Supporting Information

for

CATALYST FREE SYNTHESIS OF 3,1-BENZOXATHIIN-4-ONES / 1,3-BENZODIOXIN-4-ONES

Sengodagounder Muthusamy[a,*] Muthukumar Malarvizhi[a] and Eringathodi Suresh[b]

[a]*School of Chemistry, Bharathidasan University, Trichirappalli-620 024, India*

[b]*Analytical Discipline and Centralized Instrumentation Facility, Central Salt & Marine Chemicals Research Institute, Bhavnagar-364 002, India*

[*]Tel: +91-431-2407053; Fax: +91-431-2407045; E-mail: muthu@bdu.ac.in

Table of contents

1. General information

The melting points are uncorrected. Infrared spectra were recorded as neat (ATR) on a Bruker Alpha FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz FT-NMR (model: Avance DPX 400) spectrometer at room temperature (25 °C). The chemical shift (δ) and coupling constant (J) values are given in parts per million and Hertz, respectively. Tetramethylsilane (TMS) was used as an internal standard for all ^{1}H NMR studies. Carbon types were determined from DEPT-135 and ^{13}C NMR experiments. High resolution mass analyses were performed on Thermo Fisher Exactive Plus mass spectrometer using electrospray ionization (ESI) technique.

Solvents were purified by distillation prior to use according to usual methods. THF was purified through distillation using sodium wire. Reagents were transferred using perfectly dried syringe through septa. Thin layer chromatography was performed on silica plates and components were visualized by observation under iodine. Column chromatography was performed on silica-gel (100-200 mesh), for column elution process hexane-EtOAc mixture was used as the eluent. Phenyl acetylene, benzophenone derivatives, salicylic and thiosalicylic acids were purchased from M/s Aldrich and used as provided.

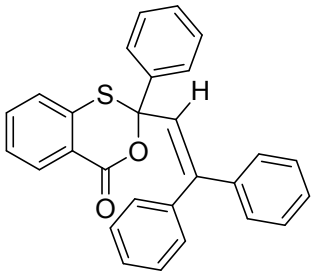
2. Typical procedure for the synthesis of 3,1-benzoxathiin-4-ones (3a-k) / 1,3-benzodioxin-4-ones (5a-e)

Propargylic alcohols[1] were prepared according to the literature.

3,1-Benzoxathiin-4-ones (3a-k): To a solution of thiosalicyclic acid (1 equiv) in toluene (10 mL), propargyl alcohol (1 equiv) was added under open-air atmosphere. The reaction mixture was refluxed with vigorous stirring and monitored using TLC until the disappearance of starting materials. After the appropriate time, toluene was concentrated under reduced pressure and diluted with ethyl acetate (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer was washed with ethyl acetate (10 mL). Concentration of combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel to afford the corresponding 3,1-benzoxathiin-4-ones **(3a-k)**.

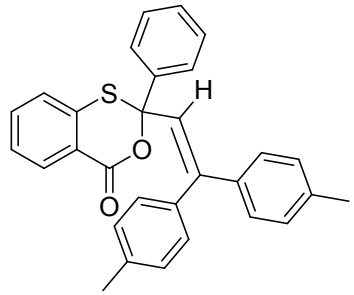
1,3-Benzodioxin-4-ones (5a-e): To a solution of salicylic acid (1 equiv) in toluene (10 mL), the controlled addition (0.2mL/h) of propargyl alcohol (1 equiv) was added using syringe pump under open-air atmosphere at reflux conditions. The reaction mixture was monitored using TLC until the disappearance of starting materials. After the appropriate time, toluene was concentrated under reduced pressure and diluted with ethyl acetate (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with ethyl acetate (10 mL). Concentration of combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel to afford the corresponding 1,3-benzodioxin-4-ones (**5a-e**).

3. Characterization data for compounds 3

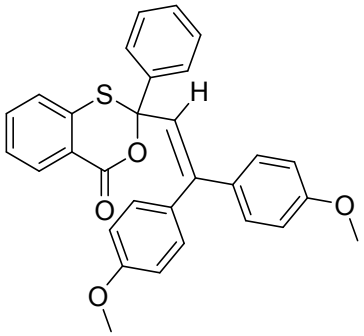


2-(2,2-Diphenylethenyl)-2-phenyl-2*H*,4*H*-3,1-benzoxathiin-4-one (3a): Yield 94%; White solid; m.p. 128-129 ºC; IR (neat): ν_{max} = 3057, 1726, 1592, 1491, 1442, 1278, 1236, 1104, 1055, 1030, 977, 743, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.77 (s, 1H), 6.93 (d, 2H, *J*

= 7.6 Hz), 7.08 (d, 2H, *J* = 6.8 Hz), 7.23-7.40 (m, 11H), 7.51-7.61 (m, 3H), 8.06 (d, 1H, *J* = 7.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 91.5, 125.6, 126.6, 126.8, 127.66, 127.71, 127.73, 128.26, 128.33, 128.6, 130.0, 130.2, 131.9, 133.7, 137.0, 137.7, 140.3, 142.2, 147.9, 163.2 ppm. HRMS (ESI): calcd for $C_{28}H_{20}O_2S$ $(M+H)^+$ 421.1257; found 421.1257.

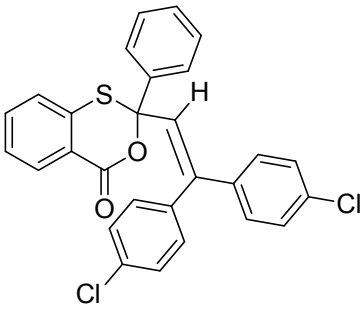


2-[2,2-Di(4-methylphenyl)ethenyl)-2-phenyl-2*H*,4*H*-3,1-benzoxathiin-4-one (3b): Yield 94%; White solid; m.p. 158-159 ºC; IR (neat): ν_{max} = 1721, 1591, 1509, 1440, 1276, 1234, 1101, 1054, 1030, 976, 816, 739, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (d, 6H, *J* = 14.4 Hz), 6.598-6.603 (m, 1H), 6.69-6.71 (m, 2H), 6.85-6.87 (m, 2H), 6.95-7.01 (m, 4H), 7.22-7.33 (m, 5H), 7.44-7.53 (m, 3H), 7.97 (d, 1H, *J* = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.5, 91.8, 125.7, 126.7, 127.7, 128.27, 128.34, 128.6, 128.9, 129.1, 130.0, 131.8, 133.6, 134.9, 137.2, 137.4, 138.3, 139.7, 140.5, 148.0, 163.3 ppm. HRMS (ESI): calcd for $C_{30}H_{24}O_2S$ $(M+H)^+$ 449.1570; found 449.1570.

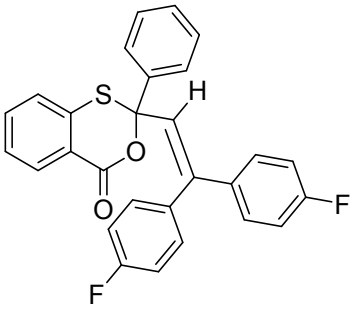


2-[2,2-Di(4-methoxyphenyl)ethenyl)-2-phenyl-2*H*,4*H*-3,1-benzoxathiin-4-one (3c): Yield 92%; White solid; m.p. 144-145 ºC; IR (neat): ν_{max} = 2933, 1724, 1600, 1508, 1448, 1284, 1243, 1176, 1105, 1031, 974, 832, 738, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 3.77 (s, 3H), 6.54 (s, 1H), 6.67-6.76 (m, 6H), 6.90-6.92 (m, 2H), 7.20-7.24 (m, 4H), 7.29-7.31 (m, 1H), 7.44 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.51-7.53 (m, 2H), 7.97 (dd, 1H, J_1 = 8.0 Hz, J_2 = 0.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 55.3, 91.8, 113.0, 113.5, 125.6, 126.6, 126.7, 127.6, 128.1, 128.2, 128.5, 129.0, 130.2, 131.3, 131.8, 133.6, 135.1,

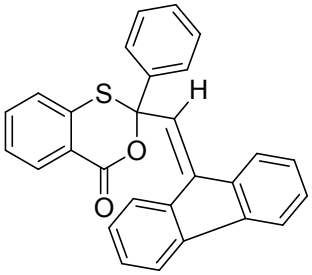
137.2, 140.5, 147.4, 159.2, 159.8, 163.4 ppm. HRMS (ESI): calcd for $C_{30}H_{24}O_4S$ $(M+H)^+$ 481.1468; found 481.1469.



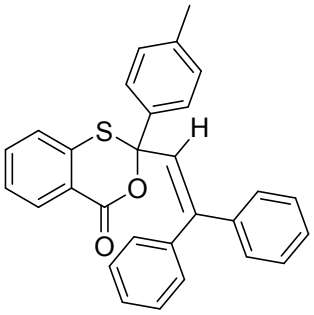
2-[2,2-Di(4-chlorophenyl)ethenyl)-2-phenyl-2*H*,4*H*-3,1-benzoxathiin-4-one (3d): Yield 89%; White solid; m.p. 132-133 ºC; IR (neat): ν_{max} = 1727, 1591, 1490, 1441, 1400, 1279, 1236, 1091, 1014, 828, 742, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.68 (s, 1H), 6.72-6.75 (m, 2H), 6.89-6.91 (m, 2H), 7.11-7.14 (m, 2H), 7.16-7.19 (m, 2H), 7.20-7.28 (m, 4H), 7.32-7.34 (m, 1H), 7.44-7.51 (m, 3H), 7.99 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 91.1, 125.3, 126.5, 126.9, 127.7, 128.0, 128.4, 128.5, 128.8, 128.9, 131.3, 131.9, 133.9, 134.0, 134.6, 135.7, 136.8, 139.97, 140.04, 145.8, 163.0 ppm. HRMS (ESI): calcd for $C_{28}H_{18}Cl_2O_2S$ $(M+H)^+$ 489.0477; found 489.0479.



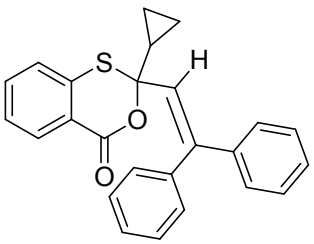
2-[2,2-Di(4-fluorophenyl)ethenyl)-2-phenyl-2*H*,4*H*-3,1-benzoxathiin-4-one (3e): Yield 90%; White solid; m.p. 142-143 ºC; IR (neat): ν_{max} = 1726, 1595, 1505, 1443, 1278, 1228, 1159, 1101, 977, 834, 735, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.63 (s, 1H), 6.76-6.96 (m, 8H), 7.21-7.33 (m, 5H), 7.45-7.49 (m, 3H), 7.99 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 91.1, 114.8 (d, J = 22.0 Hz), 115.2 (d, J =22.0 Hz), 125.4, 126.5, 126.8, 127.6, 128.4, 128.7, 129.3 (d, J =8.0 Hz), 130.5, 131.7 (d, J = 8.0 Hz), 131.9, 133.4 (d, J = 3.0 Hz), 133.8, 136.9, 138.0 (d, J = 3.0 Hz), 140.1, 146.1, 162.4 (d, J = 246.0 Hz), 162.9 (d, J = 247.0 Hz), 163.1 ppm. HRMS (ESI): calcd for $C_{28}H_{18}F_2O_2S$ $(M+H)^+$ 457.1068; found 457.1062.



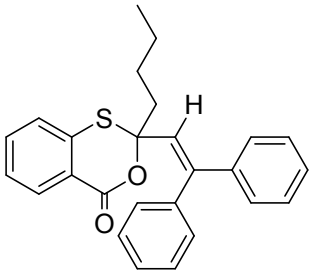
2-[(9*H*-Fluoren-9-ylidene)methyl]-2-phenyl-2*H*,4*H*-3,1-benzoxathiin-4-one (3f): Yield 74%; Yellow solid; m.p. 147-148 ºC; IR (neat): ν_{max} = 3059, 1727, 1591, 1509, 1445, 1279, 1237, 1099, 1052, 971, 737, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.07-7.17 (m, 3H), 7.21-7.31 (m, 3H), 7.34-7.36 (m, 4H), 7.41-7.49 (m, 2H), 7.56 (t, 2H, J = 7.2 Hz), 7.81-7.83 (m, 2H), 7.89-7.90 (m, 1H), 8.04 (d, 1H, J = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 90.9, 119.4, 119.6, 120.4, 124.9, 127.0, 127.05, 127.08, 127.5, 128.2, 128.7, 129.4, 129.6, 129.7, 132.5, 133.96, 134.03, 137.1, 138.8, 138.9, 139.9, 141.9, 142.9, 163.2 ppm. HRMS (ESI): calcd for $C_{28}H_{18}O_2S$ $(M+H)^+$ 419.1100; found 419.1093.



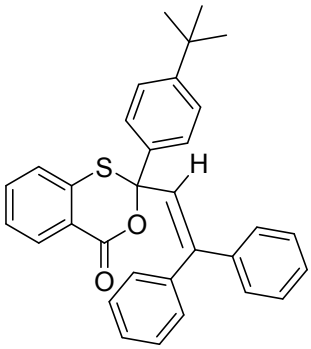
2-(4-Methylphenyl)-2-(2,2-diphenylethenyl)-2*H*,4*H*-3,1-benzoxathiin-4-one (3g): Yield 91%; Yellow oil; IR (neat): ν_{max} = 3056, 1724, 1591, 1499, 1443, 1273, 1176, 1104, 976, 905, 731, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 6.81 (s, 1H), 7.01-7.59 (m, 17H), 8.10 (d, 1H, J = 7.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 91.8, 125.7, 126.3, 126.7, 126.8, 127.7, 127.8, 128.3, 128.38, 128.42, 129.2, 129.3, 130.2, 130.3, 131.8, 133.7, 137.2, 137.5, 137.9, 138.6, 142.4, 147.7, 163.3 ppm. HRMS (ESI): calcd for $C_{29}H_{22}O_2S$ $(M+H)^+$ 435.1413; found 435.1413.



2-Cyclopropyl-2-(2,2-diphenylethenyl)-2*H*,4*H*-3,1-benzoxathiin-4-one (3h): Yield 89%; Yellow solid; m.p. 88-89 ^{o}C; IR (neat): ν_{max} = 3058, 1723, 1590, 1491, 1442, 1278, 1235, 1103, 1028, 953, 887, 837, 734, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64-0.74 (m, 2H), 0.86-0.94 (m, 2H), 1.55-1.62 (m, 1H), 6.08 (s, 1H), 6.88-6.90 (m, 2H), 7.05-7.29 (m, 7H), 7.32-7.40 (m, 4H), 7.83 (dd, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.4, 4.4, 21.5, 91.6, 125.5, 126.1, 126.5, 127.7, 127.9, 128.0, 128.1, 128.15, 128.22, 128.5, 130.4, 131.8, 133.5, 136.4, 138.0, 143.0, 145.8, 163.0 ppm. HRMS (ESI): calcd for $C_{25}H_{20}O_2S$ $(M+H)^+$ 385.1257; found 385.1256.

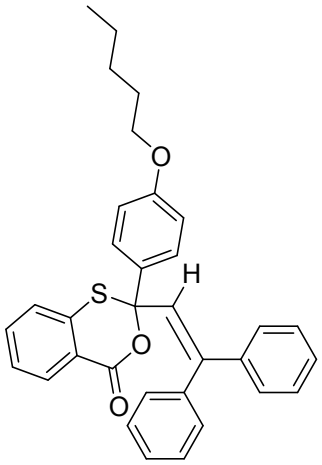


2-Butyl-2-(2,2-diphenylethenyl)-2*H*,4*H*-3,1-benzoxathiin-4-one (3i): Yield 79%; Colourless oil; IR (neat): ν_{max} = 2958, 1720, 1685, 1591, 1441, 1257, 1145, 1051, 744, 697, 646 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87-0.95 (m, 3H), 1.25-1.30 (m, 2H), 1.60-1.63 (m, 2H), 1.99-2.20 (m, 2H), 6.20 (s, 1H), 6.97-7.48 (m, 13H), 7.95-7.97 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.6, 26.5, 40.7, 91.7, 124.9, 126.4, 127.6, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 129.1, 129.6, 130.0, 131.9, 133.6, 136.5, 137.9, 142.6, 145.5, 163.2 ppm. HRMS (ESI): calcd for $C_{26}H_{24}O_2S$ $(M+H)^+$ 401.1570; found 401.1570.

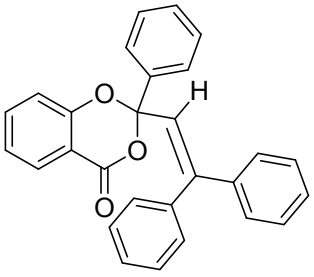


2-(4-*tert*-Butylphenyl)-2-(2,2-diphenylethenyl)-2*H*,4*H*-3,1-benzoxathiin-4-one (3j): Yield 92%; Colourless oil; IR (neat): ν_{max} = 2961, 1725, 1591, 1442, 1365, 1272, 1237, 1105, 1027, 978, 906, 736, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9H), 6.66 (s, 1H), 6.82 (d,

2H, J = 7.6 Hz), 6.98-6.99 (m, 2H), 7.12-7.23 (m, 9H), 7.30-7.32 (m, 1H), 7.40-7.46 (m, 3H), 7.97 (d, 1H, J = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.3, 34.6, 91.5, 125.2, 125.5, 126.3, 126.6, 127.6, 127.7, 128.2, 130.0, 130.3, 131.9, 133.6, 137.0, 137.2, 137.7, 142.3, 147.5, 151.5, 163.3 ppm. HRMS (ESI): calcd for $C_{32}H_{28}O_2S$ $(M+H)^+$ 477.1883; found 477.1883.

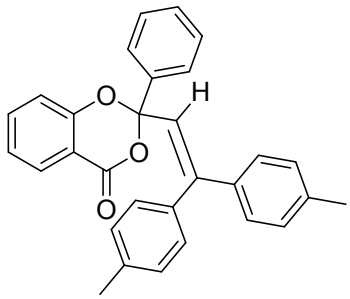


2-(4-Pentoxyphenyl)-2-(2,2-diphenylethenyl)-2*H*,4*H*-3,1-benzoxathiin-4-one (3k): Yield 95%; Colourless oil; IR (neat): ν_{max} = 2932, 1725, 1601, 1505, 1442, 1278, 1238, 1174, 1103, 1026, 975, 905, 835, 798, 737, 693 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (t, 3H, J = 6.8 Hz), 1.46-1.56 (m, 4H), 1.83-1.89 (m, 2H), 4.00 (t, 2H, J = 6.4 Hz), 6.79 (s, 1H), 6.85 (d, 2H, J = 8.8 Hz), 7.00 (d, 2H, J = 7.2 Hz), 7.09-7.11 (m, 2H), 7.27-7.38 (m, 8H), 7.48-7.58 (m, 3H), 8.08 (d, 1H, J = 7.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.6, 28.3, 29.0, 68.1, 91.8, 114.2, 125.7, 126.7, 127.6, 127.7, 127.77, 127.79, 128.28, 128.30, 128.32, 130.1, 130.3, 131.8, 132.1, 133.7, 137.6, 137.8, 142.4, 147.6, 159.4, 163.3 ppm. HRMS (ESI): calcd for $C_{33}H_{30}O_3S$ $(M+H)^+$ 507.1989; found 507.1990.

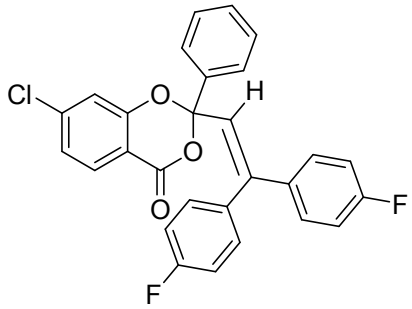


2-[2,2-Diphenylethenyl)-2-phenyl-2*H*,4*H*-1,3-benzodioxin-4-one (5a): Yield 89%; White solid; m.p. 166-167 ºC; IR (neat): ν_{max} = 1743, 1612, 1469, 1303, 1245, 1135, 1077, 1001, 965, 760, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (s, 1H), 6.67 (d, 1H, J = 8.4 Hz),

6.98-7.00 (m, 2H), 7.08 (t, 1H, J = 7.6 Hz), 7.18-7.21 (m, 2H), 7.26-7.36 (m, 9H), 7.45-7.52 (m, 3H), 7.91-7.93 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 105.8, 114.8, 117.4, 122.9, 126.5, 127.0, 127.5, 127.6, 127.7, 128.25, 128.27, 128.5, 129.0, 129.5, 129.8, 136.2, 138.2, 139.7, 141.7, 147.7, 156.0, 161.2 ppm. HRMS (ESI): calcd for $C_{28}H_{20}O_3$ $(M+H)^+$ 405.1485; found 405.1480.

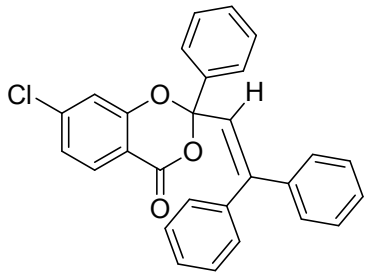


2-[2,2-Di(4-methylphenyl)ethenyl)-2-phenyl-2*H*,4*H*-1,3-benzodioxin-4-one (5b): Yield 76%; White solid; m.p. 156-157 ºC; IR (neat): ν_{max} = 1742, 1612, 1509, 1469, 1301, 1242, 1130, 1077, 1000, 963, 919, 818, 760, 731, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.35 (s, 3H), 6.47 (s, 1H), 6.60 (d, 1H, J = 8.4 Hz), 6.77 (d, 2H, J = 8.0 Hz), 6.98-7.05 (m, 7H), 7.25-7.28 (m, 3H), 7.40-7.47 (m, 3H), 7.86 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.4, 106.0, 114.9, 117.5, 122.8, 125.9, 126.5, 127.6, 128.2, 128.9, 129.0, 129.4, 129.8, 135.3, 136.1, 137.3, 138.4, 139.2, 139.8, 147.9, 156.1, 161.3 ppm. HRMS (ESI): calcd for $C_{30}H_{24}O_3$ $(M+H)^+$ 433.1798; found 433.1800.

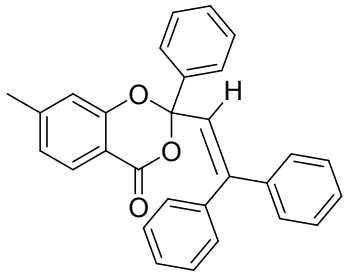


2-[2,2-Di(4-fluorophenyl)ethenyl)-2-phenyl-7-chloro-2*H*,4*H*-1,3-benzodioxin-4-one (5c): Yield 89%; Colourless oil; IR (neat): ν_{max} = 1749, 1615, 1507, 1461, 1299, 1239, 1128, 1073, 999, 961, 915, 816, 759, 727, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40 (s, 1H), 6.56 (d, 1H, J = 8.8 Hz), 6.78-6.88 (m, 6H), 6.99-7.03 (m, 2H), 7.18-7.20 (m, 3H), 7.27-7.32 (m, 3H), 7.74 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 106.0, 114.7 (d, J = 21.0 Hz), 115.3 (d, J = 21.0 Hz), 115.8, 118.9, 126.4, 126.9, 128.3, 128.4, 129.0, 129.3 (d, J = 3.0 Hz), 129.4, 131.5 (d, J = 8.0 Hz), 133.7, 133.8, 136.3, 137.4 (d, J = 3.0 Hz), 139.0, 146.3, 154.3,

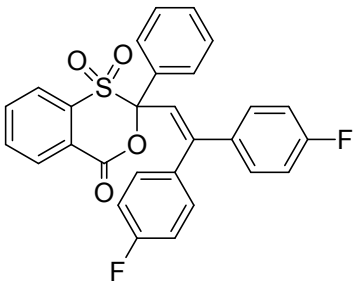
159.9, 162.4 (d, J = 246.0 Hz), 163.1 (d, J = 247.0 Hz) ppm. HRMS (ESI): calcd for $C_{28}H_{17}ClF_2O_3$ $(M+H)^+$ 475.0907; found 475.0909.



2-[2,2-(Diphenylethenyl)-2-phenyl-7-chloro-2*H*,4*H*-1,3-benzodioxin-4-one (5d): Yield 85%; Colourless oil; IR (neat): ν_{max} = 1725, 1591, 1495, 1442, 1272, 1237, 1054, 1027, 978, 835, 736, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.62-6.65 (m, 2H), 7.03-7.05 (m, 2H), 7.24-7.25 (m, 2H), 7.31-7.43 (m, 10H), 7.54-7.56 (m, 2H), 7.93-7.94 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 106.3, 115.9, 119.2, 126.45, 126.51, 127.7, 127.77, 127.83, 128.2, 128.4, 128.5, 128.7, 128.9, 129.3, 129.9, 136.2, 138.1, 139.3, 141.6, 148.2, 154.5, 160.1 ppm. HRMS (ESI): calcd for $C_{28}H_{19}{}^{35}ClO_3$ $(M+H)^+$ 440.1129; found 440.1134.



2-[2,2-(Diphenylethenyl)-2-phenyl-7-chloro-2*H*,4*H*-1,3-benzodioxin-4-one (5e): Yield 71%; Colourless oil; IR (neat): ν_{max} = 1734, 1660, 1600, 1503, 1461, 1403, 1230, 1162, 1019, 836, 750, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 6.43 (s, 1H), 6.82 (d, 1H, J = 7.2 Hz), 7.02-7.04 (m, 8H), 7.10-7.28 (m, 3H), 7.40-7.42 (m, 3H), 7.58-7.64 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1, 105.7, 112.1, 117.6, 122.5, 126.1, 126.5, 127.6, 128.3, 128.8, 129.0, 129.3, 129.9, 131.9, 138.3, 139.8, 141.9, 147.8, 156.0, 161.4 ppm. HRMS (ESI): calcd for $C_{28}H_{22}O_3$ $(M+H)^+$ 419.1642; found 419.1637.



2-[2,2-Di(4-fluorophenyl)ethenyl)-2-phenyl-2*H*,4*H*-3,1λ^6-benzoxathiine-1,1,4-trione

(7a): Yield 80%; White solid; m.p. 154-155 ºC; IR (neat): ν_{max} = 1752, 1602, 1509, 1459, 1376, 1236, 1165, 1089, 836, 751, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74-6.80 (m, 5H), 6.90-6.95 (m, 4H), 7.49-7.55 (m, 3H), 7.74-7.83 (m, 2H), 7.85-7.96 (m, 1H), 7.98-8.02 (m, 1H), 8.09-8.11 (m, 1H), 8.9-8.21 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 97.8, 115.1 (d, J = 21.0 Hz), 115.4 (d, J =21.0 Hz), 122.1, 124.8, 126.1, 128.2, 128.7, 129.6 (d, J =8.0 Hz), 130.5, 130.6, 131.58, 131.61, 131.7, 133.0 (d, J = 3.0 Hz), 134.0, 134.9, 136.8, 137.7 (d, J = 3.0 Hz), 148.7, 158.8, 162.9 (d, J = 248.0 Hz), 163.3 (d, J = 249.0 Hz), 163.1 ppm. HRMS (ESI): calcd for $C_{28}H_{18}F_2O_4S$ $(M+H)^+$ 489.0967; found 489.0959.

4. Crystal Data for Compound 3e: (CCDC 2044132) $C_{28}H_{18}F_2O_2S$, M = 456.48, 0.54 x 0.47 x 0.22 mm, Monoclinic, space group P21/n with a = 10.2296(14) Å, b = 15.605(2) Å, c = 14.042(2) Å, α = 90.00, β = 93.949(2), γ = 90.00, V = 2236.2(5) Å^3, T = 296(2) K, R_1 = 0.0506, wR_2 = 0.1346 on observed data, z = 4, D_{calcd} = 1.356 mg cm^{-3}, $F(000)$ = 944, Absorption coefficient = 0.185 mm^{-1}, λ = 0.71073 Å, 4390 reflections were collected on a smart apex CCD single crystal diffractometer 3697 observed reflections ($I \geq 2\sigma$ (I)). The largest difference peak and hole = 0.316 and -0.212 eÅ^{-3}, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL–97 software.

