

Supporting Information

An Uncommon Use of Irradiated Flavins: Brønsted Acid Catalysis

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I. General information

Melting points were measured on an AS ONE ATM-01. NMR spectra were recorded using JEOL JNM-ECX-400 (^1H , 400 MHz), JNM-ECZ-400S (^1H , 400 MHz), and JNM-ECA-500W spectrometers (^1H , 500 MHz and ^{13}C , 126 MHz). Chemical shifts are reported in ppm using TMS or the residual solvent peak as a reference. UV spectra were recorded on a HITACHI U-3000 spectrophotometer. Elemental analyses were carried out on a J-Science Lab JM10 micro corder. Steady-state emission spectra were recorded using a Hitachi F-7000 spectrometer. Visible light irradiations were performed with a blue LED (NICHIA NCSB119T, $\lambda = 465$ nm) while cooling with a fan. RFTA,¹ MFI,² DMA,³ benzaldehyde- α -d,⁴ (*E*)-*N*-benzylideneaniline,⁵ (*E*)-*N*-benzylidene-*p*-anisidine,⁶ (*E*)-2-(benzylideneamino)phenol,⁷ 1-(trimethylsilyloxy)-1-phenylethene (**5**),⁸ ((*Z*)-1-phenylprop-1-enyloxy)trimethylsilane,^{9,10} and 1-*tert*-butyldimethylsilyloxycyclopentene⁸ were prepared according to the literature procedures. Polystyrene sulfonyl hydrazide (PS-TsNHNH₂) was purchased from Biotage. All other reagents were also purchased from commercial supplies and used without purification.

II. Catalytic thioacetalization

II-1. Typical procedure (Table 2)

A 20 ϕ glass tube was charged with **1** (0.735 mmol), **2** (1.47 mmol), RFTA (11.9 mg, 21.9 μmol), and acetonitrile (3.5 mL), which was stirred and irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under air for 30 minutes. Afterwards, the LED irradiation was switched off, and the mixture was further stirred for a defined reaction time under the remaining conditions. The reaction mixture was diluted with Et₂O (35 mL) and washed with water (5 mL \times 3), 2 N NaOH (3 mL \times 5), and water (5 mL \times 5), which was dried over MgSO₄, filtered, and concentrated under reduced pressure to give the desired products either in a pure form (**3a**, **3g**) or in an impure form (**3b–3f**, **3h**, **4**). In the latter case except **3h**, the crude product was dissolved in CH₂Cl₂ and mixed with PS-TsNHNH₂ (74 mg) and shaken for 1 h. The polymer was removed by filtration and the filtrate was concentrated under reduced pressure to give **3b–3f** or **4** with high purity. Only the crude mixture for **3h** contained a small amount of unidentified byproducts, which was analyzed without further purification by ^1H NMR spectroscopy.

2-(4-Methoxyphenyl)-1,3-dithiane (3a, colorless solid, 141 mg, 85%): M.p. 113 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl₃) δ = 1.92 (dtt, J = 14.0, 12.2, 3.2 Hz, 1H, 5-CH^{ax}), 2.16 (dtt, J = 14.0, 4.1, 2.3, 1H, 5-CH^{eq}), 2.90 (ddd, J = 14.5, 4.1, 3.2 Hz, 2H, 4,6-CH^{eq}), 3.06 (ddd, J = 14.5, 12.2 2.3 Hz, 2H, 4,6-CH^{ax}), 3.80 (s, 3H, OCH₃), 5.01 (s, 1H, CH), 6.86 (d, J = 8.6 Hz, 2H, ArH), 7.40 (d, J = 8.6 Hz, 2H, ArH); ^{13}C NMR (126 MHz, CDCl₃) δ = 25.2, 32.3, 50.8, 55.4, 114.2, 129.1, 131.4, 159.7; Elemental analysis: calcd for C₁₁H₁₄OS₂: C 58.37, H 6.23; found: C 58.15, H 6.23. The proton and

¹³C are in accordance with that described in the literature (Figures S19 and S20).¹¹

2-(4-Methylphenyl)-1,3-dithiane (3b), colorless solid, 126 mg, 82%): M.p. 78–80 °C; ¹H NMR (400 MHz, CDCl₃) δ = 1.93 (dtt, *J* = 14.2, 12.4, 3.2 Hz, 1H, 5-CH^{ax}), 2.17 (dtt, *J* = 14.2, 4.4, 2.5, 1H, 5-CH^{eq}), 2.33 (s, 3H, CH₃), 2.90 (ddd, *J* = 14.4, 4.4, 3.2 Hz, 2H, 4,6-CH^{eq}), 3.06 (ddd, *J* = 14.4, 12.4 2.5 Hz, 2H, 4,6-CH^{ax}), 5.14 (s, 1H, CH), 7.15 (d, *J* = 7.8 Hz, 2H, ArH), 7.36 (d, *J* = 8.0 Hz, 2H, ArH); ¹³C NMR (126 MHz, CDCl₃) δ = 21.3, 25.3, 32.3, 51.4, 127.7, 129.6, 136.3, 138.4; Elemental analysis: calcd for C₁₁H₁₄S₂: C 62.81, H 6.71; found: C 62.83, H 6.72. The proton is in accordance with that described in the literature (Figure S21).¹²

2-Phenyl-1,3-dithiane (3c), colorless solid, 122 mg, 84%): M.p. 69 °C; ¹H NMR (400 MHz, CDCl₃) δ = 1.94 (dtt, *J* = 14.0, 12.5, 3.2 Hz, 1H, 5-CH^{ax}), 2.18 (dtt, *J* = 14.0, 4.5, 2.5, 1H, 5-CH^{eq}), 2.92 (ddd, *J* = 14.3, 4.5, 3.2 Hz, 2H, 4,6-CH^{eq}), 3.07 (ddd, *J* = 14.3, 12.5 2.5 Hz, 2H, 4,6-CH^{ax}), 5.17 (s, 1H, CH), 7.27–7.37 (m, 3H, ArH), 7.47 (d, *J* = 7.0 Hz, 2H, ArH); ¹³C NMR (126 MHz, CDCl₃) δ = 25.2, 32.2, 51.7, 127.9, 128.6, 128.9, 139.2; Elemental analysis: calcd for C₁₀H₁₂S₂: C 61.18, H 6.16; found: C 61.06, H 5.99. The proton is in accordance with that described in the literature (Figure S23).¹²

2-(4-Chlorophenyl)-1,3-dithiane (3d), colorless solid, 146 mg, 86%): M.p. 83–85 °C; ¹H NMR (400 MHz, CDCl₃) δ = 1.93 (dtt, *J* = 14.2, 12.4, 3.2 Hz, 1H, 5-CH^{ax}), 2.18 (dtt, *J* = 14.2, 4.4, 2.5, 1H, 5-CH^{eq}), 2.91 (ddd, *J* = 14.6, 4.4, 3.2 Hz, 2H, 4,6-CH^{eq}), 3.06 (ddd, *J* = 14.6, 12.4 2.5 Hz, 2H, 4,6-CH^{ax}), 5.13 (s, 1H, CH), 7.35 (d, *J* = 8.7 Hz, 2H, ArH), 7.47 (d, *J* = 8.5 Hz, 2H, ArH); ¹³C NMR (126 MHz, CDCl₃) δ = 25.1, 32.1, 50.8, 129.1, 129.3, 134.3, 137.7; Elemental analysis: calcd for C₁₀H₁₁S₂Cl: C 52.05, H 4.80; found: C 51.95, H 4.88. The proton is in accordance with that described in the literature (Figure S25).¹²

2-(4-Bromophenyl)-1,3-dithiane (3e), colorless solid, 148 mg, 73%): M.p. 86–88 °C; ¹H NMR (400 MHz, CDCl₃): δ = 1.93 (dtt, *J* = 14.2, 12.4, 3.2 Hz, 1H, 5-CH^{ax}), 2.18 (dtt, *J* = 14.2, 4.4, 2.5, 1H, 5-CH^{eq}), 2.91 (ddd, *J* = 14.4, 4.4, 3.2 Hz, 2H, 4,6-CH^{eq}), 3.05 (ddd, *J* = 14.4, 12.4 2.5 Hz, 2H, 4,6-CH^{ax}), 5.12 (s, 1H, CH), 7.35 (d, *J* = 8.2 Hz, 2H, ArH), 7.47 (d, *J* = 8.5 Hz, 2H, ArH); ¹³C NMR (126 MHz, CDCl₃) δ = 25.1, 32.1, 50.9, 122.4, 129.6, 132.0, 138.3; Elemental analysis: calcd for C₁₀H₁₁S₂Br: C 43.64, H 4.03; found: C 43.60, H 4.06. The proton and ¹³C are in accordance with that described in the literature (Figures S27 and S28).¹¹

2-(3,4-Methylenedioxyphenyl)-1,3-dithiane (3f), colorless solid, 131 mg, 74%): M.p. 84–85 °C; ¹H NMR (400 MHz, CDCl₃) δ = 1.91 (dtt, *J* = 14.0, 12.5, 3.2 Hz, 1H, 5-CH^{ax}), 2.16 (dtt, *J* = 14.0, 4.3,

2.3, 1H, 5-CH^{eq}), 2.90 (ddd, $J = 14.5, 4.1, 3.4$ Hz, 2H, 4,6-CH^{eq}), 3.05 (ddd, $J = 14.5, 12.5, 2.3$ Hz, 2H, 4,6-CH^{ax}), 5.09 (s, 1H, CH), 5.96 (s, 2H, CH₂) 6.76 (d, $J = 8.2$ Hz, 1H, ArH), 6.94 (dd, $J = 1.8, 8.2$ Hz, 1H, ArH), 6.98 (d, $J = 1.8$ Hz, 1H, ArH); ¹³C NMR (126 MHz, CDCl₃) $\delta = 25.2, 32.3, 51.4, 101.4, 108.5, 121.5, 133.0, 147.8, 147.9$; Elemental analysis: calcd for C₁₁H₁₂O₂S₂: C 54.97, H 5.03; found: C 54.76, H 5.07. The proton is in accordance with that described in the literature (Figure S29).¹²

2-tert-Butyl-1,3-dithiane (3g), yellowish oil, 76 mg, 59%): ¹H NMR (400 MHz, CDCl₃) $\delta = 1.12$ (s, 9H, CH₃), 1.80 (dqⁱⁿ, $J = 14.0, 8.0$ Hz, 1H, 5-CH^{ax}), 2.08 (dqⁱⁿ, $J = 14.0, 3.2$ Hz, 1H, 5-CH^{eq}), 2.89 (dd, $J = 8.0, 3.2$ Hz, 4H, 4,6-CH₂), 4.00 (s, 1H, CH); ¹³C NMR (126 MHz, CDCl₃) $\delta = 25.9, 27.8, 31.2, 35.7, 61.9$; The proton and ¹³C are in accordance with that described in the literature (Figures S31 and S32).¹¹

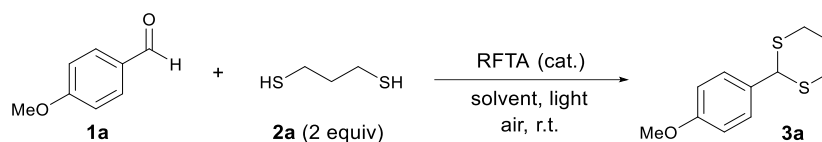
2-Isopropyl-1,3-dithiane (3h), crude): ¹H NMR (400 MHz, CDCl₃) $\delta = 1.10$ (d, $J = 6.9$ Hz, 6H), 1.86 (m, 1H), 1.97–2.15 (m, 2H), 2.88 (m, 4H), 4.04 (d, $J = 5.0$ Hz, 1H); The proton is in accordance with that described in the literature (Figure S33).¹³

2-(4-Methoxyphenyl)-1,3-dithiolane (4), colorless solid, 133 mg, 85%): M.p. 59–60 °C; ¹H NMR (400 MHz, CDCl₃) $\delta = 3.30$ – 3.39 (m, 2H, CH₂), 3.45– 3.55 (m, 2H, CH₂), 3.80 (s, 3H, CH₃), 5.64 (s, 1H, CH), 6.84 (d, $J = 8.6$ Hz, 2H, ArH), 7.45 (d, $J = 8.6$ Hz, 2H, ArH); ¹³C NMR (126 MHz, CDCl₃) $\delta = 40.4, 55.5, 56.2, 114.0, 129.3, 131.9, 159.5$; The proton is in accordance with that described in the literature (Figures S34 and S35).¹⁴

II-2. Optimization of reaction conditions

In addition to Table 1, the following experiments were carried out for optimizing reaction conditions, in which light was irradiated during the entire reaction (Table S1).

Table S1. Photoinduced thioacetalization of **1a** with **2a** under different conditions.



entry	RFTA (mol%)	light / power (W)	solvent	time (h)	yield (%) ^a
1	5	blue LED / 0.3	CH ₃ CN	1	52
2	5	blue LED / 0.3	CH ₃ OH	1	27
3	5	blue LED / 0.3	CH ₂ Cl ₂	1	18
4	5	blue LED / 0.3	EtOAc	1	2
5	5	blue LED / 0.3	THF	1	0
6	5	blue LED / 0.3	DMF	1	0
7	5	blue LED / 0.3	CH ₃ CN	6	95
8	3	blue LED / 0.3	CH ₃ CN	6	99
9	1	blue LED / 0.3	CH ₃ CN	6	80
10	5	room light	CH ₃ CN	1	0
11	5	blue LED / 0.06	CH ₃ CN	6	93
12	5	blue LED / 0.14	CH ₃ CN	6	98
13	5	blue LED / 1.1	CH ₃ CN	6	85
14	3	UV LED / 0.3	CH ₃ CN	6	96
15	3	green LED / 0.3	CH ₃ CN	6	81

^a Determined by ¹H NMR analysis.

