Solvent-free and Catalyst-free Reaction of o-Amino Benzophenone with Aryl Isothiocyanates: Expedient Access to Congested 4-Phenyl-4-Hydroxyquinazolin-2-thione Derivatives

Le Anh Nguyen,[b,c] Thi Thu Tram Nguyen,[d] Quoc Anh Ngo,[b,*] Pascal Retailleau,[a] and Thanh Binh Nguyen[a,*]

[a] Institut de Chimie des Substances Naturelles, CNRS UPR 2301 Université Paris-Sud, Université Paris-Saclay, 1, av de la Terrasse, 91198 Gif-sur-Yvette France. thanh-binh.nguyen@cnrs.fr

[b] Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam. ngoqanh@ich.vast.vn

[c] Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam.

[d] Department of Chemistry, Faculty of Basic Science, Can Tho University of Medicine and Pharmacy, Can Tho, Vietnam.

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General information

Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^1H, 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. The reactions were performed in a 7-mL closed with a plastic cap and heated in a copper or aluminium block..

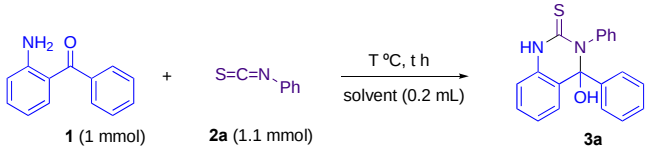
General procedure

General procedure for synthesis of quinazolin-2-thione

A mixture of *o*-aminobenzophenone **1** or *o*-aminoacetophenone **4** (1 mmol) and aryl isothiocyanate **2** (1.1 mmol) was stirred and heated in a 7-mL test tube closed with a plastic cap at 80 ºC for 1 h or 100 ºC for 10 min (for the synthesis of compounds **3e** and **3f**). The reaction mixture was progressively solidified. The crude mixture cooled down to rt was treated with methanol (2 mL, for adduct **3**) or acetonitrile (2 mL, for condensed product **5**) and the solid product was reduced to powder (with a spatula if needed), which was filtered, washed (acetonitrile 2 mL x 2) and dried in vacuo to afford the product **3** or **5**. In case of **3**, the combined filtrates could be concentrated to give addition crude products that could be further purified by recrystallization (methanol-water).

Optimization of the reaction conditions for 3a

Performing the reaction at lower temperatures (30, 40 or 60 °C, entries 1-5) and/or with shorter reaction times resulted in incomplete conversion with the reaction mixtures containing non-cyclized thiourea derived from addition of the amino group of **1** to isothiocyanate group of **2**. Reactions at 30 and 40 °C required a solvent for better mixing the starting material. At 60 °C, the use of solvent is facultative. Interestingly, heating at 80 °C for 1 h (entry 6) or 100 °C for 10 min (entry 7) resulted in full conversion into adduct 4-phenyl-4-hydrxyquinazolin-4-thione **3a**. The reaction mixture was solidified progressively with the formation of **3a**, which could be easily isolated in high purity and excellent yield by trituration with methanol or acetonitrile followed by filtration (93%).

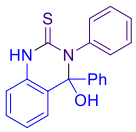


1 (1 mmol) **2a** (1.1 mmol) **3a**

entry	solvent	T (ºC)	t (h)	Isolated yield
1	DMSO	30	16	68
2	DMSO	40	16	85
3	DMSO	60	2	65
4	*N*-methylpyrrolidin-2-one	60	2	67
5	-	60	2	68
6	-	80	1	91
7	**-**	**100**	**1/6**	**93**

Characterization of products

4-Hydroxy-3,4-diphenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3a)



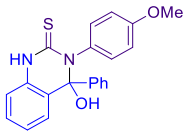
Pale yellow solid (309 mg, 93%).

^{1}H NMR (300 MHz, DMSO) δ 11.37 (s, 1H), 7.73 (s, 1H), 7.40-7.36 (m, 1H), 7.32-7.16 (m, 8H), 7.14-7.08 (m, 1H), 7.02-6.87 (m, 3H), 6.34-6.32 (broad s, 1H).

^{13}C NMR (75 MHz, DMSO) δ 131.8, 130.7, 129.0, 127.9, 127.6, 127.4, 126.9, 126.7, 126.4, 122.7, 113.8.

HRMS (ESI+) calcd for $C_{20}H_{17}N_2OS$ $[M + H]^+$ 333.1062. Found 333.1071.

4-Hydroxy-3-(4-methoxyphenyl)-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3b)



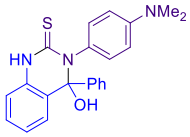
Pale yellow solid (322 mg, 89%).

^{1}H NMR (300 MHz, DMSO) δ 11.28 (s, 1H), 7.63-7.62 (m, 1H), 7.31-7.16 (m, 8H), 6.98-6.80 (m, 3H), 6.49 (dd, J = 8.8, 3.0 Hz, 1H), 6.21 (dd, J = 8.8, 2.5 Hz, 1H), 3.68 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 174.8, 157.6, 144.9, 133.8, 133.0, 132.7, 131.5, 128.9, 127.9, 127.5 (2C), 126.4 (2C), 125.9, 122.6, 113.7, 112.5, 112.2, 87.3, 55.0.

HRMS (ESI+) calcd for $C_{21}H_{19}N_2O_2S$ $[M + H]^+$ 363.1167. Found 363.1162.

3-(4-(Dimethylamino)phenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3c)



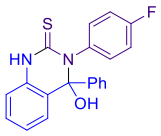
Pale yellow solid (334 mg, 89%).

^{1}H NMR (300 MHz, DMSO) δ 11.21 (s, 1H), 7.56 (s, 1H), 7.27-7.23 (m, 5H), 7.22-7.13 (m, 3H), 6.96-6.87 (m, 2H), 6.61-6.57 (m, 1H), 6.29-6.25 (m, 1H), 6.13-6.10 (m, 1H), 2.83 (s, 6H).

^{13}C NMR (75 MHz, DMSO) δ 175.0, 148.6, 145.2, 134.1, 133.8, 133.0, 132.1, 130.8, 130.2, 128.8, 128.5, 128.2, 127.8, 127.5, 127.4, 126.3, 126.0, 122.5, 116.9, 113.6, 111.0, 110.6, 87.3.

HRMS (ESI+) calcd for $C_{22}H_{12}N_3OS$ $[M + H]^+$ 376.1484. Found 376.1488.

3-(4-Fluorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3d)



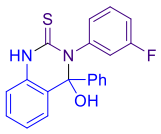
Pale yellow solid (322 mg, 92%).

^{1}H NMR (300 MHz, DMSO) δ 11.66 (s, 1H), 7.41-7.36 (m, 1H), 7.28-7.14 (m, 8H), 7.13-7.07 (m, 1H), 7.04-6.98 (m, 1H), 6.80-6.73 (m, 1H), 6.67-6.64 (m, 1H), 6.51-6.45 (m, 1H).

^{13}C NMR (75 MHz, DMSO) δ 176.1, 160.5 (d, J = 244.0 Hz), 142.9, 137.1 (d, J = 3.4 Hz), 135.2, 133.4 (d, J = 8.7 Hz), 131.5 (d, J = 9.0 Hz), 130.0, 128.5, 127.8, 127.5, 127.3, 123.3, 120.2, 114.4 (d, J = 21.1 Hz), 114.0, 113.8, 92.4, 50.0.

HRMS (ESI+) calcd for $C_{20}H_{16}FN_2OS$ $[M + H]^+$ 351.0967. Found 351.0960.

3-(3-Fluorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3e)



Pale yellow solid (315 mg, 90%).

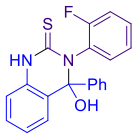
^{1}H NMR (300 MHz, DMSO) δ 11.47 (s, 1H), 7.79 (s, 1H), 7.33-7.16 (m, 9H), 7.01-6.95 (m, 2H), 6.88-6.85 (m, 1H), 6.22-6.09 (m, 1H).

^{13}C NMR (75 MHz, DMSO) δ 174.4, 144.3, 142.5 (d, J = 10.4 Hz), 133.0, 129.1, 128.6, 128.1, 127.8, 127.7, 127.6, 127.2, 126.5, 125.8, 122.9, 119.1, 118.8, 117.8, 113.9, 113.5, 87.5.

^{19}F NMR (282 MHz, DMSO) δ -114.6 and -115.1 (two isomers).

HRMS (ESI+) calcd for $C_{20}H_{16}FN_2OS$ $[M + H]$+ 351.0967. Found 351.0972.

3-(2-Fluorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3f)



Pale yellow solid (315 mg, 90%). Mixture 2:1 of two isomers

^{1}H NMR signals of the major isomer:

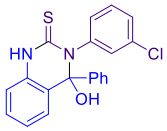
^{1}H NMR (300 MHz, DMSO) δ 11.61 (s, 1H), 7.84 (s, 1H), 7.61-7.54 (m, 1H), 7.32-7.28 (m, 2H), 7.26-7.25(m, 1H), 7.24-7.19 (m, 2H), 7.18-7.11 (m, 3H), 7.09-7.01 (m, 1H), 6.99-6.93 (m, 1H), 6.82-6.75 (m, 1H), 6.69-6.66 (m, 1H).
Some characteristic ^{1}H NMR signals of the minor isomer (300 MHz, DMSO) δ 11.46 (s, 1H), 7.35-7.34 (m, 1H), 6.22-6.16 (m, 1H).

^{13}C-NMR signals of the major isomer (75 MHz, DMSO) δ 174.3, 157.7 (d, J = 249.1 Hz), 142.8, 132.9 (d, J = 90.7 Hz), 129.3, 129.2, 129.1, 129.0, 128.2, 128.0, 127.6, 127.1, 127.0, 125.8, 125.5, 123.2 (d, J = 3.6 Hz), 122.8, 114.8 (d, J = 20.7 Hz), 113.9, 87.6.

Some characteristic ^{13}C-NMR signals of the minor isomer (75 MHz, DMSO) δ 159.4 (d, J = 249.3 Hz), 145.7, 132.1 (d, J = 105.5 Hz), 123.0 (d, J = 4.4 Hz), 115.6, 115.4 (d, J = 20.7 Hz), 88.1.

^{19}F NMR (282 MHz, DMSO) δ -115.21 (major isomer), -116.10 (minor isomer).
HRMS (ESI+) calcd for $C_{20}H_{16}FN_2OS$ $[M + H]^+$ 351.0967. Found 351.0965.

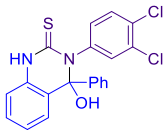
3-(3-Chlorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3g)



Pale yellow solid (330 mg, 90%).

^{1}H NMR (300 MHz, DMSO) δ 11.73 (s, 1H), 7.41-7.15 (m, 10H), 7.04-6.94 (m, 2H), 6.67-6.63 (m, 1H), 6.50-6.47 (m, 1H).
^{13}C NMR (75 MHz, DMSO) δ 176.2, 143.1, 142.4, 135.5, 132.2, 131.9, 130.9, 130.4, 129.9, 129.7, 129.0, 128.9, 128.3, 127.9, 127.8, 127.4, 123.8, 120.6, 114.3, 92.9, 50.5.
HRMS (ESI+) calcd for $C_{20}H_{16}ClN_2OS$ $[M + H]^+$ 367.0672. Found 367.0663.

3-(3,4-Dichlorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3h)



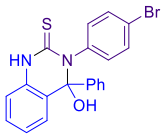
Pale yellow solid (352 mg, 88%).

^{1}H NMR (300 MHz, DMSO) δ 11.56 (s, 1H), 7.88 (s, 1H), 7.60-7.55 (m, 1H), 7.38-7.20 (m, 8H), 7.02-7.01 (m, 1H), 6.89-6.86 (m, 1H), 6.39-6.34 (m, 1H).

^{13}C NMR (75 MHz, DMSO) δ 174.3, 144.0, 140.9, 133.5, 132.9, 132.8, 132.2, 131.4, 129.6, 129.3, 129.2, 128.9, 127.9, 127.9, 127.8, 126.5, 125.6, 123.1, 114.0, 87.6 (1 signals missing due to overlap).

HRMS (ESI+) calcd for $C_{20}H_{15}Cl_2N_2OS$ $[M + H]^+$ 401.0282. Found 401.0277.

3-(4-Bromophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3i)



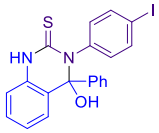
Pale yellow solid (356 mg, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.83 (s, 1H), 7.49-7.47 (m, 1H), 7.30-7.27 (m, 1H). 7.25-7.14 (m, 8H), 6.97-6.94 (m, 1H), 6.86-6.84 (m, 1H), 6.28-6.25 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5, 149.6, 145.6, 139.1, 138.2, 138.1, 135.8, 135.3, 134.4, 133.2, 133.1, 133.0, 131.7, 131.0, 128.2, 125.2, 119.1, 92.6.

HRMS (ESI+) calcd for $C_{20}H_{16}BrN_2OS$ $[M + H]^+$ 411.0167. Found 411.0158.

4-Hydroxy-3-(4-iodophenyl)-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3j)



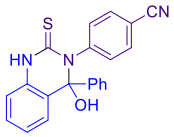
Pale yellow solid (399 mg, 87%).

^{1}H NMR (300 MHz, DMSO) δ 11.74 (s, 1H), 8.13-8.10 (m, 2H), (m, 1H), (m, 3H), (m, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.49-7.14 (m, 9H), 6.99-6.94 (m, 1H), 6.88-6.85 (m, 1H), 6.14 (d, J = 8.5 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ 174.3, 144.4, 140.9, 136.4, 135.9, 134.1, 133.0, 133.0, 129.1, 127.8, 127.7, 127.7, 126.4, 125.8, 122.9, 113.9, 92.9, 87.4.

HRMS (ESI+) calcd for $C_{20}H_{16}IN_2OS$ $[M + H]^+$ 459.0028. Found 459.0019.

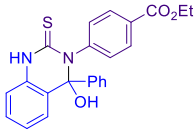
4-(4-Hydroxy-4-phenyl-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzonitrile (3k)



Pale yellow solid (325 mg, 91%).

^{1}H NMR (300 MHz, DMSO) δ 11.59 (s, 1H), 7.94 (s, 1H), 7.80-7.77 (m, 1H), 7.58-7.55 (m, 1H), 7.51-7.44 (m, 1H), 7.35-7.29 (m, 1H), 7.26-7.21 (m, 6H), 7.01-6.96 (m, 1H), 6.88-6.85 (m, 1H), 6.58-6.55 (m, 1H).
^{13}C NMR (75 MHz, DMSO) δ 174.1, 145.5, 144.0, 133.0, 132.8, 132.2, 131.7, 131.0, 129.2, 127.9, 127.8, 127.7, 126.6, 125.7, 123.0, 118.5, 114.0, 109.5, 87.7.
HRMS (ESI+) calcd for $C_{21}H_{16}N_3OS$ $[M + H]^+$ 358.1014. Found 358.1019.

Ethyl 4-(4-hydroxy-4-phenyl-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzoate (5l)

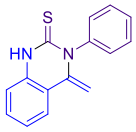


Pale yellow solid (368 mg, 91%).

^{1}H NMR (300 MHz, DMSO) δ 11.50 (s, 1H), 7.89-7.84 (m, 2H), 7.53 (dd, J = 8.3, 2.1 Hz, 1H), 7.34-7.16 (m, 8H), 6.97 (td, J = 7.5, 1.3 Hz, 1H), 6.85 (dd, J = 7.9, 1.4 Hz, 1H), 6.52 (dd, J = 8.2, 2.1 Hz, 1H), 4.27 (q, J = 7.1 Hz, 1H), 1.29 (t, J = 7.1 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 174.2, 165.3, 145.5, 144.1, 133.1, 131.9, 131.3, 129.1, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 126.6, 125.8, 122.9, 113.9, 87.6, 60.6, 14.1.
HRMS (ESI+) calcd for $C_{21}H_{21}N_2O_3S$ $[M + H]^+$ 405.1273. Found 405.1280.

4-Methylene-3-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (5a)[1]

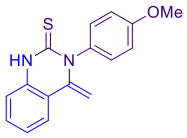
[1] Yan, H.; Xiao, X.Q.; Hider, R.C.; Ma, Y. Simple Metal-Free Cyclization for the Synthesis of 4-Methylene-3-Substituted Quinazolinone and Quinazolinthione Derivatives: Experiment and Theory. *Front. Chem.*, **2019**, 7, 584.



White solid (240 mg, 95%).

^{1}H NMR (300 MHz, DMSO) δ 11.67 (s, 1H), 7.69-7.66 (m, 1H), 7.57-7.50 (m, 2H), 7.46-7.33 (m, 2H), 7.27-7.21 (m, 2H), 7.17-7.07 (m, 2H), 4.92 (d, J = 2.2 Hz, 1H), 3.42 (d, J = 2.2 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 173.6, 141.6, 133.6, 130.7, 129.8, 129.1, 128.4, 128.1, 124.4, 123.9, 123.9, 123.6, 117.5, 115.0, 88.7.

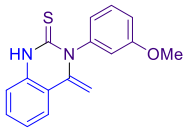
3-(4-Methoxyphenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5b)[1]



White solid (260 mg, 92%).

^{1}H NMR (300 MHz, DMSO) δ 11.59 (s, 1H), 7.66-7.63 (m, 1H), 7.39-7.33 (m, 1H), 7.17-7.03 (m, 6H), 4.90 (d, J = 2.1 Hz, 1H), 3.82 (s, 3H), 3.52 (d, J = 2.1 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 174.1, 158.5, 141.9, 134.5, 133.7, 130.6, 130.1, 123.9, 123.8, 117.6, 115.0, 114.9, 88.7, 55.3.

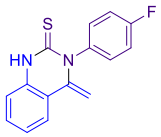
3-(3-Methoxyphenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5c)[1]



White solid (257 mg, 91%).

^{1}H NMR (300 MHz, DMSO) δ 11.61 (s, 1H), 7.68-7.65 (m, 1H), 7.47-7.34 (m, 2H), 7.17-7.06 (m, 2H), 7.03-6.98 (m, 1H), 6.82-6.79 (m, 2H), 4.92 (d, J = 2.2 Hz, 1H), 3.78 (s, 3H), 3.52 (d, J = 2.2 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 173.5, 160.5, 142.6, 141.4, 133.7, 130.7, 130.4, 123.9, 123.8, 121.2, 117.6, 115.0, 114.9, 113.7, 88.7, 55.3.

3-(4-Fluorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5d)



White solid (246 mg, 91%).

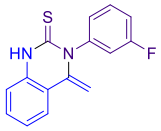
^{1}H NMR (300 MHz, DMSO) δ 11.68 (s, 1H), 7.68-7.65 (m, 1H), 7.40-7.26 (m, 5H), 7.18-7.07 (m, 2H), 4.93 (d, *J* = 2.1 Hz, 1H), 3.47(d, *J* = 2.0 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ 173.8, 162.9, 159.7, 141.7, 137.9 (d, *J* = 3.4 Hz), 133.6, 131.3 (d, *J* = 8.9 Hz), 130.7, 123.9, 117.5, 116.2 (d, *J* = 22.9 Hz), 115.1, 88.8.

^{19}F NMR (282 MHz, DMSO) δ -113.70.

HRMS (ESI+) calcd for $C_{15}H_{12}FN_2S$ $[M + H]^+$ 271.0705. Found 271.0710.

3-(3-Fluorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5e)



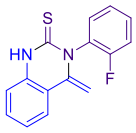
White solid (243 mg, 90%).

^{1}H NMR (300 MHz, DMSO) δ 11.70 (s, 1H), 7.69-7.66 (m, 1H), 7.62-7.54 (m, 1H), 7.42-7.35 (m, 1H), 7.33-7.24 (m, 1H), 7.23-7.08 (m, 4H), 4.94 (d, *J* = 2.4 Hz, 1H), 3.48 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ 173.5, 164.4, 161.2, (d, *J* = 10.5 Hz), 141.3, 133.6, 131.2 (d, *J* = 9.1 Hz), 130.7, 125.6 (d, *J* = 3.3 Hz), 123.9 (d, *J* = 3.5 Hz), 117.5, 116.7 (d, *J* = 22.7 Hz), 115.3, 115.1, 115.0, 88.7.

HRMS (ESI+) calcd for $C_{15}H_{12}FN_2S$ $[M + H]^+$ 271.0705. Found 271.0708.

3-(2-Fluorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5f)

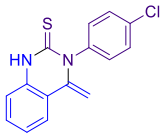


White solid (238 mg, 88%).

^{1}H NMR (300 MHz, DMSO) δ 11.78 (s, 1H), 7.70-7.67 (m, 1H), 7.55-7.48 (m, 1H), 7.46-7.35 (m, 4H), 7.19-7.09 (m, 2H), 4.94 (d, *J* = 2.5 Hz, 1H), 3.53 (d, *J* = 2.5 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ 173.6, 159.0, 155.7, 140.5, 133.5, 131.2, 130.9, 130.6 (d, J = 7.9 Hz), 128.6 (d, J = 12.9 Hz), 125.6 (d, J = 3.6 Hz), 124.0 (d, J = 9.7 Hz), 117.2, 116.7 (d, J = 19.4 Hz), 115.2, 87.9.
^{19}F NMR (282 MHz, DMSO) δ -122.72.
HRMS (ESI+) calcd for $C_{15}H_{13}FN_2S$ $[M + H]^+$ 271.0705. Found 271.0709.

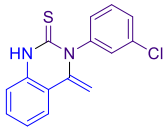
3-(4-Chlorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5g)[1]



Pale yellow solid (260 mg, 91%).

^{1}H NMR (300 MHz, DMSO) δ 11.70 (s, 1H), 7.69-7.66 (m, 1H), 7.62-7.56 (m, 2H), 7.41-7.35 (m, 1H), 7.31- 7.26 (m, 2H), 7.18-7.07 (m, 2H), 4.93 (d, J = 2.5 Hz, 1H), 3.47 (d, J = 2.4 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 173.6, 141.5, 140.5, 133.6, 132.6, 131.2, 130.8, 129.9, 123.8, 123.9, 117.5, 115.1, 88.8.

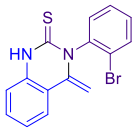
3-(3-Chlorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5h)[1]



Pale yellow solid (263 mg, 92%).

^{1}H NMR (300 MHz, DMSO) δ 11.72 (s, 1H), 7.69-7.66 (m, 1H), 7.60-7.48 (m, 2H), 7.42-7.35 (m, 2H), 7.27-7.23 (m, 1H), 7.18-7.08 (m, 2H), 4.94 (d, J = 2.5 Hz, 1H), 3.46 (d, J = 2.5 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 173.5, 142.8, 141.4, 133.7, 133.6, 131.3, 130.8, 129.4, 128.3, 128.2, 124.0, 123.9, 117.5, 115.1, 88.8.

3-(2-Bromophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5i)



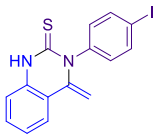
Pale yellow solid (300 mg, 91%).

^{1}H NMR (300 MHz, DMSO) δ 11.72 (s, 1H), 7.81-7.78 (m, 1H), 7.72-7.68 (m, 1H), 7.58-7.52 (m, 1H), 7.44-7.35 (m, 3H), 7.18-7.08 (m, 2H), 4.95-4.93 (m, 1H), 3.39-3.37 (m, 1H).

^{13}C NMR (75 MHz, DMSO) δ 173.0, 140.0, 139.8, 133.6, 133.5, 131.6, 130.8, 130.1, 129.2, 124.0 (2C), 122.6, 117.3, 115.2, 87.8.

HRMS (ESI+) calcd for $C_{15}H_{12}BrN_2S$ $[M + H]^+$ 330.9905. Found 330.9911.

3-(4-Iodophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5j)



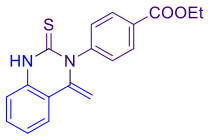
Pale yellow solid (340 mg, 90%).

^{1}H NMR (300 MHz, DMSO) δ 11.68 (s, 1H), 7.91-7.86 (m, 2H), 7.68-7.65 (m, 1H), 7.42-7.32 (m, 1H), 7.17-7.10 (m, 2H), 7.09-7.04 (m, 2H), 4.93 (d, J = 2.4 Hz, 1H), 3.47 (d, J = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ 173.5, 141.5, 141.4, 138.8, 133.6, 131.6, 130.8, 123.9, 123.9, 117.5, 115.1, 94.2, 88.9.

HRMS (ESI+) calcd for $C_{15}H_{12}IN_2S$ $[M + H]^+$ 378.9766. Found 378.9771.

Ethyl 4-(4-methylene-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzoate (5k)



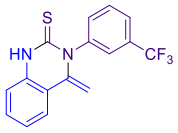
Pale yellow solid (279 mg, 86%).

^{1}H NMR (300 MHz, DMSO) δ 11.74 (s, 1H), 8.13-8.09 (m, 2H), 7.70-7.67 (m, 1H), 7.44-7.36 (m, 3H), 7.19-7.08 (m, 2H), 4.94 (d, J = 2.5 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 3.42 (d, J = 2.5 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, DMSO) δ 173.3, 165.2, 145.7, 141.3, 133.6, 130.8, 130.7, 129.9, 129.5, 124.0, 123.9, 117.5, 115.2, 88.9, 60.9, 14.1.

HRMS (ESI+) calcd for $C_{18}H_{17}N_2O_2S$ $[M + H]^+$ 325.1011. Found 325.1015.

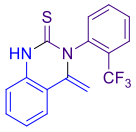
4-Methylene-3-(3-(trifluoromethyl)phenyl)-3,4-dihydroquinazoline-2(1*H*)-thione (5l)



Pale yellow solid (285 mg, 89%).

^{1}H NMR (300 MHz, DMSO) δ 11.77 (s, 1H), 7.83-7.75 (m, 2H), 7.73-7.67 (m, 2H), 7.64-7.58 (m, 1H), 7.42-7.37 (m, 1H), 7.19-7.09 (m, 2H), 4.95 (d, J = 2.6 Hz, 1H), 3.38 (d, J = 2.6 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 173.6, 142.3, 141.6, 133.9, 133.6, 131.0, 130.9, 130.2 (q, J = 32.2 Hz), 126.4 (q, J = 4.1 Hz), 125.6 (q, J = 272.1 Hz), 124.9 (q, J = 4.0 Hz), 124,0 123.9, 117.6, 115.2, 88.8.
^{19}F NMR (282 MHz, DMSO) δ -61.00.
HRMS (ESI+) calcd for $C_{16}H_{12}F_3N_2S$ $[M + H]^+$ 321.0673. Found 321.0682.

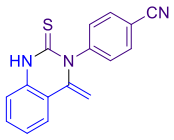
4-Methylene-3-(2-(trifluoromethyl)phenyl)-3,4-dihydroquinazoline-2(1*H*)-thione (5m)



Pale yellow solid (291 mg, 91%).

^{1}H NMR (300 MHz, DMSO) δ 11.81 (s, 1H), 7.89-7.82 (m, 2H), 7.70-7.65 (m, 2H), 7.49-7.47 (m, 1H), 7.42-7.36 (m, 1H), 7.18-7.08 (m, 2H), 4.97 (d, J = 2.7 Hz, 1H), 3.33 (d, J = 2.4 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 174.0, 141.4, 138.5, 134.1, 133.5, 132.8, 130.8, 129.3, 127.9 (q, J = 4.5 Hz), 126.3 (q, J = 30.9 Hz), 124.0, 123.9, 121.4 (q, J = 274.1 Hz), 117.4, 115.2, 88.8.
^{19}F NMR (282 MHz, DMSO) δ -60.24.
HRMS (ESI+) calcd for $C_{16}H_{12}F_3N_2S$ $[M + H]^+$ 321.0673. Found 321.0680.

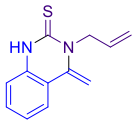
4-(4-Methylene-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzonitrile (5n)



Pale yellow solid (250 mg, 90%).