Compound **3e** contains a C-H···O interaction, a C-H···F interaction and a C-H···π interaction

i. The bond distances of C_{13}-H_{13}···O_2 interaction is 2.546 Å and the bond angle of ∠ C_{13}-H_{13}···O_2 is 165.91
ii. The bond distances of C_3-H_3···F_1 interaction is 2.399 Å and the bond angle of ∠ C_3-H_3···F_1 is 143.28
iii. The bond distances of C_{18}-H_{18}···(C_1-C_6) interaction is 3.160 Å and the bond angle of ∠ C_{18}-H_{18}···(C_1-C_6) is 169.71

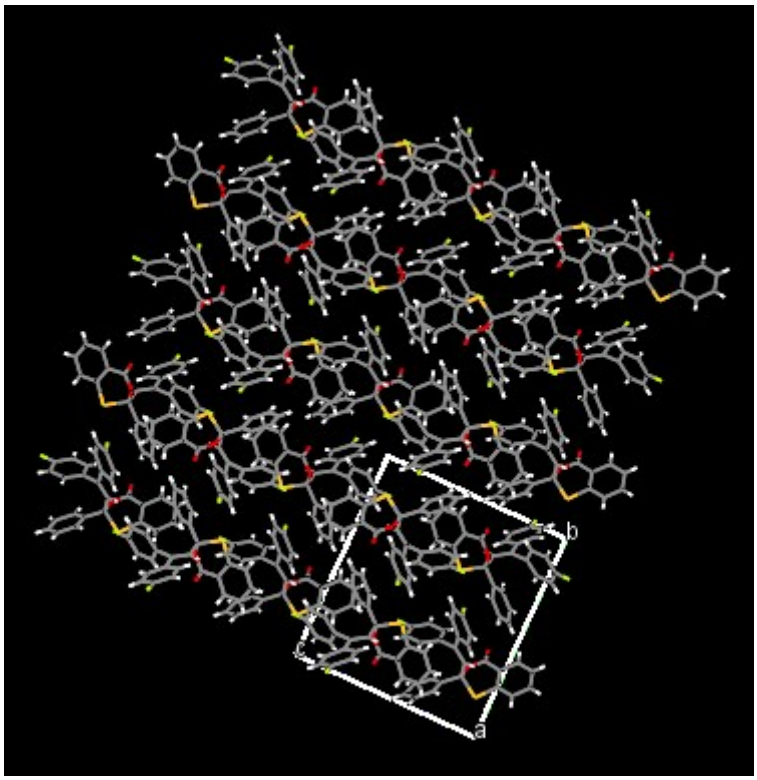


Figure 1. Partial crystal packing view of compound **3e** through a-axis

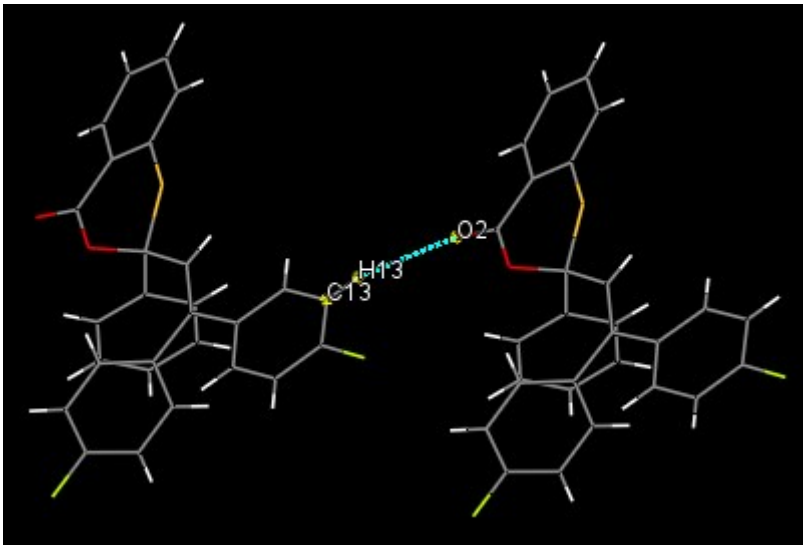


Figure 2. Partial crystal packing view of compound **3e**. The interaction between C_{13}-H_{13}...O_2

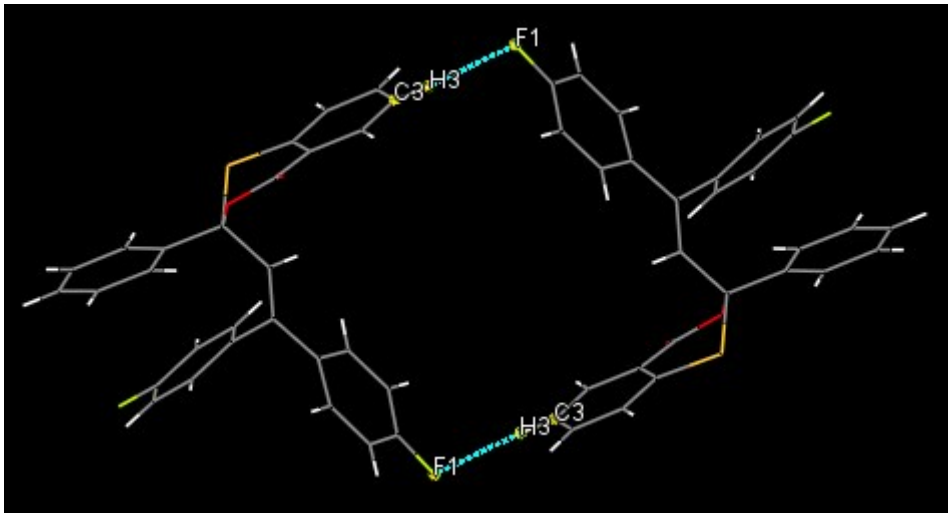


Figure 3. Partial crystal packing view of compound **3e**. The interaction between C_3-H_3...F_1

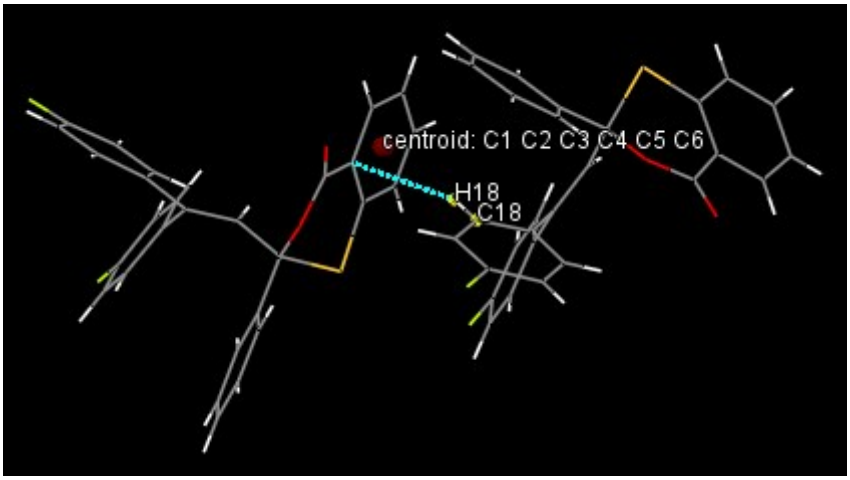


Figure 4. Partial crystal packing view of compound **3e**. The interaction between C_{18}-$H_{18}\cdots(C_1$-$C_6)$ centroid

Crystal Data for Compound 5a: (CCDC 2044131) $C_{28}H_{20}O_3$, M = 404.44, 0.451 x 0.288 x 0.102 mm, Triclinic, space group P-1 with a = 10.3275(7) Å, b = 14.0098(9) Å, c =

15.4589(11) Å, α = 90.549(2), β = 108.062(2), γ = 101.778(2), V = 2075.3(2) Å^3, T = 100.(2) K, R_1 = 0.0588, wR_2 = 0.1461 on observed data, z = 4, D_{calcd} = 1.294 mg cm^{-3}, *F(000)* = 848, Absorption coefficient = 0.083 mm^{-1}, λ = 0.71073 Å, 15905 reflections were collected on a Bruker D8 Quest 11714 observed reflections (*I > 2\s(I)*). The largest difference peak and hole = 1.370 and -0.474 eÅ^{-3}, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL–97 software.

Compound **5a** contains three C-H···O and two C-H···π interactions

i. The bond distances of C_{30}-H_{30}···O_3 interaction is 2.603 Å and the bond angle of ∠ C_{13}-H_{13}···O_2 is 164.02
ii. The bond distances of C_{37}-H_{37}···O_3 interaction is 2.377 Å and the bond angle of ∠ C_{13}-H_{13}···O_2 is 152.77
iii. The bond distances of C_{40}-H_{40}···O_3 interaction is 2.717 Å and the bond angle of ∠ C_{13}-H_{13}···O_2 is 127.91
iv. The bond distances of C_3-H_3···(C_{17}-C_{22}) interaction is 2.641 Å and the bond angle of ∠ C_3-H_3···(C_{17}-C_{22}) is 148.69
v. The bond distances of C_{19}-H_{19}···(C_{39}-C_{44}) interaction is 2.550 Å and the bond angle of ∠ C_{19}-H_{19}···(C_{39}-C_{44}) is 169.22

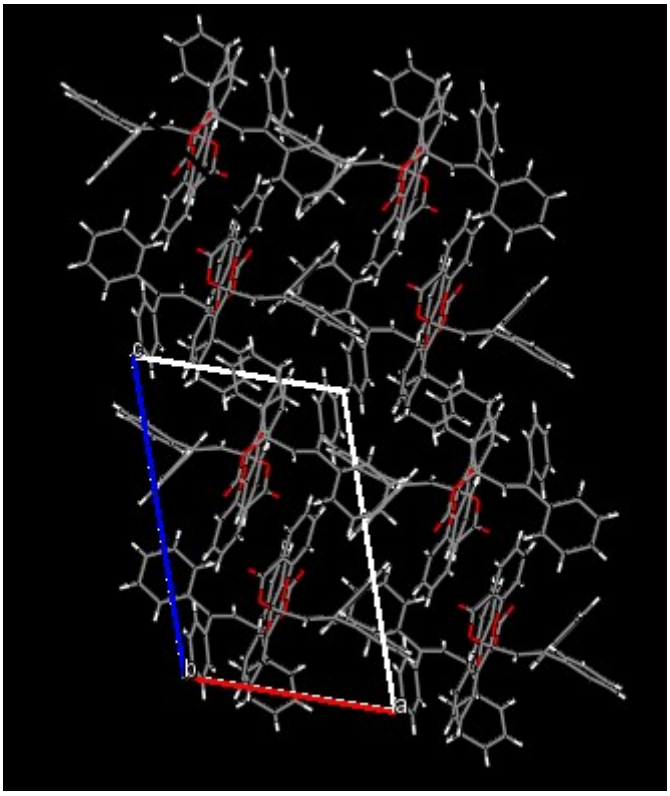


Figure 5. Partial crystal packing view of compound **5a** through b-axis

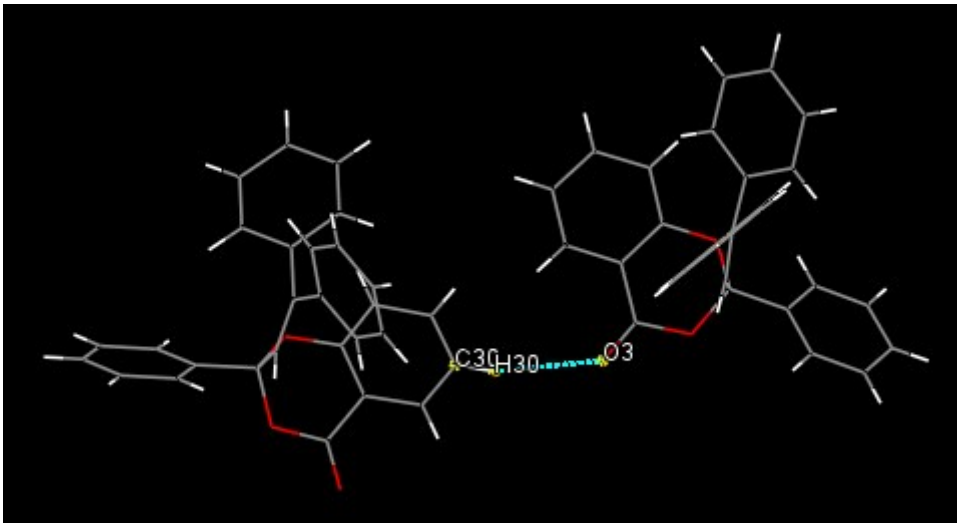


Figure 6. Partial crystal packing view of compound **5a**. The interaction between C_{30}-H_{30}...O_3

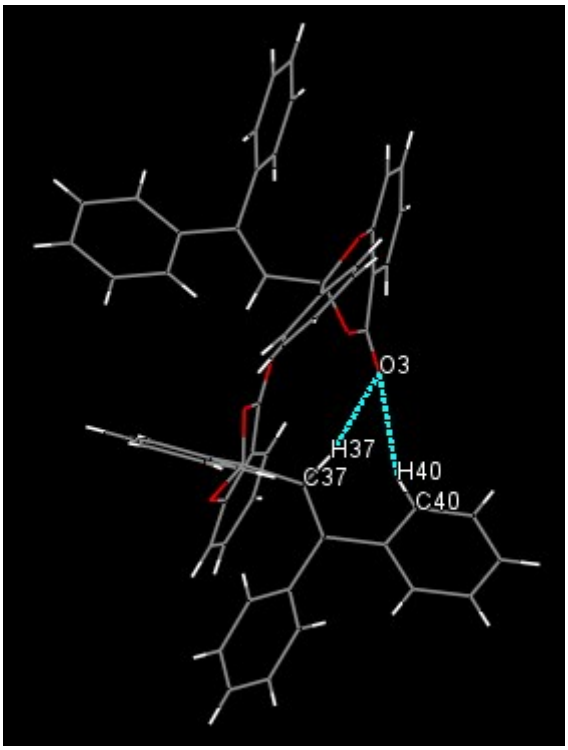


Figure 7. Partial crystal packing view of compound **5a**. The interaction between C_{37}-H_{37}...O_3 and C_{40}-H_{40}...O_3

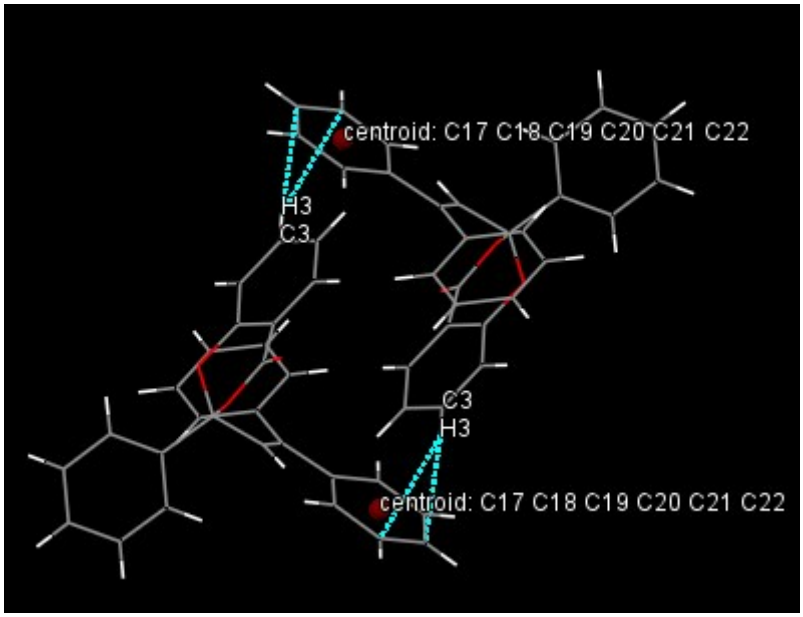


Figure 8. Partial crystal packing view of compound **5a**. The interaction between C_3-H_3···(C_{17}-C_{22}) centroid

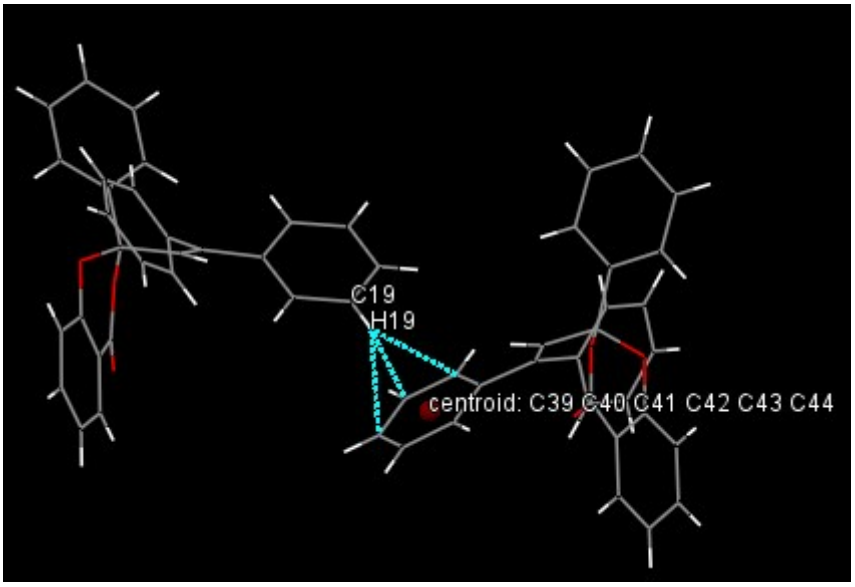
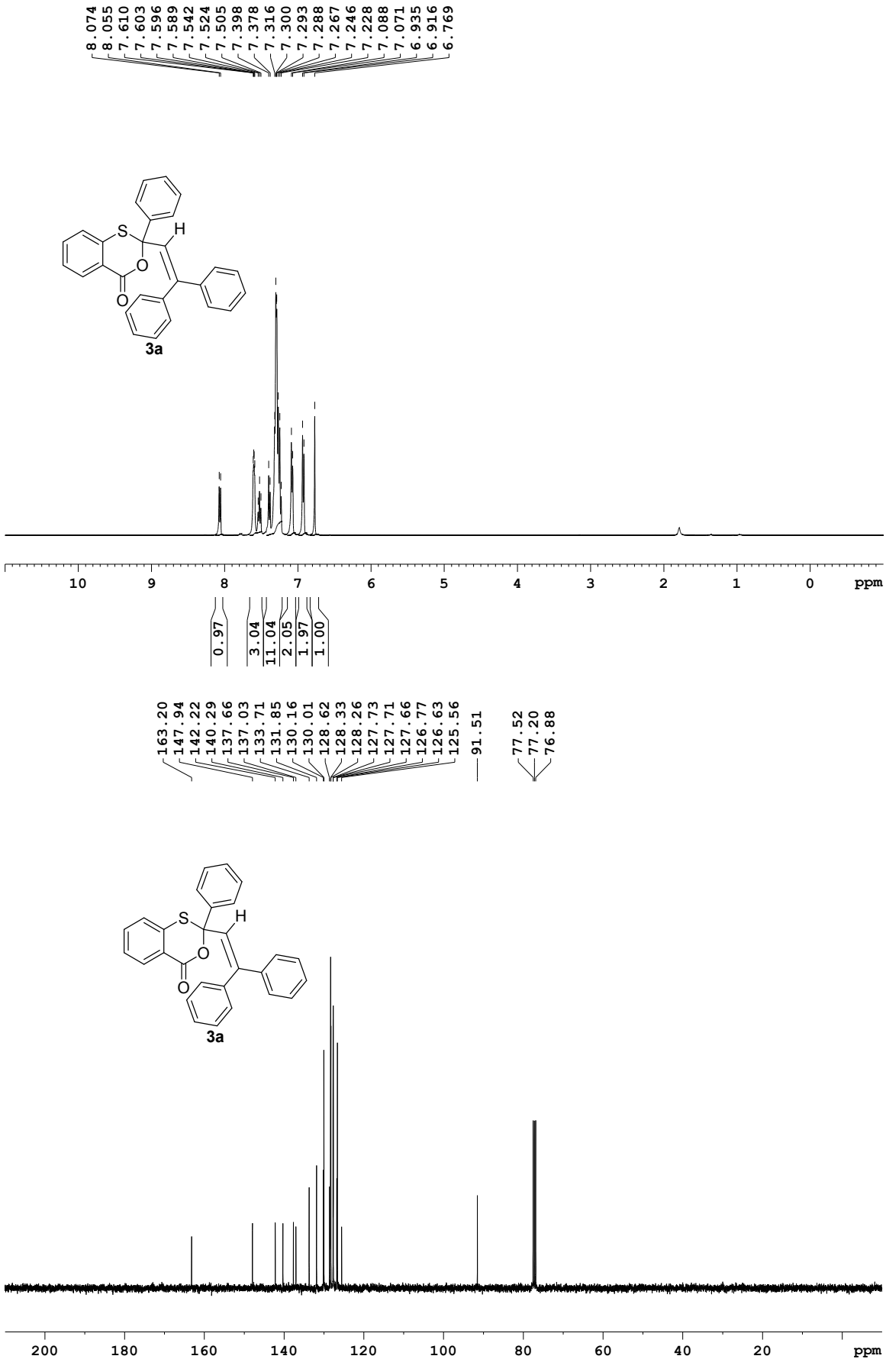


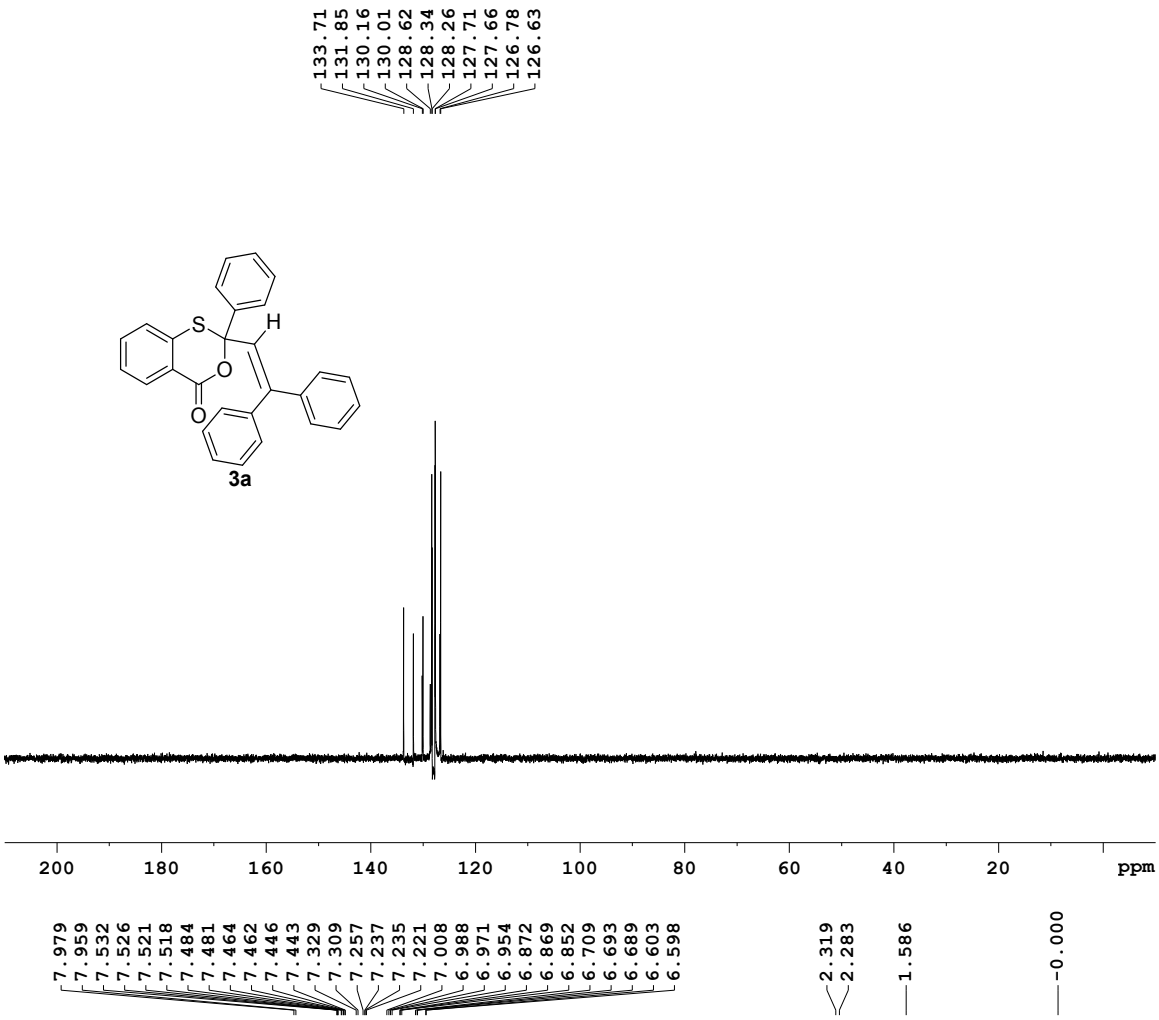
Figure 9. Partial crystal packing view of compound **5a**. The interaction between C_{19}-H_{19}···(C_{39}-C_{44}) centroid