II-3. Determination of the quantum yield of reaction

Two 20 μ glass tubes were charged with aqueous potassium ferrioxalate (2 mM, 3.5 mL) and both were bubbled with nitrogen gas for a minute and sealed with a cap. One of them (solution A) was irradiated by LED light at room temperature (465 nm, 0.3 W ($I_F = 100$ mA), distance of 1 cm) for 30 seconds, while the other one (solution B) was standing under room light. The solution A and B (1.0 mL) were added to a mixture of aqueous phenanthroline (0.1 w/v%, 2 mL) and buffer (0.54 M H₂SO₄ and 1.8 M AcONa, 0.25 mL), respectively, and then standing under light-shielding conditions for 30 min. The absolute number of photons absorbed by the reaction system was determined to be 1.98×10^{19} per an hour (3.29×10^{-5} mol/h) by UV/vis spectroscopy using a calibration curve, prepared in advance, labeled with “concentration of Fe(phen)₃SO₄” and “absorbance at 510 nm” for the X-axis and the Y-axis, respectively (Figure S1). Since the present reaction using 0.735 mmol of **1a** and 1.47 mmol of **2a** gave **3a** in 36% yield in 1 hour (2.65×10^{-4} mol/h), the corresponding quantum yield Φ was calculated to be 8.1.

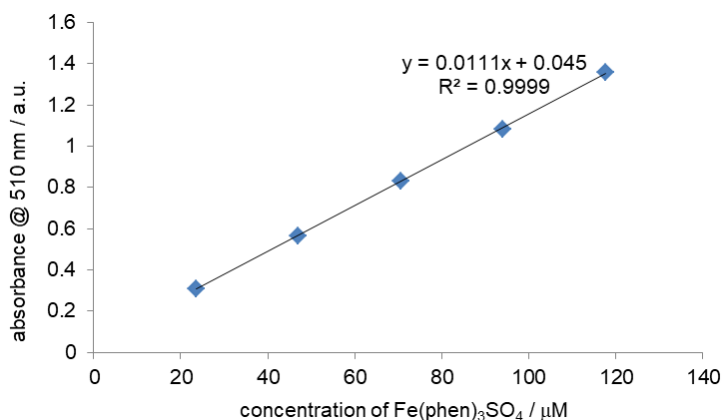


Figure S1. Calibration curve used for determining the absolute number of photons absorbed by the reaction system.

II-4. Competitive reaction using *p*-substituted benzaldehydes (Hammett plot)

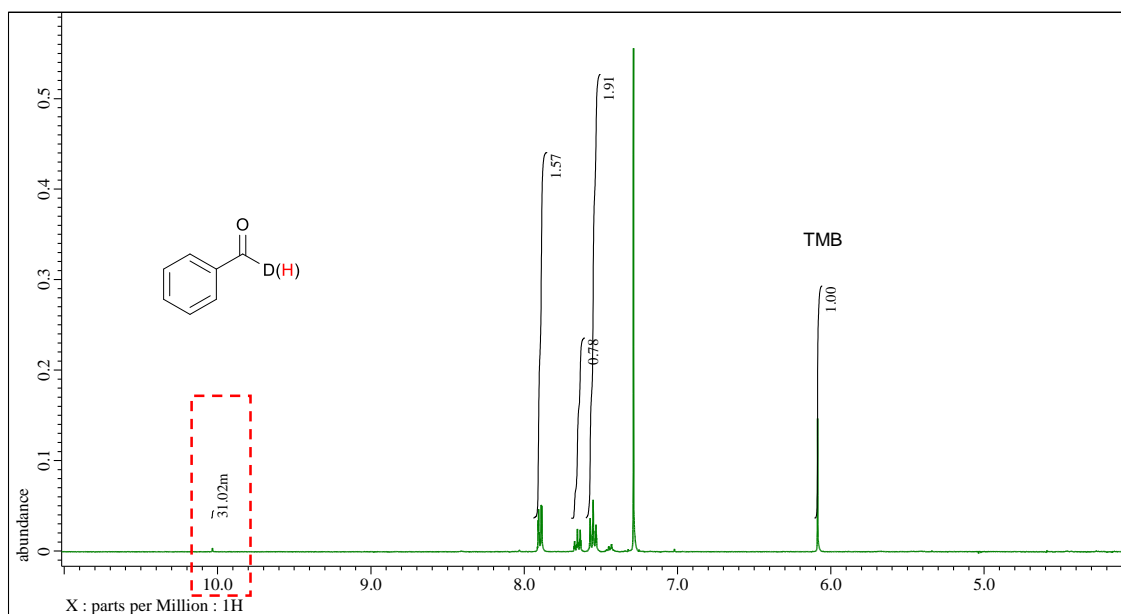
A 20 μ glass tube was charged with benzaldehyde (0.73 mmol), *p*-substituted benzaldehyde (0.73 mmol), **2a** (79.0 mg, 0.73 mmol), RFTA (11.9 mg, 21.9 μ mol, 3 mol%), 1,3,5-trimethoxybenzene (40.4 mg, 0.24 mmol) as an internal standard, and acetonitrile (3.5 mL), which was stirred and irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under air for 1 h. The reaction mixture was analyzed by ¹H NMR spectroscopy. The product ratios were determined on the basis of the integration of the methine protons, which were observed at $\delta = 5.14$ (*p*-OMe), 5.15 (*p*-Me), 5.18 (*p*-H), 5.14 (*p*-Cl), 5.13 (*p*-Br), and 5.25 ppm (*p*-NO₂), respectively. The results are summarized below (Table S2).

Table S2. Data for the Hammett plot (Fig. 3)

R	yield (%)		σ	k_R/k_H	$\log(k_R/k_H)$
	R	H			
-OMe	24	13	-0.268	1.846	0.266
-Me	18	13	-0.17	1.385	0.141
-H	—	—	0	1	0
-Cl	5	10	0.227	0.5	-0.301
-Br	6.5	13	0.227	0.5	-0.301
-NO ₂	1	13	0.778	0.0769	-1.114

II-5. Deuterium labeling experiment

A 20 μ glass tube was charged with benzaldehyde-d₁ (78.6 mg, 0.735 mmol), **2a** (0.159 g, 1.47 mmol), RFTA (11.9 mg, 21.9 μ mol), 1,3,5-trimethoxybenzene (TMB) as an internal standard, and acetonitrile (3.5 mL), which was stirred and irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under air for 6.5 h. The reaction mixture was analyzed by ¹H NMR spectroscopy, which revealed that the reaction proceeded quantitatively and the deuterium remained intact in the corresponding dithiane product (Figures S2 and S3).

Figure S2. ¹H NMR spectrum for the reaction mixture before irradiation (CDCl₃).

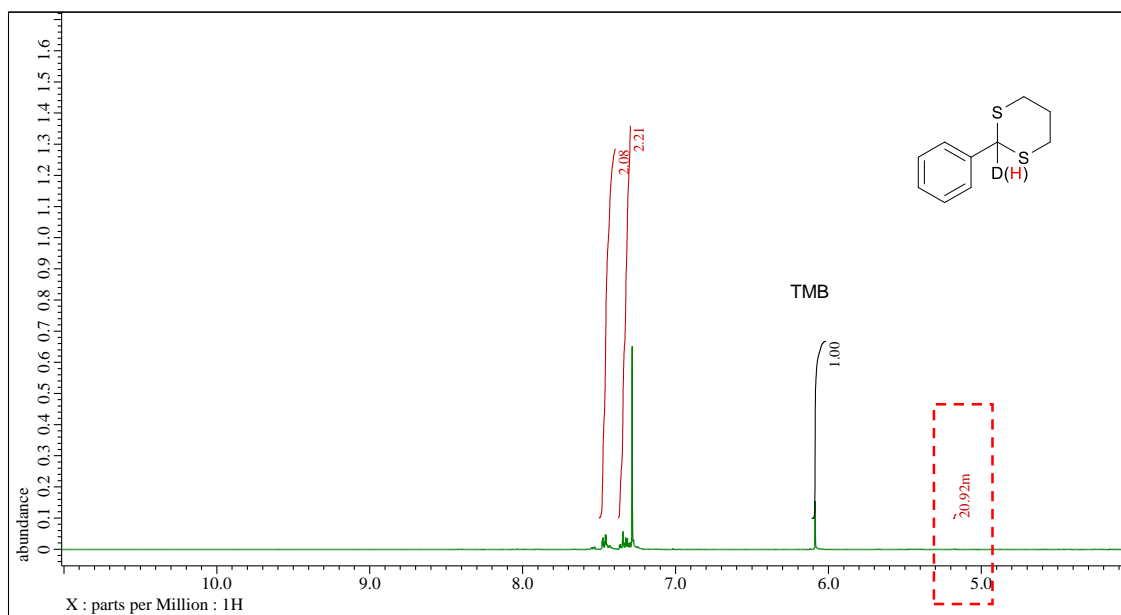


Figure S3. ^1H NMR spectrum for the reaction mixture after 6.5 h irradiation (CDCl_3).

II-6. Characterization of the product of *S,O*-acetalization

2-(4-Methoxyphenyl)-1,3-oxathiane (colorless solid): M.p. 92–93 °C; ^1H NMR (500 MHz, CDCl_3) δ = 1.76 (ddq, J = 14.0, 3.0, 2.3 Hz, 1H, 5- CH^{eq}), 2.09 (dtt, J = 14.0, 12.6, 4.0, 1H, 5- CH^{ax}), 2.82 (dtd, J = 13.2, 3.4, 1.4 Hz, 1H, SCH^{eq}), 3.21 (td, J = 13.2, 2.9 Hz, 1H, SCH^{ax}), 3.78 (td, J = 12.3, 2.0 Hz, 1H, OCH^{ax}), 3.80 (s, 3H, OCH_3), 4.32 (dddd, J = 12.3, 4.0, 2.3, 1.4 Hz, 1H, OCH^{eq}), 5.73 (s, 1H, CH), 6.87 (d, J = 8.6 Hz, 2H, ArH), 7.39 (d, J = 8.9 Hz, 2H, ArH); ^{13}C NMR (126 MHz, CDCl_3) δ = 25.8, 29.4, 55.4, 70.9, 84.3, 113.9, 127.7, 131.9, 159.8 (Figures S36 and S37).

II-7. Qualitative indication of the acidity of irradiated solution

A mixture of RFTA (11.4 mg, 20.9 μmol), **2a** (0.159 g, 1.47 mmol), and acetonitrile (3.5 mL) was irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under air for 30 minutes (Figures S4, a to b), and aqueous methyl orange (6.1 mM, 0.5 mL) was added. The resulting solution turned red (Figure S4, c). On the other hand, such a change of color by adding the same indicator was not observed without the pre-irradiation (Figure S4, d). In addition, to the above red solution was added triethylamine (3 μL , 21 μmol), which provided the original color (Figure S4, e). These results show that the acidity of the solution has increased by the irradiation due to in situ generated catalytic amount of acidic species.

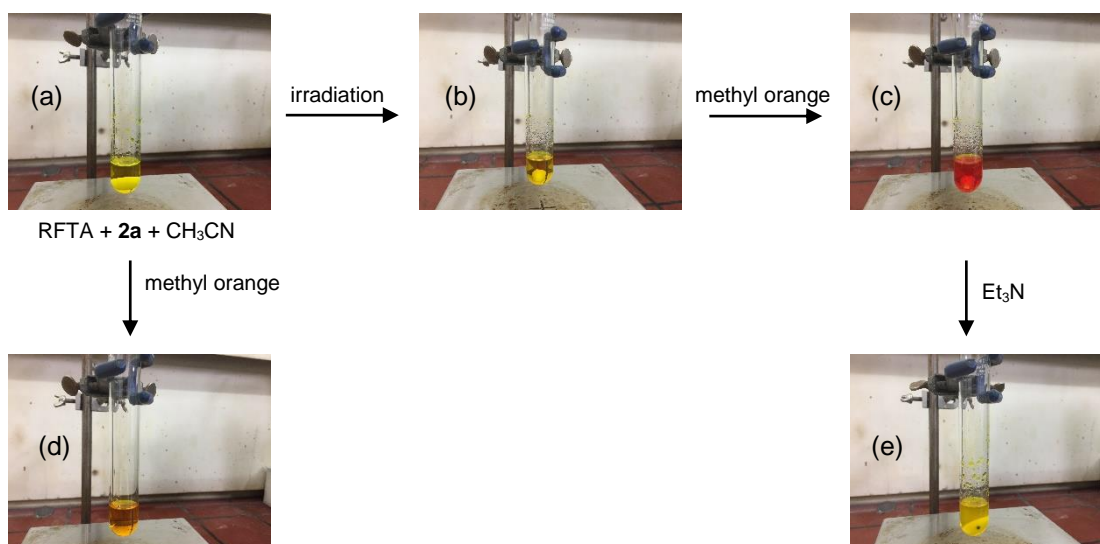


Figure S4. Qualitative indication of the acidity of irradiated solution.

II-8. Monitoring the formation of hydrogen peroxide

To a mixture of hydrogen peroxide (30%, 3.4 mg, 30 μmol) and acetonitrile (3.5 mL) was added NaI (0.2 g). A 0.1 mL of the resulting yellow solution was diluted to 10 mL with acetonitrile using a volumetric flask (*solution A*), which was analyzed by UV-Vis spectroscopy (Figure S5a). The characteristic absorption of I_3^- formed was clearly observed ($\lambda_{\text{max}} = 360 \text{ nm}$).

A mixture of RFTA (11.4 mg, 20.9 μmol), **2a** (0.159 g, 1.47 mmol), and acetonitrile (3.5 mL) was irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under air for 30 minutes, and a 0.1 mL of the reaction mixture was diluted to 10 mL with acetonitrile using a volumetric flask (*solution B*). All the residual reaction mixture was treated with NaI (0.2 g), and a 0.1 mL of the resulting solution was diluted to 10 mL with acetonitrile in the same way (*solution C*). Absorption spectrum of the *solution C* was measured with baseline set up by using the *solution B*, in which distinct peaks for I_3^- were not clearly observed (Figure S5b). These results indicate that the formation of hydrogen peroxide (in other words, recycling of RFTA) during the irradiation may take place in little.

