Supporting Information

Efficient synthesis of optically active 4-nitro-cyclohexanones via bifunctional thiourea-base catalyzed double-Michael addition of nitromethane to dienones

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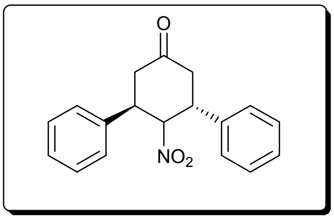
A: General Information:

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without any precautions to exclude moisture unless otherwise noted. Organic solutions were concentrated under reduced pressure on an EYELA N-1001 rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates (0.2±0.03 mm thickness, GF-254, particle size 0.01–0.04 mm) from Yantai Chemical Industry Research Institute, P. R. China. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using silica gel (particle size 0.04–0.05 mm) from Yantai Chemical Industry Research Institute, P. R. China. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in $CDCl_3$ on Varian Inova-400 NMR spectometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm for proton NMR, δ 77.00 ppm for carbon NMR). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (J) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) for all the compounds were determined on Micromass GCT-TOF mass spertrometer with EI resource. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using a Chiralcel OD-H column (0.46cm x 25 cm), Chiralpak AD-H (0.46cm x 25 cm). X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractometer. Optical rotations were measured on an Autopol IV polarimeter, and $[\alpha]_D$ values are reported in 10^{-1} dg cm^2 g^{-1}; concentration (c) is reported in g/100 ml. The divinyl ketones were prepared according to reported methods.[1-6]

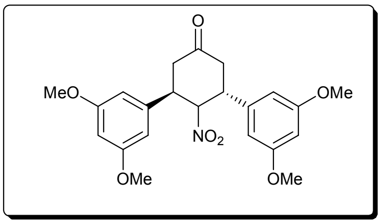
B: General Procedure for the Double-Michael addition

To a stirred solution of **1a-o** (0.25 mmol) and **IV** (0.05 mmol) in toluene (1.0 mL) was added nitromethane **2** (263.2 uL, 5.0 mmol) at room temperature. After being stirred for the right time, the mono-Michael addition product was purified by flash chromatography over silica gel (petroleum ether/ethyl acetate = 10:1 as eluent), and subsequently treated with KOH (1.1 mg, 0.025 mmol) in EtOH (2 mL) at 0 °C for 2 h. The reaction mixture was quenched with a saturated NH_4Cl solution and extracted with ethyl acetate (2×5 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Filtration and evaporation of the solvents furnished the crude product, which was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1) to afford desired product.

C: Characterization Data of Michael Addition Products

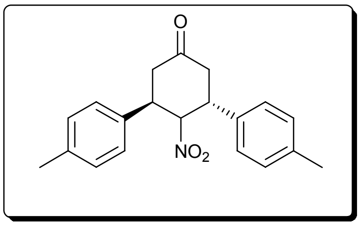


4-nitro-3,5-diphenyl cyclohexanone (3a): 86% yield, 90% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (95:5) as the eluent. Flow rate: 1.0 mL/min, λ = 210nm: t_{minor} = 23.522 min, t_{major} = 25.150 min. $[\alpha]_D^{25}$ +44.6 (c 0.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.27 – 7.22 (m, 3H), 7.23 – 7.15 (m, 3H), 6.98 (dd, *J* = 13.7, 8.6 Hz, 2H), 5.22 (dd, *J* = 6.9, 4.8 Hz, 1H), 3.87 (dd, *J* = 14.0, 7.1 Hz, 1H), 3.81 – 3.61 (m, 1H), 3.26 (dd, *J* = 15.8, 9.4 Hz, 1H), 3.00 (dd, *J* = 16.2, 6.4 Hz, 1H), 2.93 – 2.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0, 42.4, 42.6, 43.5, 91.7, 127.4, 127.8, 128.3, 128.6, 129.2, 129.5, 137.0, 139.6, 207.9 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{17}NO_3$, 295.1208, found 295.1207.

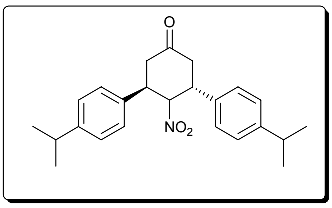


4-nitro-3,5-di(3,5-dimethoxyphenyl) cyclohexanone (3b): 77% yield, 92% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 50.982 min, t_{major} = 56.363 min. $[\alpha]_D^{25}$ +26.3 (c 1.00 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 (s, 3H), 6.20 (d, *J* = 1.8 Hz, 3H), 5.27 (dd, *J* = 6.8, 5.1 Hz, 1H), 4.12 (d, *J* = 7.1 Hz, 1H), 3.98 – 3.80 (m, 1H), 3.75 (d, *J* = 7.2 Hz, 12H), 3.25 (dd, *J* = 16.1, 9.3 Hz, 1H), 3.01 (dd, *J* = 16.3, 5.9 Hz, 1H), 2.80

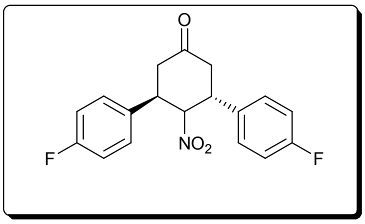
(dd, J = 15.4, 5.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.0, 42.5, 42.9, 43.4, 55.5, 91.4, 99.6, 99.7, 105.7, 106.2, 139.3, 142.0, 161.2, 161.6, 207.8 ppm. HRMS (EI) m/z: M^+ calcd. for $C_{22}H_{25}NO_7$, 415.1631, found 415.1633.



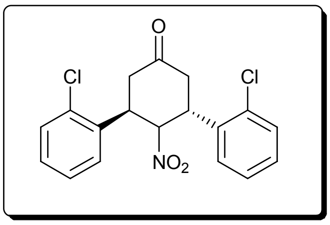
4-nitro-3,5-di(4-methylphenyl) cyclohexanone (3c): 54% yield, 90% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 10.843 min, t_{major} = 15.619 min. $[\alpha]_D^{25}$ +90.6 (c 0.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 13.4 Hz, 6H), 6.86 (d, J = 7.6 Hz, 2H), 5.26 – 5.04 (m, 1H), 3.80 (d, J = 6.9 Hz, 1H), 3.75 – 3.51 (m, 1H), 3.20 (dd, J = 15.9, 9.2 Hz, 1H), 3.05 – 2.86 (m, 1H), 2.83 – 2.63 (m, 2H), 2.24 (d, J = 5.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 41.8, 41.9, 42.0, 43.3, 91.6, 127.1, 127.4, 129.6, 129.9, 133.8, 136.3, 137.8, 138.1, 207.9 ppm. HRMS (EI) m/z: M^+ calcd. for $C_{20}H_{21}NO_3$, 323.1521, found 323.1525.



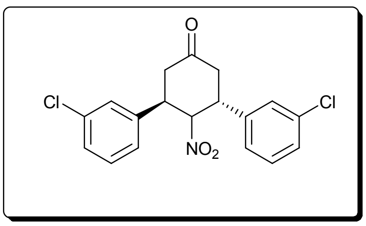
4-nitro-3,5-di(4-isopropylphenyl) cyclohexanone (3d): 67% yield, 90% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 19.759 min, t_{major} = 14.667 min. $[\alpha]_D^{25}$ +66.0 (c 1.00 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 17.6, 8.1 Hz, 6H), 6.98 (d, J = 7.9 Hz, 2H), 5.27 (s, 1H), 3.90 (d, J = 6.8 Hz, 1H), 3.79 – 3.69 (m, 1H), 3.43 – 3.21 (m, 1H), 3.01 (d, J = 5.8 Hz, 1H), 2.93 – 2.71 (m, 4H), 1.22 (t, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.7, 23.9, 33.6, 33.7, 41.7, 41.9, 42.2, 43.2, 91.5, 126.9, 127.1, 127.3, 127.4, 134.1, 136.7, 148.6, 148.8, 207.9 ppm. HRMS (EI) m/z: M^+ calcd. for $C_{24}H_{29}NO_3$, 379.2147, found 379.2154.



4-nitro-3,5-di(4-fluorophenyl) cyclohexanone (3e): 73% yield, 92% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 1.0 mL/min, λ = 210nm: t_{minor} = 25.175 min, t_{major} = 15.165 min. $[\alpha]_D^{25}$ +33.5 (c 1.00 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 2.9 Hz, 2H), 7.13 – 6.88 (m, 6H), 5.23 (dd, *J* = 6.7, 4.8 Hz, 1H), 3.96 – 3.60 (m, 2H), 3.25 (dd, *J* = 15.6, 8.5 Hz, 1H), 3.00 (d, *J* = 5.1 Hz, 1H), 2.93 – 2.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 41.6, 42.0, 43.5, 91.3, 115.8, 116.0, 116.1, 116.3, 128.6, 128.8, 129.2, 129.3, 132.4, 134.8, 206.9 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{15}F_2NO_3$, 331.1020, found 331.1014.

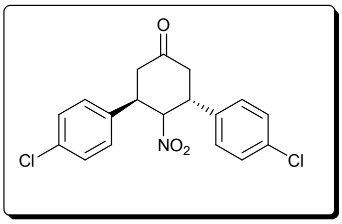


4-nitro-3,5-di(2-chlorophenyl) cyclohexanone (3f): 65% yield, 90% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 20.473 min, t_{major} = 29.946 min. $[\alpha]_D^{25}$ -88.0 (c 1.00 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.35 (m, 1H), 7.21 (dd, *J* = 18.7, 8.1 Hz, 6H), 7.06 (d, *J* = 7.0 Hz, 1H), 5.32 (s, 1H), 4.44 (d, *J* = 2.8 Hz, 1H), 3.94 (d, *J* = 14.2 Hz, 1H), 3.40 (t, *J* = 15.0 Hz, 1H), 3.22 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.88 (d, *J* = 14.3 Hz, 1H), 2.55 (dd, *J* = 15.5, 3.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.8, 39.7, 40.8, 41.0, 86.2, 127.5, 127.7, 127.8, 128.7, 129.4, 129.5, 129.9, 130.4, 130.5, 133.4, 134.1, 136.6, 208.0 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{15}Cl_2NO_3$, 363.0429, found 363.0426.

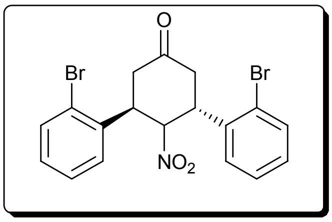


4-nitro-3,5-di(3-chlorophenyl) cyclohexanone (3g): 68% yield, 84% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 1.0 mL/min, λ = 210nm: t_{minor} = 34.468 min, t_{major} = 23.045 min. $[\alpha]_D^{25}$ +40.4 (c 0.50 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 13.3 Hz, 5H), 7.14 (s, 1H), 7.05 (s, 1H), 6.96 (d, *J* = 6.8 Hz, 1H), 5.27 (s, 1H), 3.90 (d, *J* = 6.8 Hz, 1H), 3.78 (s, 1H), 3.27 (dd, *J* = 15.8, 8.9 Hz, 1H), 3.03 (dd, *J* = 16.2, 5.0 Hz, 1H), 2.92 – 2.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.6, 41.8, 42.0, 43.1, 90.7, 114.5, 125.4, 127.4, 128.5, 130.3, 134.9, 135.2, 135.2, 138.5, 138.5, 141.0, 141.0, 206.3 ppm. HRMS (EI) *m/z*:

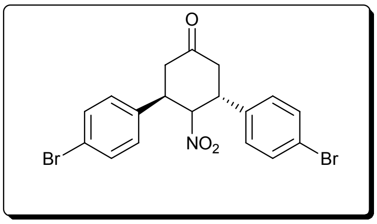
M^+ calcd. for $C_{18}H_{15}Cl_2NO_3$, 363.0429, found 363.0431.



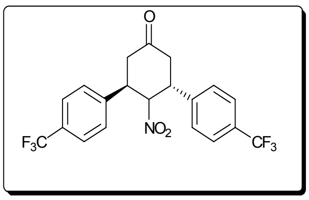
4-nitro-3,5-di(4-chlorophenyl) cyclohexanone (3h): 82% yield, 91% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (98:2) as the eluent. Flow rate: 1.0 mL/min, λ = 210nm: t_{minor} = 18.953 min, t_{major} = 17.370 min. $[\alpha]_D^{25}$ +75.2 (c 1.00 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 15.2, 7.6 Hz, 4H), 7.19 (d, *J* = 7.1 Hz, 2H), 6.99 (d, *J* = 7.1 Hz, 2H), 5.22 (d, *J* = 5.0 Hz, 1H), 3.84 (dd, *J* = 22.2, 15.6 Hz, 2H), 3.25 (dd, *J* = 15.5, 7.9 Hz, 1H), 3.02 (dd, *J* = 15.9, 5.7 Hz, 1H), 2.82 (ddd, *J* = 24.7, 15.6, 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.5, 41.7, 41.8, 43.3, 90.9, 128.5, 128.9, 129.1, 129.5, 134.0, 134.4, 135.0, 137.4, 206.6 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{15}Cl_2NO_3$, 363.0429, found 363.0427.



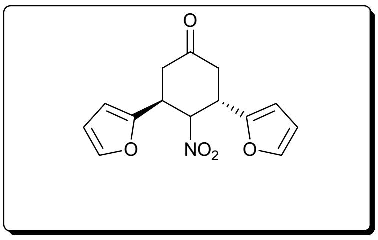
4-nitro-3,5-di(2-bromophenyl) cyclohexanone (3i): 80% yield, 90% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 21.209 min, t_{major} = 43.508 min. $[\alpha]_D^{25}$ -112.6 (c 0.50 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.15 (d, J = 7.6 Hz, 1H), 7.06 (dd, J = 21.4, 7.5 Hz, 2H), 5.28 (s, 1H), 4.42 (d, J = 3.4 Hz, 1H), 3.88 (d, J = 14.2 Hz, 1H), 3.52 – 3.18 (m, 2H), 3.04 – 2.69 (m, 1H), 2.55 (d, J = 15.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 39.9, 40.8, 43.2, 86.3, 124.1, 127.3, 127.8, 128.0, 128.4, 129.7, 130.2, 132.3, 133.3, 133.8, 135.7, 144.0, 208.0 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{15}Br_2NO_3$, 452.9419, found 452.9434.



4-nitro-3,5-di(4-bromophenyl) cyclohexanone (3j): 66% yield, 92% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 1.0 mL/min, λ = 210nm: t_{minor} = 38.787 min, t_{major} = 24.206 min. $[\alpha]_D^{25}$ +85.6 (c 0.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.32 (m, 4H), 7.05 (d, J = 7.7 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H), 5.16 (s, 1H), 3.87 – 3.64 (m, 2H), 3.27 – 3.03 (m, 1H), 2.93 (dd, J = 16.0, 4.6 Hz, 1H), 2.73 (ddd, J = 25.0, 15.8, 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 41.7, 41.8, 43.3, 90.8, 122.2, 122.7, 128.9, 129.2, 132.2, 132.5, 135.5, 138.0, 206.5 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{15}Br_2NO_3$, 450.9419, found 450.9417.

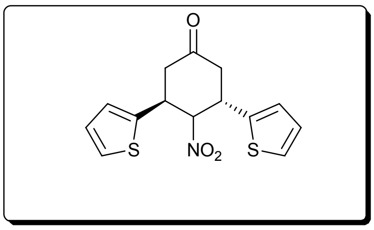


4-nitro-3,5-di(4-trifluoromethylphenyl) cyclohexanone (3k): 78% yield, 94% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 35.729 min, t_{major} = 16.428 min. $[\alpha]_D^{25}$ +42.7 (c 1.00 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 14.8, 7.8 Hz, 4H), 7.40 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 5.40 – 5.31 (m, 1H), 3.95 (dd, J = 18.3, 6.4 Hz, 2H), 3.29 (dd, J = 15.9, 7.9 Hz, 1H), 3.12 – 2.98 (m, 1H), 2.93 (dd, J = 16.0, 5.1 Hz, 1H), 2.84 (dd, J = 16.1, 9.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.1, 42.2, 42.6, 42.7, 43.7, 43.7, 90.8, 126.3, 126.7, 126.7, 128.0, 128.5, 138.3, 140.7, 140.8, 143.1, 145.5, 206.3 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{20}H_{15}F_6NO_3$, 431.0956, found 432.1037.



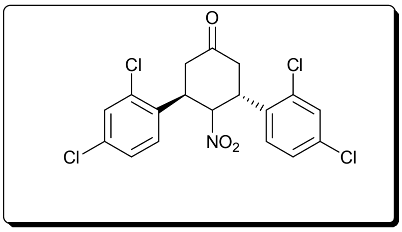
4-nitro-3,5-di(2-furyl) cyclohexanone (3l):

58% yield, 85% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 18.873 min, t_{major} = 15.009 min. $[\alpha]_D^{25}$ +19.2 (c 0.25 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.12 (m, 3H), 6.25 (s, 2H), 6.10 (d, *J* = 25.4 Hz, 1H), 5.39 (d, *J* = 4.6 Hz, 1H), 4.11 – 3.88 (m, 1H), 3.74 (d, *J* = 4.0 Hz, 1H), 3.12 – 2.83 (m, 2H), 2.83 – 2.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.1, 37.2, 40.8, 40.9, 86.0, 108.1, 108.3, 110.5, 110.6, 142.7, 142.9, 150.3, 151.2, 204.7 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{14}H_{13}NO_5$, 275.0794, found 275.0794.

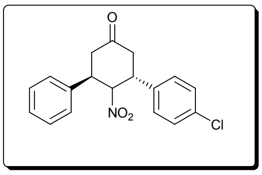


4-nitro-3,5-di(2-thienyl) cyclohexanone (3m):

74% yield, 92% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 29.212 min, t_{major} = 17.315 min. $[\alpha]_D^{25}$ +11.6 (c 0.50 in $CHCl_3$, dark sample). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.09 (m, 2H), 6.89 (s, 3H), 6.78 (s, 1H), 5.24 (d, *J* = 4.2 Hz, 1H), 4.22 (d, *J* = 6.0 Hz, 1H), 3.97 (d, *J* = 4.6 Hz, 1H), 3.24 (dd, *J* = 15.5, 9.5 Hz, 1H), 3.08 (dd, *J* = 15.7, 5.8 Hz, 1H), 2.95 – 2.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0, 38.8, 43.2, 43.3, 91.3, 125.4, 125.5, 126.0, 126.2, 127.2, 127.4, 139.3, 141.9, 205.3 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{14}H_{13}NO_3S_2$, 307.0337, found 307.0335.



4-nitro-3,5-di(2,4-dichlorophenyl) cyclohexanone (3n): 71% yield, 91% ee. The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 0.75 mL/min, λ = 210nm: t_{minor} = 24.991 min, t_{major} = 20.433 min. $[\alpha]_D^{25}$ -44.4 (c 0.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.44 – 7.16 (m, 4H), 7.07 (d, *J* = 8.2 Hz, 1H), 5.33 (s, 1H), 4.46 (s, 1H), 3.92 (d, *J* = 13.9 Hz, 1H), 3.43 (t, *J* = 14.8 Hz, 1H), 3.27 (dd, *J* = 16.1, 6.0 Hz, 1H), 2.91 (d, *J* = 16.2 Hz, 1H), 2.61 (d, *J* = 15.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.1, 40.2, 41.1, 41.2, 86.2, 128.4, 128.6, 129.3, 130.1, 130.2, 130.3, 130.9, 133.1, 134.5, 135.0, 135.4, 135.5, 207.6 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{13}Cl_4NO_3$, 432.9620, found 432.9606.



3-(4-chlorophenyl)-4-nitro-5-phenyl cyclohexanonethe (3o): product was isolated as sum of diastereoisomers in 84% yield and 64% ee on the major disteroisomer and 91% ee on the minor (d.r. = 4:1 was determined by integration of ^{1}H NMR signal: δmajor 5.20 ppm. t, δminor 5.12 ppm. t). The enantiomeric excess was determined by HPLC on Daicel Chiralcel OD-H with hexane/i-PrOH (80:20) as the eluent. Flow rate: 1.0 mL/min, λ = 210nm: major diastereoisomer t_{major} = 23.534 min., t_{minor} = 32.953 min.; minor diastereoisomer t_{major} = 18.287 min., t_{minor} = 28.448 min. $[\alpha]_D^{25}$ +54.0 (c 0.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.07 (m, 7H), 7.02 – 6.87 (m, 2H), 5.17 (dd, *J* = 20.0, 14.6 Hz, 1H), 3.90 – 3.53 (m, 2H), 3.19 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.04 – 2.88 (m, 1H), 2.86 – 2.61 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 41.4, 41.5, 41.6, 42.0, 42.3, 42.4, 43.1, 43.5, 91.0, 91.1, 126.6, 127.5, 128.5, 128.9, 129.3, 129.5, 129.8, 133.9, 133.9, 134.2, 135.2, 136.5, 137.7, 139.0, 207.0, 207.1 ppm. HRMS (EI) *m/z*: M^+ calcd. for $C_{18}H_{16}ClNO_3$, 329.0819, found 329.0817

D: X-ray Crystal Structure of 3n

Crystal structure determination of compound **3n**: $C_{18}H_{13}Cl_4NO_3$, M = 433.11; a block crystal (0.75×0.20×0.10 mm), T = 293(2), λ (Mo-Ka) = 0.71070 Å, Monoclinic, space group: P 21, a = 11.575(3) Å, b = 7.6295(19) Å, c = 21.699(6) Å, V = 1899.1(8) Å3, 18600 total reflections, 6899 unique, Rint = 0.1011, R1 = 0.0991 (I > 2σ), wR2 = 0.1687, Absolute structure parameter: -0.06 (12). An ORTEP drawing of **3n** is shown in **Figure S1**.

