Supplementary Information (SI) for Organic Chemistry Frontiers.
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1,6-Hydrosulfonylation of *p*-Quinone Methides Enabled via Strain-Release-/Aromaticity-Driven Alkyl Radical Generation and SO_2-Capture: Synthesis and Antiproliferative Studies of Sulfonylated Diarylmethanes

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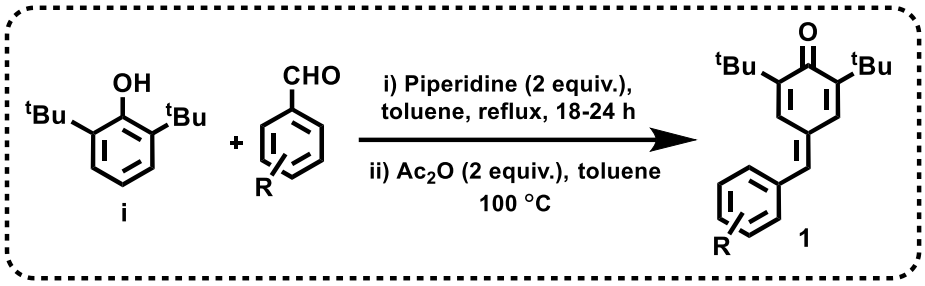
1. General Information:

All the reagents were purchased from commercial suppliers and used without further purification, while most of the desired solvents supplied by commercial suppliers were dried using the standard drying procedures. All the moisture- and air-sensitive reactions were performed under a flow of nitrogen or argon atmosphere using flame-dried or oven-dried glassware with magnetic stirring. All purifications were done using column chromatography with 100−200 mesh size SiO_2 gel as the stationary phase. Distilled ethyl acetate (EtOAc) and Hexane were typically used for column chromatography. The ^{1}H, ^{13}C {1H}, ^{19}F (Decoupled) NMR spectra were recorded on 400 MHz Bruker spectrometer using $CDCl_3$ with residual solvent peaks (H: δ = 7.26 and C: δ = 77.0 ppm) or tetramethylsilane (TMS) (δ = 0.0) as internal standard. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet/pentet, sept = septet, dd = doublet of doublet, ddd = doublet of doublet of doublet, ddt = doublet of doublet of triplet, td = triplet of doublet, dq = doublet of quartet, and m = multiplet. The chemical shifts are reported as δ values (ppm) and the coupling constant (J) values are reported in hertz. High-resolution mass spectra (HRMS) were obtained using electron spray ionization (ESI) technique and Orbitrap mass analyzer. Melting points were determined on a Buchi M-560 apparatus and are uncorrected. The emission spectra were recorded on Horiba Scientific's FluoroMax-4 spectrofluorometer. Progress of the reactions was monitored using precoated SiO_2 gel GF_{254} thin-layer chromatography (TLC) plates, while spot visualizations were done under UV light and using spot-developing stains like p-anisaldehyde, ceric ammonium molybdate or $KMnO_4$.

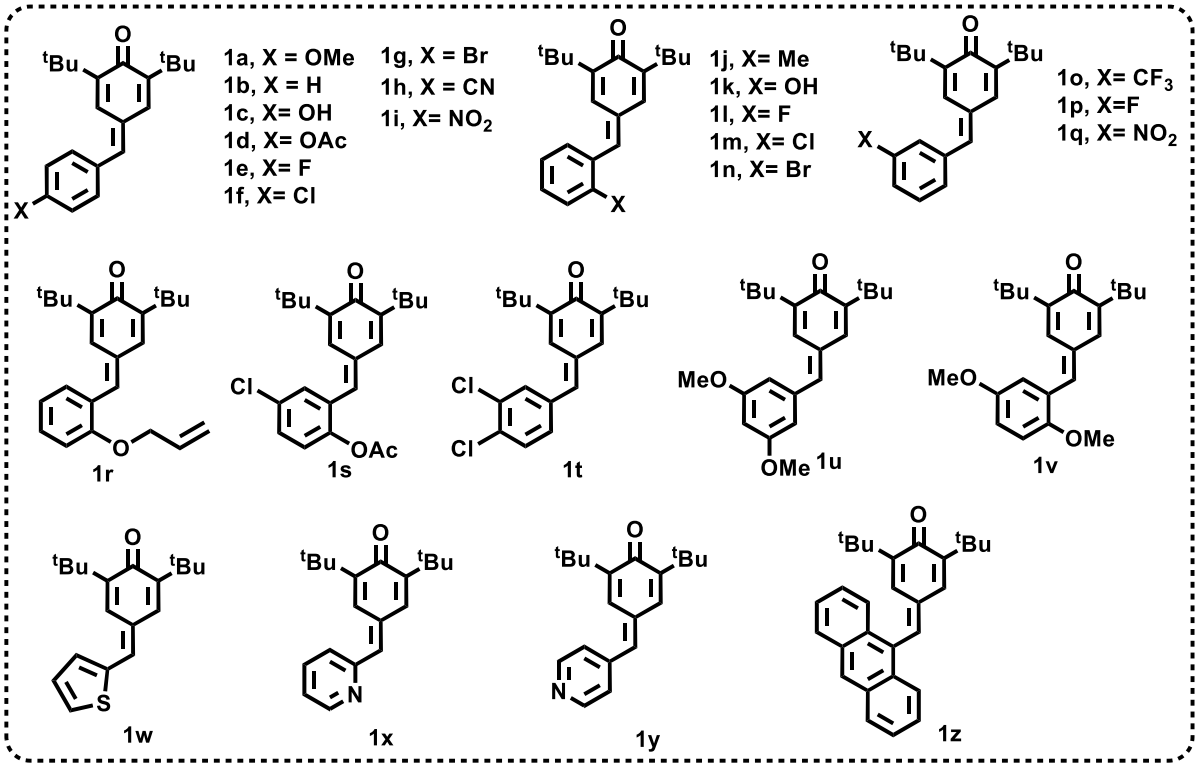
2. Synthesis of starting materials

2.1 Synthesis of *p*-Quinone Methides

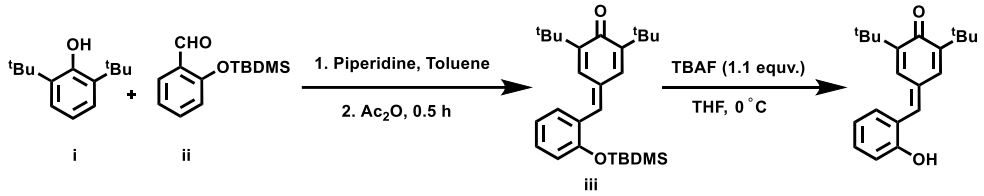


General Procedure A:[1]

Aldehydes (1 equiv.) were added to a solution of phenols (1 equiv.) in toluene (4 M). The reaction mixture was reflux in a Dean-Stark apparatus. Piperidine (2 equiv.) was added dropwise over 0.5-1 h, and the reaction mixture refluxed at 110° C, until all starting material had been consumed (nearly 18-24 h). After the mixture had cooled just below the boiling point of toluene, acetic anhydride (2 equiv.) was added, and then the solution was stirred for 15-20 min. The residue was extracted three times with dichloromethane. The combined organic layers were washed with water and brine solution sequentially, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the corresponding product.



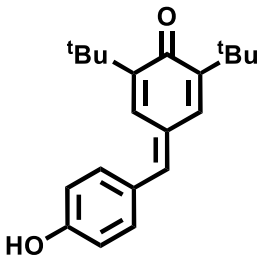
By protecting -OH group for synthesis of 2-((3,5- di-tert-butyl-4- hydroxy cyclohexa-2,5- dien-1-ylidene)methyl) phenol **ii** and following **General Procedure A,** 4-((3,5-di-tert-butyl-4- hydroxycyclohexa-2,5-dien-1 ylidene)methyl) phenol **iii** was prepared.



To a solution of **iii** (1.0 equiv.) in THF (10 mL/mmol substrate) at 0 ºC was added tetrabutylammonium fluoride trihydrate (1.1 equiv.). The reaction mixture was stirred for 10 min and a saturated NH_4Cl solution was added dropwise to quench the reaction. The resulting solution was extracted with Et_2O (3 × 20 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography to afford the desired compounds **1c** and **1k**.

The other p-Quinone methides were prepared following the general procedure **A** and the characterization data of the known *p*-Quinone methides, were found to be in accordance with the reported data, **(1a, 1b, 1g, 1i, 1k, 1m, 1q, 1w,1z)** [1], **(1e, 1f, 1h, 1j, 1l, 1t)** [2], **1o** [3], **1n** [4], **1p** [5], **1d** [6], while those for new derivatives are documented below.

***2,6-di-tert-butyl-4-(4-hydroxybenzylidene)cyclohexa-2,5-dien-1-one (1c)*:** Following the general procedure **B**, taking 2,6-di-tert-butylphenol (0.5 g, 2.42 mmol), **1c** was obtained as yellow solid 480 mg, 63% over two step. R_f = 0.5 (Hexane:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.16 (s, 1H), 7.04 (d, J = 2.5 Hz, 1H), 6.99 – 6.94 (m, 2H), 1.36 (s, 9H), 1.34 (s, 9H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.7, 156.9, 149.0, 147.3, 142.9, 135.5, 132.4 (2C), 130.6, 128.8, 127.9, 116.0 (2C), 35.4, 34.9, 29.6 (3C), 29.5 (3C). **HRMS** (ESI) m/z calcd for $C_{21}H_{27}O_2$ $(M+H)^+$: 311.2006; found: 311.2000.



4-(2-(allyloxy)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1r): Following the general procedure **A**, 2,6-di-tert-butylphenol (0.5 g, 2.42 mmol), to corresponding aldehyde (392 mg, 2.42 mmol), **1r** was obtained as yellow solid (720 mg, 85%). R_f = 0.5 (hexane:EtOAc = 19:1). m. p. 90-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.42 – 7.33 (m, 2H), 7.08 (d, J = 2.3 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.17 – 6.03 (m, 1H), 5.44 (dd, J_1 = 17.3, J_2 = 1.7 Hz, 1H), 5.37 – 5.28 (m, 1H), 4.67 – 4.60 (m, 2H), 1.35 (s, 9H), 1.30 (s, 9H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.7, 157.4, 148.9, 147.4, 138.8, 135.3, 132.9, 131.9, 131.6, 130.7, 128.4, 125.2, 120.7, 117.9, 112.1, 69.2, 35.4, 35.0, 29.6 (3C), 29.5 (3C). **HRMS** (ESI) m/z calcd for $C_{24}H_{31}O_2$ $(M+H)^+$: 351.2319; found: 351.2322.

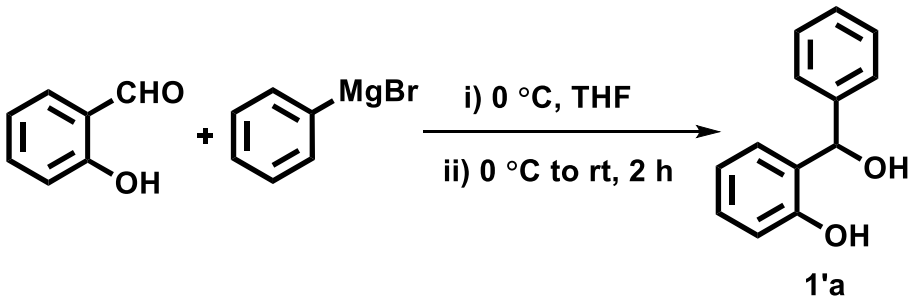
4-chloro-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl acetate (1s): Following the general procedure **A**, 2,6-di-tert-butylphenol (0.5 g, 2.42 mmol), to corresponding aldehyde (480 mg, 2.42 mmol), **1s** was obtained as yellow solid (768 mg, 82%). R_f = 0.5 (Hexane:EtOAc = 19:1). m. p. 84-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, J = 2.6 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.29 (d, J = 1.2 Hz, 1H), 7.16 (d, J = 8.6 Hz, 1H), 7.01 – 6.98 (m, 1H), 6.96 (s, 1H), 2.32 (s, 3H), 1.35 (s, 9H), 1.31 (s, 9H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.5, 168.8, 150.0, 148.6, 147.5, 134.2, 134.0, 133.9, 131.5, 131.4, 130.2, 129.9, 127.4, 124.2, 35.5, 35.1, 29.5 (6C), 20.9. **HRMS** (ESI) m/z calcd for $C_{23}H_{28}O_3Cl$ $(M+H)^+$: 387.1721; found: 387.1720.

2,6-di-tert-butyl-4-(3,5-dimethoxybenzylidene)cyclohexa-2,5-dien-1-one (1u): Following the general procedure **I**, 2,6-di-tert-butylphenol (0.5 g, 2.42 mmol), to corresponding aldehyde (403 mg, 2.42 mmol), **1u** was obtained as yellow solid (774 mg, 90%). R_f = 0.5 (hexane: EtOAc = 19:1). m. p. 80-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, J_1 = 2.5, J_2 = 0.8 Hz, 1H), 7.13 (s, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.61 (dd, J_1 = 2.3, J_2 = 0.7 Hz, 2H), 6.51 (t, J = 2.3 Hz, 1H), 3.83 (s, 6H), 1.33 (s, 9H), 1.31 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.6, 160.9 (2C), 149.3, 147.9, 142.4, 137.6, 135.1, 132.3, 127.9, 108.2 (2C), 101.7, 55.5 (2C), 35.5, 35.0, 29.6 (3C), 29.5 (3C). **HRMS** (ESI) m/z calcd for $C_{23}H_{31}O_3$ $(M+H)^+$: 355.2268; found: 355.2263.

2,6-di-tert-butyl-4-(2,5-dimethoxybenzylidene)cyclohexa-2,5-dien-1-one(1v): Following the general procedure **I**, 2,6-di-tert-butylphenol (0.5 g, 2.42 mmol), to corresponding aldehyde (403 mg, 2.42 mmol), **1v** was obtained as yellow solid (740 mg, 86%). R_f = 0.5 (hexane:EtOAc = 19:1). m. p. 84-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, J_1 = 2.3, J_2 = 0.9 Hz, 1H), 7.38 (s, 1H), 7.07 (d, J = 2.4 Hz, 1H), 6.97 (s, 1H), 6.94 (d, J = 4 Hz, 1H), 6.90 (d, J = 4 Hz, 1H) , 3.86 (s, 3H), 3.81 (s, 3H), 1.34 (s, 9H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.6, 153.3, 152.7, 149.1, 147.5, 138.4, 135.3, 131.7, 128.1, 125.4, 116.6, 116.5, 111.9, 56.1, 55.9, 35.4, 35.0, 29.6 (3C), 29.5 (3C). **HRMS** (ESI) m/z calcd for $C_{23}H_{31}O_3$ $(M+H)^+$: 355.2268; found: 355.2274.

2,6-di-tert-butyl-4-(pyridin-2-ylmethylene)cyclohexa-2,5-dien-1-one (1x): Following the general procedure **I**, 2,6-di-tert-butylphenol (0.5 g, 2.42 mmol), with corresponding aldehyde (260 mg, 2.42 mmol), **1x** was obtained as yellow semi-solid (573 mg, 80%). R_f = 0.5 (hexane:EtOAc = 19:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (dt, J_1 = 4.6, J_2 = 1.9 Hz, 1H), 8.67 (d, J = 2.4 Hz, 1H), 7.72 (tt, J_1 = 7.7, J_2 = 2.1 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.22 (ddd, J_1 = 7.2, J_2 = 4.0, J_3 = 2.8 Hz, 1H), 6.99 – 6.93 (m, 2H), 1.34 (s, 9H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.7, 155.3, 150.1, 149.9, 148.6, 138.2, 136.5, 135.4, 134.6, 129.1, 127.1, 122.8, 35.6, 35.1, 29.6 (3C), 29.6 (3C). **HRMS** (ESI) m/z calcd for $C_{20}H_{26}ON$ $(M+H)^+$:296.2009; found: 296.2006.

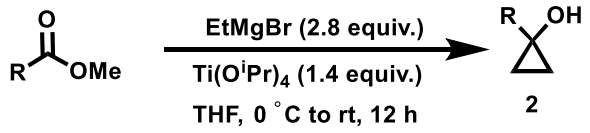
Synthesis of ortho-benzhydryl alcohol [7]



Under a nitrogen atmosphere, a solution of salicylaldehyde (1.0 mmol) in tetrahydrofuran (2 mL) was added dropwise to a solution of the Grignard reagent (2.0 mmol, 1.0 M in THF, 2 mL) at 0 °C. The mixture was then removed from the ice and stirred at room temperature for 2 hours. After complete conversion, which TLC monitored, the reaction

mixture was quenched at 0 °C with saturated ammonium chloride (10 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated. The residue was then purified on silica gel, eluting with a mixture of hexane and ethyl acetate (1:9, v/v) to obtain the product **1'a.**

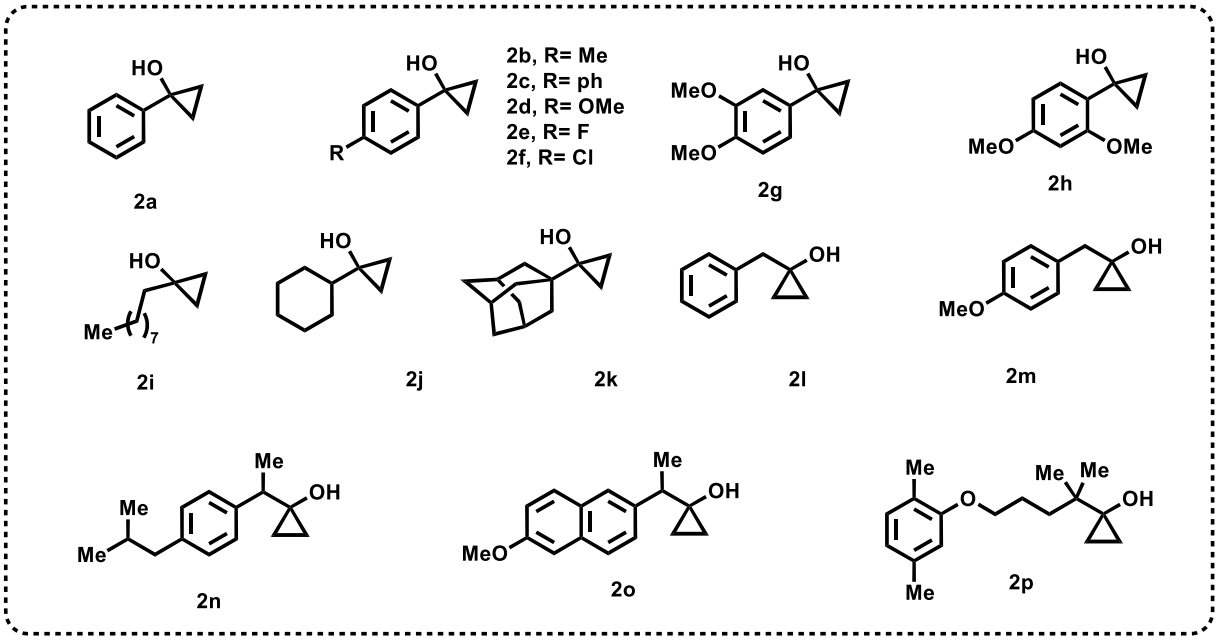
2.2 Synthesis of Cyclopropanols



General Procedure B: All the Cyclopropanols (**2**) were prepared according to the following two reported procedures.

To a stirred solution of ester (5.0 mmol) in THF (10 mL), Ti(O^{i}Pr)$_4$ (7 mmol, 1.4 equiv,) was added under N_2 atmosphere, Then, ethyl magnesuim bromide (2.8 equiv) was added dropwise via syringe at 0 °C. The black solution was allowed to warm to room temperature and stirred for 12 h. After completion, the reaction mixture was cooled to 0 °C and quenched with slow addition of sulfuric acid solution (2.0 M) and stirred until all the solid dissolved to give a clear two-phase liquid. The liquid was separated and the aqueous solution was extracted with ehyl acetate (3×30 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The organic solution was evaporated. The residue was purified by flash column chromatography on silica gel (Hexane/ EtOAc) to acquire the cyclopropanol product.

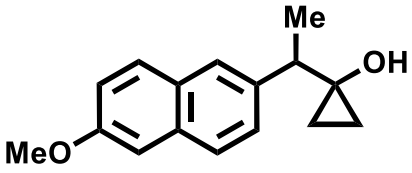
The cyclopropanols were prepared following the general procedure **B** and the characterization data of the known Cyclopropanol, were found to be in accordance with the reported data, **(2a, 2b, 2d, 2e, 2f, 2g, 2h, 2j, 2l)** [8], **(2c, 2m)** [9], **2i** [10] while those for new derivatives are documented below.



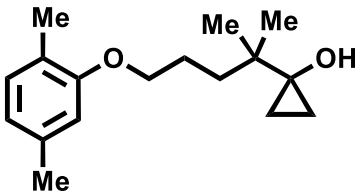
1-((1s,3s)-adamantan-1-yl)cyclopropan-1-ol (2k): Following the general procedure **B**, **2k** was obtained as white solid (624 mg 65%). R_f = 0.5 (hexane:EtOAc = 9:1). m. p. 64-66 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.06 – 1.98 (m, 3H), 1.77 – 1.62 (m, 8H), 1.57 (d, *J* = 2.9 Hz, 4H), 0.68 – 0.61 (m, 2H), 0.57 – 0.52 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 62.4, 38.2 (3C), 37.1 (3C), 34.8, 28.4 (3C), 9.3 (2C). **HRMS** (ESI) m/z calcd for $C_{13}H_{21}O$ $(M+H)^+$: 193.1587; found: 193.1587.

1-(1-(4-isobutylphenyl)ethyl)cyclopropan-1-ol (2n): Following the general procedure **B**, **2n** was obtained as colourless liquid (576 mg, 60%). R_f = 0.5 (hexane:EtOAc = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.55 (q, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.94-1.80 (m, 1H), 1.39 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H), 0.87 – 0.80 (m, 1H), 0.76 – 0.65 (m, 2H), 0.65 – 0.56 (m, 1H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 140.9, 140.0, 129.2 (2C), 127.6 (2C), 59.8, 45.4, 45.1, 30.2, 22.5, 22.4, 16.5, 13.5, 12.6. **HRMS** (ESI) m/z calcd for $C_{15}H_{23}O$ $(M+H)^+$: 219.1743; found: 219.1742.

1-(1-(6-methoxynaphthalen-2-yl)ethyl)cyclopropan-1-ol (2o): Following the general procedure **B**, **2o** was obtained as yellow solid (653 mg, 54%. R_f = 0.5 (hexane:EtOAc = 17:3). m. p. 92-94 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 3.6 Hz, 1H), 7.74 (d, *J* = 3.4 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.47 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.20 – 7.13 (m, 2H), 3.95 (s, 3H), 2.74 (q, *J* = 7.1 Hz, 1H), 1.83 (s, OH, 1H), 1.51 (d, *J* = 7.2 Hz, 3H), 0.94 – 0.65 (m, 4H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 157.5, 139.1, 133.6, 129.3, 129.0, 127.3, 126.9, 126.1, 118.9, 105.7, 59.8, 55.4, 45.8, 16.6, 13.5, 12.8. **HRMS** (ESI) m/z calcd for $C_{16}H_{19}O_2$ $(M+H)^+$: 243.1380; found: 243.1380.

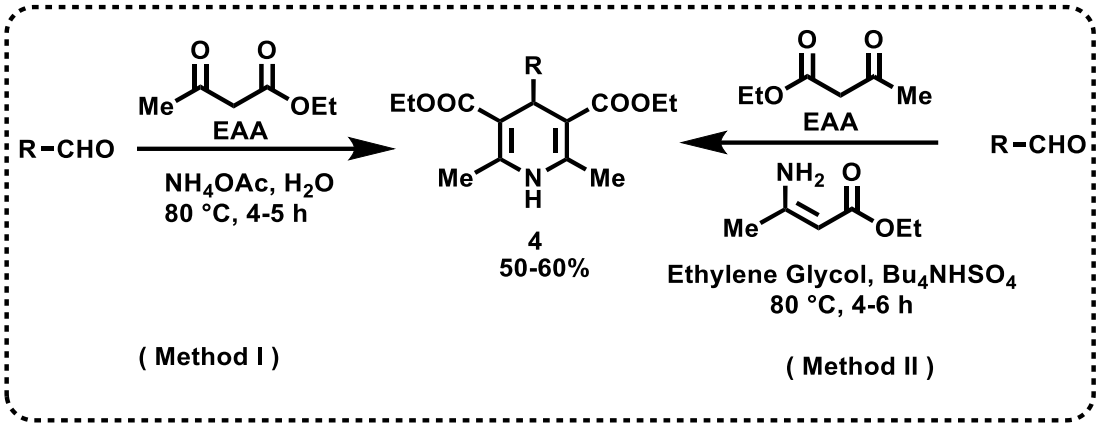


1-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)cyclopropan-1-ol (2p): Following the general procedure **B**, **2p** was obtained as yellow liquid (684 mg, 53%. R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.4 Hz, 1H), 6.77 – 6.66 (m, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 2.37 (s, 3H), 2.25 (s, 3H), 1.99 – 1.88 (m, 2H), 1.71 – 1.62 (m, 2H), 0.95 (s, 6H), 0.73 – 0.64 (m, 4H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 157.1, 136.5, 130.4, 123.6, 120.9, 112.3, 68.8, 61.1, 36.0, 35.6, 24.5, 24.1 (2C), 21.5, 15.9, 10.5 (2C). **HRMS** (ESI) m/z calcd for $C_{17}H_{27}O_2$ $(M+H)^+$: 263.2006; found: 263.2005.



2.3 Synthesis of 4-alkyl-1,4-DHPs

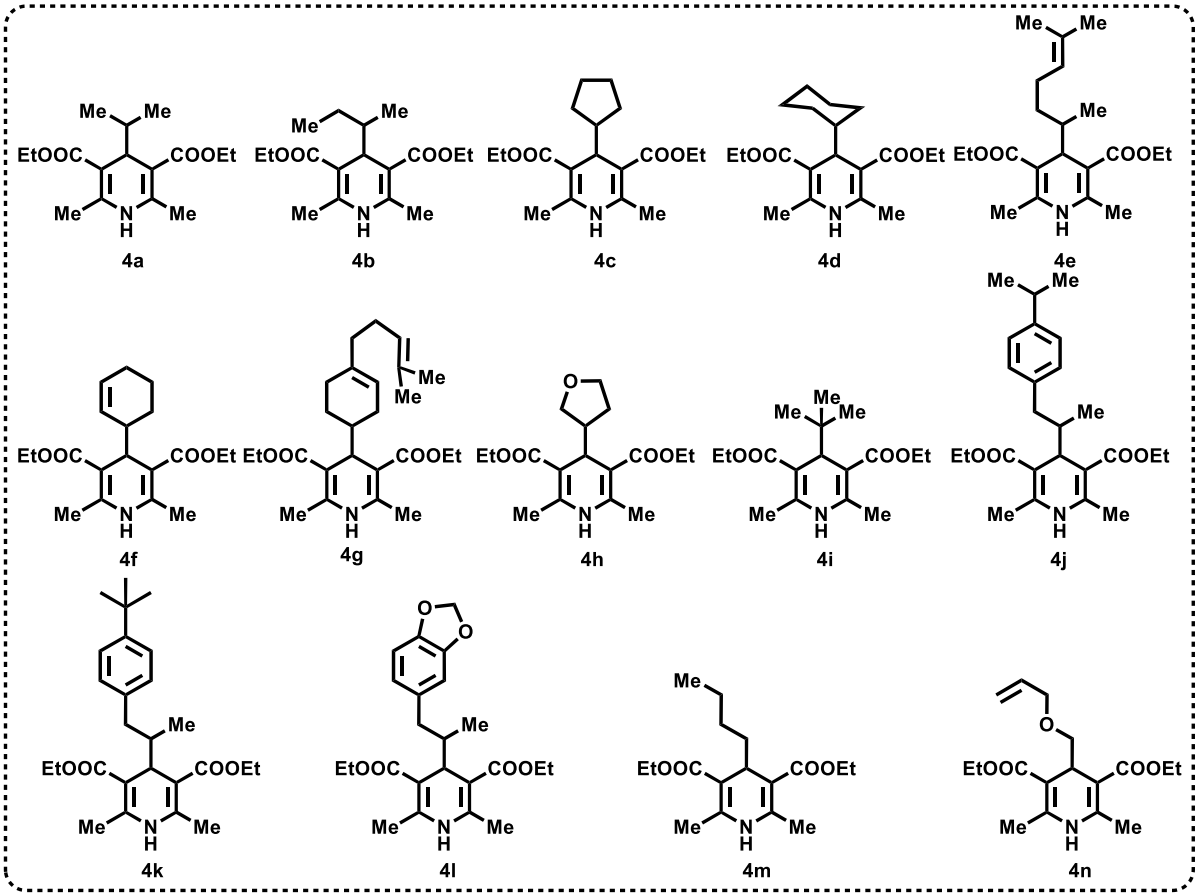
General Procedure C:



4-alkyl-1,4-DHPs (**4**) were prepared according to the following two reported procedures.[4]

Method I. A round-bottomed flask was charged with ethyl acetoacetate (2 equiv.), aldehyde (1 equiv.), ammonium acetate (2 equiv.), and water (0.3 M). The mixture was then heated to 86 – 90 °C overnight. The reaction was worked up by diluting it with DCM and further extraction of the aqueous phase with the same solvent. The organic fractions were combined, dried over Na_2SO_4, and then subjected to solvent removal in vacuo. Purification of the resultant crude material by SiO_2-gel flash column chromatography (hexane: EtOAc = 4:1) furnished the desired 4-alkyl DHP.

Method II. To the mixture of ethyl (Z)-3-aminobut-2-enoate (1 equiv.), ethyl acetoacetate (1 equiv.), and the corresponding aldehyde (1 equiv.) in ethylene glycol (2.5 M), Bu_4NHSO_4 (12 mol%) was added in one portion. The mixture was heated at 85 °C for 4 hours under N_2 atmosphere. Upon reaction completion by TLC analysis, the mixture was cooled to room temperature, diluted with DCM and water. The aqueous layer was further extracted with DCM. The combined organic layers were washed with brine and water. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The resulting crude material was purified by SiO_2-gel flash column chromatography (hexane: EtOAc = 4:1) to access the 4-alkyl DHP.

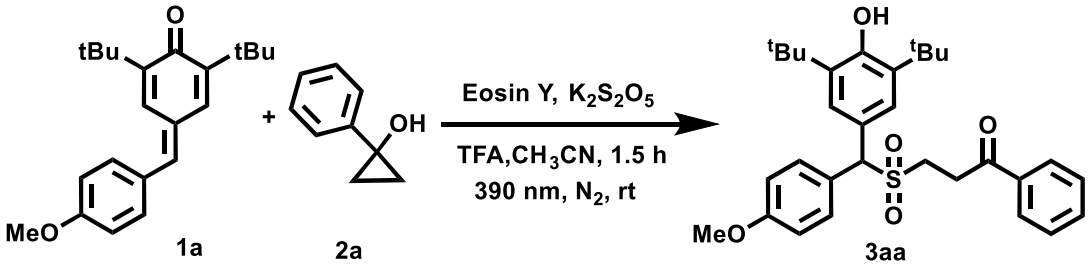


The 4-alkyl DHPs were prepared following the general procedure **C** and the characterization data of the known 4-alkyl DHPs, were found to be in accordance with the reported data, **(4a, 4b, 4c, 4d, 4f, 4g, 4i, 4j, 4k, 4l, 4m, 4n)** [11], **4h** [12], **4e** [13].

Photocatalytic Set-up procedure:

a) Wavelength of Light Source: λ_{max} = 456 nm (blue LED), 390 nm (purple LED) Kessile lamp (PR160L)
b) Intensity 100%, Operating Voltage 19 Volt, LED input Power 40 Watt (max.)
c) Irradiation Vessel: Borosilicate glass vial 20 ml
d) Distance between light source and glass vessel: 4 cm.

3. Preperation of γ- keto alkyl sulfonylated diarylmethane

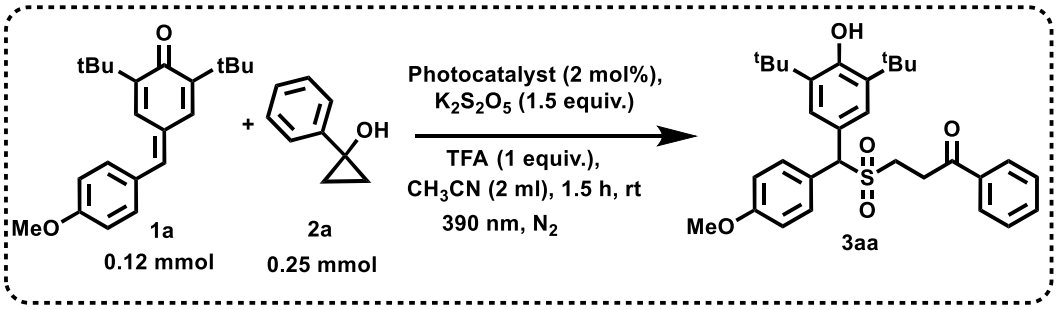


General Procedure D:

In a 20 ml borosilicate glass vial equipped with a magnet, add with *p*-QMs (0.123 mmol) Cyclopropanol (0.25 mmol) in 2 ml CH_3CN solvent (0.06 M). Then added $K_2S_2O_5$ (1.5 equiv.) followed by Eosin Y (0.02 equiv.) and TFA (1 equiv.). After that, the mixture was degassed with N_2 for 15 min, then irradiation with Purple light (390 nm) from distance 4 cm. The reaction progress was monitored by TLC. Upon complete consumption of the starting material, the reaction was quenched with water and the aqueous phase was extracted with EtOAc (3×15 mL). The organic extracts were combined and dried over Na_2SO_4. The organic phase was evaporated under reduced pressure and the resulting crude material was purified by SiO2-gel flash column chromatography to get the desired product **3aa**.

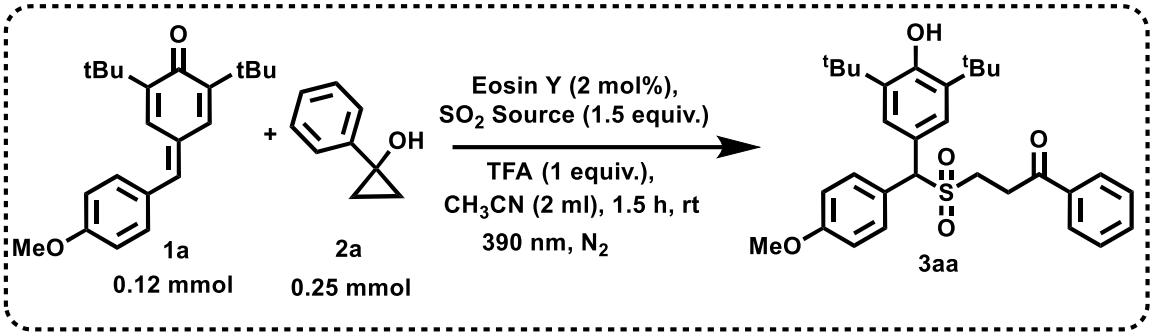
Optimization of Reaction

S1. Screening of Photocatalyst



Entry	Photocatalyst	Yield (%)
1	Eosin Y	90
2	Mes- Acr^+ ClO_4^-	60
3	CzIPN	39
4	$Ir[(dtbbpy)(ppy)_2]$ PF_6	56
5	$Ru(bpy)_3Cl_2.6H_2O$	53
6	Rose Bengal	69

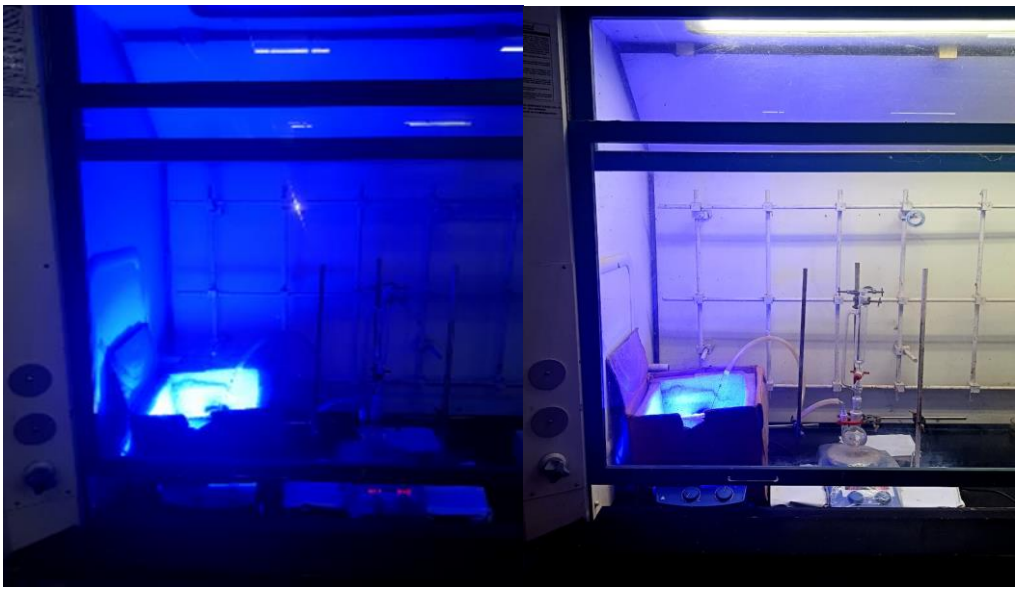
S2. Screening of SO_2 Source



Entry	SO_2 Source	Yield (%)
1	$K_2S_2O_5$	90
2	$Na_2S_2O_5$	79
3	$NaHSO_3$	70
4	DABSO	32
5	SO_2-gas bubbling*	44

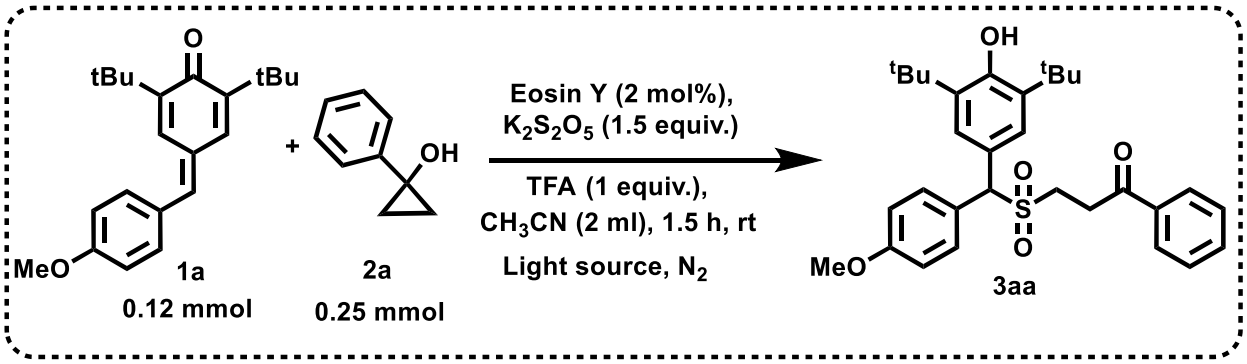
**Caution! Sulfur dioxide is a highly toxic gas, and its generation should be conducted in a well-ventilated fume hood.*

A two-necked 50 mL round-bottom flask, fitted with a 20 mL pressure-equalizing dropping funnel at the central joint and a two-way flushing adaptor at the side joint, was set up in a fume hood. The two-way flushing adaptor was connected through a Teflon tubing to a 5 mL syringe fitted with a 6-inch SS needle, which could be pierced through a rubber septum into a reaction vial used for the photoreaction. To initiate the SO_2-generation process, the two-necked R.B. flask was charged with an aqueous solution of 2 g Na_2SO_3 in 15 mL of water and allowed to stir at rt and the whole system was closed and evacuated with N_2. To this stirred solution, 1 mL of H_2SO_4 was added dropwise through the dropping funnel, and the resultant SO_2 gas was allowed to pass through the two-way flushing adaptor arrangement into the sealed photoreaction vial via the needle fitted to a plastic syringe connected through the Teflon tubing. A pictorial demonstration of the setup is as follows:



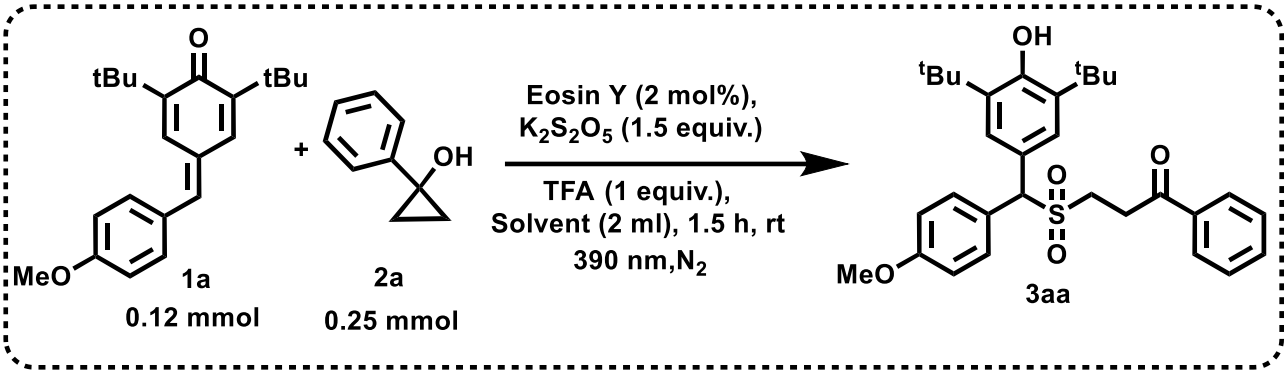
Experimental setup for SO_2-bubbling in the photoreaction.

S3. Screening of Light Source



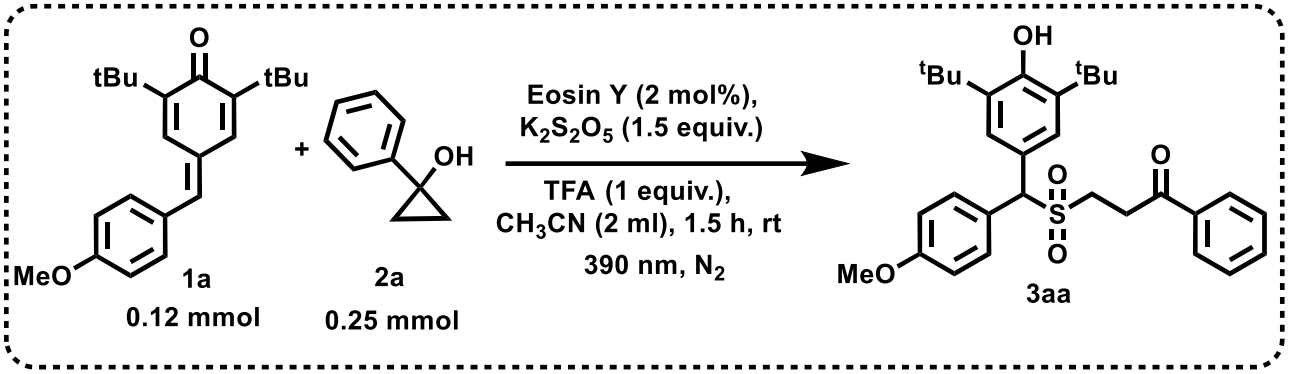
Entry	Light (nm)	Time (h)	Yield (%)
1	390	1.5	90
2	456	6	20
3	427	6	55
4	525	3	43

S4. Screening of Solvent



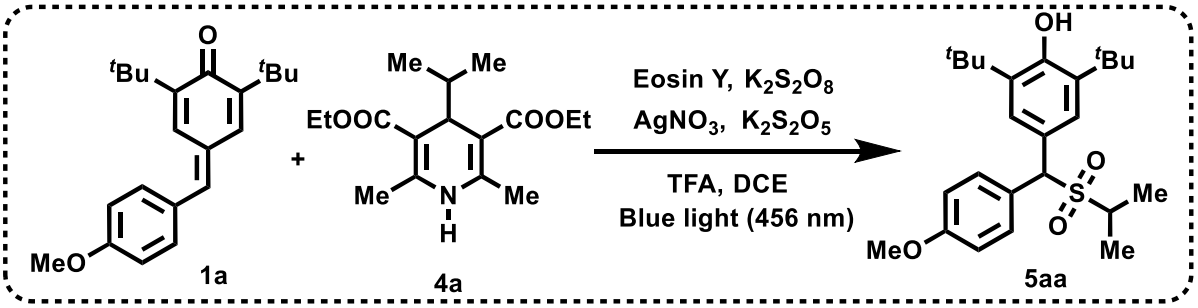
Entry	Solvent	Yield (%)
1	CH_3CN	90
2	DCE	88
3	MeOH	83
4	DCM	88
5	Toluene	80
6	EtOAc	72
7	DMSO	56

S5. Standard Deviation



Entry	Deviation from Standard condition	Time (h)	Yield (%)
1	None	1.5	90
2	Without light	24	3
3	Without Photocatalyst	5	15
4	Without Photocatalyst, acid and light	10	0
5	Without acid additive	4	18
6	Without TFA and photocatalyst	4	8
7	Without TFA (CH_3CN+ H_2O)	2	61
8	Open air	2	70
9	$K_2S_2O_5$ (1 equiv./ 2 equiv.)	2	47/ 86
10	TFA (0.5 equiv./ 1.5 equiv.)	2	58/ 84
11	Eosin Y (5 mol%)	2	84

4. Procedure for Alkyl Sulfonylated Diarylmethanes

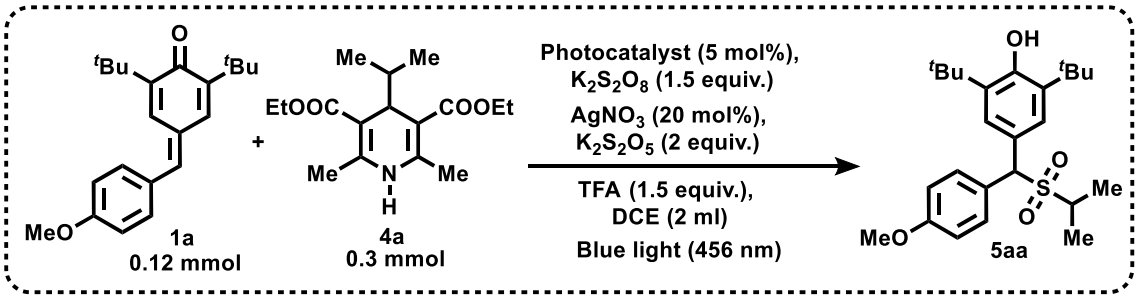


General Procedure E:

In a 20 ml borosilicate glass vial equipped with a magnet, *p*-QMs (0.123 mmol), 4-alkyl-1,4-DHPs (0.3082 mmol) was added 2 ml DCE solvent (0.06 M). Then $K_2S_2O_8$ (1.5 equiv.), $K_2S_2O_5$ (2 equiv.) was added followed by $AgNO_3$ (0.2 equiv.), Eosin Y (0.05 equiv.) and TFA (1.5 equiv.). After that, the mixture was degassed with N_2 for 15 min, then irradiation with blue Kessil light (456 nm) from a distance 4 cm. The reaction progress was monitored by TLC. Upon complete consumption of the starting material, the reaction was quenched with water (20 mL), the aqueous phase was extracted with DCM (3×15 mL) and wash with brine solution. The organic extracts were combined and dried over Na_2SO_4. The organic phase was evaporated under reduced pressure and the resulting crude material was purified by SiO2-gel flash column chromatography to get the desired product 3aa. **5aa**.

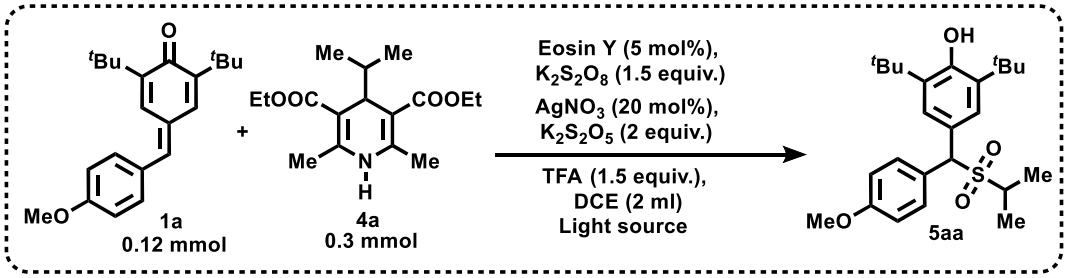
Optimization of Reaction

S1. Screening of Photocatalyst



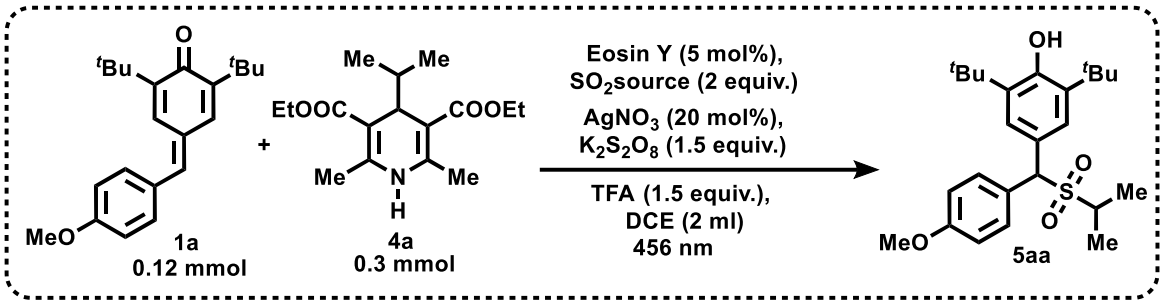
Entry	Photocatalyst	Yield (%)
1	Eosin Y	75
2	Mes-Acr$^+$ ClO_4^+	53
3	CzIPN	47
4	$[Ir(dtbbp)(ppy)_2]PF_6$	18
5	$Ru(bpy)_3Cl_2.6H_2O$	24
6	Rose Bengal	61

S2. Screening of Light source



Entry	Light source (nm)	Yield (%)
1	456	75
2	525	60
3	427	30

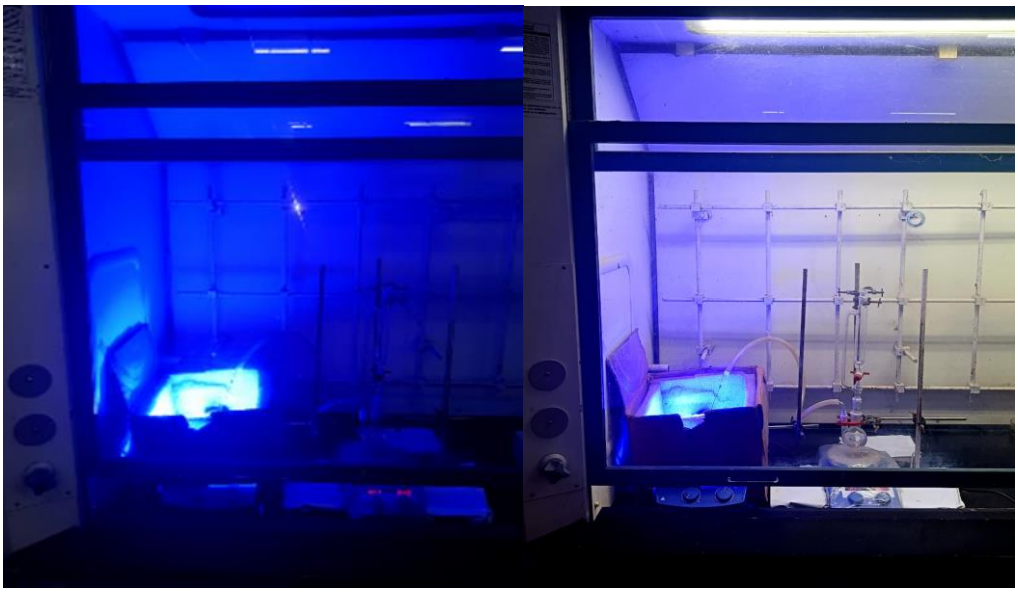
S3. Screening of SO_2 Source



Entry	SO_2 source	Yield (%)
1	$K_2S_2O_5$	75
2	$Na_2S_2O_5$	65
3	DABSO	23
4	$NaHSO_3$	15
5	SO_2-gas bubbling*	24

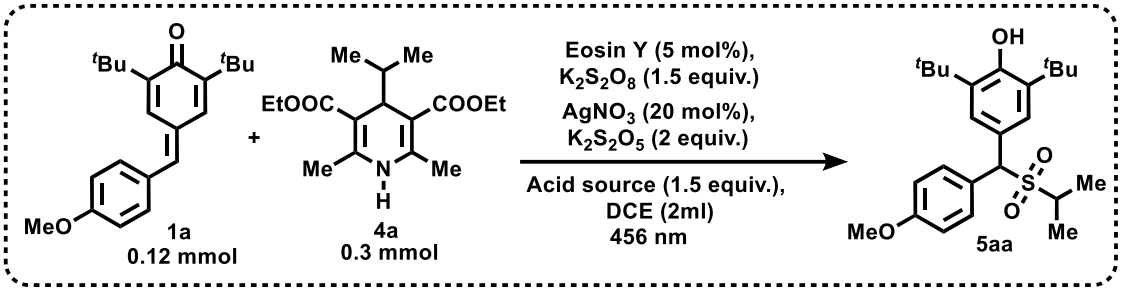
**Caution! Sulfur dioxide is a highly toxic gas, and its generation should be conducted in a well-ventilated fume hood.*

A two-necked 50 mL round-bottom flask, fitted with a 20 mL pressure-equalizing dropping funnel at the central joint and a two-way flushing adaptor at the side joint, was set up in a fume hood. The two-way flushing adaptor was connected through a Teflon tubing to a 5 mL syringe fitted with a 6-inch SS needle, which could be pierced through a rubber septum into a reaction vial used for the photoreaction. To initiate the SO_2-generation process, the two-necked R.B. flask was charged with an aqueous solution of 2 g Na_2SO_3 in 15 mL of water and allowed to stir at rt and the whole system was closed and evacuated with N_2. To this stirred solution, 1 mL of H_2SO_4 was added dropwise through the dropping funnel, and the resultant SO_2 gas was allowed to pass through the two-way flushing adaptor arrangement into the sealed photoreaction vial via the needle fitted to a plastic syringe connected through the Teflon tubing. A pictorial demonstration of the setup is as follows:



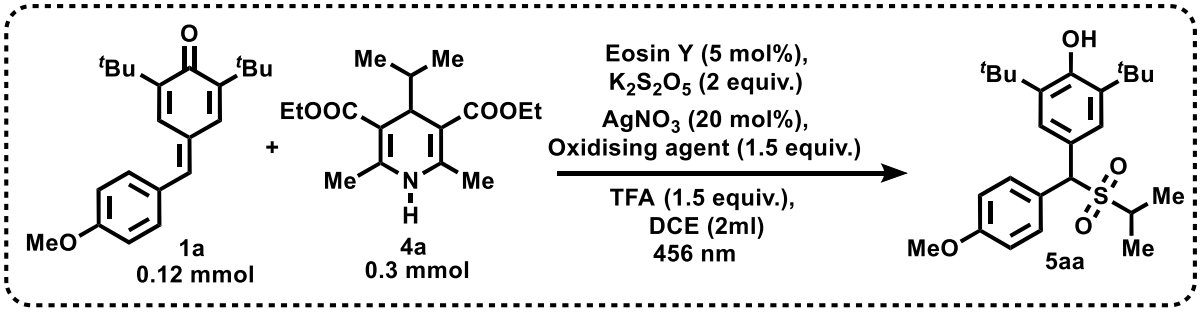
Experimental setup for SO_2-bubbling in the photoreaction.

S4. Screening of Acid Source



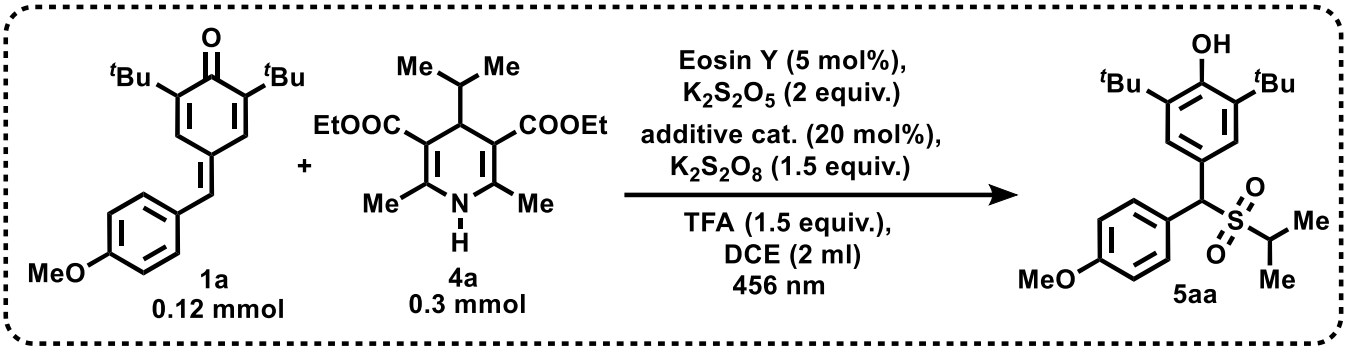
Entry	Acid source	Yield (%)
1	TFA	75
2	CH_3COOH	52
3	TsOH	45
4	Triflic acid	22
5	$BF_3.Et_2O$	25
6	o-Phosphoric acid	42

S5. Screening of additive oxidizing agent



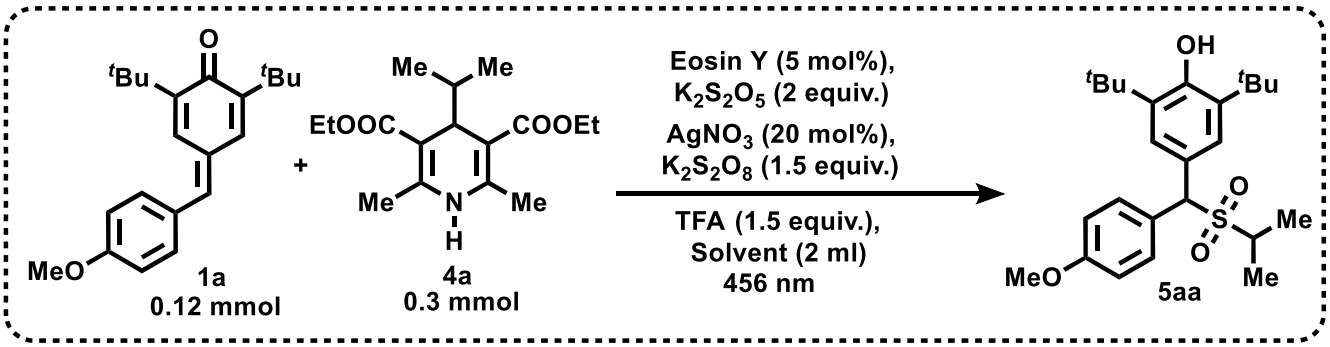
Entry	Additive Oxidising Agent	Yield (%)
1	$K_2S_2O_8$	75
2	$Na_2S_2O_8$	27
3	$(NH_4)_2 S_2O_8$	23

S6. Screening of Additive catalyst



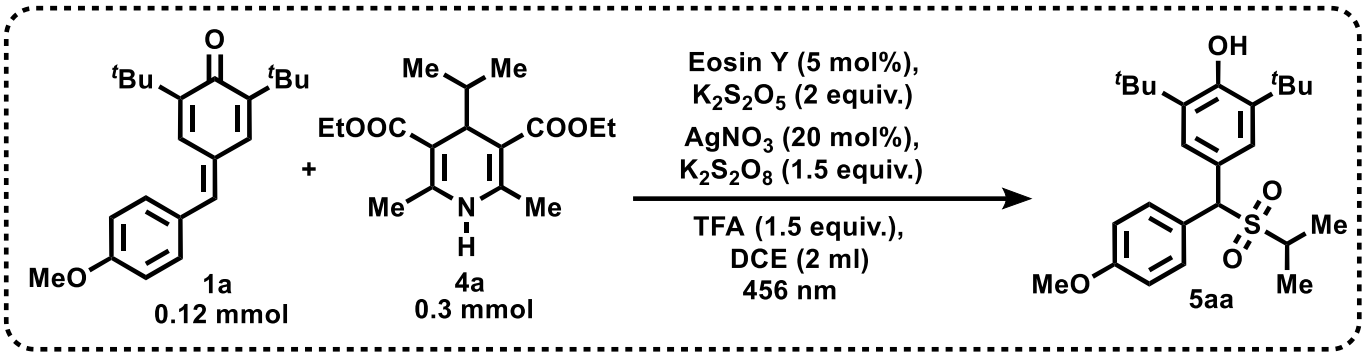
Entry	Additive Catalyst	Yield (%)
1	$AgNO_3$	75
2	AgOAc	66
3	Ag(I)O	36
4	$Ag(OCOCF_3)$	62
5	$Cu(OTf)_2$	45

S7. Screening of Solvents



Entry	Solvent	Yield (%)
1	DCE	75
2	DCM	72
3	$CHCl_3$	43
4	CCl_4	38
5	EtOAc	43
6	CH_3CN	35
7	THF	64
8	MeOH	36
9	Dioxane	46
10	DMSO/DMF/HFIP	0

S8. Standard deviation



Entry	Deviation from Standard condition	Time (h)	Yield(%)
1	None	2	75
2	Without Light	24	0
3	Without Photocatalyst	24	9
4	Without additive Catalyst	12	32
5	Without additive Oxidising agent	12	38
6	Without additive catalyst and oxidizing agent	12	46
7	Without acid additive	12	8
8	In O_2 balloon	12	20

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3aa):** Following the general procedure **D**, using **1a** (39 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3aa** was obtained as a yellow solid (56.5 mg, 90%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 8Hz, J_2 = 1.5 Hz, 2H), 7.61 (d, J = 9 Hz, 2H), 7.59 – 7.56 (m, 1H), 7.48 - 7.44 (m, 2H), 7.46 (s, 2H), 6.95 (d, J = 9 Hz, 2H), 5.32 (bs, OH, 1H), 5.29 (s, 1H), 3.81 (s, 3H), 3.47 – 3.35 (m, 2H), 3.35 – 3.27 (m, 2H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 159.9, 154.4, 136.3 (2C), 135.9, 133.7, 131.1 (2C), 128.8 (2C), 128.1 (2C), 126.6 (2C), 124.9, 123.1, 114.4 (2C), 73.9, 55.3, 46.8, 34.5 (2C), 31.0, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{31}H_{38}O_5SNa$ $(M+Na)^+$: 545.2332; found: 545.2338.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ba):** Following the General Procedure **D**, using **1b** (36 mg, 0.12 mmol), **2a** (33 mg, 0.24 mmol), **3ba** was obtained as a white solid (49 mg, 82%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 145-147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 8.4 Hz, J_2= 1.3 Hz, 2H), 7.70 (dd, J_1 = 8.4 Hz, J_2= 1.3 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.35 (m, 5H), 7.46 (s, 2H), 5.33 (s, 1H), 5.32 (bs, OH 1H), 3.47 – 3.36 (m, 2H), 3.36 – 3.28 (m, 2H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 154.5, 136.4 (2C), 135.9 133.7, 133.1, 129.8 (2C), 129.0 (2C), 128.9, 128.8 (2C), 128.1 (2C), 126.7 (2C), 122.8, 74.5, 46.9, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{36}O_4SNa$ $(M+Na)^+$: 515.2227; found: 515.2229.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ca):** Following the General Procedure **D**, using **1c** (37.3 mg, 0.12 mmol), **2a** (33 mg, 0.24 mmol), **3ca** was obtained as a white solid (46.5 mg, 76%). R_f = 0.5 (hexane:EtOAc = 3:2). m. p. 155-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8Hz, 2H), 7.58 (t, J = 8 Hz, 1H), 7.50 (d, J = 8Hz, 2H), 7.48 (s, 2H), 7.45 (d, J = 4Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 5.35 (s, 1H), 5.32 (bs, OH,1H), 3.51 – 3.39 (m, 2H), 3.39 – 3.32 (m, 2H), 1.45 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.3, 156.9, 154.5, 136.5 (2C), 135.8, 133.9, 131.3 (2C), 128.8 (2C),

128.2 (2C), 126.6 (2C), 123.9, 122.9, 116.1 (2C), 74.1, 46.7, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{36}O_5SNa$ $(M+Na)^+$: 531.2176; found: 531.2183.

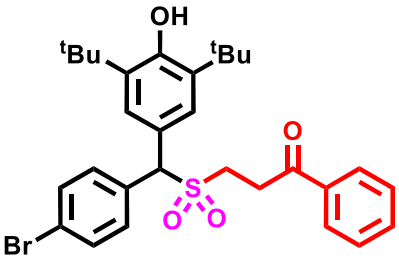
***4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl acetate* (3da):** Following the General Procedure **D**, using **1d** (42 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3da** was obtained as a black semi-solid (47.5 mg, 73%). R_f = 0.5 (hexane:EtOAc = 7:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8 Hz, 2H), 7.69 (d, J = 8 Hz, 2H), 7.58 (t, J = 16 Hz, 1H), 7.47 (d, J = 4 Hz, 2H), 7.44 (s, 2H), 7.15 (d, J = 4 Hz, 2H), 5.33 (bs, OH, 1H), 5.33 (s, 1H), 3.48 – 3.28 (m, 4H), 2.30 (s, 3H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.8, 169.2, 154.6, 151.0, 136.5 (2C), 135.8, 133.8, 131.0 (2C), 130.5, 128.8 (2C), 128.1 (2C), 126.6 (2C), 122.8, 122.1 (2C), 73.8, 46.9, 34.5 (2C), 30.9, 30.2 (6C), 21.2. **HRMS** (ESI) m/z calcd for $C_{32}H_{38}O_6SNa$ $(M+Na)^+$: 573.2281; found: 573.2284.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ea):** Following the General Procedure **D**, using **1e** (37 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ea** was obtained as a black solid (44.5 mg, 74%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 136-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, J_1 = 4 Hz, J_2 = 4 Hz, 2H), 7.66 (dd, J_1 = 4 Hz, J_2 = 4 Hz, 2H), 7.58 (t, J = 8 Hz, 1H), 7.47 (d, J = 8 Hz, 2H), 7.44 (s, 2H), 7.11 (t, J = 8.6 Hz, 2H), 5.34 (bs, OH, 1H), 5.33 (s, 1H), 3.54 – 3.26 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.8, 162.9 (d, J = 247 Hz, 1C), 154.6, 136.6 (2C), 135.8, 133.8, 131.8, 131.7, 130.9, 128.8 (2C), 128.1 (2C), 126.6 (2C), 122.8, 116.1, 115.9, 73.6, 46.8, 34.5 (2C), 30.9, 30.2 (6C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -112.8. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}FO_4SNa$ $(M+Na)^+$: 533.2132; found: 533.2142.

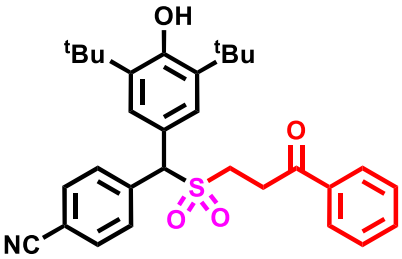
***3-(((4-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3fa):** Following the General Procedure **D**, using **1f** (39.5 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3fa** was obtained as a yellow solid (54 mg, 85%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 125-127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.62 (d,

J = 9 Hz, 2H), 7.59 (tt, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 7.47 (t, J = 8 Hz, 2H), 7.43 (s, 2H), 7.39 (d, J = 9 Hz, 2H), 5.35 (bs, OH,1H), 5.32 (s, 1H), 3.50 – 3.28 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.8,154.6, 136.6 (2C), 135.8, 135.0, 133.8, 131.5, 131.2 (2C), 129.2 (2C), 128.8 (2C), 128.1 (2C), 126.6 (2C), 122.6, 73.7, 46.9, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{35}ClO_4SNa$ $(M+Na)^+$: 549.1837; found: 549.1846.

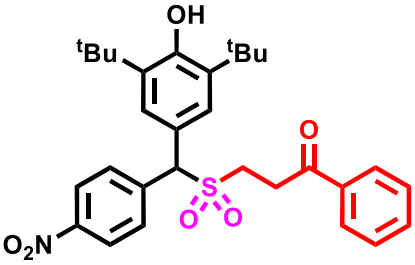
3-(((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ga)*: Following the General Procedure **D**, using **1g** (45 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ga** was obtained as a pale brown solid (59 mg, 86%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 138-140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, J_1 = 8.4, J_2 = 1.3 Hz, 2H), 7.64 – 7.53 (m, 3H), 7.55 (s, 2H), 7.48 (dt, J_1 = 8.7, J_2 = 6.7 Hz, 2H), 7.42 (s, 2H), 5.34 (bs, OH, 1H), 5.29 (s, 1H), 3.51 – 3.27 (m, 4H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.8, 154.6, 136.6 (2C), 135.8, 133.8, 132.1 (2C), 131.5 (2C), 130.2, 128.8 (2C), 128.1 (2C), 126.5 (2C), 123.3, 122.5, 73.8, 46.9, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{35}BrO_4SNa$ $(M+Na)^+$: 593.1332; found: 593.1349.



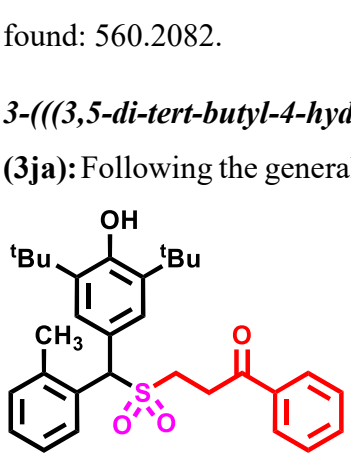
4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl) benzonitrile* (3ha)*: Following the General Procedure **D**, using **1h** (38 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ha** was obtained as a brown solid (49 mg, 80%). R_f = 0.5 (hexane:EtOAc = 7:3). m. p. 130-132 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 8 Hz, 1H), 7.46 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.43 (s, 2H), 5.41 (bs, OH,1H), 5.41 (s, 1H), 3.56 – 3.29 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.7, 154.9, 138.2, 136.9 (2C), 135.7, 133.9, 132.5 (2C), 130.7 (2C), 128.8 (2C), 128.1 (2C), 126.5 (2C), 122.2, 118.3, 112.7, 73.9, 47.1, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{31}H_{35}O_4SNaN$ $(M+Na)^+$: 540.2179; found: 540.2193.



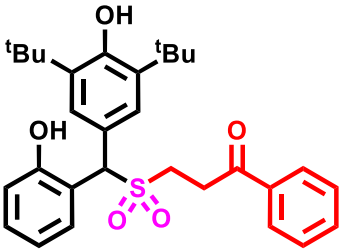
***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ia):** Following the General Procedure **D**, using **1i** (40.8 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ia** was obtained as a yellow solid (48.5 mg, 75%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 159-161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8 Hz, 2H), 7.87 (d, J = 8Hz, 2H), 7.60 (t, J = 8 Hz,1H), 7.47 dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 7.44 (s, 2H), 5.46 (bs, OH,1H), 5.40 (s, 1H), 3.55 – 3.29 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.7, 154.9, 140.0, 136.9 (2C), 135.7, 133.9, 130.9 (2C), 128.8 (2C), 128.5, 128.1 (2C), 126.5 (2C), 123.9 (2C), 122.0, 73.7, 47.1, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO_6SNa$ $(M+Na)^+$: 560.2077; found: 560.2082.



***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(o-tolyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ja):** Following the general Procedure **D**, using **1j** (37 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ja** was obtained as a light yellow solid (41 mg, 67%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 128-130 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (dd, J_1 = 7.8, J_2 = 1.4 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.62 – 7.54 (m, 1H), 7.48 – 7.43 (m, 2H),7.44 (s, 2H), 7.32 (td, J_1 = 7.4, J_2 = 2.0 Hz, 1H), 7.28 – 7.21 (m, 2H), 5.64 (s, 1H), 5.29 (bs, OH,1H), 3.53 – 3.28 (m, 4H), 2.45 (s, 3H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 154.4, 136.9, 136.2 (2C), 135.9, 133.7, 132.1, 131.3, 128.8 (2C), 128.5, 128.3, 128.1 (2C), 127.1 (2C), 126.7, 122.4, 69.6, 47.1, 34.4 (2C), 30.9, 30.2 (6C), 20.2. **HRMS** (ESI) m/z calcd for $C_{31}H_{38}O_4SNa$ $(M+Na)^+$: 529.2383; found: 529.2388.



***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ka):** Following the General Procedure **D**, using **1k** (37.3 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ka** was obtained as a dark red semi-solid (42.7 mg, 70%). R_f = 0.5 (hexane:EtOAc = 7:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.66 (dd, J_1 = 7.9, J_2 = 1.6 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.51 (s, 2H), 7.45 (dd, J_1 = 8.4, J_2 = 7.1 Hz, 2H), 7.21 (ddd, J_1 = 8.2, J_2 = 7.4, J_3 = 1.6 Hz, 1H), 6.98 (td, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 6.90 (dd, J_1 = 8.1, J_2 = 1.2 Hz, 1H), 5.96 (s, 1H), 5.33 (bs, OH,1H), 3.49 – 3.35 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.0, 154.5, 154.3, 136.4 (2C), 135.8, 133.8, 130.8, 130.3, 128.8 (2C), 128.1 (2C), 127.1 (2C), 122.1,



121.5, 120.0, 117.7, 67.6, 47.0, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{36}O_5SNa$ $(M+Na)^+$: 531.2176; found: 531.2202.

3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one(3la): Following the General Procedure **D**, using **1l** (37 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3la** was obtained as a brown solid (46 mg, 76%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 125-127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (td, J_1 = 7.6, J_2 = 1.8 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.64 – 7.57 (m, 1H), 7.51 – 7.47 (m, 2H), 7.49 (s, 2H), 7.38 (tdd, J_1 = 7.2, J_2 = 5.4, J_3 = 2.7 Hz, 1H), 7.26 (dd, J_1 = 7.6, J_2 = 1.3 Hz, 1H), 7.15 (ddd, J_1 = 9.7, J_2 = 8.2, J_3 = 1.3 Hz, 1H), 5.81 (bs, OH,1H), 5.35 (s, 1H), 3.53 – 3.41 (m, 2H), 3.40 – 3.35 (m, 2H), 1.46 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.7, 160.5 (d, J = 246 Hz, 1C) , 154.6, 136.4 (2C), 135.8, 133.8, 130.5 (d, J = 8 Hz, 1C), 130.1, 128.8 (2C), 128.1 (2C), 126.9 (2C), 124.7 (d, J = 3 Hz, 1C), 122.1, 121.1 (d, J = 14 Hz, 1C), 116.0 (d, J = 22 Hz, 1C), 64.8 (d, J = 4 Hz, 1C), 46.9, 34.5 (2C), 30.9, 30.2 (6C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.10. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}O_4SNa$ $(M+Na)^+$: 533.2132; found: 533.2124.

***3-(((2-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ma):** Following the General Procedure **D**, using **1m** (40 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ma** was obtained as a white solid (45.5 mg, 71%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 146-148 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (dd, J_1 = 7.9, J_2 = 1.7 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.47- 7.44 (m, 3H), 7.46 (s, 2H), 7.39 (td, J_1 = 7.6, J_2 = 1.4 Hz, 1H), 7.31 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1H), 6.05 (s, 1H), 5.32 (bs, OH,1H), 3.54 – 3.32 (m, 4H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.6, 154.6, 136.4 (2C), 135.8, 134.6, 133.8, 131.8, 130.3, 129.9, 129.9, 128.8 (2C), 128.1 (2C), 127.5, 126.9 (2C), 121.9, 68.6, 47.0, 34.4 (2C), 30.8, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{35}O_4SNaCl$ $(M+Na)^+$: 549.1837; found: 549.1843.

***3-(((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3na):** Following the General Procedure **D**, using **1n** (44.8 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3na** was obtained as a yellowish solid (60 mg, 88%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 131-133 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (dd, J_1 = 8.0, J_2 = 1.7 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.67 – 7.55 (m, 2H), 7.49 – 7.41 (m, 3H),7.48 (s, 2H), 7.25 – 7.18 (m, 1H), 6.06 (s, 1H), 5.32 (bs, OH, 1H), 3.53 – 3.30 (m, 4H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.6, 154.6, 136.3 (2C), 135.8, 133.8, 133.6, 133.5, 130.2, 130.0, 128.8 (2C), 128.2, 128.1 (2C), 126.9 (2C), 125.7, 121.9, 71.4, 47.1, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{35}BrO_4SNa$ $(M+Na)^+$: 593.1332; found: 593.1331.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-(trifluoromethyl)phenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3oa)**: Following the General Procedure **D**, using **1o** (44 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3oa** was obtained as a yellow solid (48.7 mg, 72%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 150-152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 4H), 7.67 – 7.52 (m, 3H), 7.49 – 7.44 (m, 2H), 7.47 (s, 2H), 5.41 (s, 1H), 5.39 (bs, OH, 1H), 3.53 – 3.29 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.7, 154.8, 136.8 (2C), 135.8, 133.9, 133.8, 133.2, 131.2 (q, J = 33 Hz, 1C), 129.4, 128.8 (2C), 128.1 (2C), 126.9 (q, J = 4 Hz, 1C), 126.7 (2C), 125.6 (q, J = 4 Hz, 1C), 123.8 (q, J = 270 Hz, 1C), 122.3, 73.8, 46.9, 34.5 (2C), 31.0, 30.2 (6C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.68. **HRMS** (ESI) m/z calcd for $C_{31}H_{35}F_3O_4SNa$ $(M+Na)^+$: 583.2100; found: 583.2090.

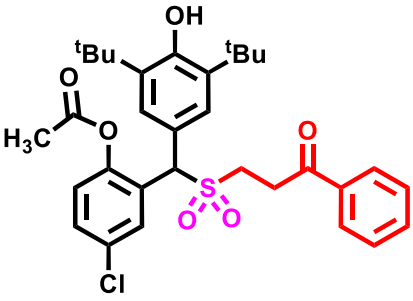
***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3pa):** Following the General Procedure **D**, using **1p** (37.5 mg, 0.12 mmol), **2a** (33 mg, 0.24 mmol), **3pa** was obtained as a yellow solid (37 mg, 60%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 138-140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.59 (t, J = 8 Hz, 1H), 7.48 – 7.44 (m, 3H),7.45 (s, 2H), 7.44-7.36 (m, 2H), 7.08 (tdd, J_1 = 8.4, J_2 = 2.6, J_3 = 1.0 Hz, 1H), 5.36 (bs, OH,1H), 5.33 (s, 1H), 3.52 – 3.31 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.8, 162.8 (d, J = 245 Hz, 1C), 154.7, 136.6 (2C), 135.8, 135.3 (d, J = 8 Hz, 1C), 133.8, 130.5(d, J = 8 Hz, 1C), 128.8 (2C), 128.1 (2C), 126.6 (2C), 125.7(d,

J = 2 Hz, 1C), 122.5, 116.9 (d, J = 23 Hz, 1C), 115.9 (d, J = 21 Hz, 1C), 73.8, 46.9, 34.5 (2C), 30.9, 30.2 (6C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.47. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}FO_4SNa$ $(M+Na)^+$: 533.2132; found: 533.2122.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3qa):** Following the General Procedure **D**, using **1q** (40.8 mg, 0.12 mmol), **2a** (33 mg, 0.24 mmol), **3qa** was obtained as a yellow solid (50.4 mg, 78%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 126-128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (t, J = 2.0 Hz, 1H), 8.23 (ddd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, J_3 = 1.0 Hz, 1H), 8.08 (dt, J_1 = 7.8, J_2 = 1.4 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.65 – 7.56 (m, 2H), 7.50 – 7.45 (m, 2H), 7.49 (s, 2H), 5.46 (bs, OH,1H), 5.41 (s, 1H), 3.56 – 3.28 (m, 4H), 1.45 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.7, 154.9, 148.4, 137.0 (2C), 135.9, 135.7, 134.7, 133.9, 129.8, 128.8 (2C), 128.1 (2C), 126.5 (2C), 125.3, 123.7, 122.1, 73.4, 47.0, 34.6 (2C), 31.0, 30.2(2C). **HRMS** (ESI) m/z calcd for $C_{30}H_{35}NO_6SNa$ $(M+Na)^+$: 560.2077; found: 560.2077.

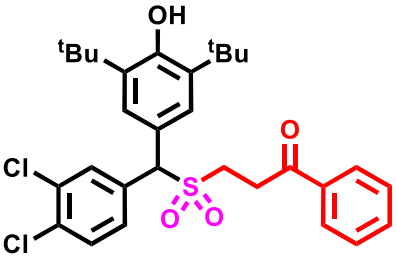
3-(((2-(allyloxy)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one (3ra): Following the General Procedure **D**, using **1r** (42 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ra** was obtained as a yellow semi-solid (48 mg, 73%). R_f = 0.5 (hexane:EtOAc = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.63 – 7.56 (m, 1H), 7.50 (s, 2H), 7.49 – 7.46 (m, 2H), 7.32 (ddd, J_1 = 8.2, J_2 = 7.4, J_3 = 1.7 Hz, 1H), 7.08 (td, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 6.92 (dd, J_1 = 8.3, J_2 = 1.1 Hz, 1H), 6.14 (s, 1H), 6.08 (ddt, J_1 = 17.2, J_2 = 10.5, J_3 = 5.2 Hz, 1H), 5.44 (dd, J_1 = 17.2, J_2 = 1.6 Hz, 1H), 5.32 (dd, J_1 = 10.5, J_2 = 1.4 Hz, 1H), 5.29 (bs, OH, 1H), 4.59 (ddt, J_1 = 5.2, J_2 = 3.5, J_3 = 1.6 Hz, 2H), 3.48 – 3.40 (m, 2H), 3.38 – 3.30 (m, 2H), 1.45 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 155.7, 154.3, 136.1 (2C), 135.9, 133.7, 132.8, 129.8, 129.6, 128.7 (2C), 128.1 (2C), 127.1 (2C), 122.8, 122.8, 121.4, 117.9, 112.4, 69.3, 64.5, 46.8, 34.4 (2C), 31.1, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{40}O_6SNa$ $(M+Na)^+$: 571.2489; found: 571.2490.

***4-chloro-2-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl acetate* (3sa):**



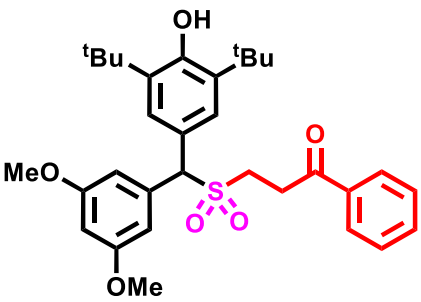
Following the General Procedure **D**, using **1s** (46.5 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3sa** was obtained as a yellow solid (52 mg, 74%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 158-160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 2.5 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.64 – 7.59 (m, 1H), 7.49 (dd, J_1 = 8.4, J_2 = 7.1 Hz, 2H), 7.40 (s, 2H), 7.36 (dd, J_1 = 8.7, J_2 = 2.5 Hz, 1H), 7.14 (d, J = 8.7 Hz, 1H), 5.66 (s, 1H), 5.36 (bs, OH,1H), 3.52 – 3.38 (m, 4H), 2.38 (s, 3H), 1.45 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.8, 168.5, 154.7, 147.3, 136.5 (2C), 135.8, 133.8, 131.9, 129.7, 129.7, 128.8 (2C), 128.1 (2C), 127.7, 126.7 (2C), 124.5, 121.8, 66.1, 47.2, 34.4 (2C), 31.0, 30.2 (6C), 21.0. **HRMS** (ESI) m/z calcd for $C_{32}H_{38}O_6SNaCl$ $(M+Na)^+$: 607.1892; found: 607.1889.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4-dichlorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ta):**



Following the General Procedure **D**, using **1t** (43.5 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ta** was obtained as a yellow solid (47 mg, 70%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 126-128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, J_1 = 8.4, J_2 = 1.3 Hz, 2H), 7.74 (d, J = 2.1 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.52 – 7.44 (m, 3H), 7.41 (s, 2H), 5.38 (s, 1H), 5.28 (bs, OH, 1H), 3.50 – 3.33 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.7, 154.8, 136.8 (2C), 135.8, 133.9, 133.3, 133.1, 133.0 131.9, 130.8, 129.0, 128.8 (2C), 128.1 (2C), 126.5 (2C), 122.2, 73.2, 46.9, 34.5 (2C), 30.9, 30.2 (2C). **HRMS** (ESI) m/z calcd for $C_{30}H_{34}Cl_2O_4SNa$ $(M+Na)^+$: 583.1447; found: 583.1446.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3,5-dimethoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3ua):**



Following the General Procedure **D**, using **1u** (42.5 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3ua** was obtained as a semi-solid (50.4 mg, 76%). R_f = 0.5 (hexane:EtOAc = 7:3).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.62 – 7.55 (m, 1H), 7.49 – 7.48- 7.44 (m, 2H), 7.47 (s, 2H), 6.87 (d, J = 2.3 Hz, 2H), 6.46 (t, J = 2.3 Hz, 1H), 5.32 (bs, OH,1H), 5.24 (s, 1H), 3.81 (s, 6H), 3.51 – 3.31 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 161.0 (2C), 154.6, 136.3 (2C), 135.9,

135.3, 133.7, 128.8 (2C), 128.1 (2C), 126.8 (2C), 122.5, 107.9 (2C), 100.9, 74.4, 55.4 (2C), 46.9, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{40}O_6SNa$ $(M+Na)^+$: 575.2438; found: 575.2437.

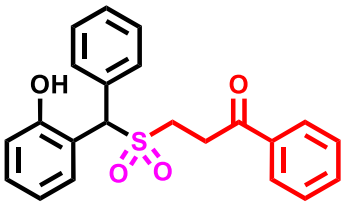
***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2,5-dimethoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3va):** Following the General Procedure **D**, using **1v** (42.5 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3va** was obtained as a semi-solid (45.7 mg, 69%). R_f = 0.5 (hexane:EtOAc = 3:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, J_1 = 8.3, J_2 = 1.4 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.50 (s, 2H), 7.48 – 7.44 (m, 2H), 6.86 (d, J = 1.7 Hz, 2H), 6.05 (s, 1H), 5.29 (bs, OH, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.46 – 3.27 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 154.4, 153.7, 151.1, 136.1 (2C), 135.9, 133.7, 128.8 (2C), 128.1 (2C), 127.1 (2C), 122.9, 122.7, 115.4, 115.1, 112.7, 64.5, 56.4, 55.7, 46.8, 34.4 (2C), 30.9, 30.3 (6C). **HRMS** (ESI) m/z calcd for $C_{30}H_{40}O_6SNa$ $(M+Na)^+$: 575.2438; found: 575.2438.

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl)sulfonyl)-1-phenylpropan-1-one* (3wa):** Following the General Procedure **D**, using **1w** (36 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3wa** was obtained as a brown solid (41 mg, 68%). R_f = 0.5 (hexane: EtOAc = 3:1). m. p. 138-140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.62 – 7.55 (m, 1H), 7.50 (s, 2H), 7.48 – 7.44 (m, 2H), 7.38 (td, J_1 = 4.4, J_2 = 3.6, J_3 = 1.3 Hz, 2H), 7.07 (dd, J_1= 5.1, J_2 = 3.6 Hz, 1H), 5.60 (s, 1H), 5.36 (bs, OH, 1H), 3.46 – 3.24 (m, 4H), 1.45 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.8, 154.8, 136.5 (2C), 135.8, 134.3, 133.8, 129.5, 128.8 (2C), 128.1 (2C), 127.4, 127.1, 126.8 (2C), 122.6, 70.4, 46.3, 34.5 (2C), 31.1, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{28}H_{34}O_4S_2Na$ $(M+Na)^+$: 521.1791; found: 521.1793.

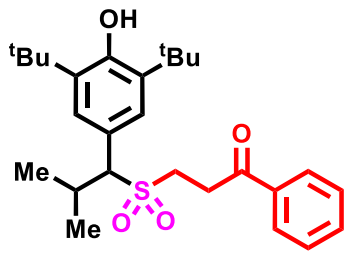
***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(pyridin-2-yl)methyl)sulfonyl)-1-phenylpropan-1-one* (3xa):** Following the General Procedure **D**, using **1x** (35.5 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3xa** was obtained as a brown solid (38 mg, 64%). R_f = 0.5 (hexane:EtOAc = 7:3). m. p. 145-147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (ddd, J_1 = 4.9 Hz, J_2 =1.8 Hz, J_3 = 0.9 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.76 (td, J_1 = 7.7, J_2 = 1.8 Hz, 1H), 7.66 (dt, J_1 = 7.8, J_2 = 1.1 Hz, 1H), 7.59 (s, 2H), 7.58-7.55 (m, 1H),

7.45 (dd, J_1 = 8.4, J_2 = 7.2 Hz, 2H), 7.31 (ddd, J_1 = 7.6, J_2 = 4.8, J_3 = 1.2 Hz, 1H), 5.56 (bs, OH, 1H), 5.34 (s, 1H), 3.75 – 3.55 (m, 2H), 3.49 – 3.25 (m, 2H), 1.42 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 154.7, 153.9, 149.4, 137.4, 136.4 (2C), 135.9, 133.6, 128.7 (2C), 128.1 (2C), 127.2 (2C), 124.9, 123.4, 122.0, 76.1, 46.5, 34.5 (2C), 31.1, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{29}H_{35}NO_4SNa$ $(M+Na)^+$: 516.2179; found: 516.2171.

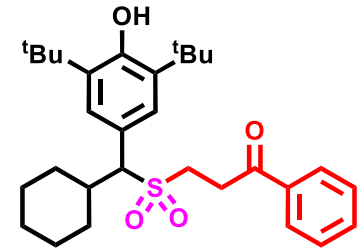
3-(((2-hydroxyphenyl)(phenyl)methyl)sulfonyl)-1-phenylpropan-1-one* (3'aa)*: Following the General Procedure **D**, using **1'a** (24 mg, 0.12 mmol), **2a** (33 mg, 0.24 mmol), **3'aa** was obtained as a brown semi-solid (28 mg, 62%). R_f = 0.5 (hexane:EtOAc = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.71 (ddd, J_1 = 7.8, J_2 = 6.3, J_3 = 1.7 Hz, 3H), 7.62 – 7.56 (m, 1H), 7.48 – 7.45 (t, J_1 = 8 Hz, 2H), 7.43- 7.38 (m, 3H), 7.21 (td, J_1 = 7.7, J_2 = 1.7 Hz, 1H), 6.98 (td, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 6.87 (dd, J_1 = 8.2, J_2 = 1.2 Hz, 1H), 6.08 (s, 1H), 3.55 – 3.46 (m, 2H), 3.45 – 3.38 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.1, 154.1, 135.7, 133.9, 132.1, 130.7, 130.4, 130.1 (2C), 129.1 (2C), 129.0, 128.8 (2C), 128.2 (2C), 121.5, 119.6, 117.4, 66.8, 47.0, 30.8. **HRMS** (ESI) m/z calcd for $C_{22}H_{21}O_4S$ $(M+H)^+$: 481.1155; found: 481.1160.



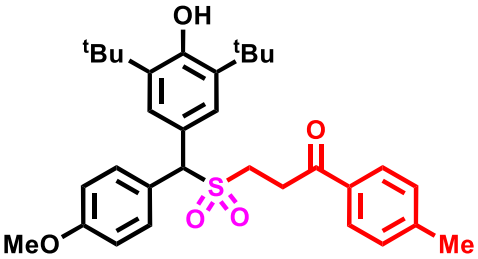
3-((1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylpropyl)sulfonyl)-1-phenylpropan-1-one* (3'ba)*: Following the General Procedure **D**, using **1'b** (32 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3'ba** was obtained as a brown semi-solid (39 mg, 68%). R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, CDCl3) δ 7.83 (d, J = 7.0 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.21 (s, 2H), 5.31 (s, 1H), 3.80 (d, J = 7.4 Hz, 1H), 3.36 – 3.24 (m, 1H), 3.17-3.10 (m, 1H), 3.07 – 2.93 (m, 2H), 2.81 (sept., J = 6.8 Hz, 1H), 1.41 (s, 18H), 1.22 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 154.4, 136.5 (2C), 135.9, 133.6 (2C), 128.7 (2C), 128.0 (2C), 126.7, 123.0, 75.6, 47.8, 34.4 (2C), 31.0, 30.3 (6C), 28.5, 22.1, 20.6. **HRMS** (ESI) m/z calcd for $C_{27}H_{38}O_4SNa$ $(M+Na)^+$: 481.2383; found: 481.2380.



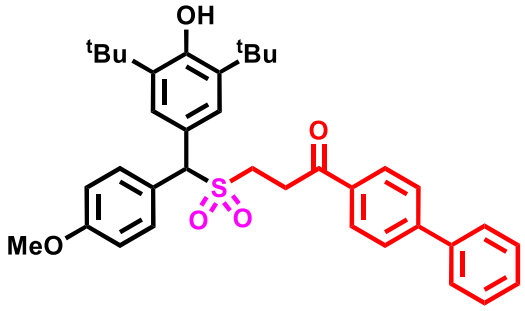
3-((cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3'ca)*:*** Following the General Procedure **D**, using **1'c** (36 mg, 0.12 mmol), **2a** (33mg, 0.24 mmol), **3'ca** was obtained as a white semi-solid (43 mg, 72%). R_f = 0.5 (hexane:EtOAc = 4:1). **^{1}H NMR** (400 MHz, CDCl3) 7.83 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.19 (s, 2H), 5.31 (s, 1H), 3.85 (d, J = 7.4 Hz, 1H), 3.35 – 3.21 (m, 1H), 3.15 – 3.05 (m, 1H), 3.05 – 2.91 (m, 2H), 2.48 (dtd, J_1 = 11.2, J_2 = 7.8, J_3 = 3.6 Hz, 1H), 2.27 – 2.13 (m, 1H), 1.90 – 1.52 (m, 6H), 1.41 (s, 18H), 1.14 – 1.06 (m, 1H), 0.95 – 0.86 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 154.3, 136.5 (2C), 135.9, 133.6 (2C), 128.7 (2C), 128.0 (2C), 125.9, 123.1, 75.3, 47.9, 37.9, 34.4 (2C), 32.2, 31.0, 30.4, 30.3 (6C), 26.1, 26.0, 25.9. **HRMS** (ESI) m/z calcd for $C_{30}H_{42}O_4SNa$ $(M+Na)^+$: 521.2696; found: 521.2693.



3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(p-tolyl)propan-1-one **(3ab)*:*** Following the general Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2b** (36 mg, 0.24 mmol), **3ab** was obtained as a brown solid (52.3 mg, 81%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 122-124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.45 (s, 2H), 7.27 – 7.23 (m, 2H), 6.94 (d, J = 8.8 Hz, 2H), 5.31 (bs, OH,1H), 5.28 (s, 1H), 3.81 (s, 3H), 3.44 – 3.24 (m, 4H), 2.41 (s, 3H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.6, 159.9, 154.4, 144.7, 136.3 (2C), 133.4, 131.1 (2C), 129.4 (2C), 128.2 (2C), 126.6 (2C), 124.9, 123.1, 114.4 (2C), 73.8, 55.3, 46.8, 34.5 (2C), 30.8, 30.2 (6C), 21.7. **HRMS** (ESI) m/z calcd for $C_{32}H_{40}O_5SNa$ $(M+Na)^+$: 559.2489; found: 559.2489.

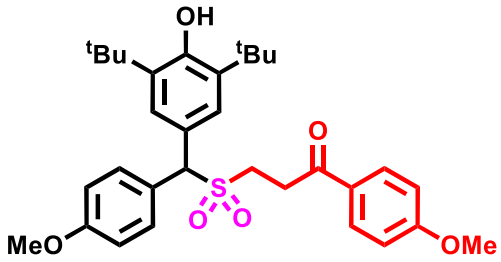


1-([1,1'-biphenyl]-4-yl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl) sulfonyl)propan-1-one **(3ac)*:*** Following the general Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2c** (51 mg, 0.24 mmol), **3ac** was obtained as a yellow solid (43.2 mg, 60%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 168-170 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.71 – 7.66 (m, 2H), 7.65 – 7.59 (m, 4H), 7.50 – 7.48 (m, 2H), 7.47 (s, 2H), 7.44- 7.40 (m, 1H), 6.98 – 6.93 (m, 2H), 5.32 (bs, OH, 1H), 5.30 (s,

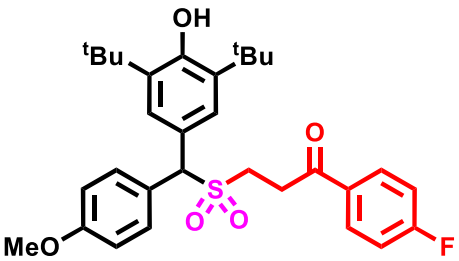


1H), 3.81 (s, 3H), 3.52 – 3.28 (m, 4H), 1.45 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.5, 160.0, 154.4, 146.4, 139.7, 136.3 (2C), 134.6, 131.1 (2C), 129.0 (2C), 128.7 (2C), 128.4, 127.4 (2C), 127.3 (2C), 126.7 (2C), 124.9, 123.1, 114.5 (2C), 73.9, 55.3, 46.8, 34.5 (2C), 31.0, 30.3 (6C). **HRMS** (ESI) m/z calcd for $C_{37}H_{42}O_5SNa$ $(M+Na)^+$: 621.2645; found: 621.2646.

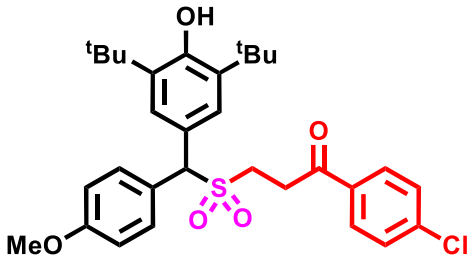
***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-methoxy phenyl)propan-1-one* (3ad):** Following the general Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2d** (40 mg, 0.24 mmol), **3ad** was obtained as a red solid (52 mg, 78%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.45 (s, 2H), 6.93 (dd, J_1 = 8.9, J_2 = 7.9 Hz, 4H), 5.31 (bs, OH,1H), 5.28 (s, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.41 – 3.24 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.4, 163.9, 159.9, 154.4, 136.3 (2C), 131.1 (2C), 130.4 (2C), 128.9, 126.6 (2C), 124.9, 123.1, 114.4 (2C), 113.9 (2C), 73.8, 55.5, 55.3, 46.9, 34.5 (2C), 30.5, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{32}H_{40}O_6SNa$ $(M+Na)^+$: 575.2438; found: 575.2448.



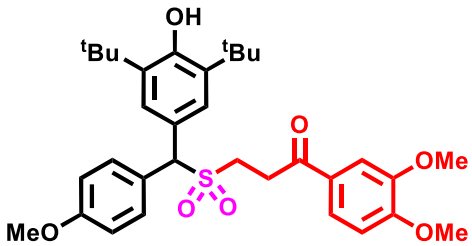
***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-fluorophenyl)propan-1-one* (3ae):** Following the general Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2e** (37 mg, 0.24 mmol), **3ae** was obtained as a yellow solid (47 mg, 72%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 140-142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.62 – 7.57 (m, 2H), 7.45 (s, 2H), 7.13 (t, J = 8.6 Hz, 2H), 6.97 – 6.92 (m, 2H), 5.32 (bs, OH,1H), 5.28 (s, 1H), 3.81 (s, 3H), 3.42 – 3.24 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.4, 166.1 (d, J = 254 Hz, 1C), 160.0, 154.4, 136.4 (2C), 132.3 (d, J = 3 Hz, 1 C), 131.1 (2C), 130.9, 130.8, 126.6 (2C), 124.9, 123.0, 116.0, 115.8, 114.4 (2C), 73.9, 55.3, 46.7, 34.5 (2C), 30.9, 30.2 (6C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -103.99. **HRMS** (ESI) m/z calcd for $C_{31}H_{37}FO_5SNa$ $(M+Na)^+$: 563.2238; found: 563.2231.



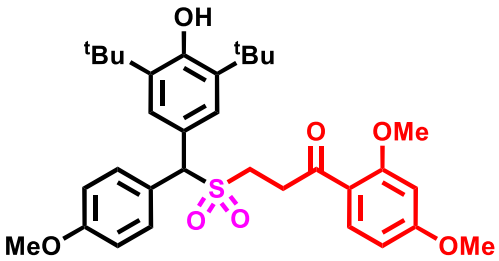
***1-(4-chlorophenyl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl) sulfonyl)propan-1-one* (3af):** Following the general Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2f** (41 mg, 0.24 mmol), **3af** was obtained as a yellow solid (47 mg, 70%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 156-158 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 7.47 – 7.40 (m, 4H), 6.94 (d, J = 8.5 Hz, 2H), 5.32 (s, 1H), 5.29 (bs, OH, 1H), 3.81 (s, 3H), 3.41 – 3.26 (m, 4H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.8, 160.01, 154.4, 140.2, 136.4 (2C), 134.2, 131.1 (2C), 129.5 (2C), 129.1 (2C), 126.6 (2C), 124.8, 123.0, 114.4 (2C), 73.9, 55.3, 46.6, 34.5 (2C), 30.9, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{31}H_{37}ClO_5SNa$ $(M+Na)^+$: 579.1942; found: 579.1941.



***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(3,4-dimethoxyphenyl)propan-1-one* (3ag):** Following the general procedure **1**, using **1a** (39 mg, 0.12 mmol), **2g** (47 mg, 0.24 mmol), **3ag** was obtained as a semi-solid (57 mg, 81%). R_f = 0.5 (hexane:EtOAc = 13:7). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.53 (dd, J_1 = 8.4, J_2 = 2.1 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.44 (s, 2H), 6.97 – 6.91 (m, 2H), 6.87 (d, J = 8.4 Hz, 1H), 5.31 (bs, OH,1H), 5.28 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.80 (s, 3H), 3.41 – 3.32 (m, 2H), 3.31 – 3.25 (m, 2H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.5, 159.9, 154.4, 153.8, 149.1, 136.3 (2C), 131.1 (2C), 129.1, 126.6 (2C), 124.9, 123.1, 122.9, 114.4 (2C), 110.2, 110.1, 73.8, 56.1, 56.0, 55.3, 46.9, 34.5 (2C), 30.3, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{33}H_{42}O_7SNa$ $(M+Na)^+$: 605.2543; found: 605.2542.



***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(2,4-dimethoxyphenyl)propan-1-one* (3ah):** Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2h** (47 mg, 0.24 mmol), **3ah** was obtained as a brown solid (52.5 mg, 75%). R_f = 0.5 (hexane:EtOAc = 13:7). m. p. 132-134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.8 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.43 (s, 2H), 6.95 – 6.91 (m, 2H), 6.52 (dd, J_1 = 8.8, J_2 = 2.3 Hz, 1H), 6.44 (d, J = 2.3 Hz, 1H), 5.28 (bs, OH, 1H), 5.26 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.48 – 3.41 (m, 2H), 3.28 – 3.20 (m, 2H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 165.1, 161.3, 159.9, 154.3, 136.2 (2C), 132.9, 131.1

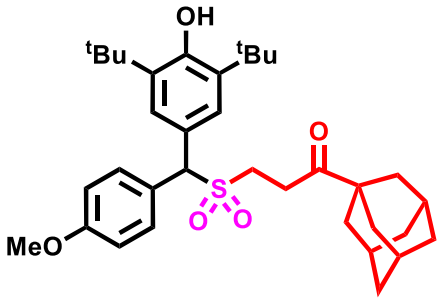


(2C), 126.6 (2C), 125.3, 123.2, 119.6, 114.4 (2C), 105.5, 98.2, 73.6, 55.6, 55.6, 55.3, 46.9, 35.5, 34.4 (2C), 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{33}H_{42}O_7SNa$ $(M+Na)^+$: 605.2543; found: 605.2537.

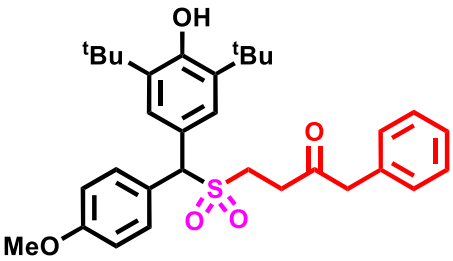
1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)dodecan-3-one (3ai): Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2i** (44 mg, 0.24 mmol), **3ai** was obtained as a yellow semi-solid (29 mg, 42%). R_f = 0.5 (hexane:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.8 Hz, 2H), 7.42 (s, 2H), 6.95 (d, J = 8.8 Hz, 2H), 5.33 (bs, OH, 1H), 5.23 (s, 1H), 3.83 (s, 3H), 3.18 – 3.05 (m, 2H), 2.90 – 2.80 (m, 2H), 2.43 (t, J = 7.5 Hz, 2H), 1.56 (t, J = 7.3 Hz, 2H), 1.27 (d, J = 4.0 Hz, 12H), 0.91 – 0.88 (m, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 206.9, 159.9, 154.4, 136.3 (2C), 131.1 (2C), 126.6 (2C), 124.9, 122.9, 114.4 (2C), 73.7, 55.3, 46.1, 42.9, 34.5 (2C), 34.2, 31.9, 30.2 (6C), 29.4, 29.4, 29.3, 29.1, 23.8, 22.7, 14.1. **HRMS** (ESI) m/z calcd for $C_{34}H_{52}O_5SNa$ $(M+Na)^+$: 595.3428; found: 595.3416.

1-cyclohexyl-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl) propan-1-one(3aj): Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2j** (34 mg, 0.24 mmol), **3aj** was obtained as a colorless semi-solid (47 mg, 75%). R_f = 0.5 (hexane:EtOAc = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.8 Hz, 2H), 7.43 (s, 2H), 6.95 (d, J = 8.8 Hz, 2H), 5.33 (bs, OH, 1H), 5.22 (s, 1H), 3.83 (s, 3H), 3.16 – 3.07 (m, 2H), 2.87 (ddd, J_1 = 8.1, J_2 = 6.5, J_3 = 3.7 Hz, 2H), 2.37 – 2.32 (m, 1H), 1.85 – 1.75 (m, 4H), 1.70 – 1.65 (m, 1H) 1.31- 1.28 (m, 5H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 209.9, 159.9, 154.4, 136.3 (2C), 131.1 (2C), 126.6 (2C), 124.9, 122.9, 114.4 (2C), 73.7, 55.3, 50.8, 46.3, 34.5 (2C), 32.4, 30.2 (6C), 28.4 (2C), 25.7, 25.5 (2C). **HRMS** (ESI) m/z calcd for $C_{31}H_{44}O_5SNa$ $(M+Na)^+$: 551.2802; found: 551.2794.

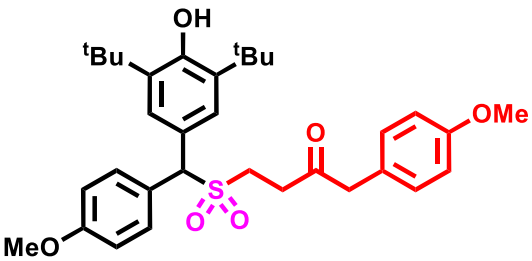
***1-((1s,3s)-adamantan-1-yl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl) methyl)sulfonyl)propan-1-one* (3ak):** Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2k** (46 mg, 0.24 mmol), **3ak** was obtained as a brown solid (52.3 mg, 75%). R_f = 0.5 (hexane:EtOAc = 4:2). m. p. 132-134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.8 Hz, 2H), 7.42 (s, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.31 (bs, OH,1H), 5.20 (s, 1H), 3.80 (s, 3H), 3.13 – 3.03 (m, 2H), 2.85 (ddd, J_1 = 9.9, J_2 = 5.9, J_3 = 2.8 Hz, 2H), 2.07 – 2.00 (m, 3H), 1.76 (d, J = 3.0 Hz, 6H), 1.74 – 1.63 (m, 6H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 211.6, 159.9, 154.4, 136.3 (2C), 131.1 (2C), 126.6 (2C), 124.9, 123.1, 114.4 (2C), 73.8, 55.3, 46.7, 46.5, 38.2 (4C), 36.4 (2C), 34.5 (2C), 30.3 (6C), 28.7, 27.8 (3C). **HRMS** (ESI) m/z calcd for $C_{35}H_{48}O_5SNa$ $(M+Na)^+$: 603.3115; found: 603.3112.



***4-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylbutan-2-one* (3al):** Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2l** (36 mg, 0.24 mmol), **3al** was obtained as a brown solid (42 mg, 65%). R_f = 0.5 (hexane:EtOAc = 7:3). m. p. 127-129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8 Hz, 2H), 7.40 (s, 2H), 7.36 – 7.25 (m, 3H), 7.17 (d, J = 8 Hz, 2H), 6.93 (d, J = 8 Hz, 2H), 5.31 (bs, OH, 1H), 5.19 (s, 1H), 3.81 (s, 3H), 3.71 (s, 2H), 3.11-3.07 (m, 2H), 2.91-2.88 (m, 2H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 204.3, 159.9, 154.3, 136.3 (2C). 133.3, 131.1 (2C), 129.4 (2C), 128.9 (2C), 127.4, 126.6 (2C), 124.8, 122.9, 114.4 (2C), 73.8, 55.3, 50.0, 46.2, 34.5 (2C), 33.77, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{32}H_{40}O_5SNa$ $(M+Na)^+$: 559.2489; found: 559.2490.



***4-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-methoxyphenyl)butan-2-one* (3am):** Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2m** (43 mg, 0.24 mmol), **3am** was obtained as a brown solid (46.3 mg, 68%). R_f = 0.5 (hexane:EtOAc = 13:7). m. p. 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8 Hz, 2H), 7.38 (s, 2H), 7.08 (d, J = 8 Hz, 2H), 6.92 (d, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 5.30 (bs, OH, 1H), 5.17 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.64 (s, 2H), 3.07 (ddt, J_1 = 7.2 Hz, J_2 = 4.8 Hz, J_3 = 3.3 Hz, 2H), 2.88 (dd, J_1 = 8.2 Hz, J_2 = 6.6 Hz, 2H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100



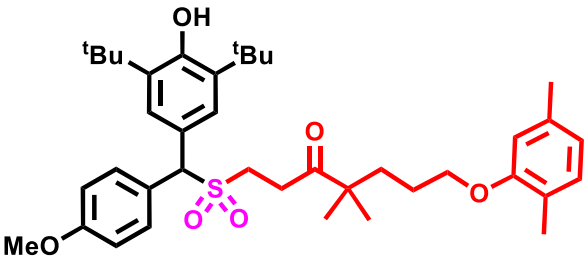
MHz, $CDCl_3$) δ 204.7, 159.9, 158.9, 154.4, 136.3 (2C), 131.0 (2C), 130.4 (2C), 126.6 (2C), 125.3, 124.8, 122.89, 114.4 (2C), 114.4 (2C), 73.8, 55.3, 55.3, 49.1, 46.2, 34.4 (2C), 33.6, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{33}H_{42}O_6SNa$ $(M+Na)^+$: 589.2594; found: 589.2593.

***1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-4-(4-isobutyl phenyl)pentan-3-one*(3an):** Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2n** (52.4 mg, 0.24 mmol), **3an** was obtained as a yellow solid (48 mg, 66%). R_f = 0.5 (hexane:EtOAc = 3:1). dr = 1:1. m. p. 124-126 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.37 (d, J = 3.1 Hz, 2H), 7.12 – 7.04 (m, 4H), 6.94 – 6.88 (m, 2H), 5.29 (bs, OH, 1H), 5.14 (s, 1H), 3.81 (d, J = 1.7 Hz, 3H), 3.73 (dd, J_1 = 7.0, J_2 = 2.8 Hz, 1H), 3.13 (dt, J_1 = 8.9, J_2 = 4.4 Hz, 1H), 3.00 – 2.86 (m, 1H), 2.86 – 2.70 (m, 2H), 2.45 (dd, J_1 = 7.2, J_2 = 1.6 Hz, 2H), 1.85 (dt, J_1 = 13.5, J_2 = 6.8 Hz, 1H), 1.42 (d, J = 1.8 Hz, 18H), 1.38 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 6.7 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 207.2, 207.1, 159.9 (2C), 154.3 (2C), 141.0 (2C), 136.9, 136.9, 136.2 (2C), 136.2 (2C), 131.0 (2C), 131.0 (2C), 129.8 (4C), 127.5 (2C), 127.5 (2C), 126.6 (2C), 126.5 (2C), 124.9 (2C), 122.9, 122.9, 114.4 (4C), 73.6, 73.6, 55.3 (2C), 52.7 (2C), 46.4, 46.3, 45.0 (2C), 34.4 (4C), 32.8 (2C), 30.2 (12C), 30.2 (2C), 22.4 (4C), 17.3, 17.3. **HRMS** (ESI) m/z calcd for $C_{37}H_{50}O_5SNa$ $(M+Na)^+$: 629.3271; found: 629.3280.

***(4S)-1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-4-(6-methoxynaphthalen-2-yl)pentan-3-on*e (3ao)**: Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2o** (58 mg, 0.24 mmol), **3ao** was obtained as a brown solid (48.5 mg, 64%). R_f = 0.5 (hexane:EtOAc = 3:1). dr = 1:1. m. p. 124-126 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.58 (d, J = 1.8 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.36 (d, J = 2.4 Hz, 2H), 7.23 (dt, J_1 = 8.5 Hz, J_2 = 2.3 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.13 (d, J = 2.4 Hz, 1H), 6.91 – 6.84 (m, 2H), 5.29 (bs, OH, 1H), 5.14 (d, J = 1.5 Hz, 1H), 3.93 (s, 3H), 3.90 (dd, J_1 = 6.9 Hz, J_2 = 3.6 Hz, 1H), 3.79 (s, 3H), 3.16 (t, J = 20 Hz, 1H), 3.00 – 2.71 (m, 3H), 1.47 (d, J = 7.0 Hz, 3H), 1.41 (d, J = 1.3 Hz, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 207.1, 207.0, 159.9 (2C), 157.9 (2C), 154.3, 154.3, 136.3 (2C), 136.2 (2C), 134.8, 134.8, 133.9 (2C), 131.0 (2C), 130.9 (2C), 129.3 (2C),

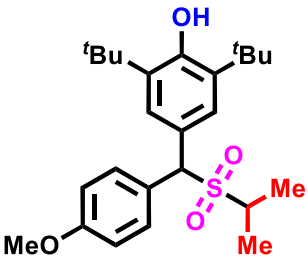
129.1 (2C), 127.8, 127.8, 126.6 (2C), 126.6 (2C), 126.5 (2C), 126.1, 126.1, 124.9 (2C), 122.9, 122.8, 119.3, 119.3, 114.4 (4C), 105.7 (2C), 73.6, 73.5, 55.4 (2C), 55.3 (2C), 53.0 (2C), 46.4 (2C), 34.4 (4C), 32.9 (2C), 30.2 (12C), 17.3, 17.3. **HRMS** (ESI) m/z calcd for $C_{38}H_{46}O_6SNa$ $(M+Na)^+$: 653.2907; found: 653.2912.

***1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-7-(2,5-dimethylphenoxy)-4,4-dimethylheptan-3-one* (3ap):** Following the General Procedure **D**, using **1a** (39 mg, 0.12 mmol), **2p** (63 mg, 0.24 mmol), **3ap** was obtained as a semi-solid (53 mg, 68%). R_f = 0.5 (hexane:EtOAc = 3:1).

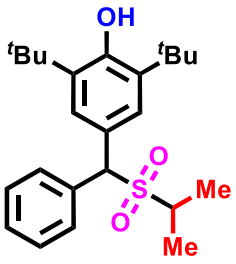


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.5 Hz, 2H), 7.43 (s, 2H), 7.02 (d, J = 7.4 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.68 (d, J = 7.5 Hz, 1H), 6.61 (s, 1H), 5.31 (bs, OH,1H), 5.22 (s, 1H), 3.90 (t, J = 5.9 Hz, 2H), 3.81 (s, 3H), 3.11 (t, J = 7.9 Hz, 2H), 2.97 – 2.90 (m, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.72 (dd, J_1 = 12.3, J_2 = 4.8 Hz, 2H), 1.64 (ddt, J_1 = 13.8 Hz, J_2 = 10.1 Hz, J_3 = 4.2 Hz, 2H), 1.45 (s, 18H), 1.17 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 211.6, 159.9, 156.9, 154.4, 136.5, 136.3 (2C), 131.1 (2C), 130.3, 126.6 (2C), 124.9, 123.6, 123.0, 120.8, 114.4 (2C), 111.9, 73.8, 67.7, 55.3, 47.5, 46.6, 36.2, 34.5 (2C), 30.3 (6C), 29.4, 24.9, 24.4, 24.3, 21.4, 15.9. **HRMS** (ESI) m/z calcd for $C_{39}H_{54}O_6SNa$ $(M+Na)^+$: 673.3533; found: 673.3538.

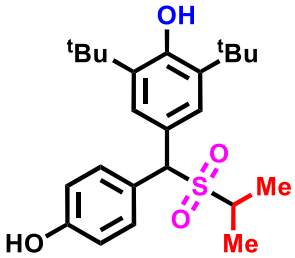
***2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-methoxyphenyl)methyl)phenol* (5aa):** Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5aa** was obtained as a yellow solid (39 mg, 75%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 155-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.8 Hz, 2H), 7.41 (s, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.28 (s, 1H), 5.27 (bs, OH, 1H), 3.81 (s, 3H), 2.97 (sept, J = 6.9 Hz, 1H), 1.43 (s, 18H), 1.31 (dd, J_1 = 6.7, J_2 = 5.3 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$)) δ 159.8, 154.2, 136.1 (2C), 131.0 (2C), 126.7 (2C), 125.3, 123.0, 114.3 (2C), 69.6, 55.3, 51.0, 34.4 (2C), 30.3 (6C), 15.6, 15.1. **HRMS** (ESI) m/z calcd for $C_{25}H_{36}O_4SNa$ $(M+Na)^+$: 455.2227; found: 455.2231.



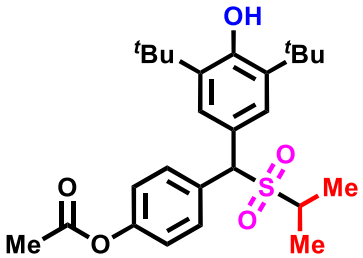
***2,6-di-tert-butyl-4-((isopropylsulfonyl)(phenyl)methyl)phenol* (5ba):** Following the General Procedure **E**, using **1b** (35 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ba** was obtained as a white solid (34.5 mg, 72%). R_f = 0.5 (hexane:EtOAc = 17:3). m. p. 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.44 – 7.34 (m, 3H), 7.43 (s, 2H), 5.32 (bs, OH,1H), 5.29 (s, 1H), 2.98 (sept, J = 6.8 Hz, 1H), 1.44 (s, 18H), 1.32 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.3, 136.1 (2C), 133.5, 129.8 (2C), 128.9 (2C), 128.6, 126.9 (2C), 122.7, 70.2, 51.2, 34.5 (2C), 30.3 (6C), 15.7, 15.1. **HRMS** (ESI) m/z calcd for $C_{24}H_{34}O_3SNa$ $(M+Na)^+$: 425.2121; found: 425.2126.



***2,6-di-tert-butyl-4-((4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenol* (5ca):** Following the General Procedure **E**, using **1c** (37 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ca** was obtained as a yellow semi-solid (35.4 mg, 71%). R_f = 0.5 (hexane:EtOAc = 7:3).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.42 (s, 2H), 6.80 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 5.30 (s, 1H), 5.28 (bs, OH, 1H), 3.01 (sept, J = 6.8 Hz, 1H), 1.45 (s, 18H), 1.34 (d, J = 4 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 156.3, 154.2, 136.2 (2C), 131.3 (2C), 126.7 (2C), 124.8, 123.0, 115.9 (2C), 69.7, 51.1, 34.5 (2C), 30.7 (6C), 15.4, 15.3. **HRMS** (ESI) m/z calcd for $C_{24}H_{34}O_4SNa$ $(M+Na)^+$: 441.2070; found: 441.2078.

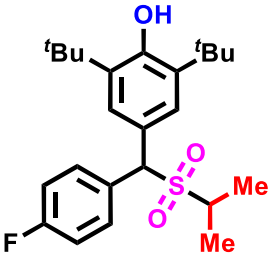


***4-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenyl acetate* (5da):** Following the General Procedure **E**, using **1d** (42.5 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5da** was obtained as a brown solid (40 mg, 72%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 140-142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.7 Hz, 2H), 7.40 (s, 2H), 7.13 (d, J = 8.7 Hz, 2H), 5.31 (s, 1H), 5.30 (bs, OH, 1H), 3.00 (sept, J = 6.8 Hz, 1H), 2.30 (s, 3H), 1.44 (s, 18H), 1.33 (d, J = 4.9 Hz, 3H), 1.32 (d, J = 4.9 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.3, 154.4, 150.9, 136.3 (2C), 130.9 (2C), 130.9, 126.7 (2C), 122.7, 121.9 (2C), 69.5, 51.2, 34.5 (2C), 30.2 (6C), 21.2, 15.4, 15.3. **HRMS** (ESI) m/z calcd for $C_{26}H_{36}O_5SNa$ $(M+Na)^+$: 483.2176; found: 483.2176.



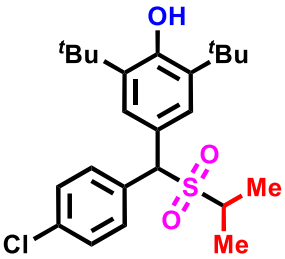
DP-03-112

***2,6-di-tert-butyl-4-((4-fluorophenyl)(isopropylsulfonyl)methyl)phenol* (5ea):** Following the



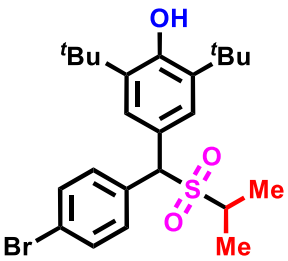
General Procedure **E**, using **1e** (37.5 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ea** was obtained as a white solid (34 mg, 68%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 178-180 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.40 (s, 2H), 7.10 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 5.30 (bs, OH, 1H), 5.30 (s, 1H), 2.97 (sept, J = 6.8 Hz, 1H), 1.44 (s, 18H), 1.32 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 162.9 (d, J = 247 Hz, 1C),154.4, 136.3 (2C), 131.7, 131.6, 129.1(d, J = 12 Hz, 1C), 126.6 (2C), 122.7, 115.9, 115.8, 69.3, 51.2, 34.5 (2C), 30.3 (6C), 15.4, 15.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -110.82. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}O_3FSNa$ $(M+Na)^+$: 443.2027; found: 443.2032.

***2,6-di-tert-butyl-4-((4-chlorophenyl)(isopropylsulfonyl)methyl)phenol* (5fa):** Following the



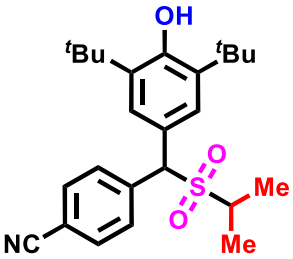
General Procedure **D**, using **1f** (40 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5fa** was obtained as a white solid (40 mg, 75%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 190-192 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.5 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.38 (s, 2H), 5.31 (s, 1H), 5.28 (bs, OH, 1H), 2.97 (sept, J = 6.8 Hz, 1H), 1.43 (s, 18H), 1.32 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.4, 136.4 (2C), 134.8, 131.8, 131.2 (2C), 129.1 (2C), 126.6 (2C), 122.46, 69.4, 51.3, 34.5 (2C), 30.2 (6C), 15.4 (2C). **HRMS** (ESI) m/z calcd for $C_{24}H_{33}O_3ClSNa$ $(M+Na)^+$: 459.1731; found: 459.1744.

