Supporting Information

Metal and Catalyst-free Strategy to Access 1, 3-Thio-heteroaryl BCP Derivatives

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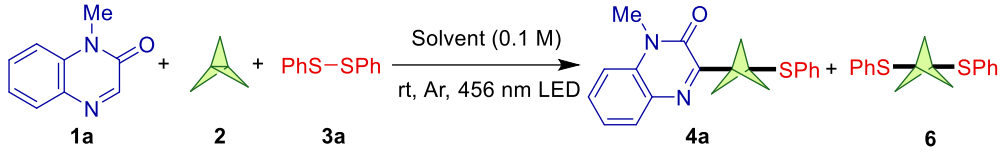
1. General Information:

Commercial reagents were purified prior to use, following the guidelines of L.L Chai and Armarego. All NMR spectra were recorded on a 500 MHz Bruker spectrometer. ^{1}H, ^{13}C, and ^{19}F spectral data are reported as chemical shifts (δ) in parts per million (ppm). Chemical shifts in ppm from tetramethylsilane (TMS) as an internal standard in $CDCl_3$. Chemical shifts (δ) are quoted in parts per million (ppm), and coupling constants (*J*) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities s=singlet, d=doublet, t=triplet, q=quartet, pent=pentet, b=broad, m=multiplet. NMR spectra were processed in Mestrenova, keeping the $CDCl_3$ residual peaks at 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C). High-resolution mass spectra (HRMS, m/z) were recorded on a Bruker MicroTOF. All fluorescence and UV−vis spectra were recorded in a HORIBA FluoroMax Plus spectrofluorometer and a Hitachi UV−vis spectrophotometer. IUPAC names were obtained using the ChemDraw service. The weighing was performed with a 4-decimal place balance. All reactions were conducted in dried glassware with magnetic stirring under an inert atmosphere unless otherwise noted. All solvents were dried following the guidelines of L.L Chai and Armarego purification of laboratory chemicals. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Flash column chromatography was performed over Merck silica gel (230−400 μm) using the eluent system described for each experiment. TLC was stained with iodine or an ethanolic solution of potassium permanganate ($KMnO_4$) or *p*-anisaldehyde. In a general experiment, 40 W blue LEDs (456 nm) brought from Kessil with a cooling fan were used as a visible light source. The light source was placed at approximately 5.0 cm distance from the reaction tube. The product yields were determined after purification by flash column chromatography using SiO_2, and the purity was determined by ^{1}H NMR spectra.

2. Optimization Studies:

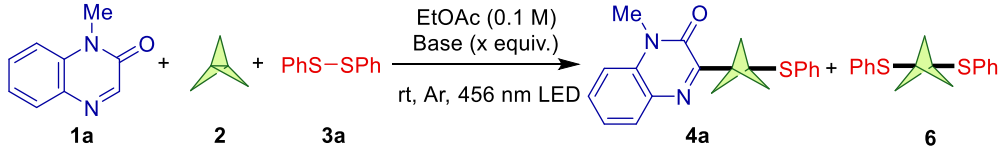
2.1 Solvent Screening: [a]



Entry	Solvent	Yield of 4a (%)	Yield of 6 (%)	RSM 1a (%)
1	EtOAc	33	28	42
2	MeCN	27	41	49
3	THF	30	46	26
4	Toluene	26	40	32
5	EtOH	26	18	41
6	DMF	28	44	22
7	DCM	28	39	32
8	Acetone	32	32	35
9[b]	**EtOAc**	**34**	**28**	**45**

[a]Performed with **1a** (0.2 mmol), **2** (0.24 mmol), **3a** (0.4 mmol) in solvent (0.1 M) at rt under 40 W, 456 nm blue LEDs irradiation for 24 h, Yields were determined by ^{1}H NMR using 1, 1, 2, 2-tetrachloroethane as an internal standard. [b]0.2 M in EtOAc.

2.2 Base Screening: [a]

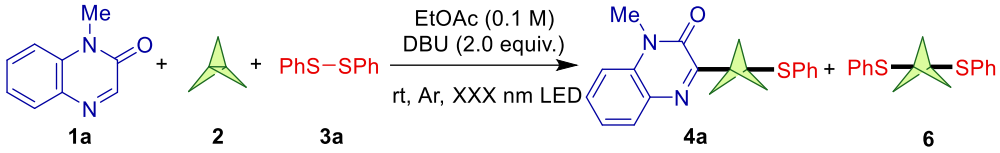


Entry	Base	Yield of 4a (%)	Yield of 6 (%)	RSM 1a (%)
1[b]	DBU	45	44	30
2	**DBU**	**58**	**50**	**15**
3[c]	DBU	48	45	23
3	DMAP	44	56	25
4	DMPU	35	46	16
5	DIPEA	45	48	25
6	DABCO	36	51	27
7	Et_3N	36	52	27
8	Pyridine	34	53	28
9	Lutidine	36	47	19
10	TMEDA	39	56	31
11	Dicyclohexyl amine	47	59	20

12	DBN	44	56	18
13	Cs_2CO_3	34	58	27
14	NaOAc	35	44	33
15	K_3PO_4	42	57	25
16	KOH	27	31	13
17	$NaHCO_3$	36	58	20

[a]Performed with **1a** (0.2 mmol), **2** (0.24 mmol), **3a** (0.4 mmol) and base (2.0 equiv.) in EtOAc (0.1 M) at rt under 40 W, 456 nm blue LEDs irradiation for 24 h, Yields were determined by ^{1}H NMR using 1, 1, 2, 2-tetrachloroethane as an internal standard. [b]1.0 equiv. of base. [c]3.0 equiv. of base.

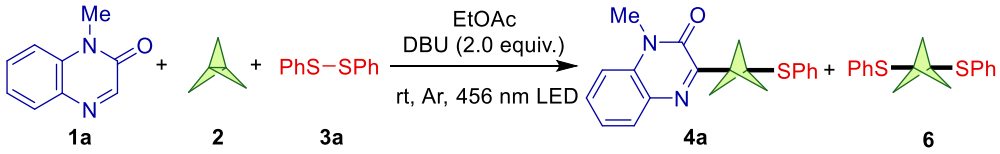
2.3 Variation of Light Source: [a]



Entry	Wavelength (nm)	Yield of 4a (%)	Yield of 6 (%)	RSM 1a (%)
1	390	0	98	12
2	440	54	44	9
3	**456**	**58**	**56**	**28**
4	467	54	54	15
5	Tuna Blue LED	26	40	15

[a]Performed with **1a** (0.2 mmol), **2** (0.24 mmol), **3a** (0.4 mmol) and DBU (2.0 equiv.) in EtOAc (0.1 M) at rt under 40 W, XXX nm blue LEDs irradiation for 24 h, Yields were determined by ^{1}H NMR using 1, 1, 2, 2-tetrachloroethane as an internal standard.

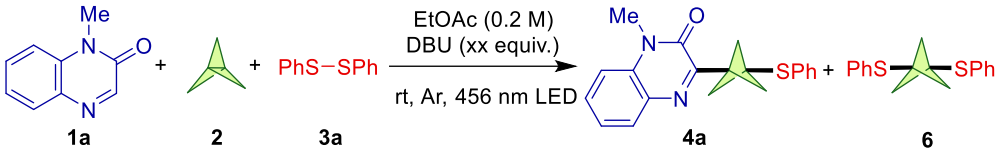
2.4 Concentration Screening: [a]



Entry	Concentration	Yield of 4a (%)	Yield of 6 (%)	RSM 2a (%)
1	0.1 M	50	46	11
2	**0.2 M**	**65**	**50**	**10**
3	0.4 M	48	48	8

[a]Performed with **1a** (0.2 mmol), **2** (0.24 mmol), **3a** (0.4 mmol) and DBU (2.0 equiv.) in EtOAc (XX M) at rt under 40 W, 456 nm blue LEDs irradiation for 24 h, Yields were determined by ^{1}H NMR using 1, 1, 2, 2-tetrachloroethane as an internal standard.

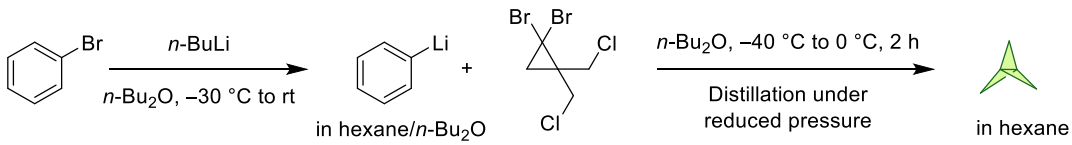
2.5 Equivalents Screening: [a]



Entry	Equiv. of 2	Equiv. of 3a	Equiv. of DBU	Yield of 4a (%)	Yield of 6 (%)	RSM 1a (%)
1	1.2	2.0	2.0	58	56	28
2[b]	1.2	2.0	2.0	65	--	29
3	1.5	1.0	2.0	39	28	21
4	1.5	1.2	2.0	63	47	20
5	1.5	1.5	2.0	65	50	10
6	1.5	1.5	2.0	65	39	17
7[b]	**1.5**	**1.5**	**1.5**	**71 (66)**[c]	**38**	**12**
8	1.5	1.5	2.5	64	42	14
9	2.0	1.0	2.0	55	27	11
10	2.0	1.2	2.0	58	41	11
11	2.0	1.5	2.0	55	46	9

[a]Performed with **1a** (0.2 mmol), **2** (xx mmol), **3a** (xx mmol) and DBU (xx equiv.) in EtOAc (0.2 M) at rt under 40 W, 456 nm blue LEDs irradiation for 24 h, Yields were determined by ^{1}H NMR using 1, 1, 2, 2-tetrachloroethane as an internal standard. [b]at 0 °C. [c]Isolated yield in the parenthesis.

3. Preparation of the solution of [1.1.1]propellane in hexane:[1]



(a) Preparation of phenyl lithium in hexane/*n*-Bu$_2$O

A 100 ml three-neck round bottom flask equipped with a magnetic stirring bar was charged with bromobenzene (100 mmol, 1.0 eq.). After the flask was evacuated and backfilled with argon three times, anhydrous dibutyl ether (20 mL) was added. Then the flask was cooled down to –30 °C, and *n*-BuLi (100 mmol, 1.0 eq., 2.5 M in hexane) was added dropwise via an addition funnel. After the addition was complete, the mixture was allowed to warm to rt and stirred at rt for 1 h. The mixture was used in the next step.

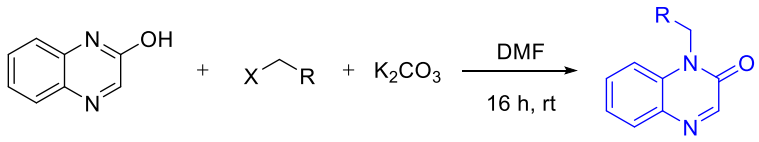
(b) Preparation of the solution of [1.1.1]propellane in hexane

A solution of the above-prepared Phenyl lithium in hexane/*n*-Bu$_2$O (65 mL) was added dropwise to a suspension of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (45.0 mmol) in anhydrous dibutyl ether (20 mL) via addition funnel under argon at –40 °C. After the addition was complete, the mixture was allowed to warm to 0 °C and stirred for 2 h, then the addition funnel was swapped out for a distillation head with an attached 100 mL round bottom flask in a –78 °C bath (dry

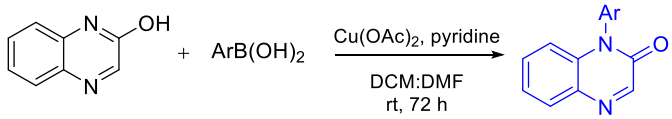
ice/acetone). A vacuum was slowly applied to the system, and the distillate was collected while maintaining the distillation flask below 0 °C. Approximately 30 mL of distillate was collected. The concentration can be checked by NMR by taking a 200 µL aliquot of the stock solution and determining the ratio of [1.1.1]propellane to an added 1,1,2,2 tetrachloroethane as standard (typically concentrations are 0.4-0.7 M with this protocol).

4. General procedure for the synthesis of substrates 1:[2,3,4]

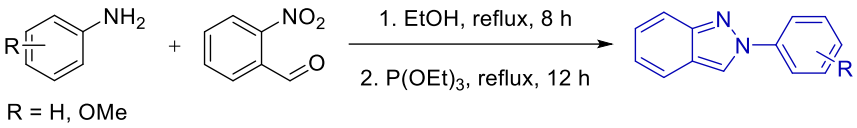
The substrates **2a-2s** were prepared according to previously reported methods and the NMR data of these compound was compared with the corresponding reported data.



In a 100 mL round bottom flask with magnetic stirrer, quinonxalin-2(1*H*)-one 6 (1.0 equiv.) was taken and dissolved in DMF. Potassium carbonate (1.2 equiv.) was added to the flask, followed by dropwise (or portion-wise for solids) addition of the haloalkane (1.6 equiv.) while stirring. The reaction was allowed to stir at room temperature for 16 hours in air atmosphere. It was quenched by adding water (20 mL) and extracted with EtOAc (40 mL). The organic layer was washed with water (2 x 20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL). Then, the organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product. The crude product is purified by flash column chromatography in EtOAc/n-hexane (15-25%) to obtain corresponding products.



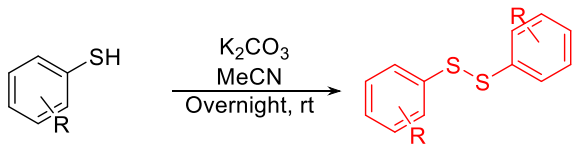
In a dried 100 mL round bottom flask, quinonxalin-2(1*H*)-one (1.0 equiv.), corresponding phenylboronic acid (1.2 equiv.), $Cu(OAc)_2$ (2.0 equiv.), molecular sieves (1.4 g, 4Å), CH_2Cl_2 (13 mL) and DMF (5 mL) was added pyridine (2.0 equiv.) under air. The reaction mixture was allowed to stir at room temperature for 72 h and then filtered through Celite pad. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography EtOAc/n-hexane (15-25%) to afford the corresponding *N*-aryl quinoxalin-2(1*H*)-ones as solids.



In EtOH (0.5 M), a solution of aniline (6 mmol, 1 equiv.), and 2-nitrobenzaldehyde (6 mmol, 1 equiv.) was refluxed for 8 h. The resulting crystalline solid was collected by filtration, and dried under reduced pressure. The solid was refluxed in triethyl phosphite (60 mmol, 10 equiv.) for 12 h. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product is purified by flash column chromatography in EtOAc/n-hexane (15-25%) to obtain corresponding products

5. General procedure for the synthesis of disulfides:[5,6]

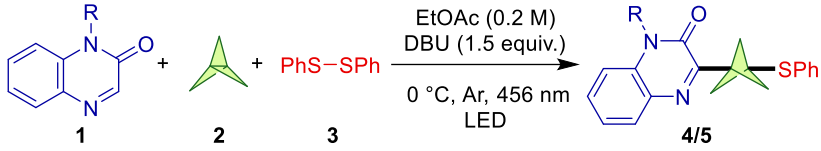
The disulfide substrates were synthesized according to previous literature reports and their NMR spectra were confirmed by comparing with the corresponding reported products.



To a 100mL round bottom flask, thiophenol (1.0 equiv.), anhydrous potassium carbonate (1.0 equiv.), and MeCN (10 mL) were added sequentially, and the reaction was conducted at room temperature under air atmosphere for 1 hour. The

corresponding disulfides were obtained after filtration and concentration. They were purified by flash column chromatography in EtOAc/n-hexane (2-5%) to obtain corresponding disulfides.

6. General procedure for 1,3-thioheteroarylation of [1.1.1]propellane:



An oven-dried borosilicate test tube equipped with a magnetic stir bar was added quinoxalin-2(1*H*)-one **1** (32.0 mg, 1.0 equiv., 0.2 mmol), diaryl disulfide **3** (65.5 mg, 1.5 equiv., 0.3 mmol), and DBU (54.7 mg, 1.5 equiv., 0.3 mmol). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.2 M EtOAC solvent (1.0 mL) and [1.1.1]propellane (0.6 mL, 0.3 mmol, 1.5 eq., 0.5 M solution in hexane) were added through the septum using a syringe and the reaction tube was placed in a 0 °C ethylene glycol, water bath approximately 5 cm from the light setup. After the reaction, 10 mL of water was added and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (mesh 230−400) using hexane and EtOAc as an eluent to afford the corresponding products (**4**/**5**).

6.1. Characterization and spectral data of the products:

6.1.1 Substrate scope:

1-methyl-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4a: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 8% EtOAc in Hexane), the product was isolated as colorless solid (66%, 44.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.34 – 7.24 (m, 5H), 3.63 (s, 3H), 2.44 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.5, 143.6, 122.8, 122.7, 122.5, 121.9, 119.2, 119.2, 118.0, 116.8, 112.7, 102.7, 44.8, 32.4, 32.2, 17.7. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{19}N_2OS$: 335.1213; found: 335.1204.

1-(3-phenylpropyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4b: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 10% EtOAc in Hexane), the product was isolated as White solid (57%, 49.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.43 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.36 – 7.25 (m, 6H), 7.24 – 7.20 (m, 3H), 7.04 (dd, *J* = 8.5, 1.2 Hz, 1H), 4.22 – 4.16 (m, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.46 (s, 6H), 2.06 (dq, *J* = 10.1, 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.4, 154.2, 140.7, 133.8, 133.7, 133.1, 132.5, 130.3, 130.1, 129.0, 128.6, 128.4, 127.8, 126.4, 123.5, 113.5, 55.8, 43.3, 43.2, 41.7, 33.3, 28.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{28}H_{27}N_2OS$: 439.1839; found: 439.1833.

1-(cyclopropylmethyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4c: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 8% EtOAc in Hexane), the product was isolated as colorless solid (66%, 49.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.38 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.35 – 7.26 (m, 4H), 4.13 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 6H), 1.24 (ddt, *J* = 13.1, 11.6, 5.8 Hz, 1H), 0.52 (ddt, *J* = 5.0, 2.6, 1.7 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.7, 154.5, 133.9, 133.7, 133.1, 133.0, 130.3, 130.1, 129.0, 127.8, 123.5, 114.0, 55.8, 45.9, 43.4, 43.2, 9.7, 4.3. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{23}H_{23}N_2OS$: 375.1526; found: 375.1519.

ethyl 2-(2-oxo-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-1(2*H*)-yl)acetate 4d: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 8% EtOAc in Hexane), the product was isolated as colorless solid (49%, 39.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.34 – 7.27 (m, 4H), 7.02 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.94 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 6H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.1, 155.3, 154.0, 133.8, 133.6, 132.9, 132.6, 130.4, 130.3, 128.9, 127.8, 124.0, 113.1, 62.2, 55.8, 43.2, 43.2, 29.8, 14.2. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{23}H_{23}N_2O_3S$: 407.1424; found: 407.1426.

1-(2-hydroxyethyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4e: Synthesised according to the general procedure and after chromatography on SiO_2 (15% to 20% EtOAc in Hexane), the product was isolated as colorless solid (46%, 33.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.37 (dd, *J* = 8.5, 1.2 Hz,

1H), 7.34 – 7.25 (m, 4H), 4.39 (t, *J* = 5.8 Hz, 2H), 3.97 (t, *J* = 5.7 Hz, 2H), 2.41 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.2, 155.2, 133.8, 133.5, 133.2, 132.9, 130.3, 130.3, 129.0, 127.8, 123.9, 113.9, 60.3, 55.7, 44.6, 43.2, 43.1. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_2S$: 365.1318; found: 365.1328.

1-allyl-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4f: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 10% EtOAc in Hexane), the product was isolated as colorless solid **(**39%, 28.1 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.35 – 7.26 (m, 4H), 7.24 (dd, *J* = 8.5, 1.2 Hz, 1H), 5.90 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.25 (dtd, *J* = 10.4, 1.7, 0.9 Hz, 1H), 5.15 (dtd, *J* = 17.2, 1.8, 0.8 Hz, 1H), 4.83 (dt, *J* = 5.2, 1.8 Hz, 2H), 2.44 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.6, 154.1, 133.9, 133.7, 133.1, 132.7, 130.7, 130.2, 130.1, 129.0, 127.8, 123.7, 118.3, 114.2, 55.8, 44.3, 43.4, 43.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{21}N_2OS$: 361.1369; found: 361.1376.

3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one 4g: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 10% EtOAc in Hexane), the product was isolated as colorless solid (36%, 25.8 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.7, 7.3, 1.5 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.42 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.38 – 7.28 (m, 4H), 4.98 (d, *J* = 2.5 Hz, 2H), 2.44 (s, 6H), 2.27 (t, *J* = 2.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.5, 153.5, 133.9, 133.6, 133.1, 132.0, 130.3, 130.3, 129.0, 127.8, 124.1, 114.2, 76.8, 73.3, 55.8, 43.3, 43.2, 31.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{19}N_2OS$: 359.1213; found: 359.1226.

1-(2-oxo-2-phenylethyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4h: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 10% EtOAc in Hexane), the product was isolated as colorless solid (51%, 44.6 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.72 – 7.63 (m, 1H), 7.59 – 7.51 (m, 2H), 7.53 – 7.47 (m, 2H), 7.41 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.35 – 7.25 (m, 4H), 6.91 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.67 (s, 2H), 2.44 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 191.2, 155.2, 154.3, 134.6, 134.5, 133.9, 133.7, 133.1, 133.0, 130.4, 130.3, 129.2, 129.0, 128.3, 127.8, 123.9, 113.6, 55.8, 48.2, 43.3, 43.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{23}N_2O_2S$: 439.1475; found: 439.1487.

1-benzyl-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4i: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 10% EtOAc in Hexane), the product was isolated as colorless solid (59%, 48.3 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.39 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.36 – 7.25 (m, 6H), 7.27 – 7.17 (m, 4H), 5.43 (s, 2H), 2.49 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.7, 154.5, 135.3, 133.9, 133.7, 133.1, 132.9, 130.2, 130.2, 129.0, 129.0, 127.8, 126.9, 123.7, 114.5, 55.8, 45.7, 43.4, 43.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{23}N_2OS$: 411.1526; found: 411.1517.

1-(4-chlorobenzyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4j: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 10% EtOAc in Hexane), the product was isolated as colorless solid (66%, 58.6 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.36 – 7.24 (m, 6H), 7.18 – 7.11 (m, 3H), 5.38 (s, 2H), 2.46 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.7, 154.5, 133.9, 133.8, 133.7, 133.6, 133.1, 132.7, 130.4, 130.3, 129.3, 129.0, 128.4, 127.9, 123.9, 114.2, 55.8, 45.1, 43.4, 43.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{22}ClN_2OS$: 445.1136; found: 445.1128.

2-((2-oxo-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-1(2*H*)-yl)methyl)benzonitrile 4k: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 12% EtOAc in Hexane), the product was isolated as colorless solid (40%, 34.7 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.73 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.47 – 7.40 (m, 2H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.03 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.97 – 6.90 (m, 1H), 5.64 (s, 2H), 2.47 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.6, 154.5, 138.8, 134.0, 133.7, 133.6, 133.4, 133.2, 132.4, 130.6, 130.5, 129.0, 128.4, 127.9, 126.7, 124.3, 117.0, 114.0, 111.2, 55.9, 43.9, 43.4, 43.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{22}N_3OS$: 436.1478; found: 436.1464.

1-(4-fluorobenzyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4l: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 10% EtOAc in Hexane), the product was isolated as white solid (60%, 51.3 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.41 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.36 – 7.24 (m, 4H), 7.25 – 7.14 (m, 3H), 7.03 – 6.94 (m, 2H), 5.38 (s, 2H), 2.47 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.5 Hz), 155.7, 154.5, 133.9, 133.6, 133.1, 132.7, 131.0 (d, *J* = 3.2 Hz), 130.3 (d, *J* = 12.4 Hz), 129.0, 128.7 (d, *J* = 8.0

Hz), 127.8, 123.9, 116.1, 115.9, 114.2, 55.8, 45.0, 43.4, 43.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.29. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{22}FN_2OS$: 429.1431; found: 429.1442.

3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one 4m: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 10% EtOAc in Hexane), the product was isolated as colorless solid (62%, 59.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.41 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.36 – 7.27 (m, 6H), 7.12 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.47 (s, 2H), 2.48 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.7, 154.4, 139.3, 133.9, 133.6, 133.1, 132.6, 130.5, 130.4, 130.2 (q, *J* = 32.6 Hz), 129.0, 127.8, 127.6, 126.0 (q, *J* = 3.8 Hz), 124.0, 124.0 (q, *J* = 272.5 Hz), 114.1, 55.8, 45.3, 43.3, 43.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.60. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{22}F_3N_2OS$: 479.1399; found: 479.1402.

1-phenyl-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4n: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 12% EtOAc in Hexane), the product was isolated as colorless solid (61%, 48.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 1H), 7.60 – 7.52 (m, 2H), 7.52 – 7.47 (m, 1H), 7.48 – 7.42 (m, 2H), 7.32 – 7.18 (m, 7H), 6.66 – 6.58 (m, 1H), 2.42 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.3, 154.2, 135.6, 134.3, 133.8, 133.7, 132.8, 130.4, 129.9, 129.7, 129.5, 128.9, 128.3, 127.7, 123.9, 115.5, 55.8, 43.3, 43.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{21}N_2OS$: 397.1369; found: 397.1381.

1-(4-fluorophenyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4o: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 12% EtOAc in Hexane), the product was isolated as colorless solid (71%, 58.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 1H), 7.50 – 7.43 (m, 2H), 7.35 – 7.18 (m, 9H), 6.66 – 6.58 (m, 1H), 2.42 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.9 (d, *J* = 249.8 Hz), 156.2, 154.3, 134.2, 133.9, 133.6, 132.8, 131.4 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 8.7 Hz), 130.0, 129.9, 129.0, 127.8, 124.1, 117.5 (d, *J* = 23.0 Hz), 115.3, 55.8, 43.3, 43.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.16. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{20}FN_2OS$: 415.1275; found: 415.1270.

3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4p: Synthesised according to the general procedure and after chromatography on SiO_2 (10% to 15% EtOAc in Hexane), the product was isolated as colorless solid (45%, 28.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.16 (s, 1H), 7.81 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.49 (ddd, *J* = 8.4, 7.3, 1.4 Hz, 1H), 7.40 – 7.28 (m, 4H), 7.24 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.48 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.4, 156.1, 134.0, 133.6, 133.0, 131.4, 130.4, 129.2, 129.0, 127.9, 124.4, 115.6, 55.8, 43.3, 43.0. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{17}N_2OS$: 321.1056; found: 321.1062.

7-bromo-1-methyl-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 4q: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 10% EtOAc in Hexane), the product was isolated as colorless solid (59%, 48.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 1H), 7.56 – 7.48 (m, 2H), 7.44 (dd, *J* = 6.7, 2.0 Hz, 2H), 7.38 – 7.29 (m, 3H), 3.62 (s, 3H), 2.44 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.9, 154.2, 134.5, 133.9, 133.6, 131.8, 131.4, 129.0, 127.9, 127.0, 124.3, 116.8, 55.8, 43.4, 43.2, 28.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{18}BrN_2OS$: 413.0318; found: 413.0315.

2-phenyl-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)-2*H*-indazole 4r: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 10% EtOAc in Hexane), the product was isolated as colorless solid (35%, 25.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.61 (m, 2H), 7.56 – 7.47 (m, 3H), 7.46 – 7.36 (m, 4H), 7.36 – 7.23 (m, 4H), 7.07 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1H), 2.21 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.2, 140.2, 133.8, 133.5, 133.1, 129.8, 129.0, 128.8, 128.0, 127.4, 126.7, 121.8, 121.3, 120.2, 117.7, 57.1, 44.3, 36.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{21}N_2S$: 369.1420; found: 369.1422.

2-(3, 5-dimethoxyphenyl)-3-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)-2*H*-indazole 4s: Synthesised according to the general procedure and after chromatography on SiO_2 (7% to 12% EtOAc in Hexane), the product was isolated as colorless solid (32%, 27.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (ddt, *J* = 18.5, 8.6, 1.1 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.39 – 7.30 (m, 4H), 7.09 (ddd, *J* = 8.5, 6.7, 0.9 Hz, 1H), 6.63 (t, *J* = 2.3 Hz, 1H), 6.60 (d, *J* = 2.3 Hz, 2H), 3.84 (s, 6H), 2.30 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.8, 148.3, 141.8, 134.0, 133.3, 133.1, 129.1, 128.1, 126.8, 121.9, 121.4, 120.3, 117.9, 106.0, 102.0, 57.2, 55.8, 44.3, 36.5. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{25}N_2O_2S$: 429.1631; found: 429.1637.

1-methyl-3-(3-(p-tolylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 5a: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 10% EtOAc in Hexane), the product was isolated as colorless solid **(**69%, 48.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.45 – 7.39 (m,

2H), 7.34 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.28 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.18 – 7.11 (m, 2H), 3.66 (s, 3H), 2.43 (s, 6H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 155.6, 154.6, 137.9, 134.2, 133.5, 132.9, 130.2, 130.2, 129.9, 129.8, 123.7, 113.7, 55.6, 43.3, 43.3, 28.7, 21.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{21}N_2OS$: 349.1369; found: 349.1369.

3-(3-((4-methoxyphenyl)thio)bicyclo[1.1.1]pentan-1-yl)-1-methylquinoxalin-2(1*H*)-one 5b: Synthesised according to the general procedure and after chromatography on SiO_2 (7% to 12% EtOAc in Hexane), the product was isolated as colorless solid (56%, 40.7mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.32 (td, *J* = 7.7, 1.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.90 – 6.84 (m, 2H), 3.82 (s, 3H), 3.64 (s, 3H), 2.38 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 159.8, 155.6, 154.5, 136.2, 133.4, 132.8, 130.1, 130.0, 123.9, 123.6, 114.5, 113.6, 55.4, 43.6, 43.1, 28.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_2S$: 365.1318; found: 365.1313.

3-(3-((4-chlorophenyl)thio)bicyclo[1.1.1]pentan-1-yl)-1-methylquinoxalin-2(1*H*)-one 5c: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 10% EtOAc in Hexane), the product was isolated as colorless solid (59%, 43.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.36 – 7.27 (m, 4H), 3.64 (s, 3H), 2.42 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 155.3, 154.5, 135.2, 134.1, 133.5, 132.9, 132.2, 130.3, 130.2, 129.2, 123.8, 113.7, 55.7, 43.4, 43.1, 28.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{18}ClN_2OS$: 369.0823; found: 369.0815.

3-(3-((4-bromophenyl)thio)bicyclo[1.1.1]pentan-1-yl)-1-methylquinoxalin-2(1*H*)-one 5d: Synthesised according to the general procedure and after chromatography on SiO_2 (4% to 10% EtOAc in Hexane), the product was isolated as colorless solid (65%, 53.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.29 – 7.25 (m, 1H), 3.65 (s, 3H), 2.45 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 155.2, 154.5, 135.3, 133.4, 132.9, 132.8, 132.1, 130.3, 130.1, 123.7, 122.1, 113.6, 55.7, 43.4, 43.0, 28.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{18}BrN_2OS$: 413.0318; found: 413.0315.

1-methyl-3-(3-(naphthalen-2-ylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 5e: Synthesised according to the general procedure and after chromatography on SiO_2 (5% to 10% EtOAc in Hexane), the product was isolated as colorless solid (45%, 34.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.7 Hz, 1H), 7.87 – 7.74 (m, 4H), 7.58 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.31 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.24 (d, *J* = 1.2 Hz, 1H), 3.62 (s, 3H), 2.49 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 155.4, 154.4, 133.7, 133.4, 132.8, 132.7, 132.6, 131.1, 131.0, 130.2, 130.0, 128.4, 127.7, 127.6, 126.4, 126.3, 123.6, 113.6, 55.8, 43.4, 43.2, 28.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{21}N_2OS$: 385.1369; found: 385.1359.

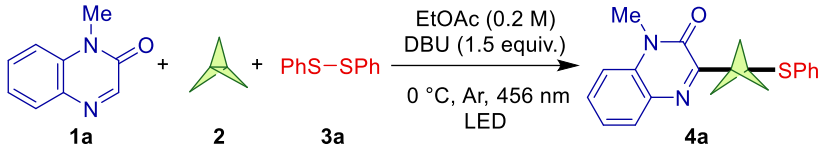
3-(3-((3-methoxyphenyl)thio)bicyclo[1.1.1]pentan-1-yl)-1-methylquinoxalin-2(1*H*)-one 5f: Synthesised according to the general procedure and after chromatography on SiO_2 (7% to 12% EtOAc in Hexane), the product was isolated as colorless solid (54%, 39.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.54 (ddt, *J* = 8.4, 7.2, 1.1 Hz, 1H), 7.34 (ddt, *J* = 8.2, 7.3, 1.0 Hz, 1H), 7.31 – 7.20 (m, 2H), 7.11 (ddt, *J* = 7.7, 1.7, 0.8 Hz, 1H), 7.07 (t, *J* = 2.1 Hz, 1H), 6.88 – 6.82 (m, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 2.48 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 159.8, 155.5, 154.6, 134.8, 133.5, 132.9, 130.2, 130.2, 129.7, 125.9, 123.7, 118.8, 113.8, 113.7, 55.8, 55.4, 43.4, 43.1, 28.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_2S$: 365.1318; found: 365.1313.

1-methyl-3-(3-(pyridin-2-ylthio)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 5g: Synthesised according to the general procedure and after chromatography on SiO_2 (10% to 20% EtOAc in Hexane), the product was isolated as colorless oily liquid (41%, 27.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.53 (dddd, *J* = 10.1, 7.3, 3.0, 1.7 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.05 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 3.66 (s, 3H), 2.69 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 159.2, 155.4, 154.6, 149.8, 136.3, 133.5, 133.0, 130.3, 130.2, 124.5, 123.7, 120.5, 113.7, 56.3, 45.0, 41.3, 28.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{18}N_3OS$: 336.1165; found: 336.1163.

3-(3-(benzo[d]thiazol-2-ylthio)bicyclo[1.1.1]pentan-1-yl)-1-methylquinoxalin-2(1*H*)-one 5h: Synthesised according to the general procedure and after chromatography on SiO_2 (10% to 20% EtOAc in Hexane), the product was isolated as colorless oily liquid (34%, 26.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.55 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.44 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.34 (dddd, *J* = 8.3, 7.3, 6.3, 1.2 Hz, 2H), 7.30 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.68 (s, 3H), 2.79 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 164.5, 154.9, 154.6, 153.3, 136.0,

133.6, 132.9, 130.5, 130.3, 126.2, 124.7, 123.8, 122.4, 121.0, 113.8, 56.6, 44.6, 41.8, 28.8. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{18}N_3OS_2$: 392.0886; found: 392.0894.

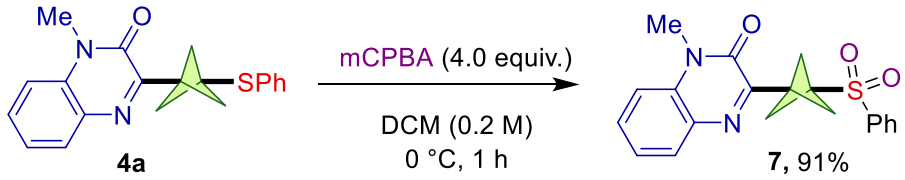
7. Gram-scale reaction:



An oven-dried two-neck round-bottom flask equipped with a magnetic stir bar was added quinoxalin-2(1*H*)-one **1a** (640.7 mg, 1.0 equiv., 4.0 mmol), diphenyl disulfide **3a** (1.31 g, 1.5 equiv., 6.0 mmol), and DBU (913.4 mg, 1.5 equiv., 6.0 mmol). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.2 M EtOAC solvent (20 mL) and [1.1.1]propellane (0.6 mL, 0.3 mmol, 1.5 eq., 0.5 M solution in hexane) were added through the septum using a syringe and the reaction tube was placed in a 0 °C ethylene glycol, water bath approximately 5 cm from the light setup. After the reaction, 50 mL of water was added and extracted with EtOAc (3 × 30 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (mesh 230–400) using 4% to 10% EtOAc in Hexane as an eluent to afford **4a** as a pale-yellow solid (58%, 778 mg).

