Electronic Supplementary Material (ESI) for Green Chemistry.

Visible-light mediated 3-Component Synthesis of Sulfonylated Coumarins from Sulfur Dioxide

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1. General Information

Reactions

Unless otherwise mentioned, all reactions were carried out under an argon atmosphere in flame dried glassware applying standard Schlenk techniques. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR. Irradiation experiments were performed using commercially available High Power 10 W LED (white 9000-15000K from AVONEC®, maximum $\lambda_{em} \approx 458$ nm).[1] For each irradiation reaction the light source was placed ≈ 1-2 cm away from the reaction vessels. A custom-made photoreactor box with an incorporated magnetic stirrer was used with 3 interchangeable heat sinks with mounted LEDs arranged around the reactions vessels (Figure SI1). The temperature inside the box was maintained below 30 °C (internal reaction temperature ≤30 °C) with an integrated fan. Experiments under sunlight were performed in an open-air lab.

Figure S1: Pictures of the custom-made photoreactor box used for reaction performed under visible-light irradiation. Reproduced with permission from Adv. Synth. Catal. ***2017****, 359, 1308-1319. Copyright 2017 Wiley-VCH.*

Chromatography

Column chromatography was performed with Silica 60 (0.04-0.063 mm, 230-400 mesh) and the specified solvent mixture. Thin layer chromatography was performed on aluminum sheets coated with SiO_2 (TLC silica gel 60 F254). The spots were visualized by ultraviolet light.

Solvents

Solvents for reactions and column chromatography were obtained from different commercial suppliers in >97% purity and used as received. All anhydrous solvents were purchased from commercial suppliers and stored over MS 4Å under an atmosphere of argon. Solvents for column chromatography were technical standard.

Materials.

All starting materials, which were obtained from commercial sources, were used without further purification. SO_2 (sulfur dioxide 3.8) was used directly without further purification. **SO_2 is a toxic and corrosive gas! It should be handled with care only in a well-ventilated fume-hood with the necessary precaution!** 1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide) was synthesized according to a literature reports either from 1,4-diazabicyclo[2.2.2]octane and sulfur dioxide gas[2] or from 1,4-diazabicyclo[2.2.2]octane and Karl Fisher solution A.[3] Commercially available diphenyliodonium salts were purchased. Following diaryliodonium salts were synthesized according to literature: diphenyliodonium tetrafluoroborate,[4] bis(*p*-chlorophenyl)iodonium triflate,[5] bis(2,5-dimethylphenyl)iodonium triflate,[5] dimesityliodonium triflate,[5] diphenyliodonium triflate (**1a**),[5] mesitylphenyliodonium triflate (**4a**),[5] (4-methoxyphenyl)phenyliodonium triflate(**4b**),[6] (2,4,6-trimethoxyphenyl)phenyliodonium tosylate (**4d**),[7] bis(*p*-methoxyphenyl) toslyate[8] and bis(*p*-tolyl)iodonium triflate.[5]

Diphenyliodonium tosylat was prepared from salt exchange with a sat. aq. NaOTs from diphenyliodonium triflate (**1a**).[5] For the synthesis of (2-(2-propenyloxy)phenyl)(2,4,6-trimethylphenyl)iodonium tosylate (**4f**) instead of a sat. aq. solution of $NaBF_4$ a sat. aq. solution of NaOTs was used.[9] (3-trifluoromethylphenyl)(2,4,6-trimethoxyphenyl)iodonium triflate (**4e**) was synthesized by adapting the literature procedure of Stuart *et al.*[7] (2,4-Dimethoxyphenyl)phenyliodonium triflate (**4c**) was synthesized by adapting the literature protocols.[6]

Propynoates were synthesized by adapting literature procedure.[10] (3-Phenoxy-1-propyn-1-yl)benzene was synthesized by using a different procedure.[11]

Analytical Data and Instrumentation

NMR spectroscopy

Proton nuclear magnetic resonance spectra (^1H NMR), carbon spectra (^{13}C NMR) and fluorine spectra (^{19}F) were recorded at 250.13, 500.18 and 600.31 MHz (^1H), 75.44, 125.77 and 150.95 MHz (^{13}C), 282.31 and 470.64 (^{19}F), respectively. Chemical shifts are reported as δ - values relative to the residual $CDCl_3$ (δ = 7.26 ppm for ^1H and δ = 77.16 ppm for ^{13}C). Coupling constants (J) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q =

quintet; sextet = sextet; m = multiplet; dd = doublet of doublets, td = triplets of doublets; ddd = doublets of doublets of doublets and ddt = doublet of doublets of triplets.

Melting points

Melting points are reported uncorrected. The solvent given in brackets after the melting points is the last solvent the compound was treated with (e.g. for transfer of the compound into a smaller flask).

Mass spectrometry

Mass spectra (MS) were measured using electrospray ionization (ESI) techniques. High resolution mass spectra (HRMS) were measured using matrix-assisted laser desorption/ionization (MALDI) techniques.

UV-Vis spectroscopy

UV-Vis Spectra were recorded at 20 °C.

Infrared spectroscopy.

Infrared spectra (IR) of neat substances were recorded on a FT-IR (Fourier transform infrared spectroscopy) spectrometer equipped with a diamond universal ATR sampling technique (attenuated total reflectance). The absorption bands are reported in wave numbers (cm^{-1}) and classified in weak (w), medium (m) and strong (s).

Crystal structure determination

Data were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK_α radiation (λ = 0.71073 Å) and were scaled using the frame scaling procedure in the *X-AREA* program system.

The structures were solved by direct methods using the program *SHELXS* and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL.*

The absolute structure for both structures was determined by refinement of the Flack parameter,

0.08(6) for ma108 (**7e**) and -0.05(14) for ma109 (**7d**).

CCDC files 1578047 and 1578048 contain the supplementary crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

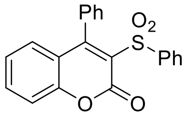
2. General procedures

TP1: Typical Procedure for visible-light induced sulfone synthesis from diaryliodonium salts, DABSO and aryl propynoate.

A 10-mL tube was charged with a magnetic stirring bar, propynoate (0.3 mmol, 1 equiv.), DABSO (144 mg, 0.600 mmol, 2.00 equiv.), diaryliodonium salt (0.36 mmol, 1.2 equiv.) and MeOH (2 mL). The tube was closed with a rubber septum. After 5 min of nitrogen sparging, the resulting reaction mixture was irradiated (9000-15000K, white light) for 8 h at ambient temperature. After the completion of the reaction, the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel (*n*-hexane/EtOAc) to afford the analytically pure product.

3. Experimental procedures and Analytical Data

4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (3a)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (94 mg, 87%).

Analytical data are consistent with the literature.[12]

R$_f$ = 0.6 (*n*-hexane/EtOAc 7:3)

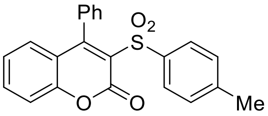
m.p. = 189-191 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) δ 8.05–7.98 (m, 2H), 7.68–7.56 (m, 3H), 7.55–7.46 (m, 1H), 7.40–7.31 (m, 2H), 7.23–7.15 (m, 1H), 7.03 (dd, *J* = 8.0, 1.5 Hz, 1H) ppm.

^{13}C NMR (75.44 MHz, CDCl$_3$) δ 159.7, 155.7, 154.0, 140.4, 134.8, 133.8, 132.7, 130.1, 129.4, 129.3, 128.8, 128.3, 127.6, 126.1, 125.0, 120.4, 116.9 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{15}O_4S_1$ [M+H]$^+$ = 363.07; found: 363.07.

4-phenyl-3-tosyl-2H-chromen-2-one (3b)



Prepared from di(*p*-tolyl)iodonium triflate (166 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a light white solid (100 mg, 89%).

Analytical data are consistent with the literature.[12]

R$_f$ = 0.6 (*n*-hexane/EtOAc 7:3)

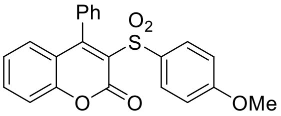
m.p. = 162-165 °C (decomp., DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) δ 7.93–7.84 (m, 2H), 7.65–7.53 (m, 4H), 7.39–7.27 (m, 5H), 7.22–7.14 (m, 1H), 7.01 (dd, *J* = 8.1, 1.4 Hz, 1H), 2.41 (s, 3H) ppm.

^{13}C NMR (75.44 MHz, $CDCl_3$) δ 159.3, 155.7, 154.0, 144.9, 137.4, 134.7, 132.8, 130.1, 129.4, 129.4, 129.4, 128.3, 127.6, 126.4, 124.9, 120.4, 116.9, 21.8 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{17}O_4S_1$ $[M+H]^+$ = 377.08; found: 377.02.

3-((4-methoxyphenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3c)



Prepared from di(*p*-methoxyphenyl)liodonium triflate (184 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a light white solid (107 mg, 91%).

R$_f$ = 0.4 (*n*-hexane/EtOAc 7:3)

m.p. = 197-198 °C (decomp., DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.00–7.89 (m, 2H), 7.67–7.53 (m, 4H), 7.40–7.30 (m, 3H), 7.24–7.13 (m, 2H), 7.04–6.89 (m, 3H), 3.86 (s, 3H) ppm.

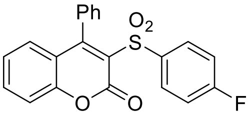
^{13}C NMR (75.44 MHz, $CDCl_3$) δ 164.0, 158.8, 155.8, 153.9, 134.6, 132.9, 131.8, 131.8, 130.0, 129.3, 128.3, 127.6, 126.6, 124.9, 120.5, 116.9, 114.0, 55.8 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{17}O_5S_1$ $[M+H]^+$ = 393.08; found: 393.01.

HRMS: m/z calcd. for $C_{22}H_{17}O_5S_1$ $[M+H]^+$ = 393.07912; found: 393.07877.

IR (cm^{-1}) 1744 (s), 1602 (w), 1322 (s), 1260 (s), 1019 (m), 830 (s), 802 (s), 701 (s), 556 (s), 542 (s).

3-((4-fluorophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3d)



Prepared from di(*p*-fluorophenyl)iodonium triflate (168 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (86 mg, 76%).

Analytical data are consistent with the literature.[12]

R$_f$ = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 164-165 °C (DCM)

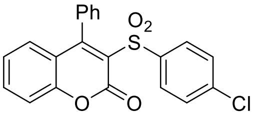
^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.09–7.96 (m, 2H), 7.69 – 7.53 (m, 4H), 7.40–7.29 (m, 3H), 7.24–7.11 (m, 3H), 7.03 (dd, *J* = 8.3, 1.5 Hz, 1H) ppm.

^{13}C NMR (125.77 MHz, $CDCl_3$) δ 166.0 (d, *J* = 256.5 Hz), 164.3, 159.8, 155.7, 154.0, 136.3 (d, *J* = 3.1 Hz), 135.0, 132.6, 132.4 (d, *J* = 9.7 Hz), 130.1, 129.5, 128.4, 127.6, 126.0, 125.1, 120.3, 117.0, 116.2, 115.9 ppm.

^{19}F NMR (282.31 MHz, $CDCl_3$) δ -103.4 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{14}F_1O_4S_1$ $[M+H]^+$ = 381.06; found: 380.84.

3-((4-chlorophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3e)



Prepared from di(*p*-chlorophenyl)iodonium triflate (180 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (100 mg, 84%).

Analytical data are consistent with the literature.[12]

R_f = 0.6 (*n*-hexane/EtOAc 7:3)

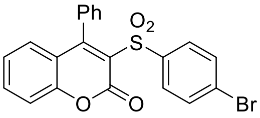
m.p. = 195-196 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2H), 7.67–7.55 (m, 4H), 7.50–7.43 (m, 2H), 7.38 – 7.30 (m, 2H), 7.24–7.17 (m, 1H), 7.04 (dd, *J* = 8.1, 1.6 Hz, 1H) ppm.

^{13}C NMR (75.44 MHz, $CDCl_3$) δ 160.0, 155.7, 154.1, 140.6, 138.8, 135.0, 132.5, 130.9, 130.2, 129.6, 129.1, 128.4, 127.6, 125.8, 125.1, 120.3, 117.0 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{14}Cl_1O_4S_1$ $[M+H]^+$ = 397.03; found: 396.94.

3-((4-bromophenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3f)



Prepared from di(*p*-bromophenyl)iodonium triflate (212 mg, 0.360 mmol, 1.2 equiv.) and phenyl phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (98 mg, 75%).

Analytical data are consistent with the literature.[12]

R$_f$ = 0.5 (*n*-hexane/EtOAc 7:3)

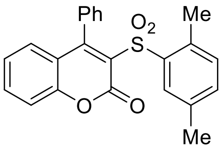
m.p. = 188-190 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) *δ* 7.92–7.80 (m, 2H), 7.69–7.53 (m, 6H), 7.39–7.31 (m, 3H), 7.24–7.16 (m, 1H), 7.04 (dd, *J* = 8.0, 1.5 Hz, 1H) ppm.

^{13}C NMR (75.44 MHz, CDCl$_3$) *δ* 160.0, 155.7, 154.1, 139.3, 135.1, 132.5, 132.1, 131.9, 130.1, 129.6, 129.3, 128.4, 127.6, 125.7, 125.1, 120.3, 117.0 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{14}Br_1O_4S_1$ $[M+H]^+$ = 442.98; found: 442.77.

3-((2,5-dimethylphenyl)sulfonyl)-4-phenyl-2H-chromen-2-one (3g)



Prepared from di(2,4-dimethylphenyl)liodonium triflate (166 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a,** 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (77 mg, 66%).

R$_f$ = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 209-210 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) *δ* 7.85 (d, *J* = 1.3 Hz, 1H), 7.68–7.58 (m, 1H), 7.57–7.49 (m, 3H), 7.42–7.32 (m, 3H), 7.25–7.17 (m, 2H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H) ppm.

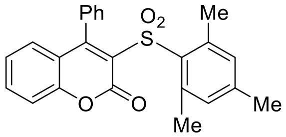
^{13}C NMR (75.44 MHz, CDCl$_3$) *δ* 159.2, 155.5, 154.1, 138.5, 136.1, 134.6, 134.3, 134.2, 132.1, 131.2, 129.8, 129.6, 128.3, 128.3, 126.2, 125.0, 120.2, 117.1, 21.0, 19.7 ppm.

MS (ESI): m/z calcd. for $C_{23}H_{19}O_4S_1$ $[M+H]^+$ = 391.10; found: 390.90.

HRMS: m/z calcd. for $C_{23}H_{19}O_4S_1$ $[M+H]^+$ = 391.09986; found: 391.09945.

IR (cm^{-1}) 2911 (w), 1723 (m), 1603 (m), 1313 (m), 1155 (m), 757 (s), 697 (s), 596 (s), 572 (s), 519 (s).

3-(mesitylsulfonyl)-4-phenyl-2H-chromen-2-one (3h)



Prepared from dimesityliodonium triflate (171 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (40 mg, 33%).

R_f = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 234-235°C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 7.67–7.52 (m, 4H), 7.42–7.32 (m, 3H), 7.26–7.12 (m, 2H), 6.88 (s, 2H), 2.59 (s, 6H), 2.26 (s, 3H) ppm.

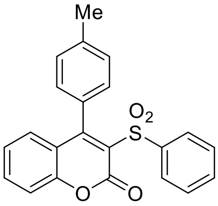
^{13}C NMR (75.44 MHz, $CDCl_3$) δ 157.6, 157.1, 155.9, 154.0, 143.1, 140.0, 135.0, 134.3, 132.1, 132.0, 129.7, 129.7, 128.4, 128.3, 127.9, 125.0, 120.1, 117.1, 22.3, 21.2 ppm.

MS (ESI): m/z calcd. for $C_{24}H_{21}O_4S_1$ $[M+H]^+$ = 405.12; found: 404.90.

HRMS: m/z calcd. for $C_{24}H_{21}O_4S_2$ $[M+H]^+$ = 405.11551; found: 405.11504.

IR (cm^{-1}) 2982 (w), 1729 (s), 1321 (s), 1151 (s), 991 (m), 757 (s), 669 (s), 640 (s), 597 (s), 513 (s).

3-(Phenylsulfonyl)-4-*p*-tolyl-2*H*-chromen-2-one (3l)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-(*p*-tolyl)propynoate (71 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (108 mg, 96%).

Analytical data are inconsistent with the literature.[13]

R_f = 0.4 (*n*-hexane/EtOAc 7:3)

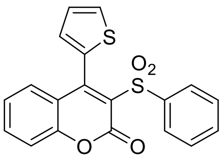
m.p. = 202-203 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.05–7.97 (m, 2H), 7.65–7.56 (m, 2H), 7.54–7.45 (m, 2H), 7.42–7.30 (m, 3H), 7.26–7.15 (m, 3H), 7.08 (dd, *J* = 8.1, 1.6 Hz, 1H), 2.50 (s, 3H) ppm.

^{13}C NMR (75.44 MHz, $CDCl_3$) δ 160.1, 155.8, 154.0, 140.5, 139.5, 134.7, 133.8, 130.2, 129.7, 129.3, 129.1, 128.7, 127.6, 126.1, 124.9, 120.5, 116.9, 21.7 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{17}O_4S_1$ $[M+H]^+$ = 377.08; found: 376.86.

3-(phenylsulfonyl)-4-(thiophen-2-yl)-2H-chromen-2-one (3m)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-(thiophen-2-yl)propynoate (69 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (26 mg, 24%).

R$_f$ = 0.4 (*n*-hexane/EtOAc 7:3)

m.p. = 186-188 °C (DCM)

^{1}H NMR (600.31 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 4.8 Hz, 1H), 7.65–7.58 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.21 (m, 3H) ppm.

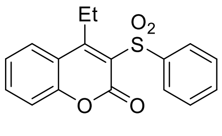
^{13}C NMR (150.95 MHz, $CDCl_3$) δ 155.4, 153.7, 153.4, 140.3, 135.0, 133.9, 130.9, 129.8, 129.7, 129.4, 128.8, 128.4, 127.4, 125.2, 120.7, 116.9 ppm.

MS (ESI): m/z calcd. for $C_{19}H_{12}O_4S_2$ $[M+H]^+$ =369.03; found: 368.81.

HRMS: m/z calcd. for $C_{19}H_{12}O_4S_2$ $[M+H]^+$ = 369.02498; found: 369.02515.

IR (cm^{-1}) 2982 (w), 1739 (s), 1307 (m), 1159 (s), 738 (m), 708 (s), 682 (s), 634 (s), 608 (s), 562 (s).

4-ethyl-3-(phenylsulfonyl)-2H-chromen-2-one (3n)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl pent-2-ynoate (52 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (36 mg, 38%).

R$_f$ = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 151-152 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) δ 8.14–8.05 (m, 1H), 7.90 (dd, J = 8.3, 1.5 Hz, 1H), 7.67–7.57 (m, 1H), 7.56–7.47 (m, 1H), 7.43–7.35 (m, 1H), 7.29 (dd, J = 8.3, 1.0 Hz, 1H), 3.69 (q, J = 7.5 Hz, 2H), 1.53 (t, J = 7.5 Hz, 3H) ppm.

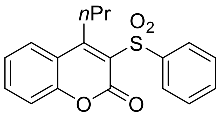
^{13}C NMR (75.44 MHz, CDCl$_3$) δ 163.9, 155.6, 154.0, 141.0, 134.6, 133.7, 128.8, 128.8, 126.7, 125.5, 125.2, 118.5, 117.6, 21.6, 15.6 ppm.

MS (ESI): m/z calcd. for $C_{17}H_{15}O_4S_1$ $[M+H]^+$ = 315.07; found: 315.08.

HRMS: m/z calcd. for $C_{17}H_{15}O_4S_1$ $[M+H]^+$ = 315.06856; found: 315.06848.

IR (cm^{-1}) 2979 (w), 1733 (m), 1598 (m), 1544 (m), 1308 (m), 1151 (m), 759 (s), 631 (s), 563 (s), 541 (s).

4-Propyl-3-(phenylsulfonyl)-2H-chromen-2-one (3o)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and phenyl hexyl-2-ynoate (56 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (38 mg, 39%).

R$_f$ = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 118-120 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) δ 8.13–8.03 (m, 2H), 7.86 (d, J = 8.2 Hz, 1H), 7.70–7.46 (m, 4H), 7.42–7.34 (m, 1H), 7.32–7.22 (m, 1H), 3.75–3.41 (m, 2H), 1.89 (sextet, J = 7.3 Hz, 1H), 1.23 (t, J = 7.4 Hz, 2H) ppm.

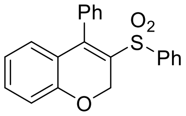
^{13}C NMR (75.44 MHz, CDCl$_3$) δ 162.6, 155.6, 153.9, 141.1, 134.6, 133.7, 128.8, 126.7, 125.6, 125.2, 118.9, 117.6, 30.0, 25.2, 14.9 ppm.

MS (ESI): m/z calcd. for $C_{18}H_{17}O_2S_1$ $[M+H]^+$ = 329.08; found: 329.09.

HRMS: m/z calcd. for $C_{18}H_{17}O_2S_1$ $[M+H]^+$ = 329.08421; found: 329.08428.

IR (cm^{-1}) 2965 (w), 1718 (s), 1534 (s), 1319 (m), 1157 (s), 716 (s), 628 (s), 567 (s), 550 (s), 539 (s).

4-phenyl-3-(phenylsulfonyl)-2H-chromene (3p)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (62 mg, 0.30 mmol, 1.0 equiv.) and isolated as a colourless oil (12 mg, 11%).

Analytical data are consistent with the literature.[13]

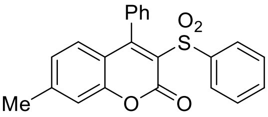
R$_f$ = 0.7 (*n*-hexane/EtOAc 7:3)

^{1}H NMR (250.13 MHz, CDCl$_3$) δ 7.53–7.44 (m, 3H), 7.42–7.29 (m, 5H), 7.28–7.20 (m, 2H), 7.06–6.97 (m, 2H), 6.92 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.80 (td, *J* = 7.6, 1.1 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.22 (s, 2H) ppm.

^{13}C NMR (75.44 MHz, CDCl$_3$) δ 155.0, 145.5, 141.5, 133.4, 133.2, 132.6, 129.8, 129.1, 128.9, 128.8, 128.6, 128.5, 128.0, 127.6, 124.3, 122.1, 116.4, 64.4 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{17}O3S_1$ $[M+Na]^+$ = 371.07; found: 371.02.

7-methyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7a)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-tolyl 3-phenylpropynoate (71 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (101 mg, 90%).

Analytical data are inconsistent with the literature.[13]

R$_f$ = 0.4 (*n*-hexane/EtOAc 7:3)

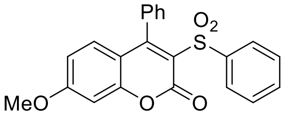
m.p. = 219-220 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) δ 8.05–7.96 (m, 2H), 7.64–7.54 (m, 4H), 7.49 (ddd, *J* = 8.5, 2.6, 1.1 Hz, 2H), 7.38–7.29 (m, 2H), 7.14 (s, 1H), 6.99 (ddd, *J* = 8.4, 1.6, 0.5 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 2.44 (s, 3H) ppm.

^{13}C NMR (75.44 MHz, CDCl$_3$) δ 159.8, 156.0, 154.2, 147.0, 140.6, 133.7, 132.1, 129.8, 129.3, 129.3, 128.7, 128.3, 127.6, 126.3, 124.8, 118.0, 117.0, 22.0 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{17}O_4S_1$ $[M+H]^+$ = 377.08; found: 376.88.

7- methoxy -4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7b)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-anisyl 3-phenylpropynoate (76 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (40 mg, 34%).

Analytical data are consistent with the literature.[13]

R

R_f = 0.3 (*n*-hexane/EtOAc 7:3)

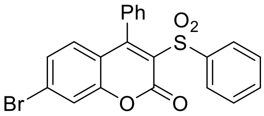
m.p. = 210-212 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.05–7.96 (m, 2H), 7.63–7.53 (m, 4H), 7.53–7.44 (m, 2H), 7.37–7.28 (m, 2H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.73 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.87 (s, 1H) ppm.

^{13}C NMR (75.44 MHz, $CDCl_3$) δ 165.4, 159.9, 156.3, 156.2, 140.8, 133.6, 133.1, 131.4, 129.3, 129.2, 128.7, 128.2, 127.6, 122.5, 113.8, 113.7, 100.4, 56.2 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{17}O_5S_1$ $[M+H]^+$ = 393.08; found: 392.87.

7-bromo-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7c)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-bromophenyl 3-phenylpropynoate (90 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (97 mg, 74%).

R_f = 0.7 (*n*-hexane/EtOAc 7:3)

m.p. = 239-240 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.03–7.94 (m, 2H), 7.65–7.56 (m, 4H), 7.55–7.47 (m, 3H), 7.37–7.28 (m, 3H), 6.87 (d, *J* = 8.5 Hz, 1H) ppm.

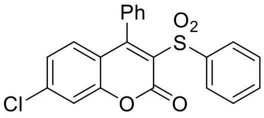
^{13}C NMR (75.44 MHz, $CDCl_3$) δ 159.0, 155.1, 154.0, 140.1, 134.0, 132.3, 131.0, 129.7, 129.5, 129.3, 128.8, 128.6, 128.5, 127.5, 126.2, 120.2, 119.4 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{14}Br_1O_4S_1$ $[M+H]^+$ = 442.98; found: 442.78.

HRMS: m/z calcd. for $C_{21}H_{14}Br_1O_4S_1$ $[M+H]^+$ = 440.97907; found: 440.97877.

IR (cm^{-1}) 1735 (w), 1583 (w), 1170 (w), 1152 (m), 988 (w), 777 (m), 761 (m), 688 (s), 607 (s), 556 (s).

7-chloro-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7d)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 4-chlorophenyl 3-phenylpropynoate (77 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (63 mg, 53%).

R_f = 0.7 (*n*-hexane/EtOAc 7:3)

m.p. = 235-236 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.03–7.95 (m, 2H), 7.66–7.56 (m, 4H), 7.55–7.45 (m, 2H), 7.38–7.29 (m, 3H), 7.16 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H) ppm.

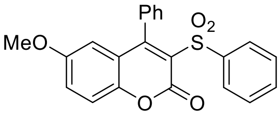
^{13}C NMR (75.44 MHz, $CDCl_3$) δ 158.9, 155.2, 154.2, 141.2, 140.2, 133.9, 132.3, 131.0, 129.7, 129.4, 128.8, 128.4, 127.5, 126.0, 125.7, 119.0, 117.2 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{14}Cl_1O_4S_1$ $[M+H]^+$ = 397.03; found: 396.81.

HRMS: m/z calcd. for $C_{21}H_{14}Cl_1O_4S_1$ $[M+H]^+$ = 397.02958; found: 397.02918.

IR (cm^{-1}) 2982 (w), 1731 (m), 1320 (m), 1156 (m), 1088 (w), 1005 (m), 683 (s), 575 (s), 551 (s), 512 (s).

6-methoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7e)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-anisyl 3-phenylpropynoate (76 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (103 mg, 88%).

R_f = 0.3 (*n*-hexane/EtOAc 7:3)

m.p. = 217-218 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.01–7.93 (m, 2H), 7.60–7.50 (m, 4H), 7.50–7.41 (m, 2H), 7.35–7.28 (m, 1H), 7.22 (s, 1H), 7.15 (dd, J = 9.1, 2.9 Hz, 1H), 6.37 (d, J = 2.8 Hz, 1H), 3.58 (s, 2H) ppm.

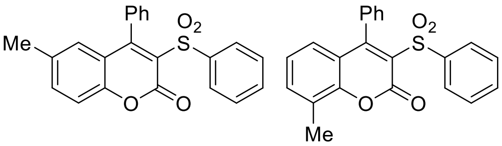
^{13}C NMR (75.44 MHz, $CDCl_3$) δ 159.4, 156.3, 155.9, 148.6, 140.4, 133.8, 132.8, 129.5, 129.3, 128.8, 128.4, 127.5, 126.3, 122.4, 120.8, 118.0, 112.2, 55.8 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{17}O_5S_1$ $[M+H]^+$ = 393.08; found: 392.88.

HRMS: m/z calcd. for $C_{22}H_{17}O_5S_1$ $[M+H]^+$ = 393.07912; found: 393.07859.

IR (cm^{-1}) 2982 (w), 1723 (m), 1156 (m), 1026 (m), 818 (m), 778 (s), 687 (s), 579 (s), 556, (s), 548 (s).

6-methyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7f) and 8-methyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7f’)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-tolyl 3-phenylpropynoate (71 mg, 0.30 mmol, 1.0 equiv.) and isolated as a waxy, low-melting white solid in a 5:1 ratio (96 mg, 86%).

Analytical data are inconsistent with the literature.[13]

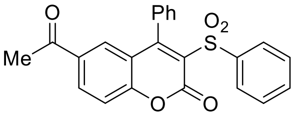
R_f = 0.5 (*n*-hexane/EtOAc 7:3)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.04–7.97 (m), 7.65–7.53 (m), 7.54–7.46 (m), 7.42 (dd, J = 8.5, 2.0 Hz), 7.36–7.31 (m), 7.24 (d, J = 8.5 Hz), 7.08 (t, J = 7.8 Hz), 6.85 (d, J = 8.0 Hz), 6.77 (d, J = 1.3 Hz), 2.43 (s), 2.26 (s) ppm.

^{13}C NMR (75.44 MHz, $CDCl_3$) δ 159.7, 155.9, 152.3, 140.5, 136.1 136.0, 134.9, 133.7, 133.0, 132.8, 129.5, 129.4, 129.3, 129.3, 128.7, 128.7, 128.3, 128.2 127.8, 127.7 127.6 125.9, 124.4, 120.1, 116.7, 21.1, 15.5 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{17}O_4S_1$ $[M+H]^+$ = 377.08; found: 376.85.

6-acetyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7g)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-acetylphenyl 3-phenylpropynoate (**1a**, 79 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (43 mg, 30%).

R$_f$ = 0.3 (*n*-hexane/EtOAc 7:3)

m.p. = 260-263 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) *δ* 8.04 (dd, *J* = 7.3, 2.3 Hz, 1H), 8.01–7.96 (m, 2H), 7.65–7.44 (m, 6H), 7.36–7.29 (m, 2H), 7.25–7.13 (m, 2H) 2.77 (s, 3H) ppm.

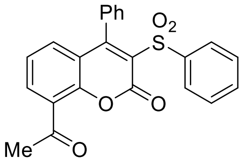
^{13}C NMR (75.44 MHz, CDCl$_3$) *δ* 196.5, 159.4, 154.5, 152.4, 140.1, 135.7, 134.3, 134.1, 132.4, 129.7, 129.4, 128.9, 128.5, 127.6, 127.5, 126.3, 124.7, 121.1, 32.2 ppm.

MS (ESI): m/z calcd. for $C_{23}H_{16}O_5S_1$ $[M+H]^+$ = 405.08; found: 404.86.

HRMS: m/z calcd. for $C_{23}H_{16}O_5S_1$ $[M+H]^+$ = 405.07912; found: 405.07913.

IR (cm^{-1}) 2923 (w), 1735 (s), 1315 (s), 1271 (s), 1153 (s), 717 (s), 689 (s), 634 (s), 561 (s), 552 (s).

8-acetyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7g')



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 3-acetylphenyl 3-phenylpropynoate (79 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (39 mg, 28%).

R$_f$ = 0.2 (*n*-hexane/EtOAc 7:3)

m.p. = 277-280 °C (DCM)

^{1}H NMR (250.13 MHz, CDCl$_3$) *δ* 8.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.05–7.97 (m, 2H), 7.66–7.58 (m, 5H), 7.56–7.48 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.39–7.33 (m, 2H), 2.42 (s, 3H) ppm.

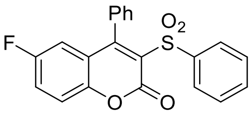
^{13}C NMR (75.44 MHz, CDCl$_3$) *δ* 195.5, 159.3, 156.6, 155.0, 140.0, 134.1, 134.0, 133.9, 131.9, 130.8, 129.9, 129.4, 128.9, 128.6, 127.6, 127.0, 120.3, 117.5, 26.4 ppm.

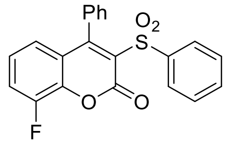
MS (ESI): m/z calcd. for $C_{23}H_{16}O_5S_1$ $[M+H]^+$ = 405.08; found:404.89.

HRMS: m/z calcd. for $C_{23}H_{16}O_5S_1$ $[M+H]^+$ = 405.07912; found:405.07930.

IR (cm^{-1}) 1730 (w), 1685 (w), 1151 (m), 782 (w), 714 (w), 690 (w), 593 (m), 566 (s), 549 (s), 453 (w).