***4-((4-bromophenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol* (5ga):** Following the



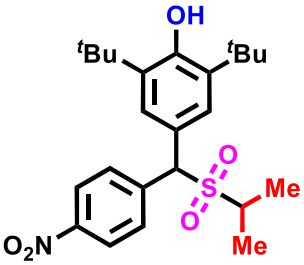
General Procedure **E**, using **1g** (45 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ga** was obtained as a brown solid (41 mg, 71%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 183-185 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 2 Hz, 4H), 7.38 (s, 2H), 5.32 (s, 1H), 5.27 (bs, OH, 1H), 2.97 (sept, J = 6.8 Hz, 1H), 1.43 (s, 18H), 1.32 (d, J = 8Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.4, 136.4 (2C), 132.4, 132.1(2C), 131.5 (2C), 126.6 (2C), 122.9, 122.4, 69.5, 51.3, 34.5 (2C), 30.2 (6C), 15.4, 15.3. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}O_3BrSNa$ $(M+Na)^+$: 503.1226; found: 503.1239.

***4-((3,5-di-tert-butyl-4-hydroxy phenyl) (isopropyl sulfonyl) methyl) benzonitrile* (5ha):**



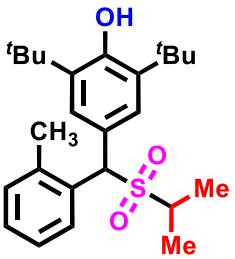
Following the General Procedure **E**, using **1h** (38.4 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ha** was obtained as a white solid (38 mg, 74%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 192-194 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8 Hz, 2H), 7.68 (d, J = 8 Hz, 2H), 7.39 (s, 2H), 5.37 (s, 1H), 5.35 (bs, OH, 1H), 2.97 (sept, J = 6.9 Hz, 1H), 1.44 (s, 18H), 1.32 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.7, 138.4, 136.8 (2C), 132.5 (2C), 130.8 (2C), 126.4 (2C), 122.1, 118.4, 112.5, 69.7, 51.7, 34.5 (2C), 30.2 (6C), 15.8, 14.9. **HRMS** (ESI) m/z calcd for $C_{25}H_{33}O_3NSNa$ $(M+Na)^+$: 450.2073; found: 450.2077.

***2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-nitrophenyl)methyl)phenol* (5ia):** Following the



General Procedure **E**, using **1i** (41 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ia** was obtained as a white solid (41.6 mg, 77%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 196-198 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (dd, J_1 = 8.7, J_2 = 1.6 Hz, 2H), 7.87 – 7.81 (m, 2H), 7.41 (d, J = 1.6 Hz, 2H), 5.41 (bs, OH, 1H), 5.38 (d, J = 1.8 Hz, 1H), 3.01 (sept, J = 6.9 Hz, 1H), 1.44 (d, J = 1.5 Hz, 18H), 1.34 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.70, 147.9, 140.3, 136.8 (2C), 130.9 (2C), 126.4 (2C), 123.9 (2C), 122.0, 69.5, 51.7, 34.5 (2C), 30.2 (6C), 15.9, 14.9. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}NO_5SNa$ $(M+Na)^+$: 470.1972; found: 470.1979.

***2,6-di-tert-butyl-4-((isopropylsulfonyl)(o-tolyl)methyl)phenol* (5ja):** Following the General



Procedure **E**, using **1j** (37 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ja** was obtained as a brown solid (32.5 mg, 65%). R_f = 0.5 (hexane:EtOAc = 17:3). m. p. 138-140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 8.12 (dd, J_1 = 7.8, J_2 = 1.4 Hz, 1H), 7.36 (s, 2H), 7.31 (td, J_1 = 7.5 Hz, J_2 = 1.9 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.24 – 7.19 (m, 1H), 5.59 (s, 1H), 5.27 (bs, OH, 1H), 3.09 (sept, J = 6.8 Hz, 1H), 2.41 (s, 3H), 1.42 (s, 18H), 1.36 (d, J = 6.9 Hz, 3H), 1.27 (d, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.3, 136.5 (2C), 135.9, 132.4, 131.2, 128.4,

128.3, 127.4 (2C), 126.6, 121.9, 65.4, 51.4, 34.4 (2C), 30.2 (6C), 20.0, 15.6, 14.9. **HRMS** (ESI) m/z calcd for $C_{25}H_{36}O_3SNa$ $(M+Na)^+$: 439.2277; found: 439.2299.

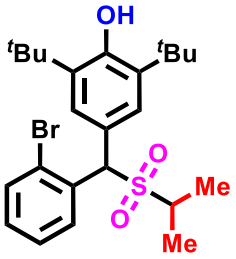
2,6-di-tert-butyl-4-((2-hydroxyphenyl)(isopropylsulfonyl)methyl)phenol* (5ka)*: Following the General Procedure **E**, using **1k** (37.3 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ka** was obtained as a yellow solid (34 mg, 67%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 151-153 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.45 (s, 2H), 7.26 – 7.21 (m, 1H), 7.02 – 6.93 (m, 2H), 5.83 (s, 1H), 5.33 (bs, OH, 1H), 3.04 (sept, J = 6.8 Hz, 1H), 1.44 (s, 18H), 1.35 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.5, 154.4, 136.4 (2C), 131.0, 130.1, 127.2 (2C), 121.8, 121.3, 120.1, 118.2, 64.7, 51.9, 34.5 (2C), 30.3 (6C), 15.4, 15.1. **HRMS** (ESI) m/z calcd for $C_{24}H_{34}O_4SNa$ $(M+Na)^+$: 441.2070; found: 441.2072.

2,6-di-tert-butyl-4-((2-fluorophenyl)(isopropylsulfonyl)methyl)phenol* (5la)*: Following the General Procedure **E**, using **1l** (38 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5la** was obtained as a white solid (25 mg, 51%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 170-172 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (td, J_1 = 7.7, J_2 = 1.8 Hz, 1H), 7.42 (s, 2H), 7.34 (dddd, J_1 = 8.2 Hz, J_2 =7.2 Hz, J_3 = 5.3Hz, J_4 = 1.8 Hz, 1H), 7.24 (td, J_1 = 7.6 Hz, J_2 = 1.3 Hz, 1H), 7.11 (ddd, J_1 = 9.8 Hz, J_2 = 8.3 Hz, J_3 = 1.3 Hz, 1H), 5.80 (s, 1H), 5.30 (bs, OH,1H), 3.00 (sept, J = 6.8 Hz, 1H), 1.43 (s, 18H), 1.34 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 160.3 (d, J = 245 Hz, 1C), 154.4, 136.2 (2C), 130.3 (d, J = 2 Hz, 1C), 130.2(d, J = 9 Hz, 1C), 127.0 (2C), 124.6 (d, J = 4 Hz, 1C), 121.9, 121.4 (d, J = 13 Hz, 1C), 115.8 (d, J = 23 Hz, 1C), 60.4 (d, J = 4 Hz, 1C), 51.5, 34.4 (2C), 30.2 (6C), 15.6, 14.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.63. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}O_3FSNa$ $(M+Na)^+$: 443.2027; found: 443.2030.

2,6-di-tert-butyl-4-((2-chlorophenyl)(isopropylsulfonyl)methyl)phenol* (5ma)*: Following the General Procedure **E**, using **1m** (38 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ma** was obtained as a white solid (37 mg, 70%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 178-180 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.44 – 7.42 (m, 1H),7.41 (s, 2H) 7.37 (td, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 7.30 (dd, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H), 6.03 (s, 1H), 5.28 (bs, OH, 1H), 3.01 (sept, J = 6.9 Hz, 1H), 1.43 (s, 18H), 1.34 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.4, 136.1 (2C), 134.4, 132.2, 130.2, 130.1,

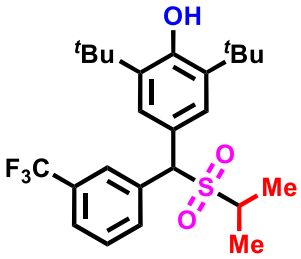
129.6, 127.4, 127.1 (2C), 121.7, 64.6, 51.7, 34.4 (2C), 30.2 (6C), 15.7, 14.9. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}O_3ClSNa$ $(M+Na)^+$: 459.1731; found: 459.1744.

***4-((2-bromophenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol* (5na):** Following the



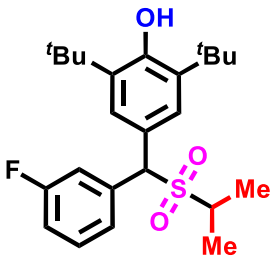
General Procedure **E**, using **1n** (45 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5na** was obtained as a yellow solid (34 mg, 58%). R_f = 0.5 (hexane:EtOAc = 17:3). m. p. 171-173 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.62 (dd, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 1H), 7.43 (s, 2H), 7.42 – 7.39 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 1H), 7.21 (td, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H), 6.03 (s, 1H), 5.28 (bs, OH,1H), 3.02 (sept, J = 6.9 Hz, 1H), 1.43 (s, 18H), 1.36 (d, J = 7.1 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.4, 136.1 (2C), 133.9, 133.6, 130.1, 129.9, 128.0, 127.1 (2C), 125.5, 121.8, 67.4, 51.7, 34.4 (2C), 30.2 (6C), 15.7, 14.9. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}O_3BrSNa$ $(M+Na)^+$: 503.1226; found: 503.1239.

***2,6-di-tert-butyl-4-((isopropylsulfonyl)(3-(trifluoromethyl)phenyl)methyl)phenol* (5oa):**



Following the General Procedure **E**, using **1o** (44 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5oa** was obtained as a white solid (37 mg, 65%). R_f = 0.5 (hexane: EtOAc = 4:1). m. p. 170-172 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dt, J_1 = 4.0, J_2 = 1.8 Hz, 2H), 7.63 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.42 (s, 2H), 5.36 (bs, OH,1H), 5.35 (s, 1H), 2.97 (sept, J = 6.8 Hz, 1H), 1.44 (s, 18H), 1.34 (d, J = 2.9 Hz, 3H), 1.32 (d, J = 3.0 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.6, 136.5 (2C), 134.2, 133.2, 131.2 (q, J = 33 Hz, 1C), 129.3, 126.9 (q, J = 3 Hz, 1C), 126.6 (2C), 125.4 (q, J = 4 Hz, 1C), 123.85 (q, J = 270 Hz, 1C), 122.2, 69.6, 51.5, 34.5 (2C), 30.2 (6C), 15.6, 15.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.67. **HRMS** (ESI) m/z calcd for $C_{25}H_{33}F_3O_3SNa$ $(M+Na)^+$: 493.1995; found: 493.1996.

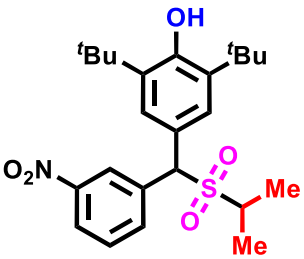
***2,6-di-tert-butyl-4-((3-fluorophenyl)(isopropylsulfonyl)methyl)phenol* (5pa):** Following the



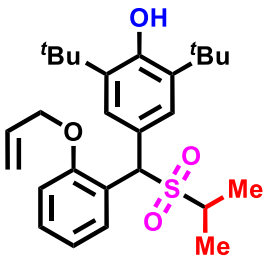
General Procedure **E**, using **1p** (38 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5pa** was obtained as a white solid (33.5 mg, 67%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 173-175 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dt, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.40 (s, 2H), 7.06 (tdd, J_1 = 8.3 Hz, J_2 = 2.6 Hz, J_3 = 1.1 Hz, 1H), 5.33 (bs, OH, 1H), 5.30 (s, 1H), 3.00 (sept, J = 6.9 Hz, 1H), 1.44 (s, 18H), 1.34 (d, J = 1.6 Hz, 3H), 1.32 (d, J = 1.6 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, J = 246 Hz, 1C), 154.5, 136.4

(2C), 135.7 (d, J = 8 Hz, 1C), 130.3 (d, J = 8 Hz, 1C), 126.7 (2C), 125.6 (d, J = 3 Hz, 1C), 122.4, 116.9 (d, J = 23 Hz, 1C), 115.6 (d, J = 21 Hz, 1 C), 69.6 (d, J = 2 Hz, 1C), 51.4, 34.5 (2C), 30.2 (6C), 15.4, 15.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.67. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}O_3FSNa$ $(M+Na)^+$: 443.2027; found: 443.2030.

***2,6-di-tert-butyl-4-((isopropylsulfonyl)(3-nitrophenyl)methyl)phenol* (5qa):** Following the General Procedure **E**, using **1q** (41 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5qa** was obtained as a white solid (37 mg, 70%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 190-192 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, J = 2.1 Hz, 1H), 8.22 (ddd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, J_3 = 1.1 Hz, 1H), 8.06 (dt, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.45 (s, 2H), 5.41 (s, 1H), 5.39 (bs, OH, 1H), 3.00 (sept, J = 6.8 Hz, 1H), 1.46 (s, 18H), 1.35 (d, J = 6.8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.7, 148.4, 136.9 (2C), 135.9, 134.9, 129.6, 126.4 (2C), 125.4, 123.5, 122.2, 69.3, 51.6, 34.5 (2C), 30.3 (6C), 16.1, 14.7. **HRMS** (ESI) m/z calcd for $C_{24}H_{33}NO_5SNa$ $(M+Na)^+$: 470.1972; found: 470.1979.



***4-((2-(allyloxy)phenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol* (5ra):** Following the General Procedure **E**, using **1r** (42 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ra** was obtained as a white solid (33.5 mg, 61%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 184-186 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.44 (s, 2H), 7.32 – 7.28 (m, 1H), 7.05 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.90 (dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, 1H), 6.13 (s, 1H), 6.05 (ddt, J_1 = 17.3 Hz, J_2 = 10.4 Hz, J_3 = 5.0 Hz, 1H), 5.43 (dd, J_1 = 17.3 Hz, J_2 = 1.6 Hz, 1H), 5.31 (dd, J_1 = 10.5 Hz, J_2 = 1.5 Hz, 1H), 5.25 (bs, OH, 1H), 4.56 (tt, J_1 = 5.1 Hz, J_2 = 1.6 Hz, 2H), 3.00 (sept, J = 6.9 Hz, 1H), 1.42 (s, 18H), 1.32 (d, J = 6.9 Hz, 3H), 1.30 (d, J = 6.7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 155.6, 154.1, 135.8 (2C), 132.9, 129.6, 129.4, 127.3 (2C), 123.2, 122.7, 121.3, 117.5, 112.4, 69.2, 60.5, 51.2, 34.4 (2C), 30.3 (d, J = 7 Hz, 6C), 15.9, 14.6. **HRMS** (ESI) m/z calcd for $C_{27}H_{38}NO_4SNa$ $(M+Na)^+$: 481.2383; found: 481.2381.

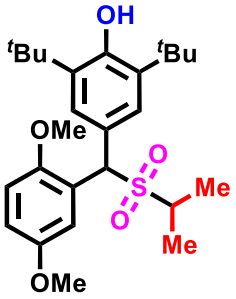


***4-chloro-2-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenyl acetate* (5sa):** Following the General Procedure **E**, using **1s** (42.4 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5sa** was obtained as a yellow solid (38 mg, 70%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 179-181 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 2.6 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.33 (s, 2H), 7.12 (d, J = 8.7 Hz, 1H), 5.59 (s, 1H), 5.32 (bs, OH,1H), 3.06 (sept, J = 6.8 Hz, 1H), 2.35 (s, 3H), 1.43 (s, 18H), 1.35 (d, J = 6.8 Hz, 3H), 1.32 (d, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.2, 154.5, 146.9, 136.4 (2C), 131.9, 129.9, 129.4, 127.9, 126.8 (2C), 124.4, 121.7, 61.6, 51.8, 34.4 (2C), 30.2 (2C), 20.9, 15.5, 15.2. **HRMS** (ESI) m/z calcd for $C_{26}H_{35}ClO_5SNa$ $(M+Na)^+$: 517.1786; found: 517.1801.

***2,6-di-tert-butyl-4-((3,4-dichlorophenyl)(isopropylsulfonyl)methyl)phenol* (5ta):** Following the General Procedure **E**, using **1t** (43.5 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ta** was obtained as a white solid (30.4 mg, 54%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 189-191 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 2.1 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.37 (s, 2H), 5.35 (s, 1H), 5.24 (bs, OH,1H), 2.99 (sept, J = 6.8 Hz, 1H), 1.44 (s, 18H), 1.34 (d, J = 2.2 Hz, 3H), 1.32 (d, J = 2.2 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.6, 136.6 (2C), 133.4, 133.1, 132.9, 131.9, 130.7, 129.0, 126.5 (2C), 122.2, 68.9, 51.5, 34.5 (2C), 30.2 (6C), 15.6, 15.1. **HRMS** (ESI) m/z calcd for $C_{24}H_{32}Cl_2O_3SNa$ $(M+Na)^+$: 493.1341; found: 493.1349.

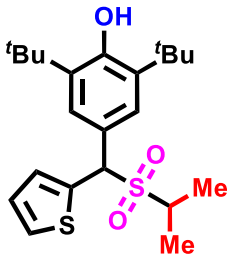
***2,6-di-tert-butyl-4-((3,5-dimethoxyphenyl)(isopropylsulfonyl)methyl)phenol* (5ua):** Following the General Procedure **E**, using **1u** (42.5 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5ua** was obtained as a yellow solid (42.7 mg, 77%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 158-160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 6.85 (d, J = 2.2 Hz, 2H), 6.45 (s, 1H), 5.29 (s, 1H), 5.22 (bs, OH, 1H), 3.80 (s, 6H), 3.04 (sept, J = 6.8 Hz, 1H), 1.43 (s, 18H), 1.33 (d, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 160.9 (2C), 154.3, 136.0 (2C), 135.7, 126.9 (2C), 122.4, 107.8 (2C), 100.8, 70.1, 55.4, 51.3, 34.4 (2C), 30.3 (6C), 15.9, 14.9. **HRMS** (ESI) m/z calcd for $C_{26}H_{38}O_5NaS$ $(M+H)^+$: 485.2332; found: 485.2336.

***2,6-di-tert-butyl-4-((2,5-dimethoxy phenyl)(isopropyl sulfonyl) methyl) phenol* (5va):**



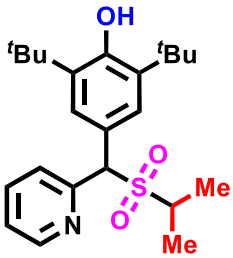
Following the General Procedure **E**, using **1v** (42.5 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5va** was obtained as a brown solid (40.4 mg, 73%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 160-162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, J_1 = 2.3 Hz, J_2 = 1.1 Hz, 1H), 7.45 (s, 2H), 6.87 – 6.84 (m, 2H), 6.04 (s, 1H), 5.25 (bs, OH,1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.99 (sept, J = 6.8 Hz, 1H), 1.43 (s, 18H), 1.31 (d, J = 6.5 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.2, 153.7, 150.9, 135.8 (2C), 127.2 (2C), 123.3, 122.5, 115.3, 114.9, 112.4, 60.5, 56.5, 55.8, 51.3, 34.4 (2C), 30.3 (6C), 15.9, 14.6. **HRMS** (ESI) m/z calcd for $C_{26}H_{38}O_5NaS$ $(M+H)^+$: 485.2332; found: 485.2336.

***2,6-di-tert-butyl-4-((isopropylsulfonyl)(thiophen-2-yl)methyl)phenol* (5wa):** Following the



General Procedure **E**, using **1w** (38 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5wa** was obtained as a black solid (33 mg, 68%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p.162-164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (s, 2H), 7.36 (dd, J_1 = 5.1 Hz, J_2 = 1.2 Hz, 1H), 7.33 (dd, J_1 = 3.7 Hz, J_2 = 1.2 Hz, 1H), 7.05 (dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz, 1H), 5.59 (s, 1H), 5.33 (bs, OH,1H), 3.01 (sept, J = 6.9 Hz, 1H), 1.45 (s, 18H), 1.35 (d, J = 6.8 Hz, 3H), 1.33 (d, J = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.6, 136.2 (2C), 134.9, 129.0, 127.0 (2C), 126.8 (2C), 122.6, 66.1, 50.9, 34.5 (2C), 30.3 (6C), 15.7, 15.3. **HRMS** (ESI) m/z calcd for $C_{22}H_{32}O_3S_2Na$ $(M+Na)^+$: 431.1685; found: 431.1690.

***2,6-di-tert-butyl-4-((isopropylsulfonyl)(pyridin-2-yl)methyl)phenol* (5xa):** Following the



General Procedure **E**, using **1x** (35.5 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5xa** was obtained as a yellow solid (22 mg, 45%). R_f = 0.5 (hexane:EtOAc = 3:1). m. p. 172-174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (ddd, J_1 = 4.8 Hz, J_2 = 1.9 Hz, J_3 = 0.9 Hz, 1H), 7.89 (dt, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 7.76 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.50 (s, 2H), 7.29 (ddd, J_1 = 7.5 Hz, J_2 = 4.9 Hz, J_3 = 1.1 Hz, 1H), 5.67 (bs, OH,1H), 5.31 (s, 1H), 3.11 (sept, J = 6.8 Hz, 1H), 1.43 (s, 18H), 1.37 (d, J = 6.8 Hz, 3H), 1.31 (d, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.5, 154.1, 149.3, 137.3, 136.3 (2C), 126.9 (2C), 124.4, 123.4, 121.9,

72.1, 51.9, 34.5 (2C), 30.2 (6C), 15.7, 15.1. **HRMS** (ESI) m/z calcd for $C_{23}H_{34}O_3NS$ $(M+H)^+$: 404.2254; found: 404.2253.

2-((isopropylsulfonyl)(phenyl)methyl)phenol (5'aa): Following the General Procedure **E**, using **1'a** (24 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5'aa** was obtained as a white solid (19 mg, 55%). R_f = 0.5 (hexane:EtOAc = 3:2). m. p. 135-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.61 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.46 – 7.35 (m, 3H), 7.23 (td, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.03 (s, 1H), 3.10 (sept, J = 6.9 Hz, 1H), 1.39 (d, J = 1.6 Hz, 3H), 1.37 (d, J = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 131.9, 130.9, 130.2 (2C), 130.2, 129.0 (2C), 128.9, 121.5, 119.9, 118.0, 63.8, 51.9, 15.5, 14.9. **HRMS** (ESI) m/z calcd for $C_{16}H_{18}O_3SNa$ $(M+Na)^+$: 313.0869; found: 313.0869.

***2,6-di-tert-butyl-4-(1-(isopropylsulfonyl)-2-methylpropyl)phenol* (5′ba):** Following the General Procedure **E**, using **1′′b** (32 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5′ba** was obtained as yellow liquid (24 mg, 52%). R_f = 0.5 (hexane:EtOAc = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 5.28 (s, 1H), 3.80 (d, J = 6.6 Hz, 1H), 2.77 (sept, J = 6.7 Hz, 1H), 2.64 (sept, J = 6.7 Hz, 1H), 1.43 (s, 18H), 1.19 (d, J = 6.9 Hz, 3H), 1.16 (d, J = 6.7 Hz, 3H), 1.15 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 154.0, 136.1 (2C), 126.6 (2C), 123.0, 71.2, 51.2, 34.4(2C), 30.4 (6C), 28.6, 22.3, 20.3, 16.7, 13.5. **HRMS** (ESI) m/z calcd for $C_{21}H_{36}O_3SNa$ $(M+Na)^+$: 391.2277; found: 391.2273.

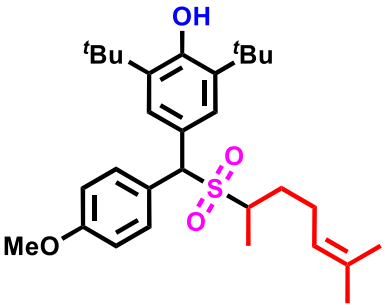
***2,6-di-tert-butyl-4-(cyclohexyl(isopropylsulfonyl)methyl)phenol* (5′ca):** Following the General Procedure **E**, using **1'c** (36 mg, 0.12 mmol), **4a** (89 mg, 0.3 mmol), **5′ca** was obtained as yellow semi-solid (22 mg, 45%). R_f = 0.5 (hexane:EtOAc = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (s, 2H), 5.28 (s, 1H), 3.83 (d, J = 6.7 Hz, 1H), 2.59 (sept, J = 6.9 Hz, 1H), 2.51 – 2.36 (m, 1H), 2.17 – 2.08 (m, 1H), 1.80 – 1.55 (m, 6H), 1.43 (s, 18H), 1.17 (d, J = 6.9 Hz, 3H), 1.13 (d, J = 6.7 Hz, 3H), 1.10 – 1.03 (m, 1H), 0.93 – 0.80 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 153.9, 136.1 (2C), 126.6 (2C), 123.2, 71.0, 51.2, 37.9, 34.4 (2C), 32.5, 30.4 (6C), 30.2, 26.2, 26.2, 26.0, 16.7, 13.5. **HRMS** (ESI) m/z calcd for $C_{24}H_{40}O_3SNa$ $(M+Na)^+$: 431.2590; found: 431.2588.

***2,6-di-tert-butyl-4-((sec-butylsulfonyl)(4-methoxyphenyl)methyl)phenol* (5ab):** Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4b** (93 mg, 0.3 mmol), **5ab** was obtained as a yellow semi-solid (24 mg, 45%). dr = 1:1. R_f = 0.5 (hexane:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8 Hz, 2H), 7.56 (d, J = 8 Hz, 2H), 7.42 (s, 2H), 7.39 (s, 2H), 7.94 (d, J = 4 Hz), 7.92 (d, J = 4 Hz), 5.30 (bs, OH, 1H), 5.30 (bs, OH, 1H), 5.29 (s, 1H), 5.28 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.73- 2.68 (m, 2H), 2.04 – 2.00 (m, 2H), 1.58- 1.52 (m, 2H), 1.44 (s, 18 H), 1.43 (s, 18H), 1.29 (d, J = 4 Hz, 3H), 1.28 (d, J = 4 Hz, 3H), 0.92 (t, J = 8 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.8, 159.8, 154.2, 154.1, 136.2 (2C), 136.0 (2C), 131.2 (2C), 131.1(2C), 126.9 (2C), 126.7 (2C), 125.4, 125.1, 123.3, 122.8, 114.3 (2C), 114.3 (2C), 69.8, 69.7, 57.0, 56.9, 55.3, 55.3, 34.5 (2C), 34.4 (2C), 30.3 (6C), 30.3 (6C), 22.5, 21.9, 12.5, 12.1, 11.1, 11.0. **HRMS** (ESI) m/z calcd for $C_{26}H_{38}O_4SNa$ $(M+Na)^+$: 469.2383; found: 469.2392.

***2,6-di-tert-butyl-4-((cyclopentylsulfonyl)(4-methoxyphenyl)methyl)phenol* (5ac):** Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4c** (97 mg, 0.3 mmol), **5ac** was obtained as a yellowish liquid (38.5 mg, 70%). R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8, 2H), 7.41 (s, 2H), 6.93 (d, J = 8, 2H), 5.28 (s, 1H), 5.18 (bs, OH, 1H), 3.81 (s, 3H), 3.16 (tt, J_1 = 8.6 Hz, J_2 = 7.2 Hz, 1H), 2.17 – 2.05 (m, 2H), 1.86 – 1.74 (m, 4H), 1.57 – 1.51 (m, 2H), 1.44 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.8, 154.2, 136.1 (2C), 131.1 (2C), 126.7 (2C), 125.6, 123.2, 114.3 (2C), 71.3, 59.4, 55.3, 34.4 (2C), 30.3 (6C), 27.1, 26.8, 26.1 (2C). **HRMS** (ESI) m/z calcd for $C_{27}H_{38}O_4SNa$ $(M+Na)^+$: 481.2383; found: 481.2399.

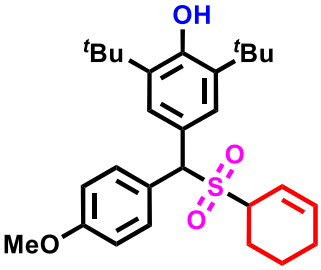
***2,6-di-tert-butyl-4-((cyclohexylsulfonyl)(4-methoxyphenyl)methyl)phenol* (5ad):** Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4d** (101 mg, 0.3 mmol), **5ad** was obtained as a yellow semi-solid (40 mg, 71%). R_f = 0.5 (hexane:EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.8 Hz, 2H), 7.39 (s, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.25 (s, 1H), 3.82 (s, 3H), 2.67 (tt, J_1 = 12.1 Hz, J_2 = 3.5 Hz, 1H), 2.07 (t, J = 14.2 Hz, 2H), 1.83 (d, J = 6.6 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.43 (s, 18H), 1.20 – 1.04 (m, 4H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.7, 154.2, 136.1 (2C), 130.9 (2C), 126.9 (2C), 125.40, 123.02, 114.3 (2C), 69.4, 59.1, 55.3, 34.4 (2C), 30.3 (6C), 25.4, 25.1, 25.0 (2C), 24.7. **HRMS** (ESI) m/z calcd for $C_{28}H_{40}O_4SNa$ $(M+Na)^+$: 495.2540; found: 495.2541.

2,6-di-tert-butyl-4-((4-methoxyphenyl)((6-methylhept-5-en-2-yl)sulfonyl)methyl)phenol



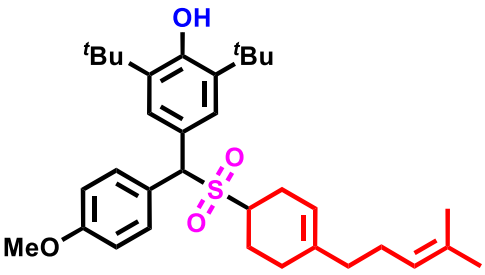
(5ae)*:* Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4e** (109 mg, 0.3 mmol), **5ae** was obtained as a yellowish semi-solid (41 mg, 68%). dr = 1:1. R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 4 Hz, 2H), 7.55 (d, *J* = 4 Hz, 2H), 7.40 (s, 2H), 7.40 (s, 2H), 6.93 (d, *J* = 8 Hz, 4H), 5.31 (s, 1H), 5.30 (s, 1H), 5.28 (s, 1H), 5.28 (s, 1H), 4.86- 4.83 (m, 2H), 3.81 (s, 6H), 2.82 – 2.78 (m, 2H), 2.07 – 1.89 (m, 8H), 1.52 (d, *J* = 8 Hz, 6H), 1.43 (s, 36H), 1.34 – 1.29 (m, 12 H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.8 (2C), 154.2 (2C), 136.1 (4C), 133.2, 133.1, 131.2 (2C), 131.1 (2C), 126.8 (2C), 126.7 (2C), 125.2, 125.1, 122.9 (2C), 122.4, 122.3, 114.3 (4C), 69.8, 69.7, 55.3 (2C), 55.2, 54.9, 34.4 (4C), 30.3 (12C), 29.2, 28.7, 25.6, 25.6, 24.8, 24.7, 17.7, 17.7, 12.7, 12.2. **HRMS** (ESI) m/z calcd for $C_{30}H_{44}O_4SNa$ $(M+Na)^+$: 523.2853; found: 523.2855.

2,6-di-tert-butyl-4-((cyclohex-2-en-1-yl sulfonyl)(4-methoxy phenyl) methyl) phenol* (5af)*:



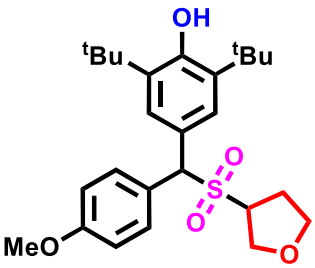
Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4f** (100 mg, 0.3 mmol), **5af** was obtained as a brown semi-solid (45 mg, 80%). dr = 1:1. R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.61 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.42 (s, 2H), 7.39 (s, 2H), 6.94 (d, *J* = 8 Hz, 4H), 5.65 – 5.62 (m, 4H), 5.28 (s, 2H), 5.27 (s, 1H), 5.25 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.97- 2.92 (m, 2H), 2.48 – 2.44 (m, 2H), 2.33 – 2.29 (m, 2H), 2.23 – 2.16 (m, 4H), 1.95 – 1.93 (m, 2H), 1.18 – 1.76 (m, 2H), 1.43 (s, 36H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.8 (2C), 154.2 (2C), 136.1 (2C), 136.1 (2C), 131.0 (2C), 130.9 (2C), 126.8 (2C), 126.7 (2C), 126.7, 126.6, 125.3 (2C), 123.9, 123.7, 122.9, 122.8, 114.4 (2C), 114.4 (2C), 69.9, 69.9, 55.6, 55.6, 55.3 (2C), 34.5 (2C), 34.4 (2C), 30.3 (12C), 24.5, 24.3, 24.2, 23.9, 21.7, 20.9. **HRMS** (ESI) m/z calcd for $C_{28}H_{38}O_4SNa$ $(M+Na)^+$: 493.2383; found: 493.2403.

2,6-di-tert-butyl-4-((4-methoxyphenyl)((4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)sulfonyl)methyl)phenol (5ag): Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4g** (100 mg, 0.3 mmol), **5ag** was obtained as a brown semi-solid (32.5 mg, 49%). dr = 1:1. R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8 Hz, 2H), 7.60 (dd, J_1 = 8 Hz, J_2 = 2



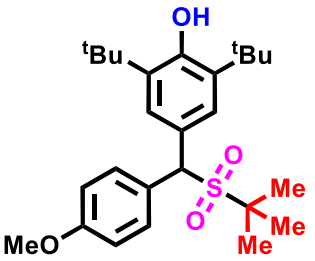
Hz, 2H), 7.45 -7.40 (m, 4H), 6.96 (s, 2H), 6.94 (s, 2H), 5.43 – 5.36 (m, 2H), 5.30 (s, 2H), 5.28 (s, 1H), 5.26 (s, 1H), 5.06 – 5.03 (m, 2H), 3.83 (s, 6H), 2.95 – 2.88 (m, 2H), 2.49 – 2.41 (m, 2H), 2.25 – 2.15 (m , 4H), 2.07 – 1.91 (m, 12H), 1.71 – 1.69 (m , 2H), 1.68 (s, 6H), 1.63 – 1.62 (m, 2H), 1.57 (s, 6H), 1.45 (s, 36H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.8, 159.8, 154.2, 154.2, 137.6, 137.5, 136.1, 136.1, 136.1, 136.0, 131.9, 131.8, 131.0, 131.0, 130.9, 130.9, 126.9, 126.8, 126.7 (2C), 125.4, 125.2, 123.8, 123.7 122.9, 122.8, 120.3, 120.2, 117.5, 117.3, 114.4, 114.3, 69.9, 69.9, 56.3, 55.7, 55.3 (2C), 37.5, 37.1, 34.5 (2C), 34.4 (2C), 30.25 (12C), 27.5, 27.4, 26.2, 26.2, 25.7 (2C), 24.6, 24.3, 23.9, 21.1, 17.8 (2C). **HRMS** (ESI) m/z calcd for $C_{34}H_{48}O_4NaS$ $(M+Na)^+$: 575.3166; found: 575.3170.

***2,6-di-tert-butyl-4-((4-methoxyphenyl)((tetrahydrofuran-3-yl)sulfonyl)methyl)phenol* (5ah):**



Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4h** (97 mg, 0.3 mmol), **5ah** was obtained as a brown liquid (40 mg, 72%). dr = 1:1. R_f = 0.5 (hexane:EtOAc = 7:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.8 Hz, 4H), 7.40 (s, 4H), 6.95 (d, J = 8.7 Hz, 4H), 5.33 (bs, OH, 1H), 5.32 (bs, OH, 1H), 5.15 (s, 1H), 5.14 (s, 1H), 4.05 – 3.98 (m, 2H), 3.89 – 3.85 (m, 2H), 3.82 (s, 6H), 3.80 – 3.75 (m, 4H), 3.50 – 3.45 (m, 2H), 2.41 – 2.36 (m, 2H), 2.05 – 2.00 (m, 2H), 1.44 (s, 36 H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 160.1, 160.0, 154.5, 154.4, 136.3 (2C), 136.3 (2C), 131.1 (2C), 131.1 (2C), 126.7 (4C), 124.6, 124.6, 122.6, 122.5, 114.4 (4C), 72.9, 72.8, 68.3, 68.2, 67.4, 67.3, 59.4, 59.3, 55.3 (2C), 34.4 (4C), 30.2 (12C), 27.4, 27.3. **HRMS** (ESI) m/z calcd for $C_{26}H_{36}O_5SNa$ $(M+Na)^+$: 483.2176; found: 483.2182.

***2,6-di-tert-butyl-4-((tert-butylsulfonyl)(4-methoxyphenyl)methyl)phenol* (5ai):** Following

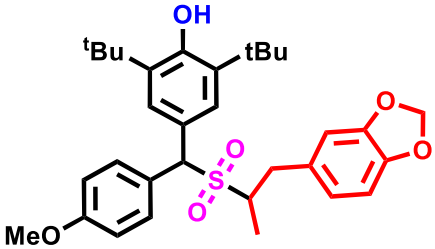


the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4i** (93 mg, 0.3 mmol), **5ai** was obtained as a white solid (22.5 mg, 42%). R_f = 0.5 (hexane:EtOAc = 4:1). m. p. 165-167 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.8 Hz, 2H), 7.45 (s, 2H), 6.91 (d, J = 8.8 Hz, 2H), 5.29 (s, 1H), 3.80 (s, 3H), 1.44 (s, 18H), 1.23 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.7, 154.1, 136.1 (2C), 131.3 (2C), 126.9 (2C), 126.4, 124.4, 114.1 (2C), 69.3, 62.4, 55.3, 34.4 (2C), 30.3 (6C), 24.7 (3C). **HRMS** (ESI) m/z calcd for $C_{26}H_{38}O_4SNa$ $(M+Na)^+$: 469.2383; found: 469.2390.

2,6-di-tert-butyl-4-(((1-(4-isopropylphenyl) propan-2-yl) sulfonyl)(4-methoxy phenyl) methyl) phenol* (5aj)*: Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4j** (125 mg, 0.3 mmol), **5aj** was obtained as a yellowish semi-solid (34.5 mg, 52%). dr = 2:1. R_f = 0.5 (hexane:EtOAc = 17:3).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8 Hz, 2H), 7.54 (d, *J* = 8 Hz, 1H), 7.45 (s, 2H), 7.40 (s, 1H), 7.13 (d, *J* = 8 Hz, 1H), 7.10 (d, *J* = 8 Hz, 2H), 6.95 (d, *J* = 8 Hz, 1H), 6.93 (d, *J* = 8 Hz, 2H), 6.91 (d, *J* = 4 Hz, 1H), 6.84 (d, *J* = 8 Hz, 2H), 5.33 (s, 1H), 5.29 (bs, OH, 1H), 5.28 (s, 0.5H), 5.23 (bs, OH, 0.5H), 3.83 (s, 1.5H), 3.81 (s, 3H), 3.34 – 3.30 (m, 1.5 H), 3.07 – 3.01 (m, 1.5H), 2.89 – 2. 82 (m, 3H), 1.45 (s, 18H), 1.44 (s, 9H), 1.24 – 1.21 (m , 13.5H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.9 (2C), 154.3, 154.2, 147.6, 147.5, 136.4 (2C), 136.1 (2C), 134.6, 134.4, 131.2 (2C), 131.2 (2C), 129.2 (2C), 129.2 (2C), 126.8 (2C), 126.7 (2C), 126.7 (4C), 125.1, 124.7, 123.3, 122.9, 114.3 (4C), 70.5, 70.4, 57.4, 57.3, 55.4, 55.3, 35.3, 34.9, 34.5 (2C), 34.5 (2C), 33.7 (2C), 30.3 (12C), 24.0 (2C), 23.9 (2C), 12.2, 11.9. **HRMS** (ESI) m/z calcd for $C_{34}H_{46}O_4SNa$ $(M+Na)^+$: 573.3009; found: 573.3013.

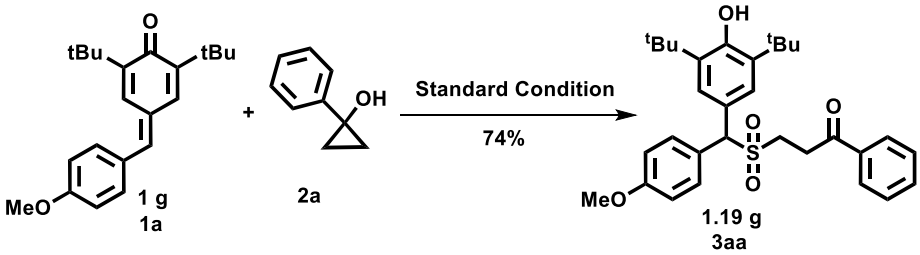
2,6-di-tert-butyl-4-(((1-(4-(tert-butyl)phenyl)propan-2-yl)sulfonyl)(4-methoxyphenyl) methyl)phenol (5ak): Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4k** (100 mg, 0.3 mmol), **5ak** was obtained as a yellow semi-solid (30.5 mg, 45%). dr = 1:0.7. R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8Hz, 2H), 7.55 (d, *J* = 8Hz, 1.4H), 7.47 (s, 2H), 7.43 (s, 1.4H), 7.33 – 7.30 (m , 2H), 7.30 – 7.29 (m, 1.4H), 6.98 – 6.97 (m, 5.1 H), 6.94 (d, *J* = 8Hz, 6.8H), 6.35 (s, 1H), 5.30 (bs, 1H), 5.30 (s, 0.7H), 5.26 (bs, 0.7H), 3.85 (s, 2.1 H), 3.83 (s, 3H), 3.38 – 3.32 (m, 1.7H), 3.10 – 3.03 (m, 2 H), 2.69 – 2.60 (m, 1.4H), 1.47 (s, 18H), 1.46 (s, 12.6H), 1.32 (s, 6.3H), 1.31 (s, 9H), 1.24 (d, *J* = 8Hz, 5.1H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.9, 159.8, 154.3, 154.2, 149.9, 149.8, 136.3 (2C), 136.1 (2C), 134.2, 134.1, 131.2 (2C), 131.2 (2C), 128.9 (2C), 128.9 (2C), 128.6, 126.8 (2C), 126.7 (2C), 125.6 (2C), 125.5 (2C), 125.3, 125.2, 124.8, 123.3, 122.9, 114.3 (2C), 70.5, 70.4, 57.3, 57.3, 55.4, 55.3, 35.2, 34.8, 34.5 (2C), 34.5 (2C), 31.4 (2C), 31.4 (3C), 31.3 (3C), 30.3 (12C), 12.3, 12.1. **HRMS** (ESI) m/z calcd for $C_{35}H_{48}O_4NaS$ $(M+Na)^+$: 587.3166; found: 587.3174.

4-(((1-(benzo[d][1,3]dioxol-5-yl)propan-2-yl)sulfonyl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol* (5al)*: Following the General Procedure **E**, using **1a** (39 mg, 0.12 mmol), **4l** (125 mg, 0.3 mmol), **5al** was obtained as a yellowish semi-solid (39 mg, 58%). dr = 1:0.9. R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7. 58 (d, J = 4 Hz, 1.8H), 7.56 (d, J = 4 Hz, 2H), 7.45 (s, 2H), 7.41 (s, 1.8H), 6.95 (d, J = 8 Hz, 3.8H), 6.69 (d, J = 4 Hz, 1H), 6.67 (d, J = 4 Hz, 0.9H), 6.45 (d, J = 4 Hz, 0.9H), 6.38 (d, J = 4 Hz, 2H), 6.30 (d, J = 4 Hz, 0.9H), 5.94 – 5.90 (m, 3.8H), 5.34 (s, 1H), 5.33 (s, 0.9H), 5.29 (s, 1H), 5.25 (s, 0.9H), 3.83 (s, 2.7H), 3.81 (s, 3H), 3.30 – 3.24 (m, 1.9H), 3.03 – 2.95 (m, 2H), 2.58 – 2.51 (m, 1.8H), 1.45 (s, 16.2H), 1.43 (s, 18H), 1.20 (d, J = 8 Hz, 5.7H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.9, 159.9, 154.4, 154.3, 147.8 (2C), 146.5 (2C), 136.5 (2C), 136.2 (2C), 131.2 (4C), 130.9, 130.7, 126.7 (2C), 126.7 (2C), 125.0, 124.6, 123.2, 122.8, 122.3, 122.3, 114.4 (2C), 114.3 (2C), 109.4, 109.2, 108.3, 108.3, 101.0 (2C), 70.6, 70.5, 57.4, 57.3, 55.4, 55.3, 35.4, 35.1, 34.5 (2C), 34.5 (2C), 30.3 (12C), 12.1, 11.8. **HRMS** (ESI) m/z calcd for $C_{32}H_{40}O_6SNa$ $(M+Na)^+$: 575.2438; found: 575.2433.



5. Gram Scale Synthesis

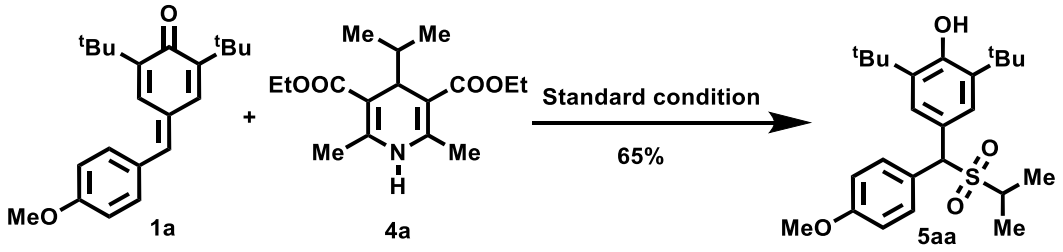
5.1 Gram Scale Synthesis of 3aa



To a 100 mL round-bottom flask equipped with a magnetic stir bar, add with *p*-QMs (3.08 mmol), Cyclopropanol (6.16 mmol) in 50 ml CH_3CN solvent (0.06 M). Then added $K_2S_2O_5$ (1.5 equiv.) followed by Eosin Y (0.02 equiv.) and TFA (1 equiv.). After that, the total mixture was degassed with N_2 for 15- 20 min, then irradiation with purple light (390 nm) from distance 4 cm. The reaction progress was monitored by TLC. Upon complete consumption of the starting material, the reaction was quenched with water and the aqueous phase was extracted with EtOAc (3×40 mL). The organic extracts were combined and dried over Na_2SO_4. The organic phase was evaporated under reduced pressure and the resulting crude material was

purified by SiO2-gel flash column chromatography to afford the desired product **3aa** (2.02 mmol, 1.18 g) with 74% yield.

5.2 Gram Scale Synthesis of 5aa

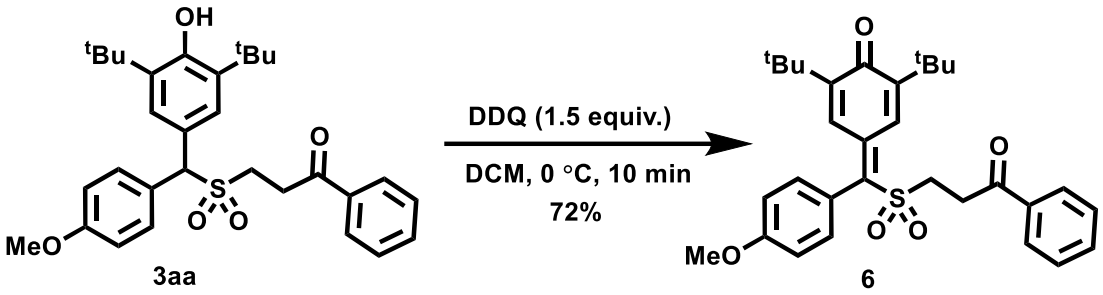


To a 100 ml round-bottom flask equipped with a magnetic stir bar, add with *p*-QMs (3.08 mmol). 4-alkyl-1,4-DHPs (7.7 mmol) in 50 ml DCE solvent (0.06 M). Then added $K_2S_2O_8$ (1.5 equiv.), $K_2S_2O_5$ (2 equiv.) followed by $AgNO_3$ (0.2 equiv.), Eosin Y (0.05 equiv.) and TFA (1.5 equiv.). After that, the total mixture was degassed with N_2 for 15- 20 min, then irradiation with blue kessil light (456 nm) from distance 4 cm. The reaction was completed in 2-3 hours. The reaction mixture was then extracted with DCM (3 x 40 ml), water (50 ml), and brine solution. The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel EtOAc/hexane to afford the desired product **5aa** (2.02 mmol, 0.87 g) with 65% yield.

6. Chemical Transformation

6.1 Oxidation of Phenols

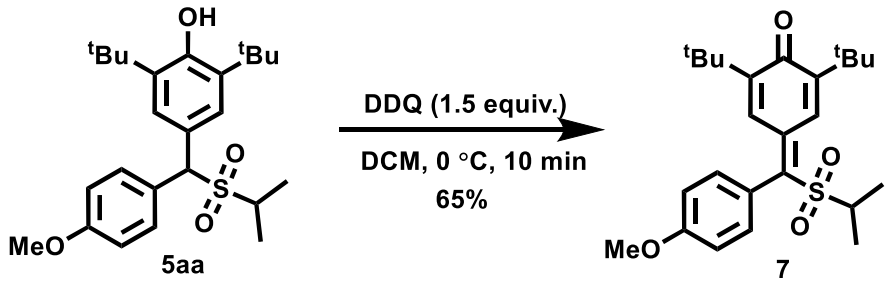
2,6-di-tert-butyl-4-((4-methoxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methylene) cyclohexa-2,5-dien-1-one* (6)*:



To a 25 ml round-bottom flask equipped with a magnetic stir bar, add **3aa** (0.0765 mmol) in 2 ml DCM in a ice bath for 5 minutes and then DDQ (0.1147 mmol) was add. The

reaction completed in 5-10 minutes, indicated by TLC, water (20 ml) was added and then extracted with DCM (3 x 15 ml). The organic layer was collected and then dried over anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel to afford the desired product **6** as a yellow solid (27 mg, 72%). R_f = 0.5 (hexane:EtOAc = 17:3).m. p. 147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, J = 2.6 Hz, 1H), 7.92 (dd, J_1 = 8 Hz, J_2 = 4, 2H), 7.64 – 7.57 (m, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.40 (dt, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.0 (dt, J_1 = 8 Hz, J_2 = 4 Hz 2H), 6.66 (d, J = 2.7 Hz, 1H), 3.88 (s, 3H), 3.49 (ddd, J_1 = 8.5 Hz, J_2 = 6.4 Hz, J_3 = 1.8 Hz, 2H), 3.41 (ddd, J_1 = 8.2 Hz, J_2 = 6.4 Hz, J_3 =1.8 Hz, 2H), 1.33 (s, 9H), 1.13 (s, 9H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.4, 186.2, 161.0, 151.4, 151.2, 145.4, 137.4, 135.8, 133.9, 132.9 (2C), 130.5, 128.9 (2C), 128.1 (2C), 126.4, 124.2, 114.1 (2C), 55.4, 49.9, 36.0, 35.7, 30.6, 29.6 (3C), 29.4 (3C). **HRMS** (ESI) m/z calcd for $C_{31}H_{37}O_5S$ $(M+H)^+$: 521.2356; found: 521.2362.

***2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one* (7):**

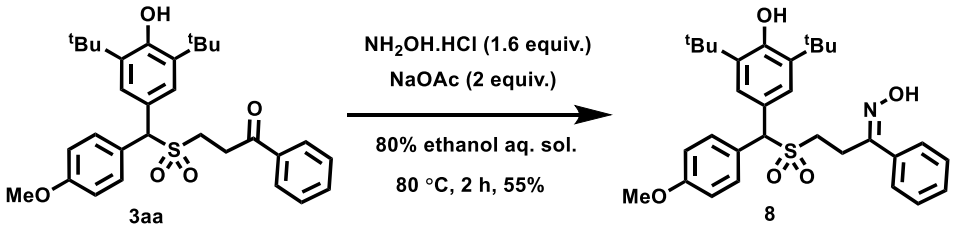


To a 25 ml round-bottom flask equipped with a magnetic stir bar, add **5aa** (0.092 mmol) in 2ml DCM in a ice bath for 5 minutes then add DDQ (0.1386 mmol). The reaction progress was monitored by TLC. Upon complete consumption of the starting material, the reaction was quenched with water and the aqueous phase was extracted with DCM (3 x 15 ml). The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel 8-15% (EtOAc/hexane) to afford the desired product **7** as a orange solid (26 mg, 65%). R_f = 0.5 (hexane:EtOAc = 9:1).m. p. 151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, J = 2.7 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 2.7 Hz, 1H), 3.88 (s, 3H), 2.99 (sept, J = 6.8 Hz, 1H), 1.33 (s, 9H), 1.32 (d, J = 6.8 Hz, 6H), 1.12 (s, 9H). **^{13}C{^{1}H} NMR** (100

MHz, $CDCl_3$) δ 186.3, 160.9, 150.9, 150.7, 144.3, 138.4, 133.2 (2C), 130.8, 126.9, 124.8, 113.9 (2C), 55.4, 53.3, 35.9, 35.6, 29.6 (3C), 29.4 (3C), 14.9 (2C). **HRMS** (ESI) m/z calcd for $C_{25}H_{35}O_4S$ $(M+H)^+$: 431.2251; found: 431.2255.

6.2 Oxime Synthesis

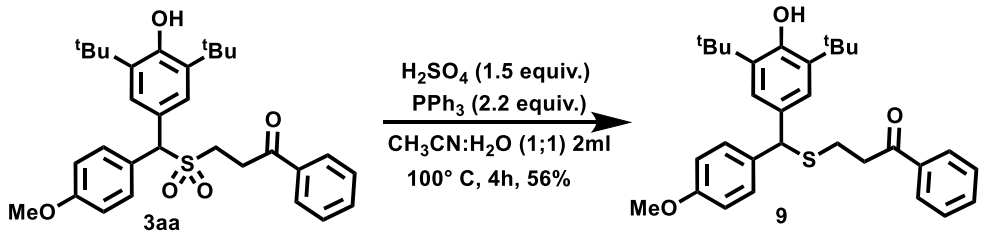
***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one oxime* (8):**.



To a 50 mL round-bottom flask equipped with a magnetic stir bar, add 3aa (0.1913 mmol) in 80% ethanol aqueous solution (16 + 4 mL), then add $NH_2OH.HCl$ (1.6 equiv.) and NaOAc (2 equiv.) and refluxed at 80 °C and the reaction was completed 1.5 h. the reaction mixture was cooled and evaporated. Then add water and extracted with DCM (3 x 25 ml). The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel 25-30% (EtOAc / hexane) to obtain pure compound **8** as a white solid. (57 mg, 55%). R_f = 0.5 (hexane:EtOAc = 3:2). m. p. 170 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (J = 8 Hz, 2H), 7.48 (dd, J_1 = 7.9 Hz, J_2 = 1.9 Hz, 2H), 7.42 (s, 2H), 7.40 – 7.36 (m, 3H), 6.93 (d, J = 8 Hz, 2H), 5.32 (bs, OH, 1H), 5.26 (s, 1H), 3.80 (s, 3H), 3.28 – 3.23 (m, 2H), 3.17 – 3.07 (m, 2H), 1.43 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) Hz, $CDCl_3$) δ 159.9, 155.7, 154.4, 136.3 (2C), 133.9, 131.1 (2C), 129.9, 128.9 (2C), 126.6 (2C), 126.1 (2C), 124.7, 122.9, 114.4 (2C), 72.7, 55.3, 47.8, 34.5 (2C), 30.3 (6C), 19.8. **HRMS** (ESI) m/z calcd for $C_{31}H_{39}O_5NNaS$ $(M+Na)^+$: 560.2441; found: 560.2442.

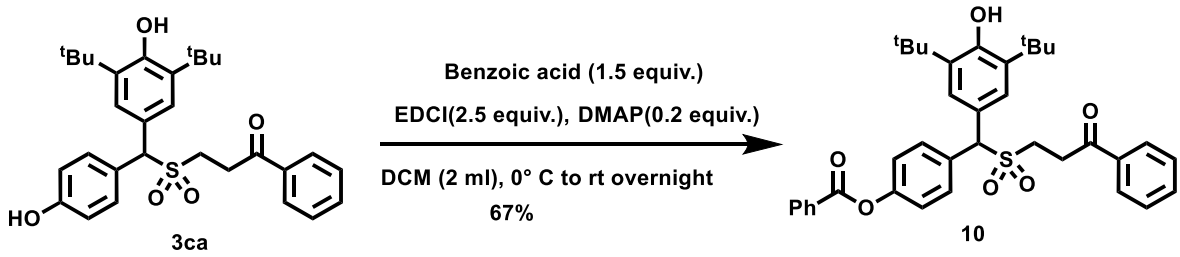
6.3 Conversion of Sulfone to Sulfer

***3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)thio)-1-phenylpropan-1-one* (9):**



To a 25 ml round-bottom flask equipped with a magnetic stir bar, **3aa** (0.095 mmol) in CH_3CN/ H_2O (1:1) 2 ml then add PPh_3 (0.2104 ml) and H_2SO_4 (0.1434 mmol) in a N_2-atmosphere for 100 °C. The reaction progress was monitored by TLC. Upon complete consumption of the starting material, the solvent was removed under reduced pressure. Then water was added and extracted with EtOAc (3 x 15 ml). The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel to afford the desired product **9** as a light yellow solid (26.2 mg, 56%). R_f = 0.5 (hexane:EtOAc = 9:1).m. p. 136 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.57 (tt, J_1 = 8 Hz, J_2 = 4 Hz 1H), 7.47 - 7.45 (m, 2H), 7.40 (d, J = 8 Hz, 2H), 7.23 (s, 2H), 6.87 (d, J = 8 Hz, 2H), 5.15 (s, 1H), 5.14 (bs, OH, 1H), 3.81 (s, 3H), 3.13 (td, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 2.81 (td, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 1.42 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.5, 158.6, 152.9, 136.6 (2C), 135.8, 134.1, 133.2, 131.9, 129.4 (2C), 128.6 (2C), 128.0 (2C), 124.8 (2C), 113.9 (2C), 55.3, 54.6, 38.8, 34.4 (2C), 30.3 (6C), 26.9. **HRMS** (ESI) m/z calcd for $C_{31}H_{38}O_3SNa$ $(M+Na)^+$: 513.2434; found: 513.2441.

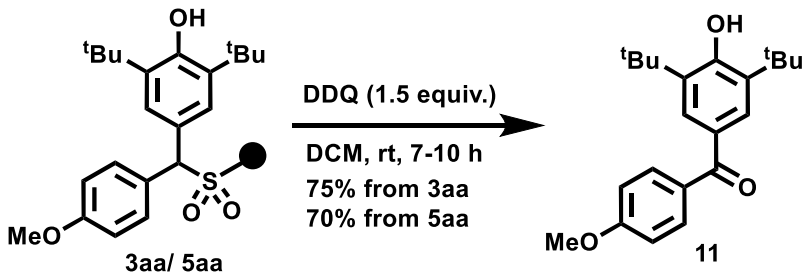
6.4 Coupling with acid



To a 10 mL round-bottom flask equipped with a magnetic stir bar, add **3ca** to 2 mL of DCM, followed by benzoic acid (1.5 equiv.). Stir the mixture in an ice bath for 5 minutes. Then, add EDCI (2.5 equiv.) and DMAP (0.2 equiv.) at room temperature for 12 hours, Completion of the reaction indicated by TLC, The reaction mixture then diluted with 20 ml distilled water and then extracted with DCM (3x15 ml). The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel 15-20 % (EtOAc / hexane) to obtain pure compound **10** with white semi-solid nature.

***4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl benzoate* (10):** To a stirred solution, using **3ca** (30 mg, 0.06 mmol), benzoic acid (11 mg, 0.09 mmol), **10** was obtained as a white solid (24 mg, 67%). R_f = 0.5 (hexane:EtOAc = 4:1).m. p. 147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (dd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 2H), 7.93 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H) 7.78 (d, J = 8.7 Hz, 2H), 7.70 – 7.57 (m, 2H), 7.56 – 7.52 (m, 2H), 7.51 – 7.47 (m, 2H), 7. 50 (s, 2H), 7.34 – 7.29 (m, 2H), 5.40 (s, 1H), 5.37 (bs, OH, 1H), 3.43 – 3.38 (m, 4H), 1.47 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 164.9, 154.6, 151.3, 136.5 (2C), 135.9, 133.8 (2C), 131.1 (2C), 130.6, 130.2 (2C), 129.3, 128.8 (2C), 128.6 (2C), 128.1 (2C), 126.6 (2C), 122.8, 122.3 (2C), 73.8, 46.9, 34.5 (2C), 31.0, 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{37}H_{40}O_6SNa$ $(M+Na)^+$: 635.2438; found: 635.2443.

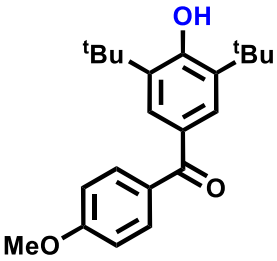
6.5 Synthesis of carbonyl-containing diarylmethanes



To a 25 ml round-bottom flask equipped with a magnetic stir bar, add **3aa/5aa** (0.0765 mmol) in 2 ml DCM in rt then add DDQ (0.1147 mmol). The reaction progress was monitored by TLC. Upon complete consumption of the starting material, the reaction was quenched with

water and the aqueous phase was extracted with DCM (3x15 ml). The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel to afford the desired product **11** with orange semi-solid.

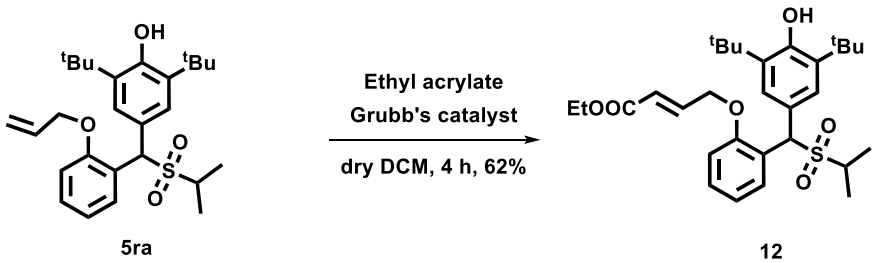
(3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methanone* (11)*: To a stirred solution



at rt, using **3aa/ 5aa** (0.076 mmol), DDQ (1.5 equiv.), **11** was obtained as a light orange semi-solid. R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 2H), 7.68 (s, 2H), 6.97 (d, J = 8.8 Hz, 2H), 5.68 (s, 1H), 3.90 (s, 3H), 1.46 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 162.7, 157.7, 135.5 (2C), 132.3 (2C), 131.1, 129.5, 127.9 (2C), 113.4 (2C), 55.5, 34.4 (2C), 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{22}H_{28}O_3Na$ $(M+Na)^+$: 363.1931; found: 363.1939.

6.6 Olefin metathesis using Grubb's 2nd generation catalyst

***ethyl (E)-4-(2-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenoxy)but-2-enoate* (12):**

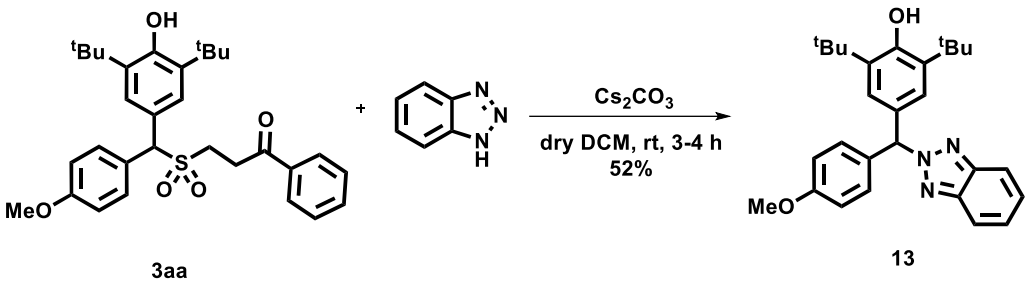


To a 25 ml round-bottom flask equipped with a magnetic stir bar, add **5ra** (0.1091 mmol) in 2 ml of dry DCM and degassed for 15 min, then add ethyl acrylate (3 equiv.) followed by Grubb's 2nd generation catalyst (3 mol%) in rt. The reaction progress was monitored by TLC. Upon complete consumption of the starting material (4 h), the reaction was quenched with water and the aqueous phase was extracted with DCM (3 x 15 ml). The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel, **12** was obtained as a pale semi-solid (36 mg, 62%). R_f = 0.5 (hexane:EtOAc = 7:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (dd, J_1 = 7.8 Hz, J_2 =1.7 Hz, 1H), 7.45 (s, 2H), 7.33 (ddd, J_1 = 8.2 Hz, J_2 = 7.4 Hz, J_3 = 1.7 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.89 (dd, J_1 = 8.3 Hz, J_2 = 1.1 Hz, 1H), 6.23 (dt, J_1 = 15.7 Hz, J_2 = 2.1 Hz, 1H), 6.12 (s, 1H), 5.28 (bs, OH, 1H), 4.74 (td, J_1 = 3.9 Hz, J_2 = 2.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 3.03 (sept, J = 6.8 Hz, 1H), 1.44 (s, 18H), 1.36 – 1.35 (m, 3H), 1.33

– 1.30 (m, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 165.9, 155.0, 154.2, 141.9, 135.9 (2C), 129.8, 129.6, 127.3 (2C), 123.1, 122.4, 121.9, 121.9, 112.6, 67.0, 60.7, 60.6, 51.3, 34.4 (2C), 30.2 (6C), 15.7, 14.7, 14.3. **HRMS** (ESI) m/z calcd for $C_{30}H_{42}O_6SNa$ $(M+Na)^+$: 553.2594; found: 553.2596.

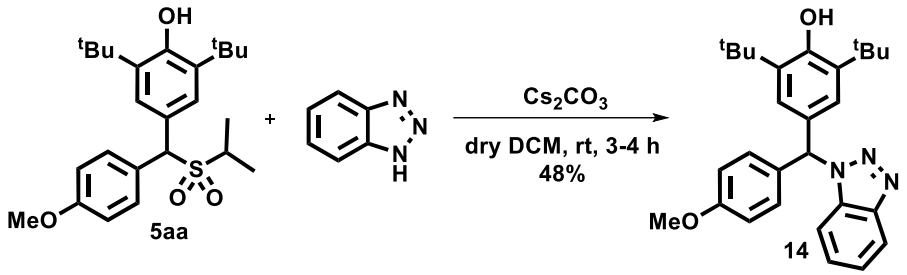
6.7 Synthesis of benzotriazole-containing diarylmethanes

4-((2H-benzo[d][1,2,3]triazol-2-yl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol (13):



To a 10 ml round-bottom flask equipped with a magnetic stir bar, add **3aa** (0.0573 mmol) in 2 ml of dry DCM, then add benzotriazole (1.5 equiv.), Cs_2CO_3 (1.5 equiv.). The reaction was completed in 3h at rt. The reaction mixture was add water and then extracted with DCM (3 x 15 ml. The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel, **13** was obtained as a brown semi-solid (13 mg, 52%). R_f = 0.5 (hexane:EtOAc = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 6.6 Hz, J_2 =3.1 Hz, 2H), 7.38 (dd, J_1 = 6.6 Hz, J_2 = 3.1 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 7.24 (bs, OH, 1H), 7.18 (s, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.26 (s, 1H), 3.82 (s, 3H), 1.39 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.4, 153.8, 144.3 (2C), 135.9 (2C), 131.0, 129.7 (2C), 128.8, 126.2 (2C), 125.2 (2C), 118.4 (2C), 113.9 (2C), 74.0, 55.3, 34.4 (2C), 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{28}H_{33}O_2N_3Na$ $(M+Na)^+$: 466.2465; found: 466.2467.

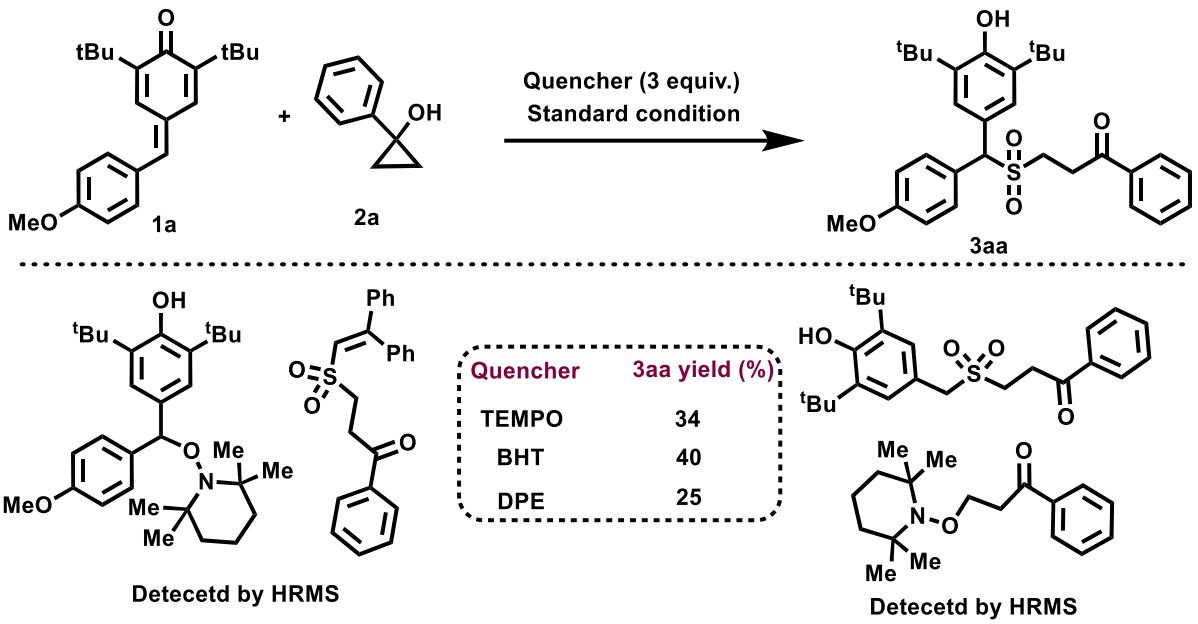
4-((1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol (14):



To a 10 ml round-bottom flask equipped with a magnetic stir bar, add **5aa** (0.0573 mmol) in 2 ml of dry DCM, then add benzotriazole (1.5 equiv.), Cs_2CO_3 (1.5 equiv.). The reaction was completed in 3 h at rt. The reaction mixture was then extracted with DCM (3 x 15 ml), water (20 ml). The organic layer was collected and then dried using anhydrous Na_2SO_4. The organic solution was evaporated, and the residue was purified by flash column chromatography on silica gel, **14** was obtained as a brown semi-solid (1 mg, 48%). R_f = 0.5 (hexane:EtOAc = 17:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 1H), 7.33 (dd, J_1 = 6.4, J_2 = 3.1 Hz, 2H), 7.30 (bs, OH, 1H), 7.14 (d, J = 8 Hz, 2H), 7.12 – 7.08 (m, 1H), 7.06 (s, 2H), 6.88 (d, J = 8 Hz, 2H), 5.28 (s, 1H), 3.82 (s, 3H), 1.35 (s, 18H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 159.4, 153.7, 146.4, 136.1 (2C), 132.9, 130.6, 129.5 (2C), 128.4, 126.9, 125.1 (2C), 123.7, 120.1, 113.9 (2C), 110.9, 67.2, 55.30, 34.4 (2C), 30.2 (6C). **HRMS** (ESI) m/z calcd for $C_{28}H_{33}O_2N_3Na$ $(M+Na)^+$: 466.2465; found: 466.2462.

7. Mechanistic Study γ- keto sulfonylated diarylmethanes

7.1 Radical Trapping Experiment



In a 20 ml borosilicate glass vial equipped with a magnet, add with *p*-QMs (39 mg, 0.123 mmol), Cyclopropanol (33 mg, 0.25 mmol) in 2 ml CH_3CN solvent (0.06 M). Then added $K_2S_2O_5$ (40 mg, 0.184 mmol) followed by Eosin Y (1.6 mg, 0.0024 mmol) and TFA (14 mg, 0.123 mg), TEMPO/ BHT/ DPE (0.37 mmol, 3 equiv.). After that, the mixture was degassed with N_2 for 15 min, then irradiation with Purple kessil light (390 nm) from distance 4 cm, and the reaction mixture was stirred for 1.5 h. The TEMPO/ BHT/ DPE adduct of **1a** and **2a** was detected by HRMS.

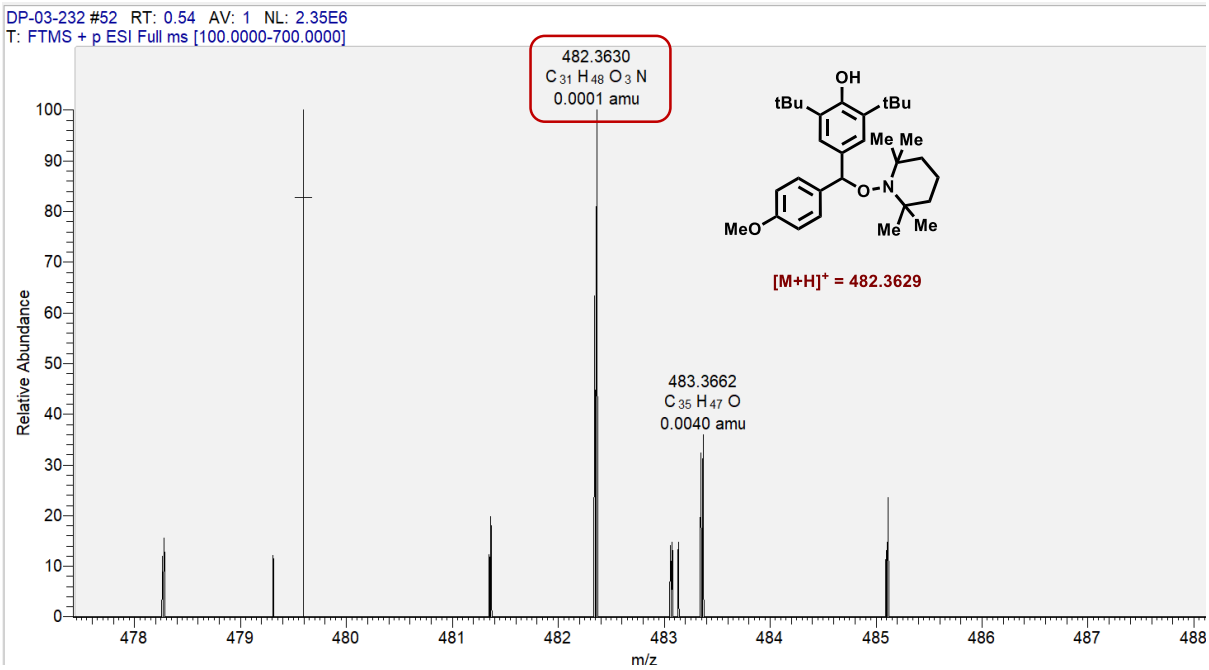


Figure S1a: HRMS spectra of the TEMPO-adduct.

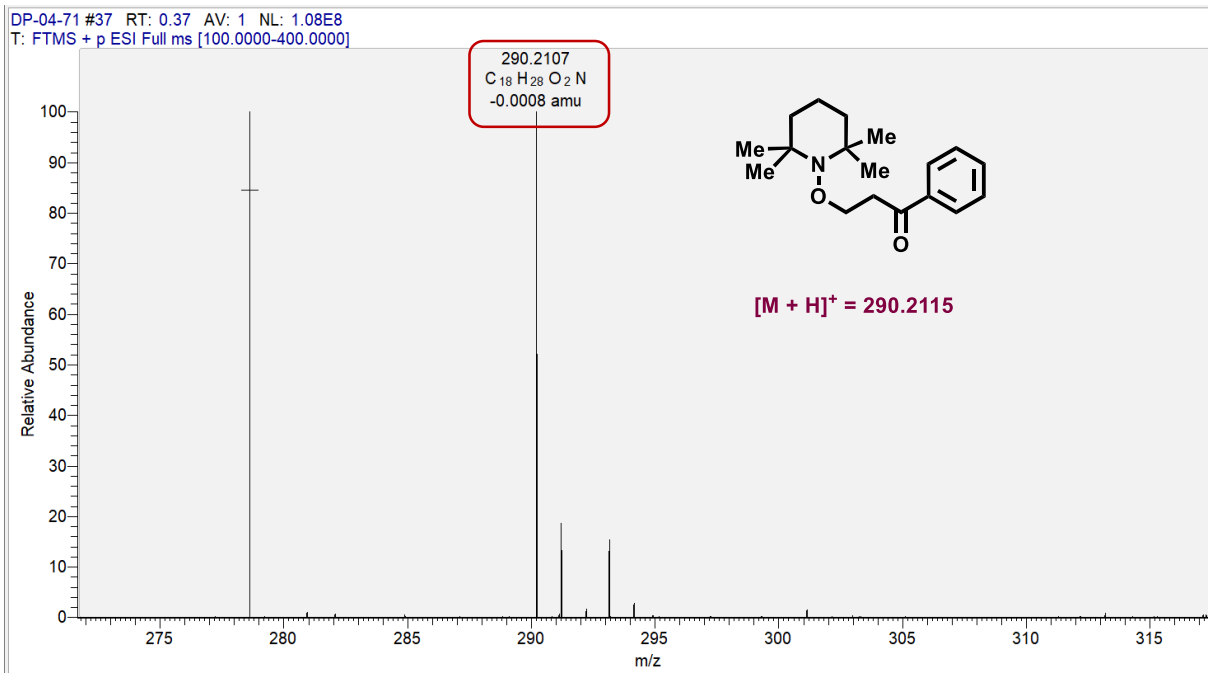


Figure S1b: HRMS spectra of the TEMPO-adduct.

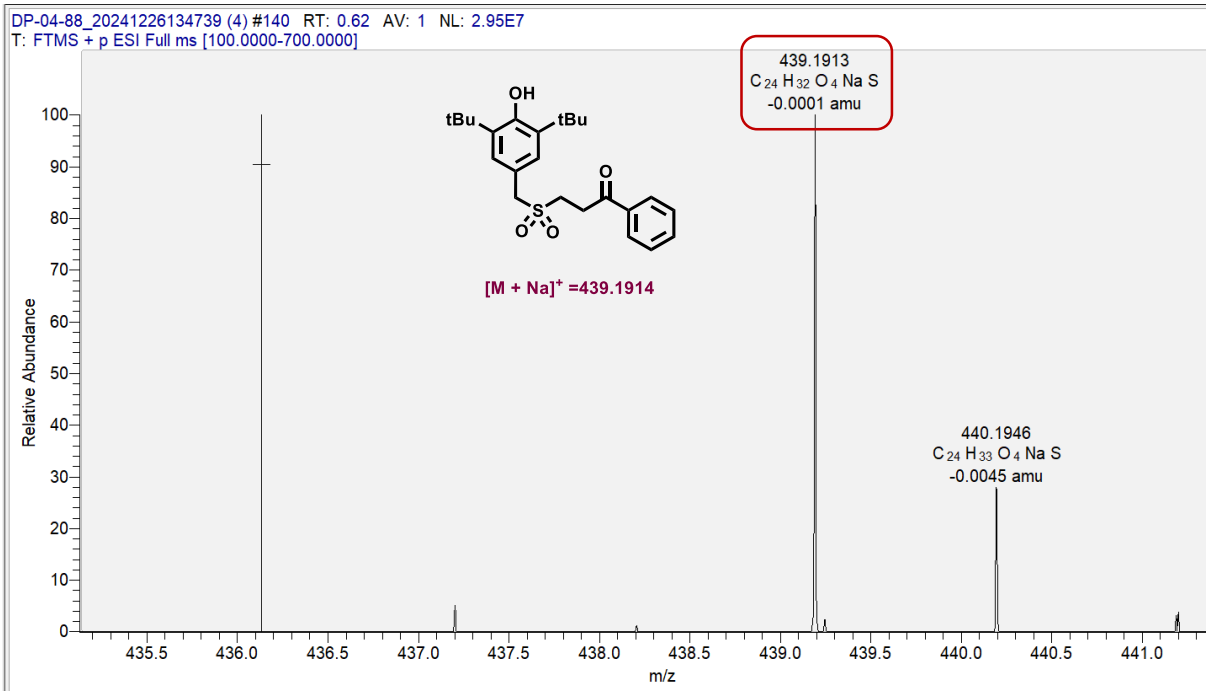


Figure S1c: HRMS spectra of the BHT-adduct

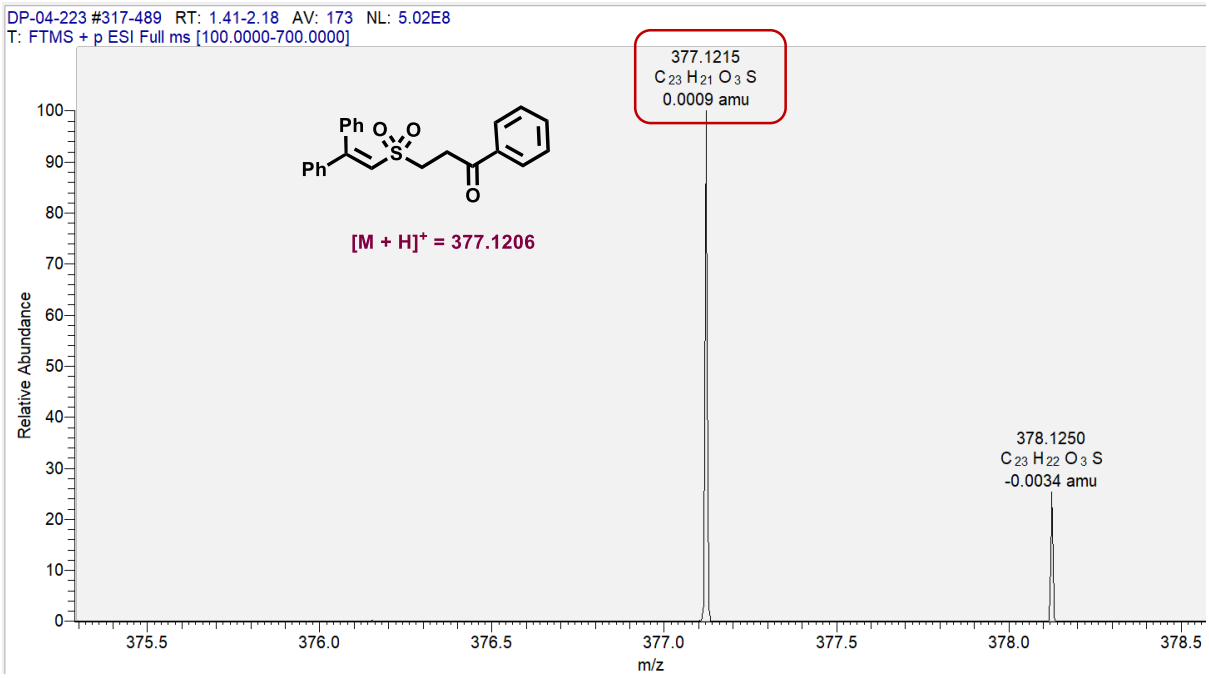


Figure S1d: HRMS spectra of the DPE-adduct

7.2 UV-Visible Study

UV-Visible absorption spectra were recorded using Horiba Scientific's FluoroMax-4 spectrophotometer. First, the solution of 0.1 mM of **1a**, **2a**, TFA, and 0.01 mM of Eosin Y was prepared in dry CH_3CN separately. The absorbance of each individual solution as well as several combinations of them, was measured over a wavelength range of 250 to 600 nm using a quartz cuvette with a path length of 1 cm.

a) b)

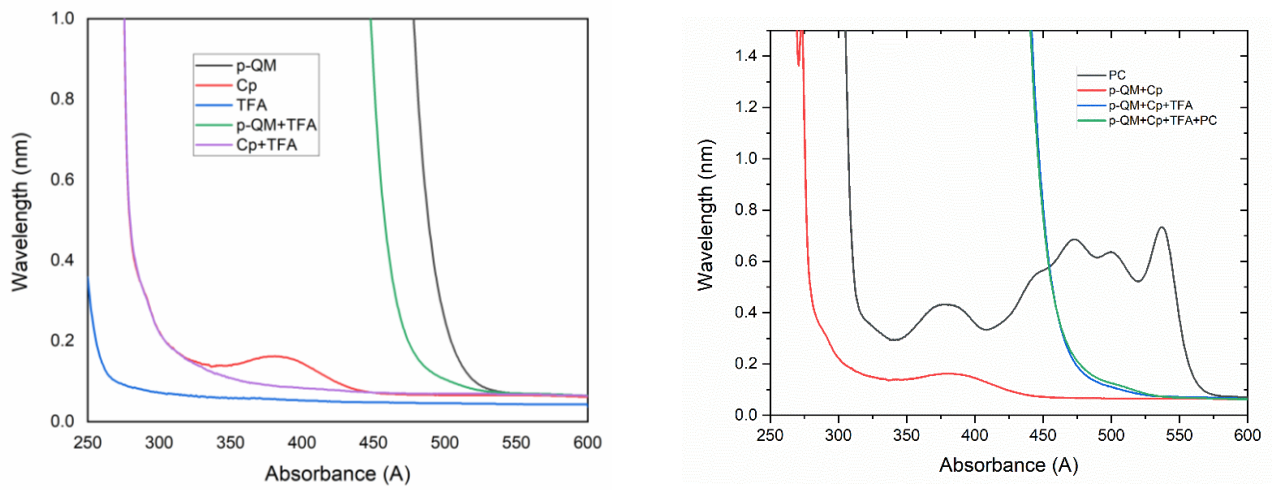


Figure S2: a) UV-Vis Spectra of reactants, b) UV-Vis Spectra of Eosin Y, individual reactants [**1a**, **2a** and TFA] and their combined mixtures.

In the first graph, there is an interaction between p-QMs and TFA indicated by a blue shift. The second graph shows a new absorption band near 390nm formed due to the addition of a photocatalyst to the mixture of **1a**, **2a** and TFA. Also, the absorption peak of combination of **1a** and **2a** in the range of 350 to 400 which was esteemed with 390 nm light irradiation.

7.3 Fluorescence Quenching Experiments

All emission spectra were recorded using the FluoroMax-4 spectrofluorometer from Horiba Scientific. Photocatalyst Eosin Y solutions were prepared in dry CH_3CN without any reactants, followed by an incremental addition of **1a** and **2a**. We conducted quenching experiments with a photocatalyst concentration of 0.5 mM, varying the concentration of **1a** from 0 to 30 mM and

6a from 0 to 25 mM. The solutions were excited at 490 nm, and the emission intensity was measured at 500 nm..

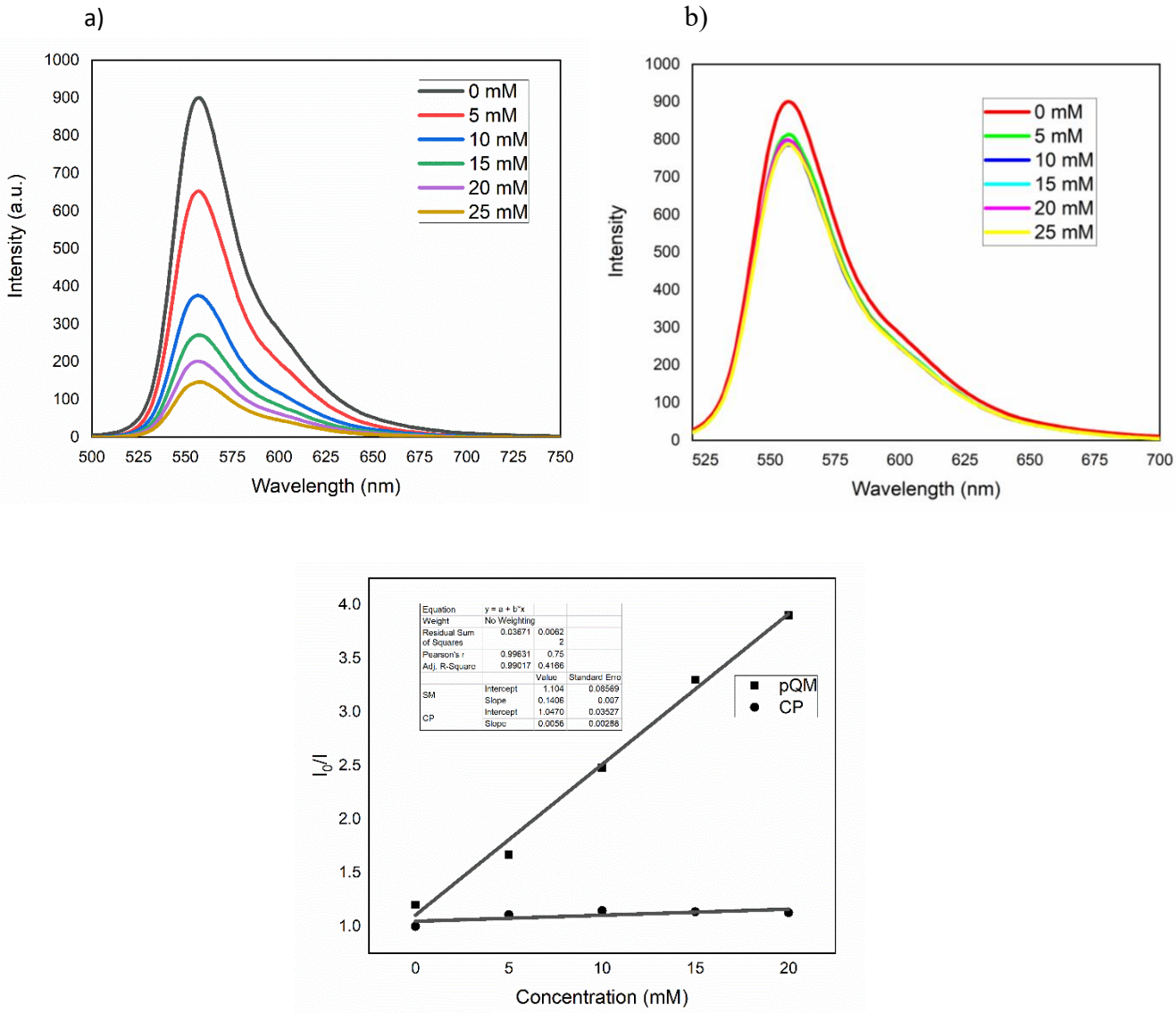


Figure S3: Fluorescence quenching spectrum of Eosin Y on incremental addition of (a) *p*-QM **1a** (b) Cyclopropanol **2a** in CH_3CN (c) Linear fit to Stern-Volmer quenching plots.

7.4 Light ON-OFF Experiment

In a 20 ml borosilicate glass vial equipped with a magnetic stir bar, *p*-QMs **1a** (39 mg, 0.123 mmol), Cyclopropanol **2a** (33 mg, 0.25 mmol), $K_2S_2O_5$ (40 mg, 0.184 mmol), TFA (14 mg, 0.123 mmol), Eosin Y (1.6 mg, 2 mol %) was dissolved in 2 ml CH_3CN solvent (0.06 M). After that, the mixture was degassed under N_2 for 15 min, then the reaction vial was irradiated with

390 nm Purple kessil light while maintaining a distance of 4 cm from the light source. The progress of the reaction was monitored in the presence and absence of light, and the product yield for the reaction was determined each time by ^{1}H NMR experiment using 1,3,5–trimethoxy benzene as internal standard until the complete consumption of starting material.

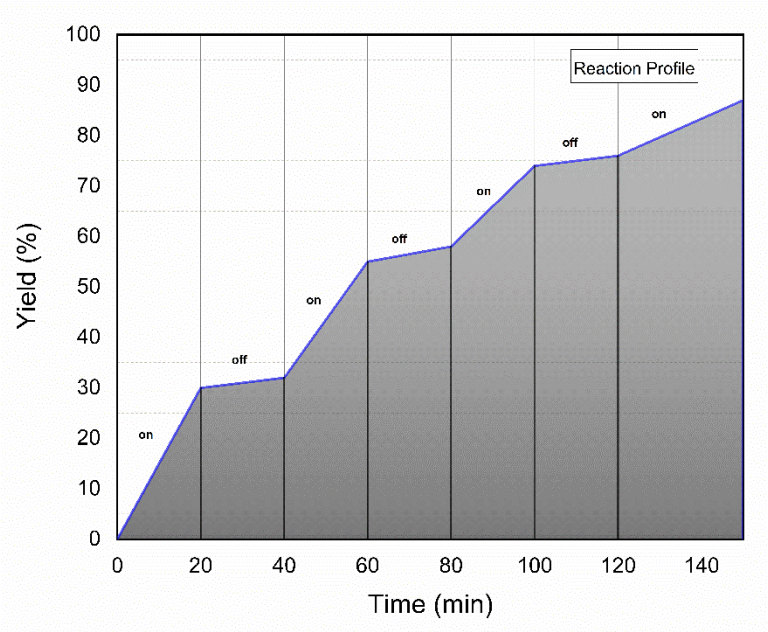
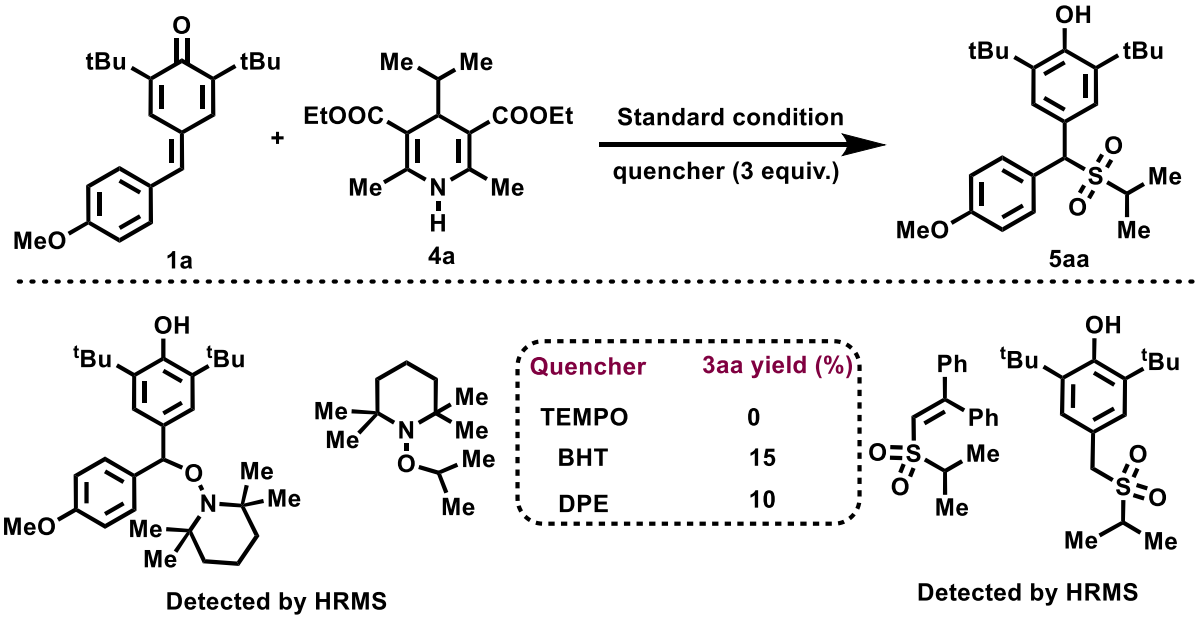


Figure S4: The result of light ON-OFF experiment clearly indicates that the reaction progresses only when the light source is on, and there is very little progress when the light source is turned off.

8. Mechanistic Studies for alkyl sulfonylated Diarylmethanes

8.1 Radical trapping experiments



In a 20 ml reaction vial equipped with a PTFE coated magnetic stir bar, *p*-QMs **1a** (39 mg, 0.123 mmol), 4-Isopropyl Hantzsch ester **4a** (91 mg, 0.3082 mmol), $K_2S_2O_8$ (50 mg, 0.184 mmol), $K_2S_2O_5$ (54 mg, 0.25 mmol), TFA (21 mg, 0.184 mmol), Eosin Y (1.6 mg, 2 mol %) and quencher [TEMPO/BHT/DPE (0.37 mmol, 3 equiv.] were taken and dissolved in 2 ml DCE solvent (0.06 M). After that, the total mixture was degassed under N_2 for 15 min, then the reaction vial was irradiated with 456 nm Blue kessil light while maintaining a distance of 4 cm from the light source. The reaction mixture was stirred for 2 h and the TEMPO/ BHT/ DPE adduct of **1a** and **4a** was detected by HRMS.

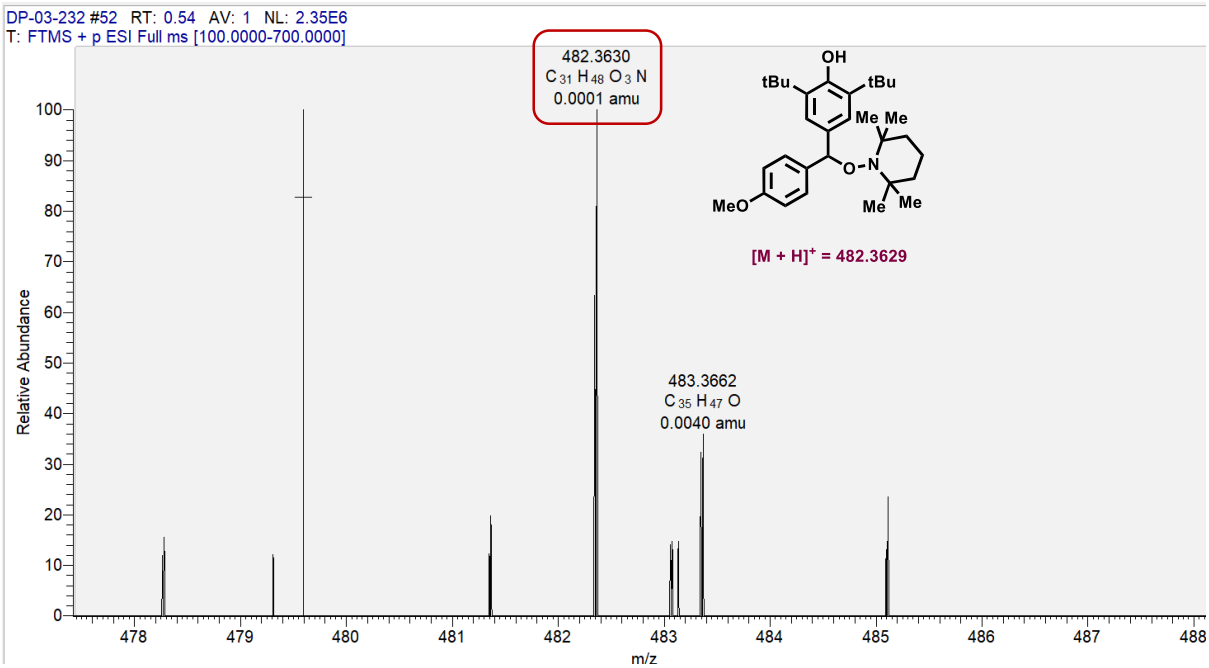


Figure S5a: HRMS spectra of the TEMPO-adduct

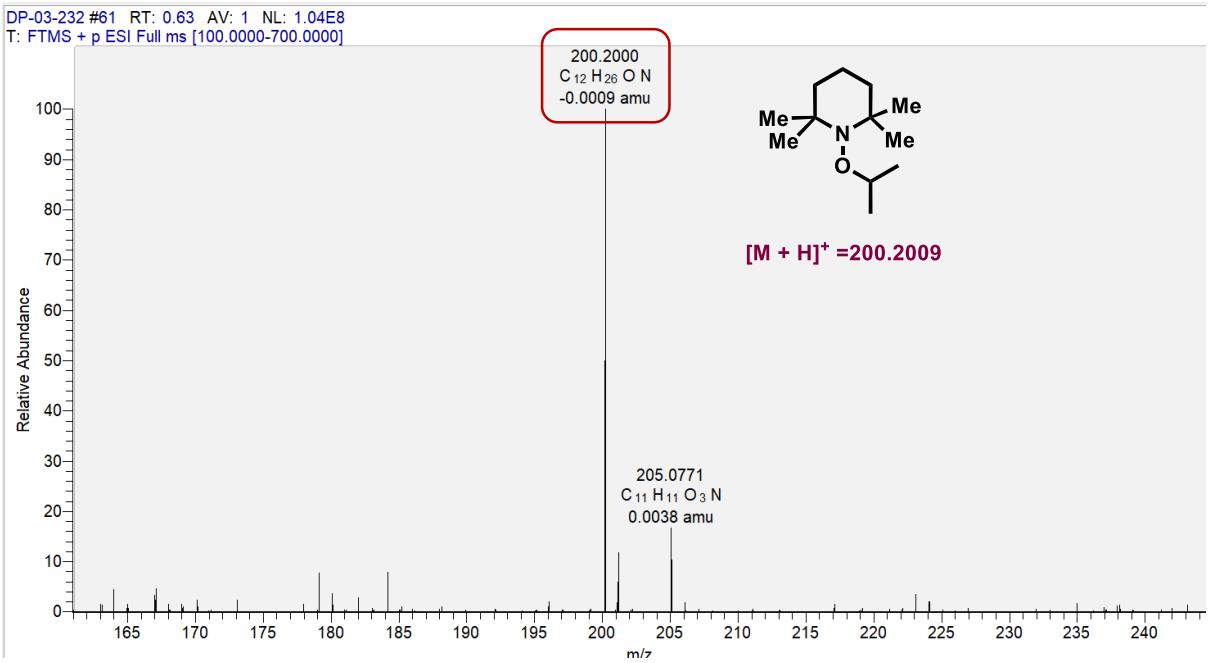


Figure S5b: HRMS spectra of the TEMPO-adduct

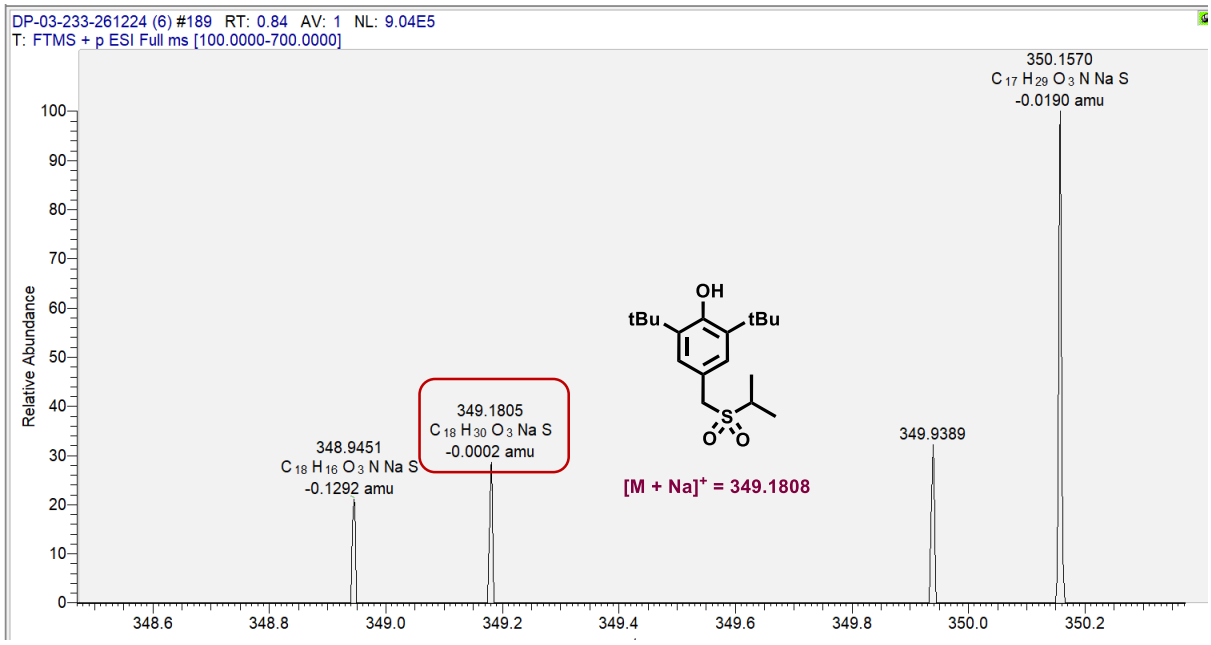


Figure S5c: HRMS spectra of the BHT-adduct

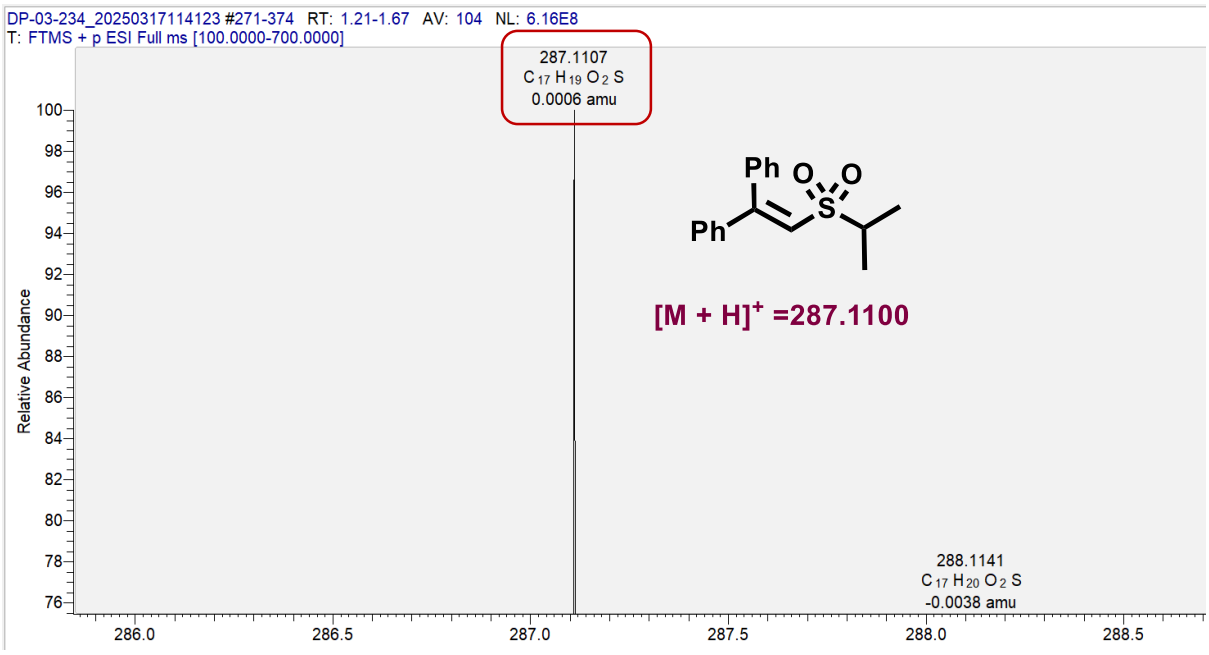


Figure S5d: HRMS spectra of the DPE-adduct

8.2 UV-Visible Study

UV-Visible absorption spectra were recorded using Horiba Scientific's FluoroMax-4 spectrophotometer. First, the solution of 0.1 mM of **1a**, **4a**, TFA, and 0.01 mM of Eosin Y was prepared in dry DCE separately. The absorbance of each individual solution, as well as several combinations of them, was measured over a wavelength range of 250 to 600 nm using a quartz cuvette with a path length of 1 cm.

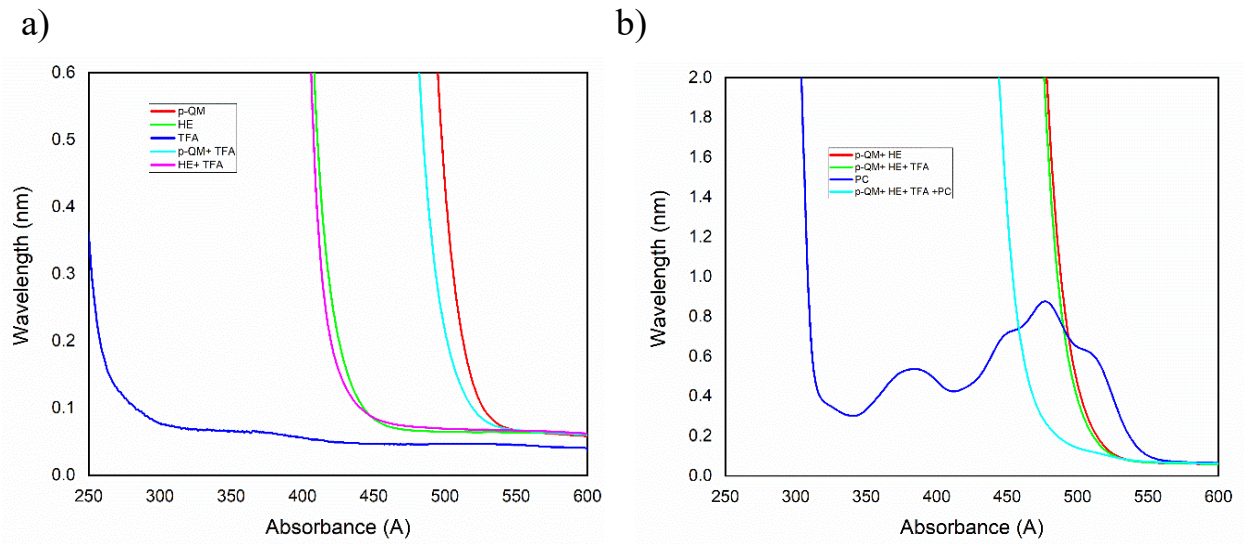


Figure S6: a) UV-Vis Spectra of reactants, b) UV-Vis Spectra of Eosin Y, individual reactants [**1a**, **4a** and TFA] and their combined mixtures.

In the first graph, there is an interaction between p-QMs and TFA indicated by a blue shift. The second graph shows a new absorption band formed due to the addition of a photocatalyst to the mixture of **1a**, **4a** and TFA. From this, the photocatalyst may interact with any species that are involved in the reaction. And the absorption peaks were in the range 450-480 which matched with blue LEDs (456 nm).

8.3 Fluorescence Quenching Experiments

All emission spectra were recorded using the FluoroMax-4 spectrofluorometer from Horiba Scientific. Photocatalyst Eosin Y solutions are prepared in dry DCE without any reactants, followed by an incremental addition of **1a** and **4a**. We conducted quenching experiments with a photocatalyst concentration of 1 mM, varying the concentration of **1a** from 0 to 30 mM and **4a** from 0 to 25 mM. The solutions were excited at 490 nm, and the emission intensity was measured at 500 nm.

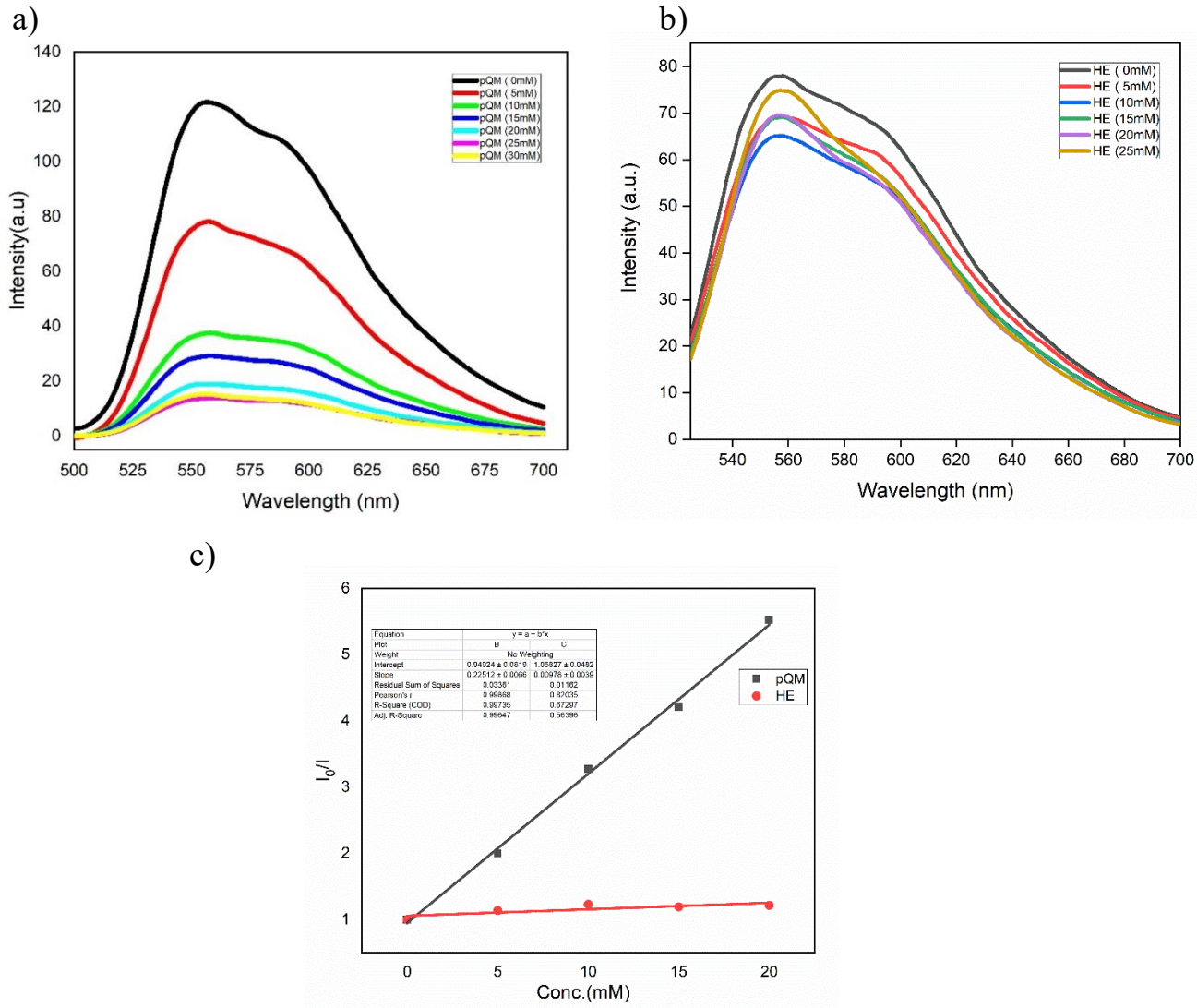


Figure S7: Fluorescence quenching spectrum of Eosin Y on incremental addition of (a) *p*-QM **1a** (b) 4-isopropyl DHP **4a** in DCE (c) Linear fit to Stern-Volmer quenching plots.

Plots were derived according to the Stern–Volmer equation, where I_0 is the luminescence intensity of the photocatalyst in the absence of a quencher, I is the intensity of the photocatalyst in the presence of quenchers.

8.4 Light ON-OFF Experiment

In a 20 ml borosilicate glass vial equipped with a magnetic stir bar, *p*-QMs **1a** (39 mg, 0.123 mmol), 4-Isopropyl Hantzsch ester **4a** (91 mg, 0.3082 mmol), $K_2S_2O_8$ (50 mg, 0.184 mmol), $K_2S_2O_5$ (54 mg, 0.25 mmol), TFA (21 mg, 0.184 mmol), Eosin Y (1.6 mg, 2 mol %) was dissolved in 2 ml DCE solvent. After that, the mixture was degassed under N_2 for 15 min, then the reaction vial was irradiated with 456 nm Blue kessil light while maintaining a distance of 4 cm from the light source. The progress of the reaction was monitored in the presence and absence of light, and the product yield for the reaction was determined each time by ^{1}H NMR experiment using 1,3,5–trimethoxy benzene as internal standard until the complete consumption of starting materials.

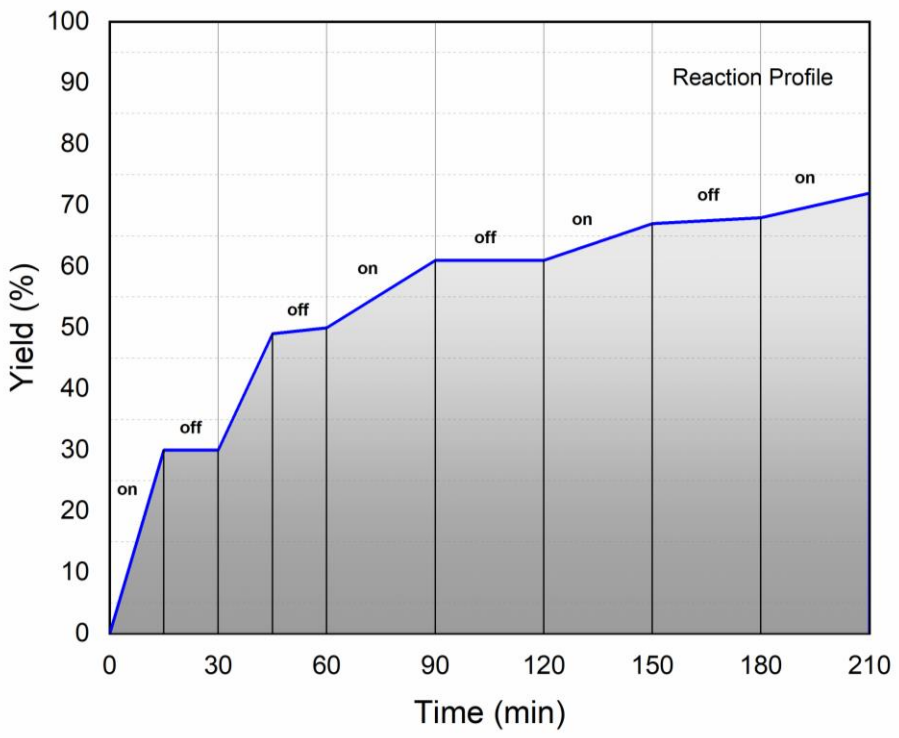
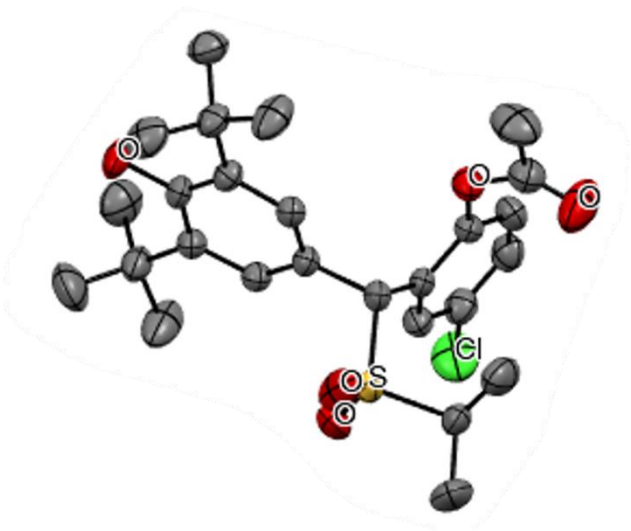


Figure S8: The result of light ON-OFF experiment clearly indicates that the reaction progresses only when the light source is on, which discard the possibility of radical chain process in the reaction course.

9. Crystallography Data:

Sample Preparation: A glass vial was contained by 10 mg of the compound, followed by 0.5 mL of hexane and 1 ml of DCM was added. Then sealed by some cotton and left at room temperature for crystal grow through slow evaporation.

