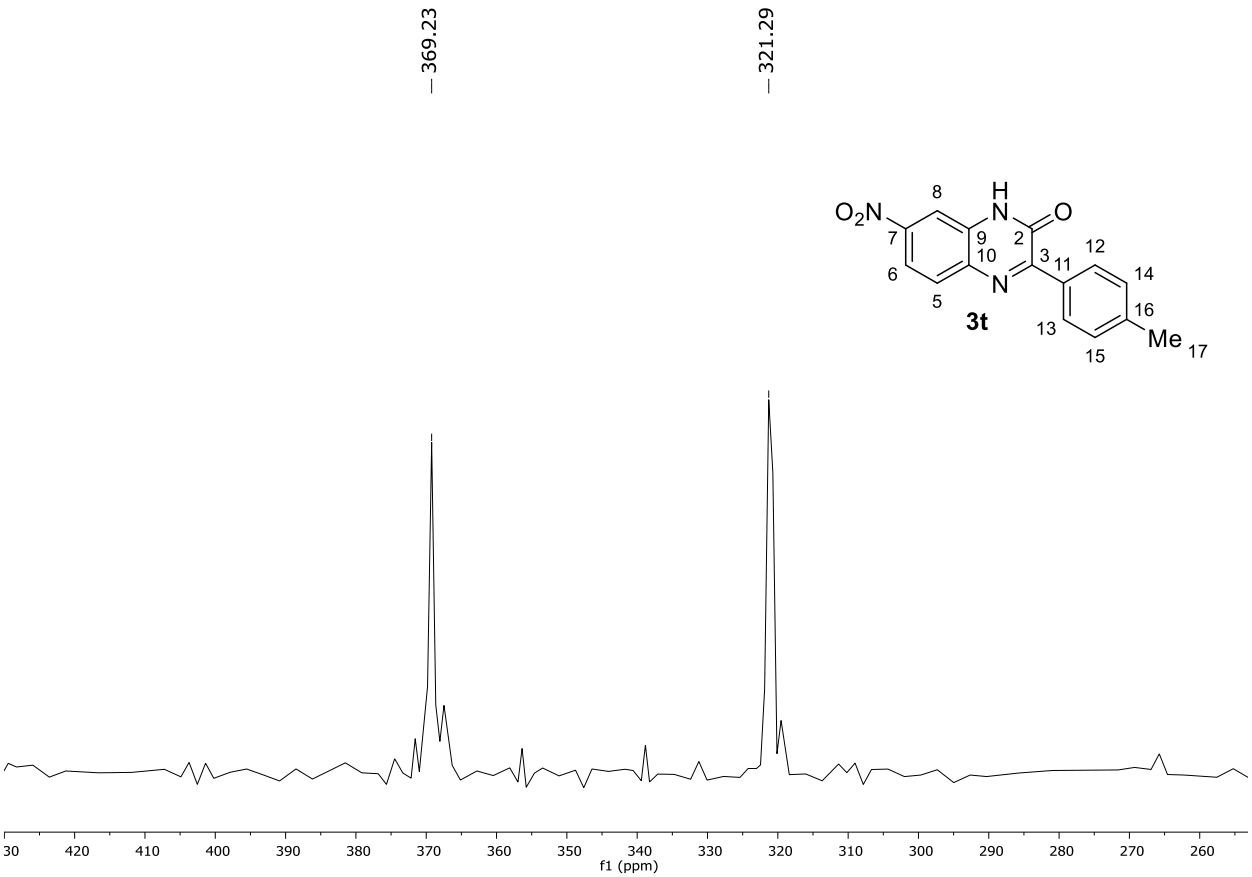
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3t**.



