Electronic Supplementary Information

Visible-light-initiated *selective synthesis of thiolated-, sulfoxinated-, and sulfonated benzoxazines from N-(2-vinylaryl)amides and thiols*

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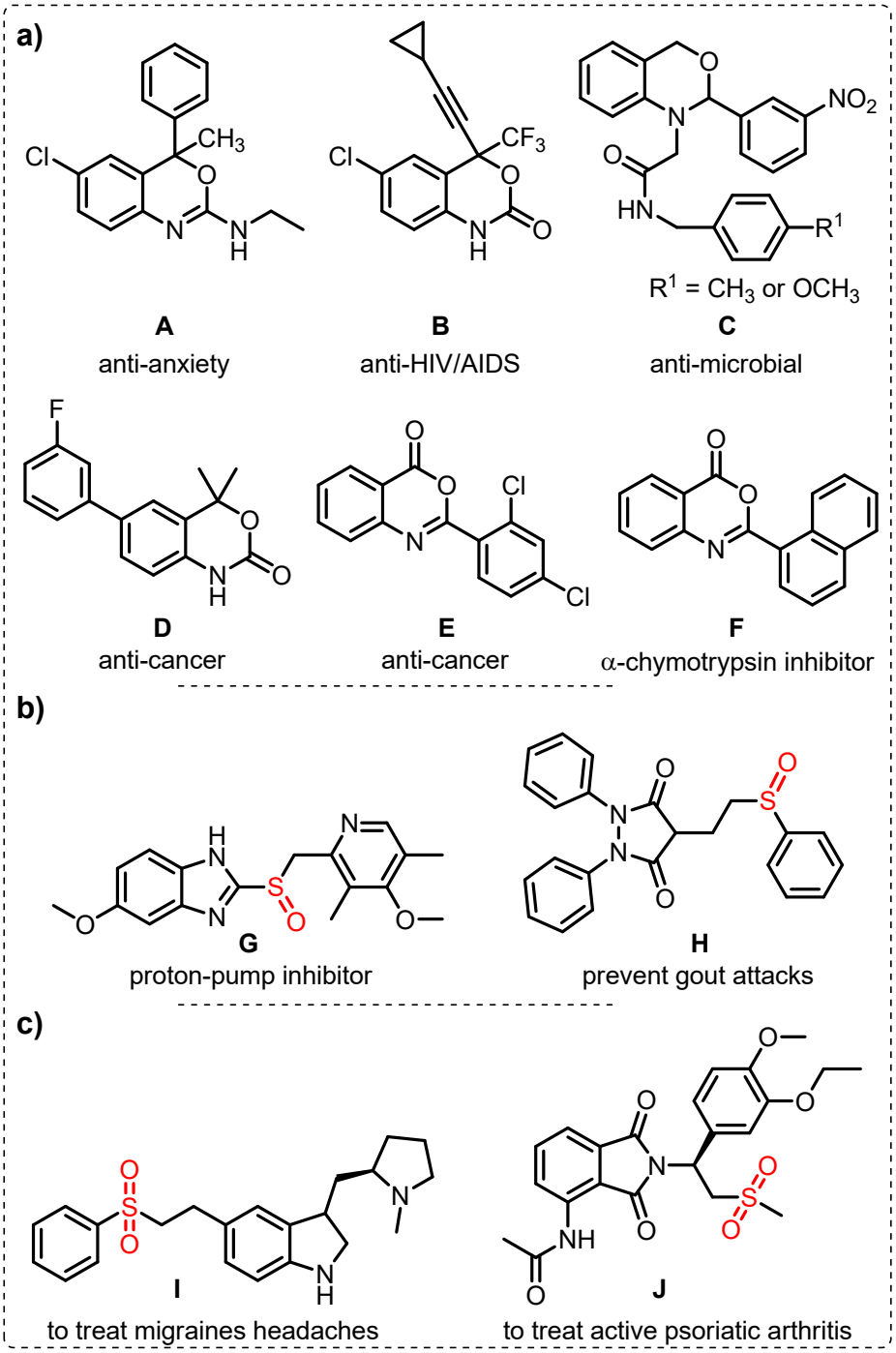
1. General Information

Unless otherwise stated, all reagents and precursors including thiols were purchased from commercial sources with the best quality and they were used without further purification. All of the reactions were carried out under aerobic conditions or O_2 atmosphere unless otherwise noted. All solvents were distilled prior to use and stored over 3 Å/4 Å molecular sieves. The progress of the optimization reactions were monitored by gas chromatography. The progress of the substrate scope was monitored by analytical thin layer chromatography and visualization was accomplished by irradiation with short wave UV light at 254 nm and by staining in phosphomolybdic acid. NMR spectra of all compounds were recorded on Bruker Avance 300 MHz (300.13 MHz Proton – Bruker BioSpin GmbH) spectrometer in deuterated solvents. Chemical shifts are expressed as δ-value in parts per million (ppm) and were calibrated using the residual protonated solvent as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet and so on. The coupling constants, J, are reported in hertz (Hz). High resolution mass spectroscopic (HRMS) data of new products were collected on Agilent Technologies Accurate-Mass Q-TOF LC/MS using ESI. Photochemical reactions were performed with 400 nm (OSRAM Oslon SSL 80 royal-blue LEDs (λ = 400 nm (± 5 nm), 3.0 V, 741 mW).

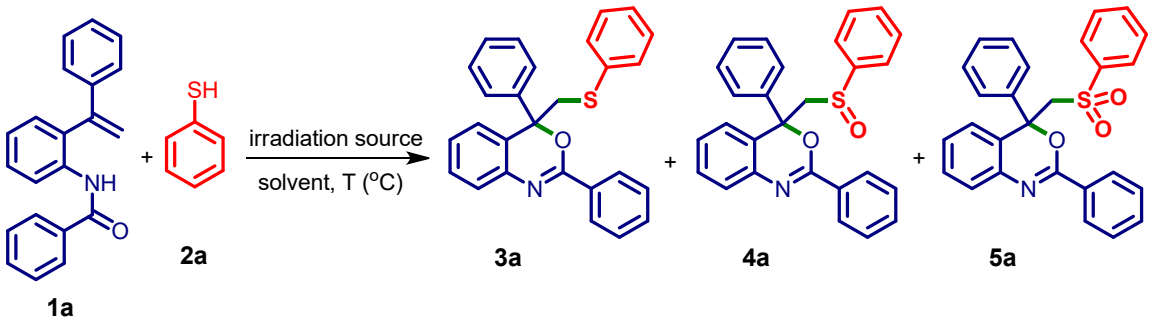
Procedure for the distillation of acetonitrile

Acetonitrile (CH_3CN) with grade: extrapure was purchased from "s d fine-CHEM Limited, Mumbai, India" and was purified by following the procedure described in a book, i.e., *B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, in Vogel's Textbook of Practical Organic Chemistry, Pearson Education, 5th edn, 1989, ch. 4, 395-409 (ISBN: 978-81-7758-957-3)*. About 1000 mL of acetonitrile solvent was added with 5.0 g of CaH_2, and the mixture was stirred for 6 h (until the hydrogen evolution stopped). Acetonitrile was then decanted from the CaH_2 and distilled at 90 °C in a nitrogen gas atmosphere. Around 90% of the solvent was collected and stored on activated 3Å molecular sieves. Unless otherwise stated, this distilled acetonitrile has been used as a solvent to carry out all studies described herein.



Scheme S1. Structure of few selected examples of pharmaceutically active compounds and drugs based on (a) benzoxazine skeleton, (b) sulfoxide (or sulfinyl) substituent, and (c) sulfone functionality.

Table S1. Selected results of screening the optimal conditions for the photocatalyst-free synthesis of thiolated benzoxazines (**3**), sulfoxinated benzoxazines (**4**), and sulfonated benzoxazines (**5**) from N-(2-vinylphenyl)amides (**1**), and thiols (**2**) under light[a]



1a **2a** **3a** **4a** **5a**

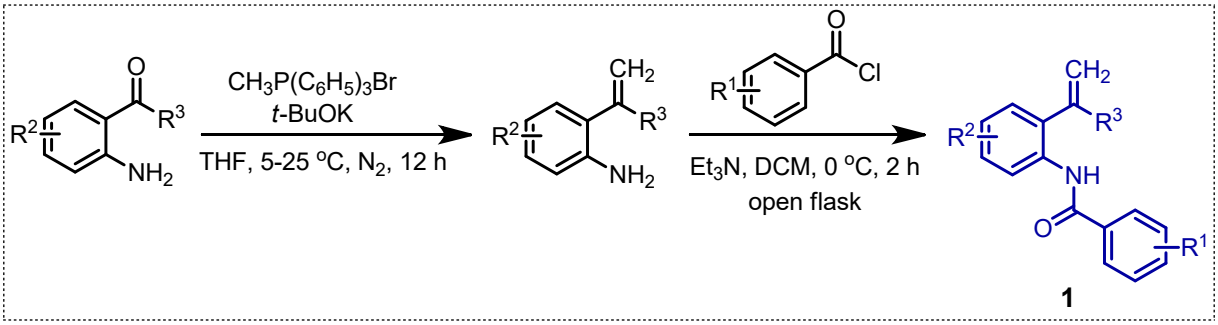
Entry	Irradiation source (λ, nm)	Reaction atm.	Solvent [b] (vol. mL)	Temp. (°C)	Time (h)	Yield (%)[c,d]		
						3a	**4a**	**5a**
1	blue LED (450-455)	open to air	CH_3CN (2)	25	14	66	ND	ND
2	white LED (420-700)	open to air	CH_3CN (2)	25	14	33	ND	ND
3	green LED (520-530)	open to air	CH_3CN (2)	25	14	17	ND	ND
4	**blue LED (400-405)**	**open to air**	**CH_3CN (2)**	**25**	**6**	**93**	**ND**	**ND**
5[e,f]	dark	open to air	CH_3CN (2)	25	6	NR	NR	NR
6	blue LED (400-405)	open to air	CH_3CN (2)	25	4	72	ND	ND
7	blue LED (400-405)	open to air	CH_3CN (2)	25	8	92	ND	ND
8	blue LED (400-405)	open to air	CH_3CN (2)	25	16	88	2	ND
9	blue LED (400-405)	open to air	CH_3CN (2)	25	24	82	4	2
10	blue LED (400-405)	open to air	CH_3CN (2)	25	30	82	5	3
11	blue LED (400-405)	open to air	DCM (2)	25	24	36	ND	ND
12	blue LED (400-405)	open to air	ethanol (2)	25	24	ND	ND	ND
13	blue LED (400-405)	open to air	DMF (1)	25	24	44	27	ND

14	blue LED (400-405)	open to air	THF (2)	25	24	12	ND	ND
15	blue LED (400-405)	open to air	H_2O (2)	25	24	9	5	ND
16	blue LED (400-405)	open to air	CH_3CN-H_2O (9:1)	25	24	33	55	ND
17	blue LED (400-405)	open to air	CH_3CN-H_2O (8:2)	25	24	9	82	ND
18	**blue LED (400-405)**	**open to air**	**CH_3CN-H_2O (8:2)**	**25**	**18**	**7**	**81**	**ND**
19	blue LED (400-405)	open to air	CH_3CN-H_2O (6:4)	25	18	5	35	ND
20	blue LED (400-405)	open to air	DMF-H_2O (8:2)	25	18	12	50	ND
21	blue LED (400-405)	O_2-balloon	CH_3CN (2)	25	27	43	6	38
22	blue LED (400-405)	O_2-balloon	CH_3CN (2)	25	36	45	5	40
23	blue LED (400-405)	O_2-balloon	CH_3CN (2)	30	27	28	7	51
24	blue LED (400-405)	O_2-balloon	CH_3CN (2)	35	27	13	3	68
25	**blue LED (400-405)**	**O_2-balloon**	**CH_3CN (2)**	**40**	**27**	**4**	**ND**	**84**
26	blue LED (400-405)	O_2-balloon	CH_3CN (2)	50	27	6	ND	83
27	blue LED (400-405)	O_2-balloon	CH_3CN (2)	40	36	3	ND	85
28	blue LED (400-405)	O_2-balloon	CH_3CN-H_2O (8:2)	40	27	19	33	29

[a] Unless stated otherwise, all reactions were performed in a vial equipped with N-(2-(1-phenylvinyl)phenyl)benzamide (**1a**, 150 mg, 0.5 mmol, 1.0 equiv.) and benzenethiol (**2a**, 61 mg, 0.55 mmol, 1.1 equiv.) in a solvent under irradiation using 5W blue LED (λ = 400-405 nm, luminous flux: 741 mW) as irradiation source, and open to air/O_2–balloon atmosphere with constant stirring. [b] Solvents were distilled before use. [c] Isolated yield. [d] The unreacted **1a** was collected from an entry where there was no reaction or no quantitative conversion. [e] Diphenyl disulphide (14%) was detected. [f] Diphenyl disulphide (51%) was detected after 36 h under dark. ND; not detected. NR; no reaction.

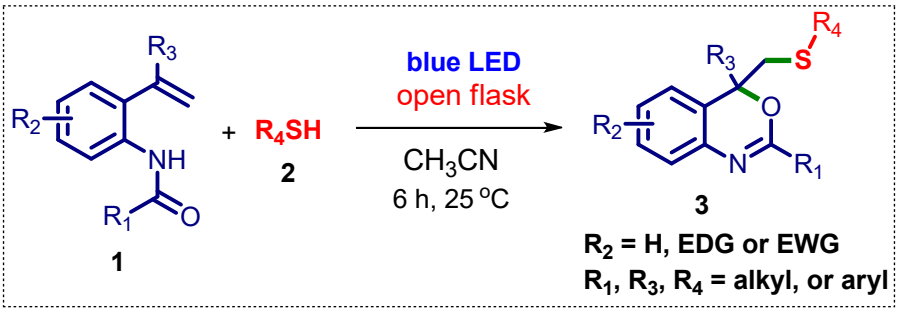
2. Experimental Section

2.1 General procedure for the preparation of precursor 1



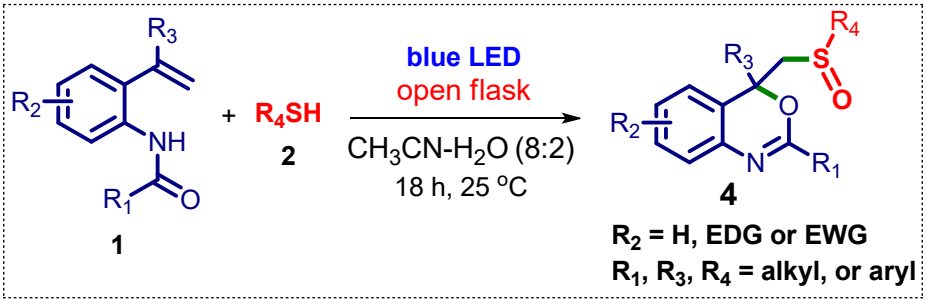
All precursors (**1**) were synthesized by following a literature known procedure.[1] An oven-dried round-bottom flask equipped with a magnetic stir bar, methyltriphenylphosphonium bromide (1.5 equiv.) and dry THF under N_2 gas atmosphere was added potassium *tert*-butoxide (1.5 equiv.) at 0 °C. Resultant mixture was stirred and allowed to warm to room temperature over the period of 30 minutes. Afterwards, 2-aminoalkylarylketone (1.0 equiv.) was added and then the reaction mixture was stirred further for 12 h at room temperature. Subsequently, the reaction mixture was quenched with cold water, extracted with ethyl acetate (three times), the organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Resultant waxy material was passed through a chromatography column with silica gel using CH_2Cl_2 and concentrated. The yellow materials obtained was dissolved in minimum quantity of CH_2Cl_2 and then added Et_3N (1.5 equiv.) followed by benzoylchloride (1.2 equiv.) at 0 °C. After 2 h of stirring, reaction mixture was purified via column chromatography to afford compound **1**.

2.2 General procedure for the synthesis of thiolated benzoxazines (3)



An oven-dried glass vial equipped with a magnetic stir bar was added N-(2-vinylphenyl)amide (**1**, 1.0 mmol, 1.0 equiv.), thiol (**2**, 1.1 mmol, 1.1 equiv.), and CH_3CN (5.0 mL). Resultant mixture was stirred few minutes to dissolve well and then with constant stirring irradiated through the plane bottom side of the vial using a blue LED (5W, λ = 400-405 nm, luminous flux: 741 mW) at a distance of 2 cm under open to air atmosphere for 6 h. Subsequently, the organic matter (product) was completely precipitated by adding cold aqueous brine (1-2 mL) solution. Filtration was used to isolate the precipitates, which were then washed with excess of water to remove any residual quantity of solvent and other inorganic impurity. The ultimate purification was accomplished either by recrystallization using aqueous ethanol solution or column chromatography on silica gel using 5-15% ethyl acetate in hexane to provide the desired product **3**.

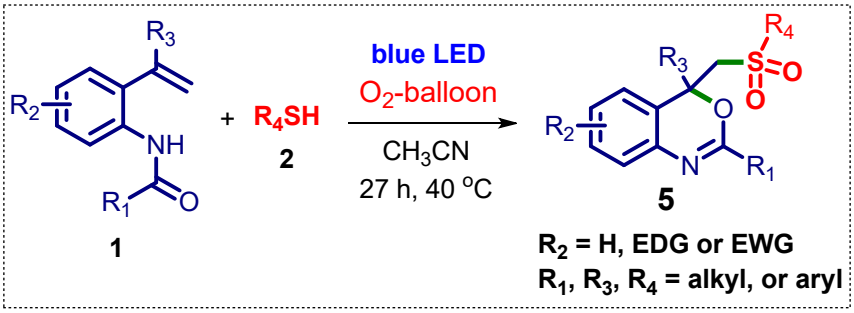
2.3 General procedure for the synthesis of sulfoxinated benzoxazines (4)



An oven-dried glass vial equipped with a magnetic stir bar was added N-(2-vinylphenyl)amide (**1**, 1.0 mmol, 1.0 equiv.), thiol (**2**, 1.1 mmol, 1.1 equiv.), and CH_3CN-H_2O (8:2, v/v, 5.0 mL). Resultant mixture was stirred few minutes to dissolve well and then with constant stirring irradiated through the plane bottom side of the vial using a blue LED (5W, λ = 400-405 nm, luminous flux: 741 mW) at a distance of 2 cm under open to air atmosphere for 18 h.

