Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information (78 Pages)

Near-Visible Light Active Biomass Derived Benzoin Photoinitiators for Energy Curing Applications

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1. General methods

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar®, Sigma-Aldrich®, Acros organics®, TCI America®, and Oakwood® Products, and were used as received without further purification. Spectrophotometric grade solvents (e.g. acetonitrile, ethanol) were purchased from Sigma-Aldrich® and used without further purification for emission measurements. Unless stated otherwise, reactions were conducted in oven-dried glassware under nitrogen atmosphere. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 500 MHz (125 MHz for ^{13}C) spectrometers. Data from the ^{1}H-NMR spectroscopy are reported as chemical shift (δ ppm) with the corresponding integration values. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), m (multiplet) and virt (virtual). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm).

When necessary, the compounds were purified by combiflash equipped with dual wavelength UV-Vis absorbance detector (Teledyne ISCO) using hexanes: ethyl acetate as the mobile phase and Redisep® cartridge filled with silica (Teledyne ISCO) as stationary phase. In some cases, compounds were purified by column chromatography on silica gel (Sorbent Technologies®, silica gel standard grade: porosity 60 Å, particle size: 230 x 400 mesh, surface area: 500 – 600 m^{2}/g, bulk density: 0.4 g/mL, pH range: 6.5 – 7.5). Unless indicated, the Retention Factor (R_f) values were recorded using a 5-50% hexanes:ethyl acetate as mobile phase and on Sorbent Technologies®, silica Gel TLC plates (200 mm thickness w/UV254).

1.1. Photophysical Methods.

Spectrophotometric solvents (Sigma-Aldrich®) were used whenever necessary unless or otherwise mentioned. UV quality fluorimeter cells (with range until 190 nm) were purchased from Luzchem®. Absorbance measurements were performed using a Cary 300 UV-Vis spectrophotometer. Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150-30 Nd:YAG laser (266 nm, ca 5 mJ/pulse, 7 nanosecond pulse length) and a computer controlled system that has been described previously.[1] Solution of the chlorobenzoin **1b** and **1g** were prepared at concentrations such that the absorbance was 0.3 at the excitation wavelength (355 nm) and deoxygenated by argon purging.

Phosphorescence emission, and lifetime experiments were carried out using Edinburgh instruments FLS 1000® photoluminescence Spectrometer. A microsecond-pulsed Xenon lamp source was used to record phosphorescence spectra and phosphorescence lifetimes.

1.2. Gel permeation Chromatography (GPC) Analysis.

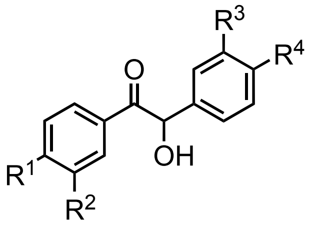
Polymer sample analysis were performed on EcoSEC GPC System (HLC-8320) equipped with a dual flow refractive index detector (RI) detector. Separation of injections occurred over a column bank consisting of two 67.8 mm ID × 30 cm, 5 μm particle size TSKgel® multiporeH xL (exclusion limit 6 × 104 g/mol) and one 6 mm ID × 15 cm, 4 μm particle size TSKgel SuperH-RC (exclusion limit 5 × 105 g/mol) columns (Tosoh Bioscience LLC). Tetrahydrofuran (THF) (HPLC grade, EMD Omnisolv®) was used as mobile phase and solvent for sample preparation. were at flow rate of 1 mL/min. Detector, pump oven, and column oven were maintained at 40 °C. Polystyrene kits with PStQuick C (Lot No: PSQ-D02C) and PStQuick C (Lot No: PSQ-C04C) All the molecular weight values (M_w, M_n and $Đ_M$) results are calculated based on a polystyrene calibration curve. The polymers were dissolved overnight in THF (1 mg polymer in 1 mL in THF) . The solutions were filtered through a 0.2 μm PTFE membrane filter and analyzed by GPC.

1.3. Curing analysis with Omnicure 365

Curing of resins with photoinitiator was performed by utilizing Omnicure AC8150 365 nm air cooled UV LED curing system equipped with specialized front-end optics at working distances 3-4 cm. Optical power of 260 W. With a peak irradiance of over 8 W/cm^2, the system ensures rapid and uniform curing even at long distances. Sample was irradiated with 100% intensity

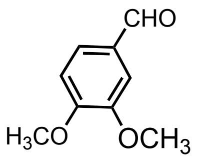
2. Chemical structures of benzoin photoinitiators, monomer and polymers.

2.1. Chemical structures of benzoin photoinitiators, monomer and corresponding polymers.

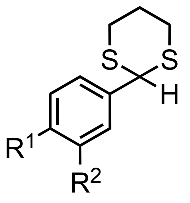


1

1a ; $R^1 = R^2 = R^3 = R^4 = OCH_3$
1b ; $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = Cl$
1c ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CN$
1d ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CF_3$
1e ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = SCH_3$
1f ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = F$
1g ; $R^1 = Cl$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
1h ; $R^1 = SCH_3$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
1i ; $R^1 = F$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
1j ; $R^1 = R^2 = R^3 = R^4 = H$

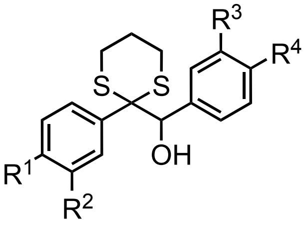


2



3

3a ; $R^1 = R^2 = OCH_3$
3g ; $R^1 = Cl$; $R^2 = H$
3h ; $R^1 = SCH_3$; $R^2 = H$
3i ; $R^1 = F$; $R^2 = H$



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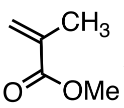

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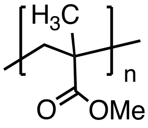
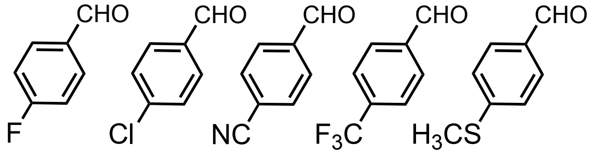


7

4 =



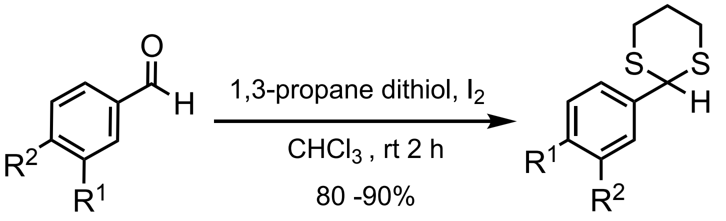
4a **4b** **4c** **4d** **4e**

5a ; $R^1 = R^2 = R^3 = R^4 = OCH_3$
5b ; $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = Cl$
5c ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CN$
5d ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CF_3$
5e ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = SCH_3$
5f ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = F$
5g ; $R^1 = Cl$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
5h ; $R^1 = SCH_3$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
5i ; $R^1 = F$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$

Chart S1**:** Chemical structures of benzoin photoinitiators, monomers and corresponding polymers

3. General procedure for synthesis of benzoin derivatives.

3.1. Synthesis of dithiane derivatives **3a**, **3g-i.**

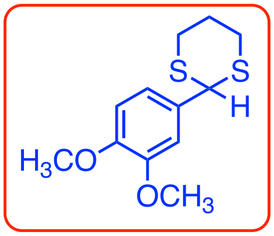


2 or **4** **3**

3a ; $R^1 = R^2 = OCH_3$
3g ; R^1 = Cl; R^2 = H
3h ; $R^1 = SCH_3$; R^2 = H
3i ; R^1 = F; R^2 = H

Scheme S1: Synthesis of dithiane derivatives **3a**, **3g-i.**

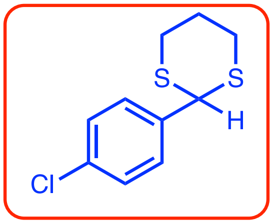
To a solution of **2** or **4** (1.0 *equiv*) Iodine (0.1 *equiv*) was dissolved in $CHCl_3$ (45 mL) and 1,3-propane dithiol [2] (1.4 *equiv*) was added and the resulting mixture was stirred for 2 h at room temperature. After the completion of reaction, the solution was diluted with $CHCl_3$ (3 × 50 mL) and quenched with NaOH (2.5 M, 25 mL) and Na_2SO_3 (0.1M, 25 mL) respectively. The obtained organic layer was washed with brine solution. The combined organic layer was dried over *anhyd.* Na_2SO_4, and solvent was removed under reduced pressure to get the crude product. The crude product was purified by Combiflash using hexanes: ethyl acetate mixture.



R*f* = 0.47 (30% ethyl acetate: 70% hexanes) for **3a**, (Yield = 89%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.03 – 6.98 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.12 (s, 1H), 3.87 (d, *J* = 17.5 Hz, 6H), 3.11 – 3.00 (m, 2H), 2.94 – 2.83 (m, 2H), 2.15 (dtt, *J* = 13.9, 4.6, 2.5 Hz, 1H), 1.98 – 1.82 (m, 1H).

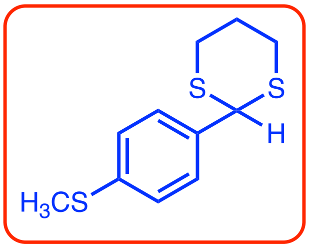
^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 149.0, 149.0, 131.7, 120.0, 111.1, 110.7, 55.9, 51.2, 32.2, 25.1.



R*f* = 0.35 (30% ethyl acetate: 70% hexanes) for **3g**, (Yield = 90%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.43 – 7.39 (m, 2H), 7.33 – 7.29 (m, 2H), 5.13 (s, 1H), 3.09 – 3.01 (m, 2H), 2.91 (dddd, *J* = 13.5, 4.4, 3.0, 1.0 Hz, 2H), 2.17 (dtt, *J* = 14.0, 4.6, 2.4 Hz, 1H), 1.92 (dtt, *J* = 14.2, 12.4, 3.1 Hz, 1H).

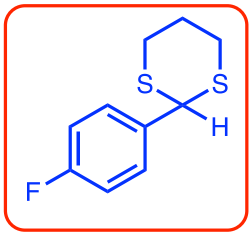
^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 137.7, 134.3, 129.3, 129.1, 50.7, 32.1, 25.1.



R*f* = 0.40 (20% ethyl acetate: 80% hexanes) for **3h**, (Yield = 87%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.39 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.18 (m, 2H), 5.13 (s, 1H), 3.05 (ddd, *J* = 14.8, 12.5, 2.4 Hz, 2H), 2.95 – 2.85 (m, 2H), 2.47 (s, 3H), 2.22 – 2.10 (m, 1H), 1.98 – 1.85 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 139.0, 135.9, 128.3, 126.7, 51.0, 32.2, 25.2, 15.8.

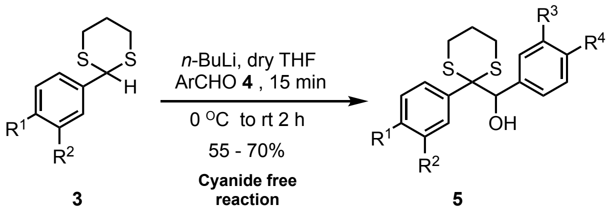


R*f* = 0.40 (20% ethyl acetate: 80% hexanes) for **3i**, (Yield = 95%).

^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm) 1H NMR (500 MHz, CDCl3) δ 7.47 – 7.42 (m, 2H), 7.05 – 6.99 (m, 2H), 5.15 (s, 1H), 3.09 – 3.01 (m, 2H), 2.91 (ddd, J = 14.6, 4.3, 3.1 Hz, 2H), 2.17 (dtt, J = 14.0, 4.6, 2.5 Hz, 1H), 1.92 (dtt, J = 14.2, 12.4, 3.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 163.5, 161.6, 135.0, 129.5, 115.7, 50.5, 32.1, 25.0.

3.2. Synthesis of hydroxy derivatives **5a-i.**

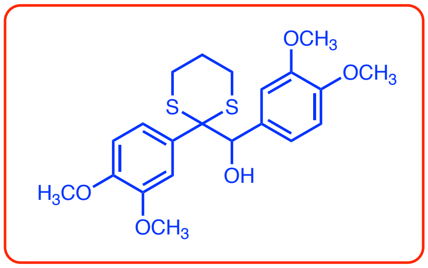


3a ; $R^1 = R^2 = OCH_3$
3g ; $R^1 = Cl$; $R^2 = H$
3h ; $R^1 = SCH_3$; $R^2 = H$
3i ; $R^1 = F$; $R^2 = H$

5a ;$R^1 = R^2 = R^3 = R^4 = OCH_3$
5b ; $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = Cl$
5c ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CN$
5d ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CF_3$
5e ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = SCH_3$
5f ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = F$
5g ; $R^1 = Cl$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
5h ; $R^1 = SCH_3$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
5i ; $R^1 = F$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$

Scheme S2: Synthesis of hydroxy derivatives **5a-i.**

To solution of **3** (1.0 *equiv*) in dry THF (30 mL) at 0°C, n-BuLi (1.6 mM in hexane, 1.5 *equiv*) was added slowly over 15 min. The resulting mixture was allowed to stir at 0 °C for 30 minutes. A solution of **4** (in dry THF) was added slowly. The mixture was then brought to room temperature and stirred for 2 h. After completion of reaction, the mixture was quenched with saturated NH_4Cl solution and washed with brine and ethyl acetate (3 × 50 mL). The combined organic layers were dried over *anhyd.* Na_2SO_4. Ethyl acetate was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes: ethyl acetate mixture.

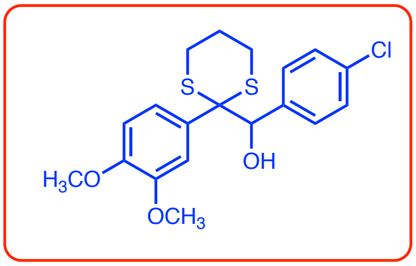


R*f* = 0.25 (50% ethyl acetate: 50% hexanes) for **5a**, (Yield = 70%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.28 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.52 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.25 (d, *J* = 2.0 Hz, 1H), 4.93 – 4.85 (m, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 2.95 (d, *J* = 3.4 Hz, 1H), 2.72 – 2.61 (m, 4H), 1.93 – 1.84 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm)148.7, 148.4, 148.3, 147.5, 129.8, 129.5, 123.5, 120.8, 114.1, 111.2, 110.3, 109.4, 80.9, 66.5, 55.9, 55.9, 55.8, 55.5, 27.4, 27.1, 24.9.

HRMS-ESI (m/z) ($[M + Na]^+$):Calculated: 445.1120, Observed: 445.1119, |Δm| = 0.22 ppm.

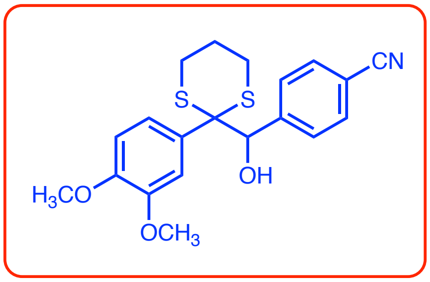


R*f* = 0.45 (30% ethyl acetate: 70% hexanes) for **5b**, (Yield = 68%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.29 – 7.25 (m, 1H), 7.11 – 7.07 (m, 2H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.79 (dd, *J* = 8.5, 7.7 Hz, 3H), 4.88 (d, *J* = 3.5 Hz, 1H), 3.88 (s, 3H), 3.66 (s, 3H), 3.09 (d, *J* = 3.6 Hz, 1H), 2.75 – 2.61 (m, 4H), 1.93 – 1.86 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm)148.4, 148.4, 135.9, 133.8, 129.6, 129.2, 127.1, 123.1, 113.6, 110.4, 80.4, 66.3, 55.8, 55.8, 27.4, 27.0, 24.7.

HRMS-ESI (m/z) ($[M + Na]^+$):Calculated: 419.0510, Observed: 419.0518, |Δm| = 1.90 ppm.

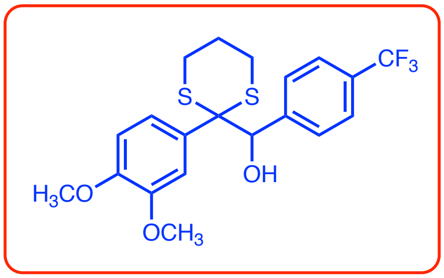


R*f* = 0.30 (30% ethyl acetate: 70% hexanes) for **5c**, (Yield = 65%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.43 (d, *J* = 8.3 Hz, 2H), 7.22 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.79 (d, *J* = 8.5 Hz, 1H), 4.96 (d, *J* = 3.2 Hz, 1H), 3.90 (s, 3H), 3.69 (s, 3H), 3.18 (d, *J* = 3.3 Hz, 1H), 2.82 – 2.58 (m, 4H), 1.99 – 1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 148.6, 148.6, 142.7, 130.7, 129.0, 122.9, 118.7, 113.1, 111.6, 110.5, 80.3, 66.1, 55.8, 27.3, 26.9, 24.5.

HRMS-ESI (m/z) ($[M + Na]^+$):Calculated: 410.0850, Observed: 410.0861, |Δm| = 2.68 ppm.

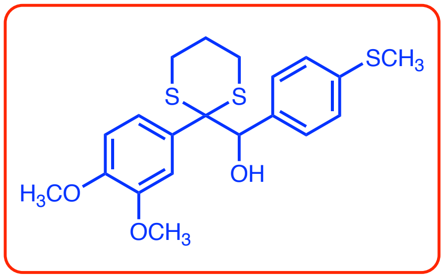


R*f* = 0.35 (30% ethyl acetate: 70% hexanes) for **5d**, (Yield = 60%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.42 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.04 – 6.98 (m, 3H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.98 (d, *J* = 2.6 Hz, 1H), 3.91 (s, 3H), 3.62 (s, 3H), 3.12 (d, *J* = 3.4 Hz, 1H), 2.79 – 2.65 (m, 4H), 1.97 – 1.90 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$, δ ppm) 148.5, 141.3, 130.5, 130.2, 130.0, 129.7, 129.1, 128.6, 123.9, 123.8, 122.9, 113.5, 110.5, 80.5, 66.3, 55.9, 55.7, 27.4, 27.0, 24.7.

HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 453.0778, Observed: 453.0782, |Δm| = 0.88 ppm.

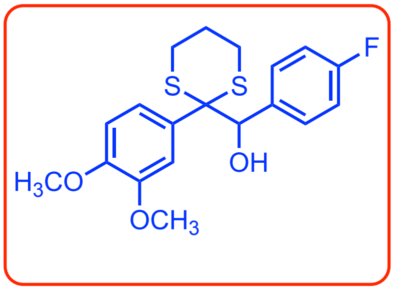


Rf = 0.30 (30% ethyl acetate: 70% hexanes) for **5e** (Yield = 65%).

^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 7.33 (dd, J = 8.5, 2.3 Hz, 1H), 7.06 (d, J = 2.3 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.83 – 6.78 (m, 3H), 4.90 (s, 1H), 3.89 (s, 3H), 3.65 (s, 3H), 2.78 – 2.61 (m, 4H), 2.41 (d, J = 1.2 Hz, 3H), 1.94 – 1.83 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$, δ ppm) 163.5, 161.5, 148.4, 148.3, 133.2, 133.2, 129.9, 129.7, 129.3, 123.1, 113.9, 113.8, 113.7, 110.4, 66.4, 55.8, 55.8, 27.3, 27.0, 24.7.

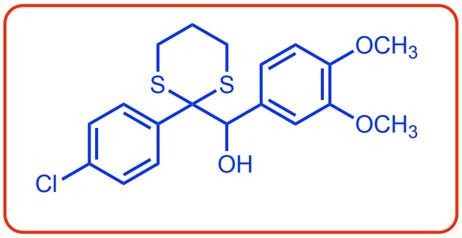
HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 431.0776, Observed: 431.0785, |Δm| = 2.08 ppm.



Rf = 0.30 (30% ethyl acetate: 70% hexanes) for **5f**, (Yield = 65%).

^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 77.30 (dd, J = 8.5, 2.3 Hz, 1H), 7.09 (d, J = 2.3 Hz, 1H), 6.93 – 6.73 (m, 5H), 4.93 (s, 1H), 3.90 (s, 3H), 3.70 (d, J = 9.2 Hz, 3H), 2.79 – 2.62 (m, 4H), 1.98 – 1.84 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$, δ ppm) 148.6, 148.6, 142.7, 130.7, 129.0, 122.9, 118.7, 113.1, 111.6, 110.5, 80.3, 66.1, 55.8, 27.3, 26.9, 24.5.

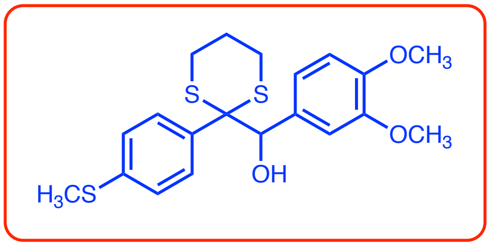


R*f* = 0.35 (30% ethyl acetate: 70% hexanes) for **5g**, (Yield = 65%).

^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 7.67 – 7.63 (m, 2H), 7.32 – 7.15 (m, 2H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.62 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.15 (d, *J* = 1.9 Hz, 1H), 4.97 (d, *J* = 3.2 Hz, 1H), 3.86 (s, 3H), 3.59 (s, 3H), 2.91 (d, *J* = 3.3 Hz, 1H), 2.80 – 2.58 (m, 4H), 1.95 (tdt, *J* = 10.5, 7.4, 3.8 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$, δ ppm) 148.8, 147.6, 136.1, 133.6, 132.5, 129.3, 129.0, 128.2, 128.1, 120.7, 110.9, 109.4, 80.7, 65.8, 55.7, 55.4, 27.3, 27.0, 24.7.

HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 419.0515, Observed: 419.0518, |Δm| = 0.72 ppm.

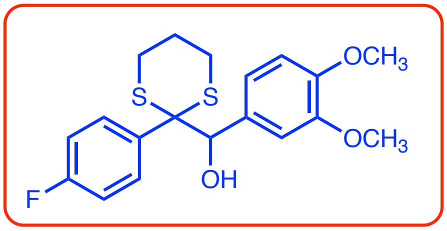


R*f* = 0.48 (20% ethyl acetate: 70% hexanes) for **5h**, (Yield = 68%).

^{1}H NMR (500 MHz, CDCl$_3$, δ ppm) 7.58 – 7.51 (m, 2H), 7.14 – 7.08 (m, 2H), 6.66 – 6.56 (m, 2H), 6.01 (d, *J* = 1.8 Hz, 1H), 4.87 (d, *J* = 2.4 Hz, 1H), 3.77 (s, 3H), 3.47 (s, 3H), 3.06 (d, *J* = 3.3 Hz, 1H), 2.70 – 2.54 (m, 4H), 2.42 (s, 3H), 1.85 (tq, *J* = 6.6, 3.3, 2.8 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$, δ ppm) 148.5, 147.3, 137.9, 133.9, 131.3, 129.6, 125.4, 120.5, 110.9, 109.2, 80.4, 65.9, 55.6, 55.2, 27.1, 26.9, 24.7, 15.2.

HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 431.0776, Observed: 431.0785, |Δm| = 2.08 ppm.



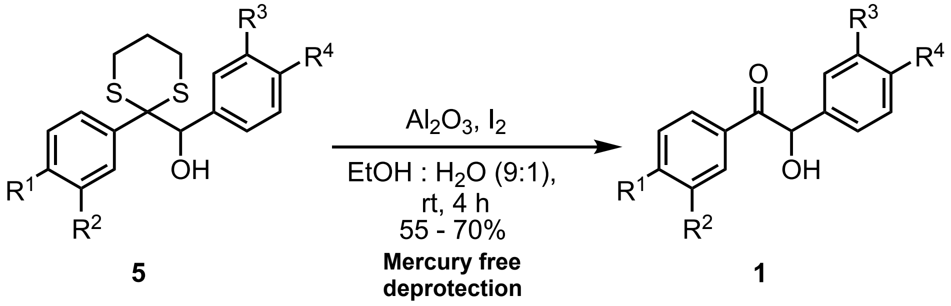
R*f* = 0.48 (20% ethyl acetate: 70% hexanes) for **5i**, (Yield = 70%).

^{1}H NMR (500 MHz, CDCl$_3$, δ ppm)7.75 – 7.53 (m, 2H), 7.08 – 6.89 (m, 2H), 6.68 (d, J = 8.3 Hz, 1H), 6.57 (dd, J = 8.3, 1.9 Hz, 1H), 6.18 (d, J = 1.9 Hz, 1H), 4.96 (s, 1H), 3.83 (s, 3H), 3.59 (s, 3H), 2.80 – 2.50 (m, 4H), 1.94 (dd, J = 7.5, 4.0 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$, δ ppm) 149.01, 147.83, 133.00, 132.94, 129.66, 120.89, 114.96, 114.80, 111.19, 109.69, 80.90, 65.92, 55.89, 55.59, 27.41, 27.15, 24.89.

HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 419.0515, Observed: 419.0518, |Δm| = 0.72 ppm.

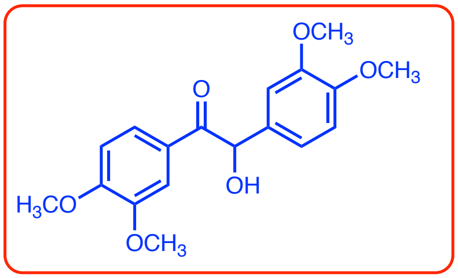
3.3. Synthesis of benzoin derivatives **1a-i**



5a ;$R^1 = R^2 = R^3 = R^4 = OCH_3$	**1a** ; $R^1 = R^2 = R^3 = R^4 = OCH_3$
5b ; $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = Cl$	**1b** ; $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = Cl$
5c ; $R^1 = R^2 = OCH_3$; $R^3 =H$, $R^4 = CN$	**1c** ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CN$
5d ; $R^1 = R^2 = OCH_3$; $R^3 =H$, $R^4 = CF_3$	**1d** ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = CF_3$
5e ; $R^1 = R^2 = OCH_3$; $R^3 =H$, $R^4 = SCH_3$	**1e** ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = SCH_3$
5f ; $R^1 = R^2 = OCH_3$; $R^3 =H$, $R^4 = F$	**1f** ; $R^1 = R^2 = OCH_3$; $R^3 = H$, $R^4 = F$
5g ; $R^1 = Cl$; $R^2 = H$; $R^3 =OCH_3$, $R^4 = OCH_3$	**1g ;** $R^1 = Cl$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
5h ; $R^1 = SCH_3$; $R^2 = H$; $R^3 =OCH_3$, $R^4 = OCH_3$	**1h** ; $R^1 = SCH_3$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$
5i ; $R^1 = F$; $R^2 = H$; $R^3 =OCH_3$, $R^4 = OCH_3$	**1i** ; $R^1 = F$; $R^2 = H$; $R^3 = OCH_3$, $R^4 = OCH_3$

Scheme S3: Synthesis of benzoin derivatives **1a-i**.

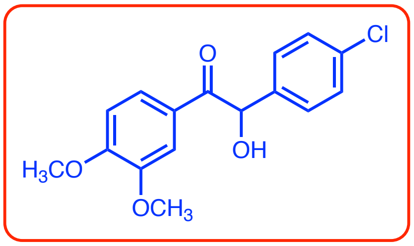
Deprotection of dithiane protecting group was carried out based on the reported literature.[3] To a solution of hydroxy derivative **5** (1.0 *equiv*) in EtOH (30 mL), freshly prepared catalyst (1.4 *equiv* iodine adsorbed on 7.5 *equiv* Al_2O_3) was added and the mixture and was stirred for 20 minutes at room temperature. Water (3 mL) was added to the reaction mixture and continued stirring for ~ 4 h. After the completion of reaction, the mixture was filtered through celite bed and washed with ethyl acetate (2 x 20 mL). The organic layers were washed with saturated sodium bisulfate solution (10 mL) and ethyl acetate (10 mL). Further the combined organic layer was dried over *anhyd.* Na_2SO_4, filtered and the solvent was removed under reduced pressure. The obtained crude product was purified by combiflash using hexanes: ethyl acetate mixture.



R*f* = 0.45 (50% ethyl acetate: 50% hexanes) for **1a**, (Yield = 65%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.55 – 7.49 (m, 2H), 6.91 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.81 (d, *J* = 3.9 Hz, 1H), 6.79 (dd, *J* = 3.1, 0.9 Hz, 2H), 5.84 (d, *J* = 6.0 Hz, 1H), 4.57 (d, *J* = 6.0 Hz, 1H), 3.88 (d, *J* = 7.4 Hz, 6H), 3.83 (d, *J* = 1.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 197.3, 153.8, 149.4, 149.1, 148.9, 132.2, 126.3, 124.2, 120.4, 111.3, 111.0, 110.1, 110.0, 75.5, 56.0, 55.9, 55.8, 55.8. HRMS-ESI (m/z) ($[M + Na]^+$):Calculated: 355.1149, Observed: 355.1158, |Δm| = 2.53 ppm.

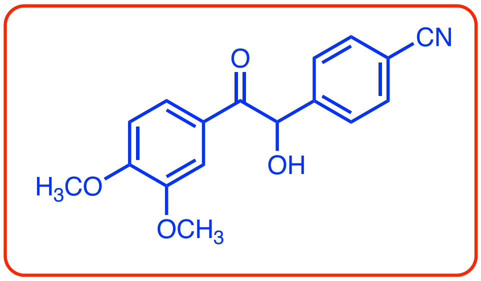


R*f* = 0.40 (50% ethyl acetate: 50% hexanes) for **1b**, (Yield = 68%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.48 – 7.43 (m, 2H), 7.26 (d, *J* = 1.0 Hz, 4H), 6.78 (d, *J* = 9.0 Hz, 1H), 5.87 (d, *J* = 6.0 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 3.87 (d, *J* = 8.3 Hz, 6H) 3.85 (d, *J* = 8.3 Hz, 6H

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 196.9, 154.1, 149.2, 138.3, 134.4, 129.3, 129.0, 126.1, 124.3, 111.1, 110.1, 75.0, 56.1, 56.0.

HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 329.0543, Observed: 355.0557, |Δm| = 4.25 ppm.

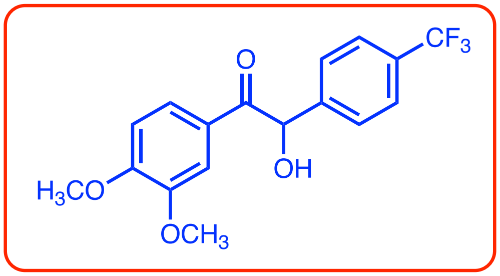


R*f* = 0.34 (50% ethyl acetate: 50% hexanes) for **1c**, (Yield = 55%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm)7.65 – 7.58 (m, 2H), 7.47 (td, *J* = 5.4, 1.9 Hz, 4H), 6.82 (d, *J* = 9.0 Hz, 1H), 5.96 (d, *J* = 6.0 Hz, 1H), 4.68 (d, *J* = 6.2 Hz, 1H), 3.90 (d, *J* = 11.6 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 196.2, 154.4, 149.4, 144.6, 132.8, 128.3, 125.8, 124.2, 118.3, 112.4, 111.0, 110.2, 74.9, 56.2, 56.0.

HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 320.0885, Observed: 355.0899, |Δm| = 4.37 ppm.

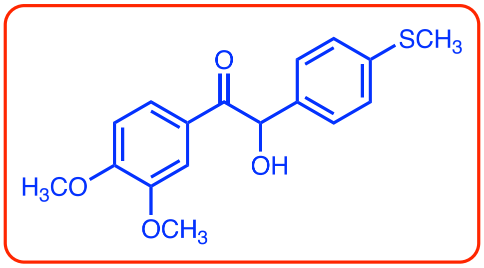


R*f* = 0.30 (50% ethyl acetate: 50% hexanes) for **1d**, (Yield = 68%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.58 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.53 – 7.44 (m, 4H), 6.86 – 6.78 (m, 1H), 5.97 (s, 1H), 4.69 (s, 1H), 3.90 (d, *J* = 9.2 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 196.5, 154.3, 149.2, 143.5, 130.9, 130.7, 130.4, 130.2, 127.9, 126.1, 126.0, 126.0, 126.0, 125.9, 124.9, 124.2, 122.7, 110.9, 110.1, 75.0, 56.1, 55.9.

HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 363.0821, Observed: 363.0820, |Δm| = 0.28 ppm.

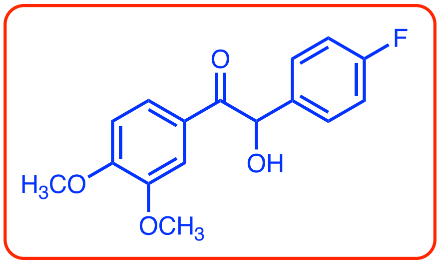


Rf = 0.34 (50% ethyl acetate: 50% hexanes) for **1e** (Yield = 55%).

^{1}H NMR ((500 MHz, $CDCl_3$, δ ppm) 7.53 (dd, J = 7.5, 1.8 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.13 (m, 2H), 6.93 – 6.72 (m, 1H), 5.89 (s, 1H), 3.91 (d, J = 7.4 Hz, 6H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 197.1, 154.0, 149.1, 139.2, 136.3, 128.1, 126.8, 126.1, 124.3, 111.0, 110.1, 75.3, 56.1, 56.0, 15.5.

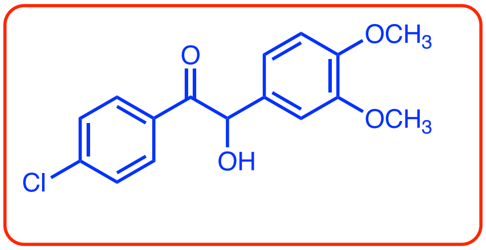
HRMS-ESI (m/z) ([M + Na]$^+$):Calculated: 341.0814, Observed: 341.0823, |Δm| = 2.63 ppm.



Rf = 0.34 (50% ethyl acetate: 50% hexanes) for **1f** (Yield = 55%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.61 – 7.43 (m, 2H), 7.40 – 7.29 (m, 2H), 7.02 (t, J = 8.7 Hz, 2H), 6.81 (d, J = 8.9 Hz, 1H), 5.90 (s, 1H), 3.89 (d, J = 9.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 197.2, 163.8, 161.8, 154.2, 149.3, 135.9, 135.8, 129.6, 129.5, 126.2, 124.4, 116.3, 116.2, 111.2, 110.2, 75.1, 56.2, 56.1.

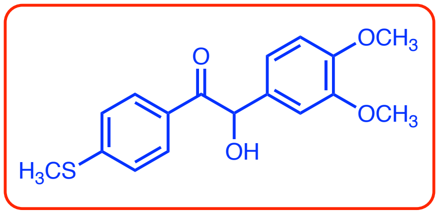


R*f* = 0.48 (50% ethyl acetate: 50% hexanes) for **1g**, (Yield = 56%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.90 – 7.85 (m, 2H), 7.42 – 7.37 (m, 2H), 6.91 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 2.1 Hz, 1H), 5.86 (d, *J* = 5.9 Hz, 1H), 4.45 (d, *J* = 5.9 Hz, 1H), 3.83 (s, 3H), 3.83 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 198.0, 149.7, 149.5, 140.5, 131.9, 131.2, 130.6, 129.2, 120.8, 111.5, 110.3, 76.3, 56.1, 56.0.

HRMS-ESI (m/z) ($[M + Na]^+$):Calculated: 329.0547, Observed: 329.0557, |Δm| = 3.04 ppm.

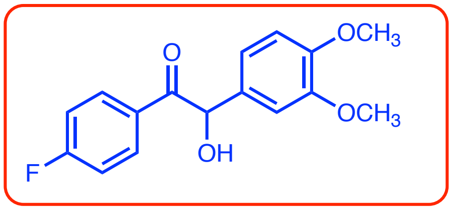


R*f* = 0.30 (50% ethyl acetate: 50% hexanes) for **1h**, (Yield = 58%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.86 – 7.81 (m, 2H), 7.22 – 7.16 (m, 2H), 6.91 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.83 – 6.78 (m, 2H), 5.85 (d, *J* = 5.9 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.84 (s, 3H) 2.48 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm). 197.6, 149.3, 149.1, 147.2, 131.6, 129.3, 124.6, 120.4, 111.2, 110.0, 75.6, 55.7, 55.7, 14.4

HRMS-ESI (m/z) ($[M + Na]^+$):Calculated: 341.0817, Observed: 341.0817, |Δm| = 1.76 ppm.



Rf = 0.34 (50% ethyl acetate: 50% hexanes) for **1i** (Yield = 58%).

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 8.02 – 7.84 (m, 2H), 7.15 – 7.03 (m, 2H), 6.90 (dd, J = 8.2, 2.0 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 6.76 (d, J = 2.0 Hz, 1H), 5.84 (s, 1H), 3.84 (d, J = 1.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm) 197.6, 149.7, 149.5, 132.1, 132.0, 131.4, 120.8, 116.2, 116.0, 111.5, 110.3, 76.1, 56.1, 56.0.

HRMS-ESI (m/z) ($[M + Na]^+$):Calculated: 313.0834, Observed: 313.0852, |Δm| = 5.75 ppm.

4. UV-Vis absorption studies

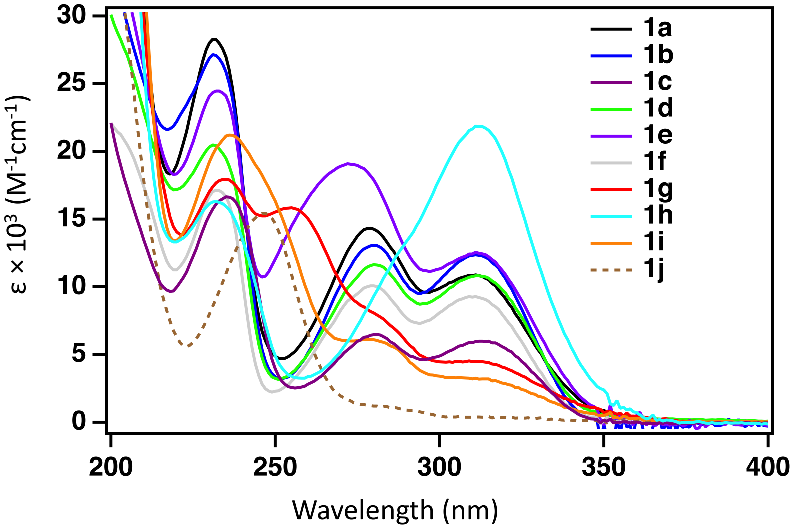


Figure S1: UV-Vis absorption spectra of photoinitiators **1a-j** with concentration of 0.16 μM in MeCN.

5. Table S1: Molar extinction co-efficient of photoinitiators 1a-1j

Entry	PI	$\varepsilon \times 10^3$ ($M^{-1}cm^{-1}$ at λ_{max} 311 nm)	ε ($M^{-1}cm^{-1}$ at λ_{max} 390 nm)
1	**1a**	10.9	10.0
2	**1b**	12.4	5.4
3	**1c**	5.96	117.6
4	**1d**	10.8	48.8
5	**1e**	12.6	13.3
6	**1f**	9.28	3.3
7	**1g**	4.49	24.1
8	**1h**	312	1.8
9	**1i**	3.25	3.3
10[a]	**1j**	15.4	-

[a] For **1j** molar extinction coefficient ε was reported at λ_{max} 246 nm due to the absence of 311 nm peak.

6. Photophysical Studies:

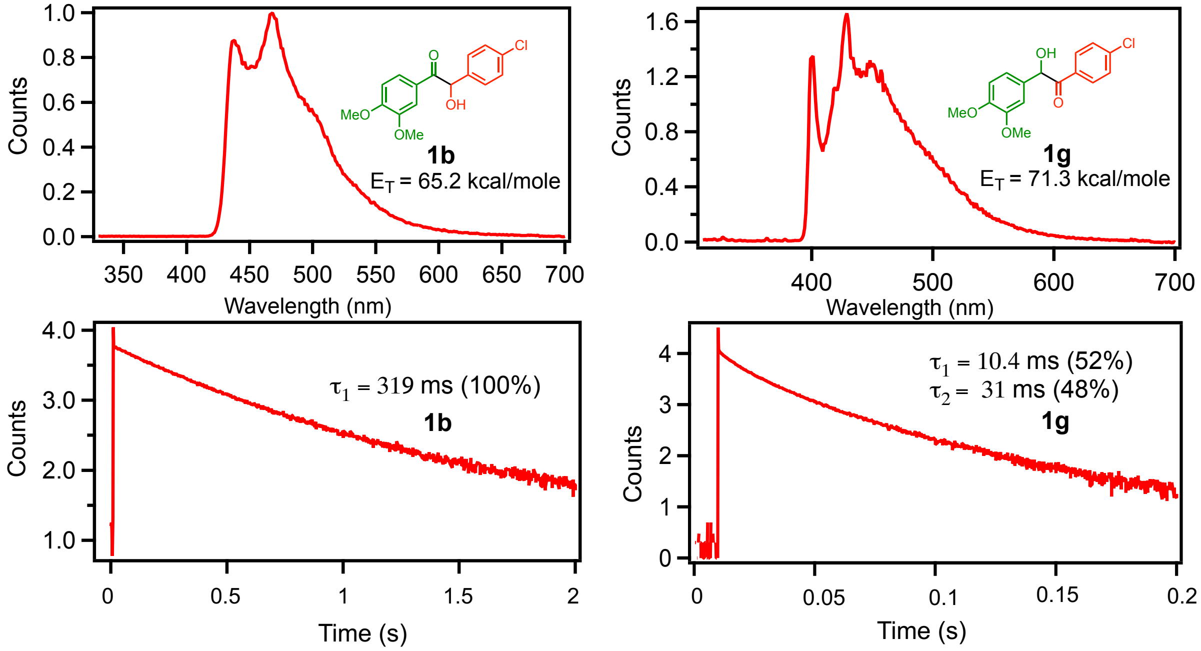
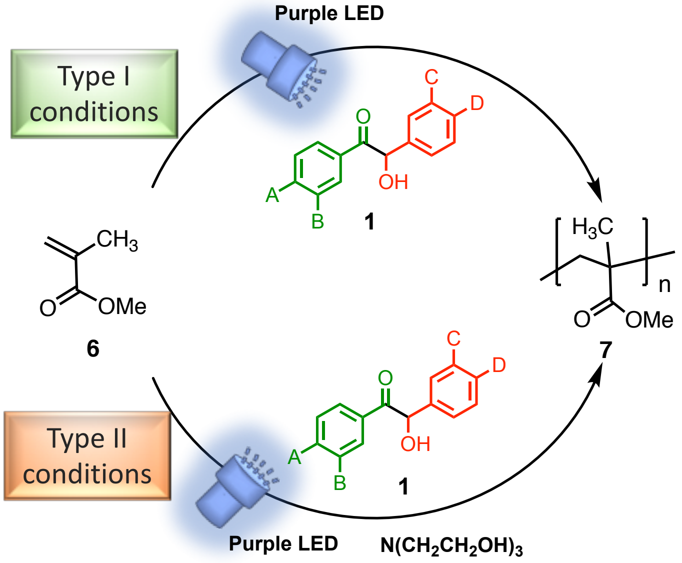


Figure S2: (Top) Time-resolved phosphorescence spectra of **1b** (λ_{ex} = 310 nm) (left) and **1g** (λ_{ex} = 290 nm) **(**right) in ethanol glass (10 ms delay after light pulse, 80 ms gate width). (Bottom) Phosphorescence decay kinetics at 77 K in ethanol glass for **1b** (λ_{ex} = 310 nm, λ_{em} = 438 nm) (left) and **1g** (λ_{ex} = 290 nm, λ_{em} = 401 nm) (right).

7. Photopolymerization of methylmethacrylate 6 with benzoin photoinitiators

7.1. Photopolymerization of methylmethacrylate **6**



Scheme S4: Photopolymerization of methylmethacrylate **6** with biomass derived benzoin photoinitiators.

Freshly distilled methyl methacrylate (MMA) **6**, benzoin photoinitiators **1a-h** and co-initiator (Table S2 and Table S3) were dissolved in MeCN. The solutions were taken in a sealed pyrex test tubes and was purged with N_2 to remove dissolved oxygen. The resulting mixture was irradiated with purple LED (~390 nm) (LED strip winded around glass jar) for 4 h. After the photopolymerization polymethylmethacrylate (PMMA) **7** was crashed out by addition of ~30 mL of cold methanol. Polymers were separated out by filtration and vacuum dried at ~35 °C for ~24 h.

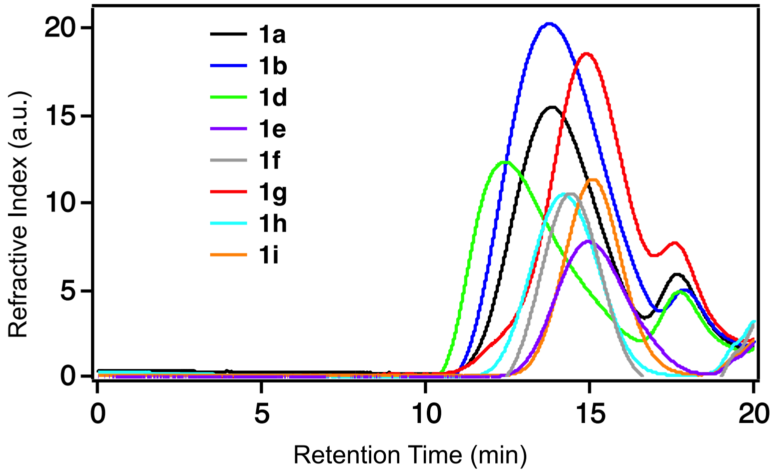


Figure S3: GPC analysis of polymers generated for Table 1 in the main manuscript.

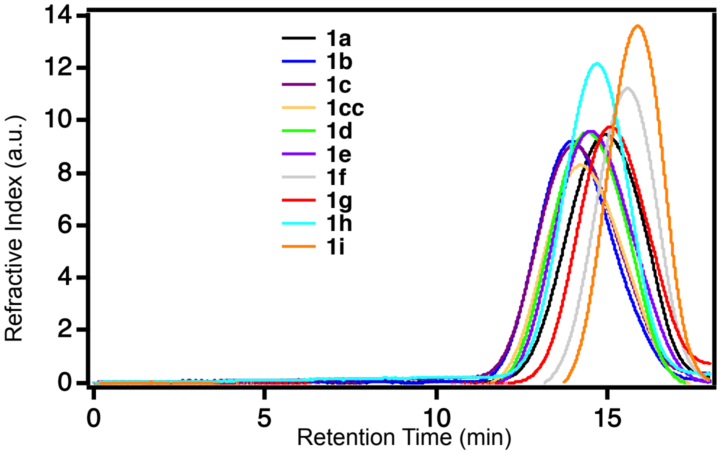


Figure S4: GPC analysis of polymers generated for Table 2 in the main manuscript.

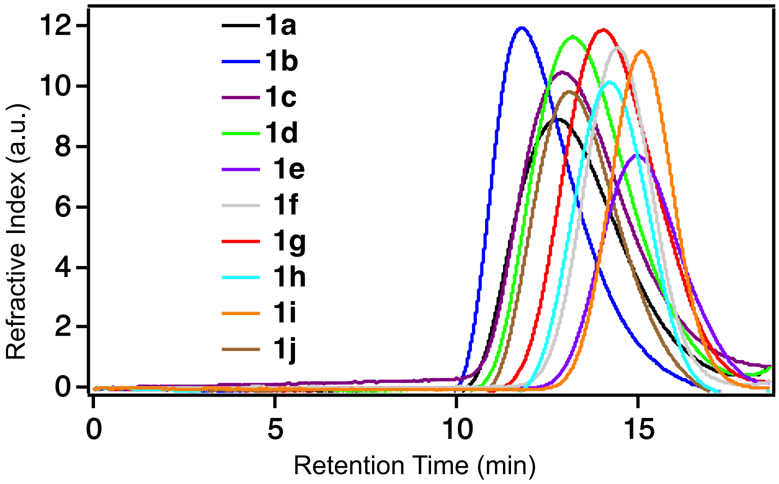


Figure S5: GPC analysis of polymers generated for Table 3 in the main manuscript.

8. Photocuring with high power LED

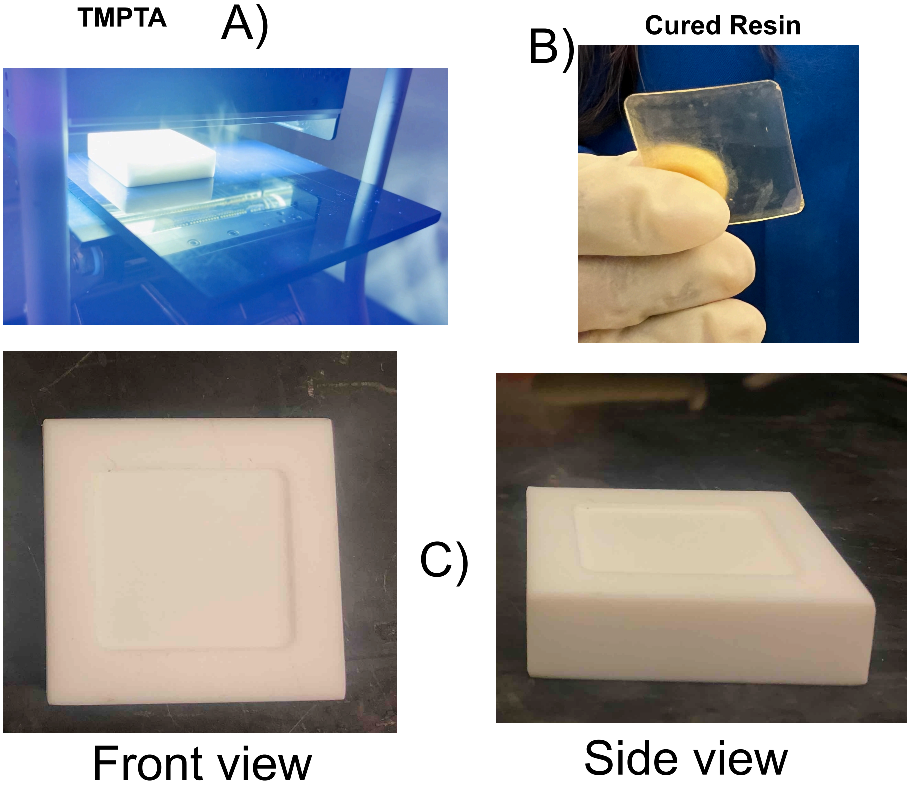
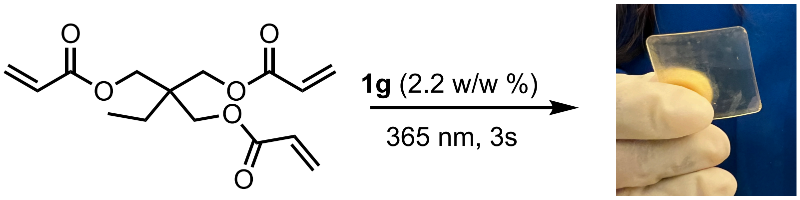


Figure S6: Reaction set up for photocuring A) Omnicure AC1850 LED set up B) Sample under irradiation C) Front and side view of the mold.



TMPTA (liquid)

cured resin (solid)

Scheme S5: Photopolymerization of **TMPTA** with biomass derived benzoin photoinitiator **1g** with 365 nm light curing

Homogeneous mixture of 2.2 w/w% of **1g** in TMPTA (Trimethylolpropane triacrylate) was poured in a mould and the sample were subjected to Omicure high power 365 nm LED irradiation for 3s to yield a transparent solid. The transparent solid material did not exhibit any tackiness or unpleasant odour. Thickness of the material was determined to be ~1.3 mm using a vernier calliper.

9. NMR spectra of 3a, 3g-i.

9.1. Characterization of **3a**

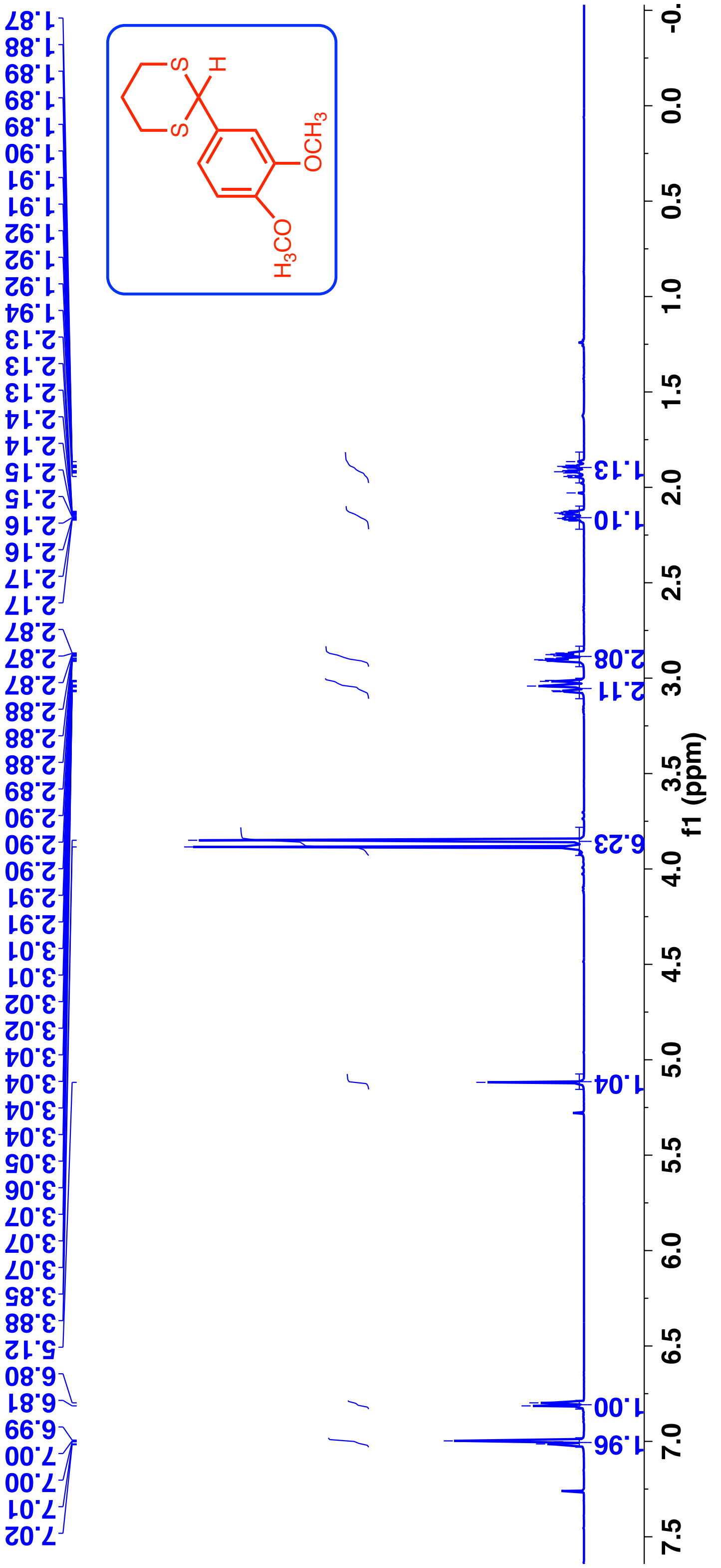


Figure S7: ^{1}H NMR spectra of **3a**.

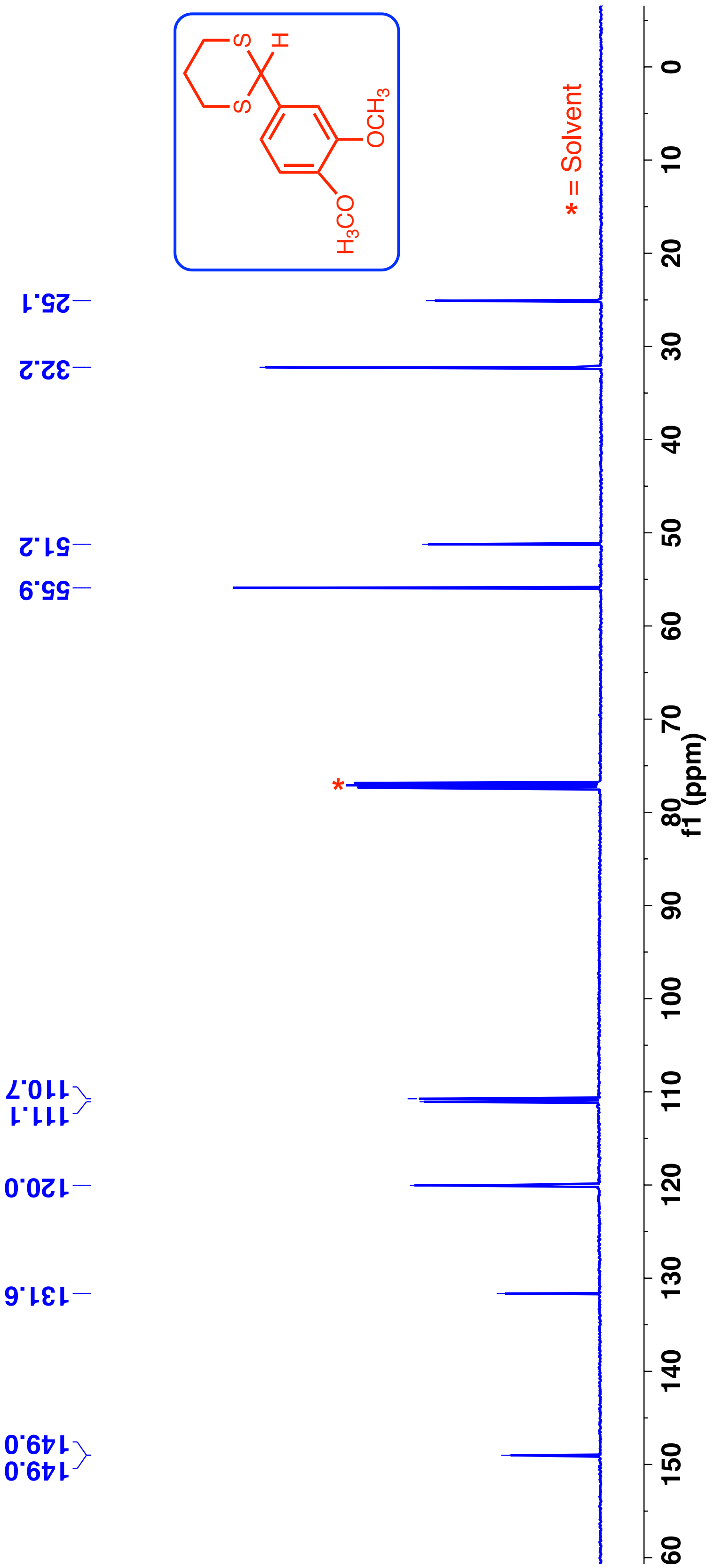


Figure S8: ^{13}C NMR spectra of **3a**.

9.2. Characterization of **3g**

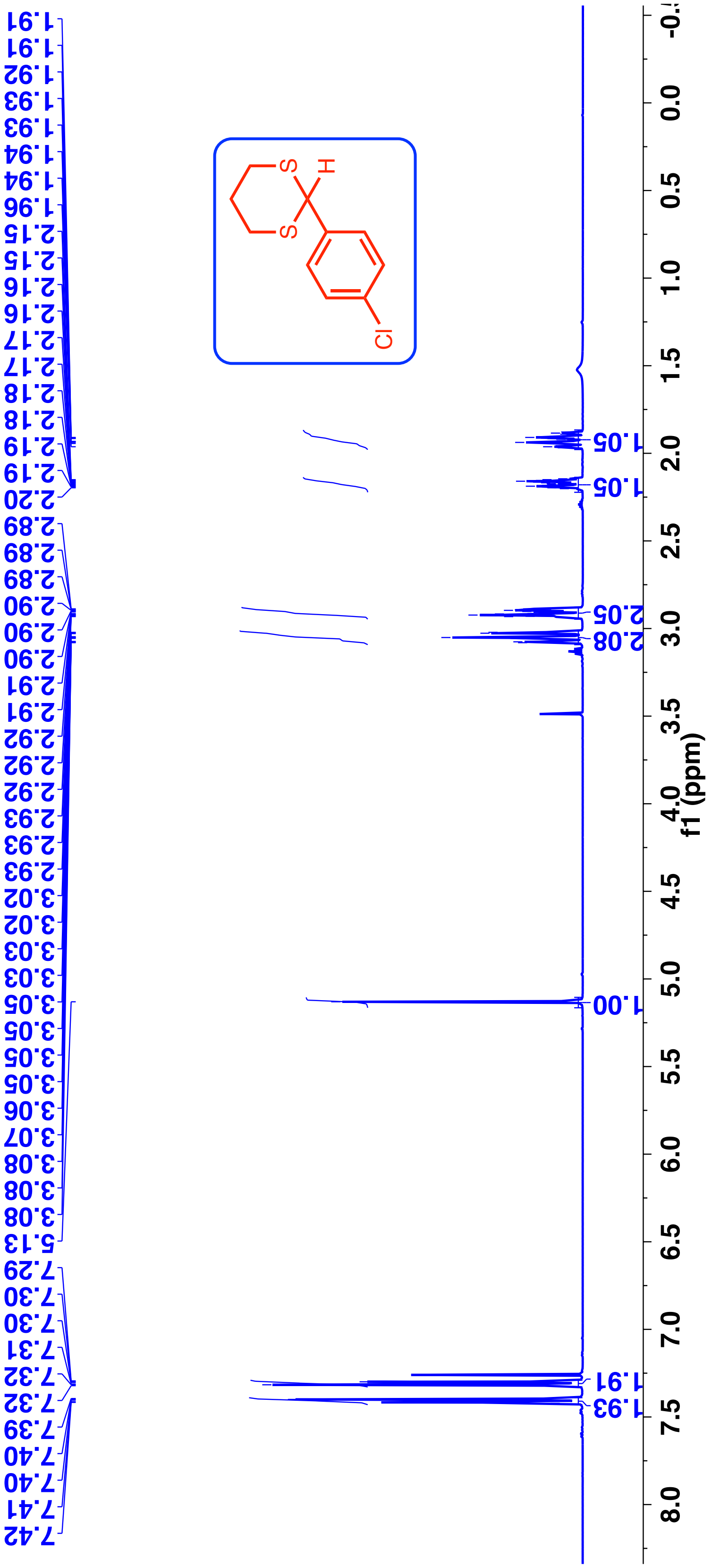


Figure S9: ^{1}H NMR spectra of **3g**.