8-fluoro-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7h) and 6-fluoro-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7h')





Prepared from diphenyliodonium triflate (155 mg, 0.360 mmol, 1.2 equiv.) and 3-fluorophenyl 3-phenylpropynoate (72 mg, 0.30 mmol, 1.0 equiv.) and isolated as an inseparable waxy, low-melting solid in a 7.5:1 ratio (93 mg, 82%).

$\mathbf{R_f}$ = 0.4 (*n*-hexane/EtOAc 7:3)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.07–7.96 (m), 7.68–7.56 (m), 7.56–7.45 (m), 7.43–7.30 (m), 7.12 (td, J = 8.2, 4.7 Hz), 6.81 (dt, J = 8.3, 1.4 Hz), 6.69 (dt, J = 8.8, 1.7 Hz) ppm.

^{13}C NMR (75.44 MHz, $CDCl_3$) δ 160.5, 158.7, 158.7, 157.2, 155.4, 150.2, 150.2, 140.1, 134.0, 132.4, 132.2, 129.8, 129.6, 129.4, 128.8, 128.6, 128.4, 127.6, 127.5, 127.1, 125.2, 124.5, 122.6, 122.3, 121.4, 121.3, 118.7, 118.6, 115.5, 115.1 ppm.

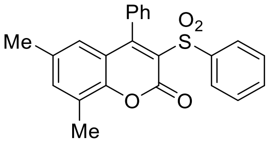
^{19}F NMR (470.64 MHz, $CDCl_3$) δ -115.1, 132.7 ppm.

MS (ESI): m/z calcd. for $C_{21}H_{14}F_1O_4S_1$ $[M+H]^+$ = 381.06; found: 380.85.

HRMS: m/z calcd. for $C_{21}H_{14}F_1O_4S_1$ $[M+H]^+$ = 381.05913; found: 381.05850.

IR (cm^{-1}) 3074 (w), 1734 (m), 1311 (m), 1155 (m), 1082 (m), 839 (m), 716 (s), 682 (s), 555 (s), 539 (s).

6,8-dimethyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one (7i)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and 3,5-dimethylphenyl 3-phenylpropynoate (75 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (110 mg, 94%).

$\mathbf{R_f}$ = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 204-205 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.04–7.97 (m, 2H), 7.64–7.45 (m, 6H), 7.38–7.27 (m, 3H), 6.60 (s, 1H), 2.39 (s, 3H), 2.21 (s, 3H) ppm.

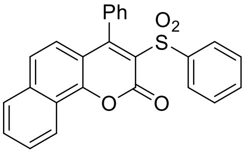
^{13}C NMR (75.44 MHz, $CDCl_3$) δ 160.0, 156.0, 150.7, 140.6, 137.4, 134.2, 133.7, 133.0, 129.3, 129.3, 128.7, 128.2, 127.7, 127.3, 126.2, 125.5, 124.8, 119.9, 21.0, 15.5 ppm.

MS (ESI): m/z calcd. for $C_{23}H_{19}O_4S_1$ $[M+H]^+$ = 391.10; found: 390.99.

HRMS: m/z calcd. for $C_{23}H_{19}O_4S_1$ $[M+H]^+$ = 391.09986; found: 391.09961.

IR (cm^{-1}) 3066 (w), 1727 (m), 1323 (m), 1152 (m), 779 (s), 701 (m), 646 (m), 599 (m), 571 (s), 552 (s).

4-phenyl-3-(phenylsulfonyl)-2*H*-benzo[*h*]chromen-2-one (7j)



Prepared from diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.2 equiv.) and naphthalen-2-yl 3-phenylpropynoate (82 mg, 0.30 mmol, 1.0 equiv.) and isolated as a white solid (85 mg, 69%).

R$_f$ = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 259-260 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 7.92–7.80 (m, 2H), 7.69–7.53 (m, 6H), 7.38–7.31 (m, 3H), 7.24–7.17 (m, 1H), 7.04 (dd, *J* = 8.0, 1.05 Hz, 1H) ppm.

^{13}C NMR (75.44 MHz, $CDCl_3$) δ 160.5, 155.8, 152.4, 140.5, 136.1, 133.8, 133.2, 130.6, 129.4, 129.3, 128.8, 128.4, 127.9, 127.9, 127.6, 125.1, 124.8, 123.7, 123.4, 122.5, 115.5 ppm.

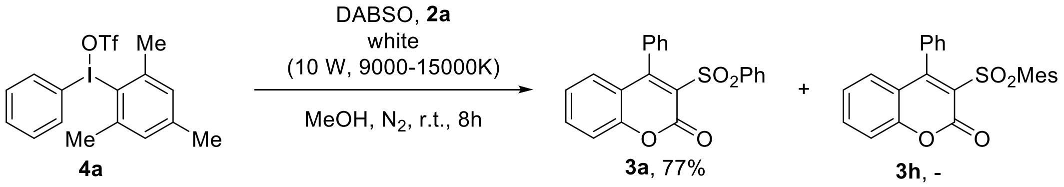
MS (ESI): m/z calcd. for for $C_{25}H_{17}O_4S_1$ $[M+H]^+$ = 413.08; found: 412.88.

HRMS: m/z calcd. for $C_{25}H_{17}O_4S_1$ $[M+H]^+$ = 413.08421; found: 413.08404.

IR (cm^{-1}) 2982 (w), 1735 (m), 1537 (m), 1155 (m), 1142 (m), 766 (s), 689 (m), 592 (s), 560 (s), 518 (s).

4. Selectivity studies

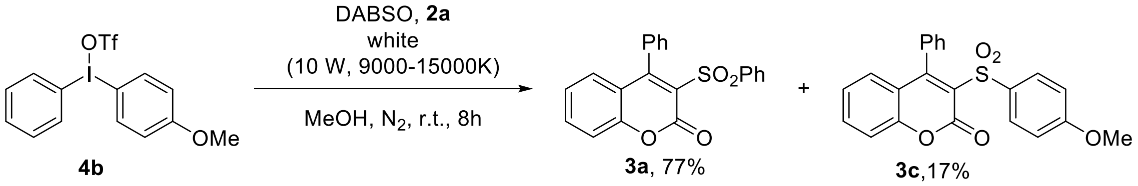
4.1 Selectivity studies with sterically differentiated diaryliodonium salts



Prepared from mesitylphenyliodonium triflate (**4a,** 142 mg, 0.300 mmol, 1.00 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (**2a**, 62 mg, 0.30 mmol, 1.0 equiv.). **3a** was isolated as a white solid (83 mg, 77%).

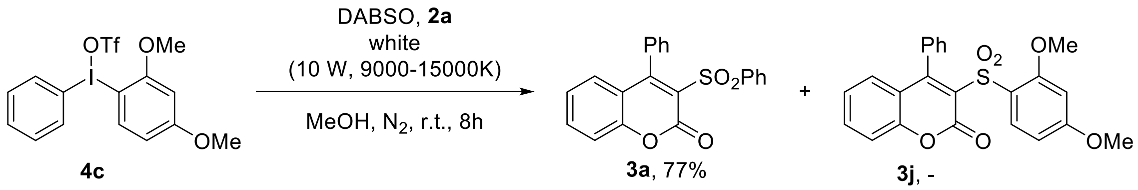
Analytical data of **3a** are in agreement with the data of **3a** prepared from the corresponding symmetrical iodonium salt (see page 5).[12]

4.2 Selectivity studies with methoxybenzenes



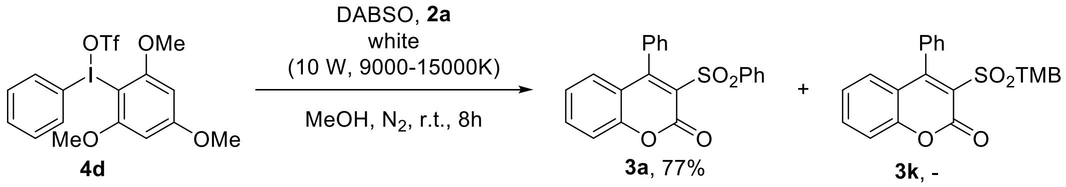
Prepared from (4-methoxyphenyl)phenyliodonium triflate (**4b**, 166 mg, 0.360 mmol, 1.2 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (**2a**, 62 mg, 0.30 mmol, 1.0 equiv.). **3a** (71 mg, 66%) and **3c** (24 mg, 17%) were isolated as white solids.

Analytical data of **3a** and **3c** are in agreement with the data of **3a** and **3c** prepared from the corresponding symmetrical iodonium salts (see page 5 and 6) and with the literature.[12]



Prepared from (2,4-dimethoxyphenyl)phenyliodonium triflate (**4c**, 147 mg, 0.36 mmol, 1.20 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (**2a**, 62 mg, 0.30 mmol, 1.0 equiv.). **3a** was isolated as white solids (70 mg, 65%).

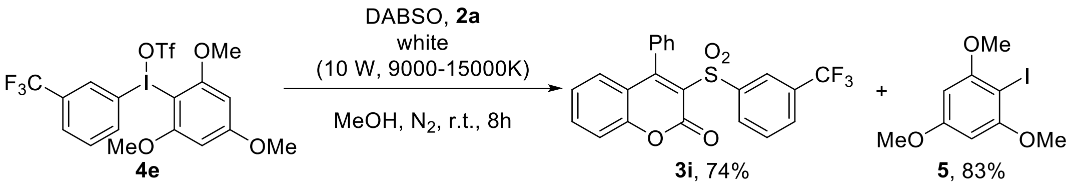
Analytical data of **3a** are in agreement with the data of **3a** prepared from the corresponding symmetrical iodonium salt (see page 5) and with the literature.[12]



Prepared from (2,4-dimethoxyphenyl)phenyliodonium triflate (**4d**, 195 mg, 0.360 mmol, 1.20 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (**2a**, 62 mg, 0.30 mmol, 1.0 equiv.). **3a** was isolated as white solids (94 mg, 87%).

Analytical data of **3a** are in agreement with the data of **3a** prepared from the corresponding symmetrical iodonium salt (see page 5) and with the literature.[12]

4.3 Selectivity studies with electronically differentiated diaryliodonium salts



Prepared from (2,4,6-trimethoxyphenyl)(3-trifluoromethylpheny)liodonium triflate (**4e**, 183 mg, 0.300 mmol, 1.20 equiv.) and (3-phenoxyprop-1-yn-1-yl)benzene (**2a**, 62 mg, 0.30 mmol, 1.0 equiv.). **3i** (95 mg, 74%) and **5** (73 mg, 83%) were isolated as white solids.

Analytical Data of **3i**

R_f = 0.3 (*n*-hexane/EtOAc 7:3)

m.p. = 202-203 °C (DCM)

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 1H), 8.20 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.72–7.57 (m, 5H), 7.40–7.31 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 8.0, 1.5 Hz, 1H) ppm.

^{13}C NMR (125.77 MHz, $CDCl_3$) δ 160.6, 155.7, 154.1, 141.5, 135.3, 132.9, 132.3, 131.5 (q, *J* = 33.5 Hz), 130.5 (q, *J* = 3.5 Hz), 130.2, 129.7, 129.6, 128.5, 127.5, 125.4, 125.2, 123.3 (q, *J* = 272.9 Hz), 120.2, 117.1.

^{19}F NMR (282.31 MHz, $CDCl_3$) δ -62.8 ppm.

MS (ESI): m/z calcd. for $C_{22}H_{13}F_3O_4S_1$ $[M+H]^+$ = 431.06; found: 430.84.

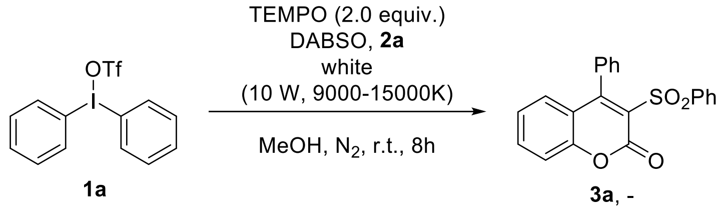
HRMS: m/z calcd. for $C_{22}H_{13}F_3O_4S_1$ $[M+H]^+$ = 431.05594; found: 431.05549.

IR (cm^{-1}) 1731 (s), 1345 (s), 1324 (s), 1163 (s), 1130 (s), 762 (s), 692 (s), 647 (s), 569 (s), 538 (s).

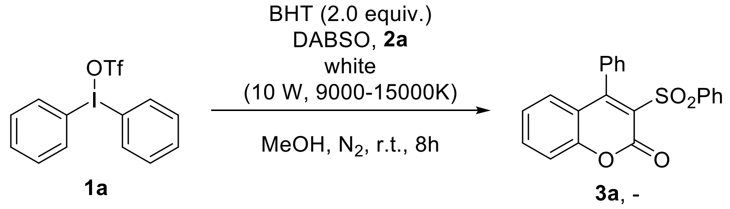
Analytical data of **5** are in agreement with literature.[14]

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 6.15 (s, 2H), 3.87 (s, 6H), 3.83 (s, 3H) ppm.

5. Radical trap experiments

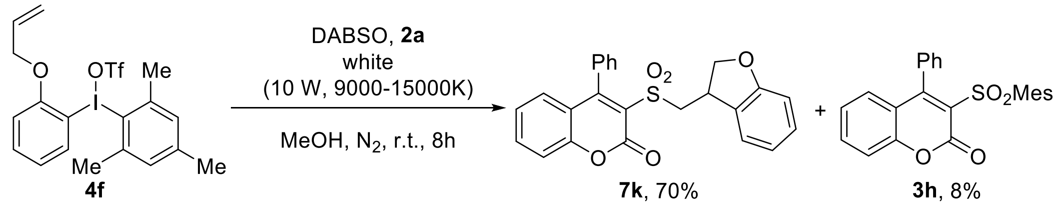


A 10-mL tube was charged with a stirring bar, phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.), DABSO (144 mg, 0.600 mmol, 2.00 equiv.), diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.20 equiv.), TEMPO (94 mg, 0.60 mmol, 2.0 equiv.) and MeOH (2 mL). The tube was closed with a rubber septum. After 5 min of nitrogen sparging, the resulting reaction mixture was irradiated (9000-15000K, white light) for 8 h at ambient temperature. Afterwards no formation of product **3a** was observed.



A 10-mL tube was charged with a stirring bar, phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.), DABSO (144 mg, 0.600 mmol, 2.00 equiv.), diphenyliodonium triflate (**1a**, 155 mg, 0.360 mmol, 1.20 equiv.), BHT (132 mg, 0.600 mmol, 2.00 equiv.) and MeOH (2 mL). The tube was closed with a rubber septum. After 5 min of nitrogen sparging, the resulting reaction mixture was irradiated (9000-15000K, white light) for 8 h at ambient temperature. Afterwards no formation of product **3a** was observed.

6. Radical clock experiment



Prepared from (2-allyloxyphenyl)(2,4,6-trimethylphenyl)iodonium tosylat (**4f**, 198 mg, 0.360 mmol, 1.2 equiv.) and phenyl 3-phenylpropynoate (**2a**, 67 mg, 0.30 mmol, 1.0 equiv.). **7k** (88 mg, 70%) and **3h** (10 mg, 8%) were isolated as a white solids.

Analytical data of **3h** are in agreement with the data of **3h** prepared from the symmetrical iodonium salt dimesityliodonium triflate (see page 9).

Analytical data of **7k**:

R$_f$ = 0.5 (*n*-hexane/EtOAc 7:3)

m.p. = 174-175 °C (DCM)

^{1}H NMR (600.31 MHz, CDCl$_3$) *δ* 7.73–7.64 (m, 1H), 7.61–7.51 (m, 3H), 7.44 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.36–7.13 (m, 5H), 7.09 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.86 (td, *J* = 7.4, 0.9 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.65 (t, *J* = 9.4 Hz, 1H), 4.53–4.40 (m, 1H), 4.17–3.96 (m, 2H), 3.75–3.61 (m, 1H) ppm.

^{13}C NMR (75.44 MHz, CDCl$_3$) *δ* 160.9, 159.9, 157.3, 153.9, 135.3, 131.9, 130.1, 129.7, 129.4, 128.4, 128.3, 128.0, 127.4, 126.9, 125.4, 124.6, 121.0, 120.1, 117.2, 110.1, 76.1, 59.6, 36.7 ppm.

MS (ESI): m/z calcd. for $C_{24}H_{19}O_5S_1$ $[M+H]^+$ = 419.10; found: 418.99.

HRMS: m/z calcd. for $C_{24}H_{19}O_5S_1$ $[M+H]^+$ = 419.09477; found: 419.09455.

IR (cm^{-1}) 1743 (m), 1482 (m), 1318 (m), 1233 (m), 1130 (m), 750 (s), 738 (m), 725 (m), 590 (m), 508 (s).

7. UV-Vis spectra

The UV-Vis absorption spectra of Ph_2IOTf (**1a**), DABSO and propynoate (**2a**) (in MeOH, 0.02M) were measured independently. Ph_2IOTf (**1a**) show almost no absorption in the visible region. The propynoate **2a** absorbs light below 400 nm but a neglectable absorbance in spectral region of sunlight or the used LEDs. Only DABSO displays a low absorbance of visible-light throughout the whole visible region. In the case of a 1:1 mixture of DABSO and Ph_2IOTf (**1a**) a slight decrease in the absorbance was detected, which could indicate some kind of interaction between those two components. Mixing of two components did not lead to significant changes in the UV/VIS spectra Contrary to a previous report by Chatani,[15] no (long-lived) charge-transfer complex could be observed.

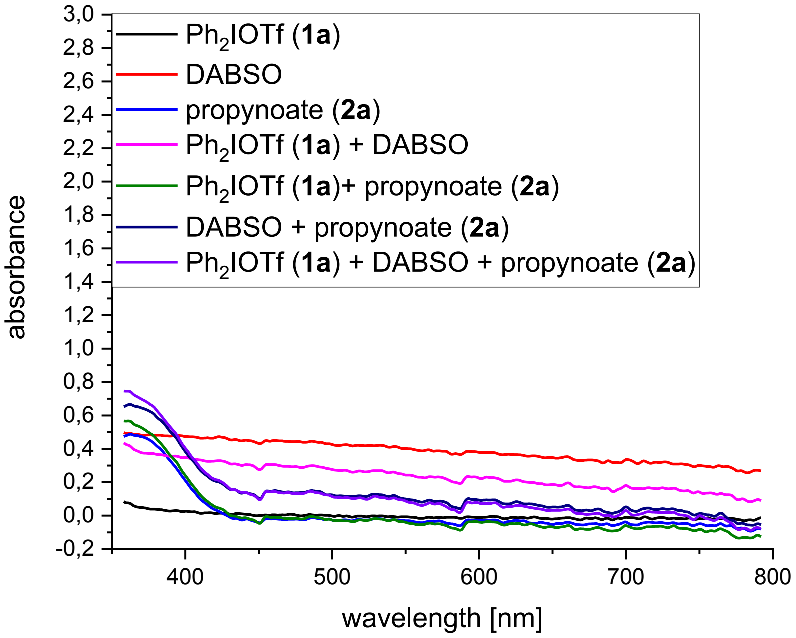


Figure S2: All UV-Vis spectra of Ph_2IOTf (**1a**), DABSO, propynoate (**2a**) independently and of their corresponding mixtures in MeOH.

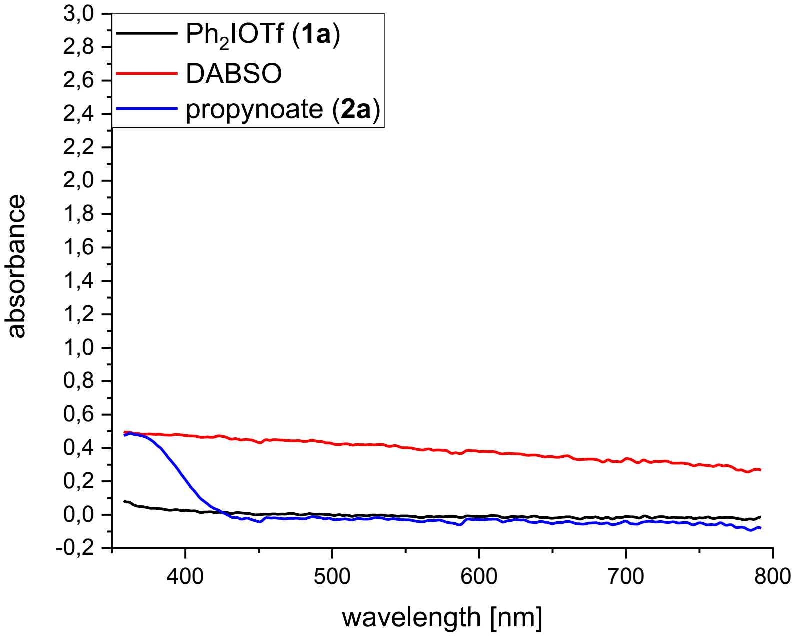


Figure S3: UV-Vis spectra of Ph$_2$IOTf (**1a**), DABSO, propynoate (**2a**) independently in MeOH.

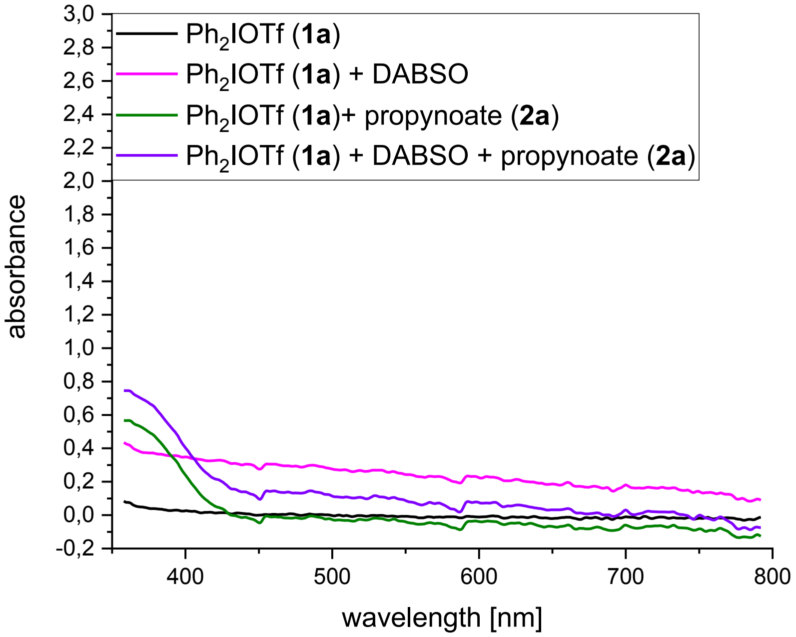


Figure S4: UV-Vis spectra of Ph$_2$IOTf (**1a**), DABSO, propynoate (**2a**) and of their corresponding mixtures in MeOH.

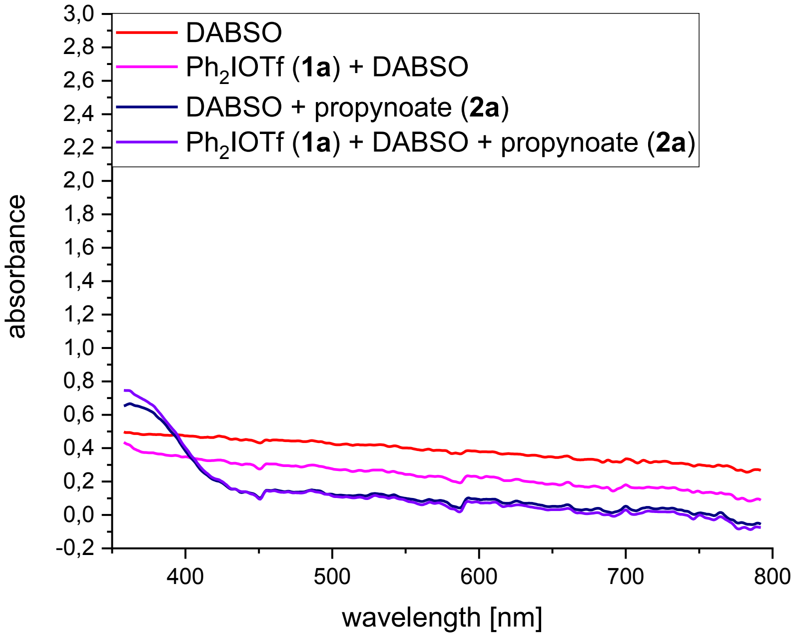


Figure S5: UV-Vis spectra of Ph$_2$IOTf (**1a**), DABSO, propynoate (**2a**) and of their corresponding mixtures in MeOH.

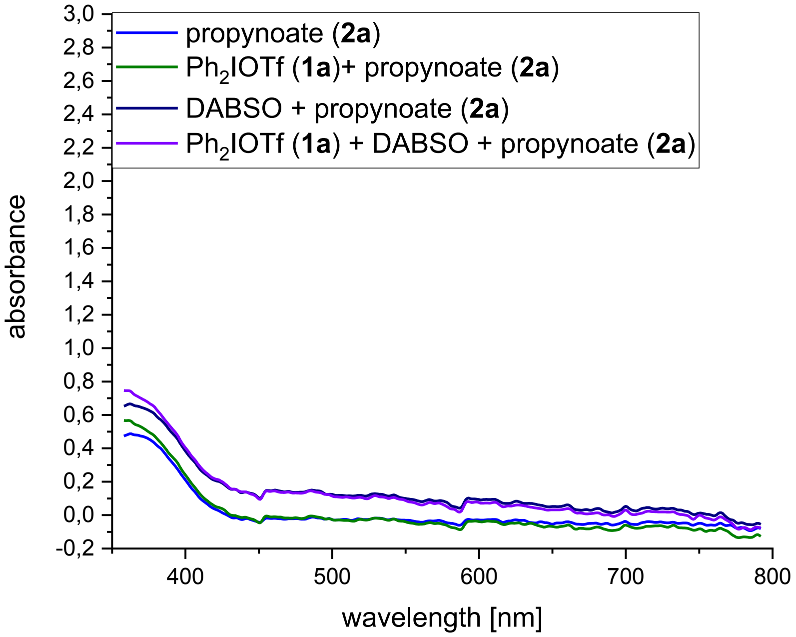


Figure S6: UV-Vis spectra of Ph$_2$IOTf (**1a**), DABSO, propynoate (**2a**) and of their corresponding mixtures in MeOH.

8. References

1 For the complete emission-spectra, see: https://www.avonec.de/images/10W-Spektrum/10W_9000k-15000k.jpg; Accessed: March 2018.
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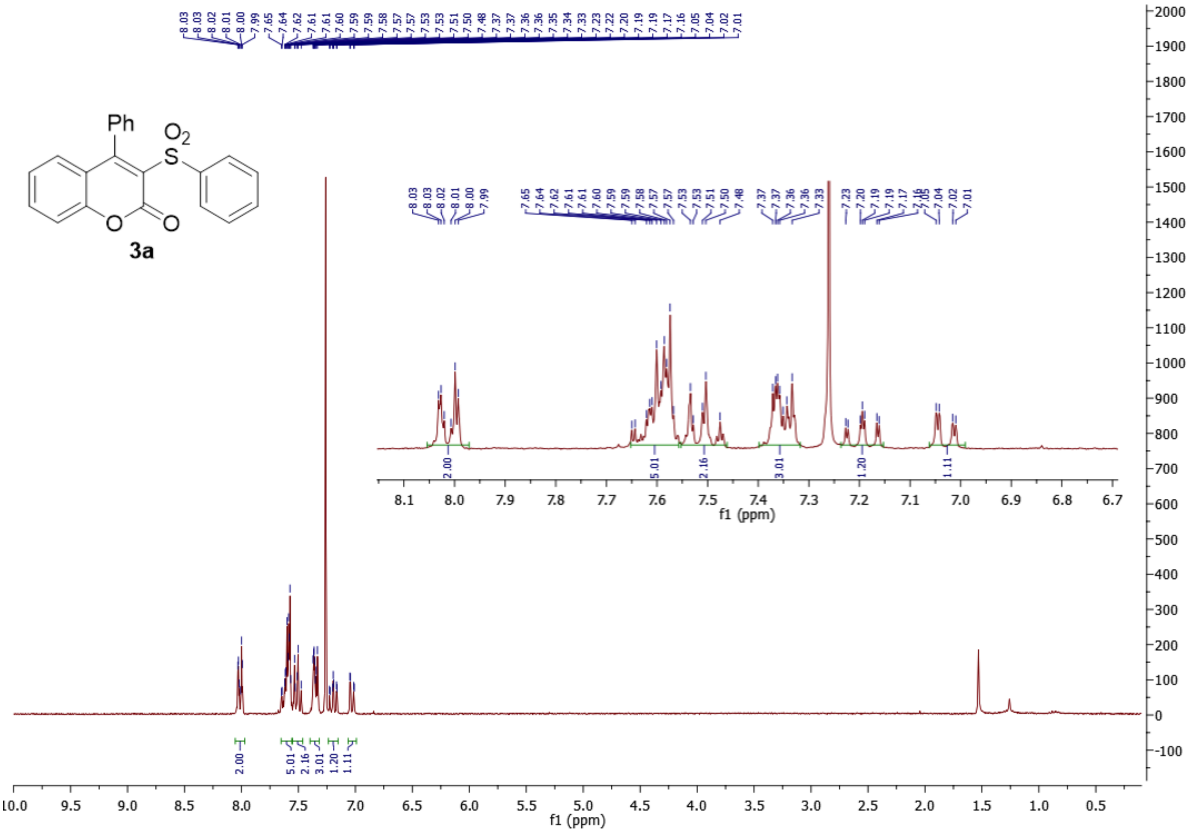
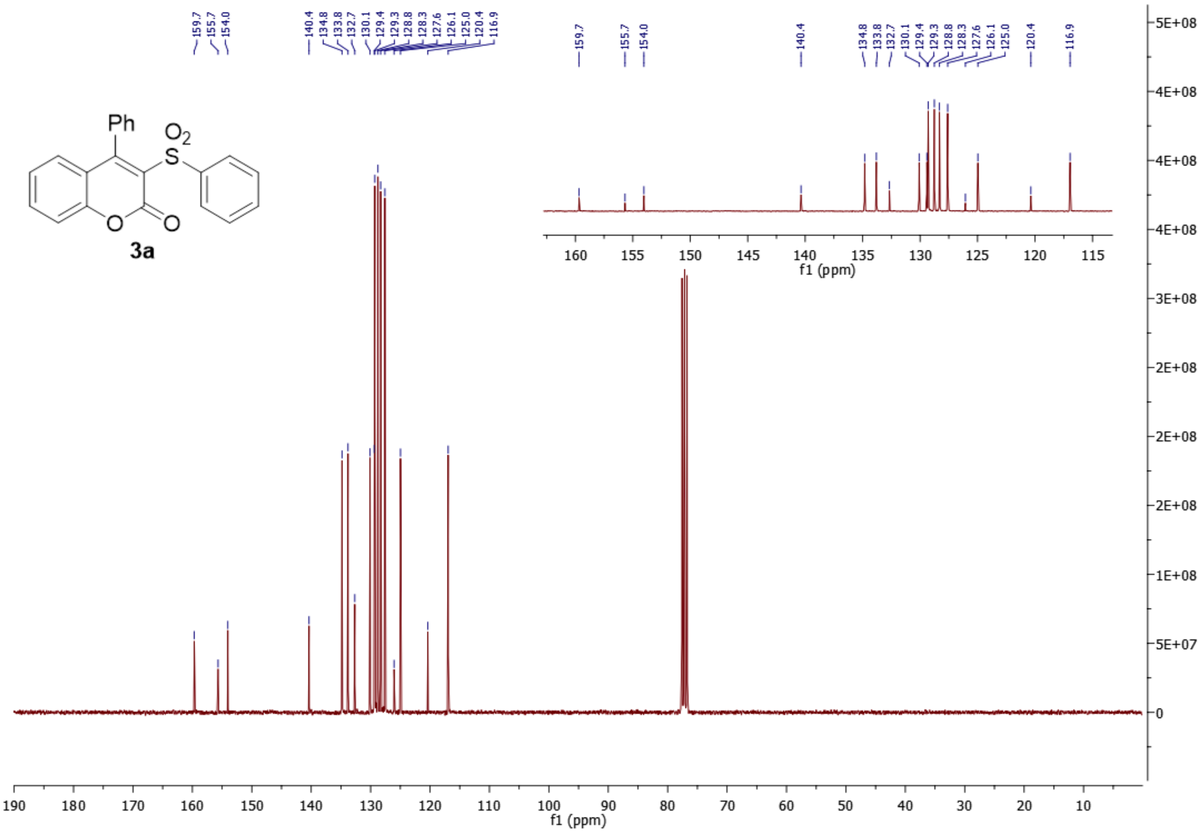
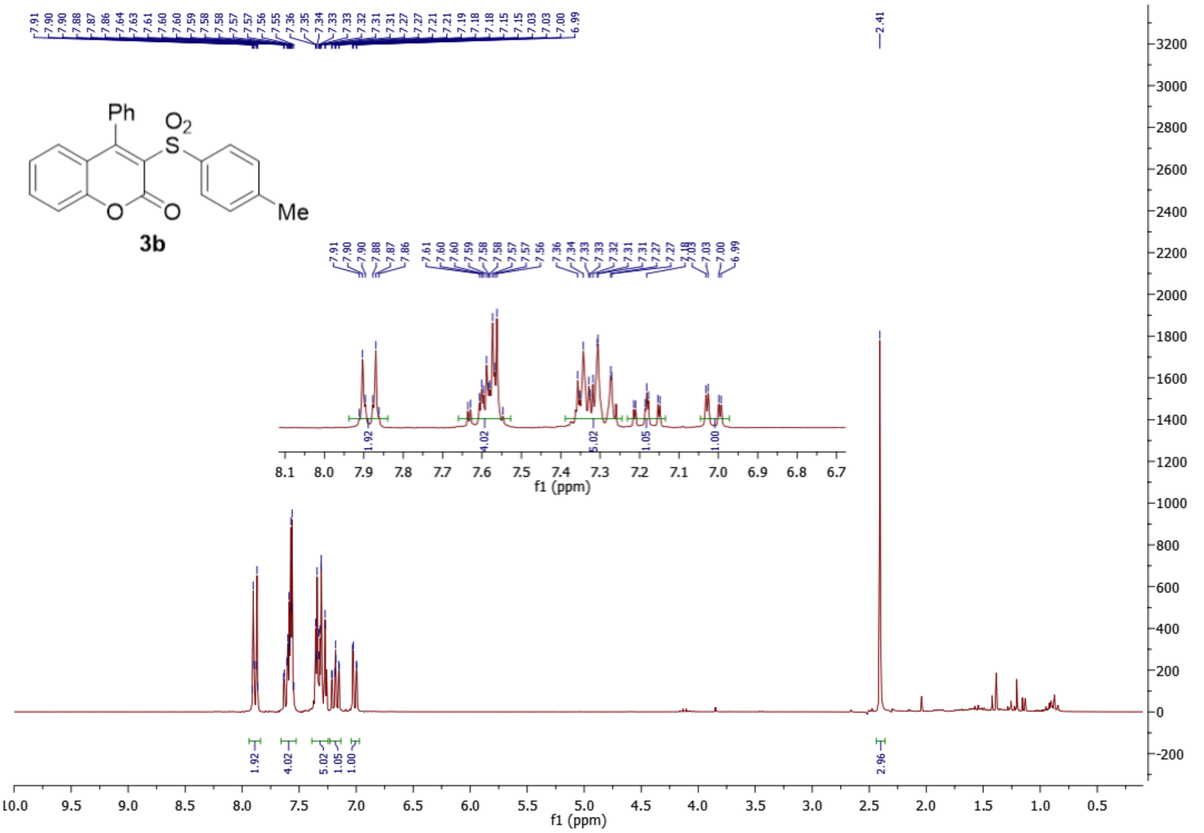
9. ^{1}H, ^{13}C, ^{19}F NMR Spectra







