Click synthesis of novel dendronized curcumin and analogs. Strengthening of physicochemical properties toward biological applications.

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Supporting Information

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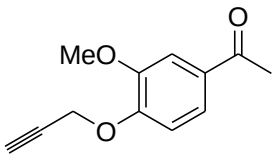
1. General

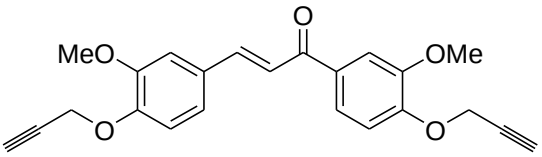
Commercially available reagents were used as received. Anhydrous solvents were obtained by distillation under the described conditions.[1] Column chromatography was carried out with Merck Silica Gel (0.040-0.063 mm). TLC was performed with Merck DC-F254 plates employing UV light or iodine vapor for visualization. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA). The spectra were recorded over the sample holder in the range of wavelengths of 400–4000 cm−1. NMR spectra were obtained with Bruker Avance 400 MHz, in $CDCl_3$ or DMSO-d6. Chemical shifts (δ) and *J* couplings are reported in ppm and Hz, respectively. Low resolution mass spectra were obtained with a JEOL The AccuTOF: JMS-T100LC, Ionization Mode: DART+. MALDI-TOF mass spectra were obtained with a Bruker microflex®, 2,5-dihydroxybenzoic acid was used as matrix in a 2/5 relation (Sample/matrix). Absorbance measurements was determined in a Shimadzu UV-1800 spectrometer, using quartz cuvettes. The wavelength range was 190-600 nm (0.5 nm step). Calibration curves were plotted with dilution of stock solution in the range of 5 to 70 µM. Emission experiments were carried out in a Horiba FluoroLog spectrophotometer FL3-22, the wavelength range was 300-700 nm (5 nm step).

2. Methodologies and Characterization.

Compounds **9**[2], **11a**[3], **A**[4] and **B**[4] were synthesized as reported in the literature.

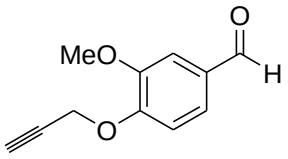


1-(3-methoxy-4-(prop-2-yn-1-yloxy)phenyl)ethan-1-one, compound **2**. In a 50 mL round bottom flask equipped with magnetically stirrer and conditioned under nitrogen, 2.19 g (13.15 mmol) of acetovanillone (4'-hydroxy-3'-methoxyacetophenone) was dissolved in 20 mL of DMF and cooled with an ice bath. The mixture was stirred in this bath for 30 minutes, then 0.63 g (15.77 mmol) of sodium hydride (NaH, 60 % dispersion in mineral oil) was added portion wise. This reaction was stirred at low temperature for 30 minutes. Finally, 2.35 g (1.76 mL, 15.77 mmol) of propargyl bromide (80 wt.% in toluene) was added drop wise, the reaction mixture was allowed to reach room temperature and stirred for 48 h. To work-up the reaction was poured into ice-water (100 mL) and the product extracted with Et_2O (3 X 50 mL). Solvent was removed by vacuum distillation and the product purified by column chromatography with silica gel (Hex-EtOAc, 7:3) or by crystallization in MeOH. The product was obtained as a pale-yellow solid in 97 % yield (2.6045 g, 12.75 mmol). **^{1}H-NMR (400 MHz, $CDCl_3$, δ = ppm)**: 7.58 (dd, *J* = 2.0 Hz, 8.3 Hz, 1H); 7.55 (d, *J* = 2.0 Hz, 1H); 7.06 (d, *J* = 8.3 Hz, 1H); 4.85 (d, *J* = 2.4 Hz, 2H); 3.94 (s, 3H); 2.58 (s, 3H); 2.56 (t, *J* = 2.4 Hz, 1H). **^{13}C-NMR (APT, 100 MHz, CDCl3, δ = ppm)**: 26.24 (*CH_3*), 55.98 (*CH_3*), 56.53 (*CH_2*), 76.47 (≡*CH*), 77.72 (*C*≡), 110.54 (*CH*), 112.23 (*CH*), 122.81 (*CH*), 131.39 (*C*), 149.45 (*C*), 150.94 (*C*), 196.75 (*C*=*O*). **FT-IR-ATR (cm^{-1})**: 3244.3, 3076.9, 3007.4, 2974.7, 2942.2, 2126.0, 1670.2, 1586.8, 1508.2, 1467.3, 1453.8, 1414.5, 1269.0, 1220.4, 1179.8, 1151.3, 1025.6, 1010.0, 979.0, 882.5, 801.9, 642.1. **MS-DART+ (M+1, low resolution):** found = 205.

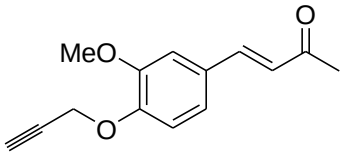


(*E*)-1,3-bis(3-methoxy-4-(prop-2-yn-1-yloxy) phenyl)prop-2-en-1-one, compound **3**. In a 25 mL round bottom flask equipped with magnetically stirrer, 0.4 g (1.96 mmol) of ketone **2** and 0.38 g (2.0 mmol) of aldehyde **5** were dissolved in 10 mL of EtOH, then 11 mg (0.196 mmol) of KOH was added and the reaction mixture stirred for 96 hour until no change was detected by TLC. Solvent was removed by vacuum distillation and the residue dissolved in EtOAc. The organic layer was washed one time with 0.1 M HCl and twice with water. Organic layer was dried with anhydrous sodium sulfate and the product purified by column chromatography in silica gel (Hex-EtOAc, 9:1 to 6:4) to achieve 0.332 g (0.88 mmol, 45 %) of the desired product as a light-yellow solid. **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 7.93 (dd, *J* = 1.8 Hz, 8.5 Hz, 1H); 7.86 (d, *J* = 15.5 Hz, 1H); 7.69 (d, *J* = 15.5 Hz, 1H); 7.62 (d, *J* = 1.8 Hz, 1H); 7.56 (d, *J* = 1.7 Hz, 1H); 7.43 (dd, *J* = 1.7 Hz, 8.4 Hz, 1H); 7.19 (d, *J* = 8.5 Hz, 1H); 7.10 (d, *J* = 8.4 Hz, 1H); 4.95 (d, *J* = 2.2 Hz, 2H); 4.88 (d, *J* = 2.2 Hz, 2H); 3.88 (s, 6H); 3.64 (t, *J* = 2.2 Hz, 1H); 3.61 (t, *J* = 2.2 Hz, 1H). **^{13}C-NMR (APT, 100 MHz, DMSO-d6, δ = ppm)**: 56.13 (*CH_3*), 56.29 (*CH_3*), 56.46 (*CH_2*), 56.54 (*CH_2*), 79.05 (≡*CH*), 79.27 (≡*CH*), 87.32 (*C*≡), 87.94 (*C*≡), 111.50 (*CH*), 111.93 (*CH*), 113.06 (*CH*), 114.03 (*CH*), 120.53 (*CH*), 123.34 (*CH*), 123.53 (*CH*), 129.04 (*C*), 131.97 (*C*), 143.95 (*CH*), 149.19 (*C*), 149.57 (*C*), 149.80

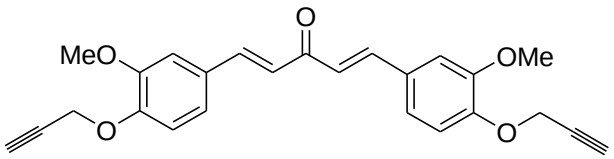
(*C*), 151.19 (*C*), 187.84 (*C*=*O*). **FT-IR-ATR (cm^{-1})**: 3245.7, 2917.0, 1742.1, 1650.3, 1574.6, 1505.7, 1417.4, 1254.3, 1134.6, 972.2, 913.4, 835.7, 787.7, 686.1, 606.7, 546.8. **MS-DART+ (M+1, low resolution):** found = 377.



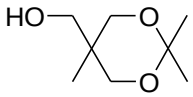
3-methoxy-4-(prop-2-yn-1-yloxy)benzaldehyde, compound **5**. In a 50 mL round bottom flask equipped with magnetically stirrer and conditioned under nitrogen, 2.0 g (13.15 mmol) of vanillin (4-hydroxy-3-methoxybenzaldehyde) was dissolved in 20 mL of DMF and cooled with an ice bath. The mixture was stirred in this bath for 30 minutes, then 0.63 g (15.77 mmol) of sodium hydride (NaH, 60 % dispersion in mineral oil) was added portion wise. This reaction was stirred at low temperature for 30 minutes. Finally, 2.35 g (1.76 mL, 15.77 mmol) of propargyl bromide (80 wt.% in toluene) was added drop wise, the reaction mixture was allowed to reach room temperature and stirred for 48 h. To work-up the reaction was poured into ice-water (100 mL) and the product extracted with Et_2O (3 X 50 mL). Solvent was removed by vacuum distillation and the product purified by column chromatography with silica gel (Hex-EtOAc, 7:3) or by crystallization in MeOH. The product was obtained as a pale-yellow solid in 96 % yield (2.3989 g, 12.61 mmol). **^{1}H-NMR (400 MHz, $CDCl_3$, δ = ppm)**: 9.89 (s, 1H, C*H*O); 7.48 (dd, *J* = 1.8 Hz, 8.2 Hz, 1H); 7.45 (d, *J* = 1.8 Hz, 1H); 7.16 (d, *J* = 8.2 Hz, 1H); 4.87 (d, *J* = 2.4 Hz, 2H); 3.96 (s, 3H); 2.58 (t, *J* = 2.4 Hz, 1H). **^{13}C-NMR (APT, 100 MHz, CDCl3, δ = ppm)**: 56.02 (*CH_3*), 56.60 (*CH_2*), 76.70 (≡*CH*), 77.48 (*C*≡), 109.49 (*CH*), 112.61 (*CH*), 126.23 (*CH*), 130.92 (*C*), 150.02 (*C*), 152.11 (*C*), 190.87 (*CHO*). **FT-IR-ATR (cm^{-1})**: 3247.7, 2922.0, 2851.8, 2114.0, 1687.1, 1668.1, 1586.7, 1506.0, 1469.3, 1451.0, 1431.1, 1406.3, 1379.3, 1221.0, 1198.8, 1157.2, 1124.7, 1033.1, 1002.2, 858.8, 804.6, 690.6. **MS-DART+ (M+1, low resolution):** found = 191.



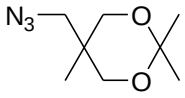
(E)-4-(3-methoxy-4-(prop-2-yn-1-yloxy)phenyl)but-3-en-2-one, compound **6**. In a 25 mL round bottom flask equipped with magnetically stirrer, 1.0 g (5.26 mmol) of aldehyde **5** were dissolved in 10 mL of MeOH, then 3.05 g (3.86 mL, 52.6 mmol) of acetone and 30 mg (0.526 mmol) of KOH was added and the reaction mixture stirred for 48 hours until no change was detected by TLC. Solvent was removed by vacuum distillation and the residue dissolved in EtOAc. The organic layer was washed one time with 0.1 M HCl and twice with water. Organic layer was dried with anhydrous sodium sulfate and the product purified by column chromatography in silica gel (Hex-EtOAc, 9:1 to 6:4) to achieve 1.09 g (4.73 mmol, 90 %) of the desired product as a light-yellow solid. **^{1}H-NMR (400 MHz, $CDCl_3$, δ = ppm)**: 7.47 (d, *J* = 16.2 Hz, 1H); 7.14 (dd, *J* = 2.0 Hz, 8.3 Hz, 1H); 7.10 (d, *J* = 2.0 Hz, 1H); 7.05 (d, *J* = 8.3 Hz, 1H); 6.63 (d, *J* = 16.2 Hz, 1H); 4.82 (d, *J* = 2.4 Hz, 2H); 3.92 (s, 3H); 2.56 (t, *J* = 2.4 Hz, 1H); 2.39 (s, 3H). **^{13}C-NMR (APT, 100 MHz, CDCl3, δ = ppm)**: 27.41 (*CH_3*), 55.94 (*CH_3*), 56.60 (*CH_2*), 76.31 (≡*CH*), 77.95 (*C*≡), 110.23 (*CH*), 113.68 (*CH*), 122.47 (*CH*), 125.74 (*CH*), 128.49 (*C*), 143.27 (*CH*), 148.99 (*C*), 149.82 (*C*), 198.31 (*C*=*O*). **FT-IR-ATR (cm^{-1})**: 3207.6, 3075.4, 3015.4, 2963.1, 2933.1, 2902.4, 2858.8, 2124.4, 1664,4, 1638.8, 1618.9, 1591.8, 1516.0, 1445.6, 1416.3, 1379.9, 1337.1, 1260.5, 1239.8, 1229.4, 1178.0, 1138.2, 1021.1, 1003.5, 962.9, 937.1, 863.0, 811.0, 701.8. **MS-DART+ (M+1, low resolution):** found = 231.



(1E,4E)-1,5-bis(3-methoxy-4-(prop-2-yn-1-yloxy)phenyl)penta-1,4-dien-3-one, compound **7**. In a 25 mL round bottom flask equipped with magnetically stirrer, 0.2 g (0.87 mmol) of enone **6** and 0.2 g (1.04 mmol) of aldehyde **5** were dissolved in 10 mL of EtOH, then 5 mg (0.09 mmol) of KOH was added and the reaction mixture stirred for 192 hour until no change was detected by TLC. Solvent was removed by vacuum distillation and the residue dissolved in EtOAc. The organic layer was washed one time with 0.1 M HCl and twice with water. Organic layer was dried with anhydrous sodium sulfate and the product purified by column chromatography in silica gel (Hex-EtOAc, 9:1 to 6:4) to achieve 0.1118 g (0.28 mmol, 32 %) of the desired product as a yellow solid. **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 7.71 (d, *J* = 15.9 Hz, 2H); 7.44 (d, *J* = 1.7 Hz, 2H); 7.34 (dd, *J* = 1.7 Hz, 8.4 Hz, 2H); 7.26 (d, *J* = 15.9 Hz, 2H); 7.10 (d, *J* = 8.4 Hz, 2H); 4.87 (d, *J* = 2.4 Hz, 4H); 3.86 (s, 6H); 3.61 (t, *J* = 2.3 Hz, 2H). **^{13}C-NMR (APT, 100 MHz, DMSO-d6, δ = ppm)**: 56.81 (*CH_3*), 56.47 (*CH_2*), 79.06(≡*CH*), 79.47 (≡*C*), 111.47 (*CH*), 114.09 (*CH*), 123.15 (*CH*), 124.70 (*CH*), 128.98 (*C_{ipso}*), 142.70 (*CH*), 149.19 (*C_{ipso}*), 149.82 (*C_{ipso}*), 188.64 (*C*=*O*). **FT-IR-ATR (cm^{-1})**: 3258.9, 1615.0, 1592.9, 1581.6, 1574.4, 1463.8, 1450.7, 1218.7, 975.6, 863.1, 851.2. **MS-DART+ (M+1, low resolution):** found = 403.

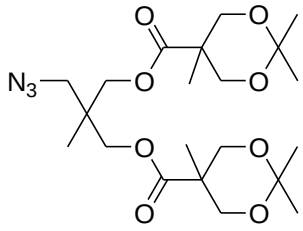


(2,2,5-trimethyl-1,3-dioxan-5yl)methanol, compound **11**. In a 250 mL round bottom flask equipped with magnetically stirrer and conditioned with Nitrogen atmosphere 10 g (82 mmol) of 2-(hydroxymethyl)-2-methylpropane-1,3-diol and 0.1 g (0.52 mmol) of *p*-Toluensulfonic acid were dissolved in 75 mL of dry acetone and stirred at room temperature for 1 h. Then 12. 88 g (15.4 mL ,123.7 mmol) of 2,2-dimethoxypropane was added and the reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with K_2CO_3 (0.4 g, 2.9 mmol). The solvent was removed by distillation and the residue was dissolved in 100 mL of CH_2Cl_2 and washed with distilled water (3 x 50 mL). The product was obtained pure as a clear oil in 90% yield (11.8 g, 73.8 mmol). **^{1}H-NMR (400 MHz, $CDCl_3$, δ = ppm)**: 3.70 (s, 2H); 3.69 (d, *J* = 11.9 Hz, 2H); 3.62 (d, *J* = 11.9 Hz, 2H); 2.21 (br, 1H); 1.45 (s, 3H); 1.40 (s, 3H); 0.84 (s, 3H). **^{13}C-NMR (APT, 100 MHz, CDCl3, δ = ppm)**: 17.58 (*CH_3*), 20.15 (*CH_3*), 27.28 (*CH_3*), 34.74 (*C*), 65. 97 (*CH_2*), 66.35 (*CH_2*), 97.97 (O-*C*-*O*). **FT-IR-ATR (cm^{-1})**: 3418.4, 2990.6, 2939.o, 2868.5, 1453.1, 1370.6, 1265.5, 1205.7, 1151.4, 1082.5, 1035.4, 932.9, 909.9, 826.6, 730.8, 520.4. Characterization is in accordance with the literature.[5]



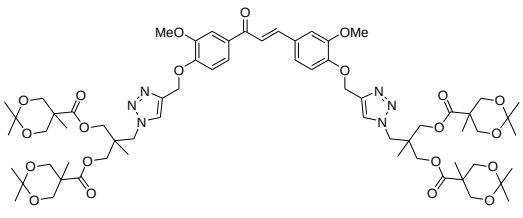
5-(azidomethyl)-2,2,5-trimethyl-1,3-dioxane, compound **12**. In a 50 mL round bottom flask, 2.0 g (12.5 mmol) of cetonide **11** was mixed with 6 mL of pyridine, then a solution of p-toluenesulfonyl chloride (2.38 g, 12.54 mmol) in 3 mL of pyridine was added. The reaction mixture was stirrer at 100° C for 2 h. Reaction was poured into ice-water (200 mL) and extracted with Et_2O (3 X 75 mL). The organic layers were mixed and dried with anhydrous Na_2SO_4 and the solvent was removed by vacuum distillation. This product (2.5 g, 7.99 mmol) was dissolved in 30 mL of DMF-DMSO (9:1) and sodium azide was added (0.57 g, 8.79 mmol). Reaction mixture was stirred at 60° C for 16 h, until no starting material was observed by TLC. The mixture was poured into 100 mL of water and extracted with Et_2O (3 x 75 mL). solvent was removed by distillation and the product was purified by column chromatography on silica gel with Hexane-EtOAc (95:5) as eluent, obtaining 1.33 g (7.2 mmol, 57.6%) of pure product as a clear oil. **^{1}H-NMR (400 MHz, $CDCl_3$, δ = ppm)**: 3.63 (d, *J* = 12.8 Hz, 2H); 3.60 (d, *J* = 12.8 Hz, 2H); 3.54 (s, 2H); 1.45

(s, 3H); 1.42 (s, 3H); 0.84 (s, 3H). **^{13}C-NMR (APT, 100 MHz, CDCl3, δ = ppm)**: 18.04 (*CH_3*), 19.65 (*CH_3*), 27.70 (*CH_3*), 34.43 (*C*), 55.99 (*CH_2*), 66.68 (*CH_2*). Characterization is in accordance with the reported literature.[5]



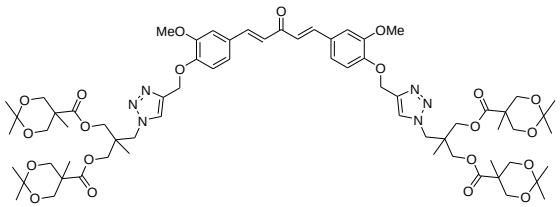
2-(azidomethyl)-2-methylpropane-1,3-diyl bis(2,2,5-trimethyl-1,3-dioxane-5-carboxylate), compound **13**. To a solution of 1.2 g (6.48 mmol) of azide **12** in 30 mL of MeOH, 0.1 g of DOWEX-H^+ resin was added. This mixture was stirred at 40° C for 45 minutes, then it was filtered through a glass porous funnel. The solvent was removed by vacuum distillation and the resulting diol (0.937 g, 6.46 mmol, 99%) was dissolved in 25 mL of dry CH_2Cl_2 and conditioned under nitrogen. To this mixture, 2.36 g (13.57 mmol) of acid **11a**, 1.33 g (4.52 mmol) of DPTS and 0.16 g (1.3 mmol) of DMAP were added. The reaction mixture was stirred at 0° C for 40 minutes, then a solution of 2.93 g (14.21 mmol) of DCC in dry CH_2Cl_2 was added dropwise. The reaction was allowed to reach room temperature and stirred for 48 h. The white precipitate (DCU) was removed by filtration and the solvent removed by vacuum distillation. The residue containing the desired product mixed with DPTS was dissolved in hot EtOAc to remove the DPTS by crystallization. This process was repeated 2 or 3 times before the final purification by column chromatography on silica gel (Hex-EtOAc, 9:1 to 7:3). The product was obtained as a clear oil, 2.54 g (5.56 mmol, 86%). **^{1}H-NMR (400 MHz, $CDCl_3$, δ = ppm)**: 4.20 (d, *J* = 12.0 Hz, 4H); 4.10 (s, 4H); 3.67 (d, *J* = 12.0 Hz, 4H); 3.40 (s, 2H); 1.45 (s, 6H); 1.38 (s, 6H); 1.16 (2, 6H); 1.07 (s, 3H). **^{13}C-NMR (APT, 100 MHz, CDCl3, δ = ppm)**: 17.69 (*CH_3*), 18.47 (*CH_3*), 21.53 (*CH_3*), 25.75 (*CH_3*), 40.03 (*C*), 42.24 (*C*), 55.15 (*CH_2*), 65.96 (*CH_2*), 66.14 (*CH_2*), 98.18 (O-*C*-*O*), 173.78 (*C*=*O*). **FT-IR-ATR (cm^{-1})**: 2939.8, 2875.7, 2102.5, 1732.2, 1197.9, 1151.2, 1120.9, 1077.9, 1039.7, 934.4, 828.7, 519.8. **MS-DART+ (M+1, low resolution):** found = 458.

General method for the Copper catalyzed Alkyne-Azide cycloaddition (CuAAC). In a 50 mL round bottom flask equipped with magnetic stirrer and conditioned under argon, 1.0 equivalents of the corresponding alkynes **3**, **7** or **9**, and 2.3 equivalents of the azide dendron **13** were dissolved in 20 mL of DMSO. Then 0.1 equivalents of $CuSO_4 \cdot 5H_2O$ was added and the mixture was stirred at 40° C for 20 minutes. Then 0.3 equivalents of Sodium Ascorbate dissolved in 4 mL of distilled water were added dropwise. The reaction mixture was stirred at 40° C for 24 h until no starting materials were detected by TLC. The reaction was poured into 60 mL of water and extracted with EtOAc (Product is not soluble in Et_2O). The organic layers were mixed and dried with Na_2SO_4, the solvent was removed by vacuum distillation and the product purified by column chromatography in silica gel with Hex-EtOAc (7:3 to 1:1).

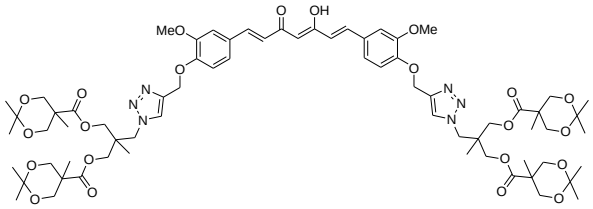


Compound **14**. General method for CuAAC chemistry was followed with 0.18 g (0.478 mmol) of alkyne **3**, 0.512 g (1.12 mmol) of azide **13**, 12.0 mg (0.048 mmol) of $CuSO_4 \cdot 5H_2O$ and 28.4 mg (0.143 mmol) of sodium ascorbate to obtain 0.413 g (0.32 mmol, 67 %) of the desired product as a pale yellow solid. **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 8.20 (s, 1H); 8.18 (s, 1H); 7.92 (dd, *J* = 2.0 Hz, 8.5 Hz, 1H); 7.84 (d, *J* = 15.4 Hz, 1H); 7.68 (d, *J* = 15.4 Hz, 1H); 7.61 (d, *J* = 2.0 Hz, 1H); 7.54 (d, *J* = 1.9 Hz, 1H); 7.41 (dd, *J* =

1.9 Hz, 8.5 Hz, 1H); 7.32 (d, *J* = 8.5 Hz, 1H); 7.21 (d, *J* = 8.4 Hz, 1H); 5.28 (s, 2H); 5.22 (s,2H); 4.51 (s, 4H); 4.08-3.99 (m, 16H); 3.85 (s, 3H); 3.84 (s, 3H); 3.65 (d, *J* = 11.6 Hz, 8H); 1.37 (s, 12H); 1.23 (s, 12H); 1.05 (s, 6H); 1.04 (s, 6H); 0.95 (s, 6H). **^{13}C-NMR (APT, 100 MHz, DMSO-d6, δ = ppm)**: 17.66 (*CH₃*), 18.31 (*CH₃*), 21.57 (*CH₃*), 26.64 (*CH₃*), 39.90 (*CH₂*), 42.16 (*CH₂*), 52.94 (*CH₂*), 56.06, 56.22, 62.10 (*CH₂*), 65.65 (*CH₂*), 65.85 (*CH₂*), 97.95 (*C, O-C-O*), 111.45 (*CH*), 111.84 (*CH*), 112.91 (*CH*), 113.91 (*CH*), 120.28 (*CH*), 122.69 (*CH*), 123.57 (*CH*), 123.79 (*CH*), 128.70 (*C*), 131.66 (*C*), 142.53 (*C*), 142.72 (*C*), 143.95 (*CH*), 149.51 (*C*), 149.77 (*C*), 150.15 (*C*), 152. 17 (*C*), 153.45 (*CH*), 173.91 (*C=O,*), 187.74 (*C=O*). **FT-IR-ATR (cm^{-1})**:1732.5, 1593.7, 1506.2, 1371.9, 1257.4, 1148.3, 1077.6, 997.8, 826.9.



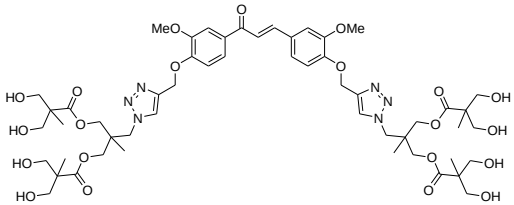
Compound **15**. General method for CuAAC chemistry was followed 70 mg (0.174 mmol) of alkyne **7**, 0.183 g (0.40 mmol) of azide **13**, 4.3 mg (0.017 mmol) of $CuSO_4 \cdot 5H_2O$ and 10.3 mg (0.052 mmol) of sodium ascorbate to obtain 0.1191 g (0.09 mmol, 54 %) of the desired product as a pale yellow solid **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 8.18 (s, 2H); 7.70 (d, *J* = 15.8 Hz, 2H); 7.42 (d, *J* = 1.8 Hz, 2H); 7.32 (dd, *J* = 8.5 Hz, 1.8 Hz, 2H); 7.24 (d, *J* = 15.8 Hz, 2H); 7.22 (d, *J* = 8.5 Hz, 2H); 5.21 (s, 4H); 4.51 (s, 4H); 4.08-3.99 (m, 16H); 3.83 (s, 6H); 3.65 (d, *J* = 11.7 Hz, 8H); 1.37 (s, 12H); 1.24 (s, 12H); 1.05 (s, 12H); 0.94 (s, 6H). **^{13}C-NMR (DEPT-Q, 100 MHz, DMSO-d6, δ = ppm)**: 17.98 (*CH₃*), 18.64 (*CH₃*), 21.88 (*CH₃*), 27.00 (*CH₃*), 40. 22 (*CH₂*), 42.50 (*CH₂*), 53.26 (*CH₂*) 56.44, 60.56 (*CH₂*), 62.44 (*CH₂*), 65.97 (*CH₂*), 66.00 (*CH₂*), 66.16 (*CH₂*), 98.28 (*C, C-O-C*), 111.67 (*CH*), 114.29 (*CH*), 123.75 (*CH*), 124.83 (*CH*), 127.16 (*CH*), 128.94 (*C*), 143.03 (*C*), 143.33 (*CH*), 150.05 (*C*), 150.43 (*C*), 174.25 (*C=O*), 188.93 (*C=O*). **FT-IR-ATR (cm^{-1})**: 1731.9, 1583.1, 1506.2, 1454.4, 1372.3, 1253.2, 1216.7, 1197.0, 1150.1, 1121.2, 1077.6, 1033.7, 994.5, 826.6, 730.2, 519.9.



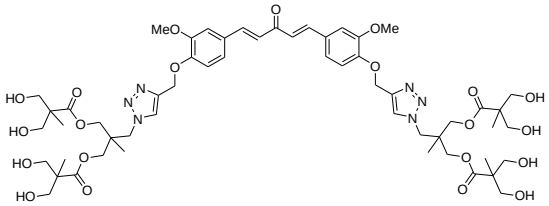
Compound **16**. General method for CuAAC chemistry was followed with 0.13 g (0.292 mmol) of alkyne **9**, 0.307 g (0.672 mmol) of azide **13**, 7.3 mg (0.03 mmol) of $CuSO_4 \cdot 5H_2O$ and 17.4 mg (0.087 mmol) of sodium ascorbate to obtain 0.19 g (0.14 mmol, 48 %) of the desired product as a pale yellow solid **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 8.18 (s, 2H); 7.70-7.10 (m, 10H); 5.20 (s, 4H); 4.51 (s, 4H); 4.08-4.02 (m, 10H); 4.01 (s, 6H); 3.87-3.78 (m, 6H); 3.69-3.63 (m, 8H); 1.37 (s, 12H), 1.23 (s, 12H); 1.05 (s, 12H); 0.94 (s, 6H). **^{13}C-NMR (DEPT-Q, 100 MHz, DMSO-d6, δ = ppm)**: 17.98 (*CH₃*), 18.64 (*CH₃*), 21.89 (*CH₃*), 26.99 (*CH₃*), 40.22 (*C*), 42.49 (*C*), 53.25 (*CH₂*), 56.23, 56.40, 56.48, 62.44 (*CH₂*), 65.97 (*CH₂*), 66.00 (*CH₂*), 66.16 (*CH₂*), 98.28 (*C, O-C-O*), 111.24 (*CH*), 111.27 (*CH*), 111.59 (*CH*), 111. 78 (*CH*), 114.24 (*CH*), 122.14 (*CH*), 123.13 (*CH*), 123.50 (*CH*), 124.01 (*CH*), 124.83 (*CH*), 127.16 (*CH*), 127.97 (*C*), 128.89 (*C*), 128.92 (*C*), 129.52 (*C*), 138.48 (*CH*), 141.16 (*CH*), 142.77 (*CH*), 143.01 (*C*), 150.11 (*C*), 152.27 (*C*), 159.93 (*C*), 161.44 (*C*), 174.24 (*C=O)*), 184.02 (*C=O*), 185.03 (*C=O*). **FT-IR-ATR (cm^{-1})**: 1736.8, 1732.4, 1585.3, 1505.3, 1455.4, 1372.2, 1252.0, 1217.0, 1197.7, 1136.0, 1077.5, 992.0, 827.6, 520.4.

