Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Enantioselective Organocatalytic Asymmetric Allylic Alkylation. Bis(phenylsulfonyl)methane addition to MBH carbonates

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-Supporting Information-

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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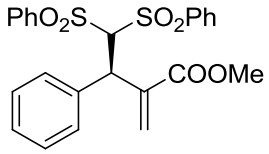
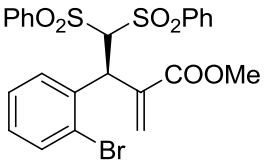
General methods.

Chemicals and solvents were either purchased *puriss p.A.* from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. H_2SO_4 (60 mL), and H_2O (940 mL) followed by heating or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating. Flash chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm), ^1H NMR and ^{13}C NMR spectra were recorded on Varian AS 400. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) and the coupling constants *J* are given in Hz. The spectra were recorded in $CDCl_3$ as solvent at room temperature. TMS served as internal standard (δ = 0 ppm) for ^1H NMR, $CDCl_3$ was used as internal standard (δ = 77.0 ppm) for ^{13}C NMR. High-resolution mass spectra were recorded on a Bruker MicrOTOF spectrometer.

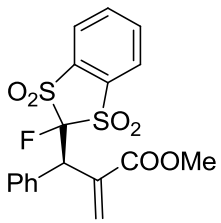
NMR spectra and HPLC traces.



(R)-methyl 2-methylene-3-phenyl-4,4-bis(phenylsulfonyl)butanoate 3a: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.94 (m, 2H), 7.65 (t, J=7.5 Hz, 1H), 7.54 (t, J=7.5 Hz, 2H), 7.47-7.42 (m, 1H), 7.26-7.20 (m, 7.13-7.07 (m, 7H), 7.05-6.99 (m, 2H), 6.27 (d, J=9.6 Hz, 1H), 6.26 (s, 1H), 5.79 (s, 1H), 4.82 (d, J=9.6 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.5, 141.9, 141.0, 138.4, 135.5, 134.8, 131.1, 130.6, 129.9, 129.4, 129.0, 85.7, 53.6, 50.0. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{24}H_{23}O_6S_2$) requires 471.0931, found 471.0928. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 203 nm, 1.0 mL/min): t_R= 28.4, 43.7 min. **[α]**$_D$=-10.5 (c=0.6, $CHCl_3$)

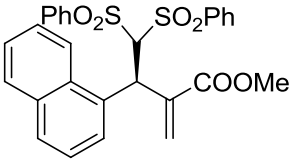


(S)-methyl 3-(2-bromophenyl)-2-methylene-4,4-bis(phenylsulfonyl)butanoate 3b: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.70-7.30 (m, 12H), 7.12-7.00 (m, 2H), 6.58 (s, 1H), 6.30 (s, 1H), 6.09 (d, J=7.6 Hz, 1H), 5.46 (d, J=7.6 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.0, 141.9, 141.7, 137.3, 136.2, 135.5, 135.4, 134.6, 133.5, 132.4, 131.0, 130.7, 130.6, 130.5, 130.4, 130.3, 130.2, 129.8, 128.8, 126.6, 85.6, 53.7, 47.8. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{24}H_{25}BrNO_6S_2$) requires 566.0301, found 566.0290. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 215 nm, 1.0 mL/min): t_R= 25.5, 27.9. **[α]**$_D$=-18.2 (c=3.0, $CHCl_3$)

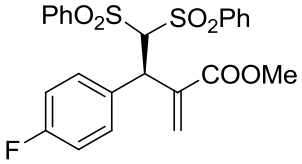


5b: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 8.07-8.01 (m, 1H), 7.96-7.89 (m, 3H), 7.63-7.57 (m, 2H), 7.41-7.35 (m, 3H), 6.71 (s, 1H), 6.59 (s, 1H), 5.65 (d, J=37.6 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 166.8, 137.6, 137.1, 137.0, 136.9, 136.3, 133.0, 132.4, 132.3, 131.1, 131.1, 130.6, 130.2, 125.2, 124.9, 110.7, 107.9, 54.2, 43.7, 43.6. **^{19}F NMR ($CDCl_3$, 376 MHz) δ (ppm):** 154.0 (d, J=37.6 Hz),

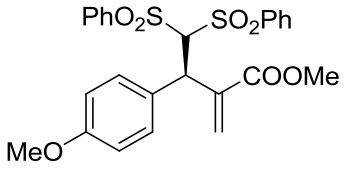
HRMS (ESI): calcd. for $[M+H]^+$ ($C_{18}H_{16}FO_6S_2$) requires 411.0367, found 411.0368. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 205 nm, 1.0 mL/min): t_R= 29.6, 37.4 min. **[α]**$_D$=-30.0 (c=1.2, $CHCl_3$)



(R)-methyl 2-methylene-3-(naphthalen-1-yl)-4,4-bis(phenylsulfonyl)butanoate 3e: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.93-7.88 (m, 1H), 7.81-7.77 (m, 1H), 7.73-7.57 (m, 4H), 7.51-7.37 (m, 5H), 7.34-7.22 (m, 4H), 7.18-7.12 (m, 1H), 6.37 (s, 1H), 6.17 (d, J=7.7 Hz, 1H), 5.93 (s, 1H), 5.89 (d, J=7.7 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.5, 141.8, 141.7, 128.9, 125.5, 135.3, 135.3, 133.0, 132.1, 131.2, 130.9, 130.6, 130.4, 130.3, 130.2, 130.1, 130.0, 128.4, 127.1, 126.6, 123.9, 87.0, 53.8, 43.5. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{28}H_{28}NO_6S_2$) requires 538.1353, found 538.1336. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 204 nm, 1.0 mL/min): t_R= 26.1, 37.2 min. **[α]**$_D$=+11.59 (c=3.1, $CHCl_3$)

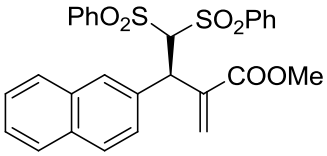


(R)-methyl 3-(4-fluorophenyl)-2-methylene-4,4-bis(phenylsulfonyl)butanoate 3c: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.96-7.90 (m, 2H), 7.68-7.60 (m, 1H), 7.56-7.43 (m, 3H), 7.30-7.18 (m, 6H), 6.71 (t, J=8.6 Hz, 1H), 6.30 (s, 1H), 6.24 (d, J=9.8 Hz, 1H), 5.76 (s, 1H), 4.82 (d, 8.6 Hz), 3.75 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.4, 164.8, 162.3, 141.9, 141.7, 140.9, 135.5, 134.9, 134.1, 134.0, 133.0, 132.9, 130.5, 130.3, 129.4, 129.1, 116.8, 116.5, 85.5, 53.7, 49.1. **^{19}F NMR ($CDCl_3$, 376 MHz) δ (ppm):** -113.7, **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{24}H_{22}FO_6S_2$) requires 489.0836, found 489.0826. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 205 nm, 1.0 mL/min): t_R= 28.3, 39.8. **[α]**$_D$=-5.15 (c=0.2, $CHCl_3$)

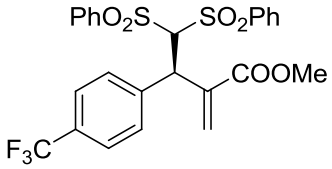


(R)-methyl 3-(4-methoxyphenyl)-2-methylene-4,4-bis(phenylsulfonyl)butanoate 3d: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.98-7.92 (m, 2H), 7.68-7.62 (m, 1H), 7.56-7.50 (m, 2H), 7.46-7.39 (m, 1H), 7.28-7.21 (m, 4H), 7.12 (d, J=8.5 Hz, 2H), 6.53 (d, J=8.5 Hz, 2H), 6.25 (d, J=9.4 Hz, 1H), 6.24 (s, 1H), 5.75 (s, 1H), 4.77 (d, J=9.9 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.5, 160.4, 142.1, 141.9, 141.4, 135.4, 134.7, 132.3, 130.5, 130.2, 130.1, 129.2, 128.9, 115.2, 85.7, 56.6, 53.6, 49.2. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{25}H_{28}NO_7S_2$) requires 518.1302, found 518.1287. **HPLC** (Chiralpak IA, *n*-hexane:

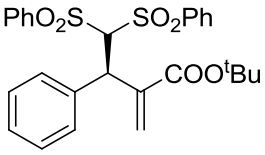
i-PrOH= 90:10, λ= 205 nm, 1.0 mL/min): t_R= 35.5, 45.1min. **[α]$_D$**=-5.3 (c=7.1, $CHCl_3$)



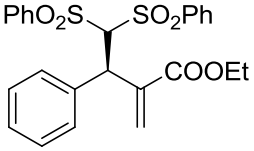
(R)-methyl 2-methylene-3-(naphthalen-2-yl)-4,4-bis(phenylsulfonyl)butanoate 3f: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 8.05-7.96 (m, 2H), 7.72-7.60 (m, 3H), 7.56-7.47 (m, 4H), 7.45-7.27 (m, 3H), 7.21-7.14 (m, 2H), 6.96-6.89 (m, 2H), 6.41 (d, J=6.2 Hz, 1H), 6.27 (s, 1H), 5.85 (s, 1H), 4.98 (d, J=9.9 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.5, 142.0, 141.9, 141.1, 135.7, 135.5, 134.7, 134.4, 134.0, 130.6, 130.2, 129.8, 129.6, 129.5, 129.2, 129.0, 128.7, 128.6, 127.8, 127.4, 85.6, 53.7, 50.1. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{28}H_{28}NO_6S_2$) requires 538.1353, found 538.1340. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 220 nm, 1.0 mL/min): t_R= 38.4, 55.6 min. **[α]$_D$**=-7.7 (c=0.9, $CHCl_3$)



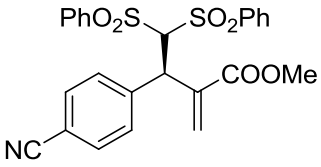
(R)-methyl 2-methylene-4,4-bis(phenylsulfonyl)-3-(4-(trifluoromethyl)phenyl)butanoate 3i: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 8.00-7.93 (m, 2H), 7.70-7.64 (m, 1H), 7.58-7.53 (m, 2H), 7.48-7.44 (m, 1H), 7.38-7.35 (m, 2H) 7.28-7.17 (m, 6H), 6.32-6.28 (m, 2H), 5.80 (s, 1H), 4.89 (d, J= 9.6 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.4, 142.6, 141.9, 140.6, 135.8, 135.1, 131.6, 131.5, 130.6, 130.5, 130.4, 130.0, 129.1, 126.8, 126.8, 85.1, 53.9, 50.0. **^{19}F NMR ($CDCl_3$, 376 MHz) δ (ppm):** -61.9. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{25}H_{25}F_3NO_6S_2$) requires 556.1070, found 556.1070. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 220 nm, 1.0 mL/min): t_R= 24.8, 41.9 min. **[α]$_D$**=-15.3 (c=1.2, $CHCl_3$)



(R)**-tert-butyl 2-methylene-3-phenyl-4,4-bis(phenylsulfonyl)butanoate 3k:** White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.95-7.90 (m, 2H), 7.64-7.60 (m, 1H), 7.53-7.47 (m, 2H), 7.45-7.40 (m, 1H), 7.30-7.20 (m, 5H), 7.10-7.06 (m, 1H), 7.05-7.00 (m, 2H), 6.29 (d, J=9.1 Hz, 1H), 6.19 (s, 1H), 5.57 (s, 1H), 4.83 (d, J=9.1 Hz, 1H), 1.48 (s, 9H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 167.2, 142.5, 142.1, 140.0, 138.7, 135.4, 134.8, 131.3, 130.6, 130.3, 130.2, 129.9, 129.4, 129.0, 128.6, 86.0, 83.1, 50.0, 29.5. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{27}H_{32}NO_6S_2$) requires 530.1666, found 530.1658. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 205 nm, 1.0 mL/min): t_R= 14.6, 19.5. **[α]$_D$**=-19.17 (c=1.2, $CHCl_3$)

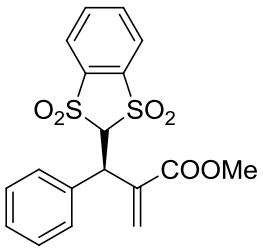


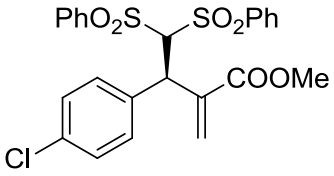
(R)-ethyl 2-methylene-3-phenyl-4,4-bis(phenylsulfonyl)butanoate 3j: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.96-7.92 (m, 2H), 7.66-7.61 (m, 1H), 7.55-7.50 (m, 2H), 7.47-7.41 (m, 1H), 7.25-7.20 (m, 5H), 7.10-7.06 (m, 1H), 7.05-6.99 (m, 2H), 6.30 (d, J=9.7 Hz, 1H), 6.27 (s, 1H), 5.76 (s, 1H), 4.83 (d, J=9.7 Hz, 1H), 4.28-4.14 (m, 2H), 1.28 (t, J=7.0 Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.0, 142.0, 141.2, 138.4, 135.4, 134.7, 131.1, 130.5, 130.2, 129.8, 129.3, 129.1, 129.0, 95.7, 62.6, 50.0, 15.6. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{25}H_{28}NNaO_6S_2$) requires 502.1353, found 502.1354. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 218 nm, 1.0 mL/min): t_R= 21.0, 29.8min. **[α]$_D$**=-20.26 (c=3.9, $CHCl_3$)



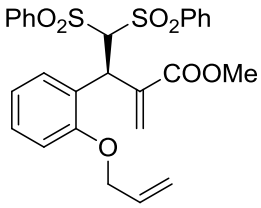
(R)-methyl 3-(4-cyanophenyl)-2-methylene-4,4-bis(phenylsulfonyl)butanoate 3h: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.94-7.90 (m, 2H), 7.70-7.64 (m, 1H), 7.58-7.53 (m, 3H), 7.45-7.25 (m, 8H), 6.32 (s, 1H), 6.23 (d, J=9.1 Hz, 1H), 5.81 (s, 1H), 4.90 (d, J=9.1 Hz, 1H),3.76 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.1, 143.7, 141.5, 141.4, 139.9, 135.8, 135.3, 133.4, 132.0, 130.5, 130.4, 130.3, 129.3, 119.8, 112.9, 84.9, 53.8, 49.7. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{25}H_{25}N_2O_6S_2$) requires 513.1149, found 513.1153. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 95:5, λ= 205 nm, 1.0 mL/min): t_R= 21.5, 32.8 min. **[α]$_D$**=+3.62 (c=2.5, $CHCl_3$)

(R)-methyl 2-(phenyl(1,1,3,3-tetraoxidobenzo[d][1,3]dithiol-2-yl)methyl)acrylate 3l: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.99-7.96 (m, 2H), 7.90-7.83 (m, 3H), 7.59-7.58 (m, 2H), 7.39-7.33 (m, 3H), 6.49 (s, 1H), 6.20 (s, 1H), 5.85 (d, J=12.0 Hz, 1H), 4.87 (d, J=12.0 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 167.1, 139.3, 138.8, 138.0, 136.5, 136.4, 135.9, 131.5, 130.9, 130.1, 129.9, 123.9, 123.8, 75.9, 53.7, 46.2. **HRMS (ESI):** calcd. for $[M-OMe]^+$ ($C_{17}H_{13}O_5S_2$) requires 361.0199, found 361.0199. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 70:30, λ= 240 nm, 1.0 mL/min): t_R= 21.4 (minor enantiomer), 32.8 min (major enantiomer). **[α]$_D$**=-16.3 (c=0.7, $CHCl_3$)

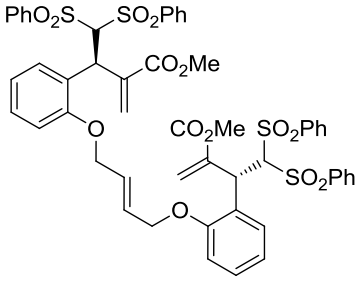




(R)-methyl 3-(4-chlorophenyl)-2-methylene-4,4-bis(phenylsulfonyl)butanoate 3g: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.96-7.94 (m, 2H), 7.68-7.64 (m, 1H), 7.56-7.52 (m, 2H), 7.50-7.47 (m, 1H), 7.29-7.23 (m, 4H), 7.19-7.16 (m, 2H), 6.27 (s, 1H), 6.25 (d, J=9.6 Hz), 5.78 (s, 1H), 4.80 (d, J=9.6 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.3, 141.8, 141.7, 140.7, 136.9, 135.6, 135.1, 134.9, 132.5, 130.5, 130.3, 129.9, 129.5, 129.1, 85.3, 53.7, 49.3. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{24}H_{25}ClNO_6S_2$) requires 522.0806, found 522.0808. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 200 nm, 1.0 mL/min): t_R= 31.2 (minor enantiomer), 42.3 min (major enantiomer). $[\alpha]_D^{25}$= -3.0 (c=1.0, $CHCl_3$, 92% ee).

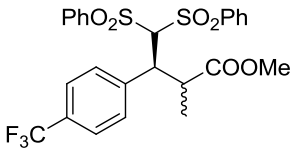


(R)-methyl 3-(2-(allyloxy)phenyl)-2-methylene-4,4-bis(phenylsulfonyl)butanoate 3m: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.74-7.72 (m, 2H), 7.60-7.58 (m, 1H), 7.51-7.47 (m, 1H), 7.45-7.41 (m, 2H), 7.36-7.34 (m, 1H), 7.31-7.29 (m, 4H), 7.09 (td, J_1=7.3 Hz, J_2=1.6 Hz, 1H), 6.90 (t, J=7.3 Hz, 1H), 6.62 (s, 1H), 6.51 (s, 1H), 6.48 (d, J=8.2 Hz, 1H), 6.08 (d, J=7.6 Hz, 1H), 5.96-5.87 (m, 1H), 5.48 (d, J=7.6 Hz, 1H), 5.30-5.26 (m, 2H), 5.26-5.25 (m, 1H), 4.80 (d, J=9.6 Hz, 1H), 4.32 (dd, J_1=12.3 Hz, J_2=5.2 Hz, 1H), 4.14-4.05 (m, 1H), 3.68 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 168.2, 156.7, 142.6, 141.8, 137.1, 136.3, 135.2, 134.8, 134.2, 132.4, 131.8, 130.8, 130.5, 130.3, 130.2, 130.0, 129.4, 125.5, 122.2, 119.7, 112.5, 85.8, 75.9, 70.1, 53.5, 41.6. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{27}H_{30}NO_7S_2$) requires 544.1458, found 544.1460. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 220 nm, 1.0 mL/min): t_R= 27.4 (major enantiomer), 29.9 min (minor enantiomer). $[\alpha]_D^{25}$= -8.8 (c=0.9, $CHCl_3$, 87% ee).

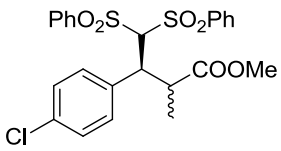


(3R,3'R)-dimethyl 3,3'-(((E)-but-2-ene-1,4-diylbis(oxy))bis(2,1-phenylene))bis(2-methylene-4,4-bis(phenylsulfonyl)butanoate) 7m: Colorless oil. **^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm):** 7.58-7.52 (m, 10H), 7.41-7.33 (m, 12H), 7.15-7.11 (m, 2H), 6.76-6.72 (m, 2H), 6.20 (d, J=8.1 Hz, 2H), 6.47 (s, 2H), 6.28 (s, 2H), 6.14 (d, J=8.1 Hz, 2H), 5.94 (s, 2H), 5.57-5.53 (m, 2H), 4.45-4.42 (m, 2H), 4.33-4.29 (m, 2H), 3.69 (s, 6H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 166.9, 155.4, 141.2, 140.4, 136.5, 133.9, 133.8, 131.0, 129.7, 129.1, 129.0, 129.0, 128.9, 128.9,

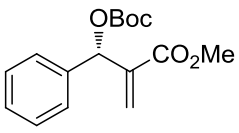
128.8, 128.4, 128.4, 128.1, 124.8, 121.0, 111.9, 84.6, 68.1, 52.2, 40.1, 31.0. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{52}H_{48}NaO_{14}S_4$) requires 1047.1825, found 1047.1819. $[\alpha]_D^{25}$= -14.6 (c=1.0, $CHCl_3$)



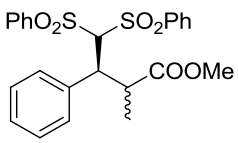
(3S)-methyl 2-methyl-4,4-bis(phenylsulfonyl)-3-(4-(trifluoromethyl)phenyl)butanoate 6i: White scum. **^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm):** Inseparable mixture of diastereomers, 7.81-7.76 (m, 2H), 7.68-7.46 (m, 8H), 7.44-7.30 (m, 4H), 5.76 (major diastereomer, d, J=2.9 Hz, 0.6H), 5.25 (major diastereomer, d, J=3.6 Hz, 0.4H), 4.23-4.17 (m, 2H), 3.78 (major diastereomer, s, 1.80H), 3.45 (minor diastereomer, s, 1.19H), 1.28 (minor enantimoer, d, J=6.9 Hz, 1.36H), 1.02 (major enantimoer, d, J=7.0 Hz, 1.87H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** Inseparable mixture of diastereomers, 176.7, 175.1, 140.8, 140.1, 139.0, 138.8, 134.6, 134.4, 134.3, 131.8, 131.0, 129.4, 129.4, 129.3, 129.2, 129.2, 129.0, 128.9, 128.8, 128.6, 125.3, 125.3, 125.2, 125.2, 125.1, 125.0, 84.8, 83.2, 77.5, 77.2, 76.9, 52.5, 52.1, 47.5, 47.4, 42.8, 42.8, 29.9, 18.1, 17.1. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{25}H_{27}NF_3O_6S_2$) requires 558.1226, found 558.1230.



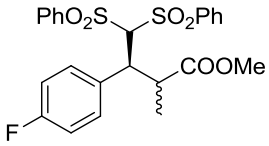
(3S)-methyl 2-methyl-4,4-bis(phenylsulfonyl)-3-(4-chlorophenyl)butanoate 6g: White scum. **^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm):** 7.81-7.83 (m, 2H), 7.62-7.59 (m, 4H), 7.49-7.47 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.30 (m, 2H), 7.12-7.09 (m, 2H), 5.25 (major diastereomer, d, J=3.1 Hz, 0.6H), 5.22 (major diastereomer, d, J=3.5 Hz, 0.4H), 3.78-3.76 (m, 2H),), 3.46 (major diastereomer, s, 2.46H), 3.42 (minor diastereomer, s, 0.69H), 1.03 (minor diastereomer, d, J=7.0 Hz, 1.53H), 0.87 (major diastereomer, d, J=8.3 Hz, 1.87H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.3, 175.1, 140.1, 134.5, 134.2, 134.1, 131.8, 130.1, 129.3, 129.1, 129.1, 129.0, 128.9, 128.8, 128.8, 128.3, 128.2, 85.0, 52.0, 47.8, 47.0, 42.8, 42.8, 42.7, 32.1, 29.9, 29.8, 29.5, 17.1, 17.0, 14.3. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{34}H_{37}ClNO_6S_2$) requires 524.0963, found 524.0967.



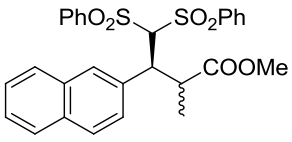
(S)-methyl 2-(((tert-butoxycarbonyl)oxy)(phenyl)methyl)acrylate 1a: Colorless oil. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 97:3, λ_1= 215 nm, λ_2= 215 nm 1.0 mL/min): t_R= 4.9 (minor enantiomer), 5.9 min (major enantiomer).



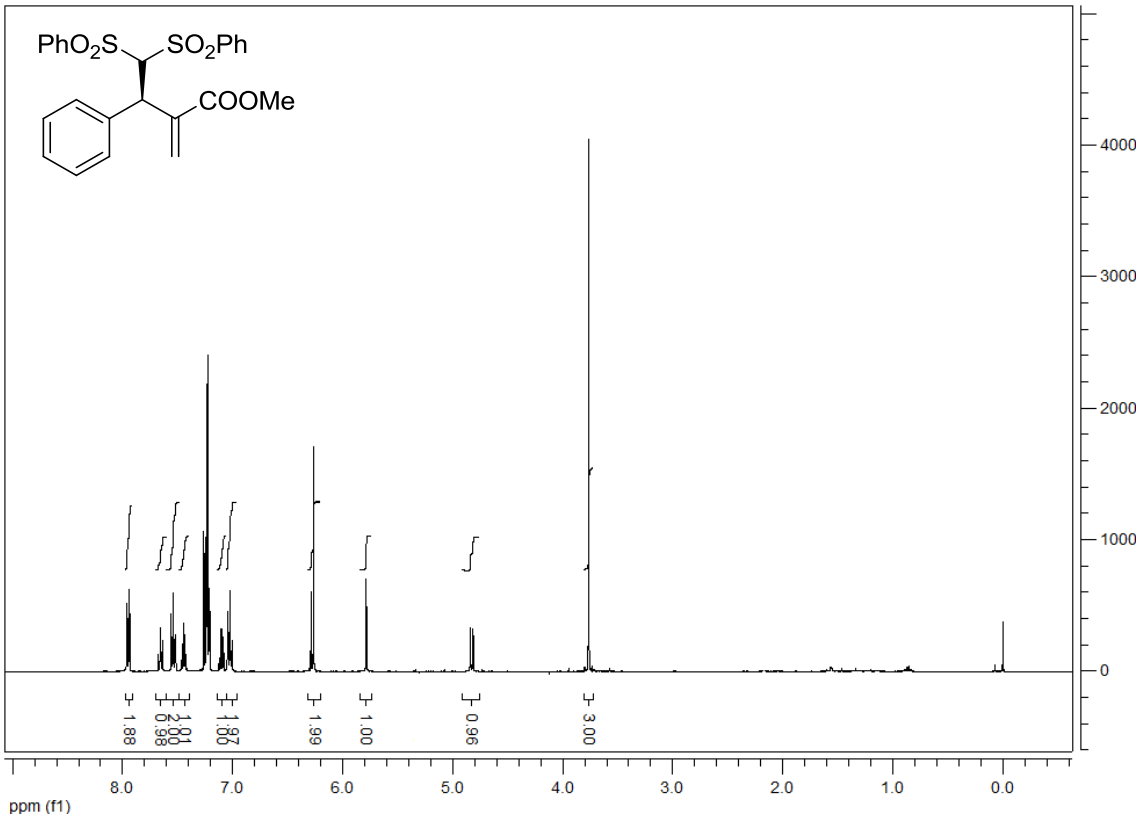
(3S)-methyl 2-methyl-4,4-bis(phenylsulfonyl)-3-phenyl-butanoate 6a: mixture of diastereomers, white scum. **^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm):** 7.80-7.25 (m, 13H), 7.18-7.12 (m, 2H), 5.70 (minor diastereomer, d, J=2.9 Hz, 1H), 5.24 (major diastereomer, d, J=3.3 Hz, 1H), 4.15-3.85 (m, 2H), 3.75 (minor diastereomer, s, 3H), 3.40 (major diastereomer, s, 3H), 1.31 (major diastereomer, d, J=6.8 Hz, 3H), 1.00 (minor diastereomer, d, J=7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 178.2, 176.6, 142.4, 141.4, 141.3, 140.4, 139.9, 138.5, 136.2, 135.9, 135.7, 135.5, 135.4, 132.5, 131.4, 130.8, 130.7, 130.5, 130.4, 130.4, 130.3, 130.2, 130.1, 130.1, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 86.9, 84.9, 75.9, 53.6, 53.1, 49.0, 44.2, 44.-0, 19.4, 18.4. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{24}H_{28}NO_6S_2$) requires 490.1353, found 490.1358.