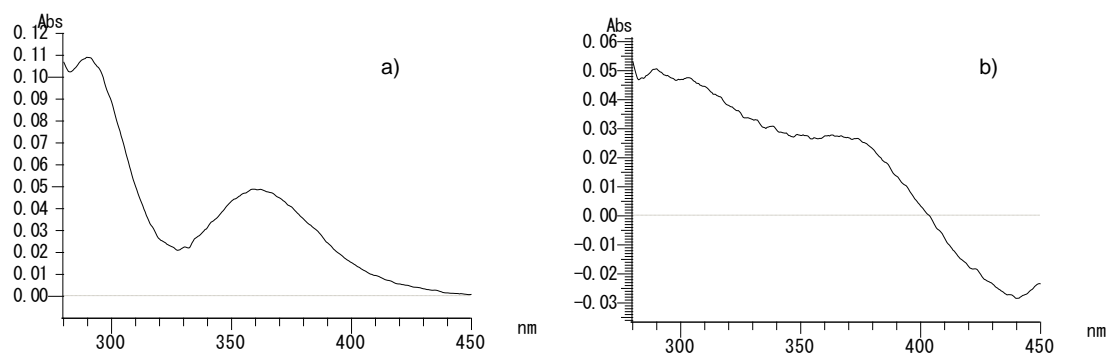


Figure S5. Absorption spectra for a) the *solution A* and b) the *solution C* (measured with baseline set up by using the *solution B*)

III. Fluorescence quenching experiment

Fluorescence spectra of RFTA in the absence and presence of **1a** and/or **2a** at different concentrations are shown below (Figure S6–S8), indicating that a high possibility of electron transfer between the excited state of RFTA and **2a**.

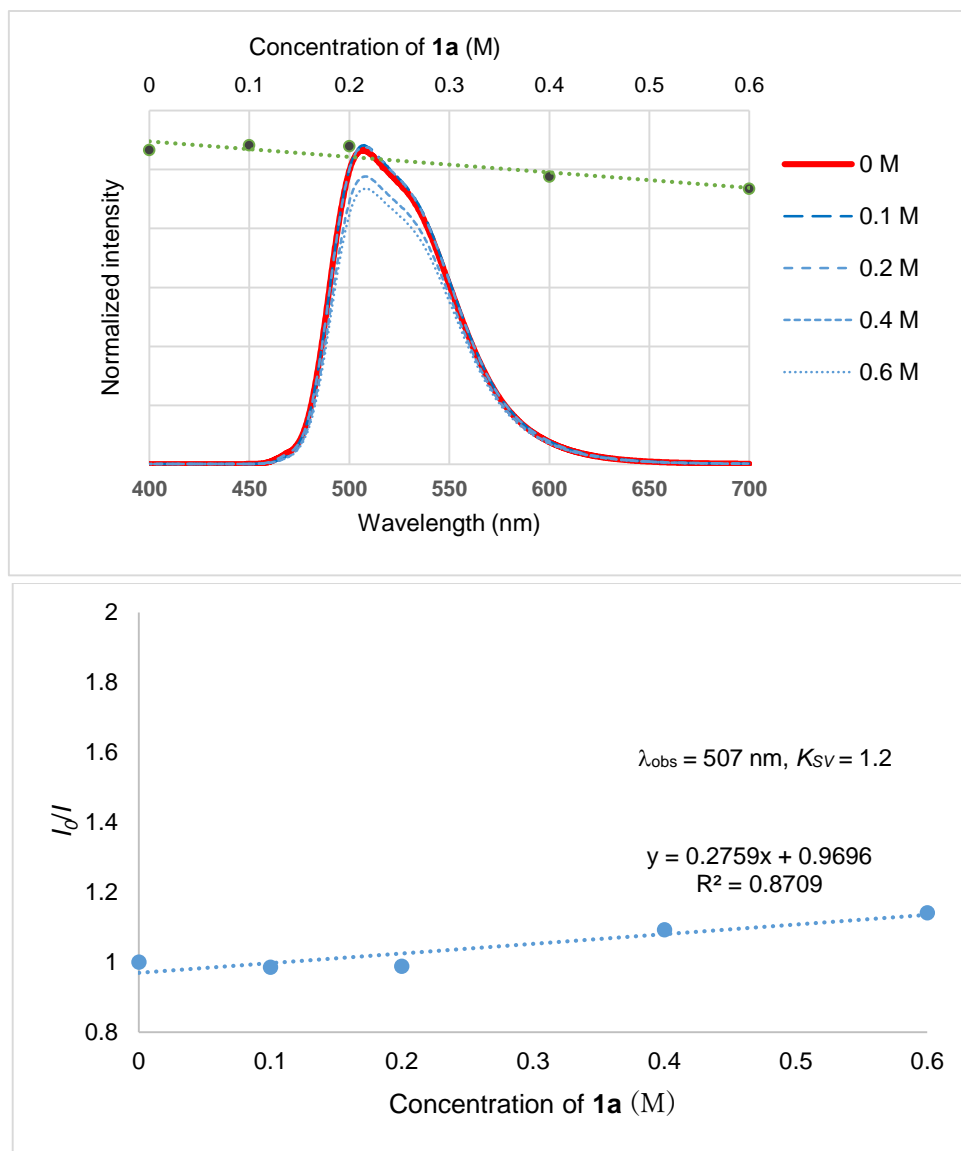


Figure S6. Fluorescence spectra of RFTA in acetonitrile (0.1 mM) in the absence and the presence of **1a** at different concentrations (0.1 M, 0.2 M, 0.4 M, 0.6 M) and the corresponding Stern-Volmer plot ($\lambda_{\text{ex}} = 465 \text{ nm}$).

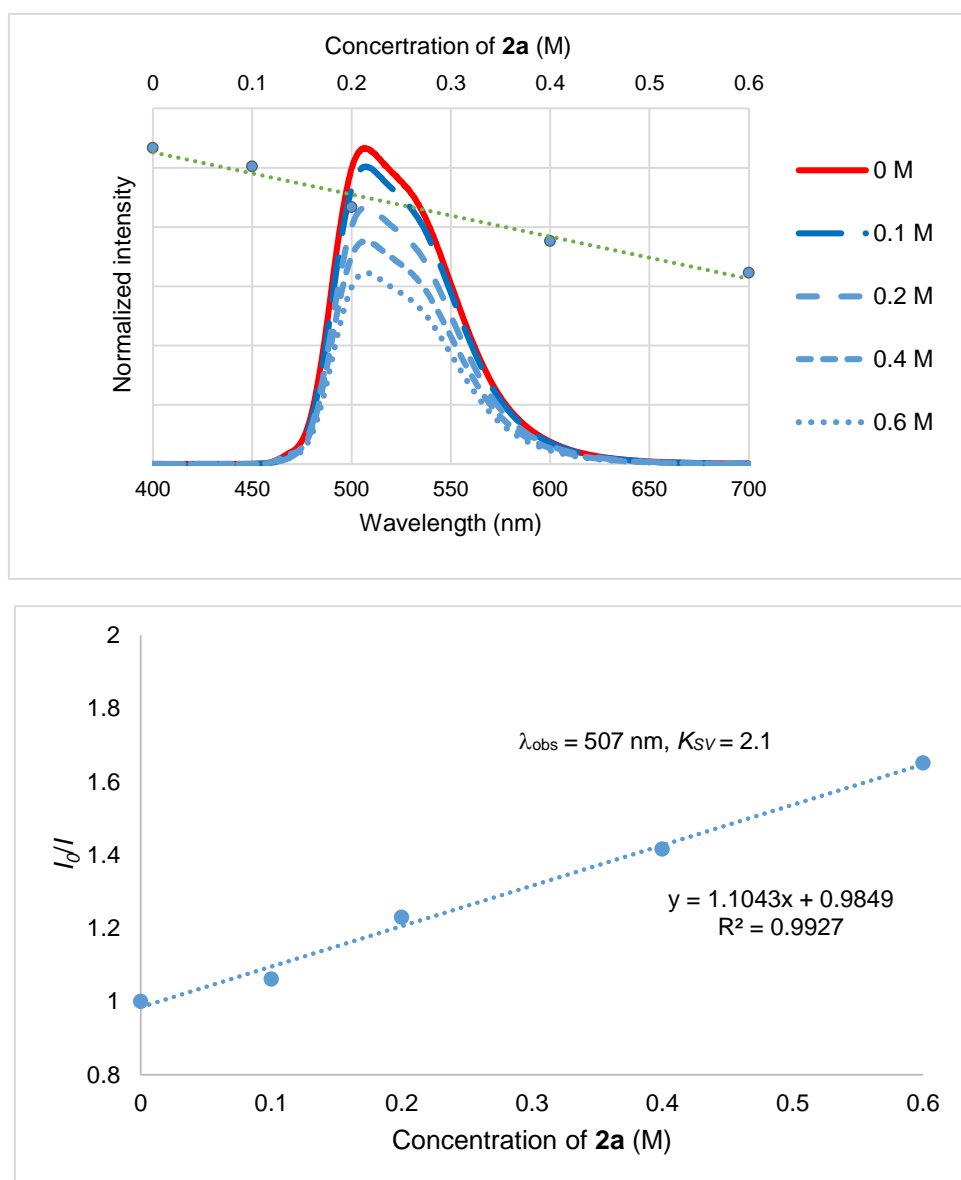


Figure S7. Fluorescence spectra of RFTA in acetonitrile (0.1 mM) in the absence and the presence of **2a** at different concentrations (0.1 M, 0.2 M, 0.4 M, 0.6 M) and the corresponding Stern-Volmer plot ($\lambda_{\text{ex}} = 465 \text{ nm}$).

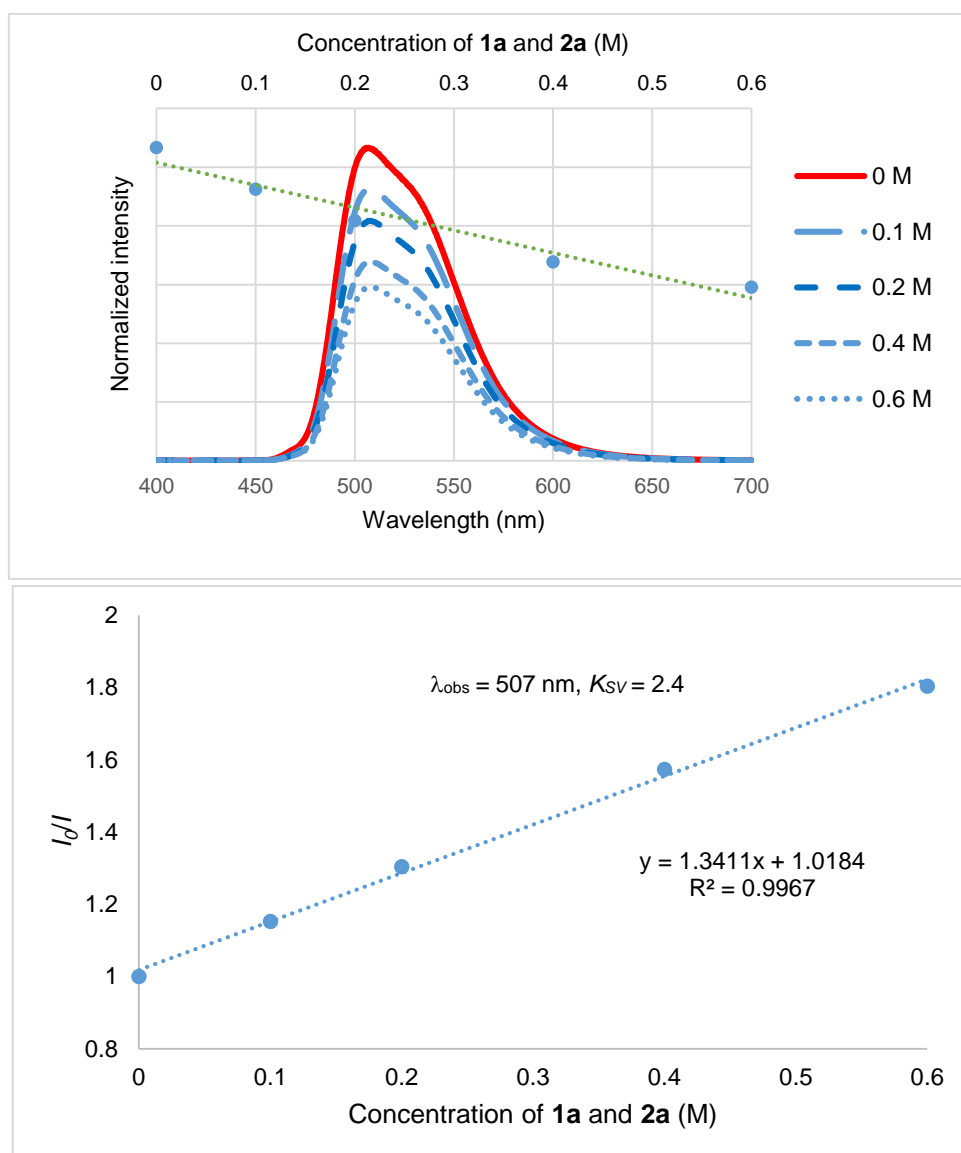


Figure S8. Fluorescence spectra of RFTA in acetonitrile (0.1 mM) in the absence and the presence of **1a** and **2a** at different concentrations (0.1 M, 0.2 M, 0.4 M, 0.6 M) and the corresponding Stern-Volmer plot ($\lambda_{\text{ex}} = 465 \text{ nm}$).

IV. Exposing thiols under the present reaction conditions in the absence of any aldehydes

A 20φ glass tube was charged with 1-dodecanethiol (0.297 g, 1.47mmol), RFTA (11.9 mg, 21.9 μmol), and acetonitrile (3.5 mL), which was stirred and irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under air. After 3 h, the reaction mixture analyzed by ¹H NMR spectroscopy was found to contain only 1-dodecanethiol and dodecyl disulfide¹⁵ in a ratio of 90:10 without any other products (Equation S1 and Figure S9).