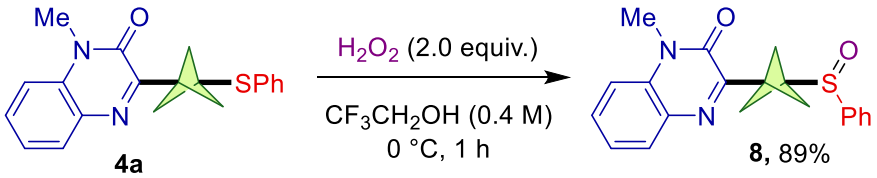
7.1 Further transformation of final products:

1-methyl-3-(3-(phenylsulfonyl)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 7:



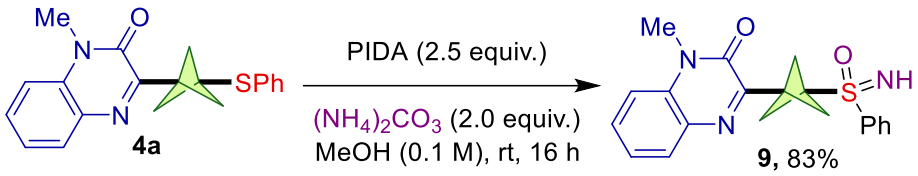
To a solution of **4a** (66.8 mg, 0.2 mmol) in DCM at 0 °C was added 3-chloroperoxybenzoic acid (138.1 mg, 0.8 mmol, 4.0 equiv.). The precipitate was filtered and the filtrate was washed with $Na_2S_2O_3$ solution and 1 M NaOH solution. The organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230–400 using 35-50% ethyl acetate in hexane as an eluent to afford product **7** (91%, 66.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.82 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.63 – 7.50 (m, 3H), 7.35 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.29 (dd, *J* = 8.7, 1.4 Hz, 1H), 3.64 (s, 3H), 2.56 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 154.2, 137.0, 133.8, 133.5, 132.8, 130.8, 130.3, 129.3, 128.8, 123.9, 113.8, 52.5, 41.1, 28.8. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_2O_3S$: 367.1111; found: 367.1113.

1-methyl-3-(3-(phenylsulfinyl)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 8:



To a solution of **4a** (66.8 mg, 0.2 mmol) in 2, 2, 2-trifluoroethanol (0.4 M) was cooled to 0 °C and treated with H_2O_2 (45 μL, 30% in water, 0.4 mmol, 2.0 equiv.). The reaction mixture was allowed to warm to room temperature and stirred it for overnight. Solid Na_2SO_3 was added to quench the reaction and the resulting mixture was stirred for 10 min. The resulting mixture was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230–400 using 60-70% ethyl acetate in hexane as an eluent to afford product **8** (89%, 62.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.55 – 7.43 (m, 4H), 7.31 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.28 – 7.23 (m, 1H), 3.61 (s, 3H), 2.40 – 2.28 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 154.4, 141.5, 133.5, 132.8, 131.1, 130.6, 130.2, 129.1, 124.3, 123.8, 113.7, 52.7, 50.9, 42.2, 28.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_2O_2S$: 351.1162; found: 351.1169.

1-methyl-3-(3-(phenylsulfonimidoyl)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one 9:

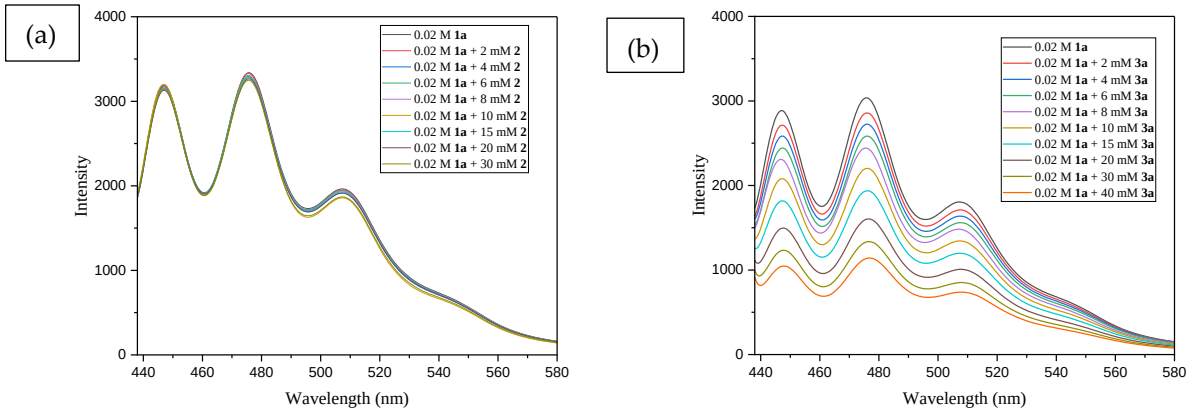


An oven-dried borosilicate test tube equipped with a magnetic stirring bar was added **4a** (66.8 mg, 0.2 mmol), PIDA (161 mg, 5.0 mmol, 2.5 equiv.) and $(NH_4)_2CO_3$ (38.4 mg, 0.4 mmol, 2.0 eq.). The reaction tube was vacuumed, backfilled with nitrogen (3 times), and fitted with a septum. Then, 2 mL of dry MeOH (0.1 M) and allowed to stir at room temperature for 16 h. The mixture was diluted with a saturated solution of brine and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230–400 using 5 to 7% MeOH in DCM as an eluent to afford product **9** (83%, 60.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (q, *J* = 8.1 Hz, 3H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.1 Hz, 1H), 3.62 (s, 3H), 2.58 (s, 1H), 2.52 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 154.3, 139.0, 133.4, 133.1, 132.7, 130.6, 130.2, 129.0, 129.0, 123.8, 113.7, 53.6, 52.2, 40.0, 28.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{20}N_3O_2S$: 366.1271; found: 366.1278.

8. Luminescence quenching studies and Stern-Volmer studies:

A 0.02 M solution of *N*-methyl quinoxalin-2(1*H*)-one (**1a**) in EtOAc was prepared and taken in a 1 mL fluorescence cuvette. For collection of data, the excitation and emission slit widths were fixed at 3 and 6 nm, respectively. Fluorescence emission spectra of *N*-methyl quinoxalin-2(1*H*)-one were recorded from 425 nm to 550 nm with an excitation wavelength of 415 nm. λ_{max}(emission) of *N*-methyl quinoxalin-2(1*H*)-one was observed at 442 nm. For each fluorescence quenching experiment, a 10 µL of 0.2 M solution of the diphenyl disulfide (**3a**), [1.1.1]propellane, DBU (prepared in EtOAc) was added individually to *N*-methyl quinoxalin-2(1*H*)-one solution (0.02 M) taken in a fluorescence cuvette, and emission spectra were recorded after each sequential addition. Figure S1b shows a decrease in emission intensity after each addition of diphenyl disulphide (0.2 M) and respective Stern-Volmer plot are shown in Figure S1d.

In a similar fashion fluorescence quenching experiment of *N*-methyl quinoxalin-2(1*H*)-one solution (0.02 M) was performed with [1.1.1]propellane (0.2 M) and DBU (0.2 M). The collective emission spectra and the Stern Volmer plot shown in Figure S1d.



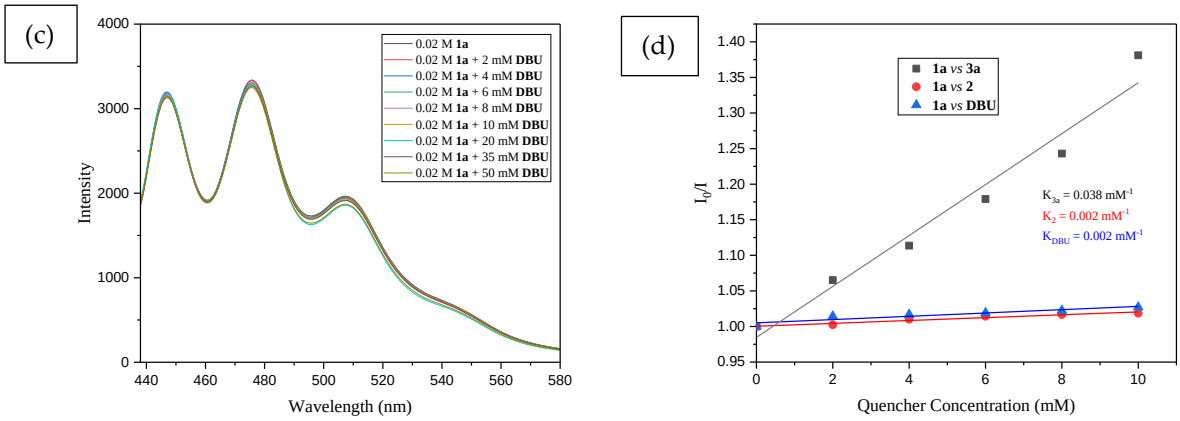
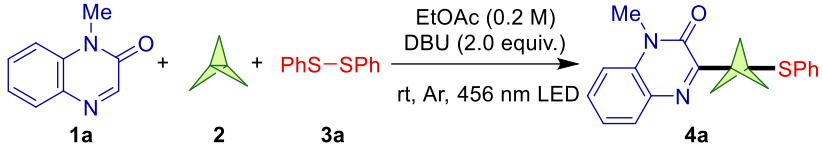


Figure S1. Luminescence quenching spectra of *N*-methyl quinoxalin-2(1*H*)-one

In EtOAc Solution: a) 0.02 M *N*-methyl quinoxalin-2(1*H*)-one (**1a**) *vs.* **2**; b) 0.02 M *N*-methyl quinoxalin-2(1*H*)-one (**1a**) *vs.* **3a**; c) 0.02 M *N*-methyl quinoxalin-2(1*H*)-one (**1a**) *vs.* **DBU** at 440 nm; d) Stern-Volmer plot of Luminescence quenching of 0.02 M *N*-methyl quinoxalin-2(1*H*)-one (**1a**) *vs.* **2, 3a,** and **DBU**.

9. Light on/off experiment over time:



An oven-dried borosilicate test tube equipped with a magnetic stir bar was added quinoxalin-2(1*H*)-one **1a** (32.0 mg, 1.0 equiv., 0.2 mmol), diaryl disulfide **3a** (65.5 mg, 1.5 equiv.), and DBU (54.7 mg, 1.5 equiv.). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.2 M EtOAC solvent (1.0 mL) and [1.1.1]propellane (0.6 mL, 0.3 mmol, 1.5 eq., 0.5 M solution in hexane) were added through the septum using a syringe and the reaction tube was placed in a 0 °C ethylene glycol, water bath approximately 5 cm from the light setup and stirred for 2 h. After the completion, the reaction mixture was quenched and extracted with EtOAc. Then, the crude ^{1}H NMR of resultant residue was taken using the 1, 1, 2, 2-tetrachloro ethane as an internal standard to obtain the yield of **4a** product. Thereafter, for a fresh batch of reaction was irradiated for 2 hours and then the light source was switched off with continuous stirring for the next 2 hours. After that, the crude ^{1}H NMR of the resultant residue was taken using the 1, 1, 2, 2-tetrachloro ethane as an internal standard to obtain the yield of **4a**. This cycle was repeated three times and the yield of **4a** with respect to time was plotted as shown in Figure S2. From the experiment, we conclude that a continuous light supply is needed for the reaction and confirms that the reaction does not proceed through a chain propagation mechanism.

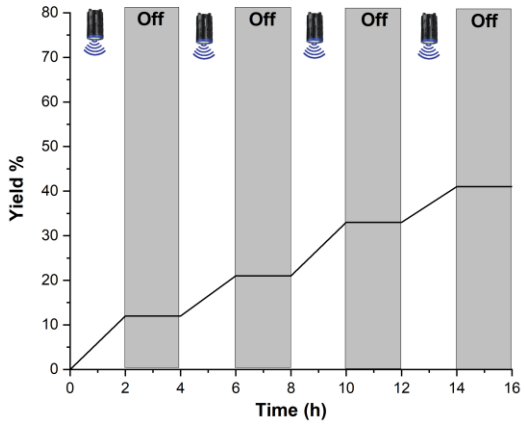
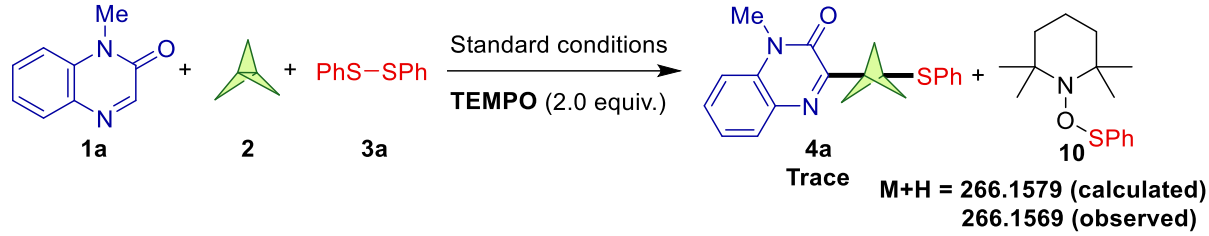


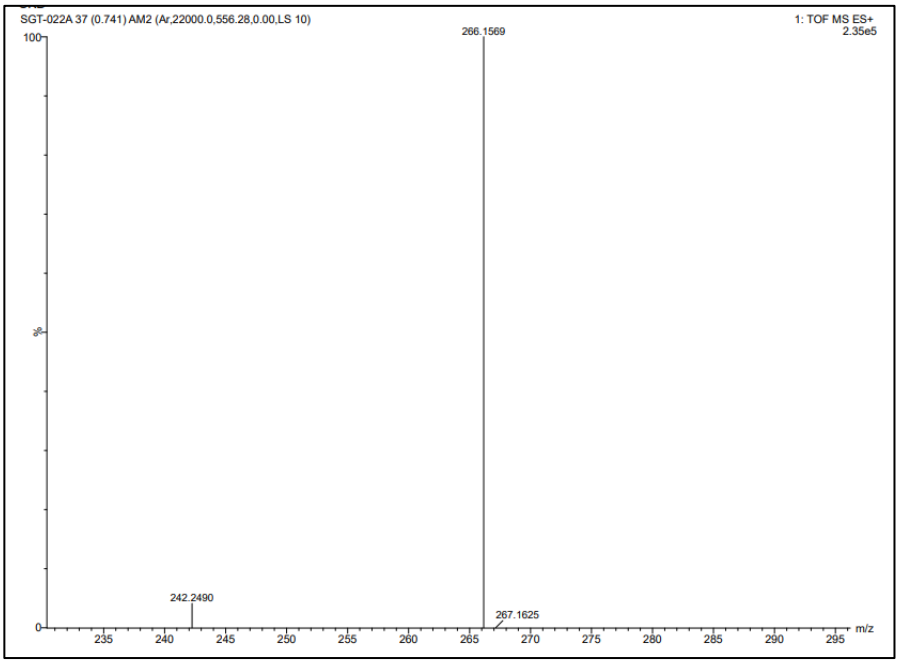
Figure S2: Light on/off experiments

10. Control Experiments:

10.1 Radical inhibition experiment with TEMPO:



An oven-dried borosilicate test tube equipped with a magnetic stir bar was added quinoxalin-2(1*H*)-one **1a** (1.0 equiv., 0.2 mmol), diaryl disulfide **3a** (1.5 equiv.), DBU (1.5 equiv.) and TEMPO (2.0 equiv.). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.2 M EtOAC solvent (1.0 mL) and [1.1.1]propellane (0.6 mL, 0.3 mmol, 1.5 eq., 0.5 M solution in hexane) were added through the septum using a syringe and the reaction tube was placed in a 0 °C ethylene glycol, water bath approximately 5 cm from the light setup. After the reaction, 10 mL of water was added and extracted with EtOAc (3 × 20 mL). The product **4a** was not observed rather TEMPO adduct **10** was observed in HRMS, which suggest that our reaction proceeds through the radical mechanism.



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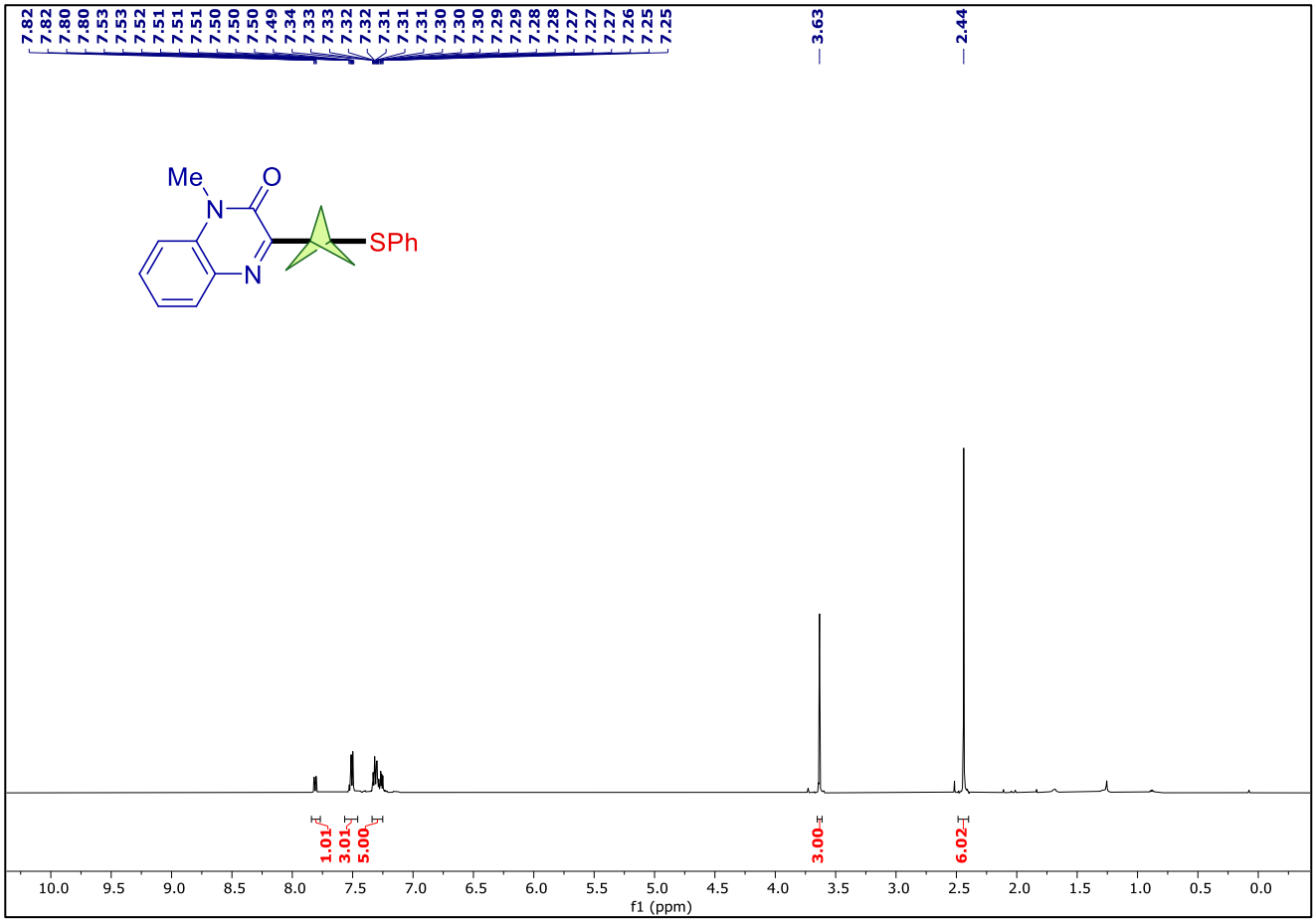
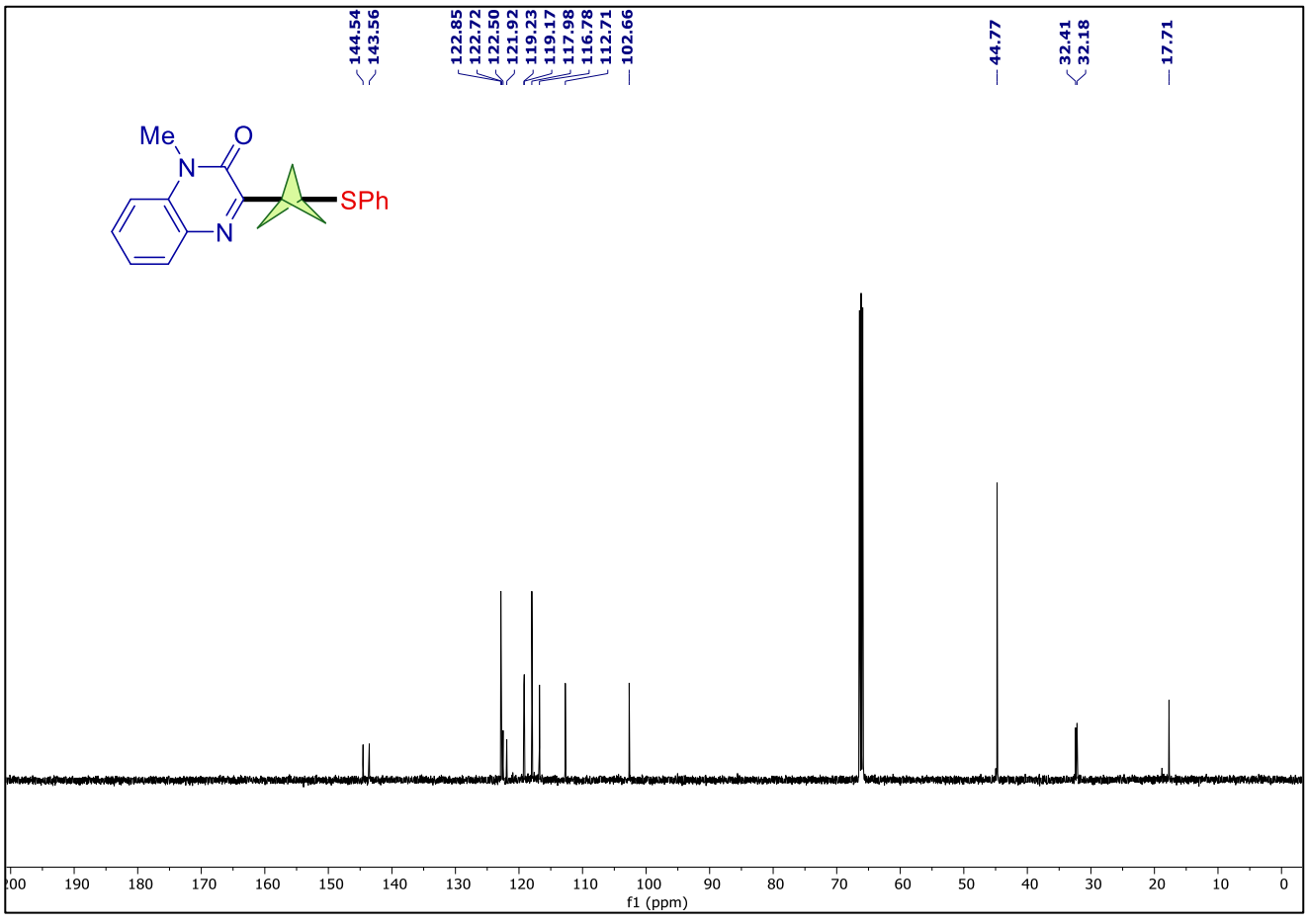
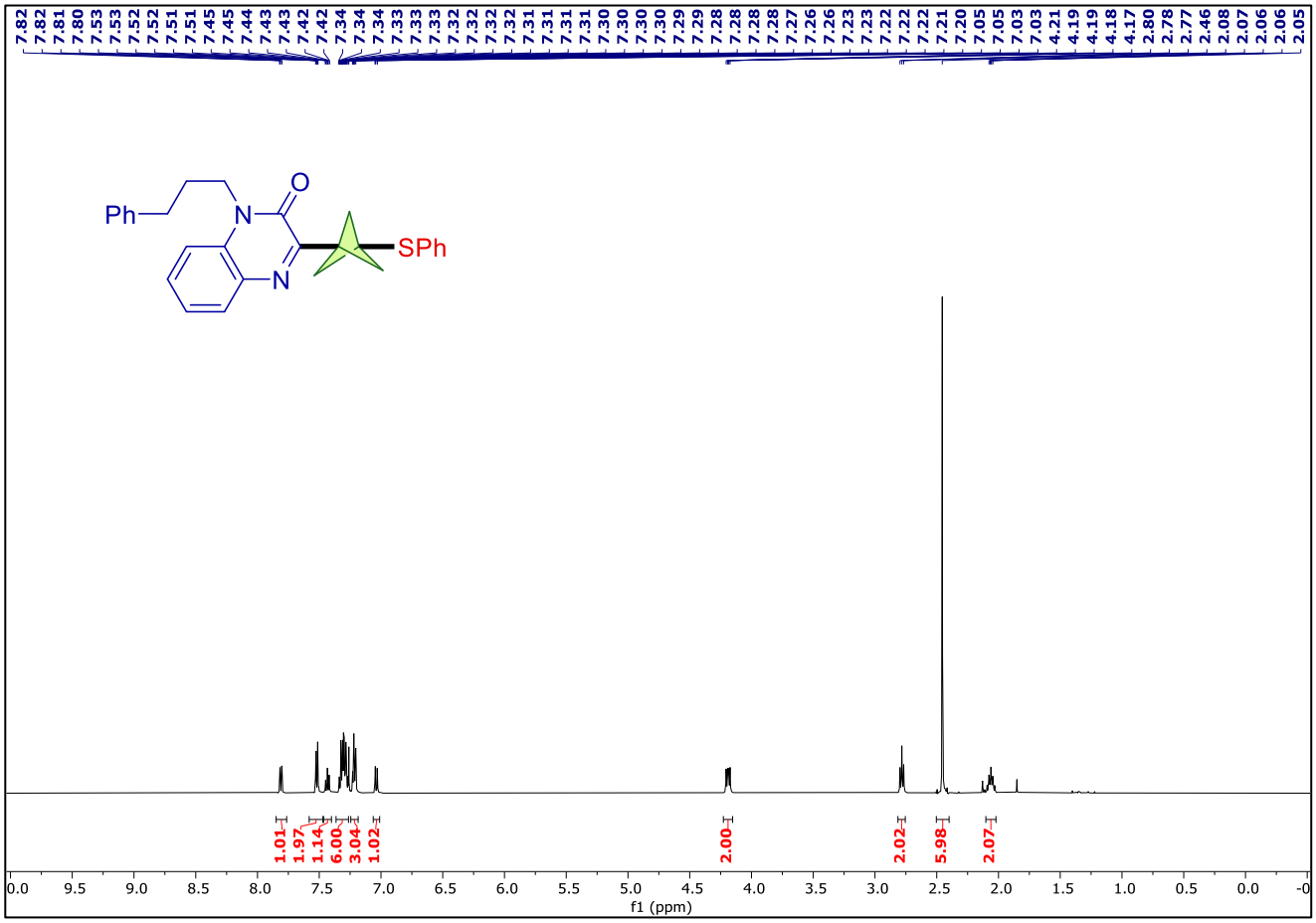
11. NMR spectral data:



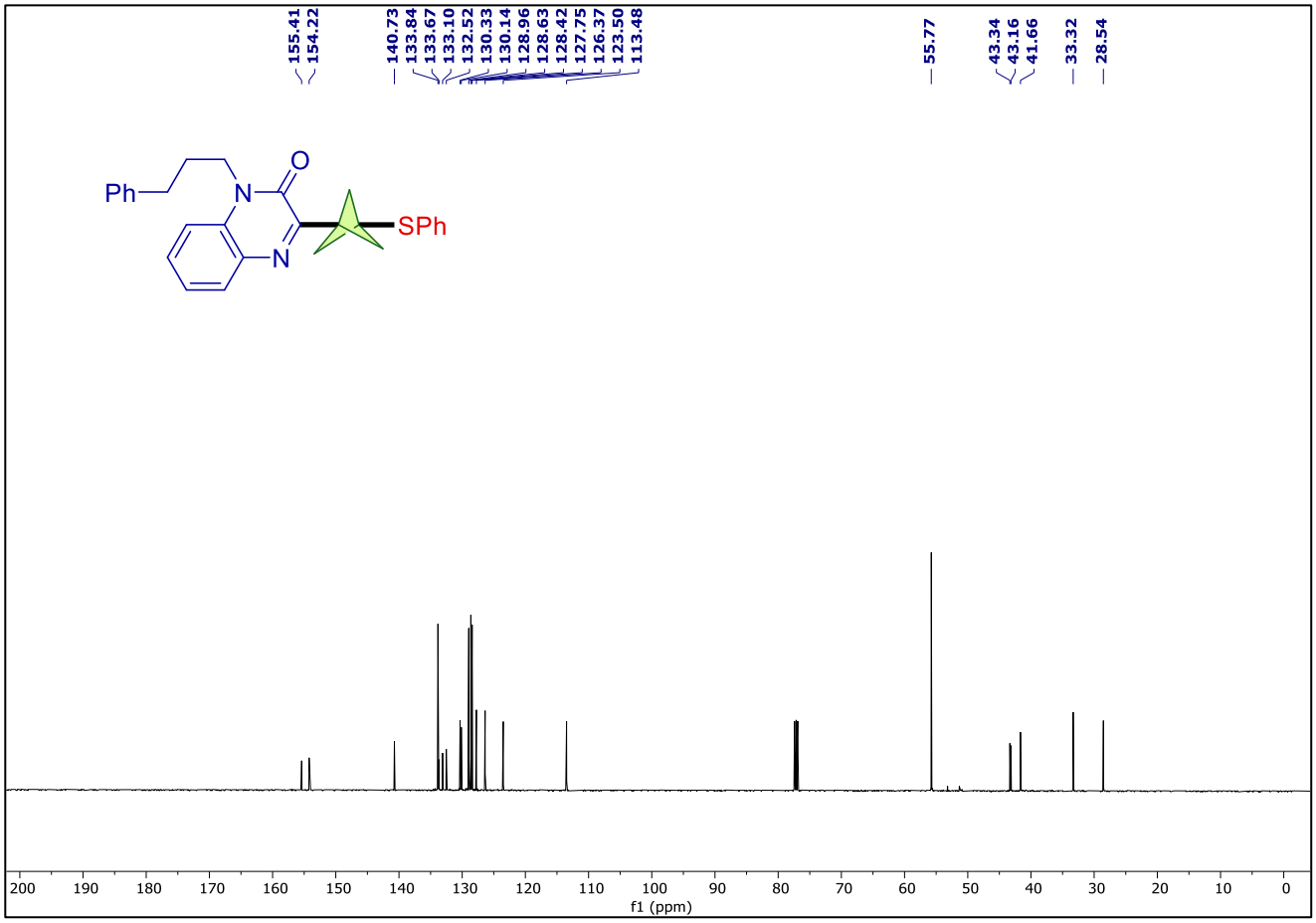
^{1}H NMR of compound **4a** (500 MHz, $CDCl_3$)



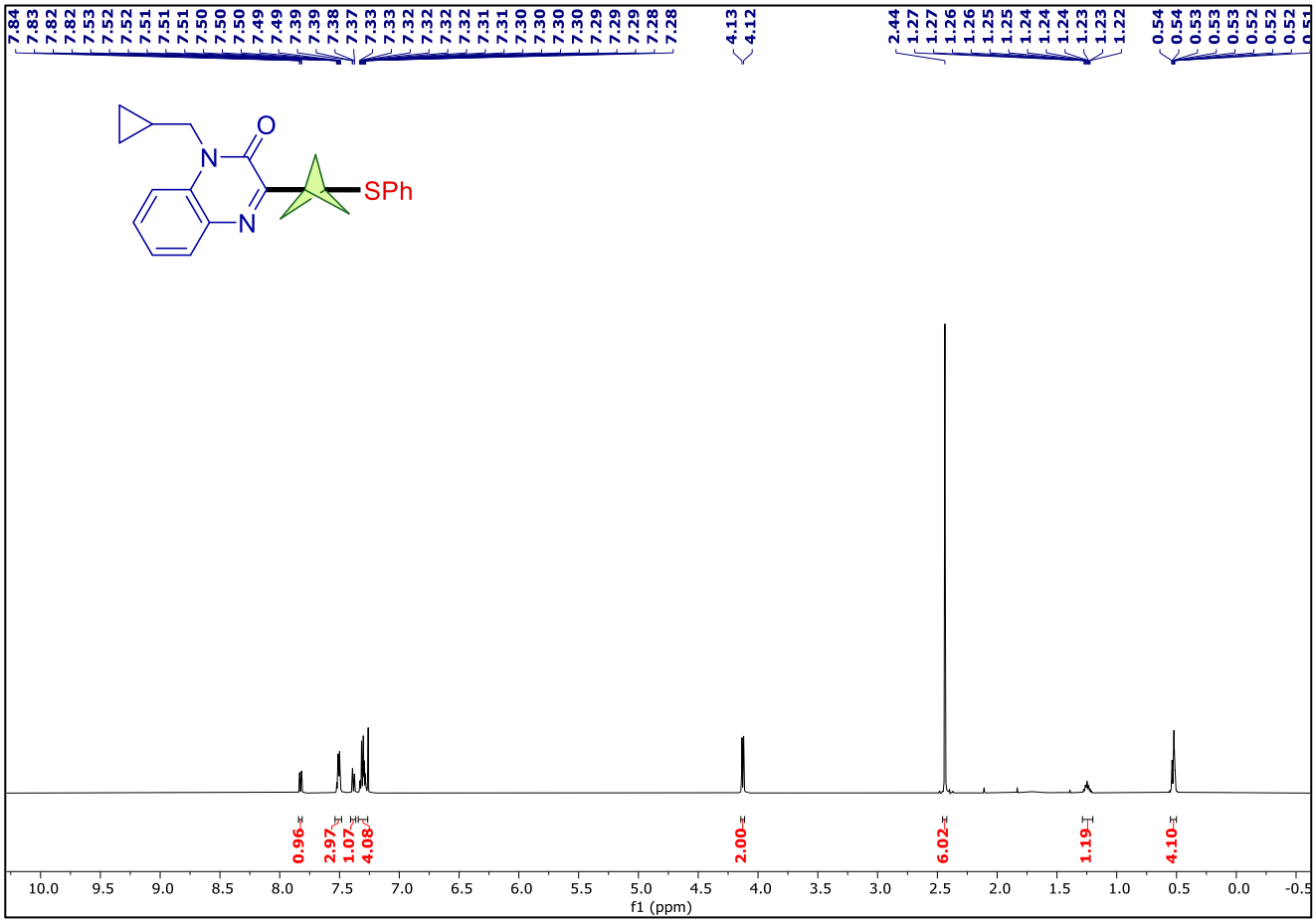
^{13}C{^{1}H} NMR of compound **4a** (126 MHz, $CDCl_3$)



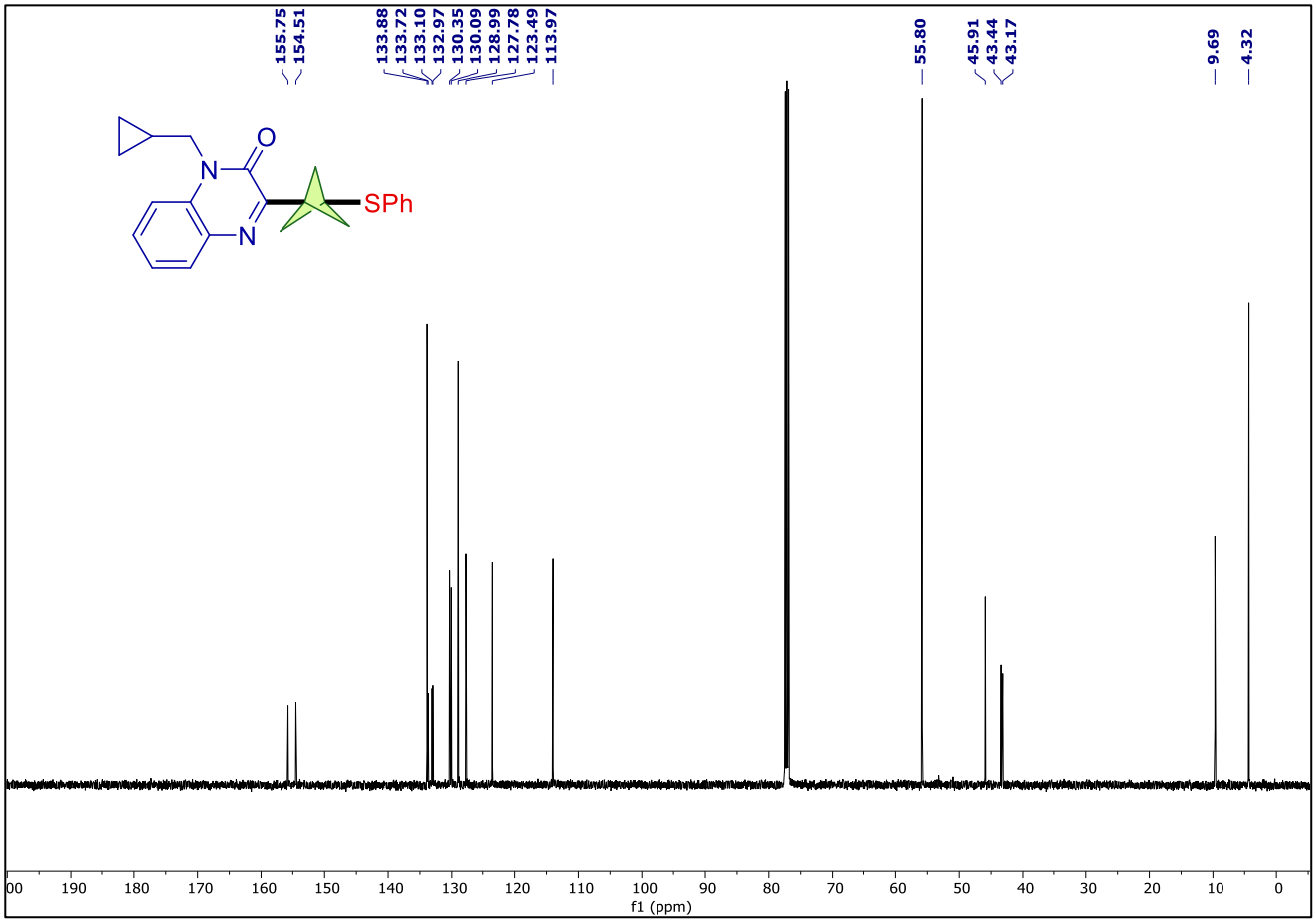
^{1}H NMR of compound **4b** (500 MHz, $CDCl_3$)