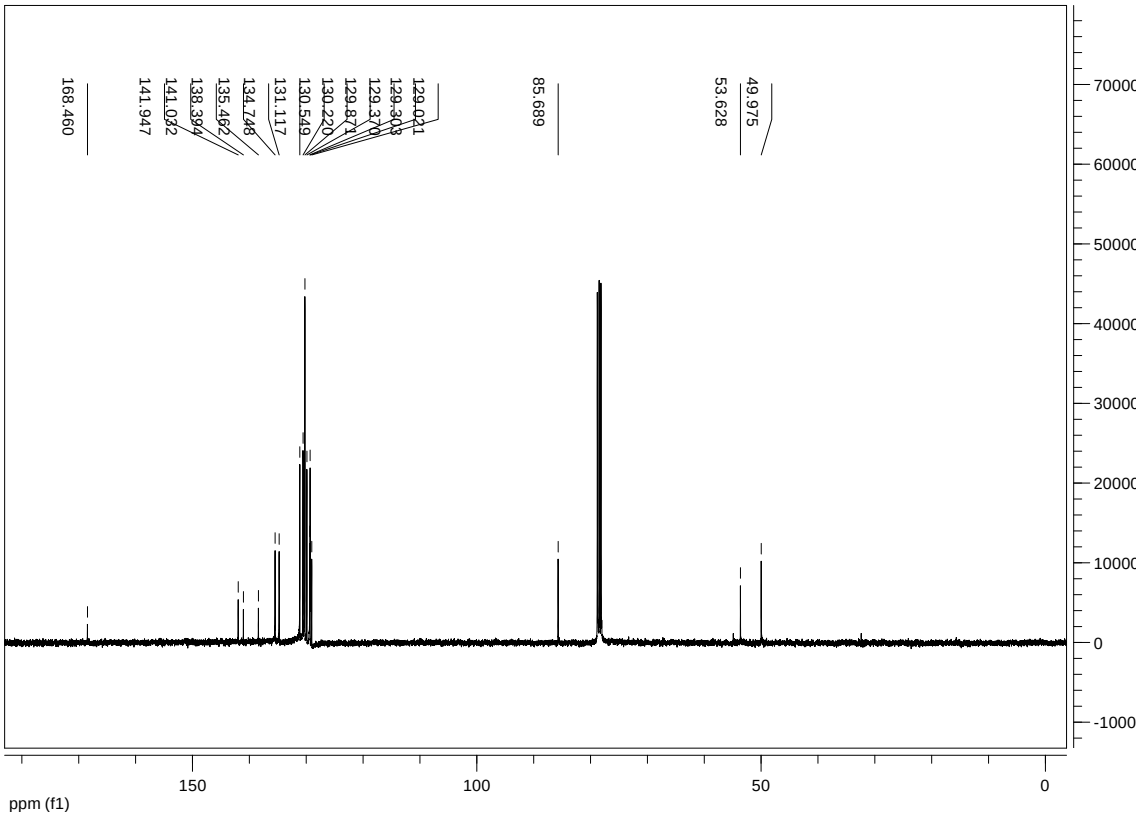


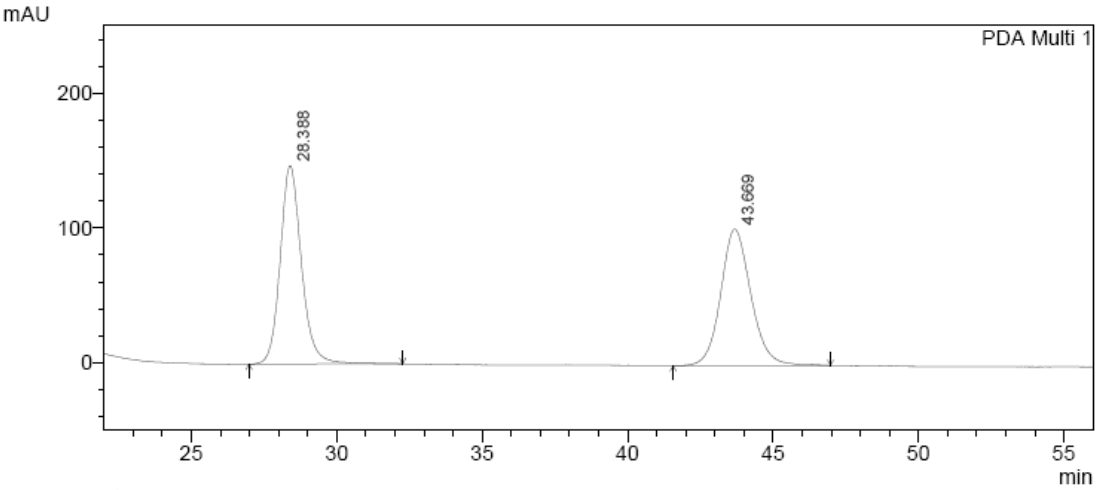
(3S)-methyl 2-methyl-4,4-bis(phenylsulfonyl)-3-(4-fluorophenyl)butanoate 6c: White scum. **^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm):** 7.80-7.83 (m, 2H), 7.62-7.59 (m, 4H), 7.49-7.47 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.30 (m, 2H), 7.12-7.09 (m, 2H), 5.25 (major diastereomer, d, J=3.1 Hz, 0.6H), 5.22 (major diastereomer, d, J=3.5 Hz, 0.4H), 3.78-3.76 (m, 2H),), 3.46 (major diastereomer, s, 2.46H), 3.42 (minor diastereomer, s, 0.69H), 1.03 (minor enantimoer, d, J=7.0 Hz, 1.53H), 0.87 (major enantimoer, d, J=8.3 Hz, 1.87H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.3, 175.1, 140.1, 134.5, 134.2, 134.1, 131.8, 130.1, 129.3, 129.1, 129.1, 129.0, 128.9, 128.8, 128.8, 128.3, 128.2, 85.0, 52.0, 47.8, 47.0, 42.8, 42.8, 42.7, 32.1, 29.9, 29.8, 29.5, 17.1, 17.0, 14.3. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{24}H_{27}FNO_6S_2$) requires 508.1258, found 508.1255.



(3S)-methyl 2-methyl-4,4-bis(phenylsulfonyl)-3-naphtyl-butanoate 6f: mixture of diastereomers, white scum. **^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm):** 7.80-7.25 (m, 15H), 7.18-7.12 (m, 2H), 5.70 (minor diastereomer, d, J=2.7 Hz, 1H), 5.19 (major diastereomer, d, J=3.3 Hz, 1H), 4.15-3.85 (m, 2H), 3.78 (minor diastereomer, s, 3H), 3.44 (major diastereomer, s, 3H), 1.31 (major diastereomer, d, J=6.8 Hz, 3H), 1.02 (minor diastereomer, d, J=7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.5, 164.9, 162.4, 141.5, 141.1, 135.8, 135.6, 135.5, 133.7, 133.5, 130.9, 130.6, 130.3, 130.2, 130.1, 129.9, 116.4, 116.2, 86.3, 84.5, 53.3, 48.3, 48.2, 44.4, 44.4, 19.4, 18.4. **HRMS (ESI):** calcd. for $[M+NH_4]^+$ ($C_{28}H_{30}NO_6S_2$) requires 540.150, found 540.1506.







1 PDA Multi 1/203nm 4nm

PeakTable

PDA Ch1 203nm 4nm

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Total		14751193	248279	100.000	100.000

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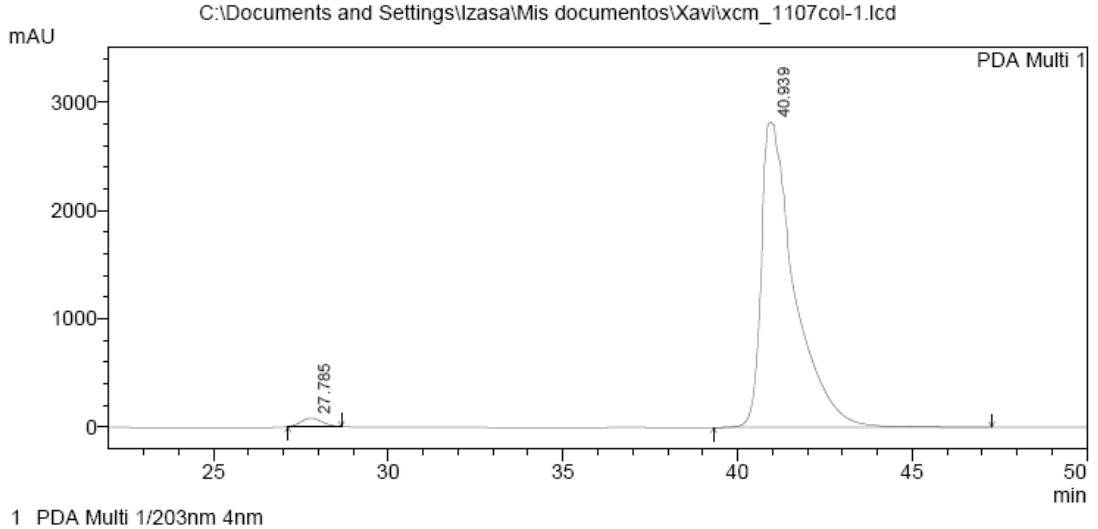

1 PDA Multi 1/203nm 4nm

PeakTable

PDA Ch1 203nm 4nm

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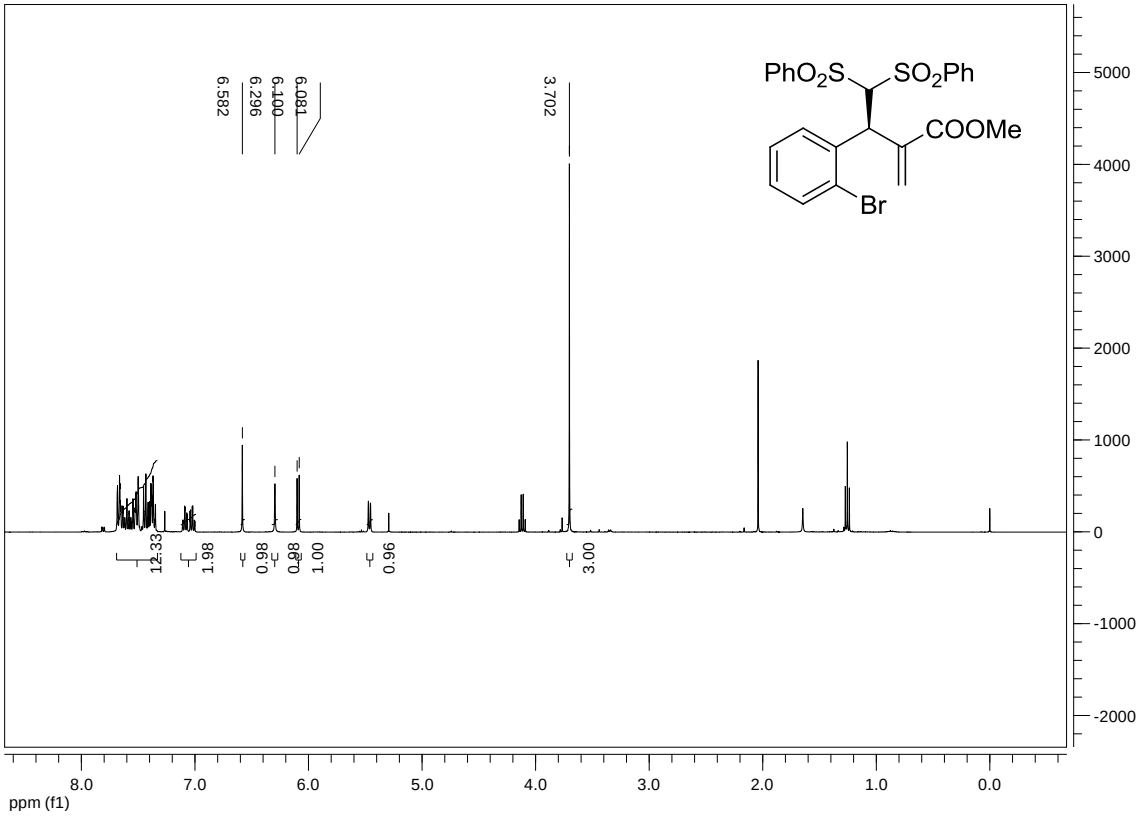

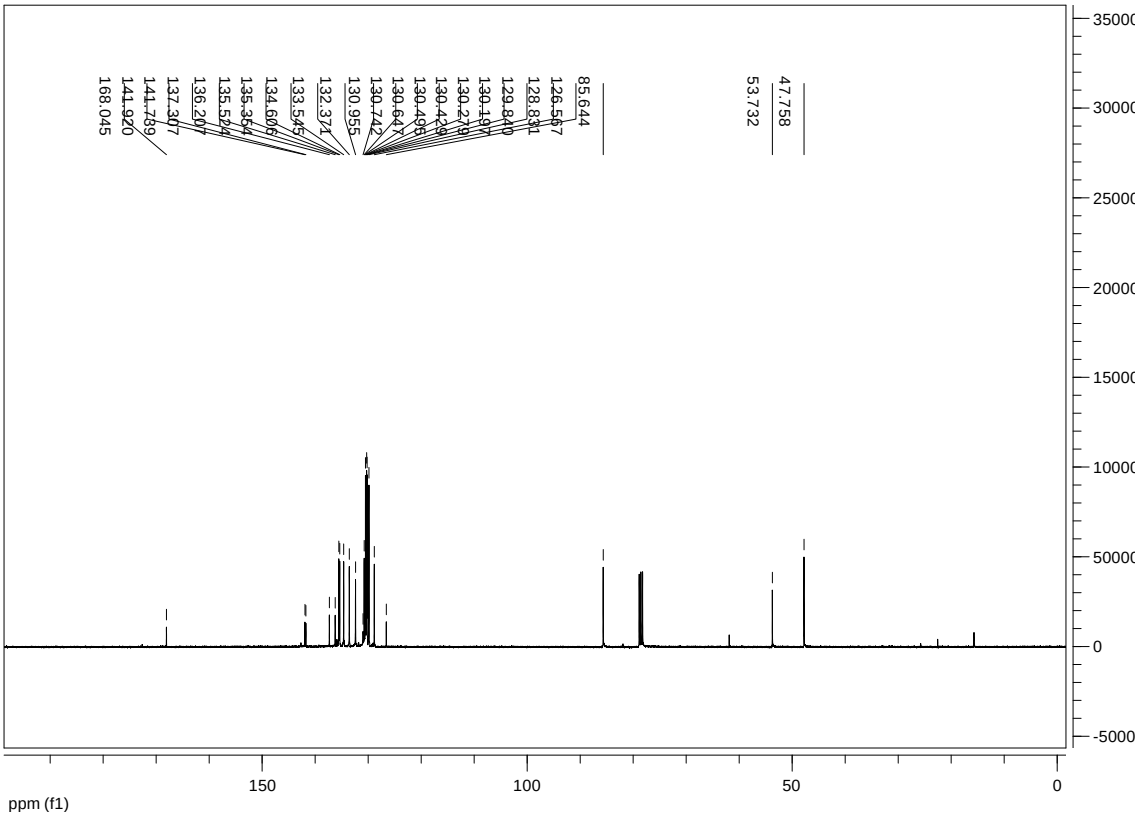

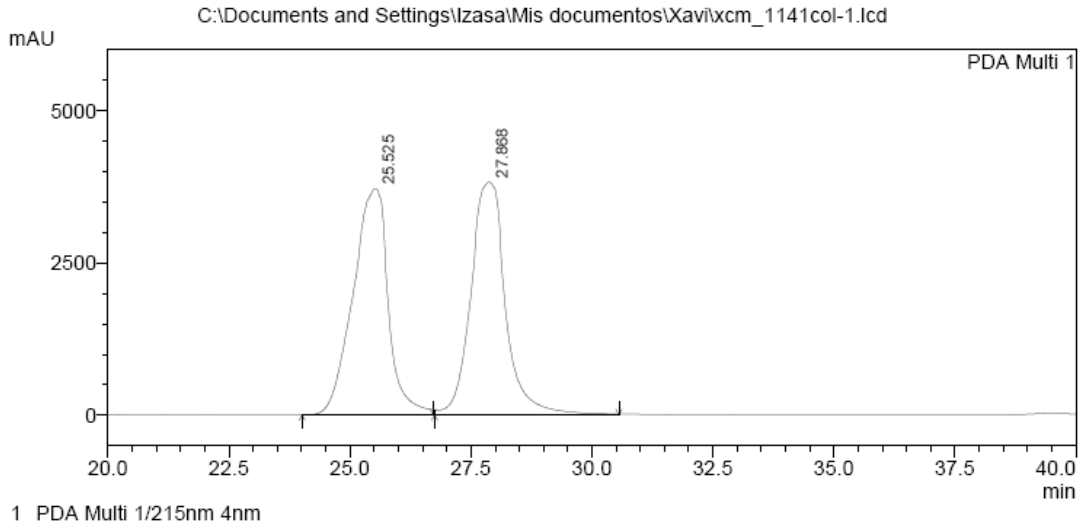

PeakTable

PDA Ch1 215nm 4nm

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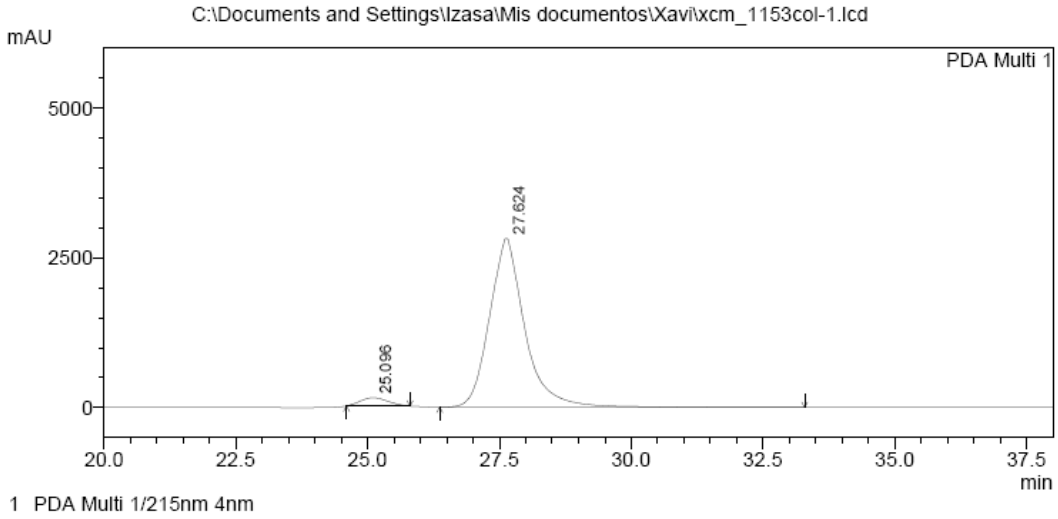

