Supplementary Materials

for

Cobalt Complexes of Redox Noninnocent Azo-aromatic Pincers. Isolation, Characterization, and Application as Catalyst for the Synthesis of Quinazolin-4(3H)-ones

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X-ray Crystallography. The X-ray single crystal data of all the complexes were collected with monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART Apex II diffractometer equipped with a CCD area detector. The crystals were positioned at 60 mm from the CCD and the spots were measured using 10s counting time. Data reduction was carried out using the SAINT-NT software package.[1] Multi-scan absorption correction was applied to all intensity data using the SADABS program.[2,3] The structure was solved by a combination of direct methods with subsequent difference Fourier syntheses and refined by full matrix least squares on F^2 using the SHELX-2013 suite.[4] All non-hydrogen atoms were refined with anisotropic thermal displacements. The crystal data together with refinement details are given in Table S1. In complex **2**, the cobalt center was found to be severely disordered, for which the cobalt sites were treated with a split model.

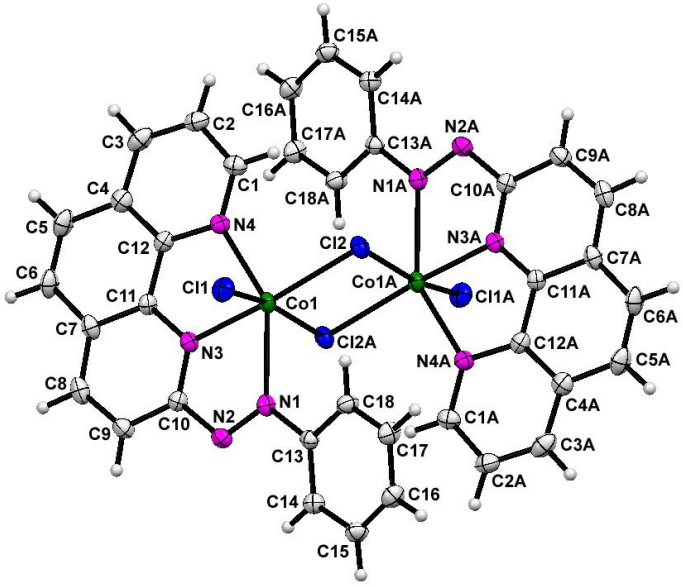


Figure S1. Oak Ridge thermal-ellipsoid plot (ORTEP) with complete atom numbering scheme of **1a.** Ellipsoids are drawn at the 50% probability level.

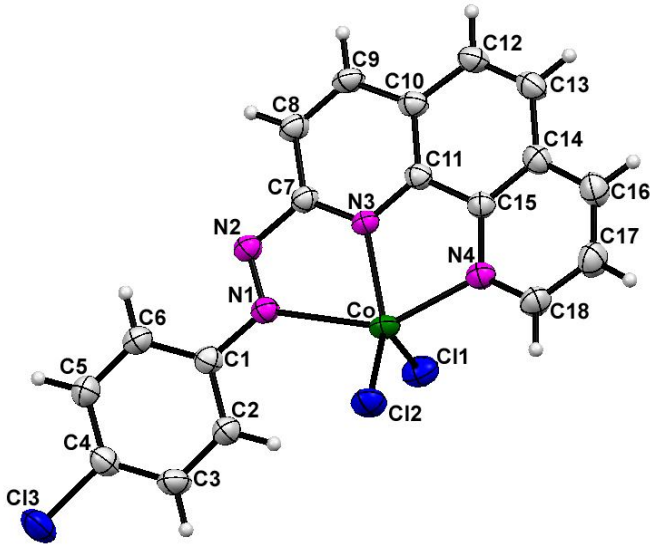


Figure S2. Oak Ridge thermal-ellipsoid plot (ORTEP) with complete atom numbering scheme of **1b.** Ellipsoids are drawn at the 50% probability level.

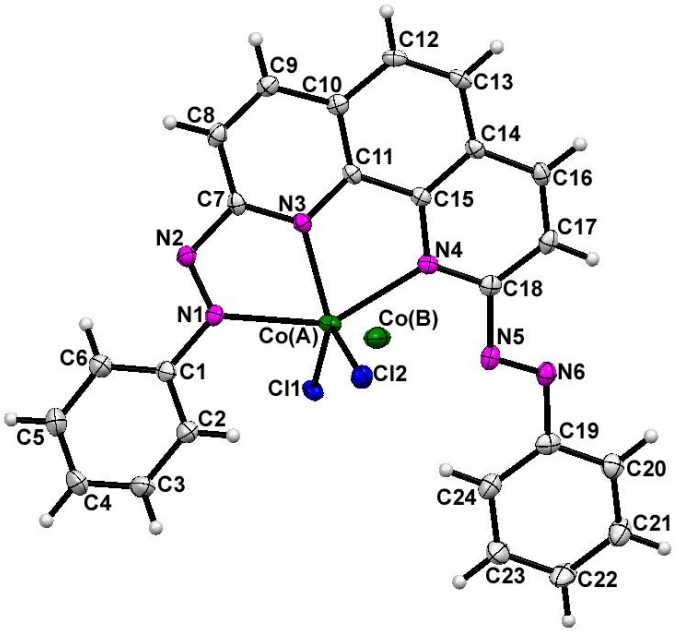
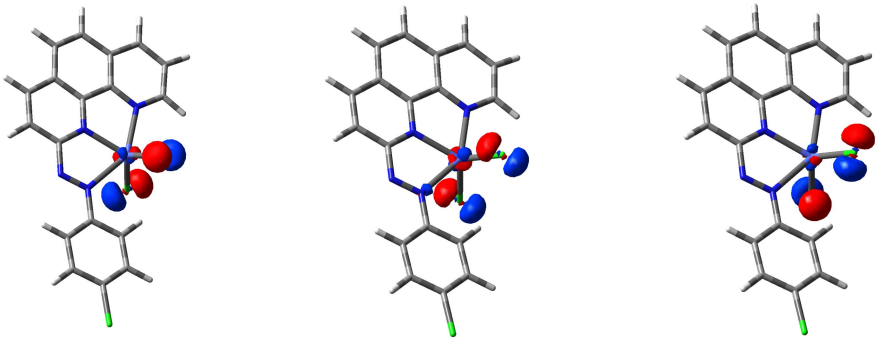


Figure S3. Oak Ridge thermal-ellipsoid plot (ORTEP) with complete atom numbering scheme of **2.** Ellipsoids are drawn at the 50% probability level.

Table S1. Crystal data and structure refinement parameters of **1a**, **1b** and **2**.

	1a	**1b**	**2**
Empirical Formula	$C_{36}H_{24}Cl_4Co_2N_8$	$C_{18}H_{11}Cl_3CoN_4$	$C_{24}H_{16}Cl_2CoN_6$
Formula Weight	828.29	448.59	518.26
Temp (K)	296	294	127
Crystal System	monoclinic	triclinic	triclinic
Space Group	P 21/n	P-1	P-1
a (Å)	12.76(3)	8.9454(9)	8.4667(7)
b (Å)	8.66(2)	9.7562(9)	10.9982(9)
c (Å)	15.29(4)	10.7268(10)	12.1179(10)
α(°)	90	89.496(4)	101.699(2)
β (°)	104.64(10)	87.482(5)	98.267(2)
γ (°)	90	71.661(4)	90.736(2)
Volume ($Å^3$)	1635(7)	887.74(15)	1092.45(16)
Z	2	2	2
D_c (Mg m^{-3})	1.683	1.678	1.576
Crystal Dimens (mm)	0.06 x 0.30 x 0.35	0.05 x 0.25 x 0.27	0.06 x 0.22 x 0.24
Theta Min-Max (º)	2.4, 25.1	2.19, 25.87	2.3, 27.162
Reflections Collected	37875	21314	31435
Unique Reflections	2898	3406	4840
Goodness-of-fit on F^2	0.973	1.04	1.08
Final *R* indices [I > 2σ(I)]	R= 0.0518, WR2= 0.1275	R = 0.0399, WR2= 0.1186	R = 0.0324, WR2=0.0848
Largest diff. peak and hole	-0.47, 0.43	-0.52, 0.61	-0.68, 0.56



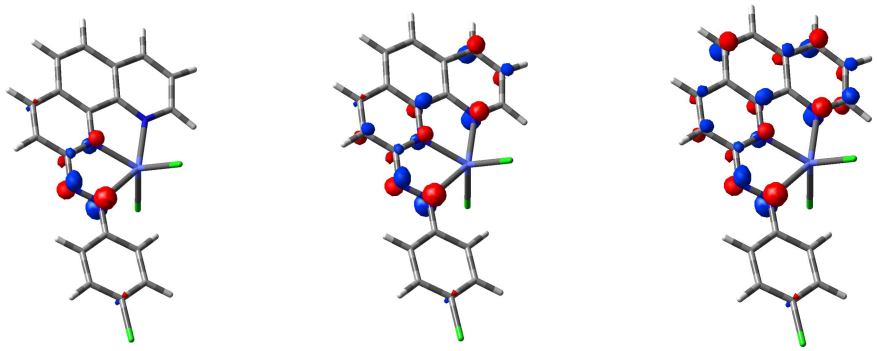


Figure S4. The representation of FMOs of **1b**.

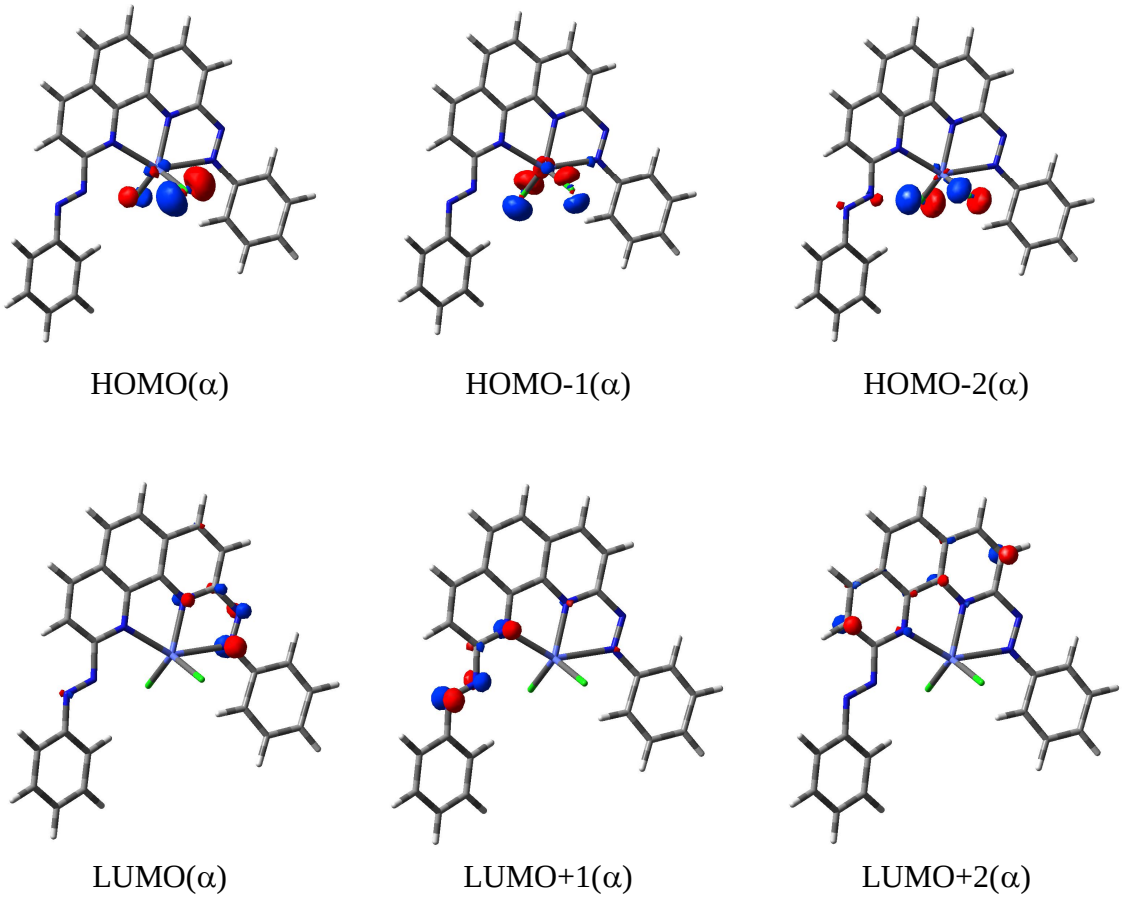


Figure S5. The representation of FMOs of **2**.

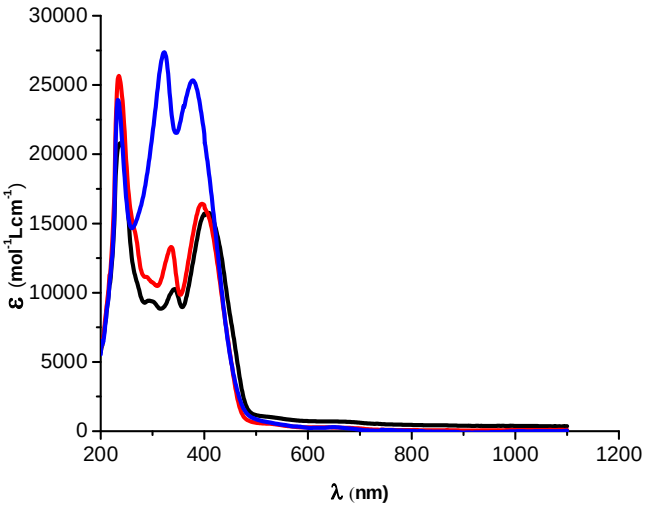


Figure S6. UV-vis spectra of catalyst **1a** (black), **1b** (red), and **2** (blue).

Table S2. UV-vis data of **1a**, **1b** and **2.**

Compound	λ_{max}, nm (ε, M^{-1} cm^{-1})
1a	404, (15,734), 342, (10,292), 300(9,422), 237, (20,749)
1b	396, (16,524), 335, (13,372), 235, (25,712)
2	376, (25,410), 321,(27,514), 233, (23,998)

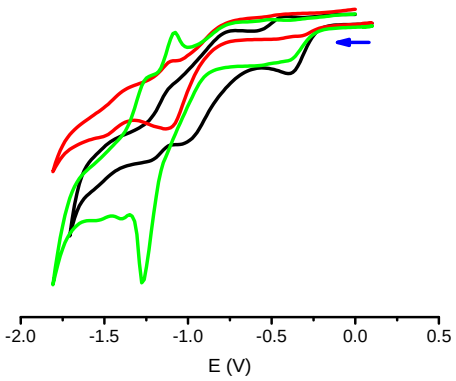


Figure S7. Cyclic voltammogram of **1a** (black), **1b** (red), **2** (green).

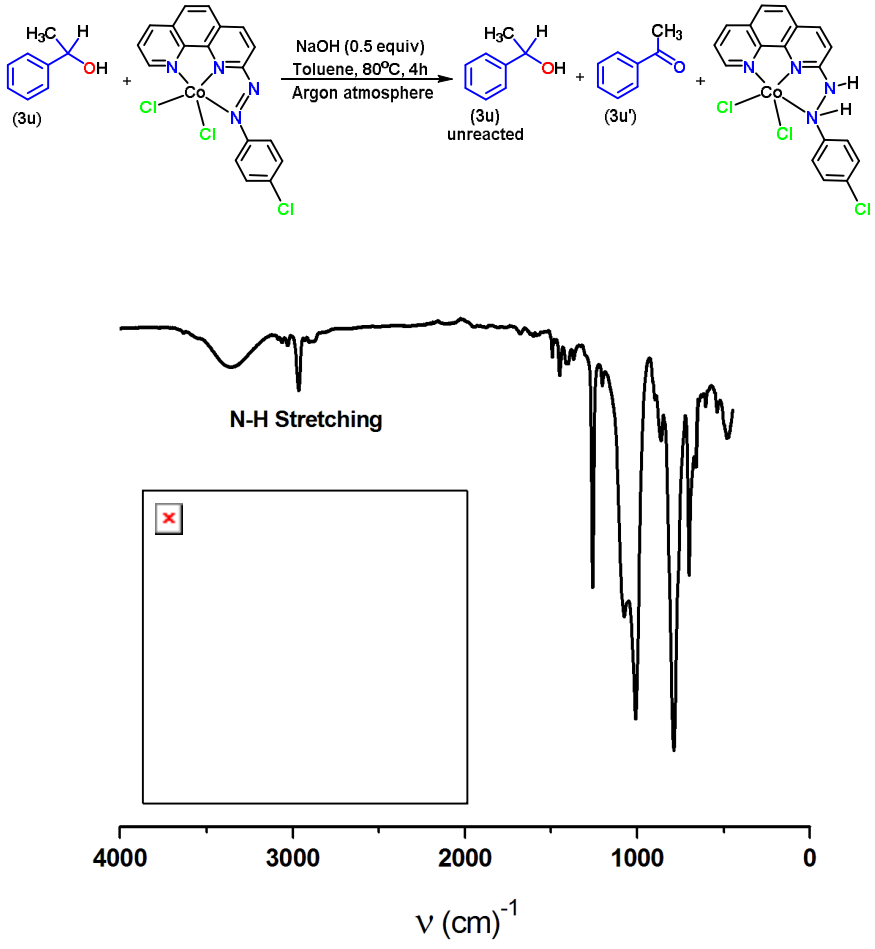


Figure S8. IR spectroscopic analysis of the reaction mixture obtained after stoichiometric alcohol dehydrogenation of 1-phenylethanol (**3u**) under argon: involvement of azo/hydrazo redox couple with catalyst **1b**.

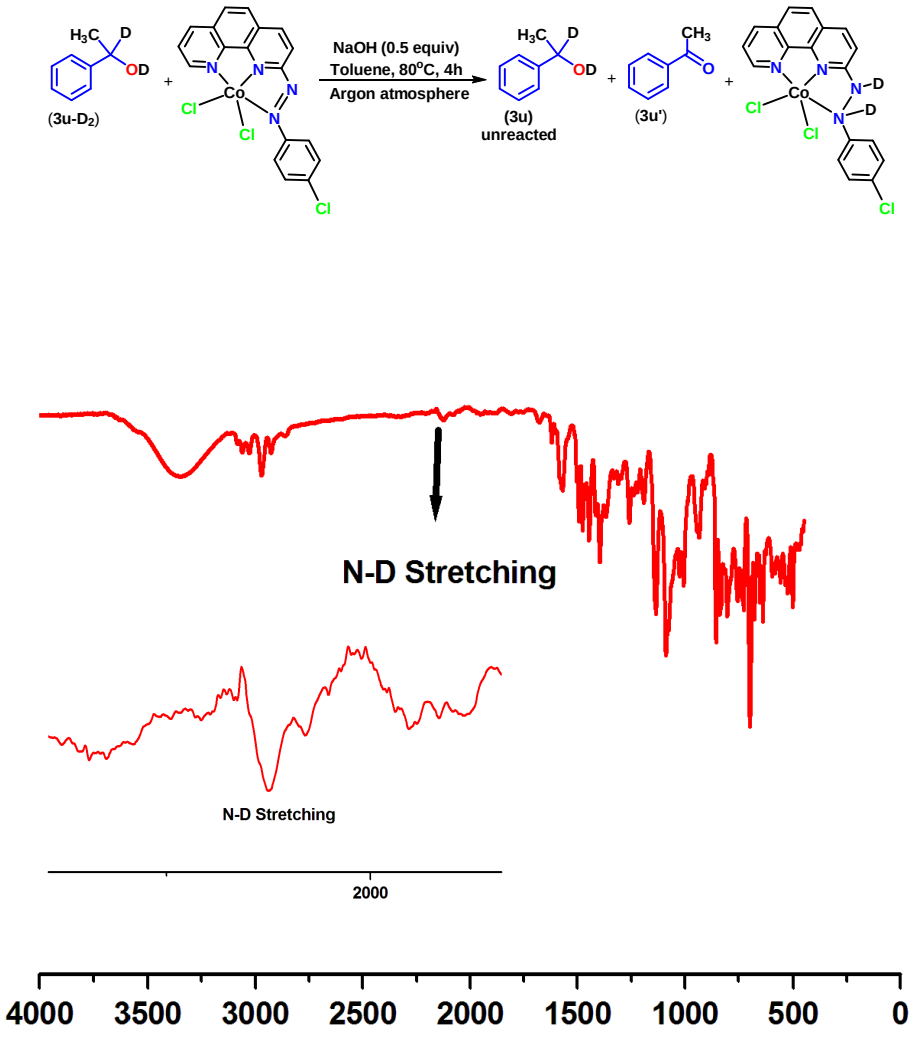


Figure S9. IR spectroscopic analysis of the reaction mixture obtained after stoichiometric alcohol dehydrogenation of deuterated 1-phenylethanol (**3u-D$_2$**) under argon: involvement of azo/hydrazo redox couple with catalyst **1b**.

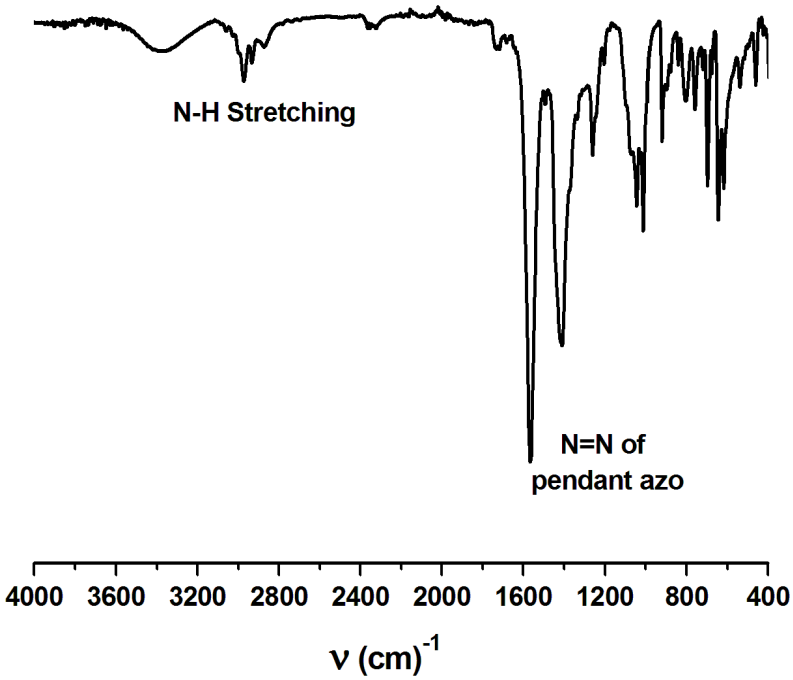


Figure S10. IR spectroscopic analysis of the reaction mixture obtained after stoichiometric alcohol dehydrogenation of 1-phenylethanol (**3u**) under argon: involvement of azo/hydrazo redox couple with catalyst **2**.

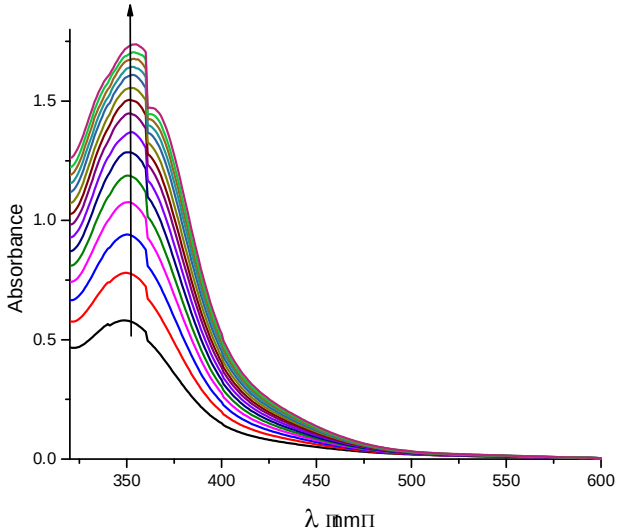


Figure S11. Detection of H_2O_2. Absorption spectral changes during formation of I_3^- at 351 nm in presence of H_2O_2.