^{1}H NMR (300 MHz, DMSO) δ 11.79 (s, 1H), 8.03-8.00 (m, 2H), 7.71, 7.68 (m, 1H), 7.52-7.49 (m, 2H), 7.42-7.36 (m, 1H), 7.18-7.09 (m, 2H), 4.95 (d, J = 2.7 Hz, 1H), 3.39 (d, J = 2.7 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 173.2, 145.7, 141.3, 134.0, 133.5, 130.9, 130.8, 124.0, 123.9, 118.4, 117.5, 115.2, 111.0, 89.0.
HRMS (ESI+) calcd for $C_{16}H_{12}N_3S$ $[M + H]^+$ 278.0752. Found 278.0760.

3-Allyl-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5o)



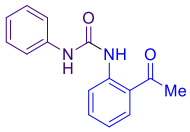
Pale yellow solid (195 mg, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.49 (s, 1H), 7.64-7.62 (m, 1H), 7.32-7.29 (m, 1H), 7.08-7.04 (m, 2H), 5.87-5.80 (m, 1H), 5.24-5.19 (m, 2H), 5.03-5.01 (m, 3H), 4.47-4.46 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 143.1, 138.5, 136.9, 135.6, 129.2, 129.0, 122.8, 122.0, 120.0, 93.5, 56.7.

HRMS (ESI+) calcd for $C_{12}H_{13}N_2S$ $[M + H]^+$ 217.0799. Found 217.0805.

1-(2-Acetylphenyl)-3-phenylurea (8)[2]

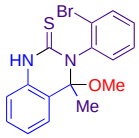


Pale yellow solid (216 mg, 85%).

^{1}H NMR (300 MHz, DMSO) δ 10.74 (s, 1H), 9.78 (s, 1H), 8.41-8.38 (m, 1H), 8.03-7.99 (m, 1H), 7.59-7.51 (m, 2H), 7.33-7.26 (m, 2H), 7.12-7.07 (m, 1H), 7.02-6.97 (m, 1H), 2.66 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 202.3, 152.4, 141.1, 139.7, 134.1, 131.9, 128.6 (2C), 122.3, 122.1, 120.9, 120.1, 118.8 (2C), 28.7.

3-(2-Bromophenyl)-4-methoxy-4-methyl-3,4-dihydroquinazoline-2(1*H*)-thione (9i)



^{1}H NMR (300 MHz, DMSO) δ 11.64 (s, 1H), 7.73-7.70 (m, 1H), 7.55-7.49 (m, 2H), 7.47-7.41 (m, 1H), 7.39 (m, 2H), 7.36-7.31 (m, 2H), 7.22-7.14 (m, 2H), 1.55 (s, 3H).

HRMS (ESI+) calcd for $C_{16}H_{16}BrN_2OS$ $[M + H]^+$ 363.0167. Found 363.0175.

[2] Singh, A. S.; Agrahari, A. K.; Singh, S. K.; Yadav, M. S.;Tiwari. V. K. An Improved Synthesis of Urea Derivatives from N-Acylbenzotriazole via Curtius Rearrangement. *Synthesis*, **2019**, *51*, 3443-3450.

Crystallographic data collection, structure determination and refinement

Colorless tab-like crystals of **5a•H_2O** were obtained in the presence of DMSO solvent. X-ray diffraction data were recorded at room temperature from a couple of *j* scans (for technical reasons) using a Rigaku XtaLabPro single-crystal diffractometer equipped with a microfocus Mo Kα radiation and a HPAD PILATUS3 R 200K detector. *CrysAlisPro*[1] was used for data processing applying an empirical absorption correction using spherical harmonics, combined with a numerical approach, as implemented in the *SCALE3 ABSPACK* scaling algorithm. The structure was readily solved by intrinsic phasing methods (*SHELXT* program),[2] then refined using full-matrix least-squares methods on F^2 with *SHELX-L*.[3] The displacement parameters for all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were freely refined in an isotropic manner whenever it was possible. The model in the asymmetric unit (asu) of the racemic monoclinic unit cell, comprises the molecule of interest and one molecule of DMSO, disordered over two sites flipped over a pseudo-mirror plane in an occupancy ratio of 0.734(2)/0.266(2) (Figure S2). The molecule of interest forms a hydrogen bonds with the solvent molecule through its hydroxyl group (*d* (O–H) = 1.01(3)Å, *d* (*O*–H···O) = 1.65(3)Å, *d* (O···O) = 2.655(8)Å, ∠(*O*–H···O) = 176(2)°). The DELU and SIMU commands were employed to restrain the thermal factors of the disordered DMSO atoms. The refinement of the model was continued using the Transferable aspherical atom model (TAAM) approach within *Olex2*.[4] The aspherical atomic scattering factors computed by the DiSCaMB library [5] from the multipole model [6] and parametrized using the MATTS2021 data bank [7] were transferred into *NoSpherA2* [8] as a tsc file format. These form factors are utilized during the least-squares refinement against experimental intensities in an iterative cycle until convergence is achieved through olex2.refine.[4] In order to achieve this, the methyl groups of the DMSO molecule had to be re-idealized as rigid groups with *U*(H) values were fixed at 1.2U_{eq} (C). A search in the Cambridge Structural Database (version 5.45, last update June 2024;[9]) of quinazolinthione derivatives reveals two reports of crystal structures, CCDC Refcodes BULQEH [10] and JOGQOP [11]. The overlays on the bicycle moiety are displayed in figure S3. If the molecule of interest differs from BULQEH by the presence of an hydroxyl group instead of a methoxy group after an incubation of 4-Methylene-3-phenyl-3,4-dihydroquinazoline-2(1H)-thione in methanol, the puckering of the six-heteromembered ring at the asymmetric carbon is more apparent in than in one of the BULQEH conformers (absent in the second conformer).

CP Puckering parameters [12]	#####	**BULQEH**	**JOGQOP**
Q_2 (Å)	0.1642(16)	0.087(4)	0.344(2)
Q_3 (Å)	0.0470(15)	-0.032(4)	-0.099(2)
Q ($Q^2=Q_2^2+Q_3^2$) (Å)	0.1708(16)	0.093(4)	0.359(2)
q (°)	74.0(5)	110(2)	106.1(3)
j_2 (°)	298.3(5)	359(2)	235.8(4)

Crystal data, data collection and structure refinement details are summarized in Table 1. CCDC 2368944 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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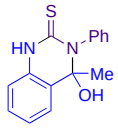
Table 1 Crystal data, data collection and structure refinement details for the **5a•H_2O**

Compound	(rac-*R*,*S*)-4-hydroxy-4-methyl-3-phenyl-3,4-dihydroquinazoline-2(1H)-thione, dmso solvate
2D	
Empirical formula	C_{15} H_{14} N_2 O S, *[C2 H6 O S]*
Formula weight	348.49
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, *P* 2_1/c
Unit cell dimensions | (Å) | (°)	12.4378(7) 7.5087(5) 19.5257(11) 96.794(5)
Volume (Å^3)	1810.74(18)
Z, Calculated density (Mg/m^3)	4, 1.278
Absorption coefficient (mm^{-1})	0.304
F(000)	736
Crystal size (mm)	0.40 x 0.18 x 0.15
θ range for data collection (°)	2.82 to 27.48
Limiting indices	-16 ≤ h ≤ 15, -10 ≤ k ≤ 10, -23 ≤ l ≤ 23
Reflections collected / unique [R(int)	24181 / 3934 0.0449
Completeness to θ_{full} (%)	99.6
Absorption correction	Sphere and equivalence
Max. and min. transmission	1.000 and 0.911
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters		3933 / 66 / 311
Goodness-of-fit on F^2		1.082
Final R indices [$I>2\sigma(I)$]	R1 wR2	0.0389 0.0869
R indices (all data)	R1 wR2	0.0533 0.0929
Largest Δ peak and hole (e.Å^{-3})		0.2929 and -0.229
CCDC deposit number		2368944

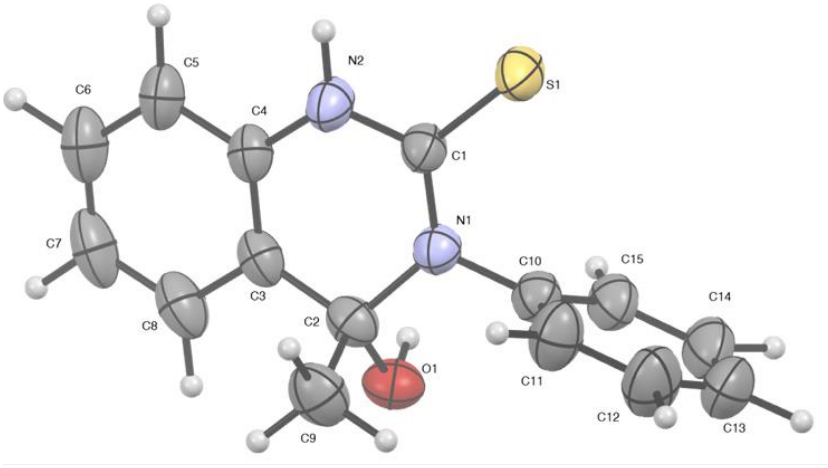
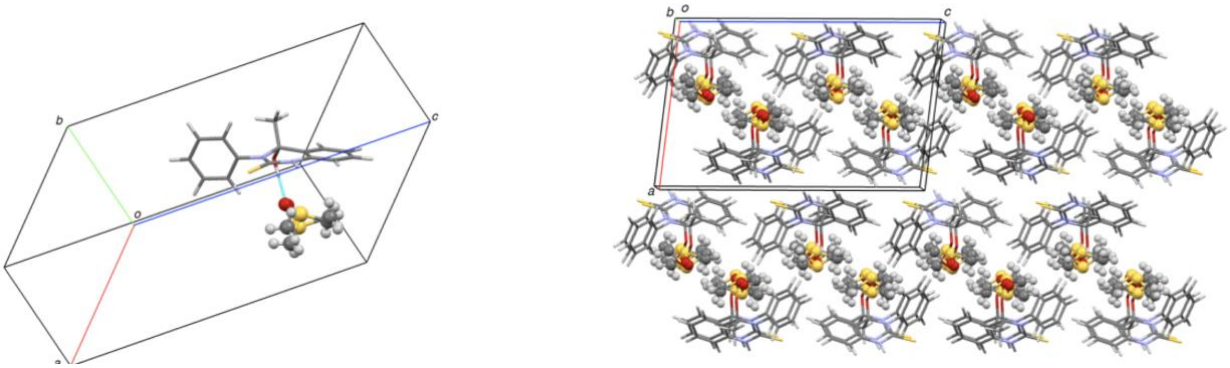


Figure S1 Ortep view of the structure of **5a•H_2O** with the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. The disordered DMSO molecule is not shown for clarity.



(a) *(b)*

Figure S2 View of the asymmetric unit of the crystal (the cyan dashed line indicates the h-bond between the two molecules present in the asu) *(a)* and partial view of the crystal packing down the ***b*** direction *(b)*. The molecule of interest is represented in capped sticks whereas the disordered DMSO is in ball-and-stick representation.

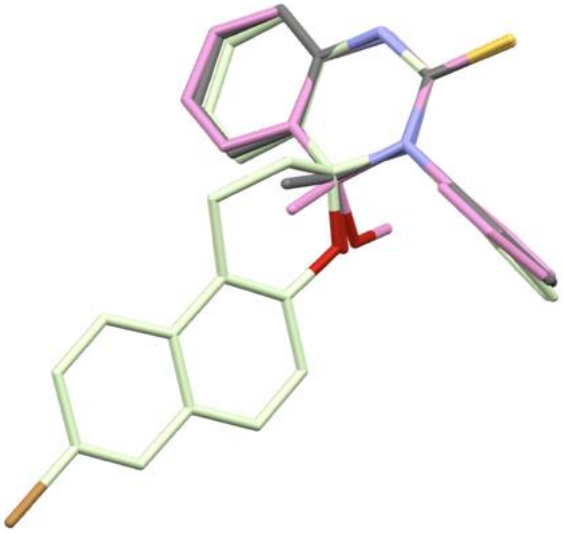


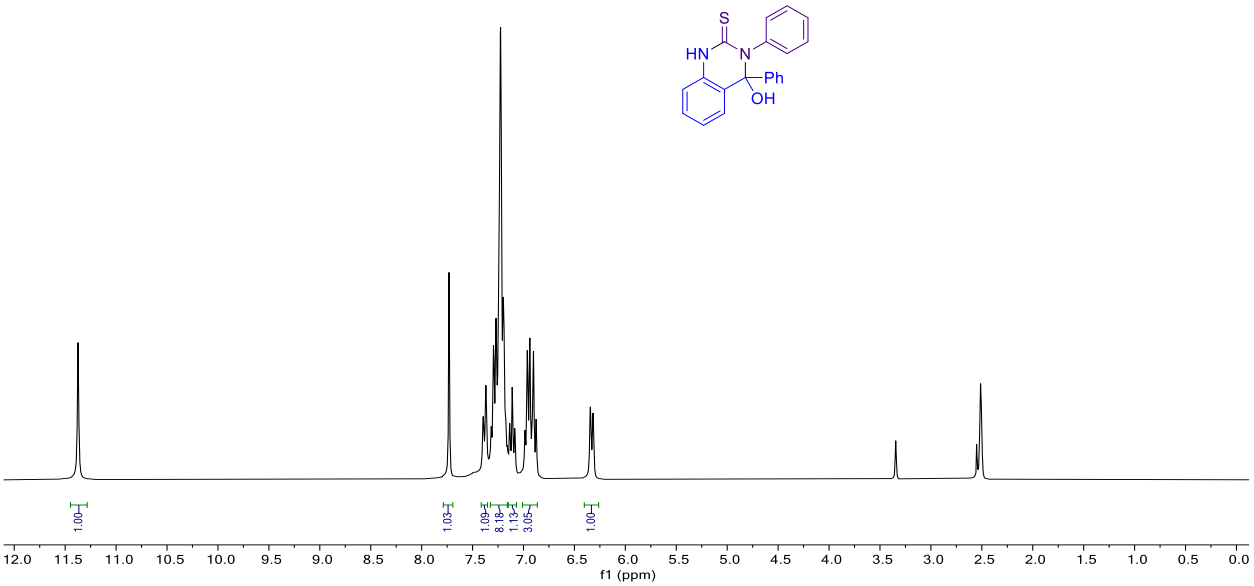
Figure S3

Overlay between the structure (carbon atoms in grey) and CSD Refcode BULQEH [7] (carbon atoms in pink) and JOGQOP (in green water). [11]

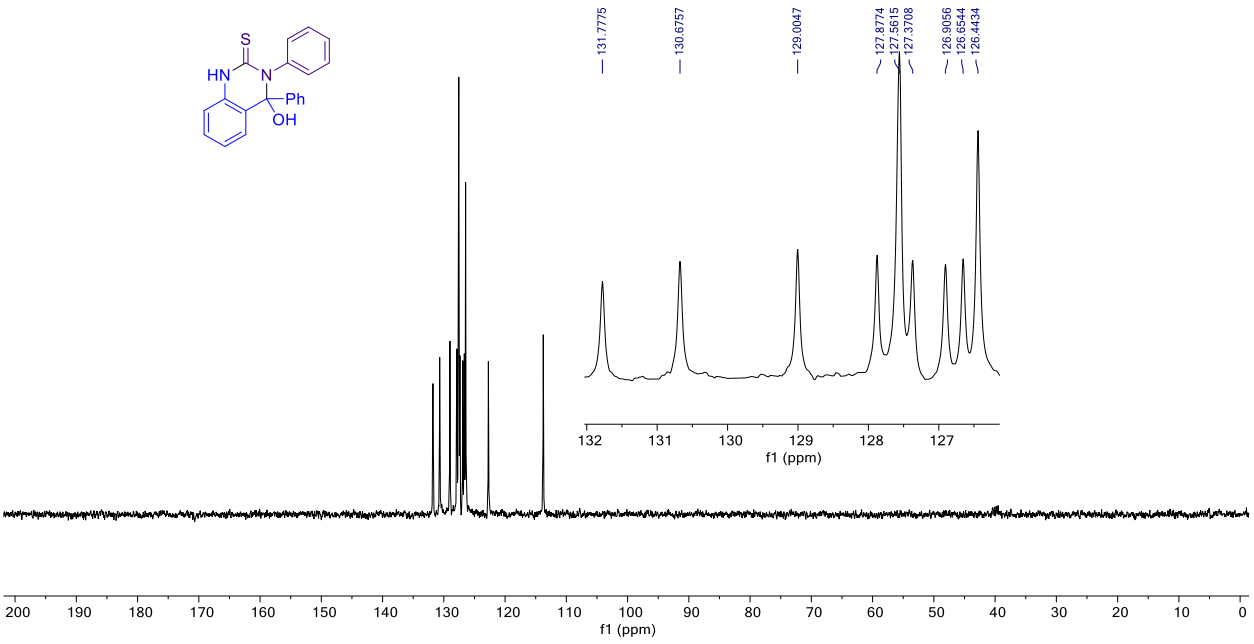
Copies of ^{1}H and ^{13}NMR spectra

4-Hydroxy-3,4-diphenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3a)

^{1}H NMR (300 MHz, DMSO-d_6)

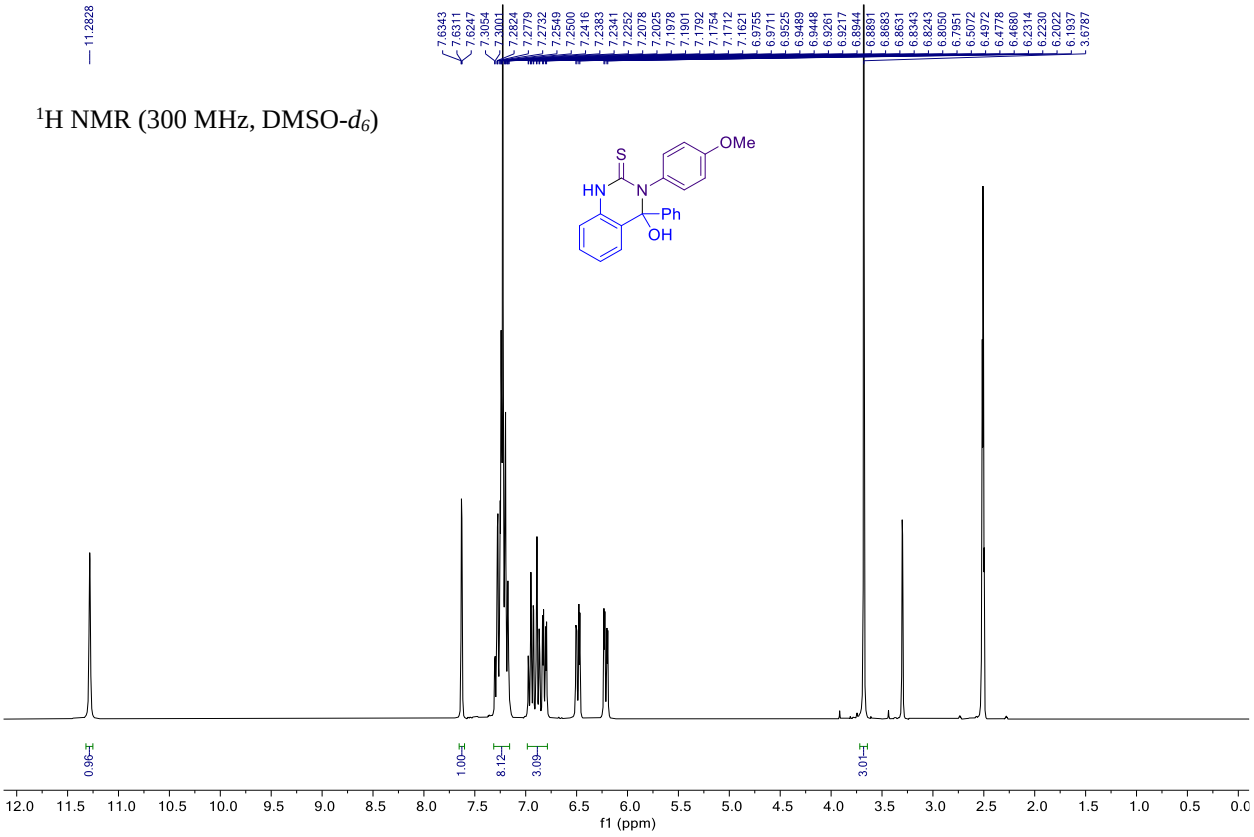


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

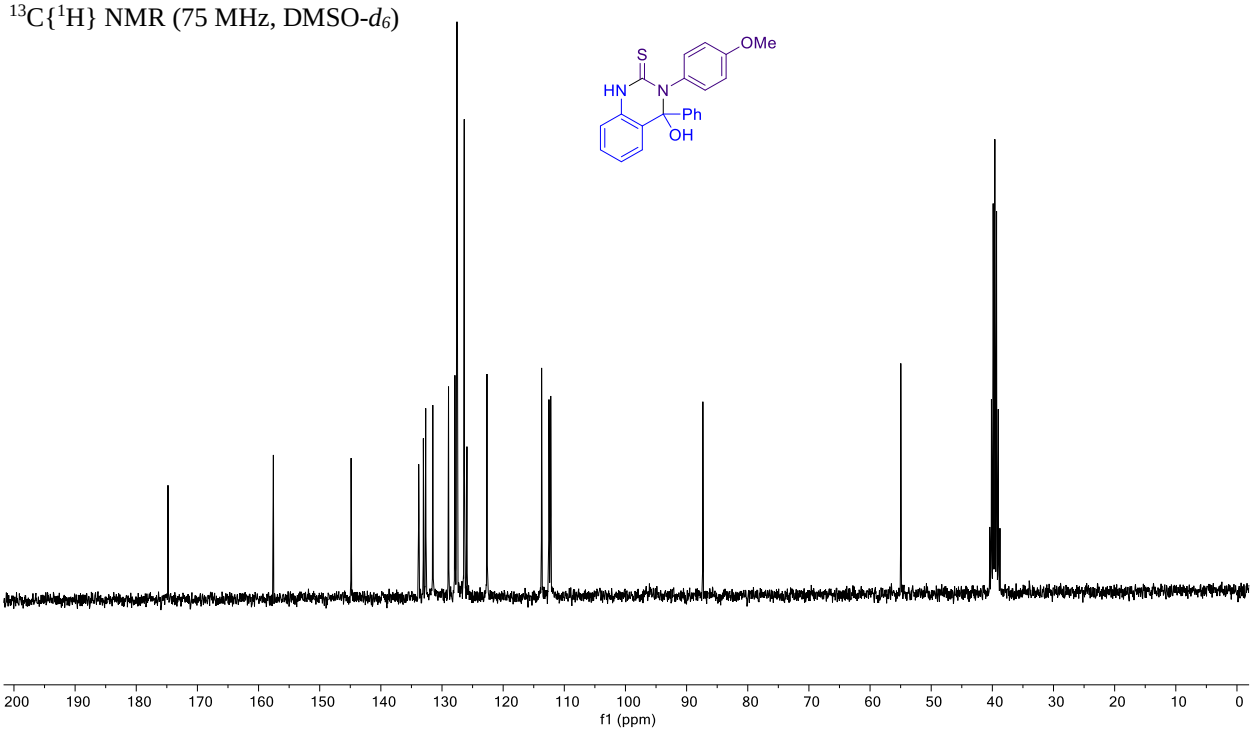


4-Hydroxy-3-(4-methoxyphenyl)-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3b)

^{1}H NMR (300 MHz, DMSO-d_6)

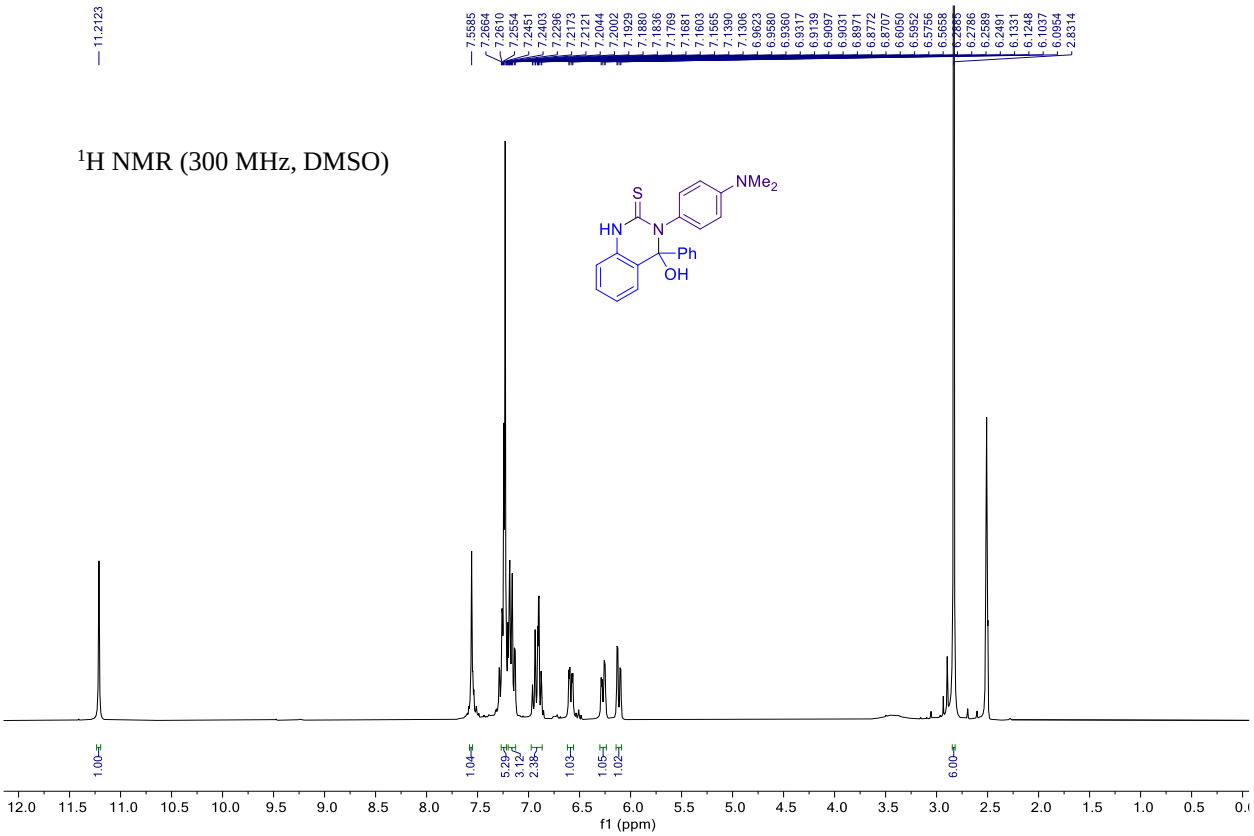


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

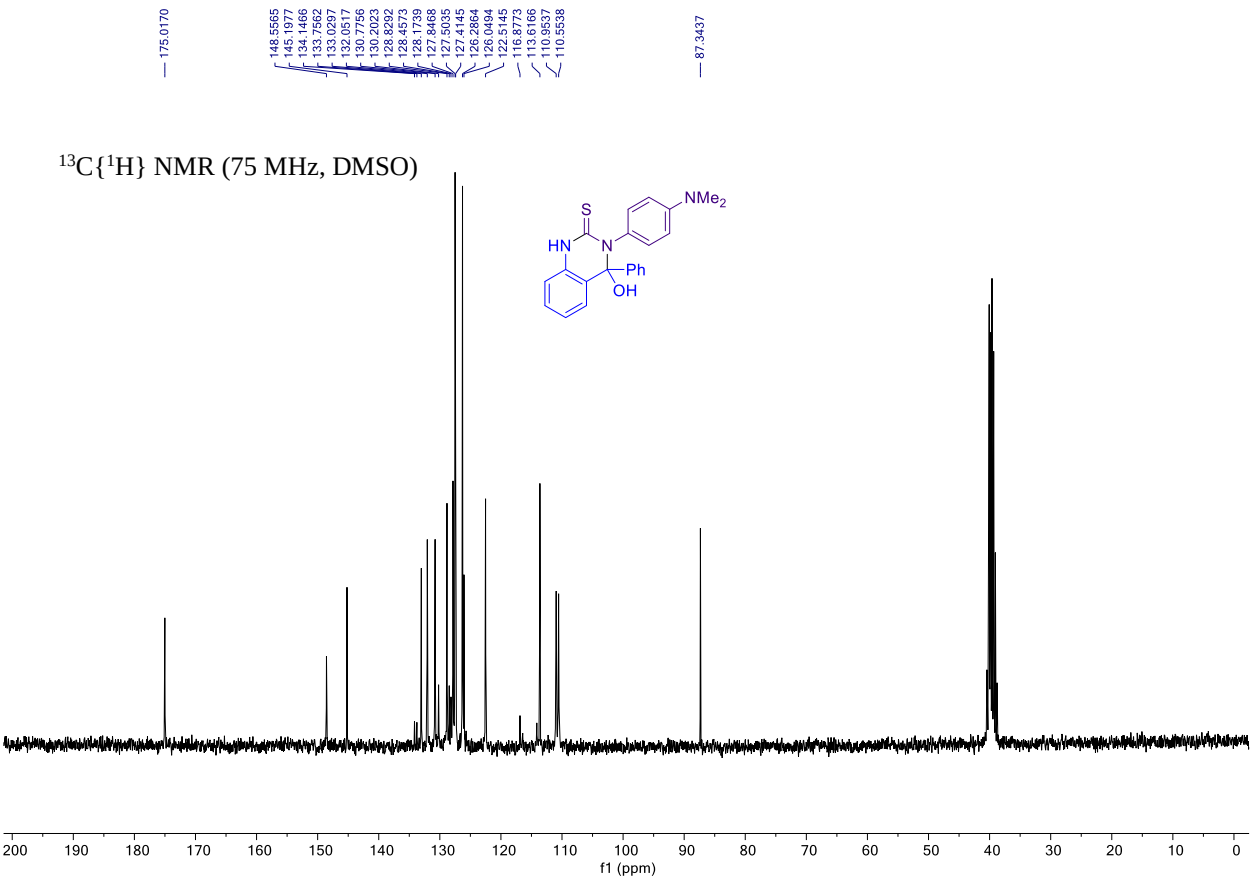


3-(4-(Dimethylamino)phenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3c)