PeakTable

PDA Ch1 215nm 4nm

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1	25.096	5026049	137290	3.700	4.642
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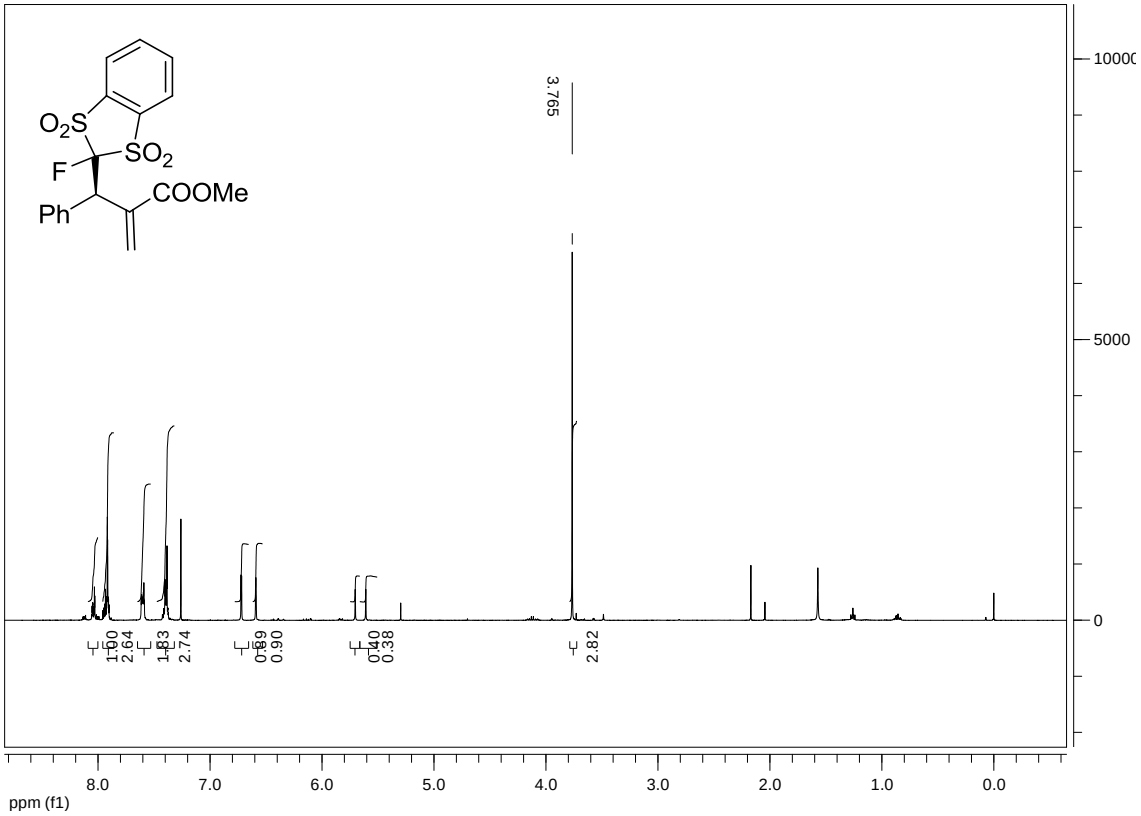
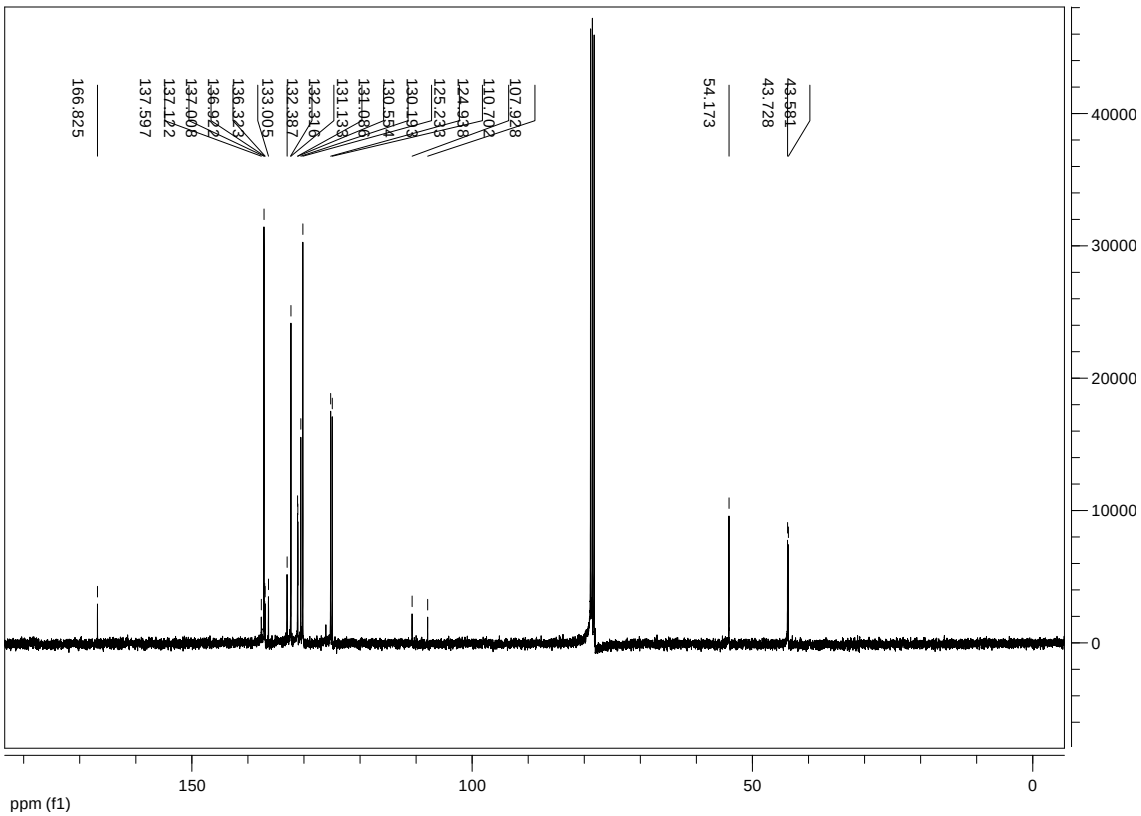
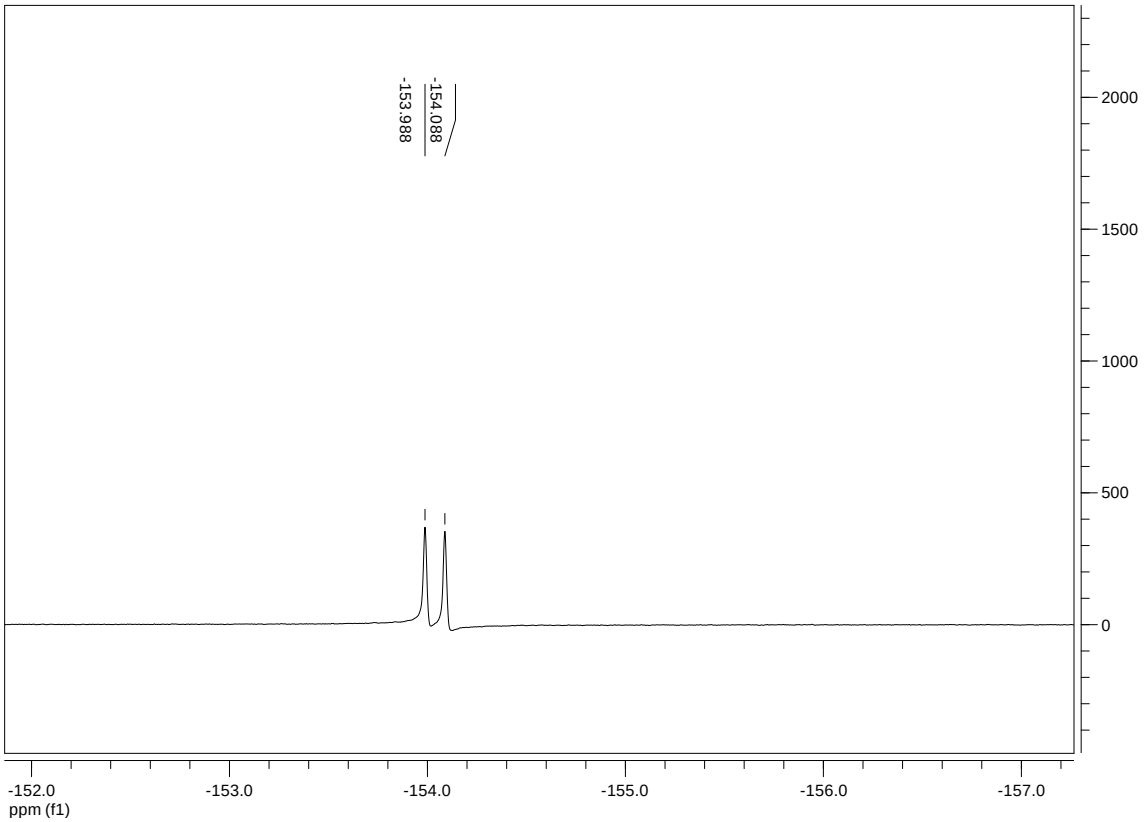
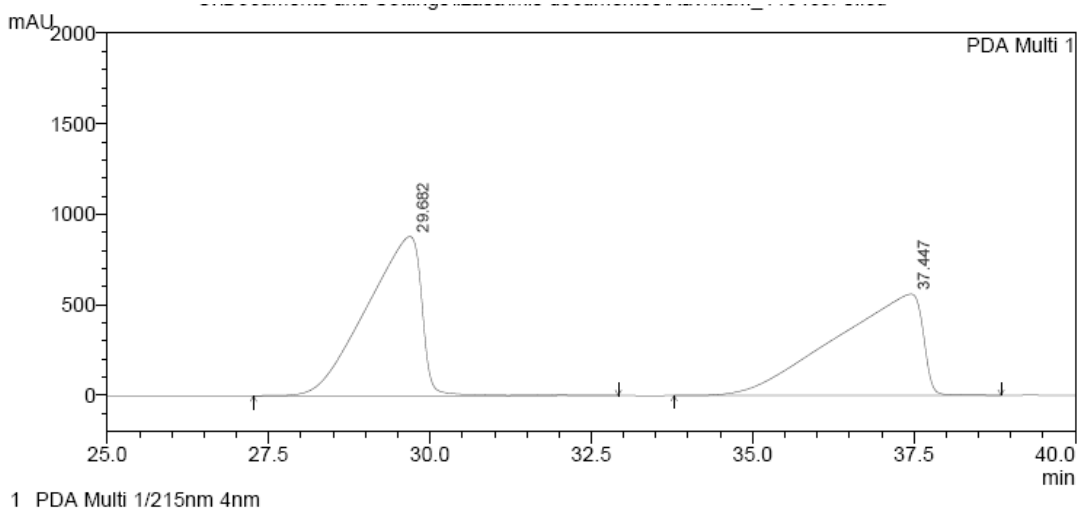
Total		135839052	2957556	100.000	100.000









1 PDA Multi 1/215nm 4nm

PeakTable

PDA Ch1 215nm 4nm

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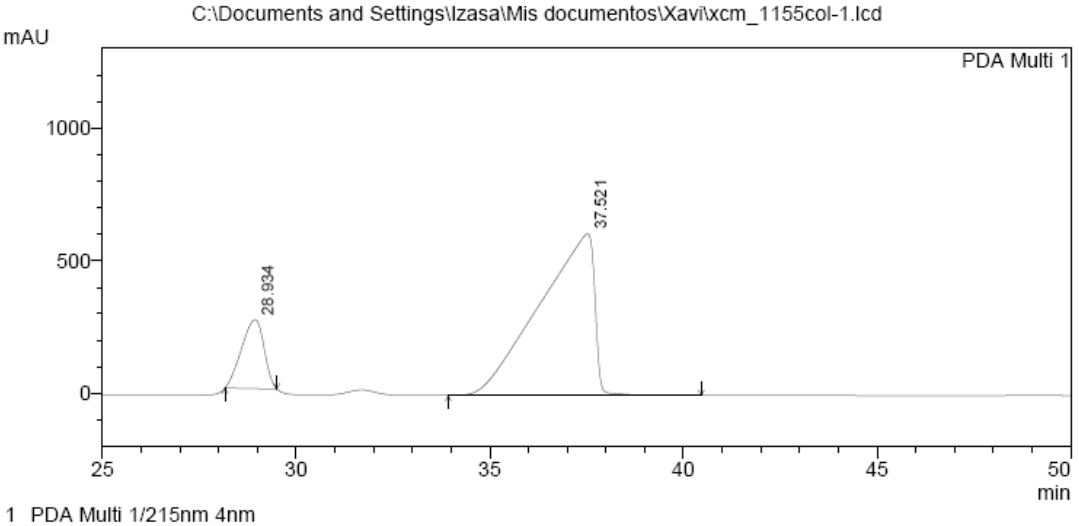

1 PDA Multi 1/215nm 4nm

PeakTable

PDA Ch1 215nm 4nm

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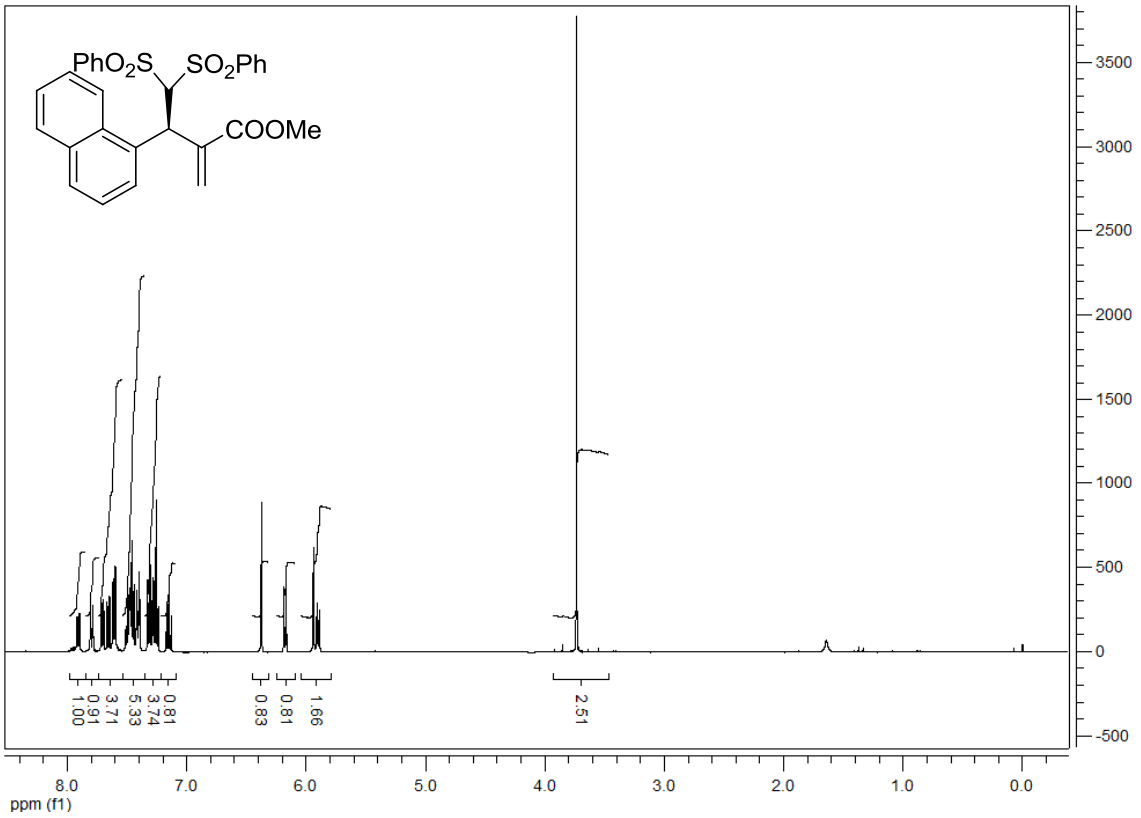

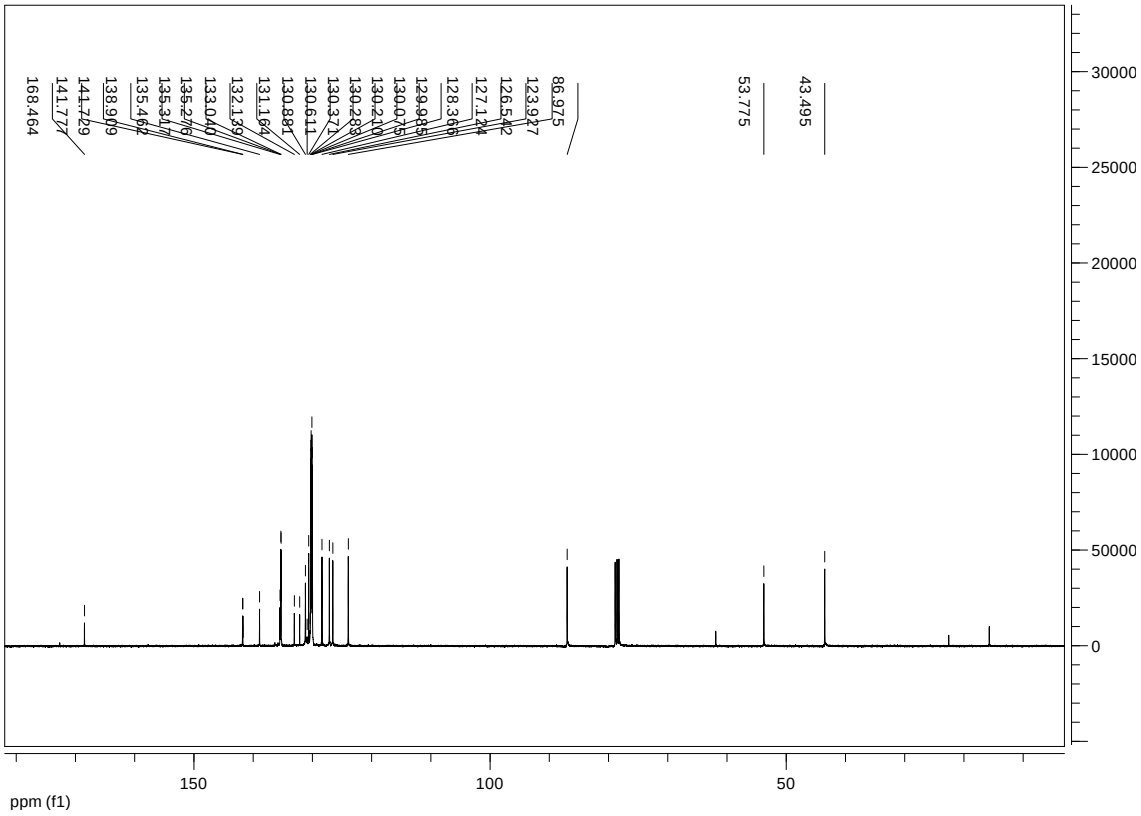

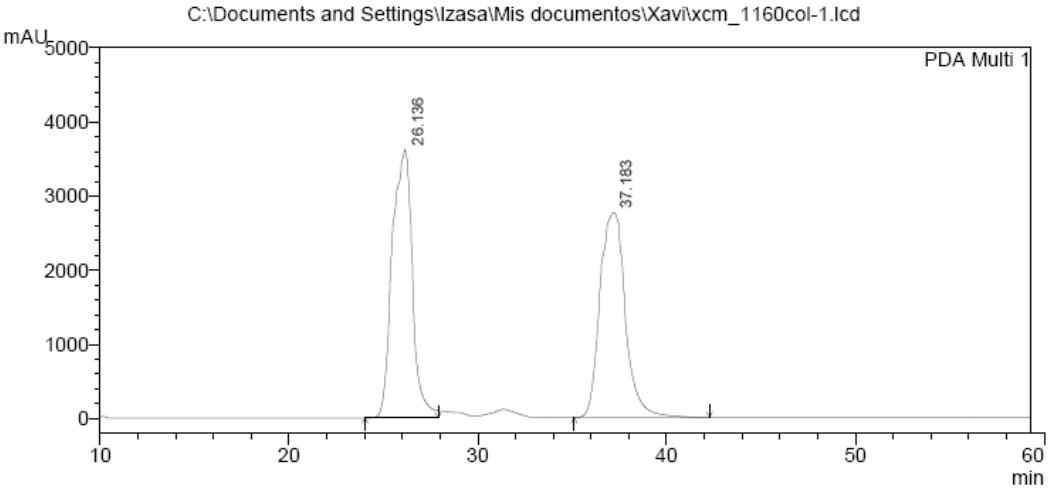

PeakTable

PDA Ch1 204nm 4nm

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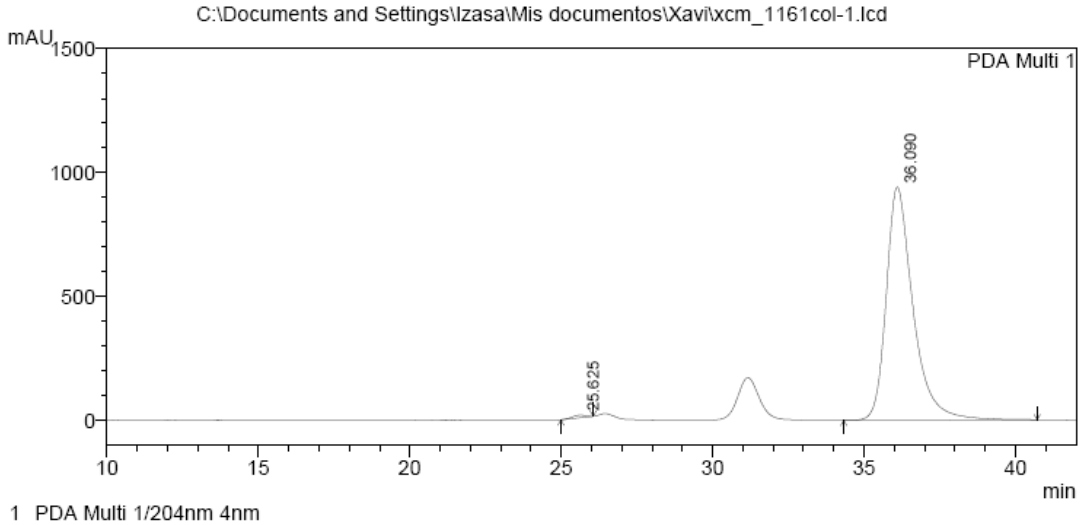

PeakTable

PDA Ch1 204nm 4nm

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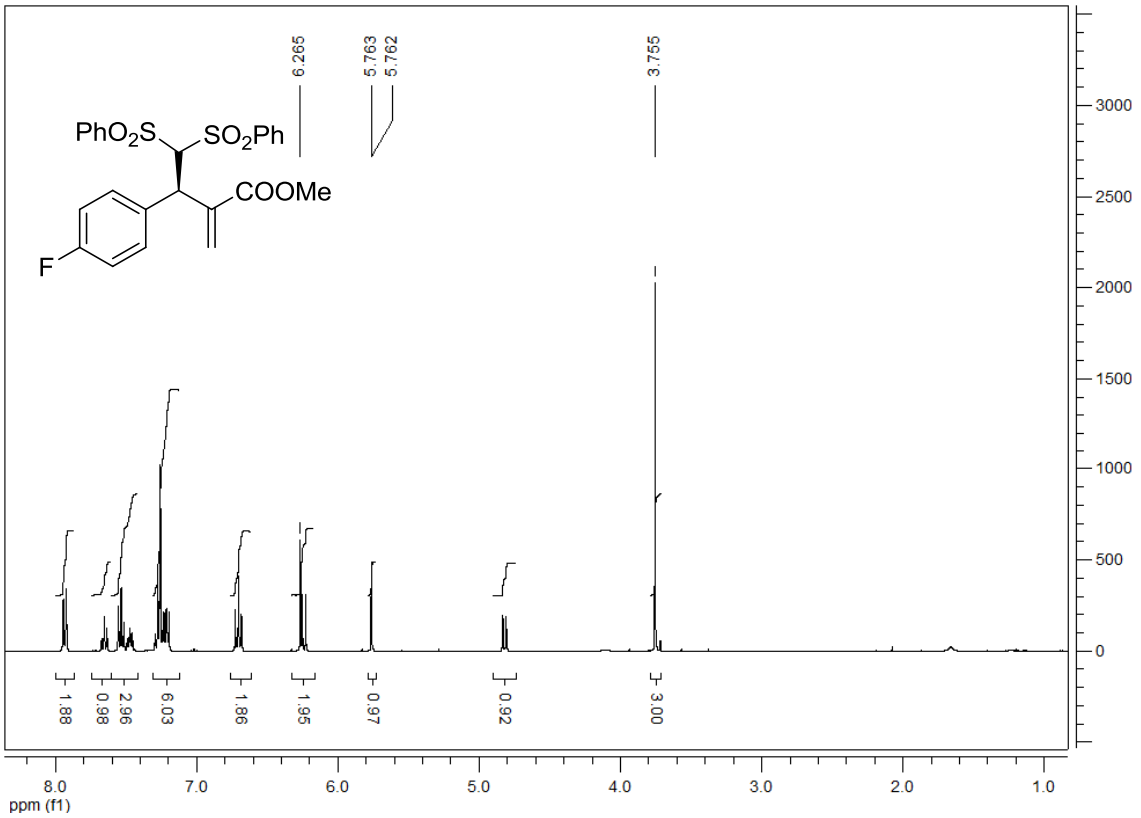
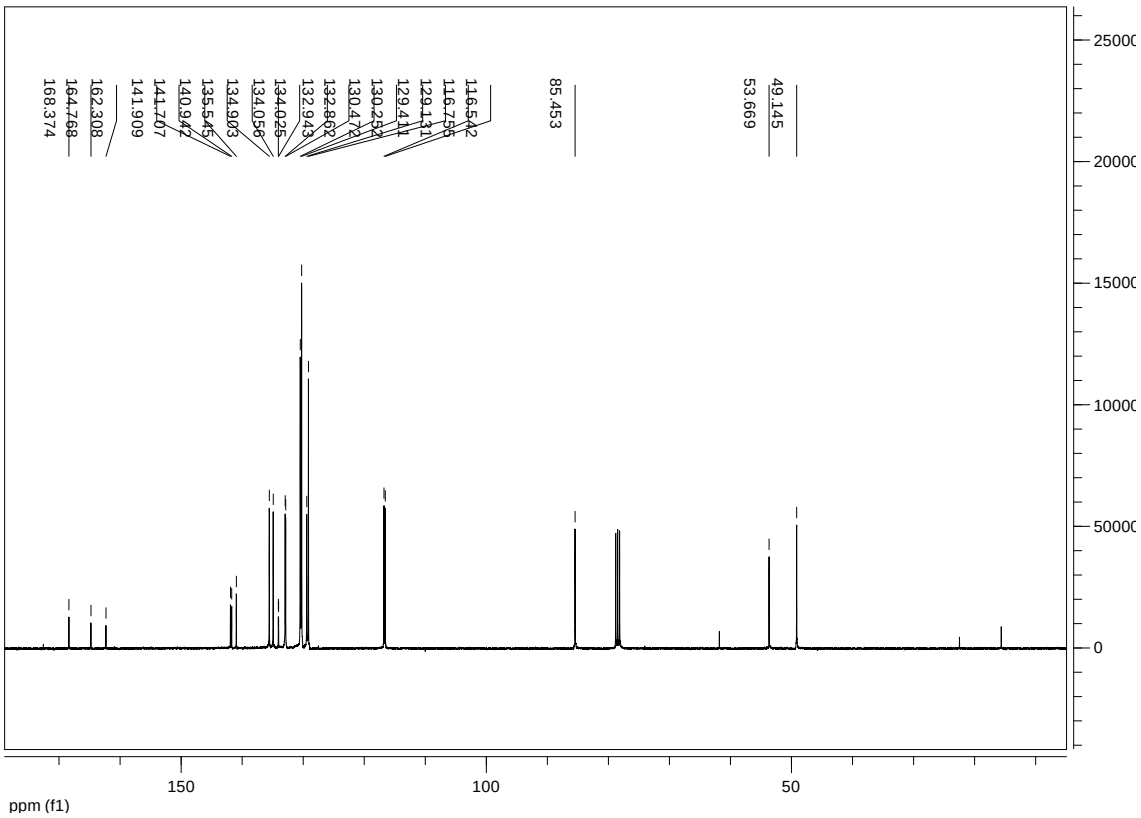
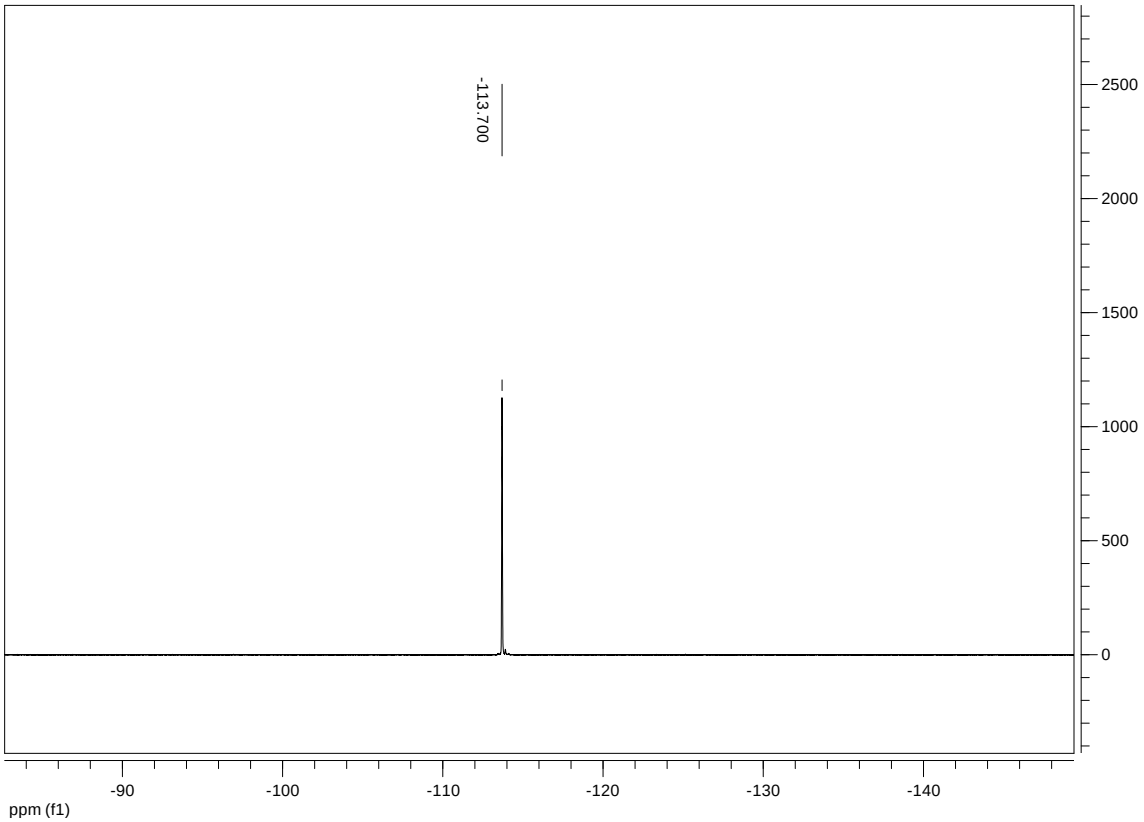
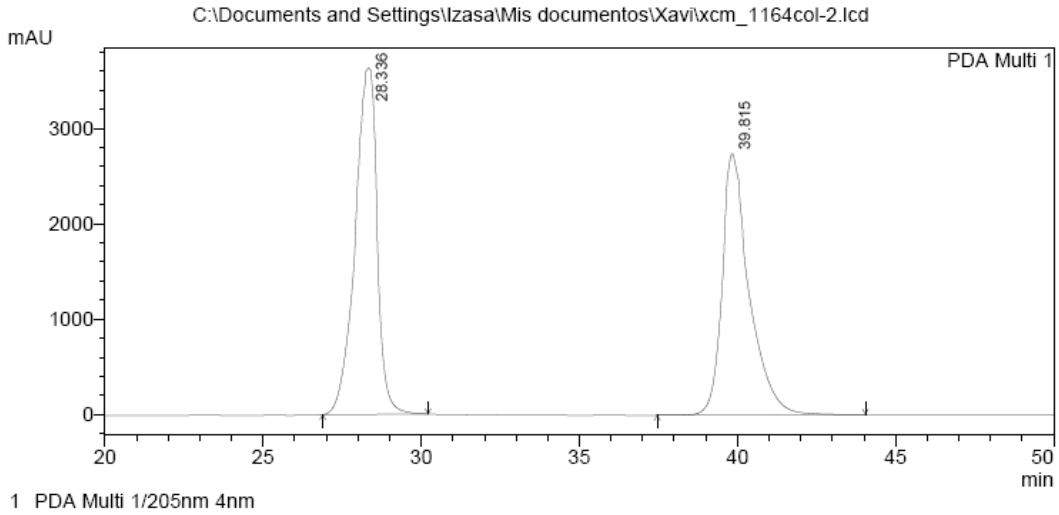
Total		58340831	951752	100.000	100.000