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2.41
Ph
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S
O
O
Me
3b
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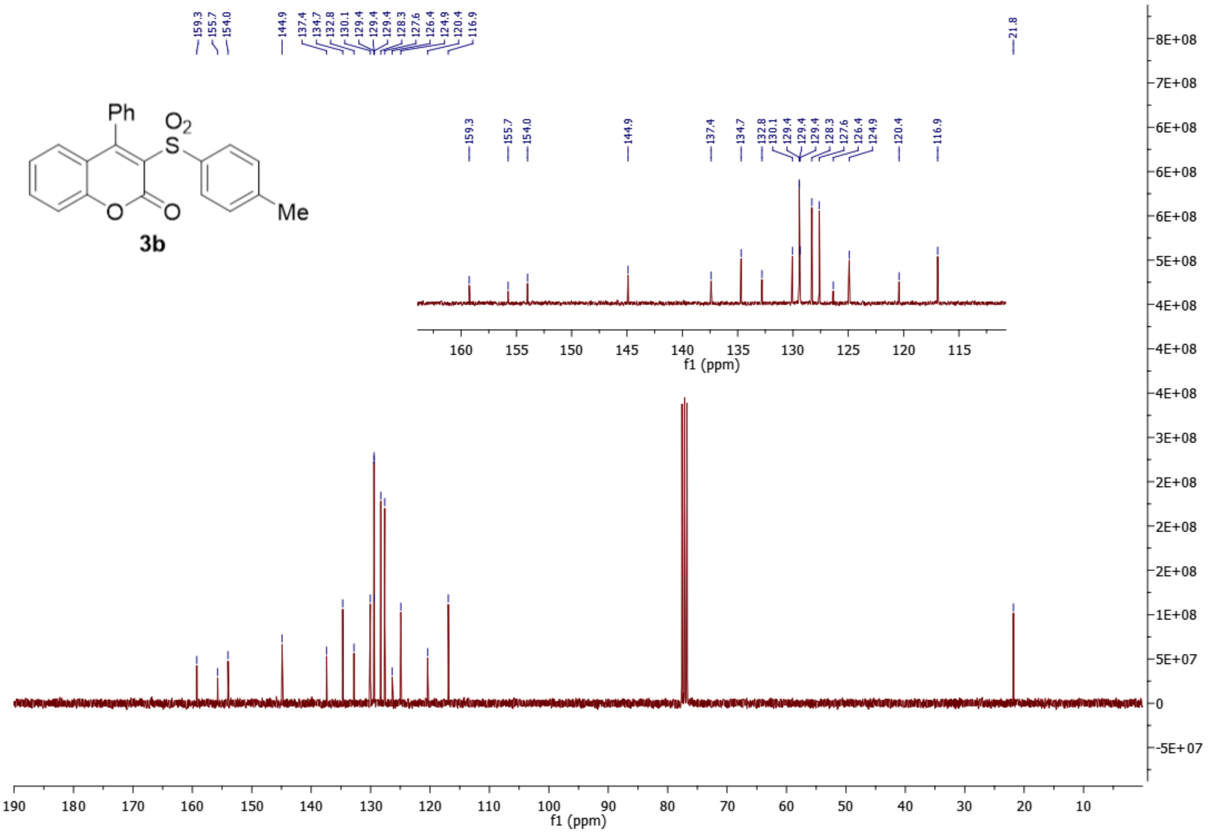
4.02
5.02
1.05
1.00
2.96
f1 (ppm)



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O
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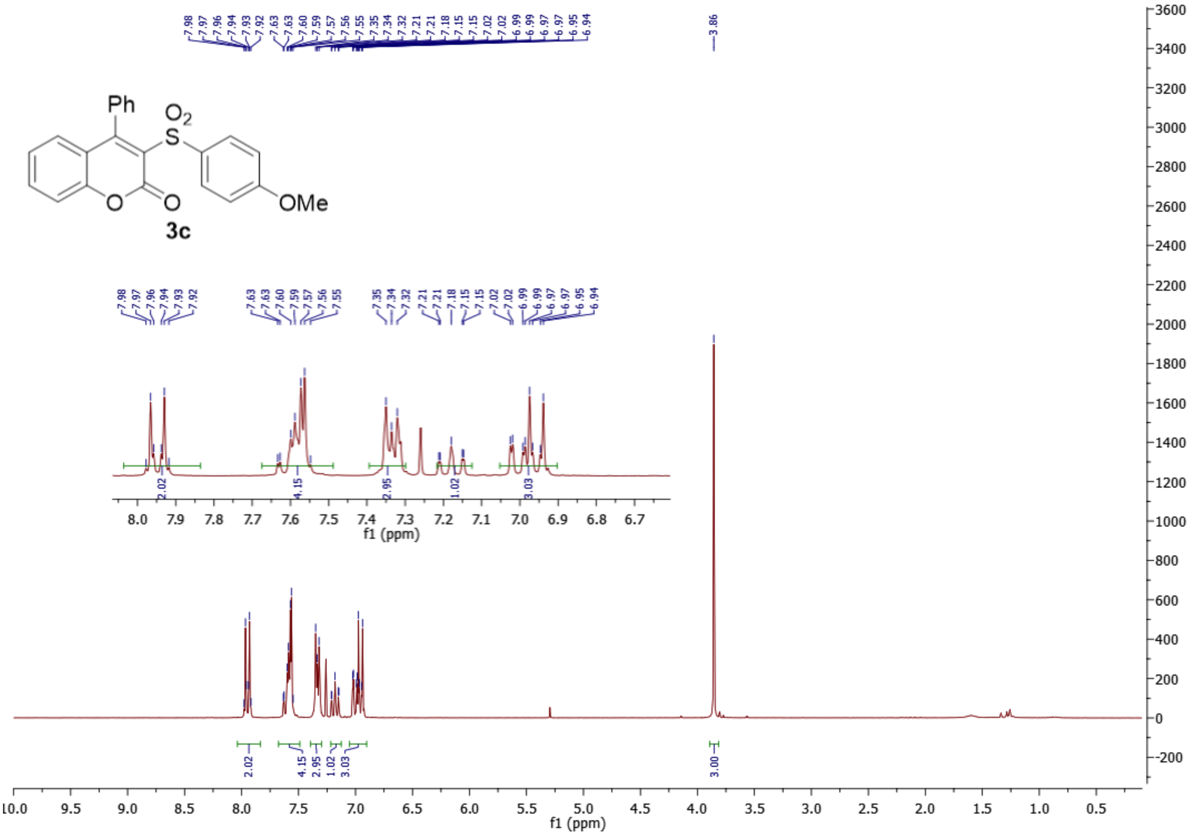
3b
f1 (ppm)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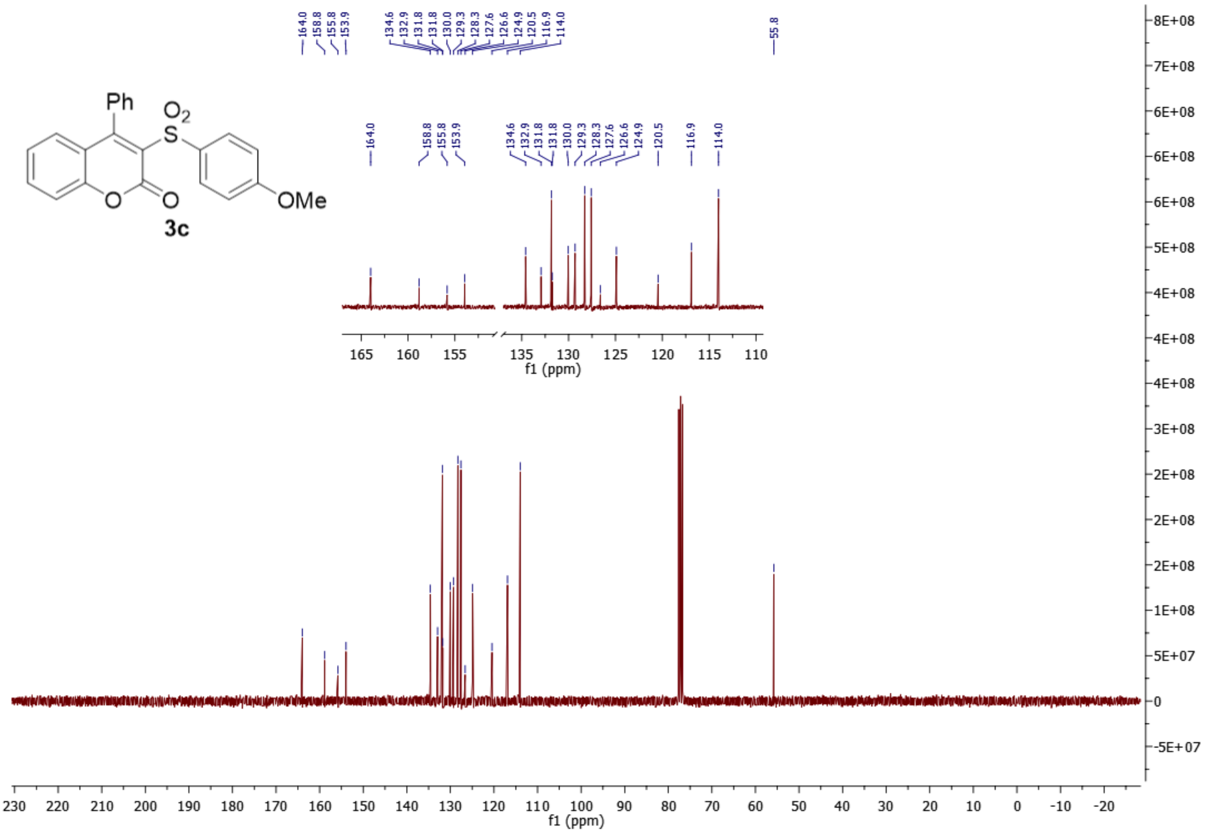
3c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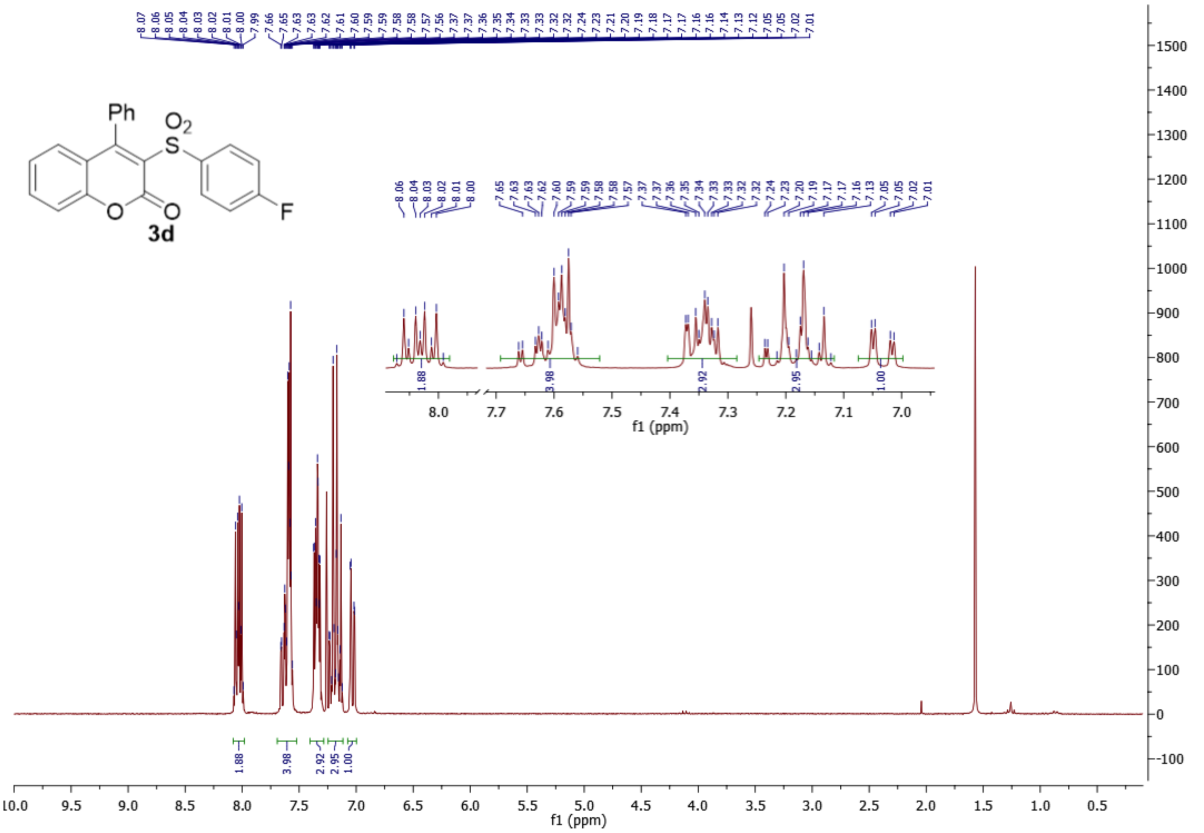
f1 (ppm)

3c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O
O
F
3d
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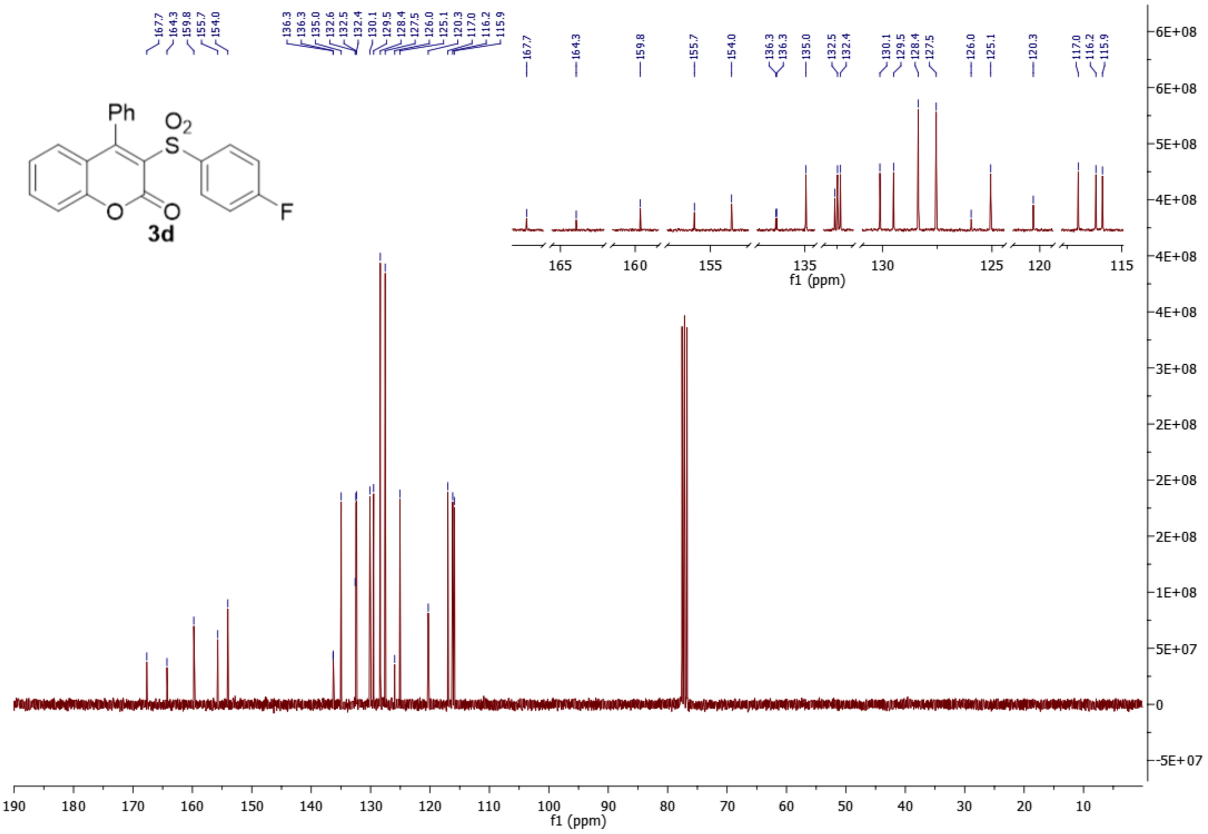
f1 (ppm)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F
3d
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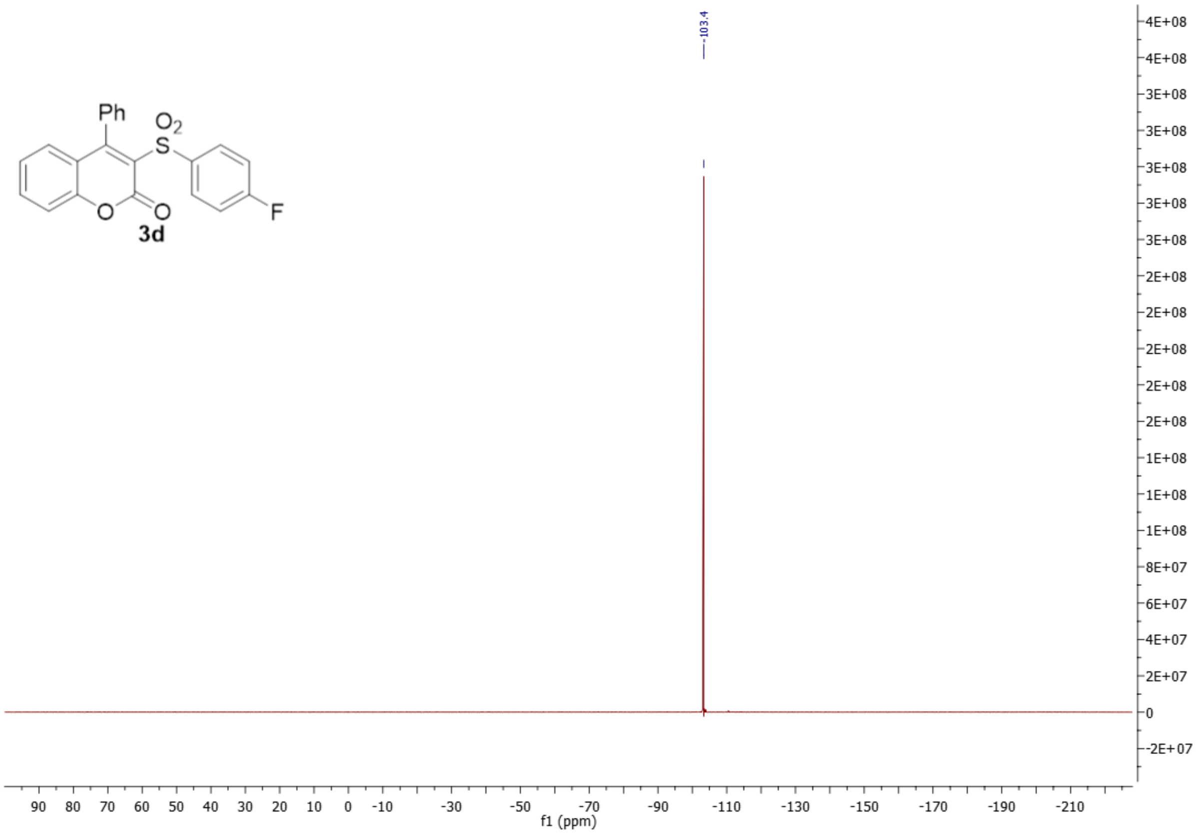
f1 (ppm)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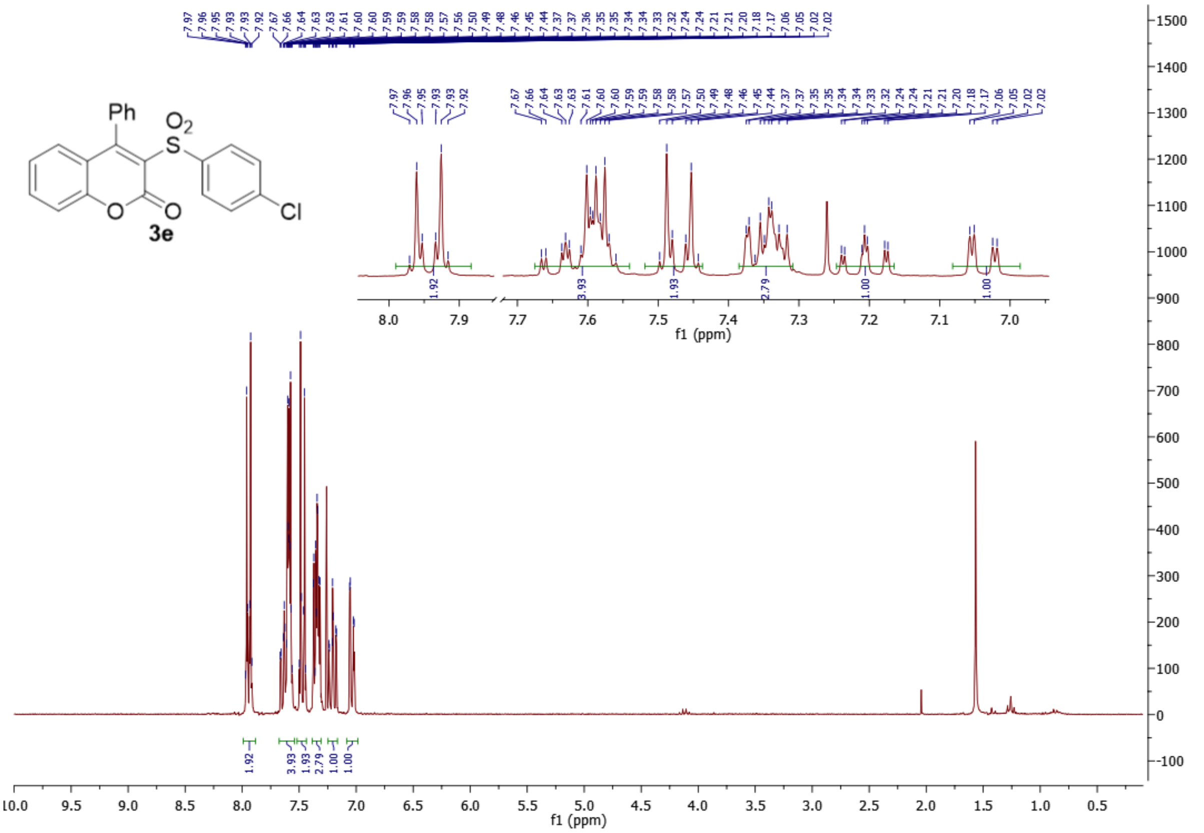
3d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f1 (ppm)
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1300
1200
1100
1000
900
800
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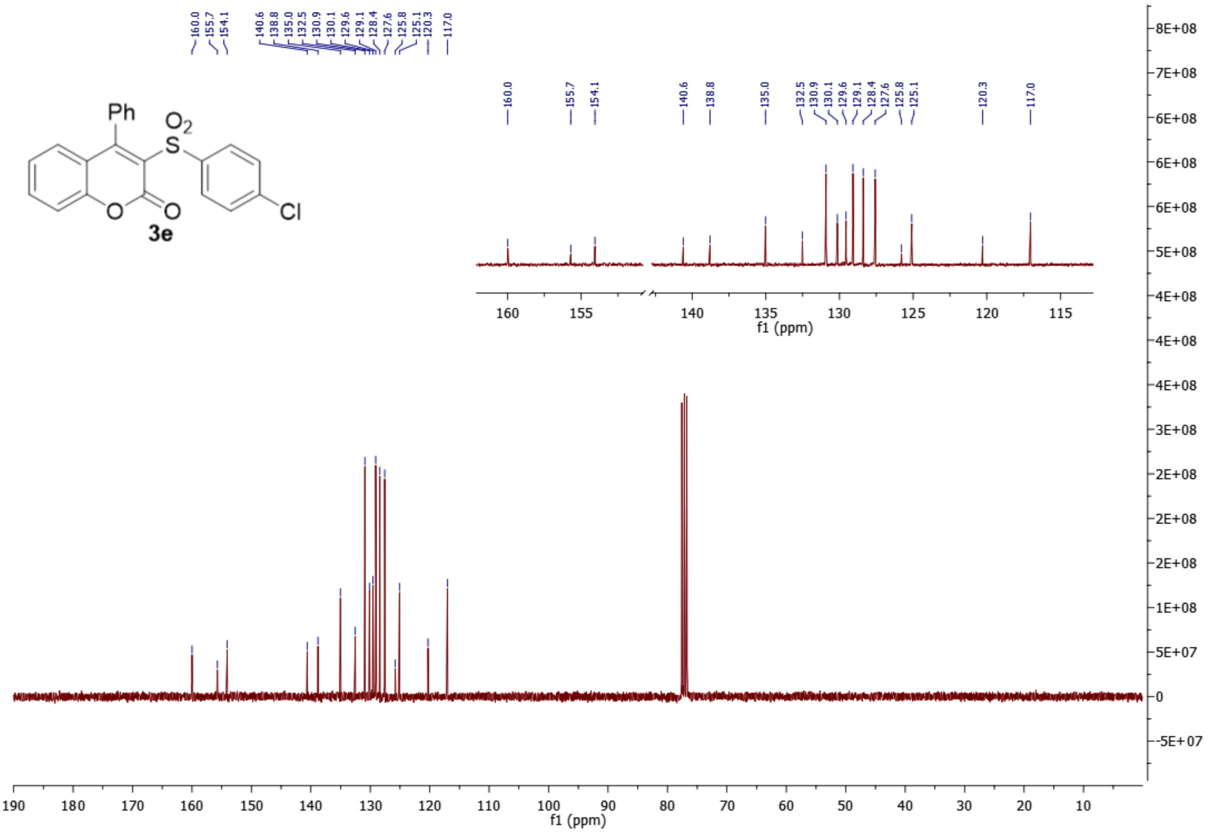
500
400
300
200
100
0
-100
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