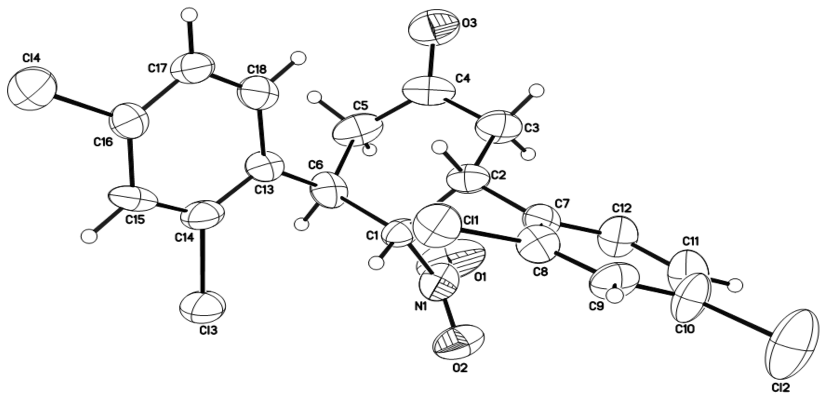


Figure S1. ORTEP drawing of **3n** (40% thermal ellipsoids)

The crystal was prepared from the solution of **3n** in acetone and n-hexane. CCDC 799931 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

E: Reference

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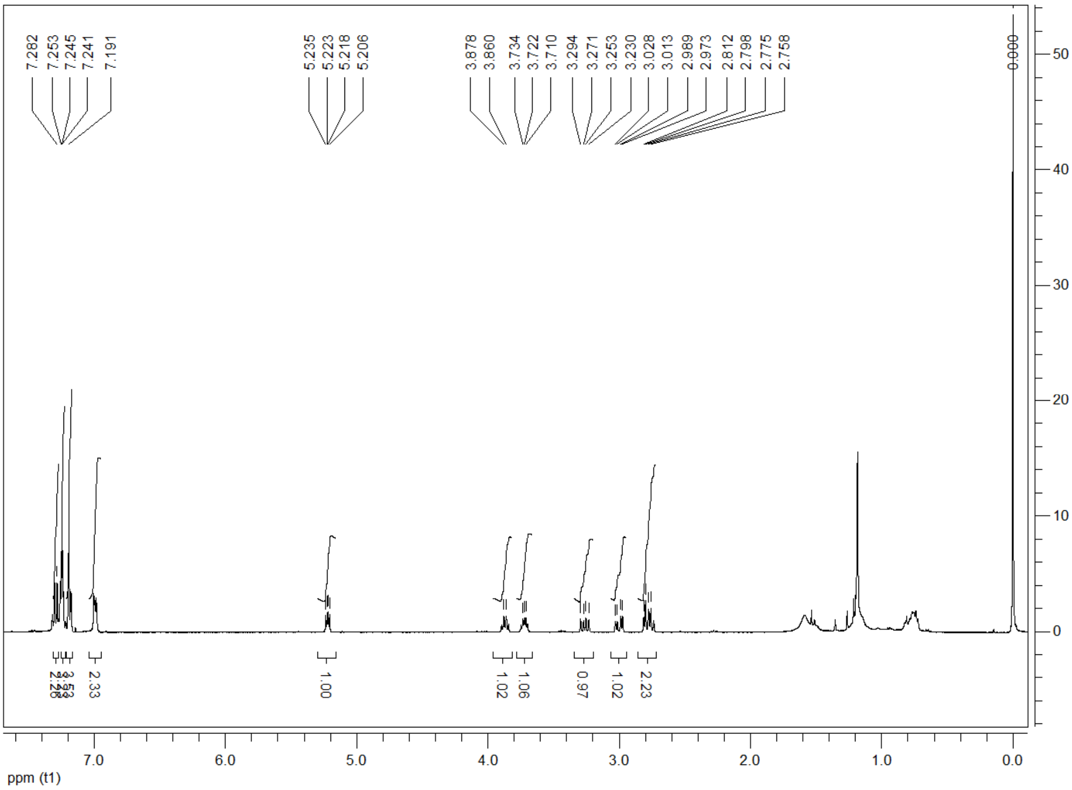
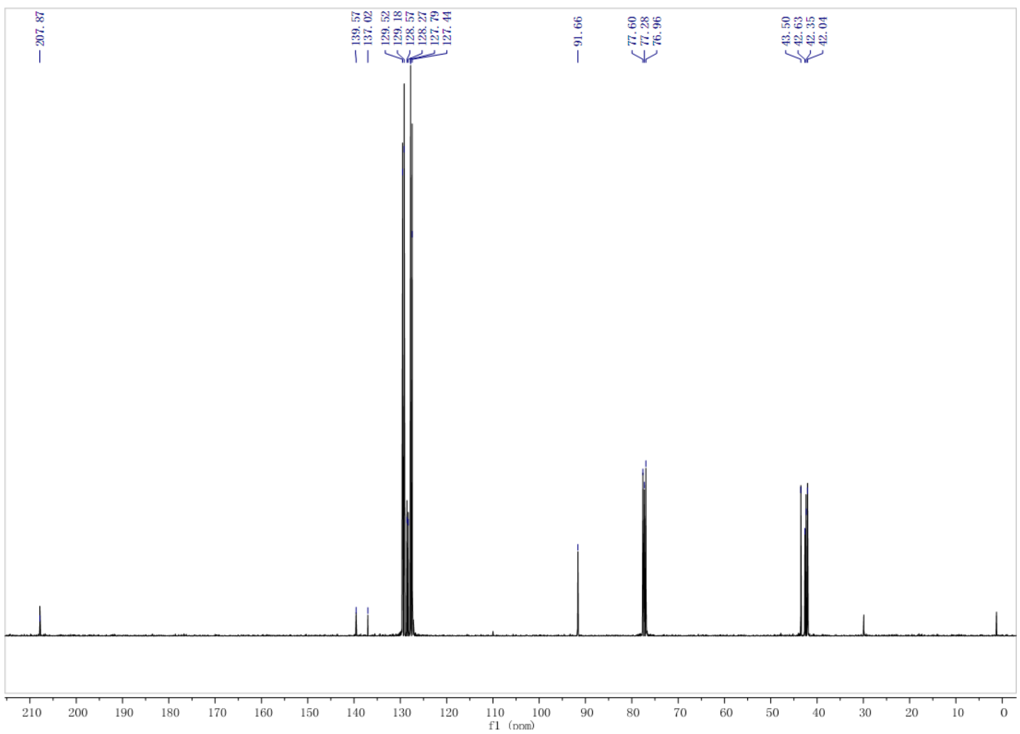
6 A. Arnold, M. Markert, R. Mahrwald, *Synthesis.,* 2006, 1099.

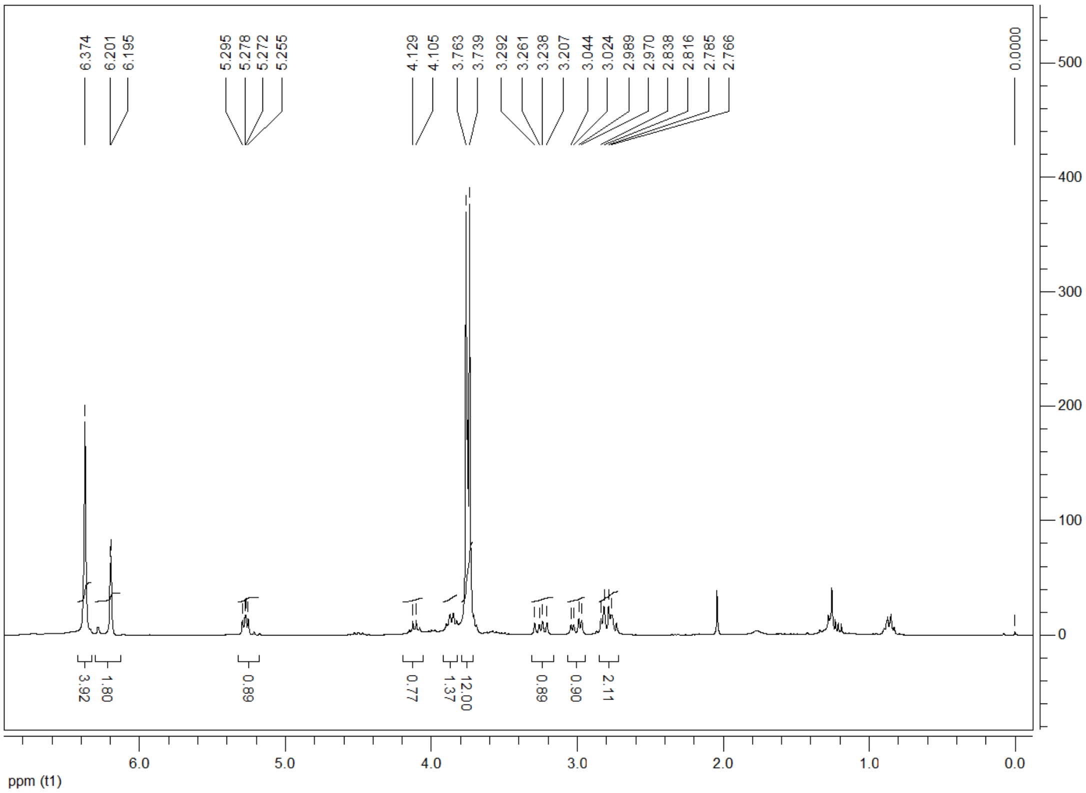
F: NMR Analysis of Michael Addition Products

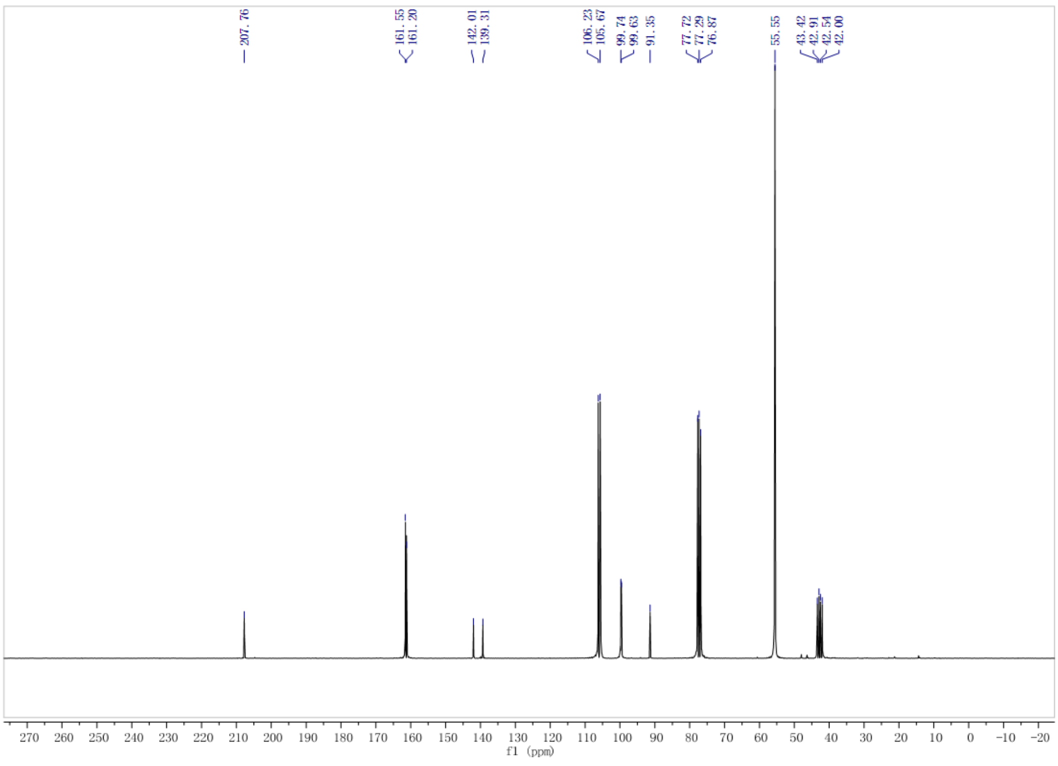
3a





3b





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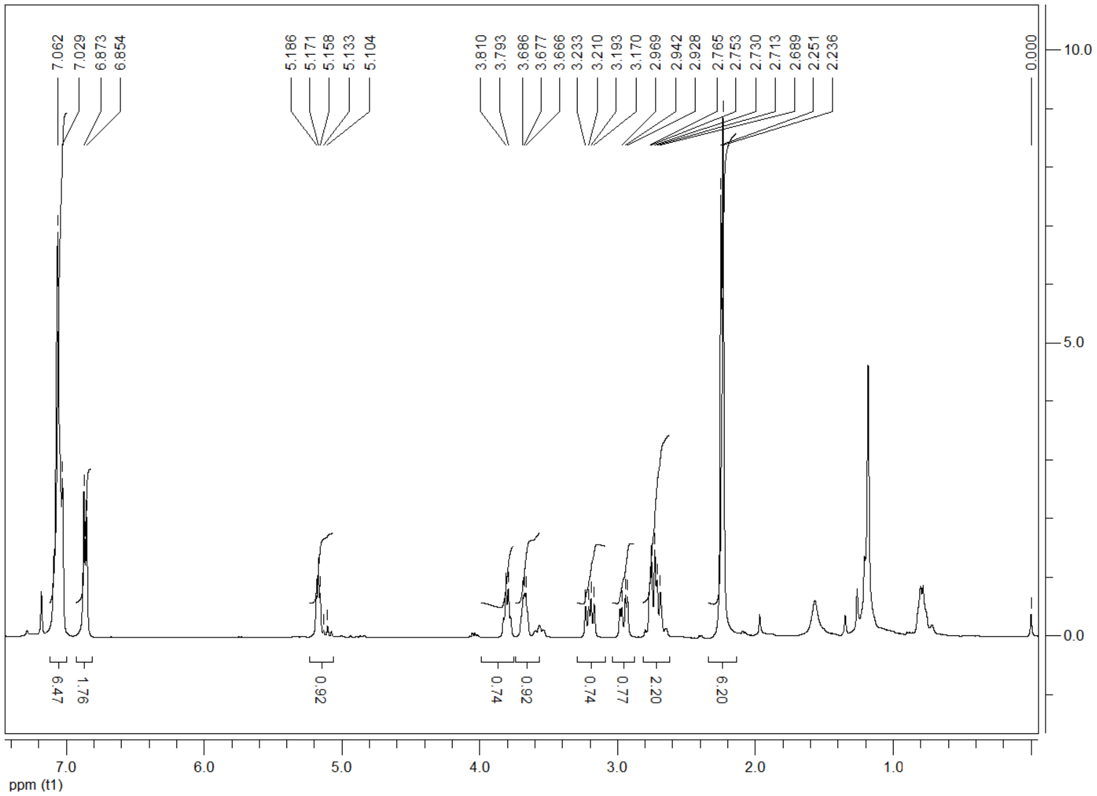

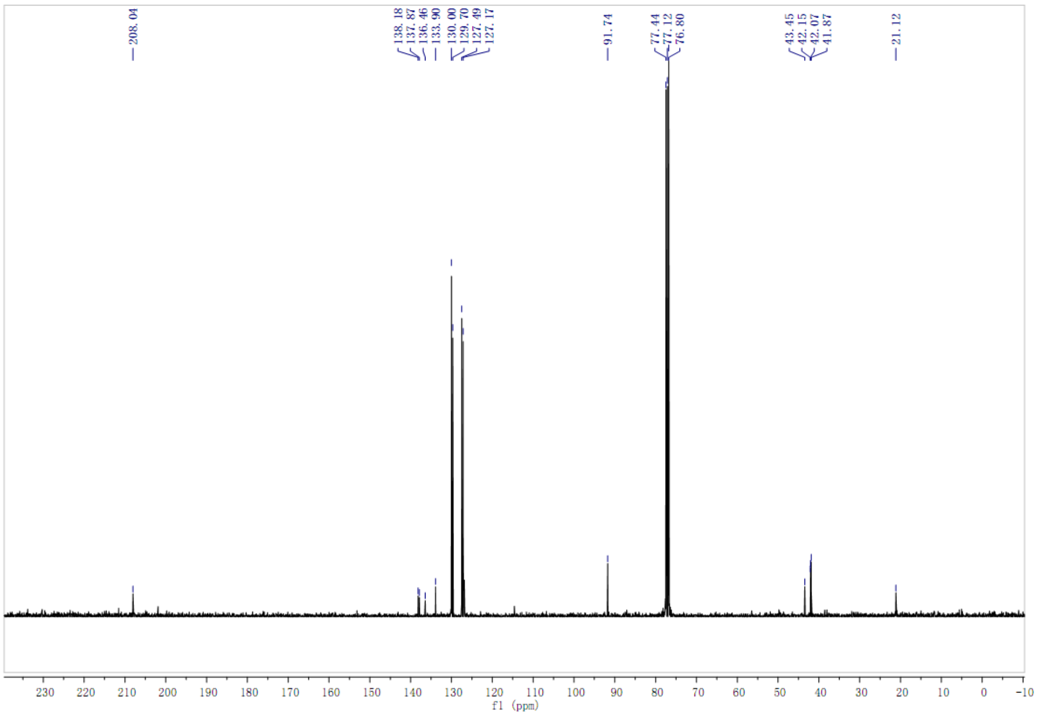

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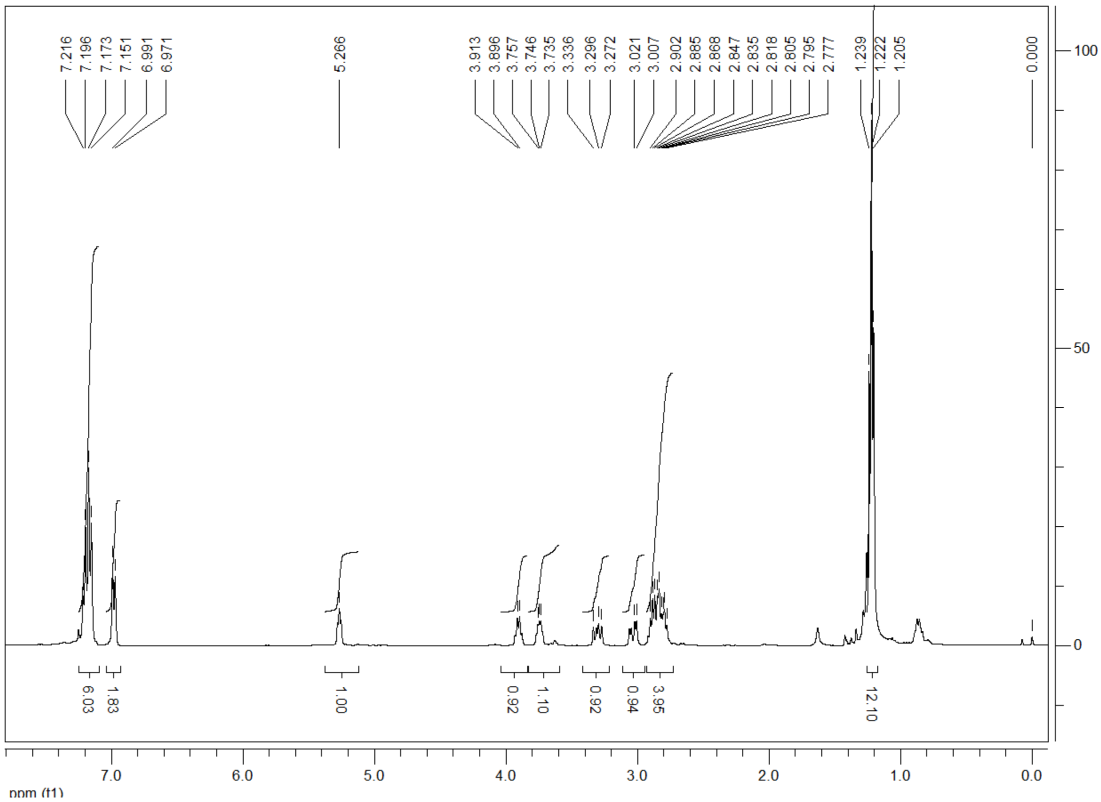
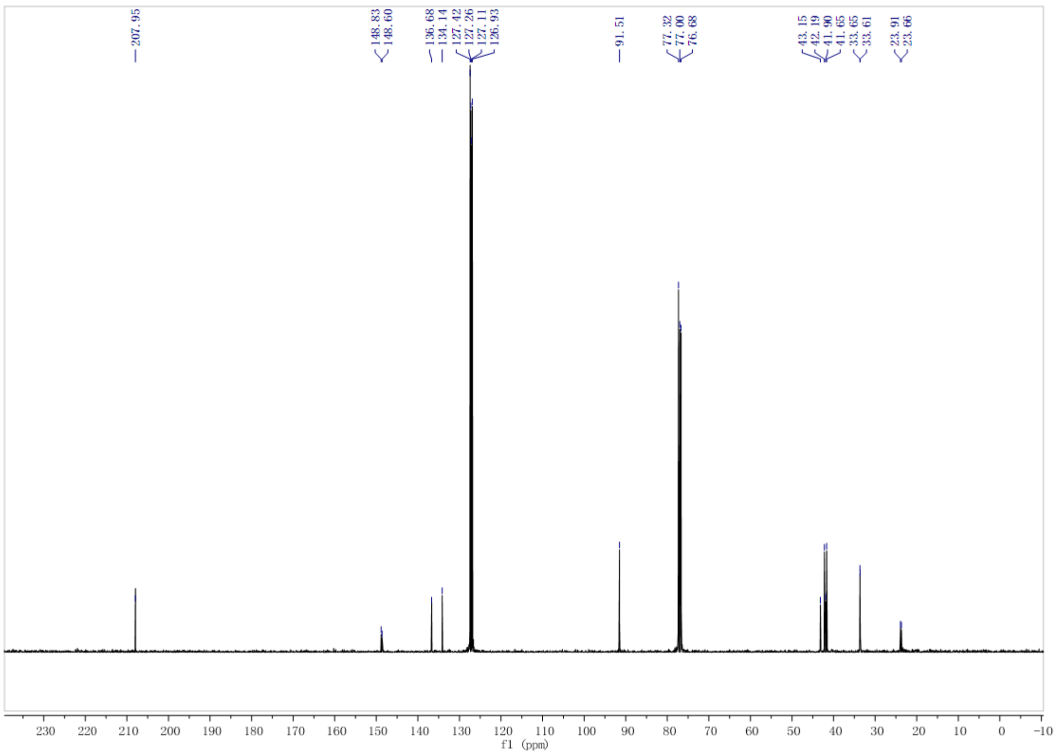
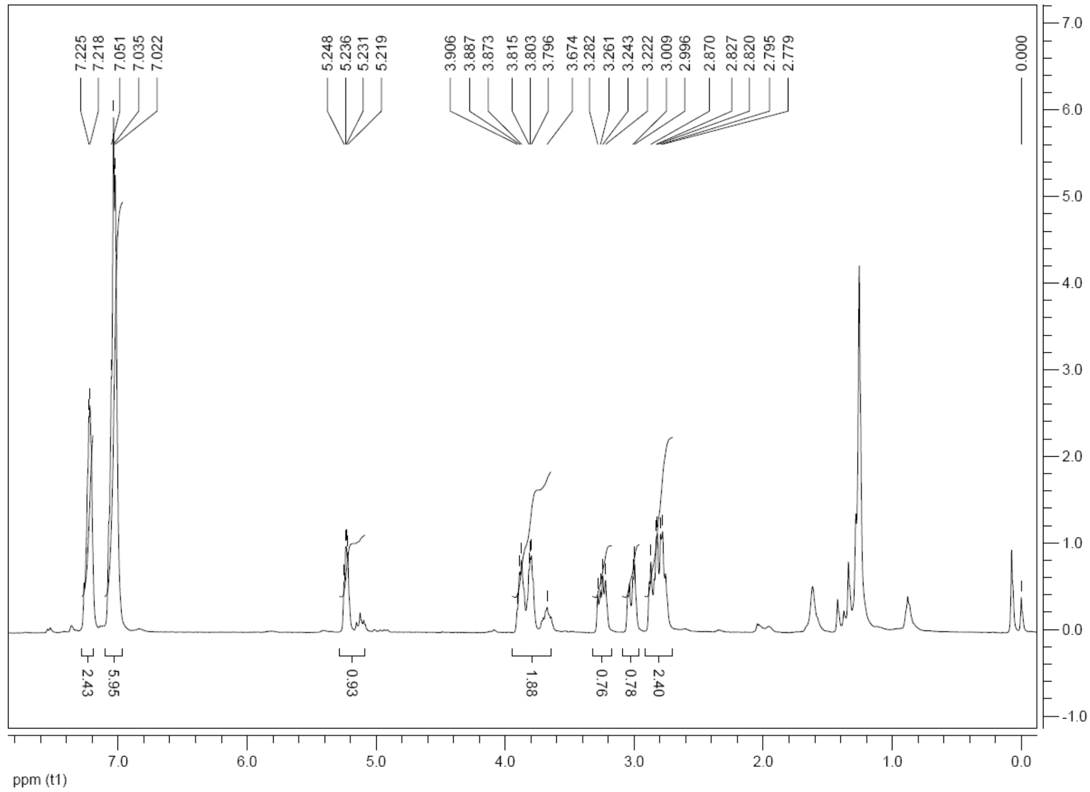