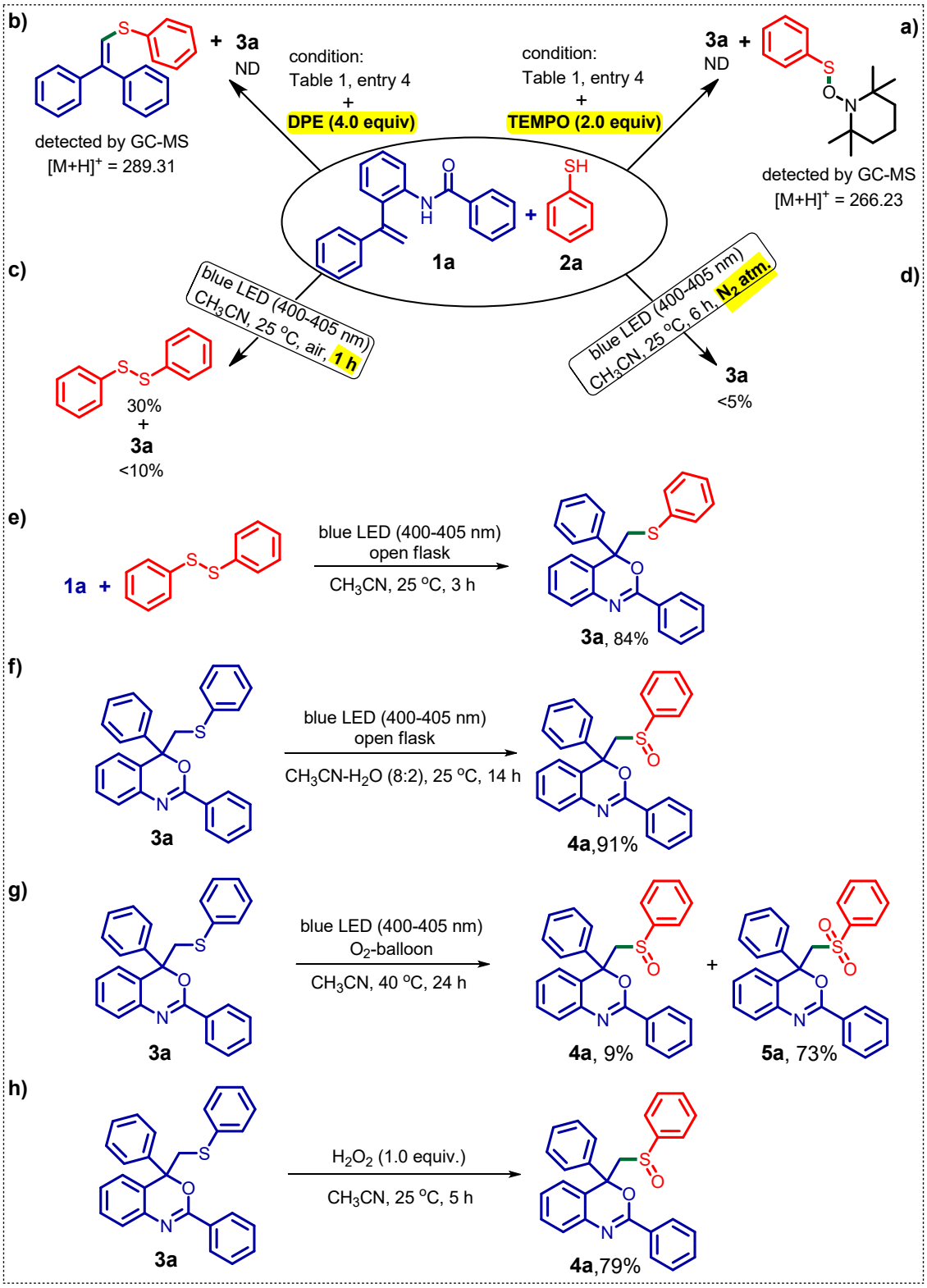
Subsequently, the reaction mixture was diluted with 3 mL of water, transferred into a separating funnel, and then the organic matter (product) was extracted using ethyl acetate (15 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Resultant residue was purified by column chromatography on silica gel using 10-20% ethyl acetate in hexane to provide the desired product **4**.

2.4 General procedure for the synthesis of sulfonated benzoxazines (5)



An oven-dried glass vial equipped with a magnetic stir bar was added N-(2-vinylphenyl)amide (**1**, 1.0 mmol, 1.0 equiv.), thiol (**2**, 1.1 mmol, 1.1 equiv.), and CH_3CN (5.0 mL). Resultant mixture was stirred few minutes to dissolve well and then with constant stirring irradiated through the plane bottom side of the vial using a blue LED (5W, λ = 400-405 nm, luminous flux: 741 mW) at a distance of 2 cm under O_2-balloon atmosphere at 40 °C for 27 h. Subsequently, the reaction mixture was diluted with 5 mL of water, transferred into a separating funnel, and then the organic matter (product) was extracted using ethyl acetate (15 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Resultant residue was purified by column chromatography on silica gel using 10-20% ethyl acetate in hexane to provide the desired product **5**.

2.5 Procedure for control experiments



Scheme S2. Control experiments for mechanistic studies

To investigate the possible reaction mechanism, a series of control experiments were carried out. *Reaction in presence of TEMPO*: A radical scavenger such as 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 2.0 equiv.) was added to the general procedure described in section 2.2. After 6 h, the crude reaction mixture was diluted with ethyl acetate, dried using anhydrous Na_2SO_4, filtered and analyzed by GCMS. GCMS analysis revealed that the formation of 2,2,6,6-tetramethyl-1-((phenylthio)oxy)piperidine (m/z = 265, Figure S1) and no **3a** was detected.

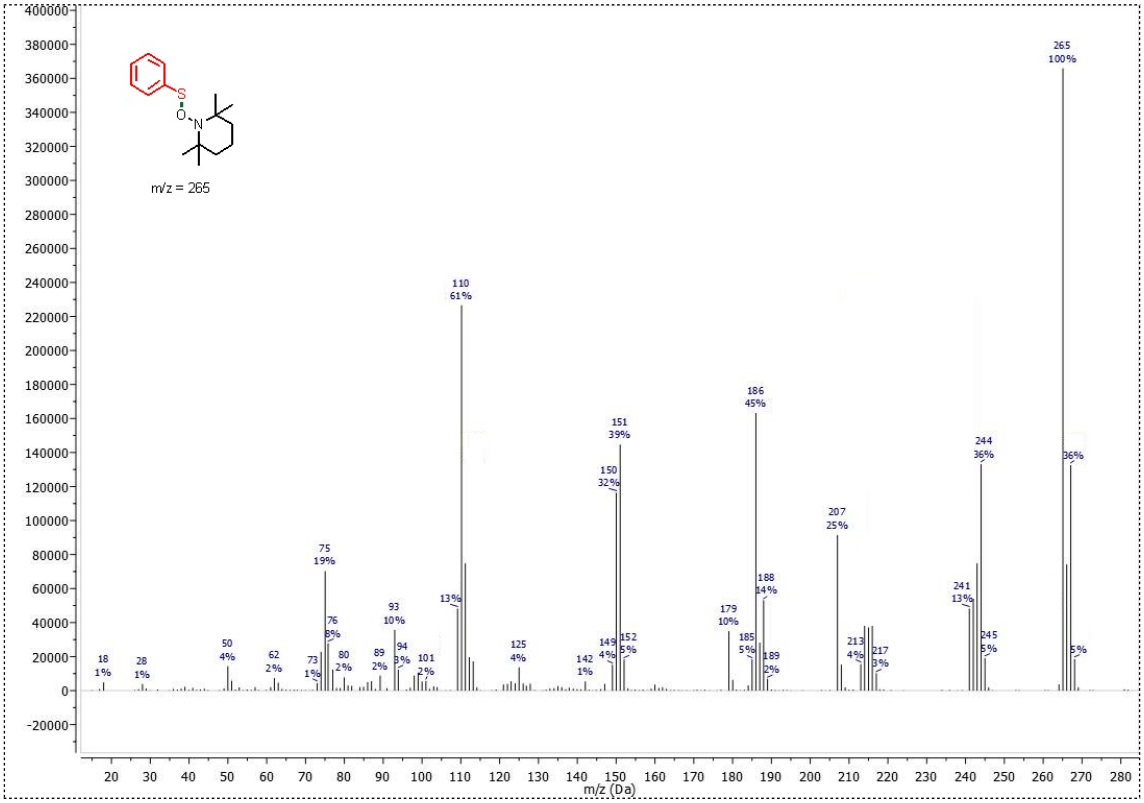


Figure S1. The GC-MS profile of TEMPO-SC_6H_5 (m/z = 265) adduct detected in the TEMPO radical trap experiment.

Reaction in presence of DPE: A radical scavenger such as 1,1-diphenylethene (**DPE**, 4.0 equiv.) was added to the general procedure described in section 2.2. After 6 h, the crude reaction mixture was diluted with ethyl acetate, dried using anhydrous Na_2SO_4, filtered and analyzed by GCMS. GCMS analysis revealed that the formation of (2,2-diphenylvinyl)(phenyl)sulfane (m/z = 288, Figure S2) and no **3a** was detected.

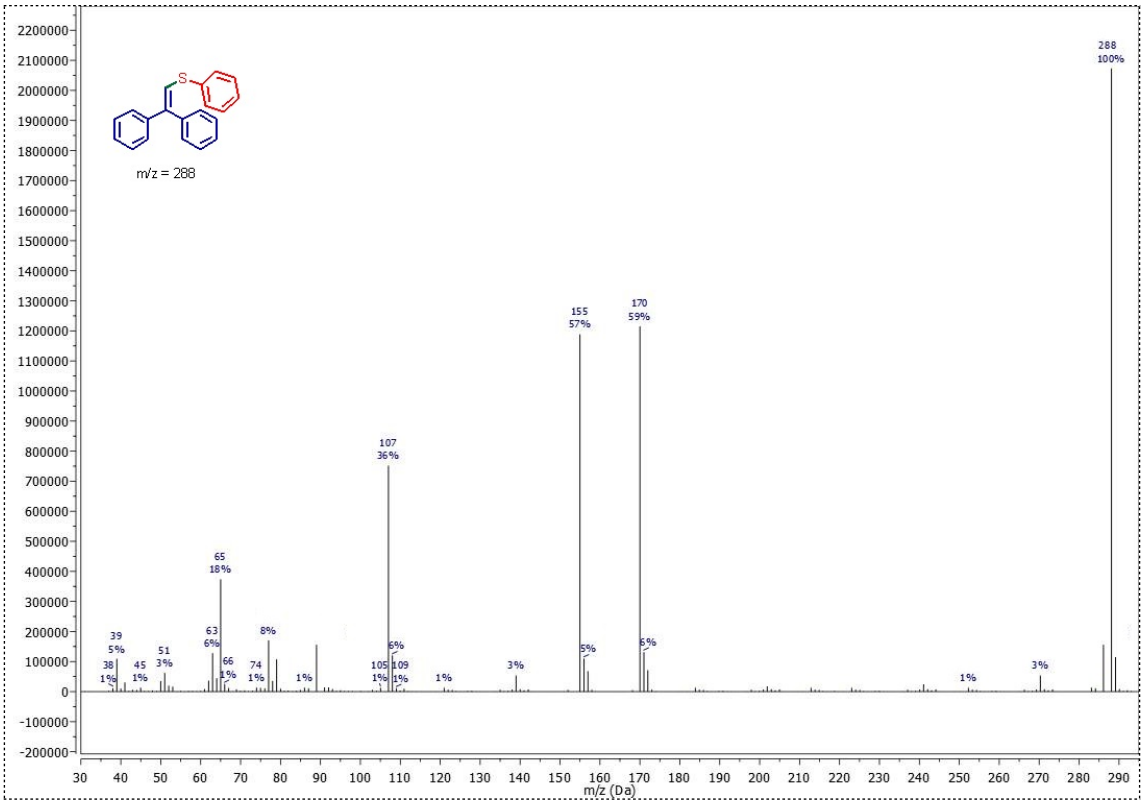


Figure S2. The GC-MS profile of DPE-SC_6H_5 (m/z = 288) adduct detected in the DPE radical trap experiment.

Reaction stopped in short duration: The general procedure described in section 2.2 was carried out for 1.0 h instead of 6.0 h. Afterwards, the crude reaction mixture was diluted with ethyl acetate, dried using anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography. Afforded **3a** in 9% yield and diphenyl disulphide in 30% yield (Figure S3). Diphenyl disulphide: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.296 (d, J = 7.7 Hz, 4H), 7.06-6.91 (m, 6H).[2] ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 129.1, 127.6, 127.1.[2]

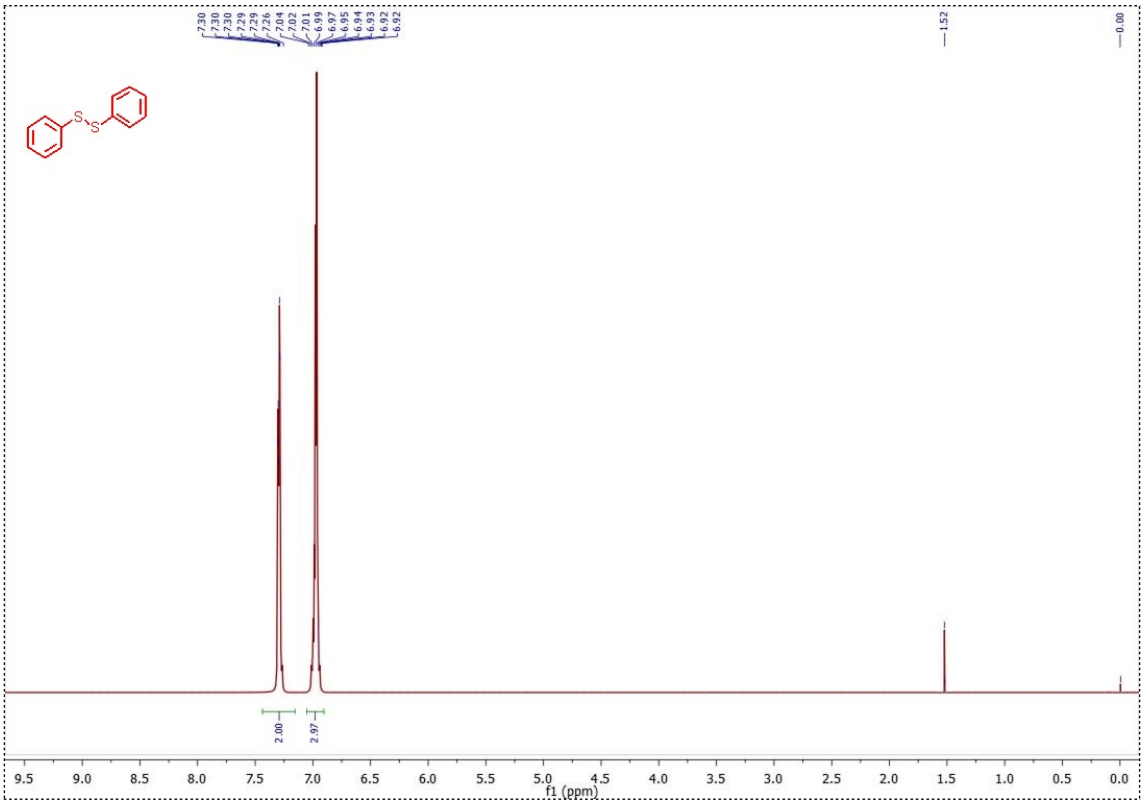


Figure S3. ^{1}H NMR spectra of diphenyl disulphide in $CDCl_3$.

Reaction under N_2 atmosphere: The general procedure described in section 2.2 was carried out under N_2 gas atmosphere instead of open air atmosphere. After 6 h, the crude reaction mixture was diluted with ethyl acetate, dried using anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography. Afforded **3a** in very poor yield and the maximum quantity of starting materials were isolated.

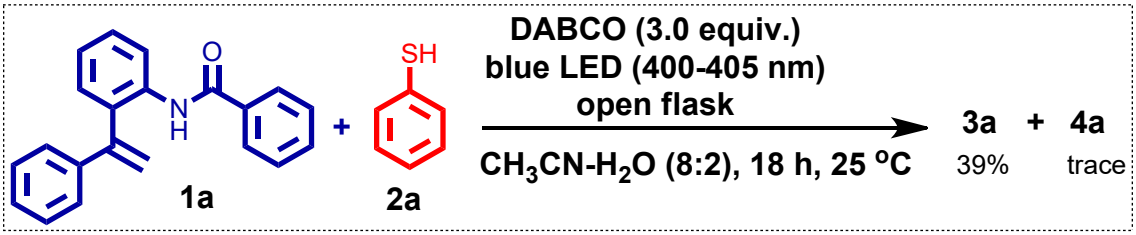
Reaction using diphenyl disulphide: The general procedure described in section 2.2 was carried out using diphenyl disulphide (0.5 mmol) as source of thiyl radicals instead of thiophenol. After 3h, the crude reaction mixture was diluted with ethyl acetate, dried using anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography. Afforded **3a** in 84% yield.

*2,4-Diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (**3a**) as a starting precursor*: An oven-dried glass vial equipped with a magnetic stir bar was added 2,4-diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (**3a**, 0.5 mmol.), and CH_3CN-H_2O (8:2, v/v, 3.0 mL). Resultant mixture was stirred few minutes to dissolve well and then with constant stirring

irradiated through the plane bottom side of the vial using a blue LED (5W, λ = 400-405 nm, luminous flux: 741 mW) at a distance of 2 cm under open to air atmosphere for 14 h. Subsequently, the reaction mixture was diluted with 2 mL of water, transferred into a separating funnel, and then the organic matter (product) was extracted using ethyl acetate (10 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Resultant residue was purified by column chromatography on silica gel using 10-20% ethyl acetate in hexane to provide **4a** in 91% yield.

Reaction in presence of H_2O_2: An oven-dried glass vial equipped with a magnetic stir bar was added 2,4-diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (**3a**, 0.5 mmol.), hydrogen peroxide (H_2O_2, 0.5 mmol) and CH_3CN (3.0 mL). Resultant mixture was stirred at 25 °C for 5 h under open air atmosphere. Afterwards, the reaction mixture was diluted with 2 mL of water, transferred into a separating funnel, and then the organic matter (product) was extracted using ethyl acetate (10 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Resultant residue was purified by column chromatography on silica gel using 10-20% ethyl acetate in hexane to provide **4a** in 79% yield.

Reaction in presence of singlet-oxygen ($^1O_2$) quencher DABCO



A singlet-oxygen ($^1O_2$) quencher such as 1,4-diazabicyclo[2.2.2]octane (DABCO, 3 equiv.) was added to the general procedure described in section 2.3. After 18 h, the crude reaction mixture was diluted with ethyl acetate, dried using anhydrous Na2SO4, filtered, concentrated and purified by column chromatography. Subsequently, **3a** was obtained in 39% yield and **4a** in negligible yield. This result indicates that the singlet-oxygen is involved in the product formation.

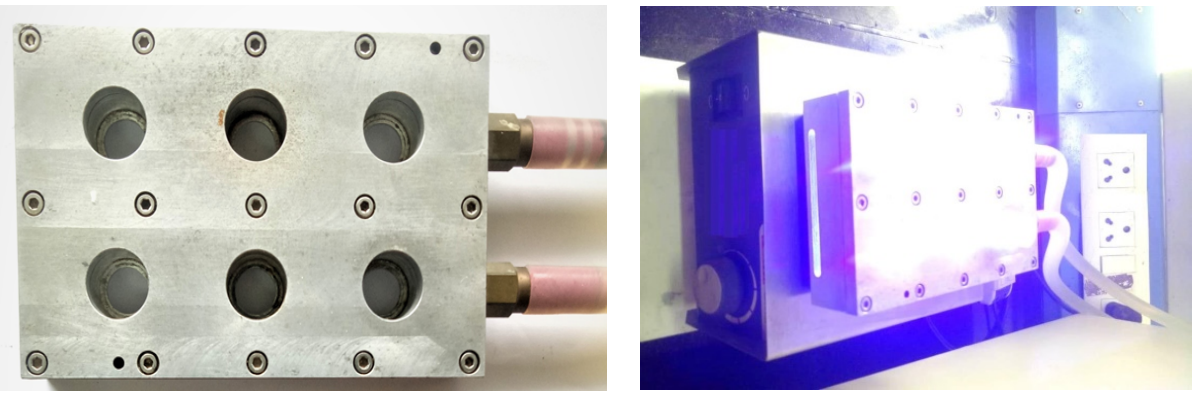
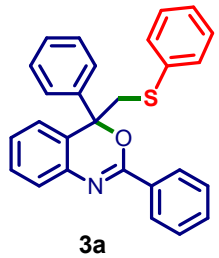


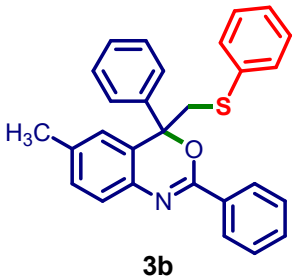
Figure S4. Photochemical reaction set-up. The photographs of parts of a custom made photochemical reactor setup used to perform reactions described in this work. holding *cum* water-cooling unit (left) and a complete reaction setup under running conditions with turn-on LEDs with water inlet/outlet (right).

