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Rhodium Catalysed Enantioselective Synthesis of mono-(halo)-methyl-cyclopropanes.

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Table of Contents

General considerations

Solvents and commercially available reagents were purchased from standard chemical suppliers (Fisher, Sigma-Aldrich, Fluorochem, Alfa Aesar) and used as received without further purification. All glassware was stored in the oven prior to use under an inert atmosphere of gas. Tetrahydrofuran and diethylether were distilled from sodium and benzophenone. Dichloromethane was distilled from calcium hydride. Reactions were performed under an atmosphere of dry nitrogen or argon unless otherwise stated. Thin layer chromatography (TLC) were done using aluminum sheets coated with silica gel 60 F254. Flash column chromatography (FC) was carried out using silica gel 60 Å (0.04−0.06 mm). NMR spectra were recorded with Bruker DXC 300 instrument (^{1}H: 300 MHz, ^{19}F: 282 MHz and ^{13}C: 75 MHz), spectrometers in $CDCl_3$ or $(CD_3)_2CO$. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as an internal standard (δ: 0.0 ppm). Chemical shifts are given in ppm, calibrated to the residual solvent peak, and coupling constants "*J*" are expressed in hertz (multiplicity: s = singlet, bs = broad singlet, d = doublet, dd = double doublet, dt = double triplet, t = triplet, m = multiplet). High-resolution mass spectra (HRMS) were recorded on Waters LCT Premier, IR spectra were recorded on a PerkinElmer Spectrum 100, optical rotations were recorded on a PerkinElmer Polarimeter 341 at 20 °C in $CHCl_3$. Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC). Crystallographic data were collected using a Bruker D8 VENTURE diffractometer configured with a METALJET liquid-metal source and a PHOTON 100 CMOS-based.

Synthesis of starting materials

Rh_2((*S*)-BTPCP)$_4$ was synthesized according to the procedure described by H. M. L. Davies.[1]

α-Aryl-diazoacetates **1a-l** were synthesized according to the literature.[2]

Synthesis of α-CH_2F-stryenes

To a solution of selectfluor (3.2 g, 9 mmol, 0.9 equiv) in dry DMF (30 mL), α-Methylstyrene (1.2 g, 10 mmol, 1.0 equiv) was added dropwise at room temperature under argon. Then the solution was stirred at 75 °C for 4 h. Water (150 mL) was added after the mixture was cooled down to room temperature and extracted with *n*-pentane (3 x 50 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (*n*-pentane 100%) to deliver the desired α-CH_2F-stryene.[3]

Synthesis of α-CH_2Cl-stryene

To a solution of α-Methylstyrene (1.2 g, 10 mmol, 1.0 equiv) in 20 mL DCM/THF (4:1) was added $Yb(OTf)_3$ (310 mg, 0.5 mmol, 0.05 equiv) and TMSCl (54 mg, 0.5 mmol, 0.05 equiv). NCS (1.6 g, 12 mmol, 1.2 equiv) was added to the mixture and stirred at room temperature for 1 h. Water (50 mL) was added to the reaction mixture and extracted with *n*-pentane (2 x 50 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (*n*-pentane 100%) to deliver the desired α-CH_2Cl-stryene (0.9g, 63 % yield) as a colorless liquid.[4] Analytic data is the same as described in the literature.

Synthesis of α-CH_2Br-stryene

To a solution of α-Methylstyrene (1.2 g, 10 mmol, 1.0 equiv) in $CHCl_3$ (2 mL) was added NBS (2.0 g, 11.5 mmol, 1.15 equiv). The mixture was stirred under reflux for 4 h. Then the mixture was cooled to room temperature and *n*-pentane was added. The precipitate was filtered off and the liquid phase was concentrated. The crude product was purified by column chromatography on silica gel (*n*-pentane 100%) to give the α-CH_2Br-stryene (1.3 g, 65 % yield)

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[1] C. Qin, V. Boyarskikh, J. H. Hansen, K. I. Hardcastle, D. G. Musaev, H. M. L. Davies, *J. Am. Chem. Soc.* **2011**, *133*, 19198-19204.

[2] H. Saito, D. Morita, T. Uchiyama, M. Miyake, S. Miyairi, *Tetrahedron Lett.* **2012**, *53*, 6662-6664.

[3] H. Q. Luo, T. P. Loh, *Tetrahedron Letters,* **2009***, 50*, 1554–1556.

[4] M. Yamanaka, M. Arisawa, A. Nishida, M. Nakagawa, *Tetrahedron Letters*, **2002**, *43*, 2403–2406.

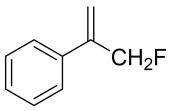
as a light yellow liquid.[5] Analytic data is the same as described in the literature.

General procedure synthesis of chiral monofluoromethylated cyclopropanes

A oven-dried 2 mL reaction vial equipped with a magnetic stirring bar was charged with Rh_2[(*S*)-BTPCP)]$_4$ (4.4 mg, 1 mol%), filled with argon and sealed. DCM (0.15 mL) was added followed by the olefin **2a** (0.25 mmol, 1 equiv.) and the reaction was cooled to -20 °C. A solution of diazo compound **1** (0.38 mmol, 1.3 equiv.) in DCM (0.2 mL) was added over 30 min at -20 °C. The reaction was stirred at -20 °C until completion of the reaction (monitored by ^{19}F NMR). At this point, pyridine (20 µL) was added to quench the reaction and the mixture was allowed to warm to room temperature. The crude material was directly purified by flash chromatography on silica gel (PE/Et_2O = 100:0 to 90:10) affording the desired monofluoromethylated cyclopropane.

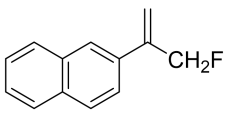
Note that all racemic cyclopropanes were obtained using general procedure with $Rh_2(OPiv)_4$ as a catalyst.

Analytical data



2a was obtained as a colorless oil after silica gel column chromatography (pentane 100%). Rf = 0.72 (PE).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.32 – 7.18 (m, 3H), 5.54 (s, 1H), 5.35 (d, *J* = 1.7 Hz, 1H), 5.17 (d, *J* = 47.0 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0 (d, *J* = 14.6 Hz), 137.3, 128.6, 128.2, 126.0, 115.4 (d, *J* = 10.6 Hz), 84.4 (d, *J* = 169.1 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -212.7 (td, *J* = 47.1, 3.0 Hz).
HRMS (EI+) calcd for C_9H_9F ([M]$^+$) 136.0688, found: 136.0696. (5.28 ppm).
IR (Neat) 2960, 1633, 1575, 1497, 1020, 1008, 986, 910, 777, 705, 608, 515 cm^{-1}.



2b was obtained as a white solid after silica gel column chromatography (pentane 100%). Rf = 0.57 (PE). **Mp**：42-43 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 4H), 7.64 (d, *J* = 1.4 Hz, 1H), 7.51 – 7.48 (m, 2H), 5.78 (s, 1H), 5.54 (d, *J* = 2.1 Hz, 1H), 5.42 (d, *J* = 48.0 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8 (d, *J* = 14.6 Hz), 134.5 (d, *J* = 2.1 Hz), 133.3, 133.1, 128.3, 128.2, 127.6, 126.4, 126.3, 124.9, 123.9, 115.9 (d, *J* = 10.6 Hz), 84.5 (d, *J* = 169.1 Hz).

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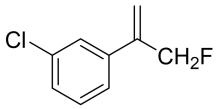
[5] X. Dong, Y. Han, F. C. Yan, Q. Liu, P. Wang, K. X. Chen, Y. Y. Li, Z. D. Zhao, Y. H. Dong, H. Liu, *Org. Lett*. **2016**, *18*, 3774-3777.

^{19}F NMR (282 MHz, $CDCl_3$) δ -212.4 (td, *J* = 47.2, 2.3 Hz).

HRMS (EI+) calcd for $C_{13}H_{11}F$ ([M]$^+$) 186.0845, found: 186.0853. (4.35 ppm).

IR (Neat) 1597, 1506, 1273, 1086, 1026, 986, 957, 916, 894, 857, 816, 716, 680, 559, 472 cm^{-1}.



2c was obtained as a colorless oil after silica gel column chromatography (pentane 100%). Rf = 0.70 (PE).

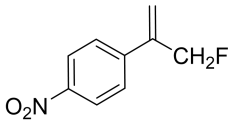
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.35 – 7.29 (m, 3H), 5.63 (s, 1H), 5.47 (m, 1H), 5.20 (dd, *J* = 47.1, 0.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1 (d, *J* = 14.9 Hz), 139.3 (d, *J* = 1.9 Hz), 134.7, 130.0, 128.4, 126.4, 124.3, 117.0 (d, *J* = 10.4 Hz), 84.3 (d, *J* = 169.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -213.0 (td, *J* = 47.1, 3.3 Hz).

HRMS (EI+) calcd for C_9H_8FCl ([M]$^+$) 170.0299, found: 170.0289. (-5.89 ppm).

IR (Neat) 1595, 1563, 1478, 1417, 1129, 1097, 1082, 1030, 1061, 1009, 988, 946, 924, 882, 811, 788, 725, 689, 676, 614, 516, 447, 414, 388 cm^{-1}.



2d was obtained as a pale yellow solid after silica gel column chromatography (pentane 100%). Rf = 0.51 (PE). **Mp：** 44-45 °C.

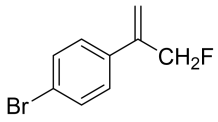
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 5.71 (s, 1H), 5.56 (d, *J* = 3.4 Hz, 1H), 5.19 (d, *J* = 47.1 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 143.7, 141.4 (d, *J* = 15.1 Hz), 126.8, 123.9, 119.6 (d, *J* = 10.1 Hz), 83.9 (d, *J* = 169.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -212.1 (td, *J* = 47.0, 3.5 Hz).

HRMS (EI+) calcd for $C_9H_8FNO_2$ ([M]$^+$) 181.0539, found: 181.0523. (-8.92 ppm).

IR (Neat) 1597, 1510, 1423, 1340, 1192, 1104, 1029, 1011, 984, 933, 855, 769, 752, 715, 681, 644, 530 cm^{-1}.



2e was obtained as a colorless oil after silica gel column chromatography (pentane 100%). Rf = 0.73 (PE).

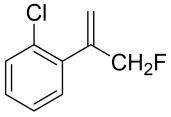
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.61 (s, 1H), 5.45 (d, *J* = 2.7 Hz, 1H), 5.20 (d, *J* = 47.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2 (d, *J* = 14.8 Hz), 136.3, 131.8, 127.7, 122.4, 116.4 (d, *J* = 10.4 Hz), 84.3 (d, *J* = 169.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -212.9 (td, *J* = 47.1, 3.3 Hz).

HRMS (EI+) calcd for C_9H_8FBr ([M]$^+$) 213.9793, found: 213.9785. (-4.06 ppm).

IR (Neat) 2956, 2914, 1491, 1470, 1395, 1380, 1117, 1073, 1030, 1008, 990, 920, 829, 779, 756, 735, 621, 530, 467, 433, 394 cm^{-1}.



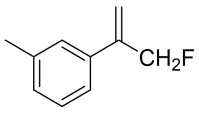
2f was obtained as a colorless oil after silica gel column chromatography (pentane 100%). Rf = 0.70 (PE).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 1H), 7.28 – 7.23 (m, 3H), 5.59 (dd, *J* = 2.4, 1.3 Hz, 1H), 5.27 (s, 1H), 5.10 (d, *J* = 46.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6 (d, *J* = 15.9 Hz), 137.6 (d, *J* = 3.2 Hz), 132.5, 131.2, 129.8, 129.4, 127.0, 118.3 (d, *J* = 9.3 Hz), 84.2 (d, *J* = 171.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -214.5 (tdd, *J* = 46.9, 2.4, 1.2 Hz).

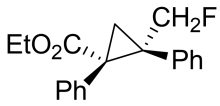
HRMS (EI+) calcd for C_9H_8FCl ($[M]^+$) 170.0299, found: 170.0308. (5.45 ppm).
IR (Neat) 1474, 1432, 1127, 1048, 1024, 991, 918, 789, 759, 737, 683, 670, 646, 613, 550, 535, 460, 430, 398 cm^{-1}.



2g was obtained as a colorless oil after silica gel column chromatography (pentane 100%). Rf = 0.72 (PE).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 4H), 5.66 (s, 1H), 5.48 (d, *J* = 1.9 Hz, 1H), 5.30 (d, *J* = 47.2 Hz, 2H), 2.45 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (d, *J* = 14.6 Hz), 138.3, 137.4 (d, *J* = 2.1 Hz), 129.1, 128.6, 126.8, 123.2, 115.3 (d, *J* = 10.7 Hz), 84.6 (d, *J* = 169.1 Hz), 21.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -212.6 (td, *J* = 47.1, 2.9 Hz).
HRMS (EI+) calcd for $C_{10}H_{11}F$ ($[M]^+$) 150.0845, found: 150.0857 (8.17 ppm).
IR (Neat) 2924, 1134, 1030, 987, 949, 905, 882, 791, 726, 684, 644, 618, 512, 444 cm^{-1}.



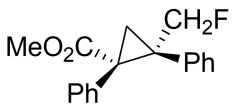
3a (69.7 mg, 93%) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.27 (PE/Et_2O = 10:1).

Enantiomeric Excess 96%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane : *i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 5.3 min, t_R = 5.6 min. **$[\alpha]^{20}_D$** = +42.6 (c = 5.3, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 – 7.07 (m, 5H), 7.04 – 6.93 (m, 5H), 4.93 – 4.69 (m, 2H), 4.21 – 3.96 (m, 2H), 2.14 – 2.07 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 137.3, 135.3, 131.5, 128.9 (d, *J* = 1.5 Hz), 128.0, 127.4, 127.03, 127.02, 87.5 (d, *J* = 171.6 Hz), 61.8, 40.9 (d, *J* = 5.3 Hz), 38.8 (d, *J* = 21.1 Hz), 20.7 (d, *J* = 7.5 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.0 (td, *J* = 47.9, 5.1 Hz).

HRMS (AP+) calcd for $C_{19}H_{20}FO_2$ ([M+H]$^+$) 299.1447, found: 299.1440. (-2.3 ppm).
IR (Neat) 2983, 1714, 1498, 1465, 1450, 1389, 1367, 1291, 1257, 1202, 1129, 1095, 1061, 1018, 989, 860, 785, 763, 742, 695, 648, 602, 556, 546, 507 cm^{-1}.



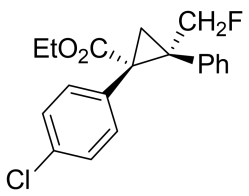
3b (65.2 mg, 92%) was obtained as a white solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.28 (PE/Et_2O =10:1). **Mp**：49-50 °C.
Enantiomeric Excess 96%. The enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-heptane/*i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 5.4 min, t_R = 5.9 min. **[α]$^{20}_D$** = +45.4 (c = 1.1, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 10H), 5.05 (d, *J* = 47.9 Hz, 2H), 3.84 (s, 3H), 2.39 – 2,32(m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 137.3, 135.2, 131.6, 128.8 (d, *J* = 1.7 Hz), 128.0, 127.5, 127.12, 127.08, 87.5 (d, *J* = 171.4 Hz), 53.0, 40.6 (d, *J* = 5.4 Hz), 39.0 (d, *J* = 21.0 Hz), 21.0 (d, *J* = 7.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.1 (td, *J* = 47.8, 5.5 Hz).

HRMS (AP+) calcd for $C_{18}H_{18}FO_2$ ([M+H]$^+$) 285.1291, found: 285.1288. (-1.1 ppm).
IR (Neat) 2952, 1718, 1497, 1462, 1448, 1436, 1255, 1209, 1130, 1061, 1030, 987, 947, 767, 739, 709, 696, 647, 598, 558, 537, 499 cm^{-1}.



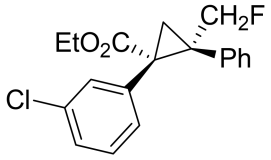
3c (88.7 mg, 98%) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.26 (PE/Et_2O = 10:1).
Enantiomeric Excess 89%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.7 min, t_R = 5.1 min. **[α]$^{20}_D$** = +39.1 (c = 6.4, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.02 (m, 9H), 4.90 (d, *J* = 47.8 Hz, 2H), 4.30 – 4.06 (m, 2H), 2.24 (dd, *J* = 5.9, 1.1 Hz, 1H), 2.15 (t, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 137.1, 134.0, 132.93, 132.90, 128.8 (d, *J* = 1.6 Hz), 128.2, 127.6, 127.3, 87.3 (d, *J* = 171.7 Hz), 61.9, 40.2 (d, *J* = 5.4 Hz), 39.0 (d, *J* = 20.9 Hz), 20.8 (d, *J* = 7.6 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -209.8 (td, *J* = 47.8, 6.1 Hz).

HRMS (AP+) calcd for $C_{19}H_{19}ClFO_2$ ([M+H]$^+$) 333.1058, found: 333.1059. (0.3 ppm).

IR (Neat) 2978, 1715, 1494, 1465, 1450, 1389, 1367, 1302, 1274, 1255, 1202, 1130, 1092, 1065, 1046, 1014, 991, 929, 860, 831, 765, 722, 563, 544, 513, 491, 470, 403 cm^{-1}.



3d (76.2 mg, 92%) was obtained as a white solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.28 (PE/Et_2O =10:1). **Mp：** 65-67 °C.

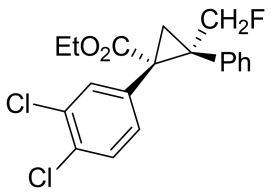
Enantiomeric Excess 82%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.8 min, t_R = 5.3 min. **$[\alpha]^{20}_D$** = +35.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.06 (m, 7H), 7.03 – 6.94 (m, 2H), 4.90 (d, *J* = 47.8 Hz, 2H), 4.31 – 4.07 (m, 2H), 2.25 – 2.15 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 137.5, 137.0, 133.2, 131.6, 129.9, 128.8 (d, *J* = 1.6 Hz), 128.6, 128.2, 127.4, 127.3 (d, *J* = 6.4 Hz), 87.3 (d, *J* = 171.8 Hz), 62.0, 40.4 (d, *J* = 5.4 Hz), 39.1 (d, *J* = 20.9 Hz), 20.8 (d, *J* = 7.6 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.0 (td, *J* = 47.9, 10.8 Hz).

HRMS (AP+) calcd for $C_{19}H_{19}ClFO_2$ ($[M+H]^+$) 333.1058, found: 333.1058. (0.0 ppm).
IR (Neat) 3109, 2989, 2952, 1705, 1453, 1390, 1367, 1272, 1257, 1207, 1132, 1100, 1076, 1050, 1018, 1002, 981, 962, 910, 884, 865, 781, 694, 681, 571, 514, 445 cm^{-1}.



3e (84.7 mg, 92%) was obtained as a pale yellow oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.27 (PE/Et_2O =10:1).

Enantiomeric Excess: 70%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.7 min, t_R = 4.9 min. **$[\alpha]^{20}_D$** = +32.7 (c = 6.7, $CHCl_3$).

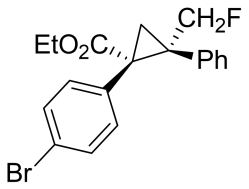
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 2.0 Hz, 1H), 7.19 – 7.09 (m, 6H), 7.03 (dd, *J* = 8.4, 2.1 Hz, 1H), 5.00 – 4.77 (m, 2H), 4.30 – 4.07 (m, 2H), 2.26 (dd, *J* = 6.0, 1.3 Hz, 1H), 2.14 (t, *J* = 6.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 136.8, 135.9, 133.4, 131.4, 131.2, 129.3, 128.72, 128.70, 128.3, 127.6, 87.1 (d, *J* = 172.0 Hz), 62.0, 39.8 (d, *J* = 5.4 Hz), 39.4 (d, *J* = 20.8 Hz), 20.9 (d, *J* = 7.7 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -209.8 (td, *J* = 47.7, 6.1 Hz).

HRMS (AP+) calcd for $C_{19}H_{18}Cl_2FO2$ ($[M+H]^+$) 367.0668, found: 367.0667. (-0.3 ppm).

IR (Neat): 2983, 1717, 1470, 1450, 1379, 1367 1255, 1203, 1132, 1095, 1068, 1055, 1030, 993, 910, 891, 861, 830, 811, 794, 766, 725, 674, 612, 519, 473, 445, 403 cm^{-1}.



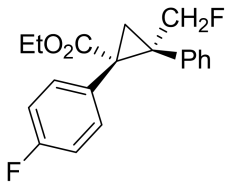
3f (89.0 mg, 94%) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.28 (PE/Et_2O = 10:1).

Enantiomeric Excess 92%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.8 min, t_R = 5.3 min. **$[\alpha]^{20}_D$** = +33.5 (c = 6.5, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.06 (m, 9H), 4.89 (d, *J* = 47.8 Hz, 2H), 4.30 – 4.06 (m, 2H), 2.24 (dd, *J* = 5.9, 1.2 Hz, 1H), 2.15 (t, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 137.0, 134.5, 133.3, 130.6, 128.8 (d, *J* = 1.7 Hz), 128.2, 127.3, 121.2, 87.3 (d, *J* = 171.8 Hz), 61.9, 40.2 (d, *J* = 5.4 Hz), 39.0 (d, *J* = 20.9 Hz), 20.8 (d, *J* = 7.6 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -209.8 (td, *J* = 47.8, 6.2 Hz).

HRMS (AP+) calcd for $C_{19}H_{19}BrFO_2$ ($[M+H]^+$) 377.0552, found: 377.0551. (-0.3 ppm).
IR (Neat) 1710, 1488, 1465, 1390, 1302, 1274, 1254, 1202, 1129, 1105, 1093, 1071, 1064, 1031, 1009, 976, 856, 828, 784, 760, 717, 697, 671, 603, 542, 515, 433 cm^{-1}.



3g (70.6 mg, 89%) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.28 (PE/Et_2O = 10:1).

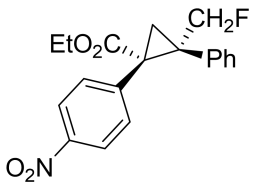
Enantiomeric Excess: 84%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.6 min, t_R = 4.9 min. **$[\alpha]^{20}_D$** = +39.2 (c = 5.4, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.06 (m, 7H), 6.79 – 6.71 (m, 2H), 4.91 (d, *J* = 47.9 Hz, 2H), 4.30 – 4.07 (m, 2H), 2.24 (dd, *J* = 5.9, 1.2 Hz, 1H), 2.16 (t, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 161.7 (d, *J* = 246.1 Hz), 137.2, 133.2 (d, *J* = 8.2 Hz), 131.2 (d, *J* = 3.3 Hz), 128.8 (d, *J* = 1.7 Hz), 128.1, 127.2, 114.4 (d, *J* = 21.4 Hz), 87.4 (d, *J* = 171.6 Hz), 61.9, 40.1 (d, *J* = 5.4 Hz), 39.0 (d, *J* = 21.0 Hz), 20.9 (d, *J* = 7.6 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -115.7 (ddd, *J* = 10.8, 7.0, 4.3 Hz), -209.7 (td, *J* = 47.8, 6.1 Hz).

HRMS (AP+) calcd for $C_{19}H_{19}F_2O_2$ ($[M+H]^+$) 317.1353, found: 317.1350. (-0.9 ppm).

IR (Neat) 1715, 1604, 1511, 1465, 1450, 1389, 1368, 1289, 1257, 1222, 1202, 1160, 1129, 1098, 1083, 1065, 1046, 1016, 767, 747, 698, 611, 582, 545, 414 cm^{-1}.



3h (69.5 mg, 81%) was obtained as a pale yellow oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.16 (PE/Et_2O =10:1).

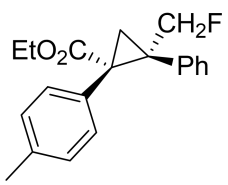
Enantiomeric Excess 55%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 7.3 min, t_R = 8.6 min. **$[\alpha]^{20}_D$** = +19.5 (c = 5.6, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 1H), 7.91 – 7.88 (m, 1H), 7.38 – 7.37 (m, 1H), 7.35 – 7.33 (m, 1H), 7.18 – 7.03 (m, 5H), 5.04 – 4.81 (m, 2H), 4.31 – 4.08 (m, 2H), 2.34 (dd, *J* = 6.1, 1.4 Hz, 1H), 2.26 (t, *J* = 6.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 146.8, 143.1, 136.6, 132.5, 128.6 (d, *J* = 1.8 Hz), 128.4, 127.7, 122.6, 87.0 (d, *J* = 172.1 Hz), 62.2, 40.3 (d, *J* = 5.4 Hz), 39.7 (d, *J* = 20.7 Hz), 21.0 (d, *J* = 7.8 Hz), 14.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ -209.7 (td, *J* = 47.7, 6.2 Hz).

HRMS (AP+): calcd for $C_{19}H_{19}FNO_4$ ($[M+H]^+$) 344.1298, found: 344.1299. (0.3 ppm).
IR (Neat): 1717, 1601, 1518, 1498, 1465, 1450, 1367, 1347, 1313, 1298, 1258, 1200, 1132, 1109, 1066, 1046, 1014, 992, 856, 766, 745, 501, 481, 465, 403 cm^{-1}.



3i (78.8 mg, 98%) was obtained as a white solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.29 (PE/Et_2O =10:1). **Mp**：62-63 °C.

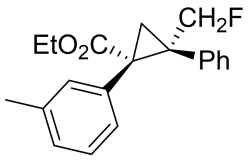
Enantiomeric Excess 96%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.4 min, t_R = 4.7 min. **$[\alpha]^{20}_D$** = +38.8 (c = 1.1, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.4 Hz, 2H), 7.16 – 7.05 (m, 5H), 6.88 (d, *J* = 7.9 Hz, 2H), 5.01 – 4.77 (m, 2H), 4.32 – 3.06 (m, 2H), 2.42 – 2.01 (m, 5H), 1.26 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 137.5, 136.6, 132.2, 131.3, 129.0 (d, *J* = 1.5 Hz), 128.2, 128.0, 127.0, 87.5 (d, *J* = 171.6 Hz), 61.7, 40.6 (d, *J* = 5.3 Hz), 38.7 (d, *J* = 21.1 Hz), 21.1, 20.6 (d, *J* = 7.4 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.2 (td, *J* = 47.9, 5.5 Hz).

HRMS (AP+) calcd for $C_{20}H_{22}FO_2$ ($[M+H]^+$) 313.1604, found: 313.1607. (1.0 ppm).

IR (Neat) 1715, 1516, 1449, 1367, 1287, 1258, 1201, 1131, 1112, 1066, 1047, 1020, 992, 861, 803, 766, 742, 699, 611, 583, 543, 514 cm^{-1}.



3j (66.3 mg, 85%) was obtained as a colorless viscous liquid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.29 (PE/Et_2O =10:1).

Enantiomeric Excess 90%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 99.5:0.5, 220 nm, 1 mL/min), t_R = 6.3 min, t_R = 6.9 min. **$[\alpha]^{20}_D$** = +35.5 (c = 1.3, $CHCl_3$).

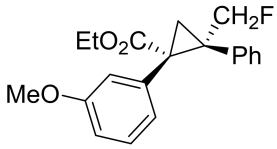
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.1 Hz, 2H), 7.16 – 7.07 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 5.03 – 4.79 (m, 2H), 4.32 – 4.08 (m, 2H), 2.22 – 2.16 (m, 5H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 137.3, 136.8, 135.1, 132.2, 128.9 (d, *J* = 1.5 Hz), 128.5, 127.8, 127.7, 127.2, 126.9, 87.5 (d, *J* = 171.6 Hz), 61.6, 40.8 (d, *J* = 5.3 Hz), 38.6 (d, *J* = 21.1 Hz), 21.2, 20.5 (d, *J* = 7.4 Hz), 14.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -209.6 (td, *J* = 47.9, 5.2 Hz).

HRMS (AP+) calcd for $C_{20}H_{22}FO_2$ ($[M+H]^+$) 313.1604, found: 313.1604. (0.0 ppm).

IR (Neat) 1741, 1450, 1367, 1286, 1258, 1219, 1181, 1129, 1096, 1056, 1020, 991, 862, 786, 765, 737, 698, 559, 444 cm^{-1}.



3k (60.4 mg, 74%) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.16 (PE/Et_2O =10:1).

Enantiomeric Excess: 92%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 6.7 min, t_R = 7.0 min. **$[\alpha]^{20}_D$** = +19.0 (c = 4.2, $CHCl_3$).

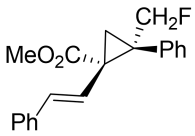
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 718 (m, 2H), 7.15 – 7.07 (m, 3H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.75 – 6.73 (m, 1H), 6.59 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.01 – 4.78 (m, 2H), 4.31 – 4.07 (m, 2H), 3.63 (s, 3H), 2.21 – 2.14 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 158.7, 137.4, 136.8, 128.9 (d, *J* = 1.5 Hz), 128.3, 128.0, 127.1, 123.8, 117.3, 113.0, 87.5 (d, *J* = 171.8 Hz), 61.8, 55.2, 40.9 (d, *J* = 5.3 Hz), 38.7 (d, *J* = 21.0 Hz), 20.8 (d, *J* = 7.4 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.1 (td, *J* = 47.9, 5.3 Hz).

HRMS (AP+) calcd for $C_{20}H_{22}FO_3$ ($[M+H]^+$) 329.1553, found: 329.1554. (0.3 ppm).

IR (Neat) 1714, 1601, 1582, 1491, 1464, 1451, 1434, 1367, 1325, 1289, 1259, 1229, 1195, 1175, 1128, 1094, 1055, 1037, 991 767, 738, 696, 651, 593, 572, 549, 463 cm^{-1}.



3l (50.1 mg, 65%) was obtained as a white solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (13:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.29 (PE/Et_2O =10:1). **Mp：** 115-116 °C.

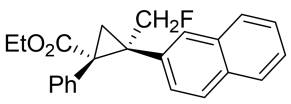
Enantiomeric Excess: 78%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.9 min, t_R = 5.3 min. **$[\alpha]^{20}_D$** = -153.2 (c = 4.6, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.26 – 7.16 (m, 4H), 7.06 – 7.03 (m, 2H), 6.16 (s, 2H), 4.75 (d, *J* = 47.8 Hz, 2H), 3.81 (s, 3H), 2.10 (d, *J* = 5.5 Hz, 1H), 1.88 (t, *J* = 5.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 137.2, 137.0, 131.6, 130.2, 128.5, 128.4, 127.7 (d, *J* = 11.1 Hz), 127.5, 126.3, 126.1, 86.8 (d, *J* = 171.8 Hz), 52.8, 40.8 (d, *J* = 21.2 Hz), 36.4 (d, *J* = 5.1 Hz), 20.8 (d, *J* = 7.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -213.9 (td, *J* = 47.8, 5.8 Hz).

HRMS (AP+) calcd for $C_{20}H_{20}FO_2$ ($[M+H]^+$) 311.1447, found: 311.1455. (2.6 ppm).
IR (Neat) 1722, 1496, 1448, 1435, 1286, 1251, 1234, 1209, 1194, 1166, 1126, 1068, 1028, 993, 964, 930, 904, 767, 745, 695, 577, 552, 538, 503, 476, 438, 405 cm^{-1}.



3m (108.7 mg, 99%) was obtained as a white solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.24 (PE/Et_2O =10:1). **Mp：** 112-114 °C.

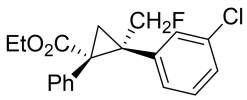
Enantiomeric Excess 64%. The enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 5.3 min, t_R = 5.8 min. **$[\alpha]^{20}_D$** = +23.8 (c = 7.9, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.64 – 7.59 (m, 2H), 7.44 – 7.36 (m, 3H), 7.29 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.05 – 6.94 (m, 3H), 4.98 (dq, *J* = 48.0, 9.9 Hz, 2H), 4.35 – 4.10 (m, 2H), 2.36 – 2.30 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 135.2, 135.1, 133.1, 132.4, 131.4, 127.98, 127.97, 127.9, 127.5, 127.14, 127.12, 127.10, 126.0, 125.9, 87.6 (d, *J* = 171.8 Hz), 61.8, 41.1 (d, *J* = 5.2 Hz), 39.0 (d, *J* = 21.2 Hz), 20.9 (d, *J* = 7.4 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.1 (td, *J* = 47.9, 4.8 Hz).
HRMS (AP+) calcd for $C_{23}H_{22}FO_2$ ($[M+H]^+$) 349.1604, found: 349.1609. (1.4 ppm).

IR (Neat) 1714, 1464, 1447, 1365, 1256, 1232, 1204, 1169, 1139, 1118, 1060, 1004, 986, 971, 918, 897, 862, 823, 754, 742, 701, 672, 663, 636, 554, 537, 508, 479, 414 cm^{-1}.

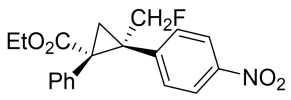


3n (70.5 mg, 85%) was obtained as a white solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.20 (PE/Et_2O =10:1). **Mp：** 65-67 °C.

Enantiomeric Excess 83%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.6 min, t_R = 4.9 min. **$[\alpha]^{20}_D$** = +35.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 3H), 7.13 – 7.07 (m, 3H), 7.04 – 7.02 (m, 3H), 4.99 – 4.75 (m, 2H), 4.28 – 4.06 (m, 2H), 2.22 (dd, *J* = 6.0, 1.1 Hz, 1H), 2.15 (t, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 137.5, 137.0, 133.2, 131.6, 129.9, 128.8 (d, *J* = 1.6 Hz), 128.6, 128.2, 127.4, 127.3 (d, *J* = 6.4 Hz), 87.3 (d, *J* = 171.8 Hz), 62.0, 40.4 (d, *J* = 5.4 Hz), 39.1 (d, *J* = 20.9 Hz), 20.8 (d, *J* = 7.6 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.2 (td, *J* = 47.8, 6.0 Hz).
HRMS (AP+) calcd for $C_{19}H_{19}ClFO_2$ ($[M+H]^+$) 333.1058, found: 333.1058. (0.0 ppm).
IR (Neat) 1705, 1453, 1390, 1367, 1272, 1257, 1207, 1132, 1100, 1076, 1050, 1018, 1002, 981, 962, 910, 884, 865, 781, 766, 717, 694, 681, 571, 554, 514, 445 cm^{-1}.

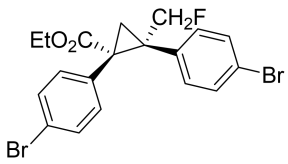


3o (50.6 mg, 59%) was obtained as a pale yellow oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.11 (PE/Et_2O =10:1). **Enantiomeric Excess** 93%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 8.5 min, t_R =9.0 min. **$[\alpha]^{20}_D$** = +19.5 (c = 5.6, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.18 – 7.14 (m, 2H), 7.10 – 7.05 (m, 3H), 4.98 (dq, *J* = 48.0, 10.2 Hz, 2H), 4.31 – 407 (m, 2H), 2.31 (dd, *J* = 6.3, 0.8 Hz, 1H), 2.25 (t, *J* = 6.1 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 146.8, 143.1, 136.6, 132.5, 128.6 (d, *J* = 1.8 Hz), 128.4, 127.7, 122.6, 87.0 (d, *J* = 172.1 Hz), 62.2, 40.3 (d, *J* = 5.4 Hz), 39.7 (d, *J* = 20.7 Hz), 21.0 (d, *J* = 7.8 Hz), 14.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -209.7 (td, *J* = 47.7, 6.2 Hz).

HRMS (AP+) calcd for $C_{19}H_{19}FNO_4$ ($[M+H]^+$) 344.1298, found: 344.1303. (1.5 ppm).
IR (Neat) 1717, 1601, 1518, 1498, 1465, 1450, 1367, 1347, 1313, 1298, 1258, 1200, 1132, 1109, 1066, 1046, 1014, 992, 856, 803, 780, 766, 745, 481, 465, 403 cm^{-1}.



3p (26.8 mg, 24%) was obtained as a white solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.28 (PE/Et_2O =10:1).**Mp：** 97-98 °C.

Enantiomeric Excess 92%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 5.6 min, t_R = 6.4 min. **$[\alpha]^{20}_D$** = +45.3 (c = 2.0, $CHCl_3$).

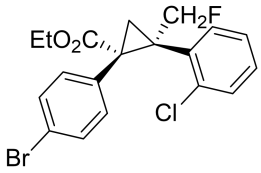
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 4H), 6.99 – 6.94 (m, 4H), 4.75 (d, *J* = 47.8 Hz, 2H), 4.21 – 3.98 (m, 2H), 2.15 (dd, *J* = 6.0, 1.3 Hz, 1H), 2.00 (t, *J* = 6.1 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 136.2, 134.0, 133.0, 131.2, 130.8, 130.4 (d, *J* = 1.8 Hz), 121.5, 121.4, 86.9 (d, *J* = 172.1 Hz), 62.0, 40.2 (d, *J* = 5.2 Hz), 38.4 (d, *J* = 21.1 Hz), 20.8 (d, *J* = 7.5 Hz), 14.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -209.5 (td, *J* = 47.8, 6.1 Hz).

HRMS (AP+) calcd for $C_{19}H_{18}Br_2FO_2$ ($[M+H]^+$) 456.9637, found: 456.9651. (3.1 ppm).

IR (Neat) 1716, 1490, 1465, 1444, 1385, 1367, 1303, 1277, 1255, 1202, 1132, 1105, 1075, 1063, 1046, 1010, 994, 860, 827, 762, 736, 719, 558, 516, 440 cm^{-1}.



3q (47.1 mg, 46%) was obtained as a colorless viscous liquid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.28 (PE/Et_2O =10:1).

Enantiomeric Excess 98%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 5.4 min, t_R = 5.9 min. **$[\alpha]^{20}_D$** = +46.7 (c = 7.6, $CHCl_3$).

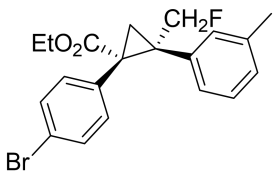
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 6H), 7.07 – 7.04 (m, 2H), 4.93 (dd, *J* = 176.6, 40.0 Hz, 2H), 4.35 – 4.15 (m, 2H), 2.23 – 2.16 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 135.2, 134.0, 133.7, 132.2, 131.3, 130.8, 130.3, 129.2, 126.6, 121.5, 85.4 (d, *J* = 171.8 Hz), 61.9, 40.4, 39.1 (d, *J* = 23.4 Hz), 20.1, 14.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -214.8 (t, *J* = 47.8 Hz).

HRMS (AP+) calcd for $C_{19}H_{18}BrClFO_2$ ($[M+H]^+$) 411.0163, found: 411.0164. (0.2 ppm).

IR (Neat) 1719, 1492, 1476, 1438, 1389, 1367, 1283, 1252, 1232, 1188, 1138, 1080, 1038, 1008, 994, 859, 829, 758, 740, 714, 666, 619, 570, 545, 503, 469, 442, 421 cm^{-1}.



3r (85.0 mg, 87%) was obtained as a colorless viscous liquid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{19}F NMR of the crude mixture. Rf = 0.22 (PE/Et_2O =10:1).

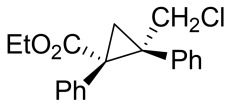
Enantiomeric Excess 86%. The enantiomeric excess was determined by HPLC with a Chiralcel IA-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.4 min, t_R = 4.8 min. **$[\alpha]^{20}_D$** = +33.4 (c = 7.2, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 2H), 7.09 – 7.06 (m, 2H), 7.01 – 6.98 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 2H), 4.86 (d, *J* = 47.8 Hz, 2H), 4.28 – 4.05 (m, 2H), 2.21 – 2.19 (m, 4H), 2.11 (t, *J* = 5.9 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 137.7, 136.9, 134.6, 133.3, 130.6, 129.6 (d, *J* = 1.6 Hz), 128.1, 128.0, 125.9 (d, *J* = 1.4 Hz), 121.3, 87.2 (d, *J* = 171.7 Hz), 61.8, 40.2 (d, *J* = 5.4 Hz), 39.0 (d, *J* = 20.9 Hz), 21.5, 20.8 (d, *J* = 7.6 Hz), 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -210.0 (td, *J* = 47.8, 6.0 Hz).

HRMS (AP+) calcd for $C_{20}H_{21}BrFO_2$ ($[M+H]^+$) 391.0709, found: 391.0700. (-2.3 ppm).
IR (Neat) 1716, 1490, 1464, 1445, 1388, 1367, 1301, 1272, 1255, 1199, 1129, 1096, 1073, 1044, 1010, 992, 931, 860, 827, 787, 759, 707, 674, 592, 513, 448, 432 cm^{-1}.



6a (50.2 mg, 64%) was obtained as a yellow solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{1}H NMR of the crude mixture. Rf = 0.28 (PE/Et_2O =10:1). **Mp**：75-76 °C.

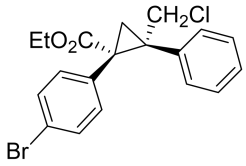
Enantiomeric Excess 92%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 5.2 min, t_R = 5.5 min. **$[\alpha]^{20}_D$** = +33.9 (c = 3.8, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 4H), 7.15 – 7.01 (m, 6H), 4.34 (d, *J* = 11.3 Hz, 1H), 4.29 – 4.10 (m, 2H), 3.93 (d, *J* = 11.3 Hz, 1H), 2.24 (dd, *J* = 14.8, 6.0 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 137.1, 135.3, 131.2, 129.4, 127.9, 127.5, 127.2, 127.1, 61.9, 51.1, 43.5, 40.4, 23.0, 14.2.

HRMS (AP+) calcd for $C_{19}H_{20}ClO_2$ ($[M+H]^+$) 315.1152, found: 315.1147. (-1.6 ppm).

IR (Neat) 1704, 1497, 1448, 1366, 1293, 1272, 1250, 1213, 1167, 1131, 1114, 1082, 1057, 1038, 1025, 1005, 928, 871, 781, 765, 751, 718, 556, 527, 495, 467, 427 cm^{-1}.



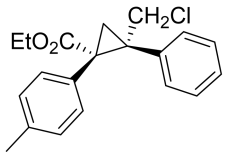
6b (76.0 mg, 77% yield) was obtained as a yellow solid after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^1H NMR of the crude mixture. Rf = 0.23 (PE/Et_2O =10:1). **Mp：** 76-77 °C.

Enantiomeric Excess 93%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 5.1 min, t_R = 6.0 min. **$[\alpha]^{20}_D$** = +28.2 (c = 2.1, $CHCl_3$).

^1H NMR (300 MHz, $CDCl_3$) δ 7.22 – 7.08 (m, 9H), 4.32 – 4.09 (m, 3H), 3.93 (d, *J* = 11.3 Hz, 1H), 2.23 (dd, *J* = 12.1, 5.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 136.8, 134.4, 132.9, 130.6, 129.2, 128.0, 127.4, 121.2, 62.0, 50.6, 42.7, 40.6, 23.2, 14.1.

HRMS (AP+) calcd for $C_{19}H_{19}O_2ClBr$ ($[M]^+$) 393.0257, found: 393.0266. (2.3 ppm).

IR (Neat) 1714, 1489, 1447, 1367, 1272, 1248, 1210, 1169, 1128, 1074, 1010, 827, 762, 713, 698, 632, 599, 557 cm^{-1}.



6c (63.0 mg, 77% yield) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^1H NMR of the crude mixture. Rf = 0.23 (PE/Et_2O =10:1).

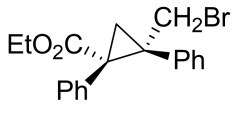
Enantiomeric Excess 96%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 4.5 min, t_R = 4.8 min. **$[\alpha]^{20}_D$** = +31.6 (c = 2.3, $CHCl_3$).

^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.0 Hz, 2H), 7.17 – 7.05 (m, 5H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.33 (d, *J* = 11.2 Hz, 1H), 4.30 – 4.09 (m, 2H), 3.90 (d, *J* = 11.3 Hz, 1H), 2.24 – 2.18 (m, 5H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 137.2, 136.6, 132.1, 130.9, 129.4, 128.2, 127.8, 127.0, 61.8, 51.2, 43.2, 40.2, 22.9, 21.0, 14.1.

HRMS (AP+) calcd for $C_{20}H_{22}O_2Cl$ ($[M+H]^+$) 329.1038, found: 329.1312. (1.2 ppm).

IR (Neat): 2980, 1711, 1514, 1447, 1366, 1248, 1206, 1168, 1127, 1051, 1023, 822, 763, 697, 599, 541, 514 cm^{-1}.



7a (57.3 mg, 64%) was obtained as a white solid after silica gel column chromatography (PE/Et2O 100:0 to 90:10). The diastereomeric ratio (17:1) was determined by ^1H NMR of the crude mixture. Rf = 0.30 (PE/Et_2O =10:1). **Mp：** 90-92 °C.

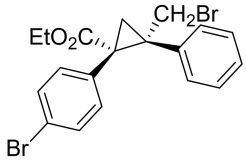
Enantiomeric Excess 90%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 5.3 min, t_R = 5.6 min. **$[\alpha]^{20}_D$** = +30.3 (c =4.9, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 7.15 – 7.00 (m, 6H), 4.32 – 4.11 (m, 3H), 3.83 (d, *J* = 10.3 Hz, 1H), 2.31 (dd, *J* = 6.0, 0.8 Hz, 1H), 2.18 (d, *J* = 6.0 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 137.2, 135.4, 131.1, 129.3, 127.9, 127.5, 127.2, 127.1, 61.9, 45.5, 40.5, 40.4, 23.8, 14.2.

HRMS (AP+) calcd for $C_{19}H_{20}BrO_2$ ($[M+H]^+$) 359.0647, found: 359.0654. (1.9 ppm).

IR (Neat) 1712, 1497, 1449, 1367, 1290, 1250, 1206, 1150, 1126, 1080, 1052, 1024, 1005, 994, 861, 800, 756, 695, 662, 638, 619, 569, 553, 512, 488 cm^{-1}.



7b (70.0 mg, 64% yield) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O = 100:0 to 90:10). The diastereomeric ratio (>20:1) was determined by ^{1}H NMR of the crude mixture.**Rf** = 0.26 (PE/Et_2O = 9:1).

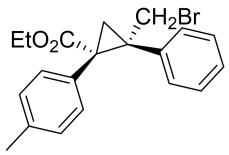
Enantiomeric Excess: 94%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 5.2 min, t_R = 6.1 min. **$[\alpha]^{20}_D$** = +20.5 (c = 2.4, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.07 (m, 9H), 4.30 – 4.10 (m, 3H), 3.82 (d, *J* = 10.4 Hz, 1H), 2.25 (d, *J* = 6.1 Hz, 1H), 2.20 (d, *J* = 6.0 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 136.8, 134.5, 132.7, 130.6, 129.1, 128.1, 127.4, 121.2, 62.0, 44.6, 40.6, 40.0, 24.0, 14.1.

HRMS (AP+) calcd for $C_{19}H_{19}O_2Br_2$ ($[M+H]^+$) 436.9752, found: 436.9761. (2.1 ppm).

IR (Neat) 1712, 1489, 1447, 1366, 1272, 1247, 1205, 1127, 1022, 1010, 825, 760, 698, 575, 555, 517 cm^{-1}.



7c (65.1 mg, 70% yield) was obtained as a colorless oil after silica gel column chromatography (PE/Et_2O = 100:0 to 90:10). The diastereomeric ratio (17:1) was determined by ^{1}H NMR of the crude mixture. **Rf** = 0.24 (PE/Et_2O = 9:1).

Enantiomeric Excess 92%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 98:2, 220 nm, 1 mL/min), t_R = 5.5 min, t_R = 5.7 min. **$[\alpha]^{20}_D$** = +32 (c = 2.5, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 – 7.10 (m, 2H), 7.05 – 6.96 (m, 5H), 6.77 (d, *J* = 8.0 Hz, 2H), 4.21 – 3.99 (m, 3H), 3.69 (d, *J* = 10.3 Hz, 1H), 2.16 (d, *J* = 5.9 Hz, 1H), 2.05 (d, *J* = 8.1 Hz, 4H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 137.2, 136.7, 132.2, 130.8, 129.3, 128.2, 127.8, 127.1, 61.8, 45.2, 40.7, 40.2, 23.7, 21.0, 14.2.

HRMS (AP+) calcd for $C_{20}H_{21}O_2Br$ ([M+H]$^+$) 373.0803, found: 373.0798. (-1.3 ppm).

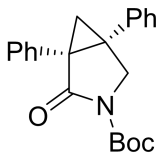
IR (Neat) 1711, 1514, 1447, 1366, 1248, 1201, 1169, 1150, 1108, 1021, 860, 762, 698, 656, 597, 540, 515 cm^{-1}.

Procedure for synthesis of lactam 8, 9

NaN_3 (130 mg, 2 mmol, 8 equiv) was added to a solution of **7a** or **7c** (0.25 mmol, 1.0 equiv) and 15-crown-5 (55 mg, 0.25 mmol, 1.0 equiv) in DMF (1 mL). The mixture was stirred at 60 °C for 6 h. Cooled down the reaction and $NaHCO_3$ (1 M, 20 mL) was added to the mixture and extracted with Et_2O (2 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude product was used to next step without any purification.

PPh_3 (78.7 mg, 0.3 mmol, 1.2 equiv) was added to a solution of azide in THF/water (8:1, 2mL), the mixture was stirred at room temperature for 18 h. water (20 mL) was added and extracted with Et_2O (2 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude product was used to next step without any purification.

To a solution of crude and DMAP (3.0 mg, 0.025 mmol, 0.1 equiv) in DCM (2 mL), Boc_2O (81.7 mg, 0.38 mmol, 1.5 equiv) was added to the mixture followed Triethylamine (25 mg, 0.25 mmol, 1.0 equiv) was added. The mixture was stirred at room temperature for 3 h. The crude product was purified by flash chromatography to provide the desired product



8 (62.8 mg, 72% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 100:0 to 85:15). **Rf** = 0.27 (PE/EtOAc = 5:1), **Mp:** 174-175 °C.

Enantiomeric Excess: 90%. The enantiomeric excess was determined by HPLC with a Chiralce IB -H column (*n*-heptane/*i*-PrOH = 80:20, 220 nm, 1 mL/min), t_R = 6.0 min, t_R = 7.3 min. **$[\alpha]^{20}_D$** = +38.0 (c = 3.0, $CHCl_3$).

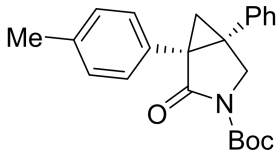
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 – 7.04 (m, 10H), 4.00 (dd, *J* = 11.4, 8.1 Hz, 2H), 2.22 (d, *J* = 5.2 Hz, 1H), 1.54 (d, *J* = 5.2 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 150.5, 135.7, 132.1, 130.0, 129.2, 128.5, 128.2, 127.7, 127.5, 83.1, 53.3, 42.8, 35.3, 28.1, 21.5.

HRMS (ES+) calcd for $C_{22}H_{24}NO_3$ ([M+H]$^+$) 350.1756, found: 350.1754. (-0.6 ppm).

IR (Neat): 2980, 1776, 1699, 1598, 1450, 1352, 1323, 1289, 1155, 1082, 971, 846, 754, 698,

610, 562, 464, 386 cm^{-1}.



9 (70.7 mg, 78% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 100:0 to 85:15). **Rf** = 0.28 (PE/EtOAc = 5:1), **Mp:** 165-166 °C.

Enantiomeric Excess: 95%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 80:20, 220 nm, 1 mL/min), t_R = 14.2 min, t_R = 17.2 min. **$[\alpha]^{20}_D$** = +13.8 (c = 3.3, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 2.8 Hz, 5H), 6.93 (d, *J* = 5.1 Hz, 4H), 4.00 (q, *J* = 11.4 Hz, 2H), 2.18 (d, *J* = 5.1 Hz, 1H), 2.13 (s, 3H), 1.52 (d, *J* = 5.1 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 150.5, 137.2, 136.0, 129.9, 129.2, 129.1, 129.0, 128.5, 127.6, 83.0, 53.3, 42.6, 34.9, 28.1, 21.6, 21.1.

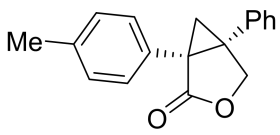
HRMS (AP+) calcd for $C_{23}H_{26}NO_3$ ($[M+H]^+$) 364.1913, found: 364.1920. (+1.9 ppm).

IR (Neat) 2983, 1776, 1697, 1448, 1358, 1285, 1156, 1135, 971, 858, 789, 770, 700, 645, 512, 487, 456 cm^{-1}.

Procedure for synthesis of lactone 10

To a mixture of **7c** (93 mg, 0.25mmol, 1.0 eq) and NaOH (100 mg, 2.5 mmol, 10 eq), EtOH (0.75 mL) was added and the reaction mixture stirred at room temperature for 8 h. HCl (0.5 M, 20 mL) was added to reaction mixture and extracted with Et_2O (2 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude product was used to next step without any purification.

To a solution of crude and DMAP (3.0 mg, 0.025 mmol, 0.1 equiv) in DCM (2 mL) was added DCC (78.3 mg, 0.38 mmol, 1.5 equiv), the reaction mixture was stirred at room temperature for 3 h. The crude product was purified by flash chromatography to provide the desired product



10 (62.7 mg, 95% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 100:0 to 90:10). **Rf** = 0.18 (PE/EtOAc = 9:1), **Mp**：154-155 °C.

Enantiomeric Excess: 91%. The enantiomeric excess was determined by HPLC with a Chiralcel IB-H column (*n*-heptane/*i*-PrOH = 80:20, 220 nm, 1 mL/min), t_R = 10.2 min, t_R = 12.1 min. **$[\alpha]^{20}_D$** = +11.8 (c = 7.4, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 5H), 6.99 – 6.92 (m, 4H), 4.47 (dd, *J* = 23.0, 9.4 Hz, 2H), 2.24 (d, *J* = 5.1 Hz, 1H), 2.15 (s, 3H), 1.60 (d, *J* = 5.2 Hz, 1H).

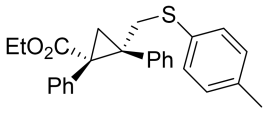
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.5, 137.5, 134.2, 129.4, 129.3, 129.2, 128.7, 128.2, 128.0, 73.4, 40.7, 38.6, 21.4, 21.1.

HRMS (AP+): calcd for $C_{18}H_{17}O_2$ ($[M+H]^+$) 265.1229, found: 265.1228. (-0.4 ppm).

IR (Neat) 1760, 1632, 1520, 1451, 1355, 1286, 1169, 1086, 1069, 1023, 1011, 971, 859, 819, 767, 701, 652, 509, 473, 423 cm^{-1}.

Procedure for synthesis of 11

An oven dried reaction tube was charged with NaH (12 mg, 0.3 mmol, 60% in mineral oil, 1.5 equiv) and DMF (0.5 mL) under Ar, a solution of *p*-Methylbenzenethiol (37.2 mg, 0.3 mmol, 1.5 equiv) in dried DMF (1 mL) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 1 h. A solution of **7c** (74.7 mg, 0.2 mmol, 1.0 equiv) in dried DMF (1 mL) was added at 0 °C and stirred at room temperature for 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (15 mL), extracted with EtOAc (3x15 mL). The combined organic layers were successively washed with water (15 mL) and brine (20 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography to provide the desired product.



11 (77.2 mg, 85% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 95:5). **Rf** = 0.21 (PE/EtOAc = 15:1), **Mp:** 124-126 °C.

Enantiomeric Excess: 89%. The enantiomeric excess was determined by HPLC with a Chiralce IA -H column (*n*-heptane/*i*-PrOH = 95:5, 230 nm, 1 mL/min), t_R = 6.1 min, t_R = 6.9 min. **$[\alpha]^{20}_D$** = +14.0 (c = 6, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.02 (m, 14H), 4.27 – 4.13 (m, 2H), 3.83 (d, *J* = 12.5 Hz, 1H), 3.35 (d, *J* = 12.5 Hz, 1H), 2.33 (s, 3H), 2.16 (t, *J* = 6.0 Hz, 1H), 2.00 (t, *J* = 7.0 Hz, 1H), 1.27 (t, *J* = 6.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 137.9, 136.5, 135.8, 132.91, 132.87, 131.12, 131.98, 129.6, 129.3, 127.8, 127.3, 126.8, 61.5, 42.5, 42.4, 38.8, 21.8, 21.1, 14.3.
HRMS (AP+) calcd for $C_{26}H_{27}O_2S$ ($[M+H]^+$) 403.1732, found: 407.1741. (2.2 ppm).

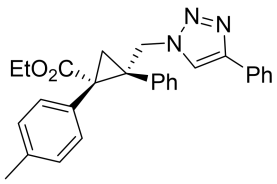
IR (Neat): 2921, 1720, 1492, 1447, 1248, 1170, 1126, 810, 733, 696, 550, 504, 481, 425 cm^{-1}.

Procedure for synthesis of 12

NaN_3 (104 mg, 1.6 mmol, 8 equiv) was added to a solution of **7c** (0.2 mmol, 1.0 equiv) and 15-crown-5 (44 mg, 0.2 mmol, 1.0 equiv) in DMF (1 mL). The mixture was stirred at 60 °C for 6 h, then cooled down to room temperature. $NaHCO_3$ (1 M, 20 mL) was added to the mixture

and extracted with Et_2O (2 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude product was used to next step without any purification.

CuBr (11.5 mg, 0.3 mmol, 0.2 equiv), phenylacetylene (22.6 mg, 0.26 mmol, 1.3 equiv) and Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) were added to a solution of azide in MeCN (2 mL). The mixture was stirred at room temperature for 3.5 h. Saturated aqueous NH_4Cl (30 mL) was added and extracted with EtOAc (3x15 mL). The combined organic layers were successively washed with water and brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography to provide the desired product.



12 (74.2 mg, 85% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 100:10 to 50:10). **Rf** = 0.17 (PE/EtOAc = 10:1), **Mp:** 124-126 °C.

Enantiomeric Excess: 96%. The enantiomeric excess was determined by HPLC with a Chiralce IA-H column (*n*-heptane/*i*-PrOH = 90:10, 220 nm, 1 mL/min), t_R = 20.9 min, t_R = 22.2 min. **$[\alpha]^{20}_D$** = -26.4 (c = 4.9, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 7.11 (s, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.00 – 6.94 (m, 3H), 6.90 – 6.86 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 5.11 (d, *J* = 14.1 Hz, 1H), 4.59 (d, *J* = 14.4 Hz, 1H), 4.29 – 4.09 (m, 2H), 2.26 (d, *J* = 6.0 Hz, 1H), 2.11 – 2.08 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H).

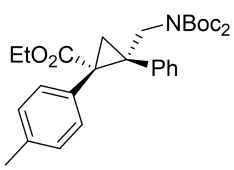
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 147.2, 136.9, 136.3, 131.8, 130.8, 130.6, 129.7, 128.8, 128.4, 128.3, 128.1, 127.5, 125.7, 120.1, 62.1, 56.1, 41.5, 39.2, 21.1, 21.0, 14.3.

HRMS (ES+) calcd for $C_{28}H_{28}N_3O_2$ ($[M+H]^+$) 438.2182, found: 438.2177. (-1.1 ppm).

IR (Neat): 3141, 2927, 1711, 1451, 1369, 1249, 1202, 1128, 1127, 1111, 1061, 1024, 1006, 765, 743, 719, 695, 566, 548, 520, 497 cm^{-1}.

Procedure for synthesis of 13

To a solution of **7c** (74.7 mg, 0.2 mmol, 1.0 eq) in DMF (2 mL) was added $NHBoc_2$ (52.1 mg, 0.24 mmol, 1.2 eq) and K_2CO_3 (55.3 mg, .4 mmol, 2 eq) at room temperature. The mixture was stirred at room temperature for 48 h. Saturated aqueous NH_4Cl (30 mL) was added and extracted with EtOAc (3x15 mL). The combined organic layers were successively washed with water (15 mL) and brine (20 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography to provide the desired product.



13 (42.8 mg, 42% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 100:10 to 50:10). **Rf** = 0.12 (PE/EtOAc = 10:1), **Mp:** 102-104 °C.

Enantiomeric Excess: 95%. The enantiomeric excess was determined by HPLC with a Chiralce IA -H column (*n*-heptane/*i*-PrOH = 95:5, 220 nm, 1 mL/min), t_R = 4.5 min, t_R = 5.6 min. **$[\alpha]^{20}_D$** = -24.0 (c = 0.6, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07-7.04 (m, 4H), 6.97 – 6.89(m, 3H), 6.80 – 6.76 (m, 2H), 4.63 (d, *J* = 14.4 Hz, 1H), 4.22 – 4.03 (m, 2H), 3.50 (d, *J* = 14.4 Hz, 1H), 2.25 (d, *J* = 5.7 Hz, 1H), 2.07 (s, 3H), 1.99 (d, *J* = 5.4 Hz, 1H), 1.28 (s, 18H), 1.21 (t, *J* = 6.9 Hz, 3H).

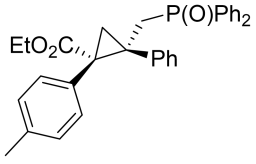
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 152.9, 137.0, 136.3, 132.8, 131.0, 130.5, 128.2, 127.5, 126.6, 82.1, 61.4, 50.5, 40.0, 39.2, 28.0, 22.4, 21.1, 14.4.

HRMS (ES+) calcd for $C_{30}H_{40}NO_6$ ($[M+H]^+$) 510.2856, found: 510.2853. (-0.6 ppm).

IR (Neat): 2982, 2927, 1739, 1721, 1699, 1512, 1451, 1394, 1342, 1316, 1305, 1256, 1223, 1176, 1147, 1121, 1050, 1024, 890, 855, 829, 760, 697, 515 cm^{-1}.

