Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

o-Hydroxycinnamate for Sequential Photouncaging of Two Different Functional Groups and its Application in Releasing Cosmeceuticals

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1. General Experimental Techniques:

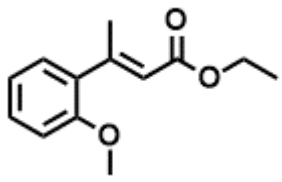
All reagents were purchased from Sigma Aldrich and were used without further purification. Dimethyl sulfoxide and dichloromethane were distilled with CaH_2 before use. All anhydrous reactions were performed under a dry nitrogen atmosphere. ^{1}H NMR spectra were recorded on a BRUKER-AC 400-MHz spectrophotometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz). ^{13}C NMR (100 MHz) spectra were recorded on a BRUKER– AC 400-MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.0 ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV–2450 UV/ Vis spectrophotometer. Photolysis of the caged compounds was carried out using 125-W medium-pressure Hg lamp supplied by SAIC (India). Chromatographic purification was done with 60–120-mesh silica gel (Merck).

2. General Procedure for the preparation of dual-caged compounds:

General procedure for the synthesis of trans ethyl cinnamates (2)

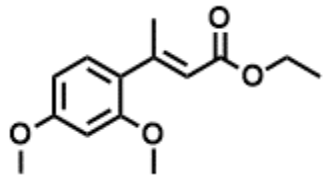
Sodium hydride (60% dispersion in mineral oil, 4 mmol) was suspended in dry THF (200 mL) and triethyl phosphonoacetate (4 mmol) was added dropwise at 0 ℃ under nitrogen atmosphere. After 10 min, appropriate methoxyacetophenone (2.7 mmol) was added to the reaction mixture, which was then allowed to warm to room temperature and stirred for 24 h. Reaction mixture was then cooled and quenched with saturated aqueous ammonium chloride solution (20 mL). The aqueous phase was extracted with ethyl acetate (4 x 50mL) and the combined organic phase was washed with brine (3 x 50mL), dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (hexanes/ethyl acetate, 95:5) yielded ester **2 a** and **b** as a clear oil with 70-80% yields.

(E)-ethyl 3-(2-methoxyphenyl)but-2-enoate (2a). Colourless liquid, yield 78 %. ^{1}H NMR



(400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.98 – 6.83 (m, 2H), 5.90 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.49 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 156.6, 156.3, 133.0, 129.5, 128.7, 120.5, 119.2, 110.99, 59.6, 55.3, 19.8, 14.3.

(E)-ethyl 3-(2,4-dimethoxyphenyl)but-2-enoate (2b). Colourless liquid, yield 73 %. ^{1}H NMR

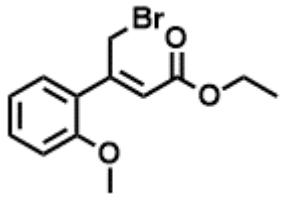


(400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 8.7 Hz, 1H), 6.46 (d, *J* = 7.3 Hz, 2H), 5.90 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 2.48 (s, 3H), 1.30 (t, *J*=7.2, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 161.0, 157.6, 156.2, 129.5, 125.8, 118.6, 104.2, 98.9, 59.6, 55.4, 55.3, 19.9, 14.3.

General procedure for allylic bromination to get bromoester (3).

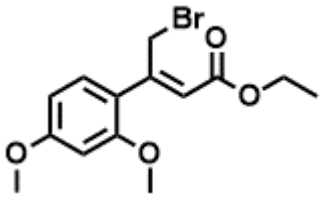
Compounds **2a** and **b** (1 mmol), NBS (1.1 mmol) and benzoylperoxide (0.04 mmol) was dissolved in dry CCl_4 (35 mL) was refluxed under nitrogen atmosphere for 10 h. Completion of the reaction was confirmed by TLC and the resulting reaction mixture was cooled to room temperature, then filtered to separate succinimide formed during the reaction. The solvent was removed from the filtrate to obtain bromoester (**3a** and **b)**. It was then purified by column chromatography packed with silica gel to give pure compounds **3a** and **b** with about 90- 92 % yield.

(Z)-ethyl 4-bromo-3-(2-methoxyphenyl)but-2-enoate (3a)



Yellow liquid, yield 91 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.95 (s, 1H), 5.03 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 156.3, 154.2, 130.7, 130.4, 128.5, 122.0, 120.7, 110.8, 60.4, 55.5, 28.6, 14.2.

(Z)-ethyl 4-bromo-3-(2,4-dimethoxyphenyl)but-2-enoate (3b).



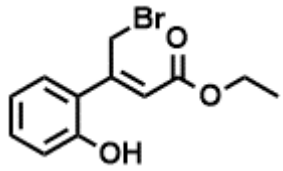
Yellow liquid, yield 92 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 8.3 Hz, 1H), 6.50 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 5.93 (s, 1H), 5.02 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.6, 161.7, 157.7, 153.9, 131.4, 121.4, 121.3, 104.5, 98.8, 60.3, 55.5, 55.4, 28.9, 14.2.

General procedure for methoxy deprotection for the synthesis of (4).

To a solution of methoxyphenyl derivatives (**3a** and **b)** (0.30 mmol) in dry dichloromethane (5 ml) at -78 °C, boron tribromide in dichloromethane (1 M, 2 equiv per methoxy function) was added dropwise. The reaction mixture was stirred for 1 h at 0 °C under nitrogen atmosphere. Water was added to quench the reaction, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried over sodium

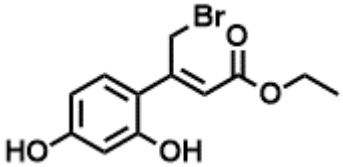
sulfate, filtered, and evaporated. The product was purified by column chromatography to get compounds **4a** and **b** with 60-65% yield.

(Z)-ethyl 4-bromo-3-(2-hydroxyphenyl)but-2-enoate (4a)



White solid, yield 65 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.02 (s, 1H), 5.02 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 161.0, 153.5, 132.4, 131.8, 122.2, 120.4, 117.1, 115.0, 60.5, 28.6, 14.2.

(Z)-ethyl 4-bromo-3-(2,4-dihydroxyphenyl)but-2-enoate (4b)

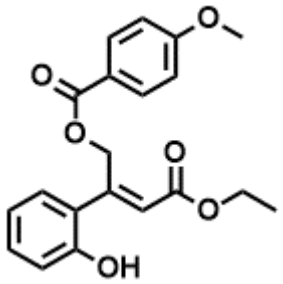


White solid, yield 62 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 8.3 Hz, 1H), 6.50 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 5.97 (s, 1H), 5.02 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.6, 161.7, 157.6, 153.9, 131.4, 121.4, 121.3, 104.5, 98.8, 60.3, 28.9, 14.2.

General procedure for the synthesis of dual-caged compounds (5a-c):

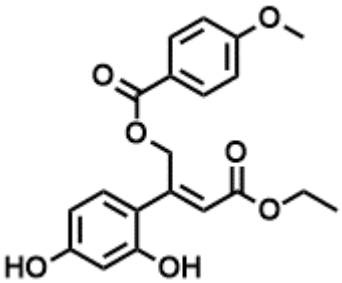
Appropriate carboxylic acid (0.33 mmol) was dissolved in dry dimethylformamide. To the solution potassium bicarbonate (0.40 mmol) was added and strirred for 10 min at room temperature. Finally compounds **4a, b** (0.33 mmol) was added to it and the reaction mixture was stirred for 3 h at room temperature. Reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and evaporated. The product i.e dual-caged compounds **(5a-c)** was purified by column chromatography with 65-67% yield.

(Z)-4-ethoxy-2-(2-hydroxyphenyl)-4-oxobut-2-en-1-yl 4-methoxybenzoate (5a)



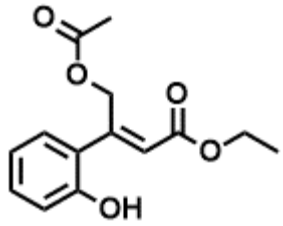
White solid, yield 65 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, J= 8.0 Hz, 2H), 7.59(t, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 7.6, 1H), 7.39 (t, *J* = 7.4, Hz, 1H), 7.33 (d, *J*= 8.0 Hz, 1H), 6.97 (d, *J*= 8.0 Hz, 2H), 6.18 (s, 1H), 5.54 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.3, 164.0, 160.8, 160.4, 153.6, 132.1, 131.9, 131.7, 122.2, 121.3, 117.4, 117.1, 115.1, 113.9, 61.3, 60.2, 55.5, 14.4. HR-MS calc for $C_{20}H_{21}O_6$ [MH^+]: 357.1333, found: 357.1305.

Z)-2-(2,4-dihydroxyphenyl)-4-ethoxy-4-oxobut-2-en-1-yl 4-methoxybenzoate (5b)



White solid, yield 67 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.44 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.37 (d, *J* = 2.2 Hz, 1H), 5.99 (s, 1H), 5.73 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.9, 165.7, 163.1, 161.5, 158.0, 154.4, 131.4, 130.4, 122.7, 121.2, 120.0, 113.4, 104.3, 98.3, 77.3, 77.03, 76.8, 63.0, 60.3, 55.3, 14.3. HR-MS calc for $C_{20}H_{21}O_7$ [MH^+]: 373.1282, found: 373.1282

(Z)-ethyl 4-acetoxy-3-(2-hydroxyphenyl)but-2-enoate (5c)



White solid, yield 66 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.95 (s, 1H), 5.52 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.77 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 165.6, 156.7, 154.6, 130.0, 129.8, 128.1, 120.8, 120.5, 110.3, 77.7, 77.1, 76.4, 62.7, 60.3, 20.4, 14.2. HR-MS calc for $C_{14}H_{17}O_5$ [MH^+]: 265.1071, found: 265.1086.

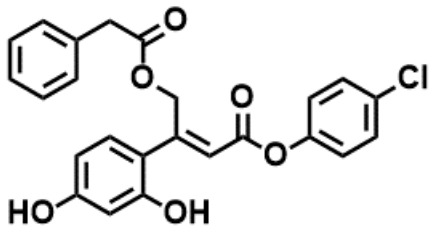
General procedure for the synthesis of dual-caged compounds (6a-c):

Compound **4a, b** (0.30 mmol) was dissolved in 2 mL trifluoroacetic acid and stirred at room temperature for 24 h. Completion of the reaction was checked by TLC analysis. Then, the mixture was quenched by the addition of aqueous $NaHCO_3$ solution and then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), filtered and the solvent was evaporated under reduced pressure to corresponding cinnamic acid derivatives with yield 90-91%. The crude product was used for the next step.

The crude cinnamic acid derivatives (0.40 mmol) was dissolved in dry DCM, cooled to 0 °C and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (0.6 mmol) was added to it. After 5 min appropriate alcohols (0.40 mmol) was added to it followed by the addition of 4-dimethylaminopyridine (0.40 mmol) at 0 °C then the reaction mixture was allowed to the room temperature. The reaction was stirred at room temperature for 6 h. Reaction was quenched with water and then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), filtered and the solvent was evaporated under reduced pressure to yield corresponding alcohol protected cinnamyl derivatives (yield 88-91 %). These crude products were used for attaching the corresponding carboxylic acids in the next step.

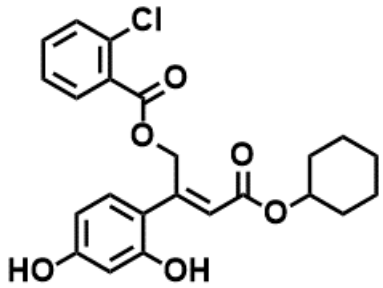
Appropriate carboxylic acid (0.30 mmol) was dissolved in dry dimethylformamide. To the solution potassium bicarbonate (0.36 mmol) was added and strirred for 10 min at room temperature. Finally the crude compounds (0.30 mmol) formed in the previous step was added to it and the reaction mixture was stirred for 3 h at room temperature. Reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and evaporated. The product i.e dual-caged compounds **(6a-c)** was purified by silica gel column chromatography (petroleum ether/ ethyl acetate 9:1 to 8:2) with 67-70 % yield.