3e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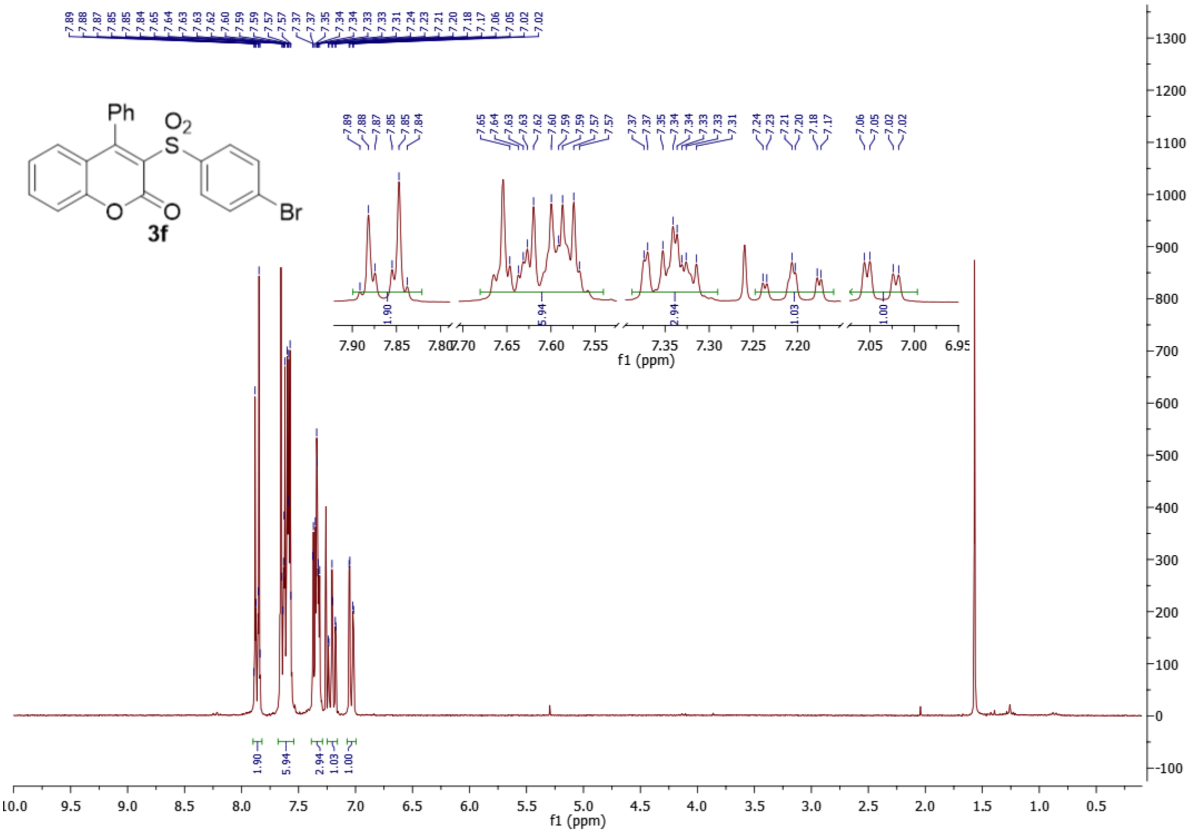
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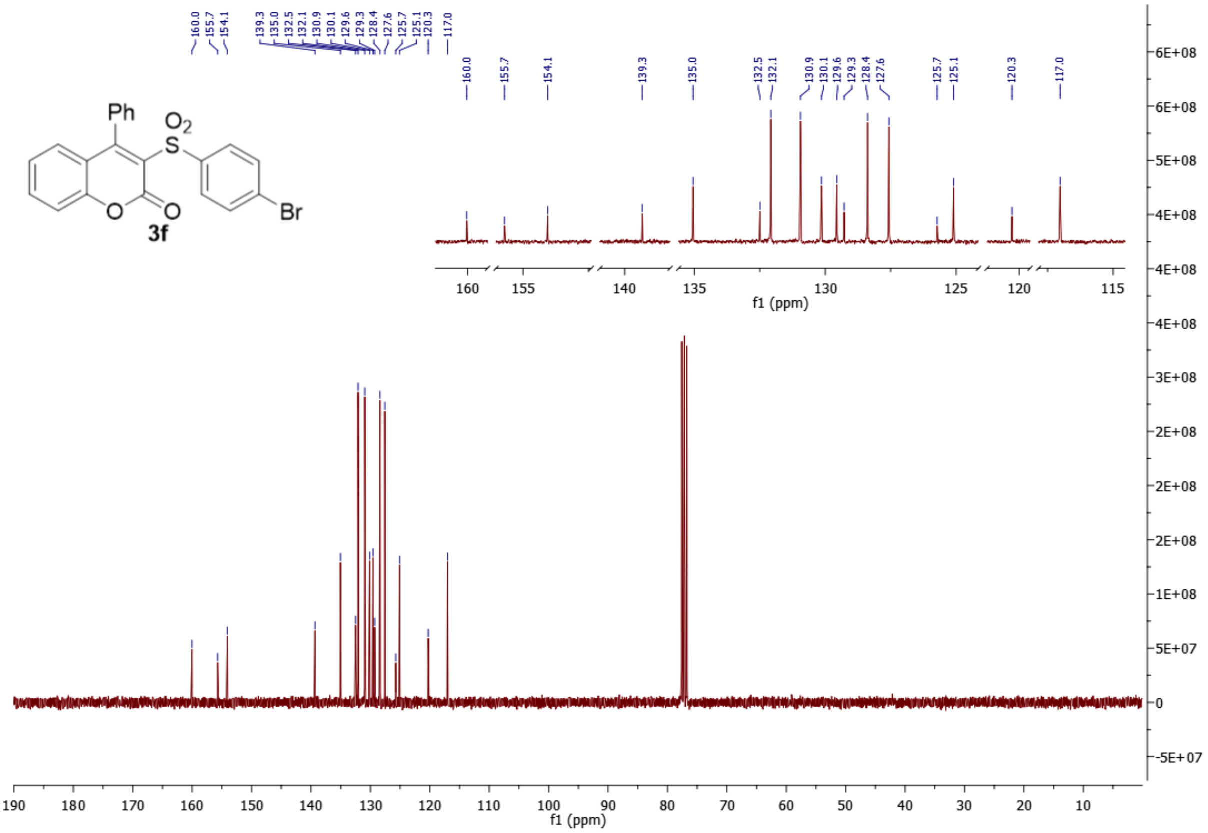
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O
Br
f1 (ppm)
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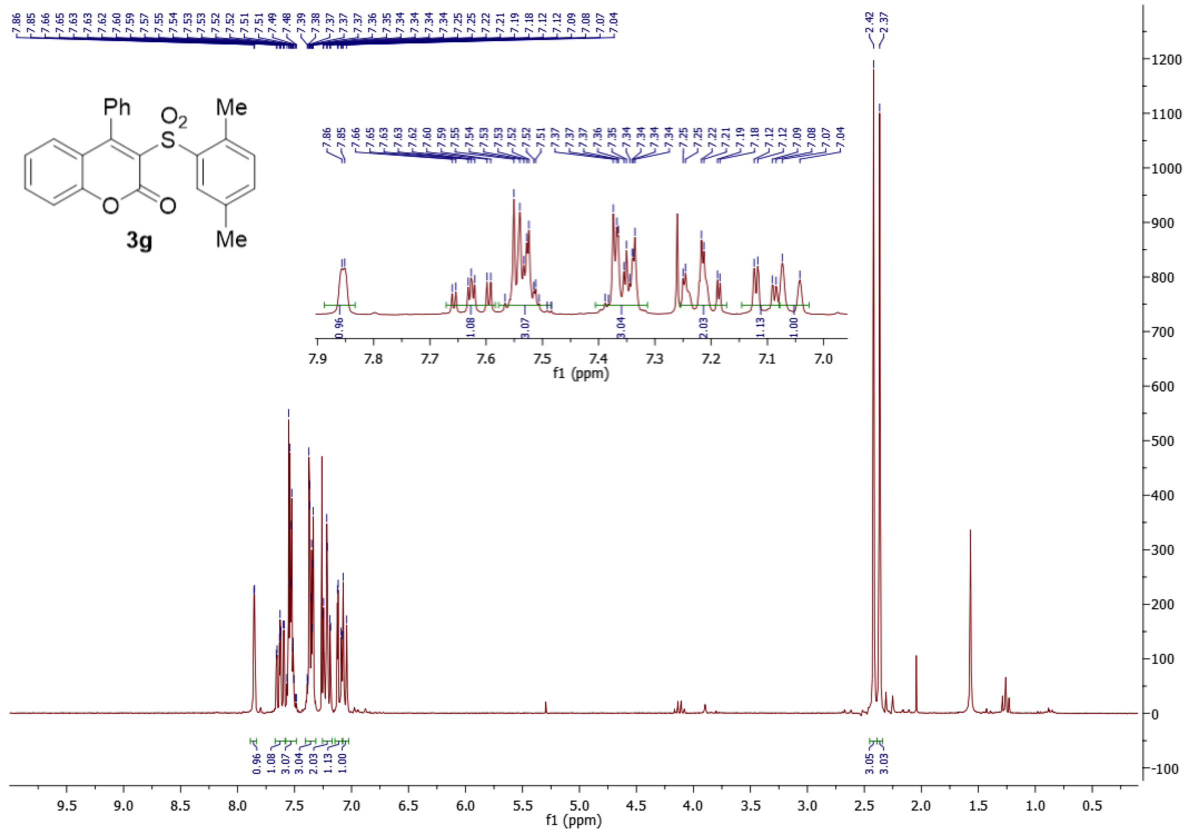
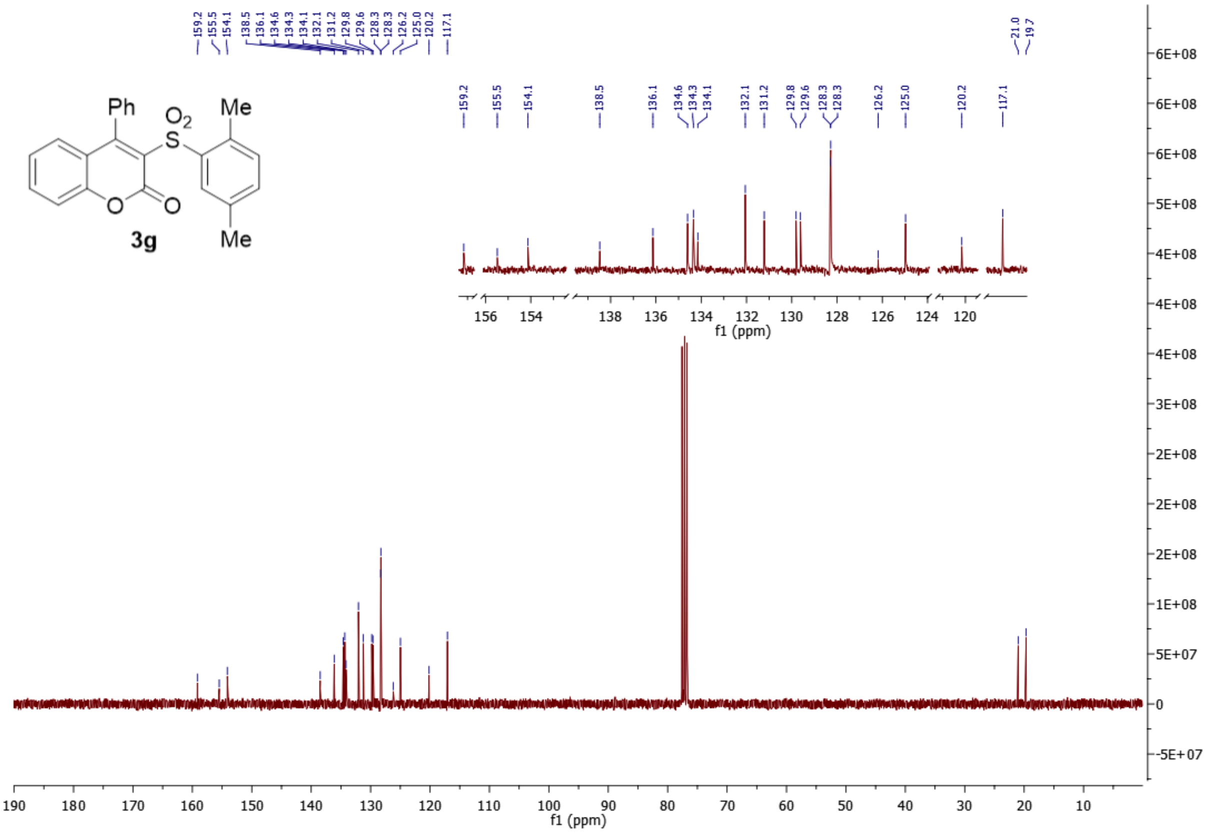
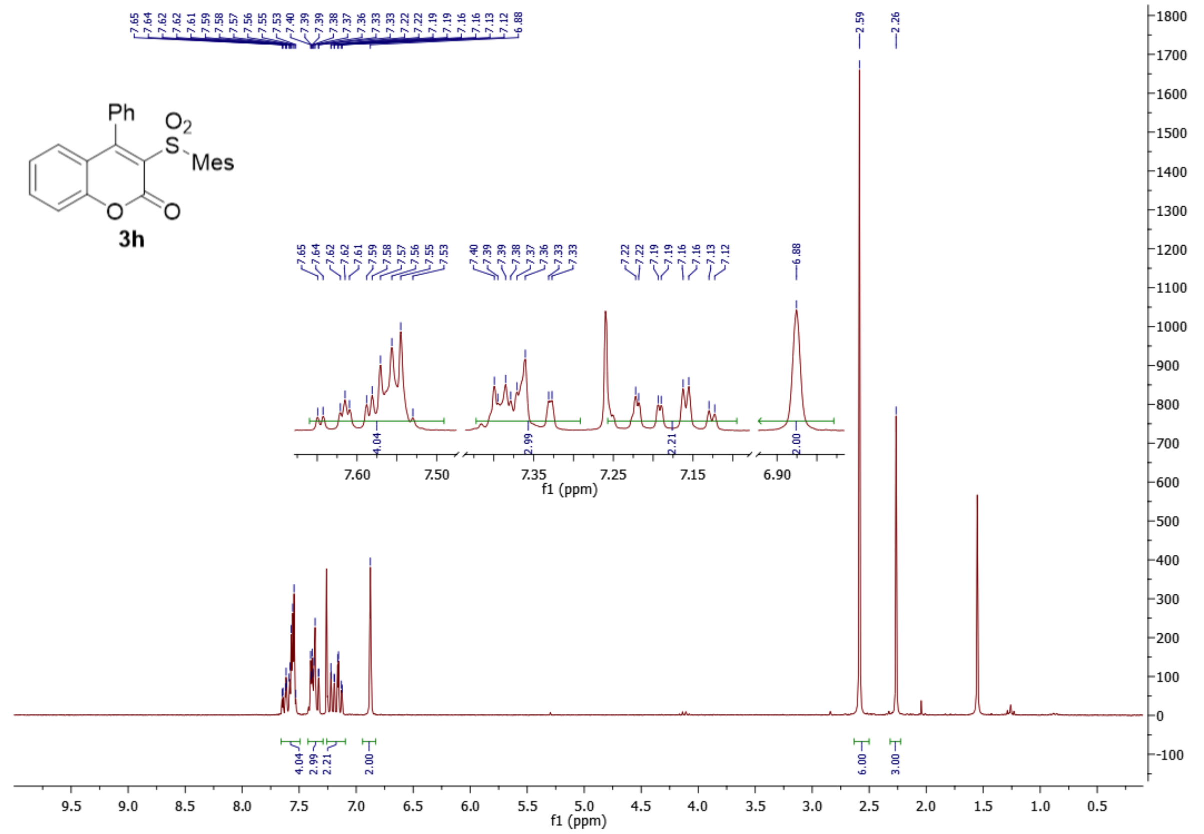
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


3g

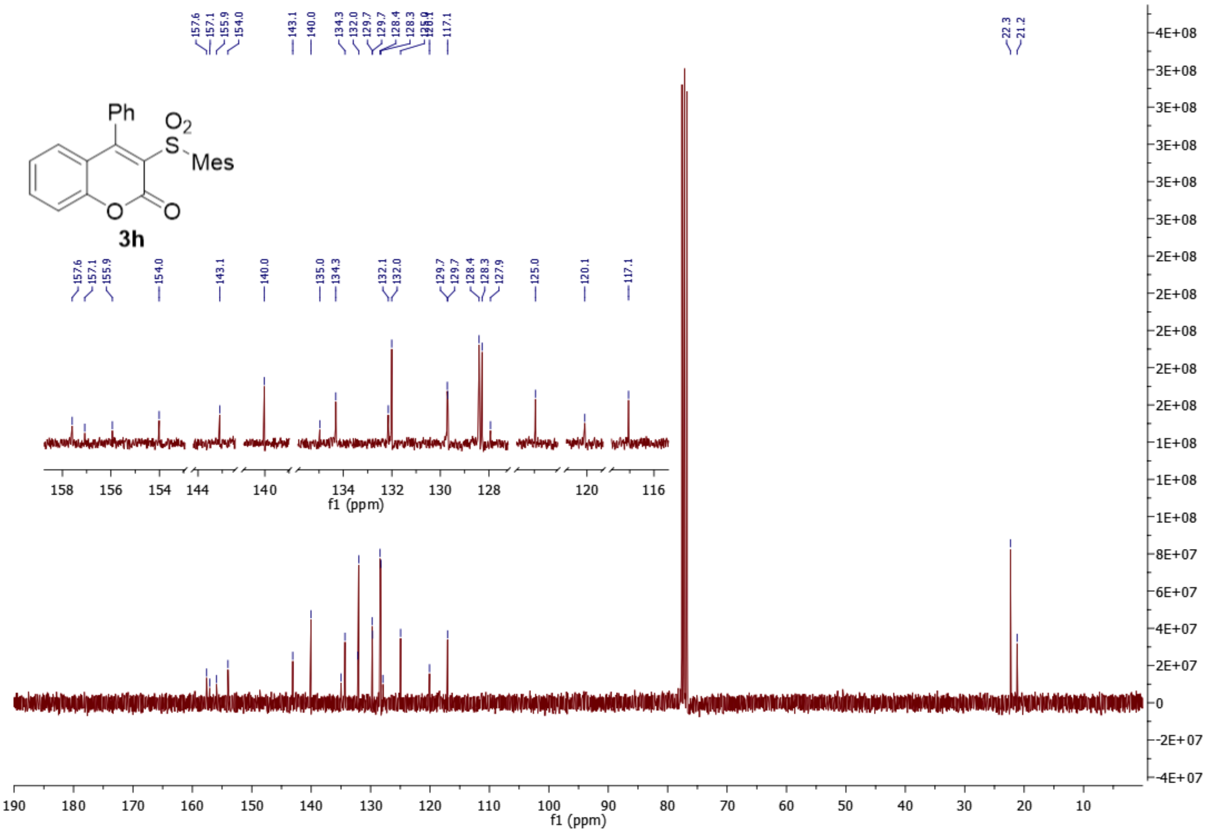
7.86
7.85
7.66
7.65
7.63
7.63
7.62
7.60
7.59
7.57
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.49
7.48
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.34
7.34
7.25
7.25
7.22
7.21
7.19
7.18
7.12
7.12
7.09
7.08
7.07
7.04
2.42
2.37
Ph
O2
S
Me
Me
O
O
0.96
1.08
3.07
3.04
2.03
1.13
1.00
3.05
3.03
f1 (ppm)
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

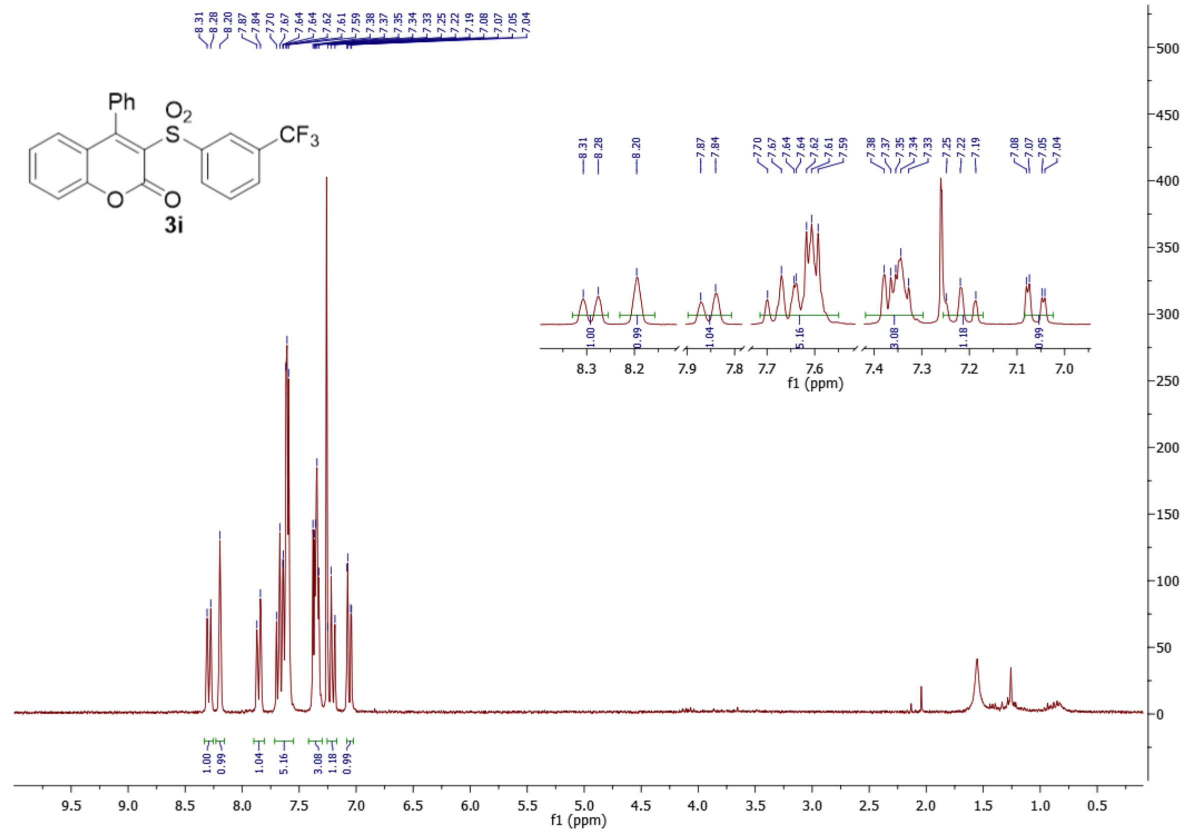


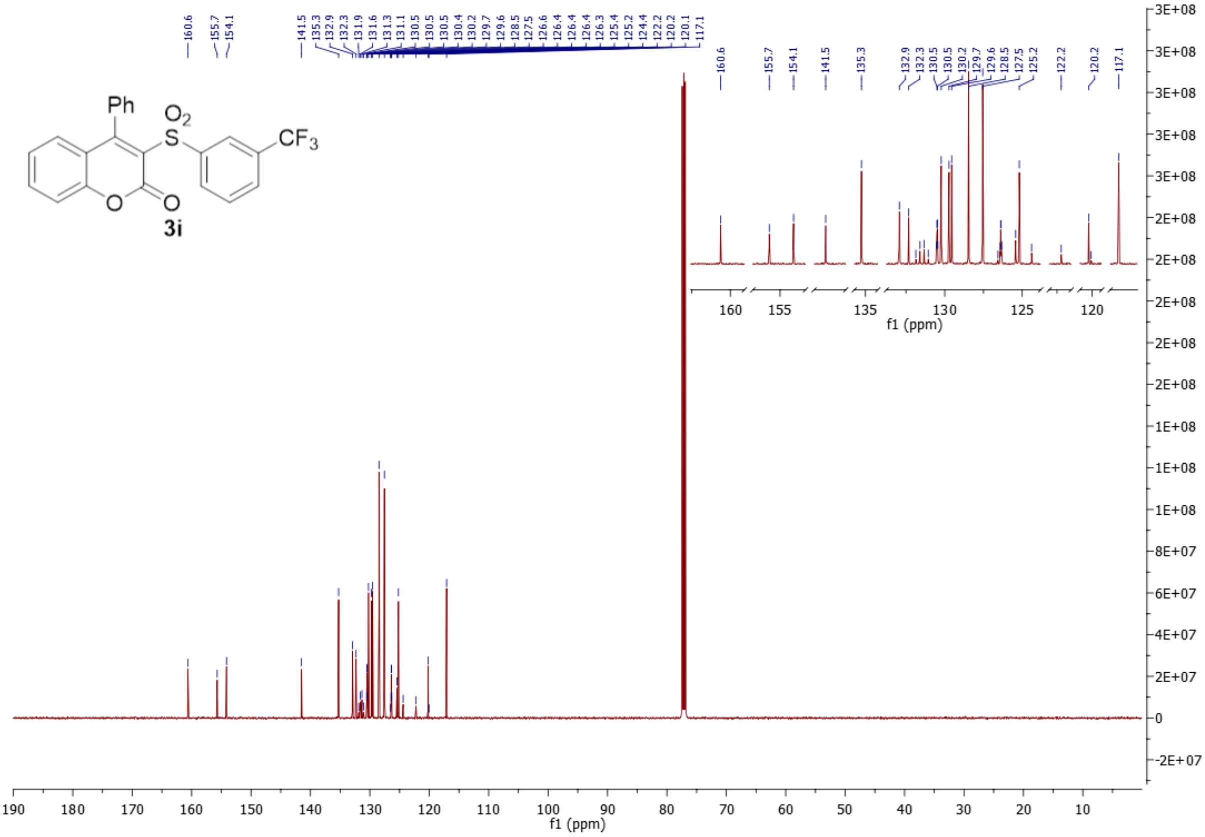
Ph
O2
S
Me
Me
O
O
3g
159.2
155.5
154.1
138.5
136.1
134.6
134.3
134.1
132.1
131.2
129.8
129.6
128.3
128.3
126.2
125.0
120.2
117.1
21.0
19.7
f1 (ppm)

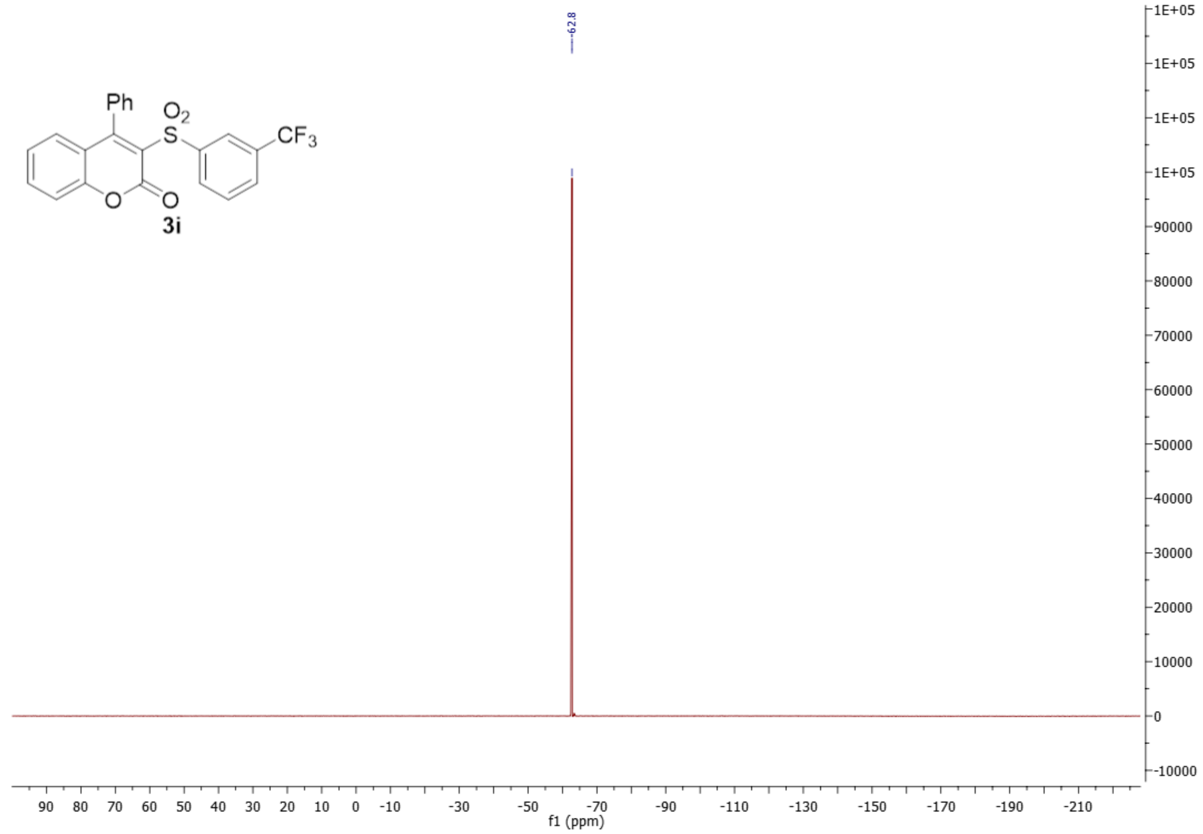


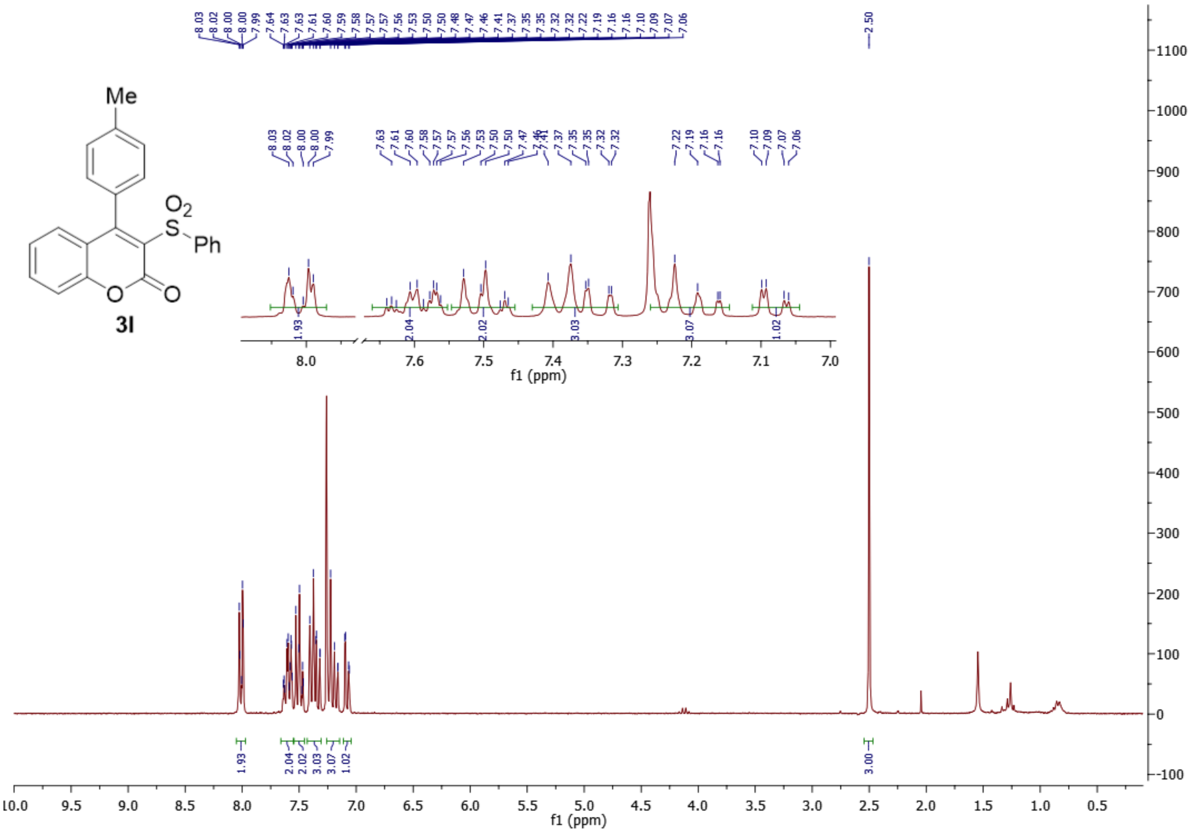
Ph
O2
S
Mes
O
O
3h
7.65
7.64
7.62
7.62
7.61
7.59
7.58
7.57
7.56
7.56
7.55
7.53
7.40
7.39
7.39
7.38
7.37
7.36
7.33
7.33
7.22
7.22
7.19
7.19
7.16
7.16
7.13
7.12
6.88
2.59
2.26
4.04
2.99
2.21
2.00
6.00
3.00
f1 (ppm)


157.6
157.1
155.9
154.0
143.1
140.0
134.3
132.0
129.7
129.7
128.4
128.3
125.0
120.1
117.1
22.3
21.2
Ph
O2
S
Mes
O
O
3h
135.0
132.1
127.9
f1 (ppm)
f1 (ppm)

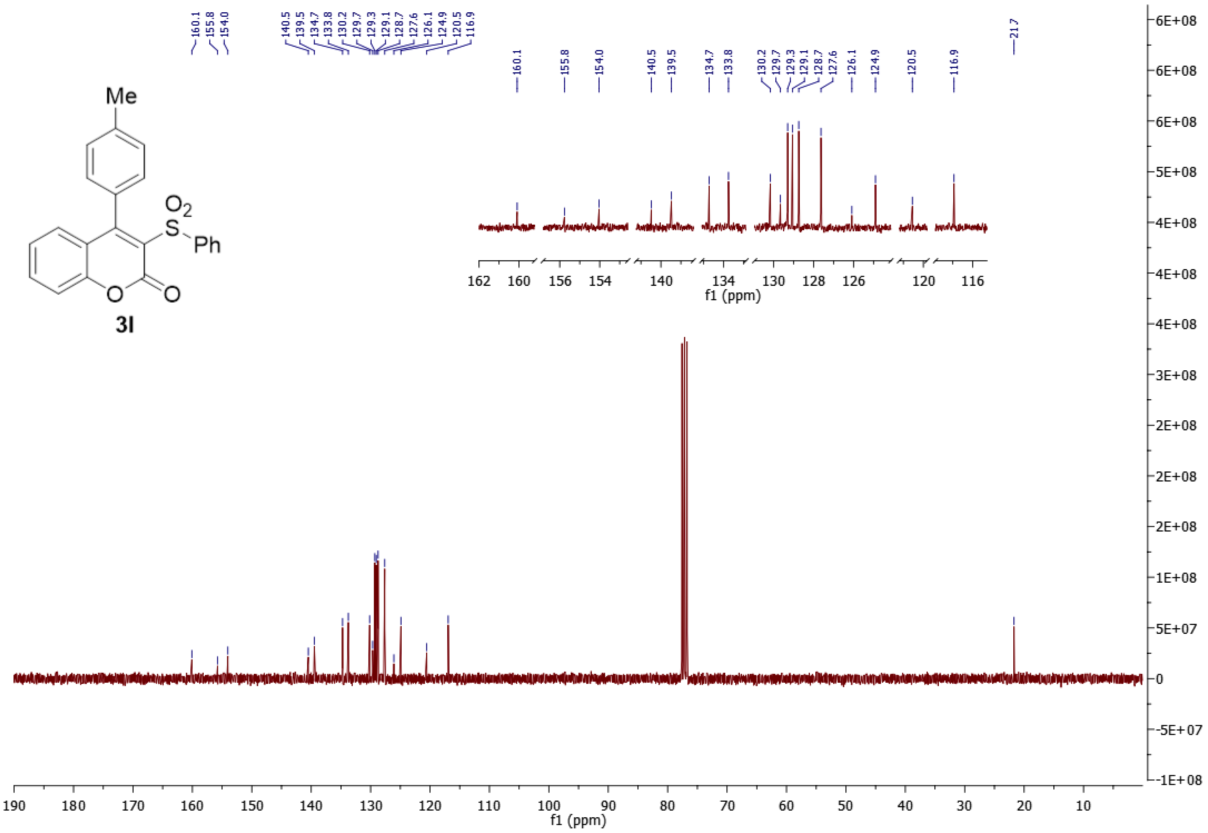

8.31
8.28
8.20
7.87
7.84
7.70
7.67
7.64
7.64
7.62
7.61
7.59
7.38
7.37
7.35
7.34
7.33
7.25
7.22
7.19
7.08
7.07
7.05
7.04
Ph
O2
S
CF3
O
O
3i
1.00
0.99
1.04
5.16
3.08
1.18
0.99
f1 (ppm)
f1 (ppm)


160.6
155.7
154.1
141.5
135.3
132.9
132.3
131.9
131.6
131.3
131.1
130.5
130.5
130.5
130.4
130.2
129.7
129.6
128.5
127.5
126.6
126.4
126.4
126.4
126.3
125.4
125.2
124.4
122.2
120.2
120.1
117.1
Ph
O2
S
CF3
O
O
3i
160
155
135
130
125
120
f1 (ppm)
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