3e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3.803
3.796
3.674
3.282
3.261
3.243
3.222
3.009
2.996
2.870
2.827
2.820
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0.000
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1.88
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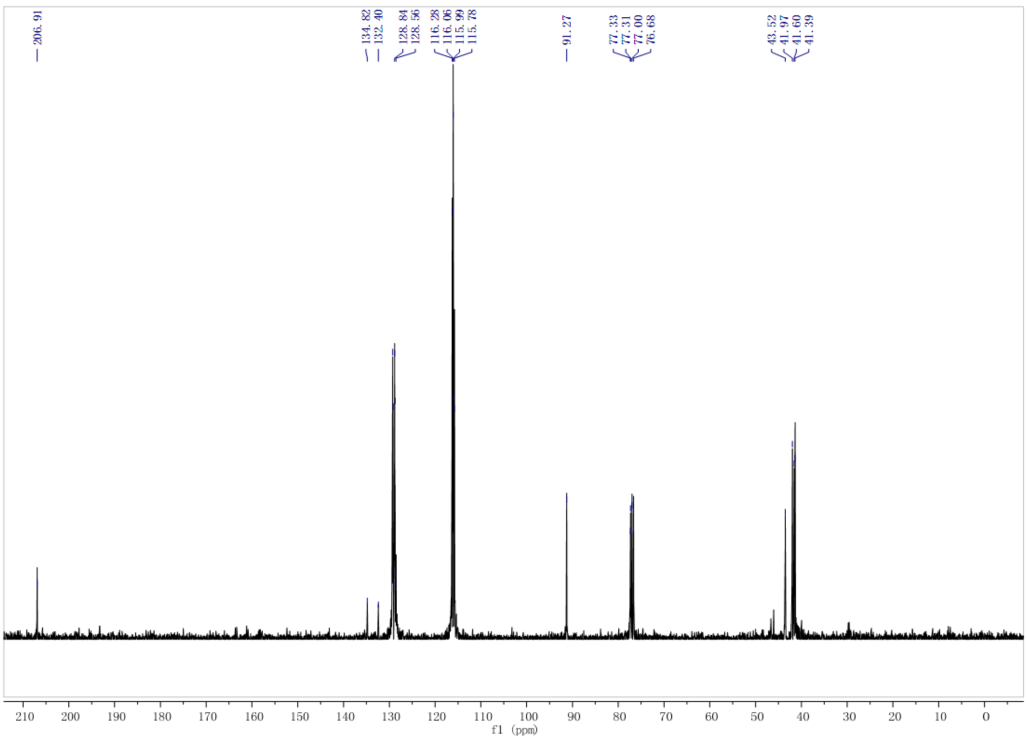
ppm (t1)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115.99
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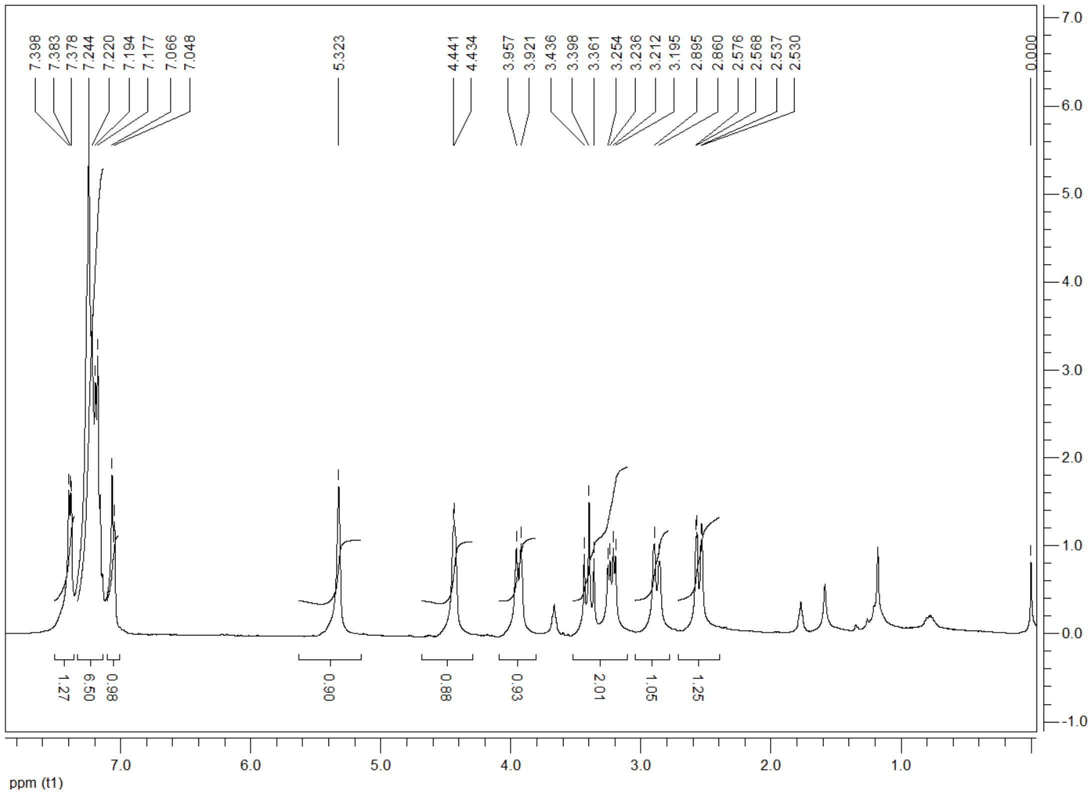
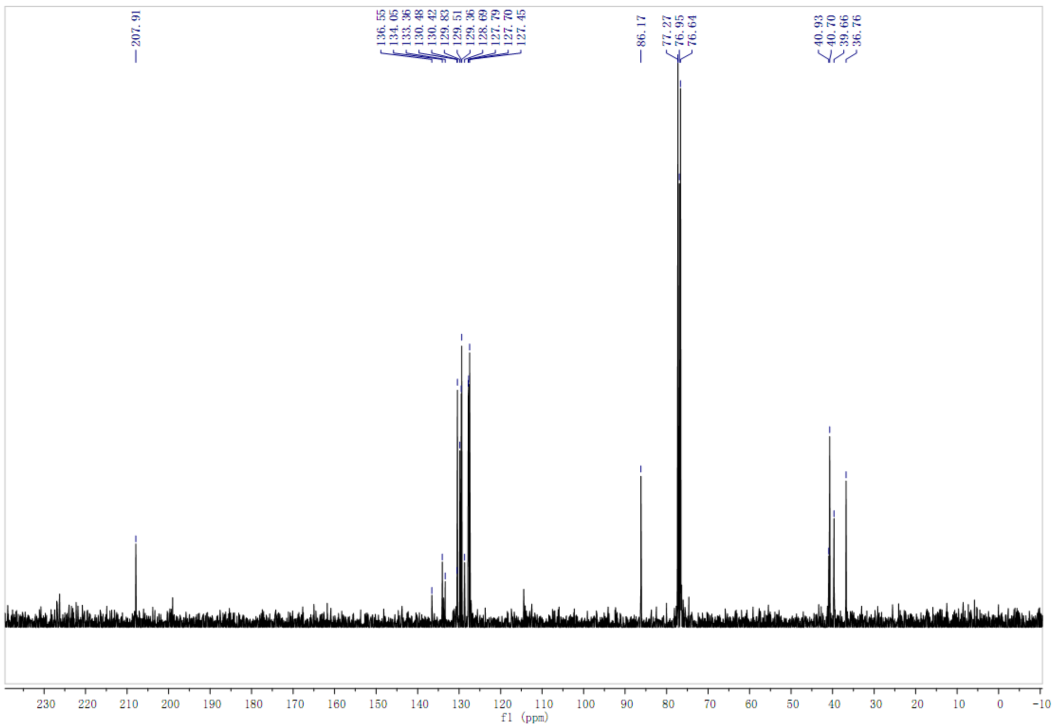
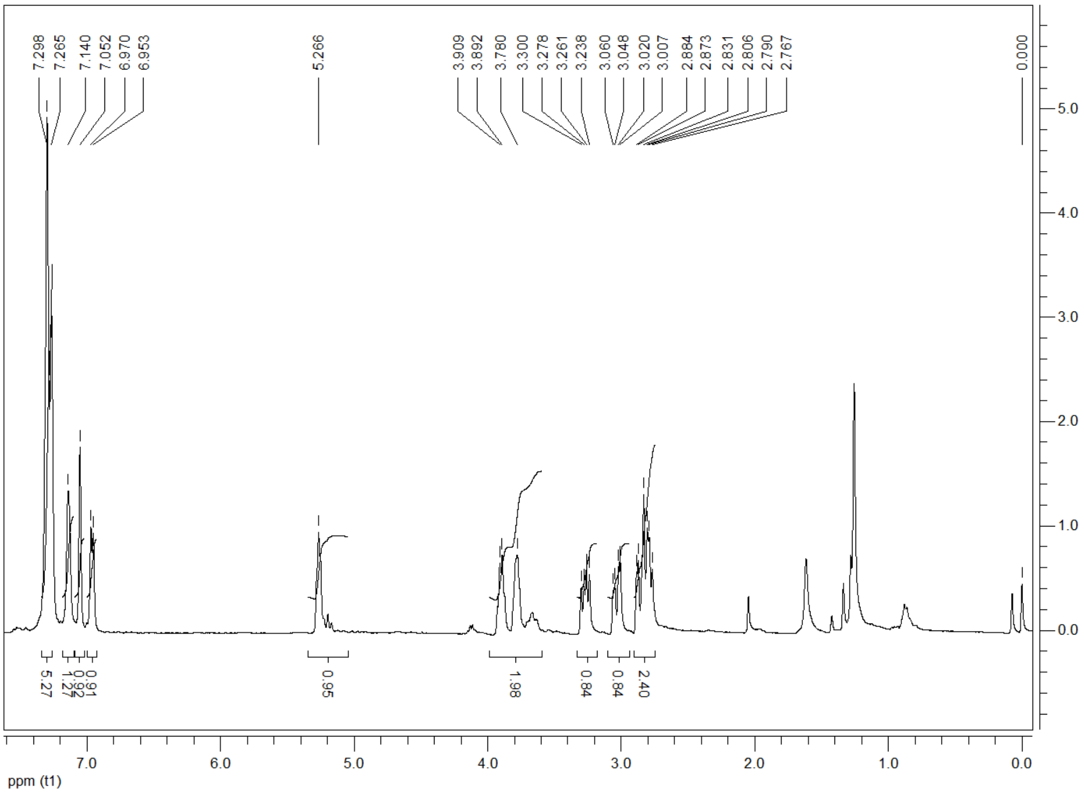
77.00
76.68
43.52
41.97
41.60
41.39
f1 (ppm)

3f





3g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3.060
3.048
3.020
3.007
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2.873
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2.806
2.790
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0.84
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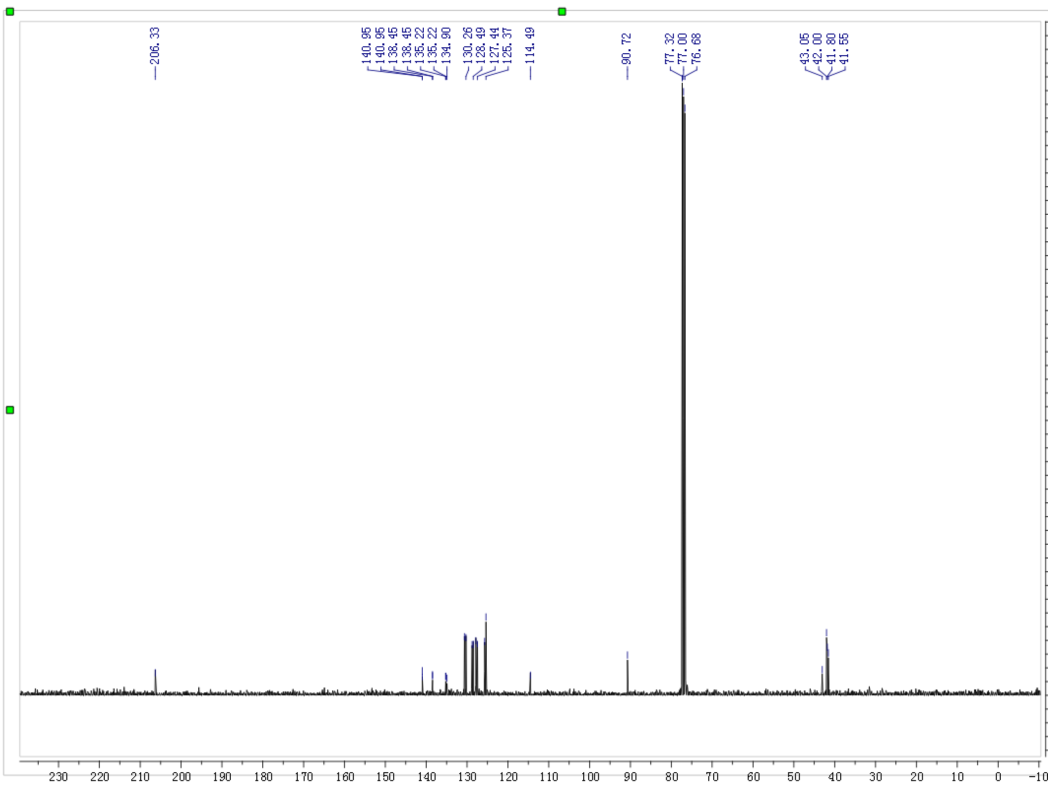
ppm (t1)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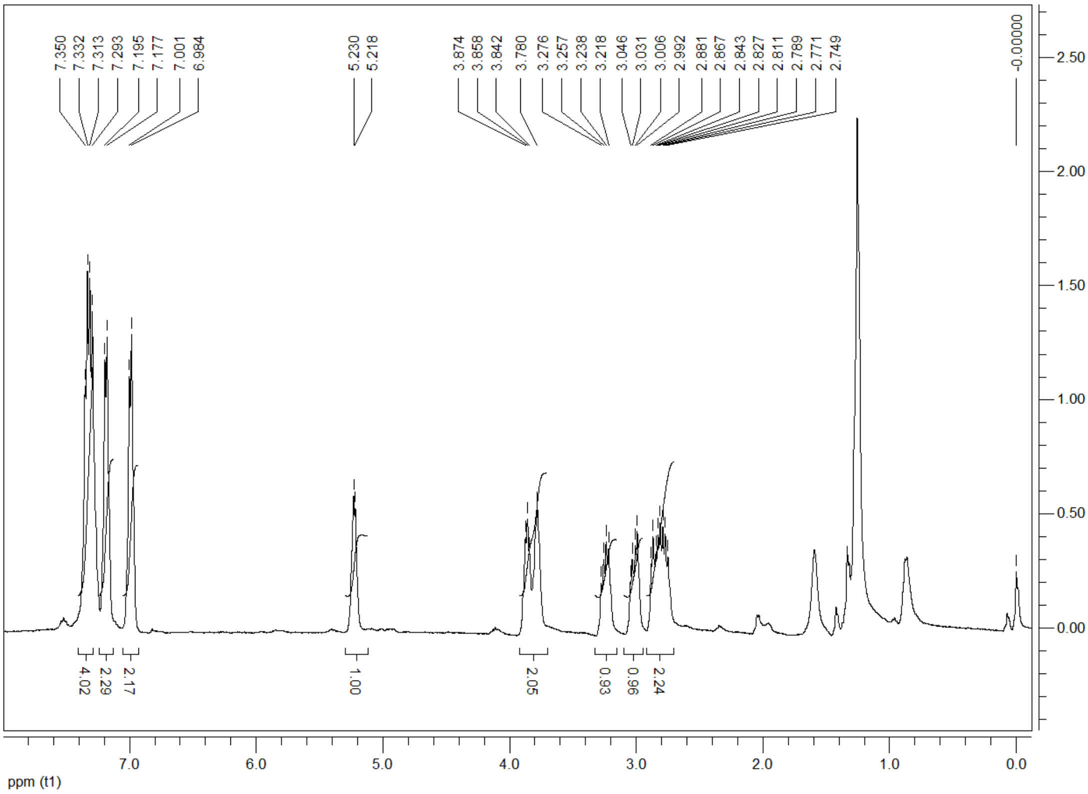
41.55

3h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3.218
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2.881
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2.843
2.827
2.811
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2.771
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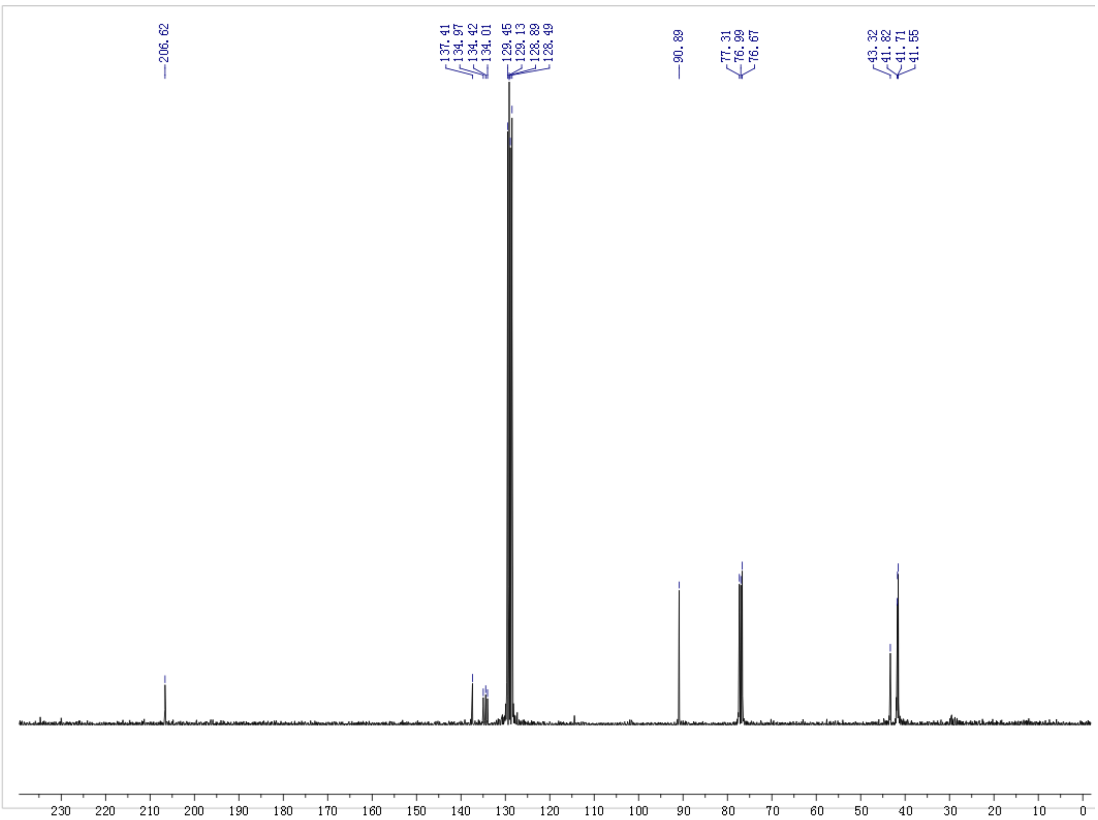
2.24
ppm (t1)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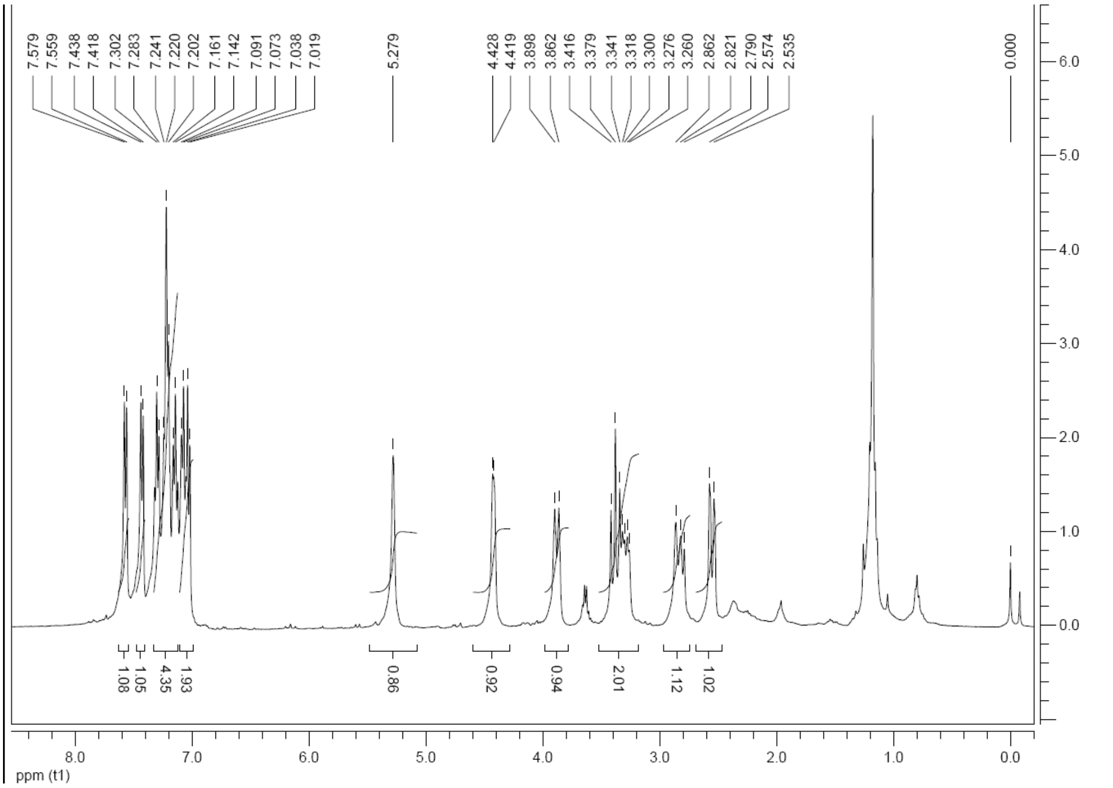
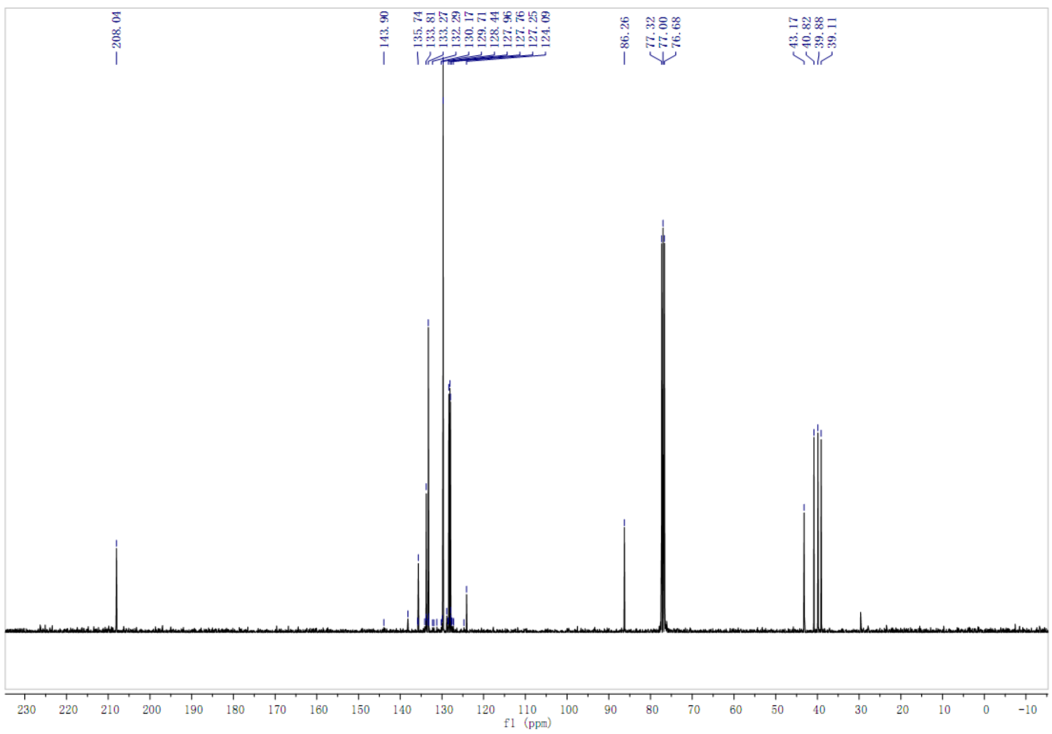
41.71
41.55

3i





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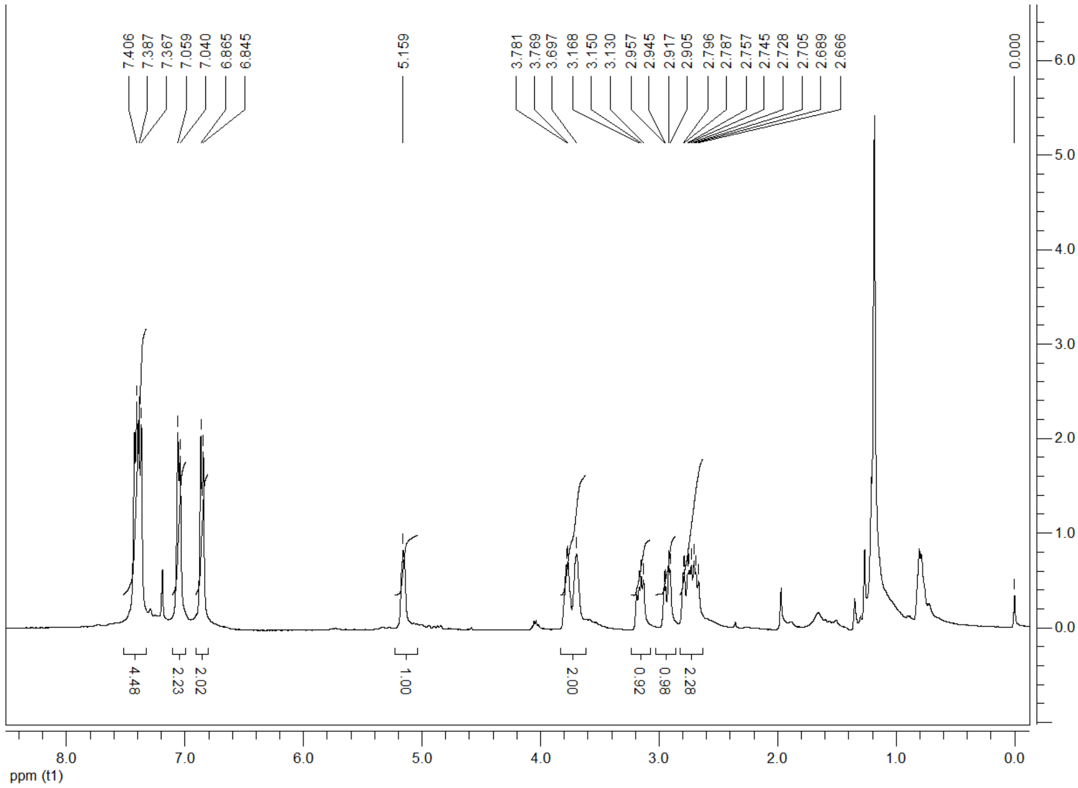