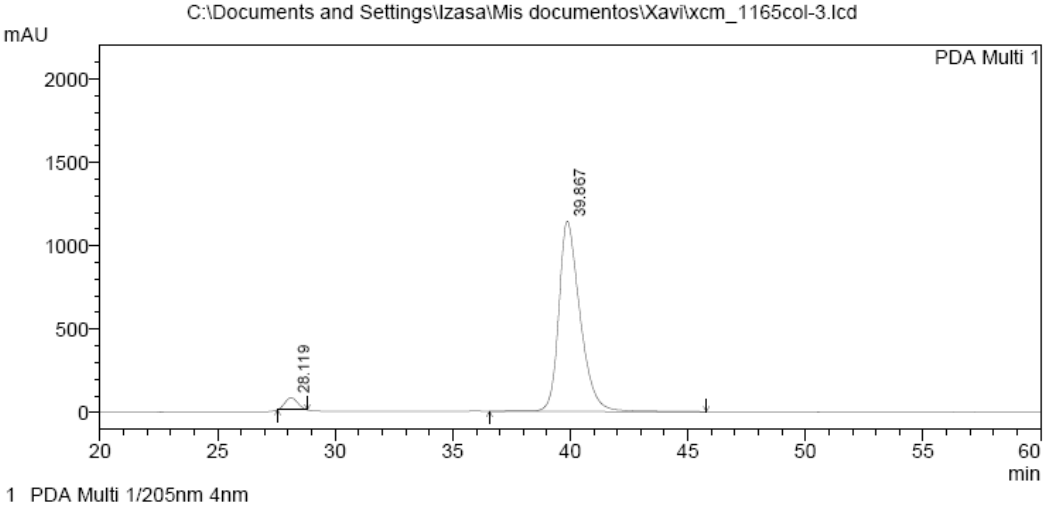


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.336	175683241	3629209	51.938	56.991
2	39.815	162571359	2738808	48.062	43.009
Total		338254600	6368017	100.000	100.000

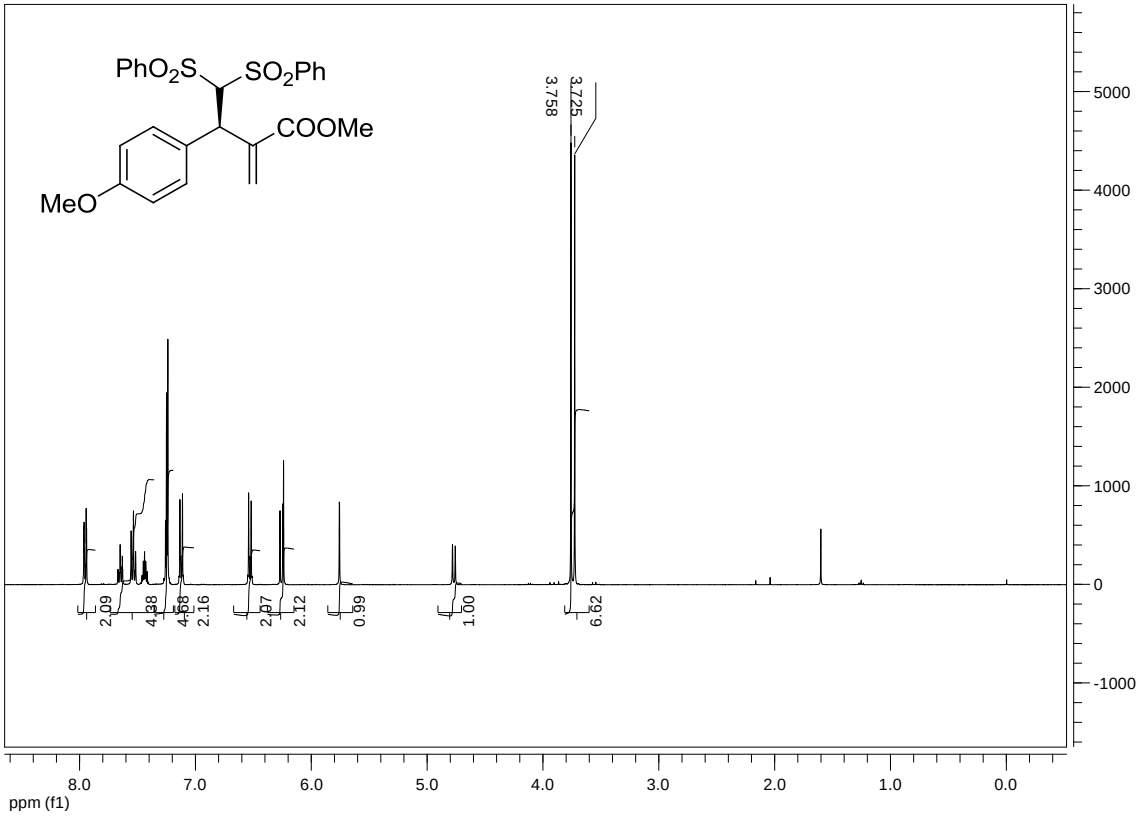


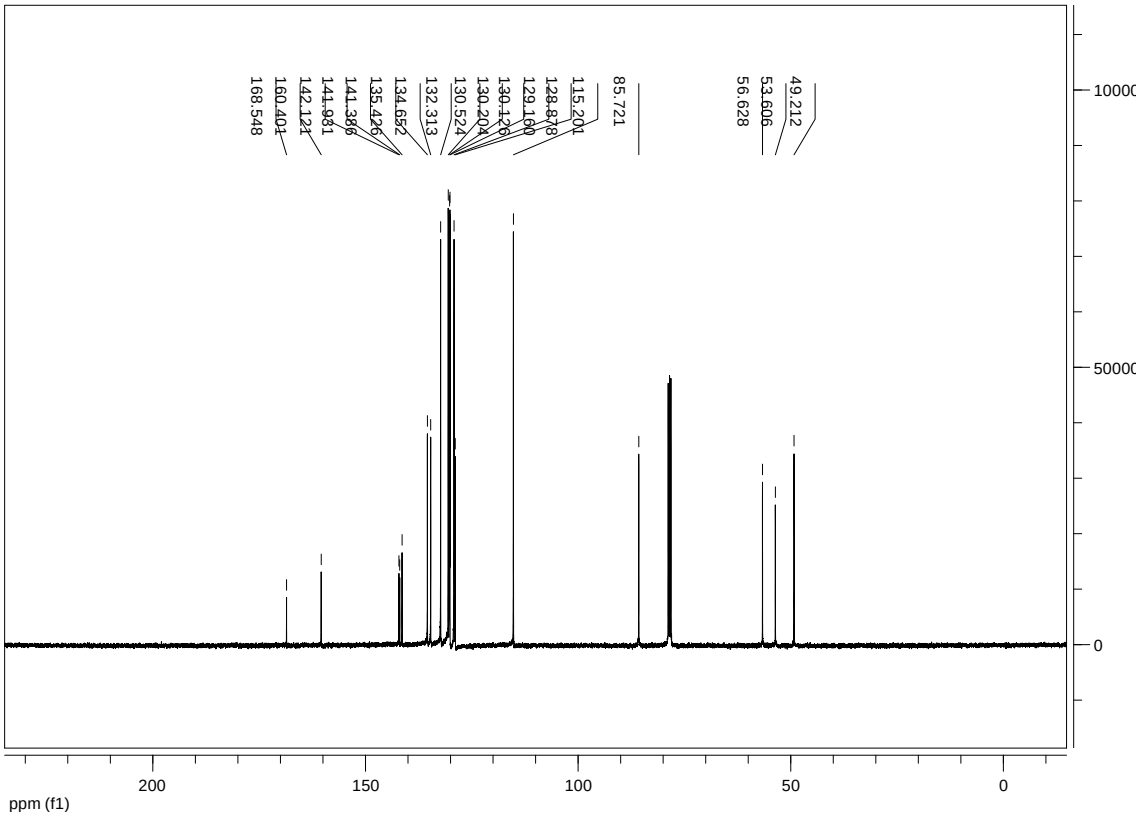
1 PDA Multi 1/205nm 4nm

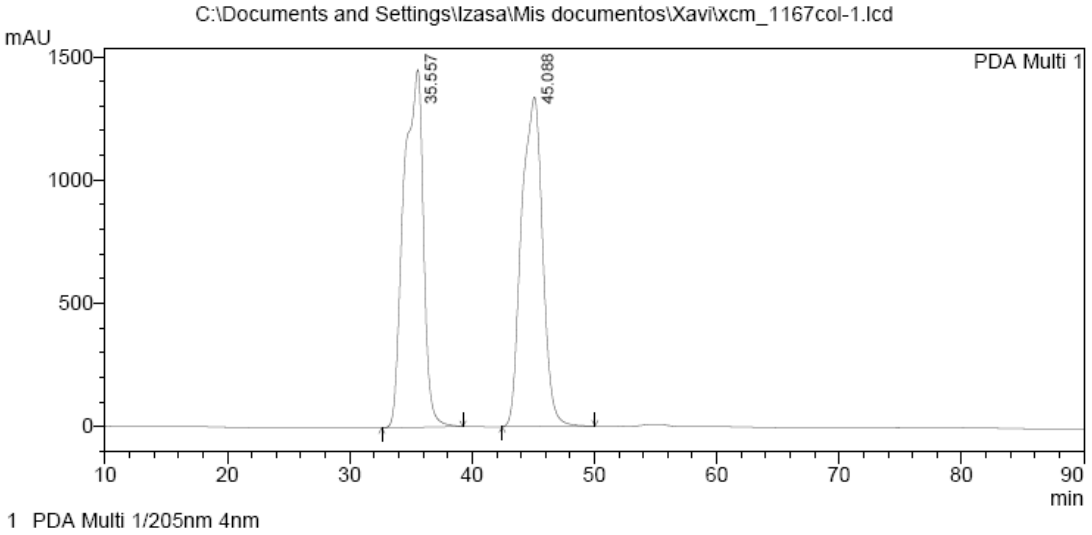
PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.119	2751421	72324	3.693	5.959
2	39.867	71749681	1141279	96.307	94.041
Total		74501101	1213604	100.000	100.000





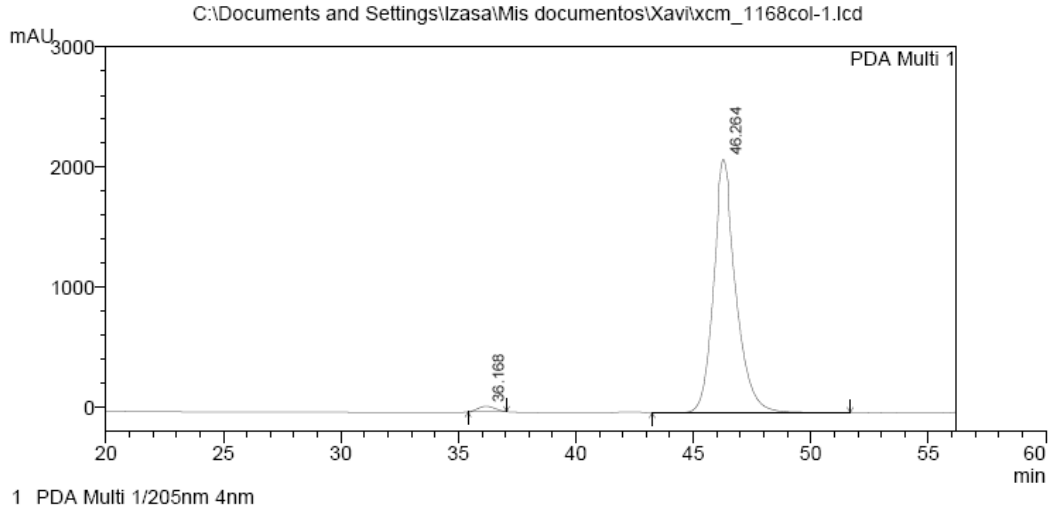


1 PDA Multi 1/205nm 4nm

PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.557	161663941	1452012	50.268	52.065
2	45.088	159941813	1336848	49.732	47.935
Total		321605754	2788860	100.000	100.000

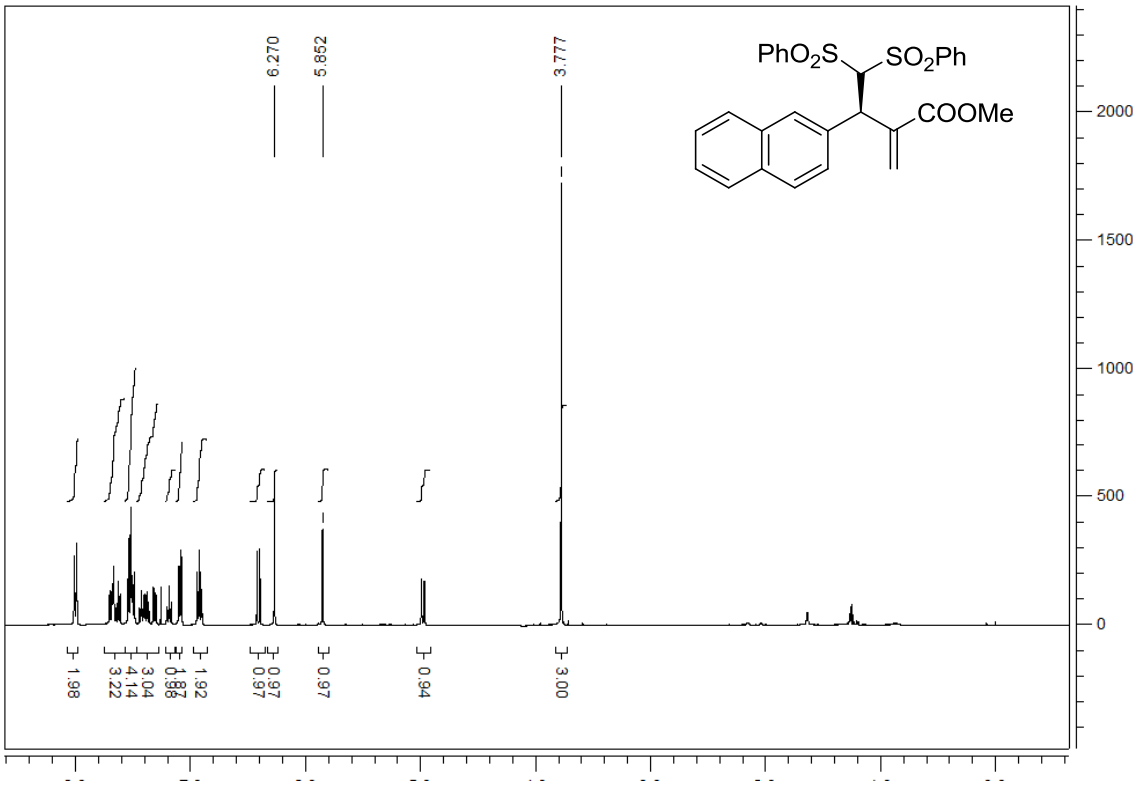


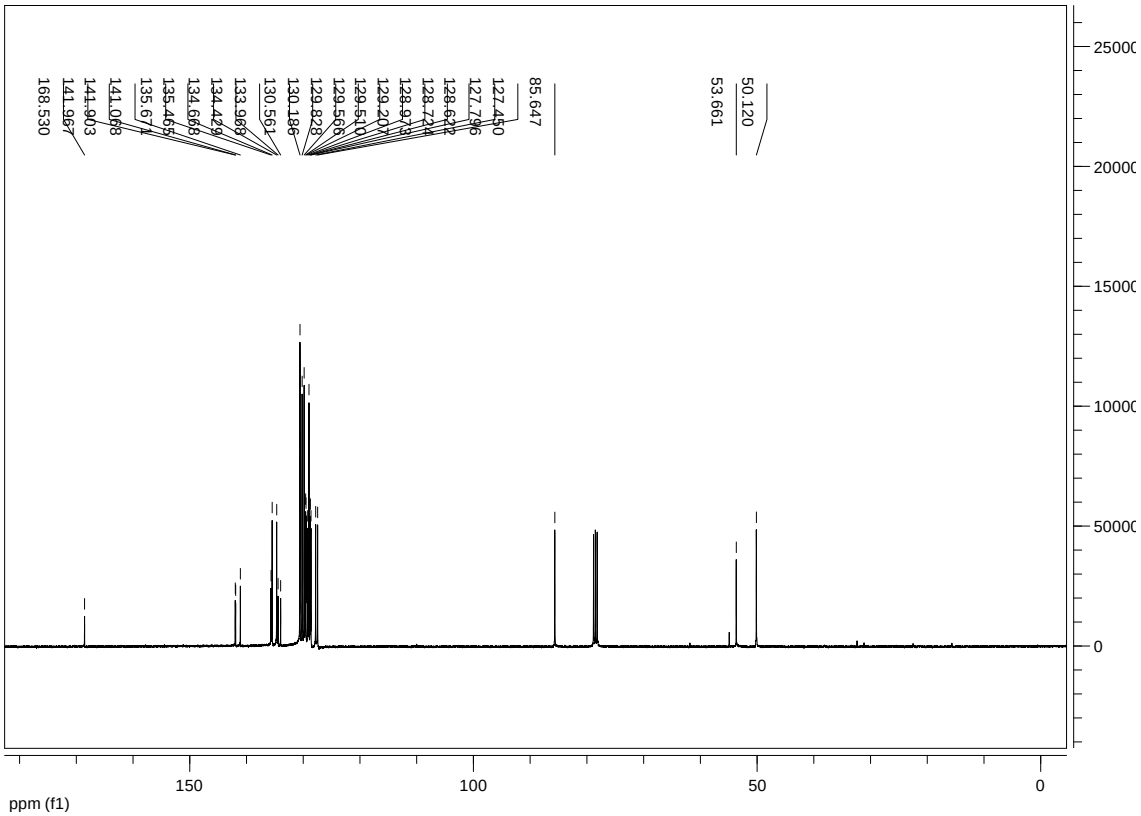
1 PDA Multi 1/205nm 4nm

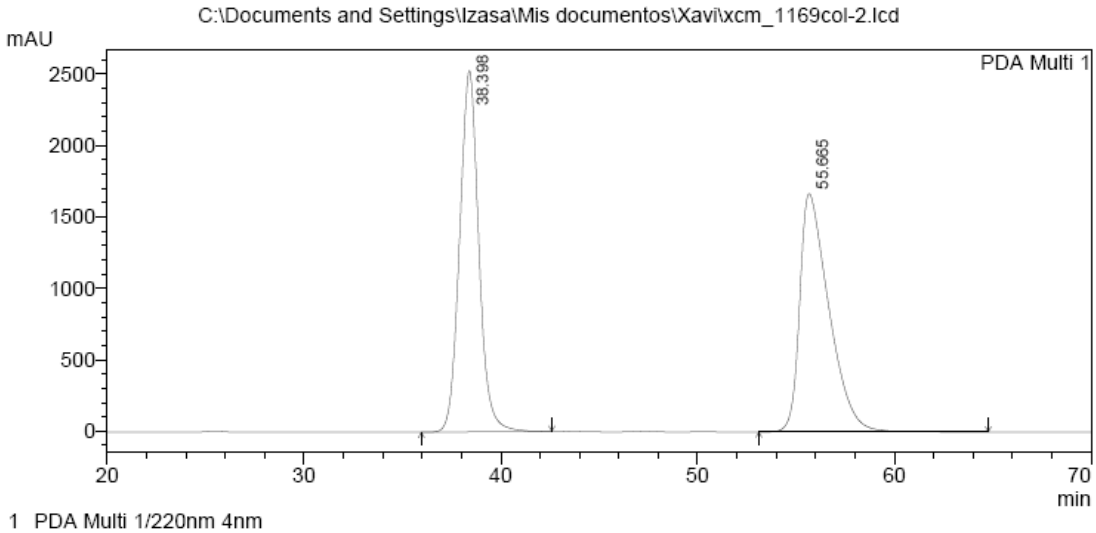
PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.168	2240660	44281	1.594	2.054
2	46.264	138330735	2111556	98.406	97.946
Total		140571395	2155836	100.000	100.000





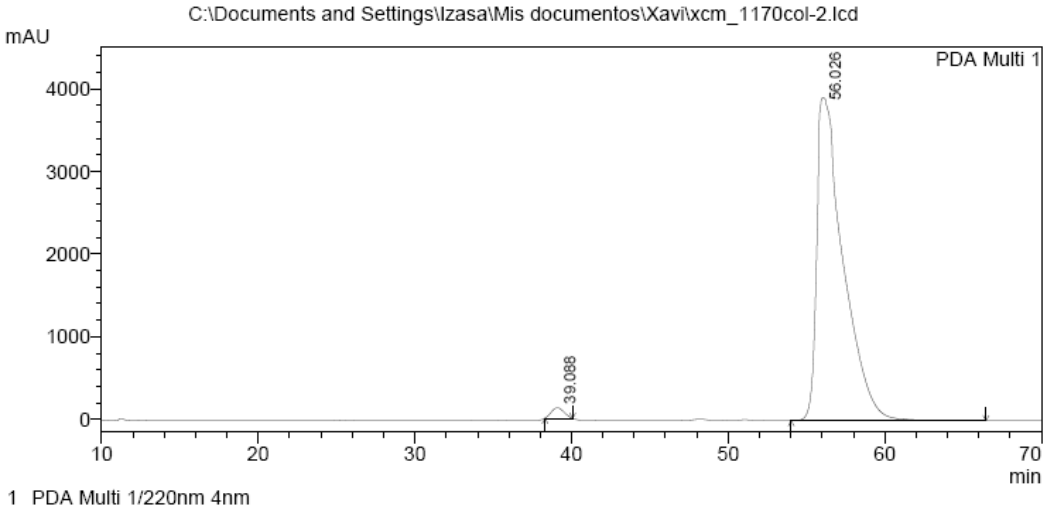


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.398	170926674	2526629	49.792	60.244
2	55.665	172351424	1667361	50.208	39.756
Total		343278098	4193989	100.000	100.000