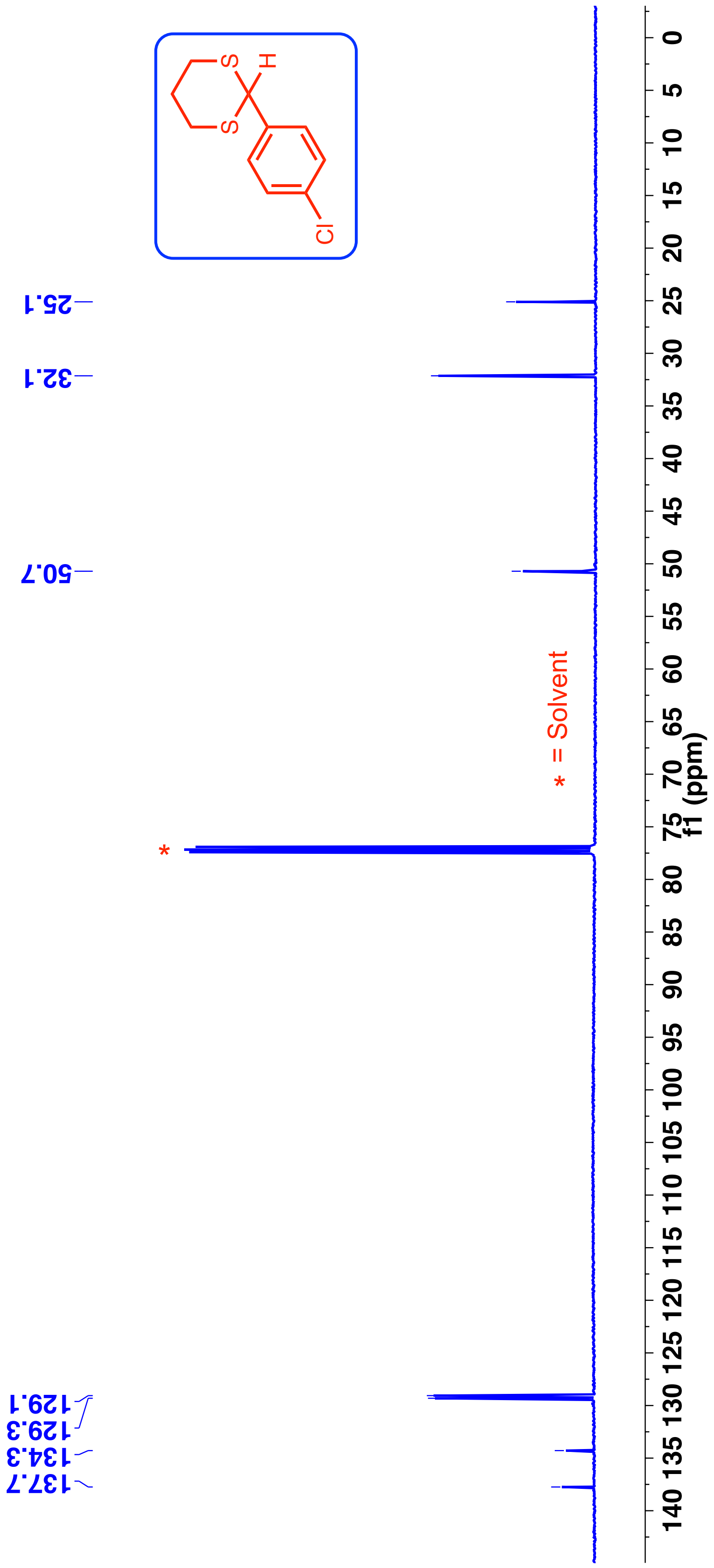


Figure S10: ^{13}C NMR spectra of **3g**.

9.3. Characterization of **3h**

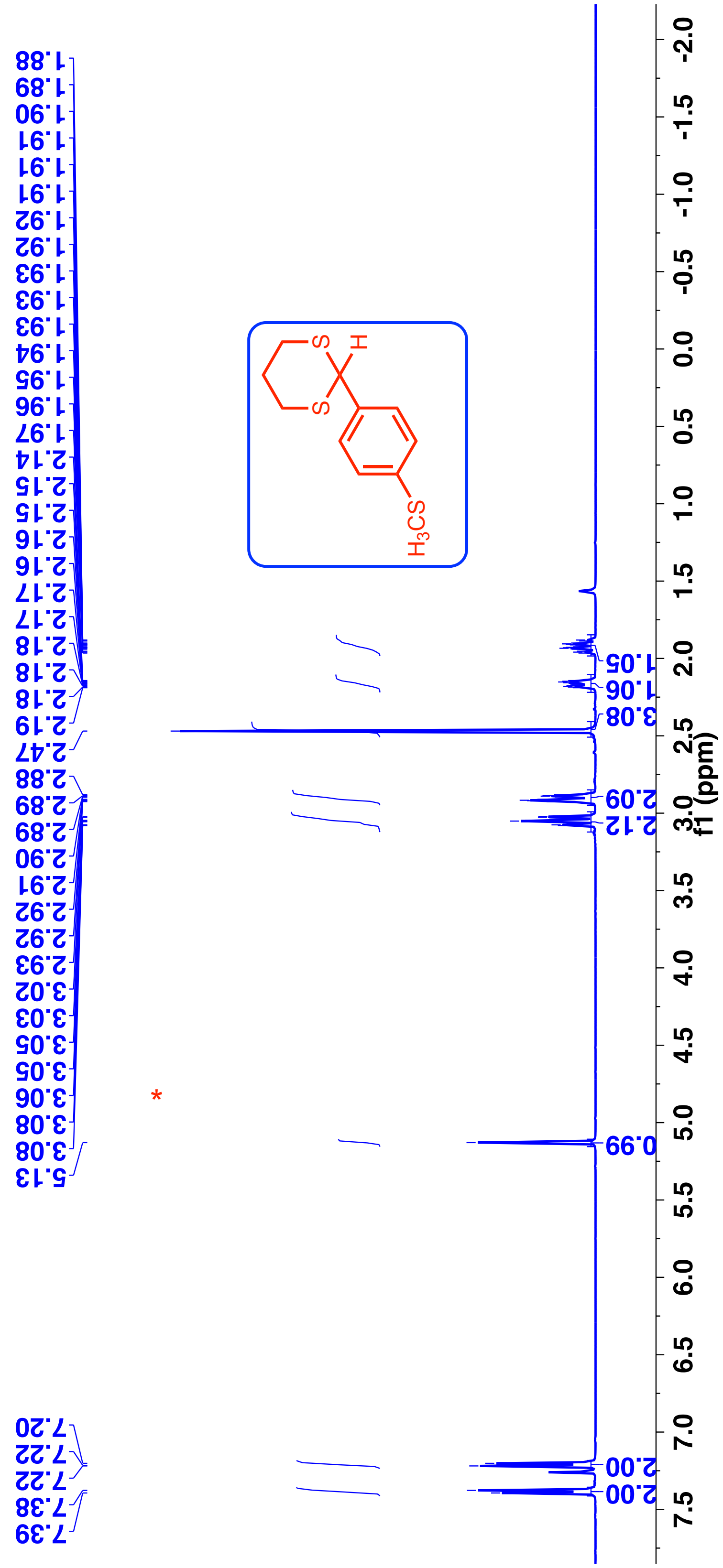


Figure S11: ^{1}H NMR spectra of **3h**.

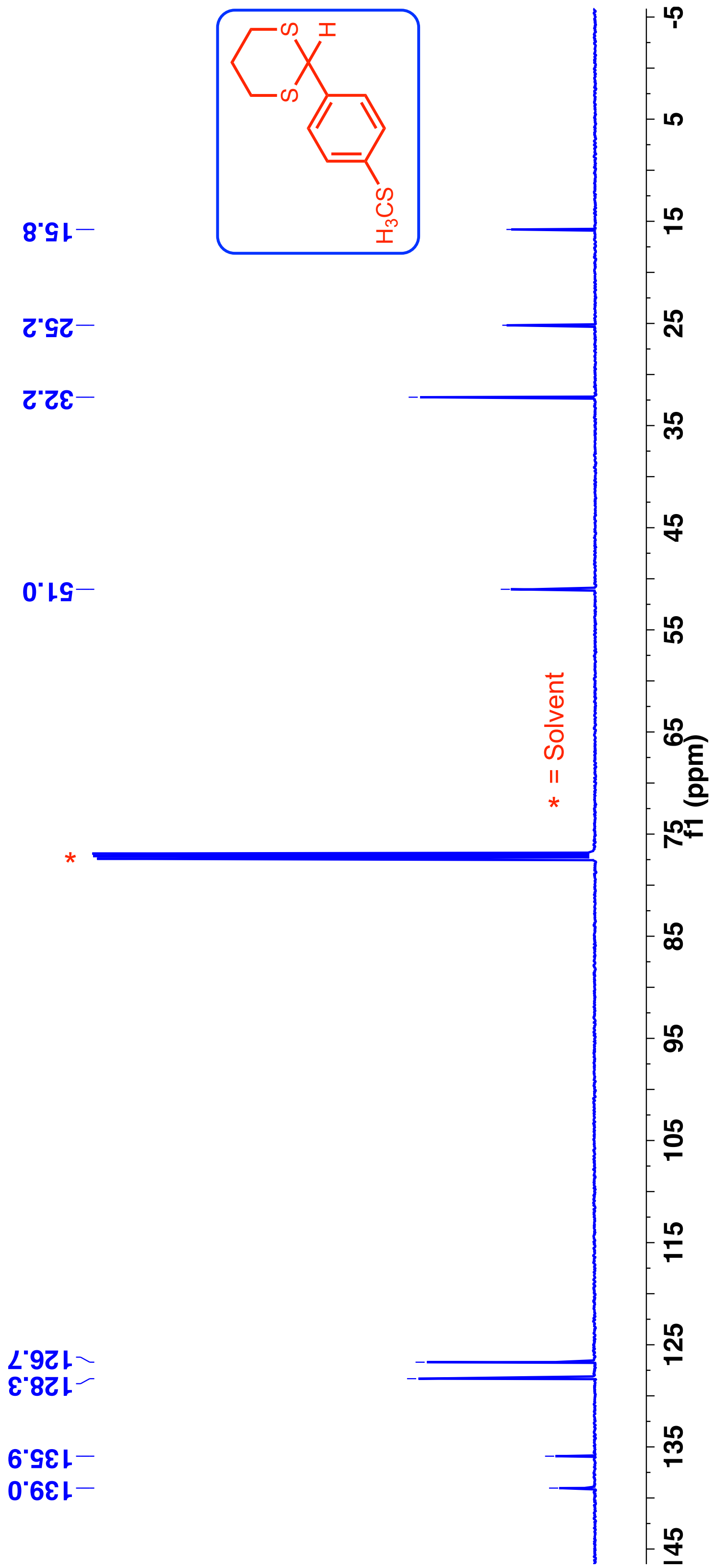


Figure S12: ^{13}C NMR spectra of **3h**.

9.4. Characterization of **3i**

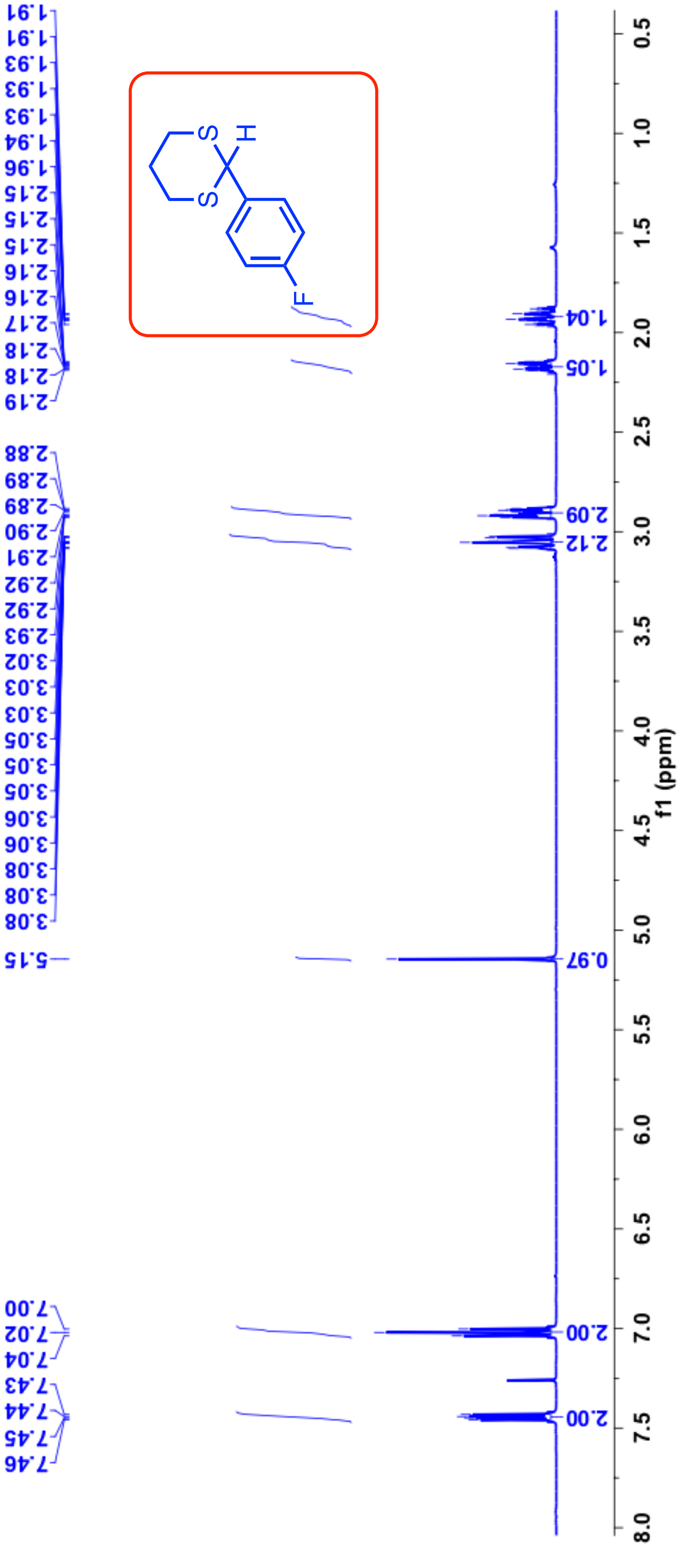


Figure S13: ^{1}H NMR spectra of **3i**.

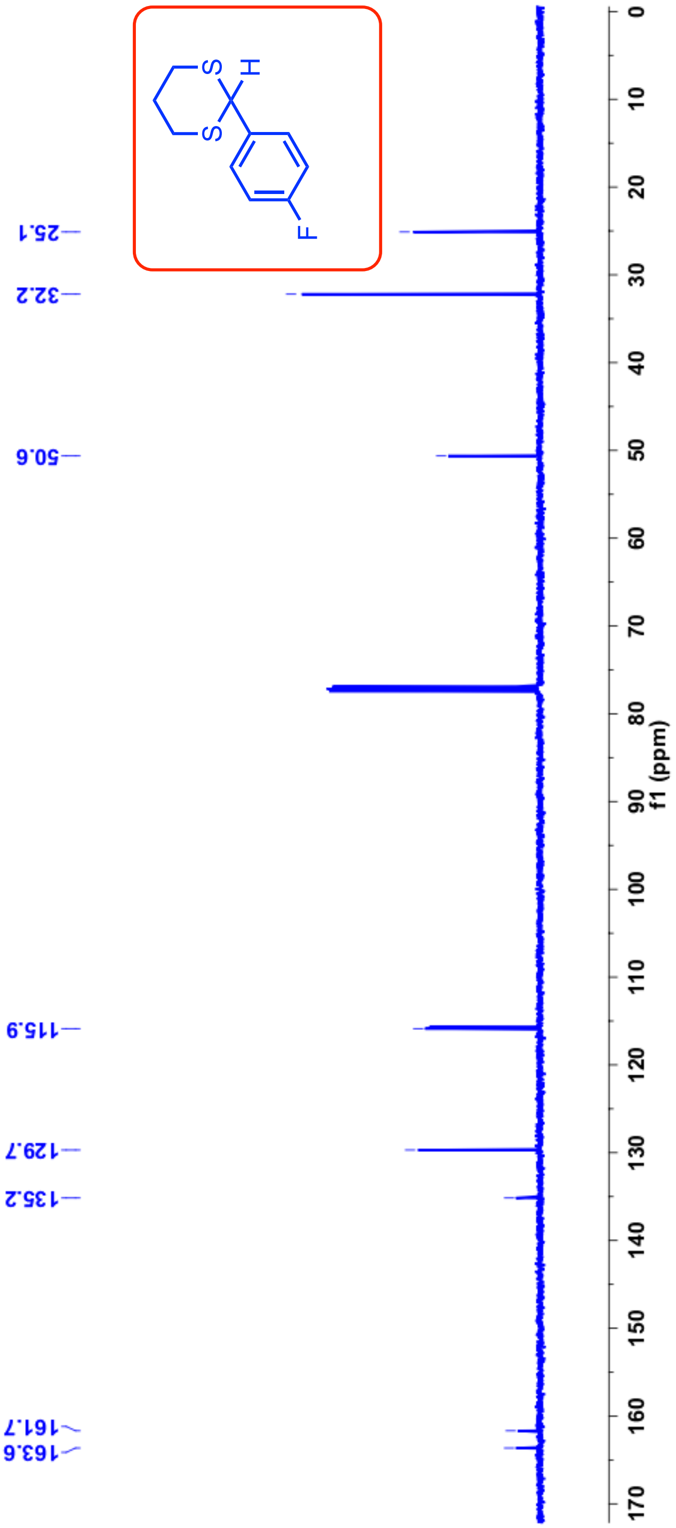


Figure S14: ^{13}C NMR spectra of **3i**.

10. NMR characterization of 5a-i

10.1. Characterization of **5a**

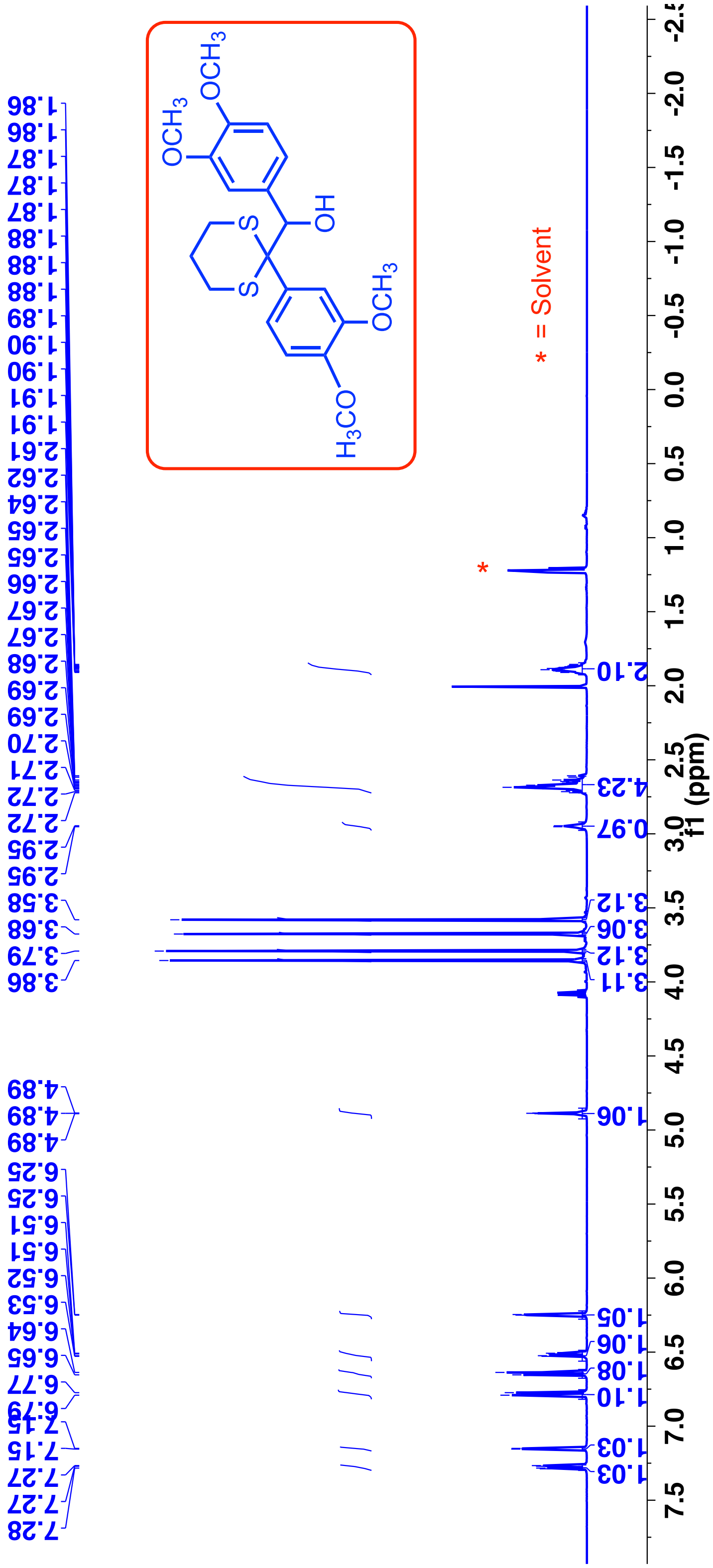


Figure S15: ^{1}H NMR spectra of **5a**.

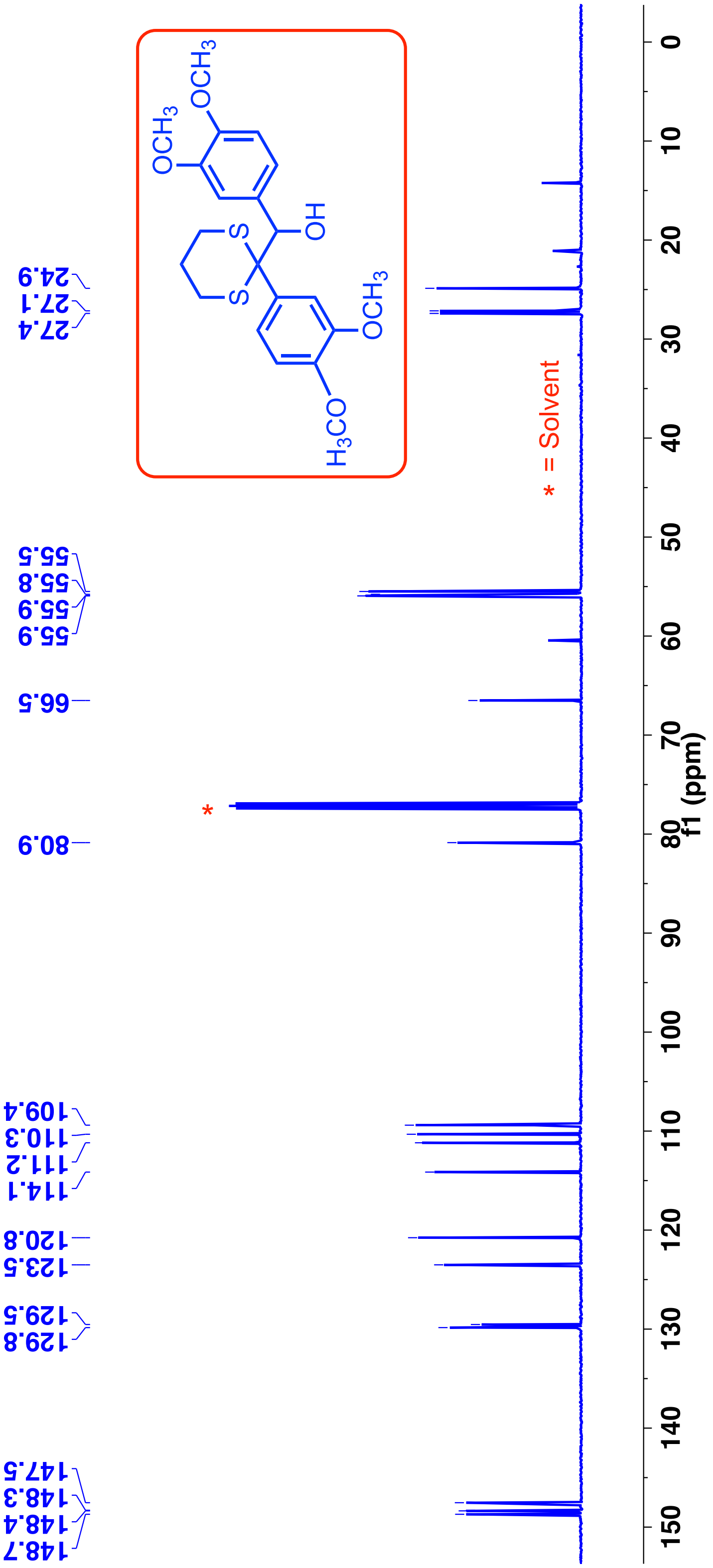


Figure S16: ^{13}C NMR spectra of **5a**.

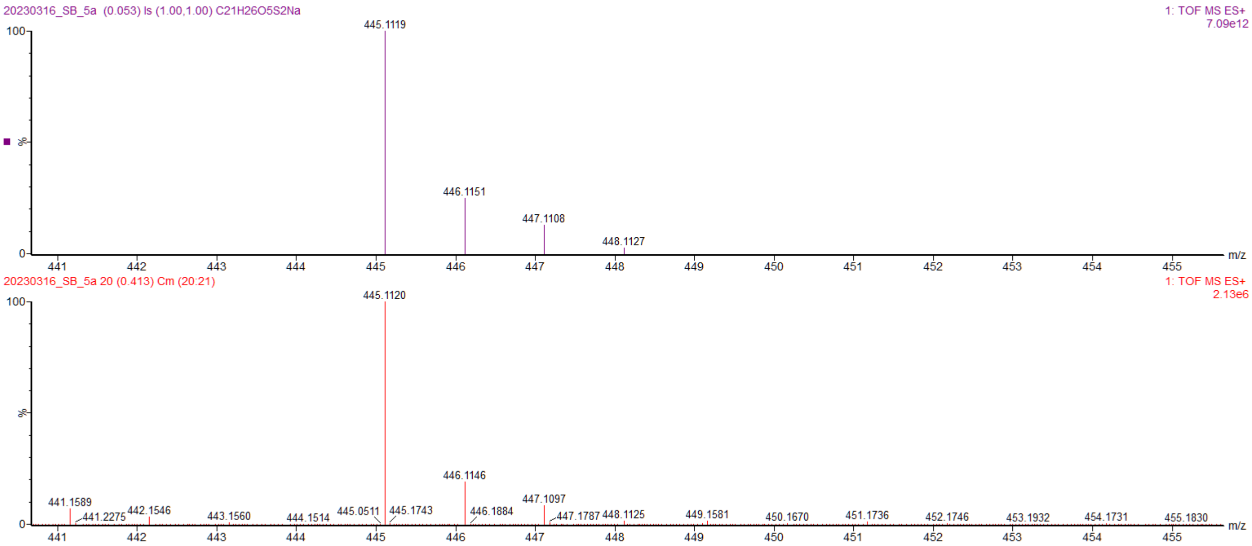


Figure S17: HRMS spectra of **5a**.

10.2. Characterization of **5b**

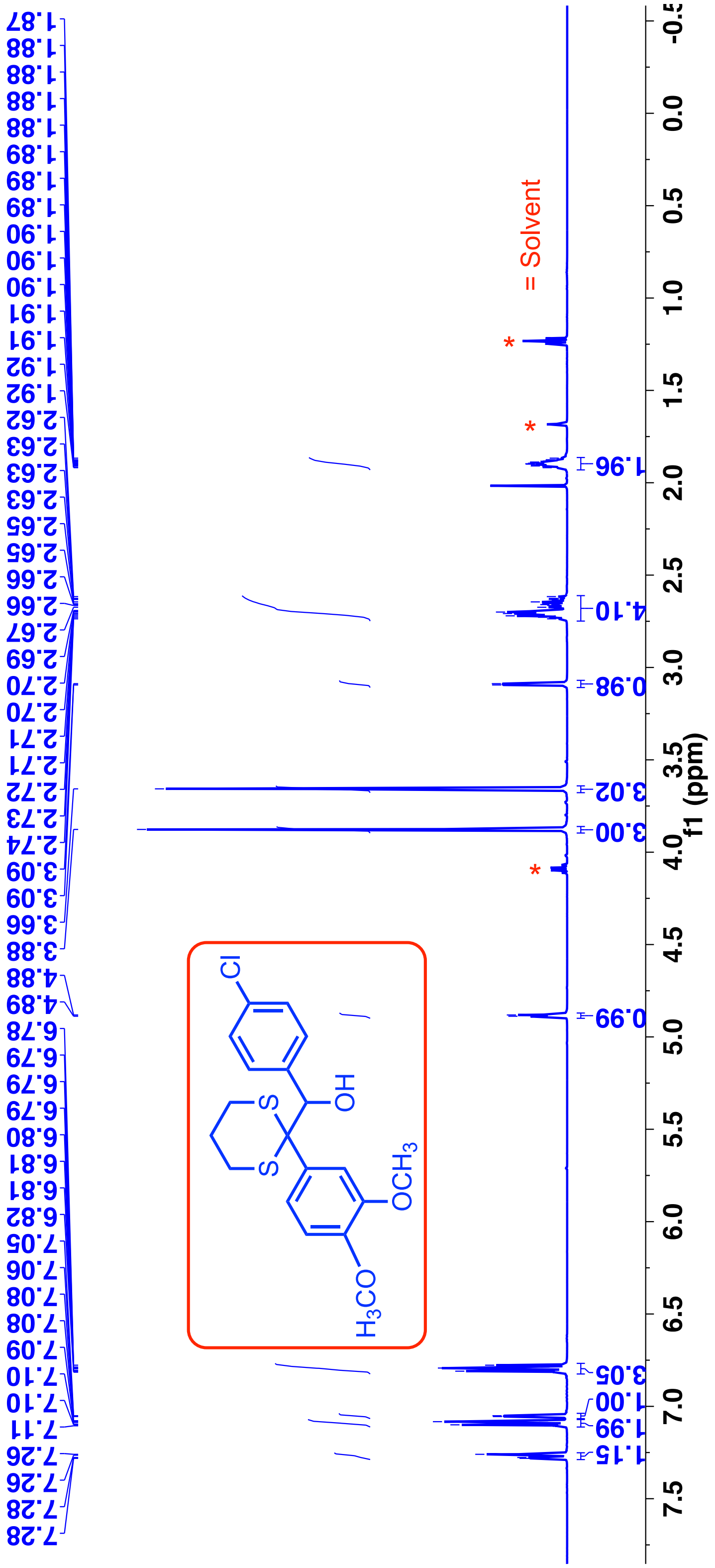


Figure S18: ^{1}H NMR spectra of **5b**.