General methodology for the removal of cetonide groups. In a round bottom flask of 25 mL, 50 mg of the corresponding triazole **14**, **16** or **18** is dissolved in 10 mL of MeOH, then 10 % wt. of DOWEX-H+ resin is added an the mixture stirred at 40° C from 30 to 45 minutes, until no starting material is

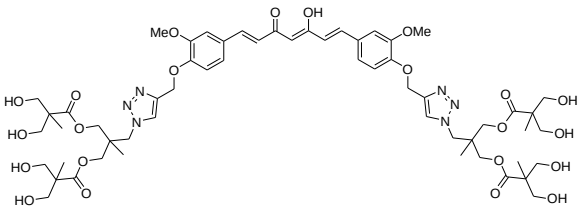
observed by TLC. The catalyst is removed by vacuum filtration and the solvent removed by vacuum distillation to afford a pure product in quantitative yield.



Compound **I**. **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 8.22 (s, 1H); 8.20 (s, 1H); 7.93 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H); 7.85 (d, *J* = 15.4 Hz, 1H); 7.68 (d, *J* = 15.4 Hz, 1H); 7.61 (d, *J* = 1.9 Hz, 1H); 7.54 (d, *J* = 2.0 Hz, 1H); 7.41 (dd, *J* = 1.9 Hz, 8.6 Hz, 1H); 7.33 (d, *J* = 8.6 Hz, 1H); 7.22 (d, *J* = 8.4 Hz, 1H); 5.28 (2, 2H); 5.20 (s, 2H); 4.80 (br, 8H); 4.47 (s, 4H); 3.94-3.82 (m, 14H); 3.56 (d, *J* = 10.3 Hz, 8H); 3.45 (d, *J* = 10.3 Hz, 8H); 1.09 (s, 12H); 0.93 (s, 6H). **^{13}C-NMR (DEPT-Q, 100 MHz, DMSO-d6, δ = ppm)**: 17.67 (*CH$_3$*), 18.09 (*CH$_3$*), 49.40, 51.32 (*CH$_2$*), 53.19 (*CH$_2$*) 56.39, 56.55, 62.43, 62.38 (*CH$_2$*), 64.73 (*CH$_2$*), 66.00 (*CH$_2$*), 111.76 (*CH*), 112.14 (*CH*), 113.22 (*CH*), 114.17 (*CH*), 120.60 (*CH*), 123.94 (*CH*), 124.18 (*CH*), 127.21 (*CH*), 127.31 (*CH*), 128.99 (*C*), 131.95 (*C*), 142.78 (*C*), 142.98 (*C*), 144.32 (*CH*), 149.80 (*C*), 150.04 (*C*), 150.52 (*C*), 152.52 (*C*), 175.14 (*C=O*), 188.10 (*C=O*). **FT-IR-ATR (cm^{-1})**: 3325.4, 2927.6, 1726.7, 1646.5, 1626.7, 1561.1, 1508.7, 1448.9, 1259.2, 1214.0, 1149.6, 1116.8, 1027.1, 1004.8, 812.0, 470.6.



Compound **II**. **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 8.20 (s, 1H); 8.17 (s, 1H); 7.71 (d, d, *J* = 16.0 Hz, 2H); 7.42 (d, *J* = 1.9 Hz, 2H); 7.33 (dd, *J* = 8.5 Hz, 1.9 Hz, 2H); 7.24 (d, *J* = 16.0 Hz, 2H); 7.23 (d, *J* = 8.6 Hz, 2H); 5.20 (s, 4H); 4.81 (br, 8H); 4.47 (s, 2H); 4.48 (s, 2H); 3.84 (s, 6H); 3.55 (d, *J* = 10.4 Hz, 8H); 3.46 (d, *J* = 10.2 Hz, 8H); 1.08 (s, 12H); 0.92 (s, 3H); 0.81 (s, (3H). **^{13}C-NMR (DEPT-Q, 100 MHz, DMSO-d6, δ = ppm)**: 17.68 (*CH$_3$*), 18.08 (*CH$_3$*), 51.34 (*CH$_2$*), 52.10 (*CH$_3$*), 53.19 (*CH$_2$*), 56.44, 62.38 (*CH$_2$*), 64.70 (*CH$_2$*), 65.99 (*CH$_2$*), 111.69 (*CH*), 114.26 (*CH*), 123. 80 (*CH*), 124. 83 (*CH*), 127.21 (*CH*), 128.90 (*C*), 142.96 (*C*), 143.34 (*CH*), 150. 07 (*C*), 150.48 (*C*), 175.14 (*C=O*), 188.94 (*C=O*). **FT-IR-ATR (cm^{-1})**: **FT-IR-ATR (cm^{-1})**: 3364.0, 2933.0, 1721.6, 1641.4, 1582.0, 1507.2, 1463.1, 1253.2, 1220.3, 1136.5, 1029.7, 996.4, 807.2.



Compound **III**. **^{1}H-NMR (400 MHz, DMSO-d6, δ = ppm)**: 8.21-8.16 (m, 2H); 7.65-7.00 (m, 10H); 5.22-5.13 (m, 4H); 4.84 (br, 8H); 4.46 (s, 4H); 3.90 (s, 6h); 3.58-3.52 (m, 8H); 3.47-3.41 (s, 8H); 1.08 (s, 12H); 0.92 (s, 6H). **FT-IR-ATR (cm^{-1})**: 3344.1, 2930.1, 1720.8, 1580.4, 1508.4, 1454.8, 1221.5, 1135.8, 1030.9, 805.7.

Solubility test. In a 5 mL vial, 5 mg of the corresponding compound **I**-**III** or **B** were placed. Subsequently, 1 mL of a phosphate buffer solution (pH 7.4 or 6.4) was added and dissolved with the help of 5 minutes under sonication. Then, 0.5 mg samples of the corresponding compound were added until the solution was saturated. For each addition of sample, it was sonicated for a time of 5 minutes to verify the solubility of the sample.

3. FT-IR comparisons

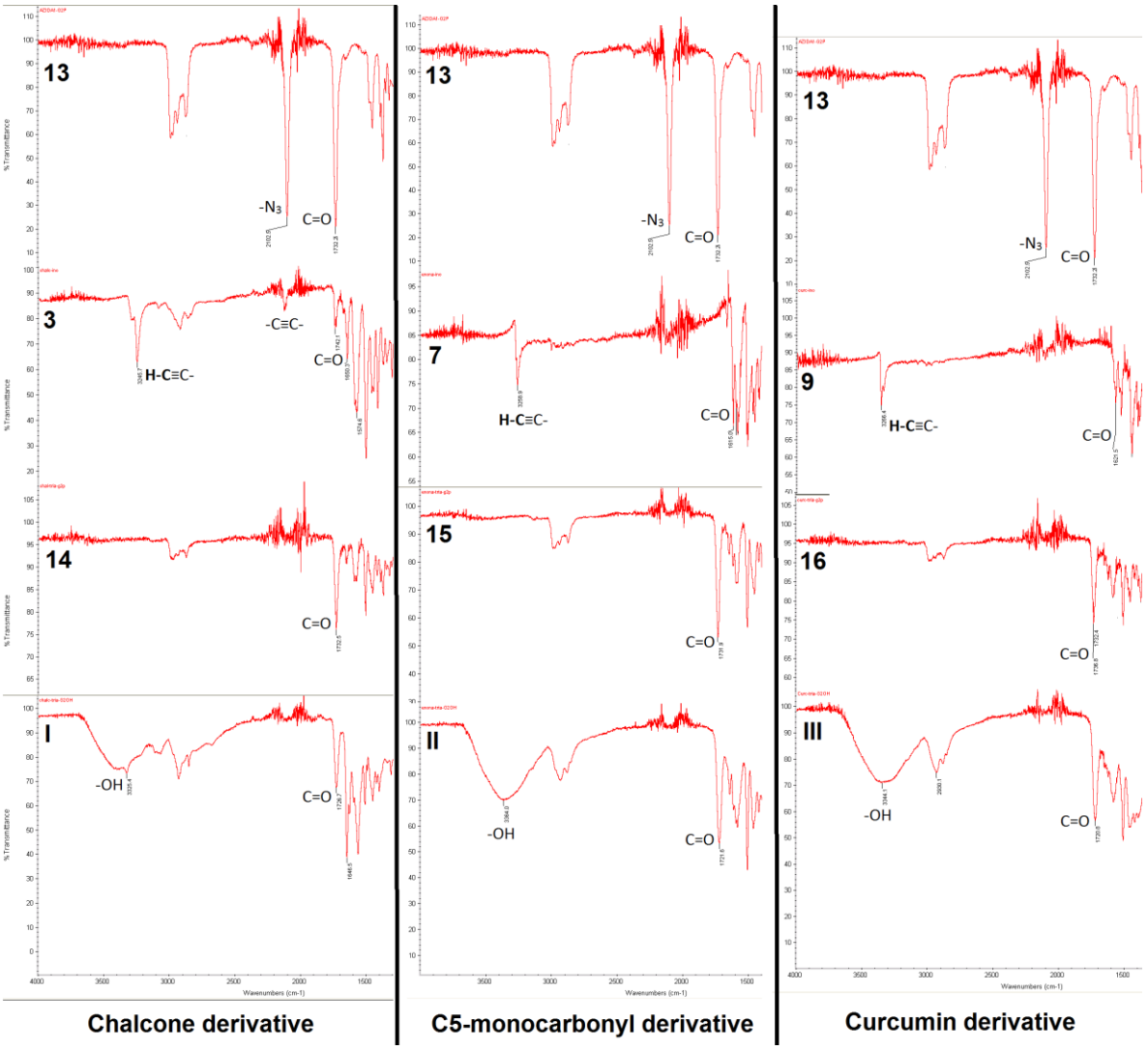


Figure S1. Comparison of the FT-IR spectra of the precursor for the obtention of derivatives **I – III**.

4. ^{1}H-NMR and DEPTQ comparison of compounds **16** and **A**.

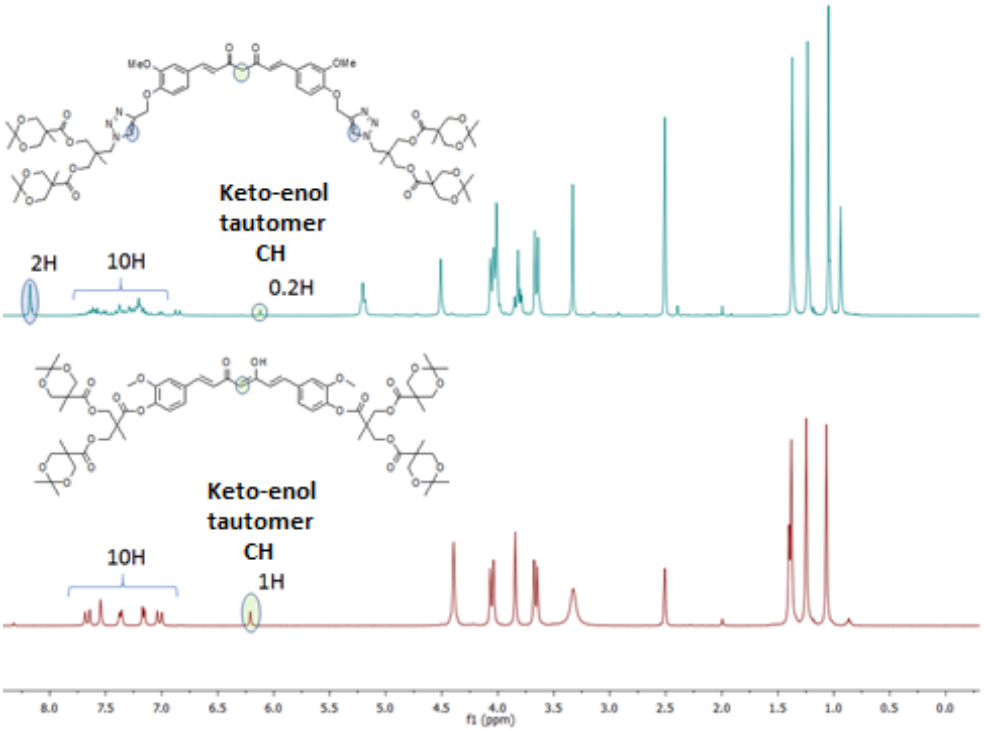


Figure S2. ^{1}H-NMR comparison of the new triazole containing dendronized derivative **16** (top) with its parent system **A** (bottom).

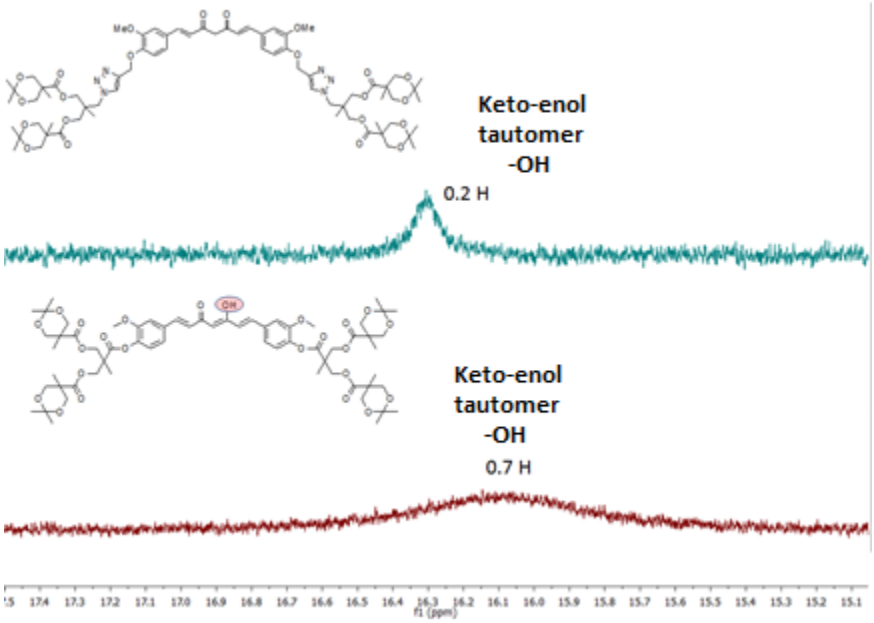


Figure S3. ^{1}H-NMR signal of the hydroxyl group related to the keto-enol tautomer of curcumin.

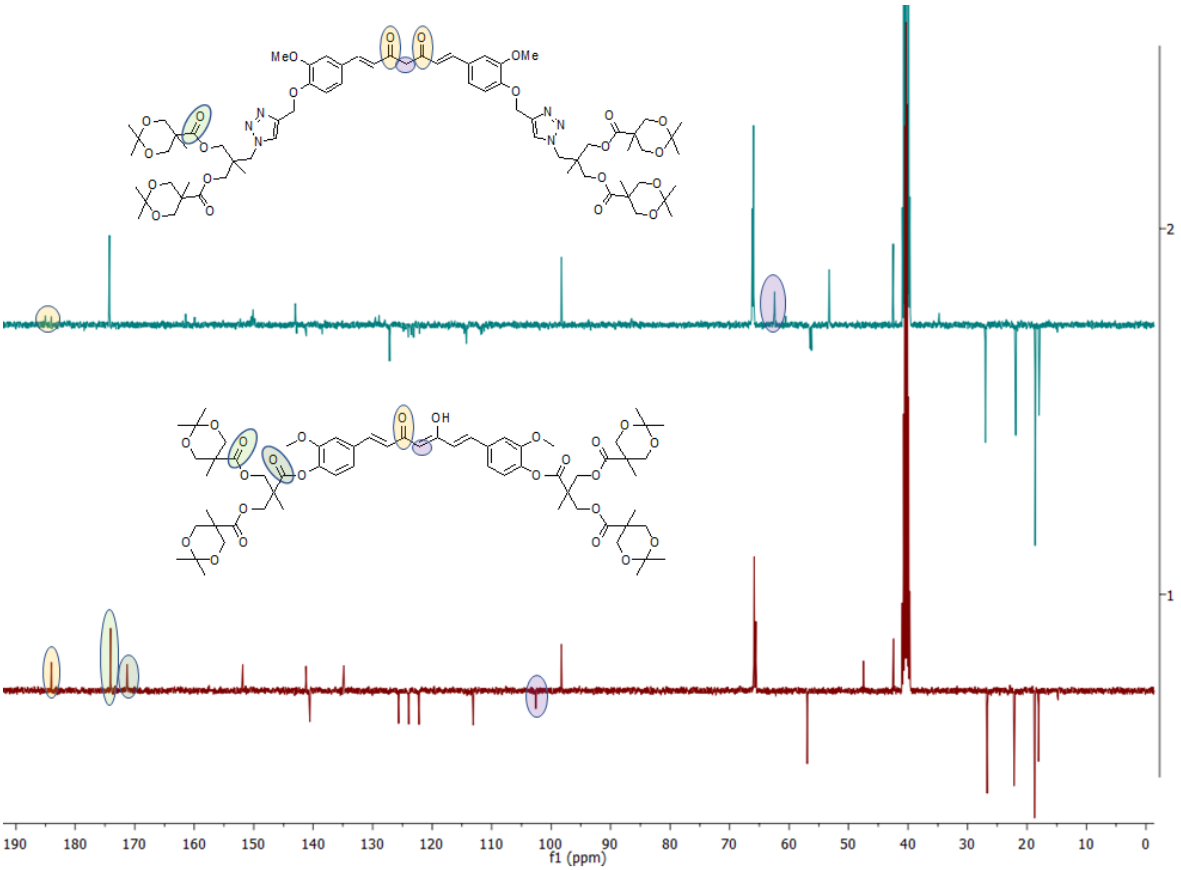


Figure S4. Full comparison of DEPTQ spectra of derivatives **16** (top) and **A** (bottom).

5. Comparison of the UV-vis spectra of chalcone and C5 monocarbonyl derivatives.

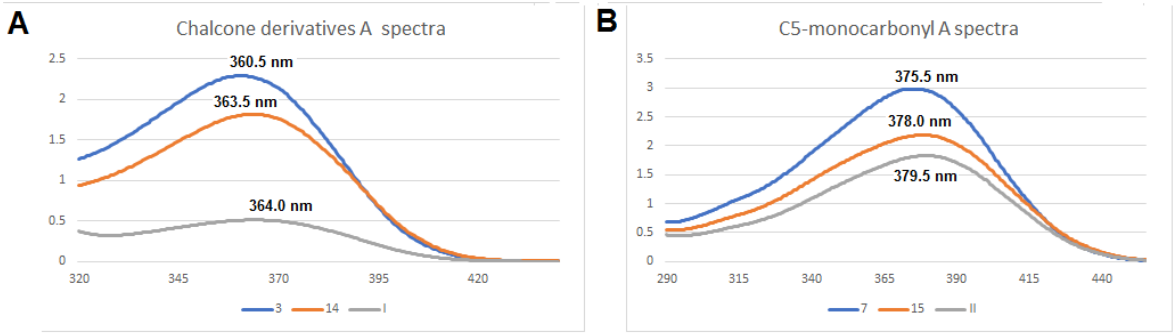


Figure S5. UV-vis spectra of curcumin analogues, A) Chalcone derivatives. B) C5 monocarbonyl derivatives. All spectra were determined at 70 µM in DMSO.

6. Table S1; λmax and ε determined by calibration curves.

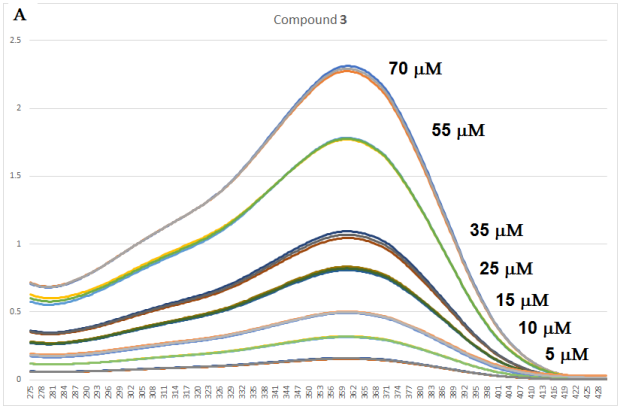
Table S1.

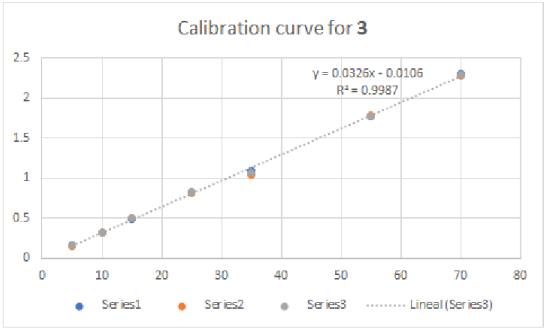
Entry	Compound	λ_{max} (nm)[a]	ε (M^{-1} cm^{-1})[b]	A[a]
1	**3**	360.5	32,600	2.2931
2	**14**	363.5	25,900	1.8122
3	**I**	364.0	7,300	0.5114
4	**7**	375.5	44,400	3.1169
5	**15**	378.0	31,300	2.1851
6	**II**	379.5	26,200	1.8287
7	**9**	437.5	48,600	3.4008
8	**16**	424.0	29,700	2.0872
9	**III**	420.5	16,600	1.1718
10	**8**	435.0	68,000	4.1708
11	**A**	406.0	50,400	3.5134
12	**B**	407.5	36,900	2.5847

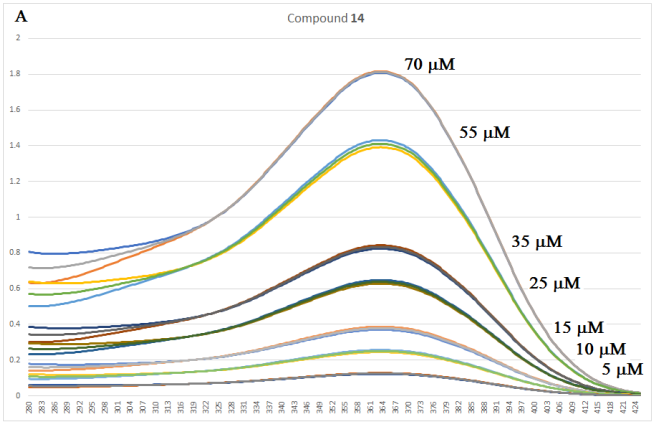
[a]Determined at 70 µM solutions in DMSO. [b]Determined by calibration curves in the range of 70 to 5 µM solutions in DMSO. [c]Molar extinction coefficient in M^{-1} cm^{-1}.

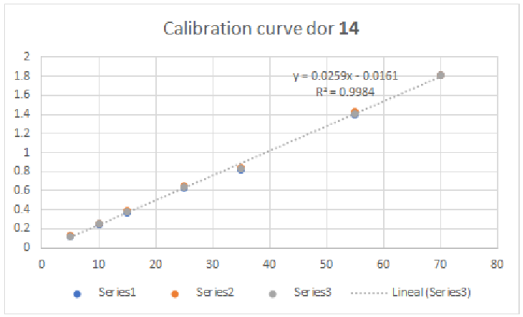
7. Complete UV-VIS spectra and calibration curves.

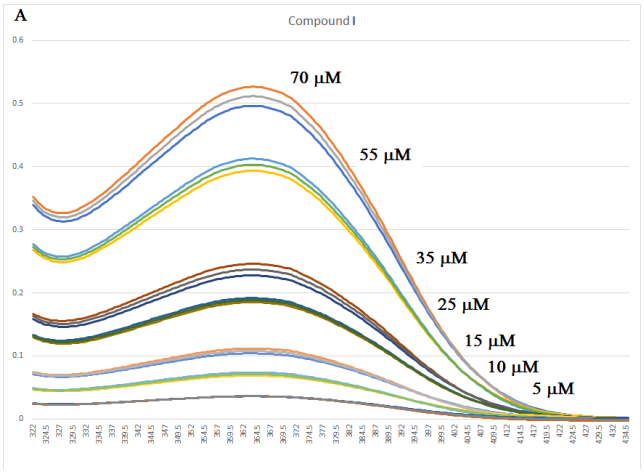
Chalcone derivatives **3**, **14** and **I**

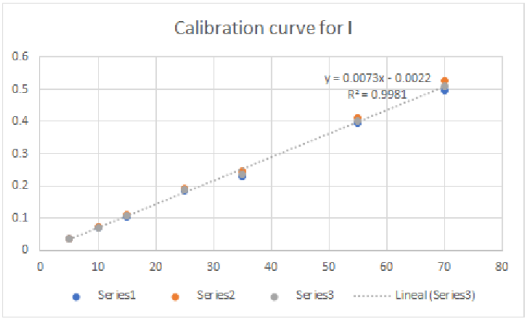




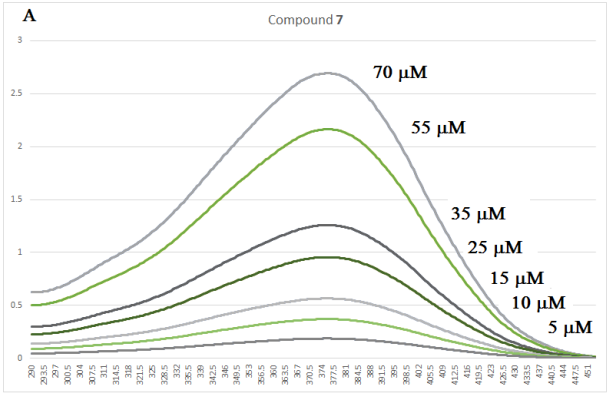


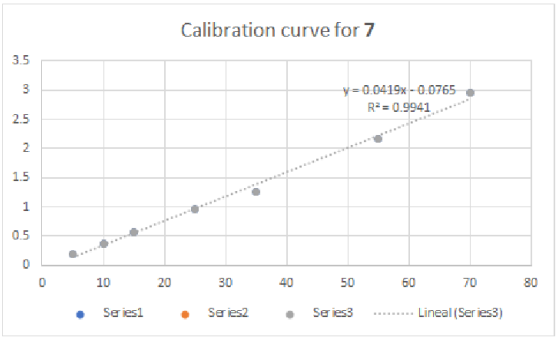


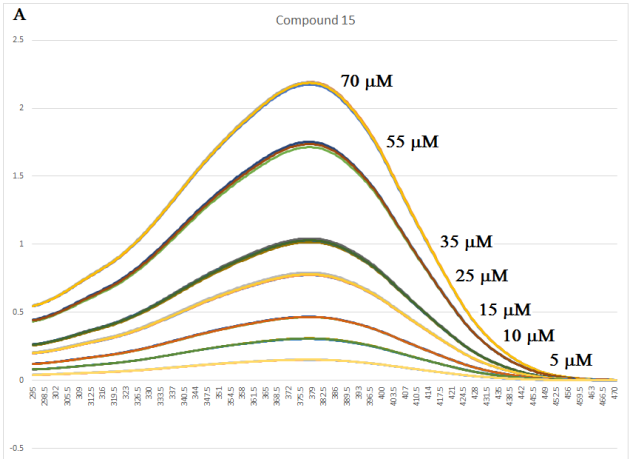


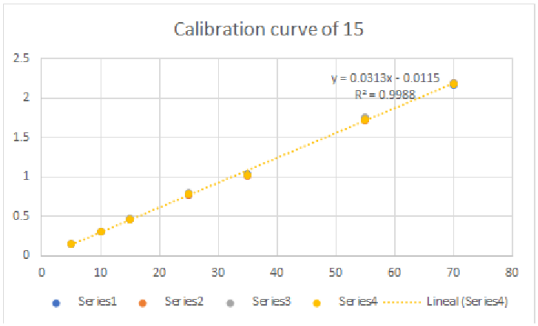


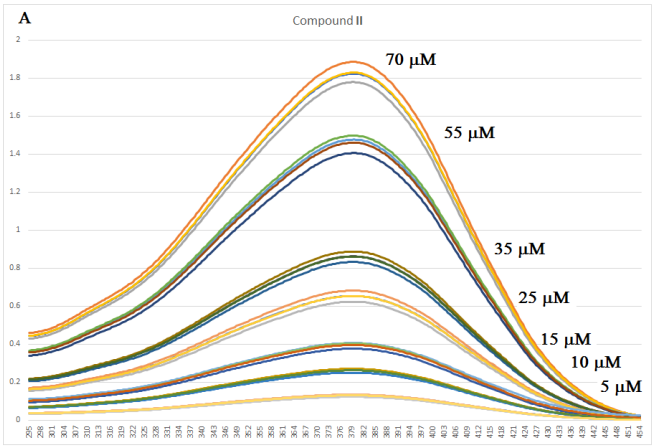
C5 monocarbonyl derivatives **7**, **15** and **II**