Procedure for synthesis of 14

An oven dried reaction tube was charged with **7c** (74.7 mg, 0.2 mmol, 1.0 eq) in dried THF (1 mL), $KPPh_2$ (0.5 mL, 0.26 mmol, 2 M in THF, 1.3 equiv) was added dropwise at -78 °C. The mixture was stirred at 0 °C for 9 h, quenched with saturated aqueous NH_4Cl (15 mL), extracted with EtOAc (3x15 mL). The combined organic layers were successively washed with water (15 mL) and brine (20 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography to provide the desired product.



14 (69.5 mg, 73% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 50:50 to 0:100). **Rf** = 0.38 (PE/EtOAc = 1:1), **Mp:** 206-207 °C.

Enantiomeric Excess: 95%. The enantiomeric excess was determined by HPLC with a Chiralce IB-H column (*n*-heptane/*i*-PrOH = 90:10, 220 nm, 1 mL/min), t_R = 11.1 min, t_R = 12.9 min. **$[\alpha]^{20}_D$** = +50.3 (c = 1.5, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.40 – 7.29 (m, 5H), 7.22 – 7.16 (m, 1H), 7.11 -7.06 (m, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.88 – 6.85 (m, 2H), 6.71 – 6.68 (m, 5H), 4.19 – 3.97 (m, 2H), 3.24 (q, *J* = 7.8 Hz, 1H), 2.83 (t, *J* = 14.7 Hz, 1H), 2.15 (dd, *J* = 11.1, 6.3 Hz, 2H), 2.02 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 137.7 (d, *J* = 1.1 Hz), 136.2, 134.7 (d, *J* = 97.0 Hz), 133.0 (d, *J* = 97.7 Hz), 132.4, 131.5 (d, *J* = 2.6 Hz), 131.1, 130.9 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.2 Hz), 130.6 (d, *J* = 9.1 Hz),129.8, 128.5 (d, *J* = 7.5 Hz), 128.1 (d, *J* = 11.6 Hz), 128.0, 127.5, 126.6, 61.5, 40.3 (d, *J* = 11.4 Hz), 35.8 (d, *J* = 70.2 Hz), 34.9 (d, *J* = 3.4 Hz), 21.8 (d, *J* = 2.9 Hz), 21.0, 14.4.

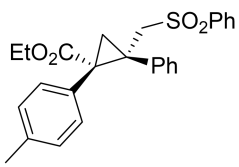
^{31}P NMR (121 MHz, $CDCl_3$) δ +28.6.

HRMS (ES+) calcd for $C_{32}H_{32}O_3P$ ($[M+H]^+$) 495.2089, found: 495.2092. (0.6 ppm).

IR (Neat): 3059, 2921, 2855, 1703, 1512, 1438, 1369, 1251, 1184, 1157, 1119, 1021, 855, 832, 817, 767, 740, 723, 690, 561, 544, 523, 501, 472, 456 cm^{-1}.

Procedure for synthesis of 15

To a solution of **7c** (74.7 mg, 0.2 mmol, 1.0 eq) in DMF (2 mL) was added sodium benzenesulfinate (42.6 mg, 0.26 mmol, 1.3 eq). The mixture was stirred at room temperature for 24 h, Saturated aqueous NH_4Cl (30 mL) was added and extracted with EtOAc (3x15 mL). The combined organic layers were successively washed with water and brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography to provide the desired product.



15 (51.2 mg, 60% yield) was obtained as a white solid after silica gel column chromatography (PE/EtOAc = 90:10). **Rf** = 0.13 (PE/EtOAc = 8:1), **Mp**:145-147 °C.

Enantiomeric Excess: 93%. The enantiomeric excess was determined by HPLC with a Chiralce IB-H column (*n*-heptane/*i*-PrOH = 90:10, 220 nm, 1 mL/min), t_R = 6.2 min, t_R = 10.4 min. **$[\alpha]^{20}_D$** = +50.3 (c = 2.3, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.90 (s, 5H), 6.77 (d, *J* = 8.0 Hz, 2H), 4.27 – 4.06 (m, 3H), 3.66 (d, *J* = 14.7 Hz, 1H), 2.26 (d, *J* = 6.4 Hz, 1H), 2.18 (d, *J* = 6.5 Hz, 1H), 2.11 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

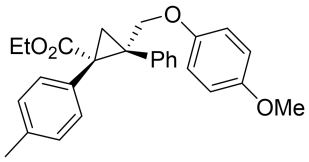
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 140.2, 136.7, 135.8, 133.2, 131.4, 131.2, 129.3, 128.9, 128.13, 128.09, 127.8, 127.0, 61.9, 61.4, 40.8, 34.2, 21.1, 20.8, 14.3.

HRMS (ES+) calcd for $C_{26}H_{30}NO_4S$ ($[M+H]^+$) 452.1896, found: 452.1896. (0 ppm).

IR (Neat): 2987, 1717, 1512, 1448, 1362, 1306, 1291, 1255, 1194, 1139, 1083, 1049, 1023, 865, 773, 736, 696, 682, 578, 551, 525, 514, 432, 404 cm^{-1}.

Procedure for synthesis of 16

An oven dried reaction tube was charged with NaH (12 mg, 0.3 mmol, 60% in mineral oil, 1.5 equiv) and THF (0.5 mL) under Ar, a solution of 4-methoxyphenol (37.2 mg, 0.3 mmol, 1.5 equiv) in dried THF (1 mL) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 30 min. A solution of **7c** (74.7 mg, 0.2 mmol, 1.0 equiv) in dried THF (1 mL) was added at 0 °C was stirred at room temperature for 30 min. The reaction was quenched with saturated aqueous NH_4Cl (15 mL), extracted with EtOAc (3x15 mL). The combined organic layers were successively washed with water (15 mL) and brine (20 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography to provide the desired product.



16 (77.4 mg, 93% yield) was obtained as a pale yellow viscous oil after silica gel column chromatography (PE/EtOAc = 90:10). **Rf** = 0.13 (PE/EtOAc = 7:1).

Enantiomeric Excess: 94%. The enantiomeric excess was determined by HPLC with a Chiralce IB-H column (*n*-heptane/*i*-PrOH = 90:10, 220 nm, 1 mL/min), t_R = 6.2 min, t_R = 10.4 min.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.15 – 7.05 (m, 5H), 6.88 – 6.79 (m, 6H), 4.38 (s, 2H), 4.11 – 3.93 (m, 2H), 3.75 (s, 3H), 2.27 (d, *J* = 5.6 Hz, 1H), 2.17 – 2.14 (m, 4H), 1.13 (t, *J* = 7.1 Hz, 3H).

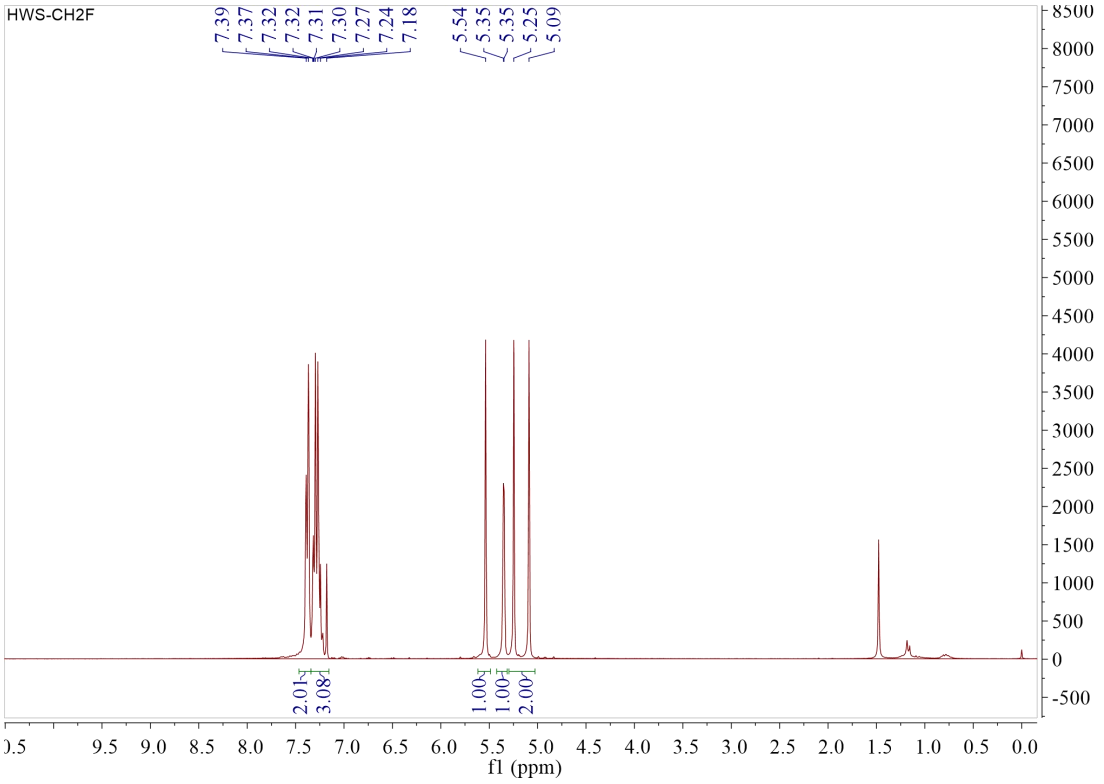
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 153.9, 153.0, 138.7, 136.3, 132.7, 131.3, 128.9, 128.1, 127.7, 126.6, 115.6, 114.6, 72.9, 61.4, 55.7, 40.2, 38.1, 21.2, 21.1, 14.1.

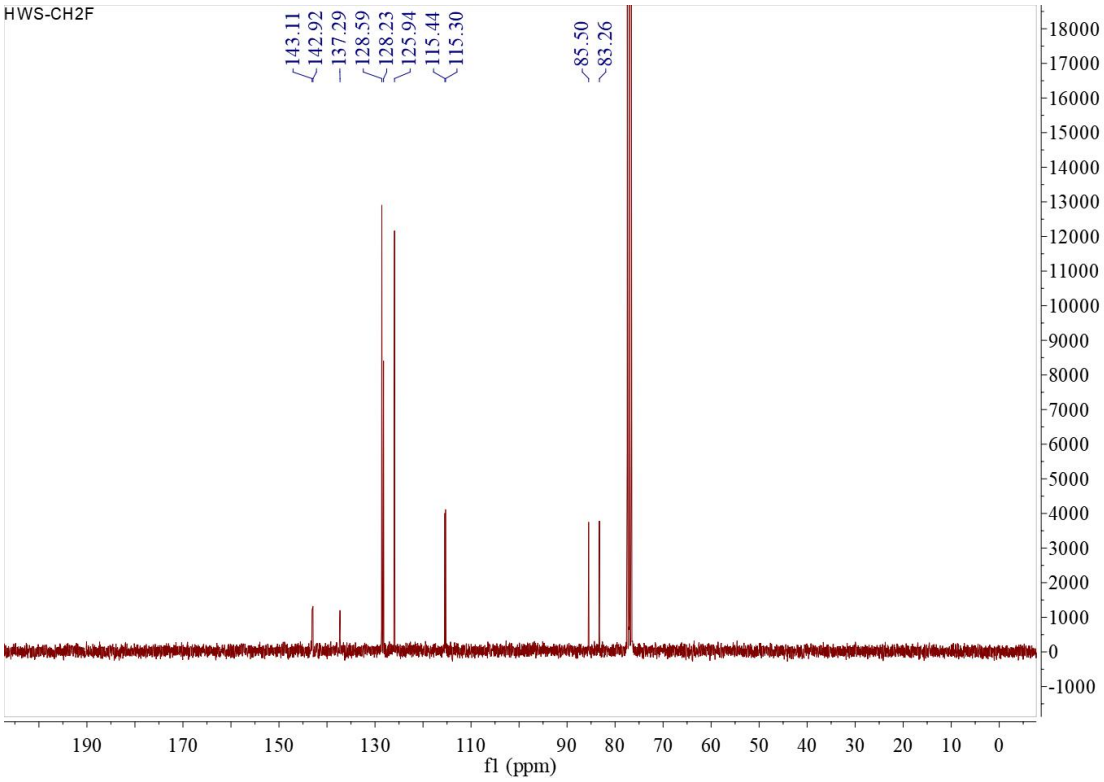
HRMS (ES+) calcd for $C_{27}H_{29}O_4$ ($[M+H]^+$) 417.2066, found: 417.2055. (-2.6 ppm).

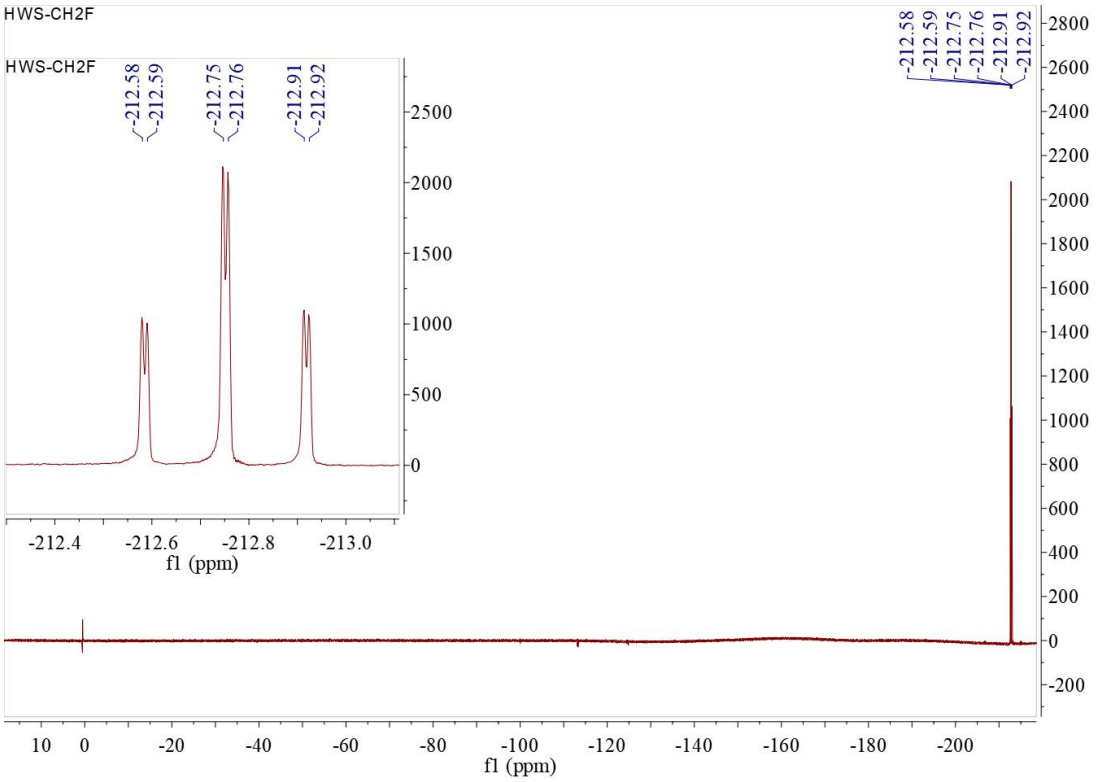
IR (Neat): 2921, 1712, 1506, 1463, 1287, 1224, 1201, 1128, 1108, 1066, 1036, 1020, 822, 741, 697, 610, 515 cm^{-1}.

NMR spectrum

2a






HWS-CH2F
HWS-CH2F
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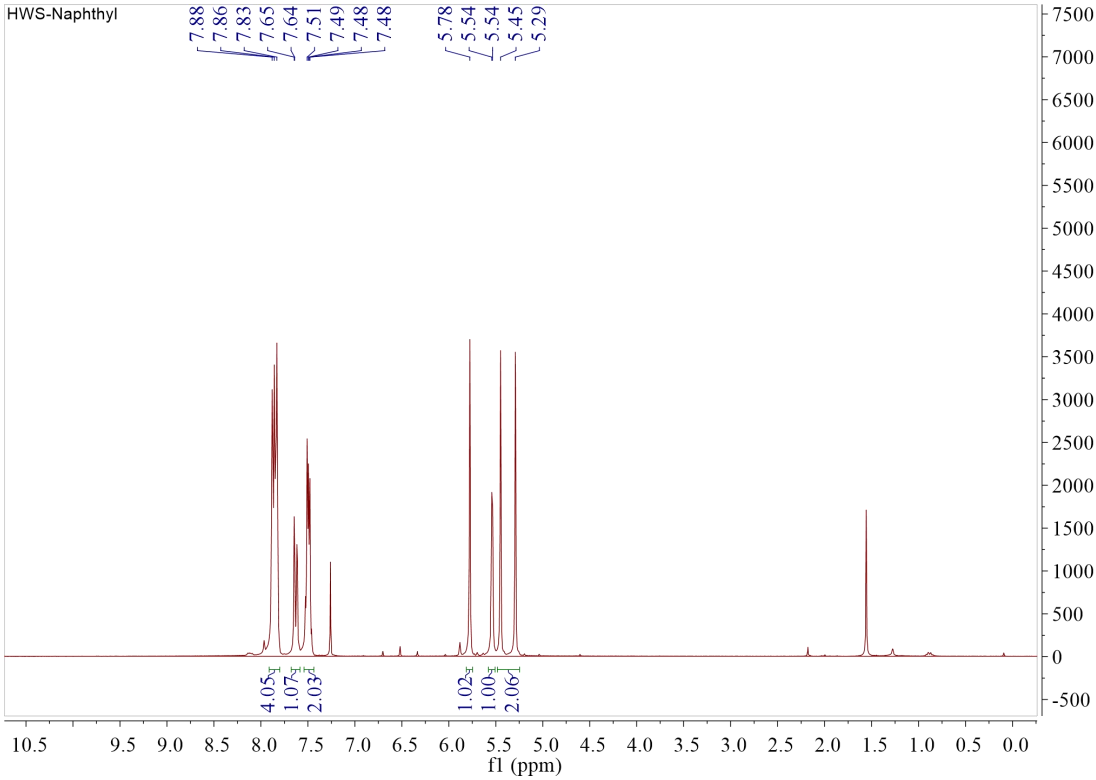
-212.59
-212.75
-212.76
-212.91
-212.92
f1 (ppm)
f1 (ppm)

2b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7.83
7.65
7.64
7.51
7.49
7.48
7.48
5.78
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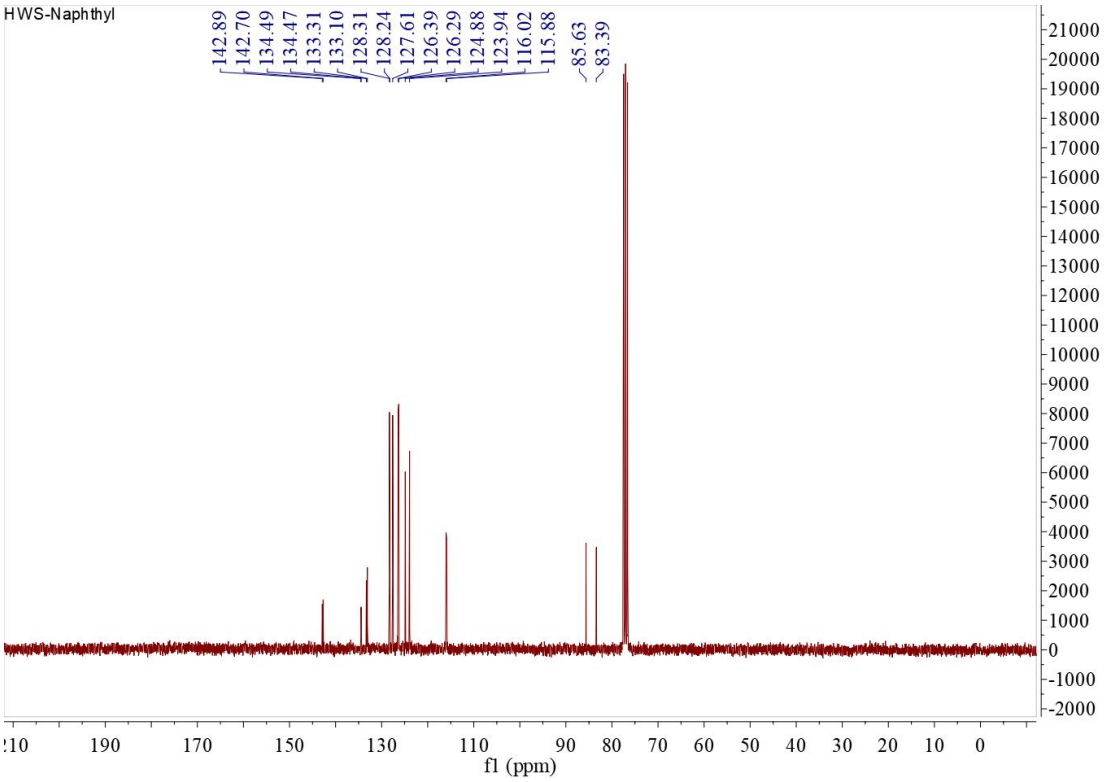
1.07
2.03
1.02
1.00
2.06
f1 (ppm)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134.47
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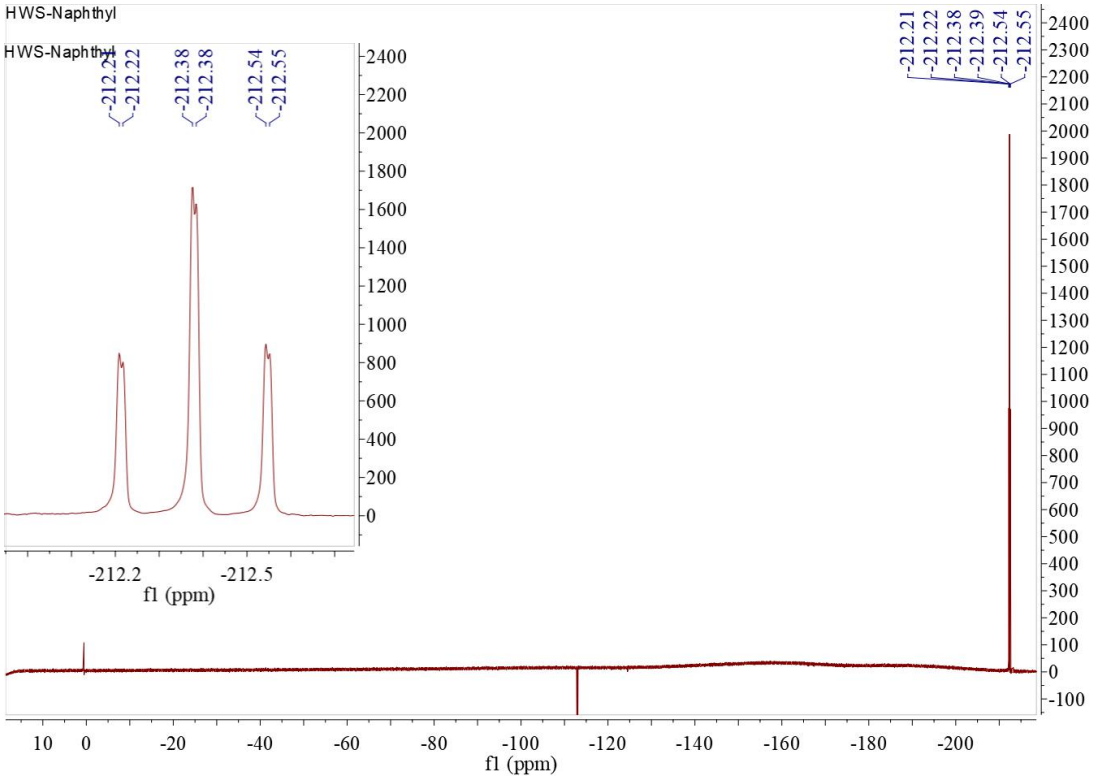
115.88
85.63
83.39
f1 (ppm)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HWS-Naphthyl
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f1 (ppm)
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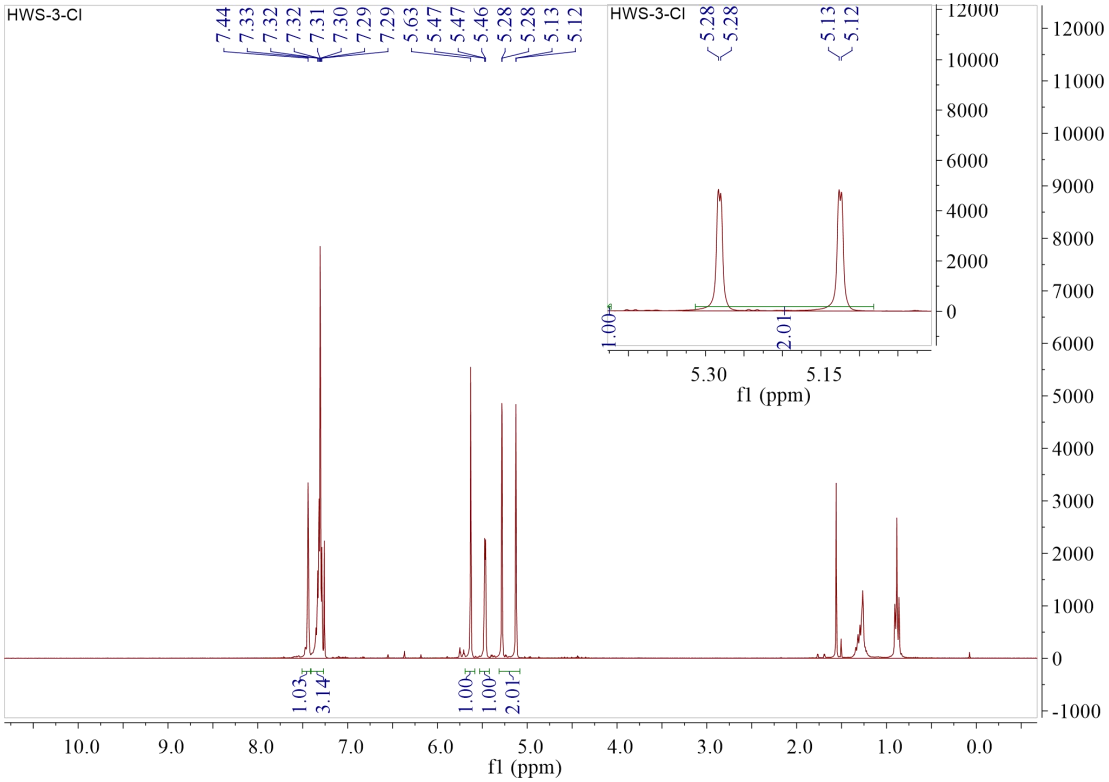
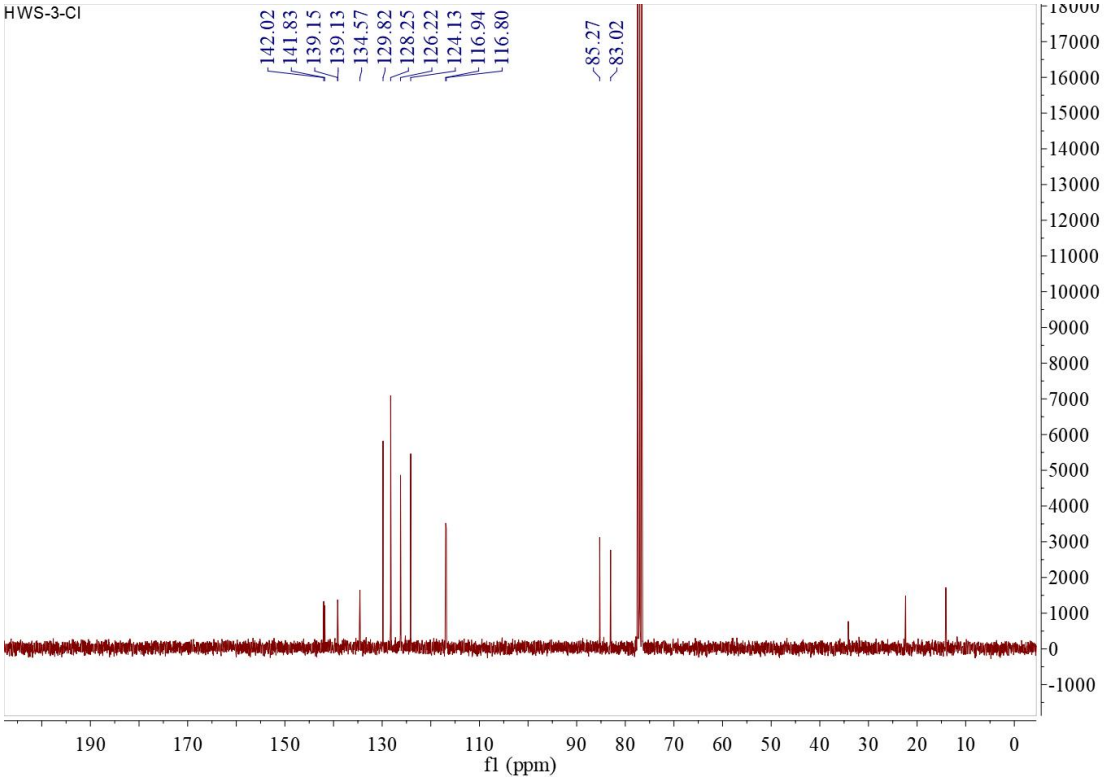
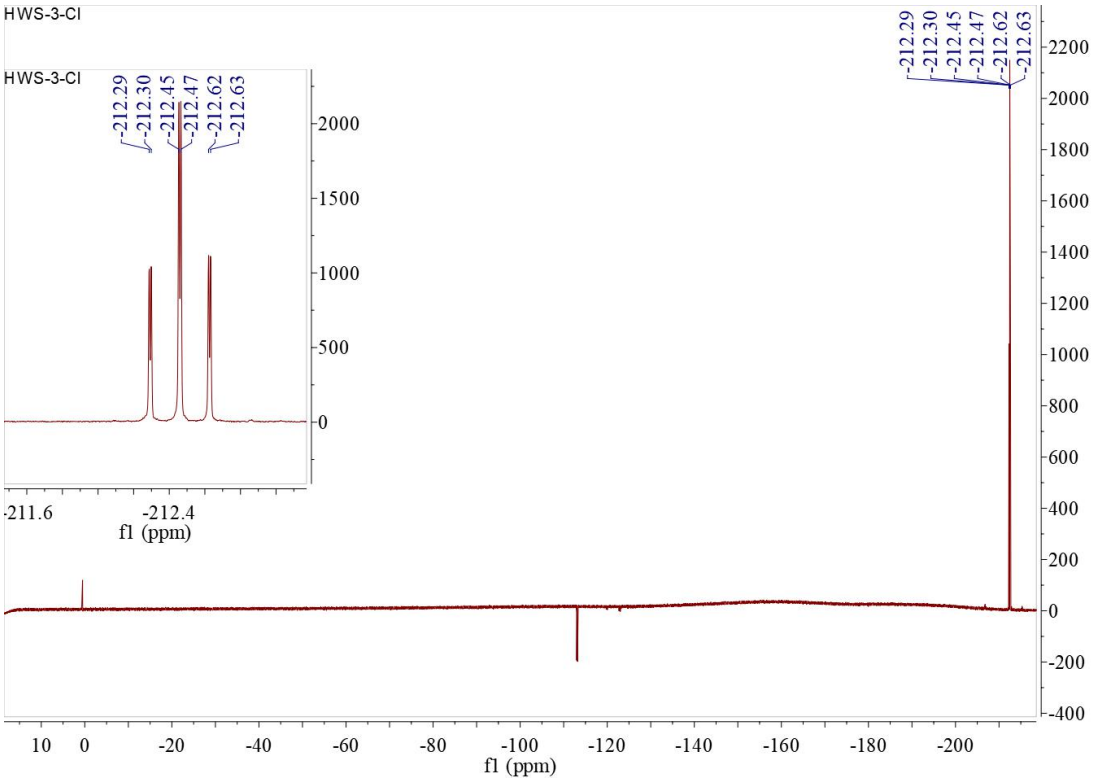
-212.22
-212.38
-212.39
-212.54
-212.55
f1 (ppm)

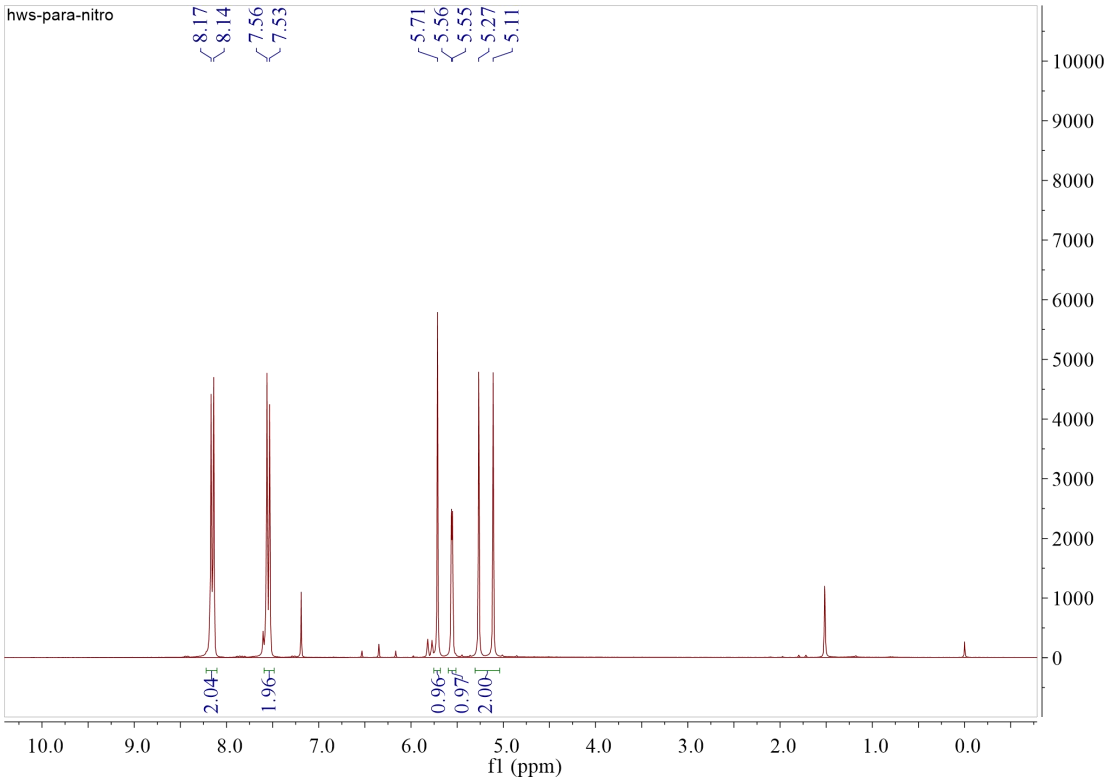
2c

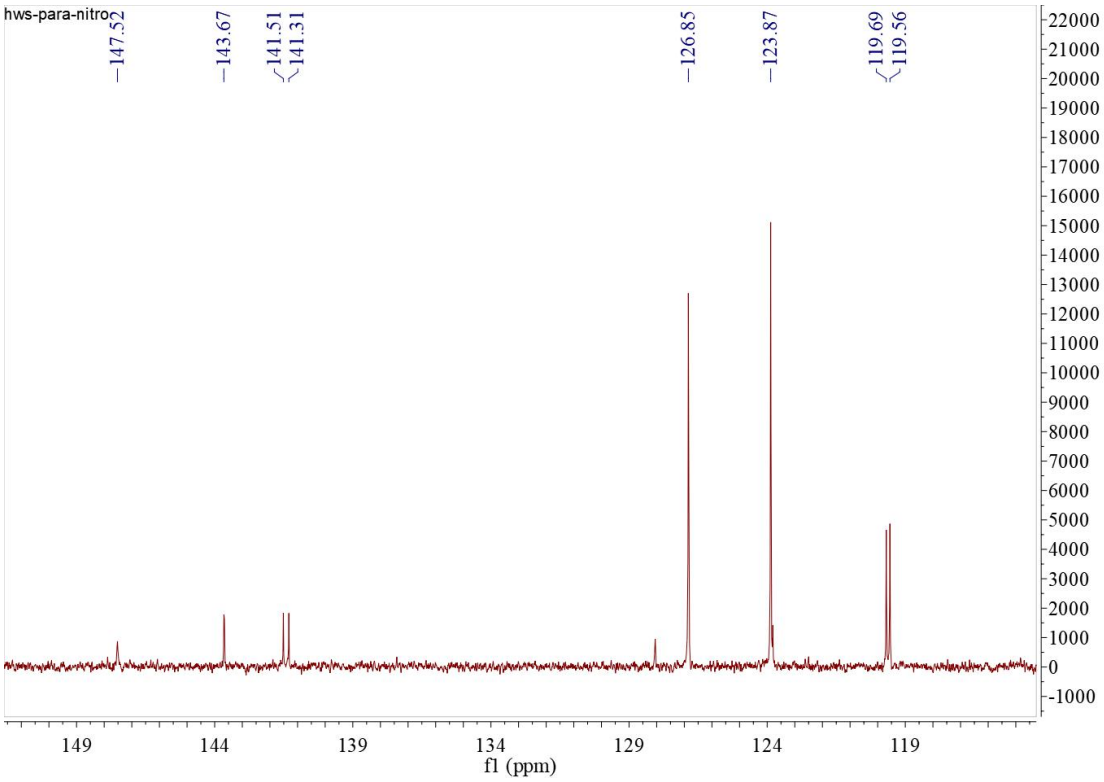

HWS-3-Cl
7.44
7.33
7.32
7.32
7.31
7.30
7.29
5.63
5.47
5.47
5.46
5.28
5.28
5.13
5.12
1.03
3.14
1.00
1.00
2.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
HWS-3-Cl
5.28
5.28
5.13
5.12
1.00
2.01
5.30
5.15
f1 (ppm)

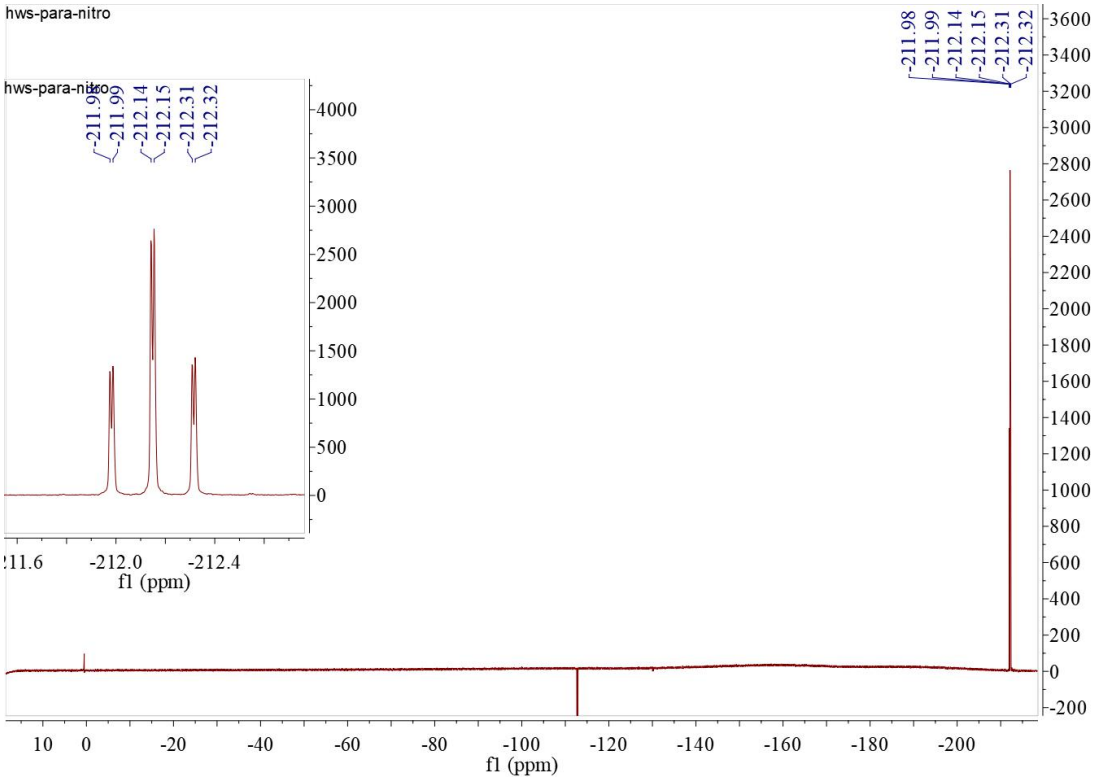

HWS-3-Cl
142.02
141.83
139.15
139.13
134.57
129.82
128.25
126.22
124.13
116.94
116.80
85.27
83.02
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HWS-3-Cl
HWS-3-Cl
-212.29
-212.30
-212.45
-212.47
-212.62
-212.63
-211.6
-212.4
f1 (ppm)
f1 (ppm)

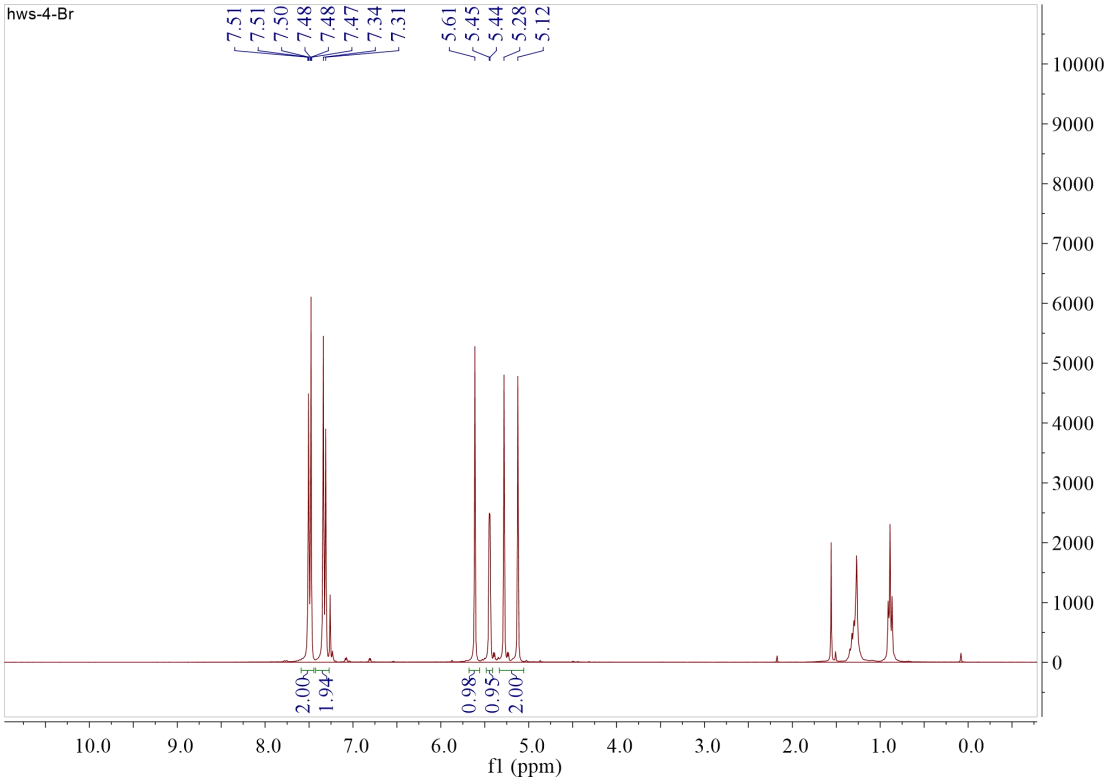
2d

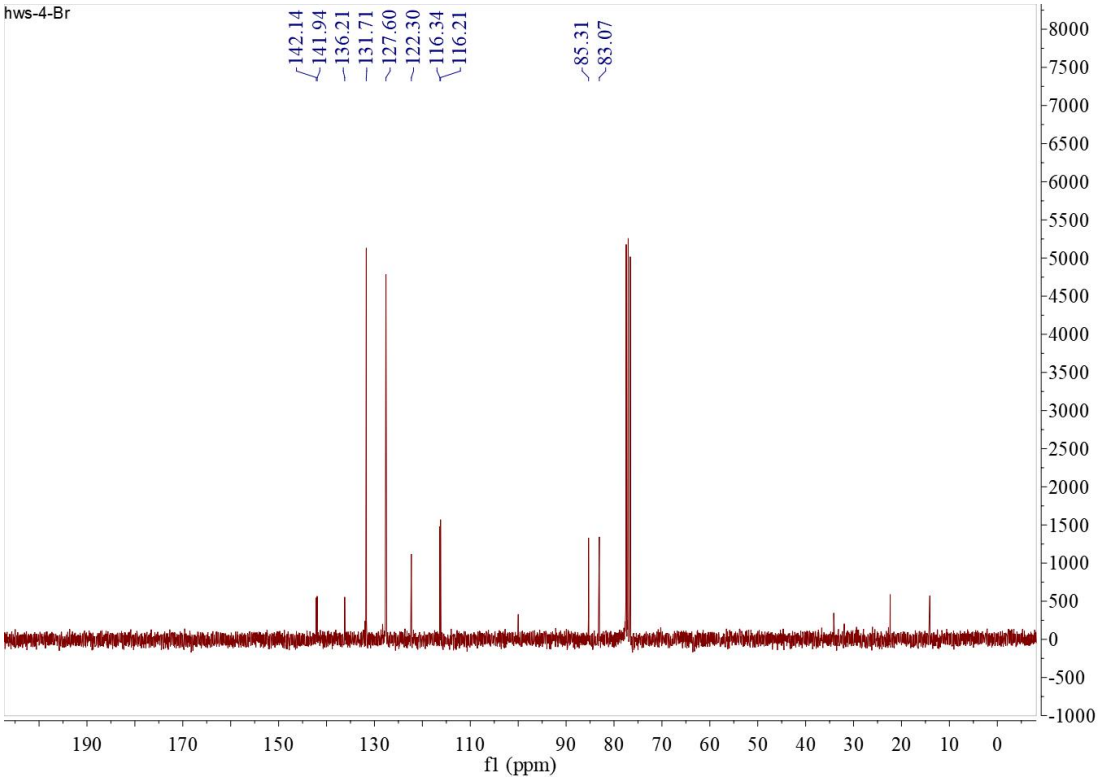

hws-para-nitro
8.17
8.14
7.56
7.53
5.71
5.56
5.55
5.27
5.11
2.04
1.96
0.96
0.97
2.00
f1 (ppm)

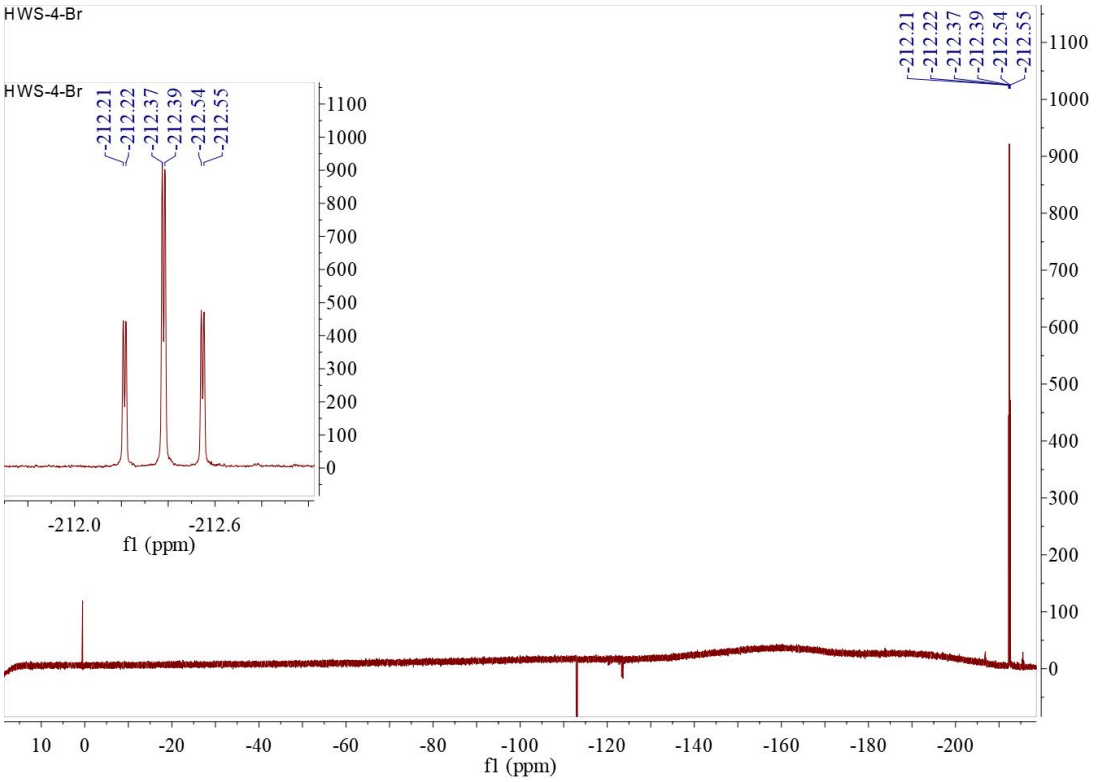

hws-para-nitro
147.52
143.67
141.51
141.31
126.85
123.87
119.69
119.56
f1 (ppm)


hws-para-nitro
hws-para-nitro
-211.98
-211.99
-212.14
-212.15
-212.31
-212.32
f1 (ppm)

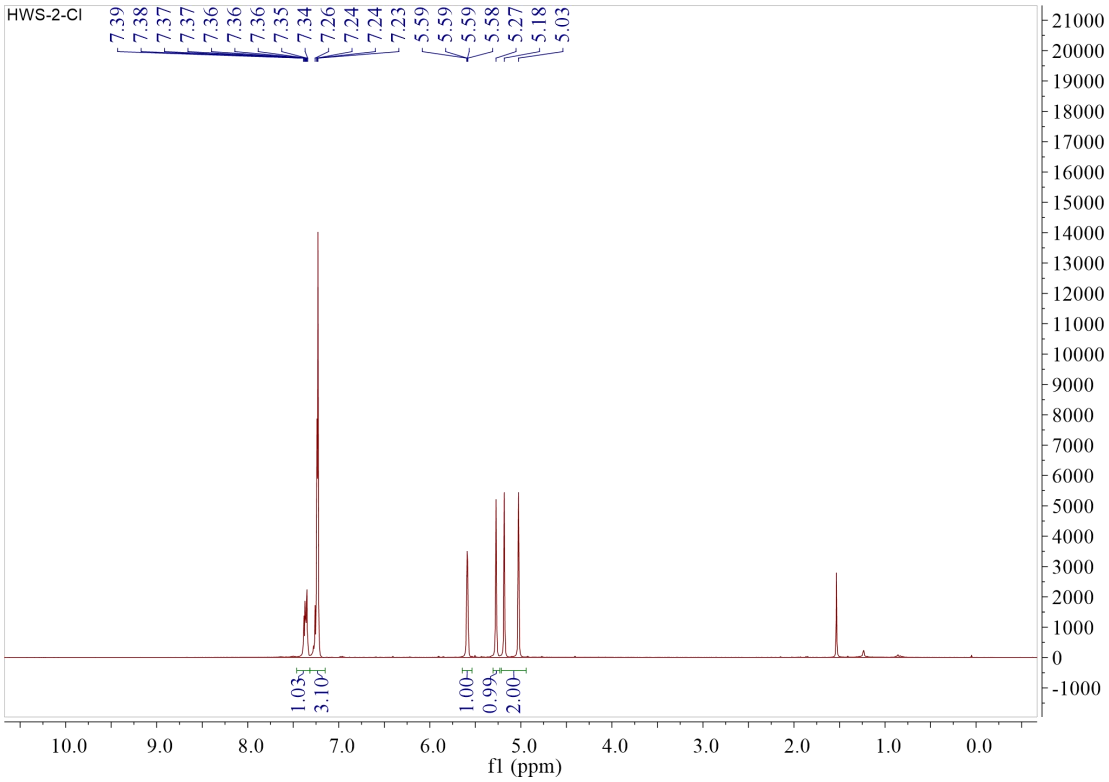
2e

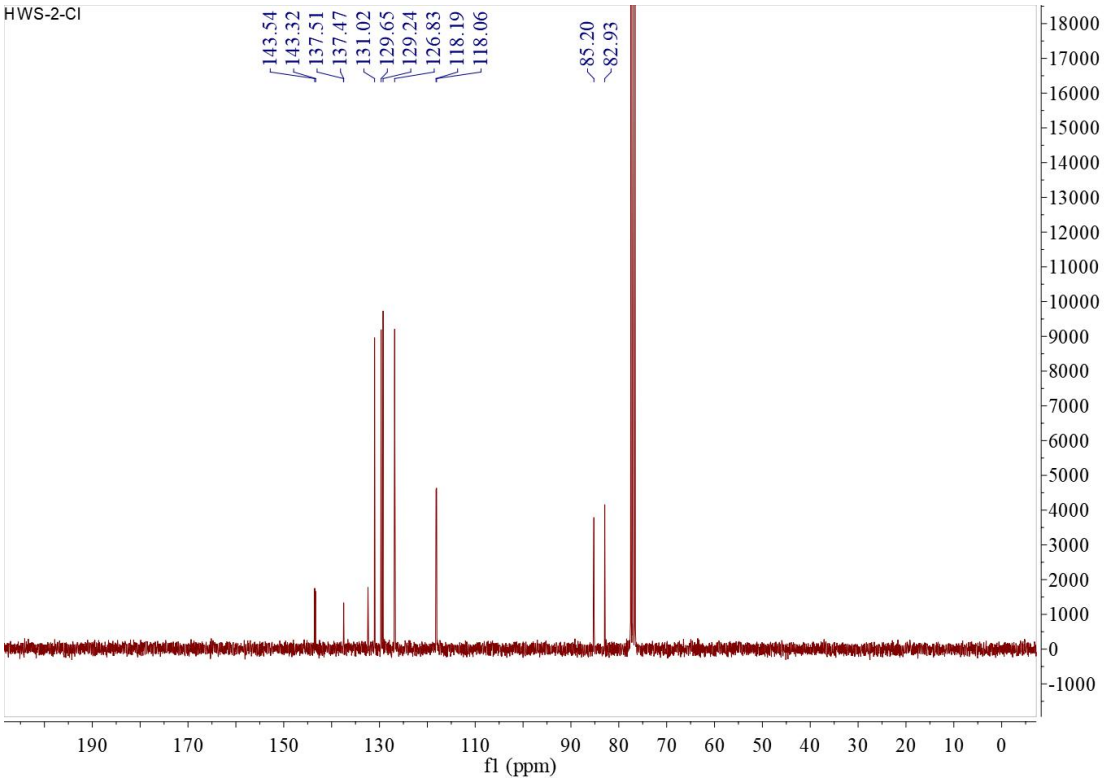

hws-4-Br
7.51
7.51
7.50
7.48
7.48
7.47
7.34
7.31
5.61
5.45
5.44
5.28
5.12
2.00
1.94
0.98
0.95
2.00
f1 (ppm)

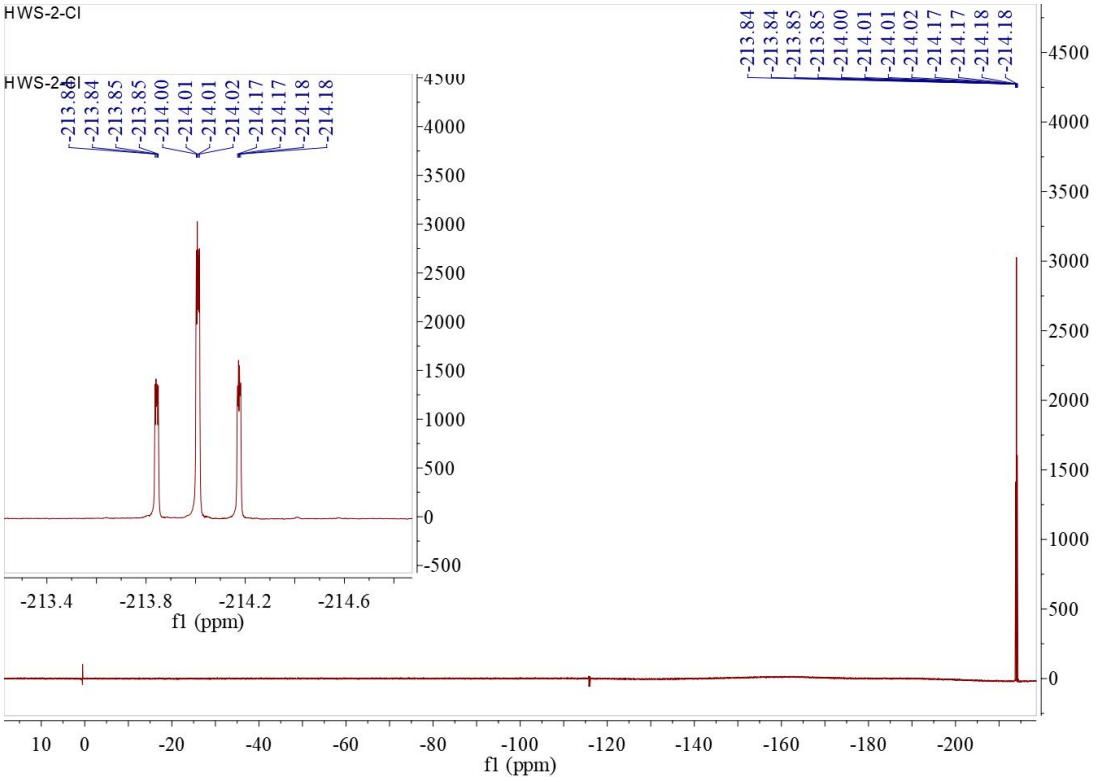

hws-4-Br
142.14
141.94
136.21
131.71
127.60
122.30
116.34
116.21
85.31
83.07
f1 (ppm)


HWS-4-Br
HWS-4-Br
-212.21
-212.22
-212.37
-212.39
-212.54
-212.55
-212.0
-212.6
f1 (ppm)
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

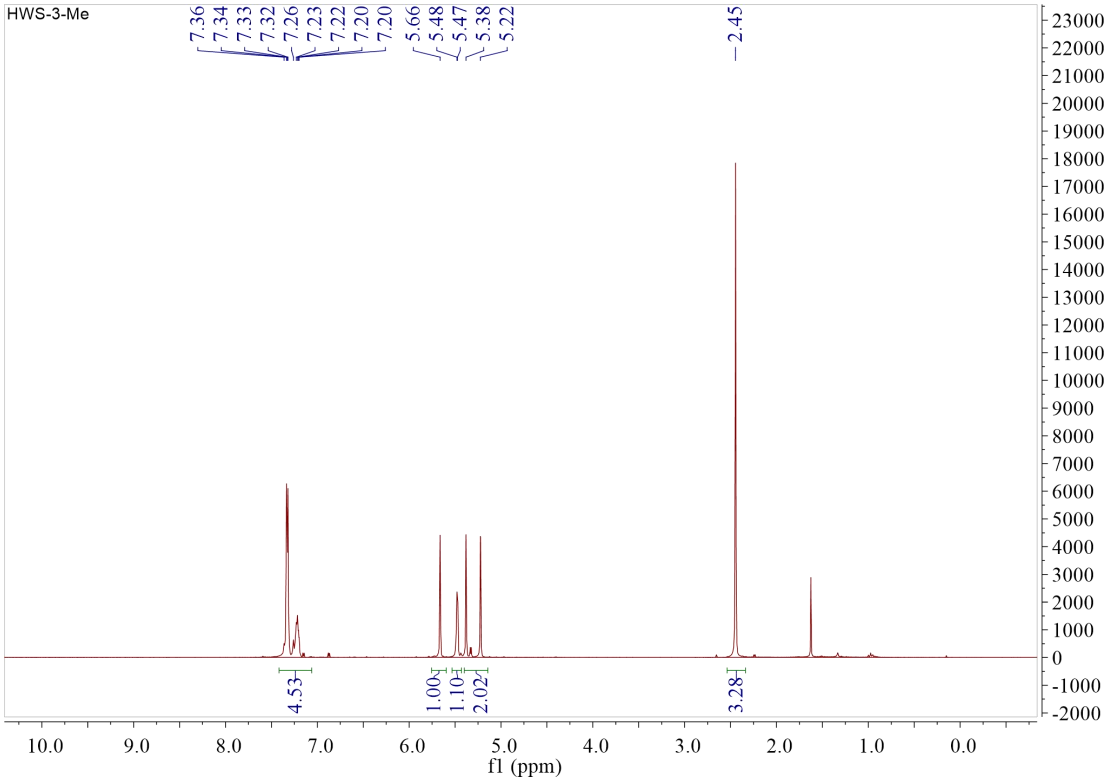
2f

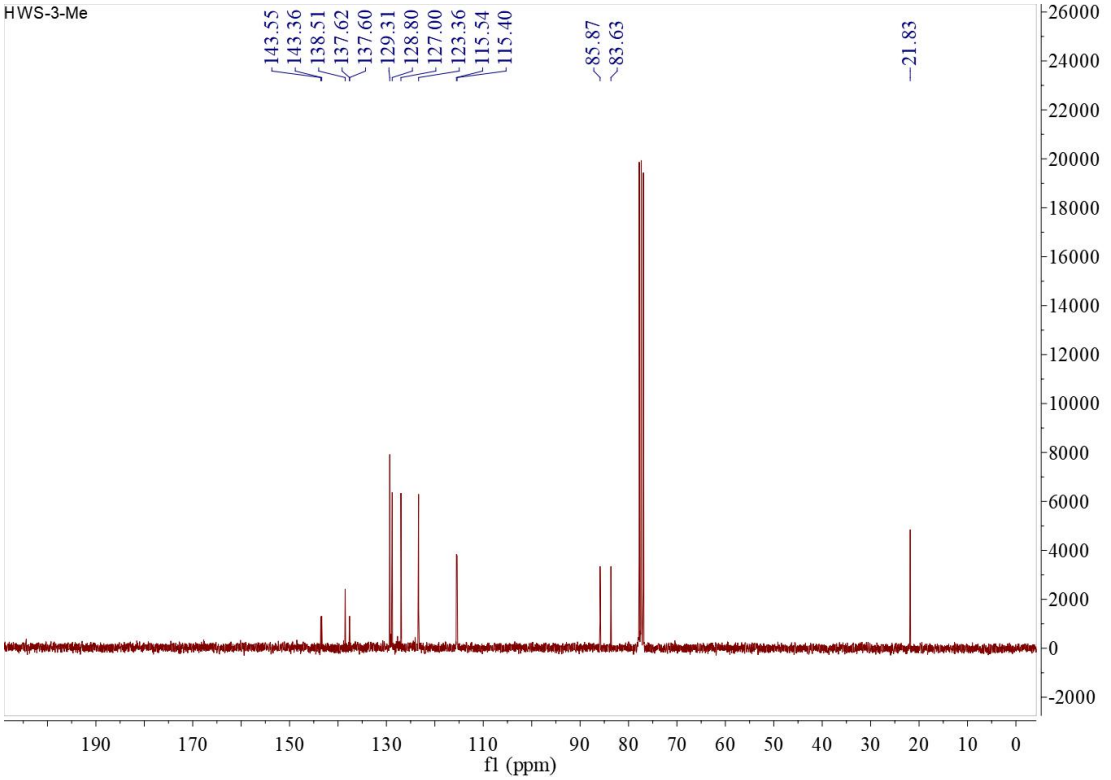

HWS-2-Cl
7.39 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.34 7.26 7.24 7.24 7.23
5.59 5.59 5.59 5.58 5.27 5.18 5.03
1.03 3.10 1.00 0.99 2.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