Single crystal X-ray diffraction data were collected on Bruker single-crystal X-ray diffractometer (D8 VENTURE) equipped with a PHOTON 100 CMOS detector. In this case, data collection was smooth without any complication and crystal was stable throughout the data collection period. The structure was determined using intrinsic phasing method followed by full-matrix least-squares refinement against F^2 using SHELXTL-13. The data of colourless crystal **(5sa)** collected



CCDC 2441977

Figure S9: ORTEP plot of 5sa (drawn at 50% probability)

Table S1. Crystal data and structure refinement for 5sa

Identification code	5sa	
Empirical formula	$C_{52}H_{68}O_{10}S_2Cl_2$	
Formula weight	988.08	
Temperature	293(2) K	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 11.0409(12) Å	α/° = 90
	b = 19.190(3) Å	β/° = 90
	c = 24.995(3) Å	γ/° = 90
Volume	5295.9(11) $Å^3$	
Z	4	
Density	1.239 g/cm^3	
Absorption coefficient	0.256 mm^{-1}	
F(000)	2104.0	
Crystal size	0.34 × 0.25 × 0.12 mm^3	
Wavelength	0.71073 Å	
Theta range for data collection	3.89 to 57.036°	
Index ranges	$-12 \leq h \leq 14$, $-25 \leq k \leq 25$, $-33 \leq l \leq 33$	
Reflections collected	108253	
Independent reflections	13329 [R_{int} = 0.0932, R_{sigma} = 0.0583]	
Data/restraints/parameters	13329/0/613	
Goodness-of-fit on F^2	1.046	
Final R indexes [I>=2σ (I)]	R_1 = 0.0540, wR_2 = 0.1237	
Final R indexes [all data]	R_1 = 0.1069, wR_2 = 0.1501	
Largest diff. peak/hole	0.30/-0.30 e $Å^{-3}$	
Flack parameter	0.41(3)	

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5sa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	6468.2(19)	3169.0(8)	6018.1(6)	90.3(5)
Cl2	11444.6(16)	3133.4(8)	545.3(7)	85.1(5)
S1	5064.3(9)	3819.0(6)	3928.4(4)	41.9(3)
S2	10088.0(10)	3793.7(6)	2625.8(4)	47.6(3)
O1	5676(3)	5729.0(16)	4820.0(15)	58.9(9)
O2	4656(3)	4037(2)	3414.1(12)	65.5(10)
O3	4572(3)	3188.3(16)	4149.6(14)	55.0(8)
O4	-288(3)	4957.8(17)	4672.7(14)	59.3(9)
O5	7603(4)	6013(3)	4700(3)	142(3)
O6	10712(3)	5710.1(15)	1729.8(13)	50.6(8)
O7	9597(3)	3977(2)	3136.5(14)	78.6(12)
O8	9690(3)	3158.1(18)	2383.2(16)	70.0(11)
O9	4734(3)	4969.0(16)	1925.1(15)	59.3(9)
O10	12669(4)	5932(2)	1883(2)	98.2(16)
C1	1462(5)	3076(3)	5248(2)	69.3(15)
C2	679(4)	3696(2)	5082(2)	49.1(11)
C3	1447(4)	4244(2)	4782.9(16)	37.2(9)
C4	2670(4)	4147(2)	4705.8(17)	38.8(9)
C5	3389(3)	4627(2)	4439.3(16)	34.5(9)
C6	4751(3)	4535(2)	4375.8(17)	38.7(9)
C7	5449(3)	4508(2)	4889.4(16)	37.0(9)
C8	5950(4)	5115(2)	5093.9(18)	41.9(10)
C9	6541(6)	6165(3)	4658(3)	76.3(16)
C10	6048(7)	6794(3)	4402(3)	92(2)
C11	5607(4)	3906(2)	5185.9(17)	44.9(10)
C12	6275(4)	3926(3)	5655.5(18)	51.4(12)
C13	6777(4)	4531(3)	5844(2)	55.1(12)
C14	6598(4)	5136(3)	5560.4(19)	52.0(12)
C15	6684(4)	3744(2)	3899.1(19)	47.5(11)
C16	6992(5)	3175(3)	3506(2)	75.0(17)
C17	7262(4)	4432(3)	3758(2)	65.4(15)
C18	2839(4)	5212(2)	4231.6(16)	37.2(9)
C19	1606(4)	5346(2)	4295.6(17)	38.0(9)
C20	930(4)	4853(2)	4579.3(18)	40.6(10)
C21	113(5)	3998(3)	5588(2)	71.3(15)
C22	-317(5)	3410(3)	4706(3)	74.2(17)
C23	1035(4)	6021(2)	4070(2)	49.5(11)
C24	620(5)	6488(3)	4528(3)	74.6(17)
C25	-16(5)	5860(3)	3689(2)	68.3(14)
C26	1980(5)	6432(3)	3747(3)	83(2)
C27	6365(5)	3050(3)	1391(3)	90(2)

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5sa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C28	5621(4)	3693(2)	1547(2)	52.3(12)
C29	6422(4)	4247(2)	1815.7(18)	40.6(10)
C30	7669(4)	4140(2)	1876.3(17)	39.2(10)
C31	8403(4)	4619(2)	2133.0(17)	37.4(9)
C32	9766(3)	4519(2)	2190.3(16)	37.3(9)
C33	10461(3)	4487(2)	1666.3(16)	35.6(9)
C34	10969(4)	5087(2)	1464.3(18)	38.8(10)
C35	11637(5)	6106(3)	1919(2)	56.8(12)
C36	11185(6)	6754(3)	2160(3)	84.5(19)
C37	10609(4)	3887(2)	1368.8(18)	44.1(10)
C38	11264(4)	3900(2)	900.9(19)	48.6(11)
C39	11769(4)	4504(3)	712(2)	52.0(12)
C40	11615(4)	5100(2)	994.6(19)	49.3(11)
C41	11704(4)	3771(2)	2688.8(18)	45.5(10)
C42	12205(5)	4463(3)	2855(3)	74.3(17)
C43	12000(5)	3187(3)	3078(3)	82.1(19)
C44	7886(4)	5213(2)	2335.7(17)	38.3(9)
C45	6654(4)	5361(2)	2285.0(16)	37.3(9)
C46	5937(4)	4868(2)	2009.2(18)	39.4(10)
C47	4624(5)	3462(3)	1926(3)	84.8(19)
C48	5062(6)	3976(3)	1031(2)	76.1(16)
C49	6109(4)	6037(2)	2513.4(19)	46.4(11)
C50	5666(5)	6515(2)	2064(2)	60.3(14)
C51	7068(5)	6445(3)	2824(2)	70.5(16)
C52	5083(5)	5880(3)	2909(2)	68.2(15)

Table S3 Bond Lengths for 5sa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C12	1.726(5)	C13	C14	1.375(7)
Cl2	C38	1.730(5)	C15	C16	1.507(6)
S1	O2	1.425(3)	C15	C17	1.508(7)
S1	O3	1.437(3)	C18	C19	1.395(5)
S1	C6	1.806(4)	C19	C20	1.397(6)
S1	C15	1.795(4)	C19	C23	1.549(6)
S2	O7	1.431(4)	C23	C24	1.524(7)
S2	O8	1.431(4)	C23	C25	1.533(7)
S2	C32	1.803(4)	C23	C26	1.537(7)
S2	C41	1.791(4)	C27	C28	1.533(7)
O1	C8	1.397(5)	C28	C29	1.536(6)

Table S3 Bond Lengths for 5sa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C9	1.333(6)	C28	C47	1.520(7)
O4	C20	1.380(5)	C28	C48	1.529(7)
O5	C9	1.213(7)	C29	C30	1.401(6)
O6	C34	1.396(5)	C29	C46	1.394(6)
O6	C35	1.358(6)	C30	C31	1.382(6)
O9	C46	1.358(5)	C31	C32	1.525(5)
O10	C35	1.191(6)	C31	C44	1.373(6)
C1	C2	1.529(7)	C32	C33	1.519(5)
C2	C3	1.544(6)	C33	C34	1.377(5)
C2	C21	1.525(7)	C33	C37	1.381(6)
C2	C22	1.547(7)	C34	C40	1.374(6)
C3	C4	1.377(6)	C35	C36	1.469(7)
C3	C20	1.397(6)	C37	C38	1.376(6)
C4	C5	1.385(6)	C38	C39	1.370(7)
C5	C6	1.523(5)	C39	C40	1.354(7)
C5	C18	1.378(5)	C41	C42	1.498(7)
C6	C7	1.498(6)	C41	C43	1.519(6)
C7	C8	1.388(6)	C44	C45	1.395(6)
C7	C11	1.383(6)	C45	C46	1.413(6)
C8	C14	1.368(6)	C45	C49	1.539(6)
C9	C10	1.470(8)	C49	C50	1.530(7)
C11	C12	1.387(6)	C49	C51	1.528(7)
C12	C13	1.369(7)	C49	C52	1.534(7)

Table S4: Bond Angles for 5sa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	O3	118.3(2)	C3	C20	C19	122.2(4)
O2	S1	C6	105.9(2)	C24	C23	C19	109.9(4)
O2	S1	C15	107.6(2)	C24	C23	C25	111.0(4)
O3	S1	C6	109.29(19)	C24	C23	C26	107.3(5)
O3	S1	C15	109.0(2)	C25	C23	C19	111.4(4)
C15	S1	C6	106.1(2)	C25	C23	C26	106.9(4)
O7	S2	O8	118.1(2)	C26	C23	C19	110.2(4)
O7	S2	C32	105.9(2)	C27	C28	C29	111.0(4)
O7	S2	C41	107.8(2)	C47	C28	C27	108.1(5)
O8	S2	C32	110.0(2)	C47	C28	C29	110.3(4)
O8	S2	C41	108.8(2)	C47	C28	C48	109.7(4)
C41	S2	C32	105.53(19)	C48	C28	C27	106.7(5)
C9	O1	C8	121.5(4)	C48	C28	C29	110.8(4)
C35	O6	C34	119.4(3)	C30	C29	C28	120.8(4)
C1	C2	C3	110.6(4)	C46	C29	C28	121.5(4)

Table S4: Bond Angles for 5sa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	C2	C22	106.9(4)	C46	C29	C30	117.7(4)
C3	C2	C22	109.7(4)	C31	C30	C29	121.9(4)
C21	C2	C1	107.6(4)	C30	C31	C32	122.6(4)
C21	C2	C3	111.6(4)	C44	C31	C30	118.7(4)
C21	C2	C22	110.3(4)	C44	C31	C32	118.6(4)
C4	C3	C2	121.0(4)	C31	C32	S2	110.3(3)
C4	C3	C20	117.5(4)	C33	C32	S2	112.9(3)
C20	C3	C2	121.5(4)	C33	C32	C31	115.0(3)
C3	C4	C5	122.7(4)	C34	C33	C32	119.2(4)
C4	C5	C6	122.6(4)	C34	C33	C37	116.9(4)
C18	C5	C4	118.1(4)	C37	C33	C32	123.9(4)
C18	C5	C6	119.3(4)	C33	C34	O6	117.3(4)
C5	C6	S1	110.0(3)	C40	C34	O6	119.8(4)
C7	C6	S1	113.9(3)	C40	C34	C33	122.6(4)
C7	C6	C5	115.0(3)	O6	C35	C36	111.2(5)
C8	C7	C6	119.4(4)	O10	C35	O6	122.4(5)
C11	C7	C6	123.6(4)	O10	C35	C36	126.4(5)
C11	C7	C8	116.9(4)	C38	C37	C33	120.3(4)
C7	C8	O1	116.2(4)	C37	C38	Cl2	118.8(4)
C14	C8	O1	120.4(4)	C39	C38	Cl2	119.7(4)
C14	C8	C7	123.2(4)	C39	C38	C37	121.4(4)
O1	C9	C10	112.5(5)	C40	C39	C38	119.0(4)
O5	C9	O1	121.0(6)	C39	C40	C34	119.7(4)
O5	C9	C10	126.4(6)	C42	C41	S2	111.8(3)
C7	C11	C12	119.8(4)	C42	C41	C43	113.4(4)
C11	C12	Cl1	119.1(4)	C43	C41	S2	106.7(3)
C13	C12	Cl1	118.9(4)	C31	C44	C45	122.7(4)
C13	C12	C11	122.0(4)	C44	C45	C46	117.0(4)
C12	C13	C14	118.8(4)	C44	C45	C49	121.2(4)
C8	C14	C13	119.2(4)	C46	C45	C49	121.7(4)
C16	C15	S1	108.0(3)	O9	C46	C29	116.3(4)
C16	C15	C17	112.7(4)	O9	C46	C45	121.9(4)
C17	C15	S1	111.1(3)	C29	C46	C45	121.8(4)
C5	C18	C19	122.4(4)	C50	C49	C45	111.0(4)
C18	C19	C20	117.1(4)	C50	C49	C52	110.7(4)
C18	C19	C23	120.6(4)	C51	C49	C45	110.5(4)
C20	C19	C23	122.3(4)	C51	C49	C50	106.7(4)
O4	C20	C3	117.3(4)	C51	C49	C52	106.5(4)
O4	C20	C19	120.5(4)	C52	C49	C45	111.3(4)

10.Computational Studies

All the geometry optimizations and frequency calculations were carried out utilizing the Gaussian16 Rev. C. 01 suite of computational chemistry software.[14] Within this framework of Density Functional Theory (DFT), the PBE0 density functional was utilized.[15,16] Geometry optimizations and vibrational frequency calculations were conducted for the gas phase using the Ahlrichs basis set def2svp.[17] To simulate the solution phase, we utilized the Solvation Model based on Density (SMD) [18] with the def2tzvp [19] basis set to predict how solvents affect molecular properties and calculate solvation-free energies. The optimized geometries were confirmed through frequency calculations, which showed no imaginary frequencies for the different intermediate species. Transition states (TSs) were identified by a single imaginary frequency (negative value) and further confirmed by intrinsic reaction coordinate (IRC) calculations to link reactants and products. Single-point energy calculations with a def2tzvp basis set were carried out to obtain more accurate energies. Grimme's empirical dispersion with Becke-Johnson parameter (GD3BJ) empirical correction was employed to describe dispersion interactions accurately.[20, 21] The standard Gibbs free energy change (ΔG^{o}) was adjusted by adding 1.89 kcal mol^{-1}, which accounts for the change in standard state from 1 atm (gas phase) to 1 M (condensed phase).

To further inclusion the proposed mechanism, we explored the proposed pathways through DFT studies at Geometries of transition states TS1a-TS2a and TS1b, free energy profile for proposed mechanism for the formation of the desired product **3ba** and **5ba**.

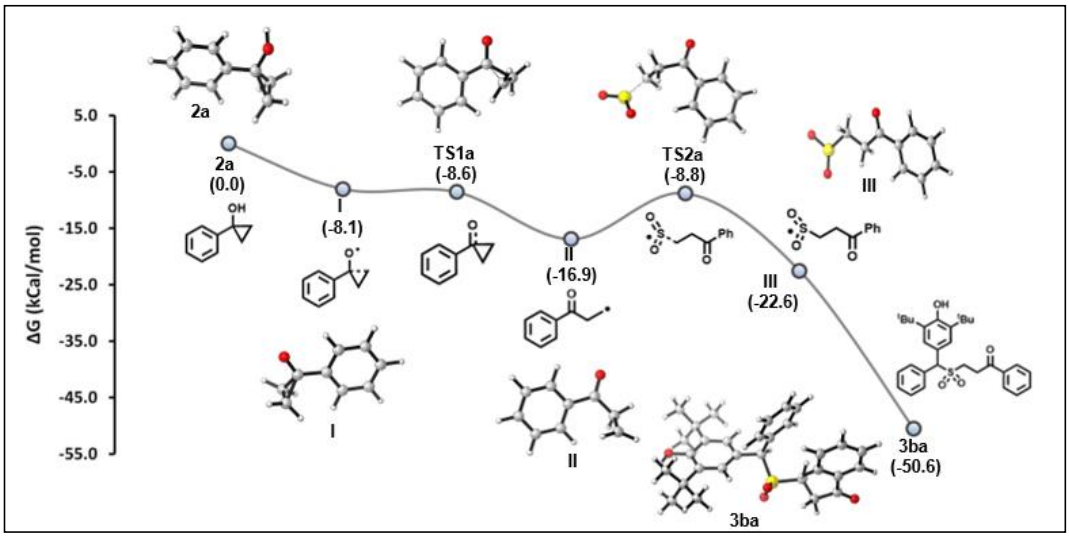


Figure S10. Free energy profile for the proposed mechanism for the formation of the desired product **(3ba)** starting from **(2a)** at the SMD/PBE0(D3BJ)/def2tzvp//PBE0(D3BJ)/def2svp level of theory. The values in parentheses represent relative free energies in kcal/mol. Optimized geometries of intermediates and transition states for the first mechanism at PBE0(D3BJ)/def2svp level of theory. Color code: white: hydrogen; grey: carbon; red: oxygen; yellow: sulfur.

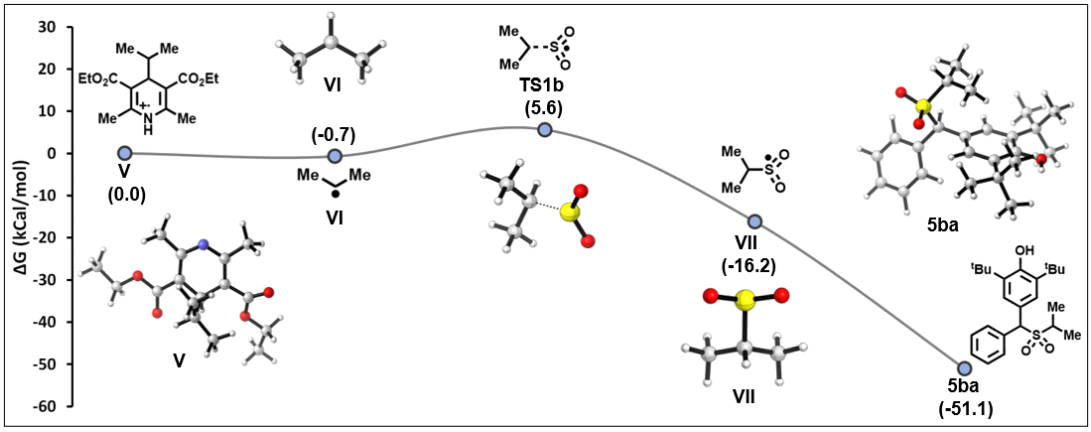


Figure S11. Free energy profile for the proposed mechanism for the formation of the desired product **5ba** starting from **V** at the SMD/PBE0(D3BJ)/def2tzvp// PBE0(D3BJ)/def2svp level of theory. The values in parentheses represent relative free energies in kcal/mol. Optimized geometries of intermediates and transition states for the first mechanism at PBE0(D3BJ)/def2svp level of theory. Color code: white: hydrogen; grey: carbon; blue: nitrogen; red: oxygen; yellow: sulfur.

Coordinates of the optimized structures

Eosin Y

Br	-2.209478000	-3.617620000	0.112279000
Br	2.316090000	-3.601625000	0.119165000
Br	-5.275913000	1.116192000	-0.354742000
Br	5.353306000	1.200010000	-0.235133000
O	0.043320000	-1.648321000	-0.047958000
O	-4.684748000	-1.817884000	-0.073232000
O	4.744295000	-1.756689000	-0.024067000
O	-0.400063000	3.929031000	2.928215000
O	-0.313643000	1.792480000	2.298270000
C	0.065659000	1.127780000	-0.278817000
C	-1.177557000	0.405343000	-0.243557000
C	1.254331000	0.435694000	-0.224653000
C	0.043077000	2.603302000	-0.448124000
C	-1.120877000	-0.993674000	-0.116053000
C	1.231988000	-1.004093000	-0.101023000
C	-2.439147000	1.020097000	-0.315877000
C	2.538931000	1.079417000	-0.257893000
C	-0.137044000	3.493723000	0.628346000
C	-2.293504000	-1.747844000	-0.058859000
C	2.378311000	-1.741112000	-0.035148000
C	0.196642000	3.121273000	-1.737352000
C	-3.600270000	0.274913000	-0.258366000
C	-3.552068000	-1.131532000	-0.125941000
C	3.682767000	0.359390000	-0.190538000
C	3.709974000	-1.123504000	-0.077592000
C	-0.156732000	4.873176000	0.392279000
C	0.172597000	4.495904000	-1.961892000
C	-0.005501000	5.374670000	-0.895679000
C	-0.288681000	2.962716000	2.010710000
H	-2.501674000	2.104095000	-0.417482000
H	2.574126000	2.166519000	-0.337803000
H	0.338176000	2.430065000	-2.571127000
H	-0.289859000	5.547536000	1.238810000
H	0.295991000	4.879902000	-2.977027000

H	-0.023195000	6.452924000	-1.066949000
H	-4.472936000	-2.762175000	0.018094000
H	-0.491489000	3.484873000	3.784943000

Eosin Y*

Br	-2.407440000	-3.503128000	0.139219000
Br	2.104003000	-3.675510000	0.102843000
Br	-5.325164000	1.332872000	-0.211406000
Br	5.362817000	0.871503000	-0.380740000
O	-0.092422000	-1.624988000	-0.066678000
O	-4.836566000	-1.632114000	0.019179000
O	4.582532000	-2.000477000	-0.087496000
O	0.931580000	3.885348000	2.880272000
O	0.428800000	1.792807000	2.308940000
C	0.009299000	1.170834000	-0.319736000
C	-1.242107000	0.490590000	-0.242827000
C	1.207665000	0.396801000	-0.272248000
C	0.062728000	2.642778000	-0.452979000
C	-1.242936000	-0.917245000	-0.114485000
C	1.105302000	-1.006600000	-0.137867000
C	-2.494065000	1.139070000	-0.263108000
C	2.500282000	0.949321000	-0.347456000
C	0.364619000	3.501527000	0.625860000
C	-2.434130000	-1.627463000	-0.028695000
C	2.234213000	-1.815391000	-0.076435000
C	-0.179606000	3.209981000	-1.709885000
C	-3.678709000	0.427179000	-0.177296000
C	-3.681674000	-0.975254000	-0.059945000
C	3.627132000	0.150791000	-0.284469000
C	3.516070000	-1.244436000	-0.146338000
C	0.433569000	4.885016000	0.417941000
C	-0.117971000	4.587392000	-1.904990000
C	0.194430000	5.428493000	-0.838928000
C	0.570088000	2.946908000	1.993295000
H	-2.528684000	2.225651000	-0.345398000
H	2.618696000	2.028279000	-0.457994000
H	-0.412850000	2.546753000	-2.546039000

H	0.670227000	5.531130000	1.263795000
H	-0.309524000	5.003739000	-2.896764000
H	0.249013000	6.509258000	-0.985701000
H	-4.646849000	-2.580729000	0.101046000
H	1.025824000	3.428751000	3.729798000

Eosin Y-H_radical

Br	-2.411302000	-3.503274000	0.138542000
Br	2.057052000	-3.669640000	0.101670000
Br	-5.339080000	1.327113000	-0.212414000
Br	5.337816000	0.912003000	-0.376324000
O	-0.100443000	-1.621149000	-0.065173000
O	-4.843417000	-1.638186000	0.018107000
O	4.583196000	-2.046591000	-0.080375000
O	0.899683000	3.902769000	2.878955000
O	0.405336000	1.806639000	2.313478000
C	-0.003303000	1.173150000	-0.315755000
C	-1.253956000	0.491851000	-0.240362000
C	1.196686000	0.400090000	-0.267667000
C	0.047595000	2.644853000	-0.453151000
C	-1.250131000	-0.915875000	-0.112776000
C	1.101127000	-1.005117000	-0.135119000
C	-2.506827000	1.138331000	-0.261655000
C	2.486109000	0.958087000	-0.342081000
C	0.342822000	3.508559000	0.623464000
C	-2.441164000	-1.627517000	-0.028235000
C	2.232474000	-1.813488000	-0.074513000
C	-0.191862000	3.207084000	-1.712917000
C	-3.690251000	0.424098000	-0.177023000
C	-3.689981000	-0.977818000	-0.060070000
C	3.607826000	0.149528000	-0.278597000
C	3.519349000	-1.247243000	-0.142753000
C	0.408482000	4.891591000	0.410839000
C	-0.133423000	4.583882000	-1.912905000
C	0.172593000	5.429895000	-0.848800000
C	0.544360000	2.959645000	1.993621000
H	-2.543613000	2.224885000	-0.343681000

H	2.598499000	2.037087000	-0.451013000
H	-0.420824000	2.540039000	-2.547207000
H	0.639670000	5.541428000	1.255361000
H	-0.322971000	4.996048000	-2.906835000
H	0.224259000	6.510320000	-0.999241000
H	-4.649428000	-2.586040000	0.099683000
H	0.989350000	3.449028000	3.730469000
H	5.382098000	-1.499239000	-0.140300000

Eosin Y_plus_radical

Br	-2.397405000	-3.529134000	0.119694000
Br	2.140187000	-3.664267000	0.106563000
Br	-5.263752000	1.328045000	-0.282608000
Br	5.343437000	1.003697000	-0.334409000
O	-0.065273000	-1.635704000	-0.050256000
O	-4.774702000	-1.594892000	-0.037975000
O	4.617666000	-1.930448000	-0.068389000
O	0.365335000	3.766912000	2.993159000
O	0.202948000	1.679140000	2.215338000
C	0.042090000	1.134856000	-0.266866000
C	-1.198352000	0.466766000	-0.234800000
C	1.234931000	0.373816000	-0.240335000
C	0.094487000	2.607551000	-0.439517000
C	-1.202248000	-0.951336000	-0.109906000
C	1.133346000	-1.035255000	-0.116638000
C	-2.443929000	1.142646000	-0.284554000
C	2.527130000	0.983307000	-0.307406000
C	0.208845000	3.473113000	0.664209000
C	-2.396210000	-1.664618000	-0.043409000
C	2.265435000	-1.840434000	-0.056527000
C	0.035567000	3.139615000	-1.729304000
C	-3.624456000	0.448564000	-0.218956000
C	-3.621854000	-0.981980000	-0.096111000
C	3.661854000	0.234742000	-0.251274000
C	3.616362000	-1.243676000	-0.120035000
C	0.265277000	4.854198000	0.462369000
C	0.094781000	4.520423000	-1.919174000

C	0.210073000	5.377111000	-0.826504000
C	0.257535000	2.873667000	2.022464000
H	-2.455248000	2.229293000	-0.374530000
H	2.585162000	2.067959000	-0.405134000
H	-0.052195000	2.471772000	-2.589349000
H	0.351164000	5.511282000	1.329179000
H	0.050185000	4.926086000	-2.932214000
H	0.255465000	6.457227000	-0.978614000
H	-4.644261000	-2.557555000	0.045789000
H	0.391595000	3.293462000	3.840102000

p-QM

symmetry c1

C	0.702460000	-1.613094000	-0.045765000
C	-0.541339000	-0.874216000	-0.066077000
C	-0.458676000	0.567921000	-0.123522000
C	0.717834000	1.239031000	-0.074387000
C	1.986295000	0.466877000	0.058785000
C	1.918722000	-1.020446000	0.022597000
H	0.619460000	-2.701380000	-0.057480000
H	-1.389636000	1.116106000	-0.254828000
C	-1.718344000	-1.572803000	-0.063989000
H	-1.631082000	-2.661468000	-0.160360000
C	-3.084774000	-1.076023000	0.026761000
C	-3.445908000	0.056363000	0.781503000
C	-4.106198000	-1.786861000	-0.631394000
C	-4.768553000	0.483371000	0.833237000
H	-2.687246000	0.578828000	1.366210000
C	-5.425460000	-1.352250000	-0.586726000
H	-3.847673000	-2.684297000	-1.199553000
C	-5.761199000	-0.210394000	0.141338000
H	-5.029439000	1.359443000	1.431594000
H	-6.199541000	-1.910590000	-1.118253000
H	-6.798895000	0.128360000	0.183916000
O	3.062267000	1.044543000	0.172615000
C	0.790088000	2.761675000	-0.162120000
C	3.219703000	-1.818091000	0.074996000

C	1.650191000	3.174149000	-1.368014000
H	1.682350000	4.272630000	-1.444249000
H	2.677198000	2.802480000	-1.268692000
H	1.221590000	2.782985000	-2.304226000
C	-0.598397000	3.379396000	-0.339376000
H	-1.089614000	3.036778000	-1.263438000
H	-1.263279000	3.154712000	0.509370000
H	-0.503934000	4.473879000	-0.401367000
C	1.397285000	3.322586000	1.135015000
H	2.415458000	2.945982000	1.289326000
H	1.432331000	4.422623000	1.084648000
H	0.781929000	3.043394000	2.004904000
C	4.110938000	-1.432084000	-1.117255000
H	4.374671000	-0.368018000	-1.086676000
H	5.040123000	-2.023461000	-1.094723000
H	3.599686000	-1.642139000	-2.070006000
C	3.952006000	-1.528236000	1.395775000
H	4.882250000	-2.116634000	1.443276000
H	4.206114000	-0.464909000	1.481589000
H	3.327514000	-1.812846000	2.257280000
C	2.957328000	-3.323313000	-0.000179000
H	2.352066000	-3.680775000	0.847526000
H	2.448977000	-3.607760000	-0.934842000
H	3.916474000	-3.861624000	0.030916000

p-QM+

C	0.603249000	1.596994000	0.083897000
C	-0.582885000	0.805061000	0.123653000
C	-0.445520000	-0.612948000	0.151617000
C	0.780553000	-1.228143000	0.078656000
C	1.932437000	-0.376630000	-0.039252000
C	1.861858000	1.053572000	-0.017381000
H	0.487680000	2.680557000	0.102229000
H	-1.336928000	-1.217719000	0.294994000
C	-1.806734000	1.472843000	0.169074000
H	-1.736614000	2.549297000	0.367113000
C	-3.141797000	0.987388000	0.010614000

C	-3.476860000	-0.205082000	-0.676999000
C	-4.187777000	1.777212000	0.547689000
C	-4.797868000	-0.609449000	-0.769619000
H	-2.702995000	-0.773639000	-1.193484000
C	-5.504796000	1.353366000	0.472476000
H	-3.943957000	2.717152000	1.049078000
C	-5.810295000	0.157573000	-0.181989000
H	-5.052553000	-1.517498000	-1.319665000
H	-6.300891000	1.958496000	0.910261000
H	-6.850183000	-0.168694000	-0.258656000
O	3.134558000	-0.900711000	-0.145248000
H	3.089964000	-1.867493000	-0.161853000
C	0.920777000	-2.756935000	0.148299000
C	3.119525000	1.926057000	-0.097040000
C	1.752621000	-3.166519000	1.379943000
H	1.811784000	-4.263288000	1.437663000
H	2.788297000	-2.792888000	1.389468000
H	1.277552000	-2.804094000	2.303358000
C	-0.449795000	-3.423893000	0.296964000
H	-0.961996000	-3.114720000	1.220261000
H	-1.106360000	-3.213713000	-0.560868000
H	-0.318525000	-4.513883000	0.346791000
C	1.537307000	-3.304997000	-1.155367000
H	2.569089000	-2.982534000	-1.371215000
H	1.563368000	-4.403766000	-1.115239000
H	0.930919000	-3.011421000	-2.024876000
C	4.042081000	1.627444000	1.097105000
H	4.410580000	0.594669000	1.096781000
H	4.916580000	2.293894000	1.056872000
H	3.523505000	1.814236000	2.050016000
C	3.849267000	1.674502000	-1.427476000
H	4.722507000	2.340387000	-1.495240000
H	4.208933000	0.642860000	-1.521694000
H	3.193059000	1.896249000	-2.283092000
C	2.754206000	3.411661000	-0.040658000
H	2.118521000	3.717985000	-0.885907000
H	2.249651000	3.682079000	0.899951000

H	3.675220000	4.008719000	-0.096304000

p-QM_radical

C	0.601747000	1.591153000	0.083540000
C	-0.580052000	0.819658000	0.160984000
C	-0.425631000	-0.582044000	0.188672000
C	0.816073000	-1.202750000	0.100596000
C	1.961848000	-0.378079000	-0.018046000
C	1.869717000	1.036879000	-0.013868000
H	0.491496000	2.675336000	0.086918000
H	-1.311901000	-1.193564000	0.331511000
C	-1.837173000	1.493845000	0.259388000
H	-1.776866000	2.554241000	0.525806000
C	-3.164833000	0.990603000	0.066645000
C	-3.476607000	-0.200642000	-0.636323000
C	-4.256612000	1.746964000	0.563870000
C	-4.791278000	-0.620773000	-0.789853000
H	-2.676867000	-0.772279000	-1.107977000
C	-5.566647000	1.319135000	0.412141000
H	-4.048243000	2.682009000	1.090883000
C	-5.846249000	0.125040000	-0.259045000
H	-4.999557000	-1.538412000	-1.346050000
H	-6.382939000	1.921356000	0.818857000
H	-6.877932000	-0.212402000	-0.380782000
O	3.203557000	-0.910965000	-0.125889000
H	3.141600000	-1.870088000	-0.119452000
C	0.929870000	-2.736645000	0.143117000
C	3.121148000	1.920254000	-0.114198000
C	1.766040000	-3.185350000	1.357377000
H	1.840369000	-4.283786000	1.383494000
H	2.792014000	-2.787896000	1.381946000
H	1.283402000	-2.853223000	2.288498000
C	-0.441712000	-3.401845000	0.295244000
H	-0.941823000	-3.103480000	1.228136000
H	-1.109385000	-3.163731000	-0.545859000
H	-0.315895000	-4.494780000	0.319902000
C	1.522956000	-3.269397000	-1.176274000

H	2.525009000	-2.885975000	-1.423270000
H	1.594689000	-4.367870000	-1.145065000
H	0.872187000	-2.992806000	-2.019110000
C	4.055722000	1.645409000	1.075208000
H	4.392793000	0.602145000	1.096295000
H	4.944330000	2.293807000	1.012116000
H	3.544331000	1.864181000	2.025586000
C	3.848407000	1.652262000	-1.441935000
H	4.735842000	2.300472000	-1.521503000
H	4.176452000	0.609070000	-1.523506000
H	3.188493000	1.876105000	-2.294552000
C	2.763932000	3.408761000	-0.080208000
H	2.118624000	3.699386000	-0.923199000
H	2.260012000	3.692095000	0.856486000
H	3.687318000	4.003182000	-0.151200000

2a

C	2.253000000	-0.683000000	0.875000000
C	2.299000000	-0.892000000	-0.608000000
C	1.430000000	0.192000000	-0.023000000
H	1.722000000	-1.410000000	1.496000000
H	3.111000000	-0.199000000	1.347000000
H	1.825000000	-1.777000000	-1.041000000
H	3.192000000	-0.545000000	-1.134000000
C	-0.061000000	0.058000000	-0.021000000
C	-0.852000000	1.208000000	0.075000000
C	-0.702000000	-1.186000000	-0.094000000
C	-2.243000000	1.121000000	0.089000000
H	-0.358000000	2.179000000	0.154000000
C	-2.091000000	-1.274000000	-0.076000000
H	-0.115000000	-2.105000000	-0.165000000
C	-2.870000000	-0.120000000	0.012000000
H	-2.840000000	2.033000000	0.165000000
H	-2.570000000	-2.255000000	-0.134000000
H	-3.960000000	-0.191000000	0.023000000
O	1.909000000	1.493000000	-0.132000000
H	1.734000000	1.789000000	-1.033000000

I

C	-2.345000000	-0.745000000	-0.725000000
C	-2.345000000	-0.745000000	0.725000000
C	-1.435000000	0.334000000	0.000000000
H	-1.780000000	-1.504000000	-1.272000000
H	-3.180000000	-0.286000000	-1.256000000
H	-1.780000000	-1.504000000	1.272000000
H	-3.180000000	-0.286000000	1.256000000
C	0.048000000	0.105000000	0.000000000
C	0.876000000	1.233000000	0.000000000
C	0.639000000	-1.165000000	0.000000000
C	2.262000000	1.095000000	0.000000000
H	0.403000000	2.216000000	0.000000000
C	2.025000000	-1.302000000	0.000000000
H	0.022000000	-2.068000000	0.000000000
C	2.842000000	-0.173000000	0.000000000
H	2.894000000	1.986000000	0.000000000
H	2.470000000	-2.300000000	0.000000000
H	3.929000000	-0.281000000	0.000000000
O	-1.901000000	1.526000000	0.000000000

II

C	2.587000000	-1.269000000	0.799000000
C	2.407000000	-0.405000000	-0.398000000
C	1.339000000	0.662000000	-0.209000000
H	3.565000000	-1.697000000	1.027000000
H	1.747000000	-1.520000000	1.451000000
H	2.145000000	-1.009000000	-1.293000000
H	3.339000000	0.125000000	-0.645000000
C	-0.093000000	0.237000000	-0.111000000
C	-0.517000000	-1.080000000	-0.332000000
C	-1.043000000	1.218000000	0.199000000
C	-1.868000000	-1.408000000	-0.241000000
H	0.207000000	-1.860000000	-0.577000000
C	-2.390000000	0.891000000	0.293000000
H	-0.688000000	2.239000000	0.359000000

C	-2.804000000	-0.424000000	0.073000000
H	-2.191000000	-2.436000000	-0.416000000
H	-3.125000000	1.662000000	0.537000000
H	-3.864000000	-0.683000000	0.145000000
O	1.645000000	1.831000000	-0.128000000

III

C	3.384000000	-1.649000000	-0.145000000
C	2.089000000	-1.138000000	-0.138000000
C	1.875000000	0.240000000	-0.007000000
C	2.977000000	1.098000000	0.118000000
C	4.269000000	0.587000000	0.111000000
C	4.474000000	-0.788000000	-0.021000000
H	3.544000000	-2.724000000	-0.246000000
H	1.246000000	-1.826000000	-0.232000000
H	2.784000000	2.168000000	0.221000000
H	5.123000000	1.261000000	0.208000000
H	5.489000000	-1.190000000	-0.027000000
C	0.516000000	0.851000000	0.008000000
O	0.360000000	2.045000000	0.151000000
C	-0.683000000	-0.063000000	-0.165000000
H	-0.588000000	-0.592000000	-1.128000000
H	-0.671000000	-0.845000000	0.611000000
C	-1.974000000	0.715000000	-0.093000000
H	-2.088000000	1.459000000	-0.892000000
H	-2.107000000	1.229000000	0.871000000
S	-3.426000000	-0.387000000	-0.222000000
O	-4.614000000	0.480000000	-0.094000000
O	-3.181000000	-1.509000000	0.713000000

5ba

C	-2.389098000	1.192327000	-0.799133000
C	-1.419829000	0.262979000	-0.426865000
C	-1.818609000	-0.890932000	0.241853000
C	-3.158385000	-1.142521000	0.540105000
C	-4.110639000	-0.171596000	0.158060000
C	-3.742808000	1.013930000	-0.518380000

C	-2.068115000	2.091541000	-1.324966000
H	-1.064166000	-1.625734000	0.515553000
C	0.026331000	0.573463000	-0.722461000
C	0.787775000	1.268538000	0.376276000
C	0.719699000	0.820074000	1.700283000
C	1.596258000	2.370730000	0.076797000
C	1.449505000	1.460129000	2.696925000
H	0.086820000	-0.033447000	1.946406000
C	2.330853000	3.009343000	1.074019000
H	1.647634000	2.738188000	-0.952509000
C	2.259610000	2.553263000	2.387663000
H	1.384693000	1.101754000	3.727143000
H	2.958550000	3.866925000	0.822117000
H	2.833937000	3.050972000	3.172370000
O	-5.429691000	-0.341463000	0.421488000
H	-5.560586000	-1.184785000	0.863829000
C	-3.563726000	-2.446077000	1.247523000
C	-4.785556000	2.059472000	-0.935809000
C	-4.497288000	-3.277029000	0.345744000
H	-4.777171000	-4.214688000	0.850779000
H	-5.431672000	-2.771083000	0.057765000
H	-3.981880000	-3.533260000	-0.591630000
C	-2.345490000	-3.329078000	1.536901000
H	-1.815427000	-3.613828000	0.616520000
H	-1.626526000	-2.832258000	2.204851000
H	-2.675912000	-4.253706000	2.033684000
C	-4.218945000	-2.144291000	2.609169000
H	-5.123405000	-1.518637000	2.558577000
H	-4.500235000	-3.082883000	3.111728000
H	-3.509380000	-1.609160000	3.257773000
C	-5.796552000	1.433616000	-1.910292000
H	-6.336555000	0.595889000	-1.453197000
H	-6.533787000	2.190089000	-2.223700000
H	-5.284717000	1.064849000	-2.812747000
C	-5.505377000	2.607620000	0.307154000
H	-6.242964000	3.369596000	0.008284000
H	-6.031207000	1.816216000	0.854550000

H	-4.785491000	3.083352000	0.991310000
C	-4.135982000	3.248054000	-1.649983000
H	-3.412803000	3.772974000	-1.006980000
H	-3.623411000	2.945174000	-2.575949000
H	-4.916203000	3.972461000	-1.928057000
H	0.073534000	1.178969000	-1.641347000
S	0.892083000	-0.966275000	-1.225943000
C	2.453833000	-0.369742000	-1.890987000
O	1.215848000	-1.737045000	-0.011365000
O	0.134536000	-1.605496000	-2.297384000
H	2.231531000	0.064583000	-2.875310000
H	2.782858000	0.427272000	-1.208397000
C	3.464479000	-1.511704000	-1.958440000
H	3.226327000	-2.251614000	-1.176693000
H	3.429321000	-2.015142000	-2.931989000
C	4.876093000	-0.998001000	-1.744737000
C	5.222413000	-0.444615000	-0.397526000
C	4.370053000	-0.542709000	0.712397000
C	6.463871000	0.190836000	-0.258924000
C	4.760452000	-0.006967000	1.937535000
H	3.394815000	-1.031696000	0.638384000
C	6.847335000	0.727535000	0.963794000
H	7.111223000	0.245512000	-1.136795000
C	5.993884000	0.629076000	2.064798000
H	4.089299000	-0.084439000	2.794872000
H	7.815759000	1.223459000	1.063803000
H	6.294025000	1.050212000	3.027647000
O	5.687181000	-1.016942000	-2.643158000

V

C	-1.419000000	1.552000000	-0.302000000
C	-1.150000000	0.202000000	-0.105000000
C	0.241000000	-0.231000000	0.213000000
C	1.258000000	0.781000000	-0.172000000
C	0.873000000	2.112000000	-0.326000000
N	-0.424000000	2.469000000	-0.328000000
C	0.333000000	-0.577000000	1.762000000

H	-0.489000000	-1.294000000	1.916000000
C	1.628000000	-1.286000000	2.131000000
H	1.814000000	-2.158000000	1.489000000
H	2.500000000	-0.616000000	2.064000000
H	1.571000000	-1.635000000	3.173000000
C	0.104000000	0.639000000	2.647000000
H	0.920000000	1.371000000	2.545000000
H	-0.841000000	1.151000000	2.416000000
H	0.067000000	0.333000000	3.704000000
C	1.840000000	3.238000000	-0.533000000
H	2.510000000	3.347000000	0.331000000
H	2.497000000	3.054000000	-1.396000000
H	1.268000000	4.161000000	-0.687000000
C	-2.785000000	2.138000000	-0.512000000
H	-3.250000000	1.748000000	-1.428000000
H	-3.467000000	1.884000000	0.312000000
H	-2.678000000	3.226000000	-0.588000000
C	2.664000000	0.370000000	-0.357000000
C	-2.133000000	-0.897000000	-0.133000000
O	3.634000000	1.086000000	-0.253000000
O	-1.825000000	-2.061000000	0.008000000
O	2.756000000	-0.925000000	-0.694000000
O	-3.399000000	-0.515000000	-0.339000000
C	-4.369000000	-1.557000000	-0.389000000
H	-4.338000000	-2.122000000	0.556000000
H	-4.094000000	-2.265000000	-1.187000000
C	-5.717000000	-0.927000000	-0.629000000
H	-6.493000000	-1.705000000	-0.674000000
H	-5.976000000	-0.229000000	0.180000000
H	-5.730000000	-0.373000000	-1.579000000
C	4.072000000	-1.441000000	-0.863000000
H	4.590000000	-0.855000000	-1.639000000
H	4.637000000	-1.292000000	0.072000000
C	3.958000000	-2.897000000	-1.231000000
H	3.387000000	-3.022000000	-2.163000000
H	4.958000000	-3.329000000	-1.378000000
H	3.450000000	-3.466000000	-0.439000000

H	0.443000000	-1.188000000	-0.292000000

VI

C	0.000000000	0.530000000	-0.050000000
C	1.293000000	-0.197000000	0.003000000
C	-1.293000000	-0.197000000	0.003000000
H	0.000000000	1.613000000	0.112000000
H	2.143000000	0.446000000	-0.274000000
H	1.509000000	-0.591000000	1.019000000
H	1.295000000	-1.074000000	-0.668000000
H	-2.143000000	0.446000000	-0.273000000
H	-1.295000000	-1.073000000	-0.668000000
H	-1.508000000	-0.591000000	1.019000000

VII

C	0.922000000	0.000000000	0.362000000
C	1.601000000	1.280000000	-0.073000000
C	1.602000000	-1.280000000	-0.073000000
H	0.739000000	0.000000000	1.451000000
H	1.022000000	2.161000000	0.232000000
H	2.597000000	1.339000000	0.393000000
H	1.739000000	1.308000000	-1.165000000
H	1.022000000	-2.161000000	0.231000000
H	1.739000000	-1.308000000	-1.165000000
H	2.598000000	-1.339000000	0.393000000
S	-0.835000000	0.000000000	-0.266000000
O	-1.428000000	1.286000000	0.161000000
O	-1.428000000	-1.286000000	0.162000000

3ba

C	-0.735980000	-1.148581000	-0.838262000
C	0.224439000	-0.284714000	-0.314609000
C	-0.189511000	0.946537000	0.190682000
C	-1.530583000	1.326448000	0.203852000
C	-2.476692000	0.416245000	-0.322165000
C	-2.095764000	-0.835992000	-0.856328000
H	-0.404131000	-2.106316000	-1.239623000

H	0.563299000	1.596734000	0.629896000
C	1.660297000	-0.714012000	-0.247033000
C	2.664639000	0.058105000	-1.076197000
C	2.337019000	1.260391000	-1.709654000
C	3.956185000	-0.462025000	-1.243873000
C	3.280769000	1.935737000	-2.481391000
H	1.329480000	1.666561000	-1.615299000
C	4.898349000	0.216918000	-2.009904000
H	4.225751000	-1.395040000	-0.747055000
C	4.565471000	1.420104000	-2.630857000
H	3.004505000	2.872195000	-2.971882000
H	5.901373000	-0.200773000	-2.124399000
H	5.305213000	1.951135000	-3.234685000
O	-3.799768000	0.708658000	-0.330945000
H	-3.936644000	1.579942000	0.051747000
C	-1.948105000	2.675241000	0.812126000
C	-3.129701000	-1.820352000	-1.418697000
C	-2.852881000	2.446873000	2.038364000
H	-3.146566000	3.411669000	2.480443000
H	-3.777750000	1.887841000	1.828321000
H	-2.308299000	1.872967000	2.802984000
C	-0.731738000	3.463675000	1.308686000
H	-0.174214000	2.920026000	2.085115000
H	-0.033999000	3.697225000	0.491083000
H	-1.068070000	4.417503000	1.742208000
C	-2.640550000	3.561079000	-0.241482000
H	-3.554290000	3.133834000	-0.683118000
H	-2.919148000	4.529483000	0.202267000
H	-1.954634000	3.755079000	-1.079532000
C	-4.118717000	-2.226448000	-0.313774000
H	-4.668231000	-1.362369000	0.078478000
H	-4.849345000	-2.949654000	-0.709942000
H	-3.586254000	-2.707515000	0.521875000
C	-3.876370000	-1.182313000	-2.601226000
H	-4.608578000	-1.895635000	-3.012098000
H	-4.412443000	-0.273978000	-2.301215000
H	-3.171777000	-0.919885000	-3.405644000

C	-2.465927000	-3.101120000	-1.932171000
H	-1.754888000	-2.901467000	-2.748367000
H	-1.935397000	-3.642516000	-1.133536000
H	-3.240108000	-3.775871000	-2.327150000
H	1.739911000	-1.780523000	-0.505712000
S	2.244973000	-0.700378000	1.509626000
C	1.083139000	-1.705780000	2.496224000
O	3.511126000	-1.442998000	1.545426000
O	2.204510000	0.673870000	2.020566000
C	0.917106000	-3.090223000	1.896818000
C	-0.212777000	-1.002660000	2.851107000
H	1.720729000	-1.775698000	3.395983000
H	1.890972000	-3.522324000	1.627292000
H	0.440352000	-3.753871000	2.633982000
H	0.268179000	-3.064852000	1.008579000
H	-0.018812000	0.034675000	3.155895000
H	-0.921691000	-0.997844000	2.011766000
H	-0.683717000	-1.529708000	3.695531000

11.Biological Studies

MATERIALS AND METHODS

Cell culture

The human tongue OSCC cell lines H357 and SCC9 were purchased from European Collection of Authenticated Cell Culture (ECACC). All OSCC cell lines were cultured and maintained in DMEM-F12 medium (Gibco, Cat #12500062) supplemented with 10% Fetal Bovine Serum (FBS; Gibco, Cat #10270106), 1x Penicillin–Streptomycin (Himedia, Cat #A001A) and 0.5µg/mL of hydrocortisone 21-hemisuccinate sodium salt (Sigma Aldrich, Cat #H2270). Cells were cultured in a humidified atmosphere maintaining a 5% CO_2 level and 37°C.

Compound Screening and cell viability assay

All the compounds were prepared as stock solutions in DMSO, at a concentration of 10 mM and 1mM. Approximately 3000 cells were seeded in 96 well polystyrene coated plate (Corning # 3599). After 24 hours, cells were treated with each compound at a final concentration of 0.5, 2.5, 5 and 10µM. After 48h of treatment, cell viability was determined by MTT assay. Here, MTT (Sigma-Aldrich, Cat #M2128) solution (0.5 mg/ml) was added to each well and then incubated for 3 hours. Post incubation, the medium was discarded and the formazan crystals were dissolved by adding 80µl of DMSO into each well. Thereafter, absorbance at 570 nm was measured by Victor Nivo Multimode Plate Reader (in-house ILS facility).

Determining 50% Inhibitory Concentration (IC_{50})

Graph representing cell viability (%) vs drug concentration (µM) in each cell line was plotted for each compound. The concentration required to inhibit growth by 50% (IC_{50}) of each compound was determined from the slope of the graph.

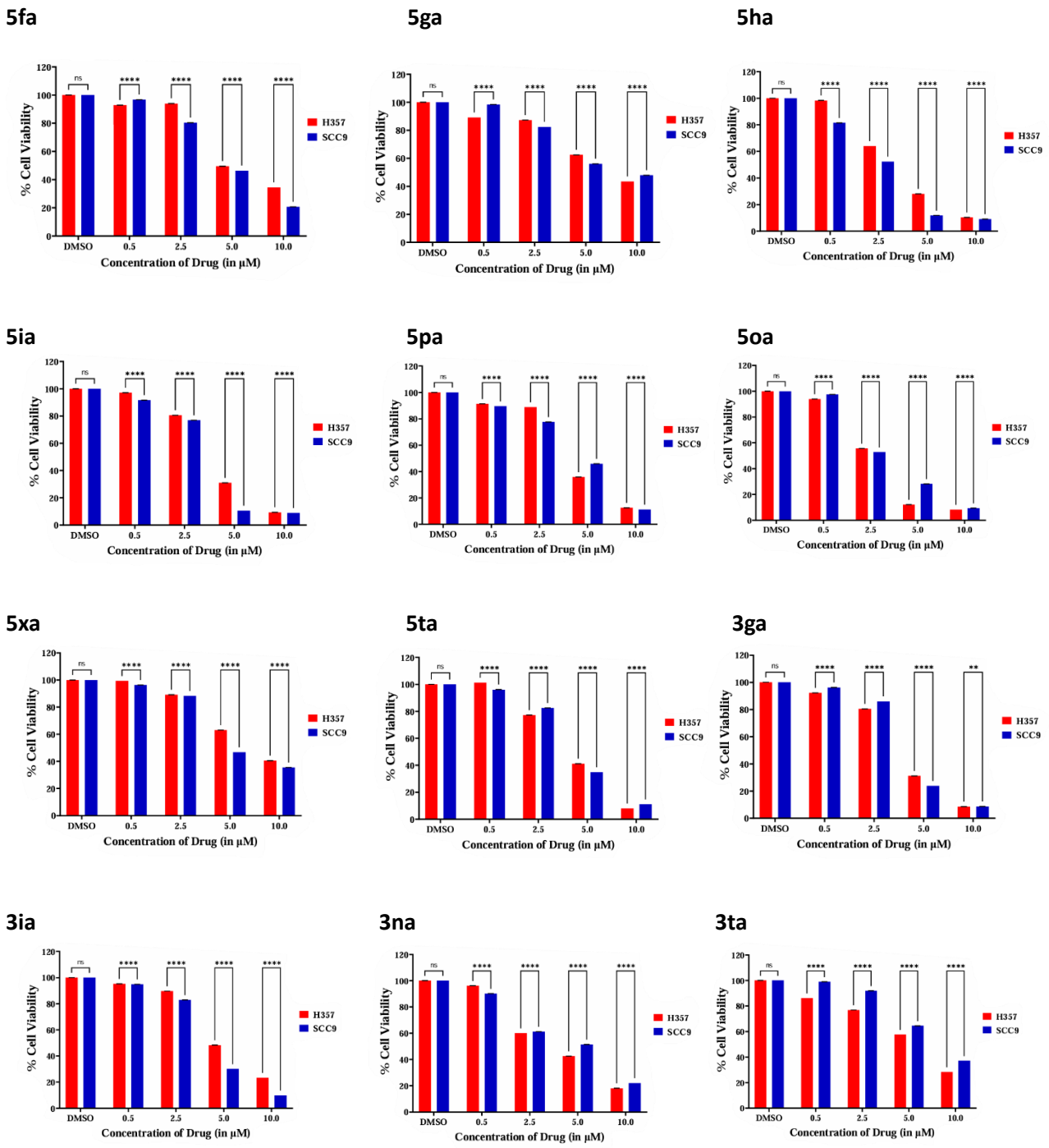


Figure S12: Screening of 20 compounds to determine their anticancer efficacies in OSCC cell lines, i.e., **H357** and **SCC9**. Cells were treated with each compound at indicated concentration for 48h and cell viability was determined by MTT assay (Technical replicates n ≥ 2 and 2-way ANOVA, **P<0.01,***P<0.001,****P.

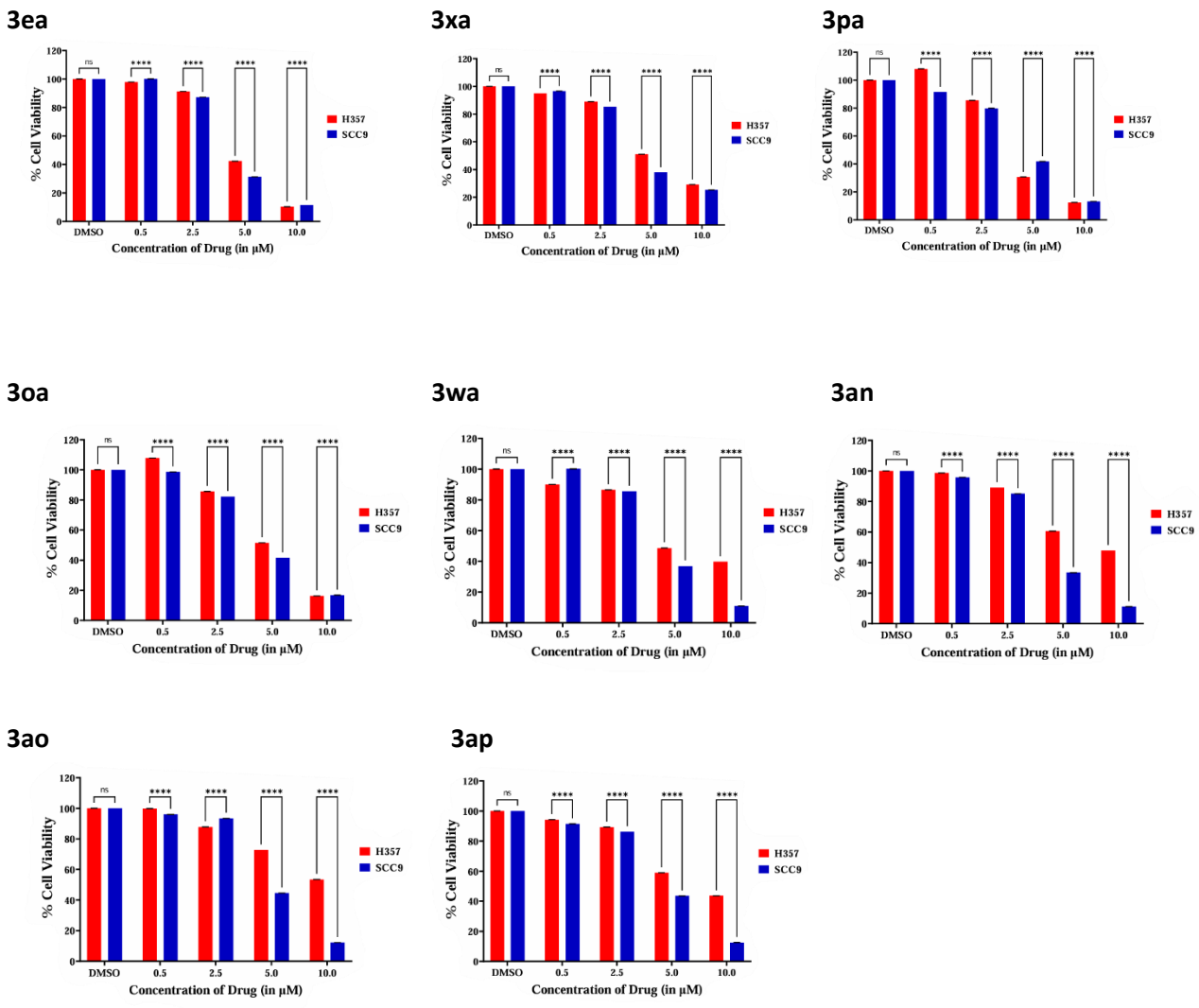
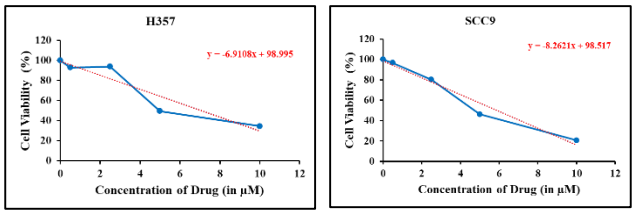


Figure S12: Screening of 20 compounds to determine their anticancer efficacies in OSCC cell lines, i.e., H357 and SCC9. Cells were treated with each compound at indicated concentration for 48h and cell viability was determined by MTT assay (Technical replicates n ≥ 2 and 2-way ANOVA, **P<0.01,***P<0.001,****P

5fa



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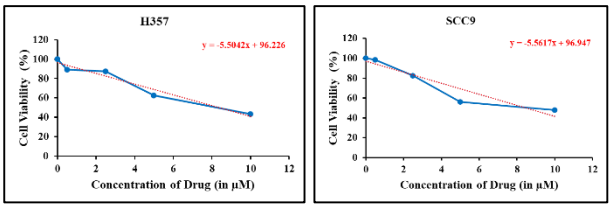

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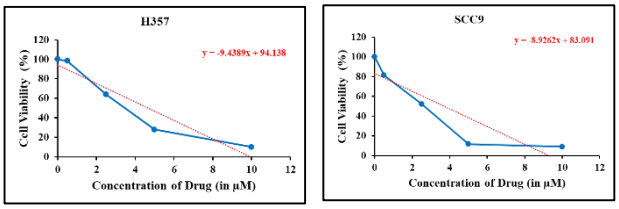

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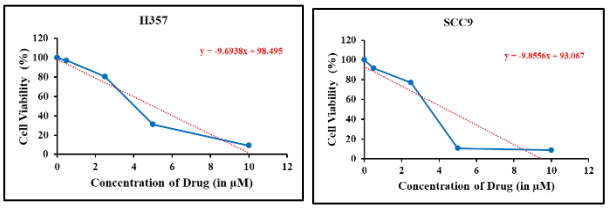

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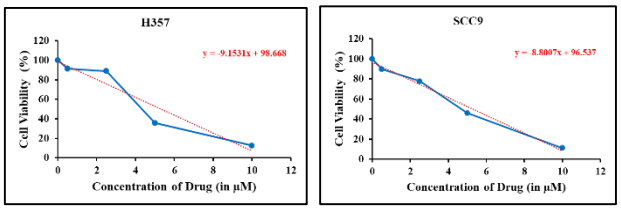

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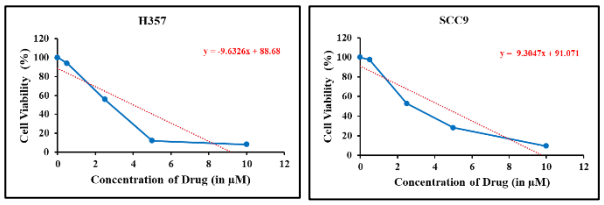

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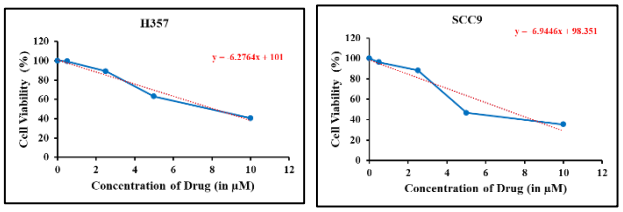

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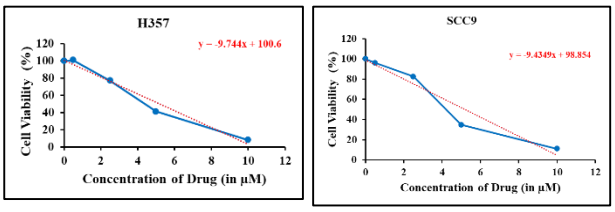

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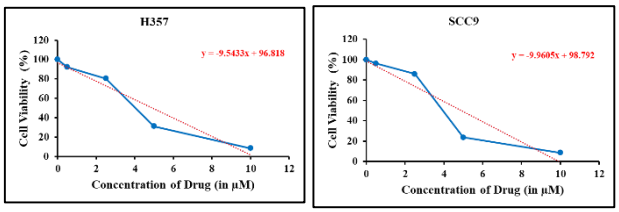

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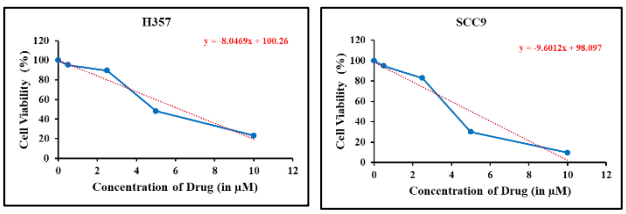
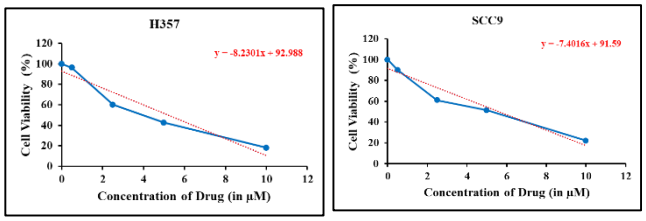


Figure S13: Cell viability versus Concentration of Compound

3na



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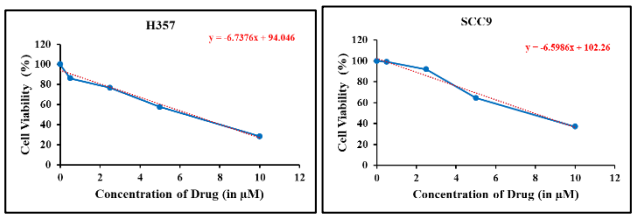

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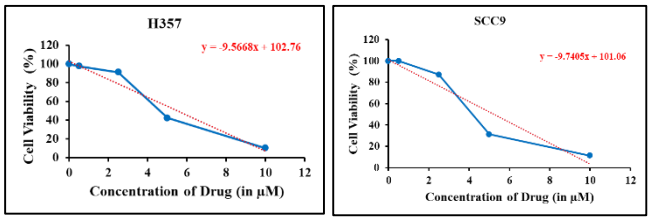

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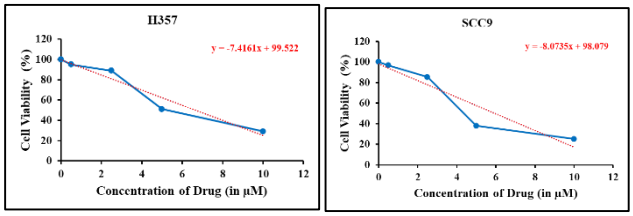

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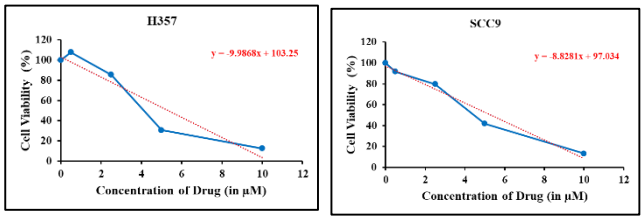

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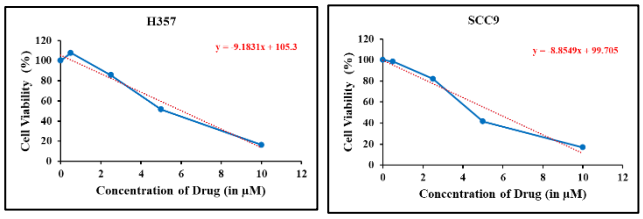

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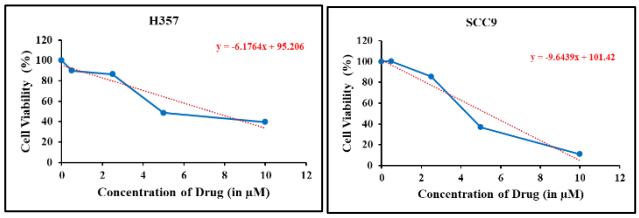

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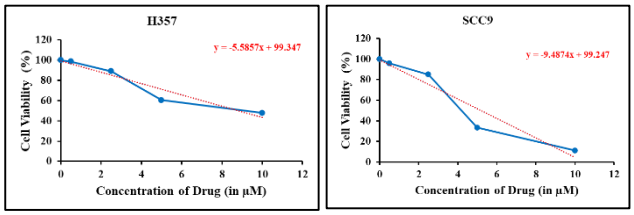

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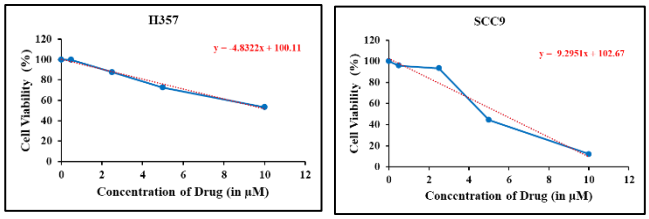

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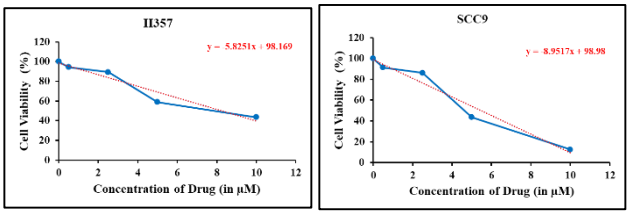

Figure S13: Cell viability versus Concentration of Compounds

Sr. No.	COMPOUND	IC_{50} values (in µM)	
		H357	**SCC9**
1	**3ga**	4.91	4.90
2	**3ia**	6.25	5.01
3	**3na**	5.22	5.62
4	**3ta**	6.54	7.92
5	**3ea**	5.51	5.24
6	**3xa**	6.68	5.96
7	**3pa**	5.33	5.33
8	**3oa**	6.02	5.61
9	**3wa**	7.32	5.33
10	**3an**	8.83	5.19
11	**3ao**	10.37	5.67
12	**3ap**	8.27	5.47
13	**5fa**	7.09	5.87
14	**5ga**	8.40	8.44
15	**5ha**	4.74	3.71
16	**5ia**	5.00	4.37
17	**5pa**	5.32	5.29
18	**5oa**	4.02	4.41
19	**5xa**	8.13	6.96
20	**5ta**	5.19	5.18

Table S5: Representing IC-50 values of 20 compounds in H357 and SCC9 cell line.

RESULTS

Compound Screening

To identify potential compounds that inhibit oral cell squamous cell carcinomas (OSCC) line growth, we performed a cell viability assay using 20 modified chemical compounds in two different human OSCC cell lines, i.e., H357 and SCC9. In brief, all the compounds were screened at a concentration of 0.5, 2.5, 5 and 10 μM and the cell viability was measured by MTT assay. All the compounds, except compound 3ao, exhibited greater than 50% reduction in cell viability within 10μM in both the cell lines. Among them, four compounds i.e., **5ha**, **5ia**, **5oa** and **3ga** had an $IC_{50} \leq 5\mu M$ in both H357 and SCC9.

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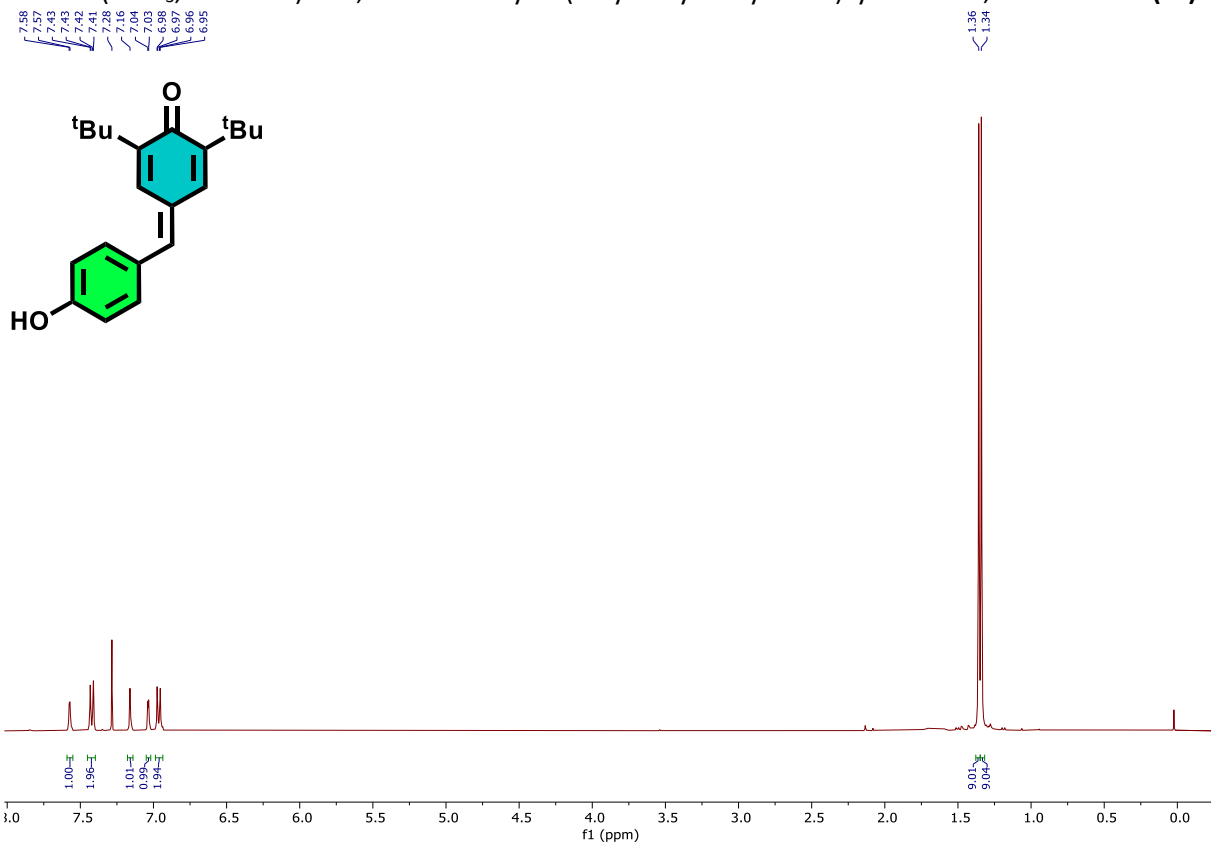
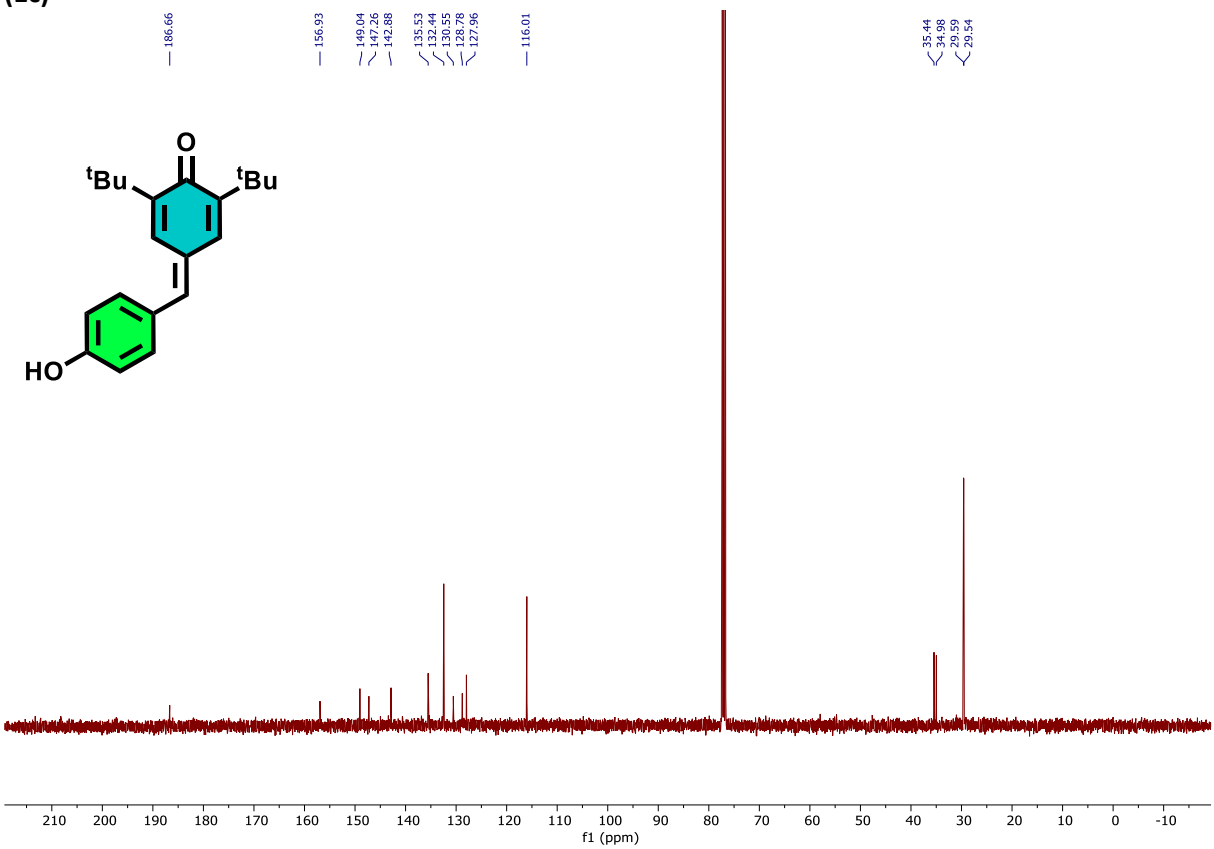
13. Spectral Data

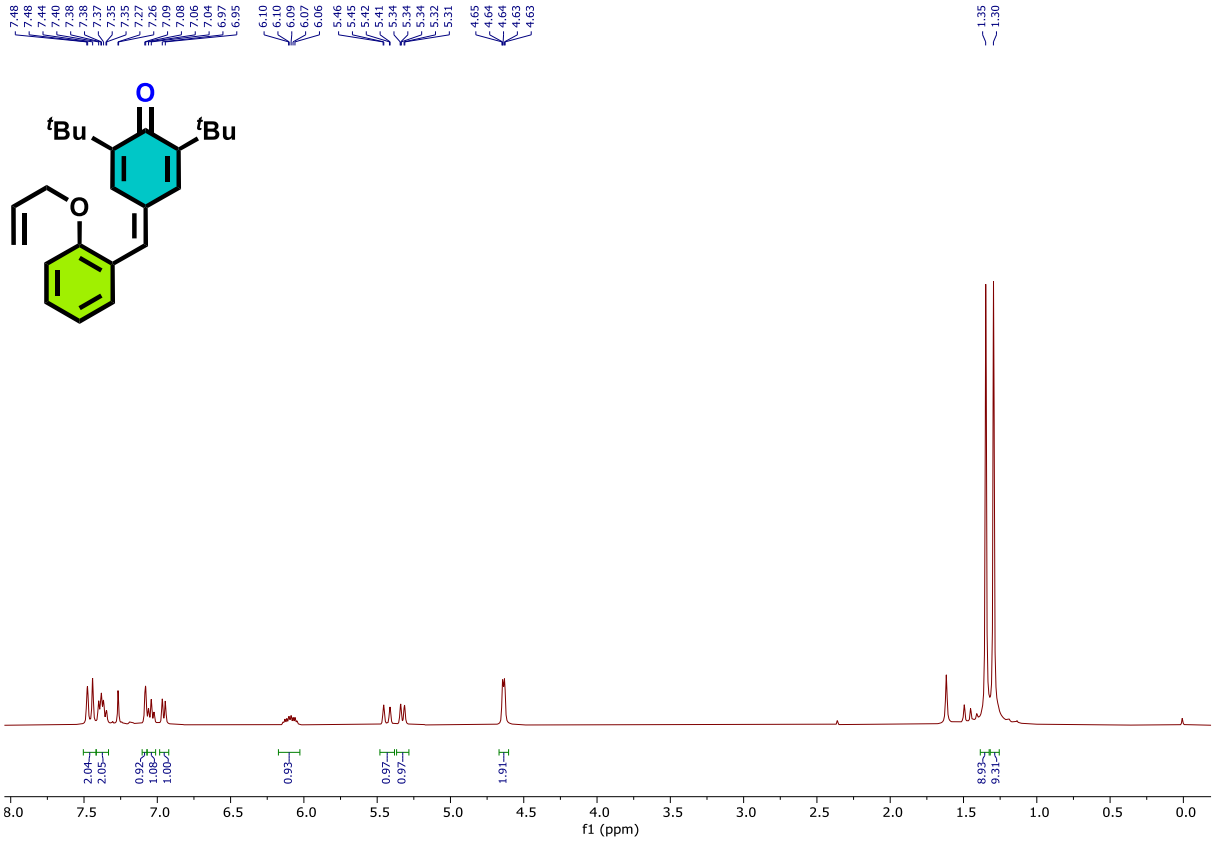
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(4-hydroxybenzylidene)cyclohexa-2,5-dien-1-one **(1c)**



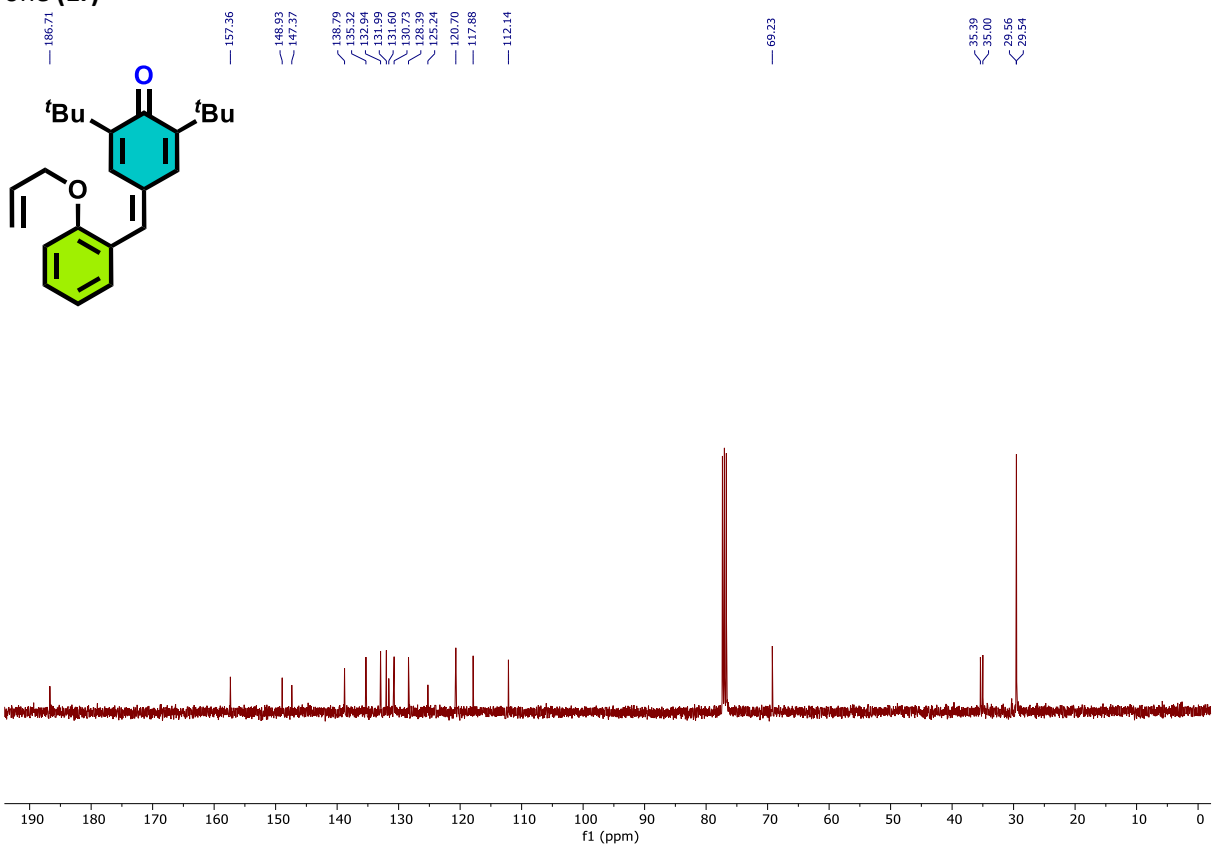
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(4-hydroxybenzylidene)cyclohexa-2,5-dien-1-one **(1c)**



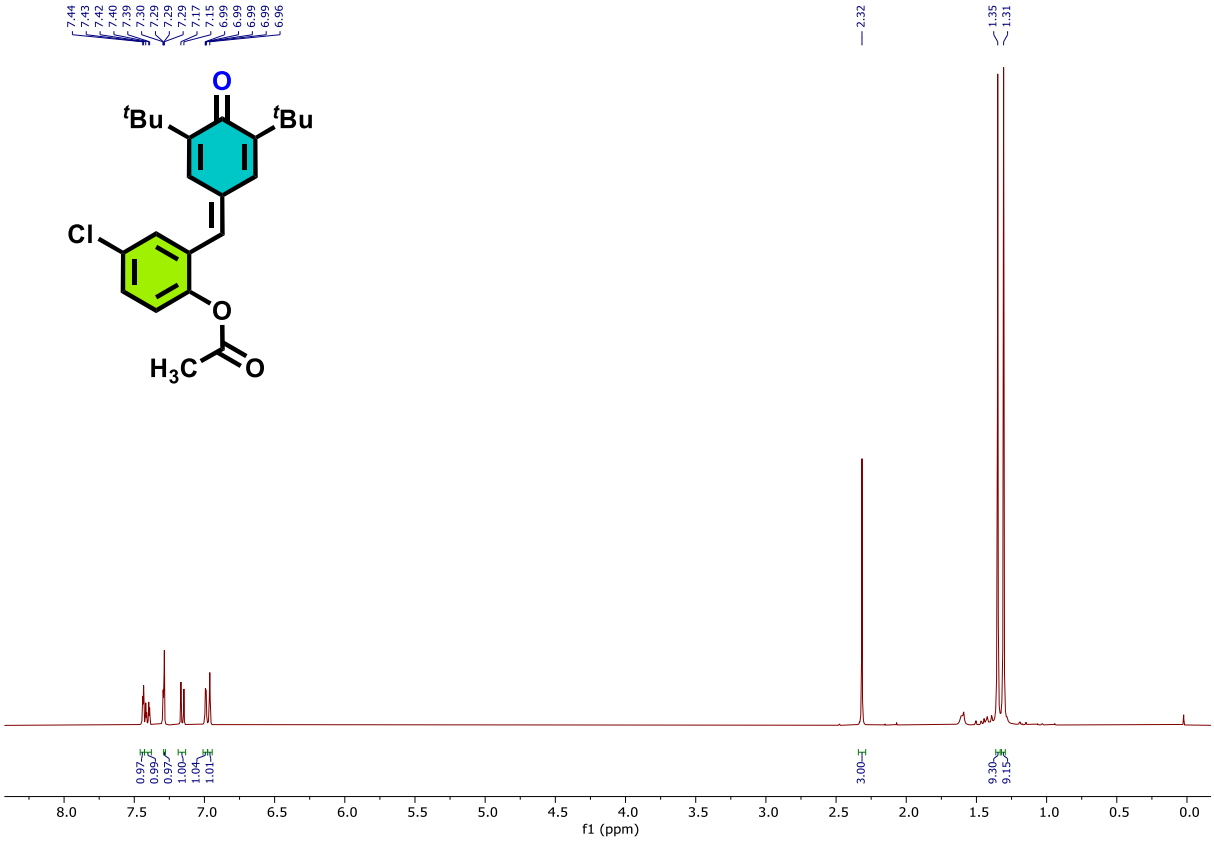
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-(2-(allyloxy)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(1r)**



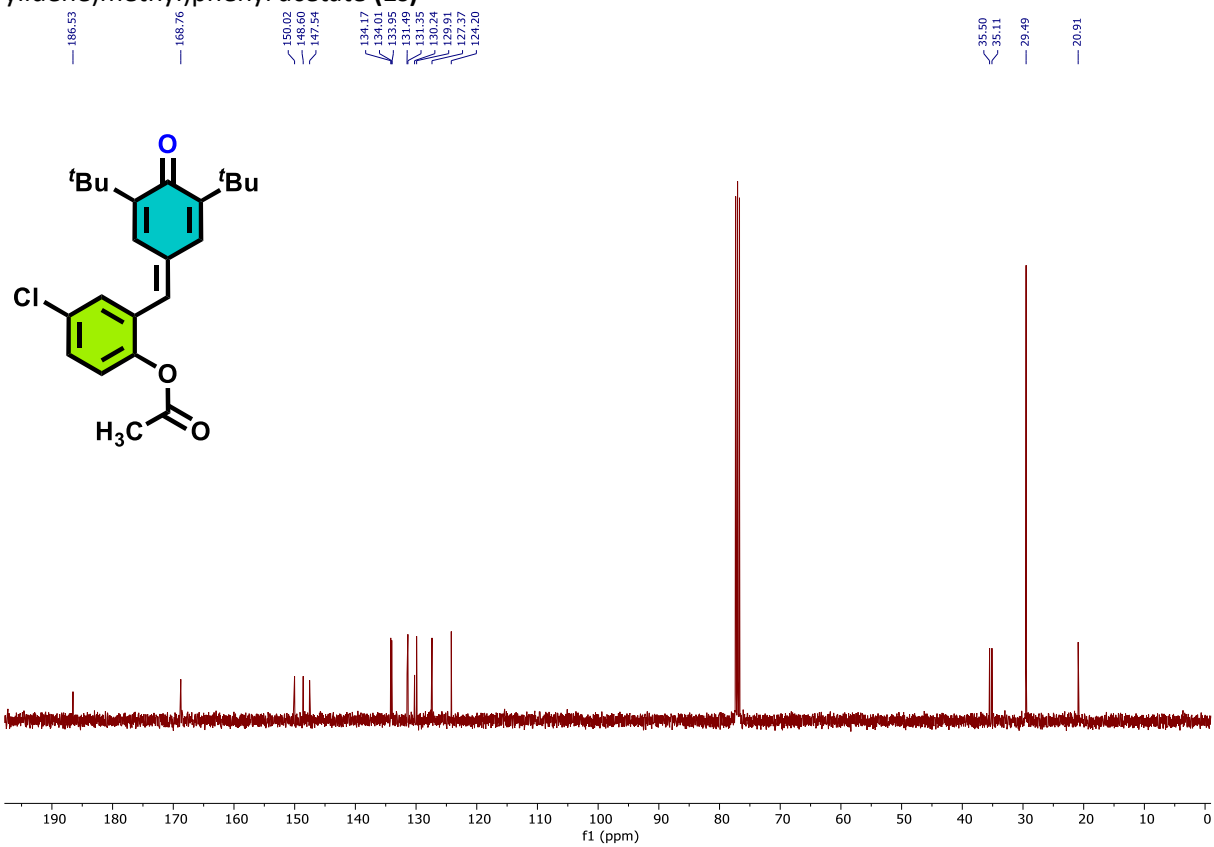
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-(2-(allyloxy)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **(1r)**



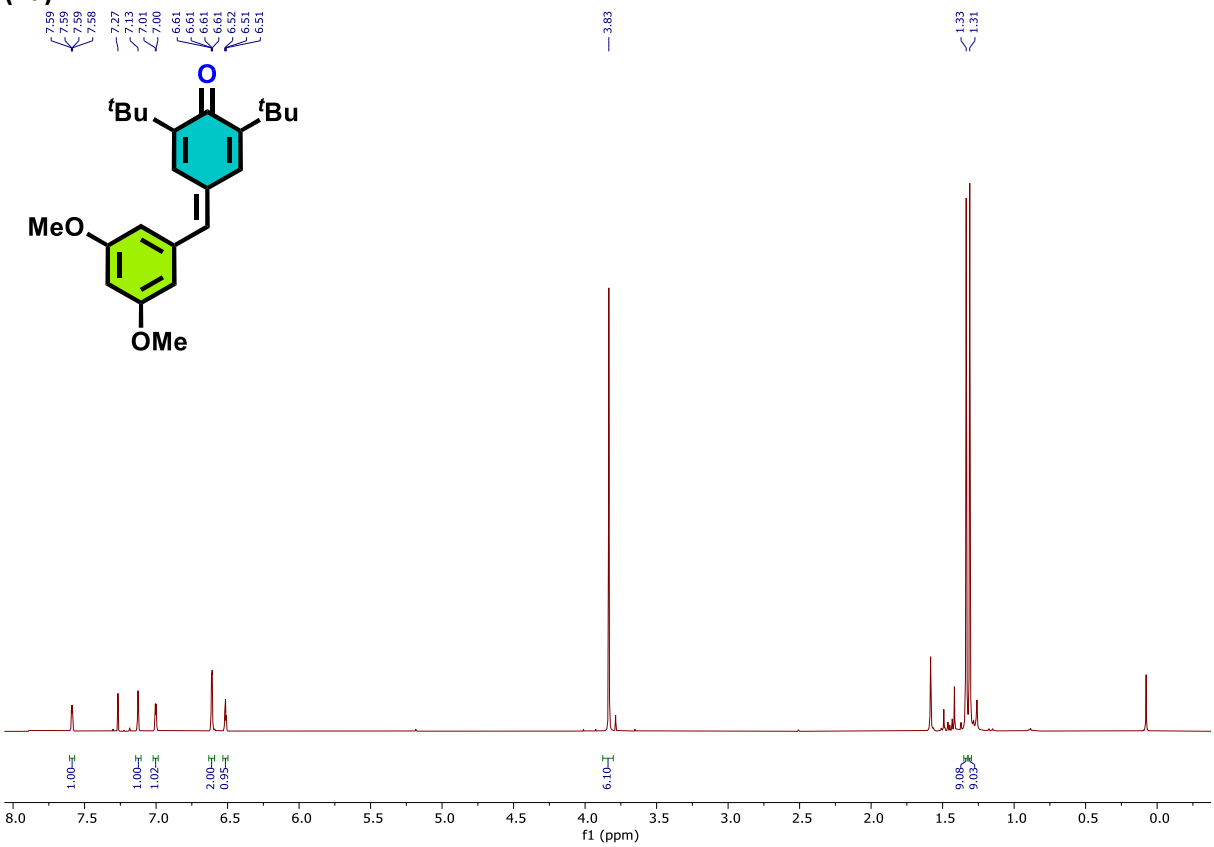
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-chloro-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl acetate **(1s)**



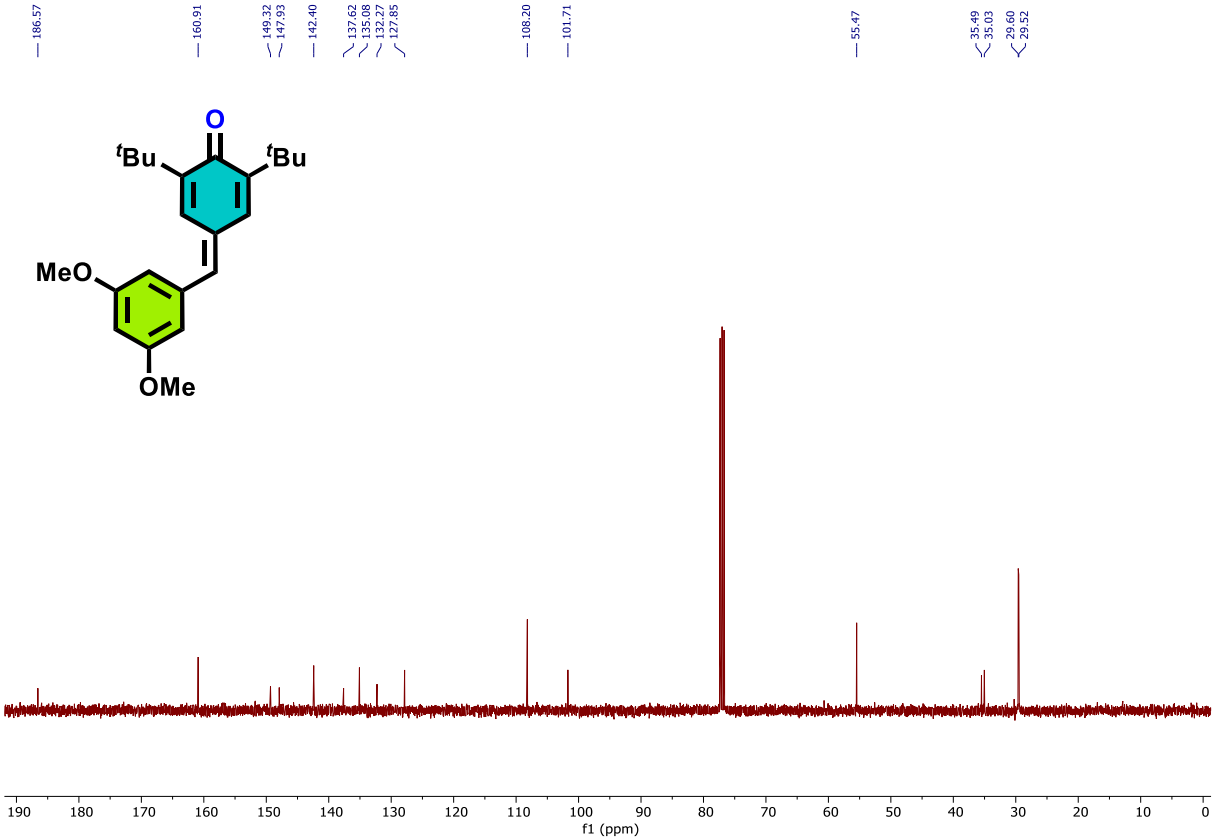
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-chloro-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl acetate **(1s)**



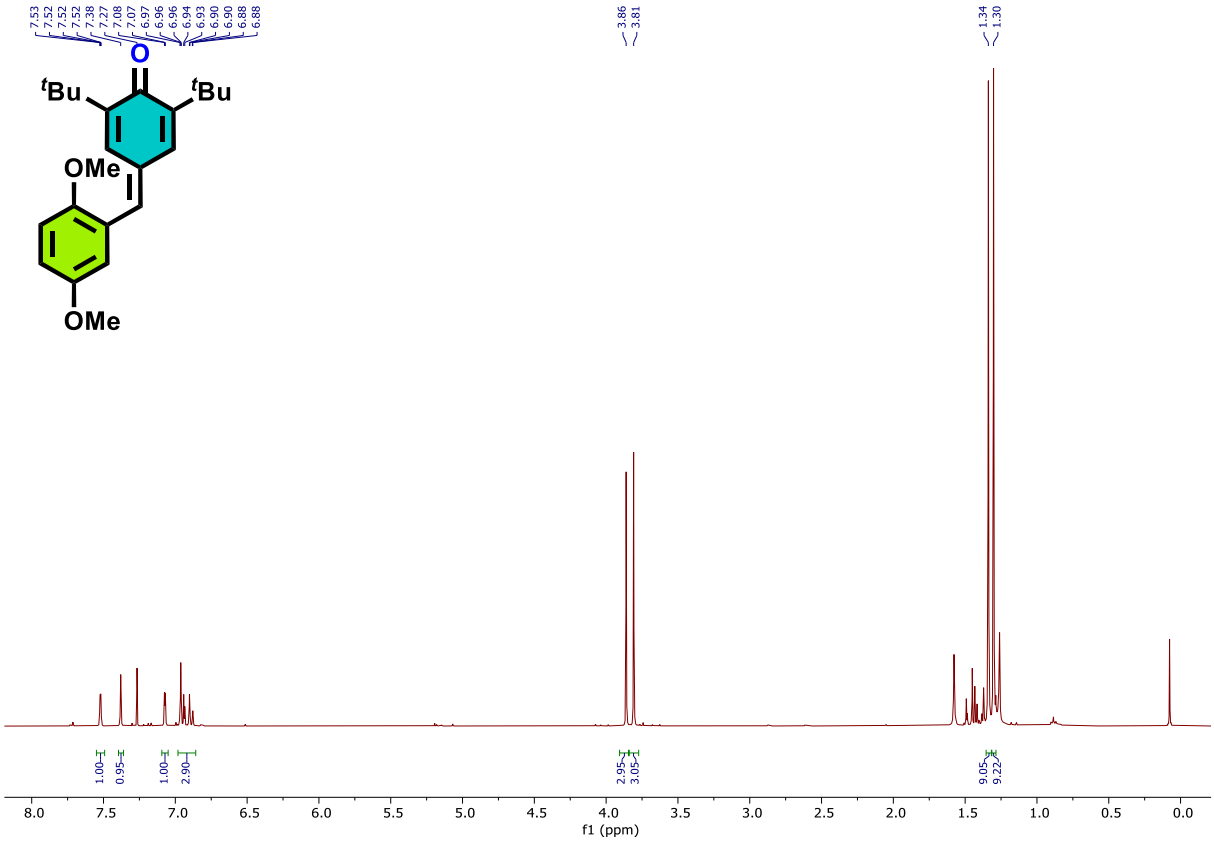
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(3,5-dimethoxybenzylidene)cyclohexa-2,5-dien-1-one **(1u)**



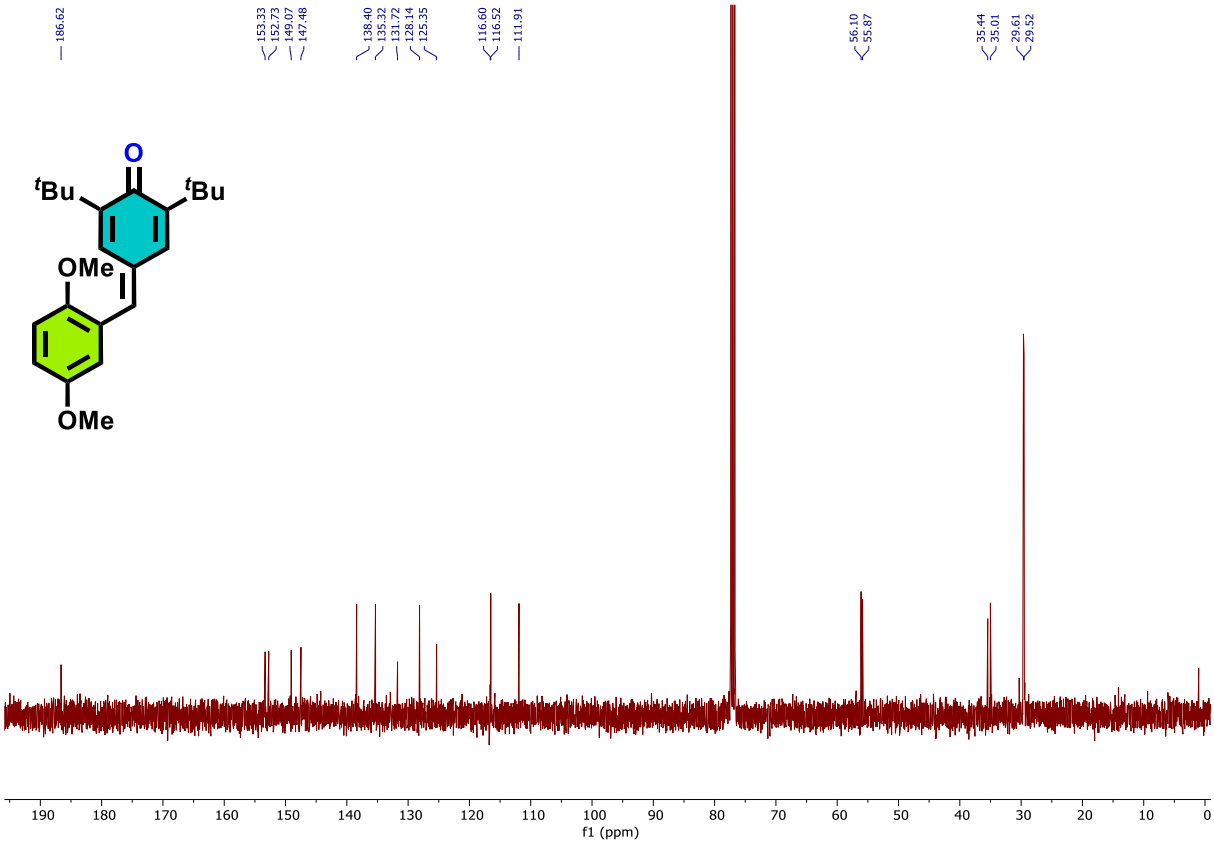
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(3,5-dimethoxybenzylidene)cyclohexa-2,5-dien-1-one **(1u)**



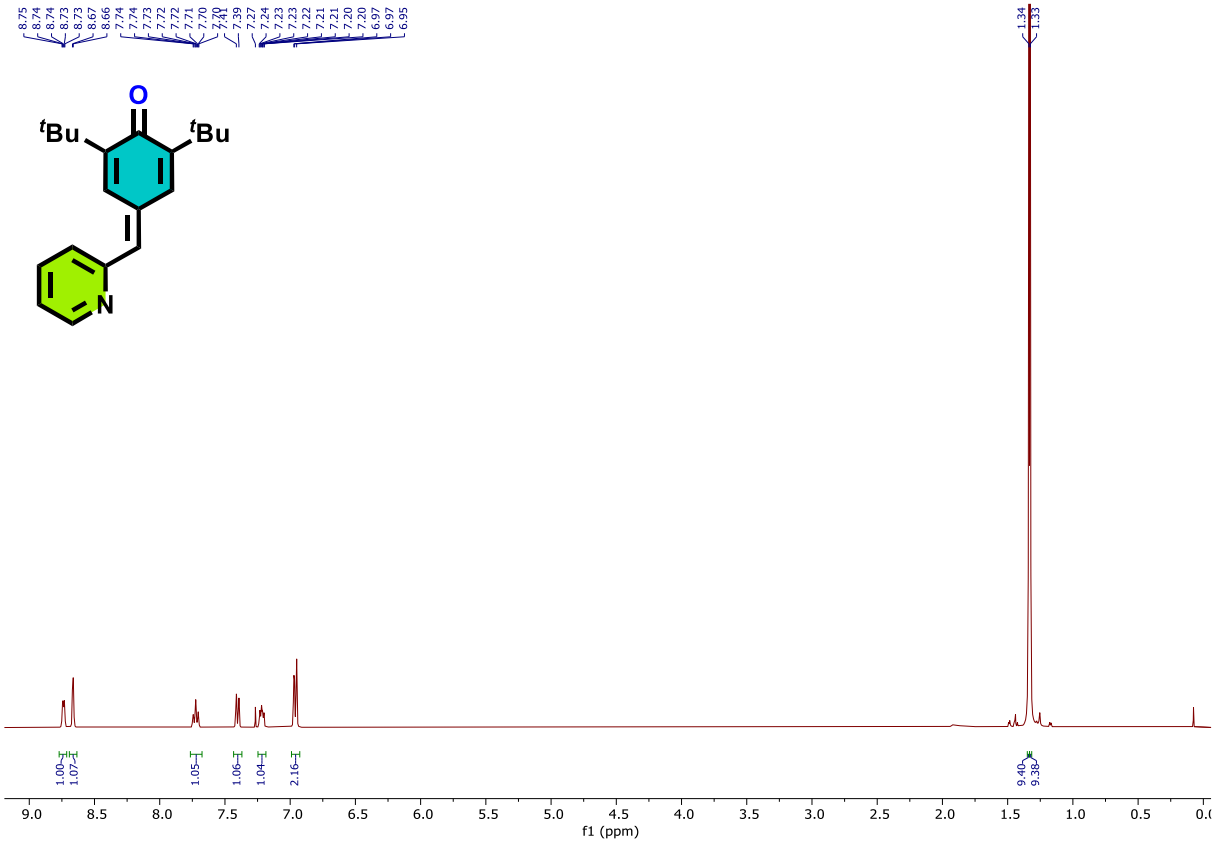
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(2,5-dimethoxybenzylidene)cyclohexa-2,5-dien-1-one **(1v)**



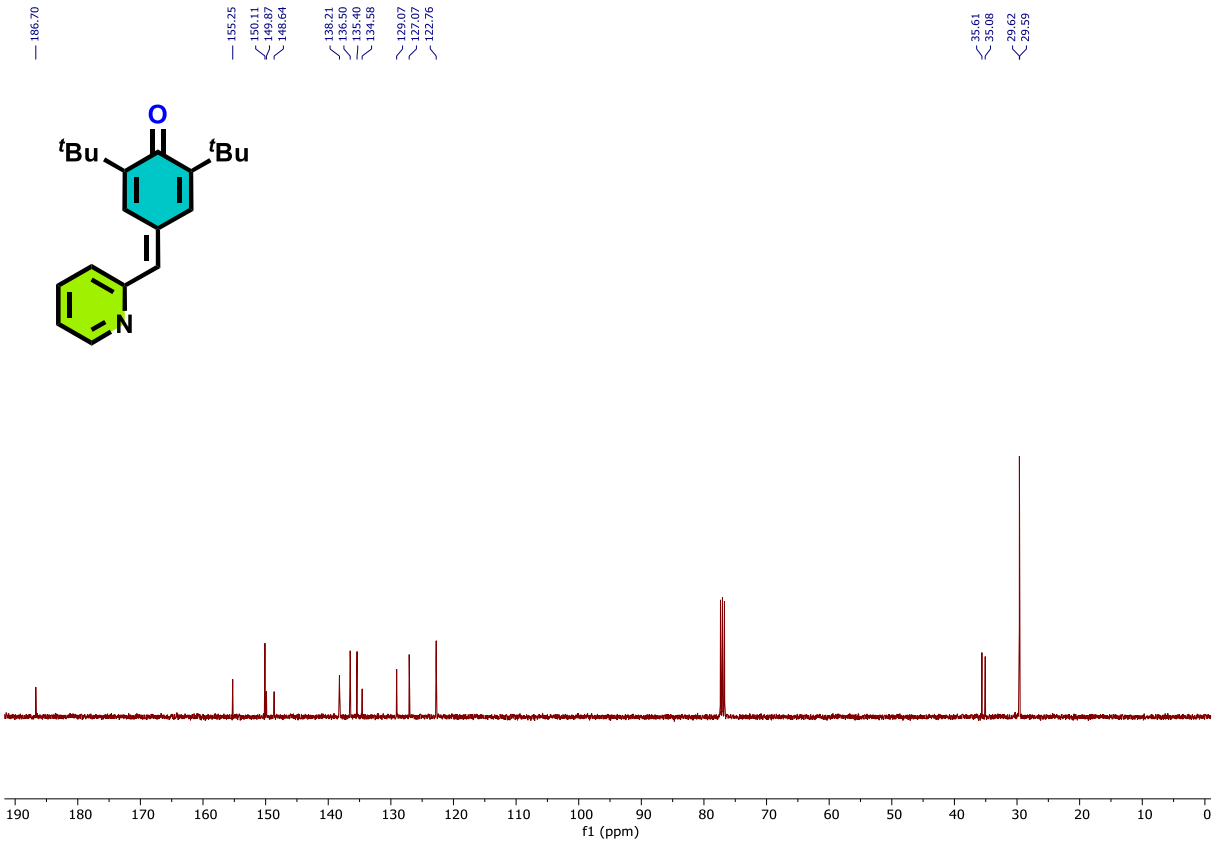
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(2,5-dimethoxybenzylidene)cyclohexa-2,5-dien-1-one **(1v)**



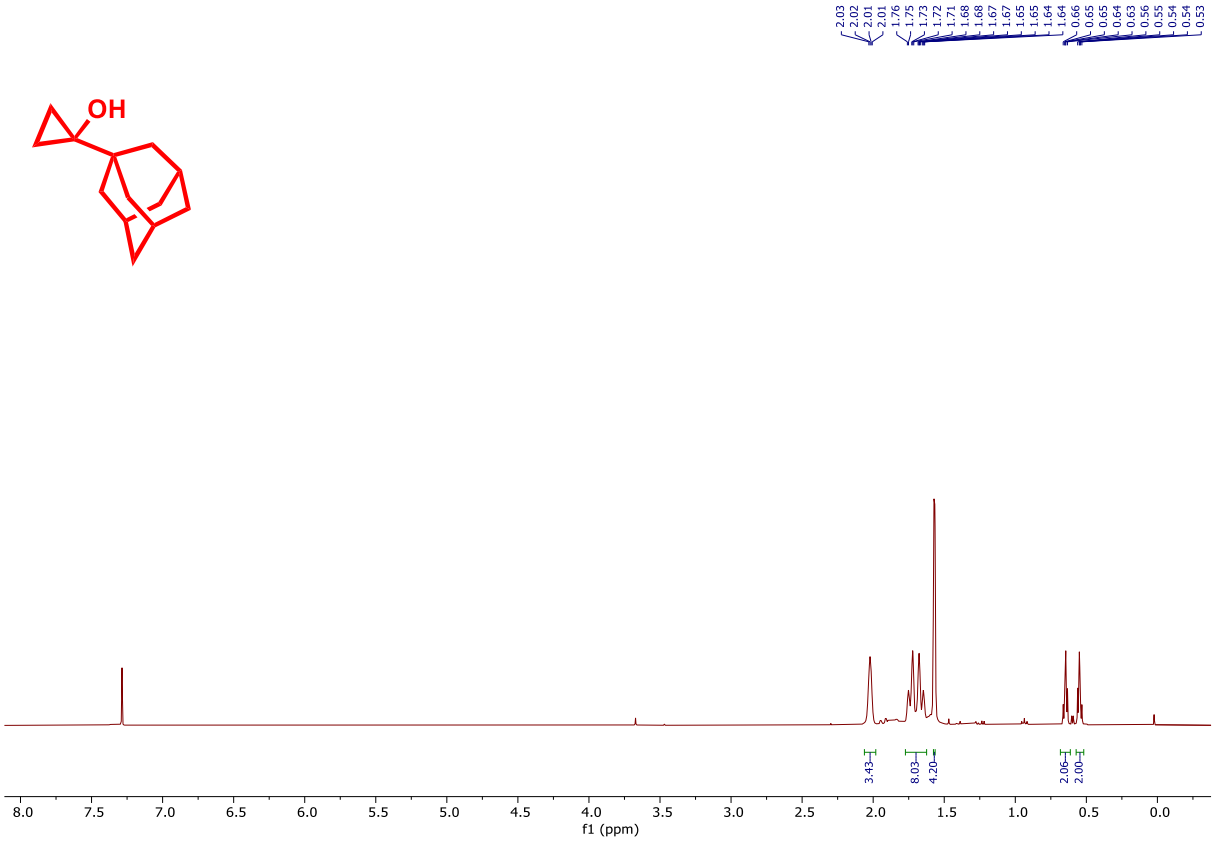
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(pyridin-2-ylmethylene)cyclohexa-2,5-dien-1-one **(1x)**



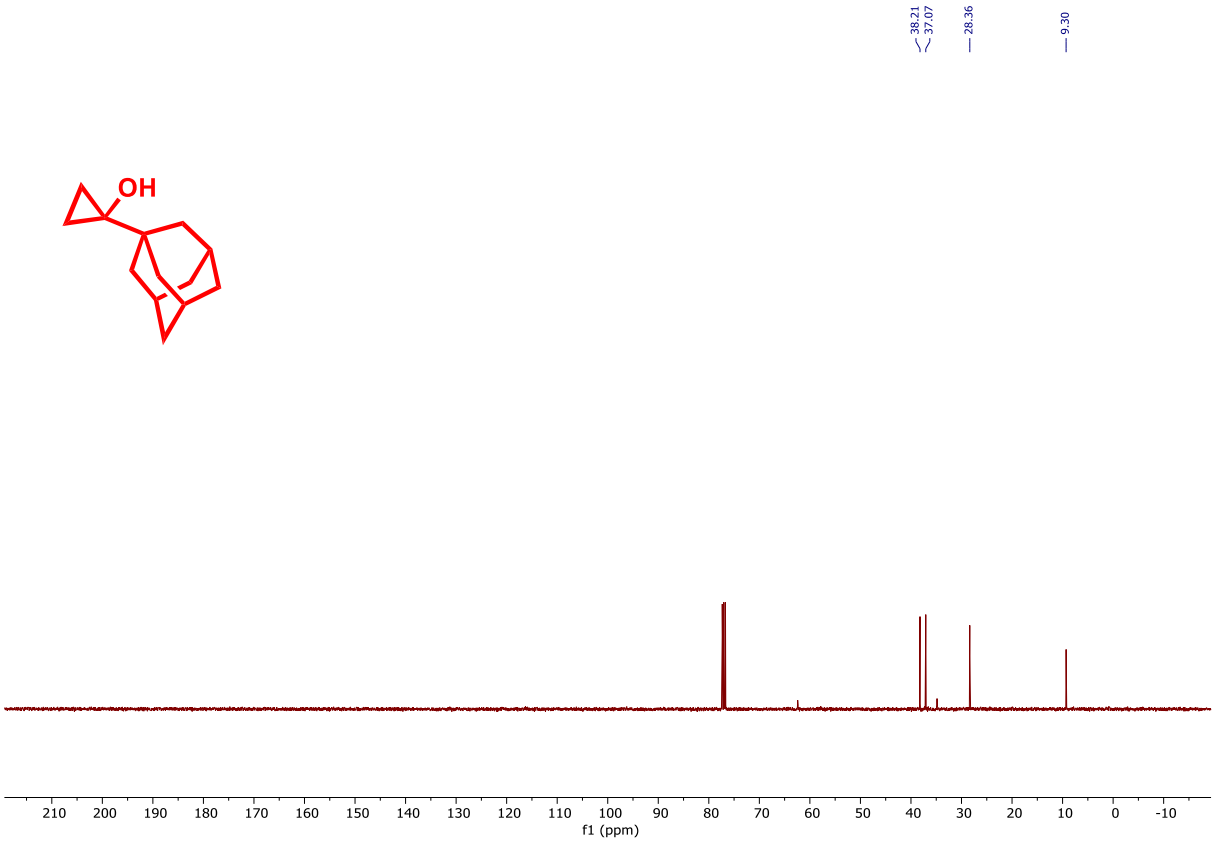
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(pyridin-2-ylmethylene)cyclohexa-2,5-dien-1-one **(1x)**



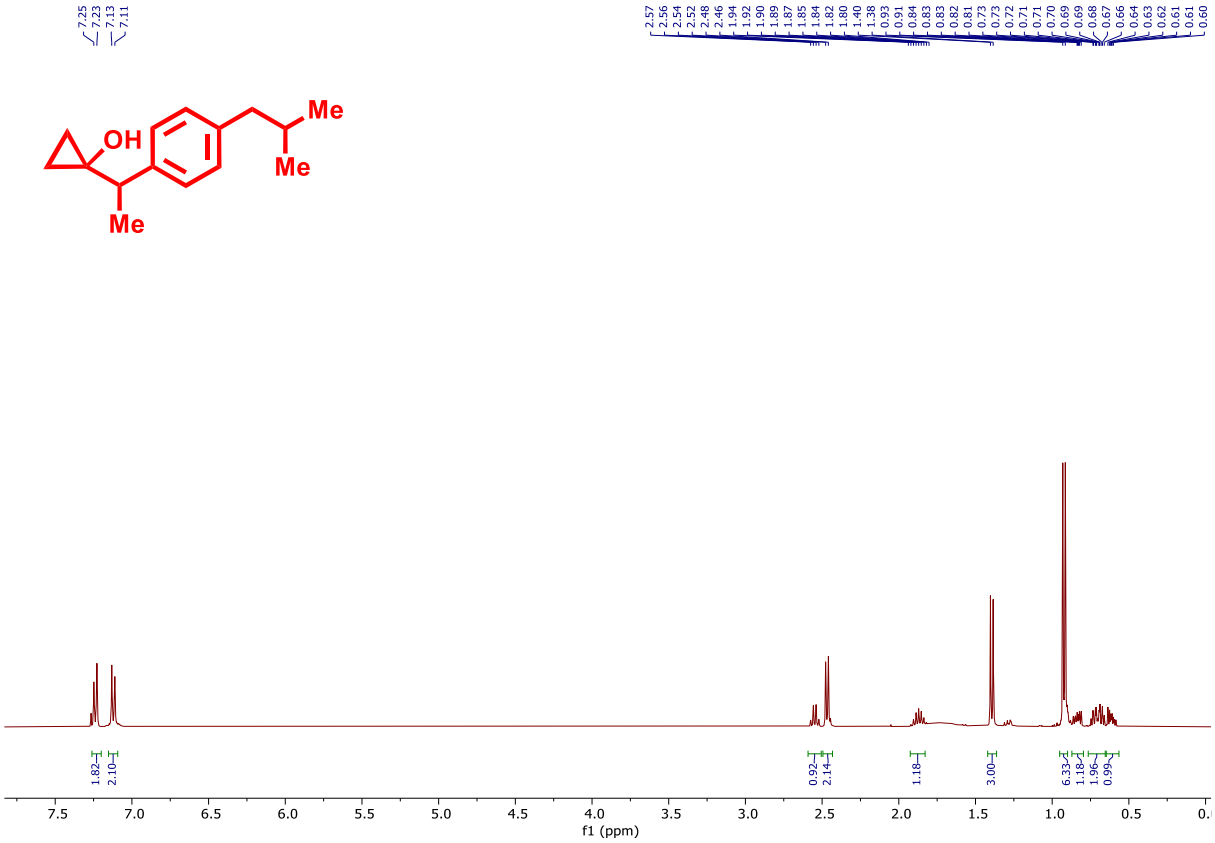
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-((1s,3s)-adamantan-1-yl)cyclopropan-1-ol **(2k)**



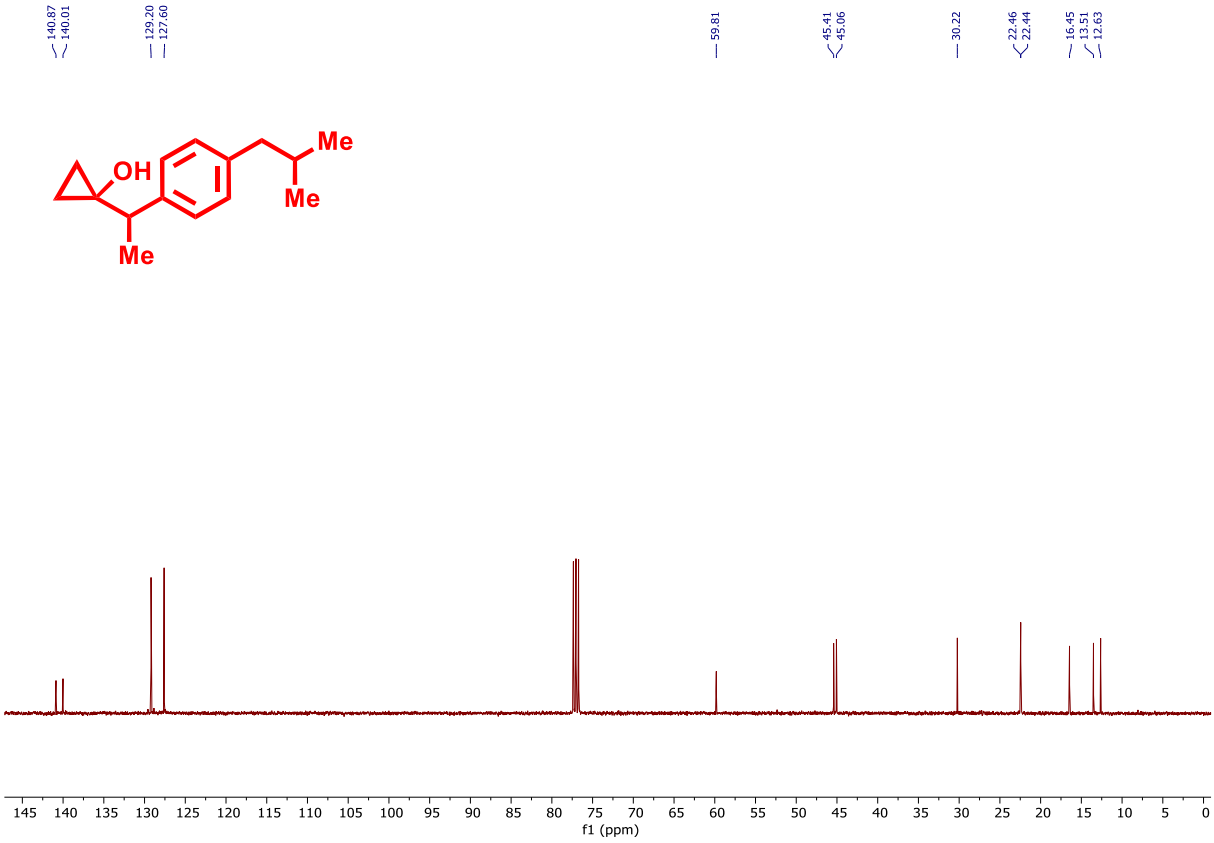
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-((1s,3s)-adamantan-1-yl)cyclopropan-1-ol **(2k)**



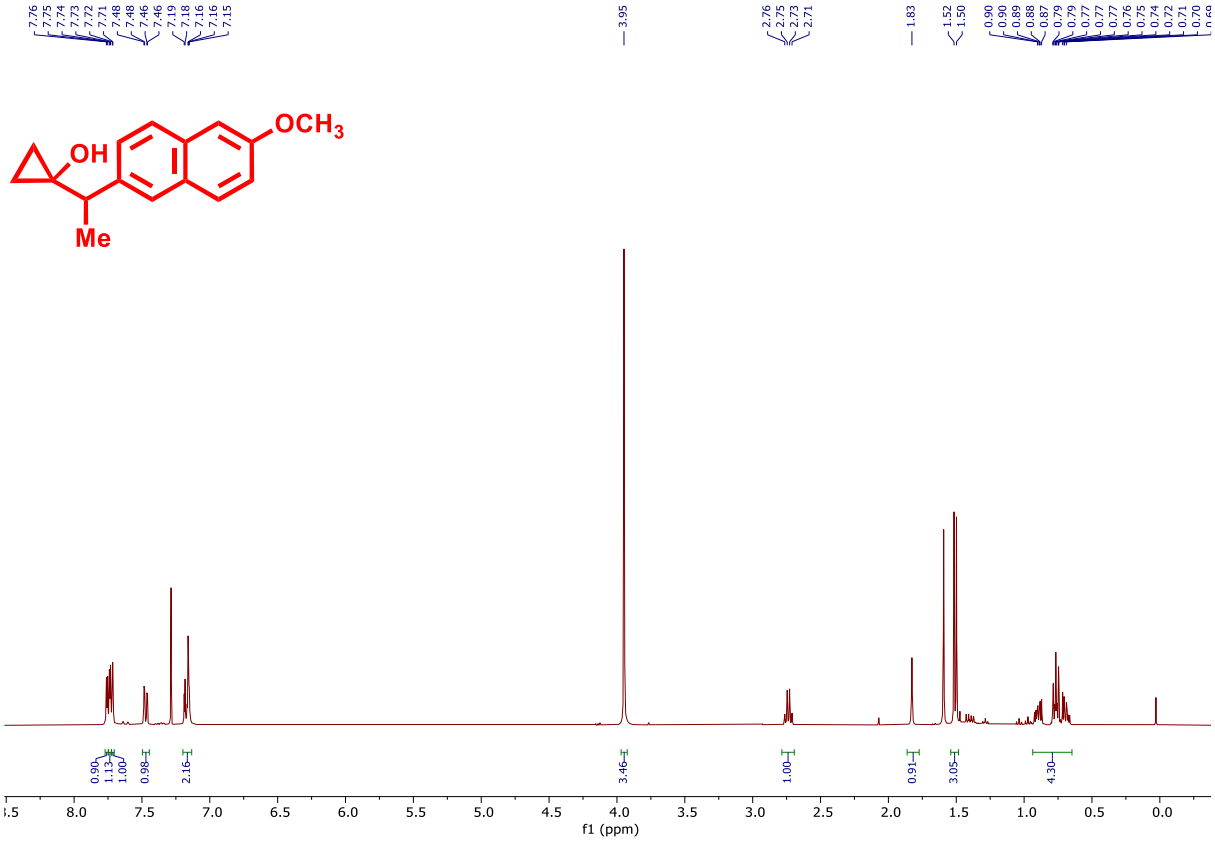
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-(1-(4-isobutylphenyl)ethyl)cyclopropan-1-ol **(2n)**



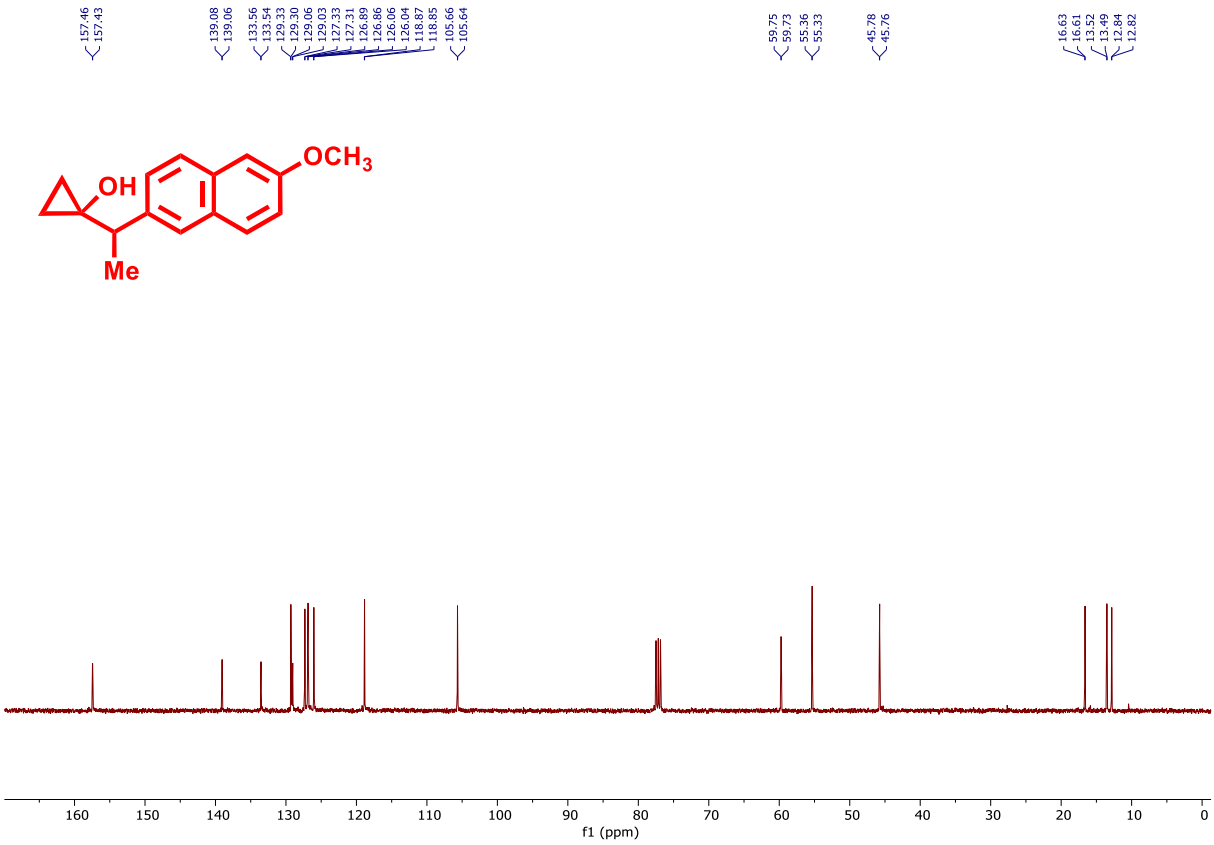
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-(1-(4-isobutylphenyl)ethyl)cyclopropan-1-ol **(2n)**