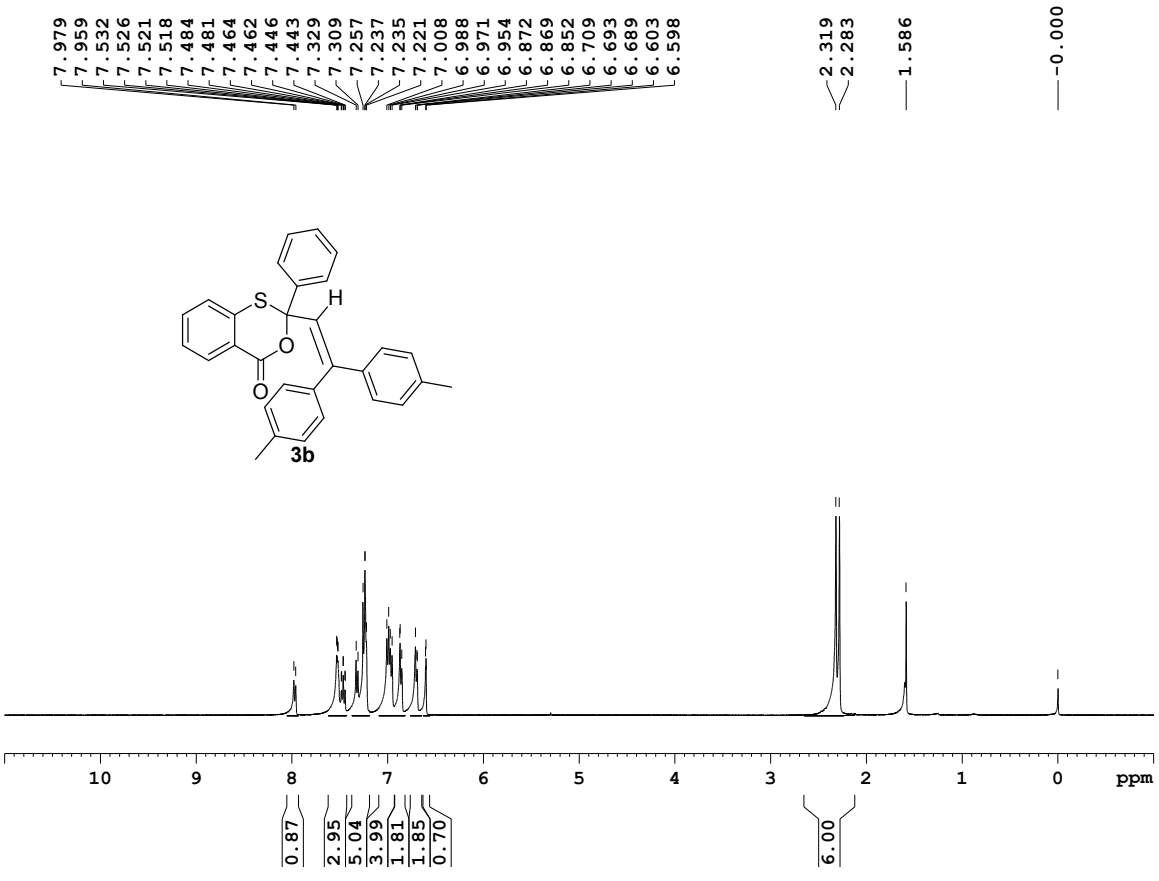
5. References

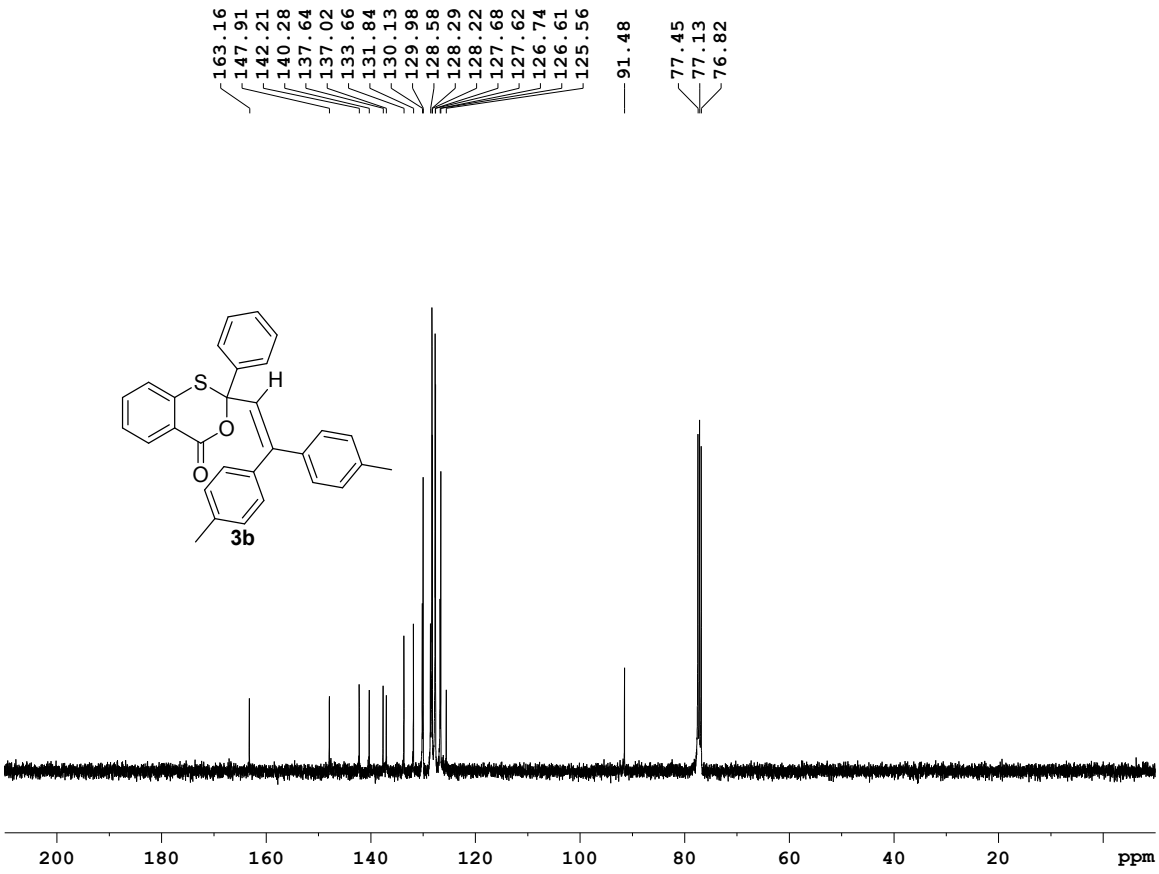
1. a) Engel, D. A.; Dudley, G. B. *Org. Lett.* **2006**, 8, 4027. b) Zhu, Y.; Yin, G.; Hong, D.; Lu, P.; Wang, Y. *Org. Lett*. **2011**, 13, 1024.

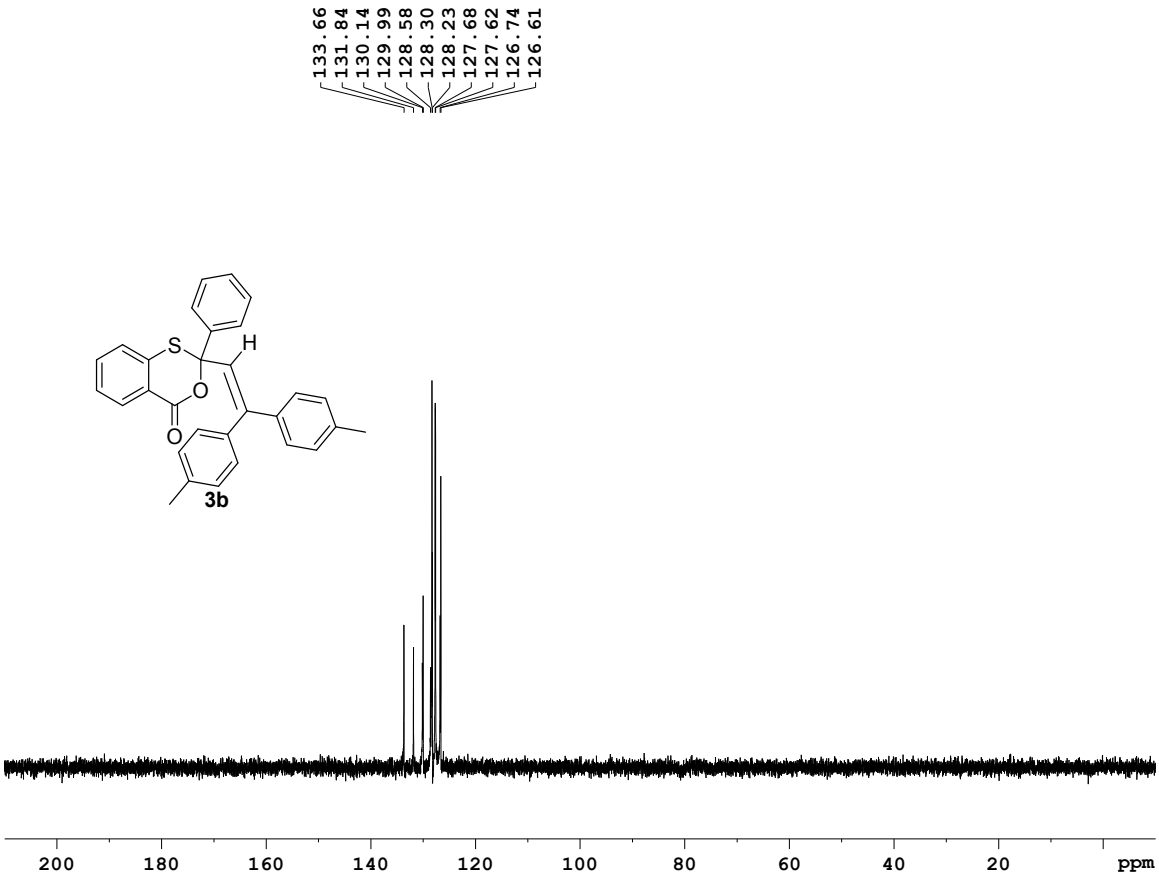
6. Scanned ^{1}H NMR and ^{13}C NMR spectra of all compounds

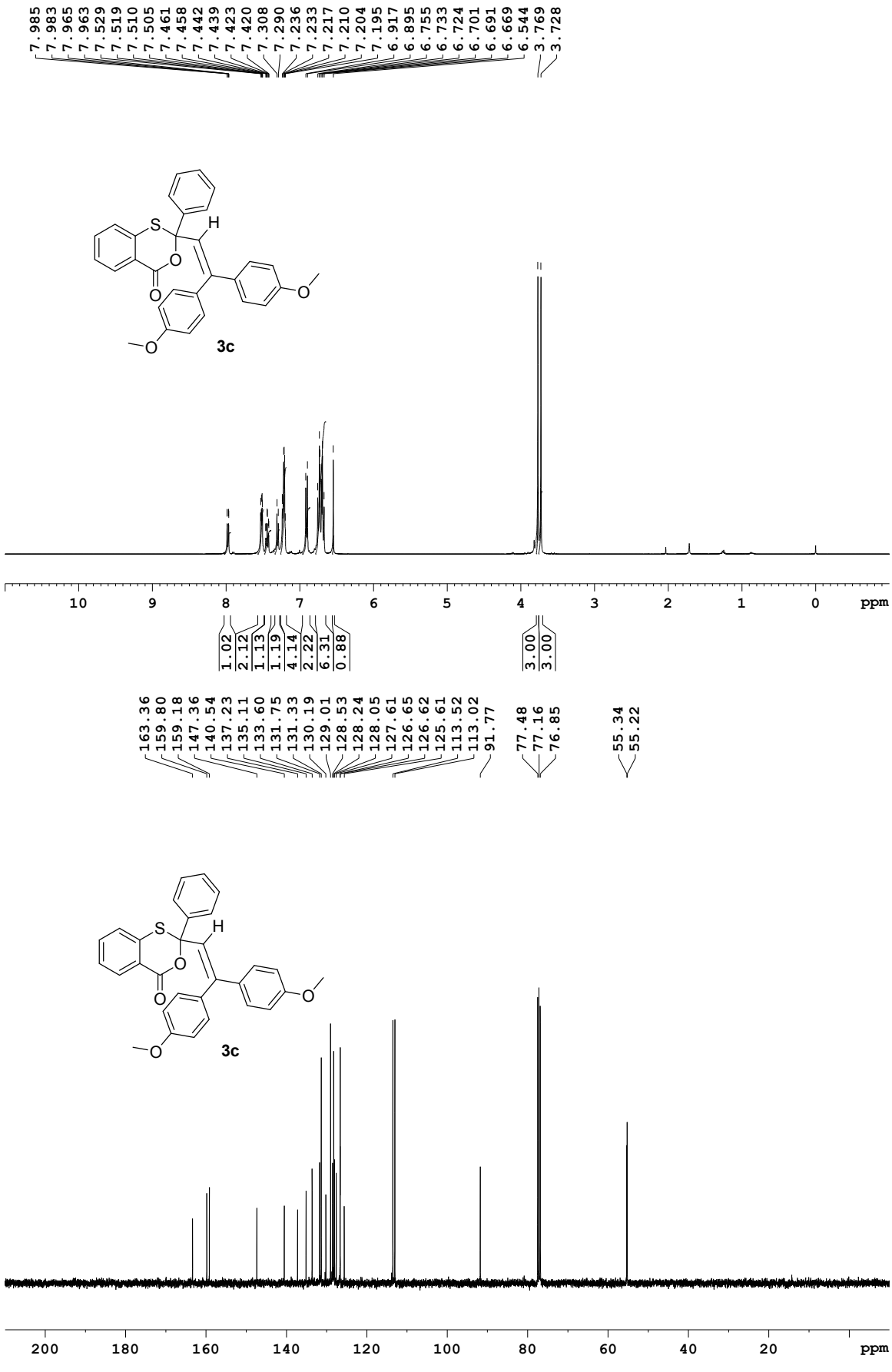


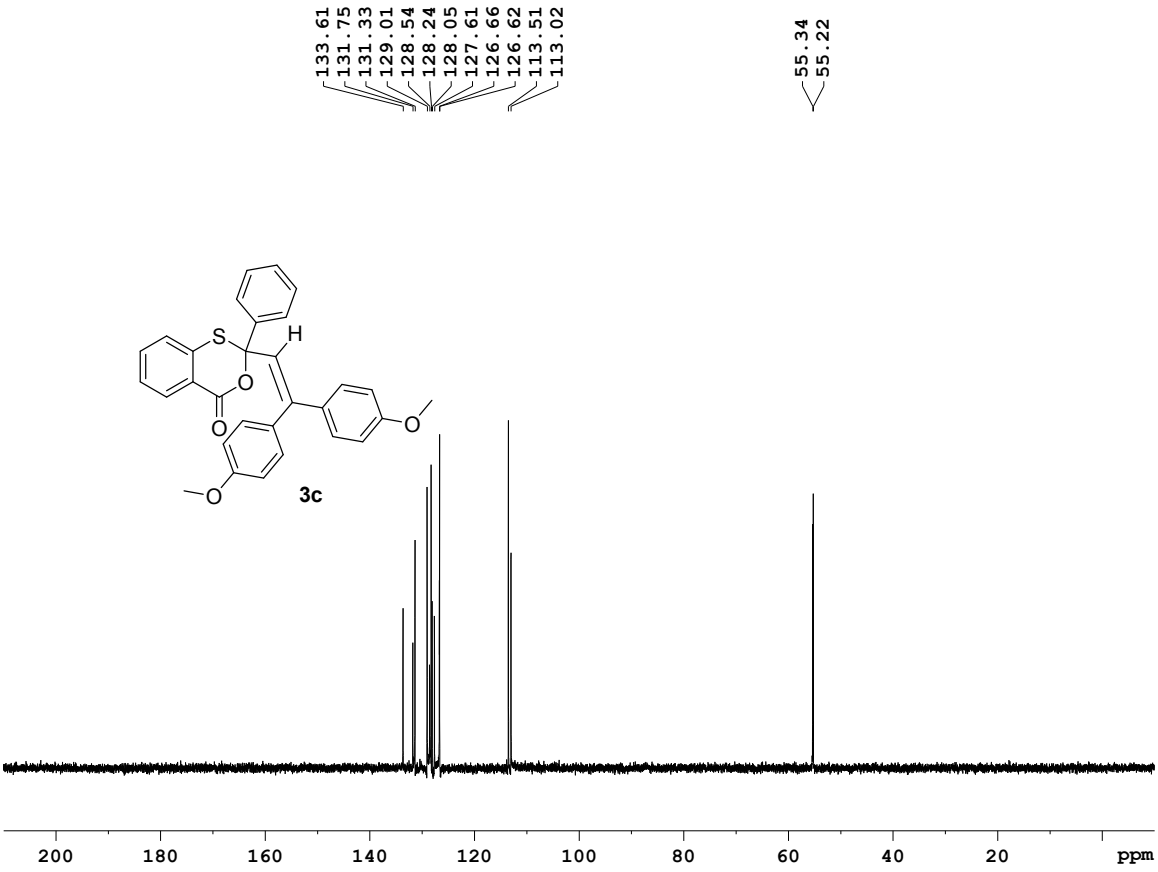

133.71
131.85
130.16
130.01
128.62
128.34
128.26
127.71
127.66
126.78
126.63
S
H
O
O
3a
200
180
160
140
120
100
80
60
40
20
ppm

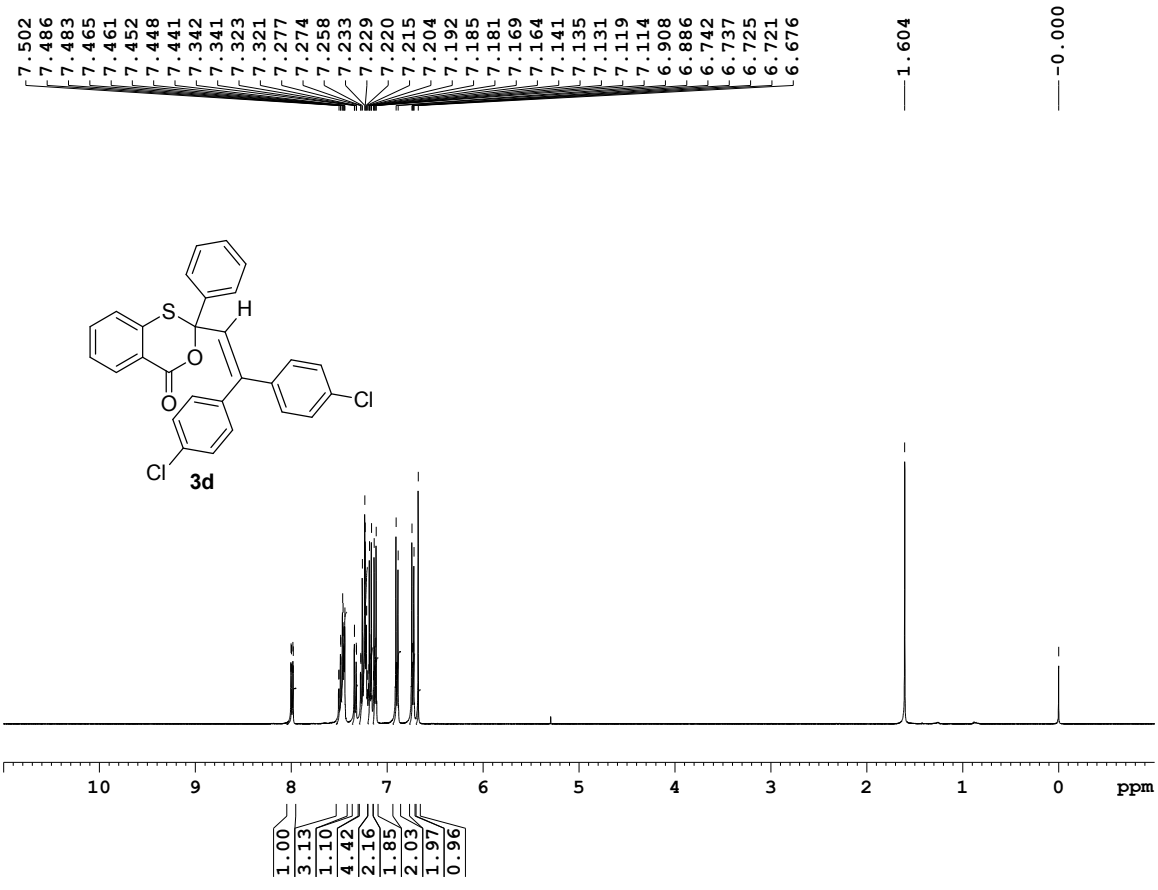

7.979
7.959
7.532
7.526
7.521
7.518
7.484
7.481
7.464
7.462
7.446
7.443
7.329
7.309
7.257
7.237
7.235
7.221
7.008
6.988
6.971
6.954
6.872
6.869
6.852
6.709
6.693
6.689
6.603
6.598
2.319
2.283
1.586
0.000
S
H
O
O
3b
10
9
8
7
6
5
4
3
2
1
0
ppm
0.87
2.95
5.04
3.99
1.81
1.85
0.70
6.00

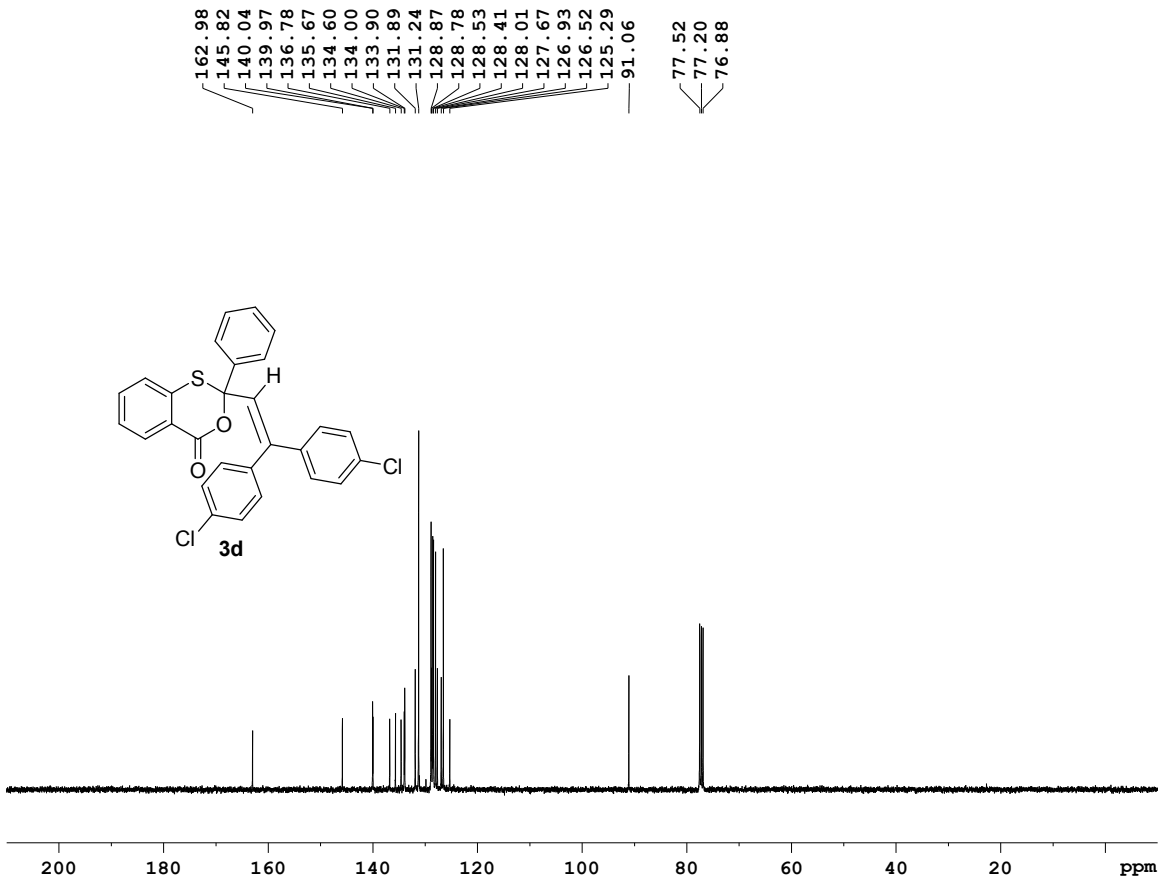

163.16
147.91
142.21
140.28
137.64
137.02
133.66
131.84
130.13
129.98
128.58
128.29
128.22
127.68
127.62
126.74
126.61
125.56
91.48
77.45
77.13
76.82
S
H
O
O
3b
200
180
160
140
120
100
80
60
40
20
ppm

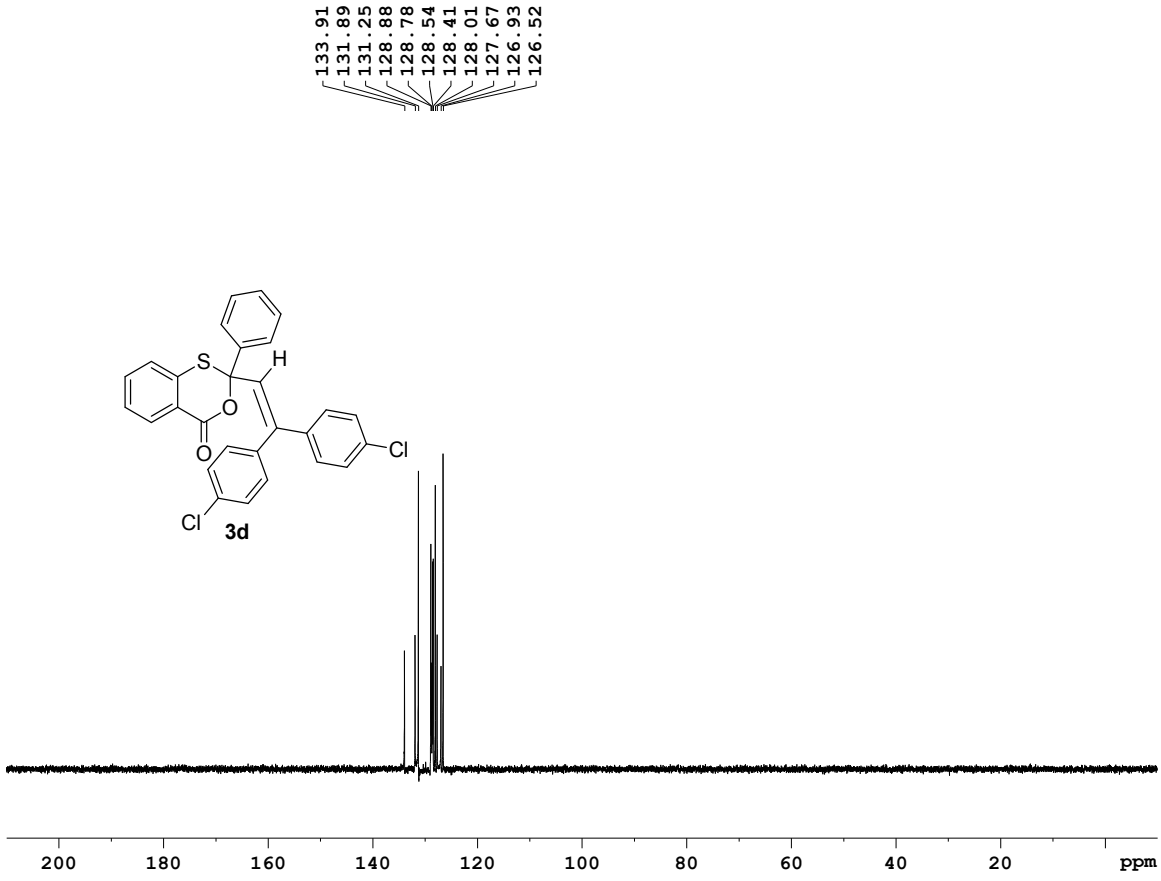

133.66
131.84
130.14
129.99
128.58
128.30
128.23
127.68
127.62
126.74
126.61
S
H
O
O
3b
200
180
160
140
120
100
80
60
40
20
ppm