4-Chlorophenyl (Z)-3-(2,4-dihydroxyphenyl)-4-(2-phenylacetoxy)but-2-enoate (6a)



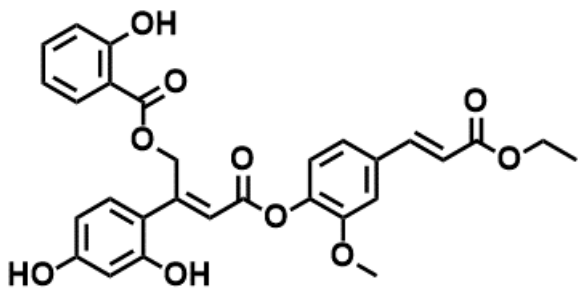
White solid, yield 67 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 2.1 Hz, 3H), 7.08 (dd, *J* = 8.3, 5.0 Hz, 3H), 6.97 (d, *J* = 3.6 Hz, 2H), 6.44 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.32 (s, 1H), 6.12 (s, 1H), 5.59 (s, 2H), 3.37 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 163.8, 161.9, 158.0, 157.9, 149.1, 133.7, 131.2, 130.54, 129.5, 129.2, 128.4, 126.8, 123.2, 120.1, 118.1, 104.4, 98.5, 63.1, 41.2. HR-MS calc for $C_{24}H_{20}ClO_6$ [MH^+]: 439.0943, found: 439.0950.

(Z)-4-(cyclohexyloxy)-2-(2,4-dihydroxyphenyl)-4-oxobut-2-en-1-yl 2-chlorobenzoate (6b)



White solid, yield 68 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 1H), 7.14 (dd, *J* = 11.3, 7.4 Hz, 1H), 6.49 – 6.42 (m, 1H), 6.41 (d, *J* = 4.5 Hz, 1H), 5.99 (d, *J* = 4.1 Hz, 1H), 5.89 – 5.67 (m, 1H), 1.90 (d, *J* = 23.1 Hz, 1H), 1.75 (dd, *J* = 14.6, 9.3 Hz, 1H), 1.51 – 1.35 (m, 1H), 1.33 – 1.23 (m, 66H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.4, 165.0, 161.6, 158.0, 153.4, 133.6, 132.2, 131.2, 130.9, 130.8, 130.0, 126.3, 121.1, 121.0, 104.4, 98.4, 72.7, 63.7, 31.74, 25.42, 23.8. HR-MS calc for $C_{23}H_{24}ClO_6$ [MH^+]: 431.1256, found: 431.1255.

(Z)-2-(2,4-dihydroxyphenyl)-4-(4-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-ethoxyphenoxy) -4-oxobut-2-en-1-yl 2-hydroxybenzoate (6c)



White solid, yield 70 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.63 (d, *J* = 1.2 Hz, 1H), 7.66 (dd, *J* = 16.0, 1.6 Hz, 1H), 7.36 (dt, *J* = 7.2, 1.5 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.13 (t, *J* = 2.2 Hz, 1H), 6.93 – 6.88 (m, 1H), 6.76 – 6.68 (m, 1H), 6.50 (dt, *J* = 3.5, 1.7 Hz, 1H), 6.44 – 6.35

(m, 1H), 6.29 (dd, *J* = 2.6, 1.5 Hz, 1H), 5.86 – 5.82 (m, 1H), 4.30 – 4.25 (m, 1H), 3.87 (d, *J* = 1.3 Hz, 1H), 1.36 – 1.33 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.4, 166.8, 163.4, 162.1, 161.4, 158.1, 156.7, 151.5, 143.9, 141.2, 135.5, 133.5, 130.7, 129.7, 123.4, 121.2, 120.3, 119.0, 118.52, 118.47, 117.4, 112.4, 111.3, 104.7, 98.4, 63.6, 60.7, 55.9, 14.3. HR-MS calc for $C_{29}H_{30}NO_{10}$ [MNH_4^+]: 552.1864, found: 552.1875.

3. ^{1}H and ^{13}C NMR of the caged compounds

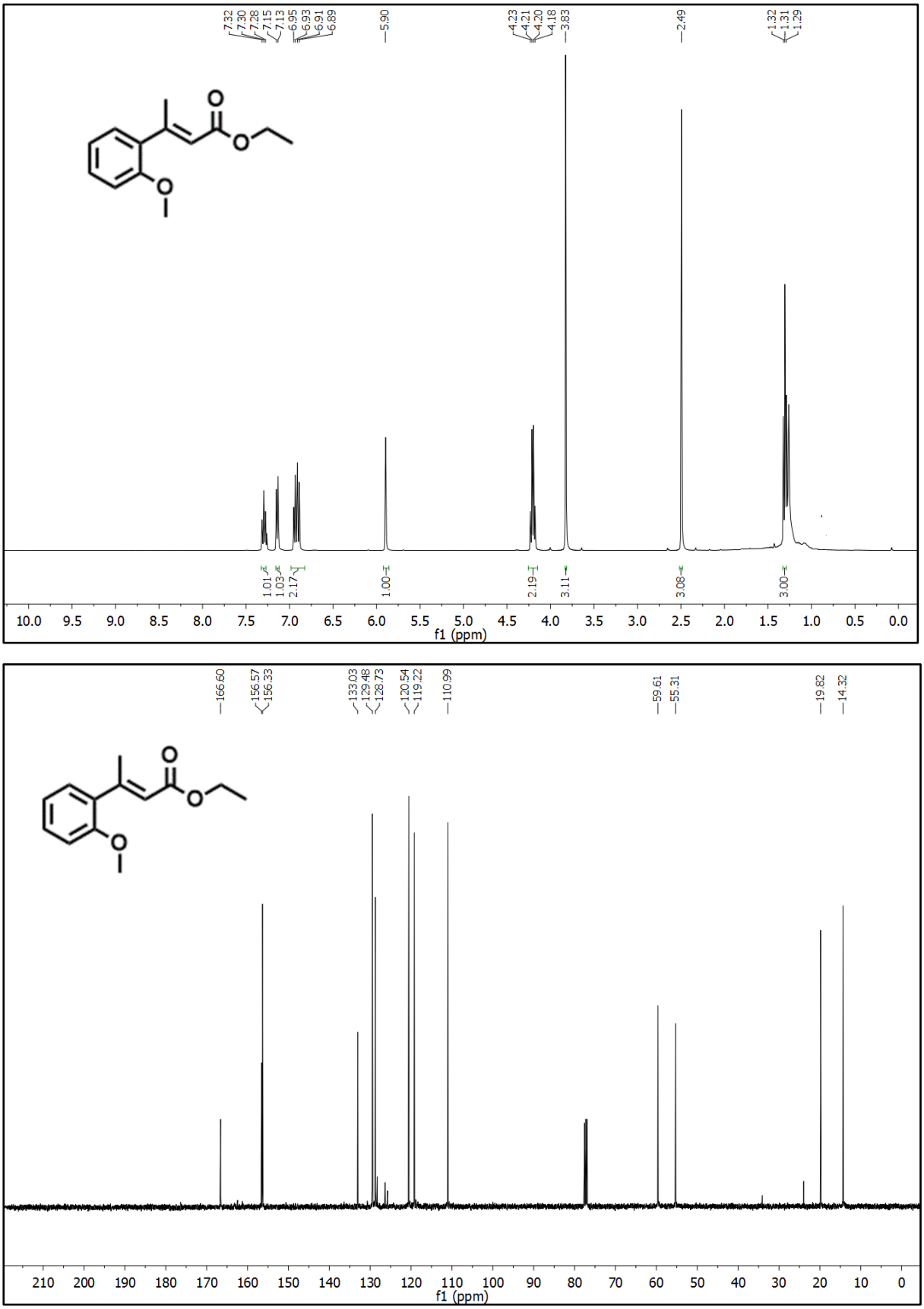


Fig. S1. ^{1}H and ^{13}C NMR spectra of **2a** in $CDCl_3$.

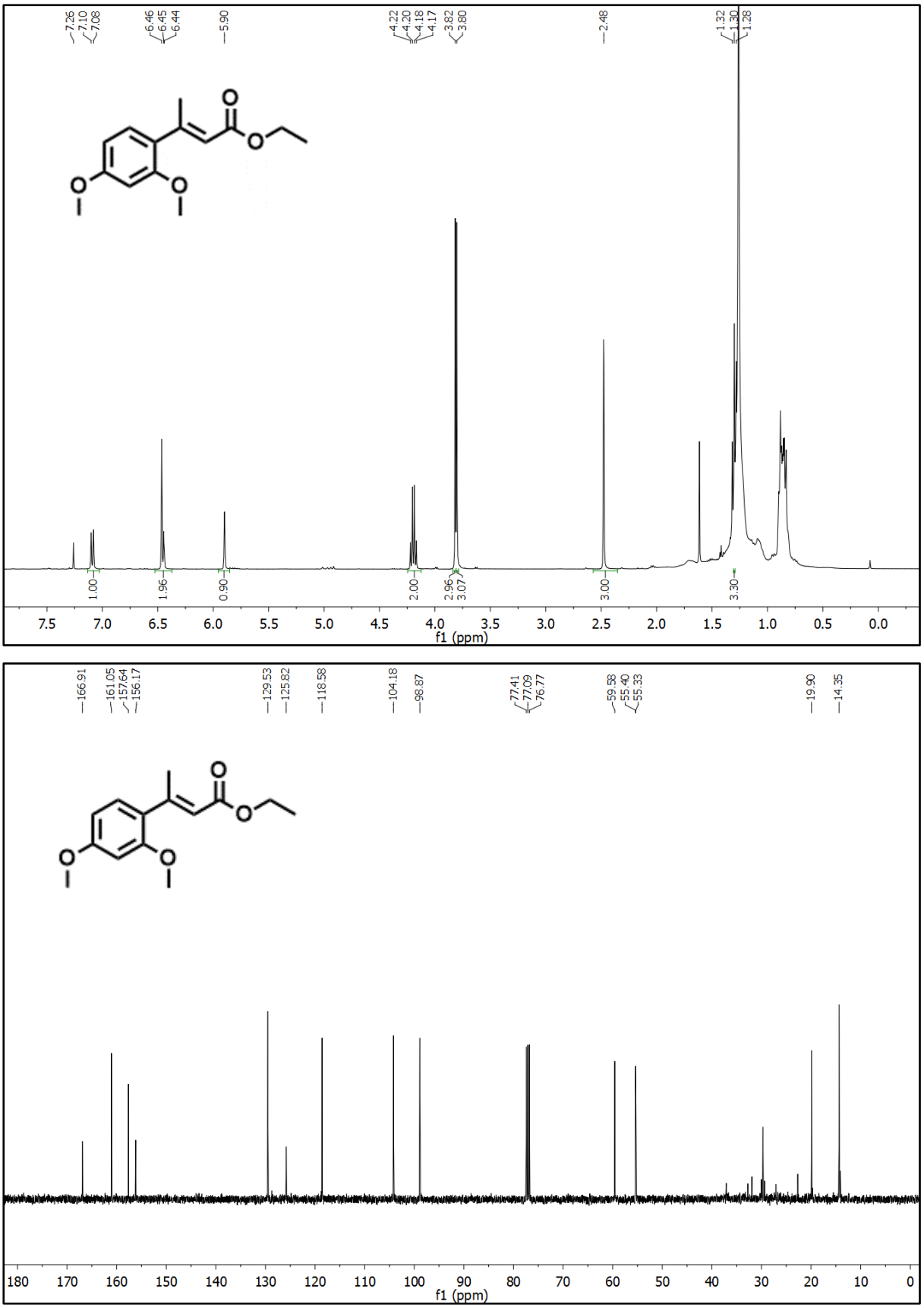


Fig. S2. ^{1}H and ^{13}C NMR spectra of **2b** in $CDCl_3$.