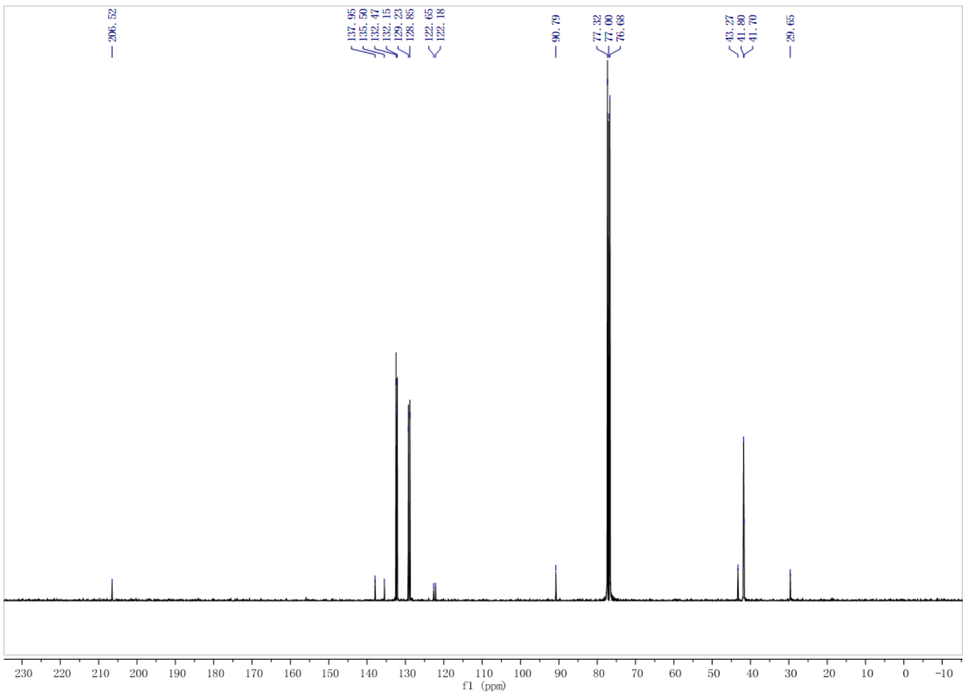

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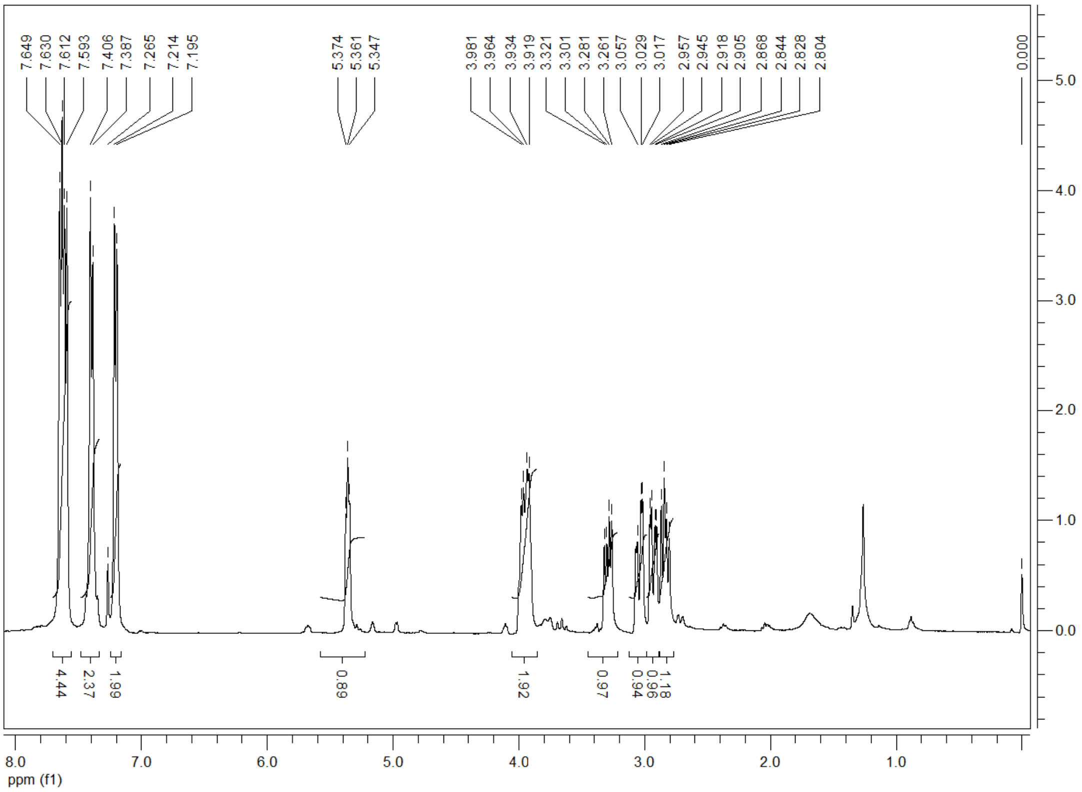
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3.0
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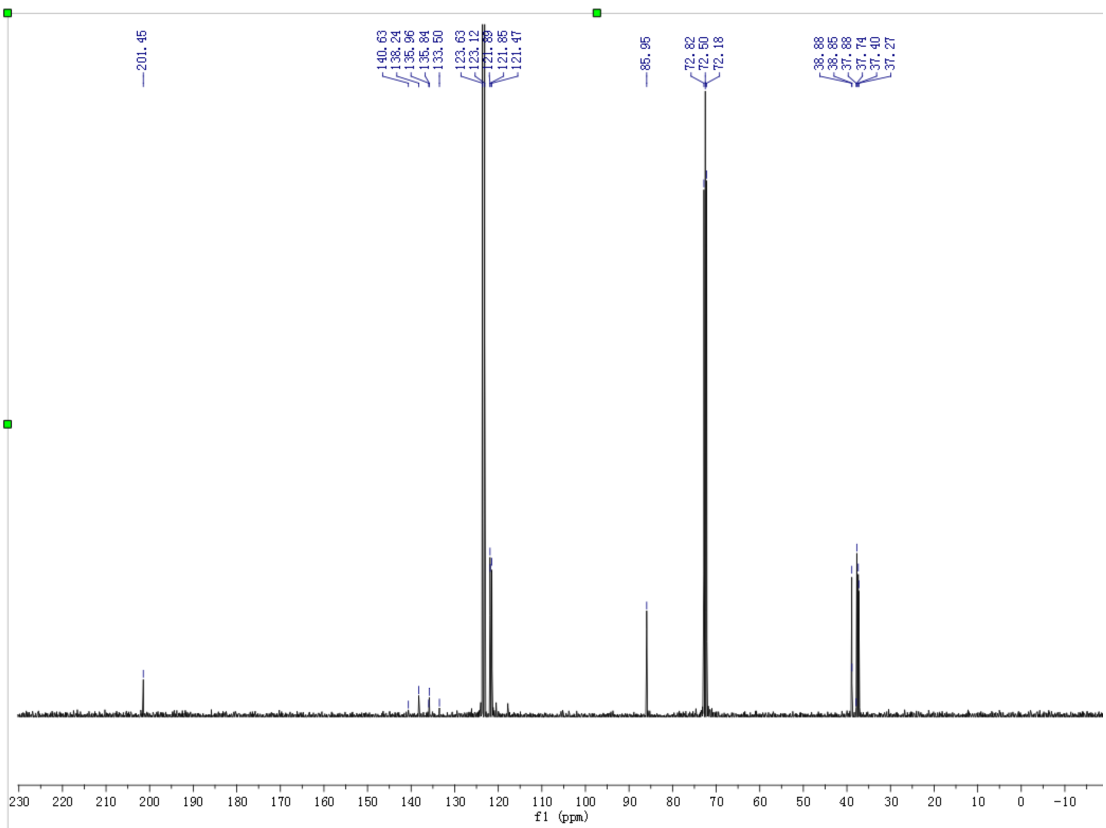
ppm (f1)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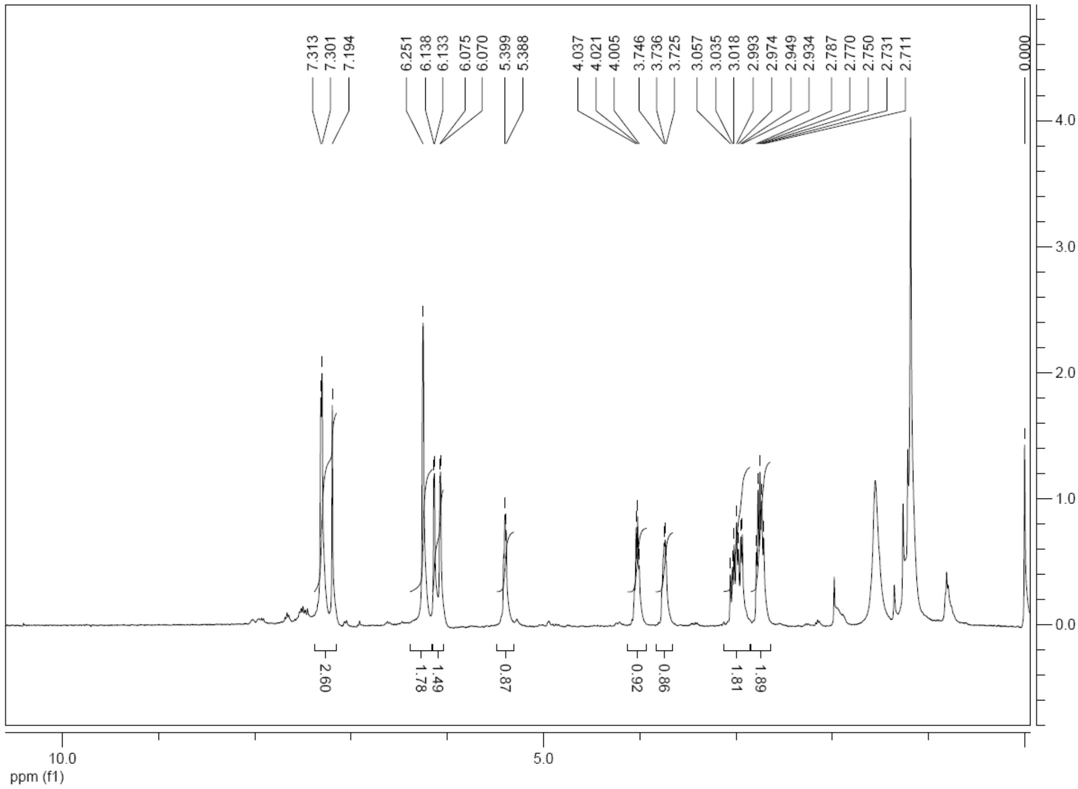
37.27
f1 (ppm)

3l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3.736
3.725
3.057
3.035
3.018
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2.949
2.934
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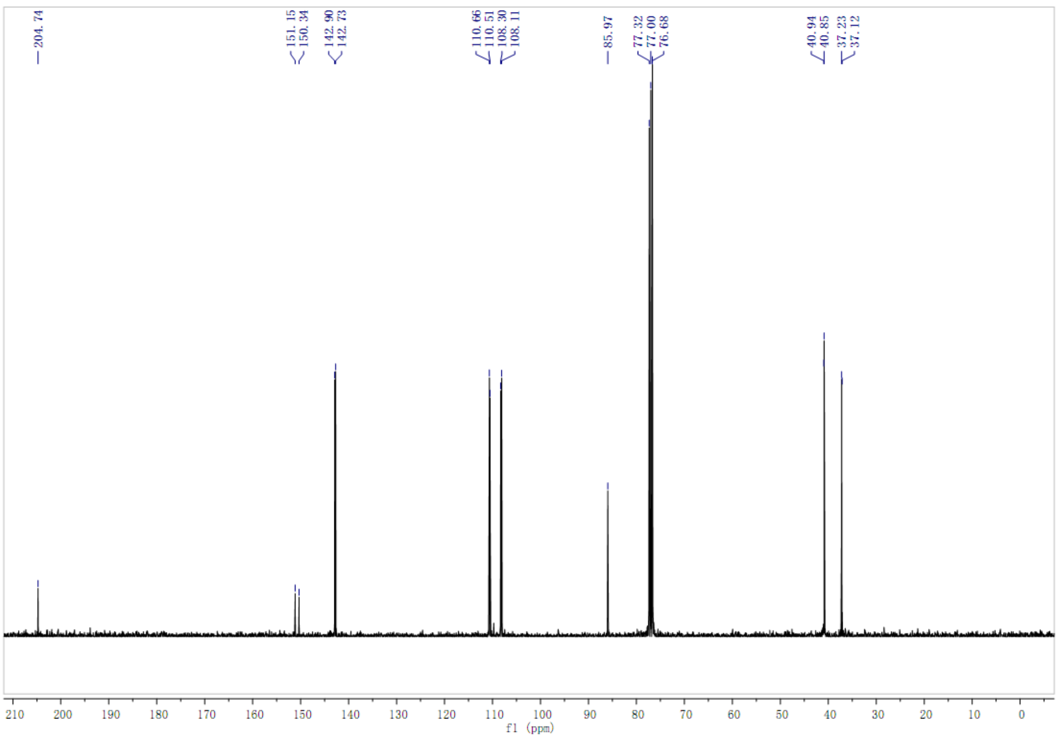
ppm (f1)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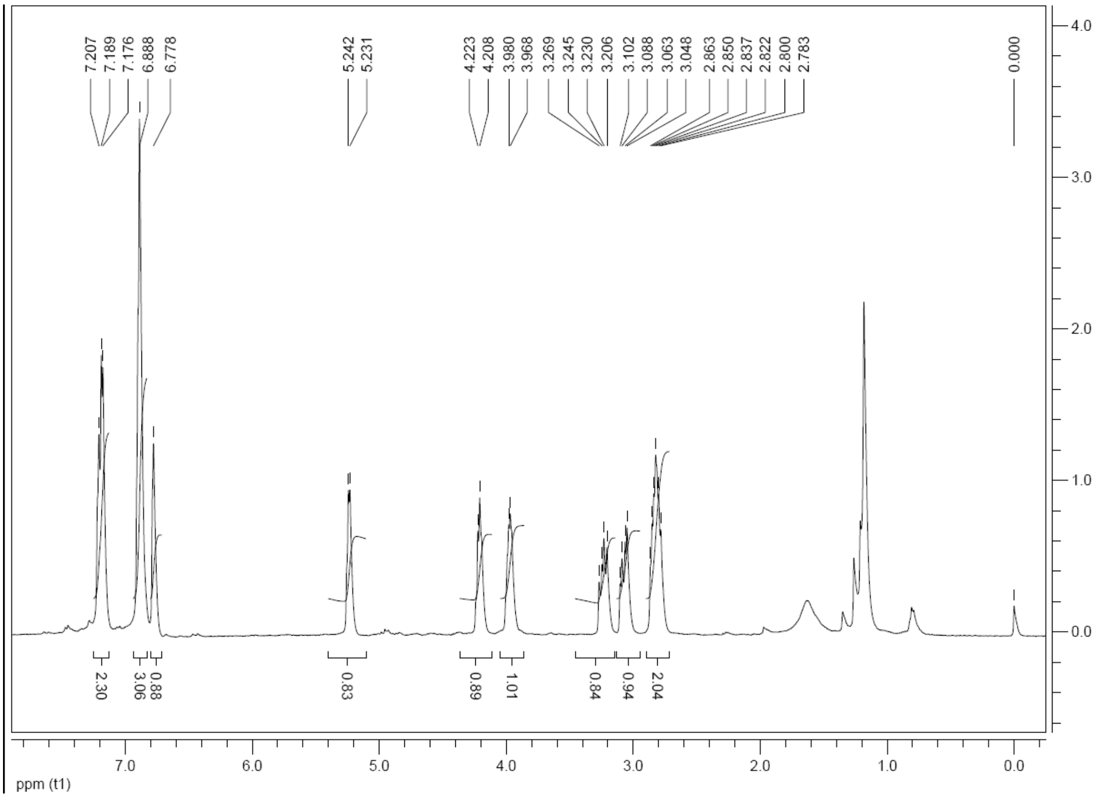
f1 (ppm)

3m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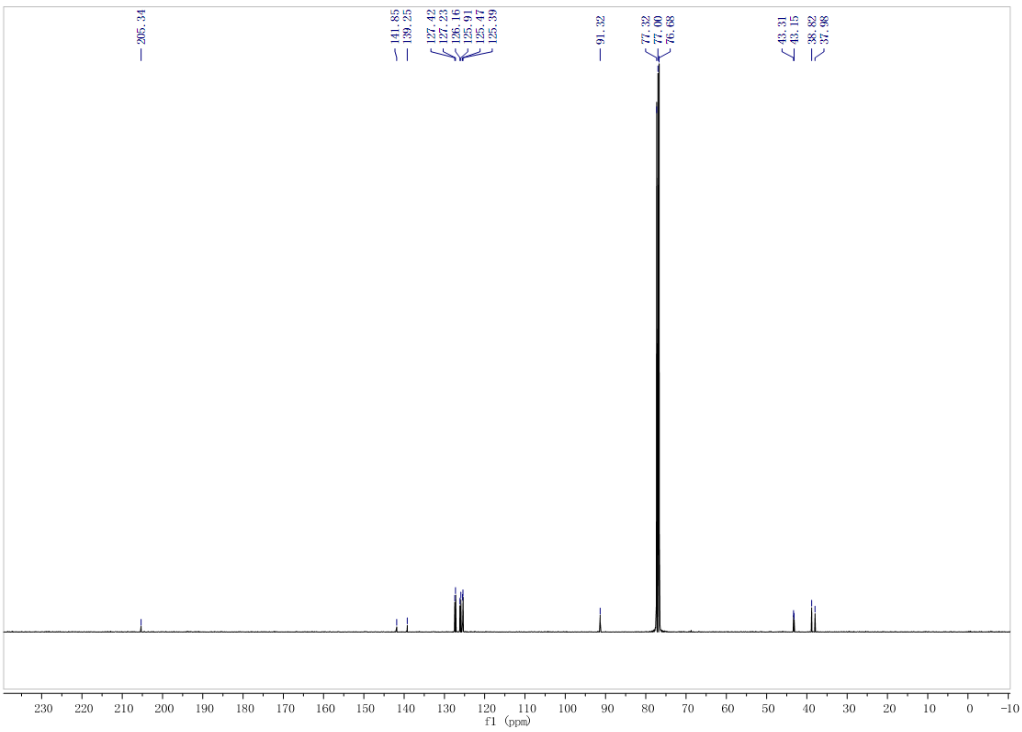
ppm (t1)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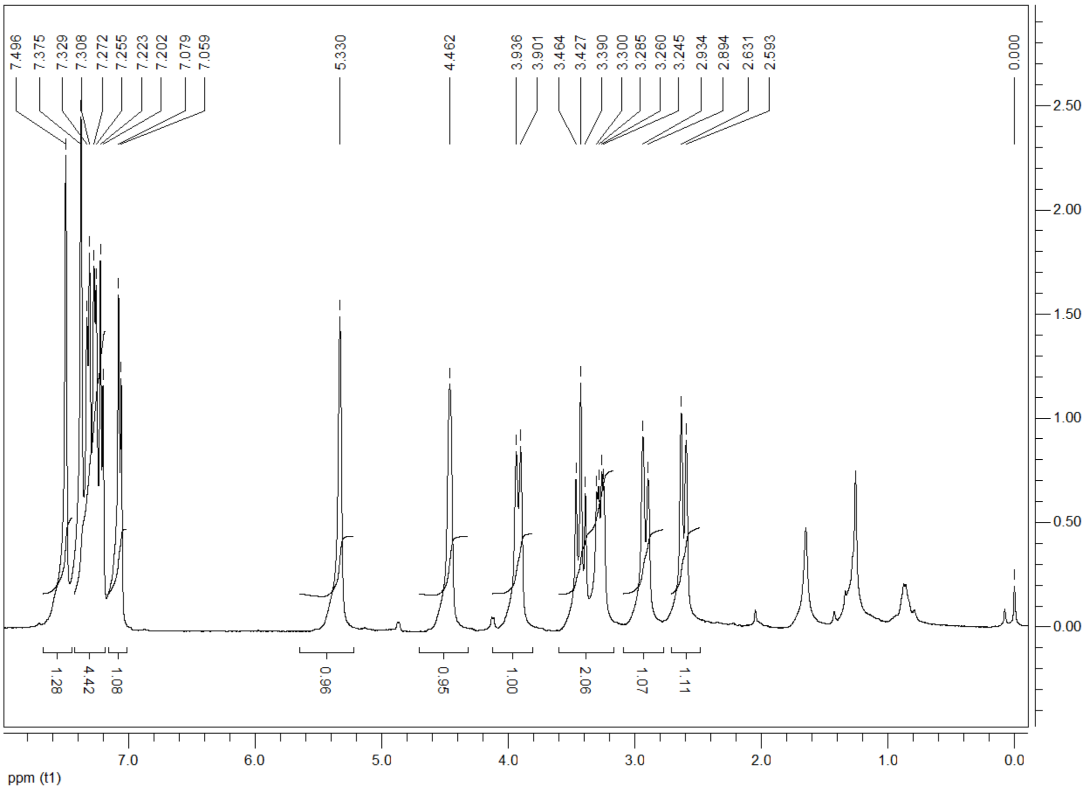
f1 (ppm)