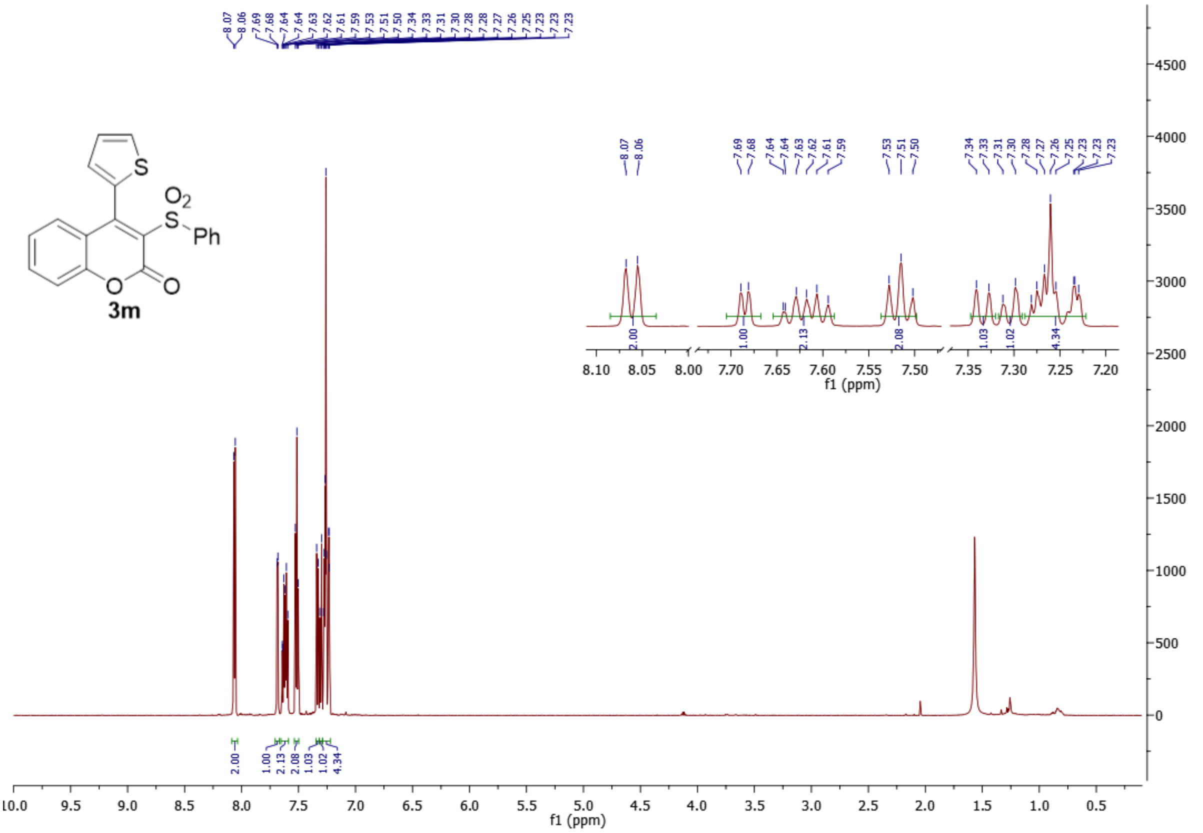

-62.8
Ph
O2
S
CF3
O
O
3i
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

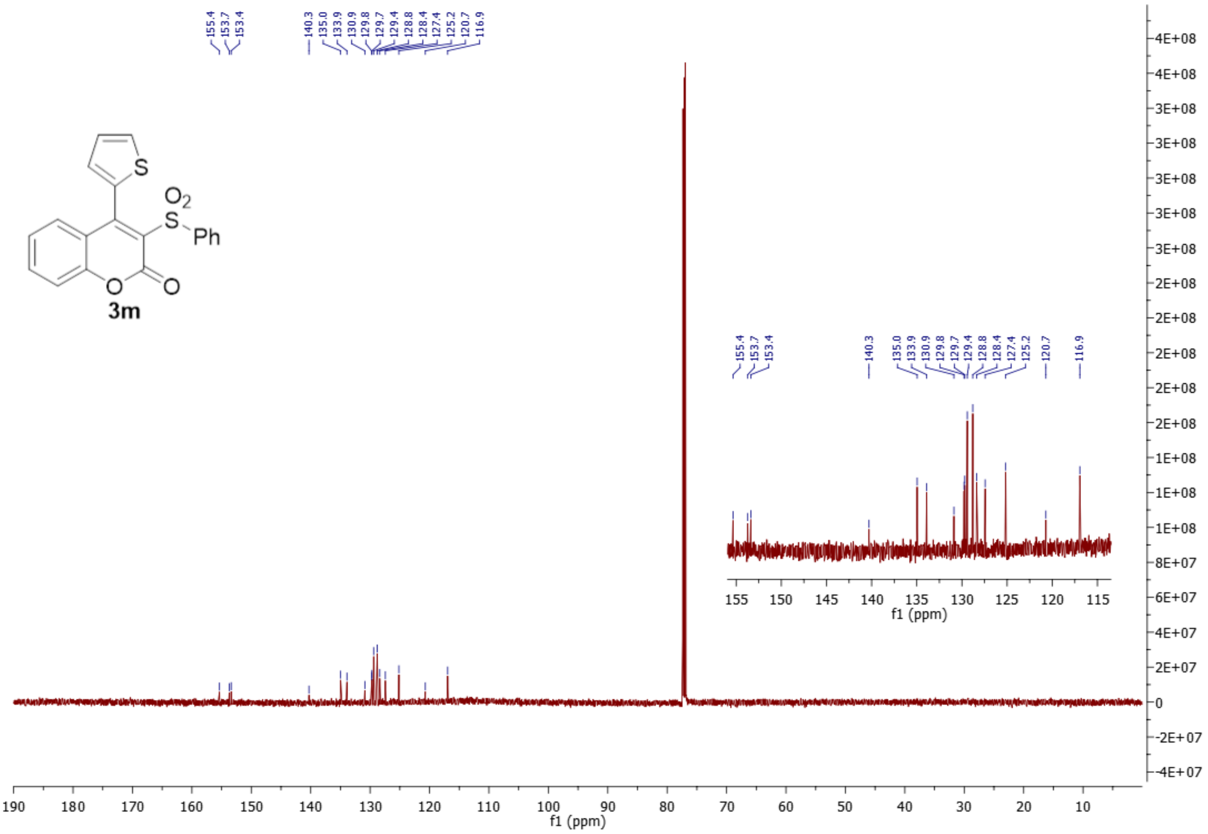

8.03
8.02
8.00
8.00
7.99
7.64
7.63
7.63
7.61
7.60
7.59
7.58
7.57
7.57
7.56
7.53
7.50
7.50
7.48
7.47
7.46
7.41
7.37
7.35
7.35
7.32
7.32
7.22
7.19
7.16
7.16
7.10
7.09
7.07
7.06
2.50
Me
O2
S
Ph
O
O
1.93
2.04
2.02
3.03
3.07
1.02
3.00
f1 (ppm)

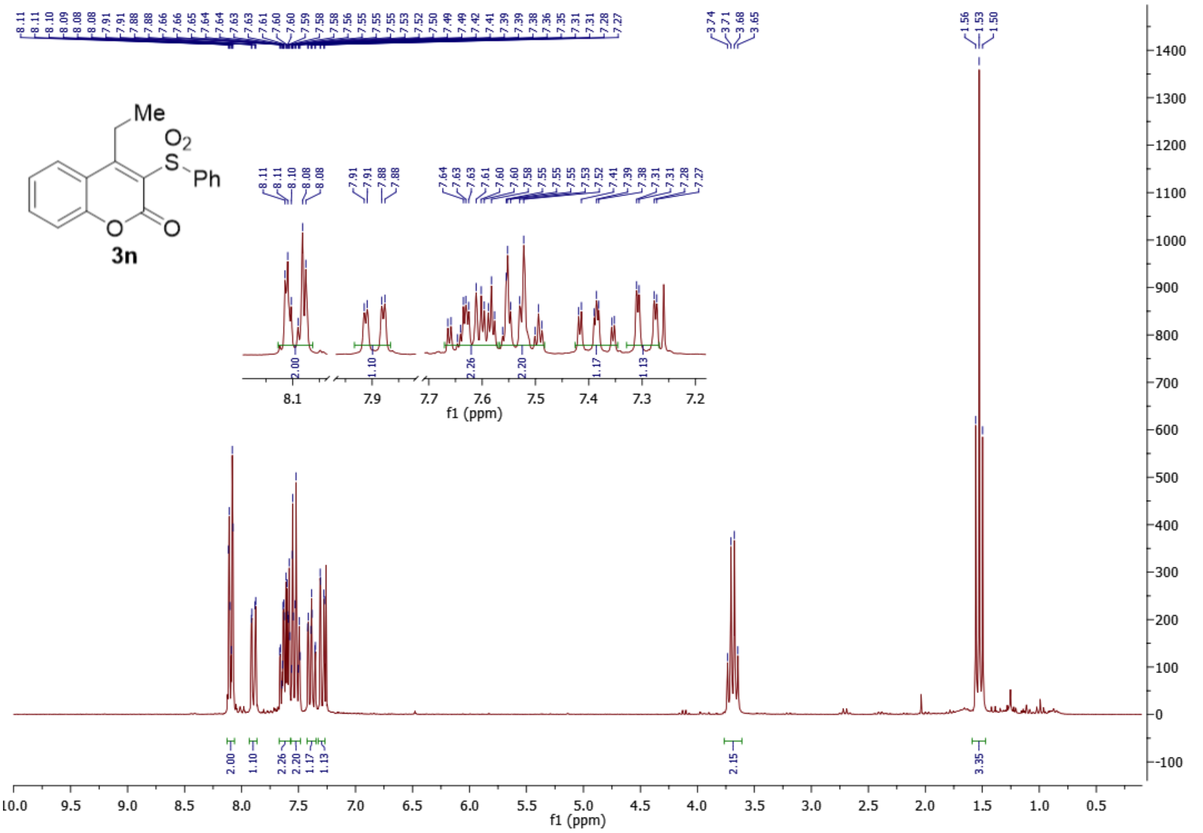
3l

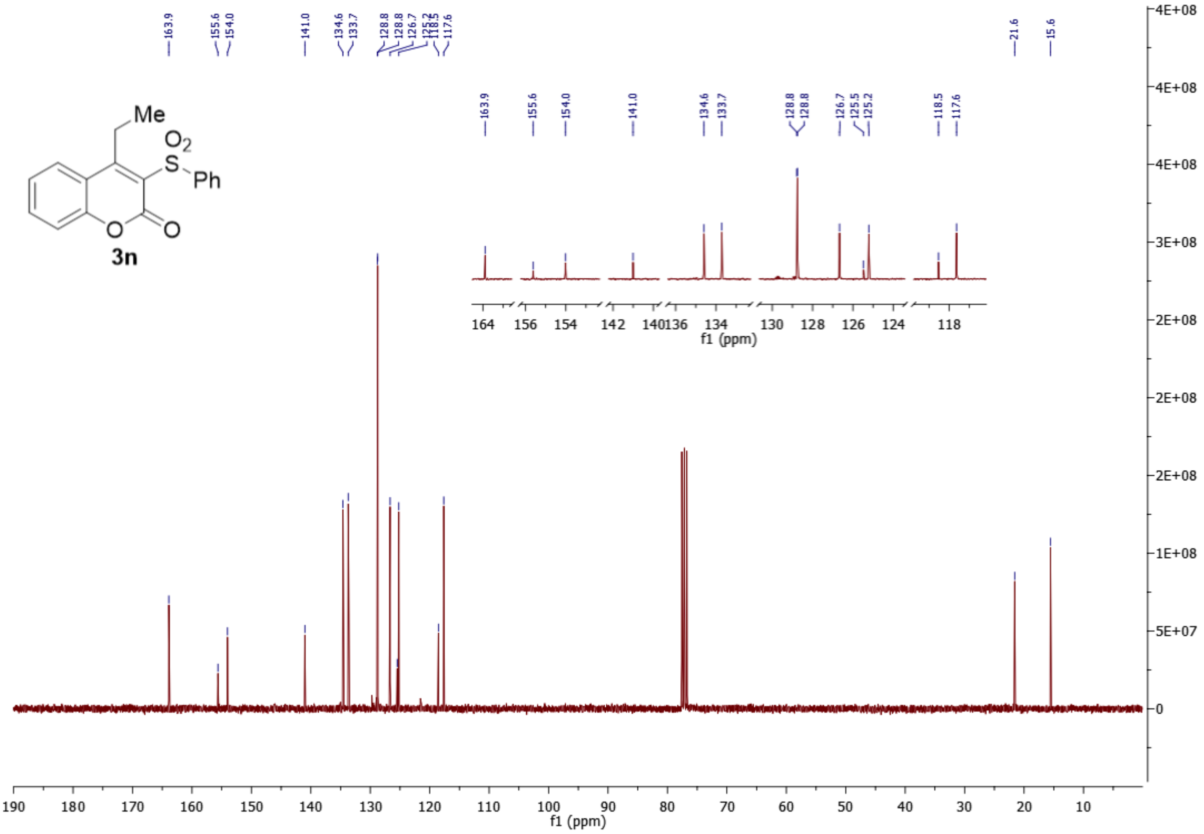

160.1
155.8
154.0
140.5
139.5
134.7
133.8
130.2
129.7
129.3
129.1
128.7
127.6
126.1
124.9
120.5
116.9
21.7
Me
O2
S
Ph
O
O
f1 (ppm)

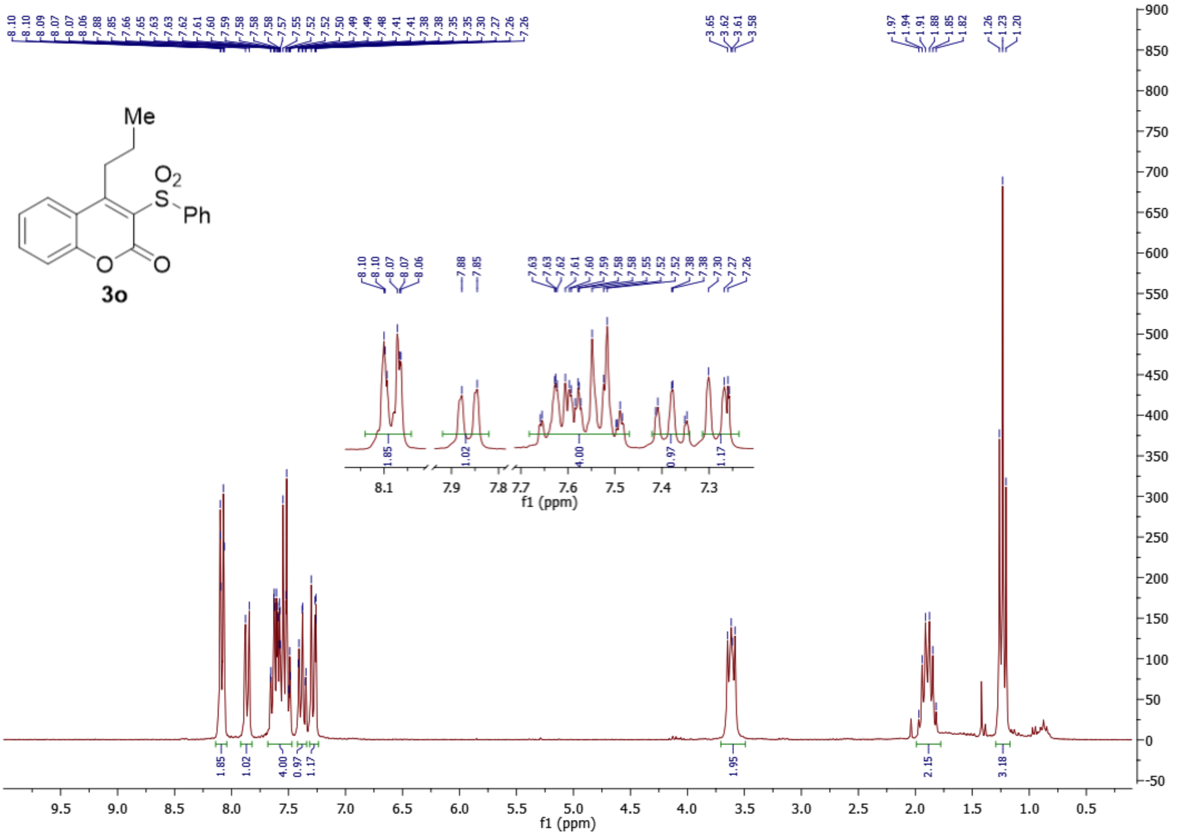
3l


8.07
8.06
7.69
7.68
7.64
7.64
7.63
7.62
7.61
7.59
7.53
7.51
7.50
7.34
7.33
7.31
7.30
7.28
7.27
7.26
7.25
7.23
7.23
7.23
O2
S
Ph
S
O
O
3m
2.00
1.00
2.13
2.08
1.03
1.02
4.34
8.10
8.05
8.00
7.70
7.65
7.60
7.55
7.50
7.35
7.30
7.25
7.20
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

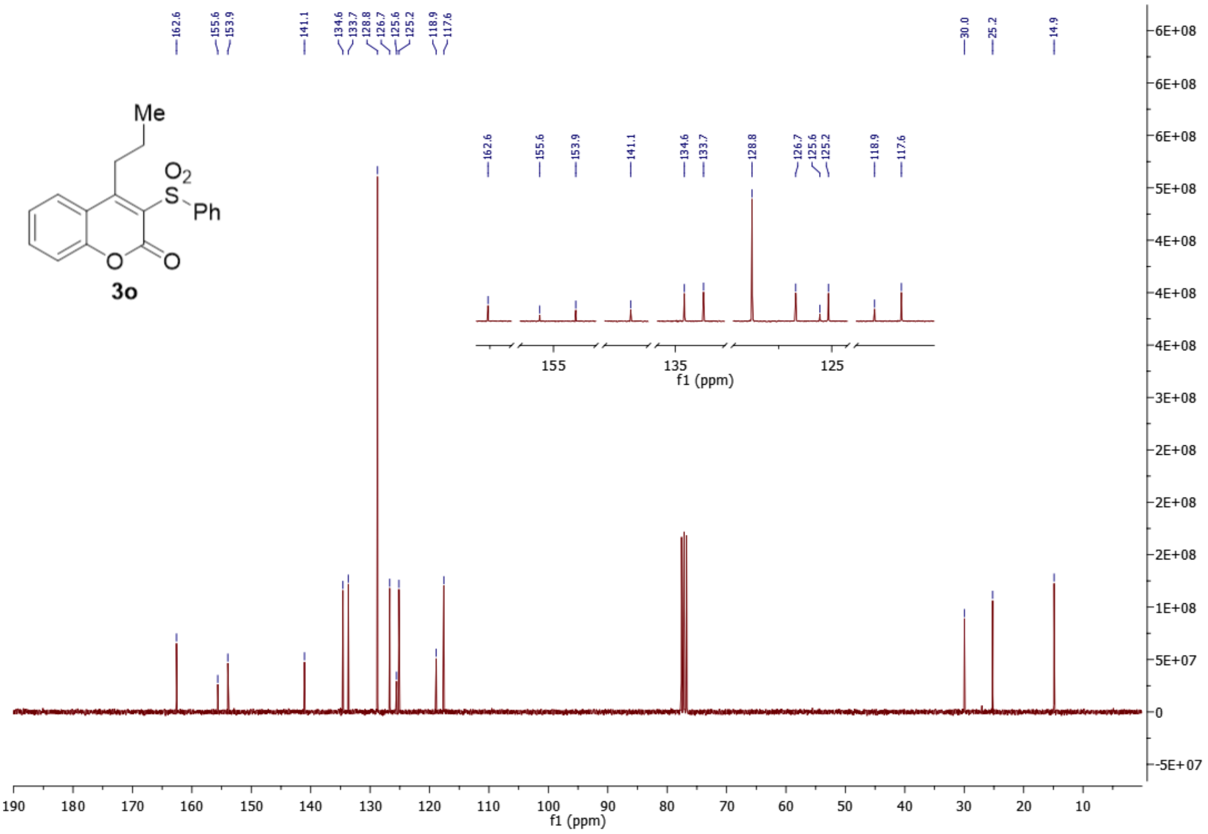

155.4
153.7
153.4
140.3
135.0
133.9
130.9
129.8
129.7
129.4
128.8
128.4
127.4
125.2
120.7
116.9
O2
S
Ph
S
O
O
3m
155
150
145
140
135
130
125
120
115
f1 (ppm)
4E+08
4E+08
3E+08
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
-4E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.11 8.11 8.10 8.09 8.08 8.08 7.91 7.91 7.88 7.88 7.66 7.66 7.65 7.64 7.64 7.63 7.63 7.61 7.60 7.60 7.59 7.58 7.58 7.56 7.55 7.55 7.55 7.53 7.52 7.50 7.49 7.49 7.42 7.41 7.39 7.39 7.38 7.36 7.35 7.31 7.31 7.28 7.27
3.74 3.71 3.68 3.65
1.56 1.53 1.50
Me
O2
S
Ph
O
O
3n
2.00
1.10
2.26
2.20
1.17
1.13
2.15
3.35
f1 (ppm)

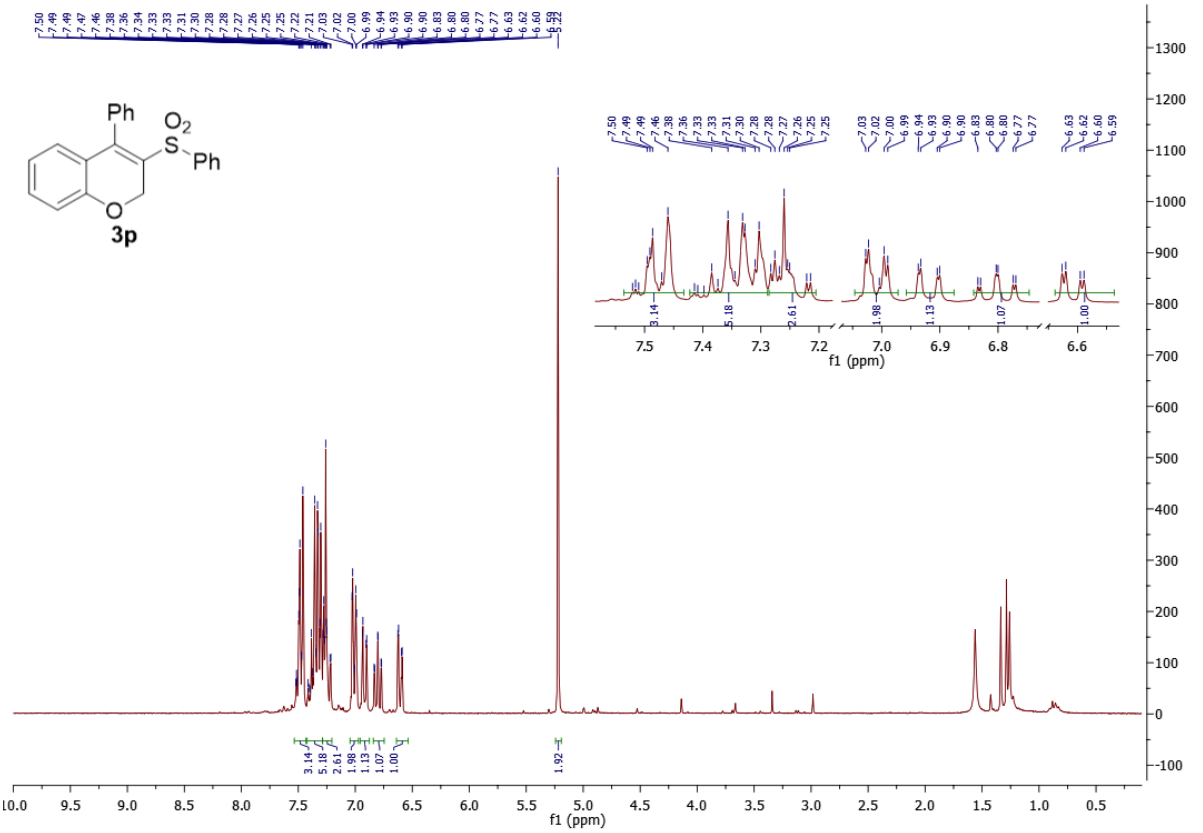

163.9
155.6 154.0
141.0
134.6 133.7
128.8 128.8 126.7 125.5 125.2 118.5 117.6
21.6
15.6
Me
O2
S
Ph
O
O
3n
f1 (ppm)

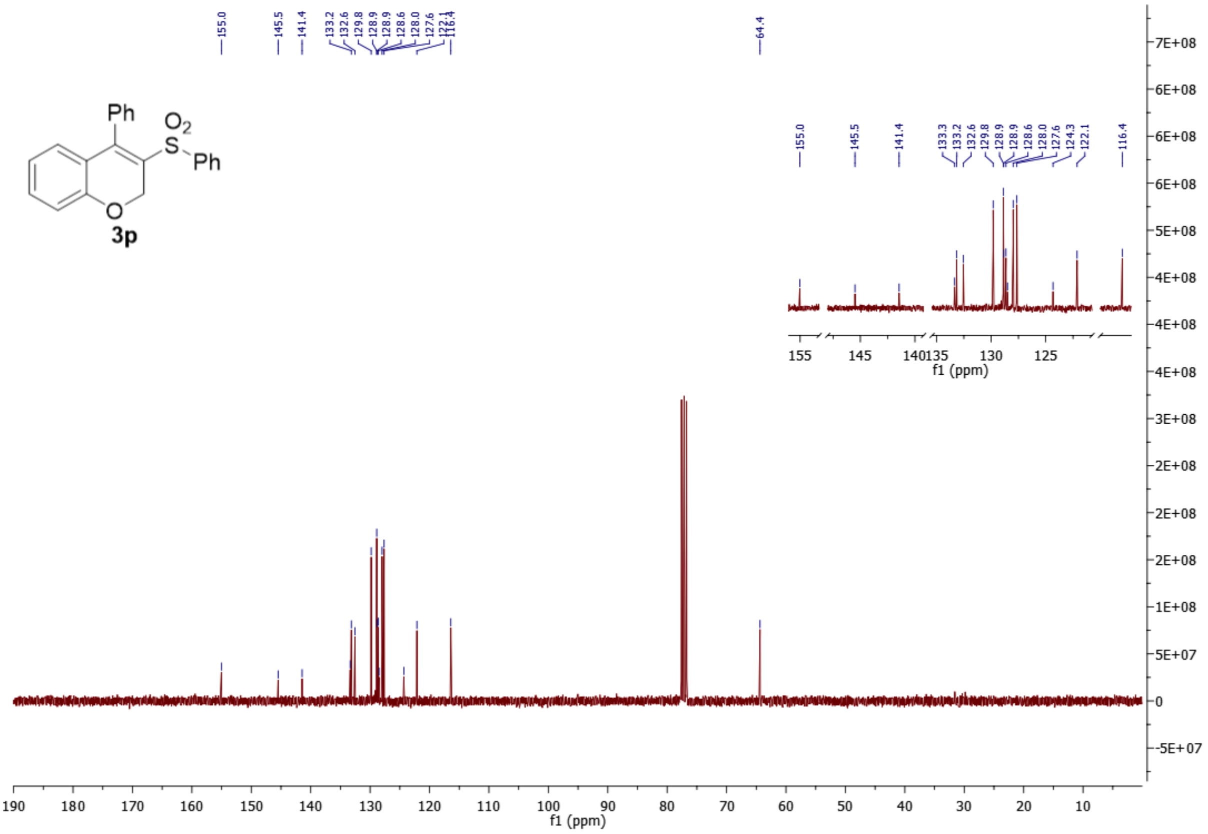

3o

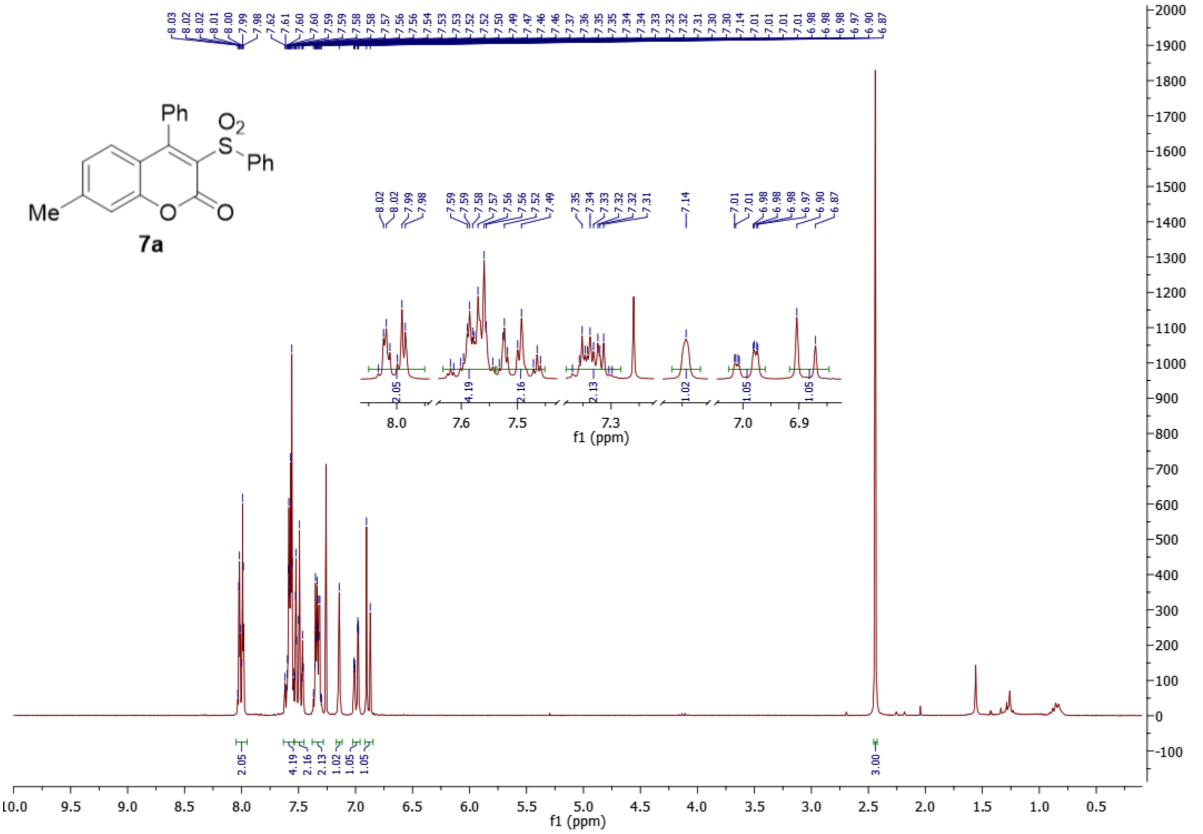
Me
O2
S
Ph
O
O
8.10, 8.10, 8.09, 8.07, 8.07, 8.06, 7.88, 7.85, 7.66, 7.65, 7.63, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.58, 7.58, 7.57, 7.55, 7.52, 7.52, 7.50, 7.49, 7.48, 7.41, 7.38, 7.38, 7.35, 7.35, 7.30, 7.27, 7.26, 7.26
3.65, 3.62, 3.61, 3.58
1.97, 1.94, 1.91, 1.88, 1.85, 1.82
1.26, 1.23, 1.20
1.85
1.02
4.00
0.97
1.17
1.95
2.15
3.18
f1 (ppm)