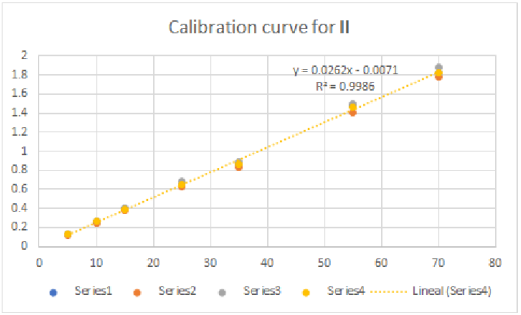




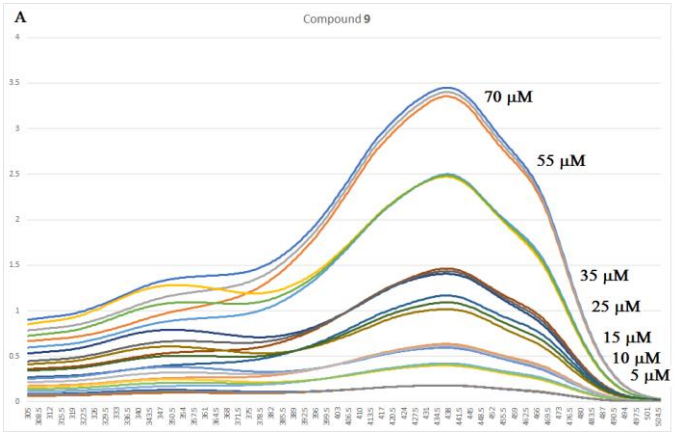


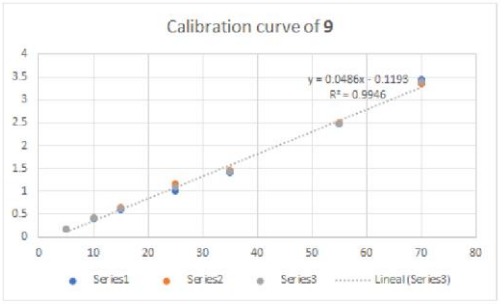


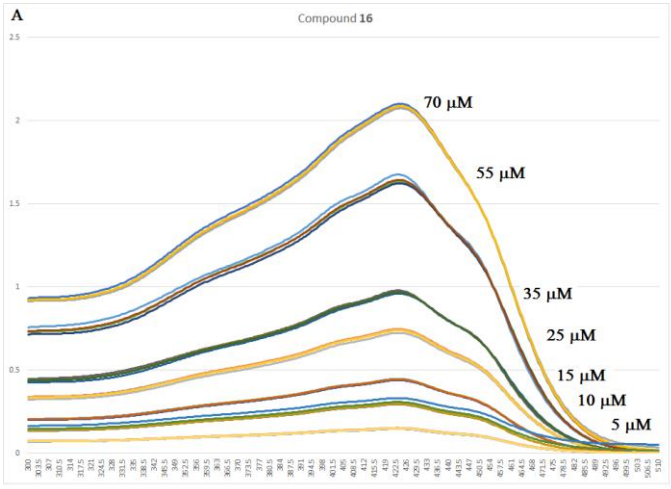


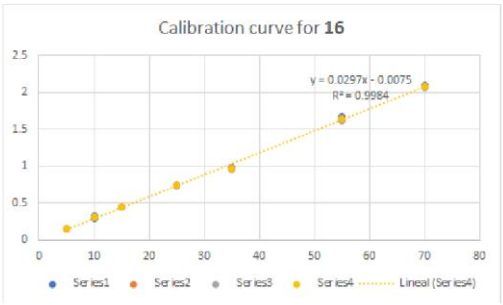


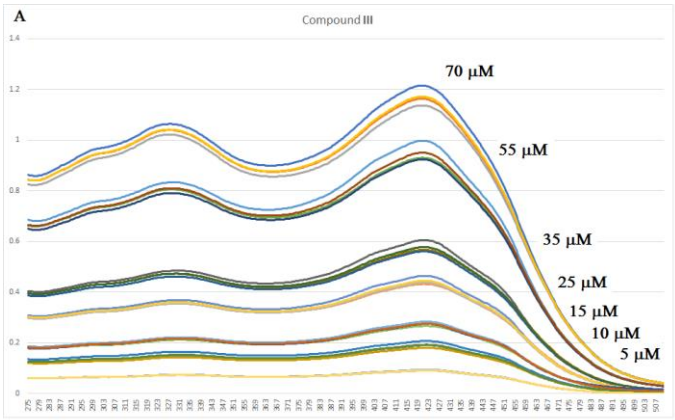
Curcumin derivatives **9**, **16** and **III**

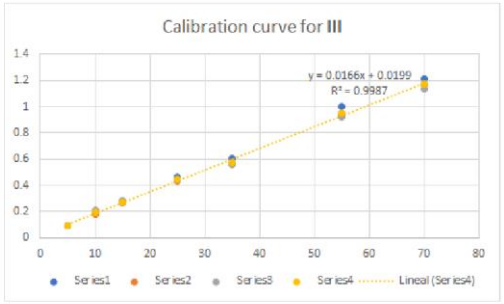




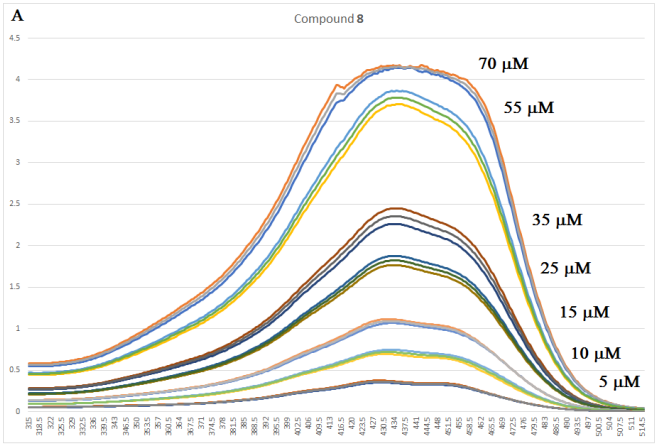


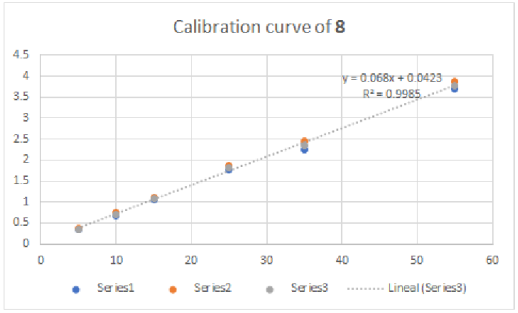


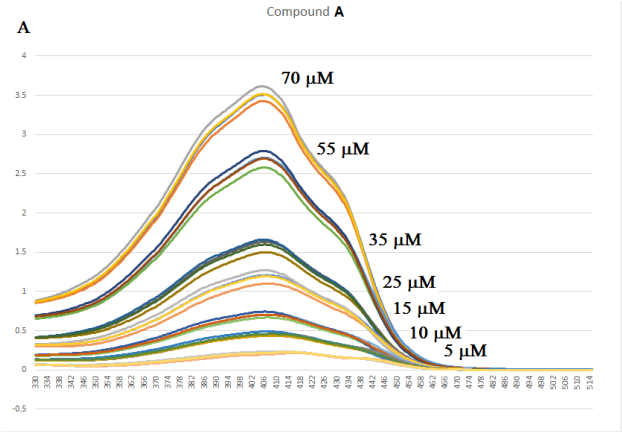


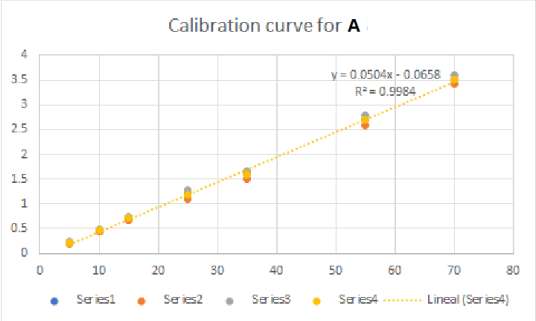


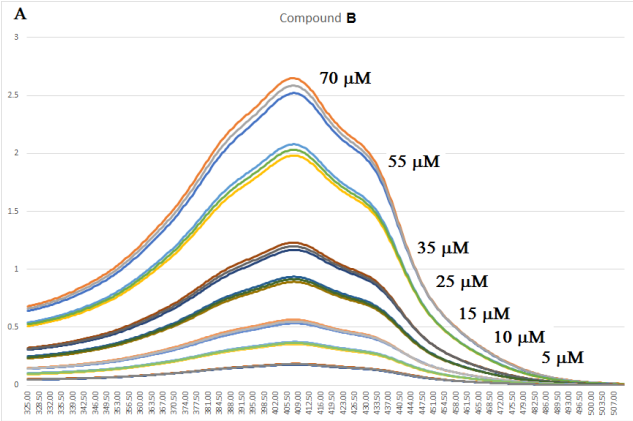
Curcumin derivatives **8**, **A** and **B**

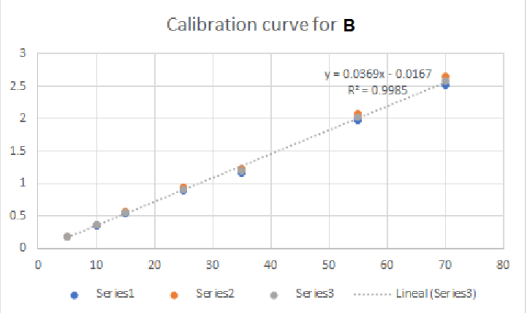










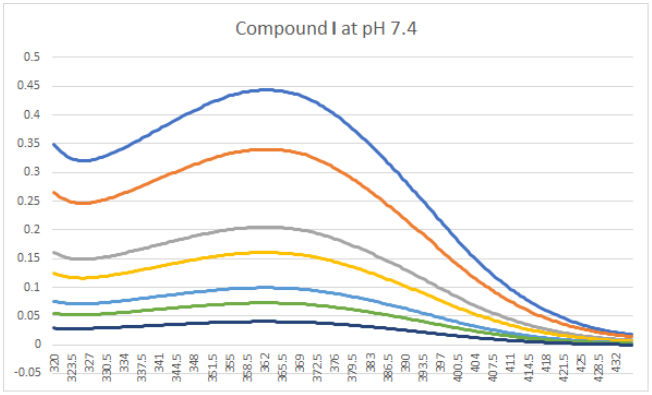


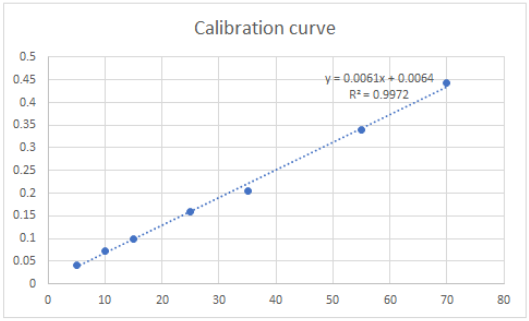
8. Table S2, λ_{max} and ε determined by calibration curves in phosphate buffered solutions.

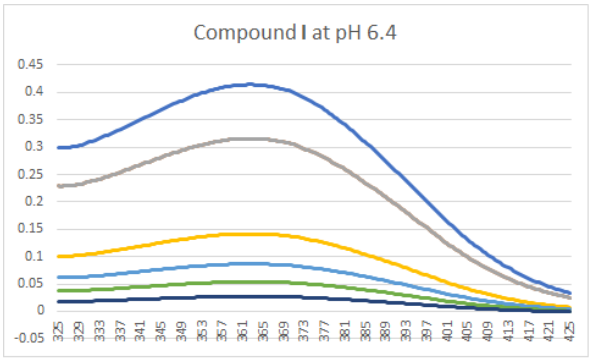
Entry	Compound	Phosphate buffered solution			
		pH 7.4		pH 6.4	
		λ_{max} (nm)[a]	ε (M^{-1} cm^{-1})[b]	λ_{max} (nm)[a]	ε (M^{-1} cm^{-1})[b]
1	**I**	362.0	6,100	362.5	5,900
2	**II**	381.5	13,000	382.0	17,500
3	**III**	317.0	5,700	363.0	3,900
4	**B**	392.0	1,900	391.5	1,700

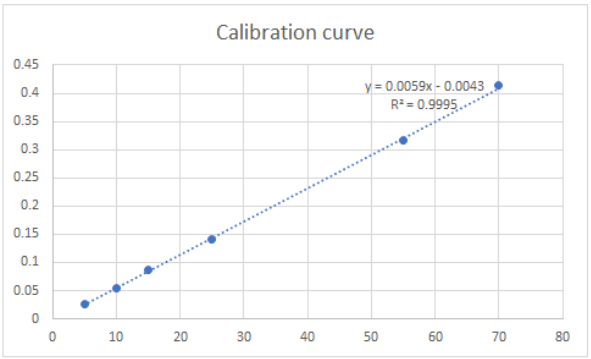
[a]Determined at 70 µM solutions in DMSO. [b]Determined by calibration curves in the range of 70 to 5 µM solutions in buffered solutions.

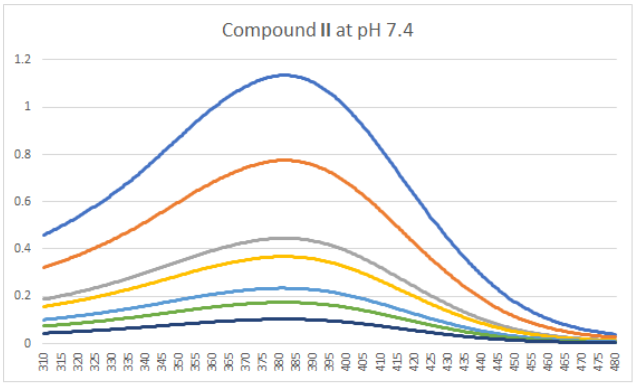
9. Complete UV-VIS spectra and calibration curves in phosphate buffered solutions.

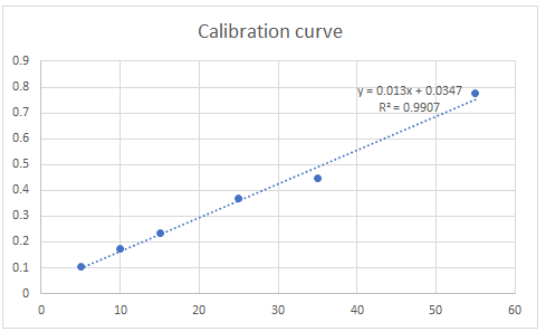


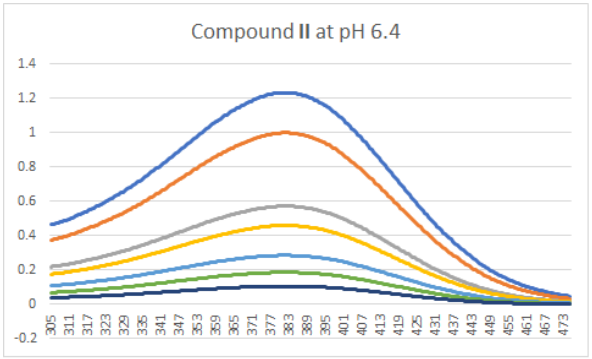


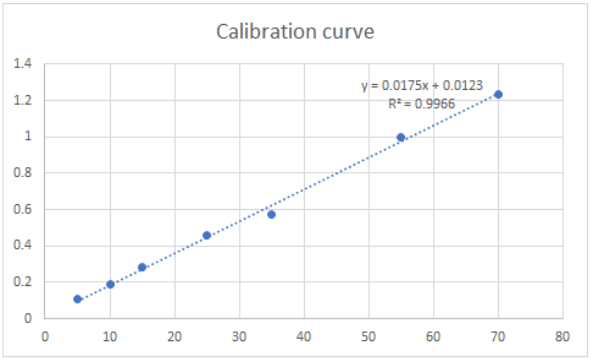


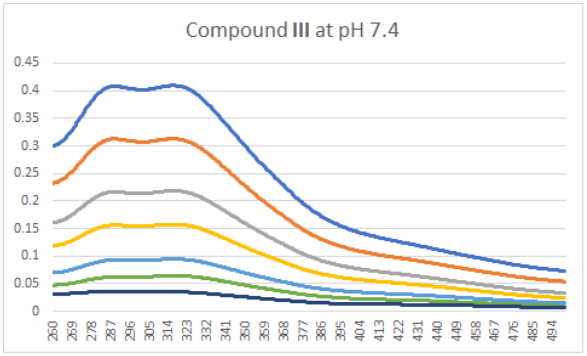


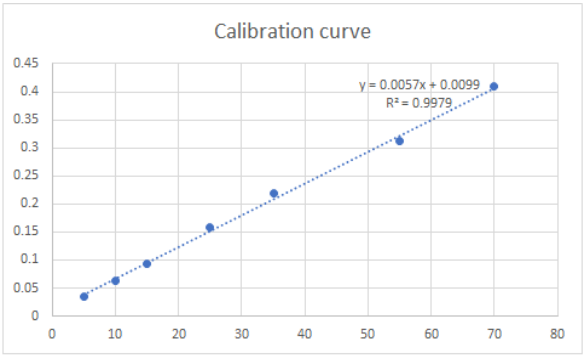


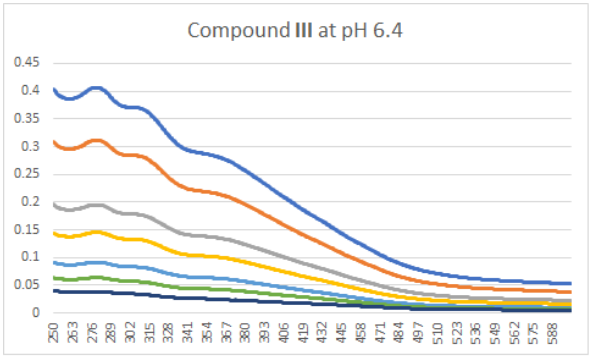


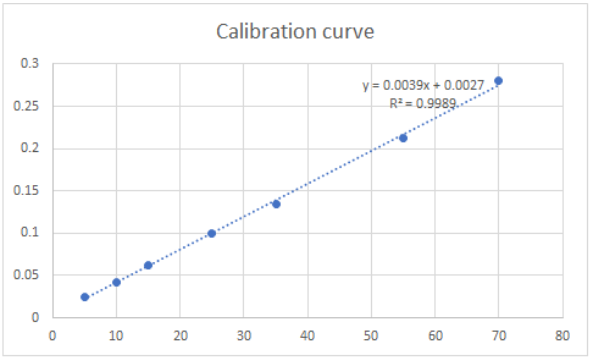


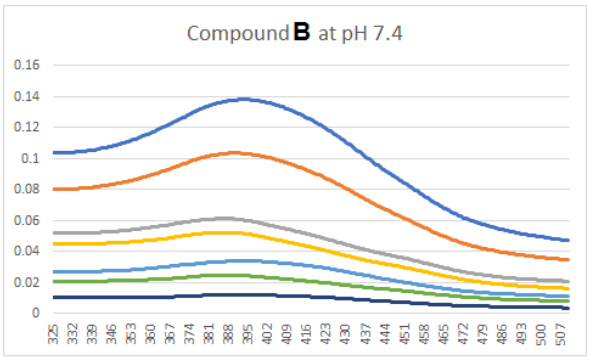


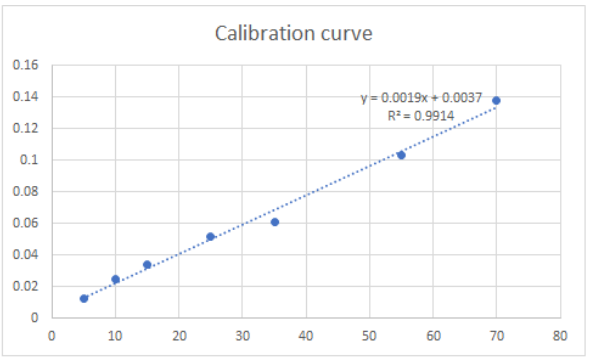


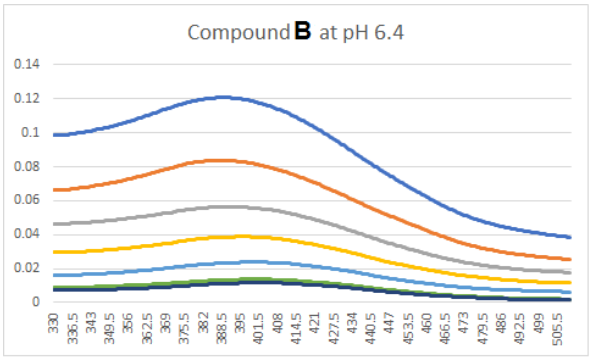


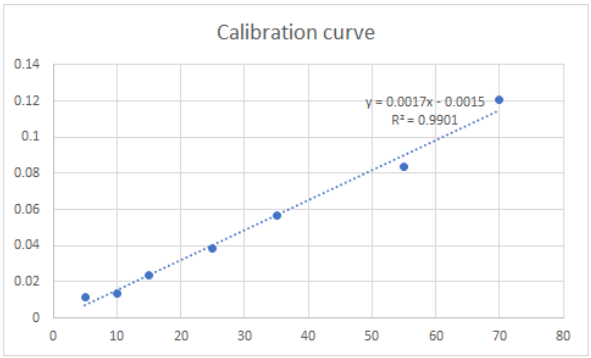












10. Stability study by UV-VIS in phosphate buffer at pH 6.4.

70 mM solutions of each compound **I-III** and **B** were prepared in phosphate buffer (7.4 and 6.4). Uv-vis spectra were taken every determined time. The samples were kept away from light for the duration of the experiment.

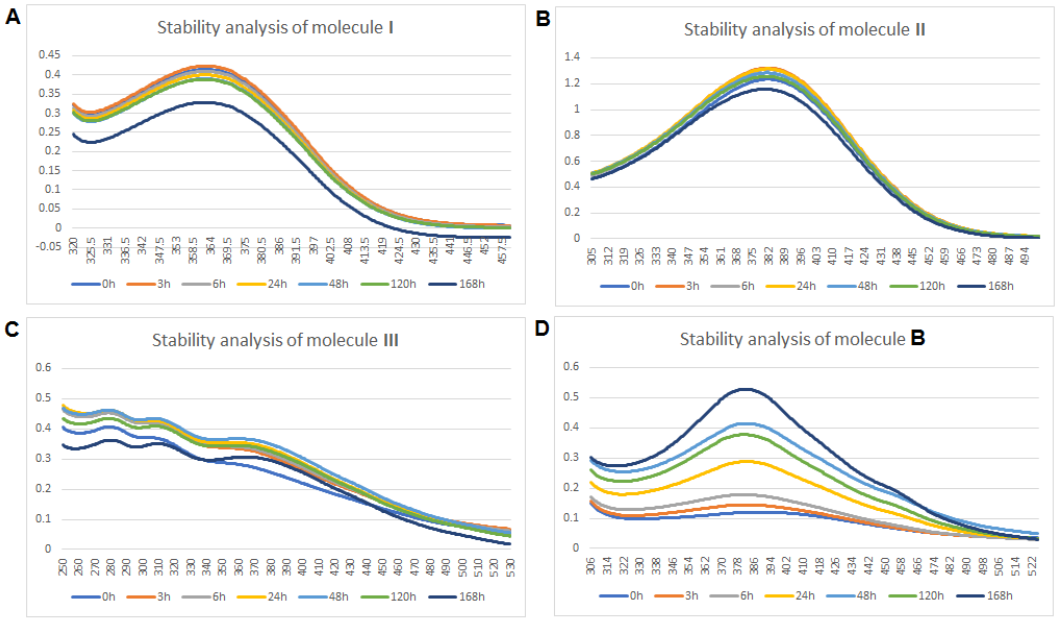


Figure S6. UV-vis stability analysis of water soluble dendronized derivatives **I**, **II**, **III** and **B** in pH 6.4 phosphate buffered solution at 70 µM.

11. Stability study under light irradiation.

5 to 10 mM solutions of Compounds **I**-**III** and **B** were prepared in DMSO. A UV-vis spectrum was taken at time zero and the sample was then irradiated under a source of 415 nm. Every given time a Uv-vis spectrum was taken until no changes in the spectra were observed (Figure S7).

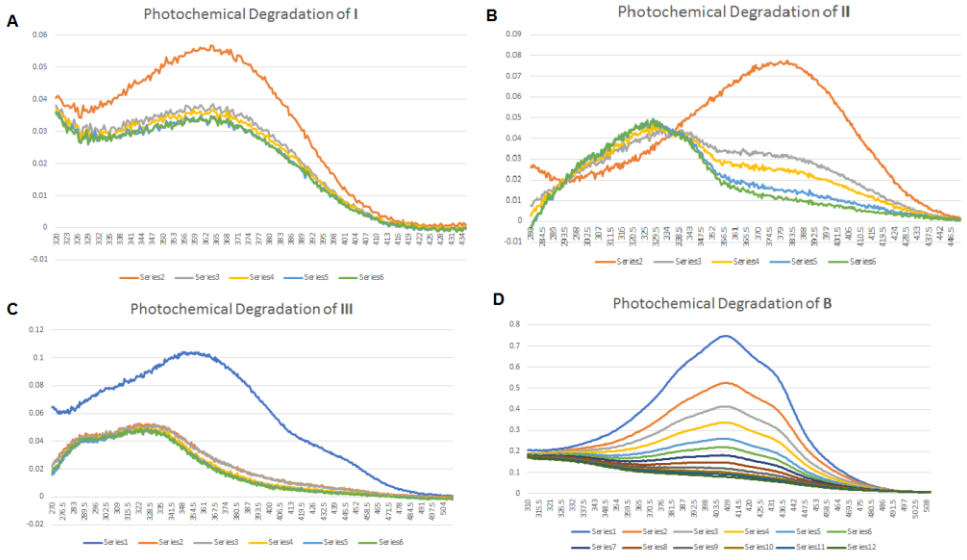
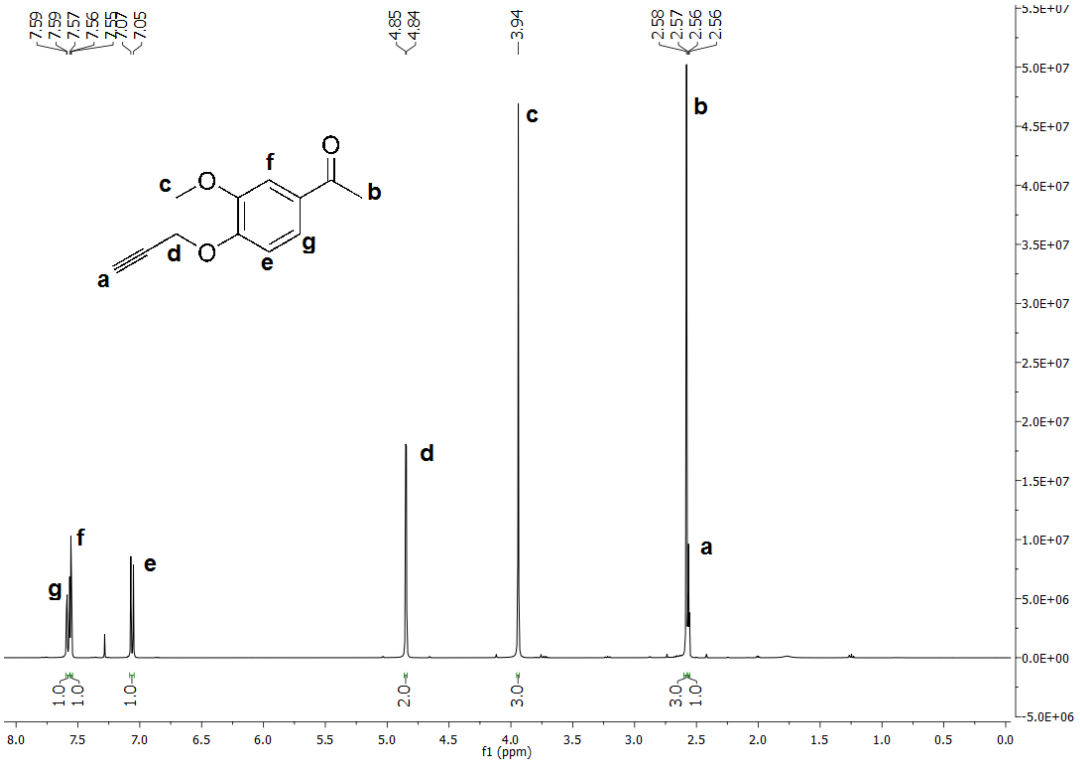
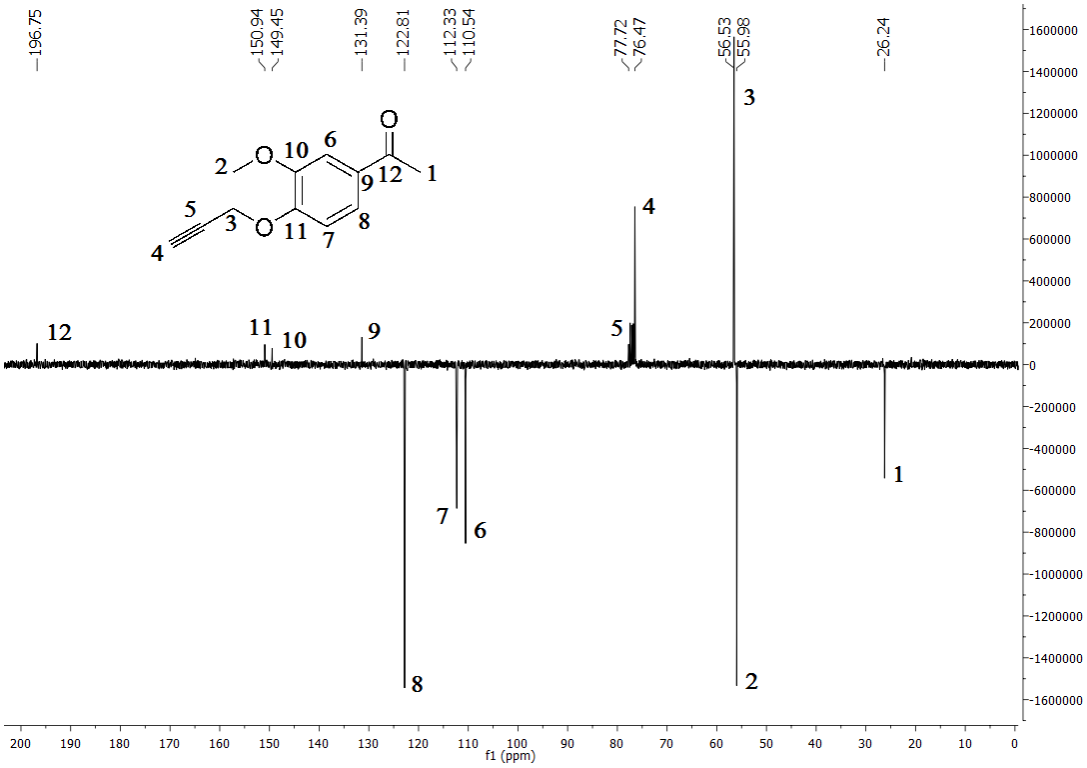
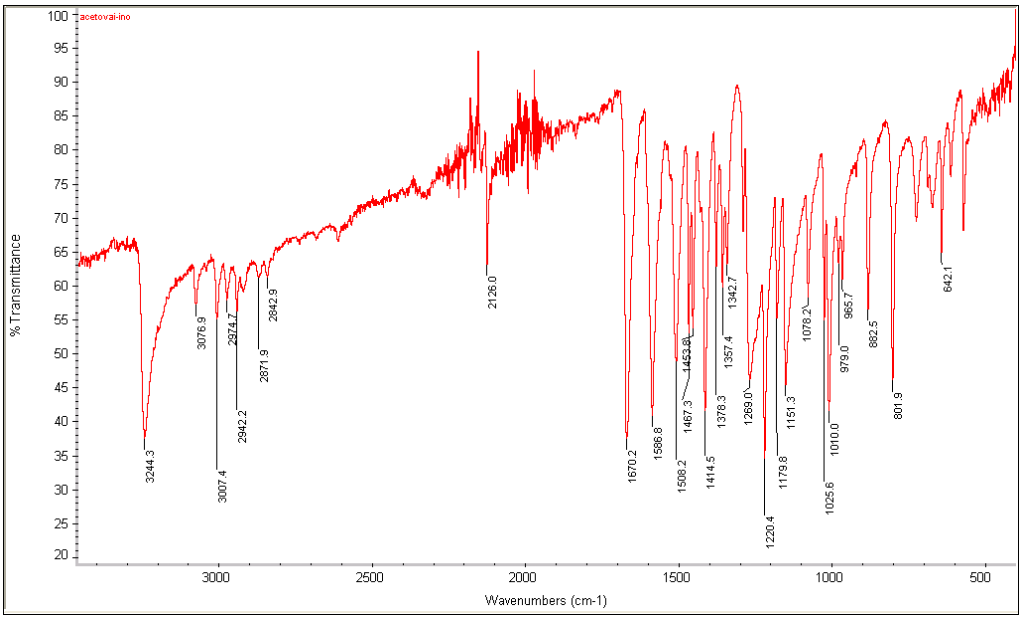


Figure S7. Stability analysis under light irradiation of curcumin analogues.