Experimental characterization data



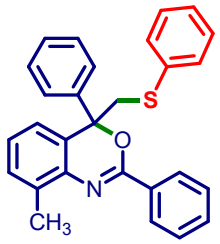
3a

2,4-Diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3a): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Pale yellow solid (379 mg, 93% yield). R_f = 0.16 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15-8.09 (m, 2H), 7.48-7.35 (m, 7H), 7.31-7.24 (m, 5H), 7.20-7.08 (m, 5H), 3.97 (d, J = 13.8 Hz, 1H), 3.90 (d, J = 13.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 141.8, 139.4, 136.7, 132.2, 131.3, 130.3, 129.2, 128.8, 128.3, 128.2, 128.1, 128.0, 126.8, 126.4, 126.3, 126.1, 125.4, 124.8, 83.6, 45.2. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{27}H_{22}NOS$ 408.1422, found 408.1438. Spectra data are consistent with those reported in the literature.[3]



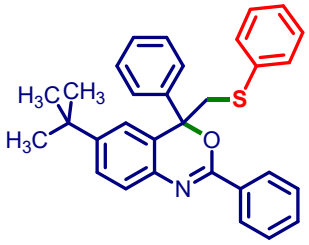
3b

6-Methyl-2,4-diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3b): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Pale yellow solid (384 mg, 91% yield). R_f = 0.15 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16-8.05 (m, 2H), 7.47-7.35 (m, 5H), 7.32-7.20 (m, 6H), 7.18-7.06 (m, 4H), 6.88 (d, J = 1.8 Hz, 1H), 3.94 (d, J = 13.8 Hz, 1H), 3.89 (d, J = 13.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 142.0, 137.2, 136.8, 136.2, 132.3, 131.2, 130.3, 129.8, 128.8, 128.3, 128.2, 128.1, 127.9, 126.6, 126.3, 126.2, 126.1, 125.3, 83.7, 45.2, 21.3. Spectra data are consistent with those reported in the literature.[3]



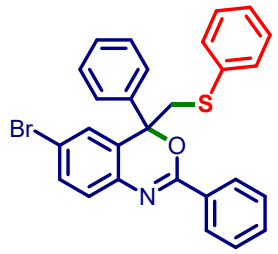
3c

8-Methyl-2,4-diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3c): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Pale yellow solid (291 mg, 69% yield). R_f = 0.15 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (dd, J = 8.0, 1.4 Hz, 2H), 7.49-7.38 (m, 5H), 7.33-7.21 (m, 6H), 7.18 (t, J = 7.6 Hz, 2H), 7.15-7.09 (m, 2H), 7.02 (d, J = 7.6 Hz, 1H), 3.96 (d, J = 13.8 Hz, 1H), 3.88 (d, J = 13.8 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 142.0, 137.6, 136.9, 134.1, 132.5, 131.2, 130.6, 130.2, 128.7, 128.3, 128.2, 128.0, 126.8, 126.3, 126.2, 125.7, 122.3, 83.4, 45.1, 17.2. Spectra data are consistent with those reported in the literature.[3]



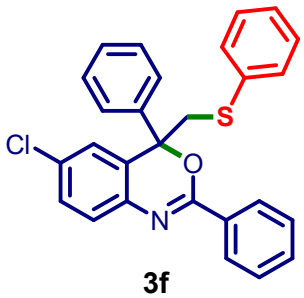
3d

6-(*tert*-Butyl)-2,4-diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3d): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Pale yellow solid (375 mg, 81% yield). R_f = 0.14 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 6.6 Hz, 2H), 7.44-7.36 (m, 6H), 7.33-7.24 (m, 6H), 7.20-7.12 (m, 3H), 7.11-7.06 (m, 1H), 3.98 (d, J = 12.0 Hz, 1H), 3.92 (d, J = 12.0 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 149.5, 142.1, 137.0, 136.9, 132.4, 131.2, 130.3, 128.8, 128.3, 128.2, 128.1, 127.8, 126.3, 126.2, 126.1, 126.0, 125.0, 121.6, 83.8, 45.3, 34.7, 31.3. Spectra data are consistent with those reported in the literature.[3]



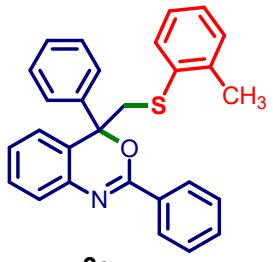
3e

6-Bromo-2,4-diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3e): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow solid (432 mg, 89% yield). R_f = 0.15 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 7.48-7.45 (m, 2H), 7.43-7.31 (m, 9H), 7.28 (d, J = 7.2 Hz, 1H), 7.23-7.14 (m, 4H), 3.89 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 141.2, 138.6, 136.1, 132.4, 131.8, 131.6, 130.7, 128.9, 128.7, 128.5, 128.3, 128.1, 127.9, 127.8, 127.2, 126.7, 126.0, 119.3, 83.4, 45.2. Spectra data are consistent with those reported in the literature.[3]



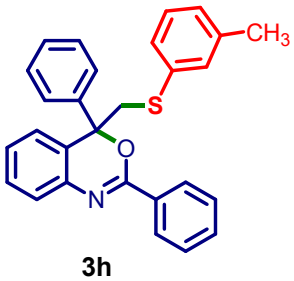
3f

6-Chloro-2,4-diphenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3f): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Pale yellow solid (406 mg, 92% yield). R_f = 0.15 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14-8.06 (m, 2H), 7.50-7.35 (m, 5H), 7.32-7.26 (m, 7H), 7.21-7.09 (m, 3H), 7.06-7.04 (m, 1H), 3.89 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 141.3, 138.2, 136.1, 131.8, 131.6, 131.4, 130.5, 129.3, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 126.8, 126.6, 126.1, 125.0, 83.5, 45.2. Spectra data are consistent with those reported in the literature.[3]



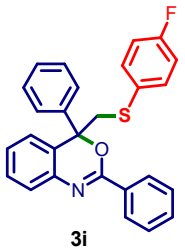
3g

2,4-Diphenyl-4-((*o*-tolylthio)methyl)-4H-benzo[d][1,3]oxazine (3g): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow solid (312 mg, 74% yield). R_f = 0.14 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.42-7.35 (m, 6H), 7.31-7.19 (m, 5H), 7.13 (d, J = 7.6 Hz, 1H), 7.07-7.02 (m, 3H), 3.91 (d, J = 13.4 Hz, 1H), 3.85 (d, J = 13.4 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 141.8, 139.5, 138.8, 135.9, 132.2, 131.4, 130.4, 130.1, 129.2, 128.3 128.2, 128.1, 128.0, 126.9, 126.5, 126.4, 126.3, 126.1, 125.5, 124.8, 83.7, 44.7, 20.6. Spectra data are consistent with those reported in the literature.[3]



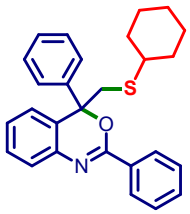
3h

2,4-Diphenyl-4-((*m*-tolylthio)methyl)-4H-benzo[d][1,3]oxazine (3h): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow solid (379 mg, 90% yield). R_f = 0.14 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.41-7.32 (m, 6H), 7.30-7.23 (m, 3H), 7.21-7.16 (m, 1H), 7.14-7.02 (m, 4H), 6.91 (d, J = 7.2 Hz, 1H), 3.94 (d, J = 13.8 Hz, 1H), 3.88 (d, J = 13.8 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 141.9, 139.6, 138.5, 136.3, 132.2, 131.3, 131.1, 129.3, 128.6, 128.3, 128.2, 128.1, 128.0, 127.4, 127.3, 126.8, 126.4, 126.1, 125.6, 124.8, 83.6, 45.2, 21.3. Spectra data are consistent with those reported in the literature.[3]



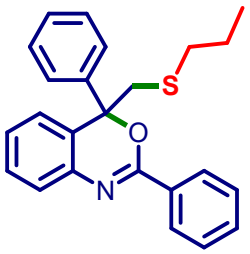
3i

4-(((4-Fluorophenyl)thio)methyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (3i): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow solid (353 mg, 83% yield). R_f = 0.16 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.43-7.34 (m, 6H), 7.31-7.23 (m, 5H), 7.21-7.16 (m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.82 (t, J = 8.4 Hz, 2H), 3.90 (d, J = 14.0 Hz, 1H), 3.85 (d, J = 14.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (d, J = 247.2 Hz), 156.0, 141.9, 139.5, 133.4 (d, J = 7.8 Hz), 132.1, 131.5 (d, J = 3.4 Hz), 131.5, 129.3, 128.4, 128.3, 128.2, 127.9, 126.8, 126.4, 126.0, 125.6, 124.8, 115.9 (d, J = 21.8 Hz), 83.7, 46.4. Spectra data are consistent with those reported in the literature.[3]



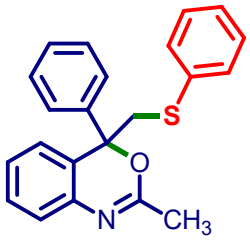
3j

4-((Cyclohexylthio)methyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (3j): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow wax (380 mg, 92% yield). R_f = 0.13 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, J = 7.4 Hz, 2H), 7.53-7.41 (m, 5H), 7.38-7.24 (m, 5H), 7.21 (t, J = 6.8 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 3.51 (s, 2H), 2.50 (t, J = 10.4 Hz, 1H), 1.93 (d, J = 12.2 Hz, 1H), 1.84 (d, J = 12.2 Hz, 1H), 1.65 (t, J = 12.2 Hz, 2H), 1.56-1.46 (m, 1H), 1.32-1.09 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 142.2, 139.4, 132.5, 131.5, 129.1, 128.3, 128.1, 128.0, 127.5, 126.3, 125.3, 125.0, 83.8, 45.1, 39.8, 33.6, 33.5, 26.0, 25.9, 25.6. Spectra data are consistent with those reported in the literature.[3]



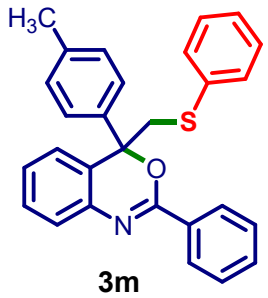
3k

2,4-Diphenyl-4-((propylthio)methyl)-4H-benzo[d][1,3]oxazine (3k): Synthesized according to the general procedure described in section 2.2. The gummy mass obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow wax (325 mg, 87% yield). R_f = 0.21 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, J = 7.2 Hz, 2H), 7.57-7.41 (m, 5H), 7.37 (d, J = 3.8 Hz, 2H), 7.33-7.21 (m, 4H), 7.12 (d, J = 7.4 Hz, 1H), 3.57-3.41 (m, 2H), 2.53-2.35 (m, 2H), 1.62-1.44 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 142.1, 139.5, 132.4, 131.6, 129.2, 128.3, 128.2, 128.1, 128.0, 127.4, 126.3, 126.2, 125.5, 124.9, 84.2, 42.3, 36.2, 22.9, 13.4. Spectra data are consistent with those reported in the literature.[3]



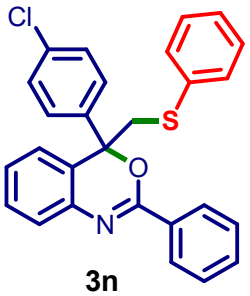
3l

2-Methyl-4-phenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3l): Synthesized according to the general procedure described in section 2.2. The gummy mass obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow wax (321 mg, 93% yield). R_f = 0.18 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.27 (m, 8H), 7.24 (t, J = 7.0 Hz, 2H), 7.19-7.12 (m, 3H), 7.02 (d, J = 7.6 Hz, 1H), 3.82 (bs, 2H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 142.4, 138.8, 136.7, 130.2, 129.3, 128.8, 128.4, 128.3, 126.4, 126.2, 126.0, 125.9, 125.0, 124.6, 83.2, 45.1, 21.4. Spectra data are consistent with those reported in the literature.[3]



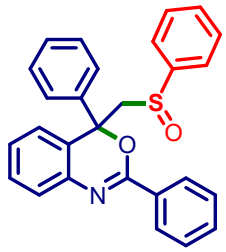
3m

2-Phenyl-4-((phenylthio)methyl)-4-(*p*-tolyl)-4H-benzo[d][1,3]oxazine (3m): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Pale yellow solid (341 mg, 81% yield). R_f = 0.14 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 2H), 7.46-7.42 (m, 1H), 7.40-7.33 (m, 4H), 7.30-7.25 (m, 4H), 7.21-7.06 (m, 7H), 3.92 (d, J = 4.2 Hz, 1H), 3.90 (d, J = 4.2 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 139.4, 139.0, 138.1, 136.8, 132.2, 131.3, 130.2, 129.2, 129.0, 128.8, 128.1, 128.0, 127.2, 126.3, 126.2, 126.0, 125.4, 124.8, 83.6, 45.0, 21.1. Spectra data are consistent with those reported in the literature.[3]



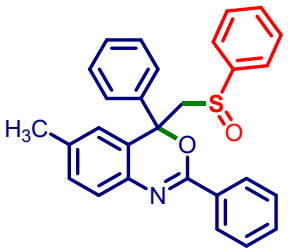
3n

4-(*p*-Chlorophenyl)-2-phenyl-4-((phenylthio)methyl)-4H-benzo[d][1,3]oxazine (3n): Synthesized according to the general procedure described in section 2.2. The precipitate obtained was purified by silica-gel column filtration using 5-10% ethyl acetate in hexane. Yellow solid (393 mg, 89% yield). R_f = 0.14 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 7.6 Hz, 2H), 7.50-7.46 (m, 1H), 7.44-7.37 (m, 4H), 7.34-7.25 (m, 7H), 7.18 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.2 Hz, 2H), 3.95 (d, J = 13.8 Hz, 1H), 3.87 (d, J = 13.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0, 140.3, 139.3, 136.3, 134.3, 132.0, 131.5, 130.4, 129.5, 128.9, 128.5, 128.3, 128.0, 127.7, 126.6, 126.55, 126.54, 125.6, 124.6, 83.1, 45.0. Spectra data are consistent with those reported in the literature.[3]



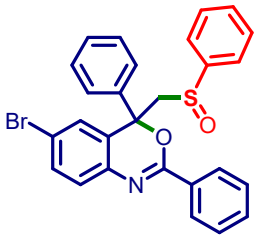
4a

2,4-Diphenyl-4-((phenylsulfinyl)methyl)-4H-benzo[d][1,3]oxazine (4a): Synthesized according to the general procedure described in section 2.3. The precipitate obtained was purified by silica-gel column chromatography using 10-20% ethyl acetate in hexane. Yellow solid (343 mg, 81% yield). R_f = 0.19 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.33-7.27 (m, 4H), 7.23-7.17 (m, 5H), 7.15-7.09 (m, 5H), 4.14 (d, J = 14.2 Hz, 1H), 4.08 (d, J = 14.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 141.3, 140.4, 138.2, 132.7, 131.2, 131.0, 129.3, 129.0, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 126.2, 126.1, 125.1, 124.0, 81.8, 63.4. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{27}H_{22}NO_2S$ 424.1293, found 424.1302.



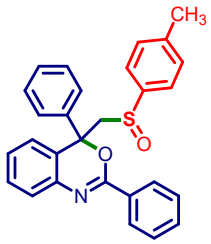
4b

6-Methyl-2,4-diphenyl-4-((phenylsulfinyl)methyl)-4H-benzo[d][1,3]oxazine (4b): Synthesized according to the general procedure described in section 2.3. The precipitate obtained was purified by silica-gel column chromatography using 10-20% ethyl acetate in hexane. Yellow solid (346 mg, 79% yield). R_f = 0.18 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19-8.09 (m, 2H), 7.49-7.37 (m, 5H), 7.33-7.22 (m, 5H), 7.21-7.08 (m, 5H), 6.92-6.89 (m, 1H), 4.12 (d, J = 14.0 Hz, 1H), 4.06 (d, J = 14.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 141.8, 137.6, 137.0, 136.2, 132.4, 131.2, 130.5, 129.9, 129.0, 128.3, 128.2, 128.1, 127.9, 126.9, 126.4, 126.3, 126.1, 125.6, 81.9, 63.3, 21.5. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{28}H_{24}NO_2S$ 438.1528, found 438.1503.



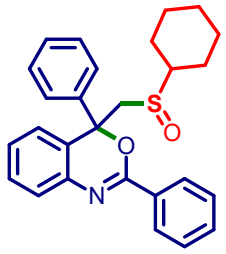
4c

6-Bromo-2,4-diphenyl-4-((phenylsulfinyl)methyl)-4H-benzo[d][1,3]oxazine (4c): Synthesized according to the general procedure described in section 2.3. The precipitate obtained was purified by silica-gel column chromatography using 10-20% ethyl acetate in hexane. Yellow solid (361 mg, 72% yield). R_f = 0.19 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12-8.09 (m, 2H), 7.49-7.47 (m, 2H), 7.44-7.34 (m, 8H), 7.29-7.27 (m, 2H), 7.22 (dd, J = 7.8, 2.4 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 4.06 (d, J = 12.8 Hz, 1H), 4.00 (d, J = 12.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 141.2, 138.6, 136.3, 132.5, 131.8, 131.4, 130.9, 129.0, 128.9, 128.8, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 127.3, 125.9, 119.3, 81.7, 63.5. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{27}H_{21}BrNO_2S$ 502.0476, found 502.0487.



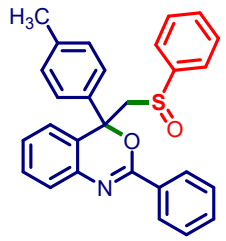
4e

2,4-Diphenyl-4-((*p*-tolylsulfinyl)methyl)-4H-benzo[d][1,3]oxazine (4e): Synthesized according to the general procedure described in section 2.3. The precipitate obtained was purified by silica-gel column chromatography using 10-20% ethyl acetate in hexane. Yellow solid (350 mg, 80% yield). R_f = 0.18 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13-8.08 (m, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.39-7.31 (m, 5H), 7.31-7.24 (m, 3H), 7.23-7.15 (m, 3H), 7.13-7.10 (m, 1H), 7.01-6.95 (m, 2H), 4.13 (d, J = 14.0 Hz, 1H), 4.05 (d, J = 14.0 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 141.9, 139.8, 136.8, 133.0, 132.4, 131.5, 131.1, 129.5, 129.3, 128.4, 128.3, 128.1, 128.0, 126.9, 126.4, 126.1, 125.5, 124.9, 81.7, 63.5, 21.0. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{28}H_{24}NO_2S$ 438.1528, found 438.1537.



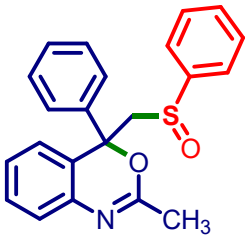
4f

4-((Cyclohexylsulfinyl)methyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (4f): Synthesized according to the general procedure described in section 2.3. The gummy mass obtained was purified by silica-gel column chromatography using 10-20% ethyl acetate in hexane. Yellow wax (348 mg, 81% yield). R_f = 0.17 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 7.2 Hz, 2H), 7.50-7.41 (m, 4H), 7.32-7.26 (m, 6H), 7.21 (t, J = 6.8 Hz, 2H), 4.02 (d, J = 13.6 Hz, 1H), 3.96 (d, J = 13.6 Hz, 1H), 2.54 (t, J = 9.8 Hz, 1H), 2.08-2.01 (m, 2H), 1.88-1.81 (m, 2H), 1.39-1.33 (m, 2H), 1.25-1.11 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 141.9, 139.5, 132.4, 131.5, 129.2, 128.4, 128.1, 128.0, 127.7, 126.3, 125.5, 125.2, 80.1, 61.2, 49.8, 26.1, 25.5, 25.0, 24.9, 24.6. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{27}H_{28}NO_2S$ 430.1841, found 430.1853.