NMR Spectral Data:

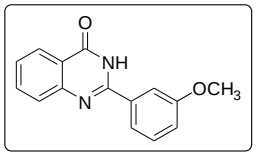
2-phenylquinazolin-4(3H)-one (5aa).[5,7,10,11] Eluent: petroleum ether/ethyl acetate (3:1): (199 mg, 90%) ; White solid, M.p :238-240 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.55 (s, 1H), 8.18-8.15 (m, 3H), 7.86-7.81 (m, 1H), 7.74 (d, J = 8.08 Hz, 1H), 7.59-7.50 (m, 4H). ^{13}C NMR (100MHz, DMSO-d_6): δ (ppm) = 162.7, 152.8, 149.2, 135.1, 133.2, 131.9, 129.4, 128.2, 128.0, 127.1, 126.3, 121.4.

2-(o-tolyl)quinazolin-4(3H)-one (5ba).[10] Eluent: petroleum ether/ethyl acetate (3:1): (169 mg, 72%), White solid; M.p: 225-226 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.44 (s, 1H), 8.17 (d, J = 7.92 Hz, 1H), 7.83 (t, J = 8.04 Hz, 1H), 7.68 (d, J = 7.68 Hz, 1H), 7.55-7.49 (m, 2H), 7.42 (t, J = 8.40, Hz,1H), 7.35-7.30 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =161.7, 154.3, 148.7, 136.1, 134.36, 134.4, 134.2, 130.5, 129.9, 129.1, 127.3, 126.6, 125.8, 125.6, 120.9, 19.6.

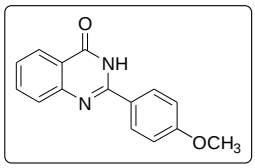
2-m-tolylquinazolin-4(3H)-one (5ca).[6,12] Eluent: petroleum ether/ethyl acetate (3:1): (167 mg, 71%), White solid; M.p: 212-213 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.56 (s, 1H), 8.24 (d, J = 8.45 Hz, 1H), 8.11(s, 1H), 8.06 (d, J = 6.80 Hz, 1H), 7.92 (t, J = 7.30 Hz, 1H), 7.83 (d, J = 7.90 Hz, 1H), 7.61 (t, J = 6.80 Hz, 1H), 7.53-7.48 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.7, 152.9, 149.3, 138.4,135.1, 133.1, 132.5, 129.0, 128.7, 128.0, 127.0,126.3, 125.4, 121.4, 21.4.

2-(p-tolyl)quinazolin-4(3H)-one (5da).[6,10-13] Eluent: petroleum ether/ethyl acetate (3:1): (177 mg, 75%)**,** White solid; M.p: 245-247 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.44 (s, 1H), 8.14 (d, J = 8.05 Hz, 1H), 8.08 (d, J = 8.05 Hz, 2H), 7.82 (dd, J = 1.90, 6.70 Hz, 1H), 7.72 (d, J = 8.55 Hz, 1H), 7.50 (t, J = 6.65 Hz, 1H), 7.34 (d, J = 8.10 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 162.2, 152.2, 148.8, 141.5, 134.6, 129.9, 129.1, 127.7, 127.4, 126.4, 125.7, 120.8, 21.0.

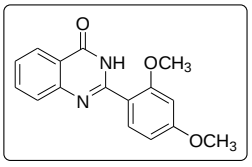
2-(3-methoxyphenyl)quinazolin-4(3H)-one (5ea).[6,12] Eluent: petroleum ether/ethyl acetate (3:1): (170 mg, 65%), White solid; M.p: 212 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.53 (s, 1H), 8.15 (d, J = 7.52 Hz, 1H), 7.83-7.77 (m, 2H), 7.73 (d, J = 4.04 Hz, 2H), 7.51 (t, J = 8.56 Hz, 1H), 7.44 (t, J = 9.04 Hz, 1H), 7.13 (dd, J = 3.52, 8.04 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.2, 159.3, 152.1, 148.6, 134.5, 134.0, 129.7, 129.3, 129.1, 126.6, 125.8, 120.1, 117.6, 112.6, 55.4.



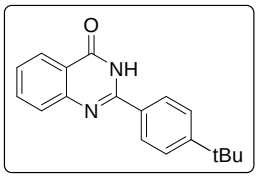
2-(4-methoxyphenyl)quinazolin-4(3H)-one (5fa).[6,10-13] Eluent: petroleum ether/ethyl acetate (3:1): (176 mg, 70%), White solid; M.p: 238-239 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.40 (s, 1H), 8.18 (d, J = 8.35 Hz, 2H), 8.12 (d, J = 7.75 Hz, 1H), 7.83-7.79 (m, 1H), 7.70 (d, J = 8.25 Hz, 1H), 7.48 (t, J = 7.60 Hz, 1H), 7.08 (d, J = 8.85 Hz, 2H), 3.84 (s, 3H).



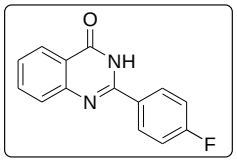
2-(2,4-dimethoxyphenyl)quinazolin-4(3H)-one (5ga).[13] Eluent: petroleum ether/ethyl acetate (3:1): (219 mg, 78%), White solid; M.p: 206-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.83 (s, 1H), 8.44 (d, J = 7.88 Hz, 1H), 8.20 (d, J = 8.64 Hz, 1H), 7.67 (d, J = 2.88 Hz, 2H), 7.37-7.33(m, 1H), 6.62 (dd, J= 7.48 Hz, 1.60 Hz,1H), 6.48 (d, J = 2.02 Hz, 1H), 3.96 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) =163.8, 162.1, 159.2, 150.7, 149.6, 134.4, 133.0, 127.6, 126.3, 126.0, 120.9, 112.6, 106.5, 98.7, 56.1, 55.6.



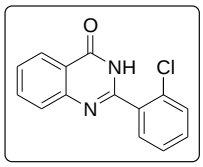
2-(4-*tert*-Butyl-phenyl)quinazolin-4(3H)-one (5ha).[9] Eluent: petroleum ether/ethyl acetate (3:1): (219 mg, 79%), White solid; M.p: 208 °C ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.49 (s, 1H), 8.16-8.11 (m, 3H), 7.83 (td, J = 1.60 Hz, 8.40 Hz, 1H), 7.73 (d, J = 8.04 Hz, 1H), 7.59 (d, J = 9.20 Hz, 2H), 7.51 (t, J = 6.92 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =162.8, 154.9, 152.7, 149.3, 135.1, 130.4, 128.1, 127.9, 126.9, 126.3, 125.9, 121.3, 35.1, 31.3.



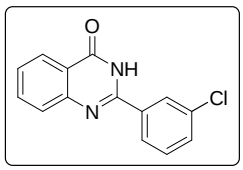
2-(4-fluorophenyl)quinazolin-4(3H)-one (5ia).[10,11] Eluent: petroleum ether/ethyl acetate (3:1): (172mg, 72%), White solid; M.p: 258-260 °C.[1]H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.66 (s, 1H), 8.34-8.30 (m, 2H), 8.23(d, J = 7.80 Hz, 1H), 7.91 (t, J = 7.24 Hz, 1H), 7.81 (d, J = 7.80 Hz, 1H), 7.60 (t, J = 6.68 Hz, 1H), 7.47 (t, J = 8.36 Hz, 2H). [13]C NMR(100 MHz, DMSO-d_6): δ (ppm) = 162.7, 151.9, 149.1, 135.1, 130.8 (d, J = 9.00 Hz), 129.7, 127.9, 127.1, 126.3, 121.3, 116.2, 116.0.



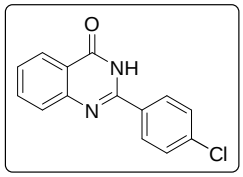
2-(2-chlorophenyl)quinazolin-4(3H)-one (5ja).[6,12,13] Eluent: petroleum ether/ethyl acetate (3:1): (174 mg 68%), White solid; M.p: 197 °C. [1]H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.68 (s, 1H), 8.18 (d, J = 7.92 Hz, 1H), 7.86 (t, J = 7.08 Hz, 1H), 7.71 (d, J = 7.96 Hz, 1H), 7.66 (d, J = 6.2 Hz, 1H), 7.62-7.55 (m, 3H), 7.49 (t, J= 8.84 Hz, 1H).



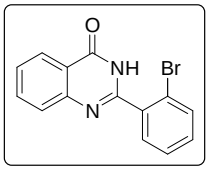
2-(3-chlorophenyl)quinazolin-4(3H)-one (5ka).[12,13] Eluent: petroleum ether/ethyl acetate (3:1): (181 mg, 71%), White solid; M.p: 295-296 °C. [1]H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.62 (s, 1H), 8.23 (s, 1H), 8.15 (t, J = 8.40 Hz, 2H), 7.86 (t, J = 8.40 Hz, 1H), 7.77 (d, J = 7.60 Hz, 1H), 7.66 (d, J = 7.60 Hz, 1H), 7.61-7.53 (m, 2H).



2-(4-chlorophenyl)quinazolin-4(3H)-one (5la).[10,12] Eluent: petroleum ether/ethyl acetate (3:1): (179 mg, 70%), White solid; M.p: 299-300 °C. [1]H NMR (400 MHz, DMSO-d_6): δ (ppm) =12.73 (s, 1H), 8.30 (d, J = 8.56 Hz, 2H), 8.26 (d, J = 9.24 Hz, 1H), 7.95 (t, J = 7.96 Hz, 1H), 7.85 (d, J = 7.48 Hz, 1H), 7.73 (d, J = 8.36 Hz, 2H), 7.64 (t, J = 7.52 Hz, 1H). [13]C NMR (100 MHz, DMSO-d_6): δ (ppm) =162.7, 149.1, 146.3, 136.8, 135.2, 132.0, 132.7, 130.1, 129.2, 128.0, 127.3, 126.4, 121.5.

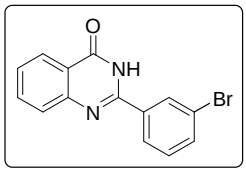


2-(2-bromophenyl)quinazolin-4(3H)-one (5ma).[11] Eluent: petroleum ether/ethyl acetate (3:1): (207 mg, 69%), White solid; M.p:185 °C. [1]H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.67 (s, 1H), 8.20 (d, J = 8.8

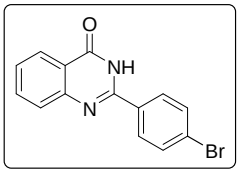


Hz, 1H), 7.87 (t, *J* = 7.28 Hz, 1H), 7.78 (d, *J* = 7.28 Hz, 1H), 7.73 (d, *J* = 8.08 Hz, 1H), 7.66 (d, *J* = 8.08 Hz, 1H), 7.61-7.55 (m, 2H), 7.53-7.47 (m, 1H).

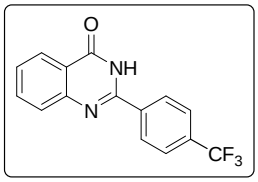
2-(3-bromophenyl)quinazolin-4(3H)-one (5na).[12] Eluent: petroleum ether/ethyl acetate (3:1): (210mg, 70%), White solid; M.p: 295-296 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.63 (s, 1H), 8.33 (s, 1H), 8.15 (d, *J* = 8.01 Hz, 2H), 7.85 (t, *J* = 7.28 Hz, 1H), 7.77 (t, *J* = 7.32 Hz, 2H),), 7.56-7.49 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =162.6, 151.4, 148.9, 135.4, 135.2, 134.5, 131.3, 130.9, 128.1, 127.4, 127.3, 126.3, 122.4, 121.6.



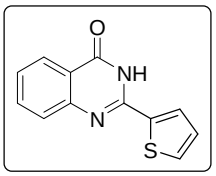
2-(4-bromophenyl)quinazolin-4(3H)-one (5oa).[5,11,12] Eluent: petroleum ether/ethyl acetate (3:1): (225 mg, 75%), White solid; M.p>300 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.62 (s, 1H), 8.17-8.11 (m, 3H), 7.85 (t, *J* = 7.92 Hz, 1H), 7.76 (t, *J*=8.60 Hz, 3H), 7.54 (t, *J*=7.96 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =162.6, 151.5, 147.9, 135.2, 132.1, 130.3, 129.6, 128.0, 127.3, 126.3, 125.7, 121.5.



2-(4-trifluoromethyl)quinazolin-4(3H)-one (5pa).[9] Eluent: petroleum ether/ethyl acetate (3:1): (218mg, 76%).White solid; M.p: 295 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) =12.81 (s, 1H), 8.42 (d, *J* = 8.92 Hz, 2H), 8.23 (d, *J* = 7.36 Hz, 1H), 7.98 (d, *J* = 8.92 Hz, 2H), 7.92 (t, *J* = 7.92 Hz, 1H), 7.83 (d, *J* = 7.64 Hz, 1H), 7.62 (t, *J* = 7.64 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 162.6, 151.7, 148.9, 137.1, 135.2, 131.8, 129.2, 128.2, 127.6, 126.4, 126.0 (q, *J* = 4.0Hz), 121.7.

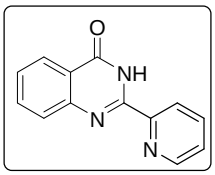


2-(thiophen-2-yl)quinazolin-4(3H)-one (5qa).[10,12] Eluent: petroleum ether/ethyl acetate (3:1): (155 mg, 68%), Yellow solid; M.p: 270-271 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.64 (s, 1H), 8.22 (d, *J* = 4.20 Hz, 1H), 8.11 (dd, *J* = 2.0, 8.10 Hz, 1H), 7.86 (d, *J* = 5.10 Hz, 1H), 7.79 (td, *J* = 1.65, 8.00 Hz 1H), 7.64 (d, *J* = 8.00 Hz, 1H), 7.48

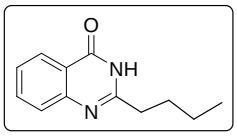


(t, *J* = 4.85 Hz, 1H), 7.23 (t , *J* = 4.20 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =162.3, 149.1, 148.3, 137.8, 135.2, 132.6, 129.9, 129.0, 127.4, 126.8, 126.5, 121.3.

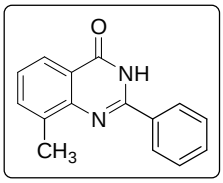
2-(pyridin-2-yl)quinazolin-4(3H)-one (5ra).[6] Eluent: petroleum ether/ethyl acetate (3:1): (140 mg, 63%), Yellow solid; ^{1}H NMR (500MHz, DMSO-d_6): δ (ppm) = 11.80 (s, 1H), 8.74 (d, *J* = 3.75 Hz, 1H), 8.43 (d, *J* = 7.50 Hz, 1H), 8.17 (d, *J* = 7.50 Hz, 1H), 8.05 (t, *J* = 7.55 Hz, 1H), 7.85 (t, *J* = 8.25 Hz, 1H), 7.78 (d, *J* = 7.50 Hz, 1H), 7.64 ((t, *J* = 6.00 Hz, 1H), 7.56 (t, *J* = 6.75, 1H).



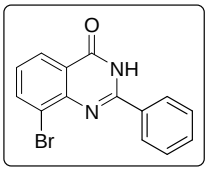
2-butylquinazolin-4(3H)-one (5sa).[6] Eluent: petroleum ether/ethyl acetate (3:1): (46 mg, 23%), White solid; Mp: 109 ^{O}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.18 (s, 1H), 8.07 (d, *J* = 8.60 Hz, 1H), 7.76 (t, *J* = 7.28 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.44 (t, *J* = 7.96 Hz, 1H), 2.58 (t, *J* = 7.64 Hz, 2H), 1.72-1.65 (m, 2H), 1.35-1.30 (m, 2H), 0.89(t, *J* = 6.08 Hz, 3H) .



8-methyl-2-phenylquinazolin-4(3H)-one (5ab).[8] Eluent: petroleum ether/ethyl acetate (3:1): (191 mg, 81%), White solid; M.p: 248-249 $^{\circ}$C ;^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.53 (s, 1H), 8.22 (d, *J* = 7.56 Hz, 2H), 7.99 (d, *J* = 7.56 Hz, 1H), 7.69 (d, *J* = 6.80 Hz, 1H), 7.59-7.54 (m, 3H), 7.39 (t, *J* =9.76 Hz, 1H), 2.63 (s, 3H).^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 163.0, 151.5, 147.6, 136.1, 135.4, 133.4, 131.8, 129.1, 128.2, 126.5, 123.9, 121.3, 17.6.

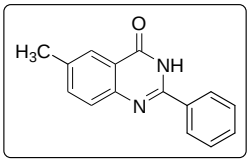


8-bromo-2-phenylquinazolin-4(3H)-one (5ac).[13] Eluent: petroleum ether/ethyl acetate (3:1): (225 mg,75%), White solid; M.p: 219-220 $^{\circ}$C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.75 (s, 1H), 8.25 (d, *J* = 7.80 Hz, 2H), 8.14 (d, *J* = 7.15 Hz, 2H), 7.63-7.56 (m, 3H), 7.41 (t, *J* = 8.30

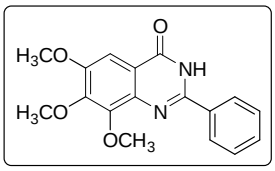


Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.4, 153.4, 146.6, 138.5, 132.9, 132.3, 129.2, 128.4, 127.8, 127.2, 126.2, 123.1, 122.7.

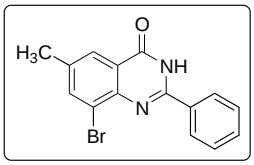
6-methyl-2-phenylquinazolin-4(3H)-one (5ad).[10,5] Eluent: petroleum ether/ethyl acetate (3:1): (195 mg, 83%), White solid; Mp: 264-265 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.47 (s, 1H), 8.16 (d, J = 6.92 Hz, 2H), 7.95 (s, 1H), 7.64 (s, 2H), 7.54 (d, J = 5.96 Hz, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.6, 152.0, 147.2, 136.8, 136.4, 133.2, 131.7, 129.1, 128.1, 127.9, 125.7, 121.2, 21.3.



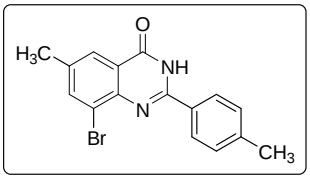
6,7,8-trimethoxy-2-phenylquinazolin-4(3H)-one (5ae).[13] Eluent: petroleum ether/ethyl acetate (3:1): (234 mg, 85%) ,White solid; M.p: 272-273 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.51 (s, 1H), 8.19 (dd, J = 2.44, 4.96 Hz, 2H), 7.56 (d, J = 6.60 Hz, 3H), 7.38 (s, 1H), 4.07(s, 3H), 3.92 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.2, 152.7, 150.1, 148.4, 147.7, 138.9, 133.4, 131.6, 129.1, 127.9, 117.6, 101.6, 62.6, 61.4, 56.4.



8-bromo-6-methyl-2-phenylquinazolin-4(3H)-one(5af).[13] Eluent: petroleum ether/ethyl acetate (3:1): (267 mg, 82%), White solid; M.p:>300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =12.68 (s, 1H), 8.23 (d, J = 8.08 Hz, 2H), 8.01 (s, 1H), 7.94 (s, 1H), 7.60-7.54 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.3, 152.5, 144.5, 139.4, 138.0, 132.9, 132.1, 129.1, 128.3, 125.7, 122.7, 122.4, 20.9.

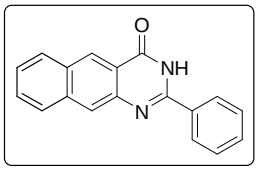


8-bromo-2-(4-methylphenyl)-6-methylquinazolin-4(3H)-one(5kf).[13] Eluent: petroleum ether/ethyl acetate (3:1): (186 mg, 75%), White solid; M.p:>300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.60 (s, 1H), 8.15 (d, J = 8.08 Hz, 2H), 8.00 (s, 1H), 7.93 (s, 1H), 7.37 (d, J = 8.08 Hz, 2H), 2.43(s, 3H), 2.39 (s, 3H).



^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.3, 152.4, 144.6, 142.3, 139.4, 137.8, 130.1, 129.7, 128.2, 125.7, 122.6, 122.3, 21.5, 20.9.

2-phenylbenzo[g]quinazolin-4(3H)-one(5ag).[13] Eluent: petroleum ether/ethyl acetate (3:1): (217m mg, 76%), White solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.37 (s, 1H), 8.87 (s, 1H), 8.32 (s, 1H), 8.22 (t, J = 6.72 Hz, 3H), 8.12 (d, J = 8.04 Hz,1H), 7.67 (t, J = 6.92 Hz, 1H), 7.59 (t, J = 7.60 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 163.3, 150.5, 144.8, 136.7, 135.5, 131.8, 131.4, 129.8, 129.1, 128.2, 127.8, 126.8, 125.4, 120.7.



Copies of ^{1}H and ^{13}C NMR spectra:

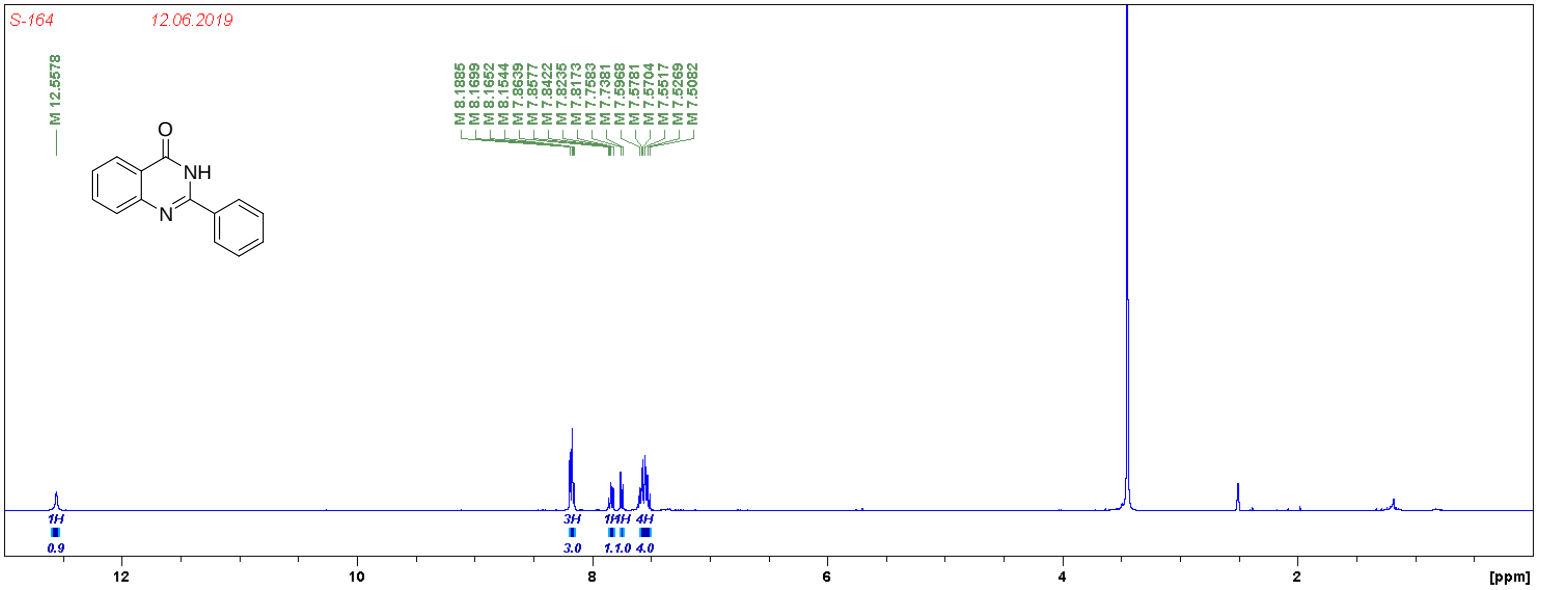


Figure S12. ^{1}H NMR spectrum of compound **5aa** (400 MHz, DMSO-d_6).