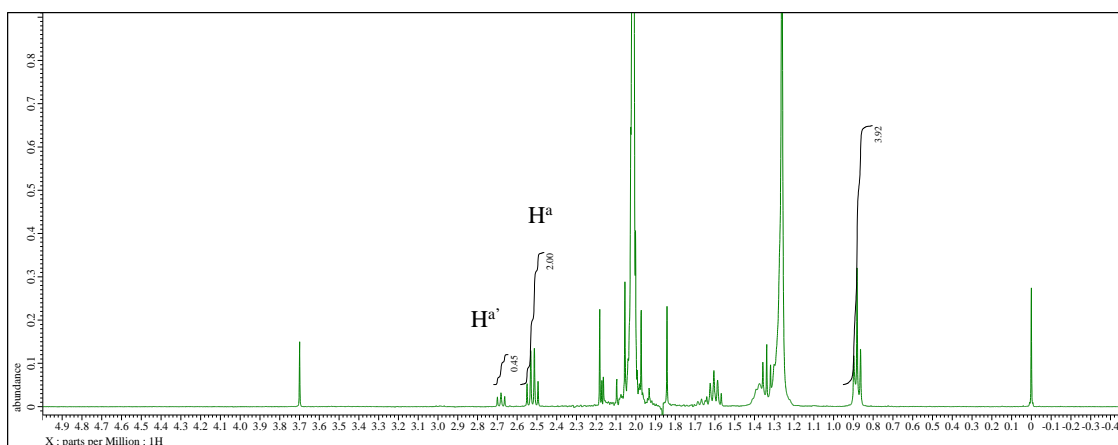
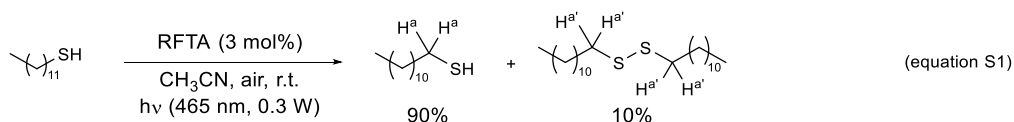
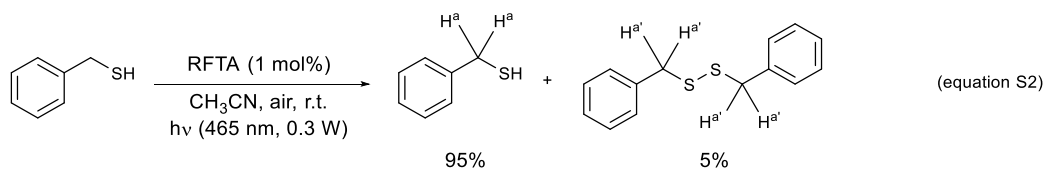


Figure S9. ¹H NMR spectrum for the reaction mixture of the equation S1 in CDCl₃.

A 20φ glass tube was charged with benzyl mercaptan (0.124 g, 1.00 mmol), RFTA (5.4 mg, 10.0 μmol), and acetonitrile (1 mL), which was stirred and irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under air. After 6 h, the reaction mixture analyzed by ¹H NMR spectroscopy was found to contain only benzyl mercaptan and benzyl disulfide in a ratio of 95:5 without any other products (Equation S2 and Figure S10).



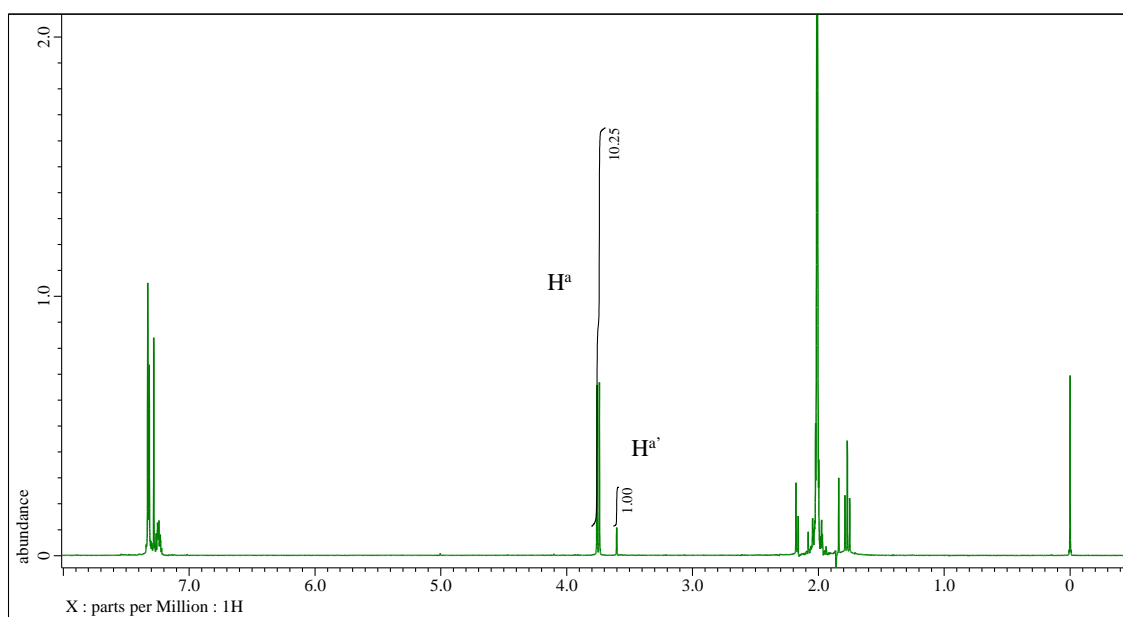


Figure S10. ^1H NMR spectrum for the reaction mixture of the equation S2 in CDCl_3 .

V. Catalytic Mannich-type reaction

V-1. Preparation of catalyst-containing solution

A 25 mL two-neck round bottom flask was charged with RFTA (12.9 mg, 23.7 μmol), 1-dodecanethiol (4.8 mg, 23.7 μmol), and acetonitrile (5.0 mL), which was stirred and irradiated by LED visible light (465 nm, 0.3 W, 1 cm distance) at room temperature under 1 atm of O_2 for 1 h. The resulting solution was immediately used as a catalyst-containing solution for the following catalytic reactions.

V-2. Typical procedure for reaction between imines and silyl enol ethers

To a mixture of the catalyst-containing solution (1.0 mL, 3 mol%), an imine (0.158 mmol), and 1,3,5-trimethoxybenzene (TMB) as an internal standard ($52.7 \mu\text{mol} \times f$) was added a silyl enol ether (0.474 mmol). The f value was determined by ^1H NMR spectrum of a pre-mixture containing imine, catalyst, TMB, and acetonitrile before adding silyl enol ether. The reaction mixture was stirred at room temperature under a nitrogen atmosphere for a defined reaction time and diluted with CH_2Cl_2 and treated with saturated aqueous NaHCO_3 solution. The organic layer was analyzed by ^1H NMR spectroscopy to determine the product yield (Figures S11–S15), which referred to the ^1H NMR spectral data described in the literature.^{16–18}

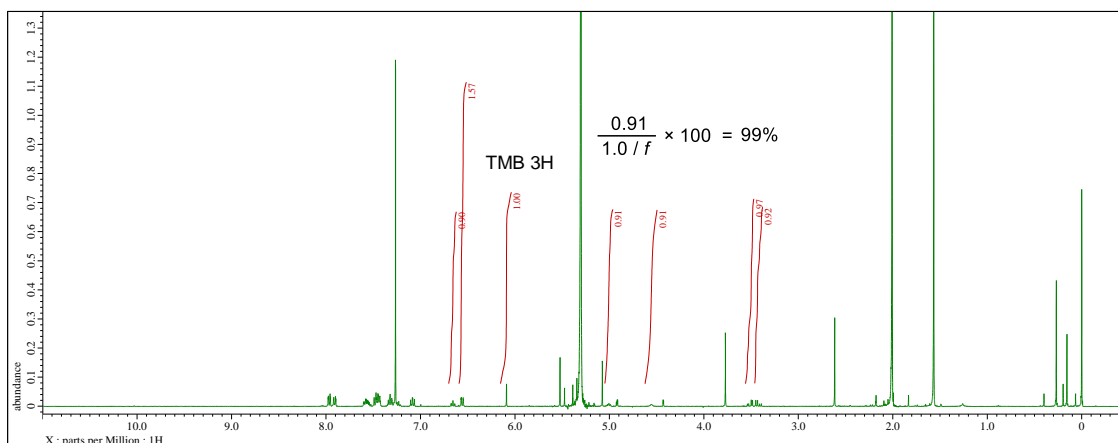


Figure S11. Determination of yield of **6a** in Fig. 3b by ^1H NMR spectroscopy (CDCl_3 , $f = 1.087$).¹⁶

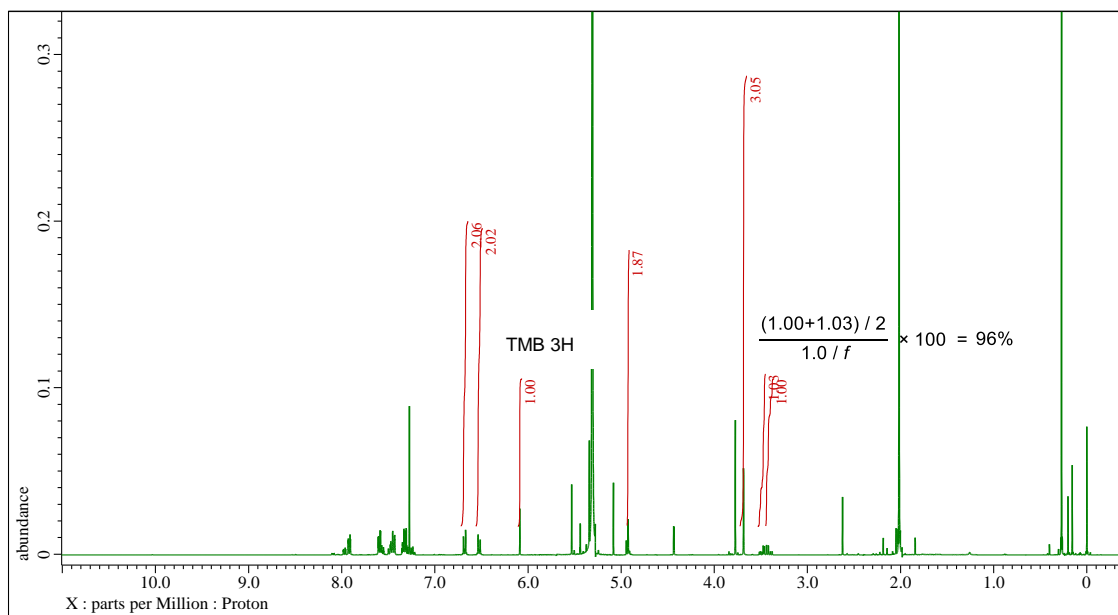


Figure S12. Determination of yield of **6b** in Fig. 3b by ^1H NMR spectroscopy (CDCl_3 , $f = 0.952$).¹⁶

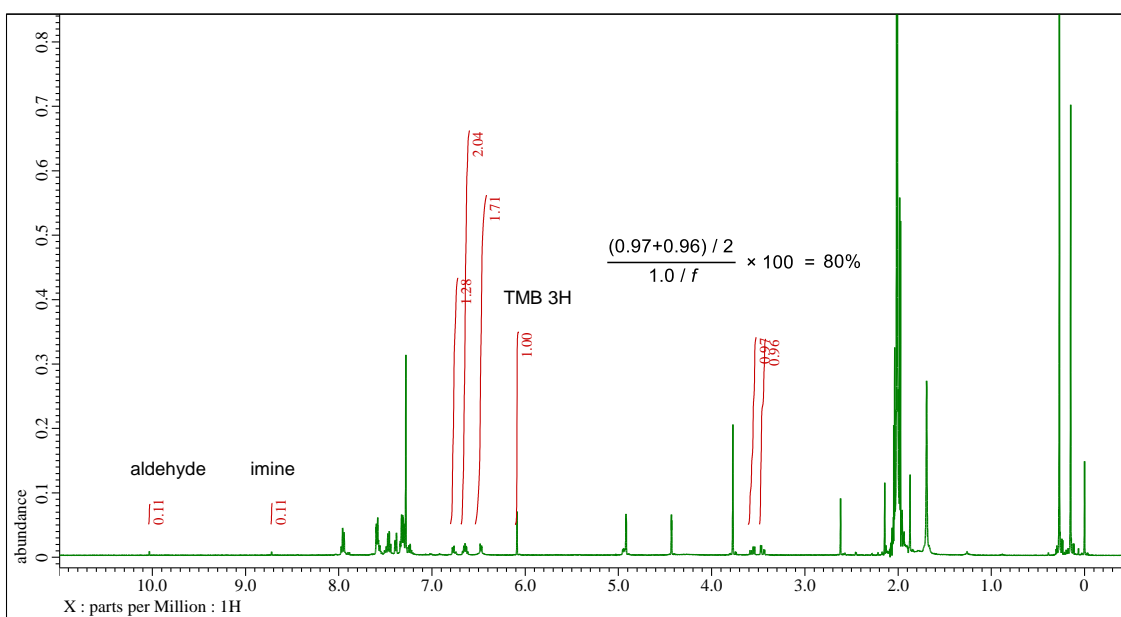


Figure S13. Determination of yield of **6c** in Fig. 3b by ^1H NMR spectroscopy (CDCl_3 , $f = 0.833$).¹⁷

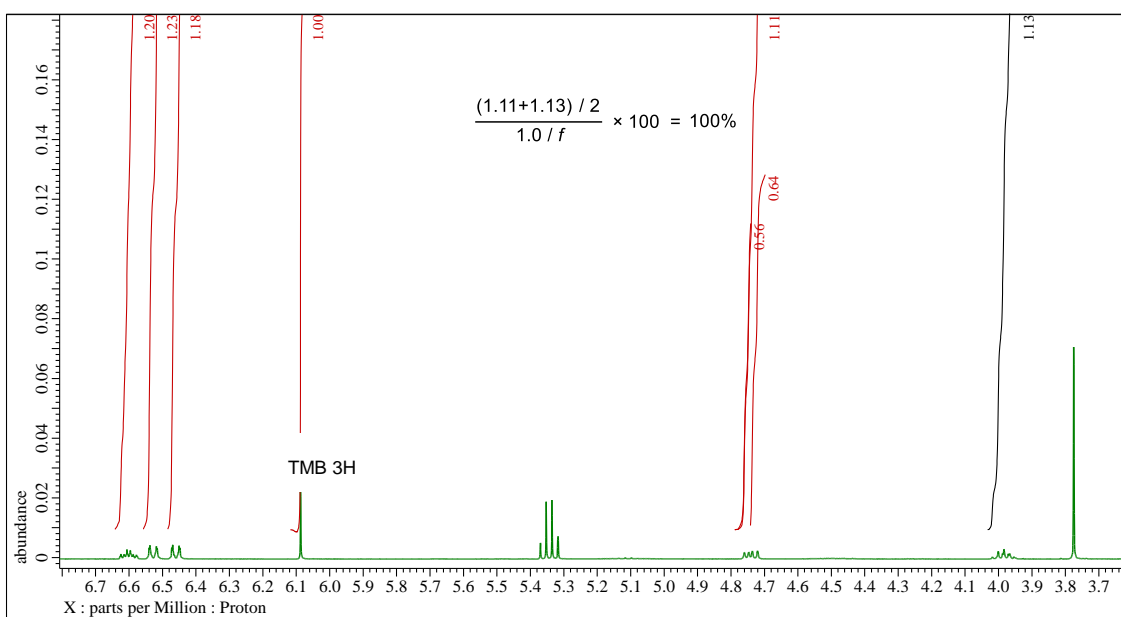


Figure S14. Determination of yield of **6d** in Fig. 3b by ^1H NMR spectroscopy (CDCl_3 , $f = 0.901$).¹⁶