3n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3.901
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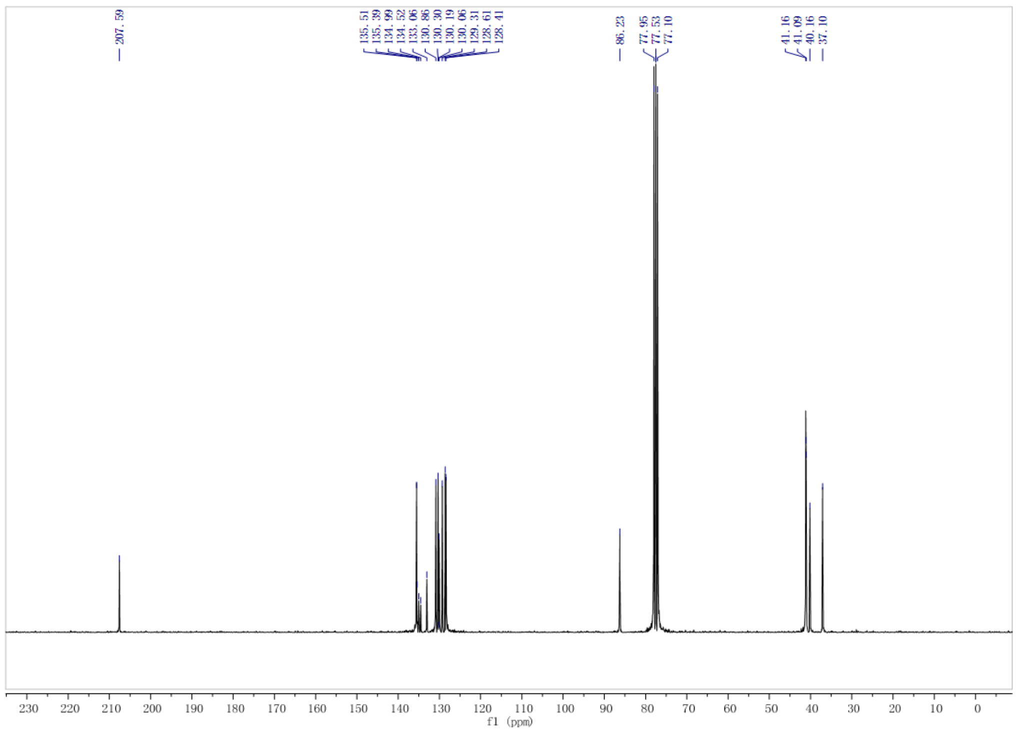
ppm (t1)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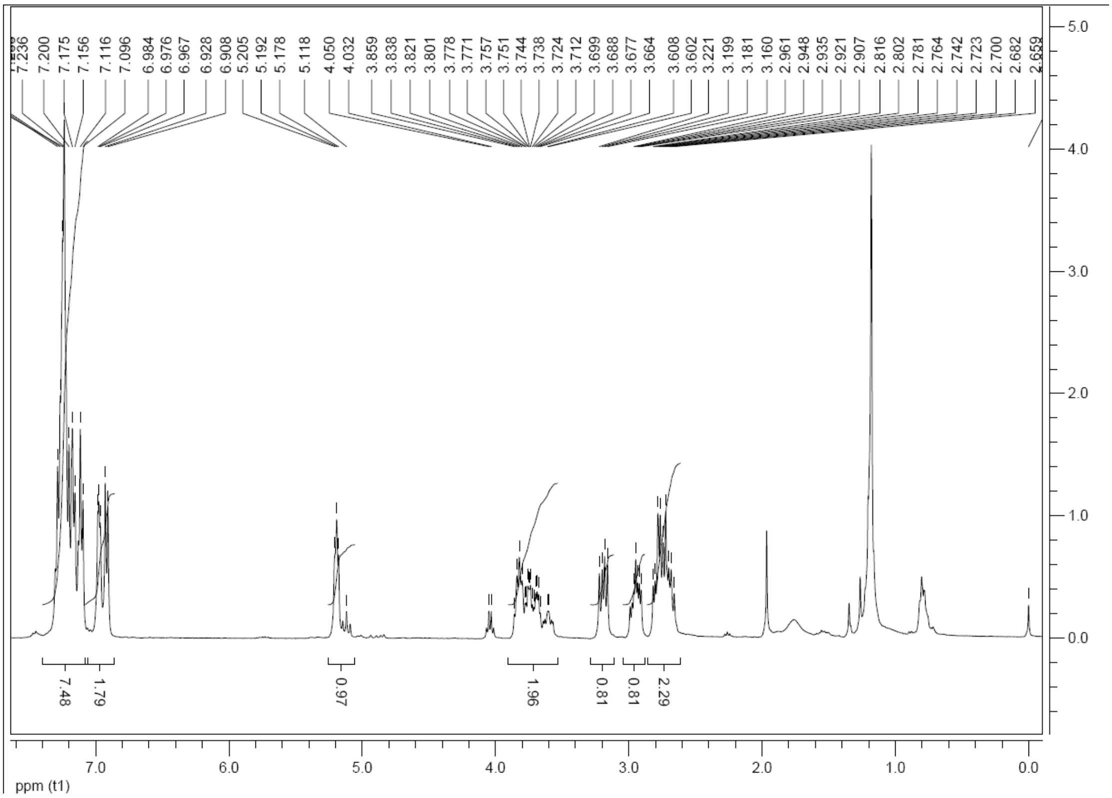
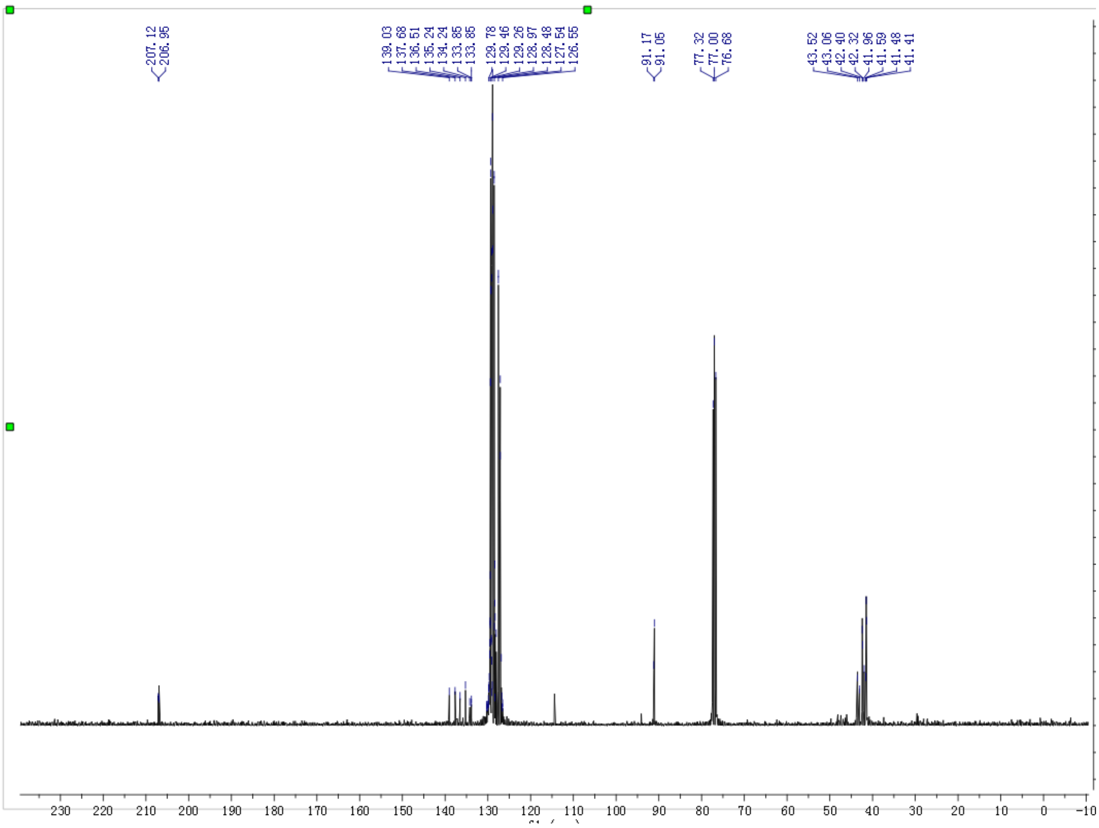
77.10
41.16
41.09
40.16
37.10
f1 (ppm)

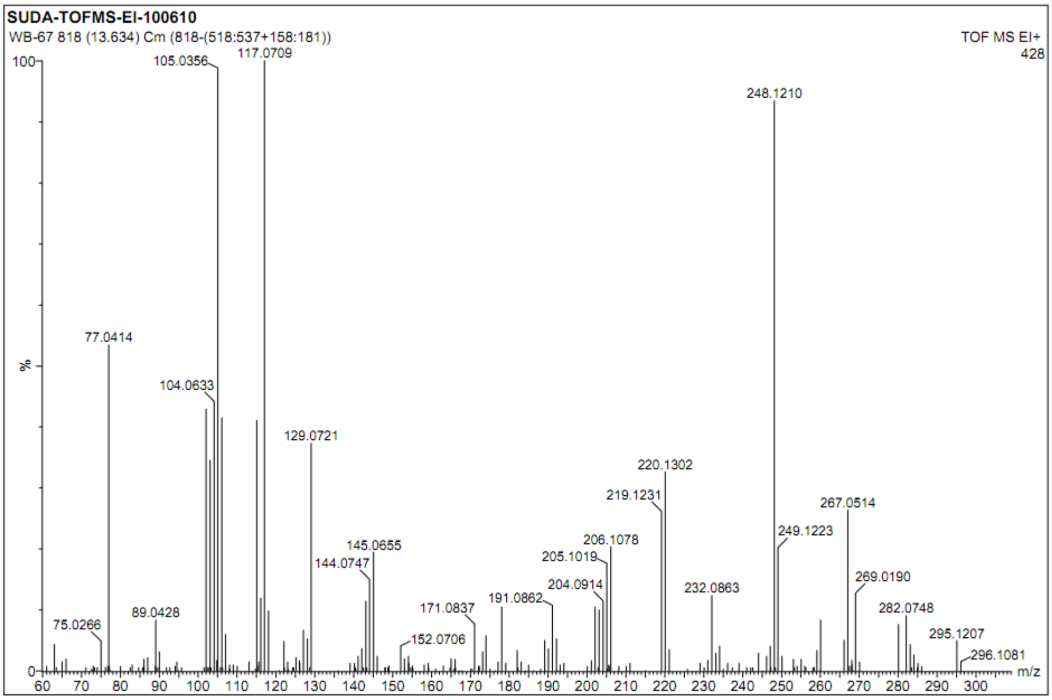
3o



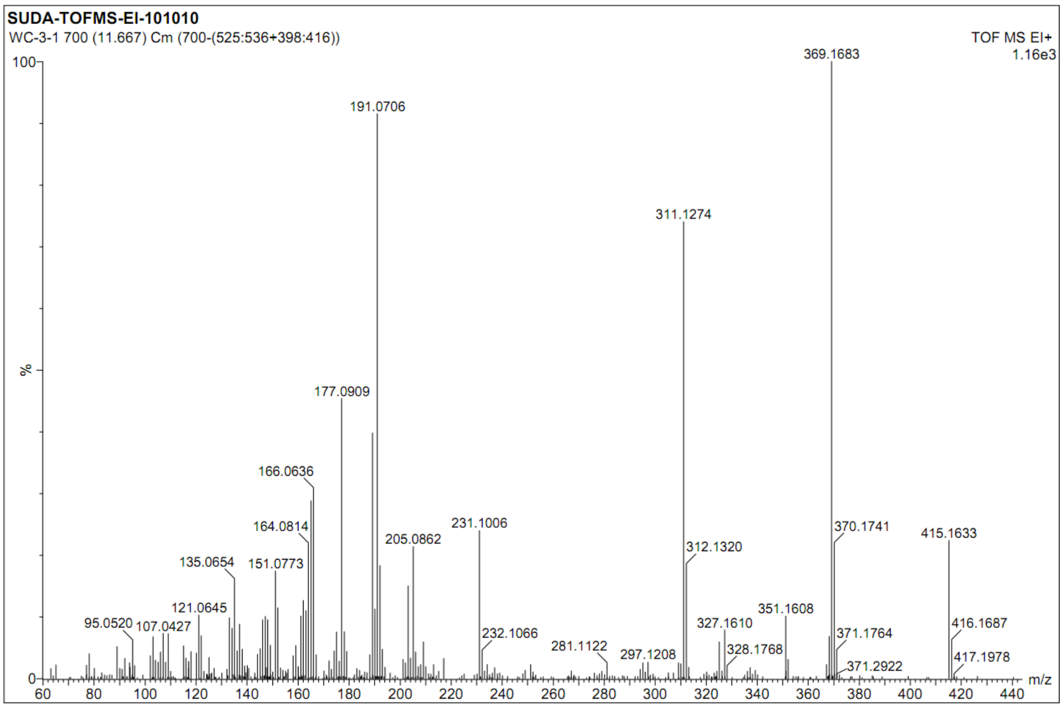


G: HRMS Analysis of Michael Addition Products

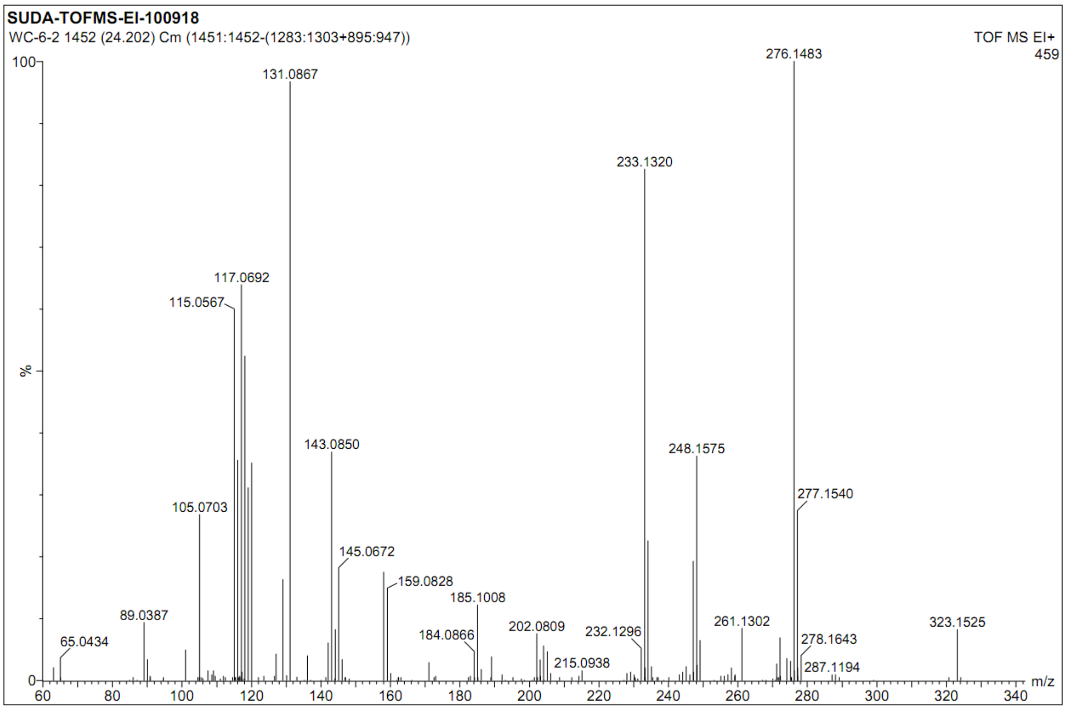
3a



3b



3c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277.1540
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159.0828
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184.0866
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261.1302
323.1525
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278.1643
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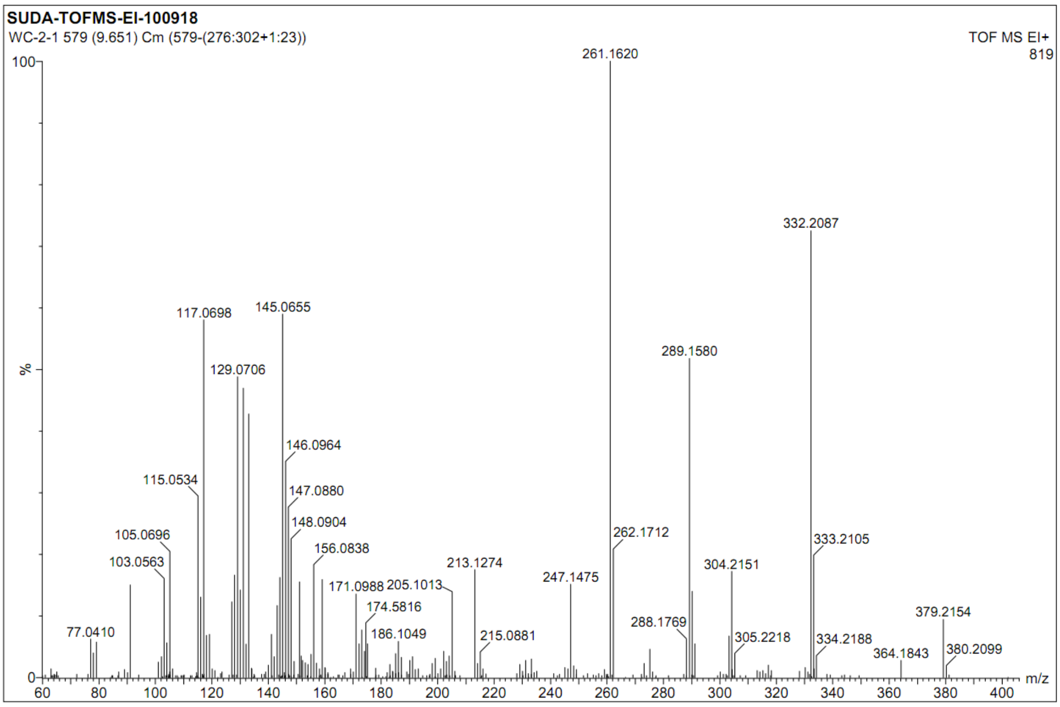
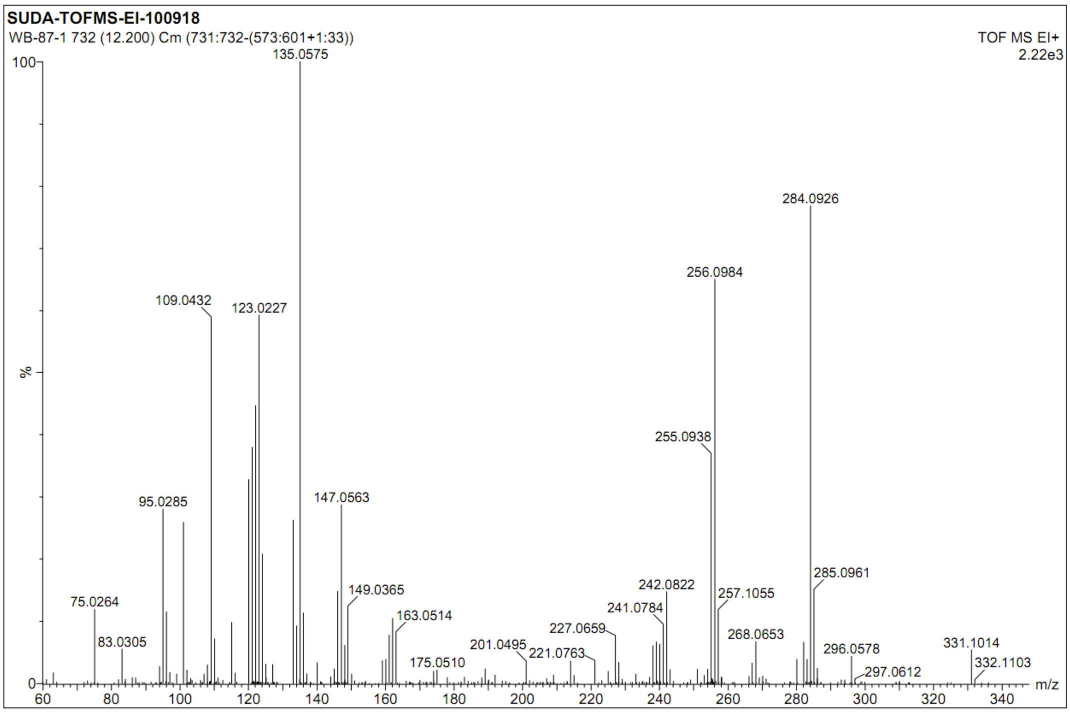
287.1194
100
%
0
m/z

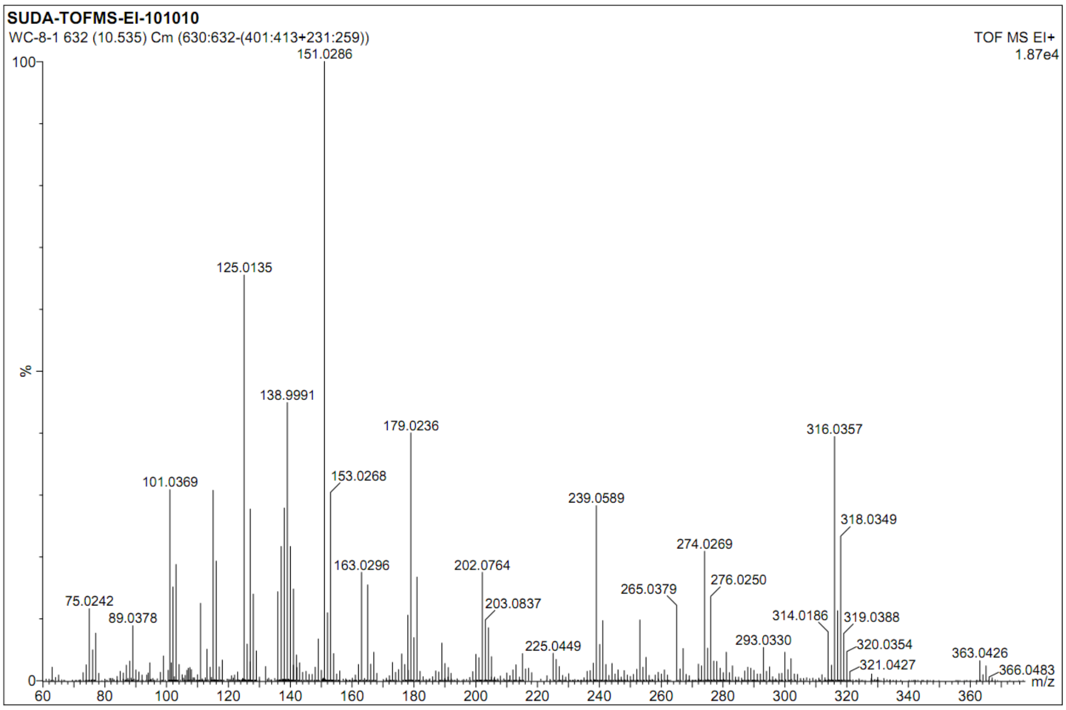
3d


SUDA-TOFMS-EI-100918
WC-2-1 579 (9.651) Cm (579-(276:302+1:23))
TOF MS EI+
819
261.1620
332.2087
117.0698
145.0655
129.0706
289.1580
146.0964
115.0534
147.0880
148.0904
105.0696
262.1712
333.2105
156.0838
103.0563
213.1274
304.2151
171.0988
205.1013
247.1475
174.5816
379.2154
288.1769
77.0410
186.1049
215.0881
305.2218
334.2188
364.1843
380.2099
100
%
0
m/z

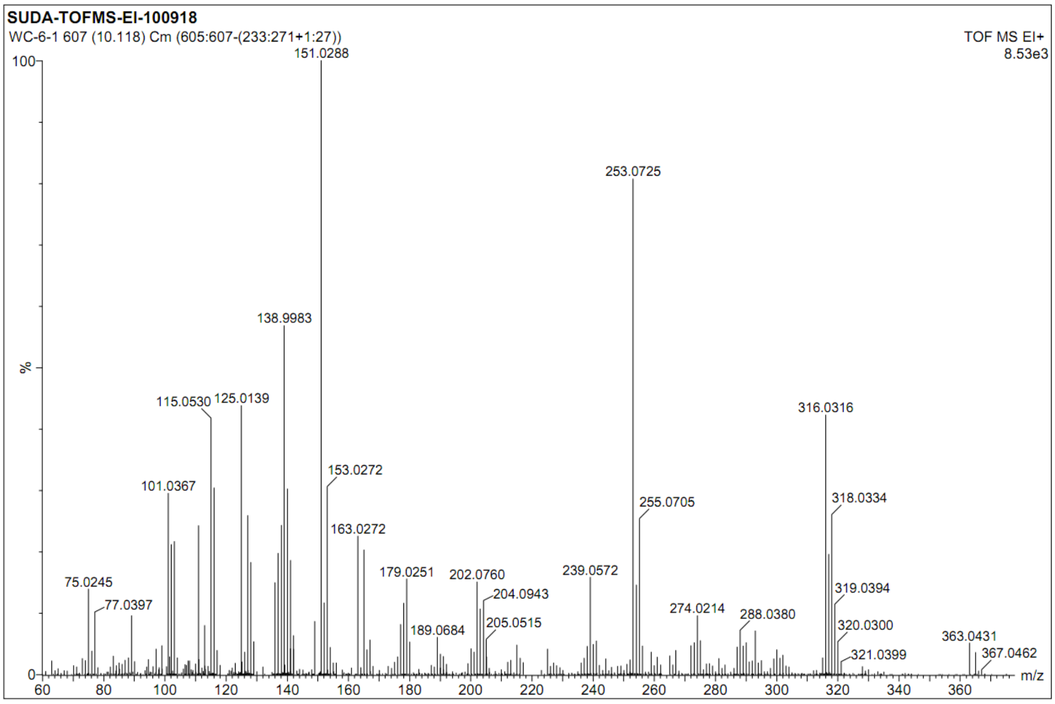
3e


SUDA-TOFMS-EI-100918
WB-87-1 732 (12.200) Cm (731:732-(573:601+1:33))
TOF MS EI+
2.22e3
135.0575
284.0926
256.0984
109.0432
123.0227
255.0938
95.0285
147.0563
285.0961
75.0264
149.0365
242.0822
257.1055
241.0784
163.0514
227.0659
268.0653
83.0305
201.0495
221.0763
296.0578
331.1014
175.0510
332.1103
297.0612
%
m/z