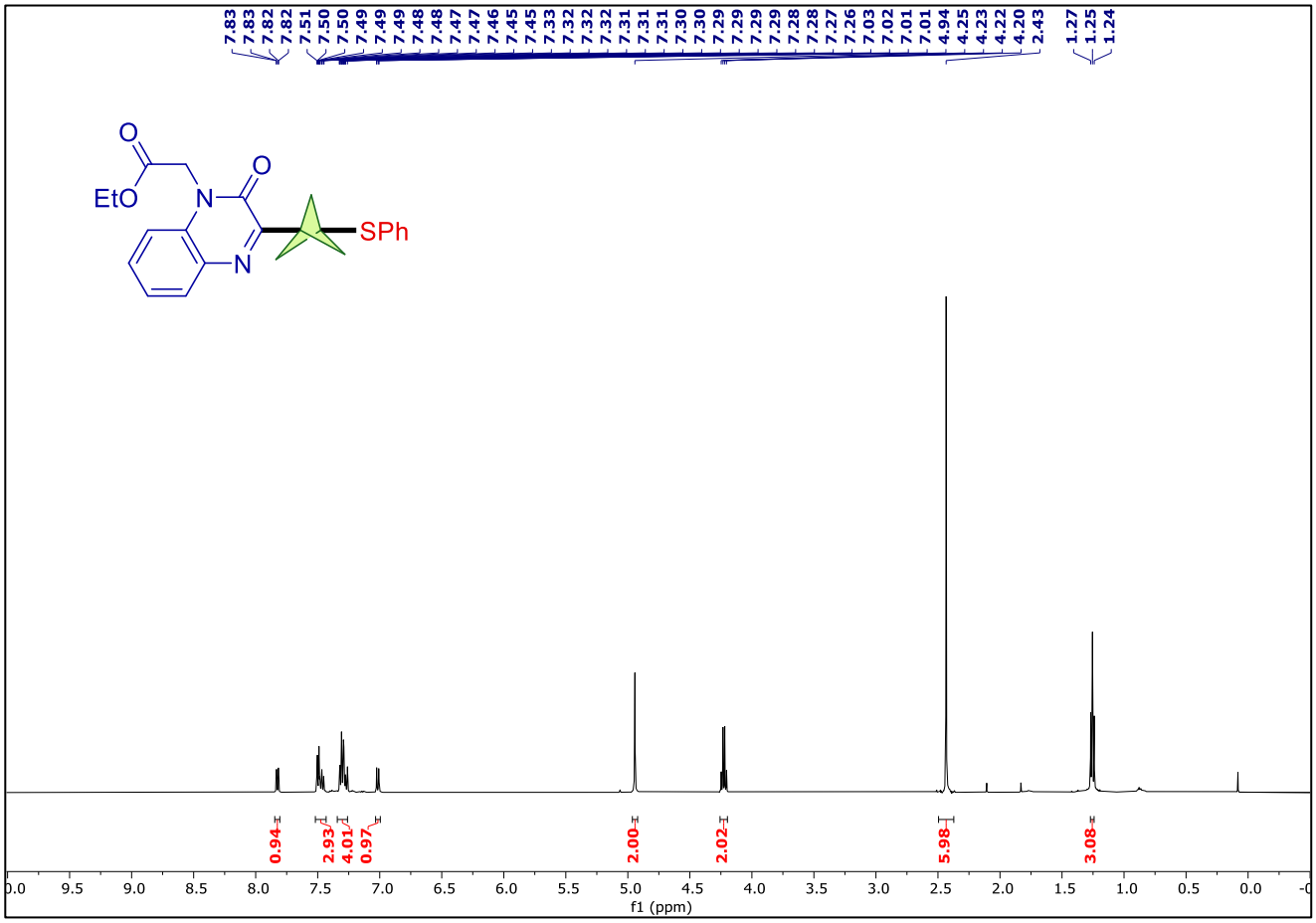
^{13}C{^{1}H} NMR of compound **4b** (126 MHz, $CDCl_3$)



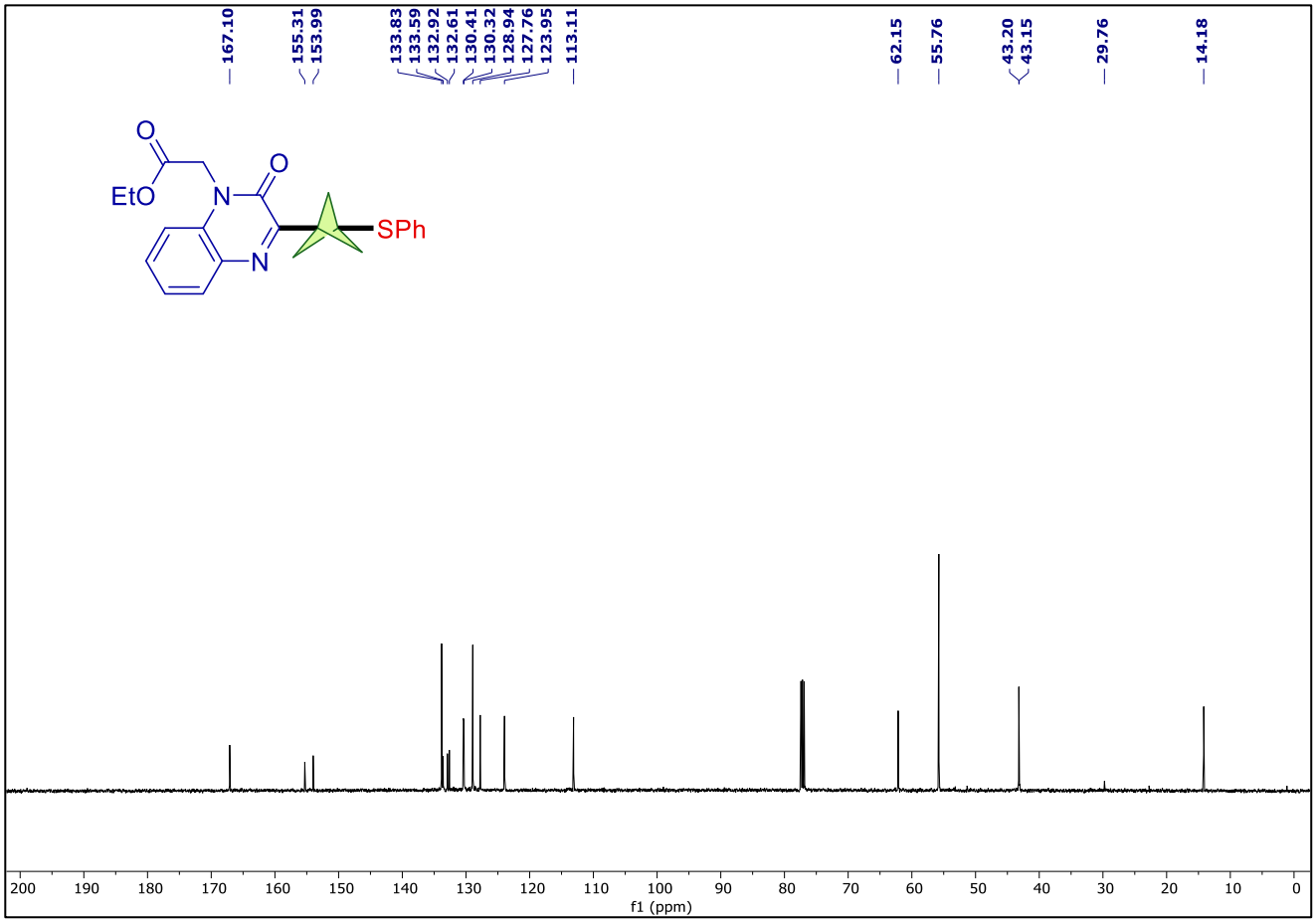
^{1}H NMR of compound **4c** (500 MHz, $CDCl_3$)



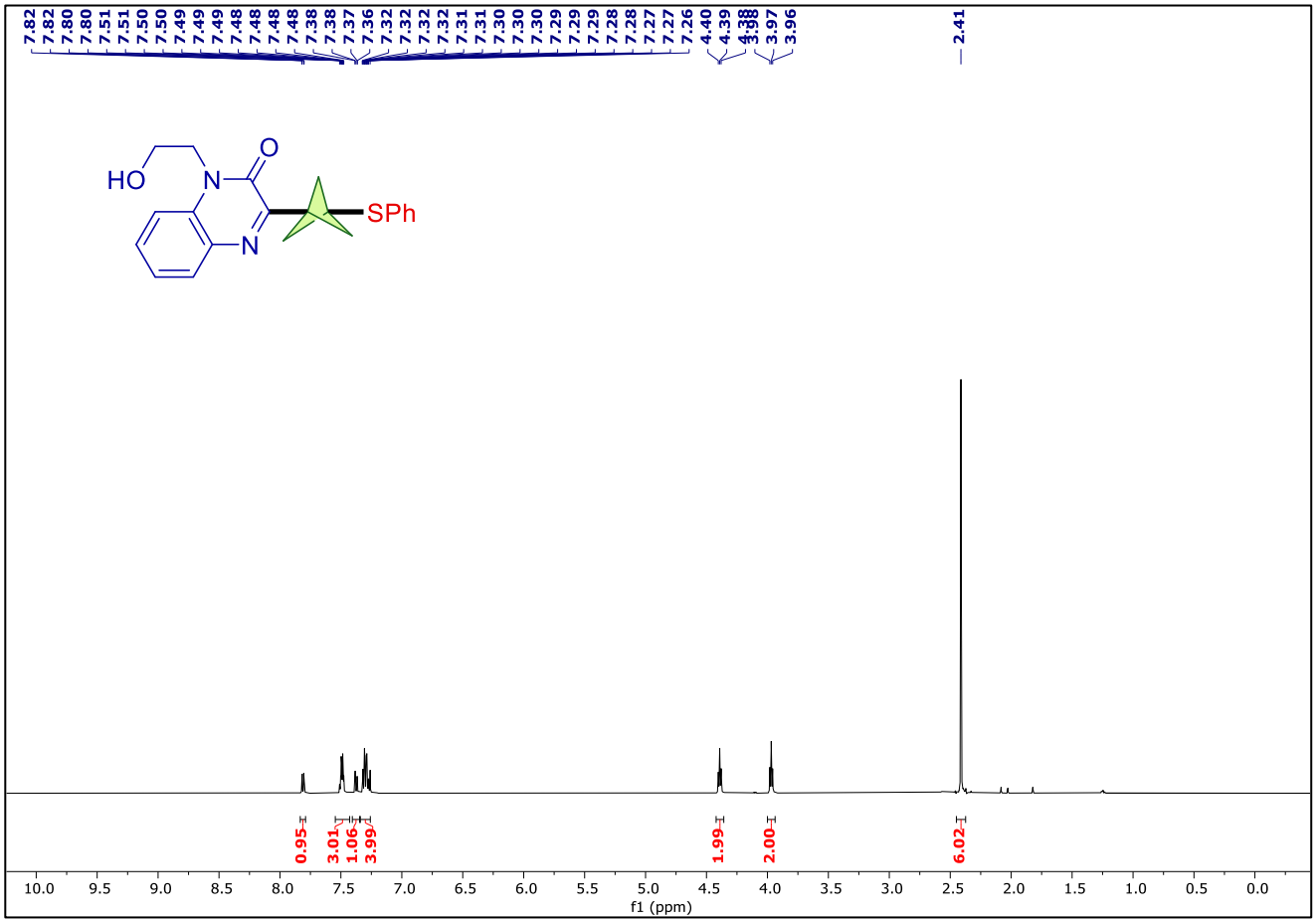
^{13}C{^{1}H} NMR of compound **4c** (126 MHz, $CDCl_3$)



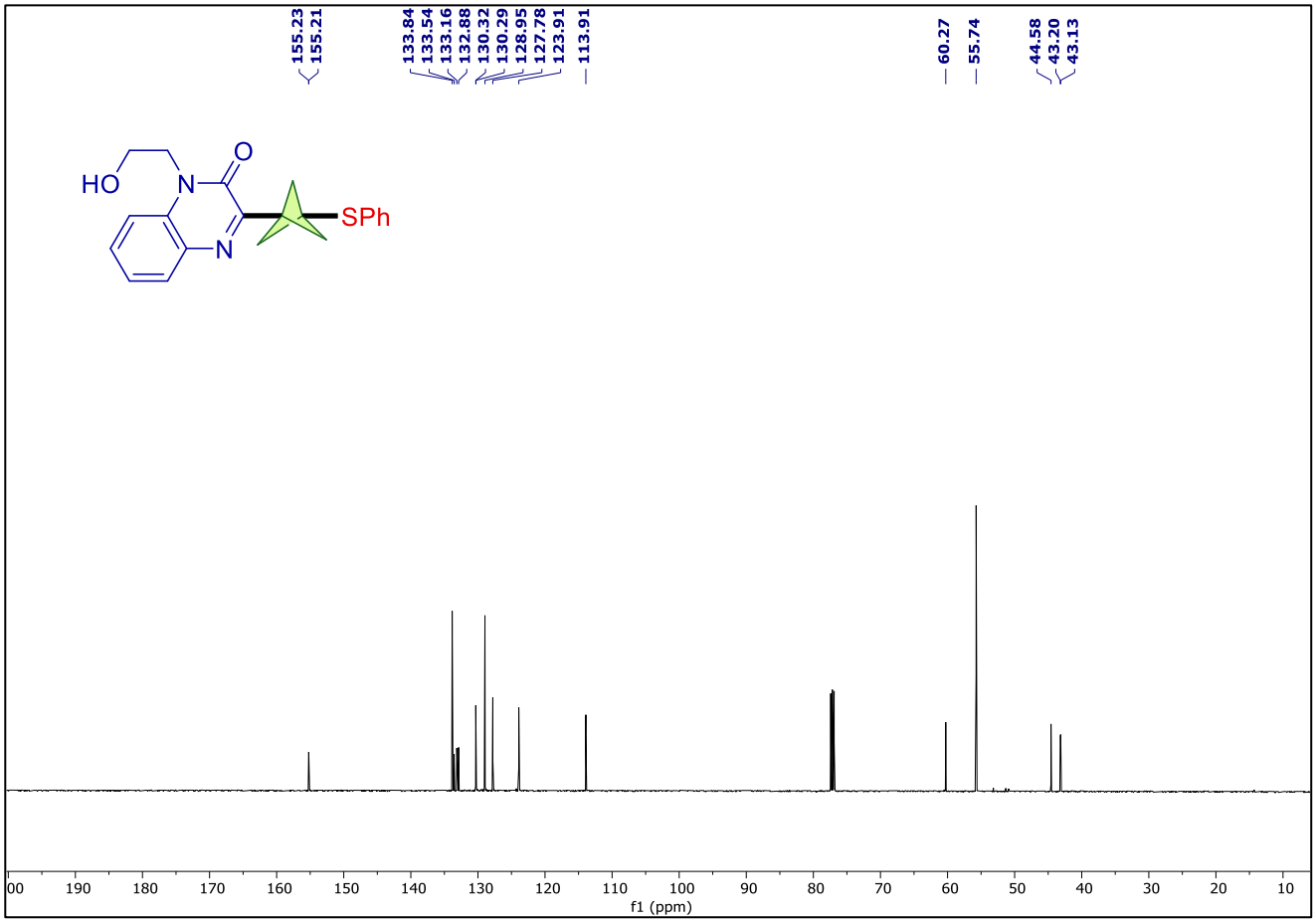
^{1}H NMR of compound **4d** (500 MHz, $CDCl_3$)



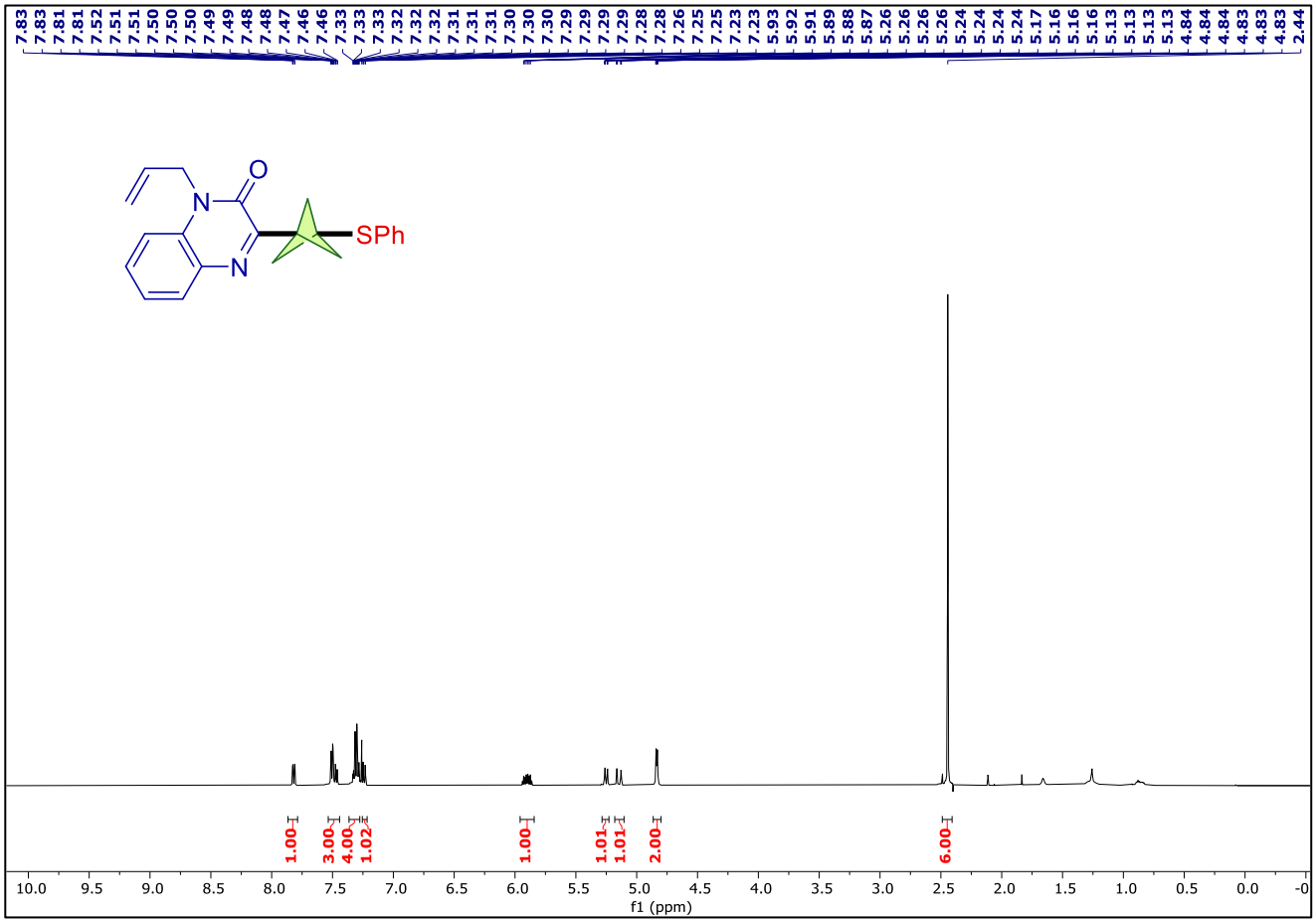
^{13}C{^{1}H} NMR of compound **4d** (126 MHz, $CDCl_3$)



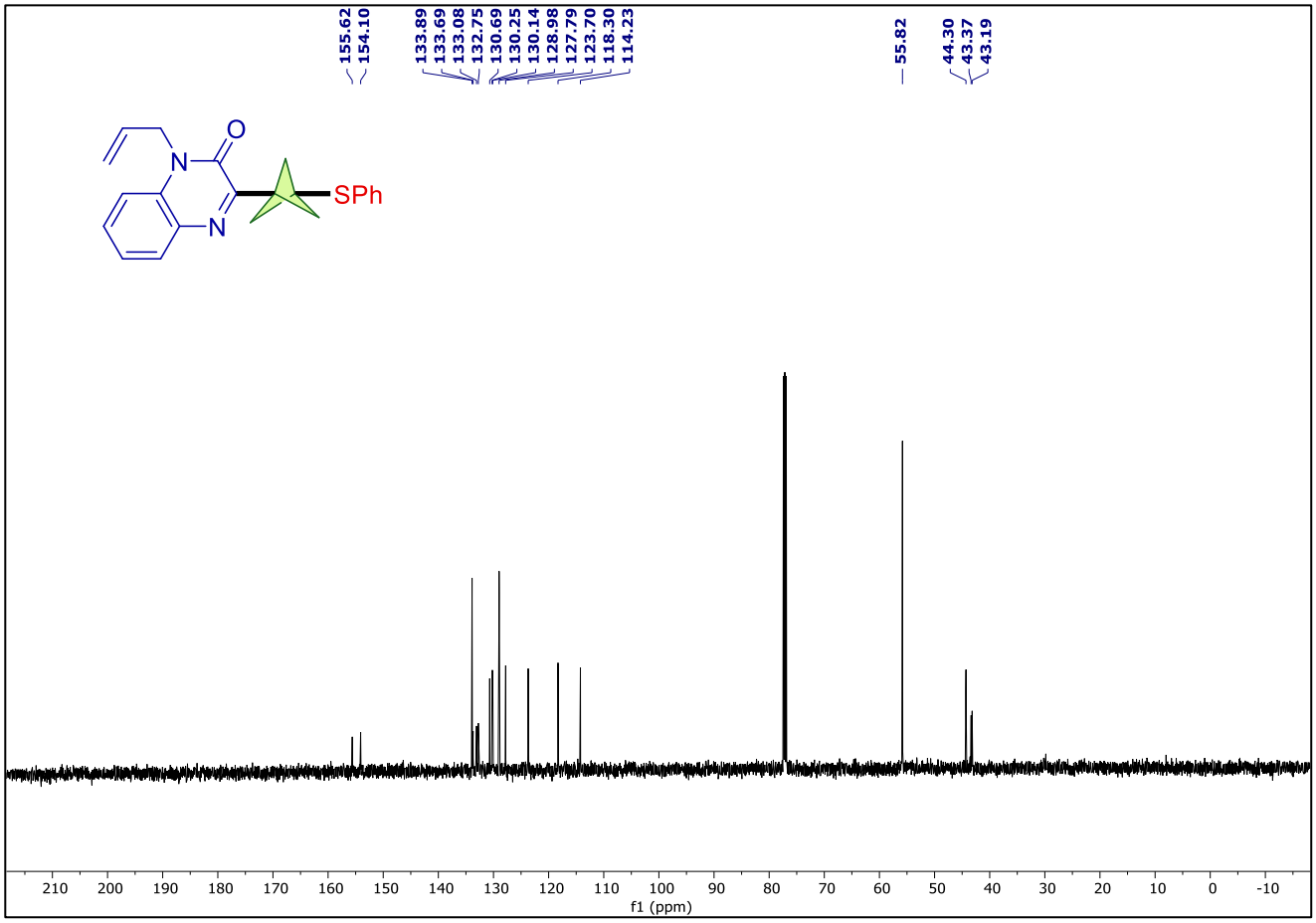
^{1}H NMR of compound **4e** (500 MHz, $CDCl_3$)



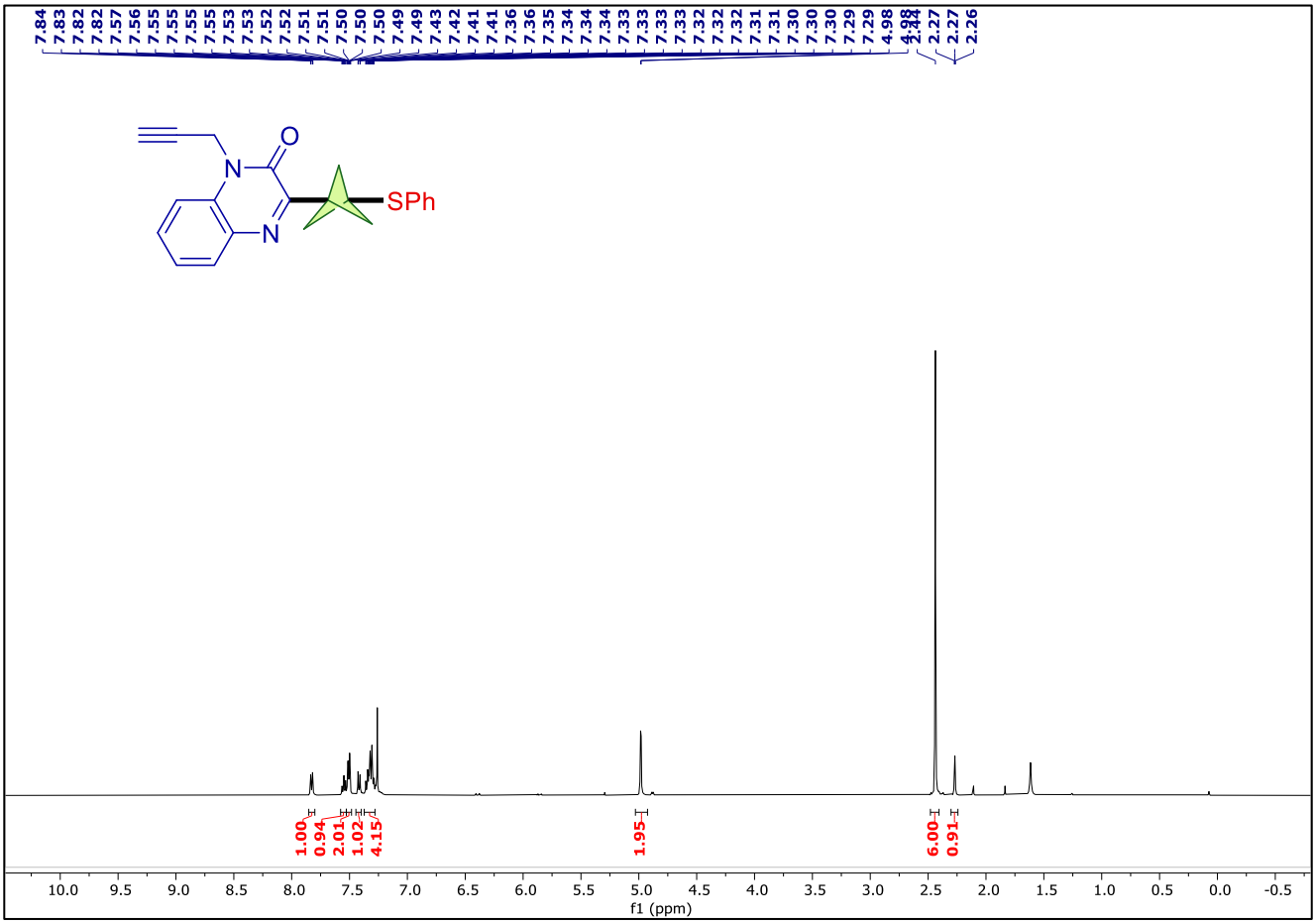
^{13}C{^{1}H} NMR of compound **4e** (126 MHz, $CDCl_3$)



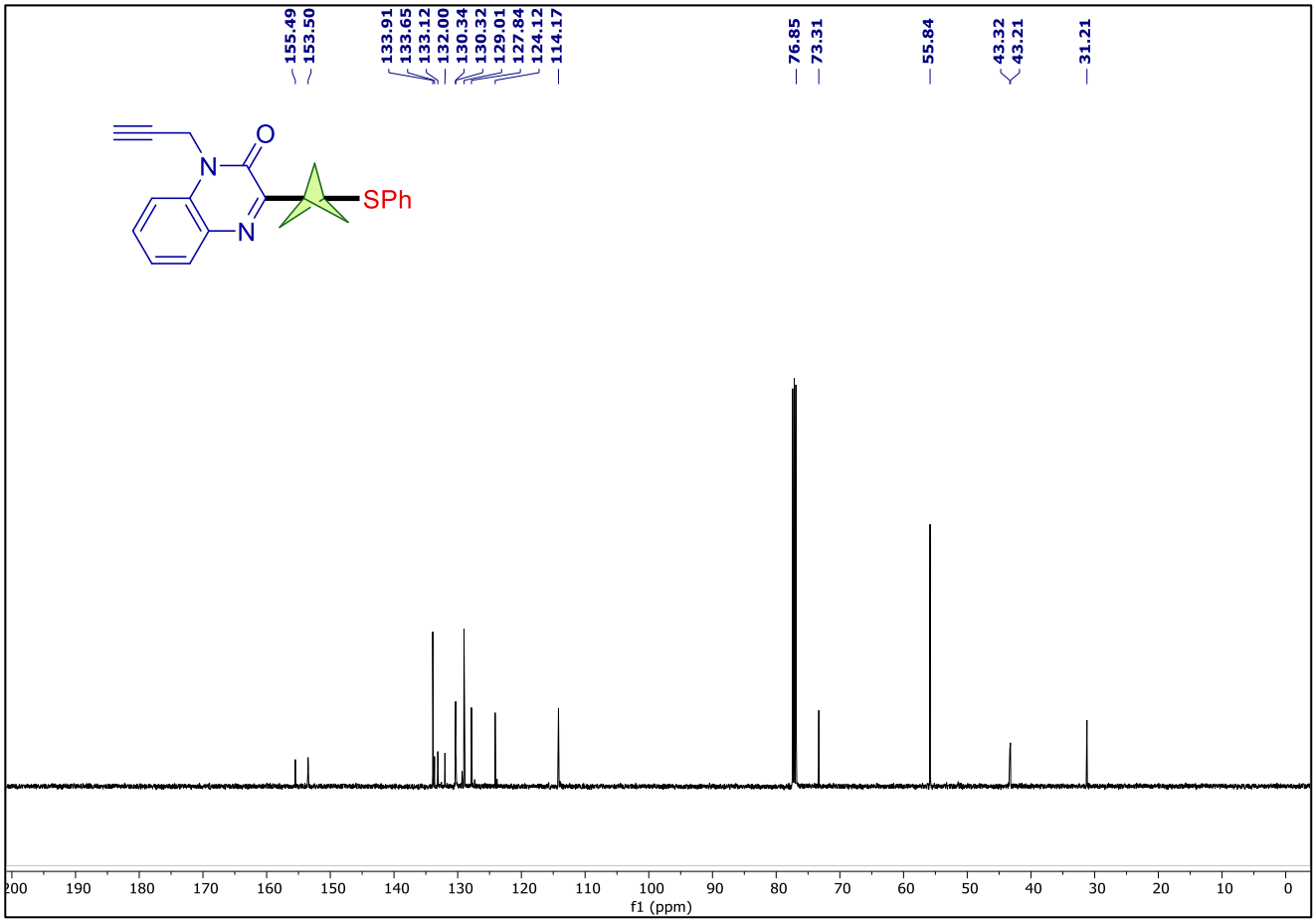
^{1}H NMR of compound **4f** (500 MHz, $CDCl_3$)



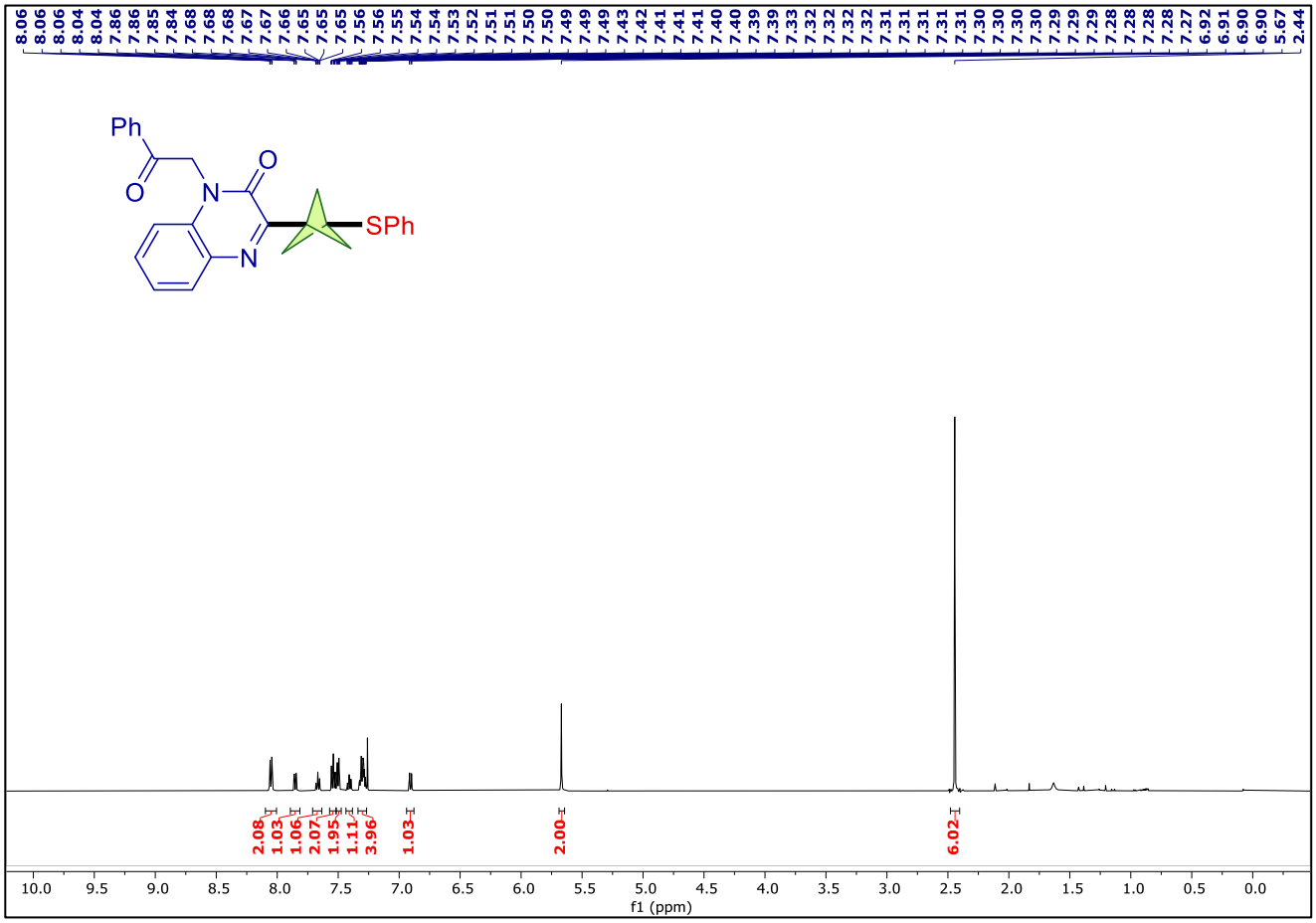
^{13}C{^{1}H} NMR of compound **4f** (126 MHz, $CDCl_3$)