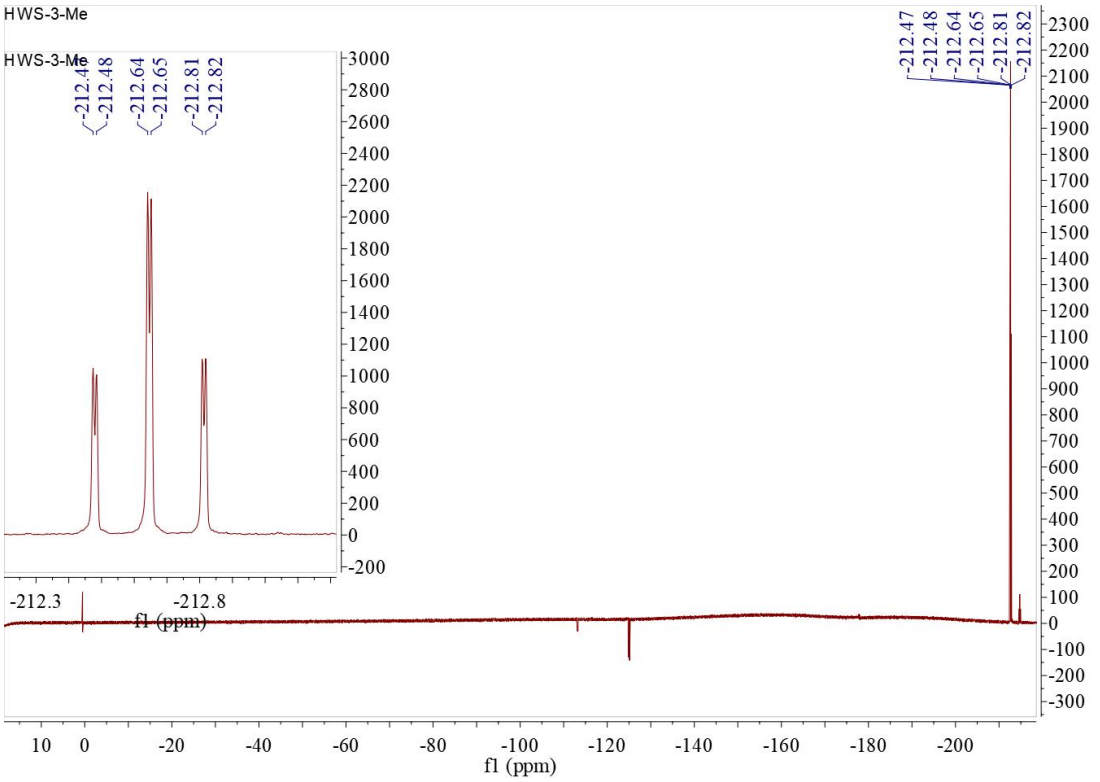

HWS-2-Cl
143.54
143.32
137.51
137.47
131.02
129.65
129.24
126.83
118.19
118.06
85.20
82.93
f1 (ppm)


HWS-2-Cl
-213.84
-213.84
-213.85
-213.85
-214.00
-214.01
-214.01
-214.02
-214.17
-214.17
-214.18
-214.18
f1 (ppm)

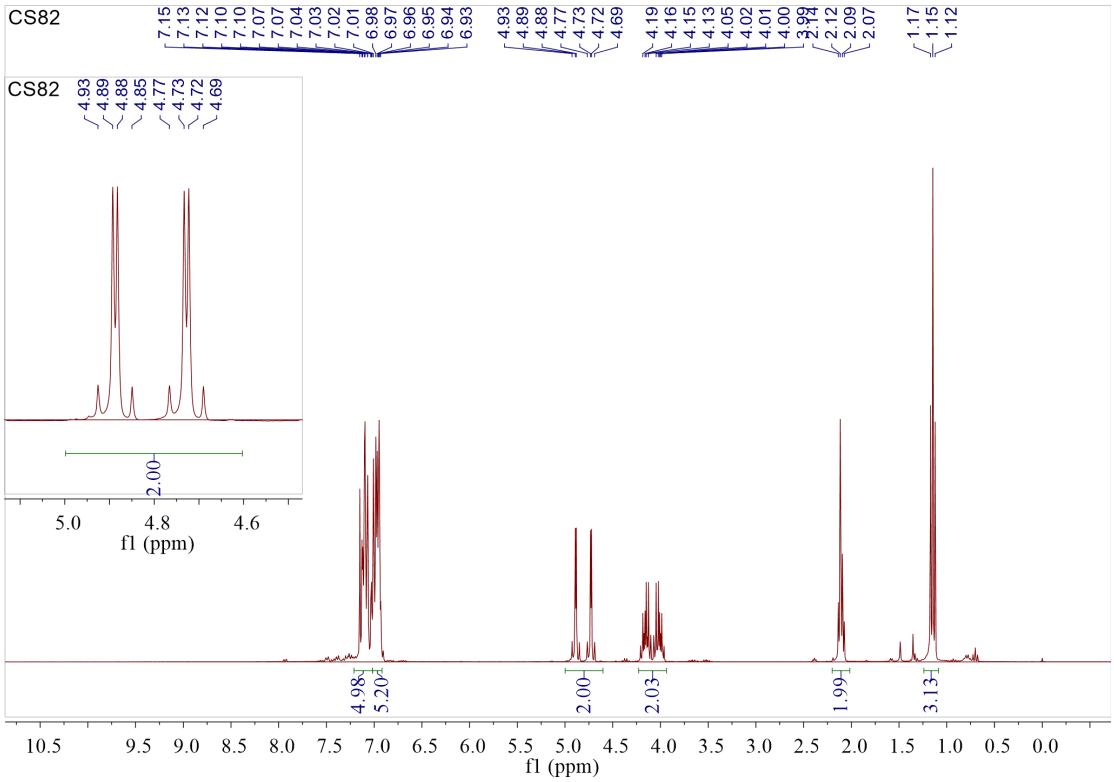
2g

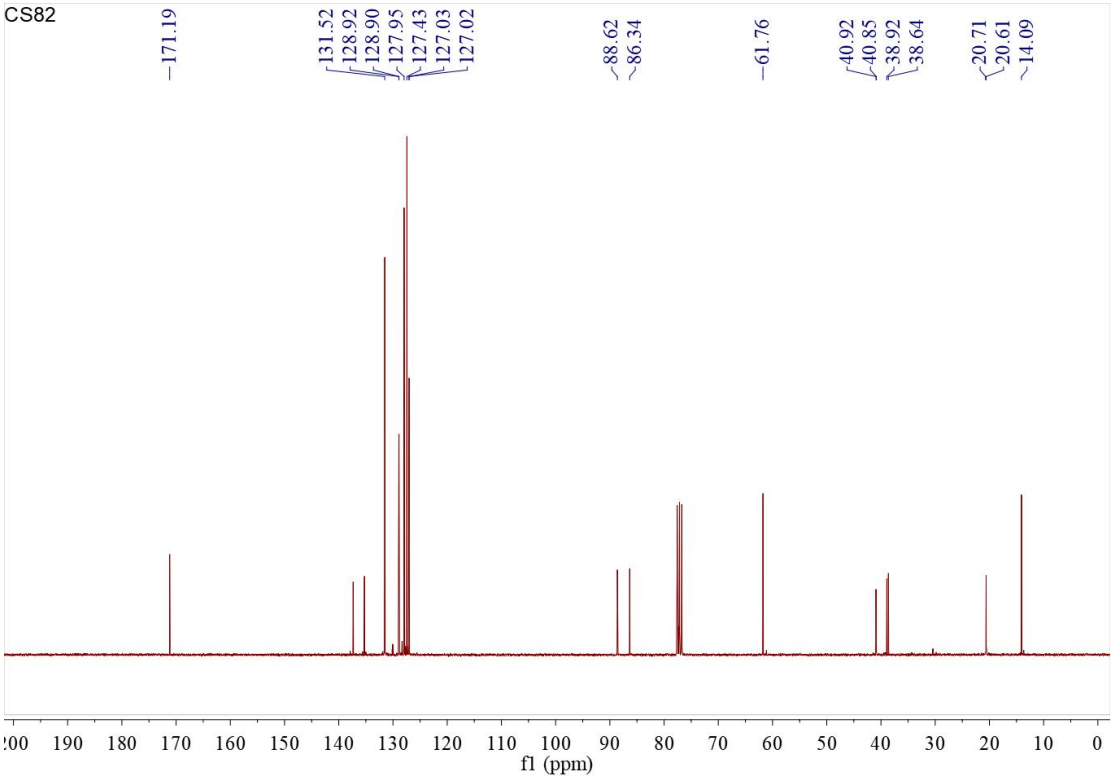

HWS-3-Me
7.36
7.34
7.33
7.32
7.26
7.23
7.22
7.20
7.20
5.66
5.48
5.47
5.38
5.22
2.45
4.53
1.00
1.10
2.02
3.28
fl (ppm)

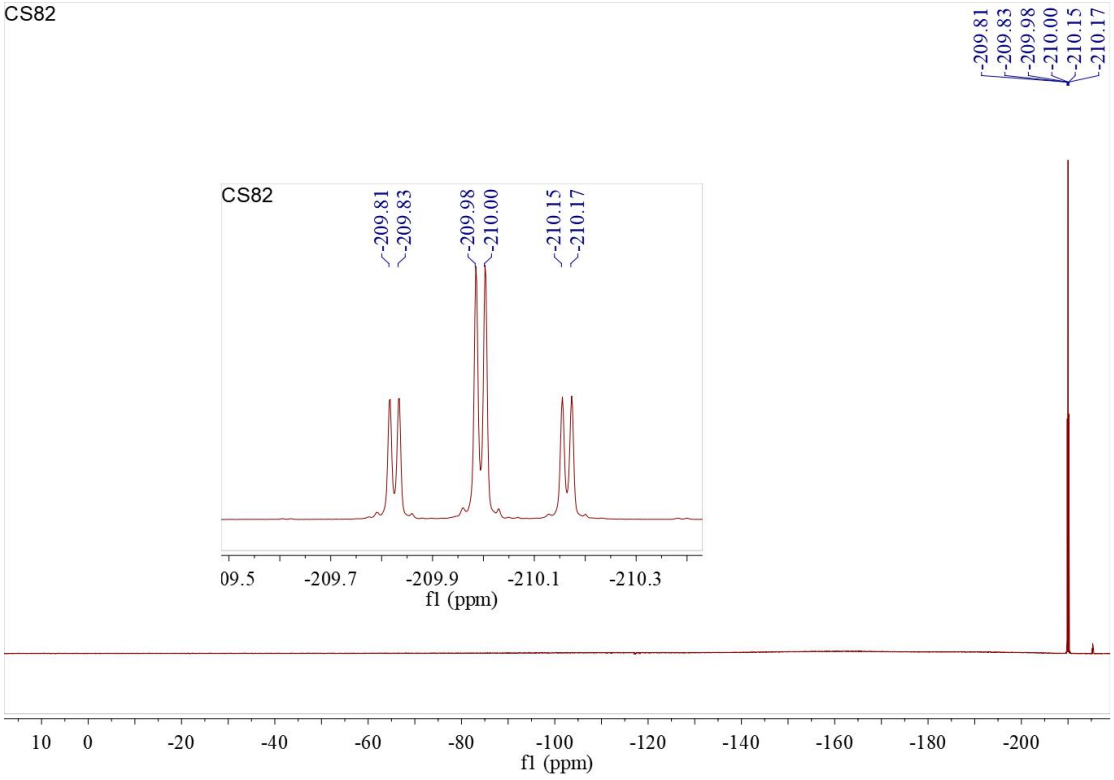

HWS-3-Me
143.55
143.36
138.51
137.62
137.60
129.31
128.80
127.00
123.36
115.54
115.40
85.87
83.63
21.83
fl (ppm)


HWS-3-Me
HWS-3-Me
-212.48
-212.64
-212.65
-212.81
-212.82
-212.47
-212.48
-212.64
-212.65
-212.81
-212.82
-212.3
-212.8
f1 (ppm)
f1 (ppm)

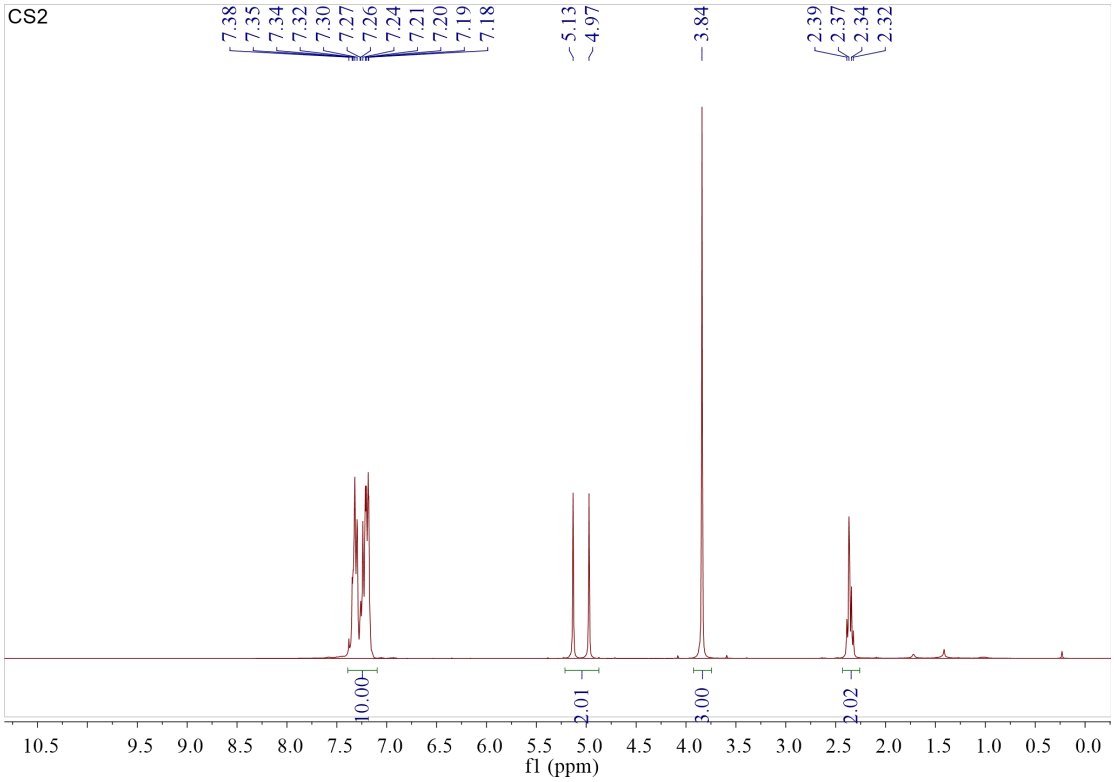
3a

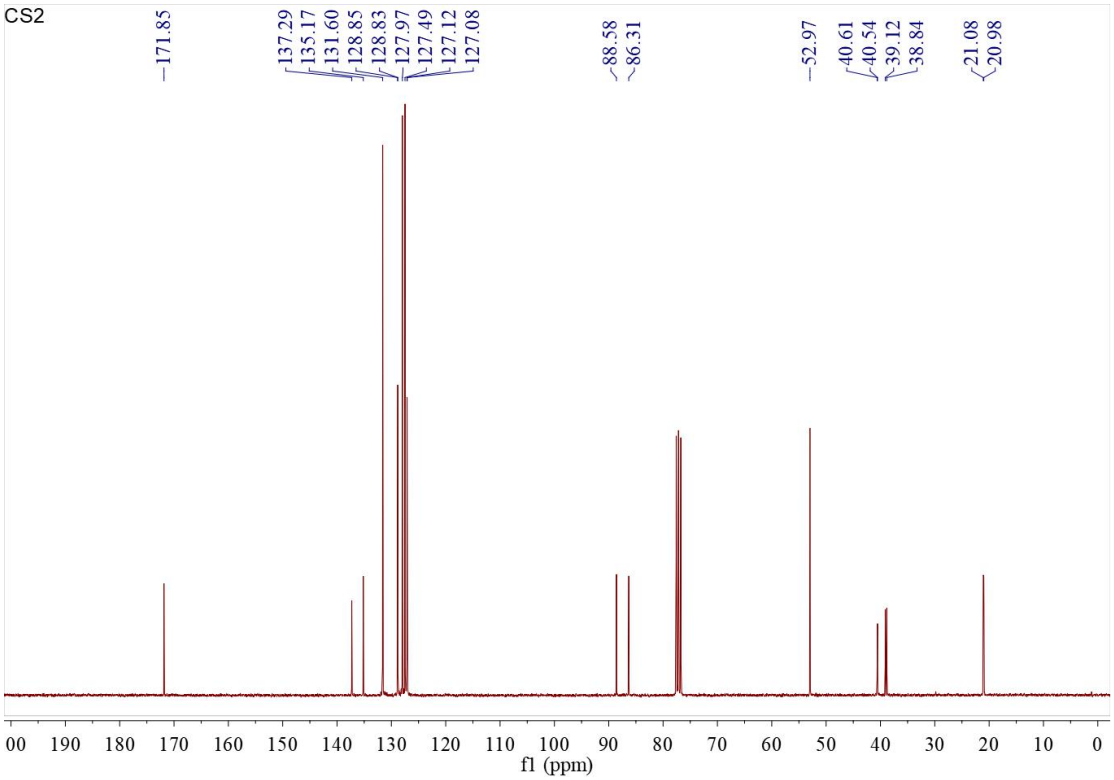

CS82
CS82
7.15
7.13
7.12
7.10
7.10
7.07
7.07
7.04
7.03
7.02
7.01
6.98
6.97
6.96
6.95
6.94
6.93
4.93
4.89
4.88
4.77
4.73
4.72
4.69
4.19
4.16
4.15
4.13
4.05
4.02
4.01
4.00
2.14
2.12
2.09
2.07
1.17
1.15
1.12
2.00
f1 (ppm)
4.98
5.20
2.00
2.03
1.99
3.13
f1 (ppm)

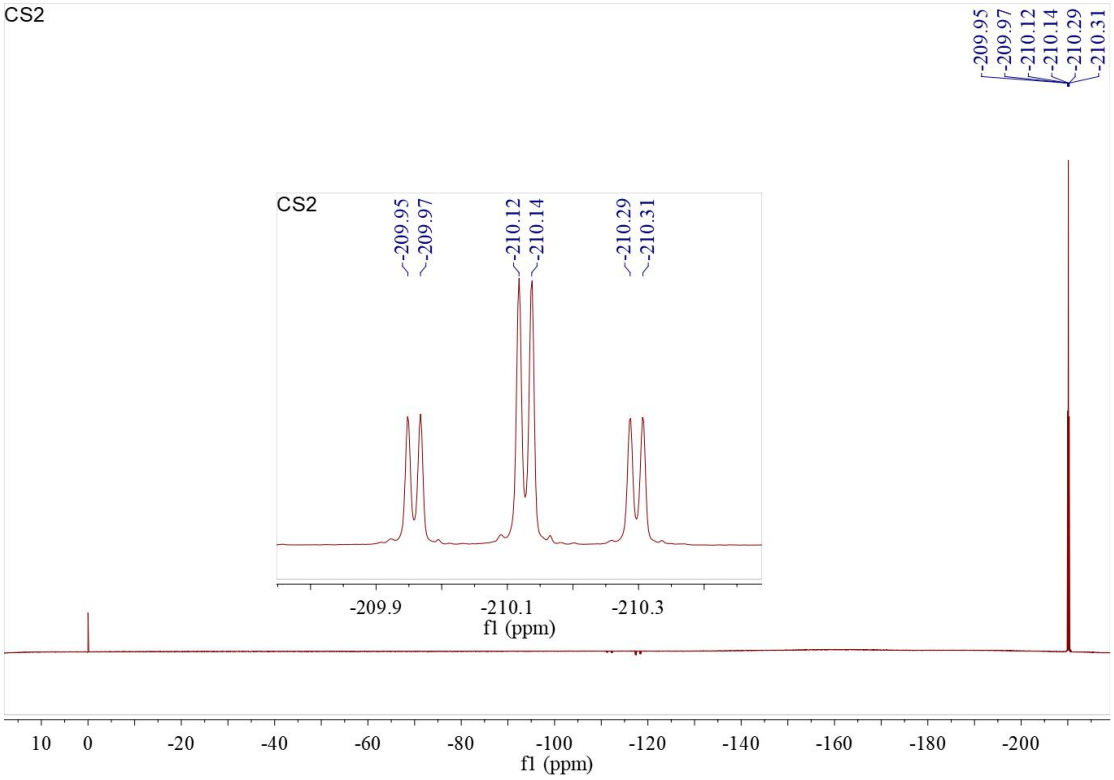

CS82
171.19
131.52
128.92
128.90
127.95
127.43
127.03
127.02
88.62
86.34
61.76
40.92
40.85
38.92
38.64
20.71
20.61
14.09
fl (ppm)


CS82
209.81
209.83
209.98
210.00
210.15
210.17
CS82
209.81
209.83
209.98
210.00
210.15
210.17
fl (ppm)
fl (ppm)

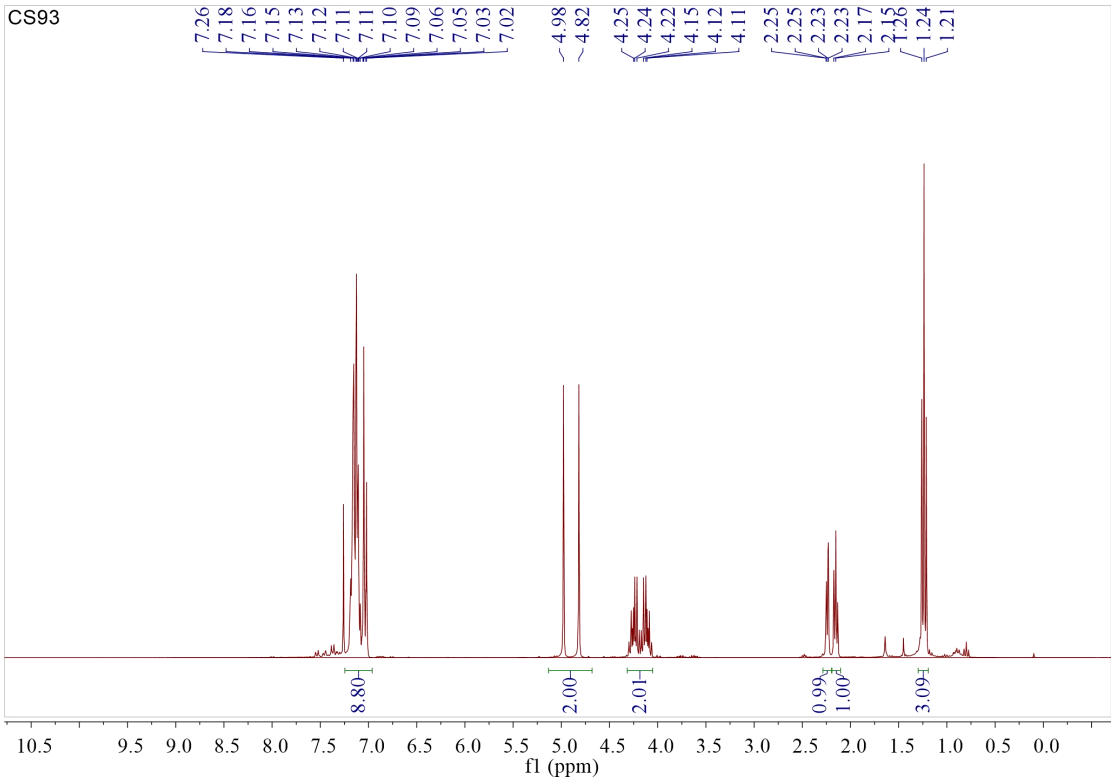
3b

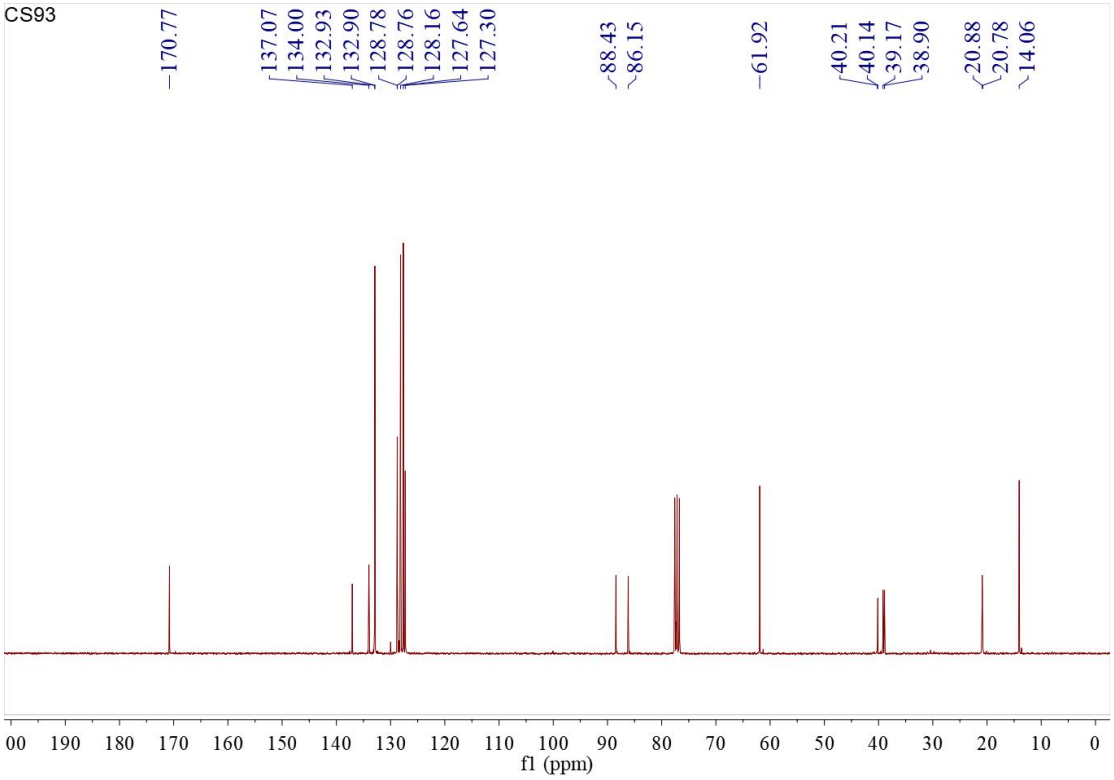

CS2
7.38
7.35
7.34
7.32
7.30
7.27
7.26
7.24
7.21
7.20
7.19
7.18
5.13
4.97
3.84
2.39
2.37
2.34
2.32
10.00
2.01
3.00
2.02
f1 (ppm)

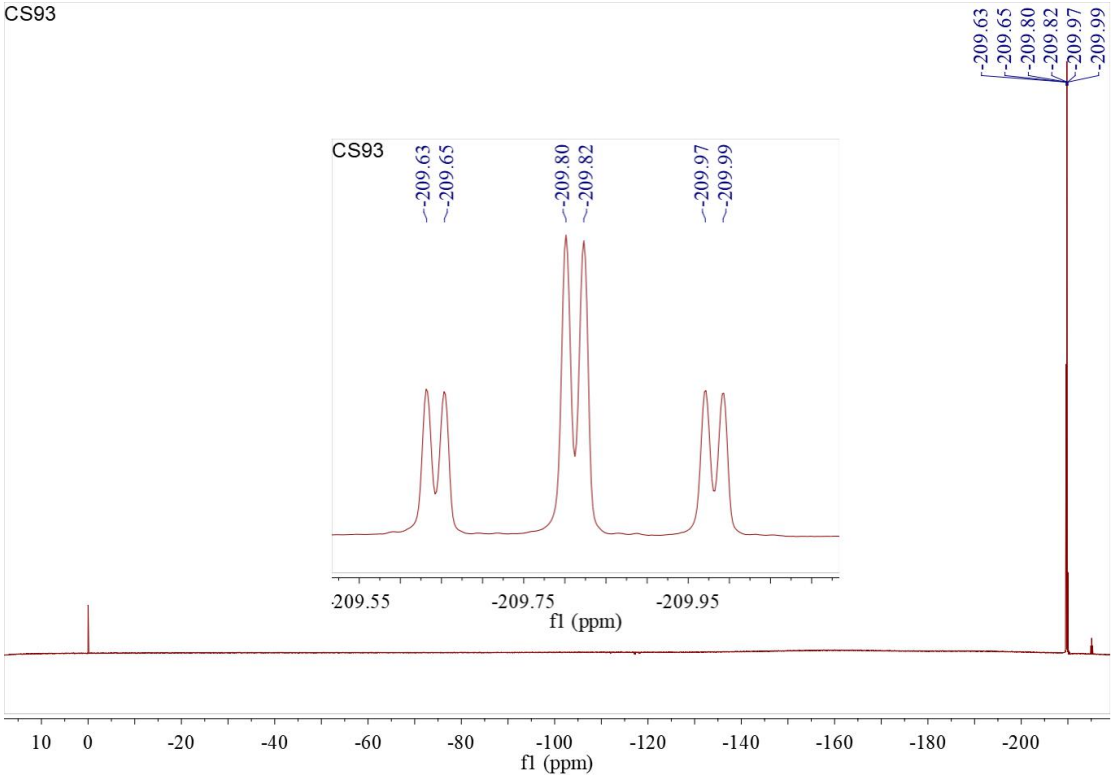

CS2
171.85
137.29
135.17
131.60
128.85
128.83
127.97
127.49
127.12
127.08
88.58
86.31
52.97
40.61
40.54
39.12
38.84
21.08
20.98
f1 (ppm)


CS2
-209.95
-209.97
-210.12
-210.14
-210.29
-210.31
CS2
-209.95
-209.97
-210.12
-210.14
-210.29
-210.31
-209.9
-210.1
-210.3
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

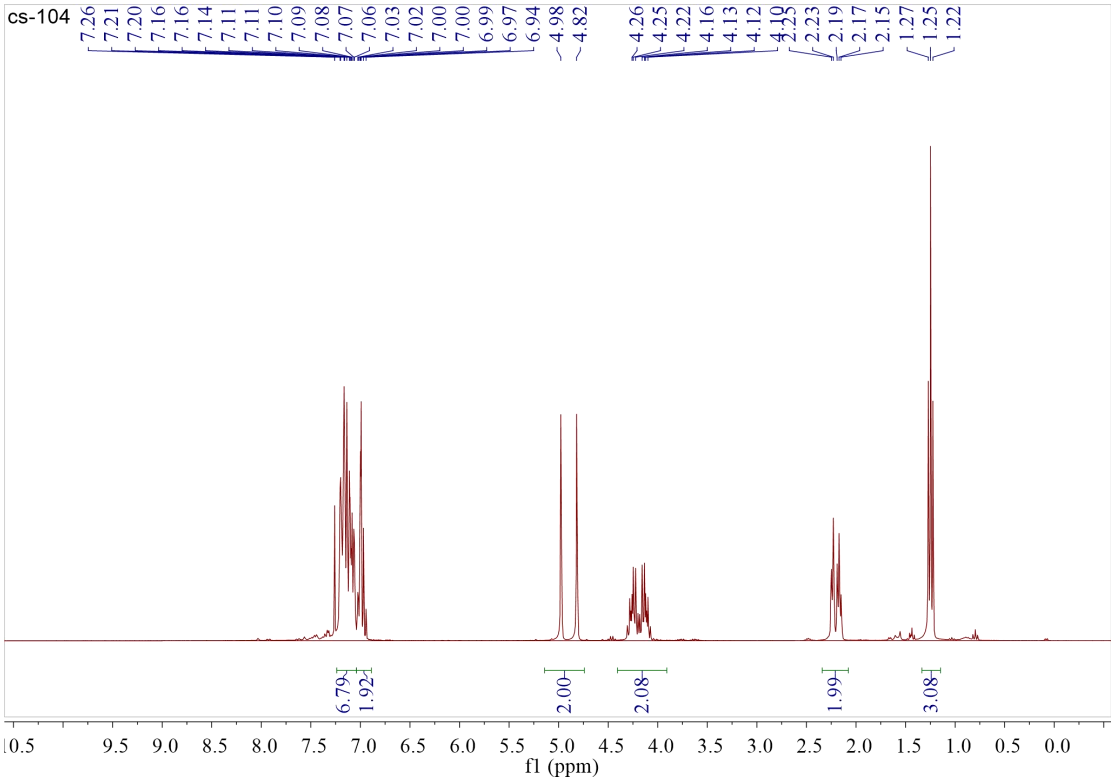
3c

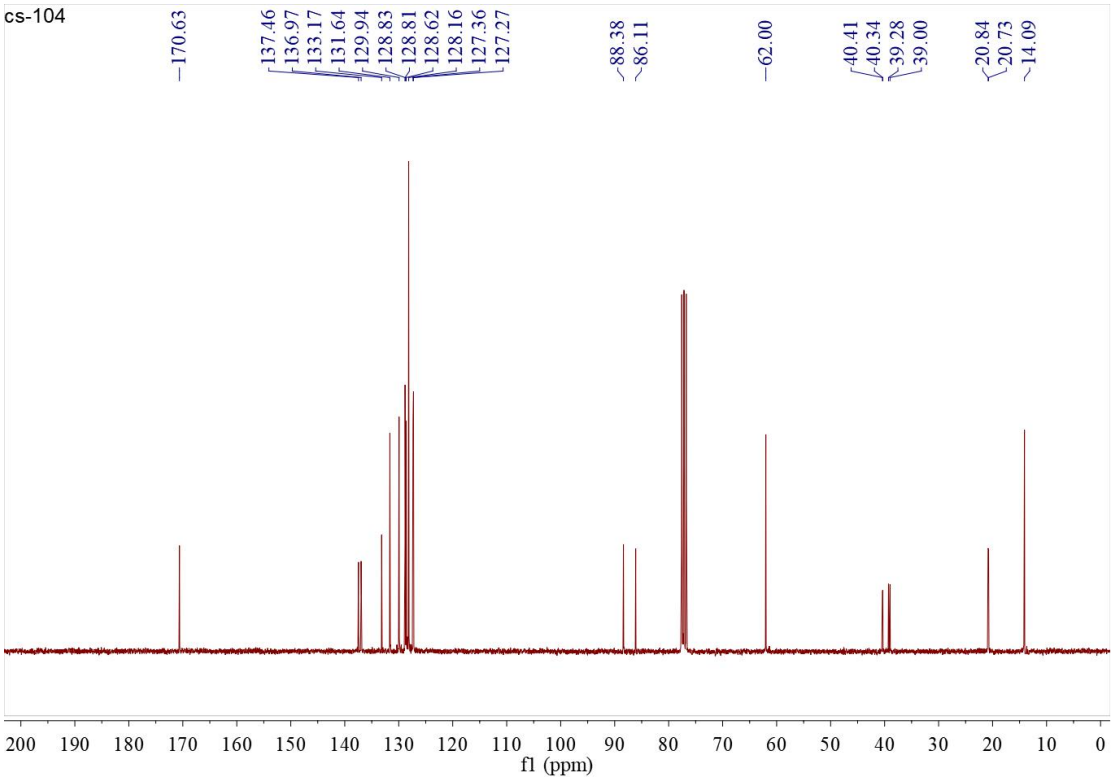

CS93
7.26
7.18
7.16
7.15
7.13
7.12
7.11
7.11
7.10
7.09
7.06
7.05
7.03
7.02
4.98
4.82
4.25
4.24
4.22
4.15
4.12
4.11
2.25
2.25
2.23
2.23
2.17
2.15
1.26
1.24
1.21
8.80
2.00
2.01
0.99
1.00
3.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

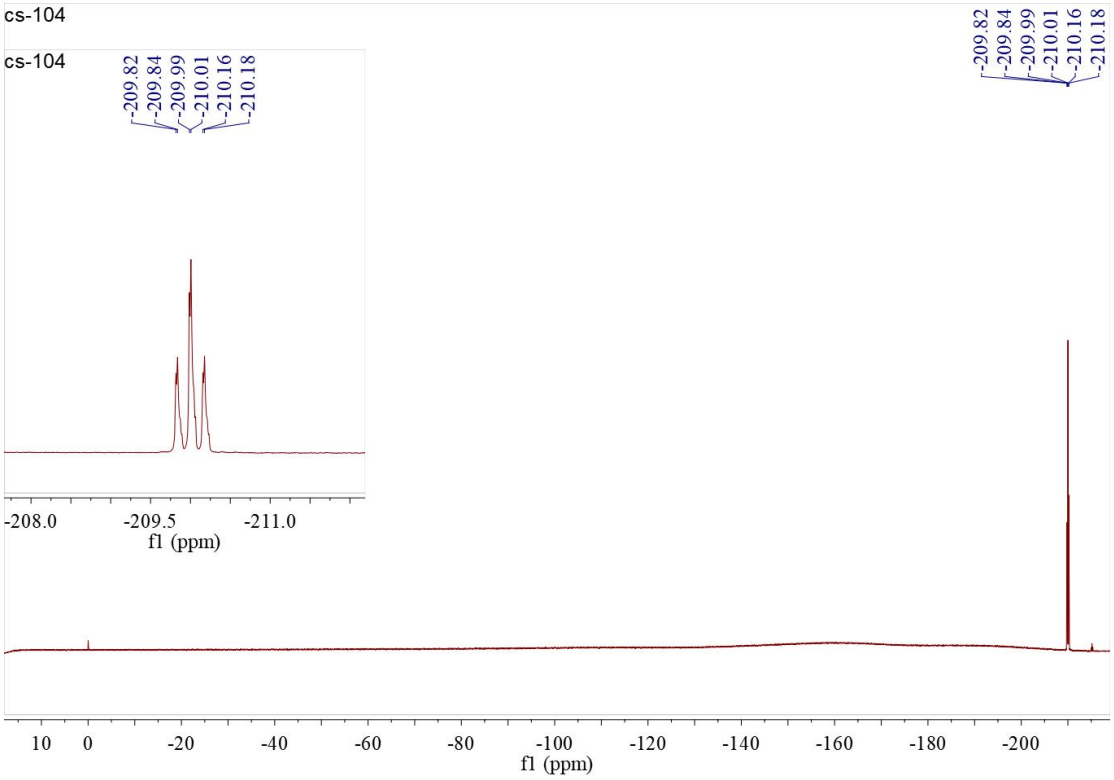

CS93
170.77
137.07
134.00
132.93
132.90
128.78
128.76
128.16
127.64
127.30
88.43
86.15
61.92
40.21
40.14
39.17
38.90
20.88
20.78
14.06
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CS93
-209.63
-209.65
-209.80
-209.82
-209.97
-209.99
CS93
-209.63
-209.65
-209.80
-209.82
-209.97
-209.99
209.55
-209.75
-209.95
f1 (ppm)
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

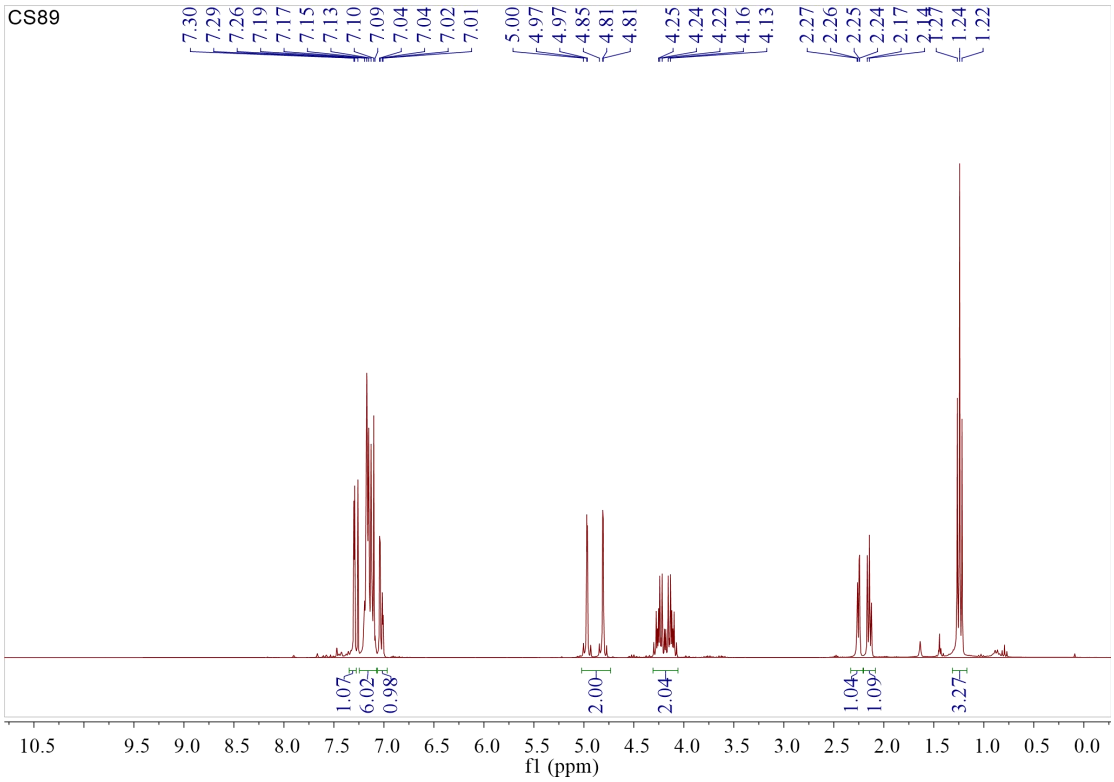
3d

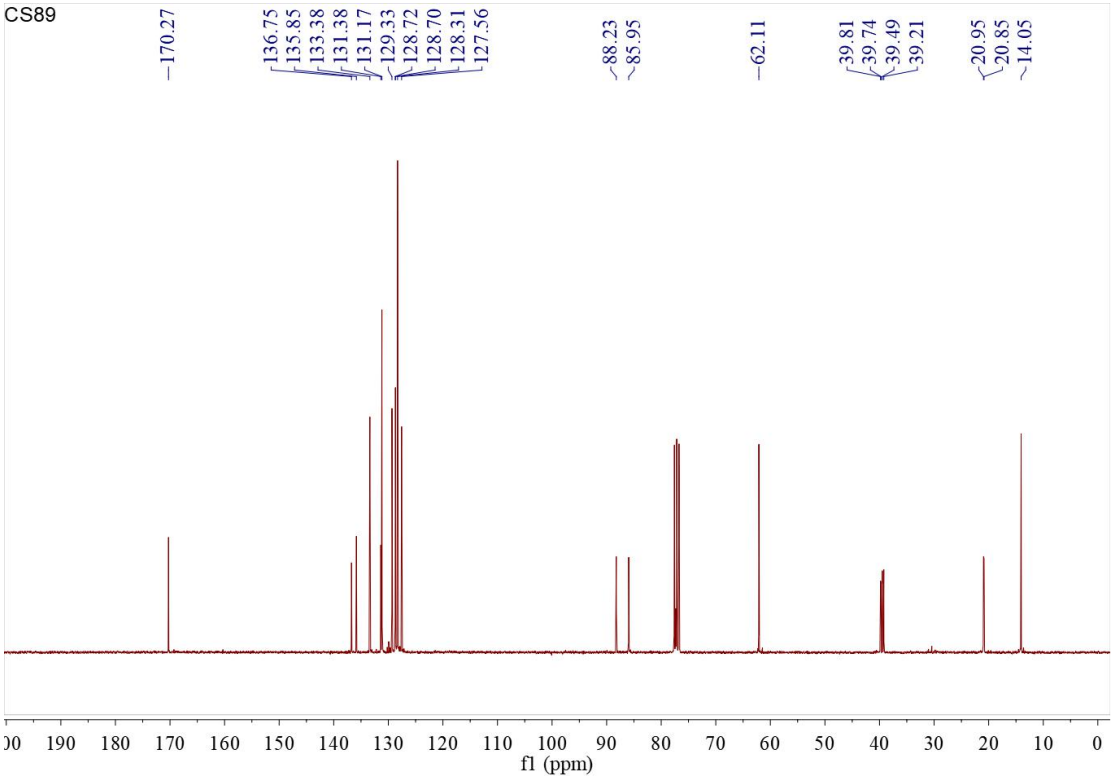

cs-104
7.26
7.21
7.20
7.16
7.16
7.14
7.11
7.11
7.10
7.09
7.08
7.07
7.06
7.03
7.02
7.00
7.00
6.99
6.97
6.94
4.98
4.82
4.26
4.25
4.22
4.16
4.13
4.12
4.10
2.25
2.23
2.19
2.17
2.15
1.27
1.25
1.22
6.79
1.92
2.00
2.08
1.99
3.08
fl (ppm)

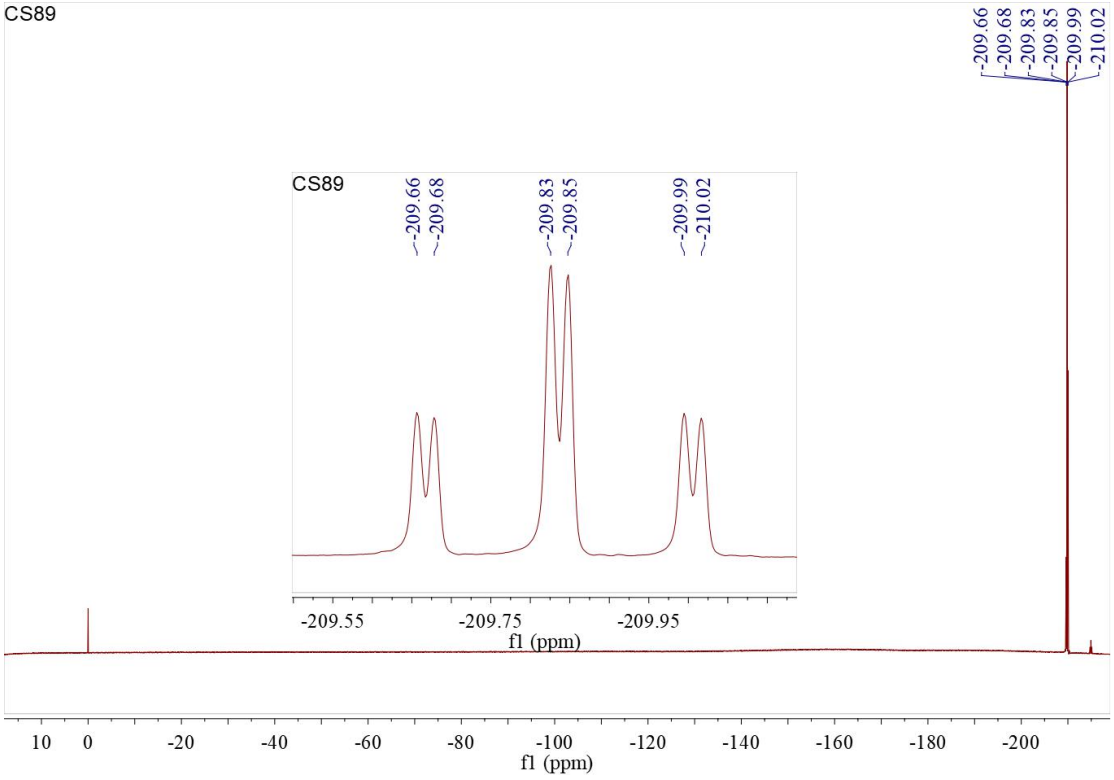

cs-104
170.63
137.46
136.97
133.17
131.64
129.94
128.83
128.81
128.62
128.16
127.36
127.27
88.38
86.11
62.00
40.41
40.34
39.28
39.00
20.84
20.73
14.09
fl (ppm)


cs-104
cs-104
209.82
209.84
209.99
210.01
210.16
210.18
-208.0
-209.5
-211.0
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

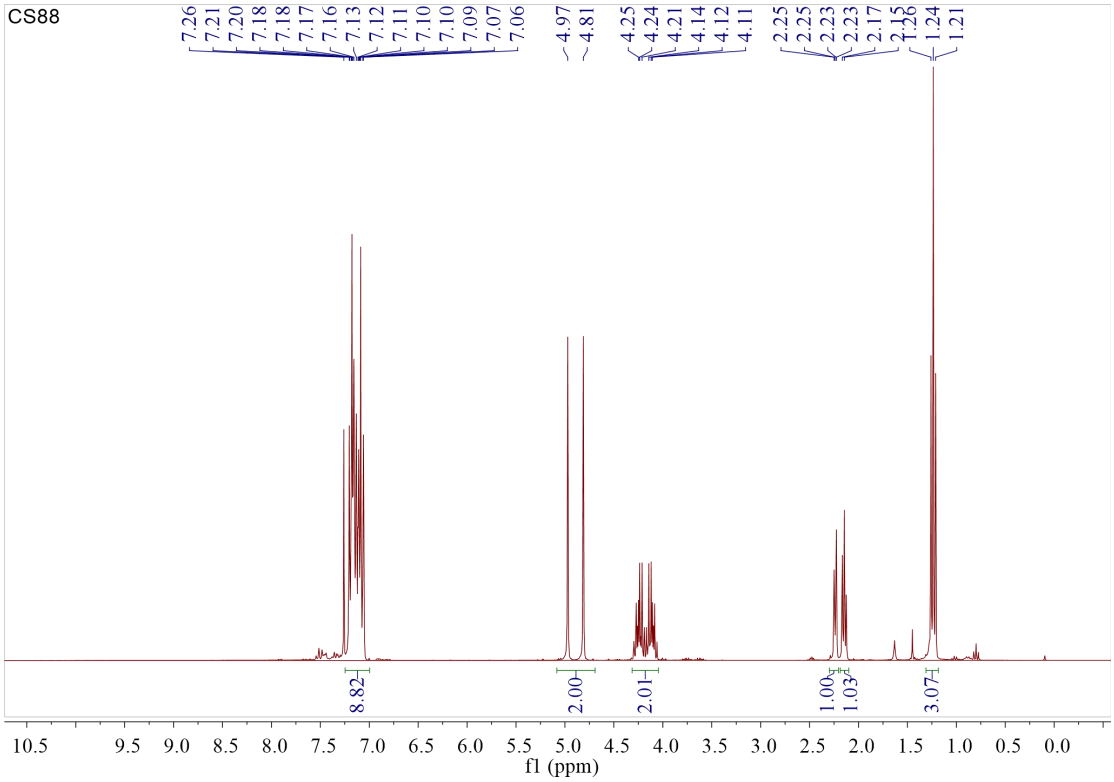
3e

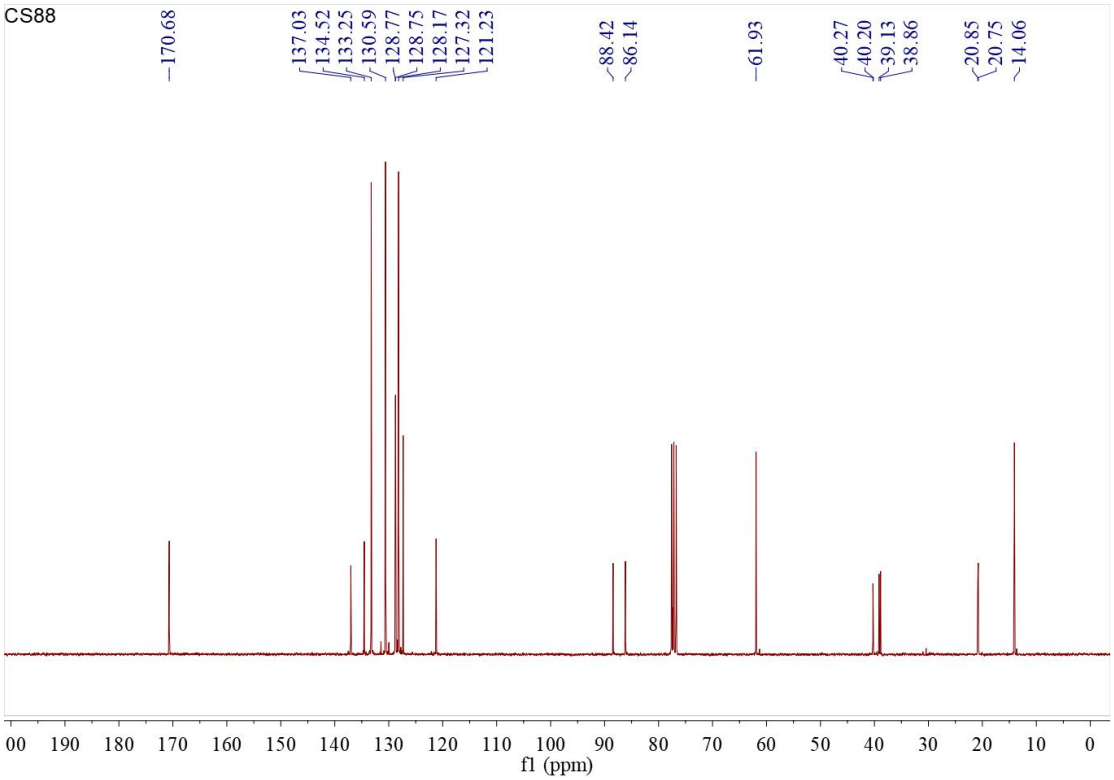

CS89
7.30
7.29
7.26
7.19
7.17
7.15
7.13
7.10
7.09
7.04
7.04
7.02
7.01
5.00
4.97
4.97
4.85
4.81
4.81
4.25
4.24
4.22
4.16
4.13
2.27
2.26
2.25
2.24
2.17
1.24
1.22
1.07
6.02
0.98
2.00
2.04
1.04
1.09
3.27
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

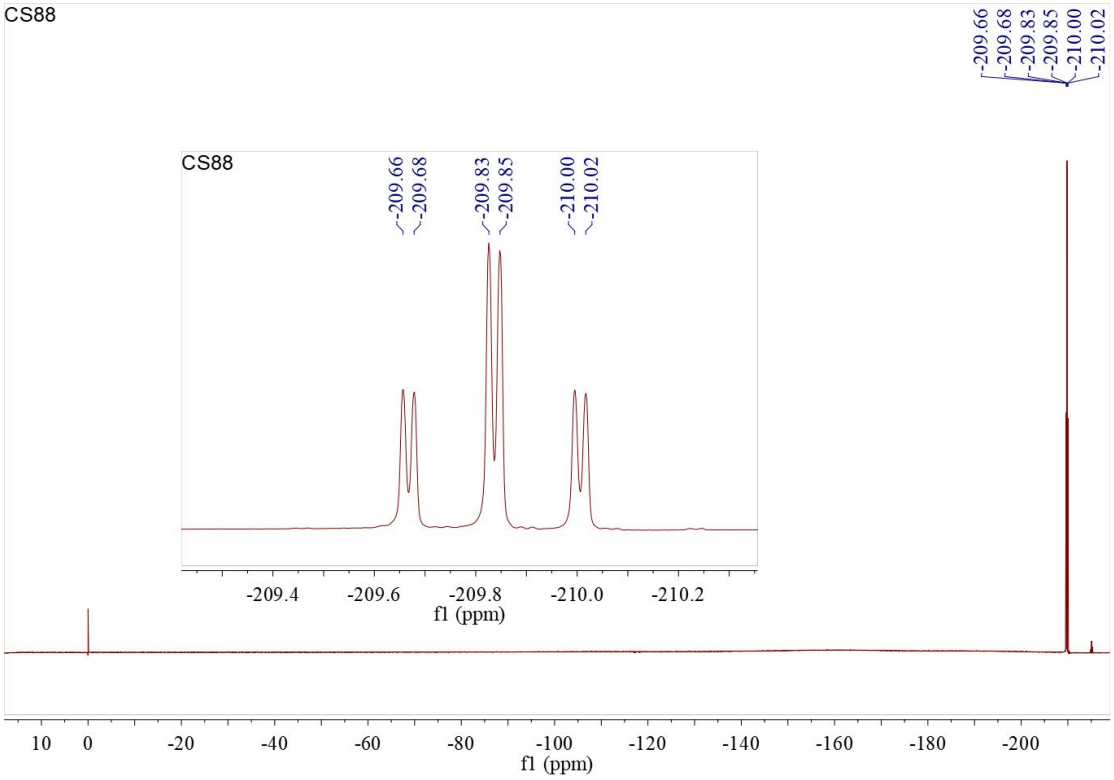

CS89
170.27
136.75
135.85
133.38
131.38
131.17
129.33
128.72
128.70
128.31
127.56
88.23
85.95
62.11
39.81
39.74
39.49
39.21
20.95
20.85
14.05
f1 (ppm)


CS89
-209.66
-209.68
-209.83
-209.85
-209.99
-210.02
CS89
-209.55
-209.75
-209.95
f1 (ppm)
f1 (ppm)

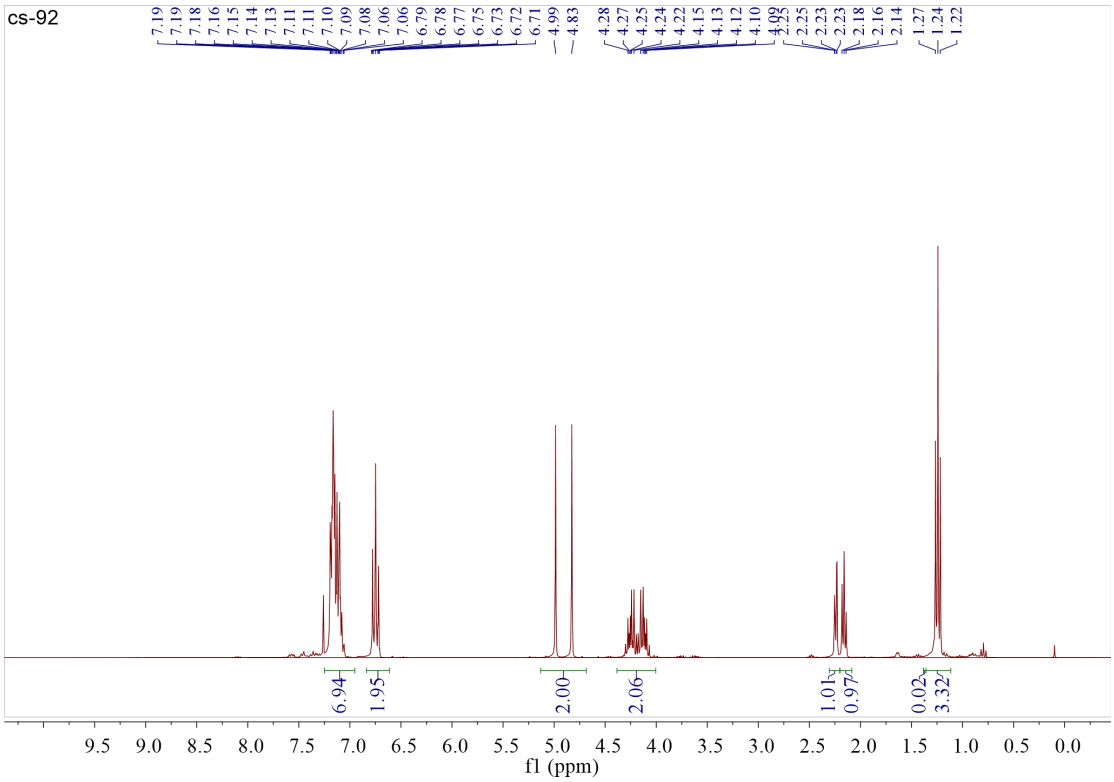
3f

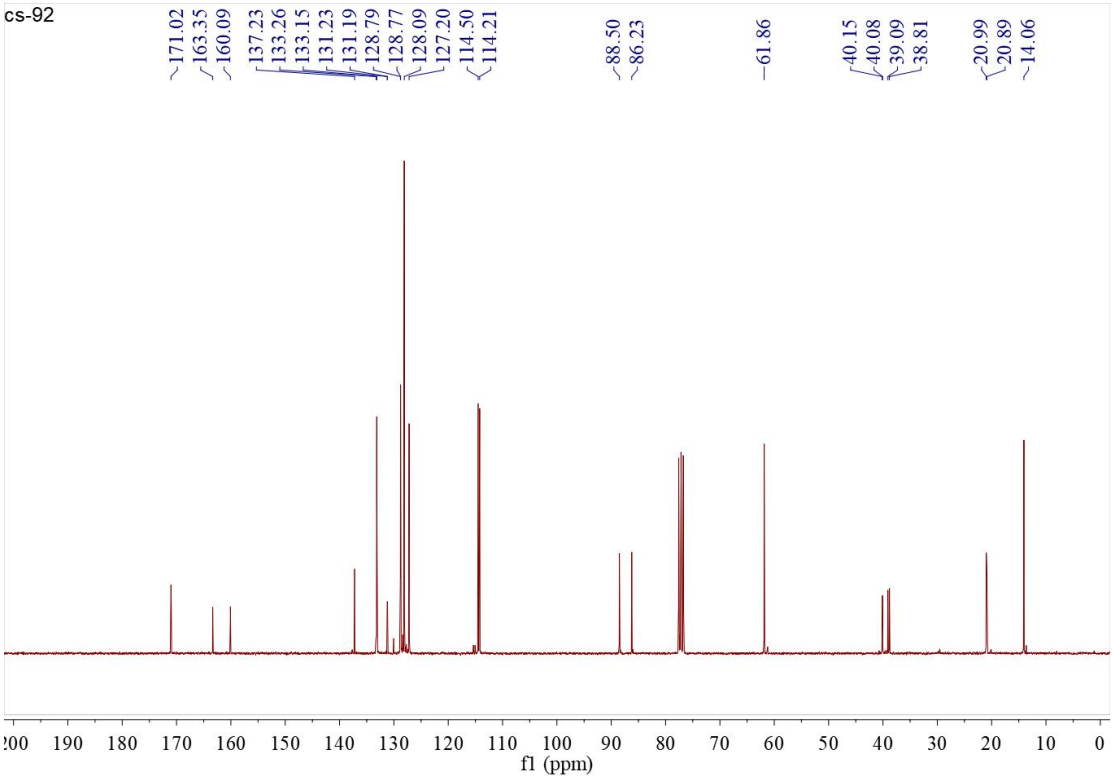

CS88
7.26
7.21
7.20
7.18
7.18
7.17
7.16
7.13
7.12
7.11
7.10
7.10
7.09
7.07
7.06
4.97
4.81
4.25
4.24
4.21
4.14
4.12
4.11
2.25
2.25
2.23
2.23
2.17
2.15
1.26
1.24
1.21
8.82
2.00
2.01
1.00
1.03
3.07
f1 (ppm)