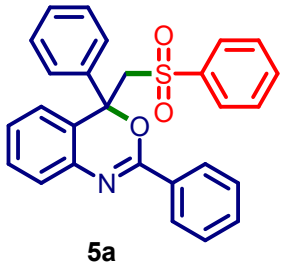
4h

2-Phenyl-4-((phenylsulfinyl)methyl)-4-(*p*-tolyl)-4H-benzo[d][1,3]oxazine (4h): Synthesized according to the general procedure described in section 2.3. The gummy mass obtained was purified by silica-gel column chromatography using 10-20% ethyl acetate in hexane. Yellow wax (337 mg, 77% yield). R_f = 0.18 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 6.8 Hz, 2H), 7.47-7.44 (m, 3H), 7.39-7.33 (m, 4H), 7.28-7.25 (m, 4H), 7.22-7.06 (m, 5H), 4.12 (d, J = 14.2 Hz, 1H), 4.07 (d, J = 14.2 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 140.2, 138.4, 138.2, 137.5, 132.7, 131.6, 130.7, 129.3, 129.1, 128.7, 128.2, 128.1, 127.4, 126.4, 126.1, 125.5, 124.4, 81.8, 63.4, 21.0. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{28}H_{24}NO_2S$ 438.1528, found 438.1529.



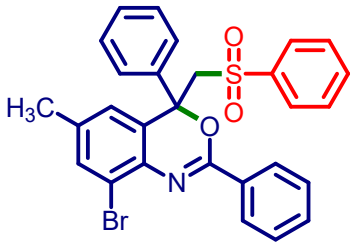
4i

2-Methyl-4-phenyl-4-((phenylsulfinyl)methyl)-4H-benzo[d][1,3]oxazine (4i): Synthesized according to the general procedure described in section 2.3. The gummy mass obtained was purified by silica-gel column chromatography using 10-20% ethyl acetate in hexane. Yellow wax (286 mg, 79% yield). R_f = 0.21 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 2H), 7.36-7.28 (m, 6H), 7.25-7.23 (m, 2H), 7.21-7.14 (m, 3H), 7.05-7.03 (m, 1H), 4.01 (d, J = 13.2 Hz, 1H), 3.96 (d, J = 13.2 Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 142.6, 138.9, 136.8, 130.4, 129.6, 128.9, 128.6, 128.4, 126.5, 126.2, 126.1, 125.9, 125.3, 124.7, 81.7, 63.4, 21.4. HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{22}H_{20}NO_2S$ 362.1215, found 362.1227.



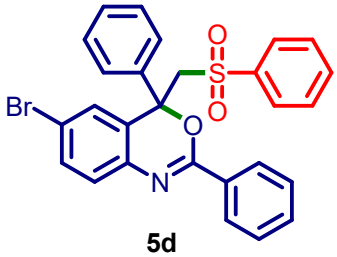
5a

2,4-Diphenyl-4-(phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5a): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Colorless solid (369 mg, 84% yield). R_f = 0.11 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.33-7.26 (m, 4H), 7.23-7.17 (m, 4H), 7.17-7.11 (m, 6H), 4.29 (d, J = 15.2 Hz, 1H), 4.27 (d, J = 15.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 141.7, 140.8, 138.7, 133.2, 131.7, 131.5, 129.6, 128.9, 128.8, 128.6, 128.5, 128.2, 128.1, 127.9, 126.3, 126.0, 125.2, 124.1, 80.8, 64.5. Spectra data are consistent with those previously reported by us.[1]



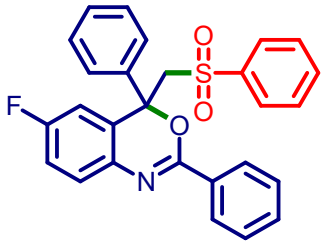
5c

8-Bromo-6-methyl-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5c): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Pale yellow solid (303 mg, 57% yield). R_f = 0.10 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 2H), 7.68 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.42-7.35 (m, 4H), 7.29 (t, J = 7.6 Hz, 2H), 7.22 (bs, 5H), 6.98 (s, 1H), 4.30 (d, J = 15.2 Hz, 1H), 4.26 (d, J = 15.2 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 141.2, 140.6, 137.1, 134.6, 133.9, 133.4, 131.7, 131.3, 128.8, 128.74, 128.68, 128.1, 128.14, 128.12, 125.5, 125.2, 125.1, 121.4, 80.9, 64.3, 21.1. Spectra data are consistent with those reported in the literature.[4]



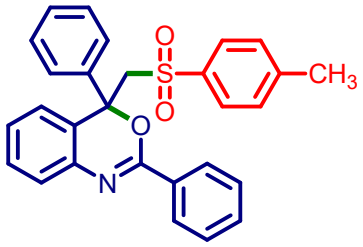
5d

6-Bromo-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5d): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Pale yellow solid (409 mg, 79% yield). R_f = 0.11 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.69-7.68 (m, 2H), 7.51-7.47 (m, 1H), 7.44-7.42 (m, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 1.8 Hz, 1H), 7.27-7.24 (m, 3H), 7.22 (dd, J = 8.4, 2.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 1H), 4.26 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 141.2, 140.6, 137.8, 133.5, 132.7, 131.7, 131.4, 130.2, 129.0, 128.89, 128.86, 128.4, 128.3, 128.1, 128.0, 127.4, 125.8, 125.2, 80.5, 64.2. Spectra data are consistent with those reported in the literature.[4]



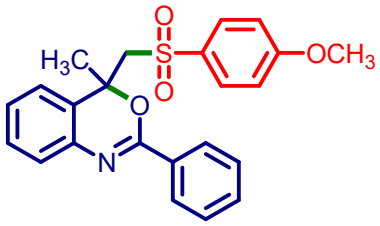
5e

6-Fluoro-2,4-diphenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5e): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Pale yellow solid (366 mg, 80% yield). R_f = 0.11 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.71-7.68 (m, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.30-7.20 (m, 8H), 7.03 (td, J = 8.2, 2.8 Hz, 1H), 6.97 (dd, J = 8.2, 2.8 Hz, 1H), 4.30 (d, J = 15.2 Hz, 1H), 4.25 (d, J = 15.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6 (d, J = 244.2 Hz), 154.2, 141.2, 140.7, 135.2, 133.4, 131.6, 131.5, 129.0, 128.8, 128.5, 128.2, 128.1, 127.8, 127.6 (d, J = 8.4 Hz), 125.7 (d, J = 7.0 Hz), 125.1, 116.3 (d, J = 21.6 Hz), 112.4 (d, J = 24.2 Hz), 80.6, 64.3. Spectra data are consistent with those reported in literature.[4]



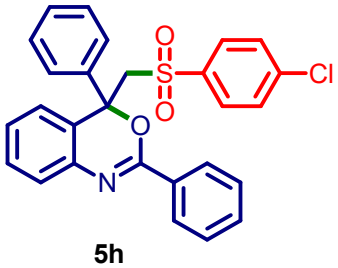
5f

2,4-Diphenyl-4-(tosylmethyl)-4H-benzo[d][1,3]oxazine (5f): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Colorless solid (376 mg, 83% yield). R_f = 0.10 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.49-7.46 (m, 1H), 7.39-7.26 (m, 6H), 7.25 (dd, J = 8.2, 1.8 Hz, 1H), 7.22-7.19 (m, 4H), 7.05 (d, J = 7.6 Hz, 2H), 4.28 (d, J = 15.2 Hz, 1H), 4.19 (d, J = 15.2 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 144.3, 141.9, 138.8, 137.8, 131.6, 131.4, 129.5, 129.4, 128.8, 128.6, 128.2, 128.1, 127.8, 126.3, 126.0, 125.5, 125.2, 123.9, 80.8, 64.6, 21.4. Spectra data are consistent with those previously reported by us.[1]



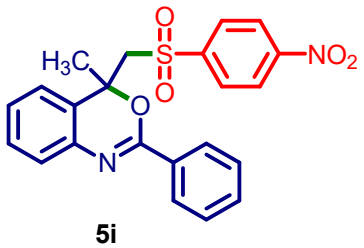
5g

4-((4-Methoxyphenyl)sulfonyl)methyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (5g): Synthesized according to the general procedure described in section 2.4. The gummy mass obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Yellow wax (350 mg, 86% yield). R_f = 0.13 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.35-7.29 (m, 2H), 7.22-7.15 (m, 2H), 6.76 (d, J = 8.6 Hz, 2H), 3.83 (d, J = 14.8 Hz, 1H), 3.73 (s, 3H), 3.60 (d, J = 14.8 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 155.4, 138.2, 132.1, 132.0, 131.5, 129.9, 129.4, 128.5, 128.1, 126.9, 126.8, 125.4, 123.2, 114.3, 77.9, 64.1, 55.6, 27.3. Spectra data are consistent with those previously reported by us.[1]



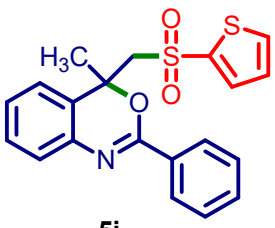
5h

4-((4-Chlorophenyl)sulfonyl)methyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (5h): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Pale yellow solid (341 mg, 72% yield). R_f = 0.11 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.58-7.55 (m, 2H), 7.51-7.48 (m, 1H), 7.41-7.39 (m, 2H), 7.35 (dd, J = 7.2, 0.8 Hz, 1H), 7.30-7.28 (m, 2H), 7.26-7.21 (m, 6H), 7.19-7.16 (m, 2H), 4.32 (d, J = 15.0 Hz, 1H), 4.28 (d, J = 15.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 141.7, 140.2, 139.1, 138.7, 131.8, 131.4, 129.7, 129.6, 129.3, 128.7, 128.6, 128.4, 127.6, 126.4, 126.1, 125.3, 125.2, 123.9, 80.8, 64.6. Spectra data are consistent with those previously reported by us.[1]



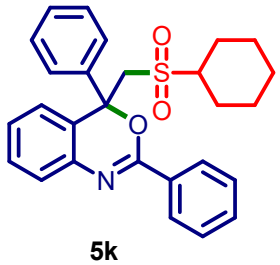
5i

4-Methyl-4-((4-nitrophenyl)sulfonyl)methyl)-2-phenyl-4H-benzo[d][1,3]oxazine (5i): Synthesized according to the general procedure described in section 2.4. The gummy mass obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Yellow wax (216 mg, 51% yield). R_f = 0.11 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.42-7.31 (m, 3H), 7.28 (d, J = 5.4 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 3.98 (d, J = 15.2 Hz, 1H), 3.79 (d, J = 15.2 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 150.3, 145.4, 138.1, 131.8, 131.6, 129.8, 129.2, 128.5, 128.1, 127.7, 127.2, 125.8, 124.2, 123.3, 77.8, 64.4, 28.2. Spectra data are consistent with those previously reported by us.[1]



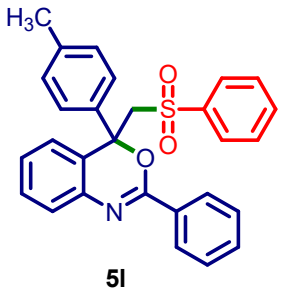
5j

4-Methyl-4-((phenylsulfonyl)methyl)-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine (5j): Synthesized according to the general procedure described in section 2.4. The gummy mass obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Yellow oil (303 mg, 79% yield). R_f = 0.12 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 7.4 Hz, 2H), 7.64-7.63 (m, 1H), 7.47 (d, J = 7.4 Hz, 2H), 7.39-7.35 (m, 2H), 7.29-7.26 (m, 1H), 7.22-7.20 (m, 1H), 7.15-7.11 (m, 2H), 7.06 (d, J = 7.8 Hz, 1H), 3.81 (d, J = 14.8 Hz, 1H), 3.62 (d, J = 14.8 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 140.7, 138.3, 136.1, 133.5, 130.9, 130.7, 129.6, 129.3, 128.4, 127.7, 126.9, 126.7, 125.3, 123.2, 78.3, 63.8, 26.9. Spectra data are consistent with those previously reported by us.[1]



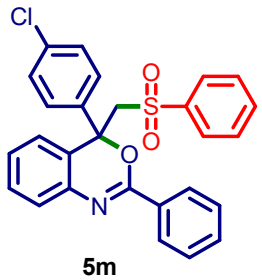
5k

4-((Cyclohexylsulfonyl)methyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (5k): Synthesized according to the general procedure described in section 2.4. The gummy mass obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Colorless oil (361 mg, 81% yield). R_f = 0.10 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (t, J = 7.2 Hz, 1H), 7.34-7.27 (m, 4H), 7.24-7.15 (m, 9H), 4.27 (d, J = 15.2 Hz, 1H), 4.08 (d, J = 15.2 Hz, 1H), 2.55-2.49 (m, 1H), 2.11-2.00 (m, 2H), 1.90-1.81 (m, 2H), 1.45-1.36 (m, 2H), 1.27-1.12 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 141.7, 140.8, 138.9, 133.2, 131.8, 131.5, 129.7, 128.7, 128.1, 127.9, 126.5, 126.0, 125.2, 124.1, 80.8, 64.6, 55.2, 26.6, 25.1, 24.7. Spectra data are consistent with those previously reported by us.[1]



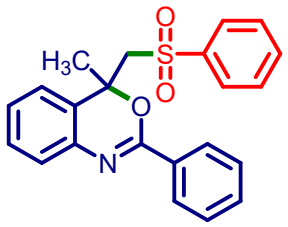
5l

2-Phenyl-4-((phenylsulfonyl)methyl)-4-(*p*-tolyl)-4H-benzo[d][1,3]oxazine (5l): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Colorless solid (385 mg, 85% yield). R_f = 0.10 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 6.4 Hz, 2H), 7.68 (d, J = 6.4 Hz, 2H), 7.47 (s, 1H), 7.38-7.34 (m, 4H), 7.26 (s, 4H), 7.24 (d, J = 6.4 Hz, 1H), 7.12 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 7.2 Hz, 2H), 4.31 (d, J = 15.2 Hz, 1H), 4.25 (d, J = 15.2 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 140.8, 138.7, 138.6, 138.5, 133.2, 131.8, 131.5, 129.5, 129.3, 128.8, 128.5, 128.3, 128.1, 127.8, 126.4, 125.9, 125.3, 124.2, 80.9, 64.6, 21.0. Spectra data are consistent with those previously reported by us.[1]



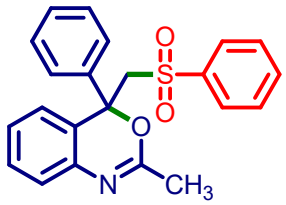
5m

4-(4-Chlorophenyl)-2-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5m): Synthesized according to the general procedure described in section 2.4. The precipitate obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Colorless solid (346 mg, 73% yield). R_f = 0.41 (10% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.71-7.65 (m, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.42-7.35 (m, 4H), 7.31-7.22 (m, 5H), 7.20-7.14 (m, 4H), 4.29 (d, J = 15.4 Hz, 1H), 4.23 (d, J = 15.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 140.7, 139.8, 138.6, 134.7, 133.2, 131.7, 131.4, 129.8, 129.1, 128.8, 128.3, 128.1, 127.8, 126.9, 126.5, 126.1, 124.9, 124.0, 80.4, 64.1. Spectra data are consistent with those previously reported by us.[1]



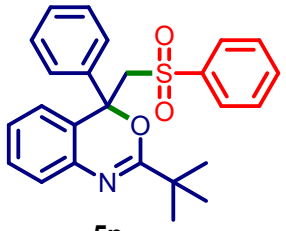
5n

4-Methyl-2-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5n): Synthesized according to the general procedure described in section 2.4. The gummy mass obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Colorless oil (313 mg, 83% yield). R_f = 0.12 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2H), 7.73 (dd, J = 8.2, 0.6 Hz, 2H), 7.51-7.45 (m, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.36 (t, J = 8.2 Hz, 2H), 7.31-7.28 (m, 1H), 7.24 (d, J = 6.0 Hz, 1H), 7.19-7.16 (m, 1H), 7.14-7.11 (m, 1H), 3.82 (d, J = 14.8 Hz, 1H), 3.64 (d, J = 14.8 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 140.6, 138.2, 133.4, 132.1, 131.5, 129.6, 129.1, 128.2, 128.1, 127.6, 127.0, 125.7, 123.2, 77.8, 64.0, 27.0. Spectra data are consistent with those previously reported by us.[1]



5o

2-Methyl-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5o): Synthesized according to the general procedure described in section 2.4. The gummy mass obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Yellow wax (294 mg, 78% yield). R_f = 0.12 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.32-7.26 (m, 4H), 7.23-7.21 (m, 2H), 7.13-7.09 (m, 2H), 7.05-7.03 (m, 1H), 4.15-4.11 (m, 2H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 141.6, 140.6, 138.1, 133.5, 129.6, 128.9, 128.7, 128.3, 126.2, 125.6, 125.4, 125.1, 123.4, 80.5, 64.2, 21.3. Spectra data are consistent with those previously reported by us.[1]



5p

2-(*tert*-Butyl)-4-phenyl-4-((phenylsulfonyl)methyl)-4H-benzo[d][1,3]oxazine (5p): Synthesized according to the general procedure described in section 2.4. The gummy mass obtained was purified by silica-gel column chromatography using 20-30% ethyl acetate in hexane. Yellow oil (336 mg, 80% yield). R_f = 0.11 (20% ethyl acetate in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-6.59 (m, 2H), 7.53-7.50 (m, 1H), 7.37 (dd, J = 8.4, 7.6 Hz, 2H), 7.28-7.24 (m, 4H), 7.19-7.16 (m, 3H), 7.01-6.98 (m, 1H), 6.93 (d, J = 1.2 Hz, 1H), 4.28 (d, J = 15.2 Hz, 1H), 4.21 (d, J = 15.2 Hz, 1H), 1.16 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 142.5, 140.8, 139.0, 133.4, 129.4, 129.1, 128.7, 128.4, 128.2, 126.0, 125.7, 125.6, 125.5, 122.4, 80.2, 64.9, 37.3, 27.4. Spectra data are consistent with those previously reported by us.[1]

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2. P. Natarajan, H. Sharma, M. Kaur, P. Sharma, Haloacid/dimethyl sulfoxide-catalyzed synthesis of symmetrical disulfides by oxidation of thiols, *Tetrahedron Lett*. 2015, **56**, 5578-5582.

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4. J. Wu, Y. Zong, C. Zhao, Q. Yan, L. Sun, Y. Li, J. Zhao, Y. Ge and Z. Li, Silver or cerium-promoted free radical cascade difunctionalization of *o*-vinylanilides with sodium aryl-or alkylsulfinates, *Org. Biomol. Chem*., 2019, **17**, 794-797.