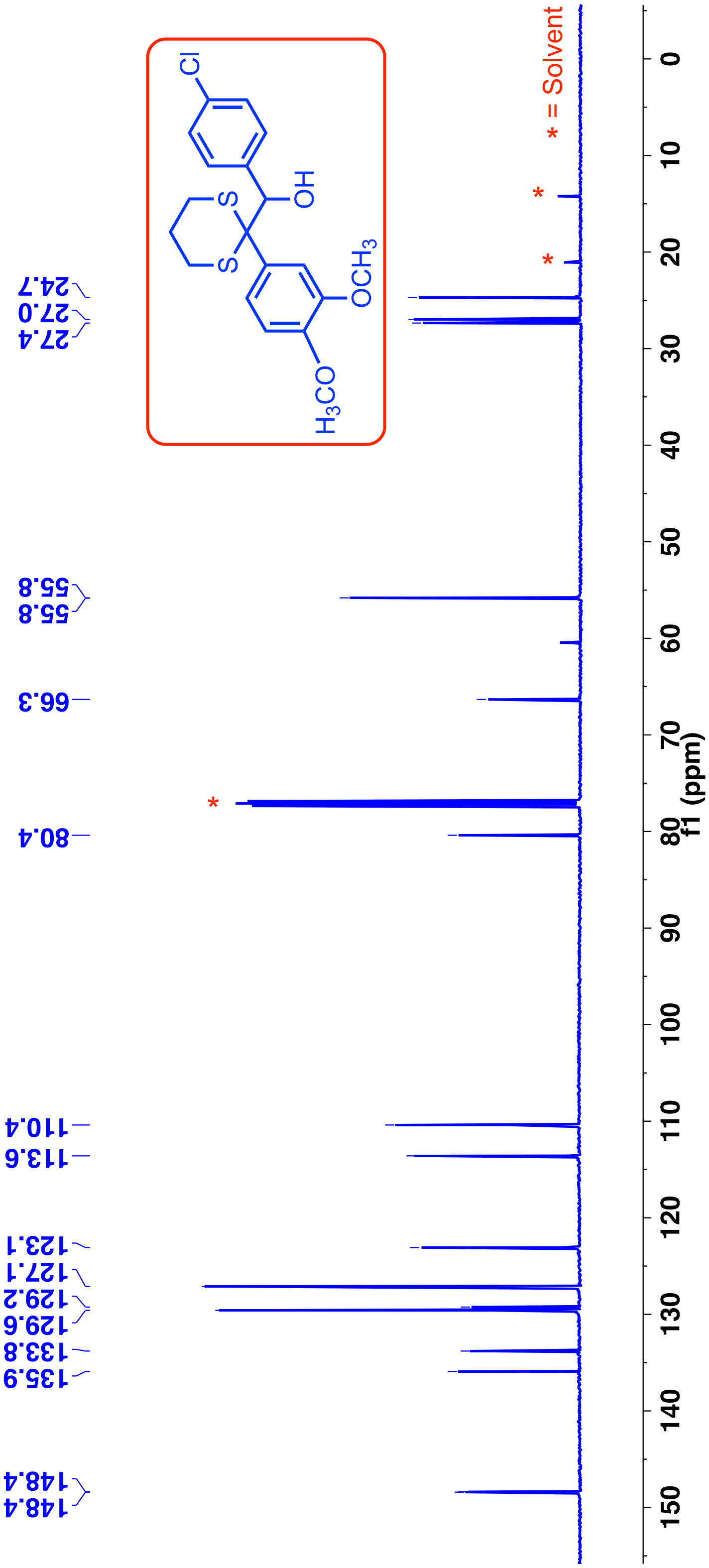


Figure S19: ^{13}C NMR spectra of **5b**.

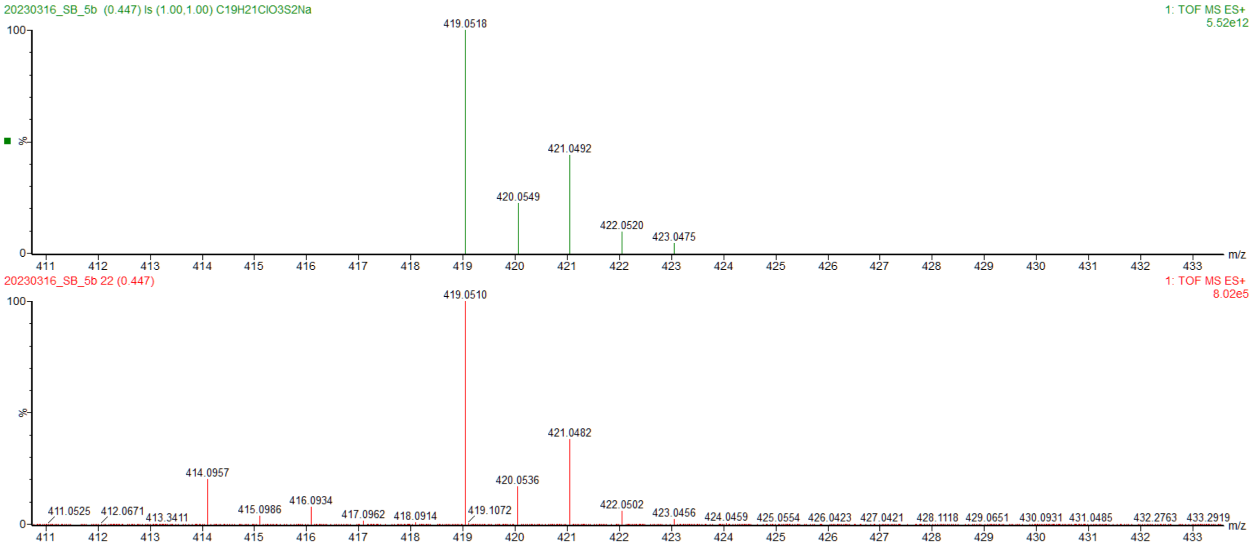


Figure S20: HRMS spectra of **5b**.

10.3. Characterization of **5c**

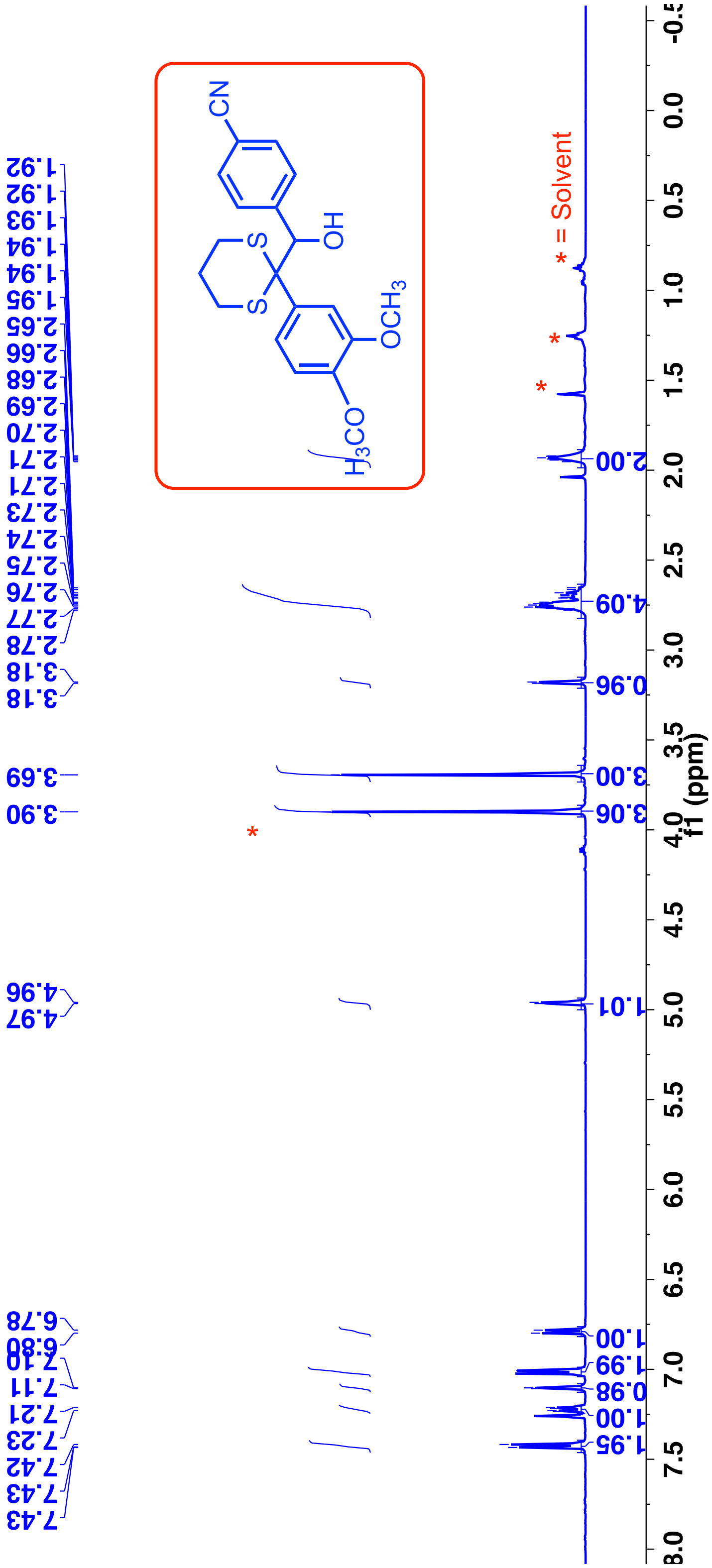


Figure S21: ^{1}H NMR spectra of **5c**.

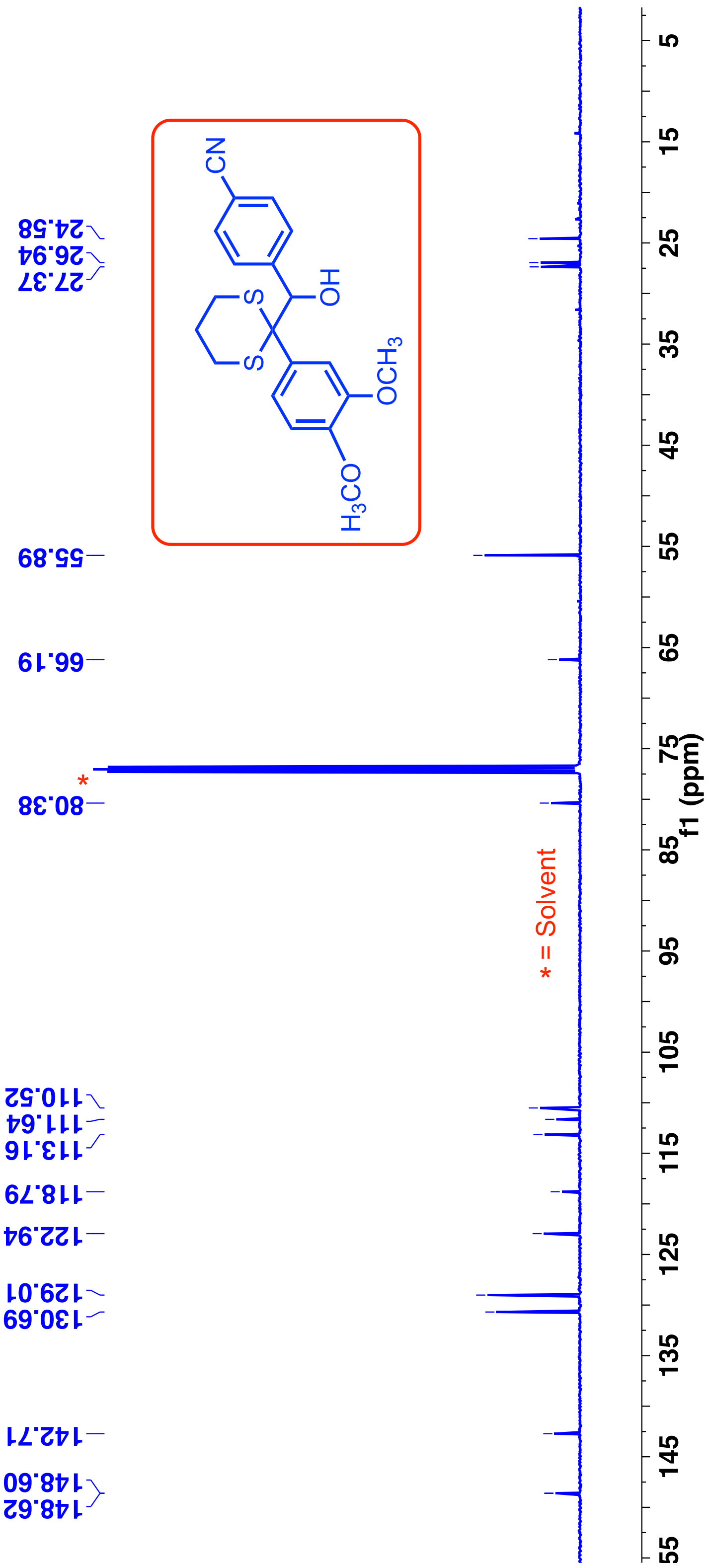


Figure S22: ^{13}C NMR spectra of **5c**.

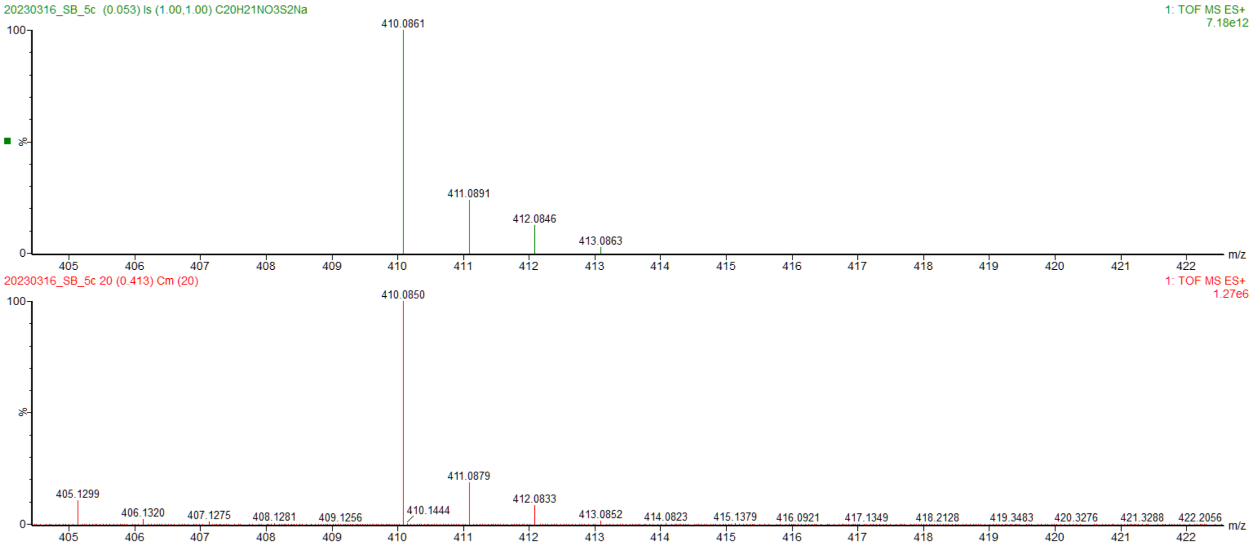


Figure S23: *HRMS* spectra of **5c**

10.4. Characterization of **5d**

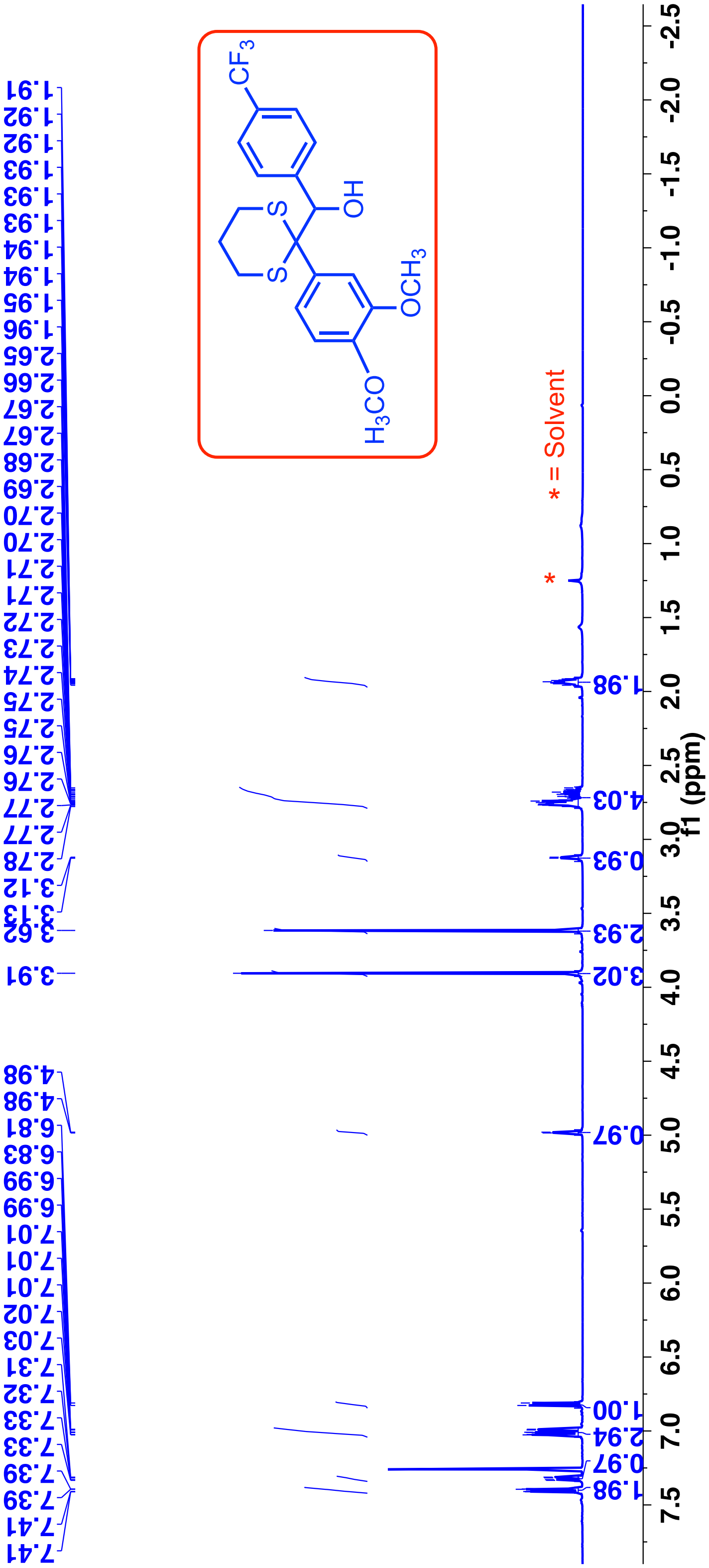


Figure S24: ^{1}H NMR spectra of **5d**.

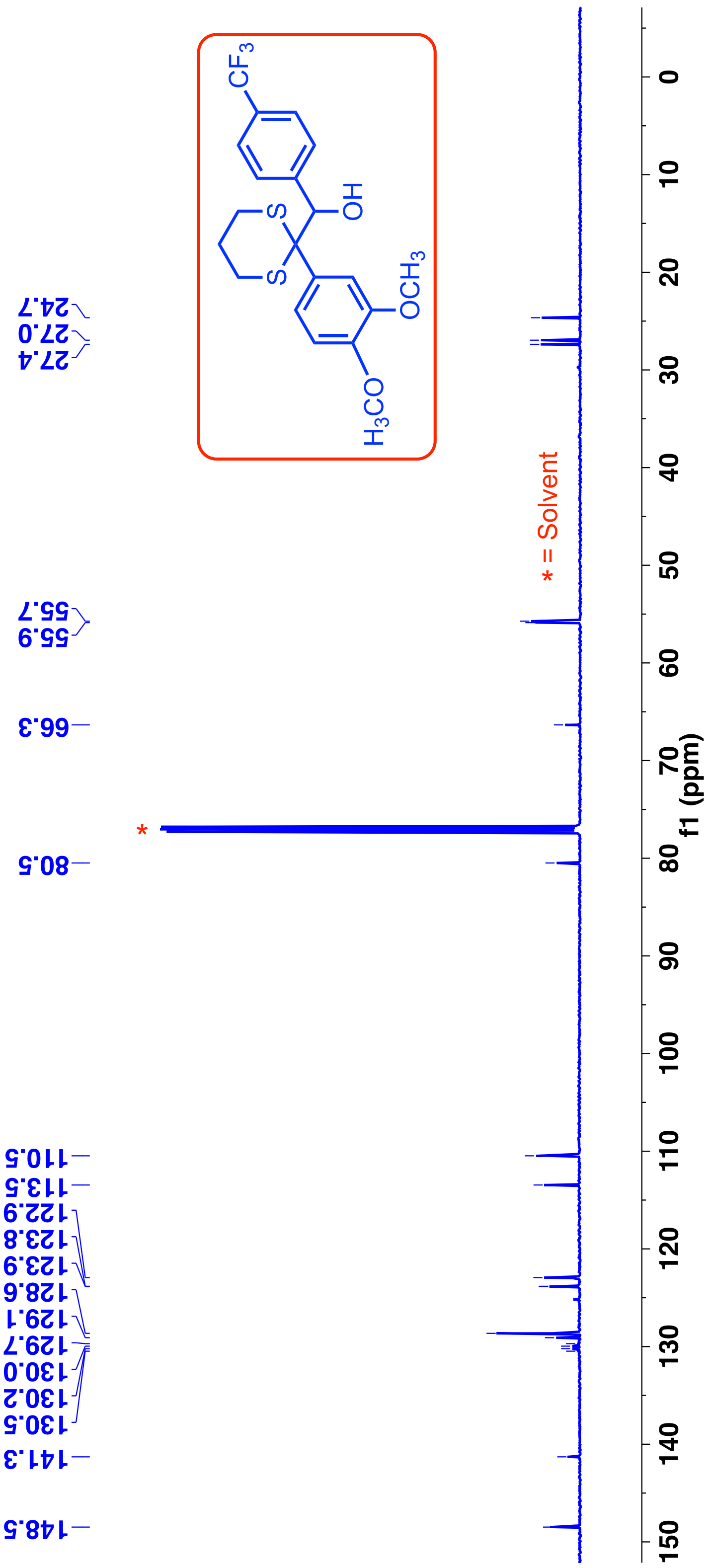


Figure S25: ^{13}C NMR spectra of **5d**.

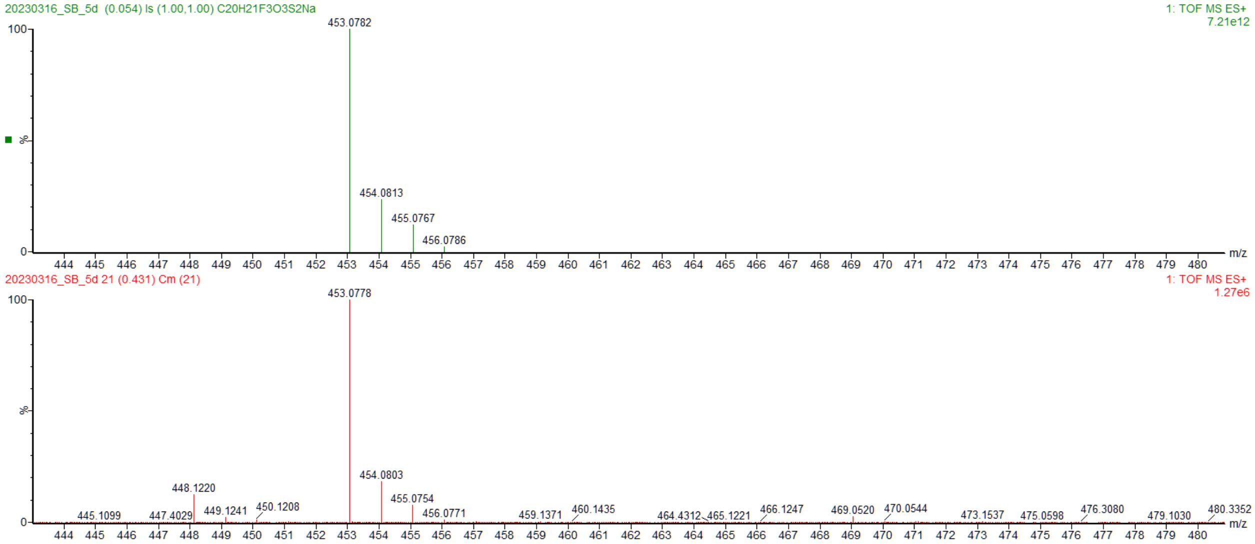


Figure S26: HRMS spectra of **5d**.

10.5. Characterization of **5e**

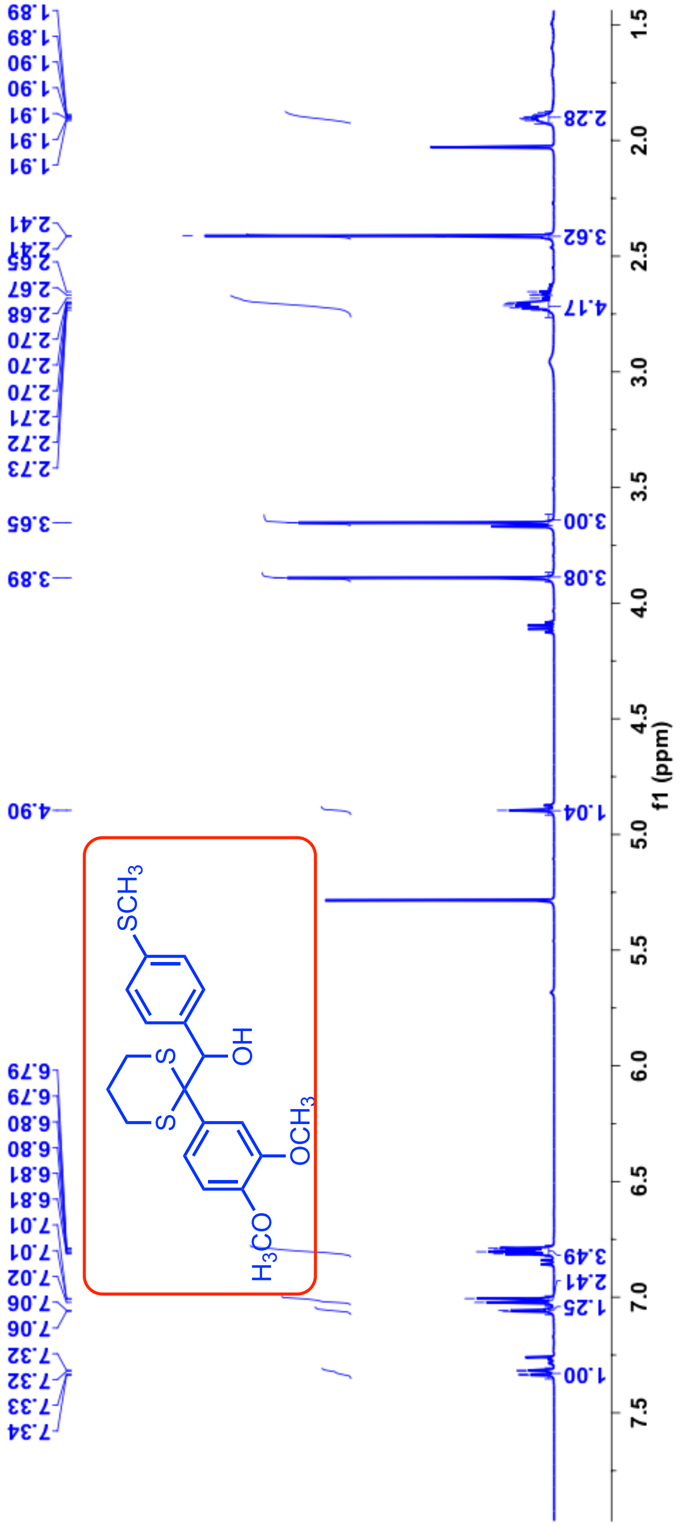


Figure S27: ^{1}H NMR spectra of **5e**.