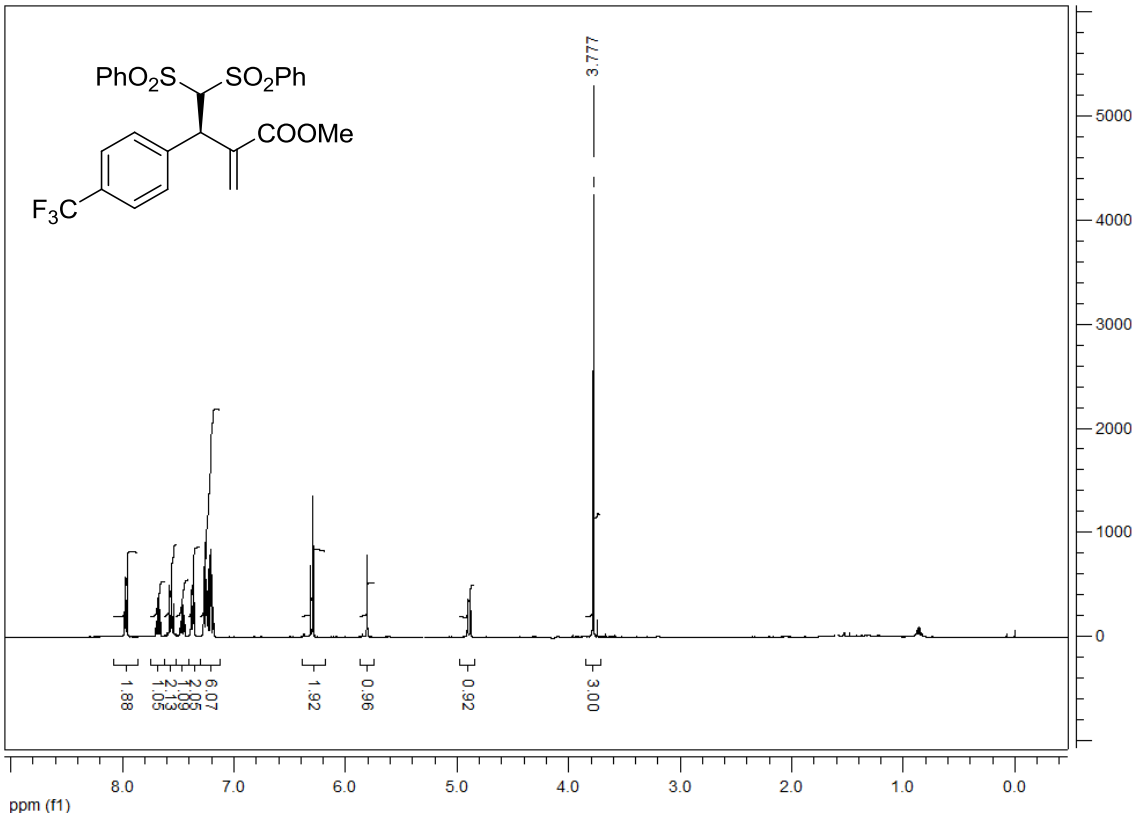


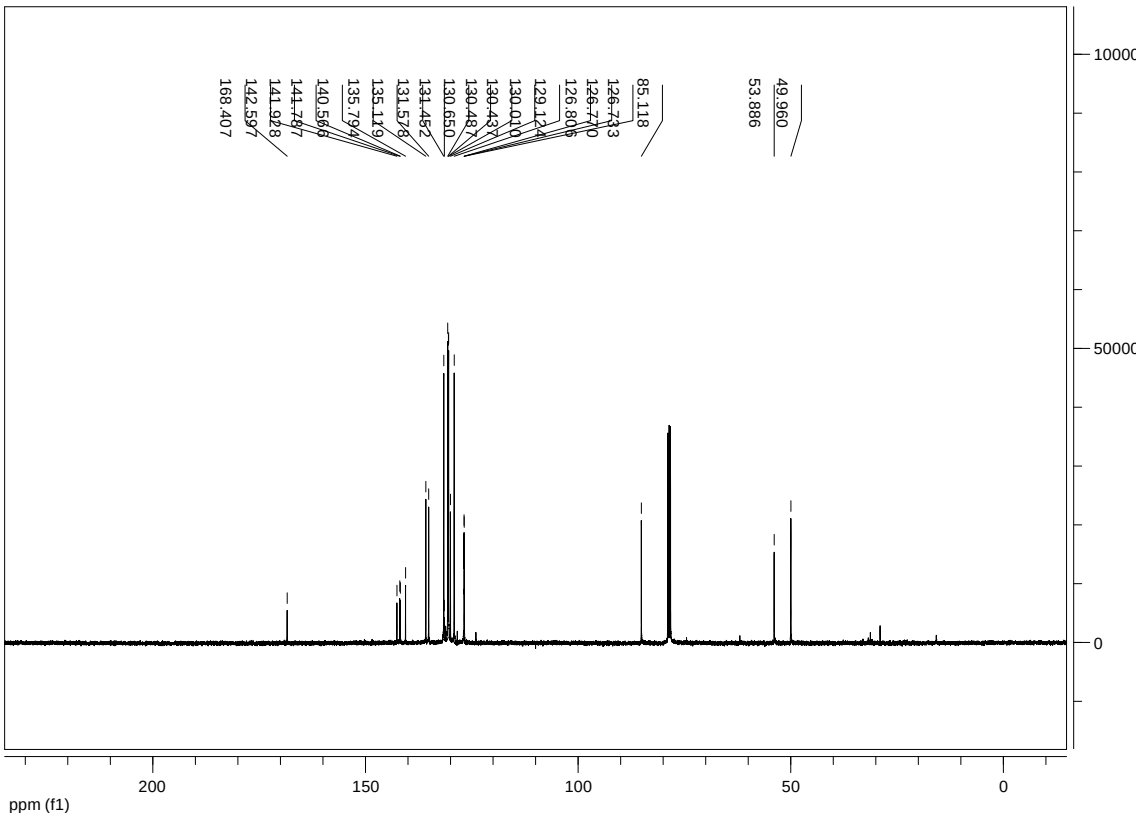
1 PDA Multi 1/220nm 4nm

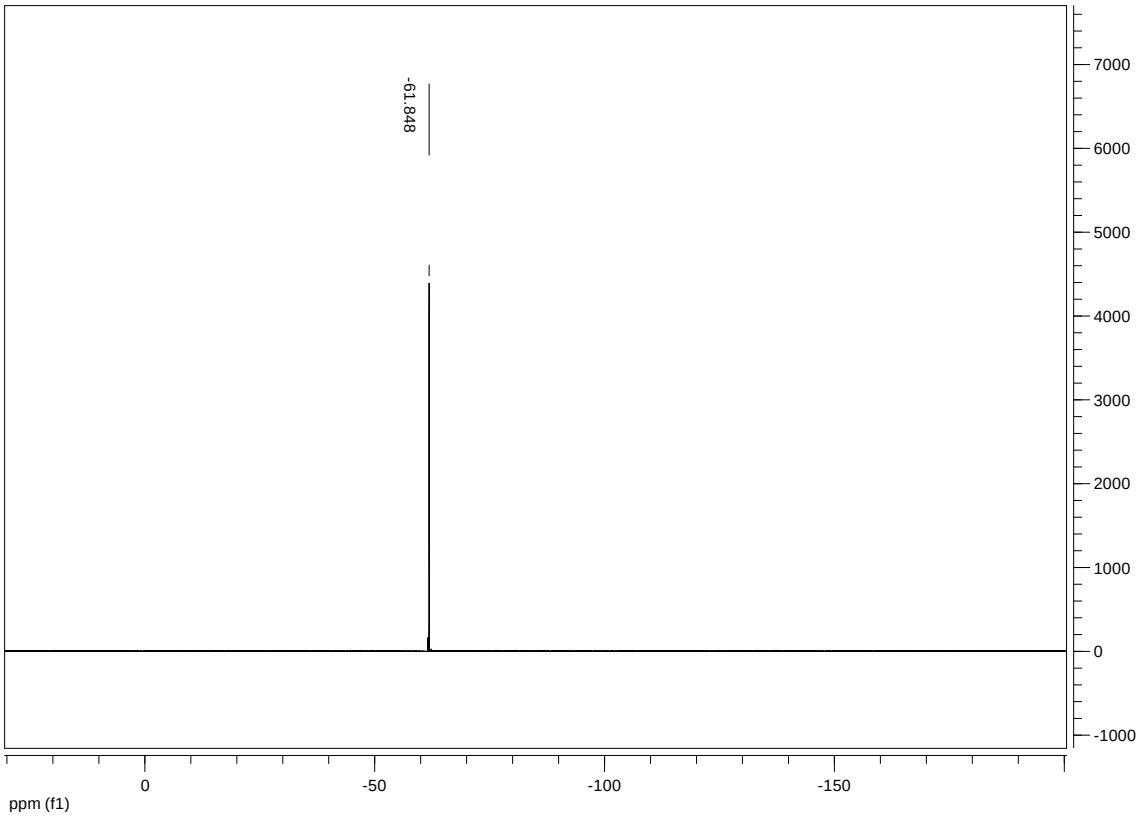
PeakTable

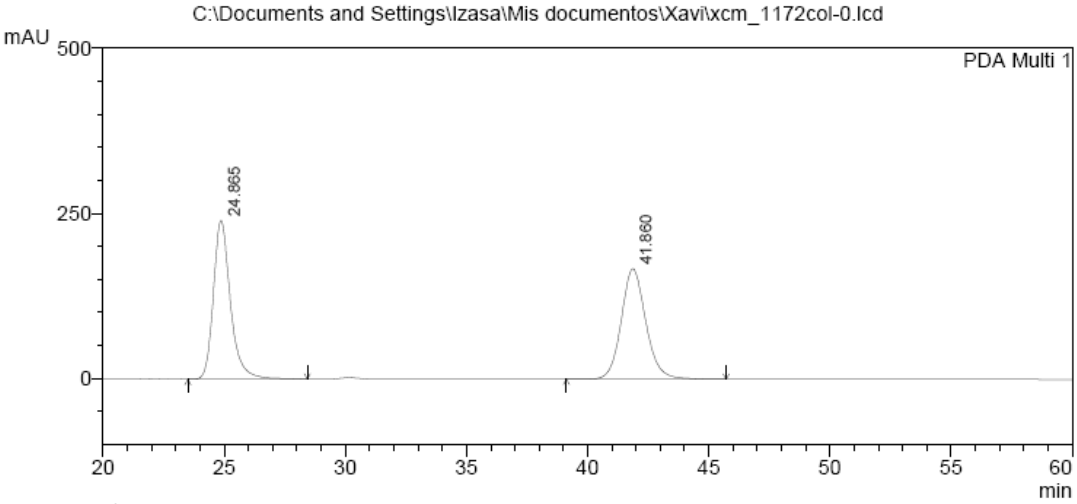
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.088	7131296	126917	1.528	3.145
2	56.026	459660654	3908980	98.472	96.855
Total		466791950	4035897	100.000	100.000







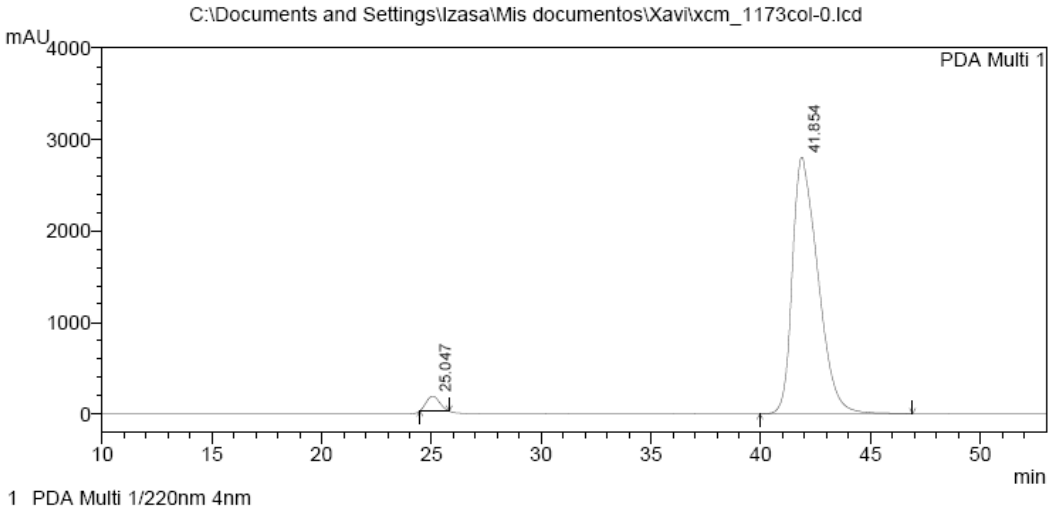


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.865	11830312	240566	49.969	58.996
2	41.860	11844791	167199	50.031	41.004
Total		23675103	407764	100.000	100.000

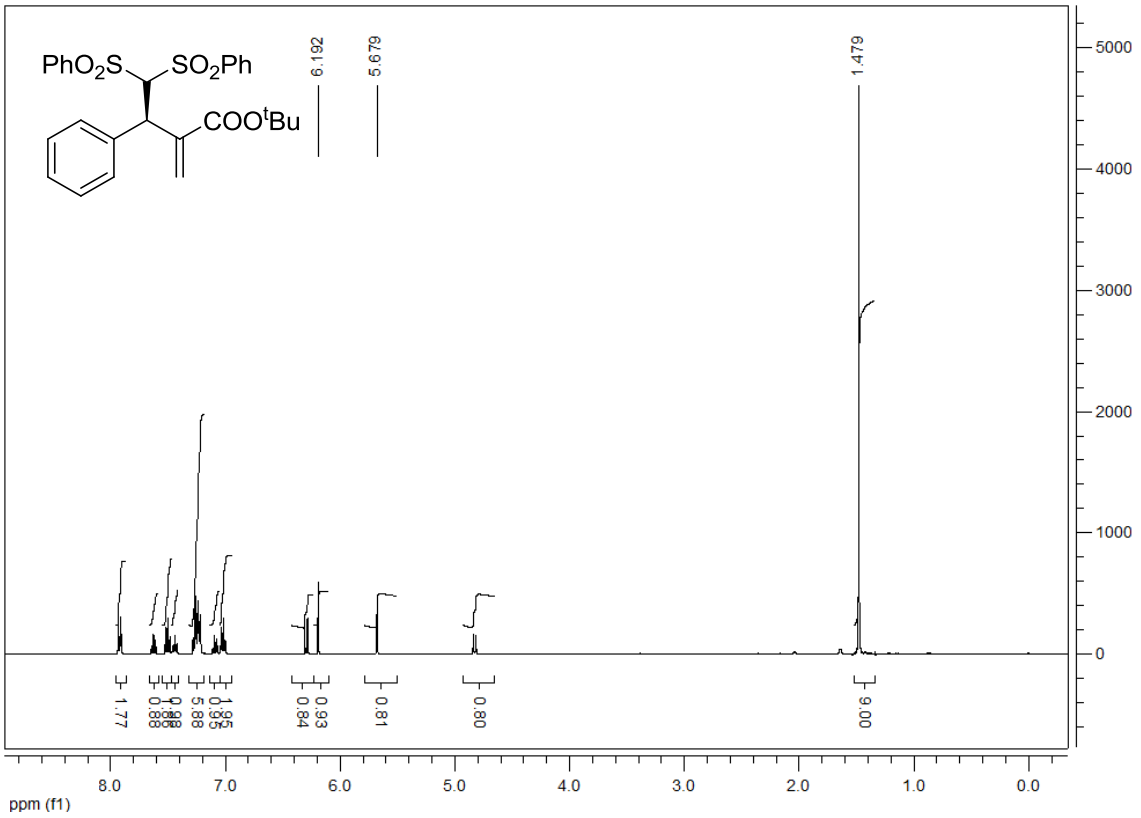


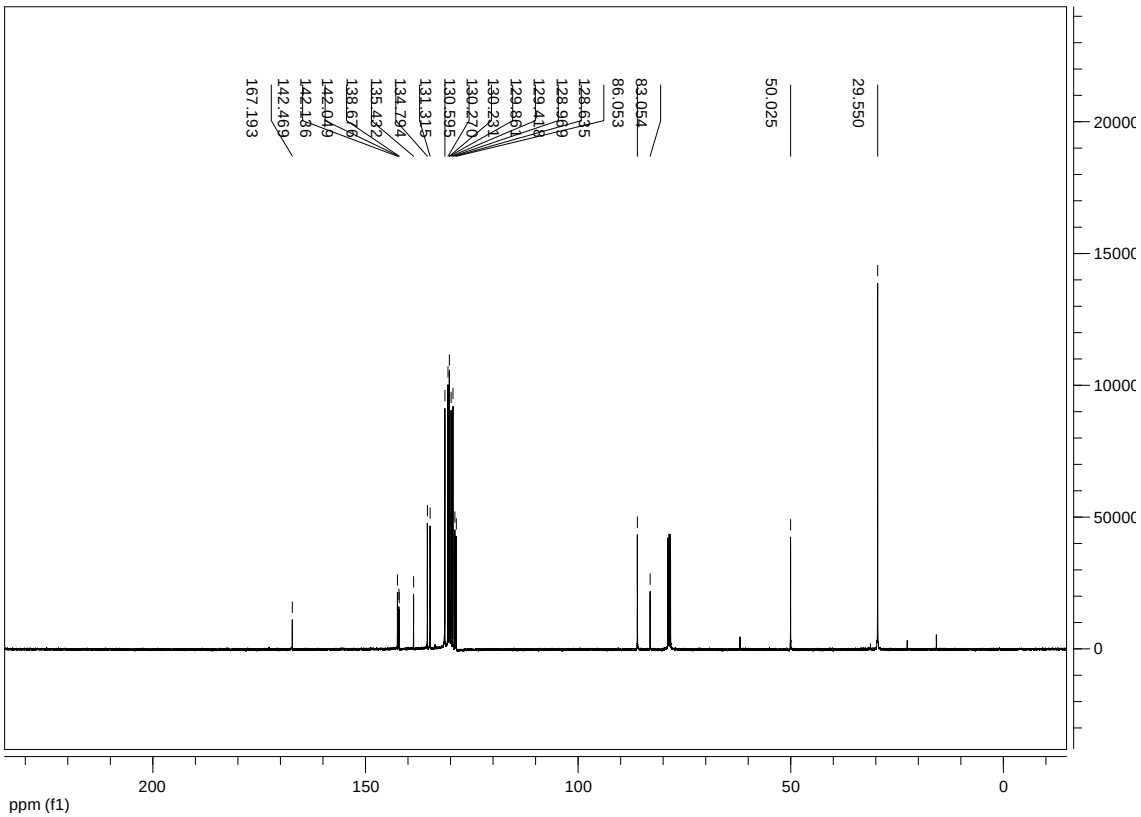
1 PDA Multi 1/220nm 4nm

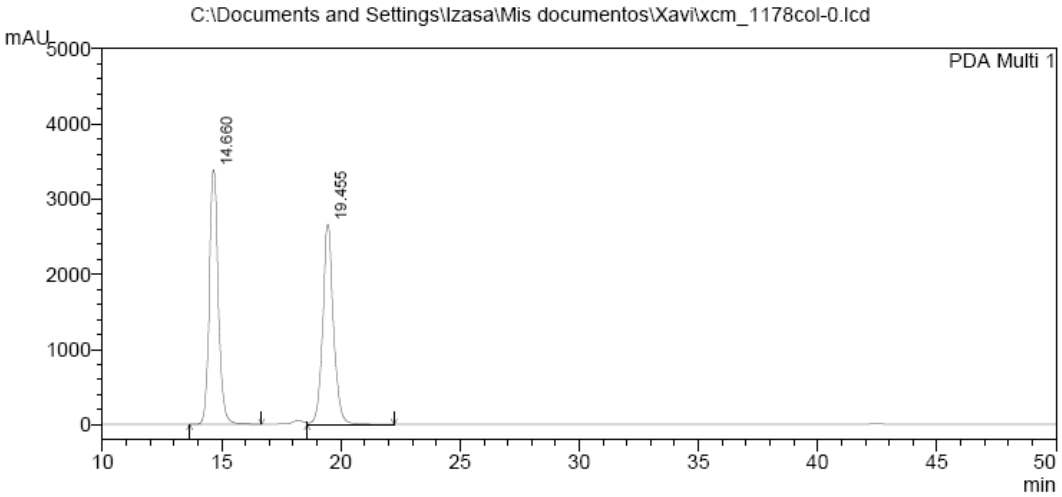
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.047	6747737	162269	2.886	5.471
2	41.854	227056874	2803763	97.114	94.529
Total		233804611	2966032	100.000	100.000



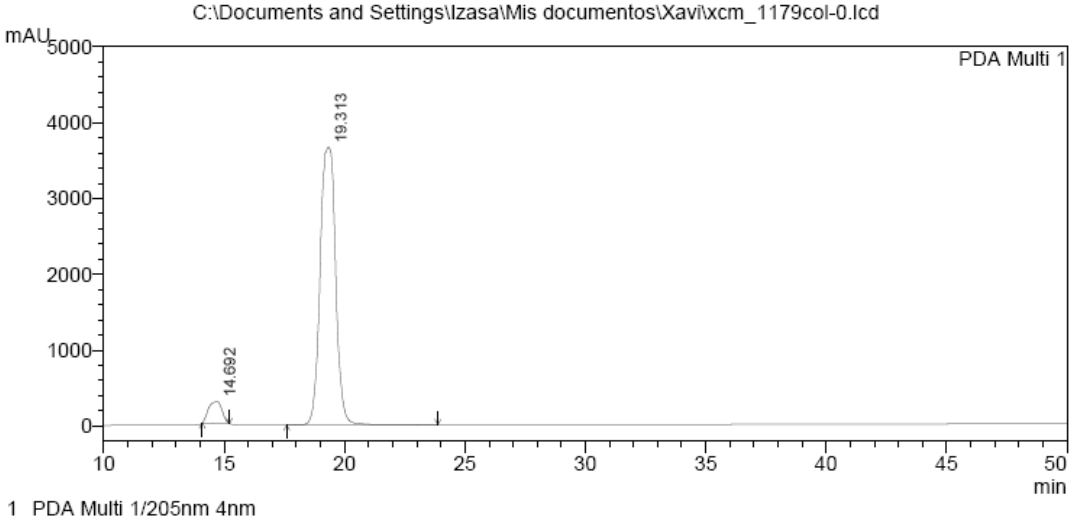




PeakTable

PDA Ch1 205nm 4nm

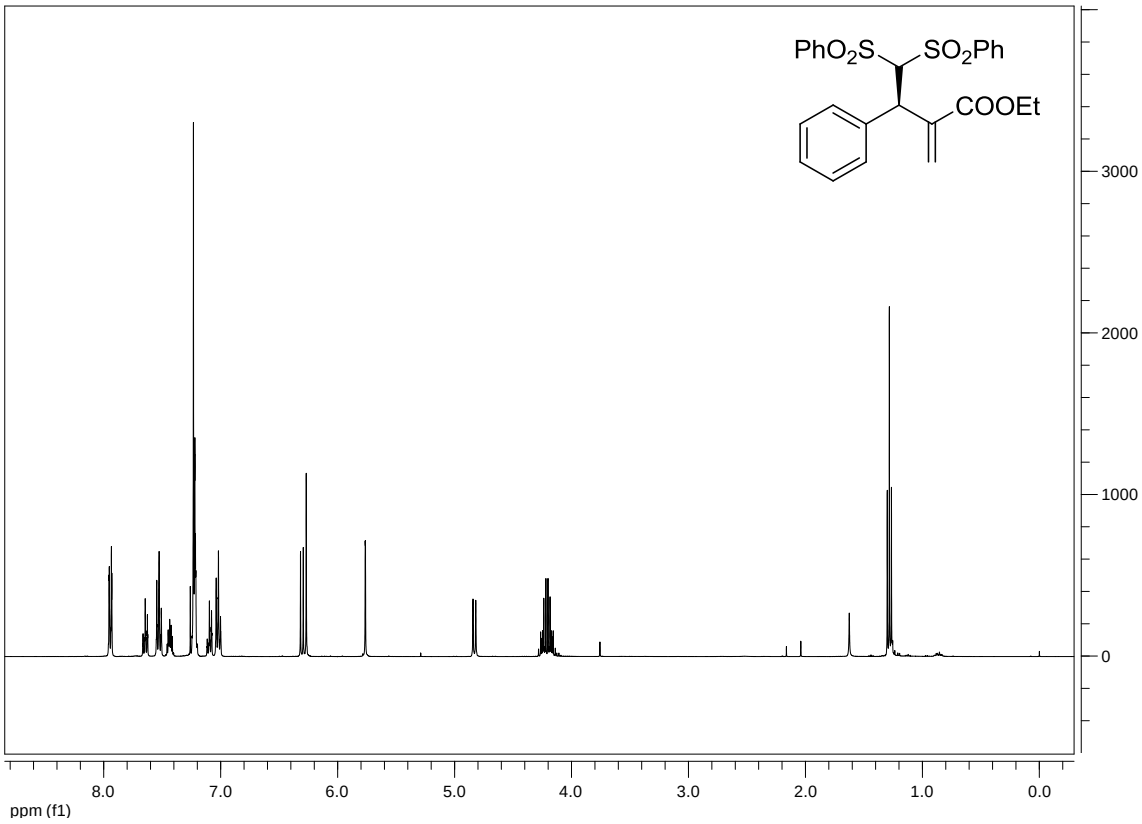
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.660	89245549	3390083	51.499	55.973
2	19.455	84049941	2666519	48.501	44.027
Total		173295490	6056602	100.000	100.000