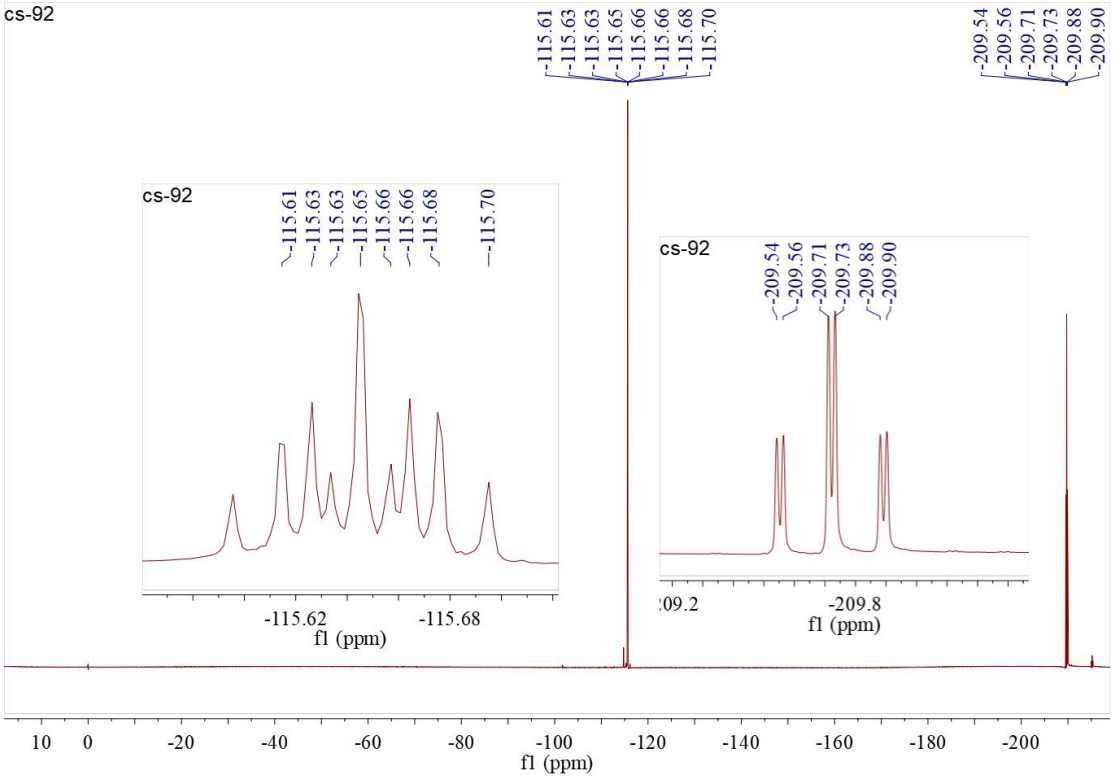

CS88
170.68
137.03
134.52
133.25
130.59
128.77
128.75
128.17
127.32
121.23
88.42
86.14
61.93
40.27
40.20
39.13
38.86
20.85
20.75
14.06
f1 (ppm)


CS88
-209.66
-209.68
-209.83
-209.85
-210.00
-210.02
CS88
-209.66
-209.68
-209.83
-209.85
-210.00
-210.02
-209.4
-209.6
-209.8
-210.0
-210.2
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

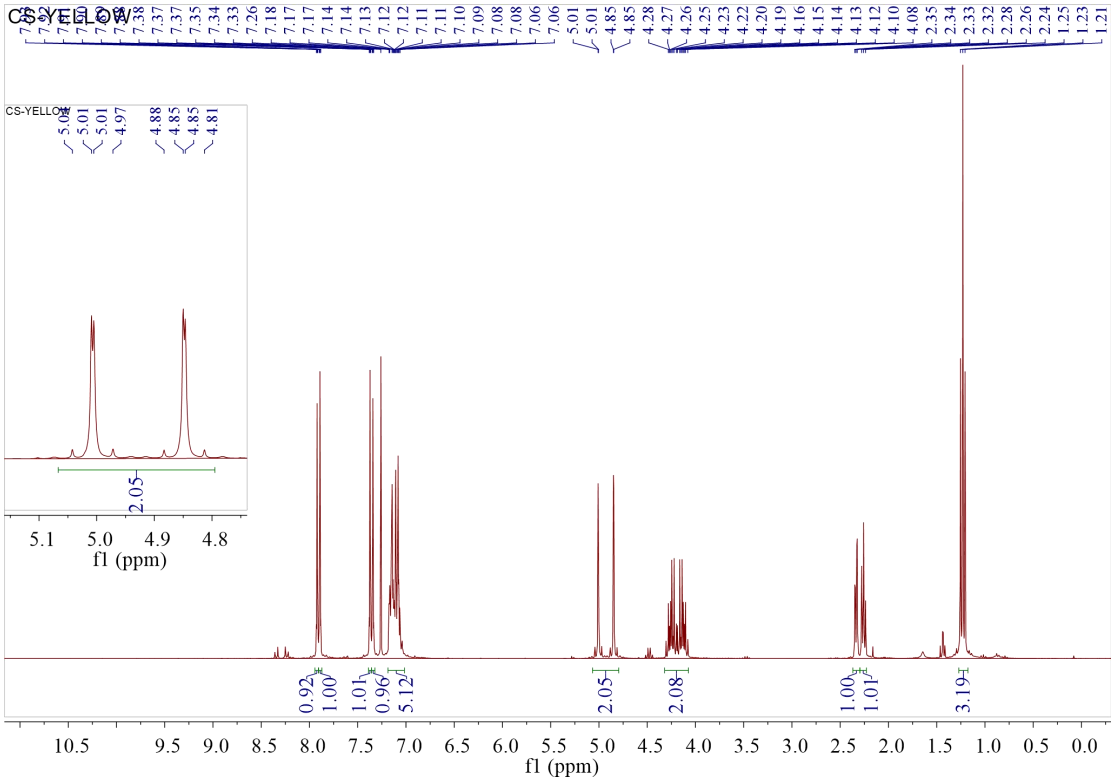
3g

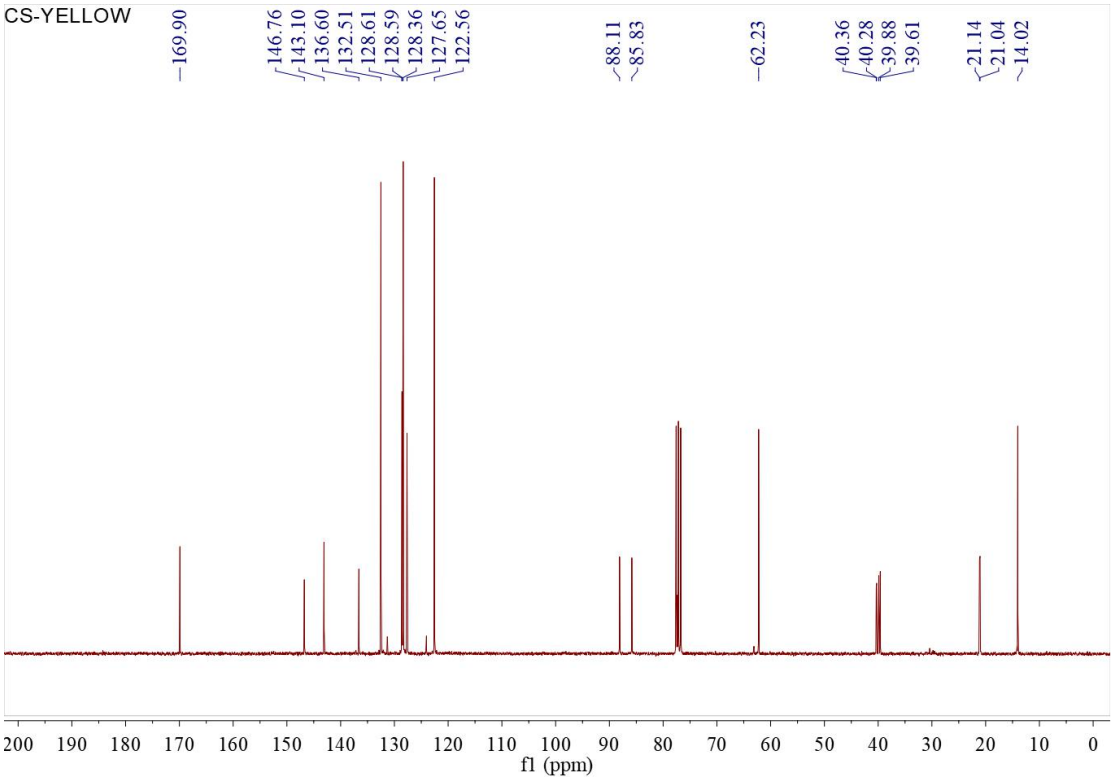

cs-92
7.19
7.19
7.18
7.16
7.15
7.14
7.13
7.11
7.11
7.10
7.09
7.08
7.06
7.06
6.79
6.78
6.77
6.75
6.73
6.72
6.71
4.99
4.83
4.28
4.27
4.25
4.24
4.22
4.15
4.13
4.12
4.10
2.25
2.23
2.23
2.18
2.16
2.14
1.27
1.24
1.22
6.94
1.95
2.00
2.06
1.01
0.97
0.02
3.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

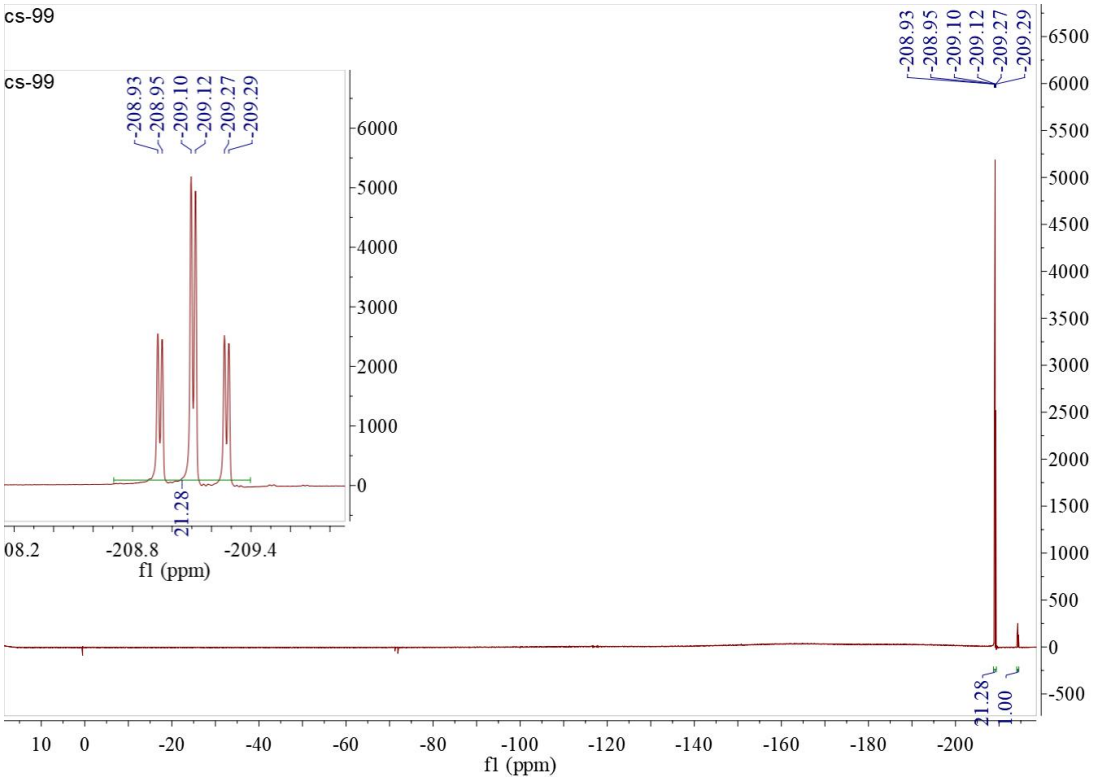

cs-92
171.02
163.35
160.09
137.23
133.26
133.15
131.23
131.19
128.79
128.77
128.09
127.20
114.50
114.21
88.50
86.23
61.86
40.15
40.08
39.09
38.81
20.99
20.89
14.06
f1 (ppm)


cs-92
-115.61
-115.63
-115.63
-115.65
-115.66
-115.66
-115.68
-115.70
-209.54
-209.56
-209.71
-209.73
-209.88
-209.90
-115.62
-115.68
f1 (ppm)
-209.8
f1 (ppm)
f1 (ppm)

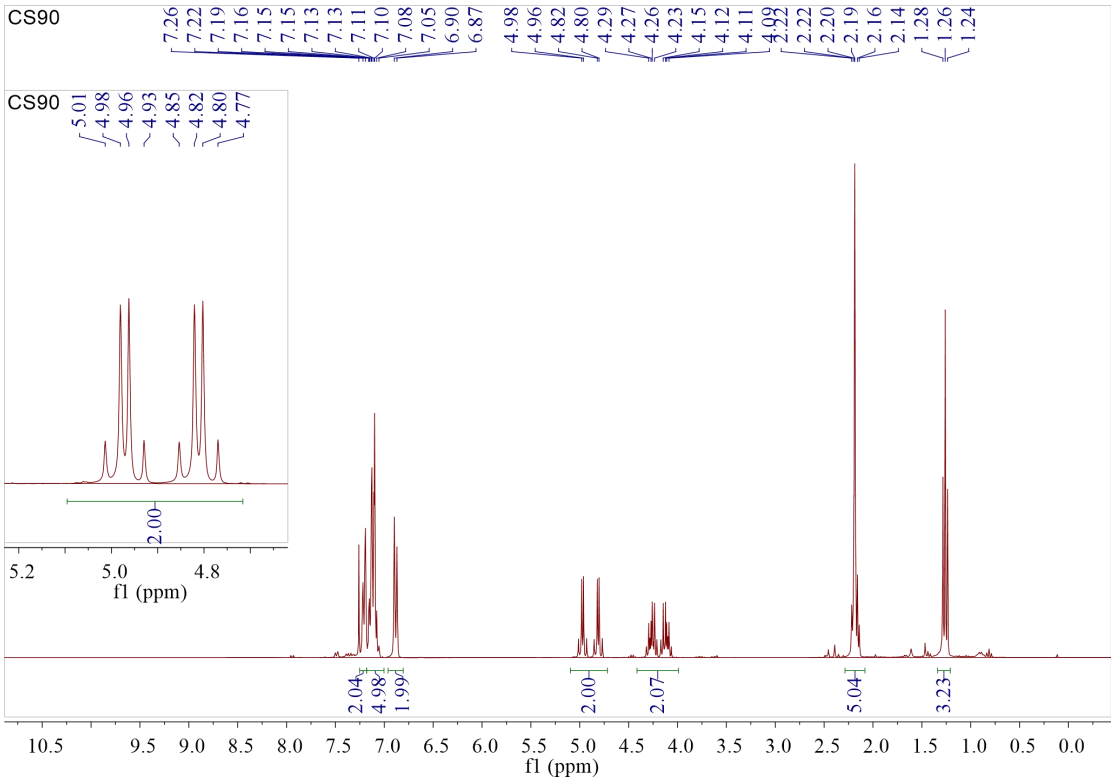
3h

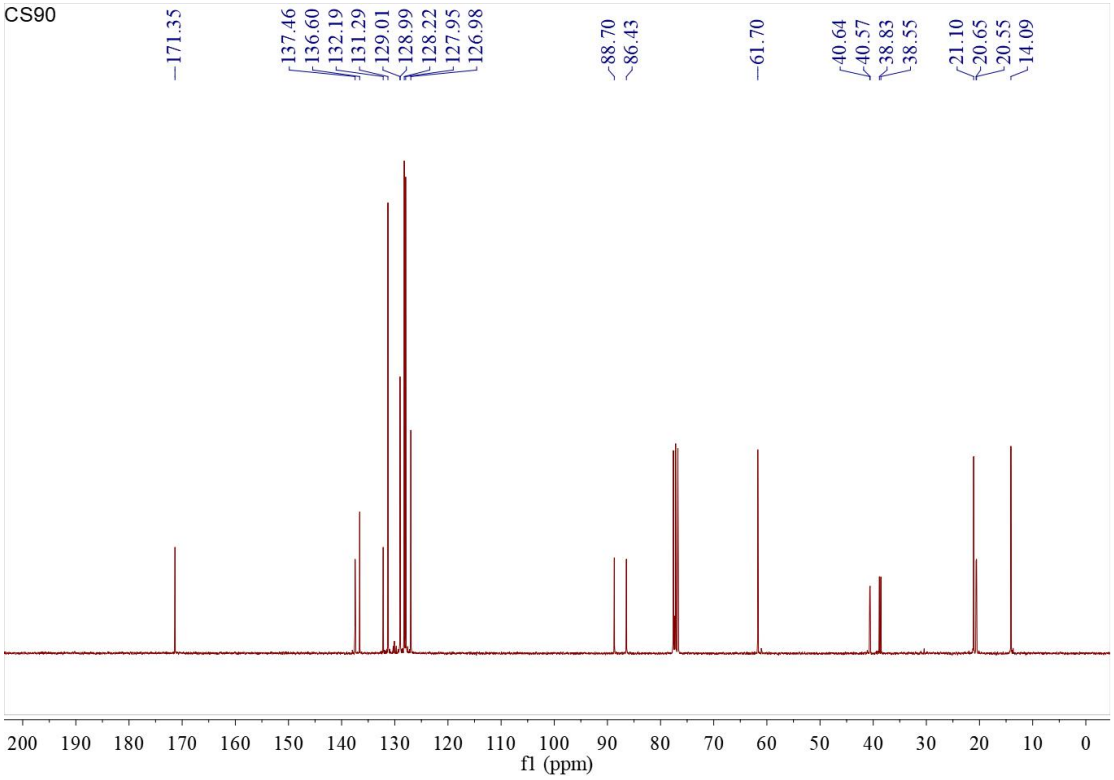


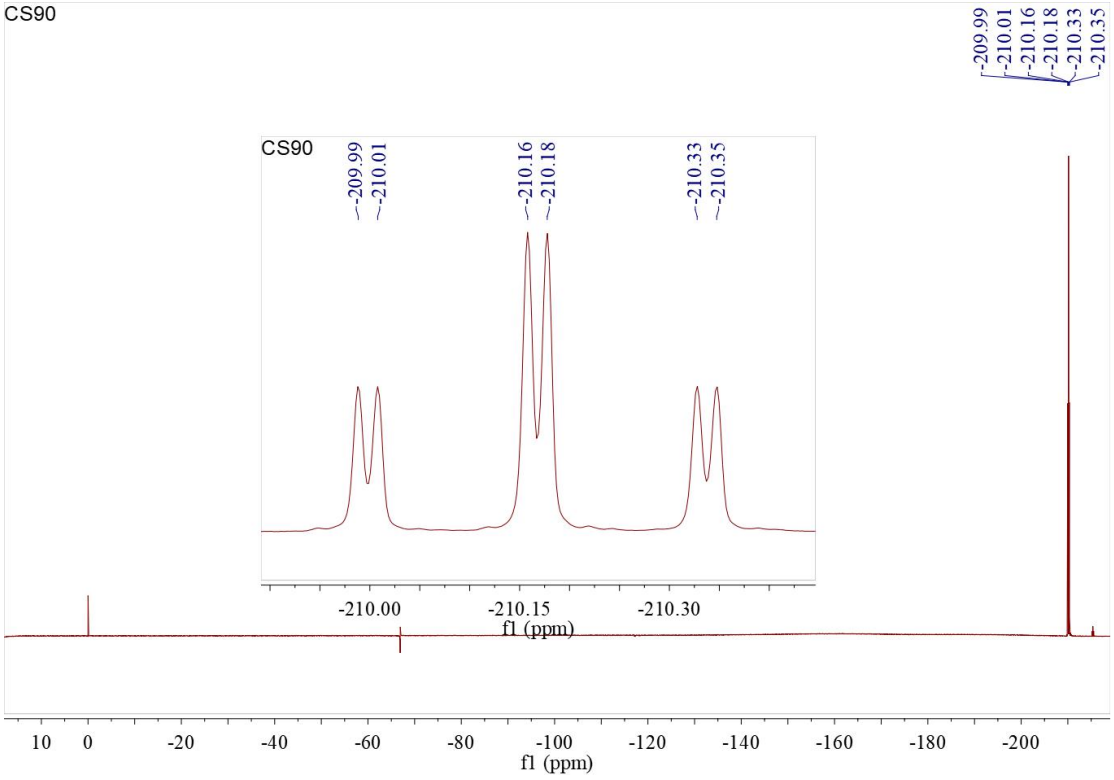



cs-99
cs-99
-208.93
-208.95
-209.10
-209.12
-209.27
-209.29
21.28
f1 (ppm)
21.28
1.00
f1 (ppm)

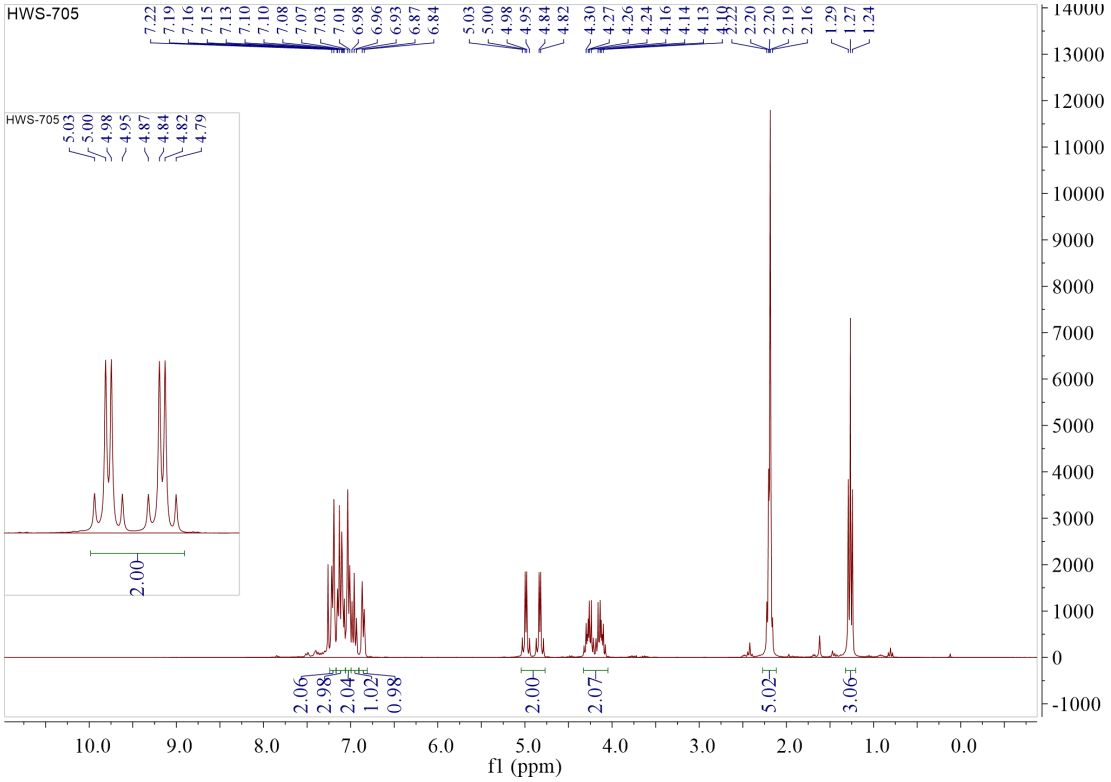
3i

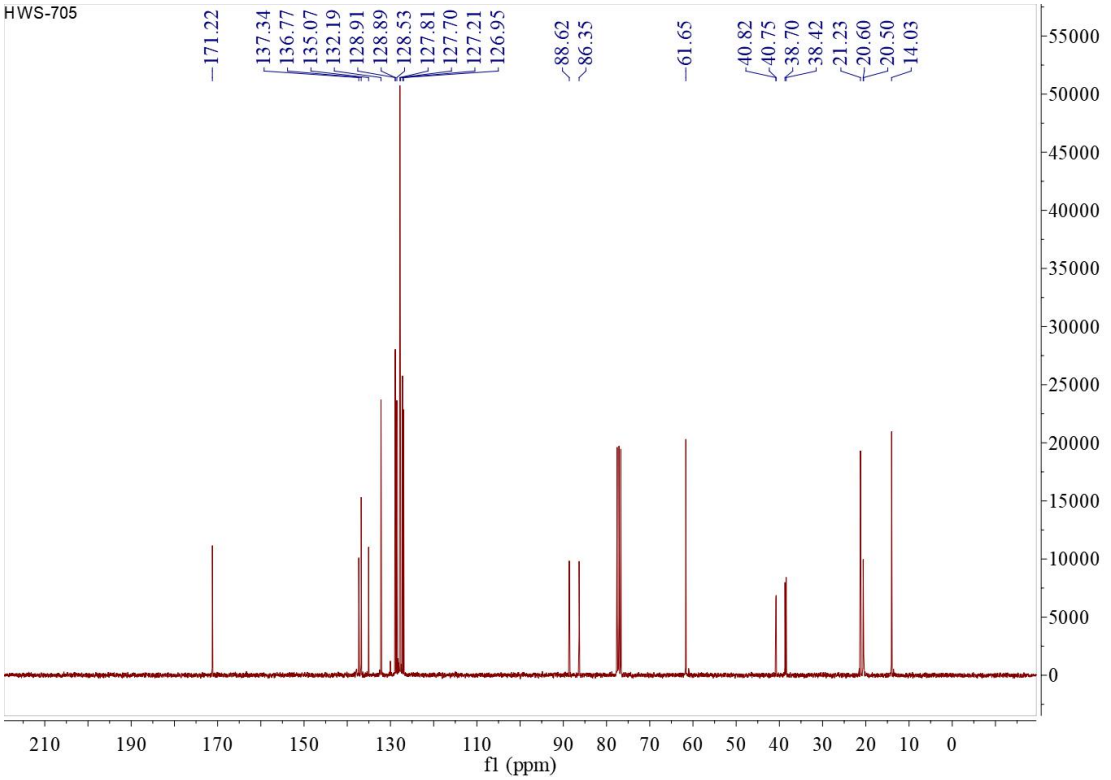

CS90
CS90
2.00
f1 (ppm)
2.04
4.98
1.99
2.00
2.07
5.04
3.23
f1 (ppm)

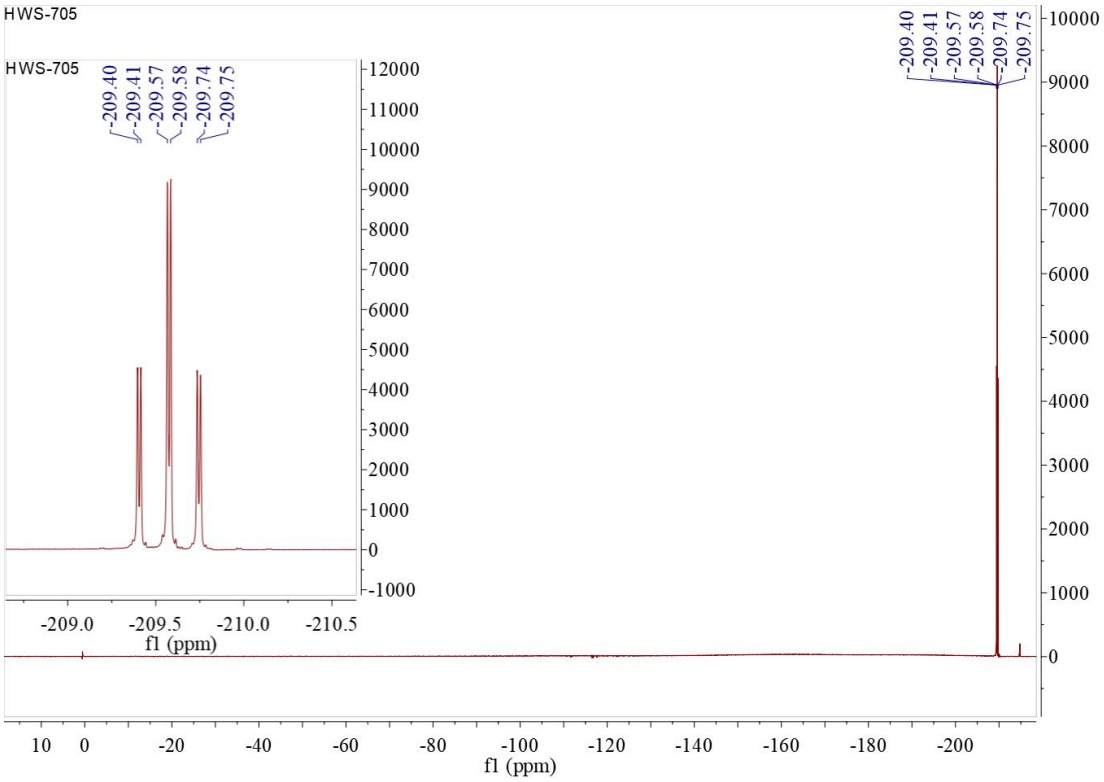

CS90
171.35
137.46
136.60
132.19
131.29
129.01
128.99
128.22
127.95
126.98
88.70
86.43
61.70
40.64
40.57
38.83
38.55
21.10
20.65
20.55
14.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CS90
-209.99
-210.01
-210.16
-210.18
-210.33
-210.35
CS90
-209.99
-210.01
-210.16
-210.18
-210.33
-210.35
-210.00
-210.15
-210.30
f1 (ppm)
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

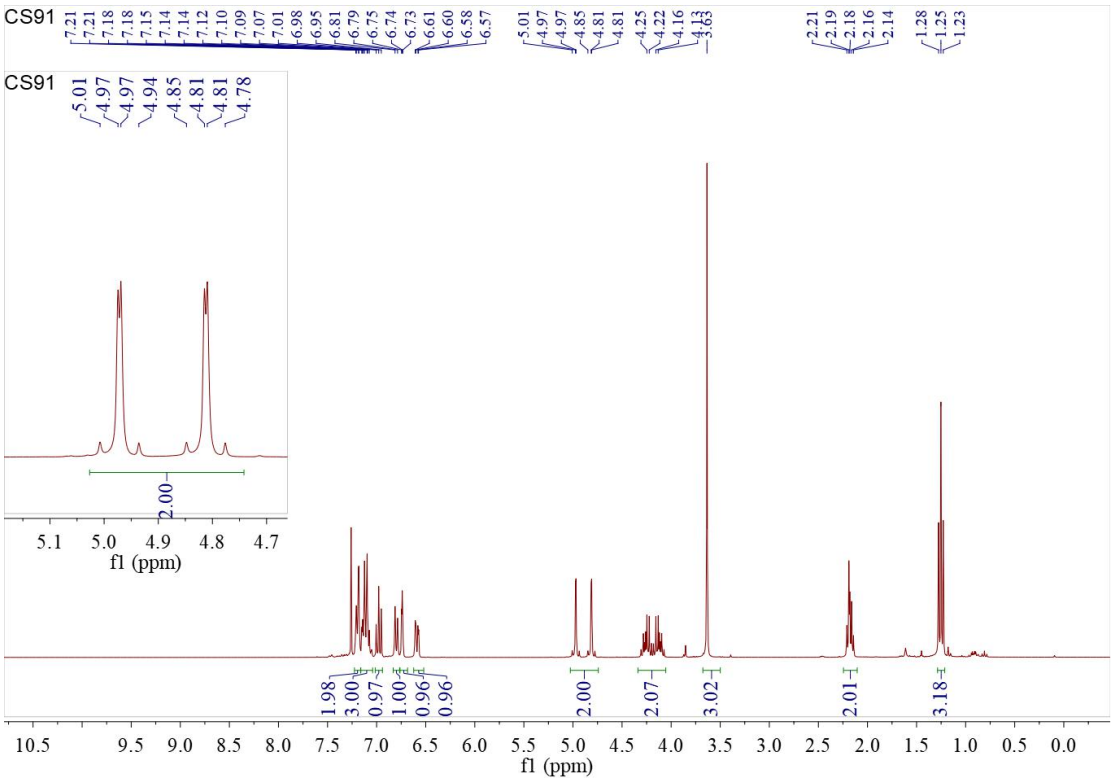
3j

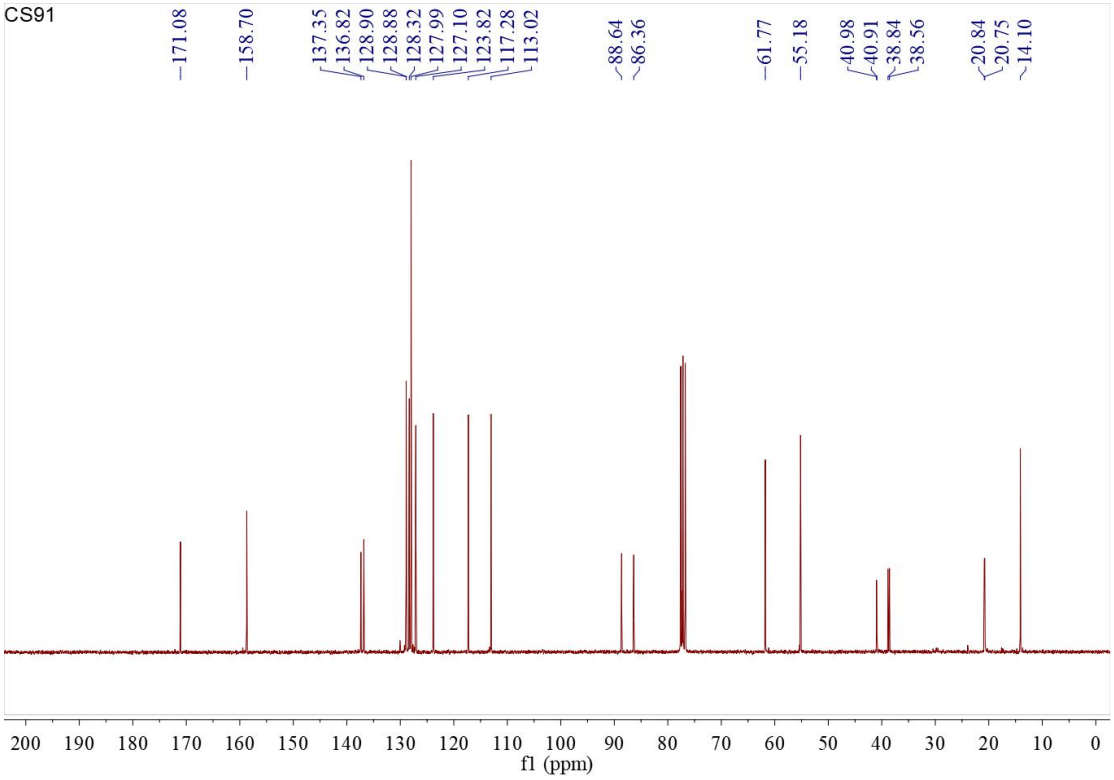

HWS-705
7.22
7.19
7.16
7.15
7.13
7.10
7.10
7.08
7.07
7.03
7.01
6.98
6.96
6.93
6.87
6.84
5.03
5.00
4.98
4.95
4.84
4.82
4.30
4.27
4.26
4.24
4.16
4.14
4.13
2.22
2.20
2.20
2.19
2.16
1.29
1.27
1.24
HWS-705
5.03
5.00
4.98
4.95
4.87
4.84
4.82
4.79
2.00
2.06
2.98
2.04
1.02
0.98
2.00
2.07
5.02
3.06
fl (ppm)

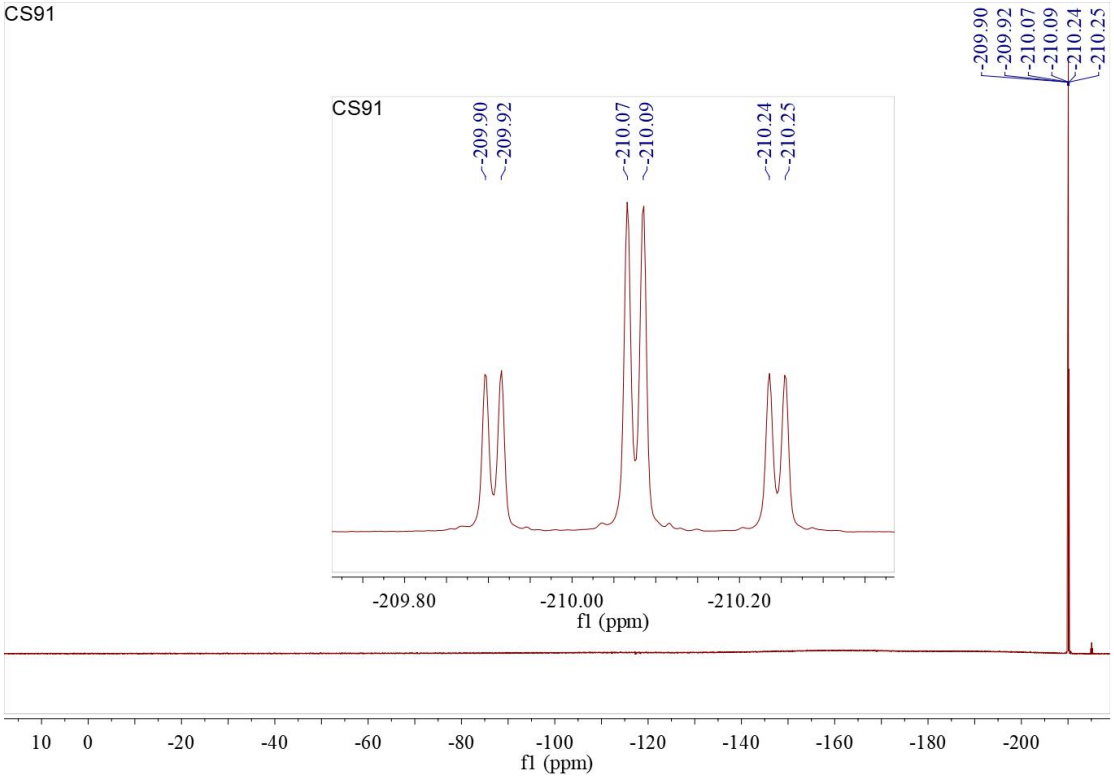

HWS-705
171.22
137.34
136.77
135.07
132.19
128.91
128.89
128.53
127.81
127.70
127.21
126.95
88.62
86.35
61.65
40.82
40.75
38.70
38.42
21.23
20.60
20.50
14.03
fl (ppm)


HWS-705
HWS-705
-209.40
-209.41
-209.57
-209.58
-209.74
-209.75
f1 (ppm)
f1 (ppm)

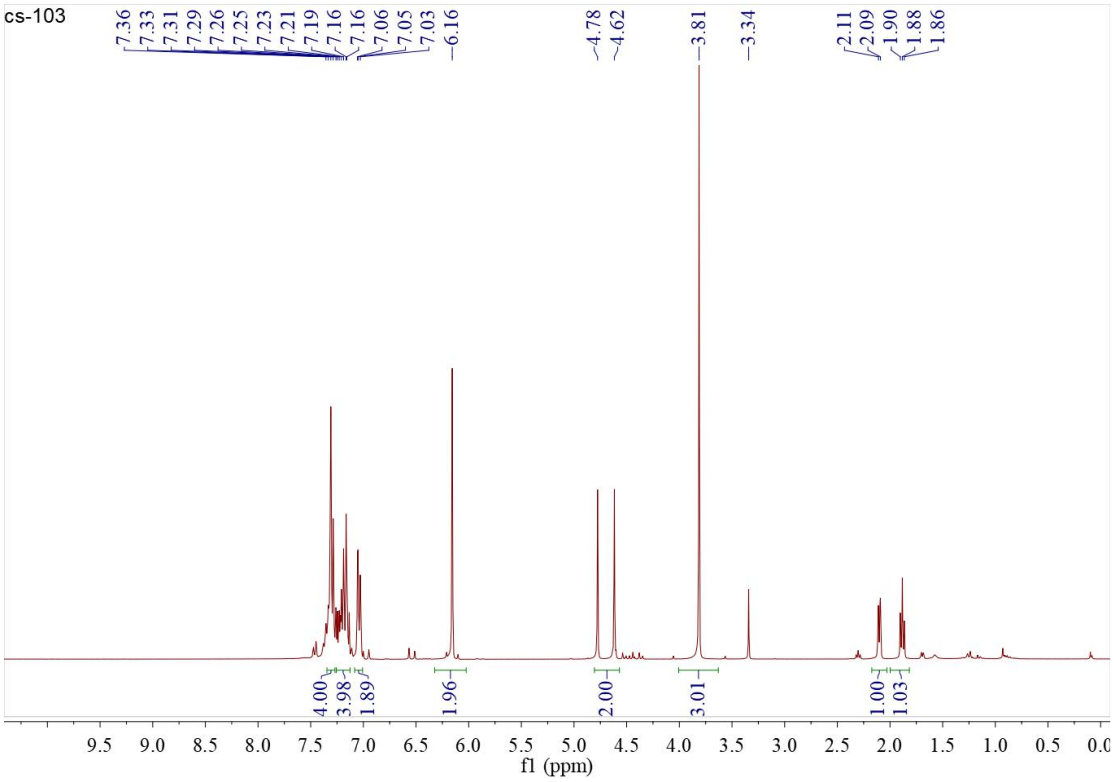
3k

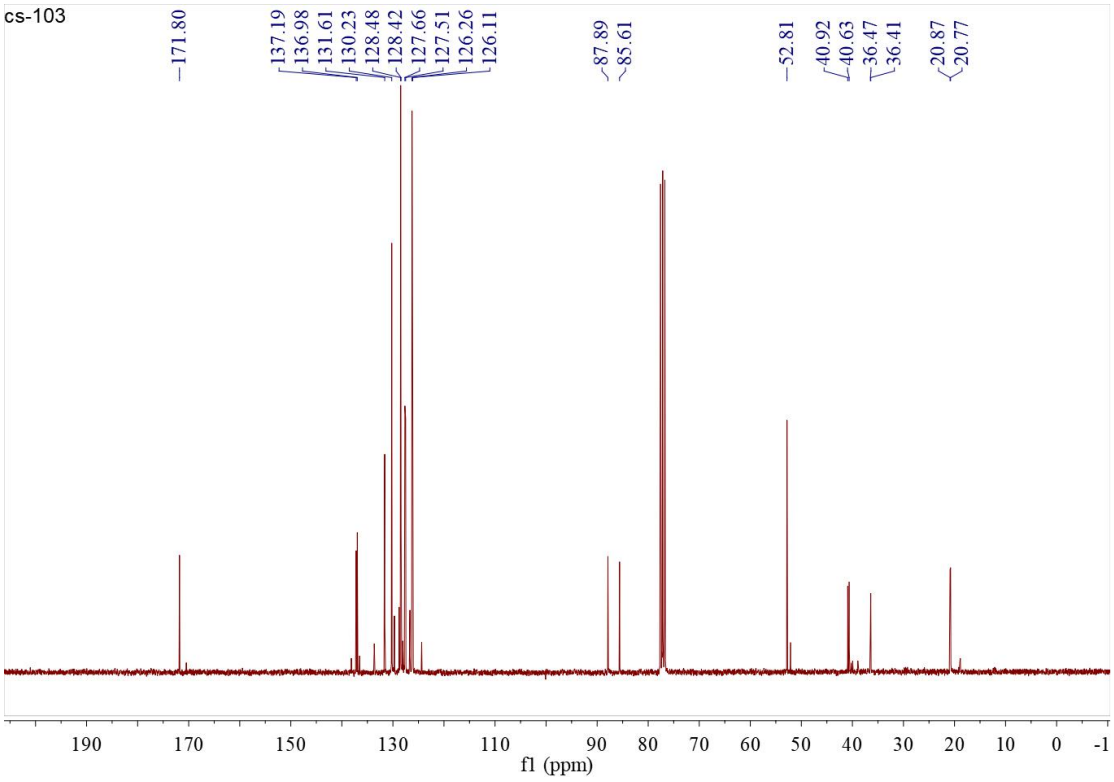

CS91
CS91
5.01
4.97
4.97
4.94
4.85
4.81
4.81
4.78
2.00
f1 (ppm)
1.98
3.00
0.97
1.00
0.96
0.96
2.00
2.07
3.02
2.01
3.18
f1 (ppm)

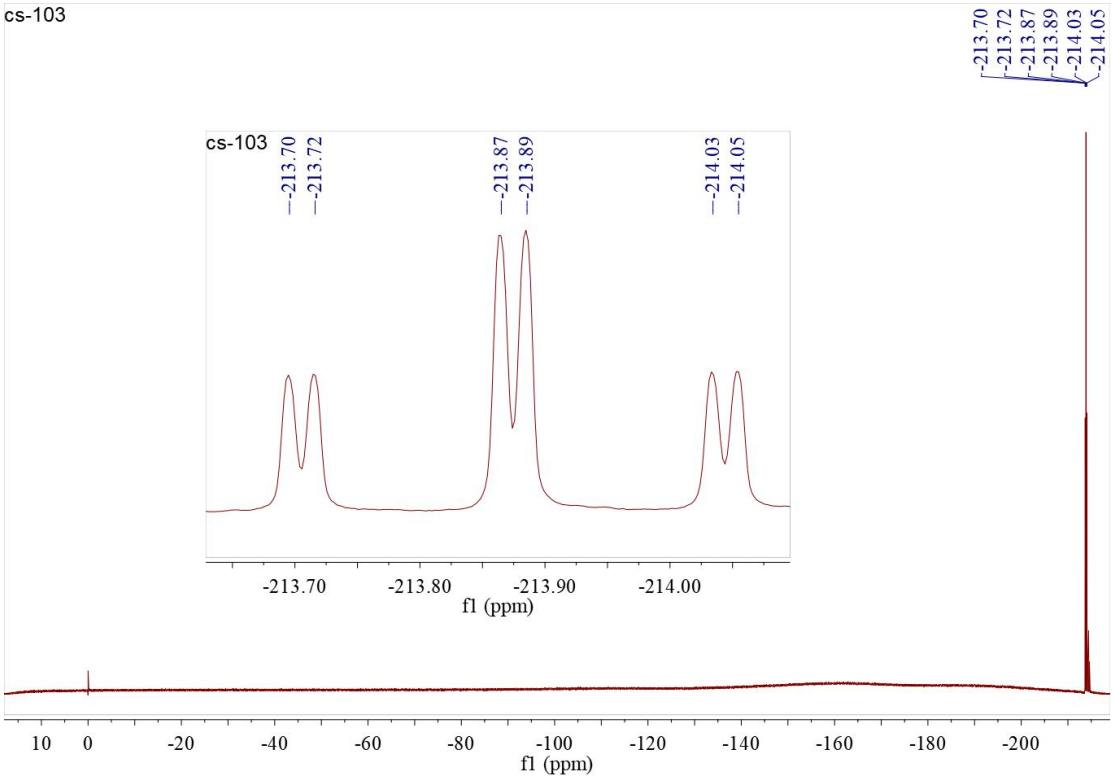

CS91
171.08
158.70
137.35
136.82
128.90
128.88
128.32
127.99
127.10
123.82
117.28
113.02
88.64
86.36
61.77
55.18
40.98
40.91
38.84
38.56
20.84
20.75
14.10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CS91
-209.90
-209.92
-210.07
-210.09
-210.24
-210.25
CS91
-209.90
-209.92
-210.07
-210.09
-210.24
-210.25
-209.80
-210.00
-210.20
f1 (ppm)
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

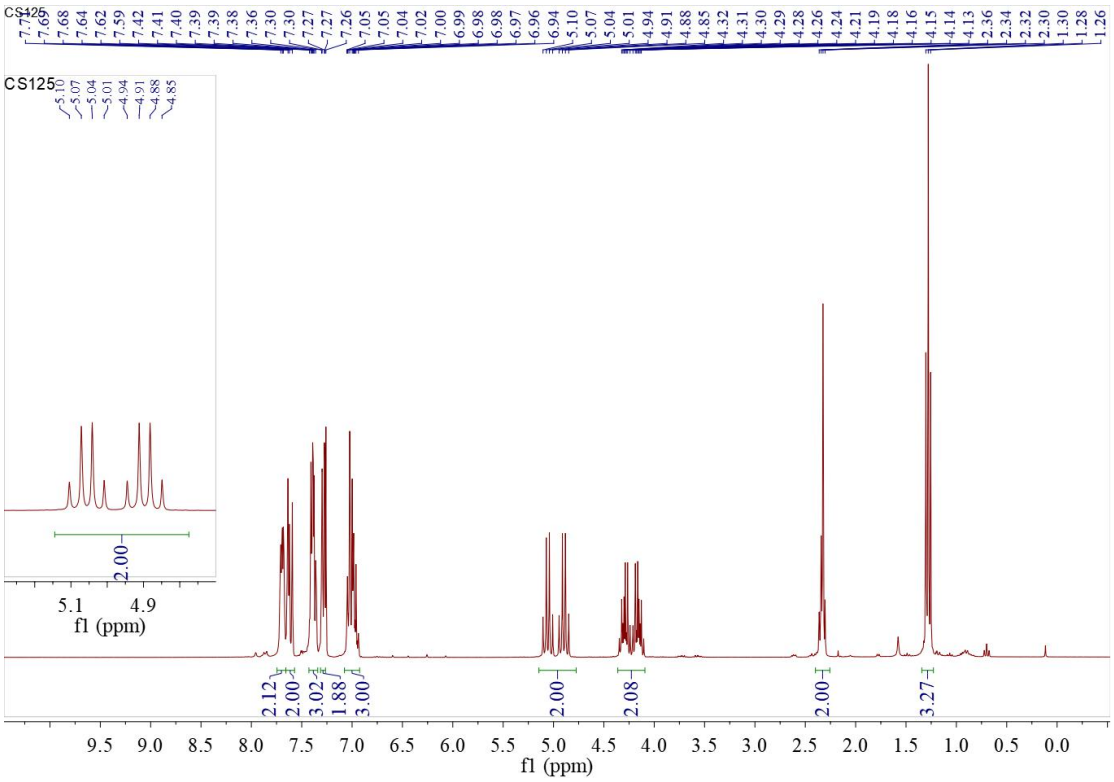
3l

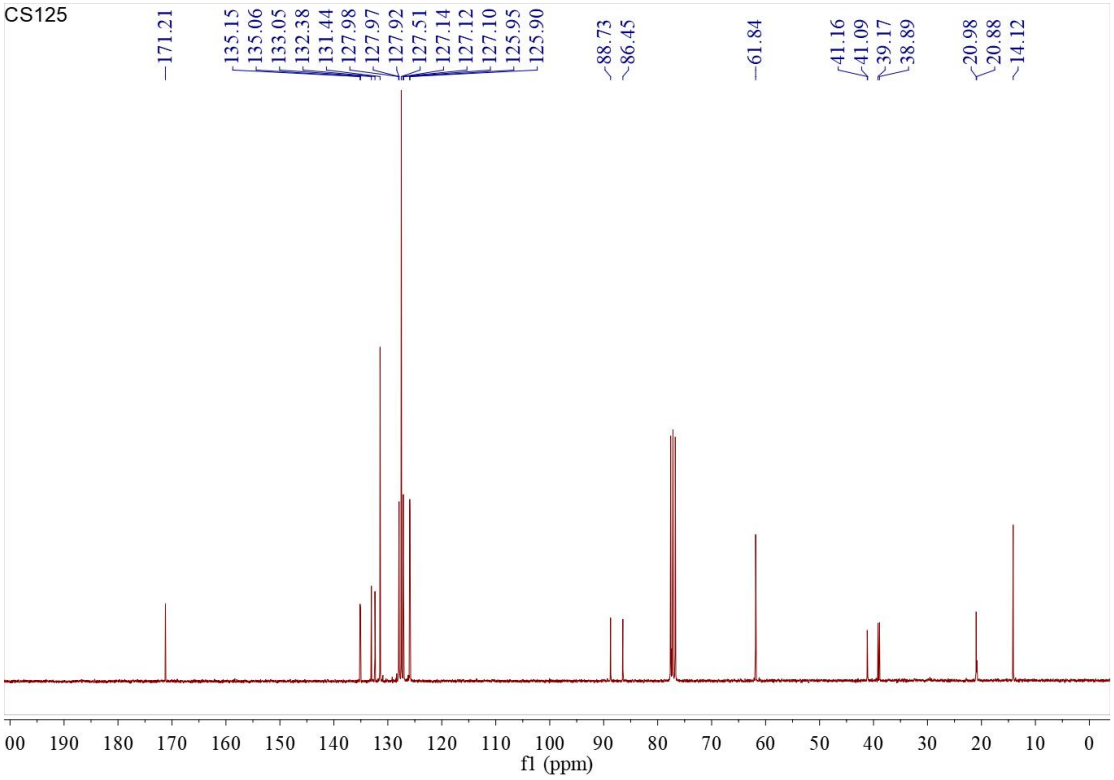

cs-103
7.36
7.33
7.31
7.29
7.26
7.25
7.23
7.21
7.19
7.16
7.16
7.06
7.05
7.03
6.16
4.78
4.62
3.81
3.34
2.11
2.09
1.90
1.88
1.86
4.00
3.98
1.89
1.96
2.00
3.01
1.00
1.03
f1 (ppm)

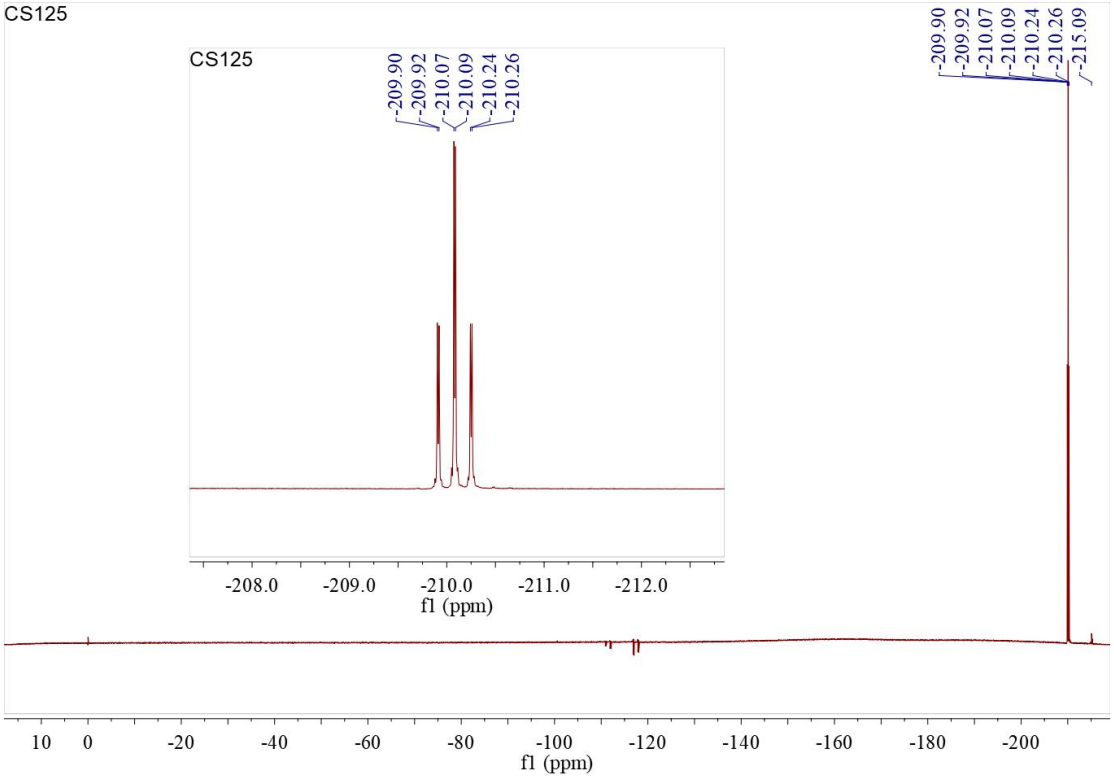

cs-103
171.80
137.19
136.98
131.61
130.23
128.48
128.42
127.66
127.51
126.26
126.11
87.89
85.61
52.81
40.92
40.63
36.47
36.41
20.87
20.77
f1 (ppm)


cs-103
-213.70
-213.72
-213.87
-213.89
-214.03
-214.05
cs-103
-213.70
-213.72
-213.87
-213.89
-214.03
-214.05
-213.70
-213.80
-213.90
-214.00
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