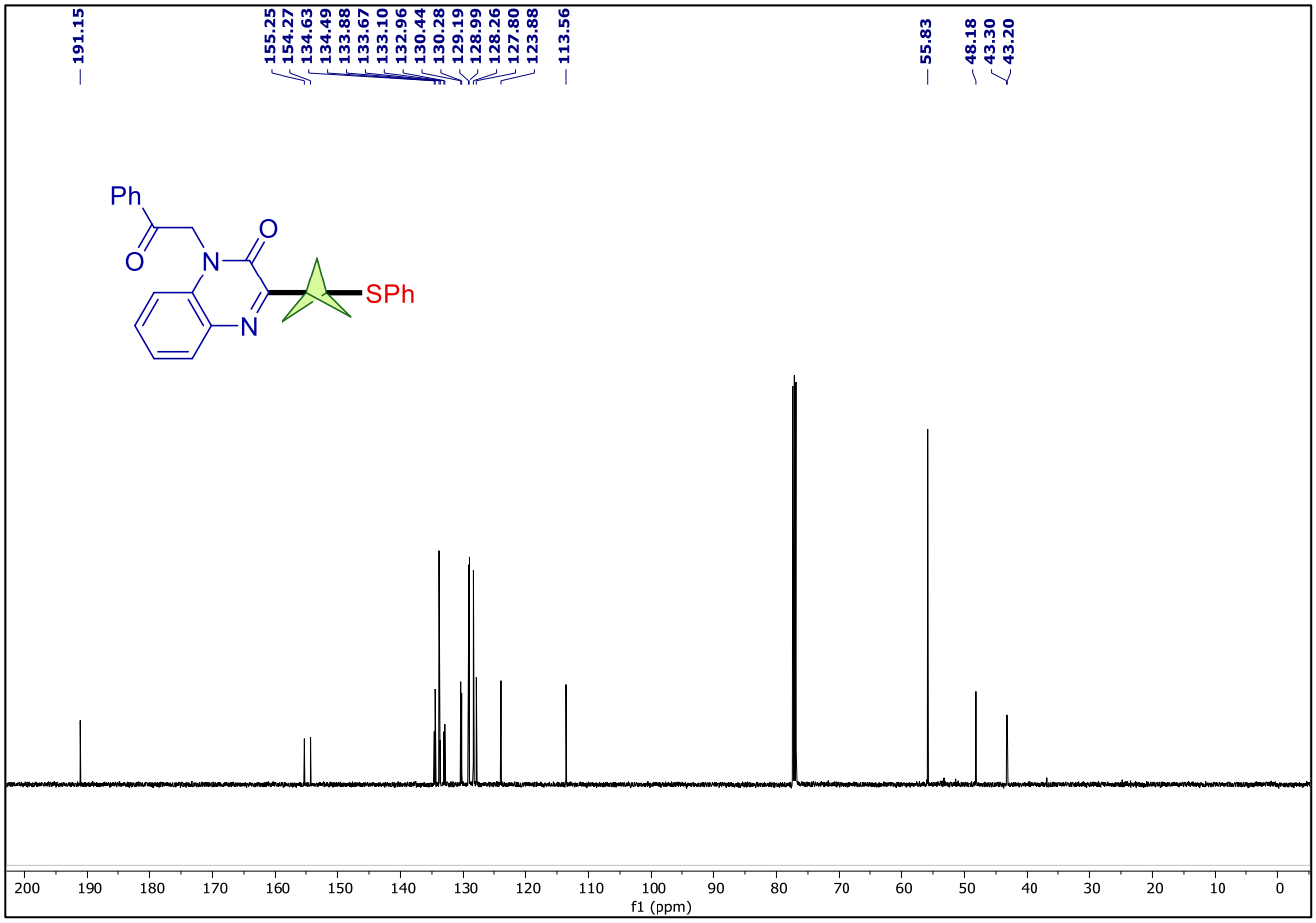
^{1}H NMR of compound **4g** (500 MHz, $CDCl_3$)



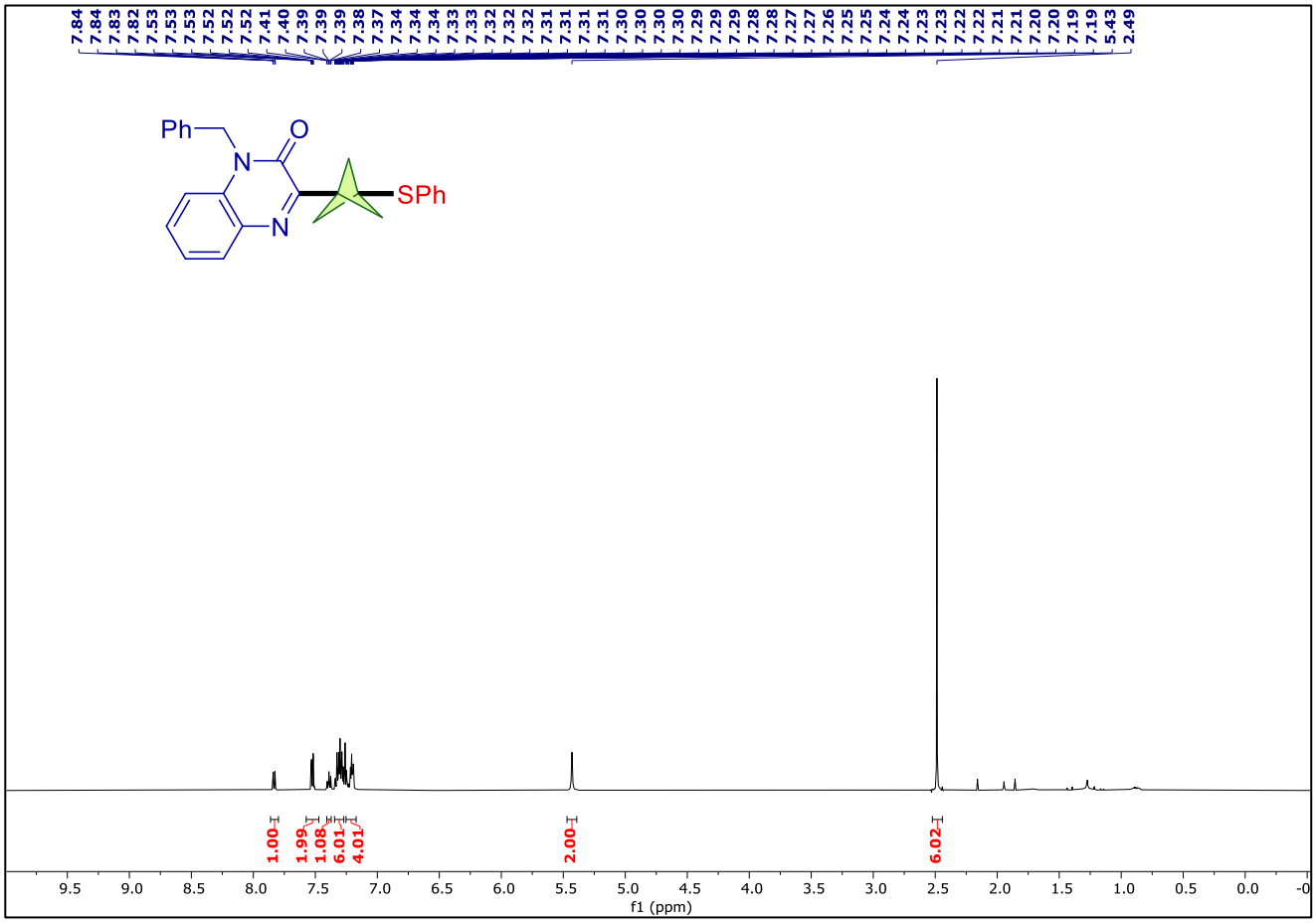
^{13}C{^{1}H} NMR of compound **4g** (126 MHz, $CDCl_3$)



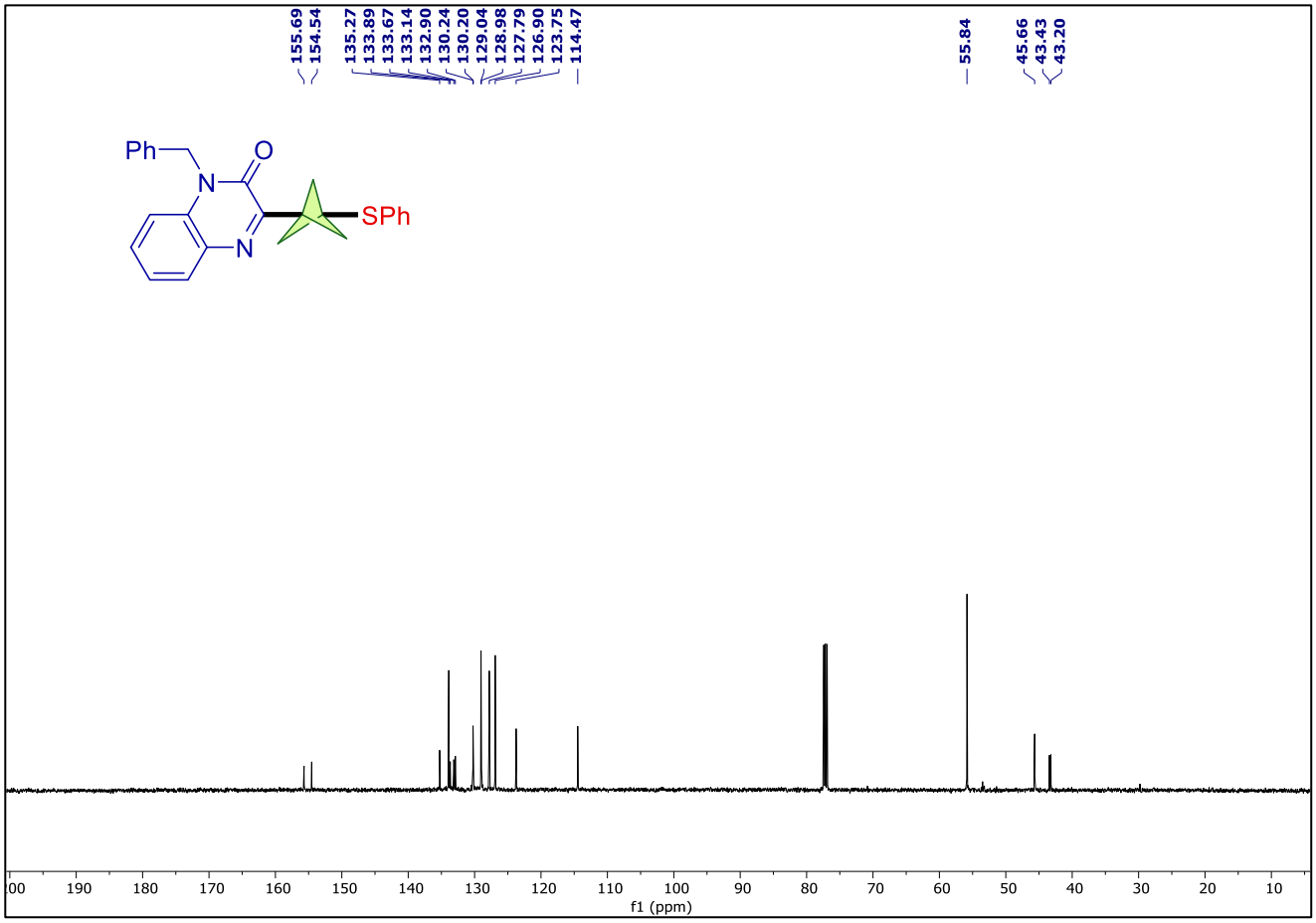
^{1}H NMR of compound **4h** (500 MHz, $CDCl_3$)



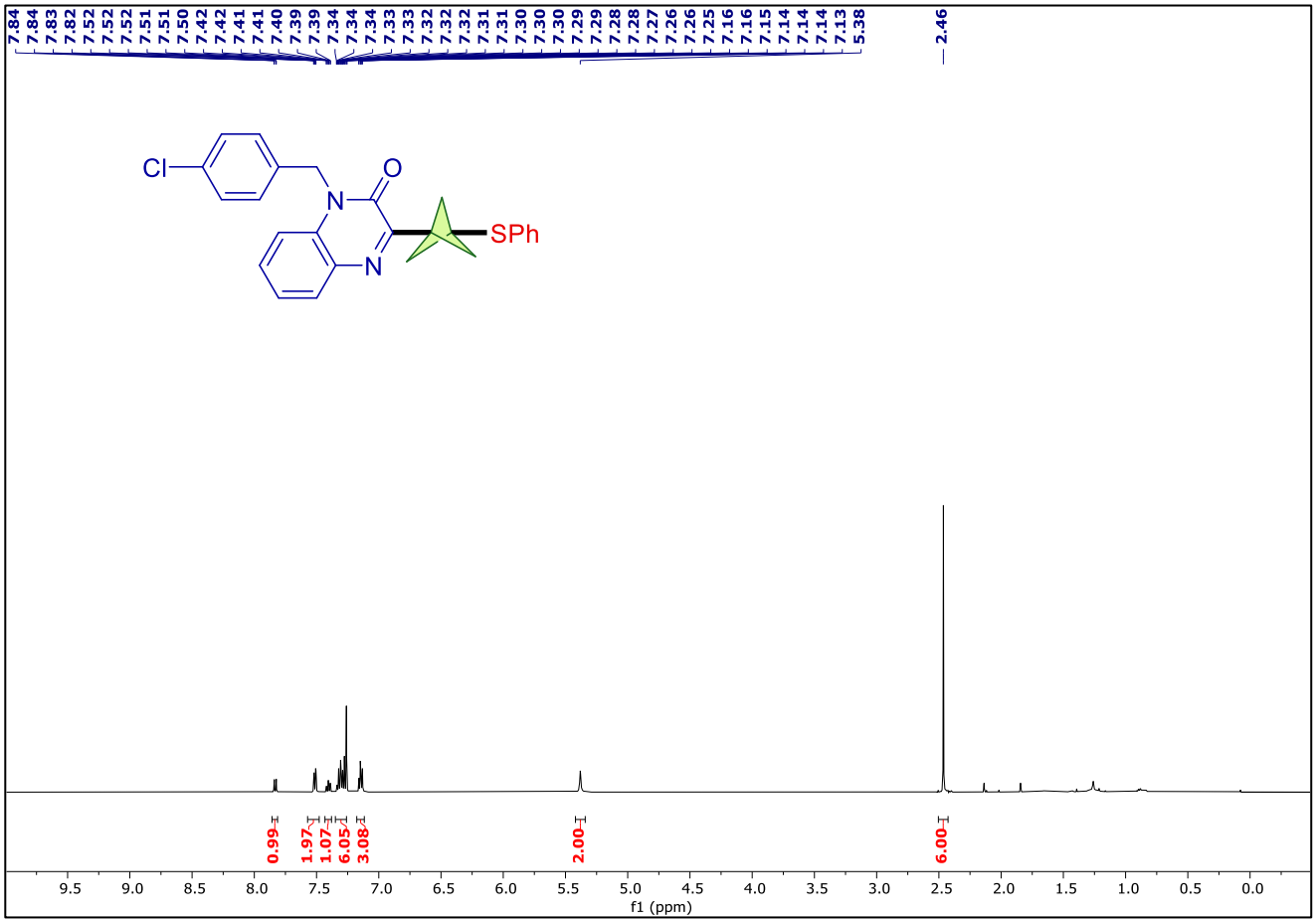
^{13}C{^{1}H} NMR of compound **4h** (126 MHz, $CDCl_3$)



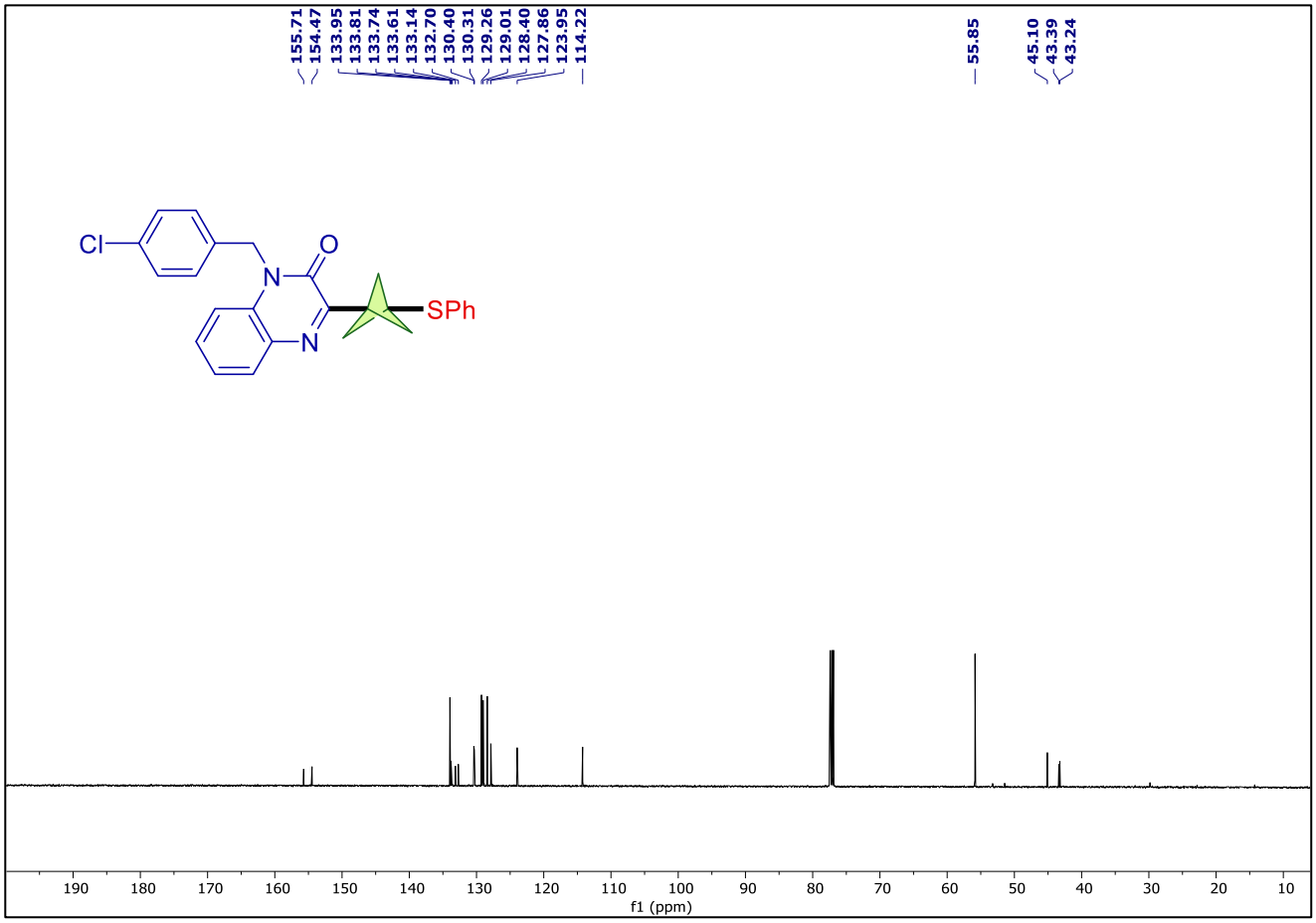
^{1}H NMR of compound **4i** (500 MHz, $CDCl_3$)



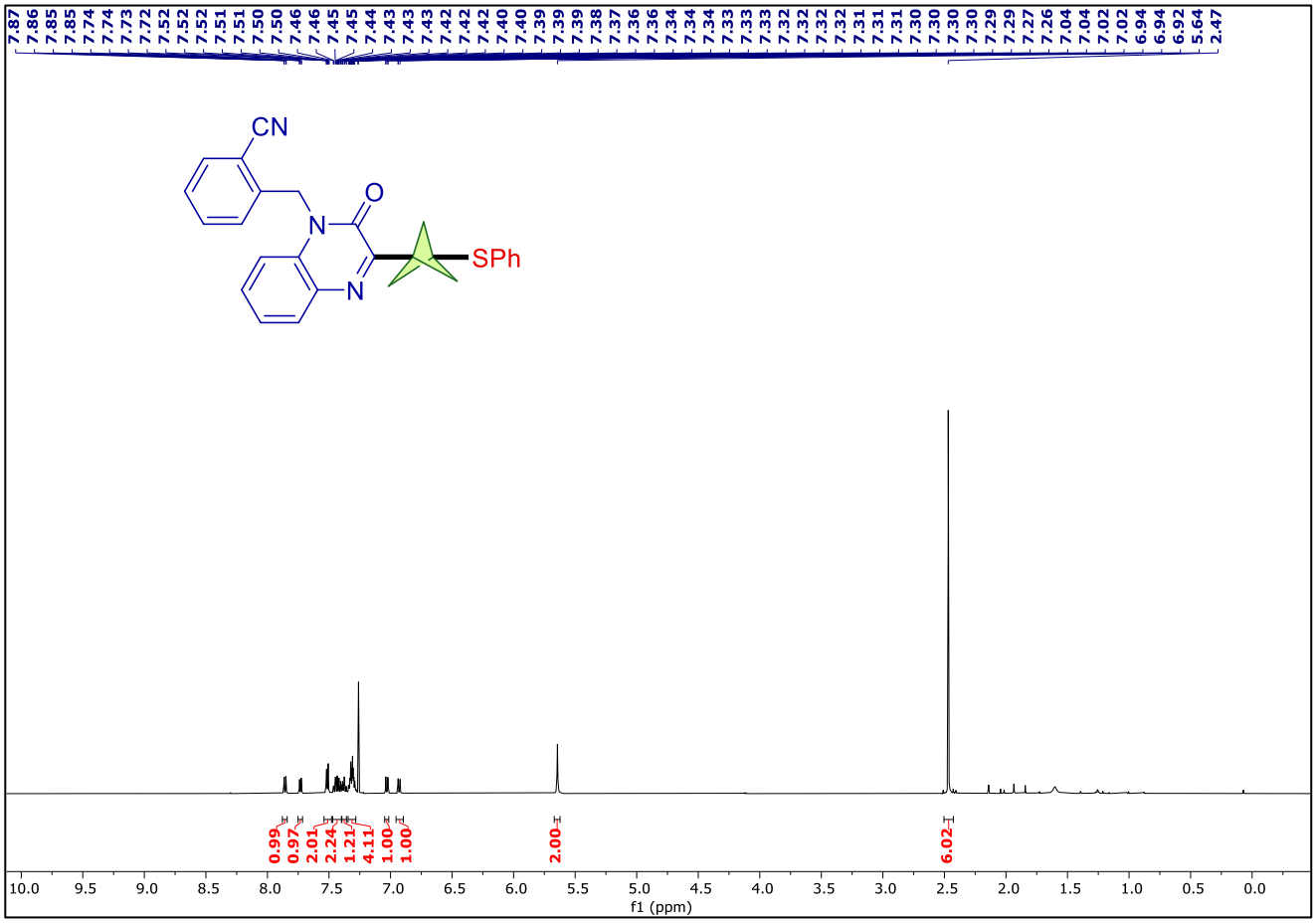
^{13}C{^{1}H} NMR of compound **4i** (126 MHz, $CDCl_3$)



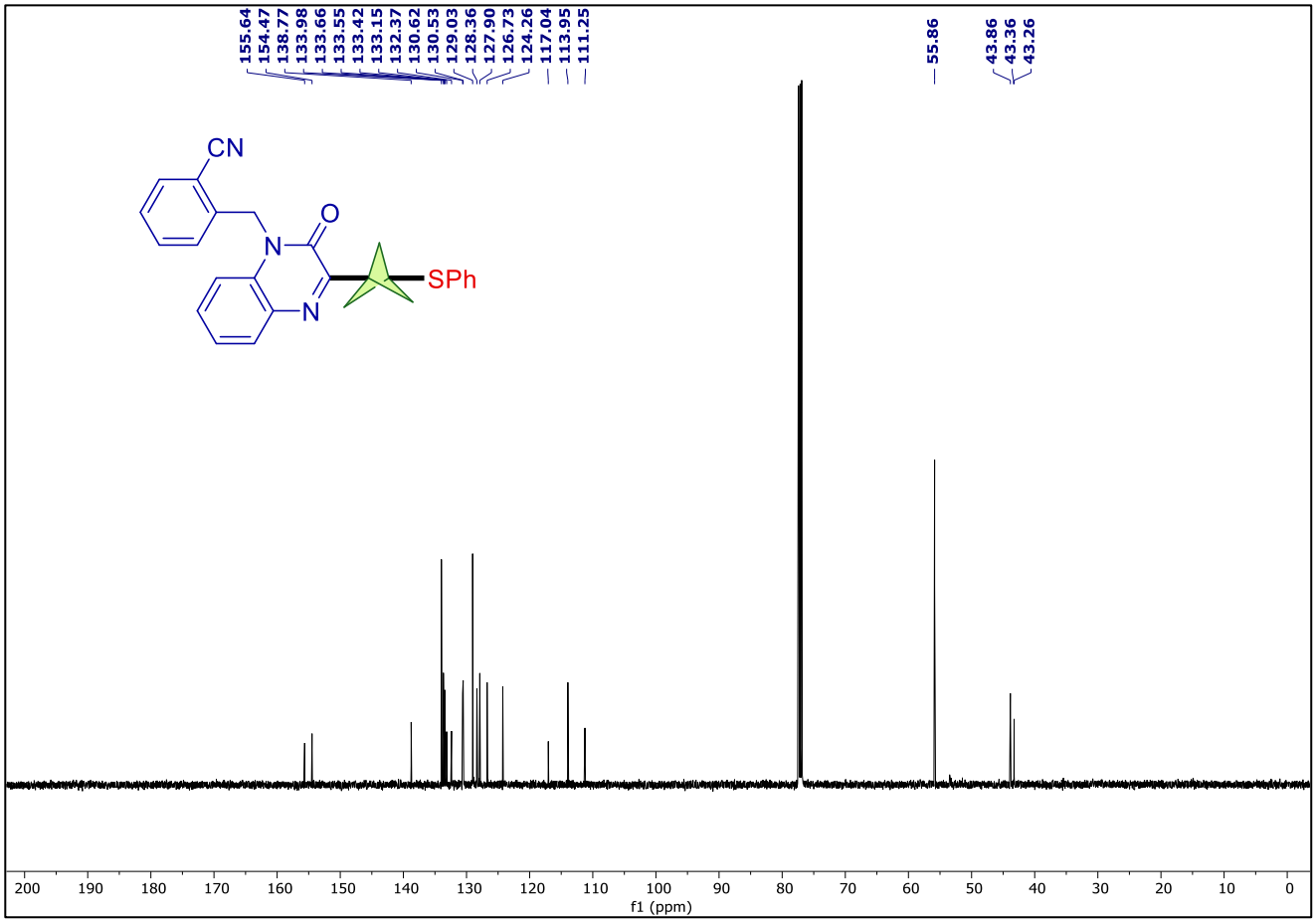
^{1}H NMR of compound **4j** (500 MHz, $CDCl_3$)



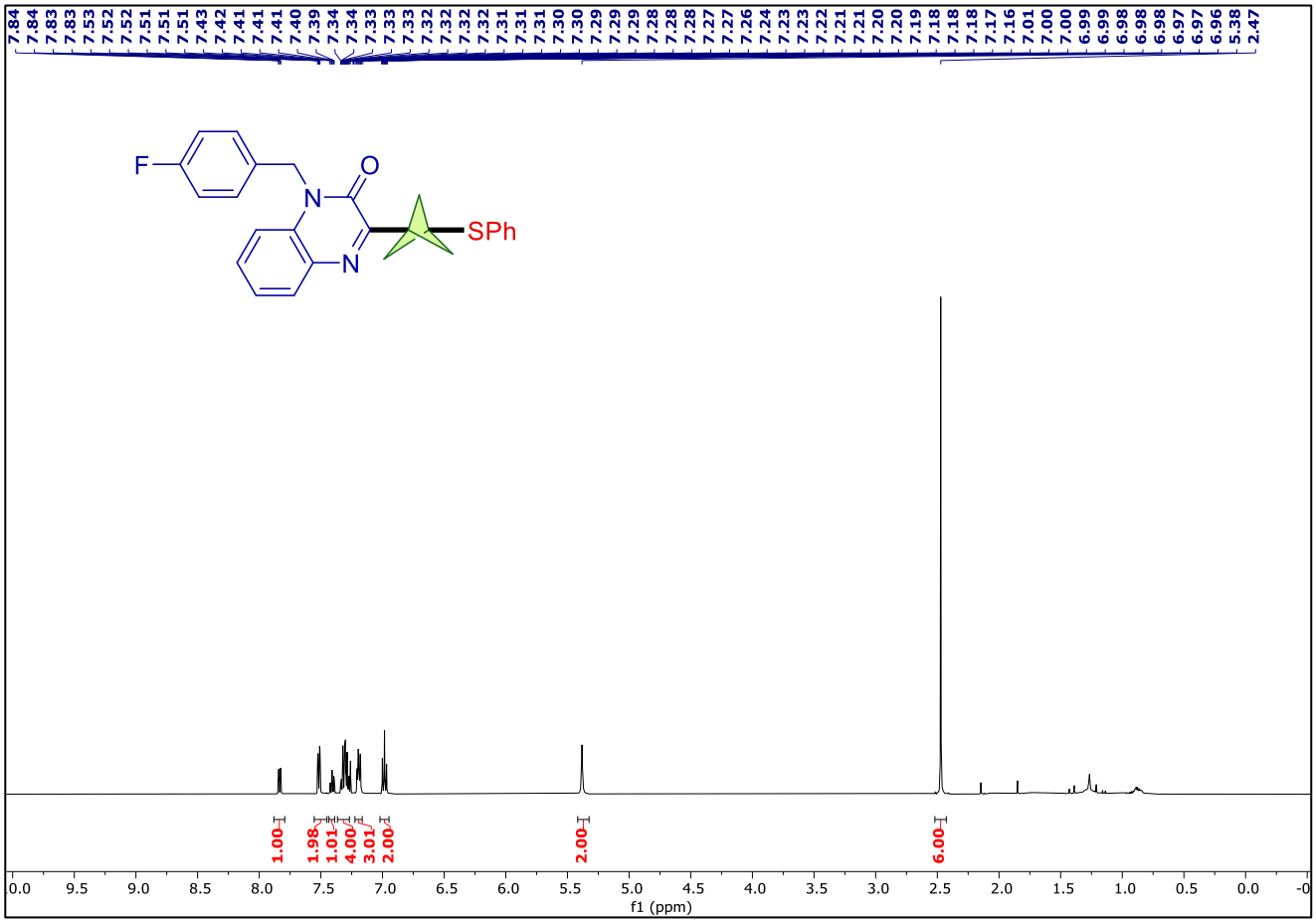
^{13}C{^{1}H} NMR of compound **4j** (126 MHz, $CDCl_3$)



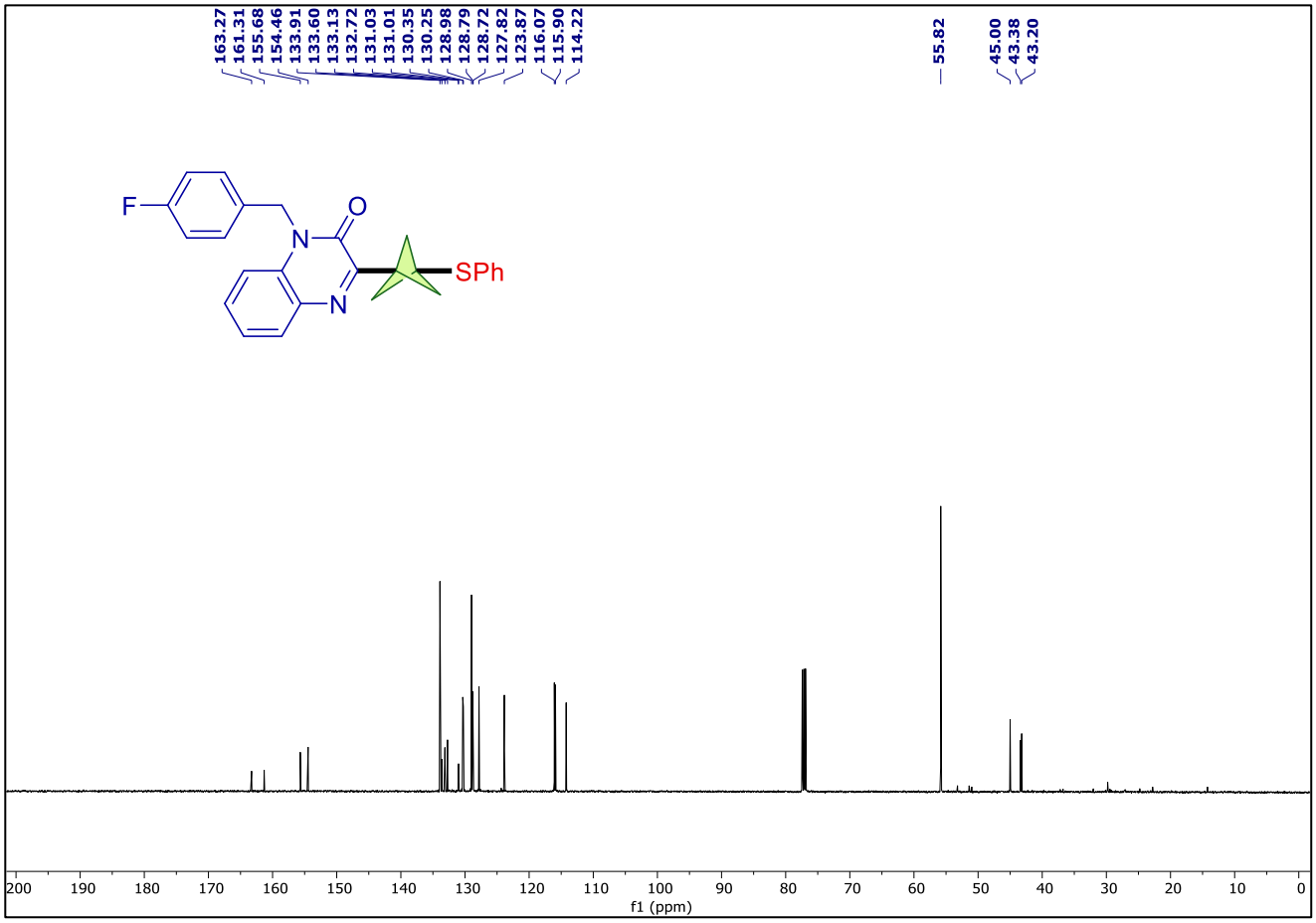
^{1}H NMR of compound **4k** (500 MHz, $CDCl_3$)



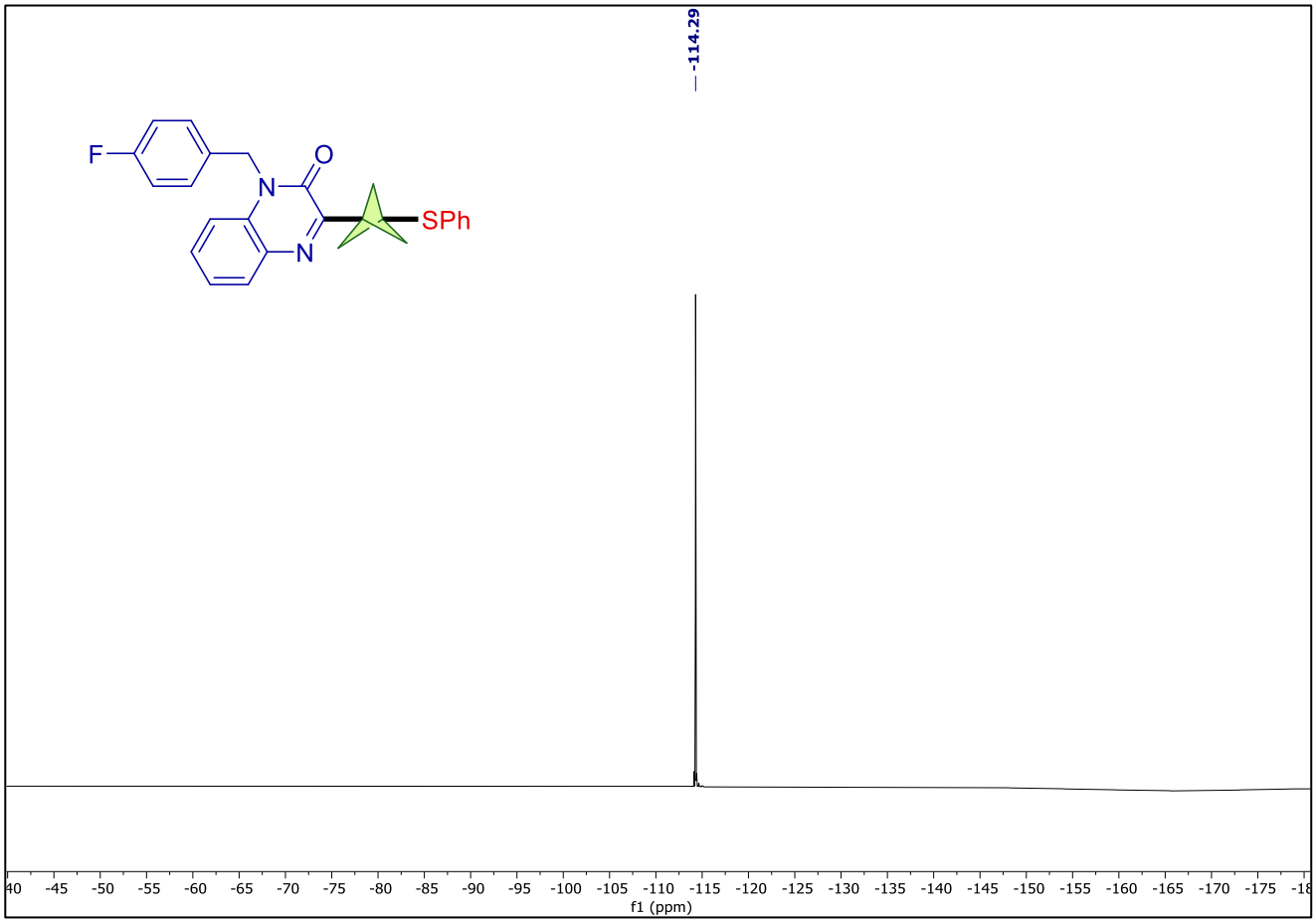
$^{13}C\{^{1}H\}$ NMR of compound **4k** (126 MHz, $CDCl_3$)