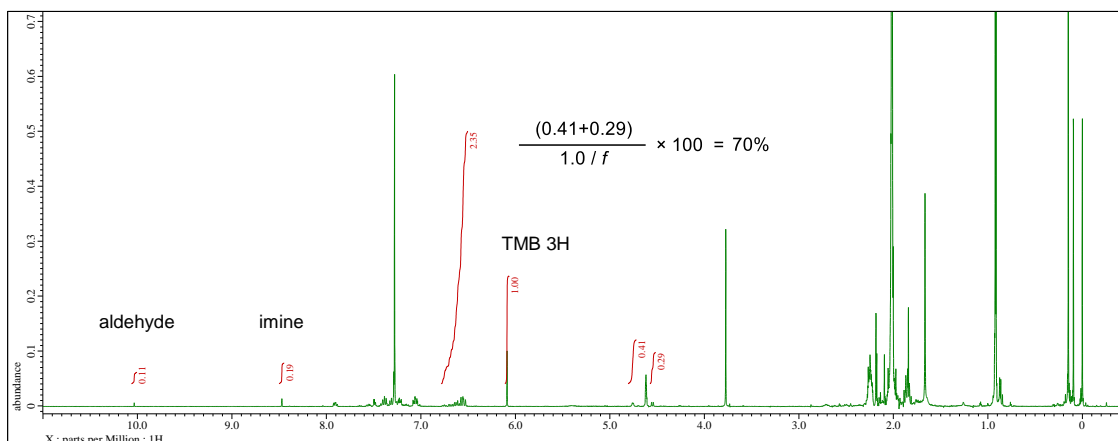


Figure S15. Determination of yield of **6e** in Fig. 3b by ^1H NMR spectroscopy (CDCl_3 , $f = 1.000$).¹⁸

V-3. Typical procedure for three-component reaction

To a mixture of an aldehyde (0.158 mmol), aniline (14.7 mg, 0.158 mmol), 1,3,5-trimethoxybenzene (TMB) as an internal standard ($52.7 \mu\text{mol} \times f$), and acetonitrile (1.0 mL) was added the catalyst-containing solution (1.0 mL, 3 mol%) and **5** (0.237 mmol). The f value was determined by ^1H NMR spectrum of a pre-mixture containing aldehyde, TMB, and acetonitrile before adding aniline. The reaction mixture was stirred at room temperature under a nitrogen atmosphere for a defined reaction time and diluted with CH_2Cl_2 and treated with saturated aqueous NaHCO_3 solution. The organic layer was analyzed by ^1H NMR spectroscopy to determine the product yield (Figures S16–S20), which referred to the ^1H NMR spectral data described in the literature.¹⁶

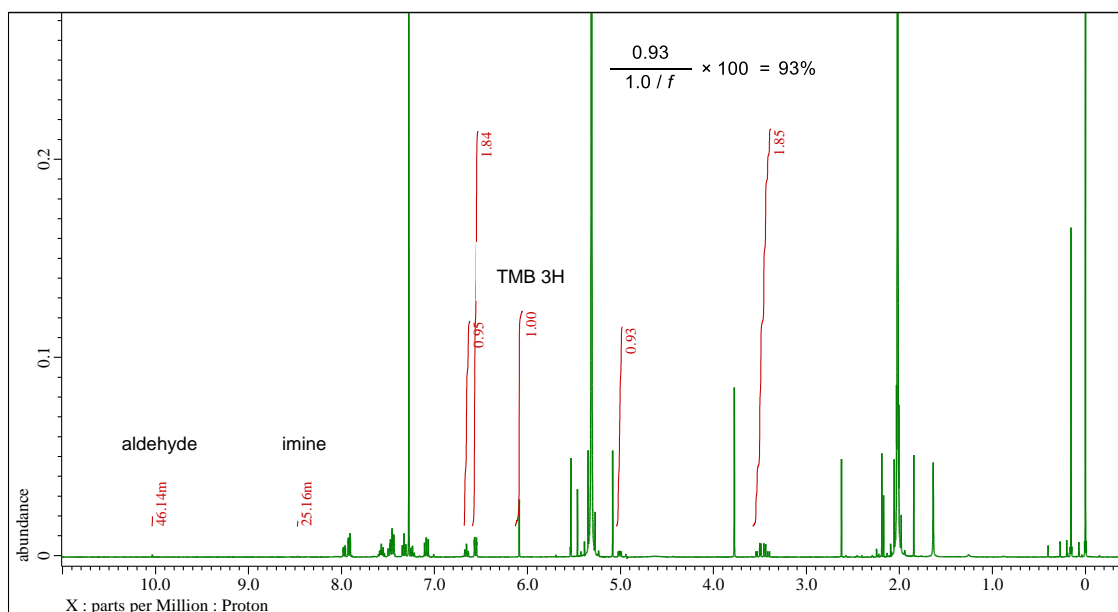


Figure S16. Determination of yield of **6a** in Fig. 3c by ^1H NMR spectroscopy (CDCl_3 , $f = 1.000$).¹⁶

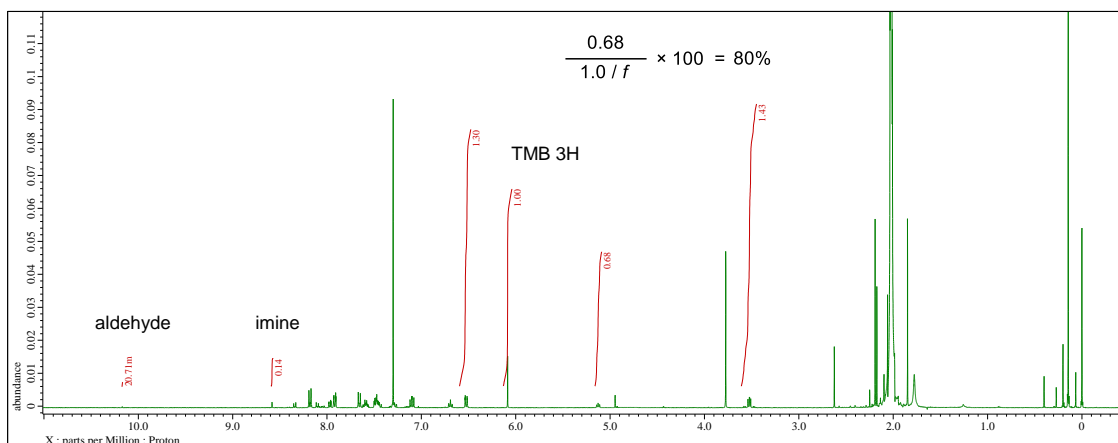


Figure S17. Determination of yield of **6f** in Fig. 3c by ^1H NMR spectroscopy (CDCl_3 , $f = 1.176$).¹⁶

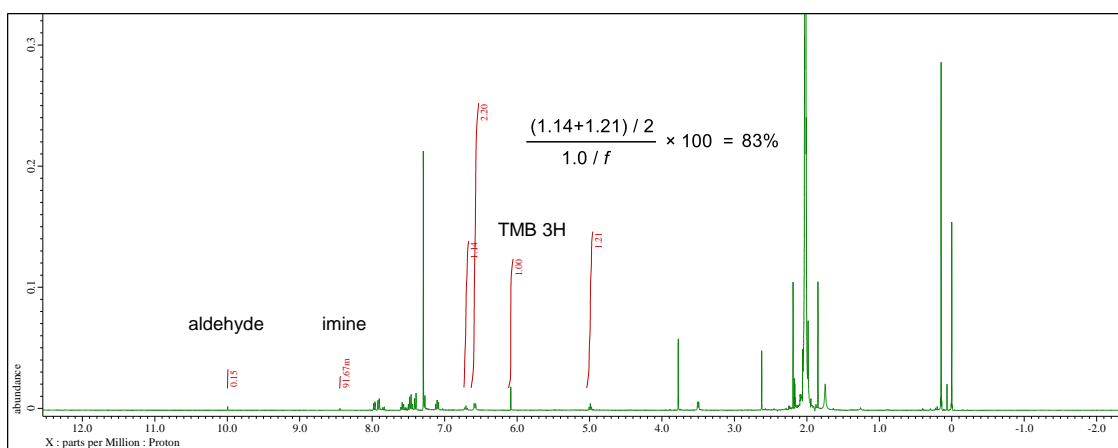


Figure S18. Determination of yield of **6g** in Fig. 3c by ^1H NMR spectroscopy (CDCl_3 , $f = 0.706$).¹⁶

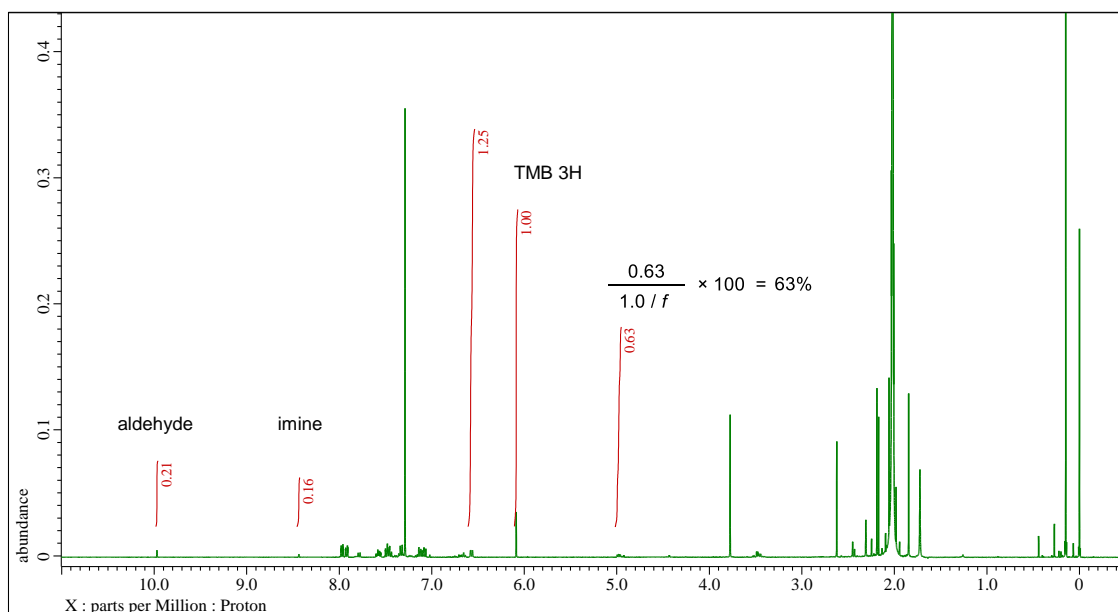


Figure S19. Determination of yield of **6h** in Fig. 3c by ^1H NMR spectroscopy (CDCl_3 , $f = 1.000$).¹⁶

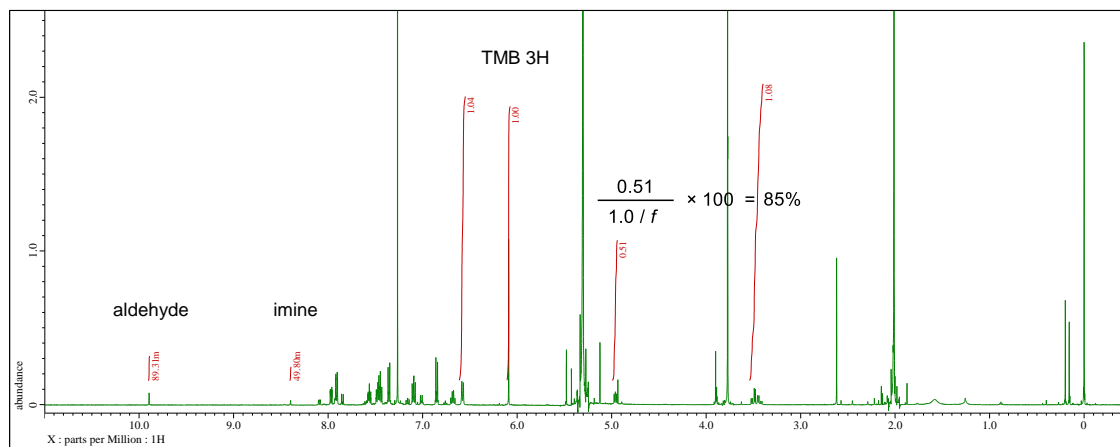


Figure S20. Determination of yield of **6i** in Fig. 3c by ^1H NMR spectroscopy (CDCl_3 , $f = 1.667$).¹⁶

VI. Spectral data

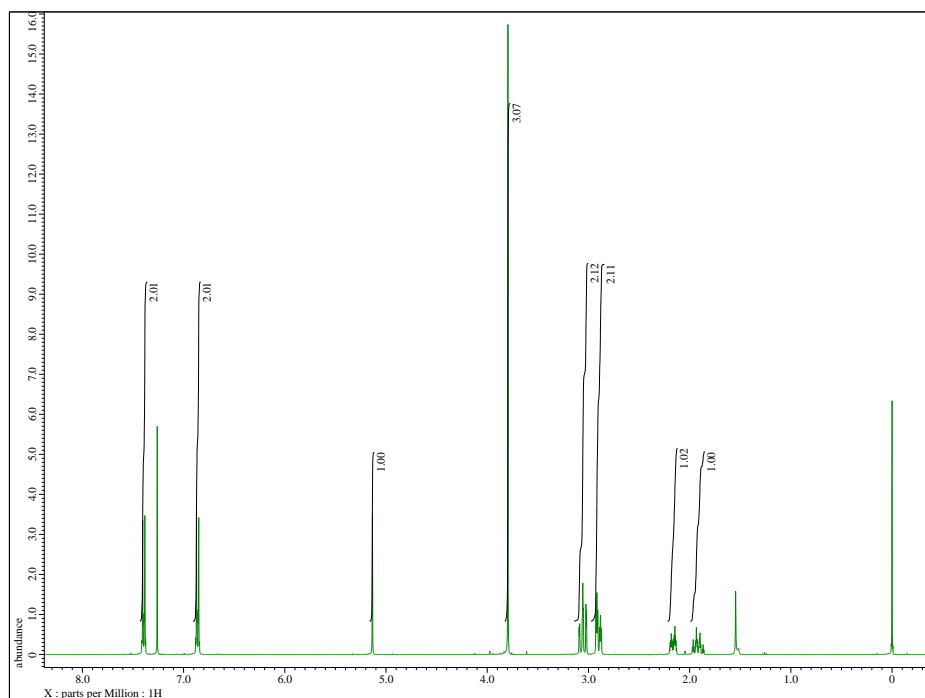


Figure S21. ¹H NMR Spectrum for **3a** in CDCl₃.