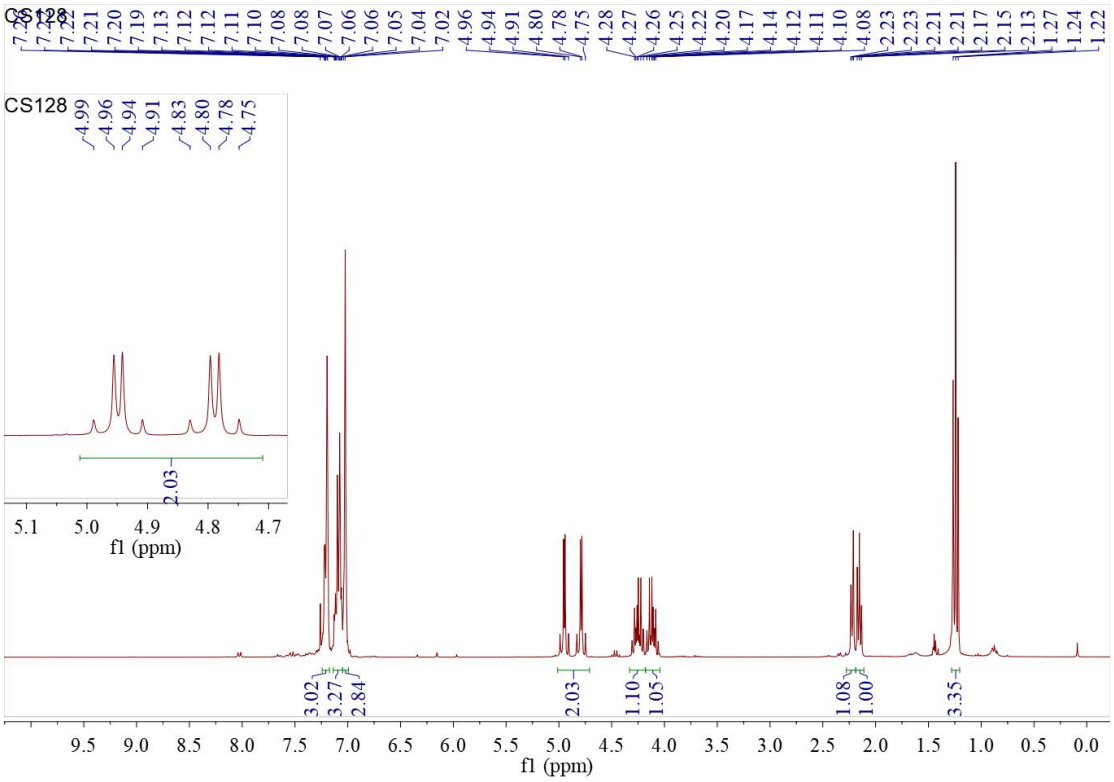
3m

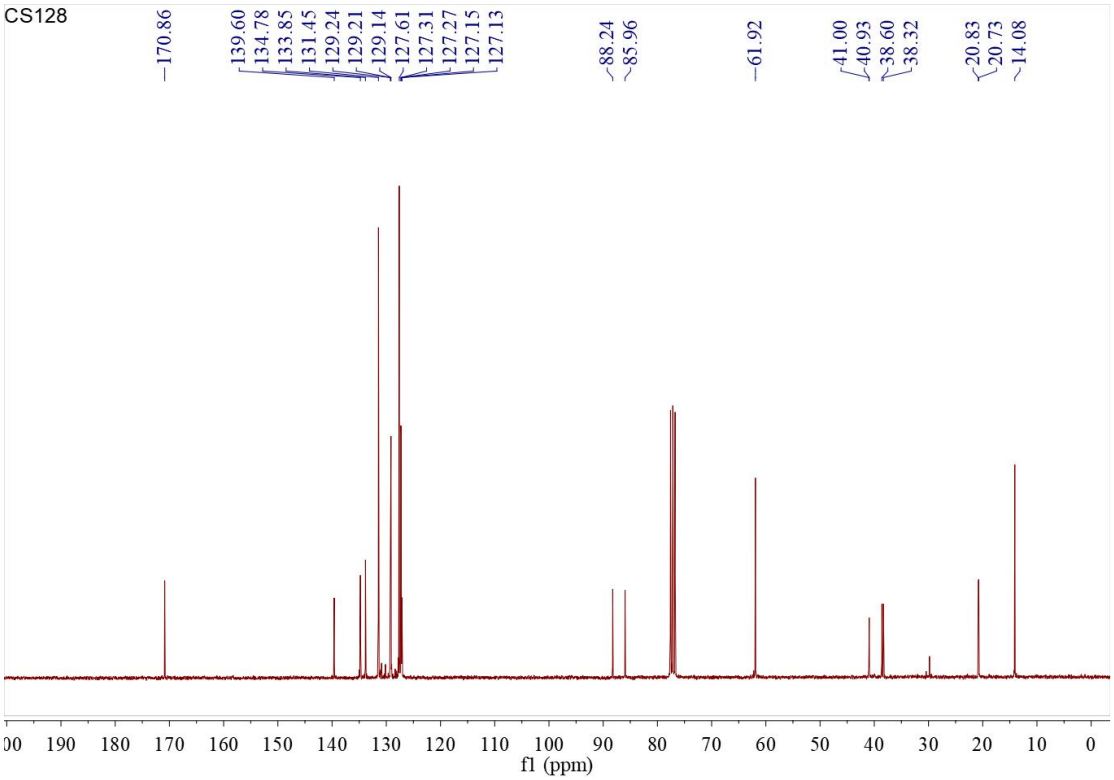

CS125
CS125
5.10
5.07
5.04
5.01
4.94
4.91
4.88
4.85
2.00
5.1
4.9
f1 (ppm)
2.12
2.00
3.02
1.88
3.00
2.00
2.08
2.00
3.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

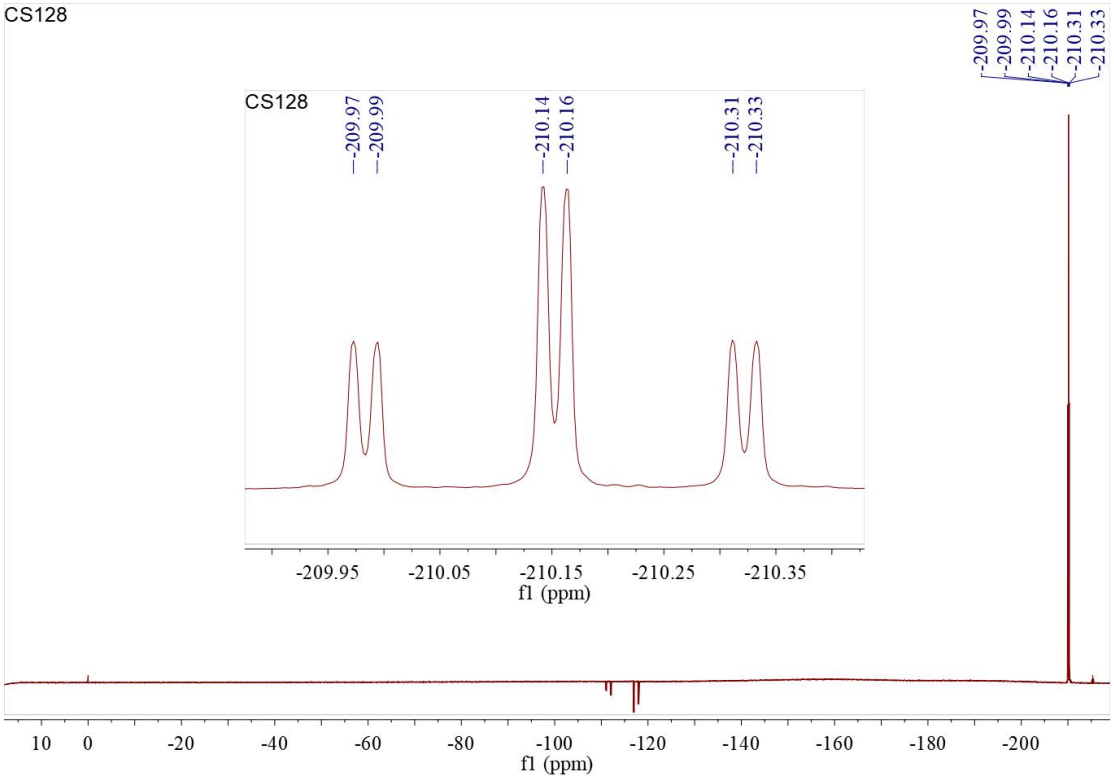

CS125
171.21
135.15
135.06
133.05
132.38
131.44
127.98
127.97
127.92
127.51
127.14
127.12
127.10
125.95
125.90
88.73
86.45
61.84
41.16
41.09
39.17
38.89
20.98
20.88
14.12
fl (ppm)


CS125
209.90
209.92
210.07
210.09
210.24
210.26
215.09
CS125
209.90
209.92
210.07
210.09
210.24
210.26
-208.0
-209.0
-210.0
-211.0
-212.0
fl (ppm)
fl (ppm)

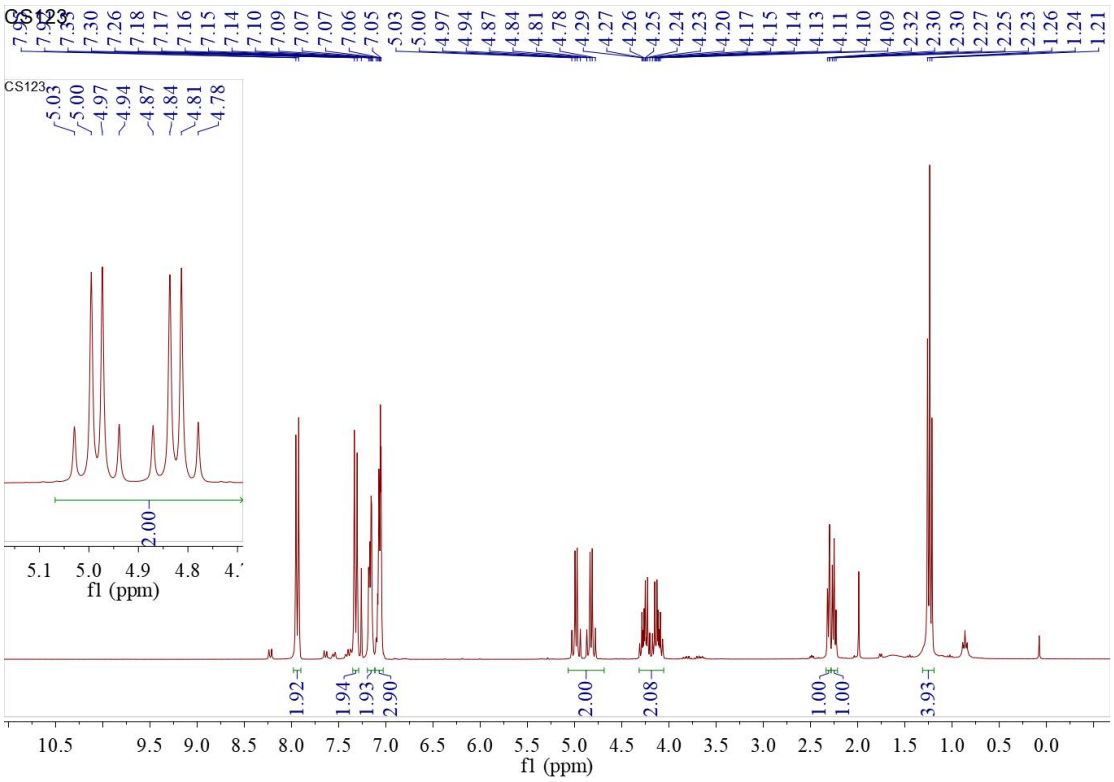
3n

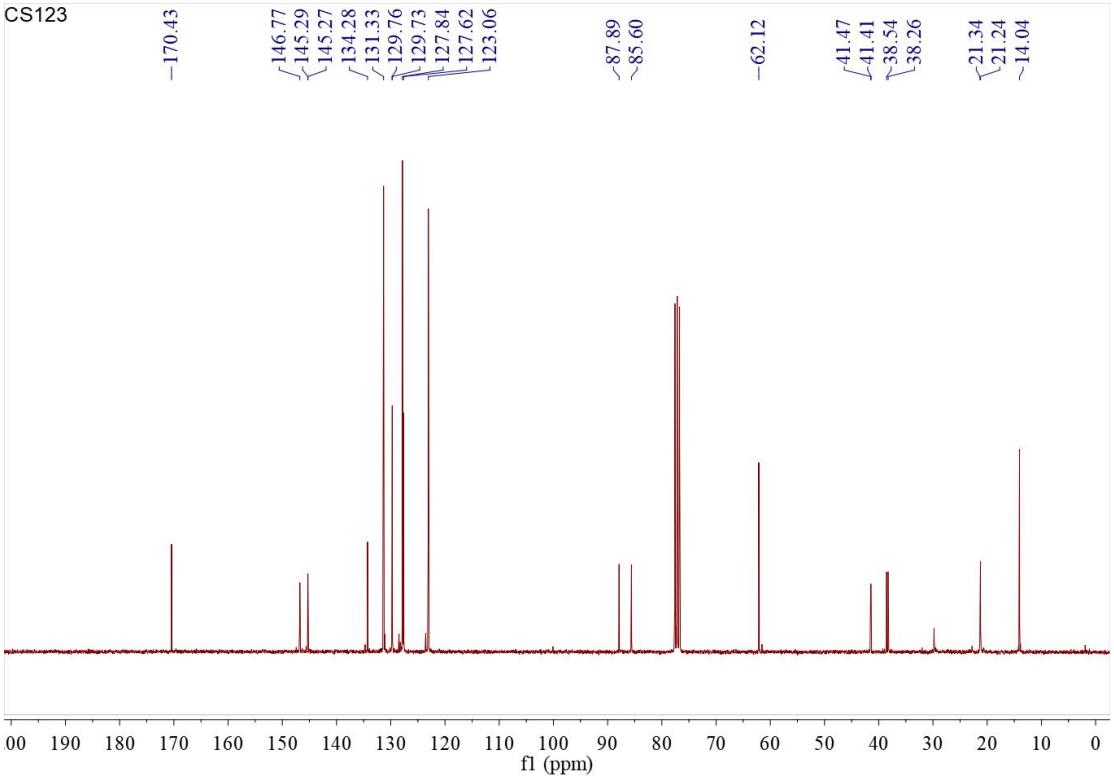


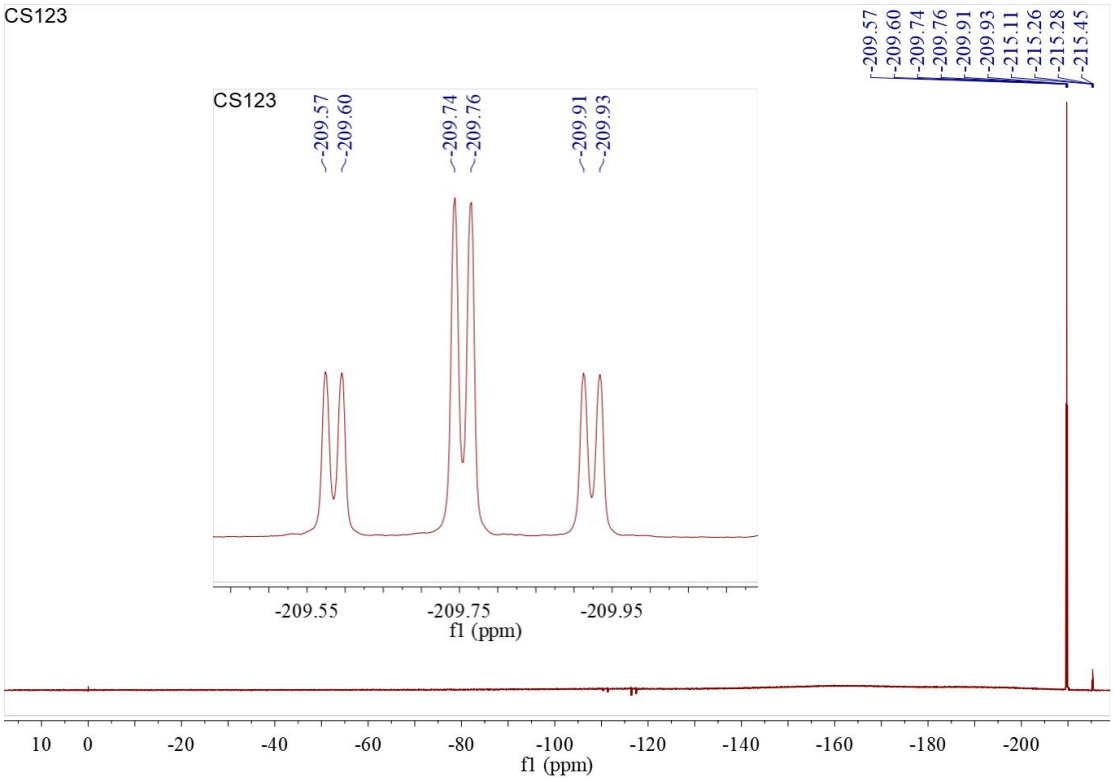



CS128
-209.97
-209.99
-210.14
-210.16
-210.31
-210.33
CS128
-209.95
-210.05
-210.15
-210.25
-210.35
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

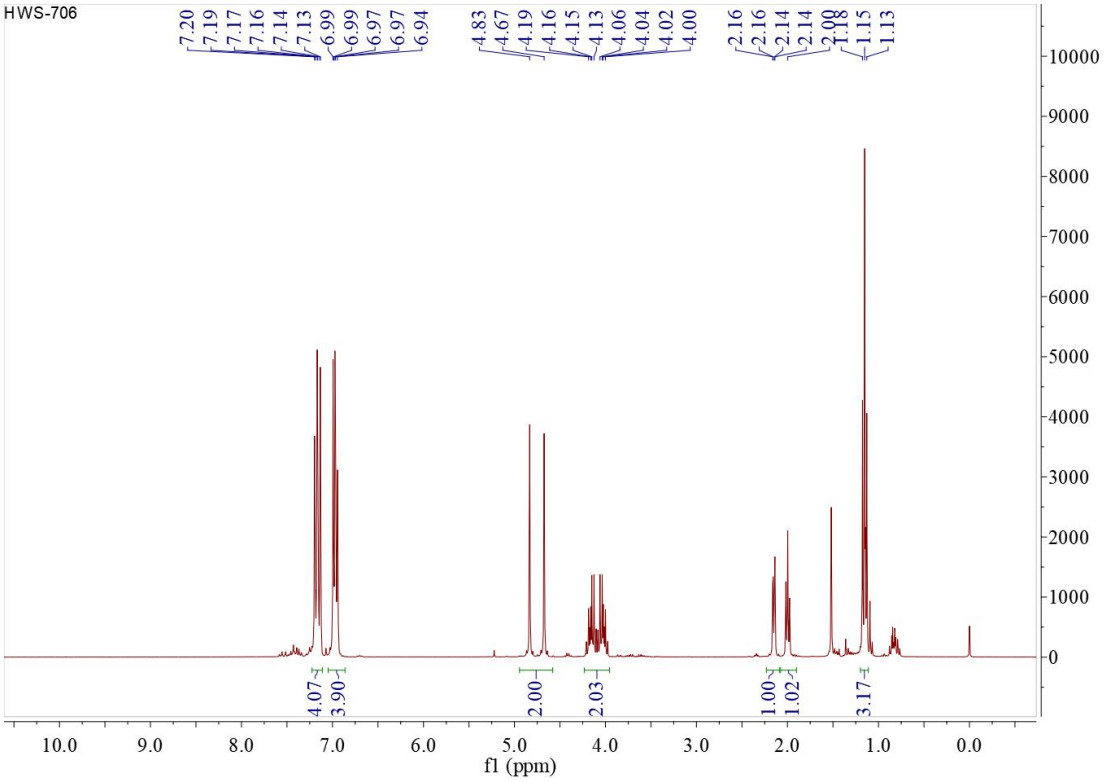
3o

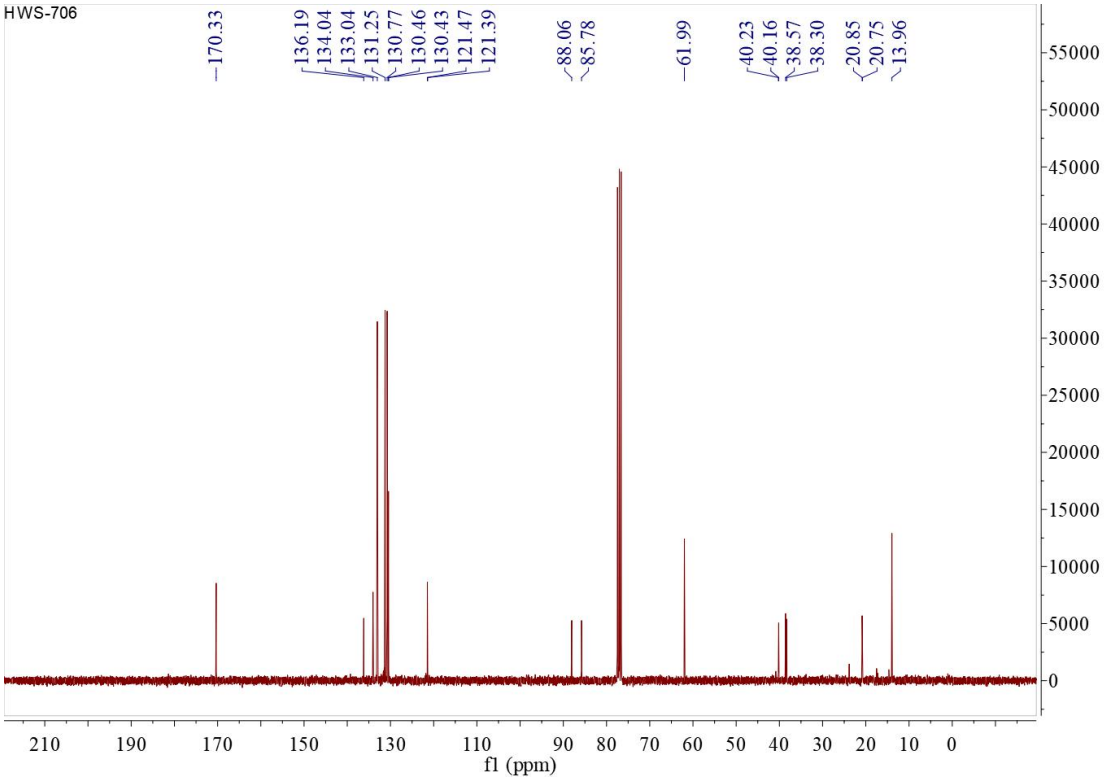

CS123
CS123
5.03
5.00
4.97
4.94
4.87
4.84
4.81
4.78
2.00
5.1
5.0
4.9
4.8
f1 (ppm)
1.92
1.94
1.93
2.90
2.00
2.08
1.00
1.00
3.93
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

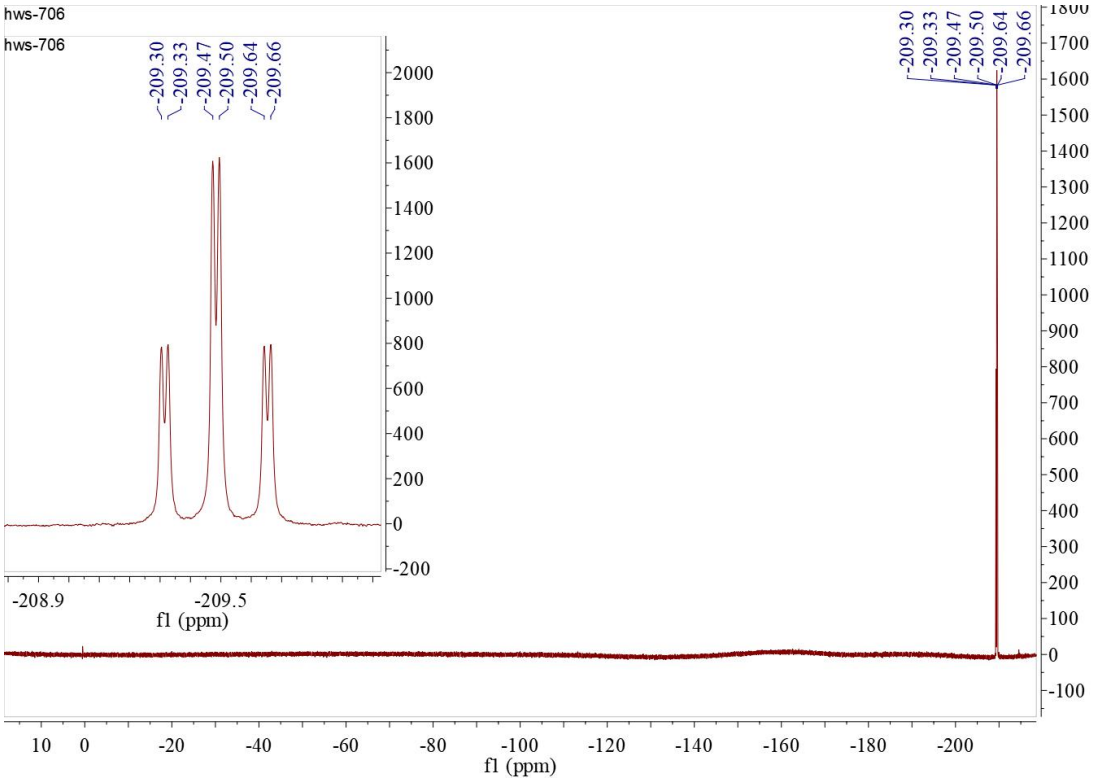

CS123
170.43
146.77
145.29
145.27
134.28
131.33
129.76
129.73
127.84
127.62
123.06
87.89
85.60
62.12
41.47
41.41
38.54
38.26
21.34
21.24
14.04
f1 (ppm)


CS123
-209.57
-209.60
-209.74
-209.76
-209.91
-209.93
-215.11
-215.26
-215.28
-215.45
CS123
-209.55
-209.75
-209.95
f1 (ppm)
f1 (ppm)

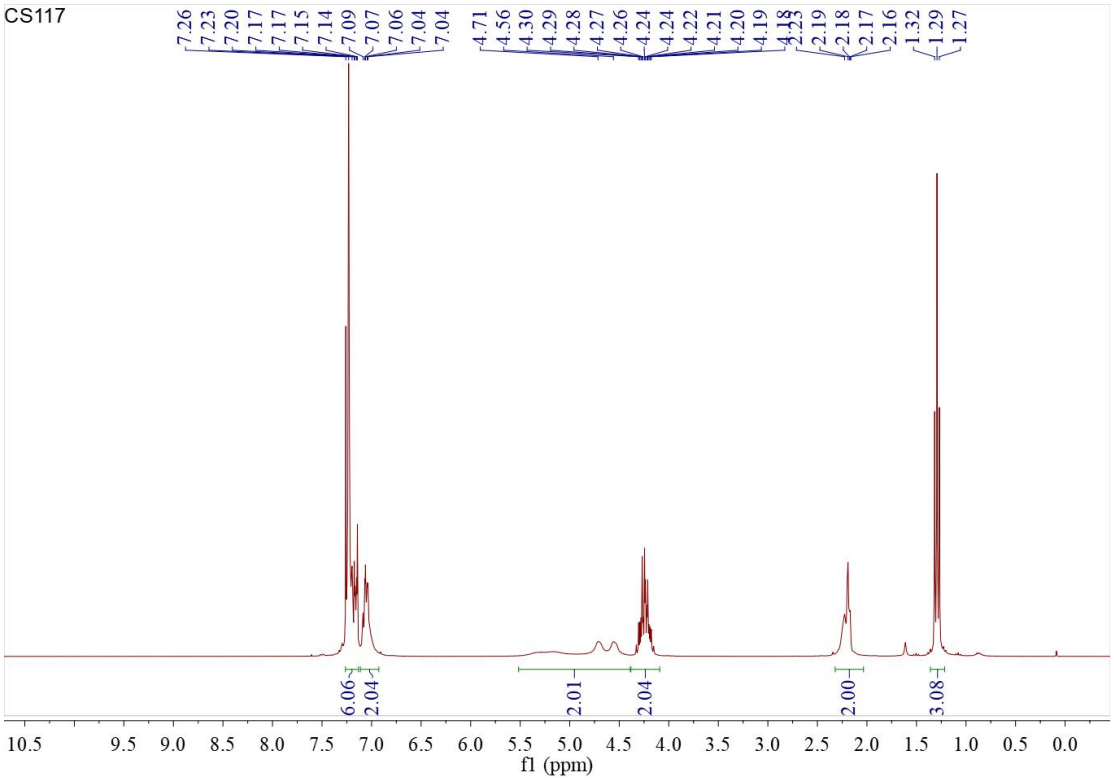
3p

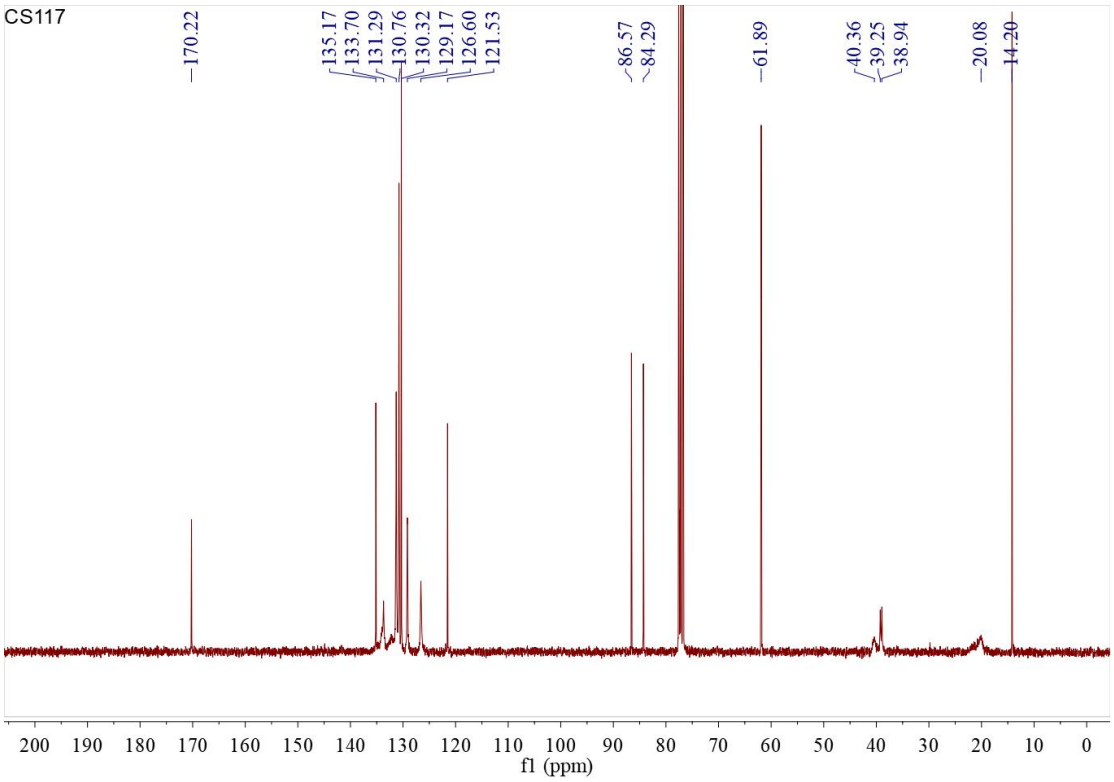

HWS-706
7.20
7.19
7.17
7.16
7.14
7.13
6.99
6.99
6.97
6.97
6.94
4.83
4.67
4.19
4.16
4.15
4.13
4.06
4.04
4.02
4.00
2.16
2.16
2.14
2.14
2.00
1.18
1.15
1.13
4.07
3.90
2.00
2.03
1.00
1.02
3.17
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

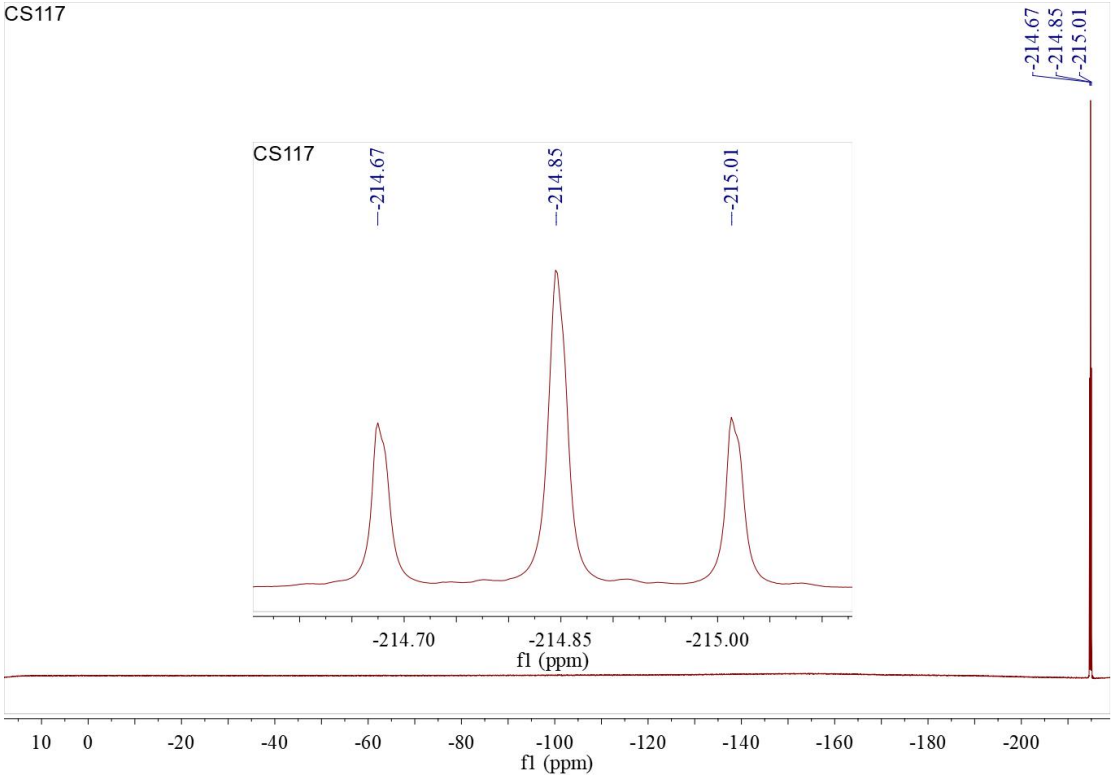

HWS-706
170.33
136.19
134.04
133.04
131.25
130.77
130.46
130.43
121.47
121.39
88.06
85.78
61.99
40.23
40.16
38.57
38.30
20.85
20.75
13.96
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


hws-706
hws-706
-209.30
-209.33
-209.47
-209.50
-209.64
-209.66
-208.9
-209.5
f1 (ppm)
f1 (ppm)

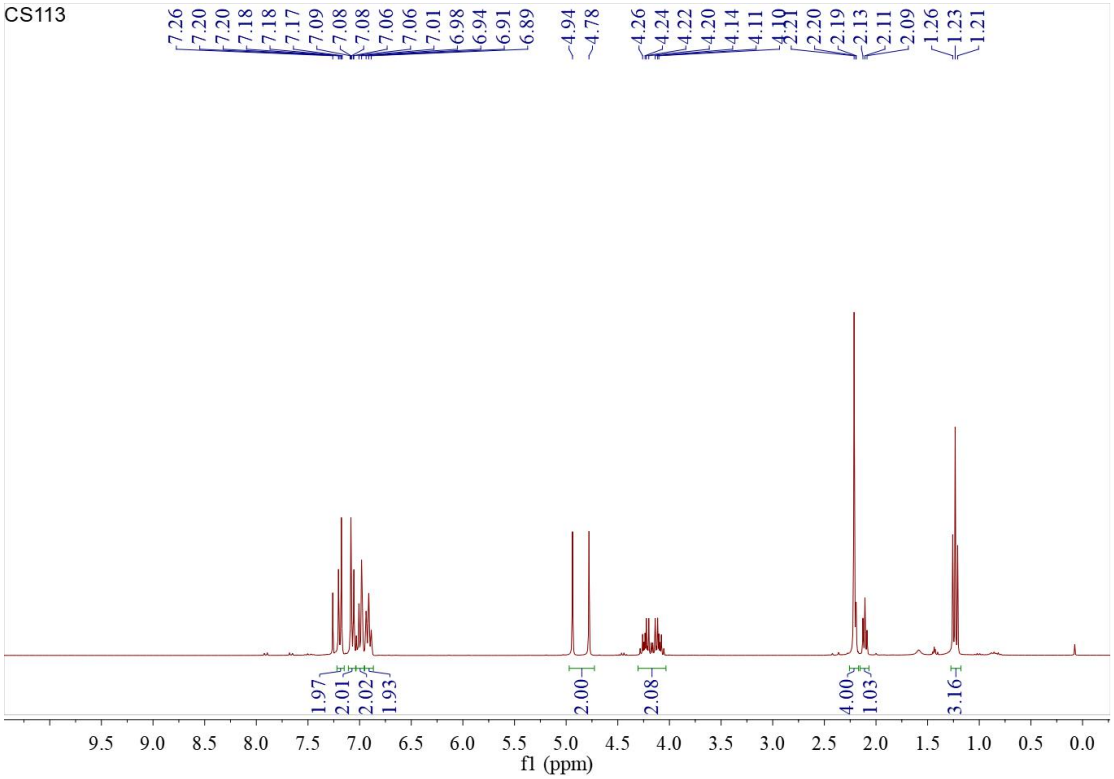
3q

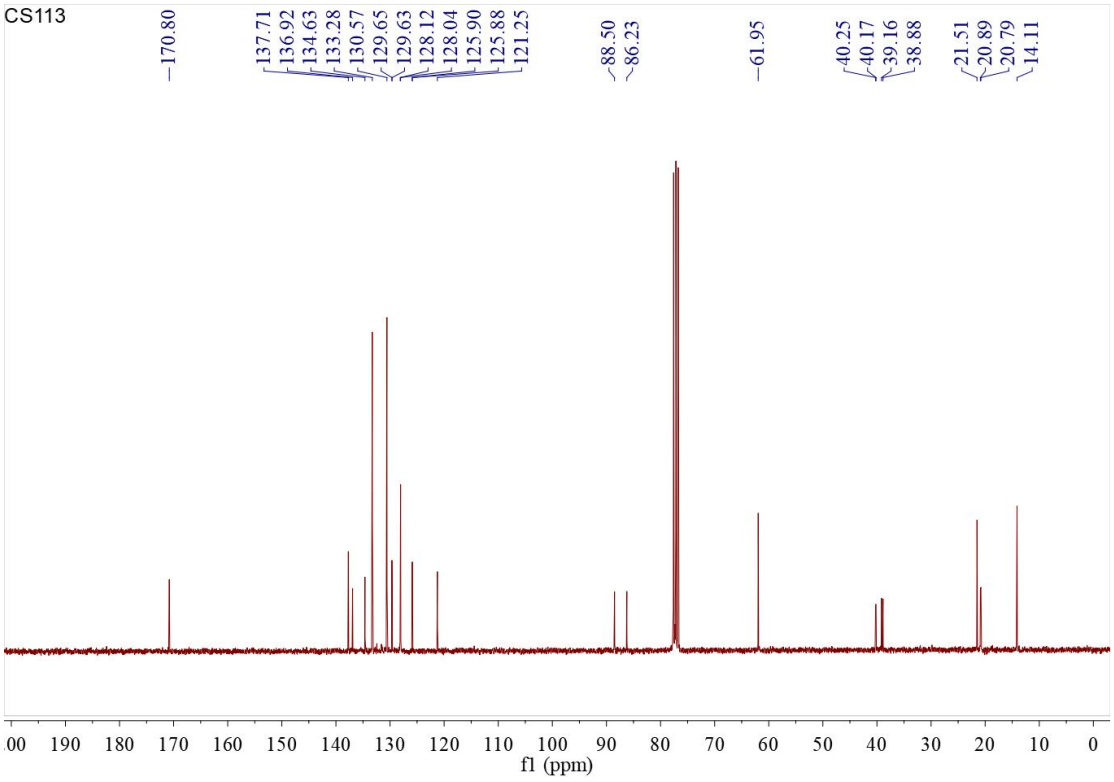

CS117
7.26
7.23
7.20
7.17
7.17
7.15
7.14
7.09
7.07
7.06
7.04
7.04
4.71
4.56
4.30
4.29
4.28
4.27
4.26
4.24
4.24
4.22
4.21
4.20
4.19
2.19
2.18
2.17
2.16
1.32
1.29
1.27
6.06
2.04
2.01
2.04
2.00
3.08
f1 (ppm)

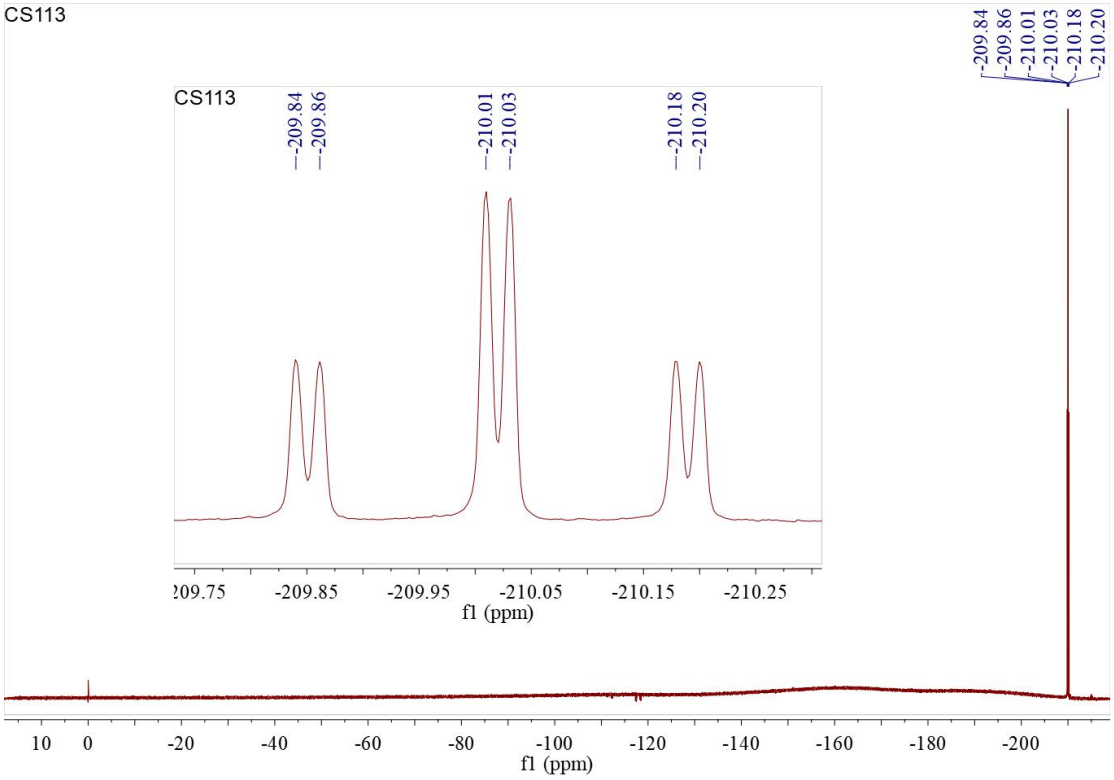

CS117
170.22
135.17
133.70
131.29
130.76
130.32
129.17
126.60
121.53
86.57
84.29
61.89
40.36
39.25
38.94
20.08
14.20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CS117
-214.67
-214.85
-215.01
CS117
-214.67
-214.85
-215.01
-214.70
-214.85
-215.00
f1 (ppm)
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

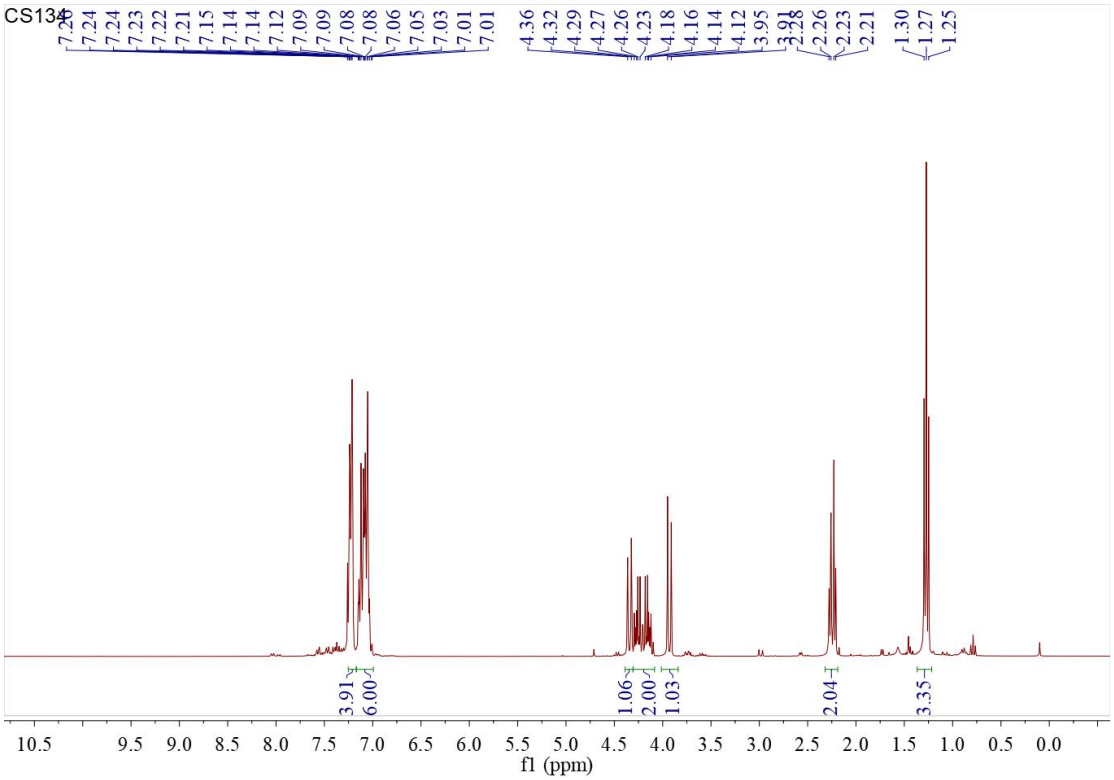
3r

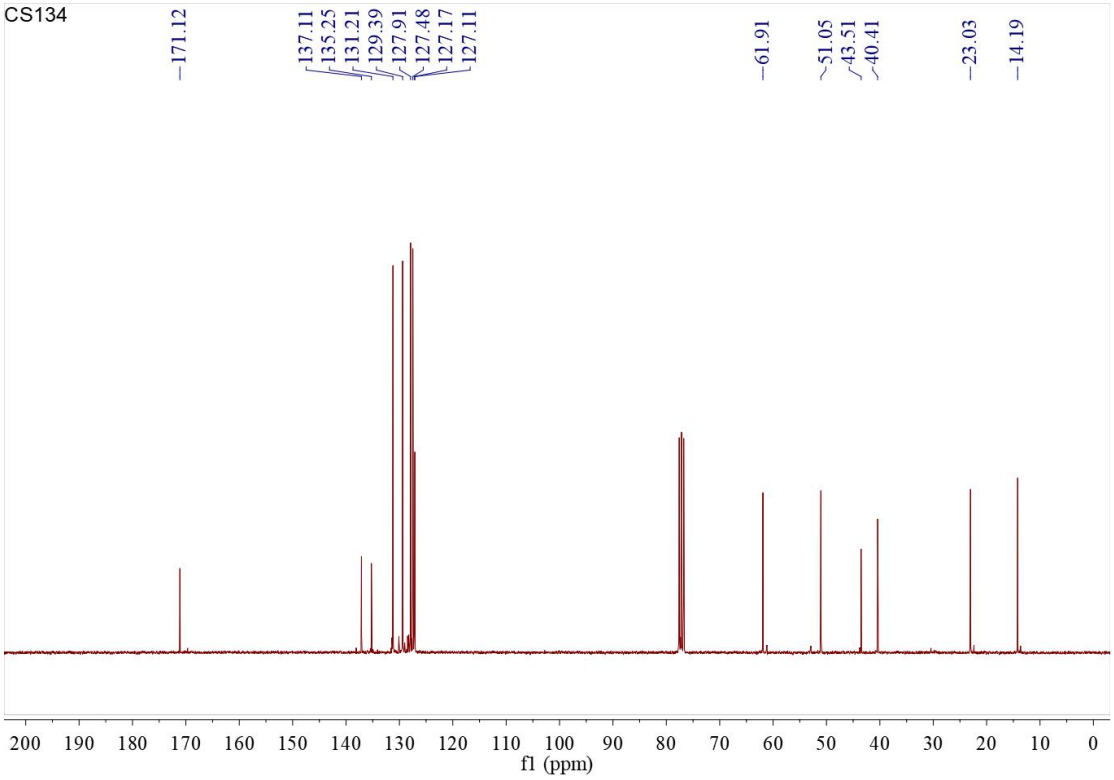

CS113
7.26
7.20
7.20
7.18
7.18
7.17
7.09
7.08
7.08
7.06
7.06
7.01
6.98
6.94
6.91
6.89
4.94
4.78
4.26
4.24
4.22
4.20
4.14
4.11
4.10
2.21
2.20
2.19
2.13
2.11
2.09
1.26
1.23
1.21
1.97
2.01
2.02
1.93
2.00
2.08
4.00
1.03
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CS113
170.80
137.71
136.92
134.63
133.28
130.57
129.65
129.63
128.12
128.04
125.90
125.88
121.25
88.50
86.23
61.95
40.25
40.17
39.16
38.88
21.51
20.89
20.79
14.11
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

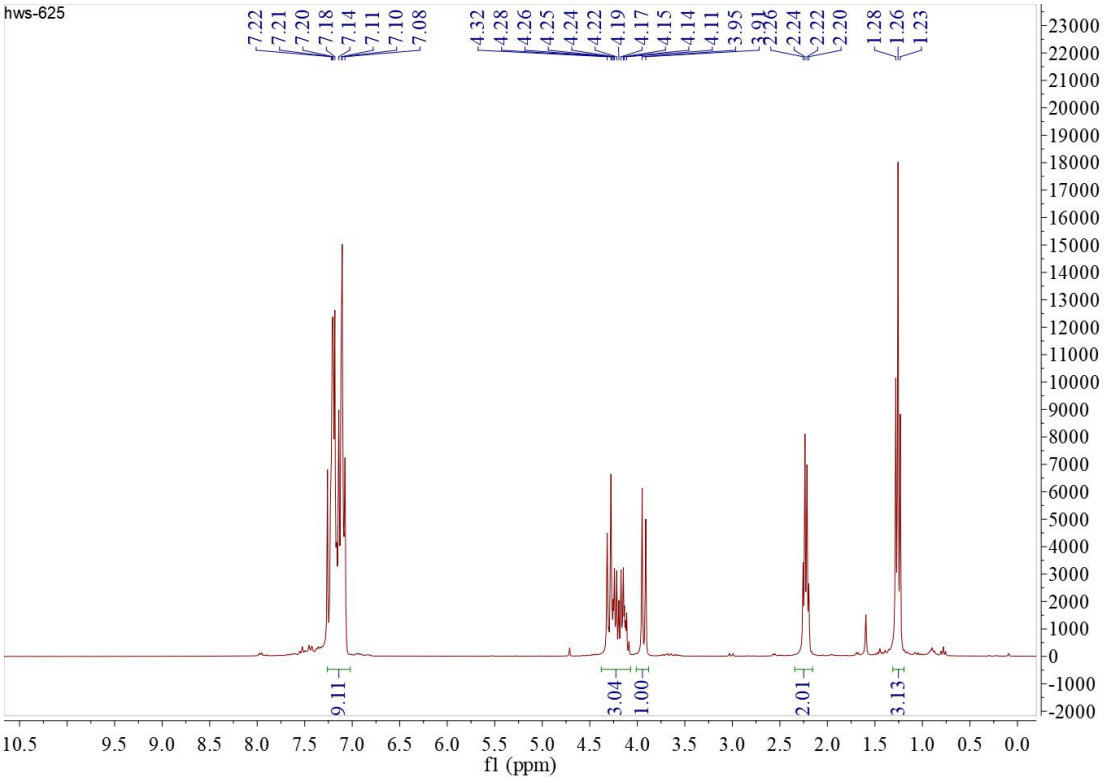

CS113
-209.84
-209.86
-210.01
-210.03
-210.18
-210.20
CS113
-209.84
-209.86
-210.01
-210.03
-210.18
-210.20
209.75
-209.85
-209.95
-210.05
-210.15
-210.25
f1 (ppm)
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

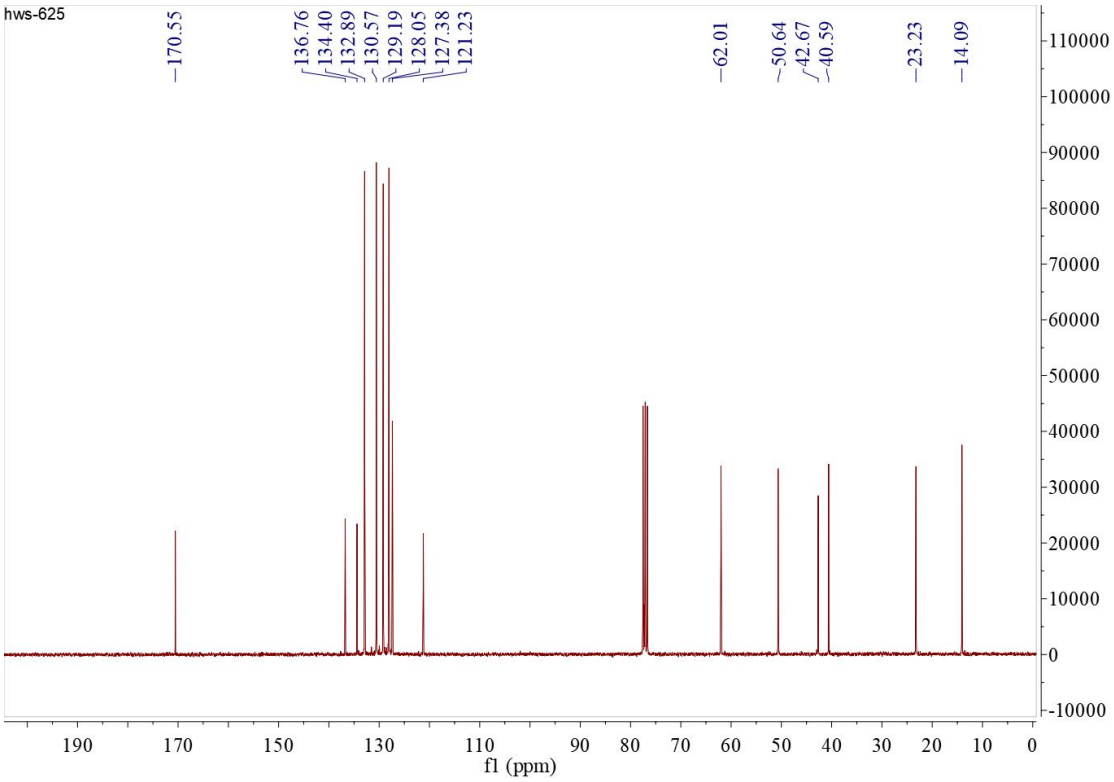
6a


CS134
7.24
7.24
7.23
7.22
7.21
7.15
7.14
7.14
7.12
7.09
7.09
7.08
7.08
7.06
7.05
7.03
7.01
7.01
4.36
4.32
4.29
4.27
4.26
4.23
4.18
4.16
4.14
4.12
3.95
2.26
2.23
2.21
1.30
1.27
1.25
3.91
6.00
1.06
2.00
1.03
2.04
3.35
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

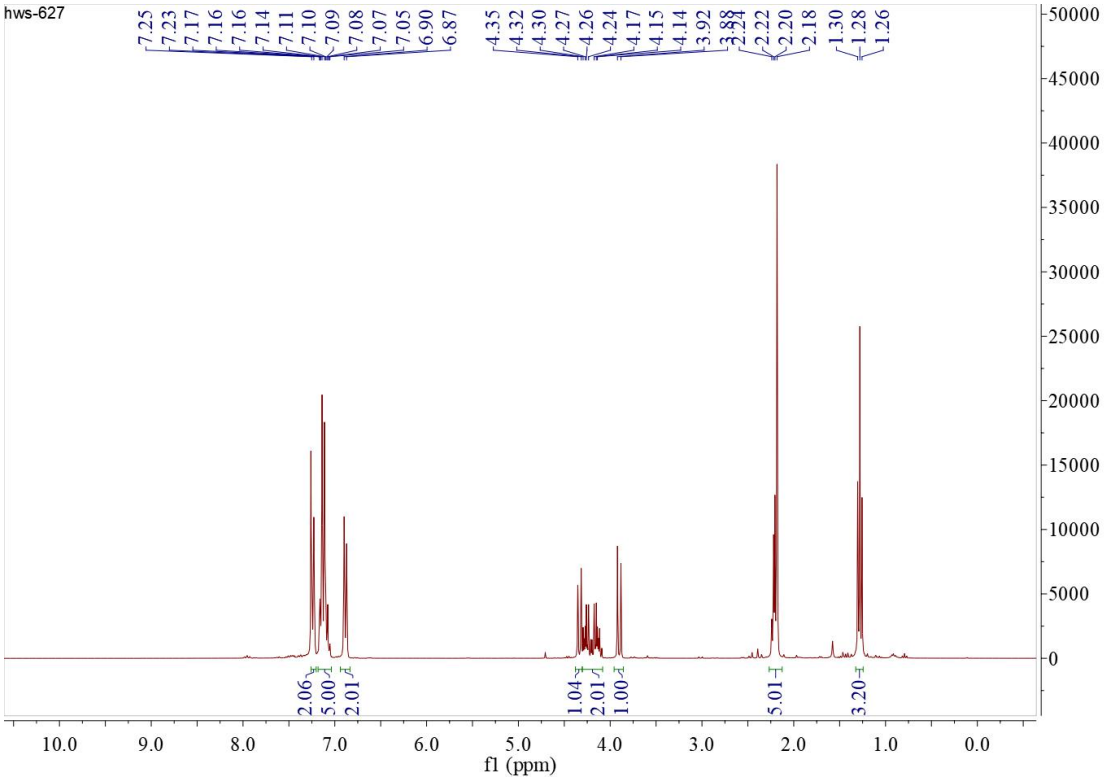

CS134
171.12
137.11
135.25
131.21
129.39
127.91
127.48
127.17
127.11
61.91
51.05
43.51
40.41
23.03
14.19
f1 (ppm)

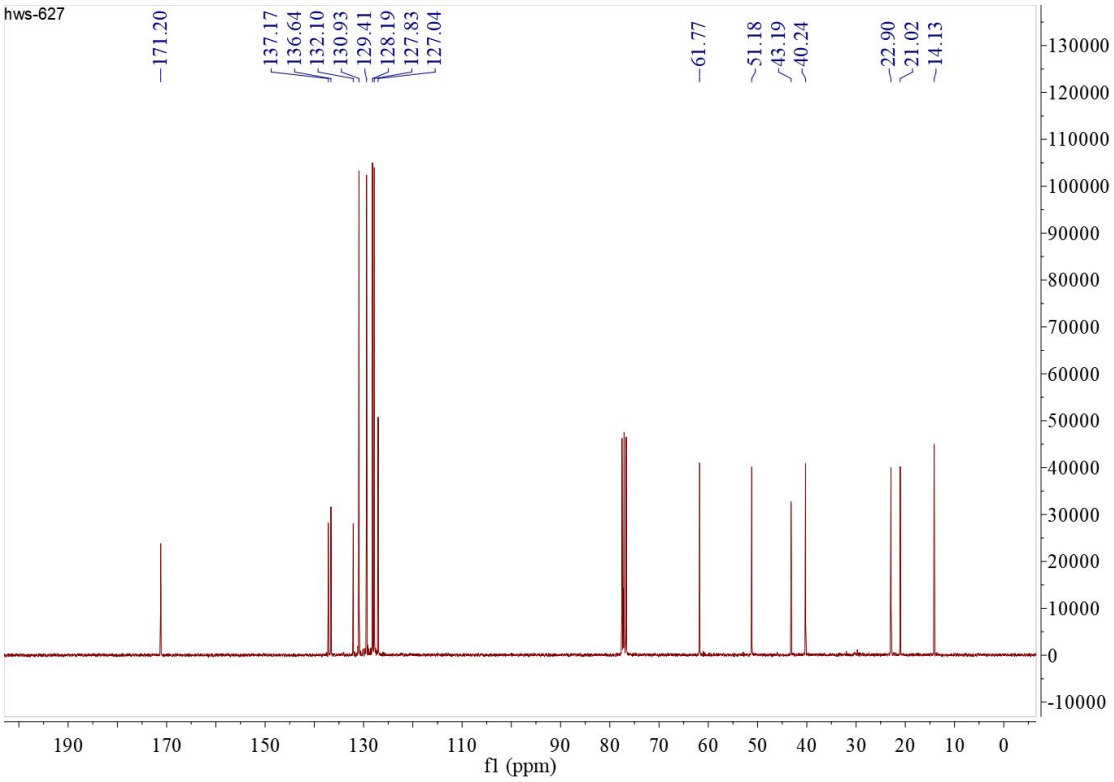
6b


hws-625
7.22
7.21
7.20
7.18
7.14
7.11
7.10
7.08
4.32
4.28
4.26
4.25
4.24
4.22
4.19
4.17
4.15
4.14
4.11
3.95
3.91
2.26
2.24
2.22
2.20
1.28
1.26
1.23
9.11
3.04
1.00
2.01
3.13
f1 (ppm)

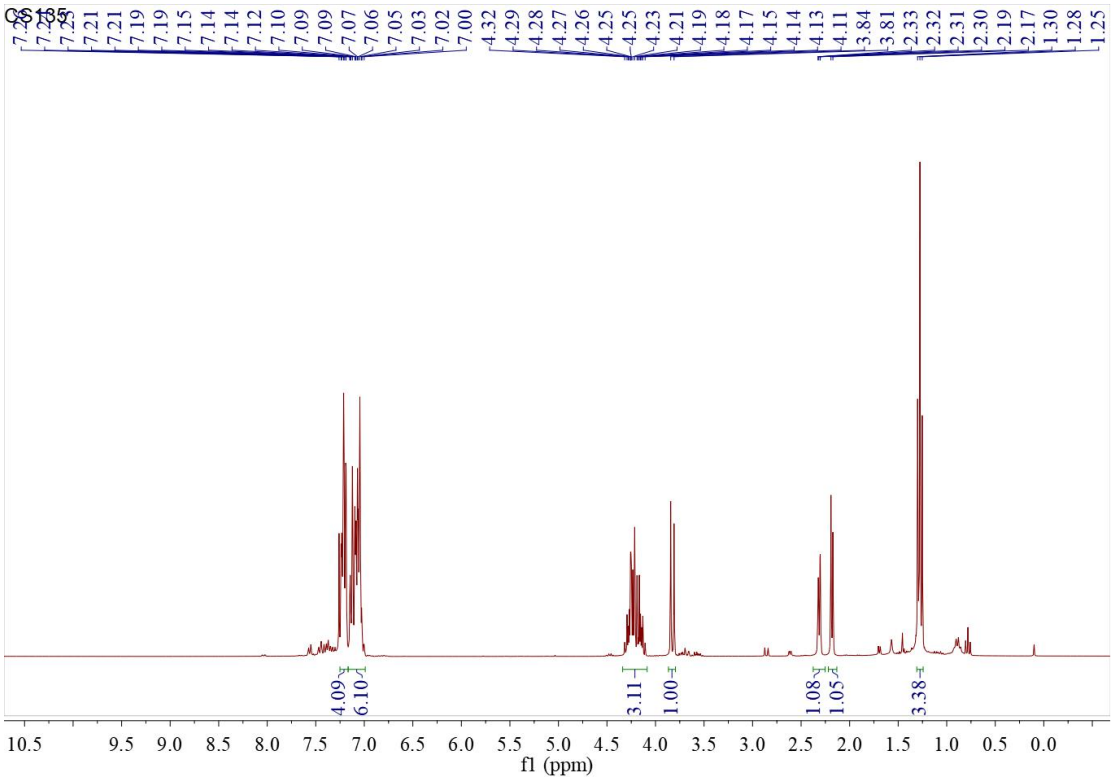

hws-625
170.55
136.76
134.40
132.89
130.57
129.19
128.05
127.38
121.23
62.01
50.64
42.67
40.59
23.23
14.09
f1 (ppm)