Copies of NMR spectra of products

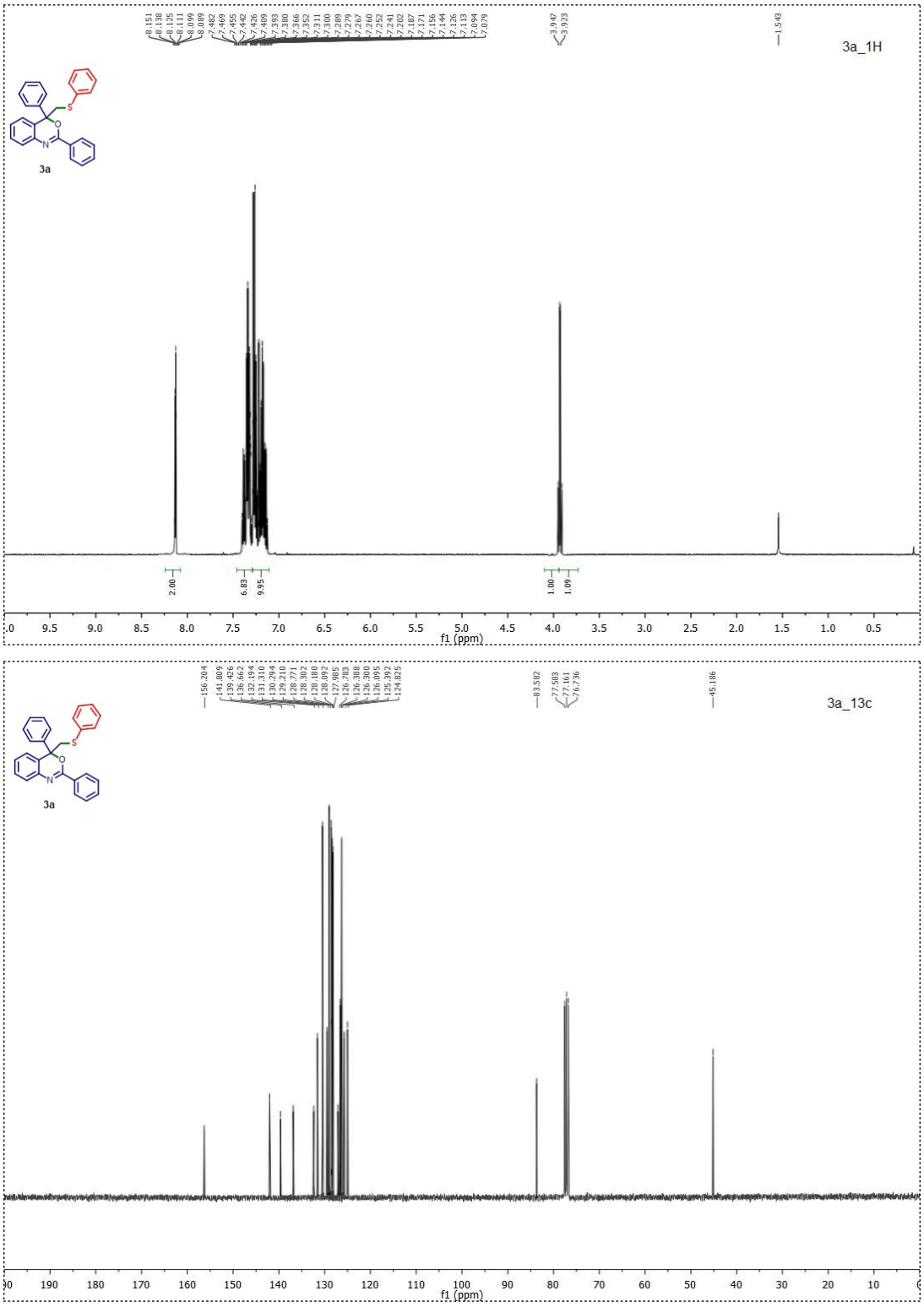

Figure S5. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3a** in $CDCl_3$.

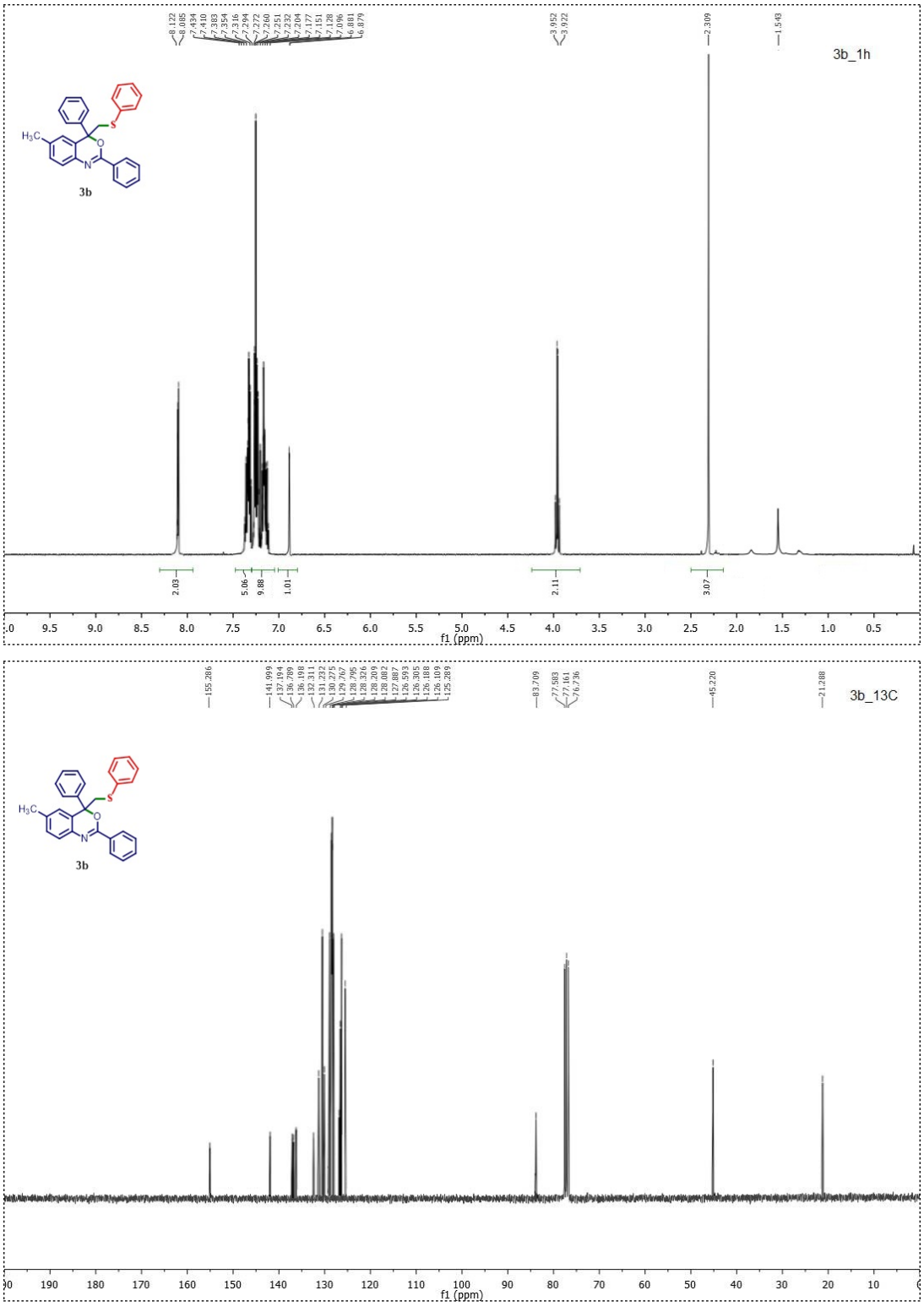

Figure S6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3b** in $CDCl_3$.

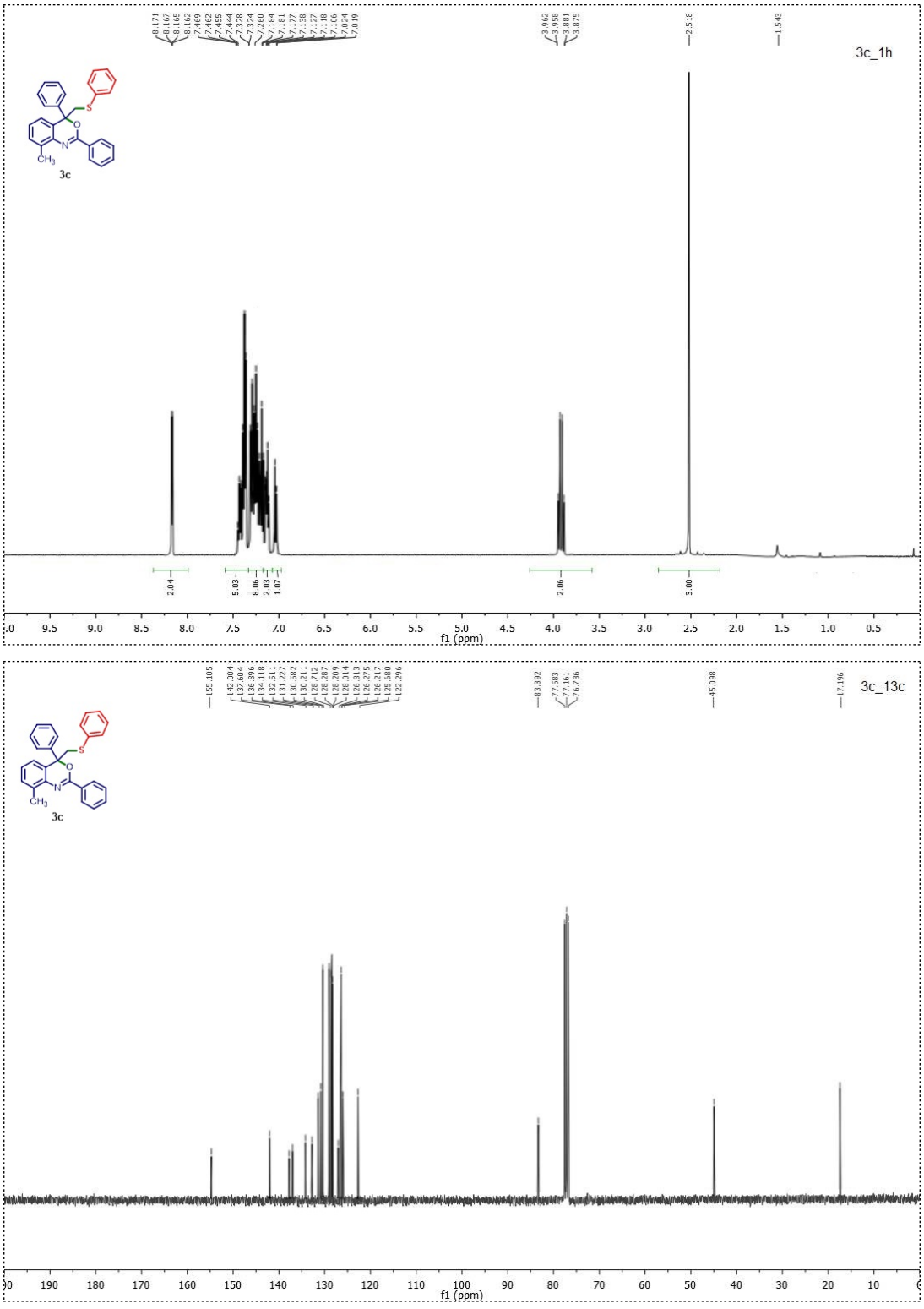

Figure S7. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3c** in $CDCl_3$.

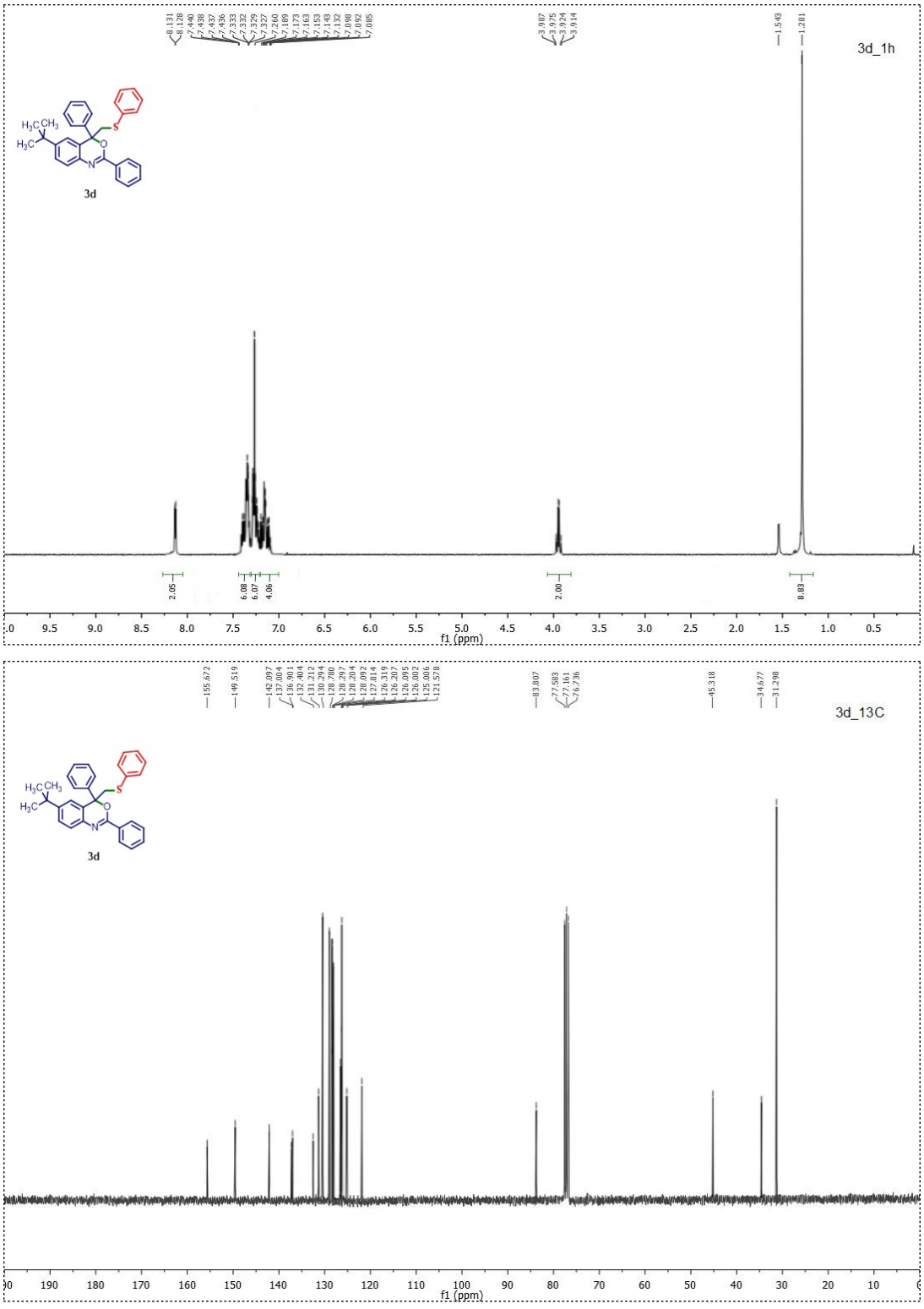

Figure S8. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3d** in $CDCl_3$.

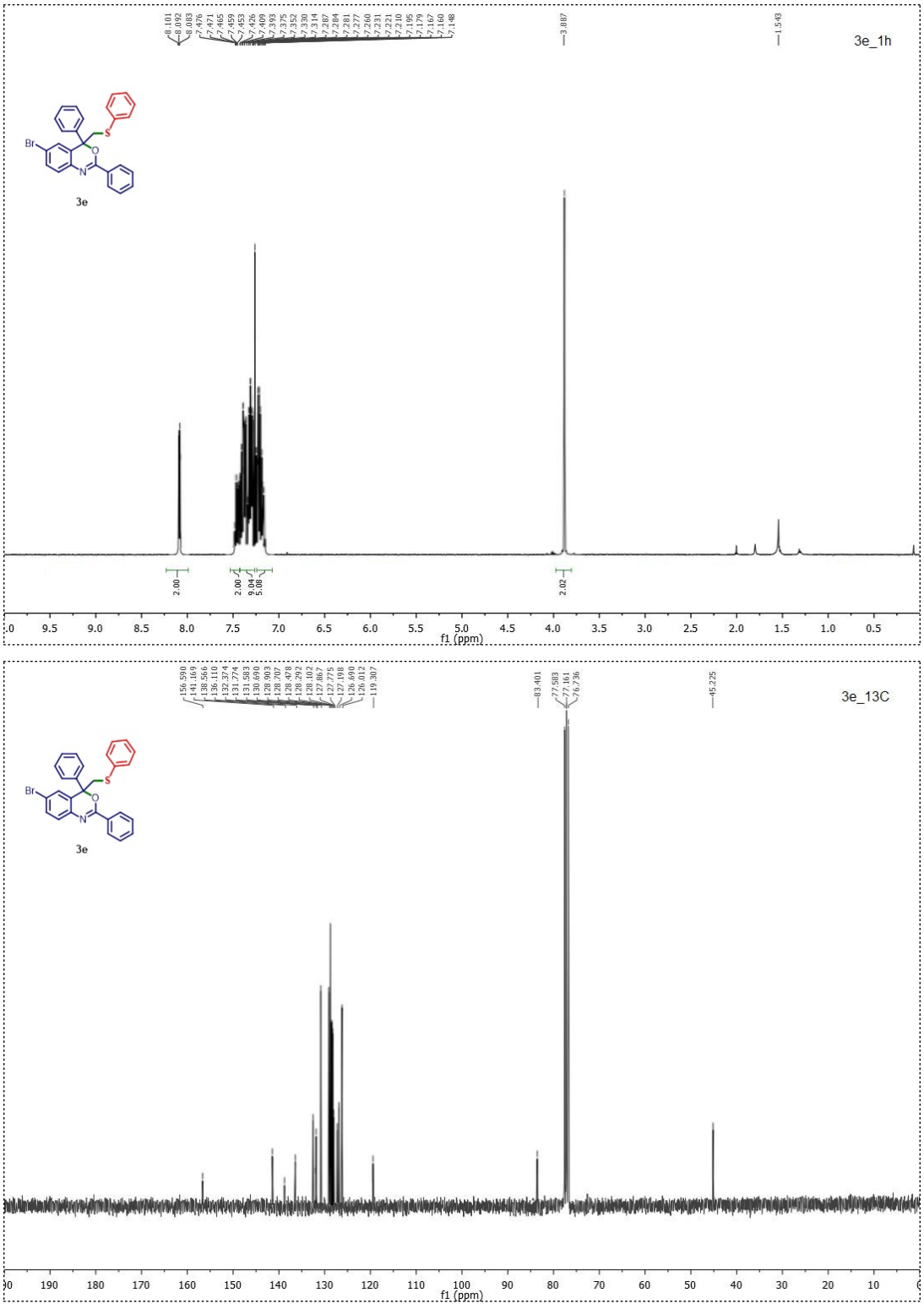

Figure S9. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3e** in $CDCl_3$.