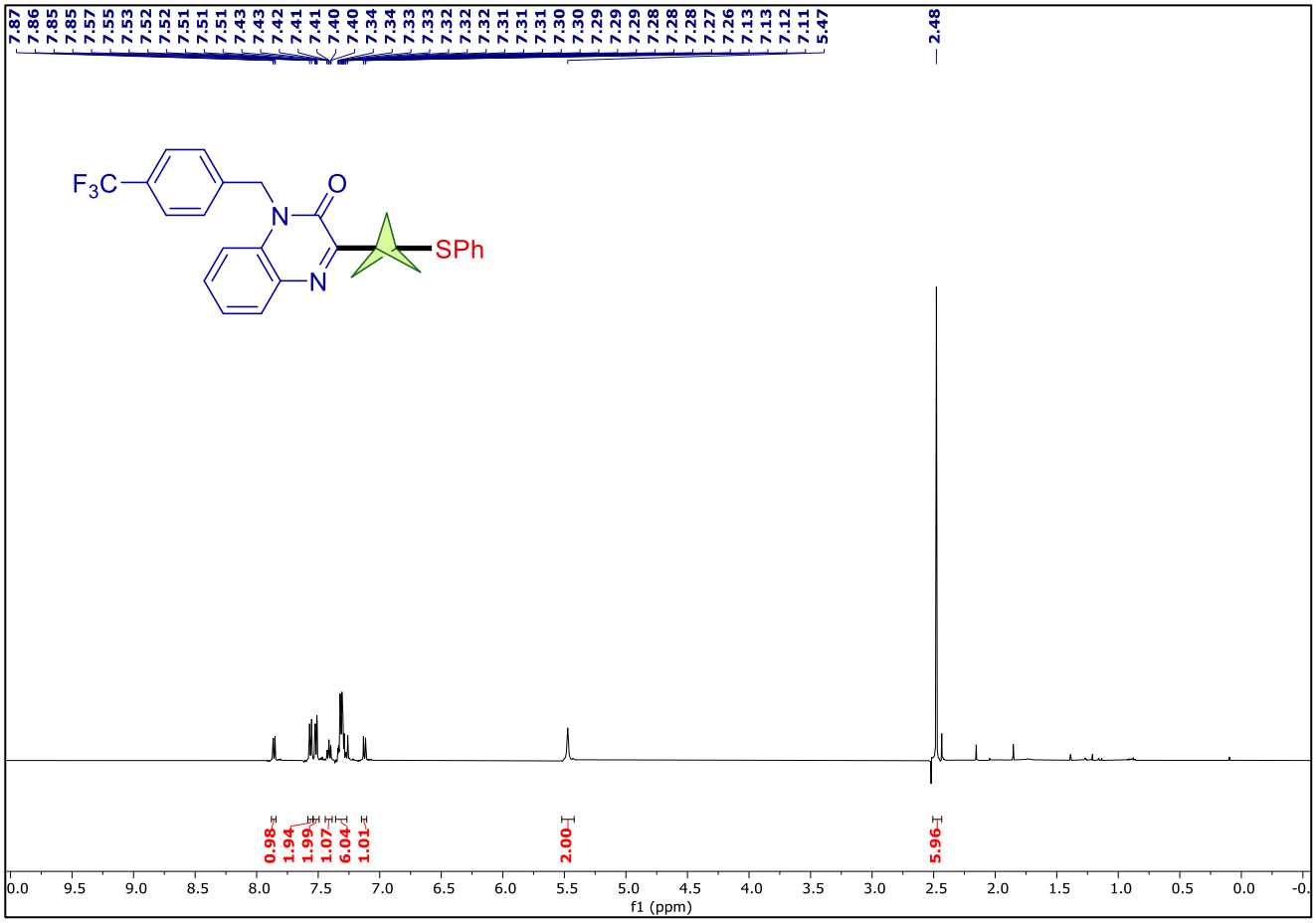
^{1}H NMR of compound **41** (500 MHz, $CDCl_3$)



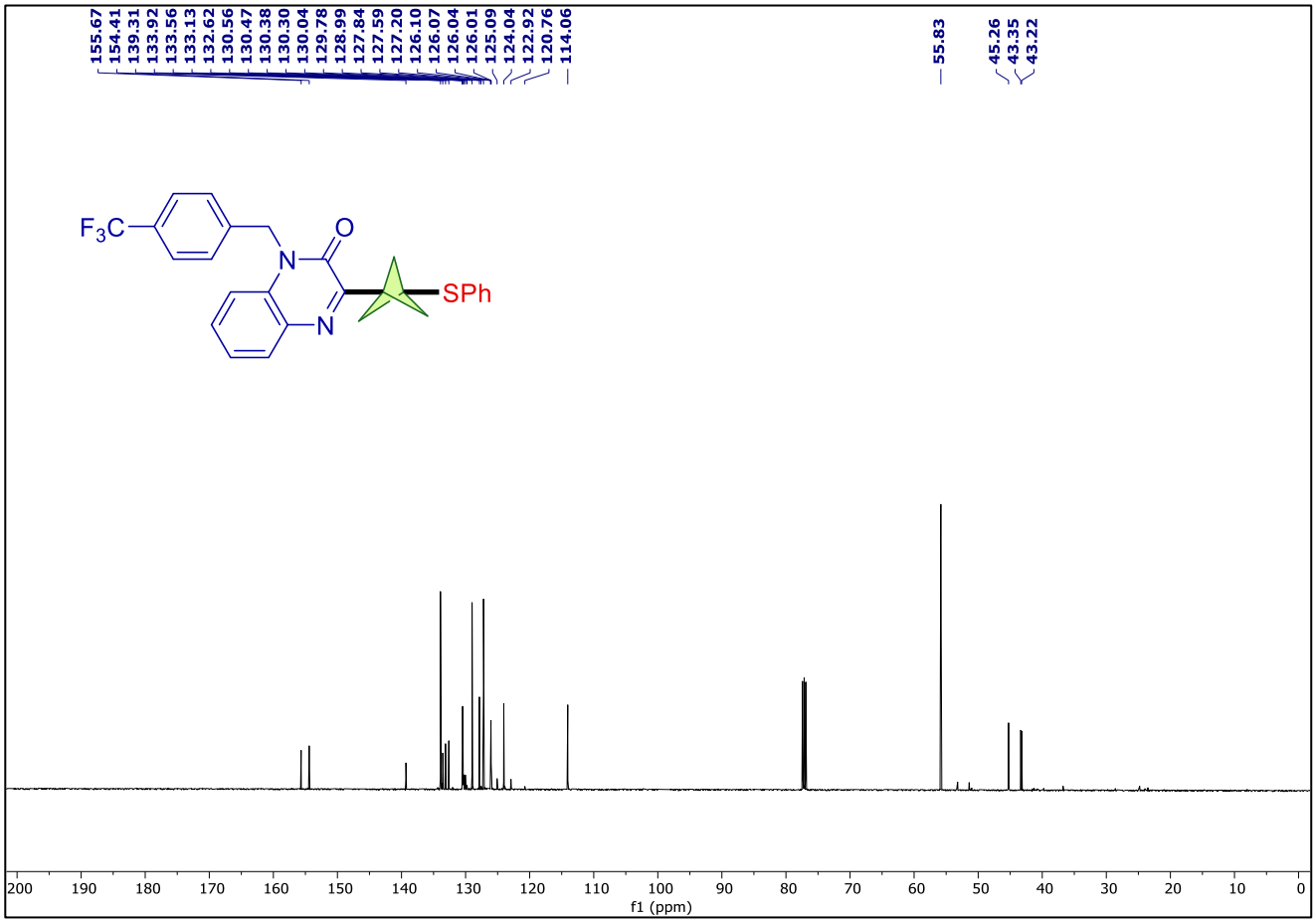
^{13}C{^{1}H} NMR of compound **41** (126 MHz, $CDCl_3$)



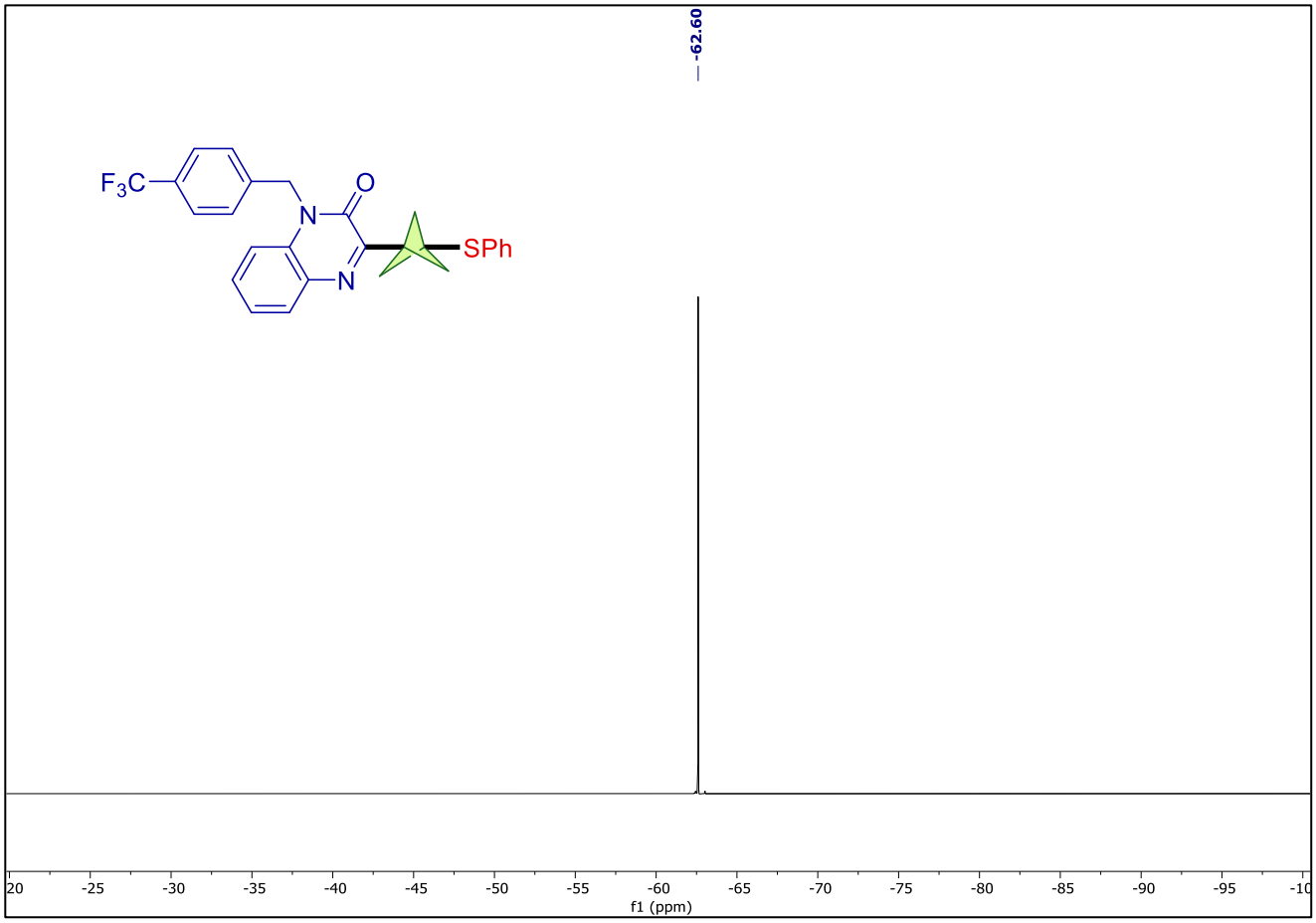
^{19}F NMR of compound **4l** (471 MHz, $CDCl_3$)



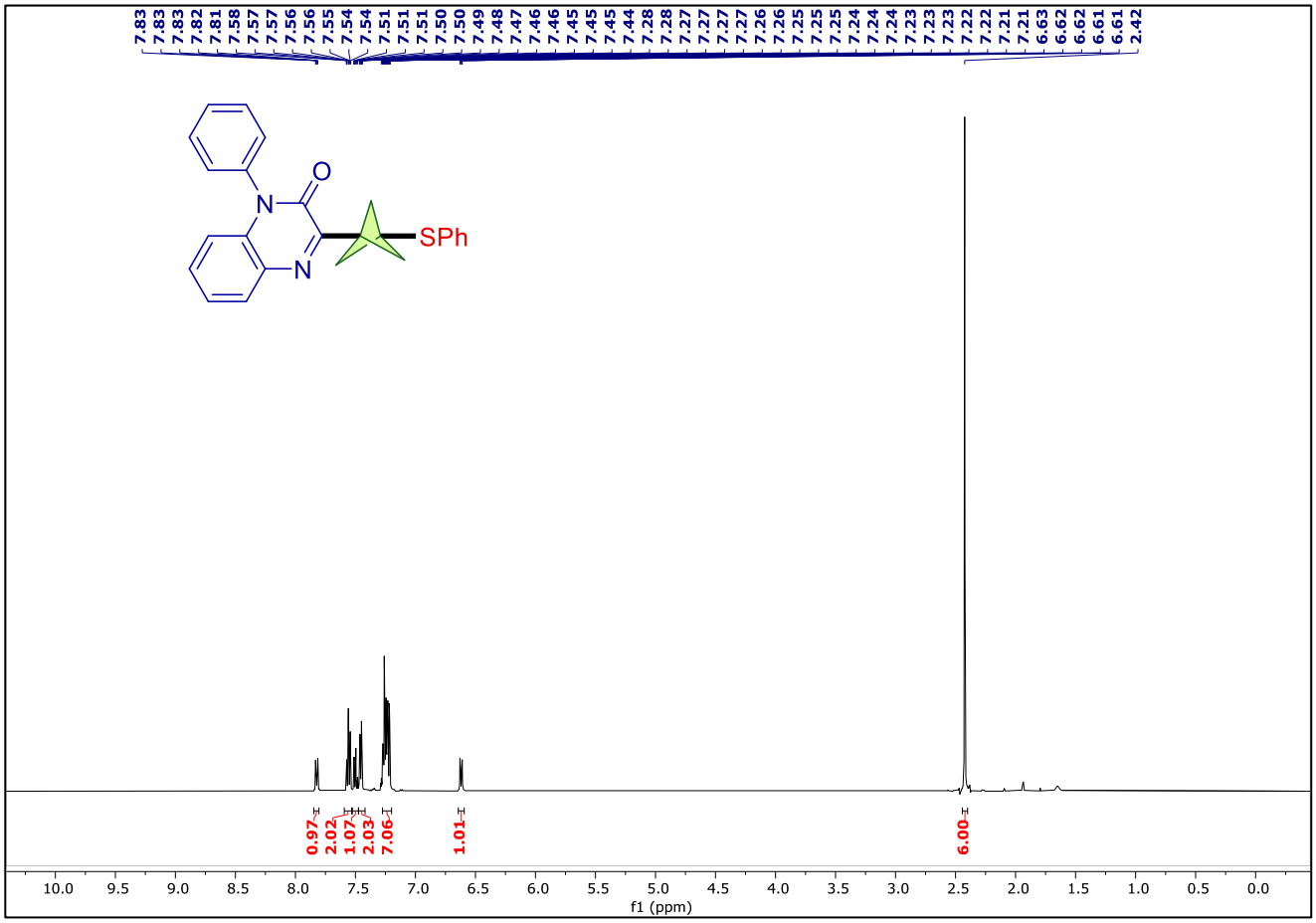
^{1}H NMR of compound **4m** (500 MHz, $CDCl_3$)



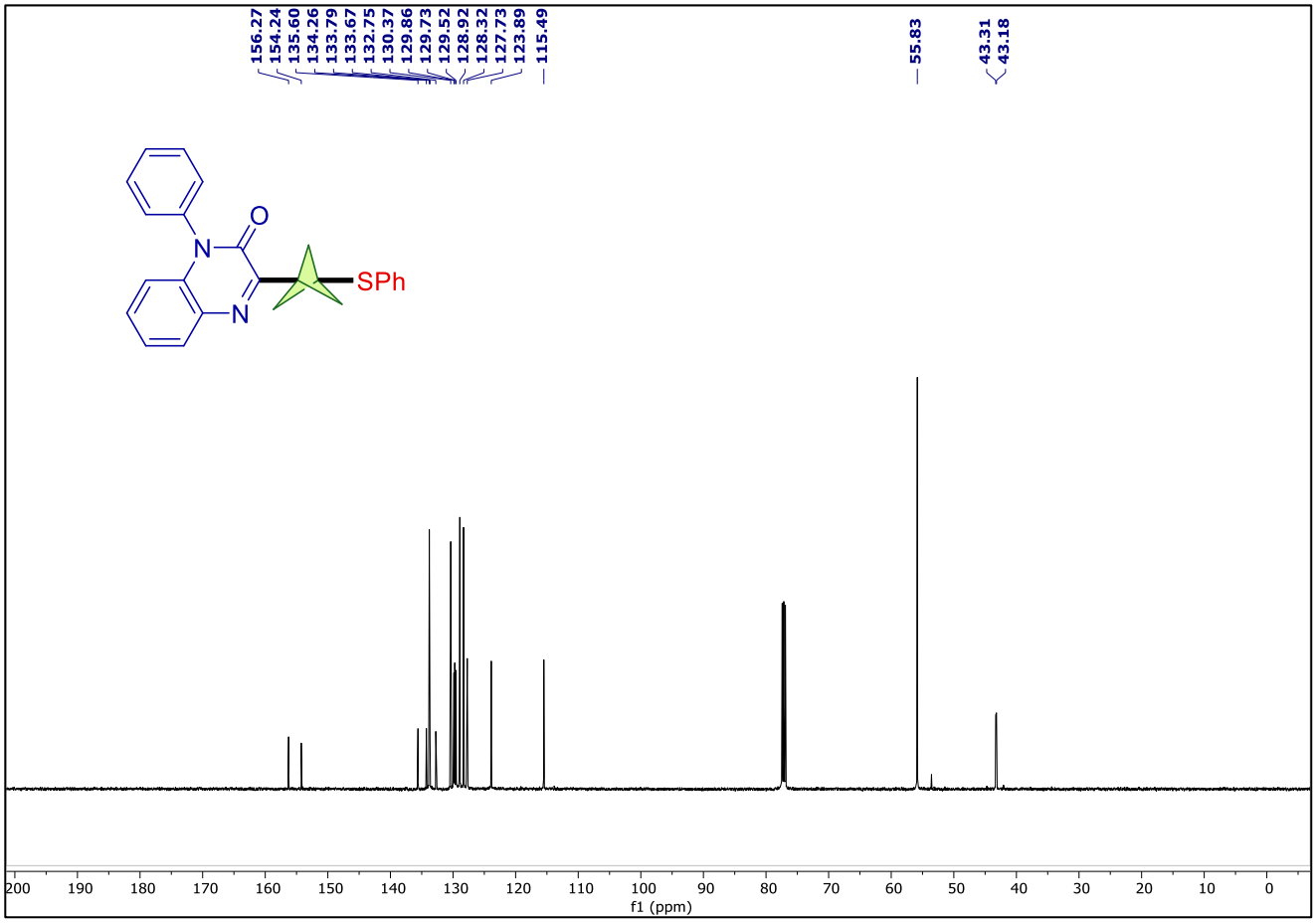
$^{13}C\{^{1}H\}$ NMR of compound **4m** (126 MHz, $CDCl_3$)



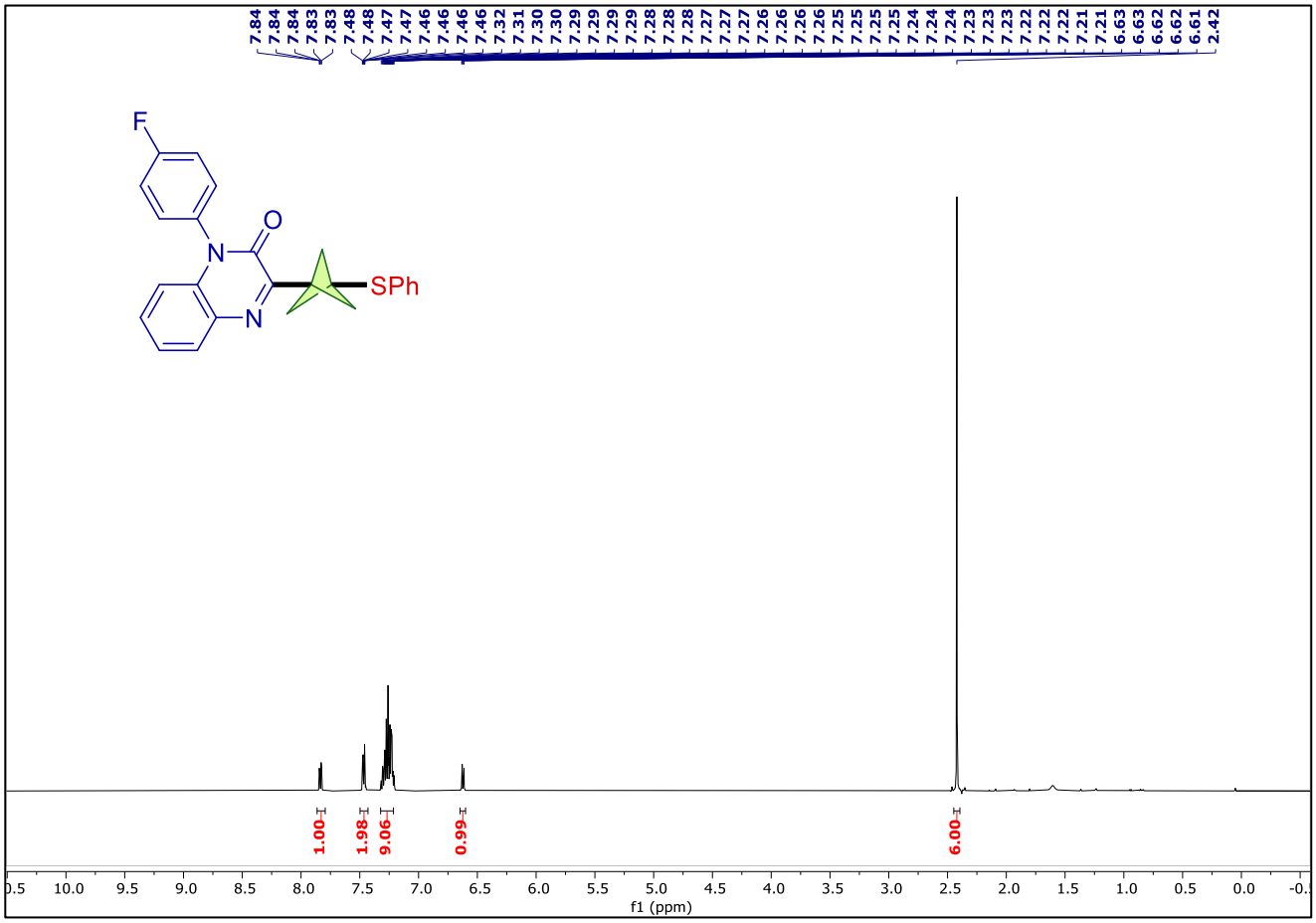
^{19}F NMR of compound **4m** (471 MHz, $CDCl_3$)



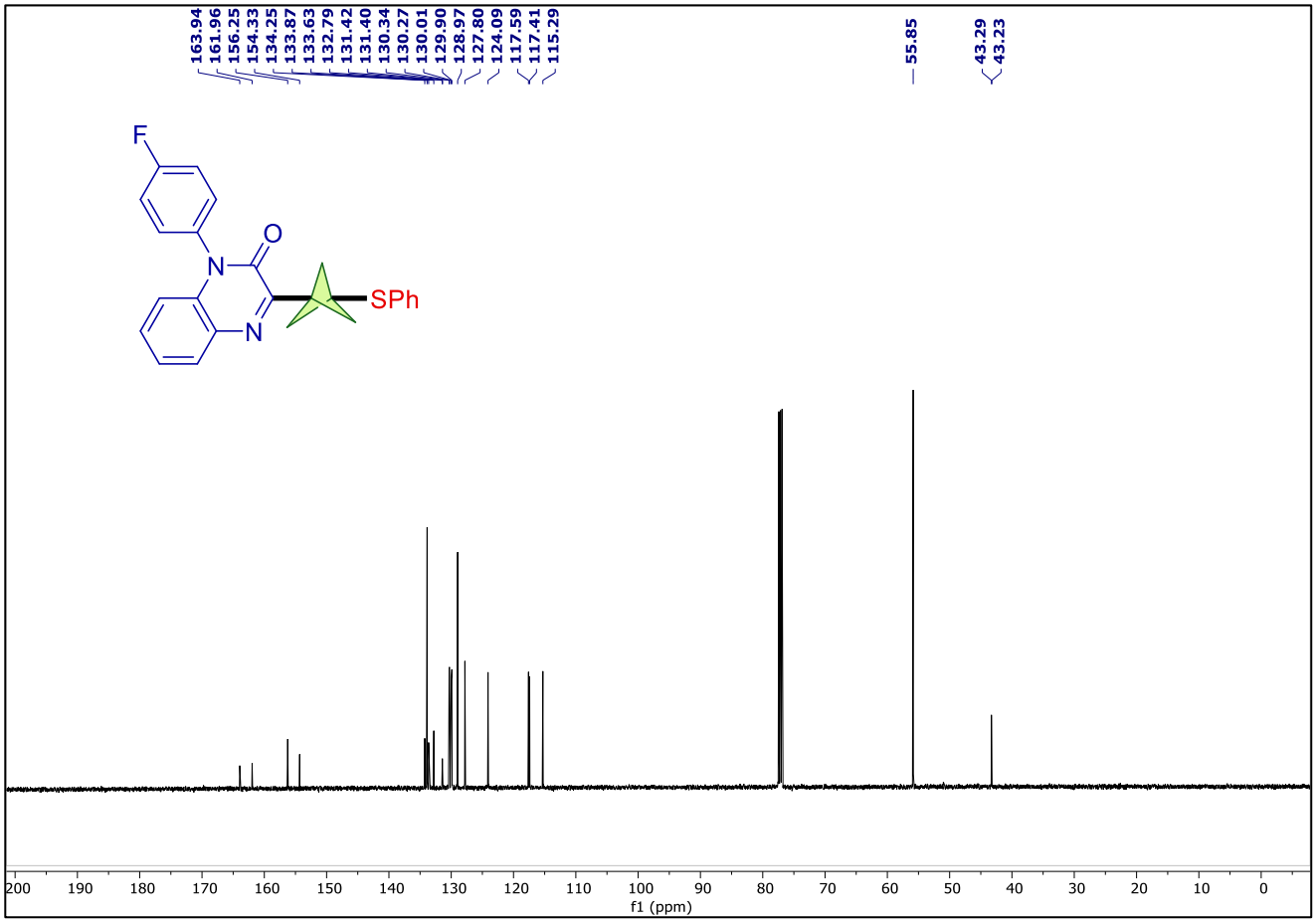
^{1}H NMR of compound **4n** (500 MHz, $CDCl_3$)



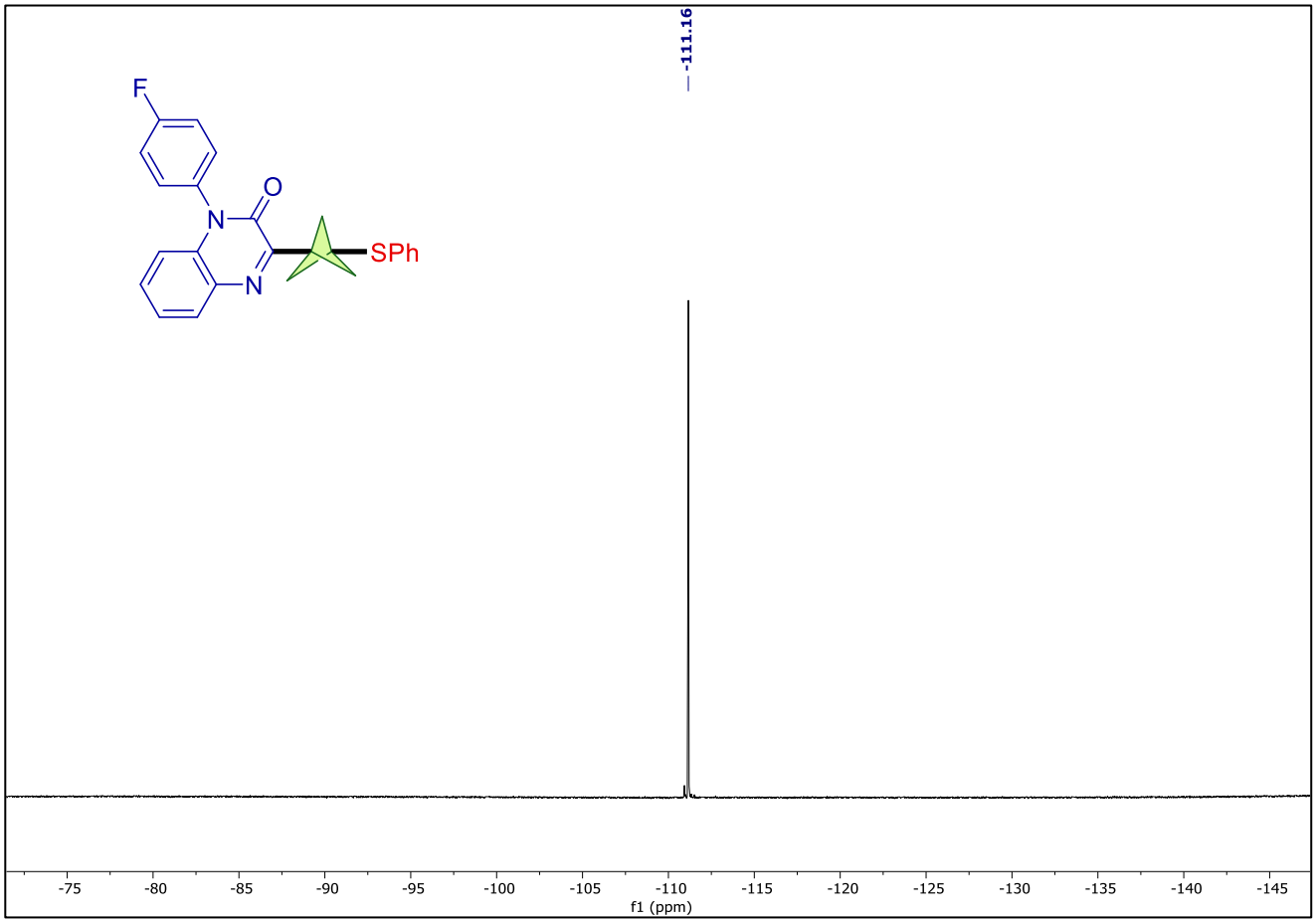
^{13}C{^{1}H} NMR of compound **4n** (126 MHz, $CDCl_3$)



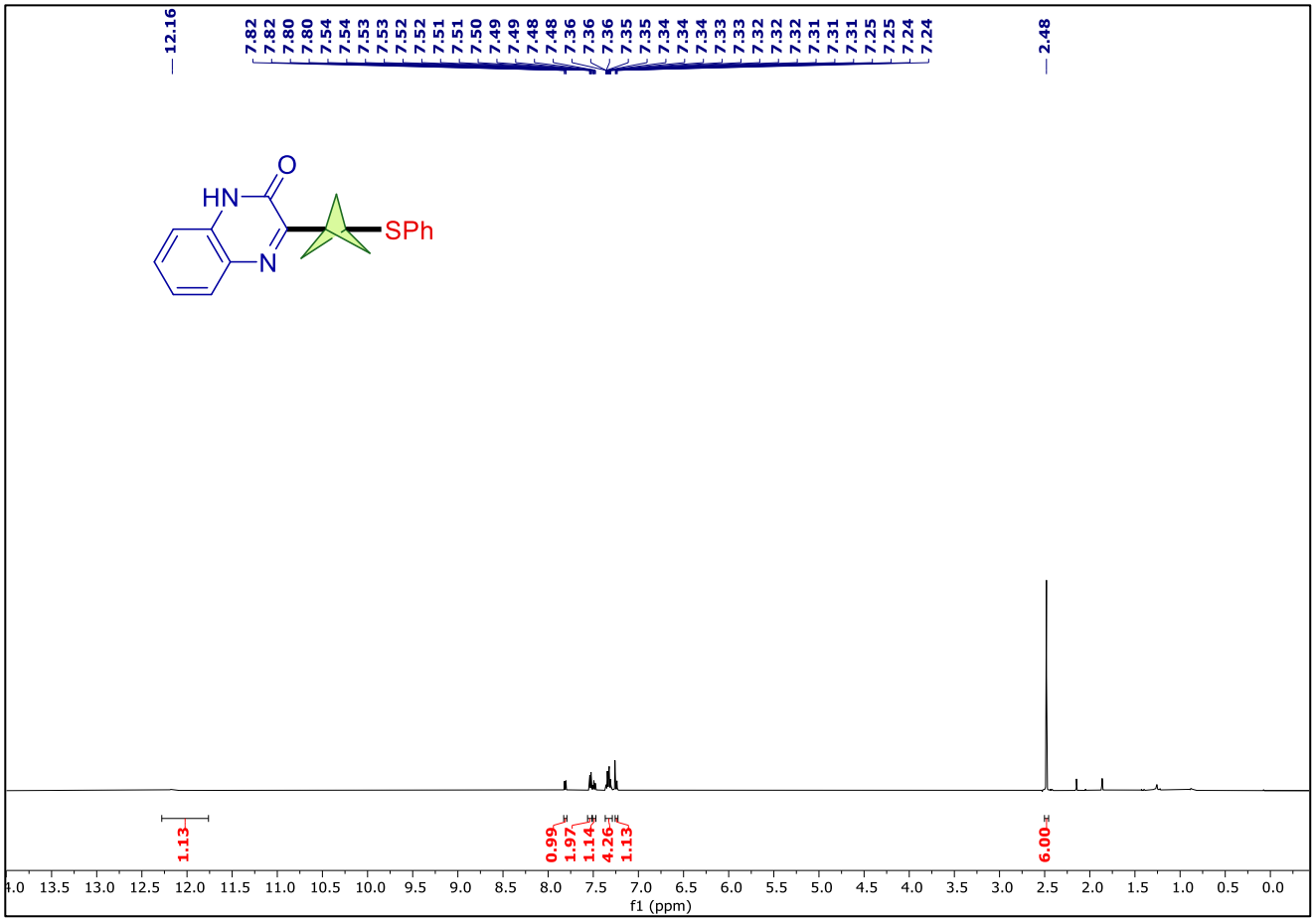
^{1}H NMR of compound **4o** (500 MHz, $CDCl_3$)