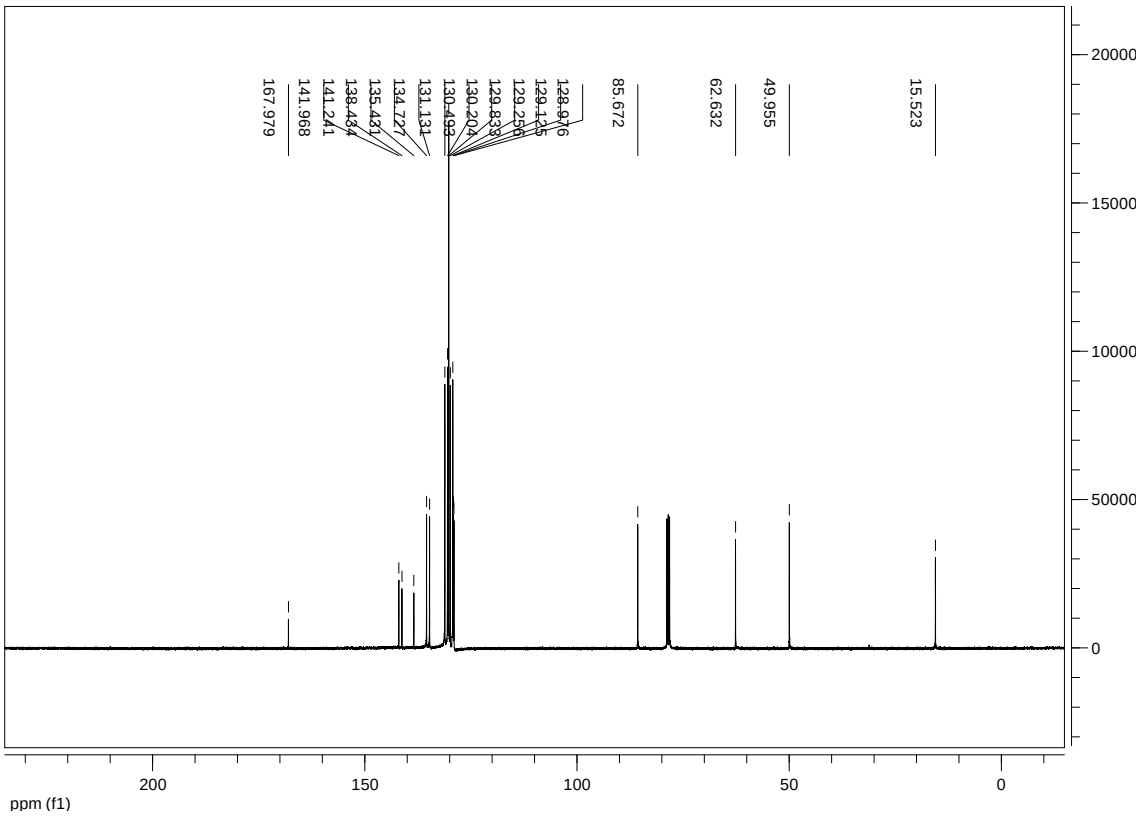


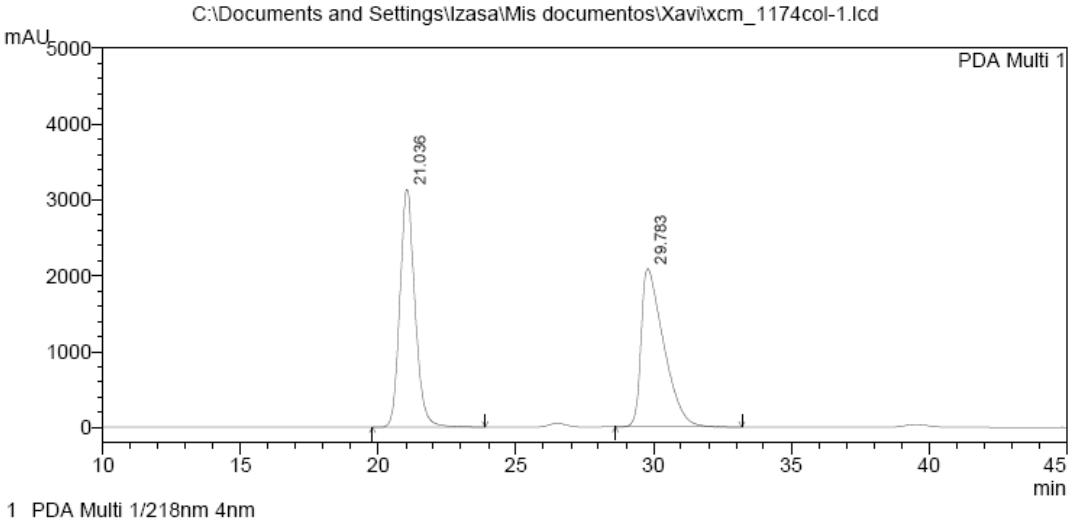
PeakTable

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.692	11050948	286844	6.322	7.258
2	19.313	163737257	3665482	93.678	92.742
Total		174788205	3952327	100.000	100.000





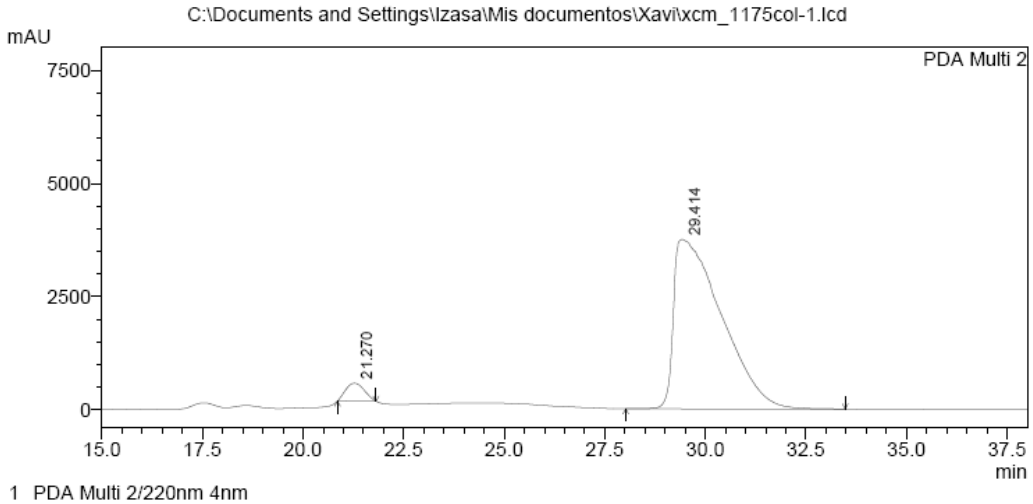


1 PDA Multi 1/218nm 4nm

PeakTable

PDA Ch1 218nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.036	119543755	3136102	50.037	60.008
2	29.783	119368378	2090046	49.963	39.992
Total		238912133	5226149	100.000	100.000

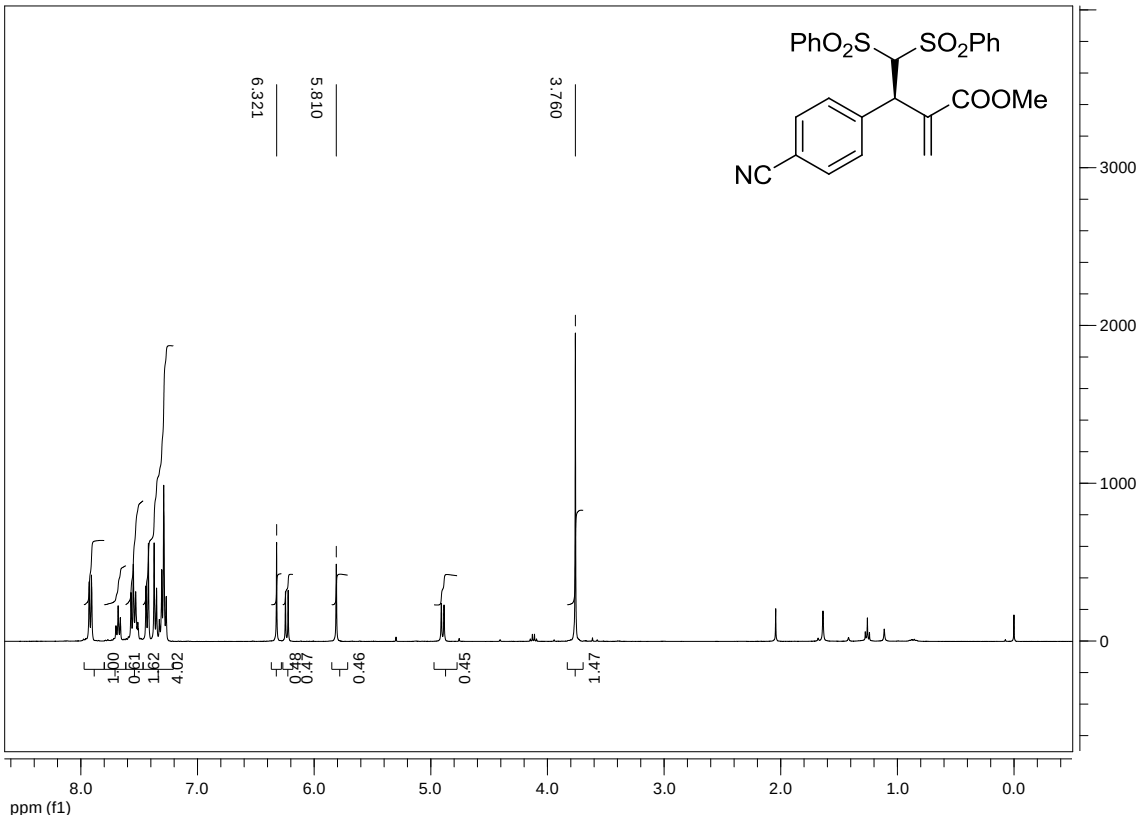


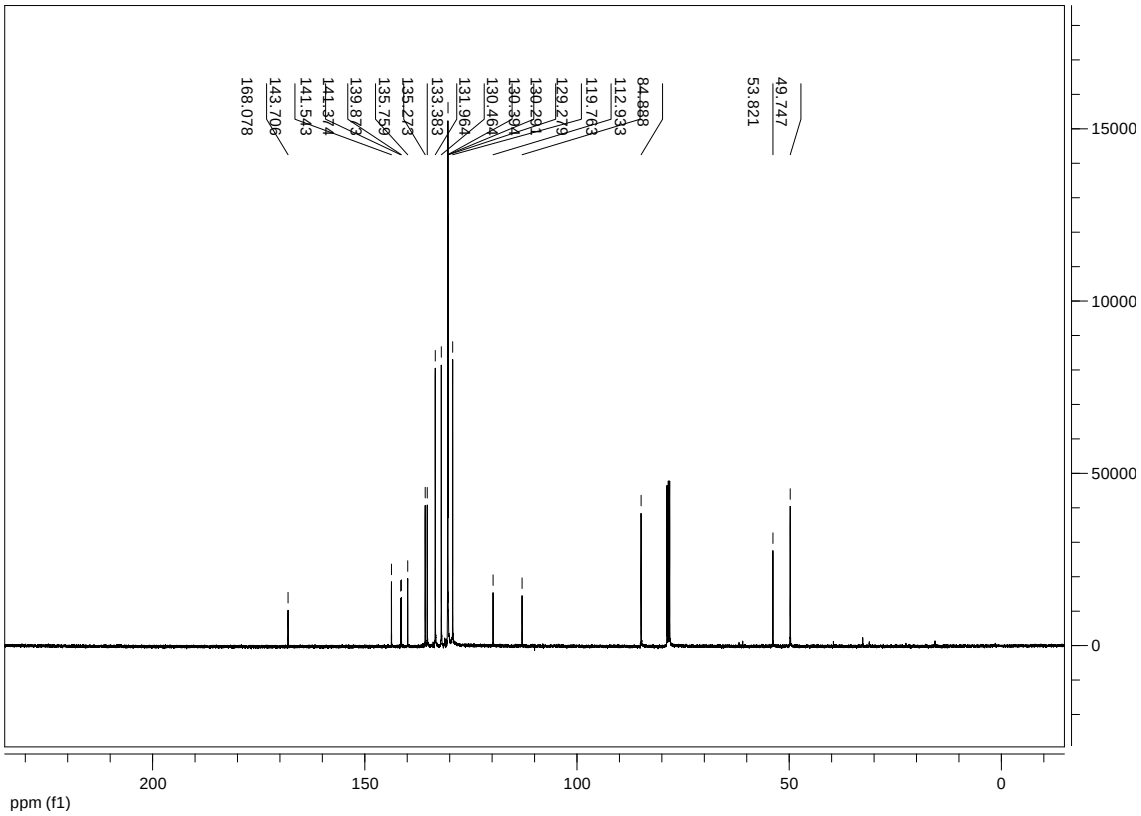
1 PDA Multi 2/220nm 4nm

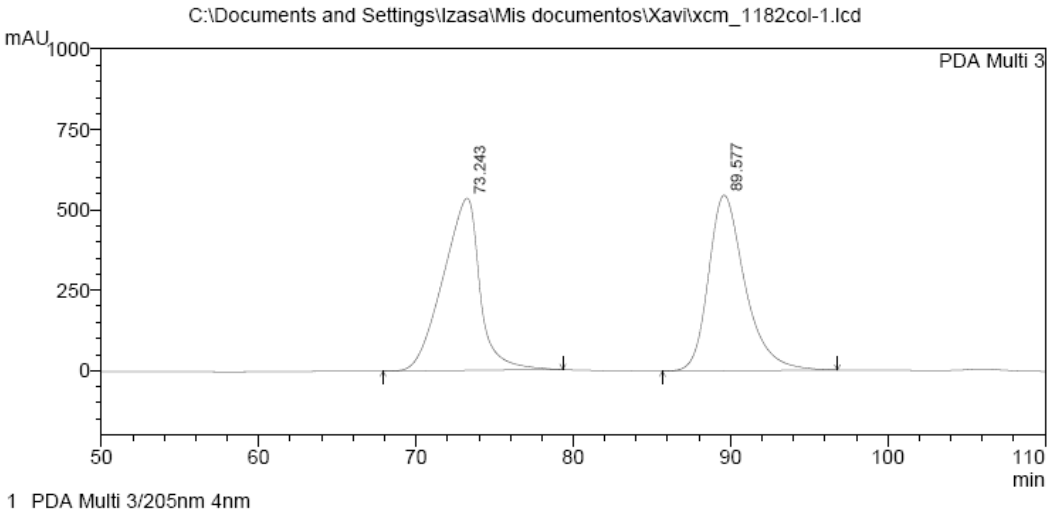
PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.270	12856331	397697	3.968	9.595
2	29.414	311151451	3747213	96.032	90.405
Total		324007783	4144910	100.000	100.000





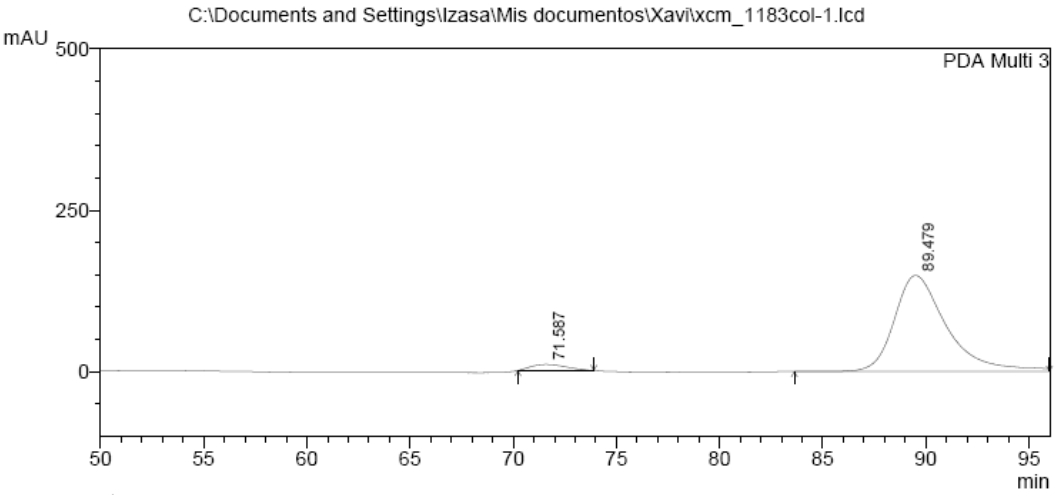


1 PDA Multi 3/205nm 4nm

PeakTable

PDA Ch3 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	73.243	87534757	535528	49.878	49.529
2	89.577	87964641	545708	50.122	50.471
Total		175499398	1081237	100.000	100.000

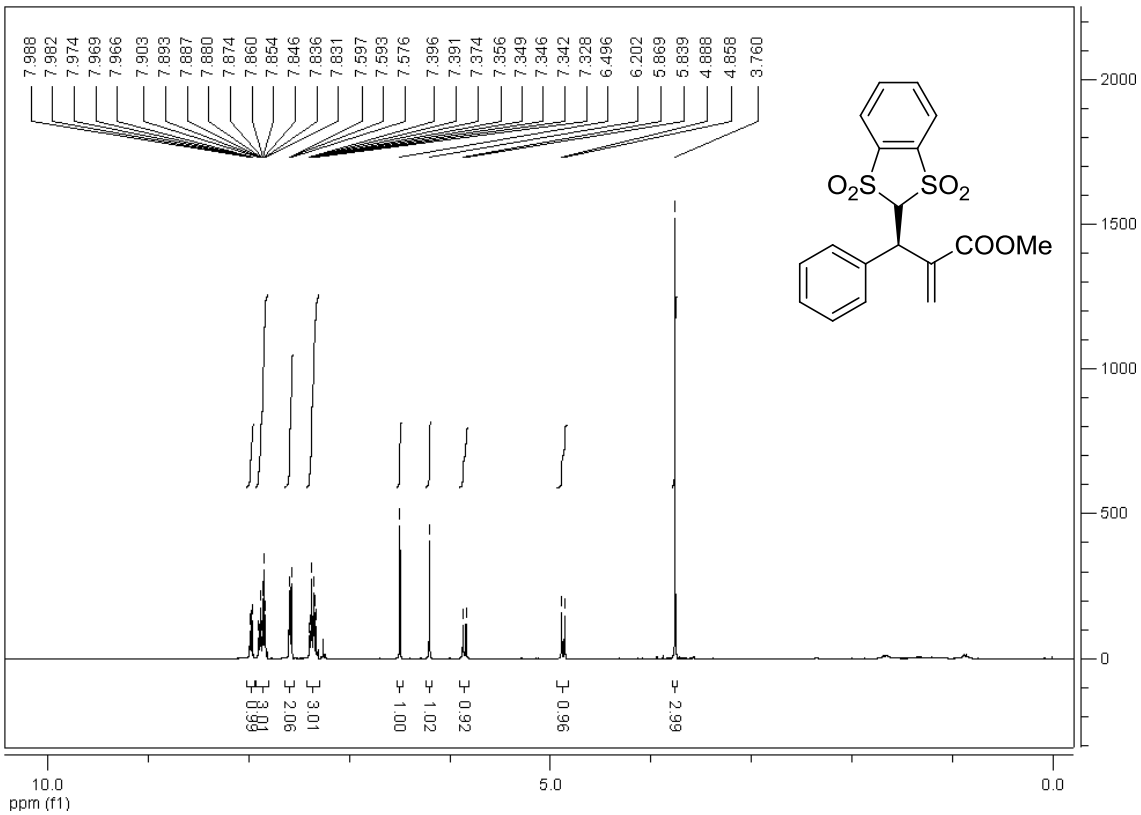


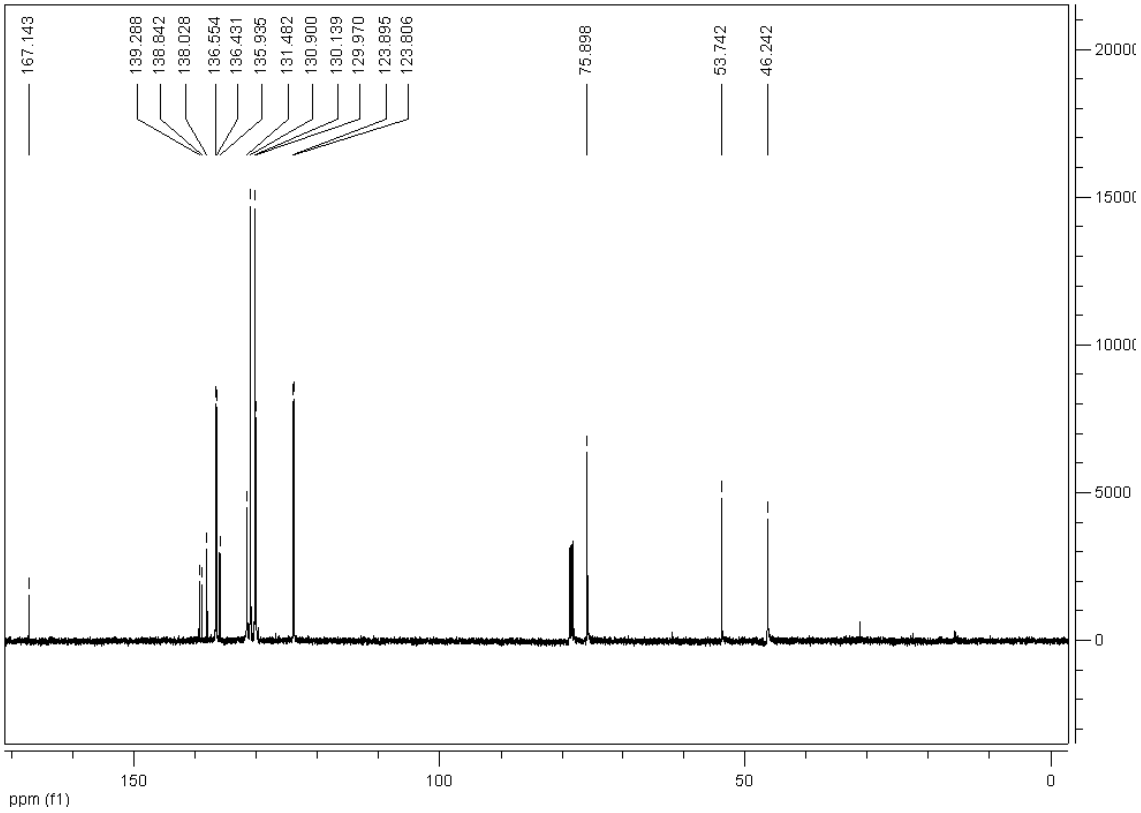
1 PDA Multi 3/205nm 4nm

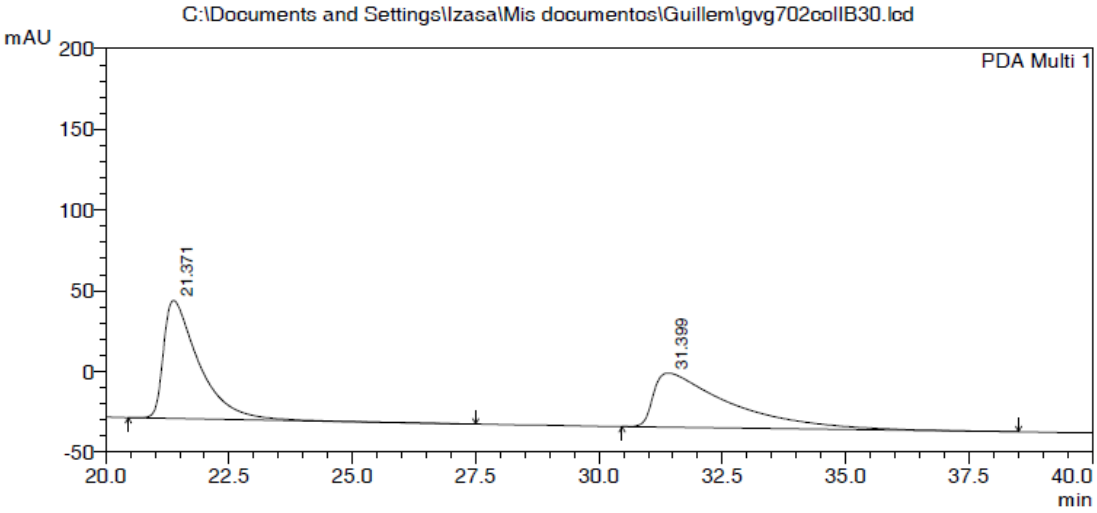
PeakTable

PDA Ch3 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	71.587	1124218	9528	4.115	6.020
2	89.479	26197336	148738	95.885	93.980
Total		27321554	158266	100.000	100.000





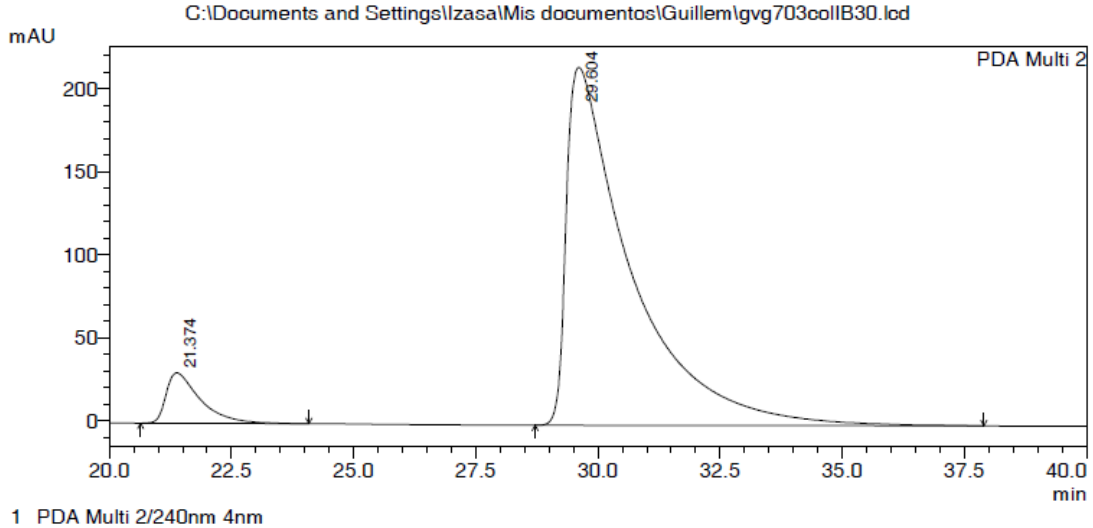


1 PDA Multi 1/240nm 4nm

PeakTable

PDA Ch1 240nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.371	3659387	73101	50.466	68.545
2	31.399	3591868	33546	49.534	31.455
Total		7251254	106647	100.000	100.000