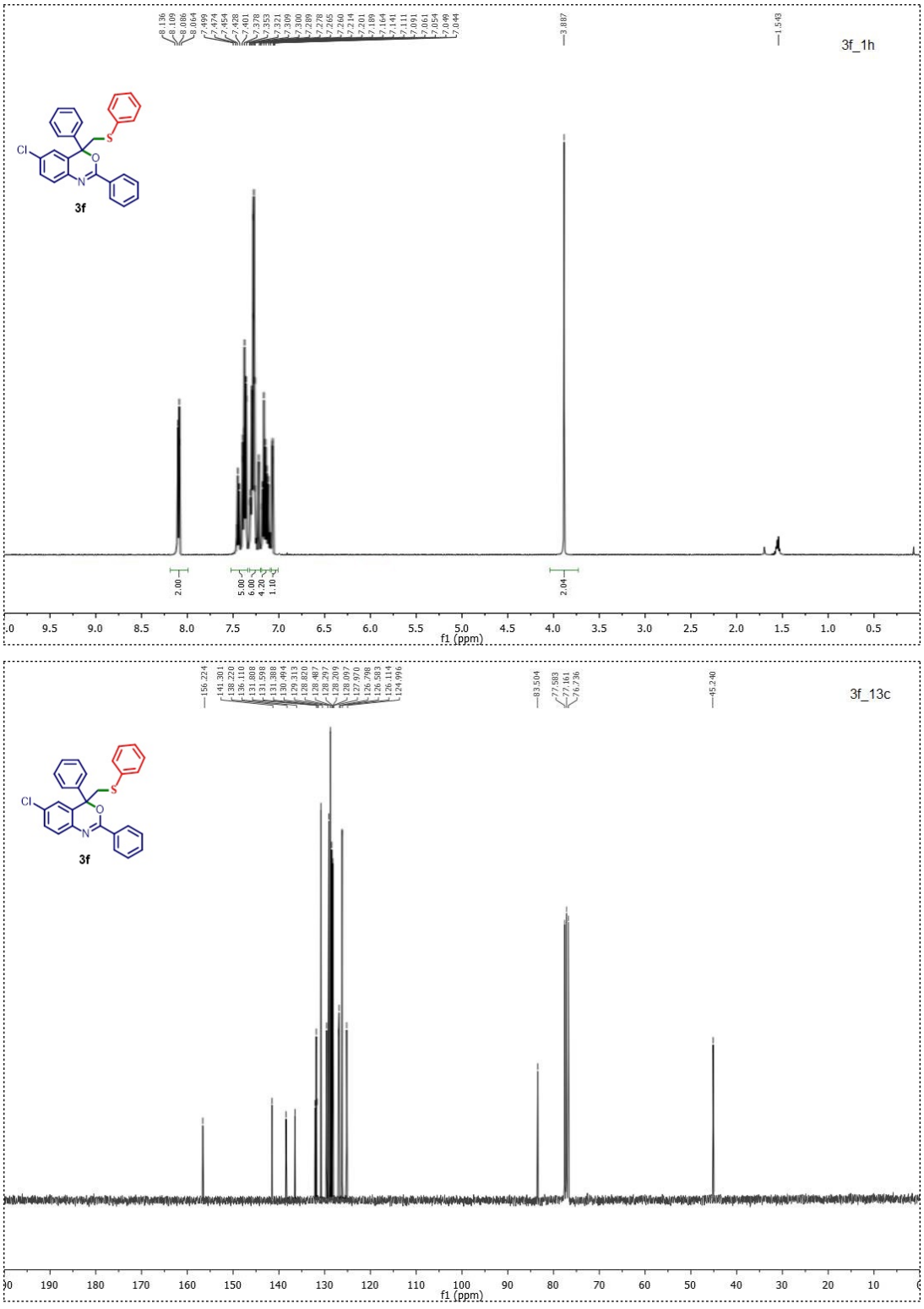

Figure S10. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3f** in $CDCl_3$.

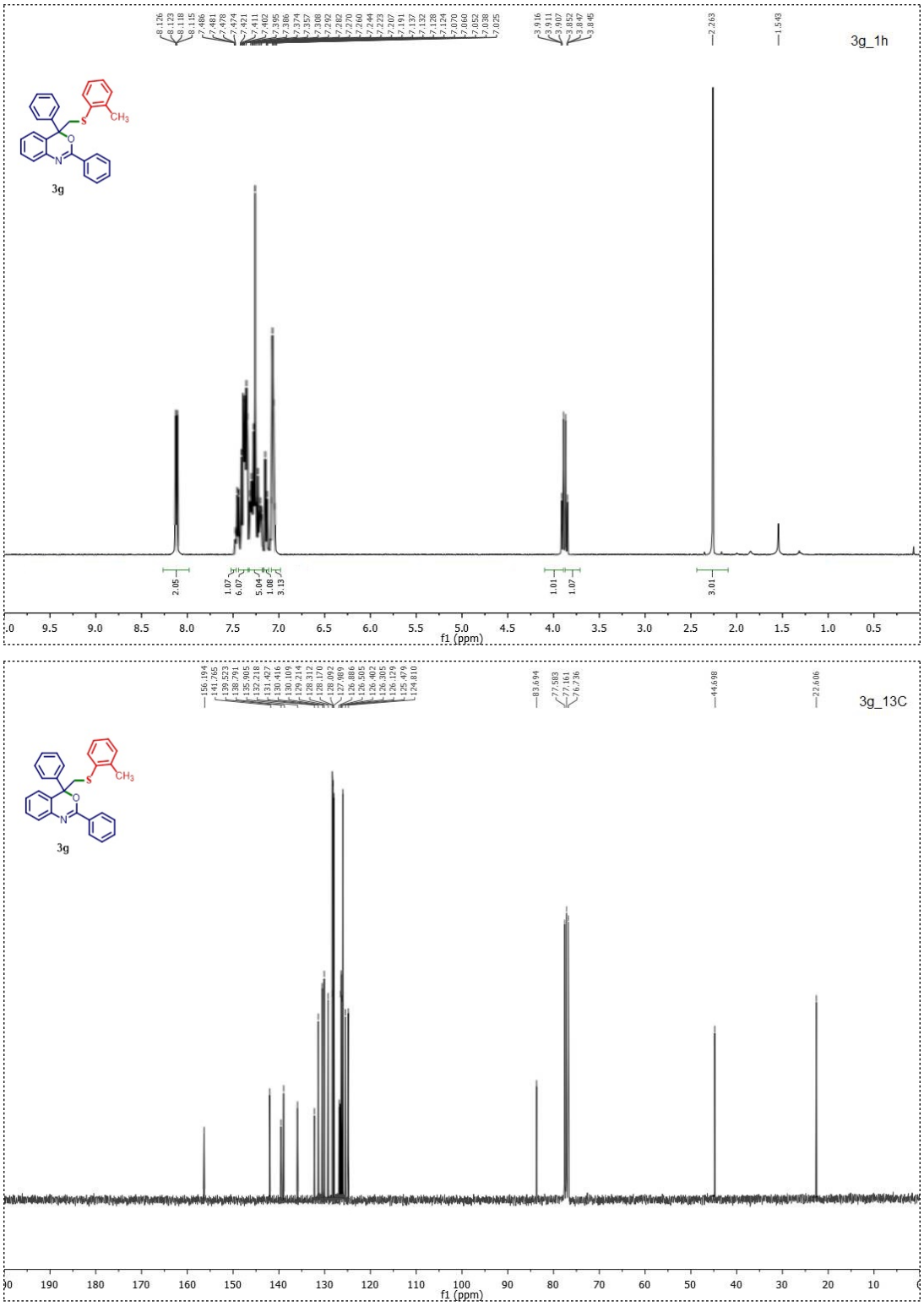

Figure S11. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3g** in $CDCl_3$.

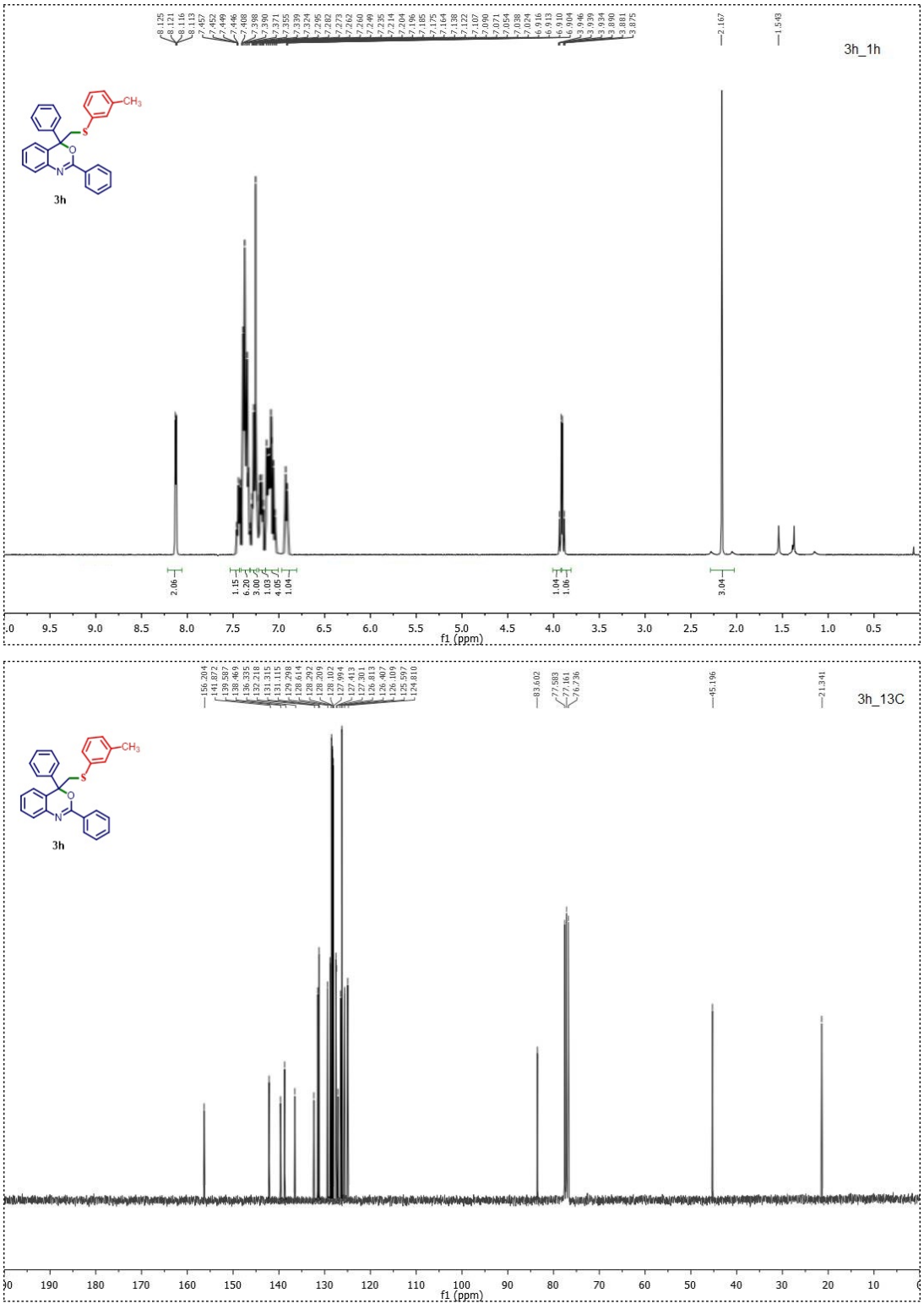

Figure S12. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3h** in $CDCl_3$.

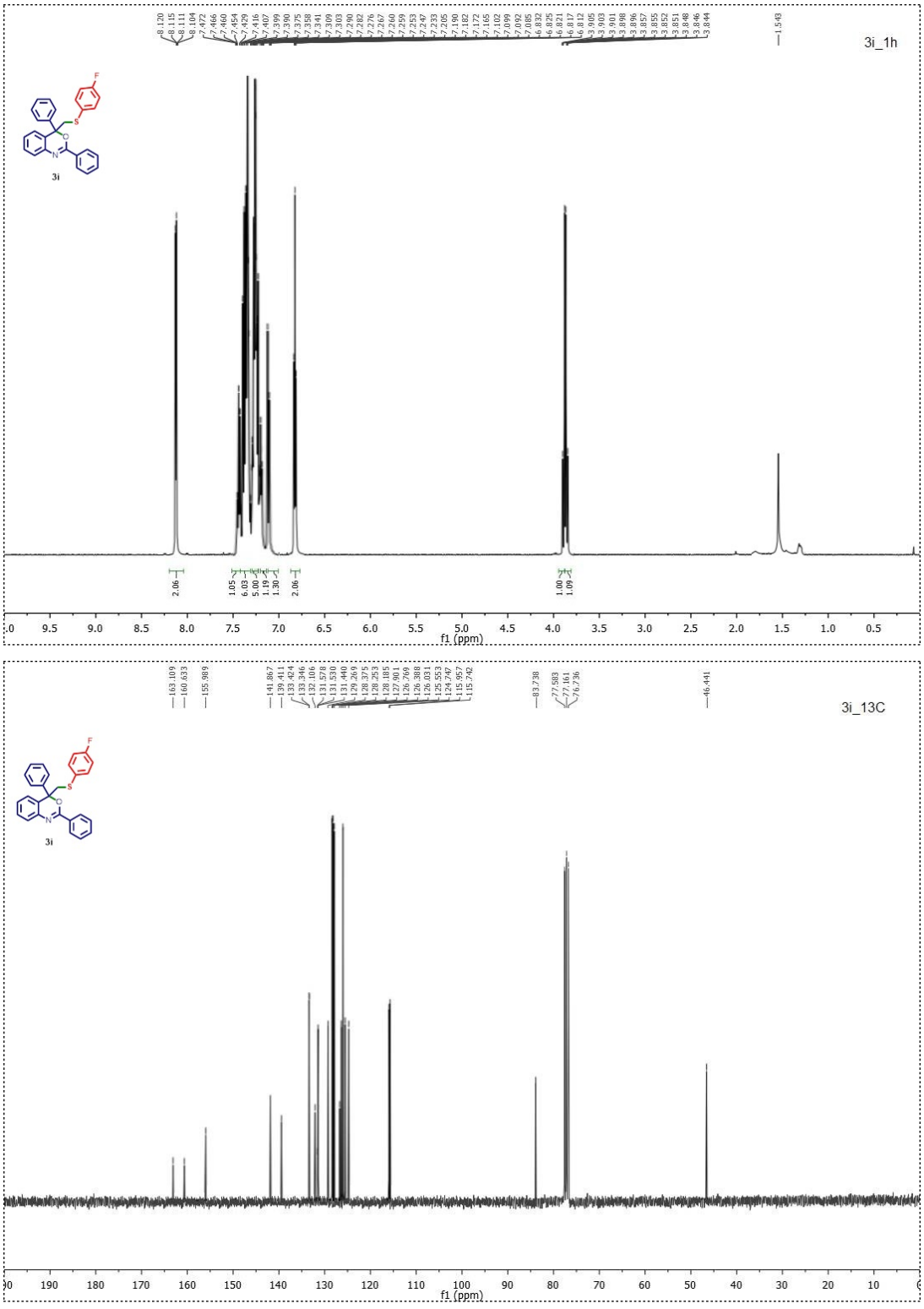

Figure S13. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3i** in $CDCl_3$.

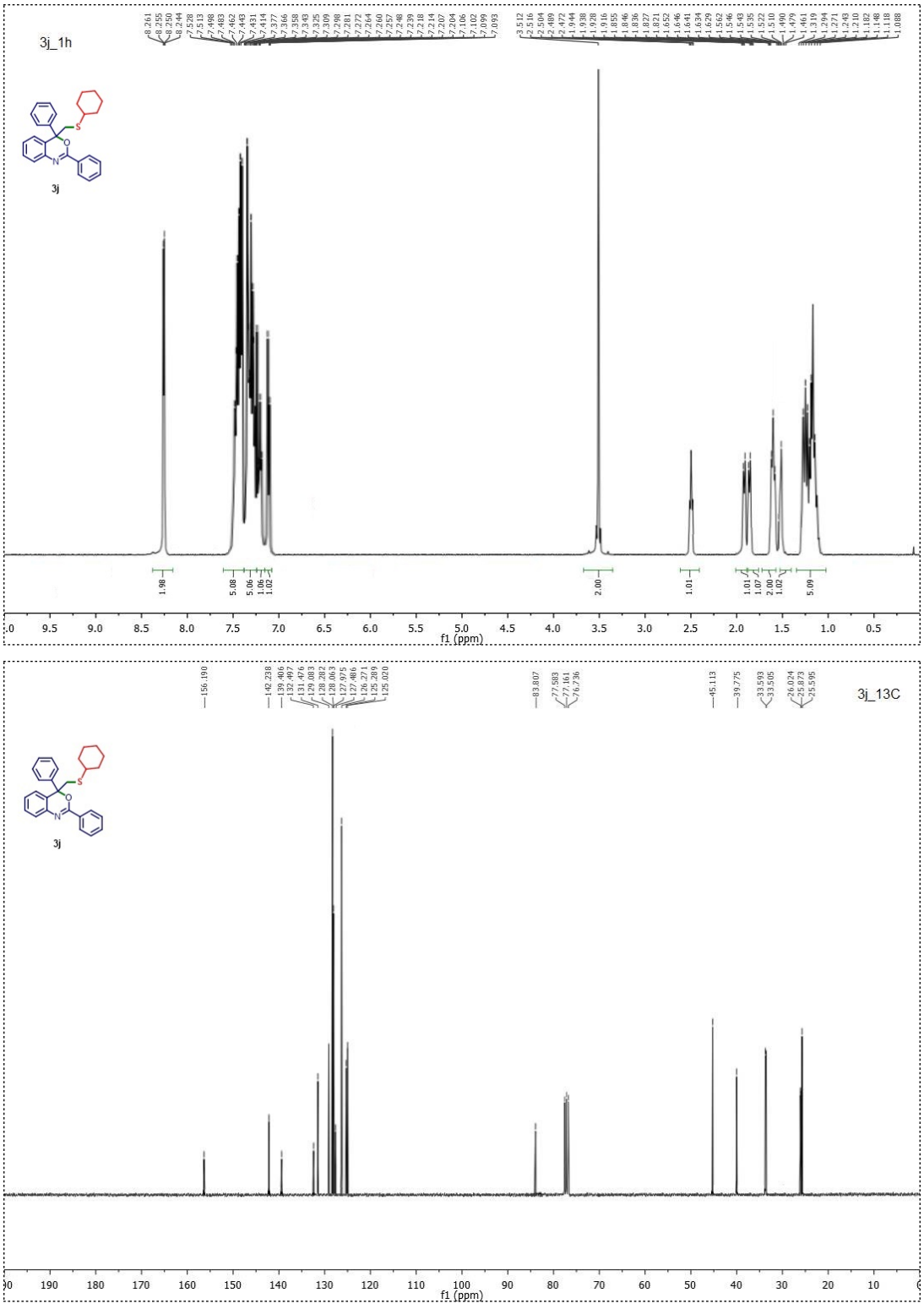

Figure S14. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3j** in $CDCl_3$.

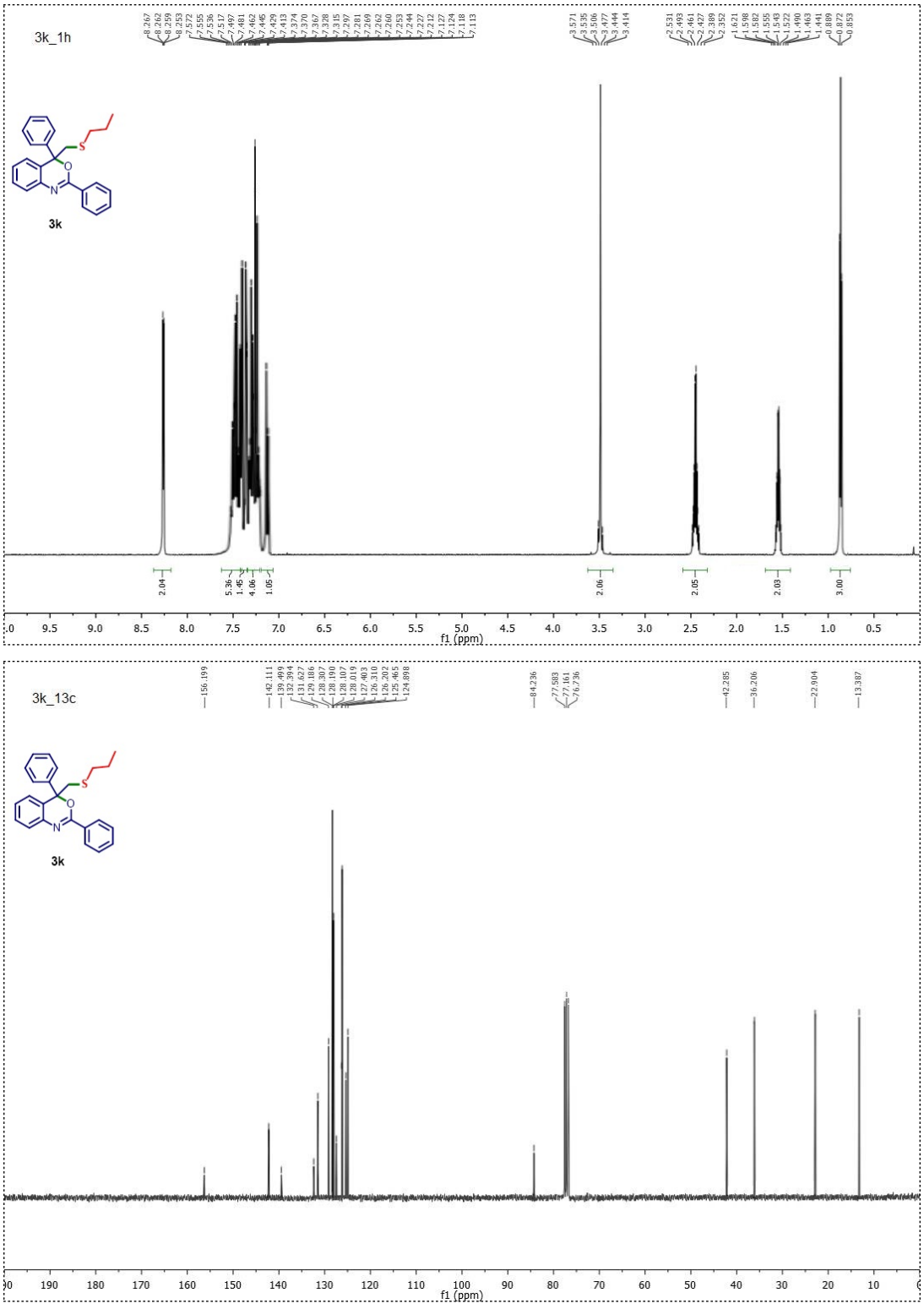

Figure S15. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3k** in $CDCl_3$.