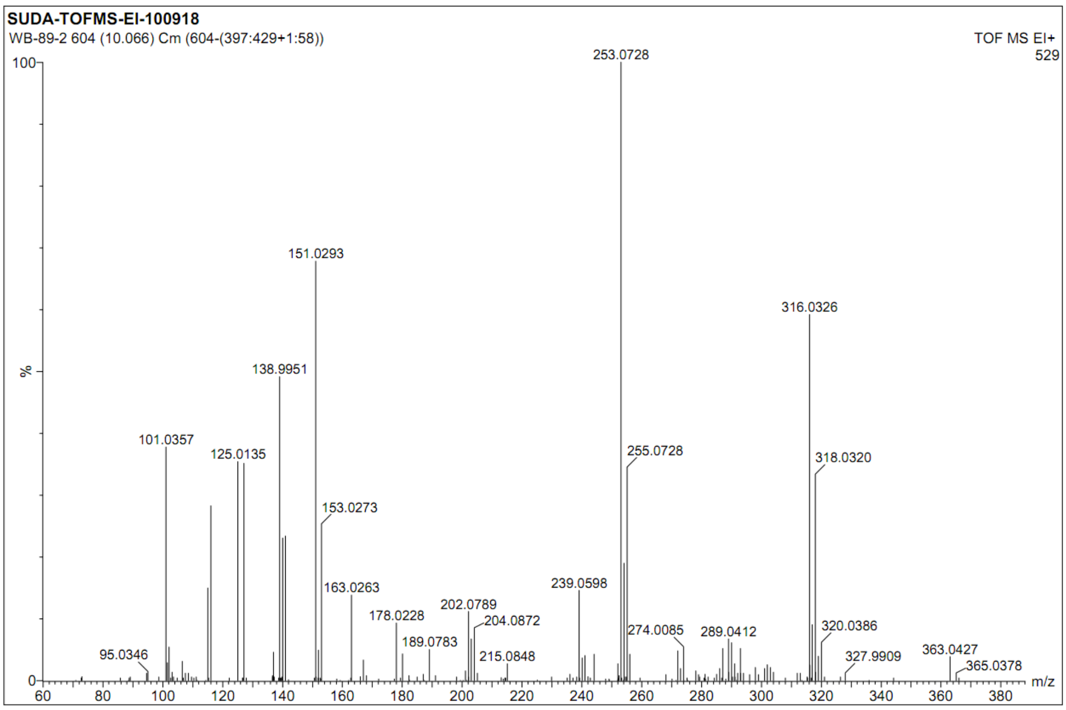
3f


SUDA-TOFMS-EI-101010
WC-8-1 632 (10.535) Cm (630:632-(401:413+231:259))
TOF MS EI+
1.87e4
151.0286
125.0135
138.9991
179.0236
316.0357
101.0369
153.0268
239.0589
318.0349
274.0269
163.0296
202.0764
276.0250
265.0379
75.0242
203.0837
314.0186
319.0388
89.0378
293.0330
320.0354
225.0449
363.0426
321.0427
366.0483
%
m/z

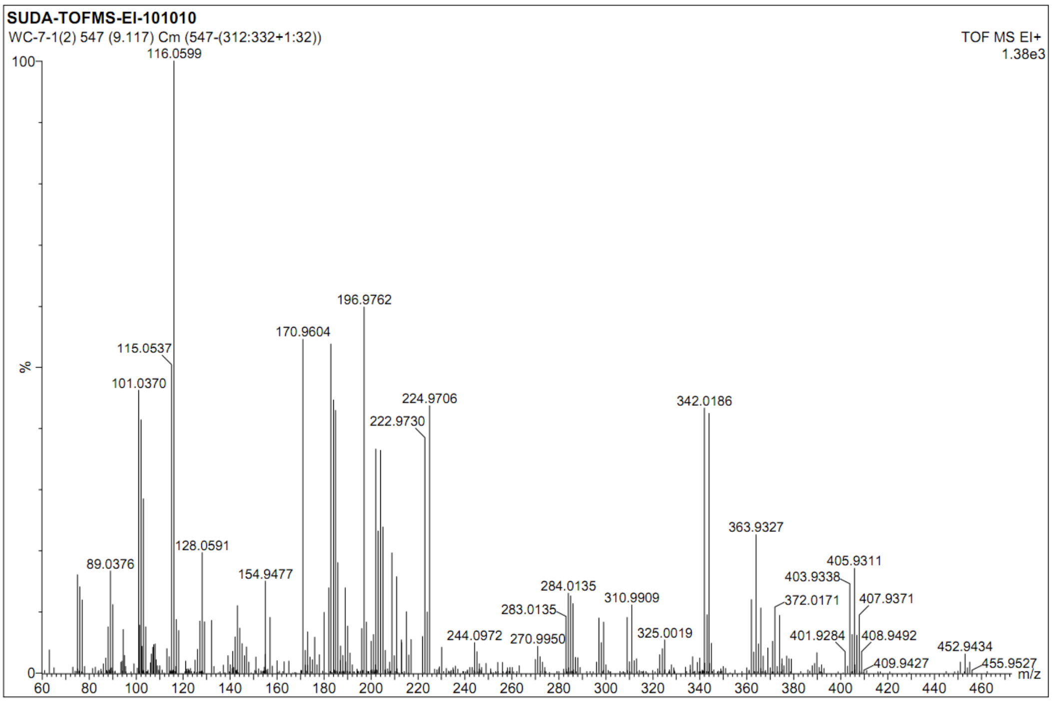
3g


SUDA-TOFMS-EI-100918
WC-6-1 607 (10.118) Cm (605:607-(233:271+1:27))
TOF MS EI+
8.53e3
151.0288
253.0725
138.9983
115.0530
125.0139
316.0316
101.0367
153.0272
255.0705
318.0334
163.0272
75.0245
77.0397
179.0251
202.0760
204.0943
239.0572
319.0394
189.0684
205.0515
274.0214
288.0380
320.0300
363.0431
367.0462
321.0399
100
%
0
m/z

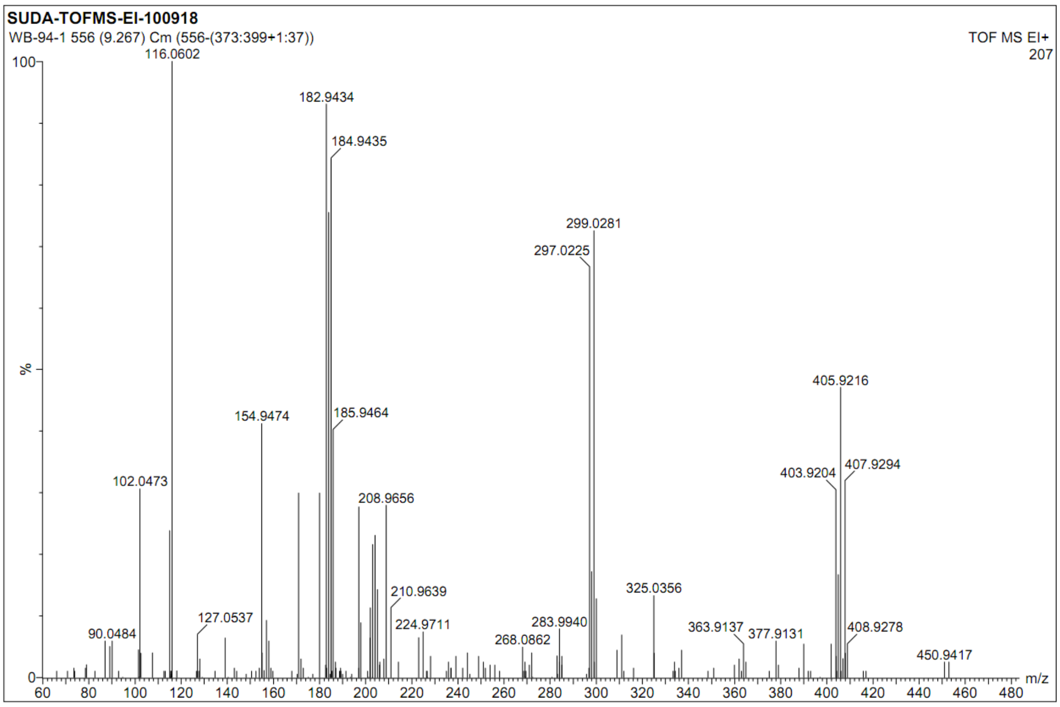
3h


SUDA-TOFMS-EI-100918
WB-89-2 604 (10.066) Cm (604-(397:429+1:58))
TOF MS EI+
529
253.0728
151.0293
316.0326
138.9951
101.0357
125.0135
255.0728
318.0320
153.0273
163.0263
239.0598
178.0228
202.0789
204.0872
189.0783
215.0848
274.0085
289.0412
320.0386
95.0346
327.9909
363.0427
365.0378
100
%
0
m/z

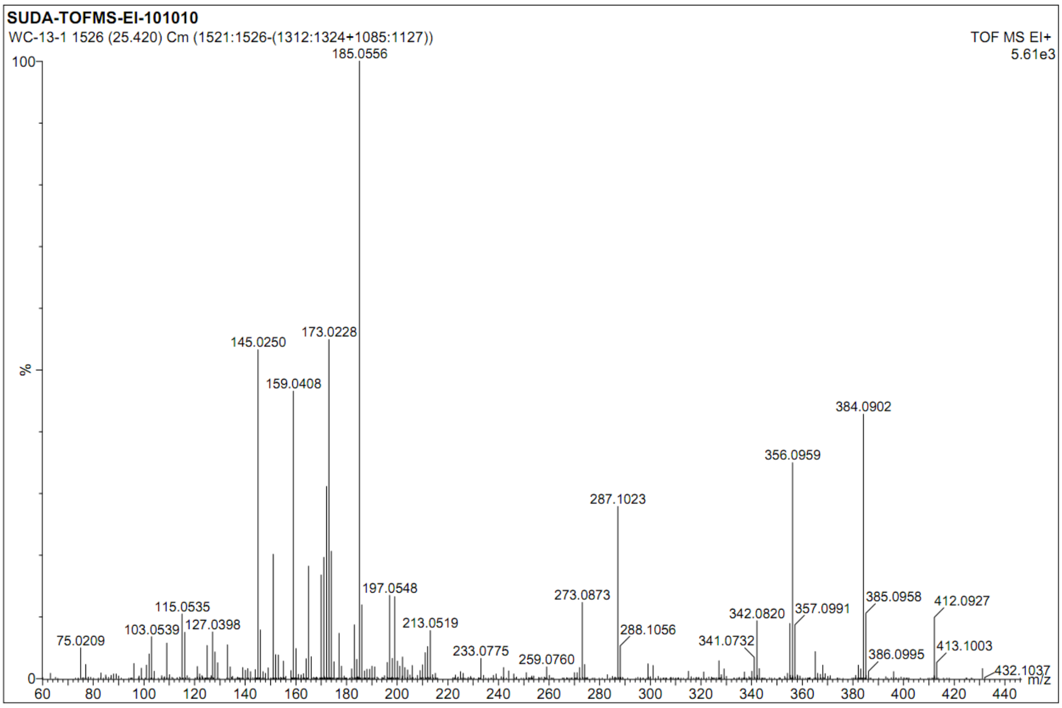
3i


SUDA-TOFMS-EI-101010
WC-7-1(2) 547 (9.117) Cm (547-(312:332+1:32))
TOF MS EI+
1.38e3
116.0599
196.9762
170.9604
115.0537
101.0370
224.9706
222.9730
342.0186
363.9327
89.0376
128.0591
154.9477
405.9311
403.9338
284.0135
310.9909
372.0171
407.9371
283.0135
244.0972
270.9950
325.0019
401.9284
408.9492
452.9434
409.9427
455.9527
%
m/z

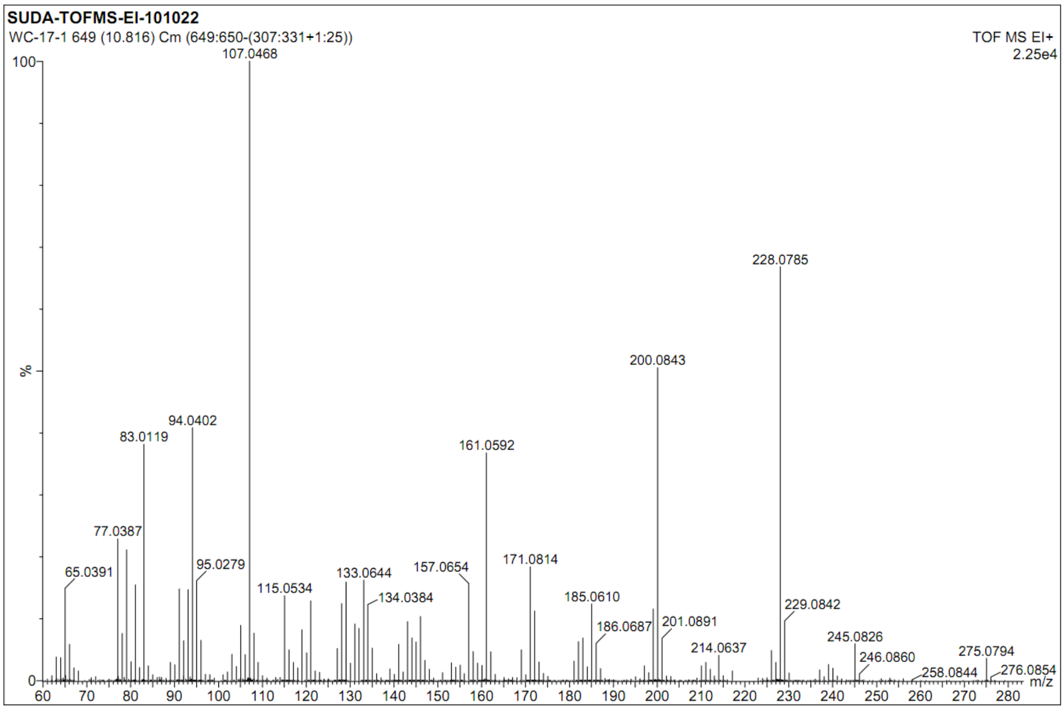
3j


SUDA-TOFMS-EI-100918
WB-94-1 556 (9.267) Cm (556-(373:399+1:37))
TOF MS EI+
207
116.0602
182.9434
184.9435
299.0281
297.0225
405.9216
154.9474
185.9464
403.9204
407.9294
102.0473
208.9656
210.9639
325.0356
127.0537
224.9711
283.9940
363.9137
377.9131
408.9278
90.0484
268.0862
450.9417
%
m/z

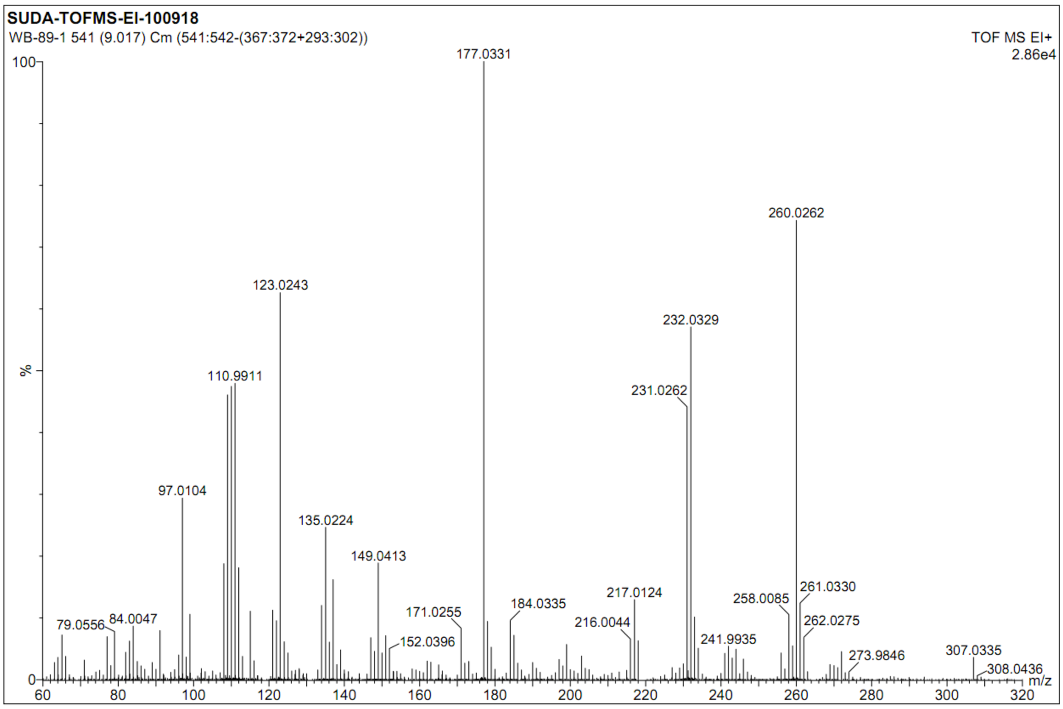
3k


SUDA-TOFMS-EI-101010
WC-13-1 1526 (25.420) Cm (1521:1526-(1312:1324+1085:1127))
TOF MS EI+
5.61e3
185.0556
145.0250
173.0228
159.0408
384.0902
356.0959
287.1023
197.0548
273.0873
213.0519
115.0535
127.0398
103.0539
75.0209
233.0775
259.0760
288.1056
342.0820
341.0732
357.0991
385.0958
386.0995
412.0927
413.1003
432.1037
%
m/z

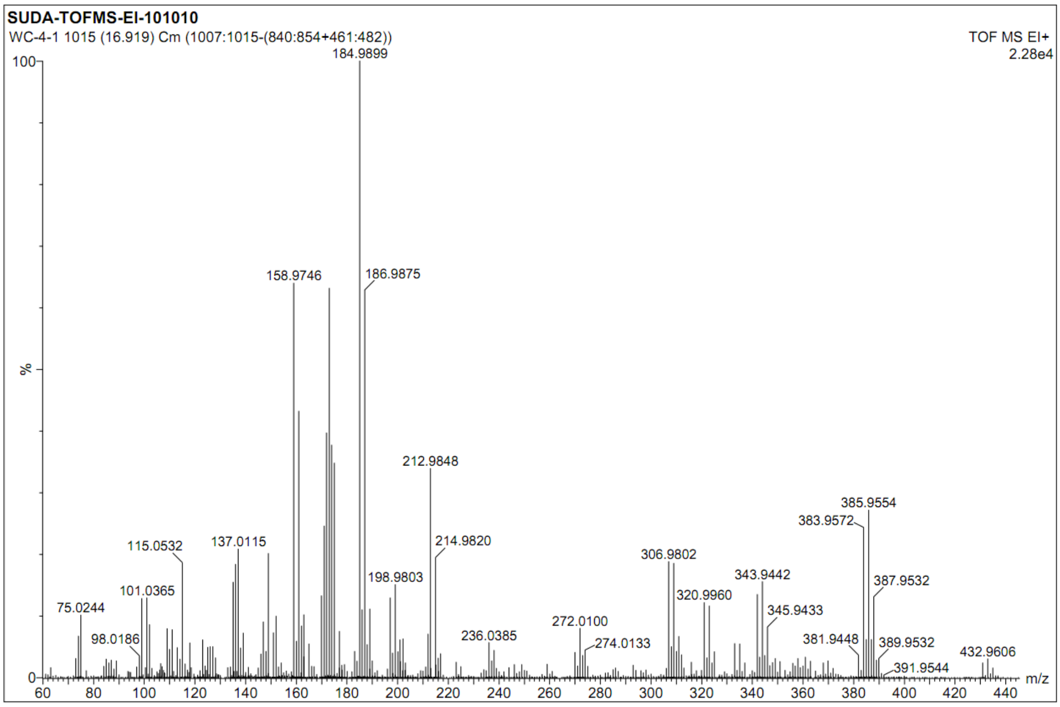
3l


SUDA-TOFMS-EI-101022
WC-17-1 649 (10.816) Cm (649:650-(307:331+1:25))
TOF MS EI+
2.25e4
107.0468
228.0785
200.0843
94.0402
83.0119
161.0592
77.0387
65.0391
95.0279
115.0534
133.0644
134.0384
157.0654
171.0814
185.0610
186.0687
201.0891
214.0637
229.0842
245.0826
246.0860
258.0844
275.0794
276.0854
%
m/z

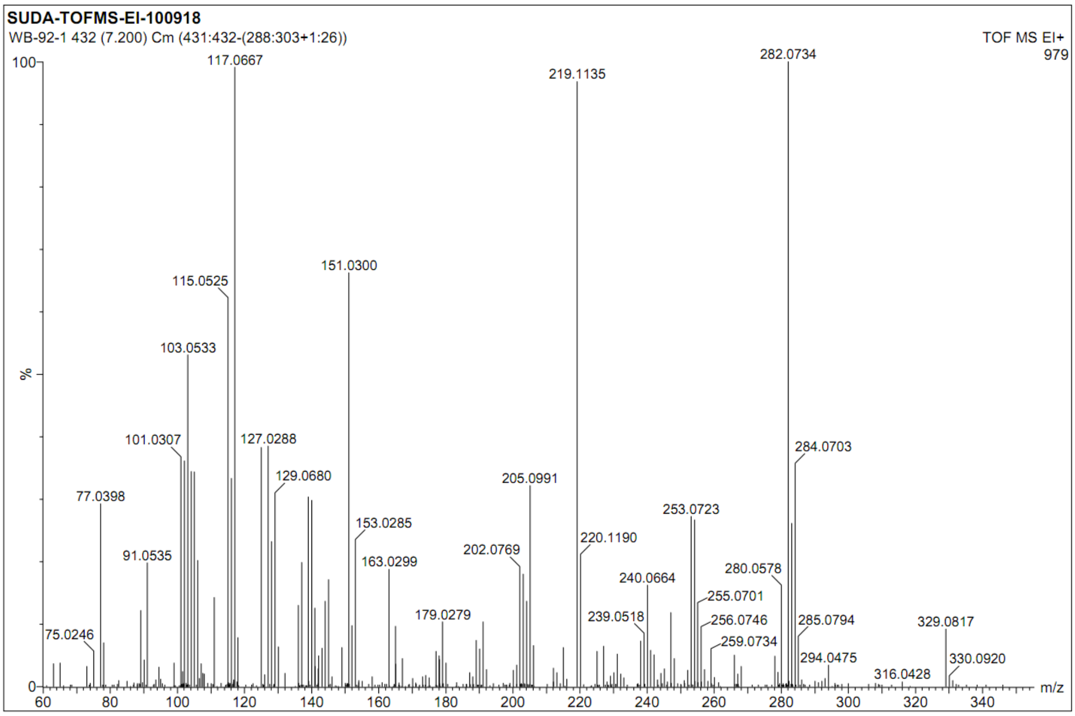
3m


SUDA-TOFMS-EI-100918
WB-89-1 541 (9.017) Cm (541:542-(367:372+293:302))
TOF MS EI+
2.86e4
177.0331
260.0262
123.0243
232.0329
110.9911
231.0262
97.0104
135.0224
149.0413
171.0255
184.0335
217.0124
216.0044
258.0085
261.0330
262.0275
79.0556
84.0047
152.0396
241.9935
273.9846
307.0335
308.0436
%
m/z

3n

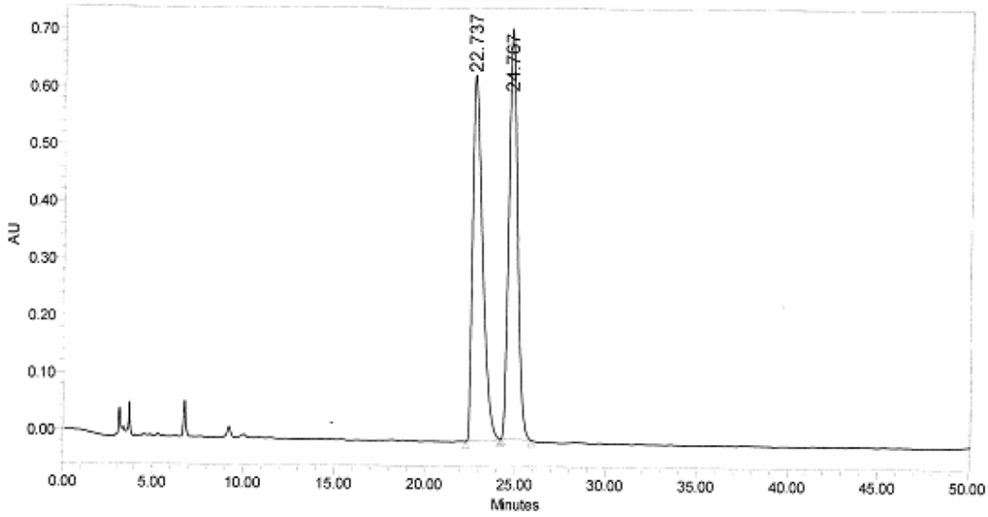

SUDA-TOFMS-EI-101010
WC-4-1 1015 (16.919) Cm (1007:1015-(840:854+461:482))
TOF MS EI+
2.28e4
184.9899
158.9746
186.9875
212.9848
385.9554
383.9572
115.0532
137.0115
214.9820
306.9802
343.9442
387.9532
198.9803
320.9960
101.0365
75.0244
345.9433
272.0100
98.0186
236.0385
274.0133
381.9448
389.9532
432.9606
391.9544
%
m/z