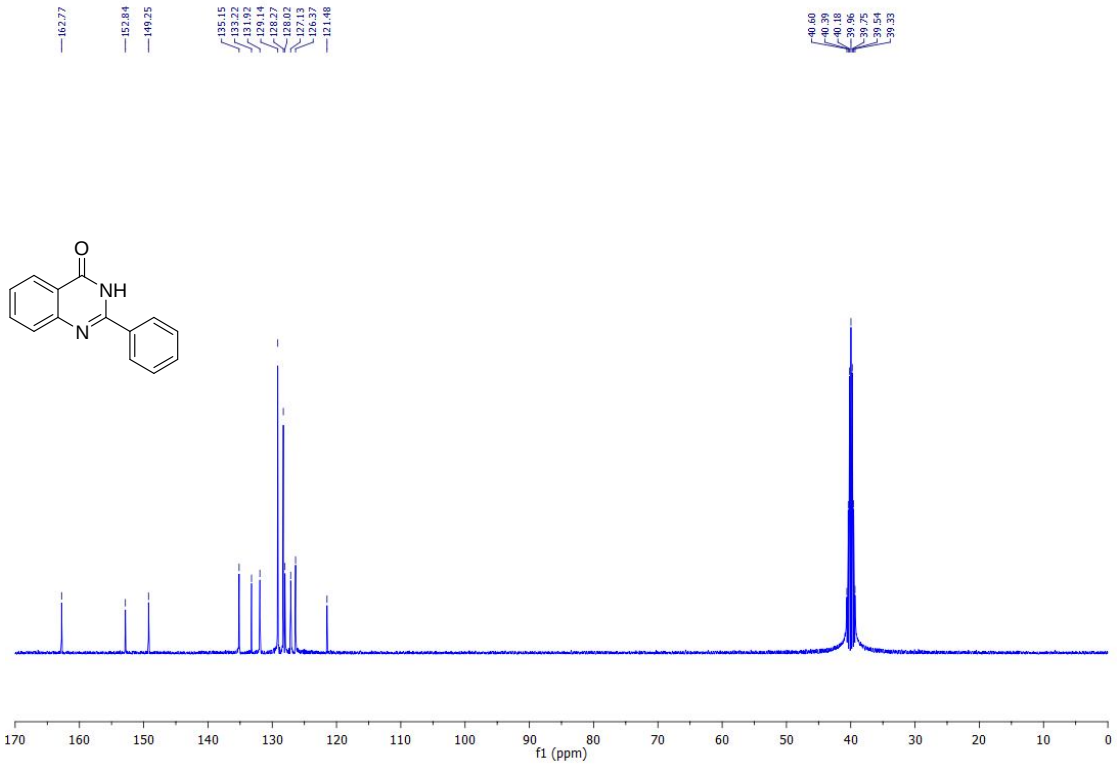


Figure S13. ^{13}C NMR spectrum of compound **5aa** (100 MHz, DMSO-d_6).

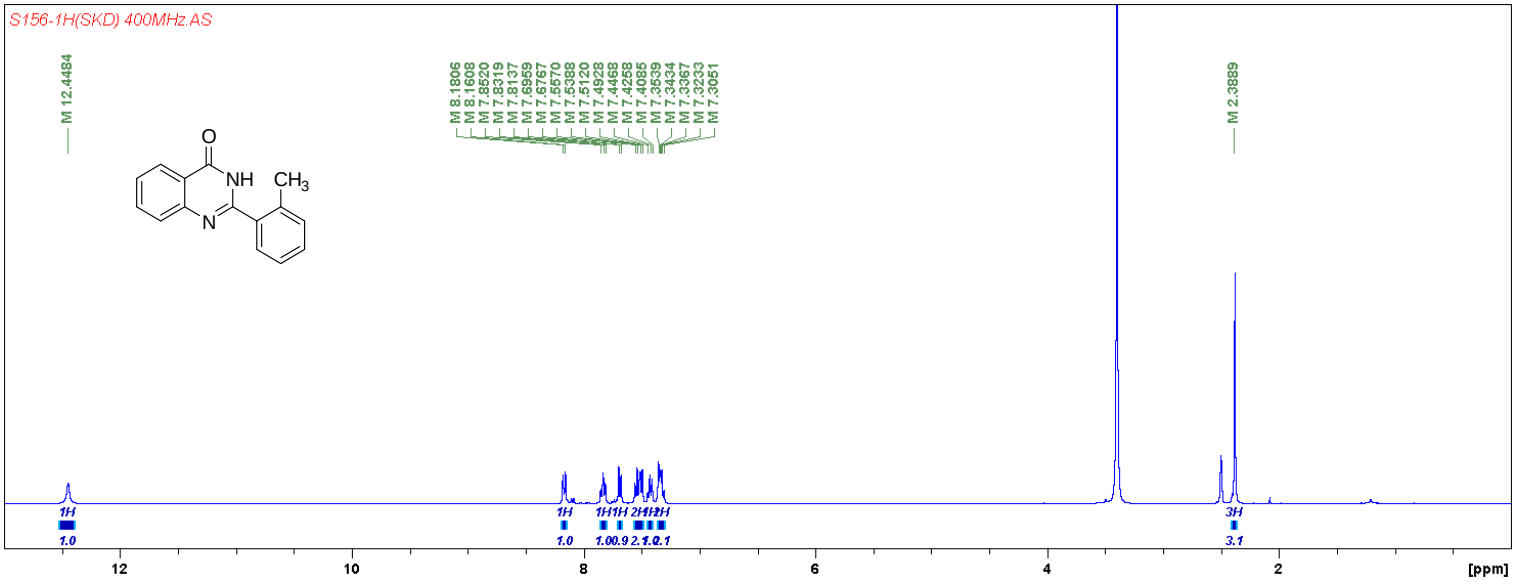


Figure S14. ^{1}H NMR spectrum of compound **5ba** (400 MHz, DMSO-d_6).

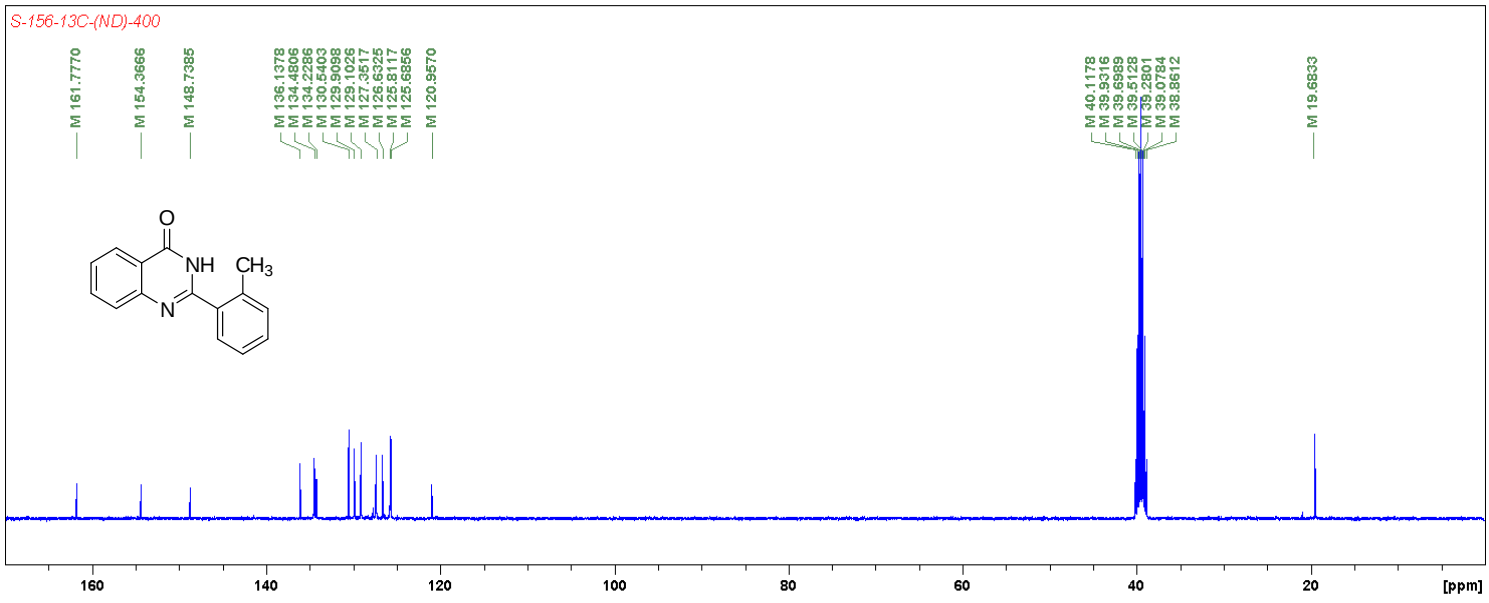


Figure S15. ^{13}C NMR spectrum of compound **5ba** (100 MHz, DMSO-d_6).

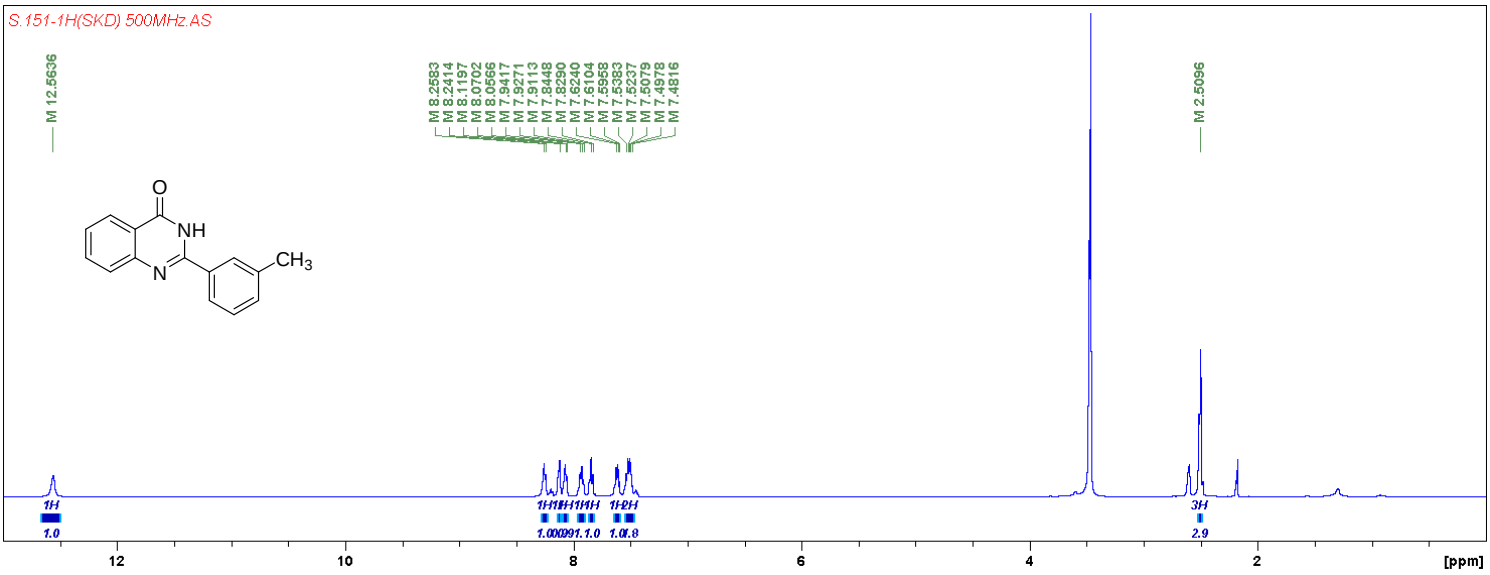


Figure S16. ^{1}H NMR spectrum of compound **5ca** (500 MHz, DMSO-d_6).

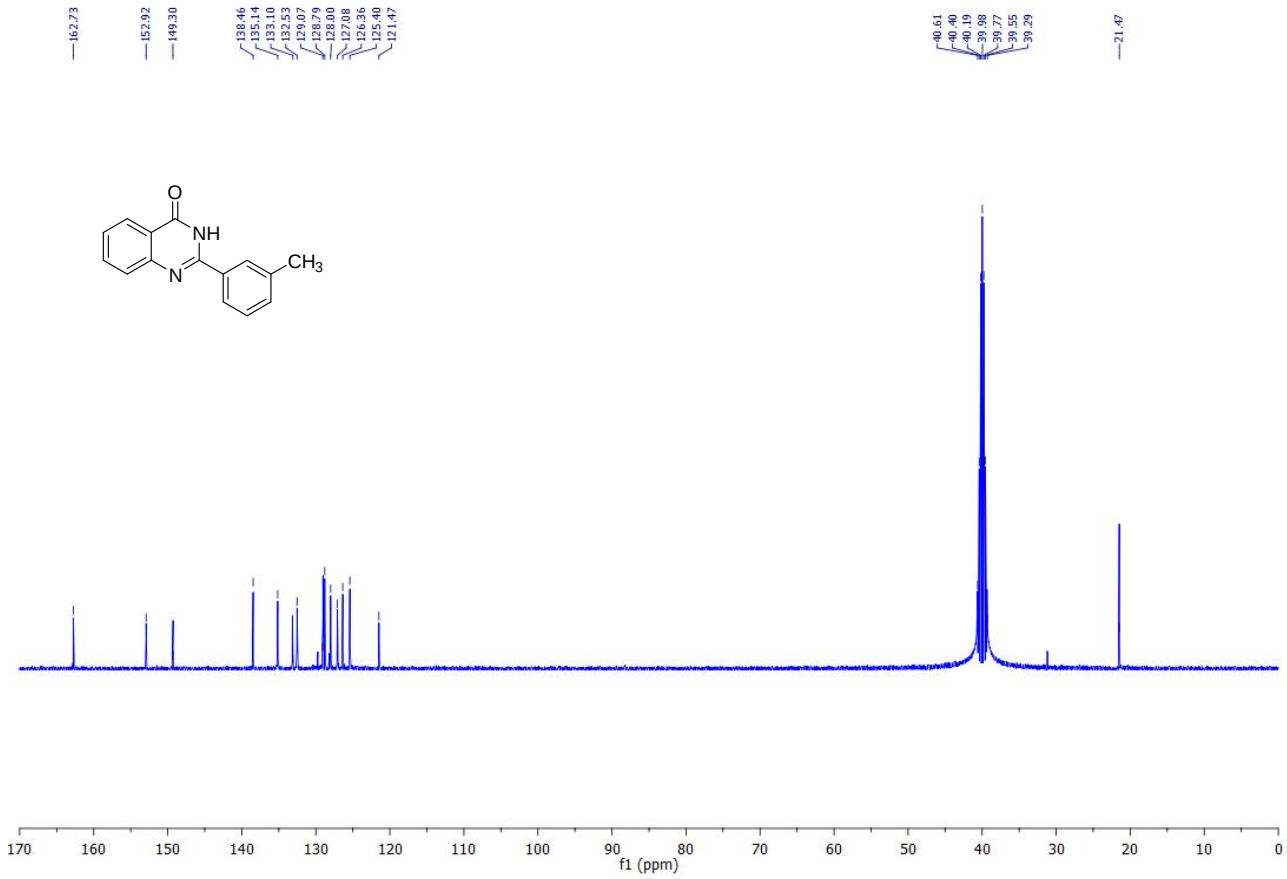


Figure S17. ^{13}C NMR spectrum of compound **5ca** (100 MHz, DMSO-d_6).

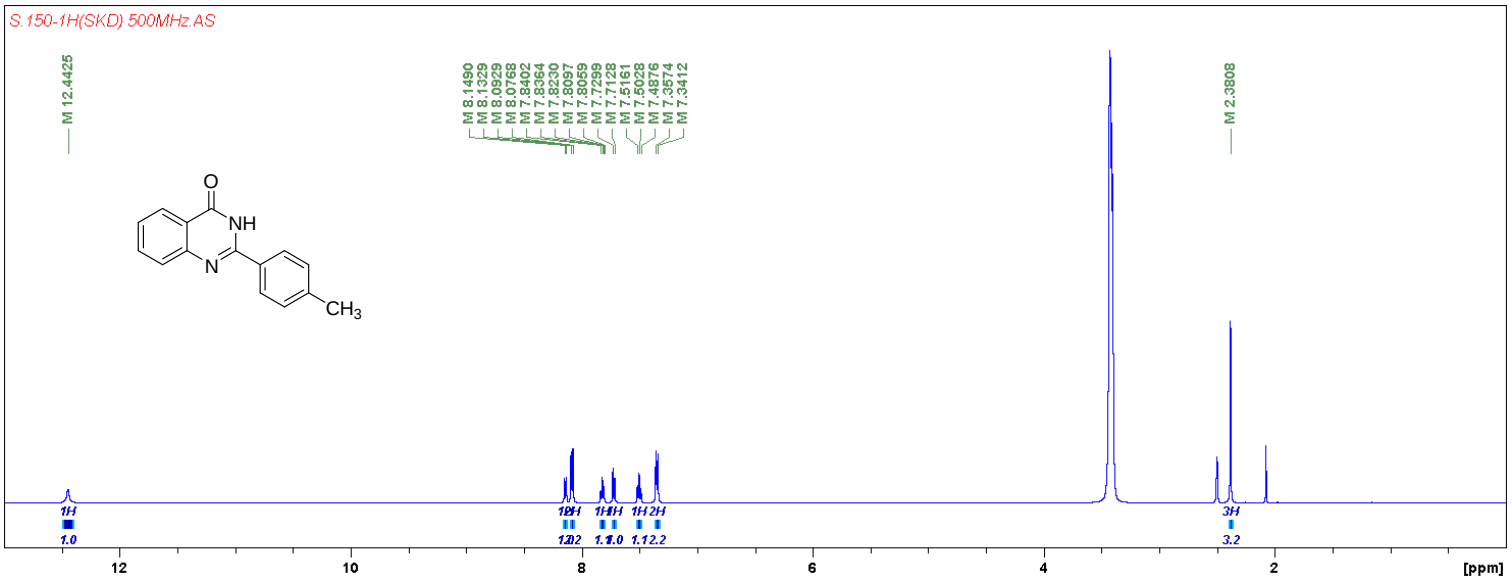


Figure 18. ^{1}H NMR spectrum of compound **5da** (500 MHz, DMSO-d_6).

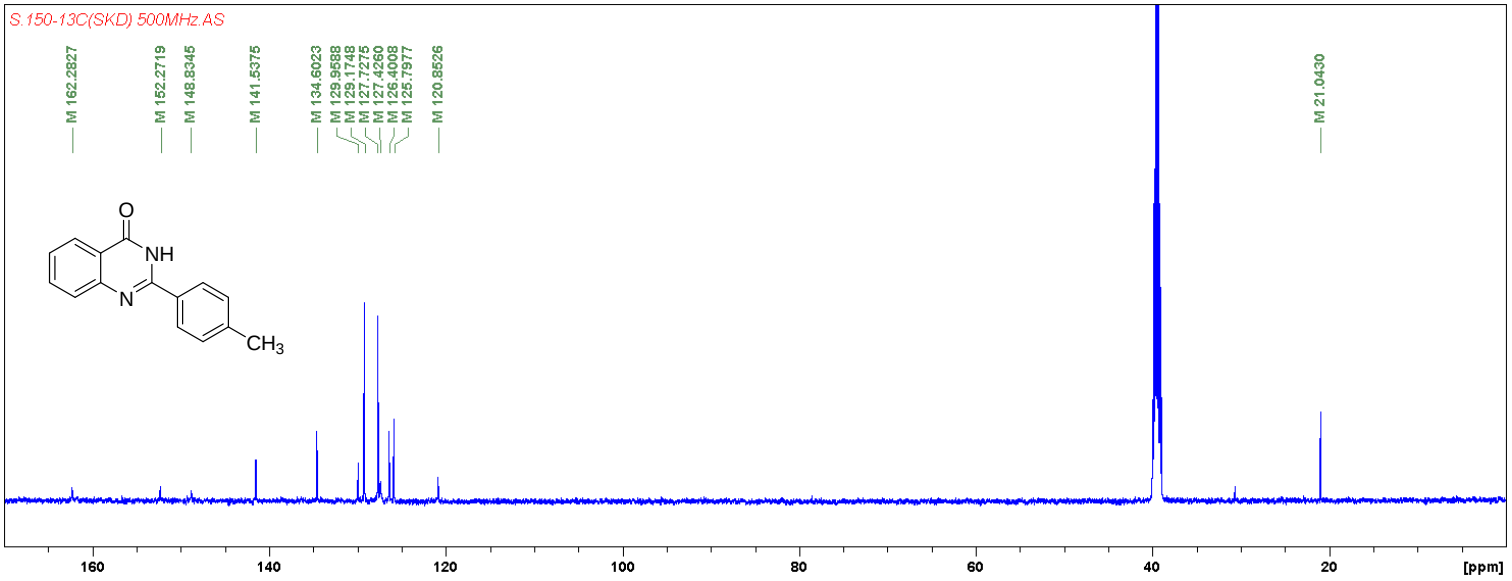


Figure S19. ^{13}C NMR spectrum of compound **5da** (125 MHz, DMSO-d_6).

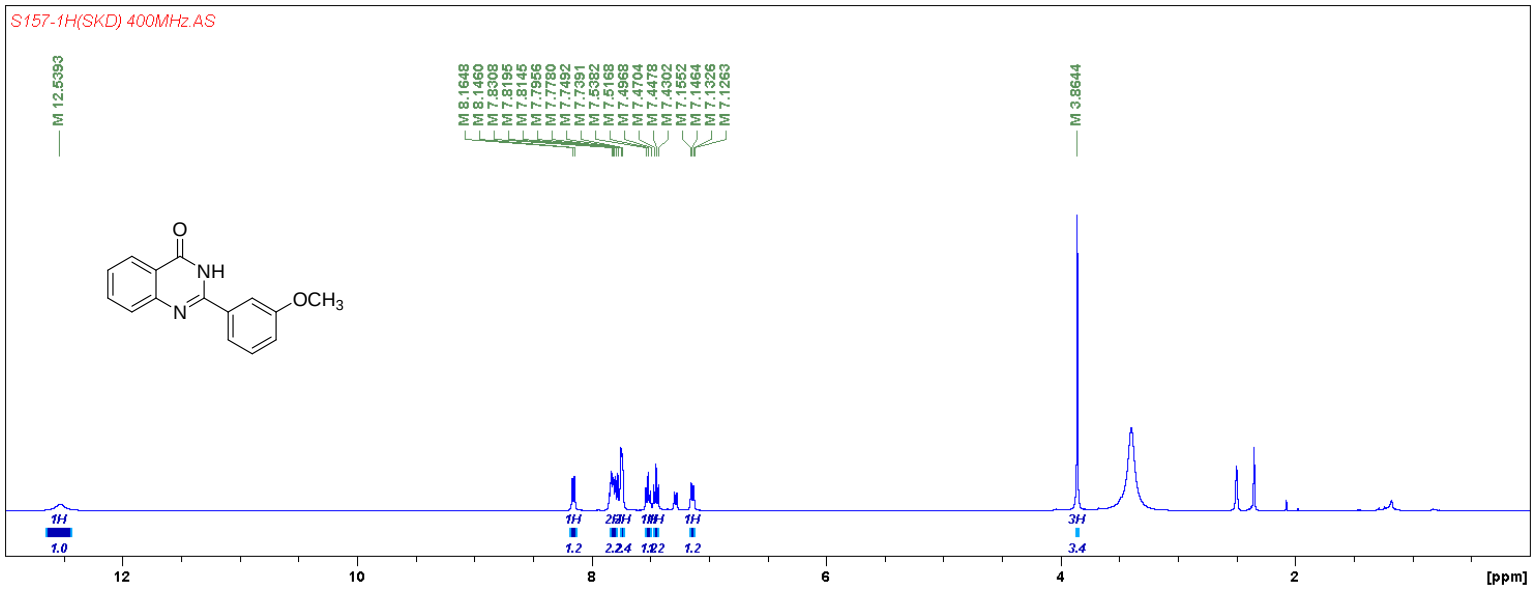


Figure S20. ^{1}H NMR spectrum of compound **5ea** (400 MHz, DMSO-d_6).