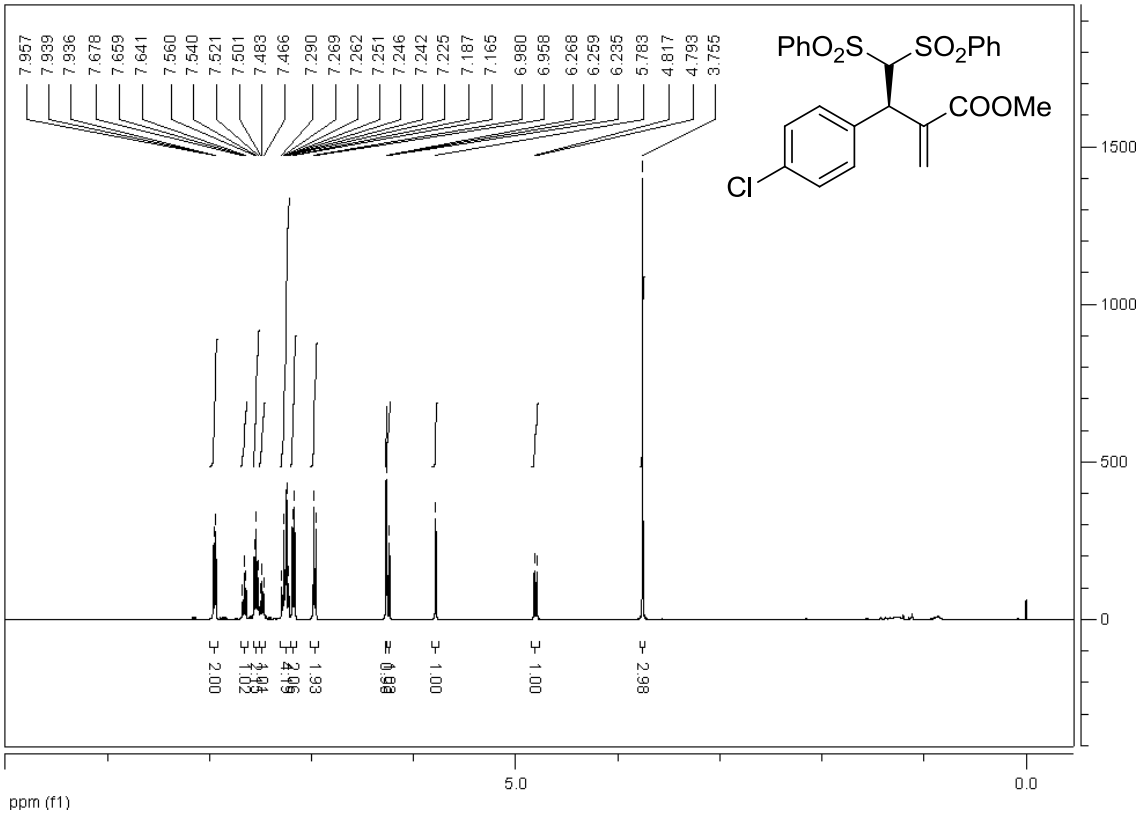


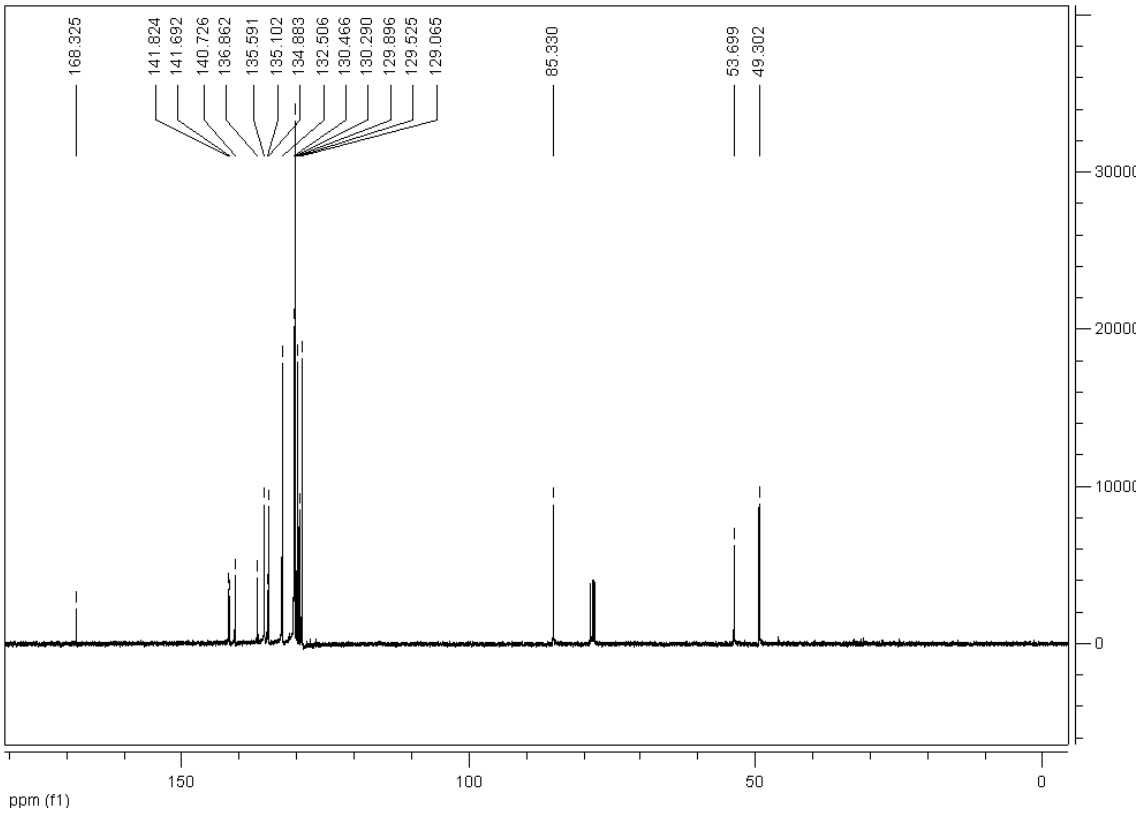
1 PDA Multi 2/240nm 4nm

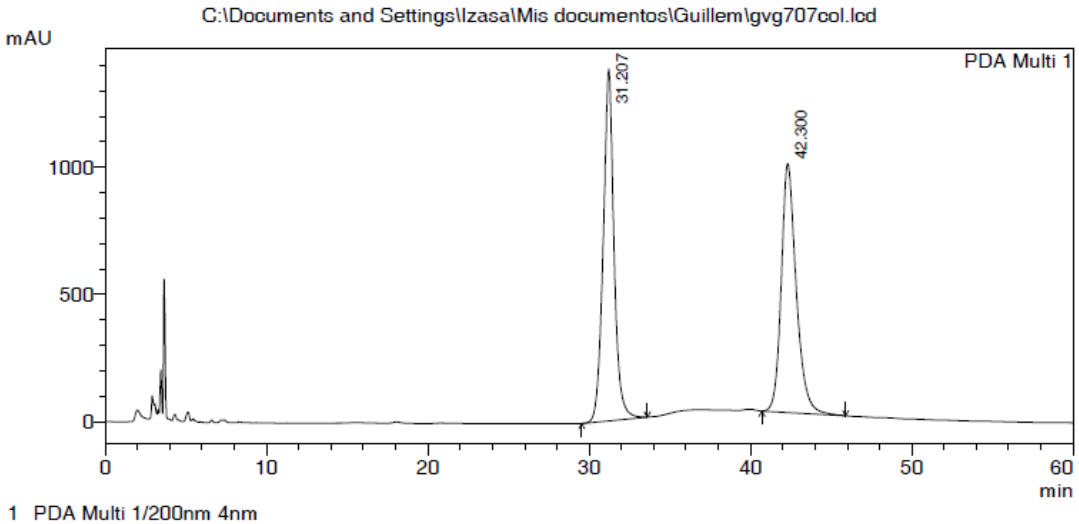
PeakTable

PDA Ch2 240nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.374	1475918	30321	6.946	12.338
2	29.604	19772984	215441	93.054	87.662
Total		21248902	245762	100.000	100.000





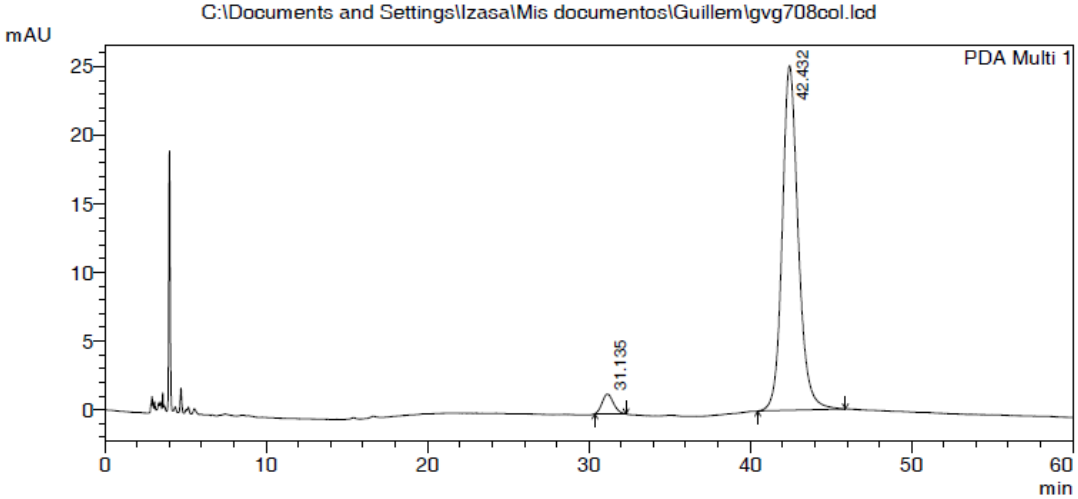


1 PDA Multi 1/200nm 4nm

PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.207	64393926	1383750	50.503	58.558
2	42.300	63111613	979299	49.497	41.442
Total		127505539	2363049	100.000	100.000

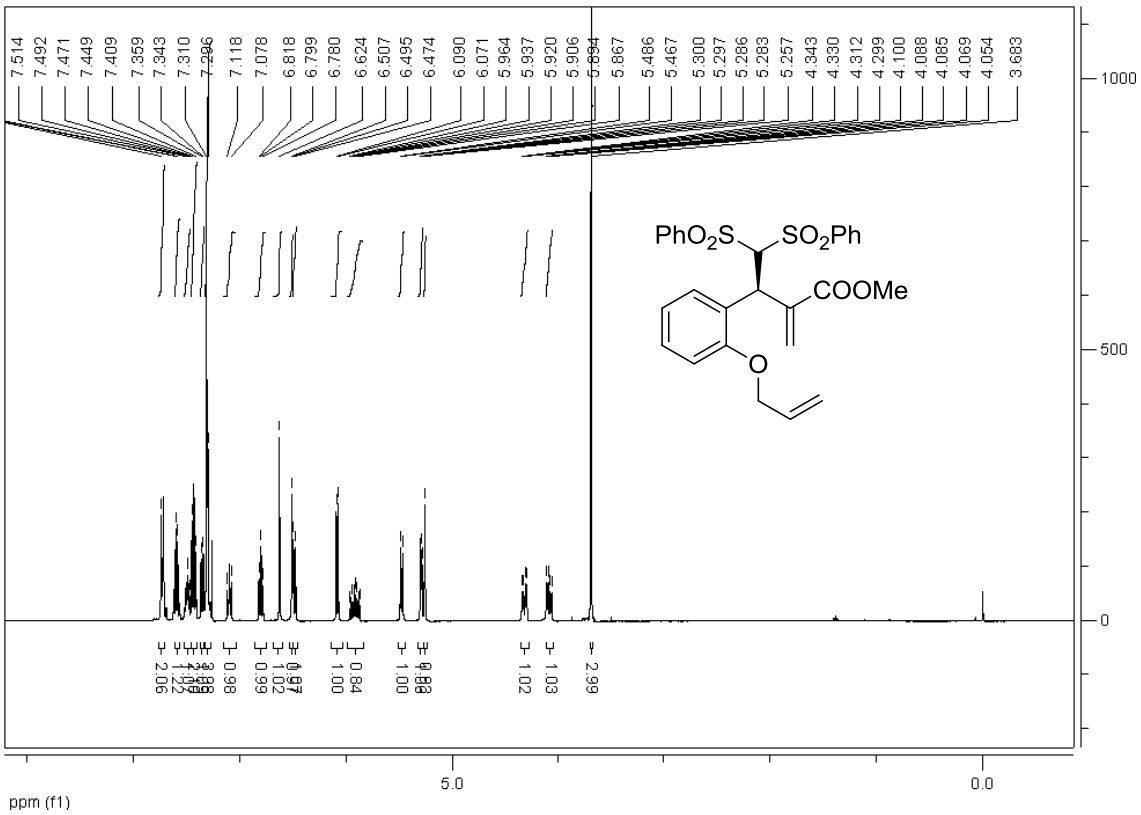


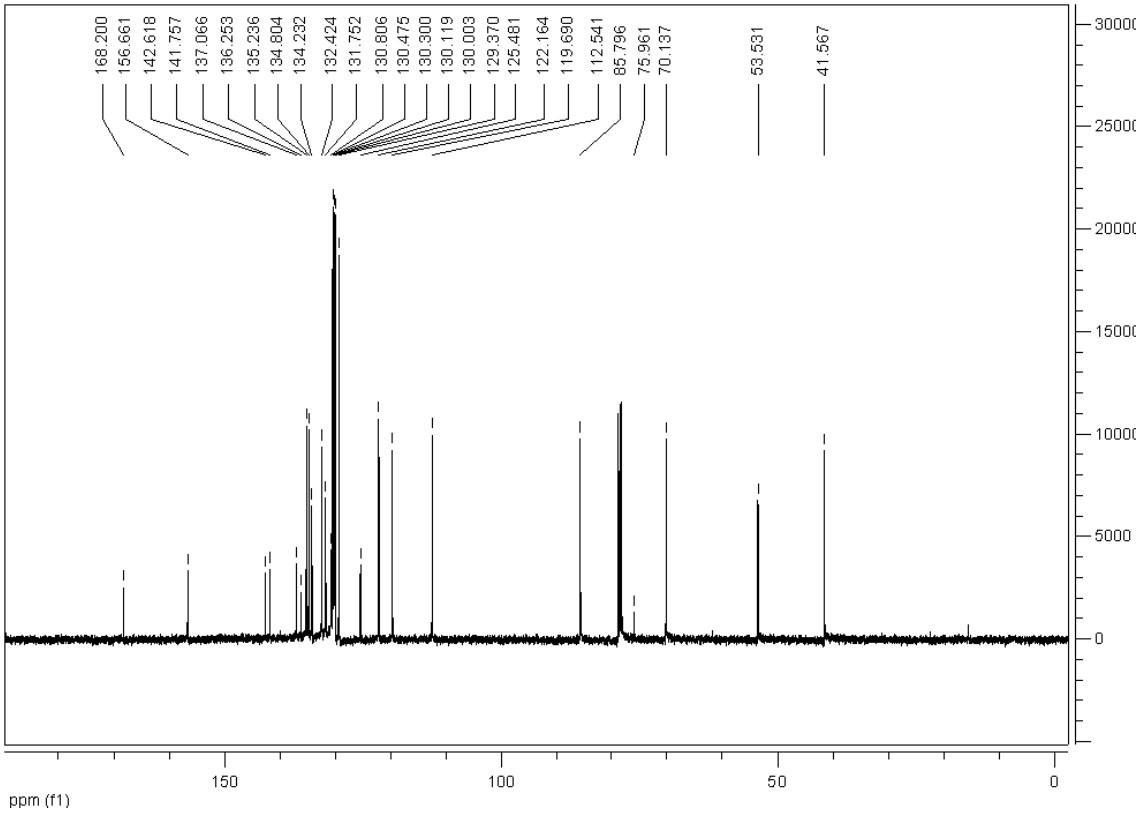
1 PDA Multi 1/254nm 4nm

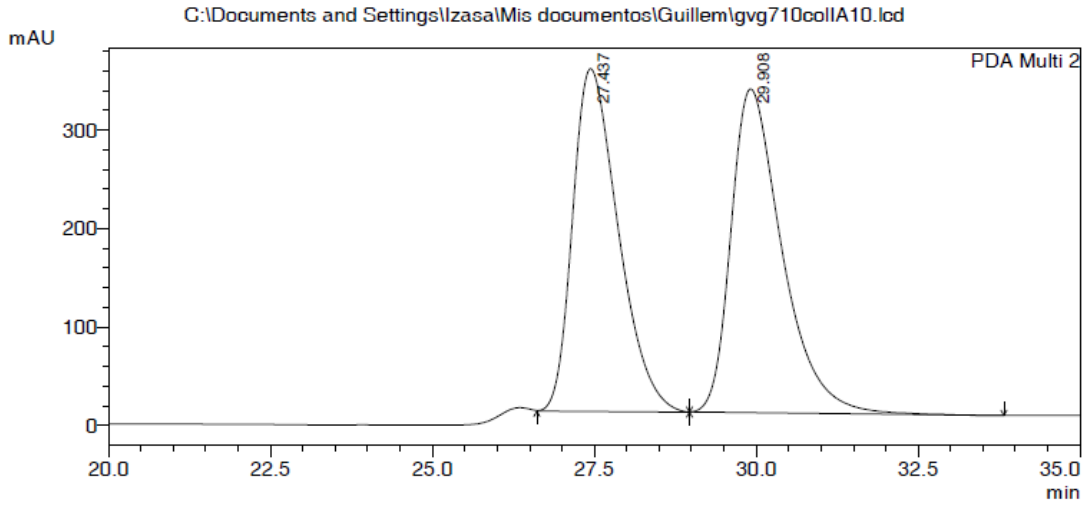
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.135	70120	1432	3.886	5.400
2	42.432	1734384	25078	96.114	94.600
Total		1804504	26509	100.000	100.000





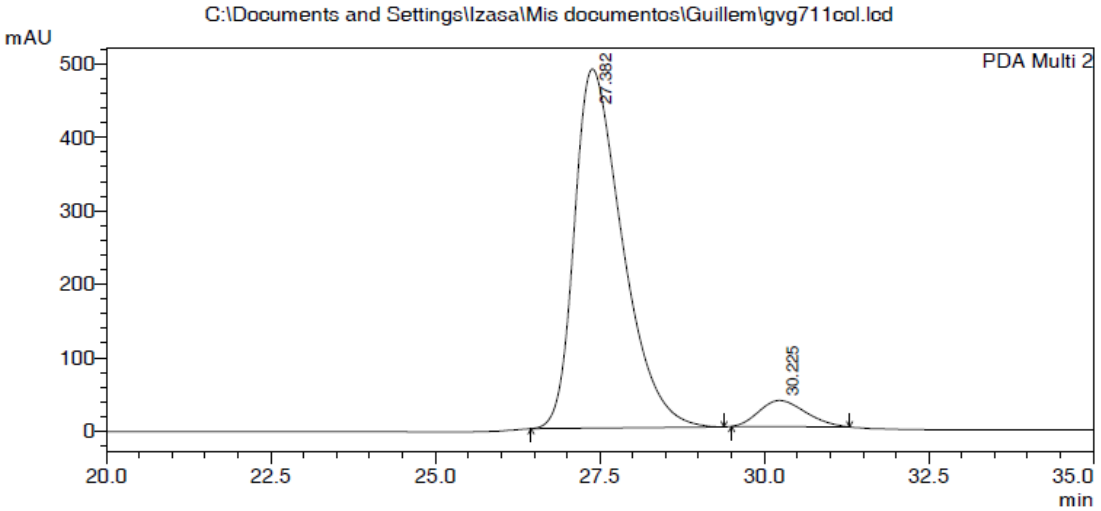


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.437	17005964	347814	48.543	51.432
2	29.908	18026982	328446	51.457	48.568
Total		35032946	676260	100.000	100.000