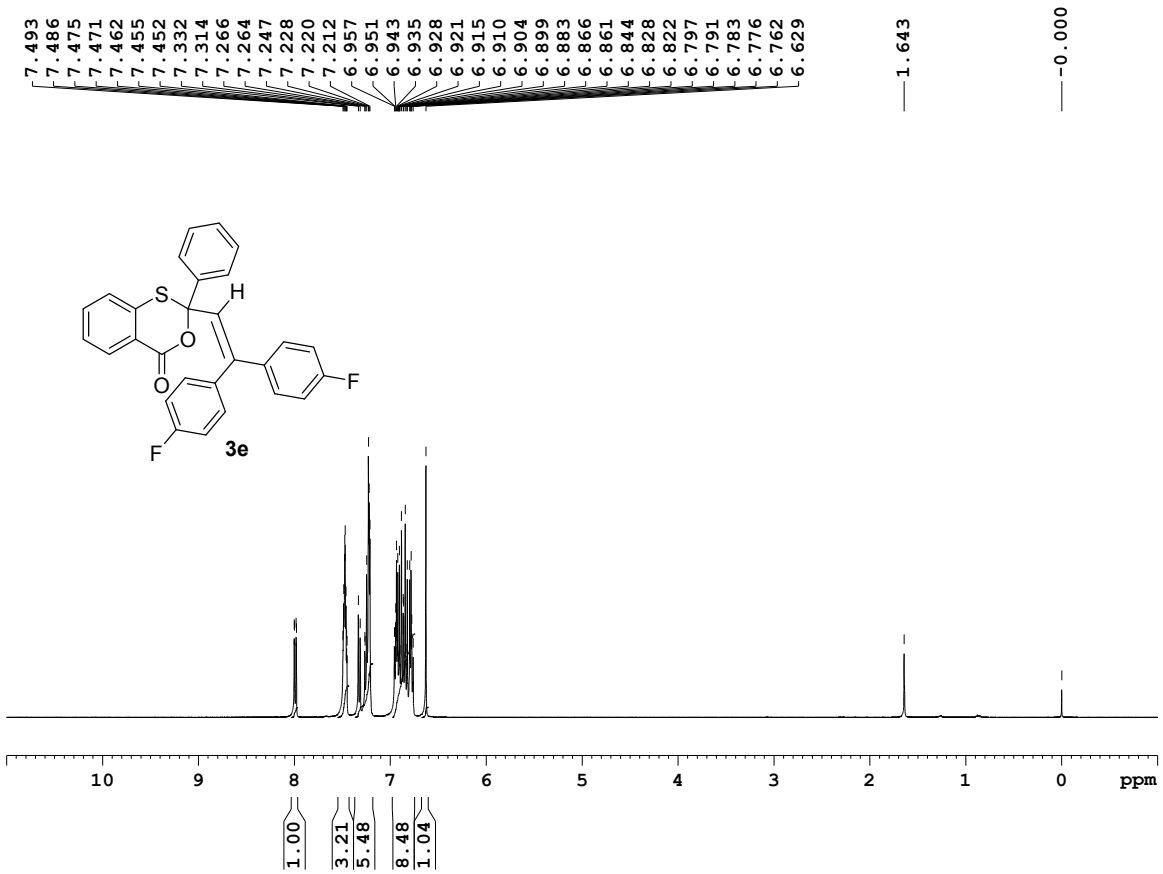

7.985
7.983
7.965
7.963
7.529
7.519
7.510
7.505
7.461
7.458
7.442
7.439
7.423
7.420
7.308
7.290
7.236
7.233
7.217
7.210
7.204
7.195
6.917
6.895
6.755
6.733
6.724
6.701
6.691
6.669
6.544
3.769
3.728
S
H
O
O
O
O
3c
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
2.12
1.13
1.19
4.14
2.22
6.31
0.88
3.00
3.00
163.36
159.80
159.18
147.36
140.54
137.23
135.11
133.60
131.75
131.33
130.19
129.01
128.53
128.24
128.05
127.61
126.65
126.62
125.61
113.52
113.02
91.77
77.48
77.16
76.85
55.34
55.22
S
H
O
O
O
O
3c
200
180
160
140
120
100
80
60
40
20
ppm

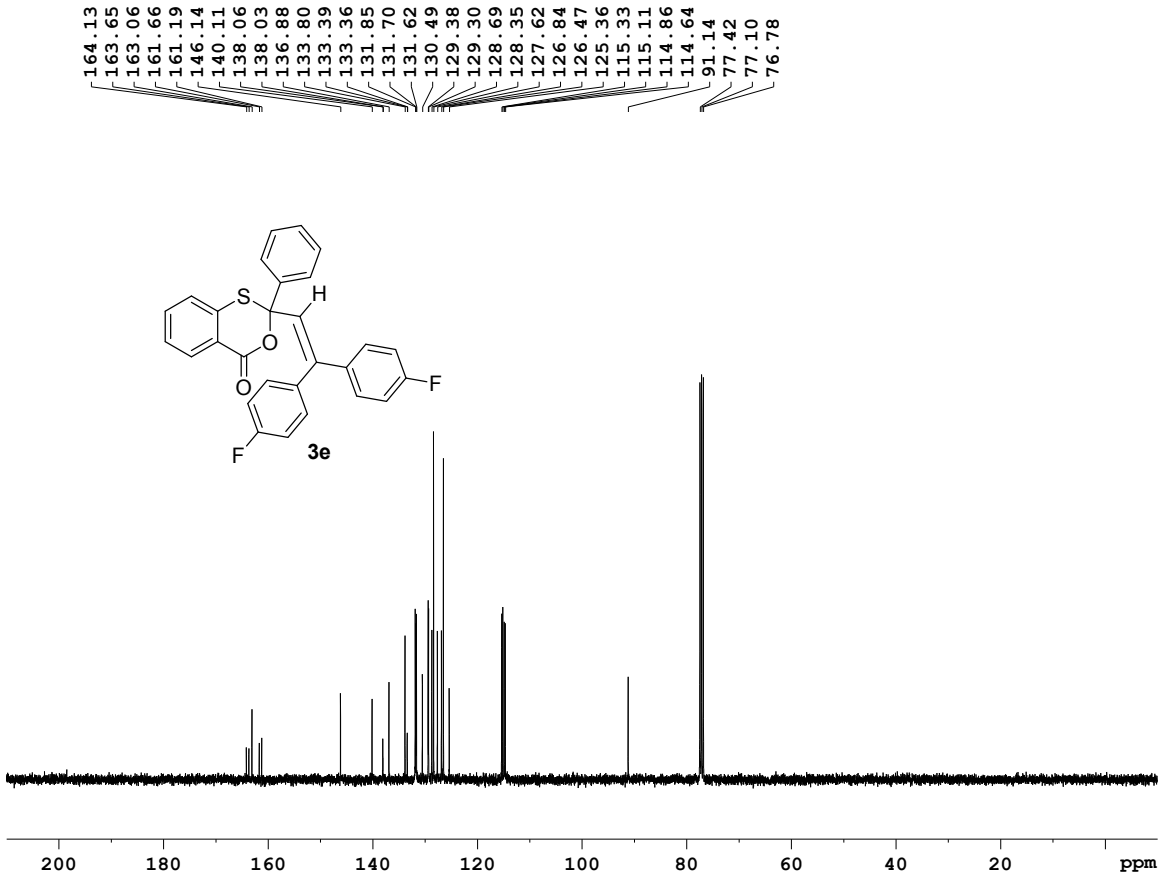

133.61
131.75
131.33
129.01
128.54
128.24
128.05
127.61
126.66
126.62
113.51
113.02
55.34
55.22
3c
200
180
160
140
120
100
80
60
40
20
ppm

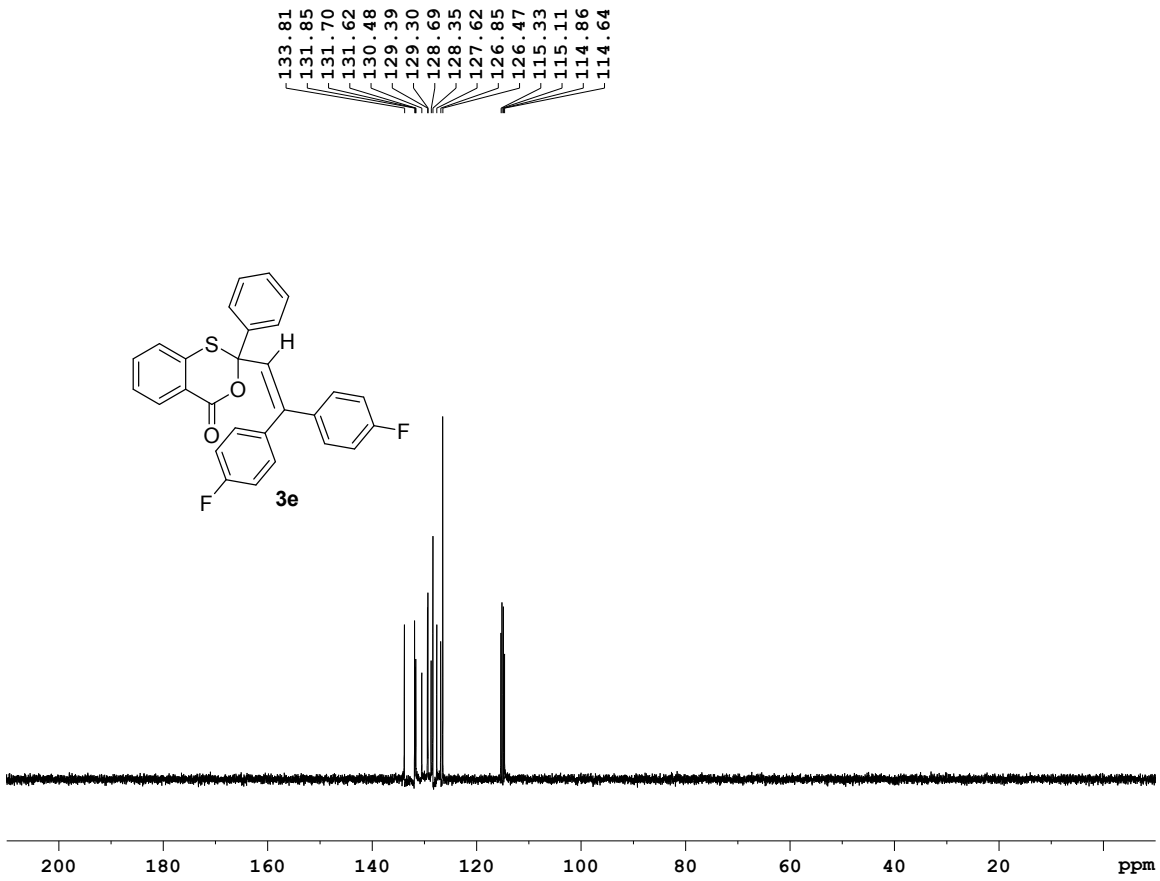

7.502
7.486
7.483
7.465
7.461
7.452
7.448
7.441
7.342
7.341
7.323
7.321
7.277
7.274
7.258
7.233
7.229
7.220
7.215
7.204
7.192
7.185
7.181
7.169
7.164
7.141
7.135
7.131
7.119
7.114
6.908
6.886
6.742
6.737
6.725
6.721
6.676
1.604
0.000
3d
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.13
1.10
4.42
2.16
1.85
2.03
1.97
0.96

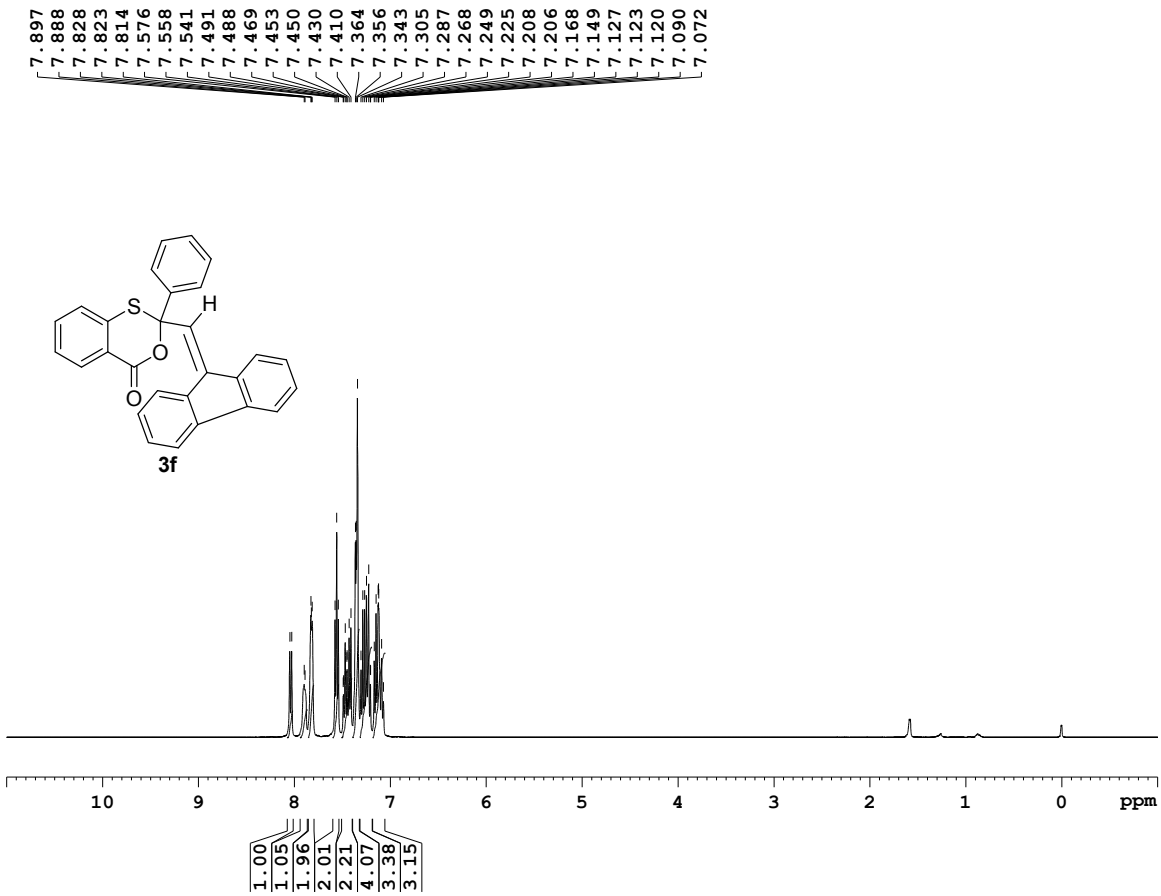

162.98
145.82
140.04
139.97
136.78
135.67
134.60
134.00
133.90
131.89
131.24
128.87
128.78
128.53
128.41
128.01
127.67
126.93
126.52
125.29
91.06
77.52
77.20
76.88
S
H
O
O
Cl
Cl
3d
200
180
160
140
120
100
80
60
40
20
ppm

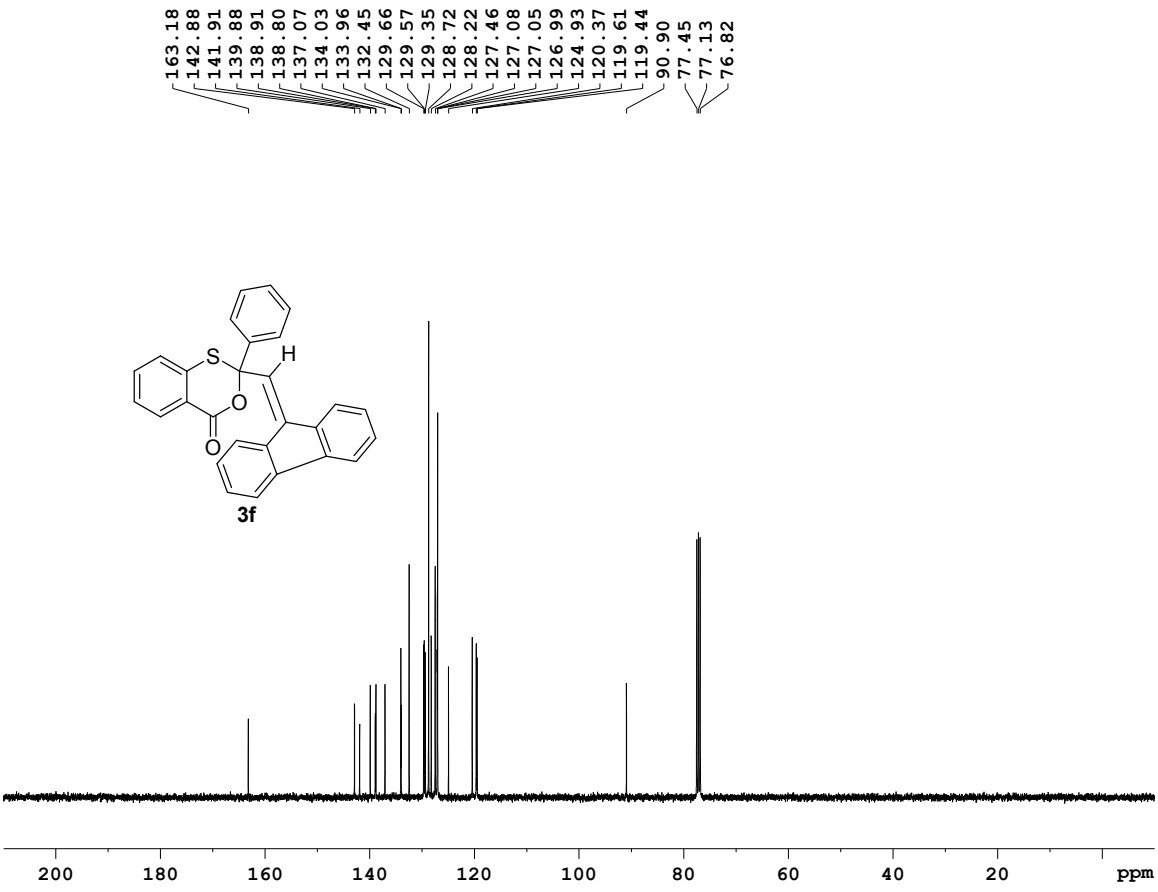

133.91
131.89
131.25
128.88
128.78
128.54
128.41
128.01
127.67
126.93
126.52
S
H
O
O
Cl
Cl
3d
200
180
160
140
120
100
80
60
40
20
ppm

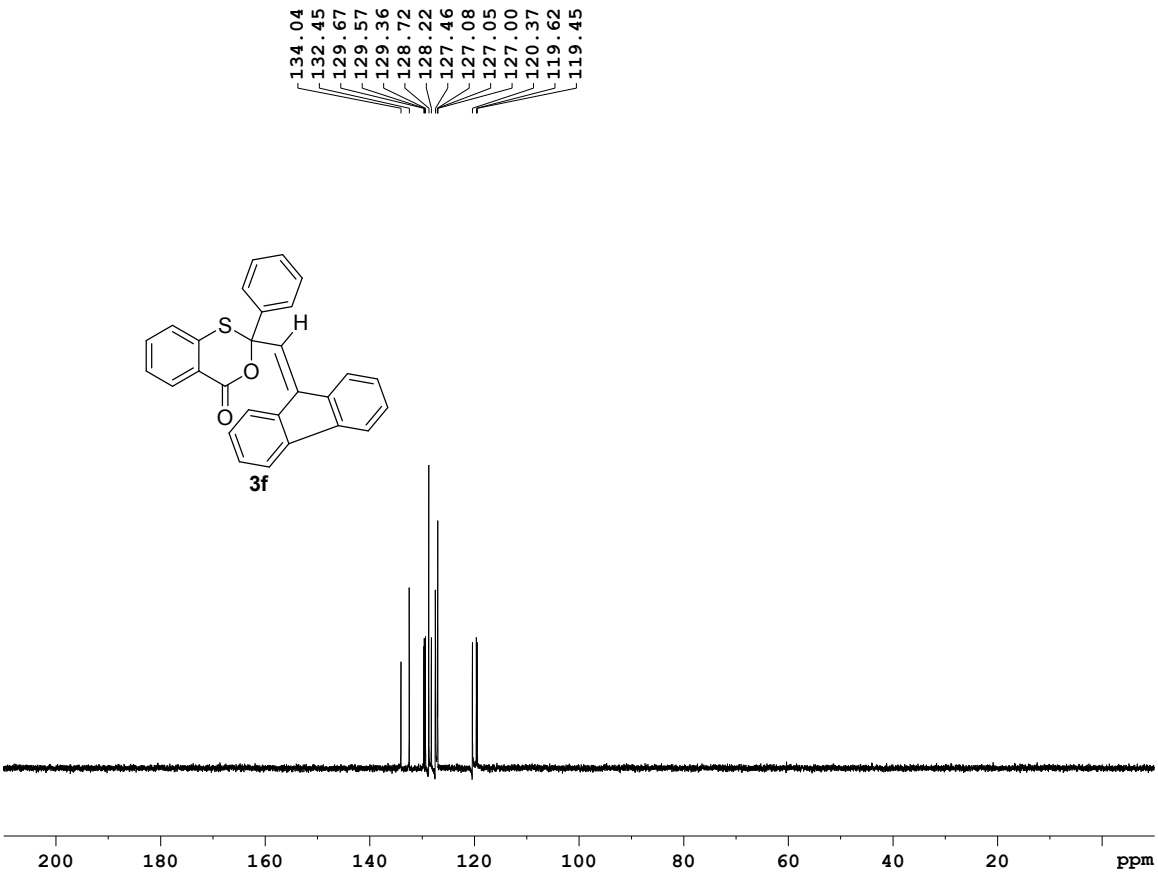

7.493
7.486
7.475
7.471
7.462
7.455
7.452
7.332
7.314
7.266
7.264
7.247
7.228
7.220
7.212
6.957
6.951
6.943
6.935
6.928
6.921
6.915
6.910
6.904
6.899
6.883
6.866
6.861
6.844
6.828
6.822
6.797
6.791
6.783
6.776
6.762
6.629
1.643
0.000
S
H
O
O
F
F
3e
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.21
5.48
8.48
1.04

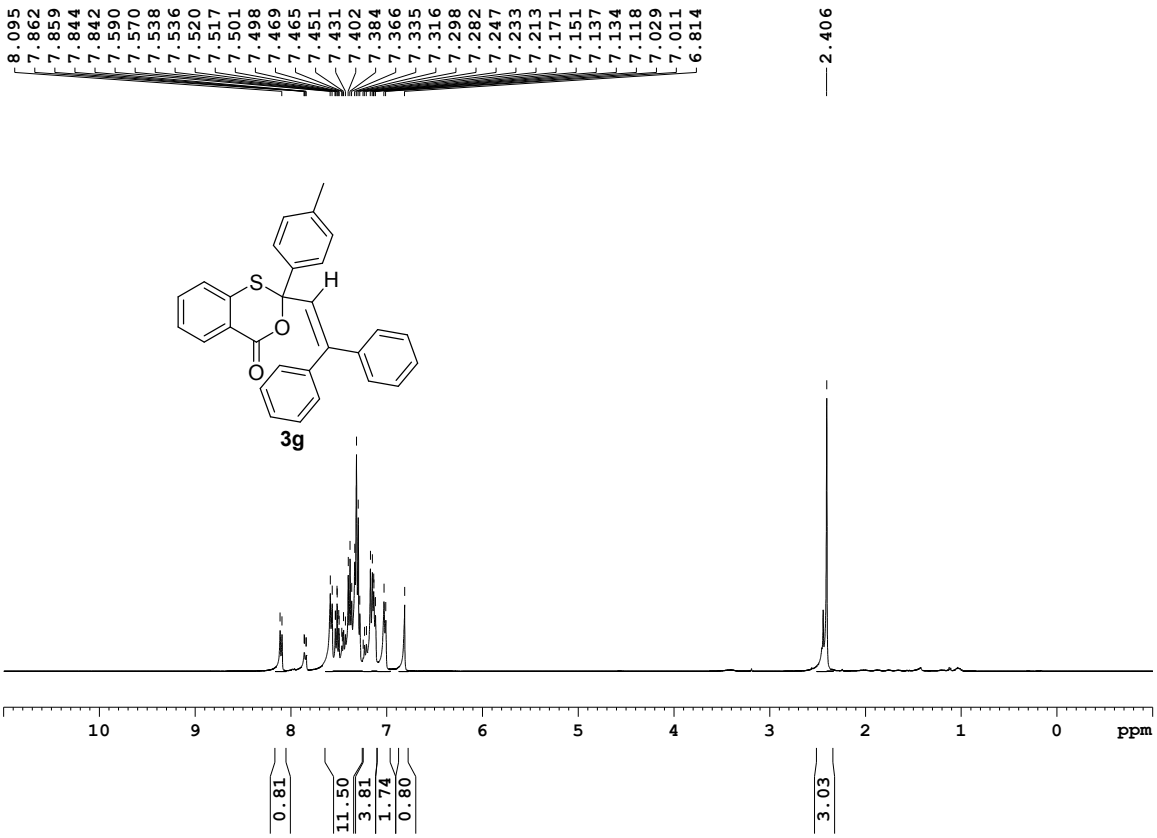

164.13
163.65
163.06
161.66
161.19
146.14
140.11
138.06
138.03
136.88
133.80
133.39
133.36
131.85
131.70
131.62
130.49
129.38
129.30
128.69
128.35
127.62
126.84
126.47
125.36
115.33
115.11
114.86
114.64
91.14
77.42
77.10
76.78
S
H
O
O
F
F
3e
200
180
160
140
120
100
80
60
40
20
ppm

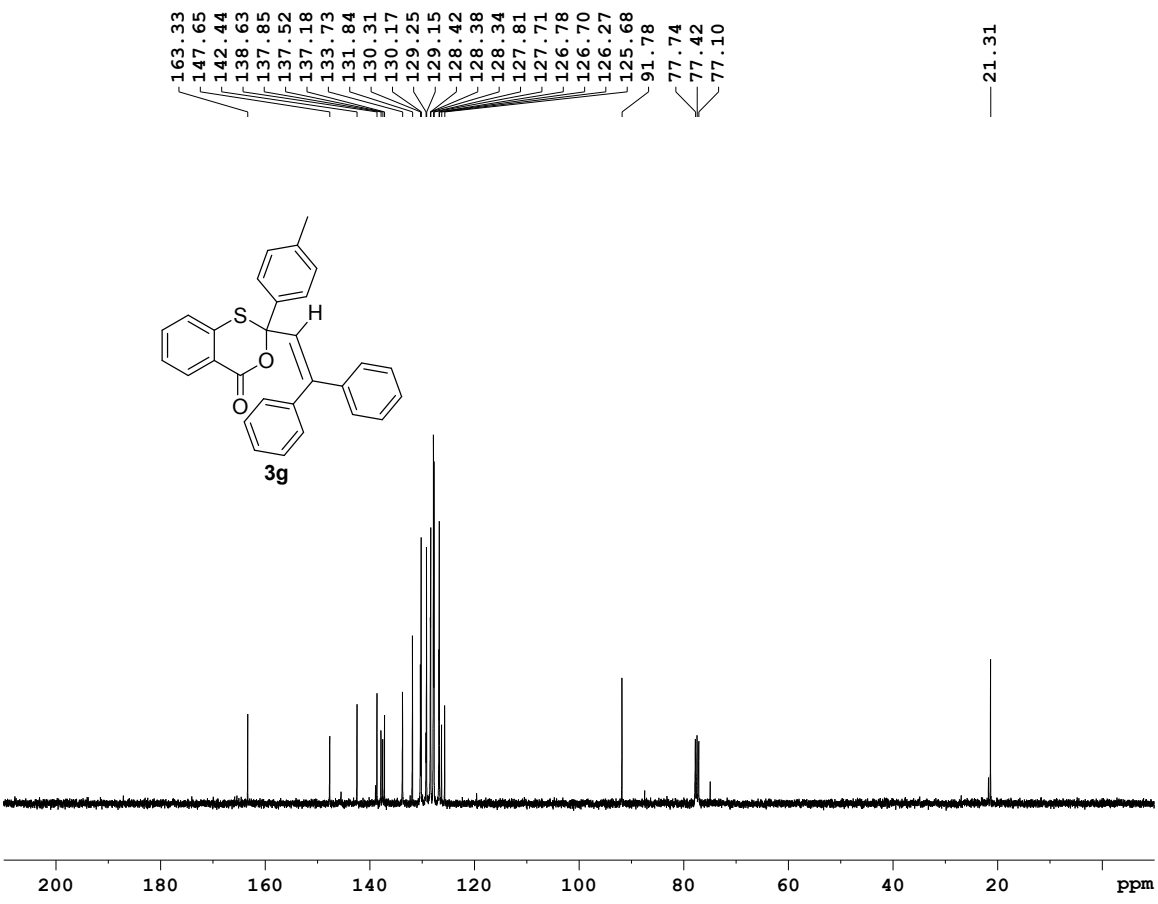

133.81
131.85
131.70
131.62
130.48
129.39
129.30
128.69
128.35
127.62
126.85
126.47
115.33
115.11
114.86
114.64
S
H
O
O
F
F
3e
200
180
160
140
120
100
80
60
40
20
ppm