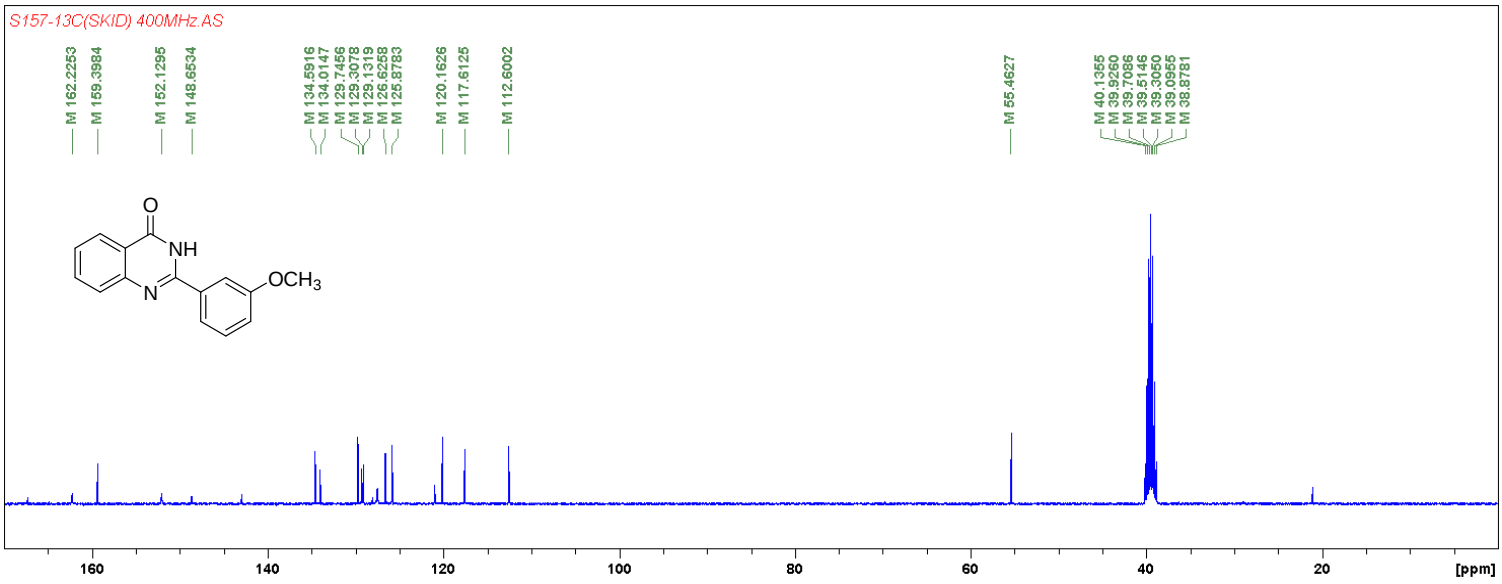


Figure S21. ^{13}C NMR spectrum of compound **5ea** (100 MHz, DMSO-d_6).

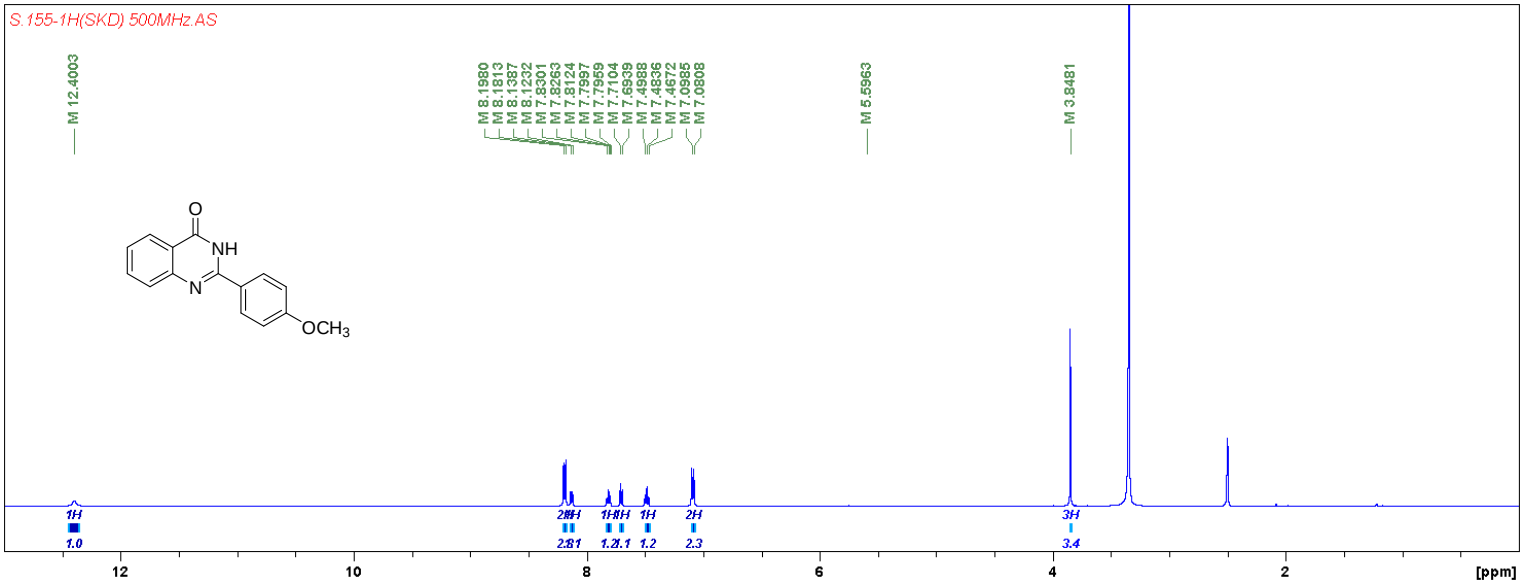


Figure S22. ^{1}H NMR spectrum of compound **5fa** (500 MHz, DMSO-d_6).

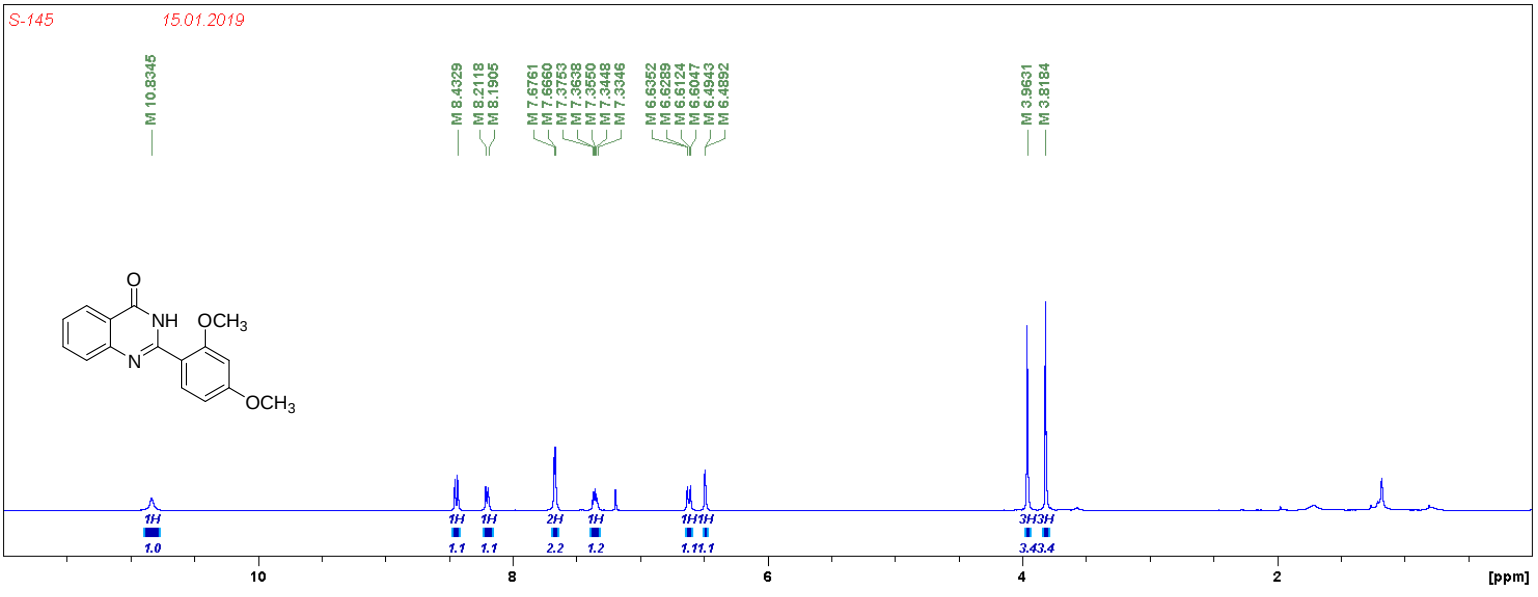


Figure S23. ^{1}H NMR spectrum of compound **5ga** (400 MHz, $CDCl_3$).

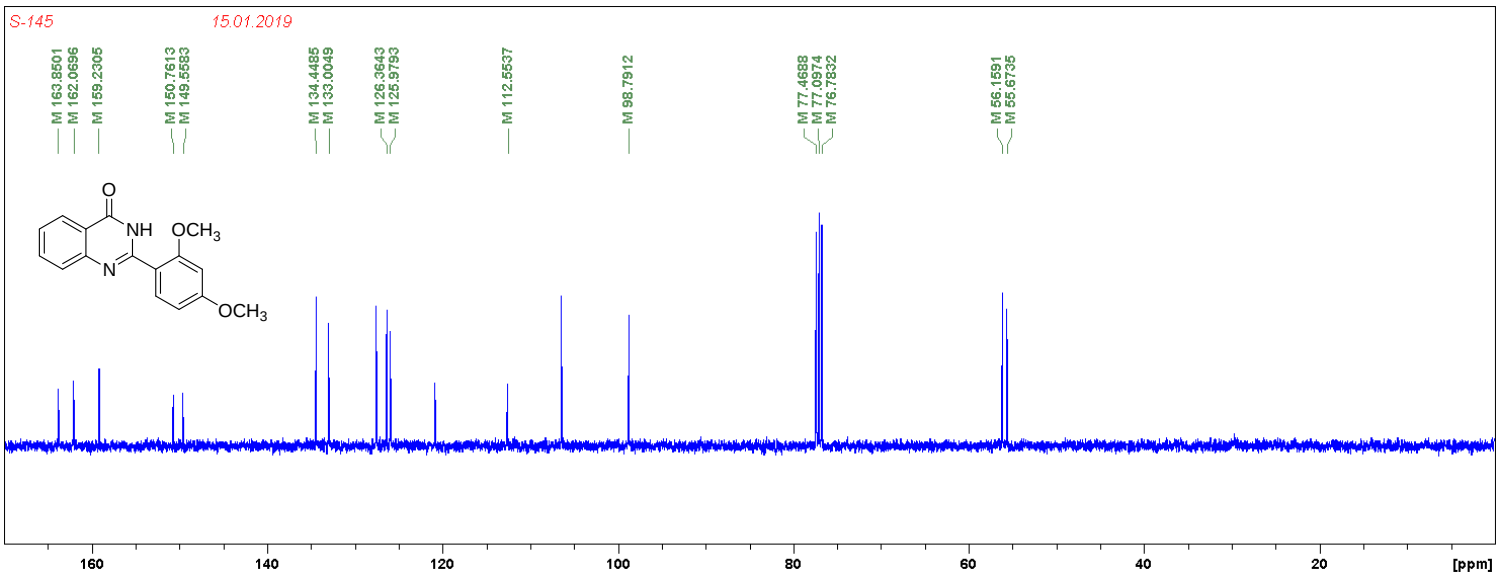


Figure S24. ^{13}C NMR spectrum of compound **5ga** (100 MHz, $CDCl_3$).

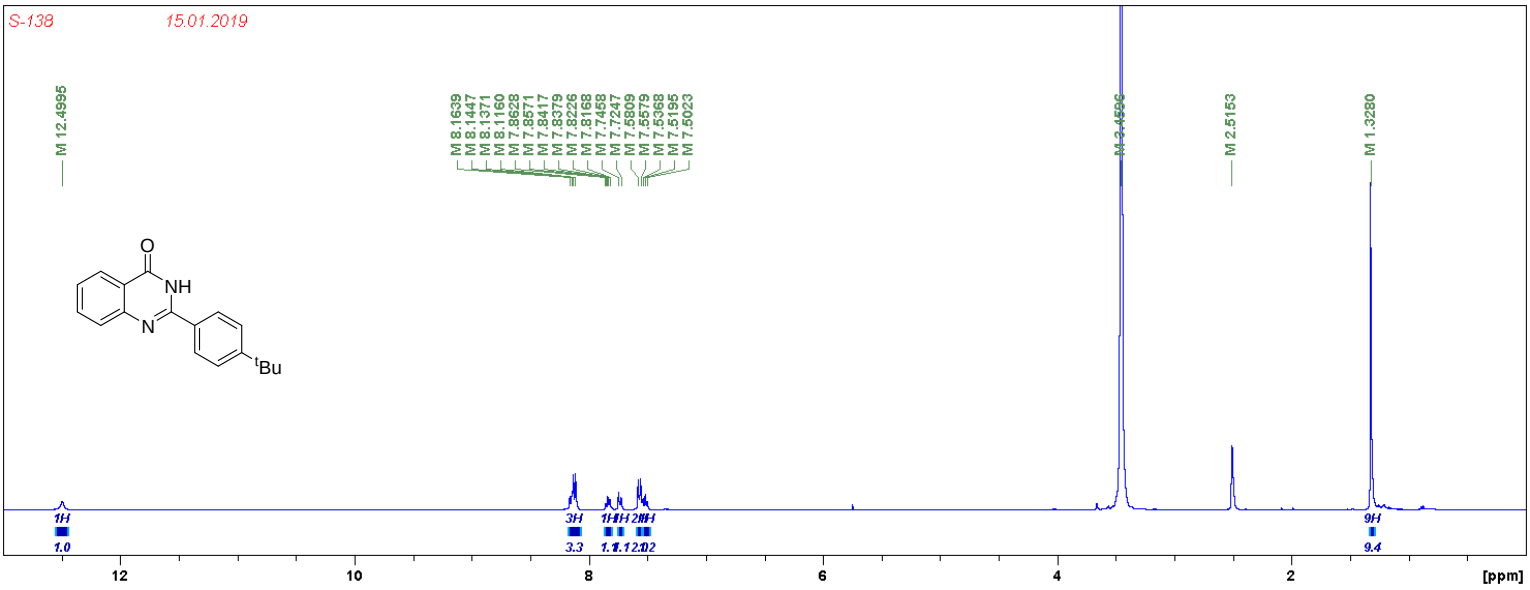


Figure S25. ^{1}H NMR spectrum of compound **5ha** (400 MHz, DMSO-d_6).

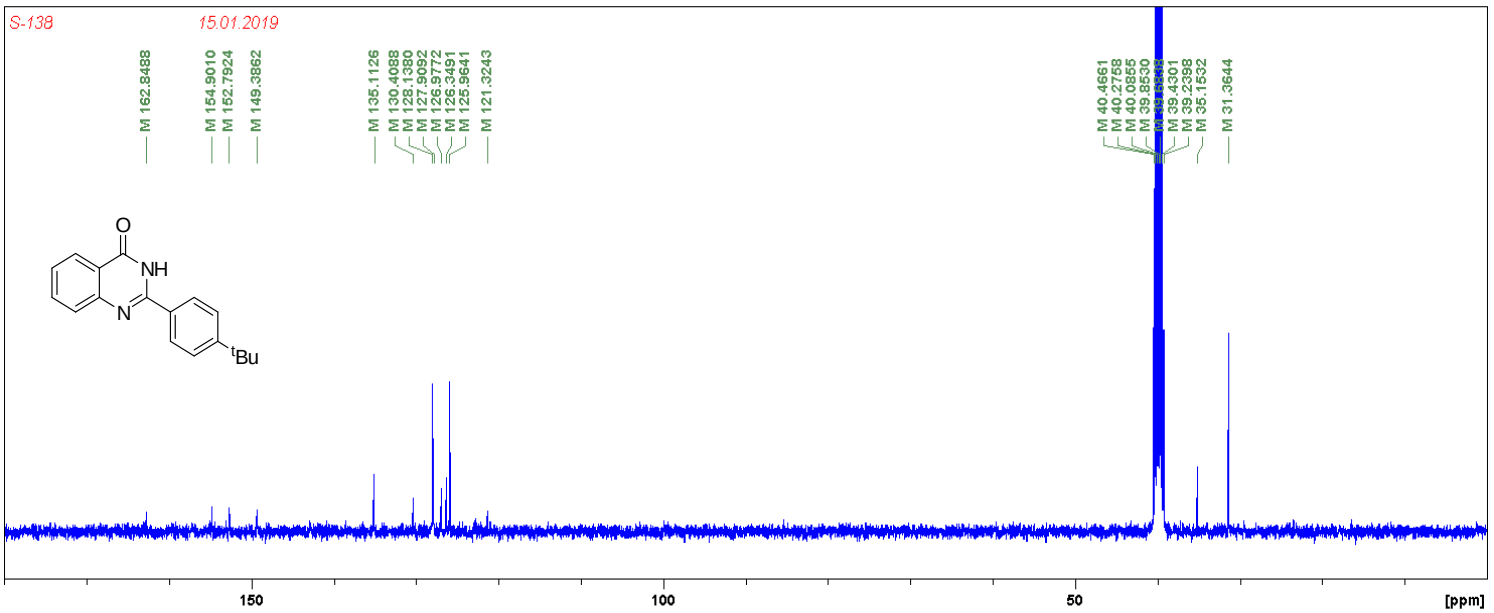


Figure S26. ^{13}C NMR spectrum of compound **5ha** (100 MHz, DMSO-d_6).

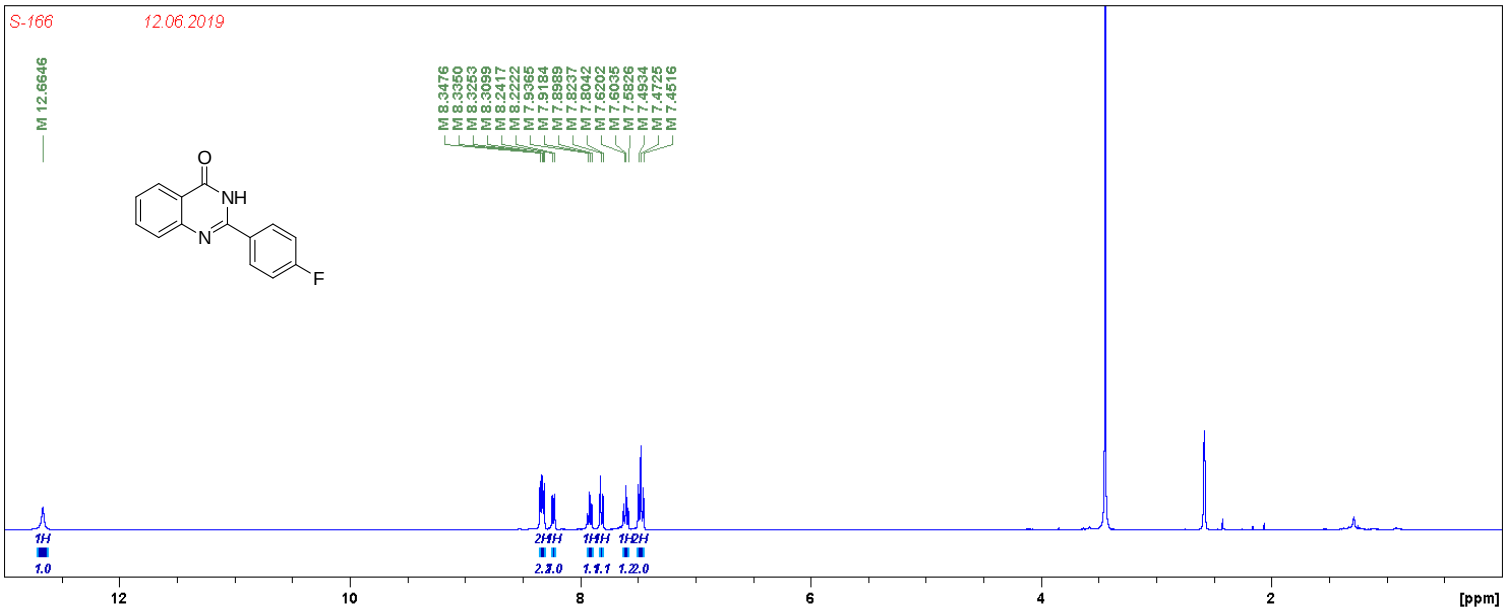


Figure S27. ^{1}H NMR spectrum of compound **5ia** (400 MHz, DMSO-d_6).

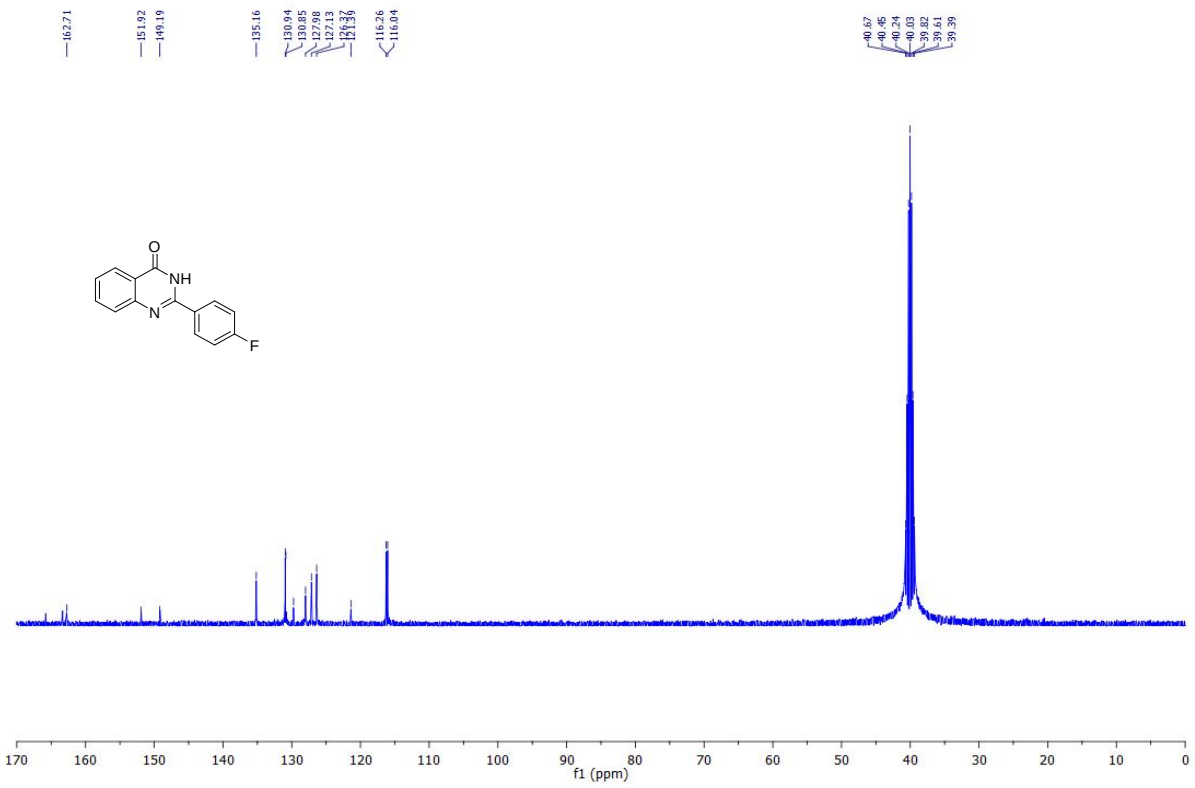


Figure S28. ^{13}C NMR spectrum of compound 5**ia** (100 MHz, DMSO-d_6).