3o

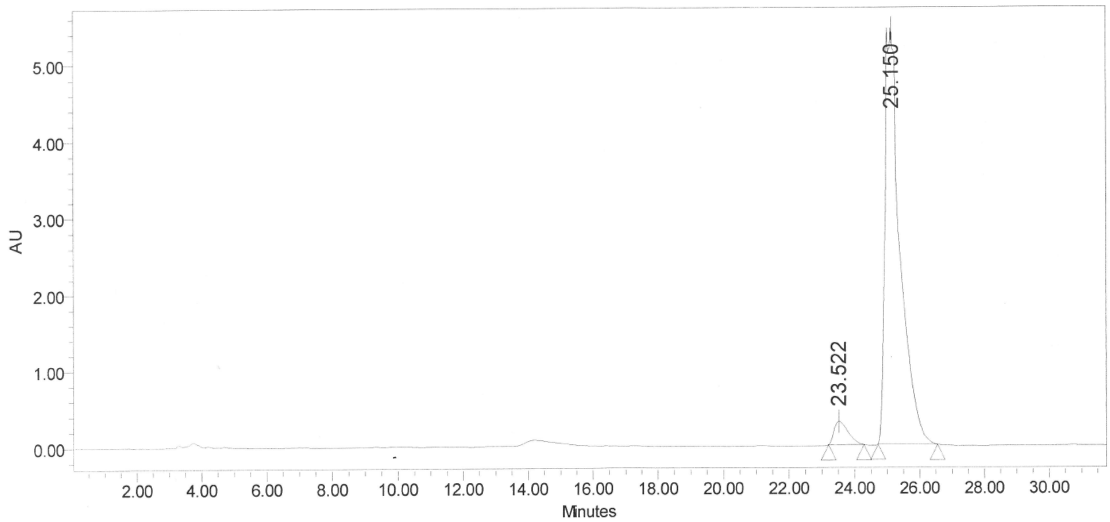

SUDA-TOFMS-EI-100918
WB-92-1 432 (7.200) Cm (431:432-(288:303+1:26))
TOF MS EI+
979
117.0667
219.1135
282.0734
151.0300
115.0525
103.0533
101.0307
127.0288
284.0703
129.0680
205.0991
77.0398
153.0285
253.0723
220.1190
91.0535
202.0769
163.0299
280.0578
240.0664
255.0701
179.0279
239.0518
256.0746
285.0794
329.0817
75.0246
259.0734
294.0475
330.0920
316.0428
%
m/z

H: HPLC Analysis of Michael Addition Products

3a

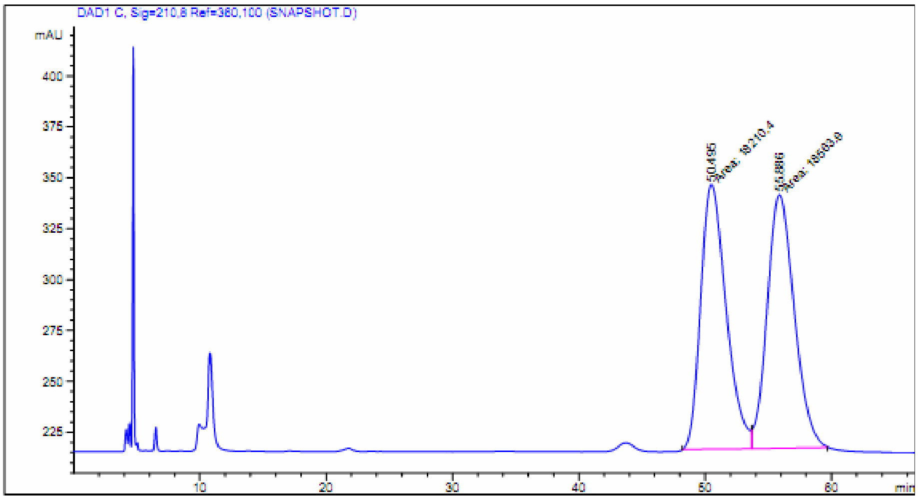


	RT	Area	% Area	Height
1	22.737	24195769	50.44	637786
2	24.767	23778090	49.56	713897

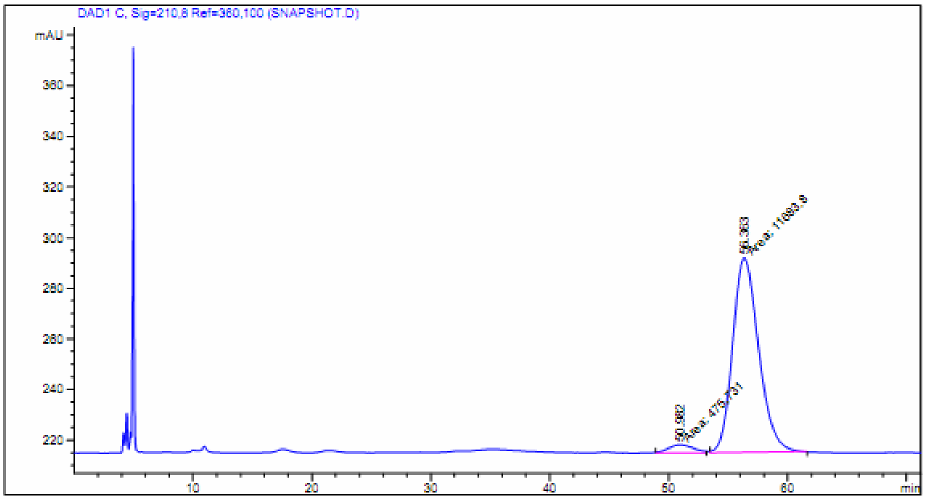


	Name	RT	Area	% Area	Height (µV)
1		23.522	8931199	4.85	301878
2		25.150	175084100	95.15	5437118

3b

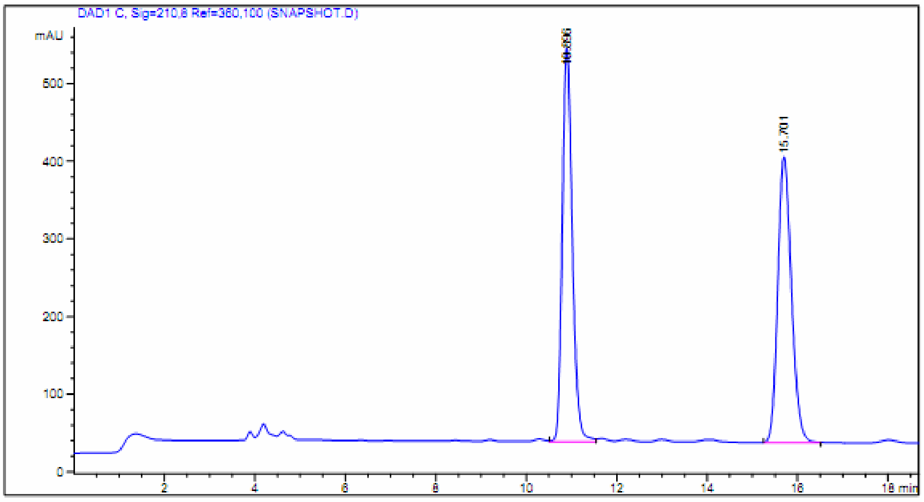


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.495	MF	2.3383	1.82104e4	129.80028	49.5194
2	55.886	FM	2.4839	1.85639e4	124.56097	50.4806
Totals :				3.67742e4	254.36125	



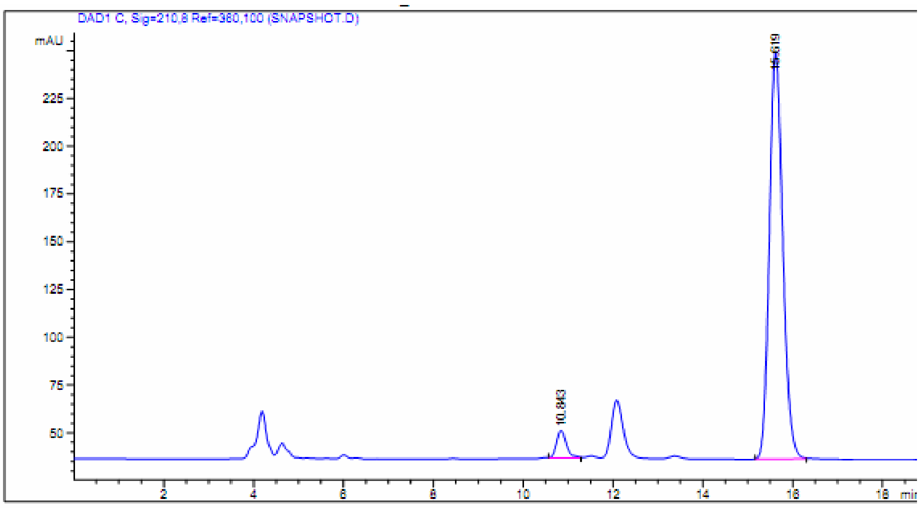
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.982	MM	2.5105	475.73080	3.15822	3.9124
2	56.363	MM	2.5388	1.16838e4	76.70048	96.0876
Totals :				1.21595e4	79.85870	

3c



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.896	VV	0.2367	7779.89600	507.79156	50.1676
2	15.701	BB	0.3248	7727.90674	368.31305	49.8324

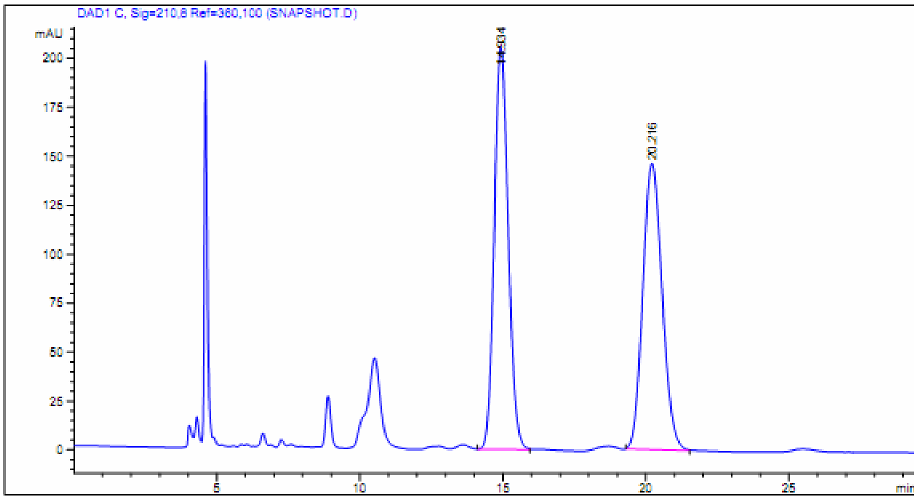
Totals : 1.55078e4 876.10461



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.843	BB	0.2356	220.40231	14.31716	4.7604
2	15.619	BB	0.3202	4409.47363	212.38193	95.2396

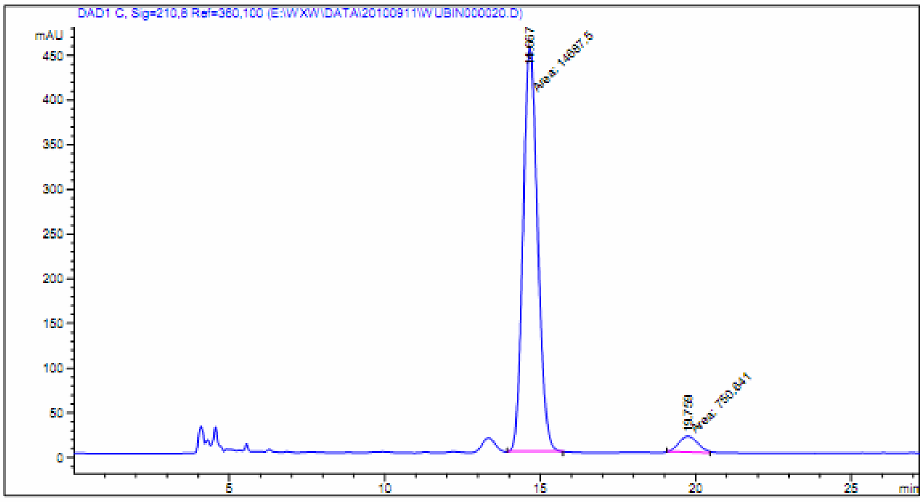
Totals : 4629.87595 226.69909

3d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.934	VB	0.5272	6952.54346	205.22092	50.3534
2	20.216	BB	0.7315	6854.94092	146.07912	49.6466

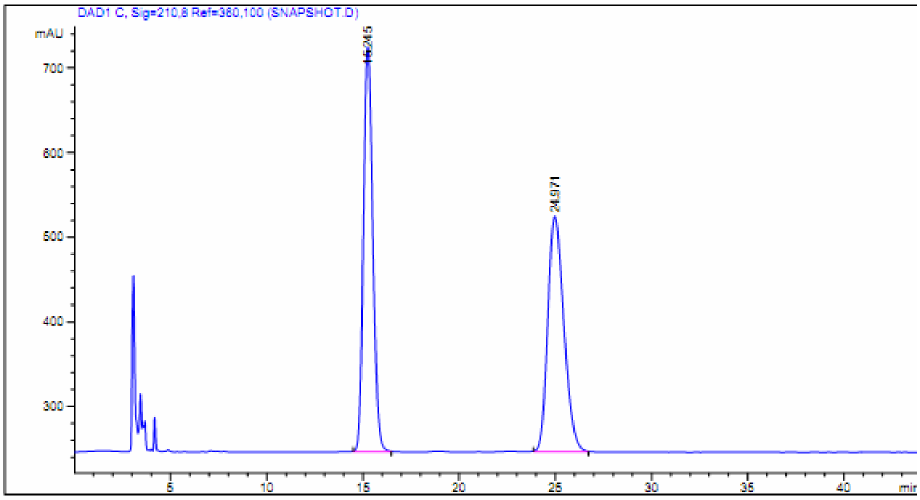
Totals : 1.38075e4 351.30003



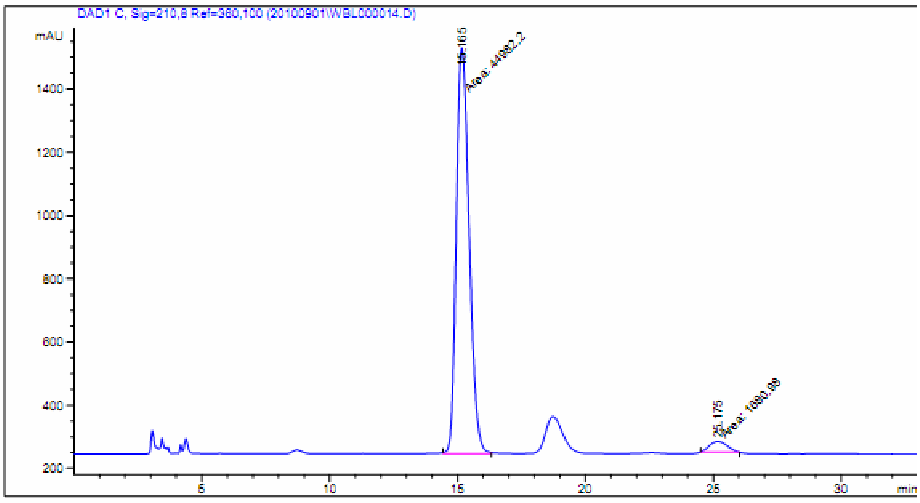
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.667	MM	0.5420	1.46875e4	451.64243	95.1377
2	19.759	MM	0.7022	750.64063	17.81737	4.8623

Totals : 1.54381e4 469.45979

3e

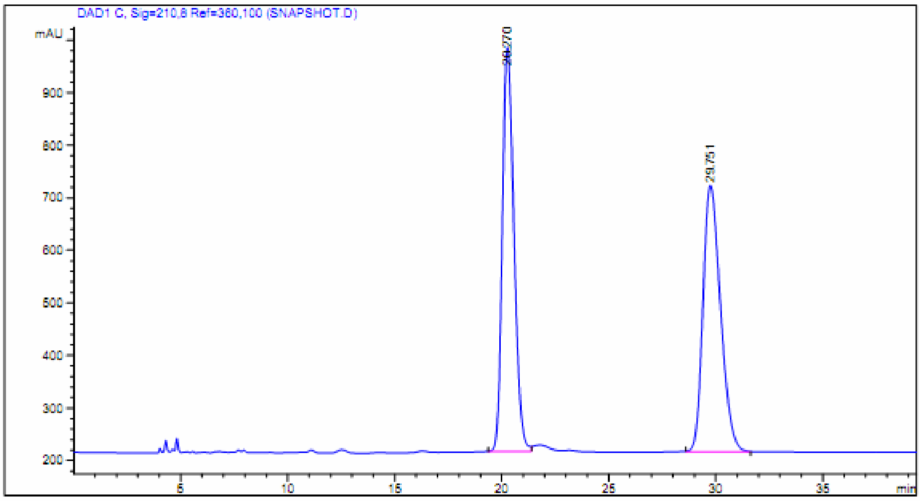


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.245	BB	0.5224	1.60833e4	478.18372	49.9761
2	24.971	BB	0.9003	1.60987e4	277.71735	50.0239
Totals :				3.21819e4	755.90106	

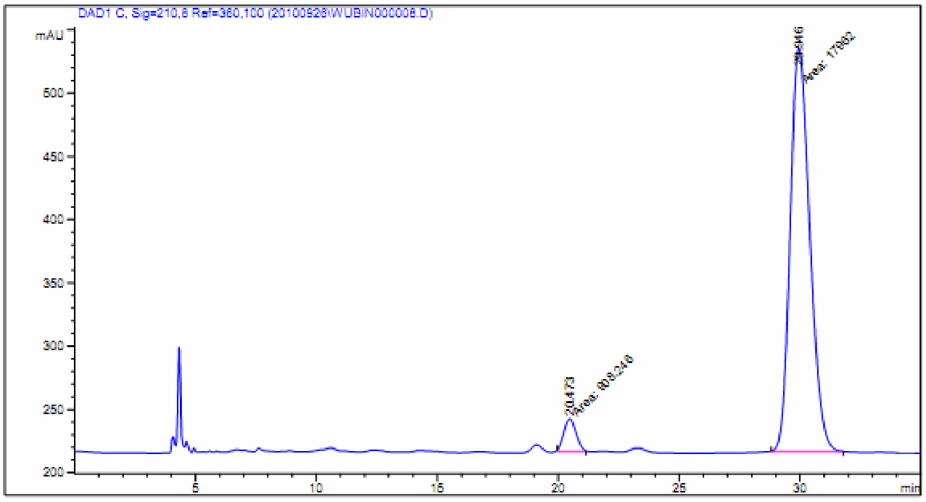


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.165	MM	0.5842	4.49822e4	1283.28906	96.3976
2	25.175	MM	0.8143	1680.98120	34.40445	3.6024
Totals :				4.66631e4	1317.69351	

3f

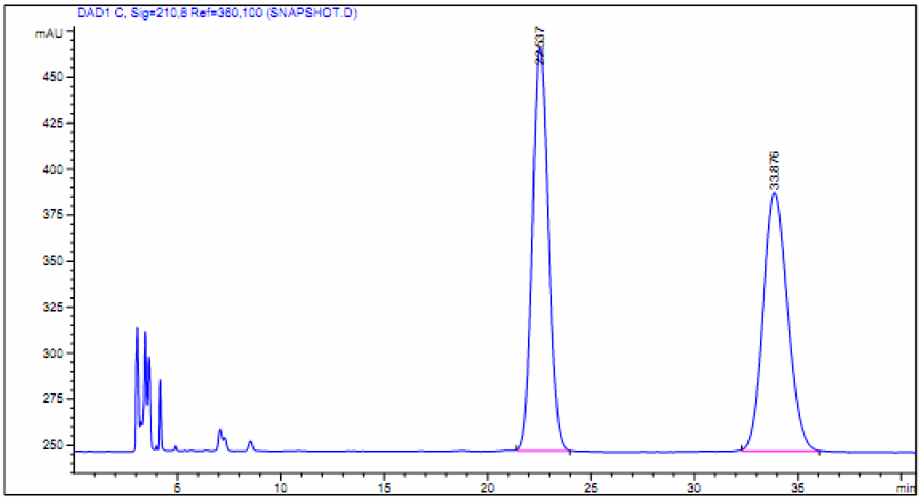


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.270	BB	0.5854	2.89746e4	769.23553	50.1016
2	29.751	BB	0.8803	2.88571e4	506.78421	49.8984
Totals :				5.78316e4	1276.01974	



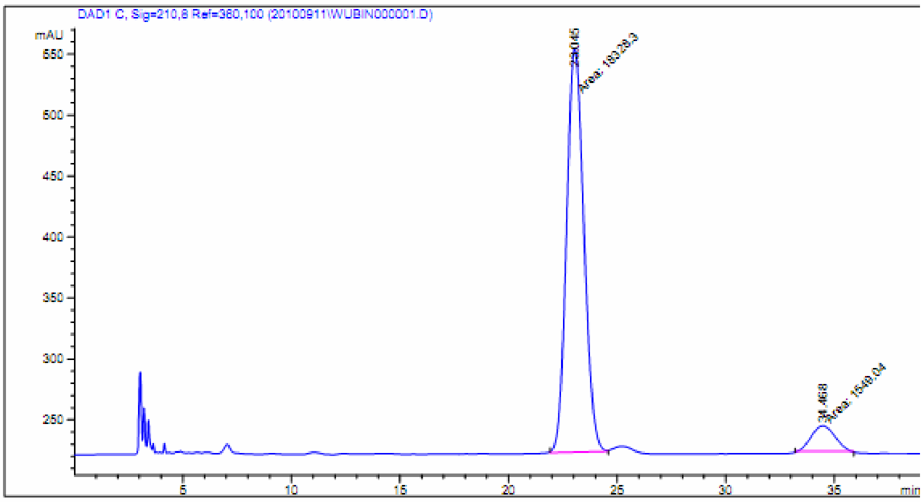
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.473	MM	0.5867	908.24615	25.80091	4.8131
2	29.946	MM	0.9379	1.79620e4	319.19394	95.1869
Totals :				1.88702e4	344.99485	

3g



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.537	BB	0.8407	1.18288e4	219.51790	50.6524
2	33.876	BB	1.2619	1.15241e4	140.36246	49.3476

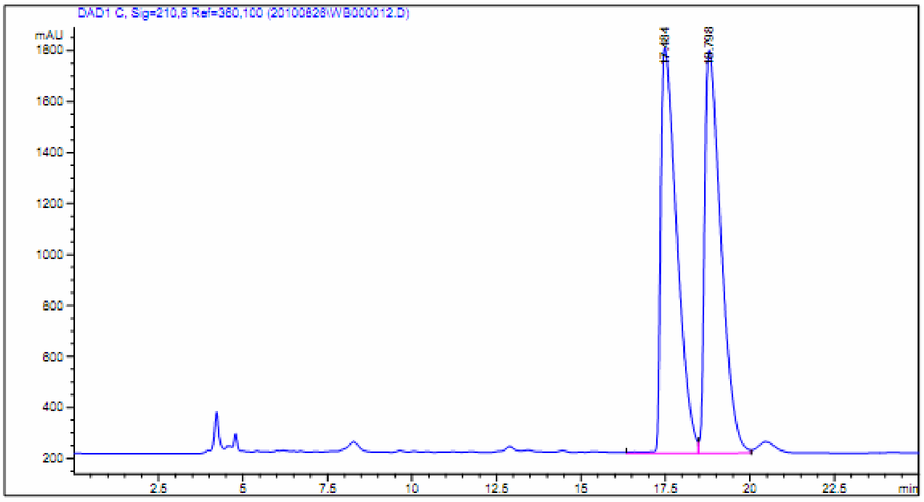
Totals : 2.33529e4 359.88036



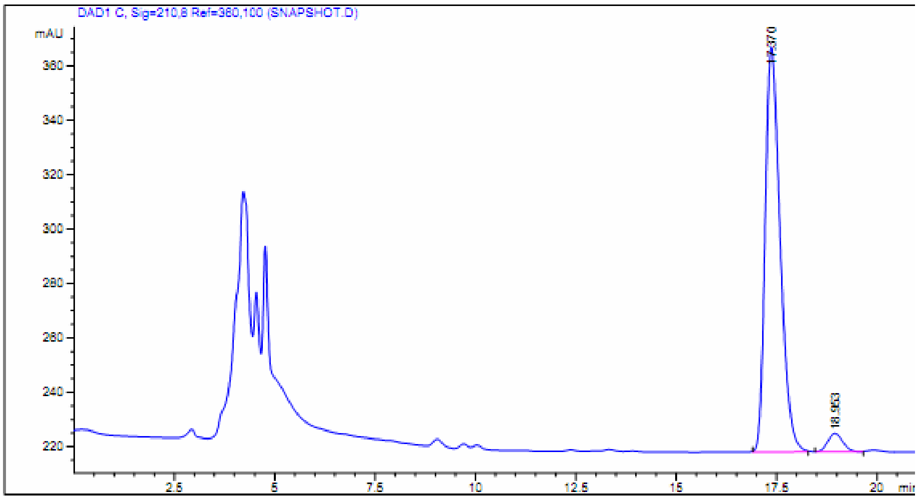
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.045	MM	0.9226	1.83283e4	331.09967	92.2070
2	34.468	MM	1.2434	1549.03772	20.76331	7.7930