12. NMR spectra and FT-IR of new compounds.






acetovai-ino
% Transmittance
Wavenumbers (cm-1)
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2974.7
2942.2
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2842.9
2126.0
1670.2
1586.8
1508.2
1467.3
1453.8
1414.5
1378.3
1357.4
1342.7
1269.0
1220.4
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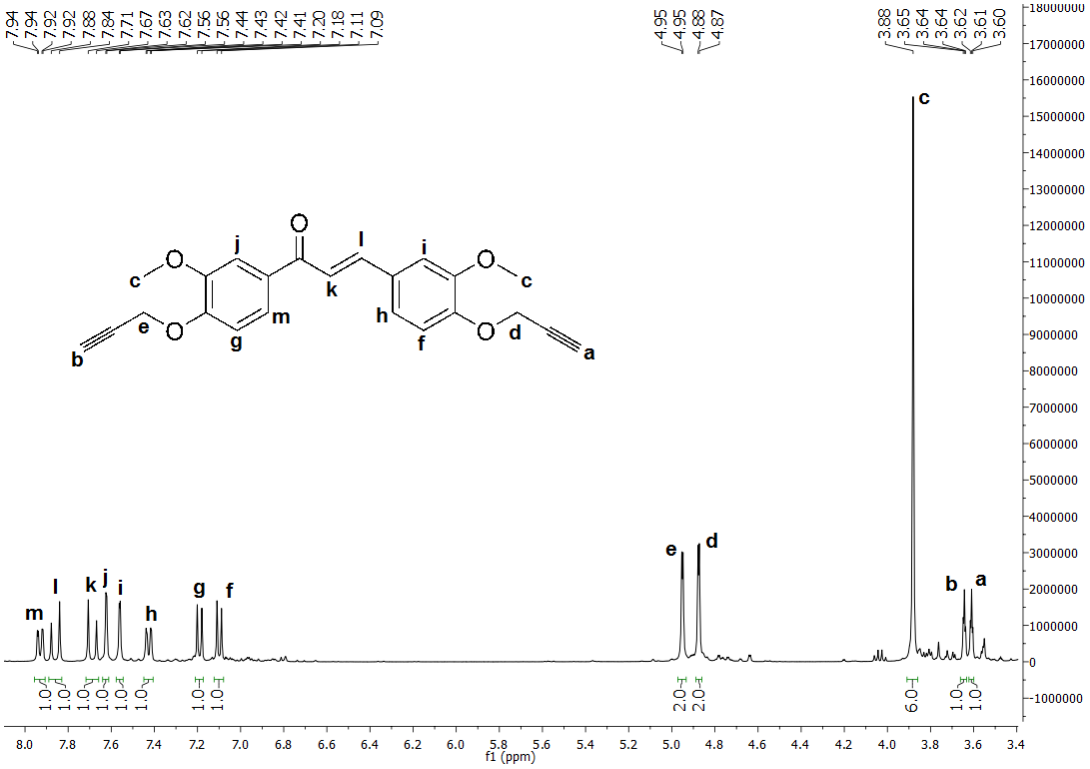
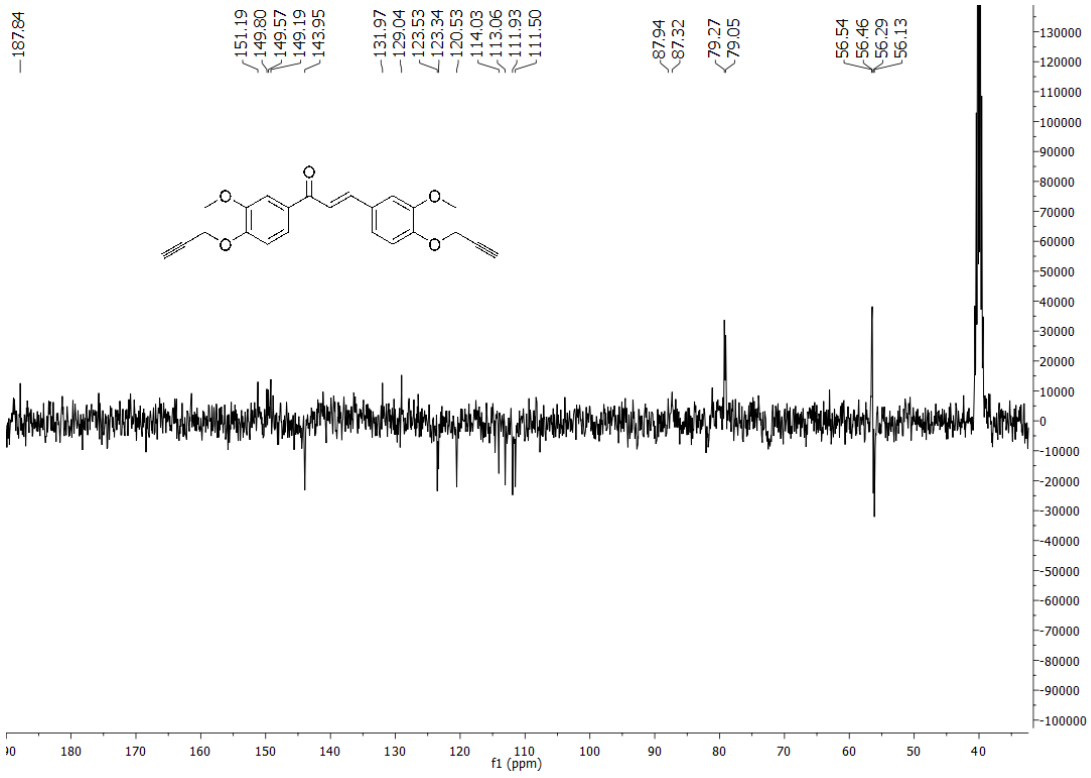
1078.2
1025.6
1010.0
979.0
965.7
882.5
801.9
642.1


f1 (ppm)
a
b
c
d
e
f
g
h
i
j
k
l
m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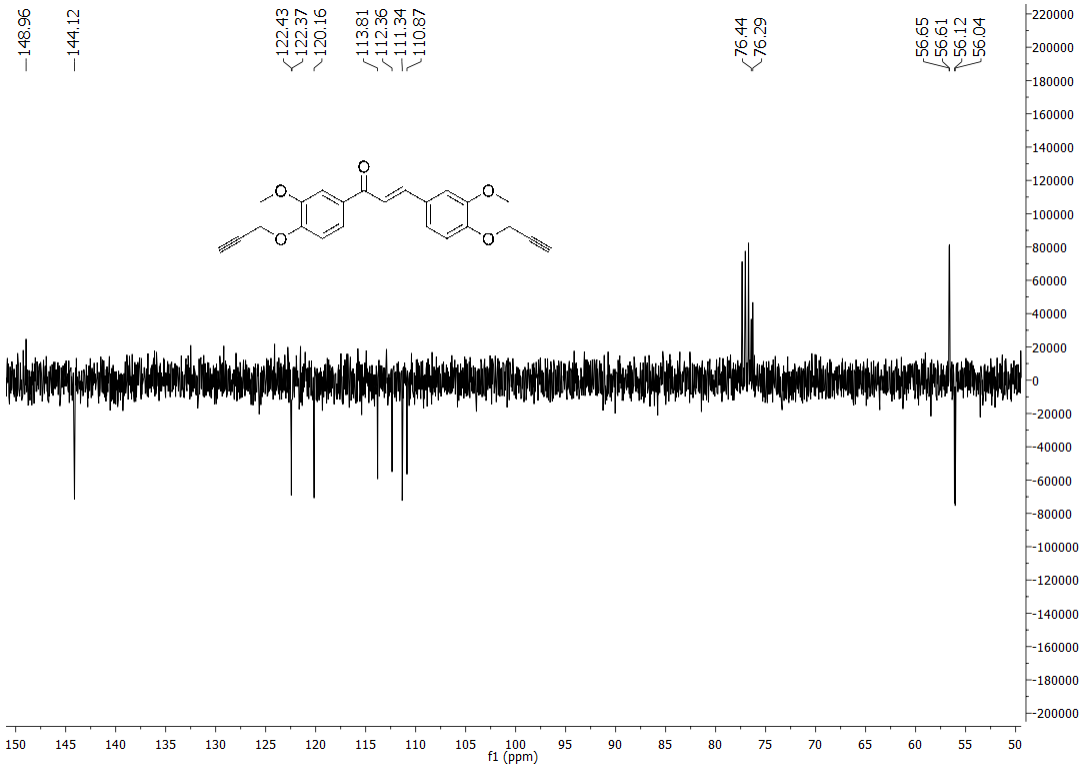
149.80
149.57
149.19
143.95
131.97
129.04
123.53
123.34
120.53
114.03
113.06
111.93
111.50
87.94
87.32
79.27
79.05
56.54
56.46
56.29
56.13
f1 (ppm)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144.12
122.43
122.37
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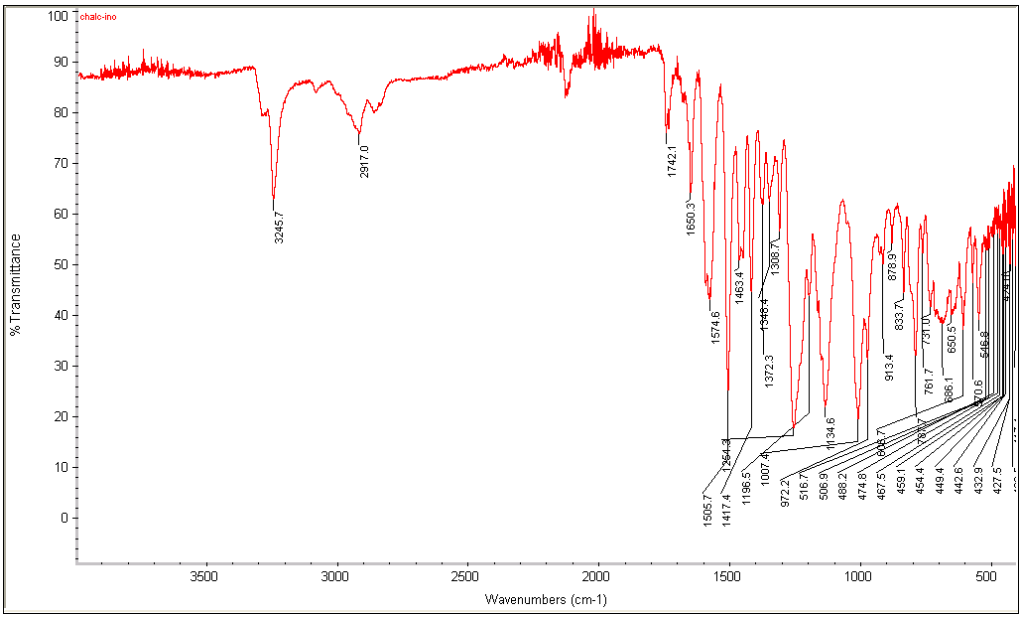
56.12
56.04
f1 (ppm)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% Transmittance
Wavenumbers (cm-1)
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1574.6
1463.4
1346.4
1308.7
1372.3
1134.6
913.4
878.9
833.7
761.7
731.0
650.5
546.8
1505.7
1417.4
1196.5
1007.4
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467.5
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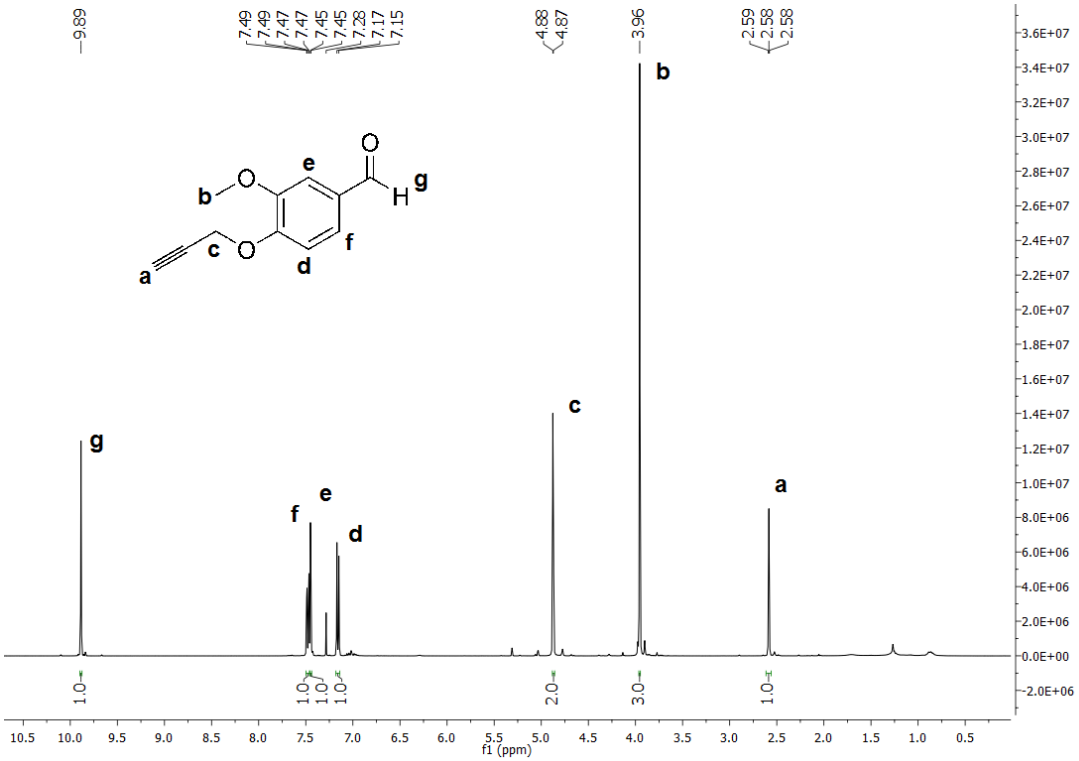
454.4
449.4
442.6
432.9
427.5


9.89
7.49
7.49
7.47
7.47
7.45
7.45
7.28
7.17
7.15
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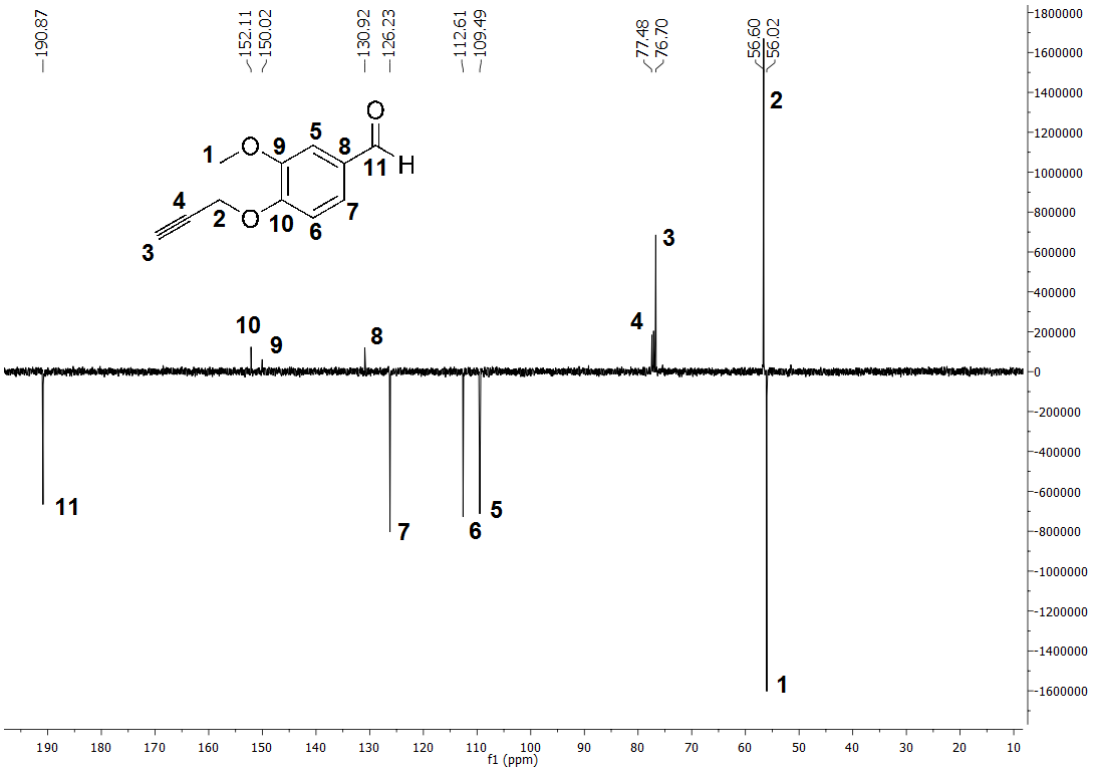
4.87
3.96
2.59
2.58
2.58
a
b
c
d
e
f
g
f1 (ppm)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126.23
112.61
109.49
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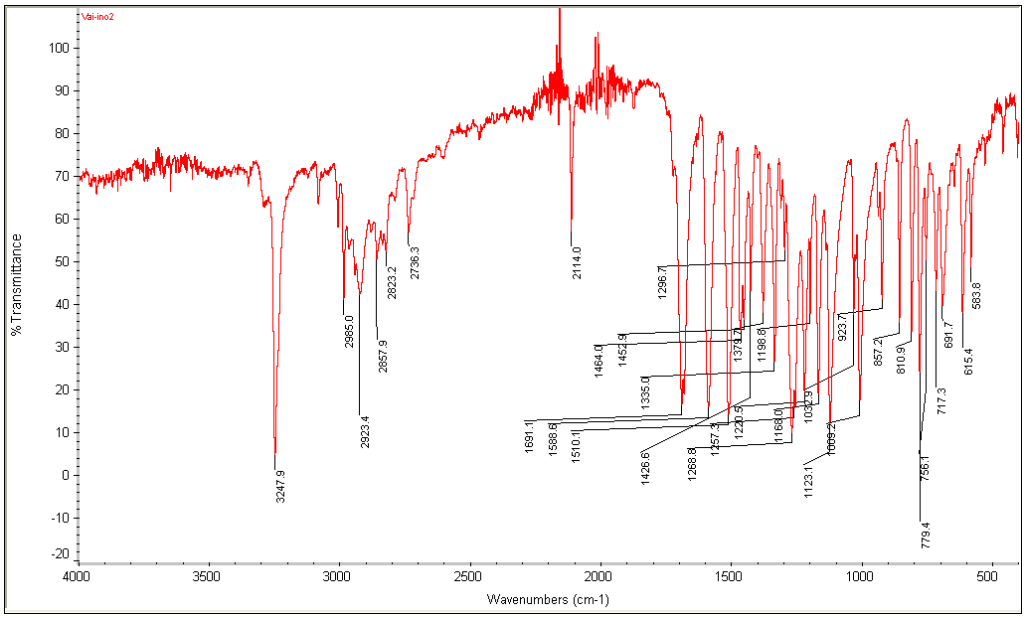
56.60
56.02
f1 (ppm)


% Transmittance
Wavenumbers (cm-1)
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1588.8
1510.1
1464.0
1451.9
1426.6
1335.0
1286.7
1266.8
1257.3
1220.5
1198.8
1168.0
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810.9
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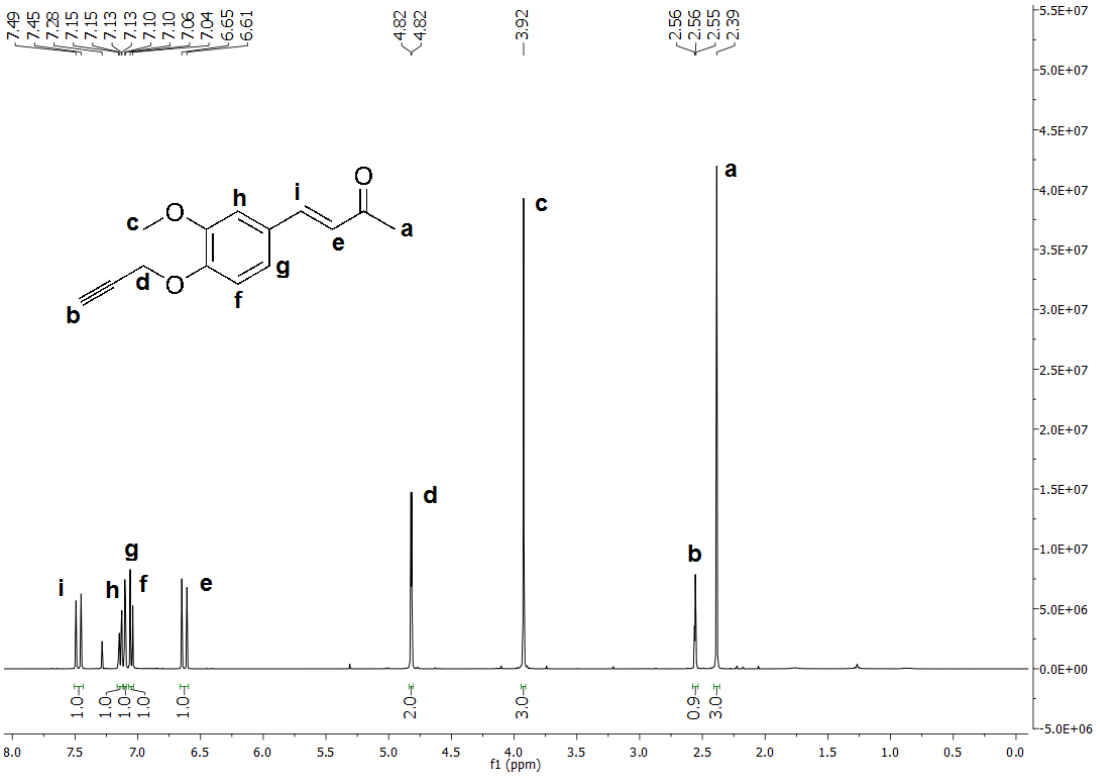
756.1
717.3
691.7
615.4
583.8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7.28
7.15
7.15
7.13
7.13
7.10
7.10
7.06
7.04
6.65
6.61
4.82
4.82
3.92
2.56
2.56
2.55
2.39
a
b
c
d
e
f
g
h
i
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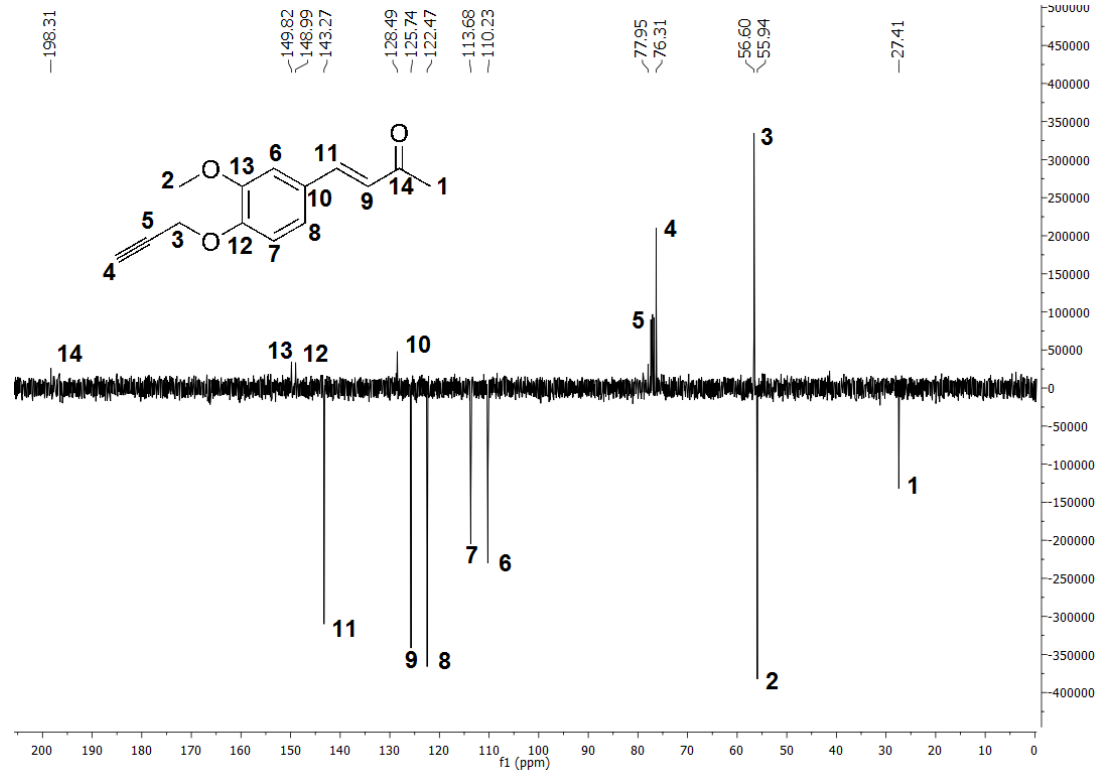
1.0
1.0
1.0
1.0
2.0
3.0
0.9
3.0
f1 (ppm)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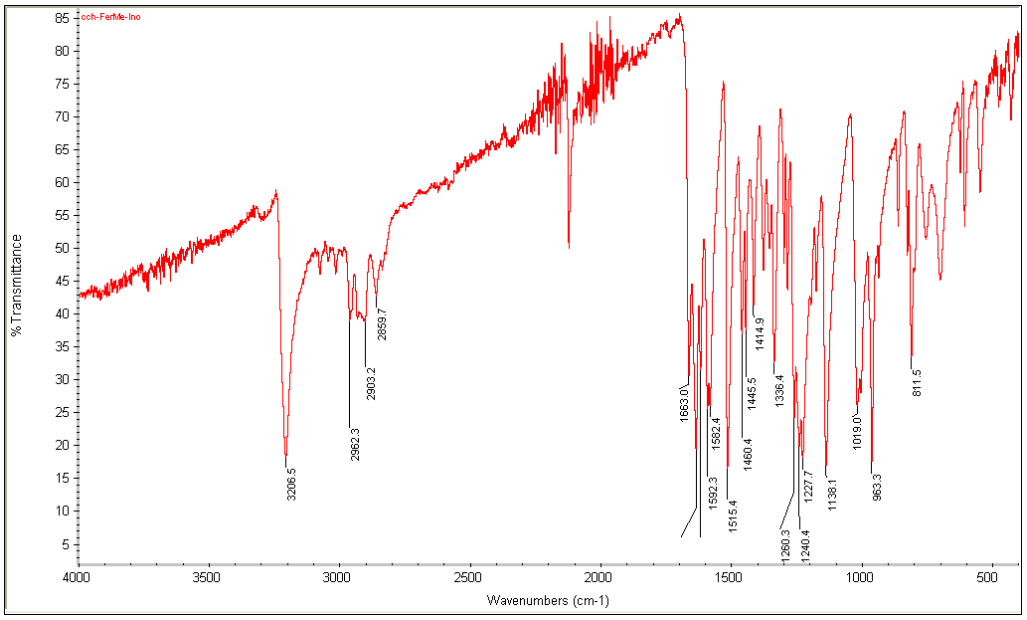
128.49
125.74
122.47
113.68
110.23
77.95
76.31
56.60
55.94
27.41
1
2
3
4
5
6
7
8
9
10
11
12
13
14
f1 (ppm)