^{1}H NMR (300 MHz, DMSO)

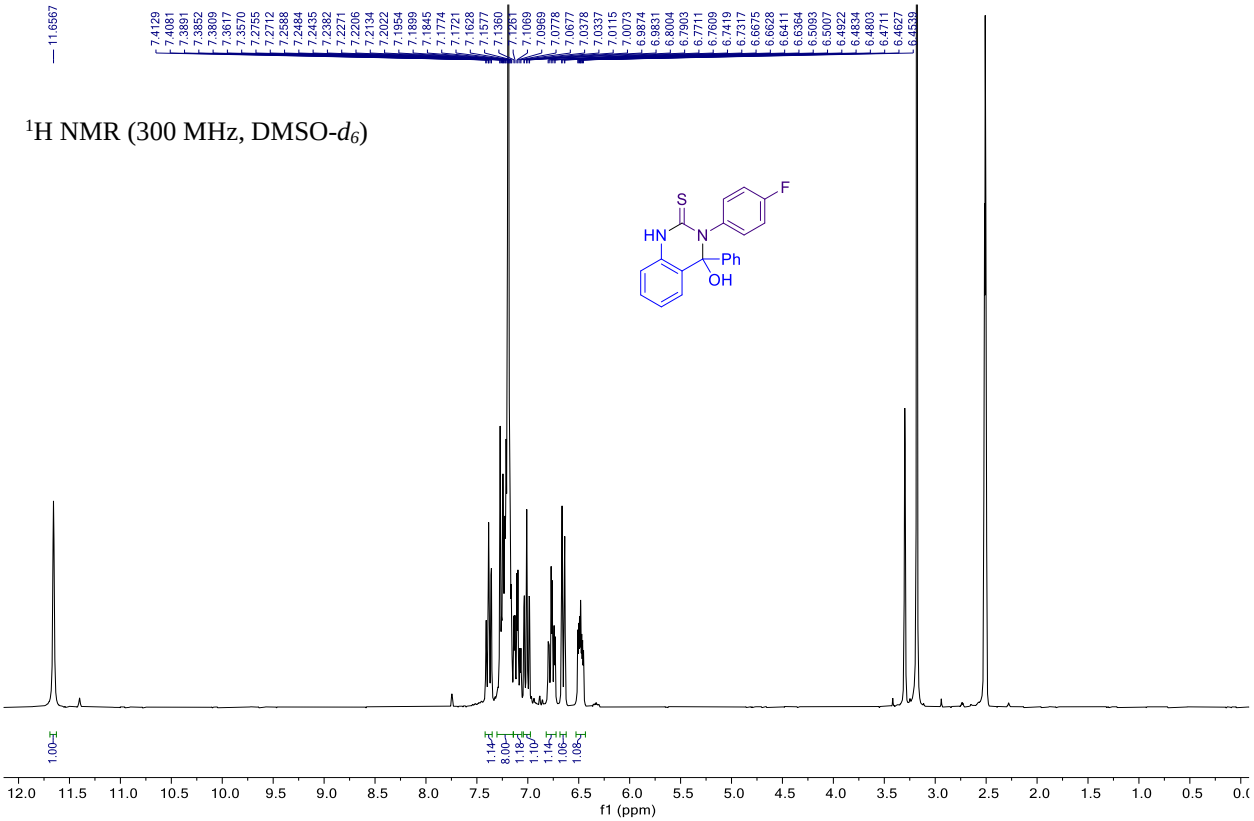


^{13}C{^{1}H} NMR (75 MHz, DMSO)

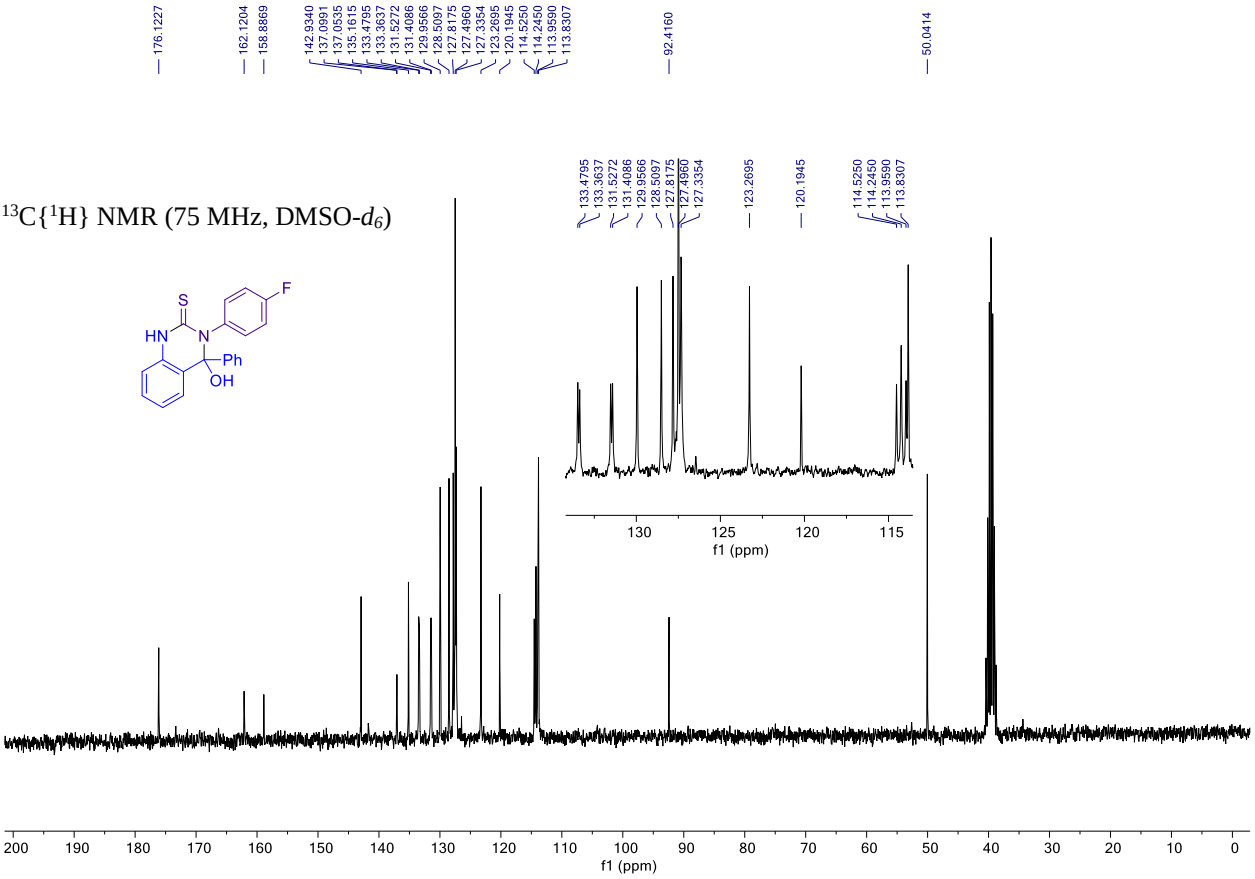


3-(4-Fluorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3d)

^{1}H NMR (300 MHz, DMSO-d_6)

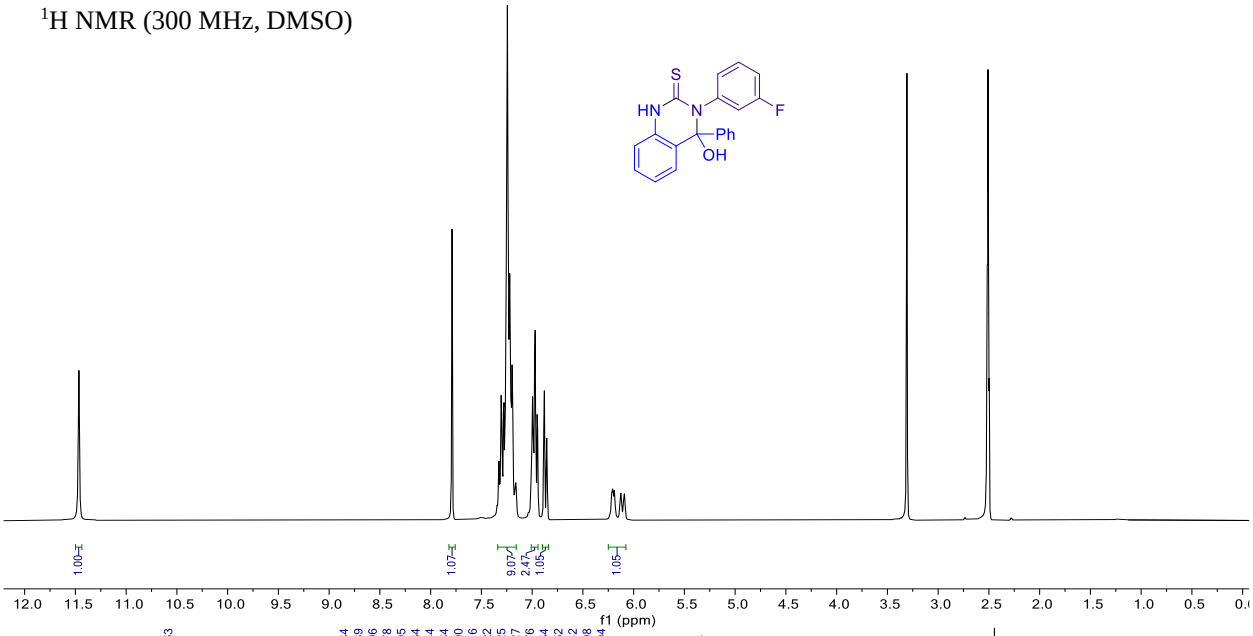


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

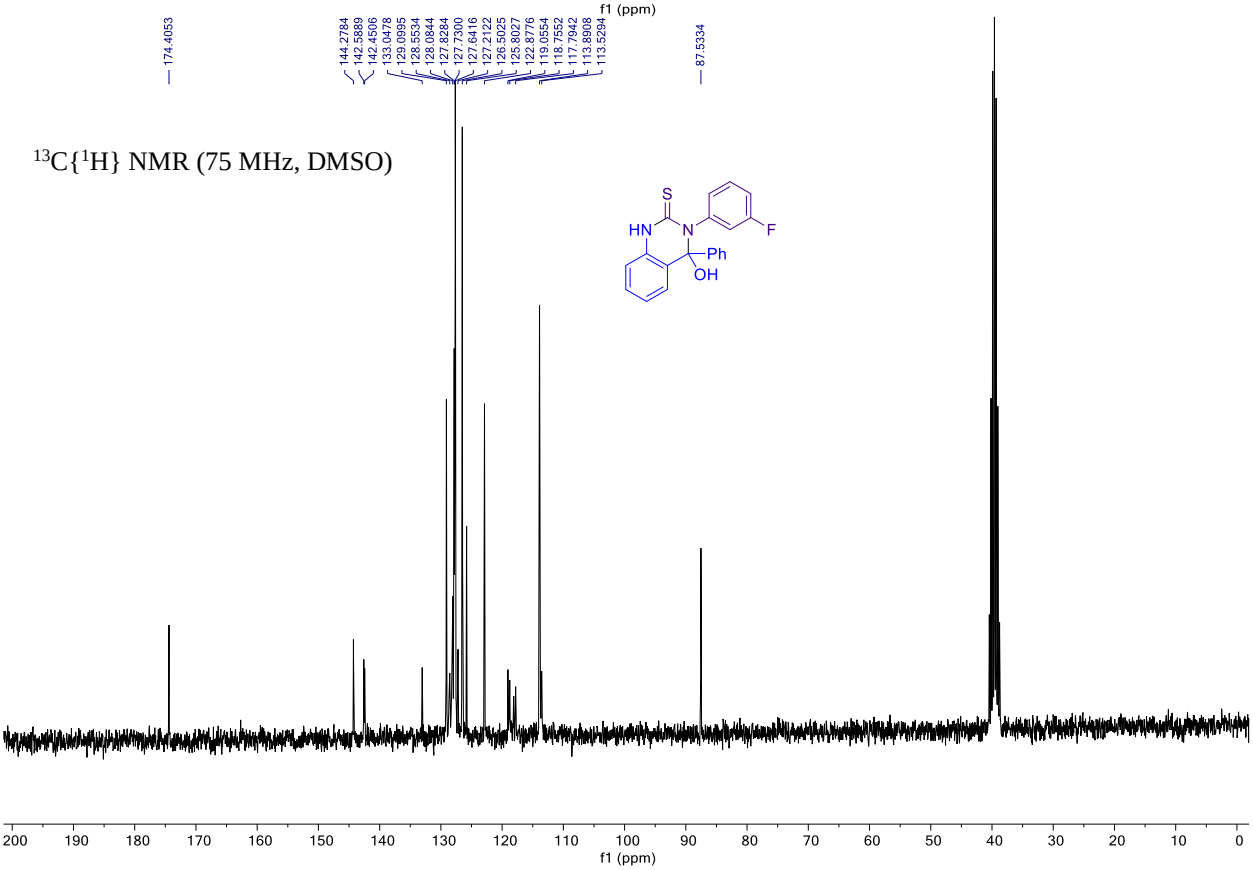


3-(3-Fluorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3e)

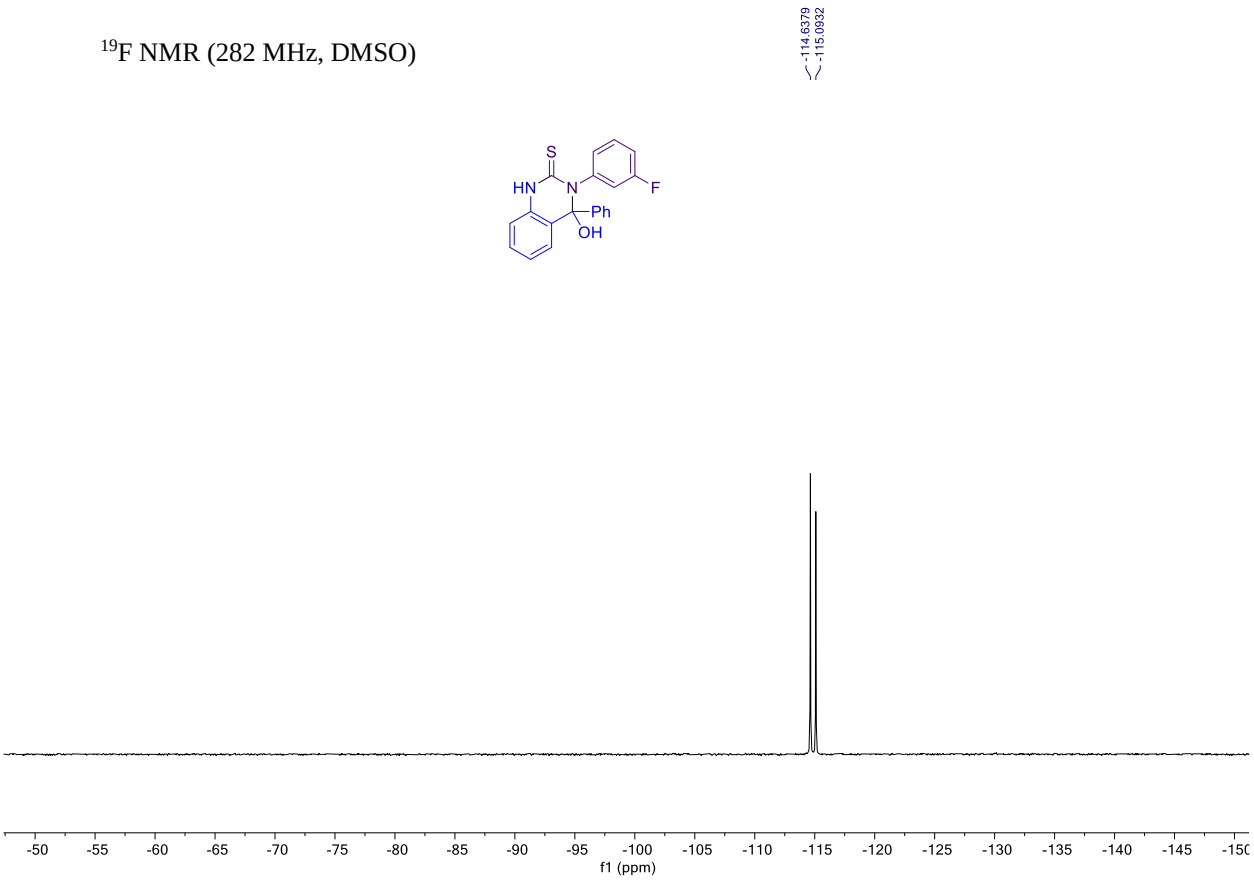
^{1}H NMR (300 MHz, DMSO)



^{13}C{^{1}H} NMR (75 MHz, DMSO)

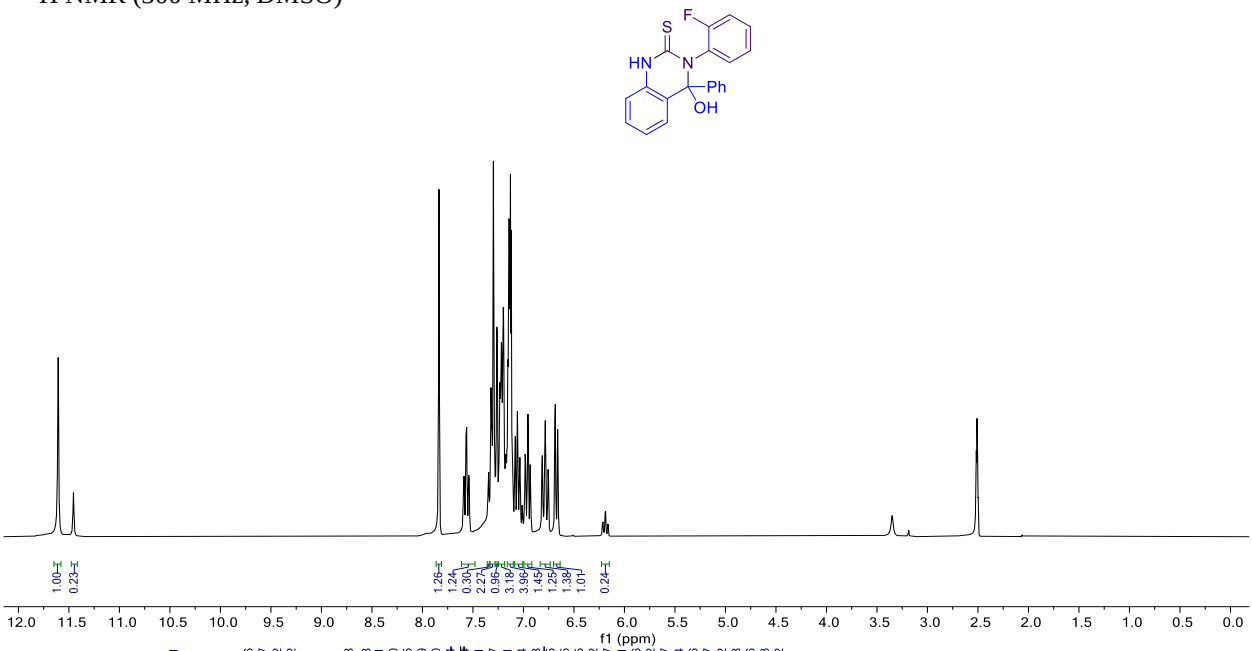


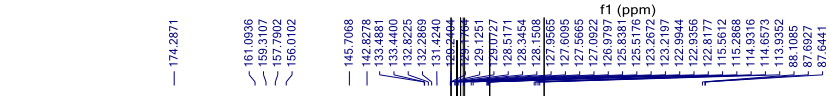
^{19}F NMR (282 MHz, DMSO)



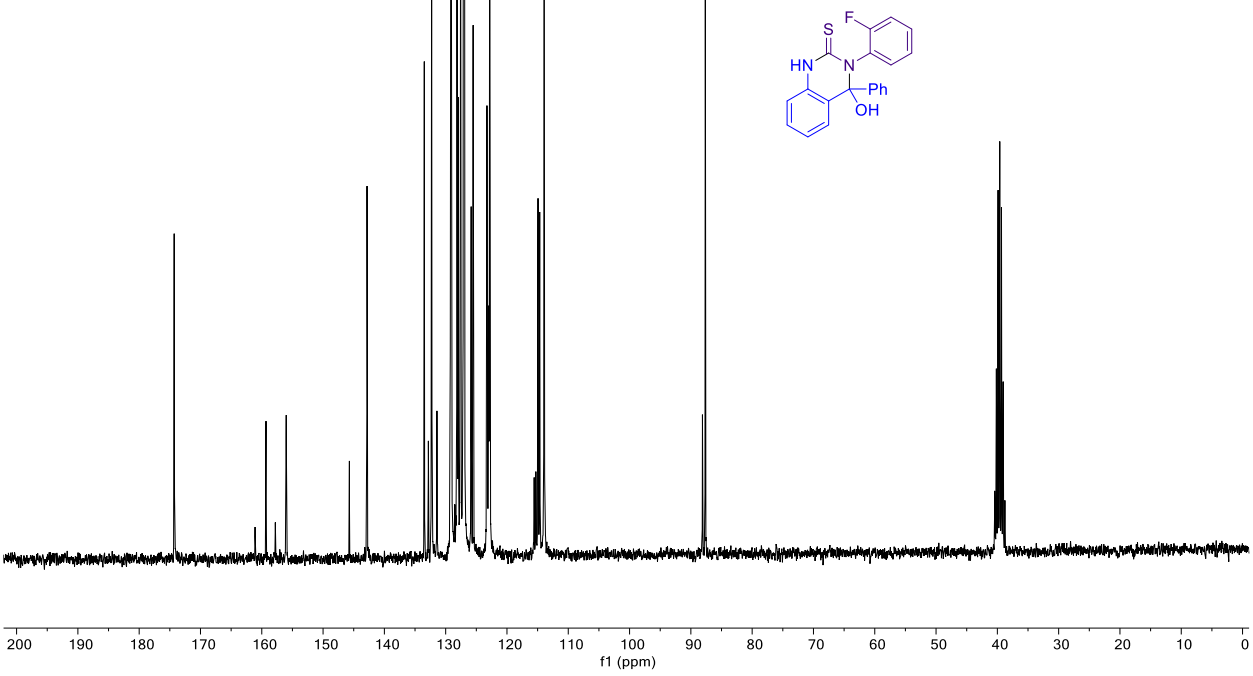
3-(2-Fluorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3f)

^{1}H NMR (300 MHz, DMSO)

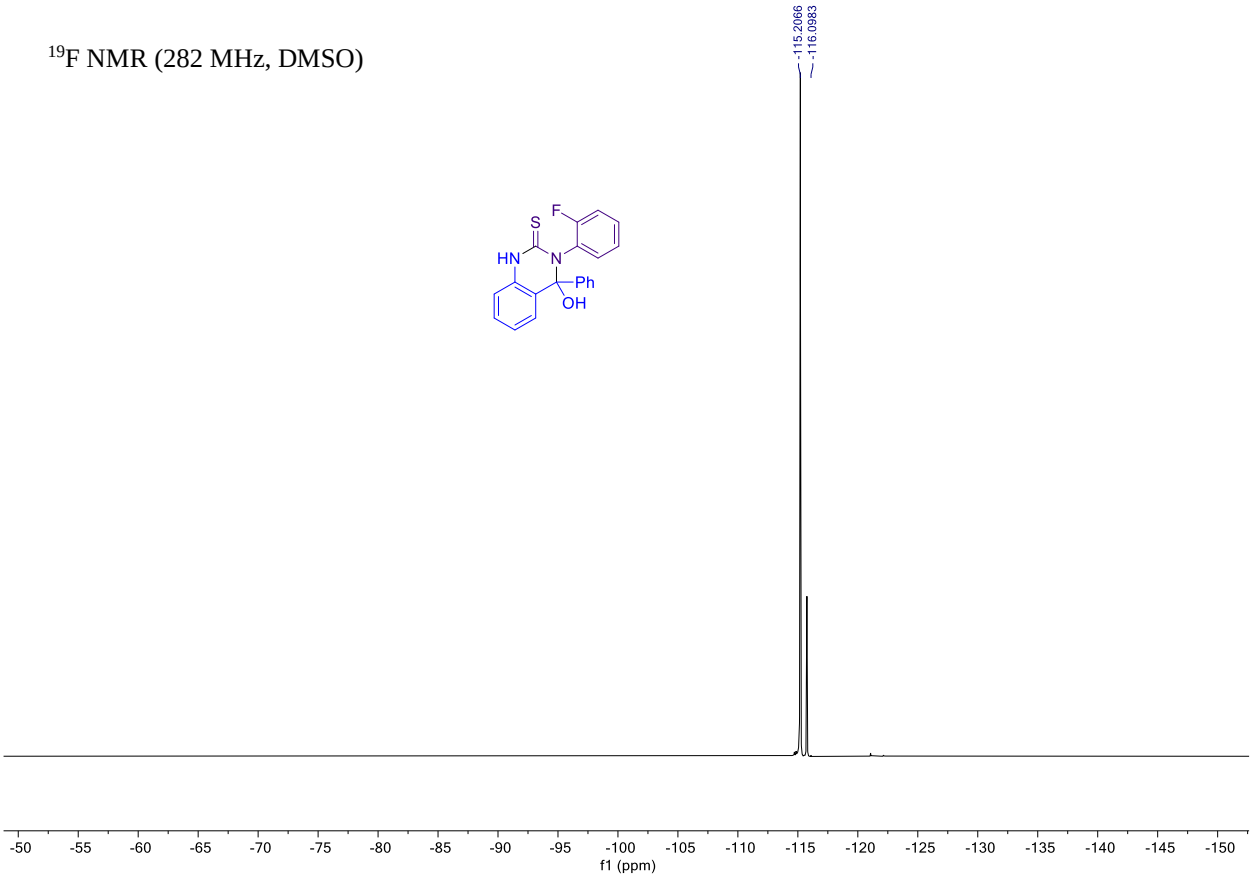




^{13}C{^{1}H} NMR (75 MHz, DMSO)