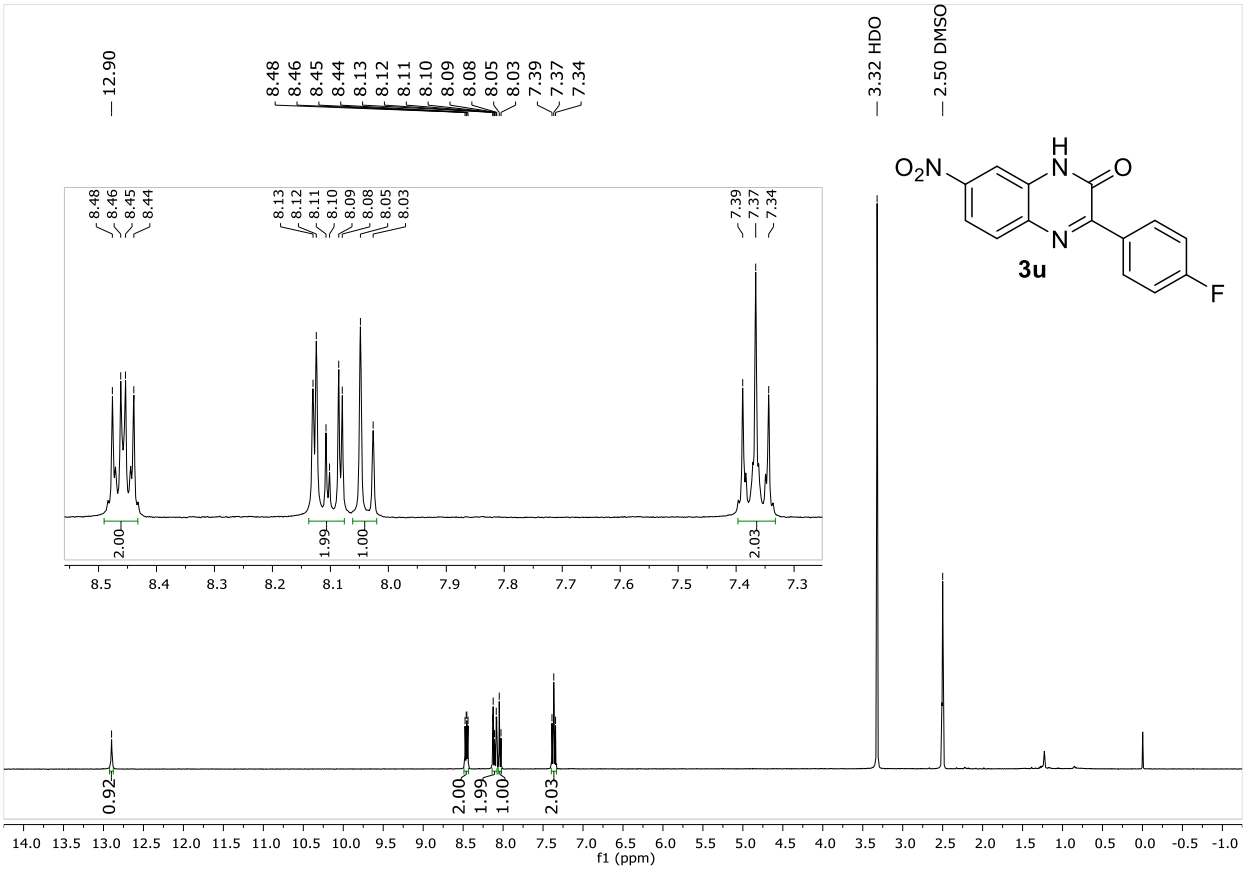
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3t**.



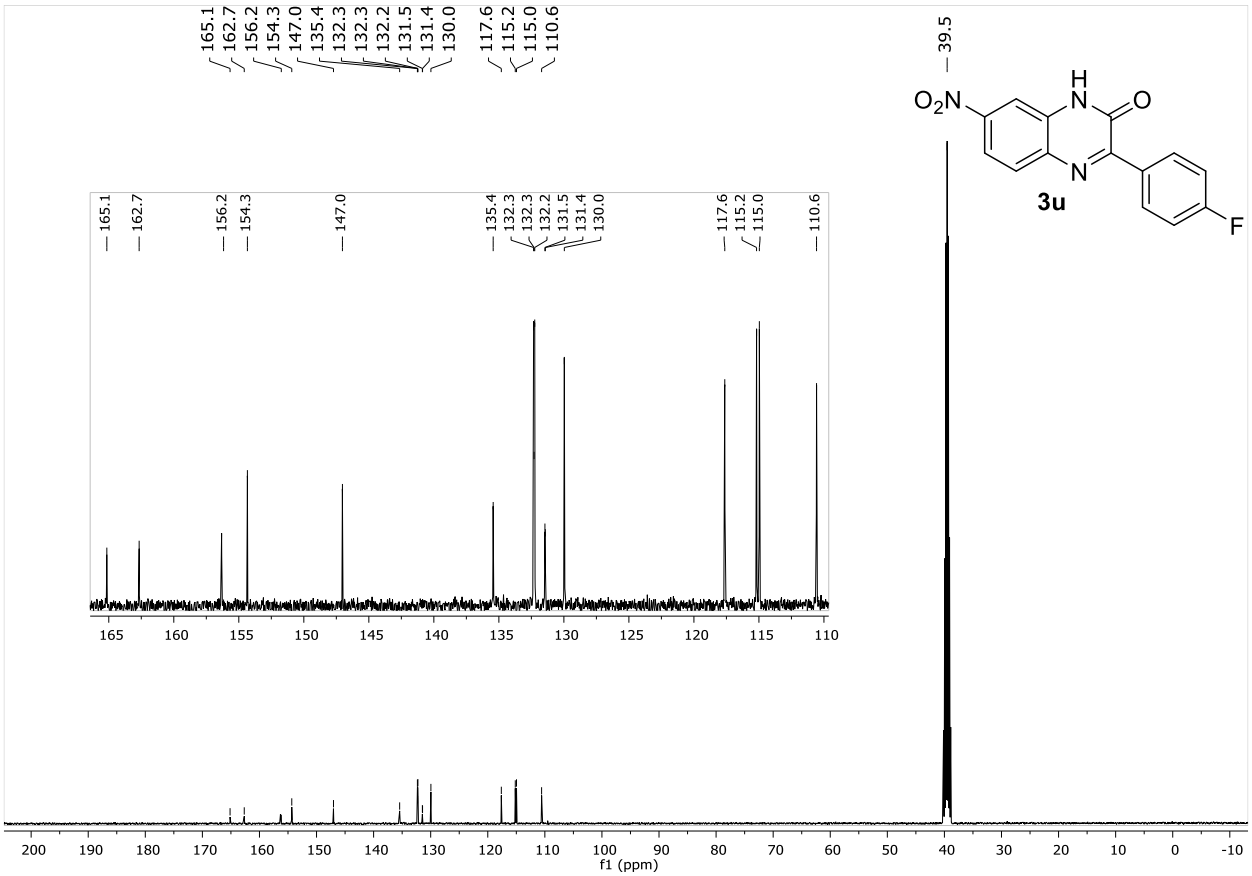
^{1}H-^{15}N HMBC NMR (DMSO-d_6) spectrum of **3t**.