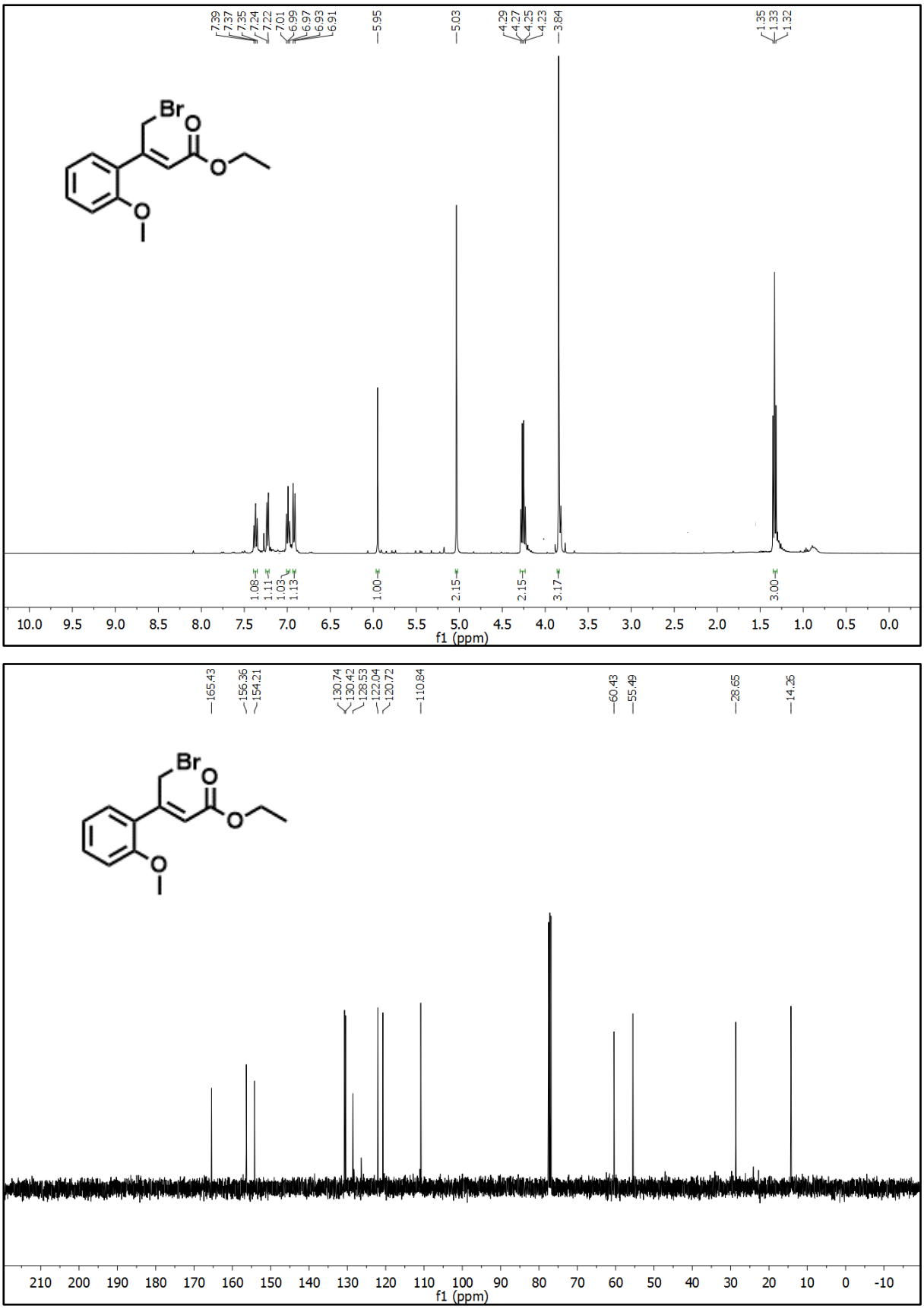


Fig. S3. ^{1}H and ^{13}C NMR spectra of **3a** in $CDCl_3$.

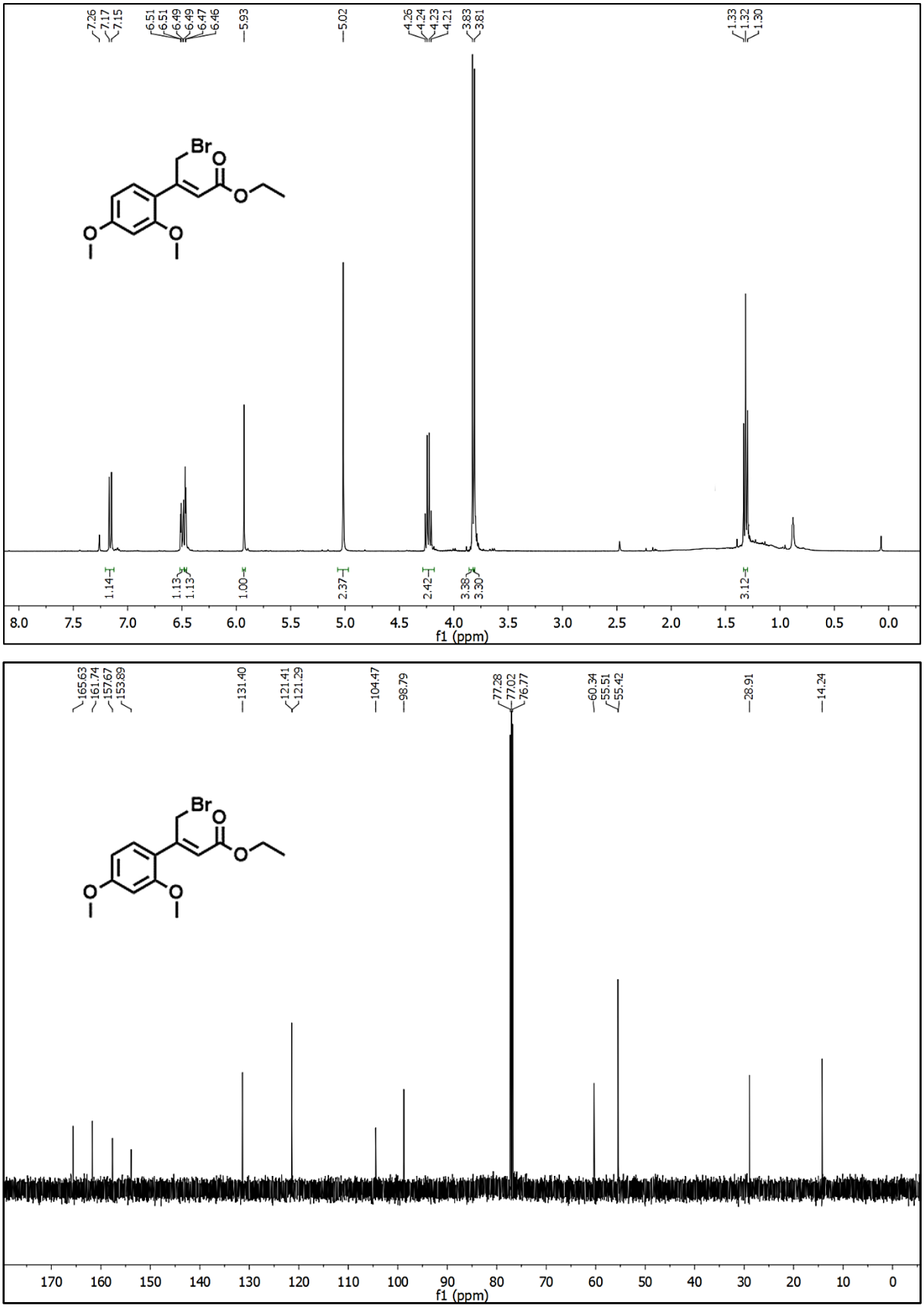


Fig. S4. ^{1}H and ^{13}C NMR spectra of **3b** in $CDCl_3$.

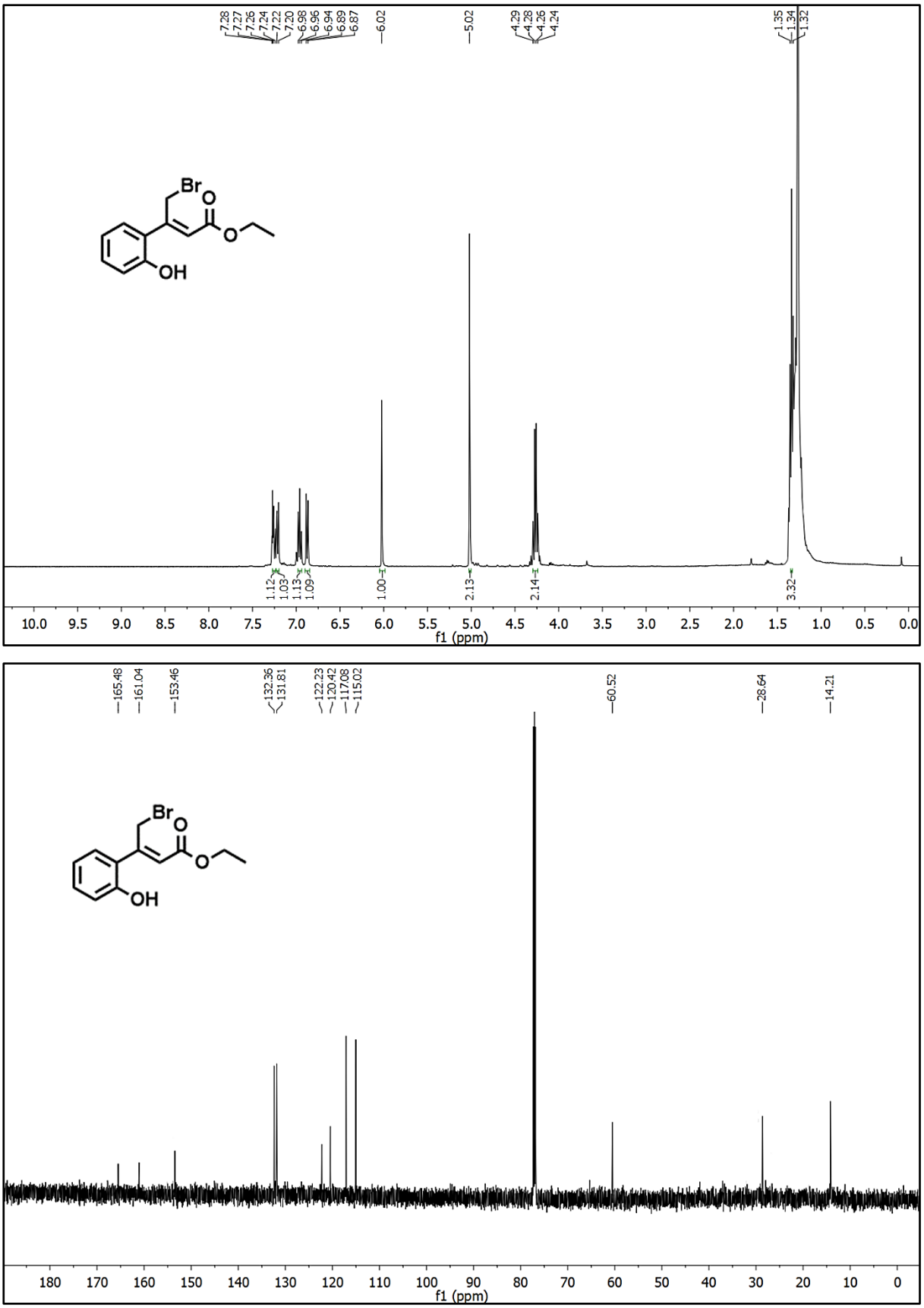


Fig. S5. ^{1}H and ^{13}C NMR spectra of **4a** in $CDCl_3$.