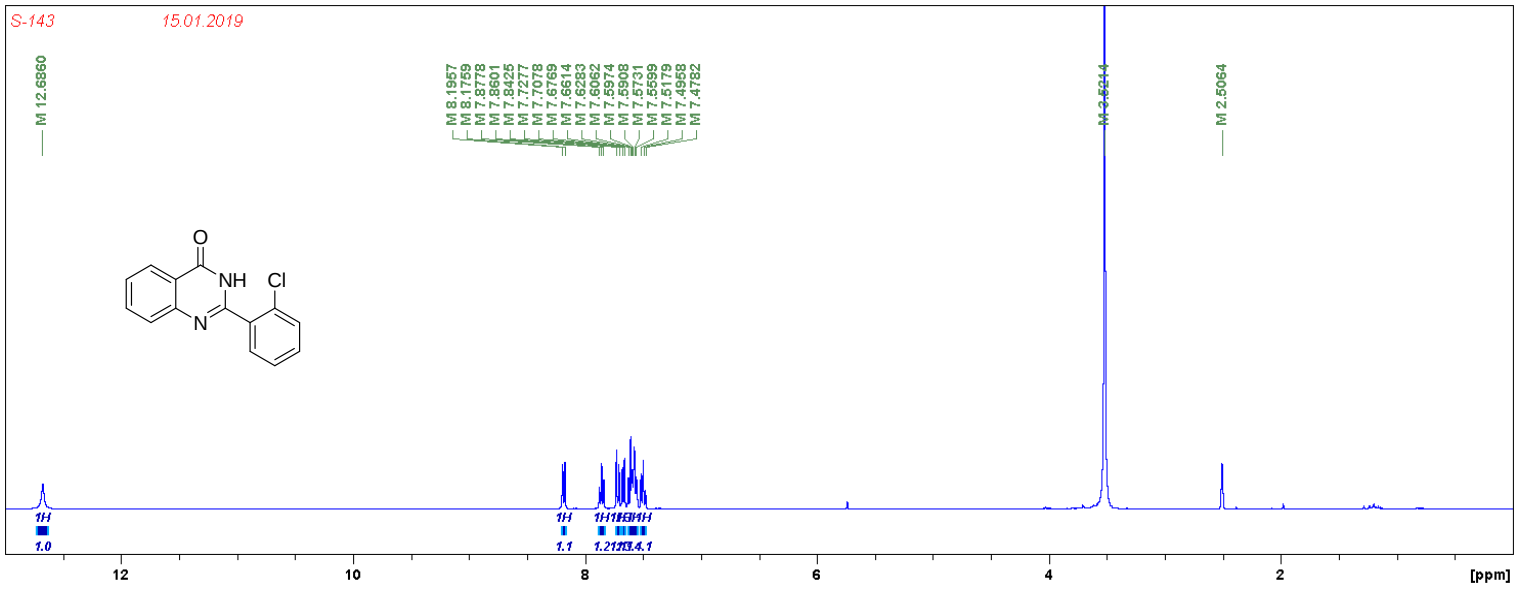


Figure S29. ^{1}H NMR spectrum of compound **5ja** (400 MHz, DMSO-d_6).

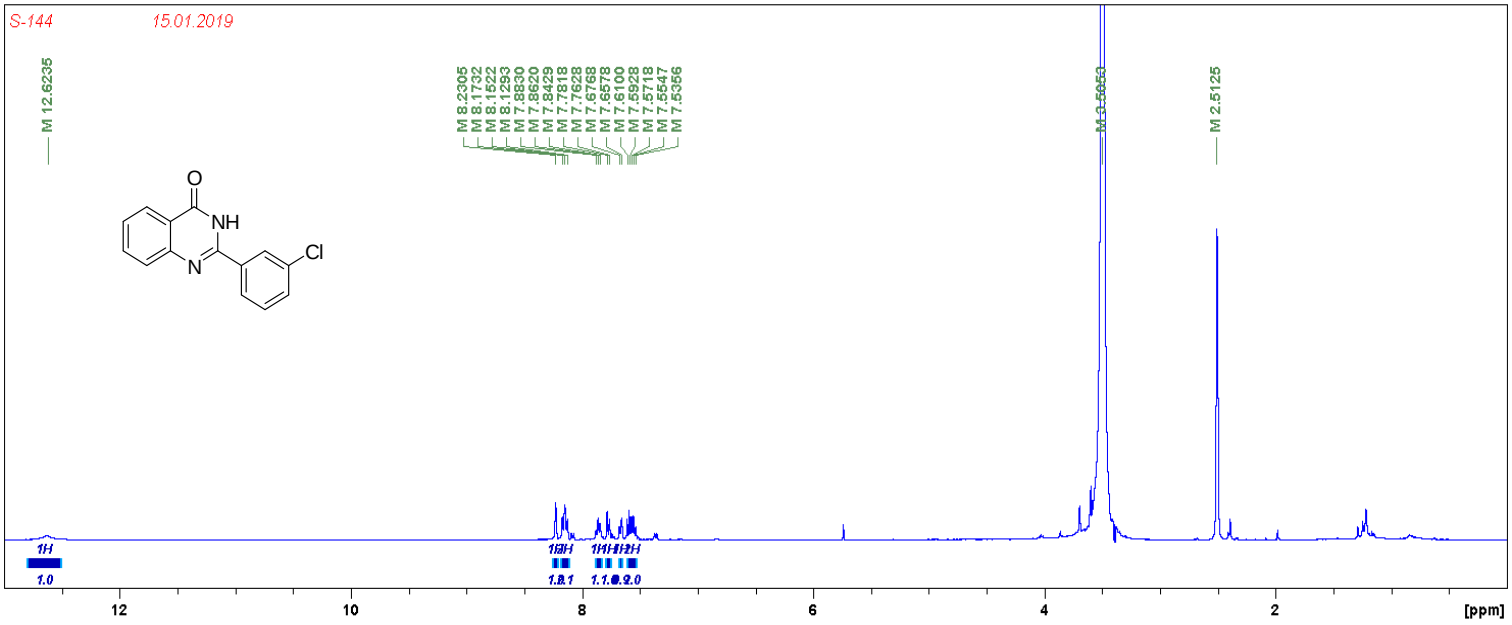


Figure S30. ^{1}H NMR spectrum of compound **5ka** (400 MHz, DMSO-d_6).

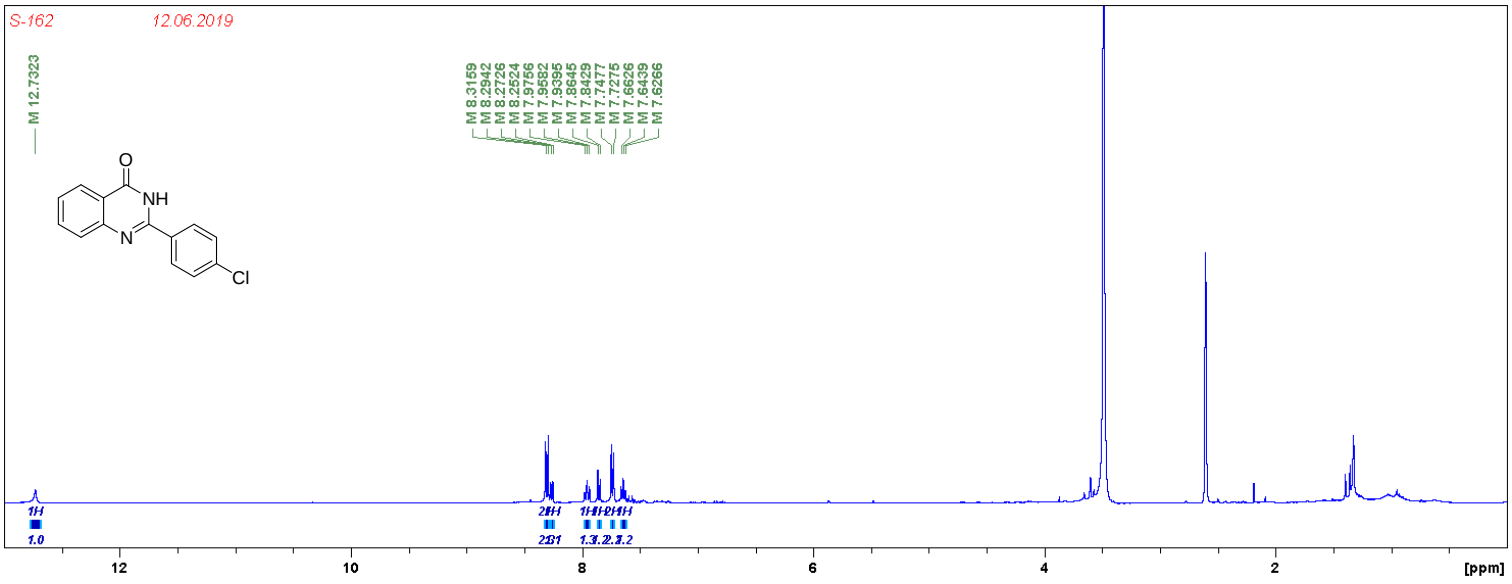


Figure S31. ^{1}H NMR spectrum of compound **5la** (400 MHz, DMSO-d_6).

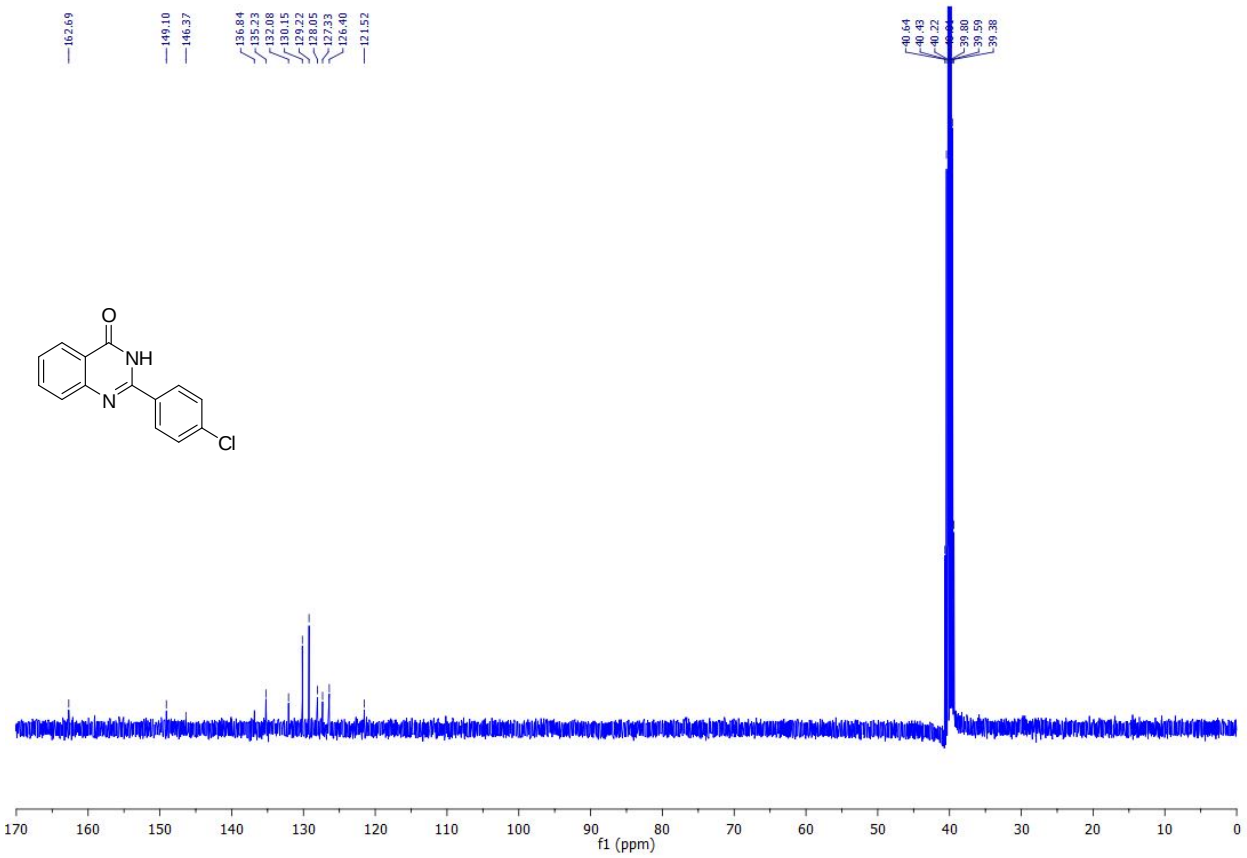


Figure S32. ^{13}C NMR spectrum of compound 5**la** (100 MHz, DMSO-d_6).

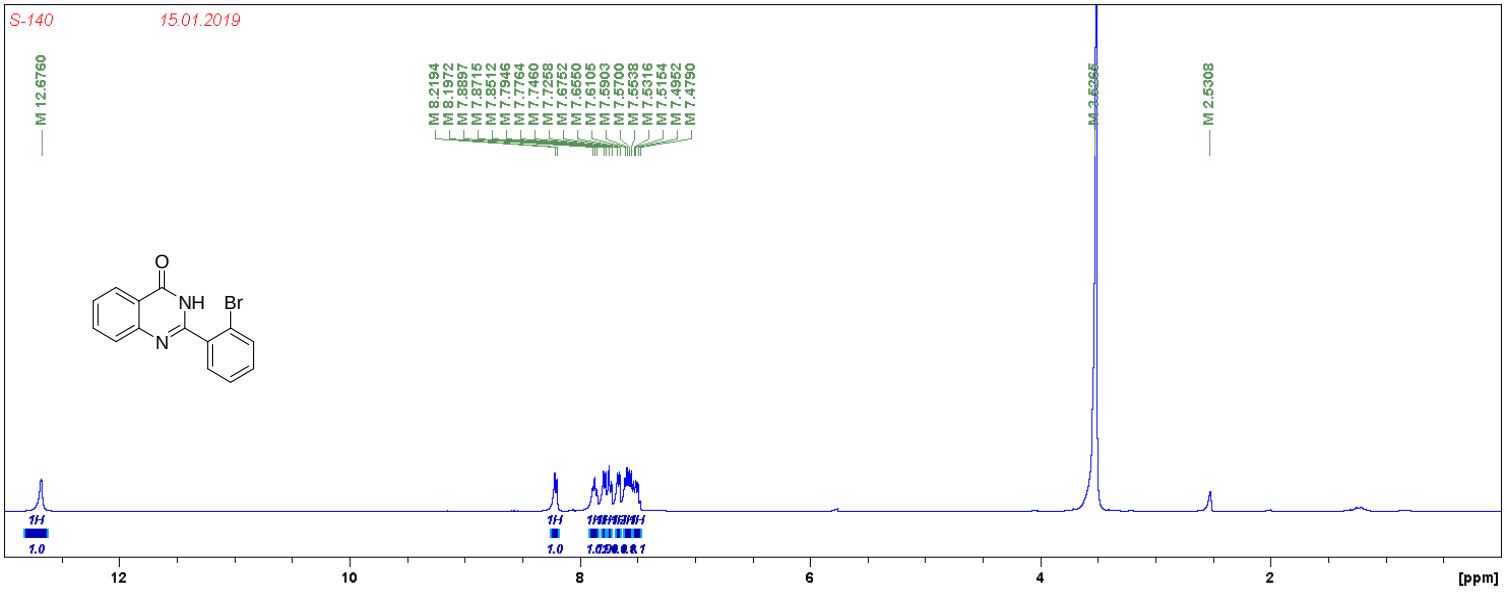


Figure S33. ^{1}H NMR spectrum of compound **5ma** (400 MHz, DMSO-d_6).

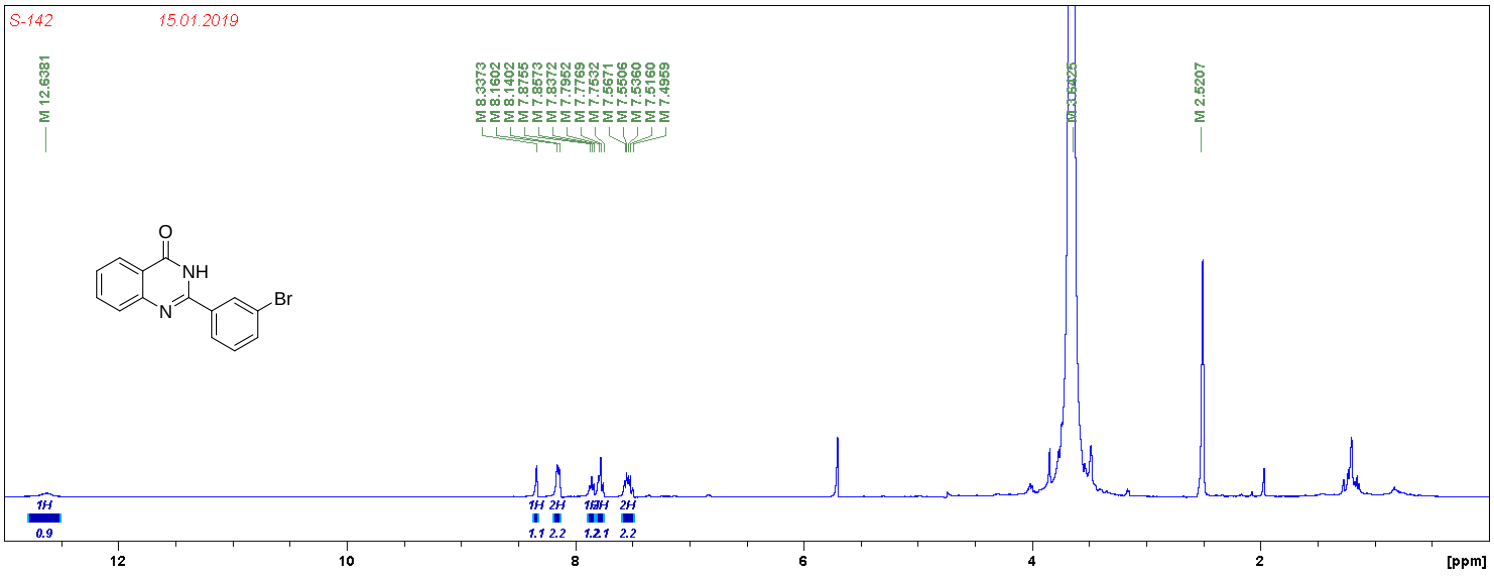


Figure S34. ^{1}H NMR spectrum of compound **5na** (400 MHz, DMSO-d_6).

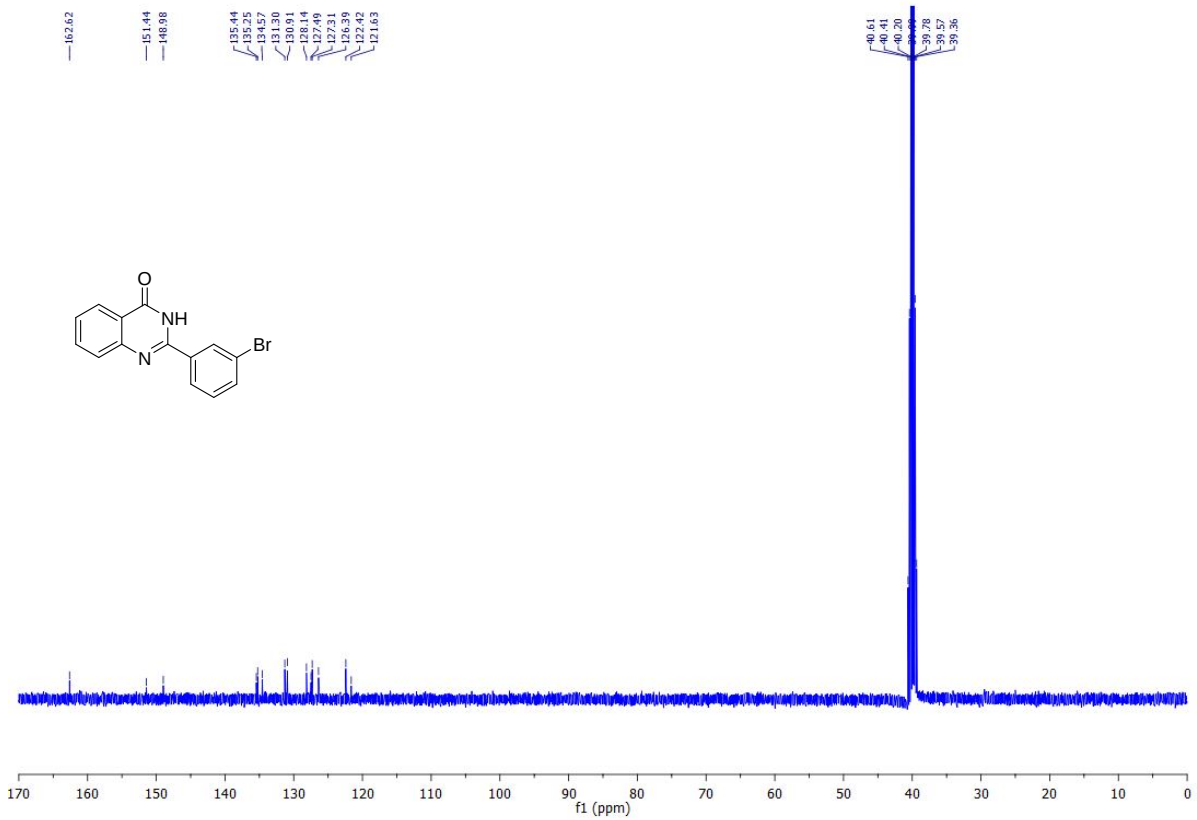


Figure S35. ^{13}C NMR spectrum of compound **5na** (100 MHz, DMSO-d_6).

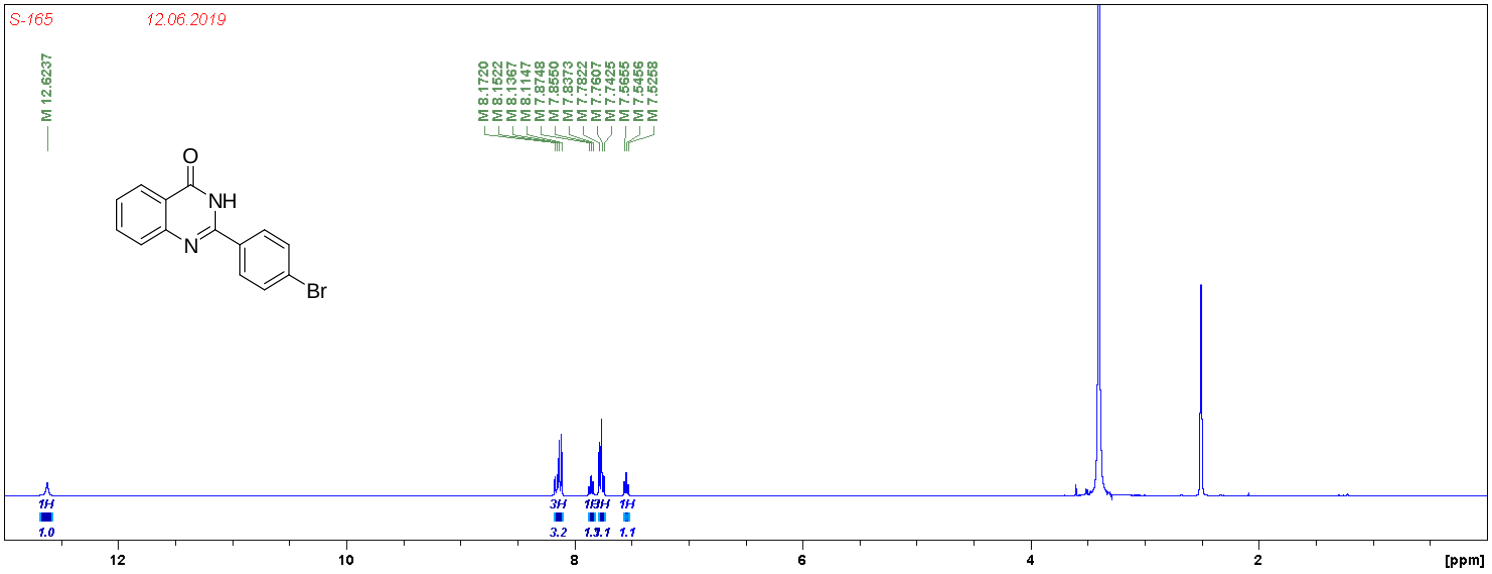


Figure S36. ^{1}H NMR spectrum of compound **5oa** (400 MHz, DMSO-d_6).