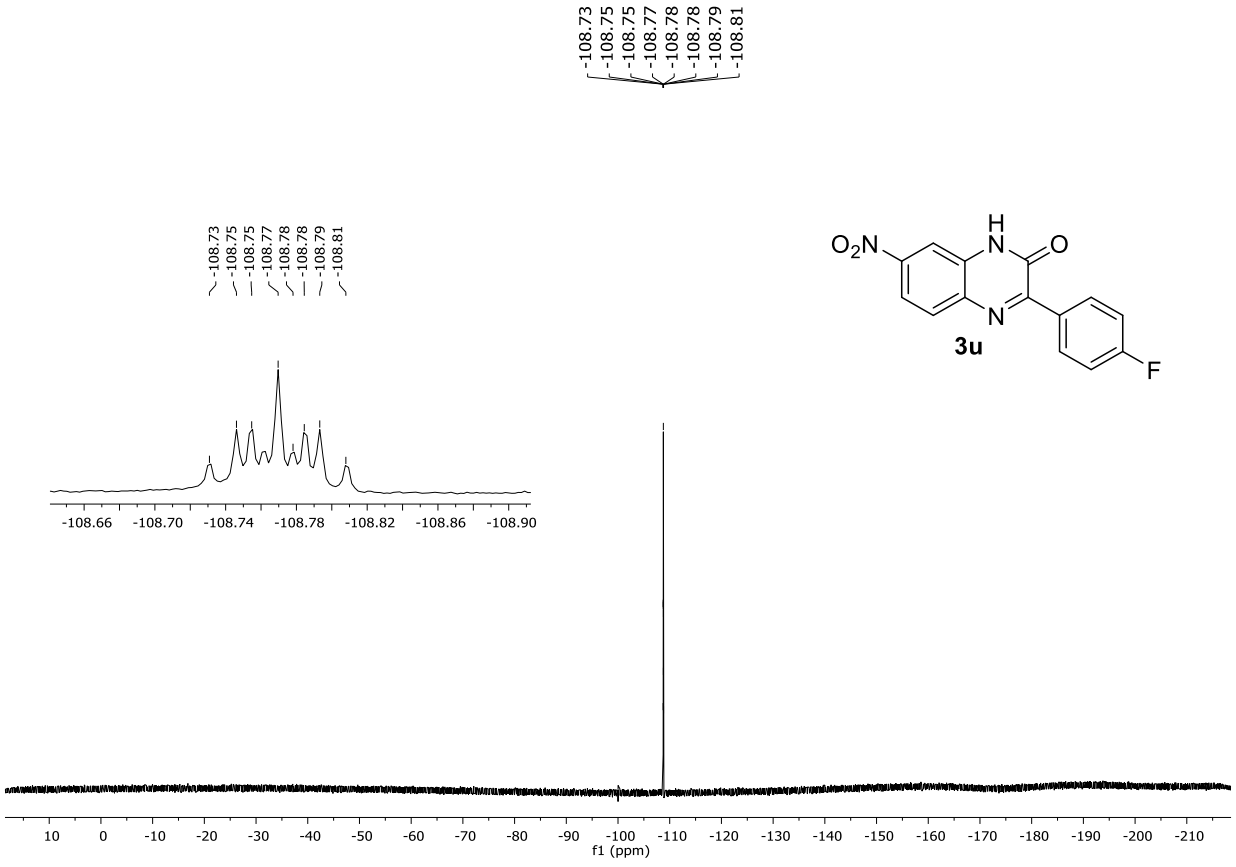
^{15}N NMR (40 MHz, DMSO-d_6) spectrum of **3t**.