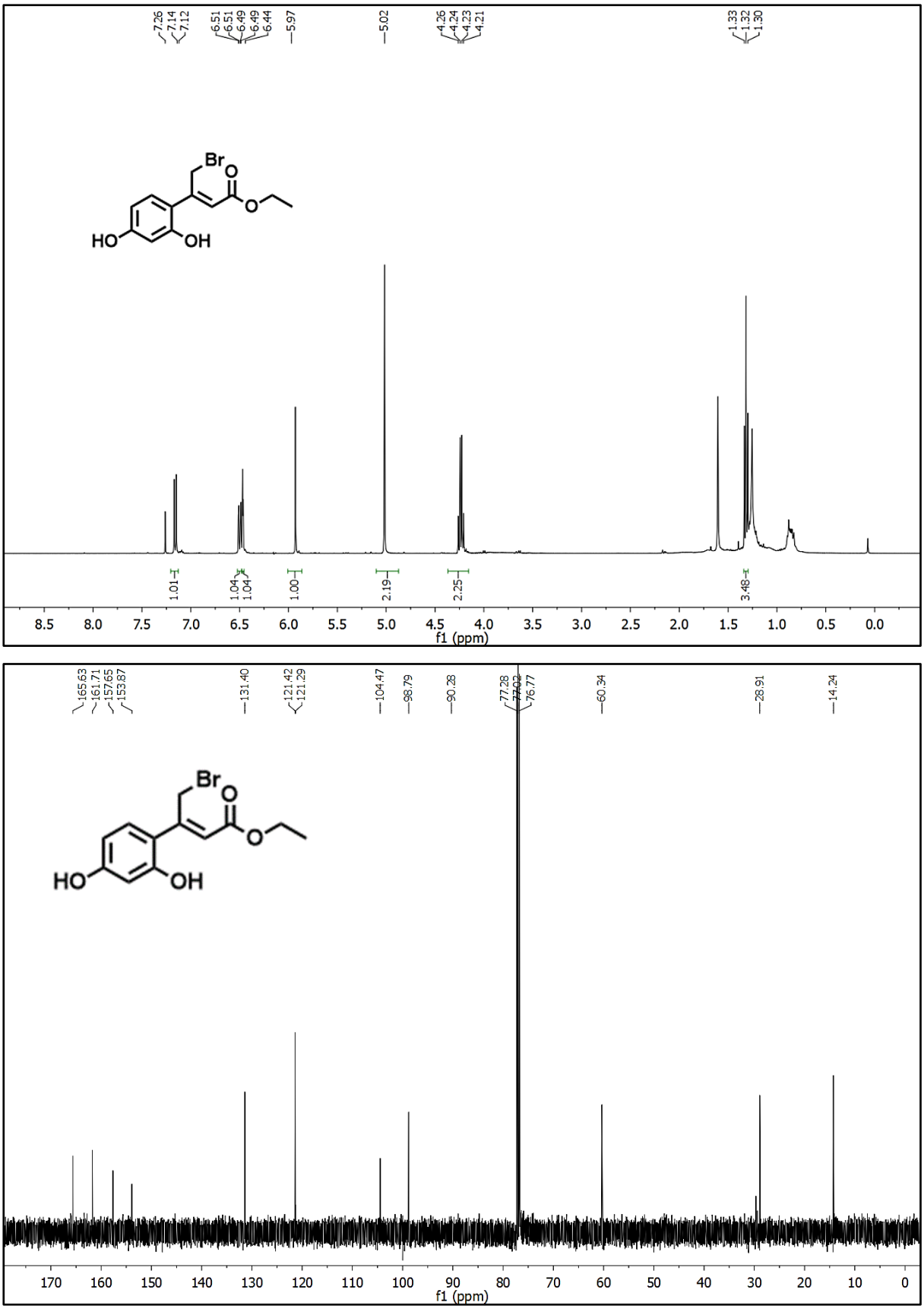


Fig. S6. ^{1}H and ^{13}C NMR spectra of **4b** in $CDCl_3$.

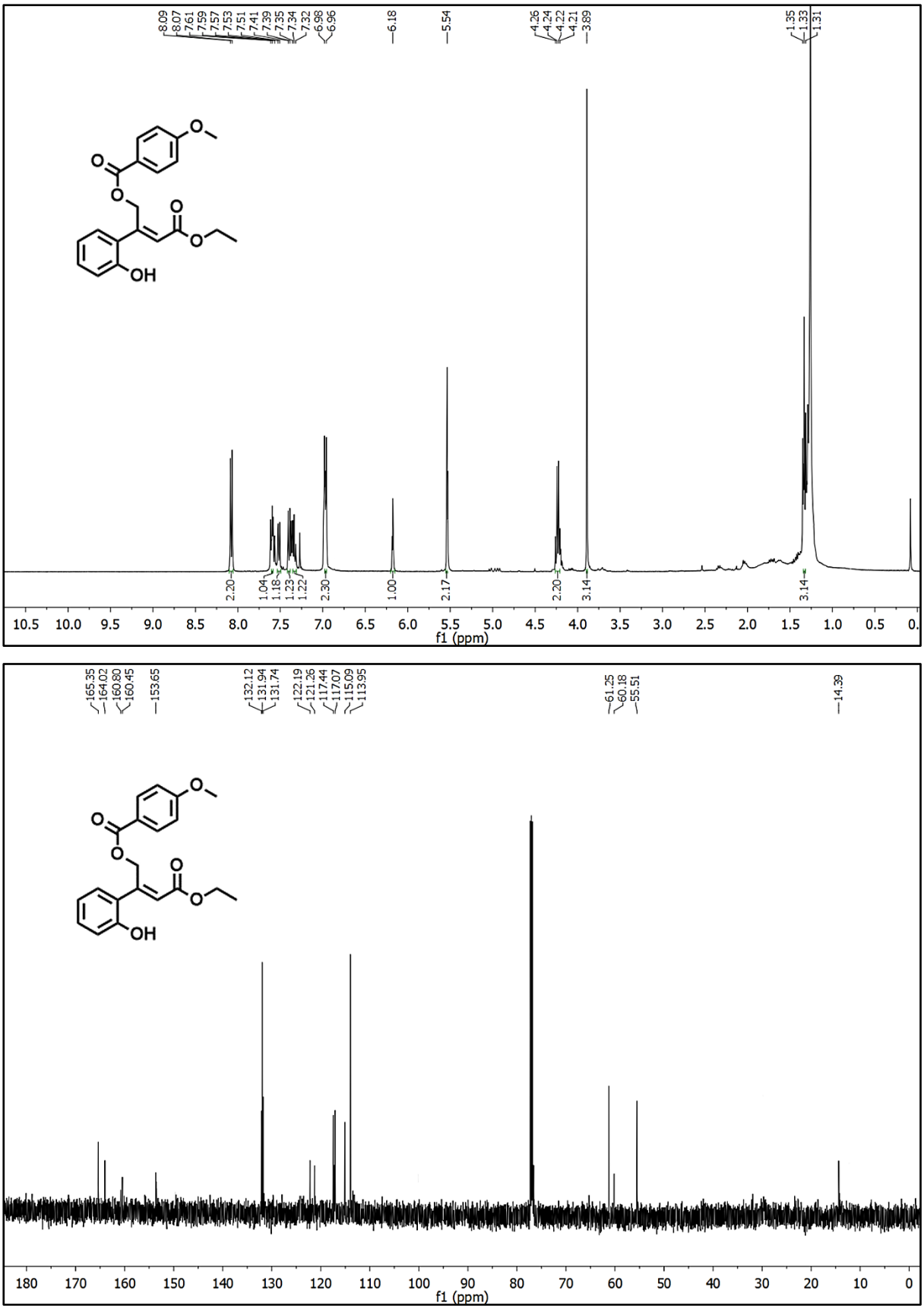


Fig. S7. ^{1}H and ^{13}C NMR spectra of **5a** in $CDCl_3$.

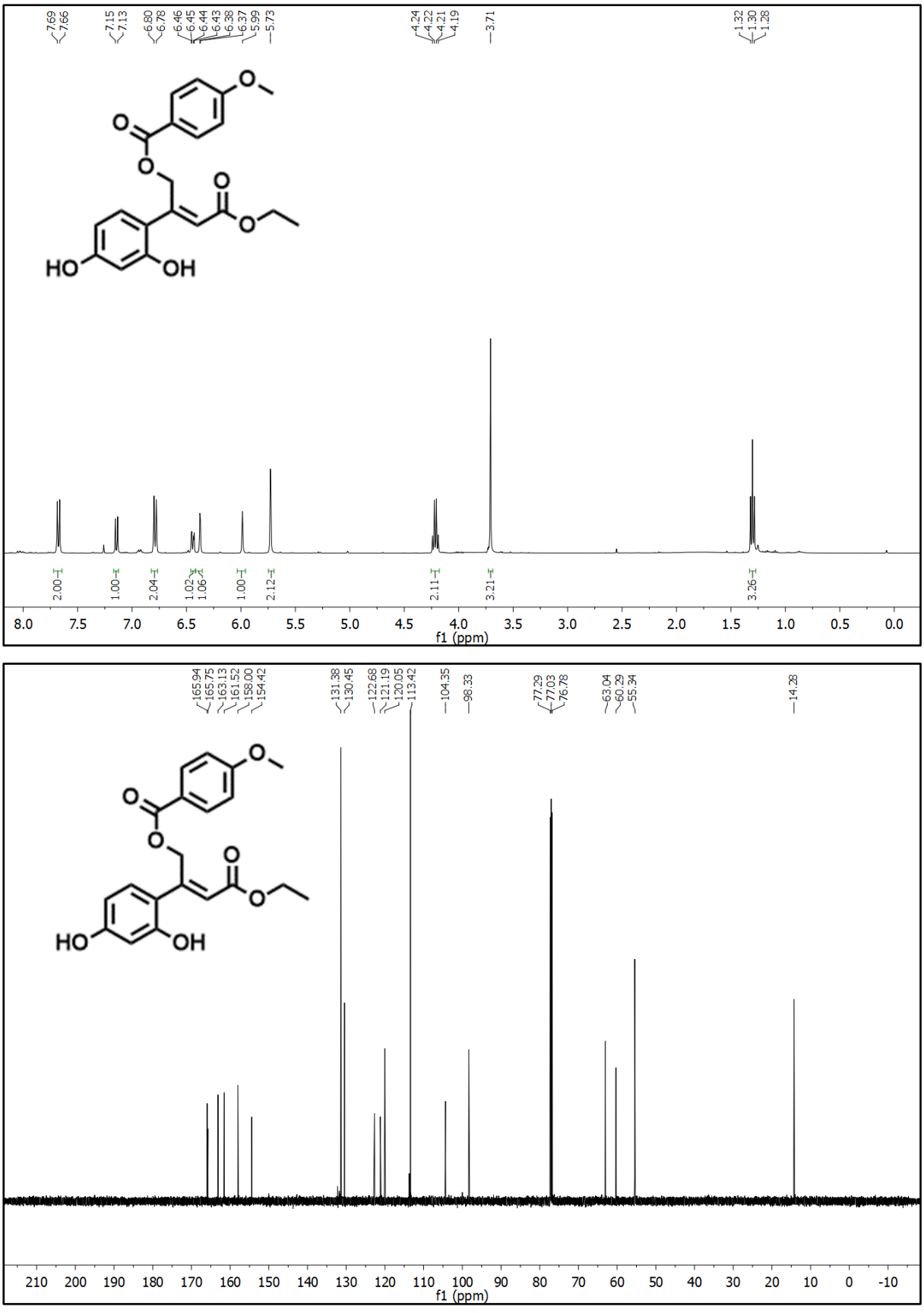


Fig. S8. ^{1}H and ^{13}C NMR spectra of **5b** in $CDCl_3$.