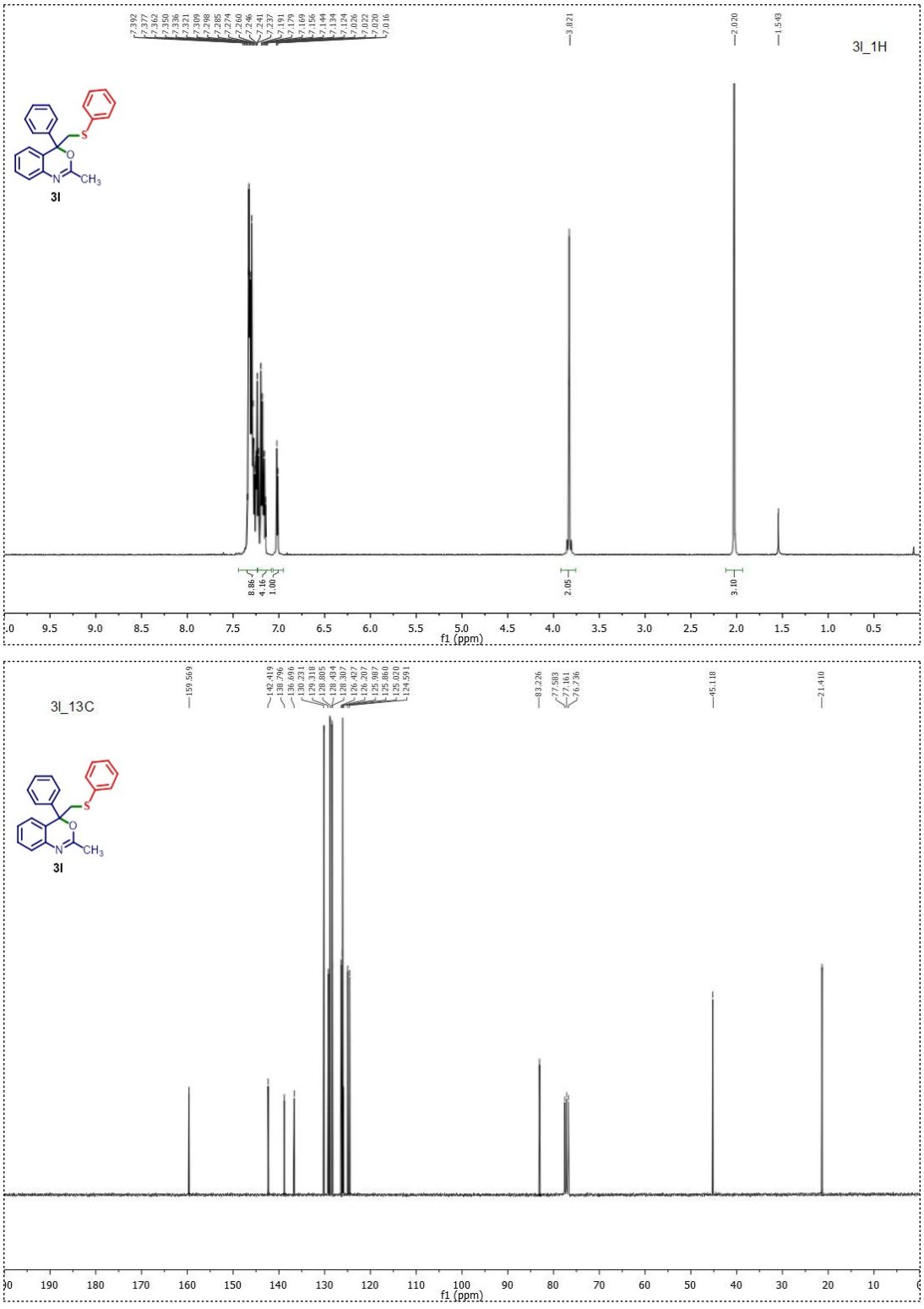

Figure S16. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3l** in $CDCl_3$.

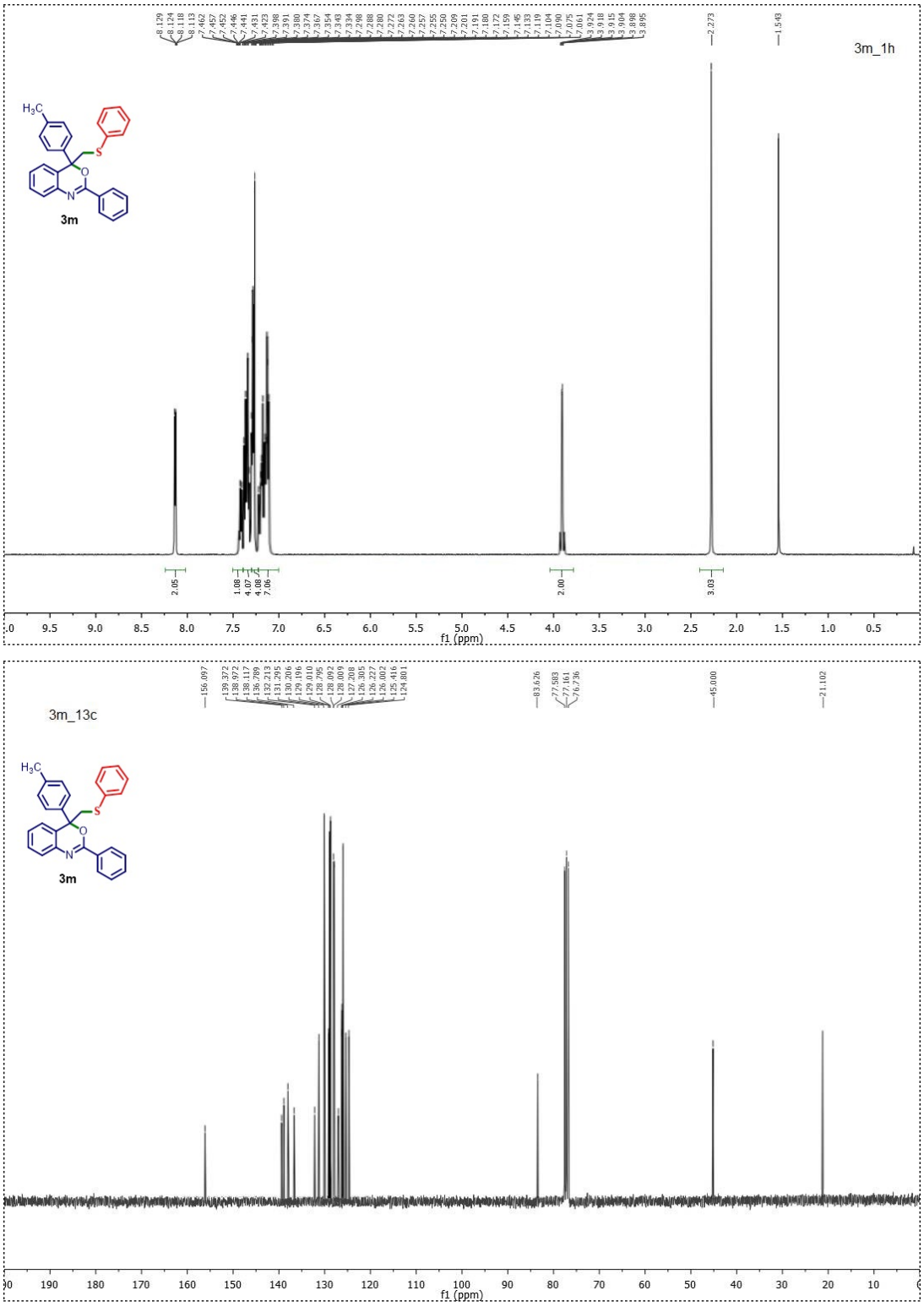

Figure S17. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3m** in $CDCl_3$.

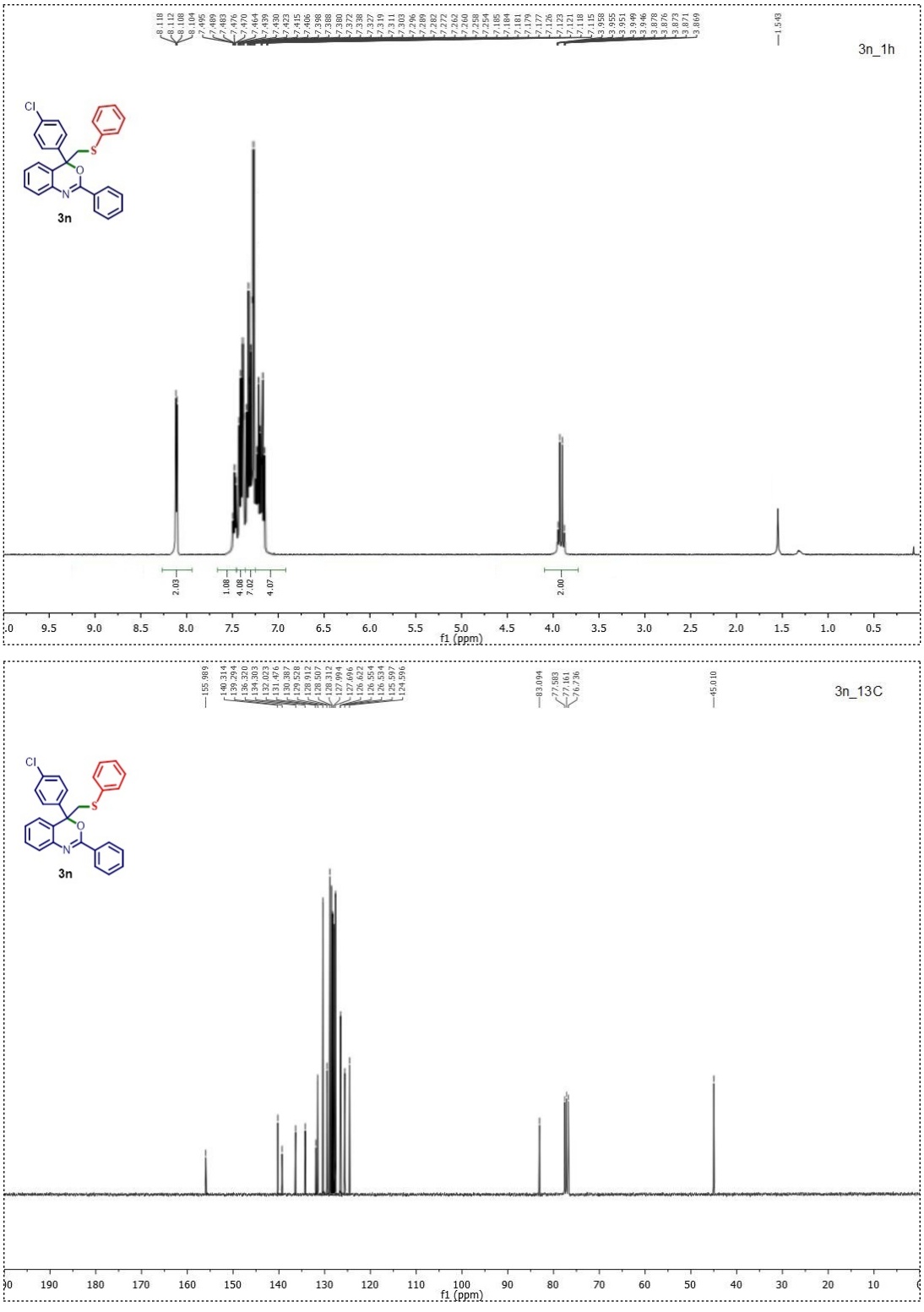

Figure S18. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3n** in $CDCl_3$.

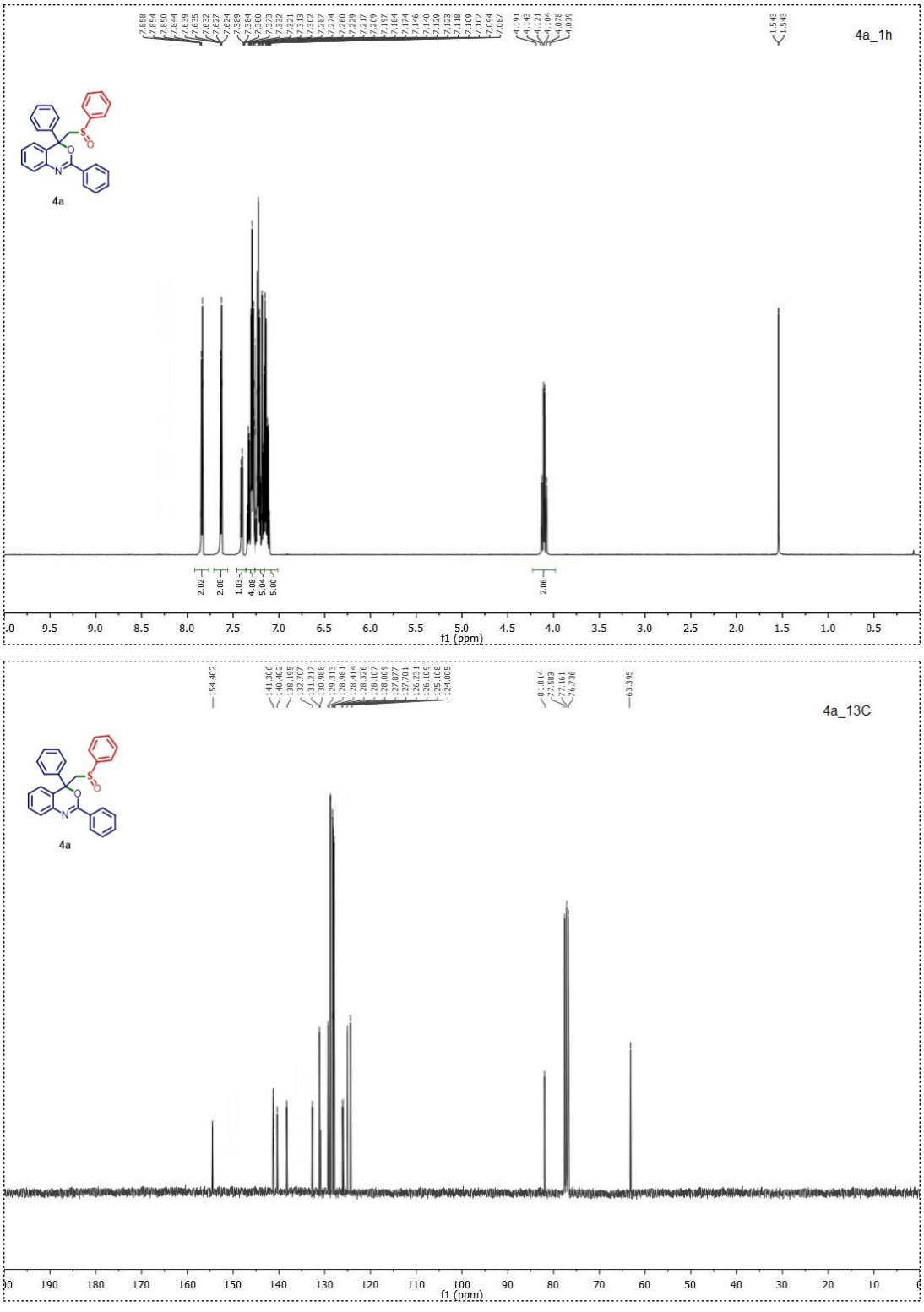

Figure S19. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4a** in $CDCl_3$.

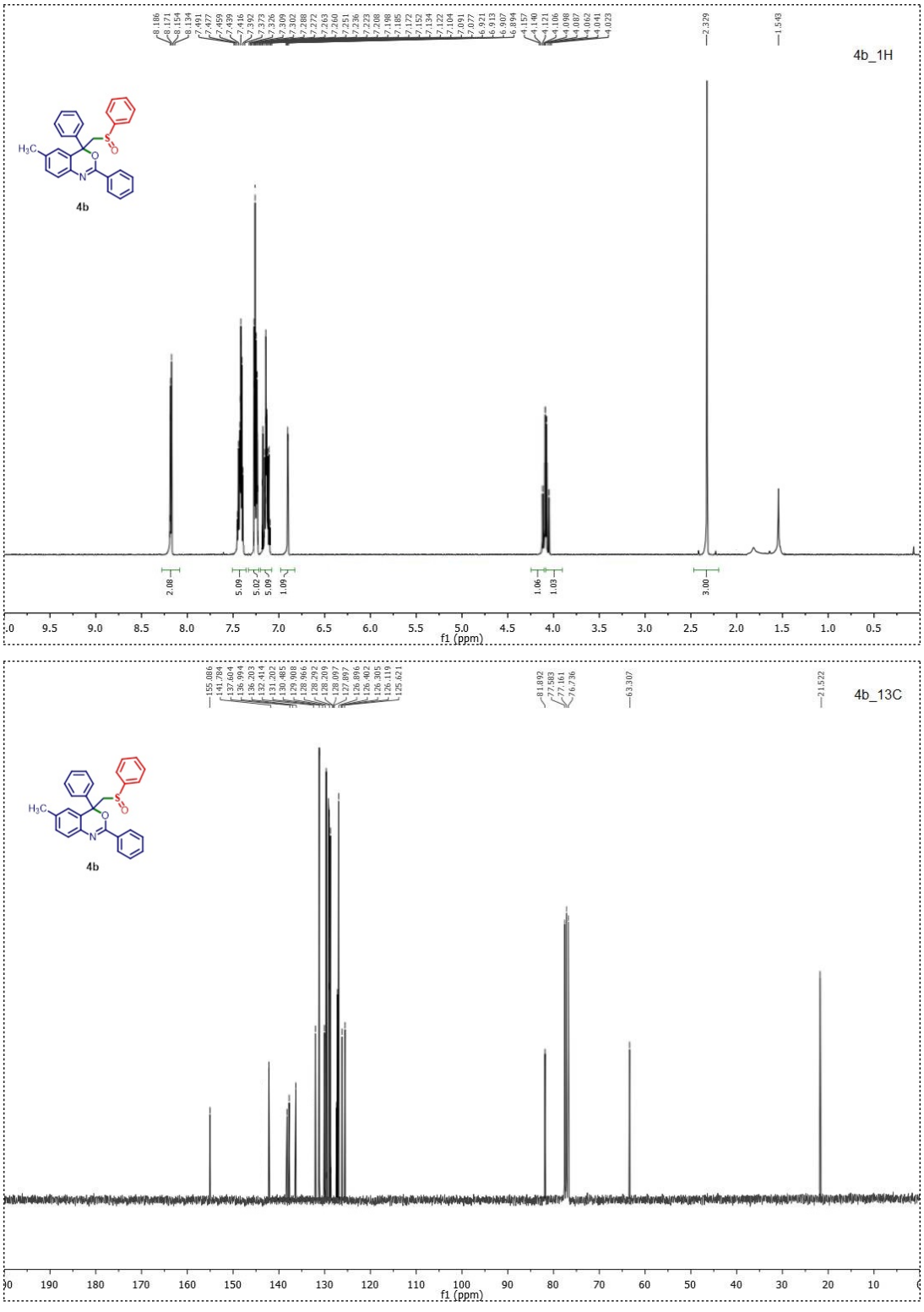

Figure S20. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4b** in $CDCl_3$.