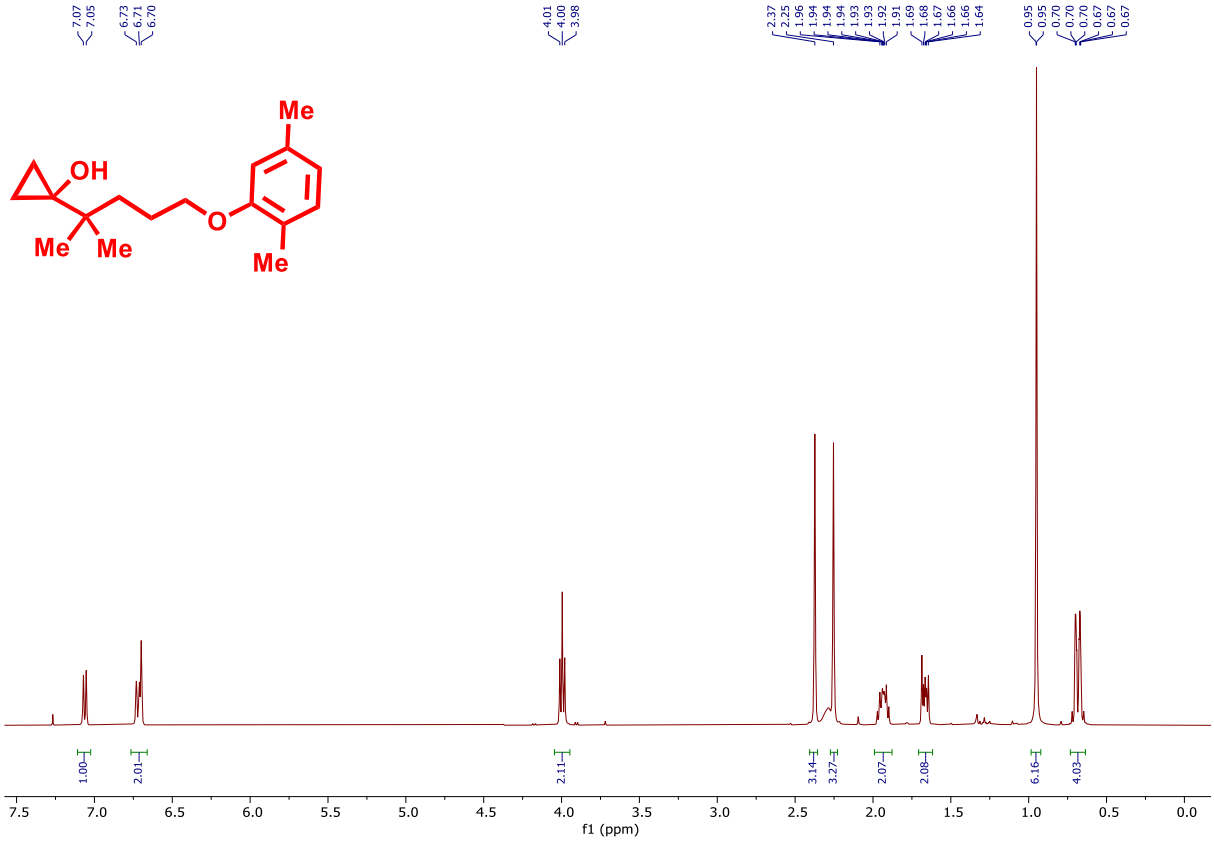
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-(1-(6-methoxynaphthalen-2-yl)ethyl)cyclopropan-1-ol **(2o)**



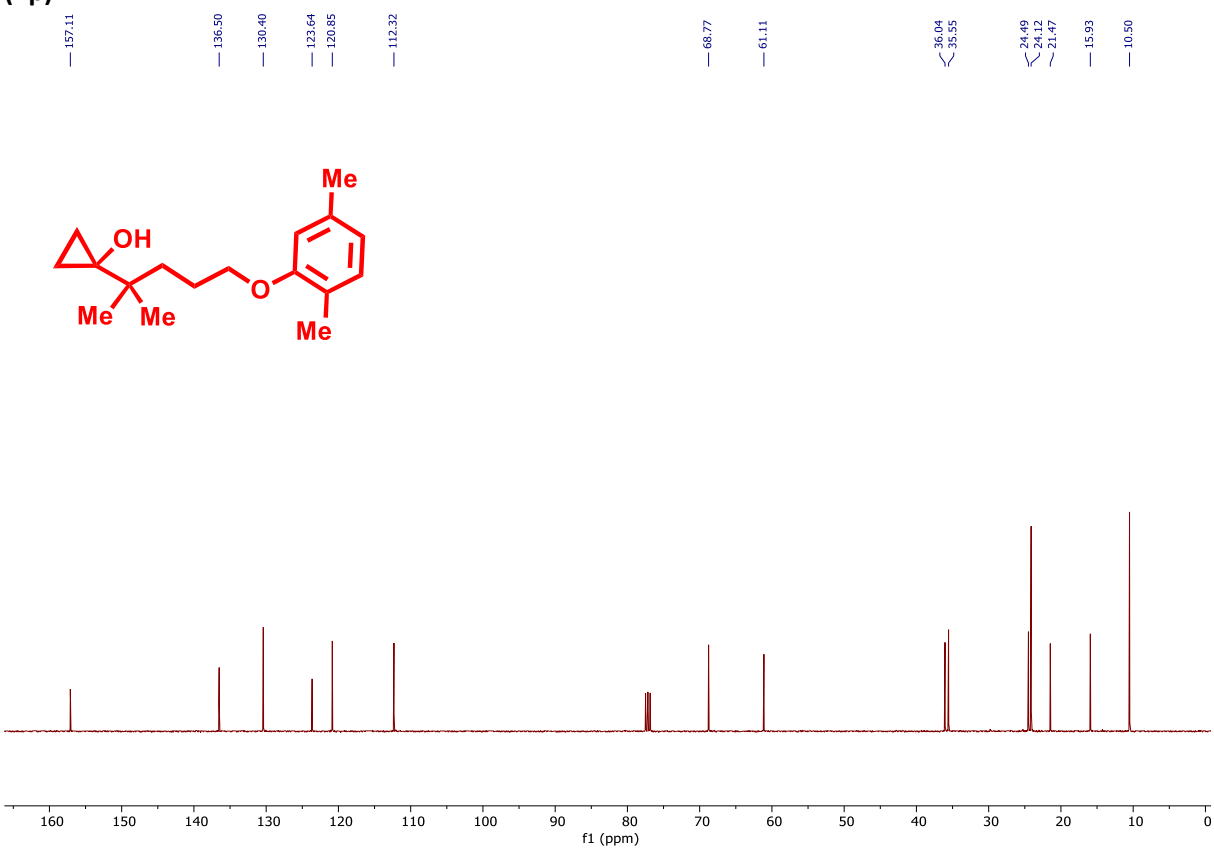
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-(1-(6-methoxynaphthalen-2-yl)ethyl)cyclopropan-1-ol **(2o)**



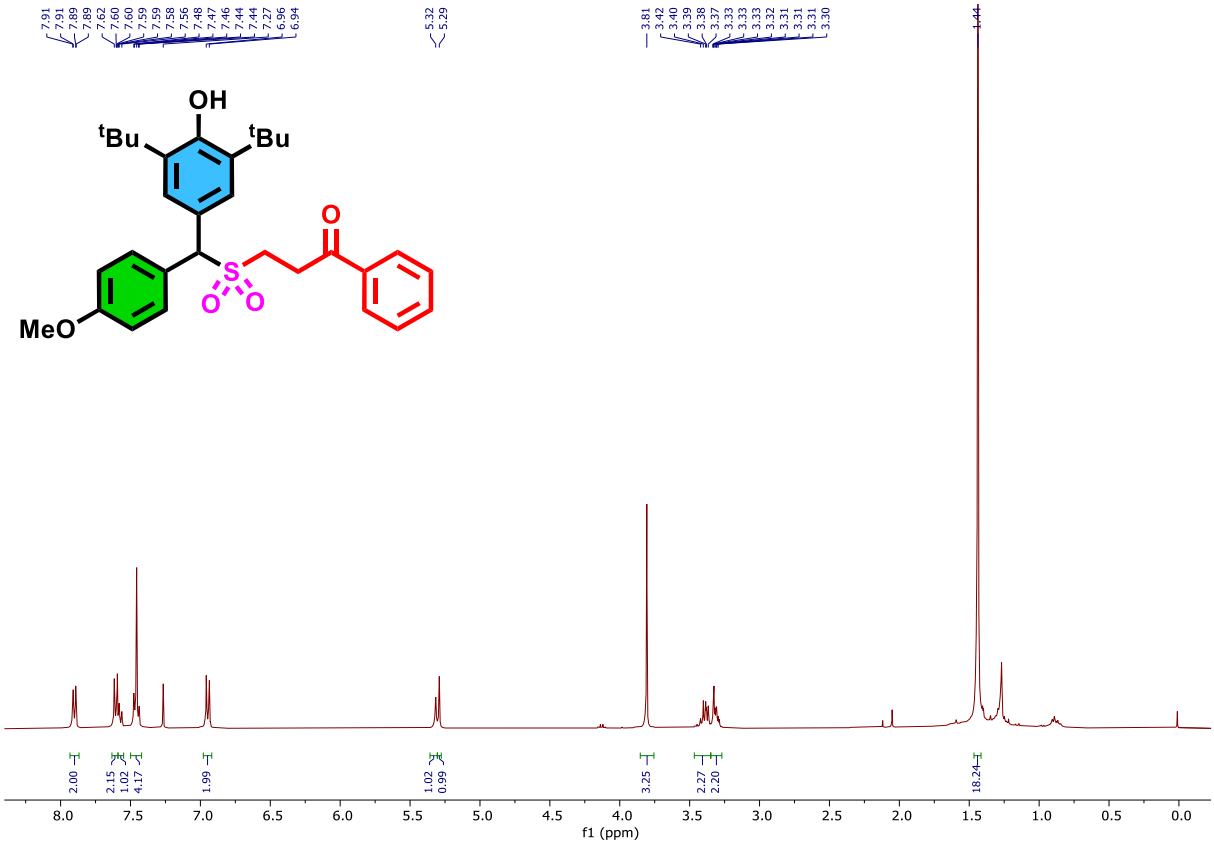
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)cyclopropan-1-ol **(2p)**



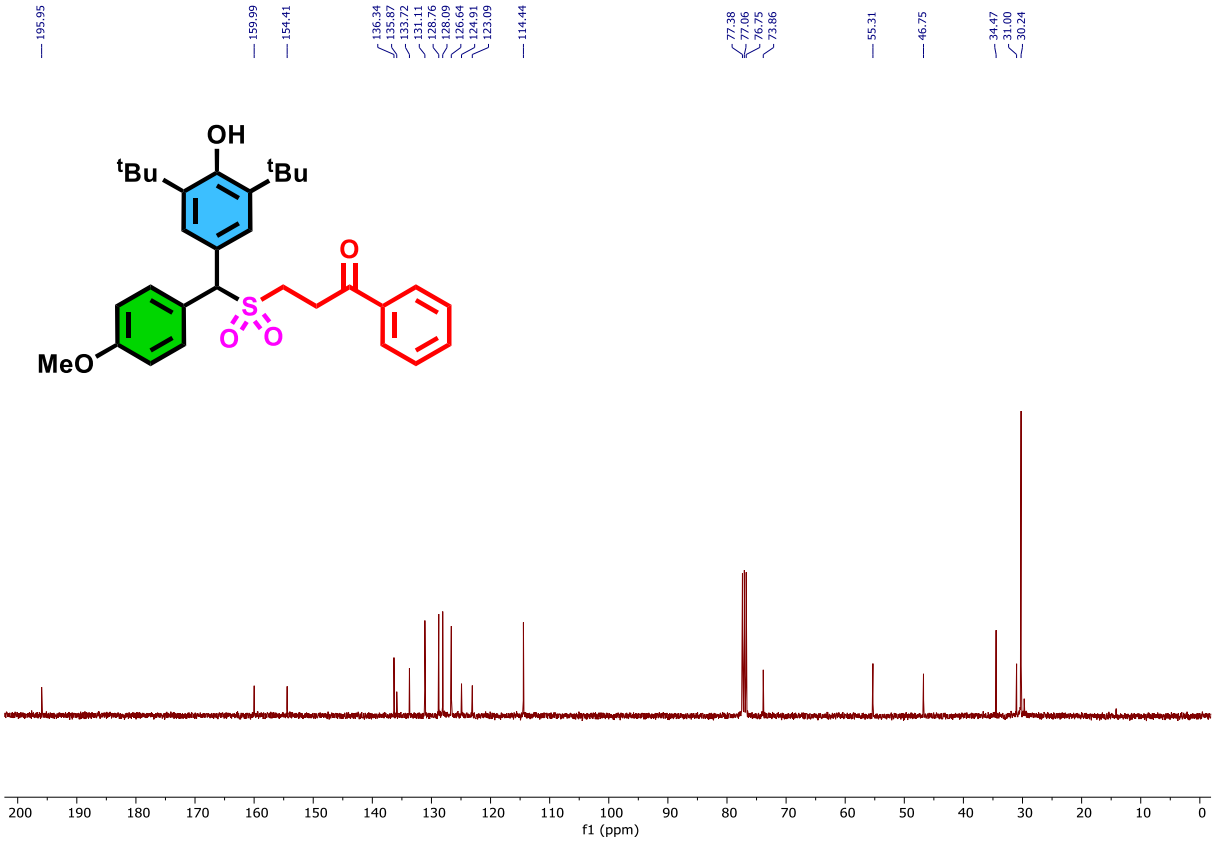
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)cyclopropan-1-ol **(2p)**



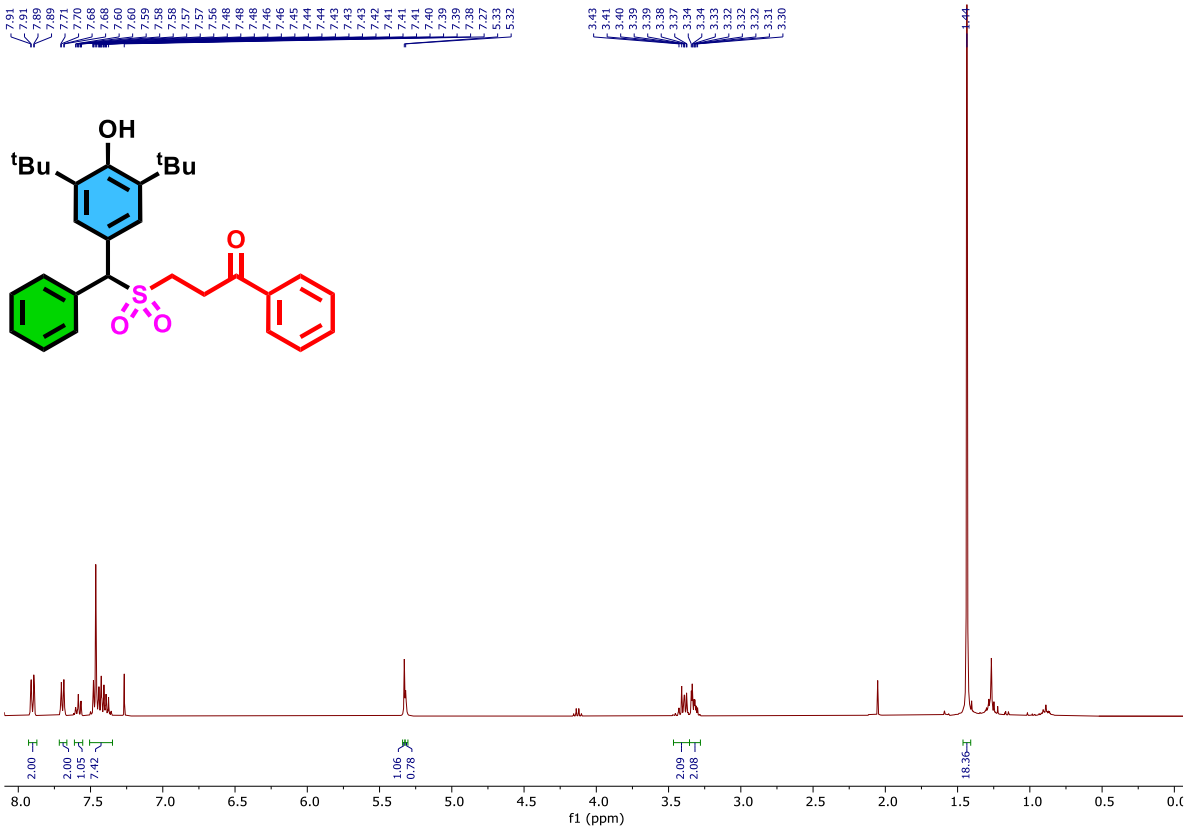
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3aa)**



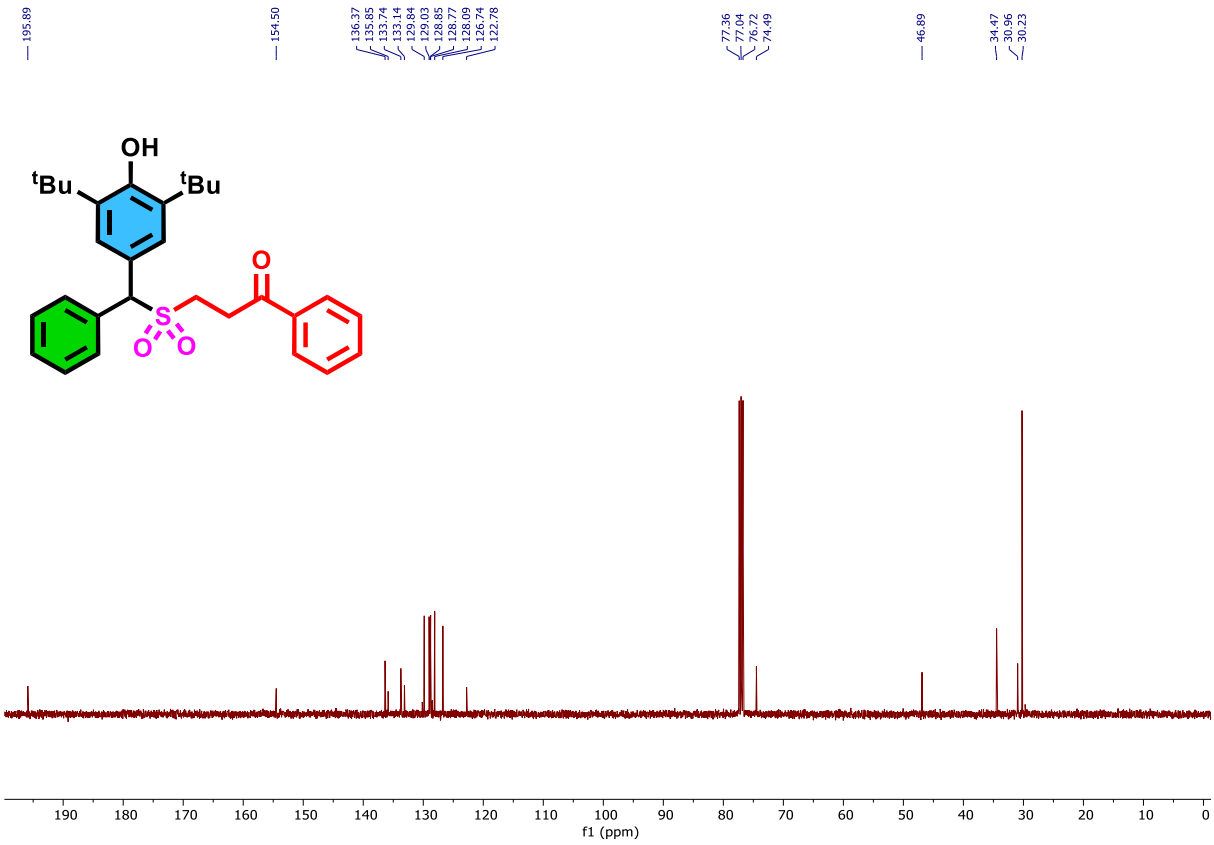
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3aa)**



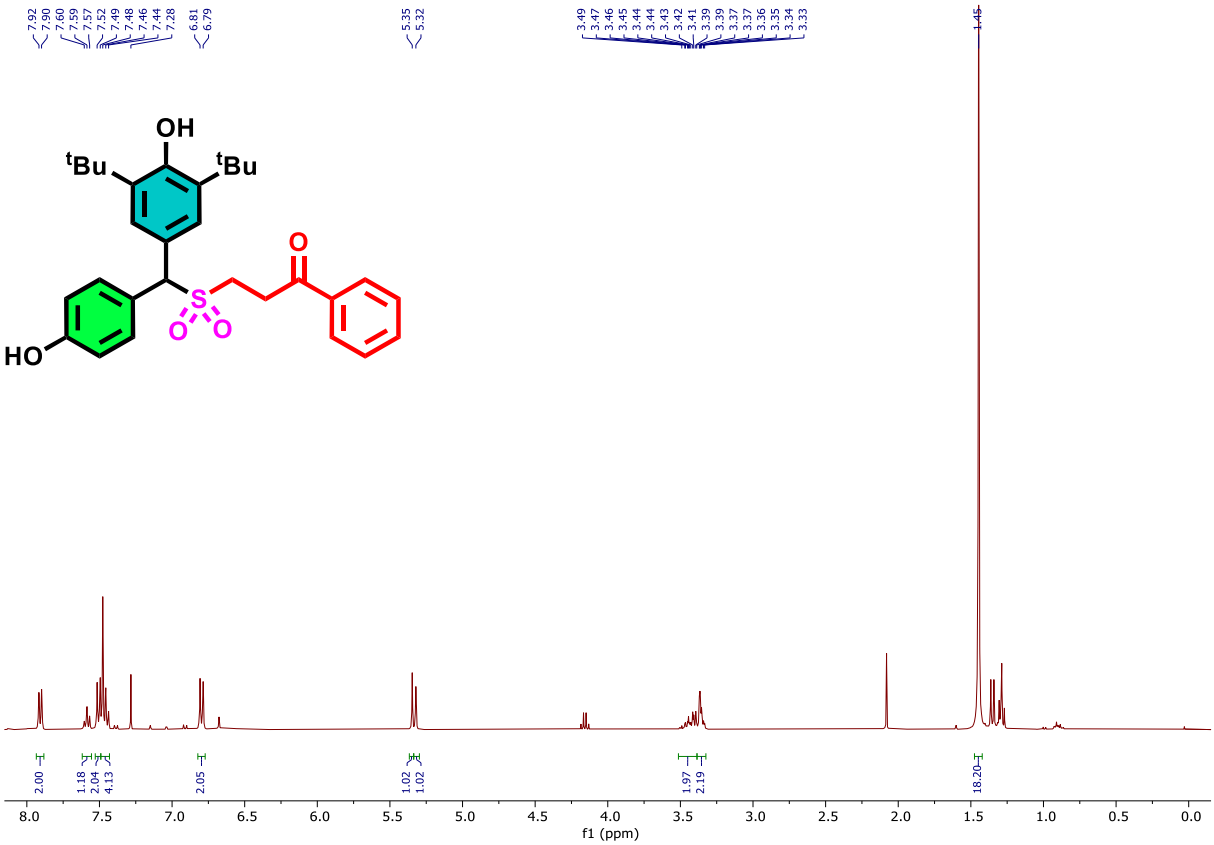
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ba)**



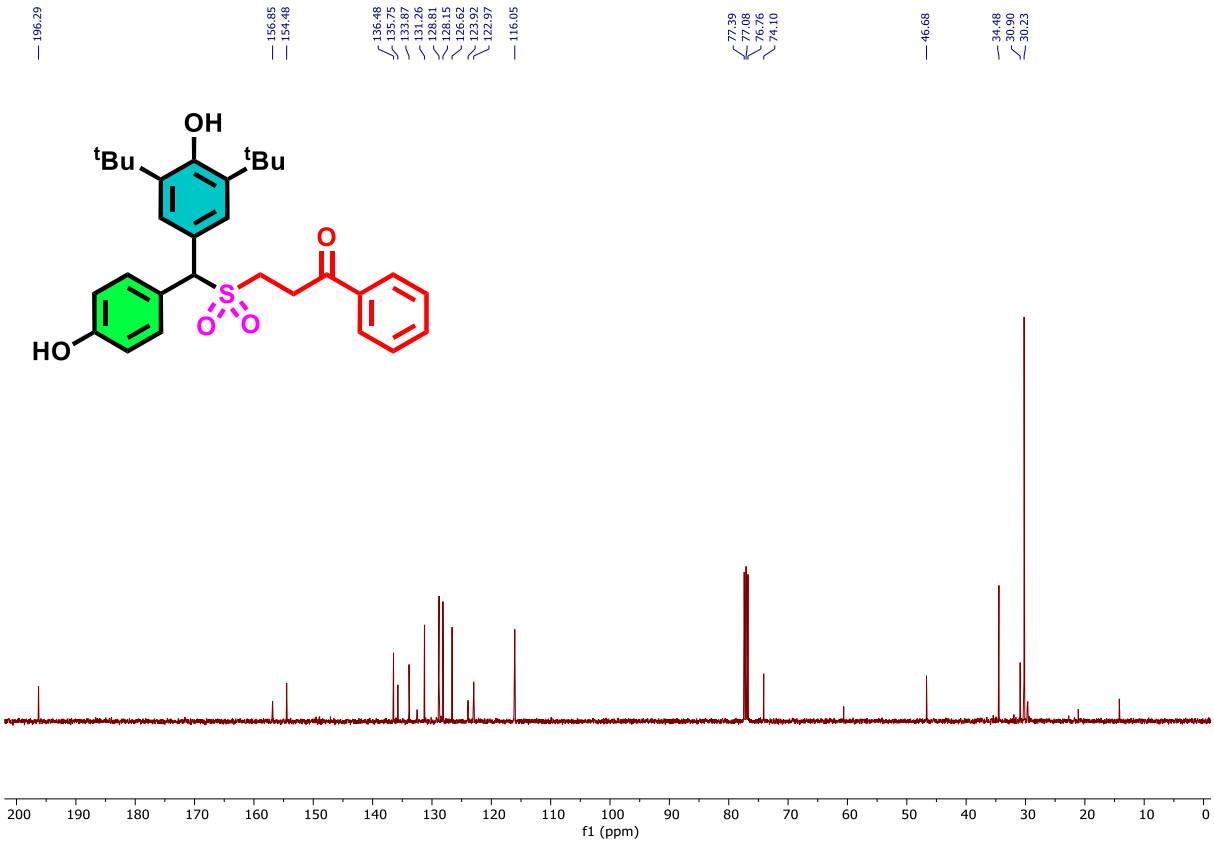
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ba)**



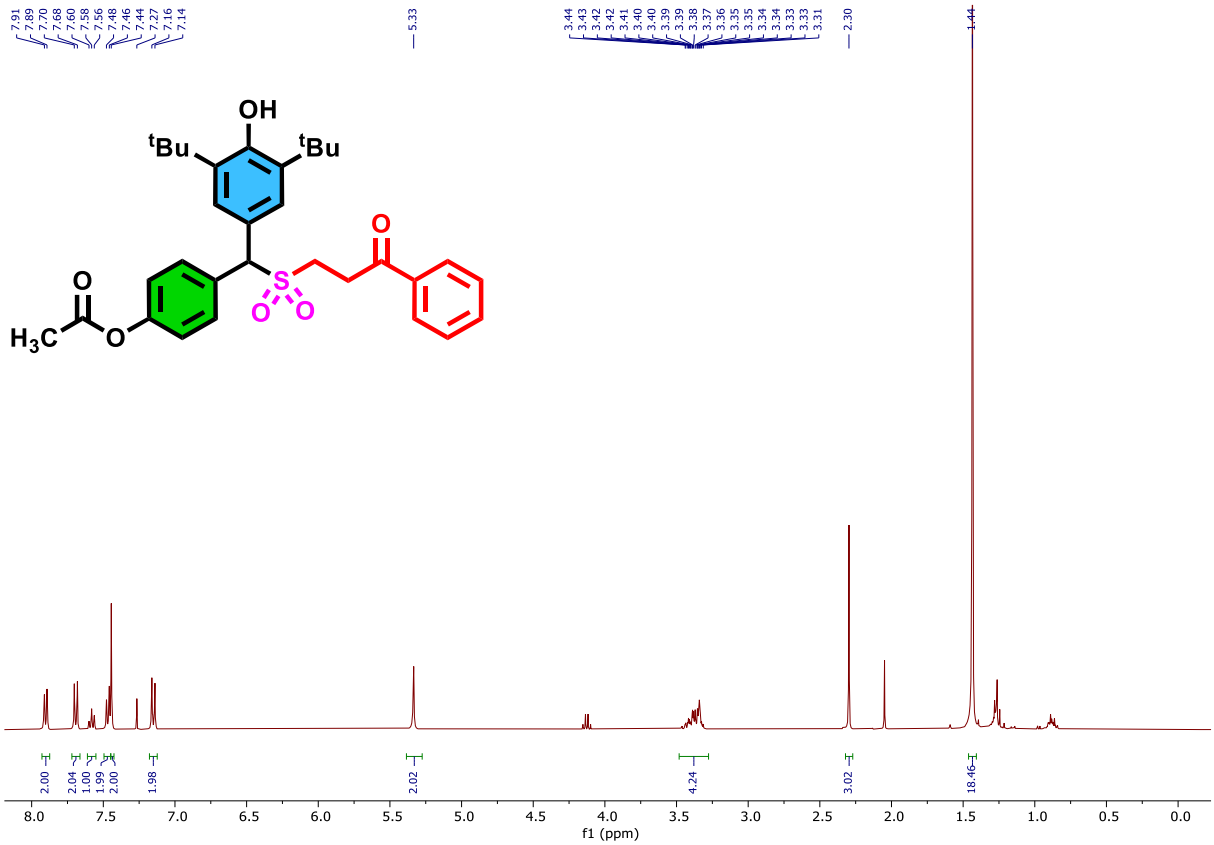
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ca)**



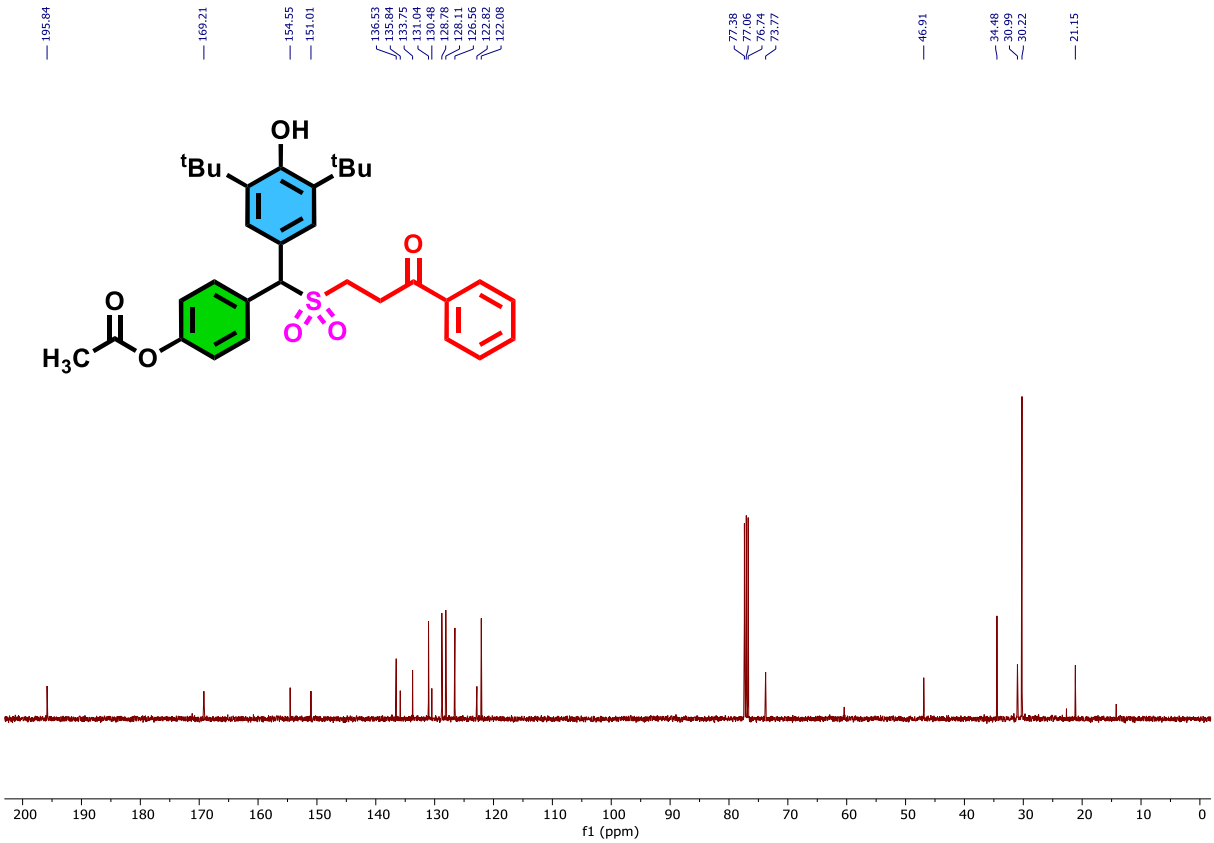
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ca)**



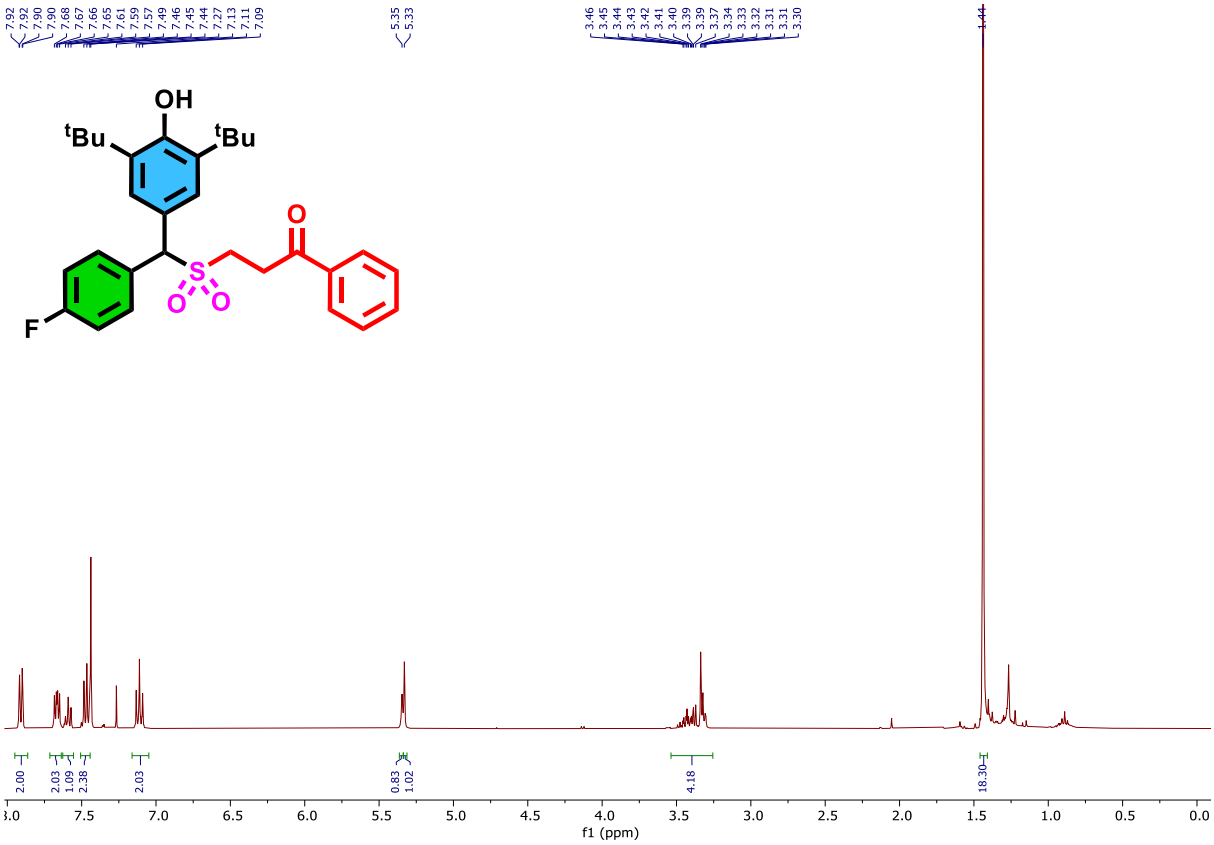
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl acetate **(3da)**



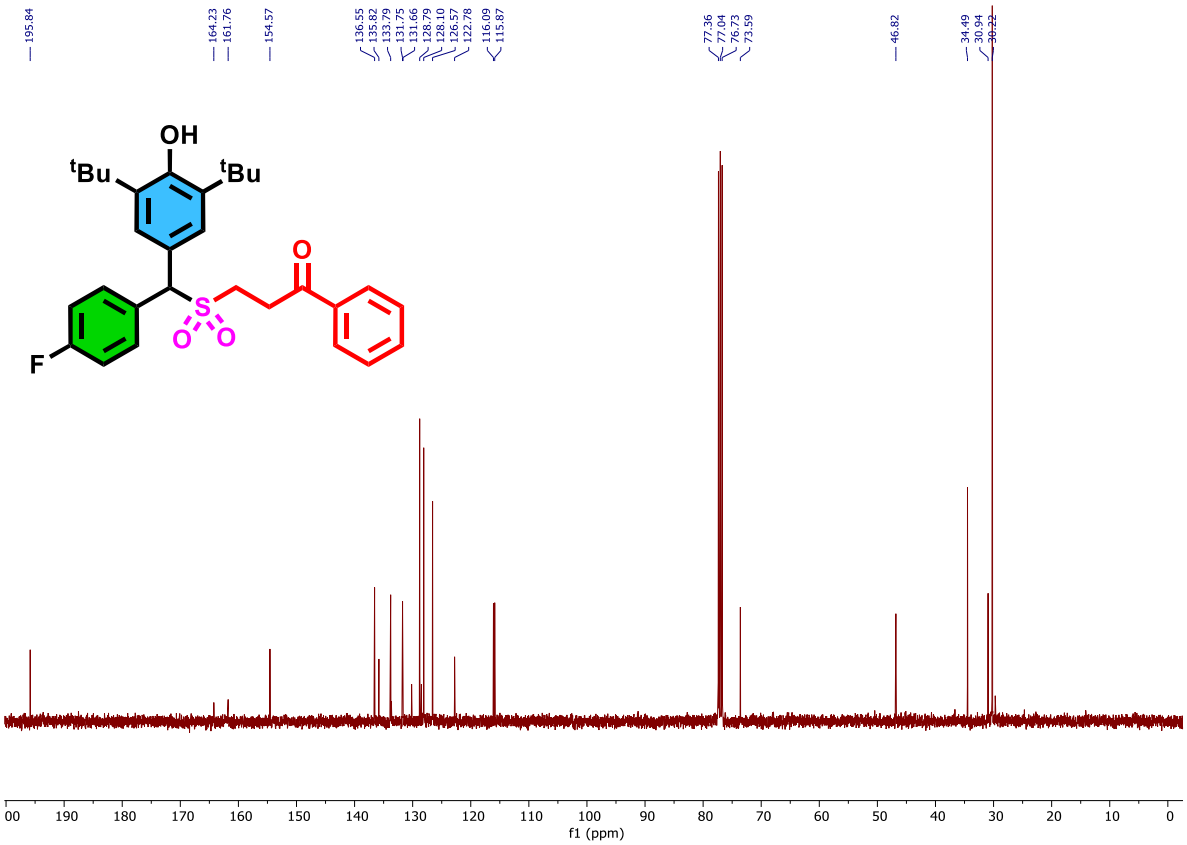
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl acetate **(3da)**



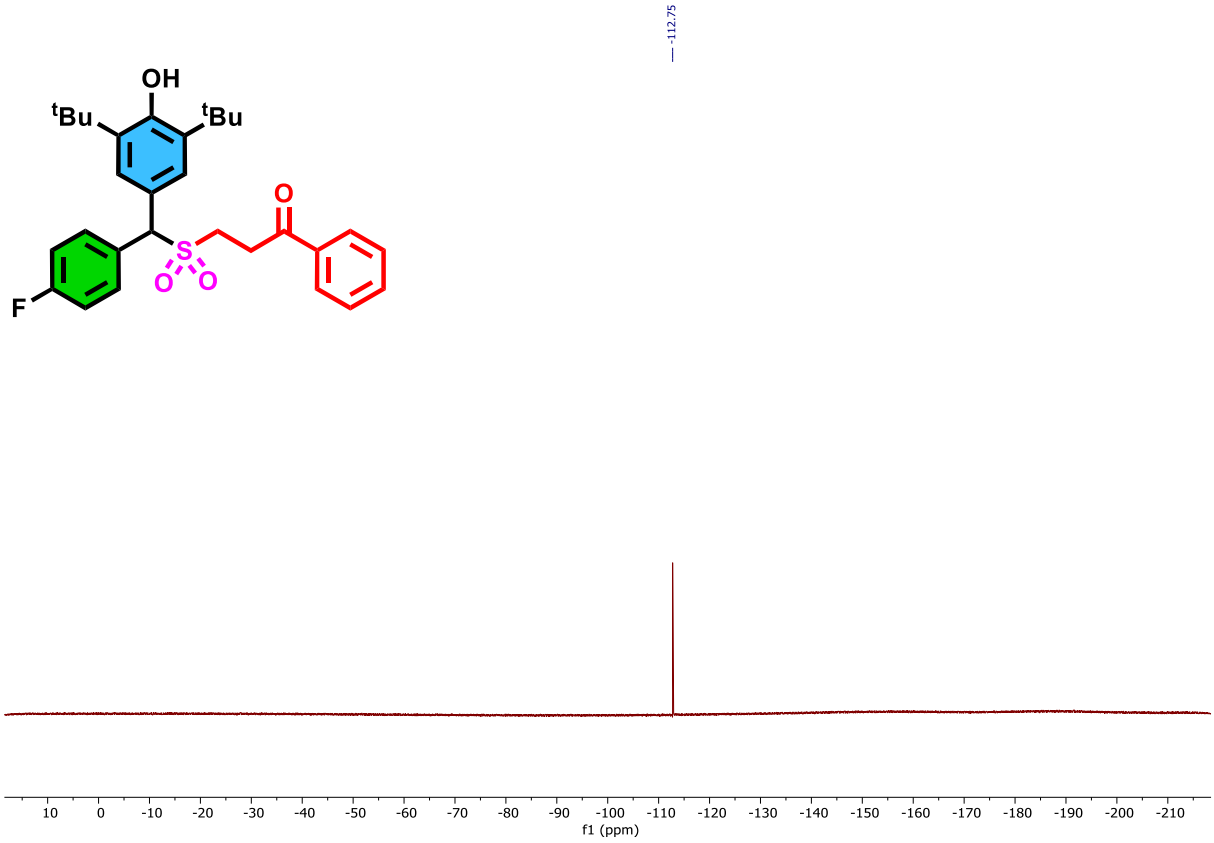
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ea)**



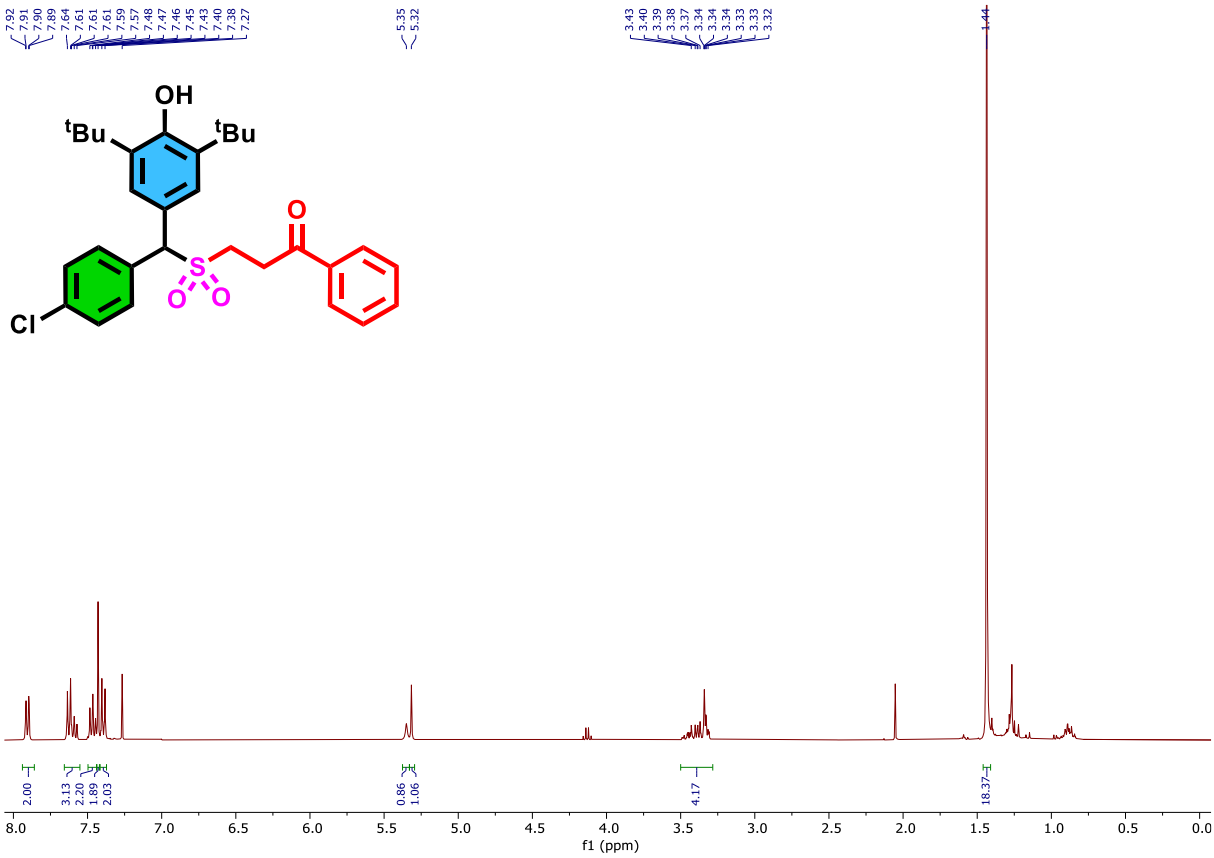
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ea)**



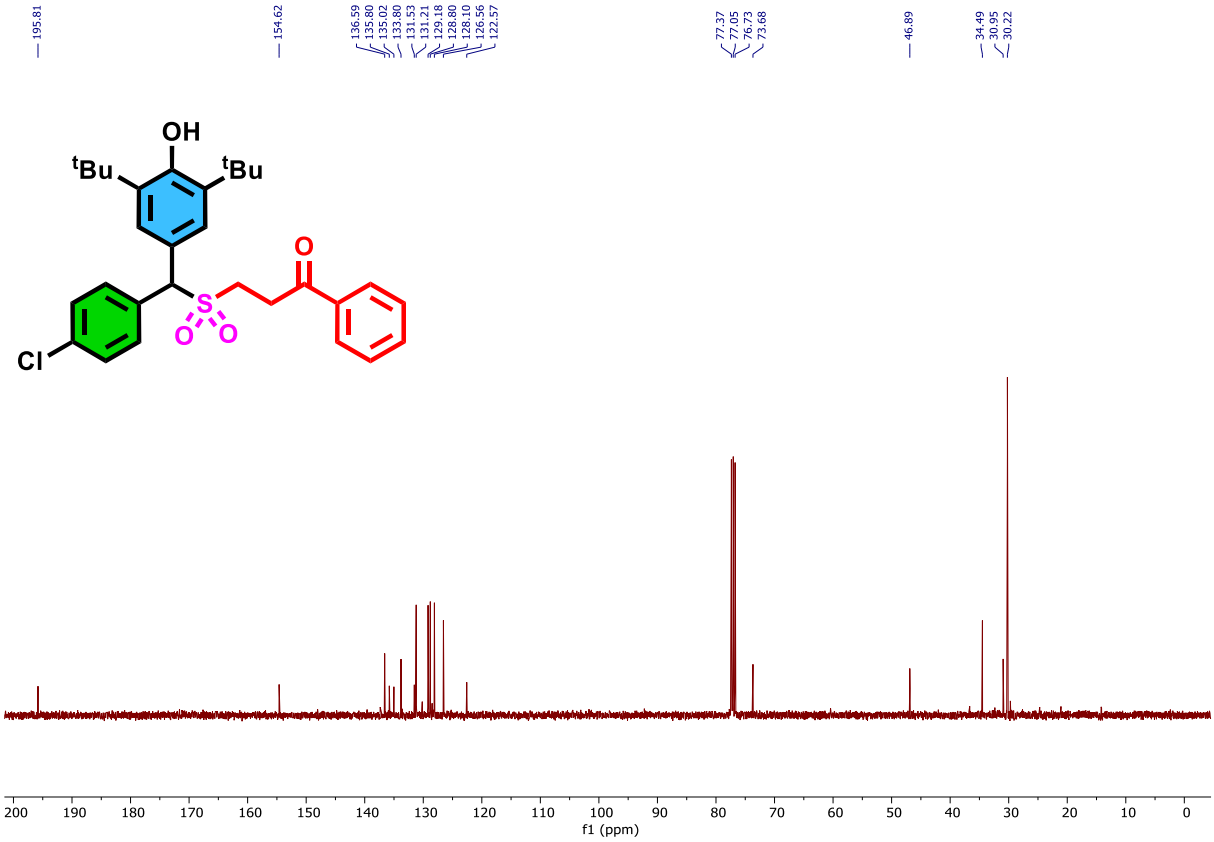
^{19}F NMR (377 MHz, $CDCl_3$) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ea**)



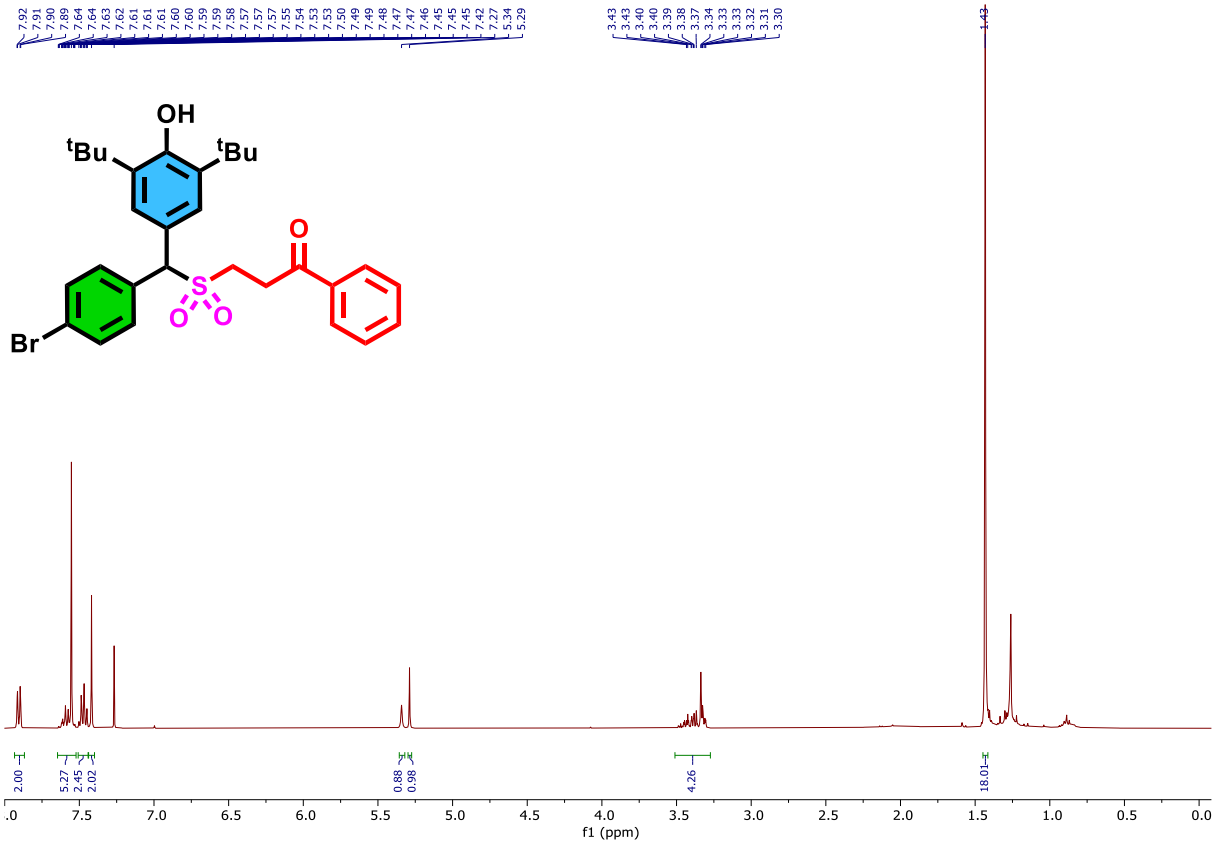
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((4-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3fa)**



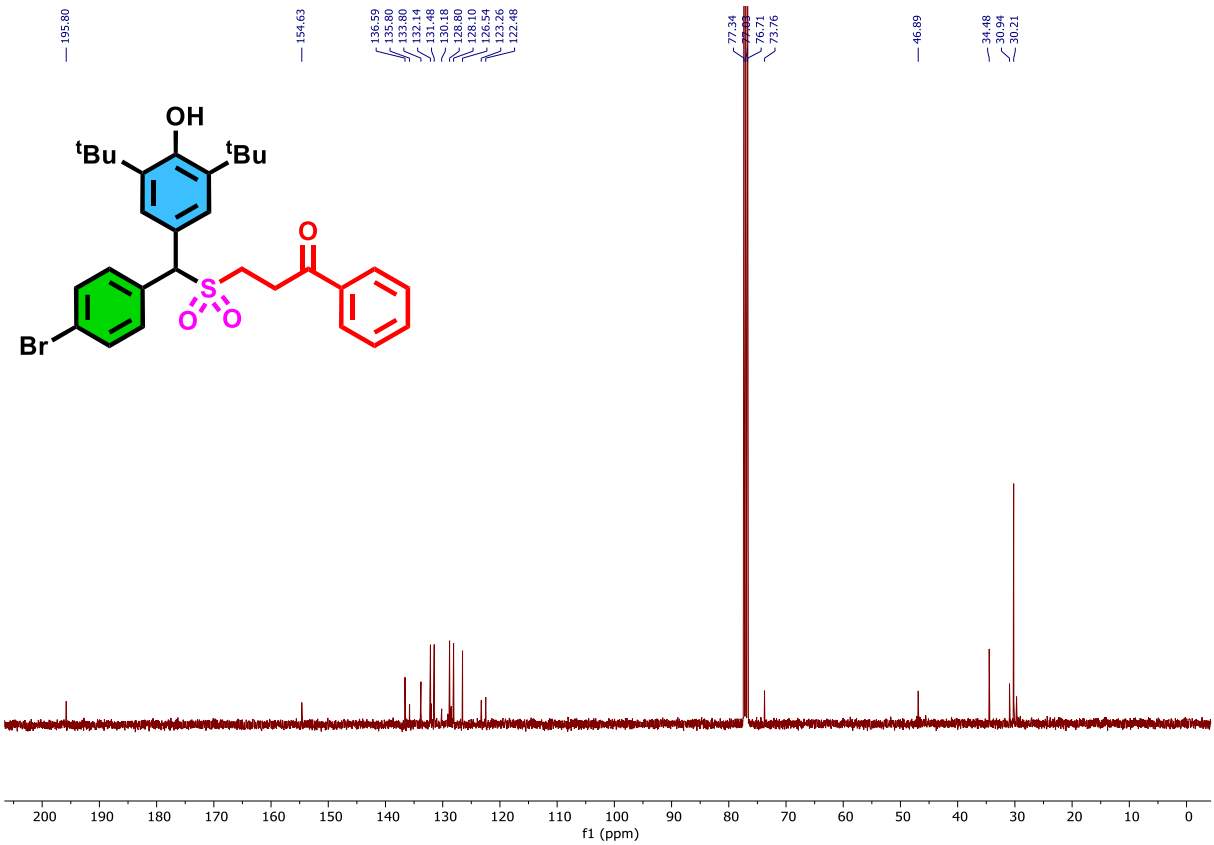
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((4-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3fa)**



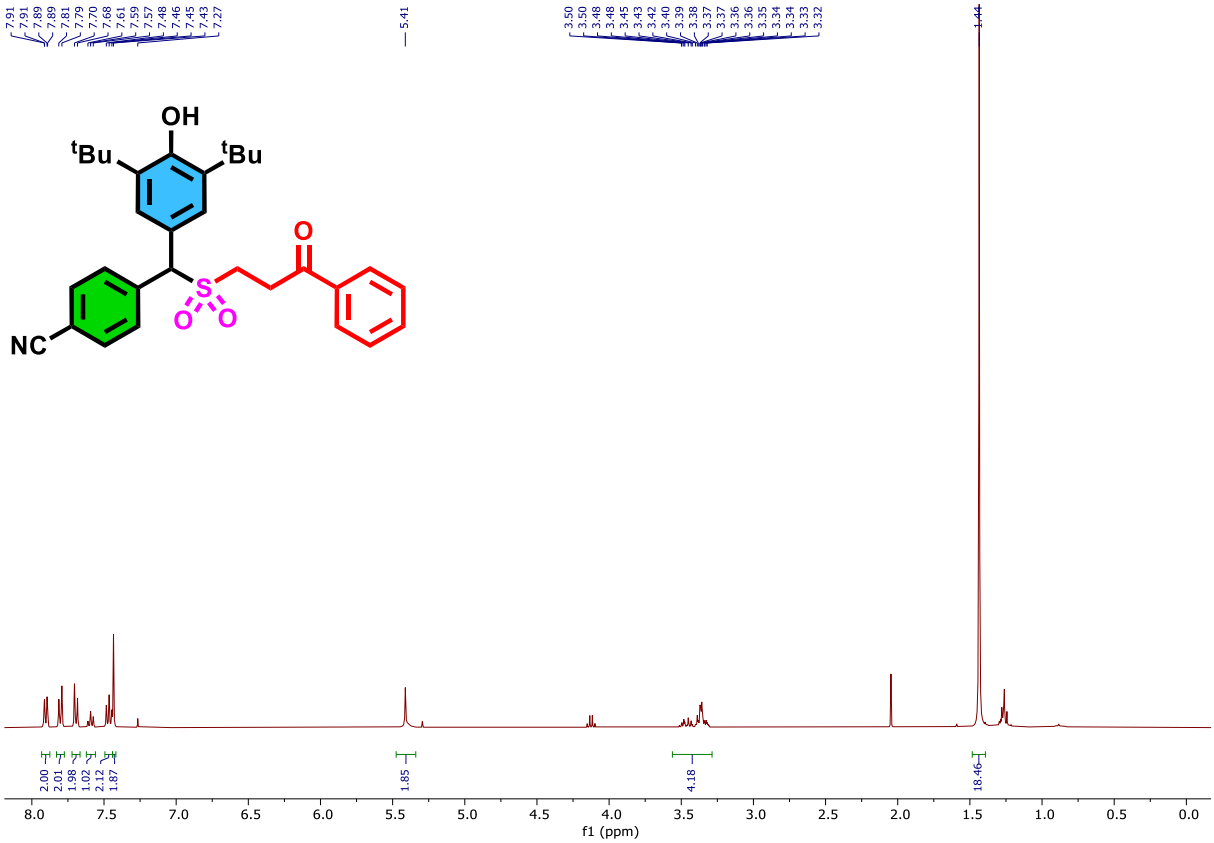
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ga)**



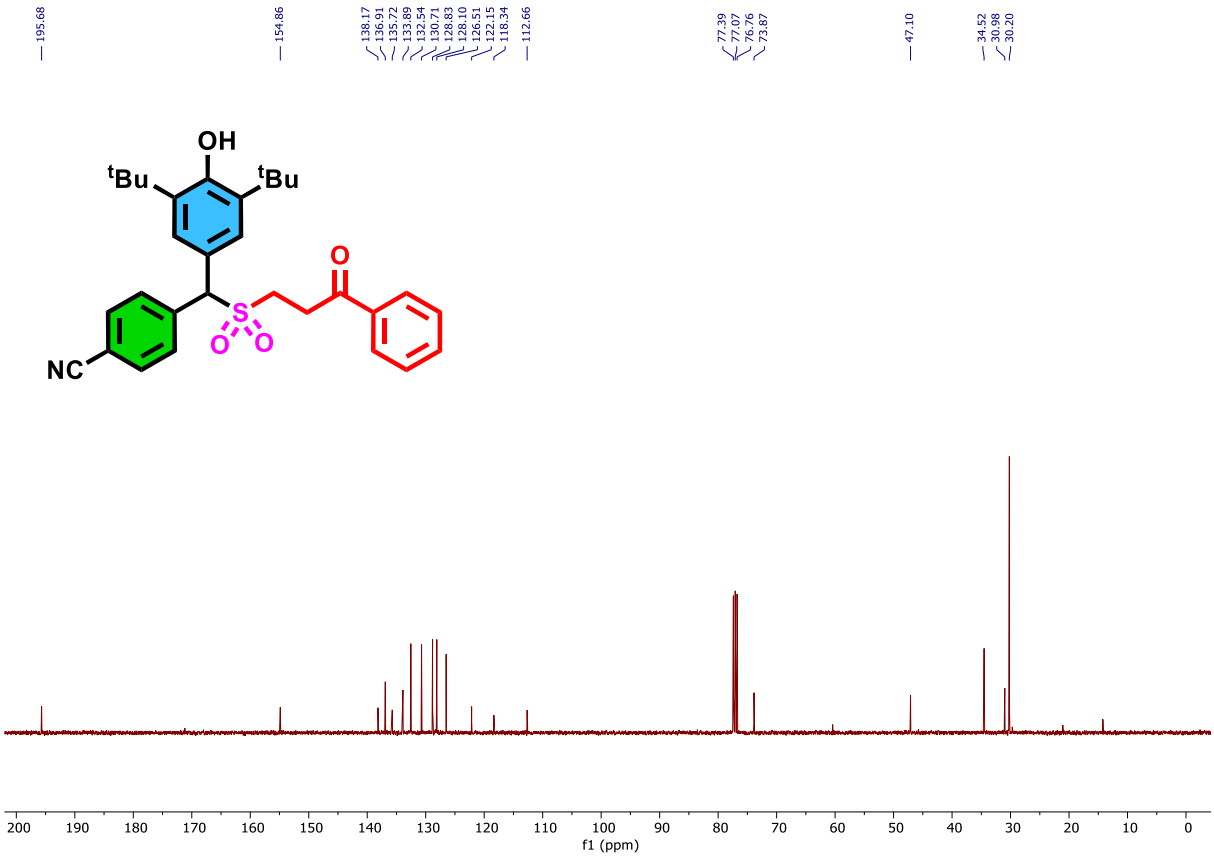
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of3-(((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ga)**



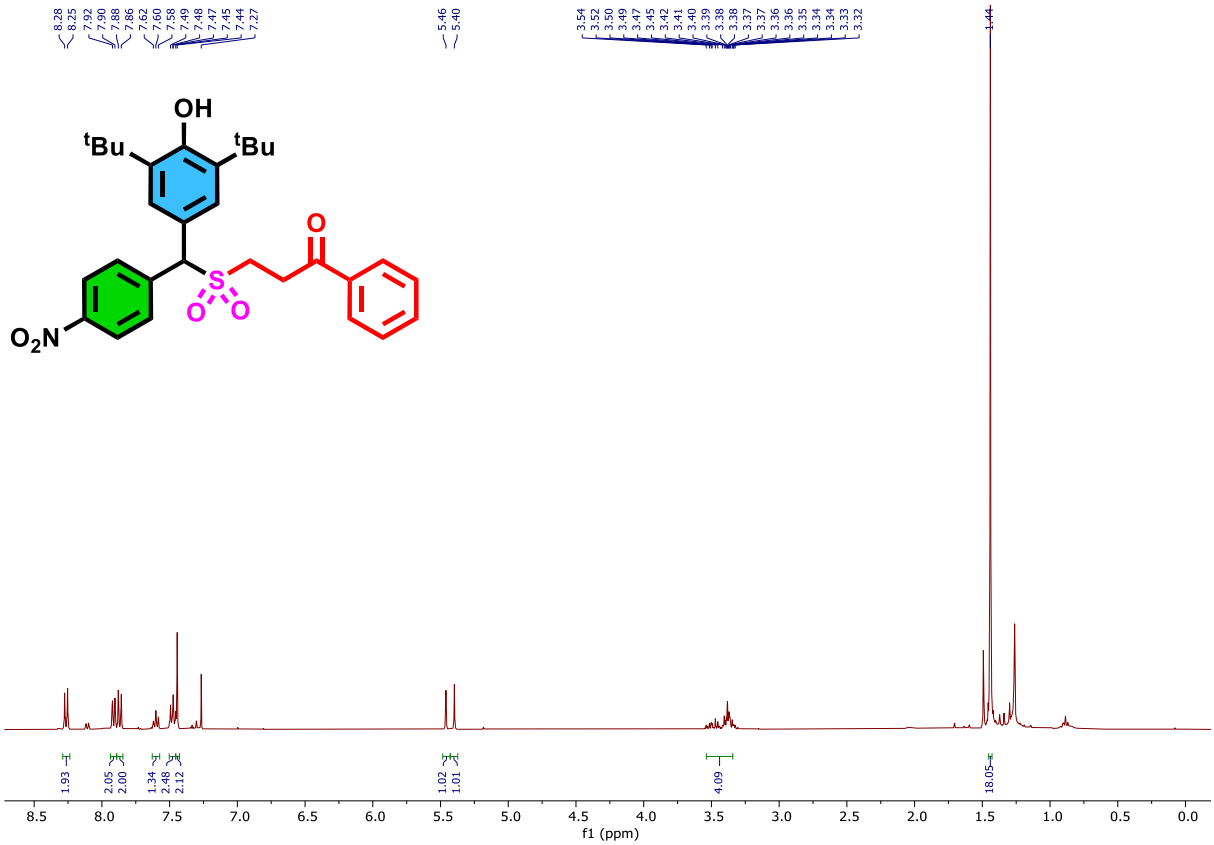
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)benzonitrile **(3ha)**



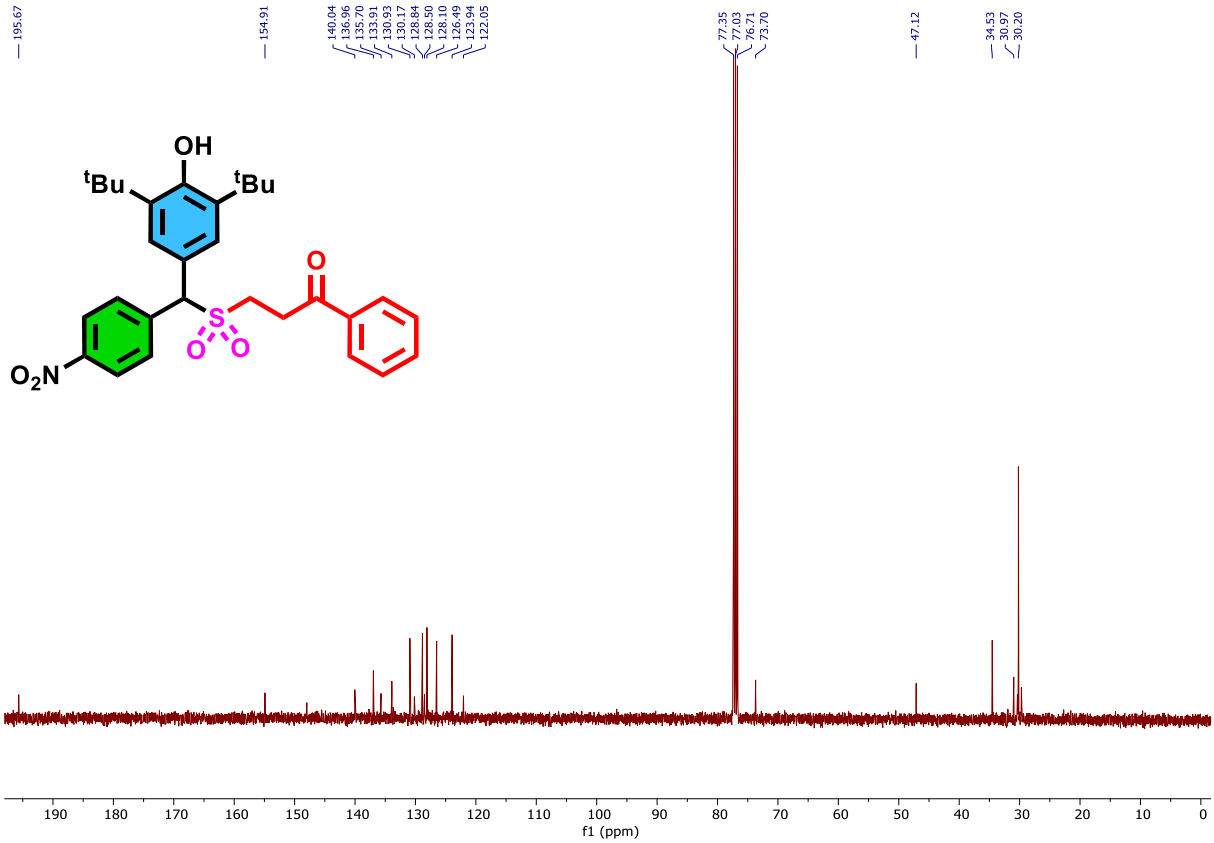
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)benzonitrile **(3ha)**



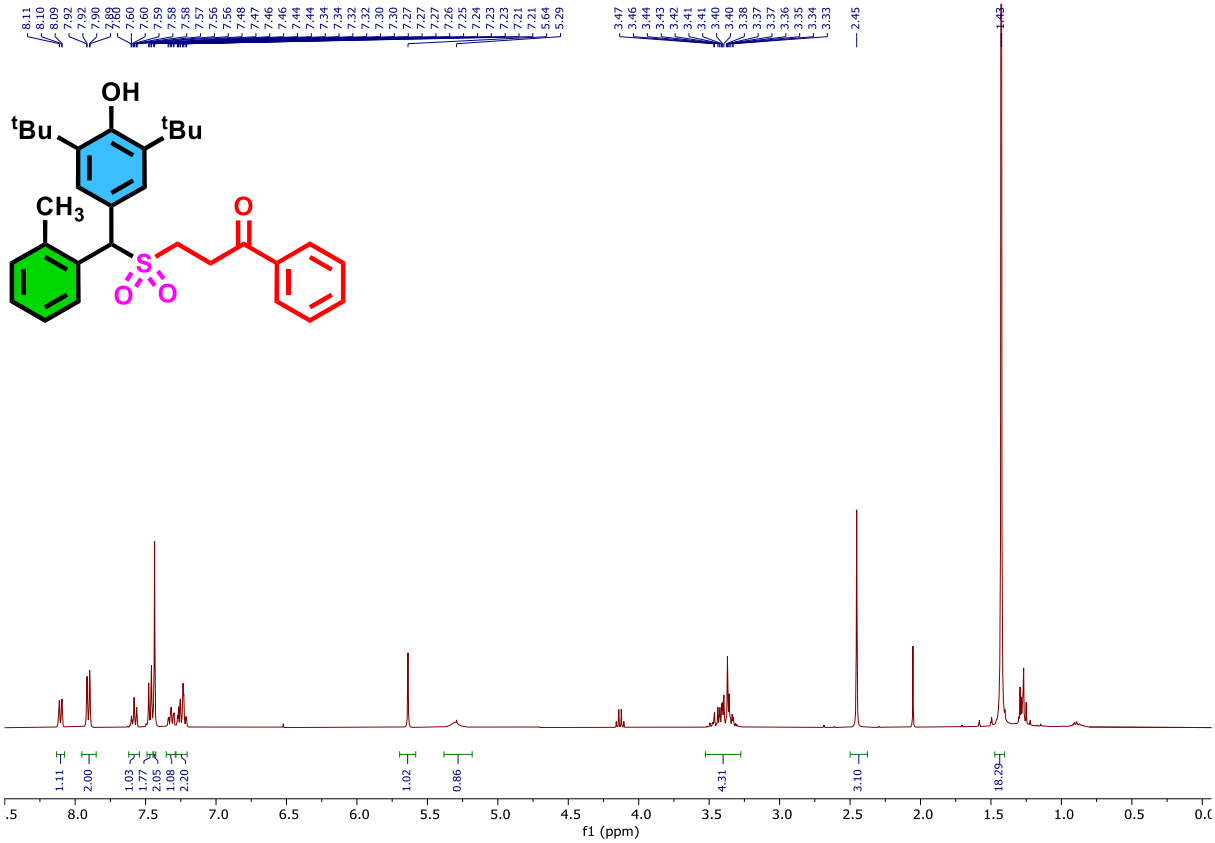
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ia)**



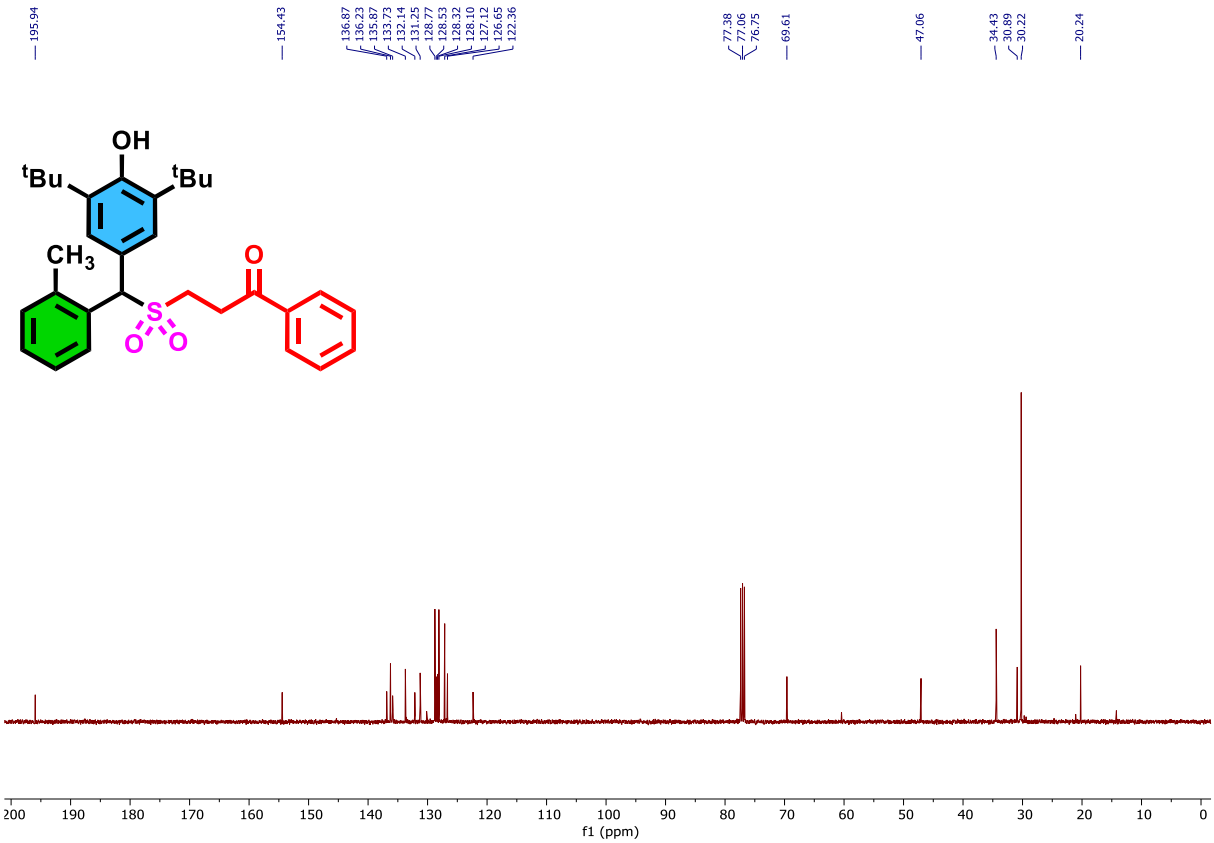
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ia)**



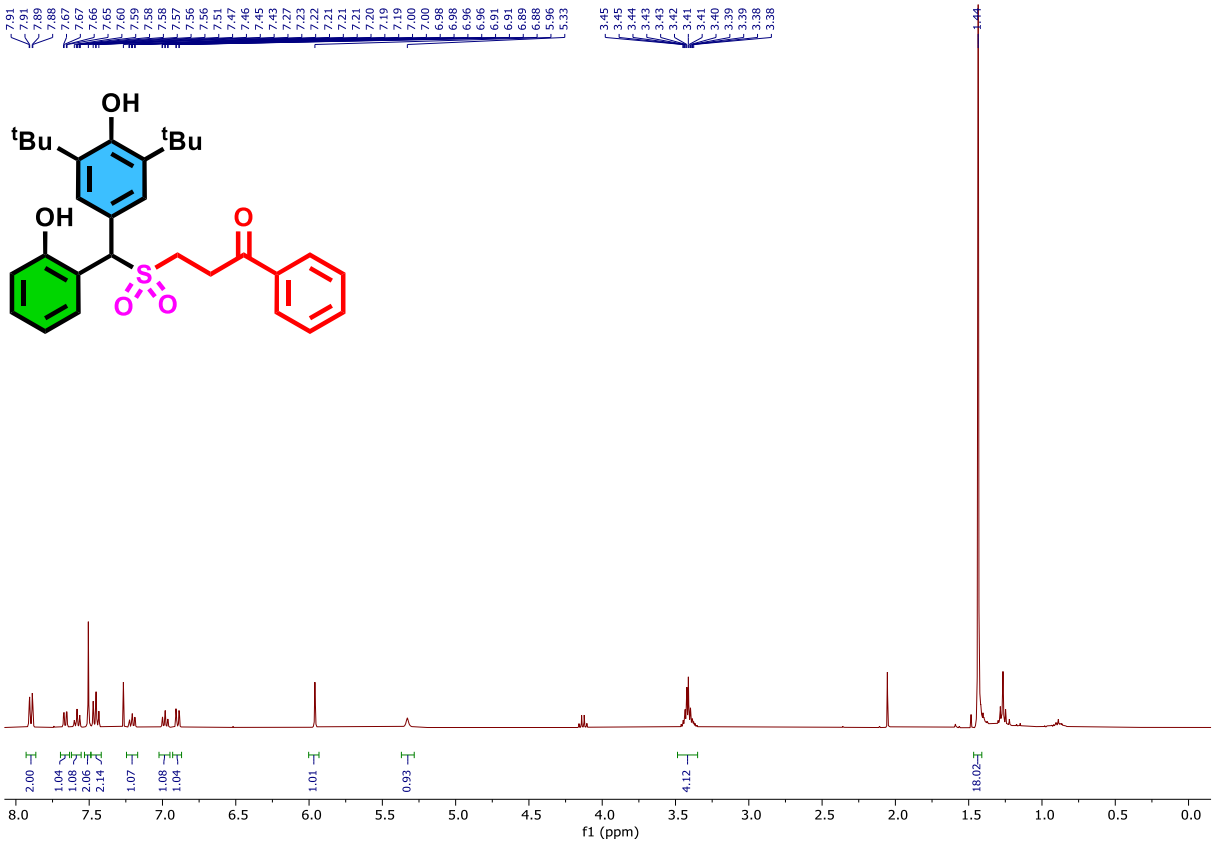
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(o-tolyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ja)**



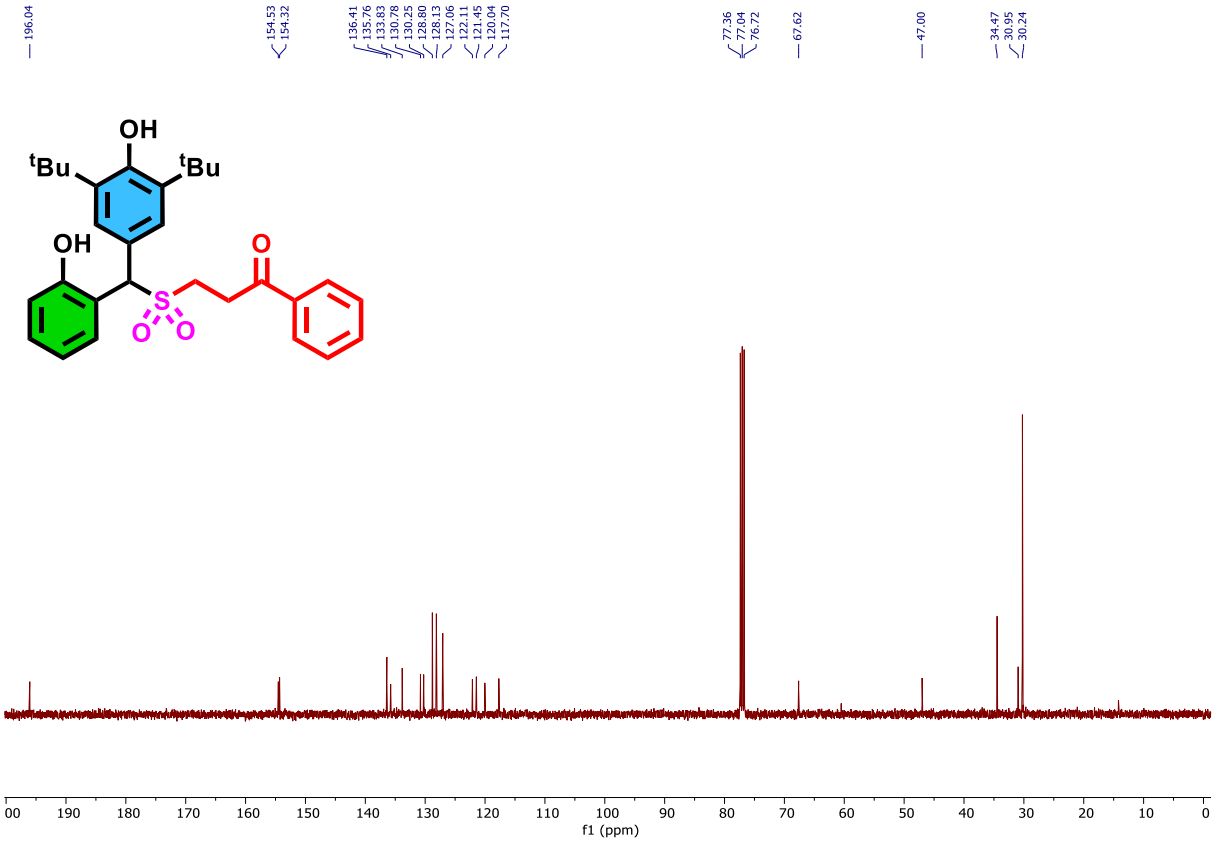
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(o-tolyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ja)**



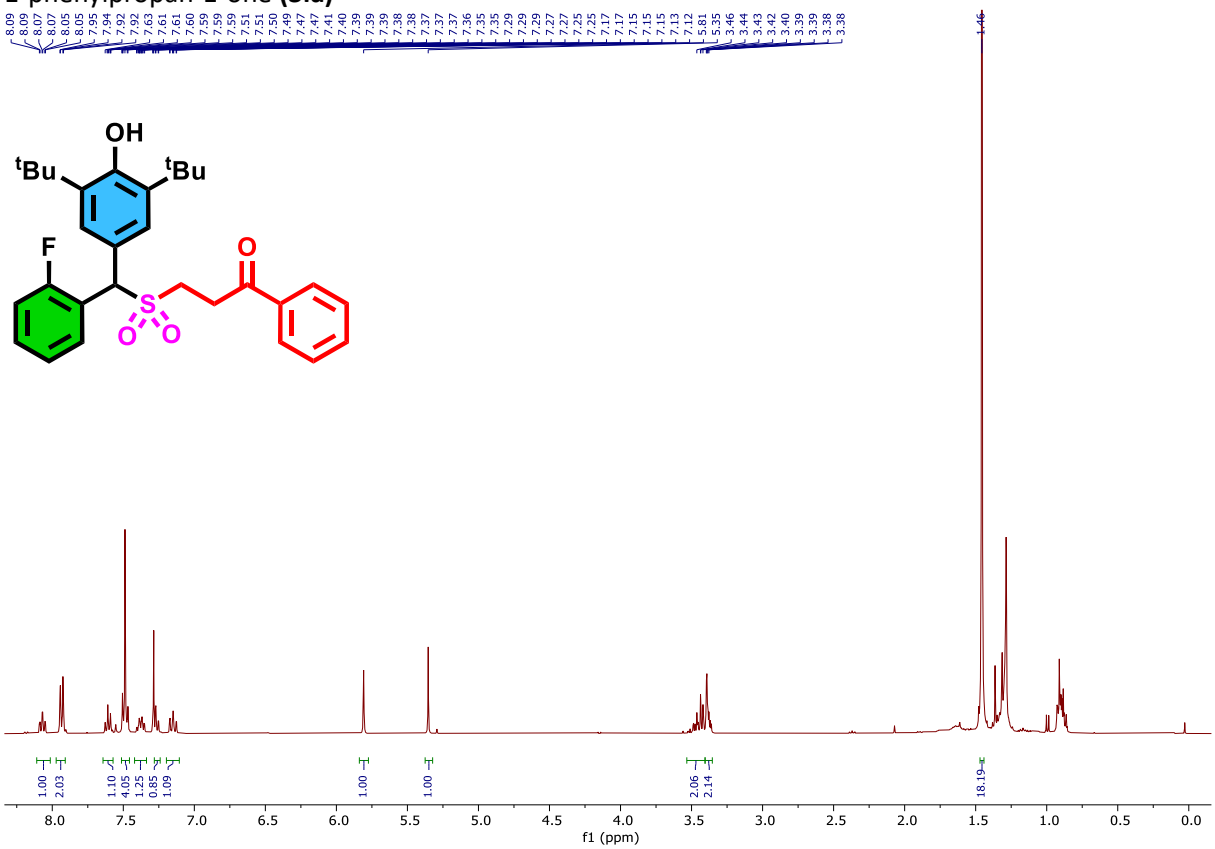
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ka)**



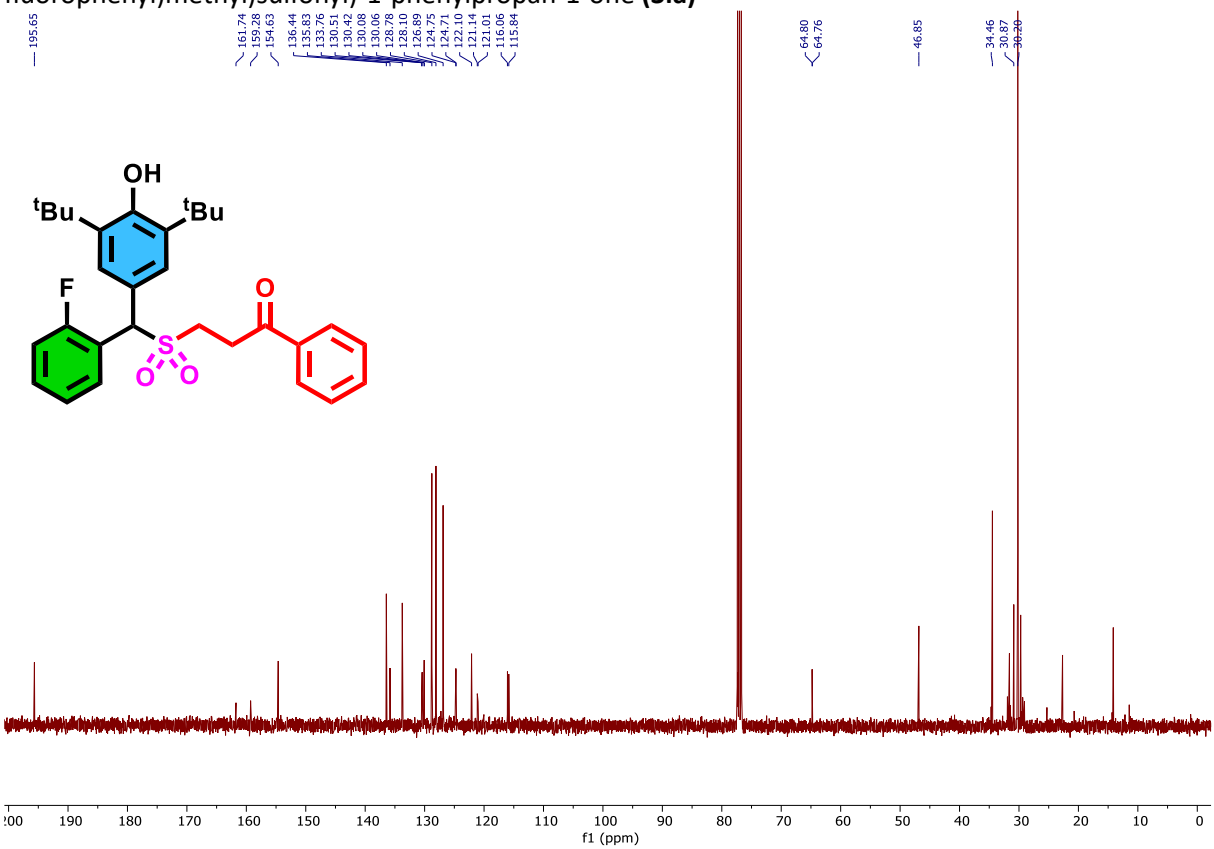
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ka)**



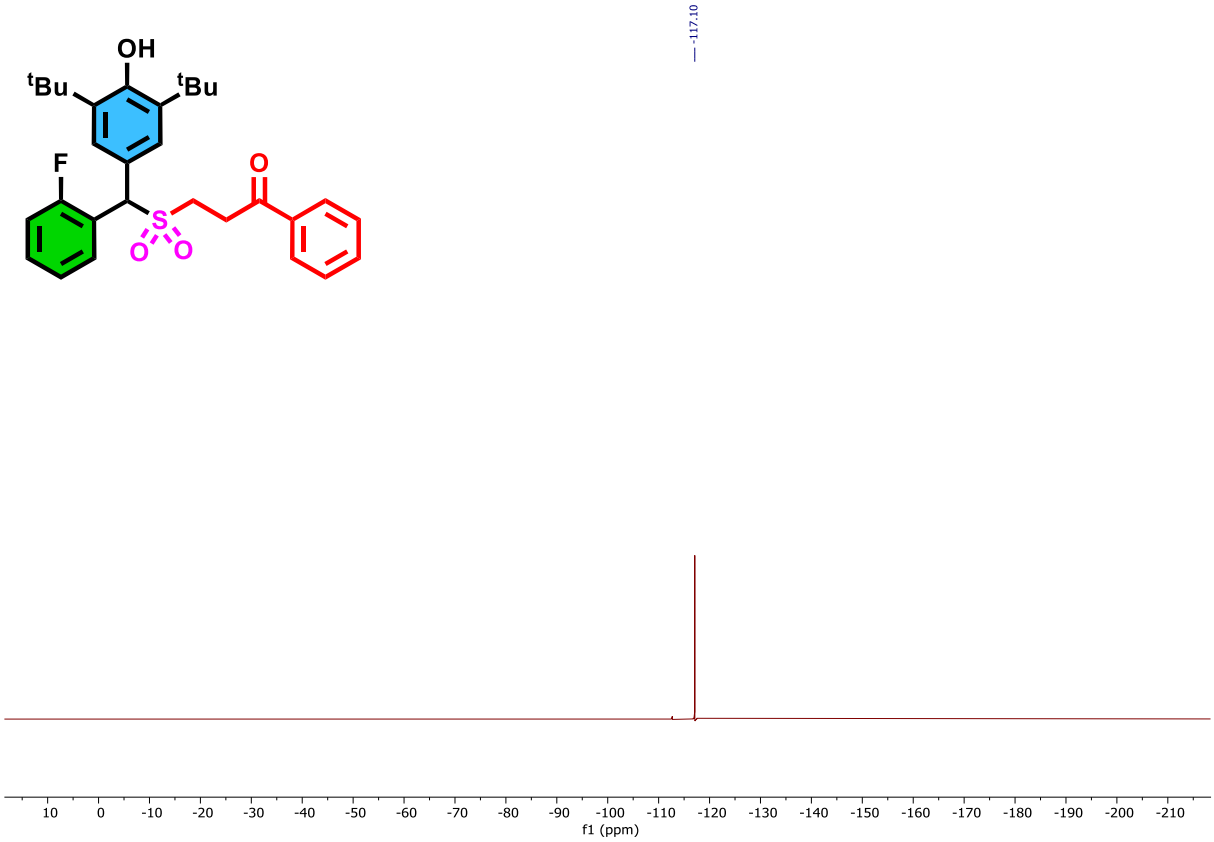
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3la)**



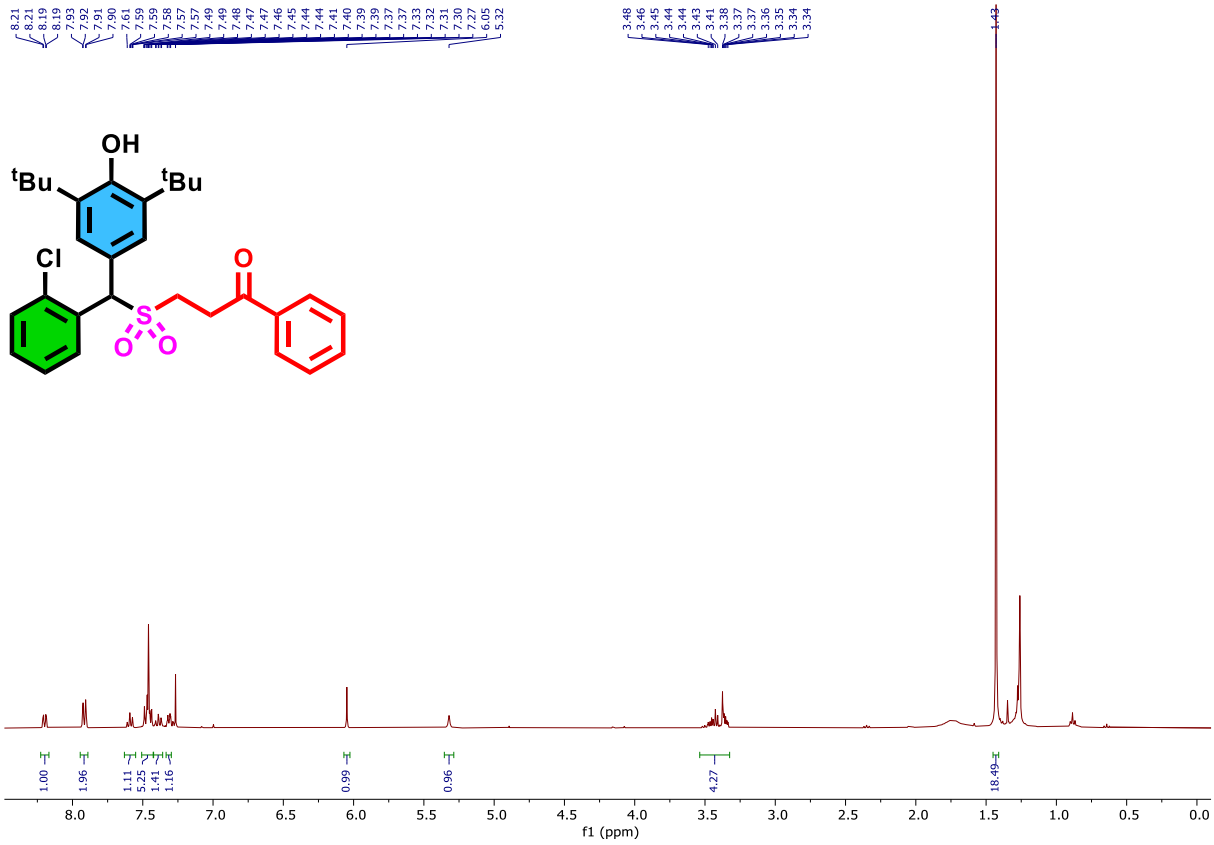
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3la)**



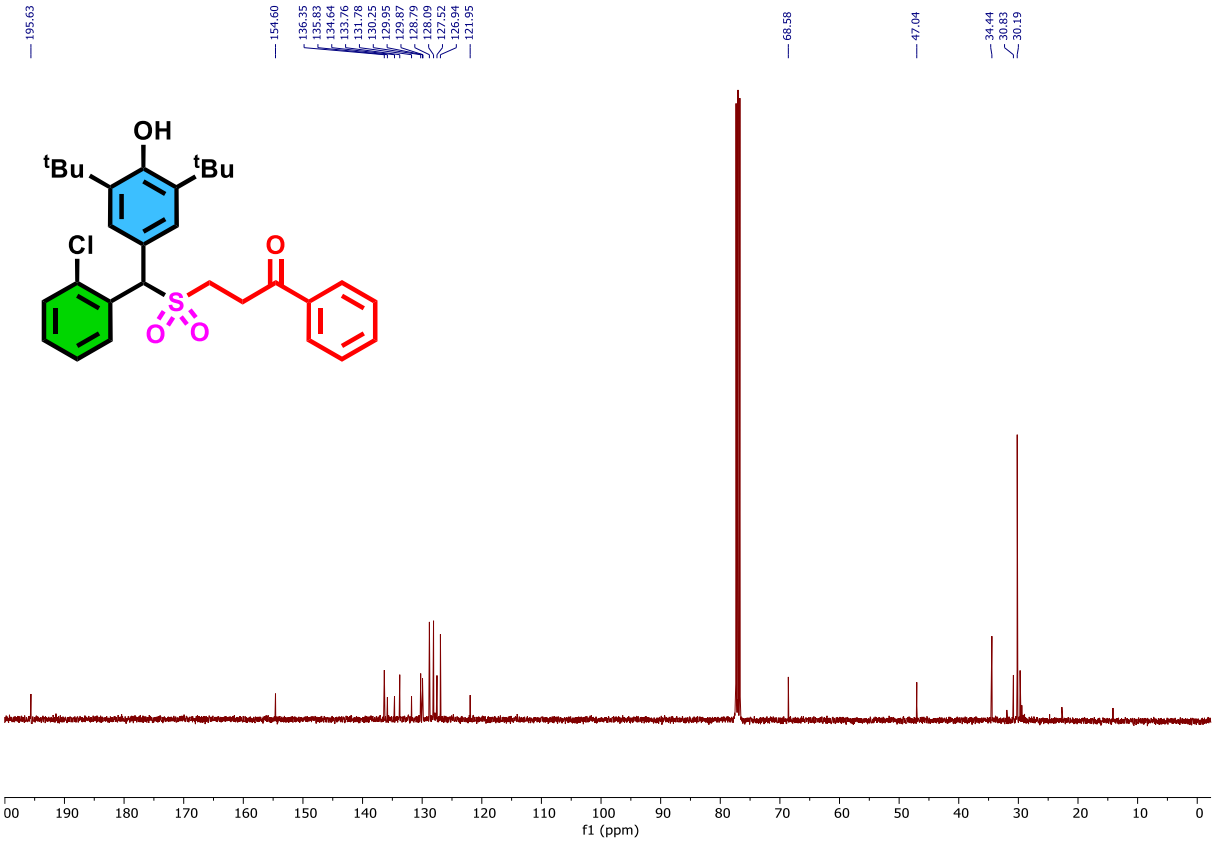
3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3la)**



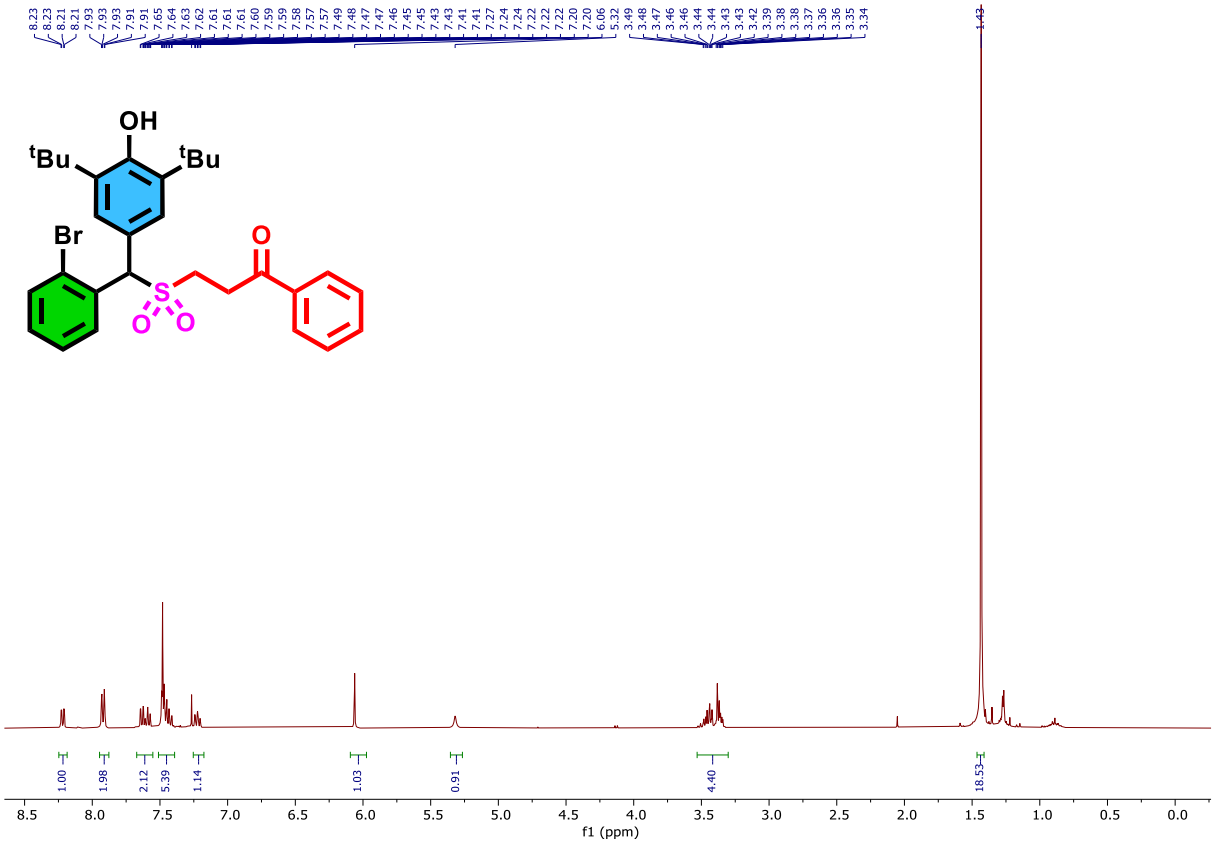
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((2-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ma)**



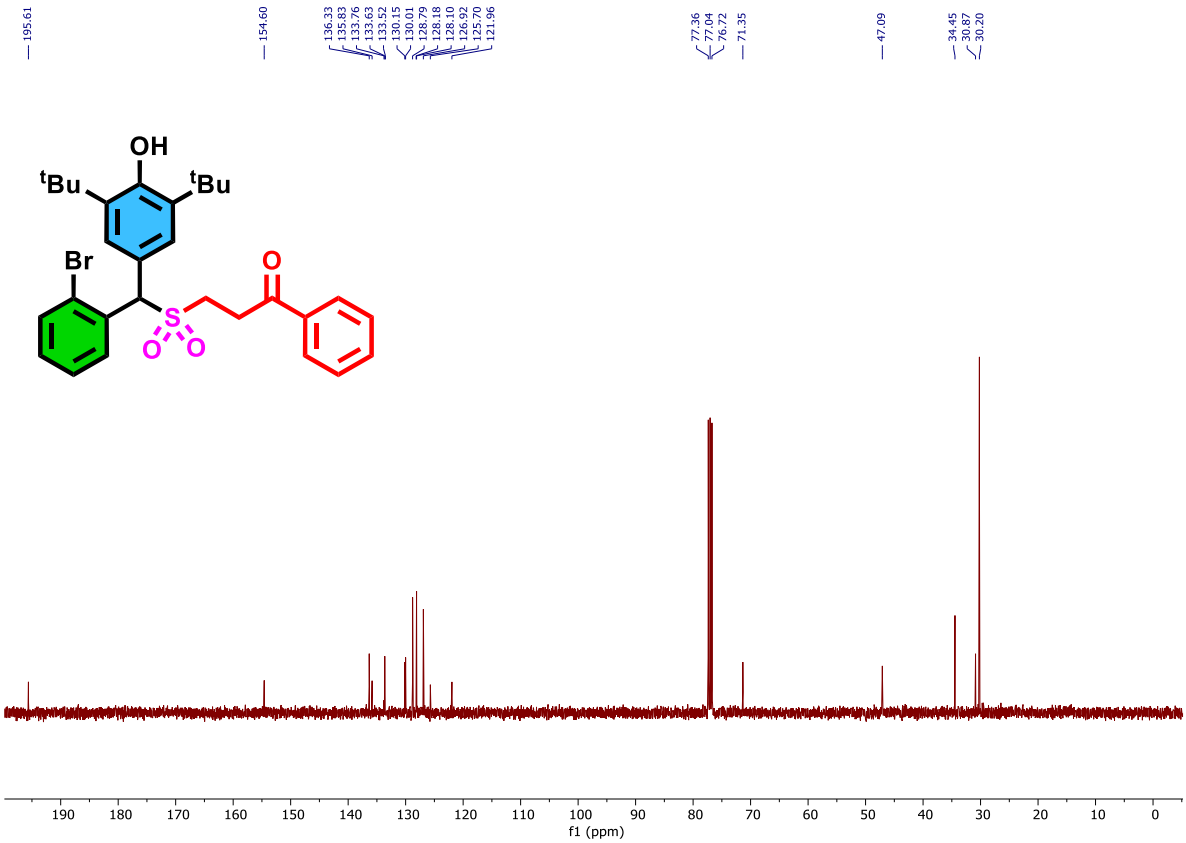
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((2-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ma)**



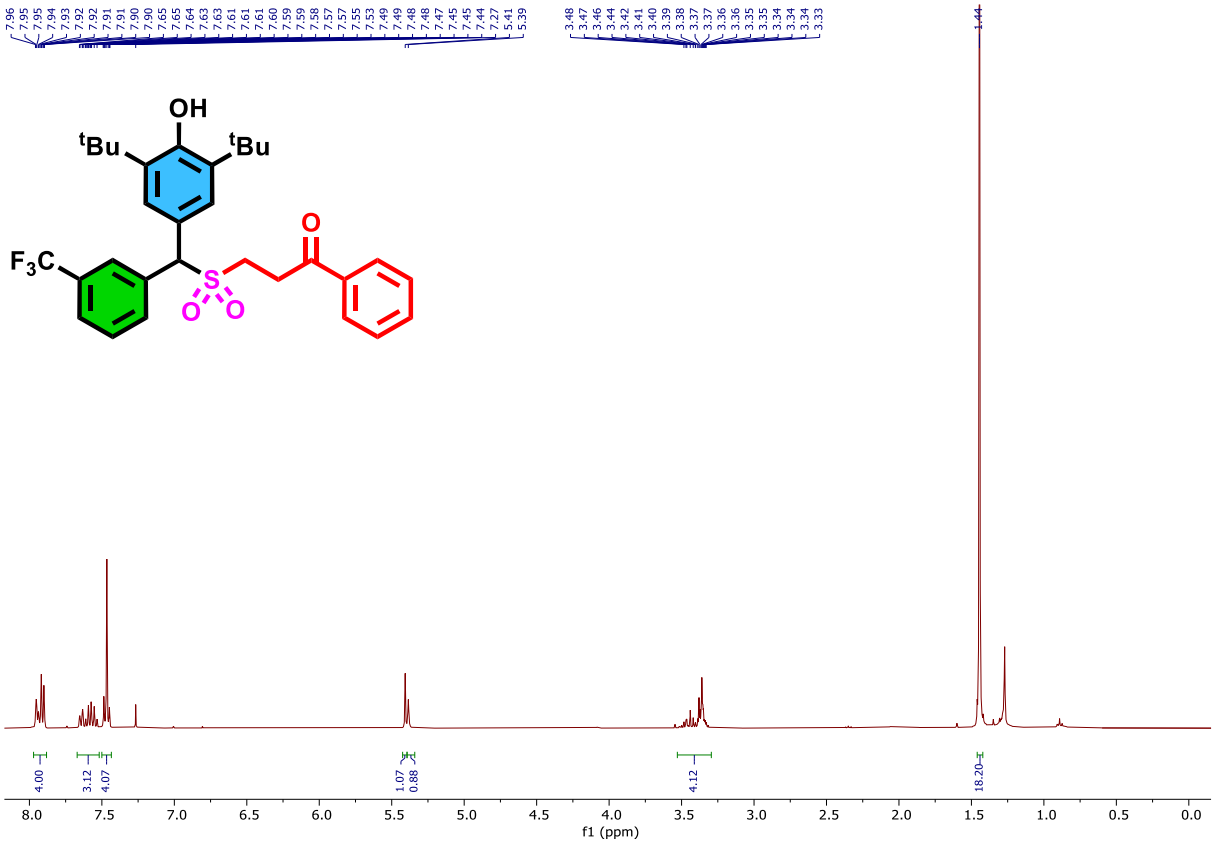
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3na)**



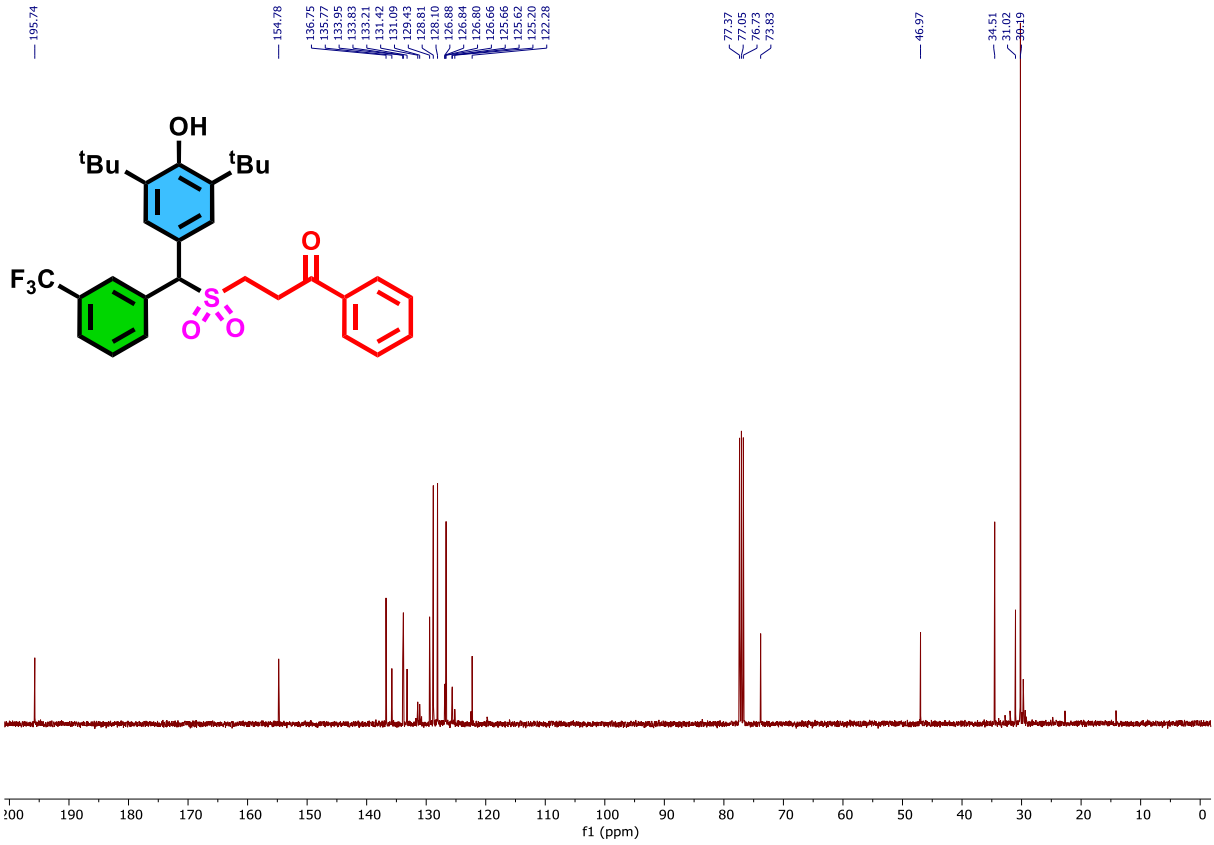
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3na)**



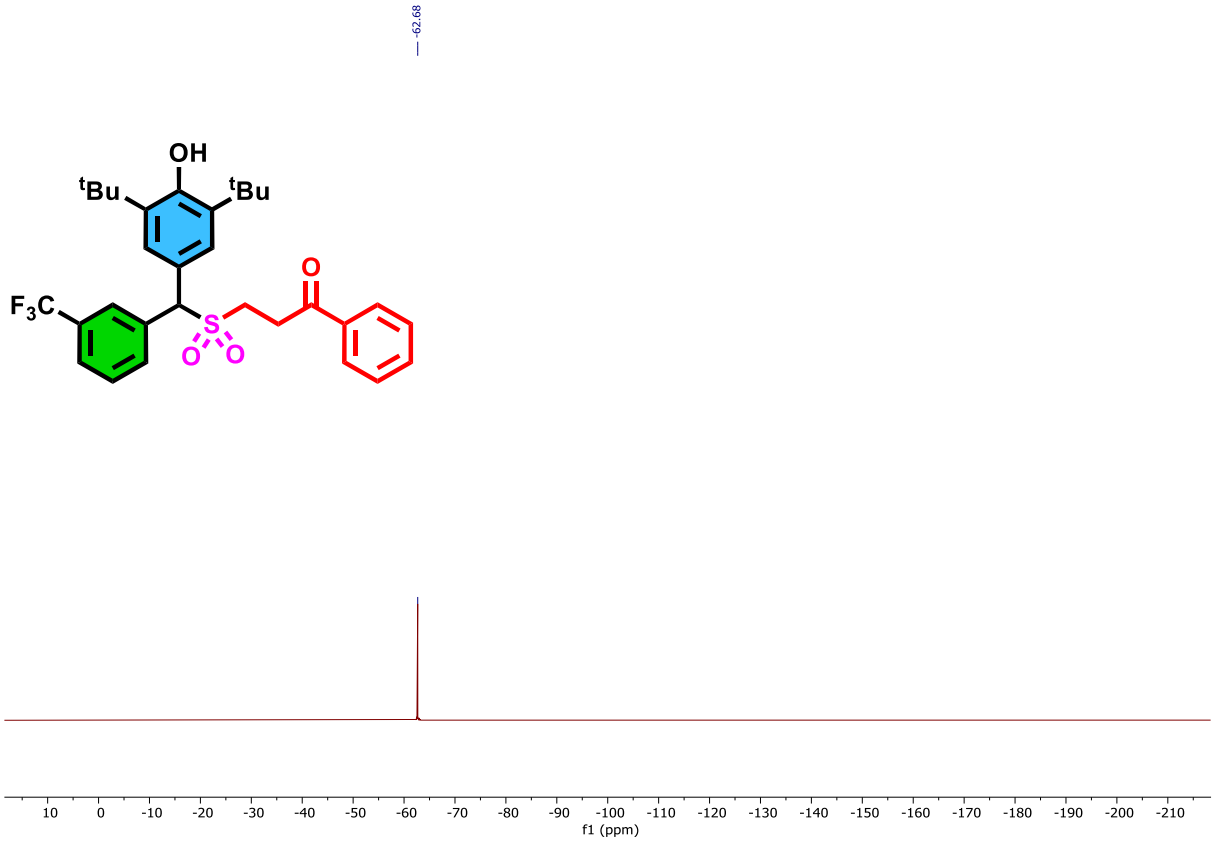
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-(trifluoromethyl)phenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3oa)**



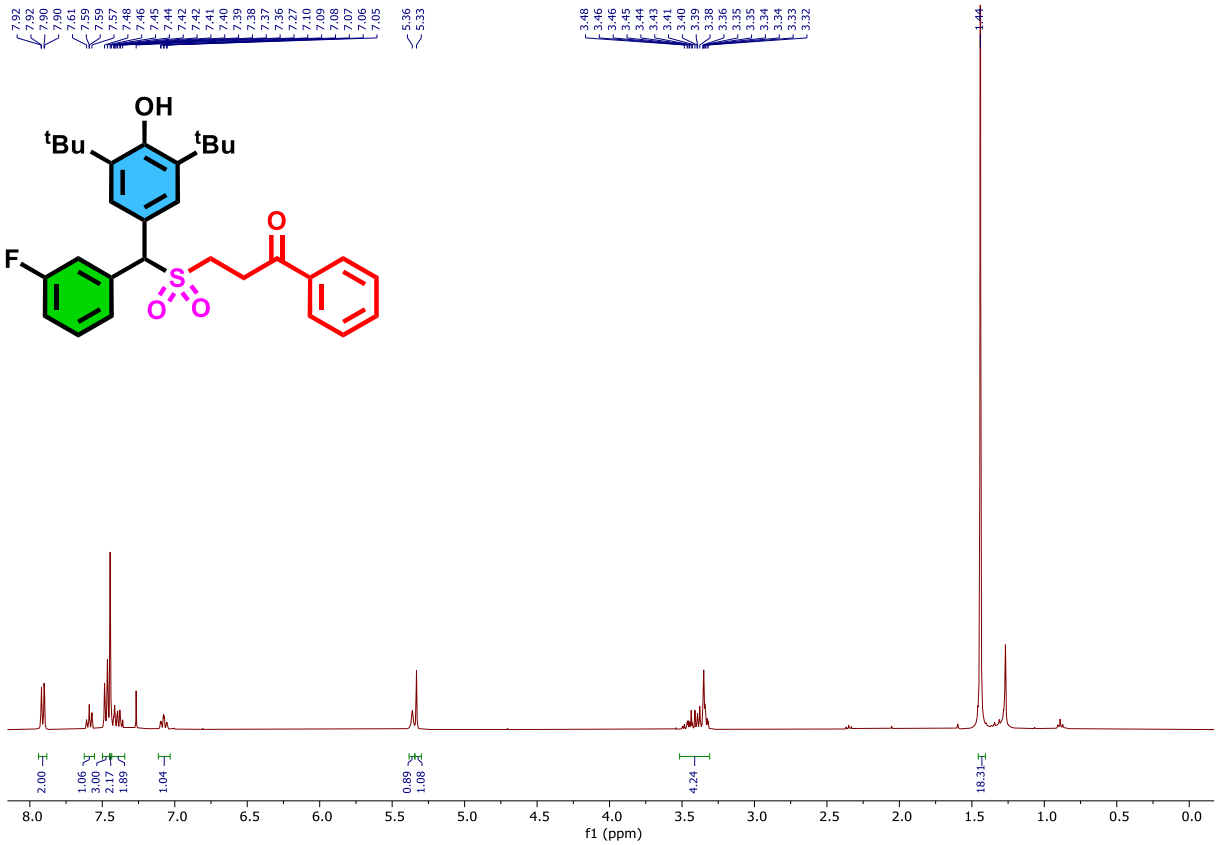
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-(trifluoromethyl)phenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3oa)**



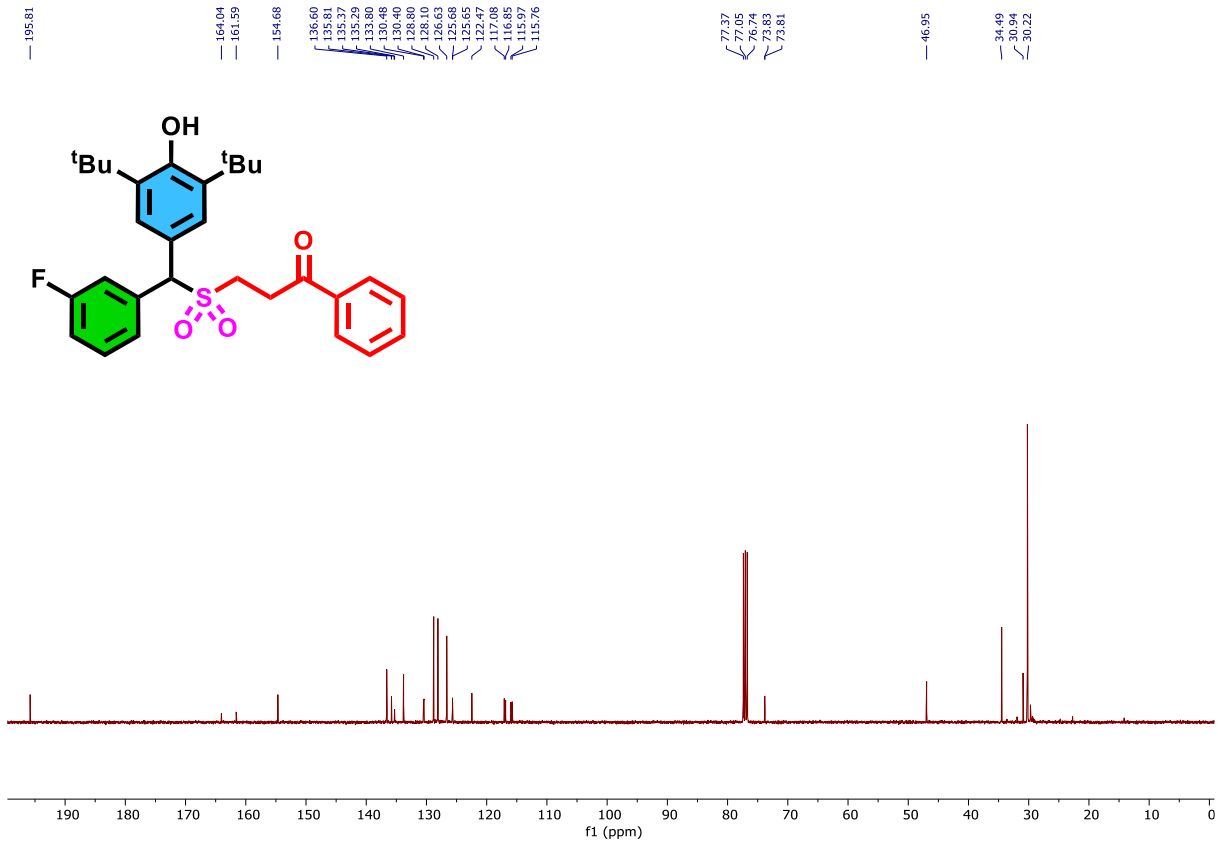
^{19}F NMR (377 MHz, $CDCl_3$) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-(trifluoromethyl)phenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3oa)**