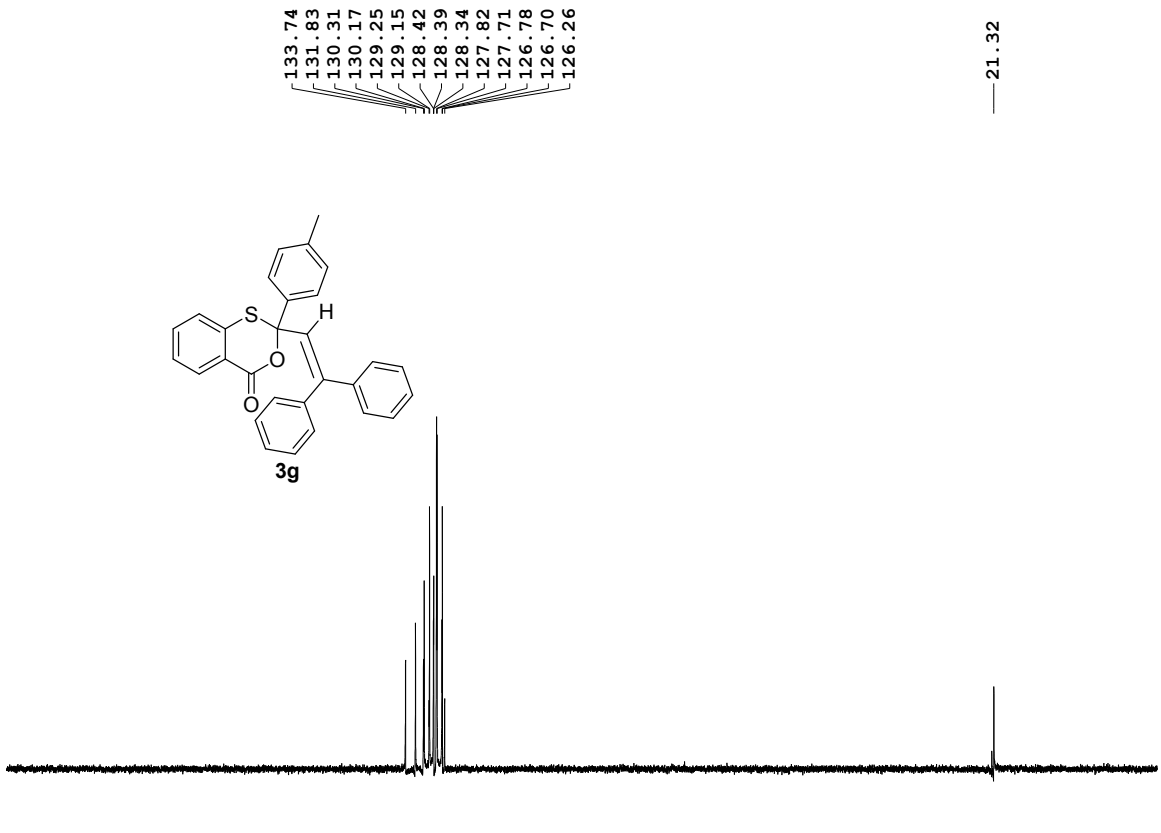

7.897
7.888
7.828
7.823
7.814
7.576
7.558
7.541
7.491
7.488
7.469
7.453
7.450
7.430
7.410
7.364
7.356
7.343
7.305
7.287
7.268
7.249
7.225
7.208
7.206
7.168
7.149
7.127
7.123
7.120
7.090
7.072
S
H
O
O
3f
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
1.96
2.01
2.21
4.07
3.38
3.15

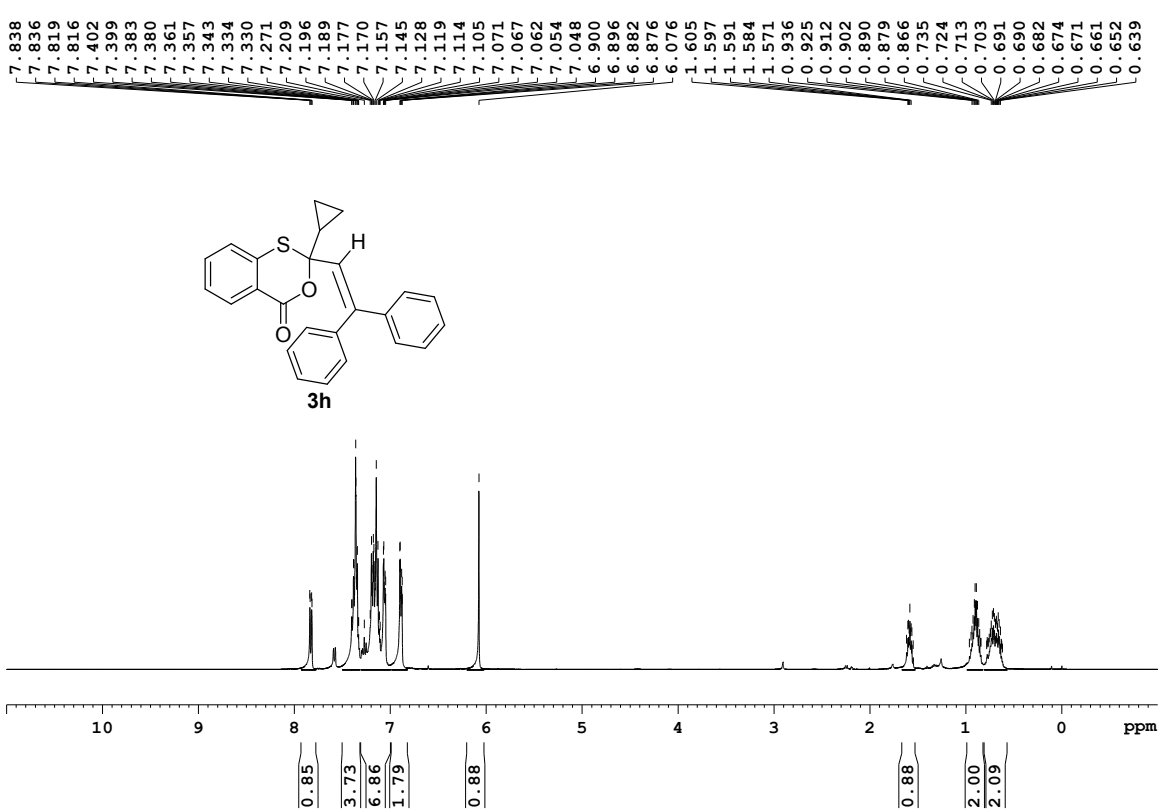

163.18
142.88
141.91
139.88
138.91
138.80
137.07
134.03
133.96
132.45
129.66
129.57
129.35
128.72
128.22
127.46
127.08
127.05
126.99
124.93
120.37
119.61
119.44
90.90
77.45
77.13
76.82
S
H
O
O
3f
200
180
160
140
120
100
80
60
40
20
ppm

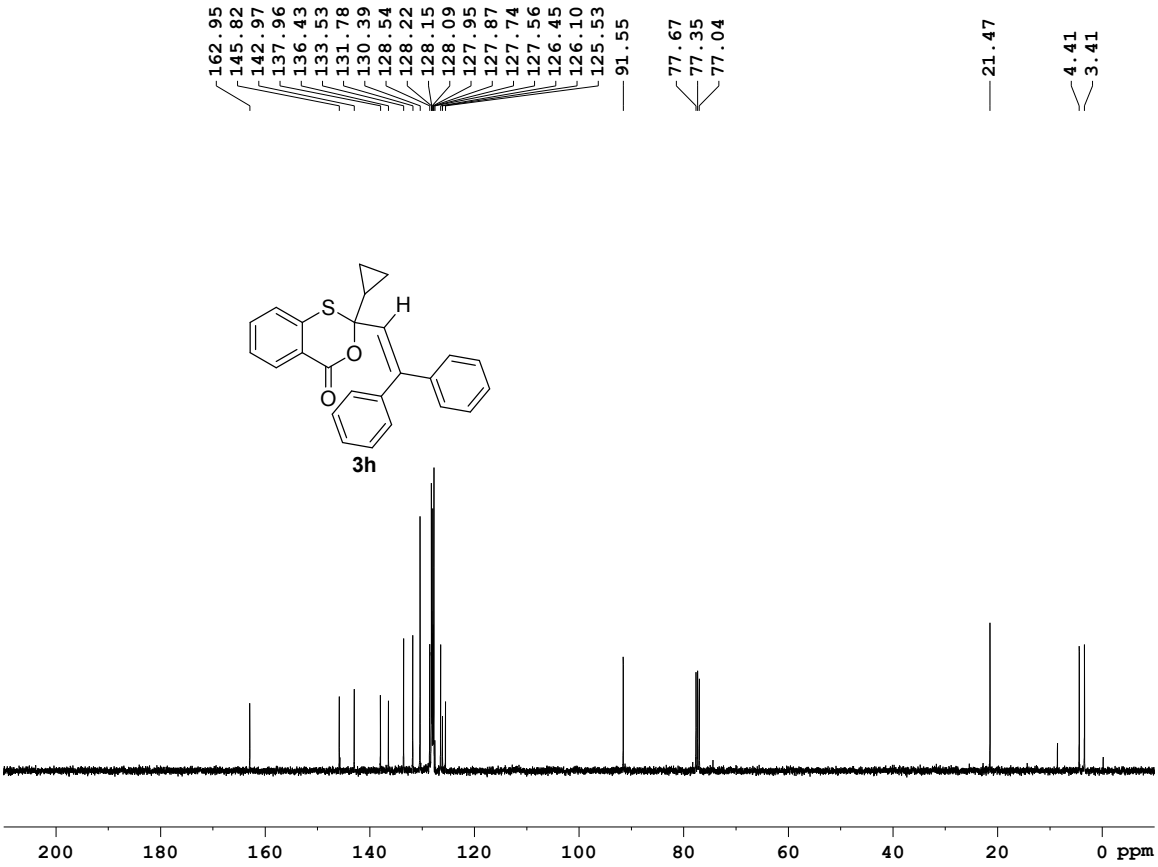

134.04
132.45
129.67
129.57
129.36
128.72
128.22
127.46
127.08
127.05
127.00
120.37
119.62
119.45
S
H
O
O
3f
200
180
160
140
120
100
80
60
40
20
ppm

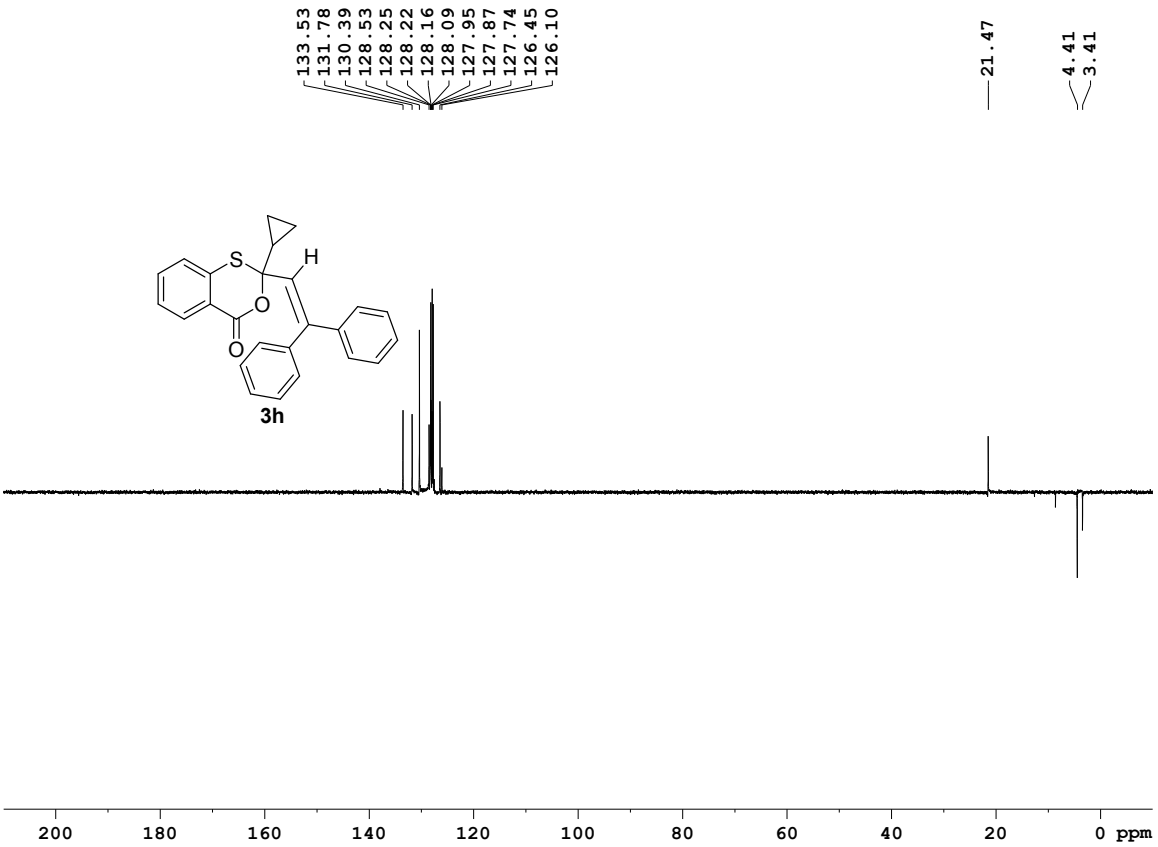

8.095
7.862
7.859
7.844
7.842
7.590
7.570
7.538
7.536
7.520
7.517
7.501
7.498
7.469
7.465
7.451
7.431
7.402
7.384
7.366
7.335
7.316
7.298
7.282
7.247
7.233
7.213
7.171
7.151
7.137
7.134
7.118
7.029
7.011
6.814
2.406
S
H
O
O
3g
10
9
8
7
6
5
4
3
2
1
0
ppm
0.81
11.50
3.81
1.74
0.80
3.03

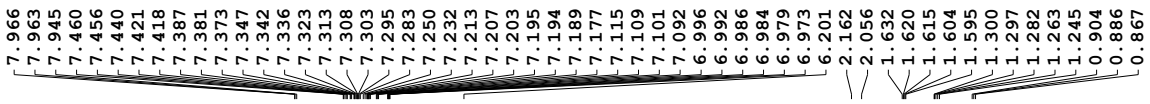

163.33
147.65
142.44
138.63
137.85
137.52
137.18
133.73
131.84
130.31
130.17
129.25
129.15
128.42
128.38
128.34
127.81
127.71
126.78
126.70
126.27
125.68
91.78
77.74
77.42
77.10
21.31
S
H
O
O
3g
200
180
160
140
120
100
80
60
40
20
ppm

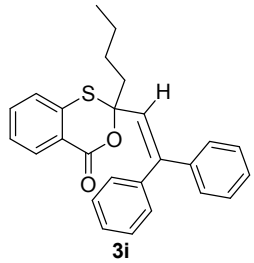

133.74
131.83
130.31
130.17
129.25
129.15
128.42
128.39
128.34
127.82
127.71
126.78
126.70
126.26
21.32
S
H
O
O
3g
200
180
160
140
120
100
80
60
40
20
ppm


7.838
7.836
7.819
7.816
7.402
7.399
7.383
7.380
7.361
7.357
7.343
7.334
7.330
7.271
7.209
7.196
7.189
7.177
7.170
7.157
7.145
7.128
7.119
7.114
7.105
7.071
7.067
7.062
7.054
7.048
6.900
6.896
6.882
6.876
6.076
1.605
1.597
1.591
1.584
1.571
0.936
0.925
0.912
0.902
0.890
0.879
0.866
0.735
0.724
0.713
0.703
0.691
0.690
0.682
0.674
0.671
0.661
0.652
0.639
S
H
O
O
3h
10
9
8
7
6
5
4
3
2
1
0
ppm
0.85
3.73
6.86
1.79
0.88
0.88
2.00
2.09

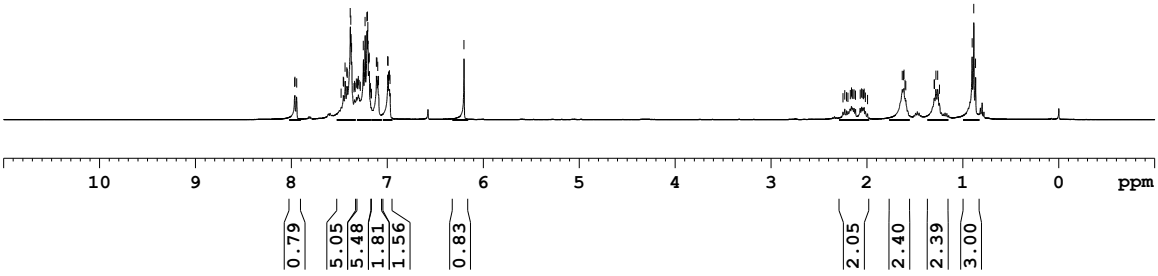

162.95
145.82
142.97
137.96
136.43
133.53
131.78
130.39
128.54
128.22
128.15
128.09
127.95
127.87
127.74
127.56
126.45
126.10
125.53
91.55
77.67
77.35
77.04
21.47
4.41
3.41
S
H
O
O
3h
200
180
160
140
120
100
80
60
40
20
0 ppm

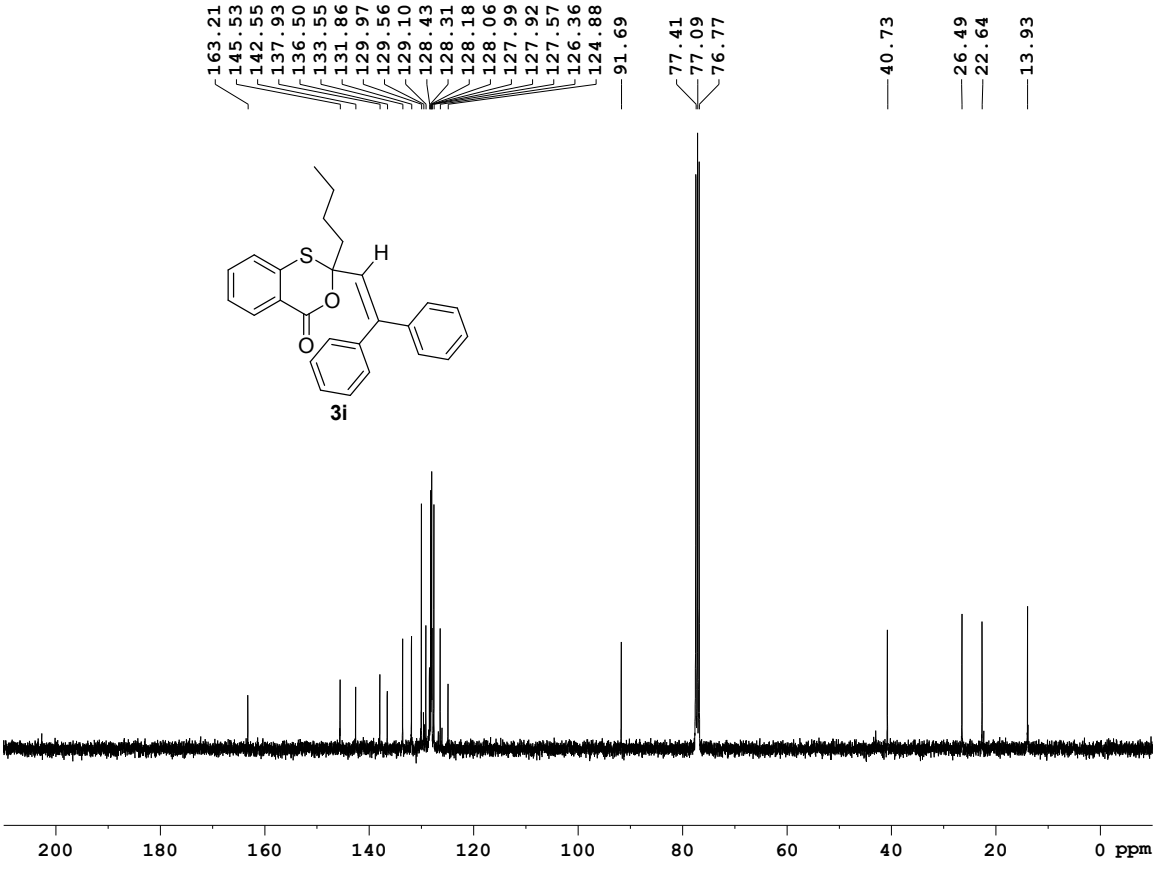

133.53
131.78
130.39
128.53
128.25
128.22
128.16
128.09
127.95
127.87
127.74
126.45
126.10
21.47
4.41
3.41
S
H
O
O
3h
200
180
160
140
120
100
80
60
40
20
0 ppm


7.966
7.963
7.945
7.460
7.456
7.440
7.421
7.418
7.387
7.381
7.373
7.347
7.342
7.336
7.323
7.313
7.308
7.303
7.295
7.283
7.250
7.232
7.213
7.207
7.203
7.195
7.194
7.189
7.177
7.115
7.109
7.101
7.092
6.996
6.992
6.986
6.984
6.979
6.973
6.201
2.162
2.056
1.632
1.620
1.615
1.604
1.595
1.300
1.297
1.282
1.263
1.245
0.904
0.886
0.867


S
H
O
O

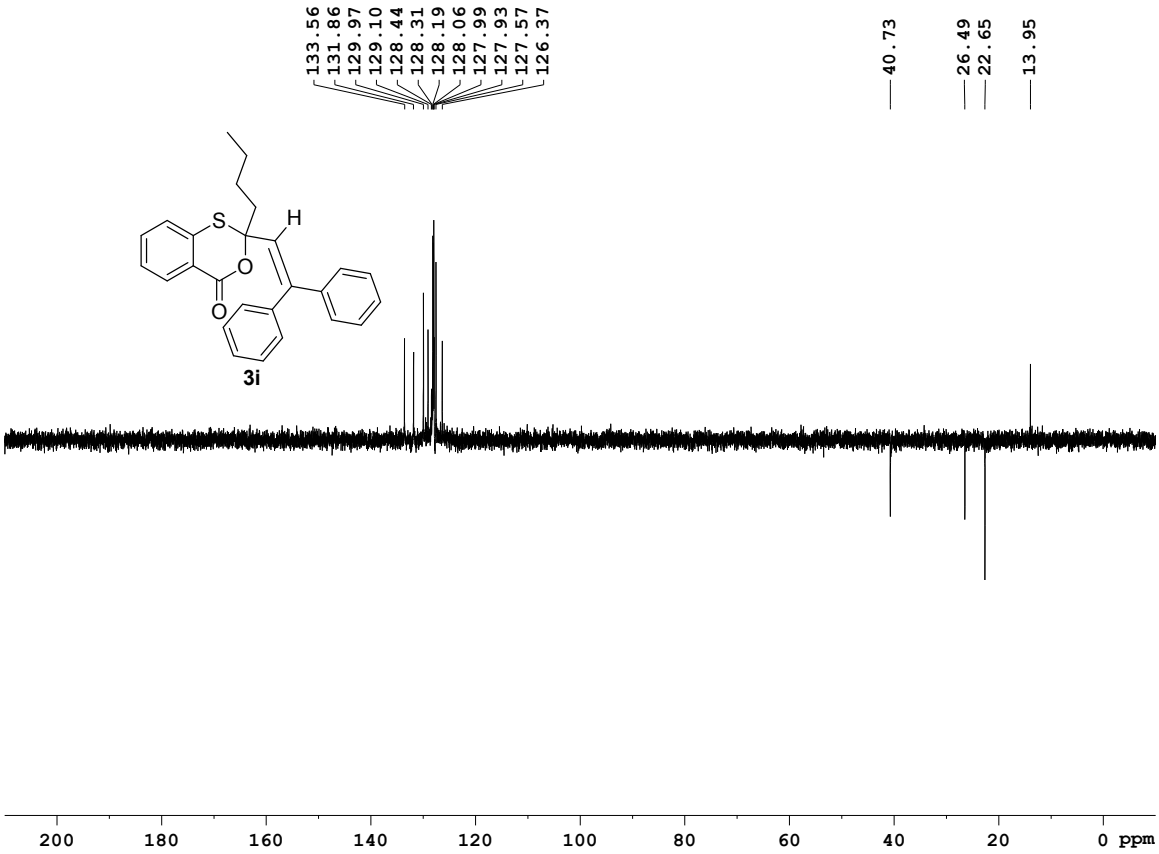
3i

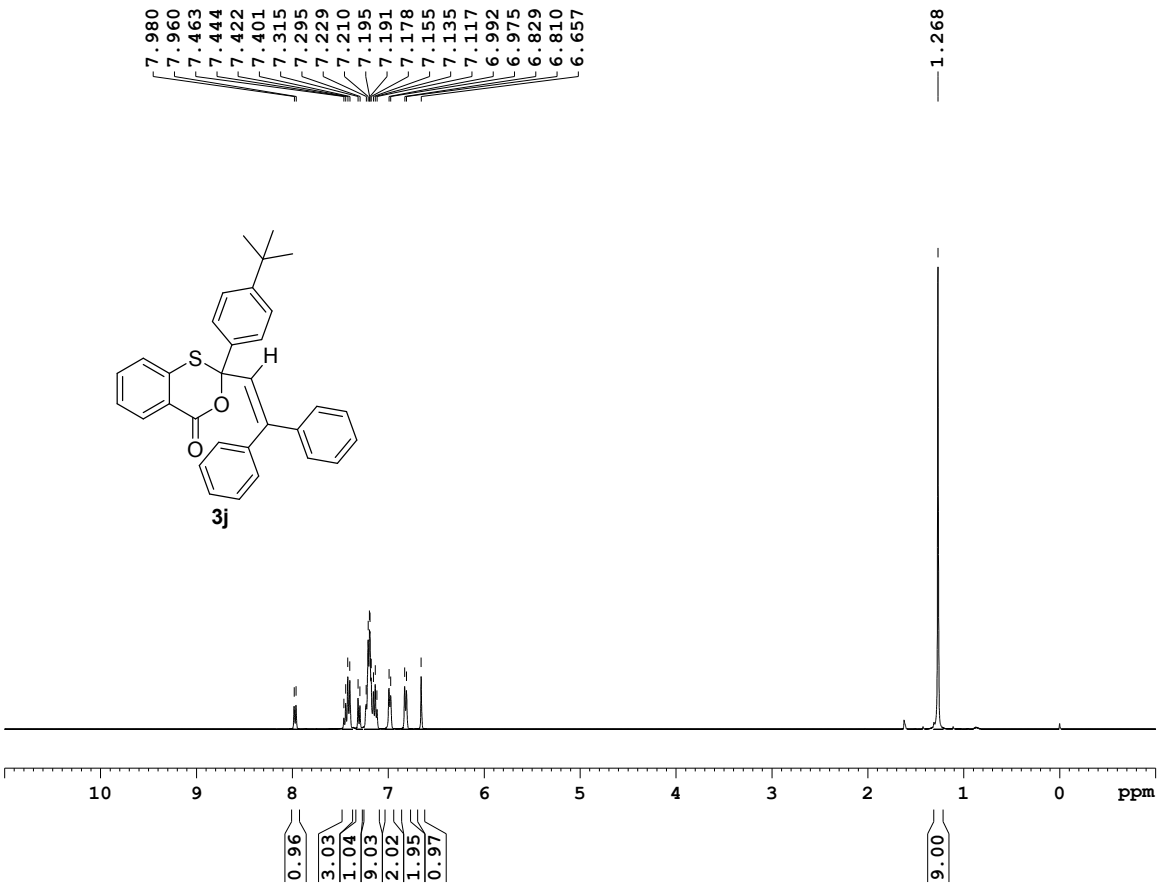

10
9
8
7
6
5
4
3
2
1
0
ppm
0.79
5.05
5.48
1.81
1.56
0.83
2.05
2.40
2.39
3.00

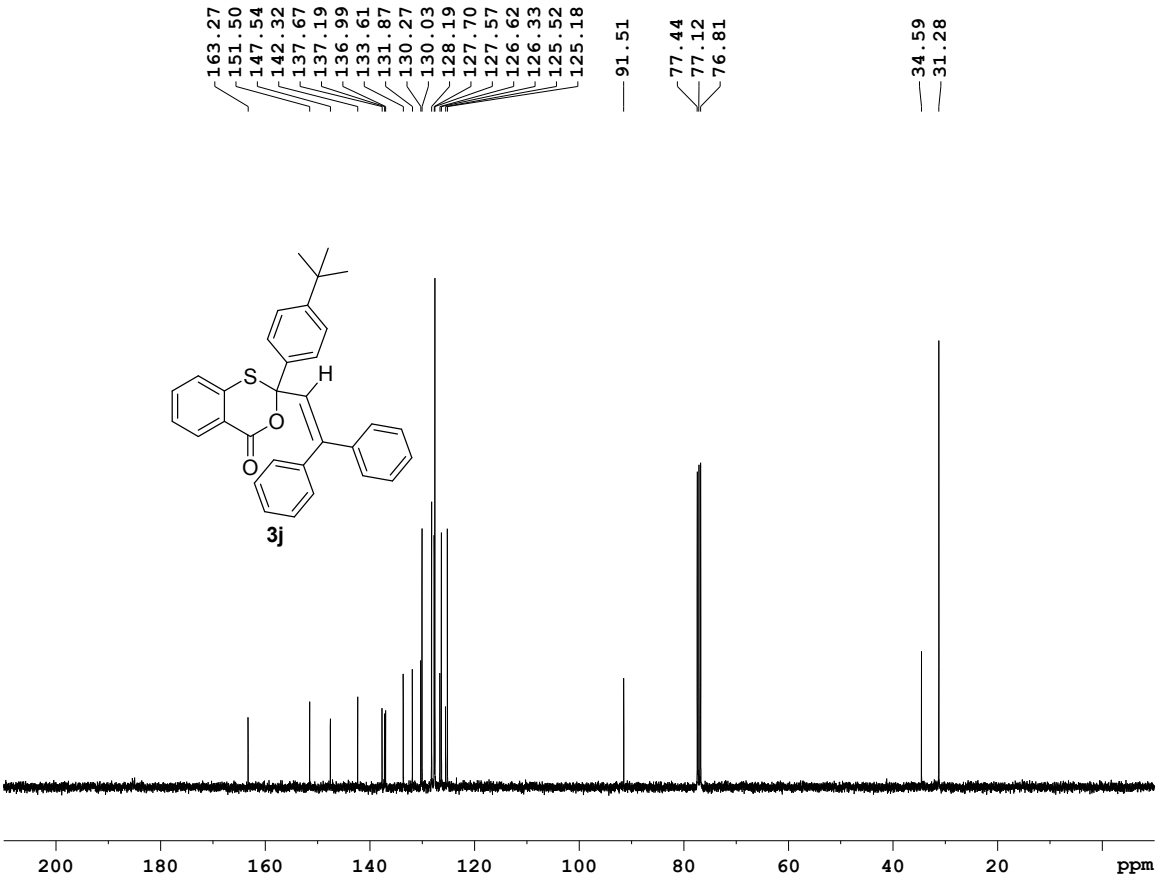

163.21
145.53
142.55
137.93
136.50
133.55
131.86
129.97
129.56
129.10
128.43
128.31
128.18
128.06
127.99
127.92
127.57
126.36
124.88
91.69
77.41
77.09
76.77
40.73
26.49
22.64
13.93
200
180
160
140
120
100
80
60
40
20
0 ppm