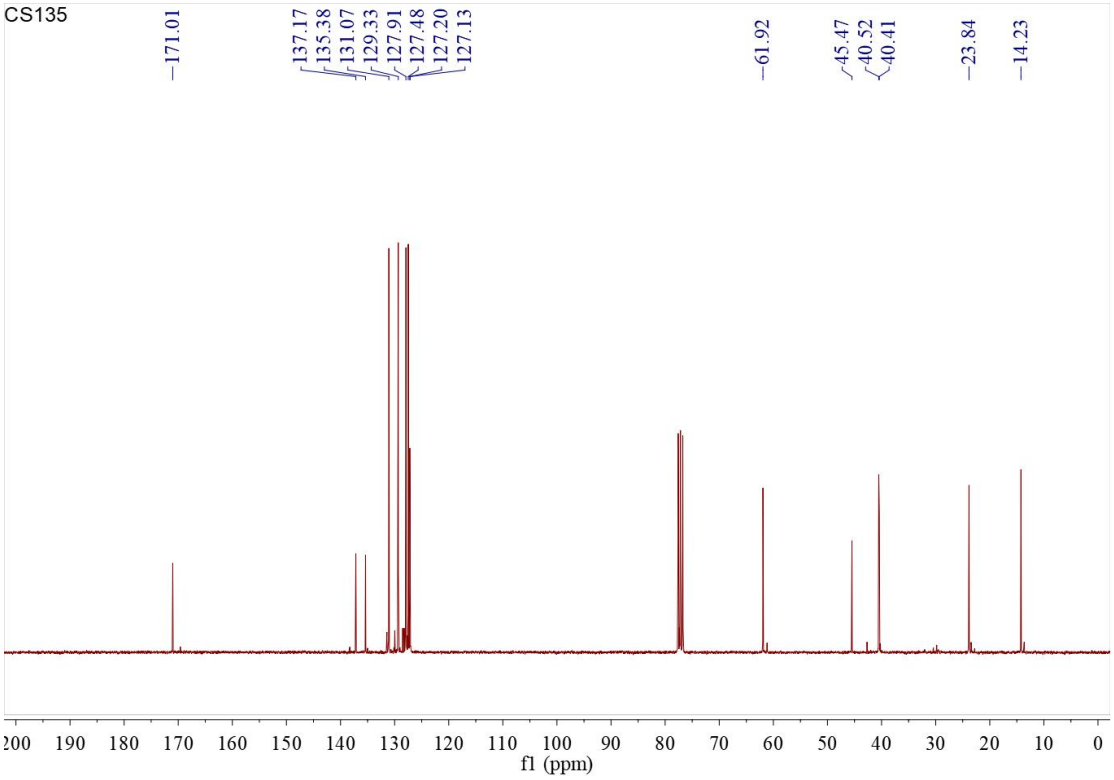
6c


hws-627
7.25
7.23
7.17
7.16
7.16
7.14
7.11
7.10
7.09
7.08
7.07
7.05
6.90
6.87
4.35
4.32
4.30
4.27
4.26
4.24
4.17
4.15
4.14
3.92
2.22
2.20
2.18
1.30
1.28
1.26
2.06
5.00
2.01
1.04
2.01
1.00
5.01
3.20
f1 (ppm)

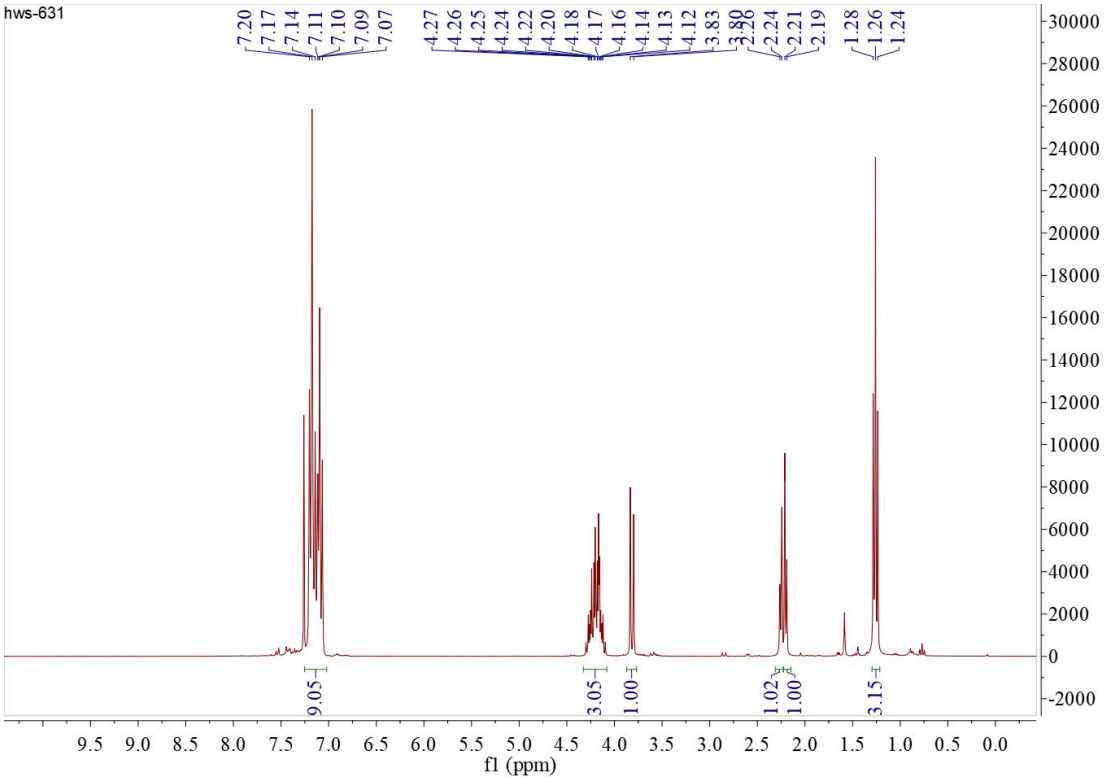

hws-627
171.20
137.17
136.64
132.10
130.93
129.41
128.19
127.83
127.04
61.77
51.18
43.19
40.24
22.90
21.02
14.13
f1 (ppm)

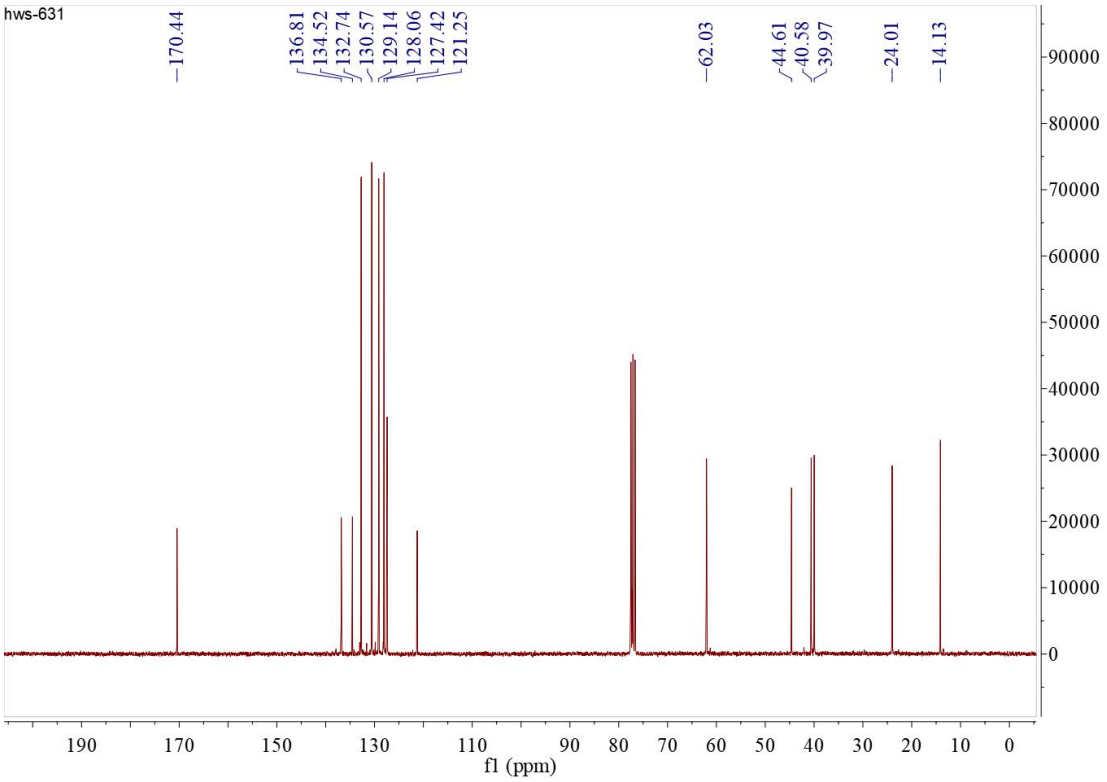
7a


CS135
4.09
6.10
3.11
1.00
1.08
1.05
3.38
f1 (ppm)

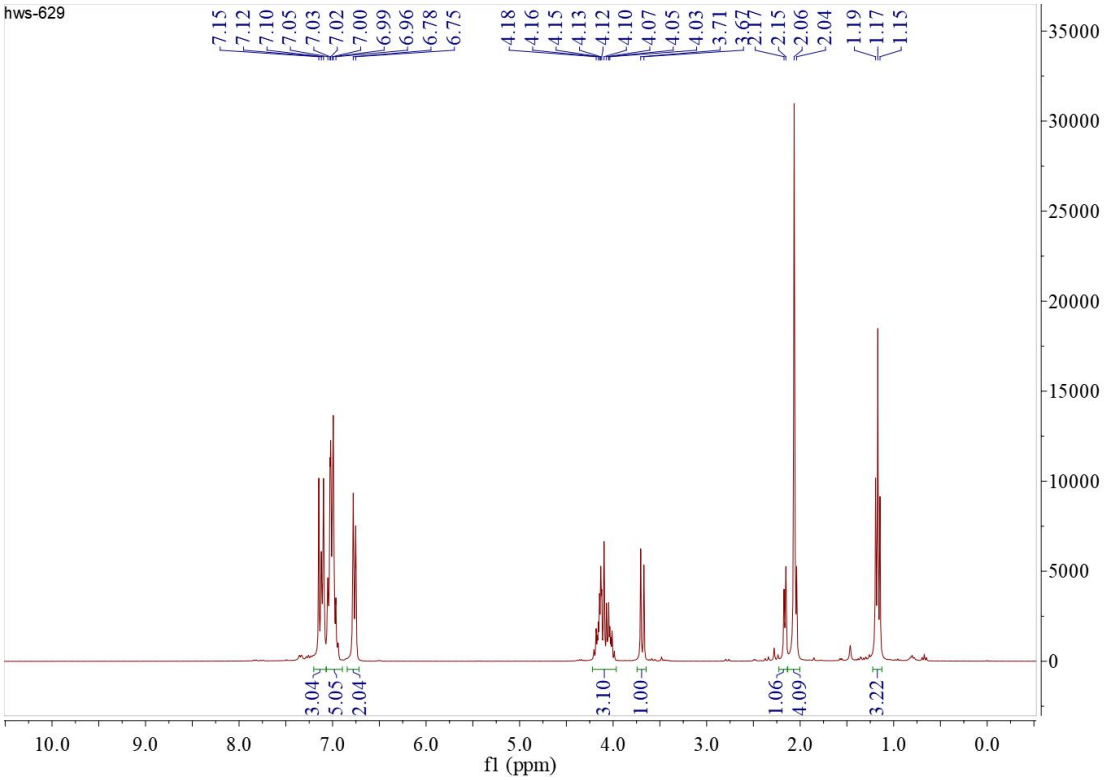

CS135
171.01
137.17
135.38
131.07
129.33
127.91
127.48
127.20
127.13
61.92
45.47
40.52
40.41
23.84
14.23
f1 (ppm)

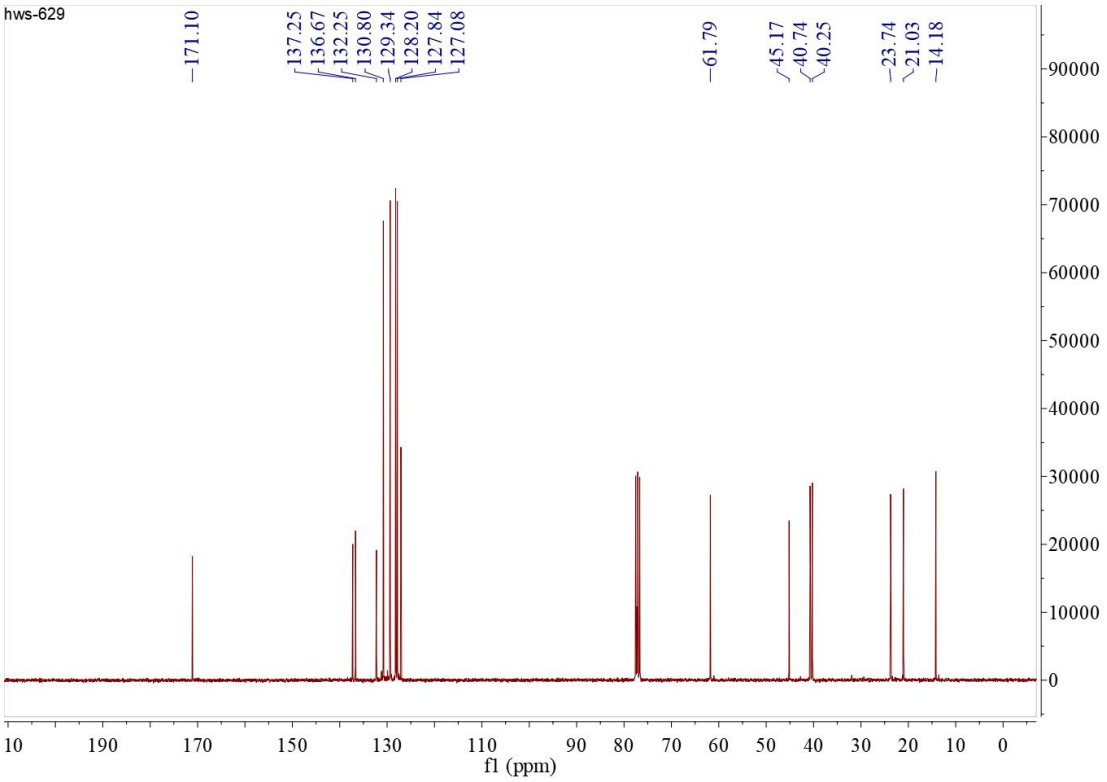
7b


hws-631
7.20
7.17
7.14
7.11
7.10
7.09
7.07
4.27
4.26
4.25
4.24
4.22
4.20
4.18
4.17
4.16
4.14
4.13
4.12
3.83
2.24
2.21
2.19
1.28
1.26
1.24
9.05
3.05
1.00
1.02
1.00
3.15
f1 (ppm)

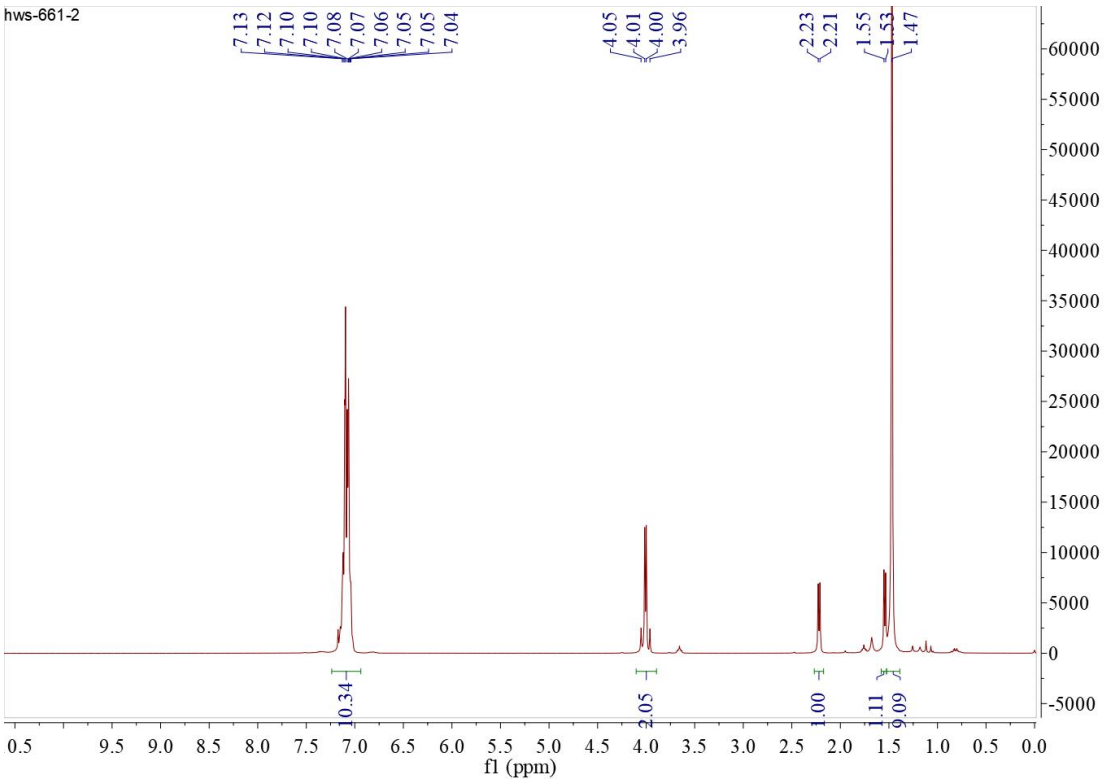

hws-631
170.44
136.81
134.52
132.74
130.57
129.14
128.06
127.42
121.25
62.03
44.61
40.58
39.97
24.01
14.13
f1 (ppm)

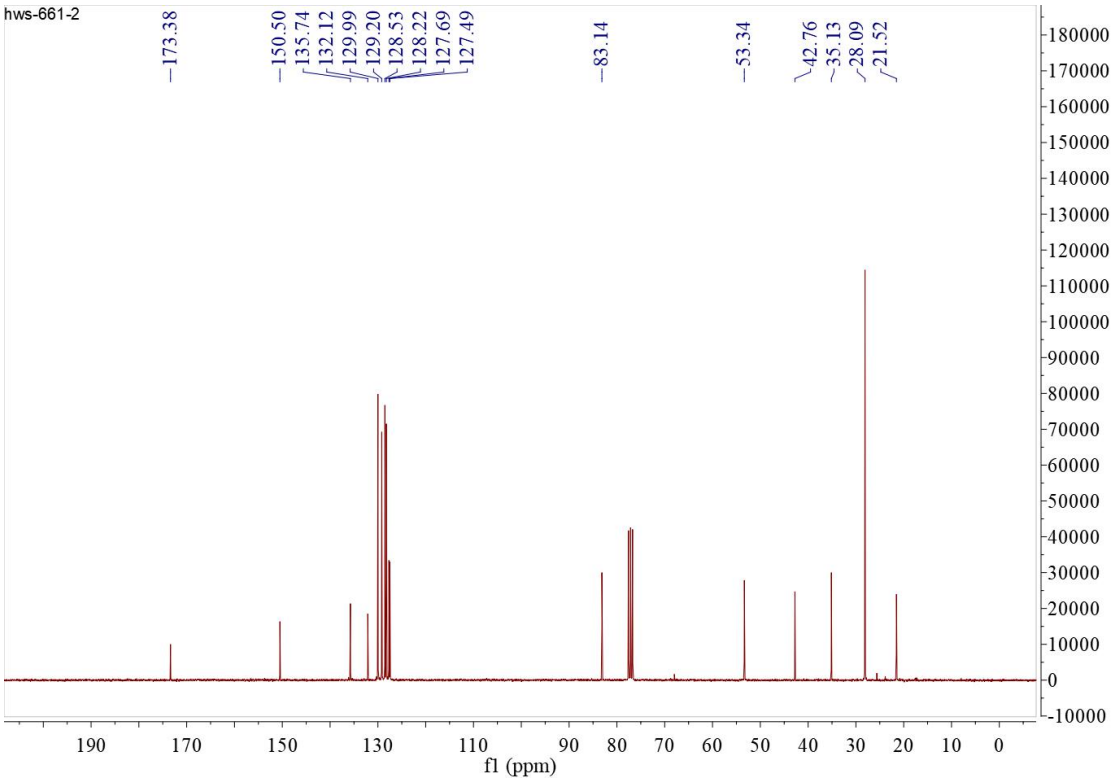
7c


hws-629
7.15
7.12
7.10
7.05
7.03
7.02
7.00
6.99
6.96
6.78
6.75
4.18
4.16
4.15
4.13
4.12
4.10
4.07
4.05
4.03
3.71
3.67
2.17
2.15
2.06
2.04
1.19
1.17
1.15
3.04
5.05
2.04
3.10
1.00
1.06
4.09
3.22
f1 (ppm)

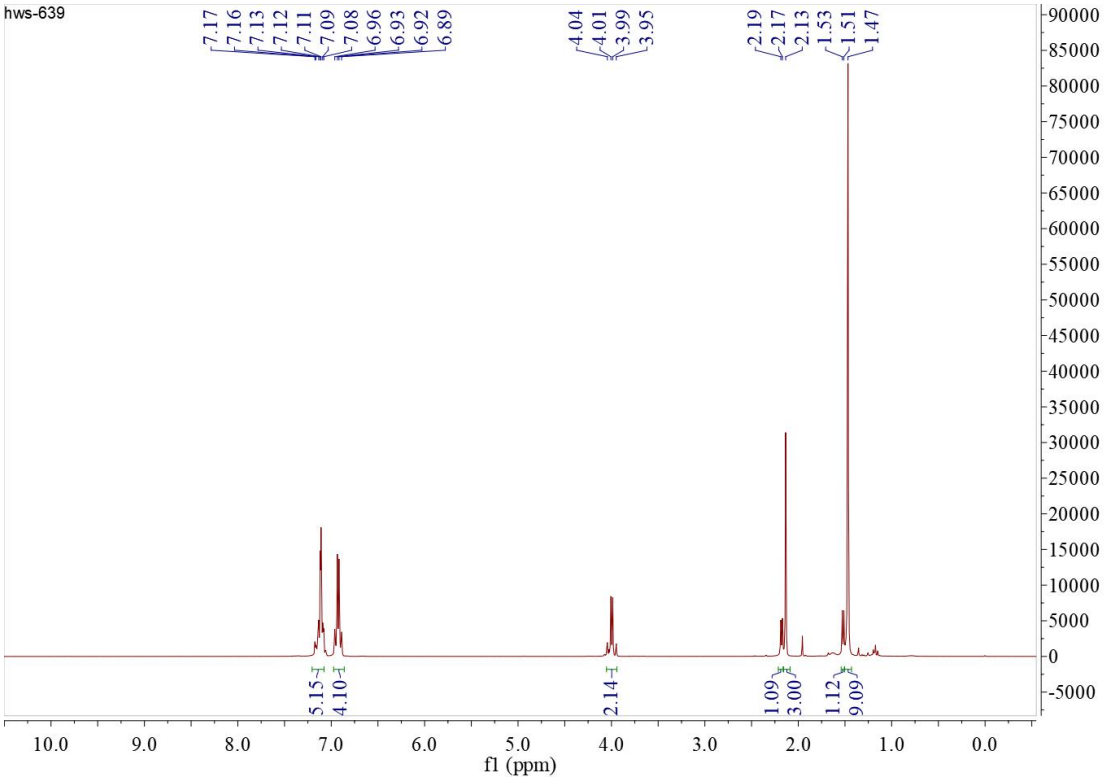

hws-629
171.10
137.25
136.67
132.25
130.80
129.34
128.20
127.84
127.08
61.79
45.17
40.74
40.25
23.74
21.03
14.18
f1 (ppm)

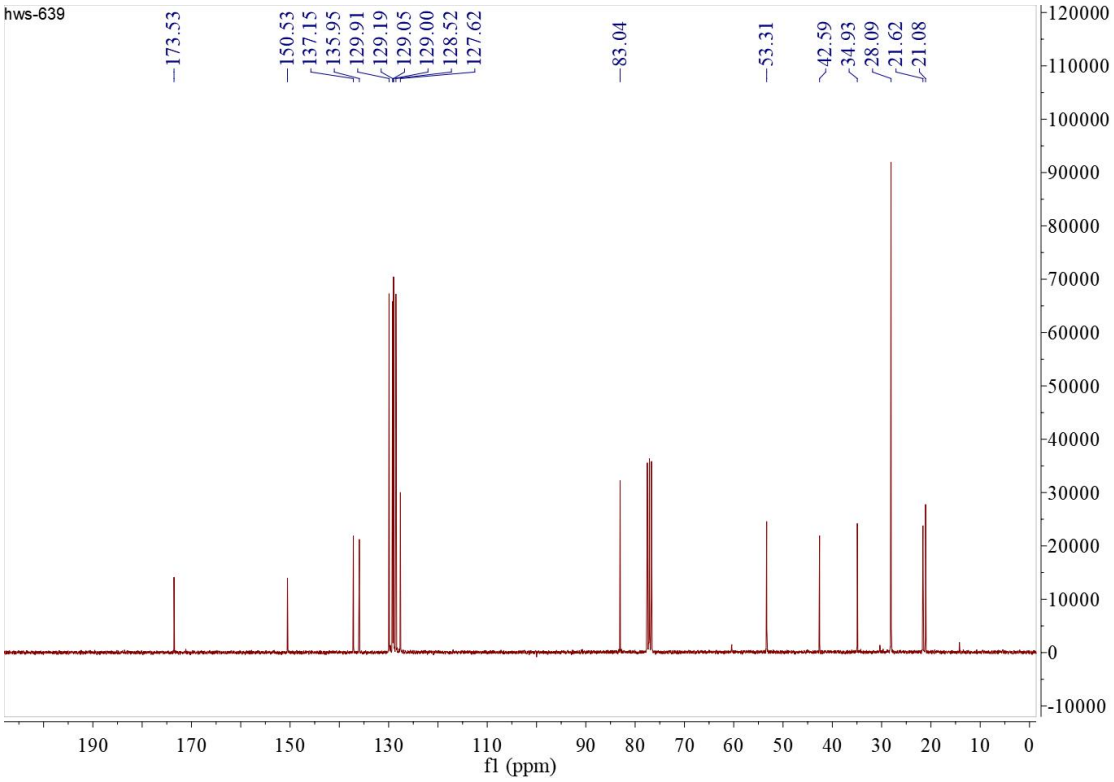
8


hws-661-2
7.13
7.12
7.10
7.10
7.08
7.07
7.06
7.05
7.05
7.04
4.05
4.01
4.00
3.96
2.23
2.21
1.55
1.53
1.47
10.34
2.05
1.00
1.11
9.09
f1 (ppm)

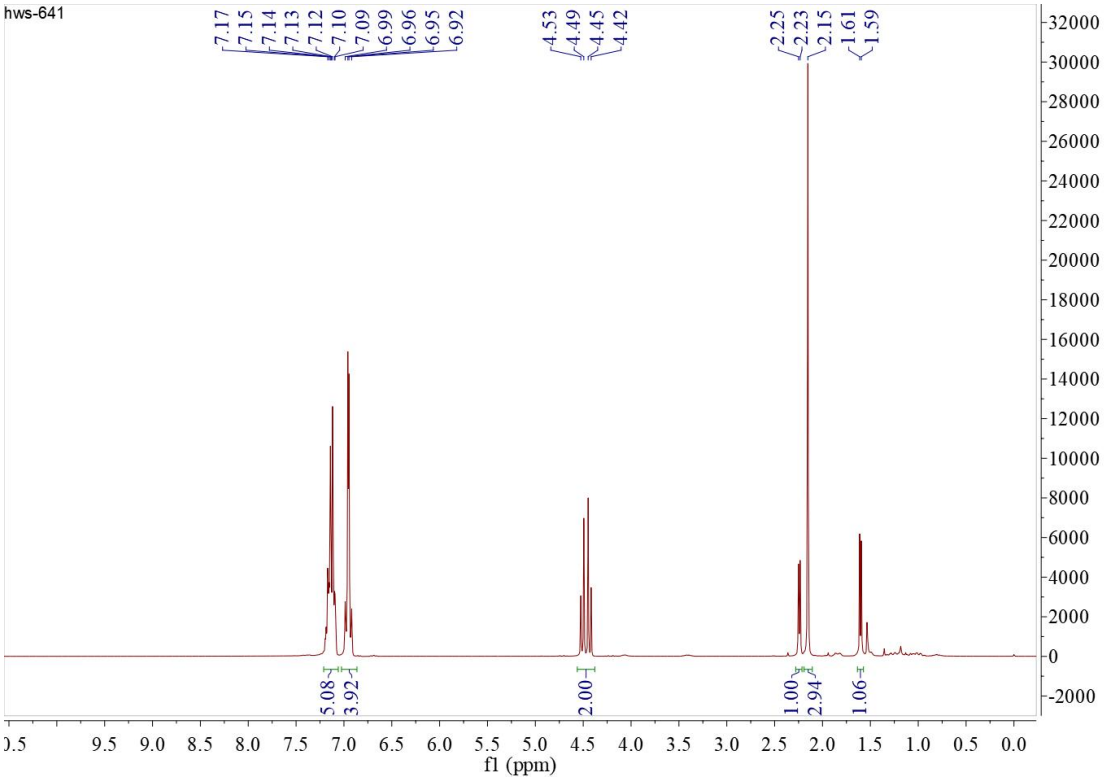

hws-661-2
173.38
150.50
135.74
132.12
129.99
129.20
128.53
128.22
127.69
127.49
83.14
53.34
42.76
35.13
28.09
21.52
f1 (ppm)

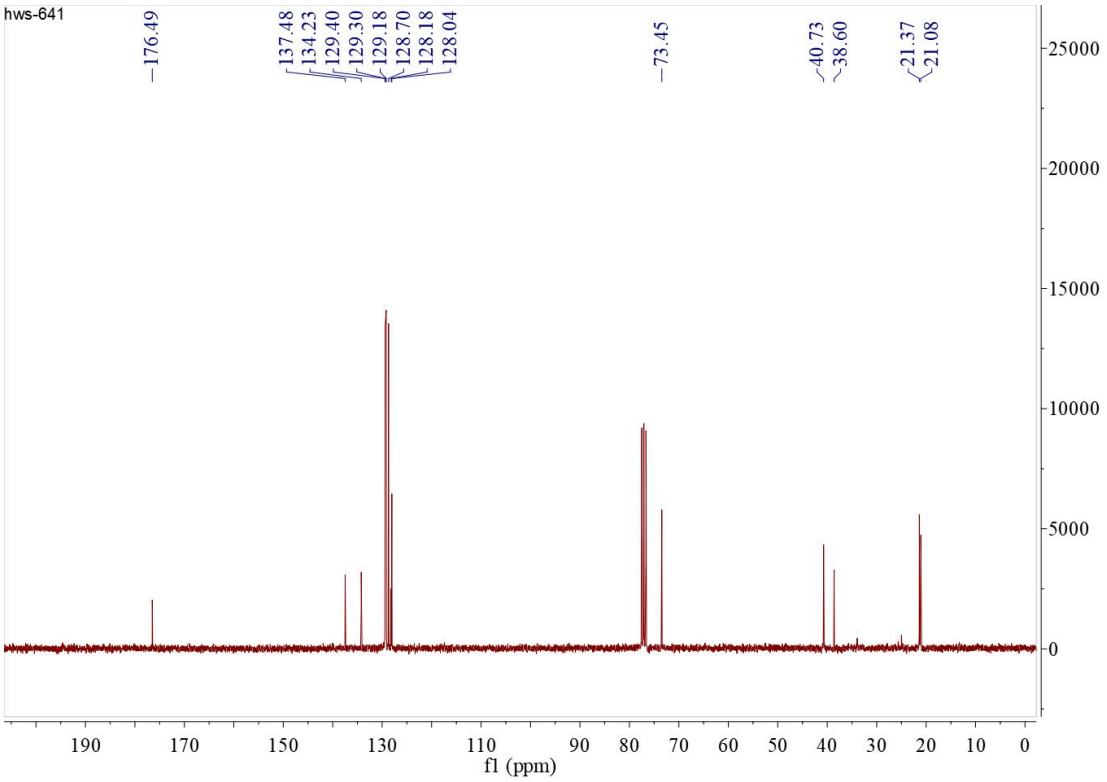
9


hws-639
7.17
7.16
7.13
7.12
7.11
7.09
7.08
6.96
6.93
6.92
6.89
4.04
4.01
3.99
3.95
2.19
2.17
2.13
1.53
1.51
1.47
5.15
4.10
2.14
1.09
3.00
1.12
9.09
f1 (ppm)

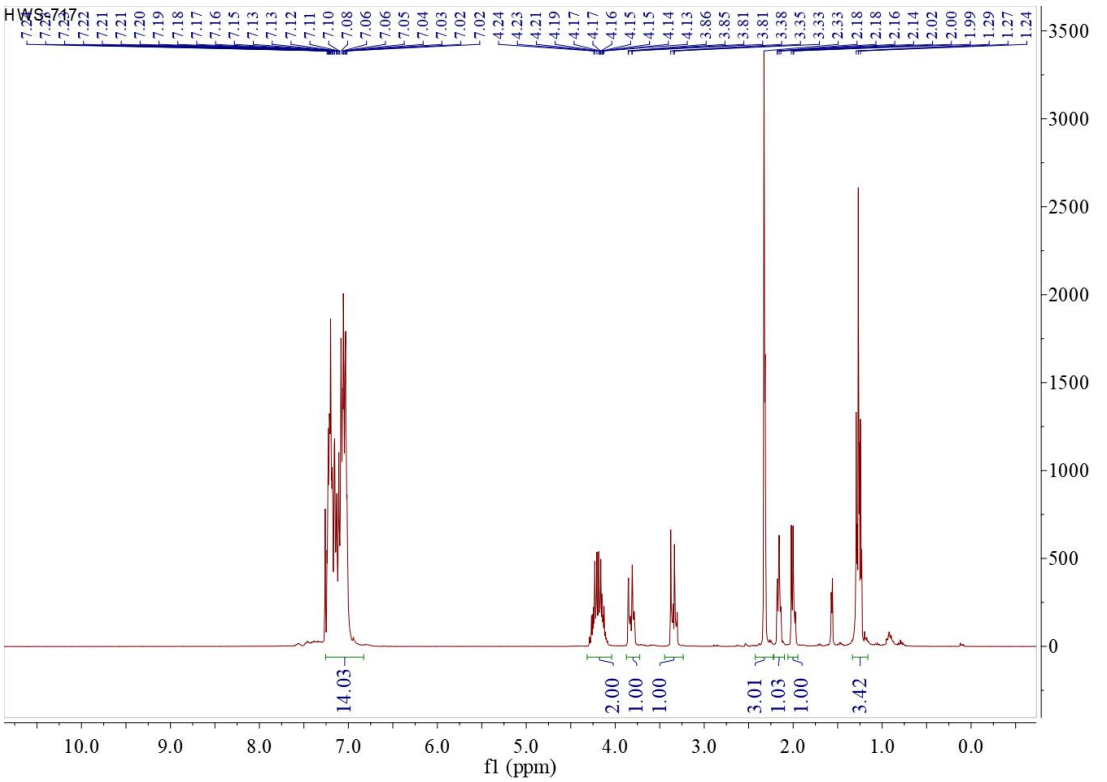

hws-639
173.53
150.53
137.15
135.95
129.91
129.19
129.05
129.00
128.52
127.62
83.04
53.31
42.59
34.93
28.09
21.62
21.08
f1 (ppm)

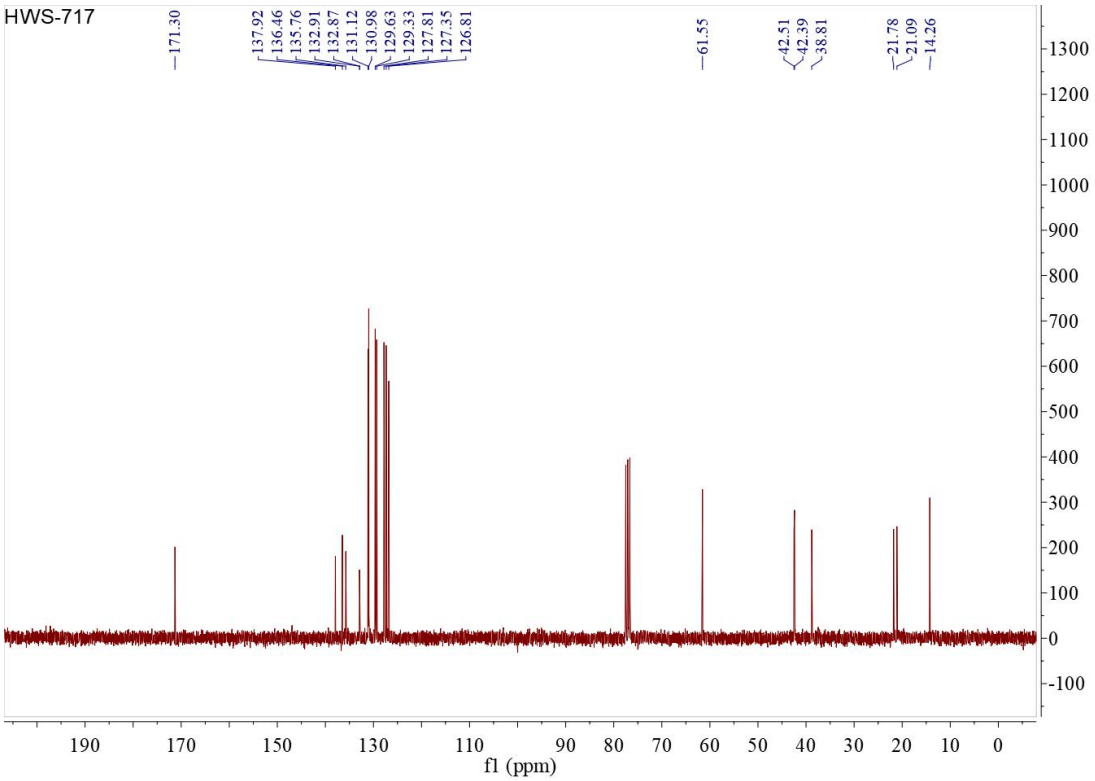
10


hws-641
7.17
7.15
7.14
7.13
7.12
7.10
7.09
6.99
6.96
6.95
6.92
4.53
4.49
4.45
4.42
2.25
2.23
2.15
1.61
1.59
5.08
3.92
2.00
1.00
2.94
1.06
f1 (ppm)

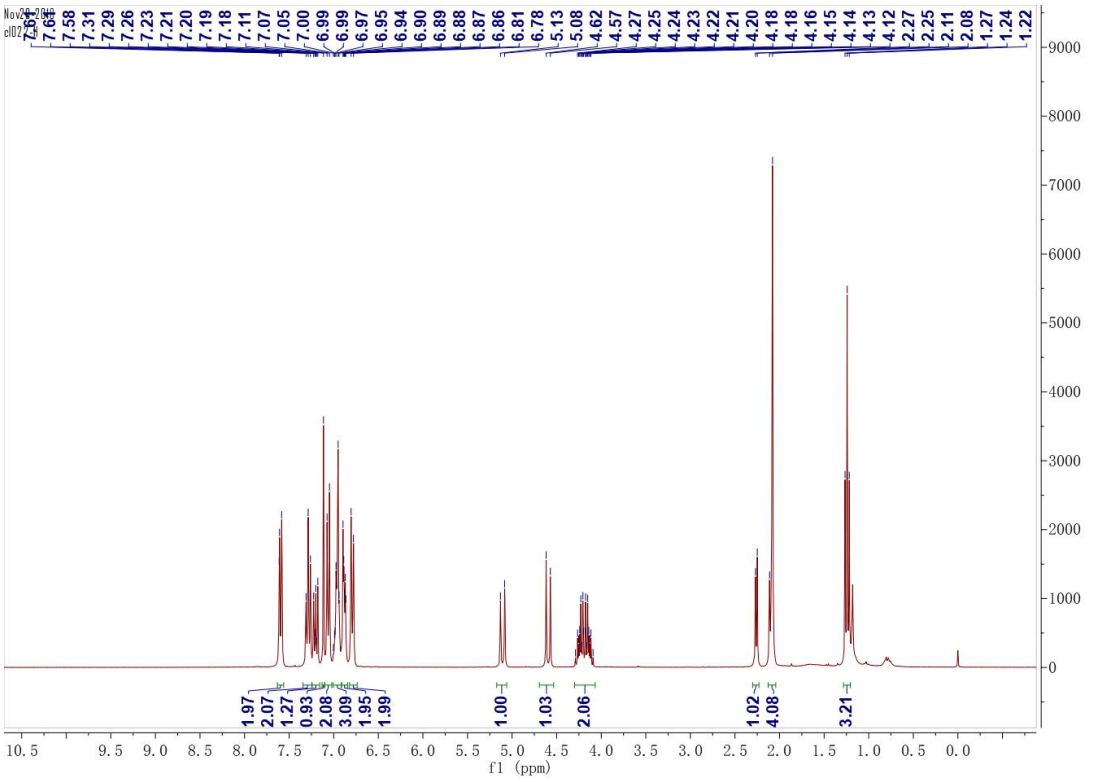

hws-641
176.49
137.48
134.23
129.40
129.30
129.18
128.70
128.18
128.04
73.45
40.73
38.60
21.37
21.08
25000
20000
15000
10000
5000
0
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

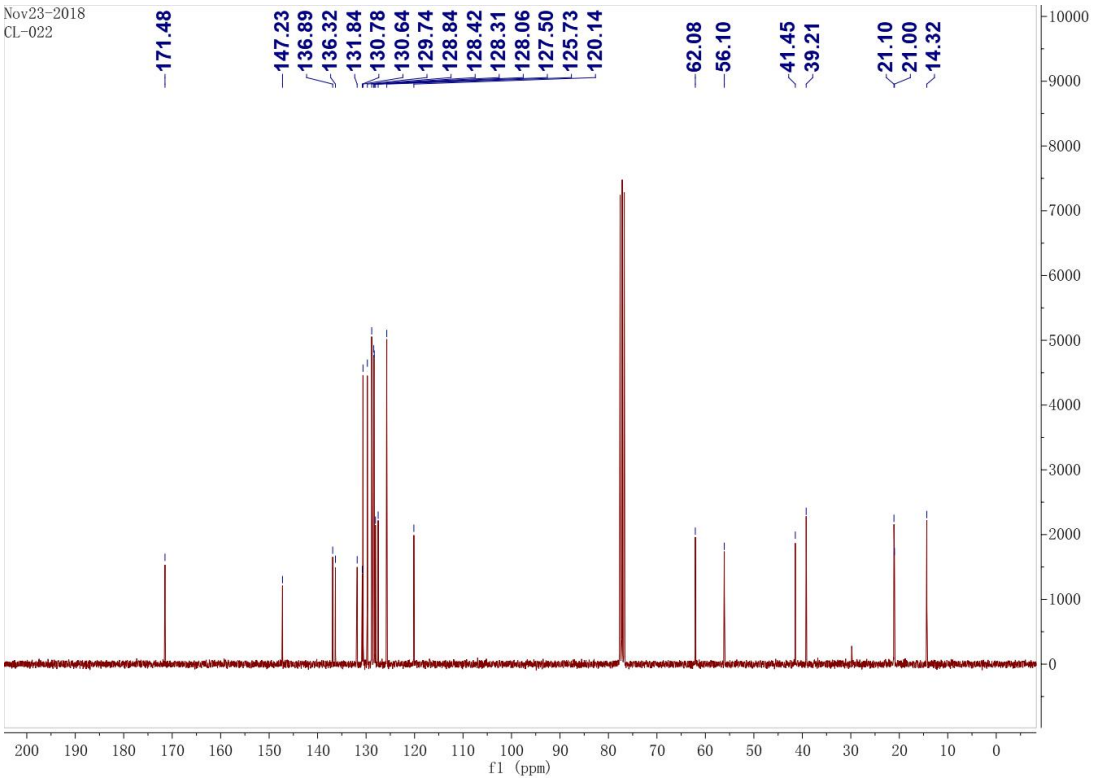
11


HWS-717
3500
3000
2500
2000
1500
1000
500
0
14.03
2.00
1.00
1.00
3.01
1.03
1.00
3.42
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


HWS-717
171.30
137.92
136.46
135.76
132.91
132.87
131.12
130.98
129.63
129.33
127.81
127.35
126.81
61.55
42.51
42.39
38.81
21.78
21.09
14.26
f1 (ppm)

12


7.65
7.58
7.31
7.29
7.26
7.23
7.21
7.20
7.19
7.18
7.11
7.07
7.05
7.00
6.99
6.99
6.97
6.95
6.94
6.90
6.89
6.88
6.87
6.86
6.81
6.78
5.13
5.08
4.62
4.57
4.27
4.25
4.24
4.23
4.22
4.21
4.20
4.18
4.18
4.16
4.15
4.14
4.13
4.12
2.27
2.25
2.11
2.08
1.27
1.24
1.22
1.97
2.07
1.27
0.93
2.08
3.09
1.95
1.99
1.00
1.03
2.06
1.02
4.08
3.21
f1 (ppm)


Nov23-2018
CL-022
171.48
147.23
136.89
136.32
131.84
130.78
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129.74
128.84
128.42
128.31
128.06
127.50
125.73
120.14
62.08
56.10
41.45
39.21
21.10
21.00
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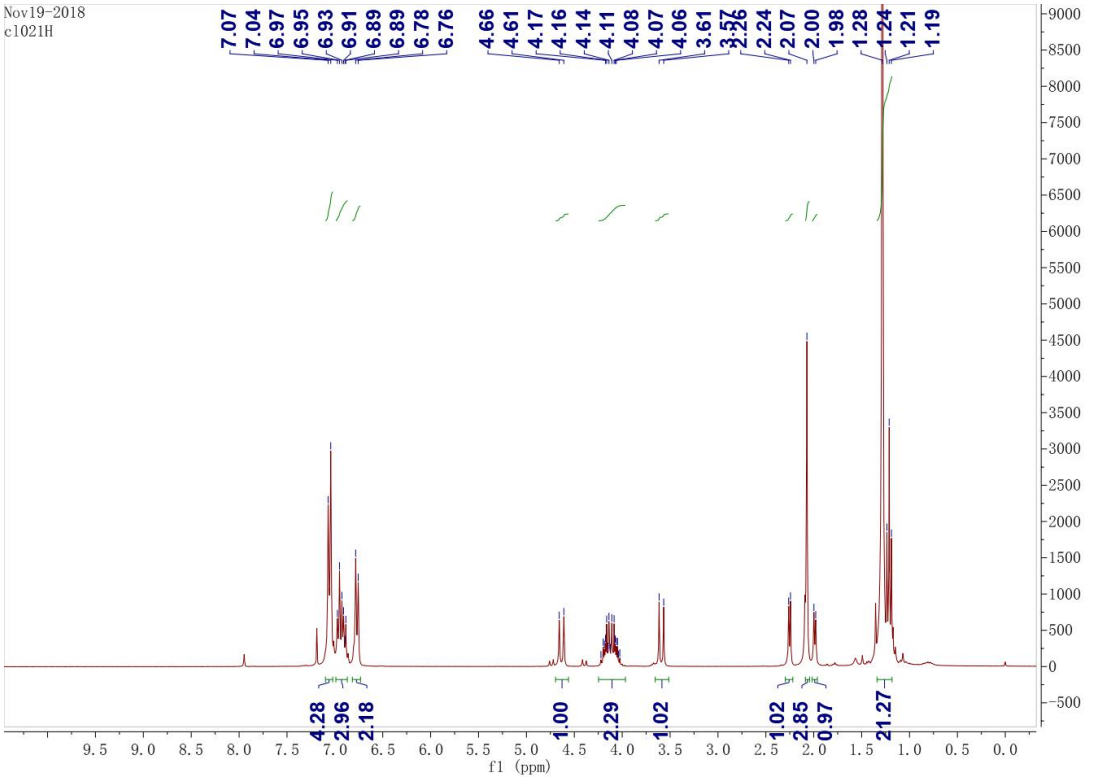
f1 (ppm)

13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1.24
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2.29
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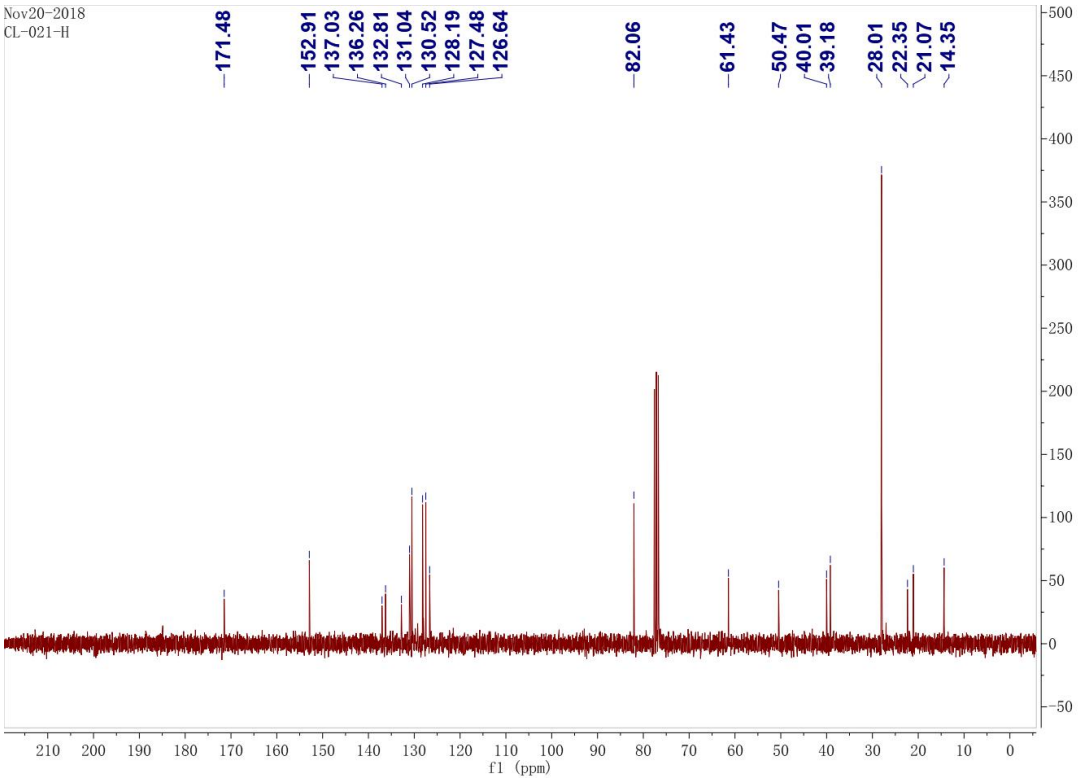
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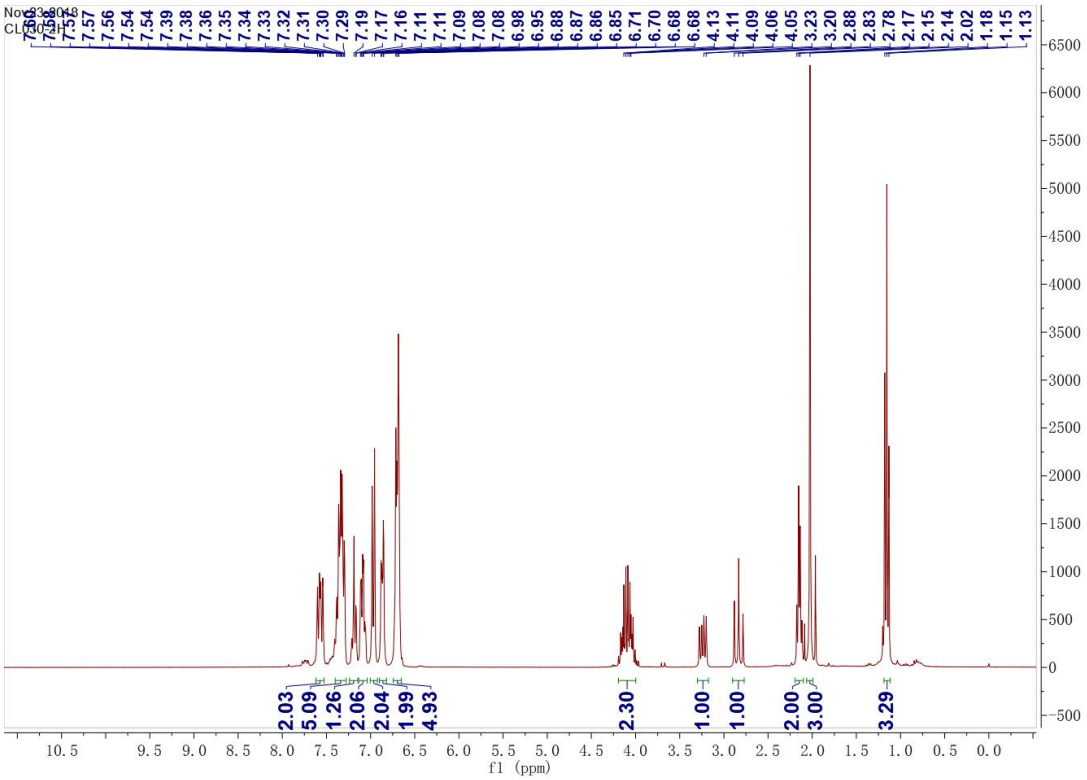
14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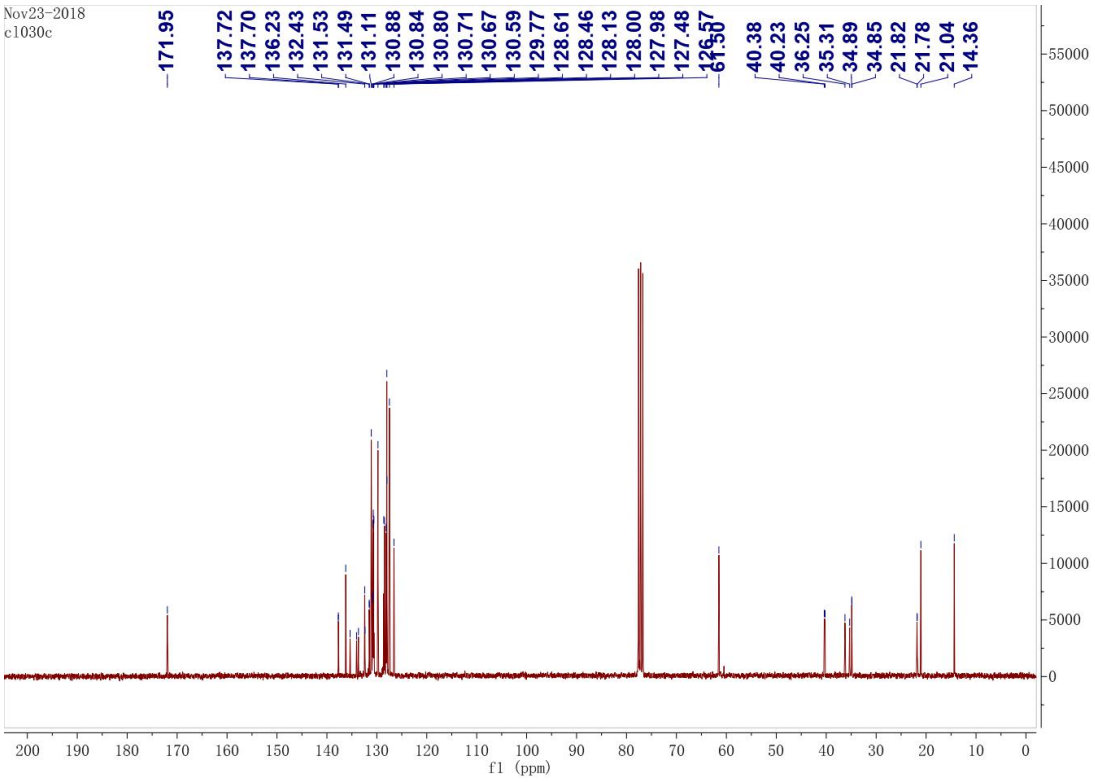
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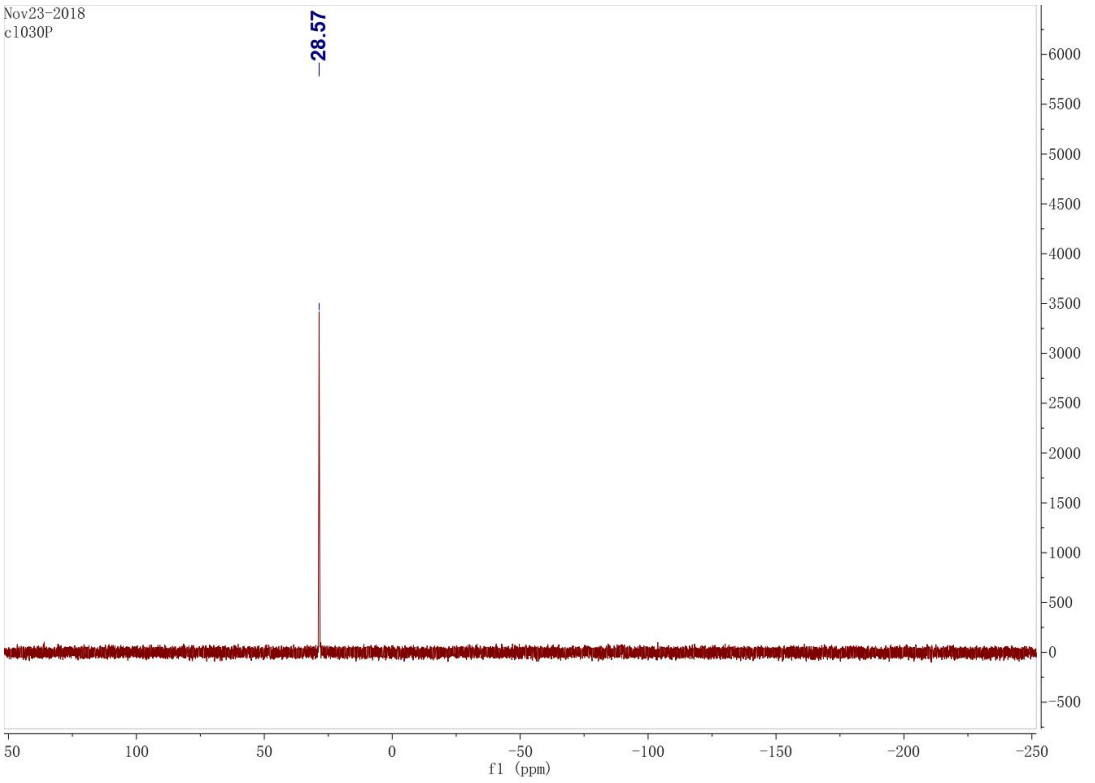
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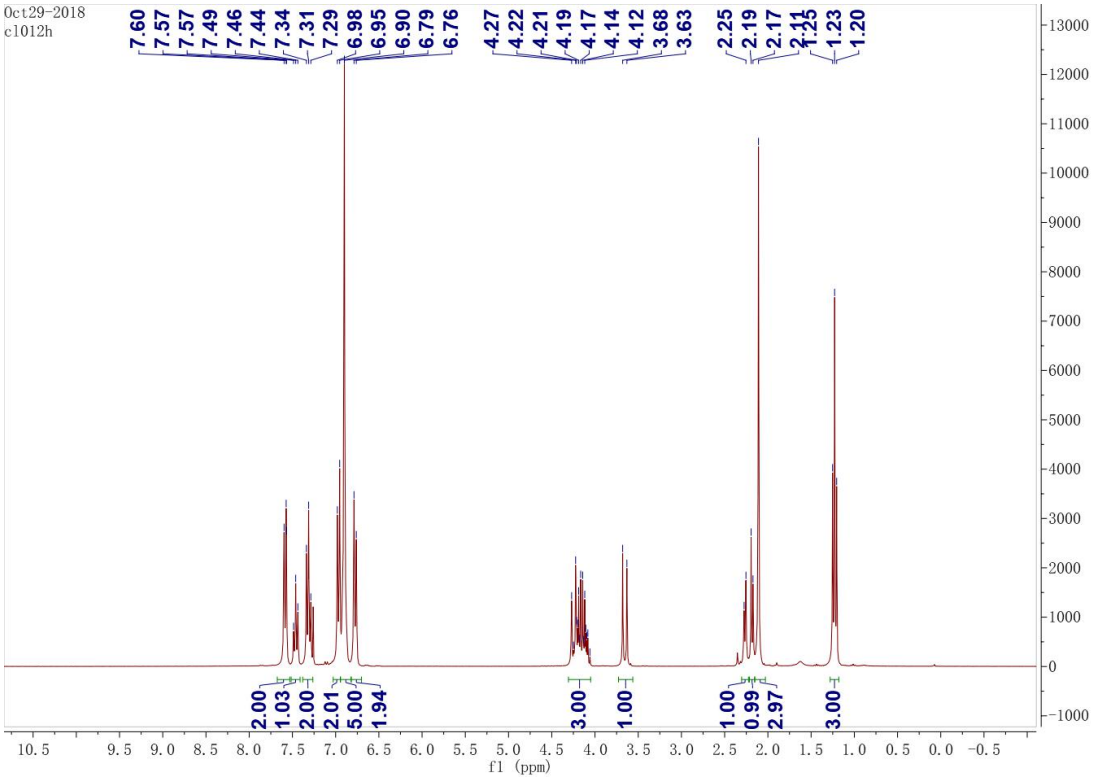
15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6.76
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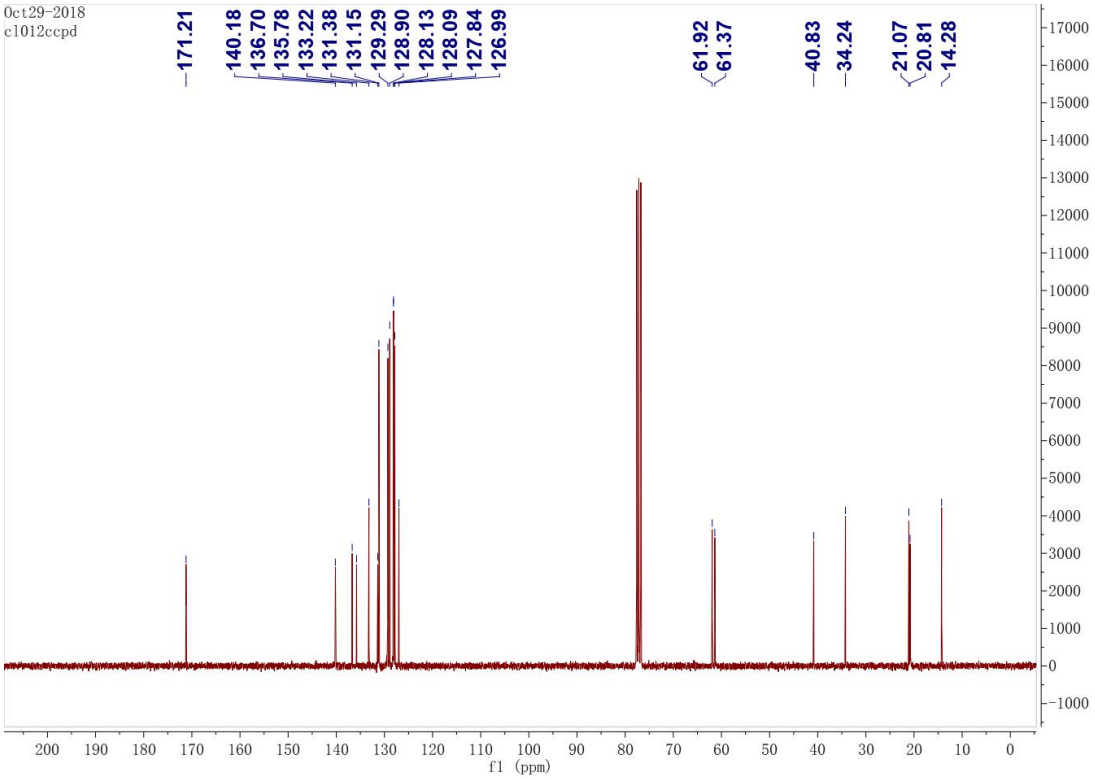
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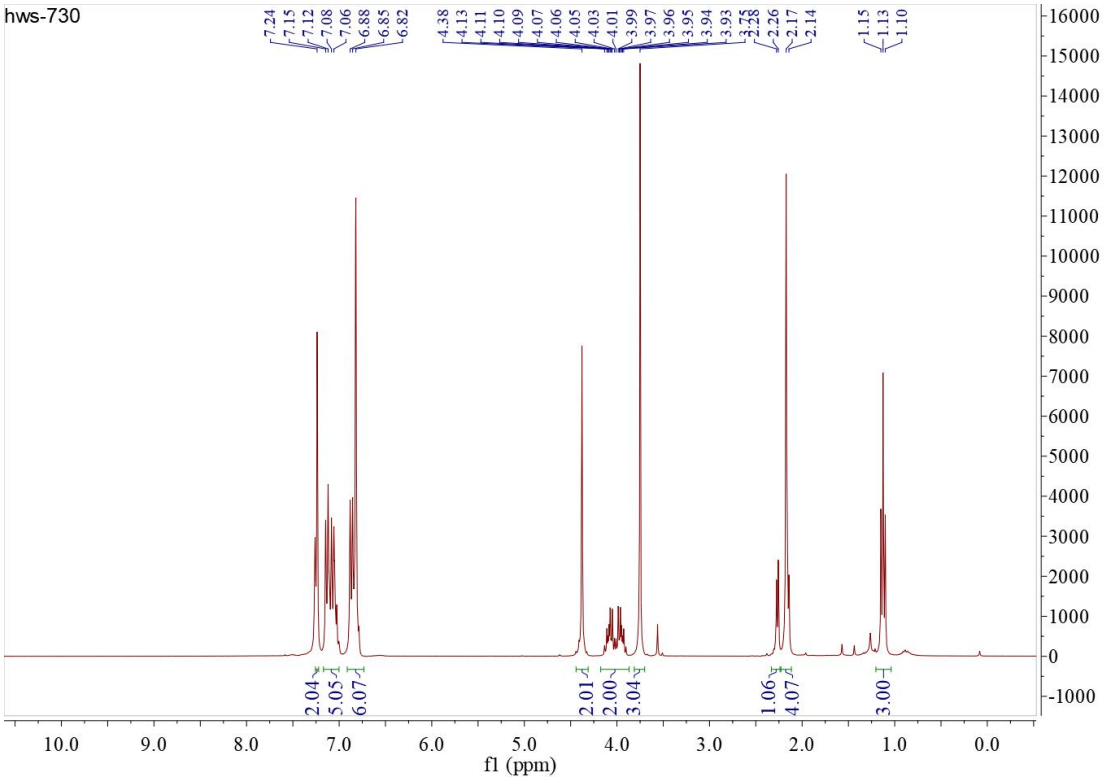
16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3.93
3.75
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1.15
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1.10
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5.05
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2.01
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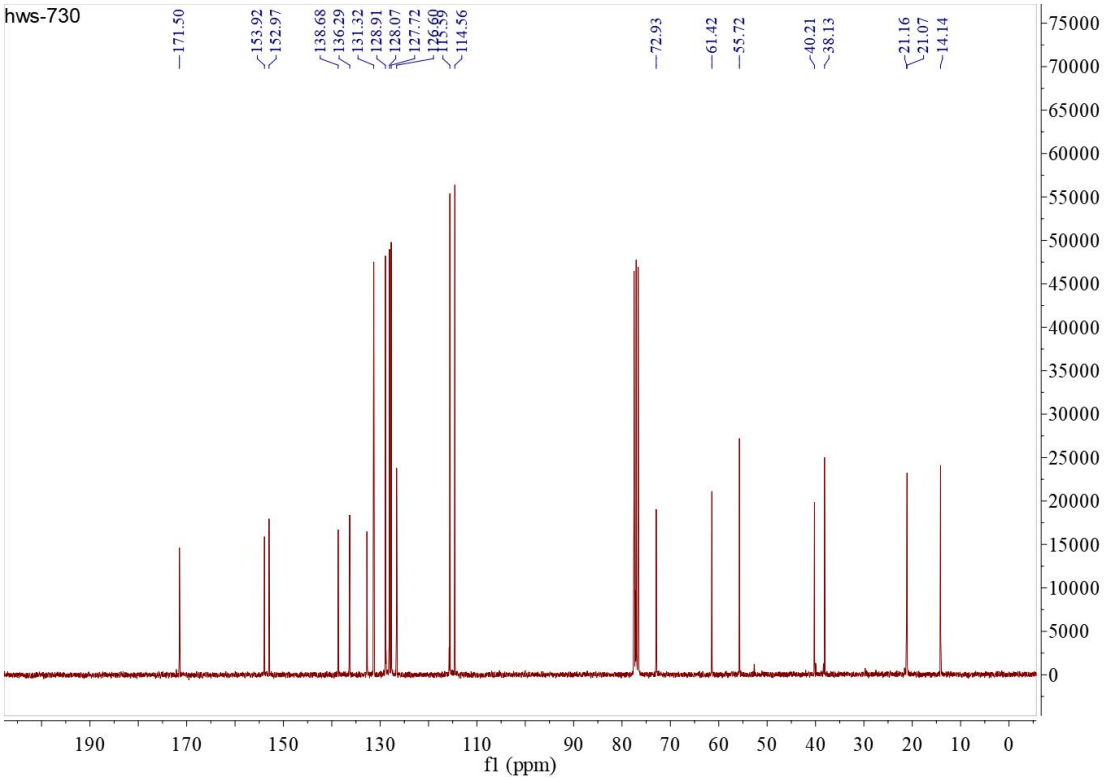
3.04
1.06
4.07
3.00
fl (ppm)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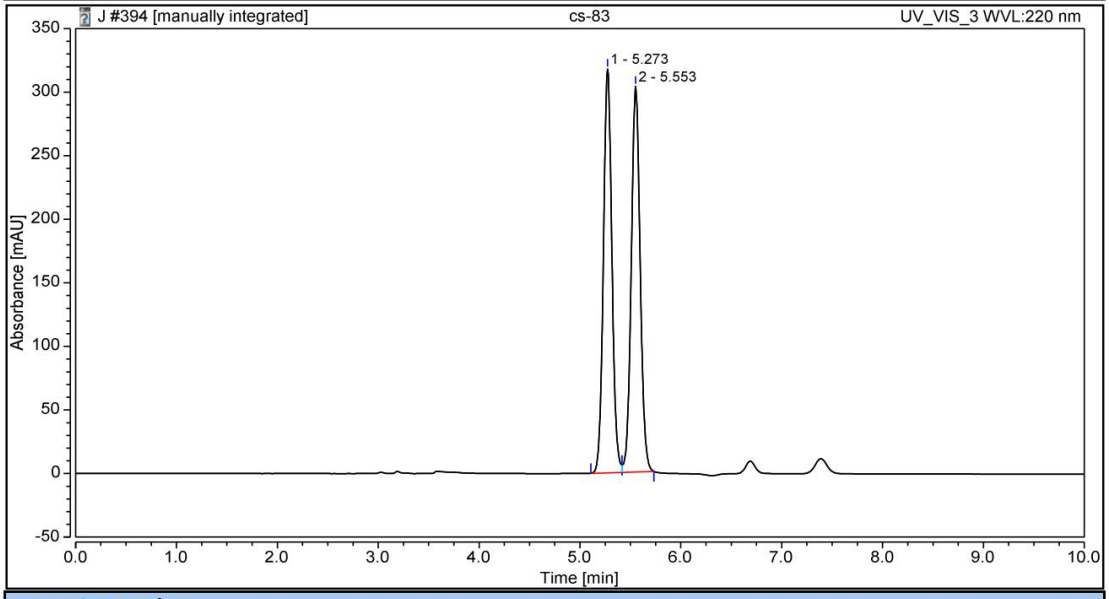
21.16
21.07
14.14
fl (ppm)