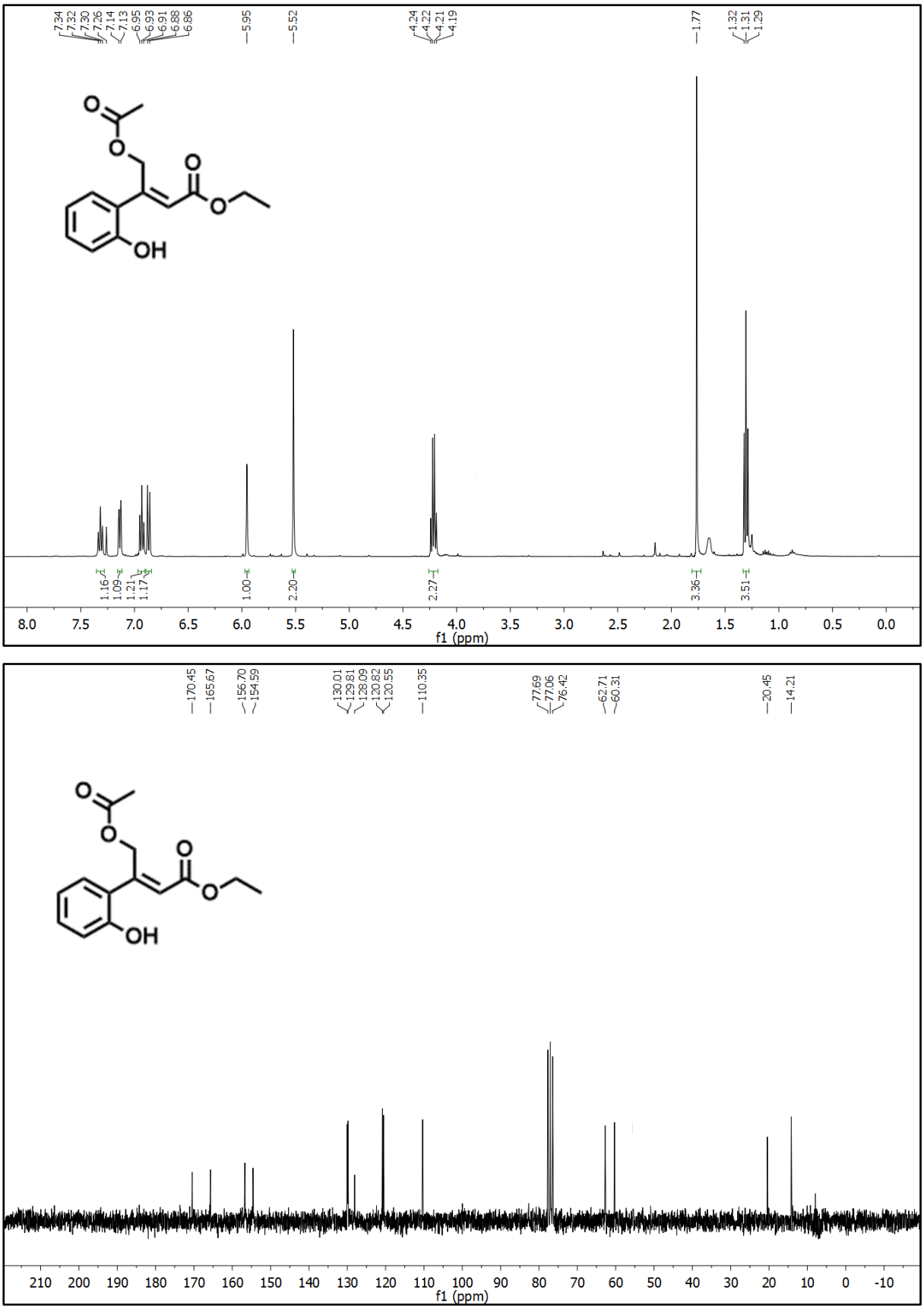


Fig. S9. ^{1}H and ^{13}C NMR spectra of **5c** in $CDCl_3$.

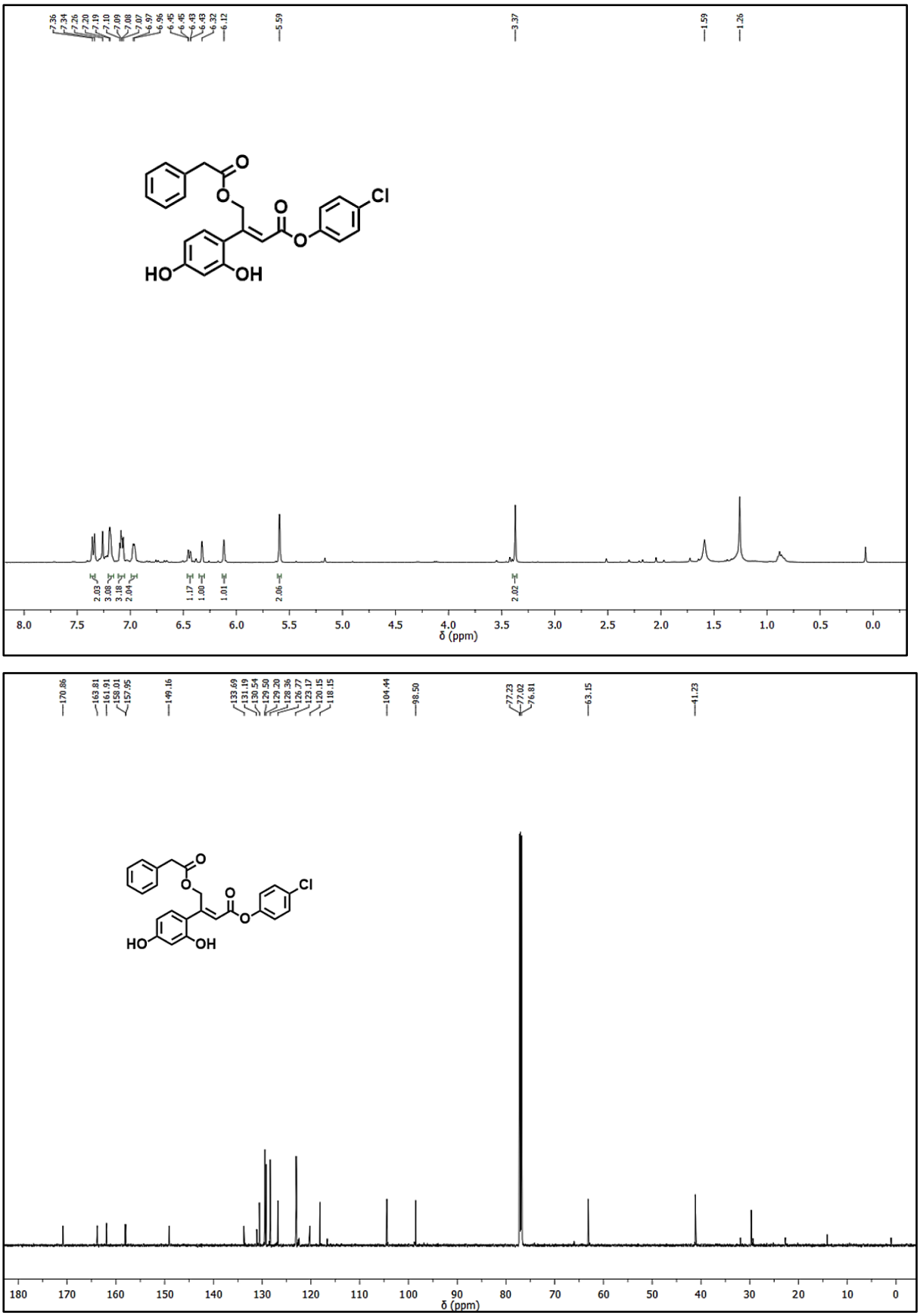


Fig. S10. ^{1}H and ^{13}C NMR spectra of **6a** in $CDCl_3$.

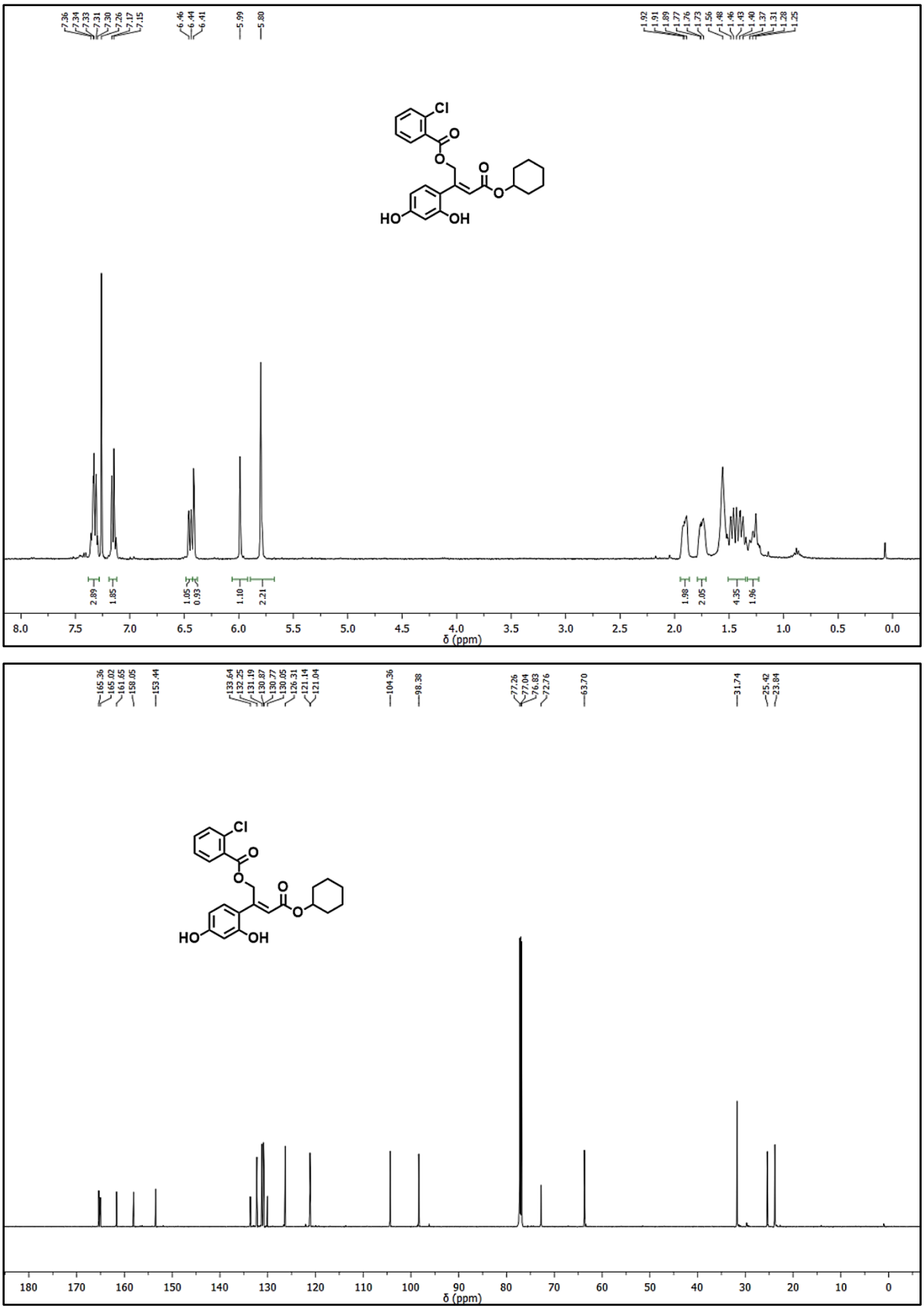


Fig. S11. ^{1}H and ^{13}C NMR spectra of **6b** in $CDCl_3$.