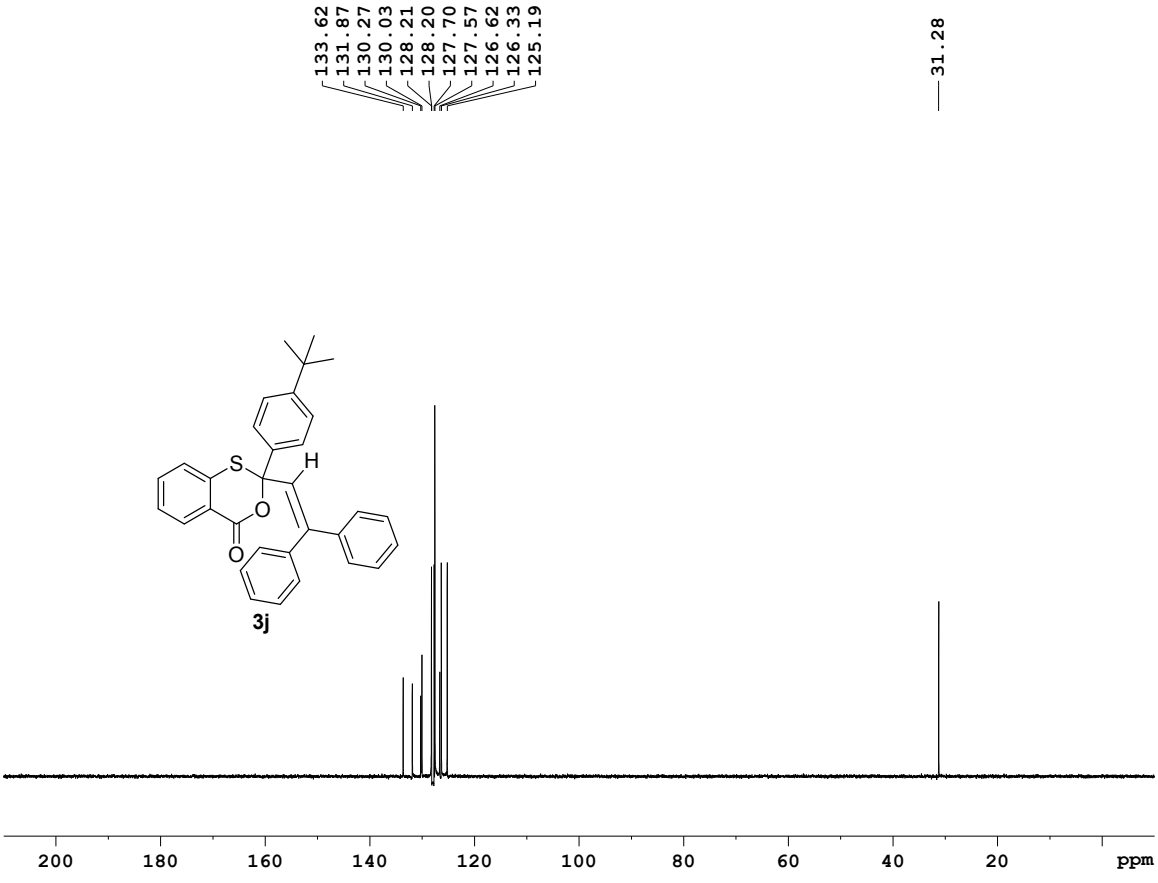
S
H
O
O

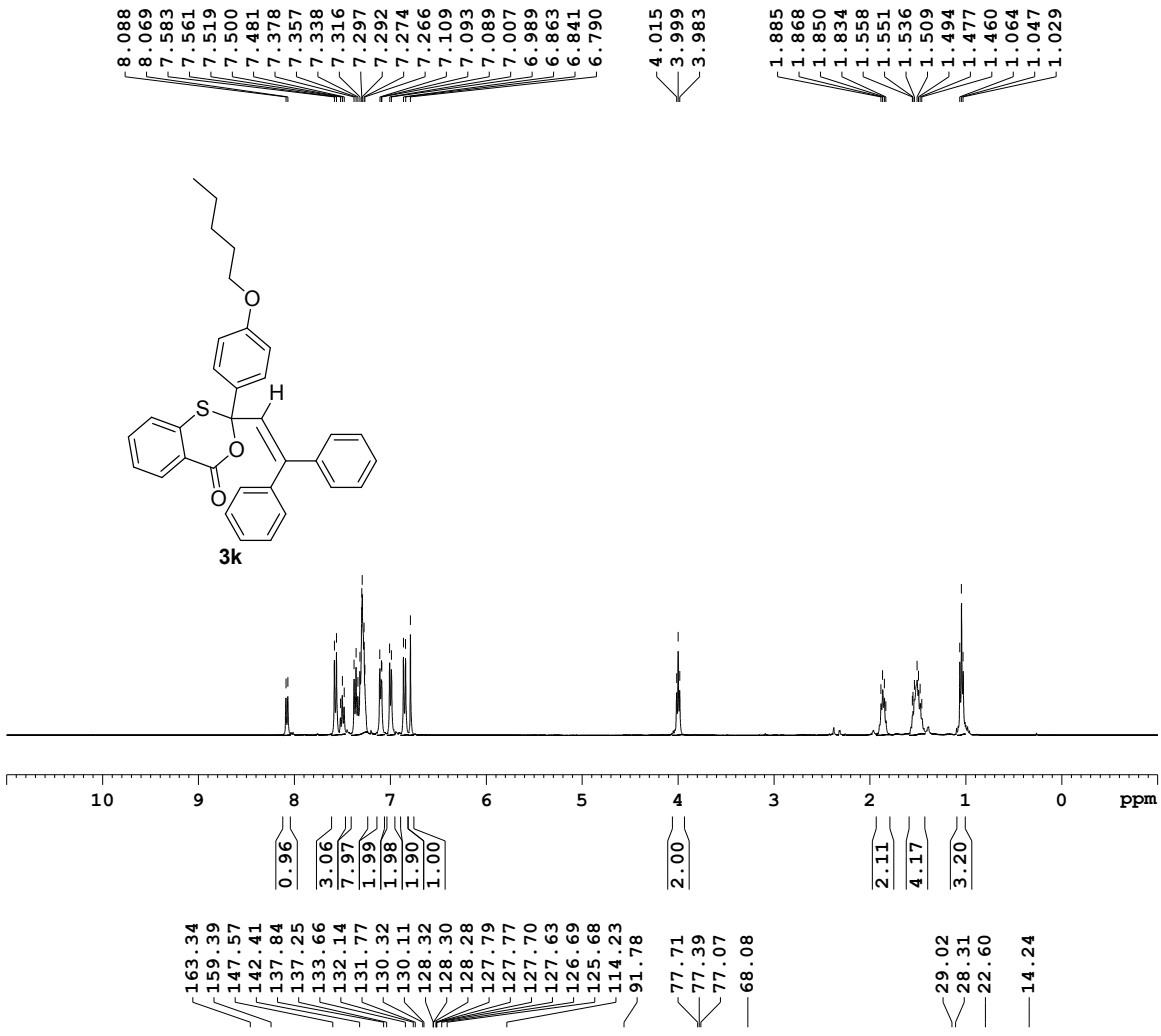
3i

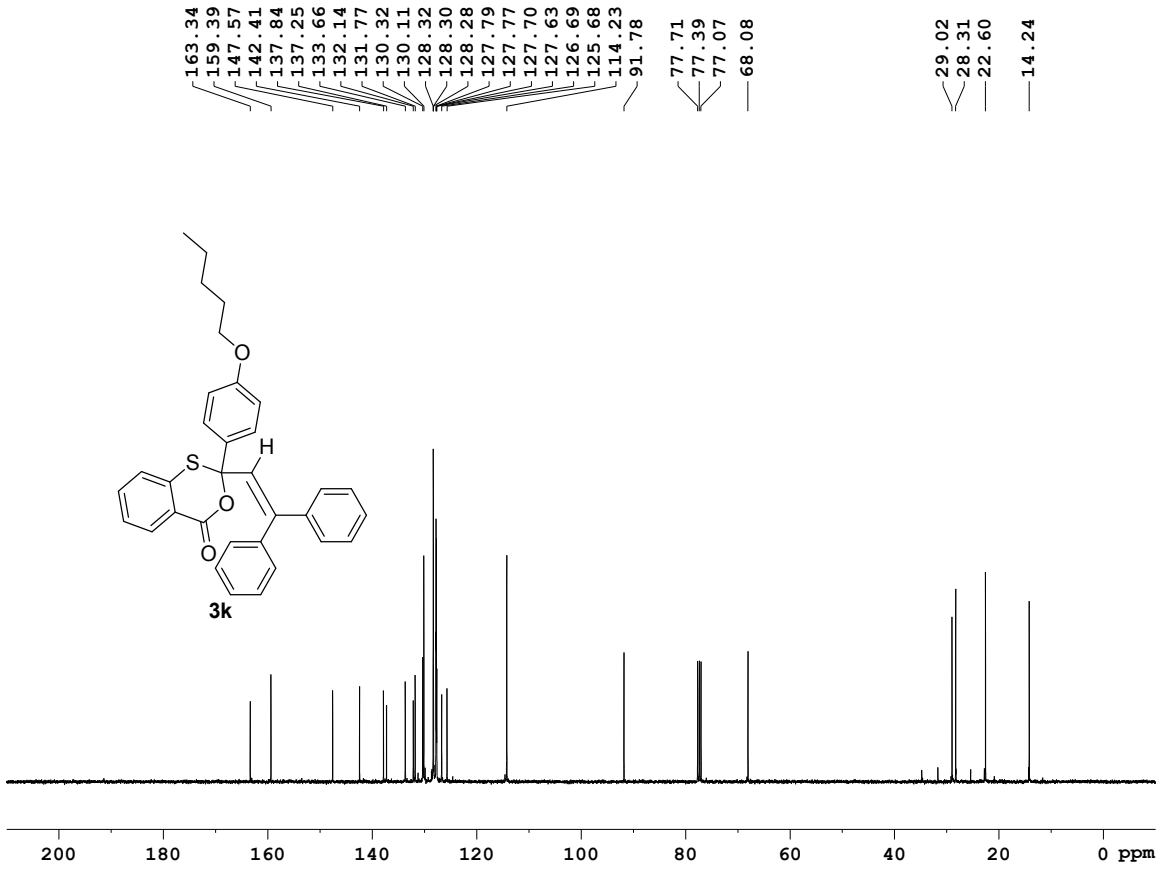

133.56
131.86
129.97
129.10
128.44
128.31
128.19
128.06
127.99
127.93
127.57
126.37
40.73
26.49
22.65
13.95
S
H
O
O
3i
200
180
160
140
120
100
80
60
40
20
0 ppm

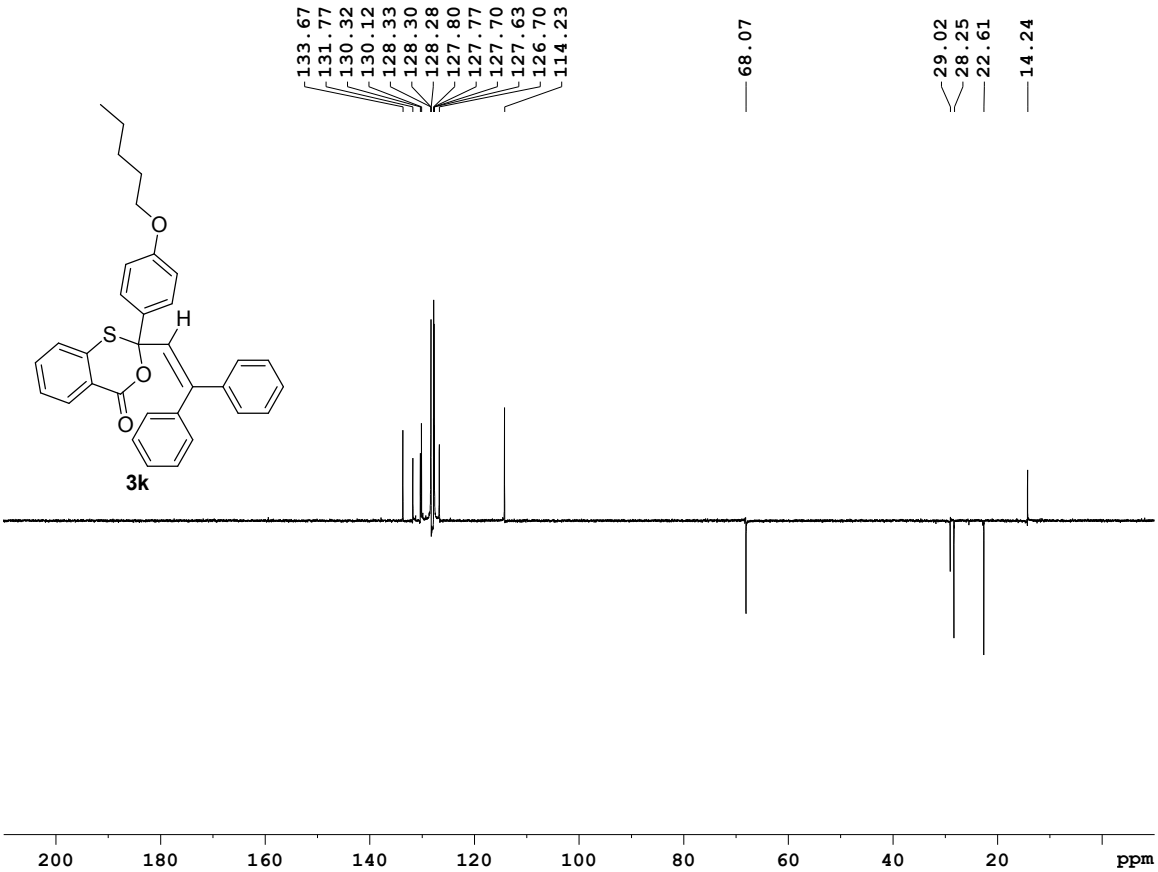

7.980
7.960
7.463
7.444
7.422
7.401
7.315
7.295
7.229
7.210
7.195
7.191
7.178
7.155
7.135
7.117
6.992
6.975
6.829
6.810
6.657
1.268
S
H
O
O
3j
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
3.03
1.04
9.03
2.02
1.95
0.97
9.00

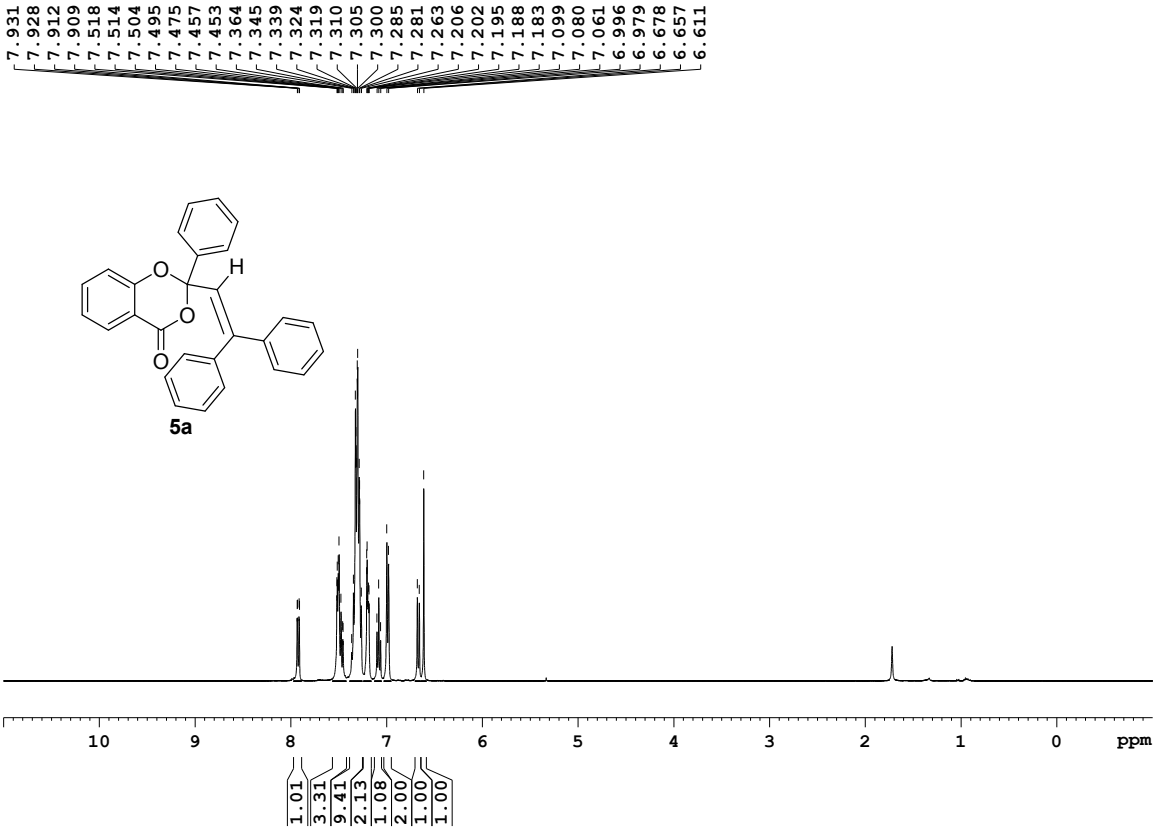

163.27
151.50
147.54
142.32
137.67
137.19
136.99
133.61
131.87
130.27
130.03
128.19
127.70
127.57
126.62
126.33
125.52
125.18
91.51
77.44
77.12
76.81
34.59
31.28
S
H
O
O
3j
200
180
160
140
120
100
80
60
40
20
ppm

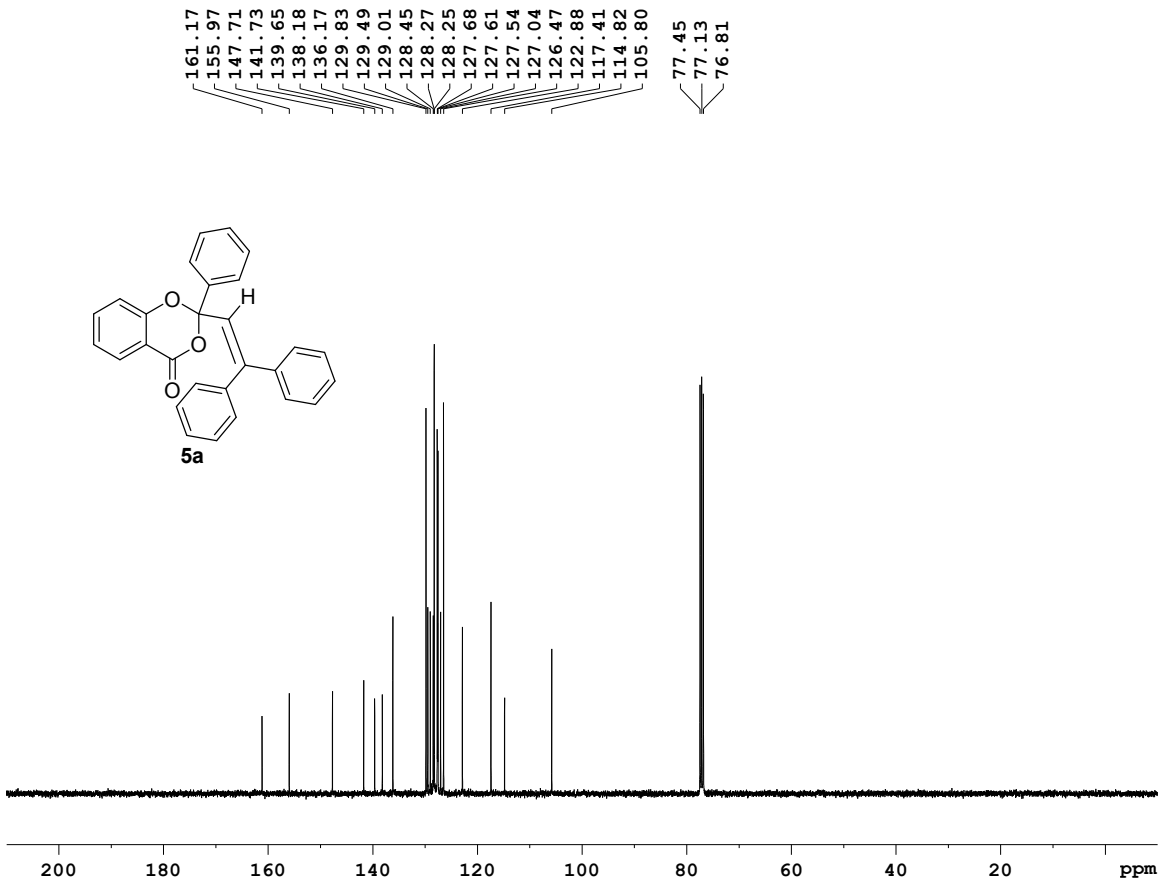

133.62
131.87
130.27
130.03
128.21
128.20
127.70
127.57
126.62
126.33
125.19
31.28
S
H
O
O
3j
200
180
160
140
120
100
80
60
40
20
ppm

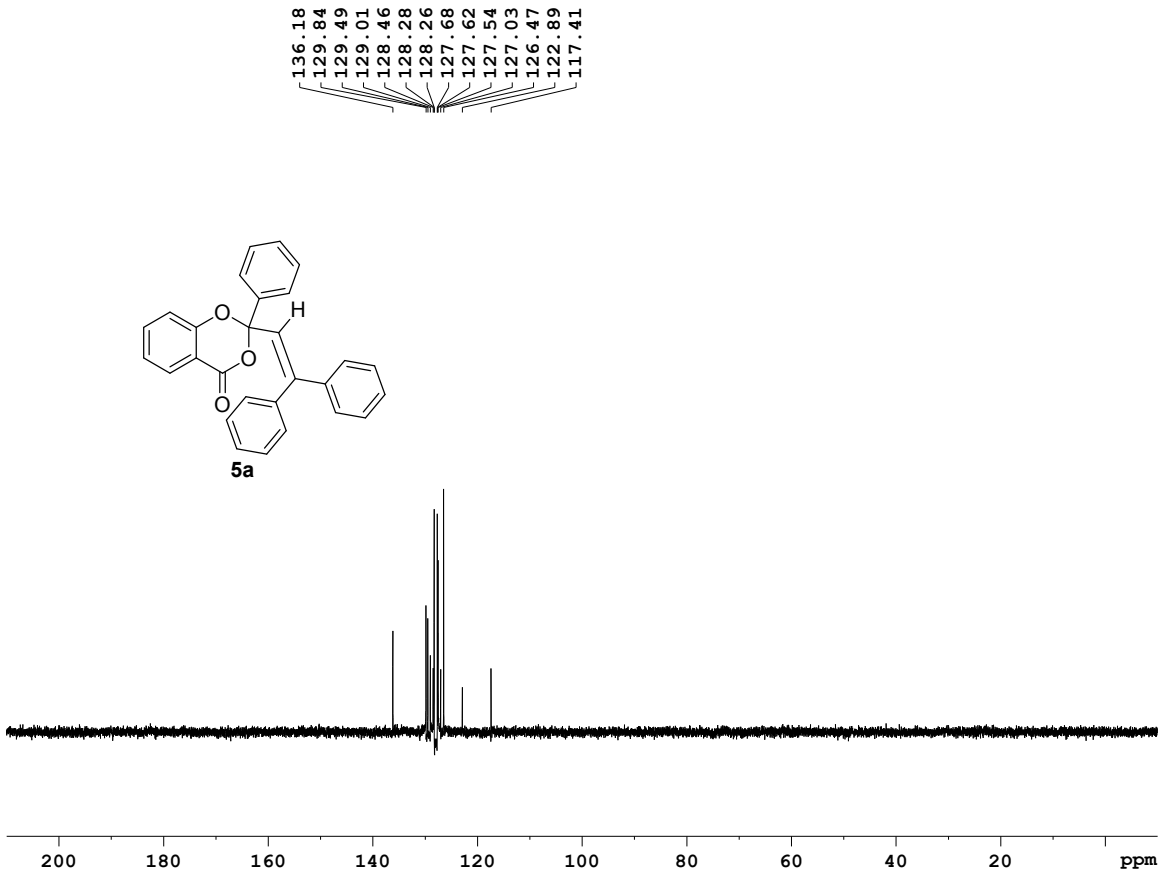

8.088
8.069
7.583
7.561
7.519
7.500
7.481
7.378
7.357
7.338
7.316
7.297
7.292
7.274
7.266
7.109
7.093
7.089
7.007
6.989
6.863
6.841
6.790
4.015
3.999
3.983
1.885
1.868
1.850
1.834
1.558
1.551
1.536
1.509
1.494
1.477
1.460
1.064
1.047
1.029
O
H
S
O
O
3k
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
3.06
7.97
1.99
1.98
1.90
1.00
2.00
2.11
4.17
3.20