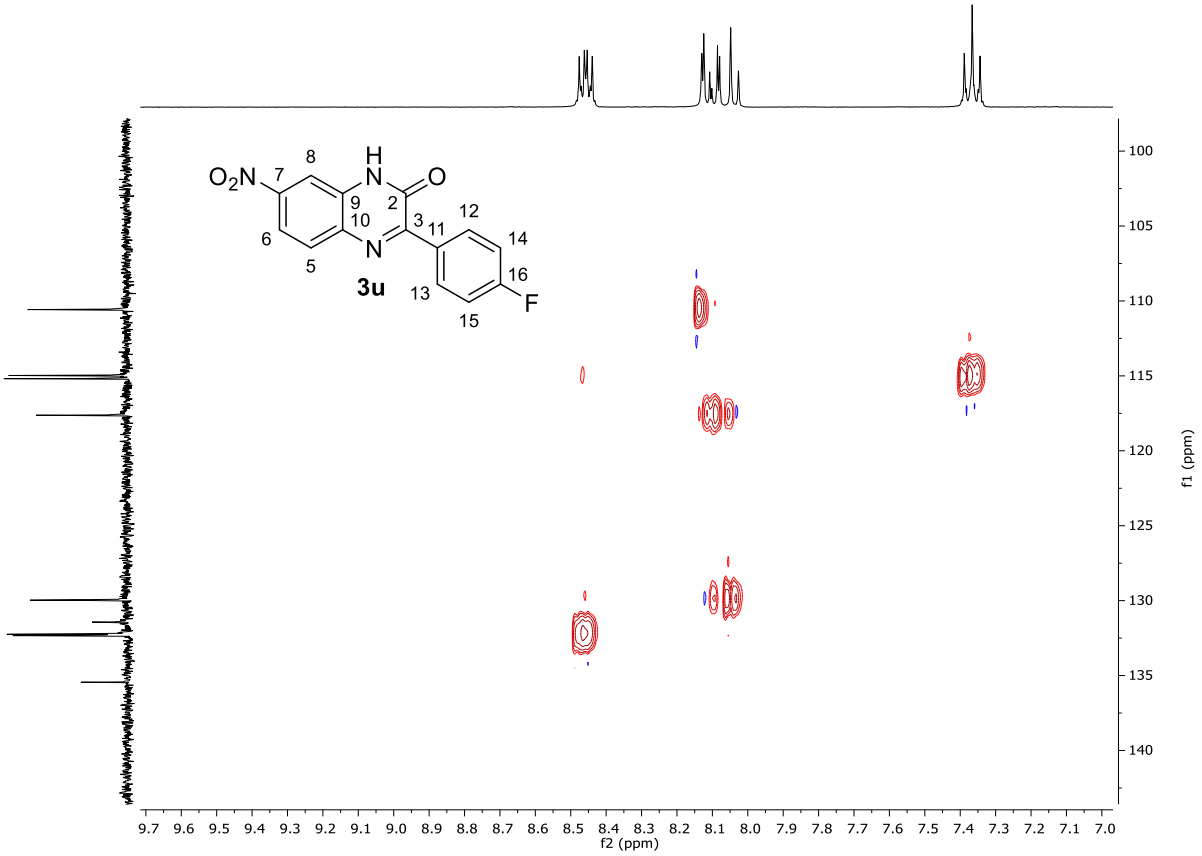
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3u**.



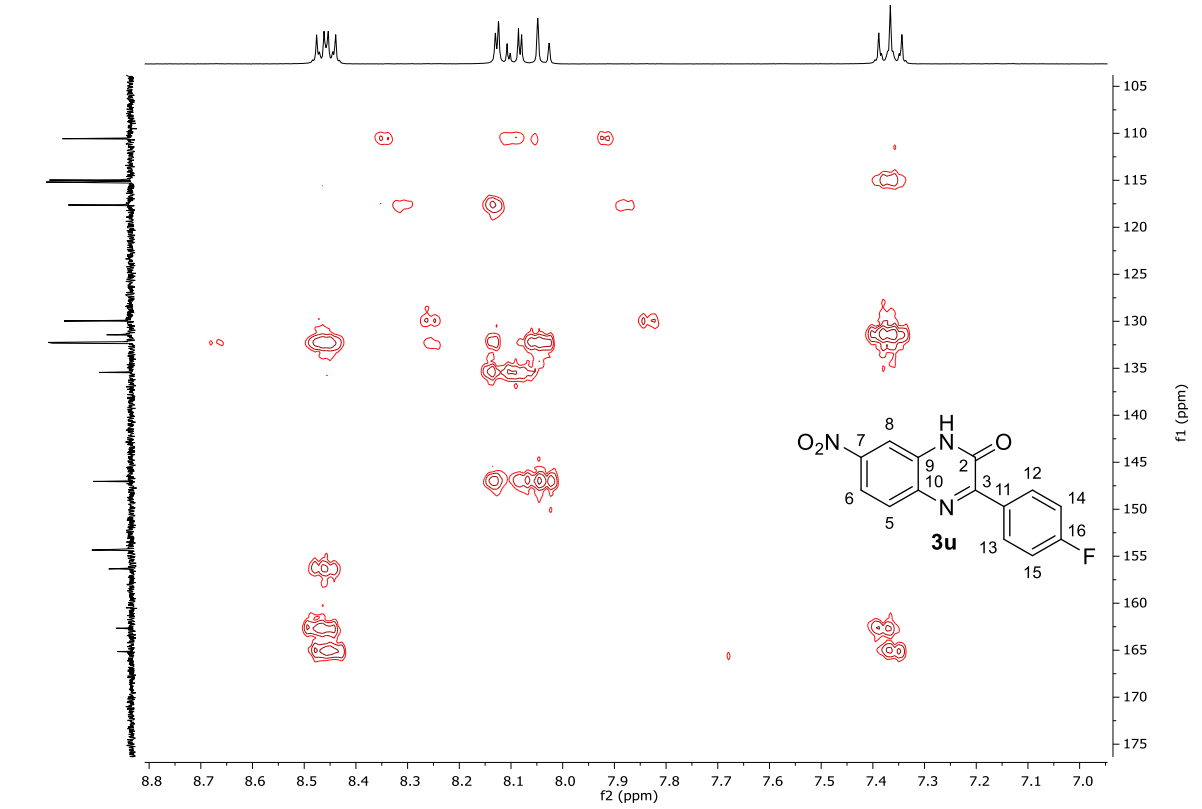
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **3u**.