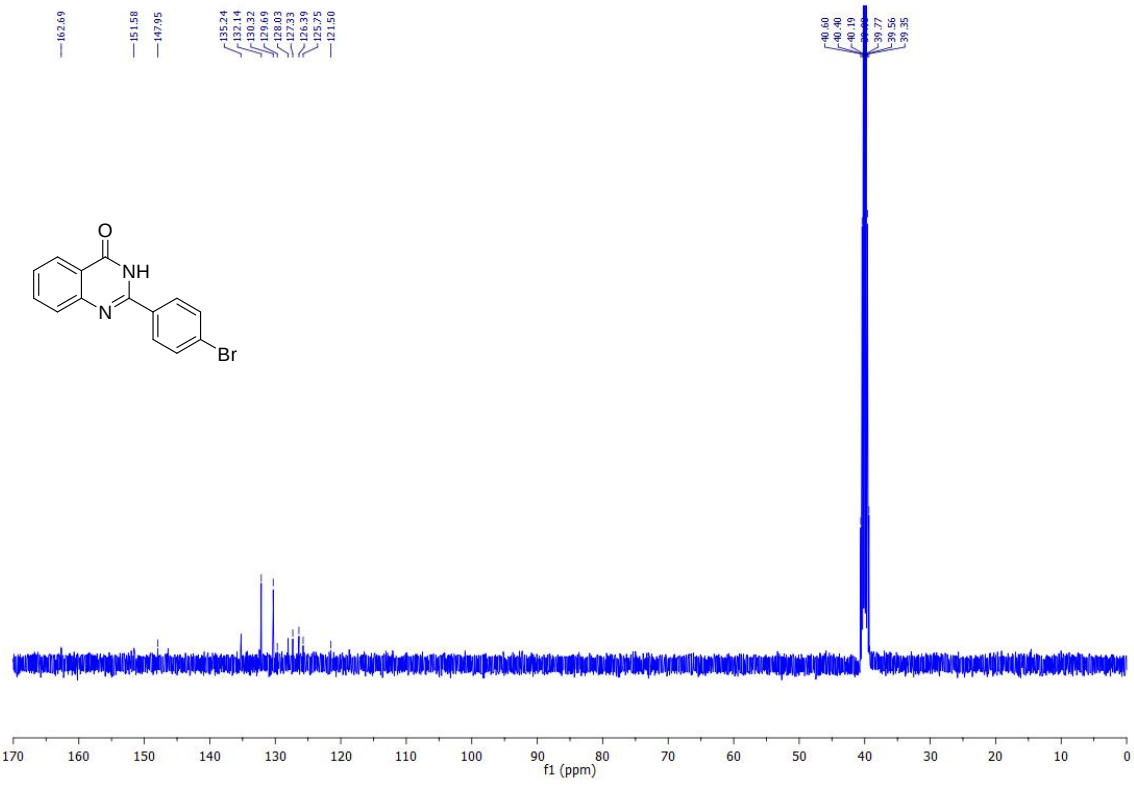


Figure S37. ^{13}C NMR spectrum of compound **5oa** (100 MHz, DMSO-d_6).

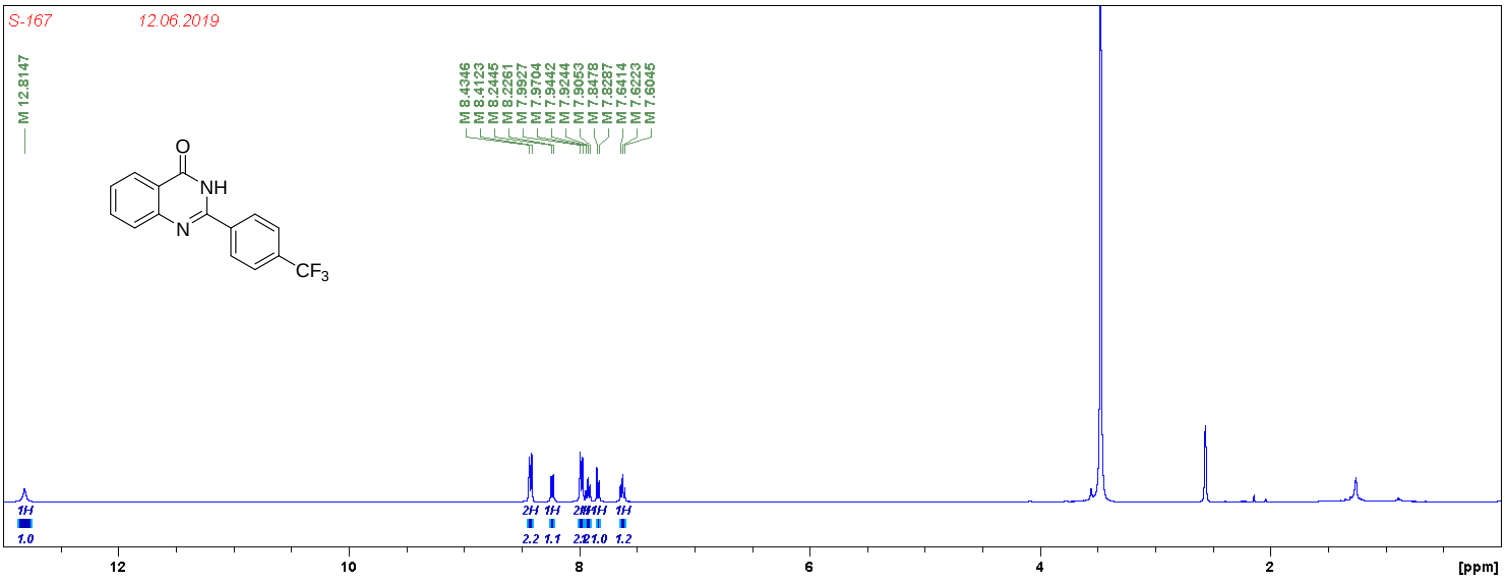


Figure S38. ^{1}H NMR spectrum of compound **5pa** (400 MHz, DMSO-d_6).

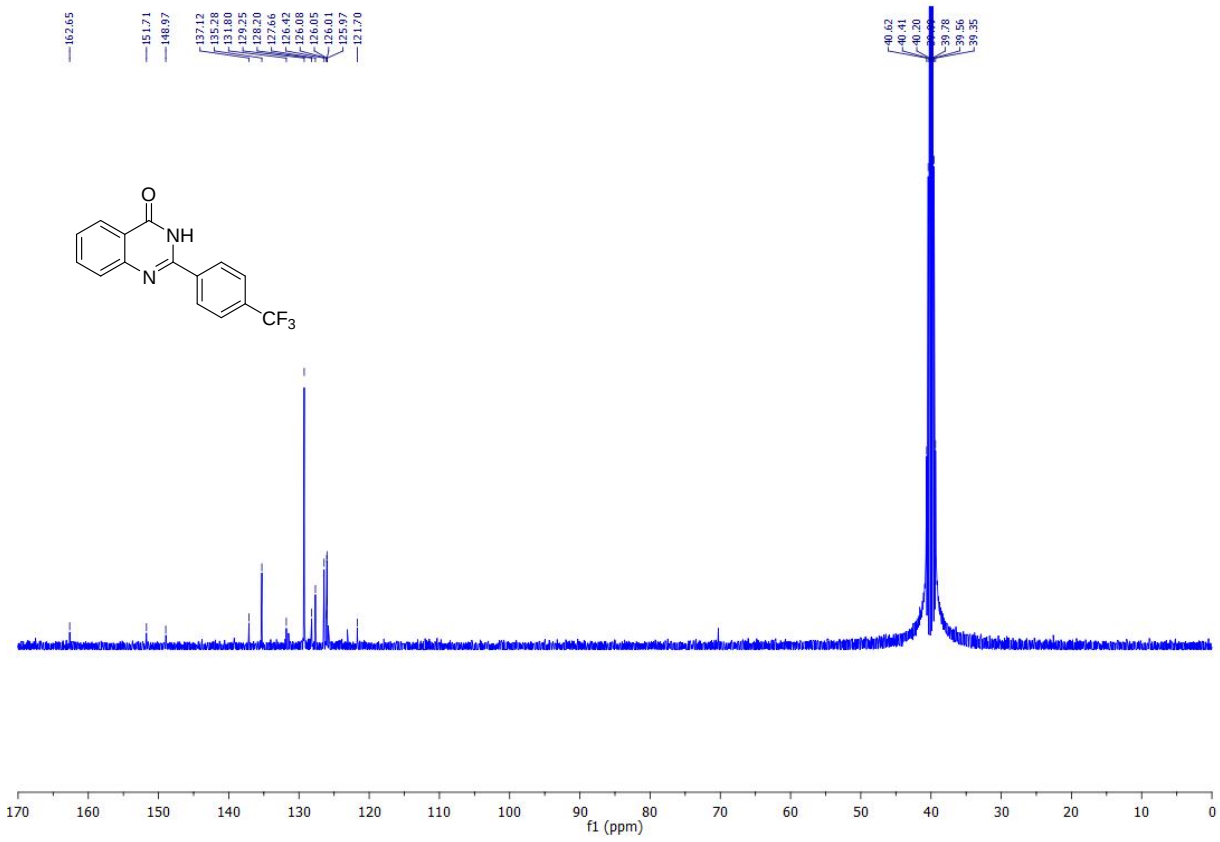


Figure S39. ^{13}C NMR spectrum of compound **5pa** (100 MHz, DMSO-d_6).

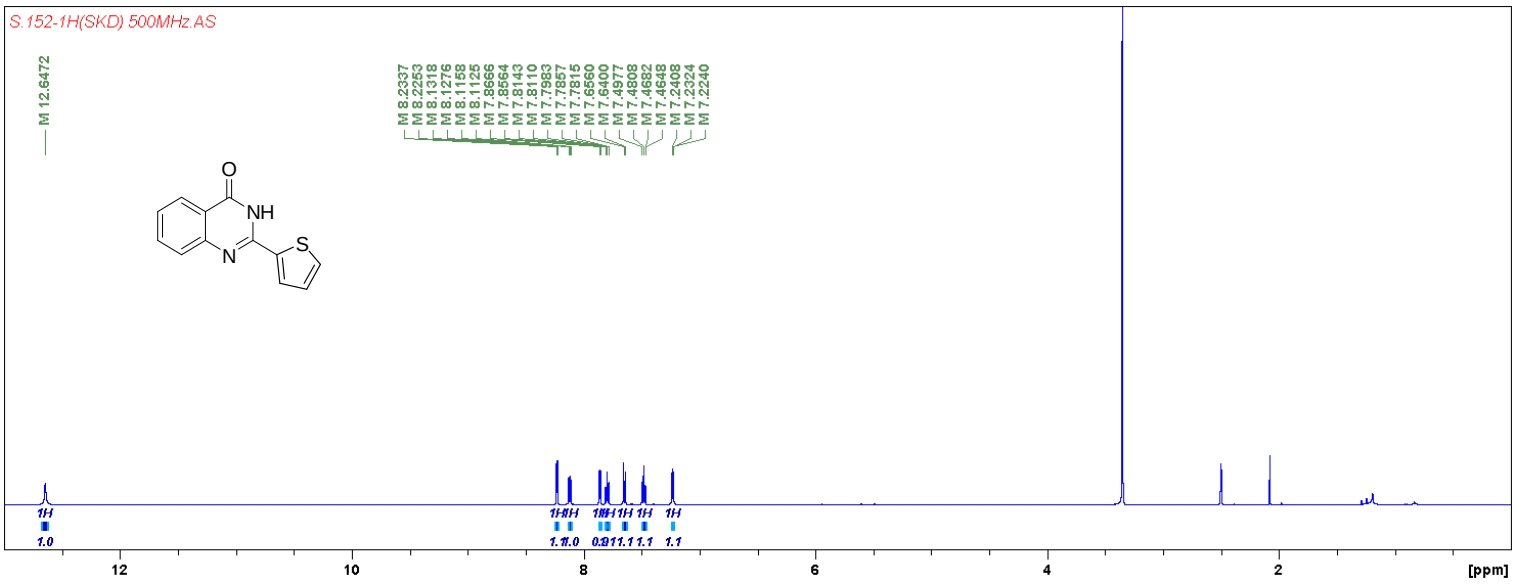


Figure S40. ^{1}H NMR spectrum of compound **5qa** (500 MHz, DMSO-d_6).

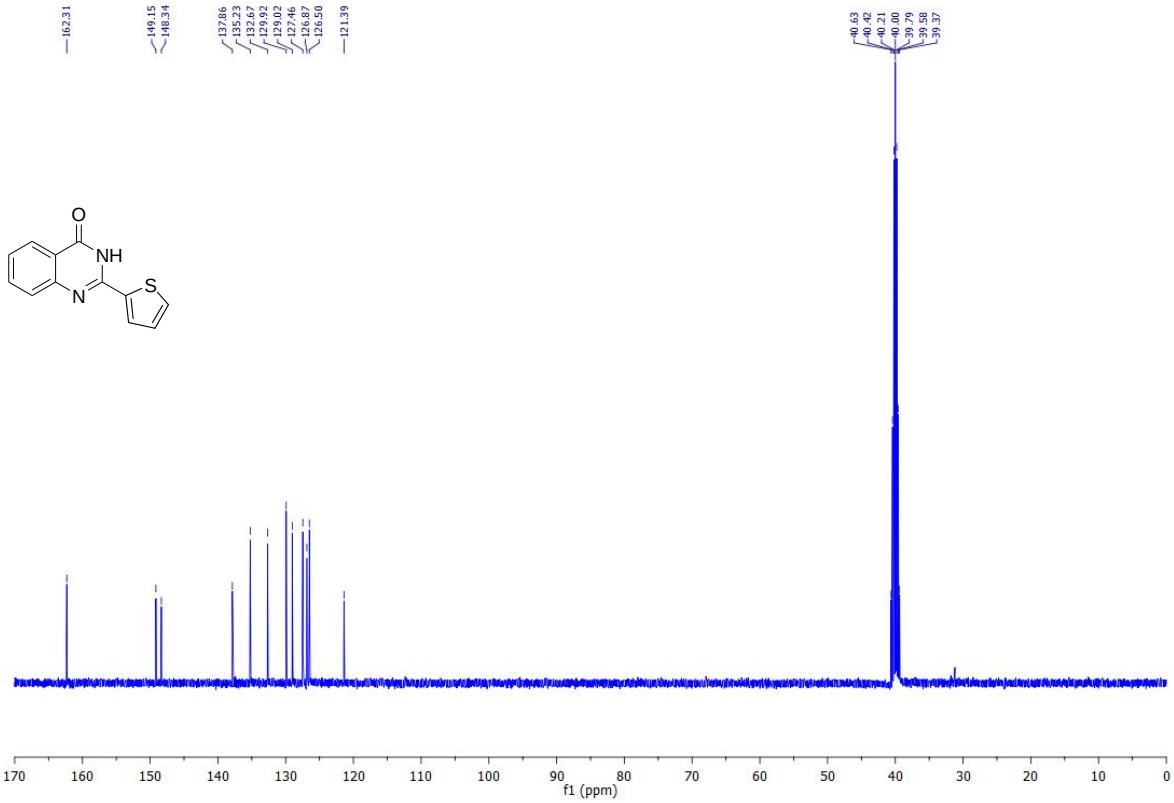


Figure S41. ^{13}C NMR spectrum of compound **5qa** (100 MHz, DMSO-d_6).

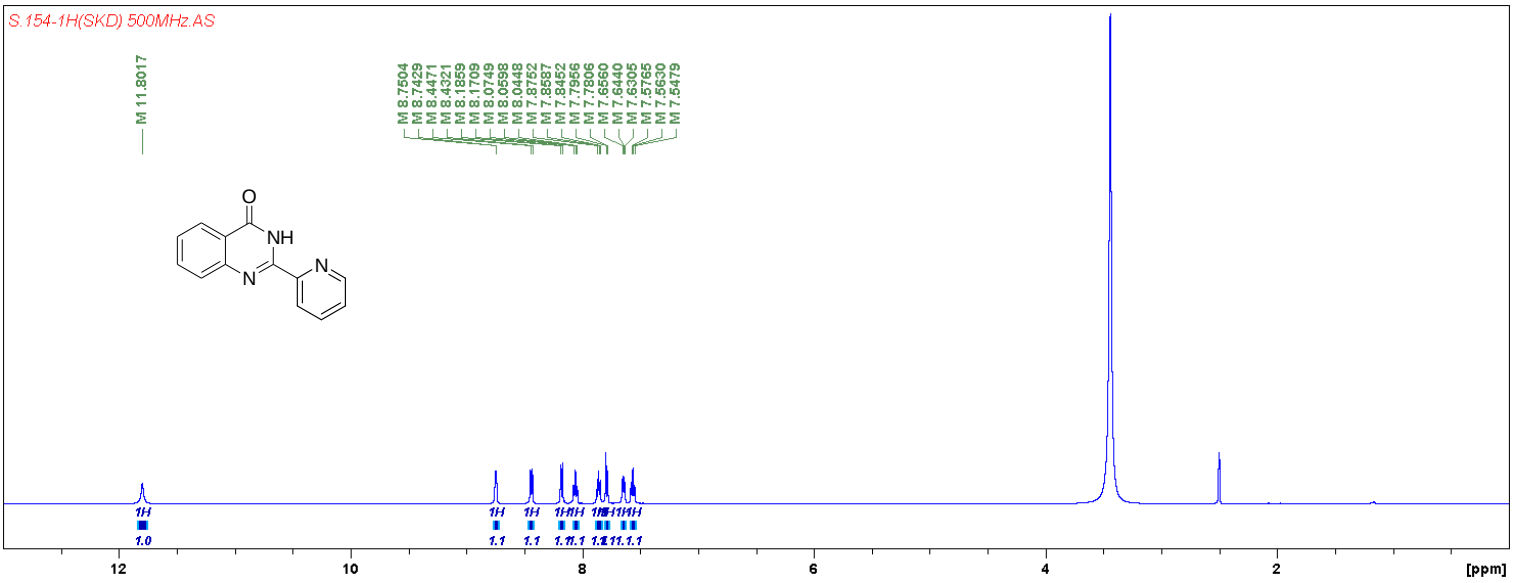


Figure S42. ^{1}H NMR spectrum of compound **5ra** (500 MHz, DMSO-d_6).

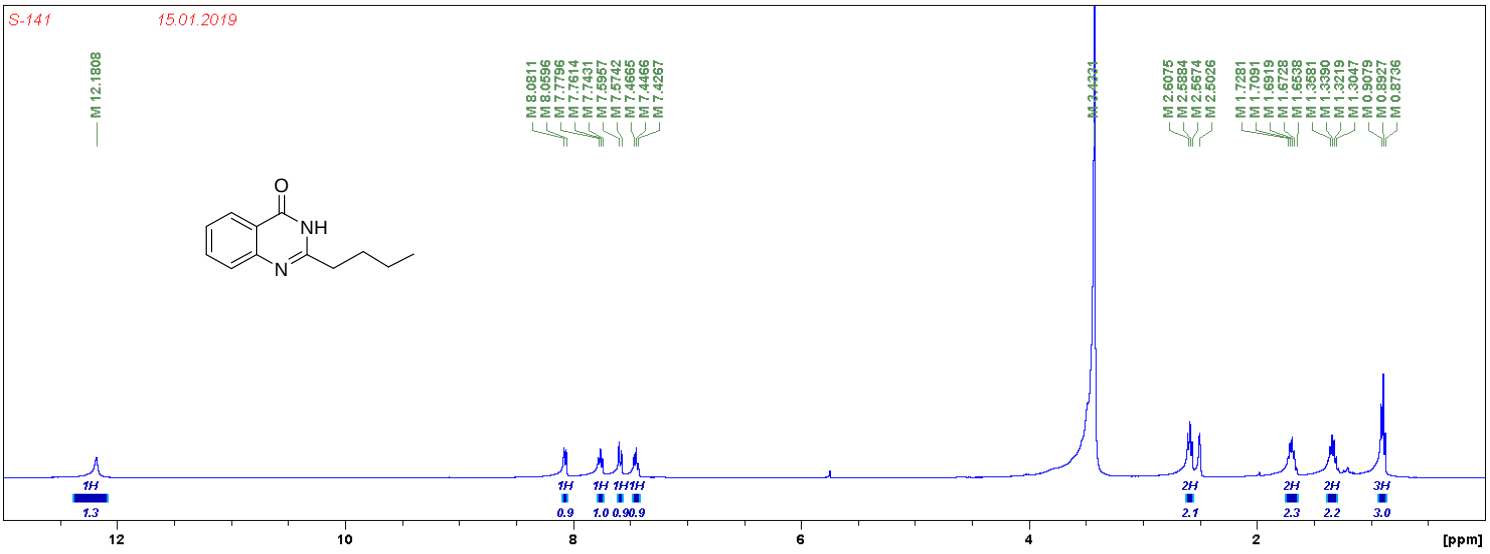


Figure S43. ^{1}H NMR spectrum of compound **5sa** (400 MHz, DMSO-d_6).

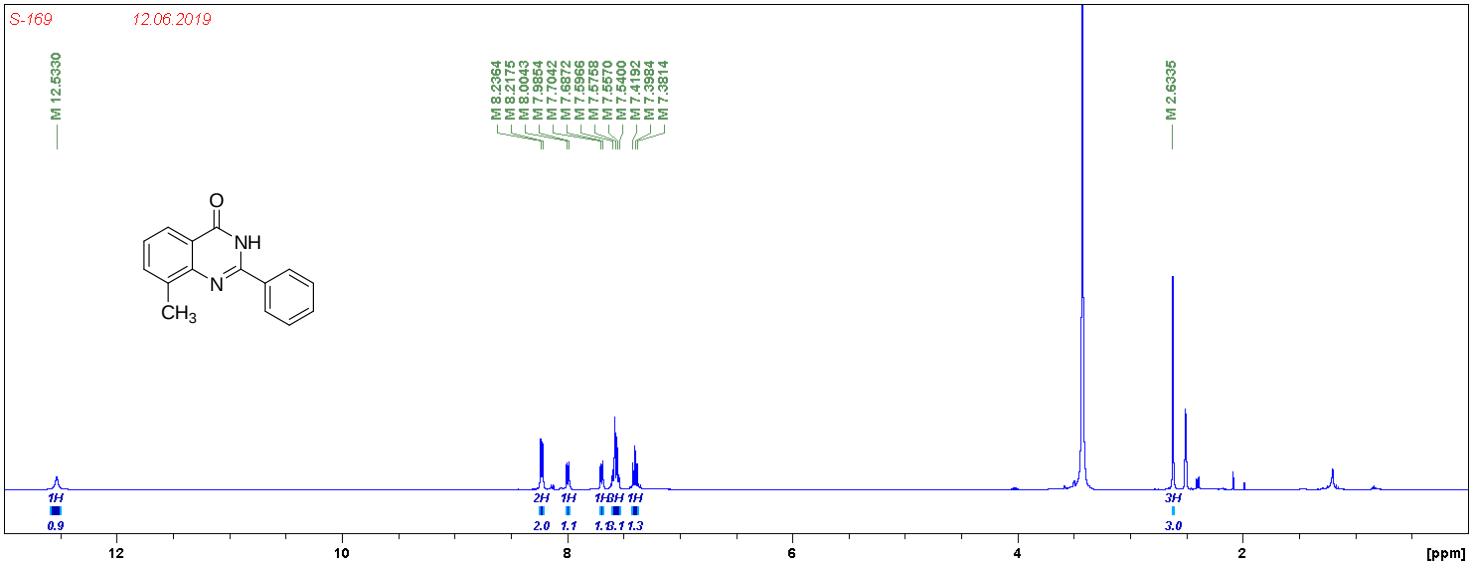


Figure S44. ^{1}H NMR spectrum of compound **5ab** (400 MHz, DMSO-d_6).