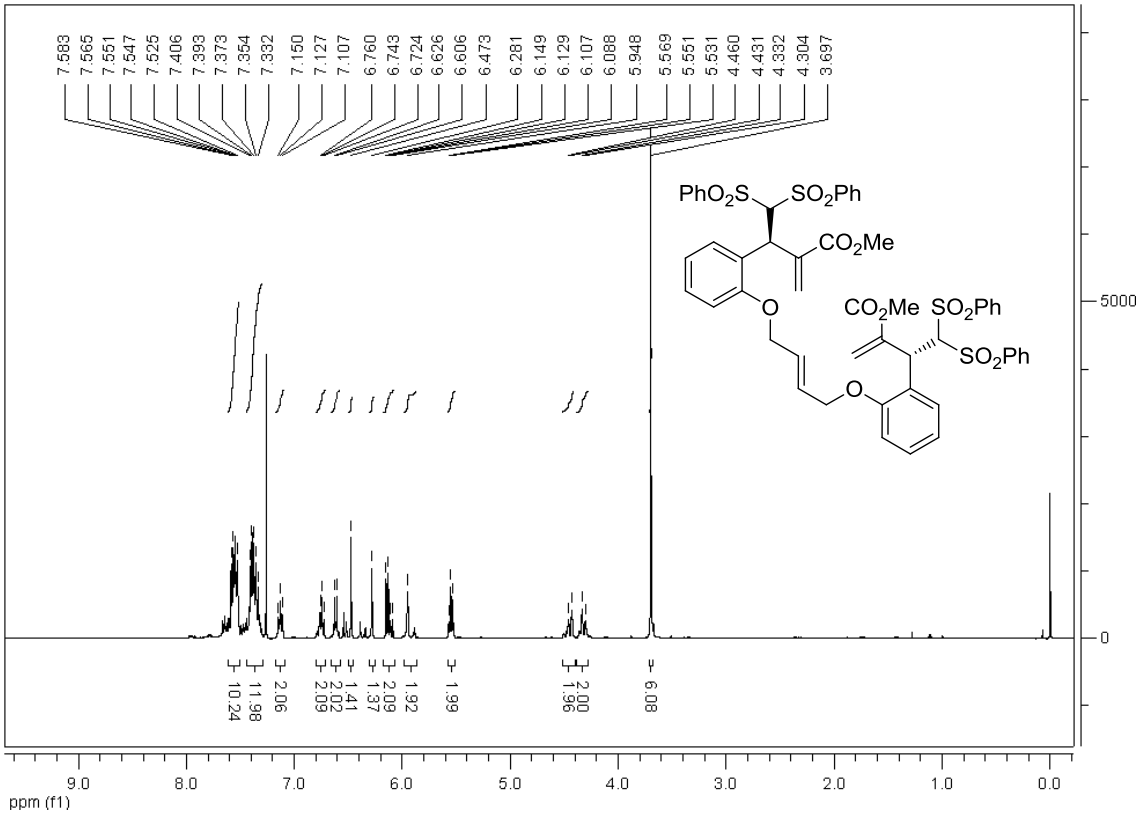


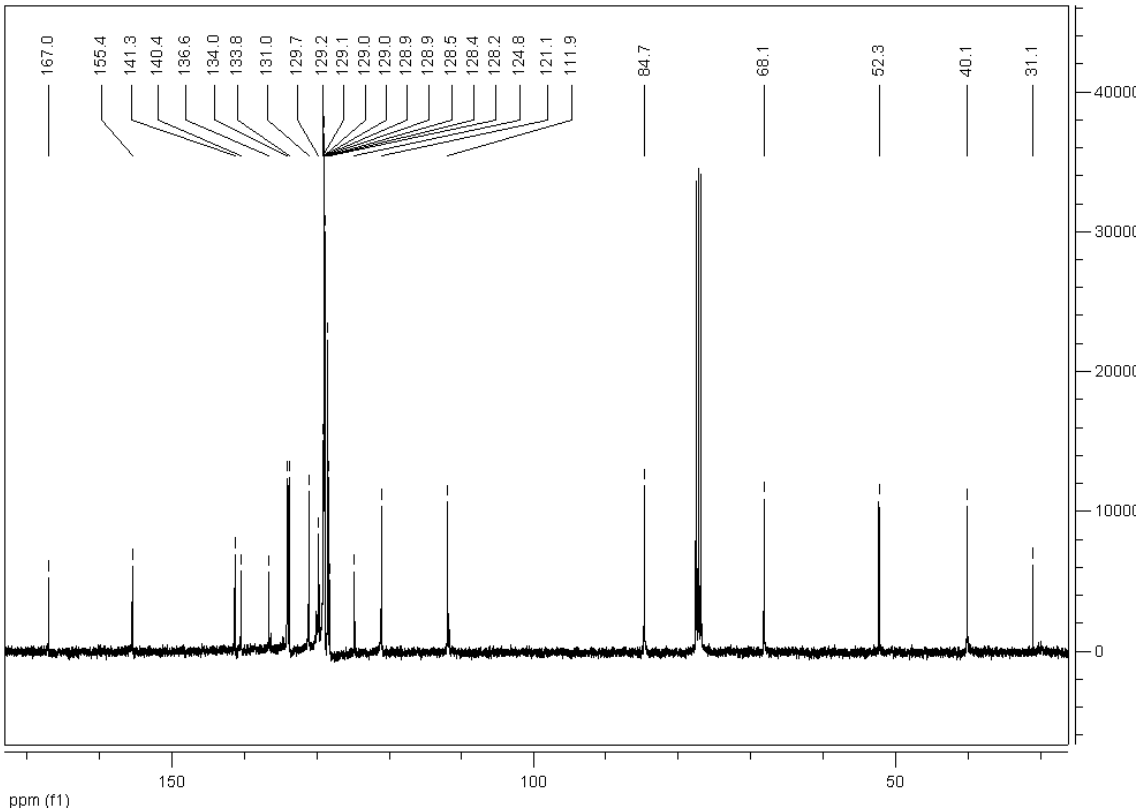
1 PDA Multi 2/220nm 4nm

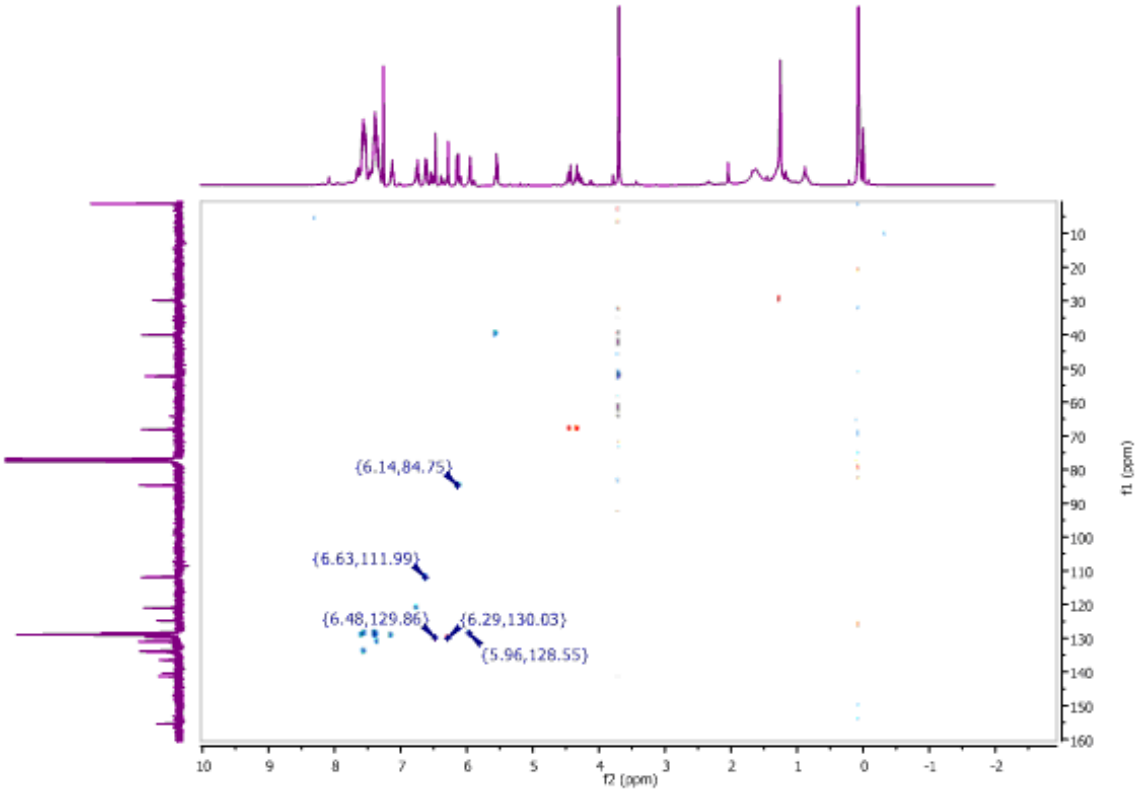
PeakTable

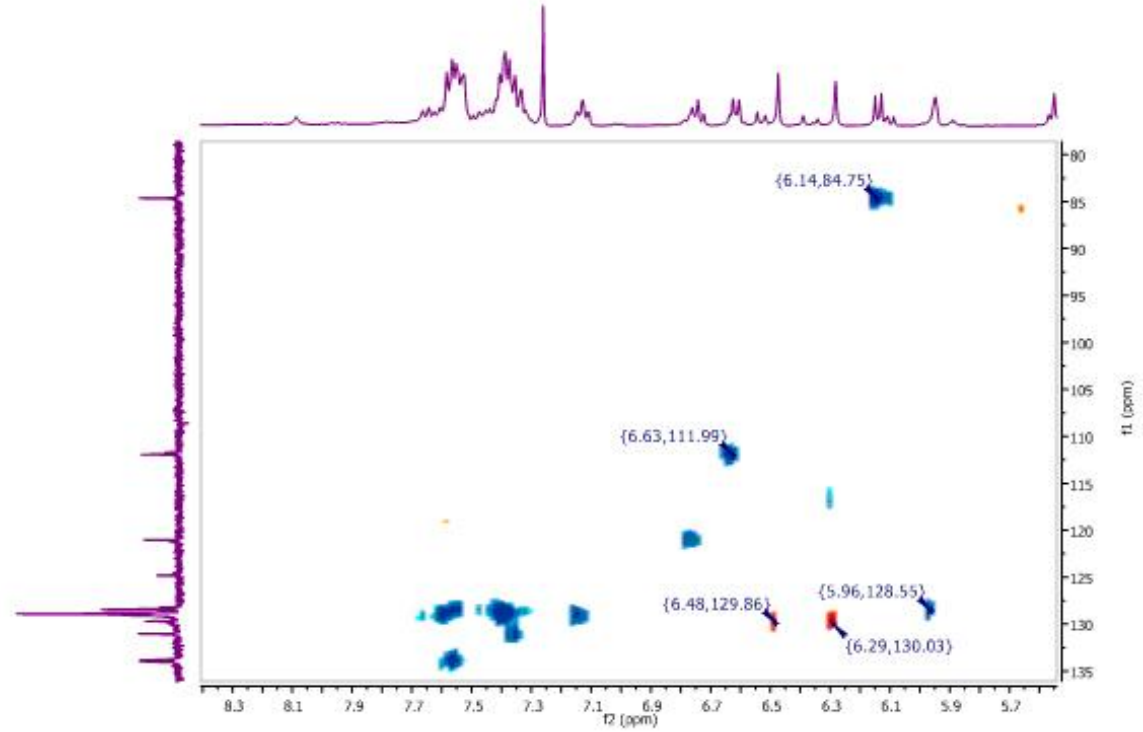
PDA Ch2 220nm 4nm

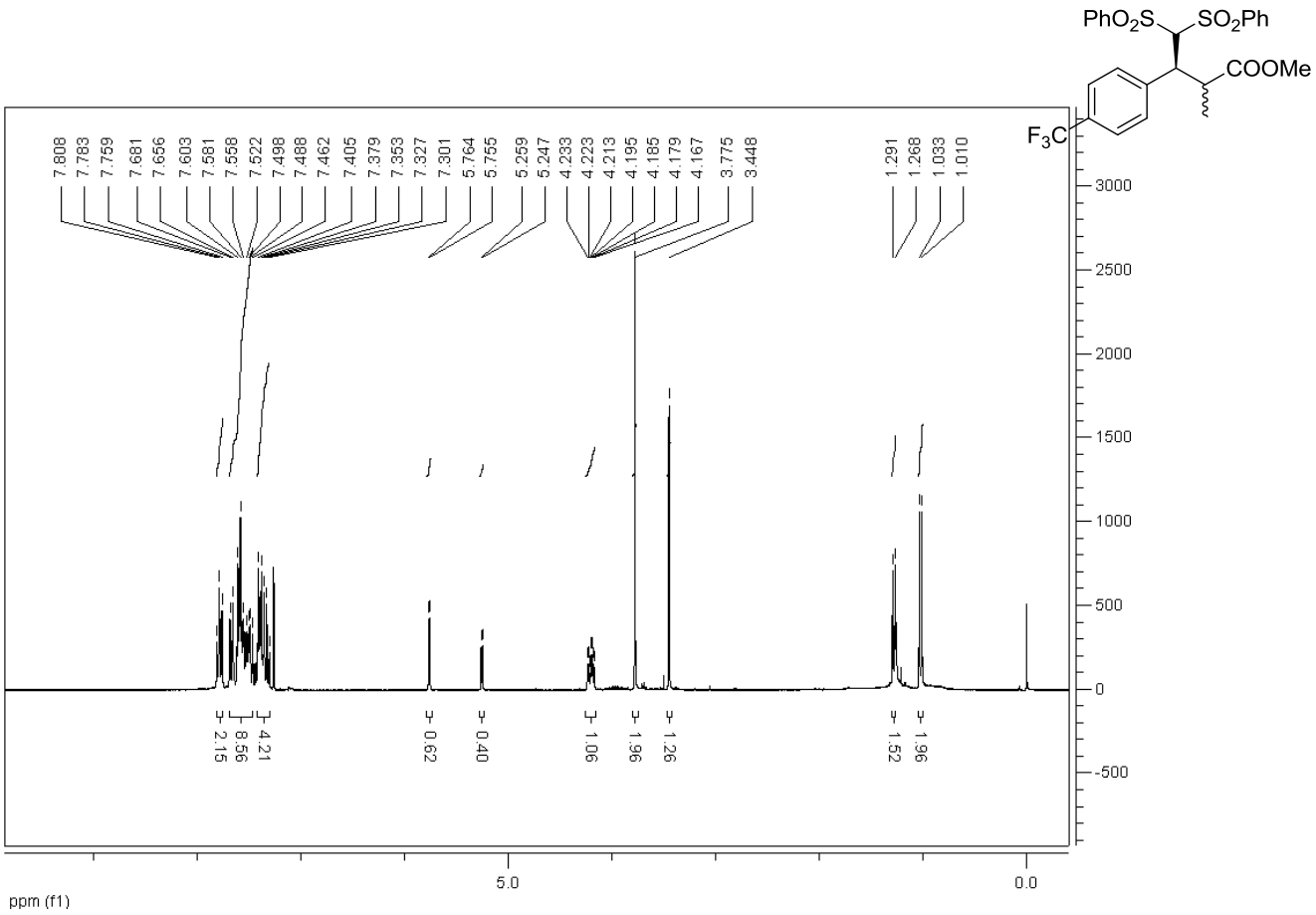
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.382	24841176	489302	93.440	93.251
2	30.225	1744062	35411	6.560	6.749
Total		26585238	524713	100.000	100.000

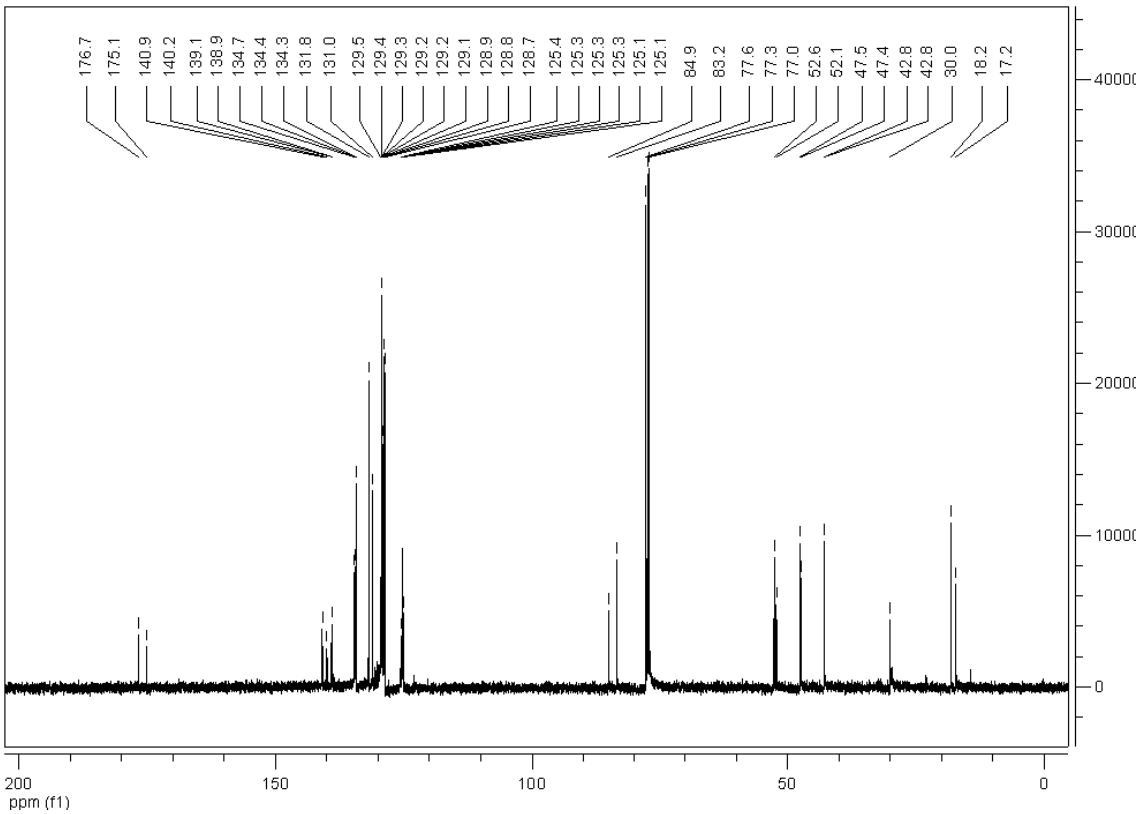


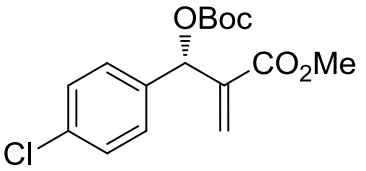


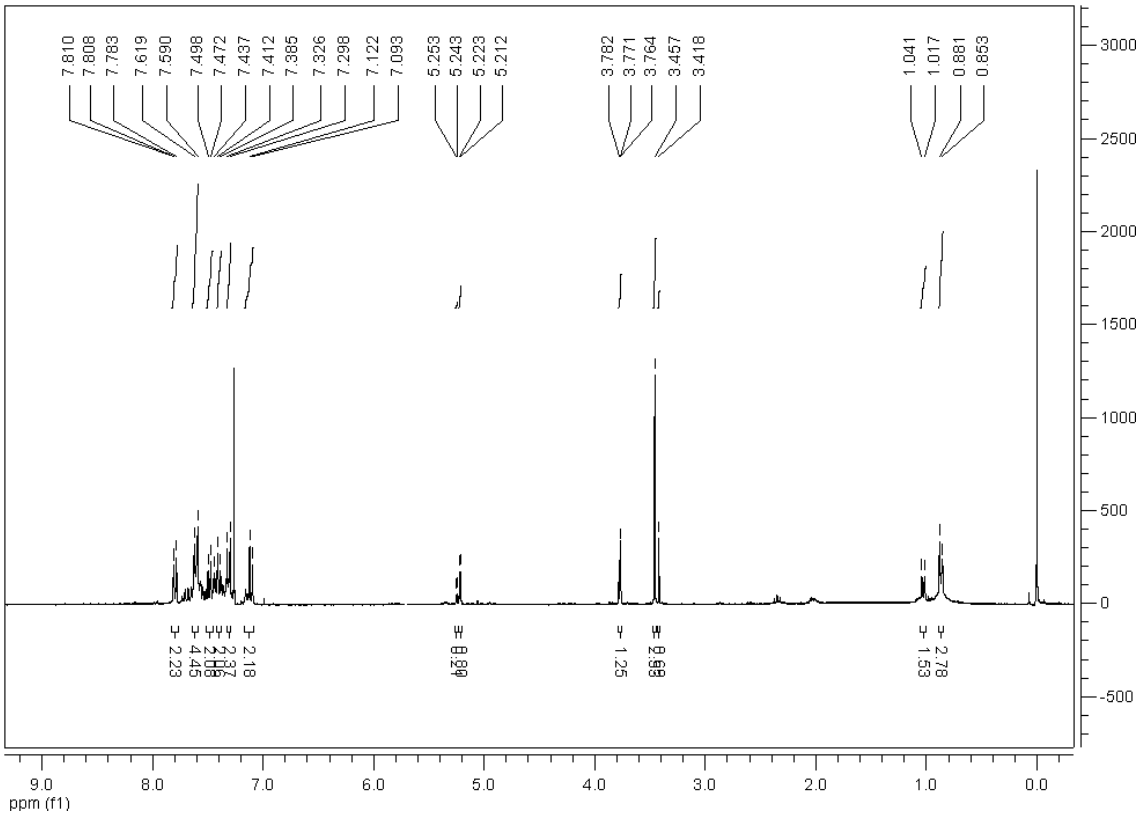


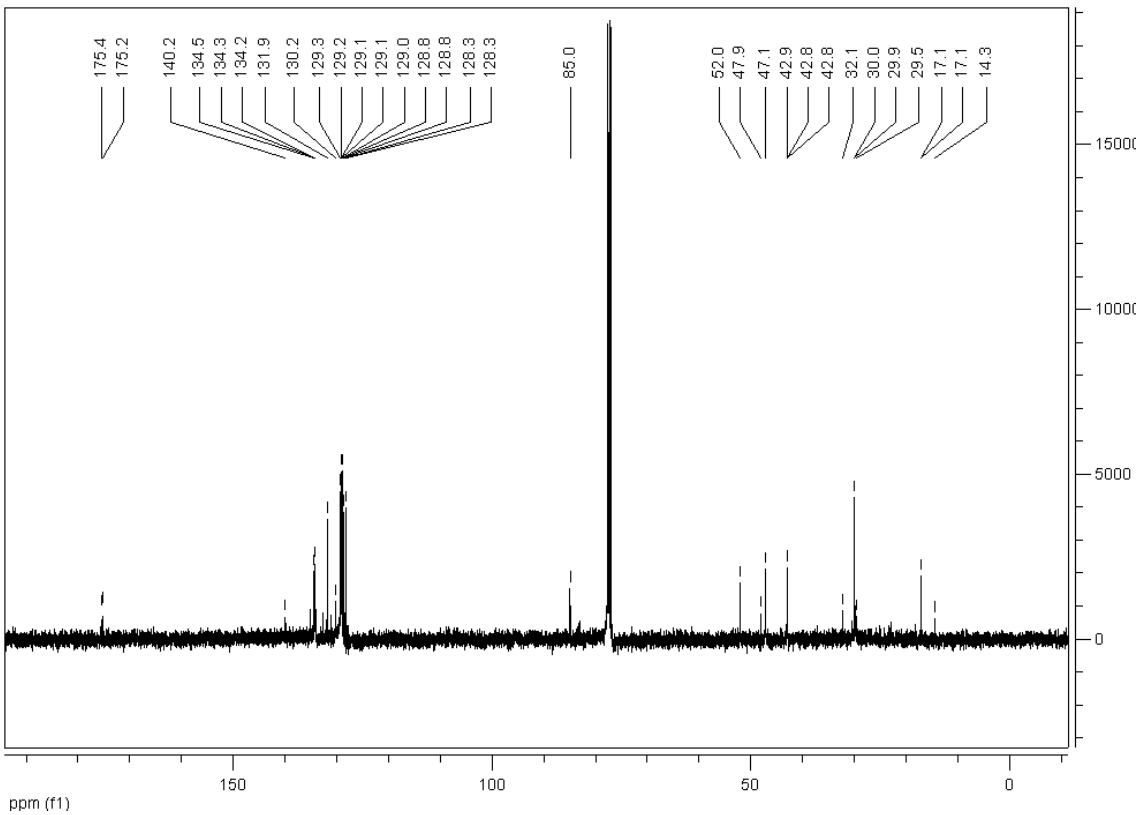


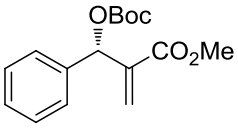


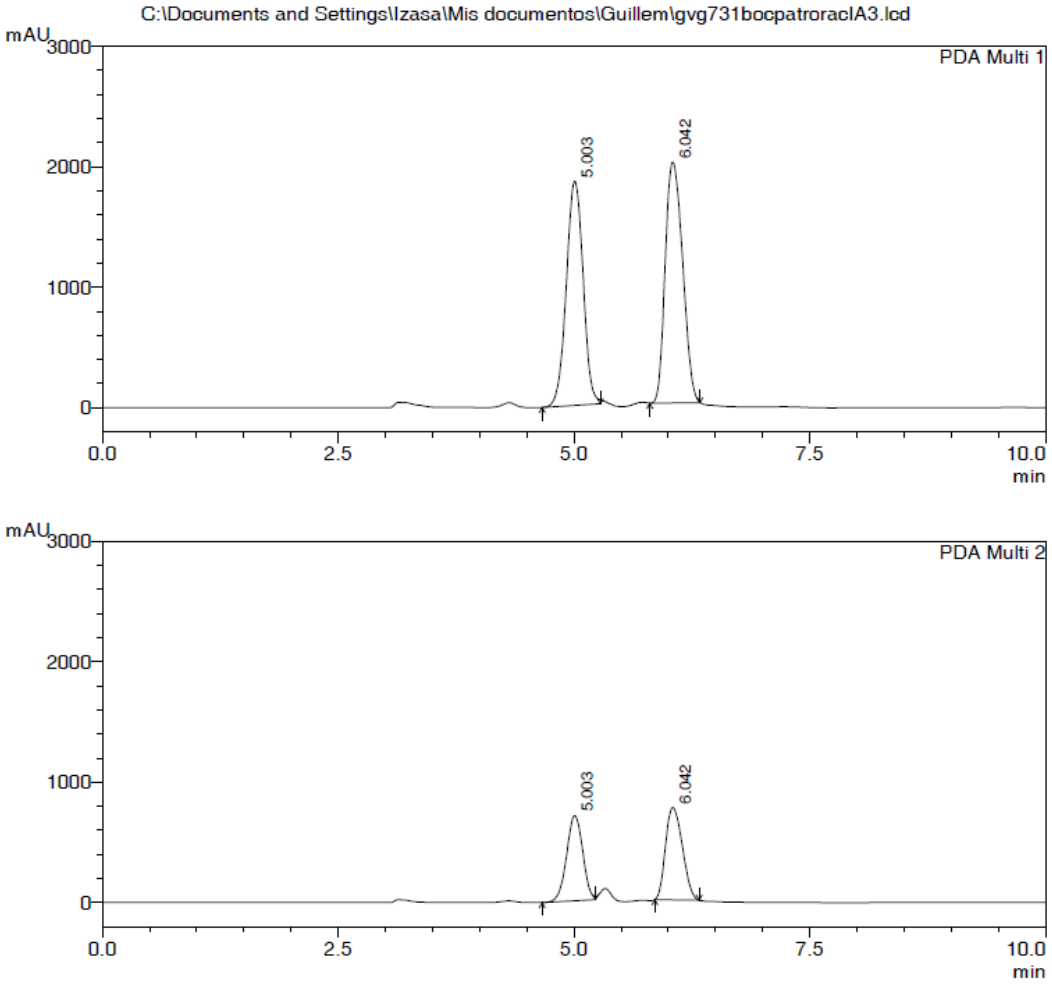












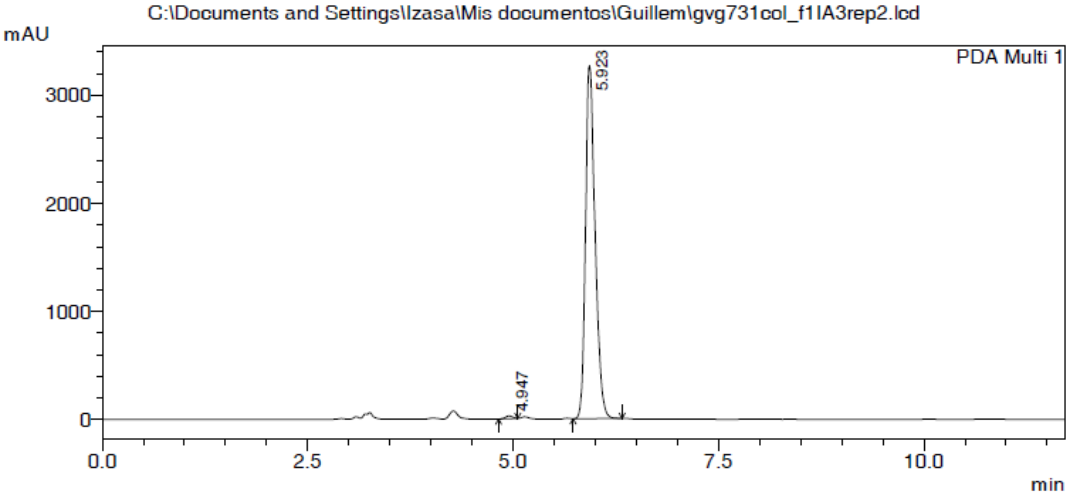
1 PDA Multi 1/215nm 4nm
2 PDA Multi 2/230nm 4nm

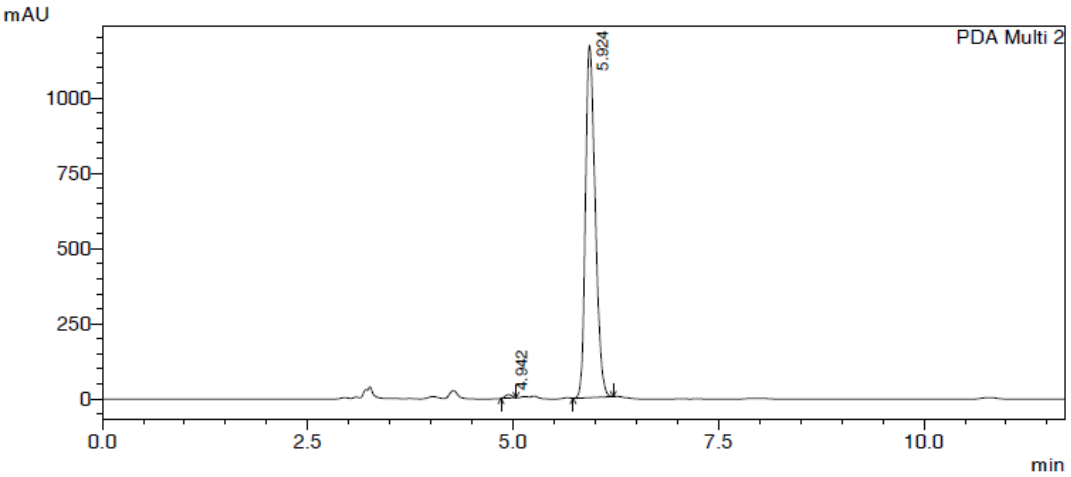
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.003	23108568	1859894	47.418	48.177
2	6.042	25625423	2000654	52.582	51.823
Total		48733991	3860548	100.000	100.000

PeakTable

PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.003	8406376	705105	46.958	47.956
2	6.042	9495626	765208	53.042	52.044
Total		17902003	1470313	100.000	100.000





1 PDA Multi 1/215nm 4nm
2 PDA Multi 2/230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.947	149679	25579	0.562	0.776
2	5.923	26506981	3268910	99.438	99.224
Total		26656660	3294489	100.000	100.000

PeakTable

PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.942	64857	11358	0.665	0.961
2	5.924	9680948	1170345	99.335	99.039
Total		9745805	1181703	100.000	100.000