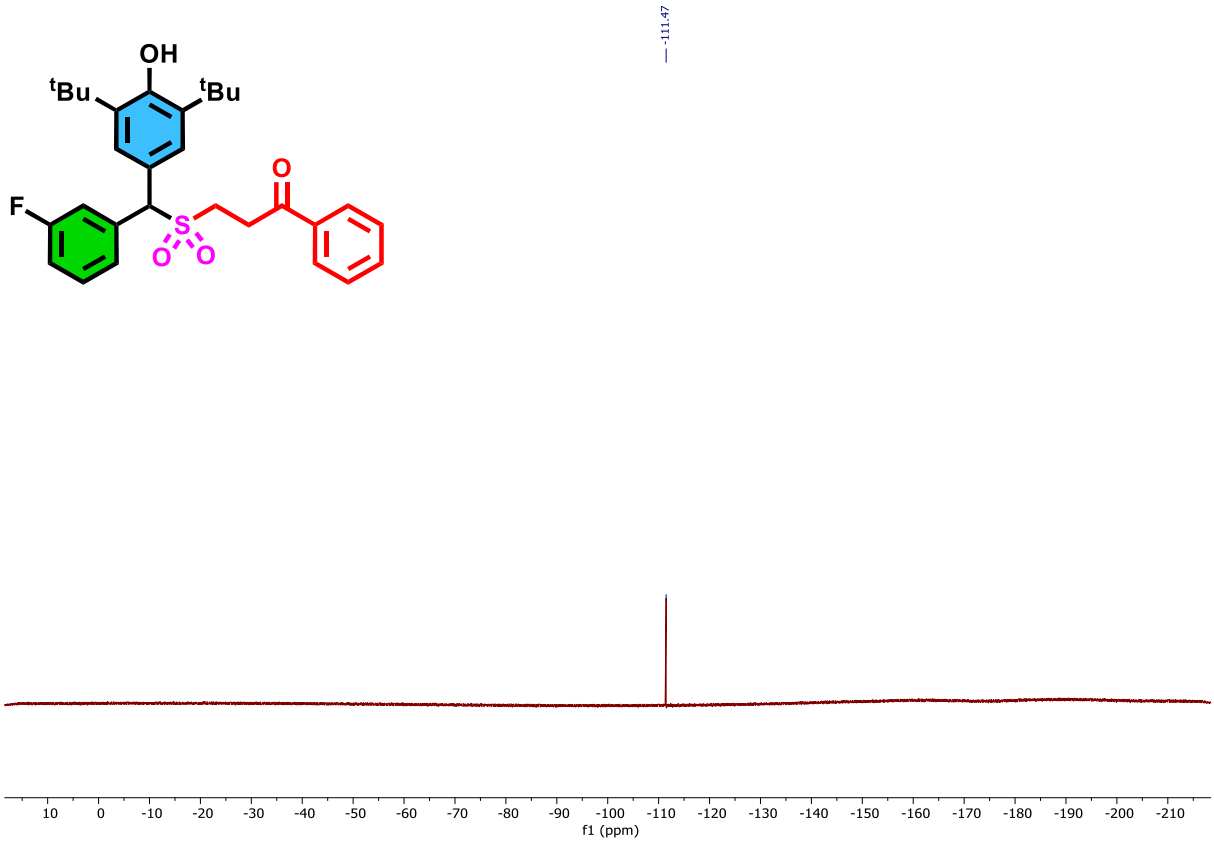
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3pa)**



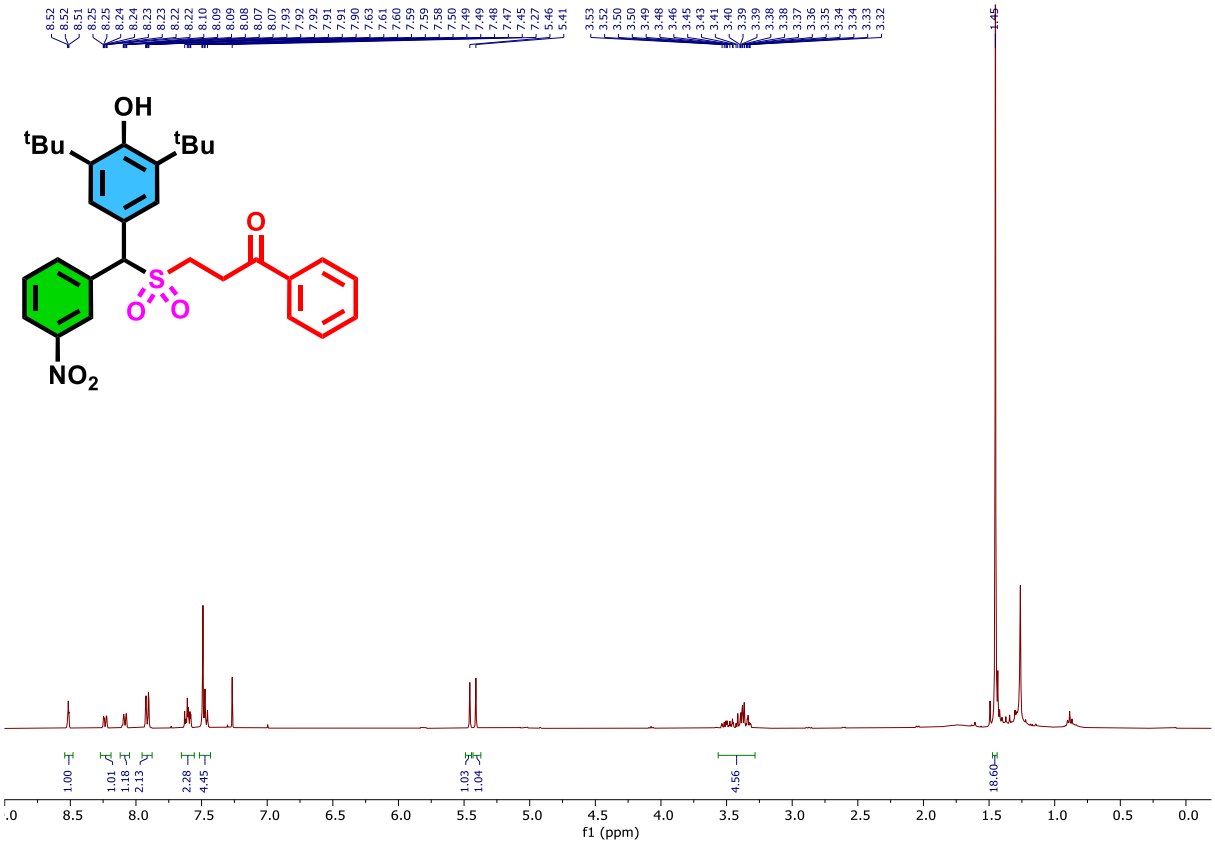
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3pa)**



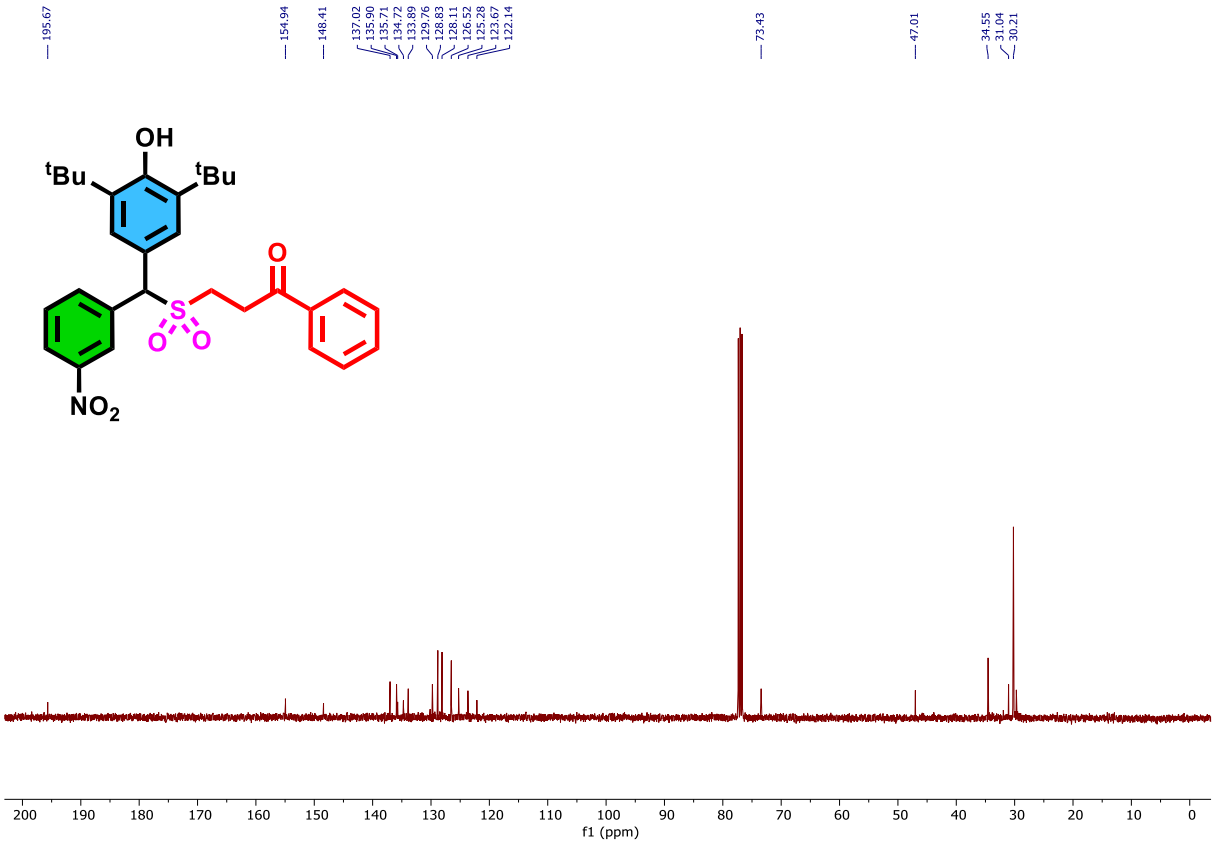
^{19}F NMR (377 MHz, $CDCl_3$) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-fluorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3pa)**



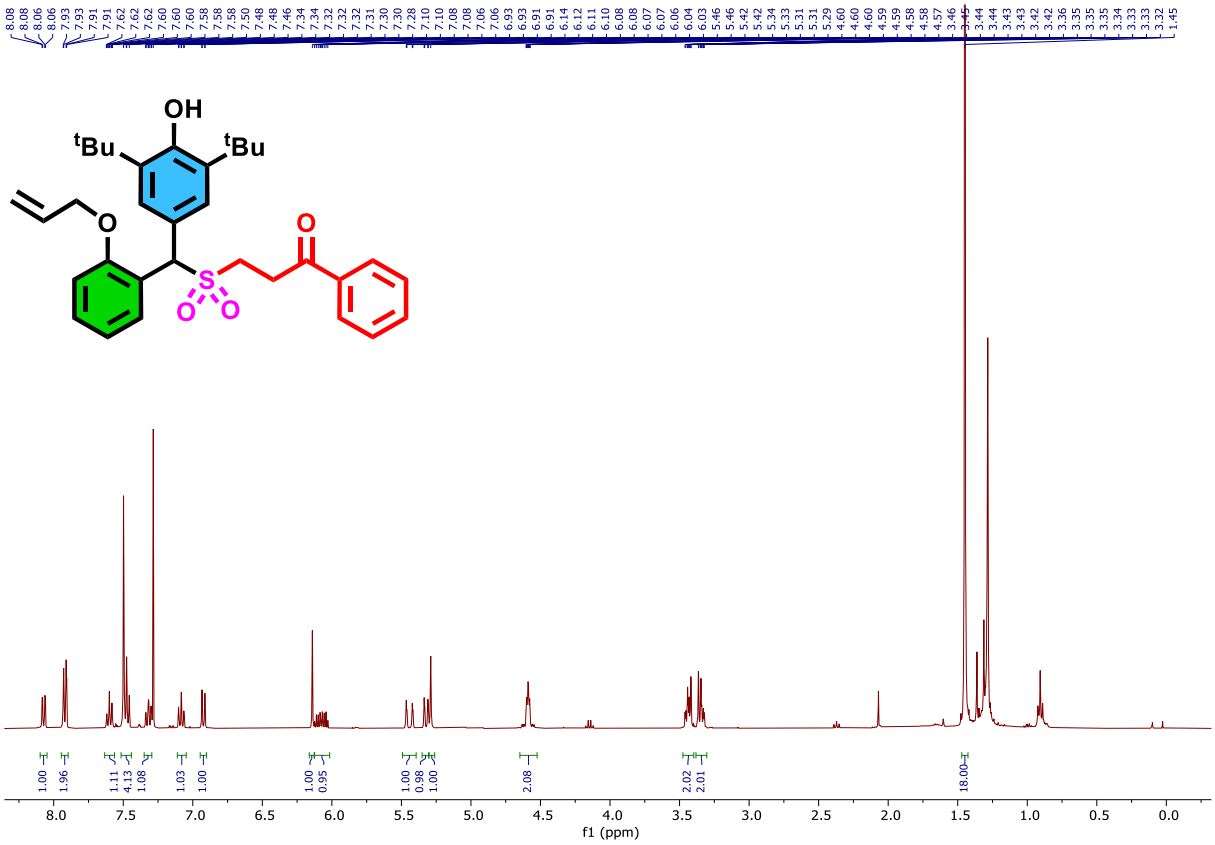
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3qa)**



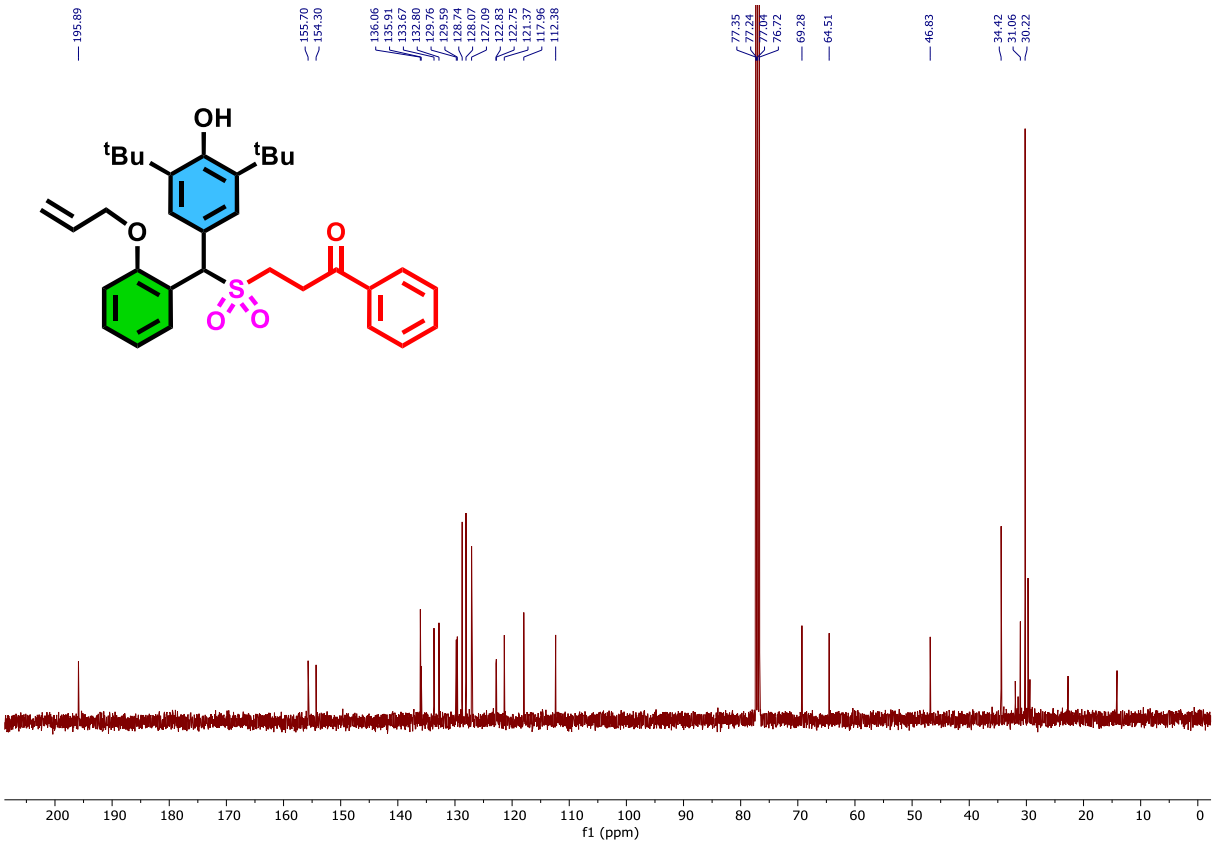
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3-nitrophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3qa)**



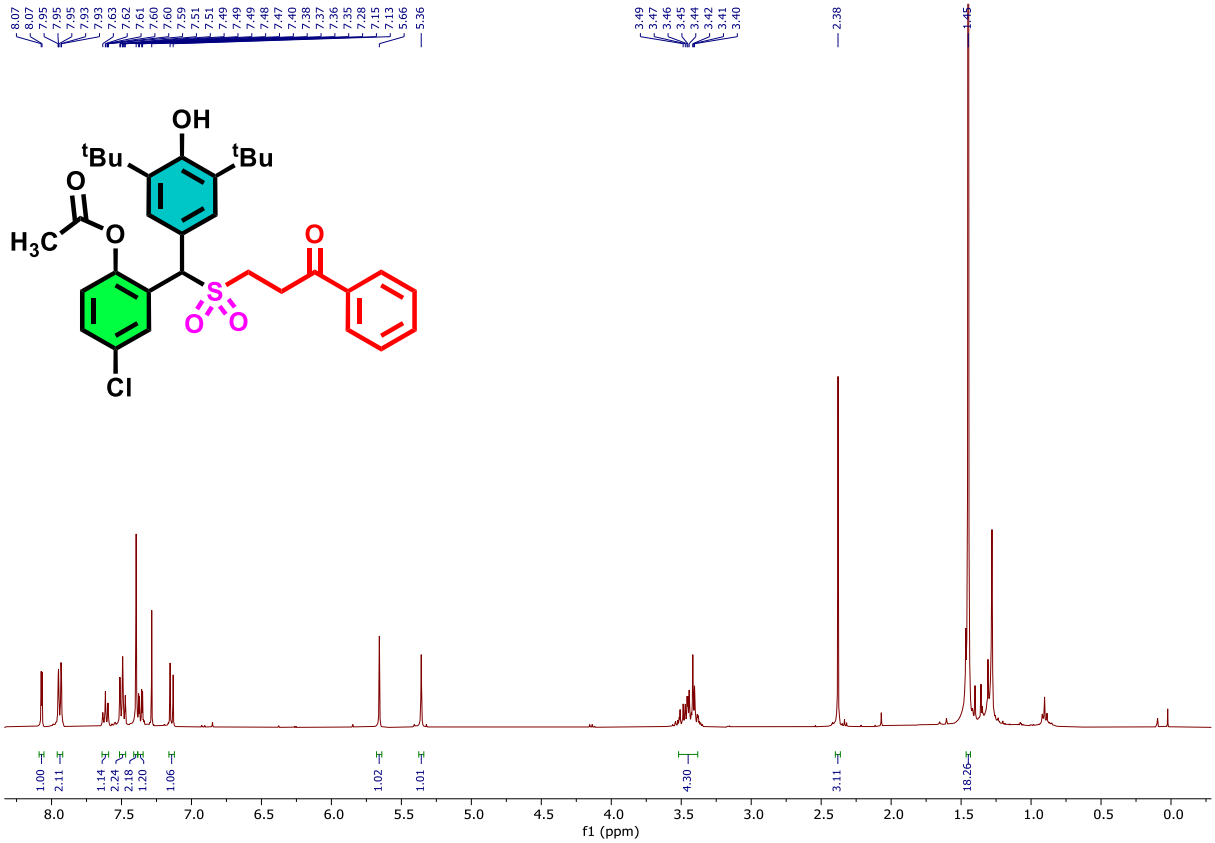
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((2-(allyloxy)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ra)**



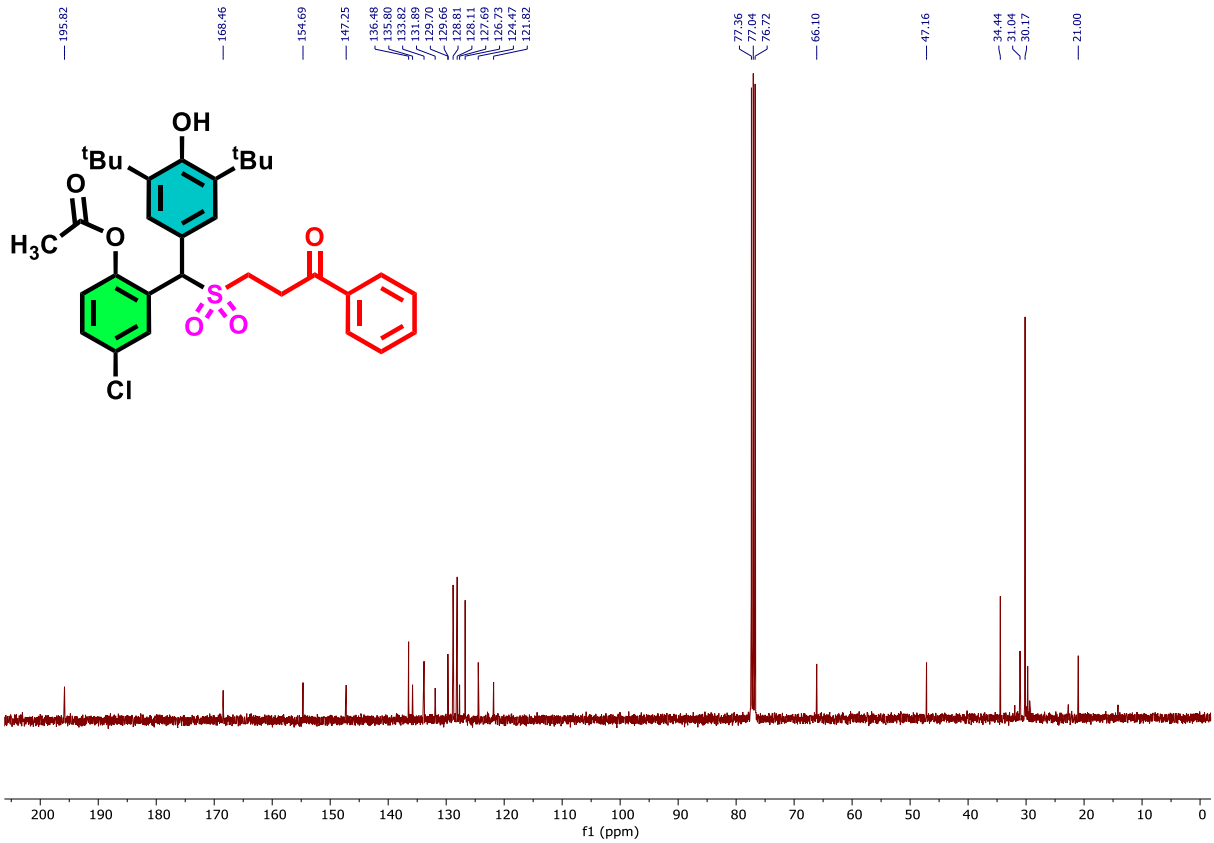
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((2-(allyloxy)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ra)**



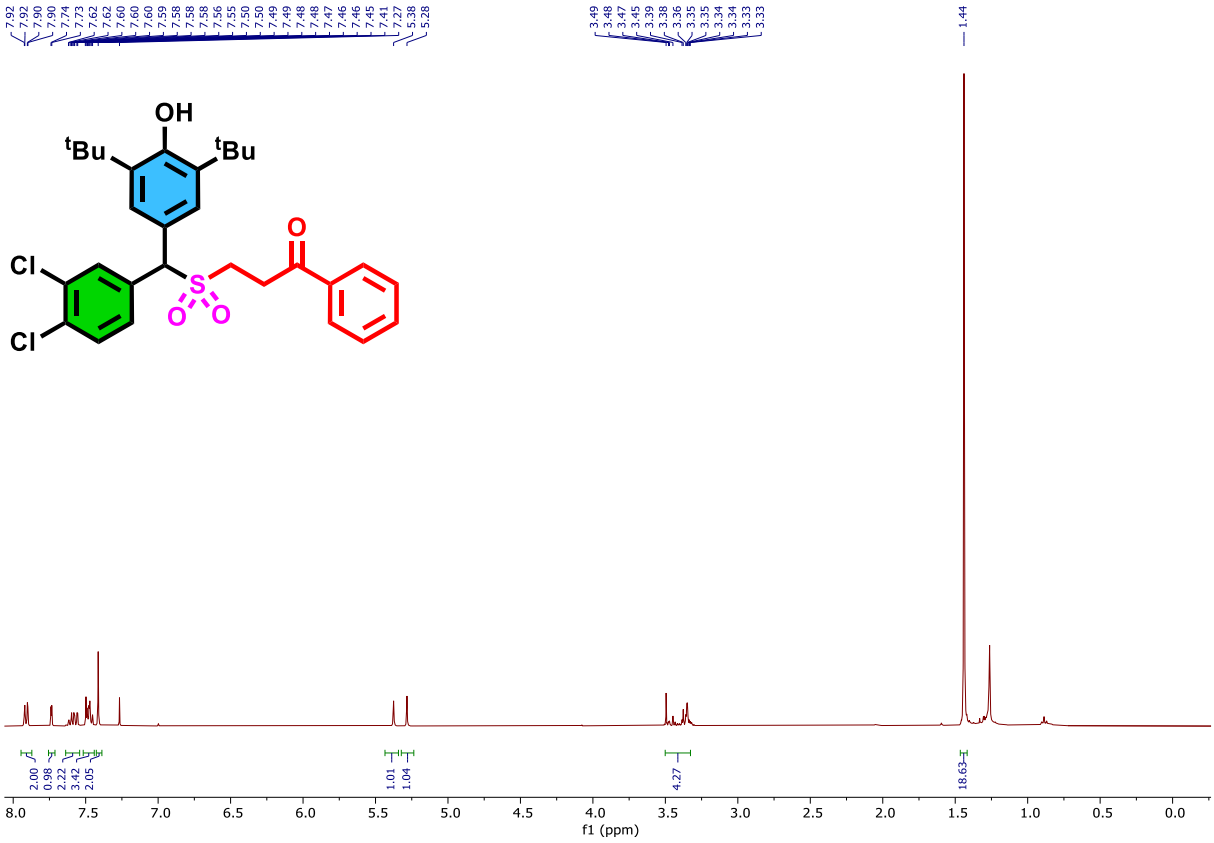
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-chloro-2-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl acetate **(3sa)**



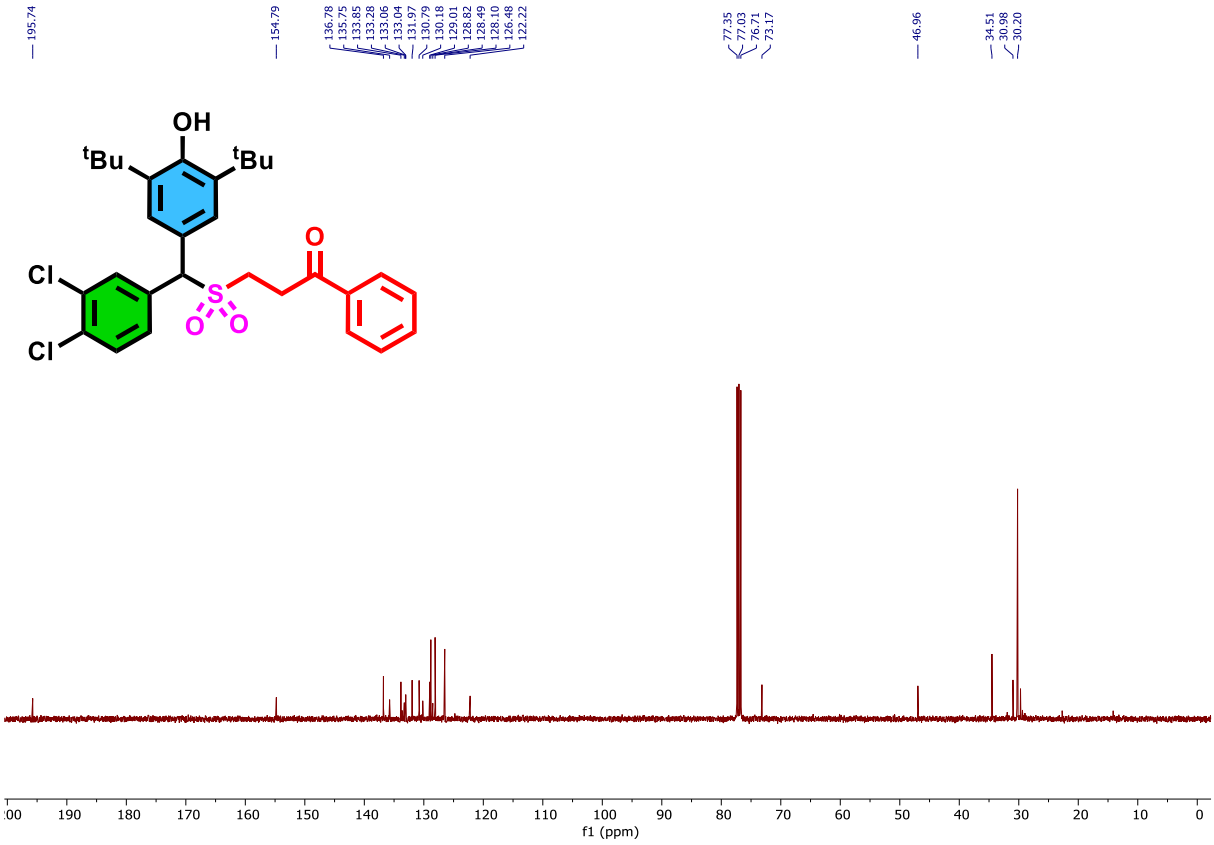
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-chloro-2-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl acetate **(3sa)**



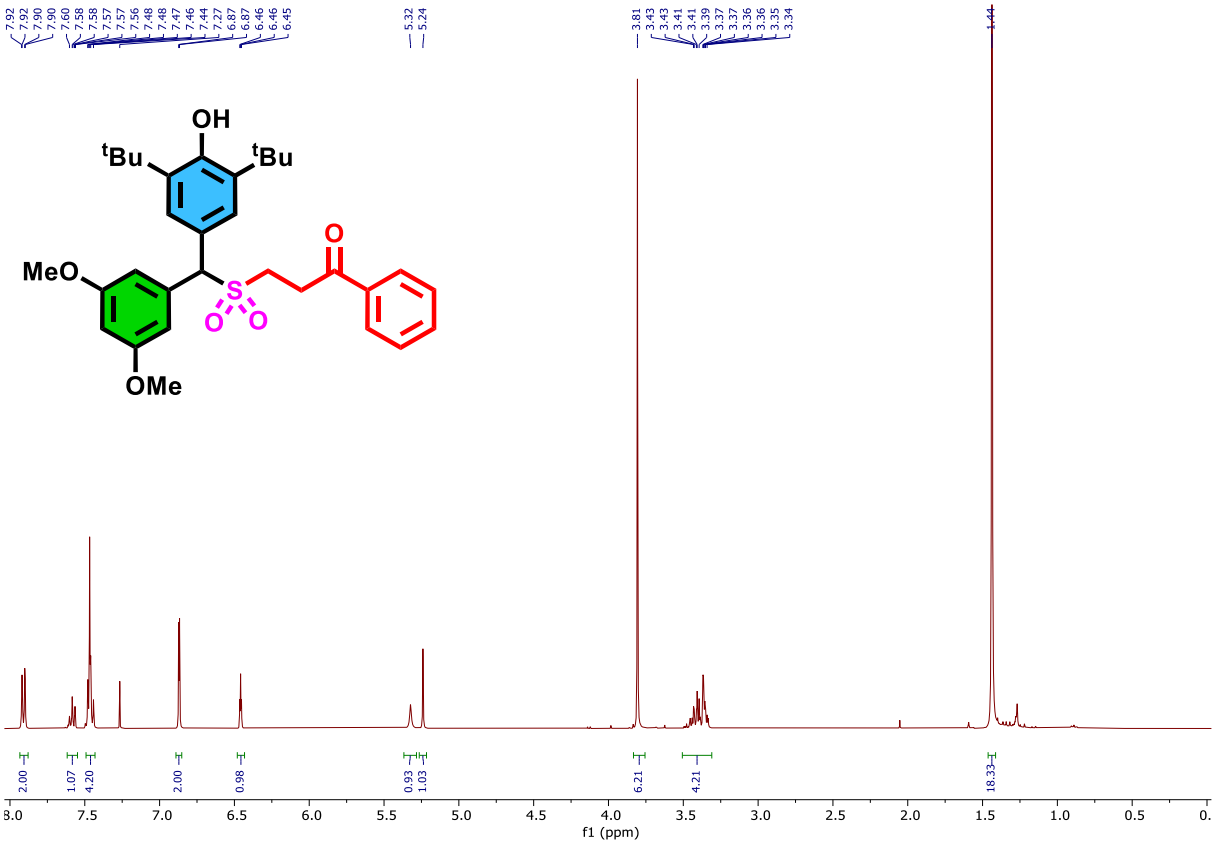
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4-dichlorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ta)**



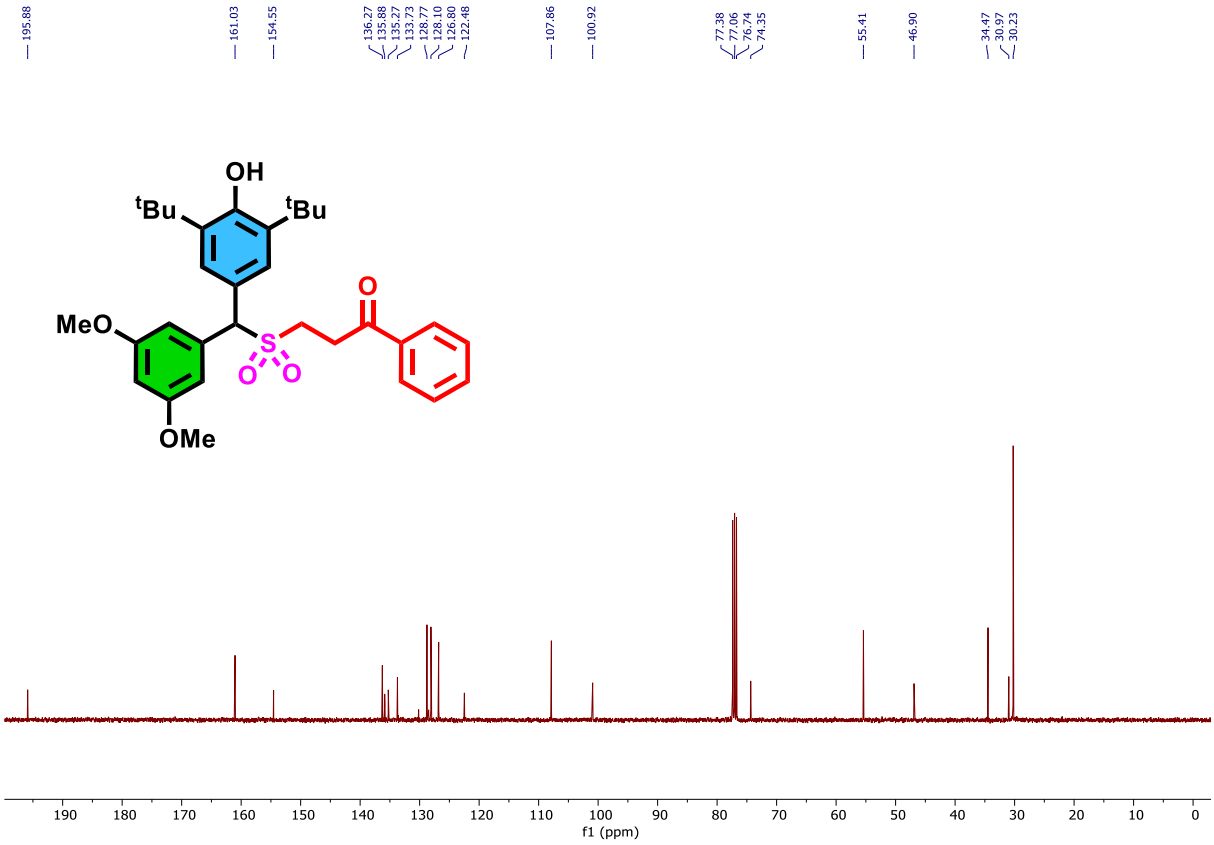
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4-dichlorophenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ta)**



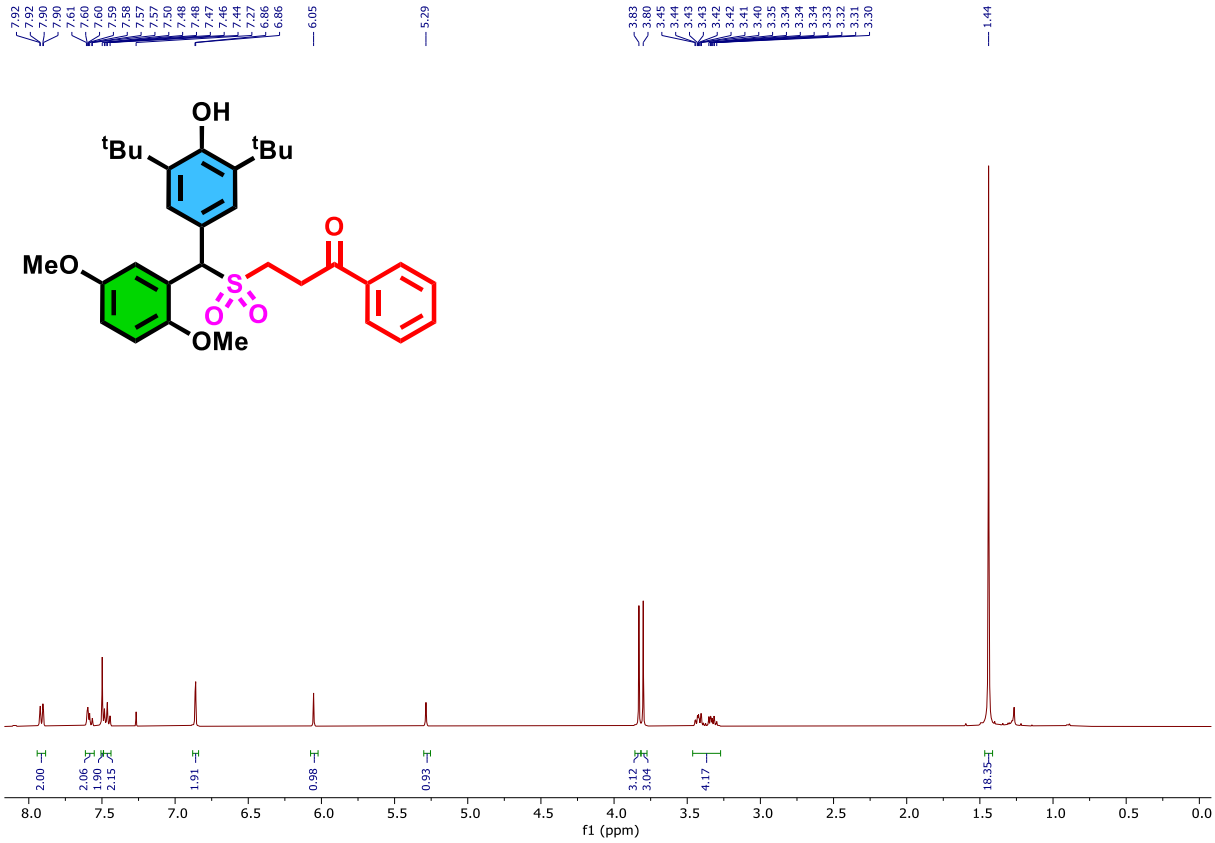
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3,5-dimethoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ua)**



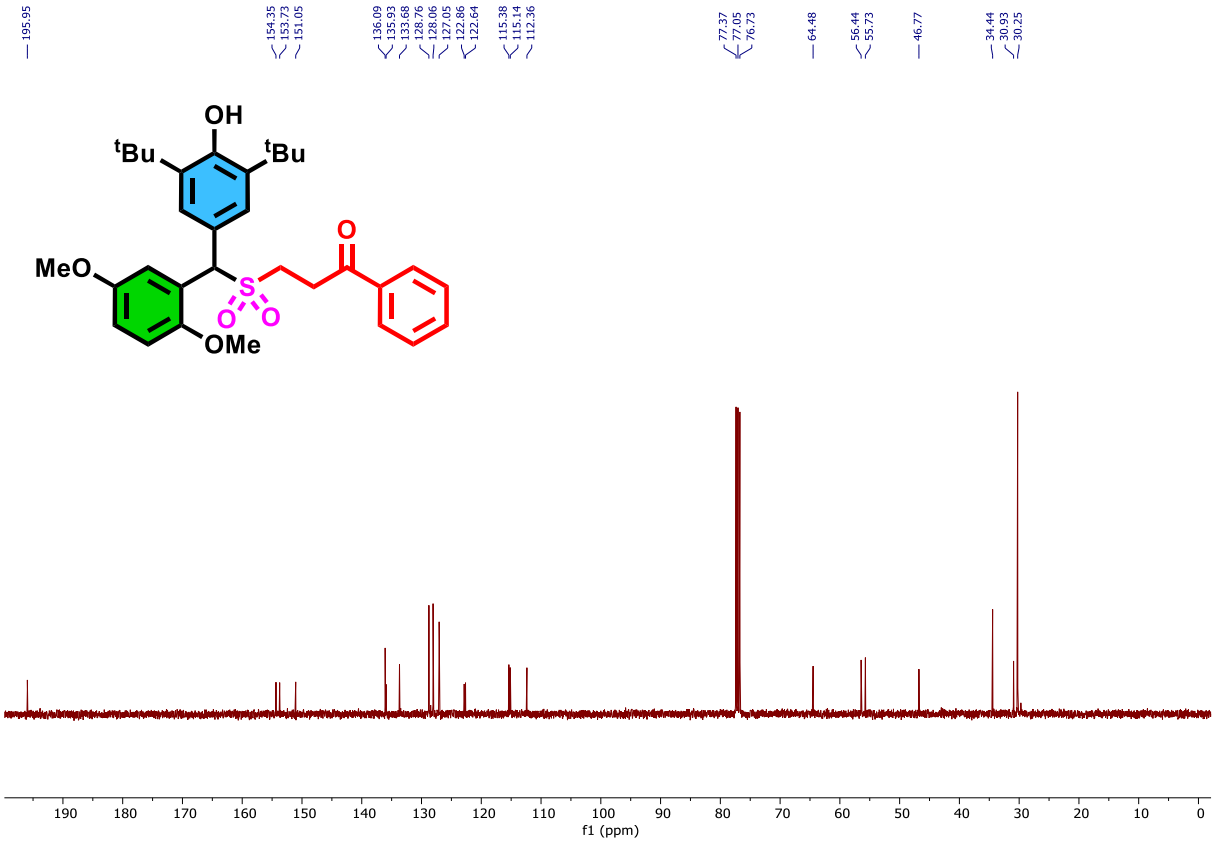
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(3,5-dimethoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3ua)**



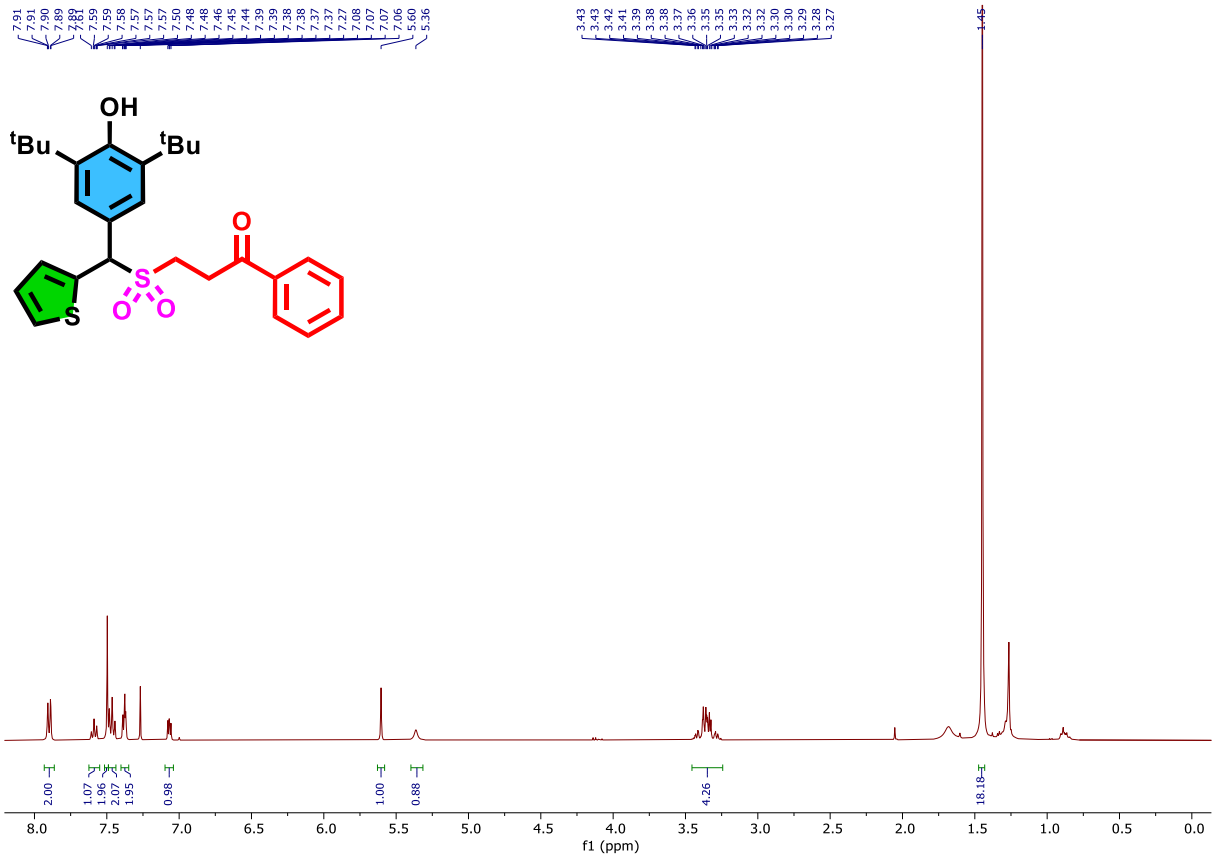
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2,5-dimethoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3va)**



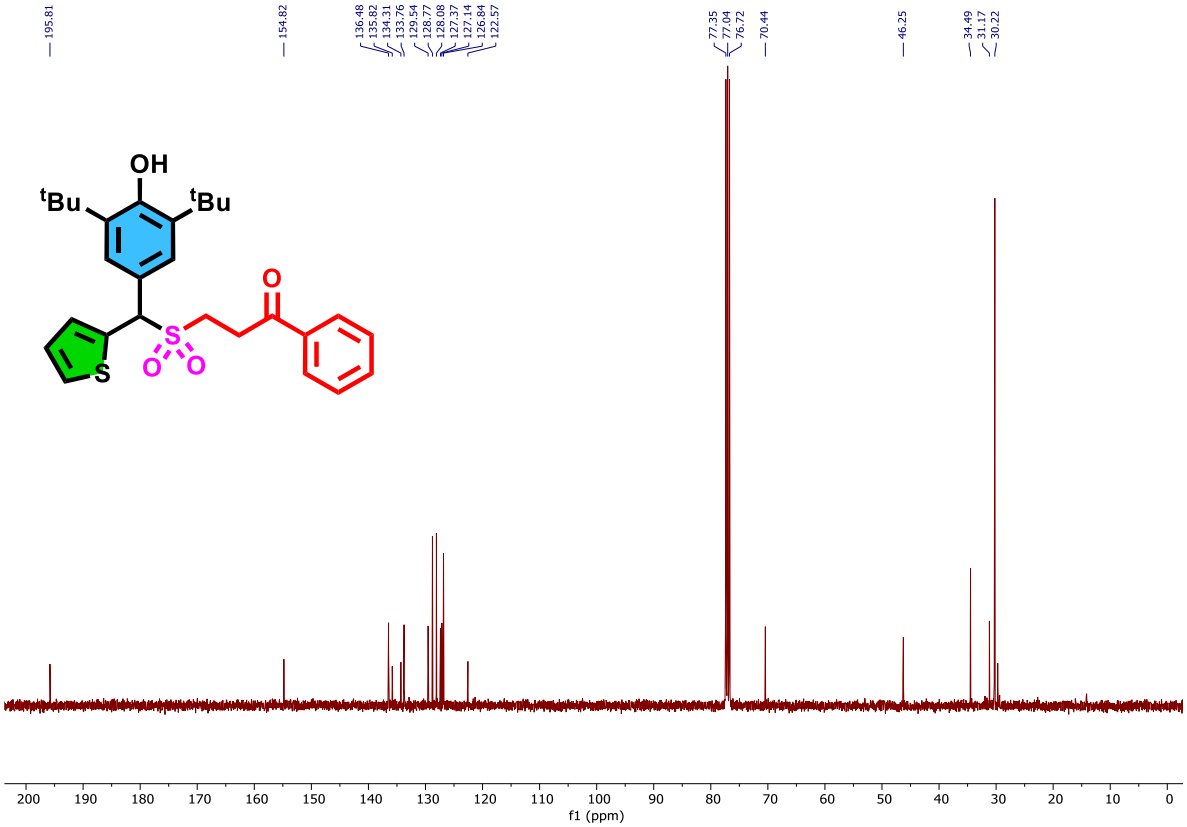
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(2,5-dimethoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3va)**



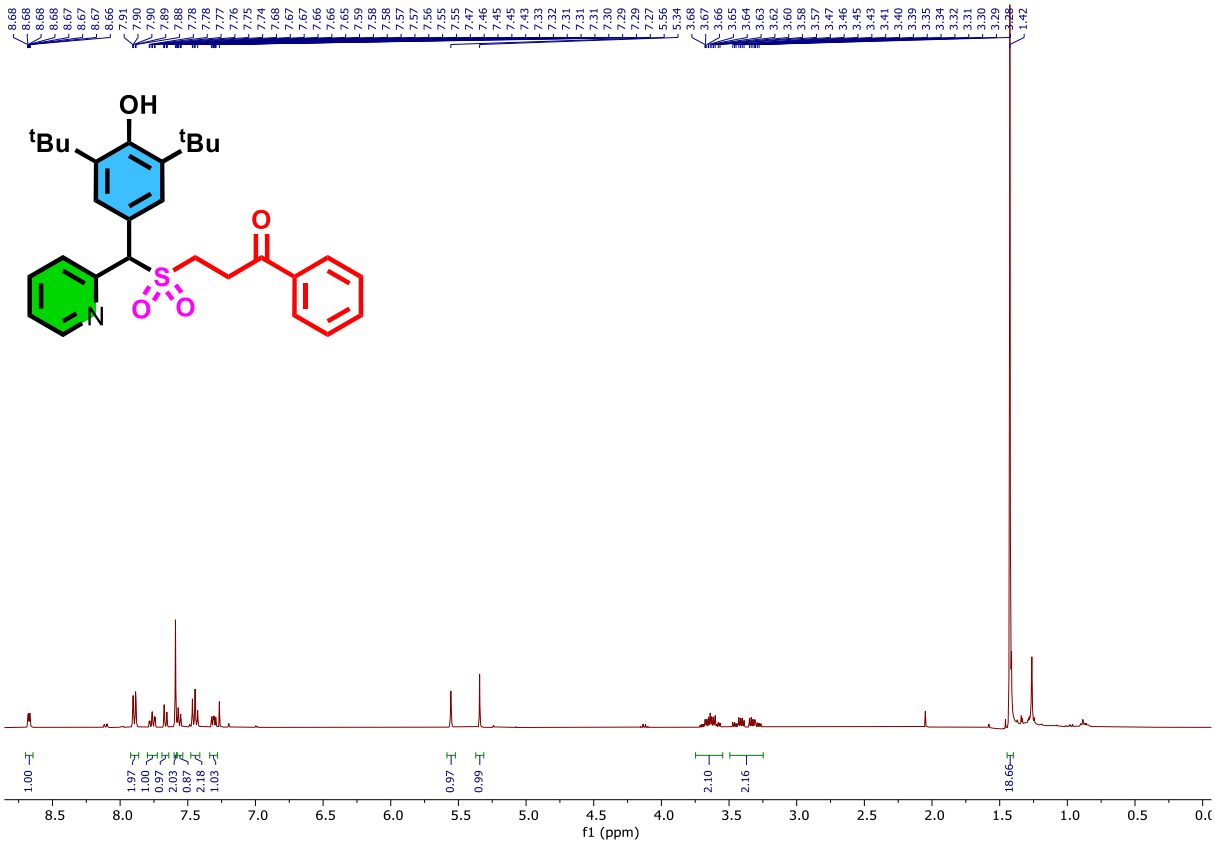
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl)sulfonyl)-1-phenylpropan-1-one **(3wa)**



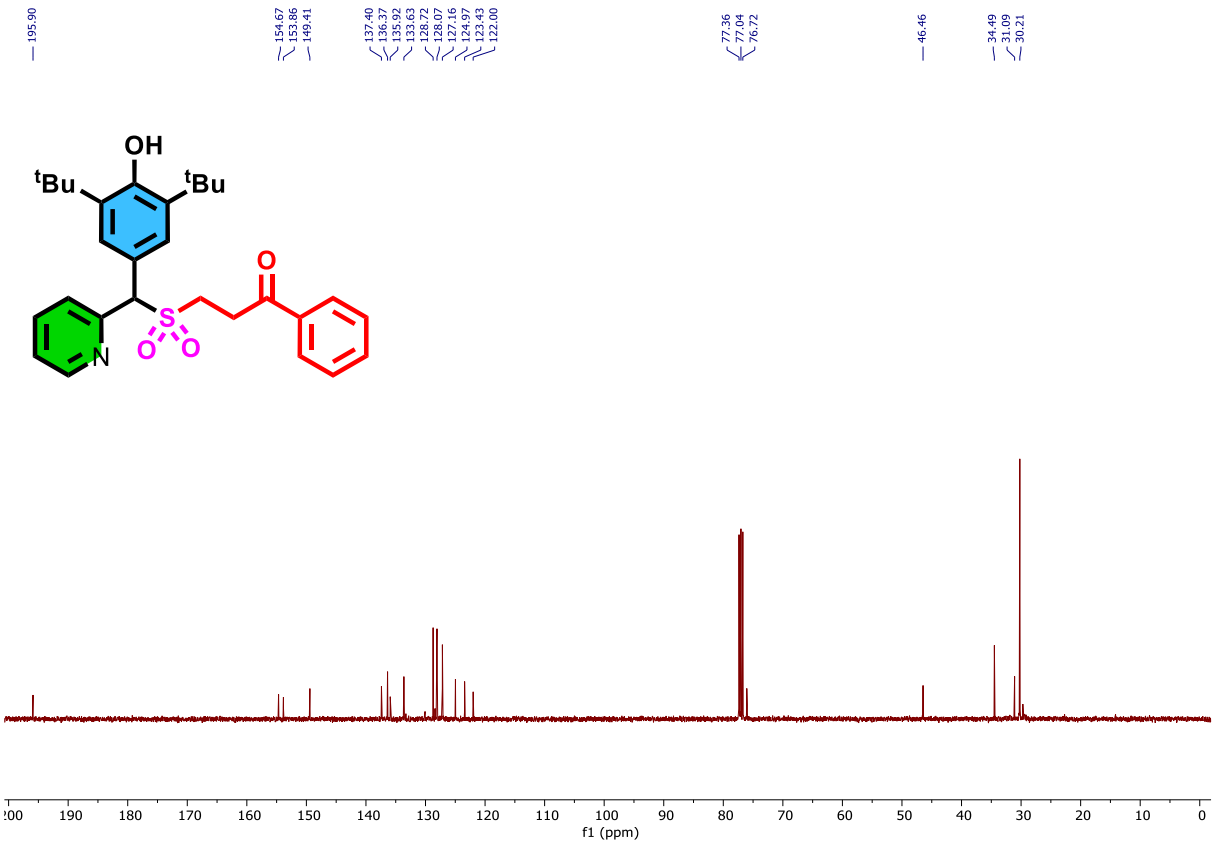
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl)sulfonyl)-1-phenylpropan-1-one **(3wa)**



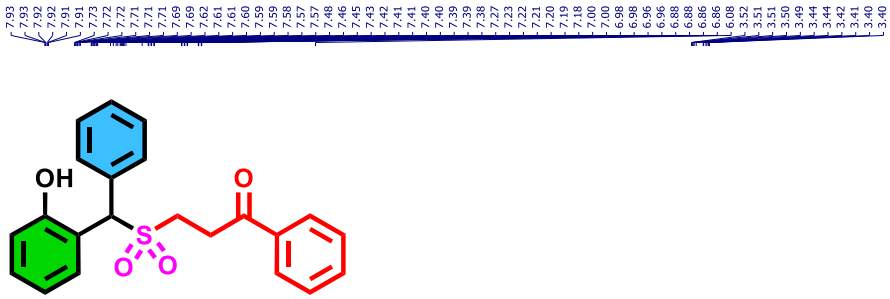
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(pyridin-2-yl)methyl)sulfonyl)-1-phenylpropan-1-one **(3xa)**

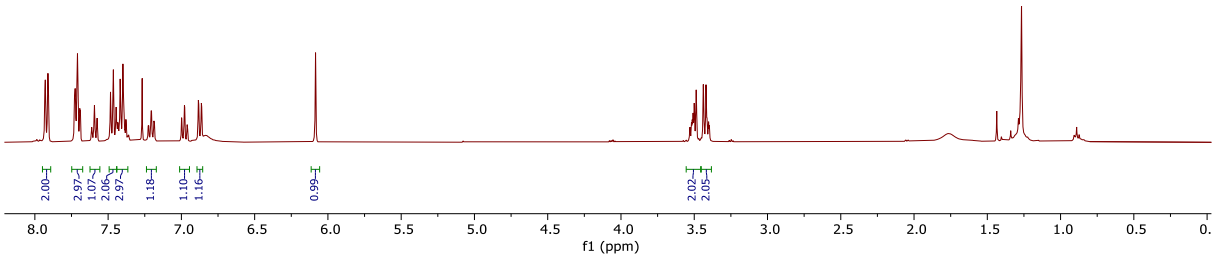


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(pyridin-2-yl)methyl)sulfonyl)-1-phenylpropan-1-one **(3xa)**

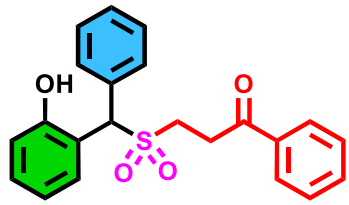


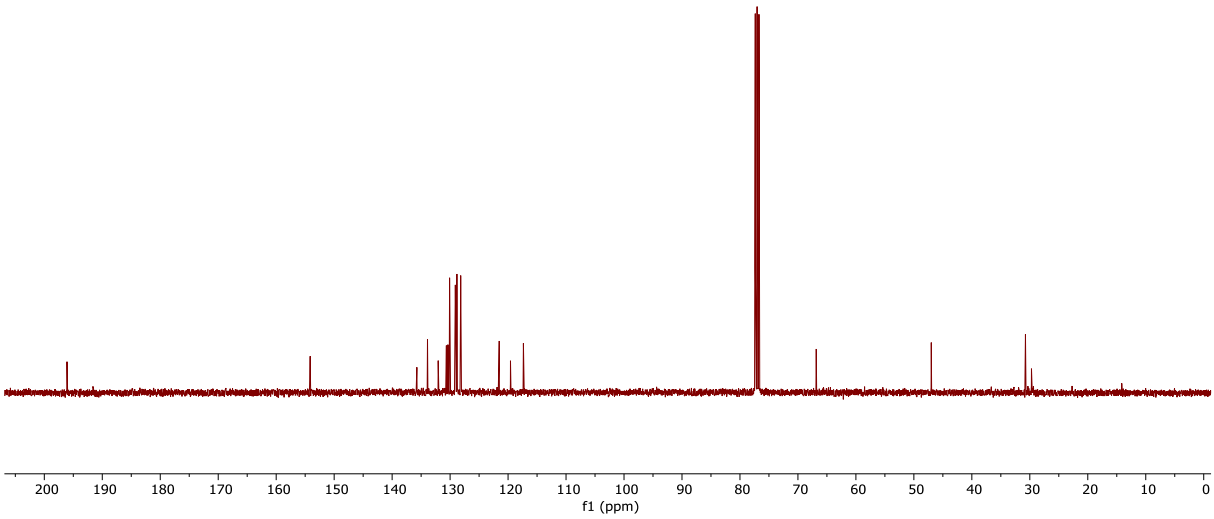
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((2-hydroxyphenyl)(phenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3'aa)**



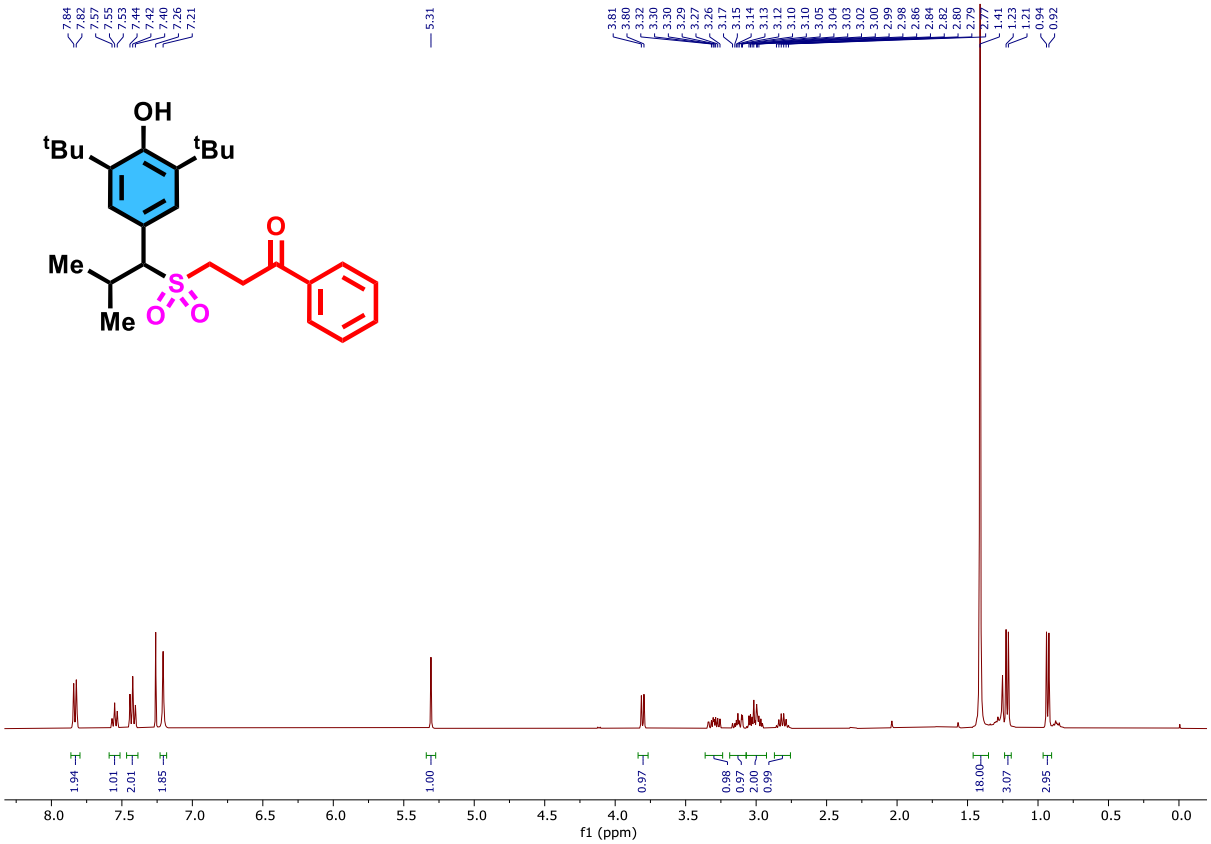


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((2-hydroxyphenyl)(phenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3'aa)**

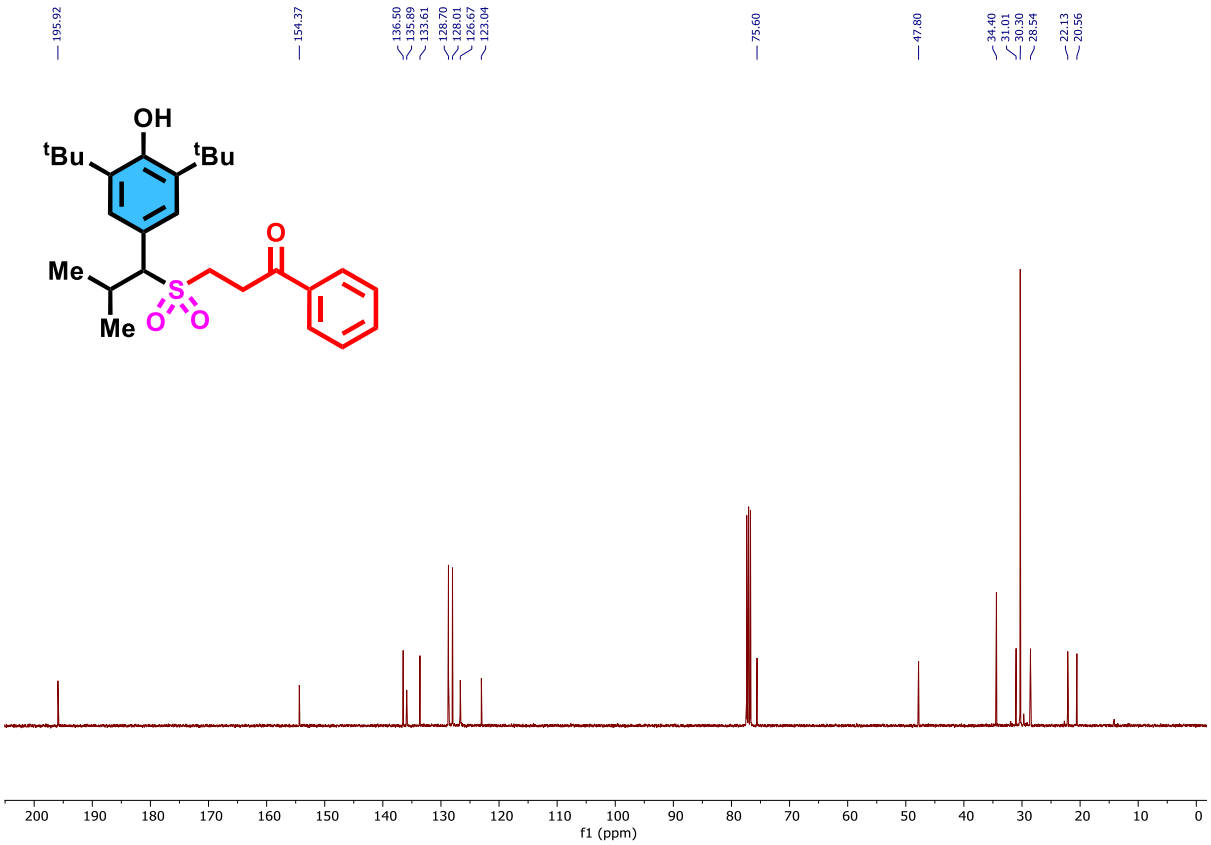




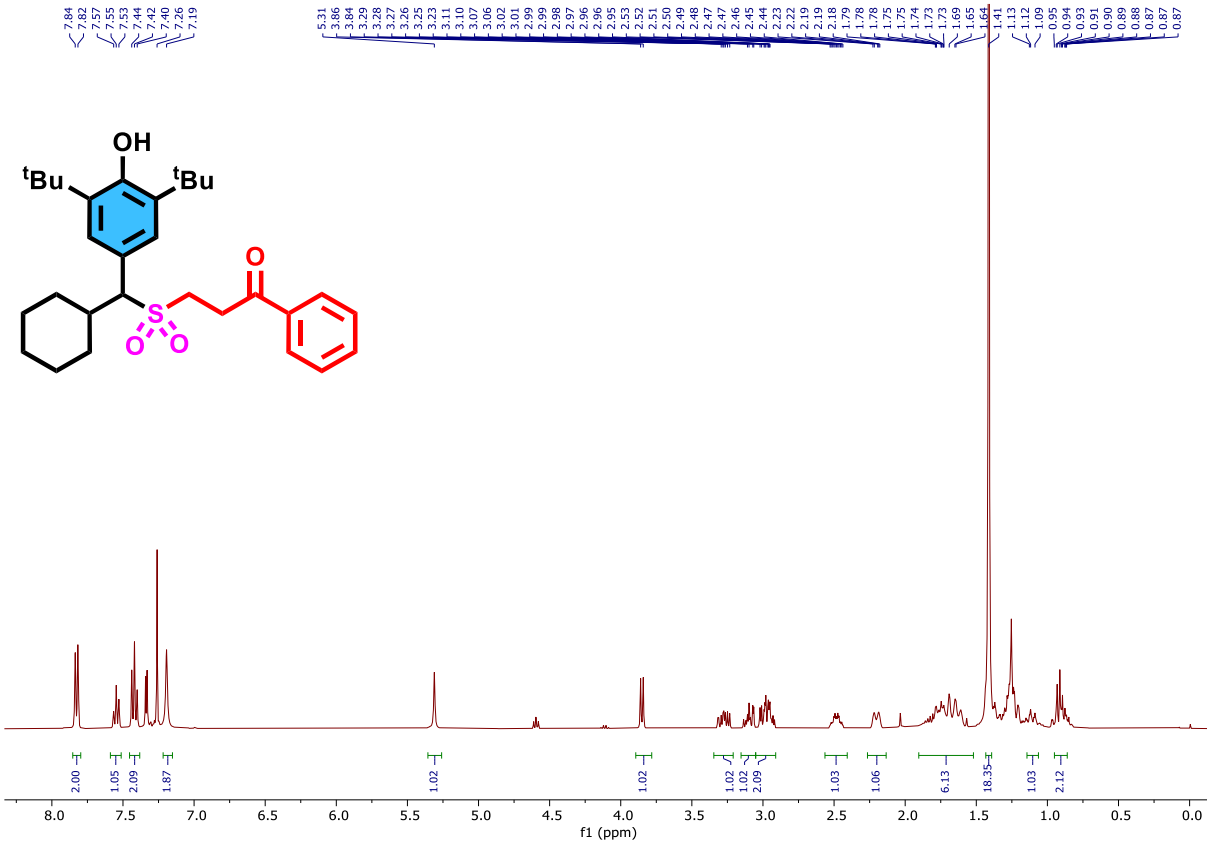
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-((1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylpropyl)sulfonyl)-1-phenylpropan-1-one **(3'ba)**



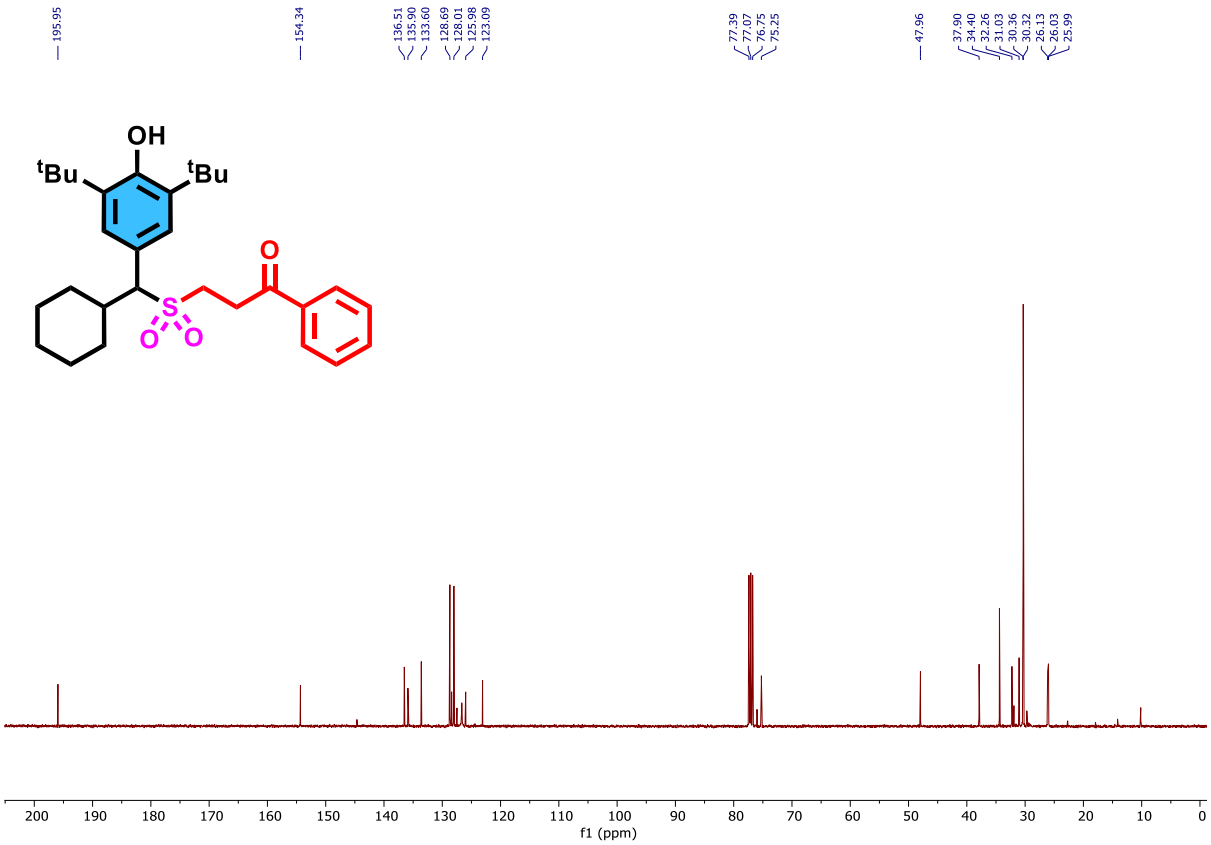
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-((1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylpropyl)sulfonyl)-1-phenylpropan-1-one **(3'ba)**



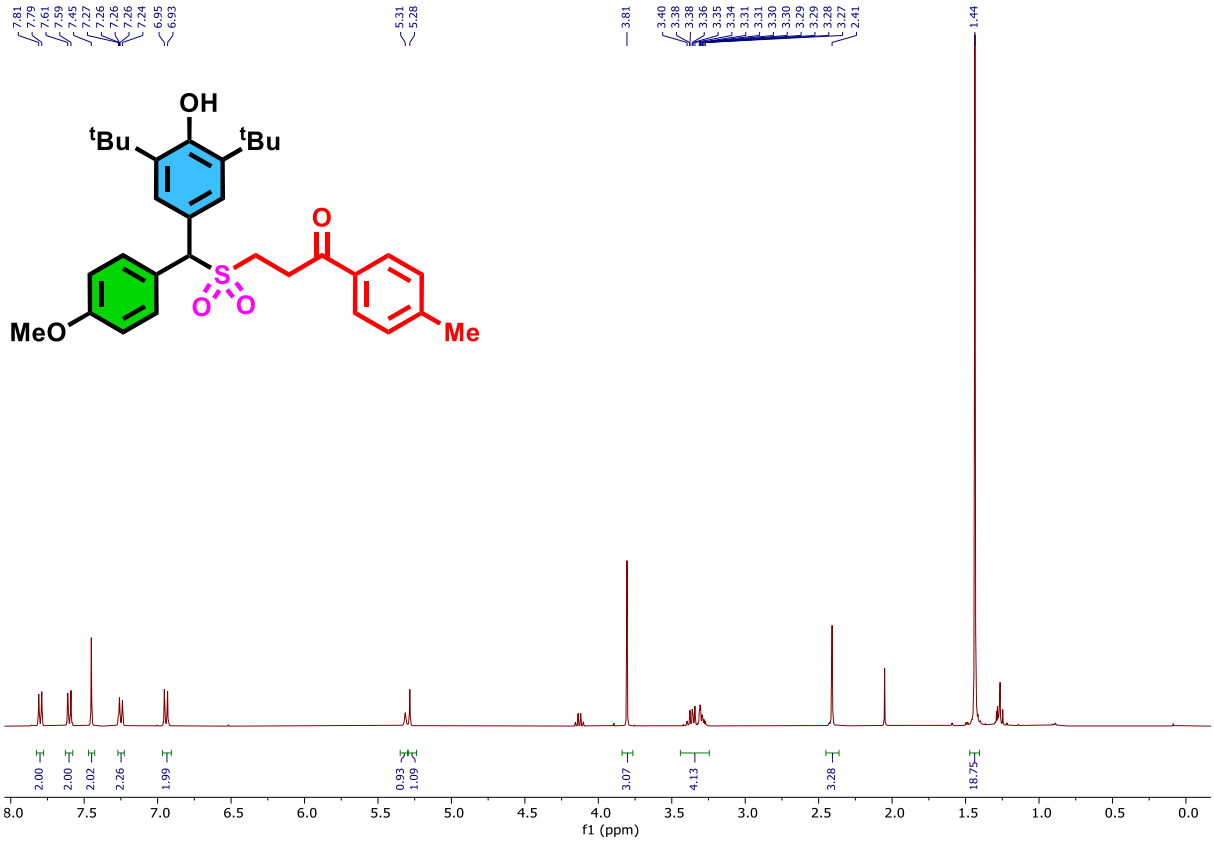
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-((cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one **(3'ca)**



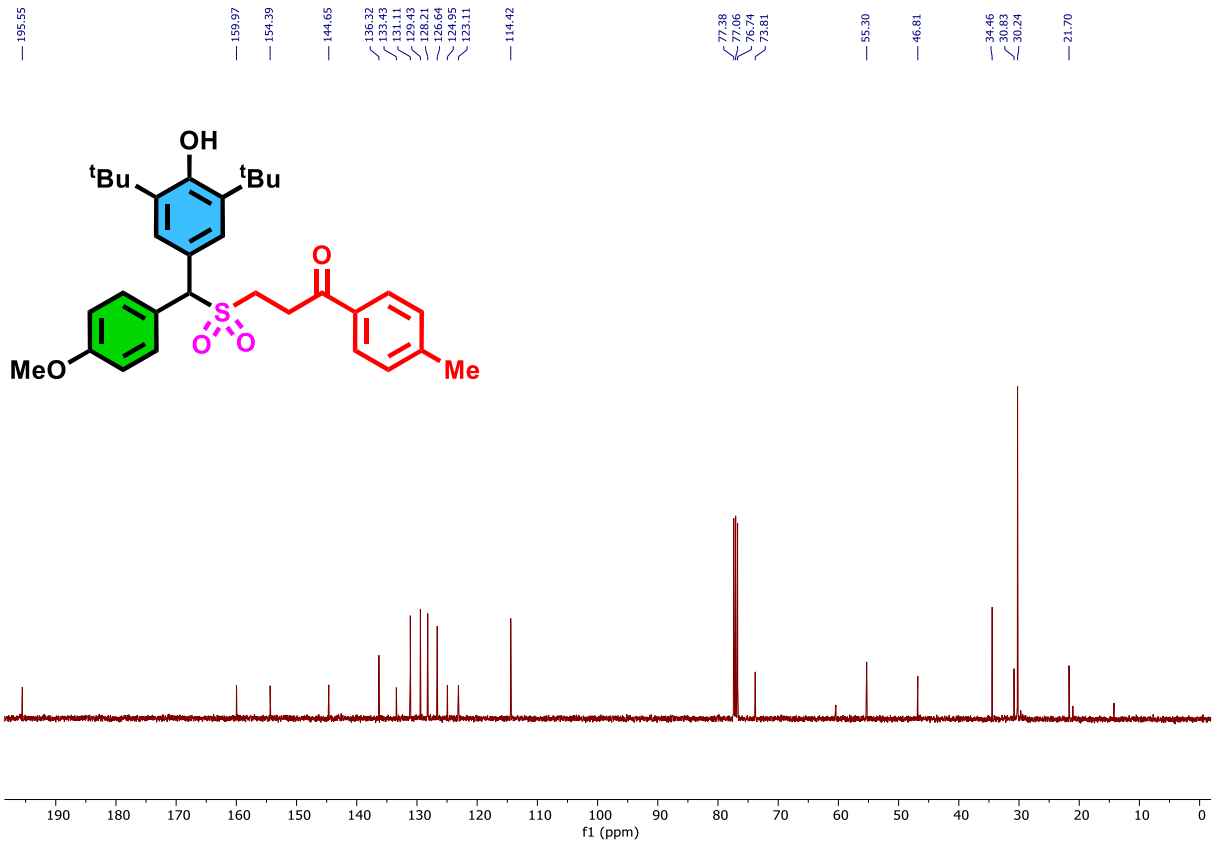
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-((cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one



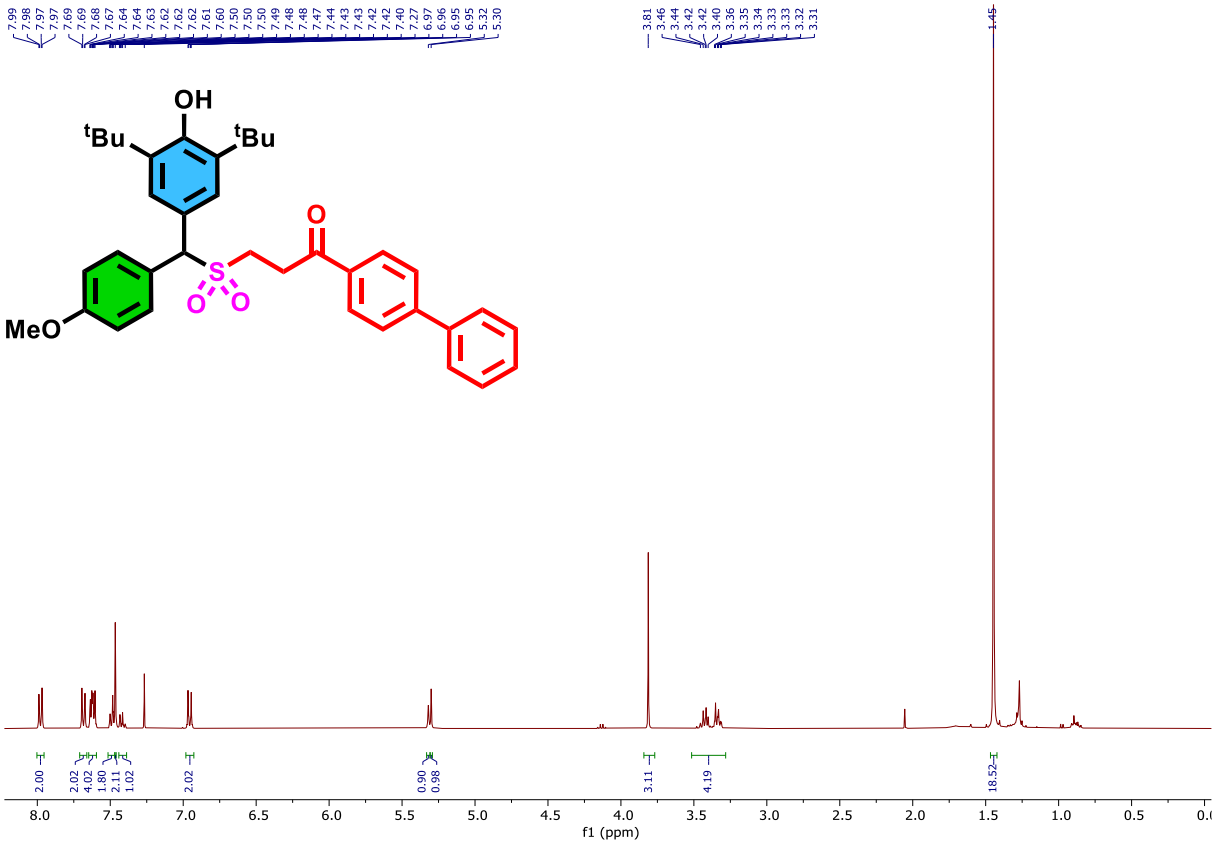
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(p-tolyl)propan-1-one **(3ab)**



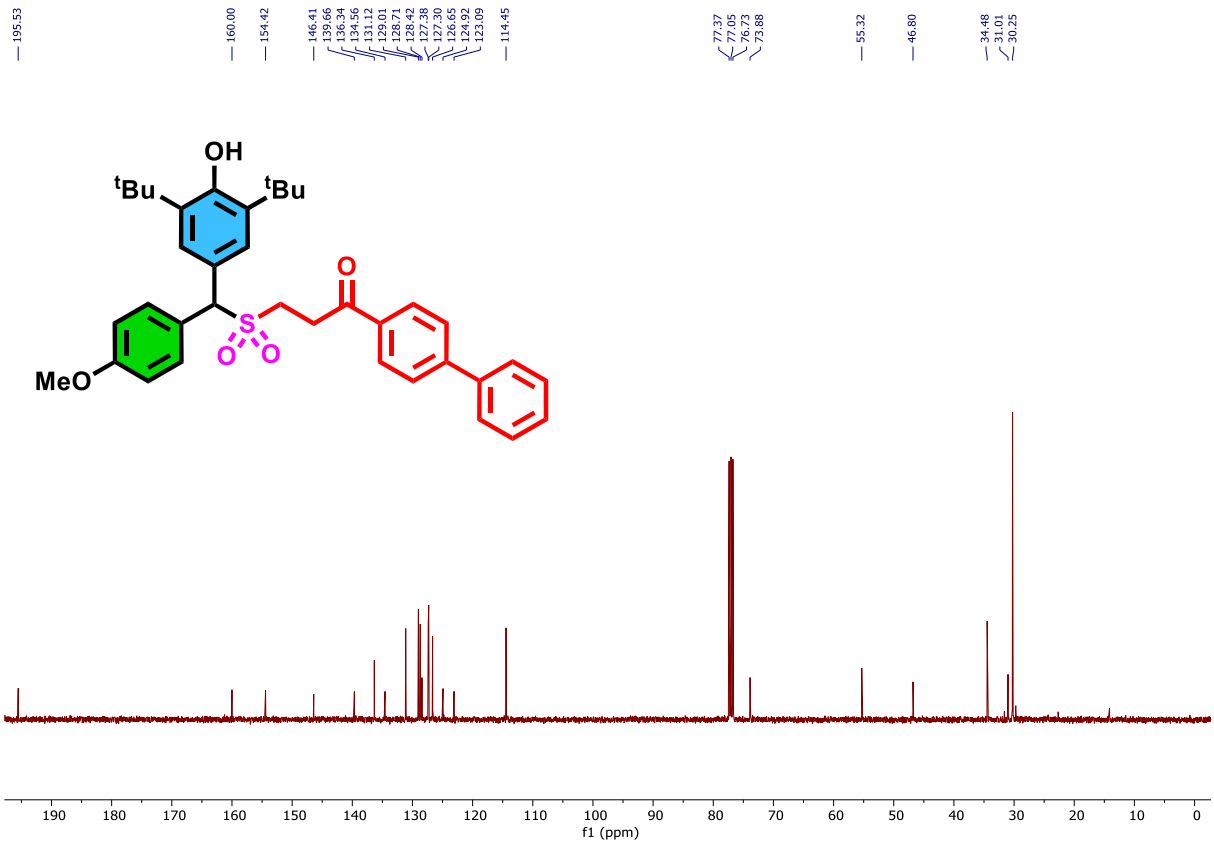
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(p-tolyl)propan-1-one **(3ab)**



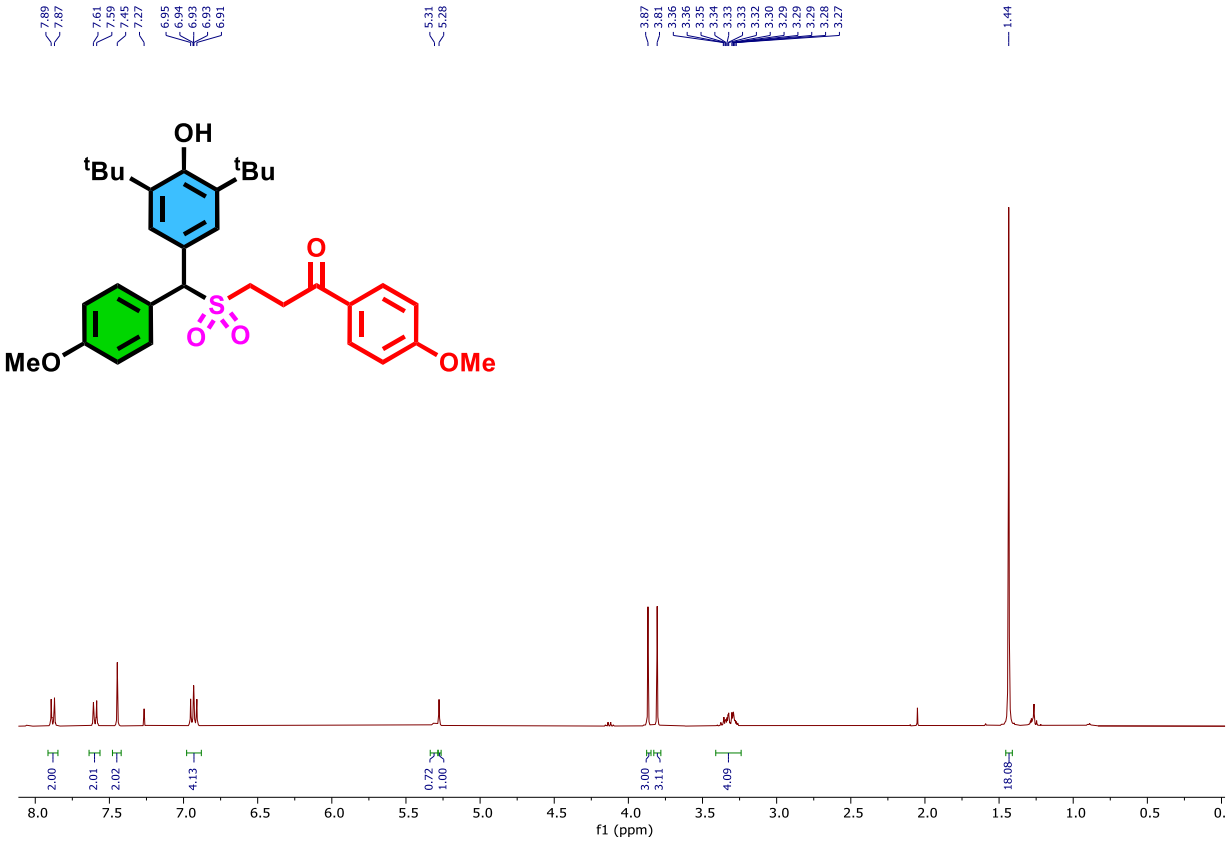
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-([1,1'-biphenyl]-4-yl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3ac)**



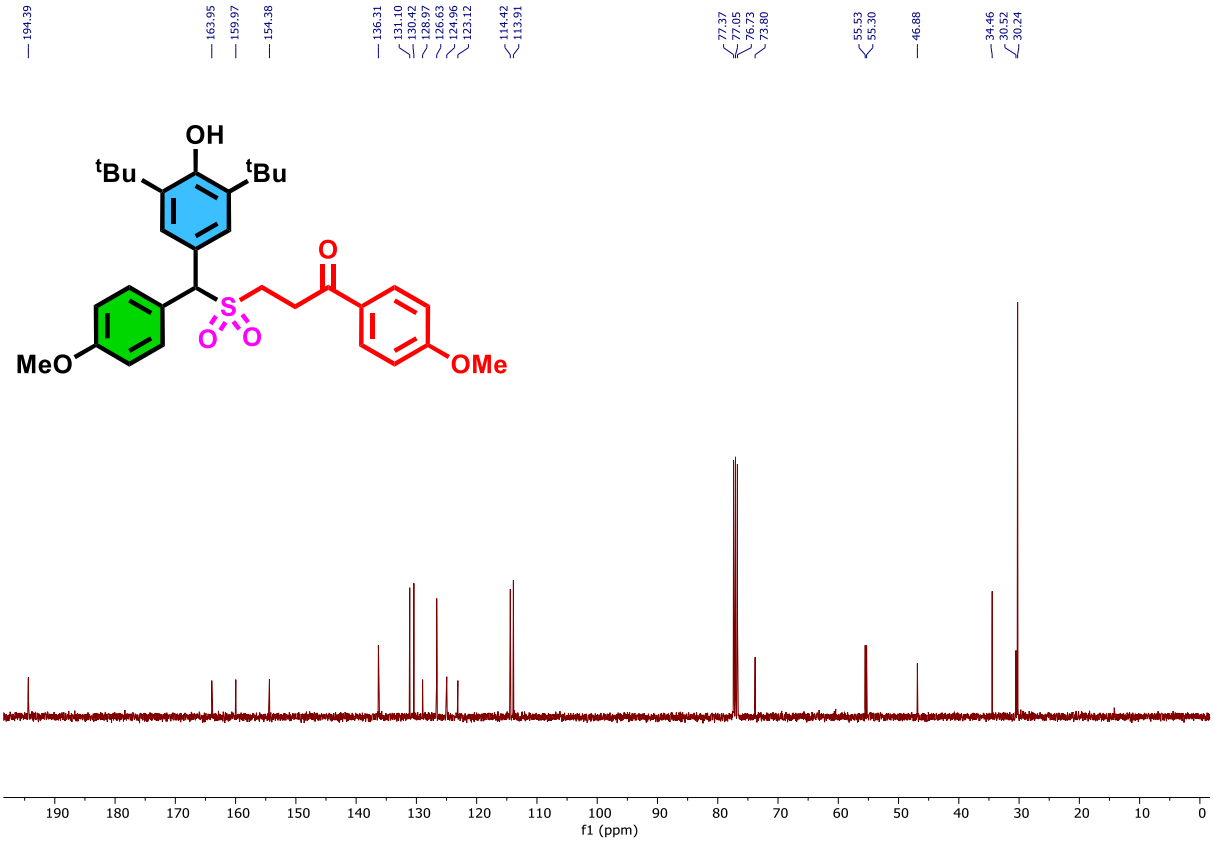
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-([1,1'-biphenyl]-4-yl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3ac)**



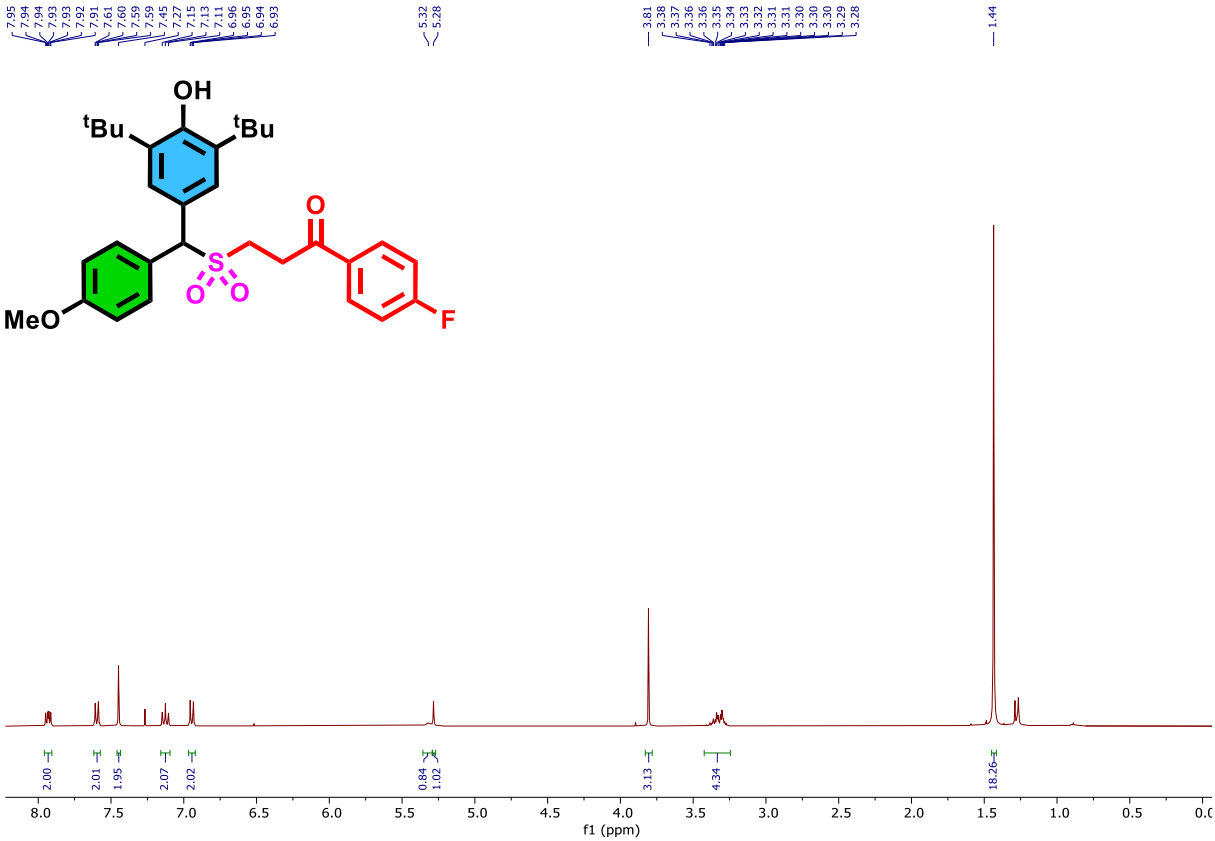
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-methoxyphenyl)propan-1-one **(3ad)**



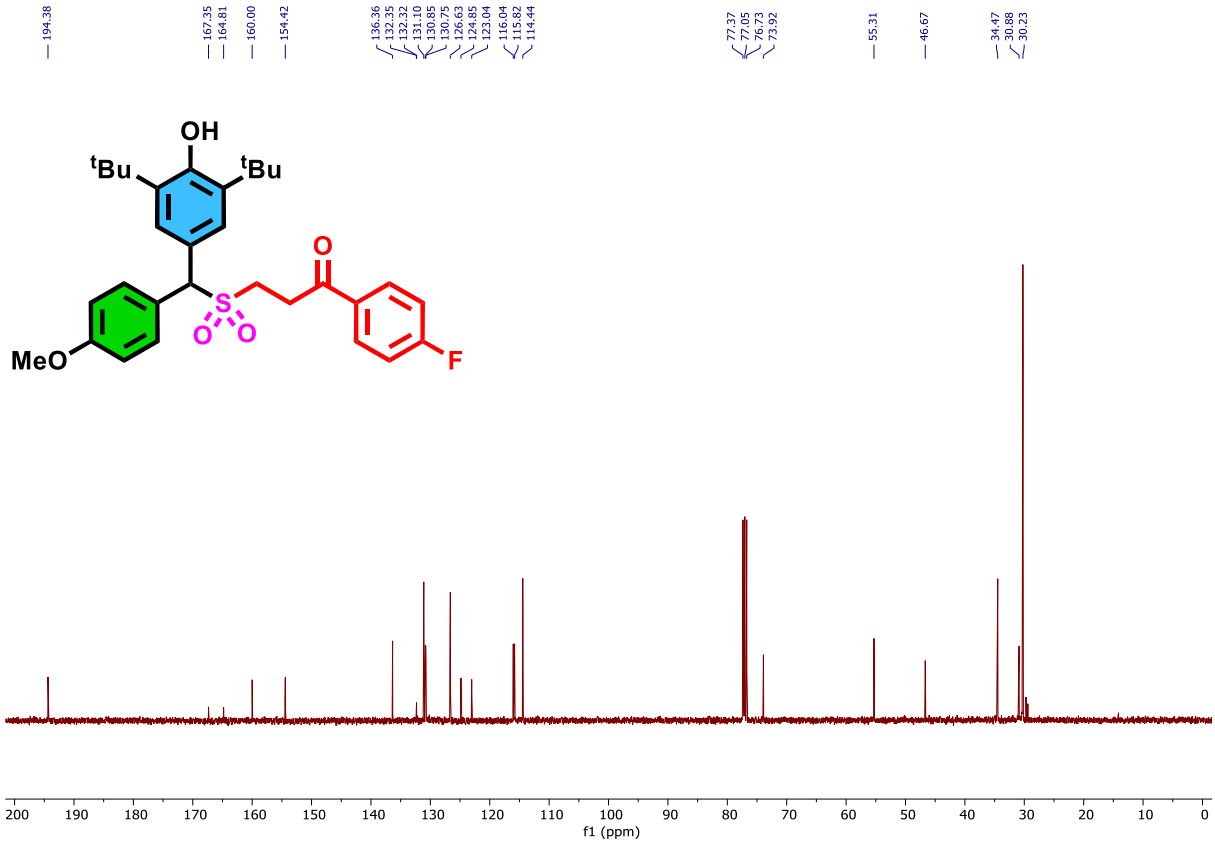
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-methoxyphenyl)propan-1-one **(3ad)**



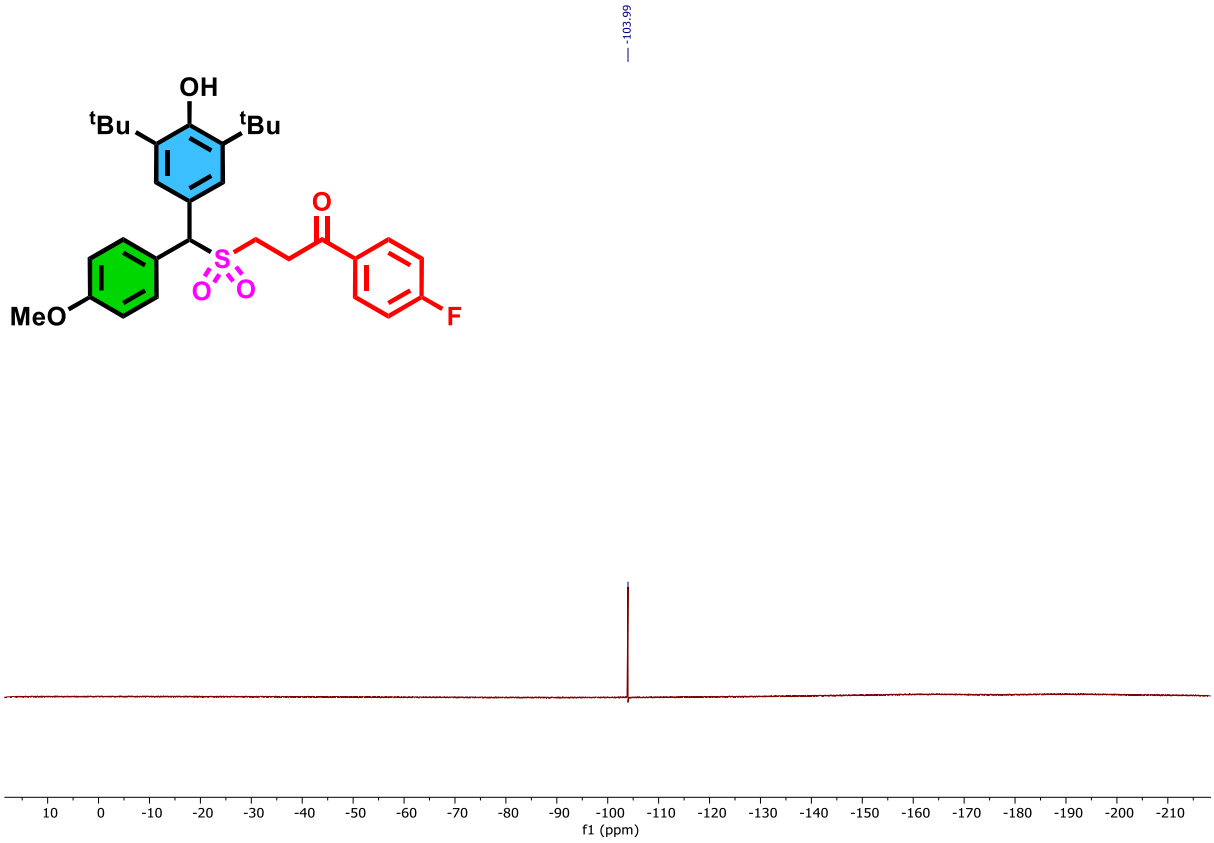
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-fluorophenyl)propan-1-one **(3ae)**



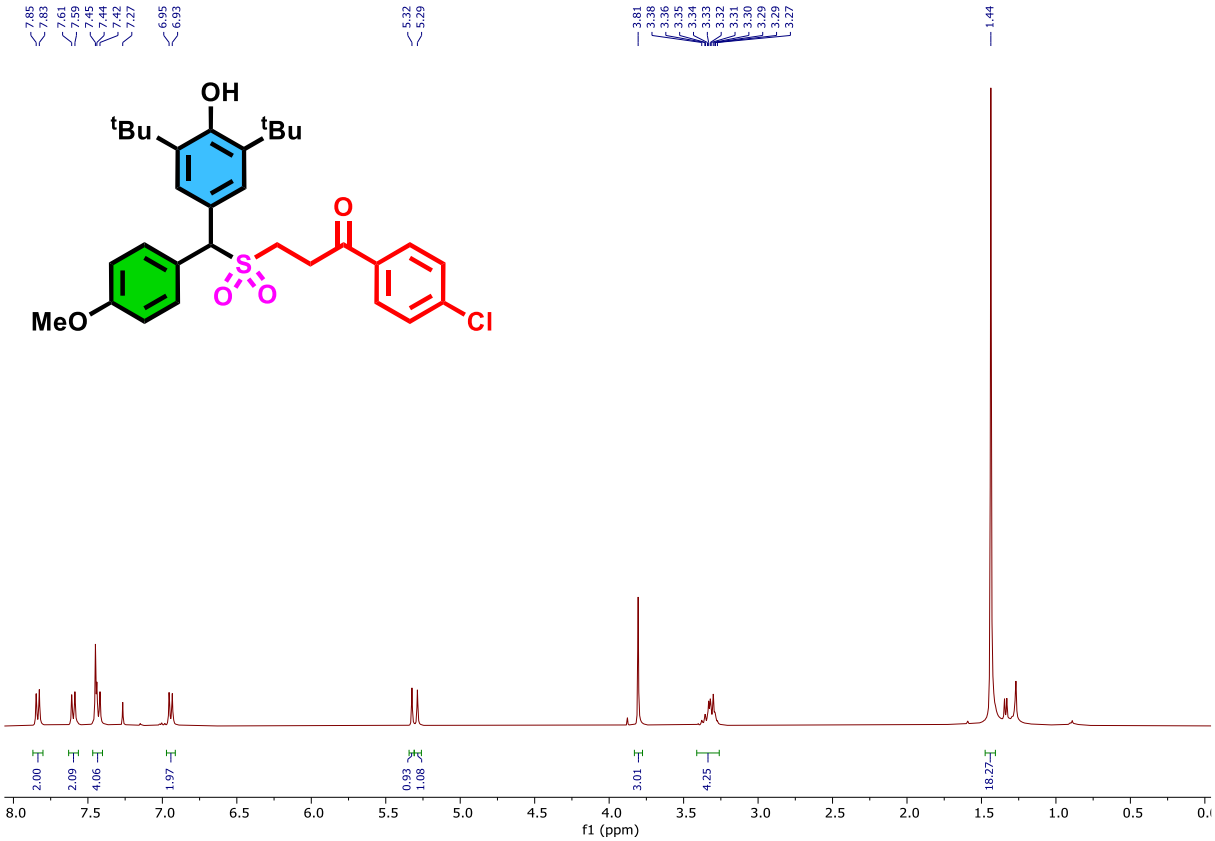
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-fluorophenyl)propan-1-one **(3ae)**



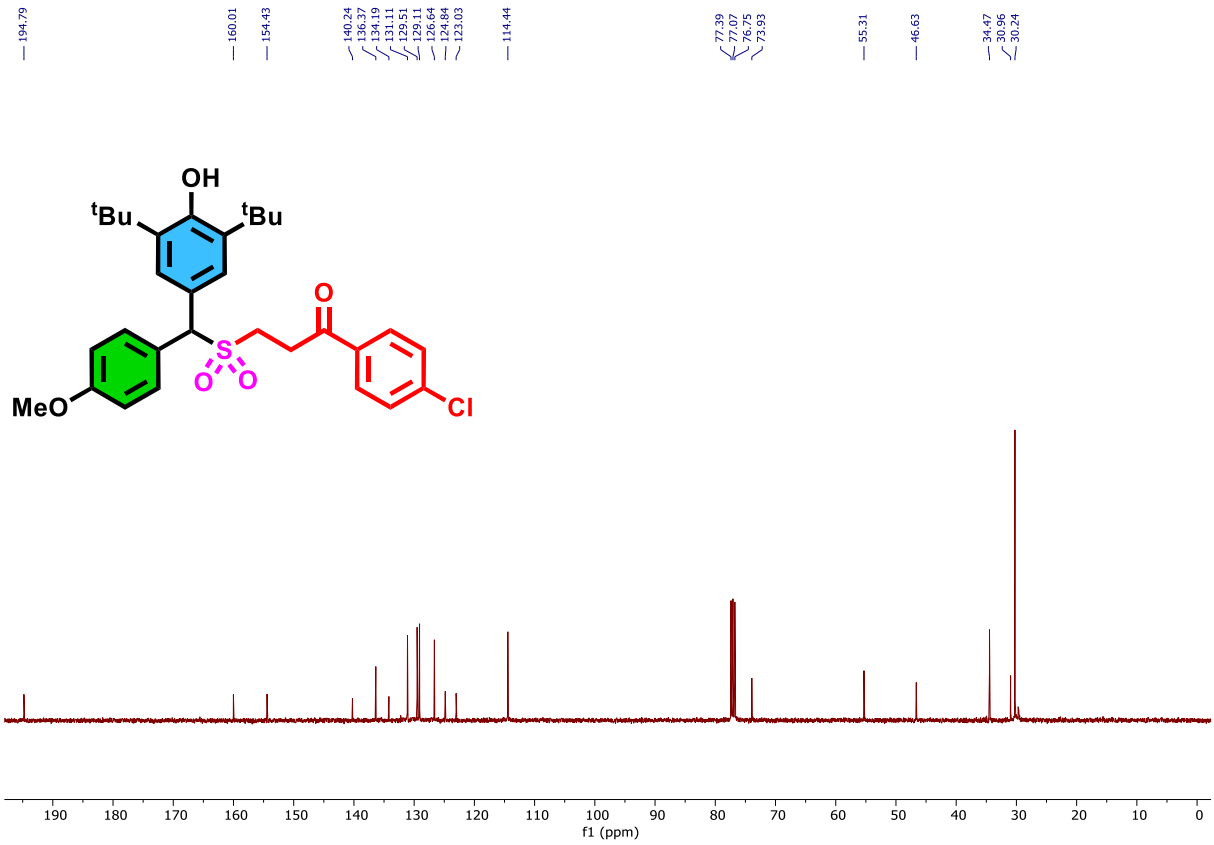
^{19}F NMR (377 MHz, $CDCl_3$) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-fluorophenyl)propan-1-one **(3ae)**



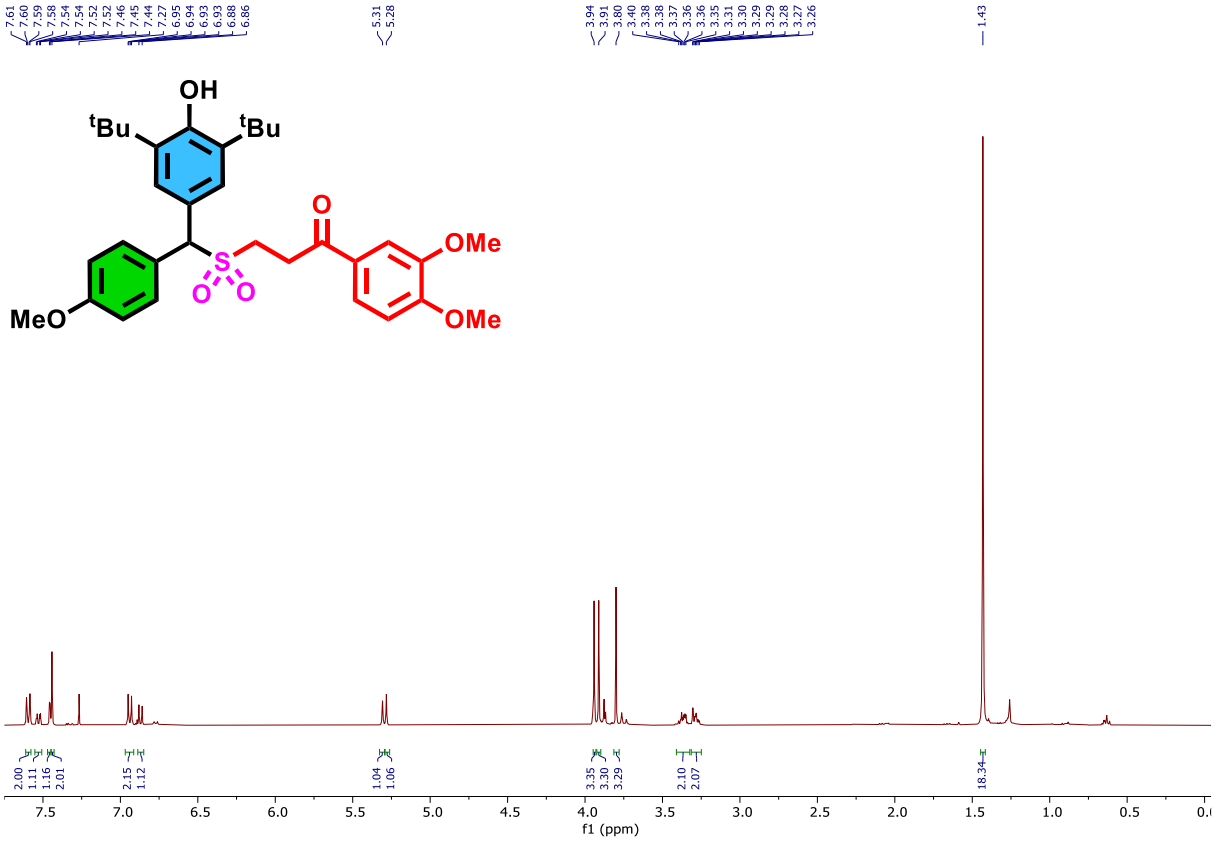
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-(4-chlorophenyl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3af)**



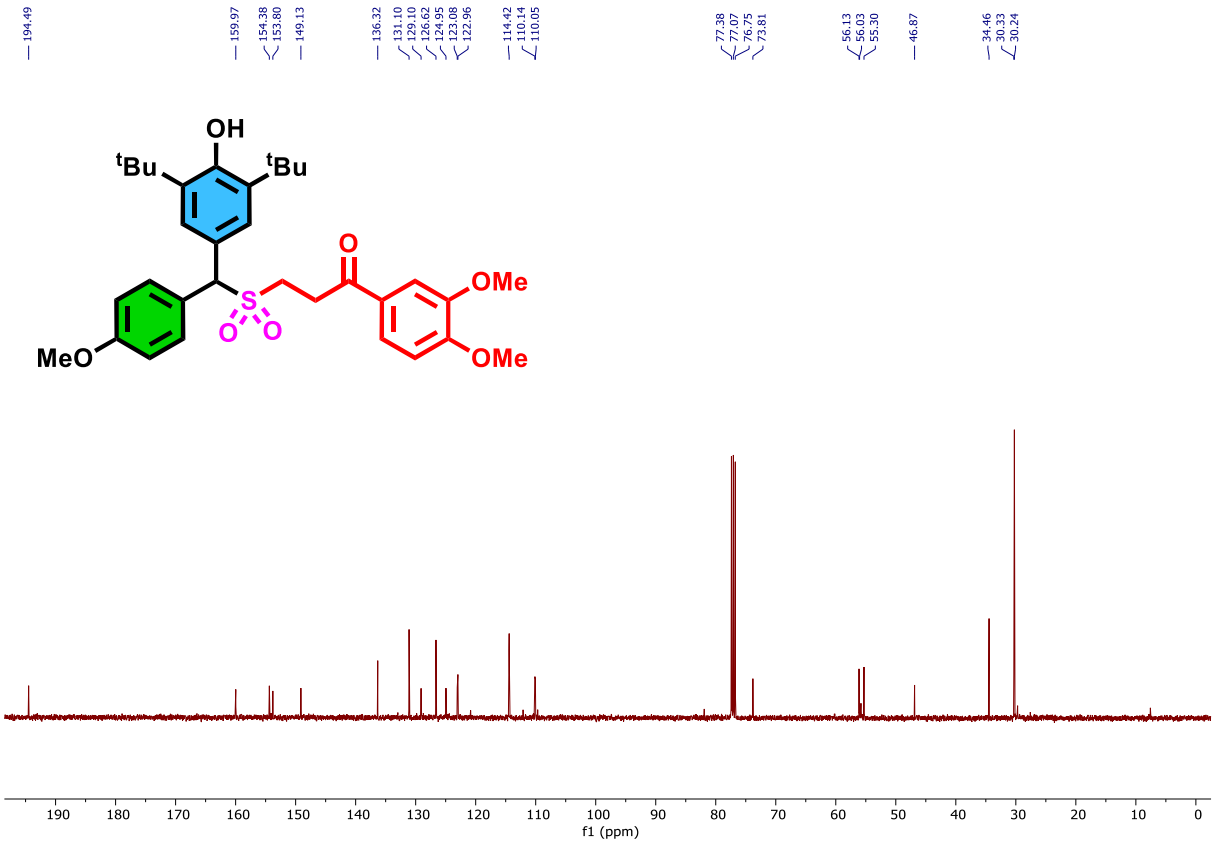
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-(4-chlorophenyl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3af)**



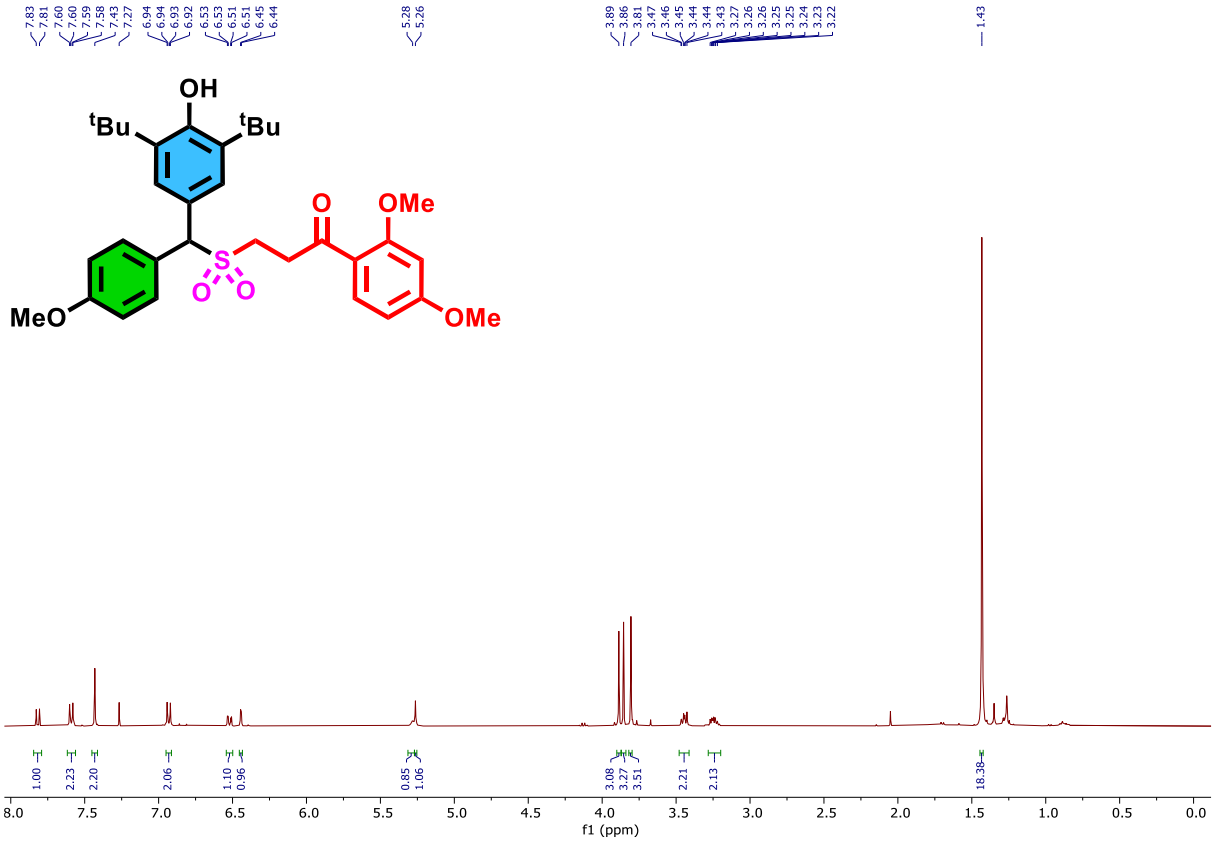
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(3,4-dimethoxyphenyl)propan-1-one **(3ag)**



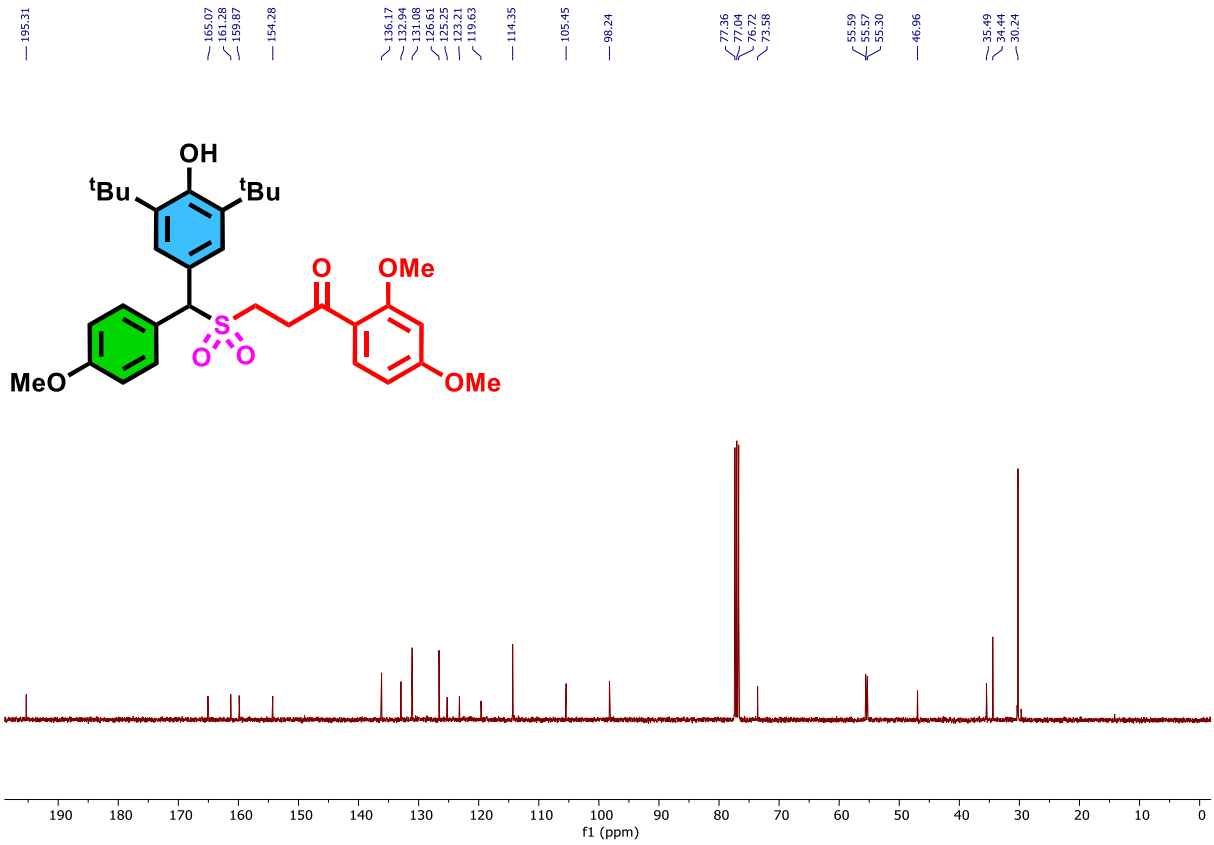
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(3,4-dimethoxyphenyl)propan-1-one **(3ag)**