cch-FerMe-Ino
% Transmittance
Wavenumbers (cm-1)
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2859.7
1663.0
1592.3
1582.4
1515.4
1460.4
1445.5
1414.9
1336.4
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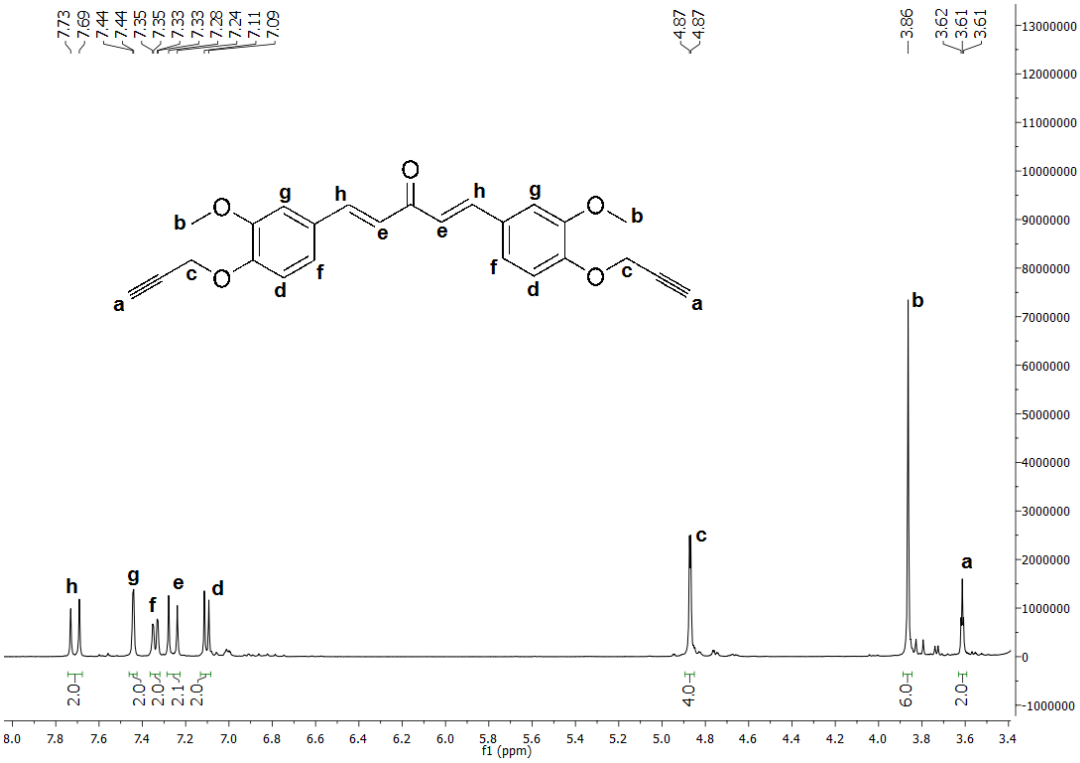
1240.4
1227.7
1138.1
1019.0
963.3
811.5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7.44
7.35
7.35
7.33
7.33
7.28
7.24
7.11
7.09
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4.87
3.86
3.62
3.61
3.61
a
b
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g
h
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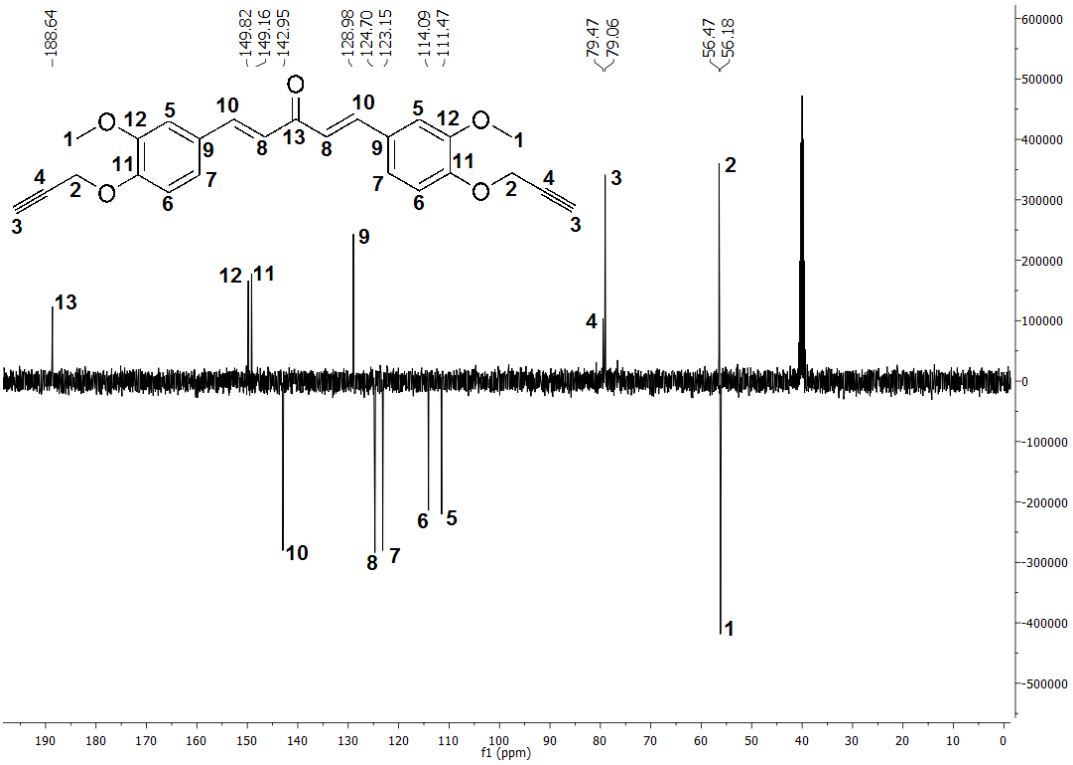
2.0
2.1
2.0
4.0
6.0
2.0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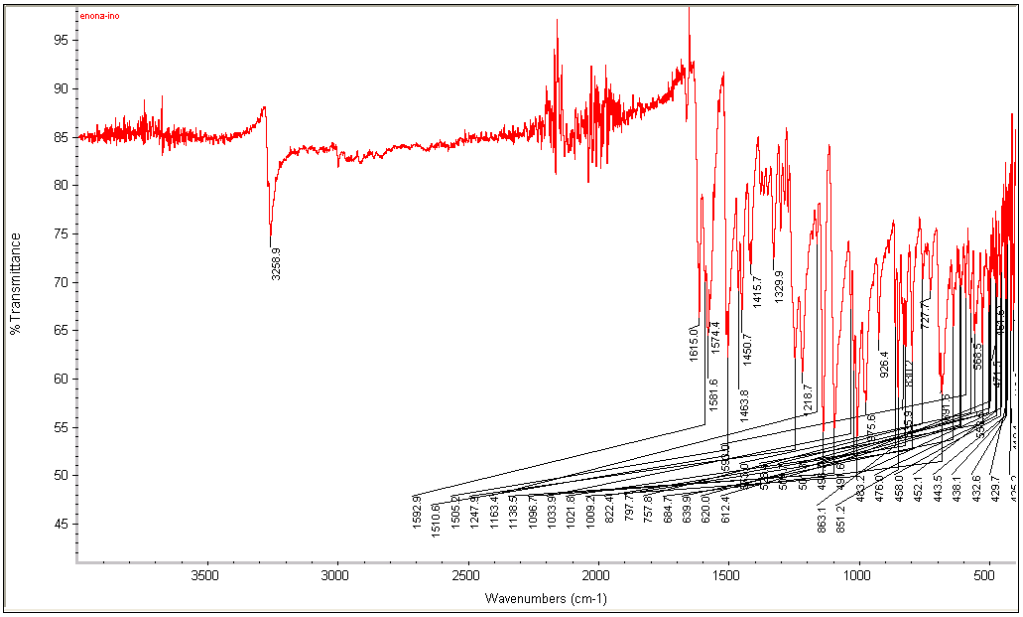
f1 (ppm)


enona-ino
% Transmittance
Wavenumbers (cm-1)
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1581.6
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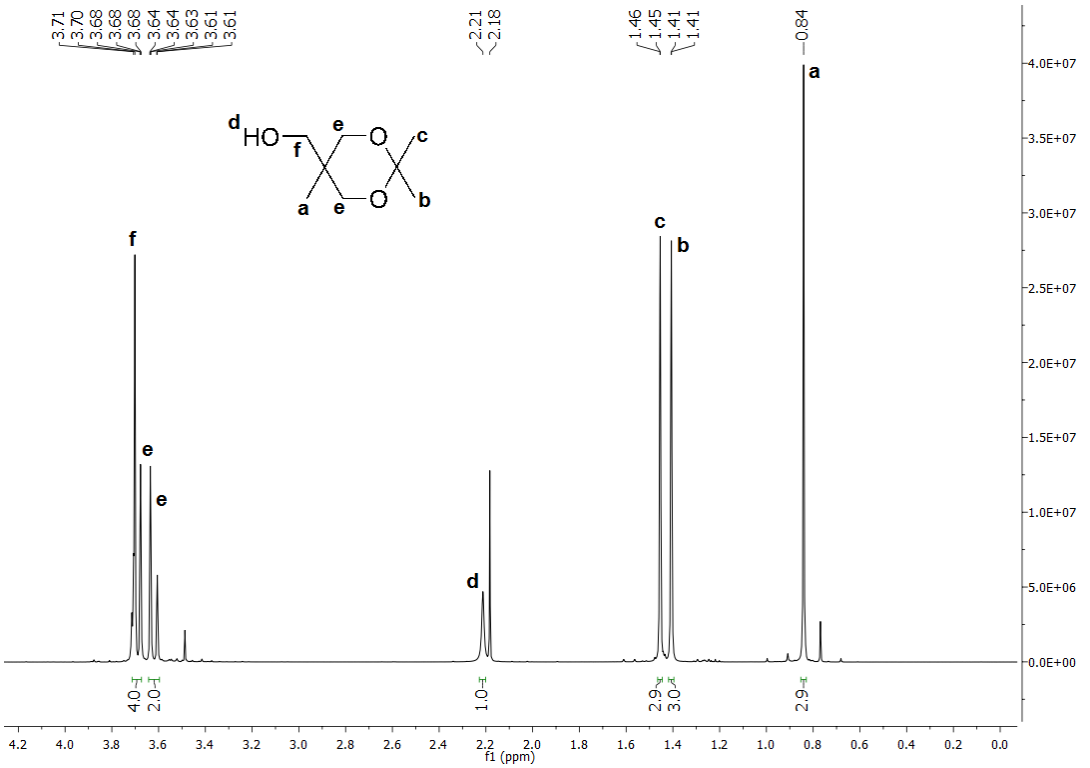
1463.8
1415.7
1329.9
1218.7
926.4
727.7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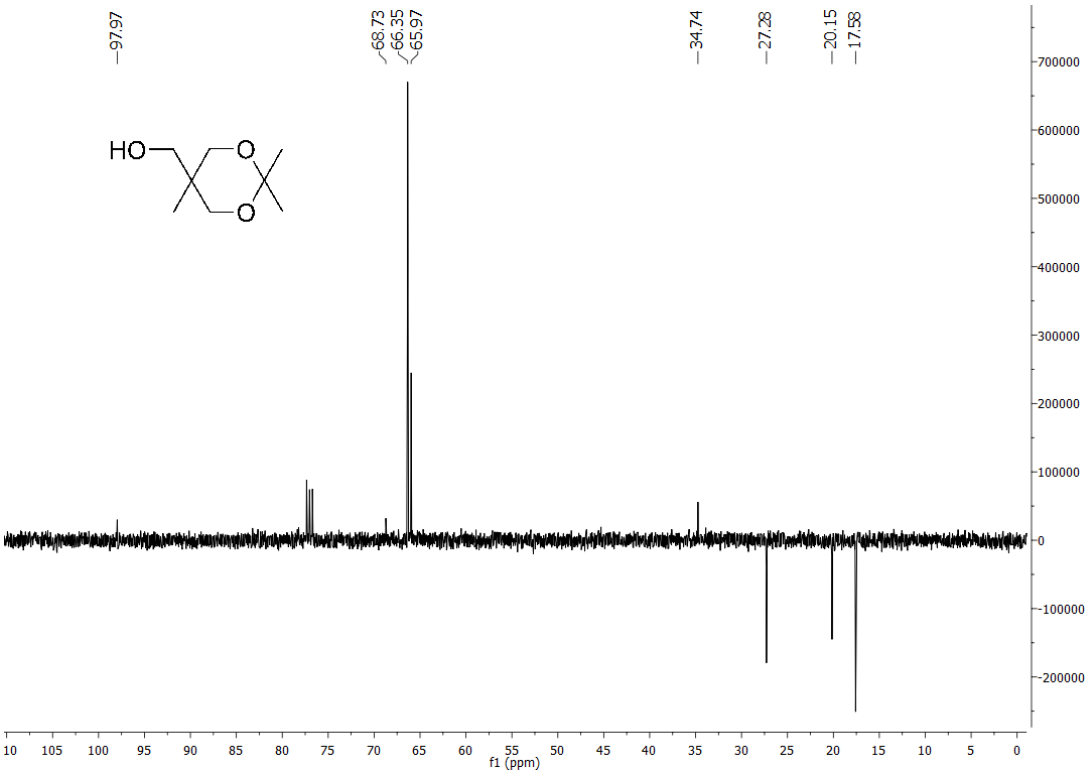
3.68
3.68
3.64
3.64
3.63
3.61
3.61
2.21
2.18
1.46
1.45
1.41
1.41
0.84
HO
a
b
c
d
e
f
4.0
2.0
1.0
2.9
3.0
2.9
f1 (ppm)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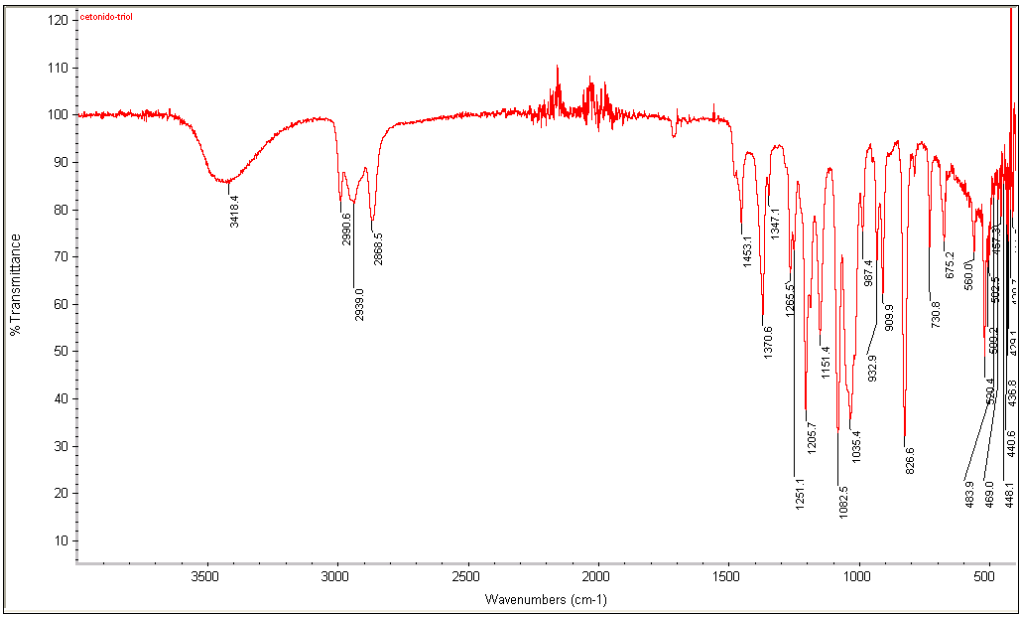
66.35
65.97
34.74
27.28
20.15
17.58
HO
f1 (ppm)


acetonido-triol
% Transmittance
Wavenumbers (cm-1)
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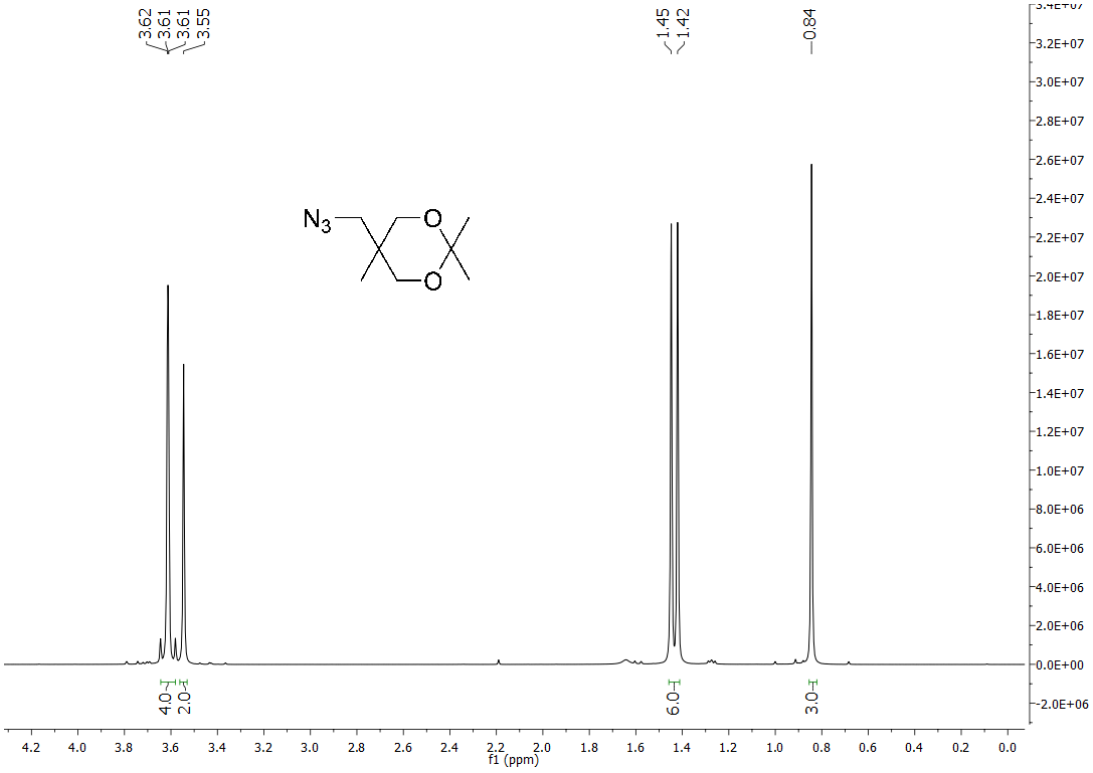
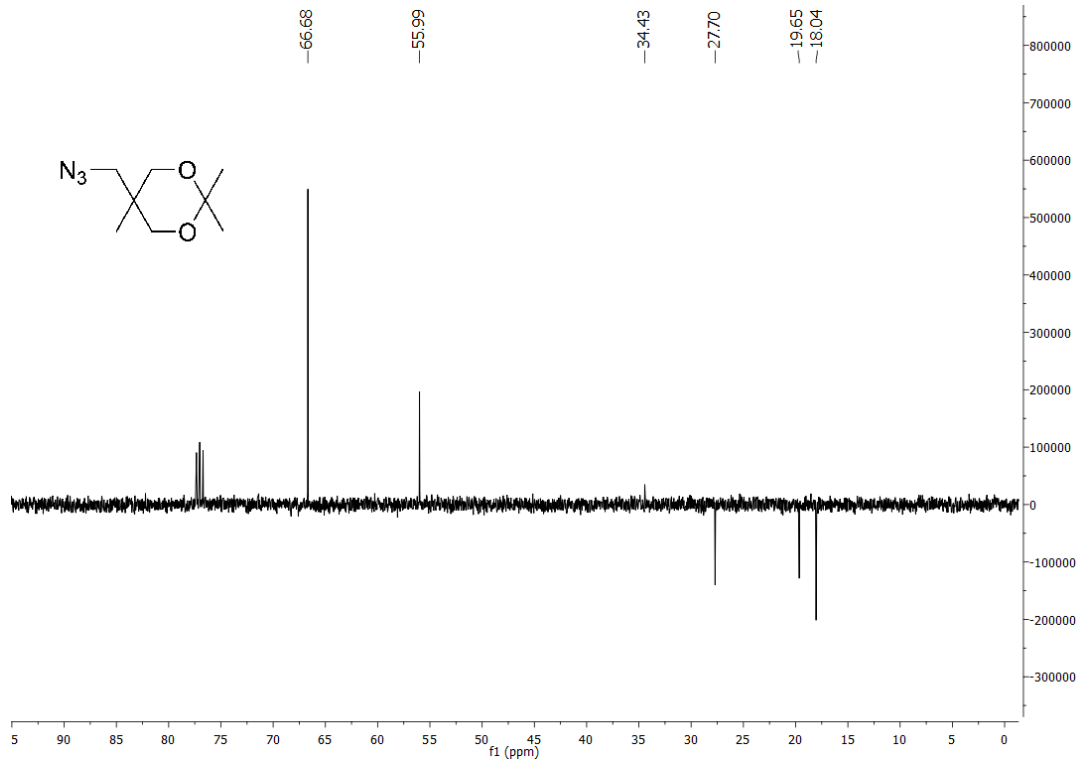
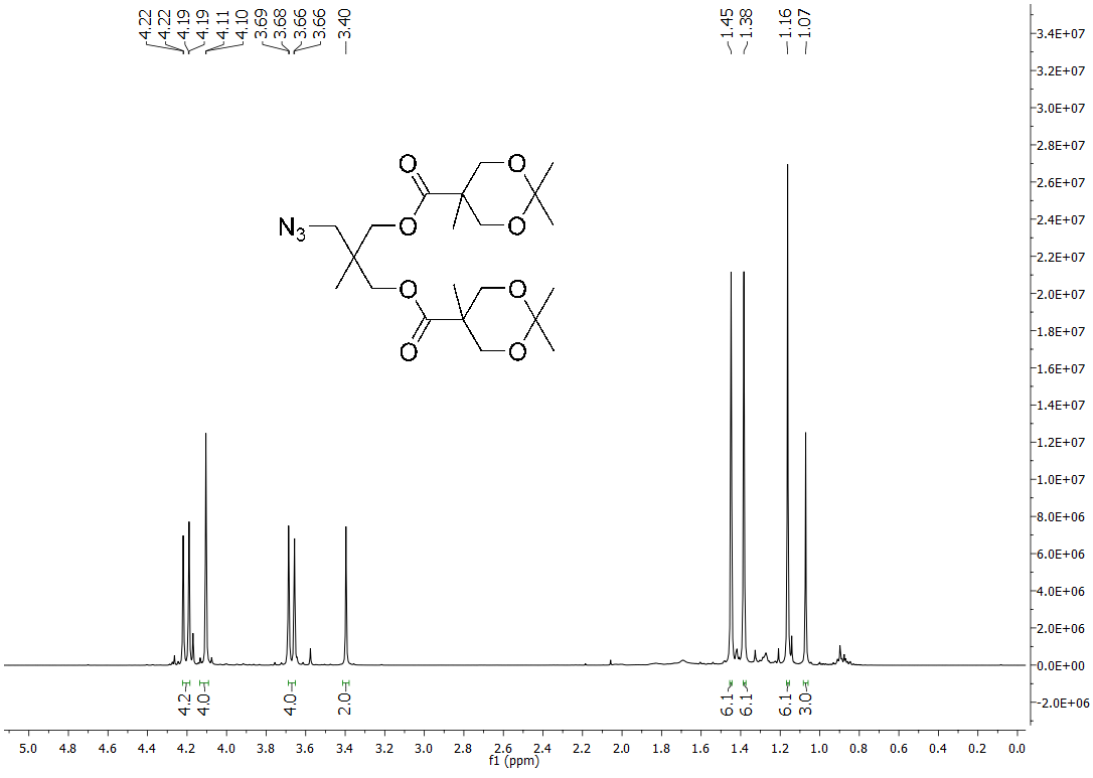
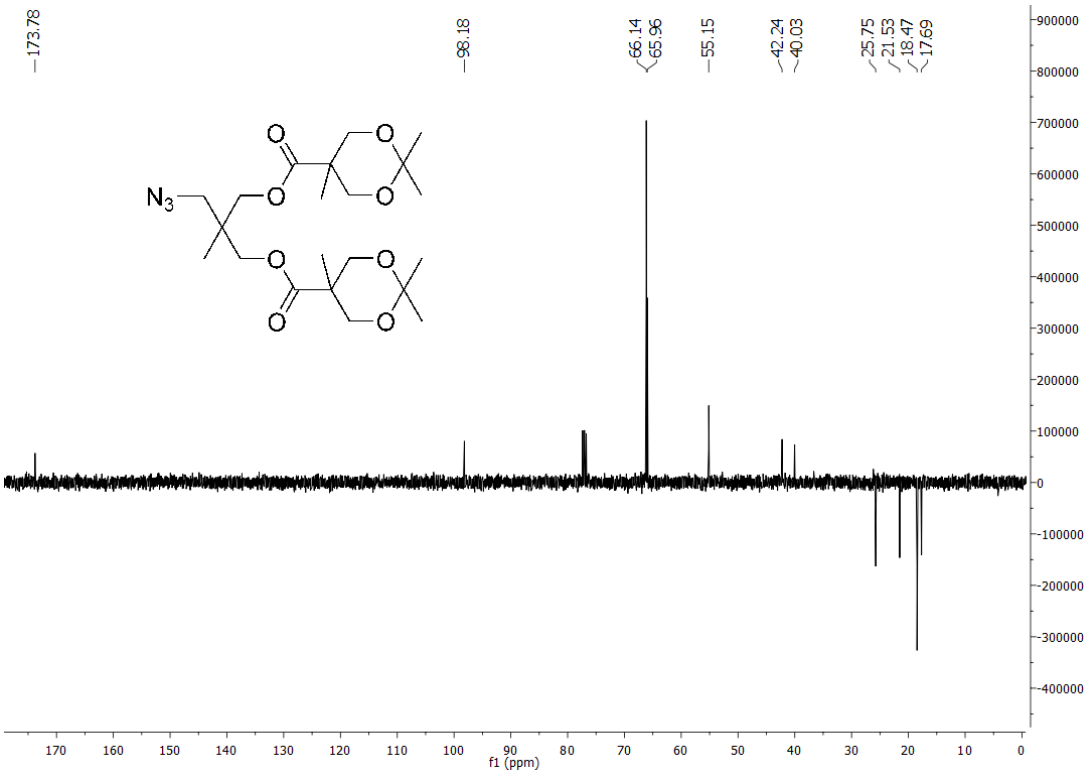
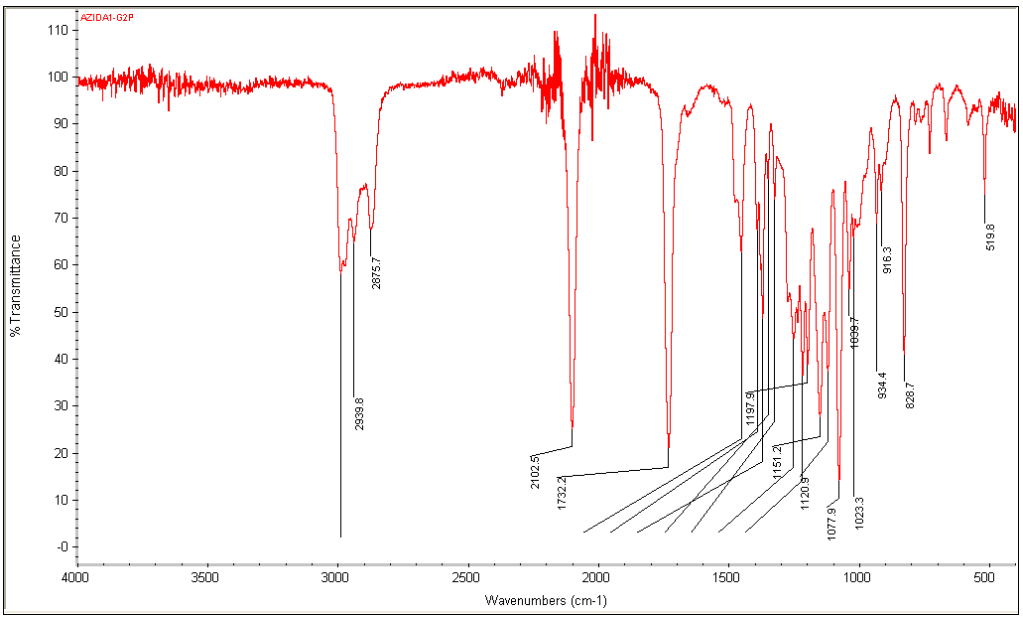
2990.6
2939.0
2868.5
1453.1
1370.6
1347.1
1265.5
1251.1
1205.7
1151.4
1082.5
1035.4
967.4
932.9
909.9
826.6
730.8
675.2
560.0
483.9
469.0
448.1
440.6
436.8