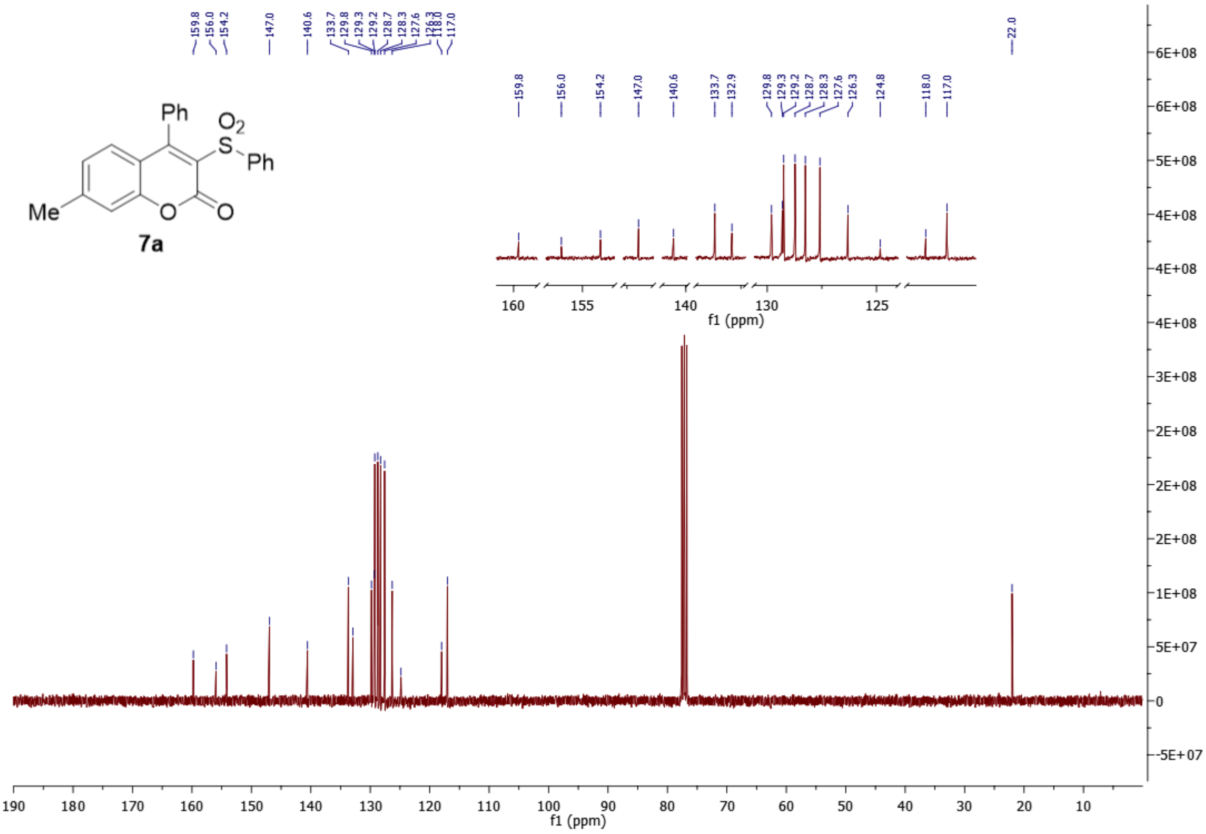

3o

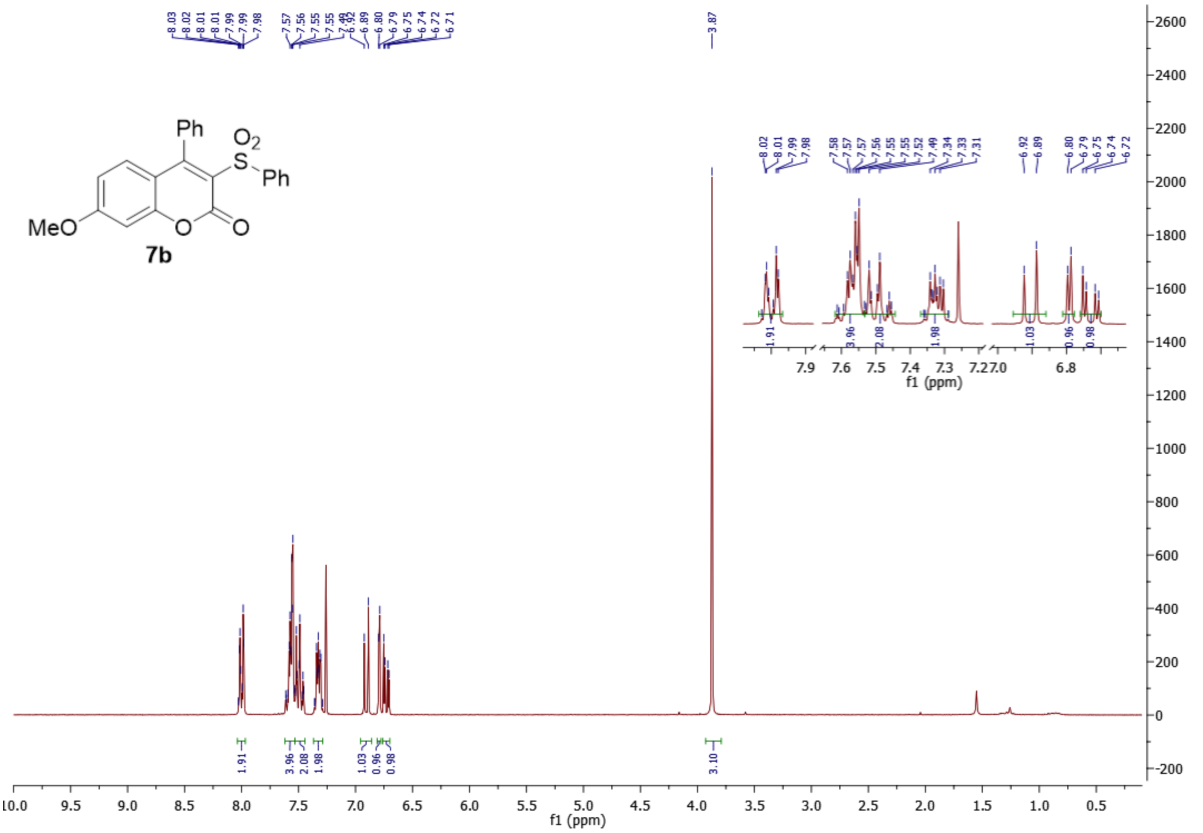
Me
O2
S
Ph
O
O
162.6
155.6
153.9
141.1
134.6
133.7
128.8
126.7
125.6
125.2
118.9
117.6
30.0
25.2
14.9
f1 (ppm)

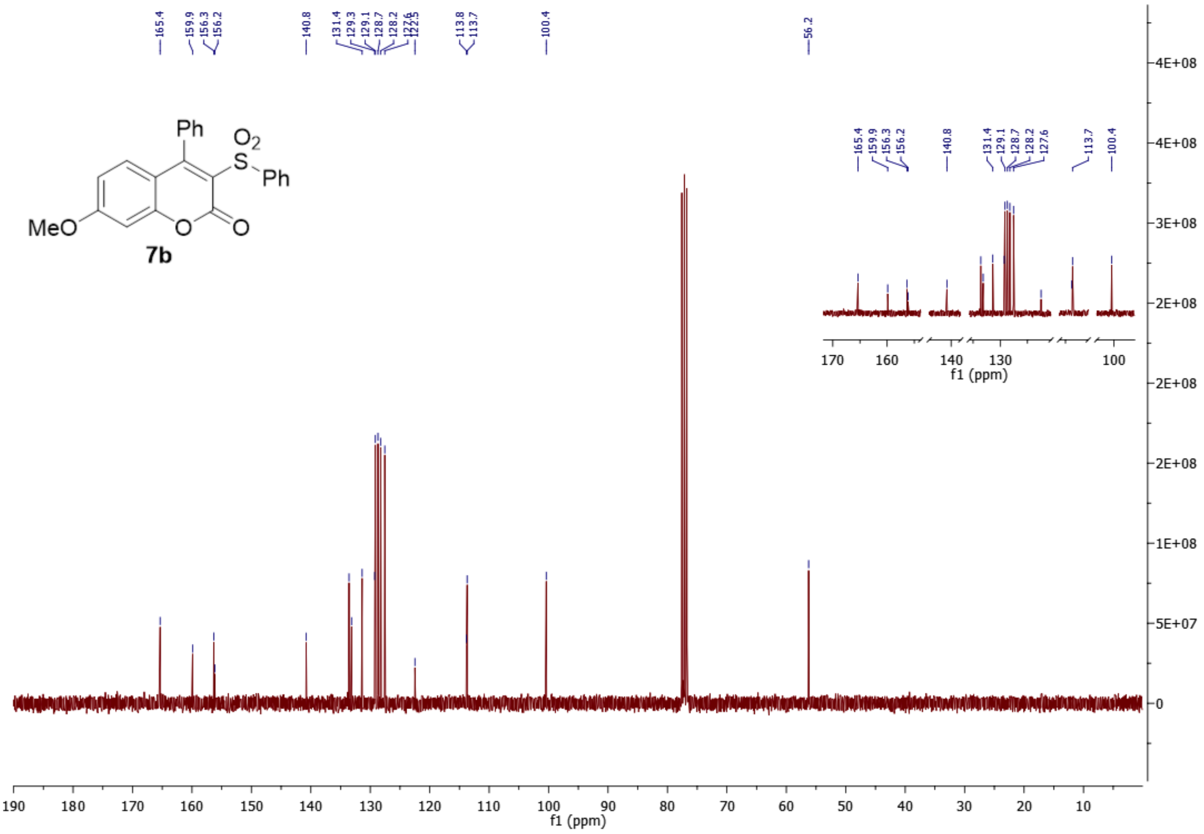

7.50
7.49
7.49
7.47
7.46
7.38
7.36
7.36
7.34
7.33
7.33
7.31
7.30
7.28
7.28
7.27
7.26
7.25
7.25
7.22
7.21
7.03
7.02
7.00
6.99
6.94
6.93
6.90
6.90
6.83
6.80
6.80
6.77
6.77
6.63
6.62
6.60
6.59
5.22
Ph
O2
S
Ph
O
3p
3.14
5.18
2.61
1.98
1.13
1.07
1.00
1.92
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

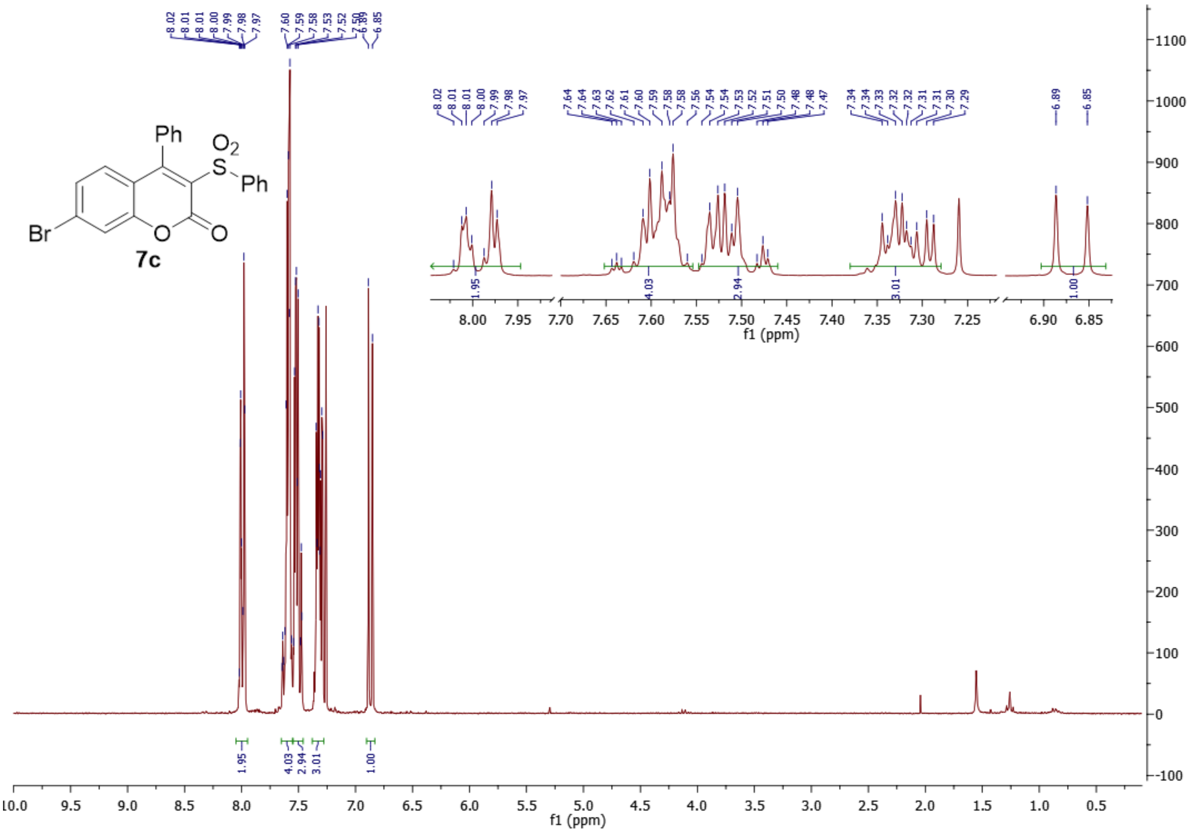

155.0
145.5
141.4
133.2
132.6
129.8
128.9
128.9
128.6
128.0
127.6
122.1
116.4
64.4
Ph
O2
S
Ph
O
3p
155.0
145.5
141.4
133.3
133.2
132.6
129.8
128.9
128.9
128.6
128.0
127.6
124.3
122.1
116.4
155
145
140135
130
125
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07

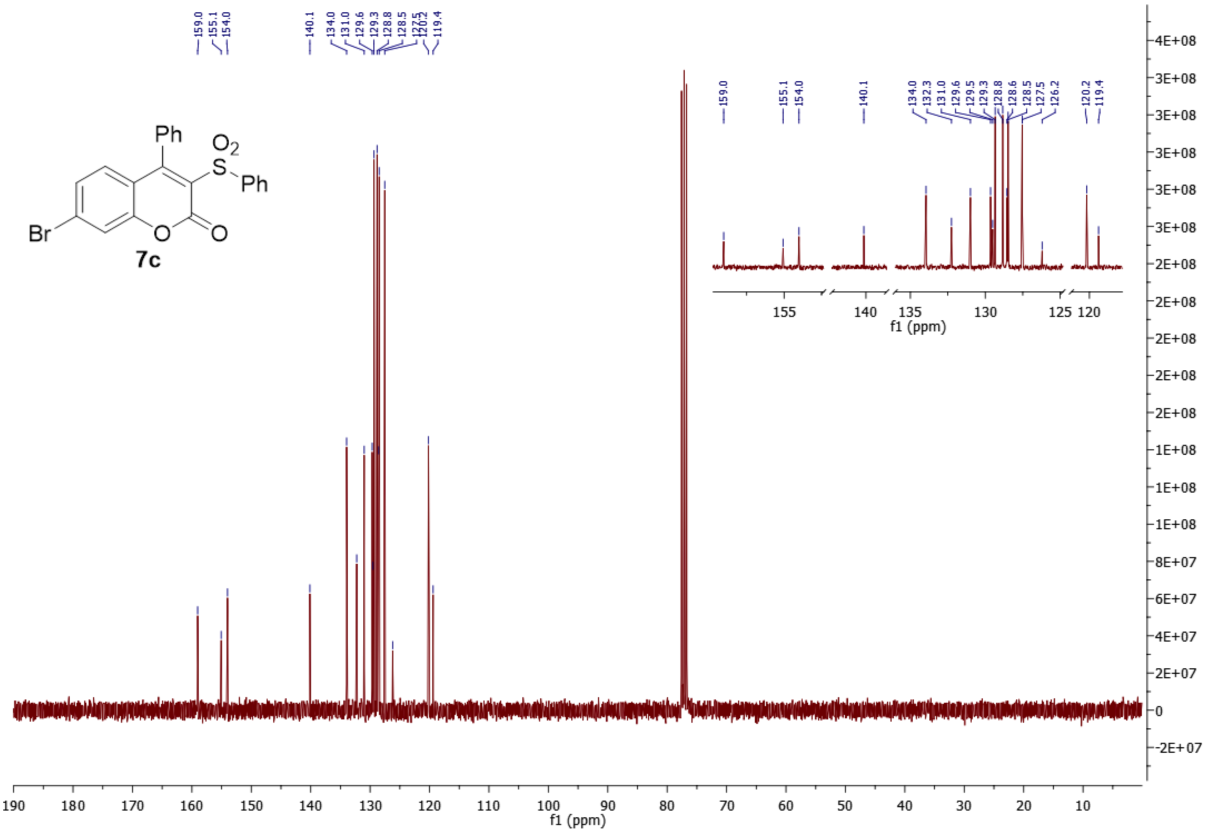

Ph
O2
S
Ph
Me
O
O
7a
8.03 8.02 8.02 8.01 8.00 7.99 7.98 7.62 7.61 7.60 7.60 7.59 7.59 7.59 7.58 7.58 7.57 7.56 7.56 7.54 7.53 7.53 7.52 7.52 7.50 7.49 7.47 7.46 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.14 7.01 7.01 7.01 7.01 6.98 6.98 6.98 6.98 6.97 6.90 6.87
8.02 8.02 7.99 7.98 7.59 7.59 7.58 7.57 7.56 7.56 7.52 7.49 7.35 7.34 7.33 7.32 7.32 7.31 7.14 7.01 7.01 6.98 6.98 6.98 6.97 6.90 6.87
2.05 4.19 2.16 2.13 1.02 1.05 1.05
8.0 7.6 7.5 7.3 7.0 6.9
f1 (ppm)
2.05 4.19 2.16 2.13 1.02 1.05 1.05 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

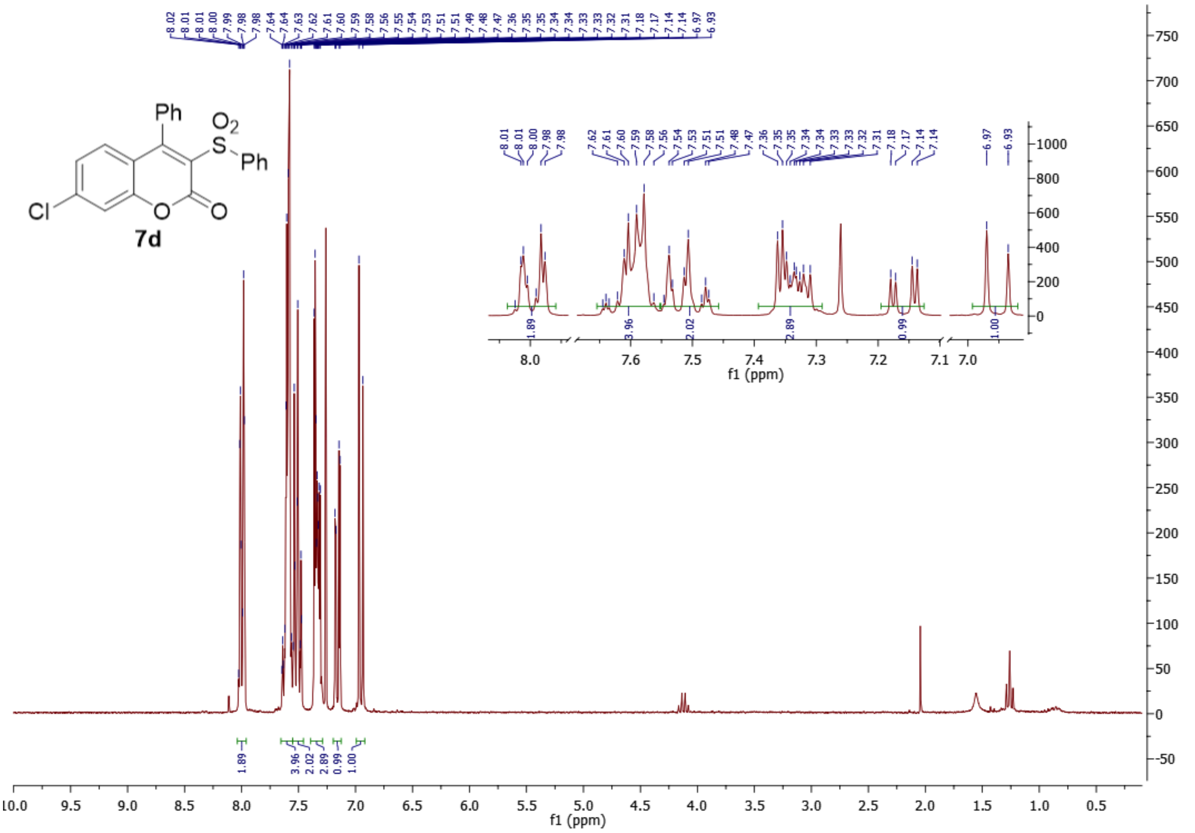

Ph
O2
S
Ph
Me
O
O
7a
159.8 156.0 154.2 147.0 140.6 133.7 132.9 129.8 129.3 129.2 128.7 128.3 127.6 126.3 124.8 118.0 117.0 22.0
159.8 156.0 154.2 147.0 140.6 133.7 132.9 129.8 129.3 129.2 128.7 128.3 127.6 126.3 124.8 118.0 117.0
160 155 140 130 125
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
6E+08 6E+08 5E+08 4E+08 4E+08 4E+08 3E+08 2E+08 2E+08 2E+08 1E+08 5E+07 0 -5E+07


8.03
8.02
8.01
8.01
7.99
7.99
7.98
7.57
7.56
7.55
7.55
7.49
6.92
6.89
6.80
6.79
6.75
6.74
6.72
6.71
3.87
Ph
O2
S
Ph
MeO
O
O
7b
8.02
8.01
7.99
7.98
7.58
7.57
7.57
7.56
7.55
7.55
7.52
7.49
7.34
7.33
7.31
6.92
6.89
6.80
6.79
6.75
6.74
6.72
1.91
3.96
2.08
1.98
1.03
0.96
0.98
3.10
7.9
7.6
7.5
7.4
7.3
7.2
7.0
6.8
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

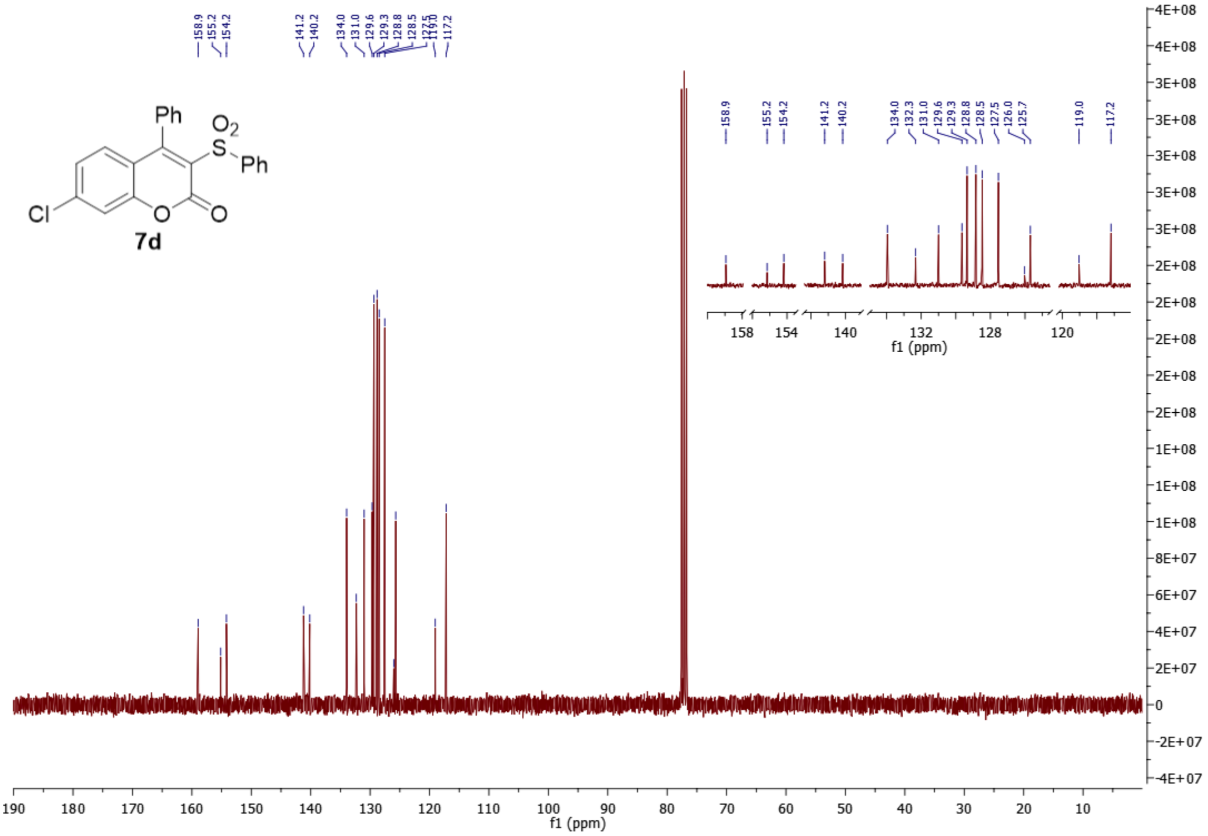

165.4
159.9
156.3
156.2
140.8
131.4
129.3
129.1
128.7
128.2
127.6
122.5
113.8
113.7
100.4
56.2
Ph
O2
S
Ph
MeO
O
O
7b
165.4
159.9
156.3
156.2
140.8
131.4
129.1
128.7
128.2
127.6
113.7
100.4
170
160
140
130
100
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0


8.02
8.01
8.01
8.00
7.99
7.98
7.97
7.60
7.59
7.58
7.53
7.52
7.50
6.89
6.85
Ph
O2
S
Ph
Br
O
O
7c
7.64
7.64
7.63
7.62
7.61
7.60
7.59
7.58
7.58
7.56
7.54
7.54
7.53
7.52
7.51
7.50
7.48
7.48
7.47
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
1.95
4.03
2.94
3.01
1.00
f1 (ppm)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

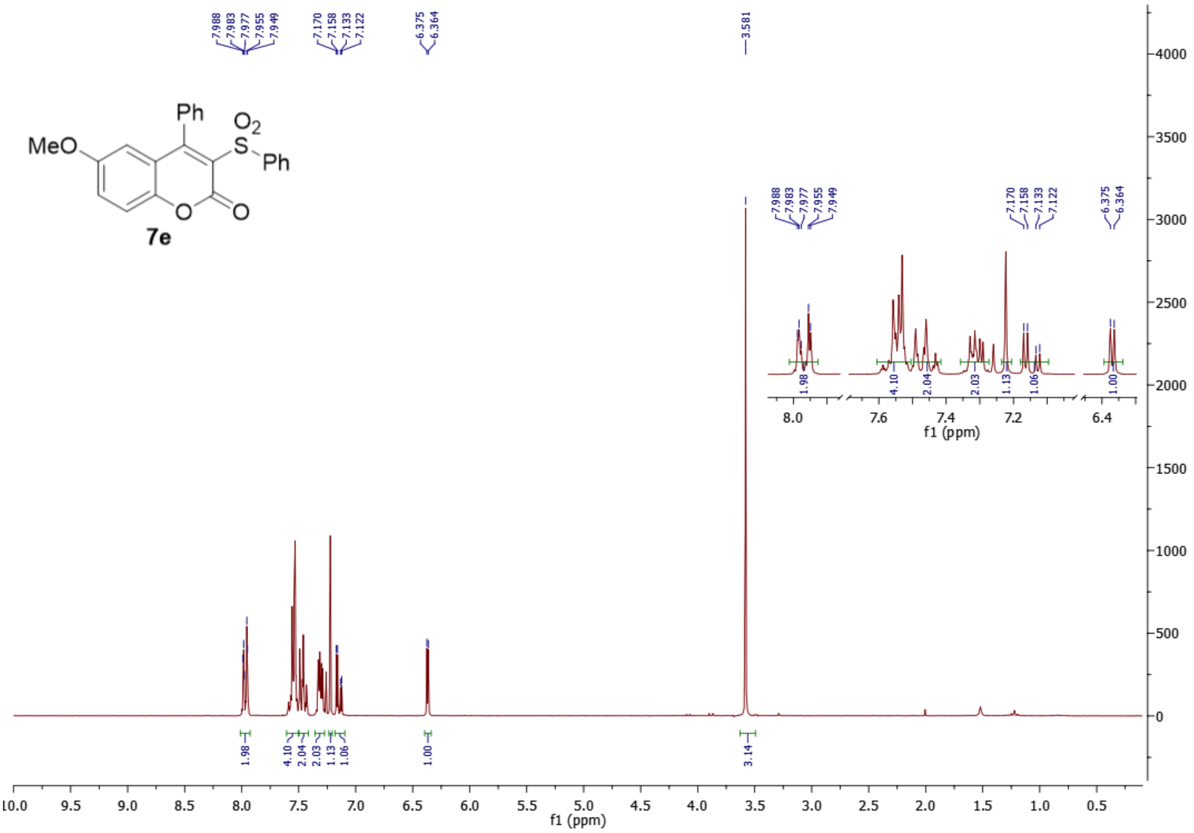

159.0
155.1
154.0
140.1
134.0
131.0
129.6
129.3
128.8
128.5
127.5
120.2
119.4
Ph
O2
S
Ph
Br
O
O
7c
132.3
129.5
128.6
126.2
155
140
135
130
125
120
f1 (ppm)
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Ph
O2
S
Ph
Cl
O
O
8.02, 8.01, 8.01, 8.00, 7.99, 7.98, 7.98, 7.64, 7.63, 7.63, 7.62, 7.62, 7.61, 7.60, 7.59, 7.58, 7.56, 7.55, 7.54, 7.54, 7.53, 7.51, 7.51, 7.49, 7.48, 7.47, 7.36, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.31, 7.18, 7.17, 7.14, 7.14, 6.97, 6.93
1.89
3.96
2.02
2.89
0.99
1.00
f1 (ppm)

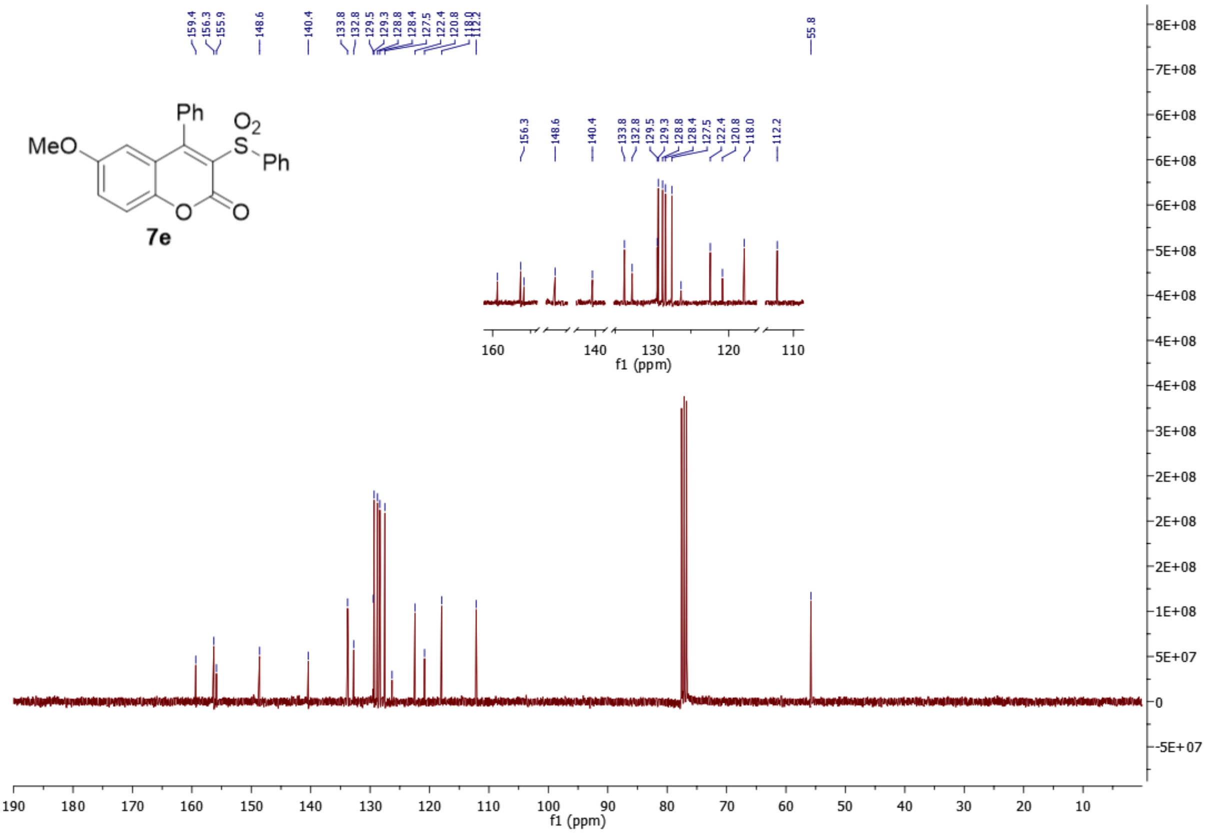
7d


Ph
O2
S
Ph
Cl
O
O
158.9, 155.2, 154.2, 141.2, 140.2, 134.0, 132.3, 131.0, 129.6, 129.3, 128.8, 128.5, 127.5, 126.0, 125.7, 119.0, 117.2
f1 (ppm)