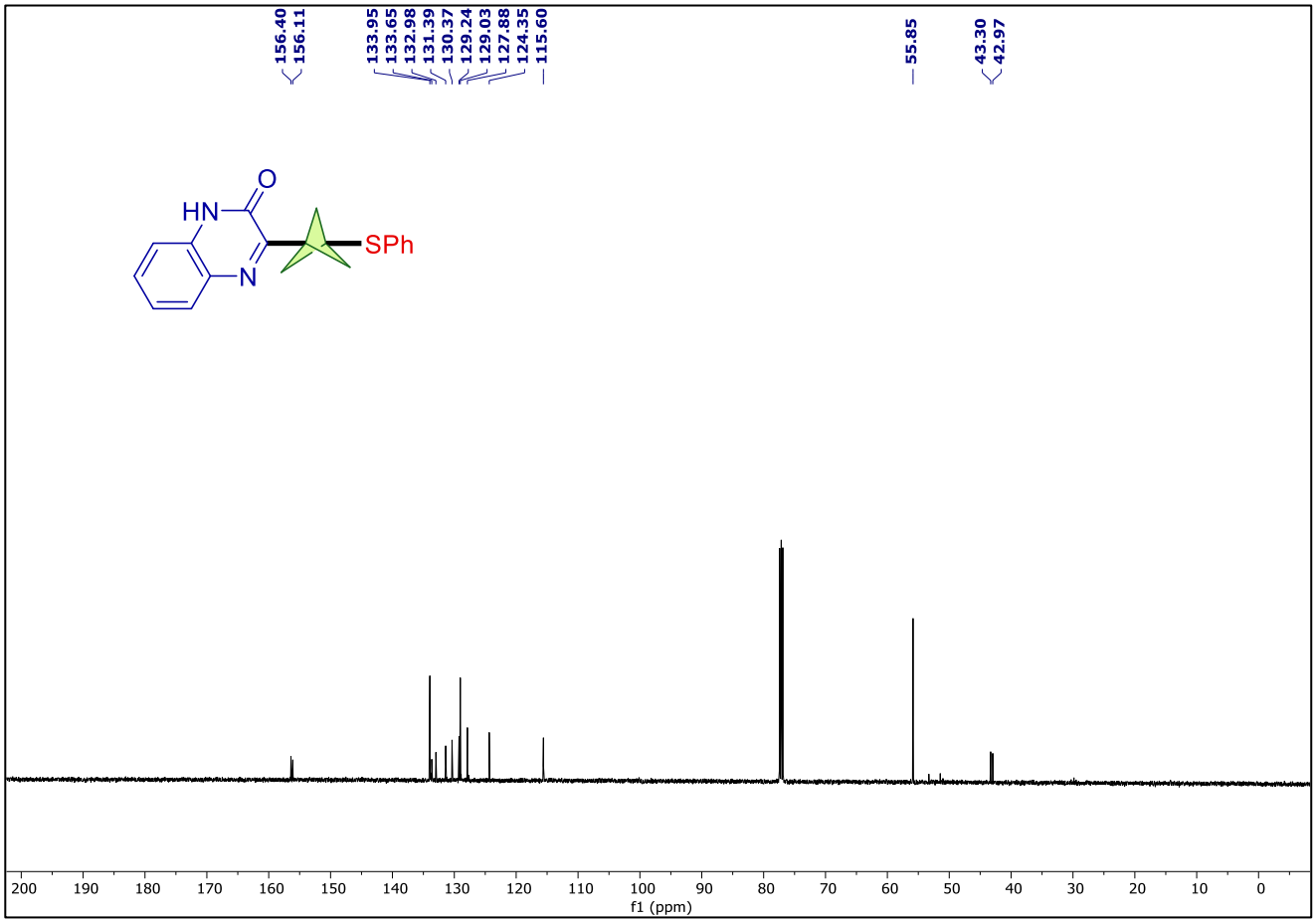
^{13}C{^{1}H} NMR of compound **4o** (126 MHz, $CDCl_3$)



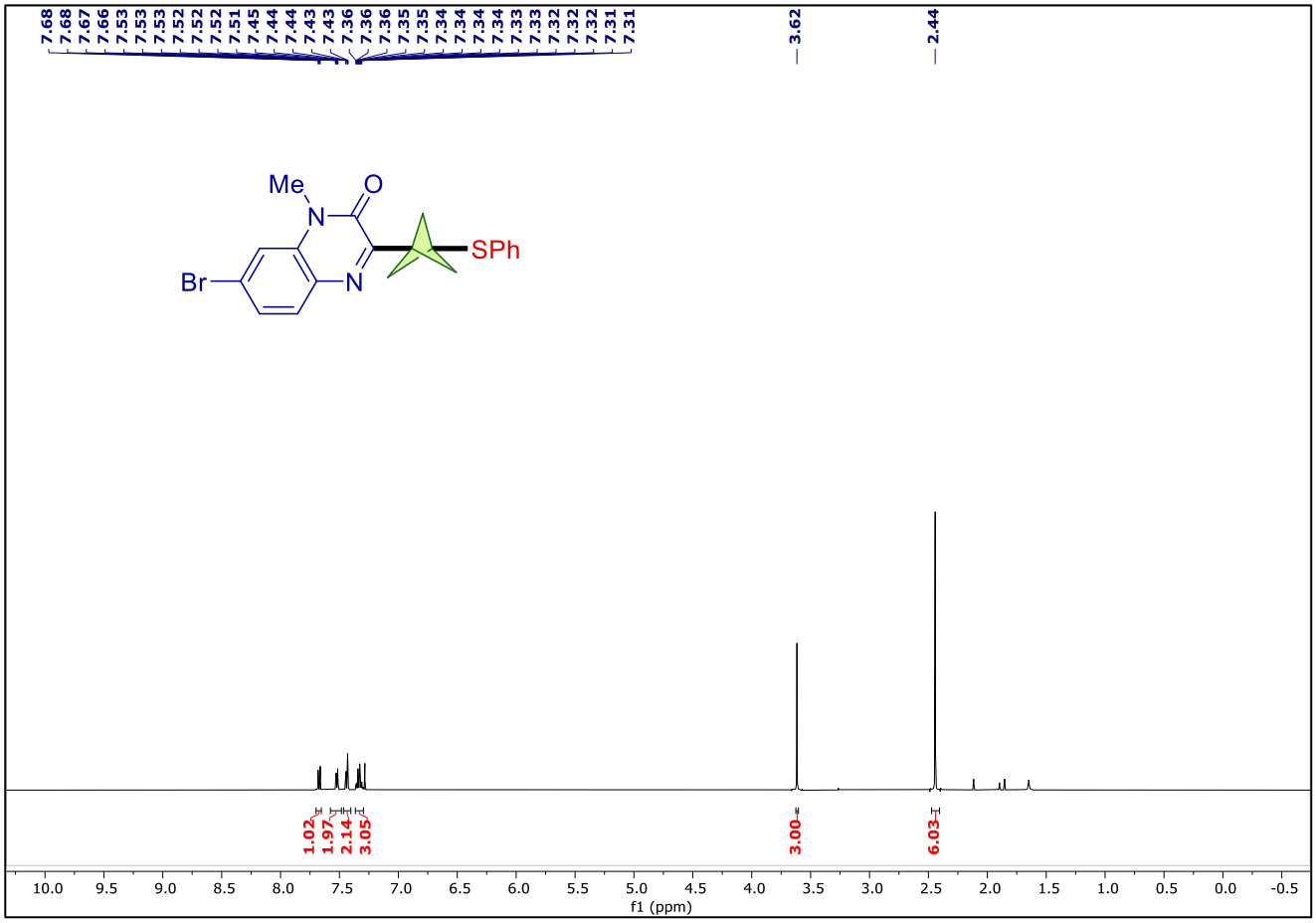
^{19}F NMR of compound **4o** (471 MHz, $CDCl_3$)



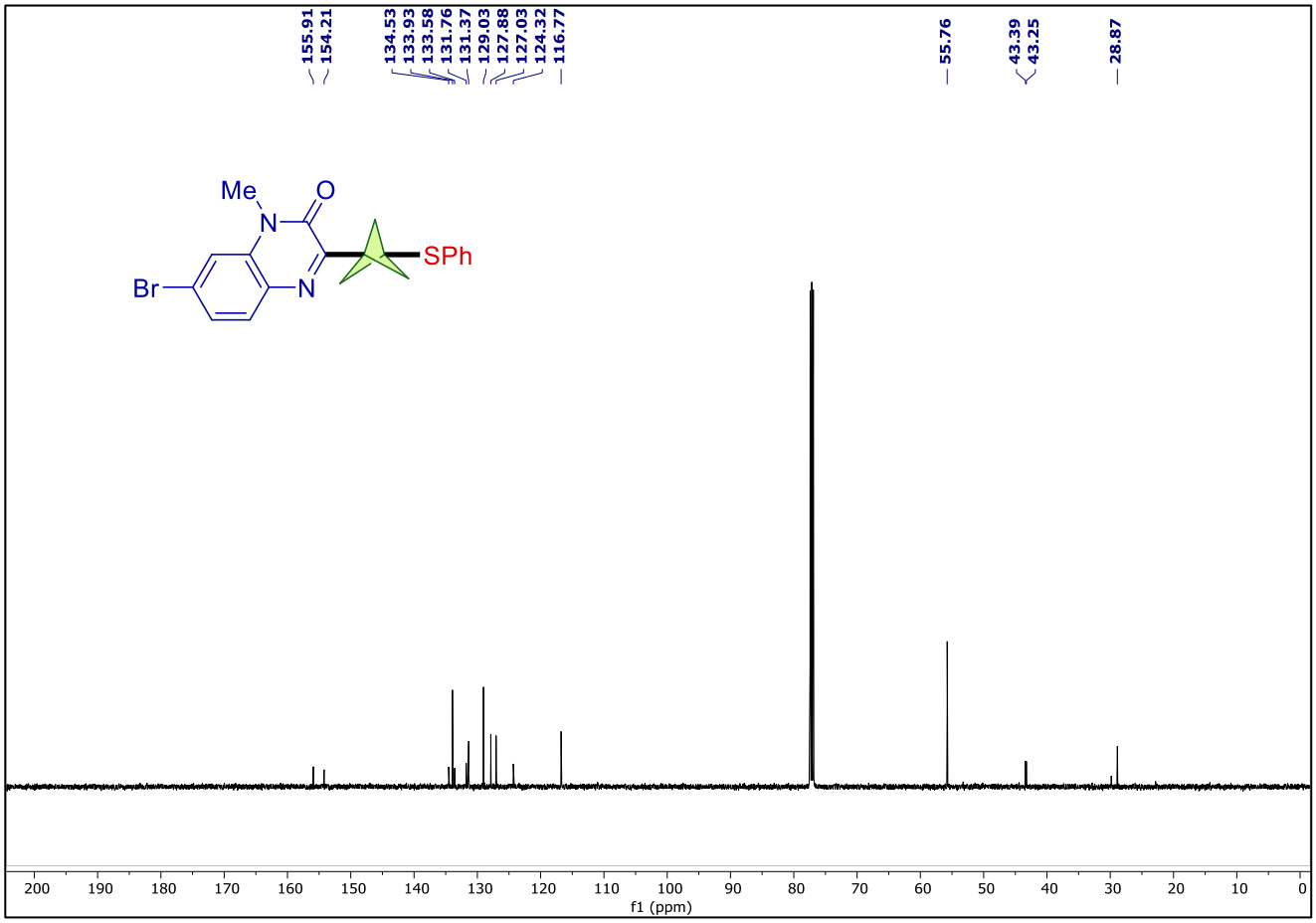
^{1}H NMR of compound **4p** (500 MHz, $CDCl_3$)



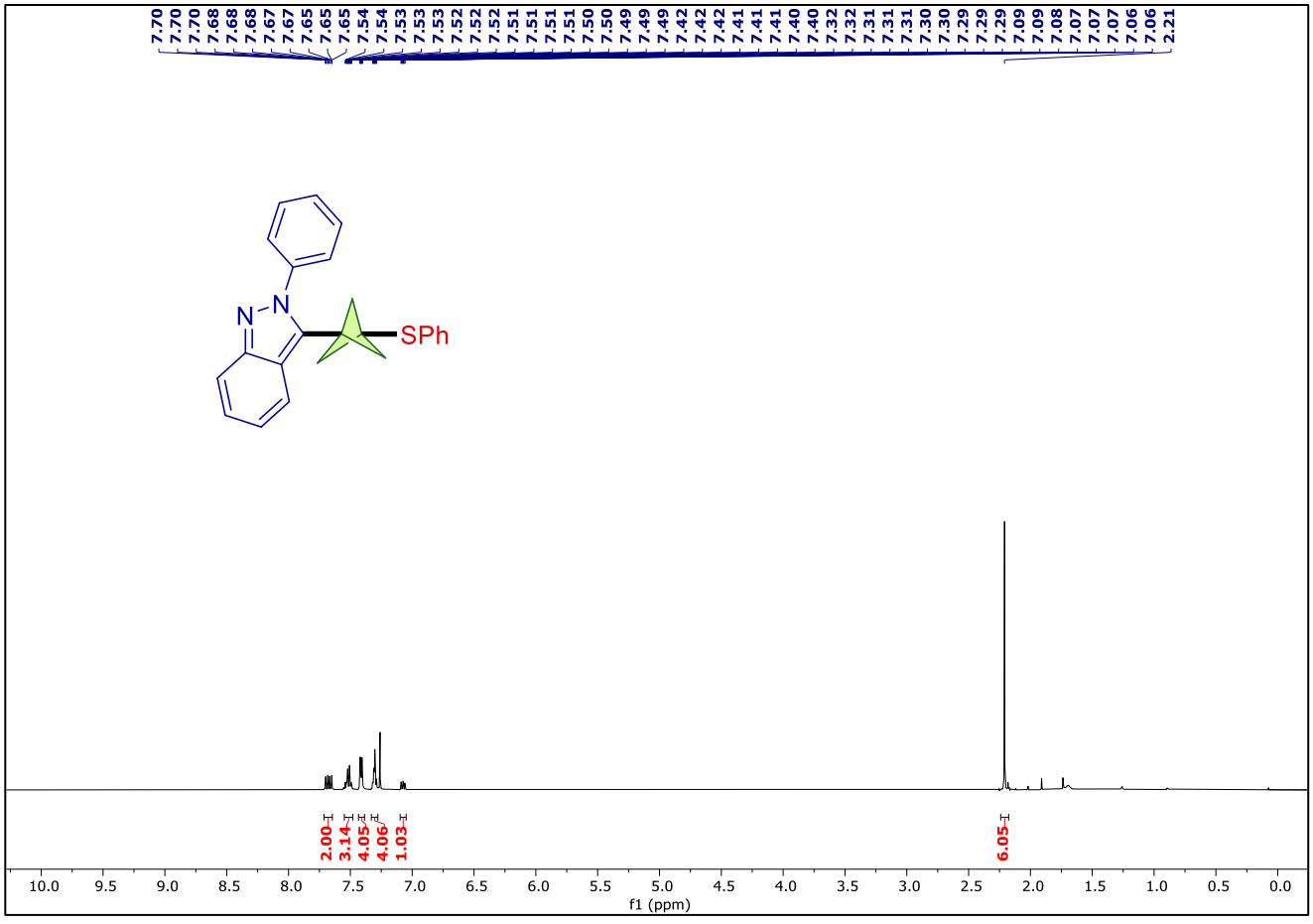
$^{13}C\{^{1}H\}$ NMR of compound **4p** (126 MHz, $CDCl_3$)



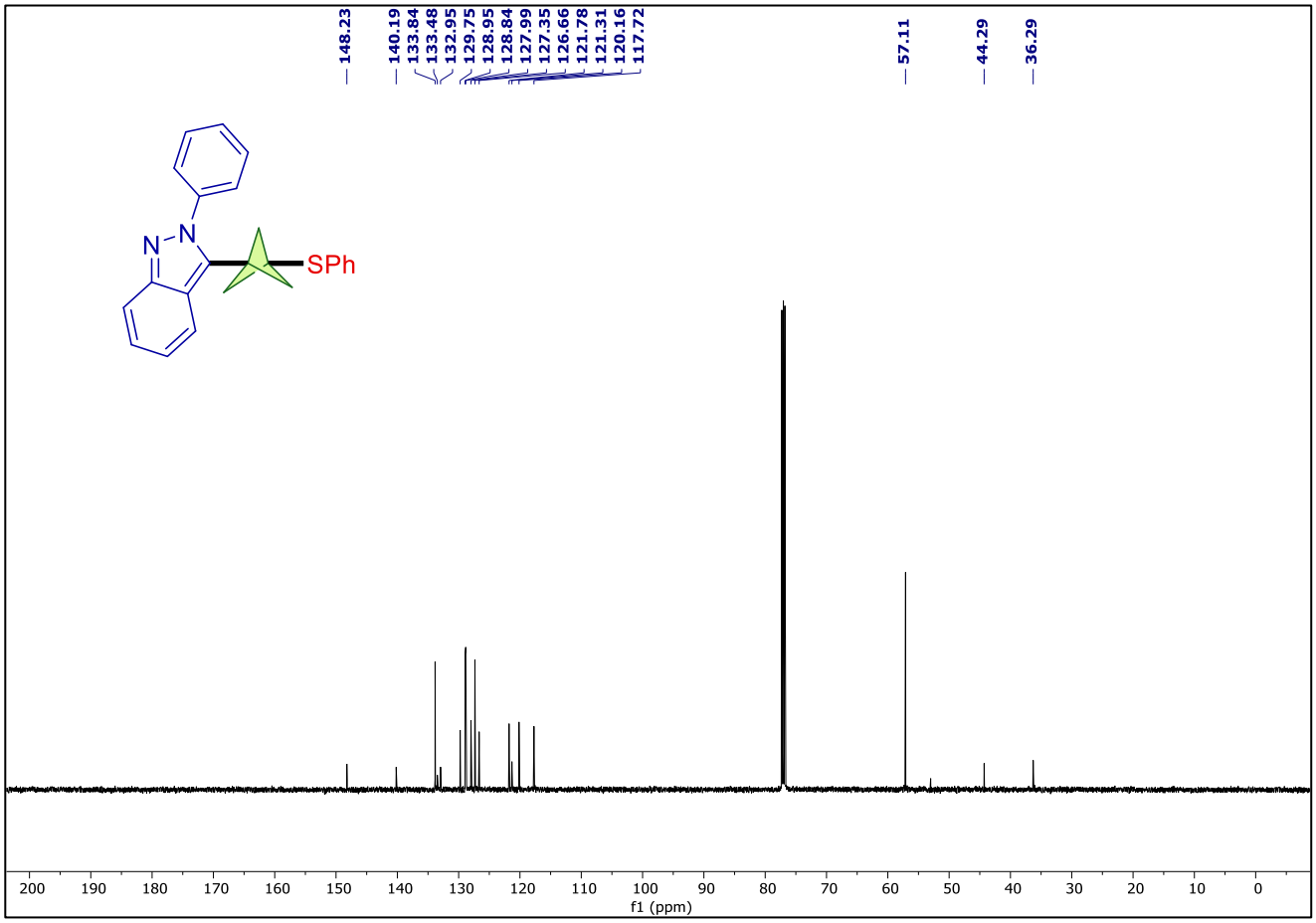
^{1}H NMR of compound **4q** (500 MHz, $CDCl_3$)



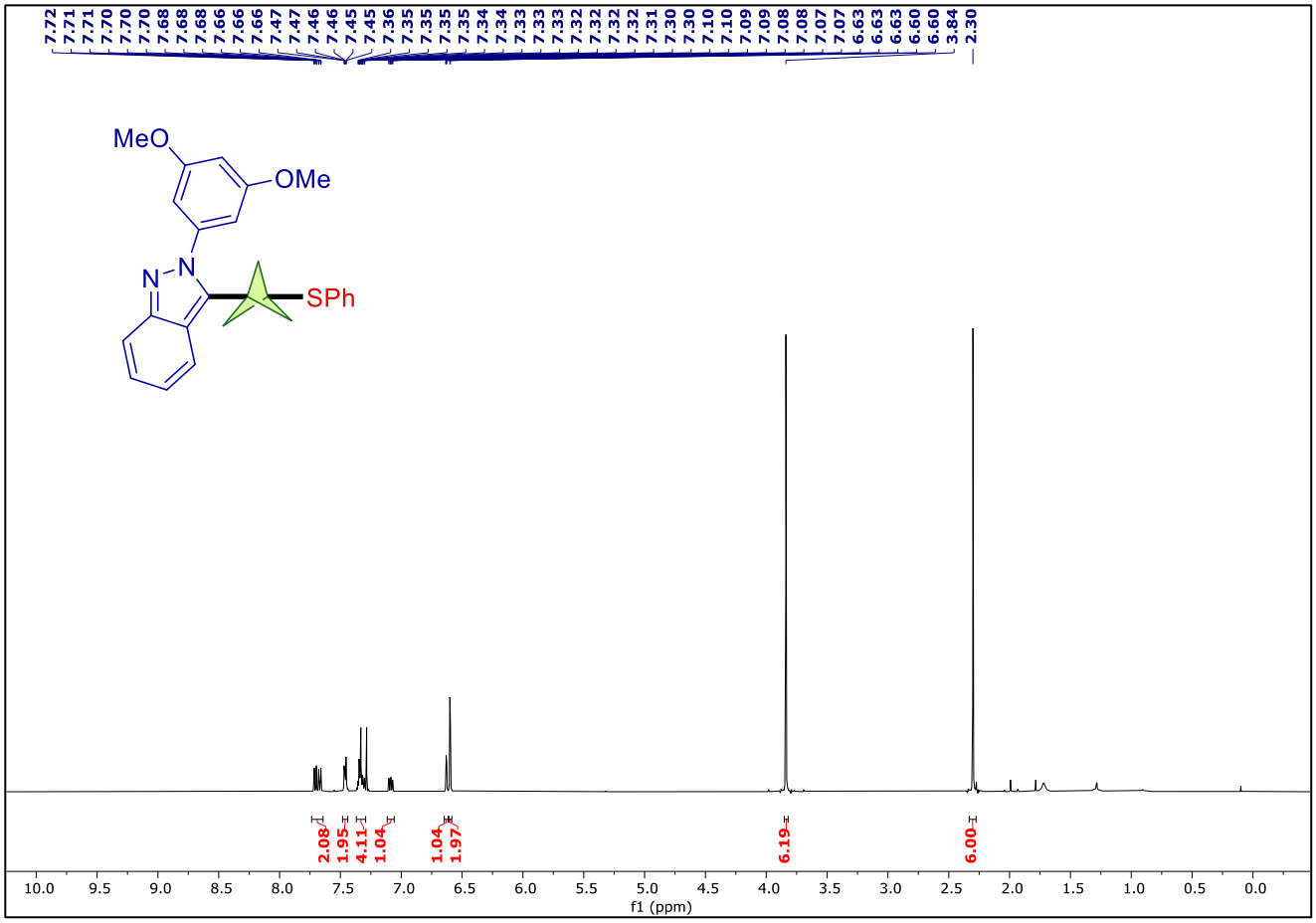
$^{13}C\{^{1}H\}$ NMR of compound **4q** (126 MHz, $CDCl_3$)



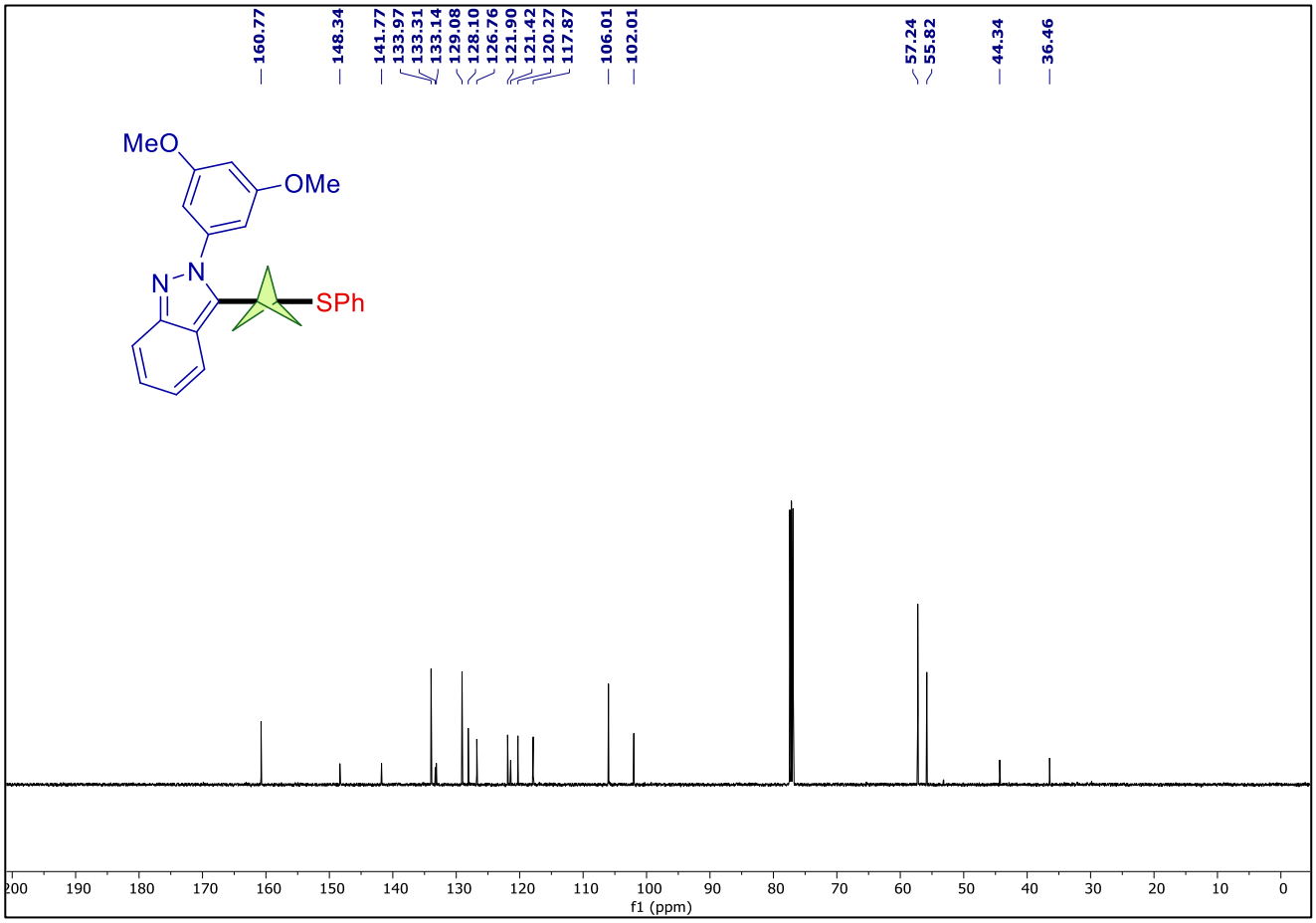
^{1}H NMR of compound **4r** (500 MHz, $CDCl_3$)



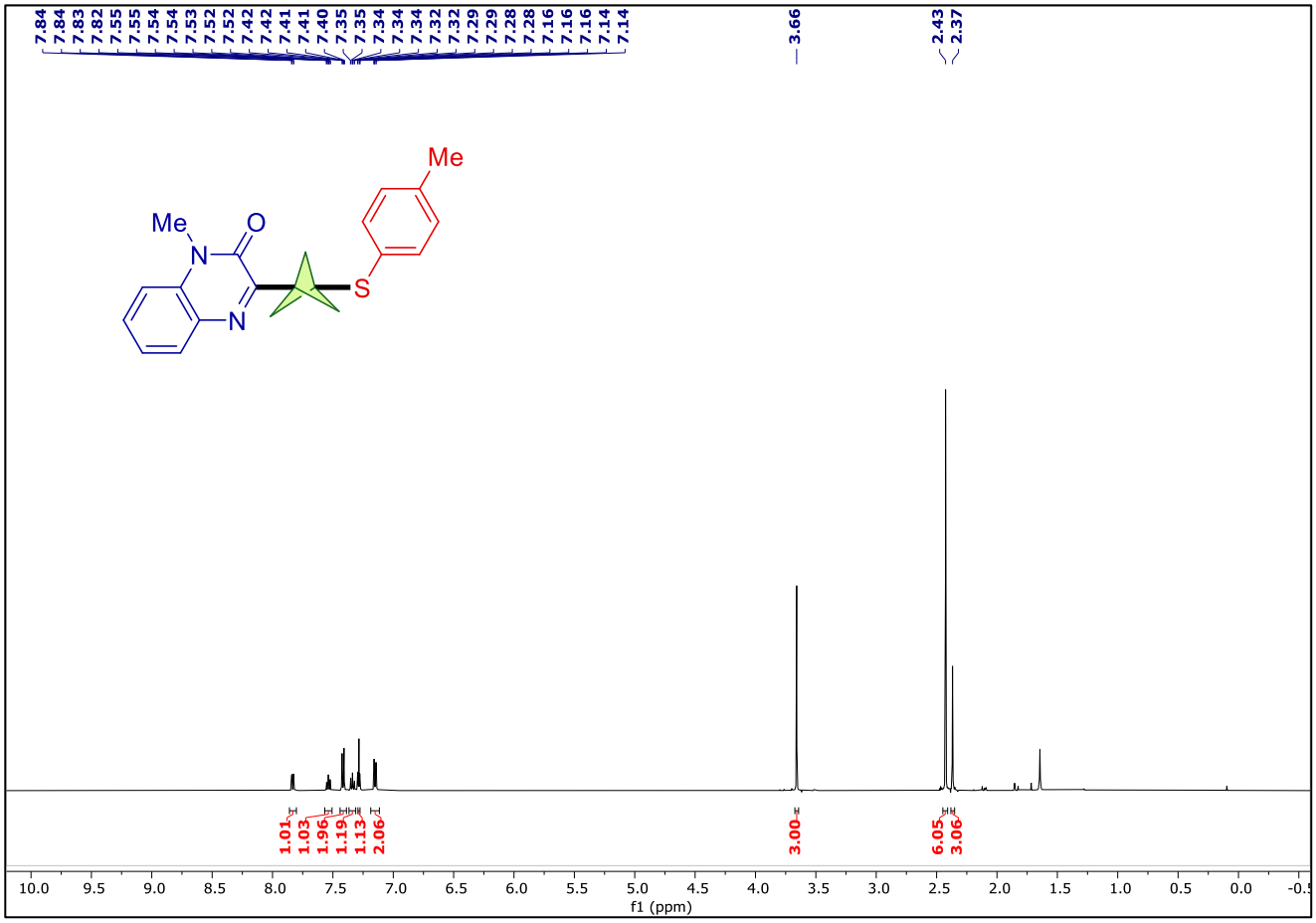
$^{13}C\{^{1}H\}$ NMR of compound **4r** (126 MHz, $CDCl_3$)



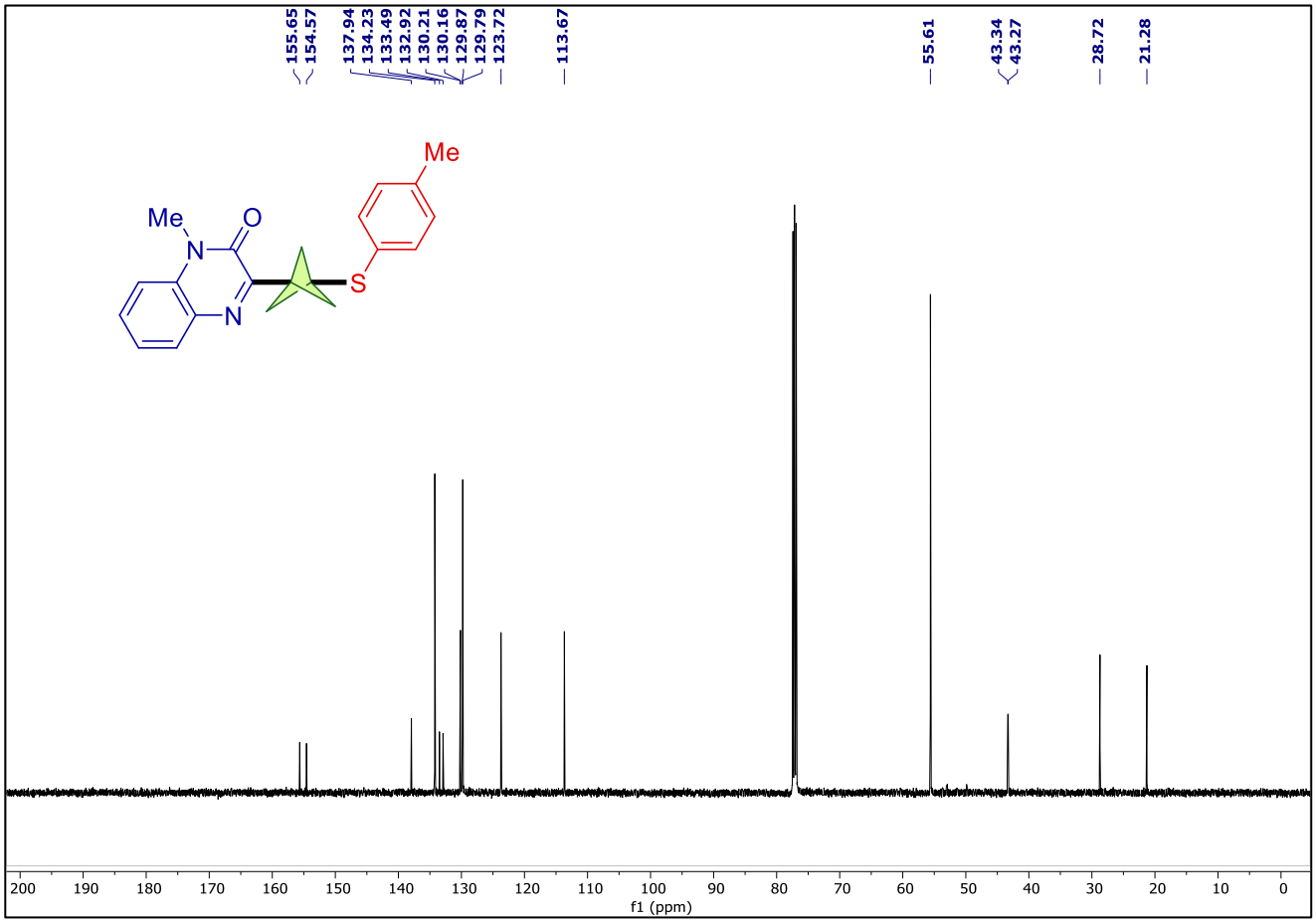
^{1}H NMR of compound **4s** (500 MHz, $CDCl_3$)



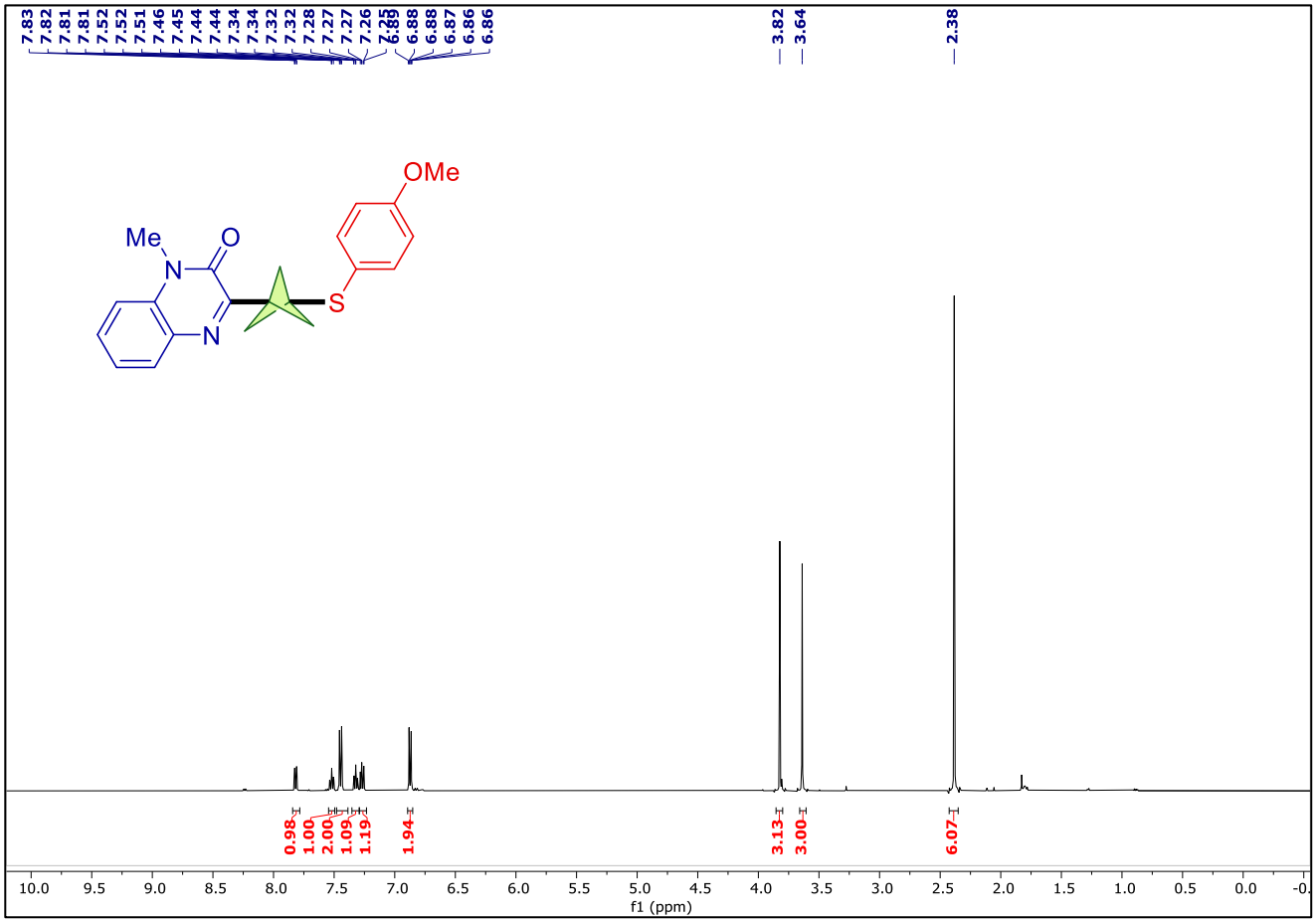
$^{13}C\{^{1}H\}$ NMR of compound **4s** (126 MHz, $CDCl_3$)