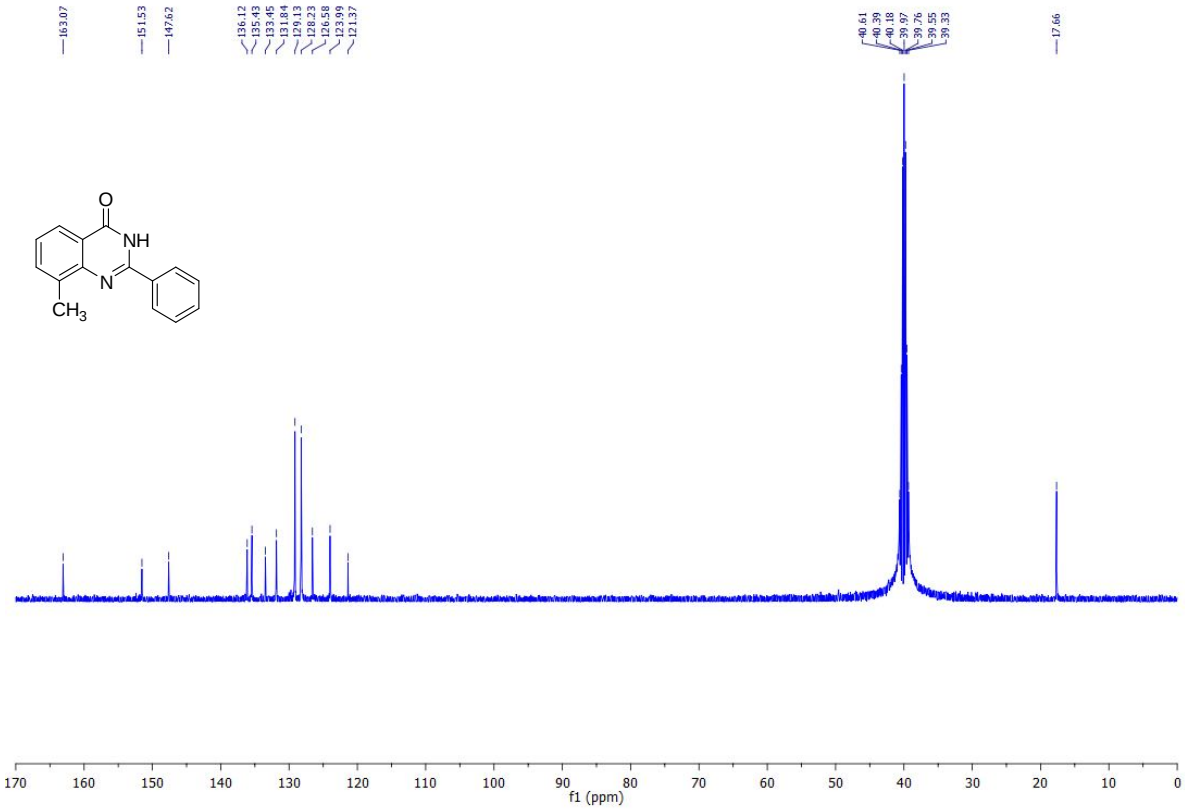


Figure S45. ^{13}C NMR spectrum of compound **5ab** (100 MHz, DMSO-d_6).

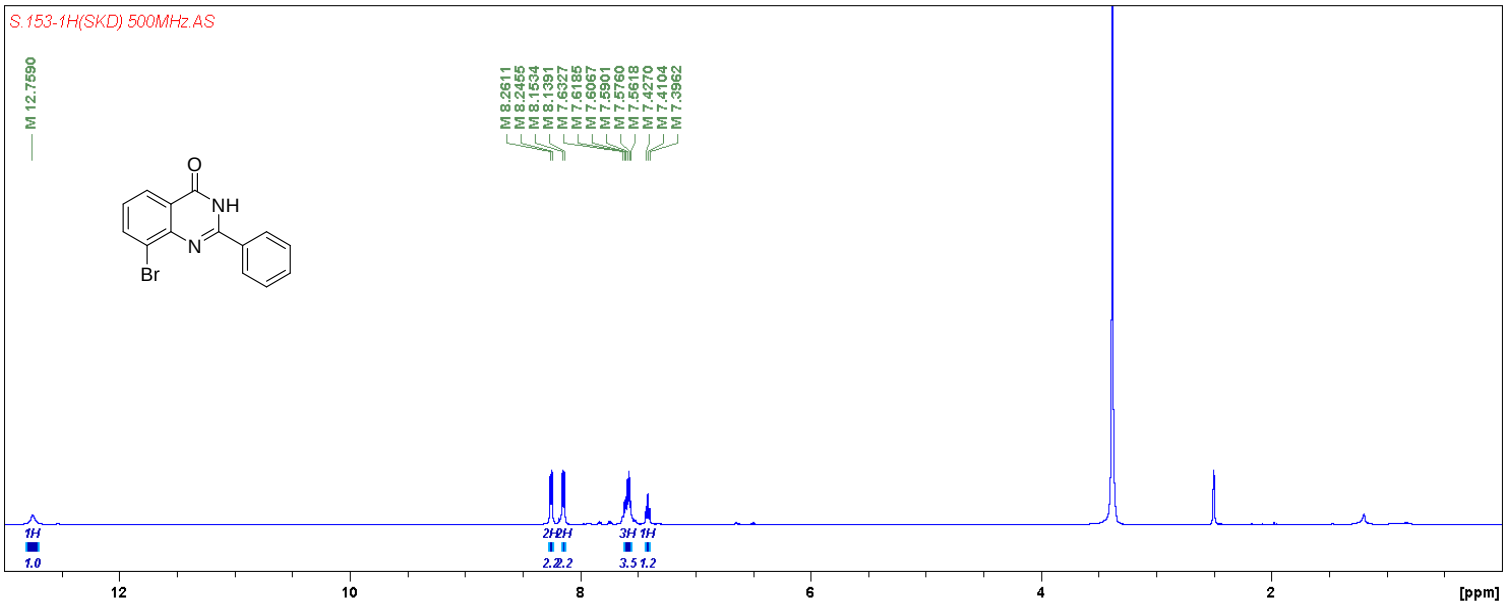


Figure S46. ^{1}H NMR spectrum of compound **5ac** (500 MHz, DMSO-d_6).

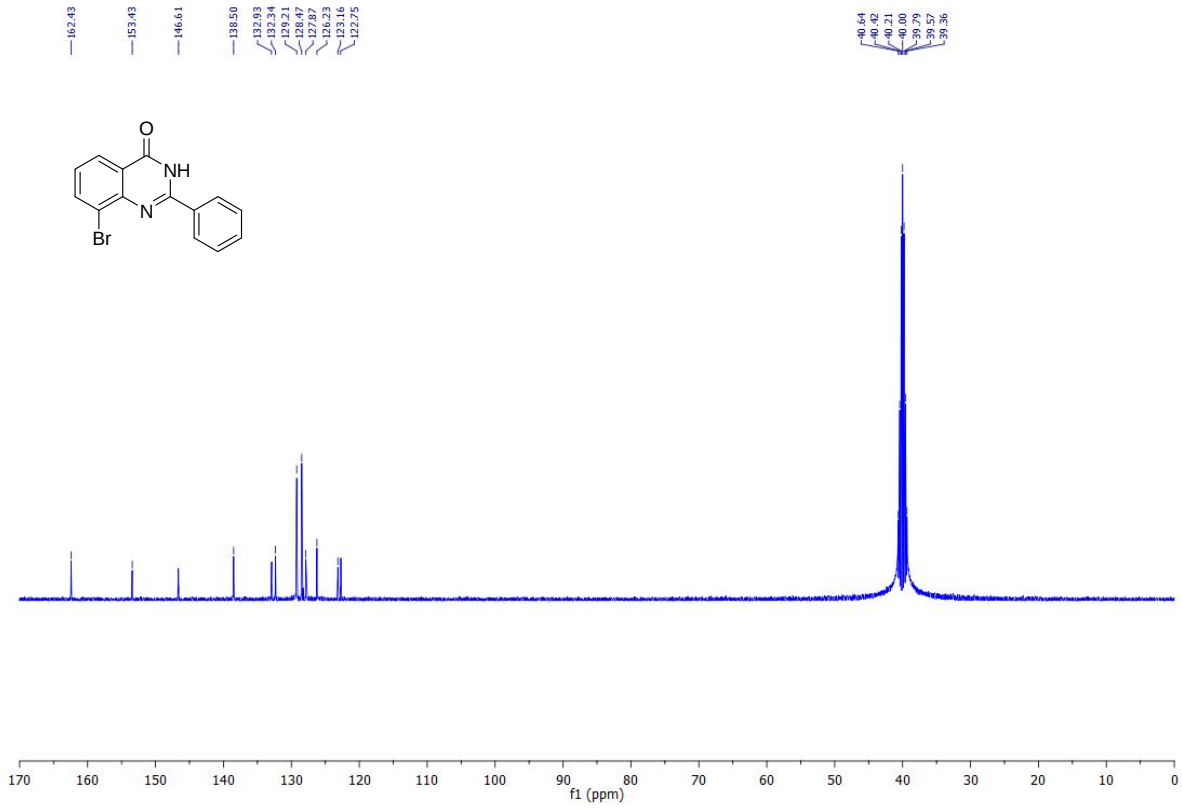


Figure S47. ^{13}C NMR spectrum of compound **5ac** (100 MHz, DMSO-d_6).

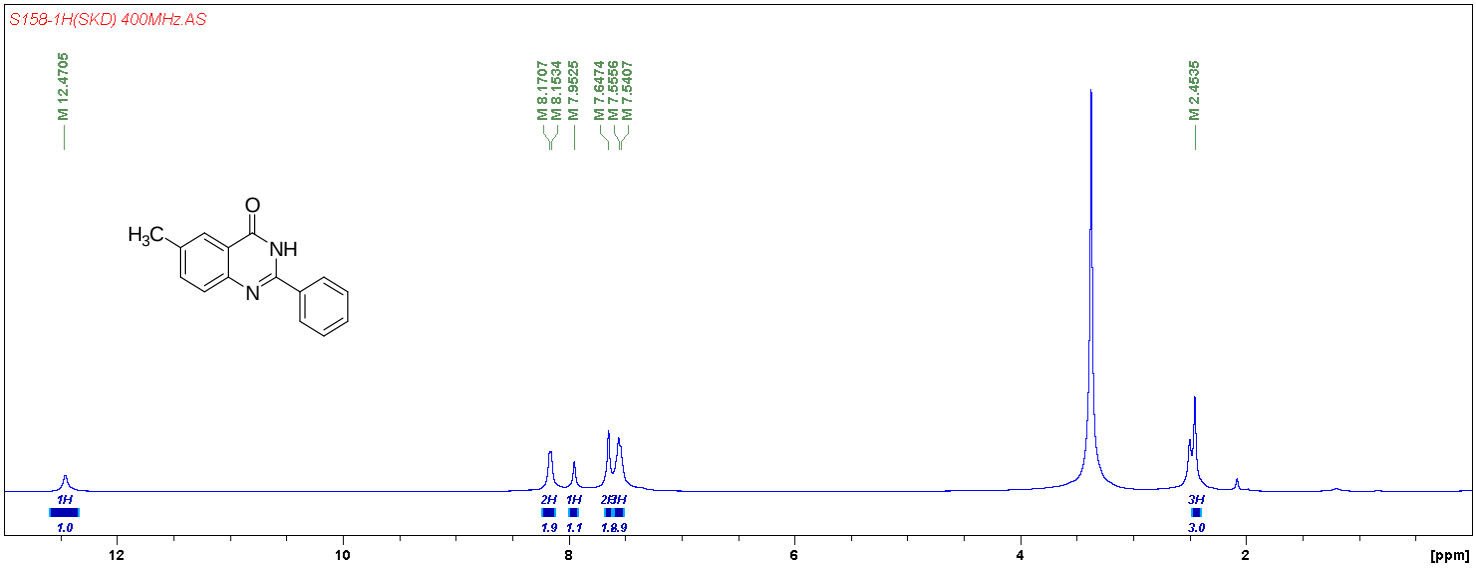


Figure S48. ^{1}H NMR spectrum of compound **5ad** (400 MHz, DMSO-d_6).

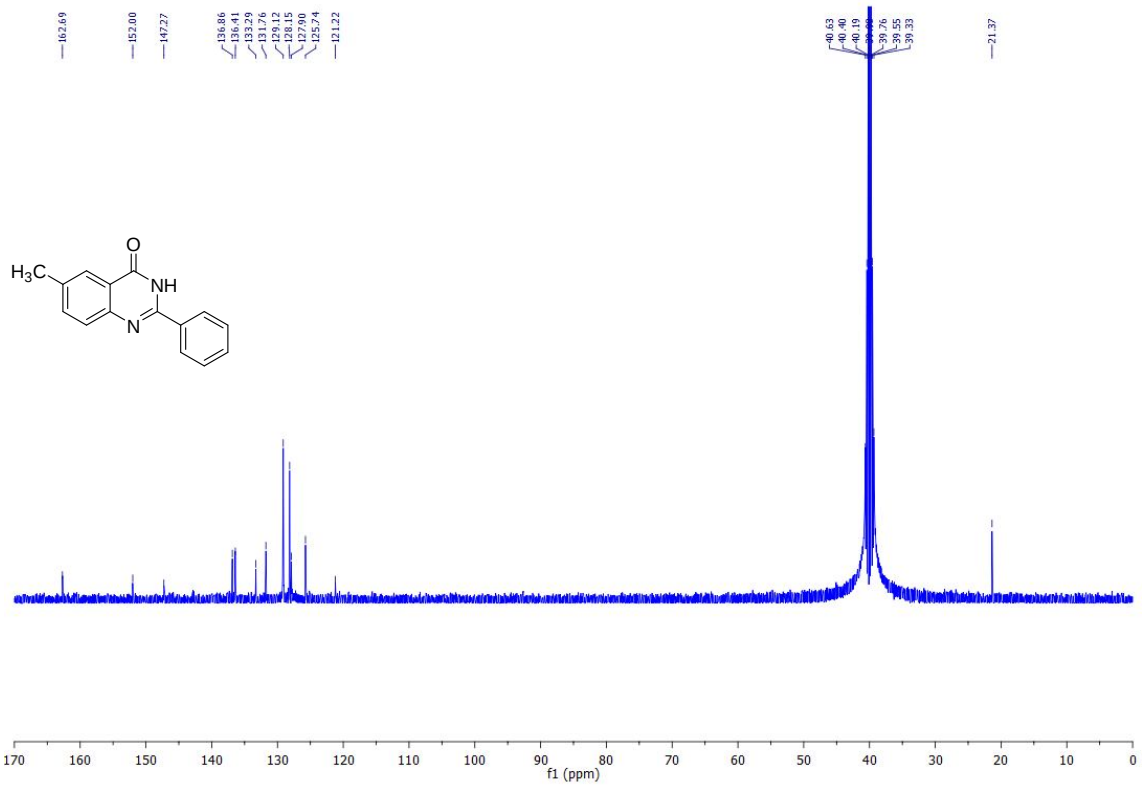


Figure S49. ^{13}C NMR spectrum of compound **5ad** (100 MHz, DMSO-d_6).

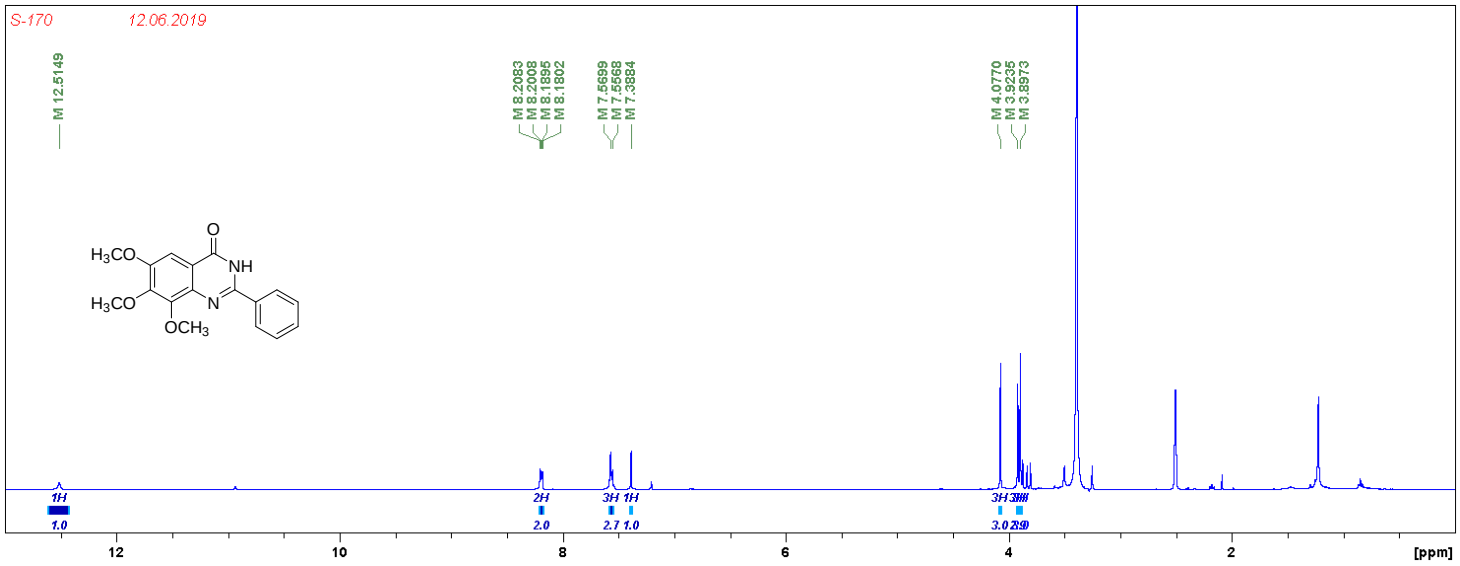


Figure S50. ^{1}H NMR spectrum of compound **5ae** (400 MHz, DMSO-d_6).

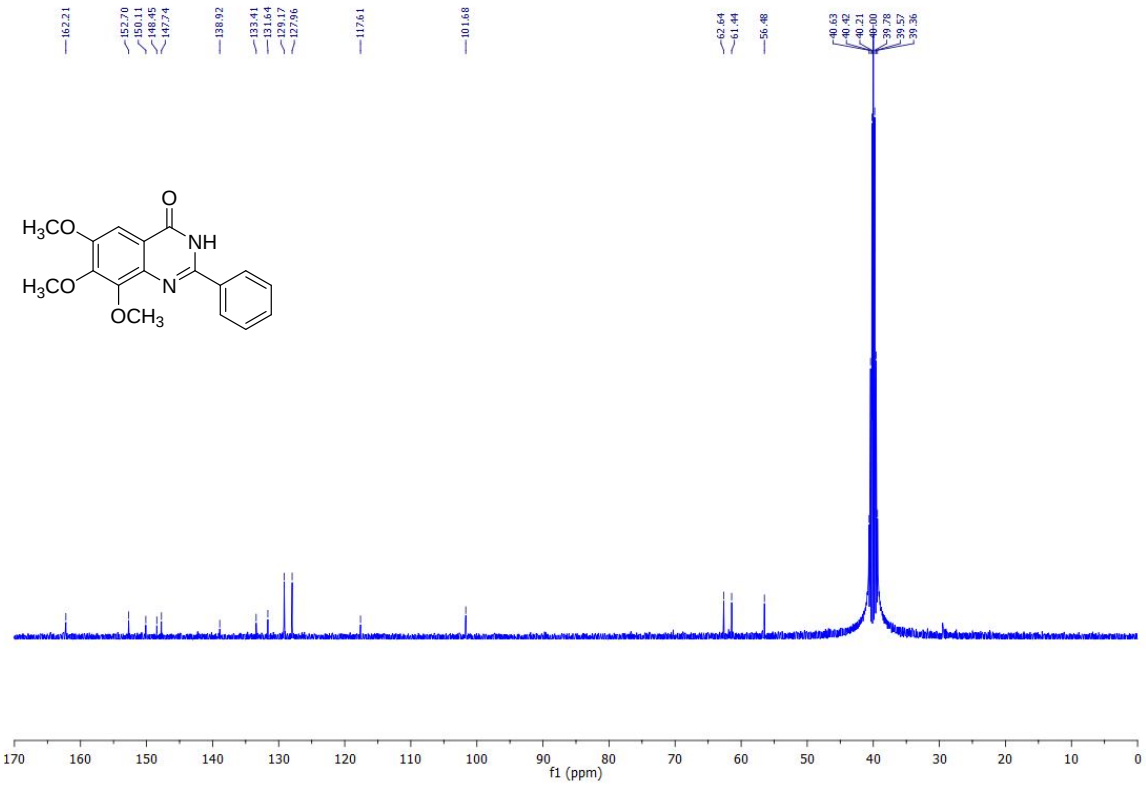


Figure S51. ^{13}C NMR spectrum of compound **5ae** (100 MHz, DMSO-d_6).

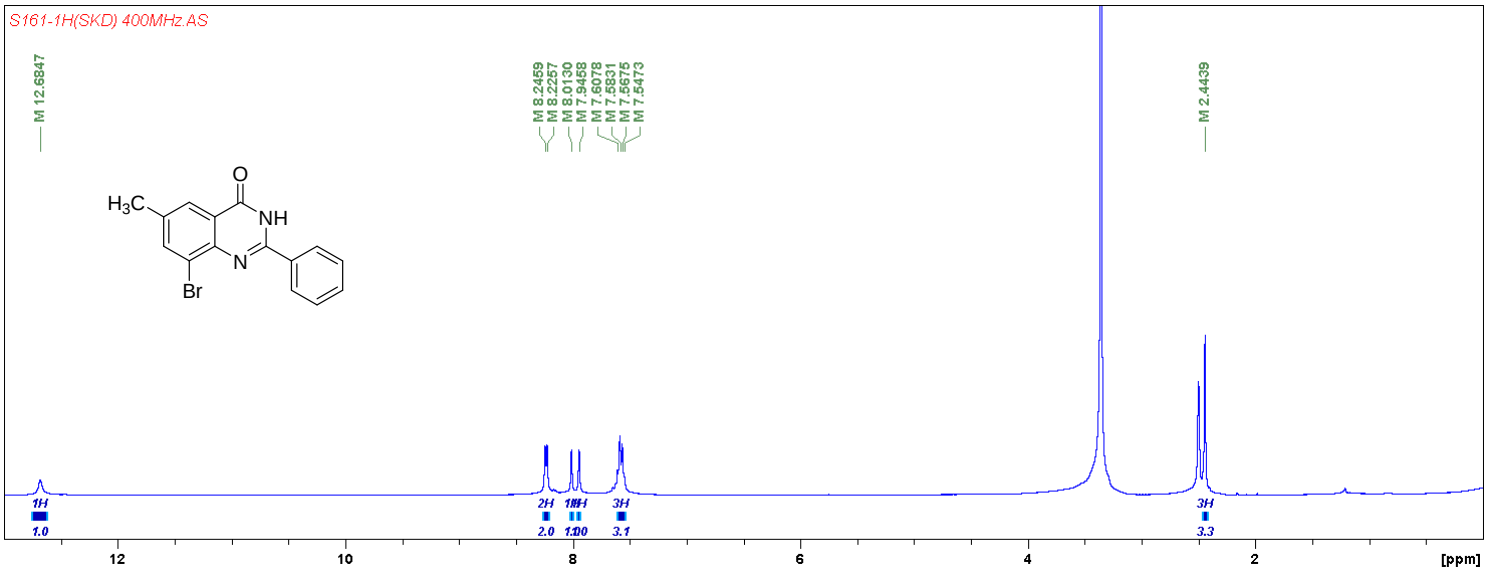


Figure S52. ^{1}H NMR spectrum of compound **5af** (400 MHz, DMSO-d_6).