Fig. S12. ^{1}H and ^{13}C NMR spectra of **6c** in $CDCl_3$.

4. Determination of incident photon flux (I_0) of the UV lamp by potassium ferrioxalate actinometry:

Potassium ferrioxalate actinometry was used for the determination of incident photon flux (I0) of the UV lamp used for irradiation. Solution of potassium ferrioxalate, 1, 10-phenanthroline and the buffer solution were prepared following the literature procedure.[1] Solution (0.006 M) of potassium ferrioxalate was irradiated using 125W medium pressure Hg lamp through a Pyrex filter as UV light source (≥ 310 nm). At a regular interval of time (3 min), 1mL of the aliquots was taken out and to it 3 mL of 1,10 phenanthroline solution and 2 mL of the buffer solution were added and the whole solution was kept in dark for 30min. The absorbance of the red phenanthroline-ferrous complex formed was then measured spectrophotometrically at 510 nm. The amount of Fe^{2+}ion was determined from the calibration graph. The calibration graph was plotted by measuring the absorbance of the phenanthroline-ferrous complex at several known concentration of Fe2+ion in dark. From the slope of the graph, the molar absorptivity of the phenanthroline-ferrous complex was calculated to be $1.10 \times 10^4\ M^{-1}\ cm^{-1}$ at 510 nm which is found to be similar to reported value. Using the known quantum yield (1.283 ± 0.023) for potassium ferrioxalate actinometer at 363.8 nm,[2] the number of Fe^{2+} ion formed during photolysis and the fraction of light absorbed by the actinometer, the incident photon flux (I_0) at 350 nm of the 125 W Hg lamp was determined as 1.88×10^{17}photons $s^{-1}cm^{-2}$.

5. Photolysis and quantum yield measurements of the two sequential photouncaging reactions for the caged compound 5a-c:

A solution of 1×10^{-4}M of the caged compounds (**5a-c**) was prepared in ACN/H_2O (3:7 v/v). Half of the solution was kept in dark and to the remaining half nitrogen was passed and irradiated using 125 W medium pressure Hg lamp through a Pyrex filter as UV light source ($\lambda \geq 310$ nm) 120 min. At a regular interval of time, the photolysis mixture was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$. The quantum yields for photodegradation of caged compounds **5a-c** and photorelease of caged carboxylic acids were calculated to determine the photochemical quantum yields of first and second photoreleases respectively using equation (1).

$$(\Phi)_{CG} = (\Phi)_{act} \times [(k_p)_{CG}/(k_p)_{act}]\times[F_{act}/F_{CG}] \text{ ---------- (1)}$$

Where the subscript 'CS' and 'act' denotes caged substrate and actinometer respectively. Ferrioxalate was used as an actinometer.[2] Φp is the photolysis quantum yield, kp is the photolysis rate constant and F is the fraction of light absorbed.

6. Characterisation of photoproducts of dual caged compound 5a by ^{1}H NMR spectroscopy

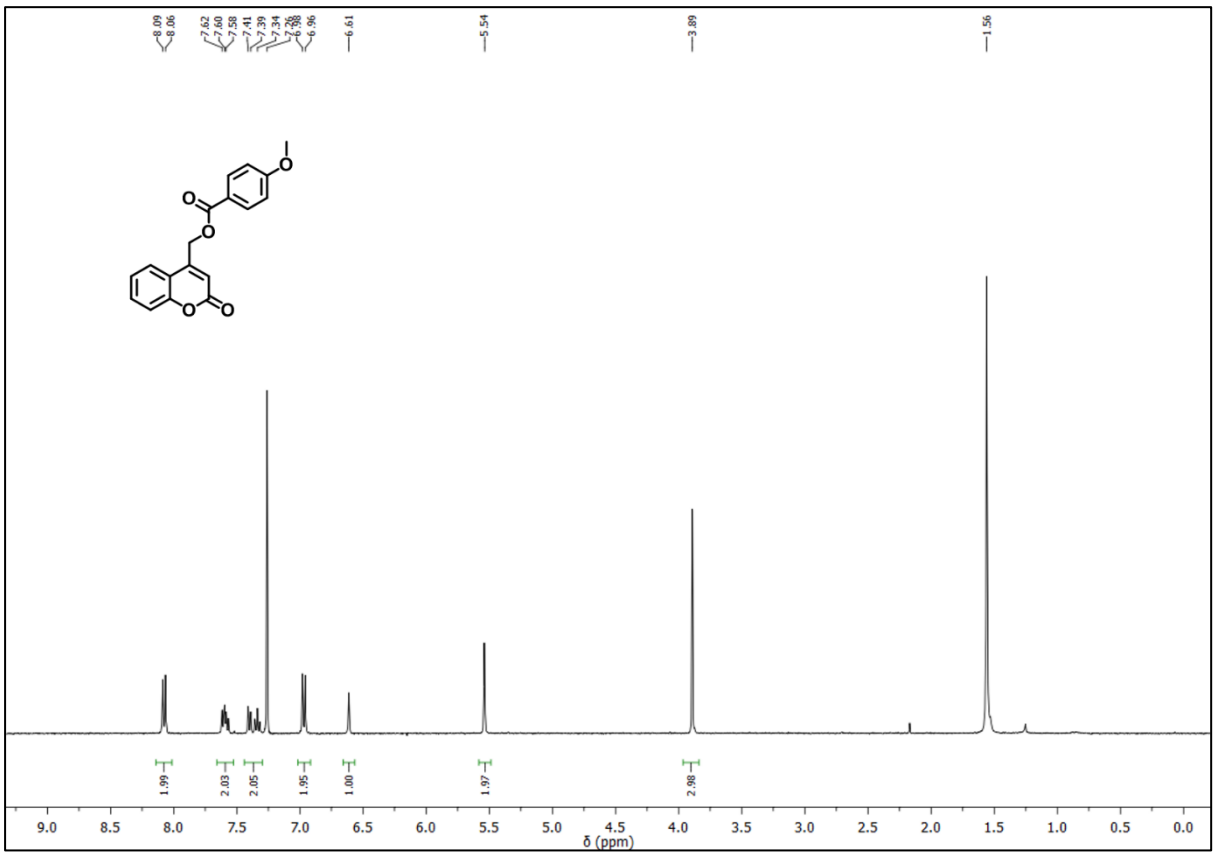


Fig. S13. ^{1}H NMR spectrum of intermediate coumarin derivative **8a** in $CDCl_3$ formed after first release from **5a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 2H), 7.66 – 7.52 (m, 2H), 7.44 – 7.30 (m, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.61 (s, 1H), 5.54 (s, 2H), 3.89 (s, 3H).

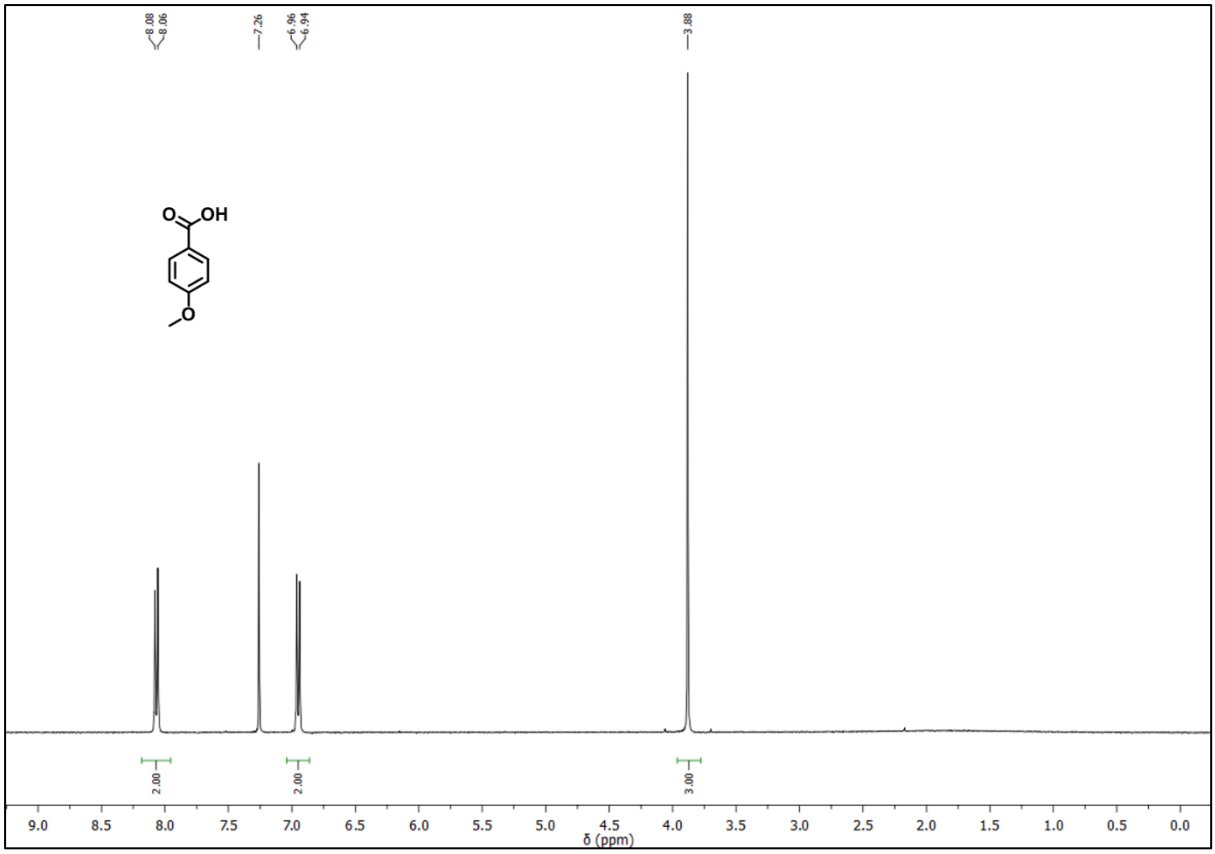


Fig. S14. ^{1}H NMR spectrum of anisic acid released from **8a** in $CDCl_3$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H).