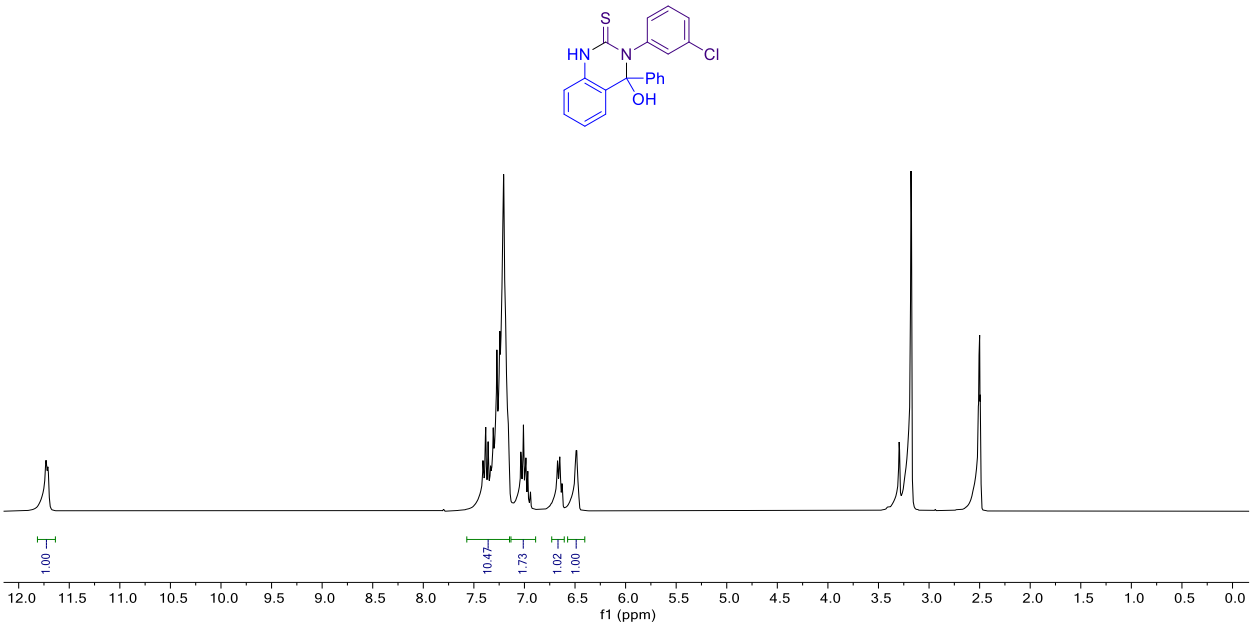


^{19}F NMR (282 MHz, DMSO)

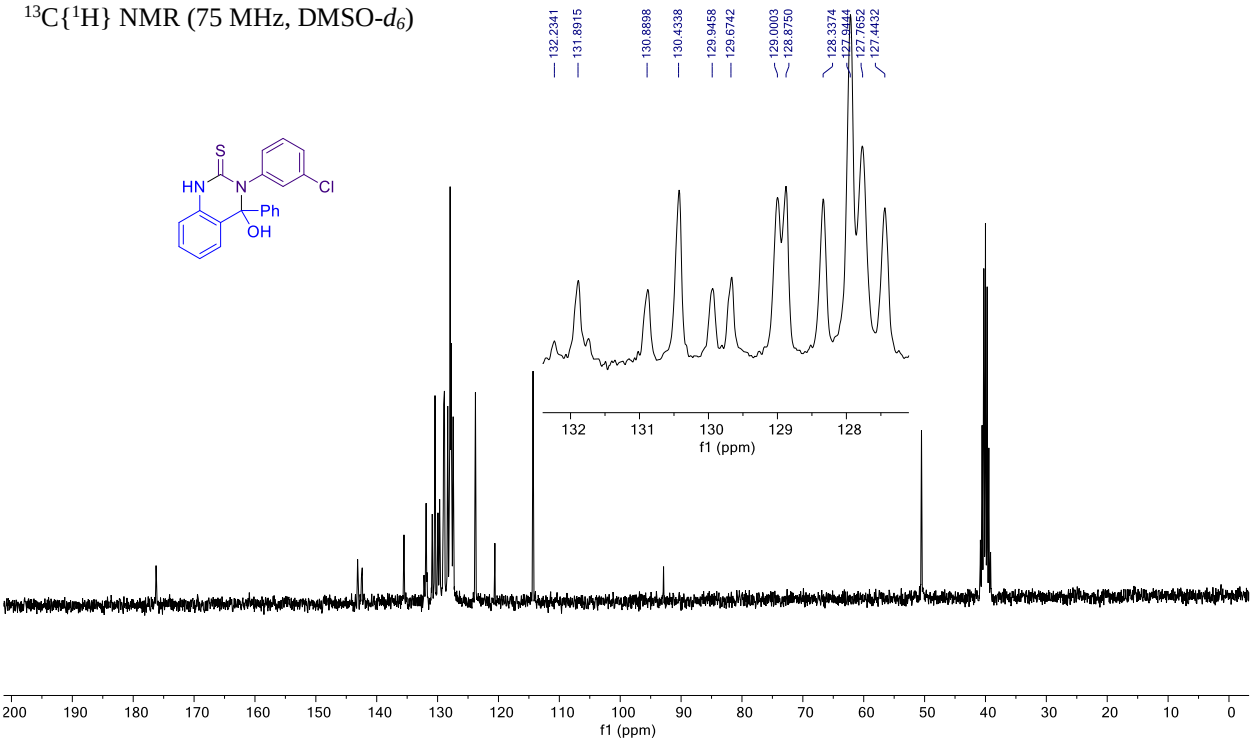


3-(3-Chlorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3g)

^{1}H NMR (300 MHz, DMSO-d_6)

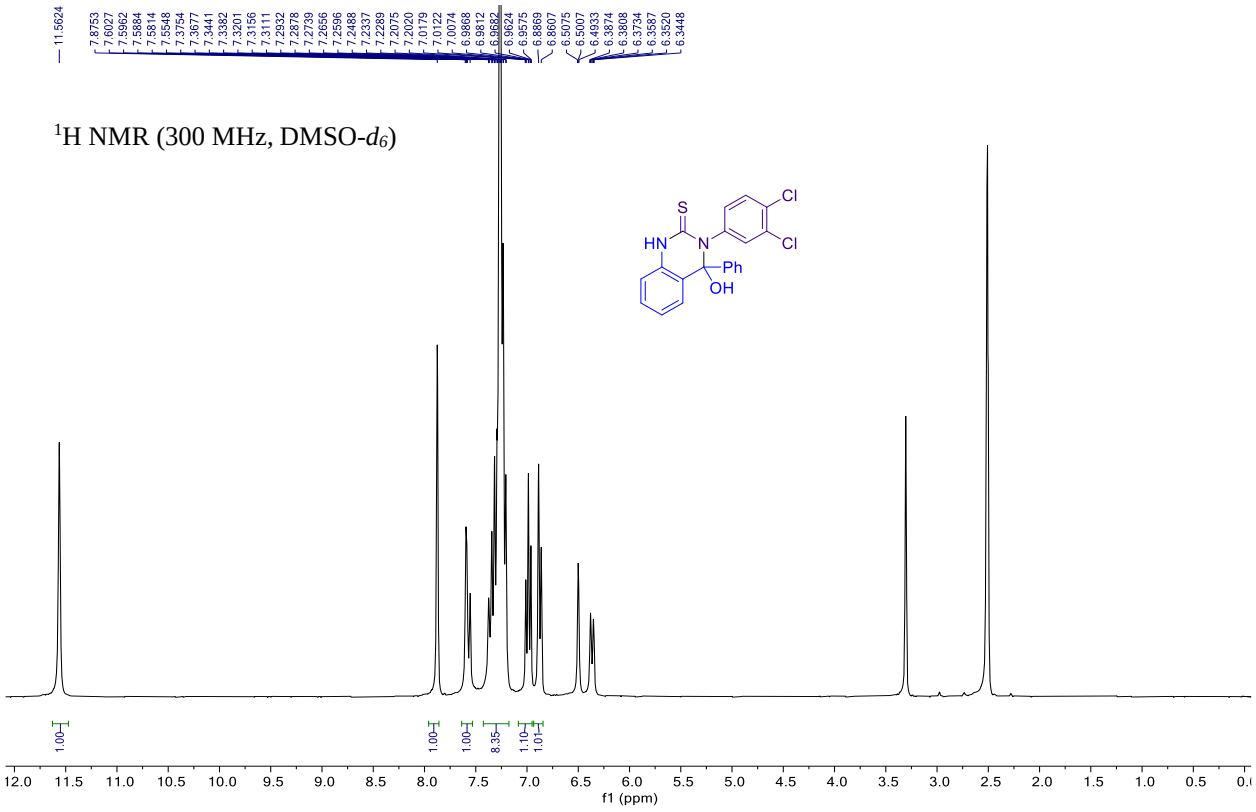


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

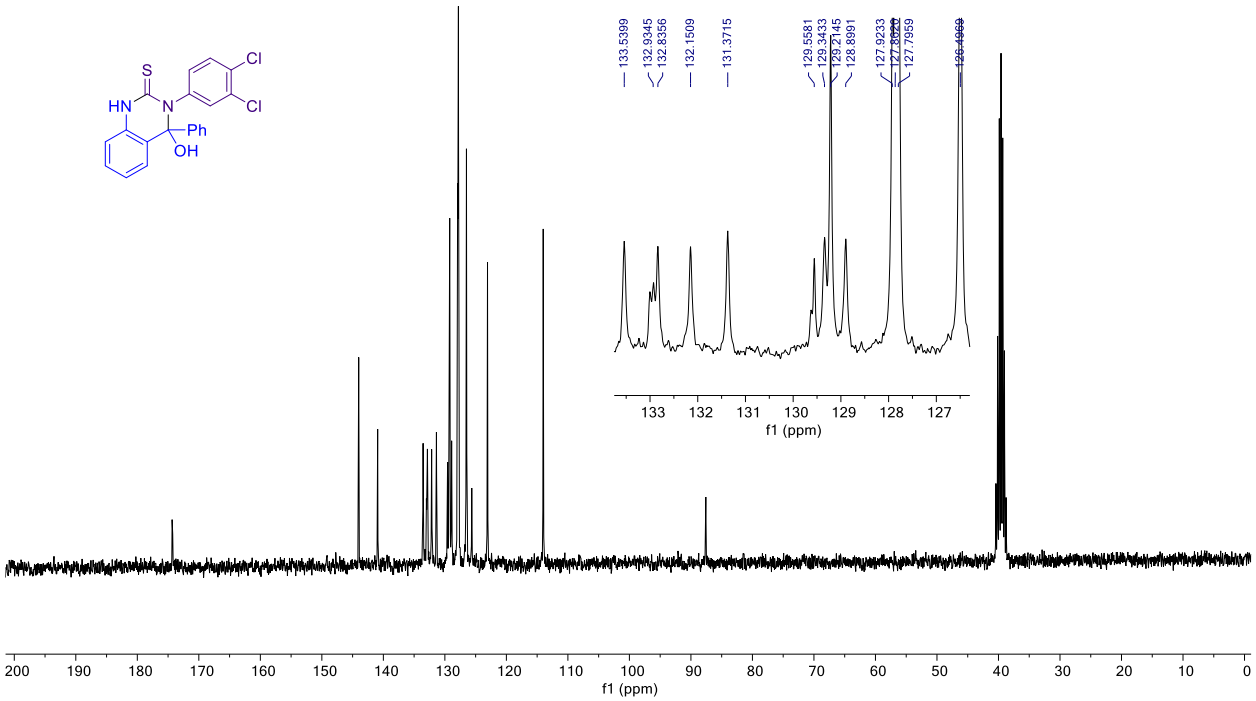


3-(3,4-Dichlorophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3h)

^{1}H NMR (300 MHz, DMSO-d_6)

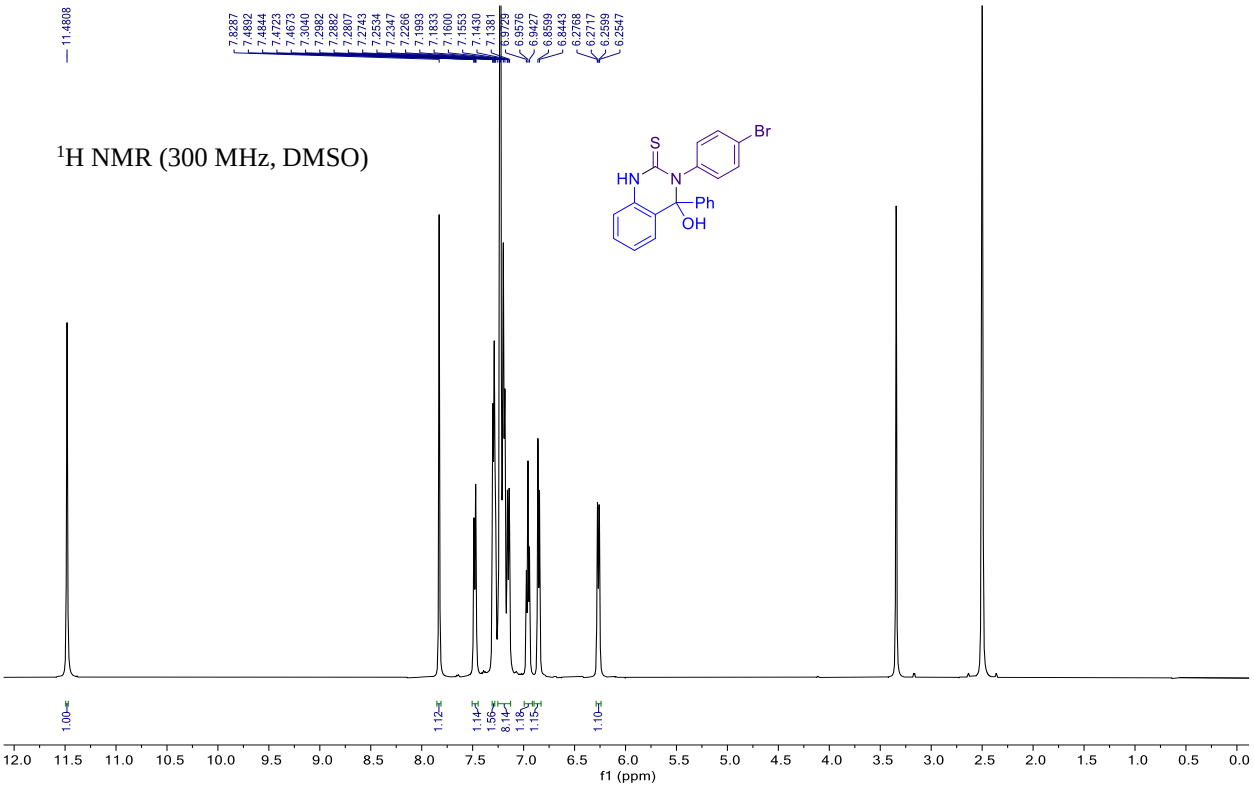


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

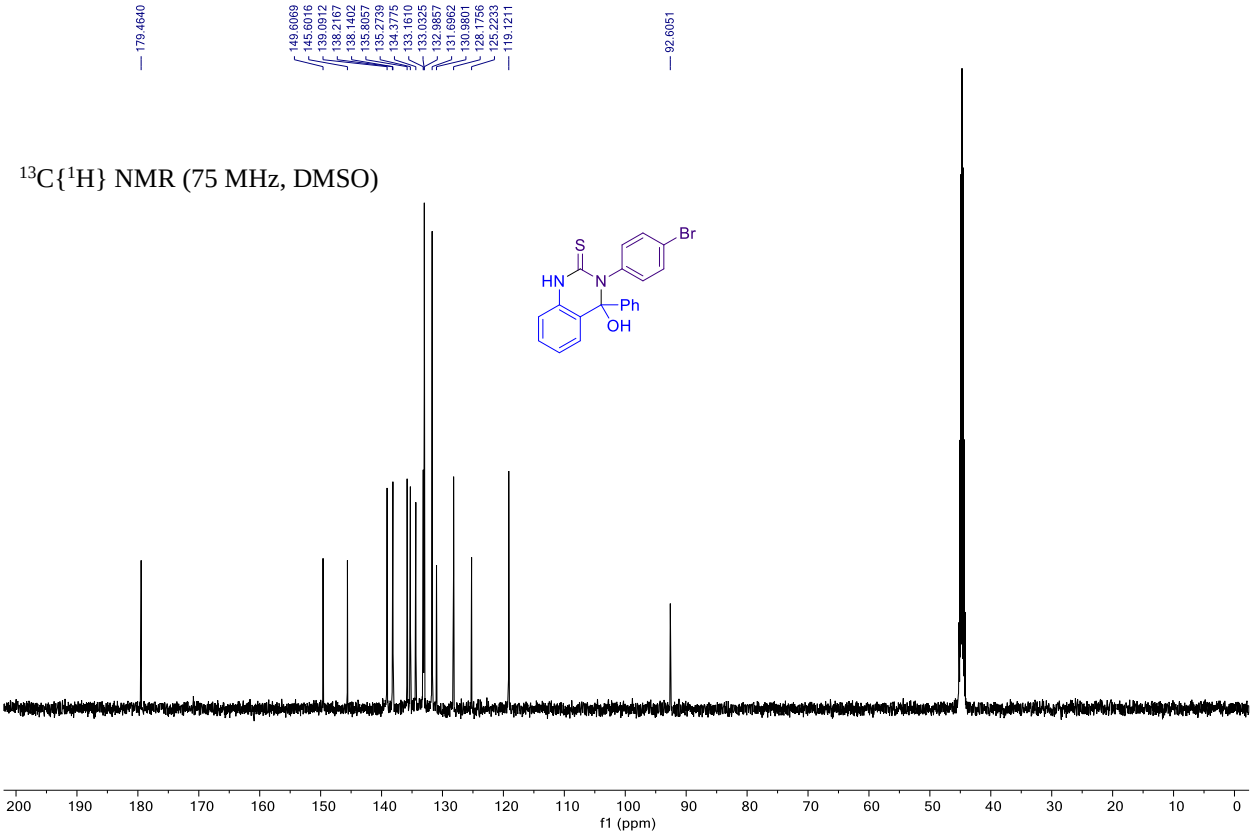


3-(4-Bromophenyl)-4-hydroxy-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3i)

^{1}H NMR (300 MHz, DMSO)

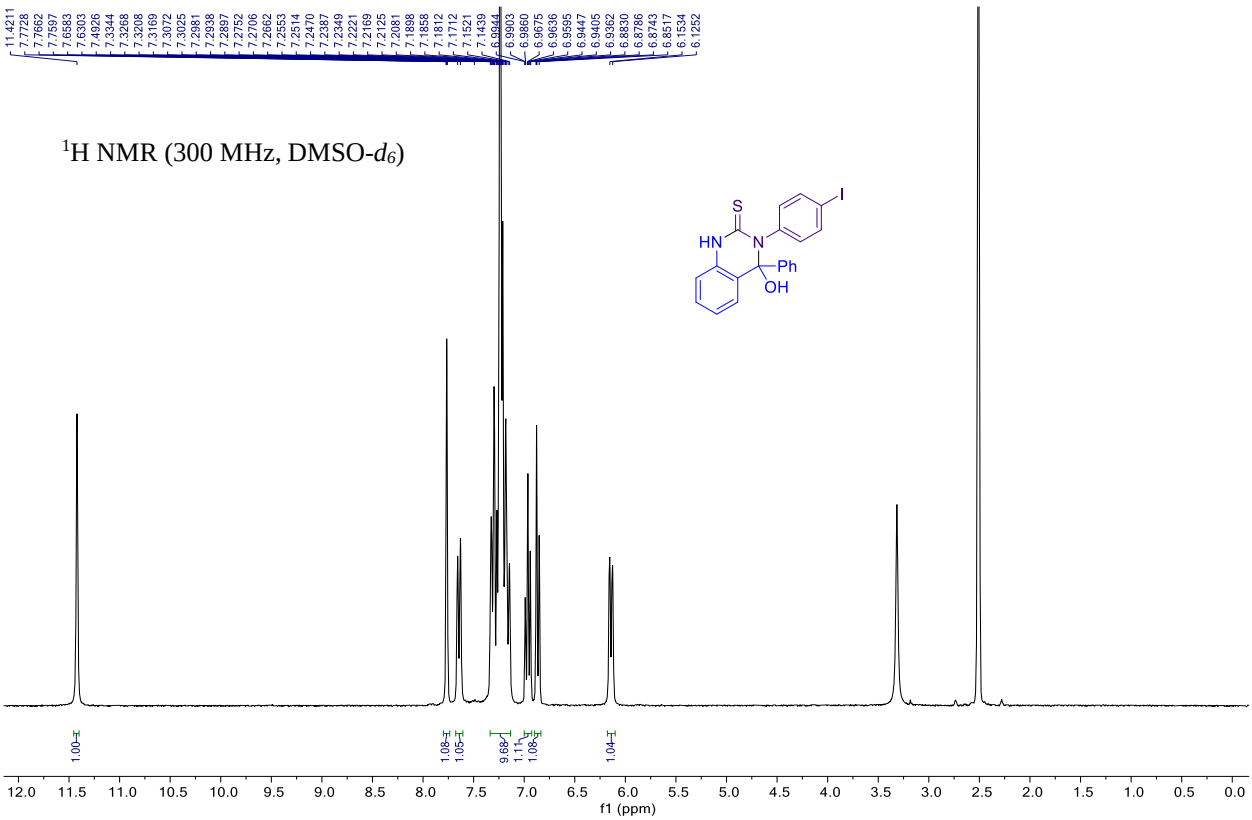


^{13}C{^{1}H} NMR (75 MHz, DMSO)

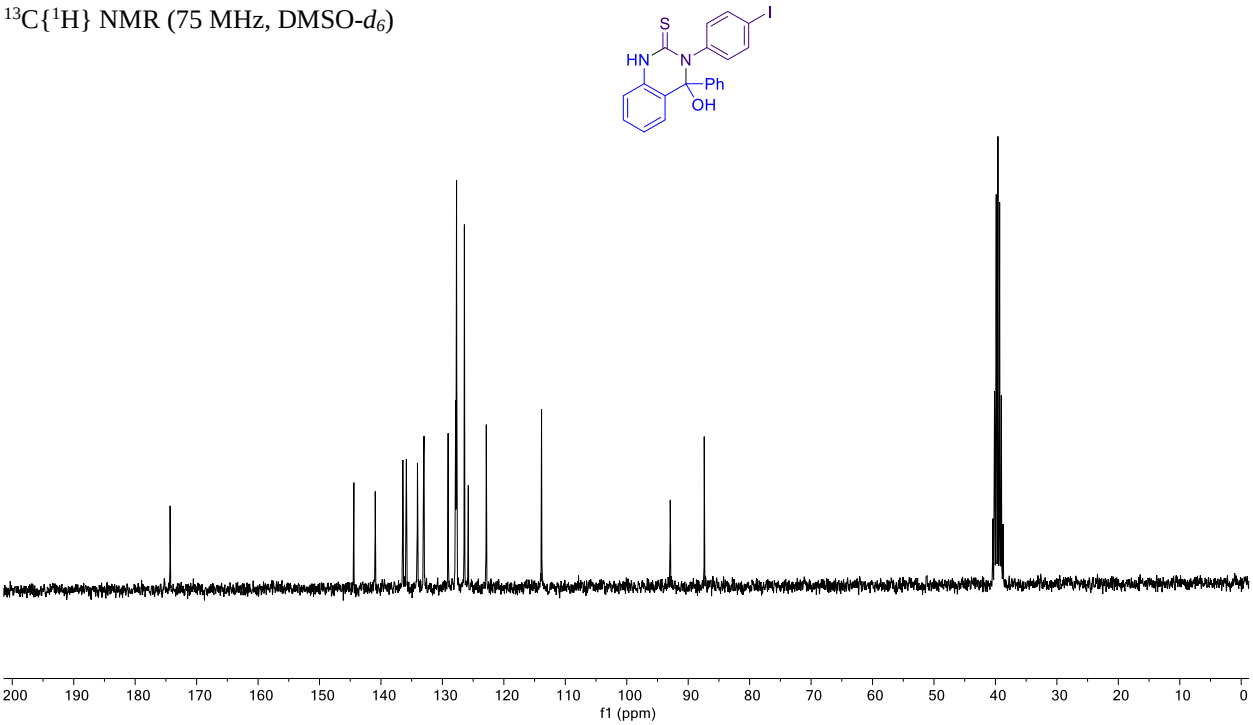


4-Hydroxy-3-(4-iodophenyl)-4-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (3j)

^{1}H NMR (300 MHz, DMSO-d_6)