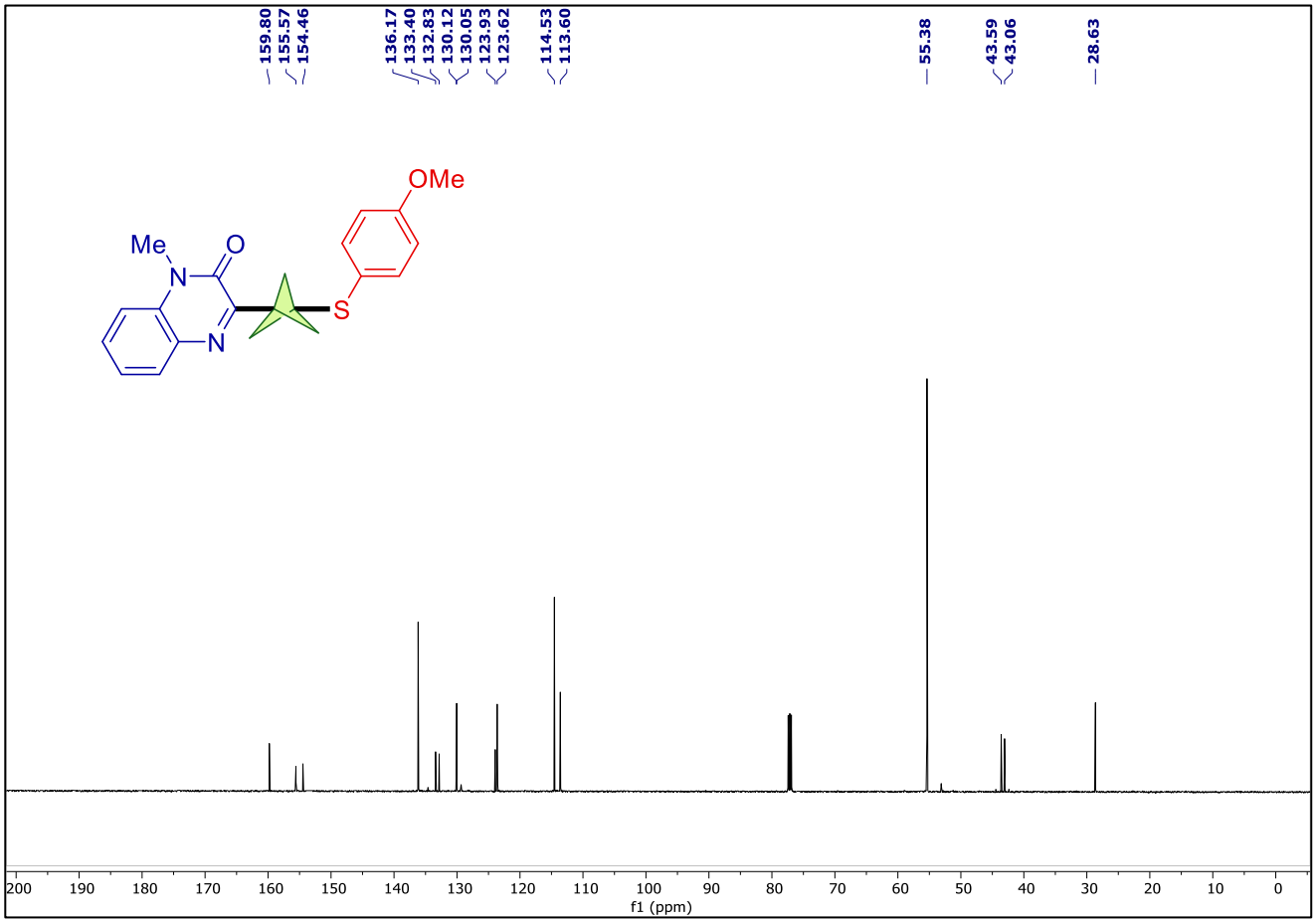
^{1}H NMR of compound **5a** (500 MHz, $CDCl_3$)



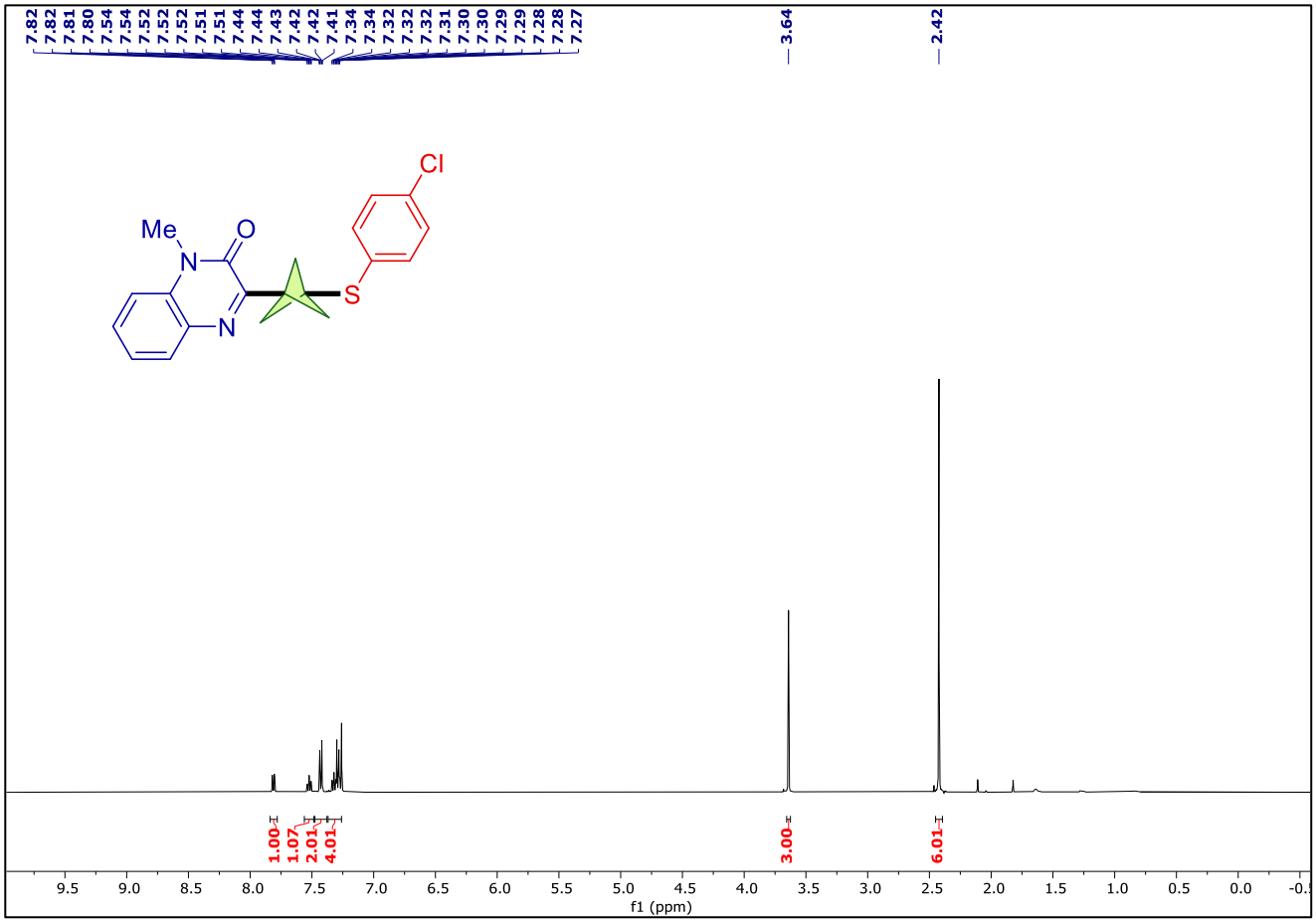
$^{13}C\{^{1}H\}$ NMR of compound **5a** (126 MHz, $CDCl_3$)



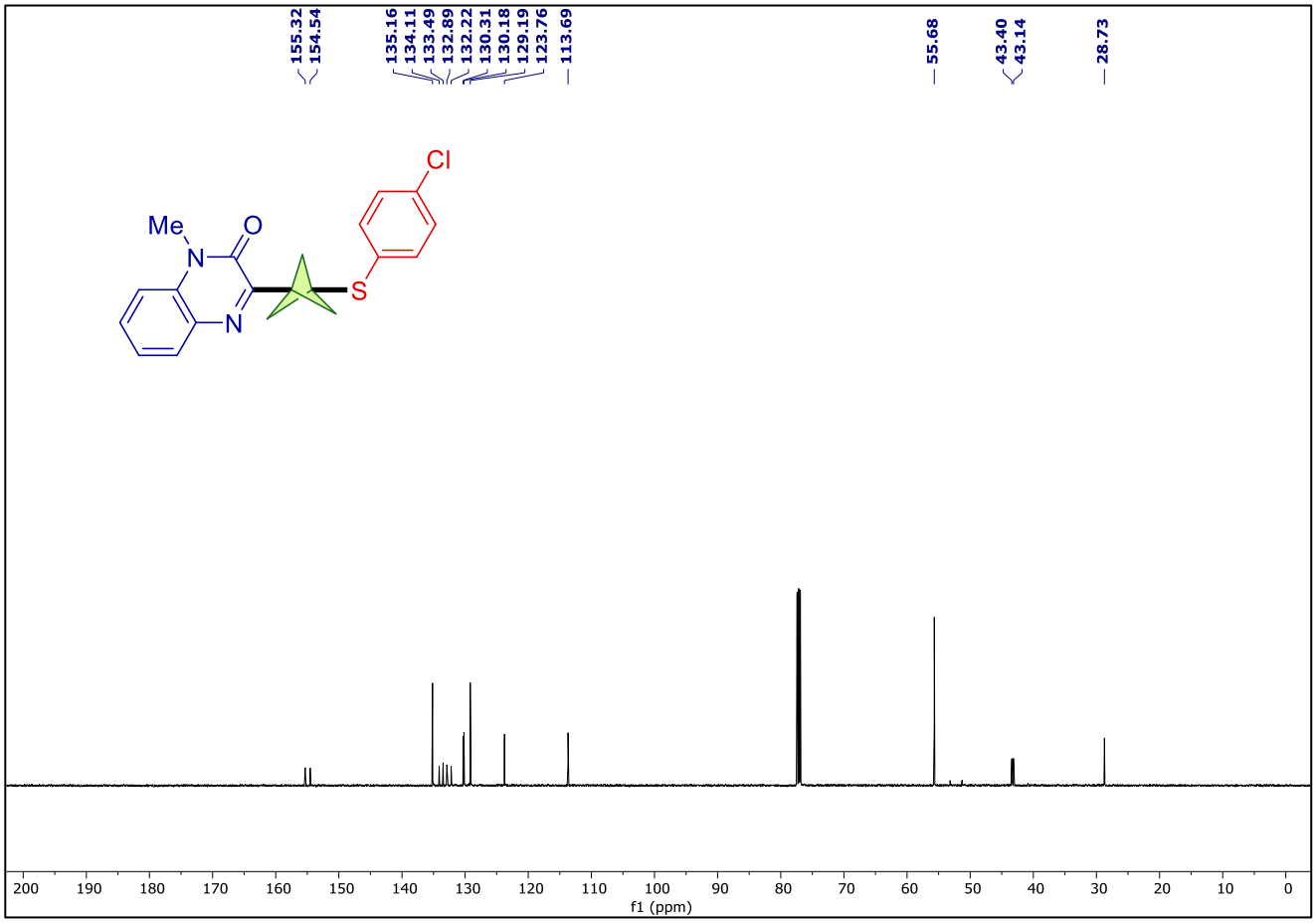
^{1}H NMR of compound **5b** (500 MHz, $CDCl_3$)



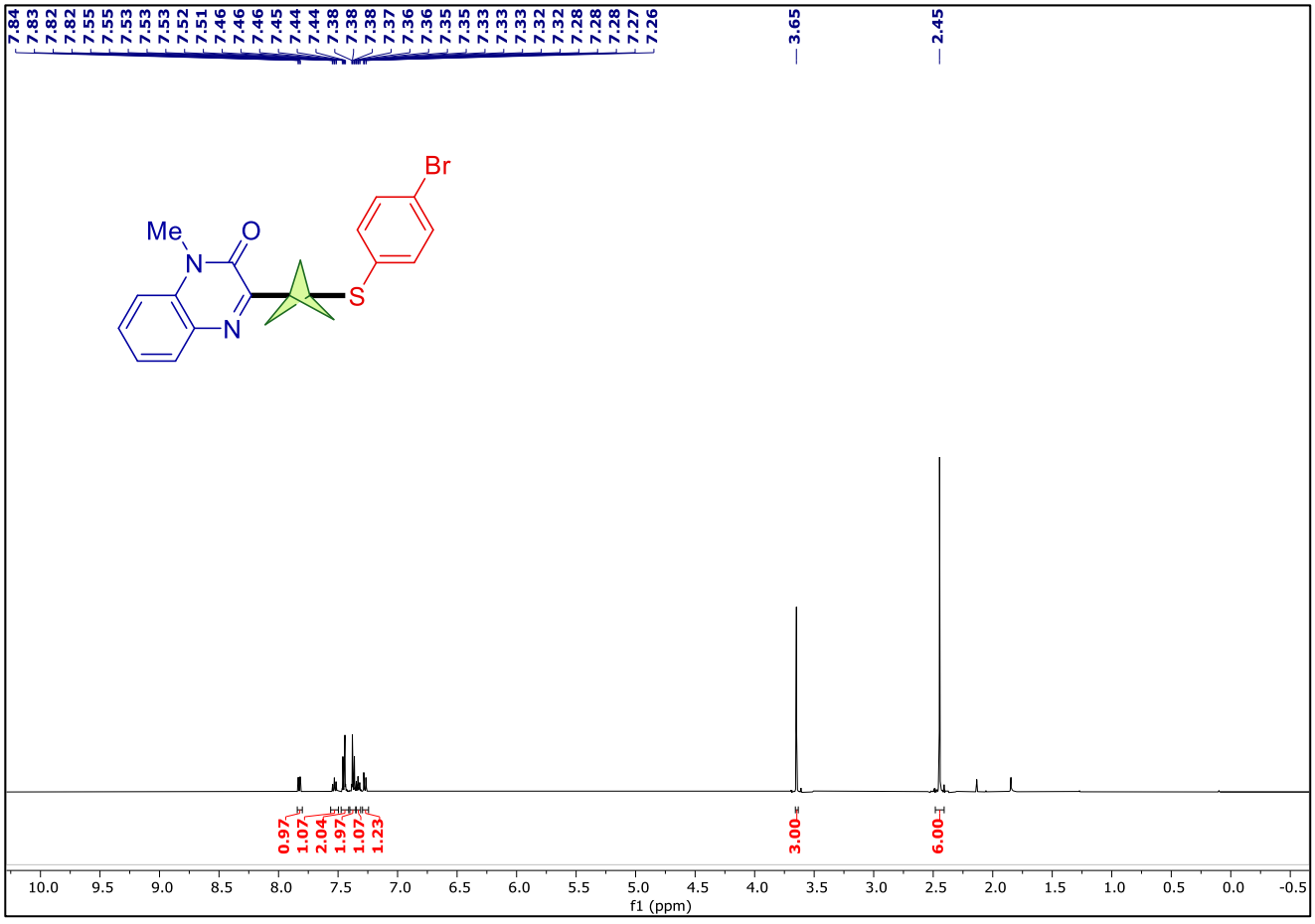
$^{13}C\{^{1}H\}$ NMR of compound **5b** (126 MHz, $CDCl_3$)



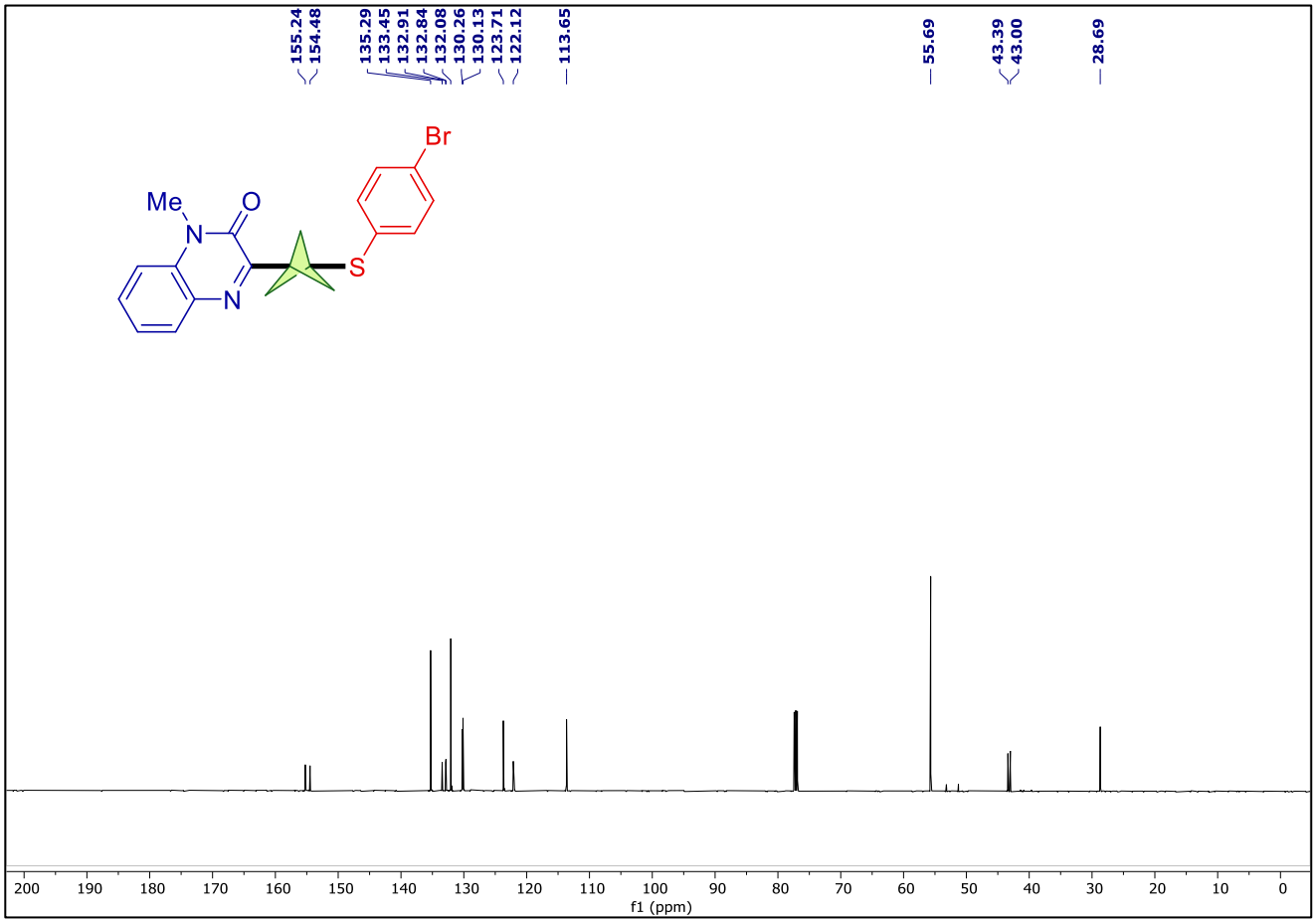
^{1}H NMR of compound **5c** (500 MHz, $CDCl_3$)



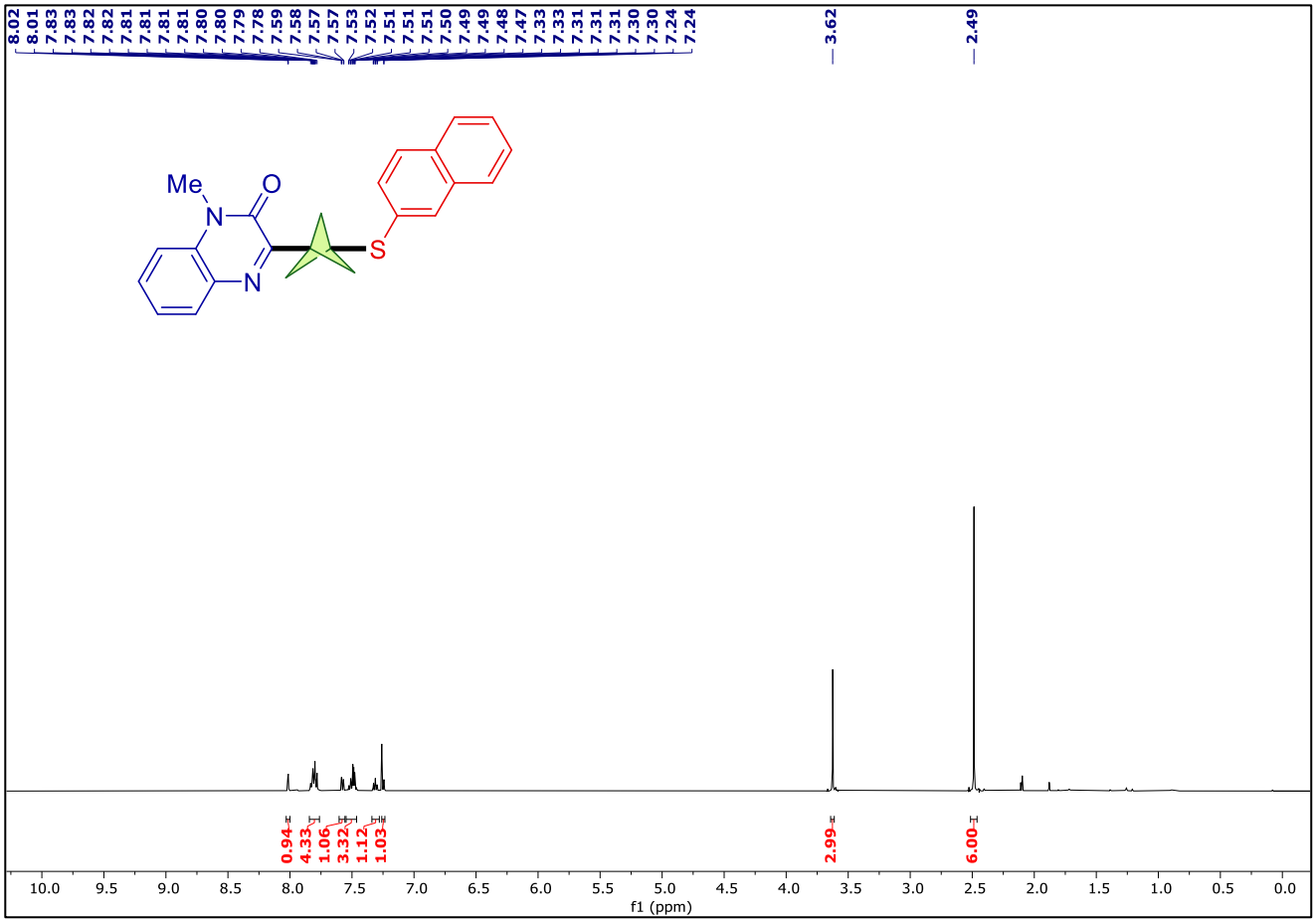
$^{13}C\{^{1}H\}$ NMR of compound **5c** (126 MHz, $CDCl_3$)



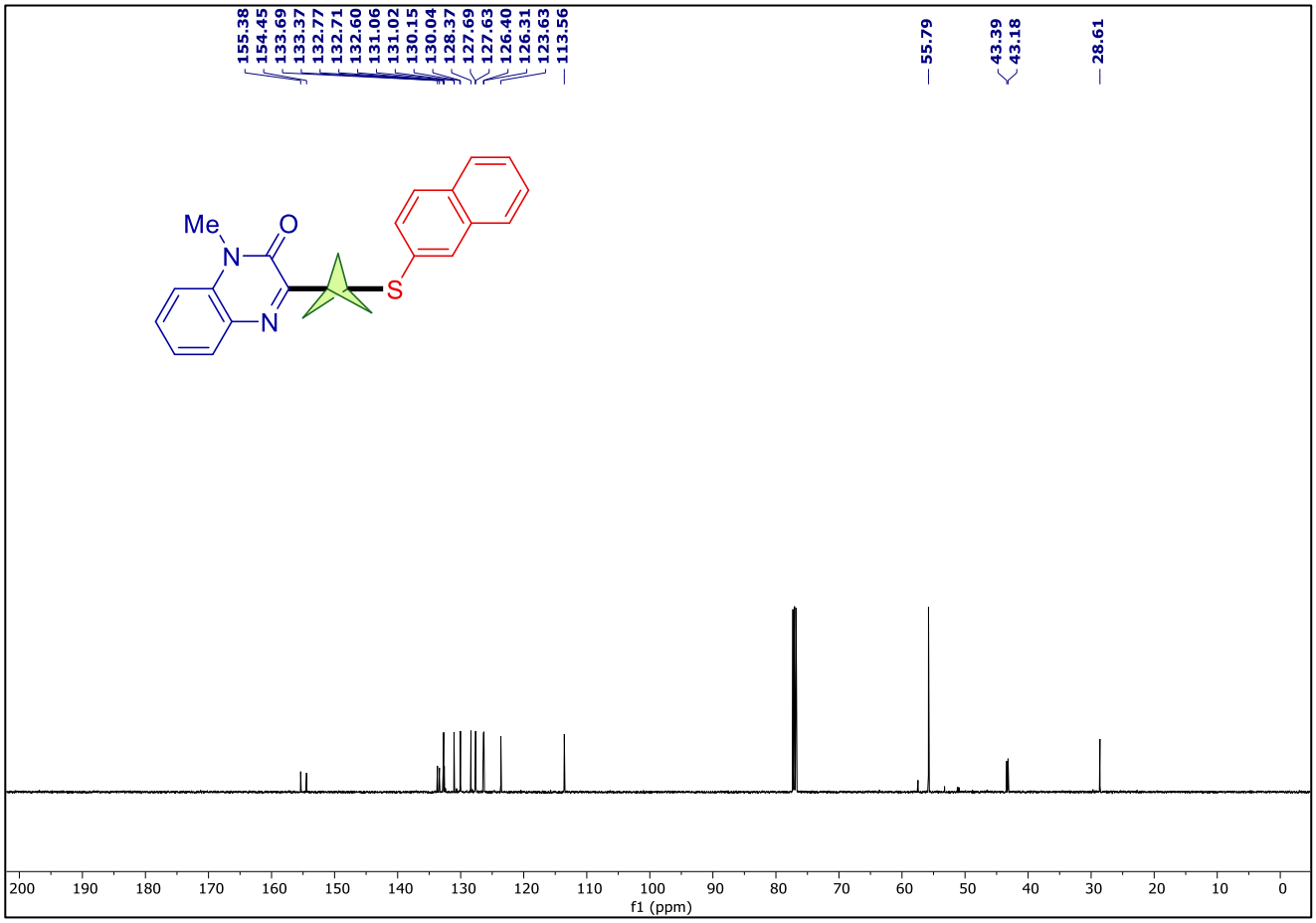
^{1}H NMR of compound **5d** (500 MHz, $CDCl_3$)



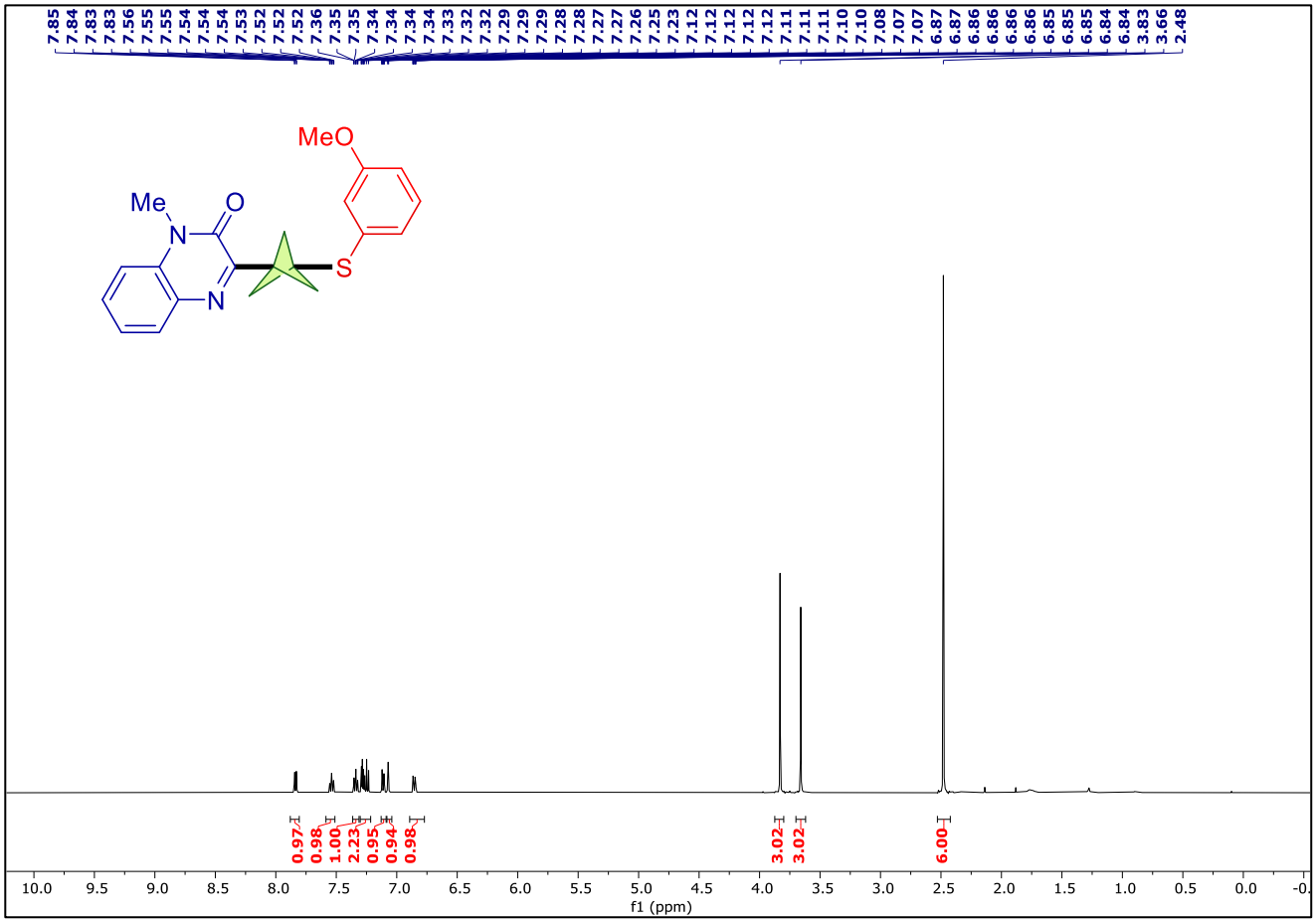
$^{13}C\{^{1}H\}$ NMR of compound **5d** (126 MHz, $CDCl_3$)



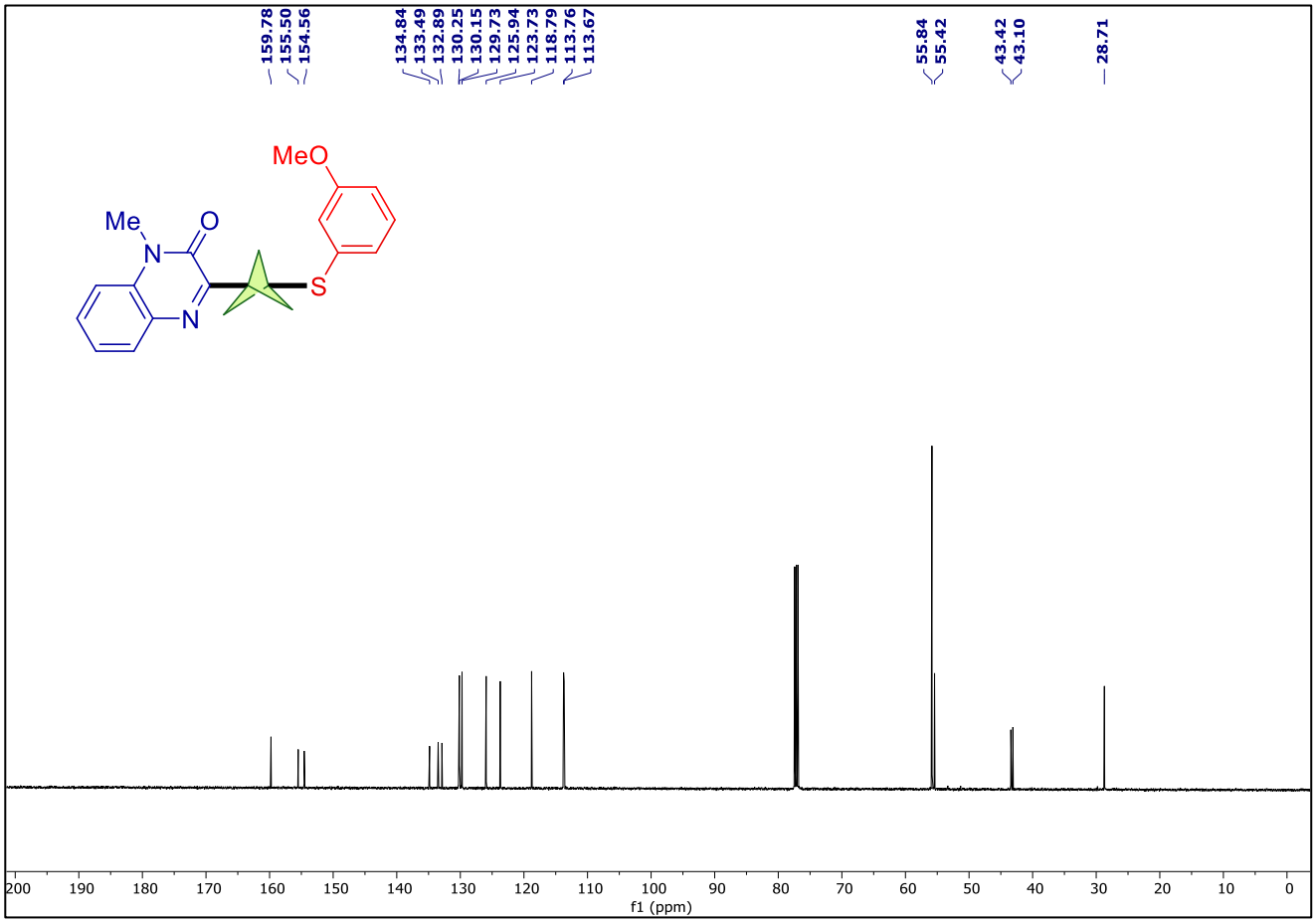
^{1}H NMR of compound **5e** (500 MHz, $CDCl_3$)