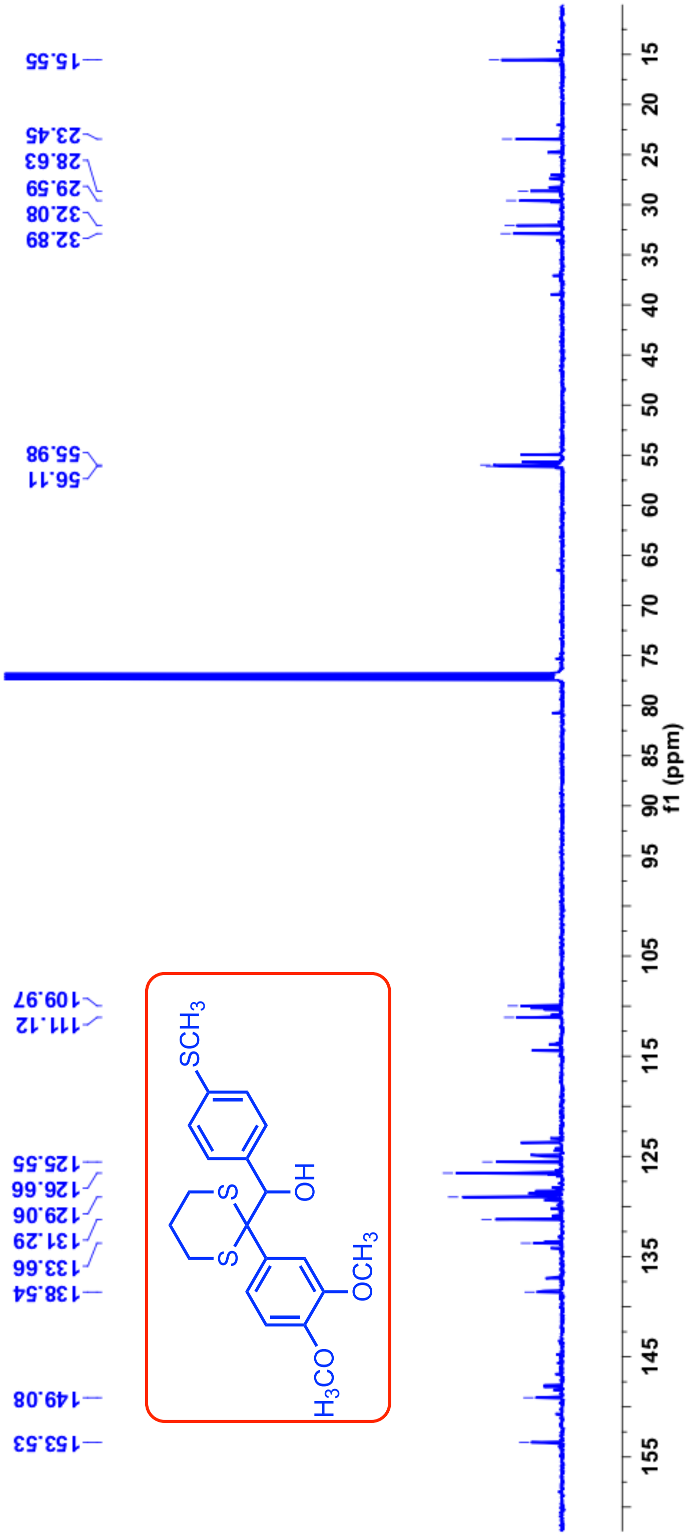


Figure S28: ^{13}C NMR spectra of **5e**.

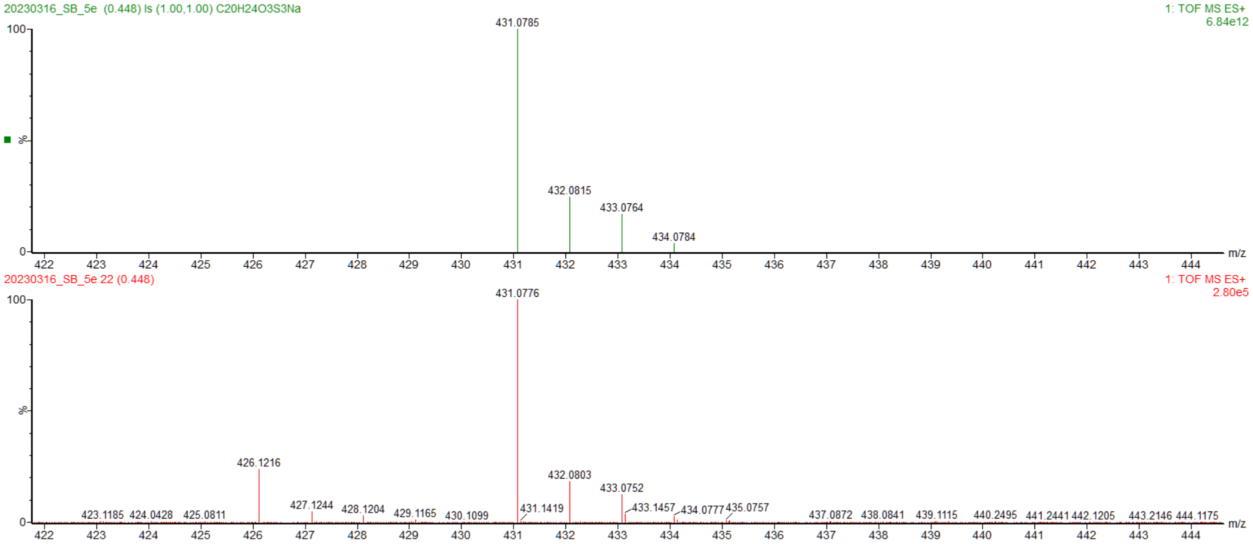


Figure S29: HRMS spectra of **5e**.

10.6. Characterization of **5f**

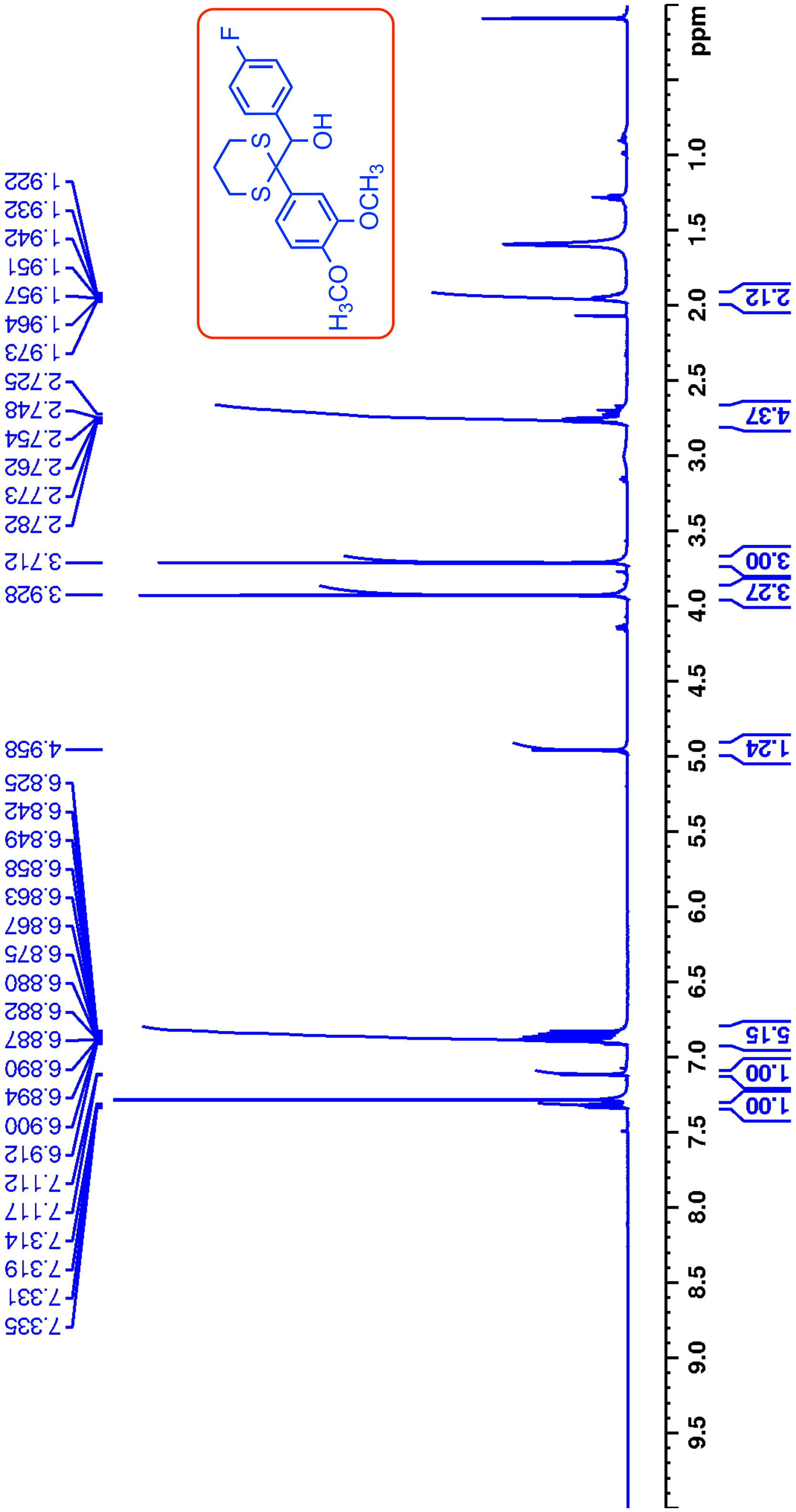


Figure S30: ^{1}H NMR spectra of **5f**.

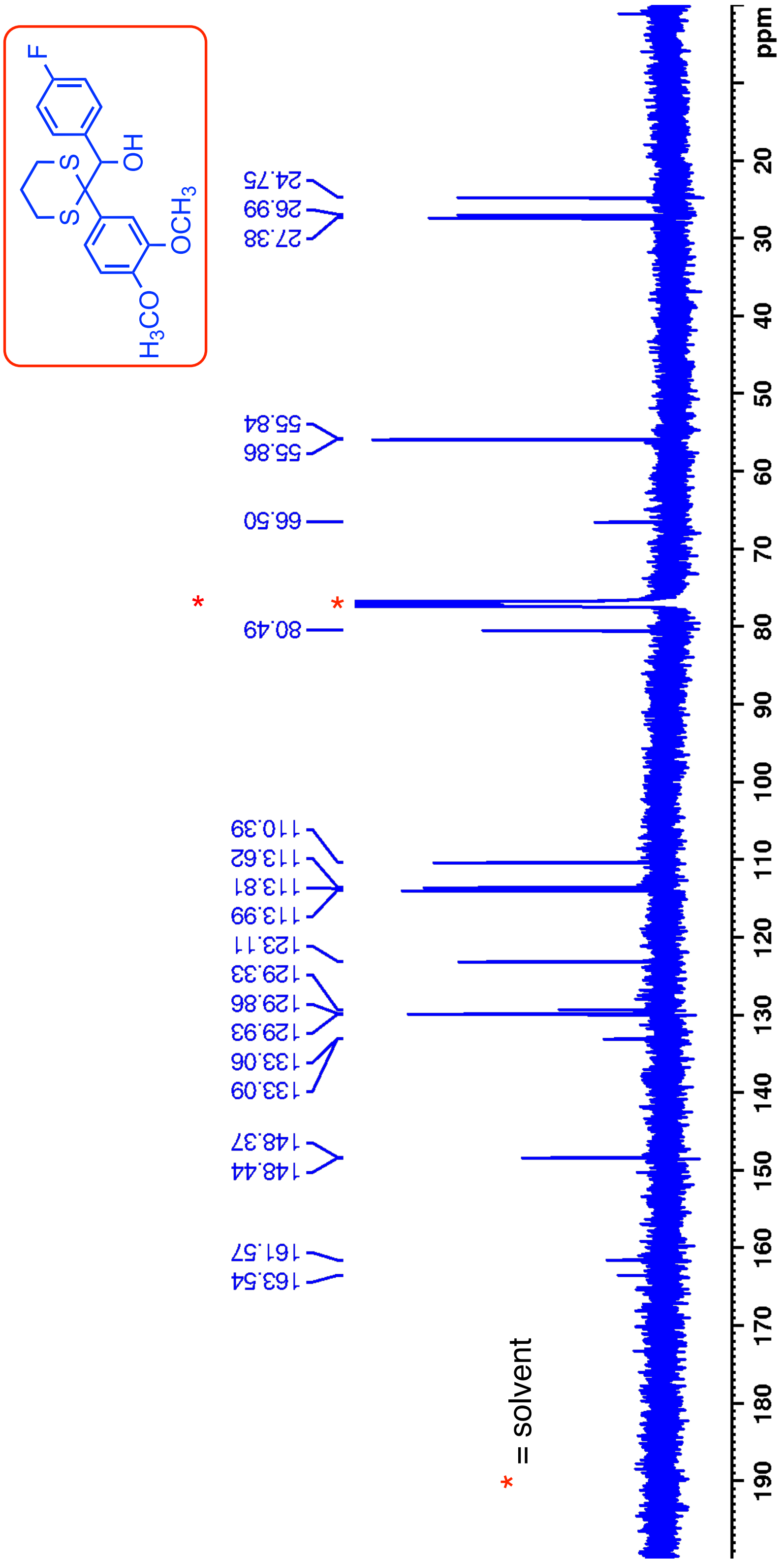


Figure S31: ^{13}C NMR spectra of **5f**.

10.7. Characterization of **5g**

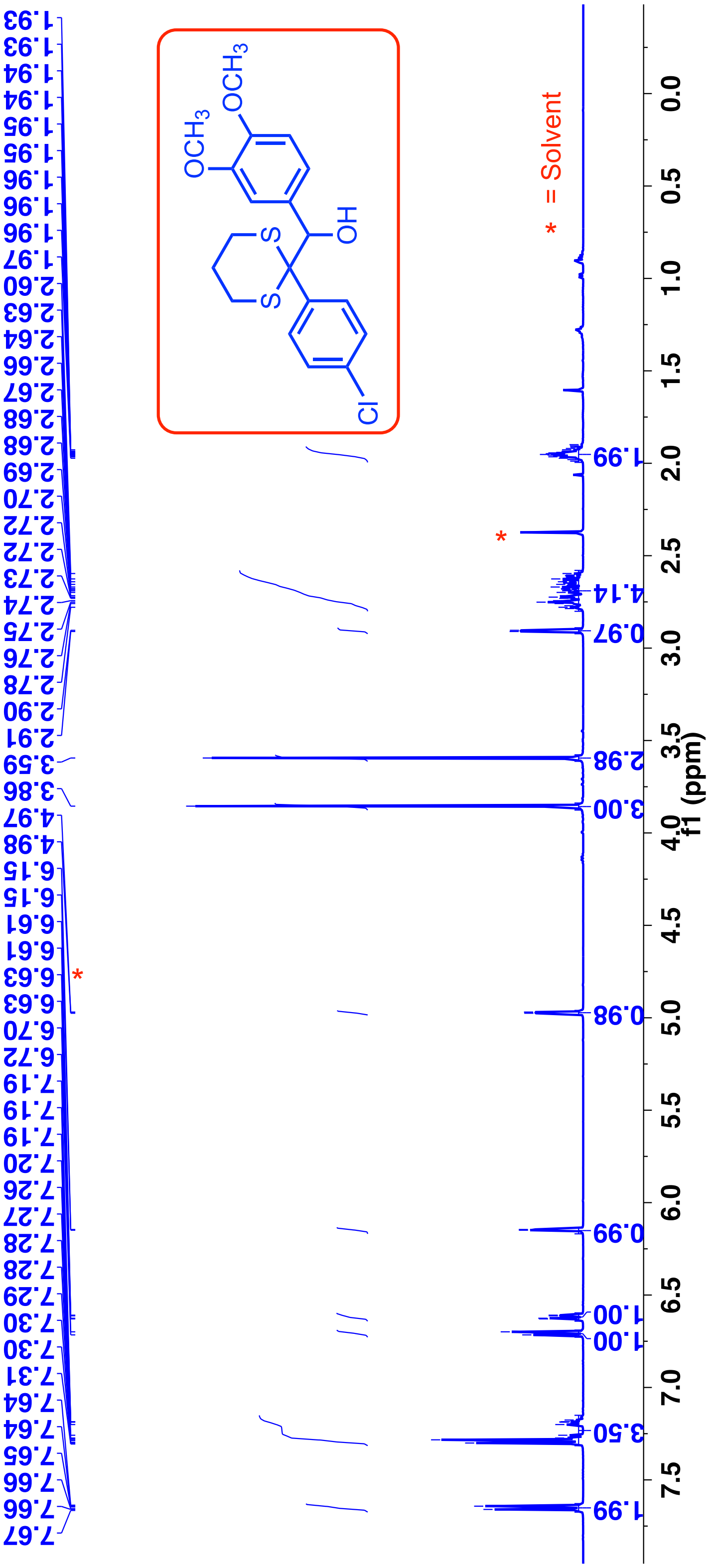


Figure S32: ^{1}H NMR spectra of **5g**.

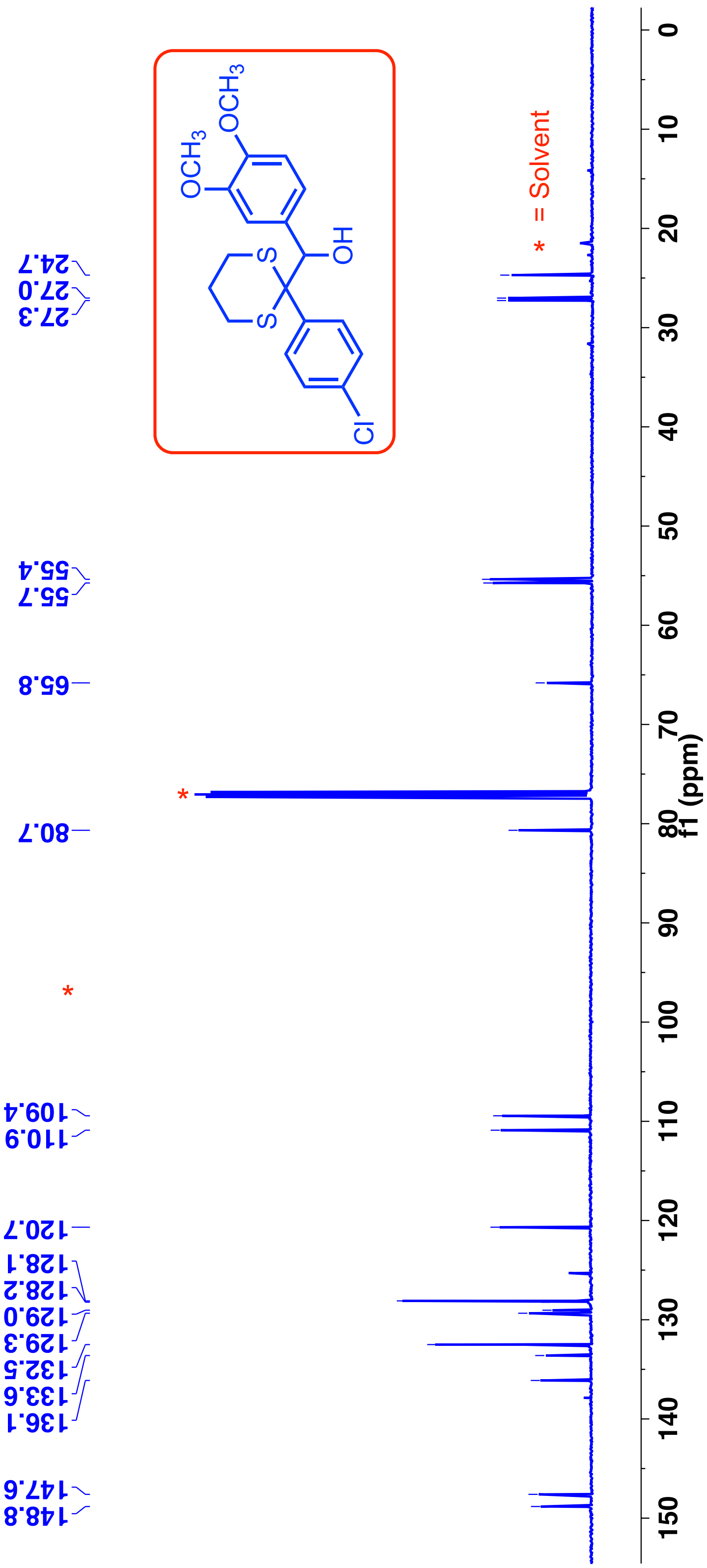


Figure S33: ^{13}C NMR spectra of **5g**.

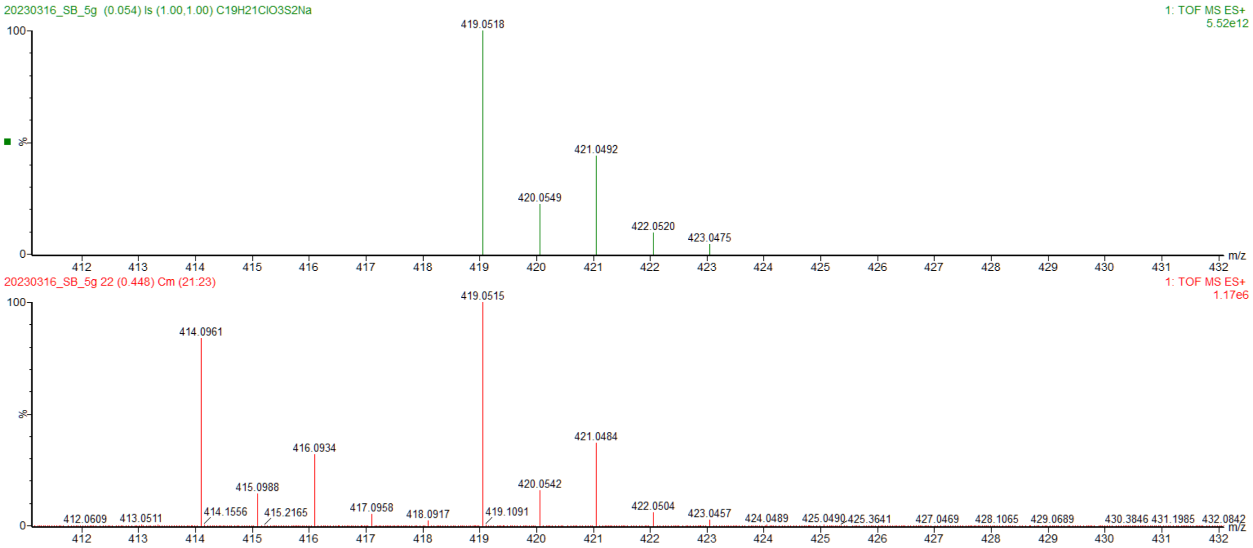


Figure S34: HRMS spectra of **5g**.

10.8. Characterization of **5h**

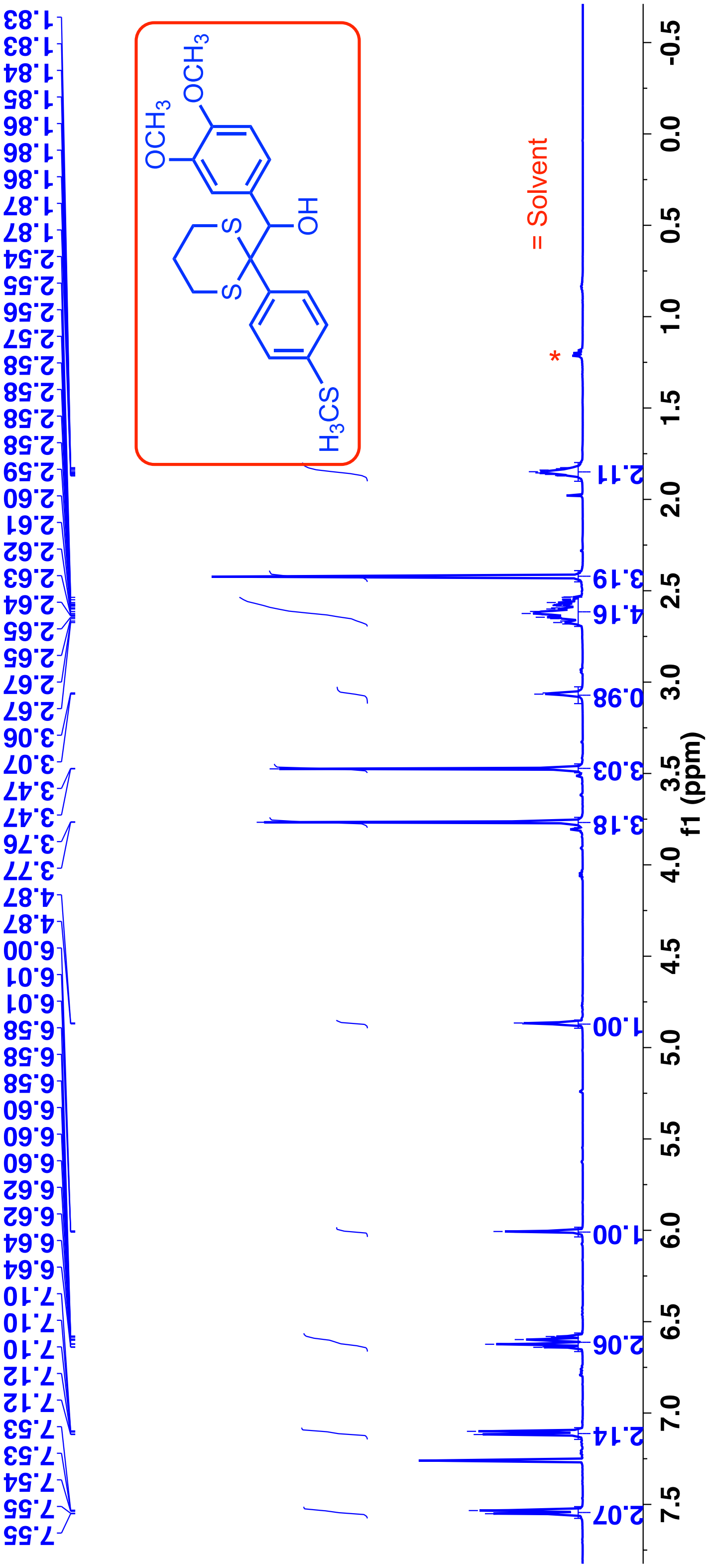


Figure S35: ^{1}H NMR spectra of **5h**.

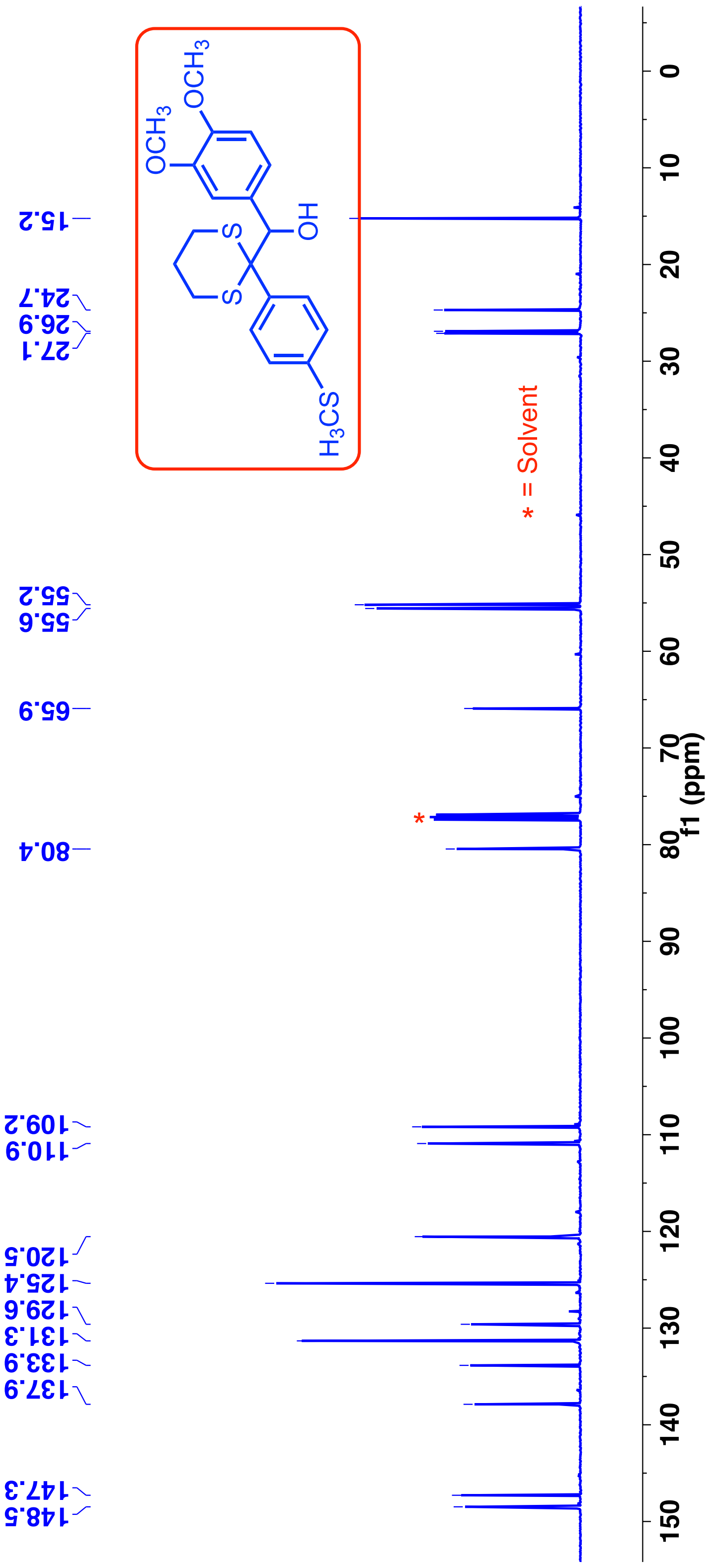


Figure S36: ^{13}C NMR spectra of **5h**.

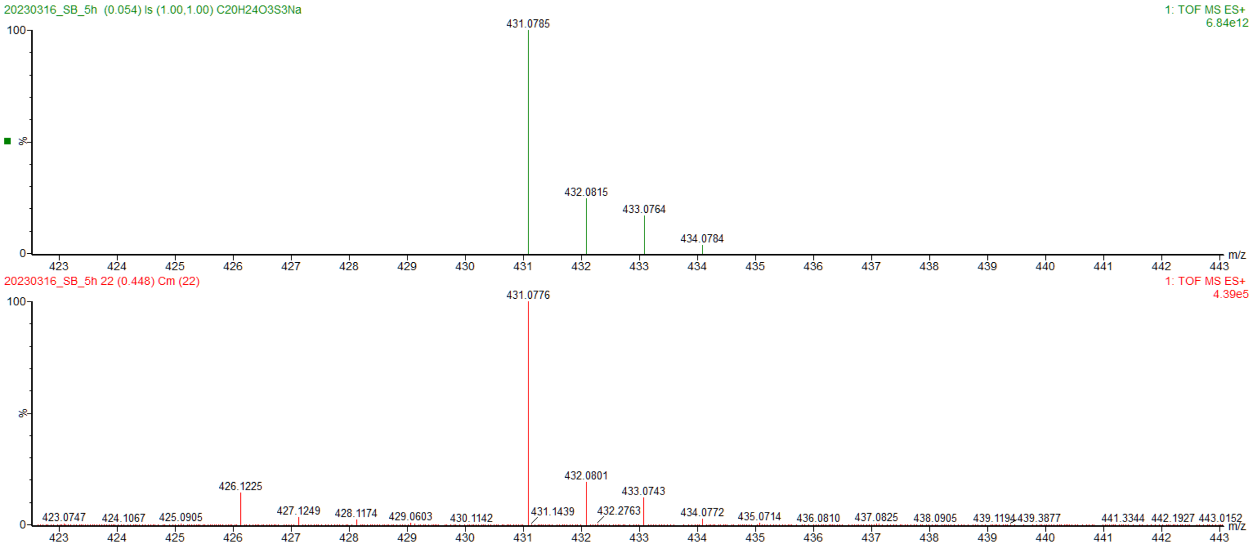


Figure S37: HRMS spectra of **5h**.