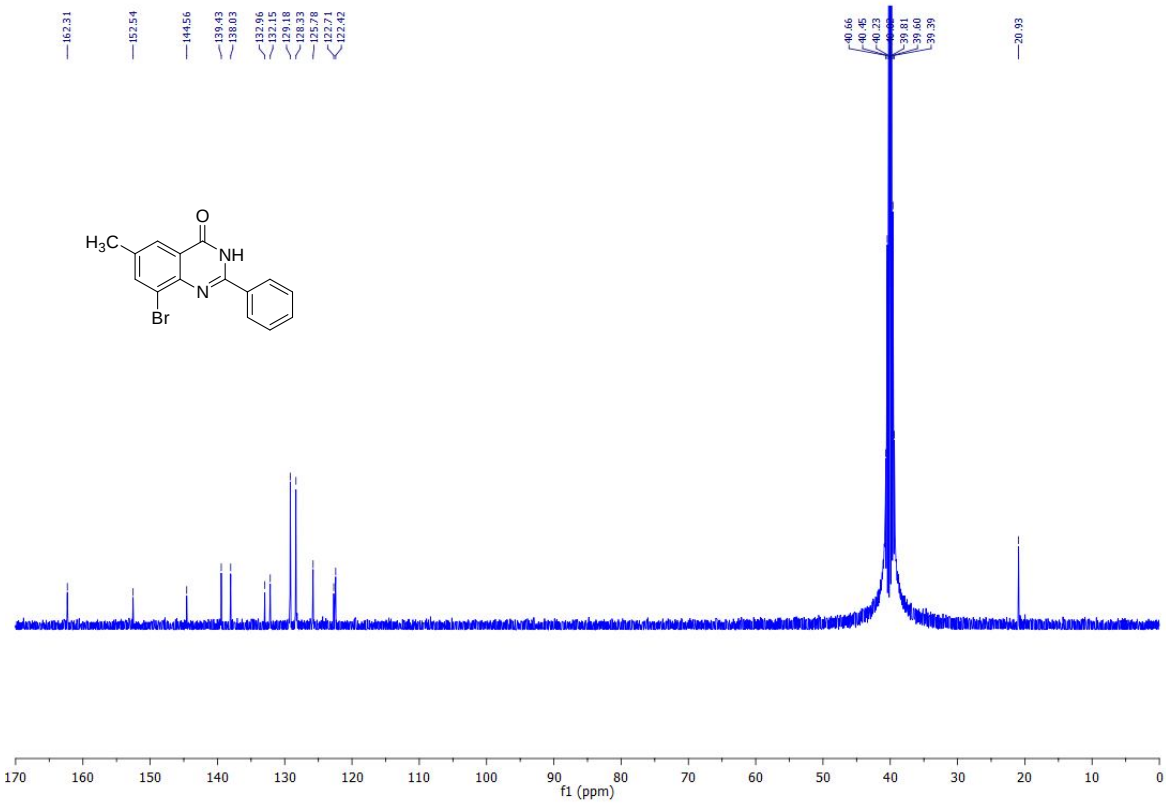


Figure S53. ^{13}C NMR spectrum of compound **5af** (100 MHz, DMSO-d_6).

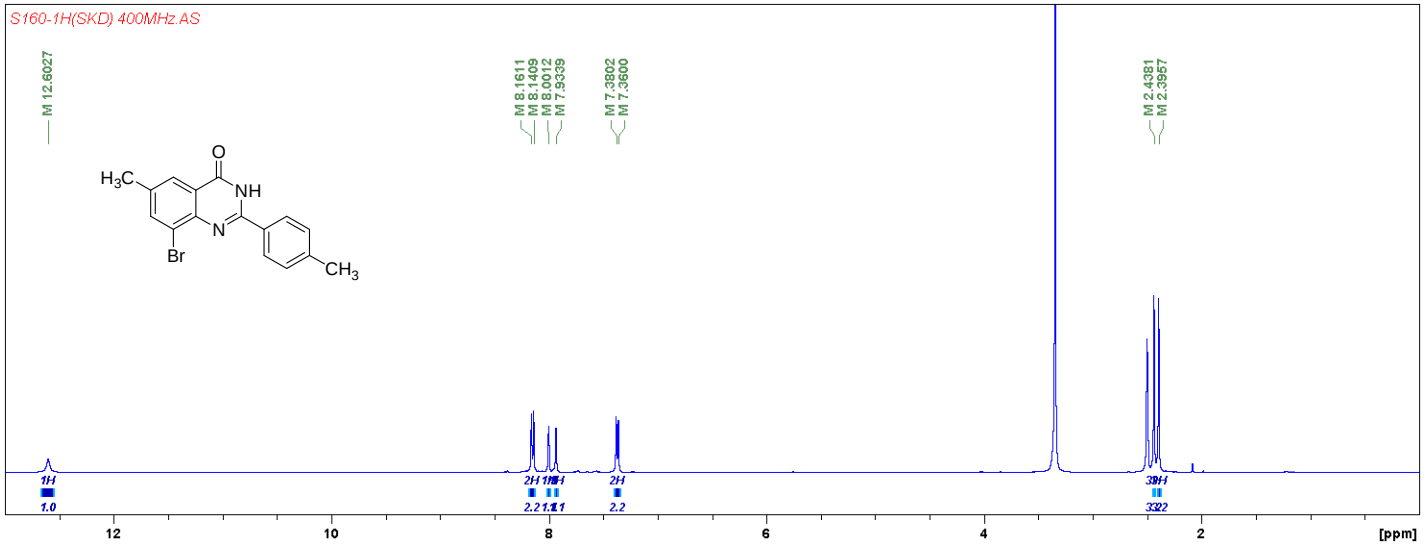


Figure S54. ^{1}H NMR spectrum of compound **5kf** (400 MHz, DMSO-d_6).

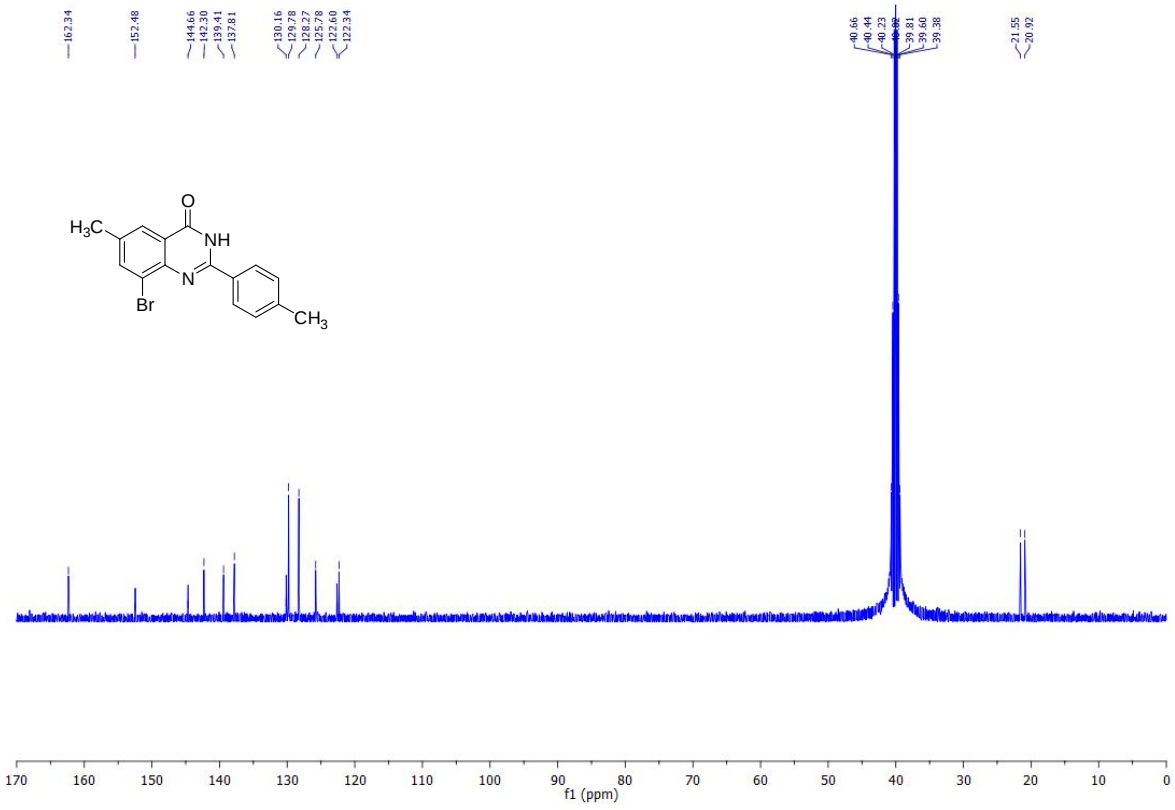


Figure S55. ^{13}C NMR spectrum of compound **5kf** (100 MHz, DMSO-d_6).

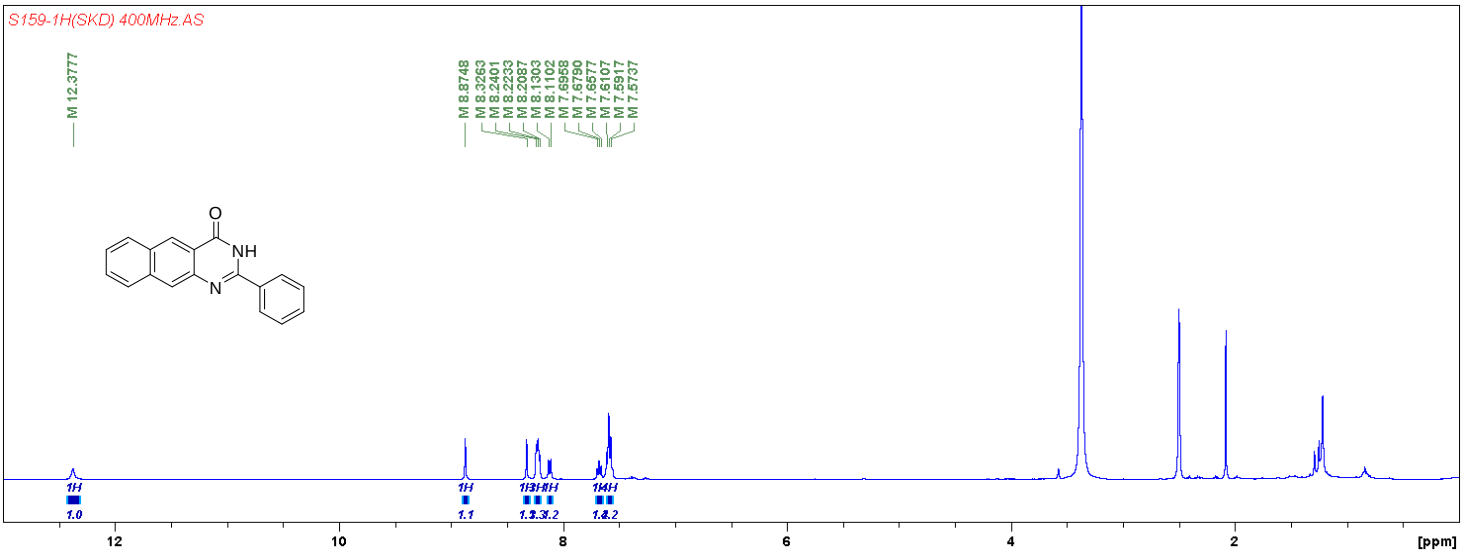


Figure S56. ^{1}H NMR spectrum of compound **5ag** (400 MHz, DMSO-d_6).

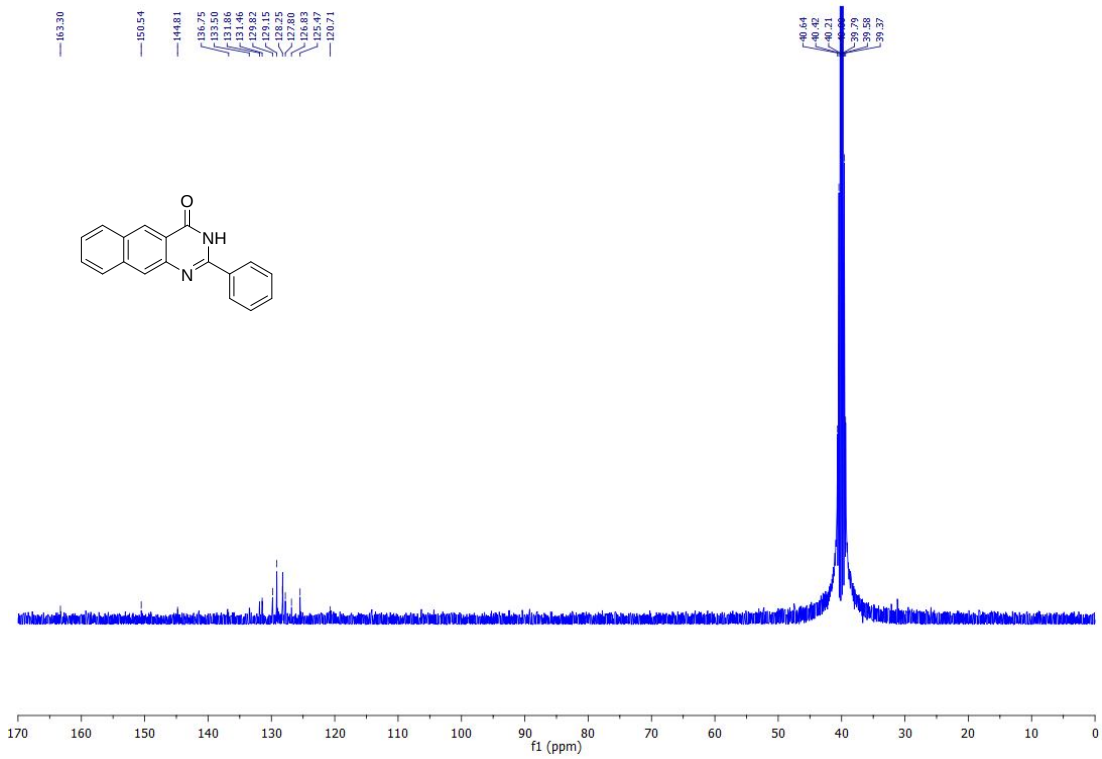


Figure S57. ^{13}C NMR spectrum of compound **5ag** (100 MHz, DMSO-d_6).

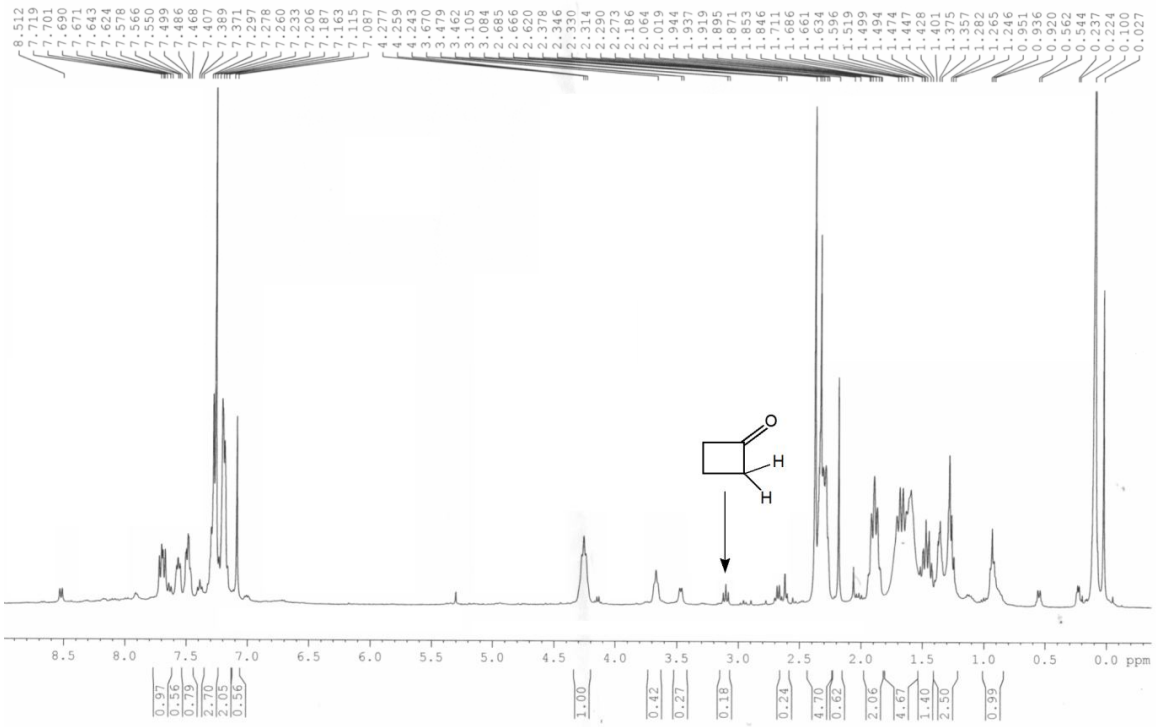


Figure S58. ^{1}H NMR spectrum of compound reaction mixture of cyclobutanol oxidation using **1b** as the catalyst.

Table S3. DFT optimized coordinates for **1b**.

Co	8.048	6.522	8.305
Cl	7.446	8.647	8.726
Cl	9.622	6.147	6.731
Cl	3.387	9.193	2.986
N	7.382	4.699	8.878
N	6.229	5.862	6.943
N	5.783	4.697	7.137
N	9.117	6.176	10.204
C	6.462	4.023	8.201
C	7.984	4.102	9.929
C	5.511	6.608	5.967

C	8.915	4.923	10.67
C	7.684	2.807	10.339
C	6.095	2.725	8.533
H	5.442	2.279	8.045
C	9.515	4.406	11.829
C	6.716	2.112	9.596
H	6.496	1.238	9.823
C	6.058	7.824	5.590
H	6.867	8.102	5.956
C	4.286	6.198	5.440
H	3.913	5.386	5.697
C	9.235	3.062	12.208
H	9.657	2.702	12.955
C	4.203	8.199	4.160
C	10.326	5.293	12.567
H	10.744	5.008	13.349
C	8.364	2.294	11.502
H	8.203	1.420	11.775
C	3.637	7.007	4.539
H	2.816	6.748	4.187
C	5.405	8.625	4.670
H	5.772	9.437	4.403
C	10.488	6.560	12.132
H	11.002	7.157	12.625
C	9.883	6.982	10.932
H	10.023	7.854	10.640

Table S4. DFT optimized coordinates for **2**.

Co	1.743	1.526	3.872
Cl	1.996	2.727	1.977
Cl	-0.288	0.603	4.274
N	1.752	3.015	5.578
N	3.275	0.935	5.077
N	2.825	-0.242	2.936
N	3.908	-0.645	3.460
N	0.286	4.481	4.594
N	-0.205	5.629	4.717
C	3.386	1.464	6.319
C	4.100	-0.067	4.732
C	2.549	2.598	6.595
C	4.282	0.972	7.277
C	3.476	2.647	8.847
H	3.494	3.027	9.718
C	4.270	1.577	8.579
H	4.827	1.224	9.263
C	2.615	3.218	7.860
C	1.040	4.118	5.770
C	1.815	4.373	8.033
H	1.809	4.828	8.866
C	-0.898	6.084	3.549
C	5.079	-0.571	5.598
H	5.680	-1.248	5.309
C	1.046	4.835	6.988
H	0.525	5.625	7.085

C	5.155	-0.070	6.872
H	5.792	-0.421	7.484
C	2.550	-0.830	1.653
C	1.217	-0.927	1.282
H	0.539	-0.575	1.846
C	-1.615	7.254	3.726
H	-1.635	7.679	4.575
C	0.878	-1.539	0.080
H	-0.035	-1.644	-0.160
C	3.556	-1.304	0.820
H	4.467	-1.237	1.081
C	-0.829	5.446	2.302
H	-0.329	4.647	2.191
C	-1.513	6.015	1.236
H	-1.475	5.608	0.378
C	-2.304	7.802	2.657
H	-2.807	8.600	2.771
C	3.210	-1.881	-0.401
H	3.889	-2.196	-0.986
C	-2.254	7.181	1.422
H	-2.731	7.554	0.690
C	1.874	-1.994	-0.766
H	1.644	-2.387	-1.600

Table S5. DFT optimized coordinates for **1b** with HOMO-LUMO mixing.

Co	8.048	6.522	8.305
Cl	7.446	8.647	8.726
Cl	9.622	6.147	6.731
Cl	3.387	9.193	2.986
N	7.382	4.699	8.878
N	6.229	5.862	6.943
N	5.783	4.697	7.137
N	9.117	6.176	10.204
C	6.462	4.023	8.201
C	7.984	4.102	9.929
C	5.511	6.608	5.967
C	8.915	4.923	10.67
C	7.684	2.807	10.339
C	6.095	2.725	8.533
H	5.442	2.279	8.045
C	9.515	4.406	11.829
C	6.716	2.112	9.596
H	6.496	1.238	9.823
C	6.058	7.824	5.590
H	6.867	8.102	5.956
C	4.286	6.198	5.440
H	3.913	5.386	5.697
C	9.235	3.062	12.208
H	9.657	2.702	12.955

C	4.203	8.199	4.160
C	10.326	5.293	12.567
H	10.744	5.008	13.349
C	8.364	2.294	11.502
H	8.203	1.420	11.775
C	3.637	7.007	4.539
H	2.816	6.748	4.187
C	5.405	8.625	4.670
H	5.772	9.437	4.403
C	10.488	6.560	12.132
H	11.002	7.157	12.625
C	9.883	6.982	10.932
H	10.023	7.854	10.64

Table S6. DFT optimized coordinates for **2** with HOMO-LUMO mixing.

Co	1.743	1.526	3.872
Cl	1.996	2.727	1.977
Cl	-0.288	0.603	4.274
N	1.752	3.015	5.578
N	3.275	0.935	5.077
N	2.825	-0.242	2.936
N	3.908	-0.645	3.460
N	0.286	4.481	4.594
N	-0.205	5.629	4.717

C	3.386	1.464	6.319
C	4.100	-0.067	4.732
C	2.549	2.598	6.595
C	4.282	0.972	7.277
C	3.476	2.647	8.847
H	3.494	3.027	9.718
C	4.270	1.577	8.579
H	4.827	1.224	9.263
C	2.615	3.218	7.860
C	1.040	4.118	5.770
C	1.815	4.373	8.033
H	1.809	4.828	8.866
C	-0.898	6.084	3.549
C	5.079	-0.571	5.598
H	5.680	-1.248	5.309
C	1.046	4.835	6.988
H	0.525	5.625	7.085
C	5.155	-0.07	6.872
H	5.792	-0.421	7.484
C	2.550	-0.830	1.653
C	1.217	-0.927	1.282
H	0.539	-0.575	1.846
C	-1.615	7.254	3.726
H	-1.635	7.679	4.575
C	0.878	-1.539	0.080

H	-0.035	-1.644	-0.160
C	3.556	-1.304	0.820
H	4.467	-1.237	1.081
C	-0.829	5.446	2.302
H	-0.329	4.647	2.191
C	-1.513	6.015	1.236
H	-1.475	5.608	0.378
C	-2.304	7.802	2.657
H	-2.807	8.600	2.771
C	3.210	-1.881	-0.401
H	3.889	-2.196	-0.986
C	-2.254	7.181	1.422
H	-2.731	7.554	0.690
C	1.874	-1.994	-0.766
H	1.644	-2.387	-1.600

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