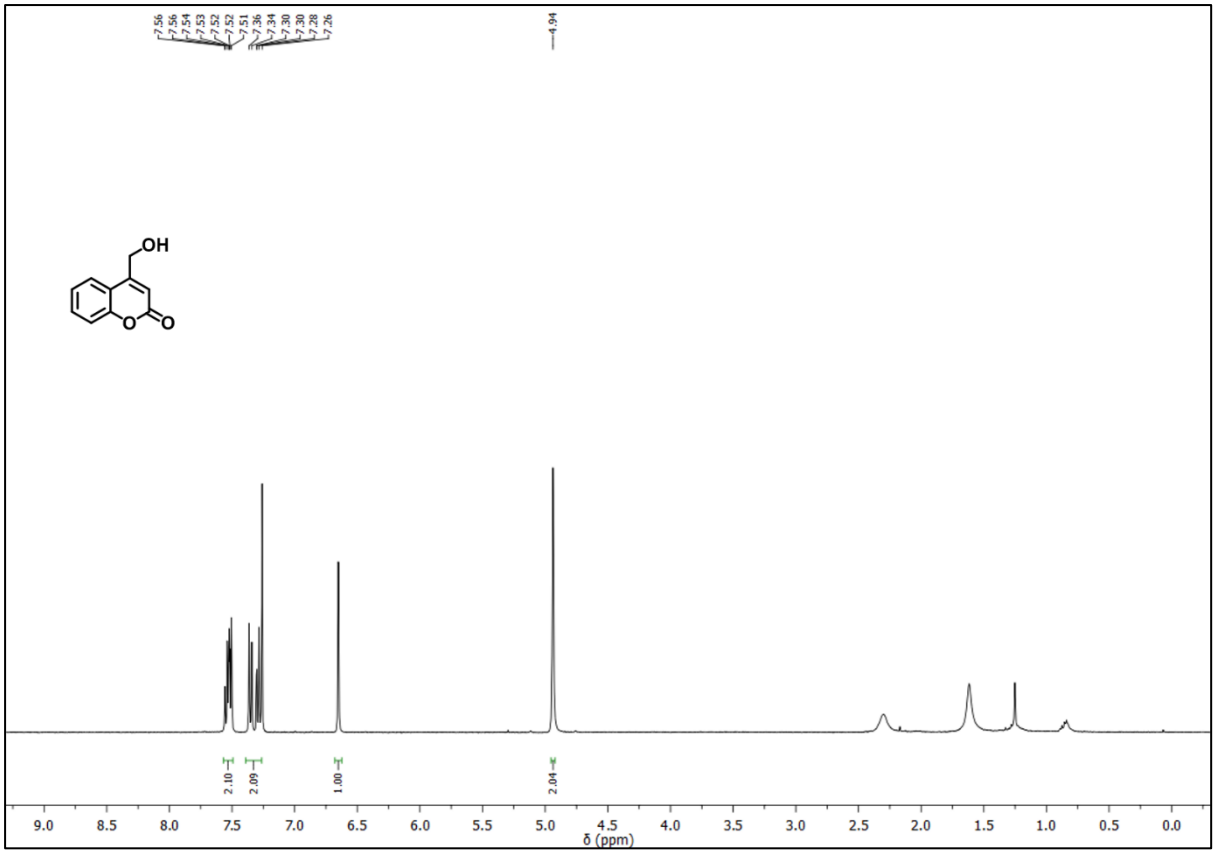


Fig. S15. ^{1}H NMR spectrum of final photoproduct **12a** in $CDCl_3$ formed after dual release from **5a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.39 – 7.26 (m, 2H), 6.65 (s, 1H), 4.94 (s, 2H).

7. Absorption spectra of photoproducts (8a, 8b)

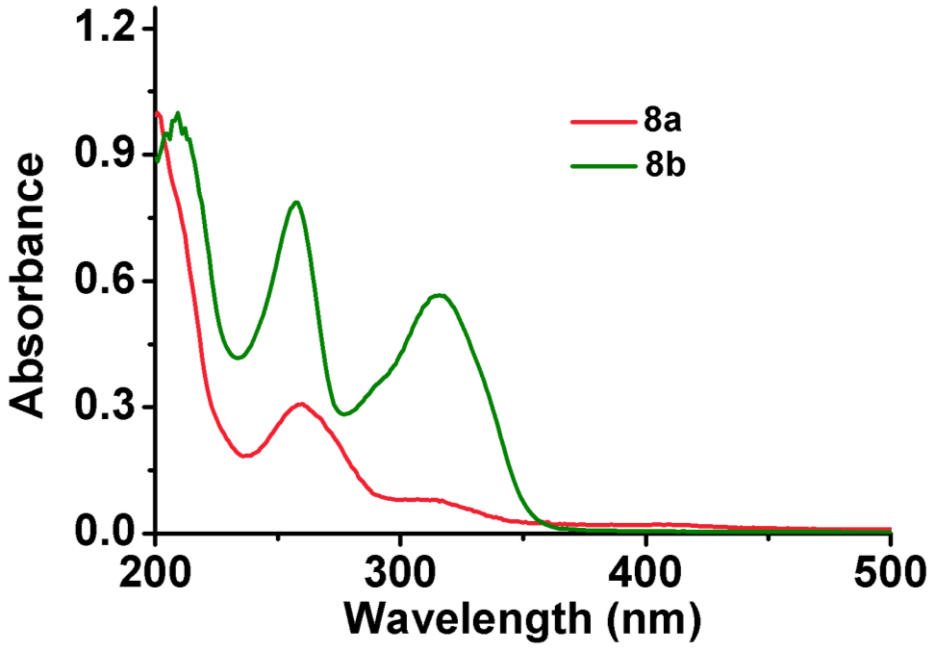


Fig. S16. Absorption spectra of photoproducts (**8a, 8b**) after the release of corresponding alcohols (first release) from **5a** and **5b** in acetonitrile (C = 10^{-5} mol/L, 298 K).

8. Photolysis of dual caged compound 5b

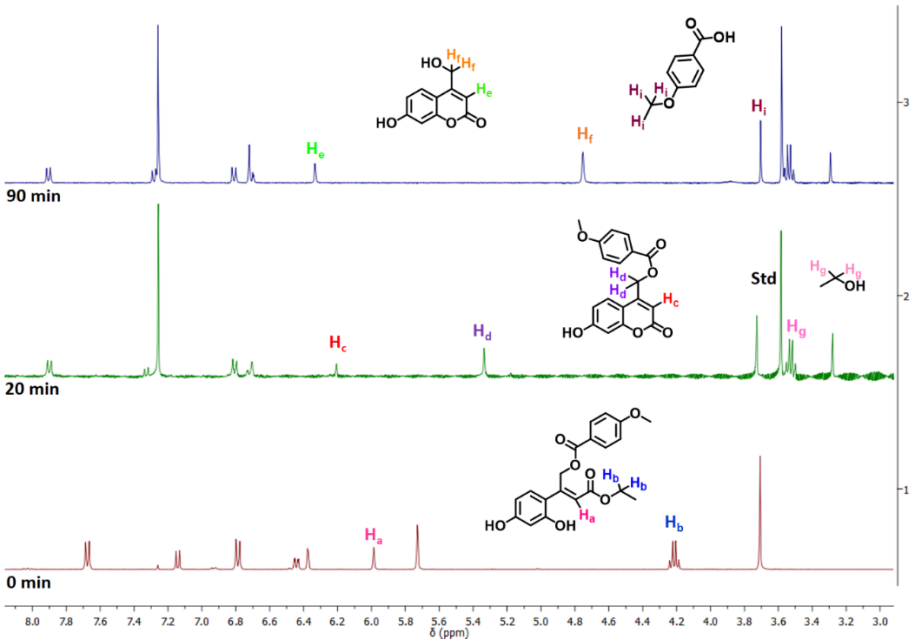


Fig. S17. Photolysis of dual caged compound **5b** monitored by ^{1}H NMR in $CDCl_3$ with 1,2-dichloroethane as an internal standard.

9. Absorption spectrum of dual caged compound 6c

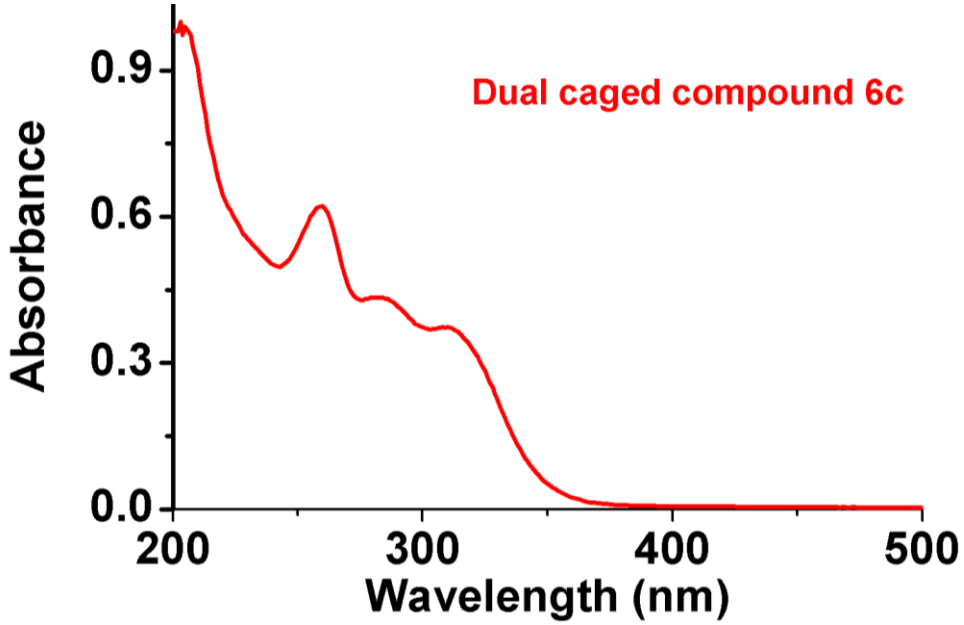


Fig. S18. Absorption spectrum of dual caged compound **6c** in acetonitrile (C = 10^{-5} mol/L, 298 K).

10. Characterisation of photoproducts of dual caged compound 6c

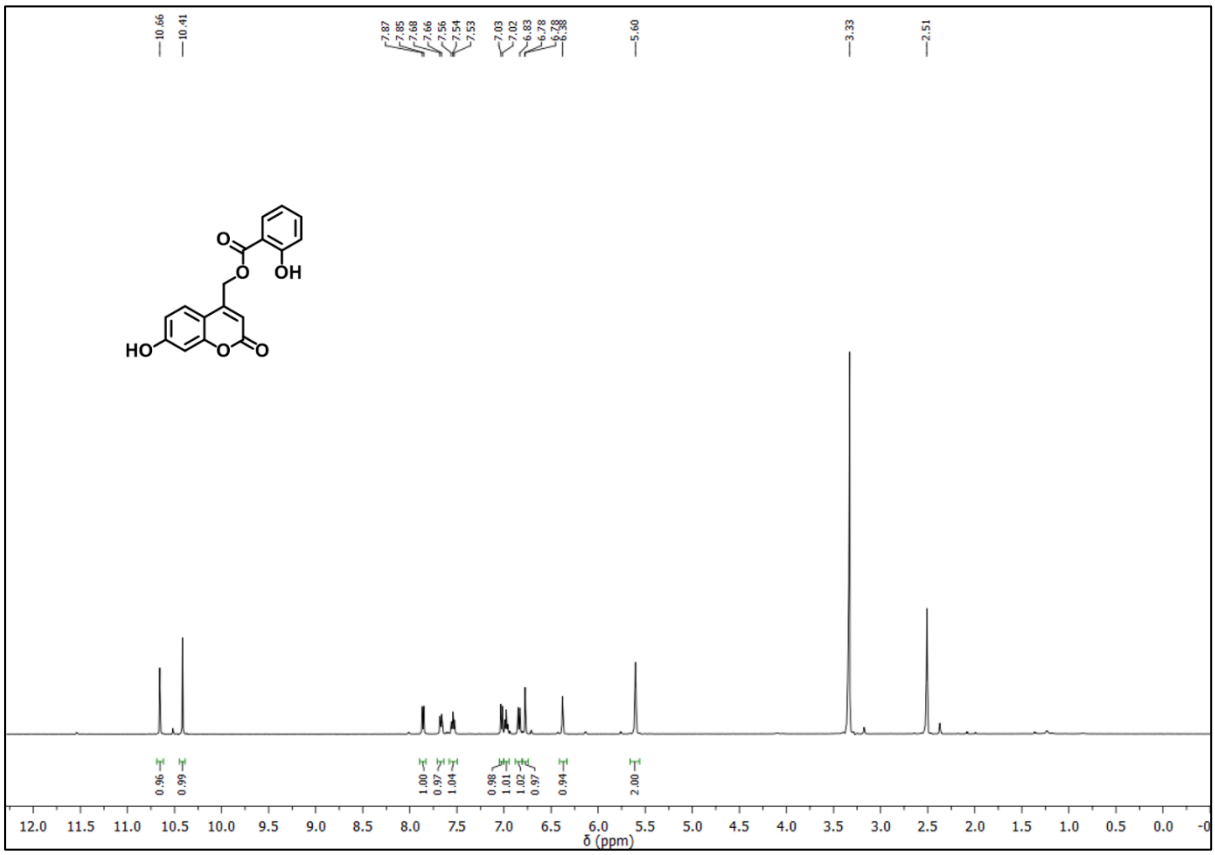


Fig. S19. ^{1}H NMR spectrum of intermediate salicylic acid caged coumarin derivative in DMSO-d_6 formed after first release from **6c**.