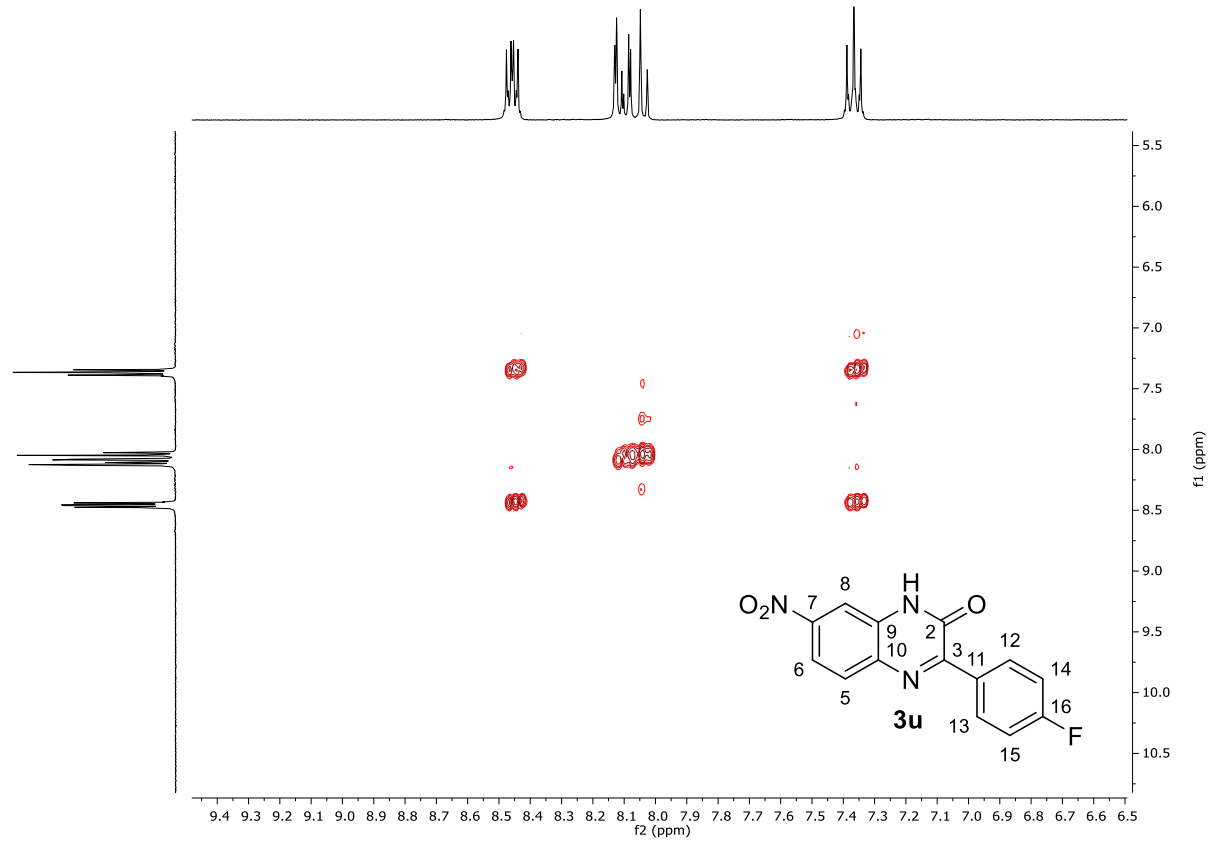
^{19}F NMR (376 MHz, DMSO-d_6) spectrum of **3u**.