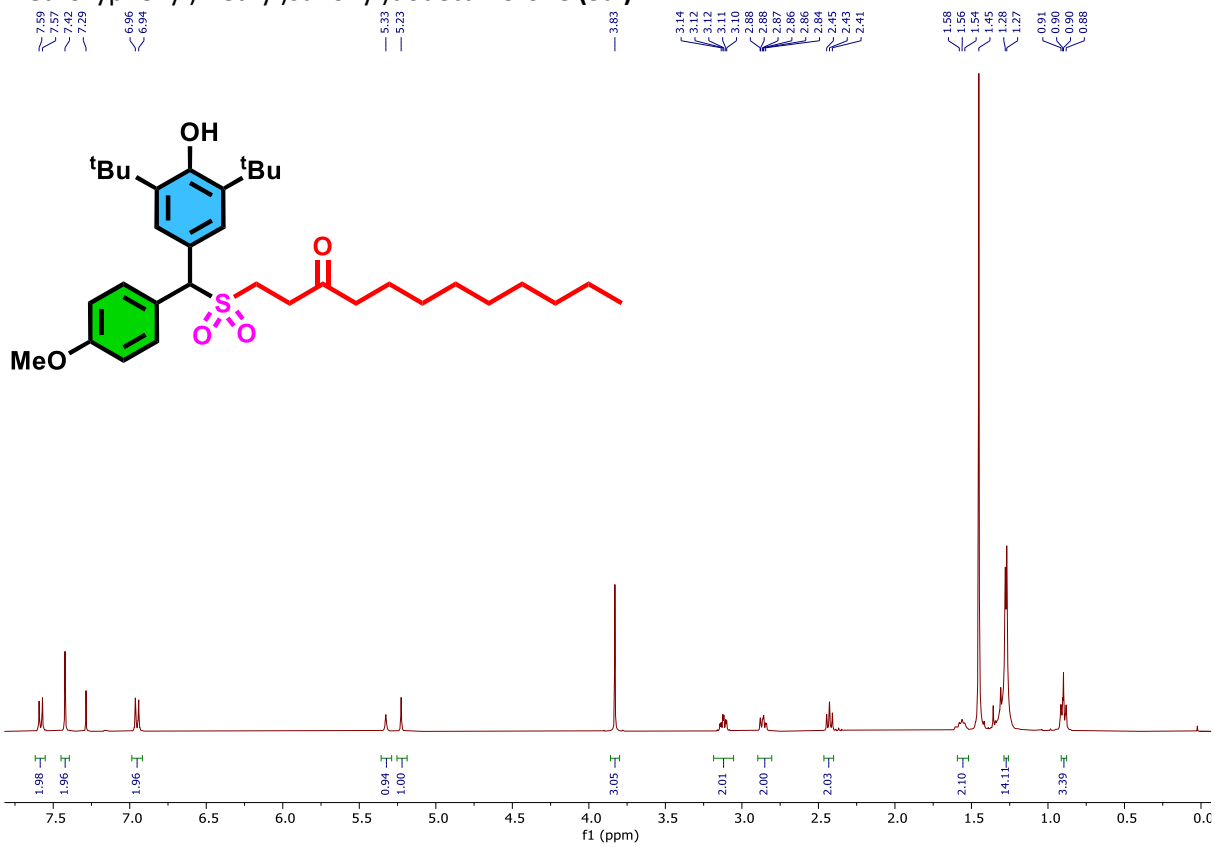
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(2,4-dimethoxyphenyl)propan-1-one **(3ah)**



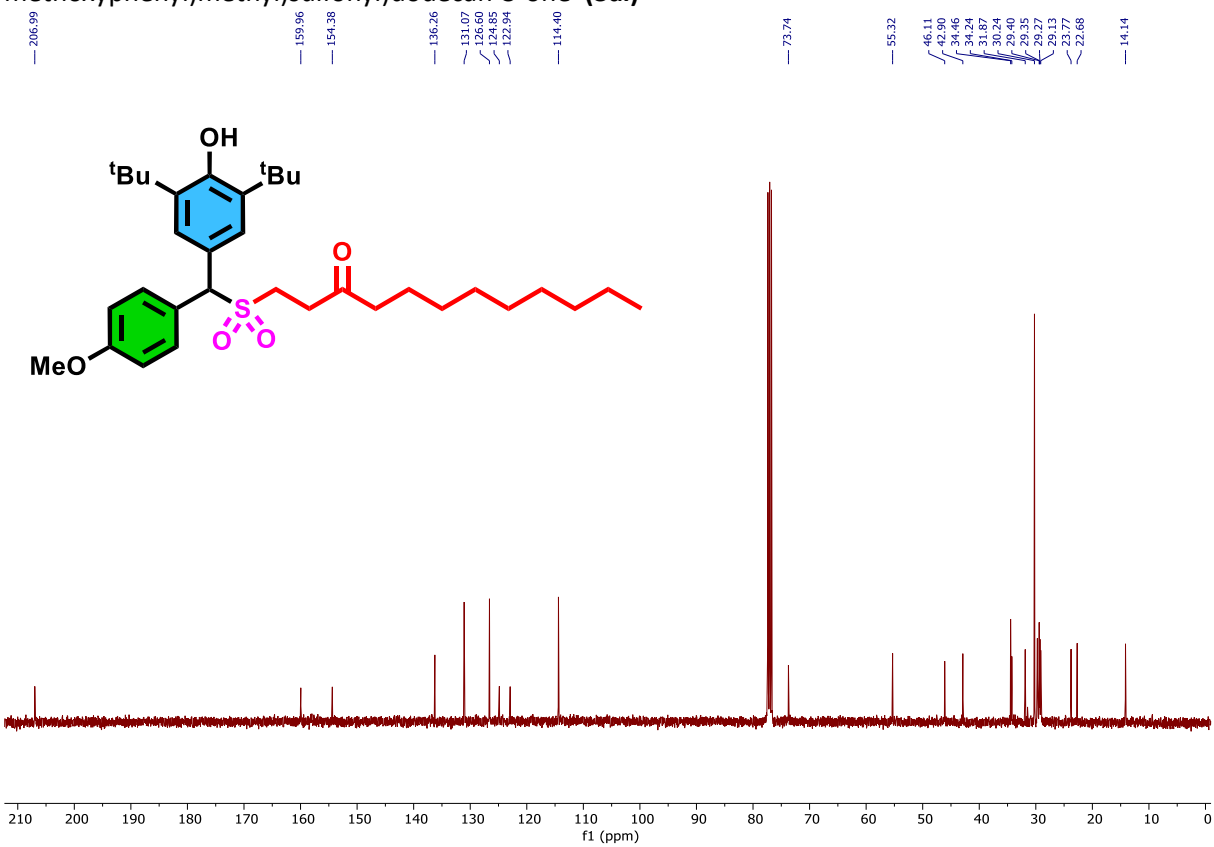
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(2,4-dimethoxyphenyl)propan-1-one **(3ah)**



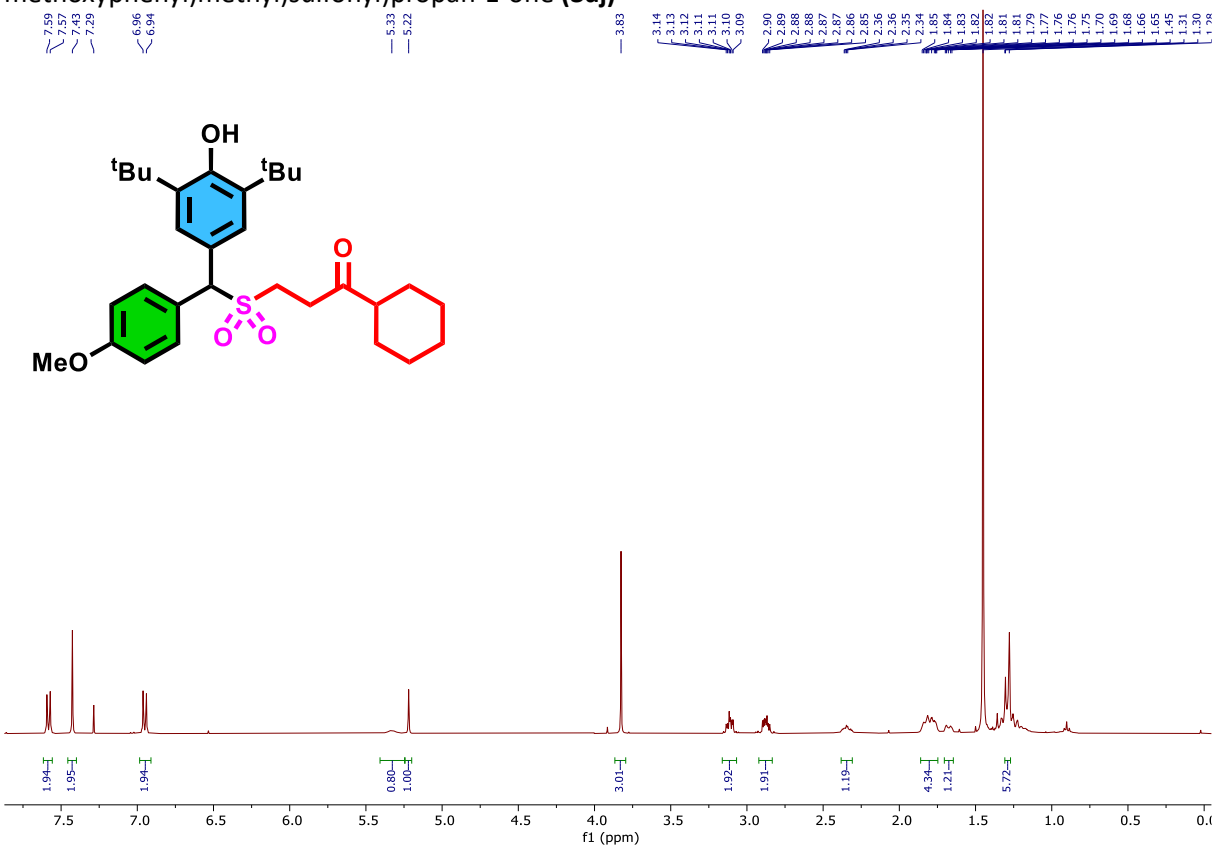
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)dodecan-3-one **(3ai)**



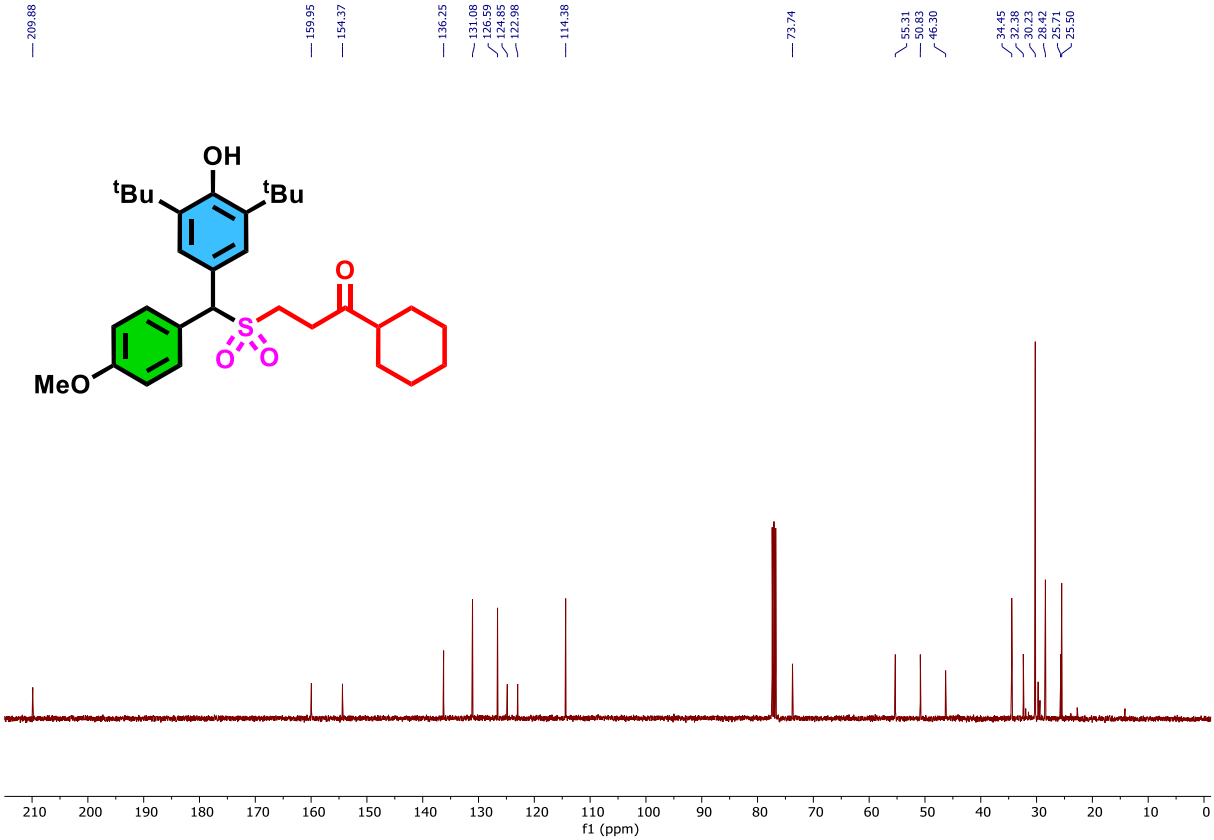
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)dodecan-3-one **(3ai)**



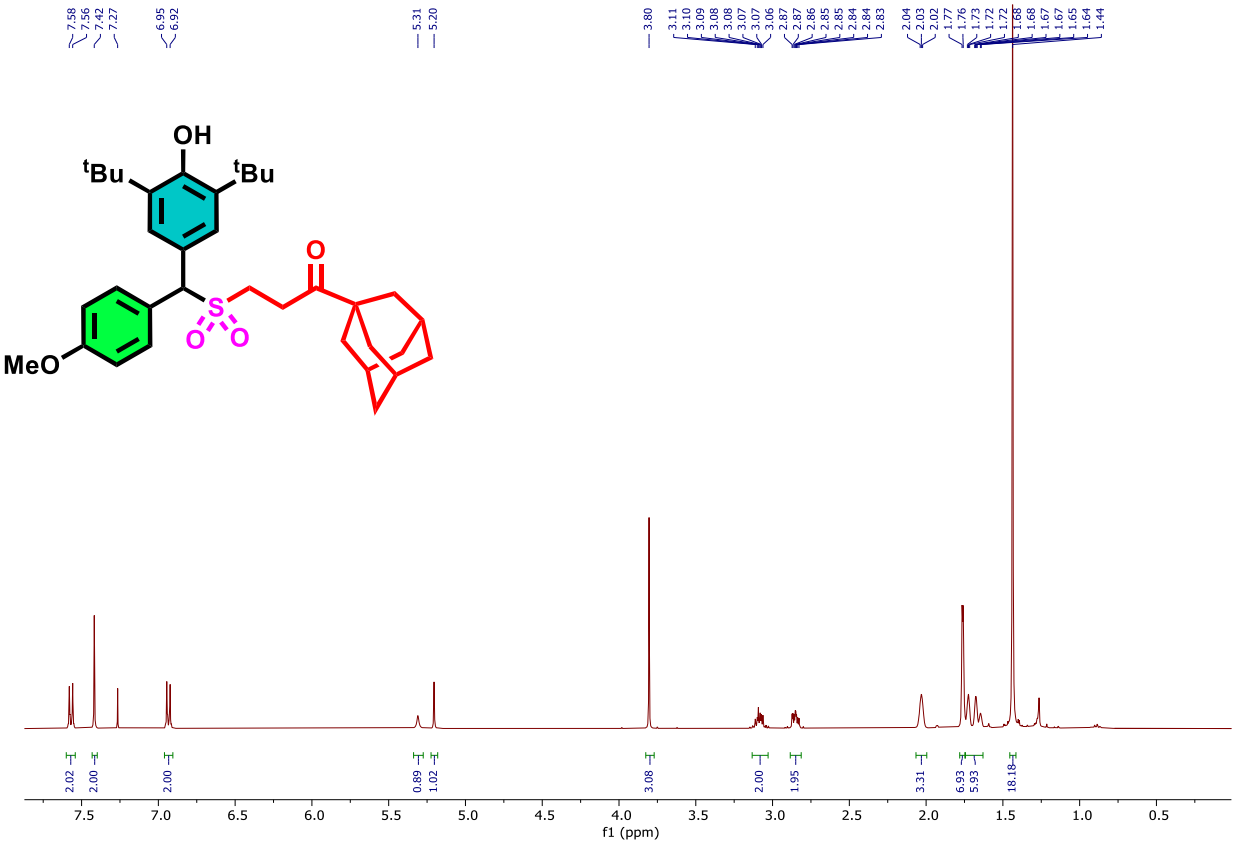
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-cyclohexyl-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3aj)**



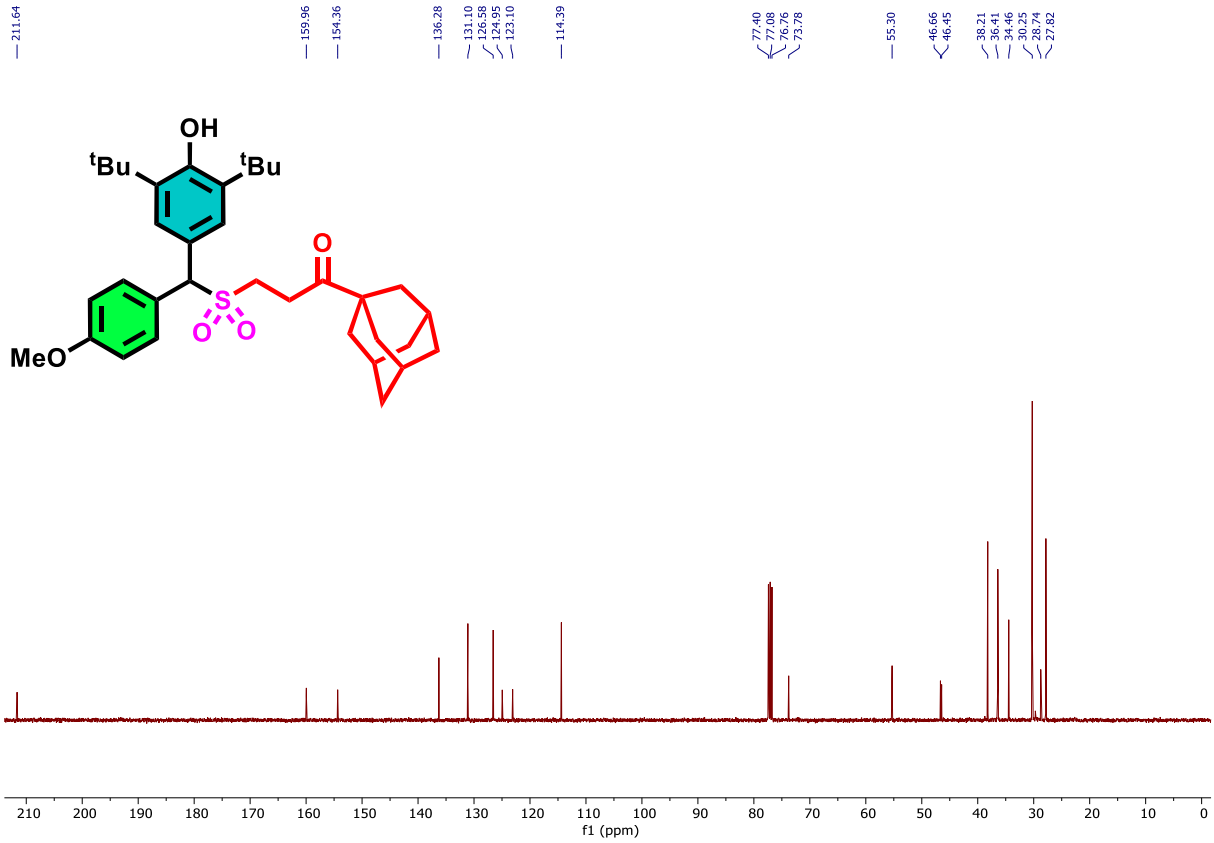
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-cyclohexyl-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3aj)**



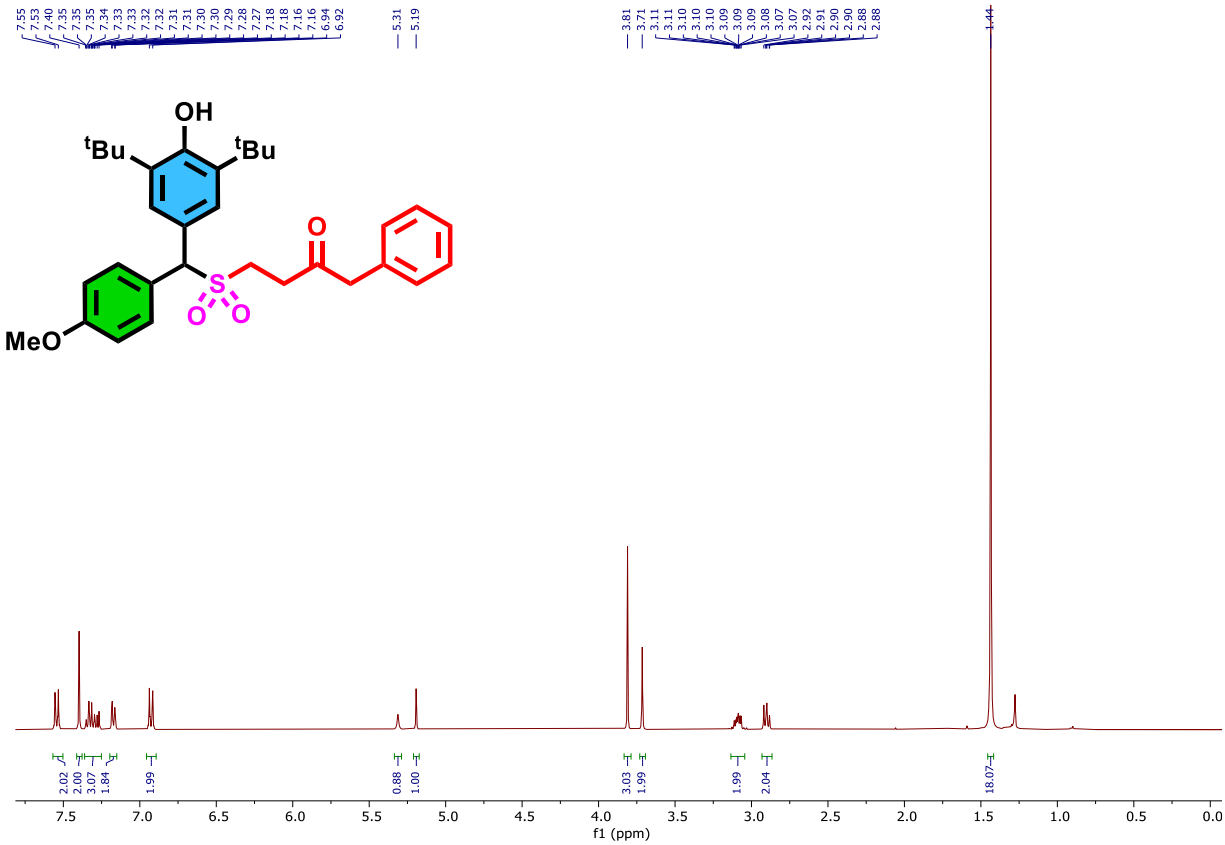
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-((1s,3s)-adamantan-1-yl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3ak)**



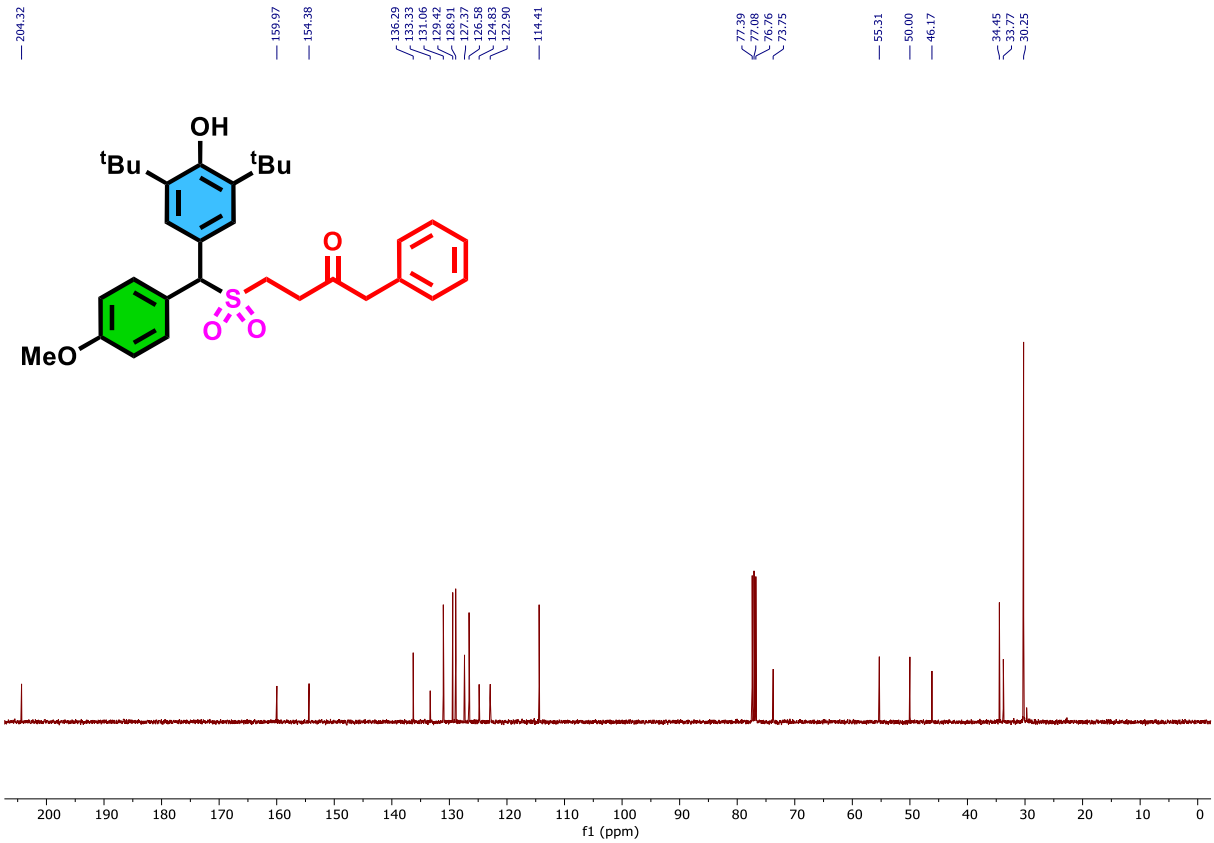
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-((1s,3s)-adamantan-1-yl)-3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)propan-1-one **(3ak)**



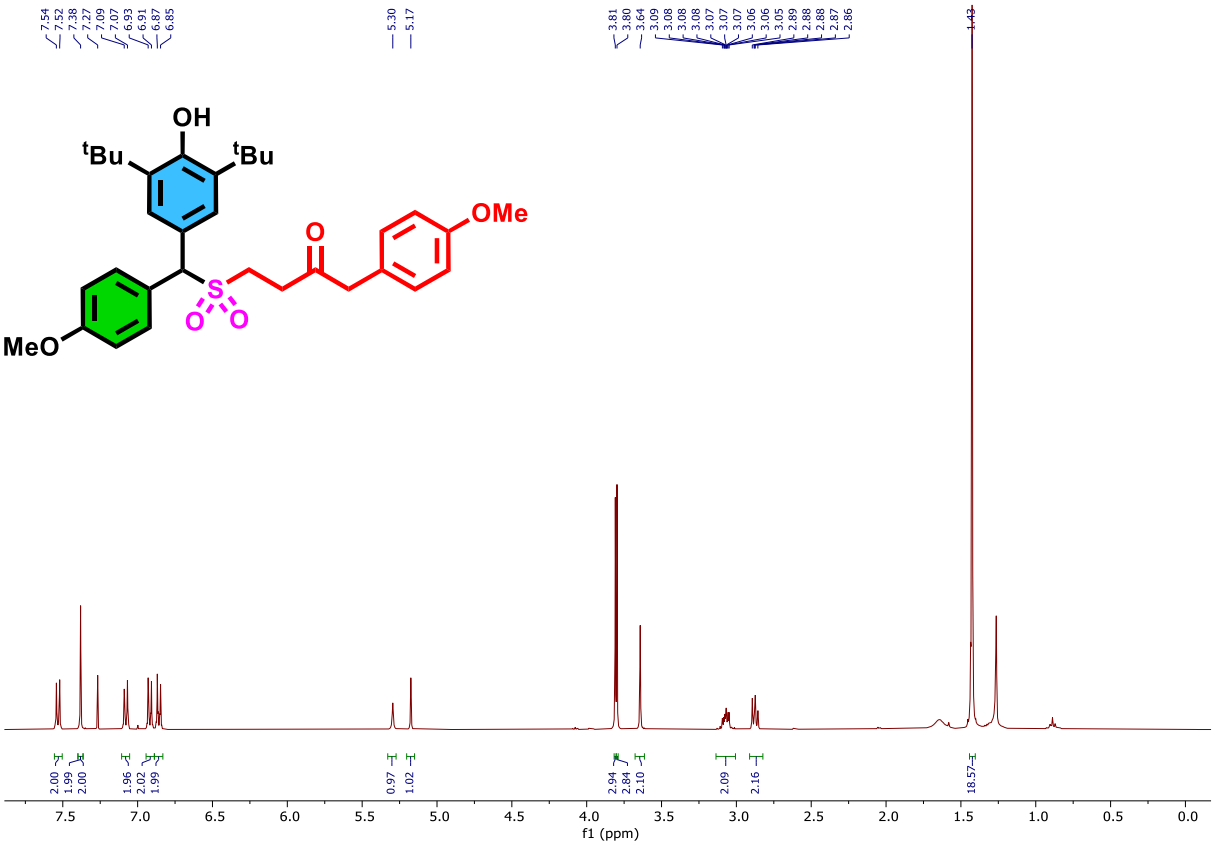
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylbutan-2-one **(3al)**



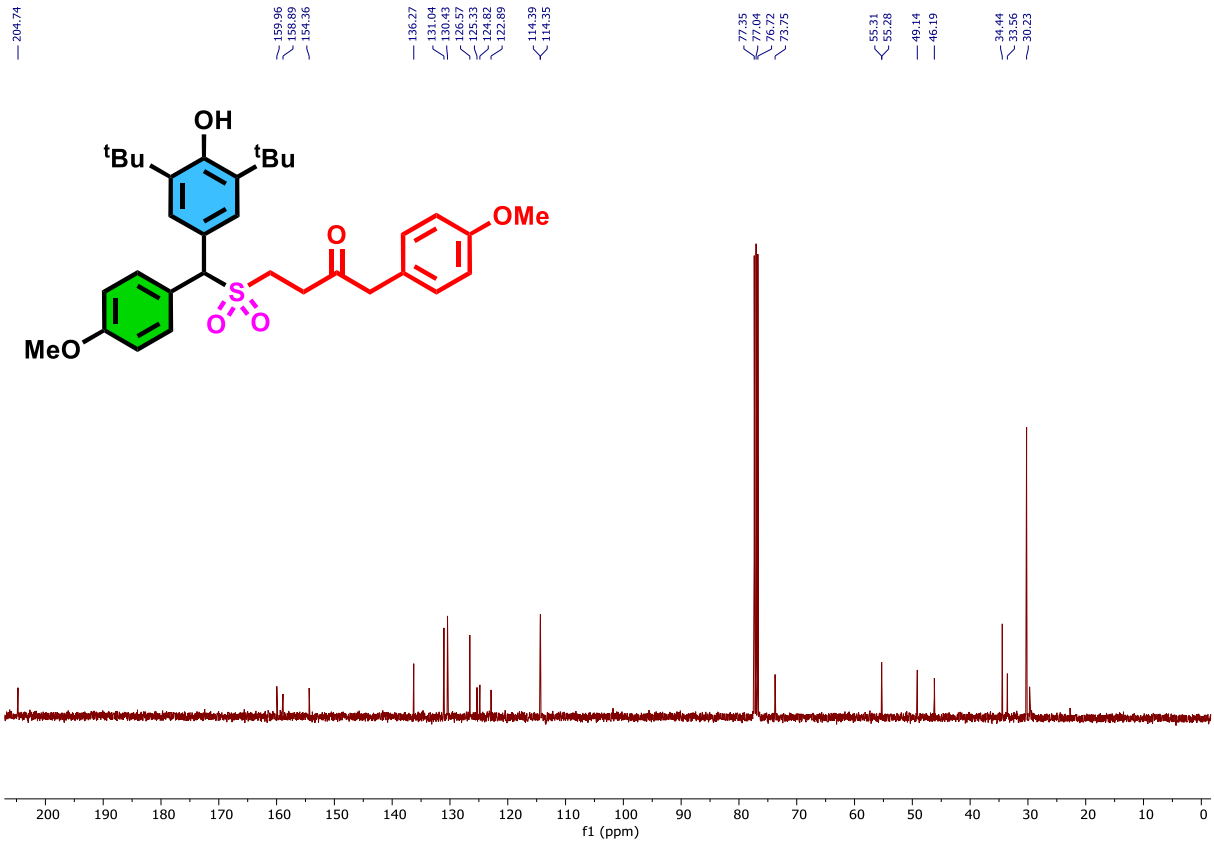
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylbutan-2-one **(3al)**



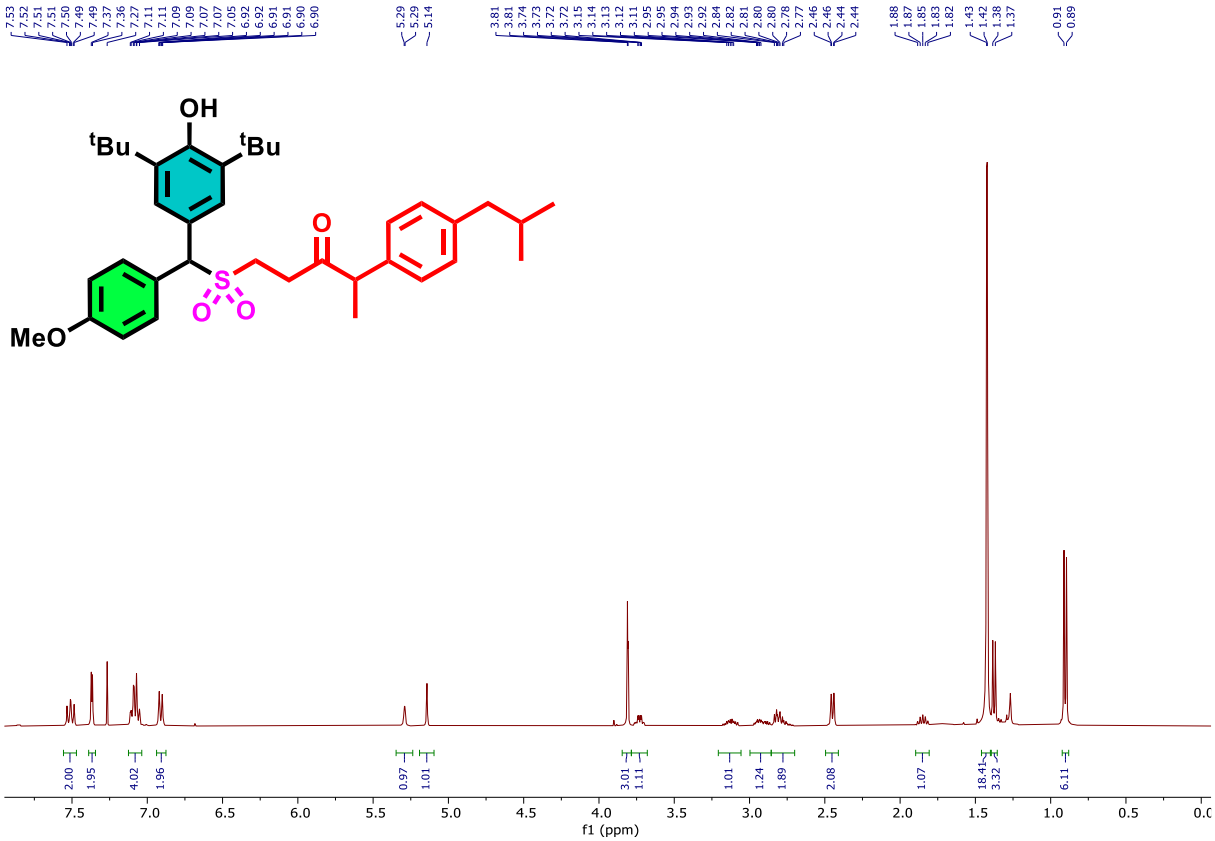
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-methoxyphenyl)butan-2-one **(3am)**



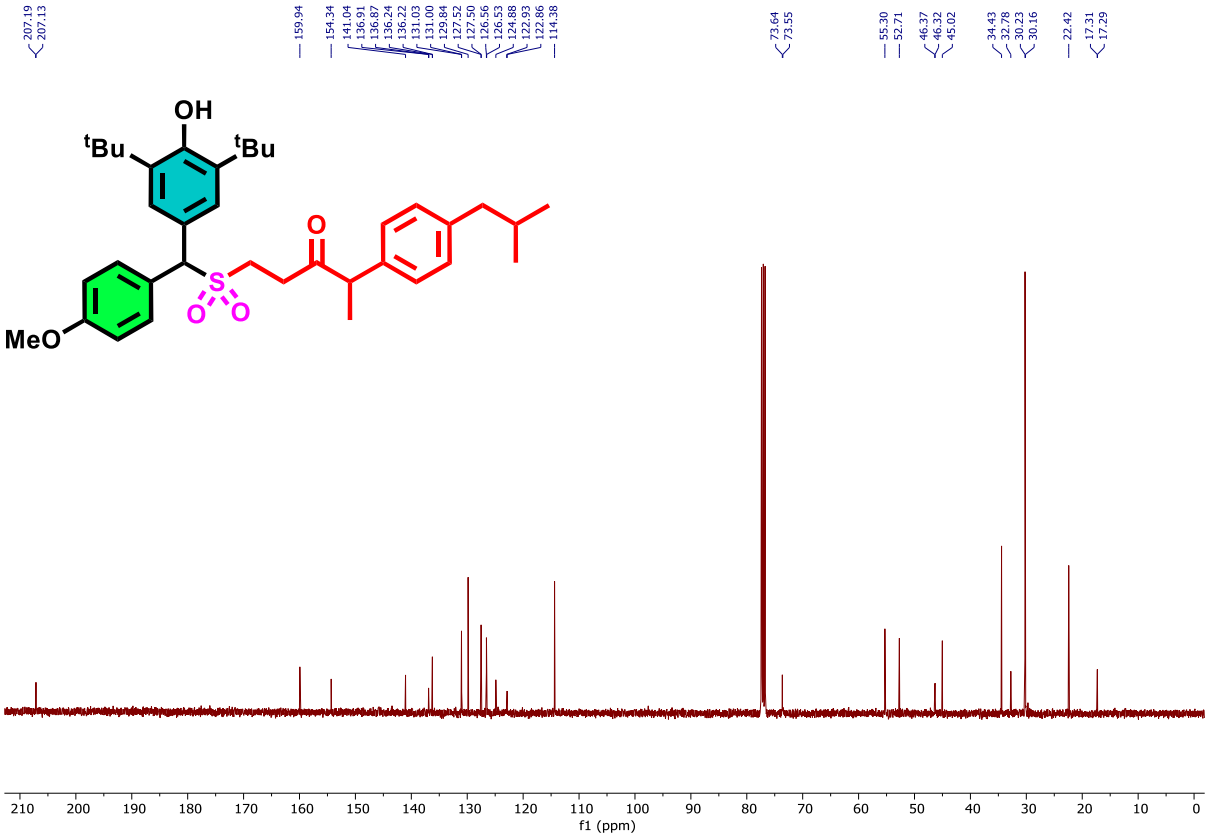
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-(4-methoxyphenyl)butan-2-one **(3am)**



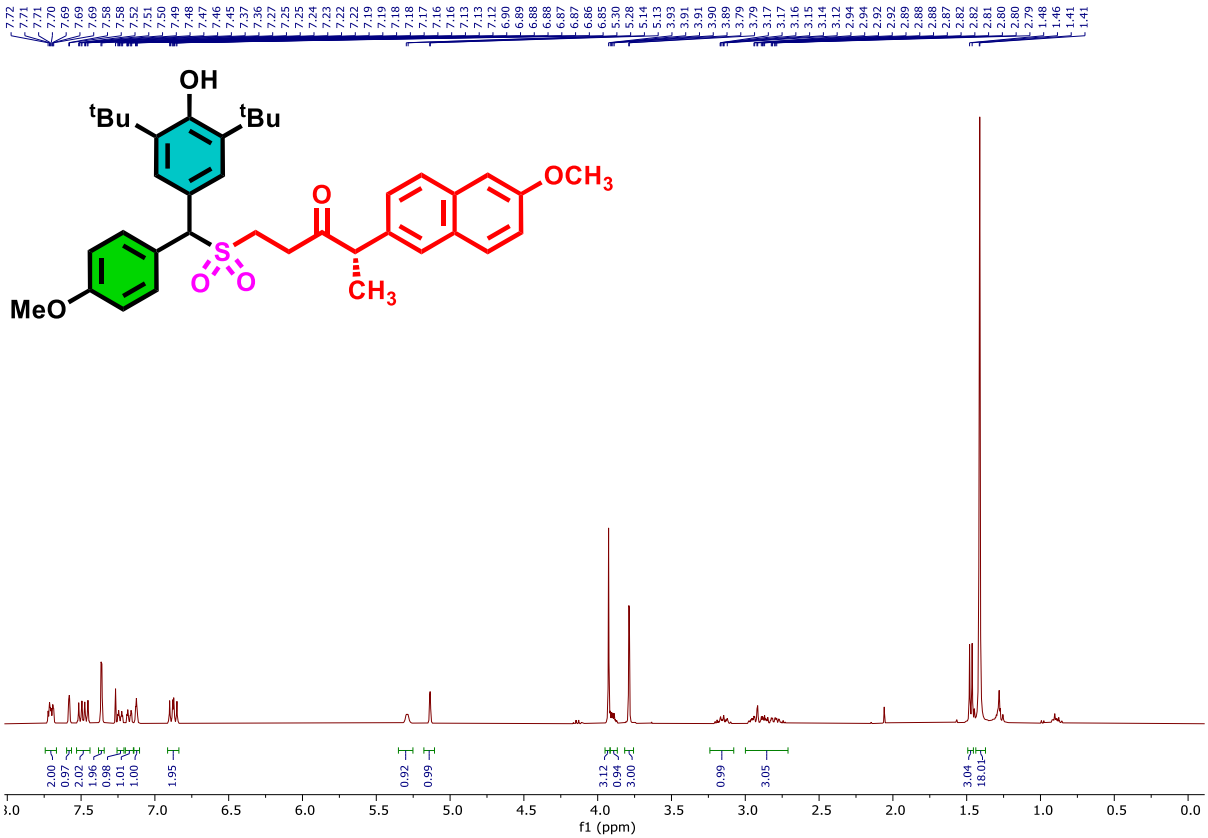
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-4-(4-isobutylphenyl)pentan-3-one **(3an)**



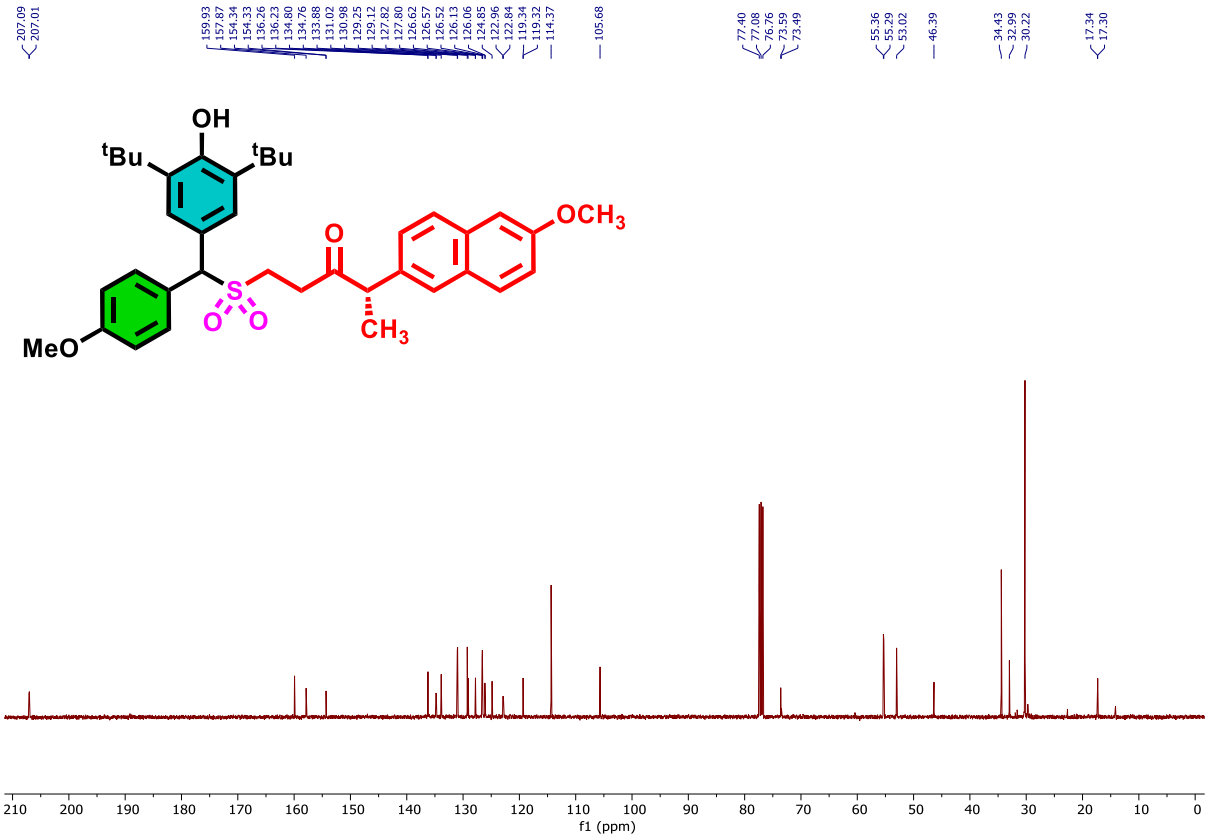
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-4-(4-isobutylphenyl)pentan-3-one **(3an)**



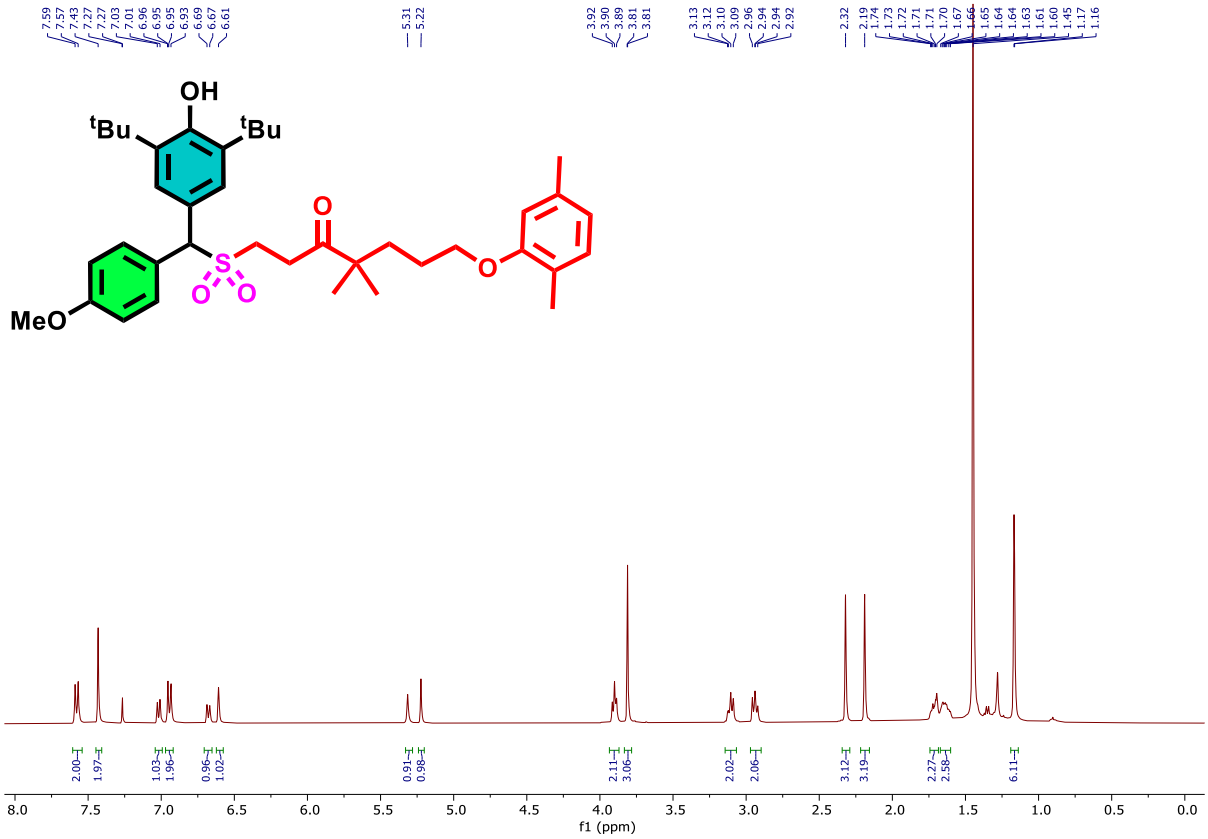
^{1}HNMR ($CDCl_3$, 400 MHz) of (4S)-1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-4-(6-methoxynaphthalen-2-yl)pentan-3-one **(3ao)**



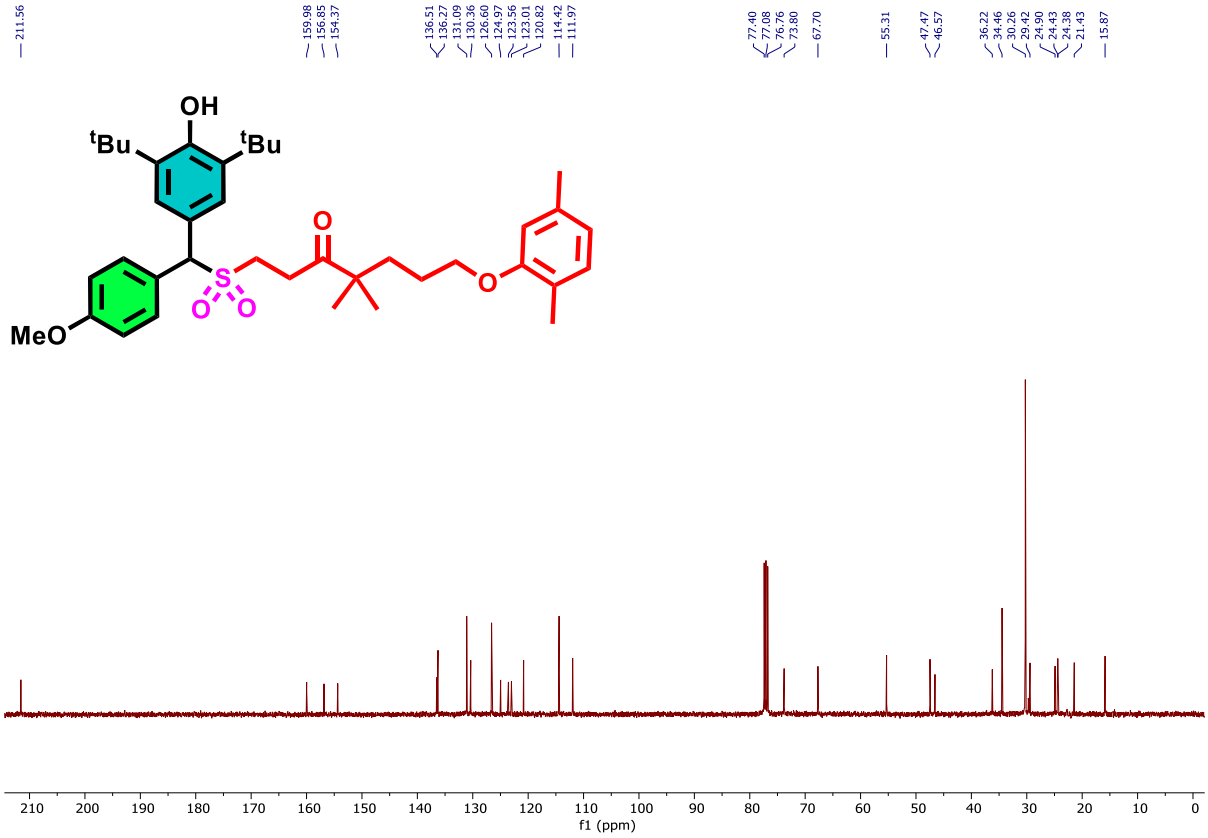
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of (4S)-1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-4-(6-methoxynaphthalen-2-yl)pentan-3-one **(3ao)**



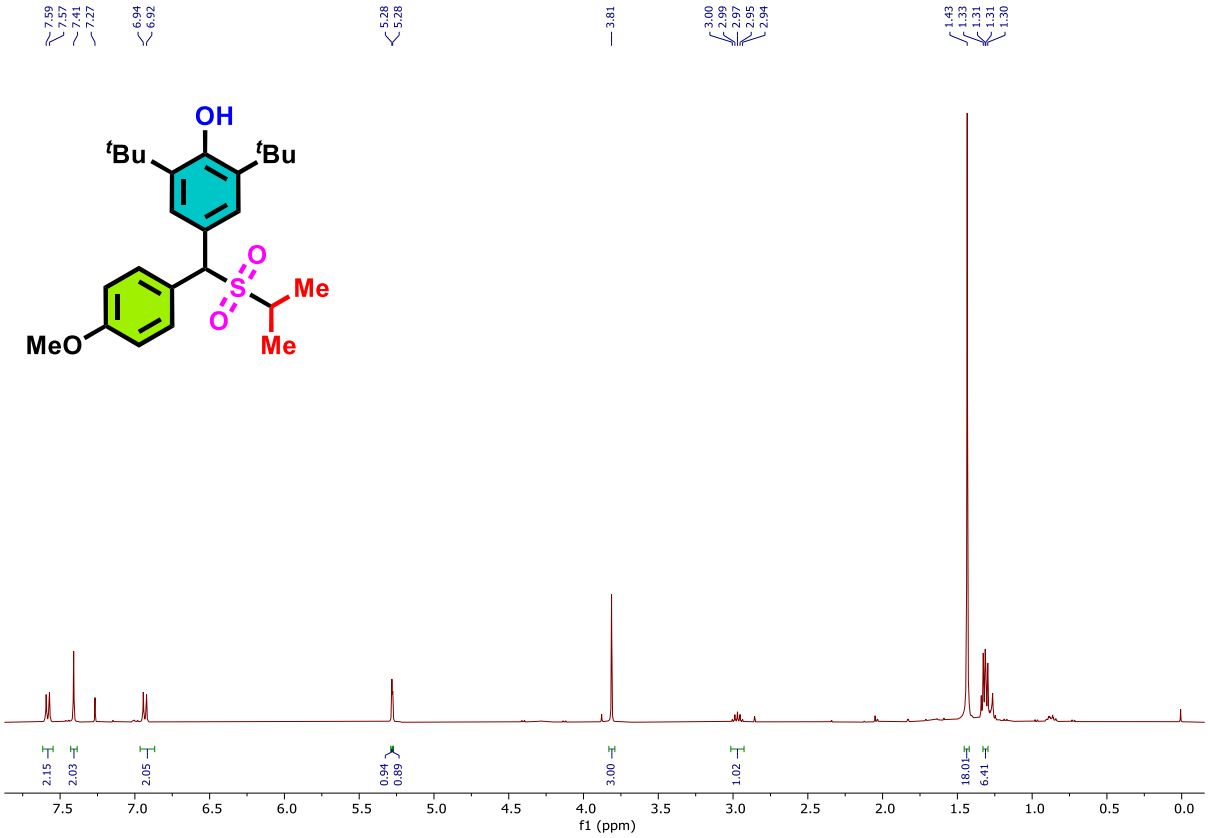
^{1}HNMR ($CDCl_3$, 400 MHz) of 1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-7-(2,5-dimethylphenoxy)-4,4-dimethylheptan-3-one **(3ap)**



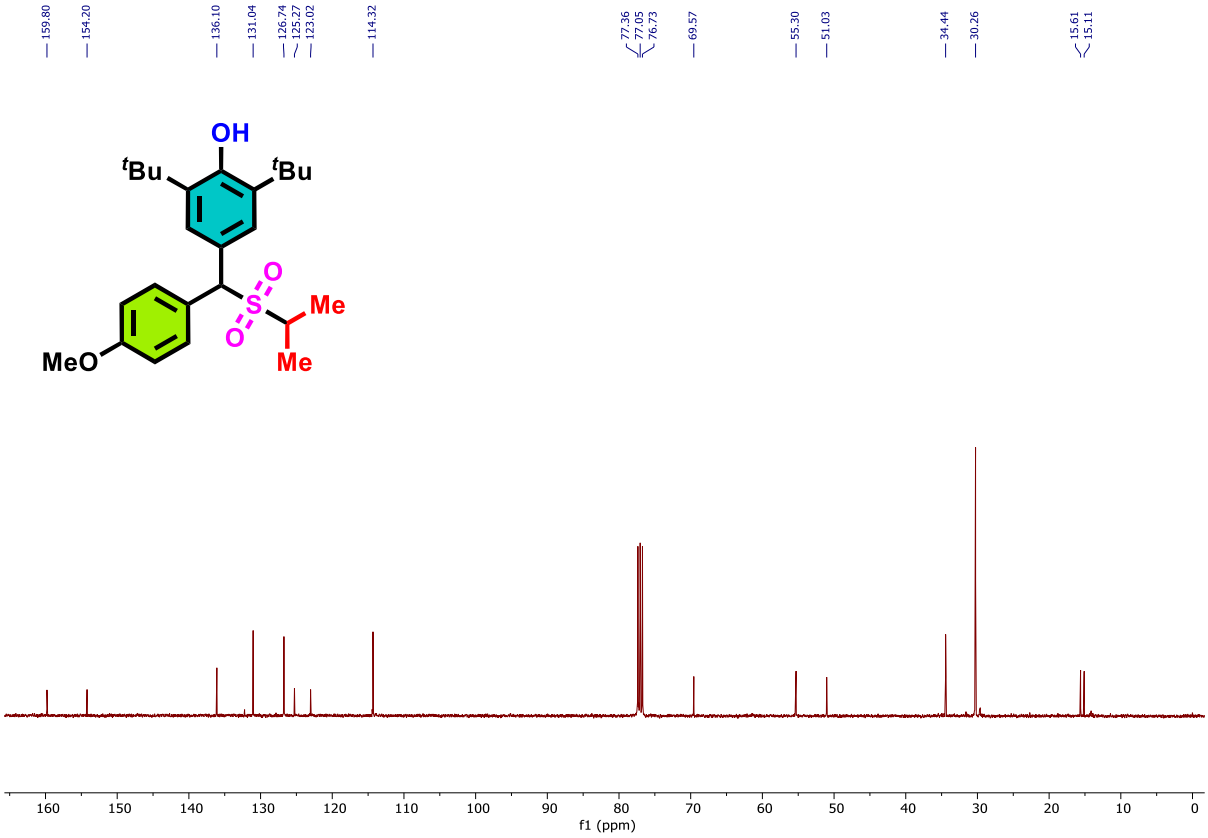
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 1-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-7-(2,5-dimethylphenoxy)-4,4-dimethylheptan-3-one **(3ap)**



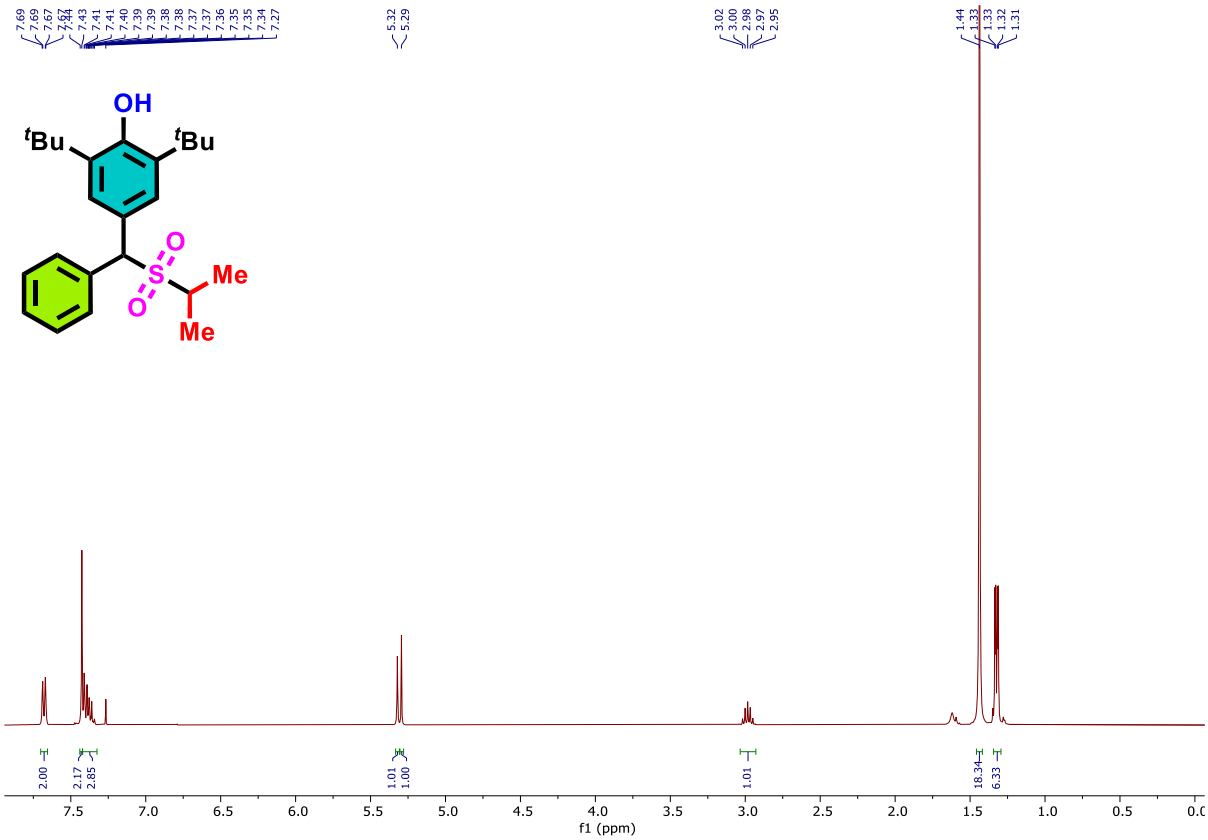
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5aa)**



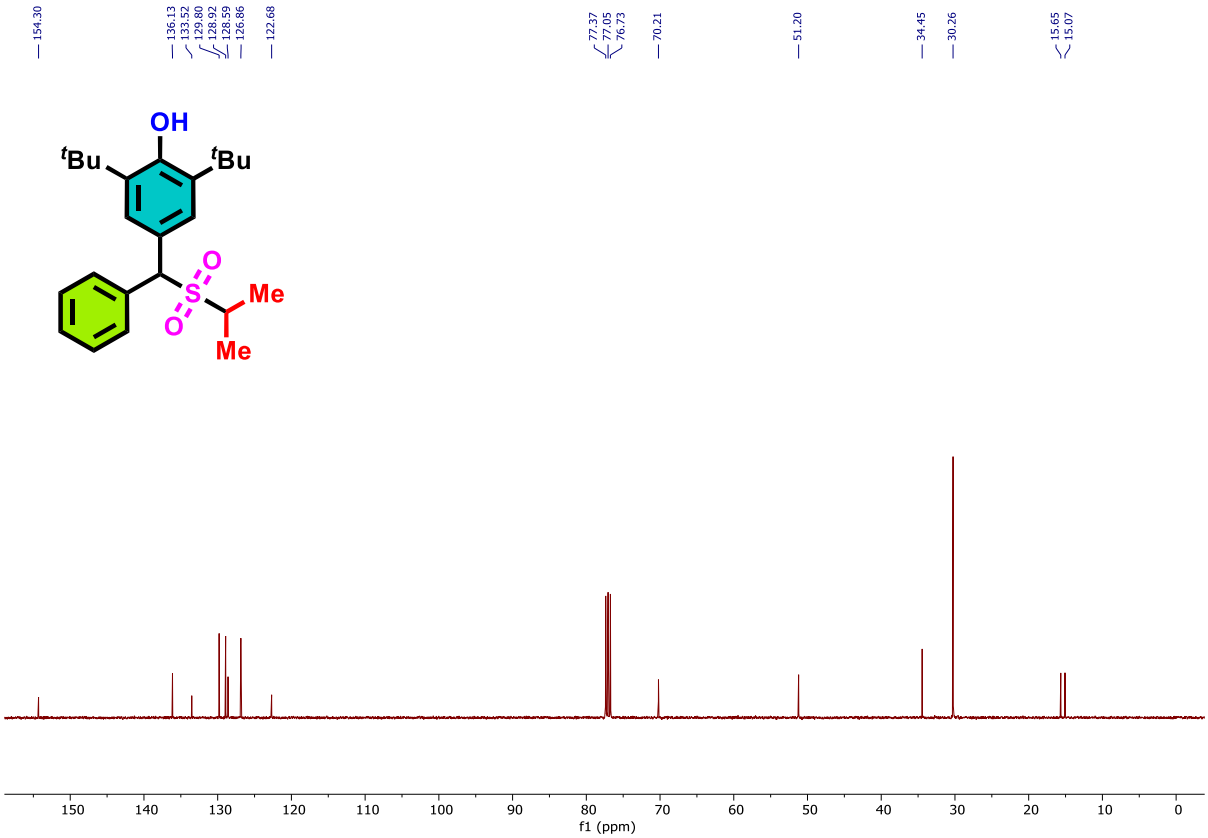
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5aa)**



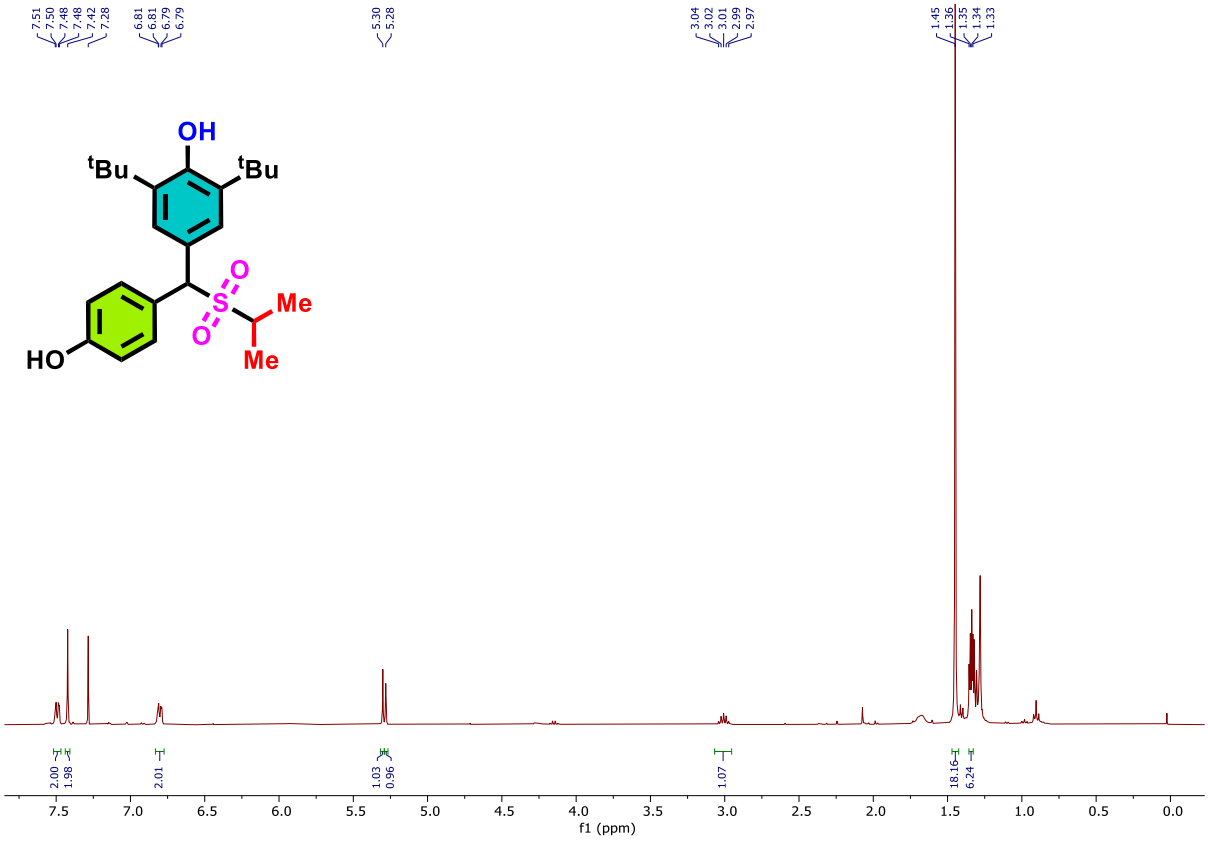
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(phenyl)methyl)phenol **(5ba)**



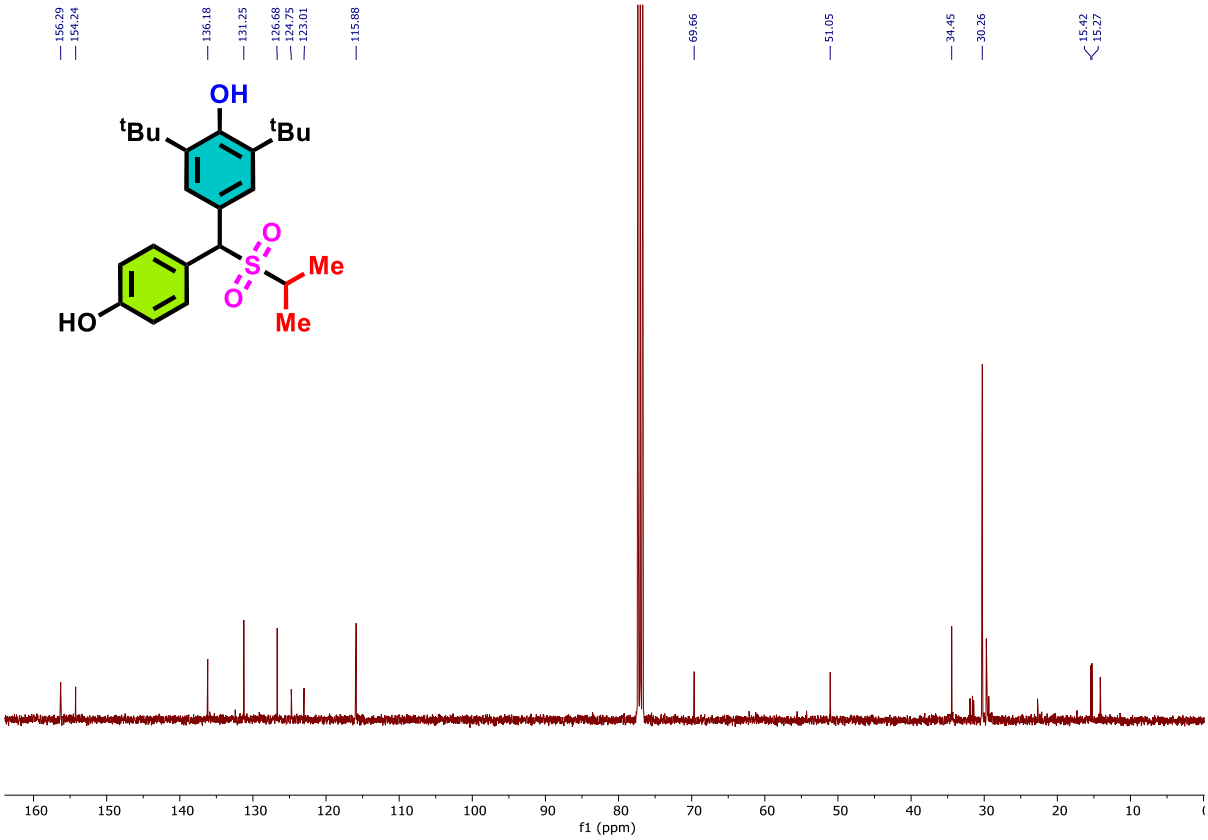
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(phenyl)methyl)phenol **(5ba)**



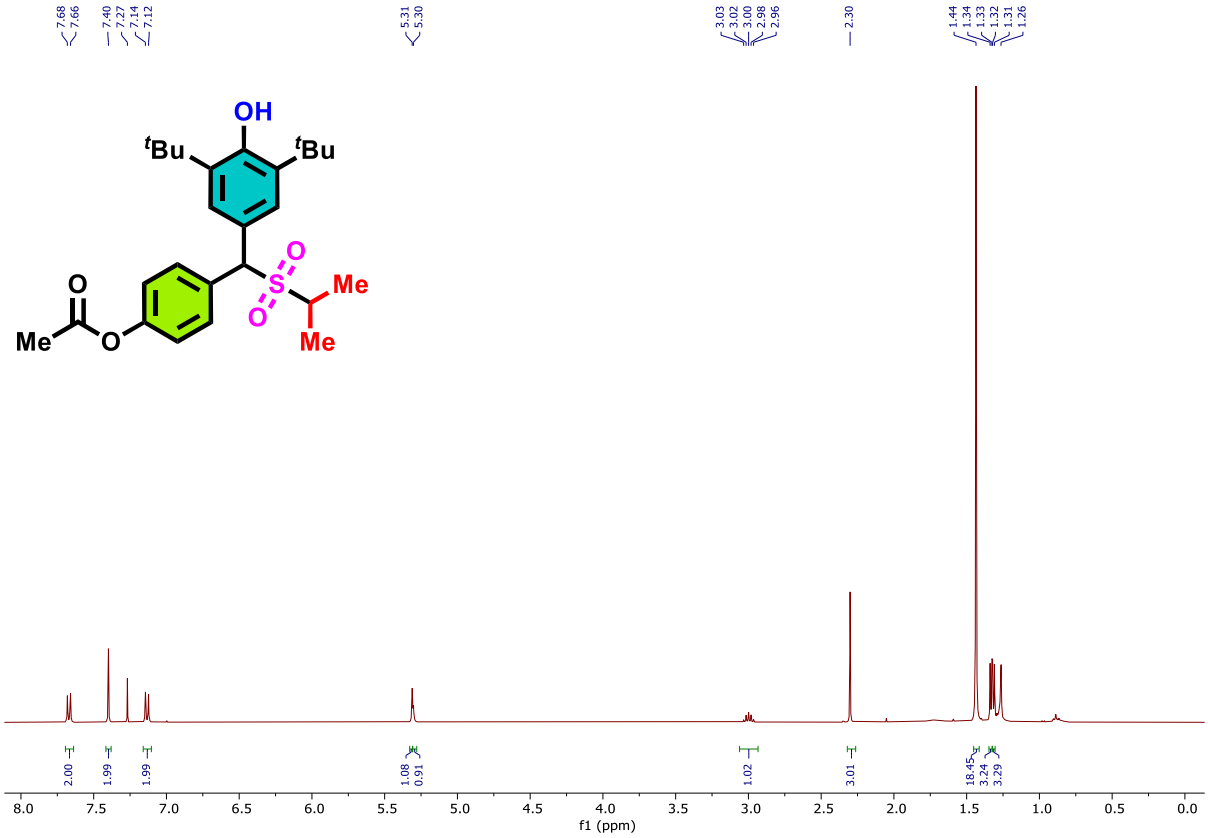
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenol **(5ca)**



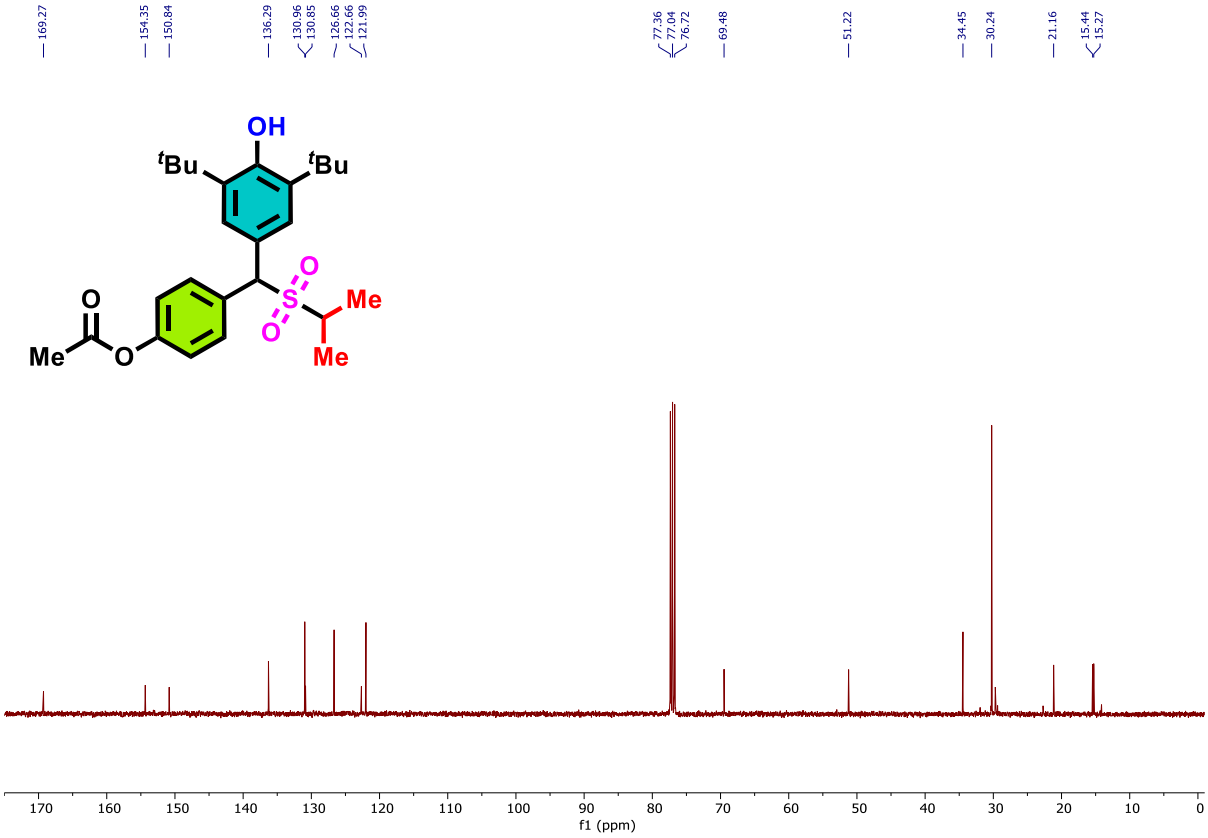
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenol **(5ca)**



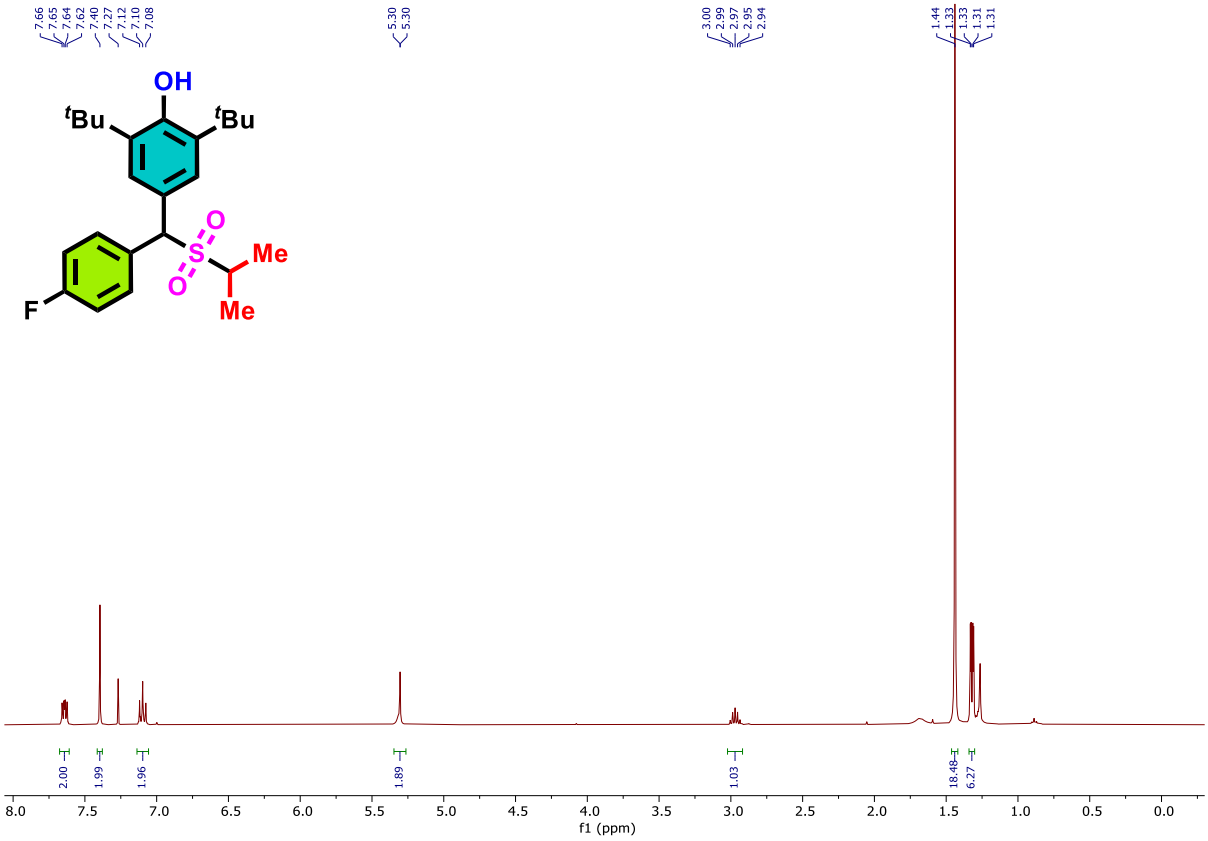
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenyl acetate **(5da)**



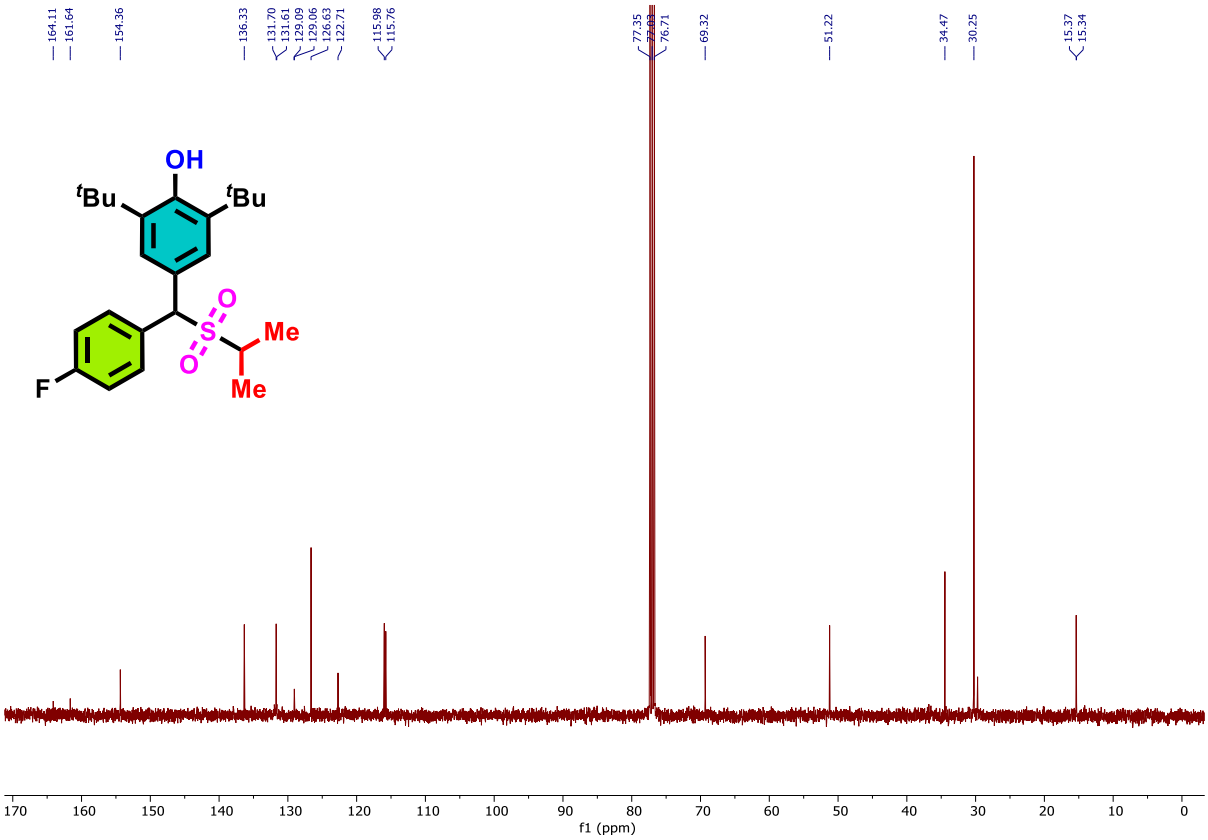
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenyl acetate **(5da)**



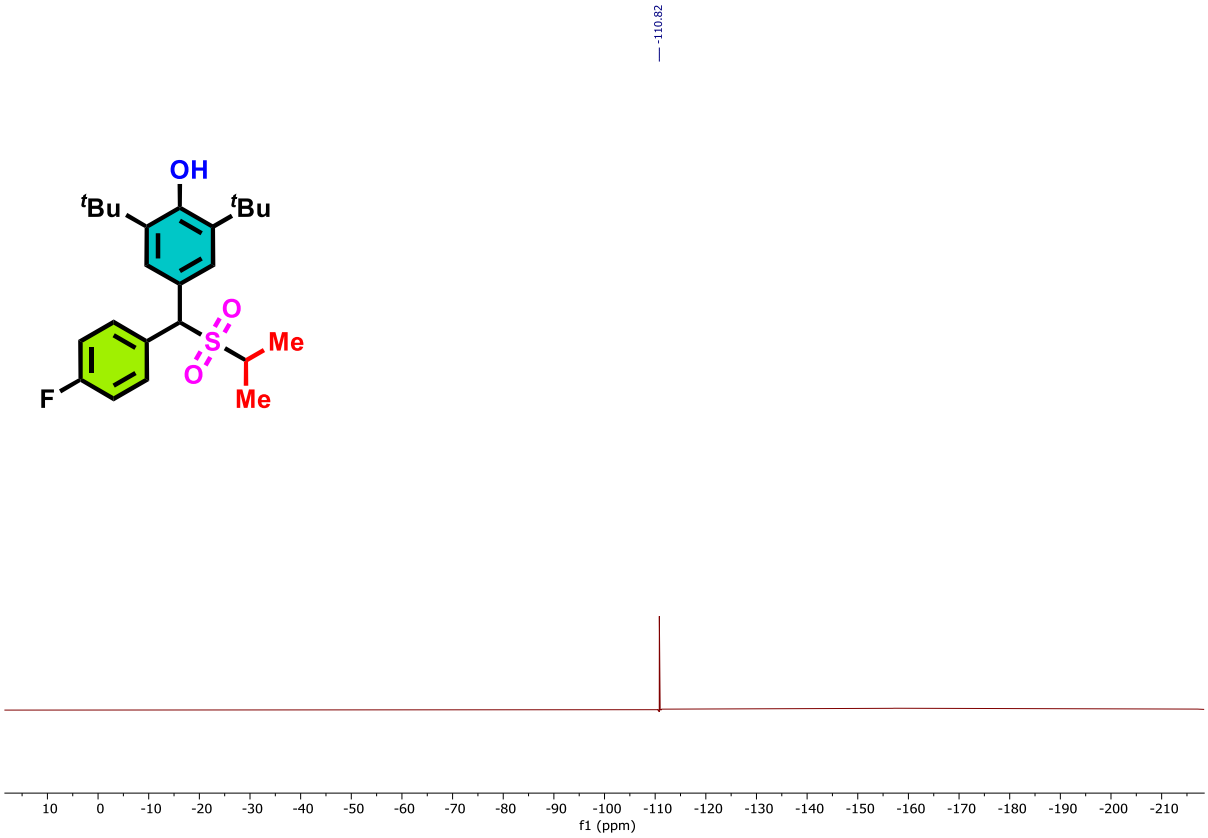
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((4-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5ea)**



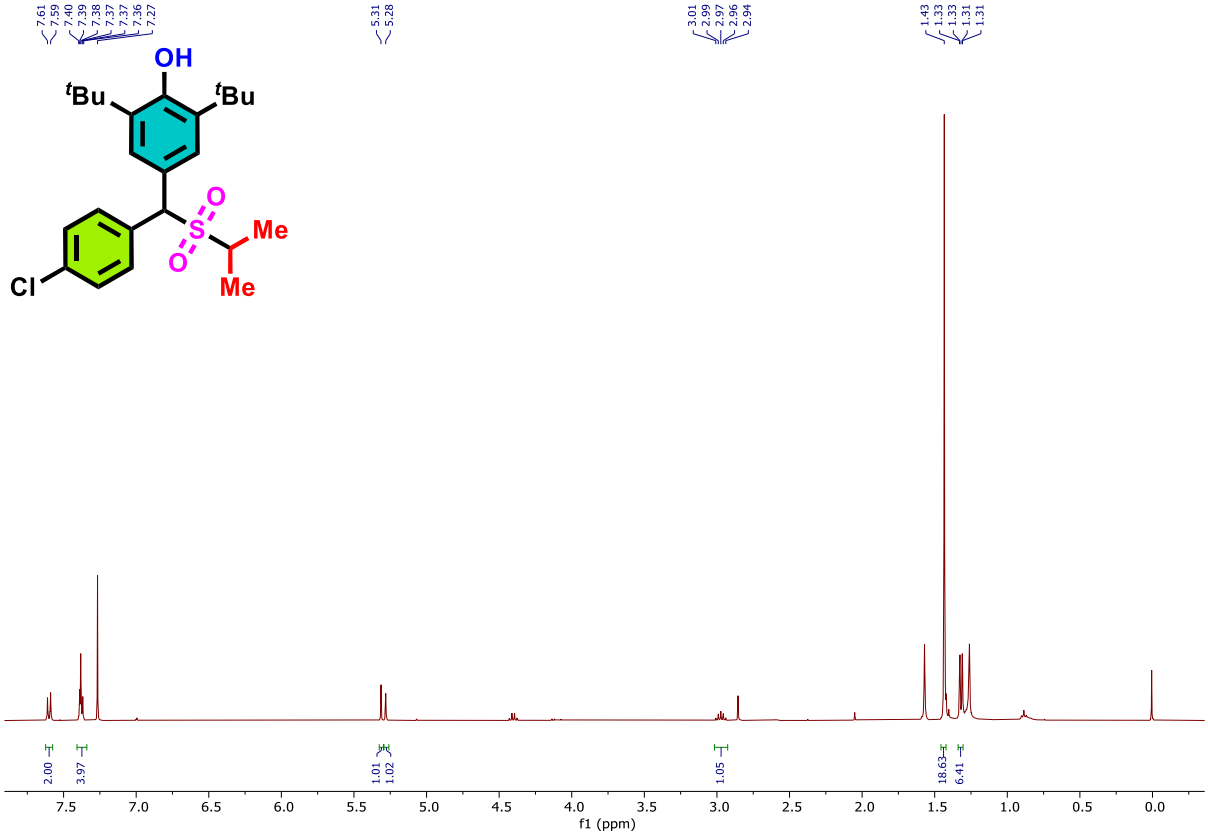
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((4-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5ea)**



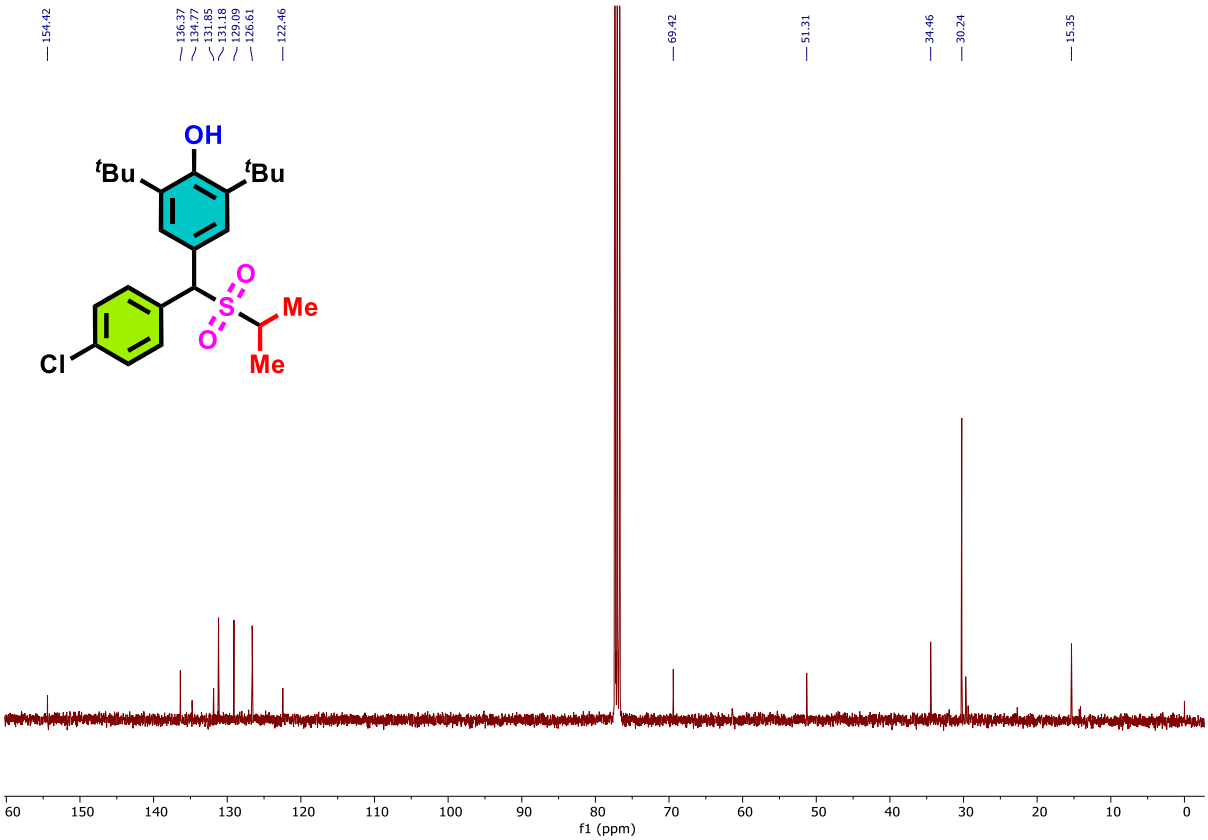
^{19}F NMR (377 MHz, $CDCl_3$) of 2,6-di-tert-butyl-4-((4-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5ea)**



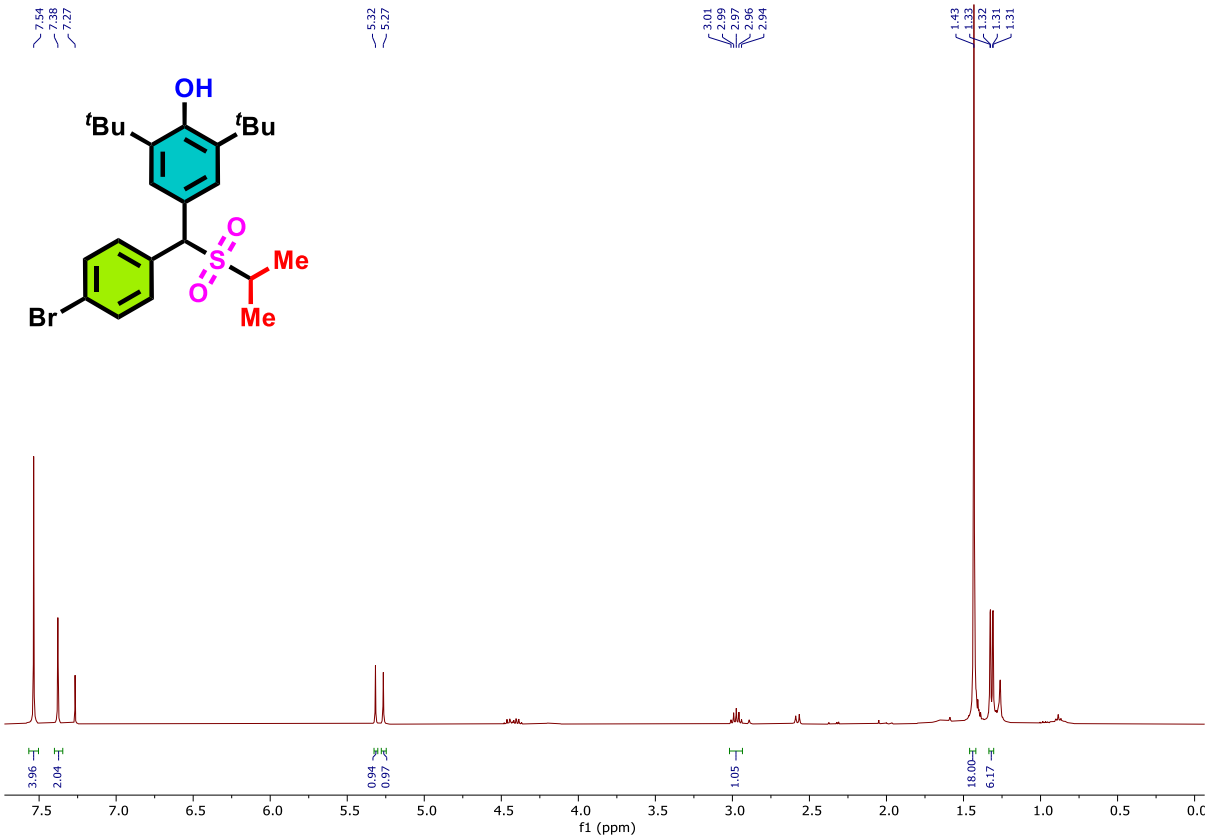
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((4-chlorophenyl)(isopropylsulfonyl)methyl)phenol **(5fa)**



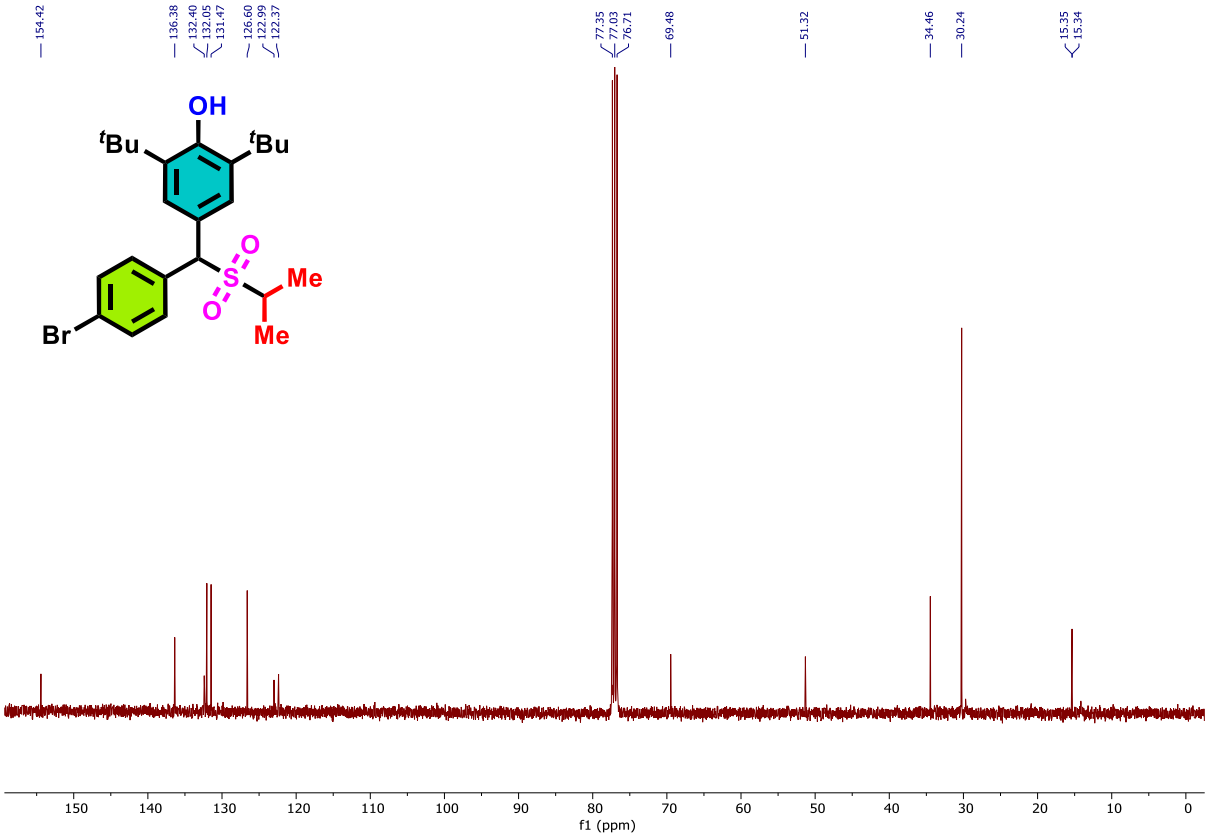
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((4-chlorophenyl)(isopropylsulfonyl)methyl)phenol **(5fa)**



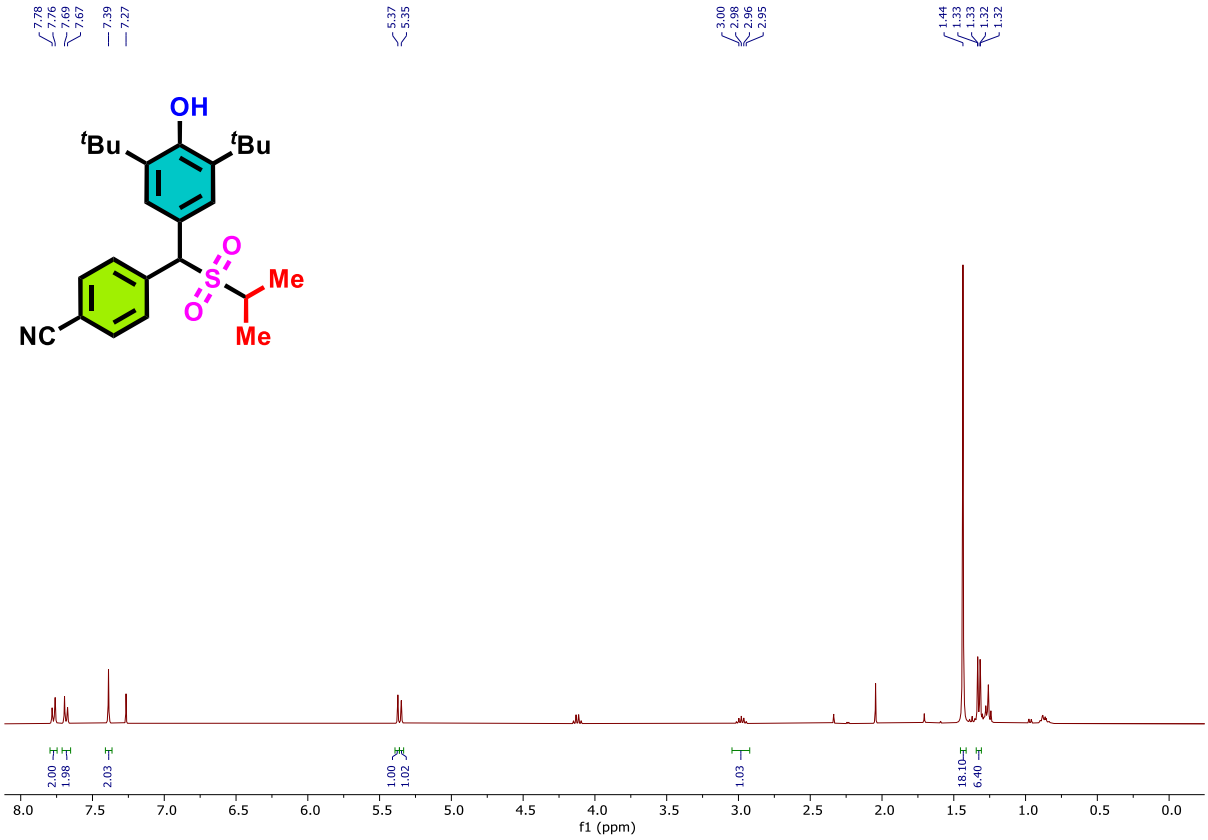
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((4-bromophenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol **(5ga)**



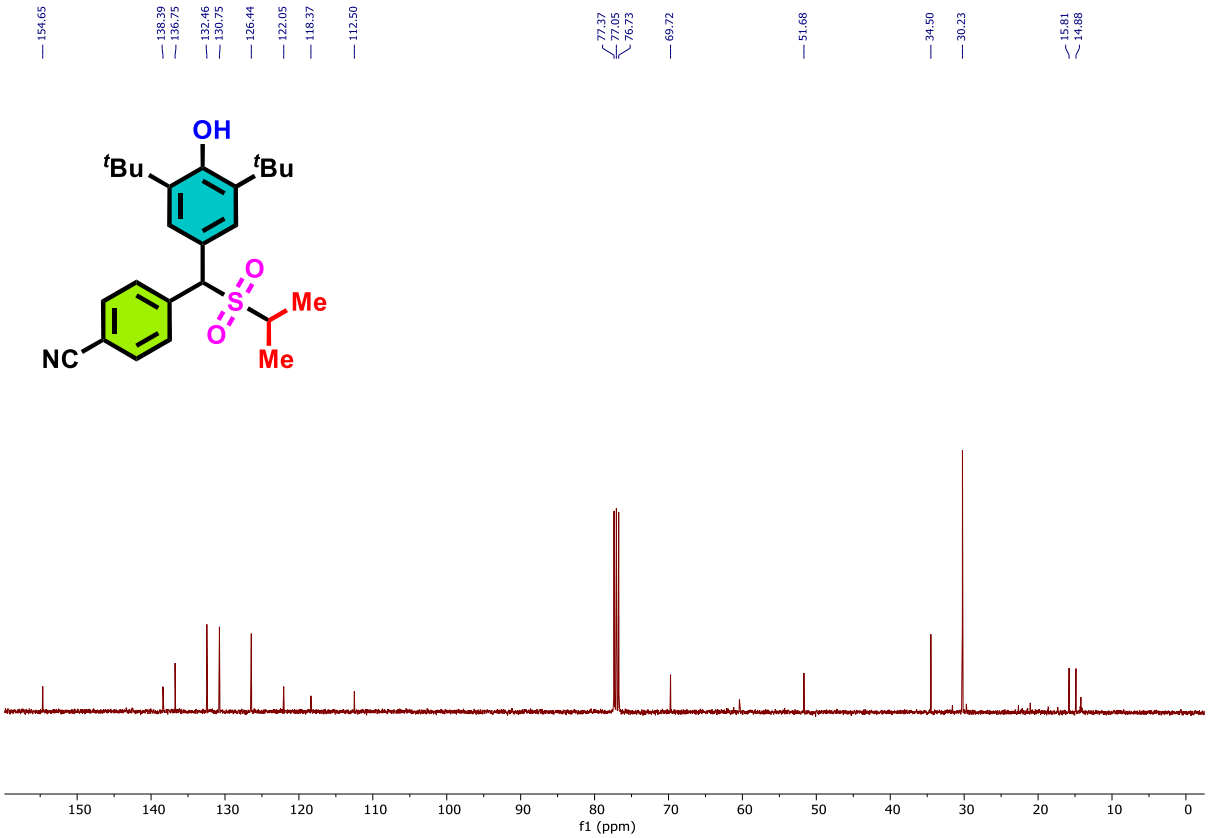
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((4-bromophenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol **(5ga)**



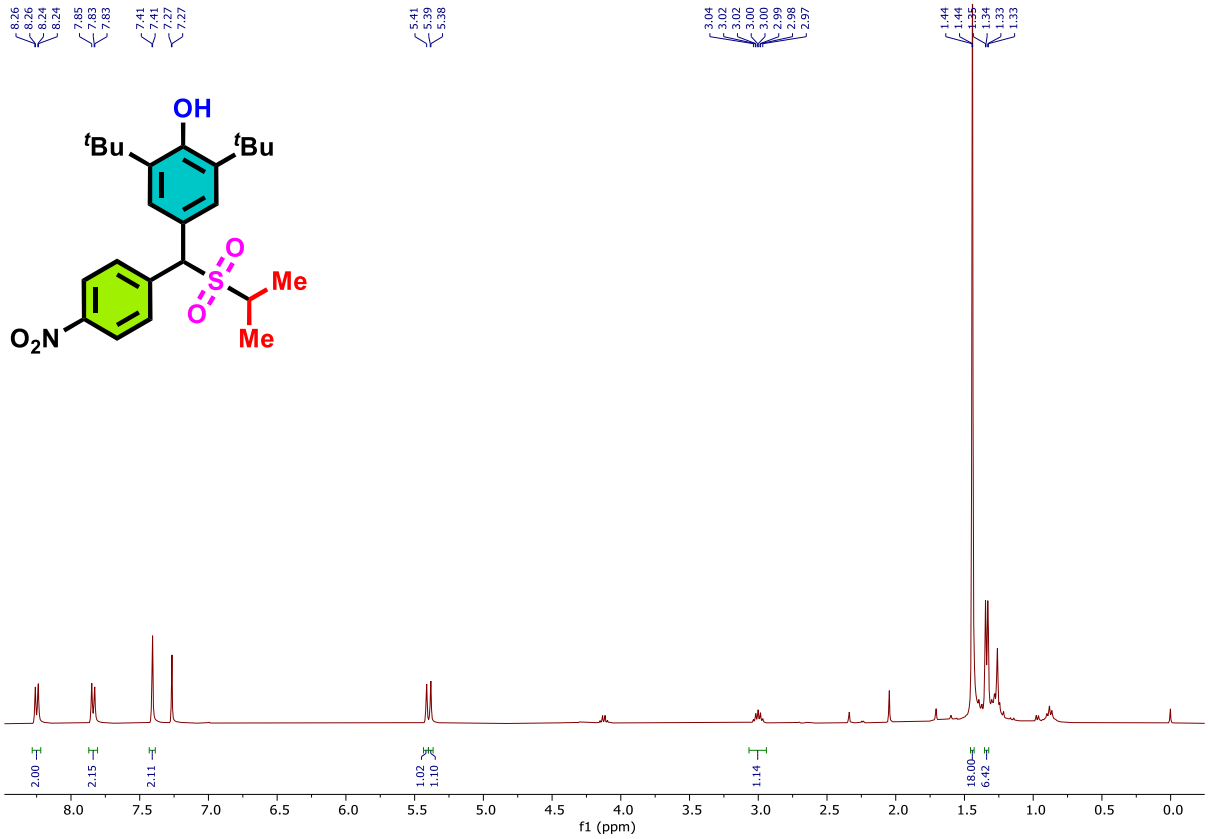
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)benzonitrile **(5ha)**



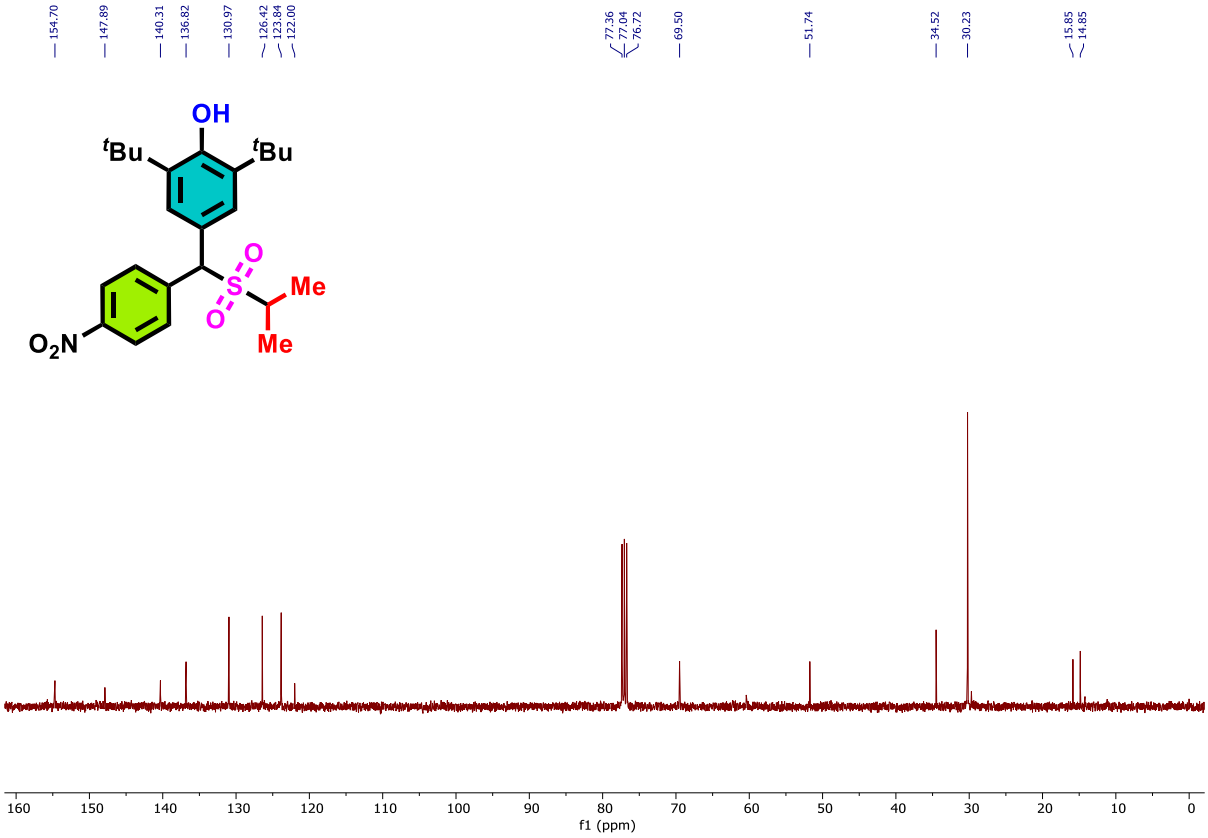
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)benzonitrile **(5ha)**



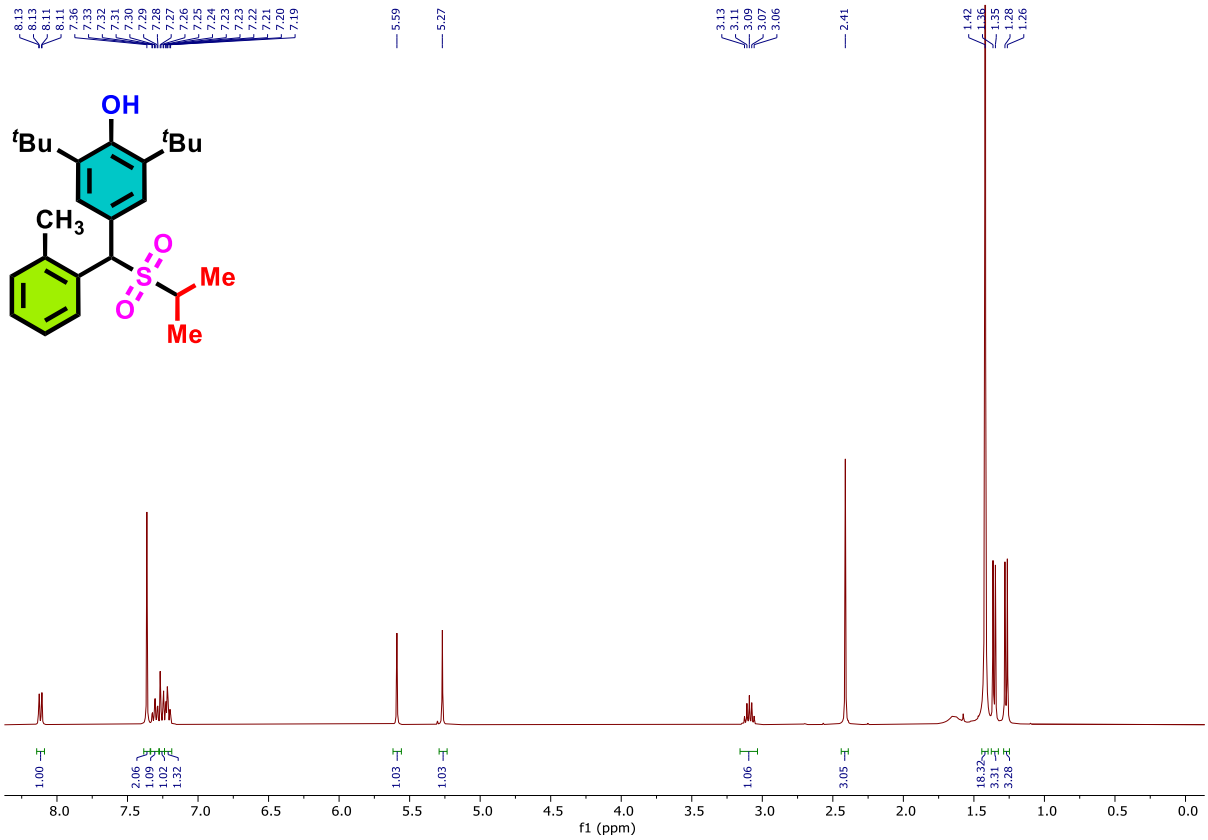
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-nitrophenyl)methyl)phenol **(5ia)**



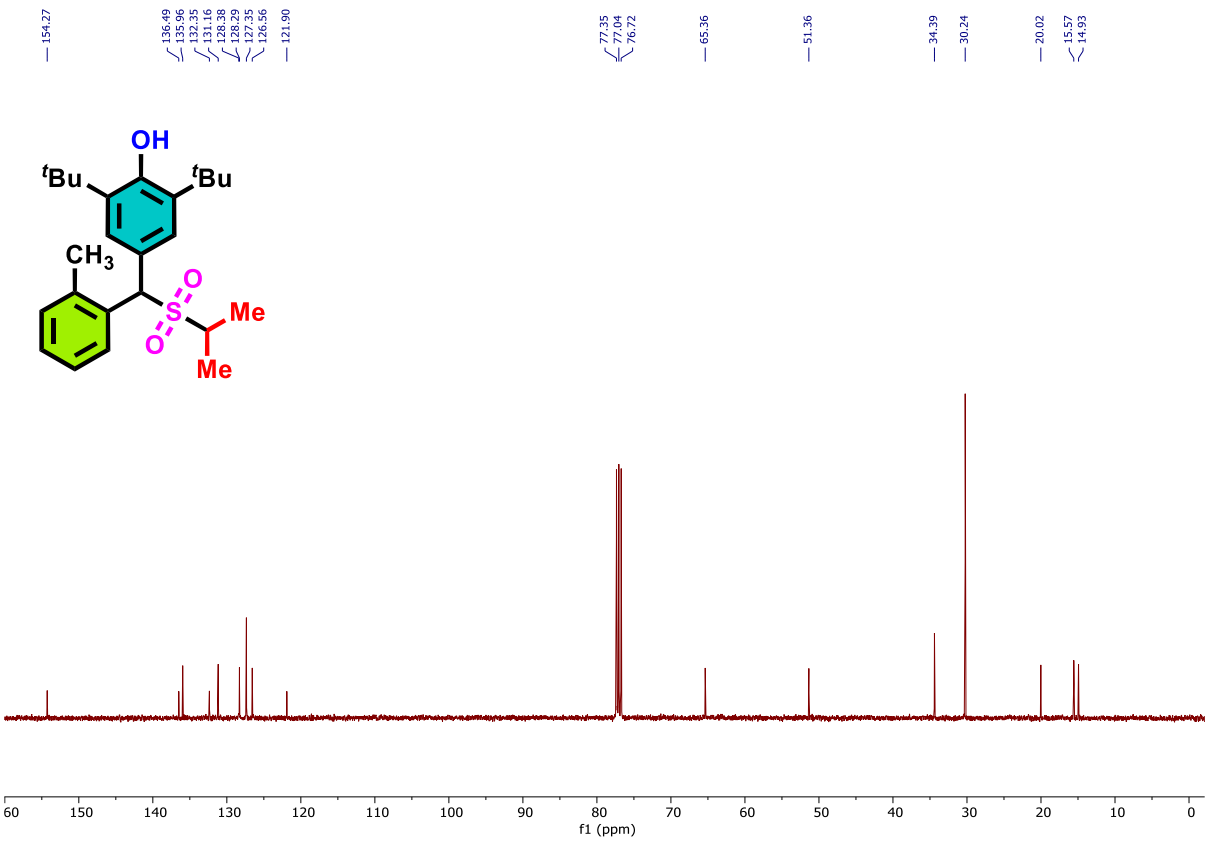
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-nitrophenyl)methyl)phenol **(5ia)**



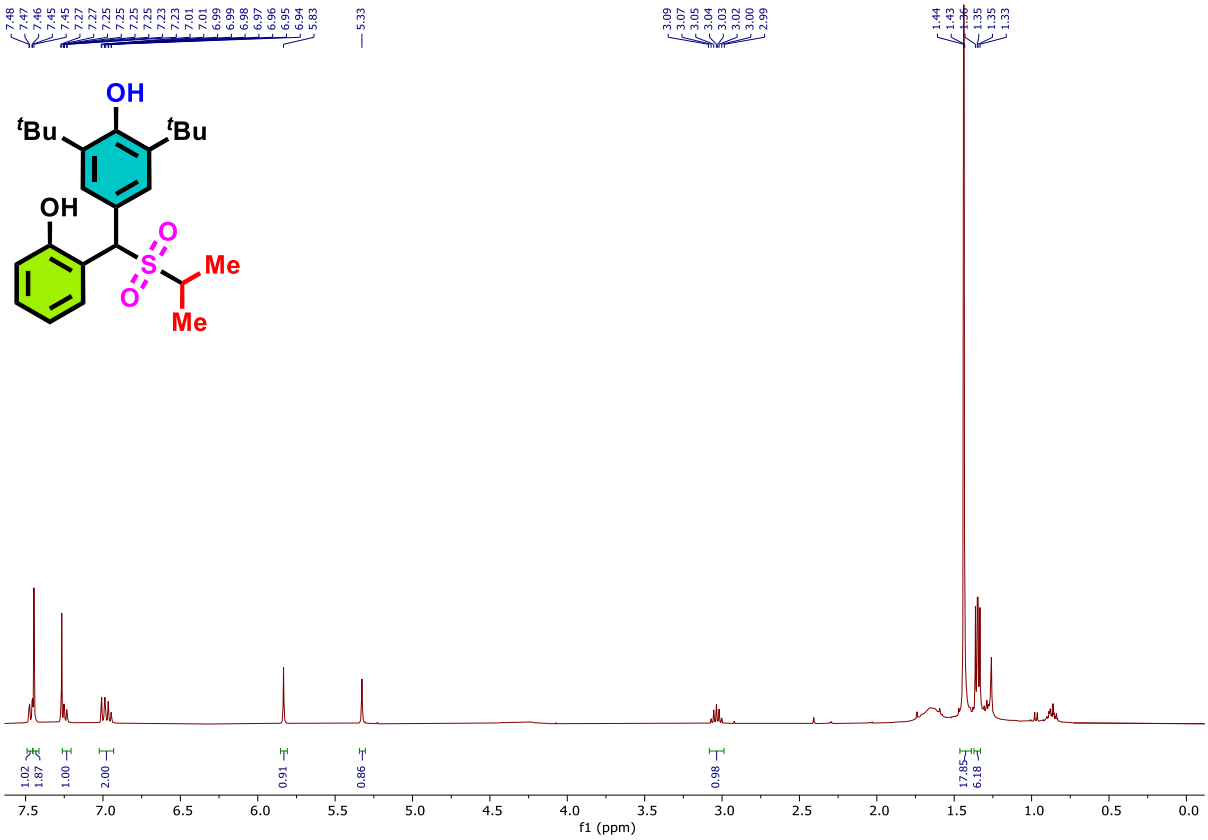
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(o-tolyl)methyl)phenol **(5ja)**