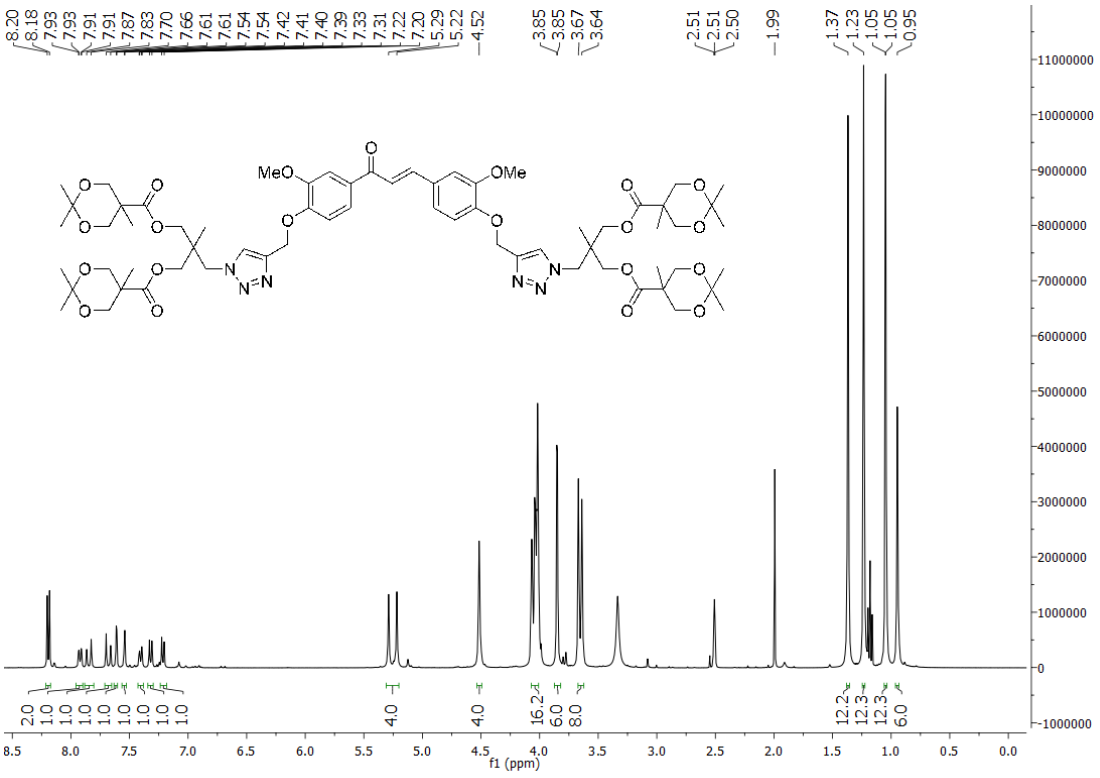

3.62
3.61
3.61
3.55
1.45
1.42
0.84
N3
O
O
4.0
2.0
6.0
3.0
f1 (ppm)

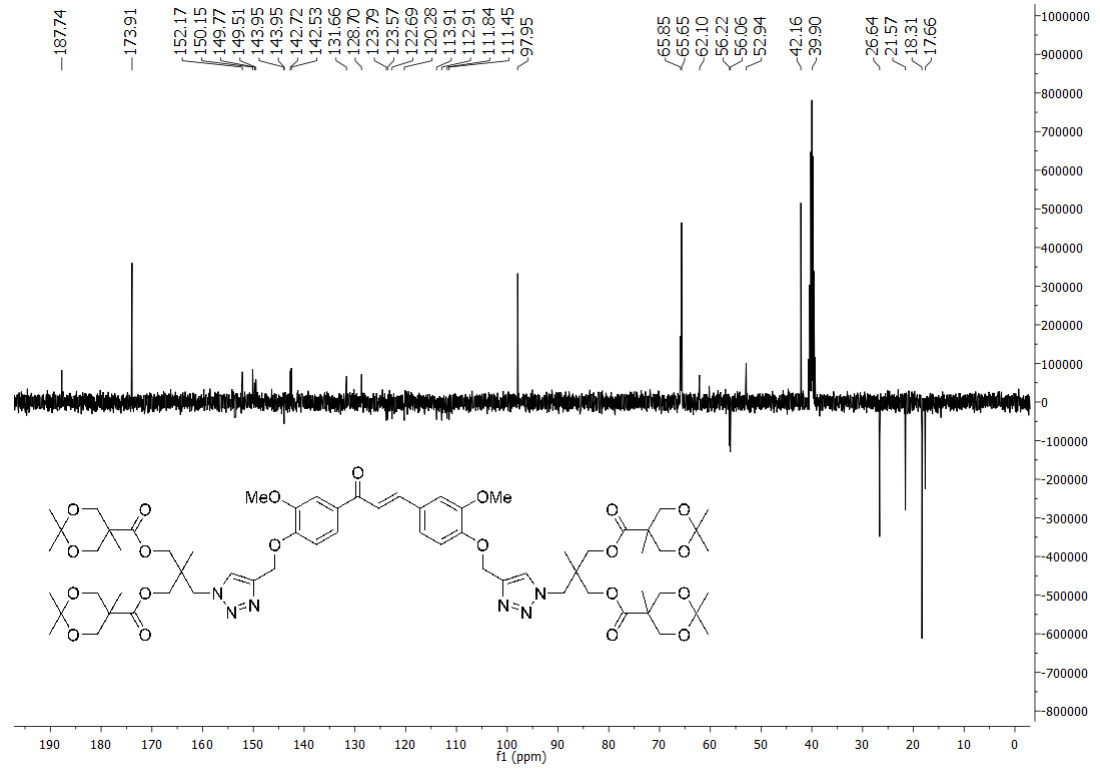

66.68
55.99
34.43
27.70
19.65
18.04
N3
O
O
f1 (ppm)

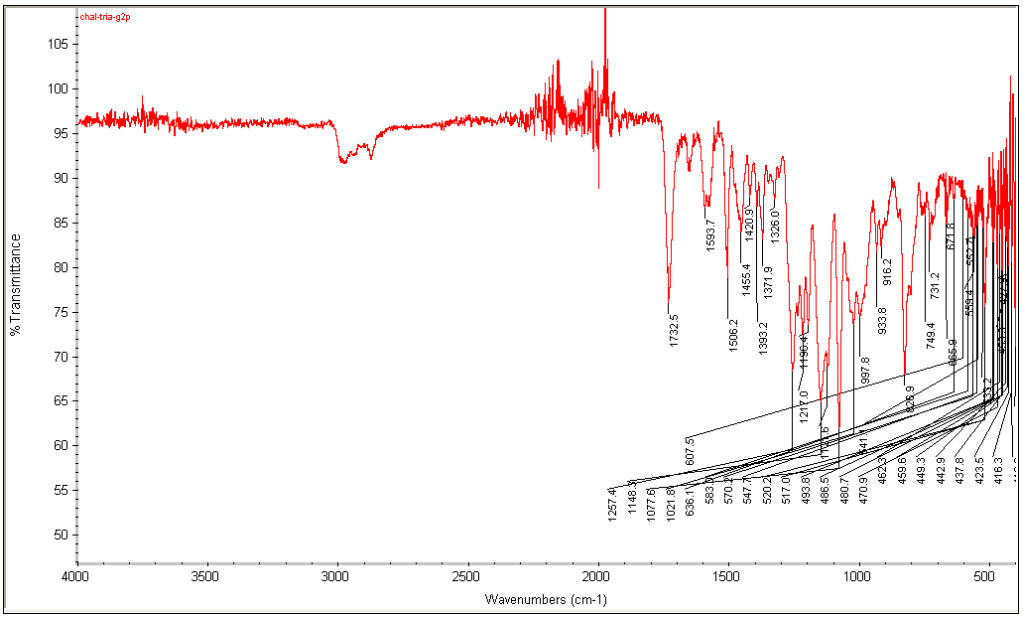

4.22
4.22
4.19
4.19
4.11
4.10
3.69
3.68
3.66
3.66
3.40
1.45
1.38
1.16
1.07
N3
O
4.2
4.0
4.0
2.0
6.1
6.1
6.1
3.0
f1 (ppm)

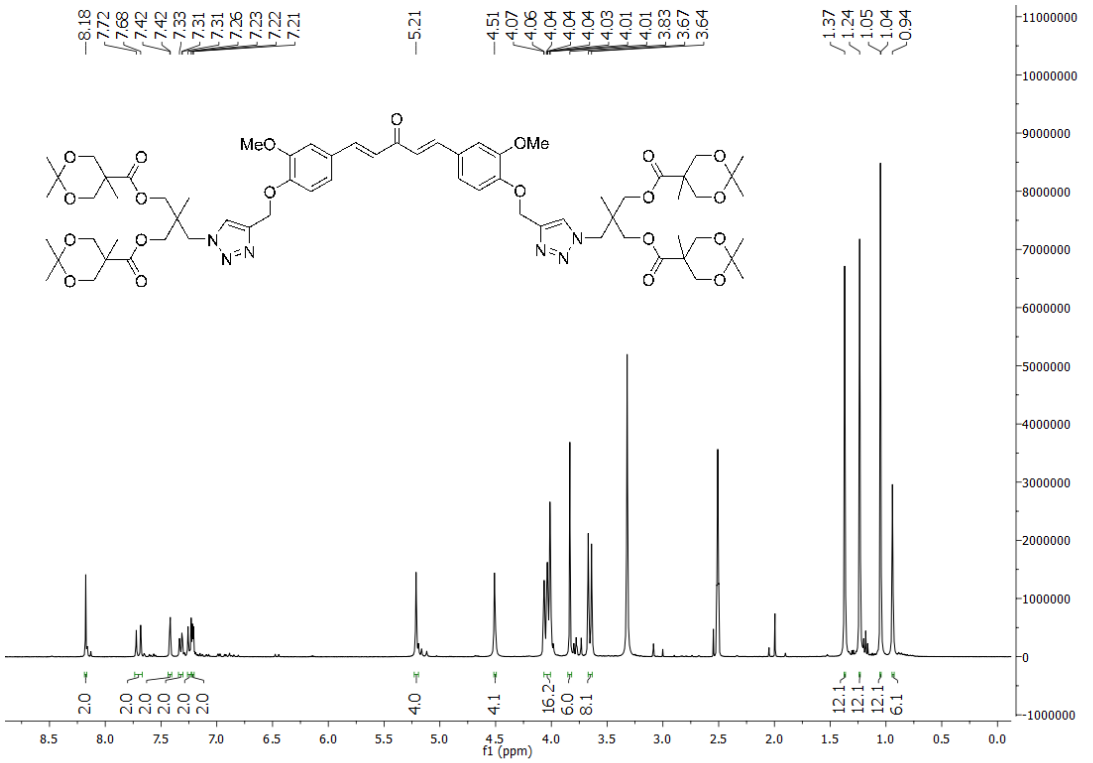

173.78
98.18
66.14
65.96
55.15
42.24
40.03
25.75
21.53
18.47
17.69
N3
f1 (ppm)

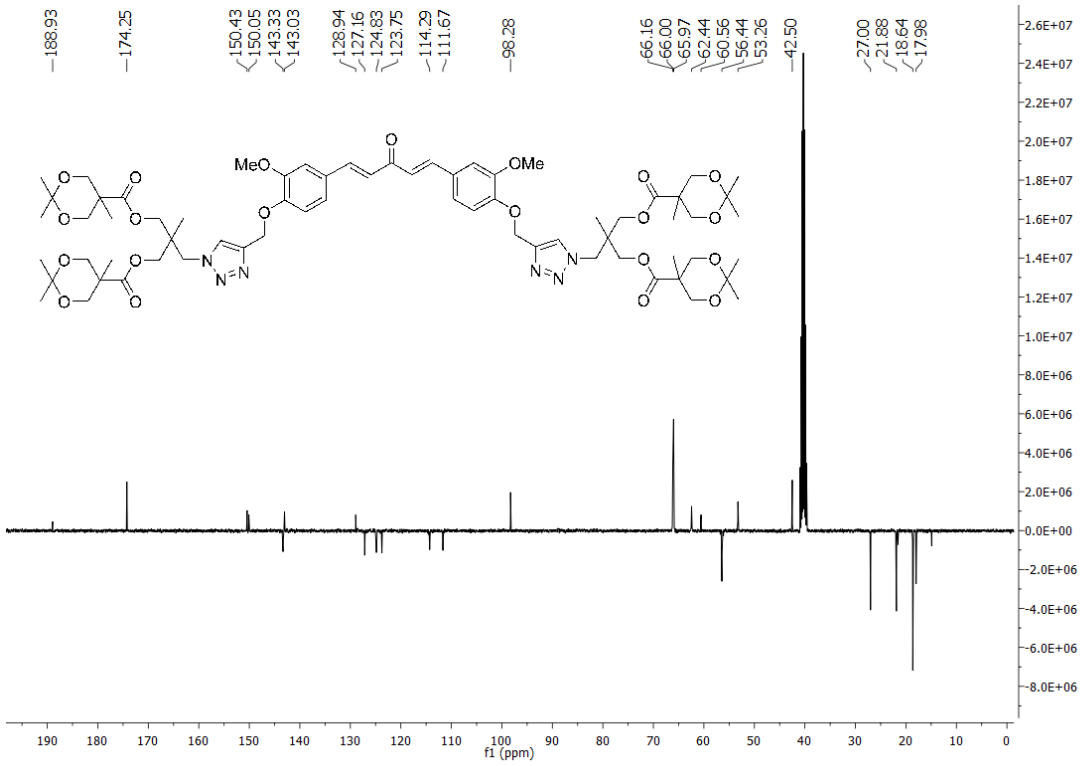

AZIDA1-02P
%Transmittance
Wavenumbers (cm-1)
2939.8
2875.7
2102.5
1732.2
1197.9
1151.2
1120.9
1077.9
1023.3
1099.7
934.4
916.3
828.7
519.8

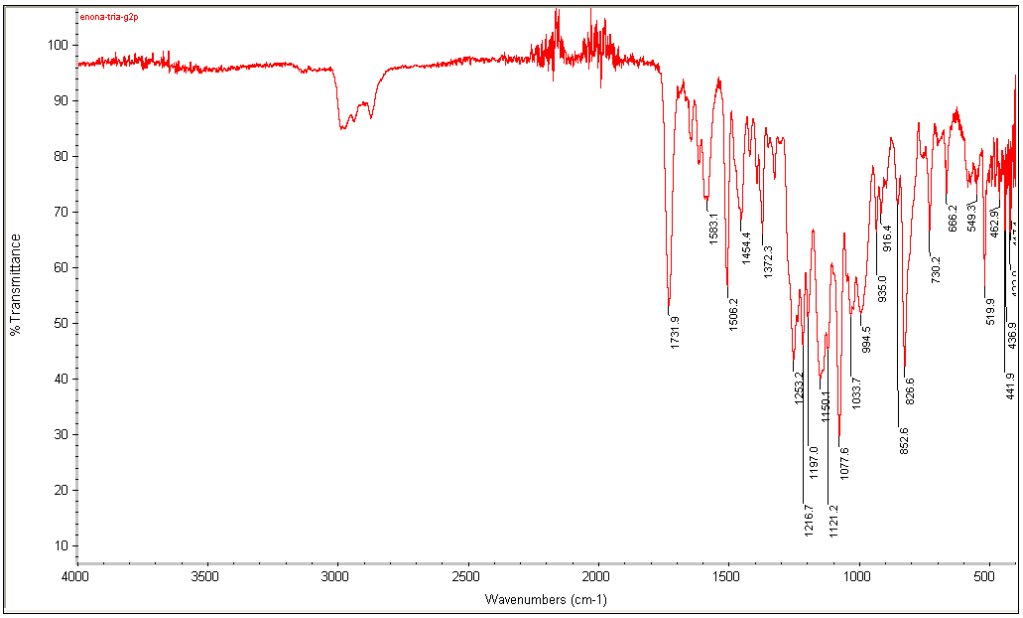

8.20
8.18
7.93
7.93
7.91
7.91
7.87
7.83
7.70
7.66
7.61
7.61
7.54
7.54
7.42
7.41
7.40
7.39
7.33
7.31
7.22
7.20
5.29
5.22
4.52
3.85
3.85
3.67
3.64
2.51
2.51
2.50
1.99
1.37
1.23
1.05
1.05
0.95
MeO
OMe
2.0
1.0
1.0
1.0
1.0
1.0
1.0
1.0
4.0
4.0
16.2
6.0
8.0
12.2
12.3
12.3
6.0
f1 (ppm)

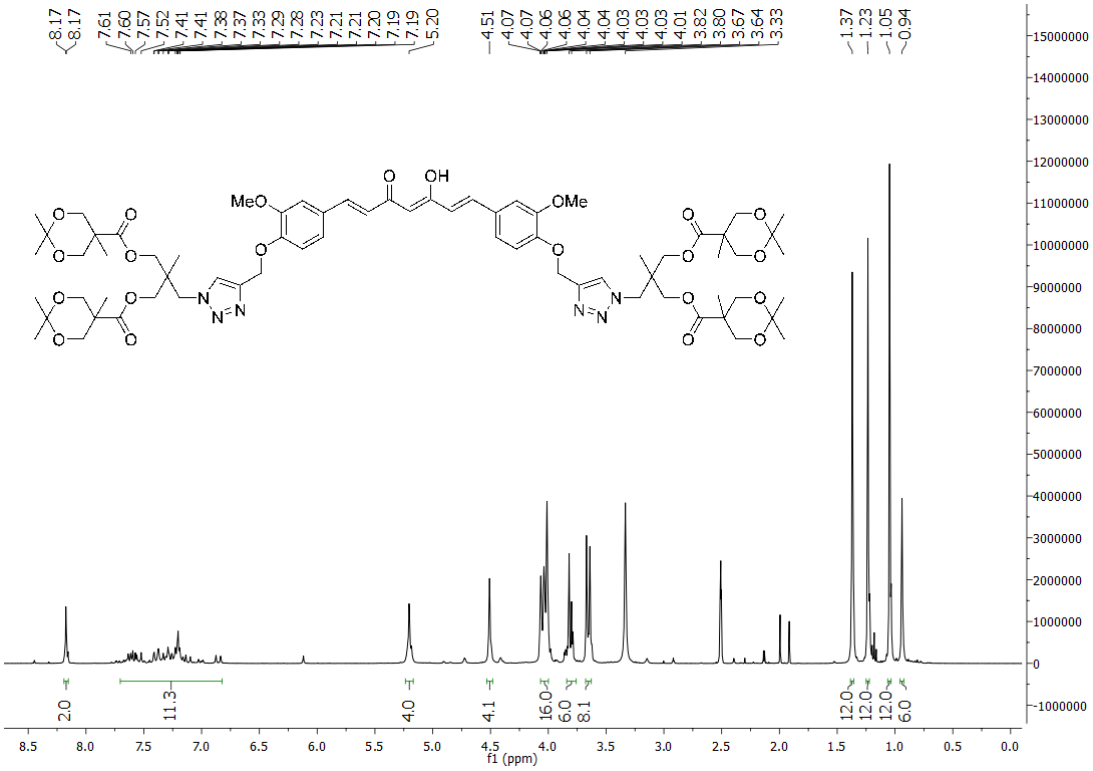

187.74
173.91
152.17
150.15
149.77
149.51
143.95
143.95
142.72
142.53
131.66
128.70
123.79
123.57
122.69
120.28
113.91
112.91
111.84
111.45
97.95
65.85
65.65
62.10
56.22
56.06
52.94
42.16
39.90
26.64
21.57
18.31
17.66
MeO
OMe
f1 (ppm)

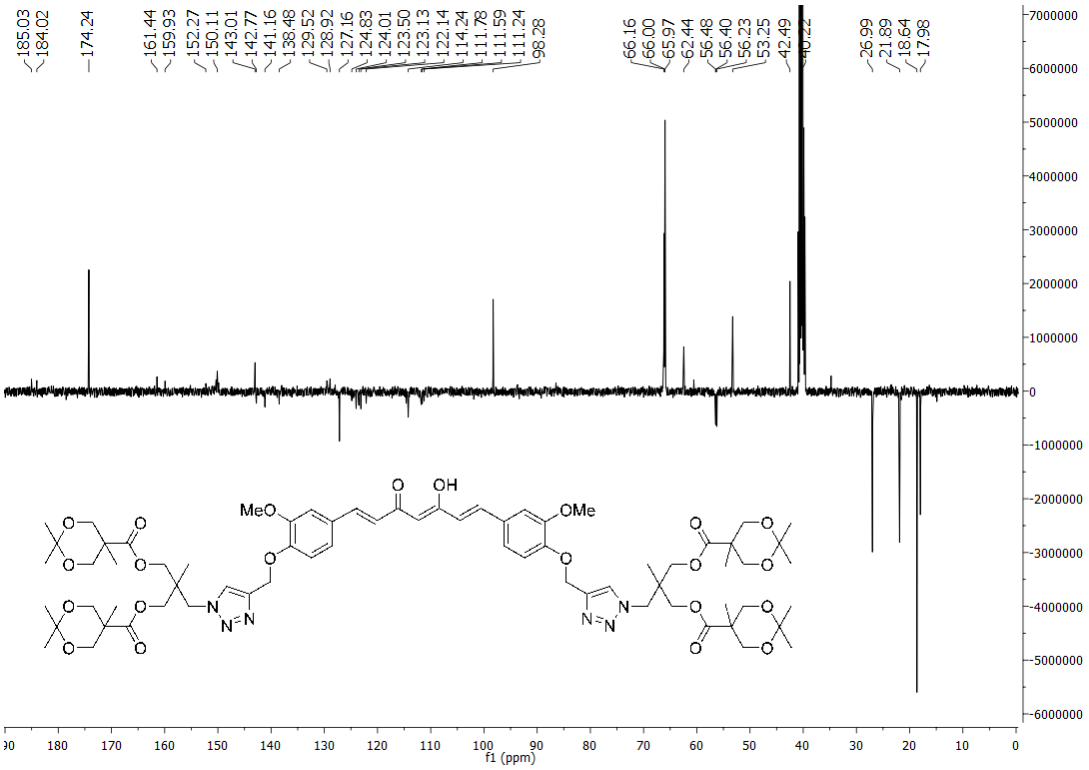

chal-tria-g2p
% Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
105
100
95
90
85
80
75
70
65
60
55
50
1732.5
1593.7
1506.2
1455.4
1420.9
1393.2
1371.9
1326.0
1257.4
1148.3
1077.6
1021.8
933.8
916.2
749.4
731.2
607.5

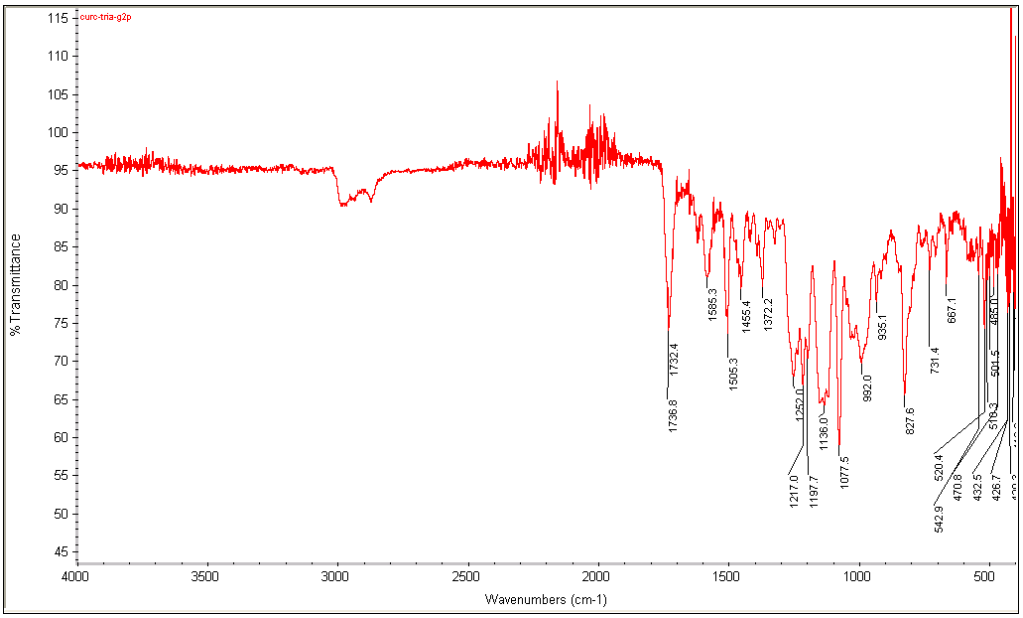

8.18
7.72
7.68
7.42
7.42
7.33
7.31
7.31
7.26
7.23
7.22
7.21
5.21
4.51
4.07
4.06
4.04
4.04
4.04
4.03
4.01
4.01
3.83
3.67
3.64
1.37
1.24
1.05
1.04
0.94
MeO
OMe
2.0
2.0
2.0
2.0
2.0
2.0
4.0
4.1
16.2
6.0
8.1
12.1
12.1
12.1
6.1
f1 (ppm)

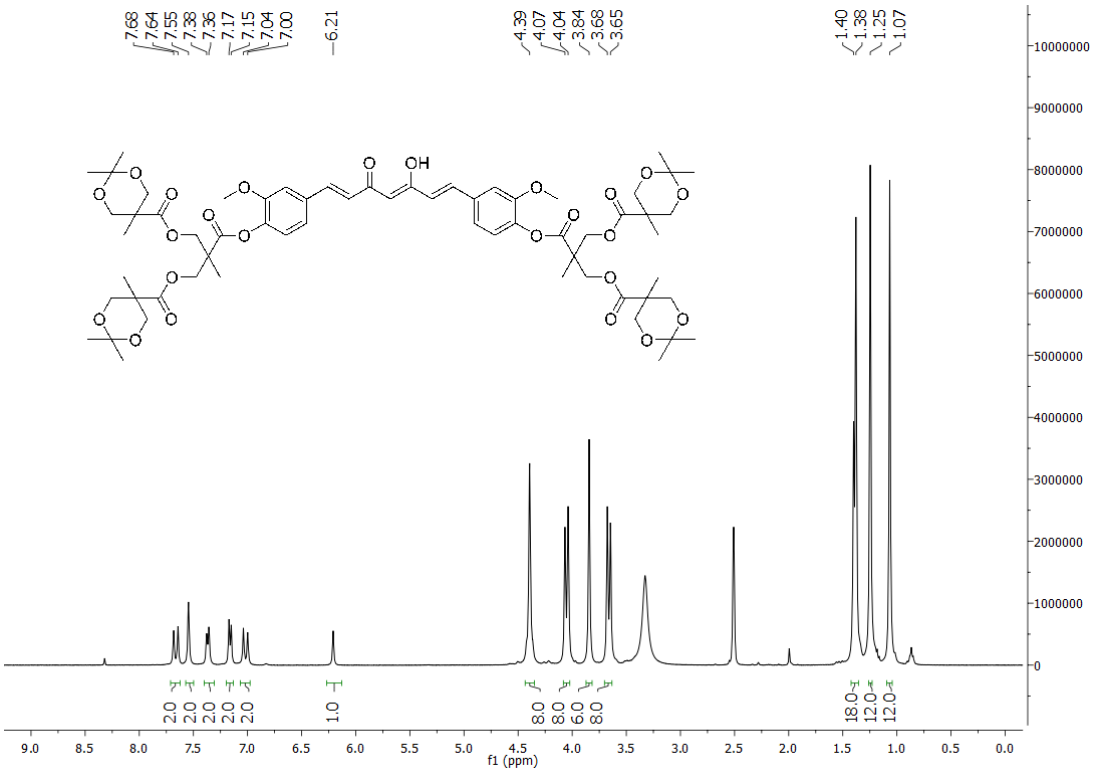

188.93
174.25
150.43
150.05
143.33
143.03
128.94
127.16
124.83
123.75
114.29
111.67
98.28
66.16
66.00
65.97
62.44
60.56
56.44
53.26
42.50
27.00
21.88
18.64
17.98
MeO
OMe
f1 (ppm)

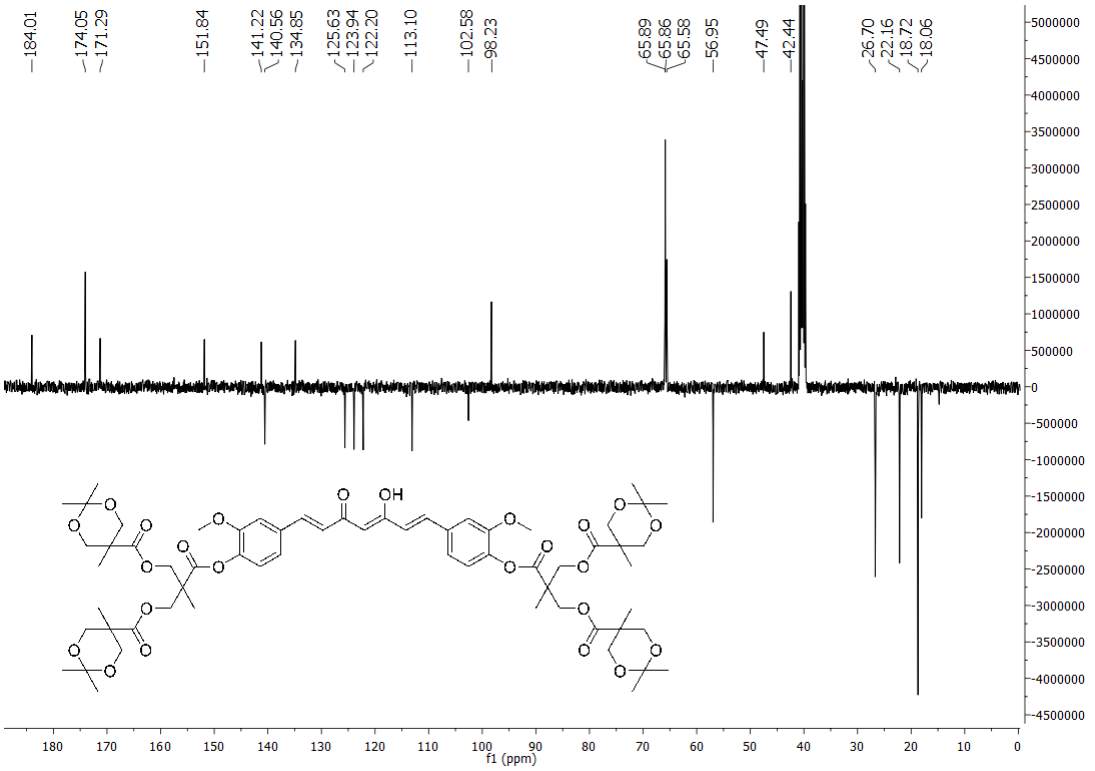

enona-tria-g2p
% Transmittance
Wavenumbers (cm-1)
1731.9
1583.1
1506.2
1454.4
1372.3
1253.2
1216.7
1197.0
1150.1
1121.2
1077.6
1033.7
994.5
935.0
916.4
852.6
826.6
730.2
666.2
549.3
519.9
462.9
441.9
436.9