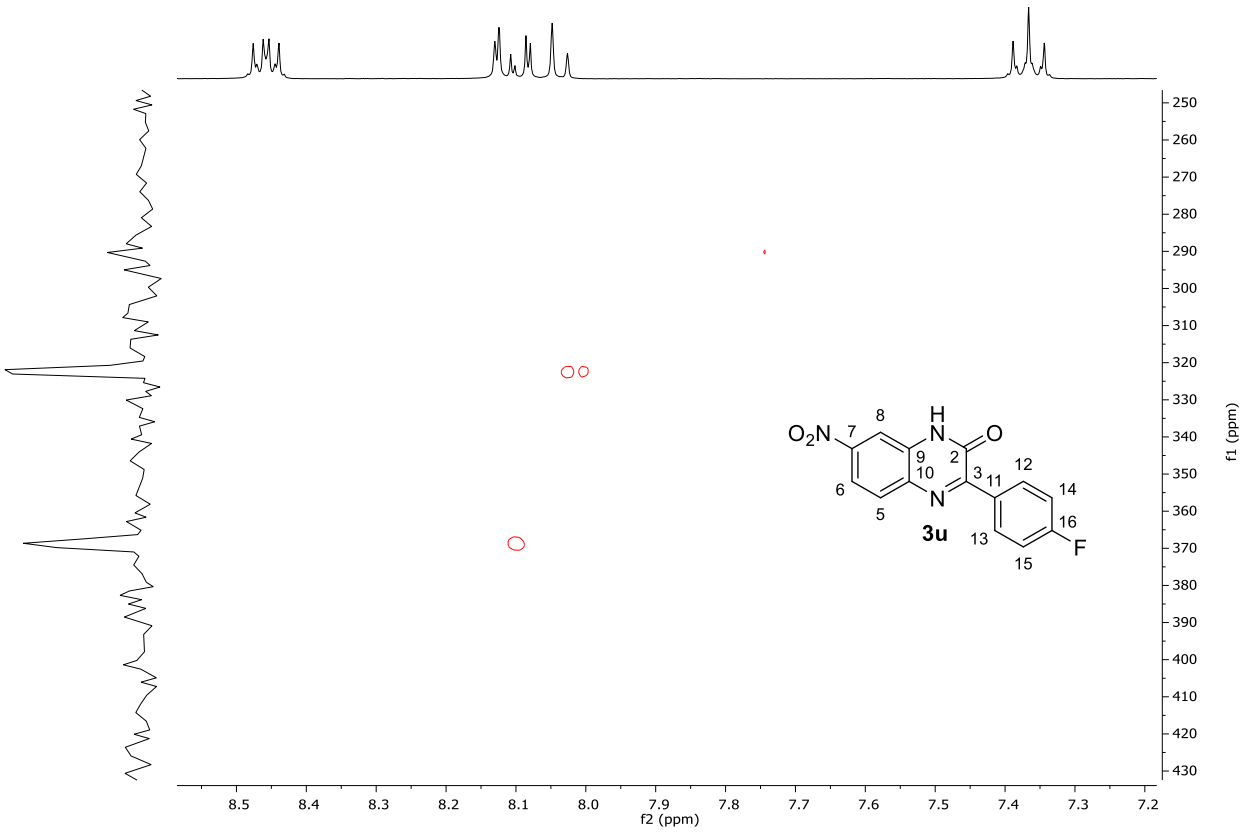
^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d$_6$) spectrum of **3u**.