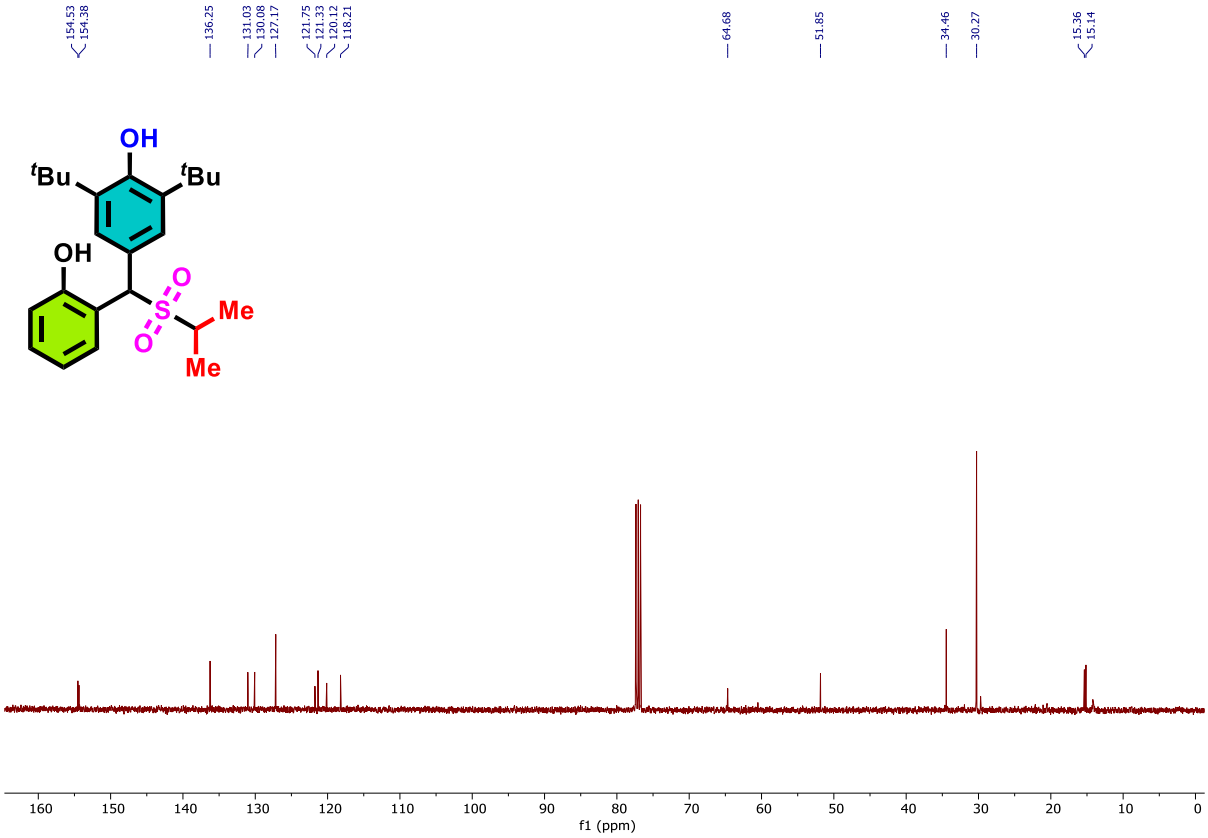
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(o-tolyl)methyl)phenol **(5ja)**



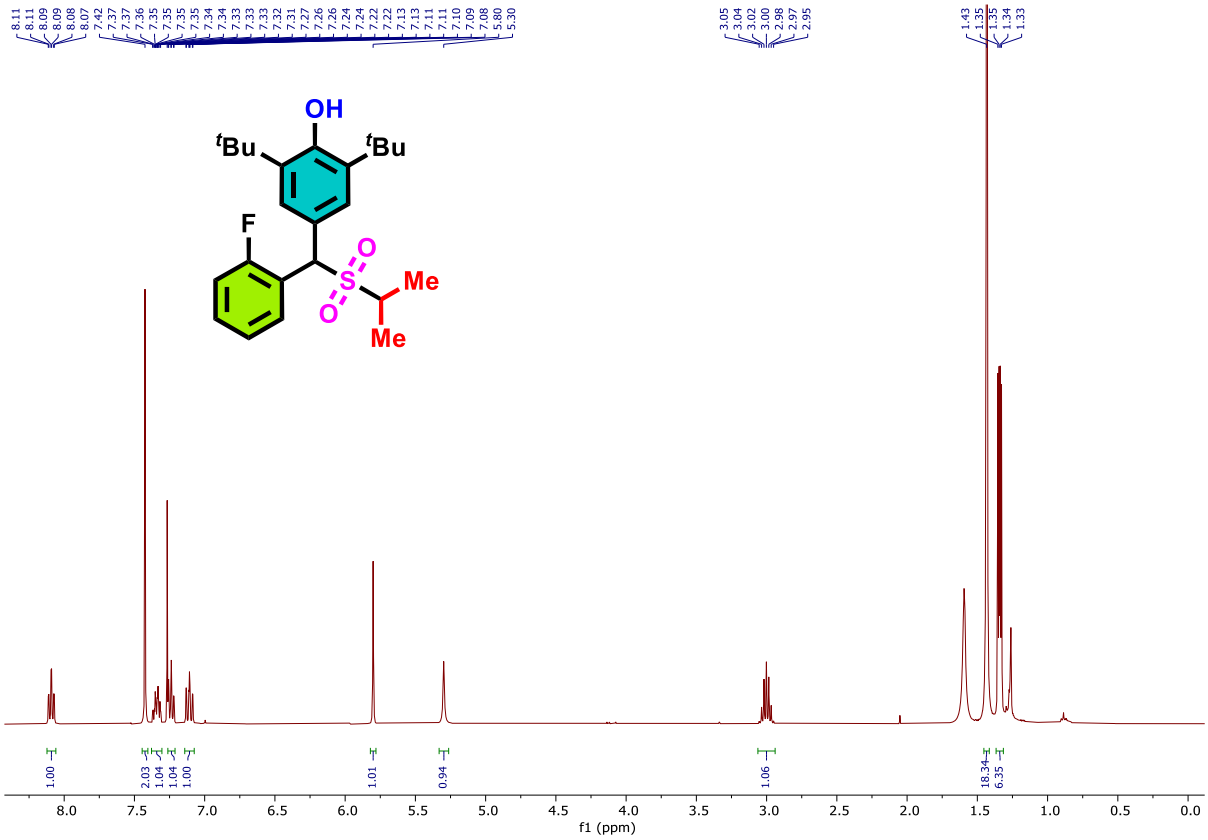
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((2-hydroxyphenyl)(isopropylsulfonyl)methyl)phenol **(5ka)**



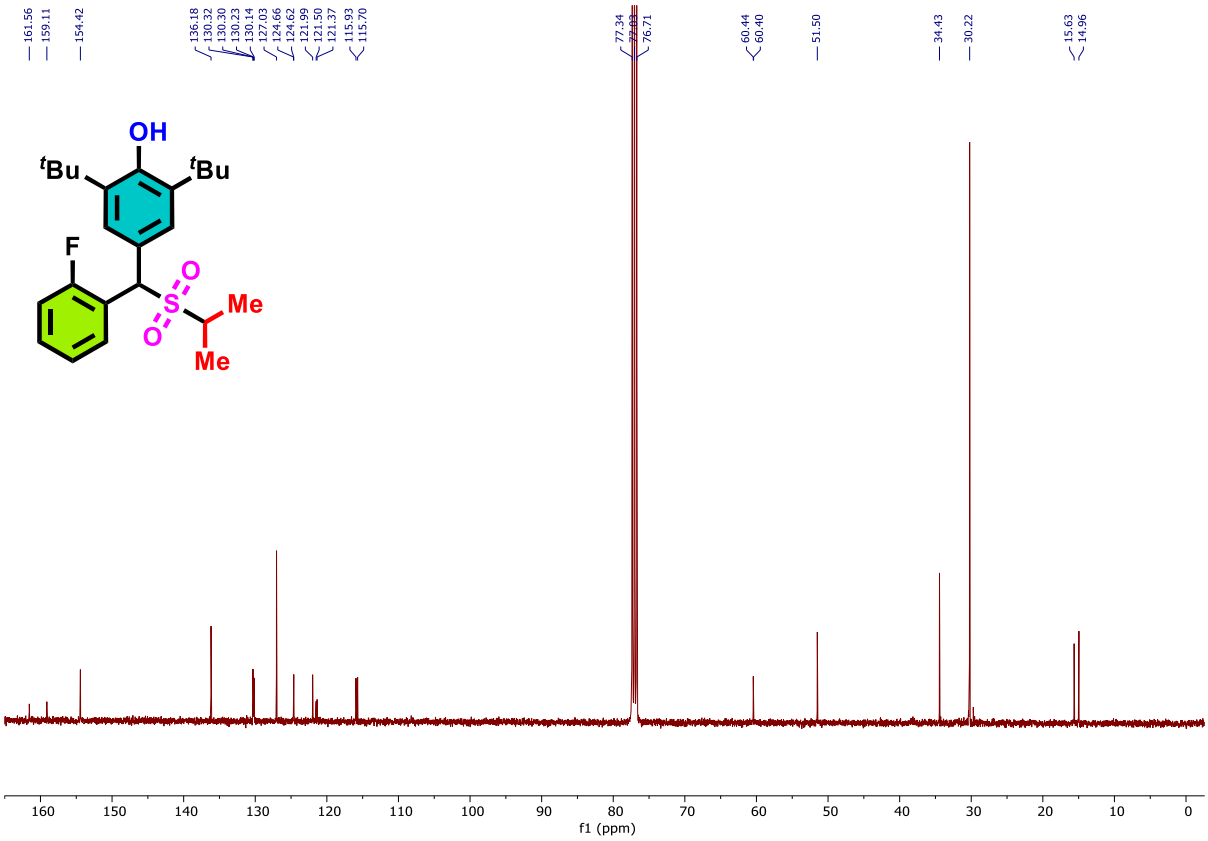
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((2-hydroxyphenyl)(isopropylsulfonyl)methyl)phenol (**5ka**)



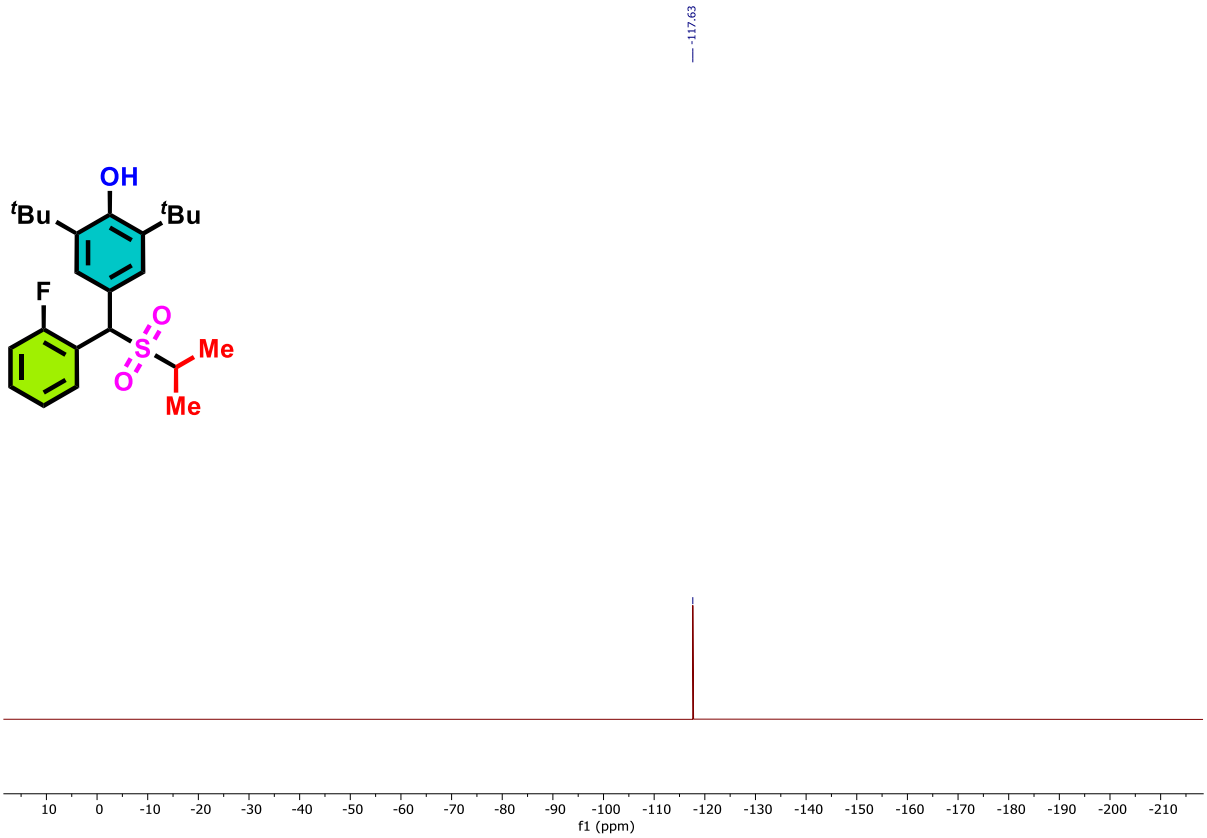
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((2-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5la)**



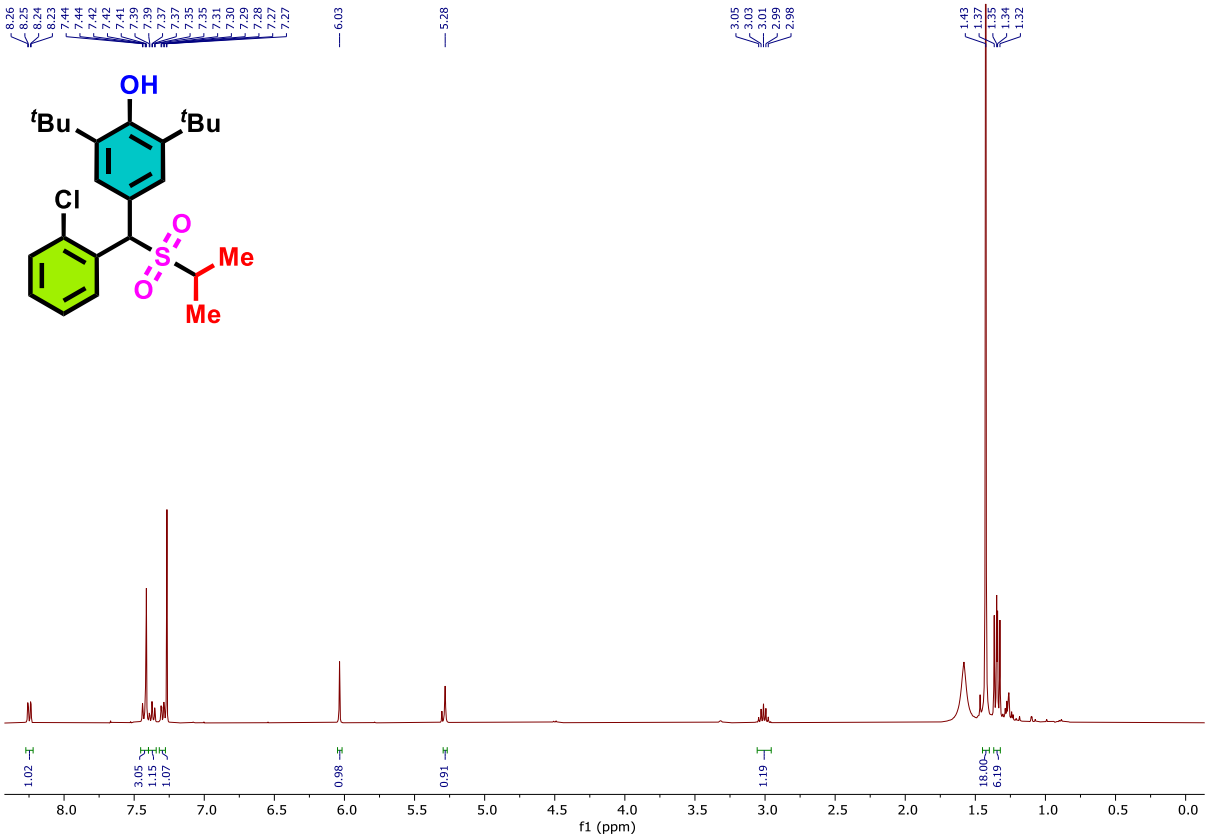
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((2-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5la)**



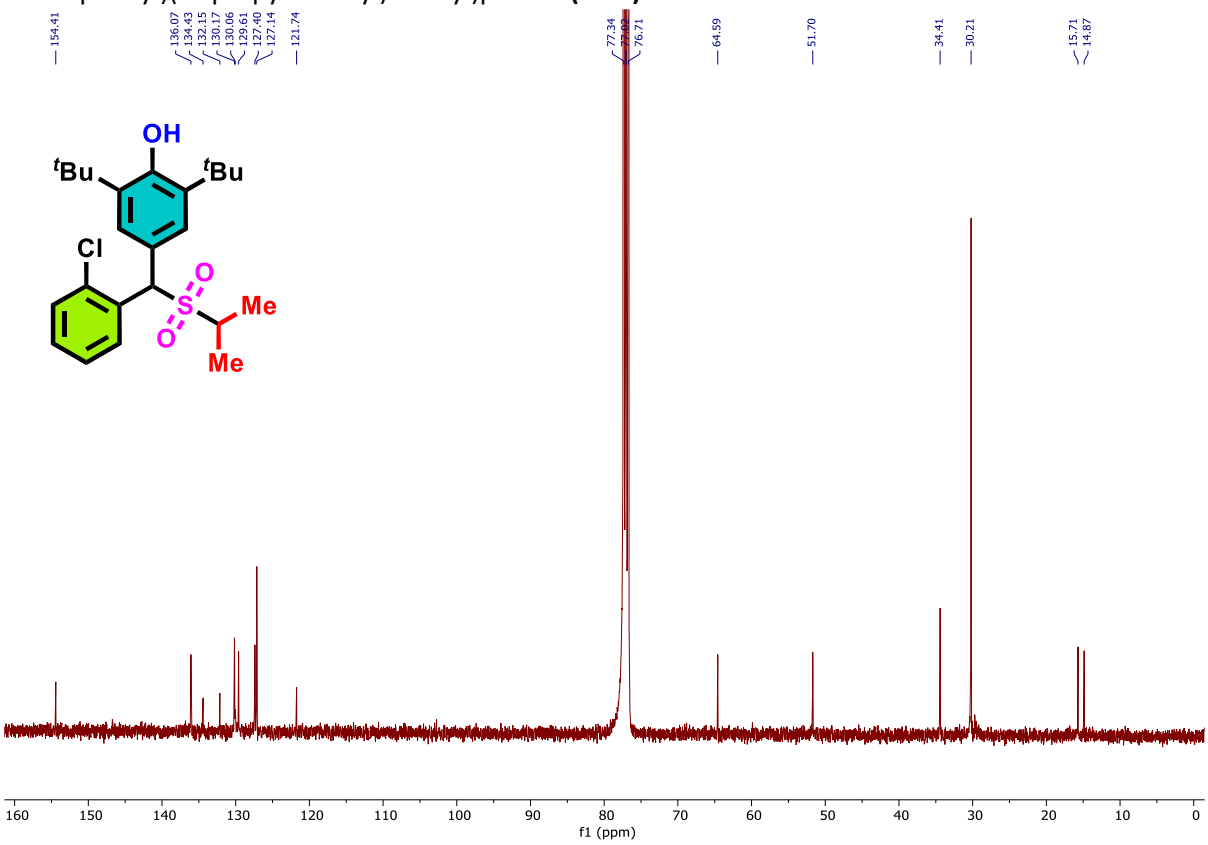
^{19}F NMR (377 MHz, $CDCl_3$) of 2,6-di-tert-butyl-4-((2-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5la)**



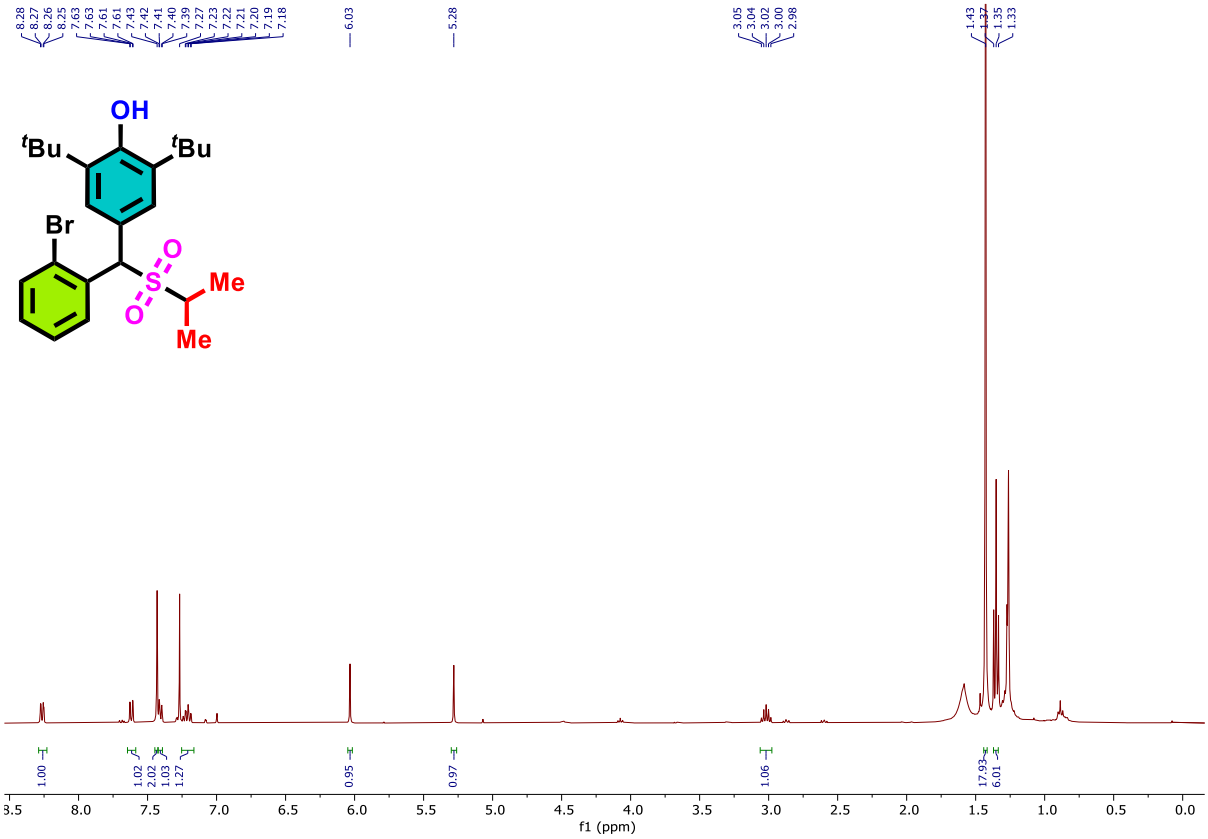
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((2-chlorophenyl)(isopropylsulfonyl)methyl)phenol **(5ma)**



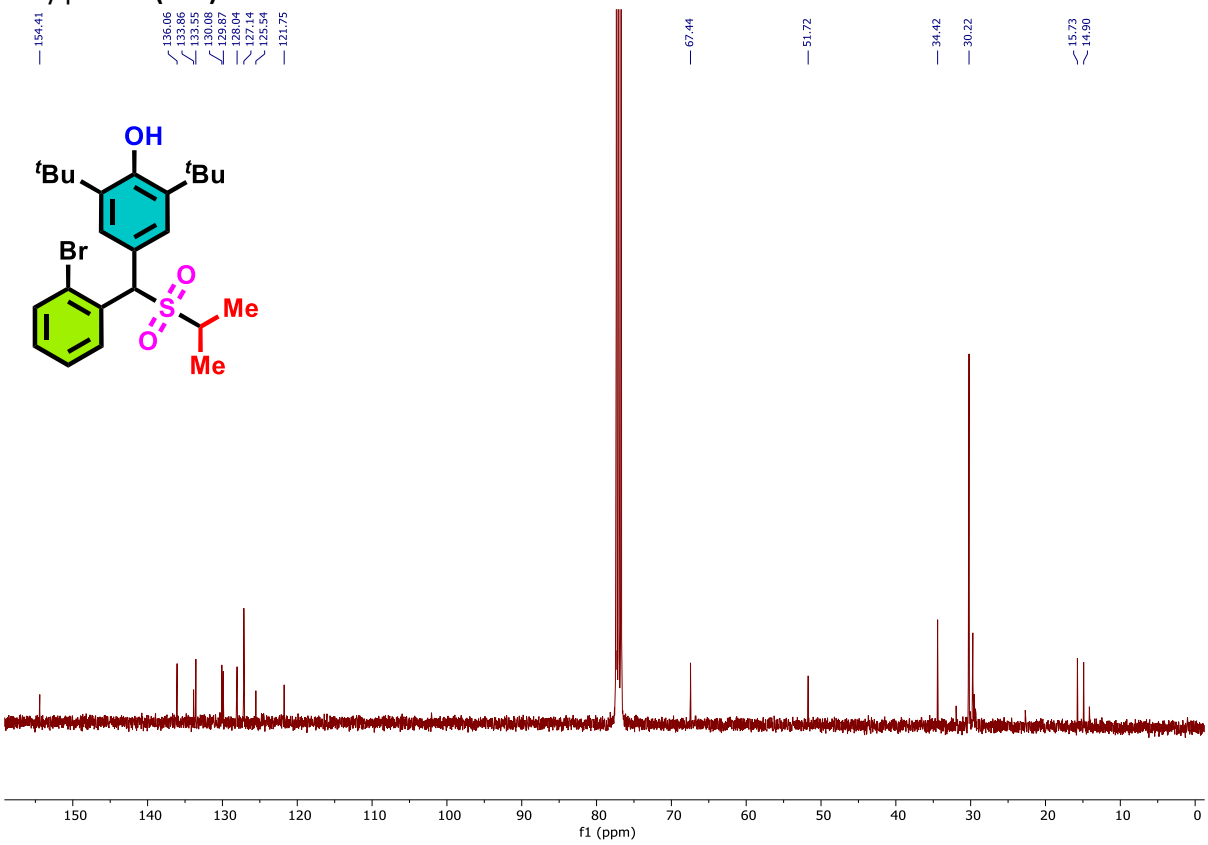
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((2-chlorophenyl)(isopropylsulfonyl)methyl)phenol **(5ma)**



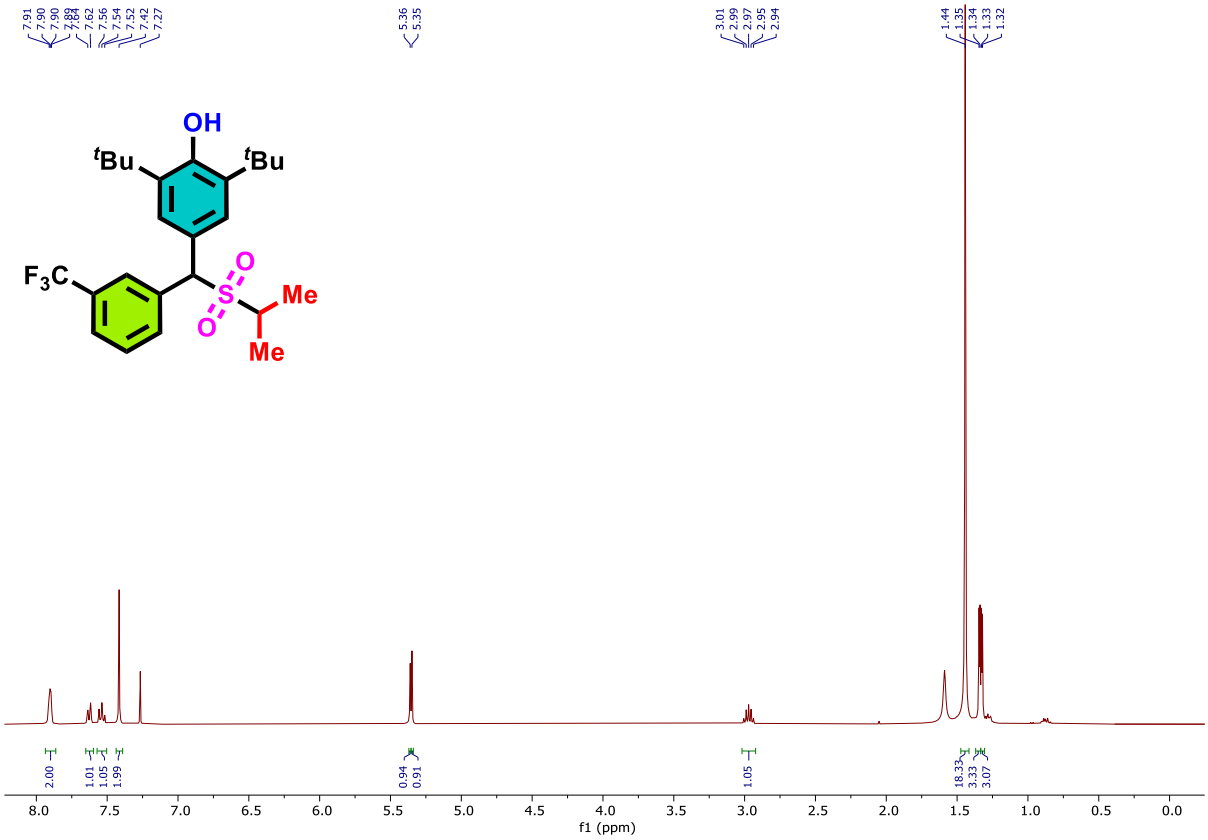
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((2-bromophenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol **(5na)**



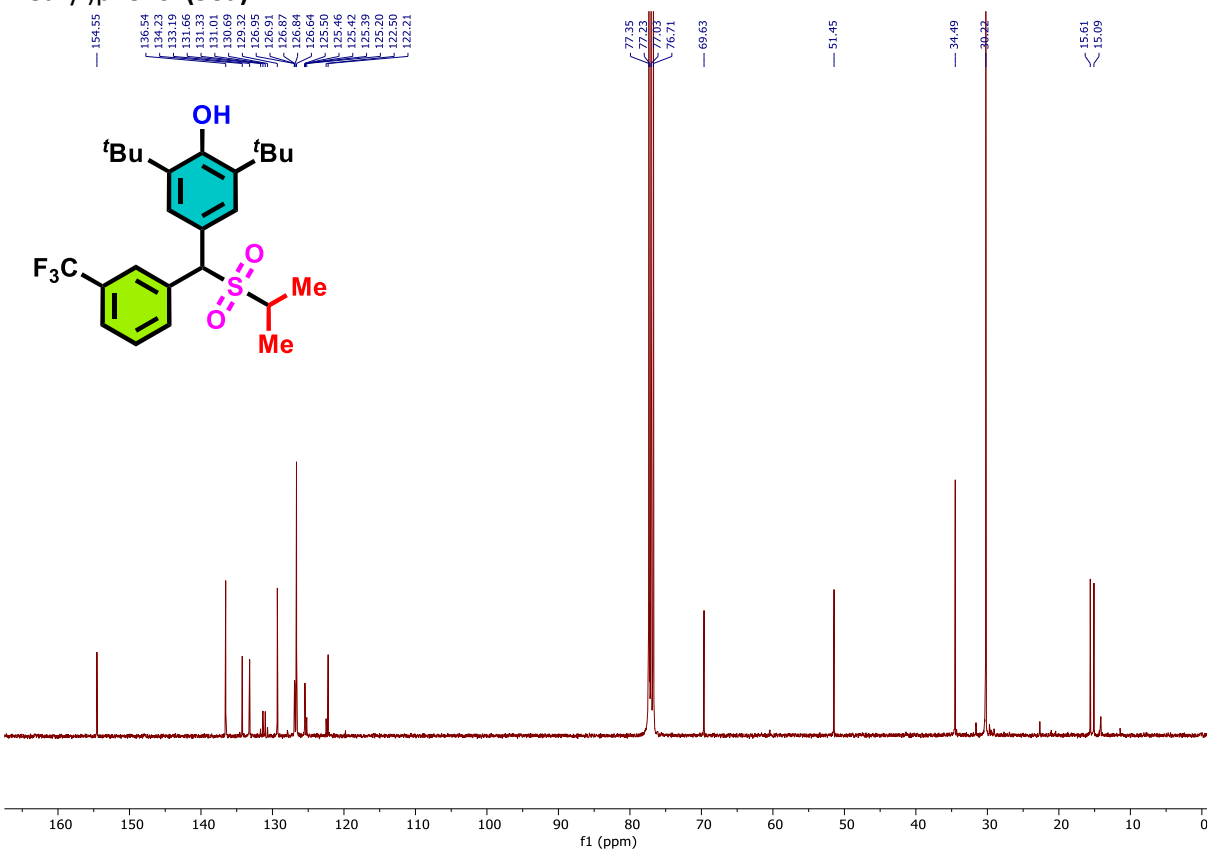
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((2-bromophenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol **(5na)**



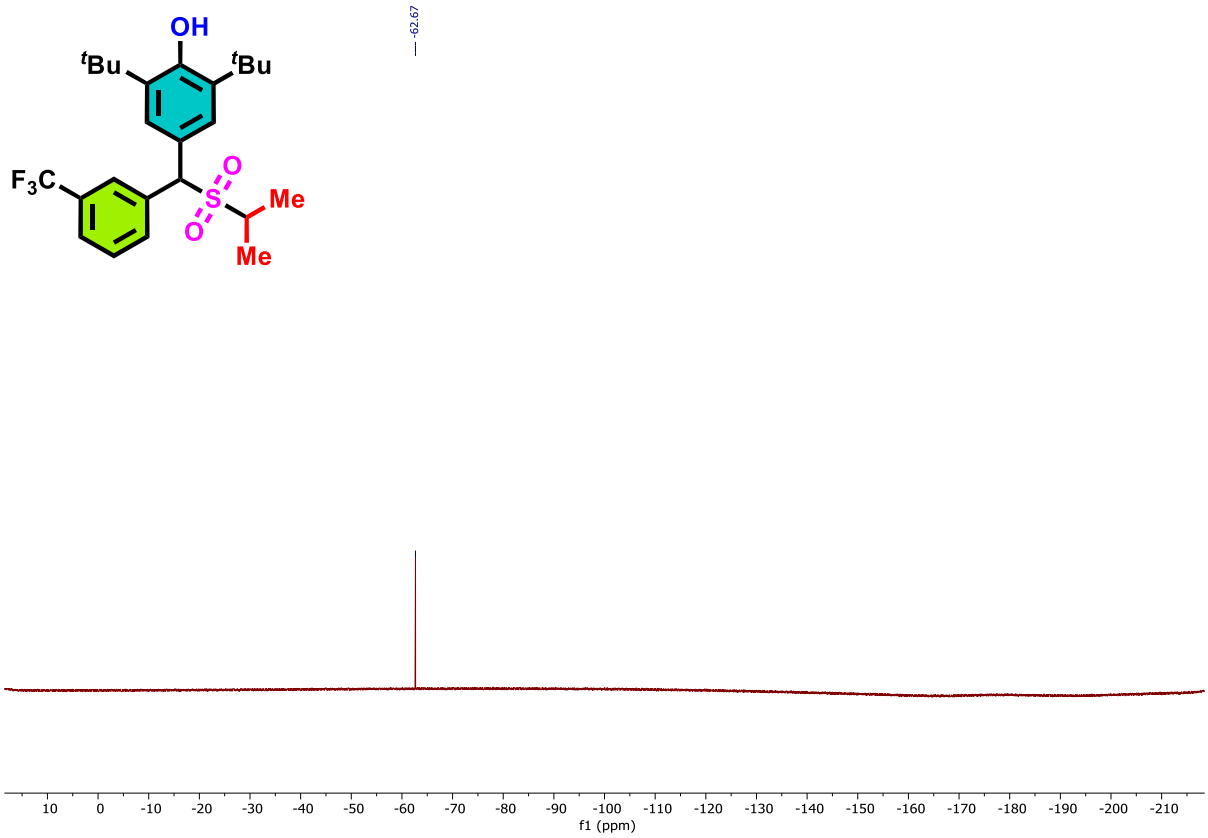
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(3-(trifluoromethyl)-phenyl)methyl)phenol **(5oa)**



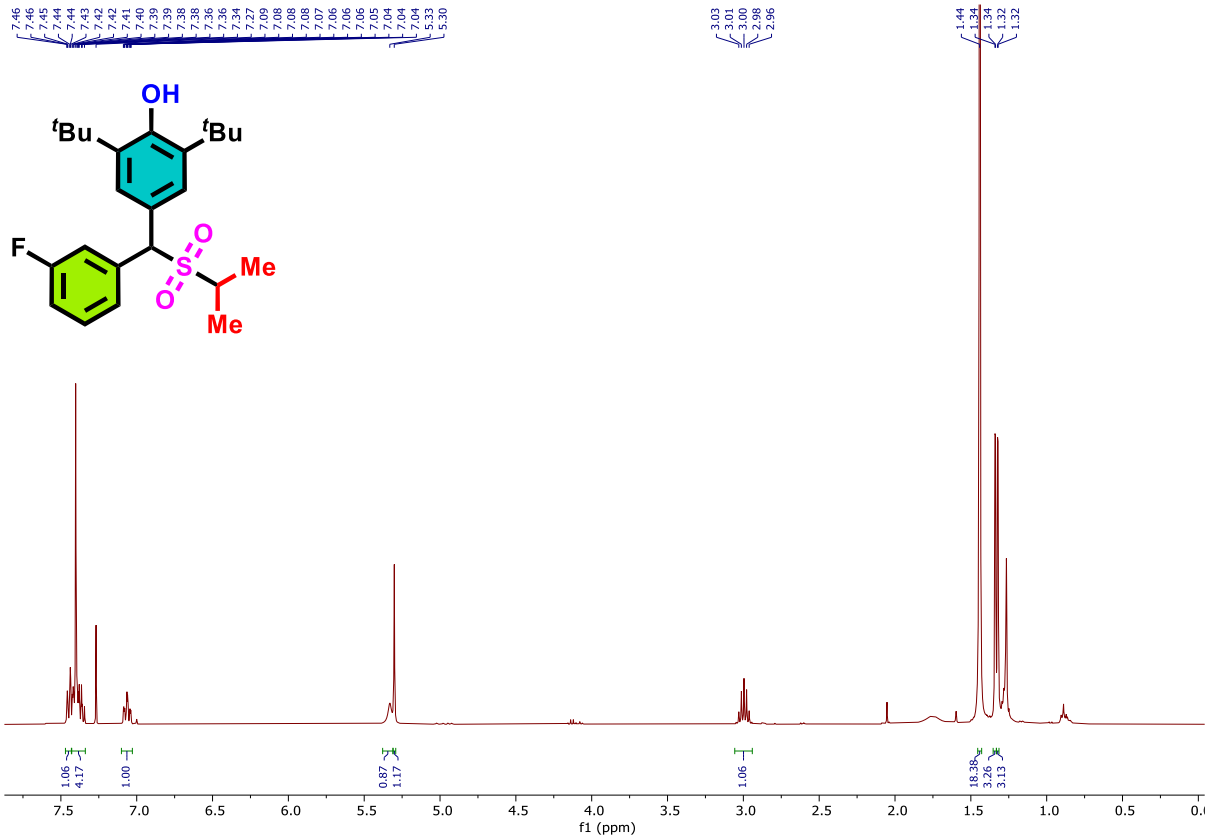
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(3-(trifluoromethyl)phenyl)-methyl)phenol **(5oa)**



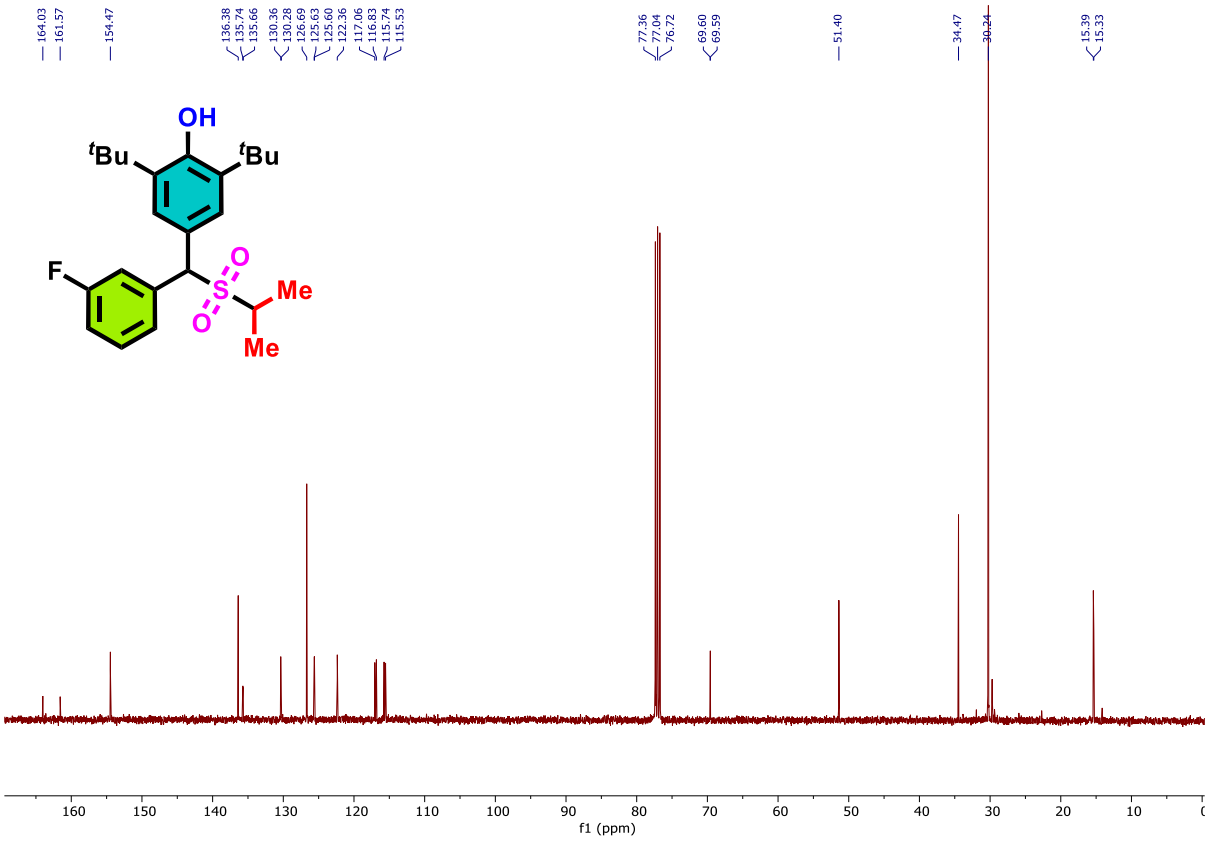
^{19}F NMR (377 MHz, $CDCl_3$) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(3-(trifluoromethyl)phenyl)-methyl)phenol **(5oa)**



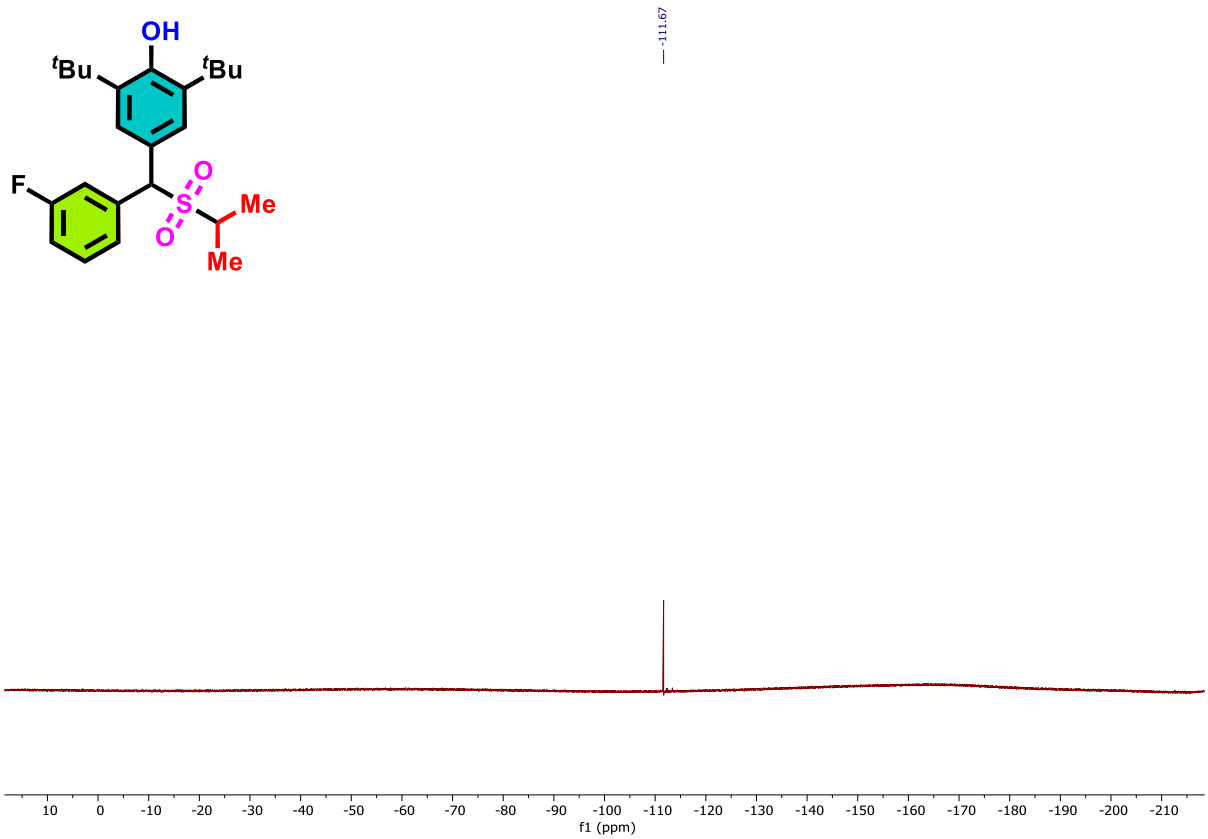
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((3-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5pa)**



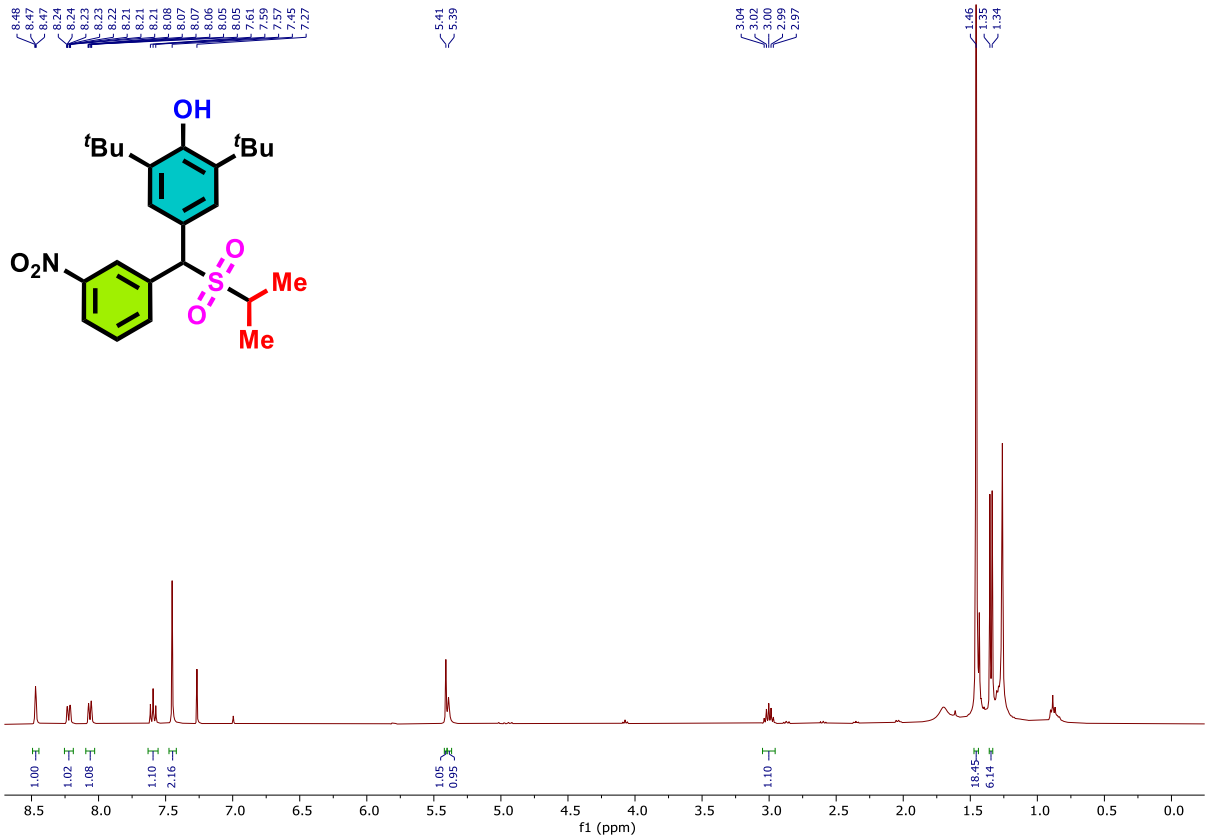
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((3-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5pa)**



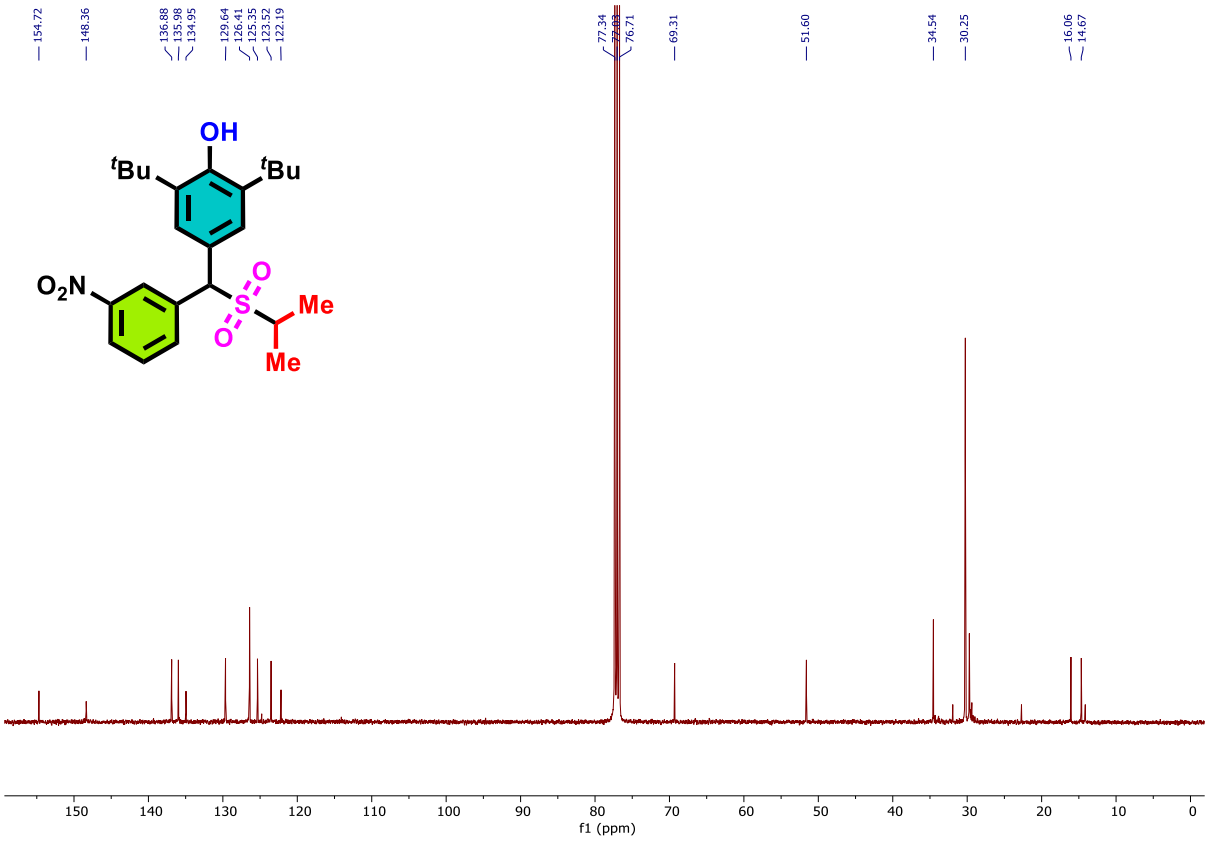
^{19}F NMR (377 MHz, $CDCl_3$) of 2,6-di-tert-butyl-4-((3-fluorophenyl)(isopropylsulfonyl)methyl)phenol **(5pa)**



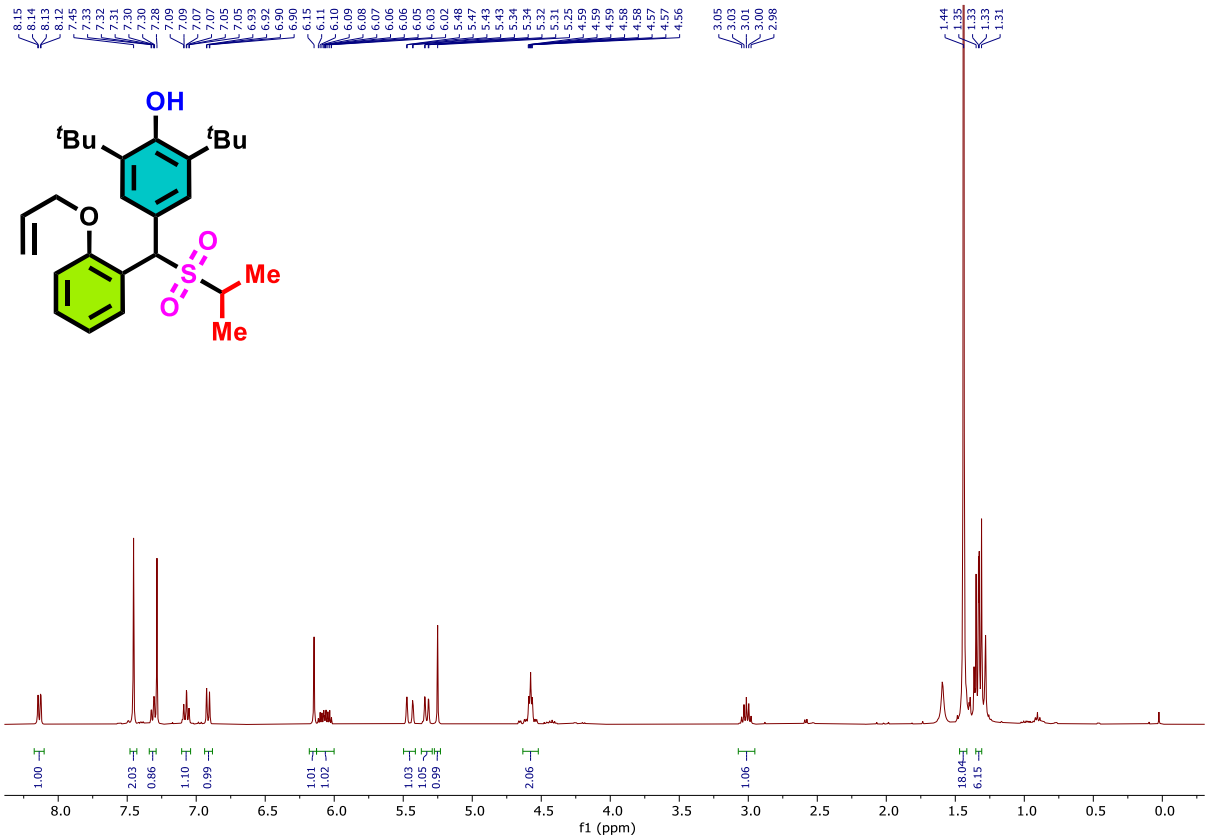
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(3-nitrophenyl)methyl)phenol **(5qa)**



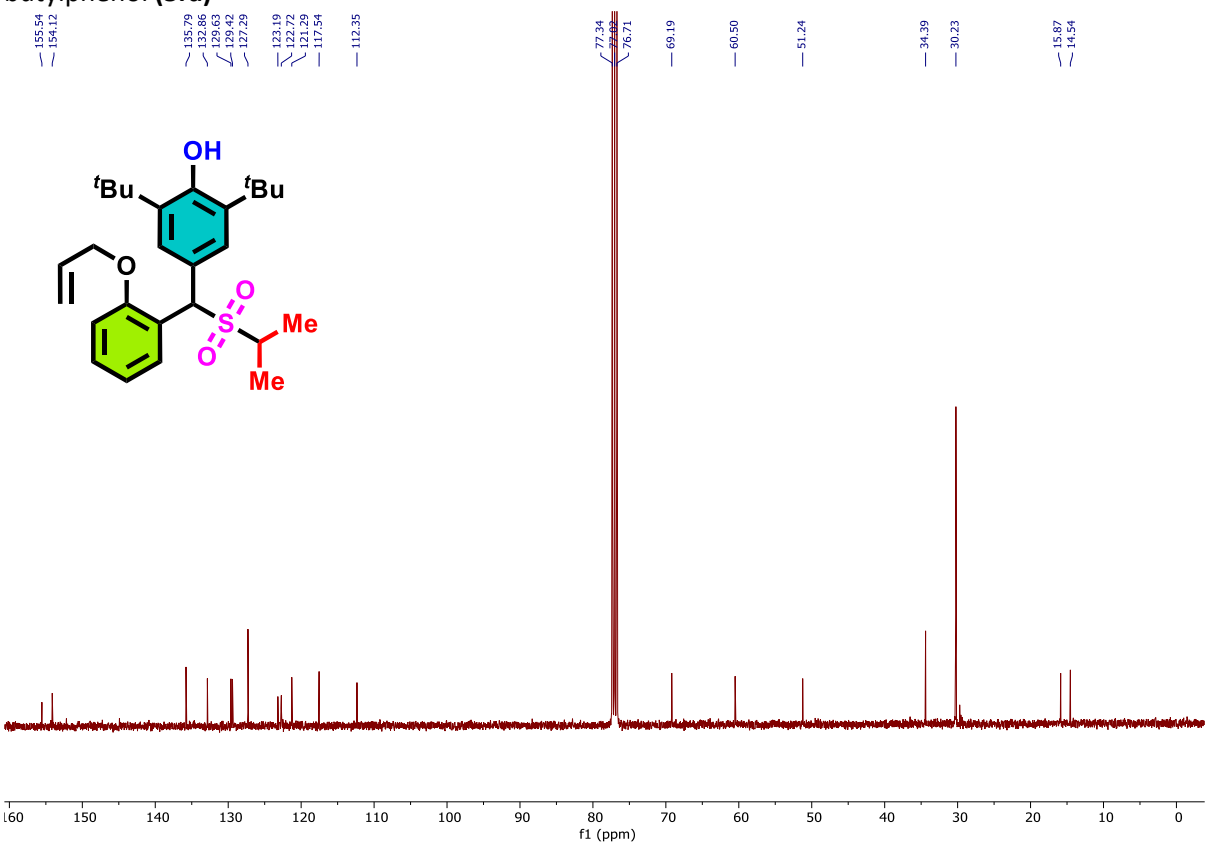
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(3-nitrophenyl)methyl)phenol **(5qa)**



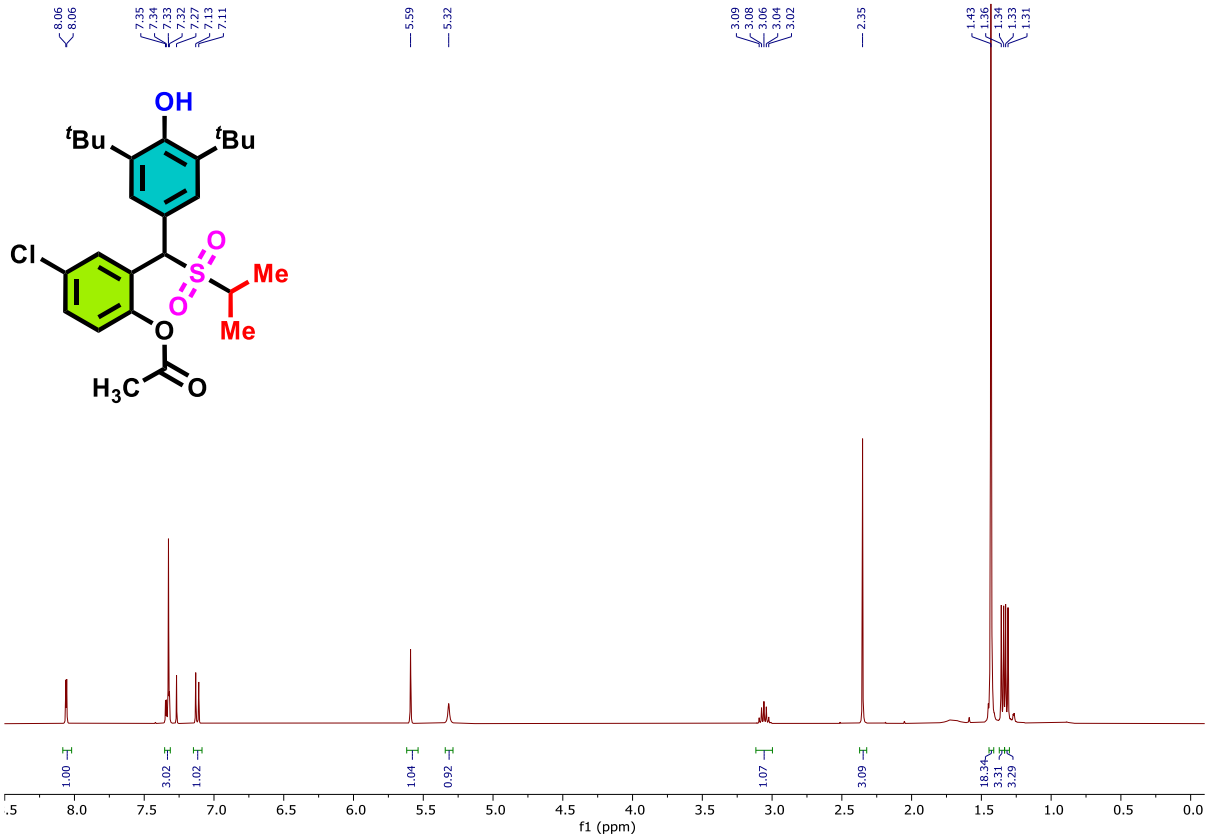
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((2-(allyloxy)phenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol **(5ra)**



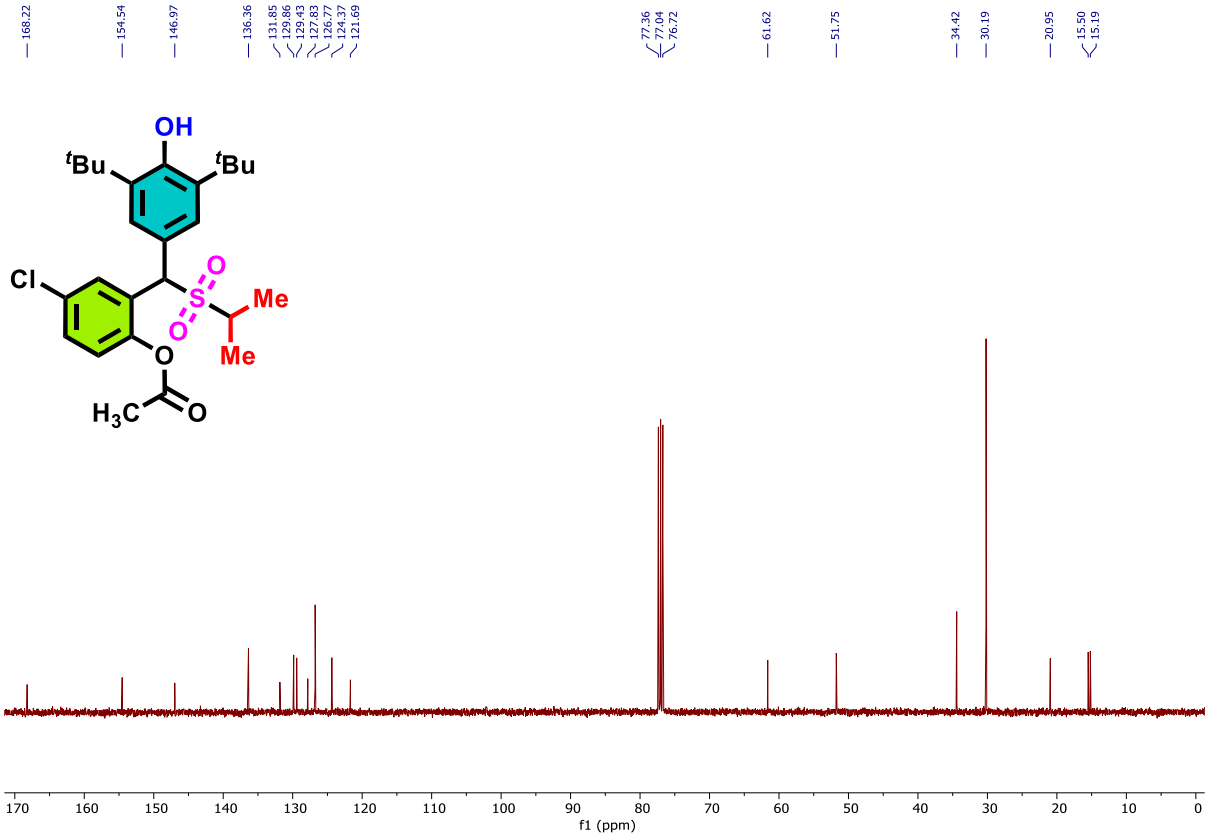
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((2-(allyloxy)phenyl)(isopropylsulfonyl)methyl)-2,6-di-tert-butylphenol **(5ra)**



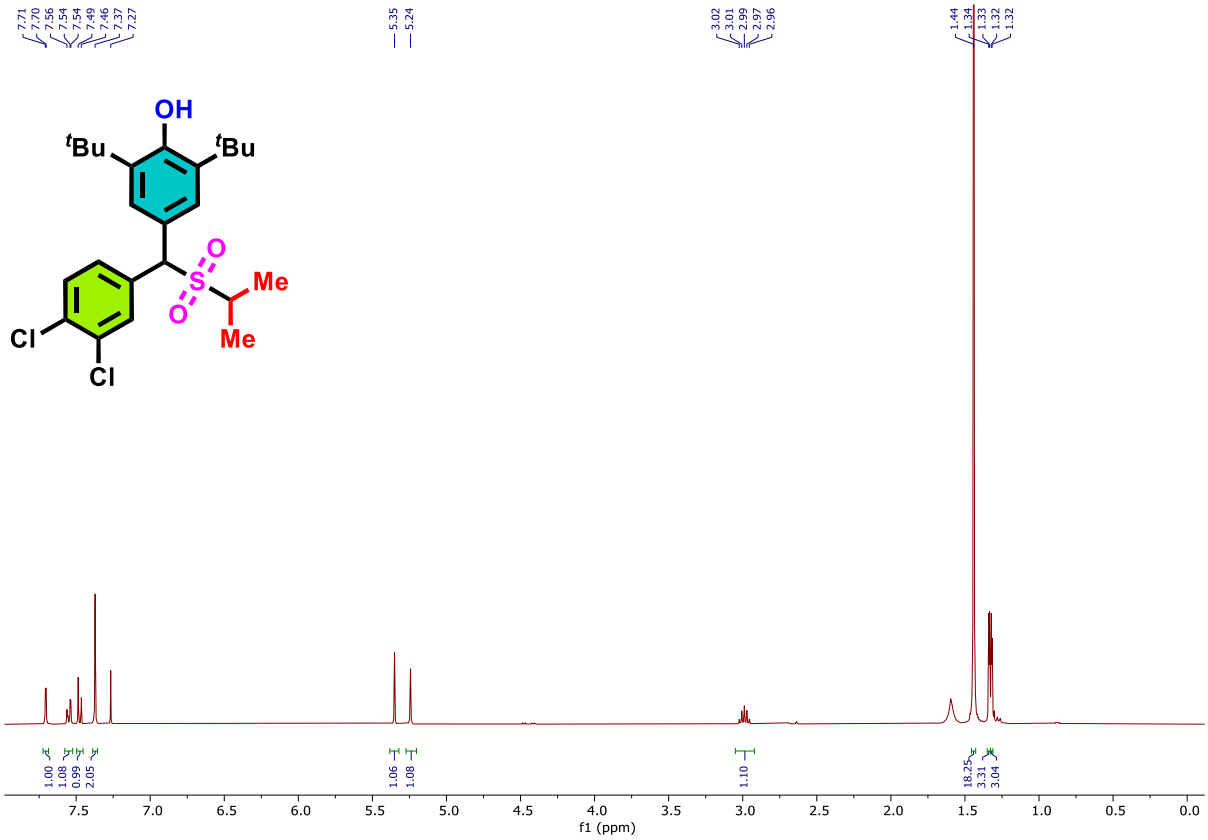
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-chloro-2-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenyl acetate **(5sa)**



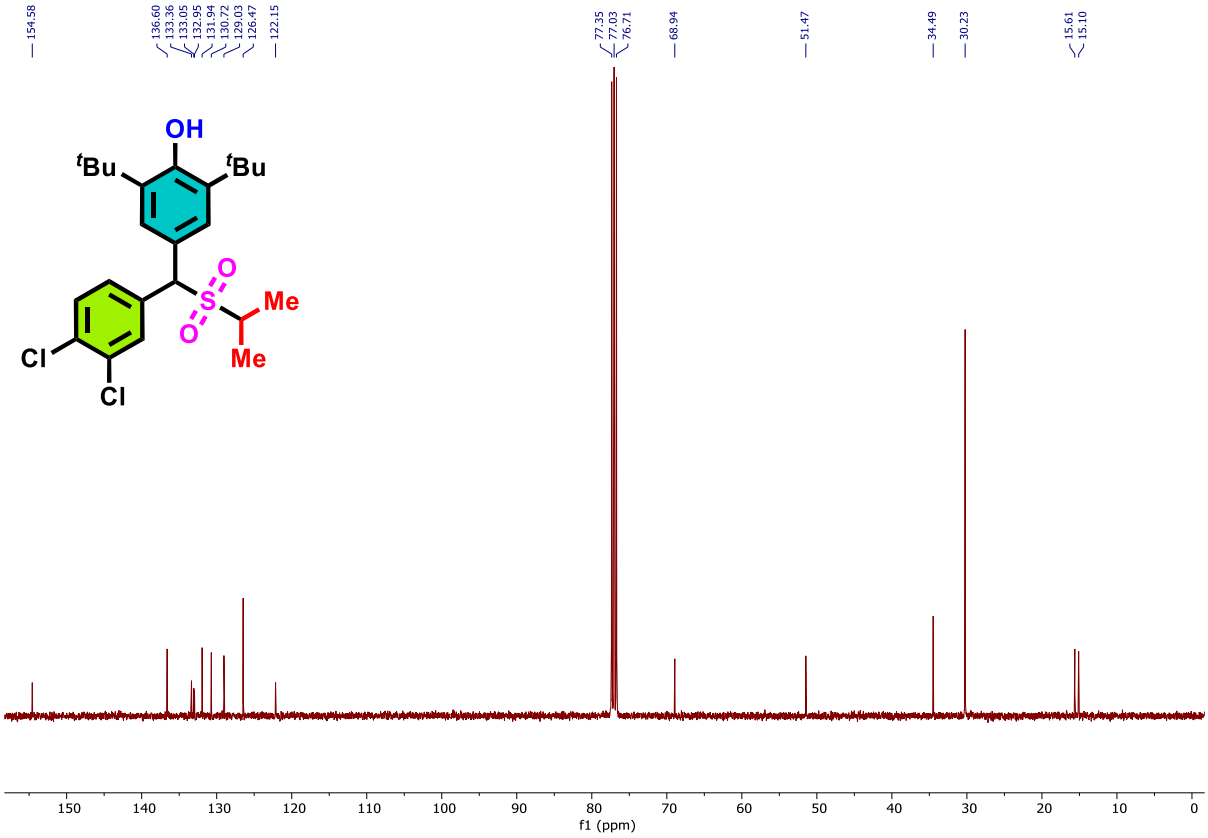
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-chloro-2-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenyl acetate **(5sa)**



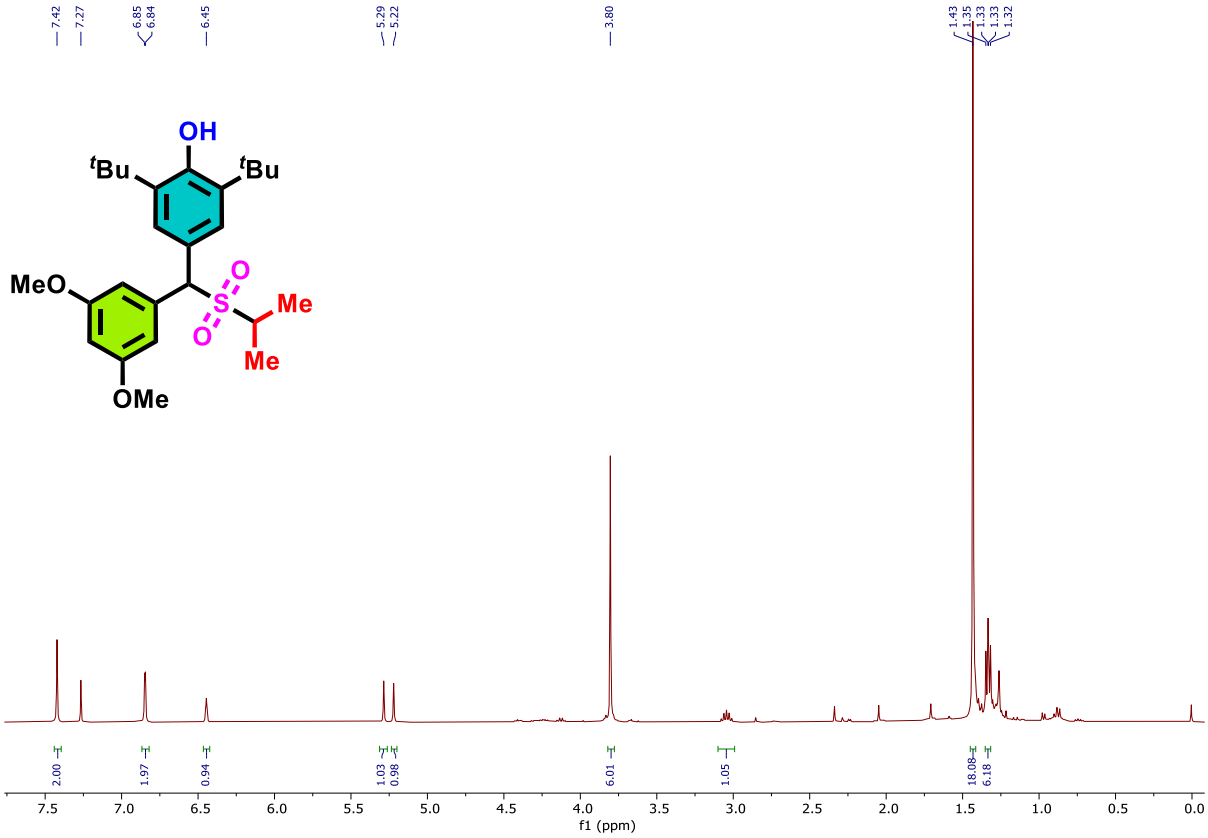
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((3,4-dichlorophenyl)(isopropylsulfonyl)methyl)phenol **(5ta)**



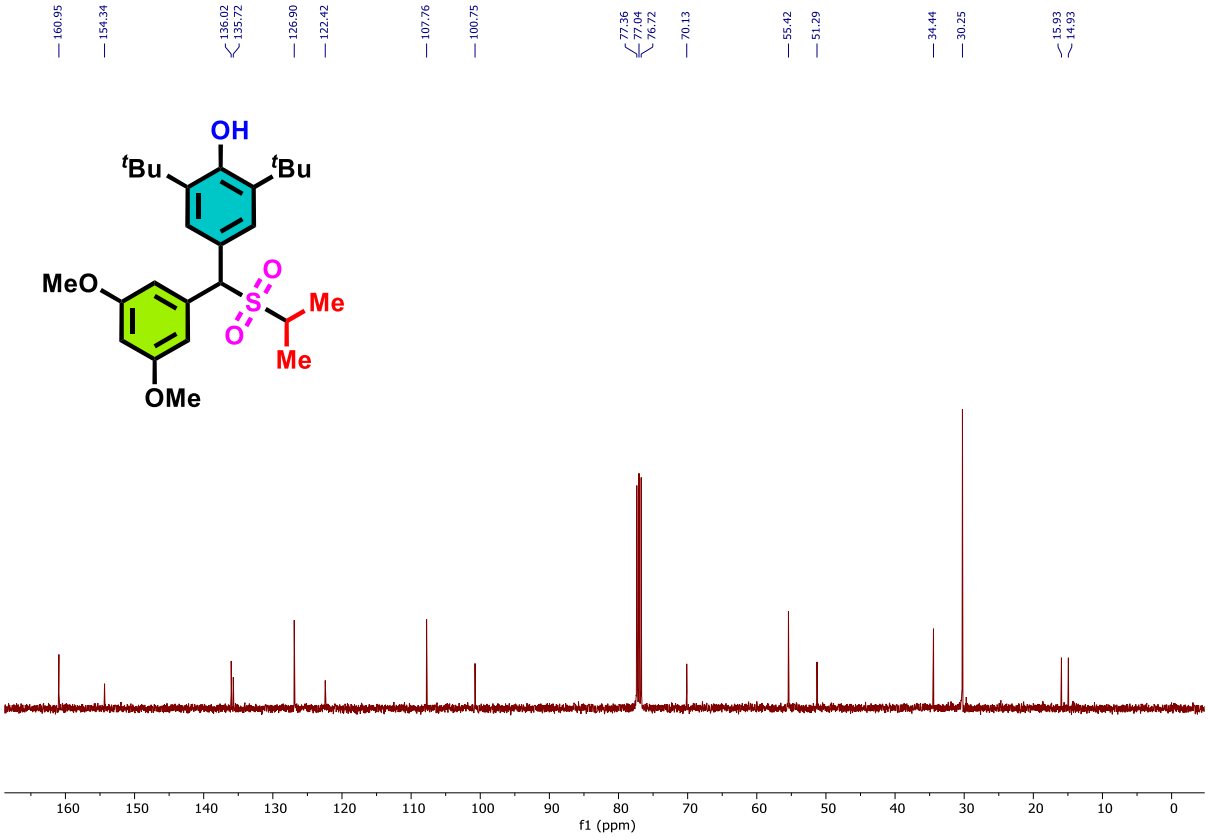
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((3,4-dichlorophenyl)(isopropylsulfonyl)methyl)phenol **(5ta)**



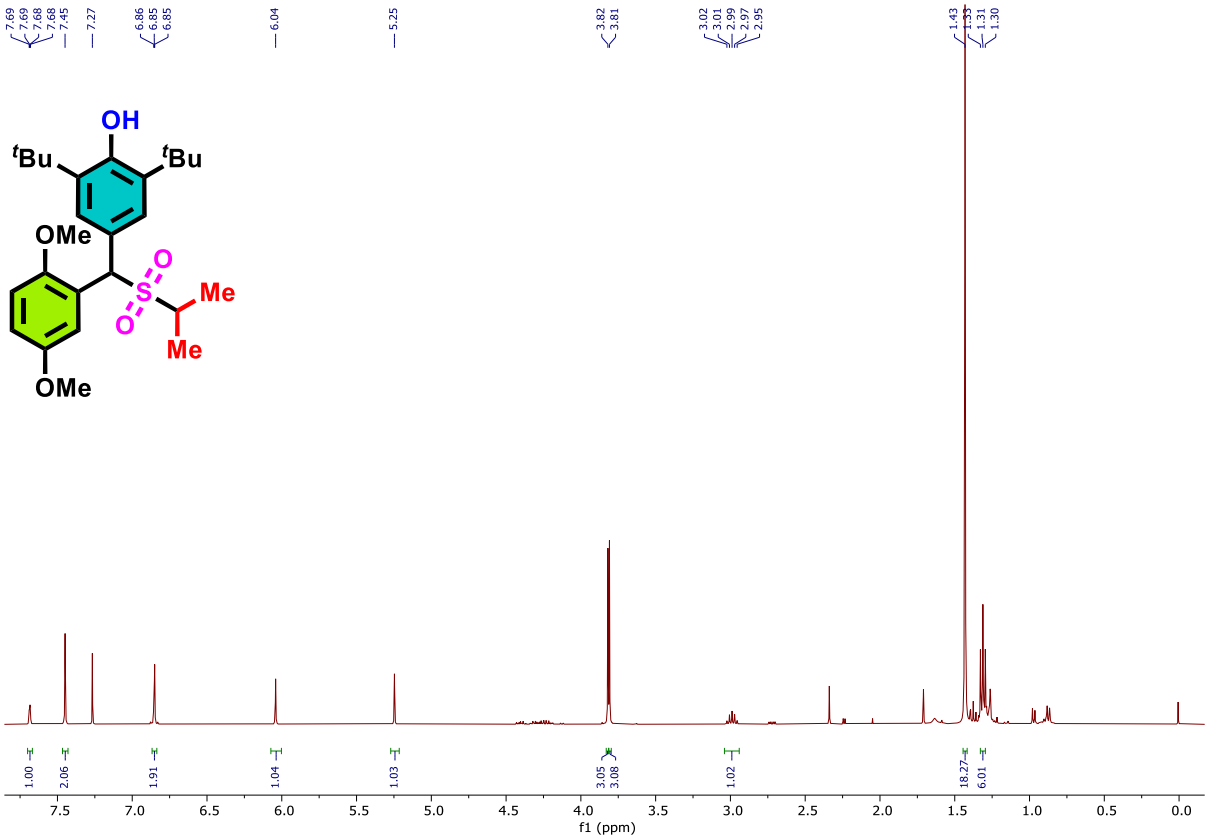
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((3,5-dimethoxyphenyl)(isopropylsulfonyl)methyl)phenol **(5ua)**



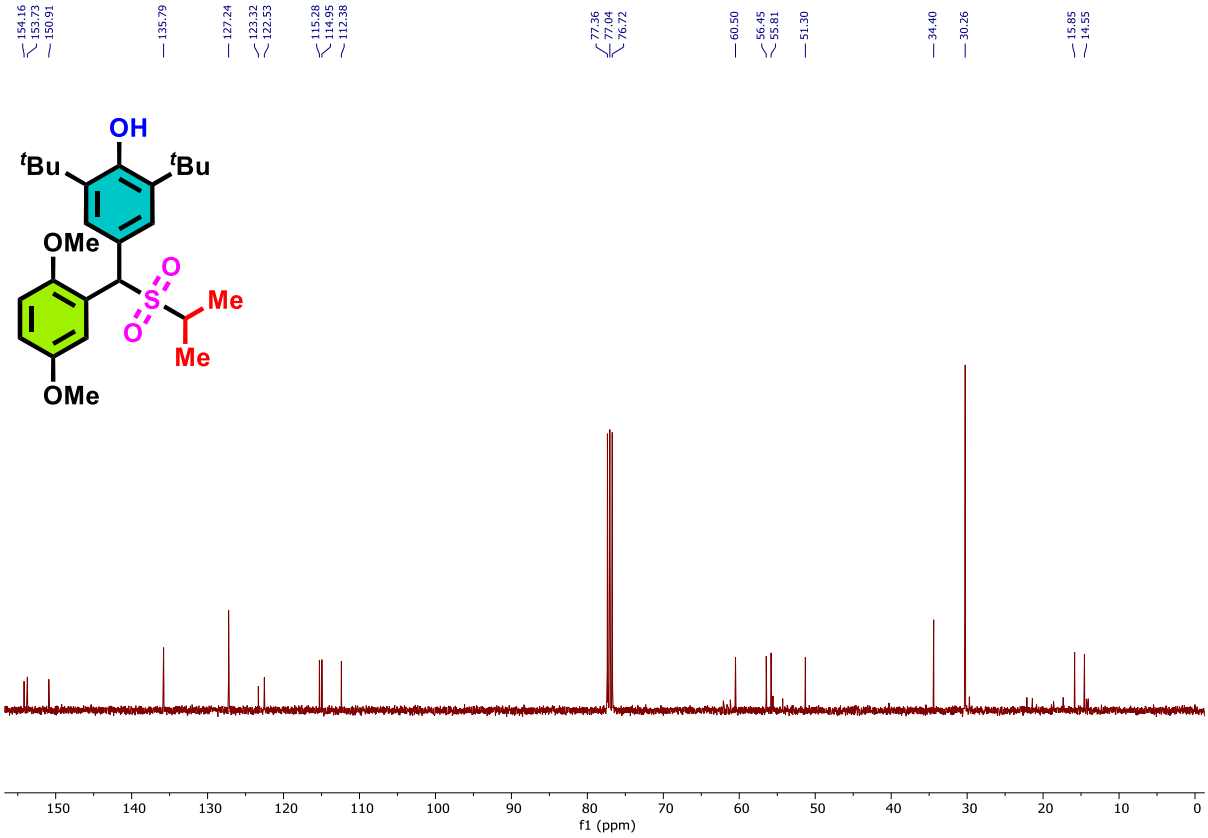
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((3,5-dimethoxyphenyl)(isopropylsulfonyl)methyl)phenol **(5ua)**



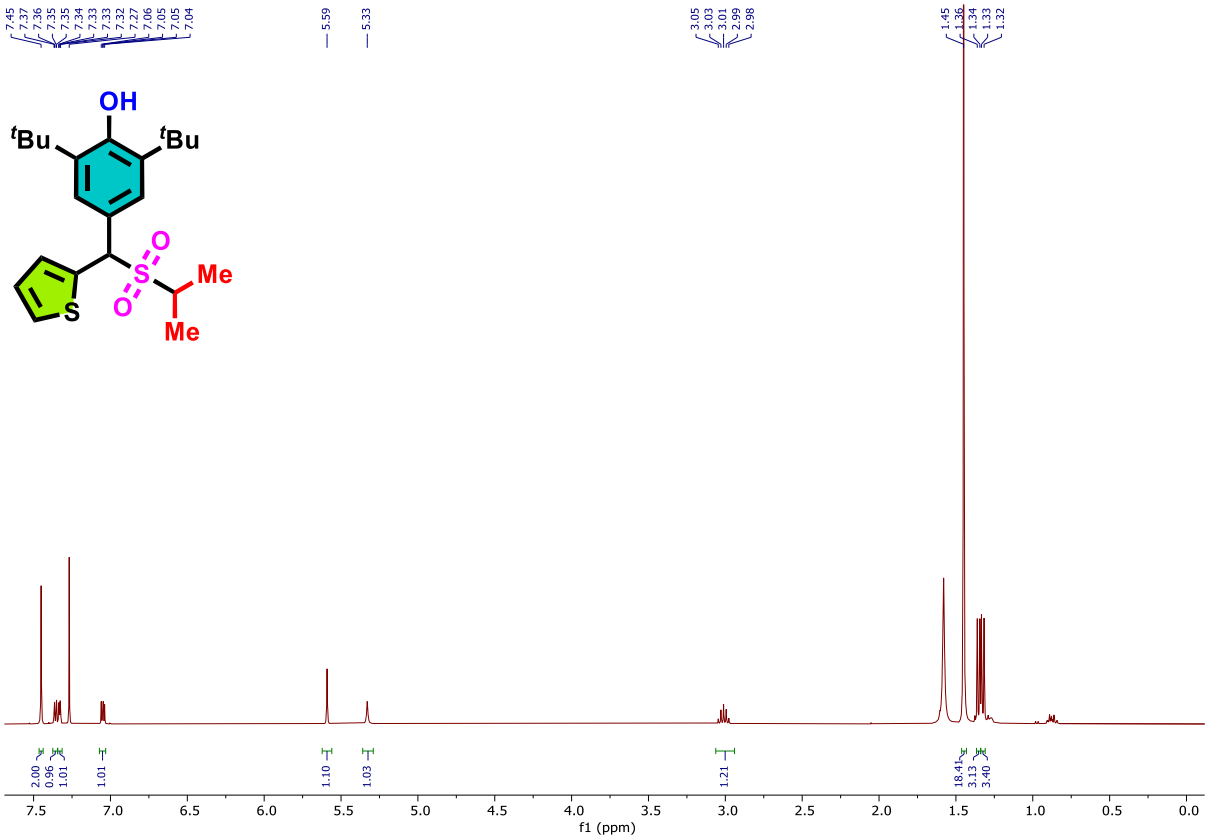
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((2,5-dimethoxyphenyl)(isopropylsulfonyl)methyl)phenol **(5va)**



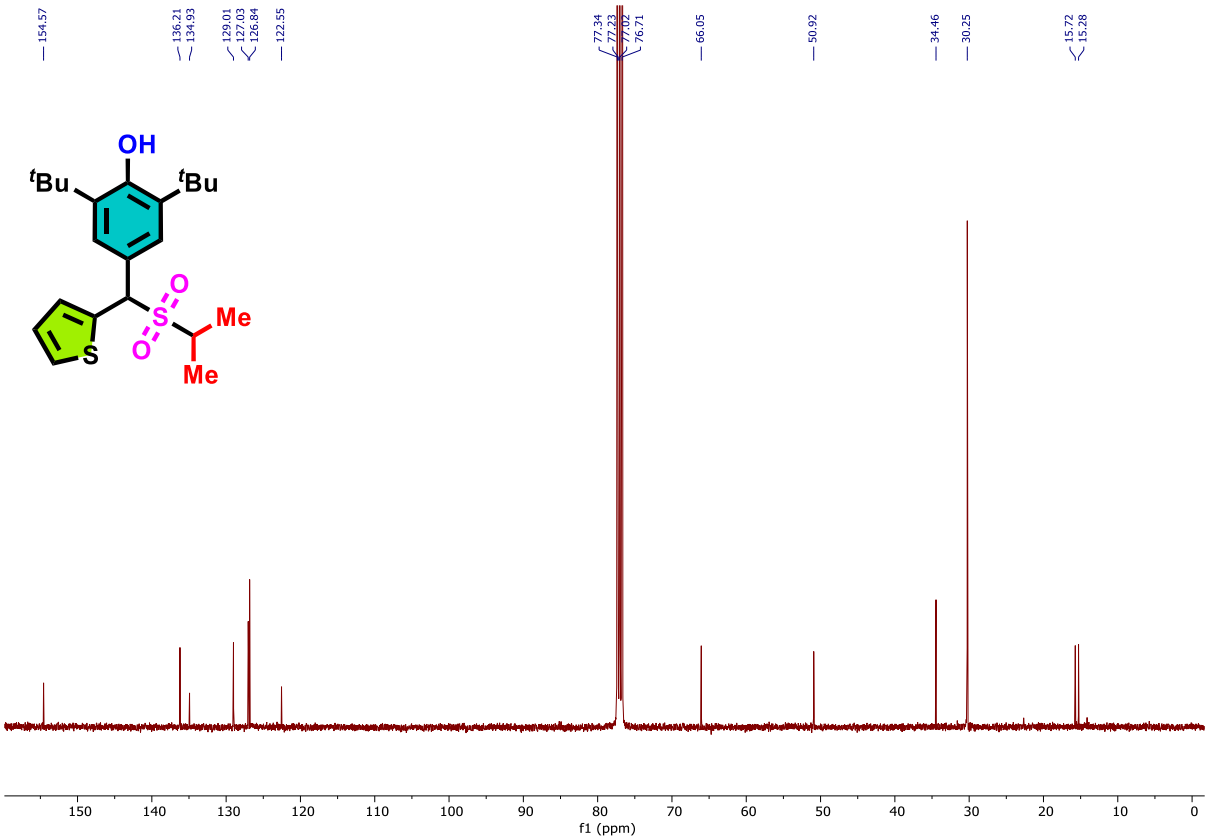
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((2,5-dimethoxyphenyl)(isopropylsulfonyl)methyl)phenol **(5va)**



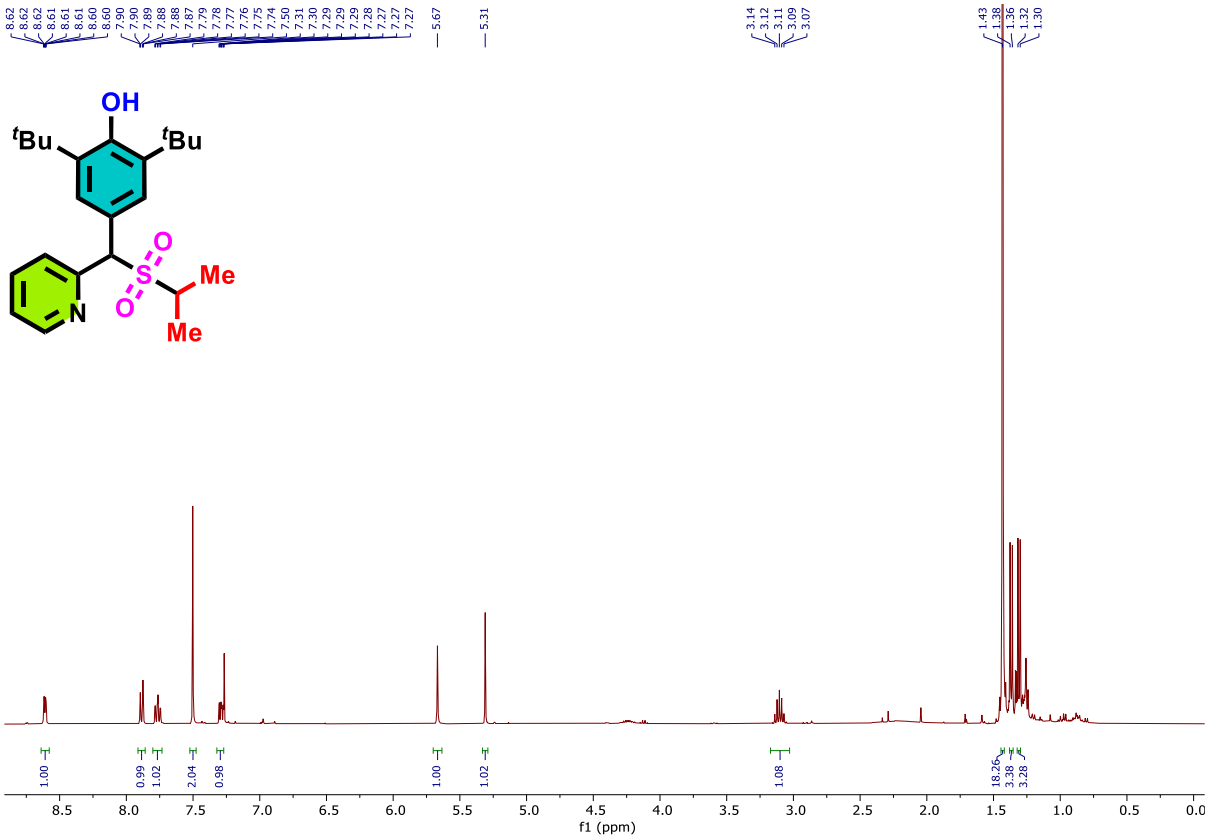
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(thiophen-2-yl)methyl)phenol **(5wa)**



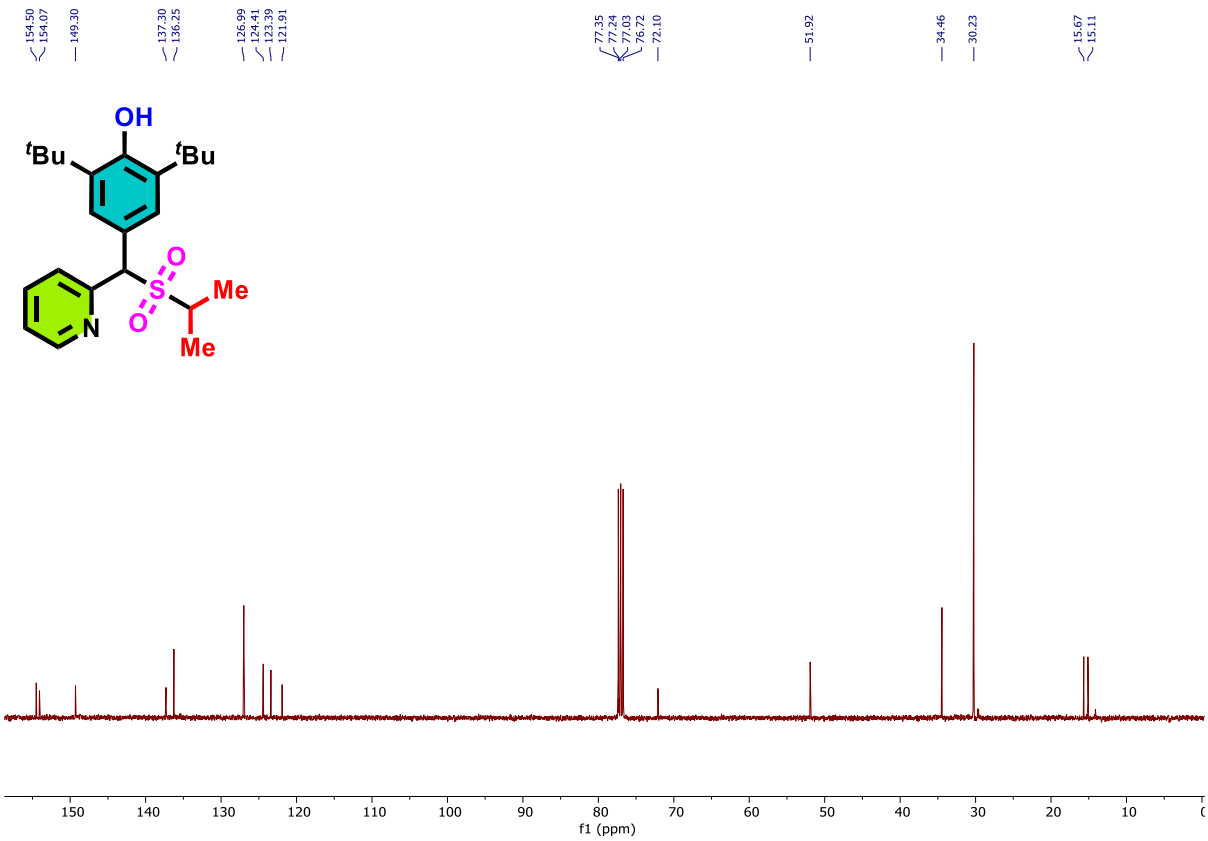
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(thiophen-2-yl)methyl)phenol **(5wa)**



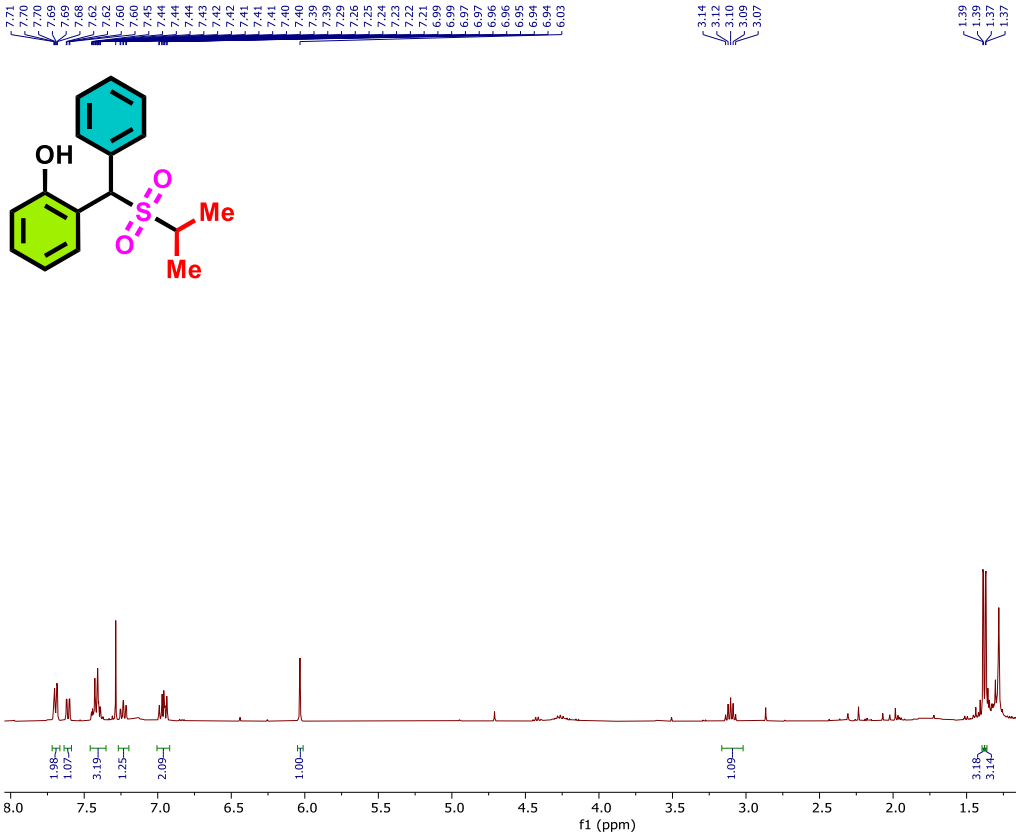
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(pyridin-2-yl)methyl)phenol **(5xa)**



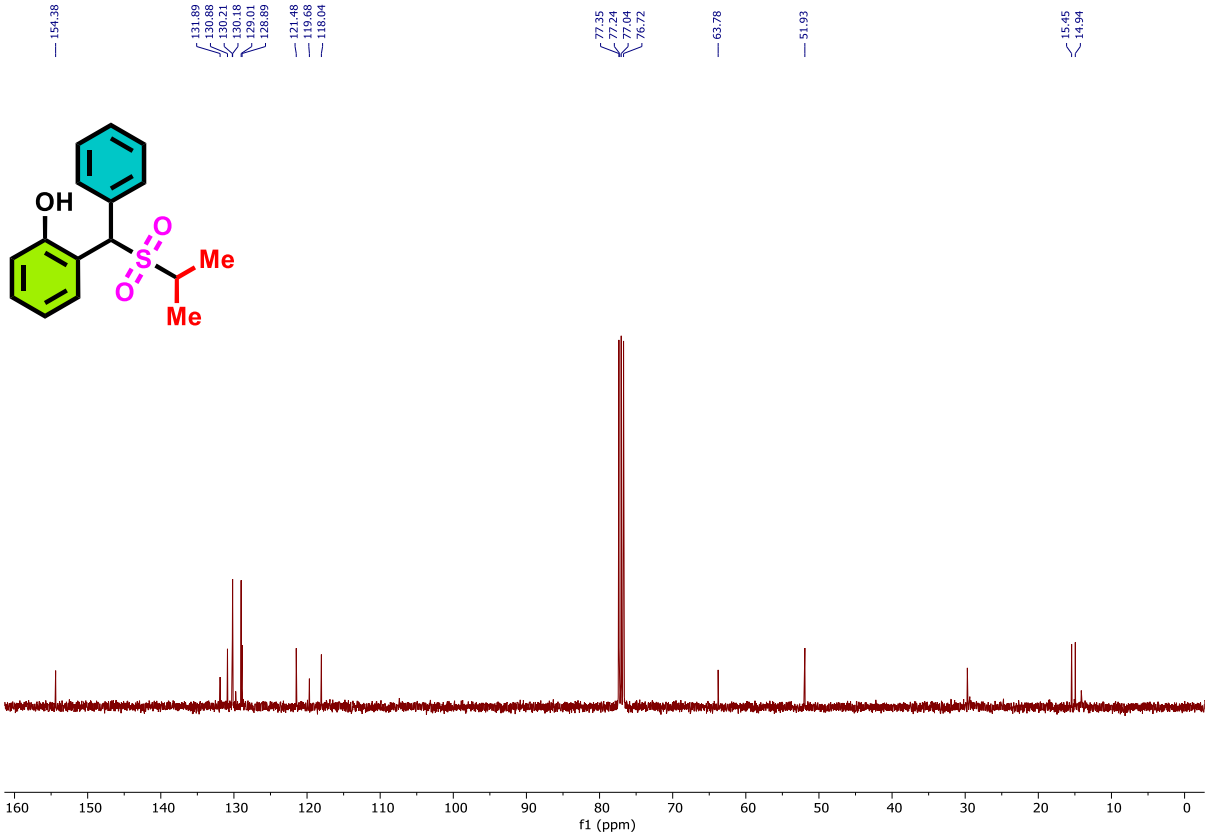
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(pyridin-2-yl)methyl)phenol **(5xa)**



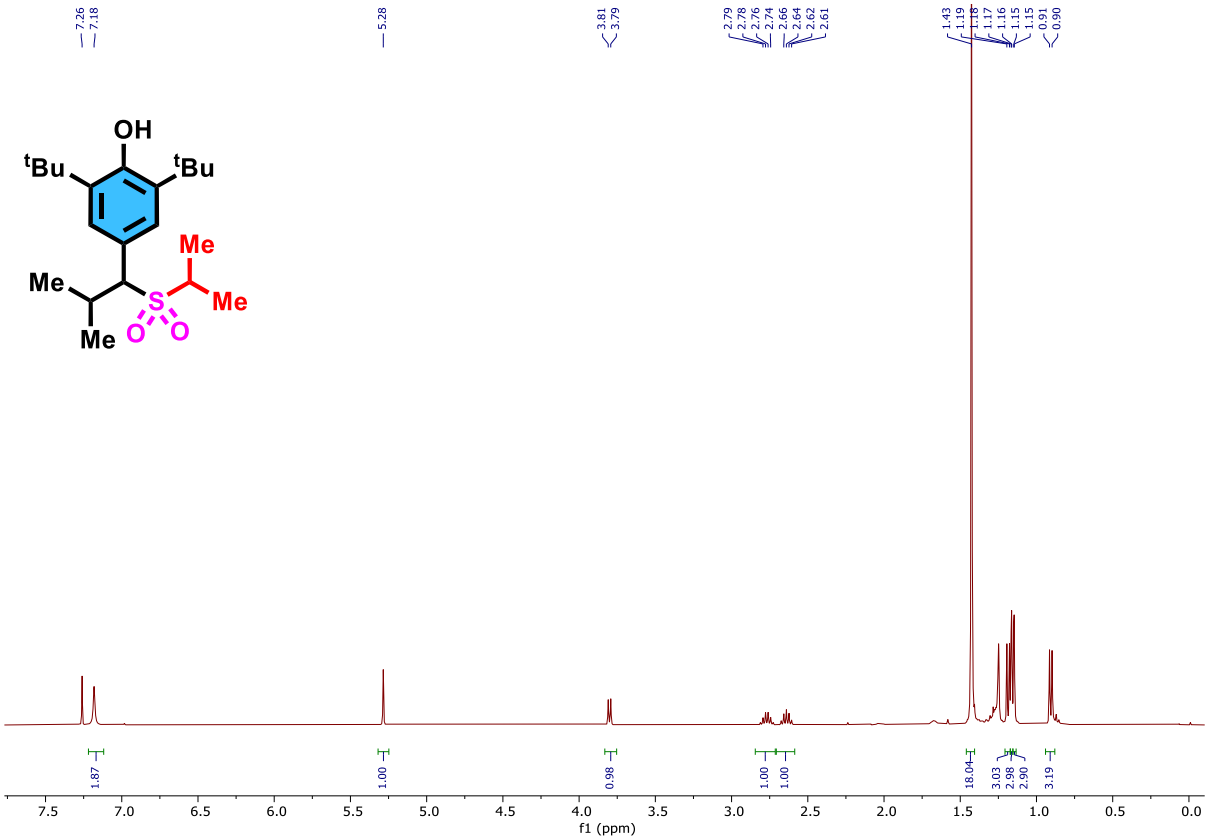
^{1}HNMR ($CDCl_3$, 400 MHz) of 2-((isopropylsulfonyl)(phenyl)methyl)phenol (**5'aa**)



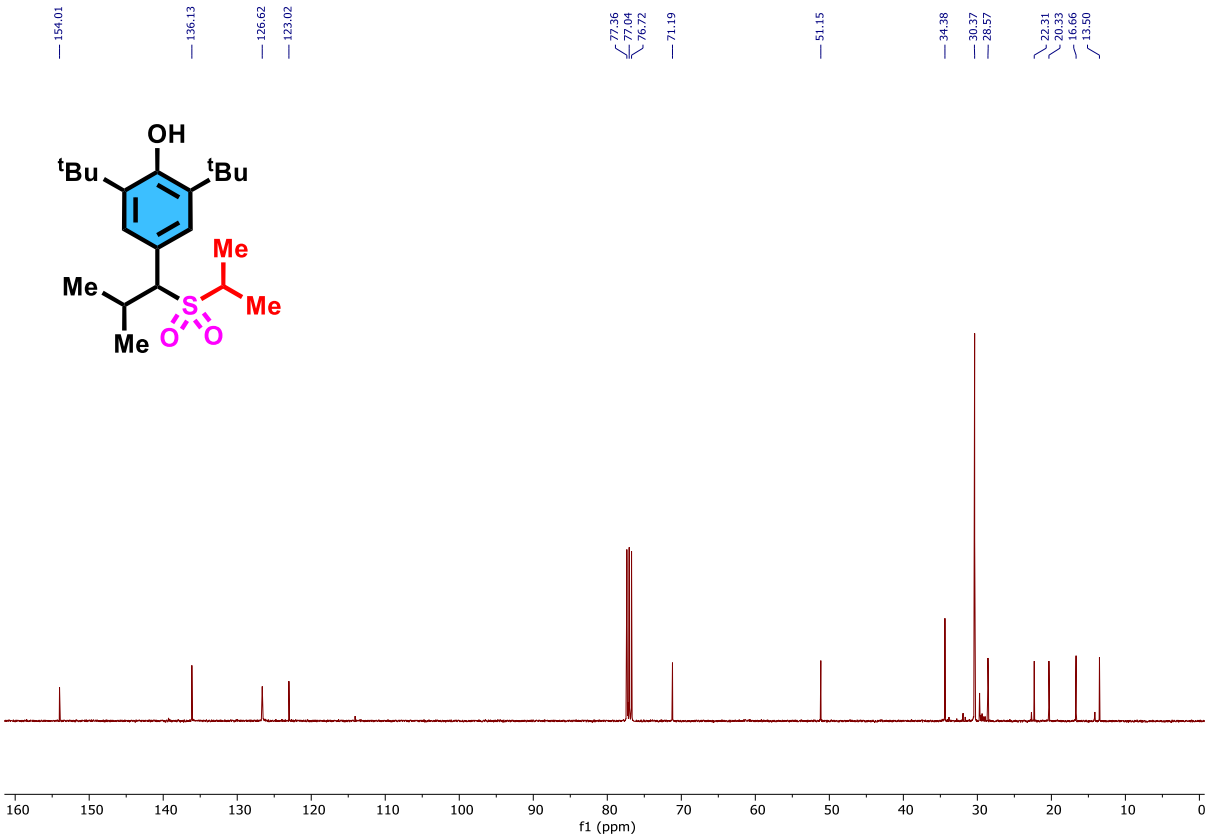
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2-((isopropylsulfonyl)(phenyl)methyl)phenol (**5'aa**)



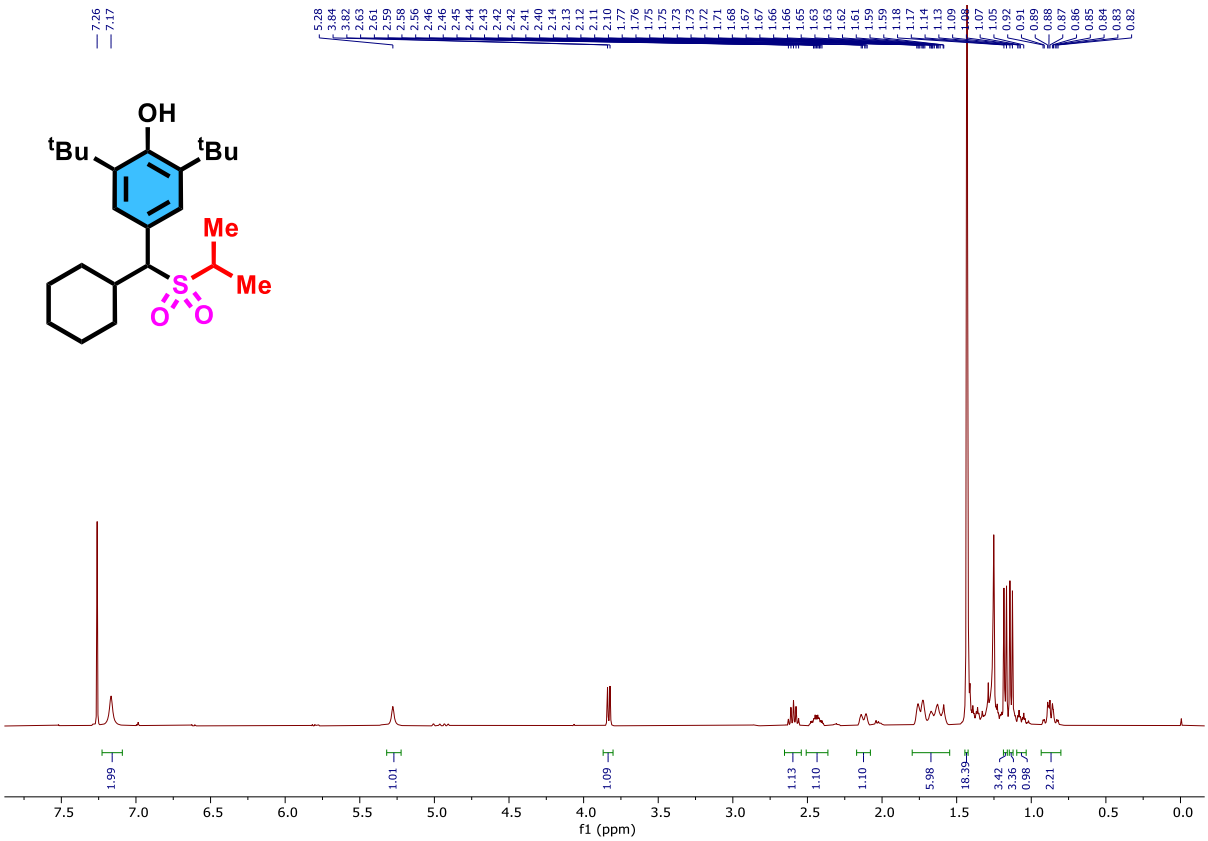
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(1-(isopropylsulfonyl)-2-methylpropyl)phenol **(5'ba)**



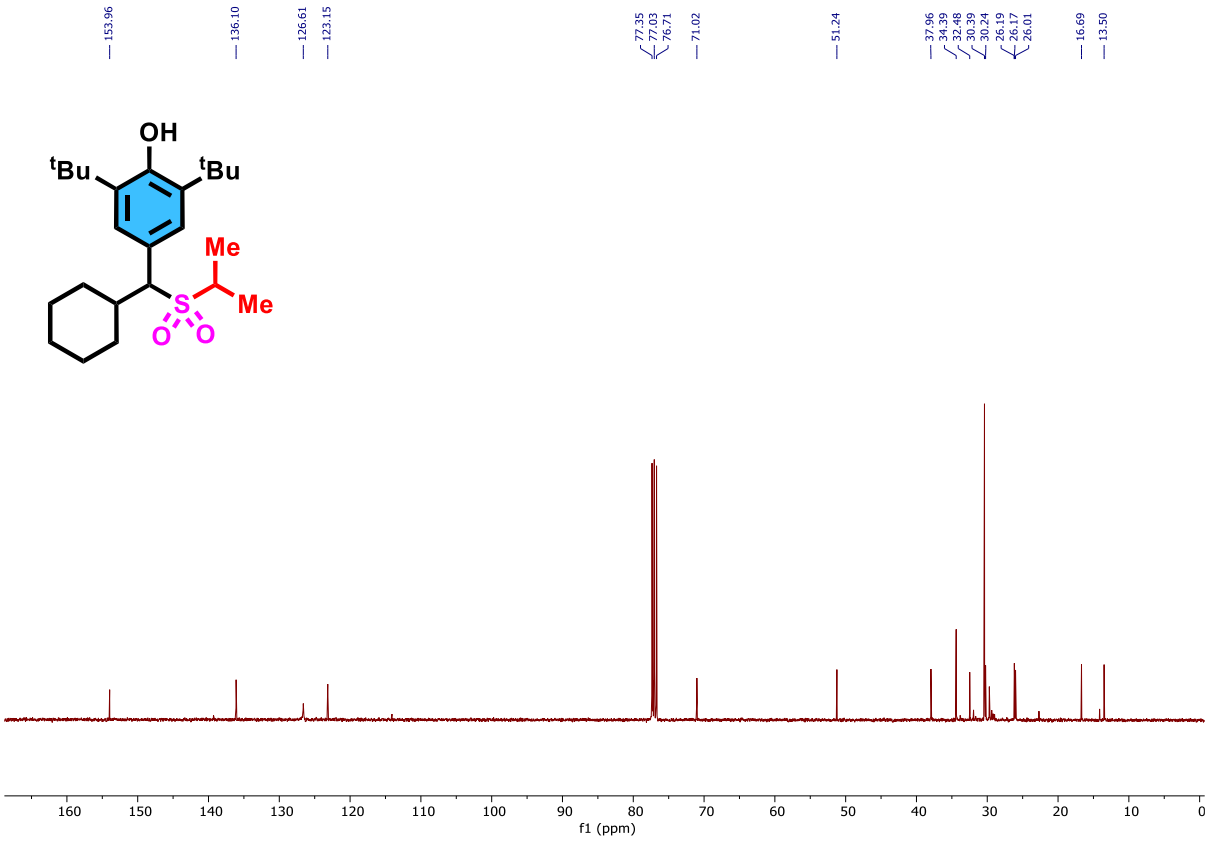
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(1-(isopropylsulfonyl)-2-methylpropyl)phenol **(5'ba)**



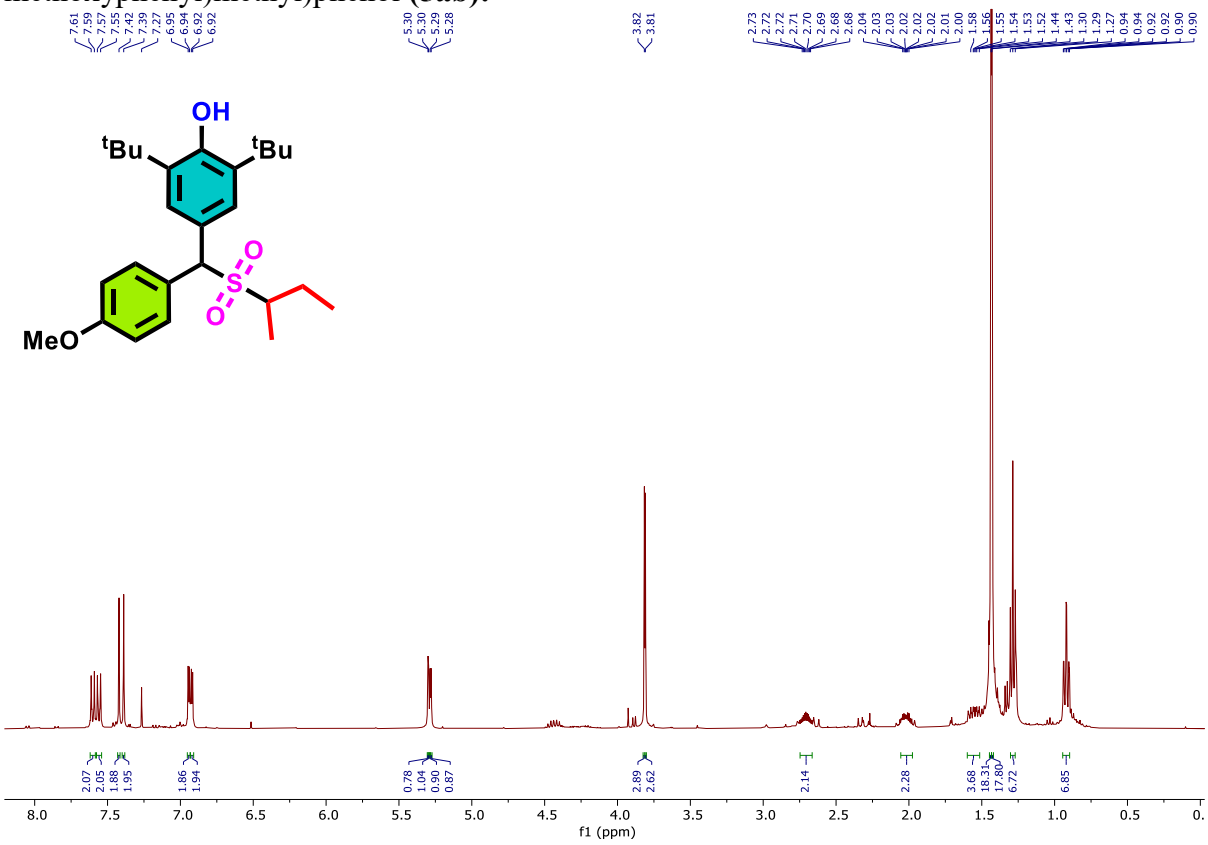
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(cyclohexyl(isopropylsulfonyl)methyl)phenol **(5'ca)**



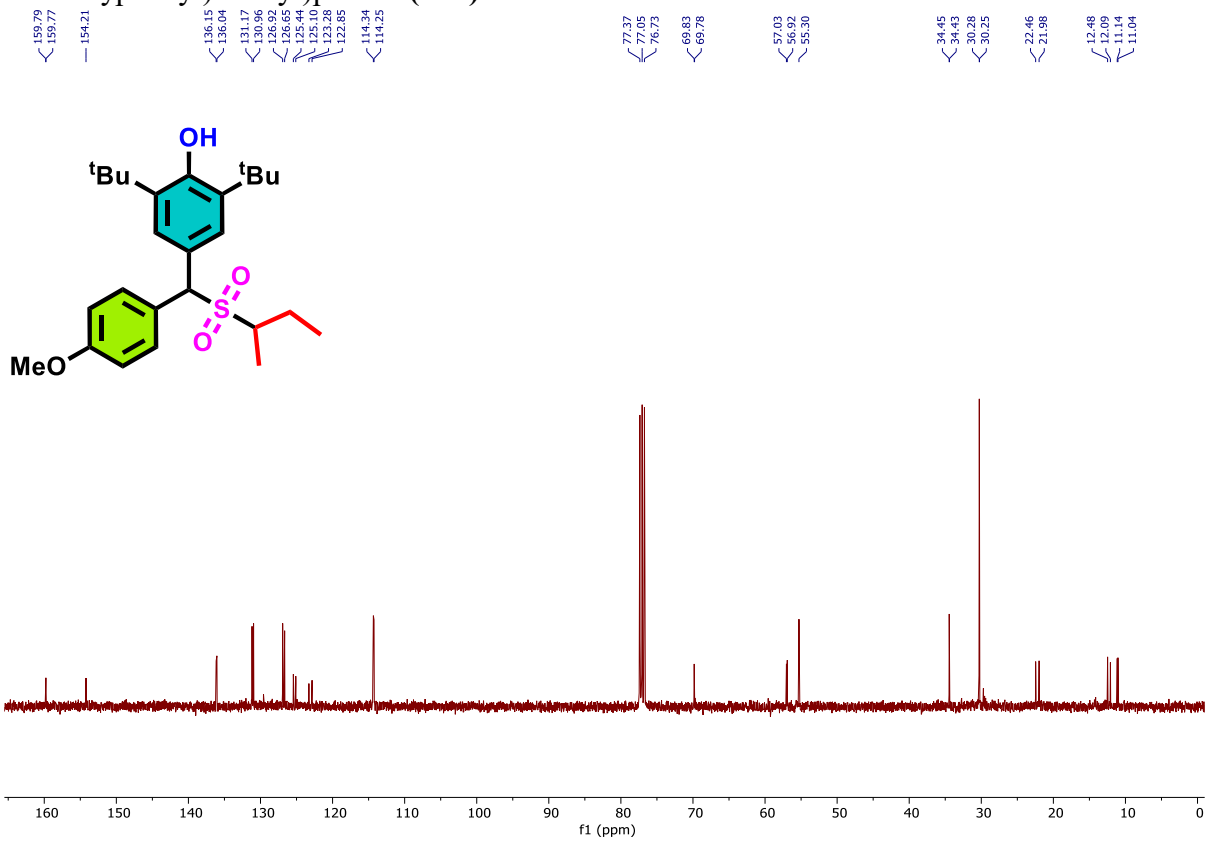
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(cyclohexyl(isopropylsulfonyl)methyl)phenol **(5'ca)**