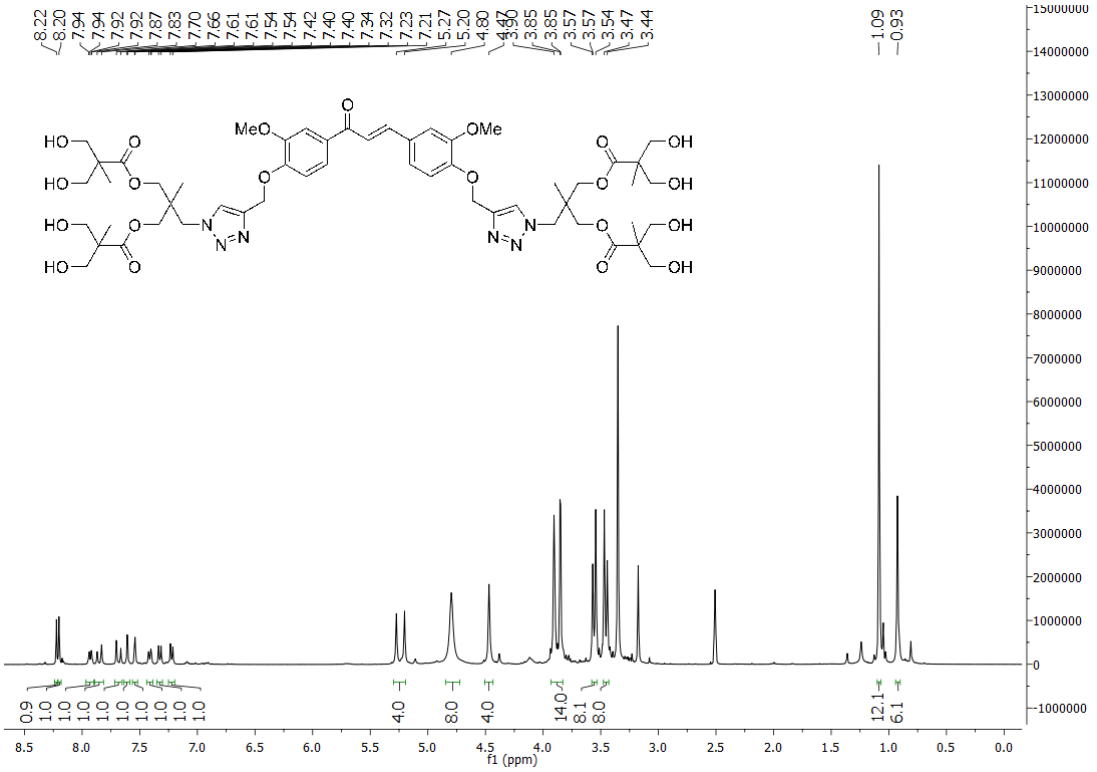

8.17
8.17
7.61
7.60
7.57
7.52
7.41
7.41
7.38
7.37
7.33
7.29
7.28
7.23
7.21
7.21
7.20
7.19
7.19
5.20
4.51
4.07
4.07
4.06
4.06
4.04
4.04
4.03
4.03
4.03
4.01
3.82
3.80
3.67
3.64
3.33
1.37
1.23
1.05
0.94
MeO
OMe
OH
2.0
11.3
4.0
4.1
16.0
6.0
8.1
12.0
12.0
12.0
6.0
f1 (ppm)

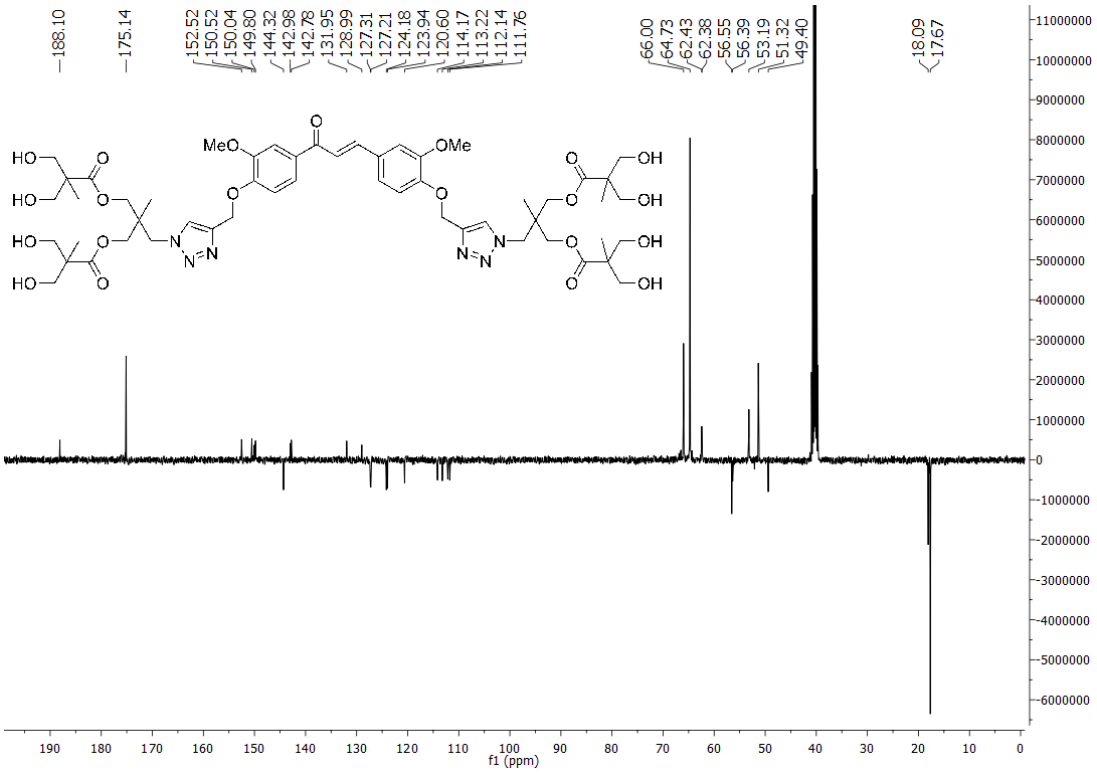

185.03
184.02
174.24
161.44
159.93
152.27
150.11
143.01
142.77
141.16
138.48
129.52
128.92
127.16
124.83
124.01
123.50
123.13
122.14
114.24
111.78
111.59
111.24
98.28
66.16
66.00
65.97
62.44
56.48
56.40
56.23
53.25
42.49
40.22
26.99
21.89
18.64
17.98
MeO
OMe
O
OH
f1 (ppm)

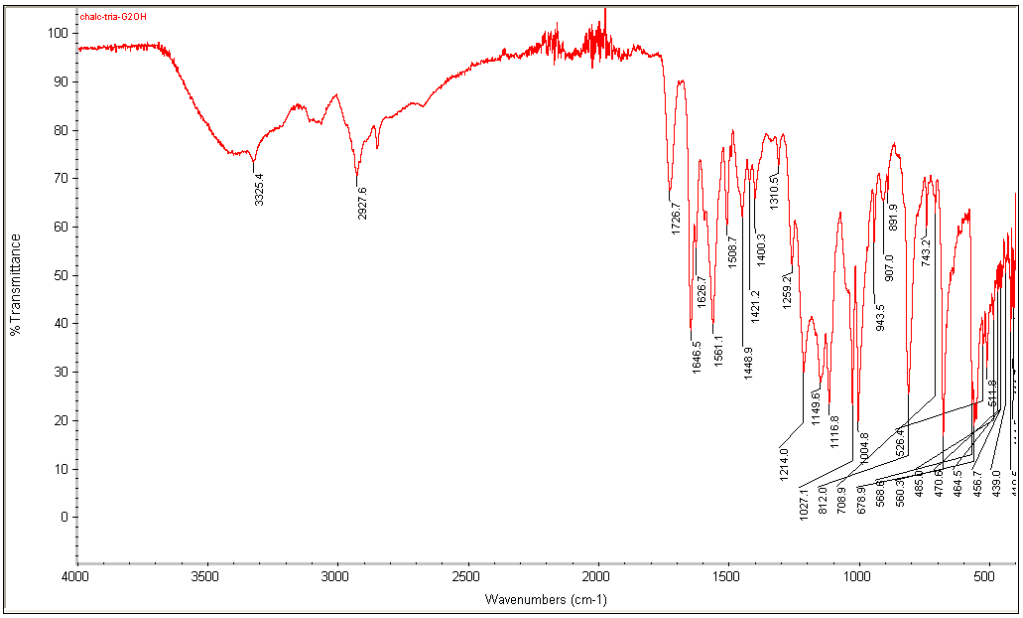

curc-tria-g2p
% Transmittance
Wavenumbers (cm-1)
1736.8
1732.4
1585.3
1505.3
1455.4
1372.2
1252.0
1217.0
1197.7
1136.0
1077.5
992.0
935.1
827.6
731.4
667.1
542.9
520.4
501.5
470.8
432.5
426.7

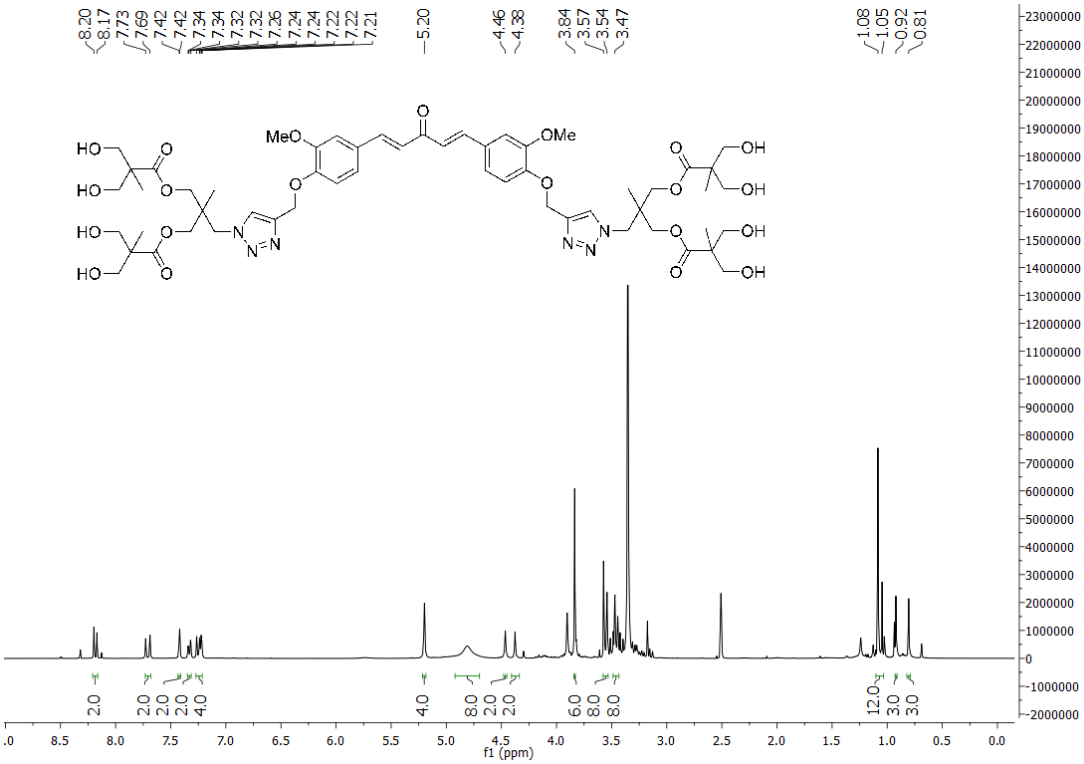

7.68
7.64
7.55
7.38
7.36
7.17
7.15
7.04
7.00
6.21
4.39
4.07
4.04
3.84
3.68
3.65
1.40
1.38
1.25
1.07
OH
2.0
2.0
2.0
2.0
2.0
1.0
8.0
8.0
6.0
8.0
18.0
12.0
12.0
f1 (ppm)

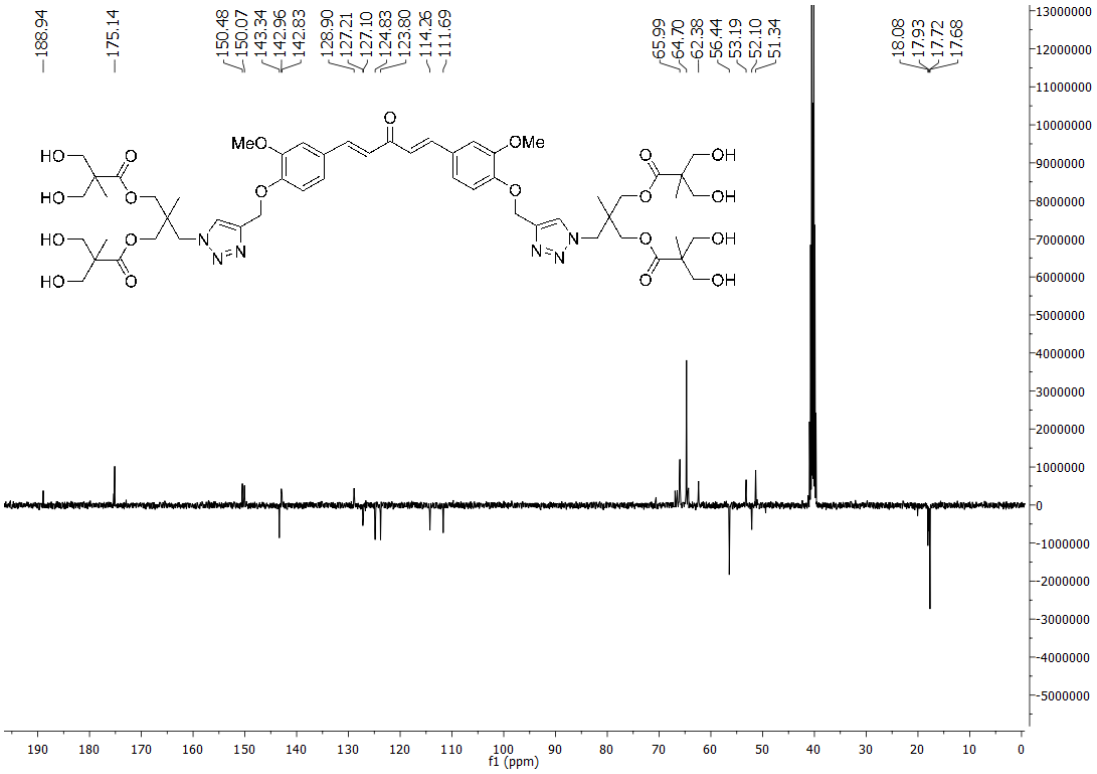

184.01
174.05
171.29
151.84
141.22
140.56
134.85
125.63
123.94
122.20
113.10
102.58
98.23
65.89
65.86
65.58
56.95
47.49
42.44
26.70
22.16
18.72
18.06
OH
f1 (ppm)

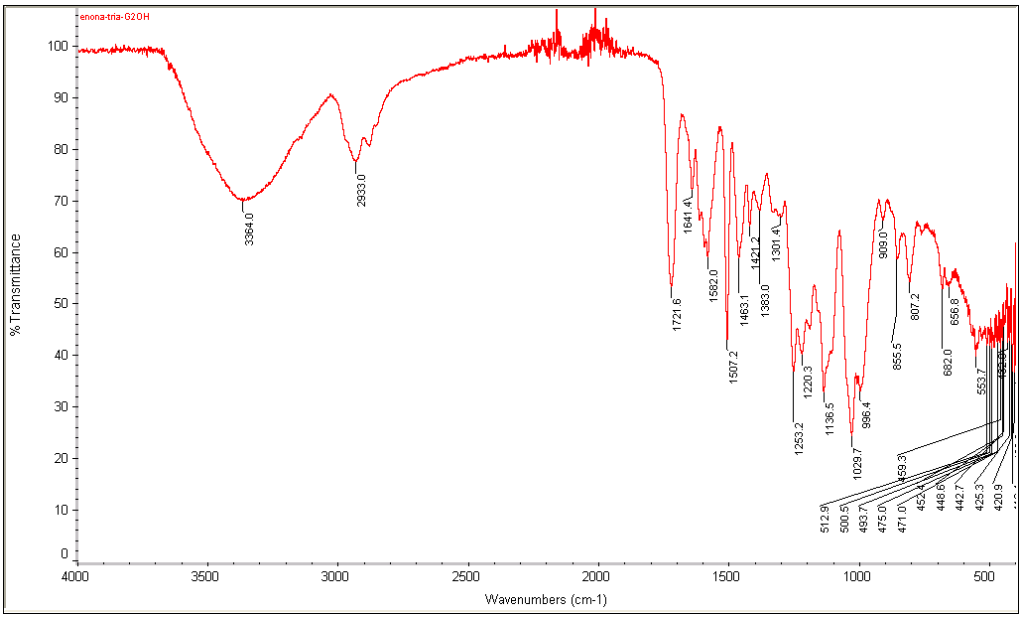

8.22
8.20
7.94
7.94
7.92
7.92
7.87
7.83
7.70
7.66
7.61
7.61
7.54
7.54
7.42
7.40
7.40
7.34
7.32
7.23
7.21
5.27
5.20
4.80
4.47
3.90
3.85
3.57
3.57
3.54
3.47
3.44
1.09
0.93
MeO
OMe
HO
OH
N
O
0.9
1.0
1.0
1.0
1.0
1.0
1.0
1.0
1.0
4.0
8.0
4.0
14.0
8.1
8.0
12.1
6.1
f1 (ppm)

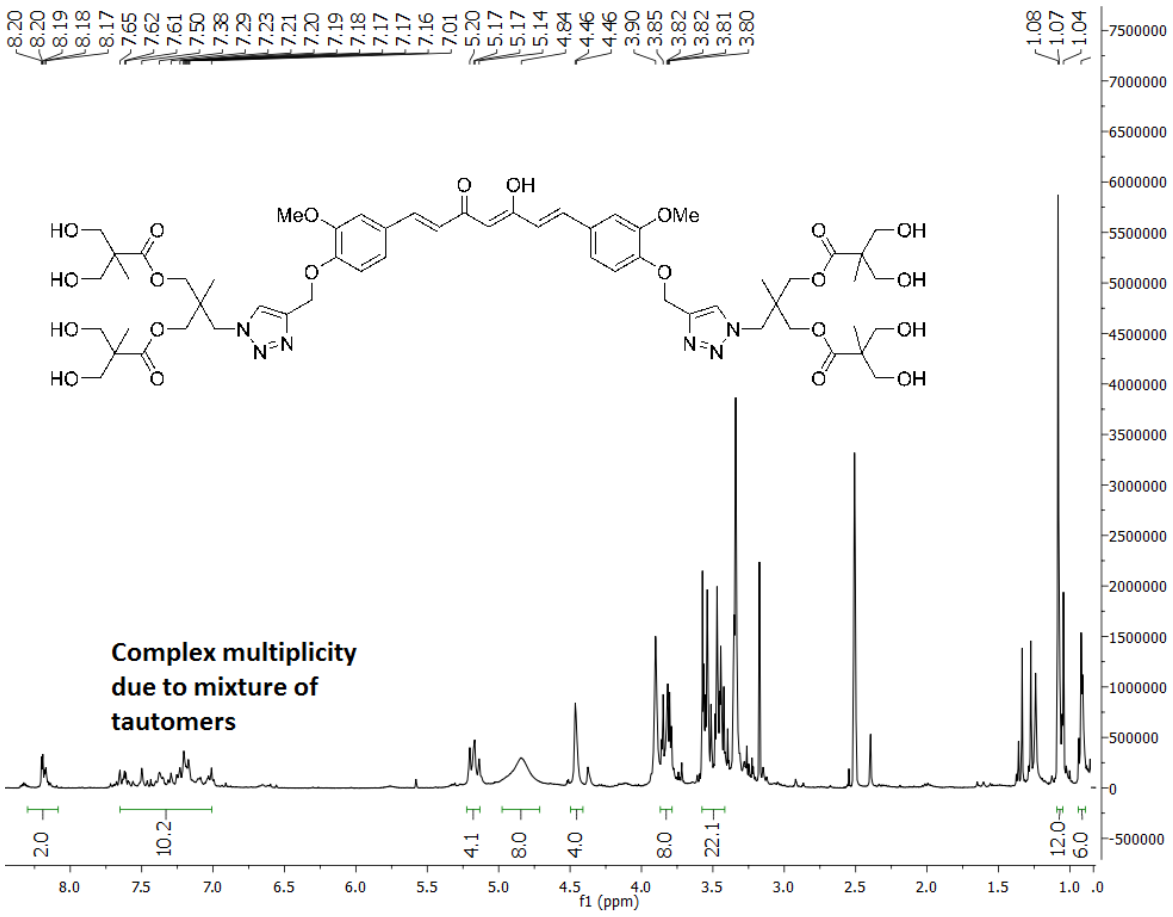

188.10
175.14
152.52
150.52
150.04
149.80
144.32
142.98
142.78
131.95
128.99
127.31
127.21
124.18
123.94
120.60
114.17
113.22
112.14
111.76
66.00
64.73
62.43
62.38
56.55
56.39
53.19
51.32
49.40
18.09
17.67
MeO
OMe
HO
OH
N
O
f1 (ppm)

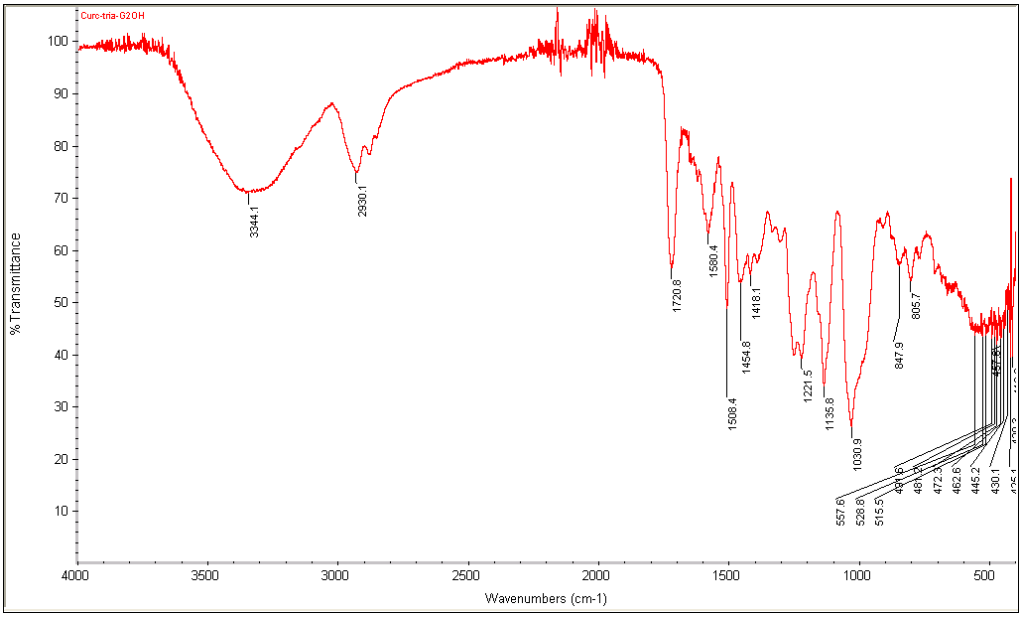

chalc-tria-G2OH
% Transmittance
Wavenumbers (cm-1)
3325.4
2927.6
1726.7
1646.5
1626.7
1561.1
1508.7
1448.9
1421.2
1400.3
1310.5
1259.2
1214.0
1149.6
1116.8
1027.1
1004.8
943.5
907.0
891.9
812.0
743.2
708.9
678.9
611.8
588.8
560.3
526.4
485.0
470.6
464.5
456.7
439.0

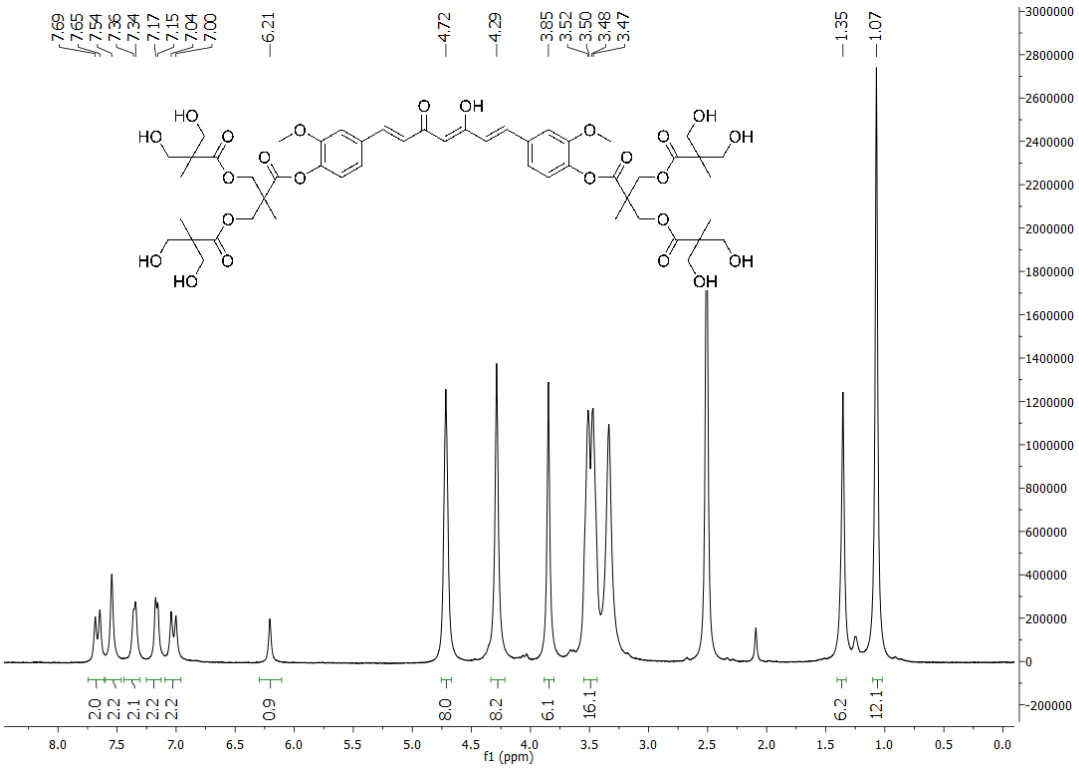

8.20
8.17
7.73
7.69
7.42
7.42
7.34
7.34
7.32
7.32
7.26
7.24
7.24
7.22
7.22
7.21
5.20
4.46
4.38
3.84
3.57
3.54
3.47
1.08
1.05
0.92
0.81
MeO
OMe
HO
OH
f1 (ppm)

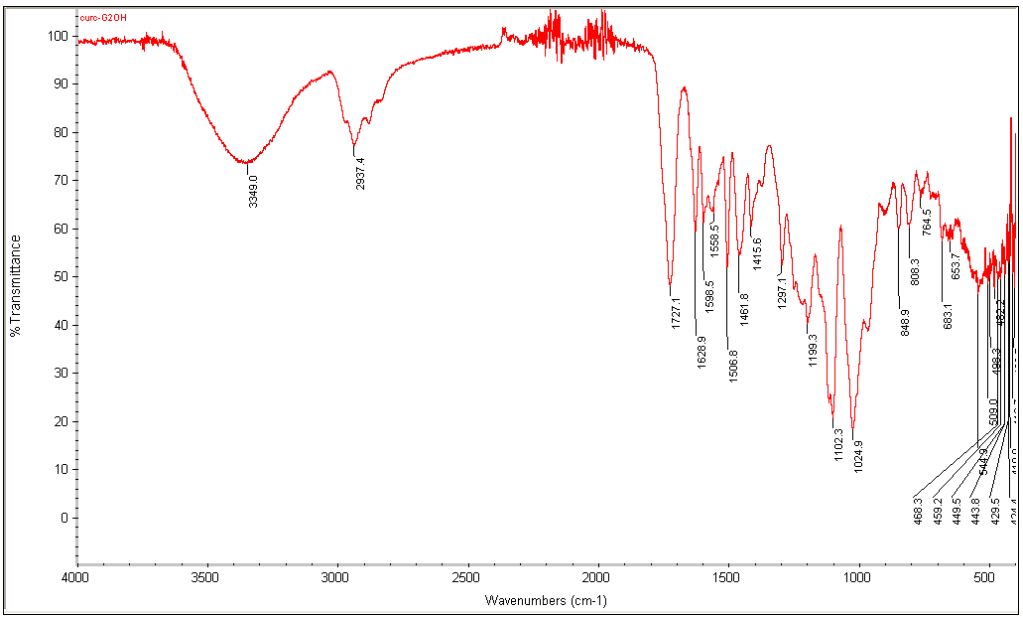

188.94
175.14
150.48
150.07
143.34
142.96
142.83
128.90
127.21
127.10
124.83
123.80
114.26
111.69
65.99
64.70
62.38
56.44
53.19
52.10
51.34
18.08
17.93
17.72
17.68
MeO
OMe
HO
OH
f1 (ppm)


enona-tria-G2OH
% Transmittance
Wavenumbers (cm-1)
3384.0
2933.0
1721.6
1641.4
1582.0
1507.2
1463.1
1421.2
1383.0
1301.4
1253.2
1220.3
1136.5
1029.7
996.4
969.0
855.5
807.2
682.0
656.8
553.7
512.9
500.5
493.7
475.0
471.0
459.3
452.4
448.6
442.7
425.3
420.9