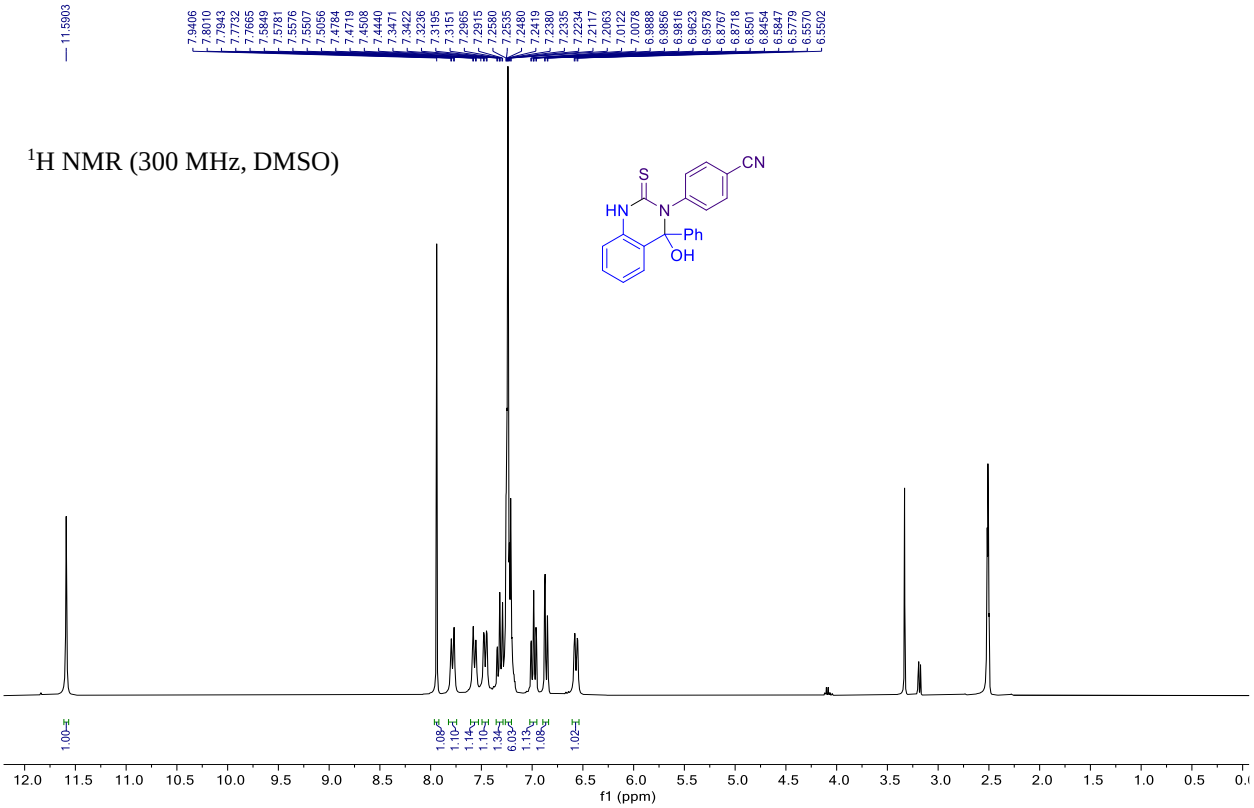


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

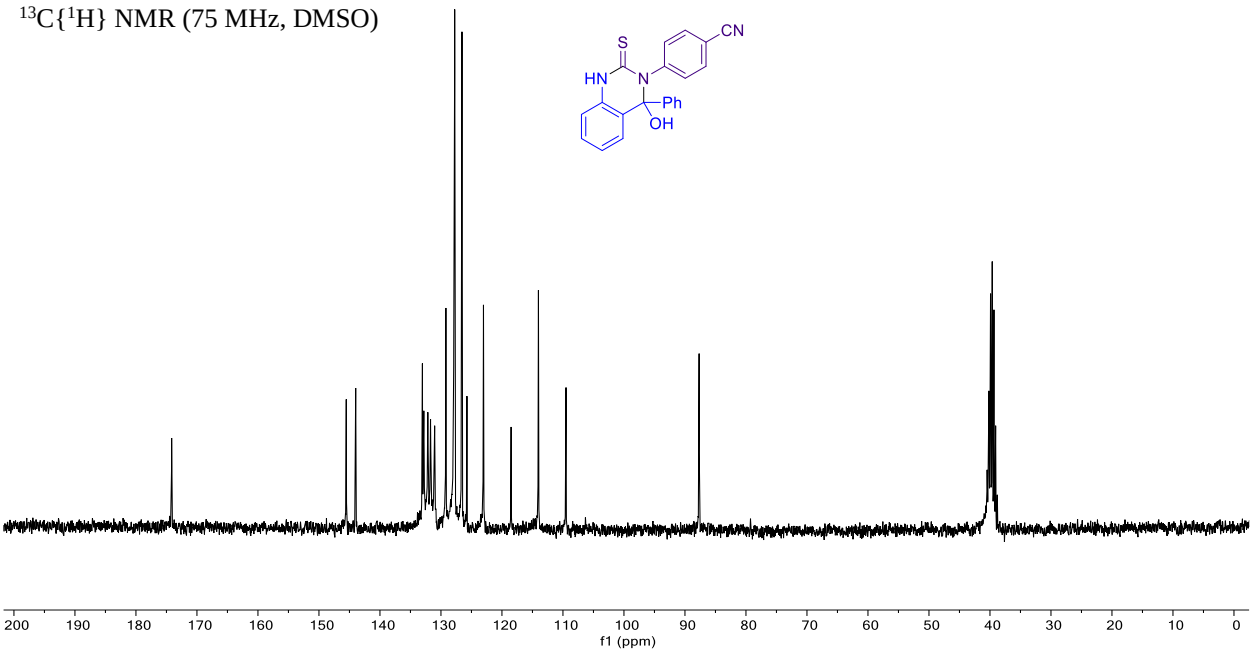


4-(4-Hydroxy-4-phenyl-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzonitrile (3k)

^{1}H NMR (300 MHz, DMSO)

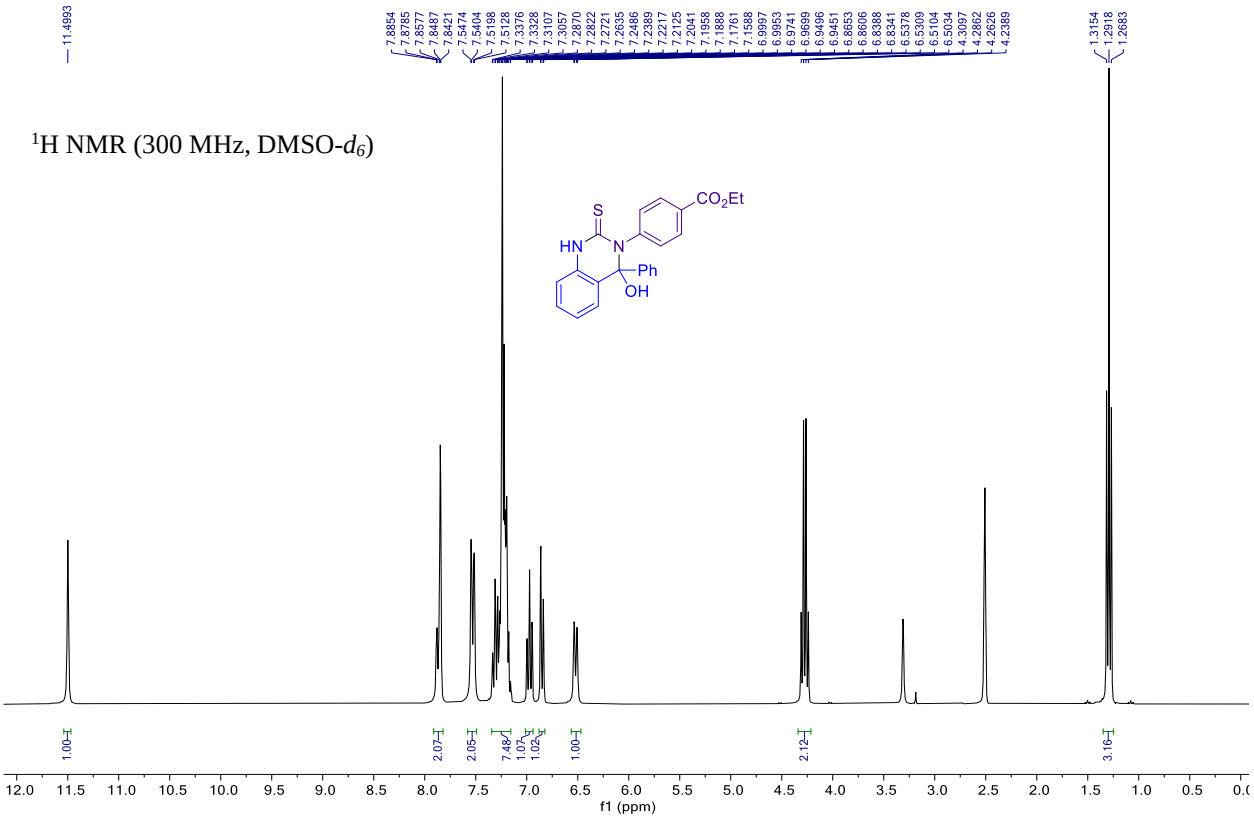


^{13}C{^{1}H} NMR (75 MHz, DMSO)

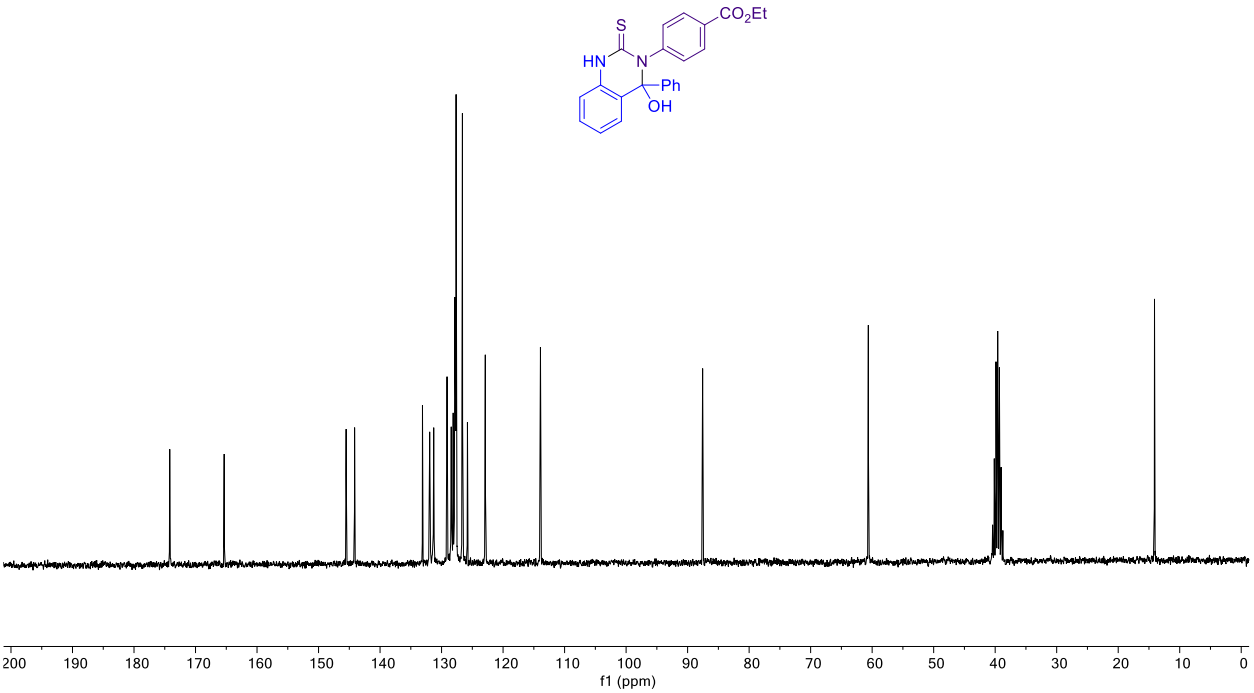


Ethyl 4-(4-hydroxy-4-phenyl-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzoate (3l)

^{1}H NMR (300 MHz, DMSO-d_6)

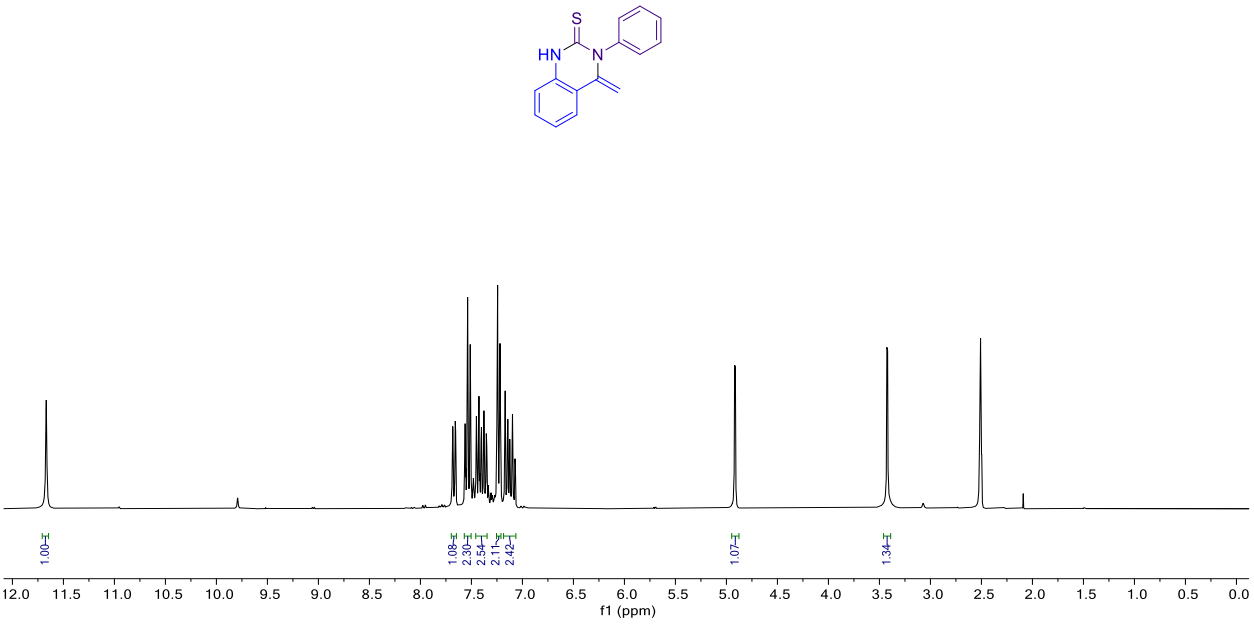


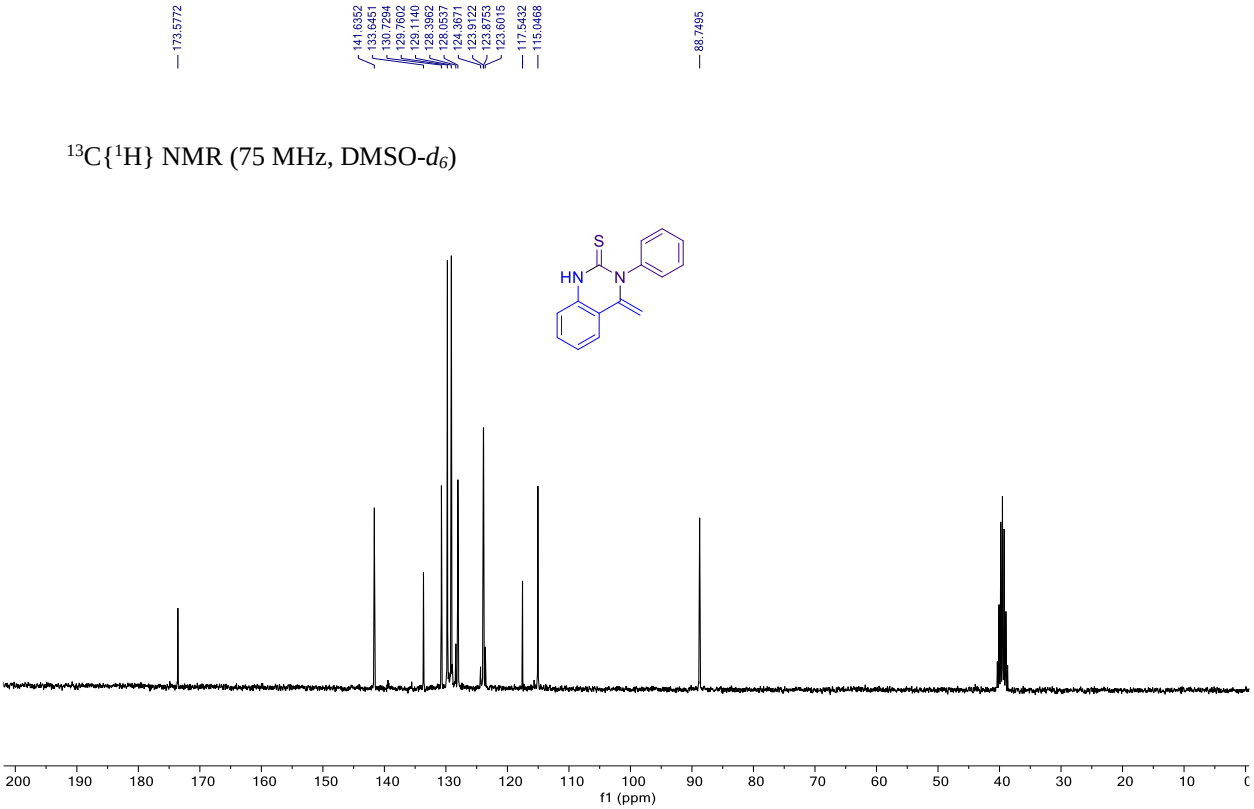
^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)



4-Methylene-3-phenyl-3,4-dihydroquinazoline-2(1*H*)-thione (5a)

^{1}H NMR (300 MHz, DMSO-d_6)

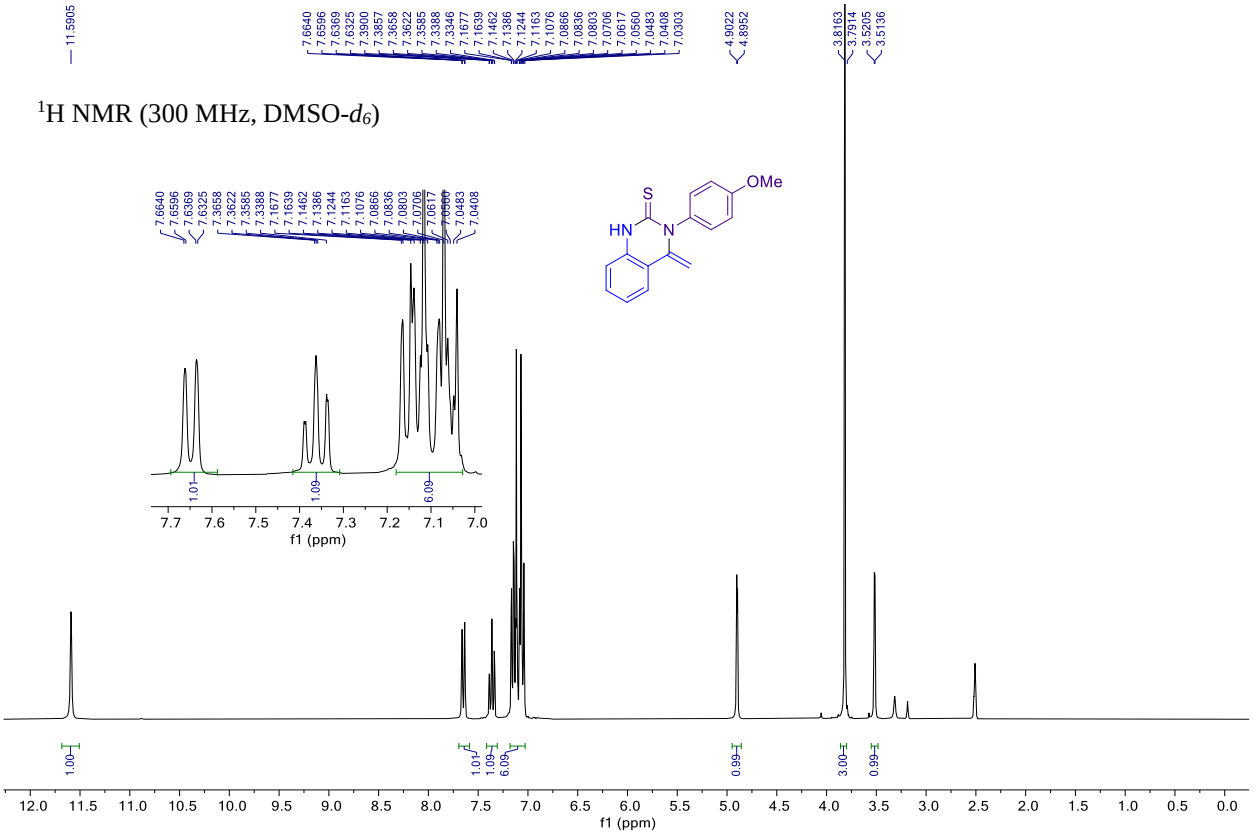




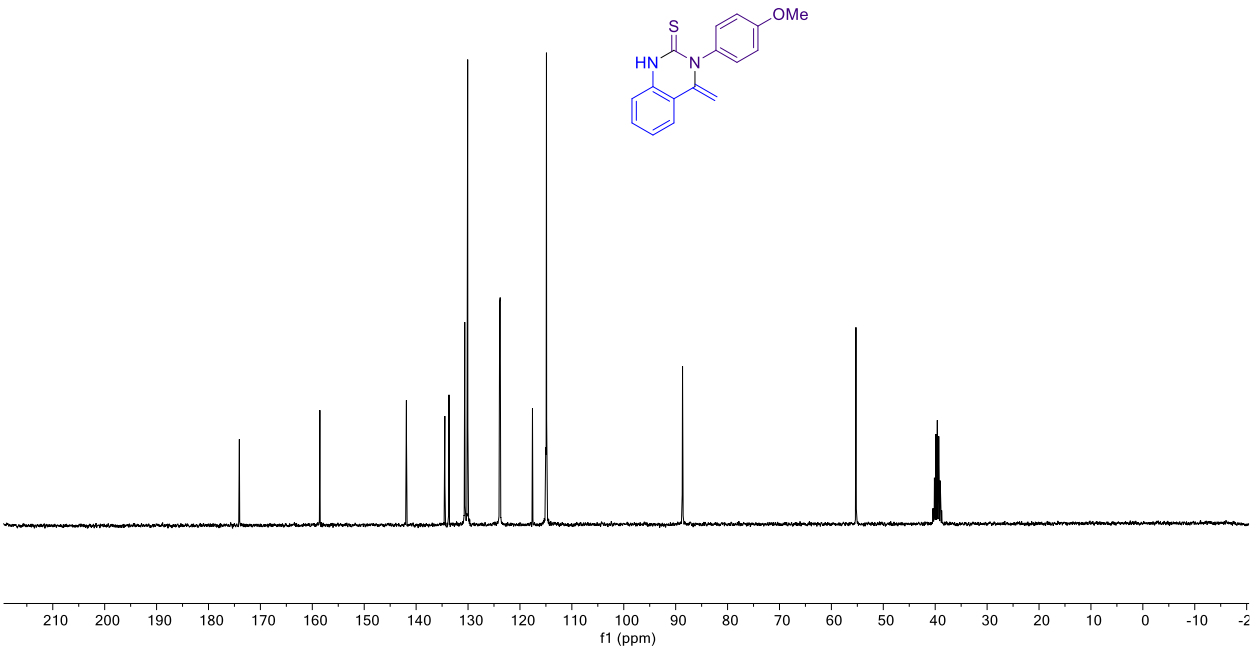
^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

3-(4-Methoxyphenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5b)

^{1}H NMR (300 MHz, DMSO-d_6)

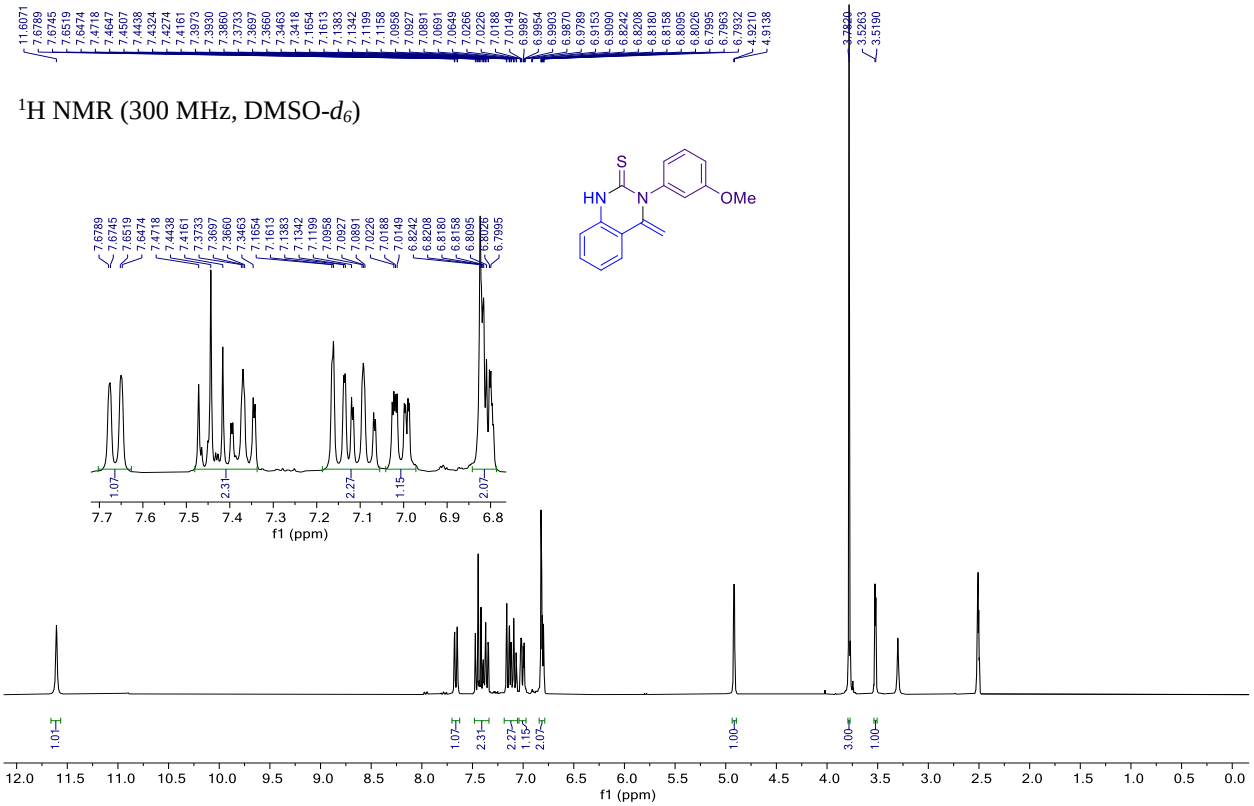


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

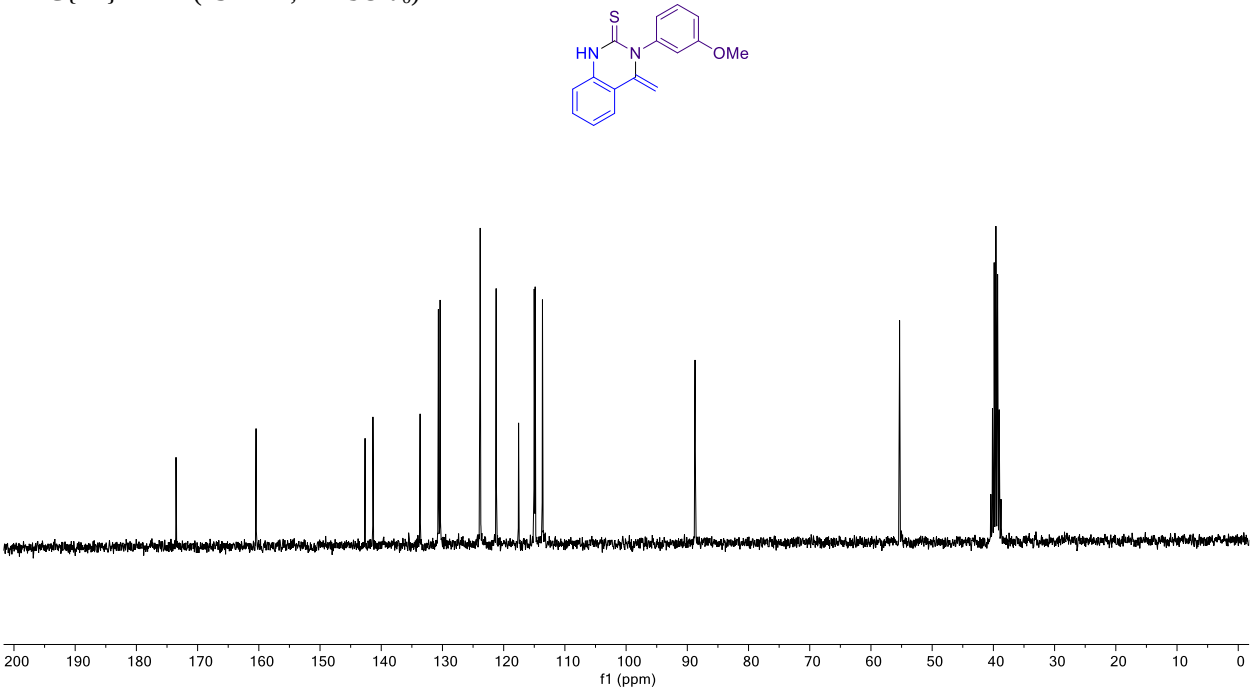


3-(3-Methoxyphenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5c)

^{1}H NMR (300 MHz, DMSO-d_6)