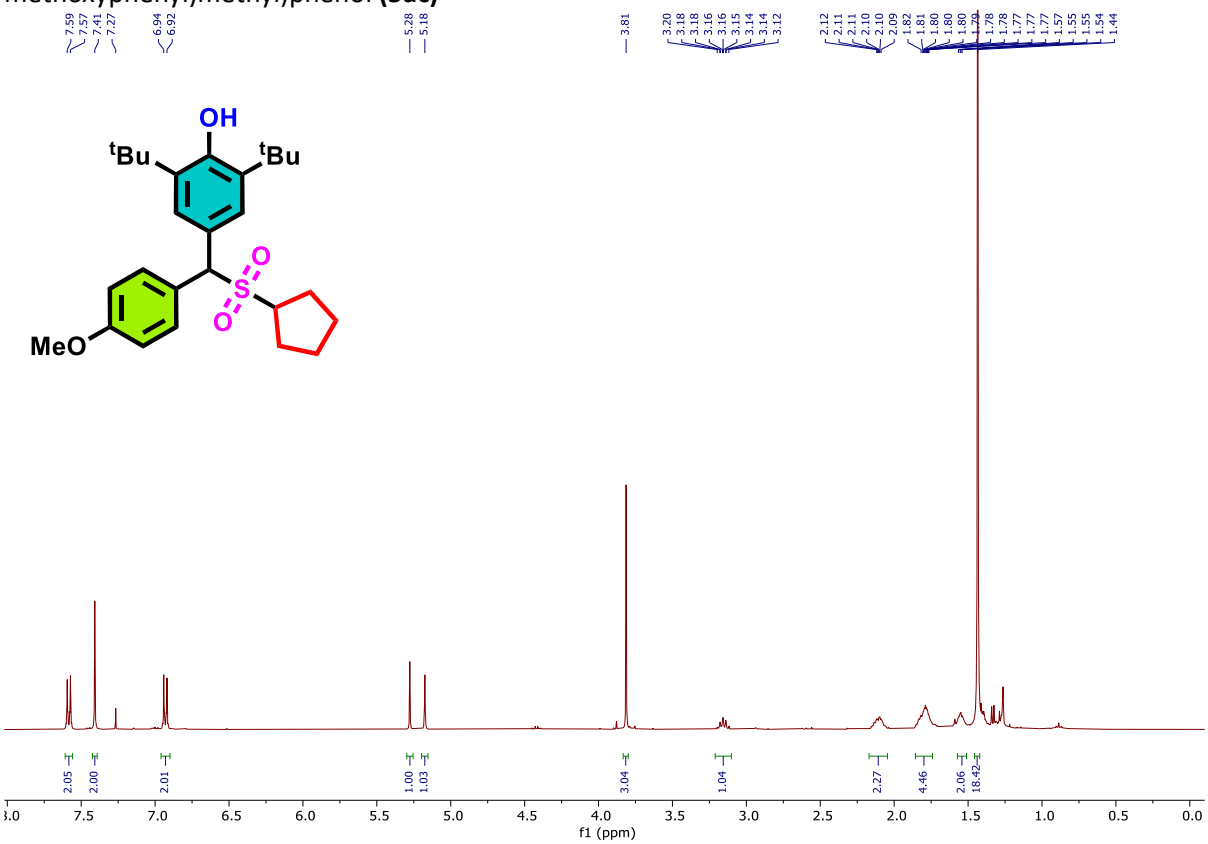
NMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((sec-butylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ab):**



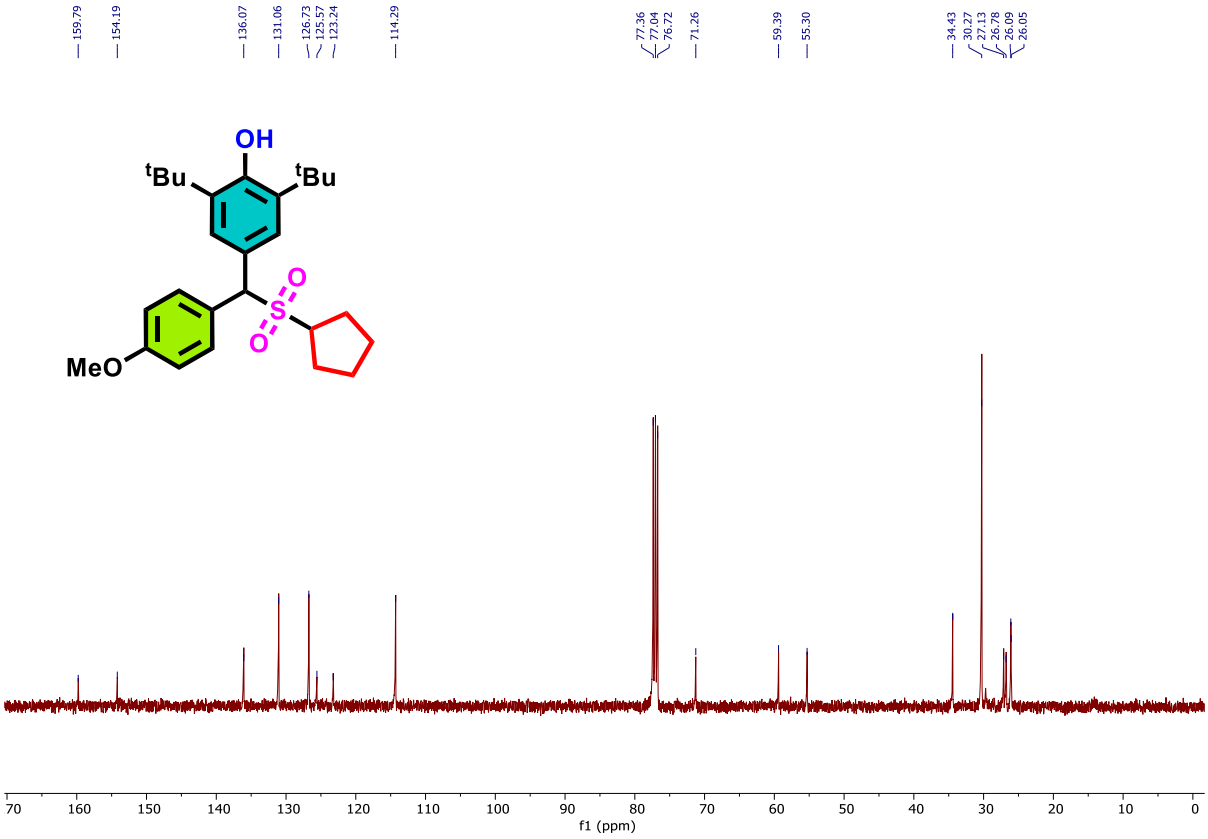
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((sec-butylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ab):**



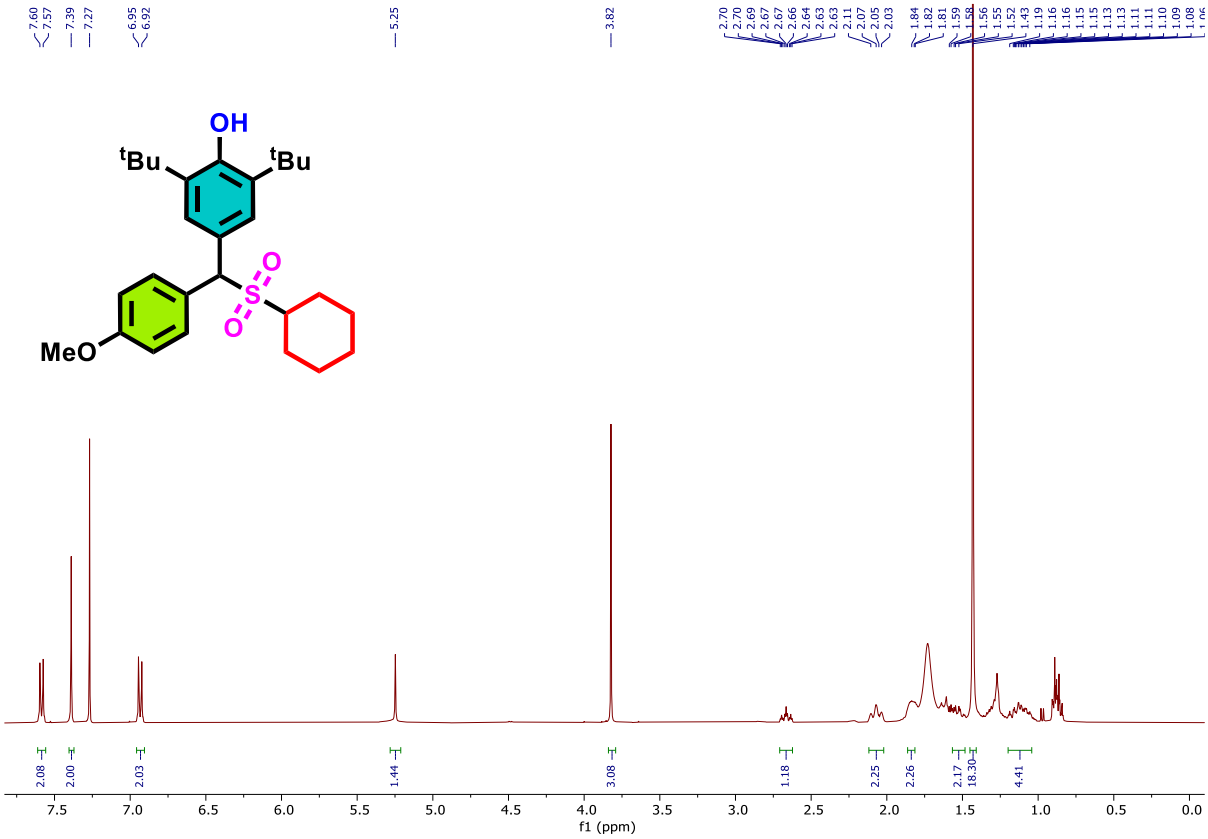
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((cyclopentylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ac)**



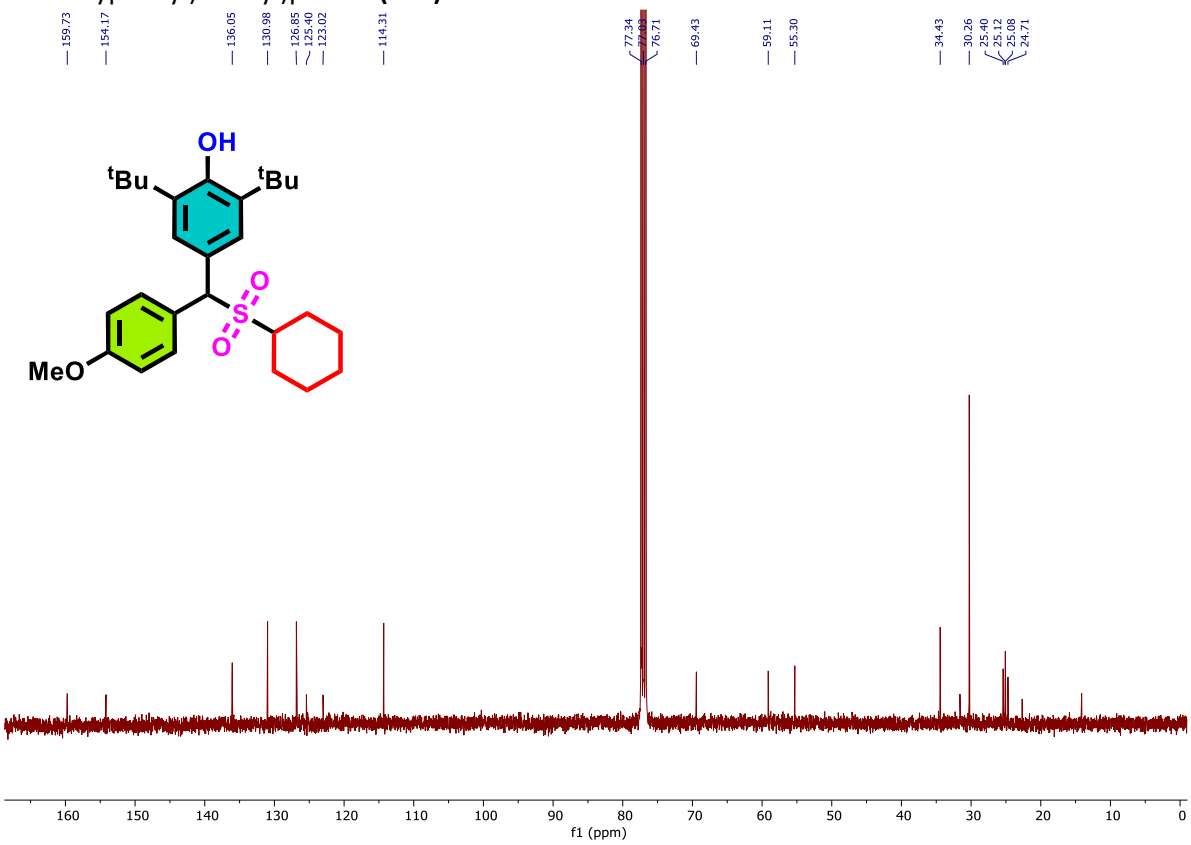
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((cyclopentylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ac)**



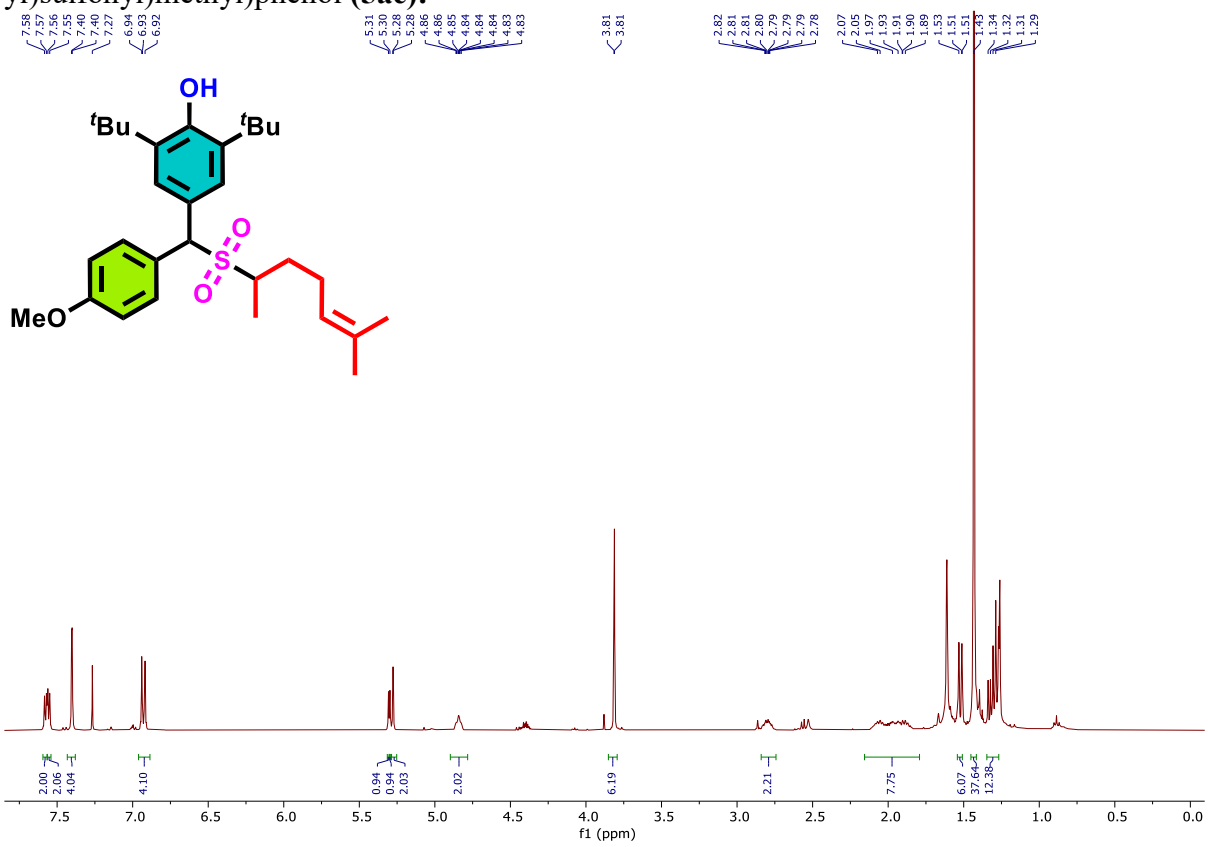
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((cyclohexylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ad)**



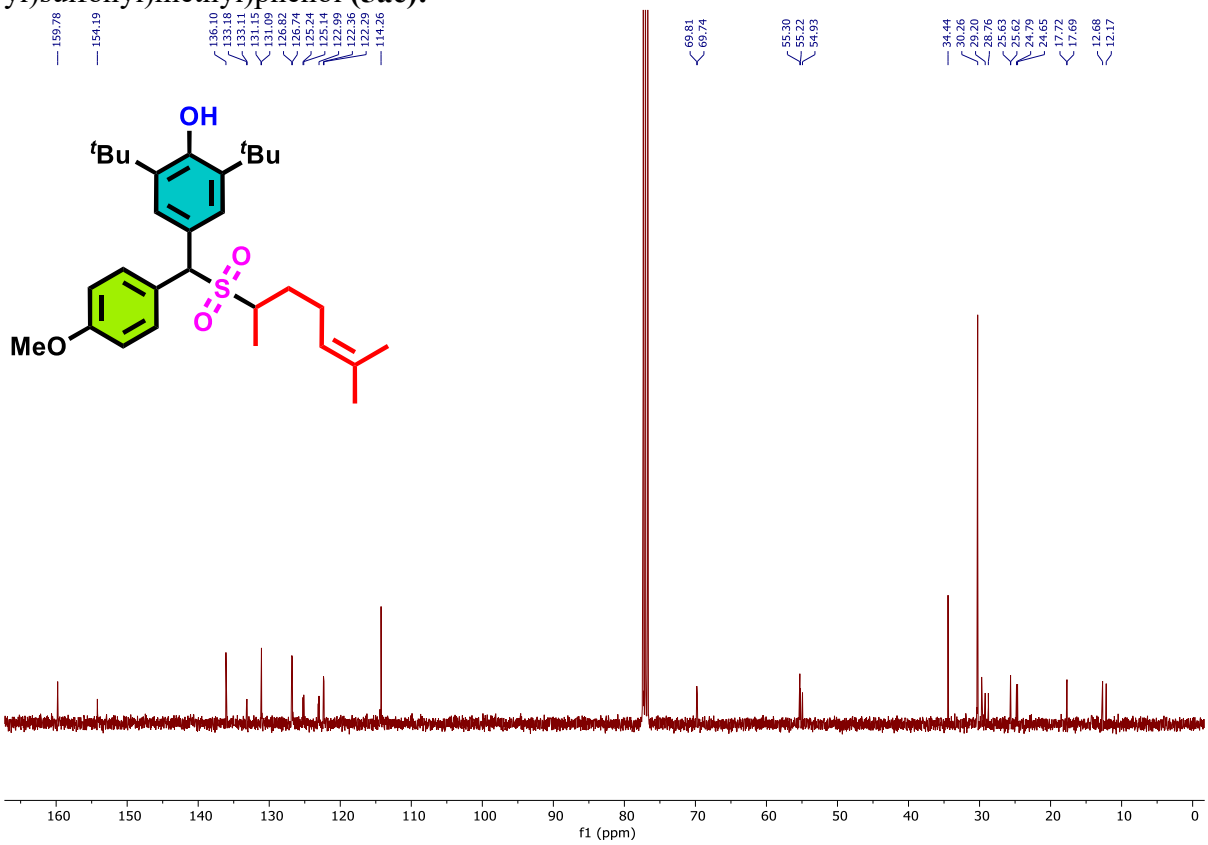
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((cyclohexylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ad)**



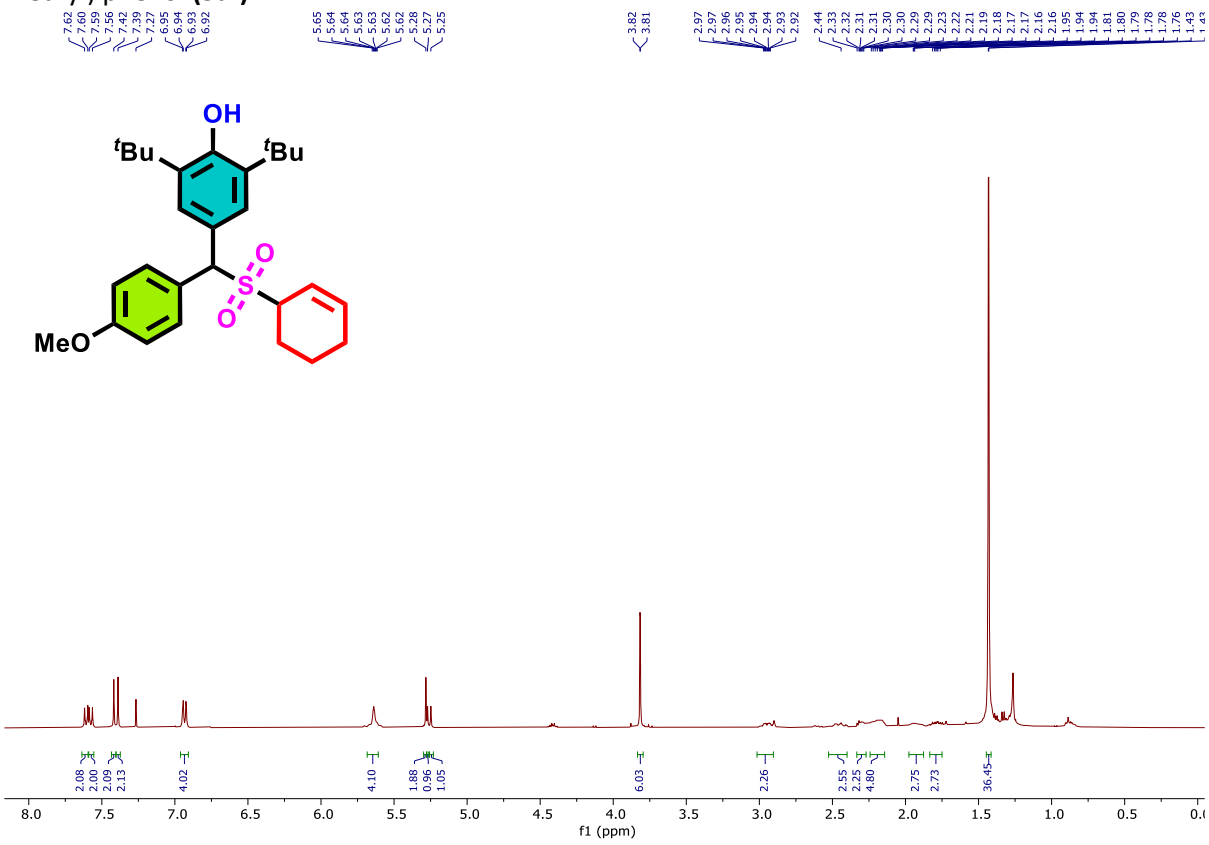
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((6-methylhept-5-en-2-yl)sulfonyl)methyl)phenol **(5ae):**



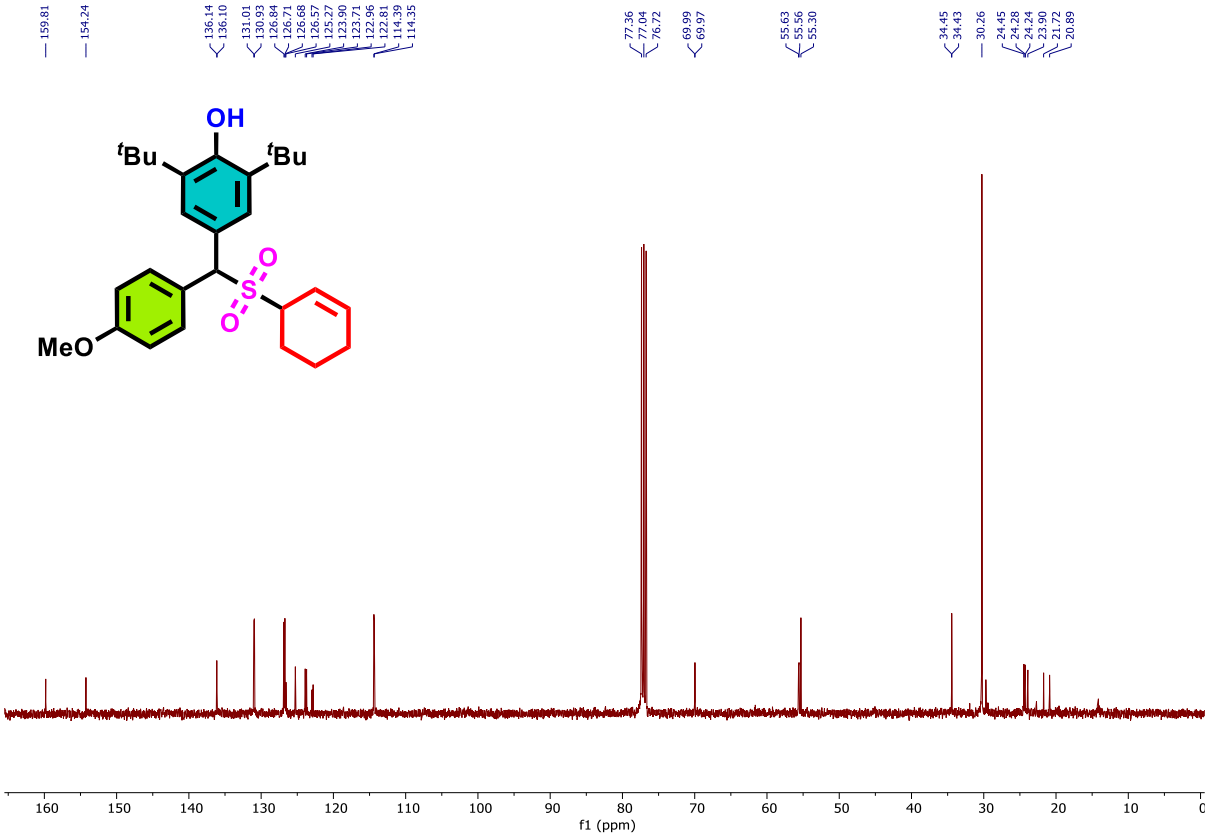
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((6-methylhept-5-en-2-yl)sulfonyl)methyl)phenol **(5ae):**



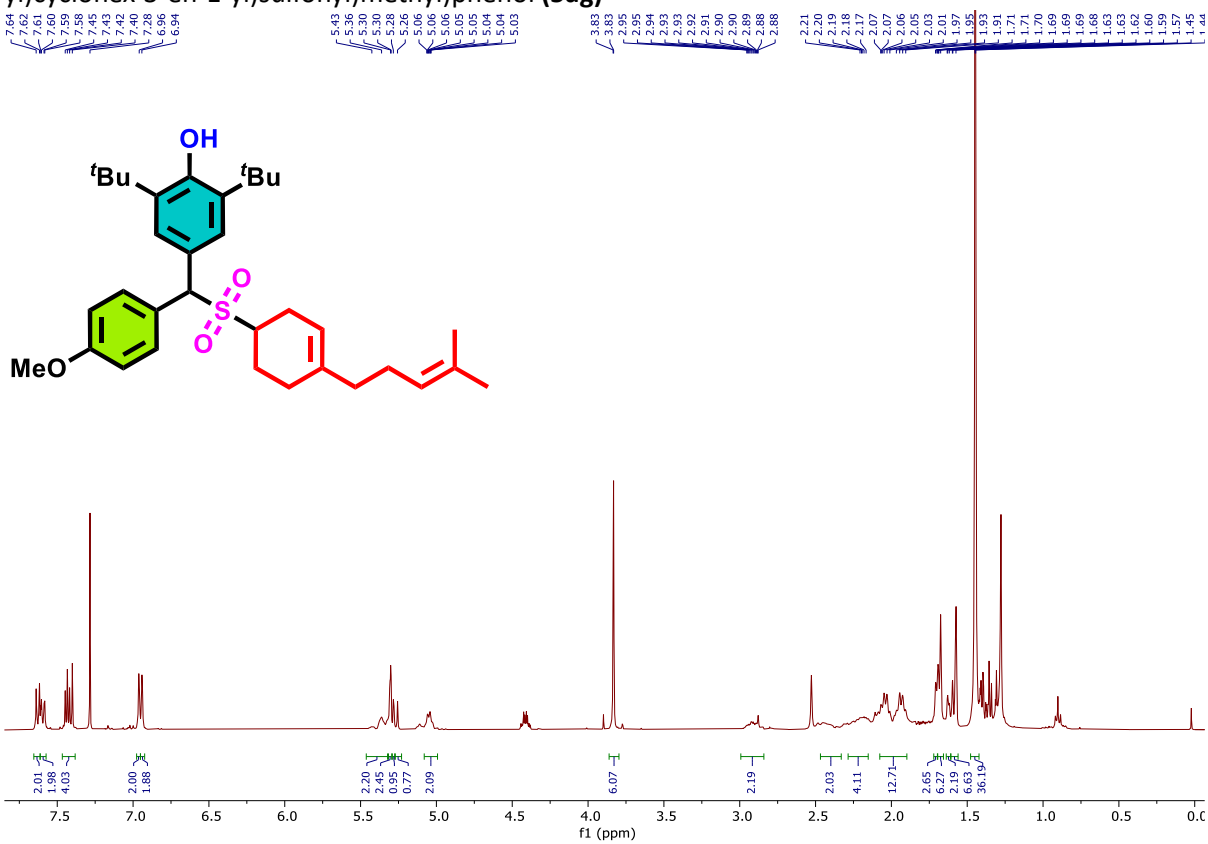
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((cyclohex-2-en-1-yl sulfonyl)(4-methoxy phenyl) methyl) phenol **(5af):**



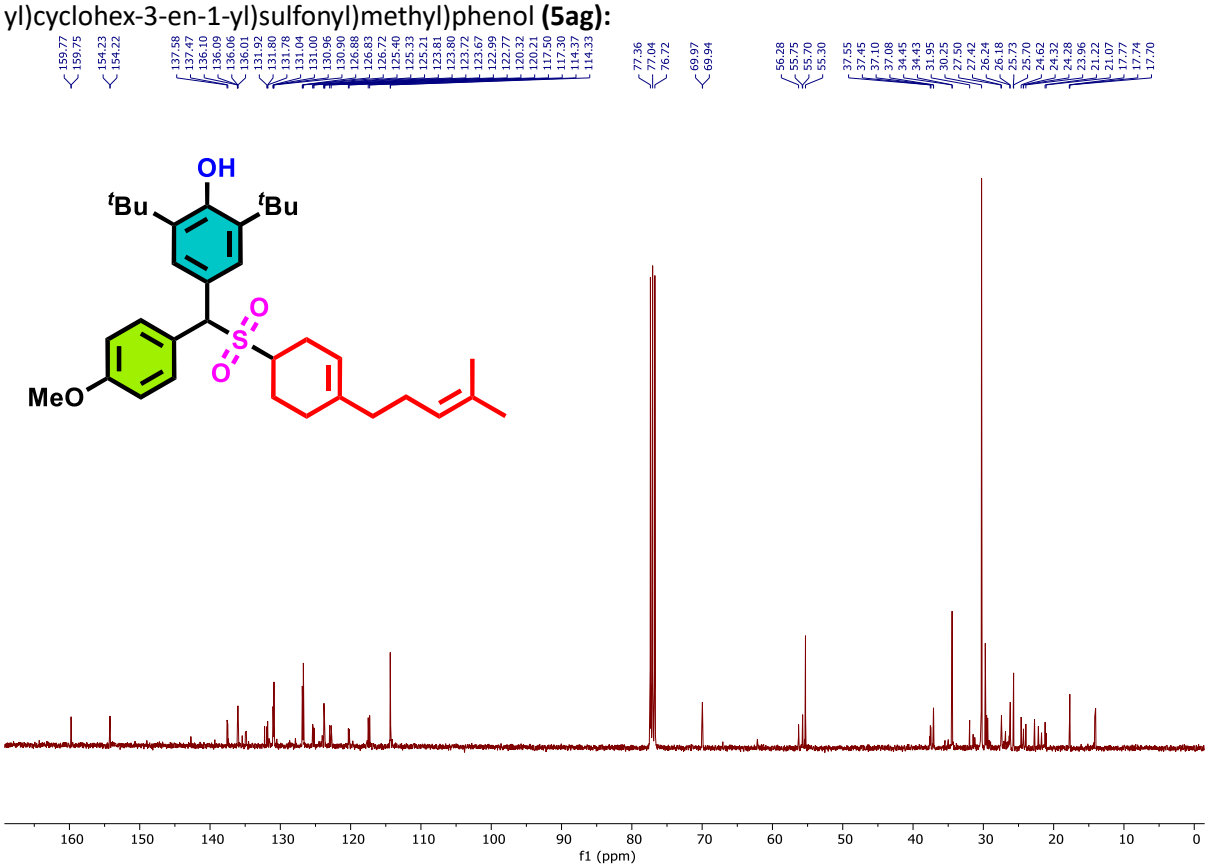
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((cyclohex-2-en-1-yl sulfonyl)(4-methoxy phenyl) methyl) phenol **(5af):**



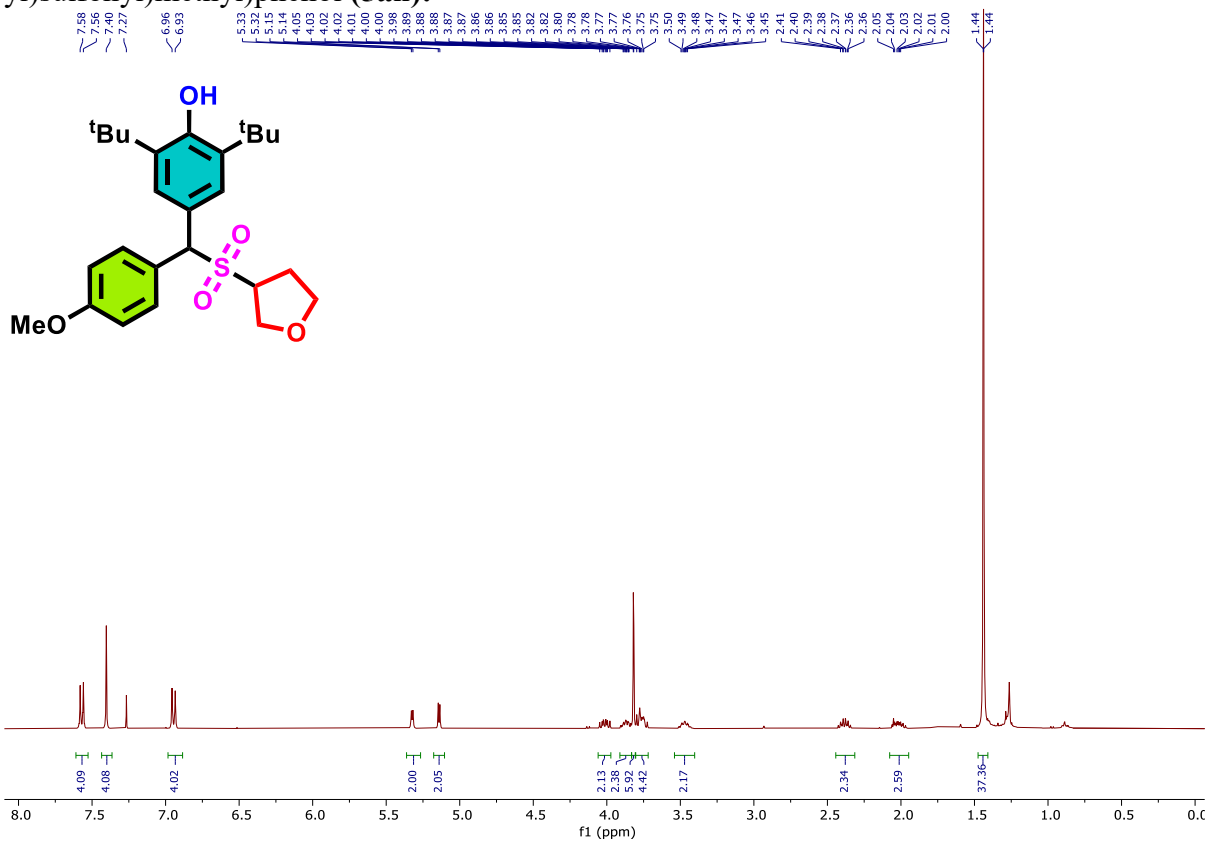
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)sulfonyl)methyl)phenol **(5ag)**



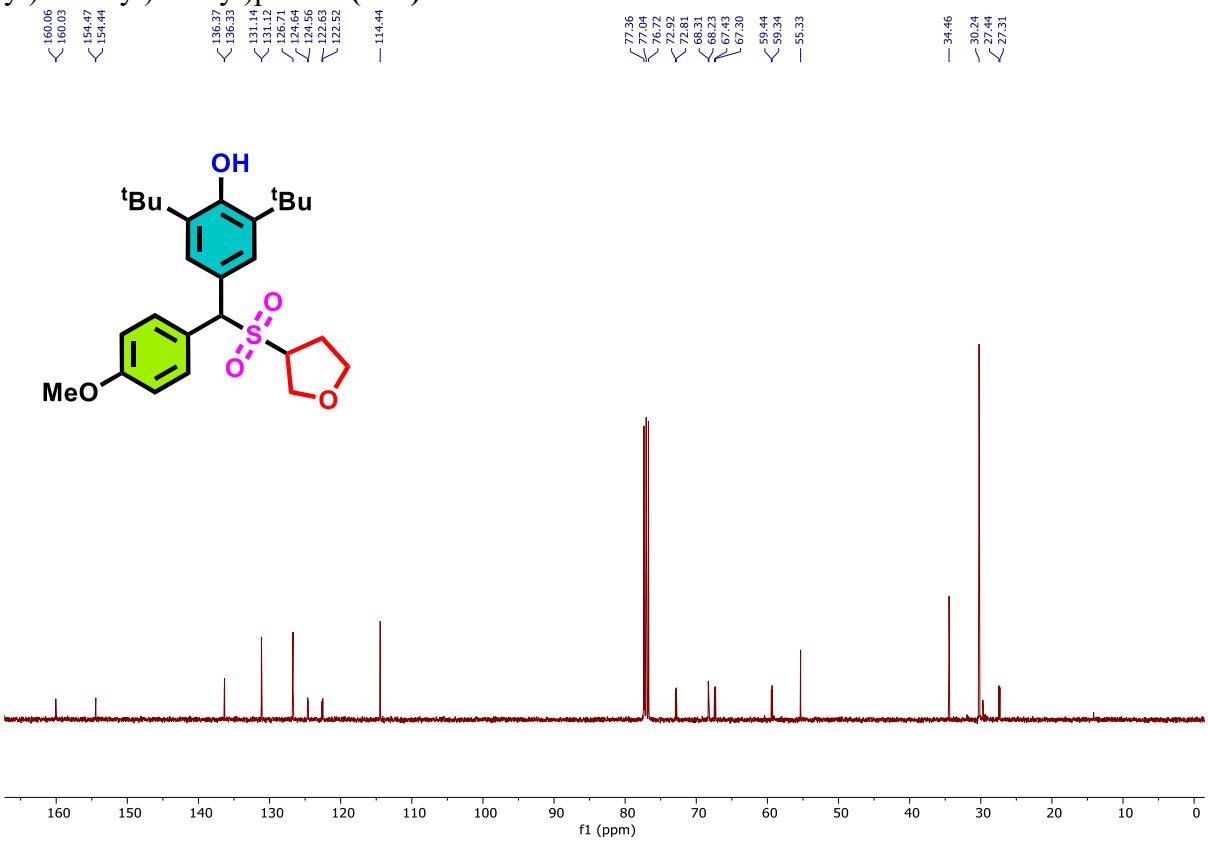
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)sulfonyl)methyl)phenol **(5ag):**



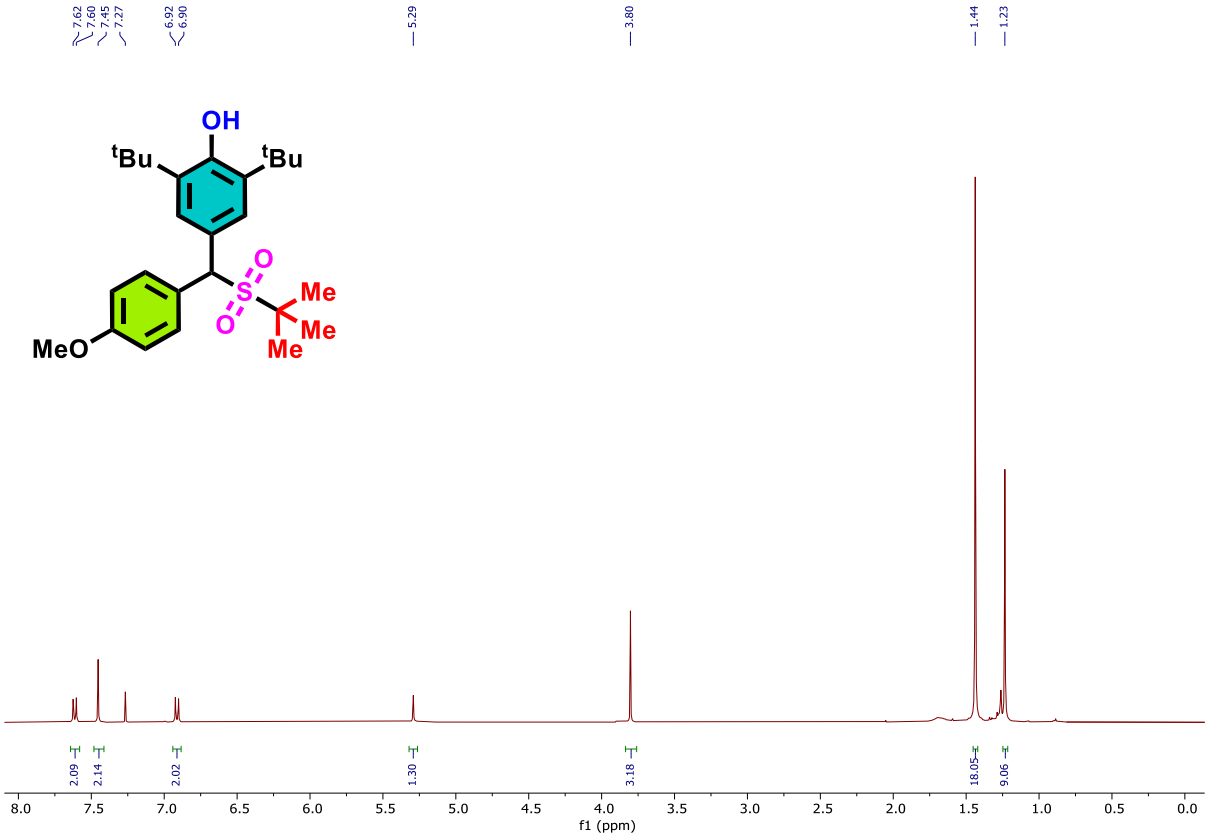
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((tetrahydrofuran-3-yl)sulfonyl)methyl)phenol **(5ah):**



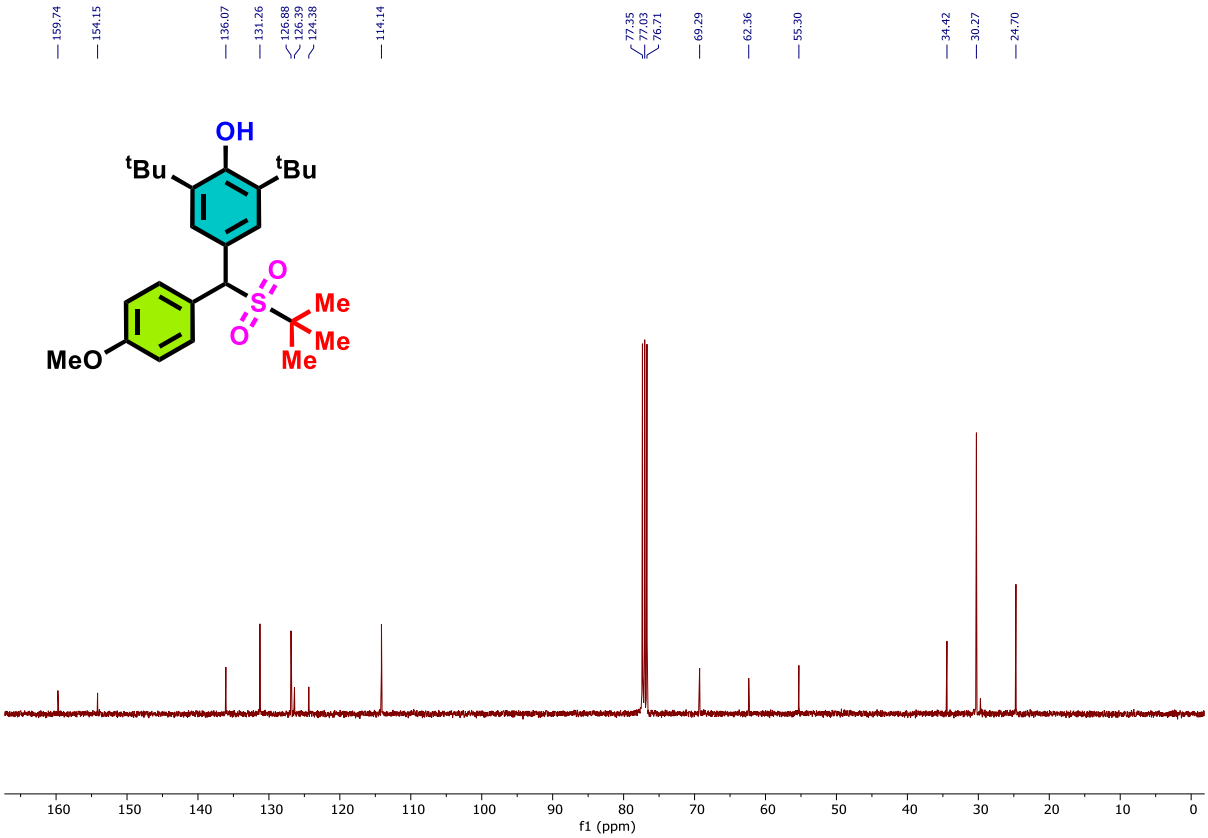
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((tetrahydrofuran-3-yl)sulfonyl)methyl)phenol **(5ah):**



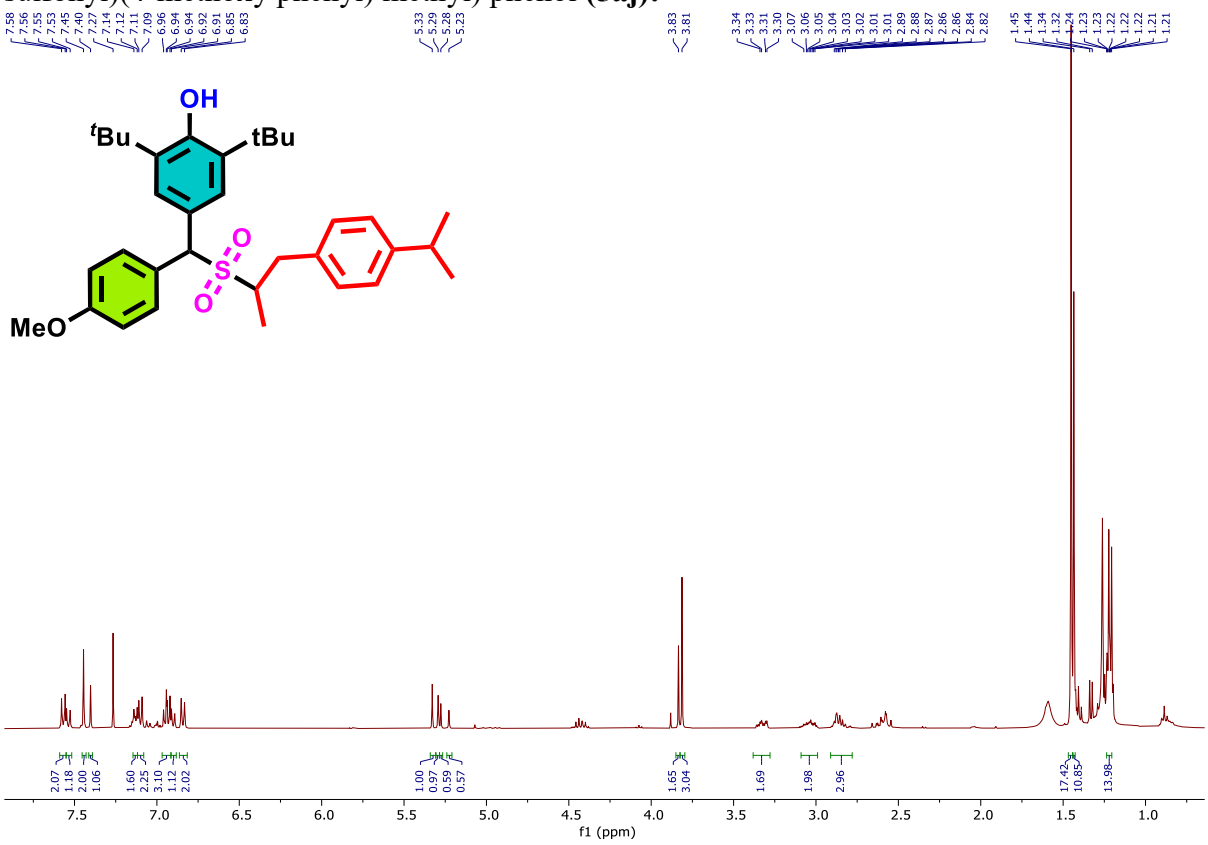
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((tert-butylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ai)**



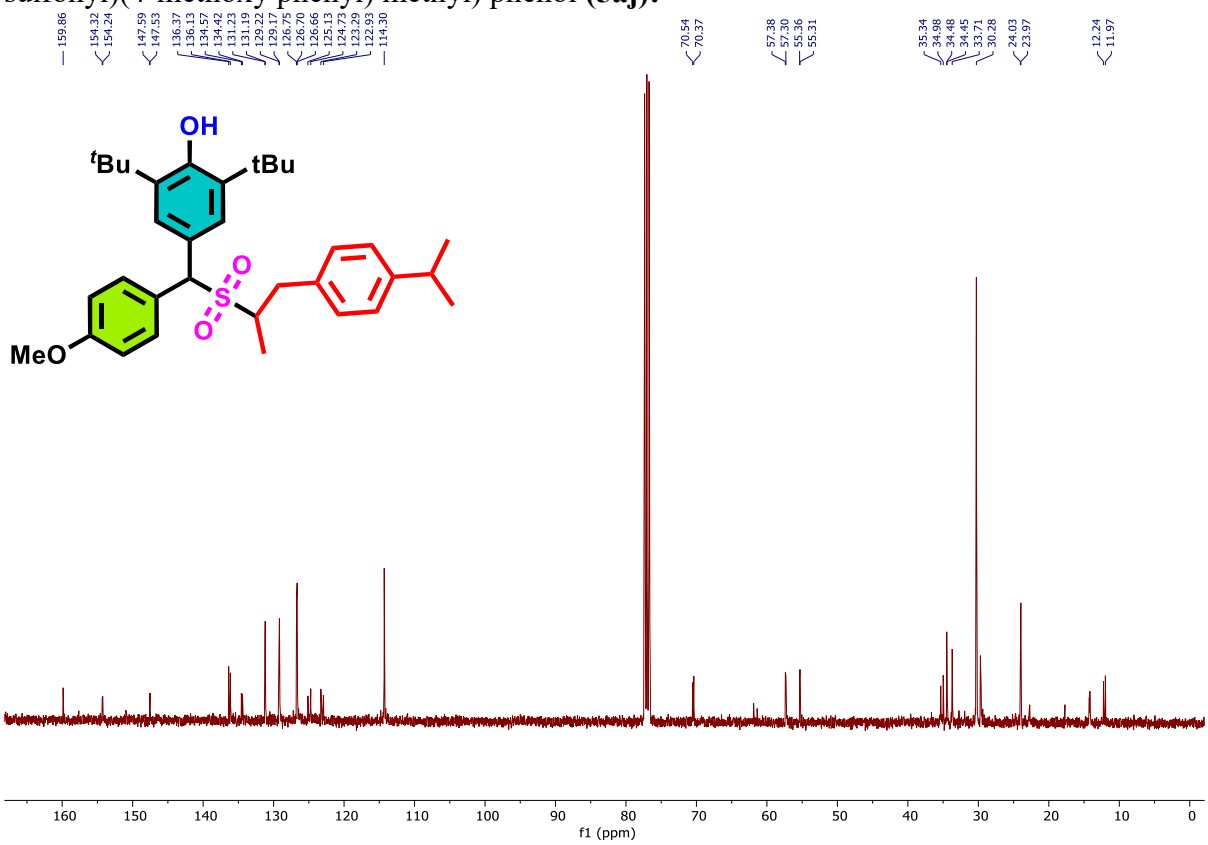
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((tert-butylsulfonyl)(4-methoxyphenyl)methyl)phenol **(5ai)**



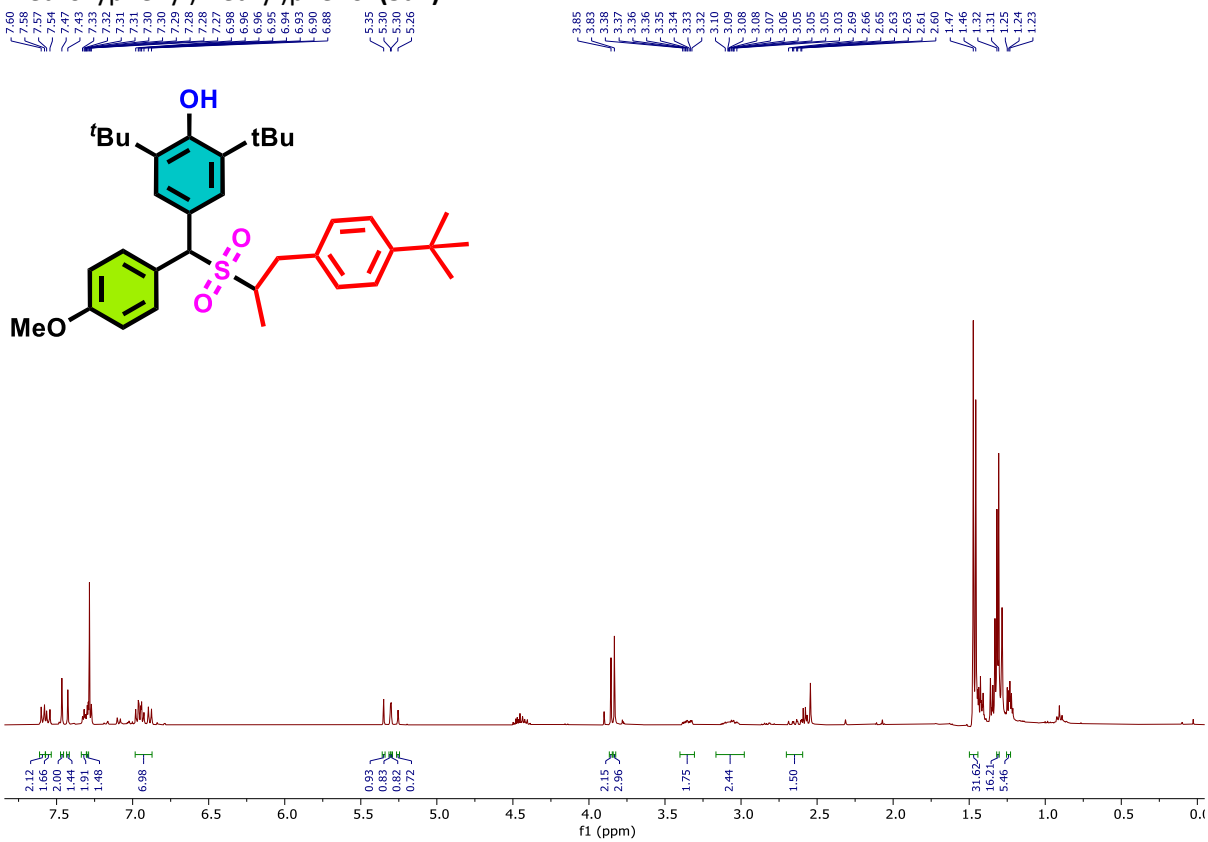
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(((1-(4-isopropy lphenyl) propan-2-yl) sulfonyl)(4-methoxy phenyl) methyl) phenol **(5aj):**



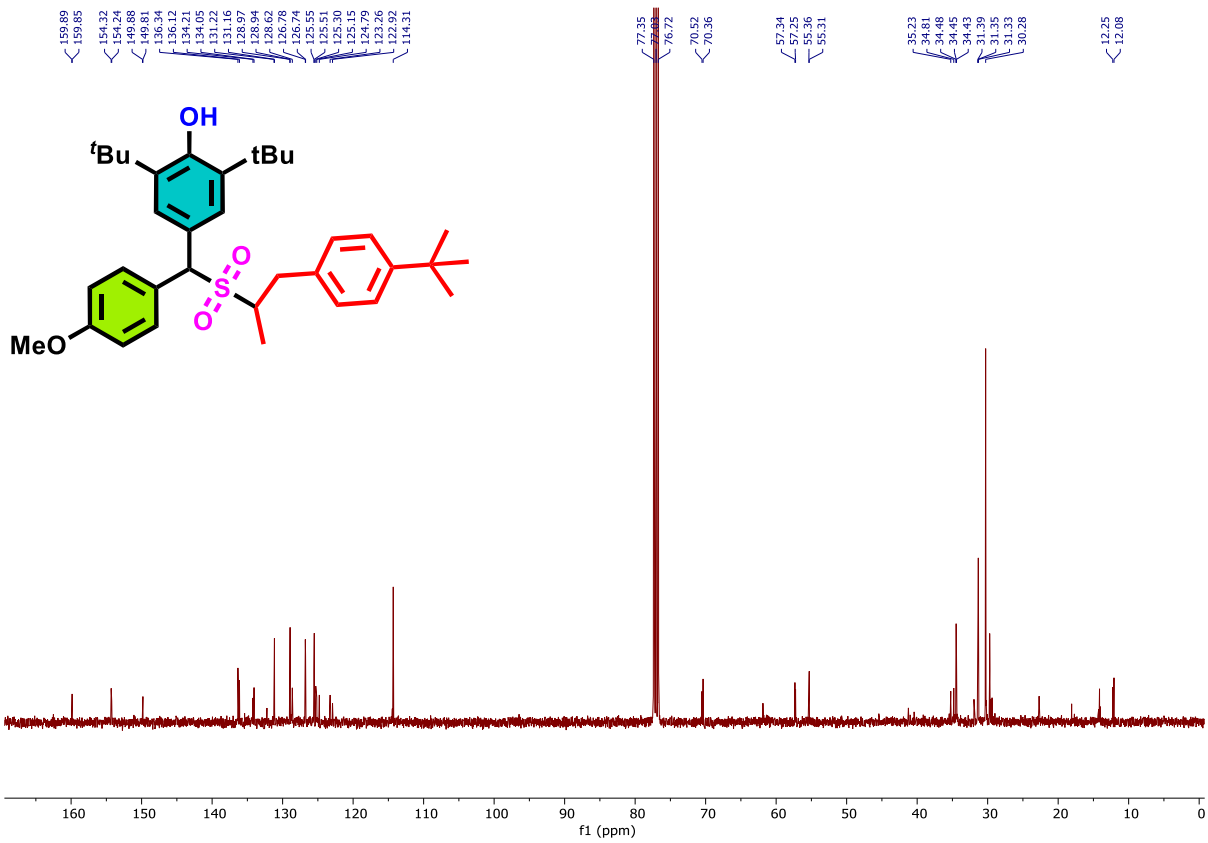
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(((1-(4-isopropy lphenyl) propan-2-yl) sulfonyl)(4-methoxy phenyl) methyl) phenol **(5aj):**



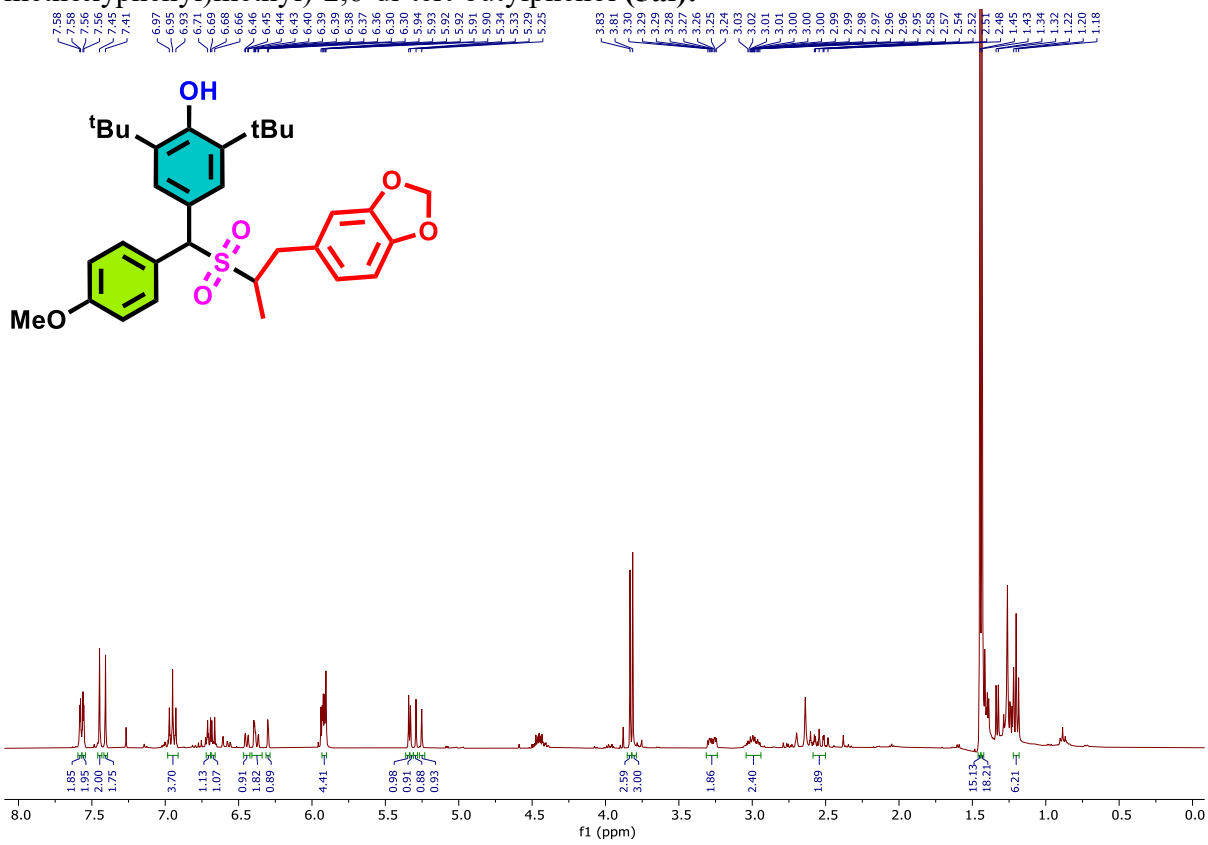
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-(((1-(4-(tert-butyl)phenyl)propan-2-yl)sulfonyl)(4-methoxyphenyl)methyl)phenol **(5ak)**



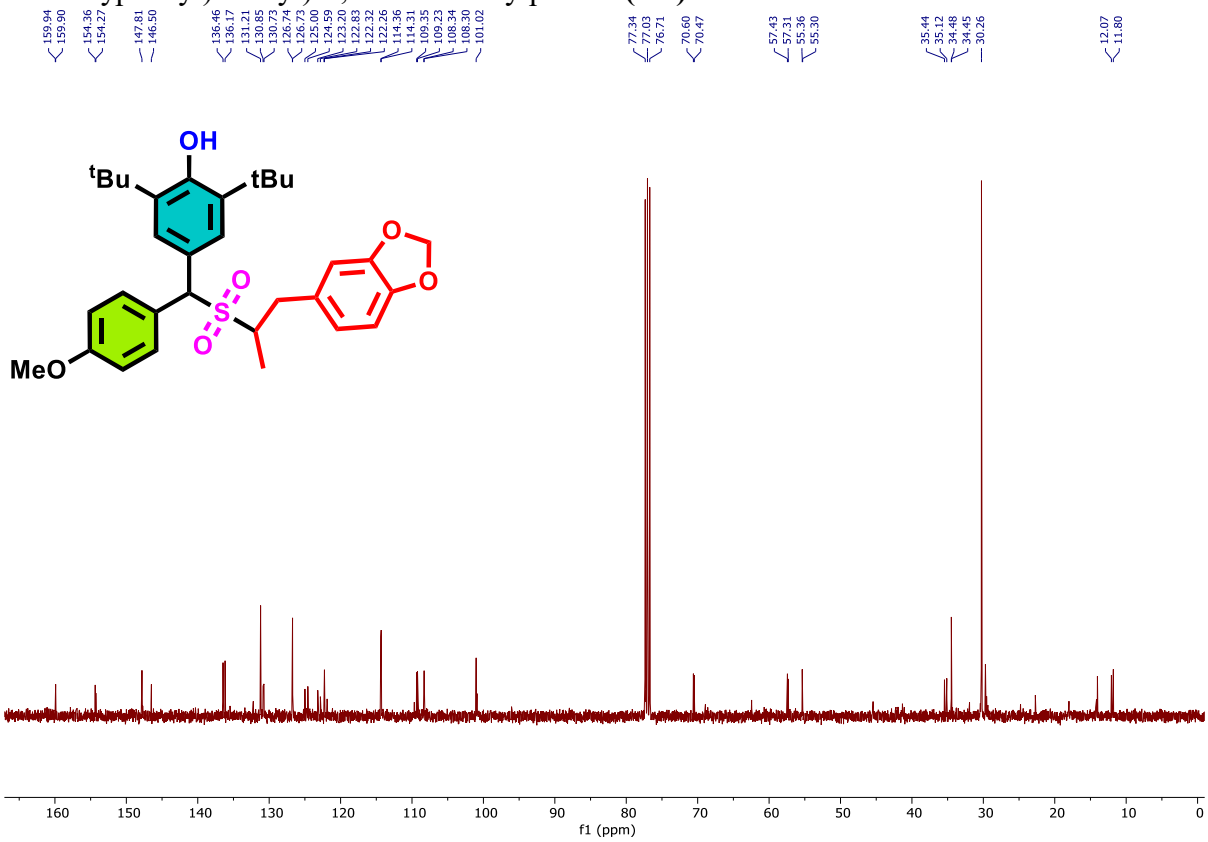
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-(((1-(4-(tert-butyl)phenyl)propan-2-yl)sulfonyl)(4-methoxyphenyl)methyl)phenol **(5ak)**



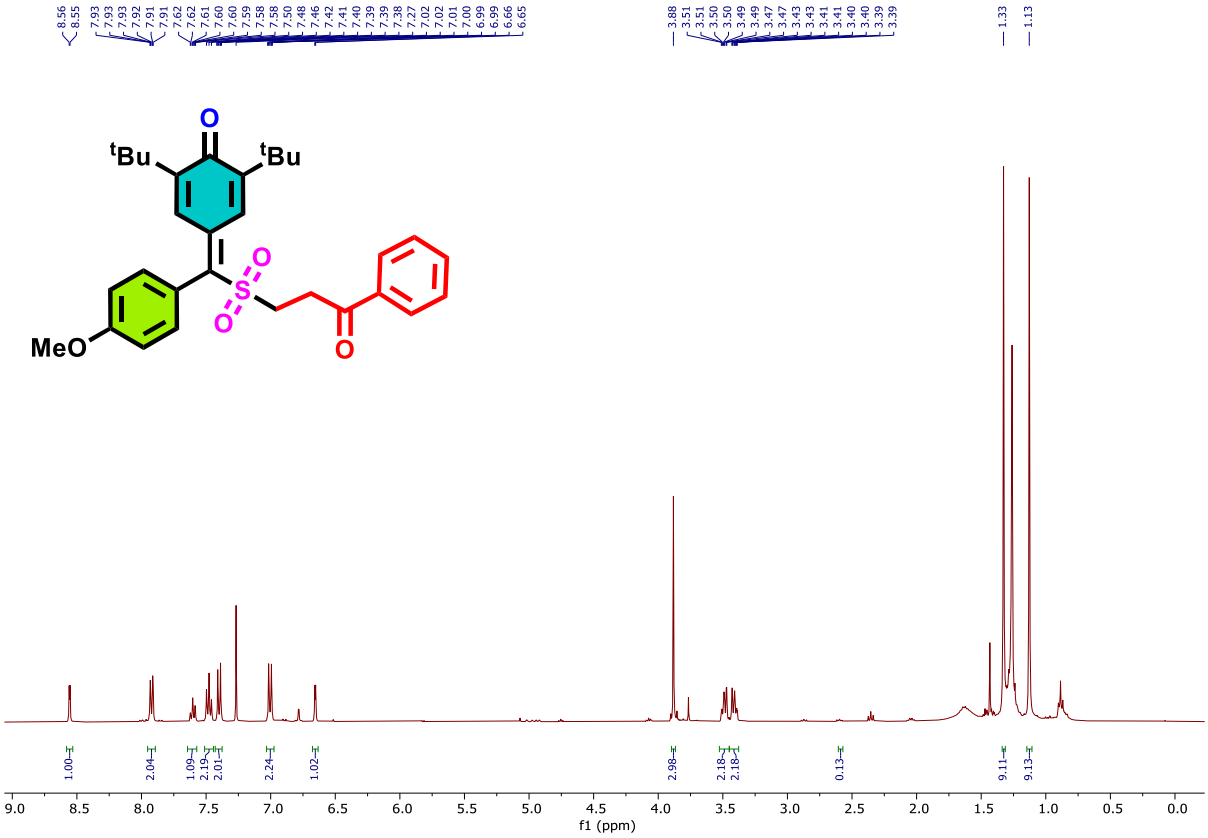
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-(((1-(benzo[d][1,3]dioxol-5-yl)propan-2-yl)sulfonyl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol **(5al):**



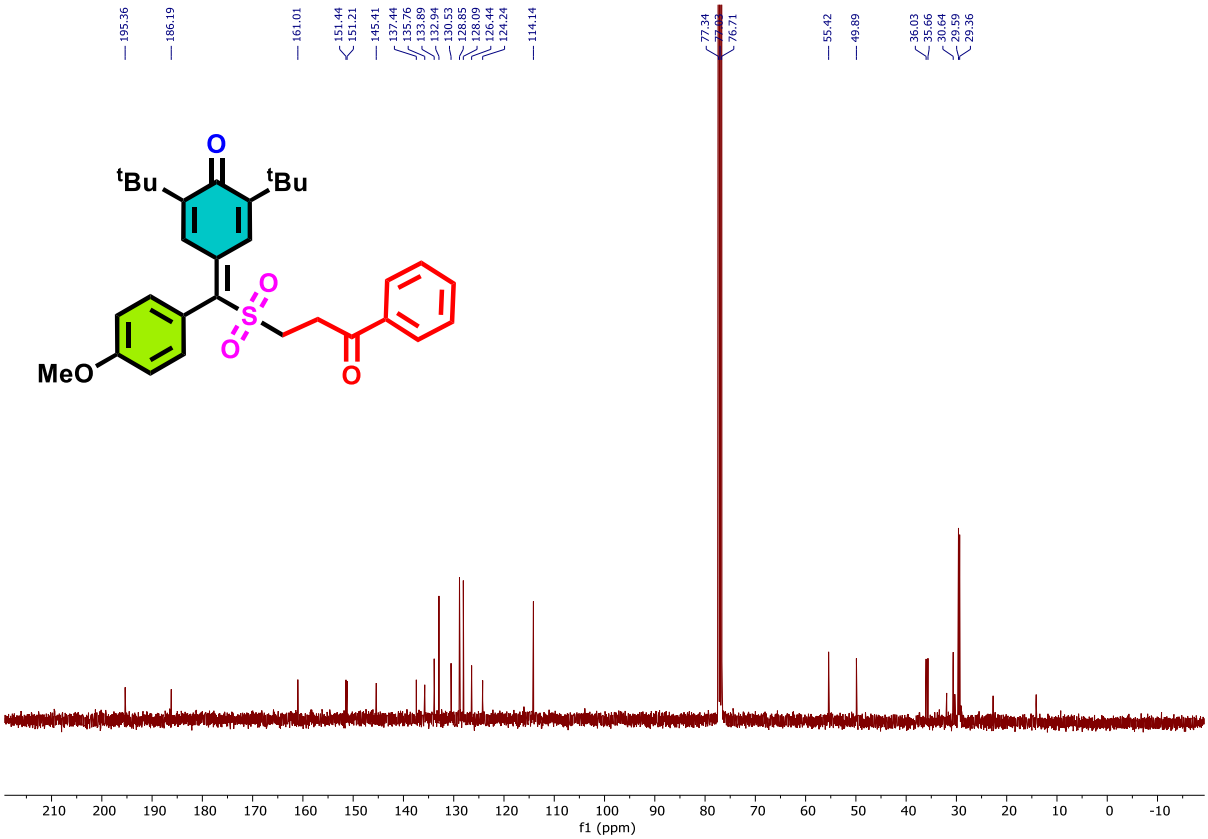
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-(((1-(benzo[d][1,3]dioxol-5-yl)propan-2-yl)sulfonyl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol **(5al):**



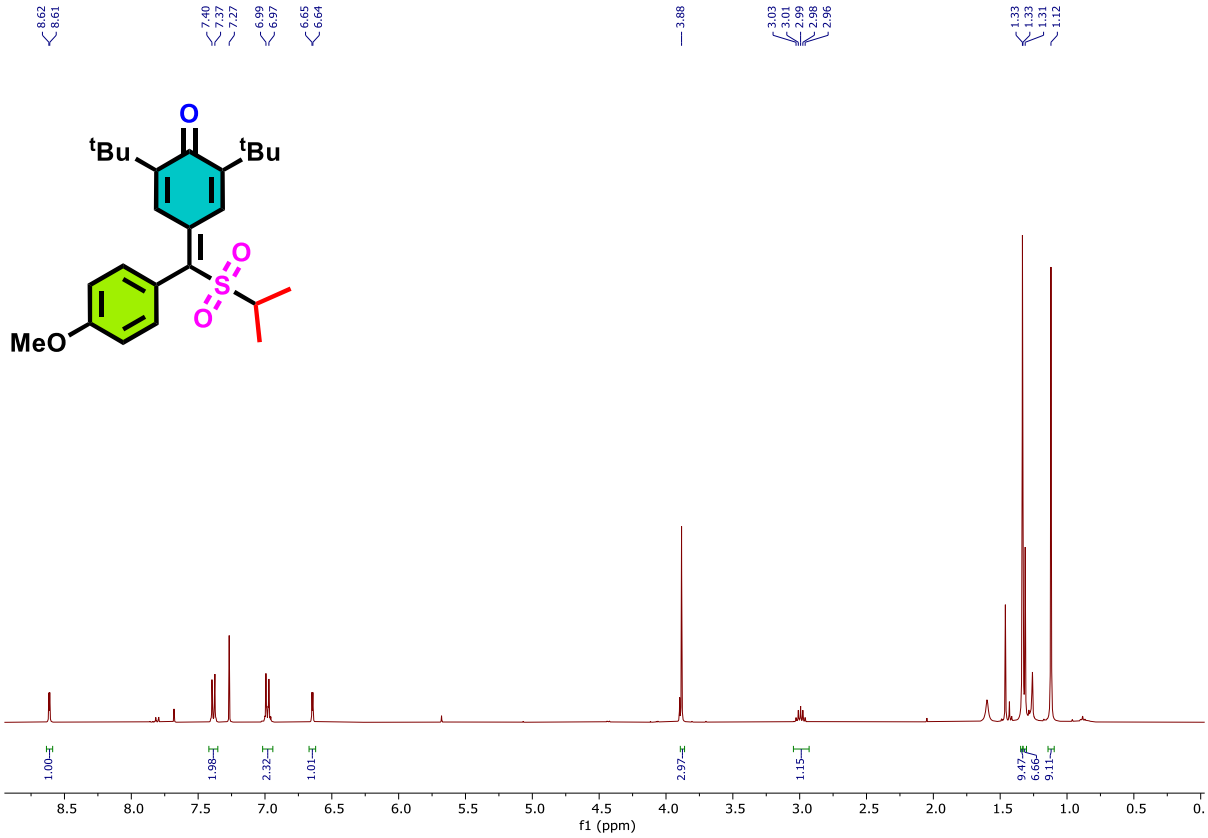
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methylene)cyclohexa-2,5-dien-1-one **(6)**



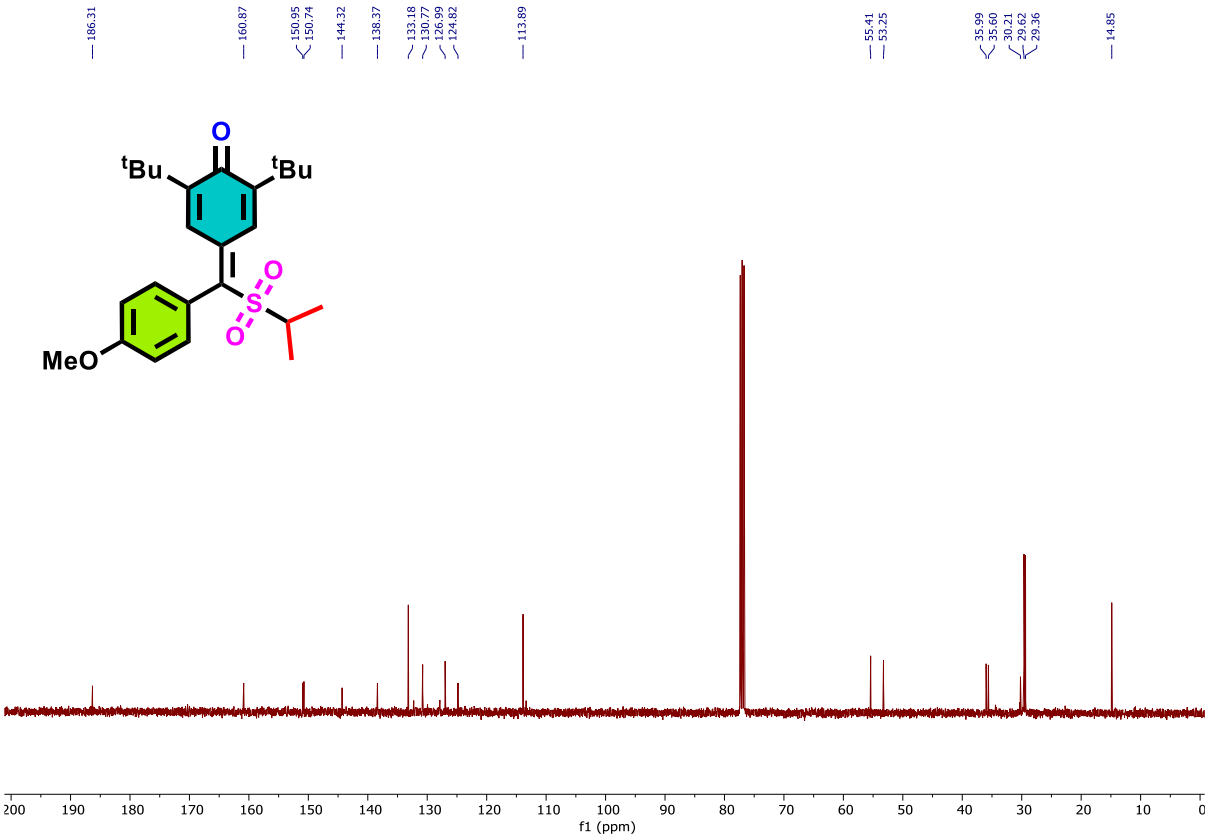
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((4-methoxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methylene)cyclohexa-2,5-dien-1-one **(6)**



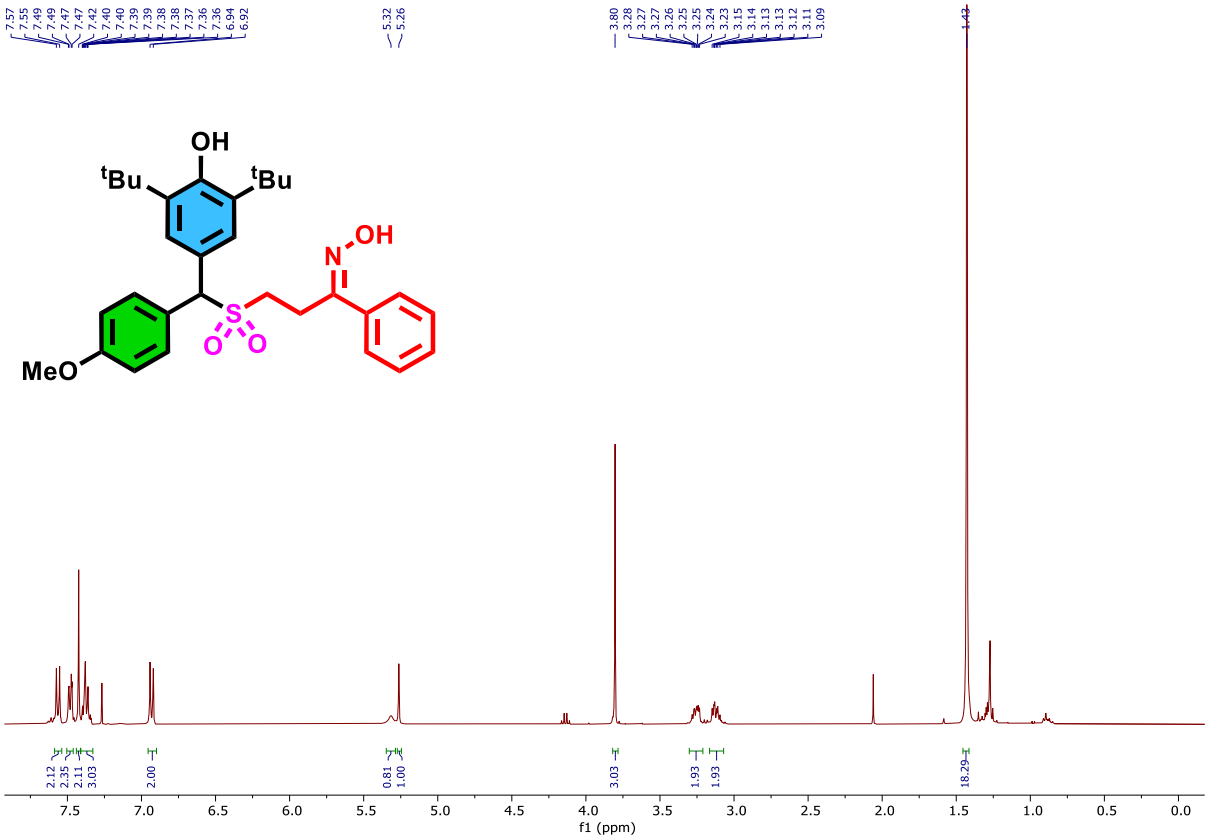
^{1}HNMR ($CDCl_3$, 400 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one **(7)**



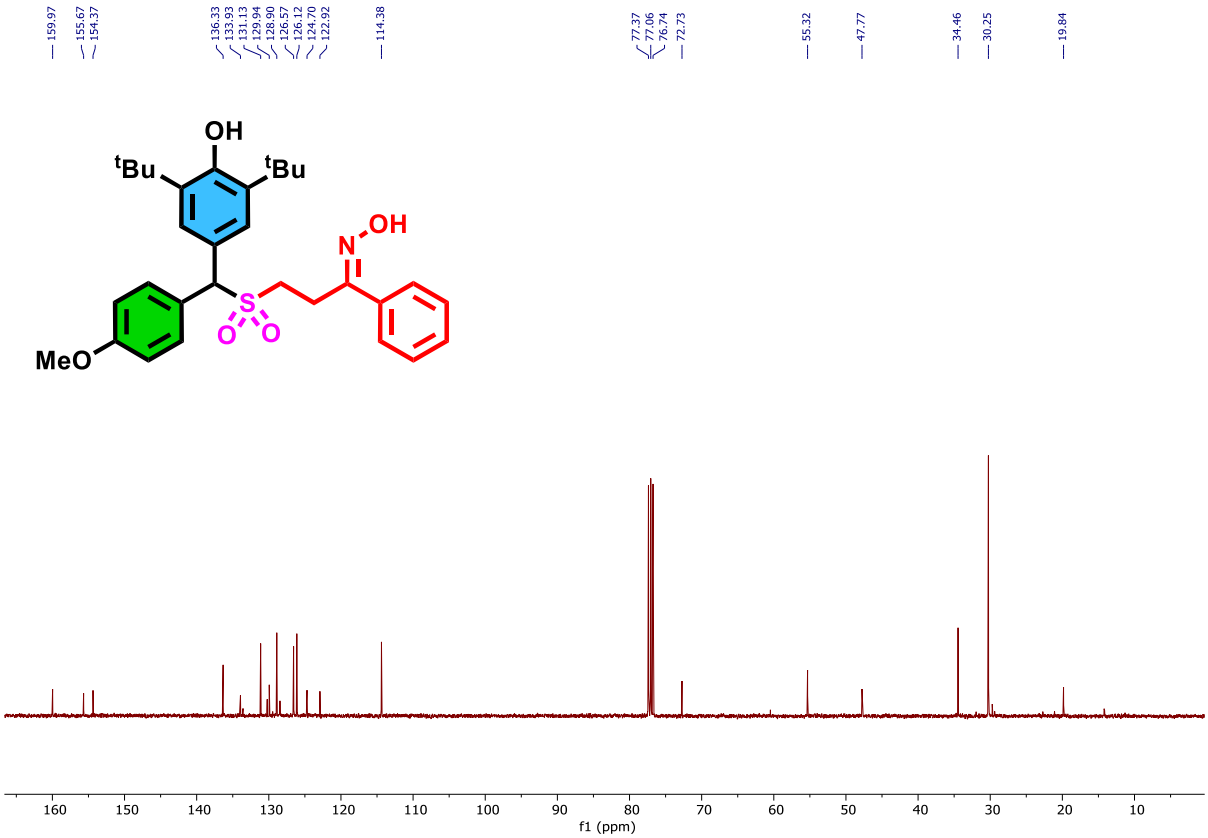
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 2,6-di-tert-butyl-4-((isopropylsulfonyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one **(7)**



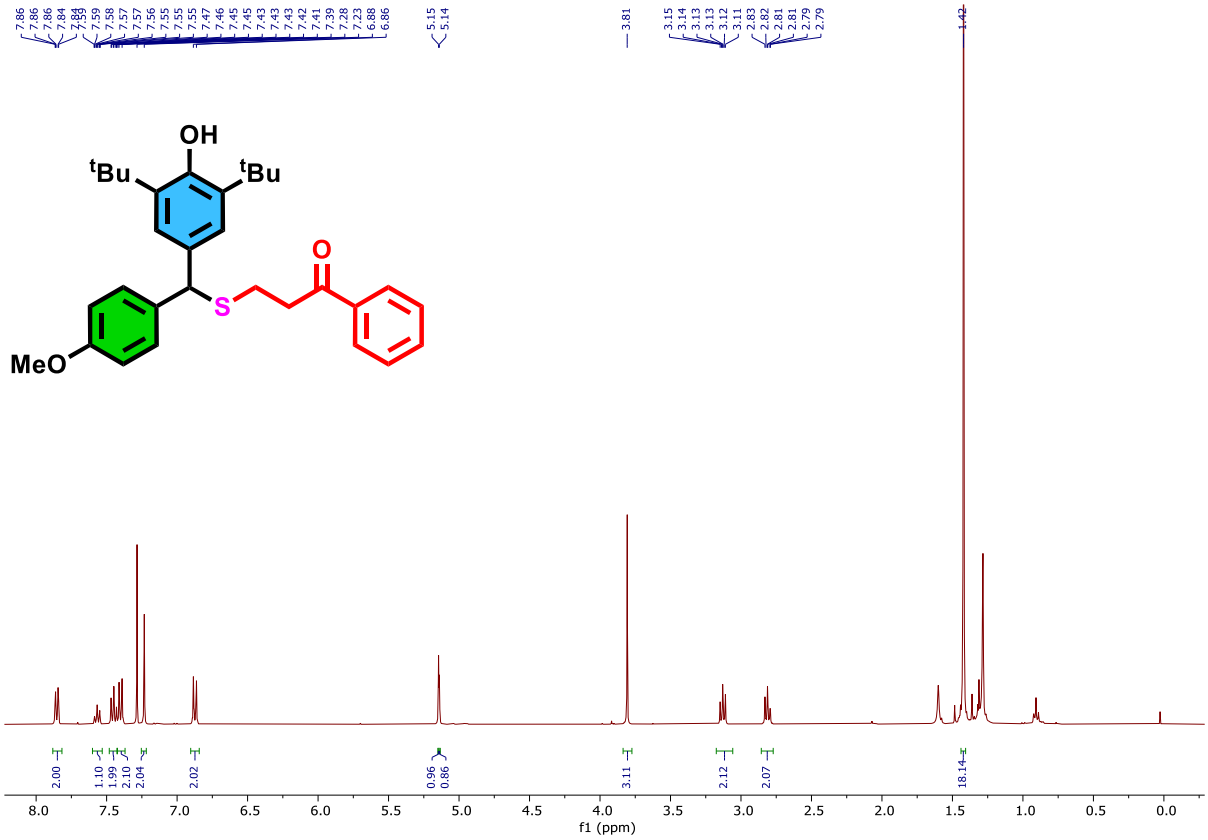
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one oxime **(8)**



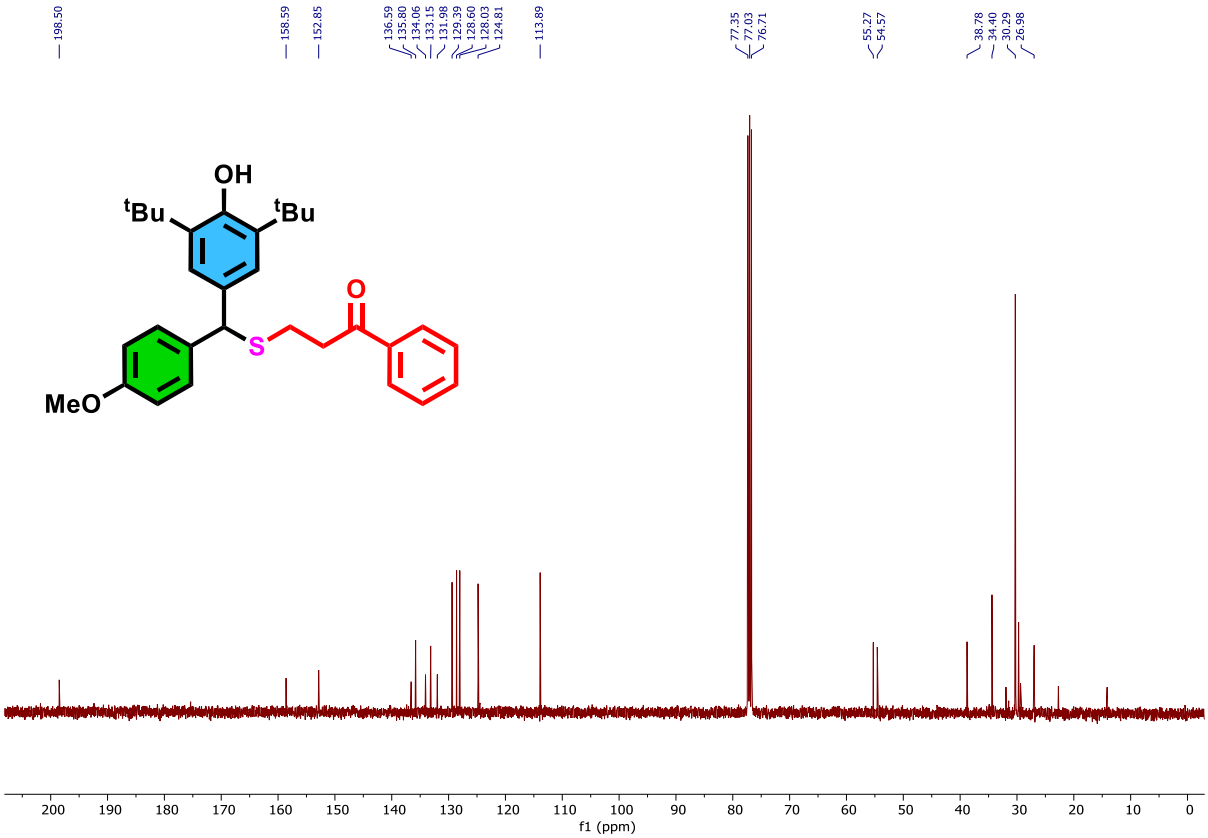
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)sulfonyl)-1-phenylpropan-1-one oxime **(8)**



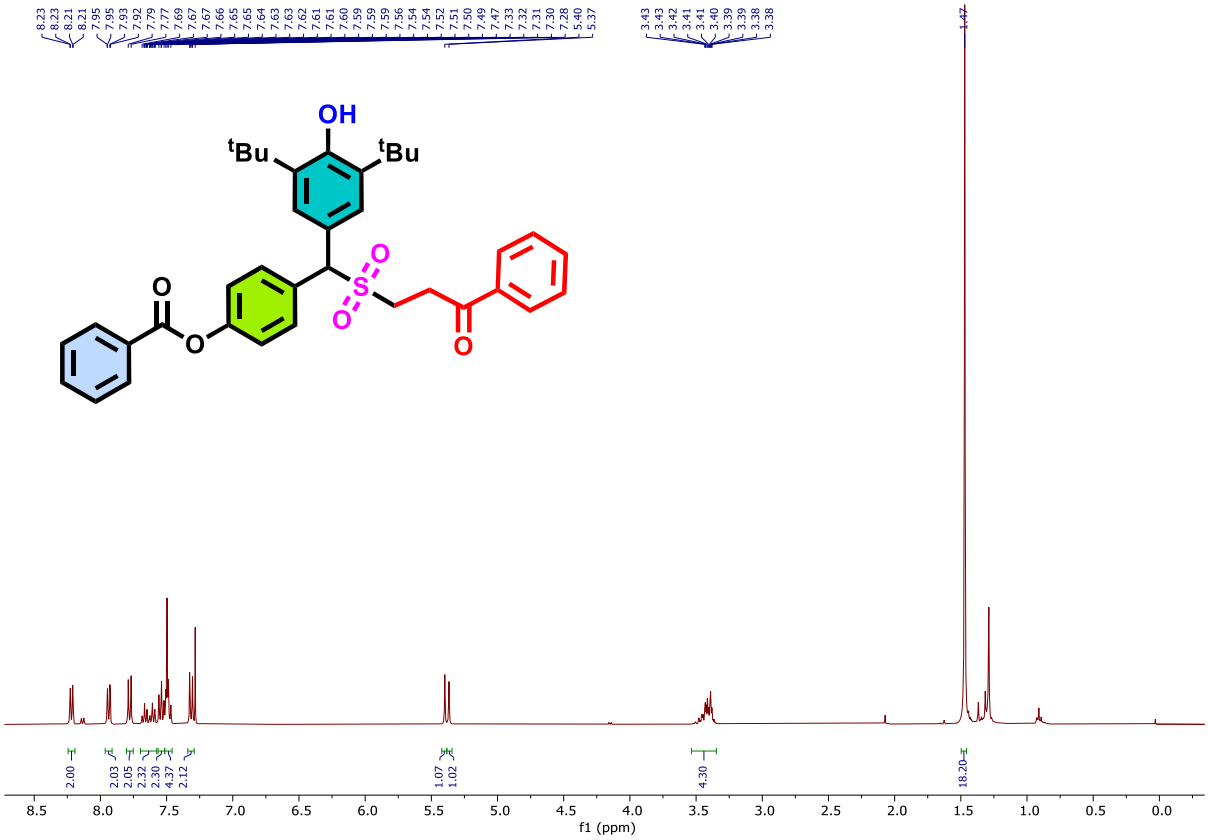
^{1}HNMR ($CDCl_3$, 400 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)thio)-1-phenylpropan-1-one **(9)**



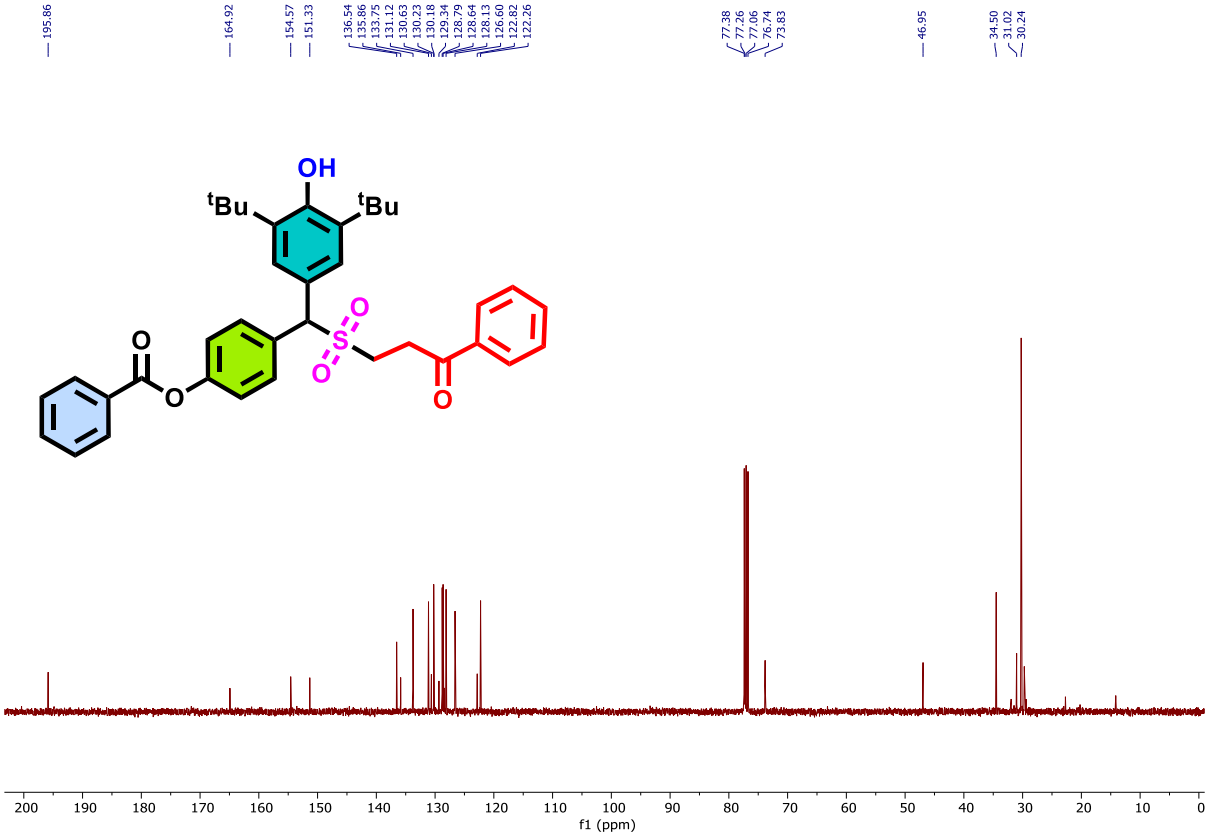
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 3-(((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)thio)-1-phenylpropan-1-one **(9)**



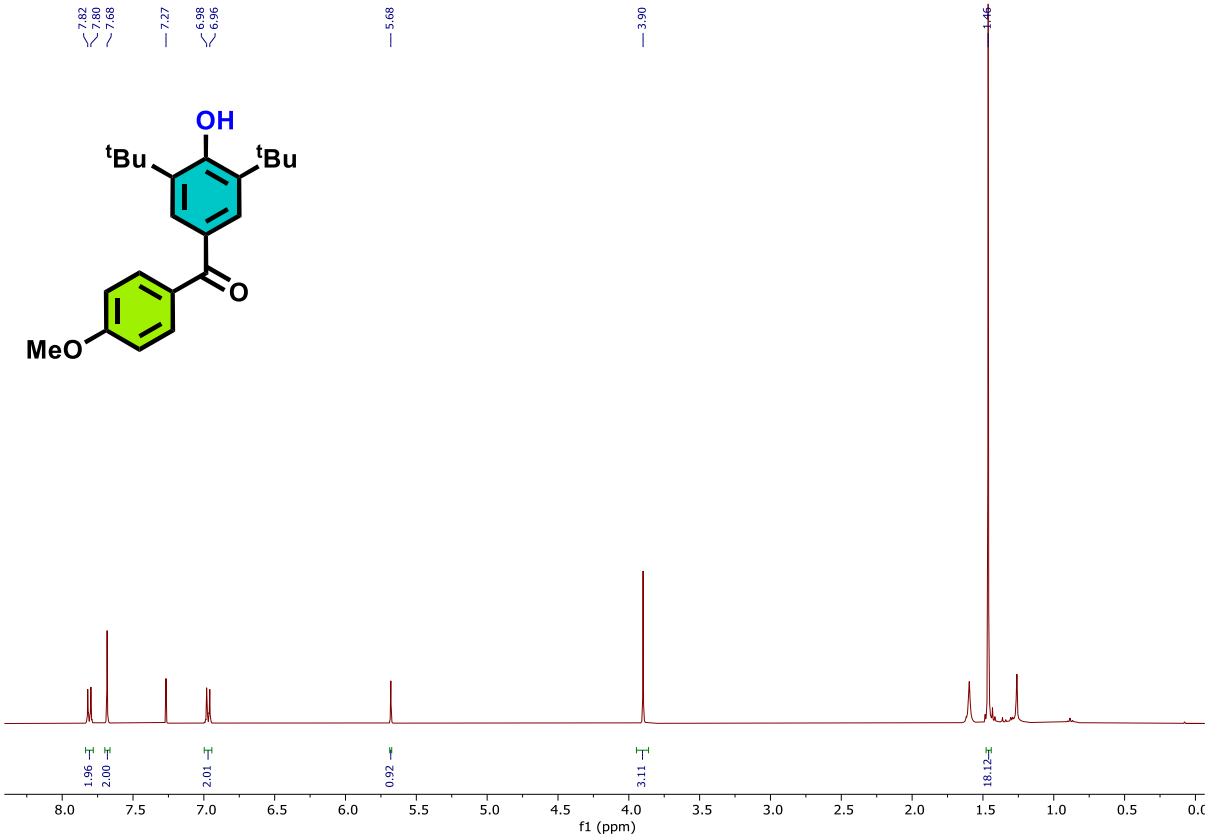
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl benzoate **(10)**



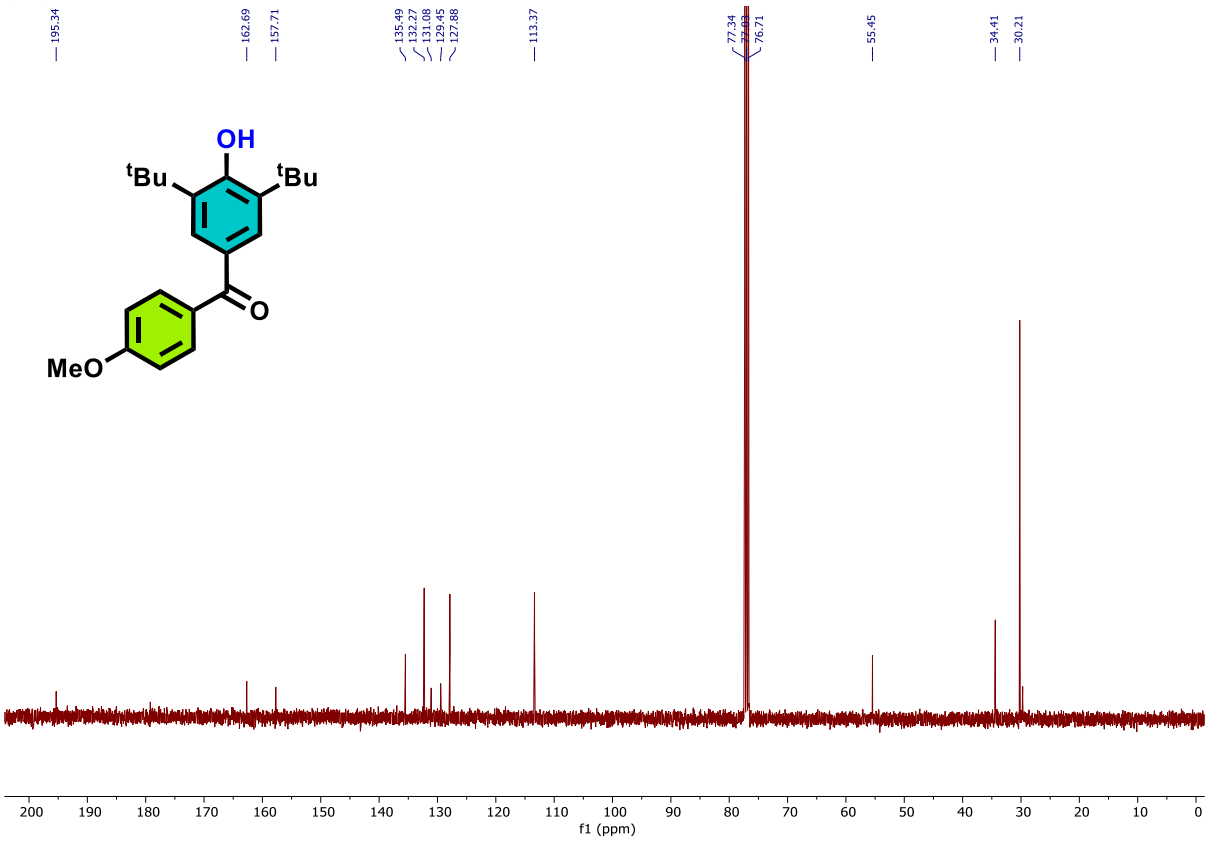
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((3,5-di-tert-butyl-4-hydroxyphenyl)((3-oxo-3-phenylpropyl)sulfonyl)methyl)phenyl benzoate **(10)**



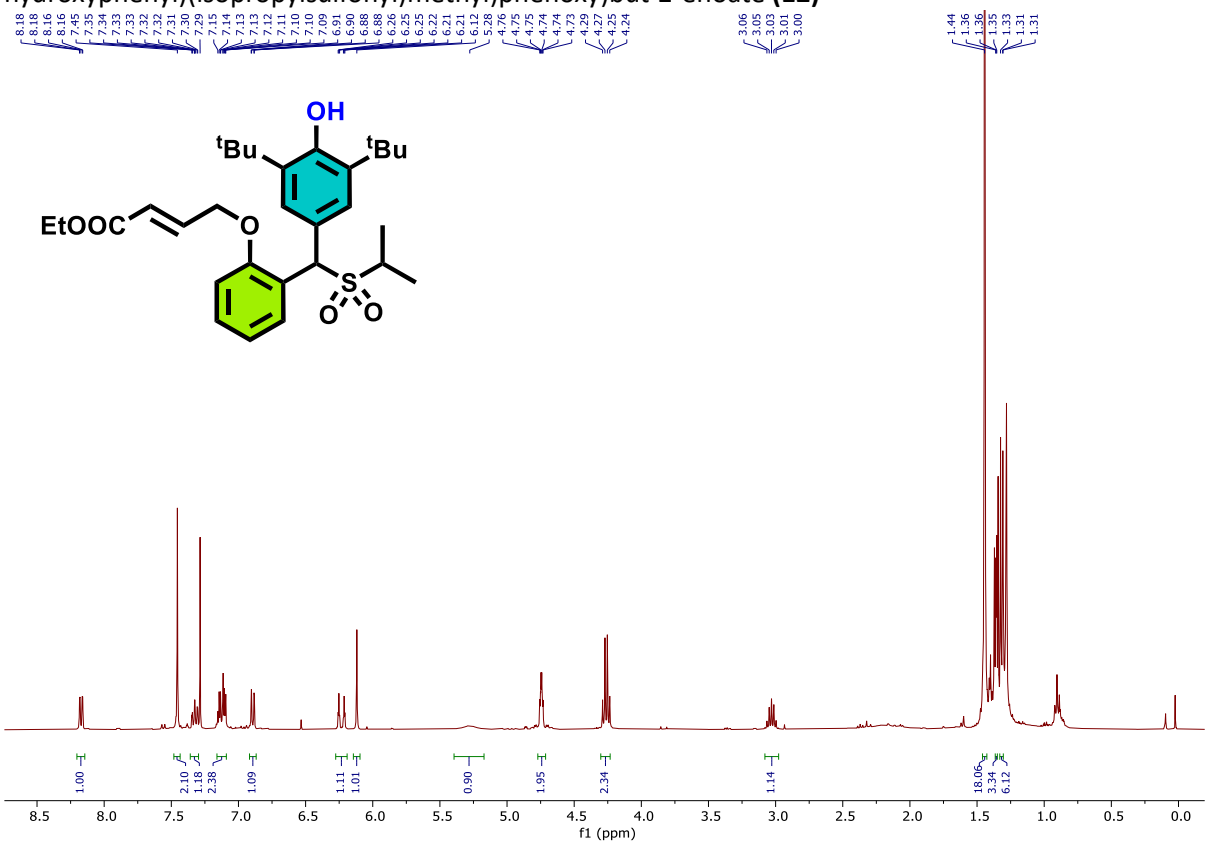
^{1}HNMR ($CDCl_3$, 400 MHz) of (3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methanone **(11)**



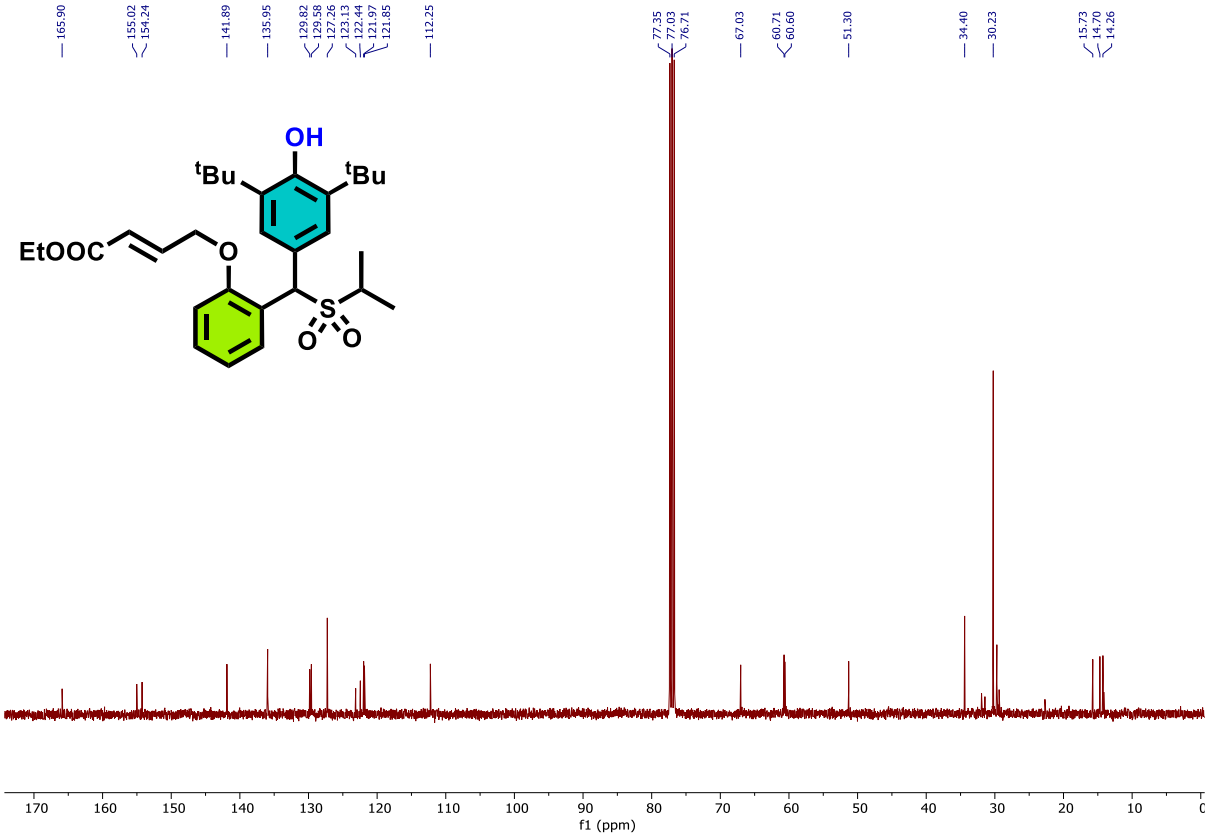
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of (3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methanone **(11)**



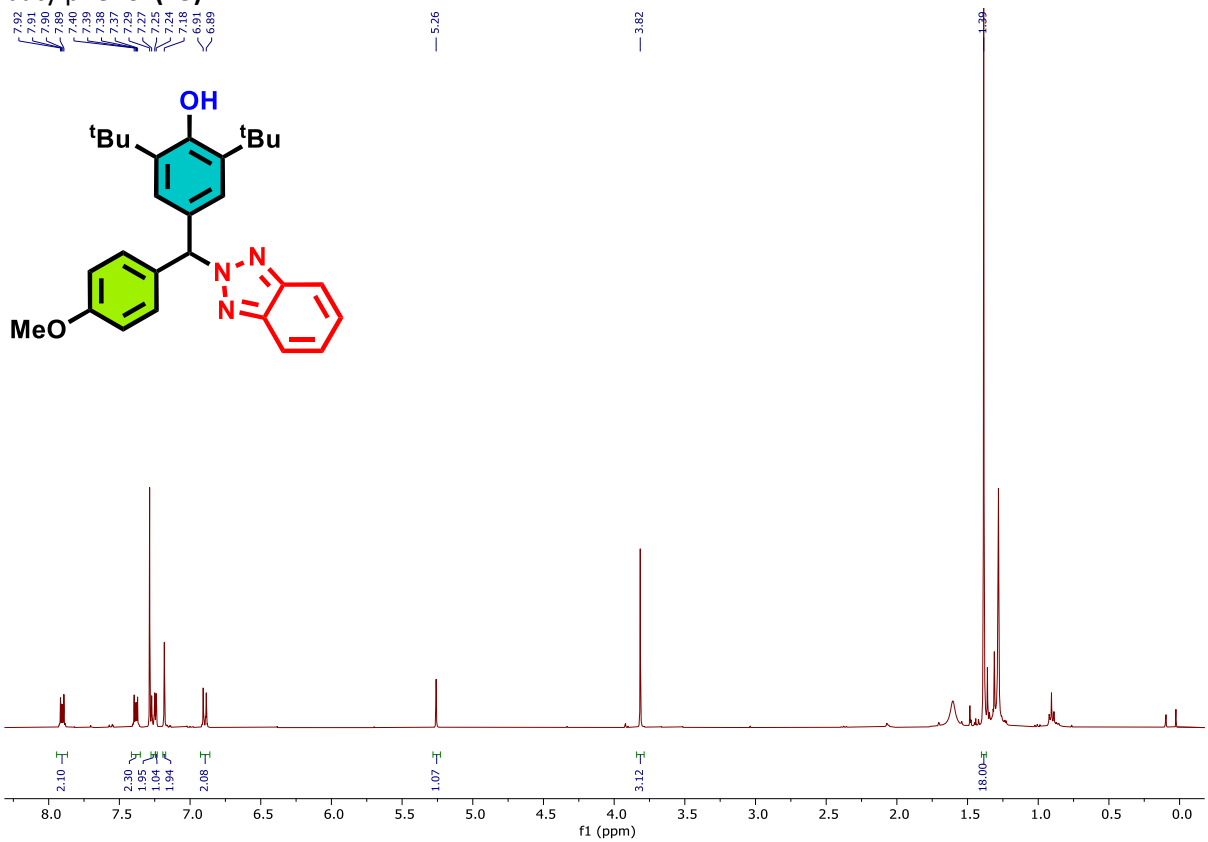
^{1}HNMR ($CDCl_3$, 400 MHz) of ethyl (E)-4-(2-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenoxy)but-2-enoate **(12)**



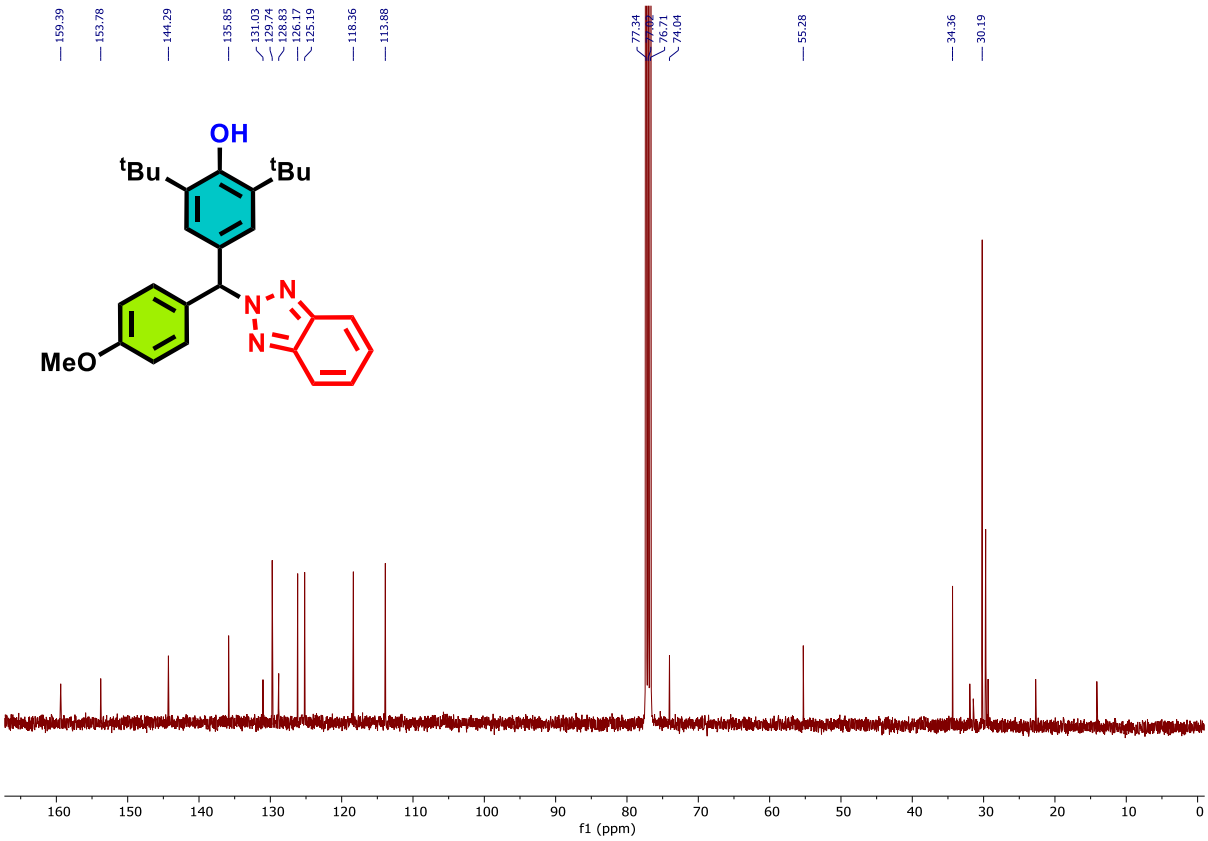
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of ethyl (E)-4-(2-((3,5-di-tert-butyl-4-hydroxyphenyl)(isopropylsulfonyl)methyl)phenoxy)but-2-enoate **(12)**



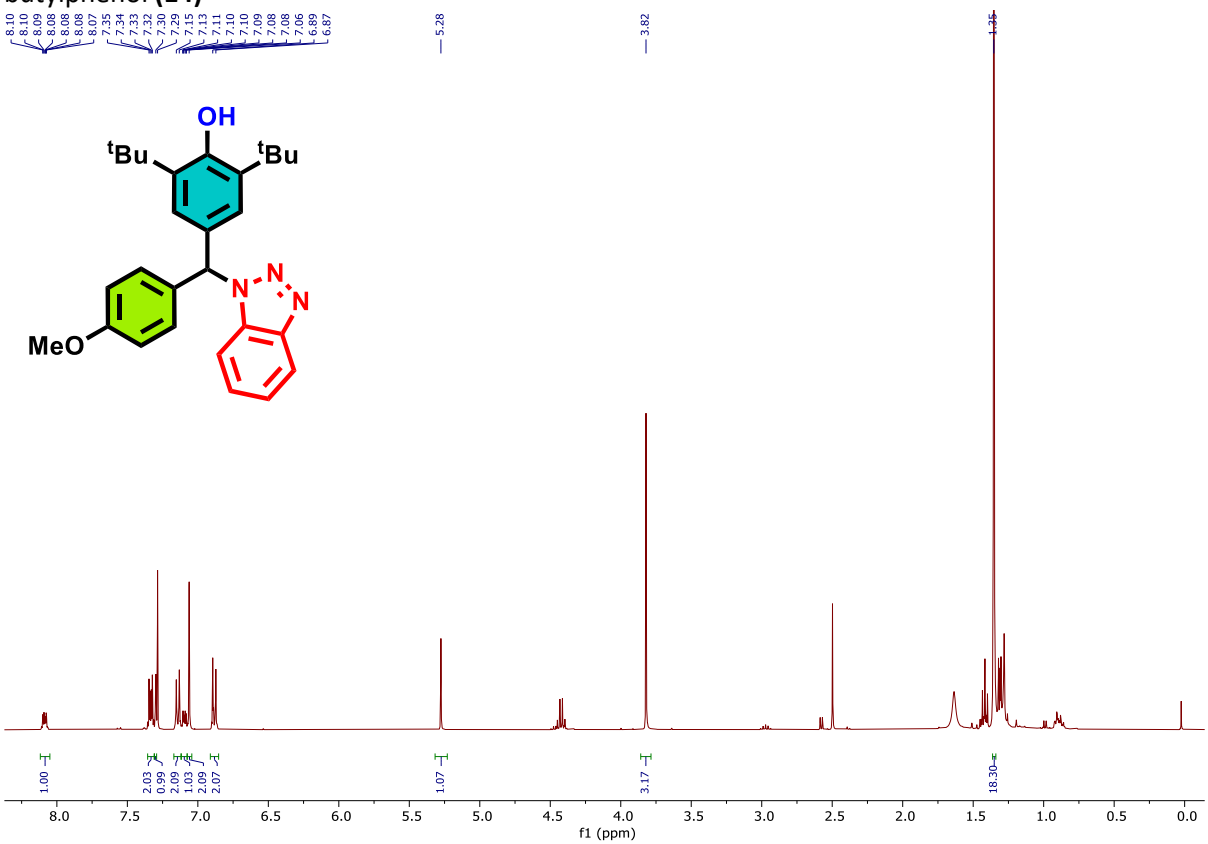
^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((2H-benzo[d][1,2,3]triazol-2-yl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol **(13)**



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((2H-benzo[d][1,2,3]triazol-2-yl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol **(13)**



^{1}HNMR ($CDCl_3$, 400 MHz) of 4-((1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol **(14)**



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of 4-((1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methyl)-2,6-di-tert-butylphenol **(14)**