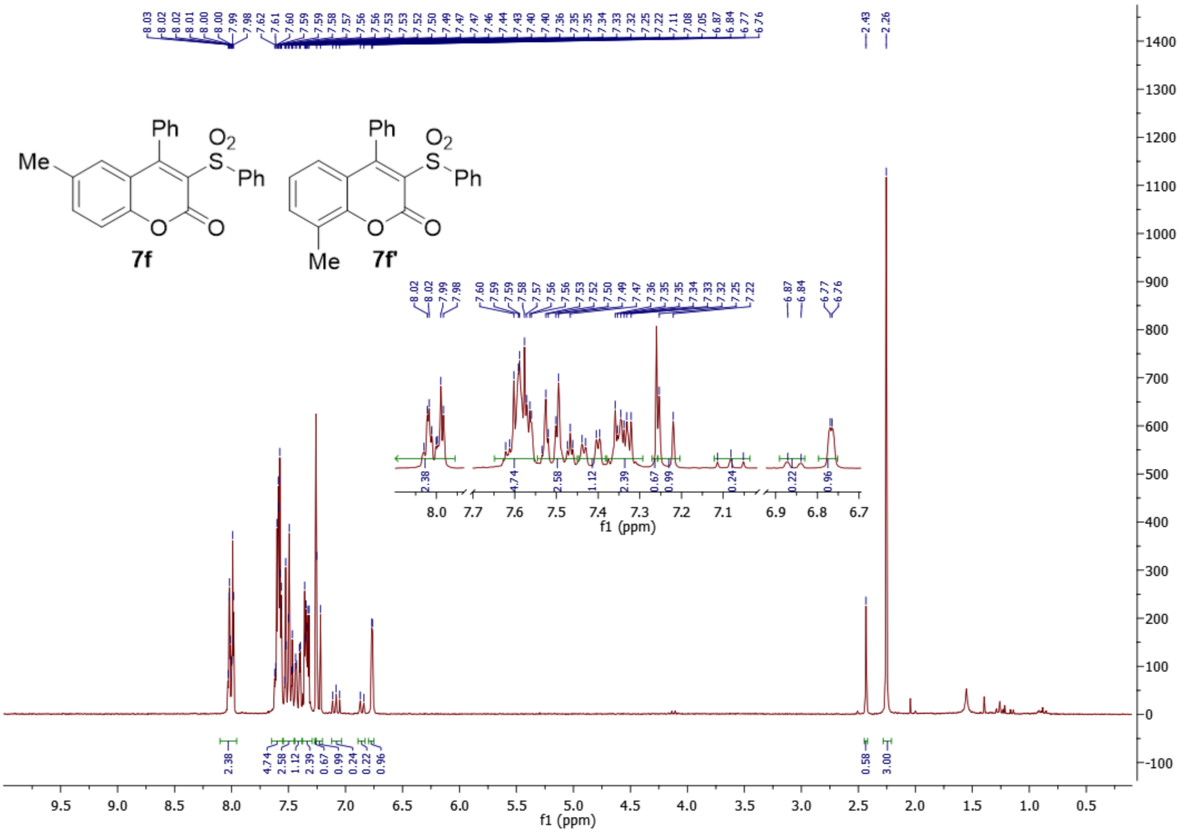
7d

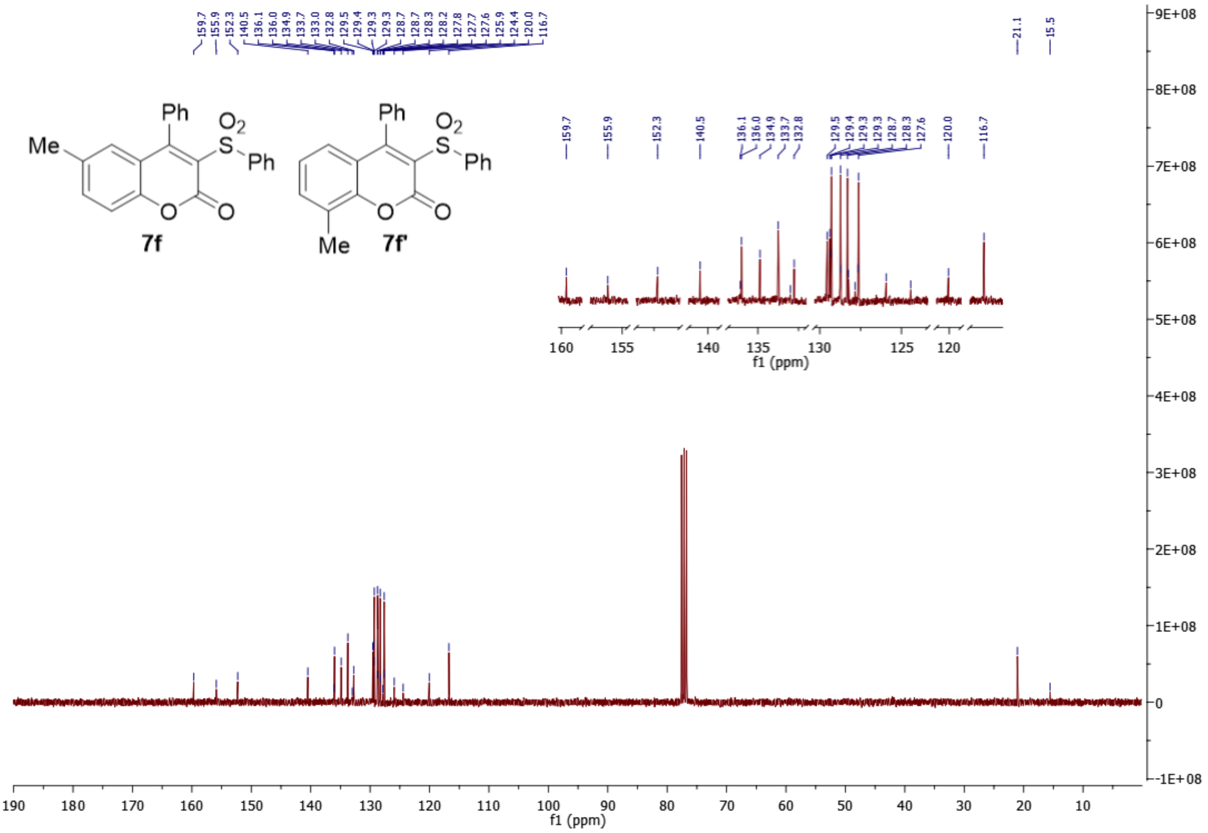

MeO
Ph
O2
S
Ph
O
O
7.988
7.983
7.977
7.955
7.949
7.170
7.158
7.133
7.122
6.375
6.364
3.581
1.98
4.10
2.04
2.03
1.13
1.06
1.00
3.14
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0

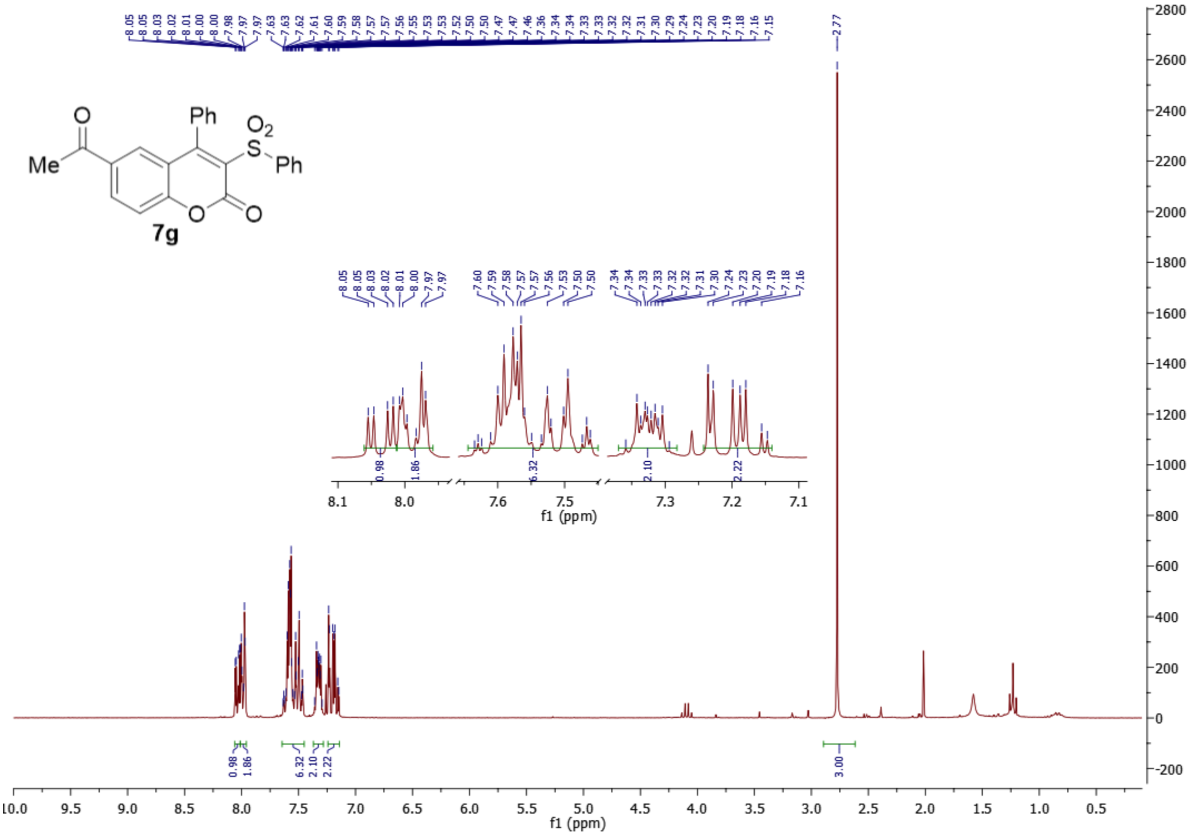
7e

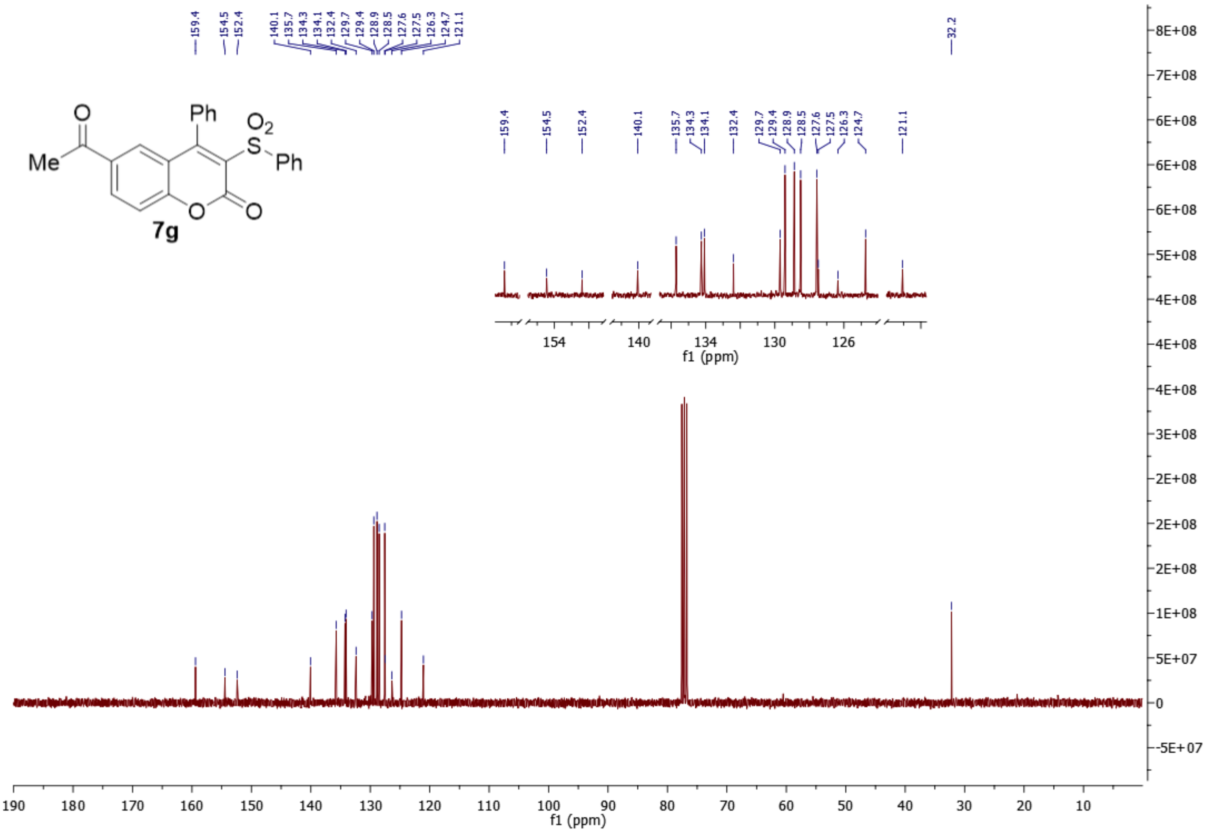

MeO
Ph
O2
S
Ph
O
O
159.4
156.3
155.9
148.6
140.4
133.8
132.8
129.5
129.3
128.8
128.4
127.5
122.4
120.8
118.0
112.2
55.8
f1 (ppm)
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07

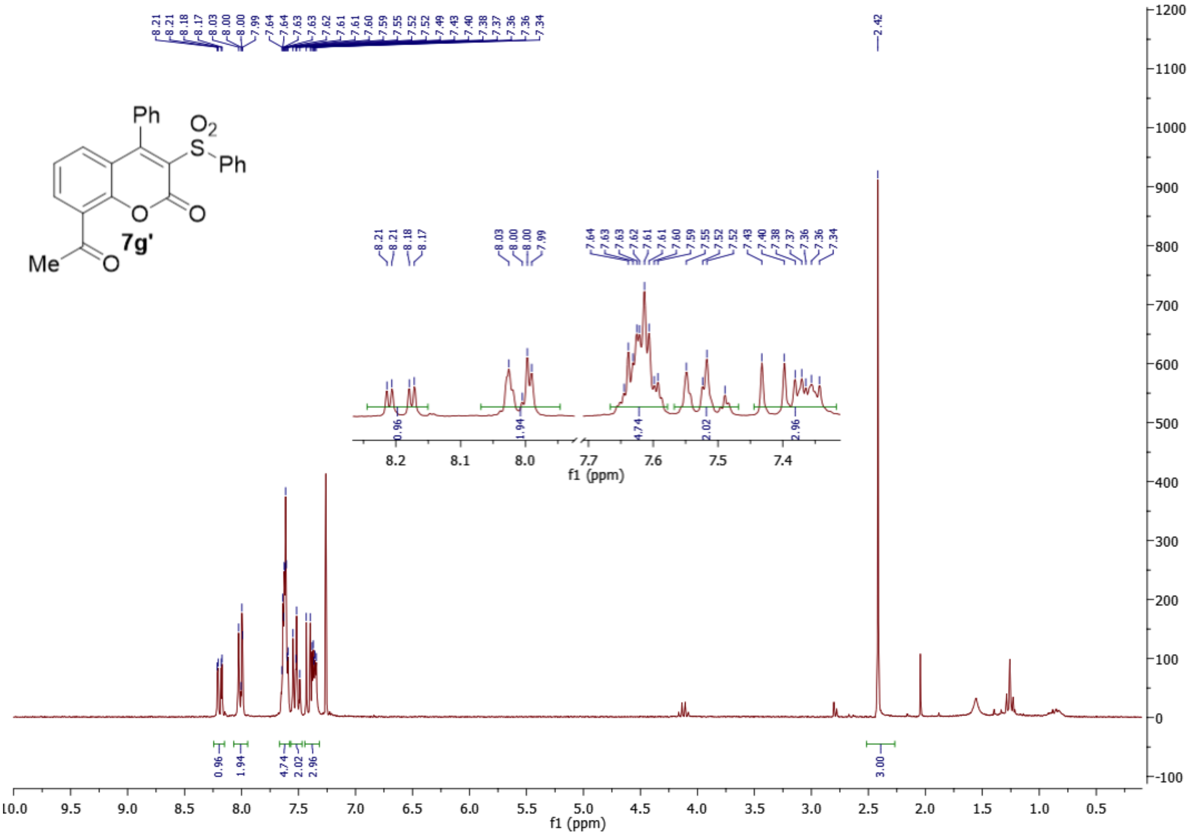
7e

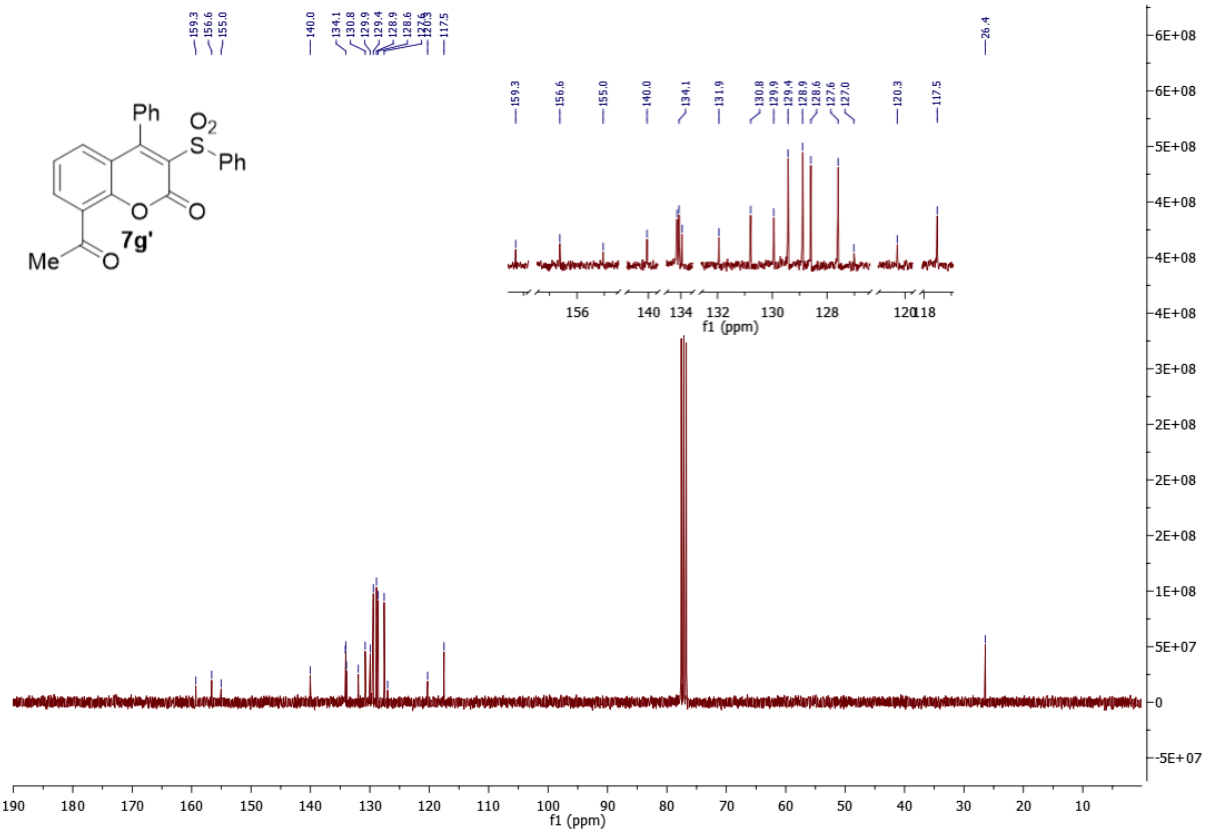

8.03 8.02 8.01 8.00 7.99 7.98 7.62 7.61 7.60 7.59 7.59 7.58 7.57 7.56 7.56 7.53 7.53 7.52 7.50 7.49 7.47 7.47 7.46 7.44 7.43 7.40 7.36 7.35 7.35 7.34 7.33 7.32 7.25 7.22 7.11 7.08 7.05 6.87 6.84 6.77 6.76
2.43
2.26
Ph
O2
S
Ph
Me
O
O
7f
Ph
O2
S
Ph
O
O
Me
7f'
8.02 8.02 7.99 7.98 7.60 7.59 7.59 7.58 7.57 7.56 7.56 7.53 7.52 7.50 7.49 7.47 7.36 7.35 7.35 7.34 7.33 7.32 7.25 7.22
6.87 6.84 6.77 6.76
2.38 4.74 2.58 1.12 2.39 0.67 0.99 0.24 0.22 0.96
8.0 7.7 7.6 7.5 7.4 7.3 7.2 7.1 6.9 6.8 6.7
f1 (ppm)
2.38 4.74 2.58 1.12 2.39 0.67 0.99 0.24 0.22 0.96 0.58 3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

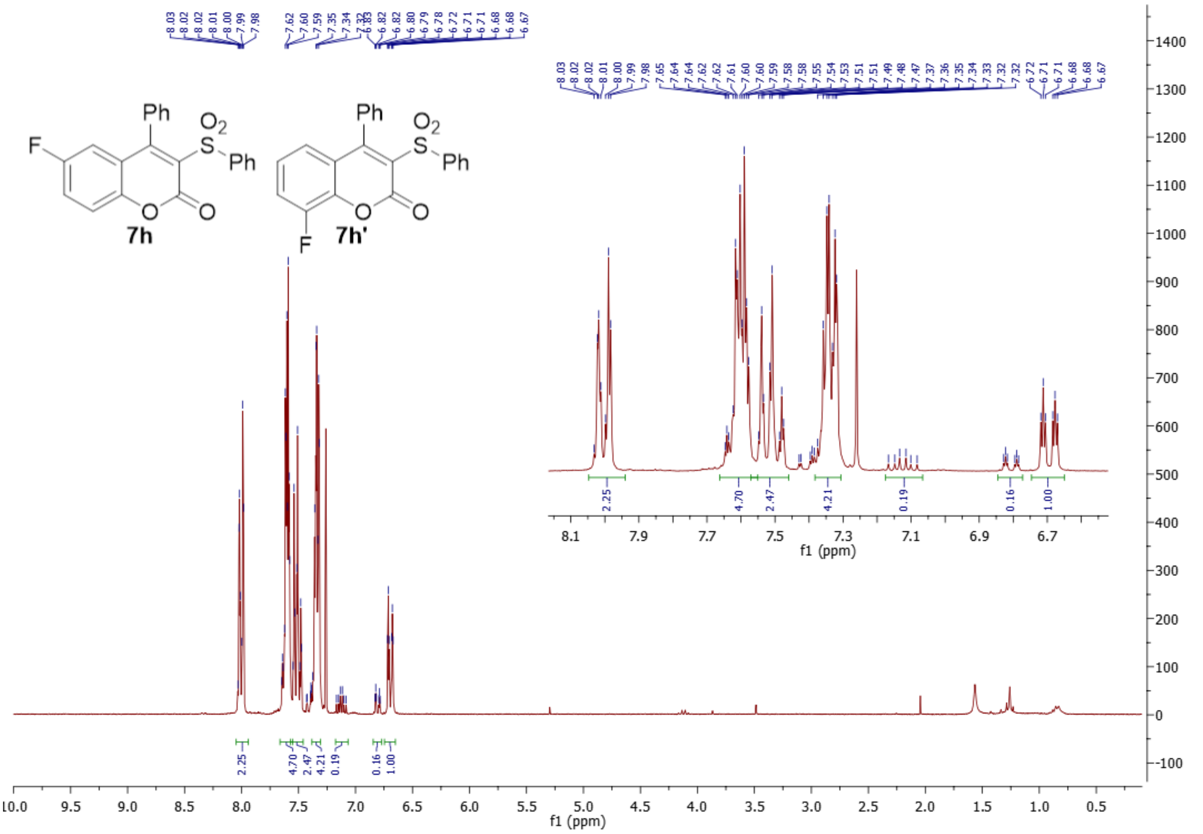

159.7 155.9 152.3 140.5 136.1 136.0 134.9 133.7 133.0 132.8 129.5 129.4 129.3 129.3 128.7 128.3 128.2 127.8 127.7 127.6 125.9 124.4 120.0 116.7
21.1
15.5
Ph
O2
S
Ph
Me
O
O
7f
Ph
O2
S
Ph
O
O
Me
7f'
159.7 155.9 152.3 140.5 136.1 136.0 134.9 133.7 132.8 129.5 129.4 129.3 129.3 128.7 128.3 127.6 120.0 116.7
160 155 140 135 130 125 120
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
9E+08 8E+08 7E+08 6E+08 5E+08 4E+08 3E+08 2E+08 1E+08 0 -1E+08

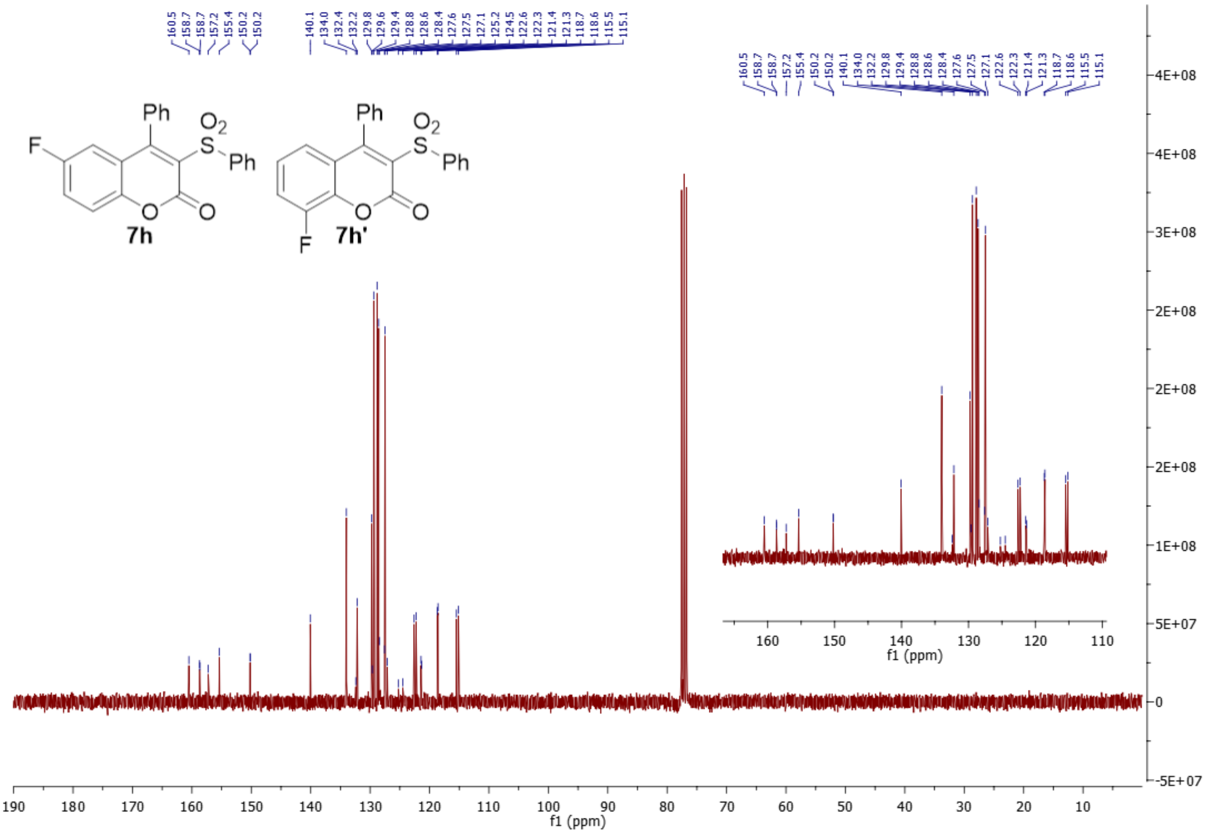

8.05 8.05 8.03 8.02 8.01 8.00 8.00 7.98 7.97 7.97 7.63 7.62 7.61 7.60 7.59 7.58 7.57 7.57 7.56 7.55 7.53 7.53 7.52 7.50 7.50 7.47 7.47 7.46 7.36 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.29 7.24 7.23 7.20 7.19 7.18 7.16 7.15
2.77
O
Ph
O2
S
Me
Ph
O
O
7g
8.05 8.05 8.03 8.02 8.01 8.00 7.97 7.97
7.60 7.59 7.58 7.57 7.57 7.56 7.53 7.50 7.50
7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.24 7.23 7.20 7.19 7.18 7.16
0.98
1.86
6.32
2.10
2.22
8.1
8.0
7.6
7.5
7.3
7.2
7.1
f1 (ppm)
0.98
1.86
6.32
2.10
2.22
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

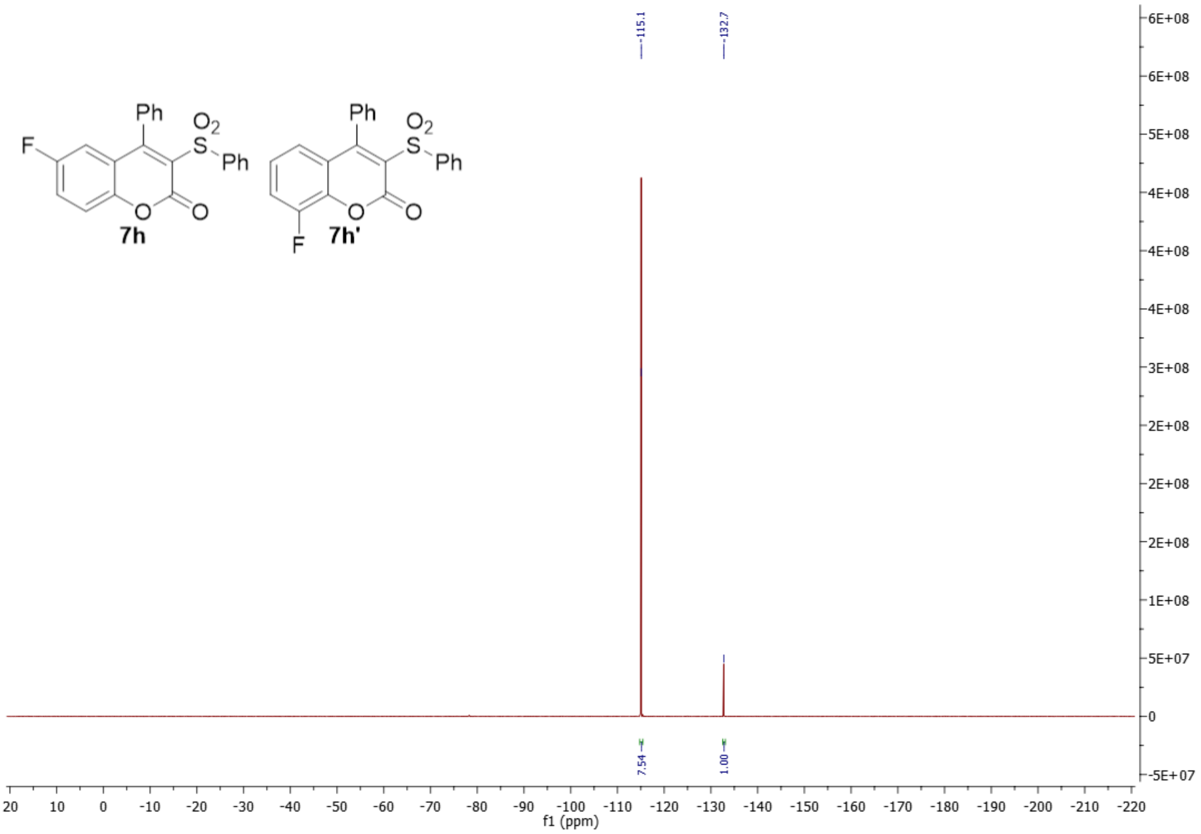

159.4
154.5
152.4
140.1 135.7 134.3 134.1 132.4 129.7 129.4 128.9 128.5 127.6 127.5 126.3 124.7 121.1
32.2
O
Ph
O2
S
Me
Ph
O
O
7g
159.4
154.5
152.4
140.1
135.7 134.3 134.1
132.4
129.7 129.4 128.9 128.5 127.6 127.5 126.3 124.7
121.1
154
140
134
130
126
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
8E+08
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07

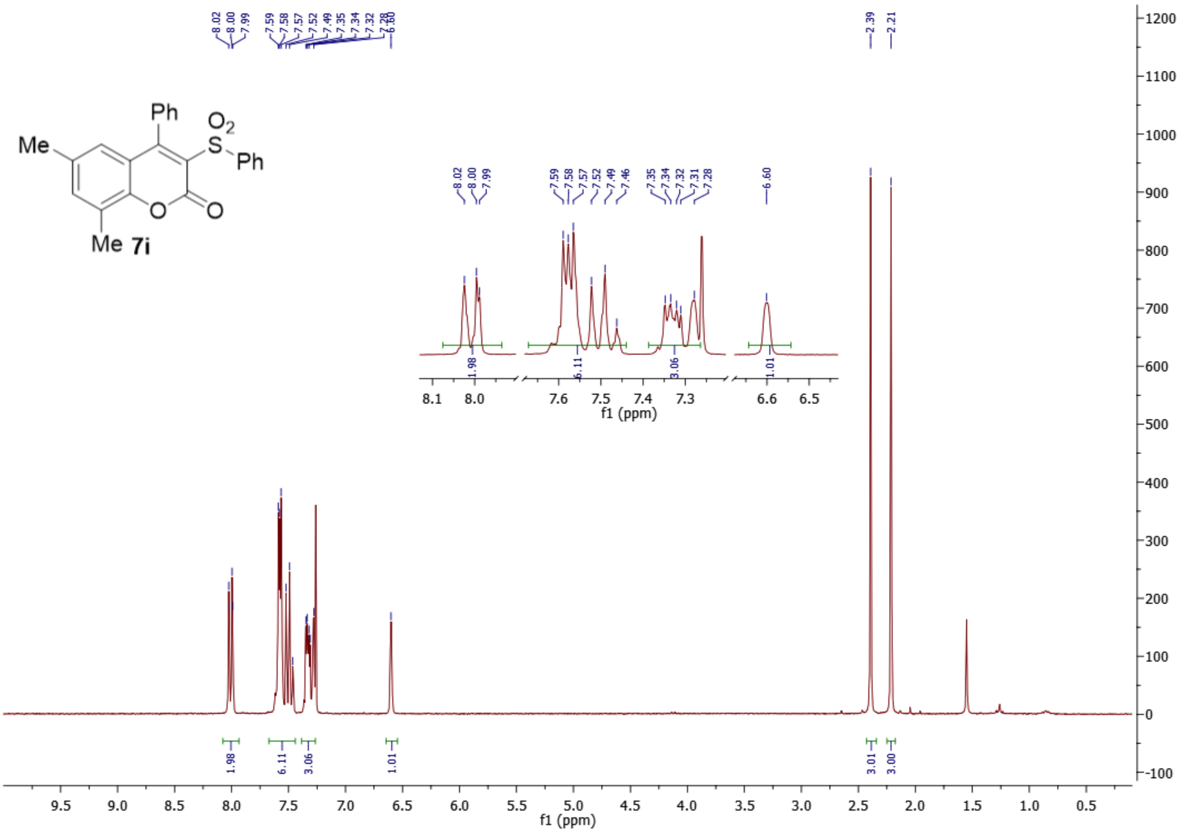

8.21
8.21
8.18
8.17
8.03
8.00
8.00
7.99
7.64
7.63
7.63
7.62
7.61
7.61
7.60
7.59
7.55
7.52
7.52
7.49
7.43
7.40
7.38
7.37
7.36
7.36
7.34
2.42
Ph
O2
S
Ph
O
O
Me
O
7g'
0.96
1.94
4.74
2.02
2.96
3.00
f1 (ppm)
-1200
-1100
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
-0
--100