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.66 (s, 1H), 10.41 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.54 (t, *J* = 8.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.38 (s, 1H), 5.60 (s, 2H).

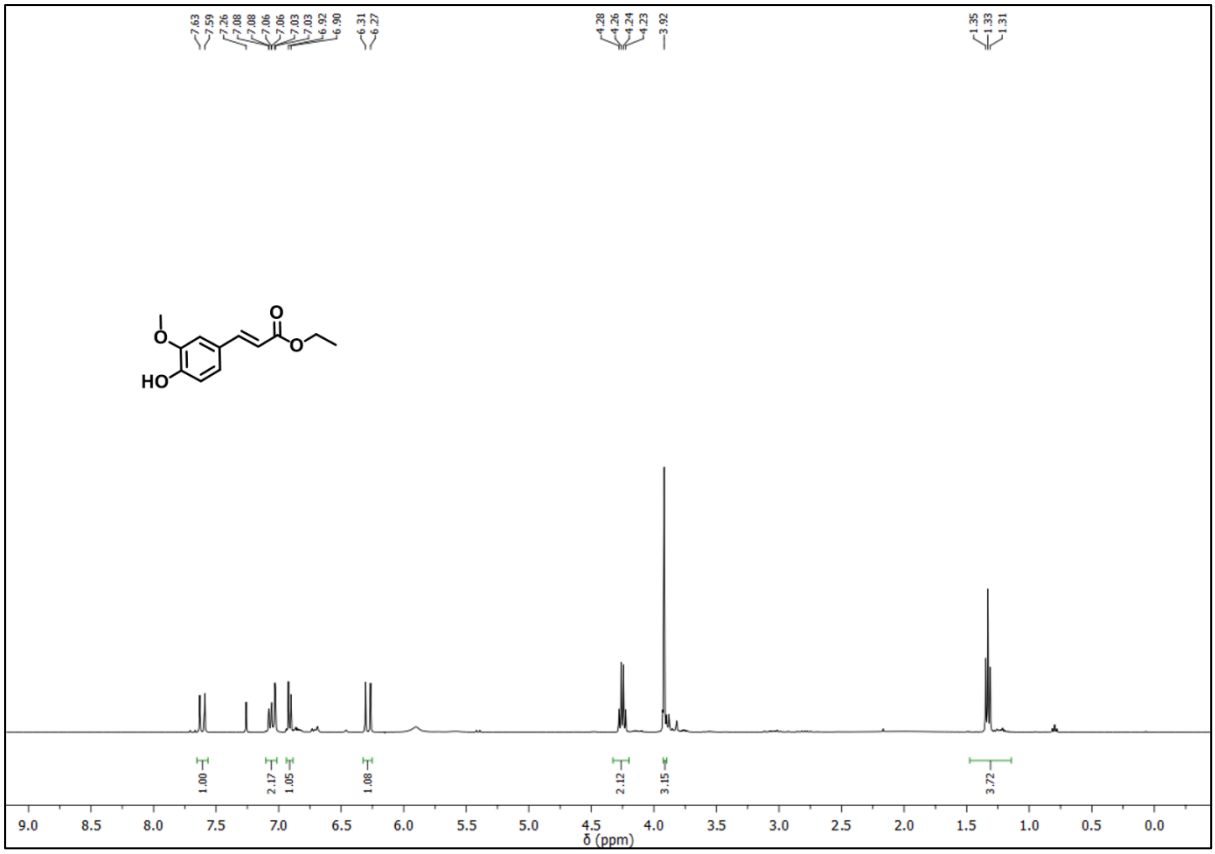


Fig. S20. ^{1}H NMR spectrum of FAEE released from **6c** in $CDCl_3$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.9 Hz, 2H), 7.10 – 7.01 (m, 4H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.29 (d, *J* = 15.9 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 4H), 3.92 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 7H).

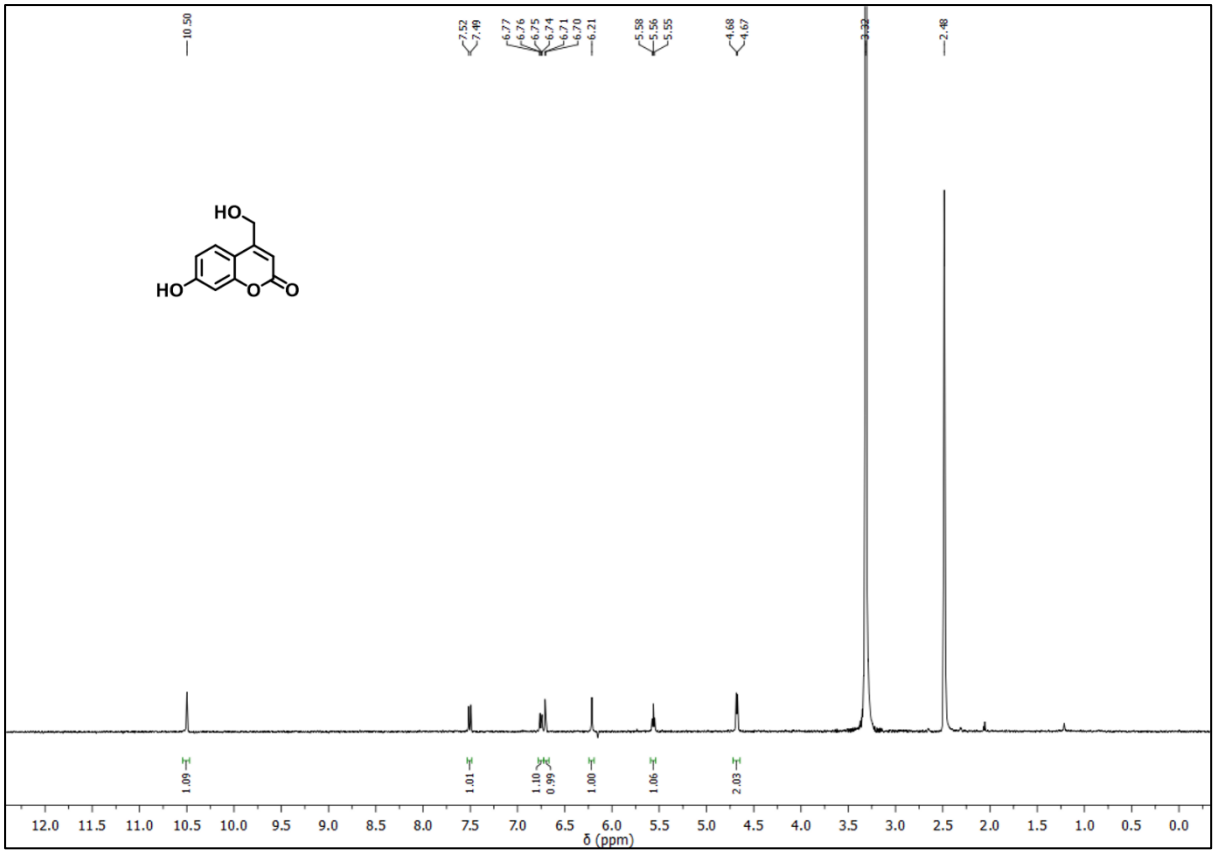


Fig. S21. ^{1}H NMR spectrum of final photoproduct formed after dual release from **6c** in DMSO-d_6.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 6.75 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 6.21 (s, 1H), 5.56 (t, *J* = 5.5 Hz, 1H), 4.68 (d, *J* = 5.4 Hz, 2H).

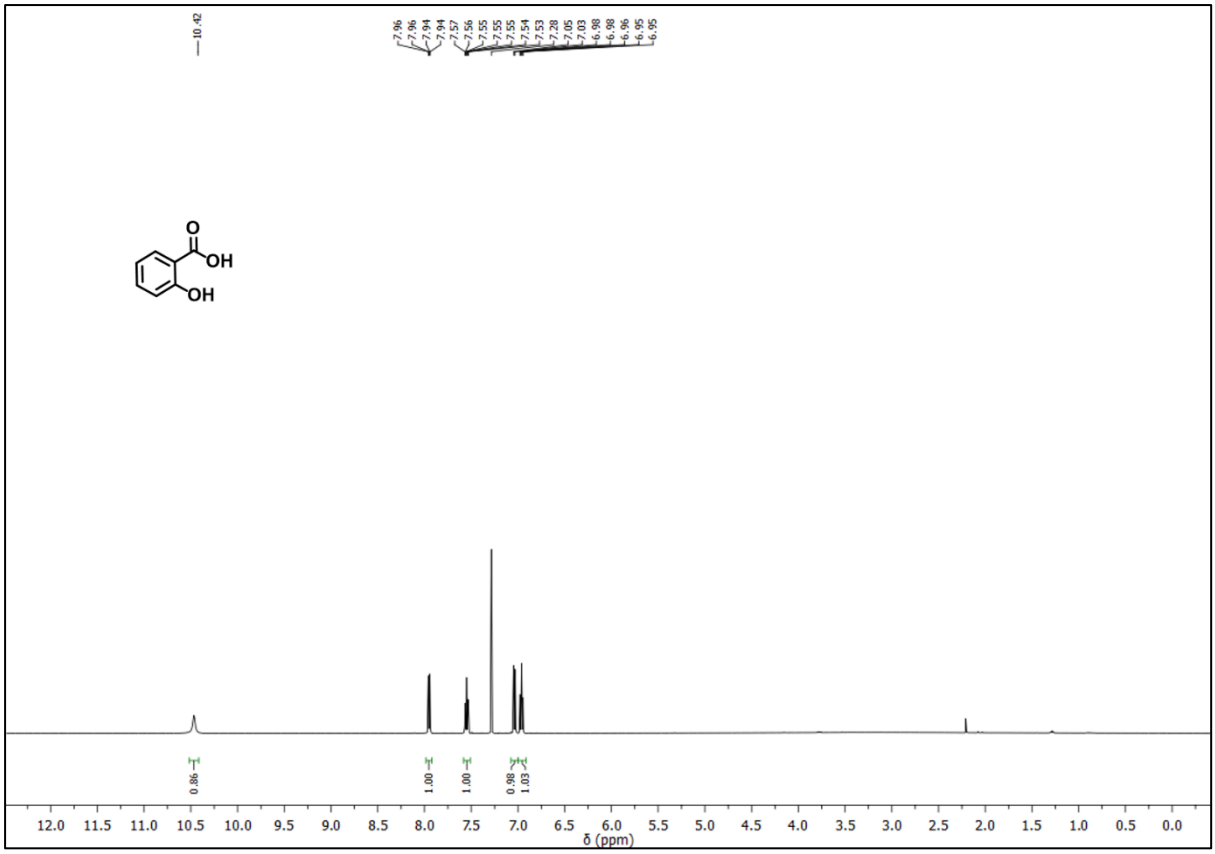


Figure S22. ^{1}H NMR spectrum of salicylic acid in $CDCl_3$ after second release from **6c**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.95 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.55 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.00 – 6.91 (m, 1H).

References:

1. (a) E. T. Ryan, T. Xiang, K. P. Johnston and M. A. Fox, *J. Phys. Chem. A*, 1997, **101**, 1827–1835. (b) A. Jana, B. Saha, M. Ikbal, S. K. Ghosh and N. D. P. Singh, *Photochem. Photobiol. Sci*. 2012, **11**, 1558.
2. H. J. Kuhn, S. E. Braslawsky and R. Schmidt, *Pure Appl. Chem*. 1989, **61**, 187-210.