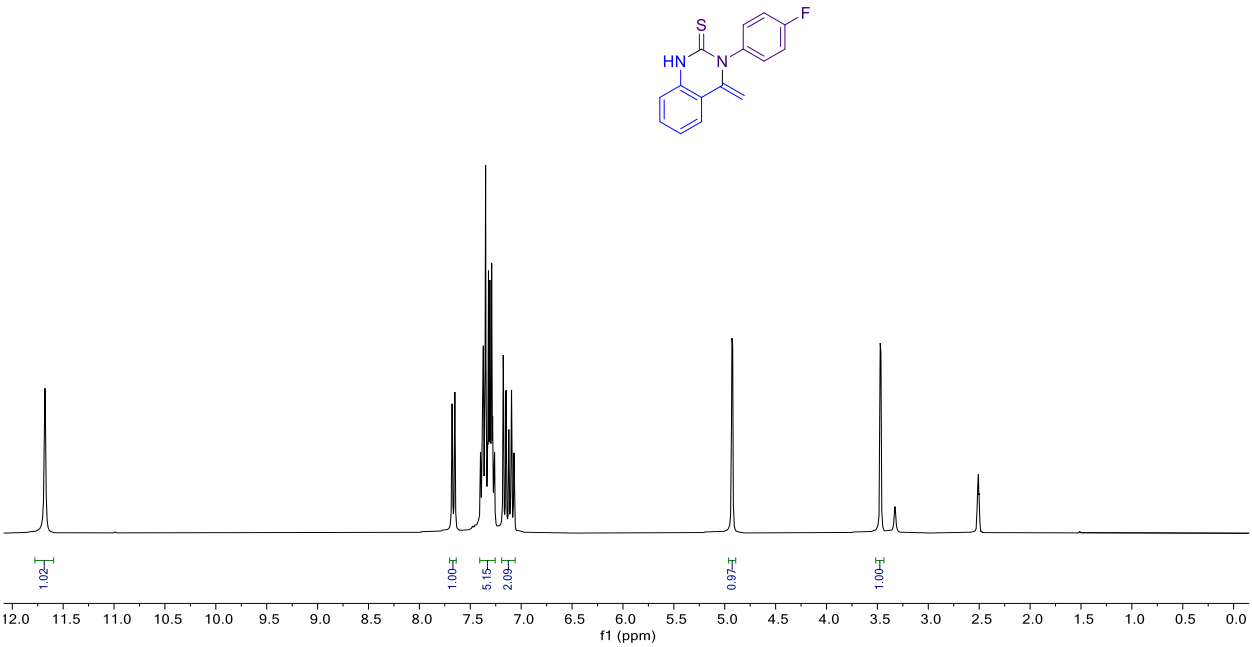


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

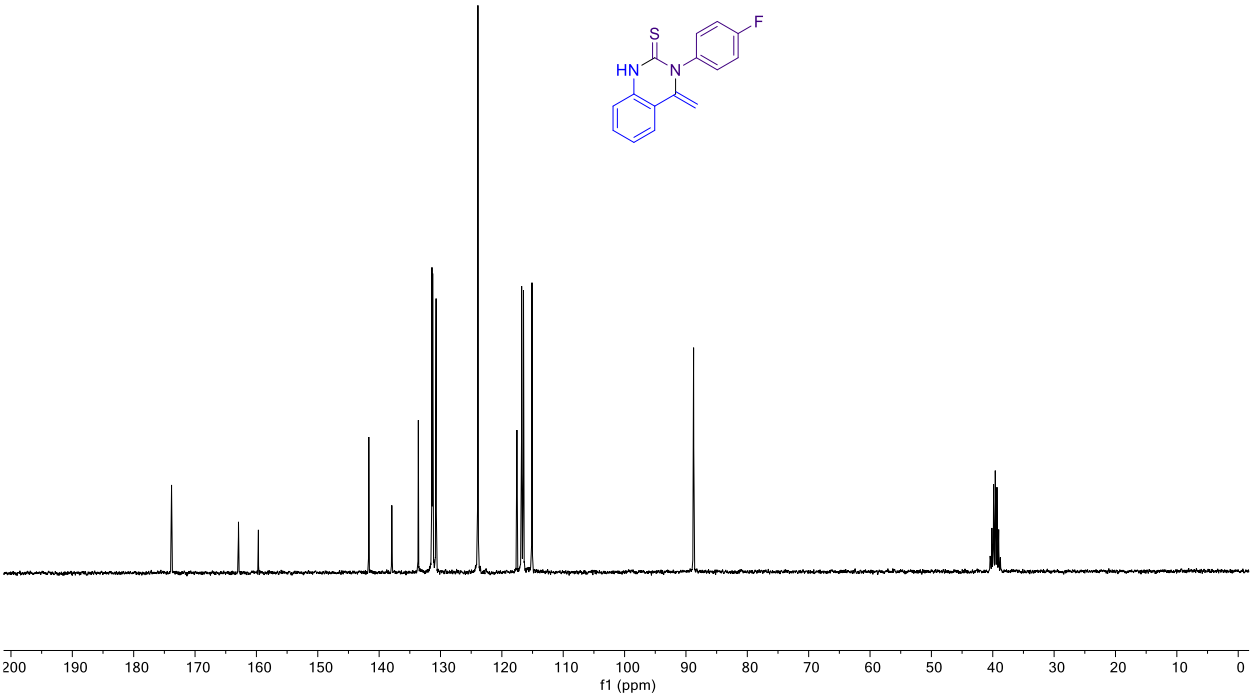


3-(4-Fluorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5d)

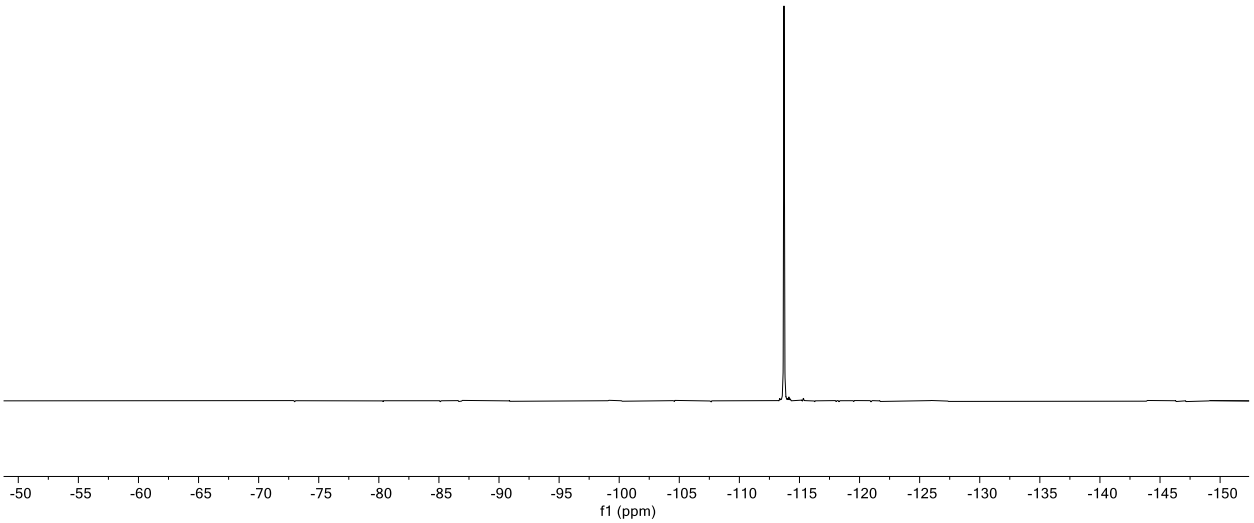
^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

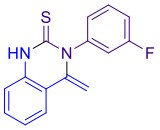


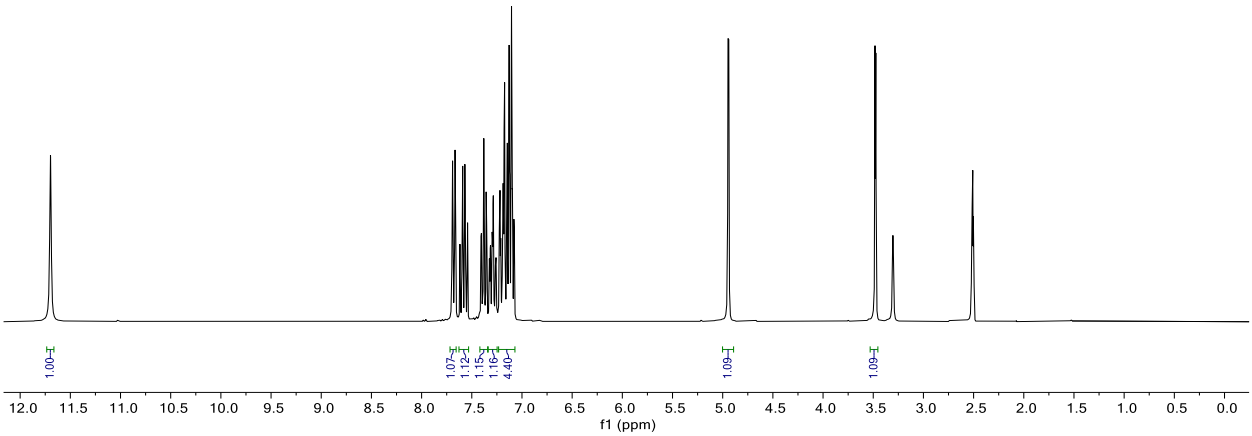
^{19}F NMR (282 MHz, DMSO-d_6)



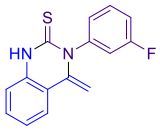
3-(3-Fluorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5e)

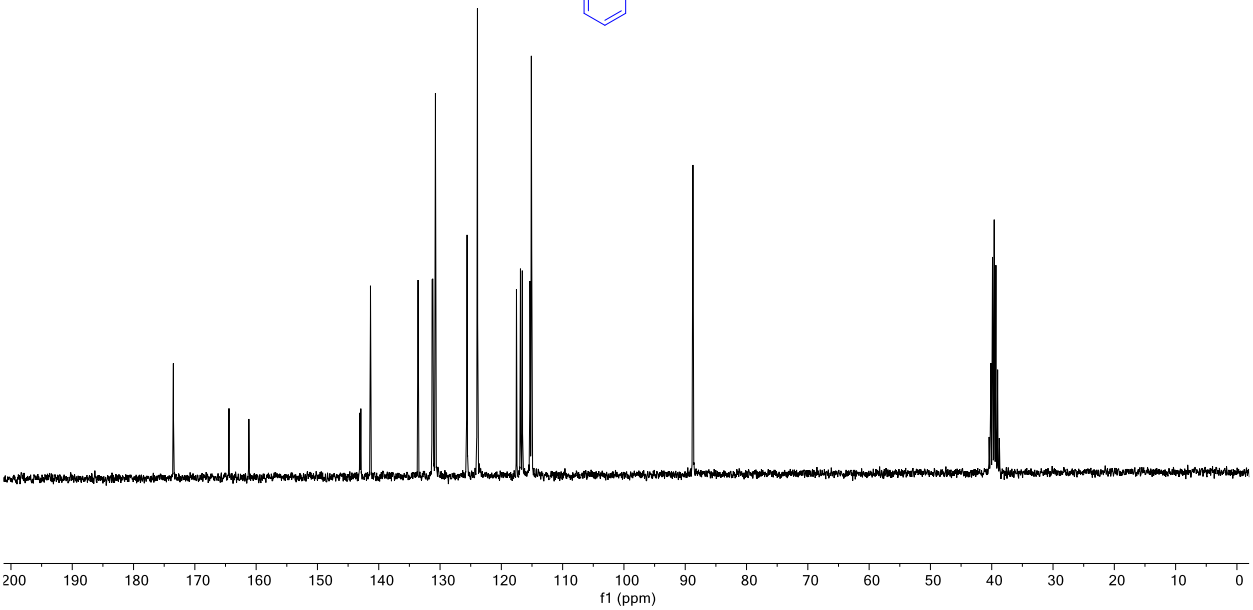
^{1}H NMR (300 MHz, DMSO-d_6)





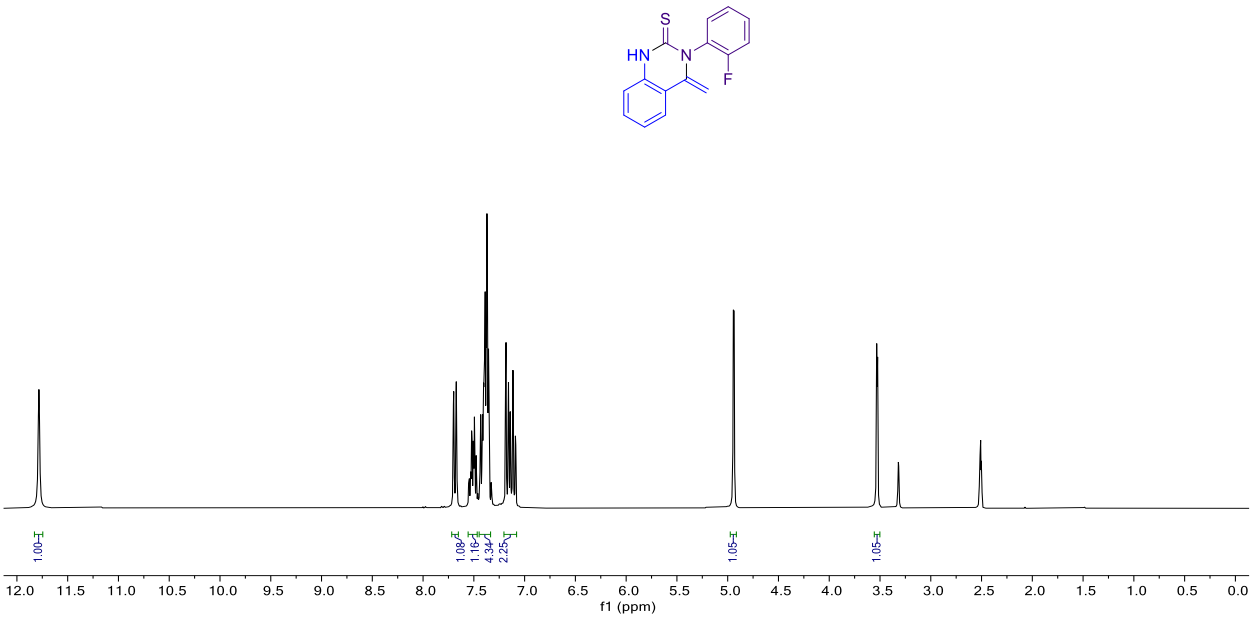
^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)



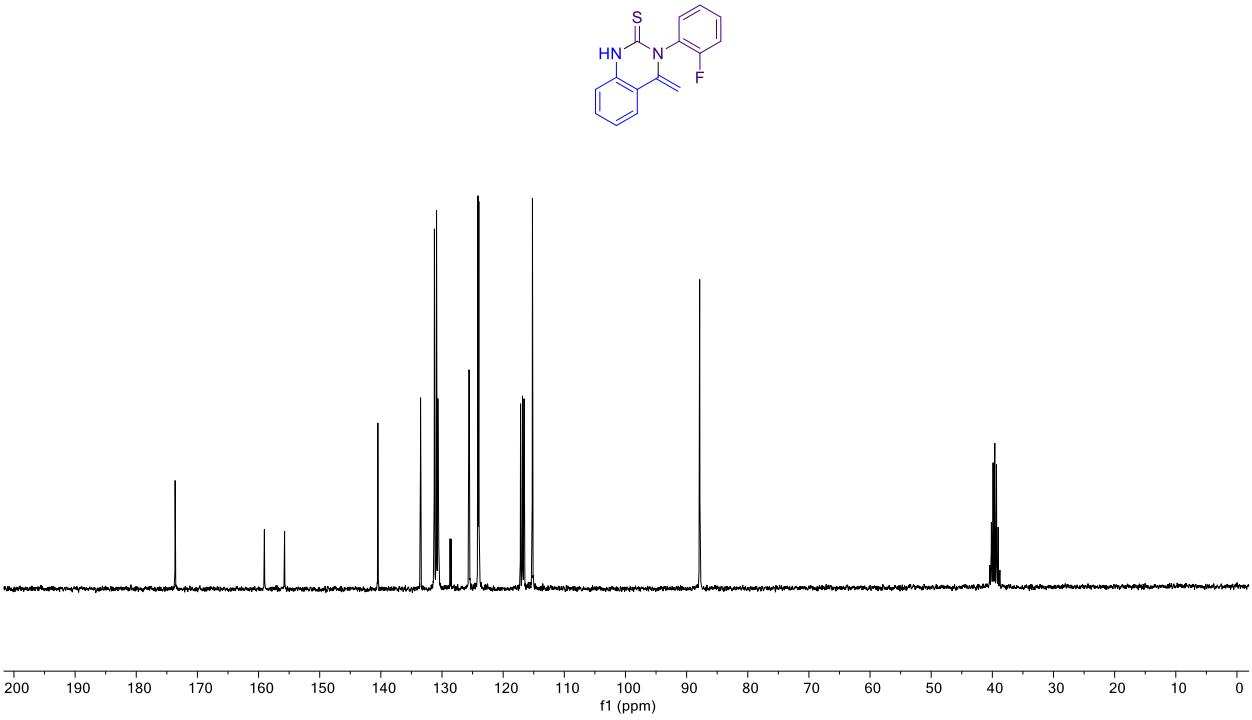


3-(2-Fluorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5f)

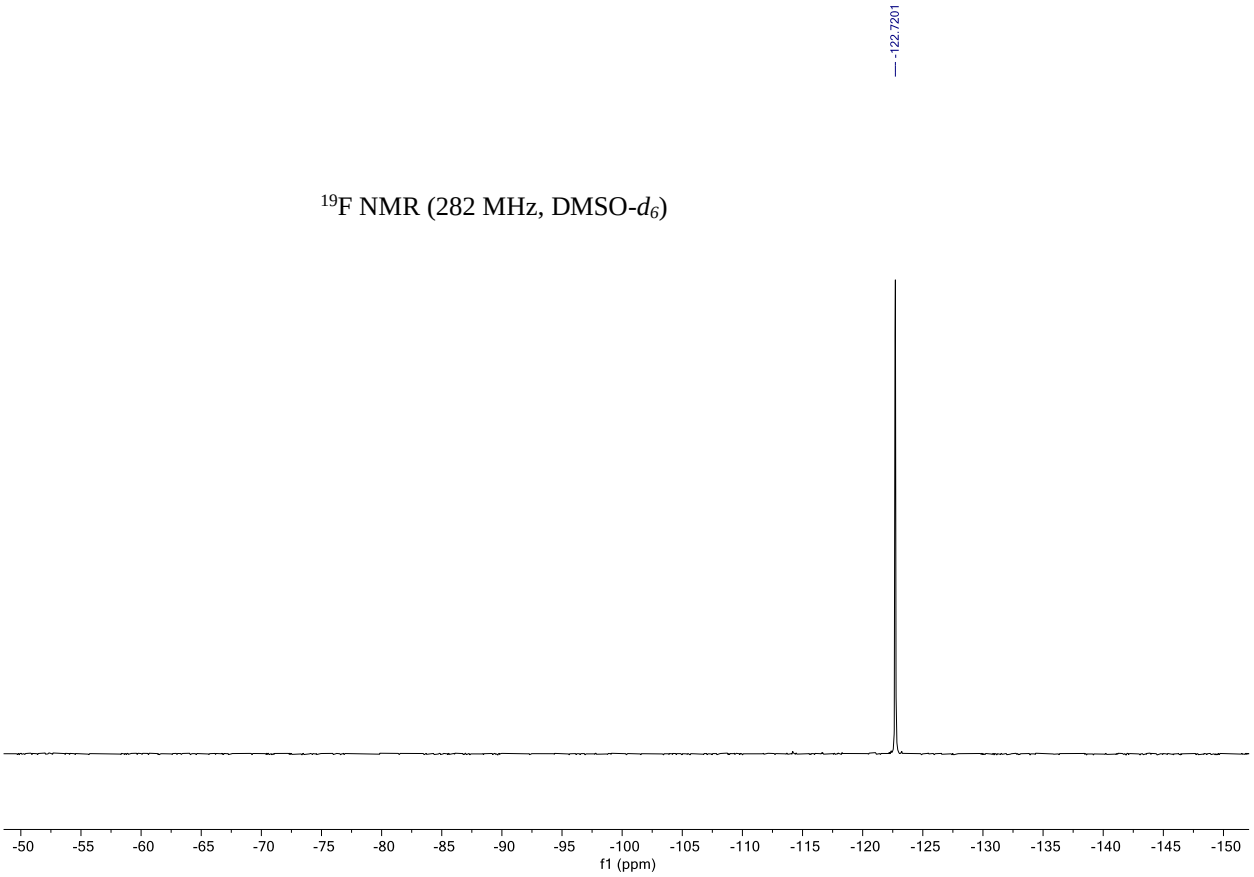
^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

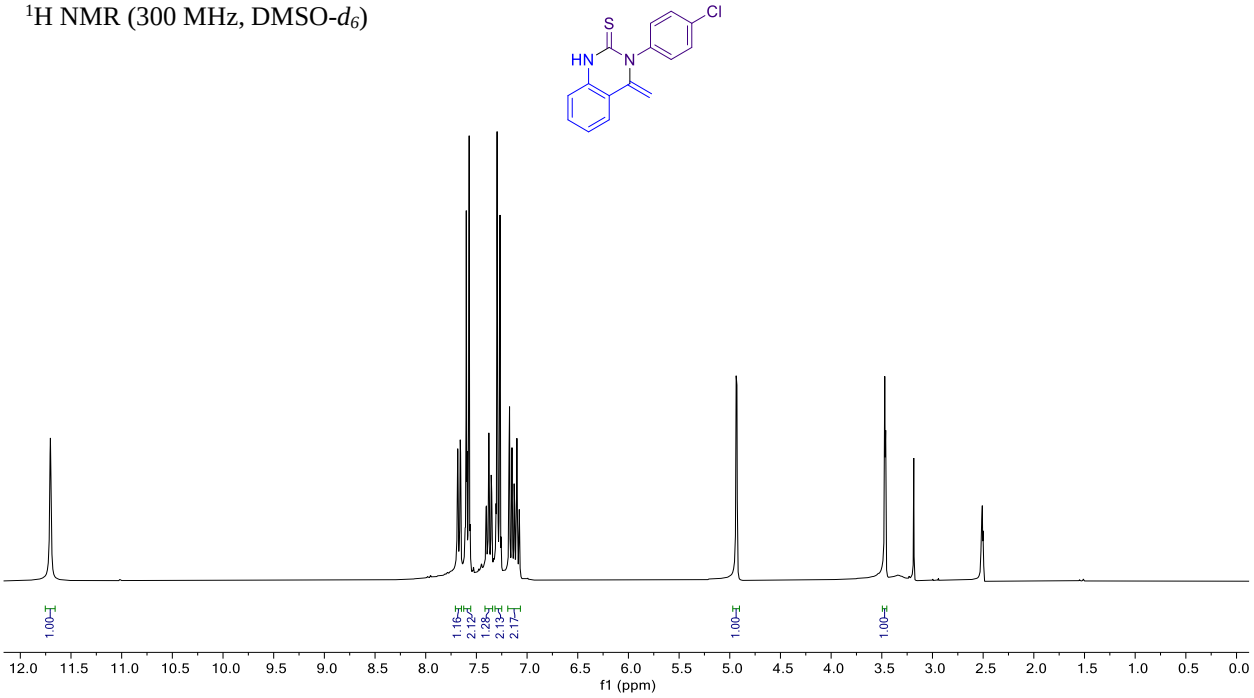


^{19}F NMR (282 MHz, DMSO-d_6)

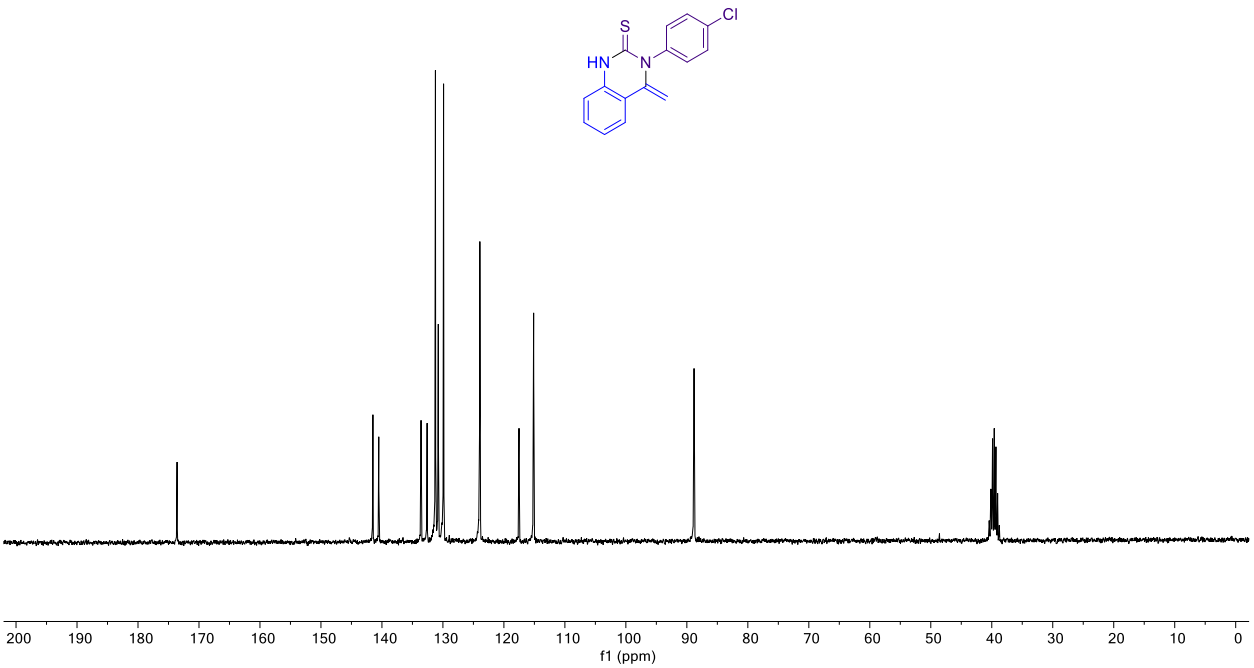


3-(4-Chlorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5g)

^{1}H NMR (300 MHz, DMSO-d_6)