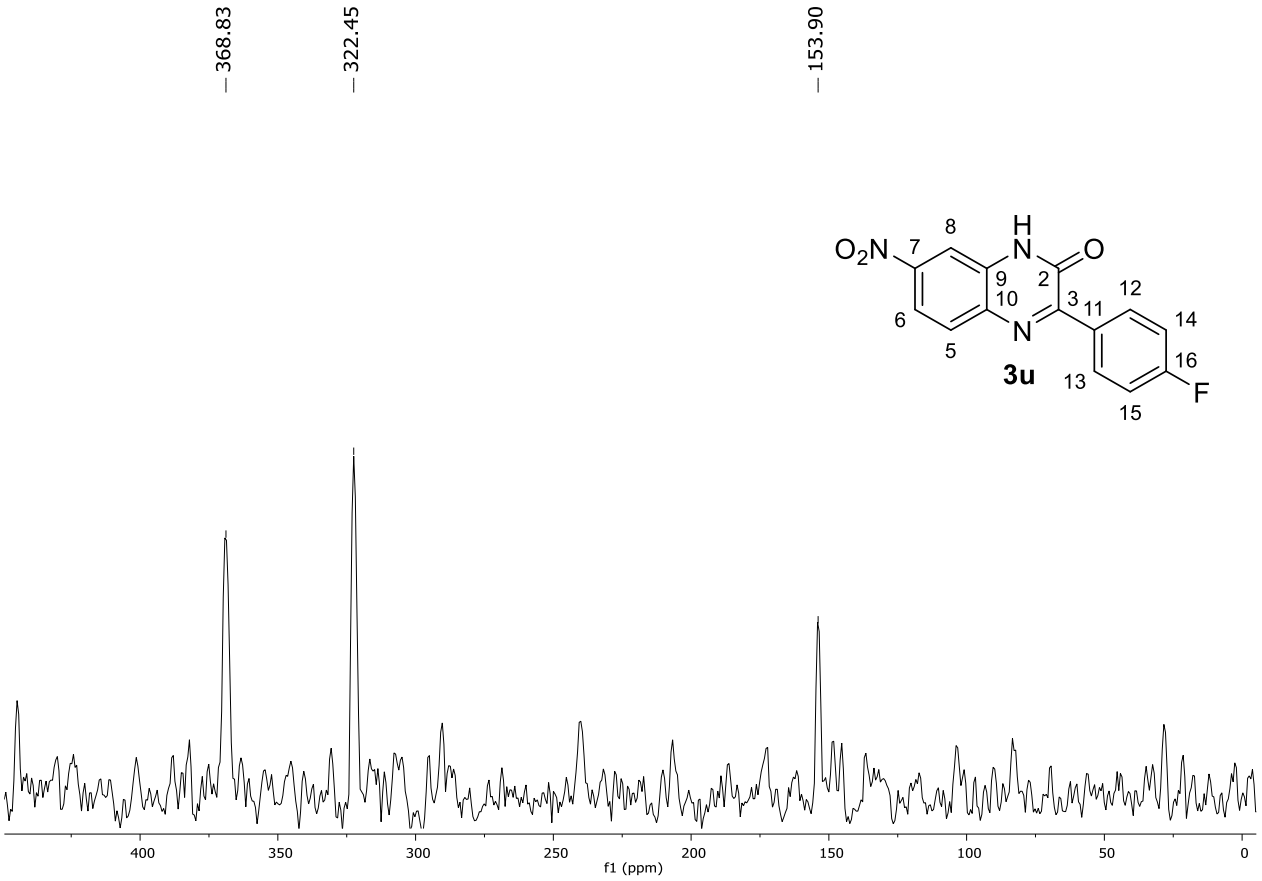
^{1}H-^{13}C HMBC NMR (400 MHz, DMSO-d$_6$) spectrum of **3u**.



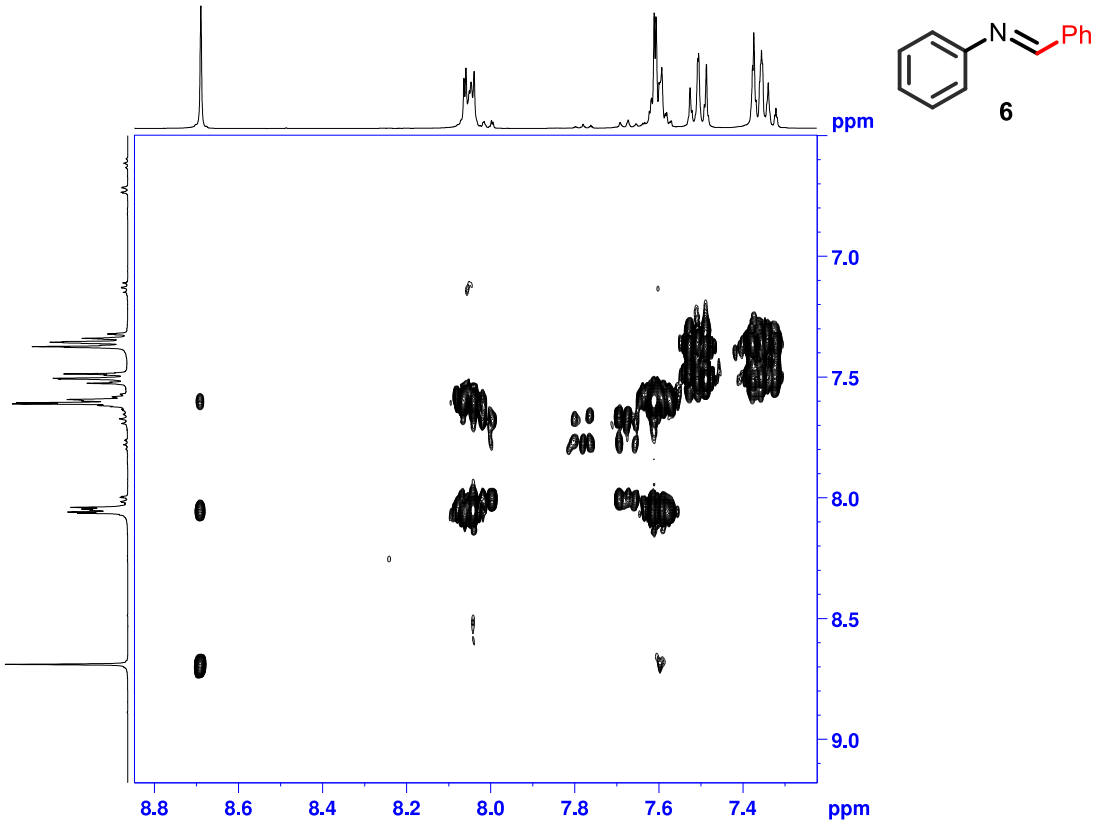
^{1}H COSY NMR (400 MHz, DMSO-d$_6$) spectrum of **3u**.