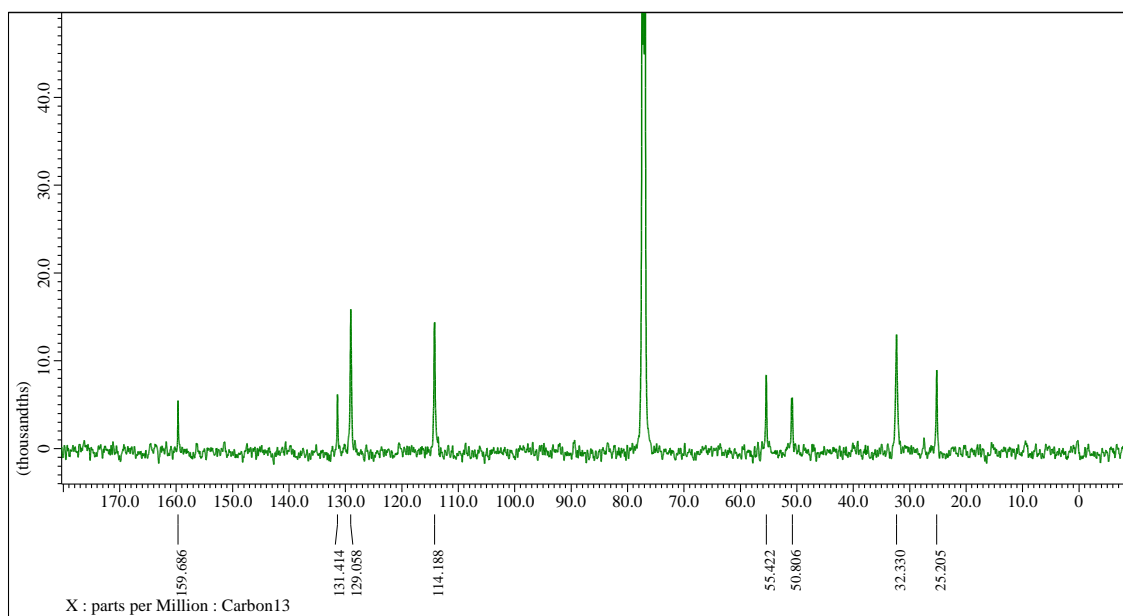


Figure S22. ¹³C NMR Spectrum for **3a** in CDCl₃.

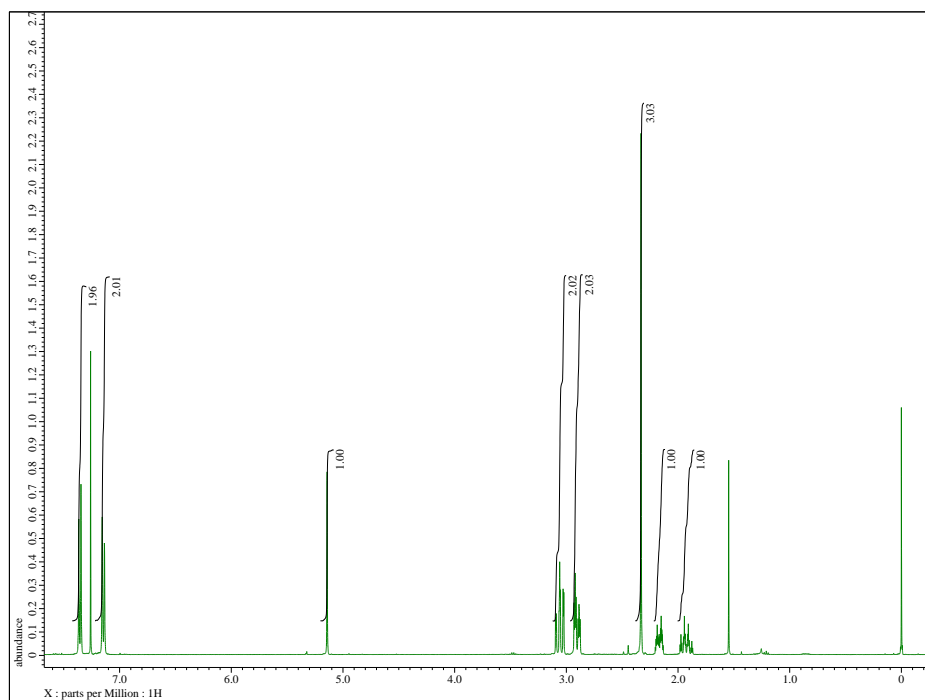


Figure S23. ^1H NMR Spectrum for **3b** in CDCl_3 .

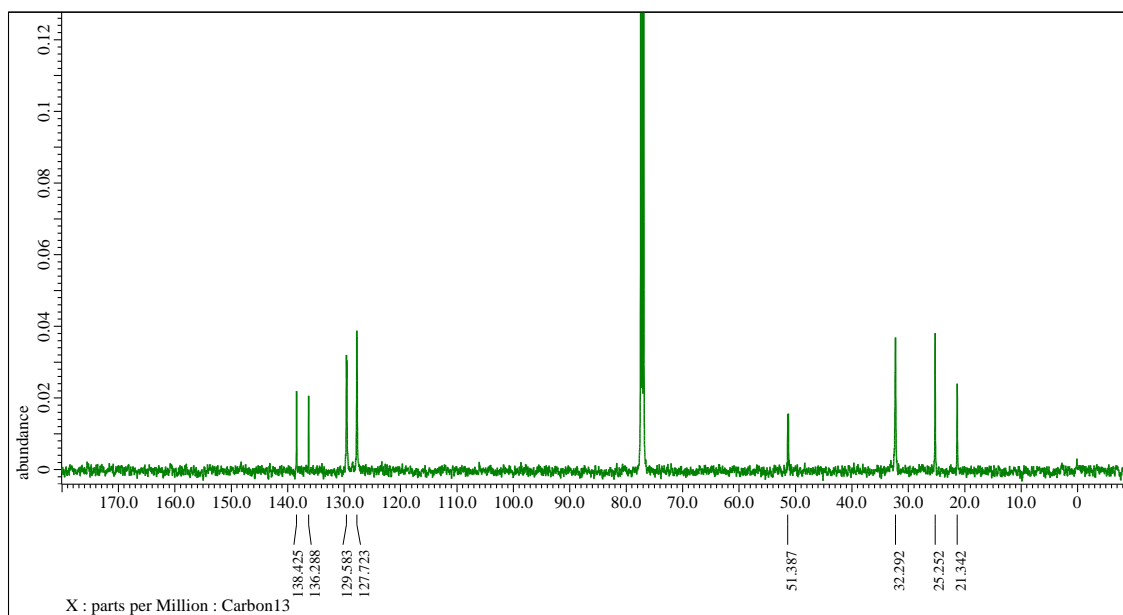


Figure S24. ^{13}C NMR Spectrum for **3b** in CDCl_3 .

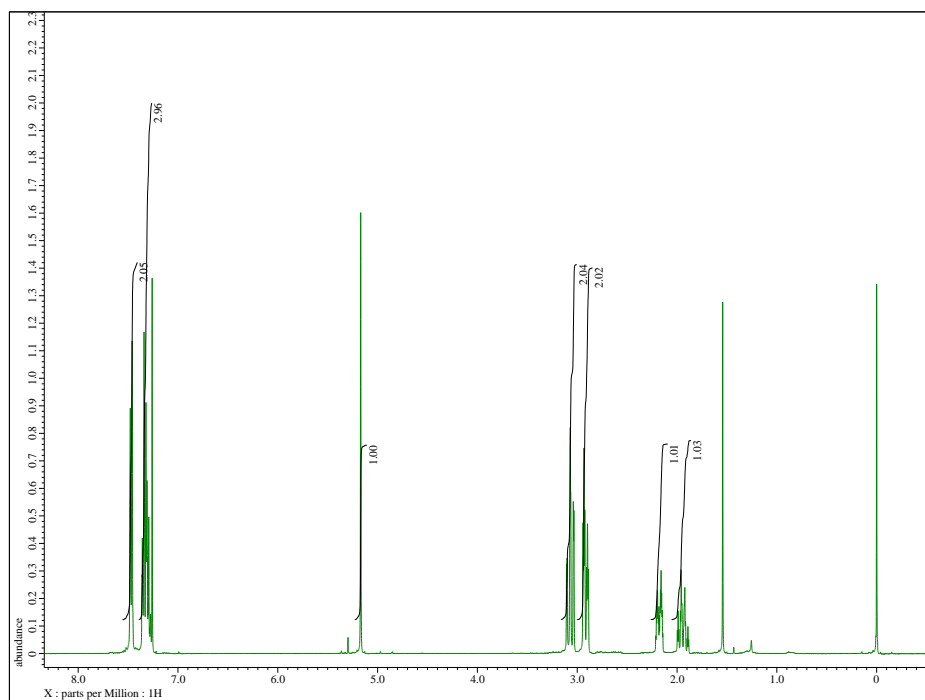


Figure S25. ^1H NMR Spectrum for **3c** in CDCl_3 .

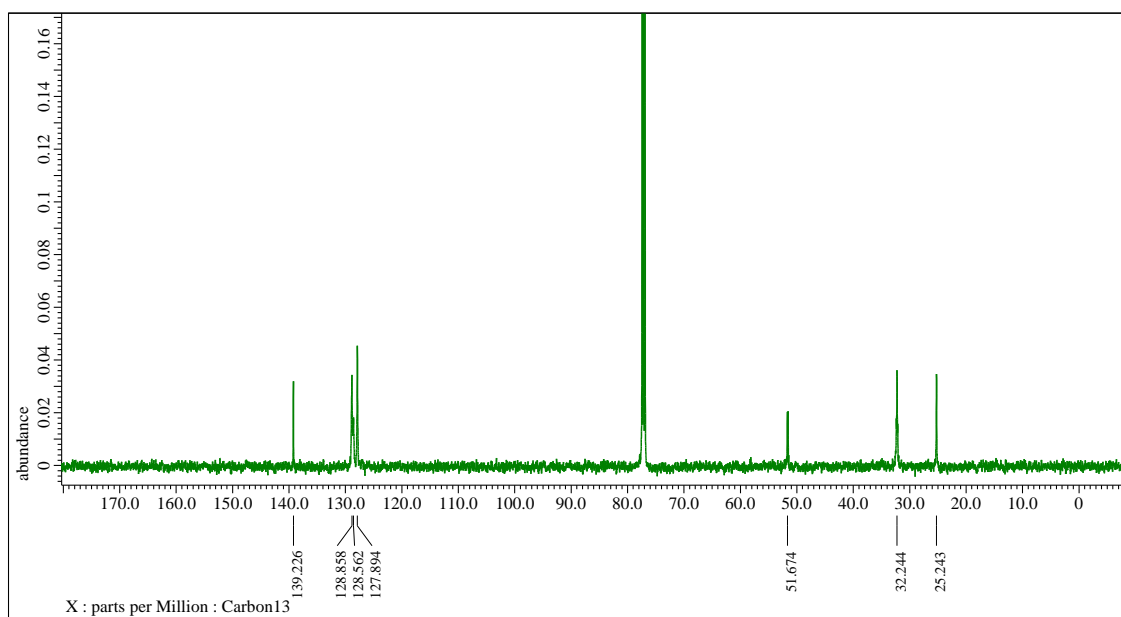


Figure S26. ^{13}C NMR Spectrum for **3c** in CDCl_3 .

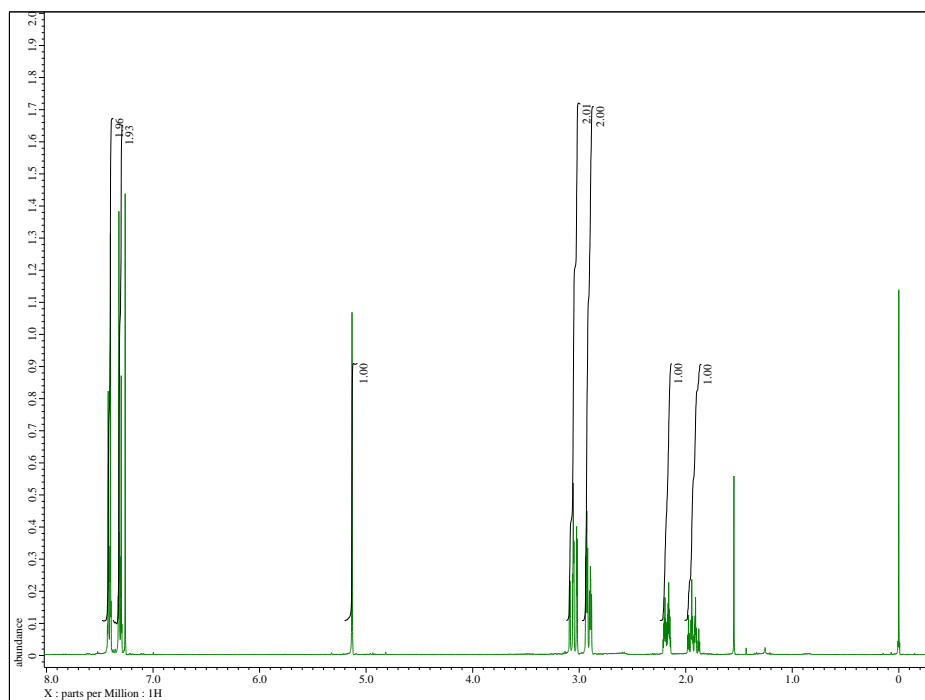


Figure S27. ^1H NMR Spectrum for **3d** in CDCl_3 .