10.9. Characterization of **5i**

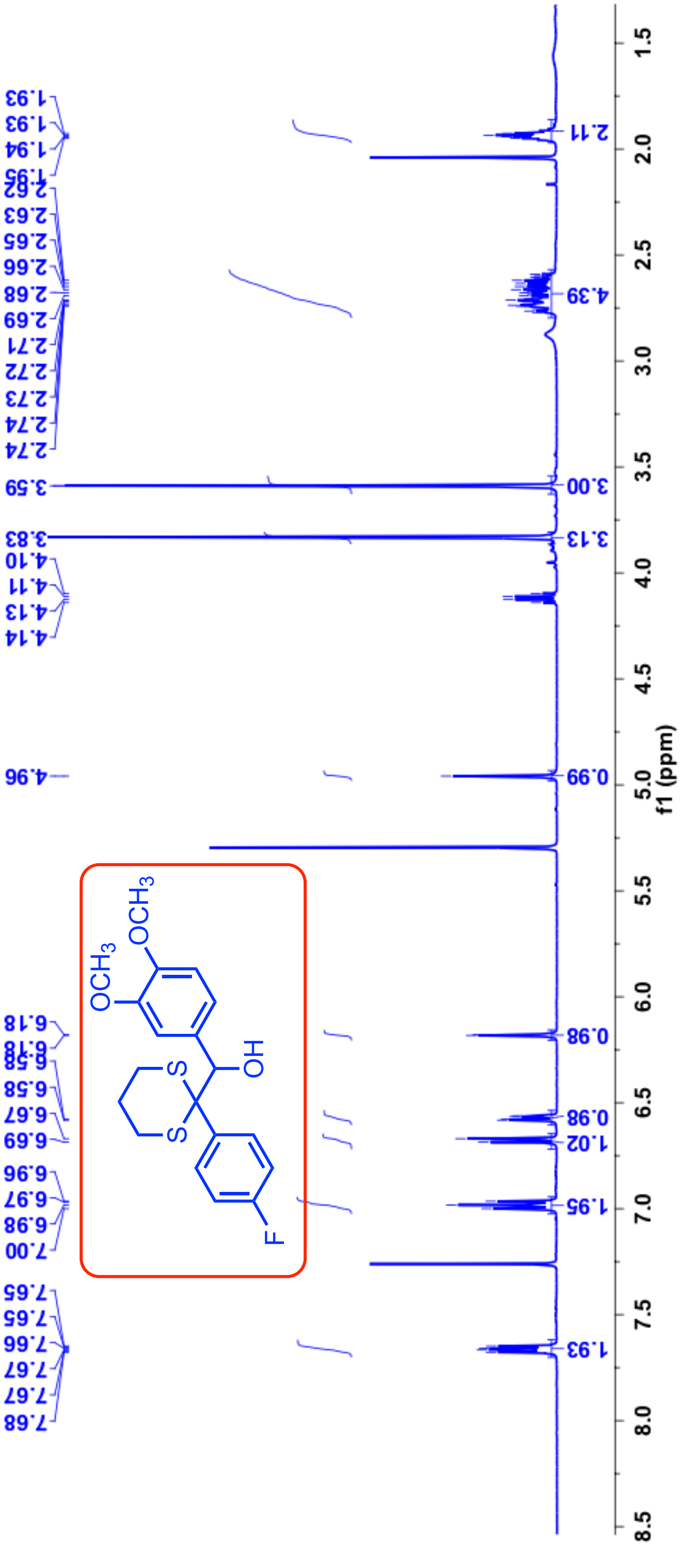


Figure S38: ^{1}H NMR spectra of **5i**.

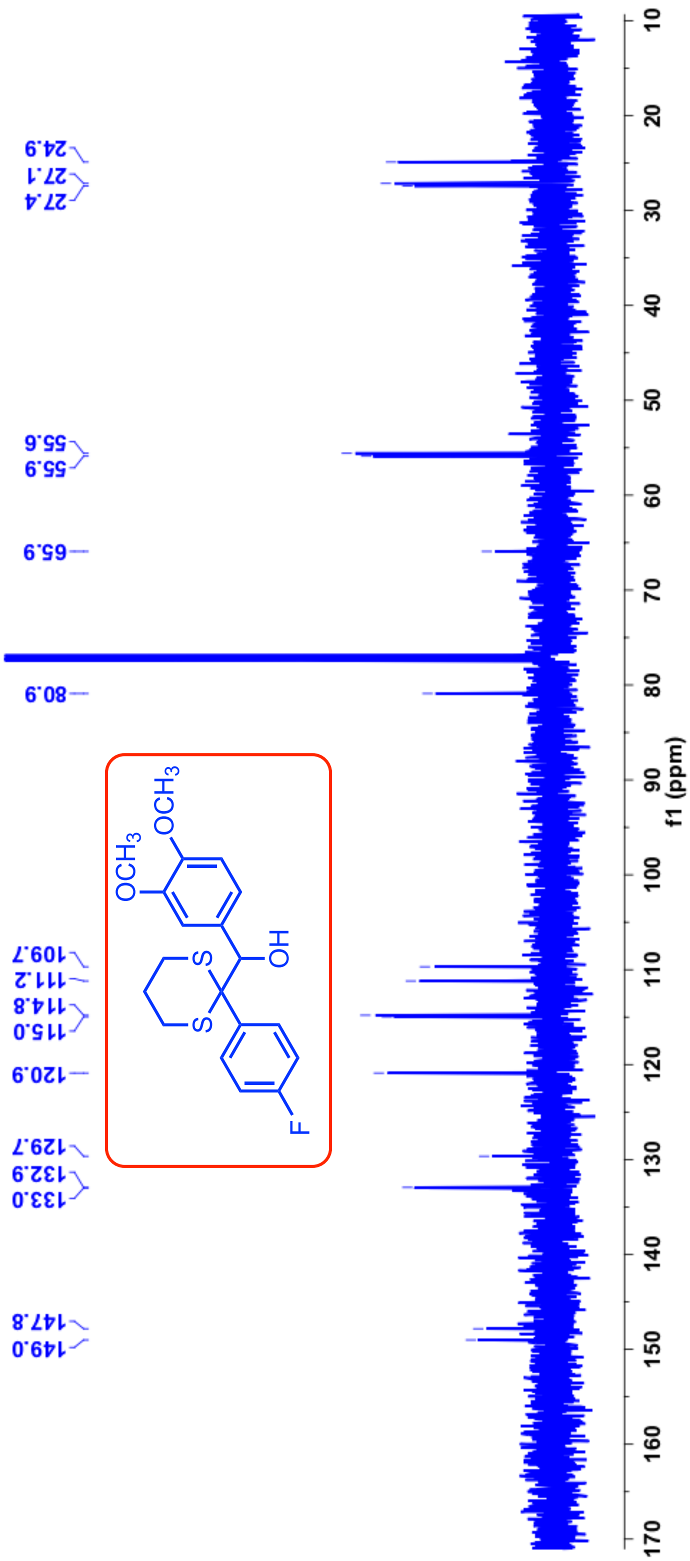


Figure S39: ^{13}C NMR spectra of **5i**.

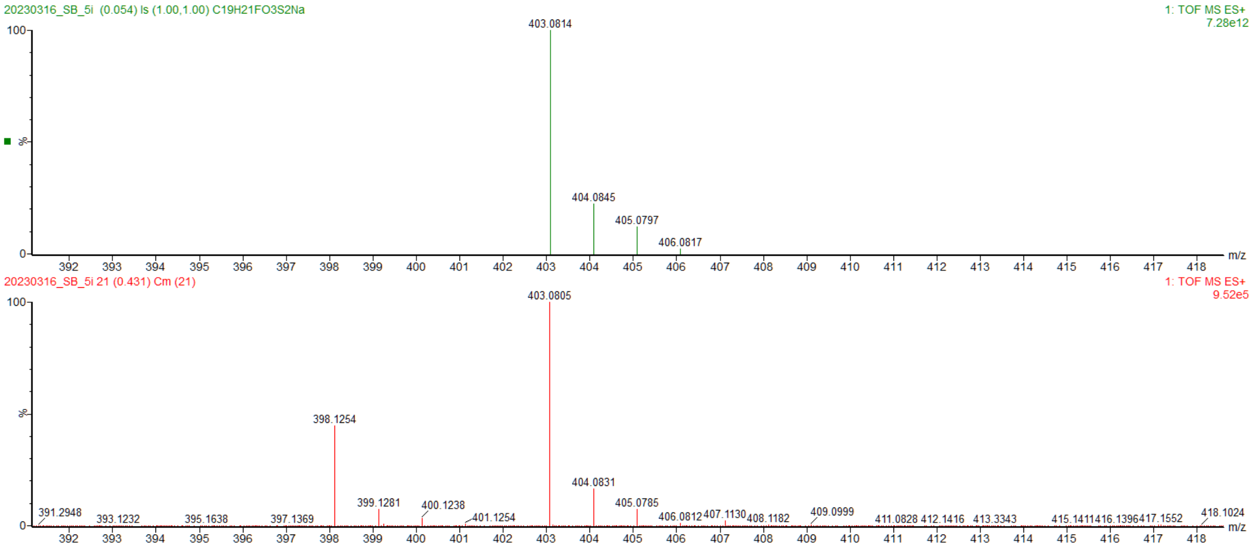


Figure S40: HRMS spectra of **5i**

11. Characterization of benzoins 1a-i

11.1. Characterization of **1a**

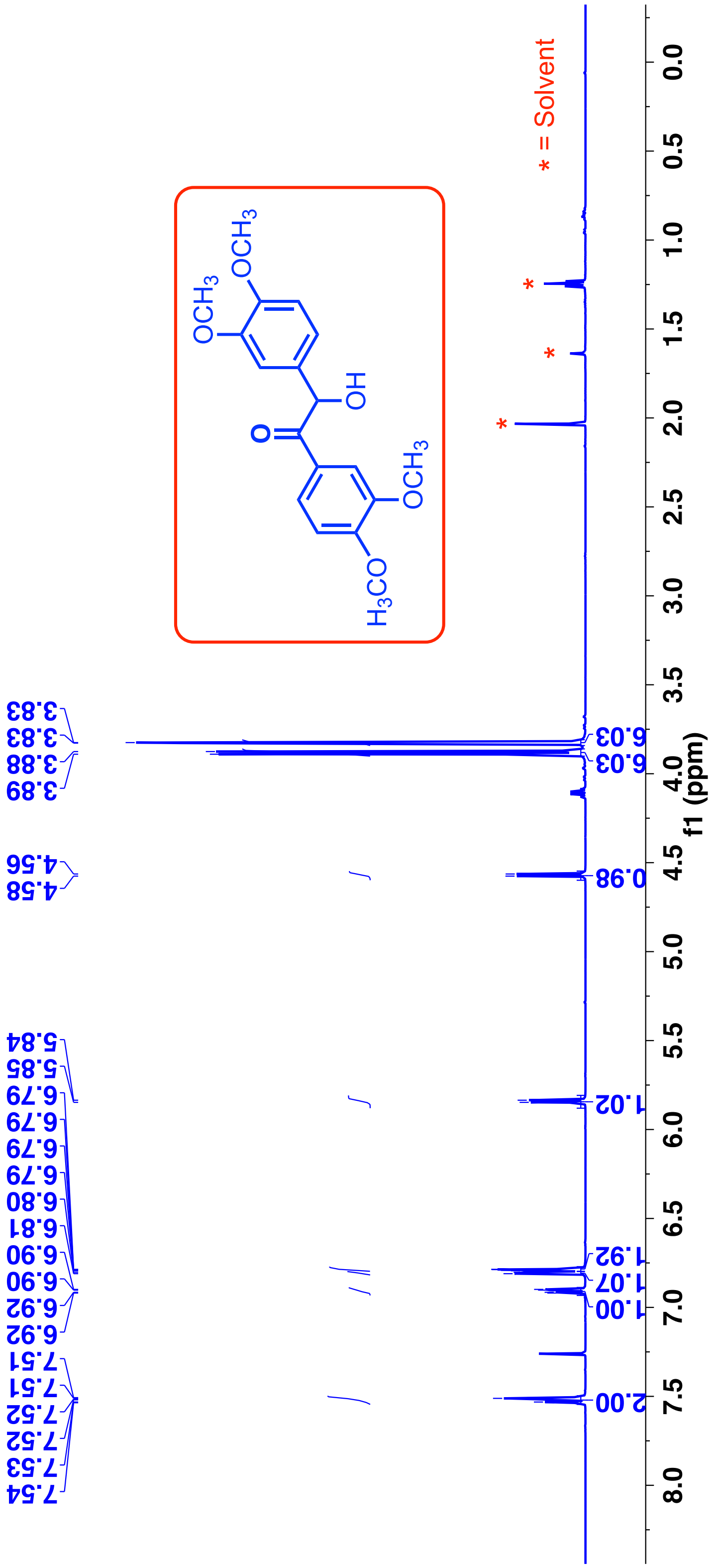


Figure S41: ^{1}H NMR spectra of **1a**.

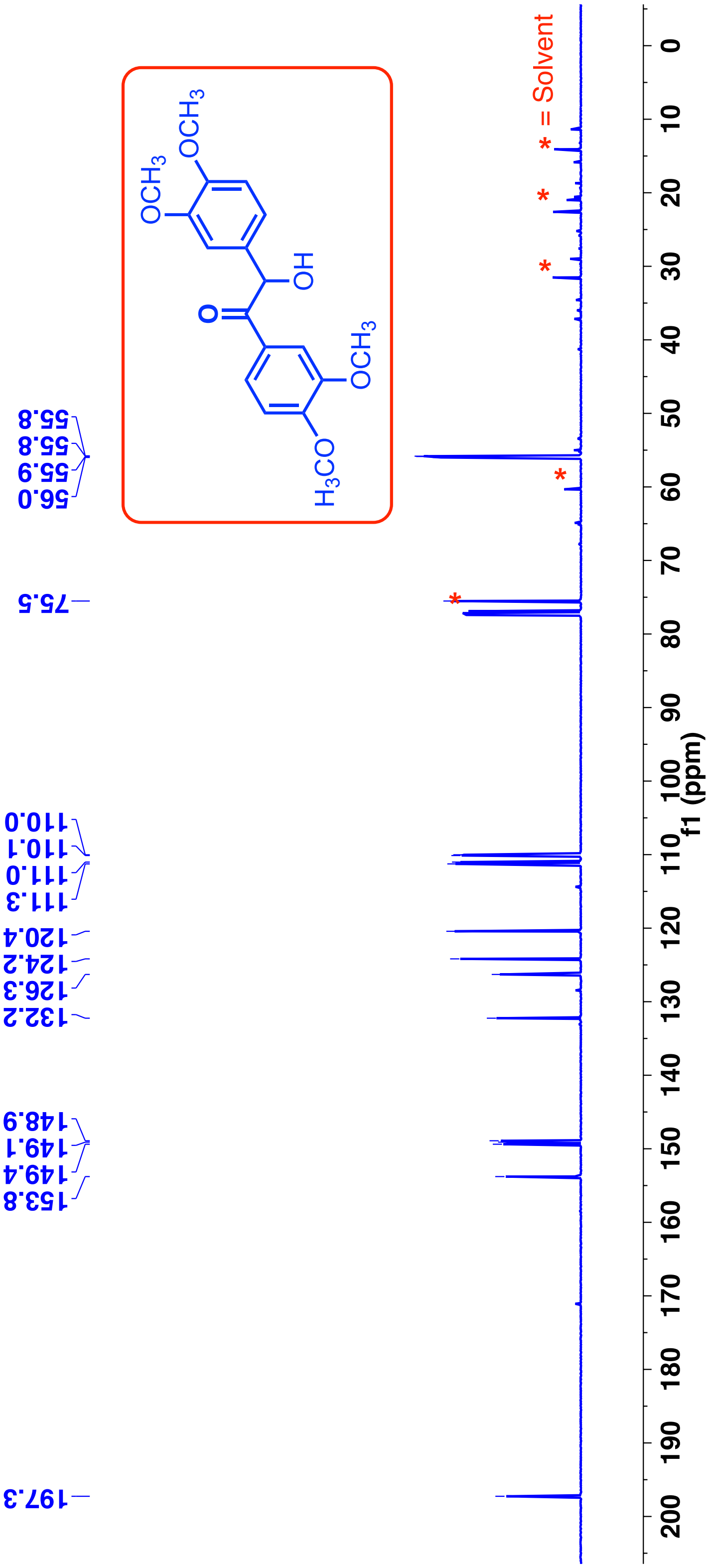


Figure S42: ^{13}C NMR spectra of **1a**.

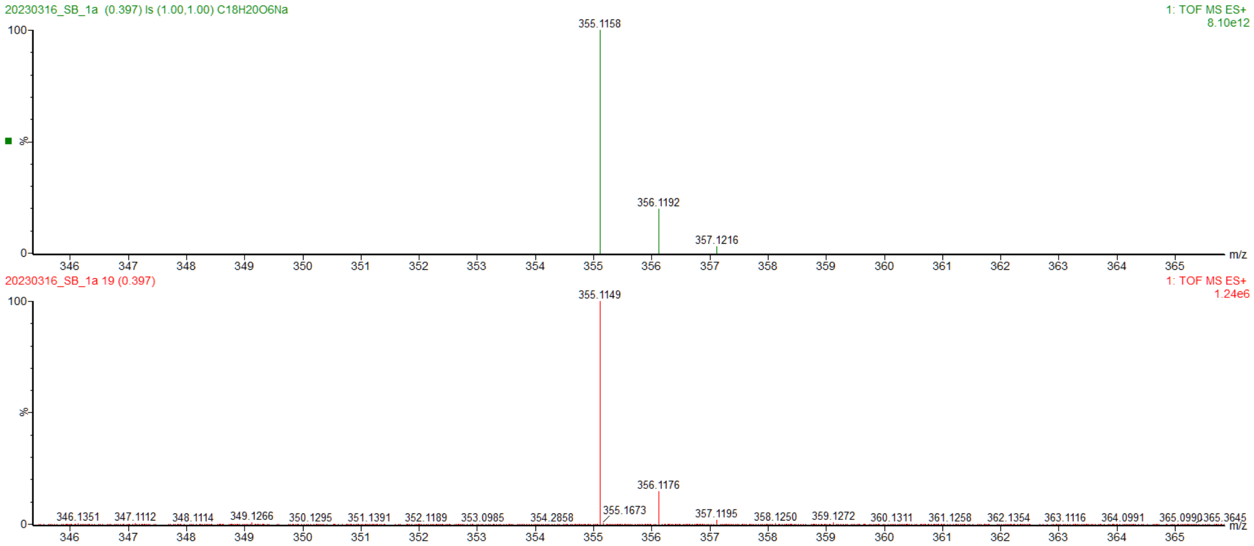


Figure S43: HRMS spectra of **1a**.

11.2. Characterization of **1b**

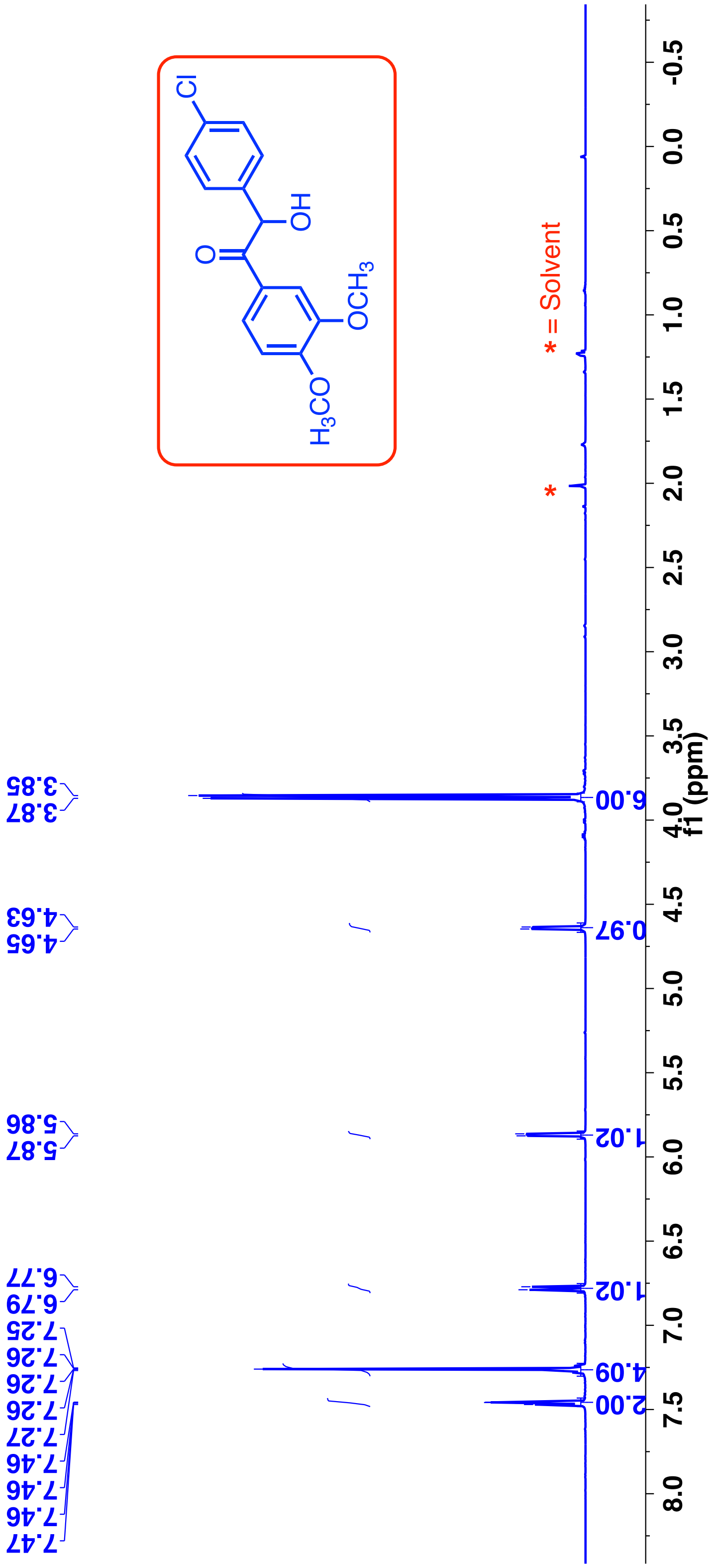


Figure S44: ^{13}C NMR spectra of **1b**.

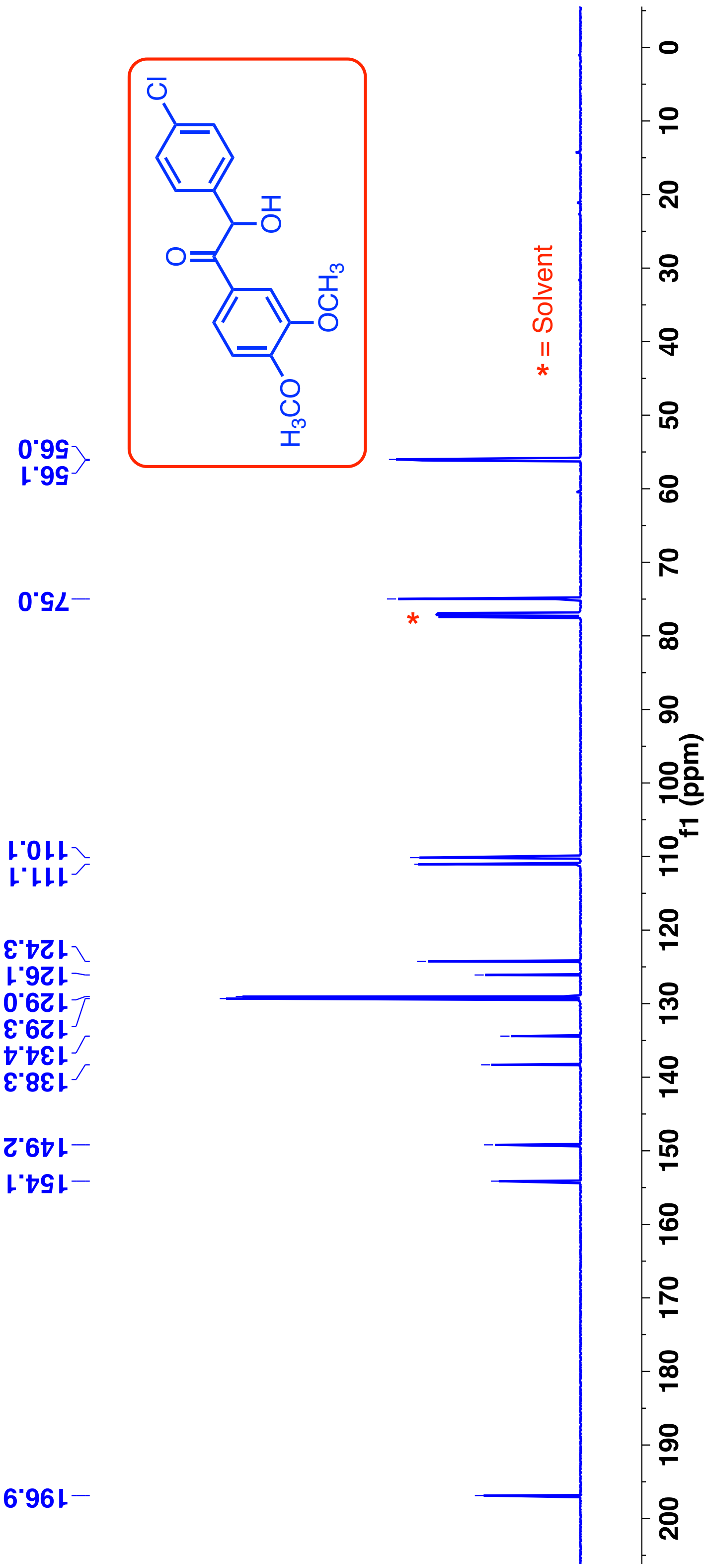


Figure S45: ^{13}C NMR spectra of **1b**.

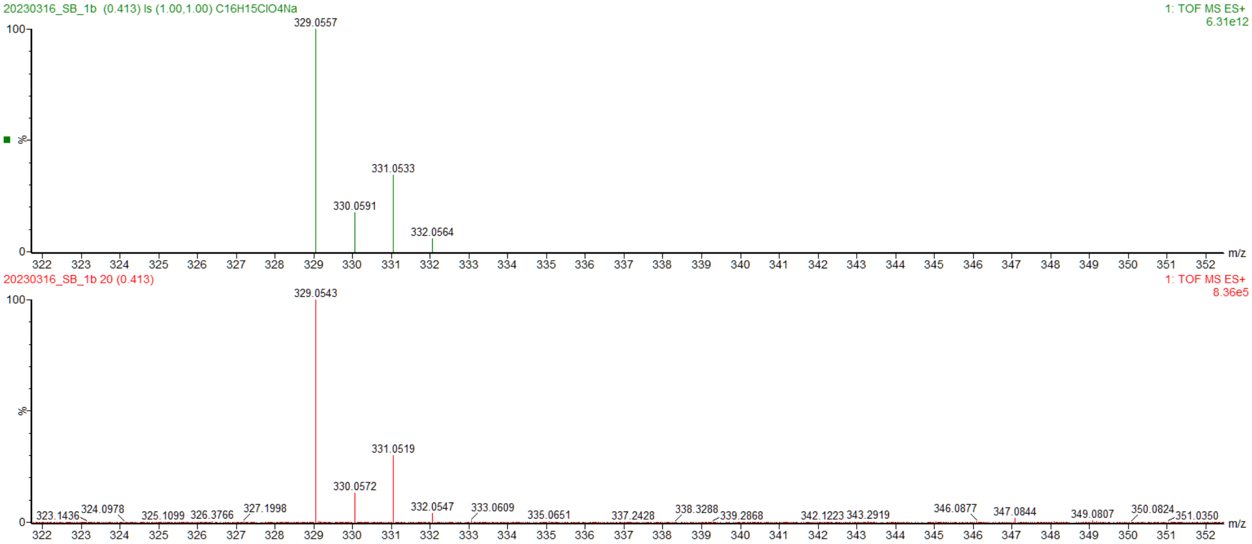


Figure S46: HRMS spectra of **1b**.

11.3. Characterization of **1c**

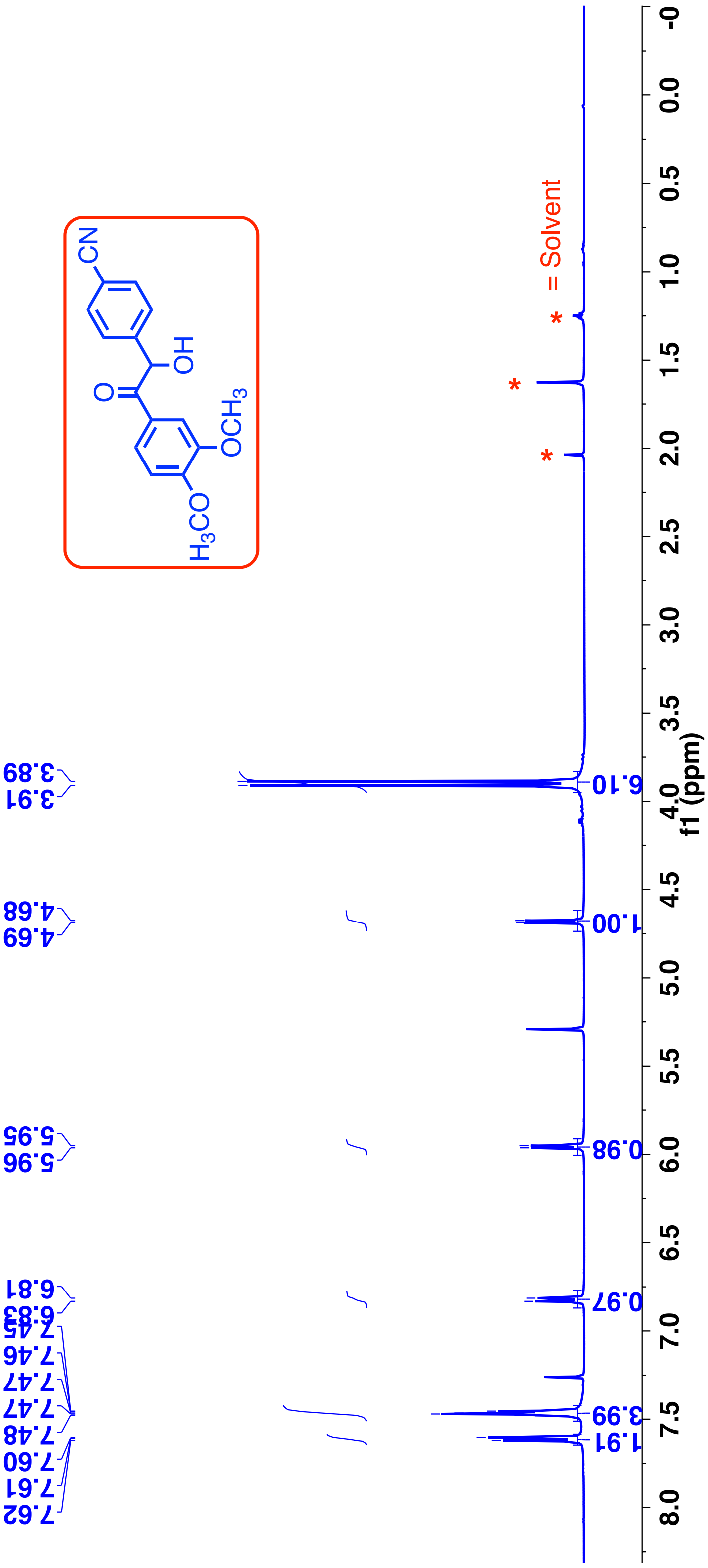


Figure S47: ^{1}H NMR spectra of **1c**.