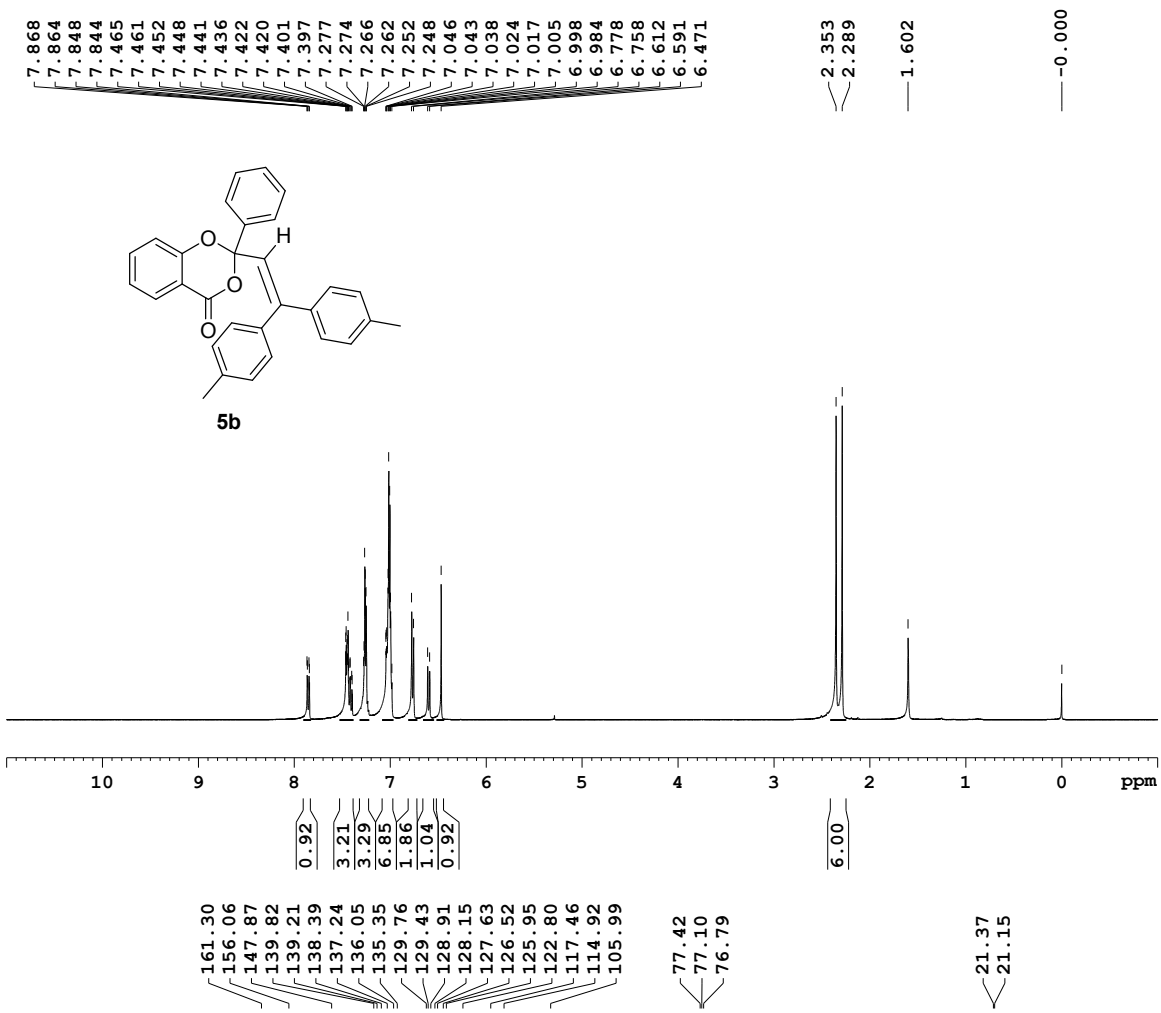

163.34
159.39
147.57
142.41
137.84
137.25
133.66
132.14
131.77
130.32
130.11
128.32
128.30
128.28
127.79
127.77
127.70
127.63
126.69
125.68
114.23
91.78
77.71
77.39
77.07
68.08
29.02
28.31
22.60
14.24
O
H
S
O
O
3k
200
180
160
140
120
100
80
60
40
20
0 ppm

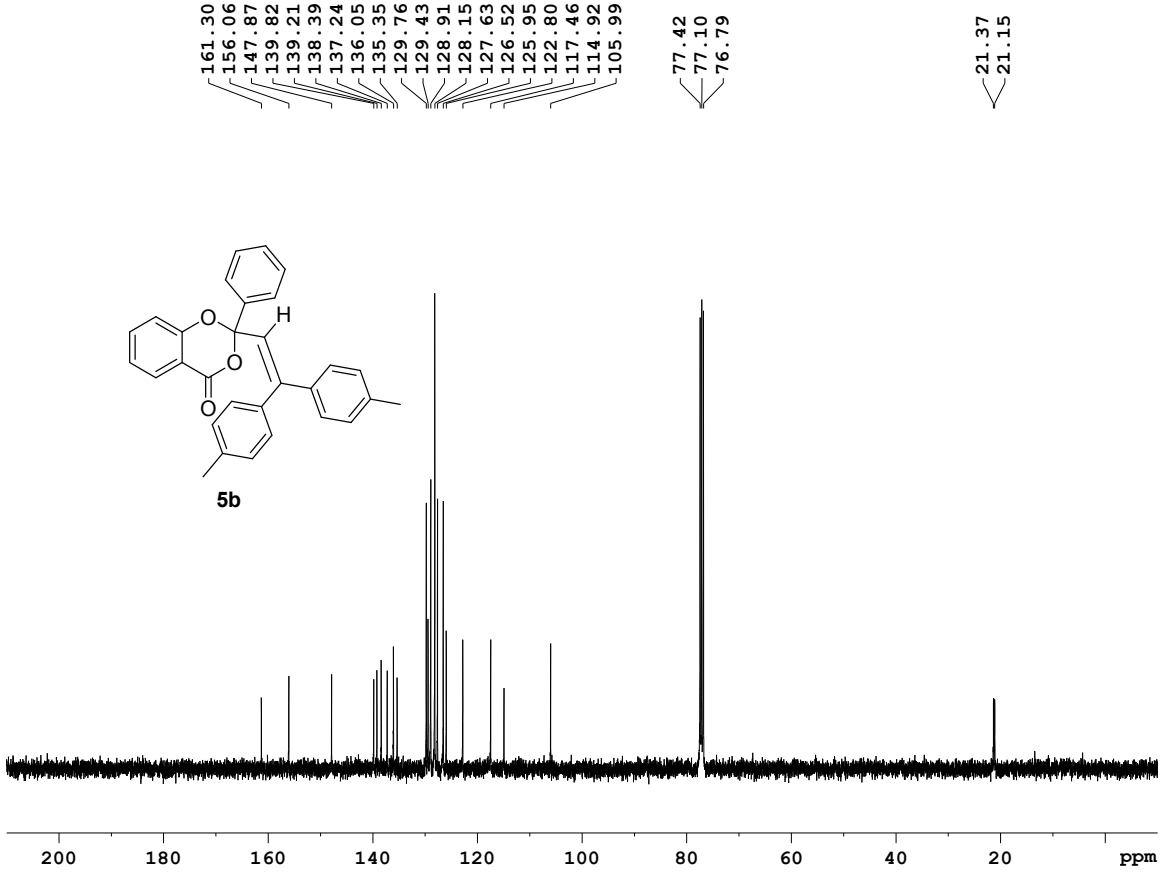

133.67
131.77
130.32
130.12
128.33
128.30
128.28
127.80
127.77
127.70
127.63
126.70
114.23
68.07
29.02
28.25
22.61
14.24
O
H
S
O
O
3k
200
180
160
140
120
100
80
60
40
20
ppm

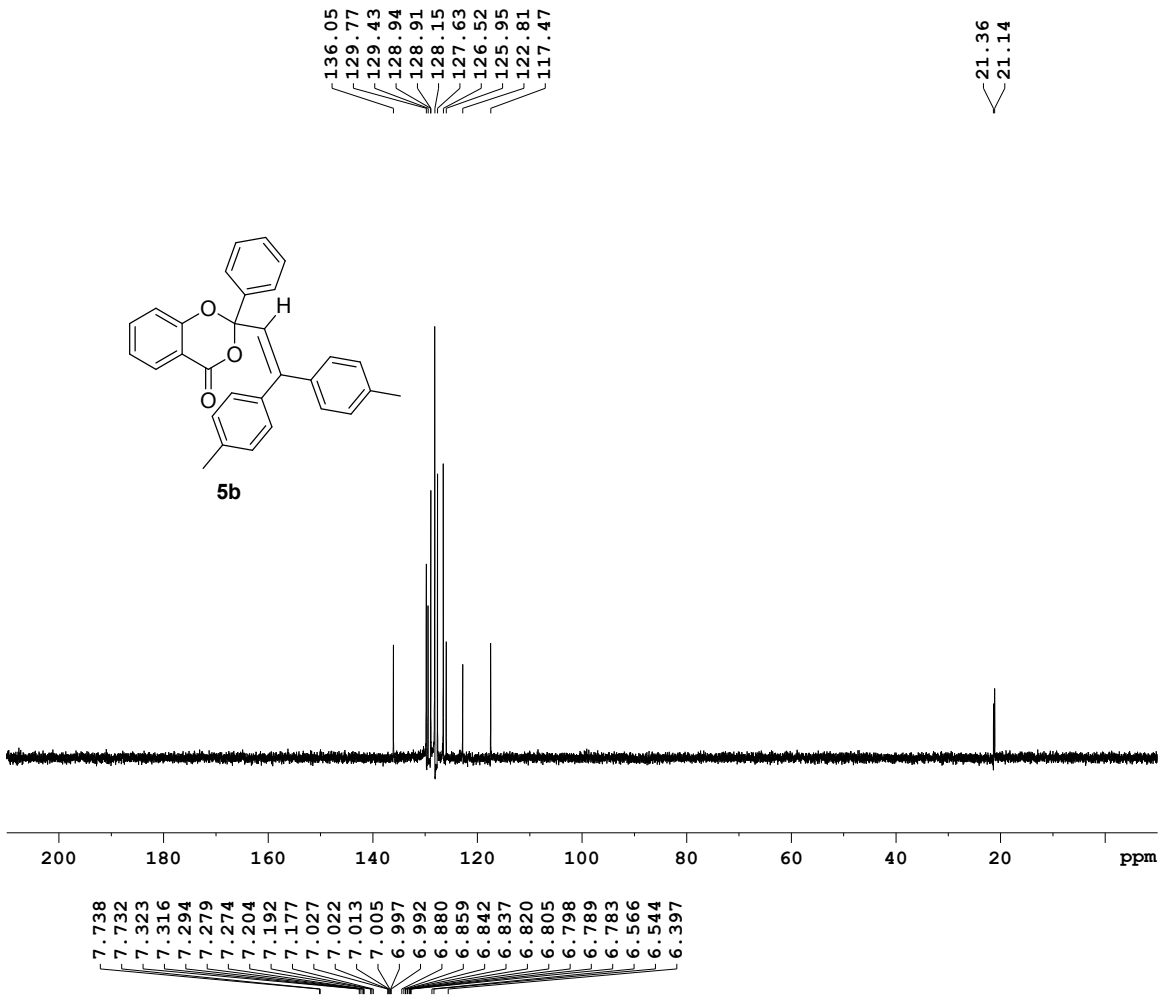

7.931
7.928
7.912
7.909
7.518
7.514
7.504
7.495
7.475
7.457
7.453
7.364
7.345
7.339
7.324
7.319
7.310
7.305
7.300
7.285
7.281
7.263
7.206
7.202
7.195
7.188
7.183
7.099
7.080
7.061
6.996
6.979
6.678
6.657
6.611
O
H
O
O
5a
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
3.31
9.41
2.13
1.08
2.00
1.00
1.00

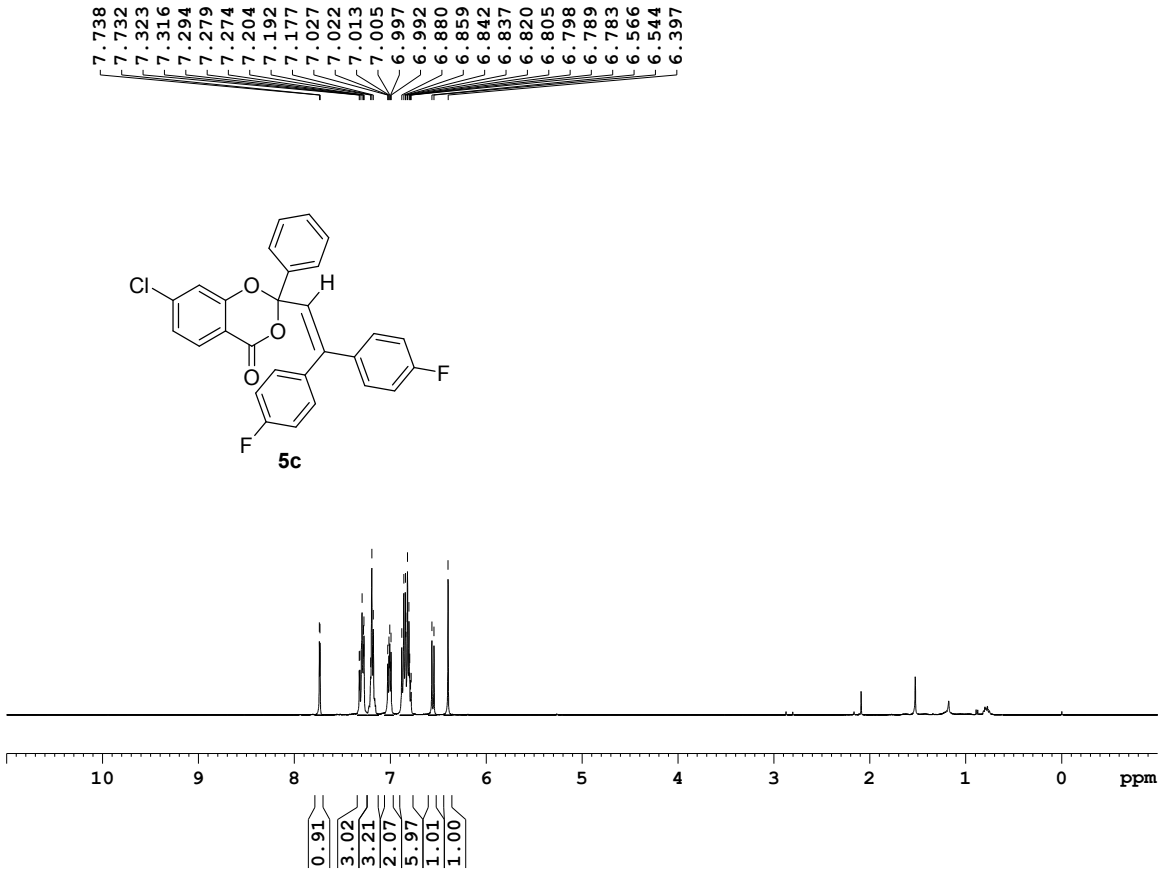

161.17
155.97
147.71
141.73
139.65
138.18
136.17
129.83
129.49
129.01
128.45
128.27
128.25
127.68
127.61
127.54
127.04
126.47
122.88
117.41
114.82
105.80
77.45
77.13
76.81
O
H
O
O
5a
200
180
160
140
120
100
80
60
40
20
ppm

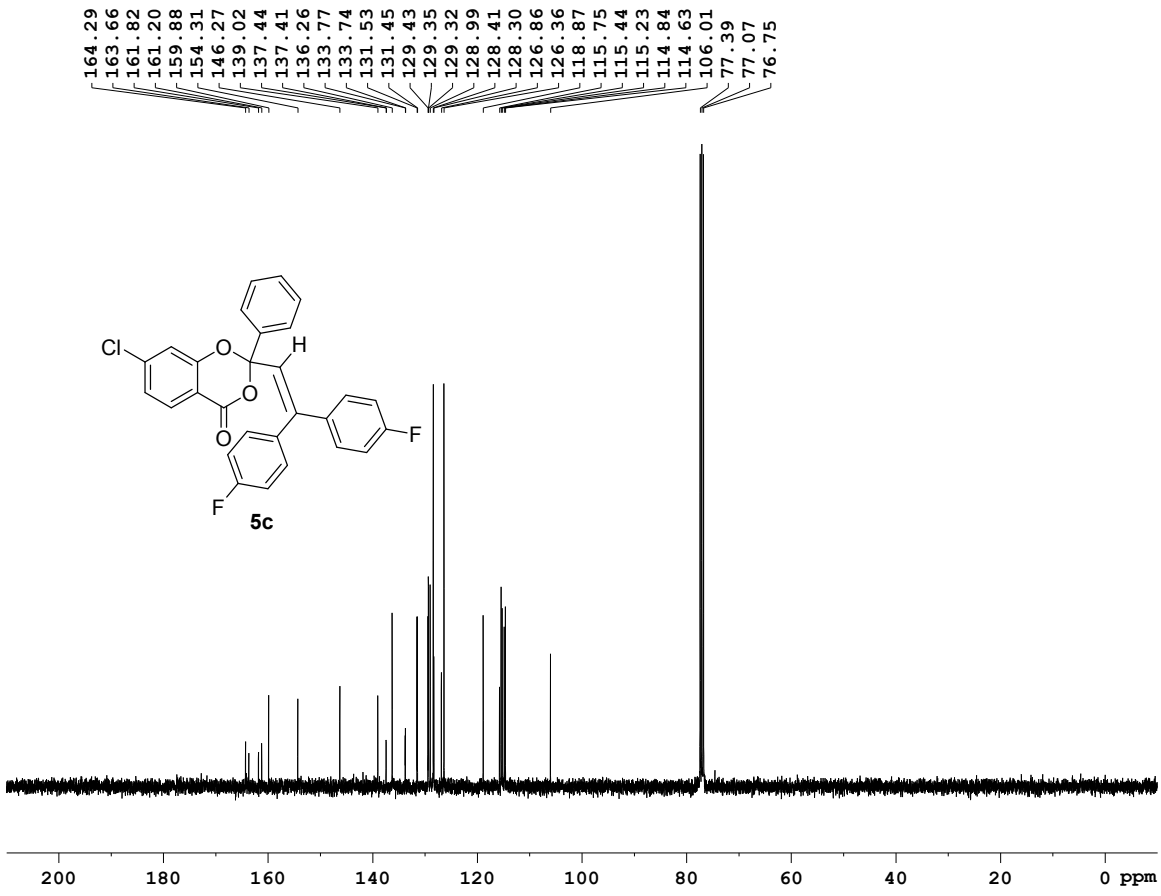

136.18
129.84
129.49
129.01
128.46
128.28
128.26
127.68
127.62
127.54
127.03
126.47
122.89
117.41
O
H
O
O
5a
200
180
160
140
120
100
80
60
40
20
ppm

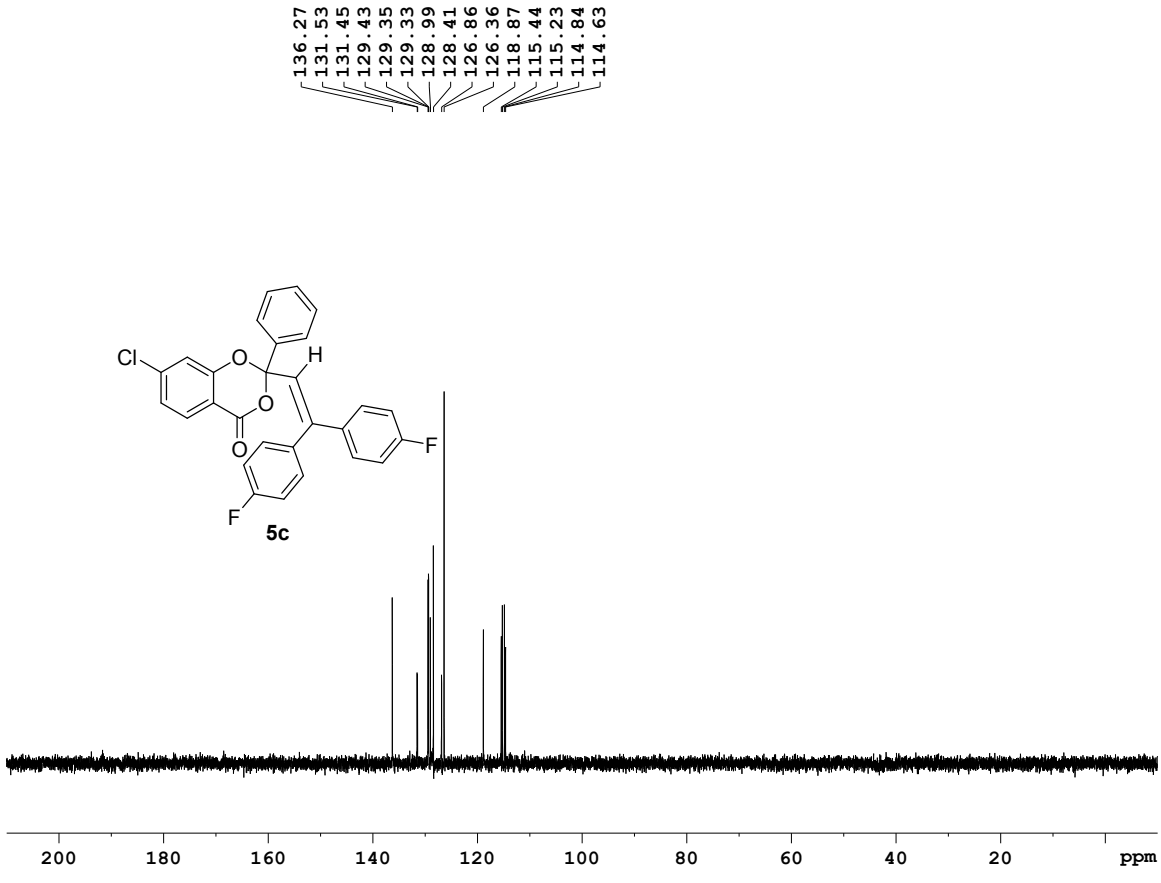

7.868
7.864
7.848
7.844
7.465
7.461
7.452
7.448
7.441
7.436
7.422
7.420
7.401
7.397
7.277
7.274
7.266
7.262
7.252
7.248
7.046
7.043
7.038
7.024
7.017
7.005
6.998
6.984
6.778
6.758
6.612
6.591
6.471
2.353
2.289
1.602
0.000
5b
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
3.21
3.29
6.85
1.86
1.04
0.92
6.00

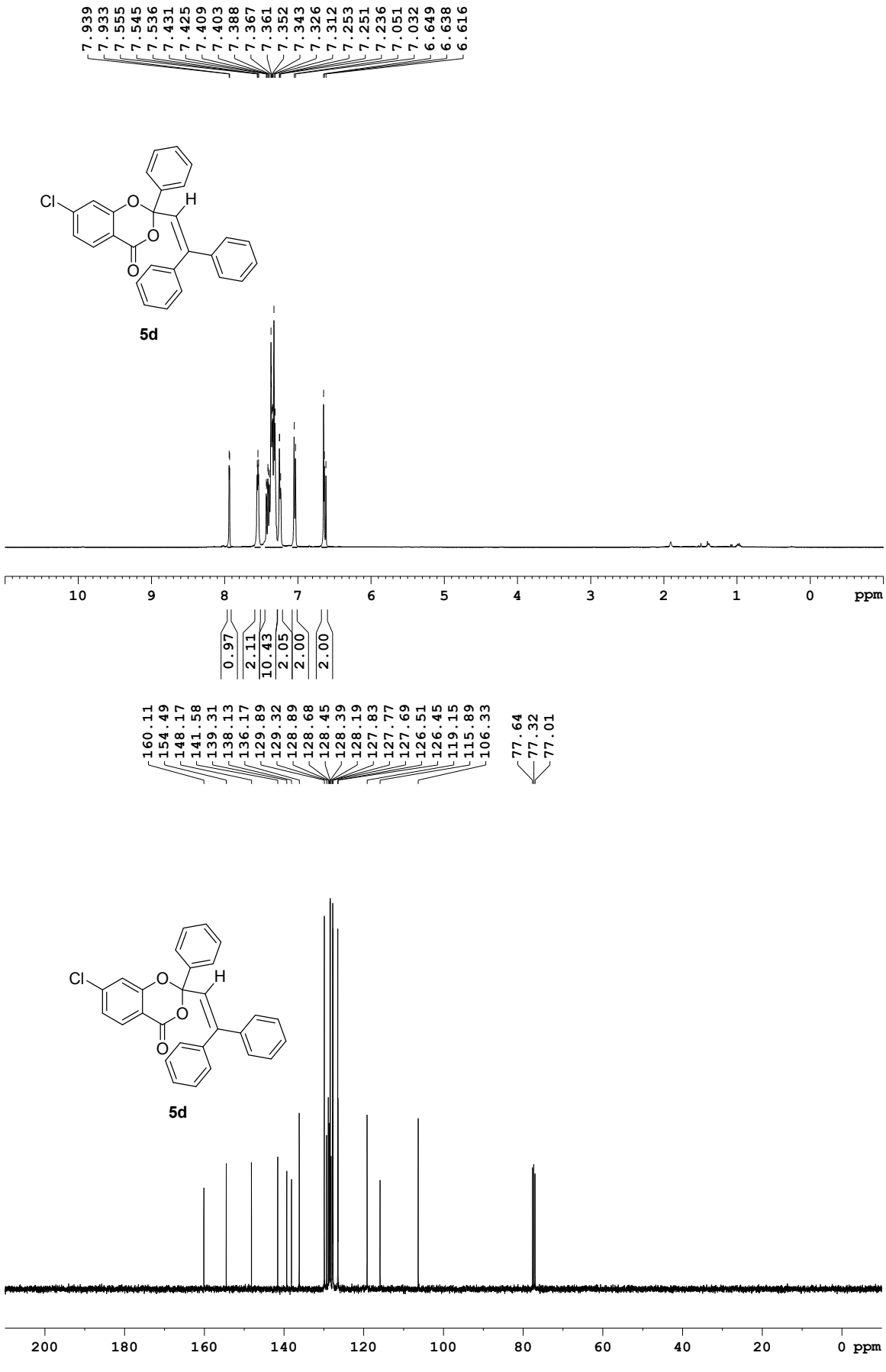

161.30
156.06
147.87
139.82
139.21
138.39
137.24
136.05
135.35
129.76
129.43
128.91
128.15
127.63
126.52
125.95
122.80
117.46
114.92
105.99
77.42
77.10
76.79
21.37
21.15
5b
200
180
160
140
120
100
80
60
40
20
ppm

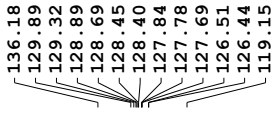

136.05
129.77
129.43
128.94
128.91
128.15
127.63
126.52
125.95
122.81
117.47
21.36
21.14
O
H
O
O
5b
200
180
160
140
120
100
80
60
40
20
ppm

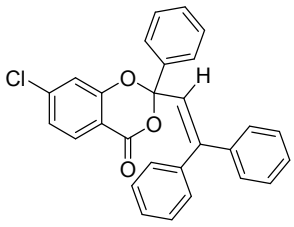

7.738
7.732
7.323
7.316
7.294
7.279
7.274
7.204
7.192
7.177
7.027
7.022
7.013
7.005
6.997
6.992
6.880
6.859
6.842
6.837
6.820
6.805
6.798
6.789
6.783
6.566
6.544
6.397
Cl
O
H
O
O
F
F
5c
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
3.02
3.21
2.07
5.97
1.01
1.00