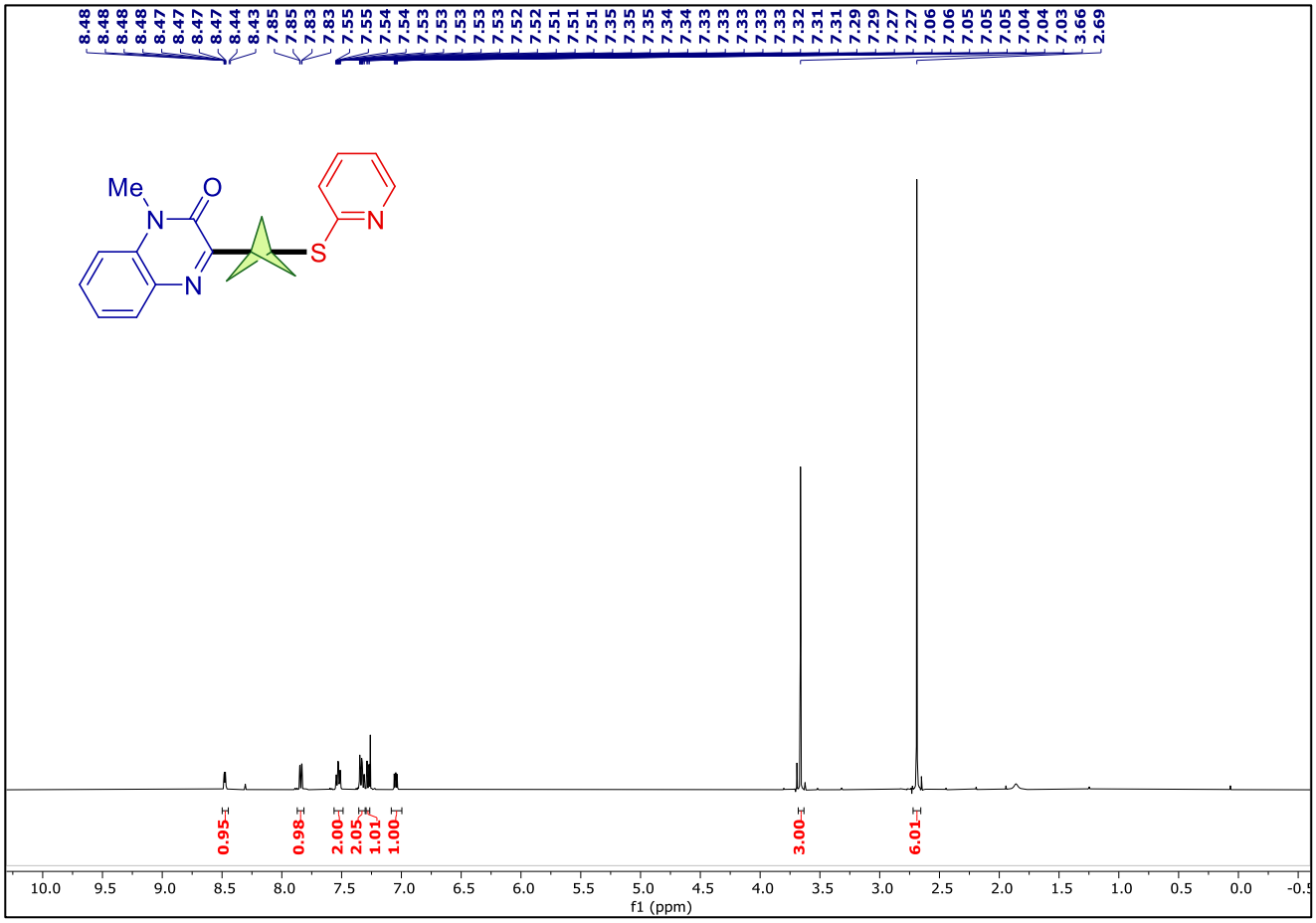
$^{13}C\{^{1}H\}$ NMR of compound **5e** (126 MHz, $CDCl_3$)



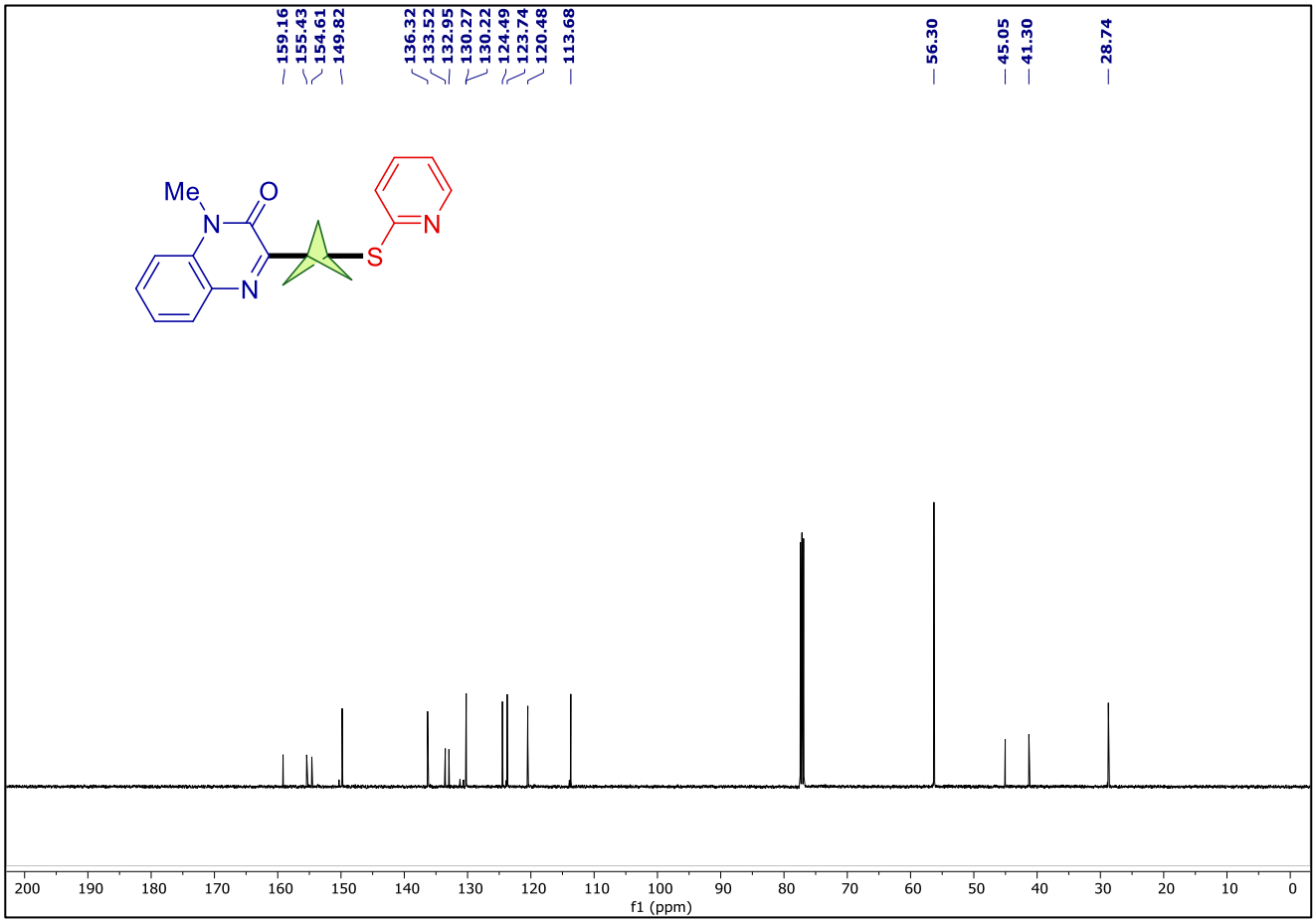
^{1}H NMR of compound **5f** (500 MHz, $CDCl_3$)



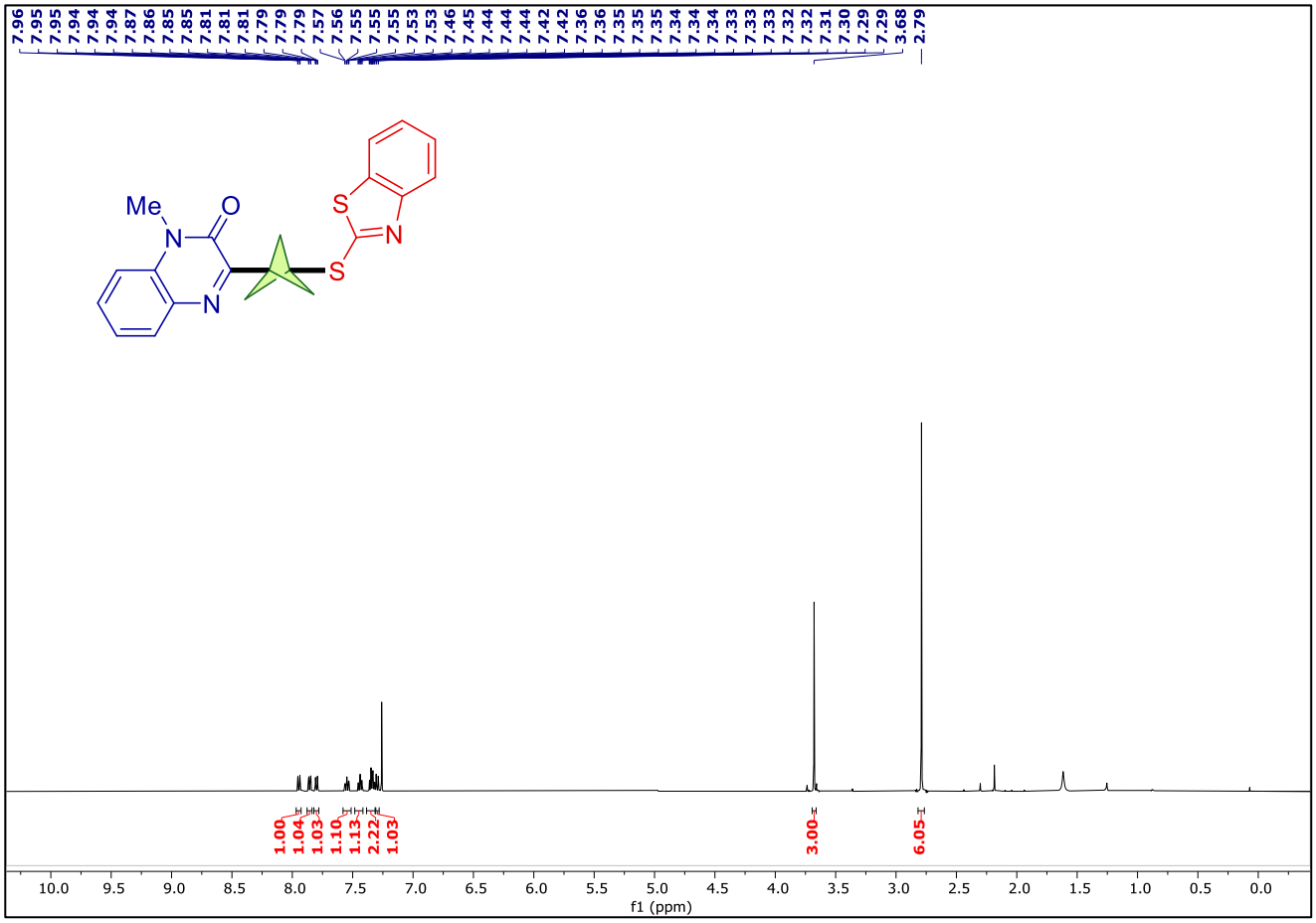
$^{13}C\{^{1}H\}$ NMR of compound **5f** (126 MHz, $CDCl_3$)



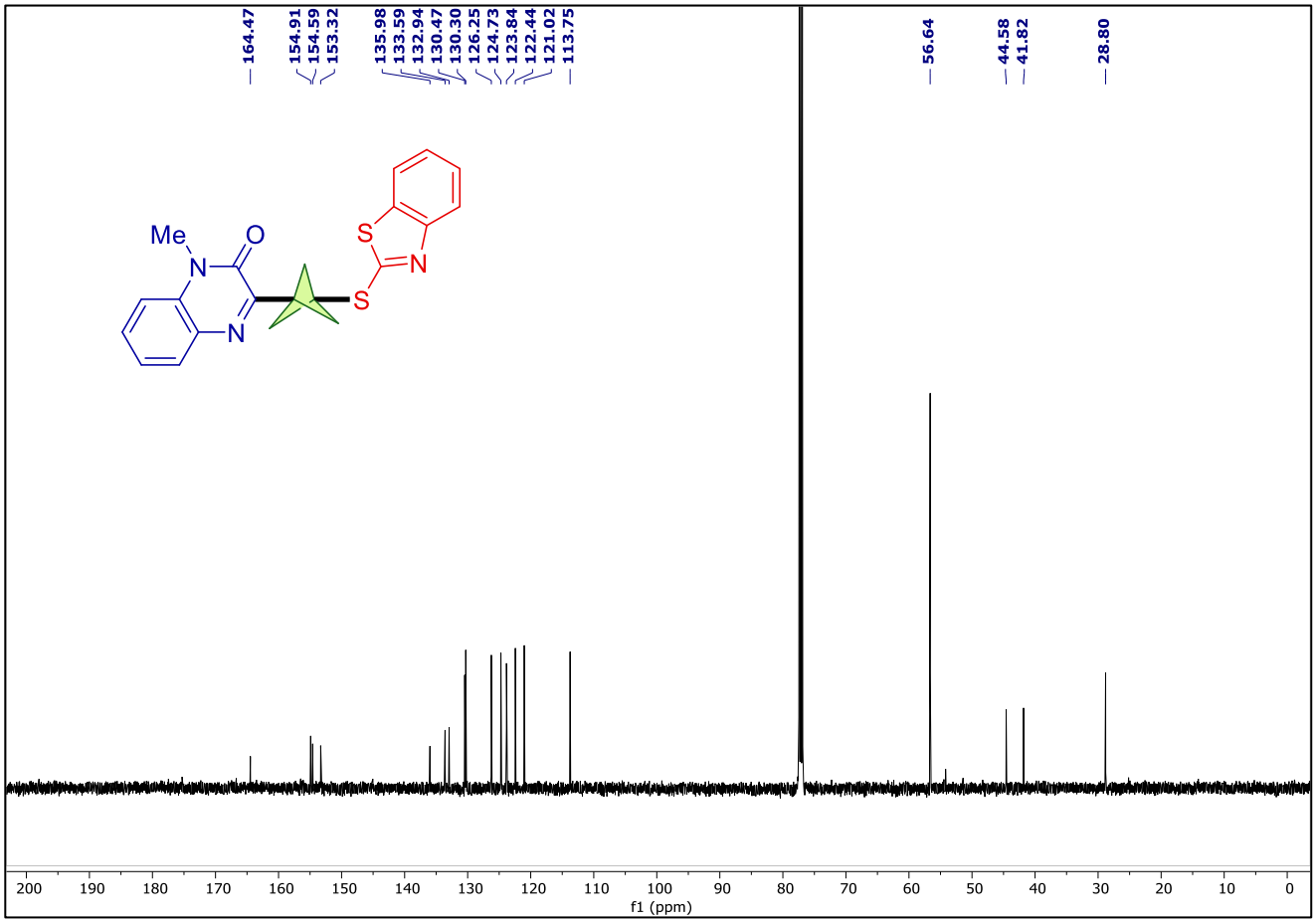
^{1}H NMR of compound **5g** (500 MHz, $CDCl_3$)



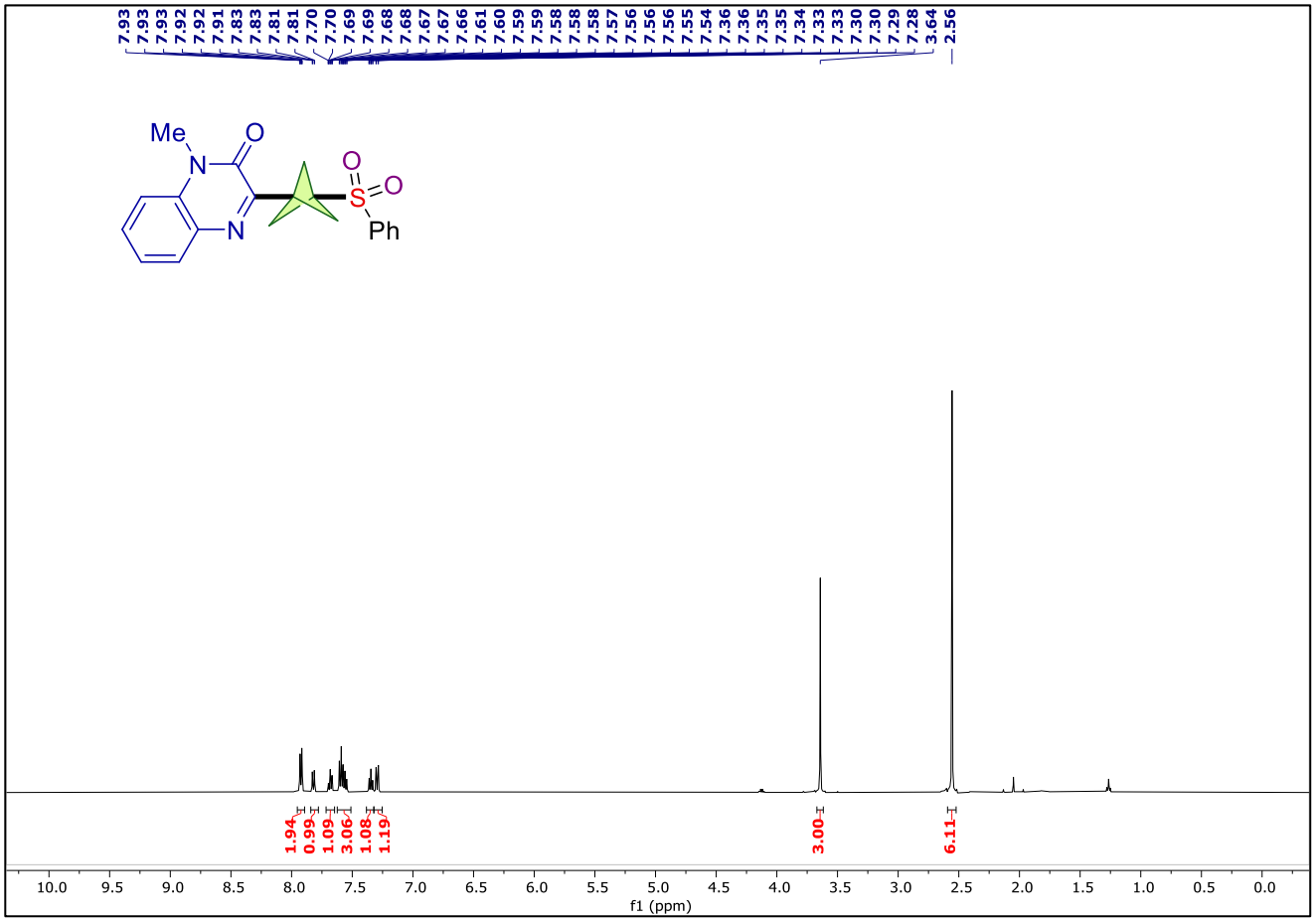
$^{13}C\{^{1}H\}$ NMR of compound **5g** (126 MHz, $CDCl_3$)



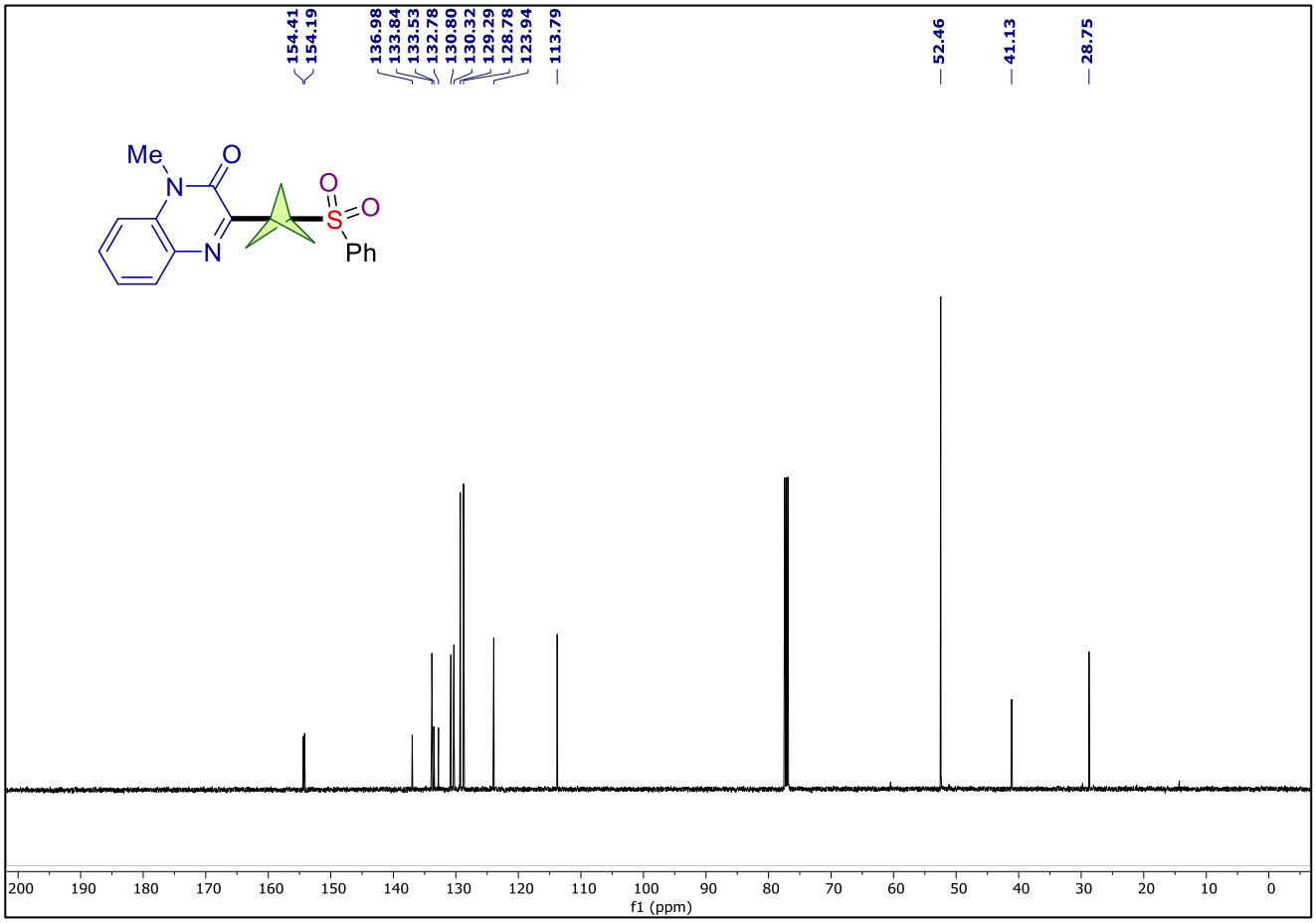
^{1}H NMR of compound **5h** (500 MHz, $CDCl_3$)



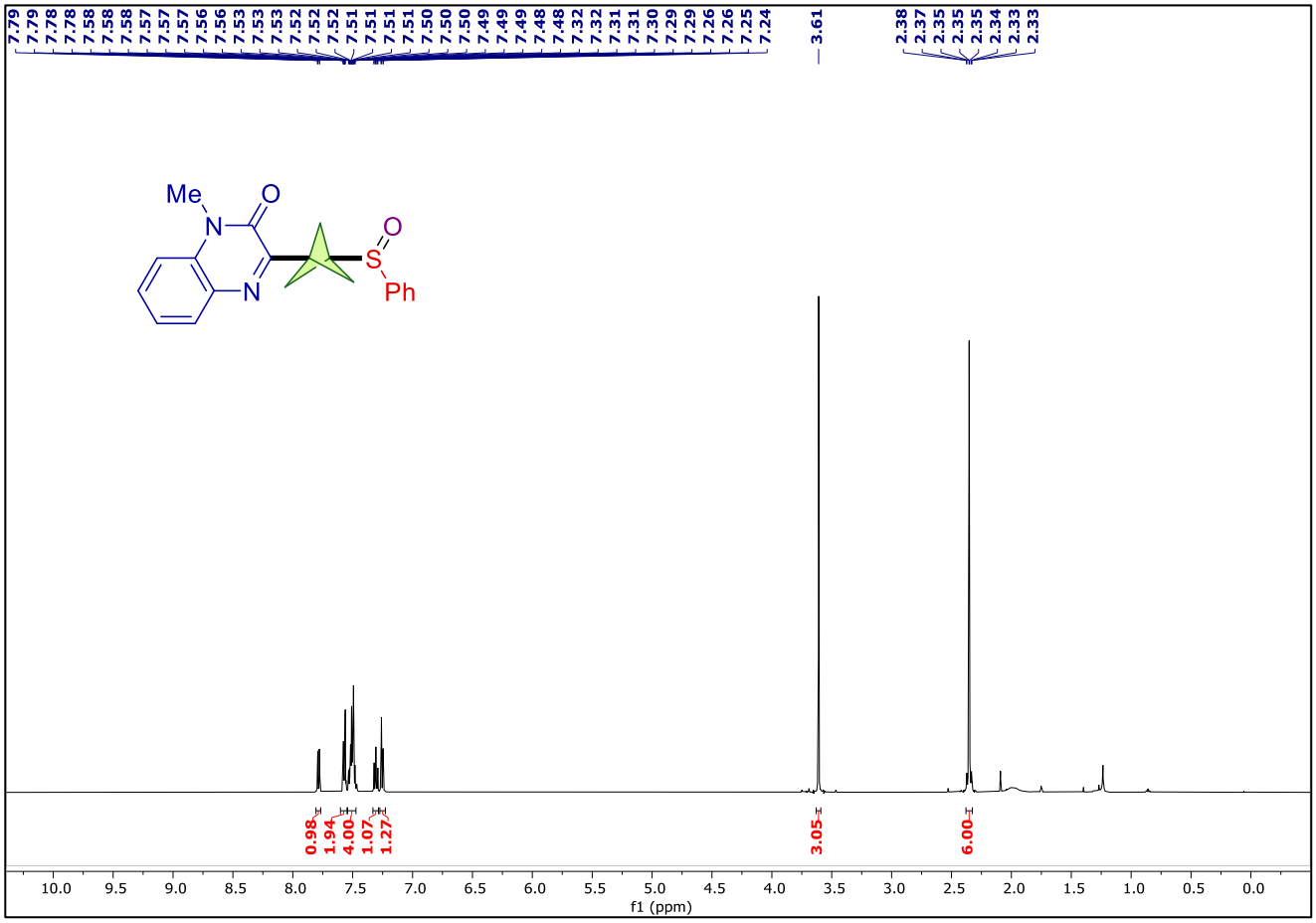
$^{13}C\{^{1}H\}$ NMR of compound **5h** (126 MHz, $CDCl_3$)



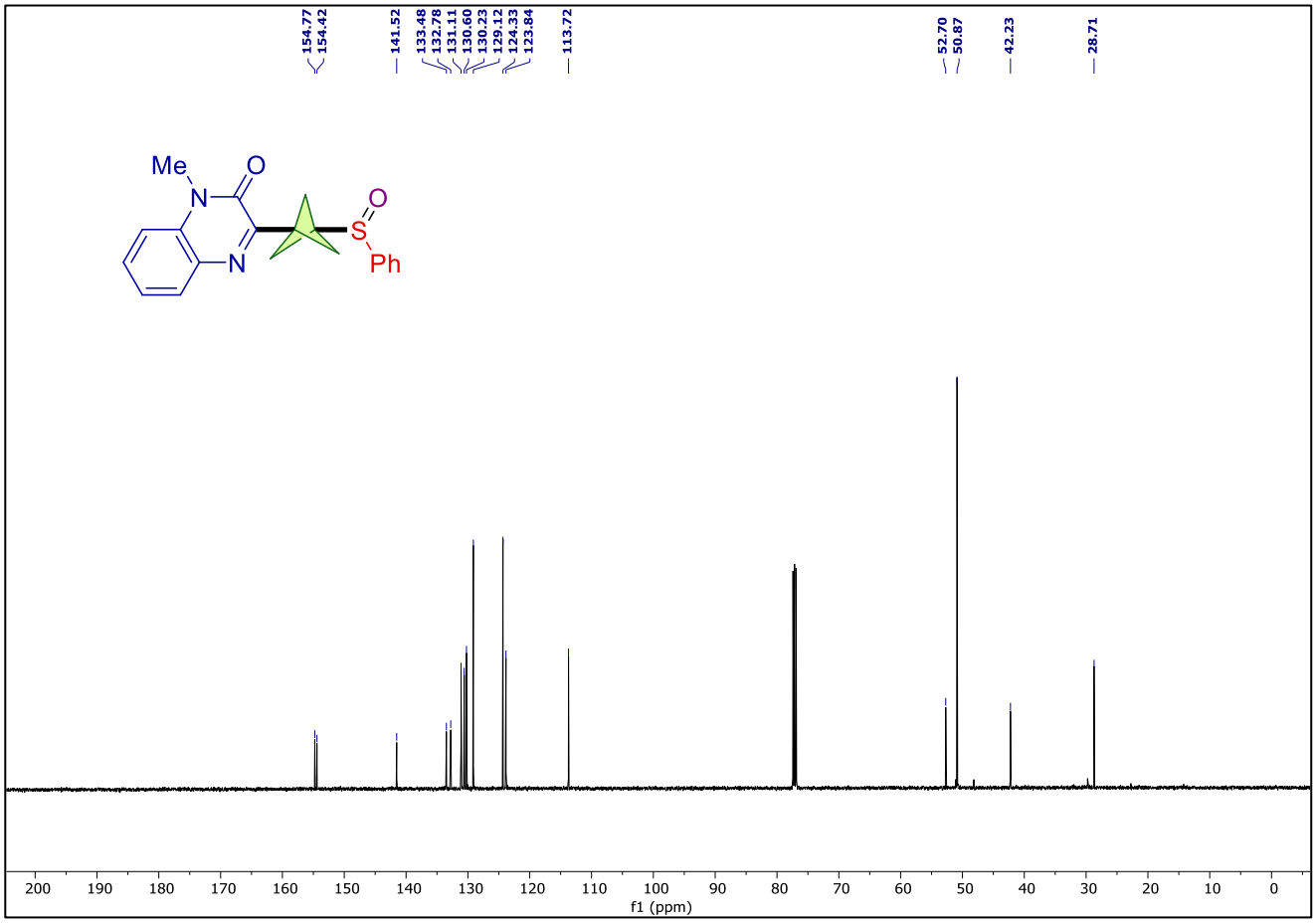
^{1}H NMR of compound **7** (500 MHz, $CDCl_3$)



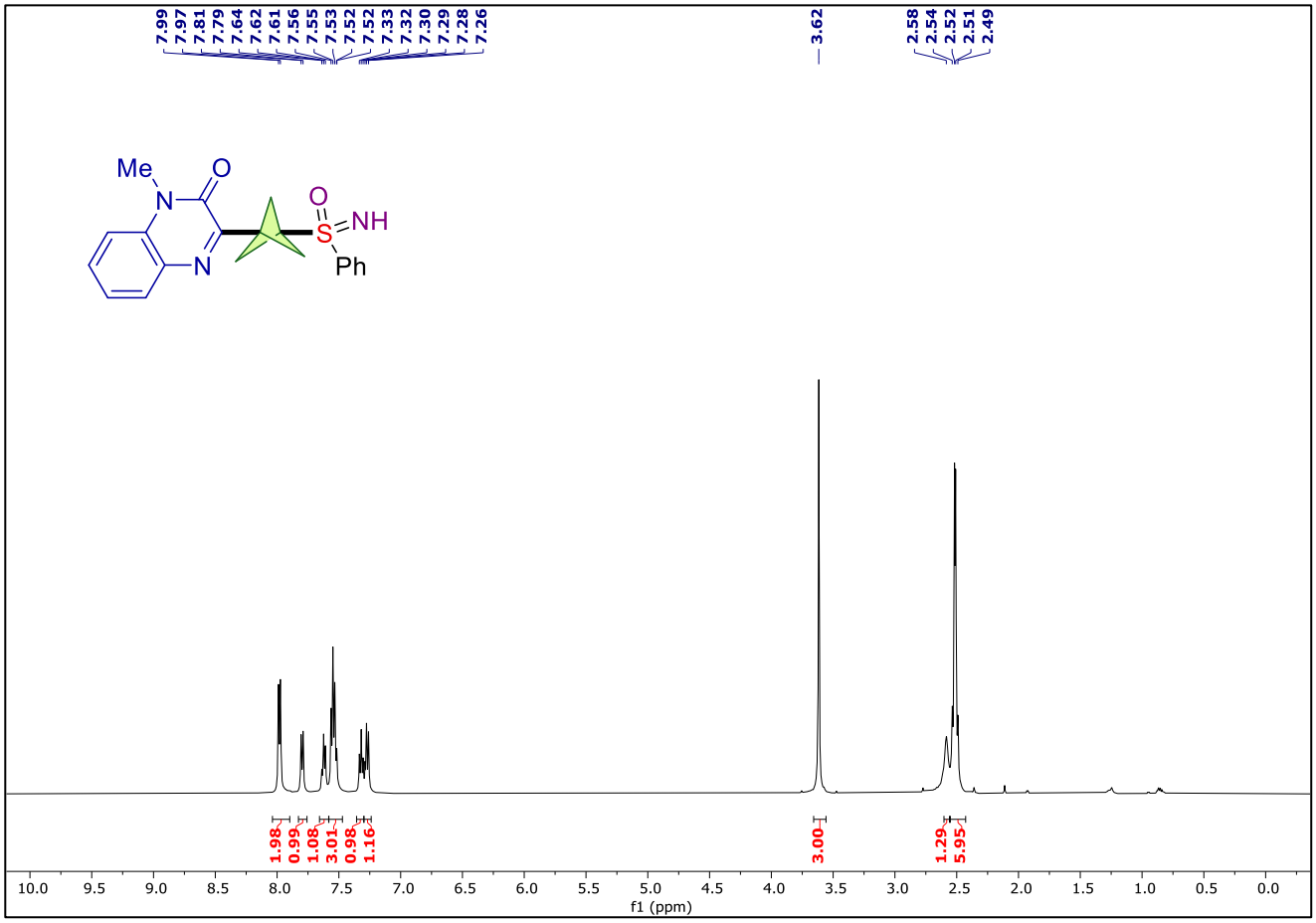
$^{13}C\{^{1}H\}$ NMR of compound **7** (126 MHz, $CDCl_3$)



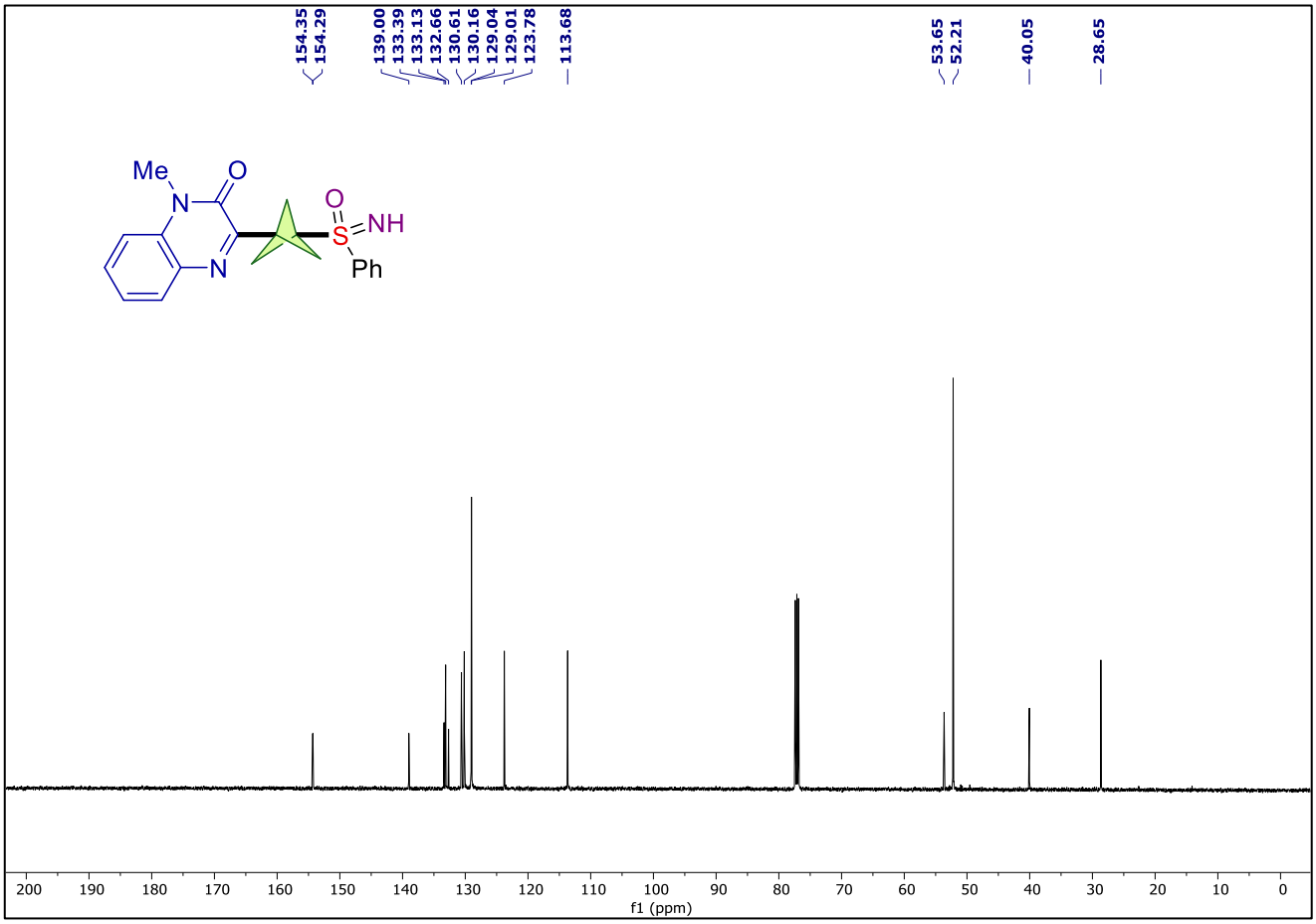
^{1}H NMR of compound **8** (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR of compound **8** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **9** (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR of compound **9** (126 MHz, $CDCl_3$)