Totals : 1.98774e4 351.86298

3h

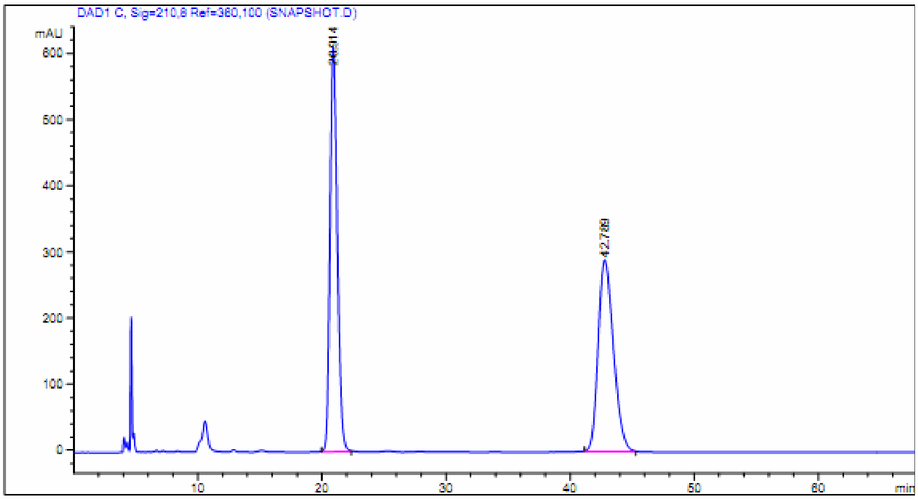


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.484	BV	0.5086	5.29886e4	1590.76990	49.8834
2	18.798	VV	0.5170	5.32362e4	1580.55835	50.1166
Totals :				1.06225e5	3171.32825	

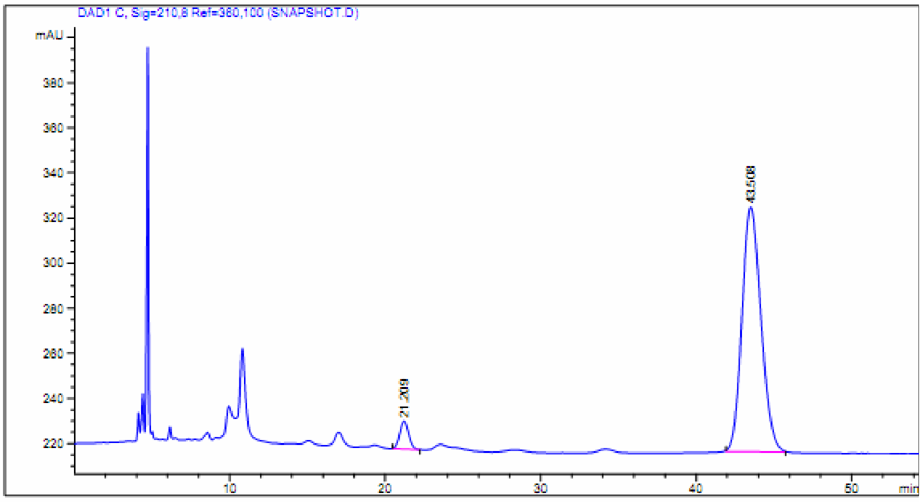


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.370	BB	0.4004	3859.76953	148.93201	95.7407
2	18.953	BB	0.3998	171.71487	6.68134	4.2593
Totals :				4031.48441	155.61335	

3i

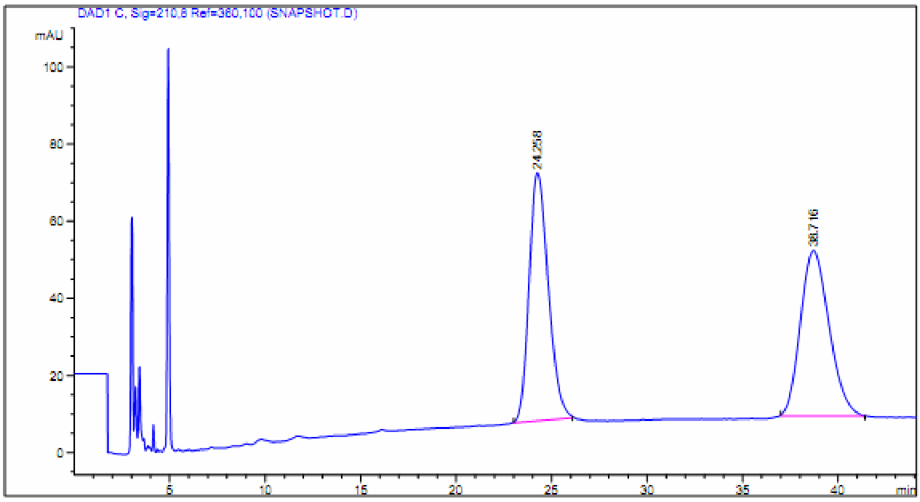


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.914	BB	0.6328	2.49936e4	611.53119	50.2303
2	42.789	BB	1.3299	2.47644e4	289.53589	49.7697
Totals :				4.97579e4	901.06708	

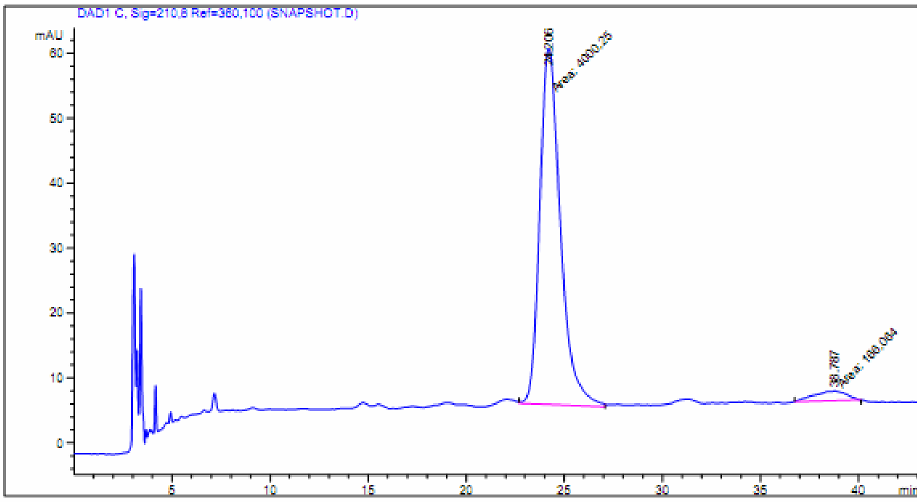


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.209	BB	0.6211	493.48630	12.37905	5.0789
2	43.508	BB	1.3167	9222.94336	108.38976	94.9211
Totals :				9716.42966	120.76881	

3j

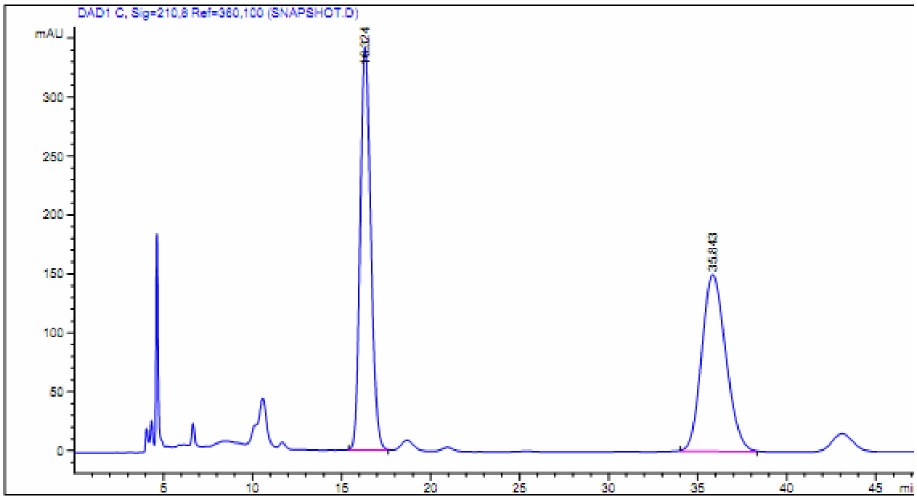


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.258	BB	1.0630	4491.58105	64.29762	50.0733
2	38.716	BB	1.5267	4478.43701	42.87309	49.9267
Totals :				8970.01807	107.17070	

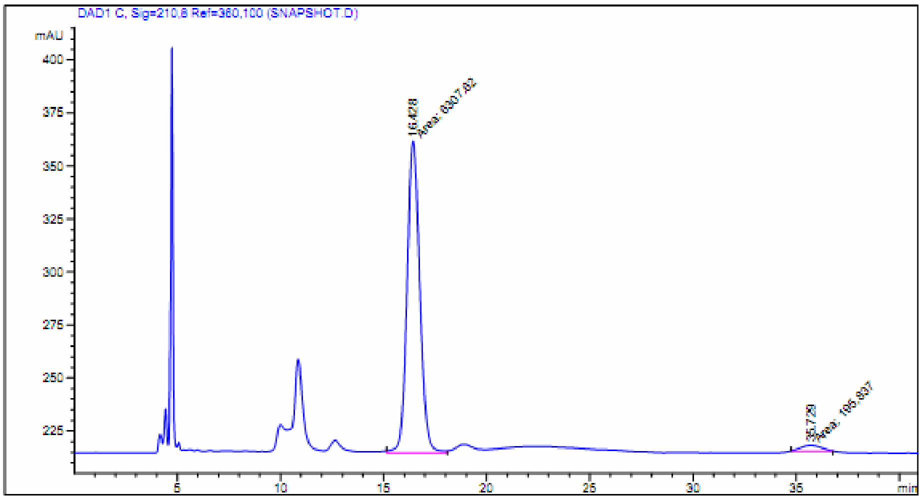


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.206	MM	1.2159	4000.24805	54.83383	96.0141
2	38.787	MM	1.8884	166.06404	1.46564	3.9859
Totals :				4166.31209	56.29947	

3k

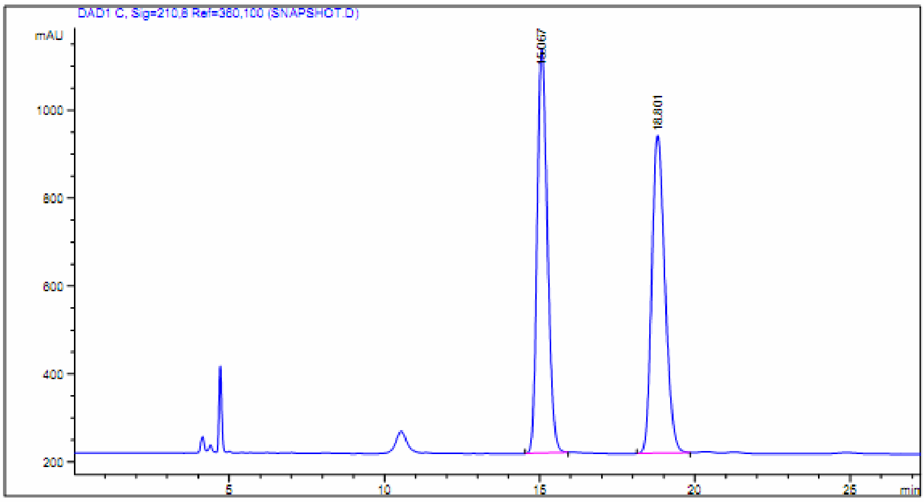


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.324	BB	0.6455	1.41691e4	341.87494	50.1529
2	35.843	BB	1.4632	1.40827e4	149.74373	49.8471
Totals :				2.82517e4	491.61867	



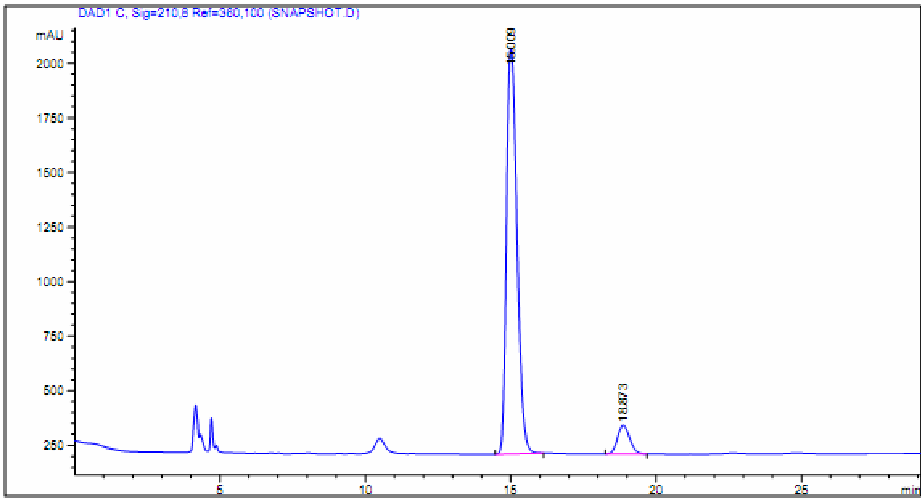
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.428	MM	0.7141	6307.61914	147.21034	96.9887
2	35.729	MM	1.1960	195.83699	2.72907	3.0113
Totals :				6503.45613	149.93941	

3l



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.067	BB	0.3563	2.11813e4	921.16528	49.8879
2	18.801	BB	0.4573	2.12765e4	722.96552	50.1121

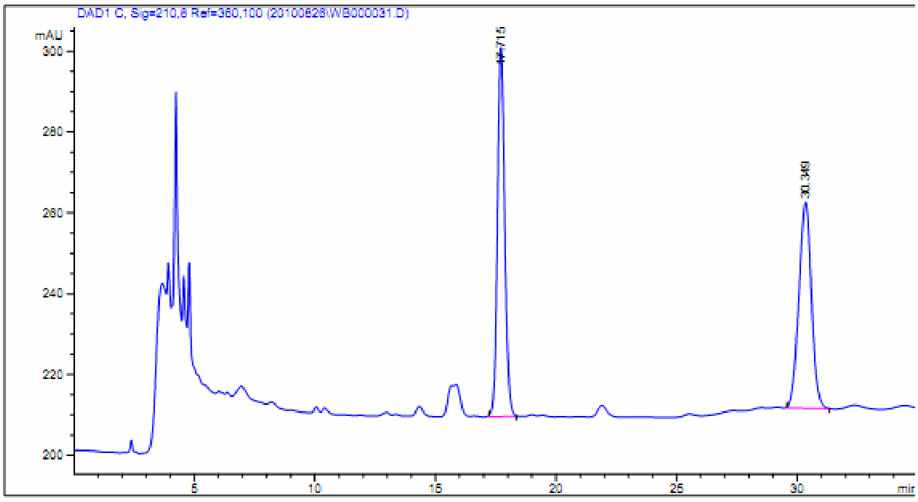
Totals : 4.24577e4 1644.13080



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.009	BB	0.3961	4.68355e4	1858.20227	92.4694
2	18.873	BB	0.4544	3814.20972	130.72366	7.5306

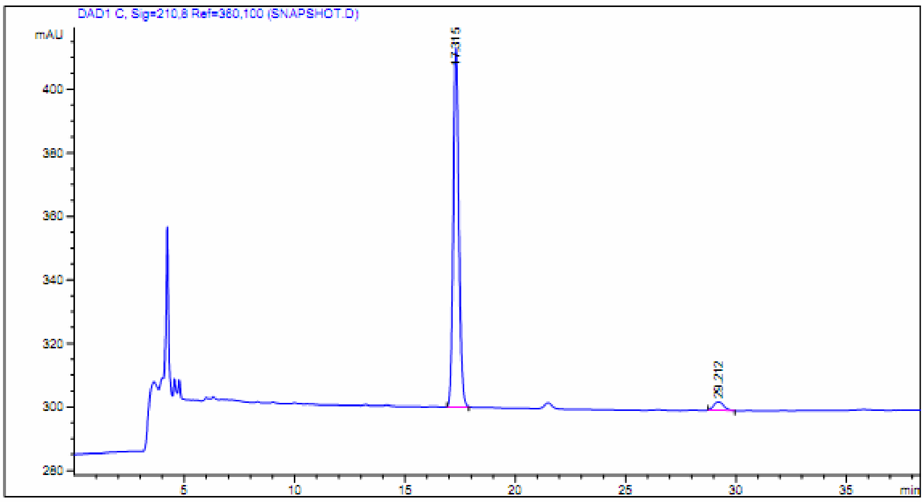
Totals : 5.06497e4 1988.92593

3m



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.715	BB	0.3190	1902.25916	91.31438	50.6276
2	30.349	BB	0.5669	1855.09753	50.93422	49.3724

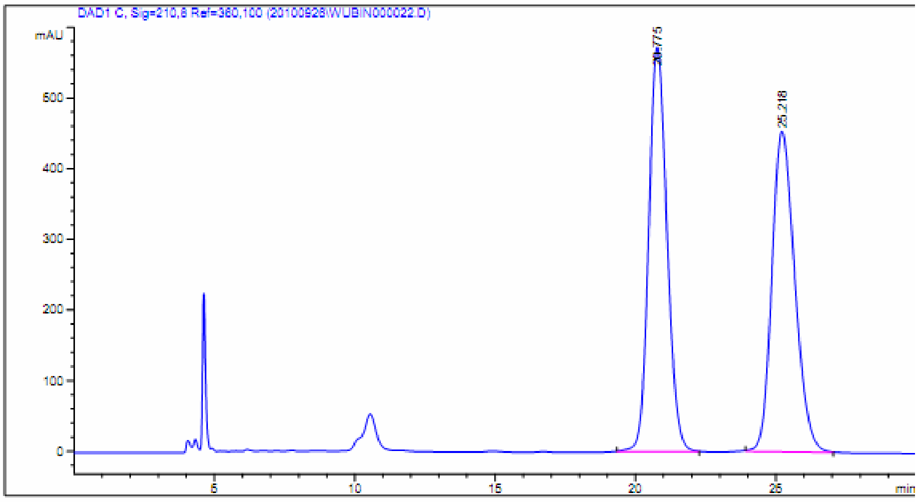
Totals : 3757.35669 142.24861



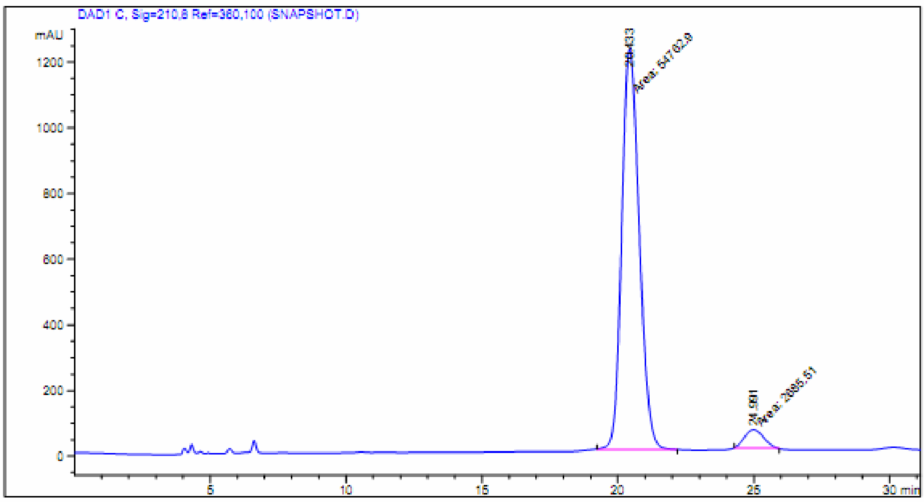
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.315	BB	0.2754	1991.28308	113.08757	95.8655
2	29.212	BB	0.4845	85.88069	2.64744	4.1345

Totals : 2077.16377 115.73501

3n

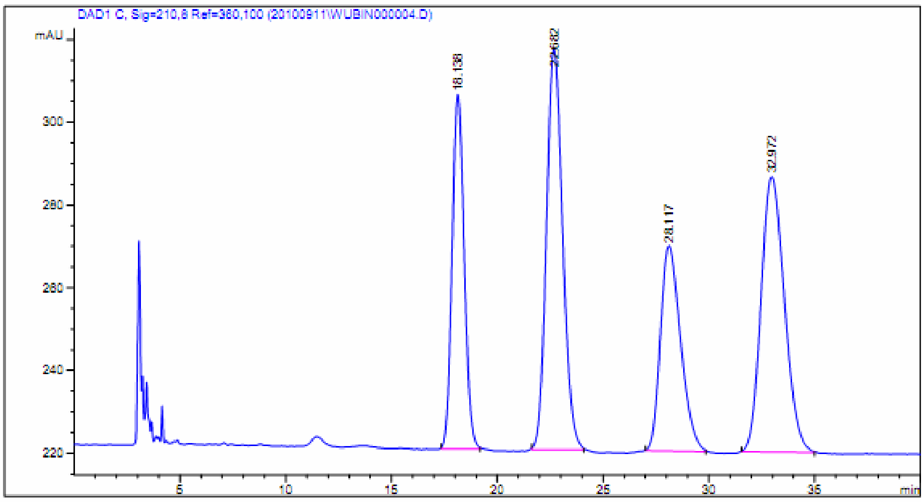


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.775	BB	0.7018	2.58878e4	572.25684	50.1240
2	25.218	BB	0.8810	2.57597e4	453.29068	49.8760
Totals :				5.16475e4	1025.54752	



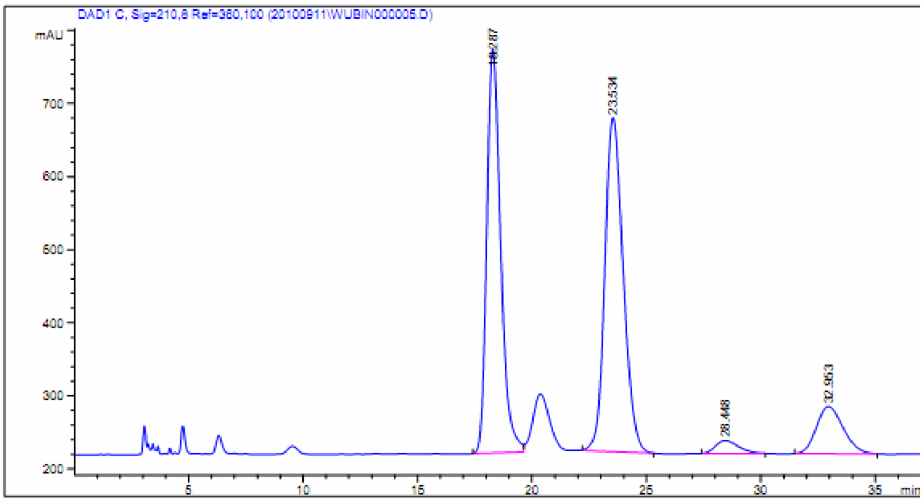
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.433	MM	0.7475	5.47629e4	1221.03650	95.3254
2	24.991	MM	0.8031	2685.50928	55.73405	4.6746
Totals :				5.74484e4	1276.77055	

3o



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.138	BB	0.6128	3383.35132	85.65783	19.9621
2	22.682	BB	0.8237	5170.38184	97.03319	30.5057
3	28.117	BB	1.0255	3297.96582	49.61621	19.4583
4	32.972	BB	1.1861	5097.21436	66.51390	30.0740

Totals : 1.69489e4 298.82113



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.287	BV	0.6477	2.32369e4	553.55780	42.1153
2	23.534	BB	0.8575	2.54345e4	456.87564	46.0983
3	28.448	BB	1.0393	1230.76978	17.61098	2.2307
4	32.953	BB	1.2589	5272.33496	64.68568	9.5558

Totals : 5.51744e4 1092.73010