164.29
163.66
161.82
161.20
159.88
154.31
146.27
139.02
137.44
137.41
136.26
133.77
133.74
131.53
131.45
129.43
129.35
129.32
128.99
128.41
128.30
126.86
126.36
118.87
115.75
115.44
115.23
114.84
114.63
106.01
77.39
77.07
76.75
Cl
O
H
O
O
F
F
5c
200
180
160
140
120
100
80
60
40
20
0 ppm

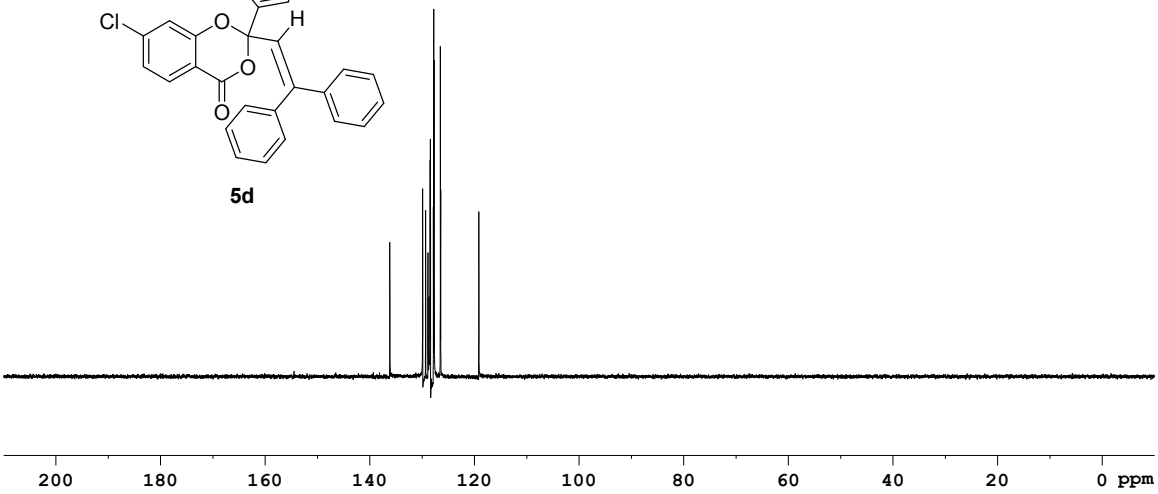

136.27
131.53
131.45
129.43
129.35
129.33
128.99
128.41
126.86
126.36
118.87
115.44
115.23
114.84
114.63
Cl
O
H
O
O
F
F
5c
200
180
160
140
120
100
80
60
40
20
ppm

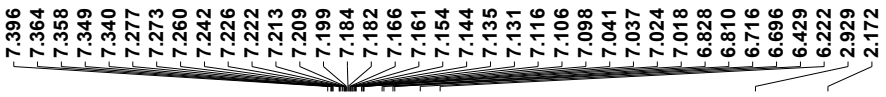

7.939
7.933
7.555
7.545
7.536
7.431
7.425
7.409
7.403
7.388
7.367
7.361
7.352
7.343
7.326
7.312
7.253
7.251
7.236
7.051
7.032
6.649
6.638
6.616
Cl
O
H
O
O
5d
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
2.11
10.43
2.05
2.00
2.00
160.11
154.49
148.17
141.58
139.31
138.13
136.17
129.89
129.32
128.89
128.68
128.45
128.39
128.19
127.83
127.77
127.69
126.51
126.45
119.15
115.89
106.33
77.64
77.32
77.01
Cl
O
H
O
O
5d
200
180
160
140
120
100
80
60
40
20
0 ppm

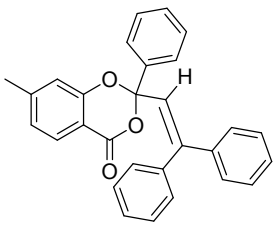

136.18
129.89
129.32
128.89
128.69
128.45
128.40
127.84
127.78
127.69
126.51
126.44
119.15


Cl
O
H
O
O

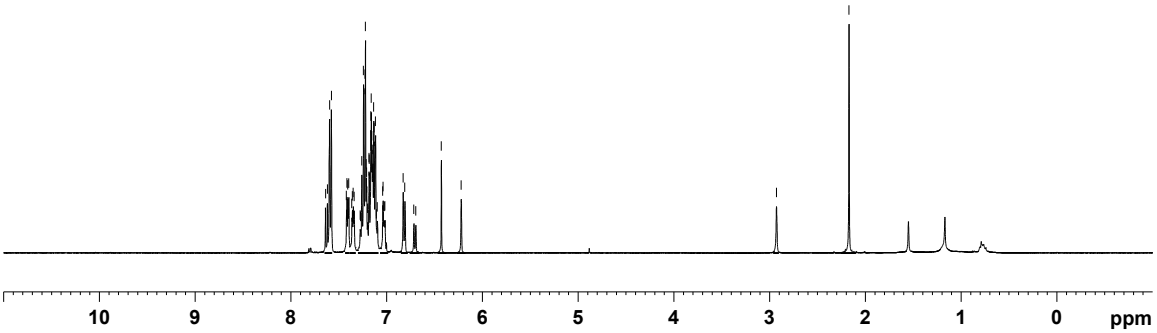
5d

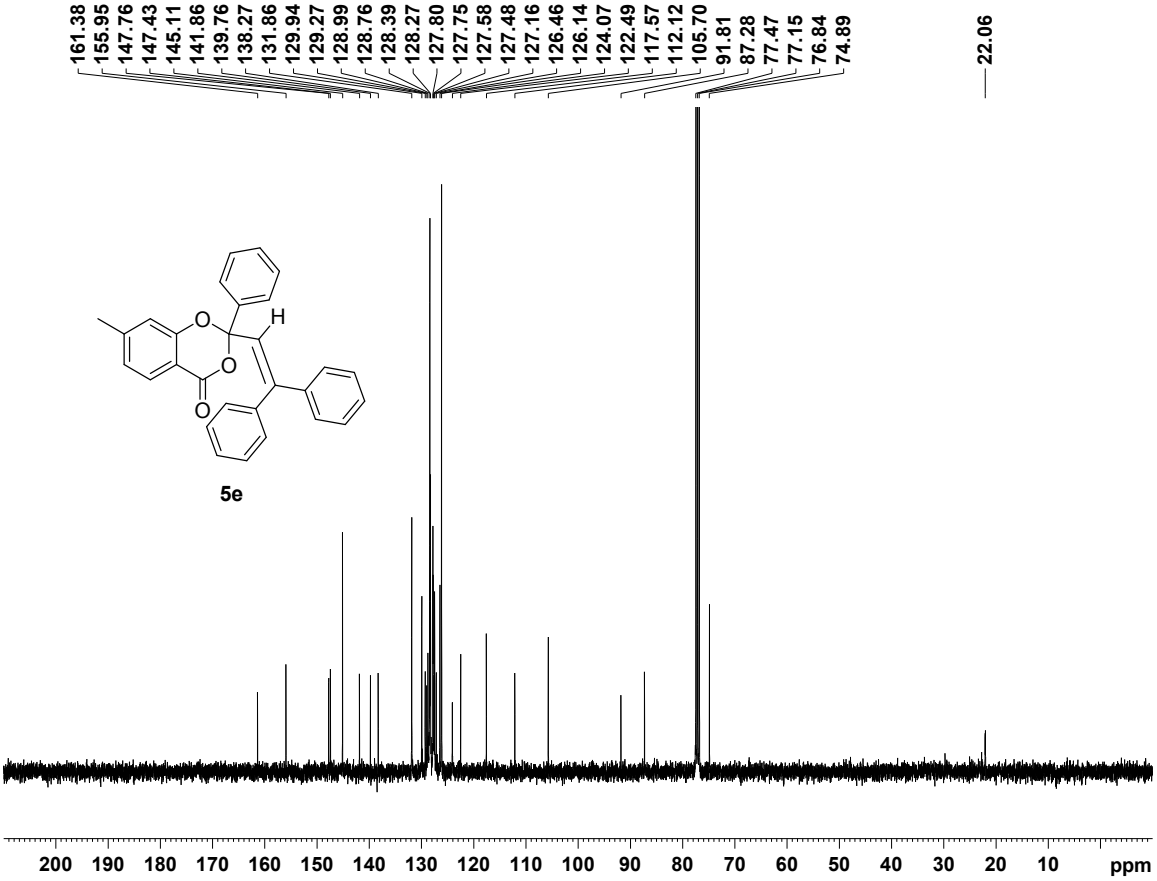

200
180
160
140
120
100
80
60
40
20
0 ppm

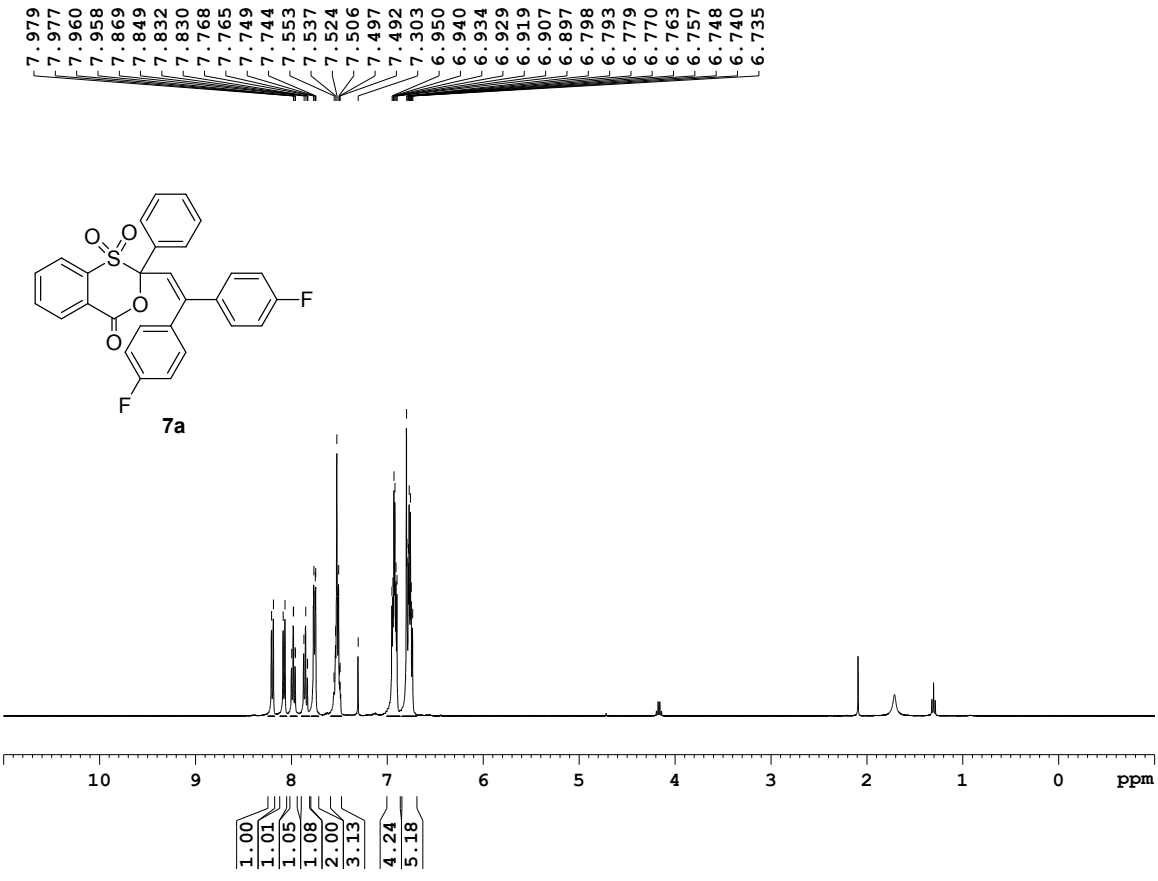

7.396
7.364
7.358
7.349
7.340
7.277
7.273
7.260
7.242
7.226
7.222
7.213
7.209
7.199
7.184
7.182
7.166
7.161
7.154
7.144
7.135
7.131
7.116
7.106
7.098
7.041
7.037
7.024
7.018
6.828
6.810
6.716
6.696
6.429
6.222
2.929
2.172

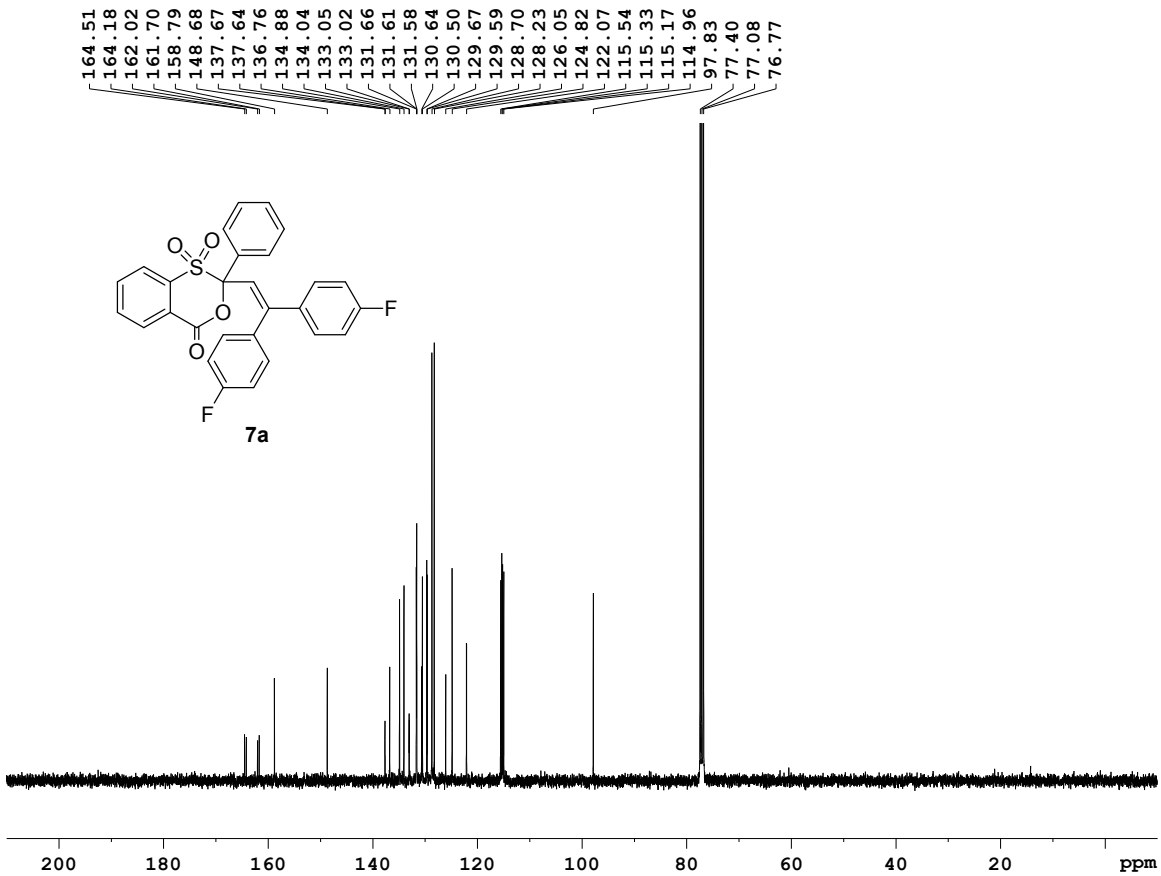

O
H
O
O

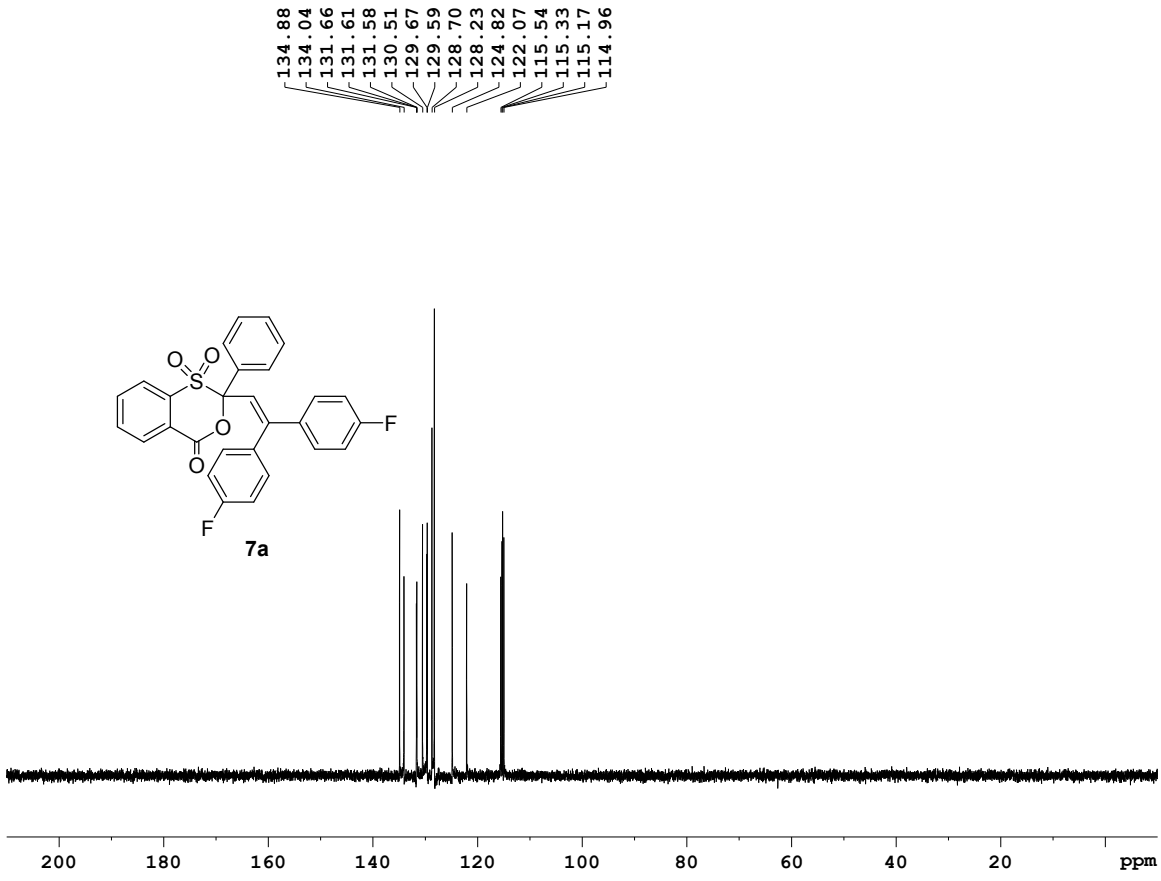
5e


10
9
8
7
6
5
4
3
2
1
0
ppm


161.38
155.95
147.76
147.43
145.11
141.86
139.76
138.27
131.86
129.94
129.27
128.99
128.76
128.39
128.27
127.80
127.75
127.58
127.48
127.16
126.46
126.14
124.07
122.49
117.57
112.12
105.70
91.81
87.28
77.47
77.15
76.84
74.89
22.06
O
H
O
O
5e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.979
7.977
7.960
7.958
7.869
7.849
7.832
7.830
7.768
7.765
7.749
7.744
7.553
7.537
7.524
7.506
7.497
7.492
7.303
6.950
6.940
6.934
6.929
6.919
6.907
6.897
6.798
6.793
6.779
6.770
6.763
6.757
6.748
6.740
6.735
O
O
S
O
O
O
F
F
7a
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.01
1.05
1.08
2.00
3.13
4.24
5.18


164.51
164.18
162.02
161.70
158.79
148.68
137.67
137.64
136.76
134.88
134.04
133.05
133.02
131.66
131.61
131.58
130.64
130.50
129.67
129.59
128.70
128.23
126.05
124.82
122.07
115.54
115.33
115.17
114.96
97.83
77.40
77.08
76.77
O
O
S
O
O
F
F
7a
200
180
160
140
120
100
80
60
40
20
ppm

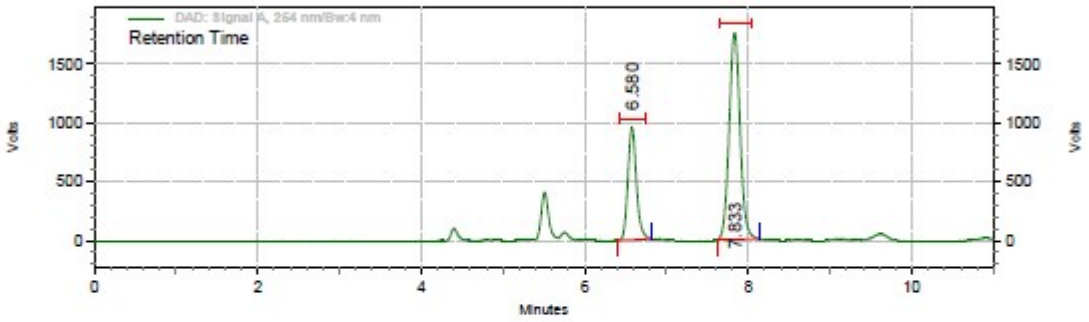

134.88
134.04
131.66
131.61
131.58
130.51
129.67
129.59
128.70
128.23
124.82
122.07
115.54
115.33
115.17
114.96
O
O
S
O
O
F
F
7a
200
180
160
140
120
100
80
60
40
20
ppm

7. HPLC chromatograms for the preparation of 1,3-benzodioxin-4-one (5a)

Reaction of propargyl alcohol **2a** and salicylic acid **4a without controlled addition** was followed by HPLC.

Area % Report

Data File: D:\Ezchrom\hplc data\mmv_141_cr_0.4ml per hr2019_abs_100ACN.met.rslt\323.dat
Method: D:\Ezchrom\Method\2020_mmv_141 crude_direct_100acn.met
Acquired: 10-Dec-20 1:19:40 PM (GMT +05:30)
Printed: 10-Dec-20 4:44:48 PM (GMT +05:30)



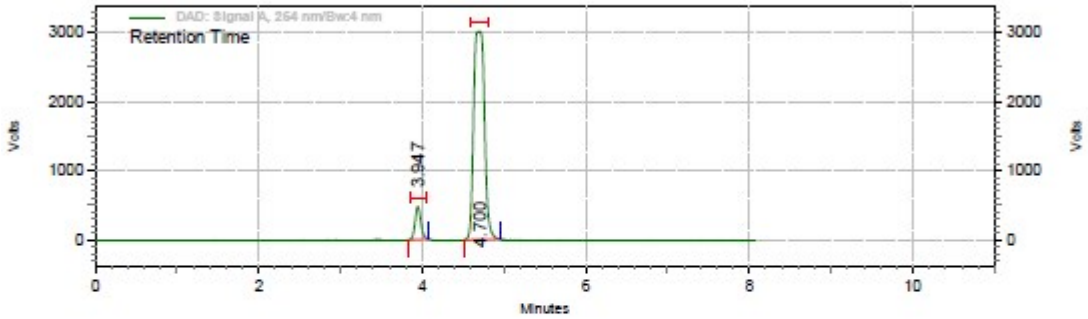
DAD: Signal A, 254 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %	Name
6.580	14545936	29.93	1993452	35.15	**chalcone**
7.833	34057275	70.07	3678303	64.85	**benzodioxinone**
Totals	48603211	100.00	5671755	100.00	

Controlled addition (**1 mL/h**) of propargyl alcohol **2a** into salicylic acid **4a**:

Area % Report

Data File: D:\Ezchrom\hplc data\mmv-141_crude2020_apr_100_ACN.met.rslt\312.dat
Method: D:\Ezchrom\Method\2020_mmv_141_crude100acn.met
Acquired: 07-Dec-20 4:19:15 PM (GMT +05:30)
Printed: 07-Dec-20 6:17:45 PM (GMT +05:30)



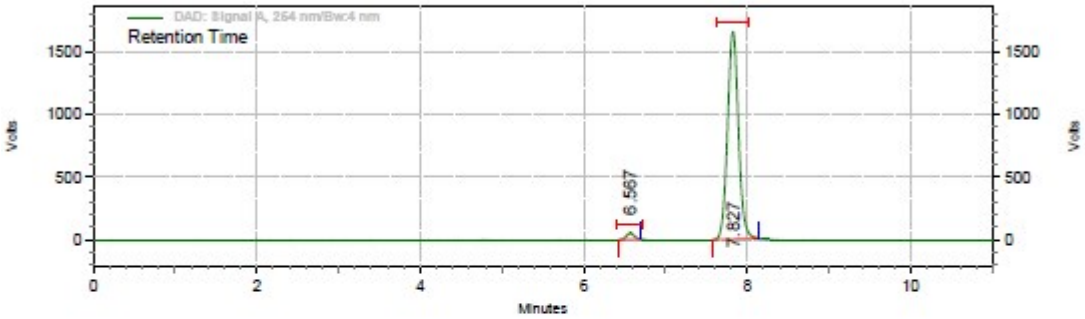
DAD: Signal A, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %	Name
3.947	4897502	7.76	997646	13.65	**chalcone**
4.700	58216675	92.24	6311781	86.35	**benzodioxinone**
Totals	63114177	100.00	7309427	100.00	

Controlled addition (**0.4 mL/h**) of propargyl alcohol **2a** into salicylic acid **4a**:

Area % Report

Data File: D:\Ezchrom\hplc data\mmv_141_cr_0.4ml_10 h2019_abs_100ACN.met.rslt\324.dat
Method: D:\Ezchrom\Method\2020_mmv_141 crude_0.4ml per hr sl add_100acn.met
Acquired: 10-Dec-20 1:34:27 PM (GMT +05:30)
Printed: 10-Dec-20 4:53:16 PM (GMT +05:30)



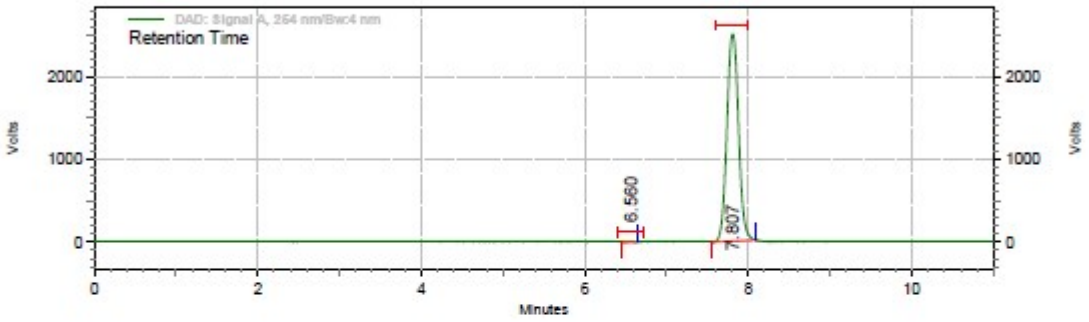
DAD: Signal A, 254 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %	Name
6.567	698433	2.12	105118	2.93	**pa chalcone_100acn_0.4ml/hr**
7.827	32195877	97.88	3483263	97.07	**benzodioxinone_100acn_0.4ml/hr**
Totals	32894310	100.00	3588381	100.00	

Controlled addition (**0.2 mL/h**) of propargyl alcohol **2a** into salicylic acid **4a**:

Area % Report

Data File: D:\Ezchrom\hplc data\mmv_141_crude_100acn_0.6ml per min in hplc2019_abs_100ACN.met.rslt\332.dat
Method: D:\Ezchrom\Method\2019_abs_100ACN.met
Acquired: 12-Dec-20 6:13:50 PM (GMT +05:30)
Printed: 12-Dec-20 7:12:57 PM (GMT +05:30)



DAD: Signal A, 254 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %	Name
6.560	144965	0.28	23719	0.45	**mpa chalcone_0.2ml per hr for 10 h(slow add)**
7.807	51643926	99.72	5246478	99.55	**benzodioxinone_0.2ml per hr for 10h(slow add)**
Totals	51788891	100.00	5270197	100.00	