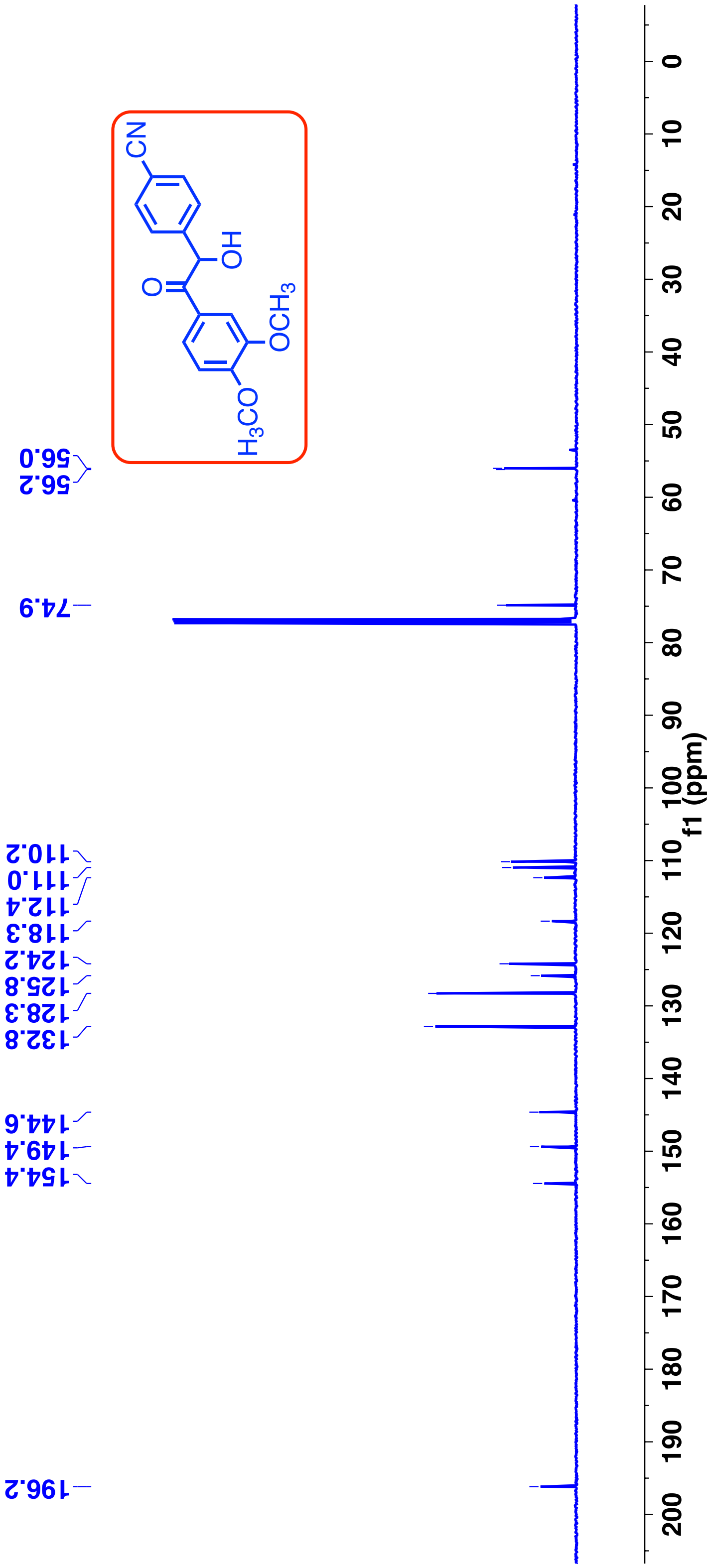


Figure S48: ^{13}C NMR spectra of **1c**.

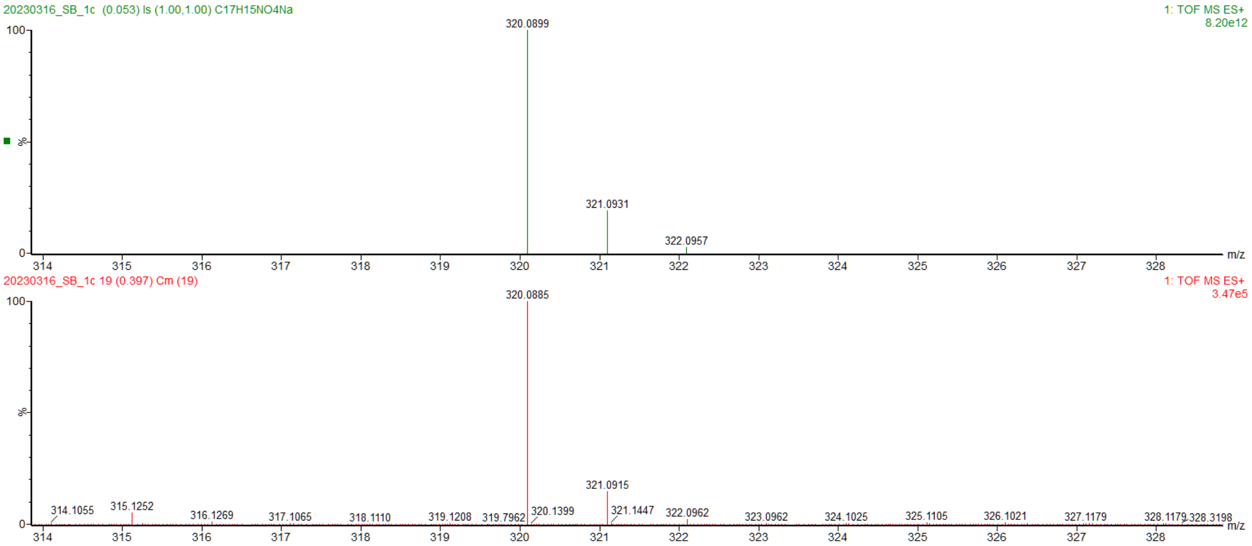


Figure S49: HRMS spectra of **1c**.

11.4. Characterization of **1d**

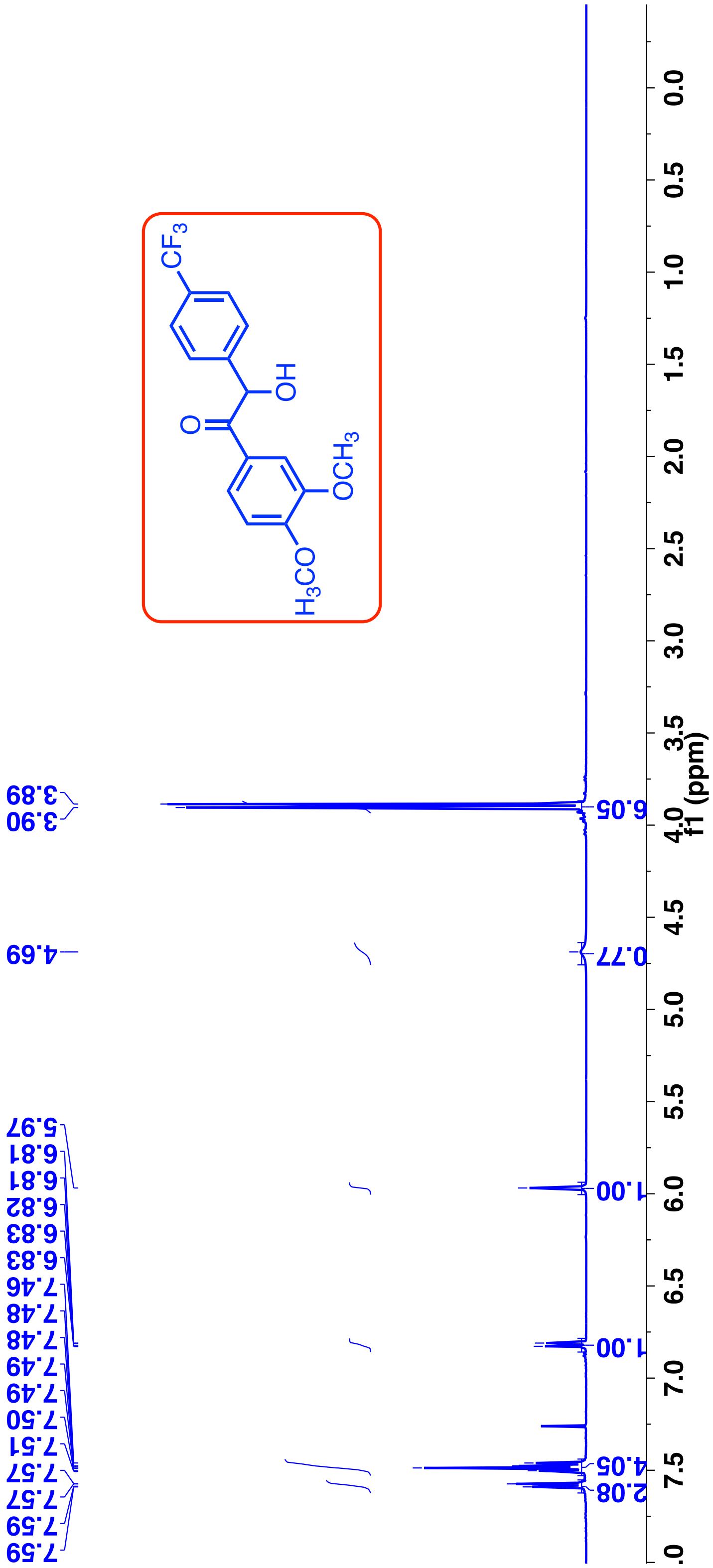


Figure S50: ^{1}H NMR spectra of **1d**.

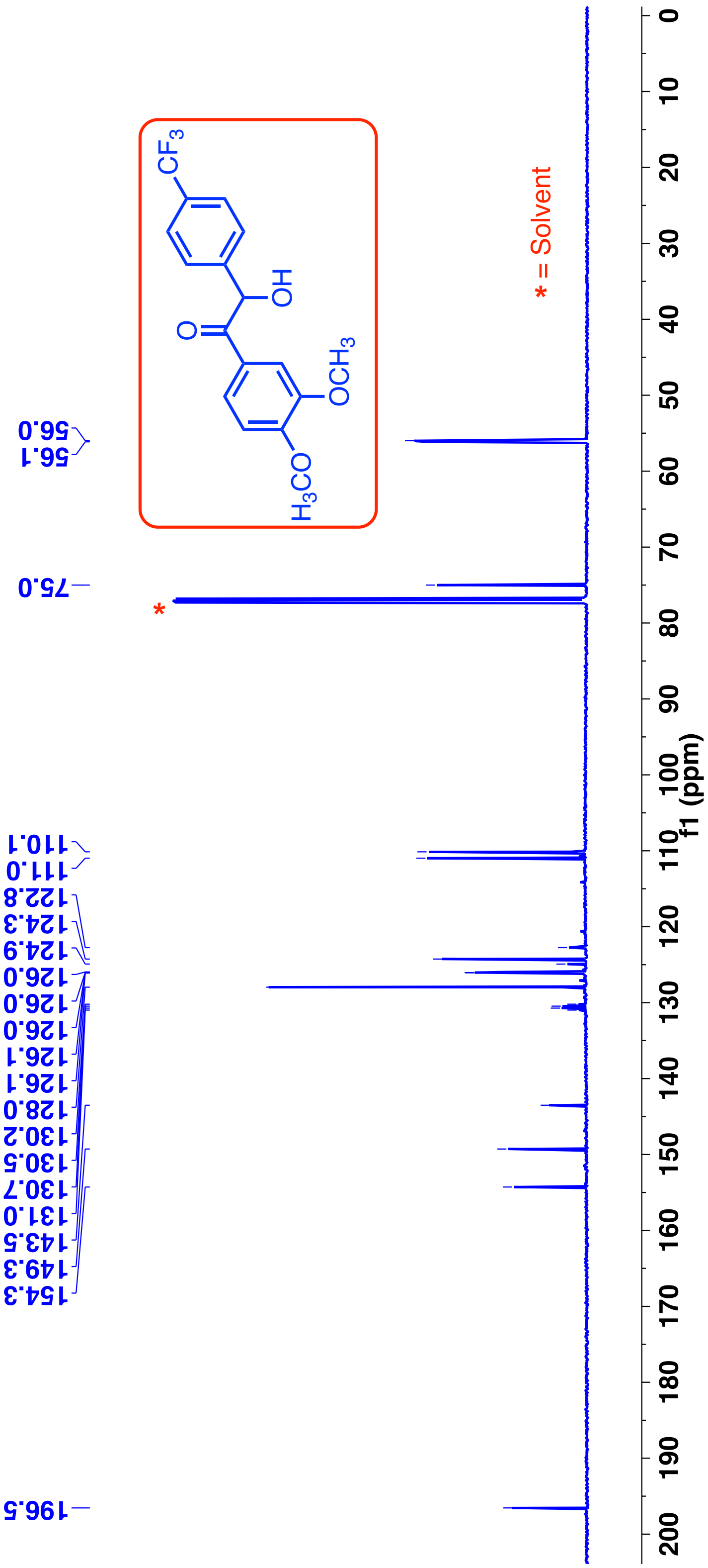


Figure S51: ^{13}C NMR spectra of **1d**.

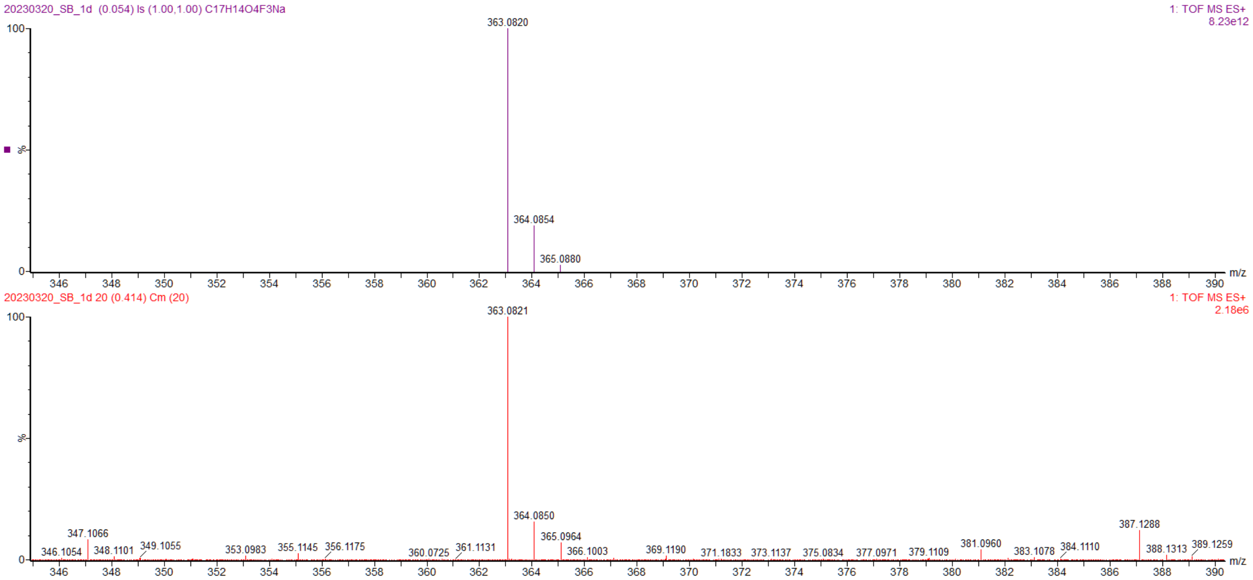


Figure S52: HRMS spectra of **1d**.

11.5. Characterization of **1e**

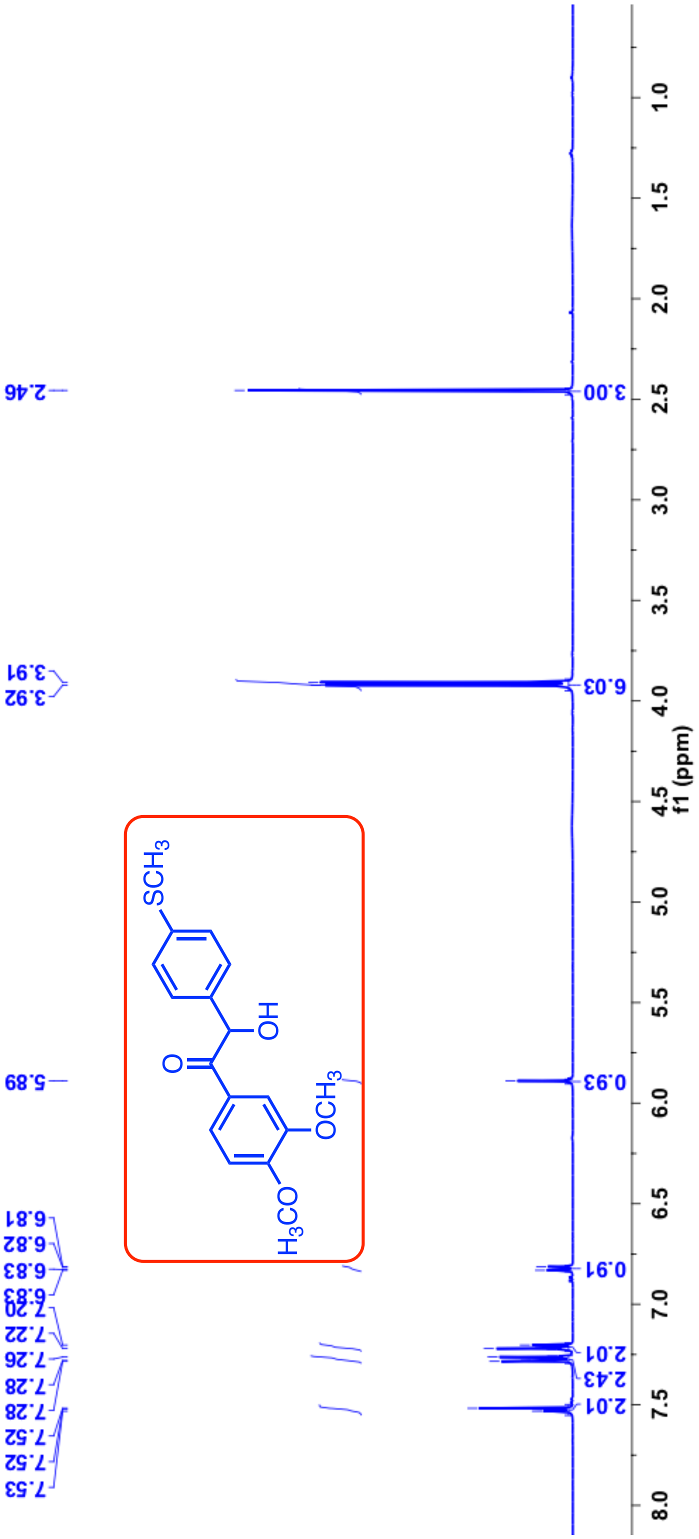


Figure S53: ^{1}H NMR spectra of **1e**.

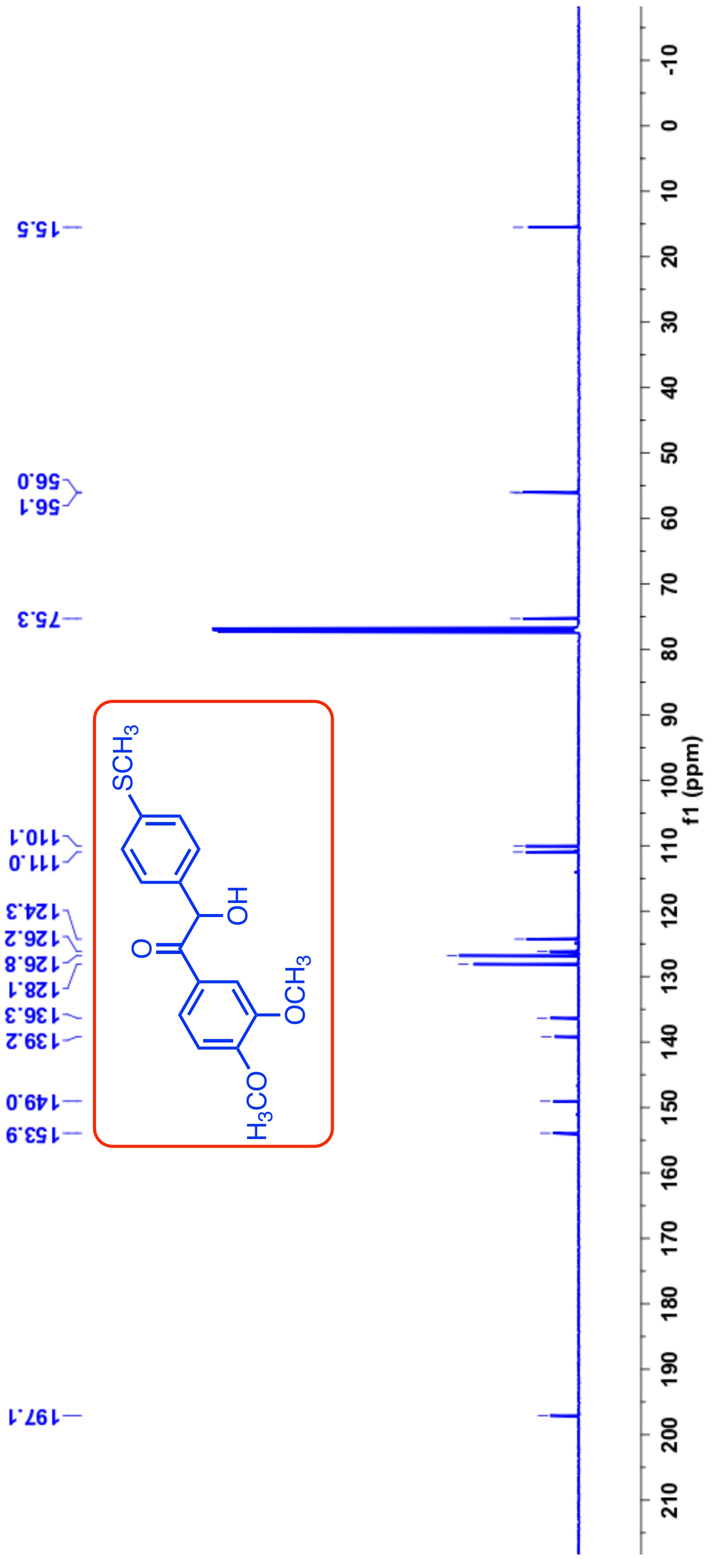


Figure S54: ^{13}C NMR spectra of **1e**.

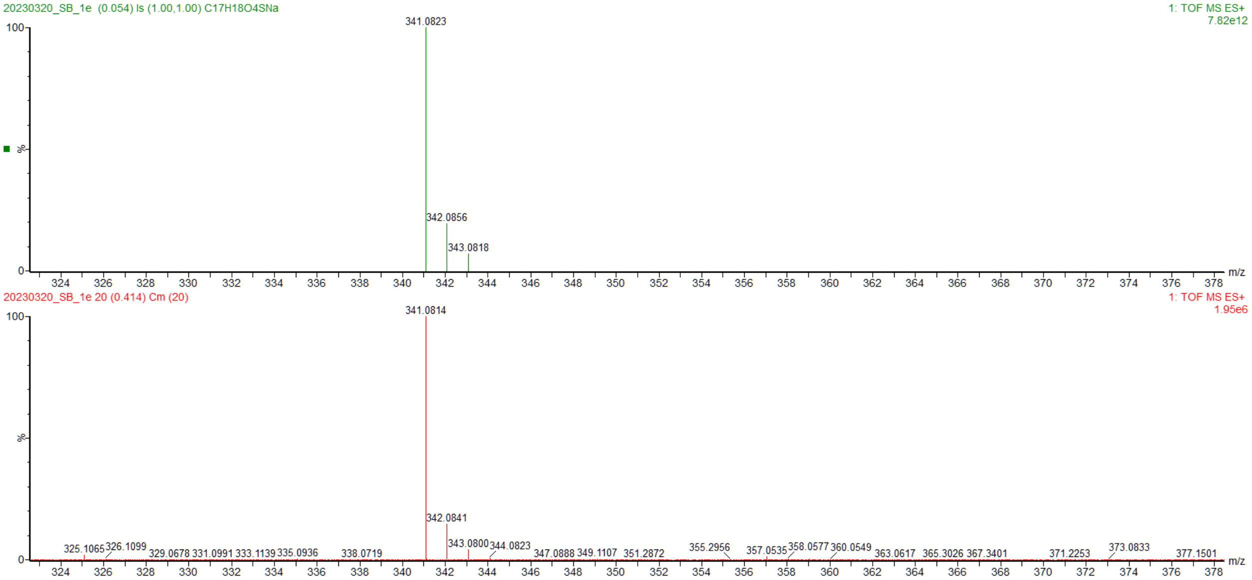


Figure S55: HRMS spectra of **1e**.

11.6. Characterization of **1f**

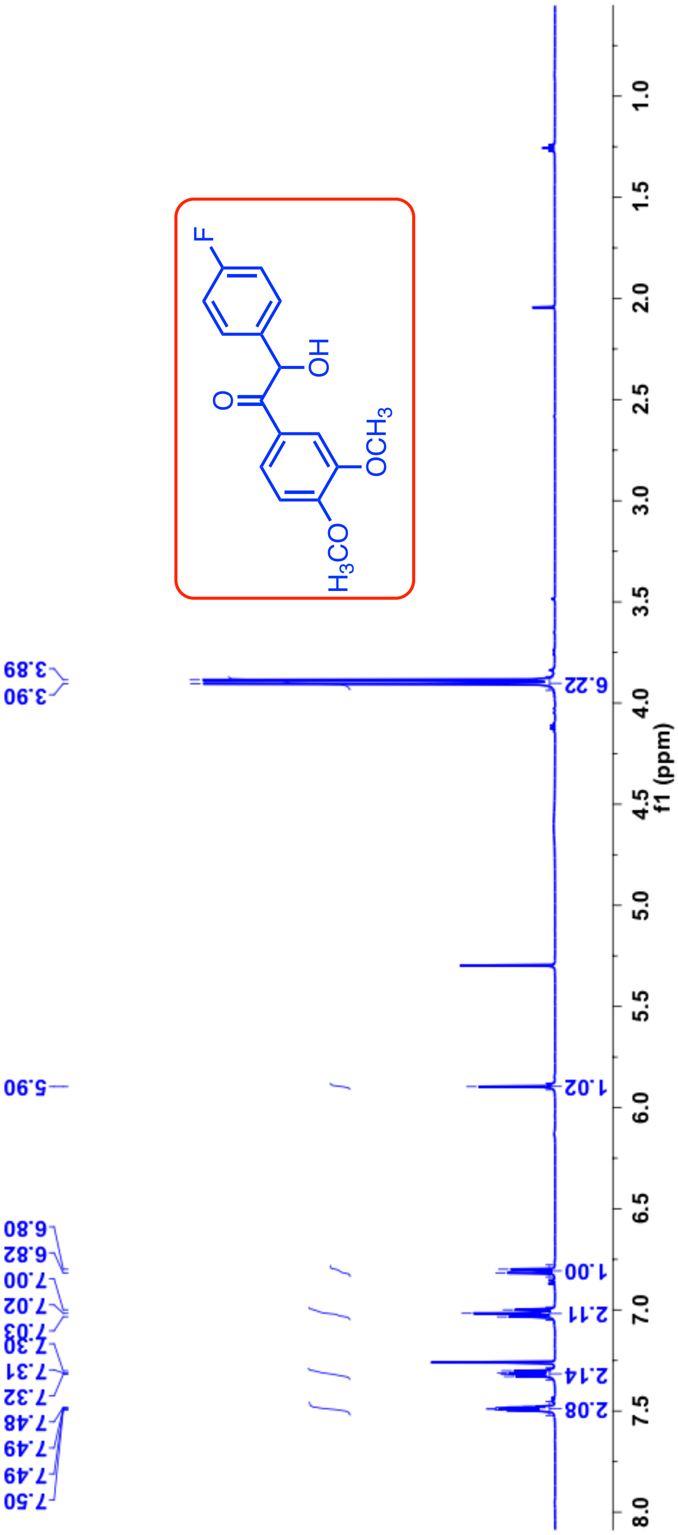


Figure S56: ^{1}H NMR spectra of **1f**.