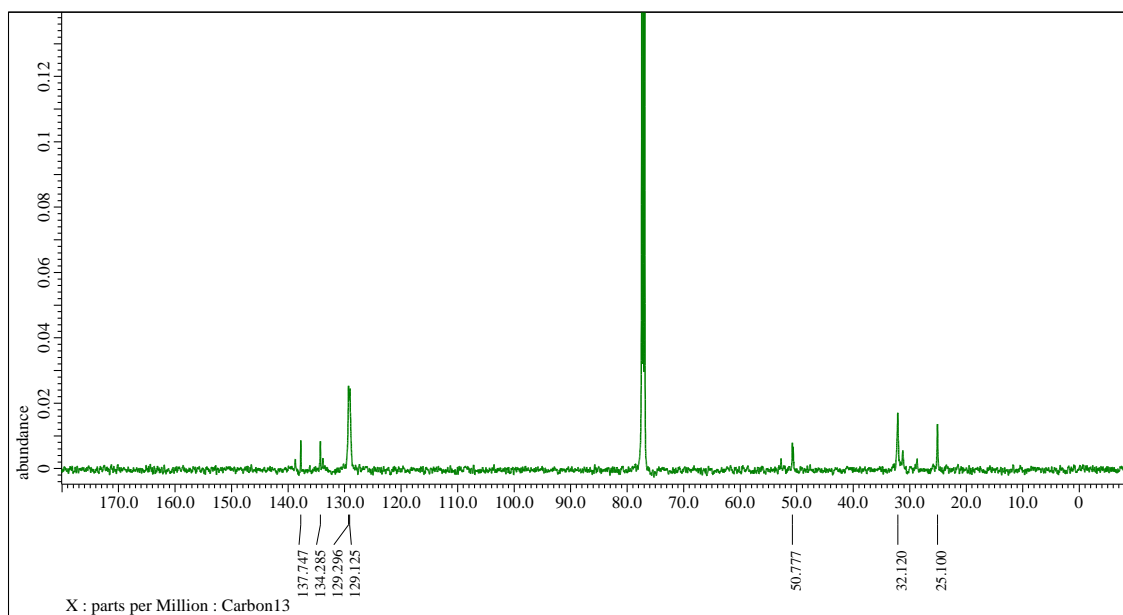
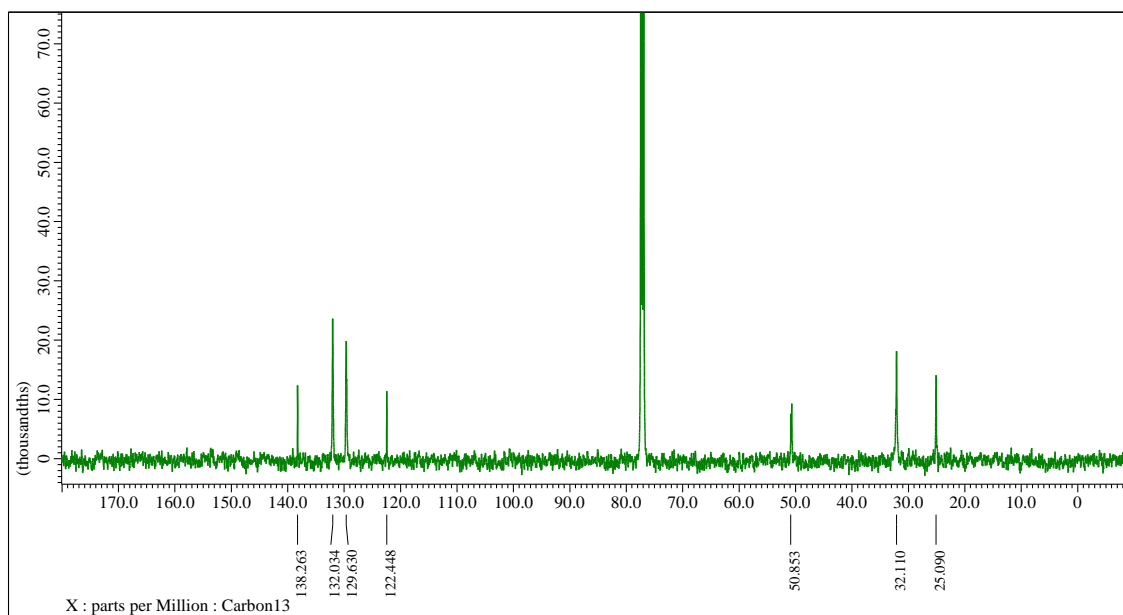
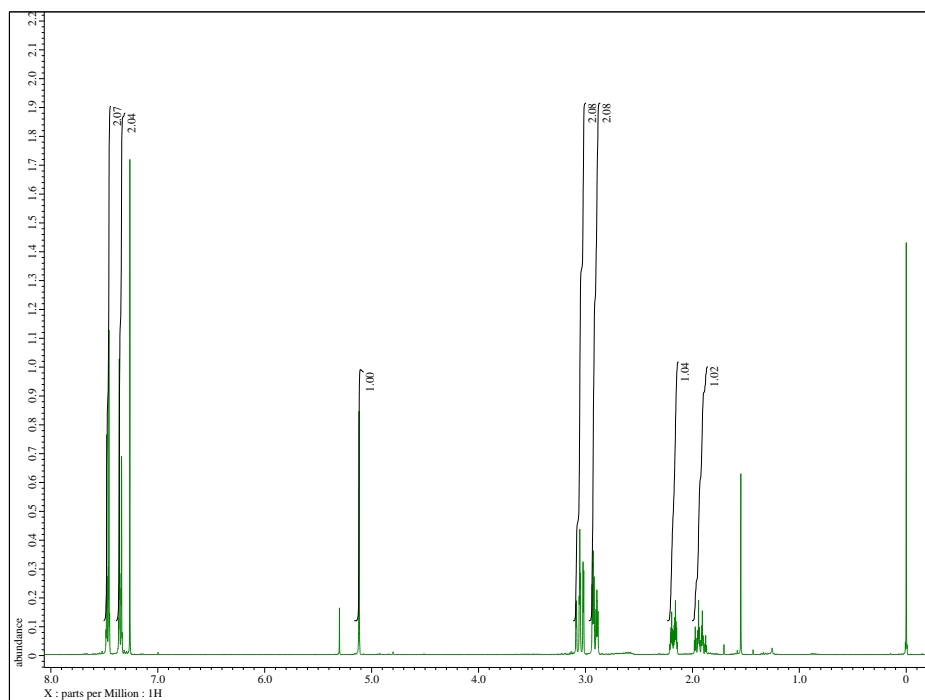


Figure S28. ^{13}C NMR Spectrum for **3d** in CDCl_3 .



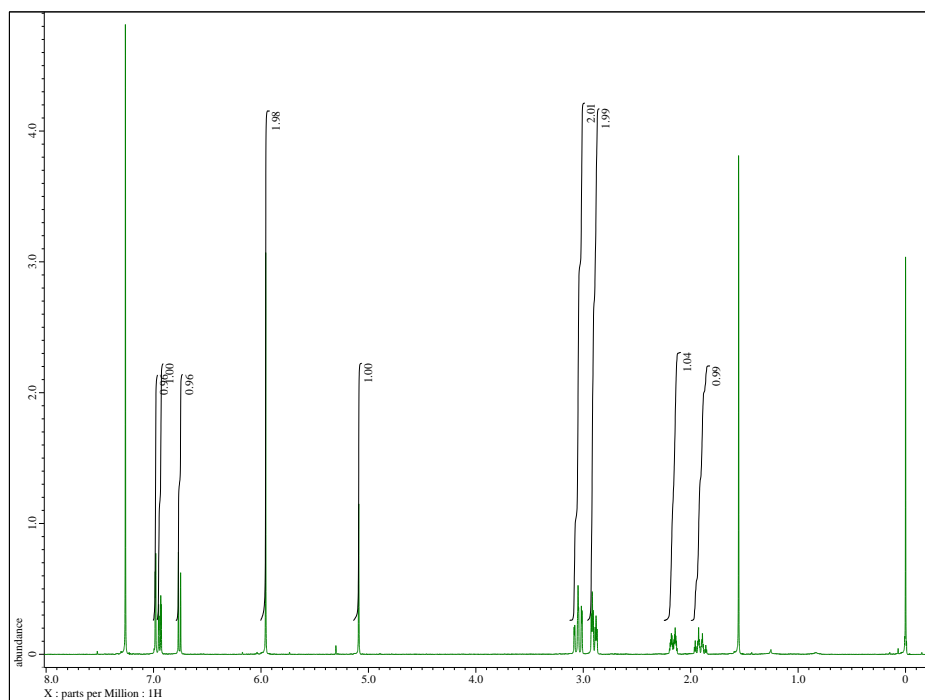


Figure S31. ^1H NMR Spectrum for **3f** in CDCl_3 .

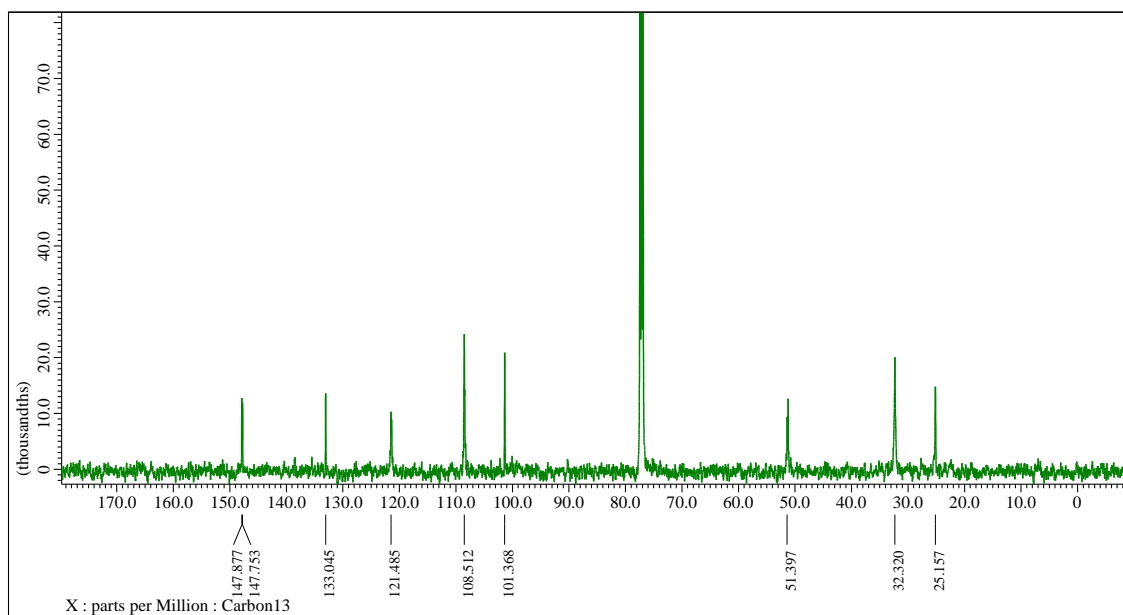


Figure S32. ^{13}C NMR Spectrum for **3f** in CDCl_3 .

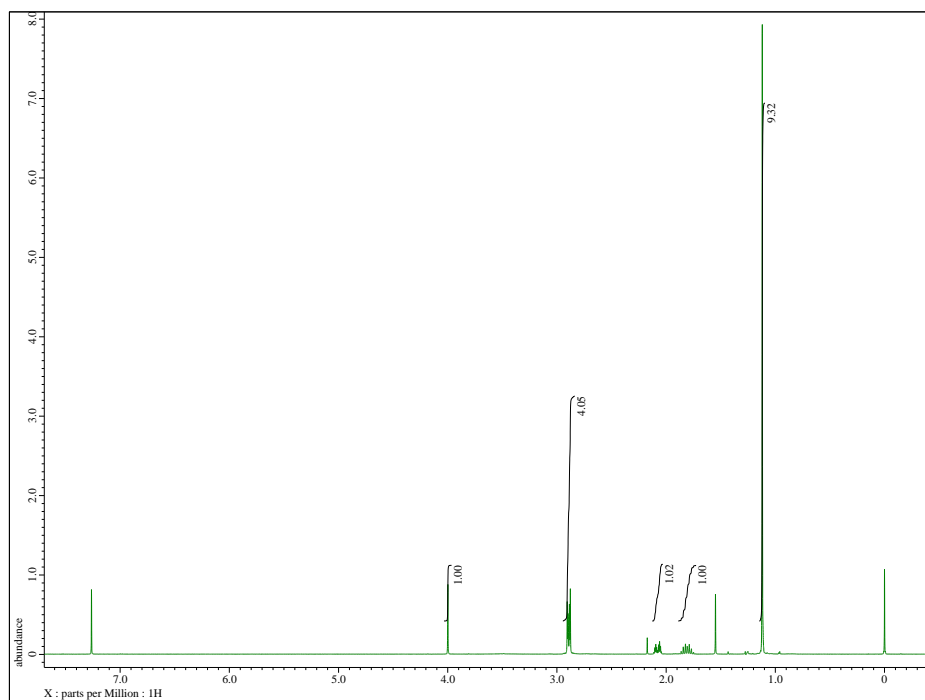


Figure S33. ^1H NMR Spectrum for **3g** in CDCl_3 .