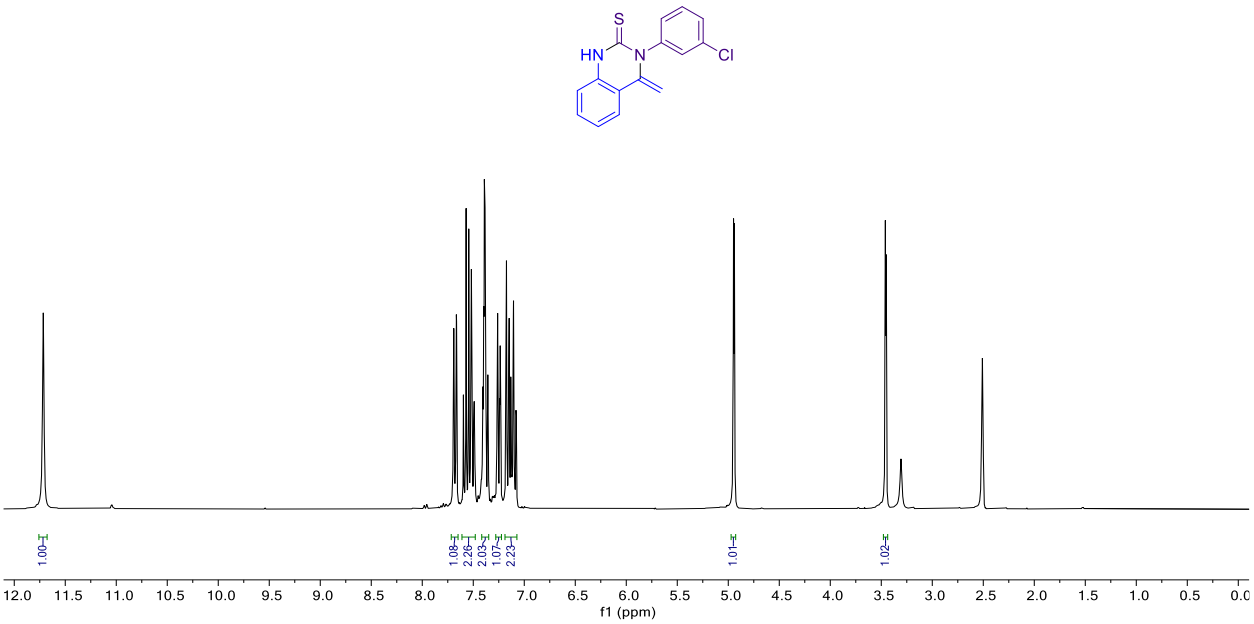


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

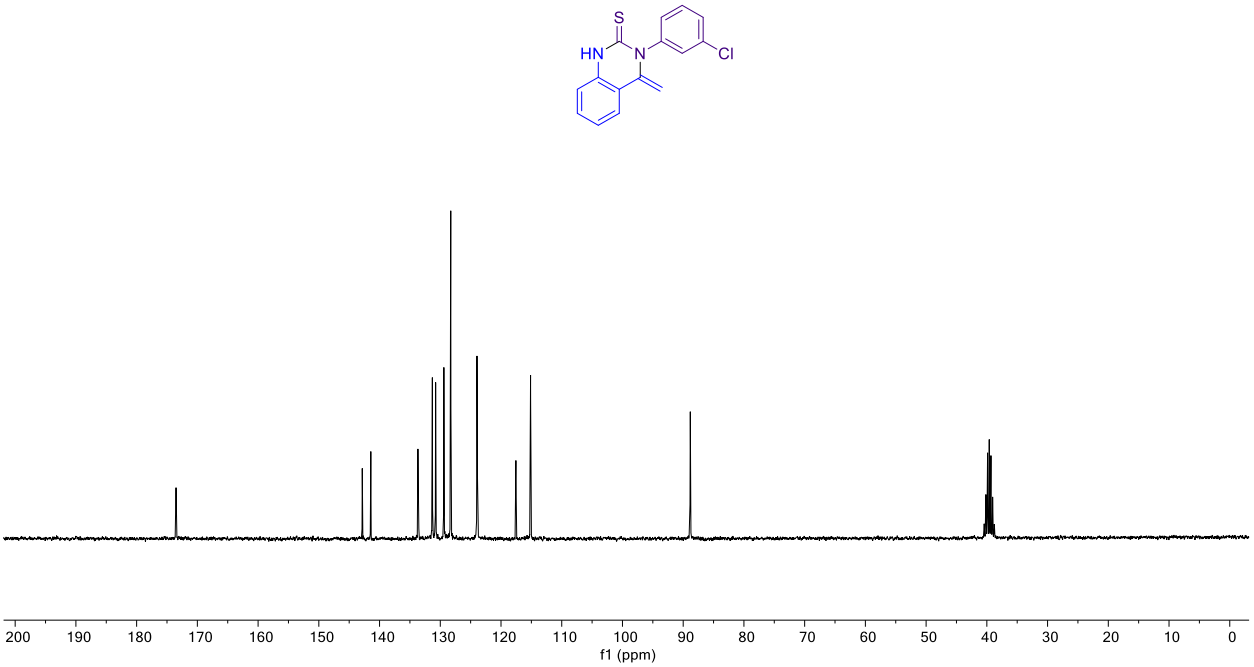


3-(3-Chlorophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5h)

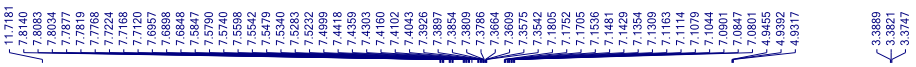
^{1}H NMR (300 MHz, DMSO-d_6)



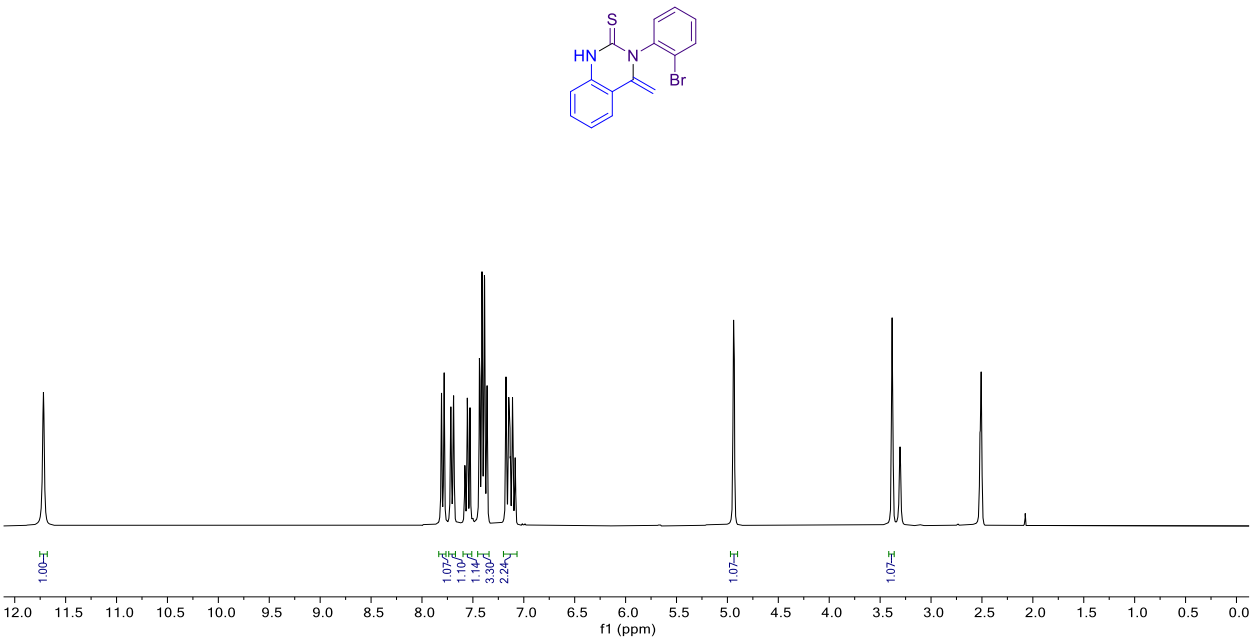
^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)



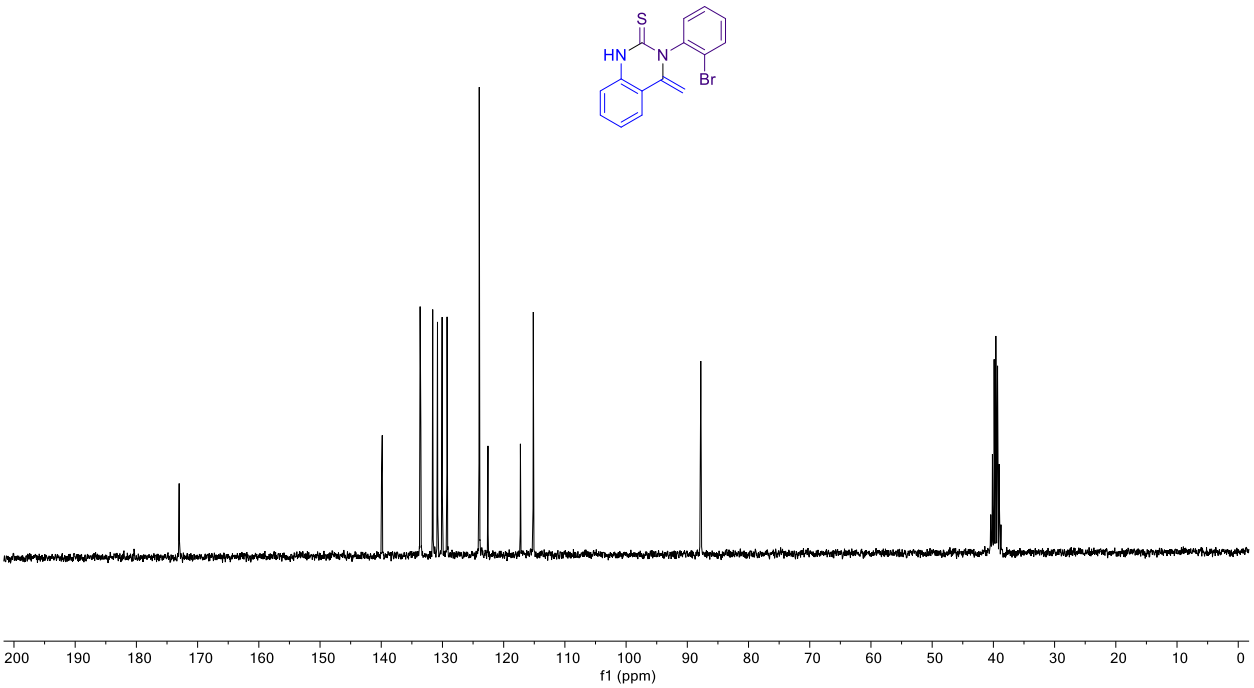
3-(2-Bromophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5i)



^{1}H NMR (300 MHz, DMSO-d_6)

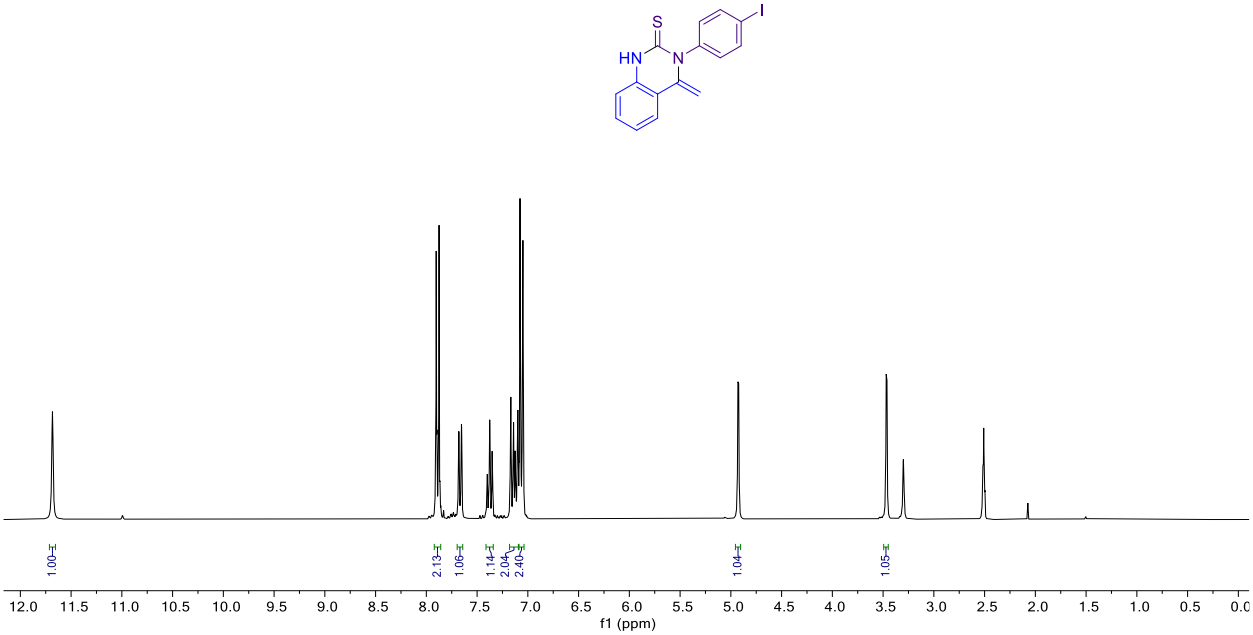


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

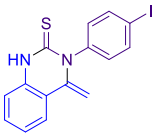


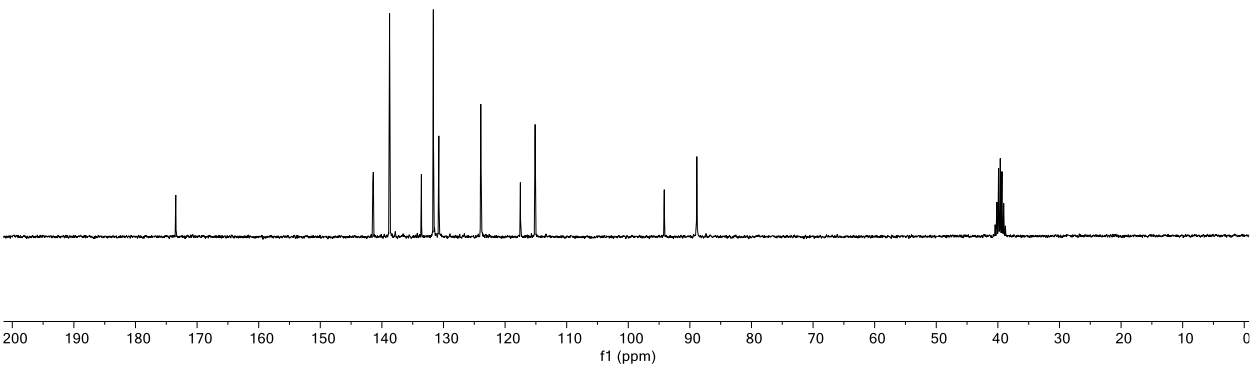
3-(4-Iodophenyl)-4-methylene-3,4-dihydroquinazoline-2(1*H*)-thione (5j)

^{1}H NMR (300 MHz, DMSO-d_6)



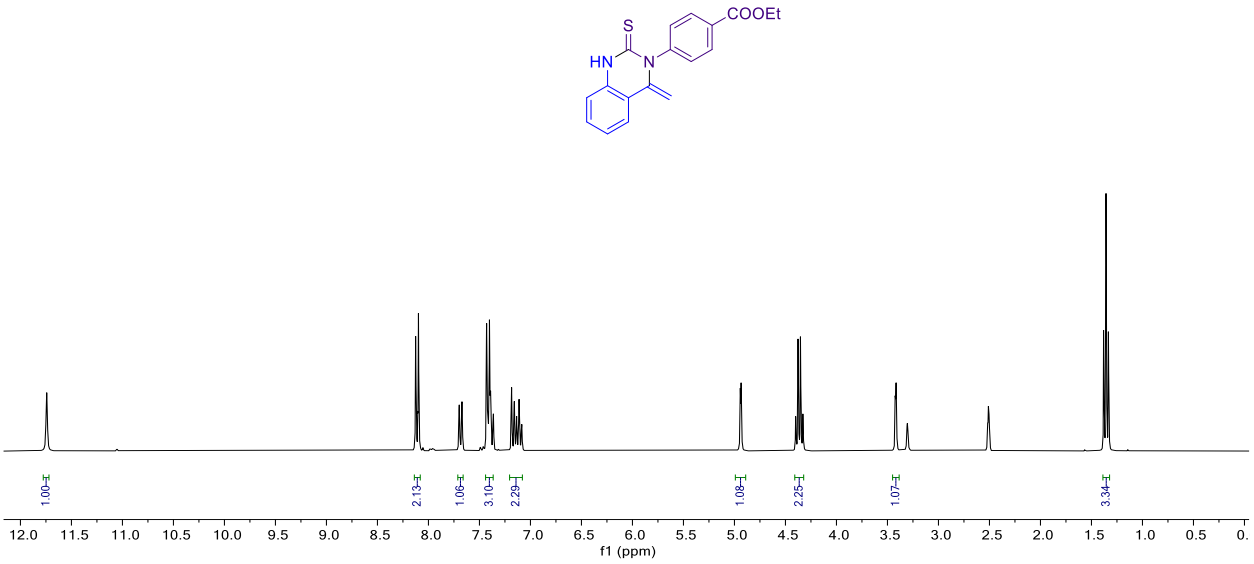
^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)



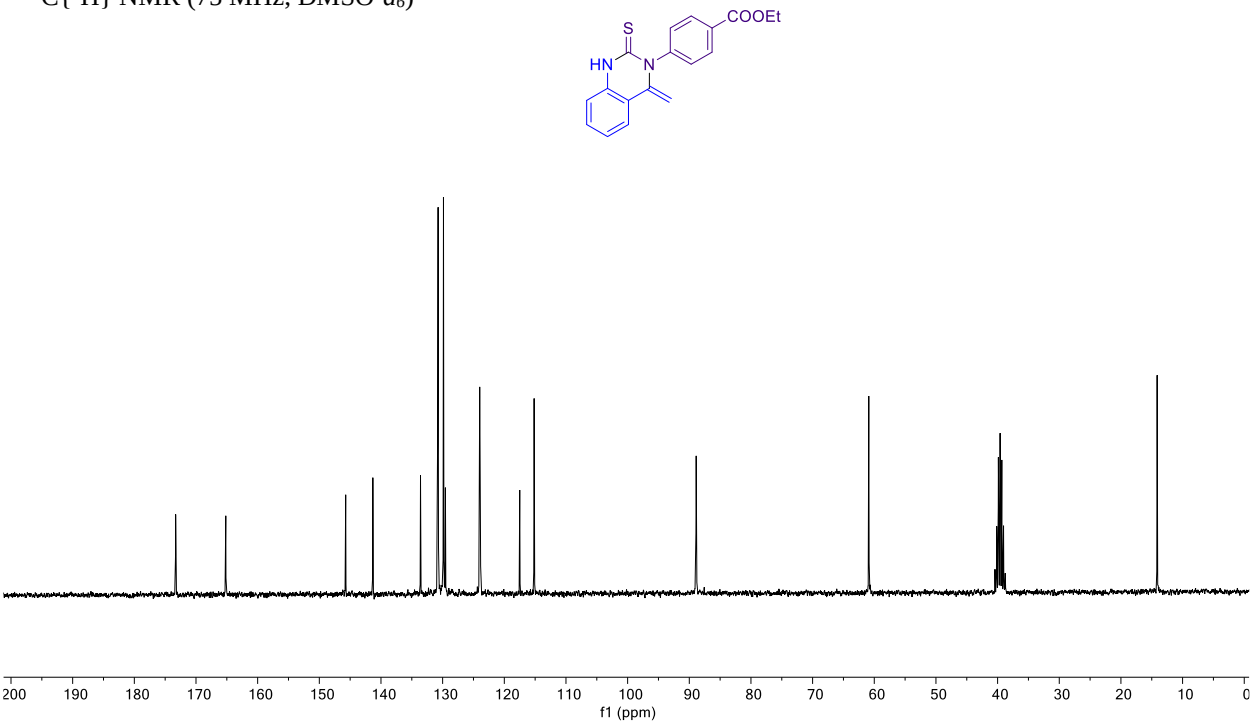


Ethyl 4-(4-methylene-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzoate (5k)

^{1}H NMR (300 MHz, DMSO-d_6)

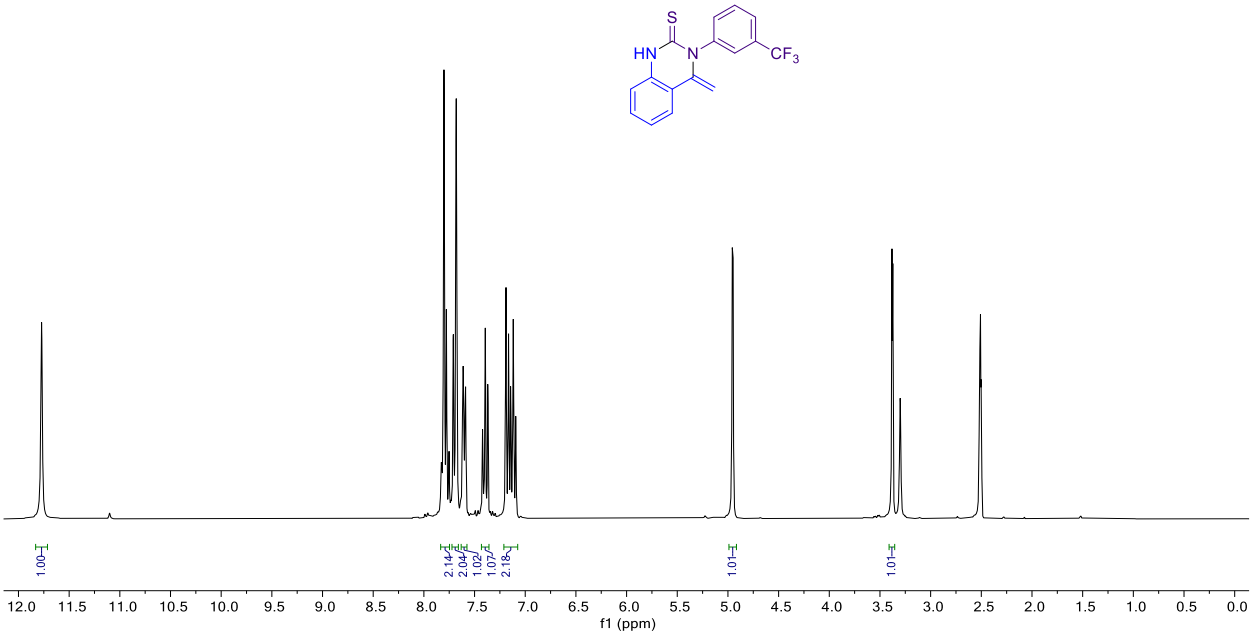


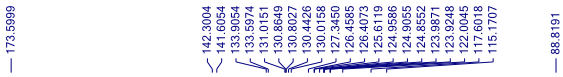
^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)



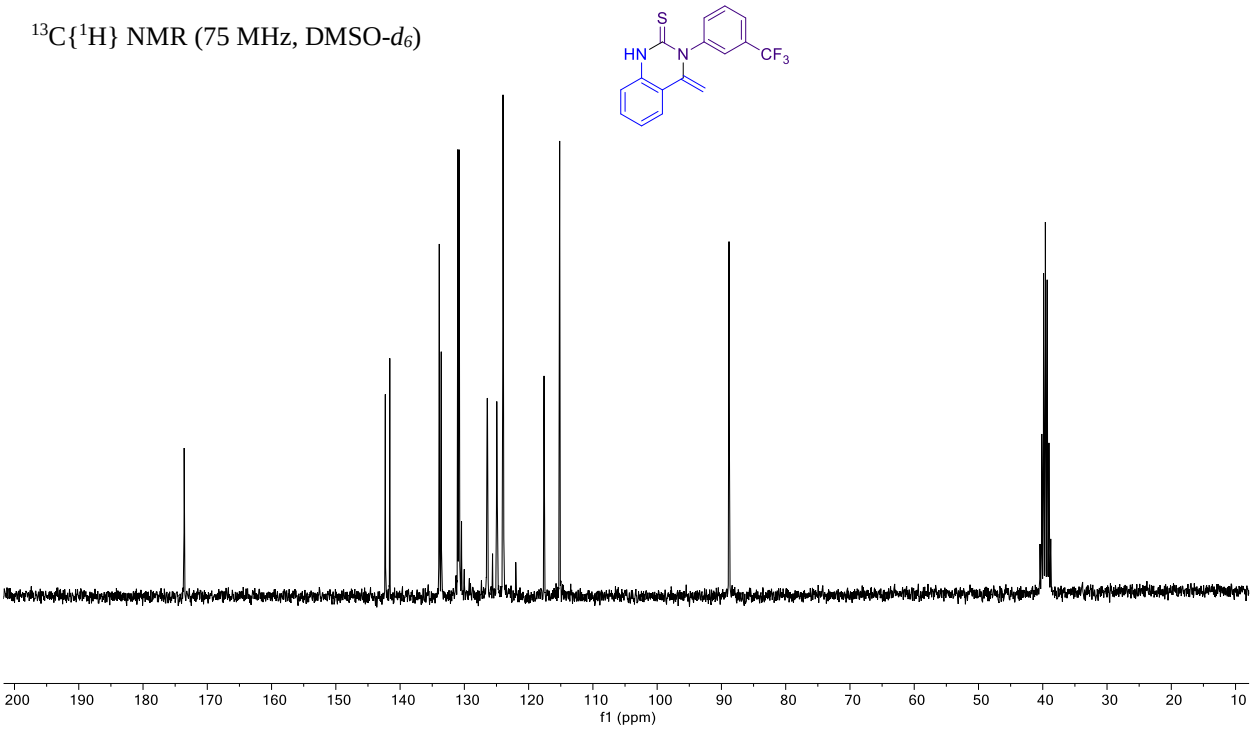
4-Methylene-3-(3-(trifluoromethyl)phenyl)-3,4-dihydroquinazoline-2(1*H*)-thione (5l)

^{1}H NMR (300 MHz, DMSO-d_6)

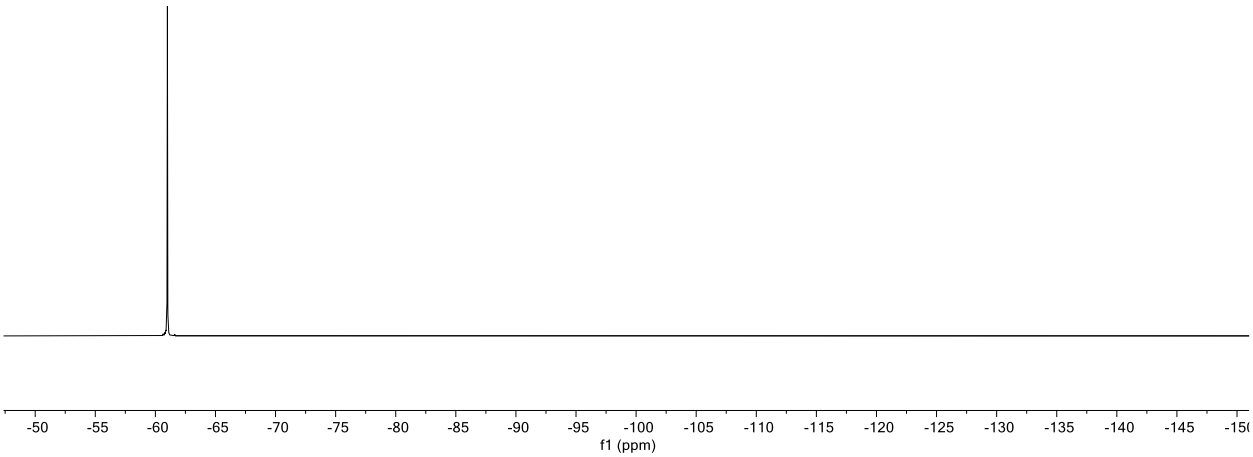




^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

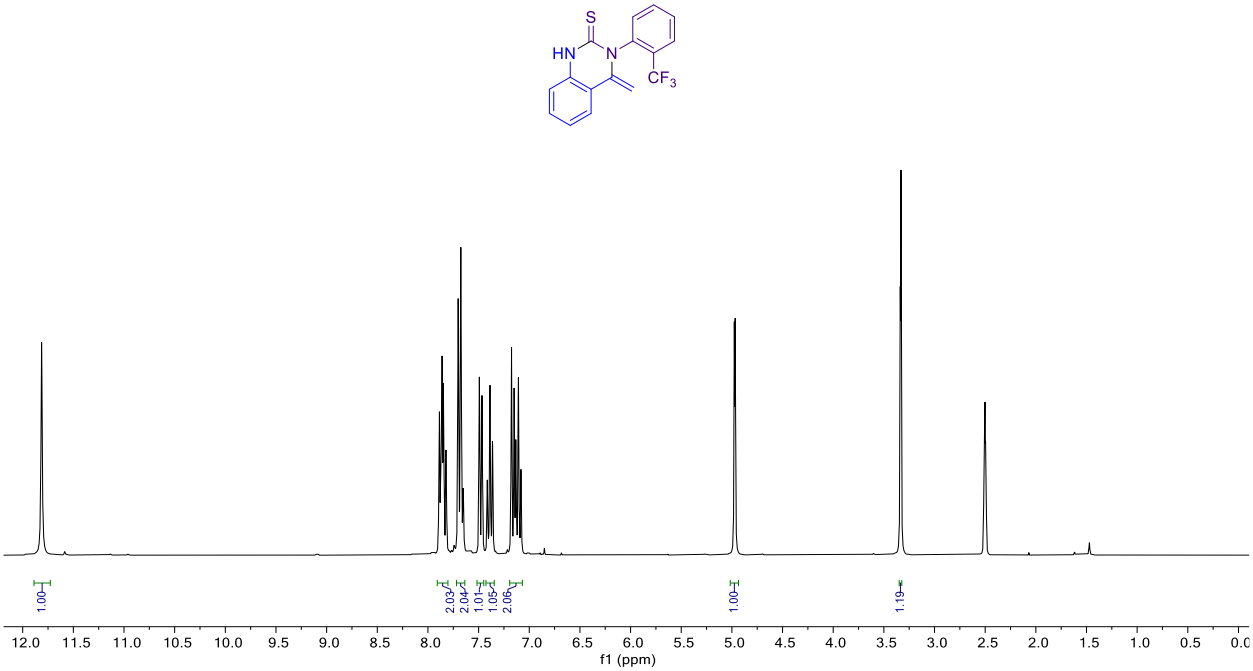


^{19}F NMR (282 MHz, DMSO-d_6)