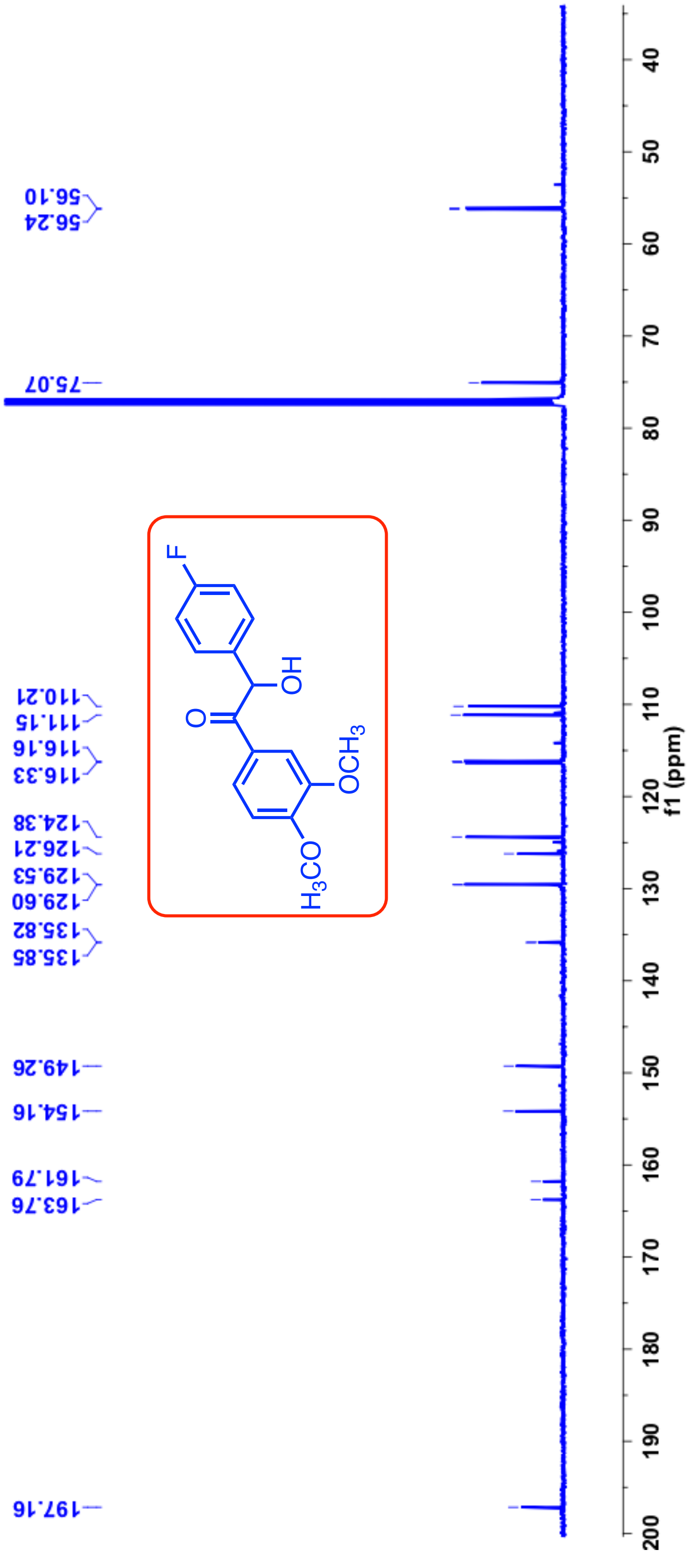


Figure S57: ^{13}C NMR spectra of **1f**.

11.7. Characterization of **1g**

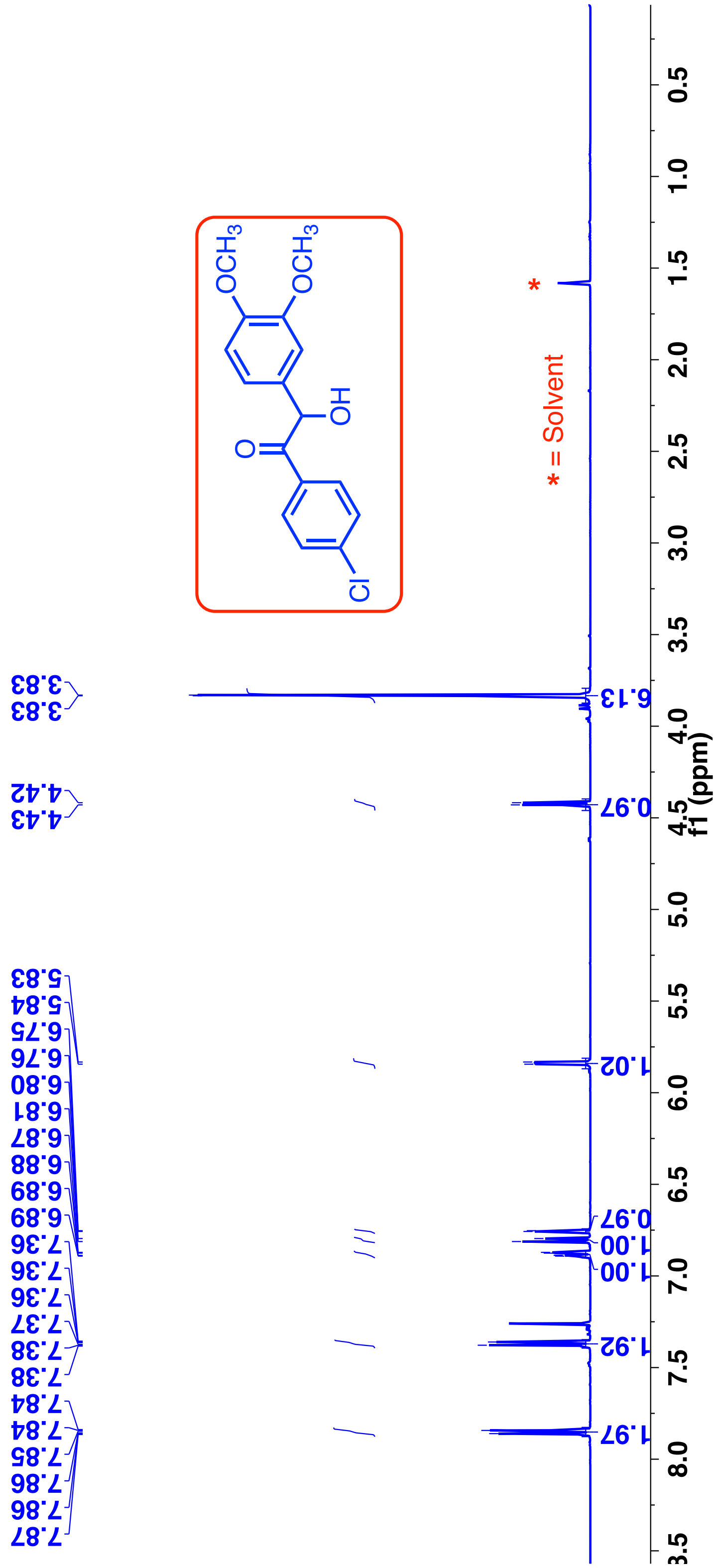


Figure S58: ^{1}H NMR spectra of **1g**.

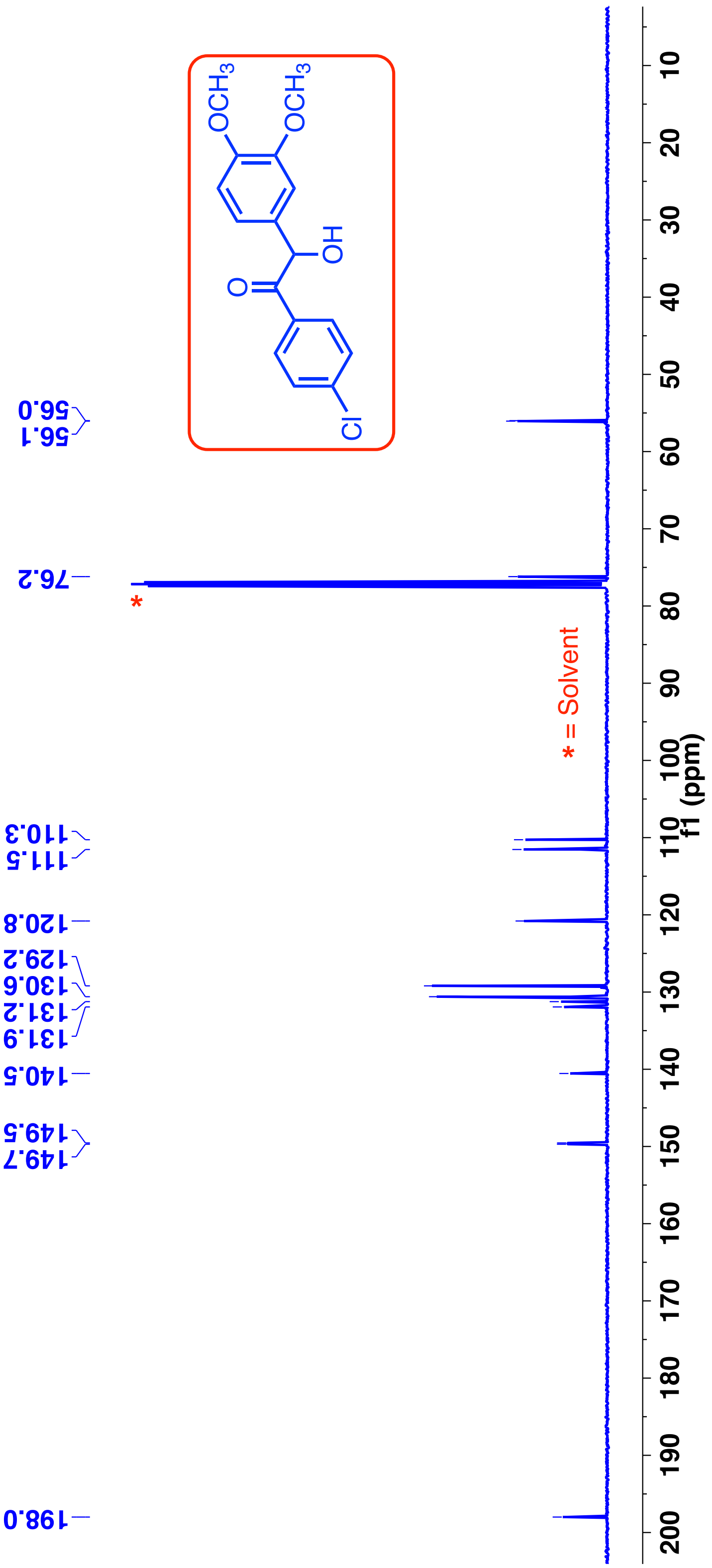


Figure S59: ^{13}C NMR spectra of **1g**.

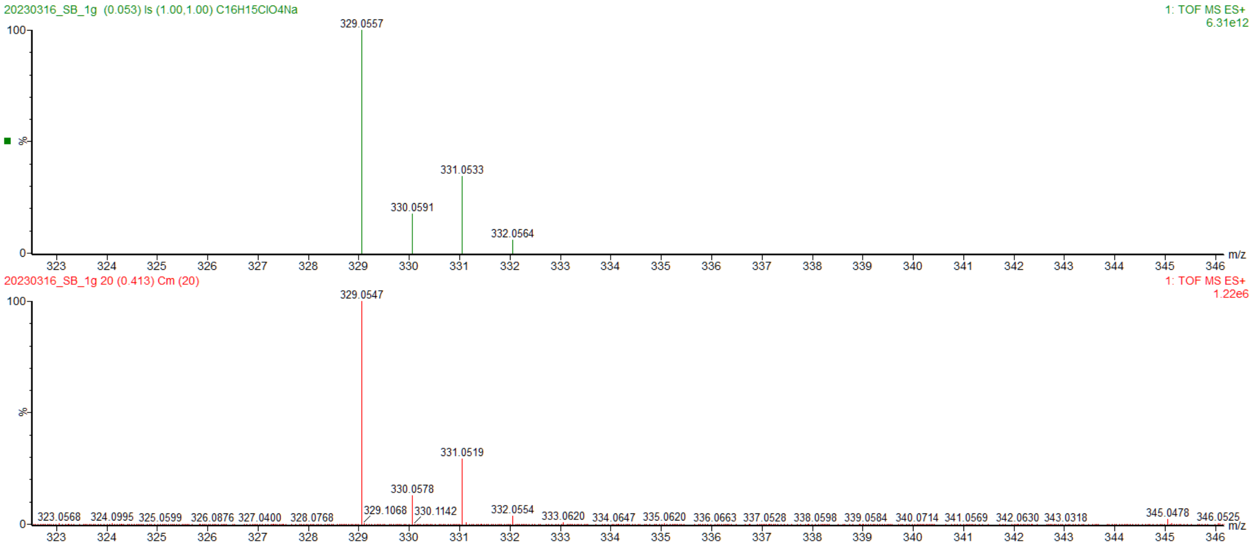


Figure S60: HRMS spectra of **1g**.

11.8. Characterization of **1h**

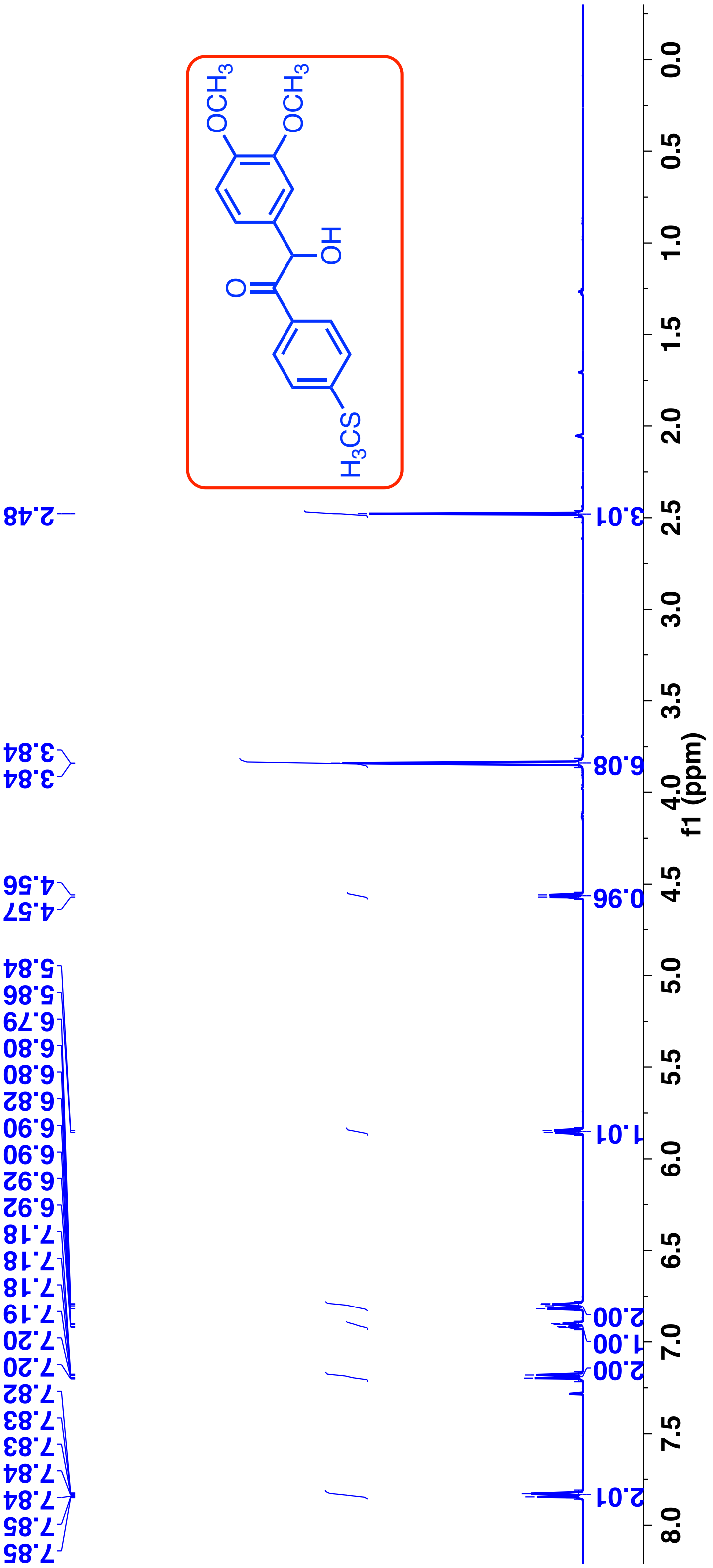


Figure S61: ^{1}H NMR spectra of **1h**.

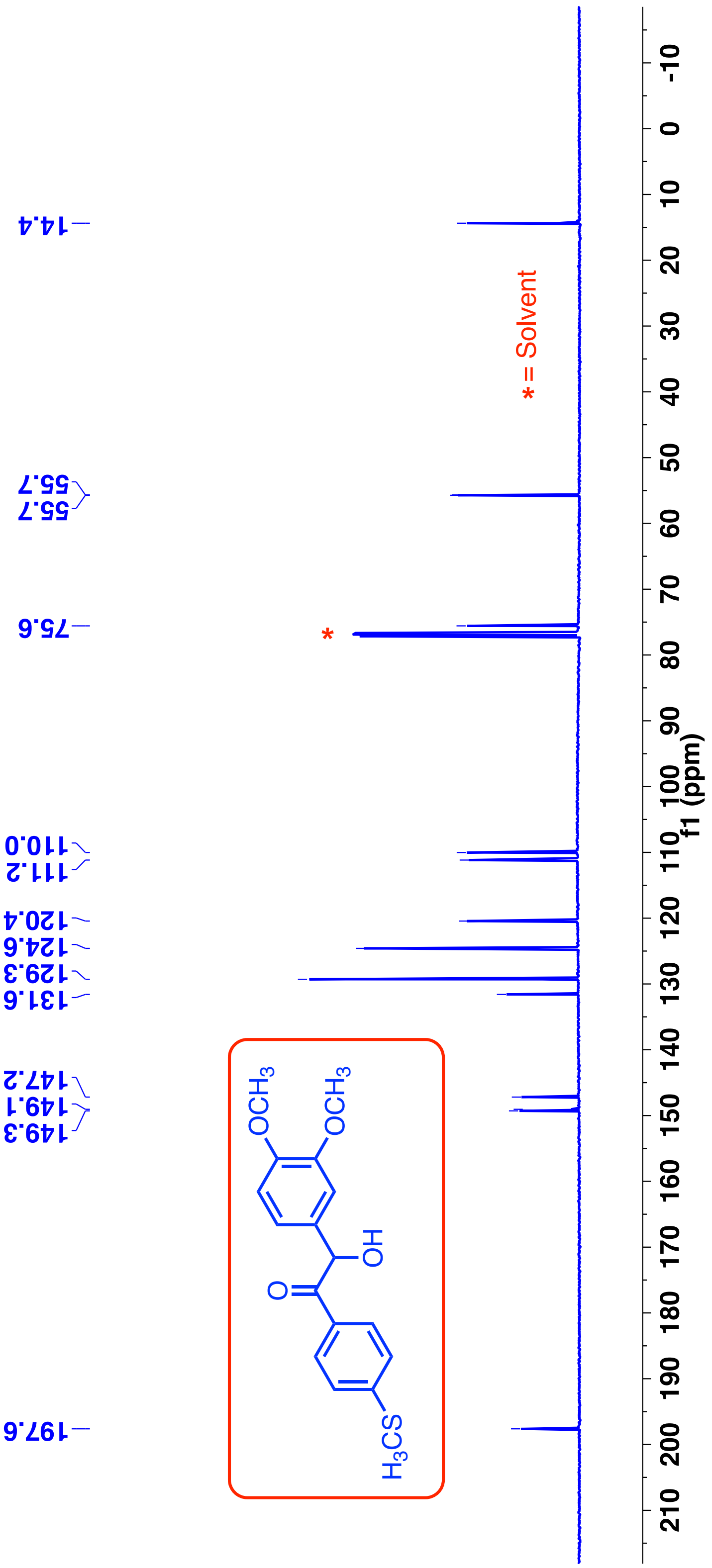


Figure S62: ^{13}C NMR spectra of **1h**.

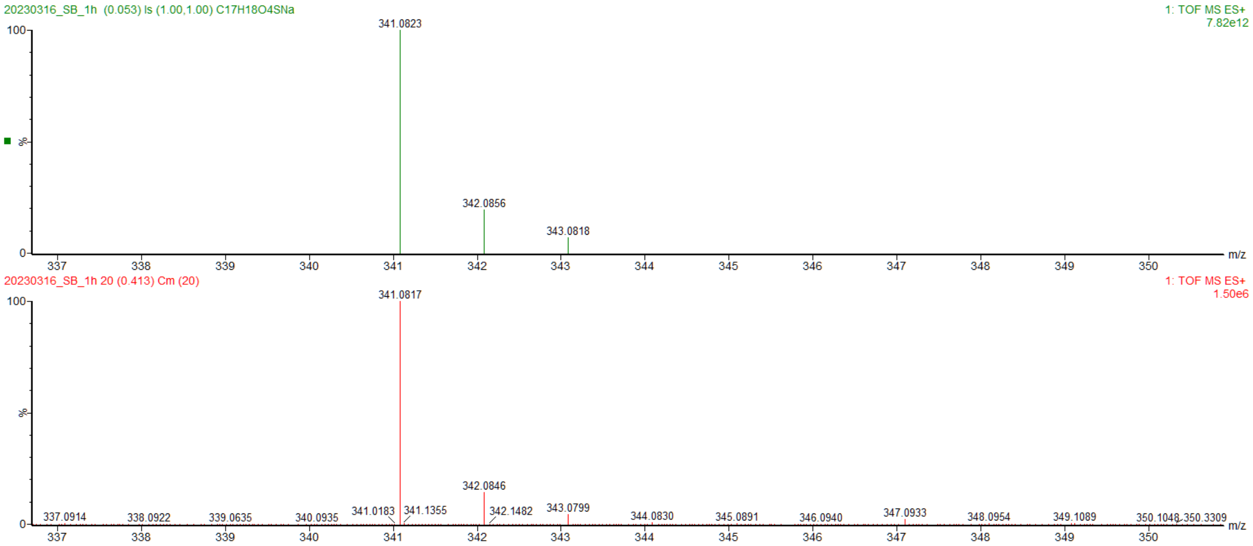


Figure S63: HRMS spectra of **1h**.

11.9. Characterization of **1i**

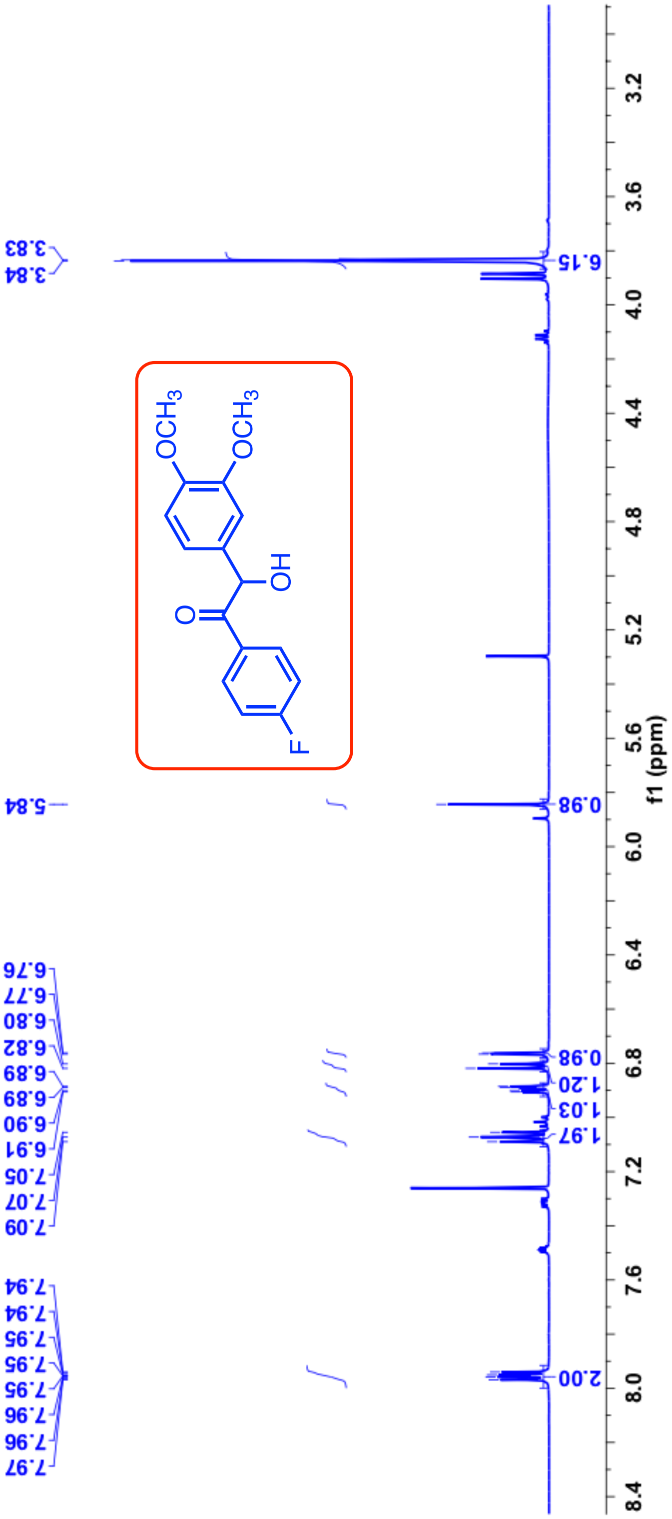


Figure S64:^{1}H NMR spectra of **1i**.

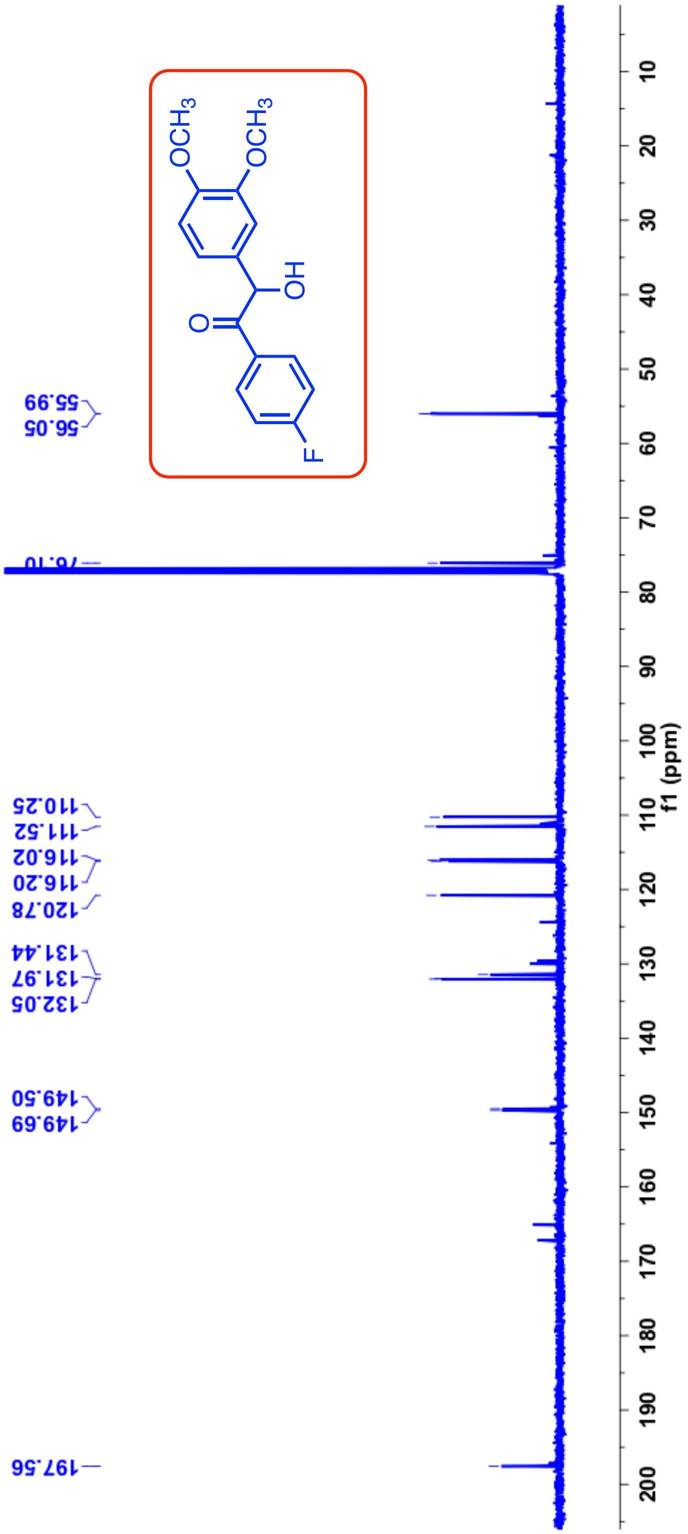


Figure S65:^{13}C NMR spectra of **1i**.

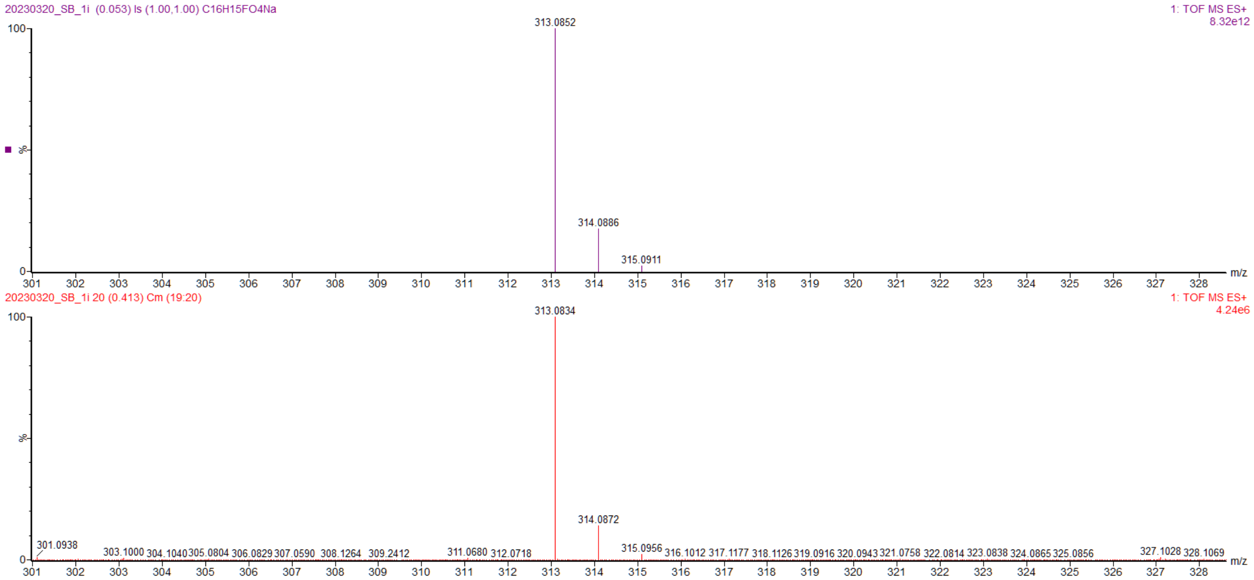


Figure S66: HRMS spectra of **1i**.

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2. H. Firouzabadi, N. Iranpoor and H. Hazarkhani, Iodine Catalyzes Efficient and Chemoselective Thioacetalization of Carbonyl Functions, Transthioacetalization of O,O- and S,O-Acetals and Acylals, *J. Org. Chem.*, 2001, **66**, 7527-7529.

3. M. R. Rohman, M. Rajbangshi, B. M. Laloo, P. R. Sahu and B. Myrboh, Iodine–alumina as an efficient and useful catalyst for the regeneration of carbonyl functionality from the corresponding 1,3-oxathiolanes and 1,3-dithiolanes in aqueous system, *Tetrahedron Lett.*, 2010, **51**, 2862-2864.