HPLC Chromatogram

3a

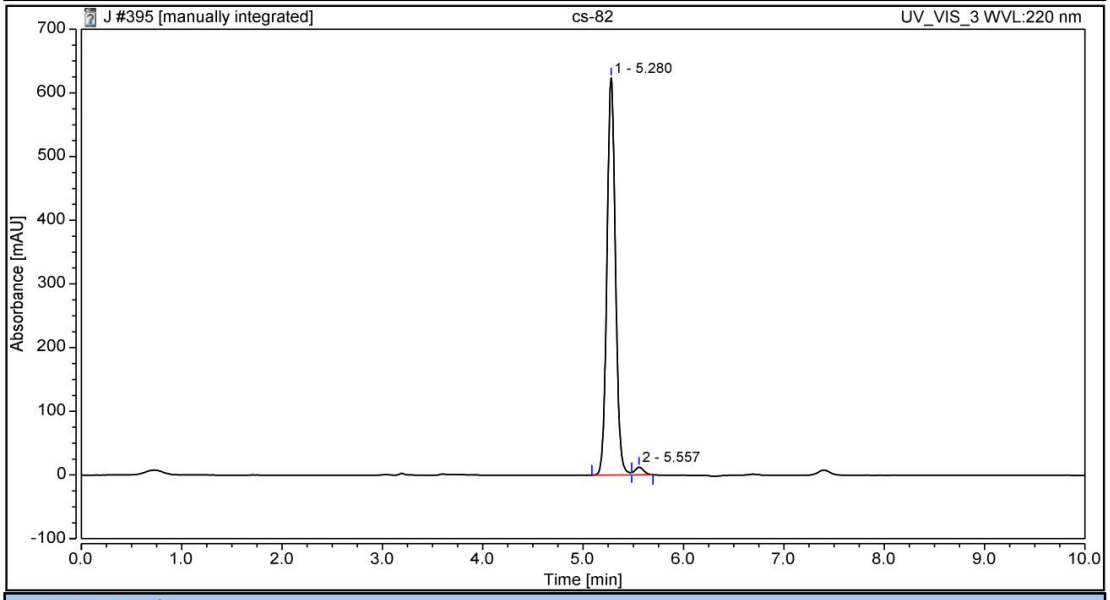
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.273	31.005	317.675	49.92	51.16	n.a.
2		5.553	31.105	303.295	50.08	48.84	n.a.
Total:			**62.111**	**620.970**	**100.00**	**100.00**	

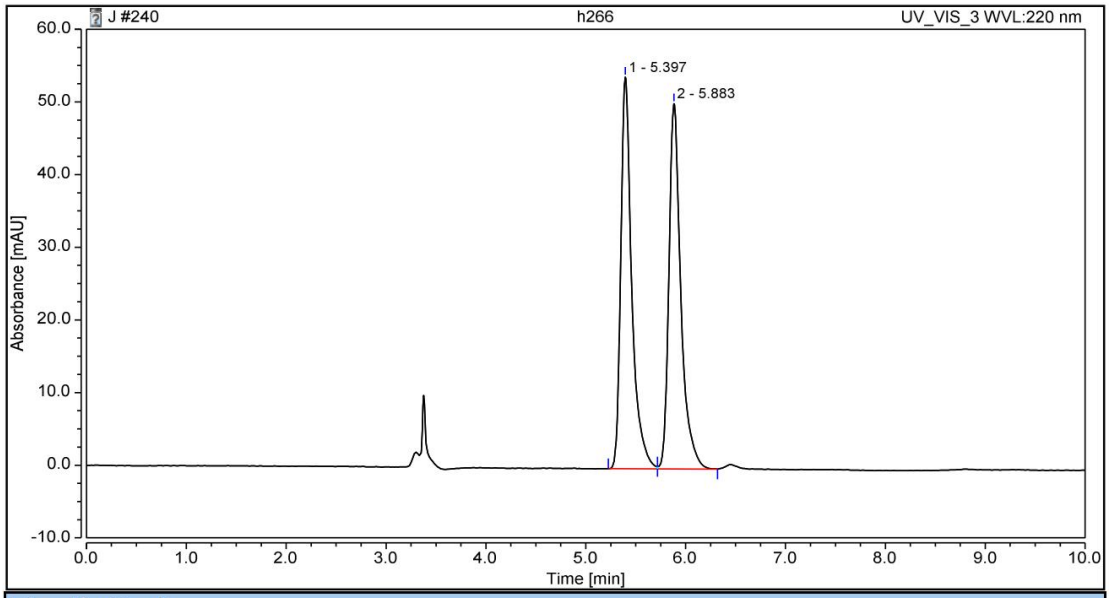
Chromatogram



Integration Results

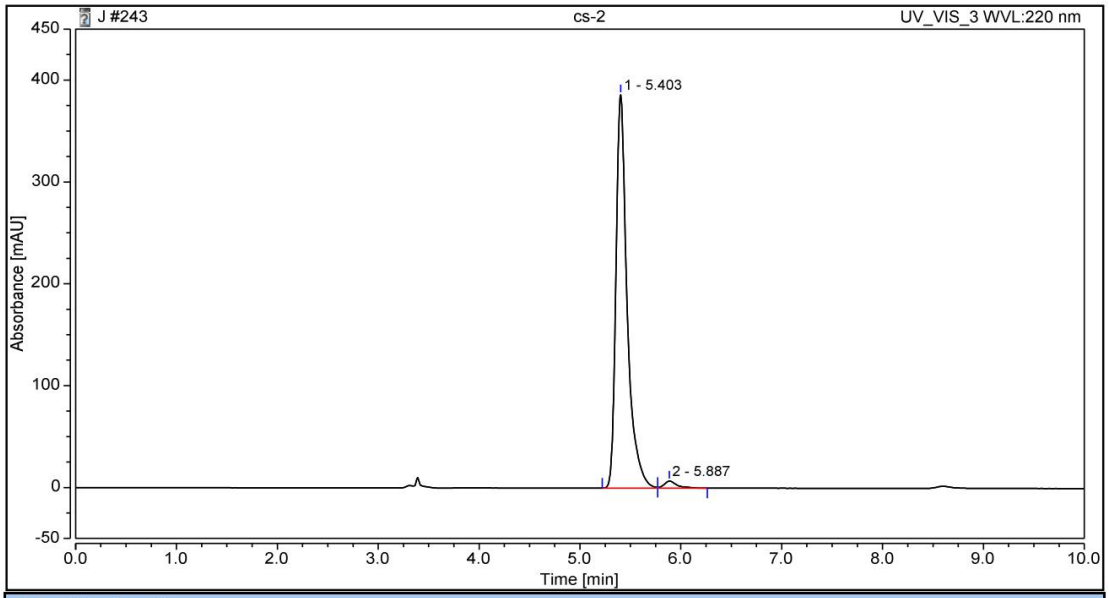
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.280	61.174	623.644	98.03	98.11	n.a.
2		5.557	1.232	11.997	1.97	1.89	n.a.
Total:			**62.405**	**635.641**	**100.00**	**100.00**	

3b



Integration Results

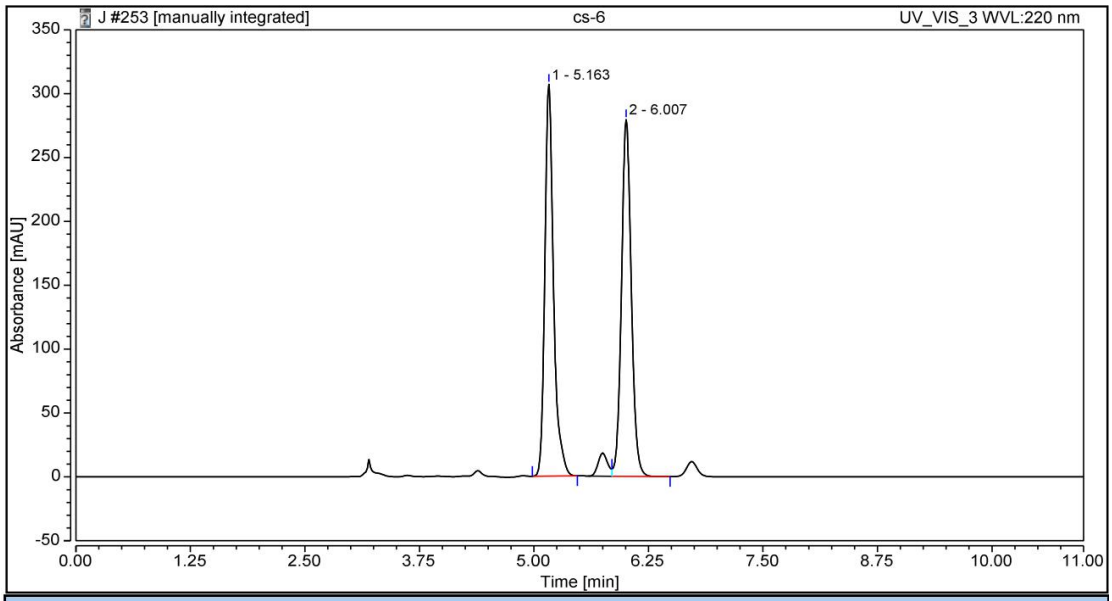
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.397	6.866	53.903	49.65	51.75	n.a.
2		5.883	6.963	50.261	50.35	48.25	n.a.
Total:			**13.829**	**104.164**	**100.00**	**100.00**	



Integration Results

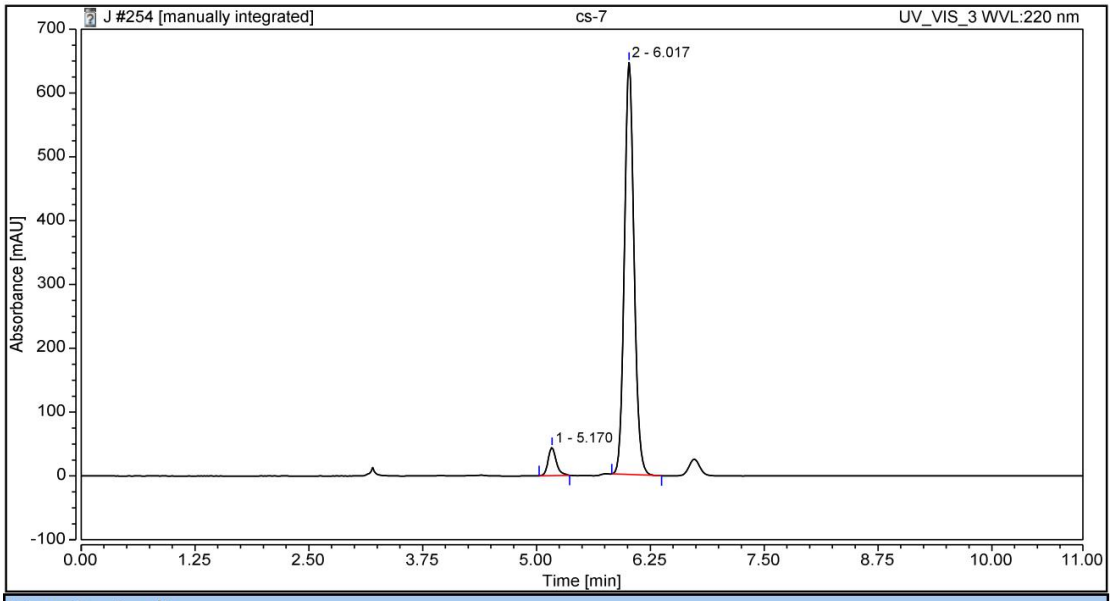
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.403	49.434	386.204	97.95	98.22	n.a.
2		5.887	1.036	6.992	2.05	1.78	n.a.
Total:			**50.469**	**393.196**	**100.00**	**100.00**	

3c



Integration Results

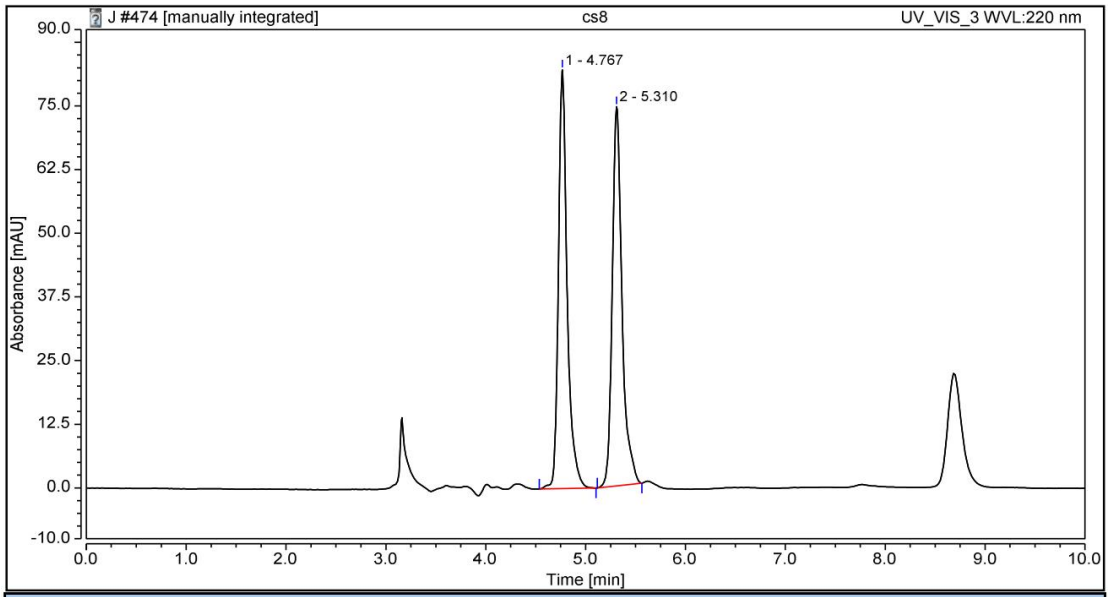
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.163	33.763	306.655	49.43	52.34	n.a.
2		6.007	34.539	279.219	50.57	47.66	n.a.
Total:			**68.301**	**585.874**	**100.00**	**100.00**	



Integration Results

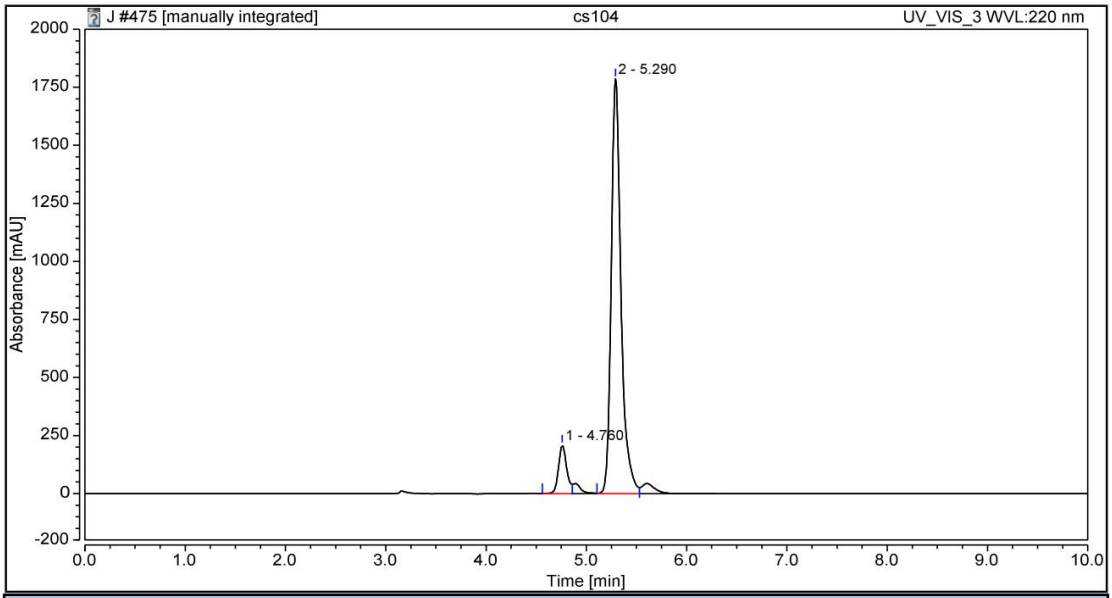
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.170	4.617	43.772	5.52	6.35	n.a.
2		6.017	79.081	645.585	94.48	93.65	n.a.
Total:			**83.698**	**689.357**	**100.00**	**100.00**	

3d



Integration Results

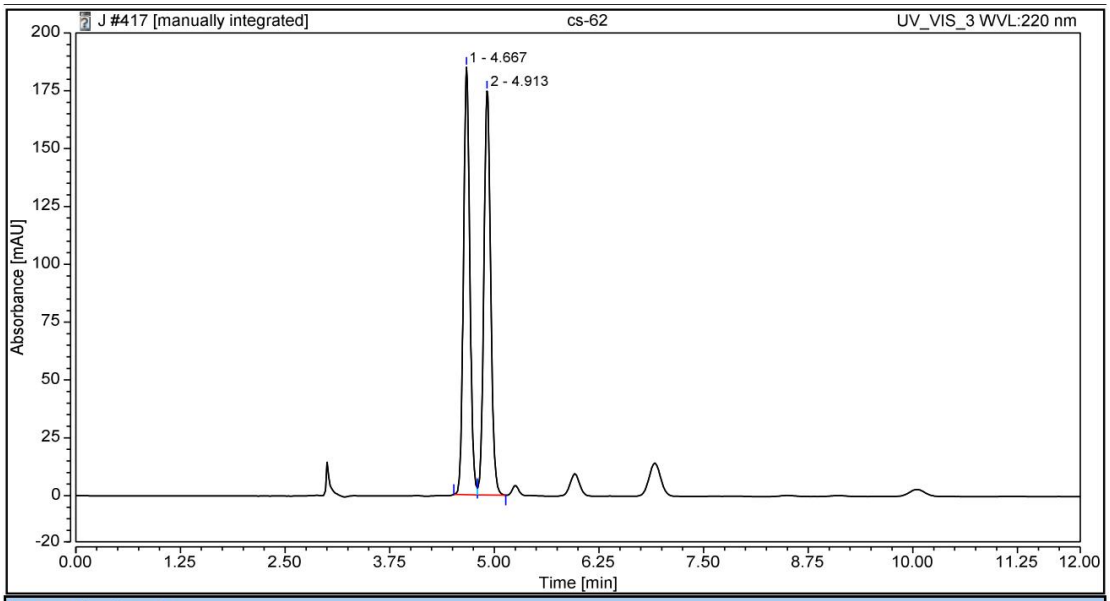
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.767	8.390	82.226	49.91	52.47	n.a.
2		5.310	8.419	74.488	50.09	47.53	n.a.
Total:			**16.809**	**156.714**	**100.00**	**100.00**	



Integration Results

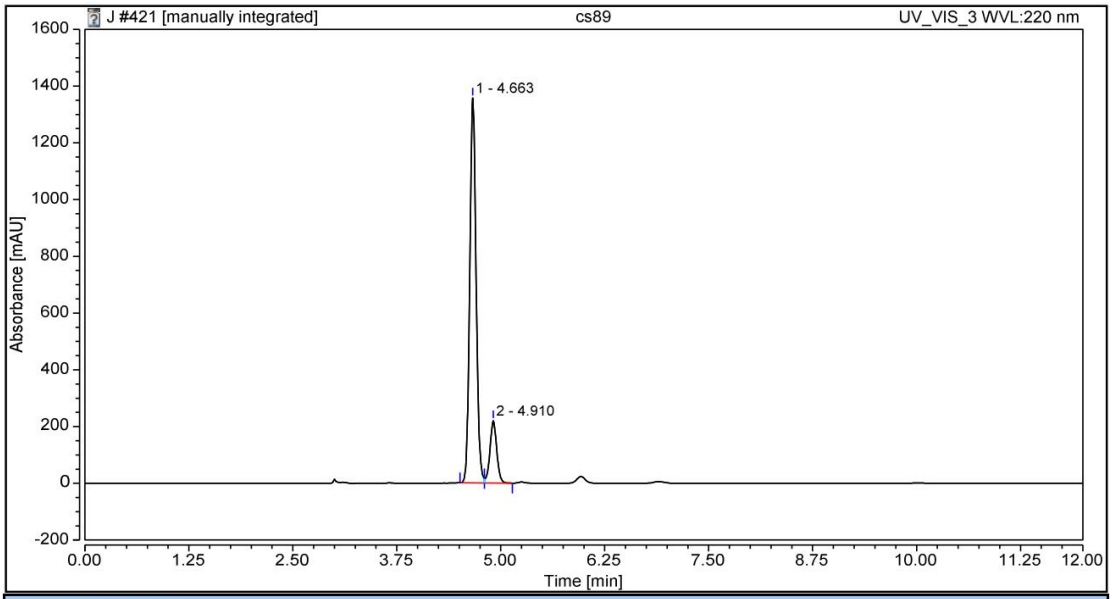
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.760	19.714	208.371	8.94	10.45	n.a.
2		5.290	200.826	1786.008	91.06	89.55	n.a.
Total:			**220.540**	**1994.379**	**100.00**	**100.00**	

3e



Integration Results

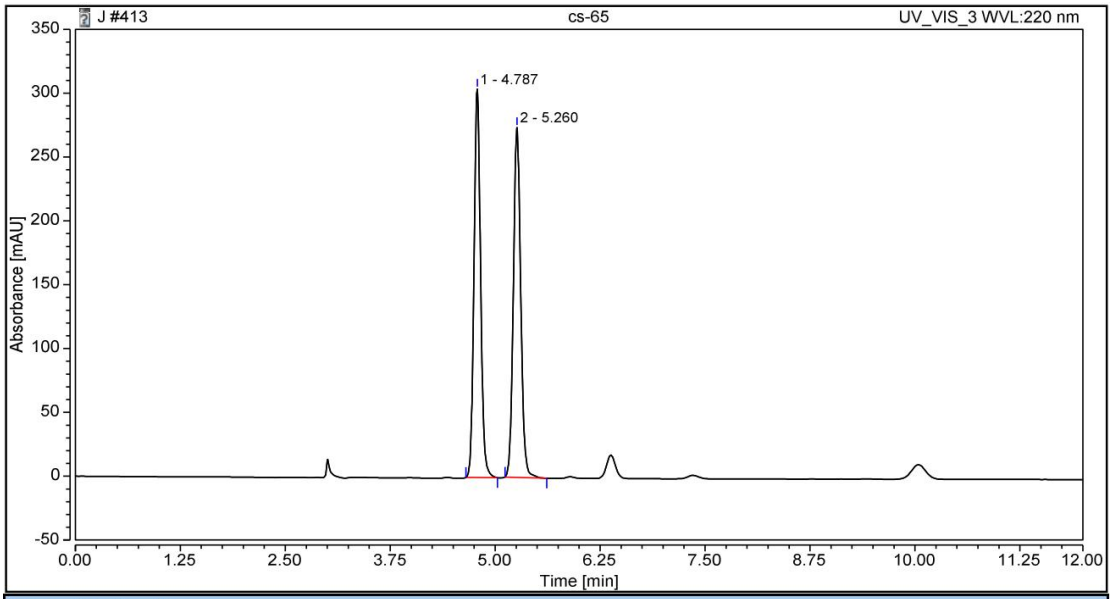
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.667	16.279	184.802	49.64	51.41	n.a.
2		4.913	16.515	174.674	50.36	48.59	n.a.
Total:			**32.794**	**359.476**	**100.00**	**100.00**	



Integration Results

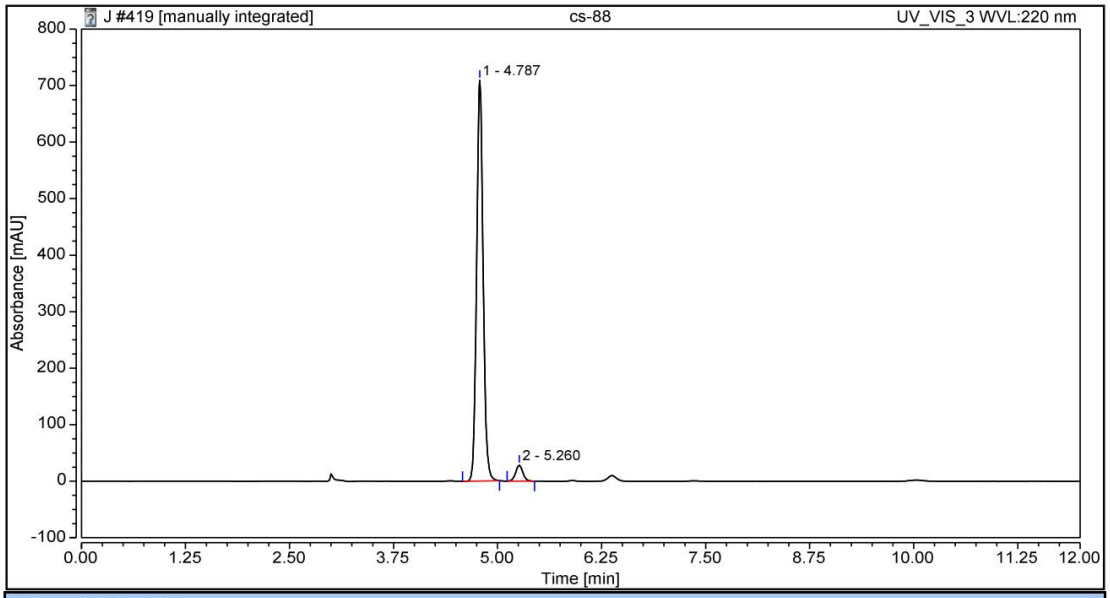
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.663	120.014	1355.929	85.21	86.08	n.a.
2		4.910	20.829	219.337	14.79	13.92	n.a.
Total:			**140.843**	**1575.266**	**100.00**	**100.00**	

3f



Integration Results

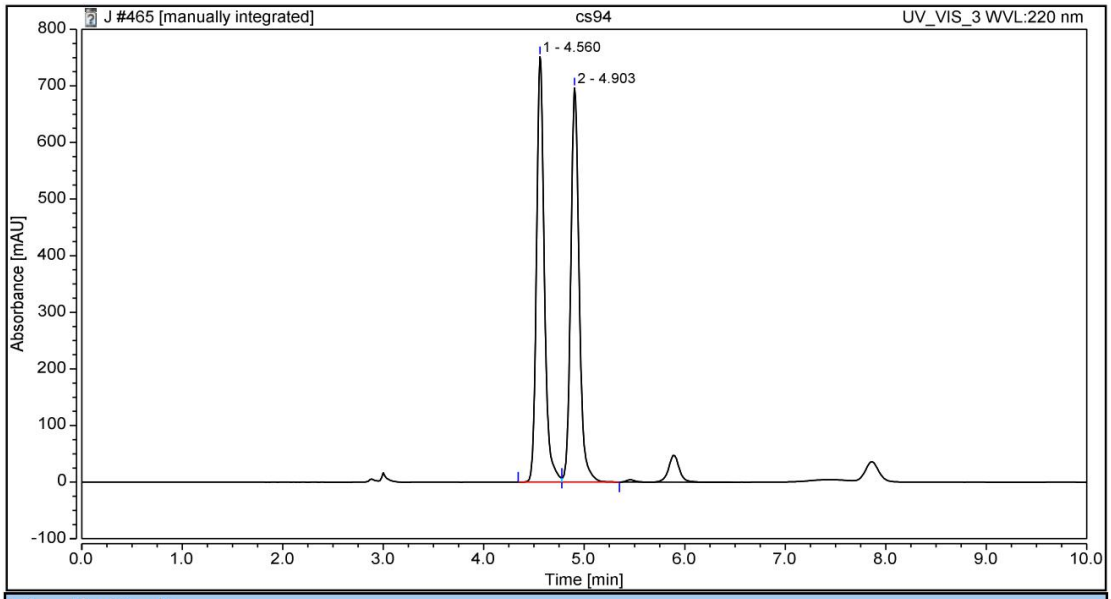
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.787	27.678	304.208	49.90	52.61	n.a.
2		5.260	27.794	274.004	50.10	47.39	n.a.
Total:			**55.472**	**578.212**	**100.00**	**100.00**	



Integration Results

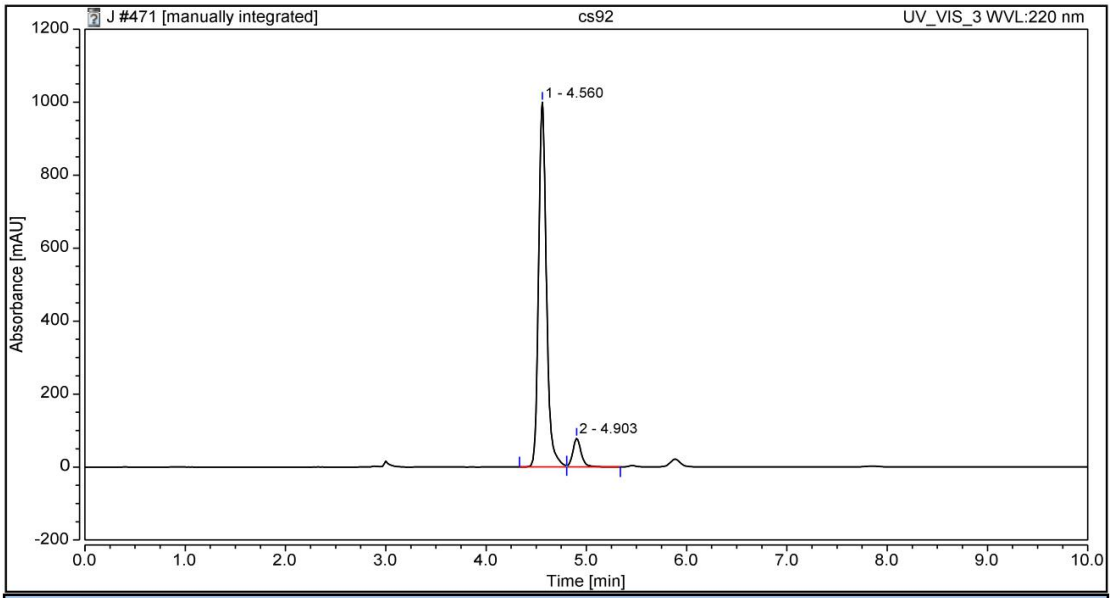
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.787	64.381	709.165	95.78	96.16	n.a.
2		5.260	2.837	28.350	4.22	3.84	n.a.
Total:			**67.217**	**737.515**	**100.00**	**100.00**	

3g



Integration Results

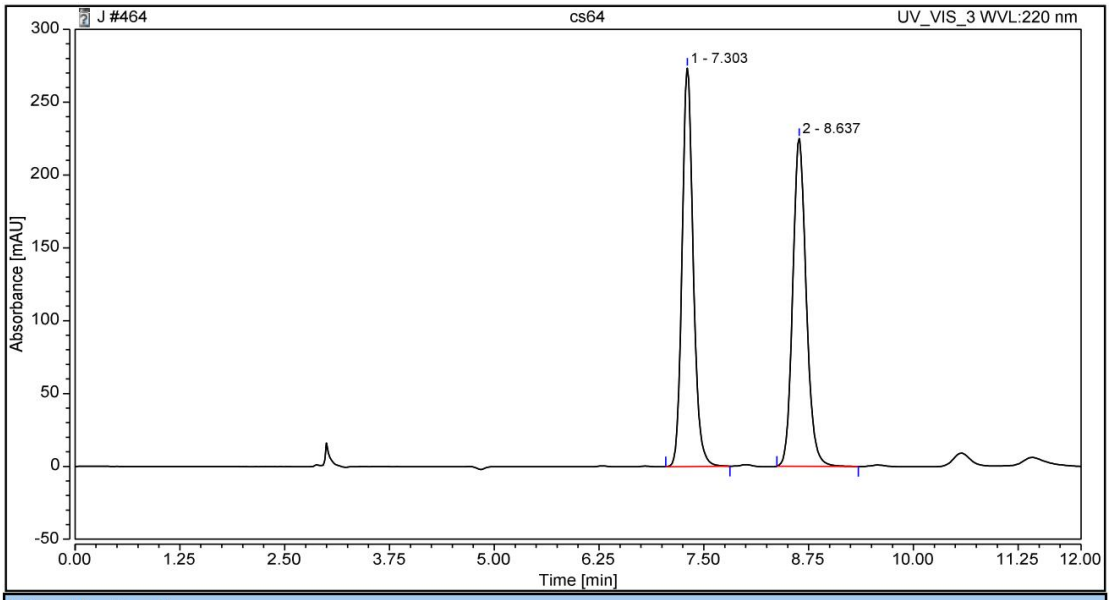
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.560	68.284	751.621	50.15	51.91	n.a.
2		4.903	67.880	696.361	49.85	48.09	n.a.
Total:			**136.164**	**1447.982**	**100.00**	**100.00**	



Integration Results

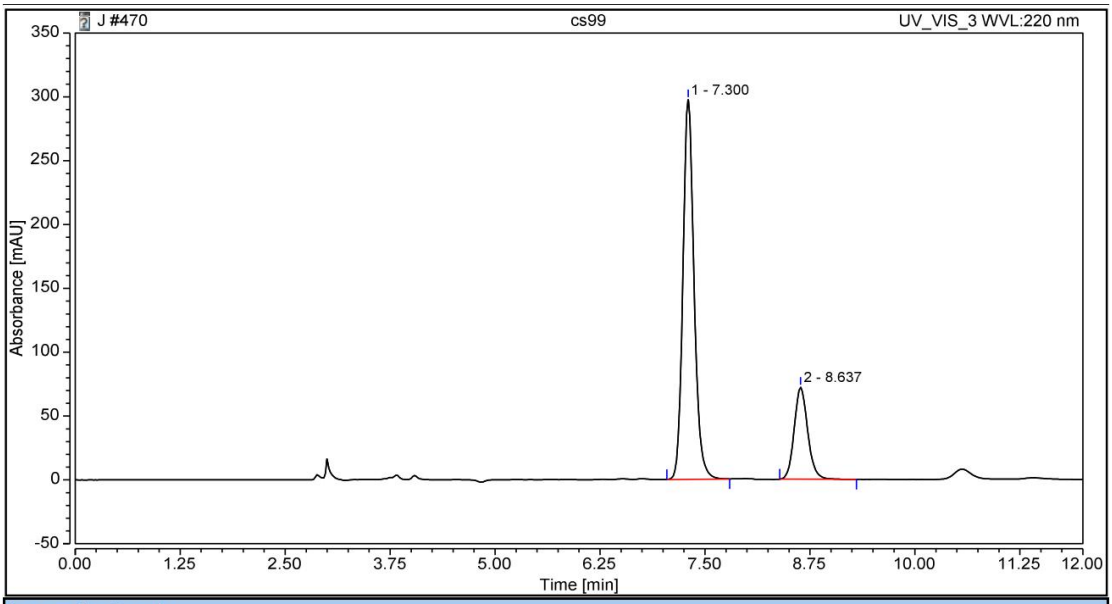
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.560	90.681	999.583	92.20	92.70	n.a.
2		4.903	7.676	78.698	7.80	7.30	n.a.
Total:			**98.358**	**1078.281**	**100.00**	**100.00**	

3h



Integration Results

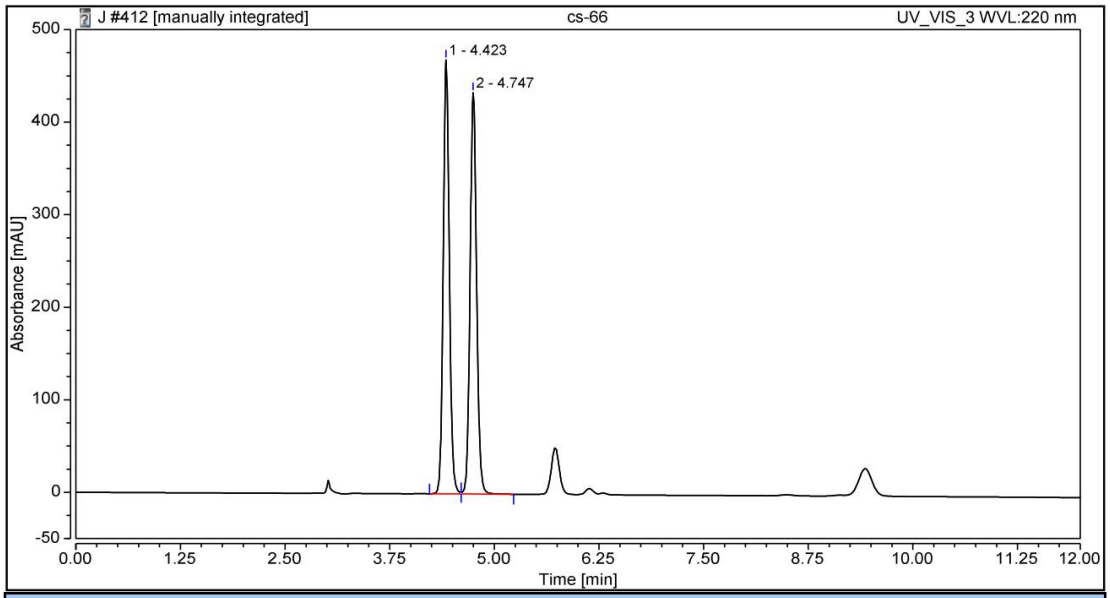
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.303	42.178	273.368	50.00	54.85	n.a.
2		8.637	42.176	225.044	50.00	45.15	n.a.
Total:			**84.354**	**498.411**	**100.00**	**100.00**	



Integration Results

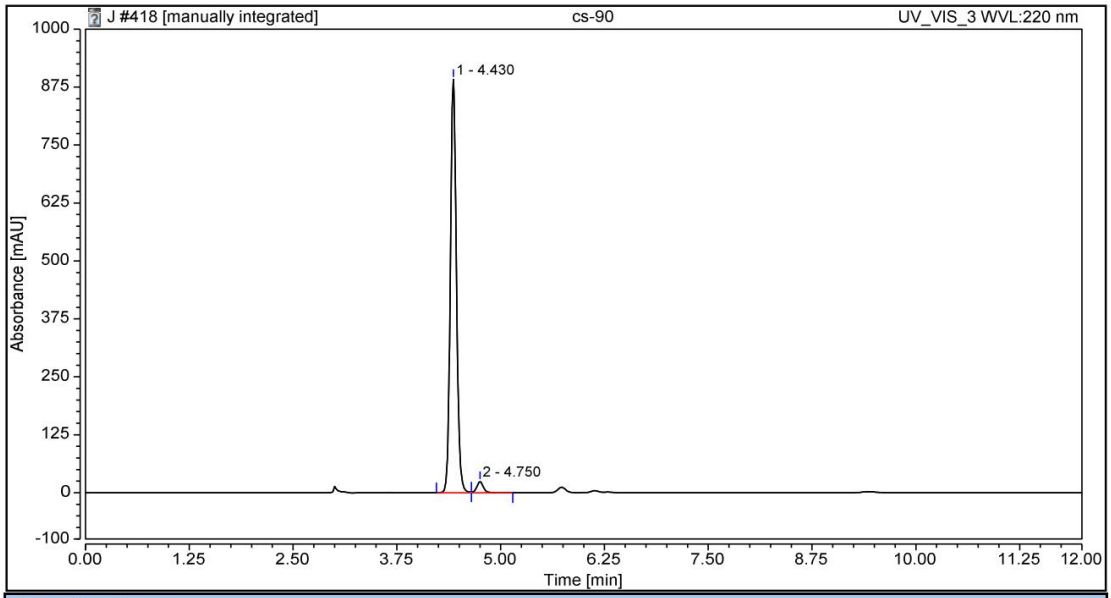
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.300	45.725	297.251	77.25	80.51	n.a.
2		8.637	13.466	71.975	22.75	19.49	n.a.
Total:			**59.191**	**369.226**	**100.00**	**100.00**	

3i



Integration Results

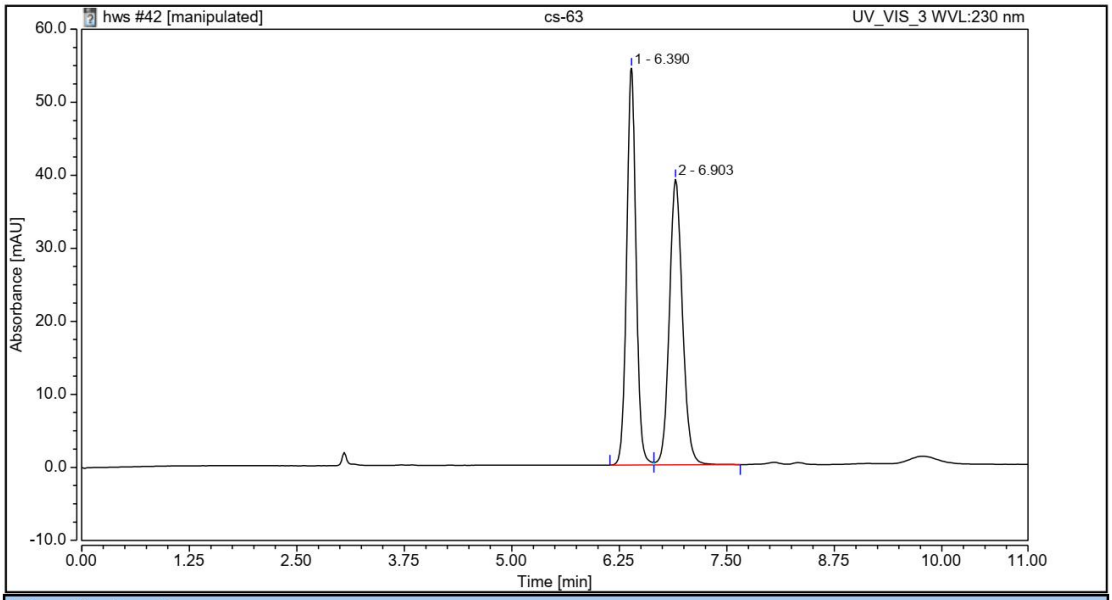
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.423	39.379	468.739	50.11	51.95	n.a.
2		4.747	39.204	433.573	49.89	48.05	n.a.
Total:			**78.583**	**902.311**	**100.00**	**100.00**	



Integration Results

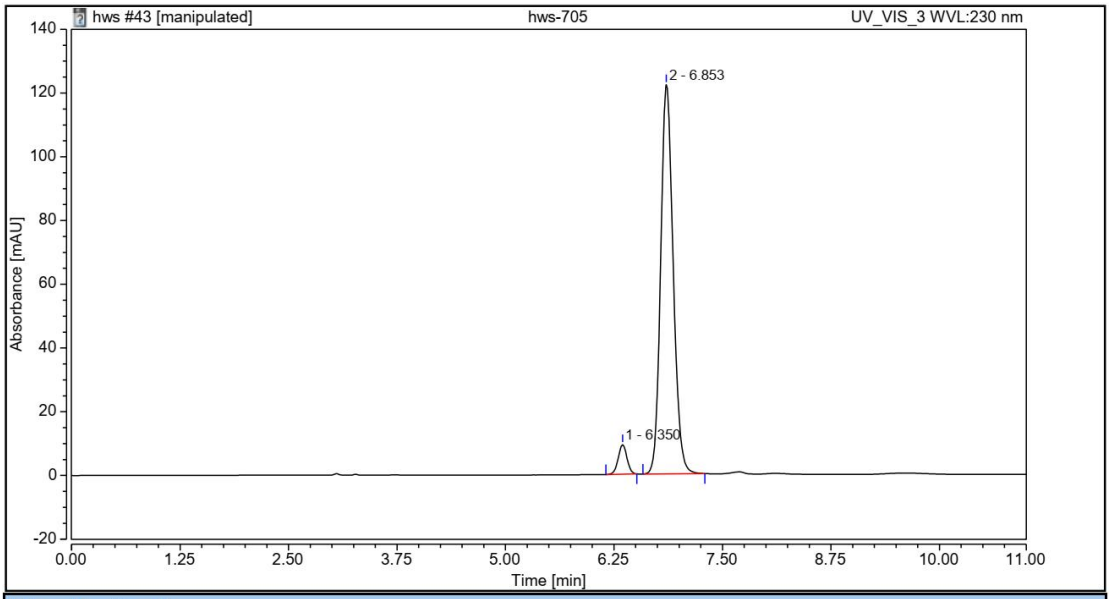
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.430	75.230	891.265	97.19	97.38	n.a.
2		4.750	2.177	23.991	2.81	2.62	n.a.
Total:			**77.407**	**915.256**	**100.00**	**100.00**	

3j



Integration Results

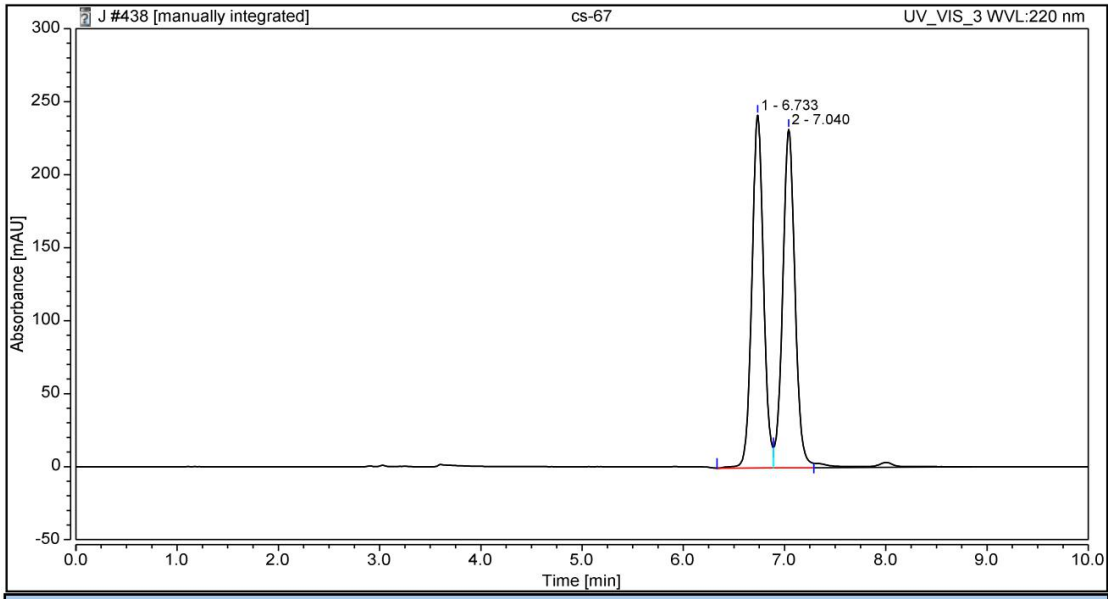
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.390	6.863	54.360	49.80	58.18	n.a.
2		6.903	6.917	39.077	50.20	41.82	n.a.
Total:			**13.780**	**93.437**	**100.00**	**100.00**	



Integration Results

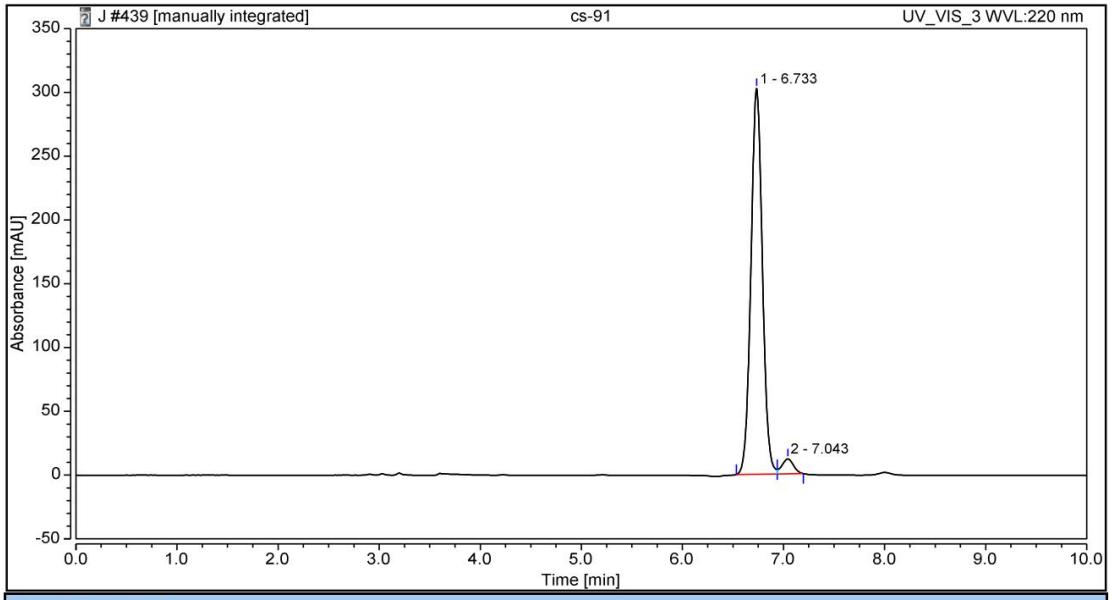
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.350	1.089	9.317	5.07	7.09	n.a.
2		6.853	20.385	122.137	94.93	92.91	n.a.
Total:			**21.474**	**131.455**	**100.00**	**100.00**	

3k



Integration Results

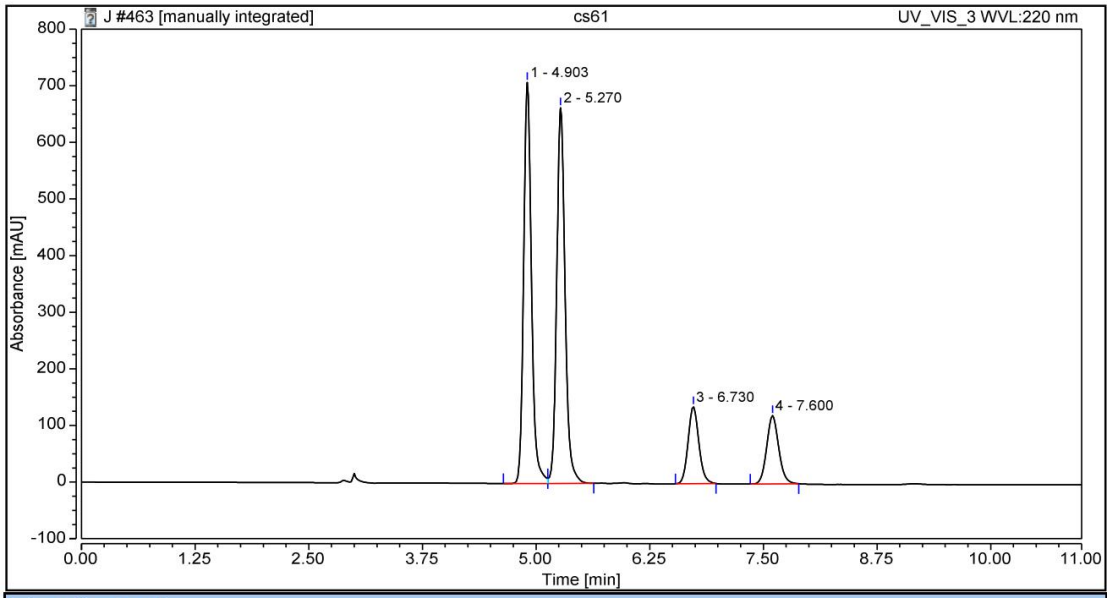
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.733	32.090	241.603	49.69	51.04	n.a.
2		7.040	32.494	231.772	50.31	48.96	n.a.
Total:			**64.583**	**473.375**	**100.00**	**100.00**	