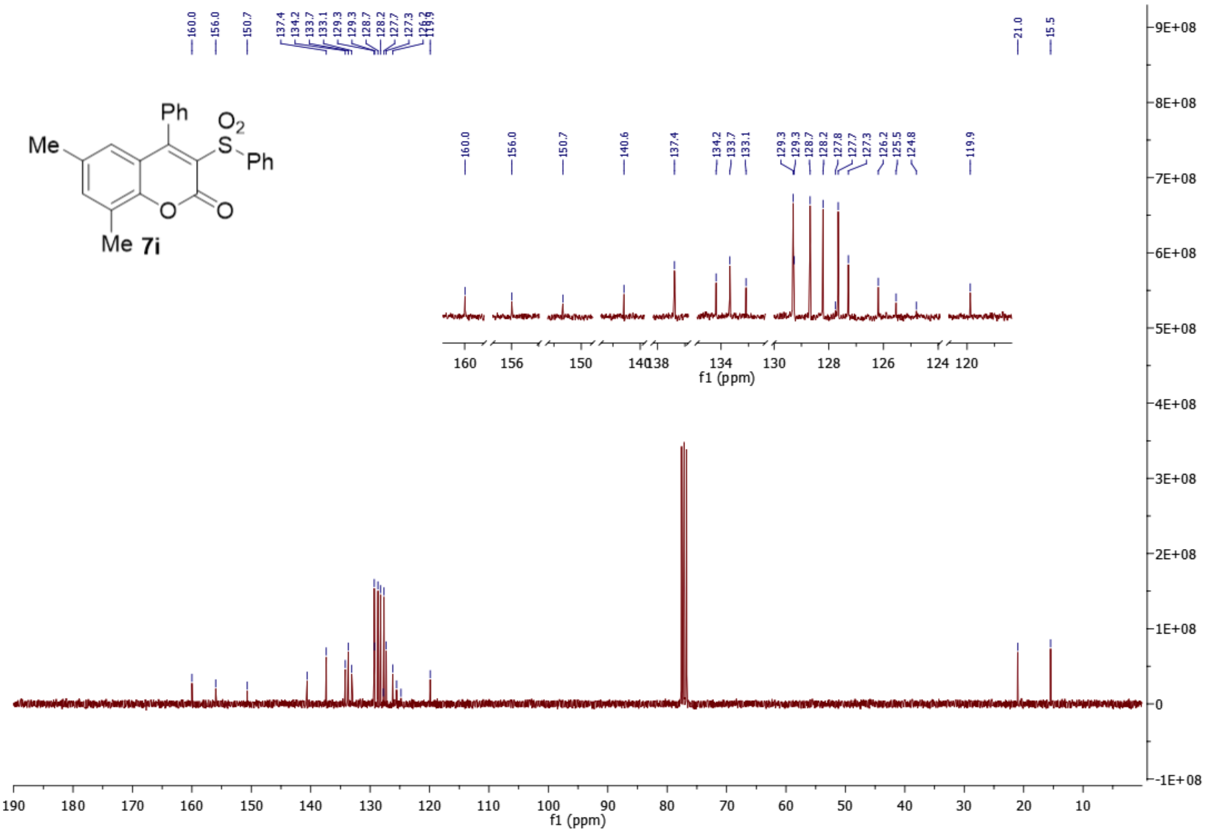

159.3
156.6
155.0
140.0
134.1
131.9
130.8
129.9
129.4
128.9
128.6
127.6
127.0
120.3
117.5
26.4
Ph
O2
S
Ph
O
O
Me
O
7g'
f1 (ppm)
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07


7h
7h'
Ph
O2
S
Ph
F
O
O
8.03
8.02
8.02
8.01
8.00
7.99
7.98
7.62
7.60
7.59
7.35
7.34
7.32
6.83
6.82
6.82
6.80
6.79
6.78
6.72
6.71
6.71
6.68
6.68
6.67
8.03
8.02
8.02
8.01
8.00
7.99
7.98
7.65
7.64
7.64
7.62
7.62
7.61
7.60
7.60
7.59
7.58
7.58
7.55
7.54
7.53
7.51
7.51
7.49
7.48
7.47
7.37
7.36
7.35
7.34
7.33
7.32
7.32
6.72
6.71
6.71
6.68
6.68
6.67
2.25
4.70
2.47
4.21
0.19
0.16
1.00
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

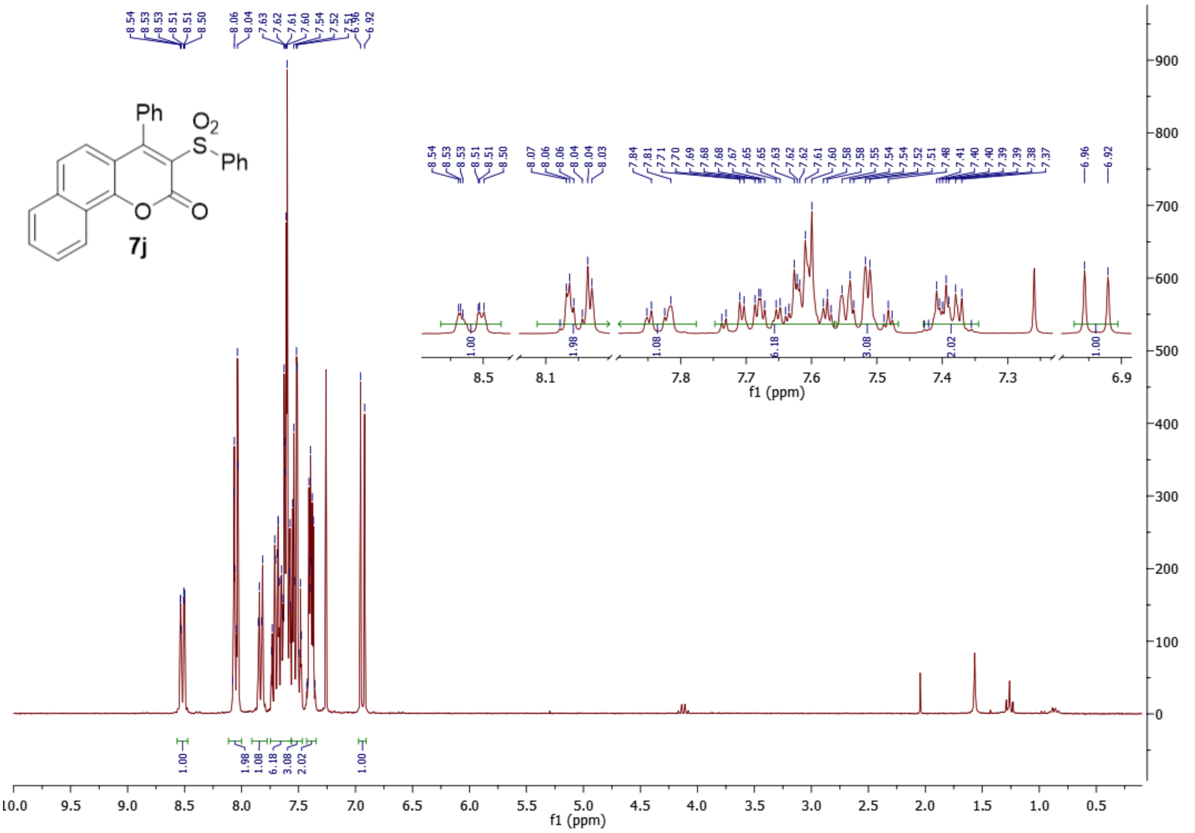

7h
7h'
Ph
O2
S
Ph
F
O
O
160.5
158.7
158.7
157.2
155.4
150.2
150.2
140.1
134.0
132.4
132.2
129.8
129.6
129.4
128.8
128.6
128.4
127.6
127.5
127.1
125.2
124.5
122.6
122.3
121.4
121.3
118.7
118.6
115.5
115.1
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07


7h
7h'
F
Ph
O2
S
Ph
O
O
-115.1
-132.7
7.54
1.00
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

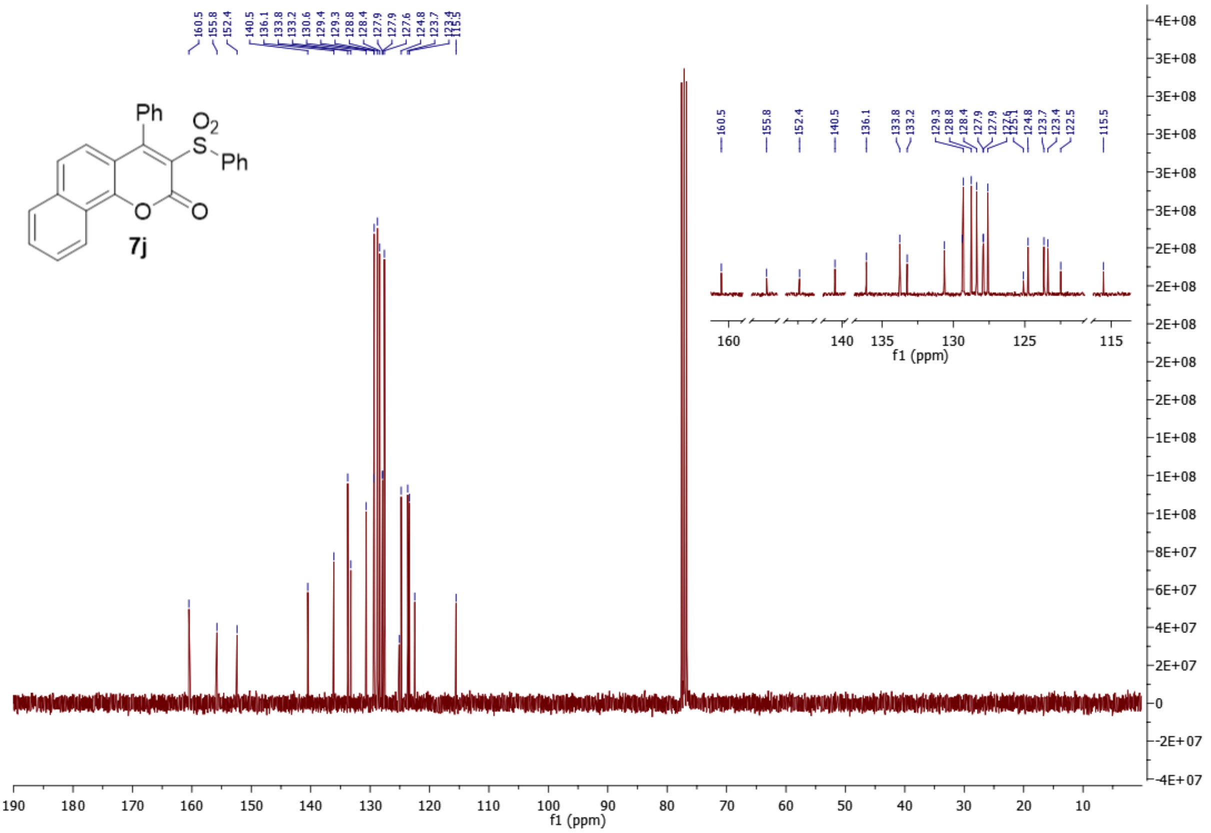

Me
Me
7i
Ph
O2
S
Ph
O
O
8.02
8.00
7.99
7.59
7.58
7.57
7.52
7.49
7.46
7.35
7.34
7.32
7.31
7.28
6.60
2.39
2.21
1.98
6.11
3.06
1.01
3.01
3.00
8.1 8.0 7.6 7.5 7.4 7.3 6.6 6.5
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



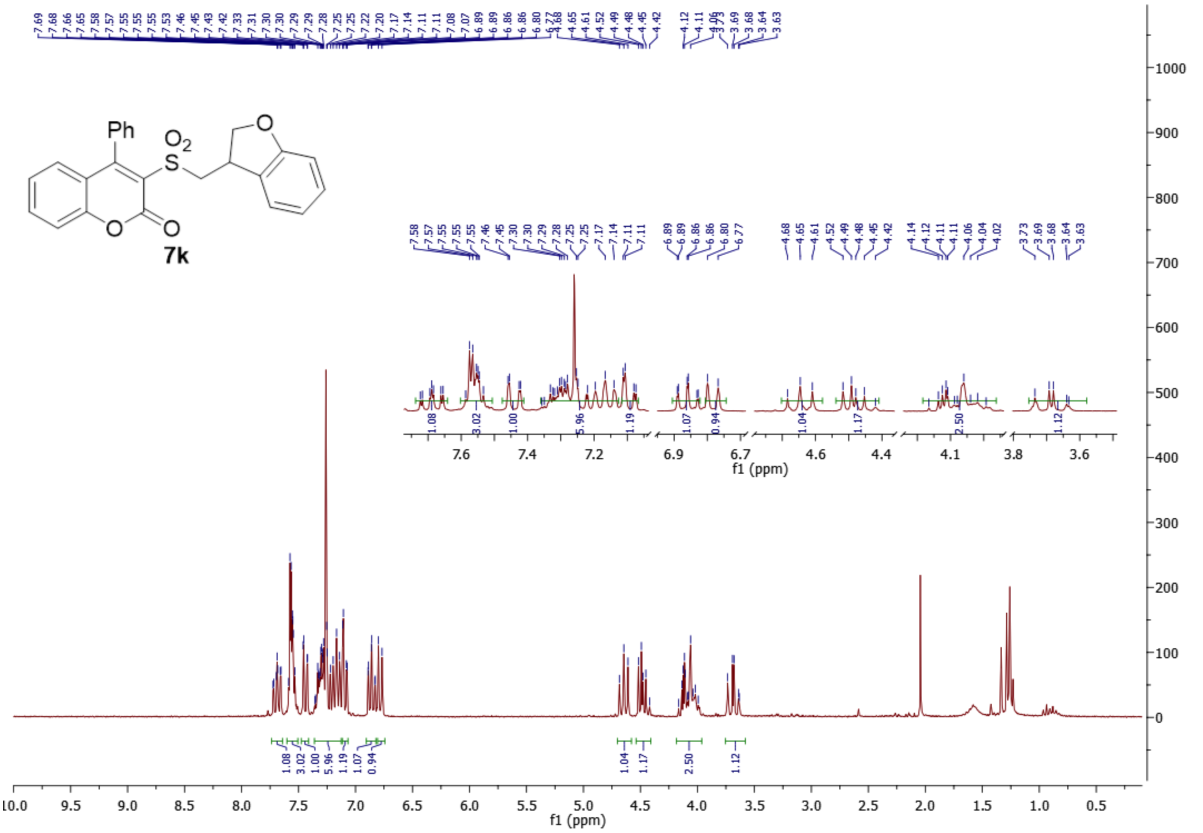
Ph
O2
S
Ph
Me
O
O
Me
7i
160.0
156.0
150.7
137.4
134.2
133.7
133.1
129.3
129.3
128.7
128.2
127.7
127.3
126.2
119.9
21.0
15.5
140.6
127.8
125.5
124.8
160
156
150
140
138
134
130
128
126
124
120
f1 (ppm)
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



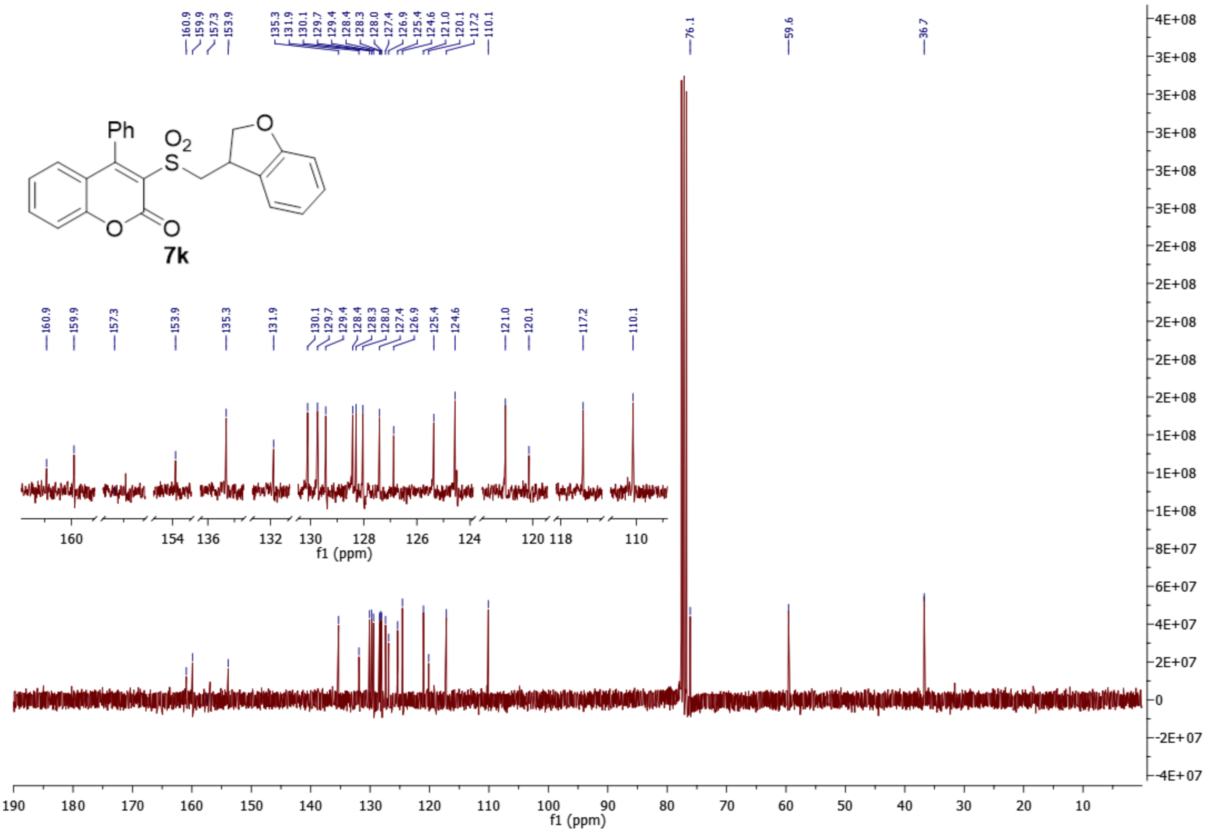
Ph
O2
S
Ph
O
O
7j
8.54
8.53
8.53
8.51
8.51
8.50
8.06
8.04
7.63
7.62
7.61
7.60
7.54
7.52
7.51
6.96
6.92
8.07
8.06
8.06
8.04
8.04
8.03
7.84
7.81
7.71
7.70
7.69
7.68
7.68
7.67
7.65
7.65
7.63
7.62
7.62
7.61
7.60
7.58
7.58
7.55
7.54
7.54
7.52
7.51
7.48
7.41
7.40
7.39
7.39
7.38
7.37
1.00
1.98
1.08
6.18
3.08
2.02
1.00
8.5
8.1
7.8
7.7
7.6
7.5
7.4
7.3
6.9
f1 (ppm)
900
800
700
600
500
400
300
200
100
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

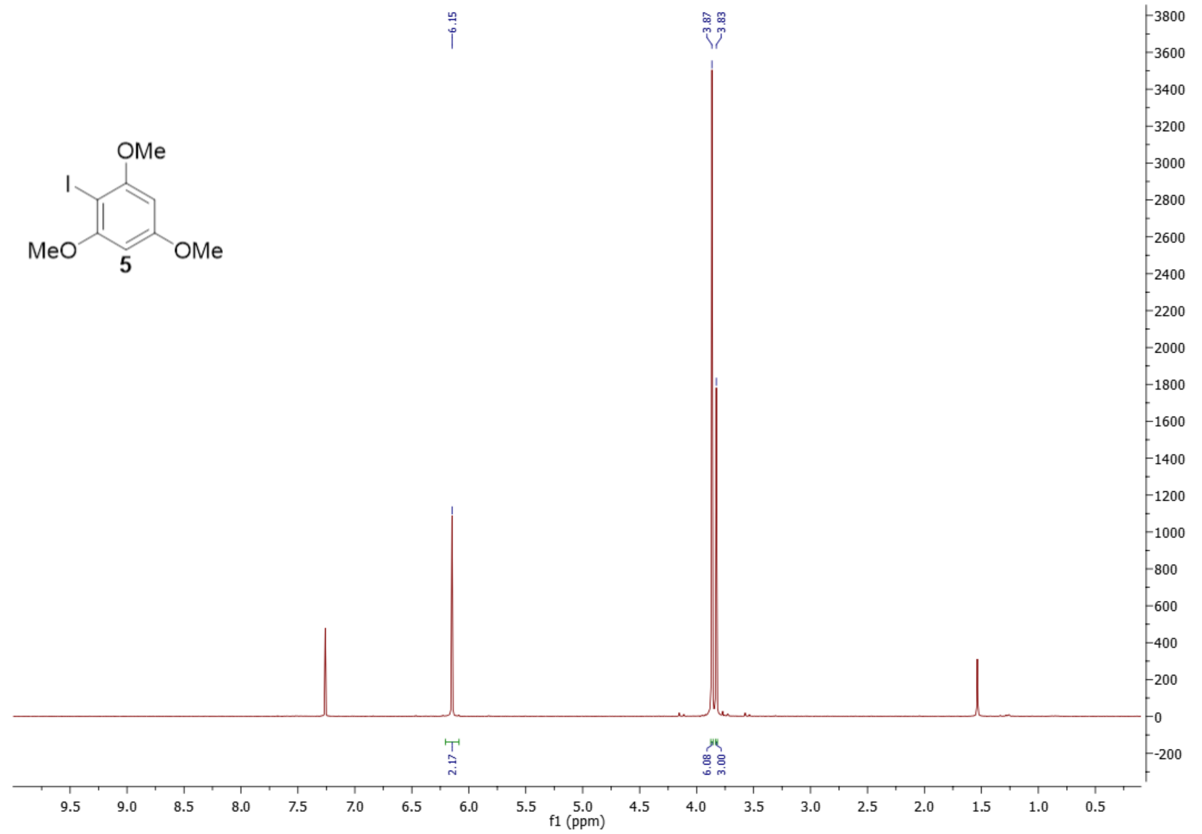

Ph
O2
S
Ph
O
O
160.5
155.8
152.4
140.5
136.1
133.8
133.2
130.6
129.4
129.3
128.8
128.4
127.9
127.9
127.6
124.8
123.7
123.4
115.5
160
140
135
130
125
115
f1 (ppm)
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
-4E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

7j

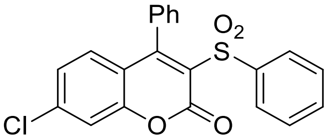
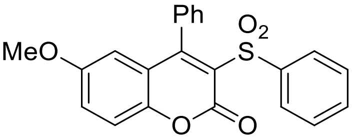

Ph
O2
S
O
O
O
7.69
7.68
7.66
7.65
7.58
7.57
7.55
7.55
7.55
7.53
7.46
7.45
7.43
7.42
7.33
7.31
7.30
7.30
7.29
7.28
7.25
7.25
7.22
7.20
7.17
7.14
7.11
7.11
7.08
7.07
6.89
6.89
6.86
6.86
6.80
6.77
4.68
4.65
4.61
4.52
4.49
4.48
4.45
4.42
4.12
4.11
4.06
3.73
3.69
3.68
3.64
3.63
1.08
3.02
1.00
5.96
1.19
1.07
0.94
1.04
1.17
2.50
1.12
7.6
7.4
7.2
6.9
6.7
4.6
4.4
4.1
3.8
3.6
f1 (ppm)
1000
900
800
700
600
500
400
300
200
100
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

7k


160.9
159.9
157.3
153.9
135.3
131.9
130.1
129.7
129.4
128.4
128.3
128.0
127.4
126.9
125.4
124.6
121.0
120.1
117.2
110.1
76.1
59.6
36.7
Ph
O2
S
O
O
O
7k
f1 (ppm)
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
-4E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


6.15
3.87
3.83
OMe
I
MeO
OMe
5
2.17
6.08
3.00
f1 (ppm)
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

10. X-ray data

	 **7d (ma109)**	 **7e (ma108)**
CCDC	1578048	1578047
Empirical formula	$C_{21}H_{13}ClO_4S$	$C_{22}H_{16}O_5S$
Formula weight	396.82	392.41
Temperature [K]	173(2)	173(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	*Pc*	$Pna2_1$
a [Å]	12.8859(12)	7.7651(6)
b [Å]	5.6317(3)	16.4066(12)
c [Å]	25.025(2)	14.1404(15)
α [°]	90	90
β [°]	92.804(8)	90
γ [°]	90	90
V [Å^3]	1813.9(2)	1801.5(3)
Z	4	4
D_{calcd}[Mg/m^3]	1.453	1.447
μ [mm^{-1}]	0.351	0.213
F(000)	816	816
Crystal size [mm^3]	0.210 x 0.120 x 0.030	0.280 x 0.120 x 0.120
Theta range for data collection [°]	2.215 to 25.517	3.240 to 25.639
Index ranges	-15<=h<=15, -6<=k<=6, -30<=l<=30	-8<=h<=9, -18<=k<=19, -17<=l<=17
Reflections collected	17139	8840
Independent reflections	6690 [R(int) = 0.0763]	3312 [R(int) = 0.0313]
Completeness to theta = 25.000°	99.9 %	99.7 %
Max. and min. transmission	1.000 and 0.525	1.000 and 0.592
Data / restraints / parameters	6690 / 2 / 487	3312 / 1 / 255
Goodness-of-fit on F^2	0.954	0.976
R_1, wR_2 [I > 2σ(I)]	0.0708, 0.1858	0.0299, 0.0632
R_1, wR_2 (all data)	0.0860, 0.1986	0.0359, 0.0647
Largest diff. peak and hole [eÅ^{-3}]	0.495 and -0.397	0.173 and -0.205

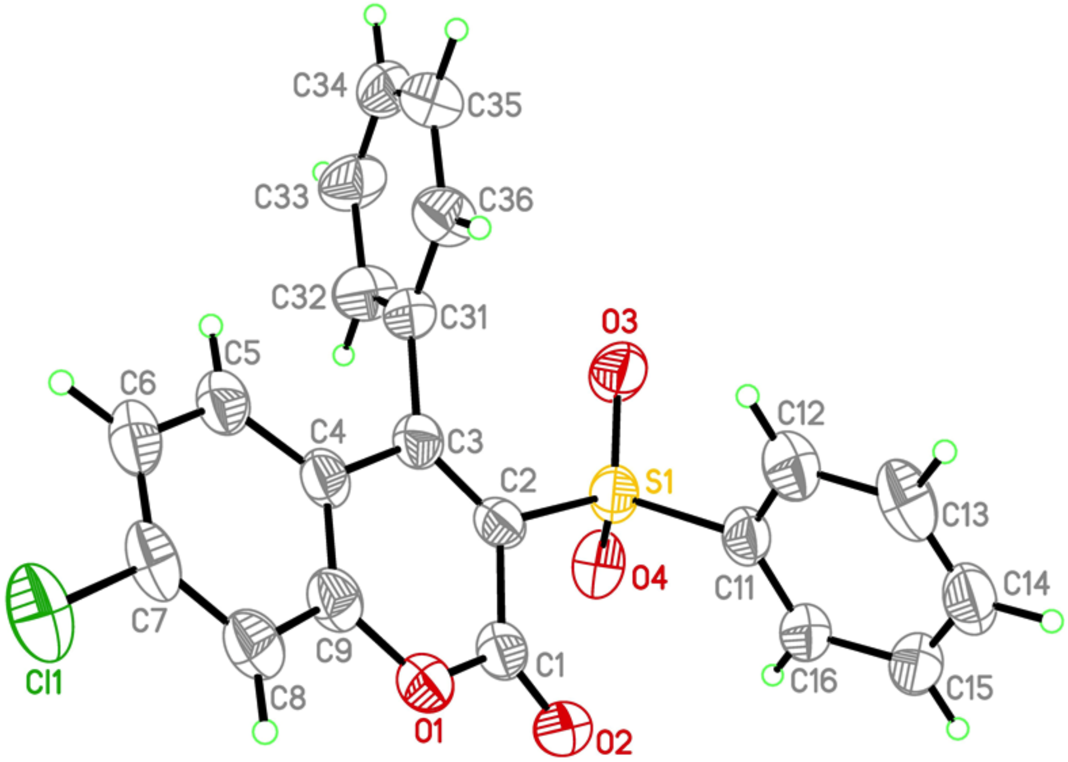


Figure S7: Perspective view of one of the two molecules in the asymmetric unit of **7d** (ma109) with displacement ellipsoids at the 50 % probability level.

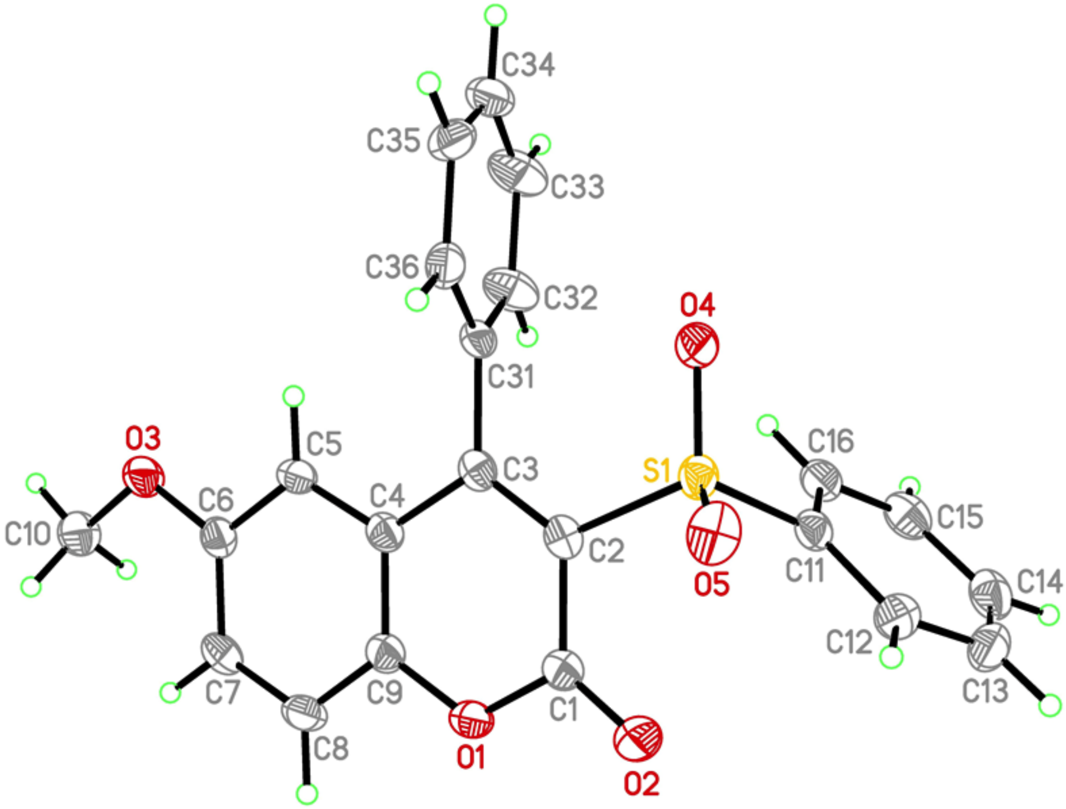


Figure S8: Perspective view of **7e** (ma108) with displacement ellipsoids at the 50 % probability level.