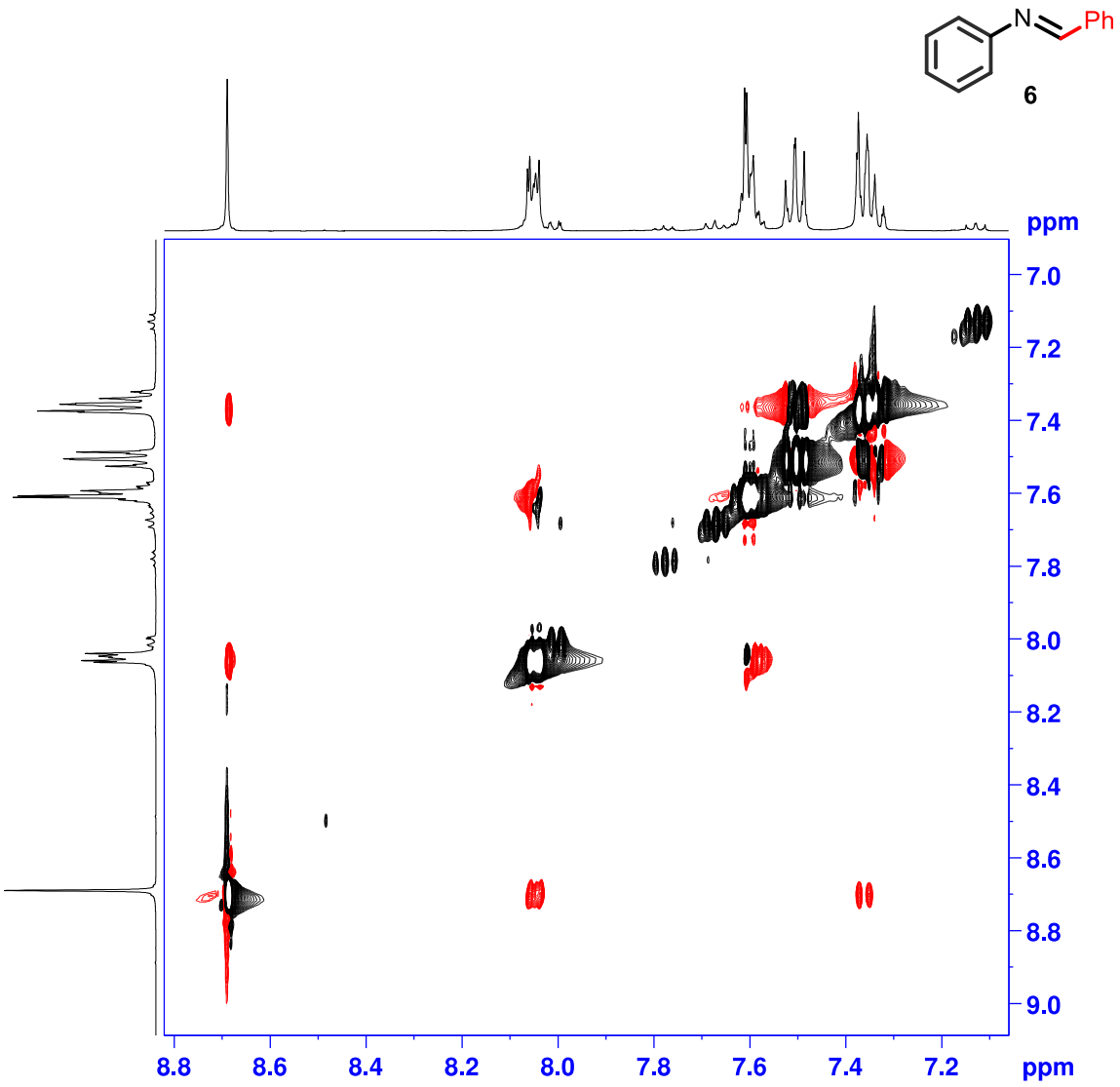
^{1}H-^{15}N HMBC NMR (400 MHz, DMSO-d$_6$) spectrum of **3u**.



^{15}N NMR (40 MHz, DMSO-d$_6$) spectrum of **3u**.



COSY 2D NMR (400 MHz, DMSO-d$_6$) spectrum of **6**.



NOESY 2D NMR (400 MHz, DMSO-d_6) spectrum of **6**.