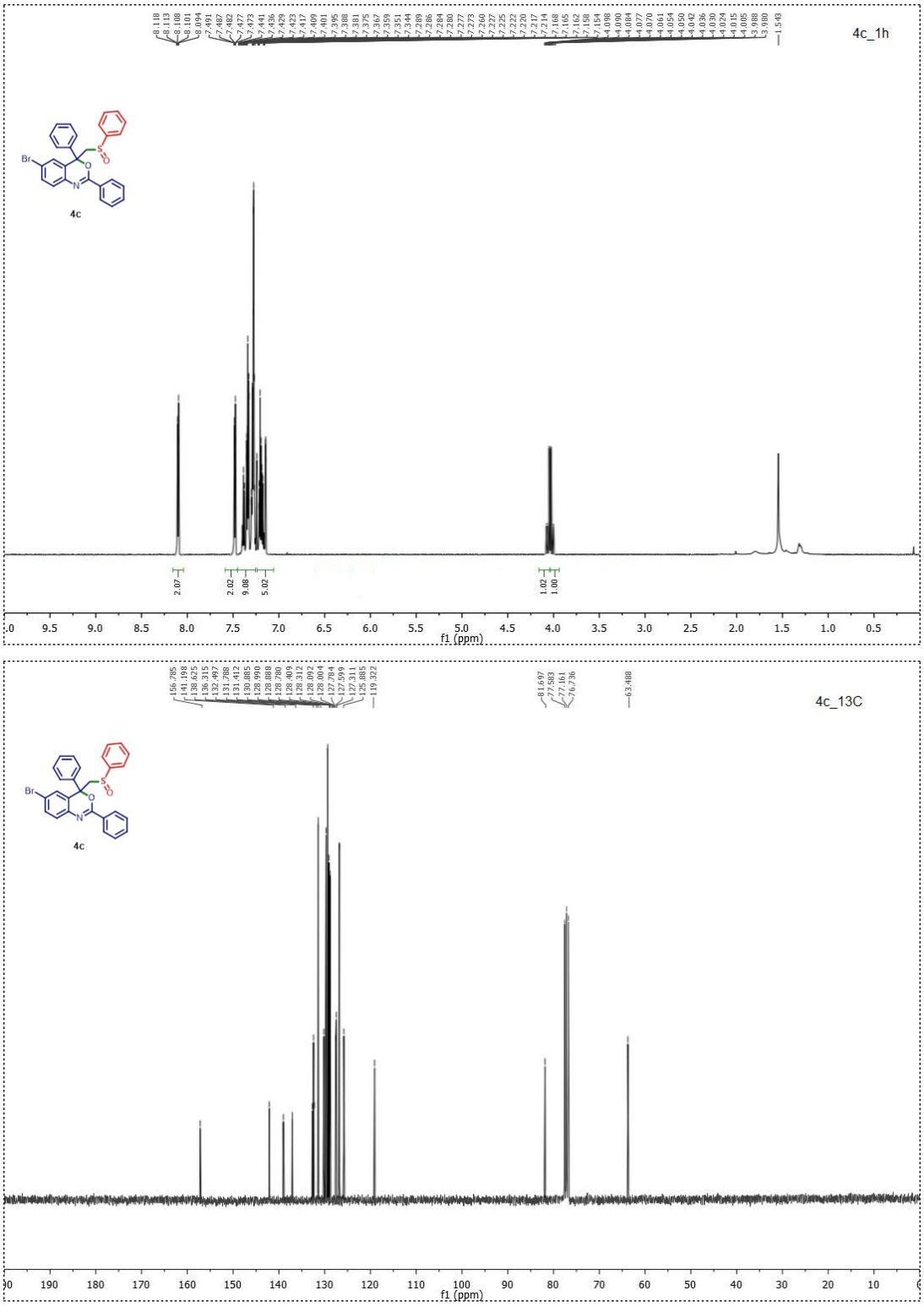

Figure S21. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4c** in $CDCl_3$.

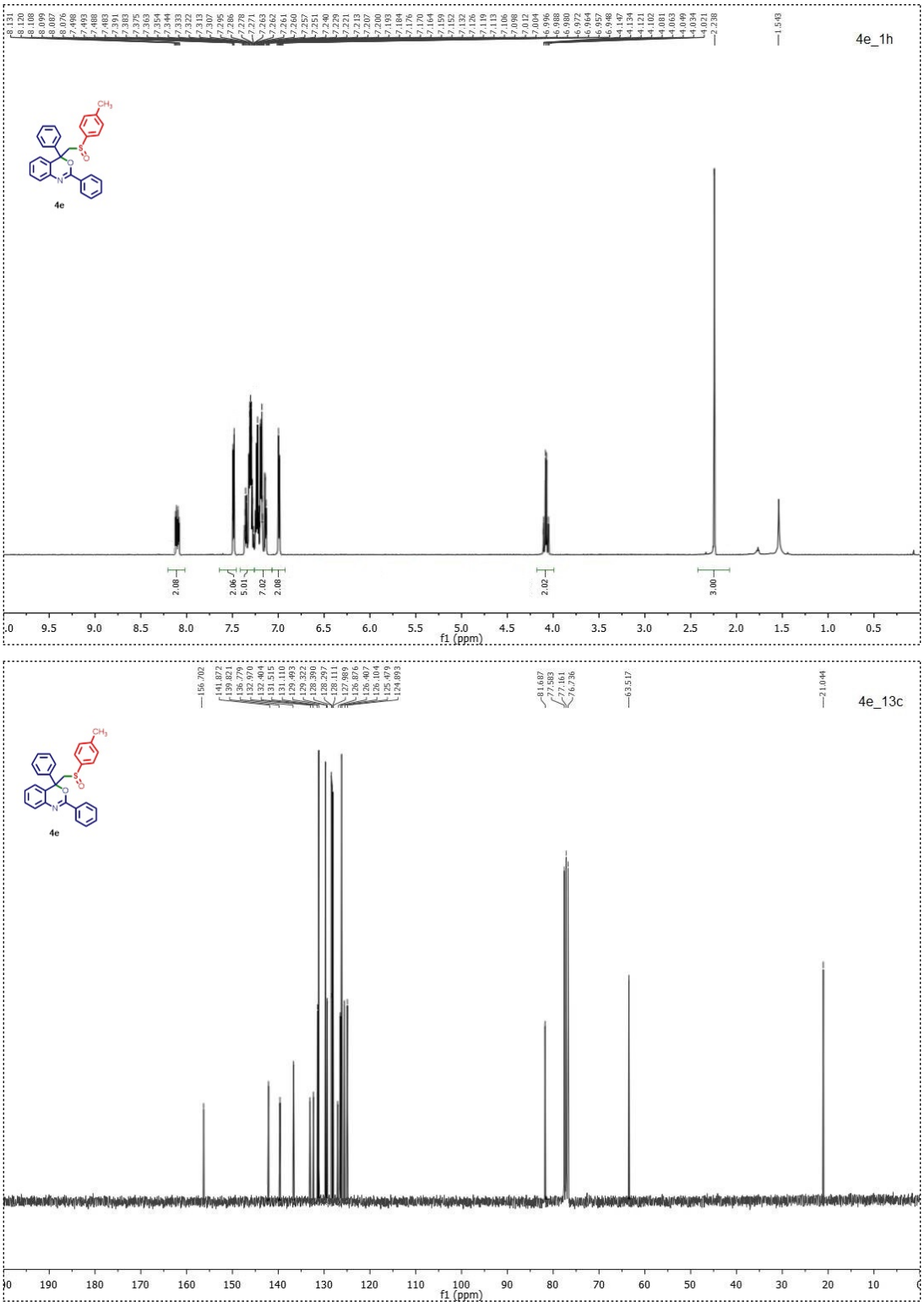

Figure S22. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4e** in $CDCl_3$.

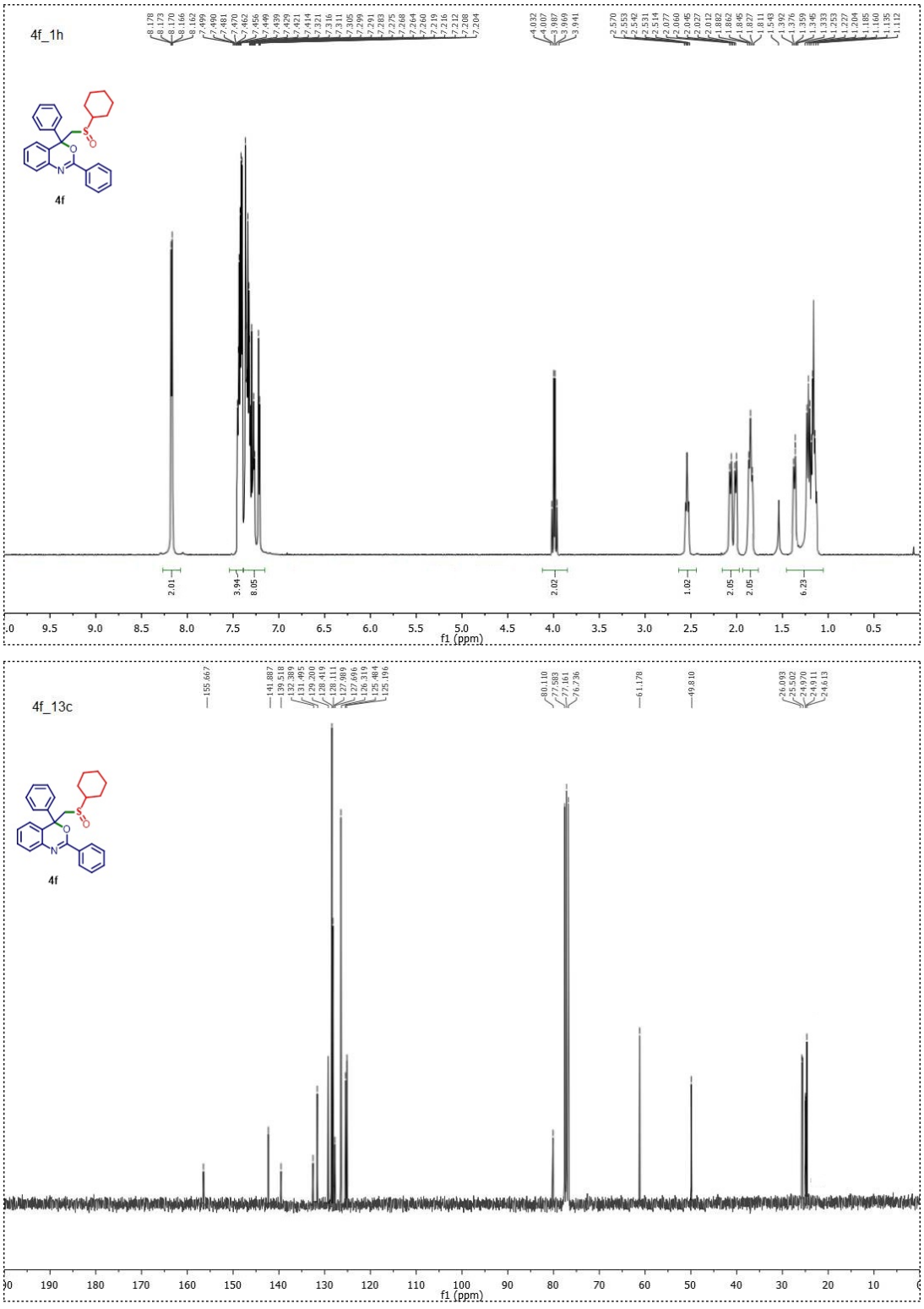

Figure S23. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4f** in $CDCl_3$.

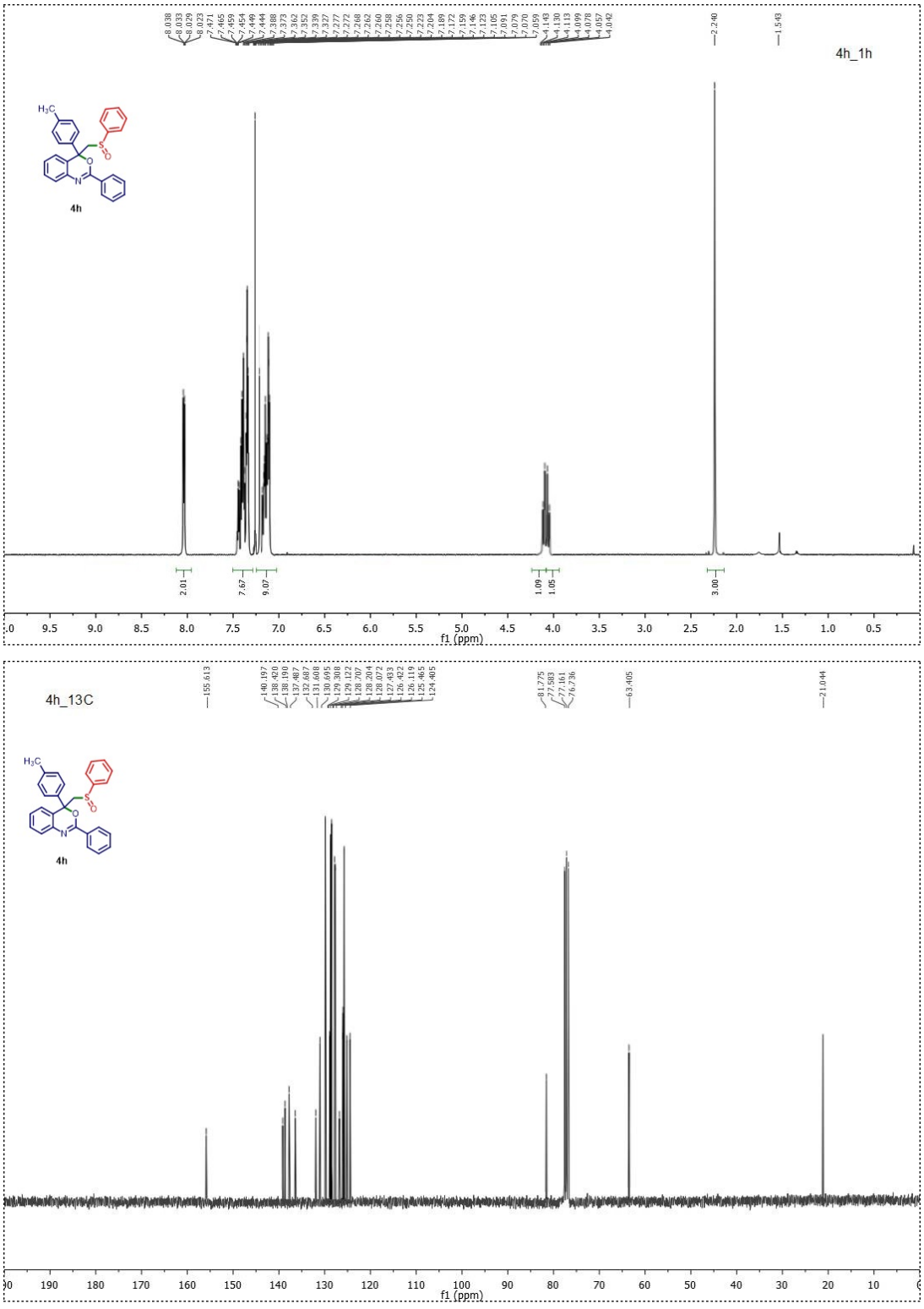

Figure S24. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4h** in $CDCl_3$.

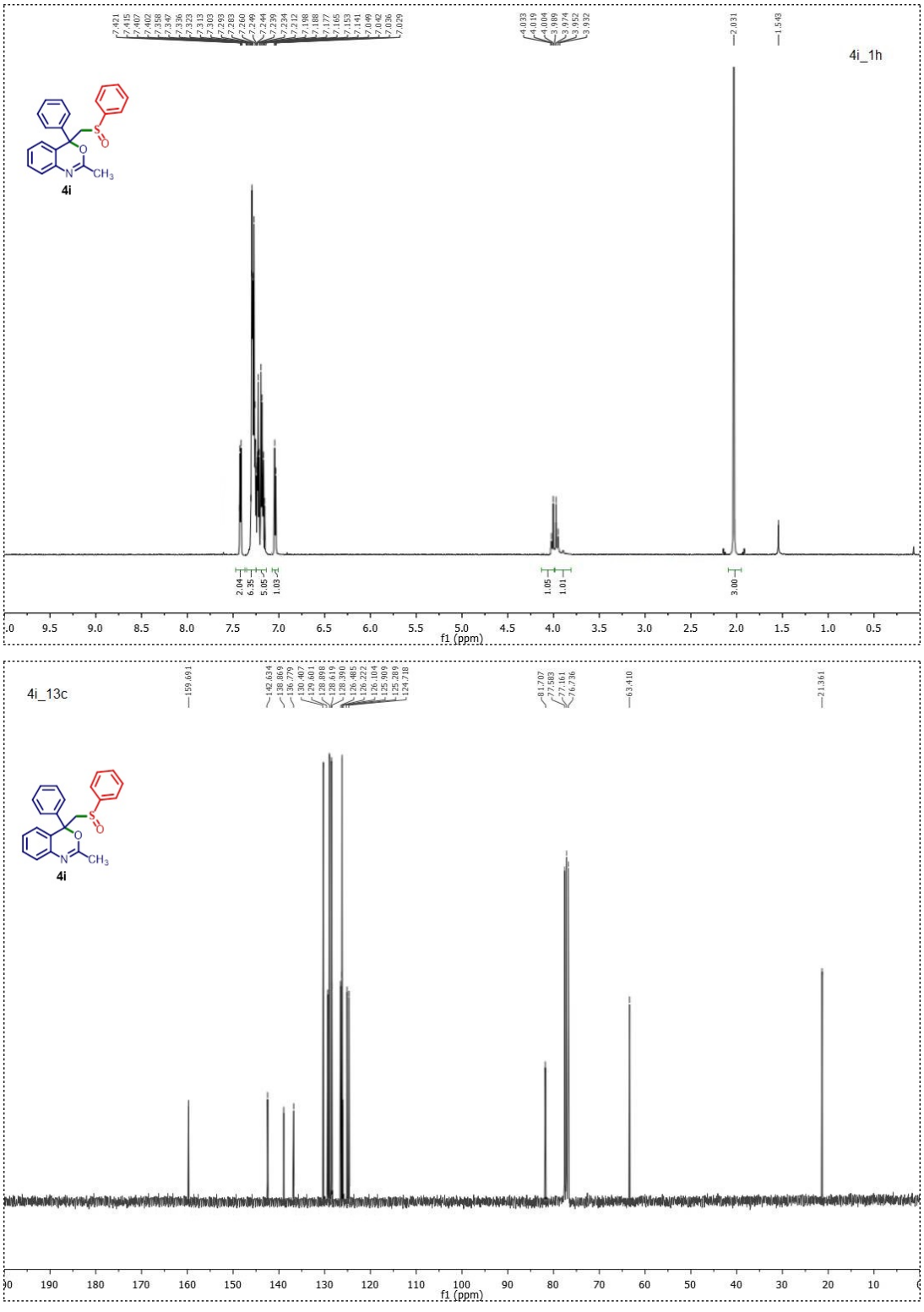

Figure S25. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4i** in $CDCl_3$.