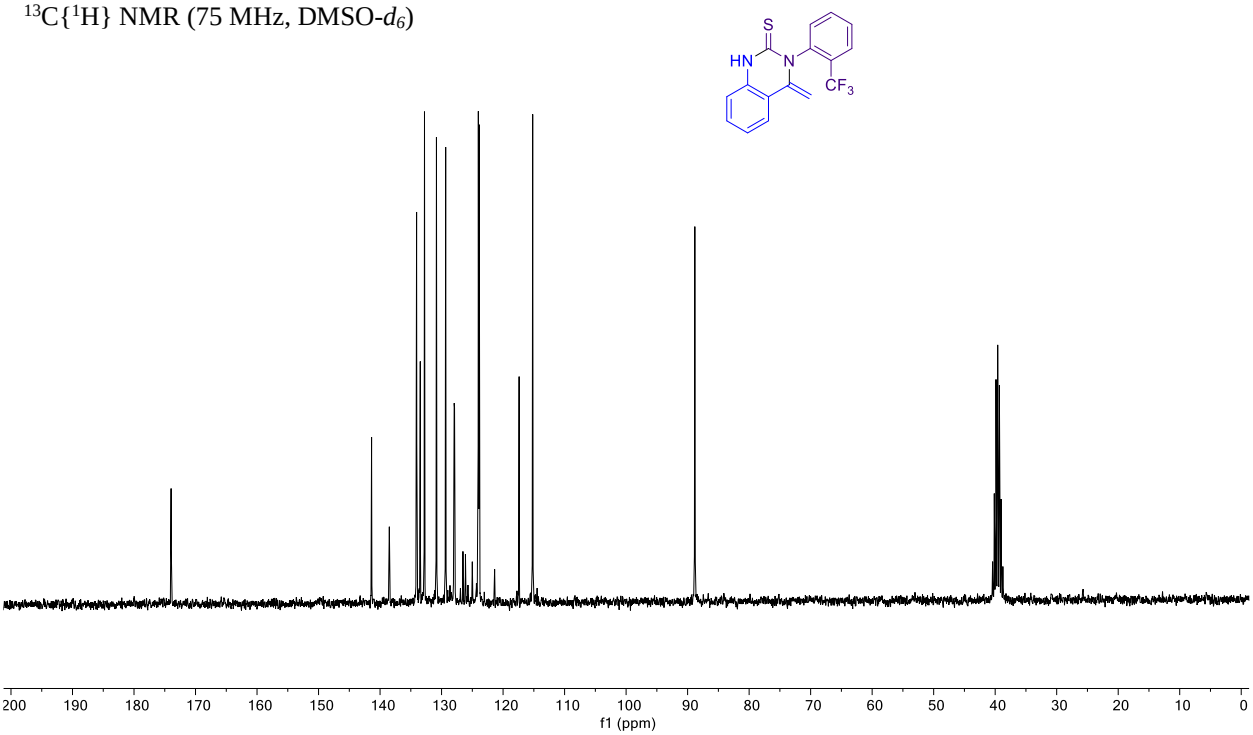


4-Methylene-3-(2-(trifluoromethyl)phenyl)-3,4-dihydroquinazoline-2(1*H*)-thione (5m)

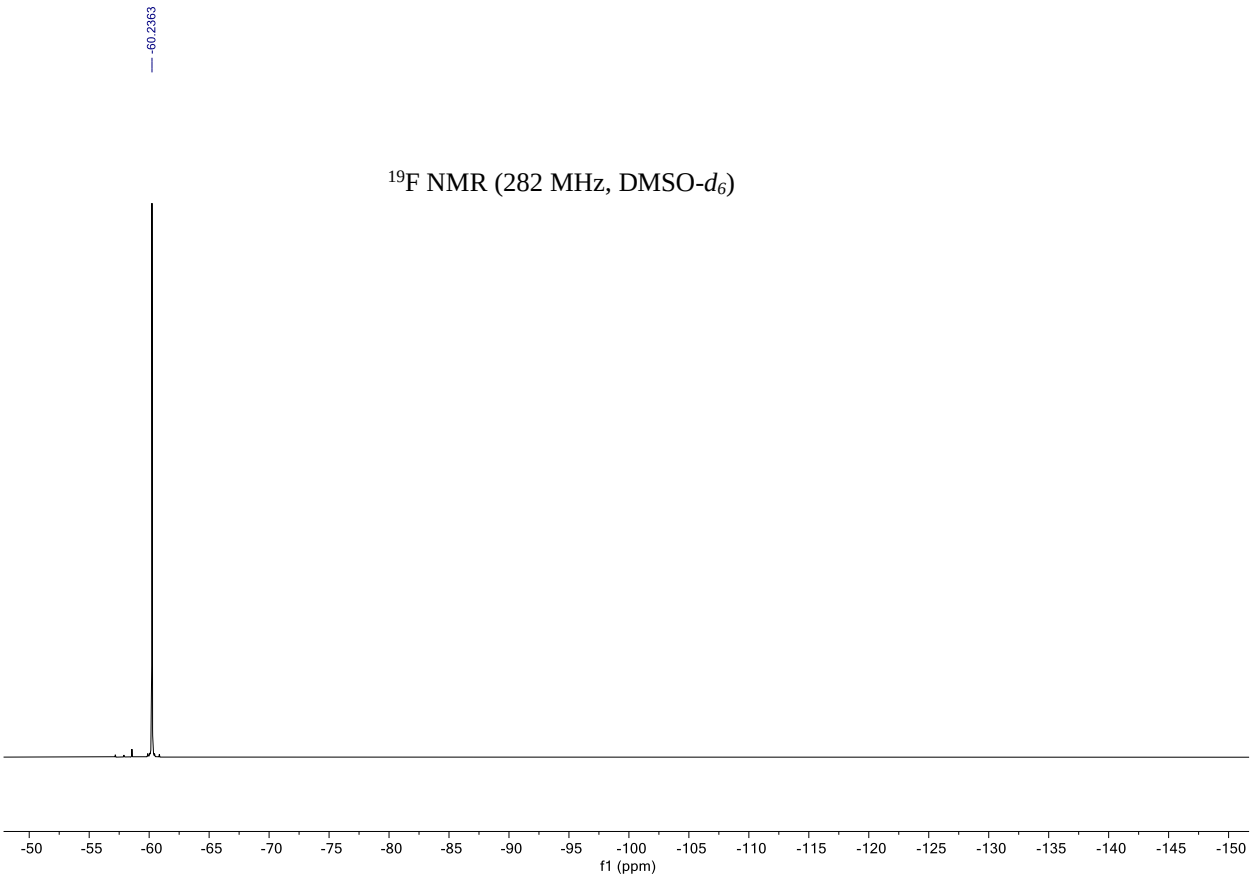
^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

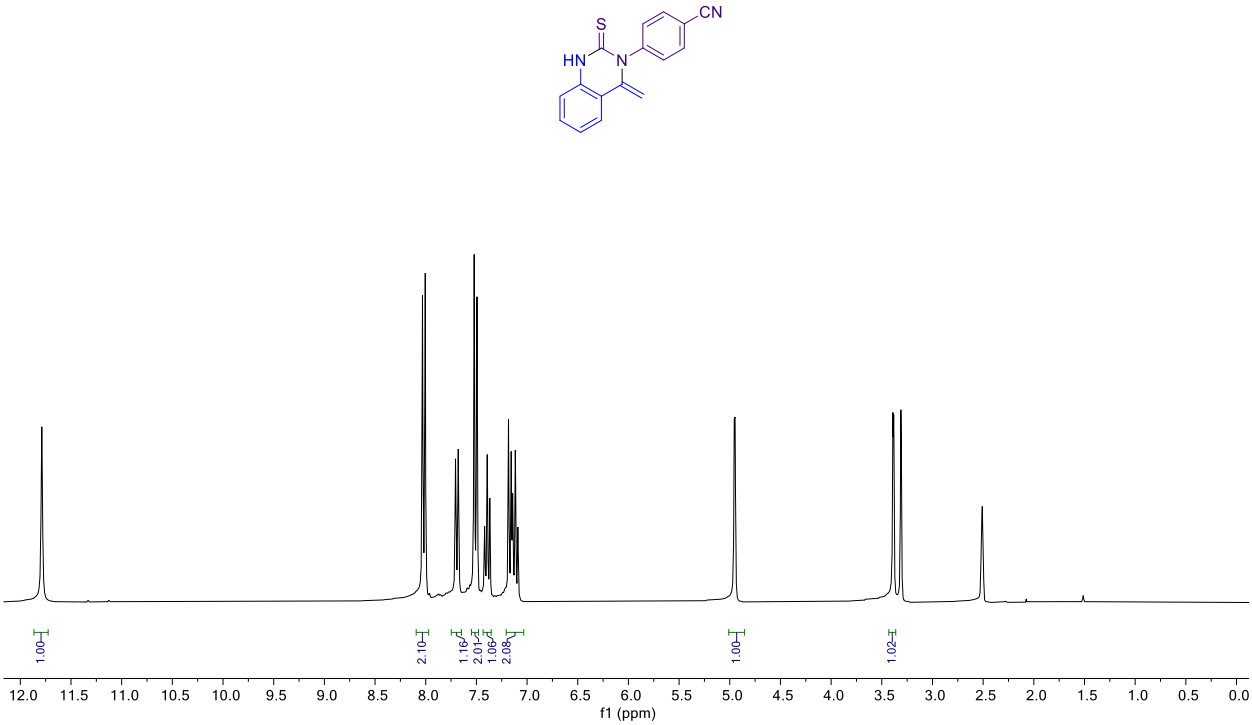


^{19}F NMR (282 MHz, DMSO-d_6)

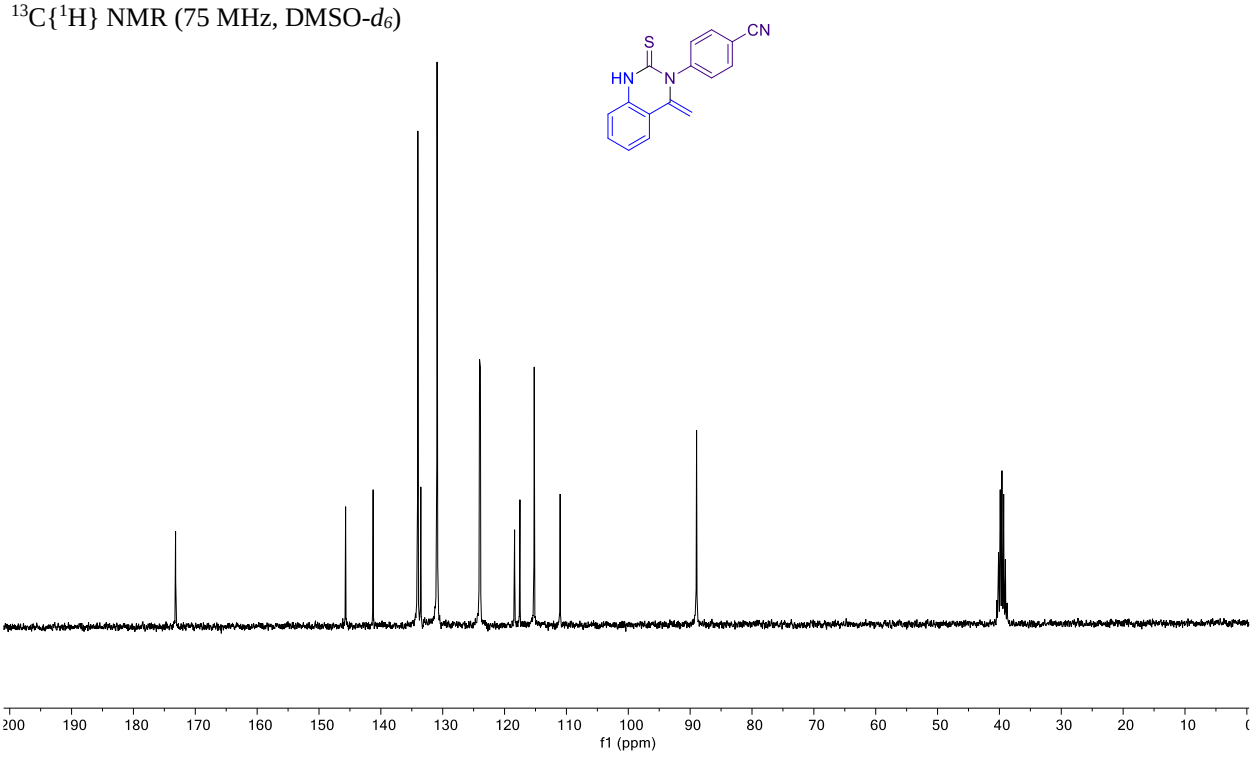


4-(4-Methylene-2-thioxo-1,4-dihydroquinazolin-3(2*H*)-yl)benzonitrile (5n)

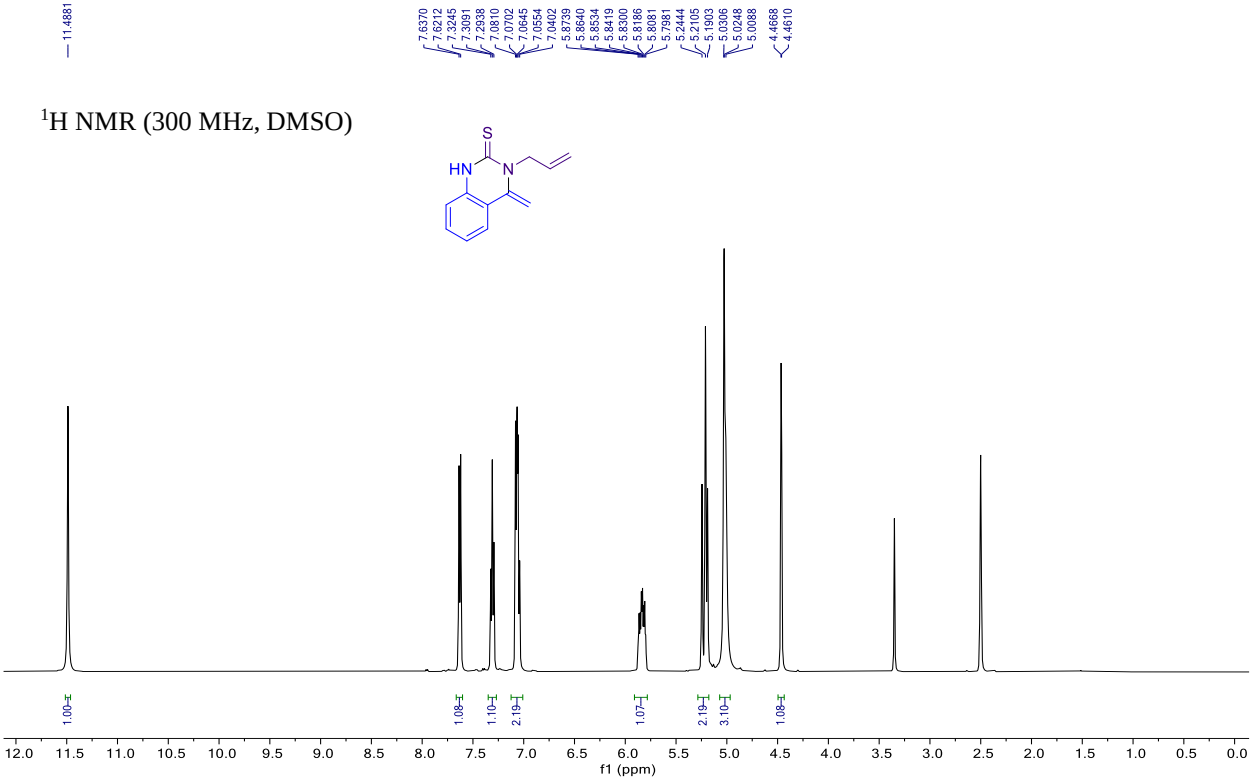
^{1}H NMR (300 MHz, DMSO-d_6)

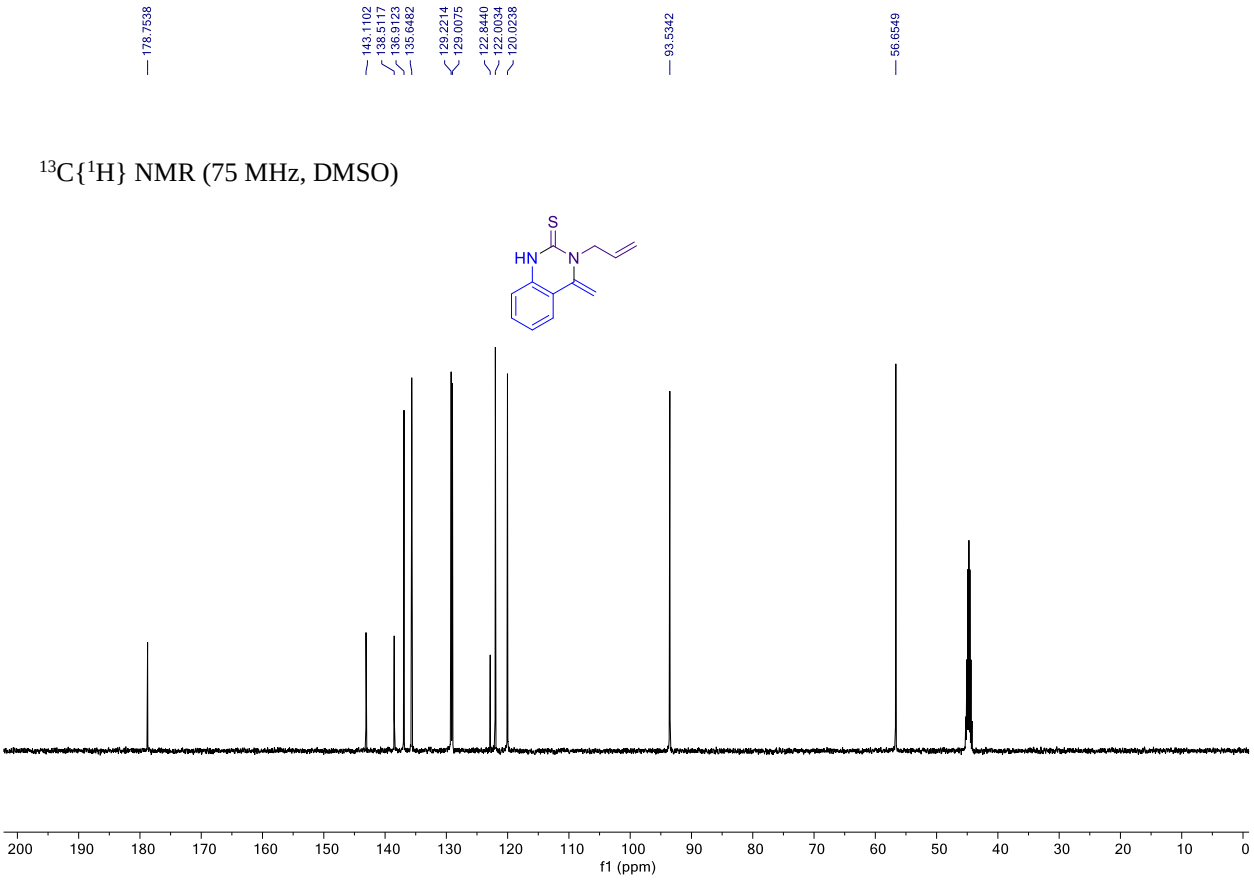


^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)



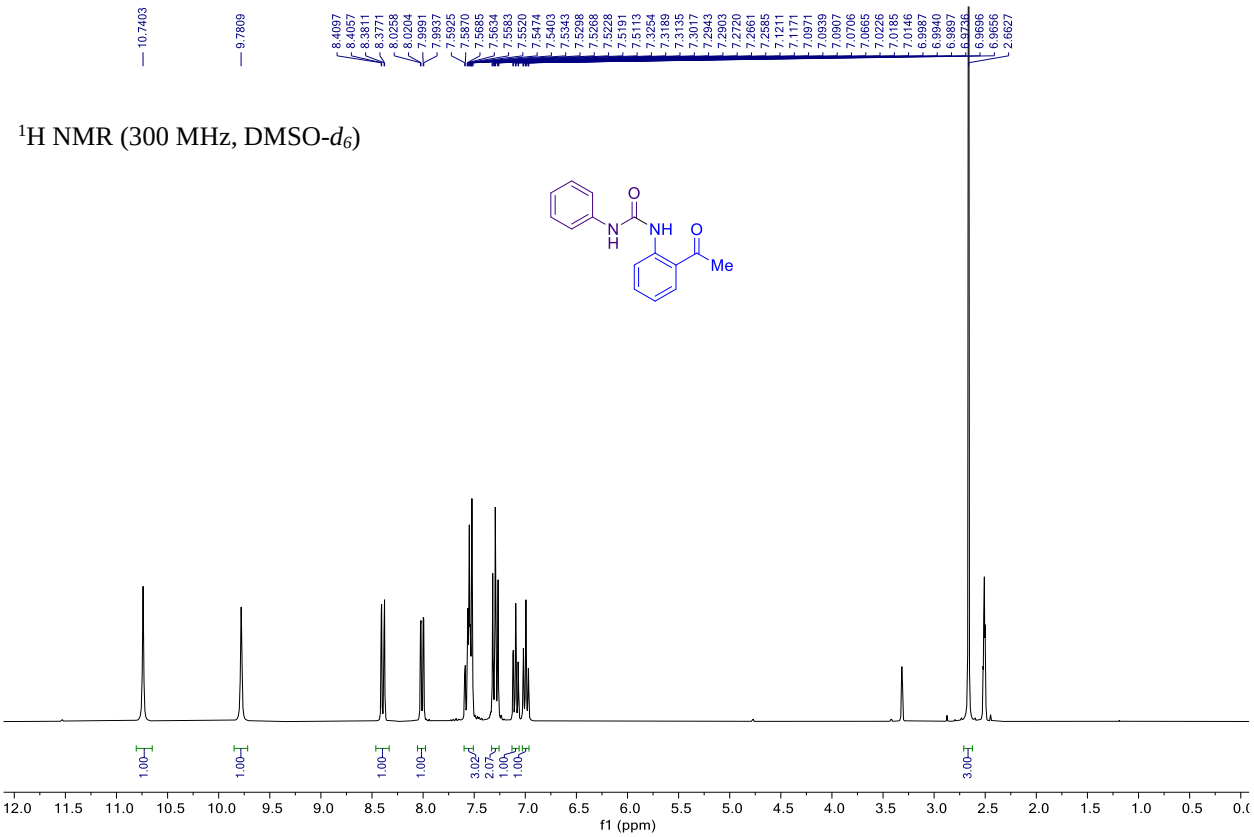
3-Allyl-4-methylene-3,4-dihydroquinazoline-2(1H)-thione (5o)



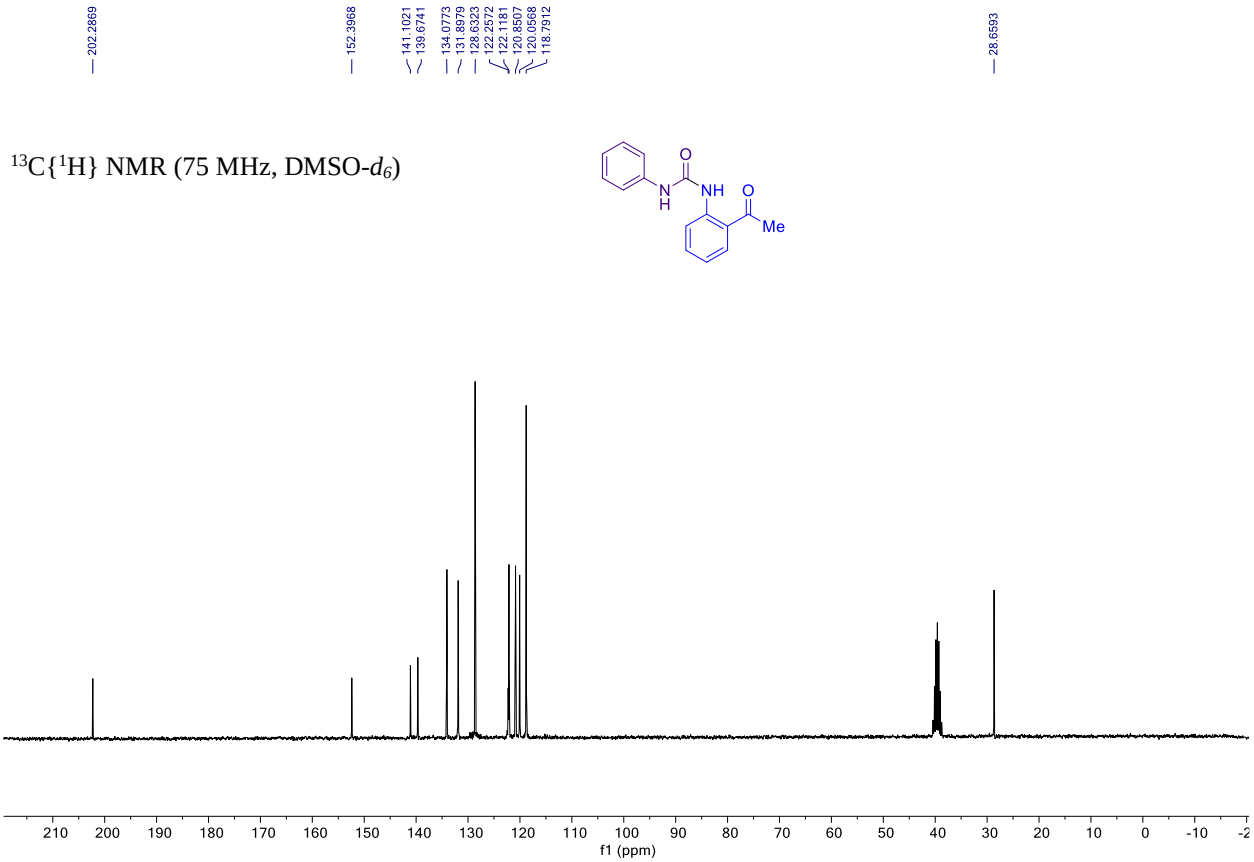


1-(2-Acetylphenyl)-3-phenylurea (8)

^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)



Transformation of 9i into 5i in the NMR tube after 16 h