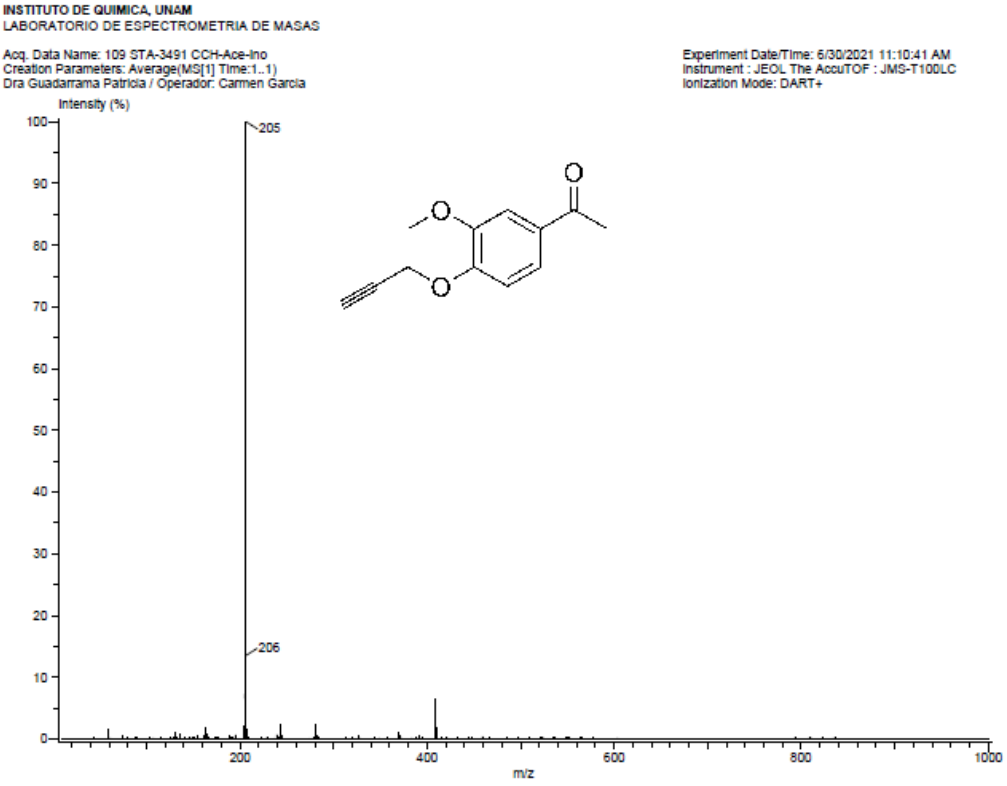

Complex multiplicity due to mixture of tautomers
f1 (ppm)

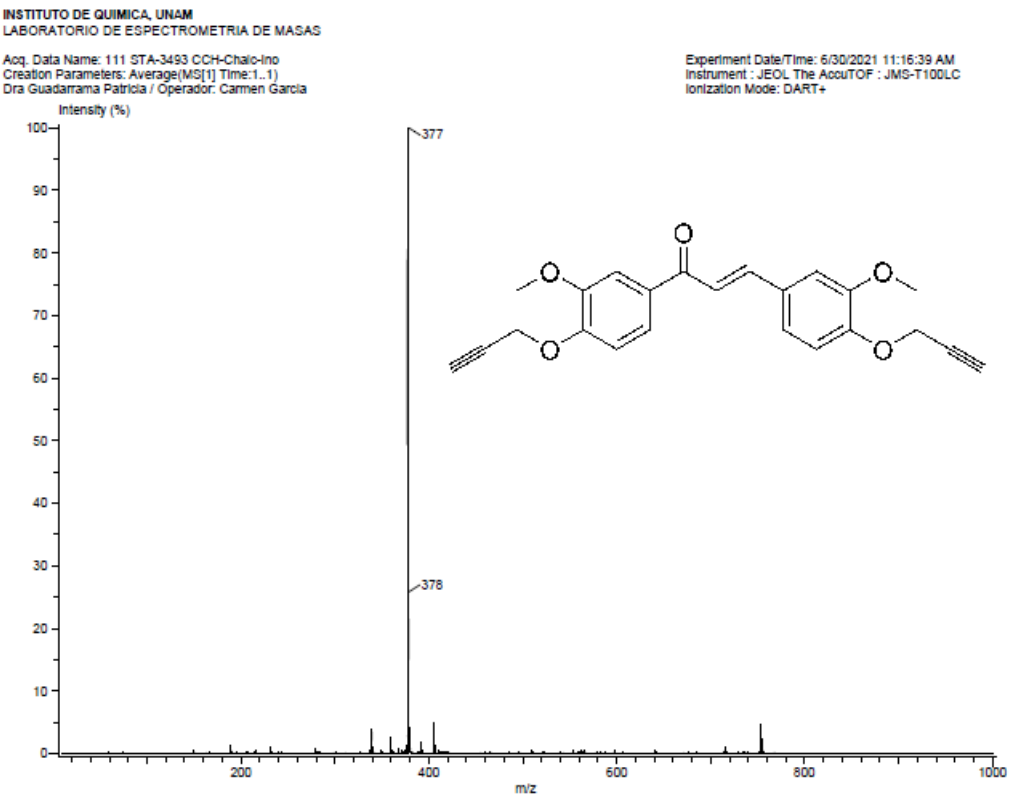

Curc-tria-G2OH
% Transmittance
Wavenumbers (cm-1)


7.69
7.65
7.54
7.36
7.34
7.17
7.15
7.04
7.00
6.21
4.72
4.29
3.85
3.52
3.50
3.48
3.47
1.35
1.07
HO
OH
2.0
2.2
2.1
2.2
2.2
0.9
8.0
8.2
6.1
16.1
6.2
12.1
f1 (ppm)


curc-G2OH
% Transmittance
Wavenumbers (cm-1)
3349.0
2937.4
1727.1
1628.9
1598.5
1558.5
1506.8
1461.8
1415.8
1297.1
1198.3
1102.3
1024.9
848.9
806.3
764.5
683.1
653.7
509.0
468.3
459.2
449.5
443.8
429.5

13. Mass spectrometry of new compounds.

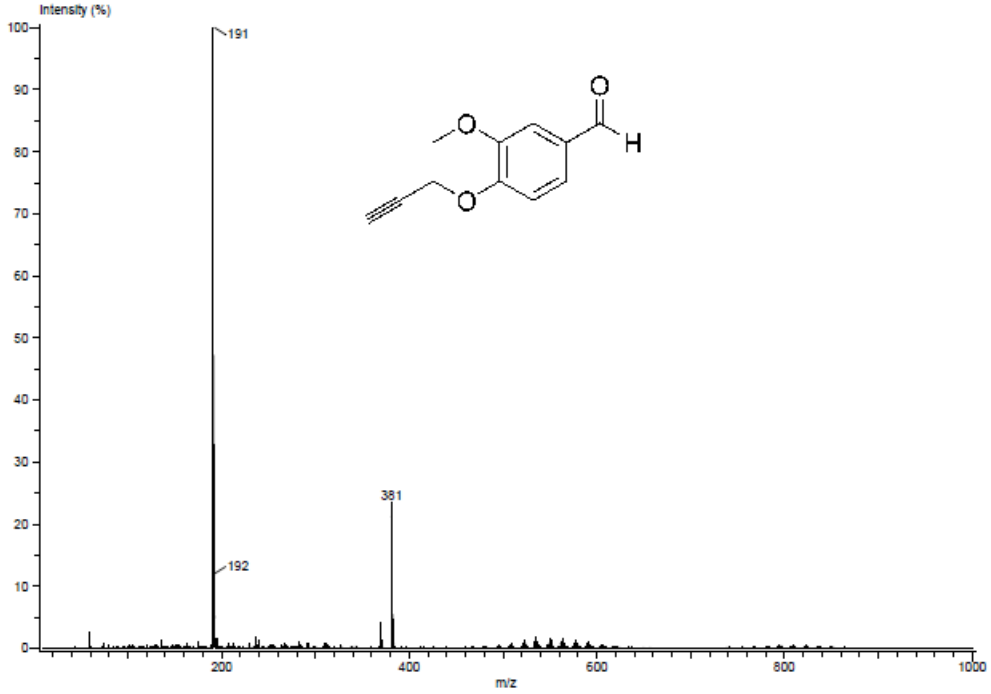




INSTITUTO DE QUIMICA, UNAM
LABORATORIO DE ESPECTROMETRIA DE MASAS

Acq. Data Name: 108 STA-3490 CCH-Val-Ino
Creation Parameters: Average(MS[1] Time:1..2)
Dra Guadarrama Patricia / Operador: Carmen Garcia

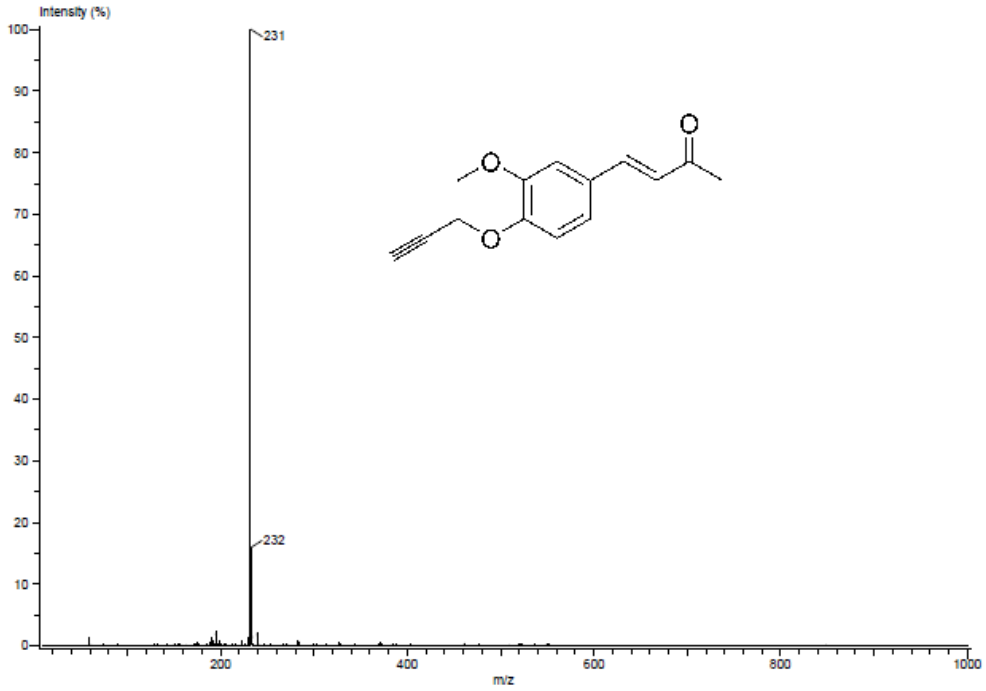
Experiment Date/Time: 6/30/2021 11:06:50 AM
Instrument : JEOL The AccuTOF : JMS-T100LC
Ionization Mode: DART+



INSTITUTO DE QUIMICA, UNAM
LABORATORIO DE ESPECTROMETRIA DE MASAS

Acq. Data Name: 110 STA-3492 CCH-FerMe-Ino
Creation Parameters: Average(MS[1] Time:0..1)
Dra Guadarrama Patricia / Operador: Carmen Garcia

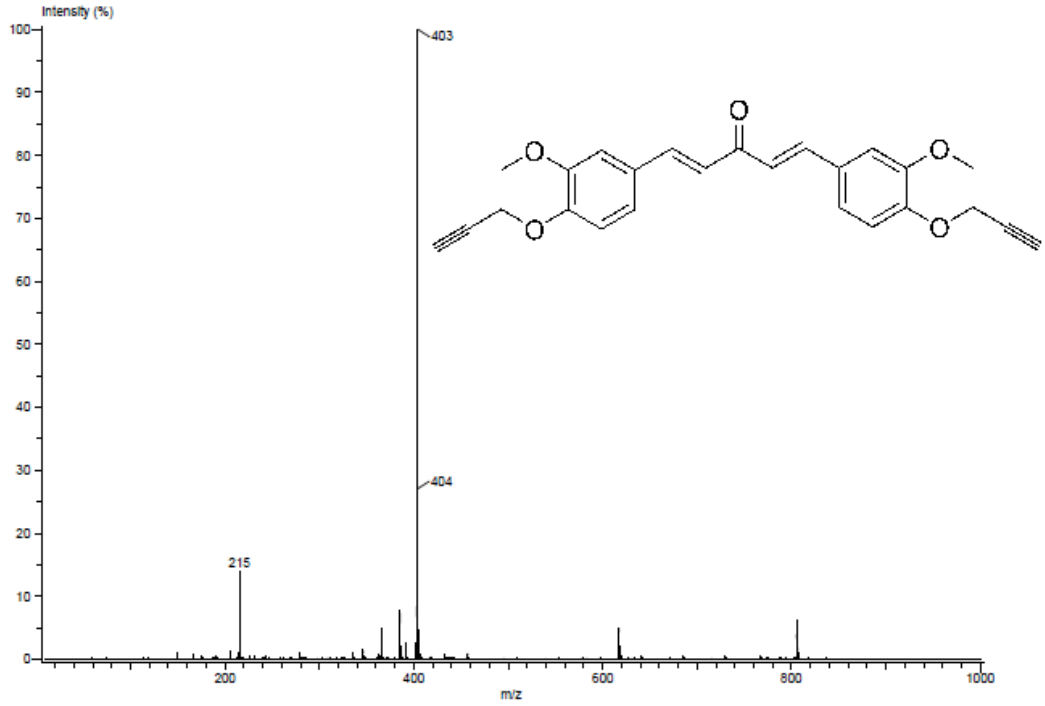
Experiment Date/Time: 6/30/2021 11:13:45 AM
Instrument : JEOL The AccuTOF : JMS-T100LC
Ionization Mode: DART+



INSTITUTO DE QUIMICA, UNAM
LABORATORIO DE ESPECTROMETRIA DE MASAS

Acq. Data Name: 112 STA-3494 CCH-Eno-Ino
Creation Parameters: Average(MS[1] Time:1..1)
Dra Guadarrama Patricia / Operador: Carmen Garcia

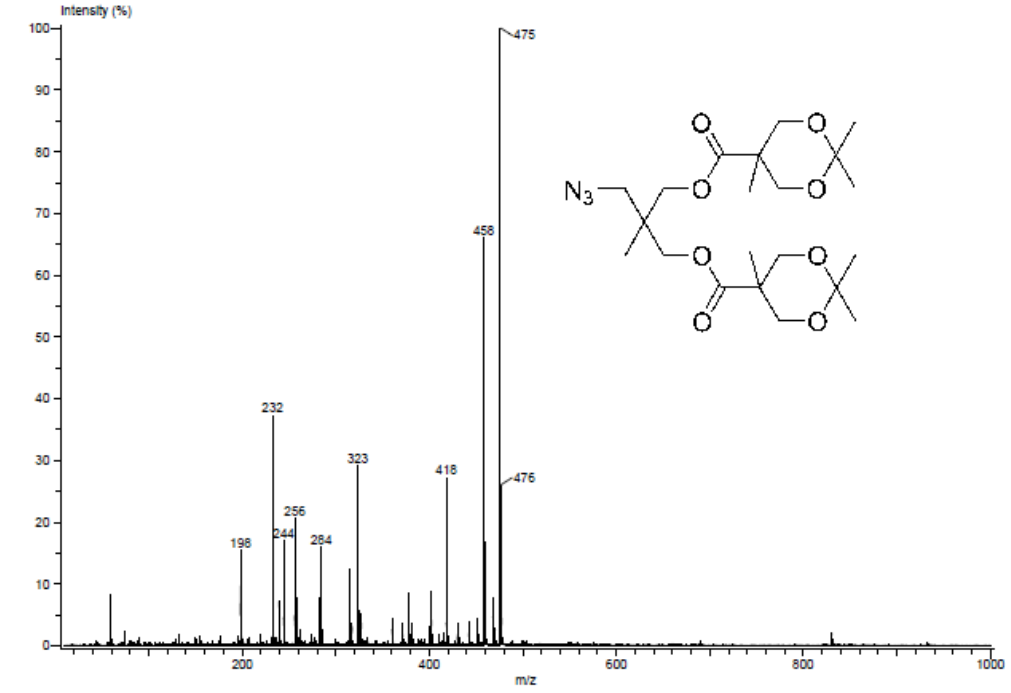
Experiment Date/Time: 6/30/2021 11:19:35 AM
Instrument : JEOL The AccuTOF : JMS-T100LC
Ionization Mode: DART+



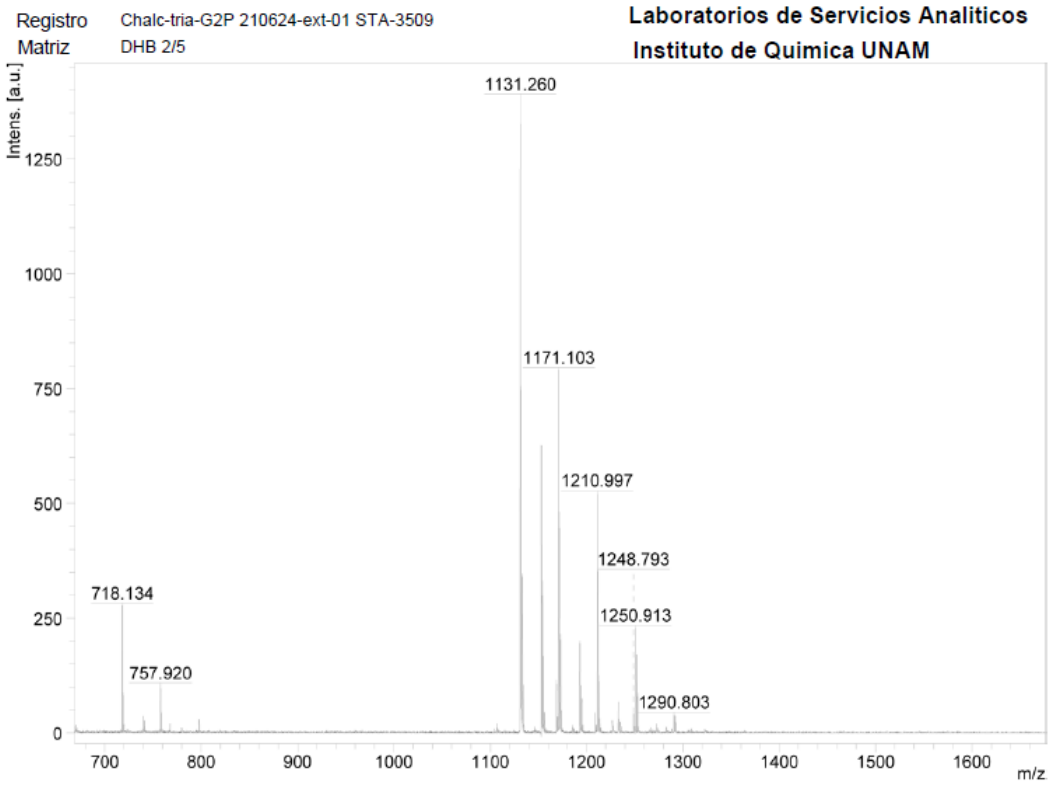
INSTITUTO DE QUIMICA, UNAM
LABORATORIO DE ESPECTROMETRIA DE MASAS

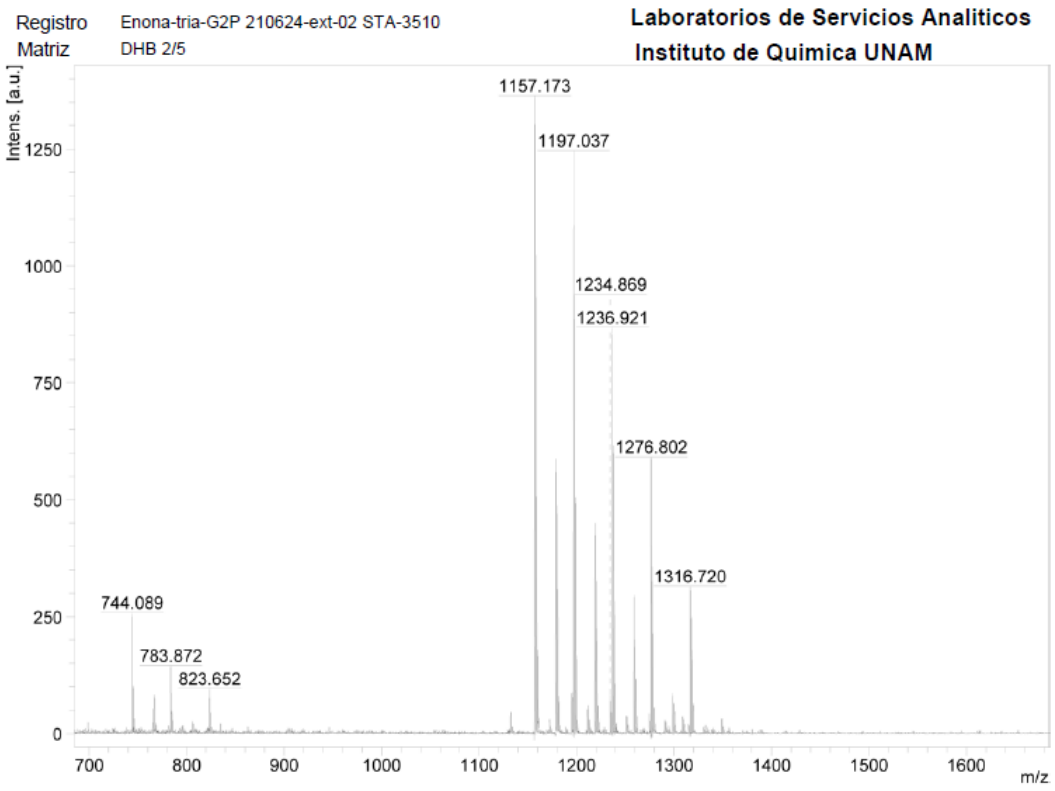
Acq. Data Name: 113 STA-3495 CCH-N3-1G2P
Creation Parameters: Average(MS[1] Time:1..1)
Dra Guadarrama Patricia / Operador: Carmen Garcia

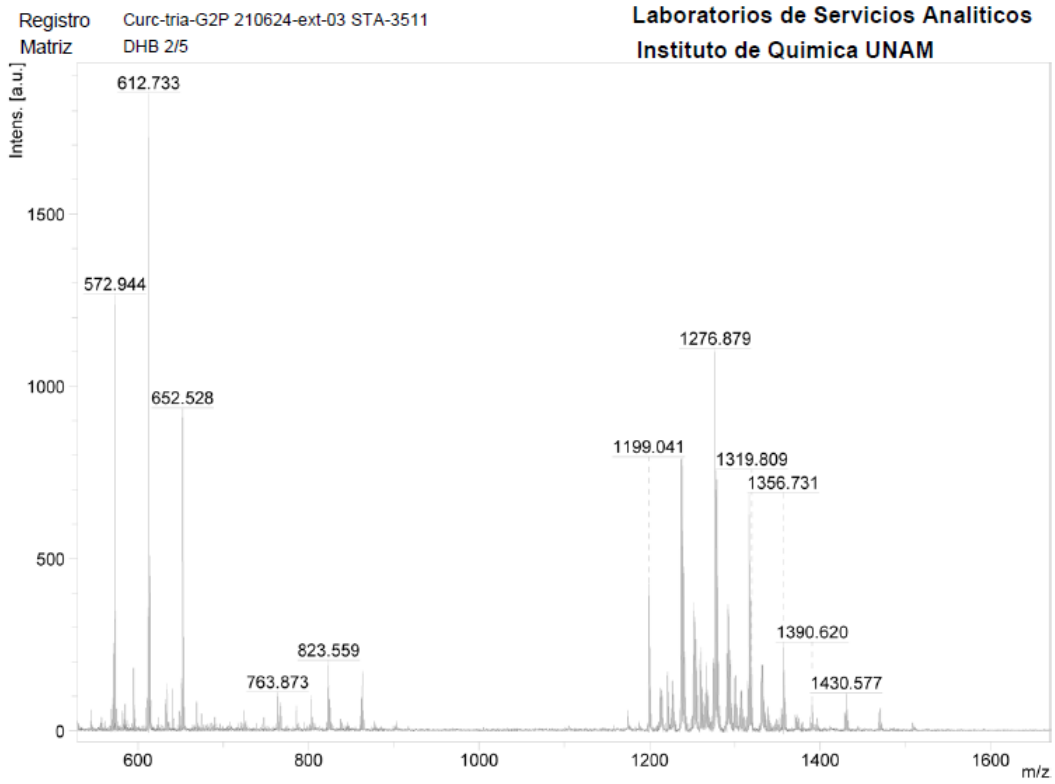
Experiment Date/Time: 6/30/2021 11:23:41 AM
Instrument : JEOL The AccuTOF : JMS-T100LC
Ionization Mode: DART+

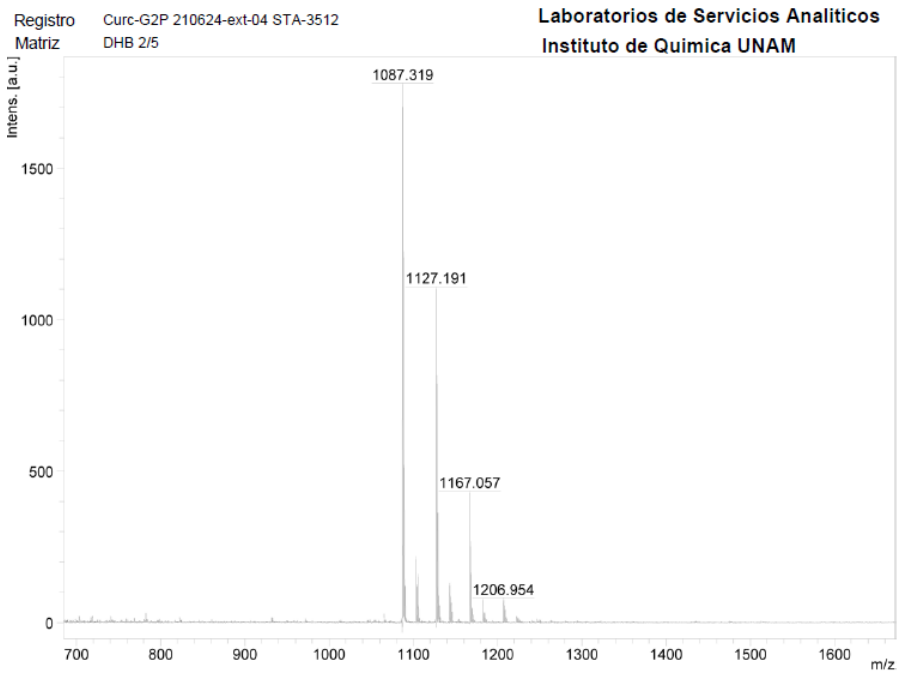


MS-MALDI-TOF showed many peaks due to the subsequent loss of cetonide groups provoked by the experimental conditions. Nevertheless, dendronized protected derivatives **14**, **15**, **16** and **A** as well as unprotected dendronized compounds **I**, **II**, **III** and **B** are pure compounds as stated by NMR experiments.




Registro Enona-tria-G2P 210624-ext-02 STA-3510
Matriz DHB 2/5
Laboratorios de Servicios Analiticos
Instituto de Quimica UNAM
Intens. [a.u.]
1157.173
1197.037
1234.869
1236.921
1276.802
1316.720
744.089
783.872
823.652
m/z


Registro Curc-tria-G2P 210624-ext-03 STA-3511
Matriz DHB 2/5
Laboratorios de Servicios Analiticos
Instituto de Quimica UNAM
Intens. [a.u.]
612.733
572.944
652.528
1276.879
1199.041
1319.809
1356.731
823.559
763.873
1390.620
1430.577
m/z



14. Fluorescence Spectra

Emission experiments were carried out in a Horiba FluoroLog spectrophotometer FL3-22, the wavelength range was 300-700 nm (5 nm step). Emission experiments of compounds **I** – **III** and **B** in DMSO solutions at 10-5 M.

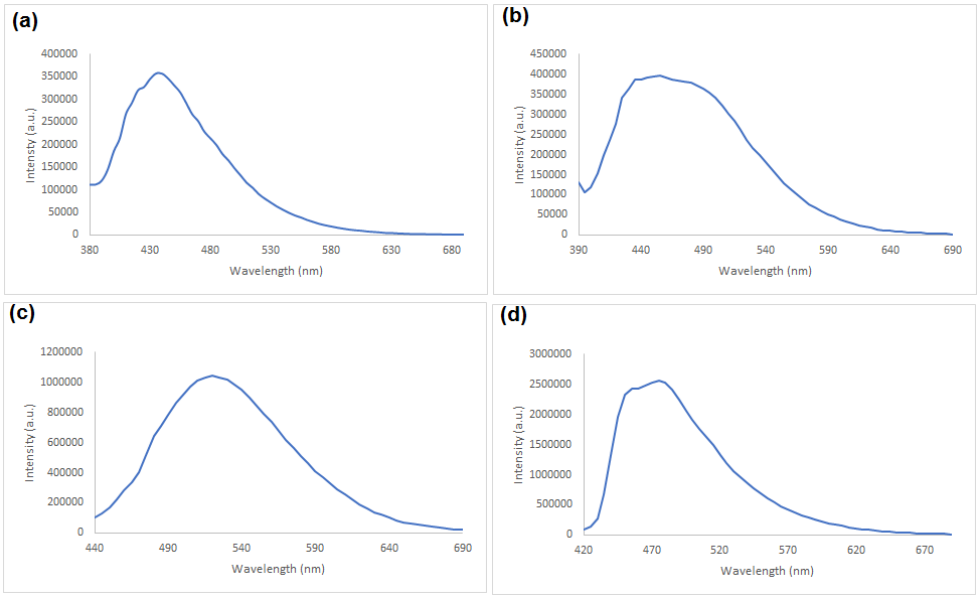


Figure S8. Emission spectra of compounds **I** (a), **II** (b), **III** (c) and **B** (d).

15. References.

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