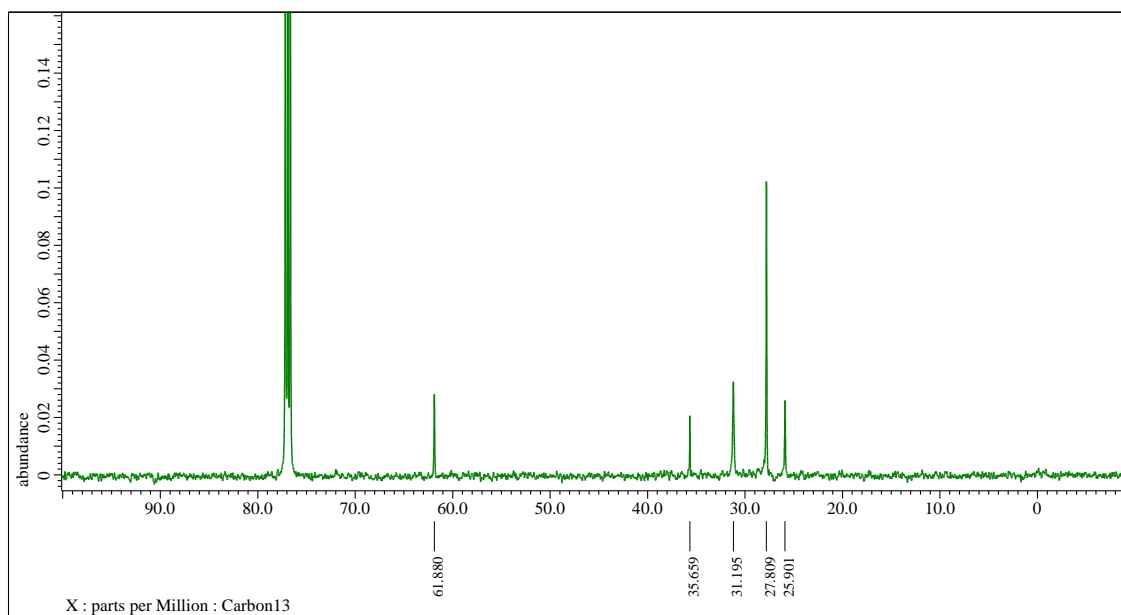


Figure S34. ^{13}C NMR Spectrum for **3g** in CDCl_3 .

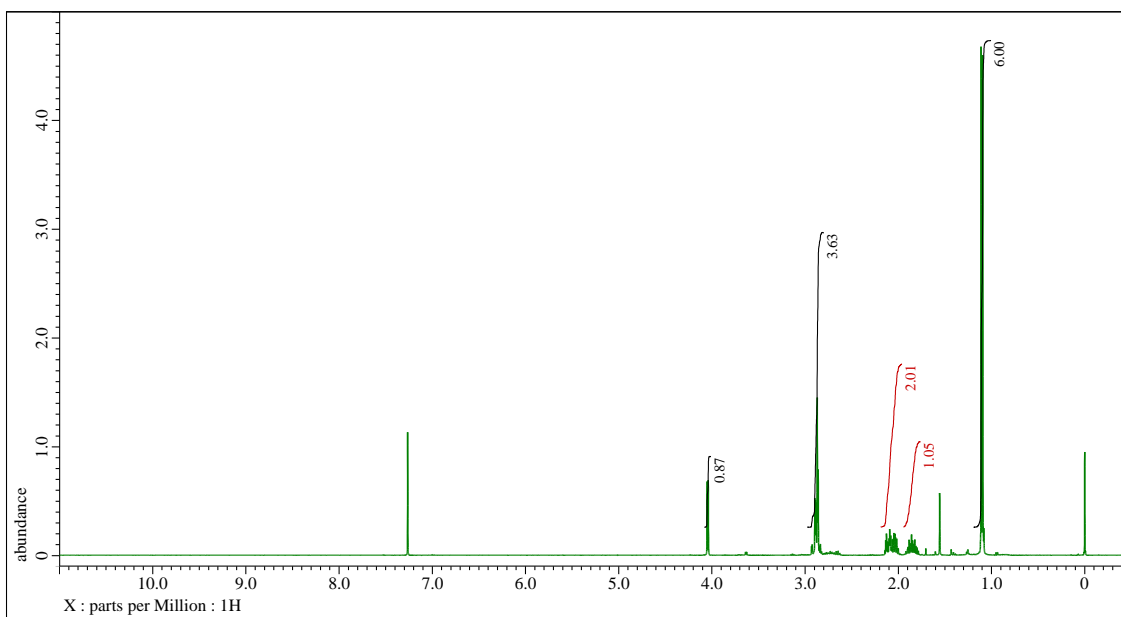


Figure S35. ^1H NMR Spectrum for **3h** in CDCl_3 .

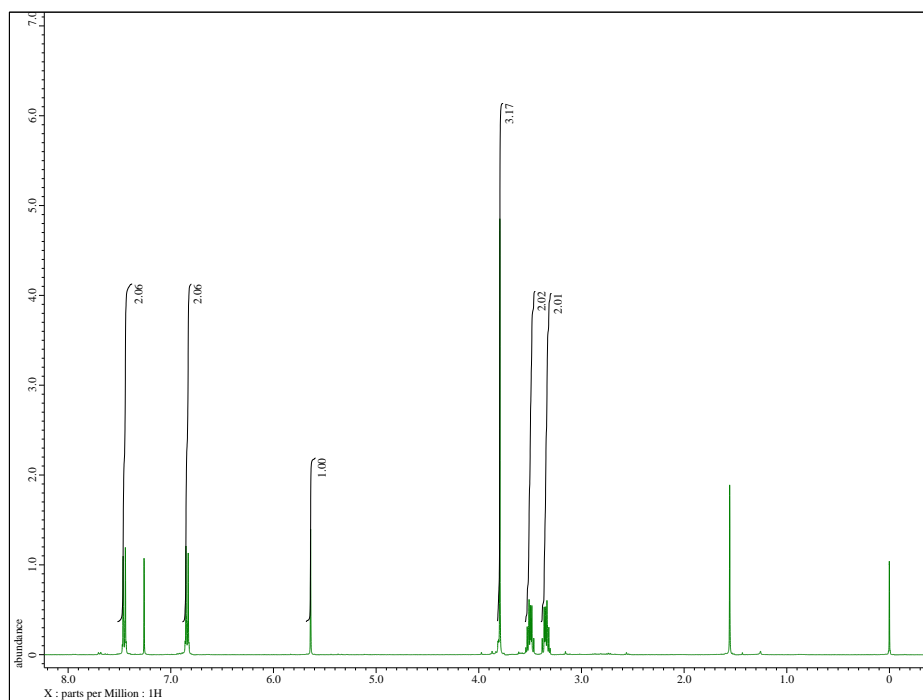


Figure S36. ^1H NMR Spectrum for **4** in CDCl_3 .

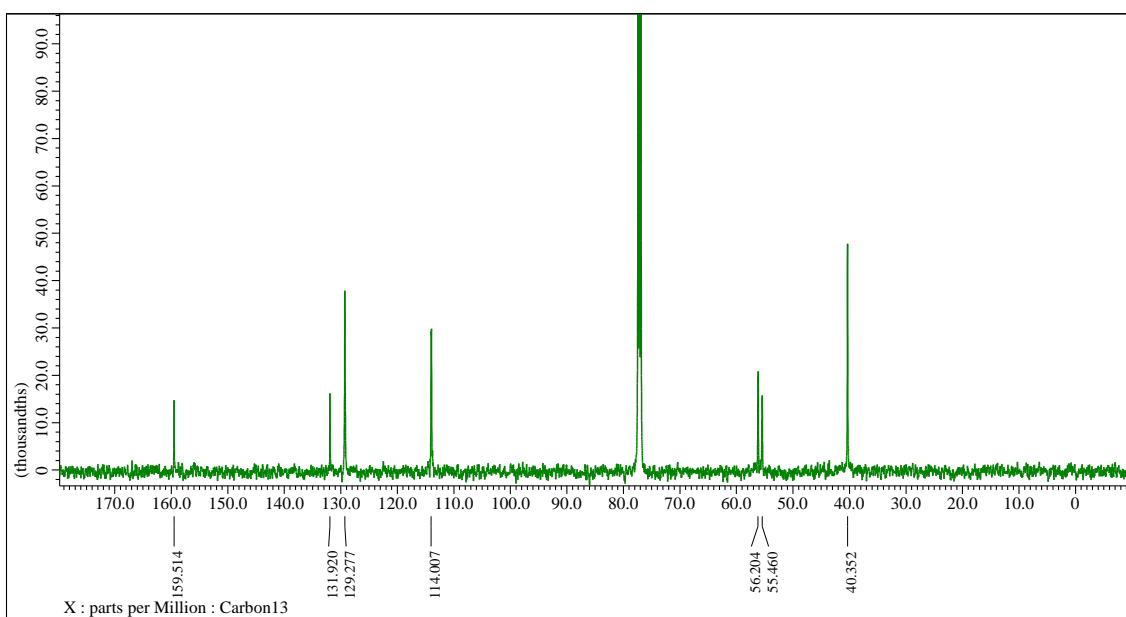


Figure S37. ^{13}C NMR Spectrum for **4** in CDCl_3 .

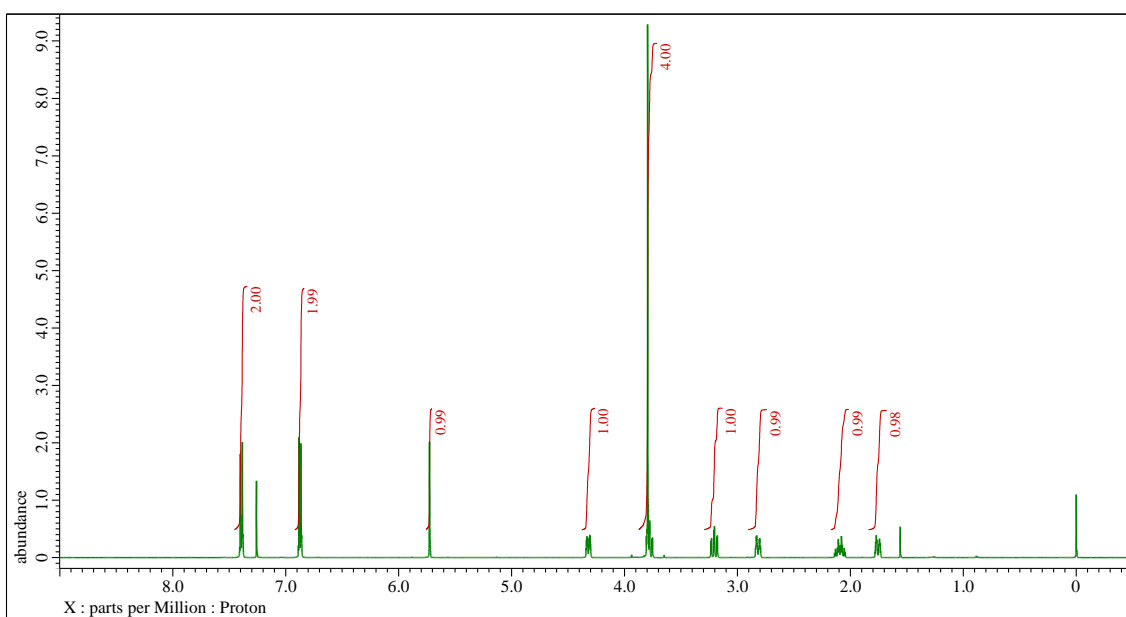


Figure S38. ^1H NMR Spectrum for 2-(4-methoxyphenyl)-1,3-oxathiane in CDCl_3 .

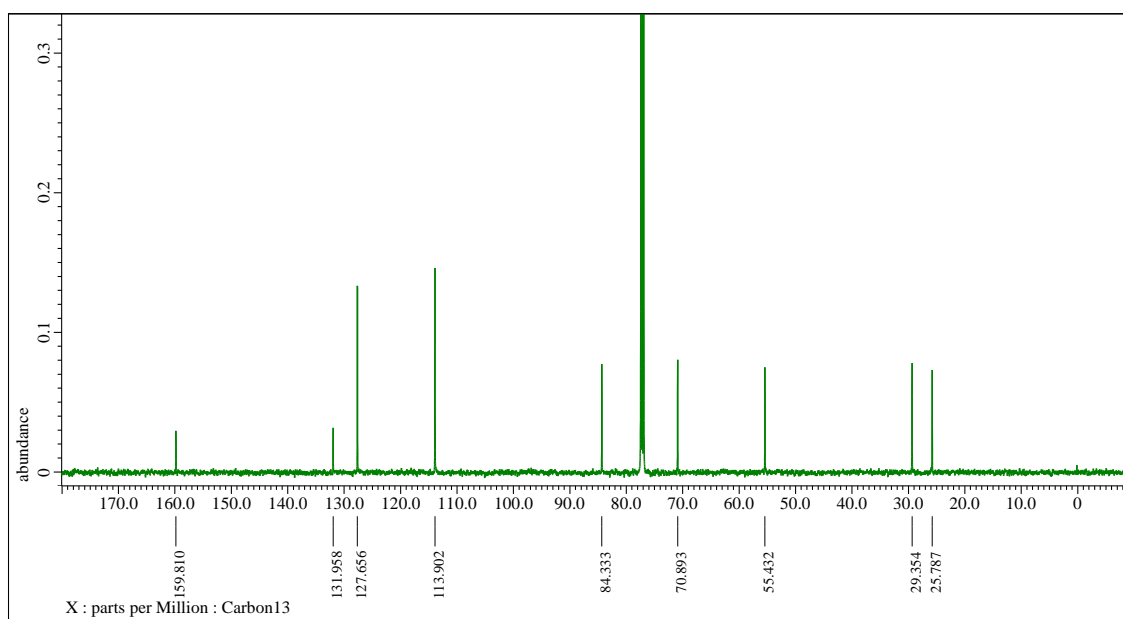


Figure S39. ^{13}C NMR Spectrum for 2-(4-methoxyphenyl)-1,3-oxathiane in CDCl_3 .

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