Integration Results

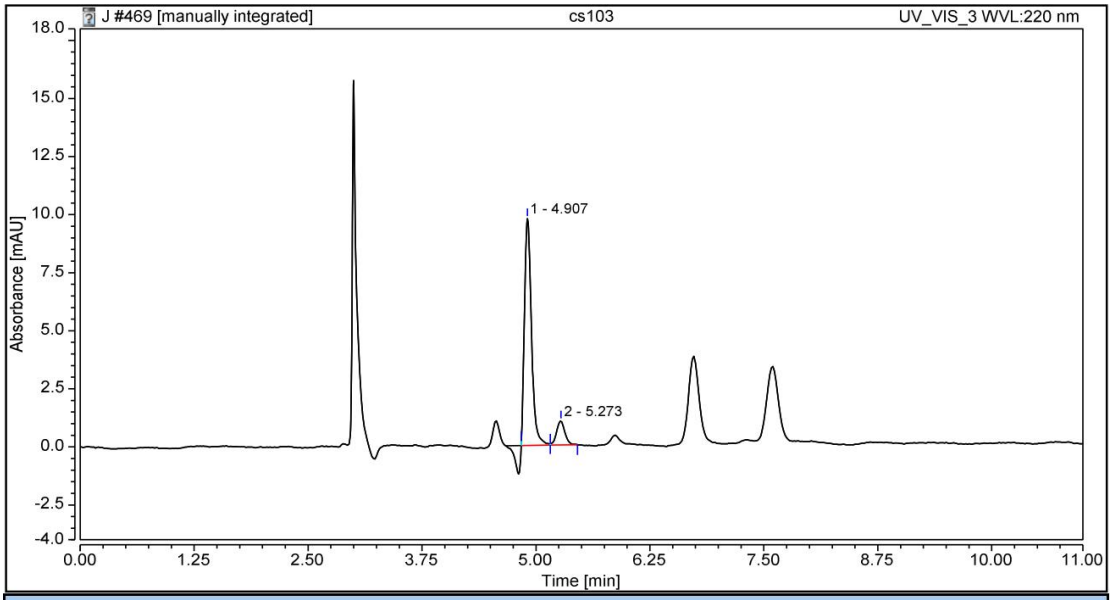
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.733	39.589	302.398	96.23	96.28	n.a.
2		7.043	1.551	11.696	3.77	3.72	n.a.
Total:			**41.140**	**314.094**	**100.00**	**100.00**	

3l



Integration Results

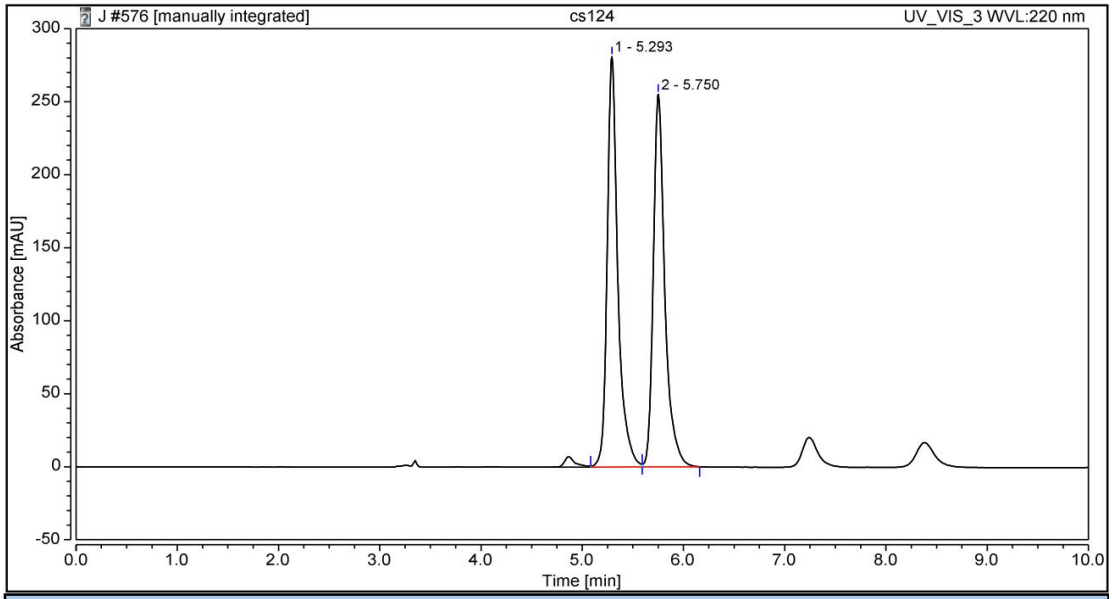
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.903	70.445	708.267	39.40	43.48	n.a.
2		5.270	70.949	663.591	39.68	40.74	n.a.
3		6.730	18.675	136.132	10.44	8.36	n.a.
4		7.600	18.733	120.900	10.48	7.42	n.a.
Total:			**178.802**	**1628.890**	**100.00**	**100.00**	



Integration Results

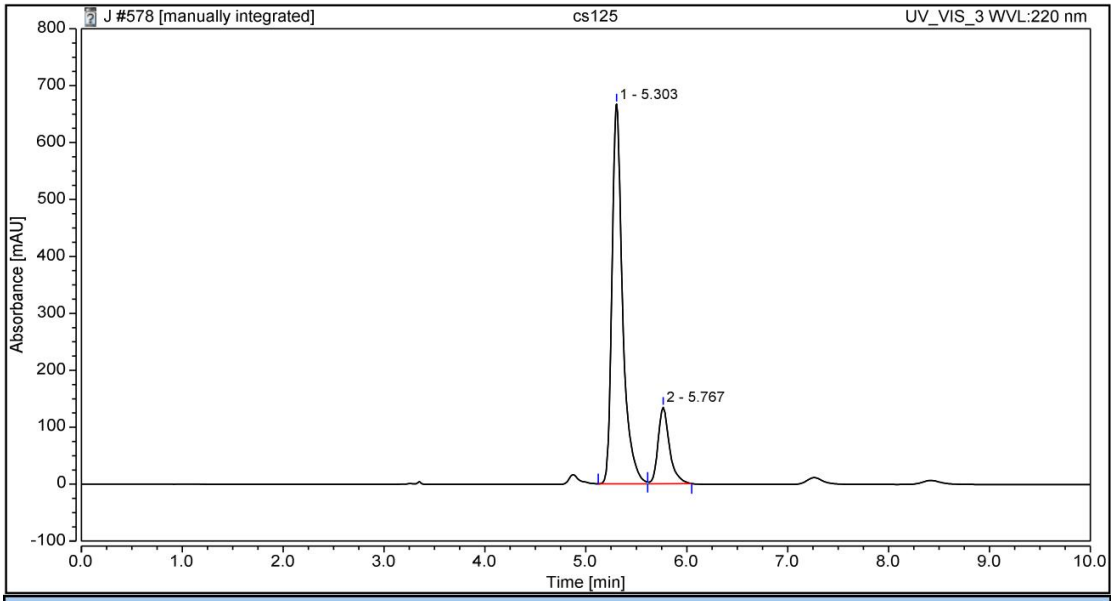
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.907	0.870	9.769	88.91	90.44	n.a.
2		5.273	0.108	1.033	11.09	9.56	n.a.
Total:			**0.978**	**10.803**	**100.00**	**100.00**	

3m



Integration Results

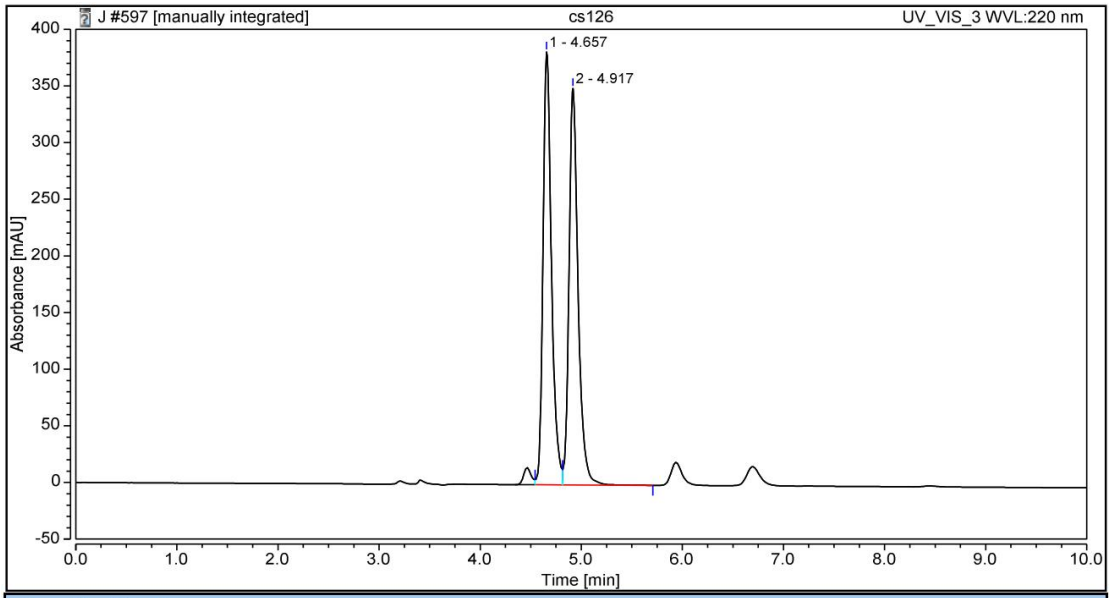
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.293	34.378	280.889	50.49	52.40	n.a.
2		5.750	33.704	255.178	49.51	47.60	n.a.
Total:			**68.082**	**536.067**	**100.00**	**100.00**	



Integration Results

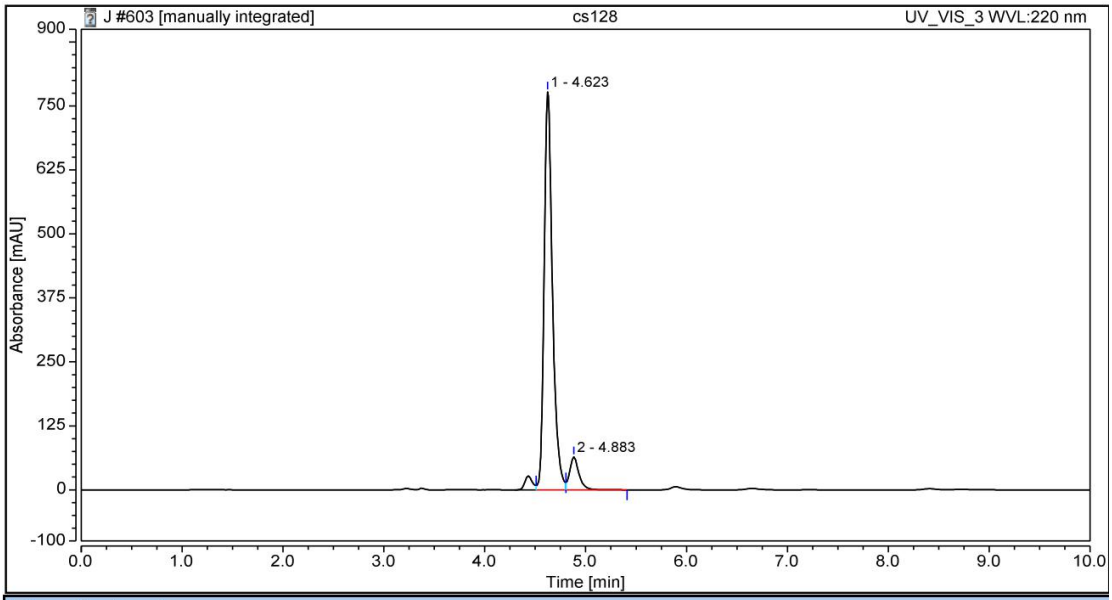
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.303	80.956	667.221	82.14	83.25	n.a.
2		5.767	17.597	134.277	17.86	16.75	n.a.
Total:			**98.553**	**801.498**	**100.00**	**100.00**	

3n



Integration Results

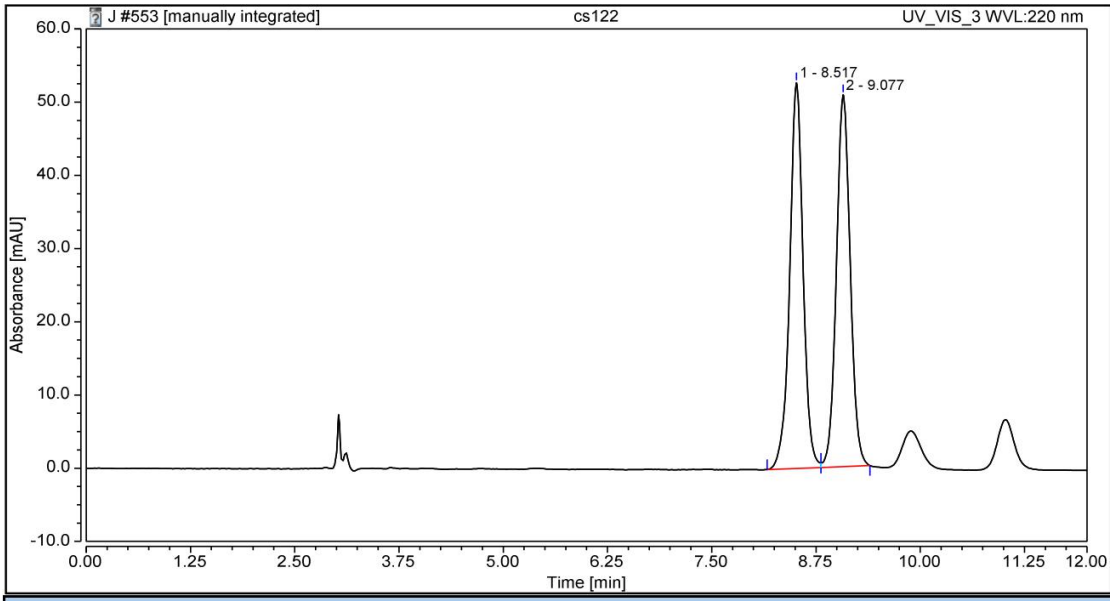
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.657	36.994	382.082	50.30	52.19	n.a.
2		4.917	36.550	349.957	49.70	47.81	n.a.
Total:			**73.544**	**732.039**	**100.00**	**100.00**	



Integration Results

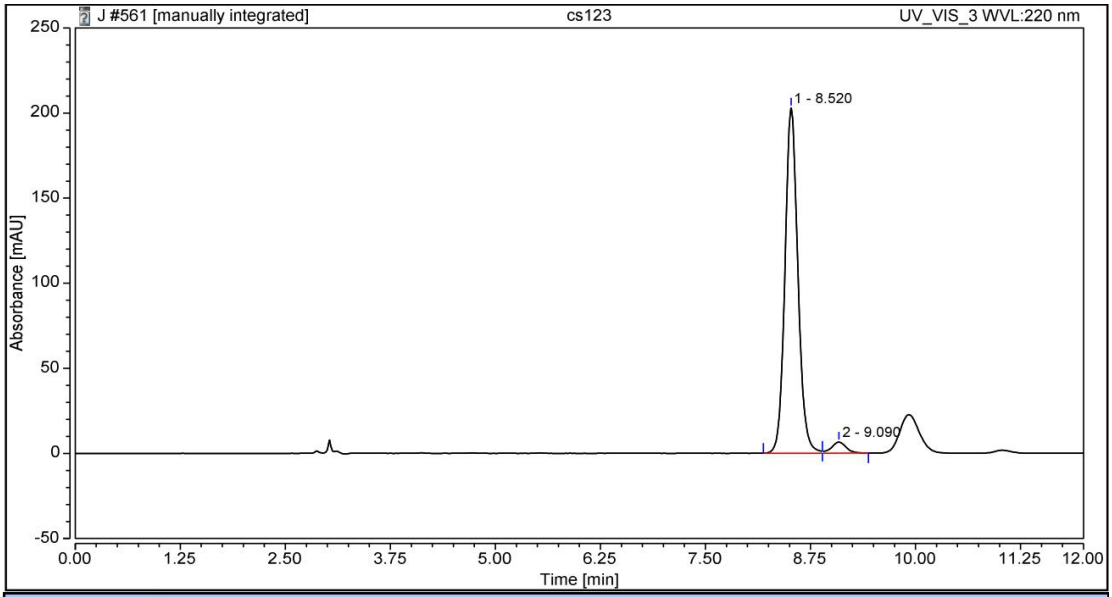
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.623	74.250	777.288	91.47	92.31	n.a.
2		4.883	6.926	64.765	8.53	7.69	n.a.
Total:			**81.176**	**842.052**	**100.00**	**100.00**	

3o



Integration Results

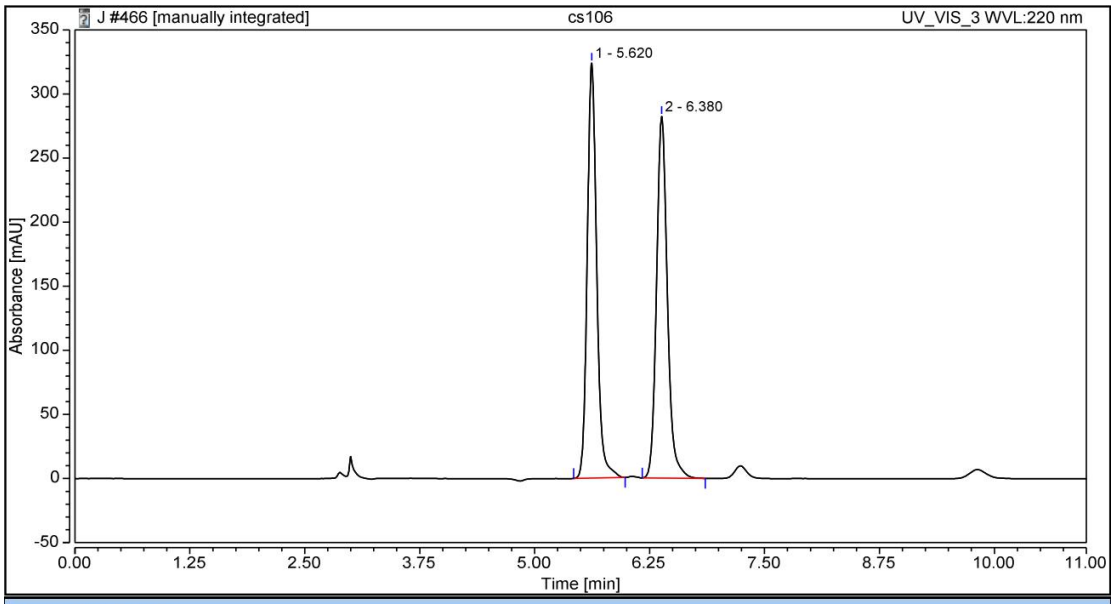
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.517	9.795	52.675	50.14	50.92	n.a.
2		9.077	9.740	50.777	49.86	49.08	n.a.
Total:			**19.535**	**103.452**	**100.00**	**100.00**	



Integration Results

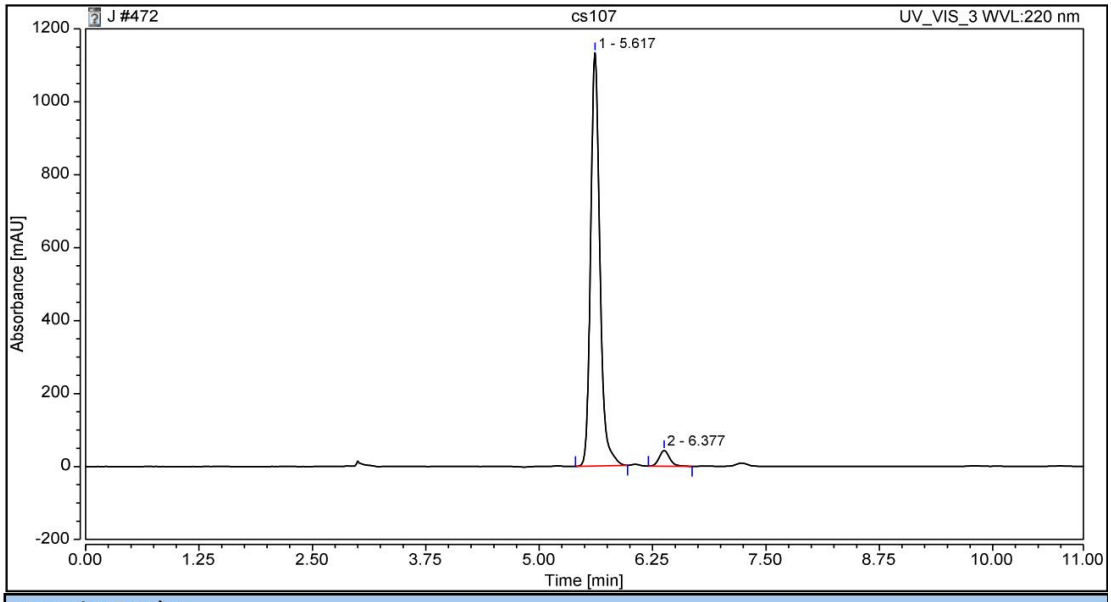
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.520	36.116	202.813	96.50	96.89	n.a.
2		9.090	1.309	6.507	3.50	3.11	n.a.
Total:			**37.425**	**209.320**	**100.00**	**100.00**	

3p



Integration Results

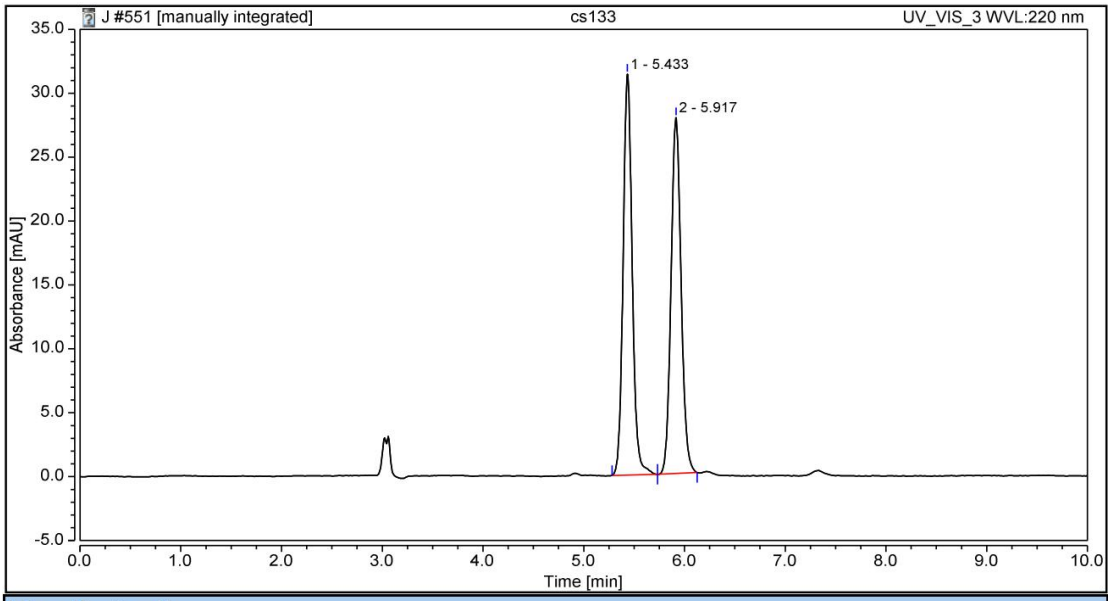
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.620	38.191	323.792	49.84	53.44	n.a.
2		6.380	38.437	282.105	50.16	46.56	n.a.
Total:			**76.629**	**605.897**	**100.00**	**100.00**	



Integration Results

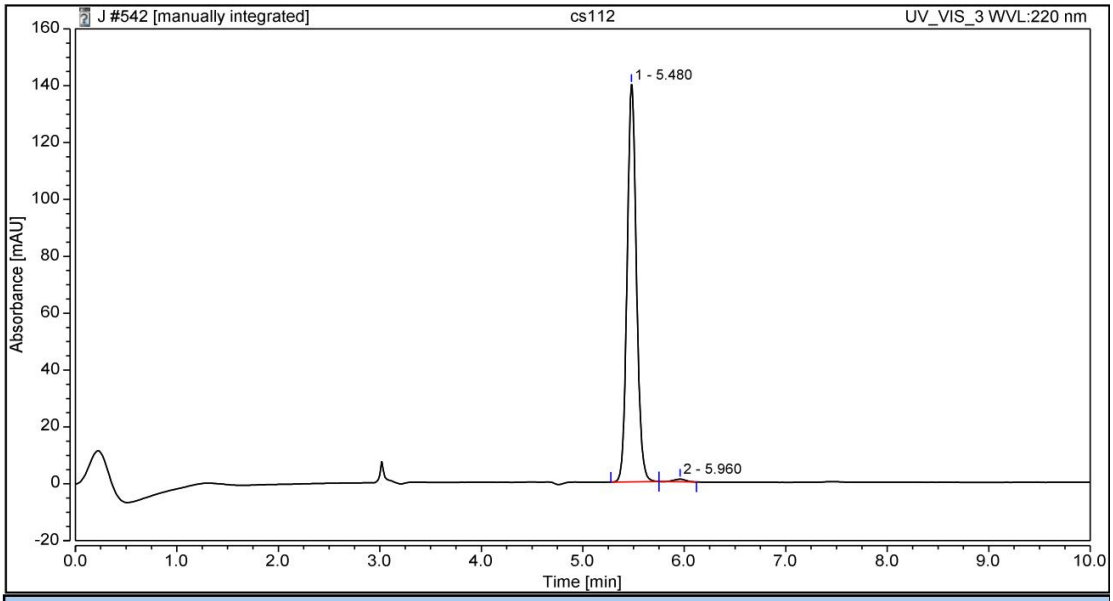
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.617	134.142	1132.898	95.92	96.35	n.a.
2		6.377	5.713	42.936	4.08	3.65	n.a.
Total:			**139.855**	**1175.834**	**100.00**	**100.00**	

3q



Integration Results

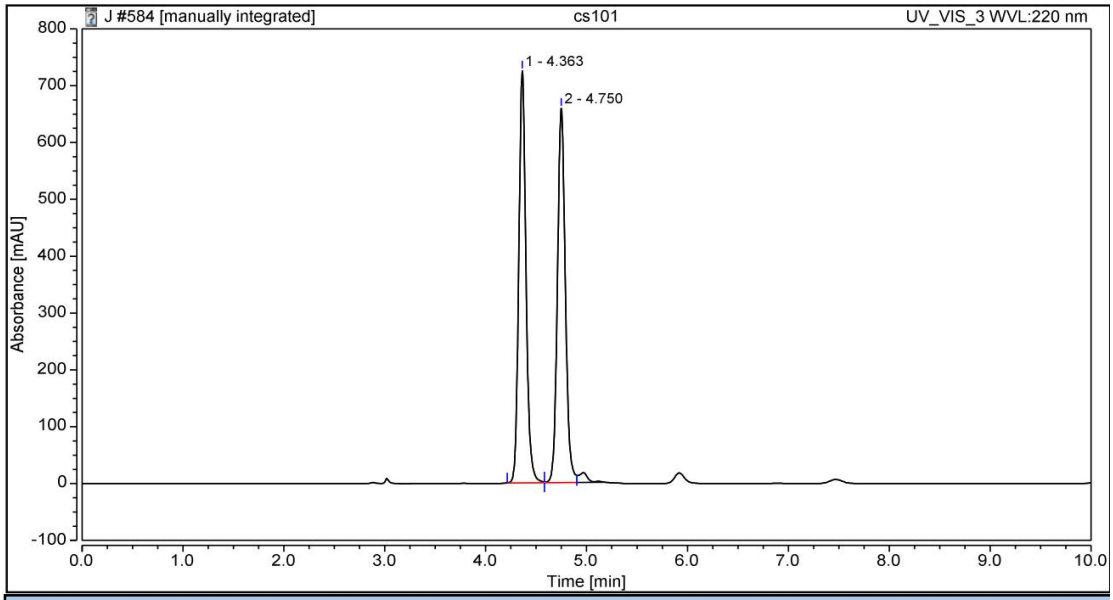
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.433	3.282	31.365	50.47	52.97	n.a.
2		5.917	3.221	27.849	49.53	47.03	n.a.
Total:			**6.503**	**59.214**	**100.00**	**100.00**	



Integration Results

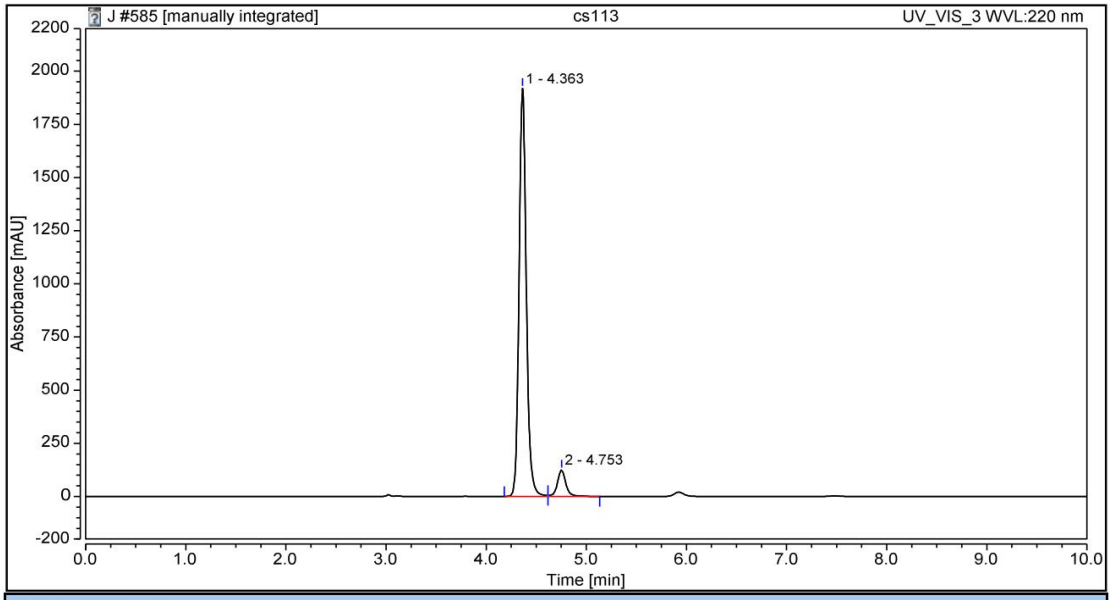
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.480	14.870	139.751	99.14	99.30	n.a.
2		5.960	0.129	0.983	0.86	0.70	n.a.
Total:			**14.999**	**140.734**	**100.00**	**100.00**	

3r



Integration Results

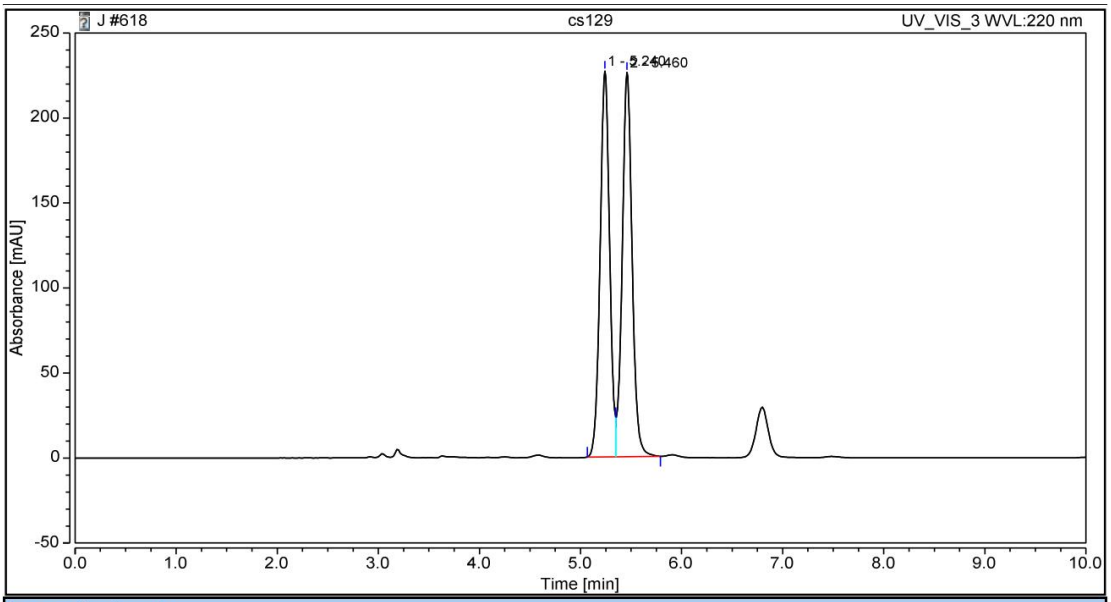
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.363	59.837	724.510	50.11	52.39	n.a.
2		4.750	59.568	658.286	49.89	47.61	n.a.
Total:			**119.405**	**1382.796**	**100.00**	**100.00**	



Integration Results

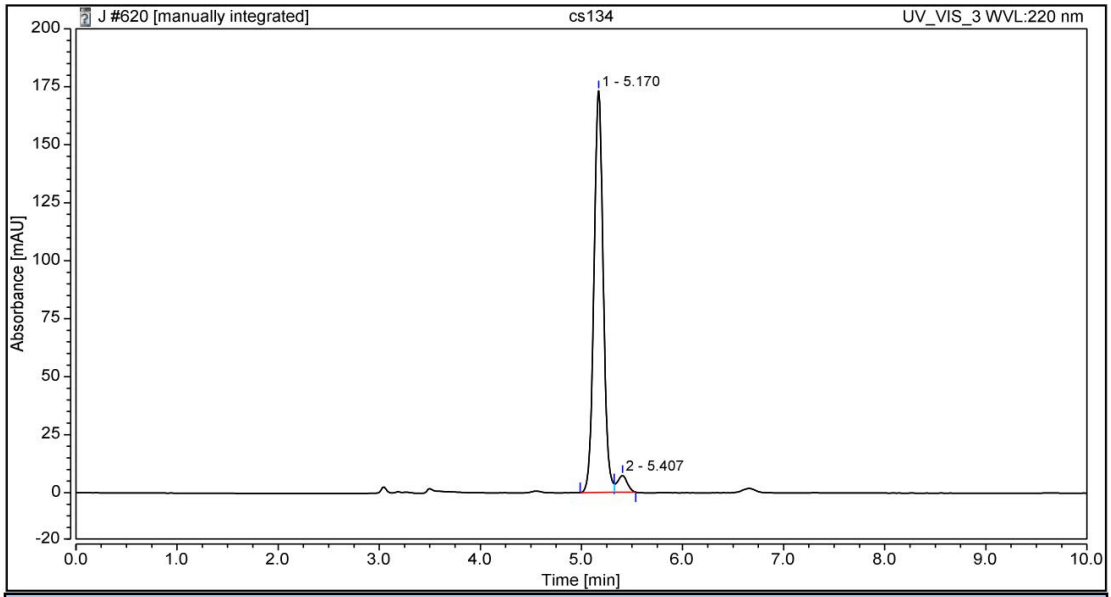
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.363	160.428	1919.330	92.90	93.90	n.a.
2		4.753	12.255	124.597	7.10	6.10	n.a.
Total:			**172.682**	**2043.927**	**100.00**	**100.00**	

6a



Integration Results

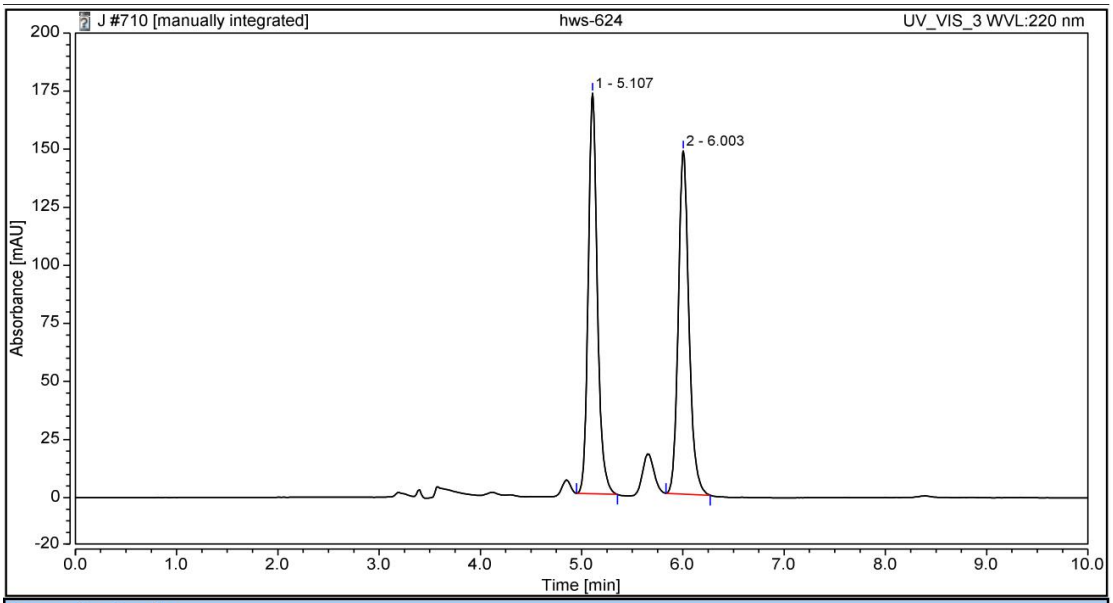
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.240	24.652	226.993	49.01	50.10	n.a.
2		5.460	25.651	226.130	50.99	49.90	n.a.
Total:			**50.303**	**453.123**	**100.00**	**100.00**	



Integration Results

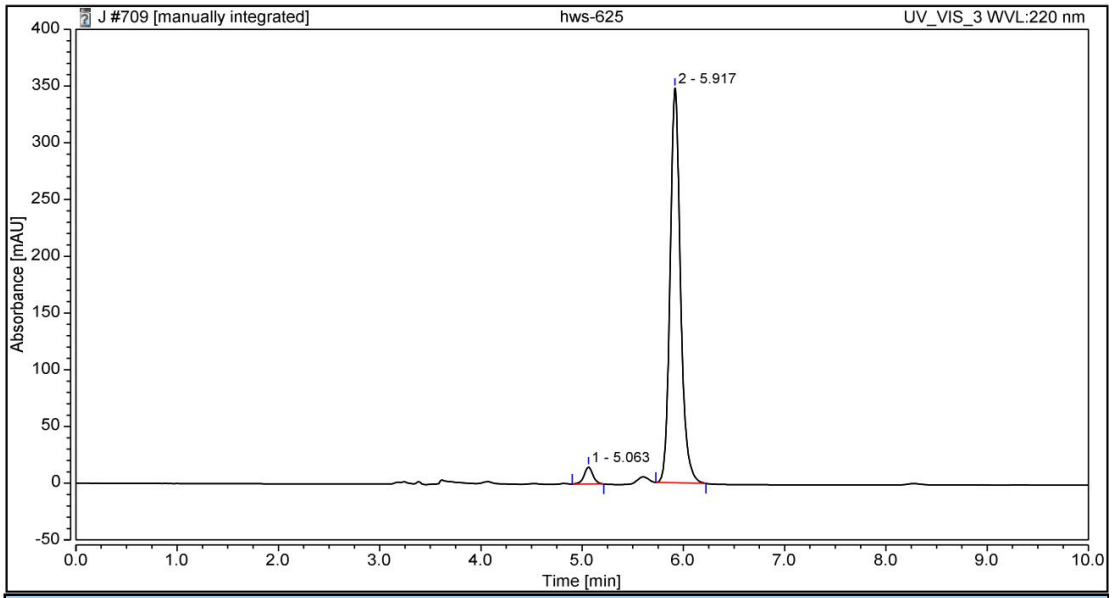
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.170	18.335	173.124	95.69	96.00	n.a.
2		5.407	0.825	7.222	4.31	4.00	n.a.
Total:			**19.160**	**180.346**	**100.00**	**100.00**	

6b



Integration Results

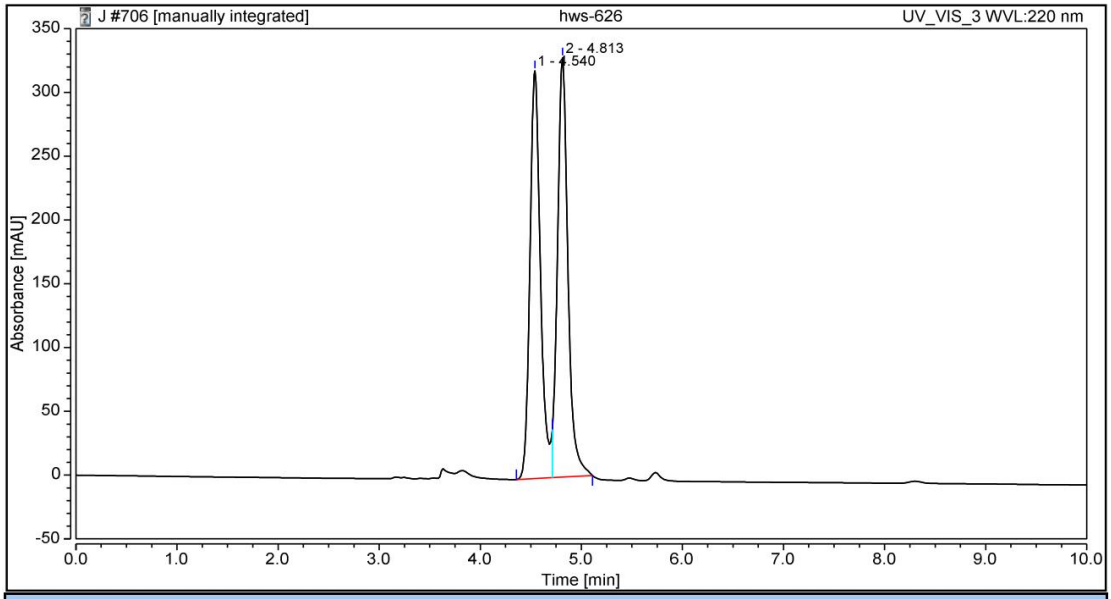
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.107	18.089	172.488	50.10	53.86	n.a.
2		6.003	18.016	147.752	49.90	46.14	n.a.
Total:			**36.105**	**320.240**	**100.00**	**100.00**	



Integration Results

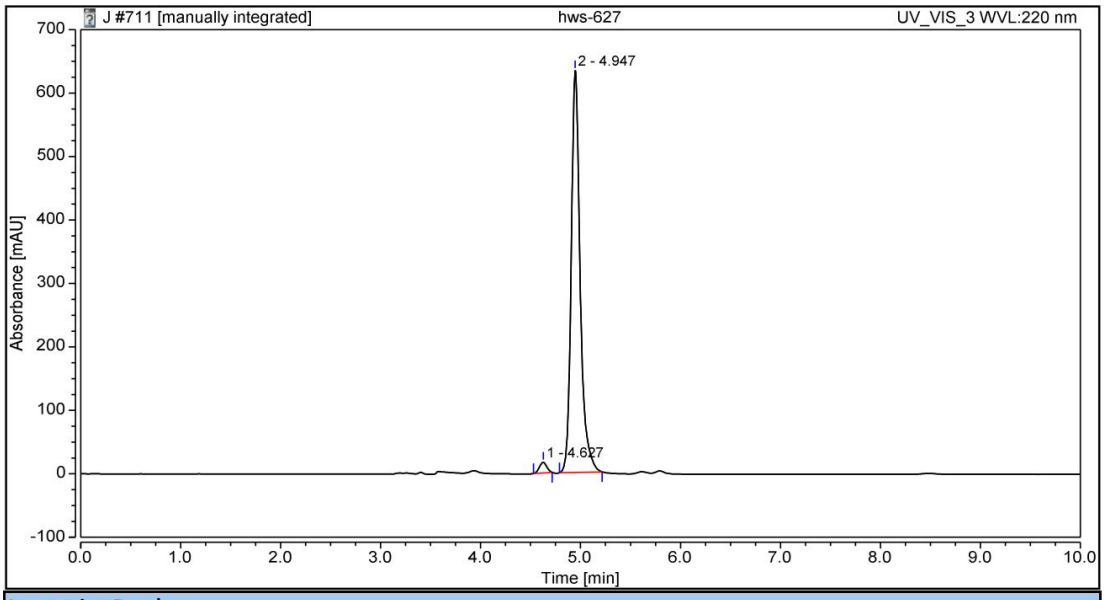
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.063	1.520	15.026	3.54	4.14	n.a.
2		5.917	41.359	347.768	96.46	95.86	n.a.
Total:			**42.879**	**362.795**	**100.00**	**100.00**	

6c



Integration Results

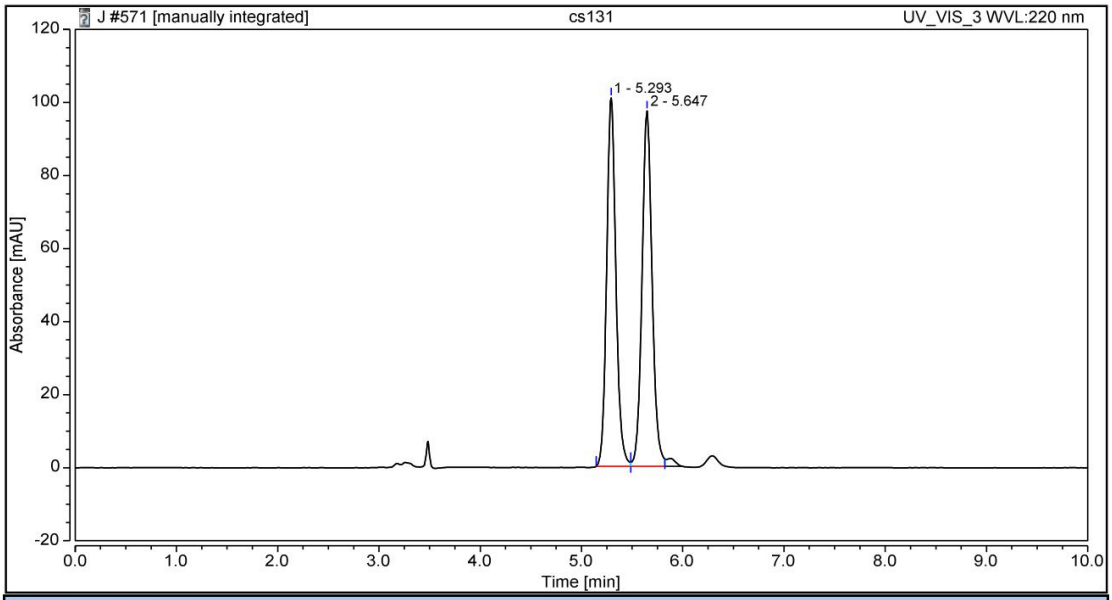
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.540	38.604	319.659	49.54	49.31	n.a.
2		4.813	39.315	328.663	50.46	50.69	n.a.
Total:			**77.920**	**648.322**	**100.00**	**100.00**	



Integration Results

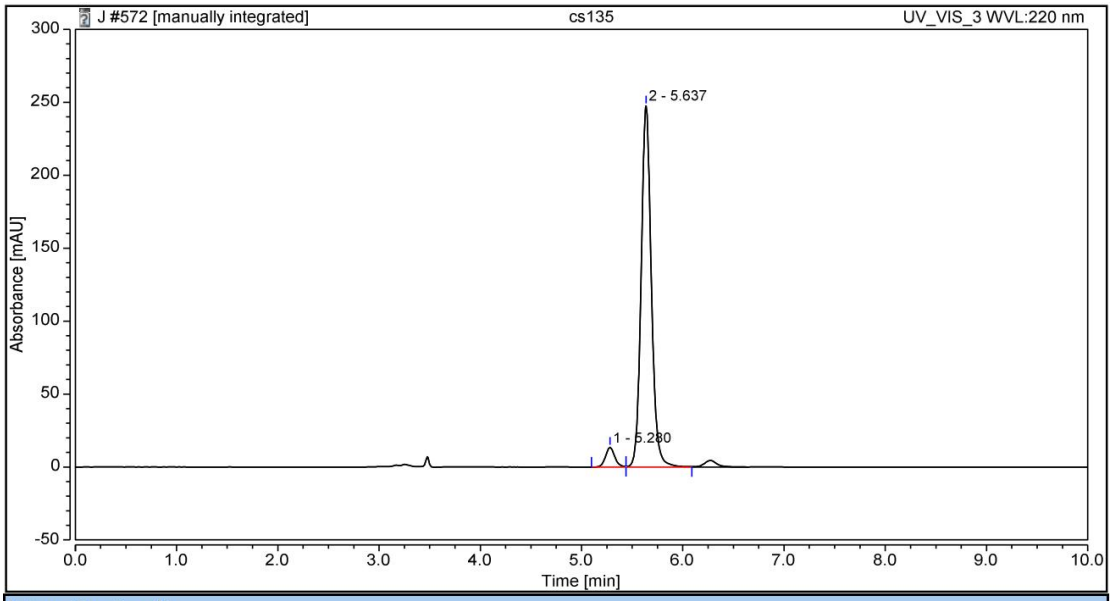
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.627	1.445	17.018	2.15	2.62	n.a.
2		4.947	65.636	633.326	97.85	97.38	n.a.
Total:			**67.081**	**650.345**	**100.00**	**100.00**	

7a



Integration Results

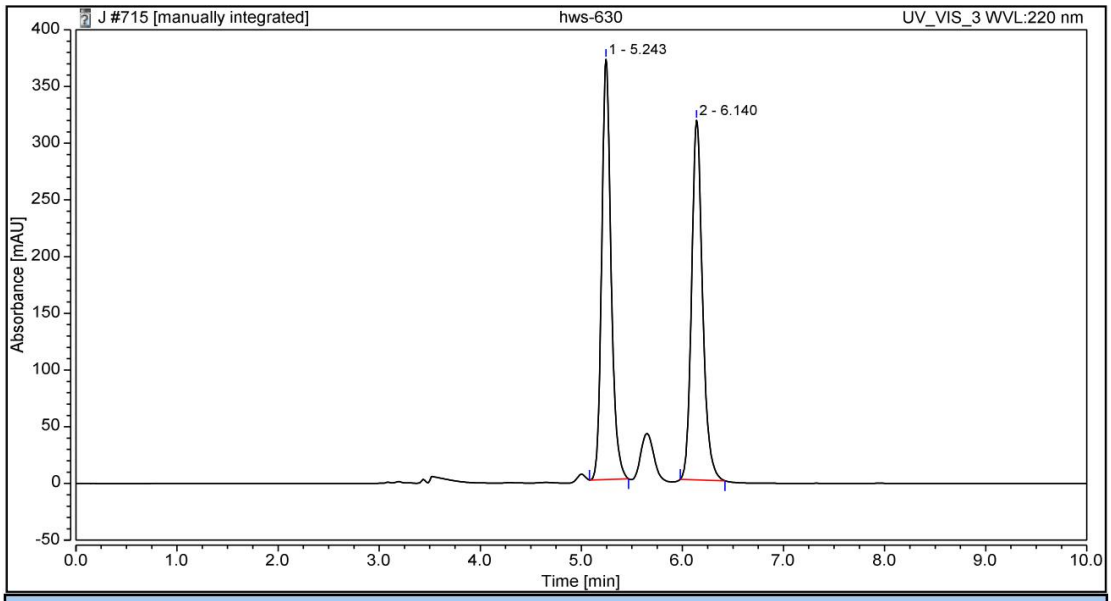
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.293	10.717	100.840	48.88	50.90	n.a.
2		5.647	11.211	97.269	51.12	49.10	n.a.
Total:			**21.928**	**198.109**	**100.00**	**100.00**	



Integration Results

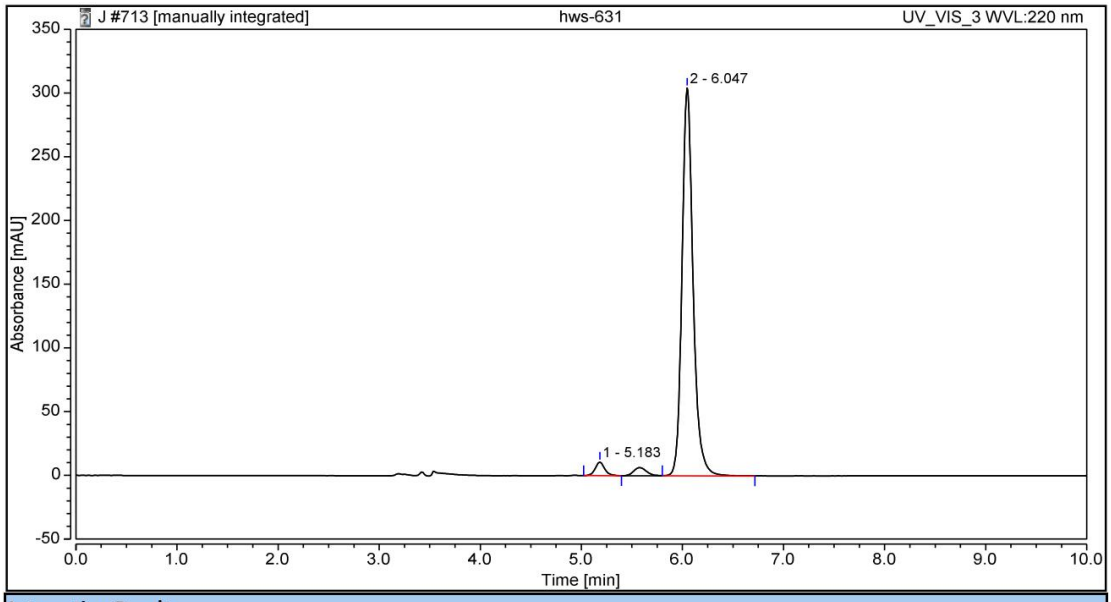
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.280	1.443	13.501	4.78	5.17	n.a.
2		5.637	28.758	247.572	95.22	94.83	n.a.
Total:			**30.201**	**261.073**	**100.00**	**100.00**	

7b



Integration Results

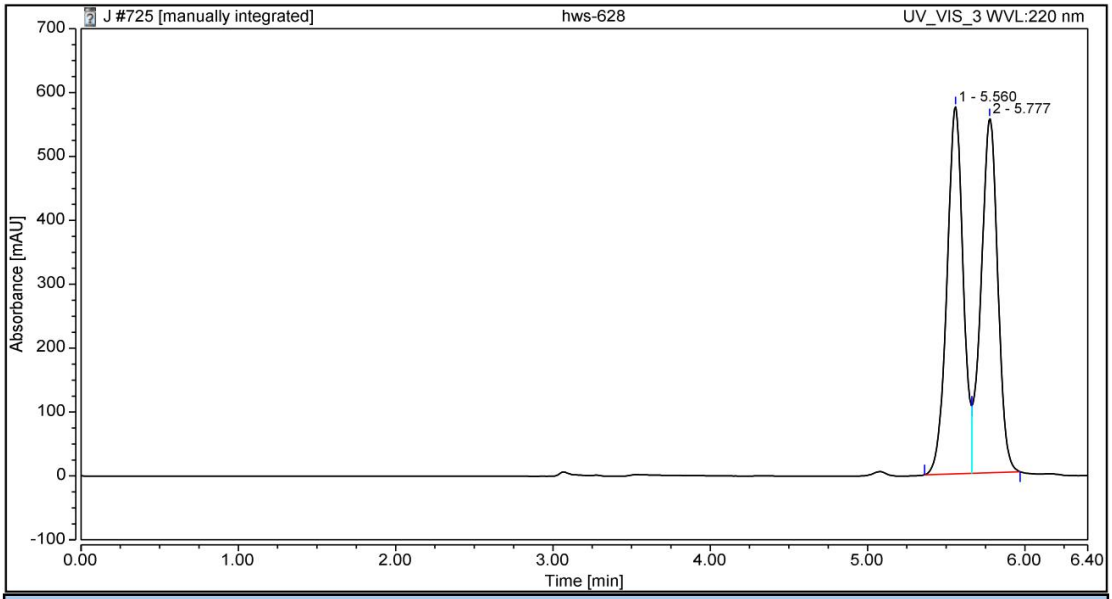
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.243	39.779	370.559	49.91	53.89	n.a.
2		6.140	39.924	317.043	50.09	46.11	n.a.
Total:			**79.703**	**687.601**	**100.00**	**100.00**	



Integration Results

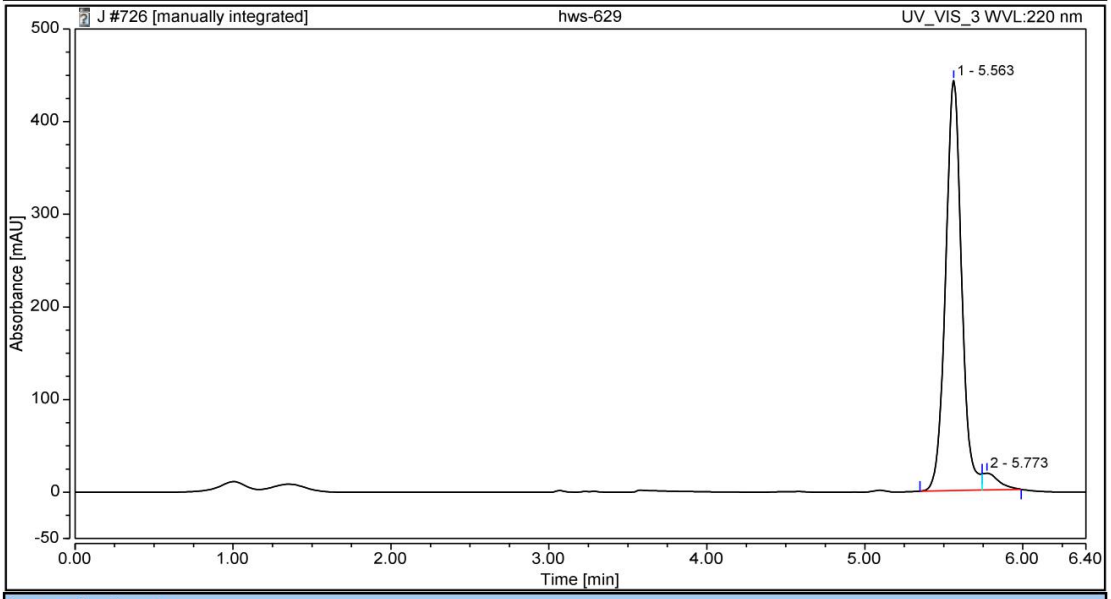
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.183	1.164	10.703	2.93	3.40	n.a.
2		6.047	38.505	304.248	97.07	96.60	n.a.
Total:			**39.669**	**314.951**	**100.00**	**100.00**	

7c



Integration Results

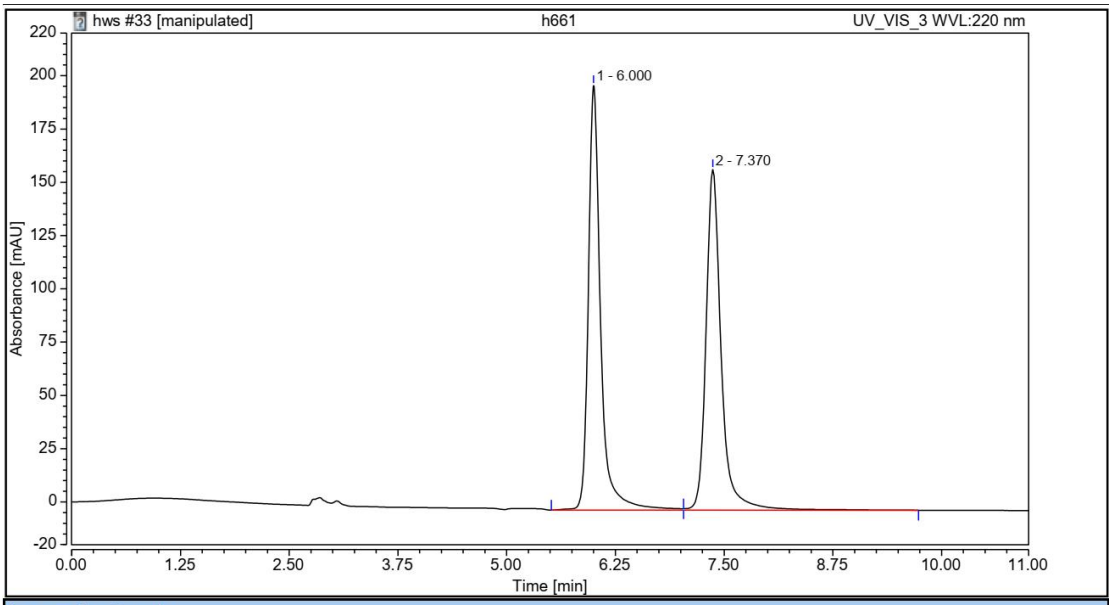
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.560	68.443	574.335	50.09	50.90	n.a.
2		5.777	68.196	554.035	49.91	49.10	n.a.
Total:			**136.639**	**1128.370**	**100.00**	**100.00**	



Integration Results

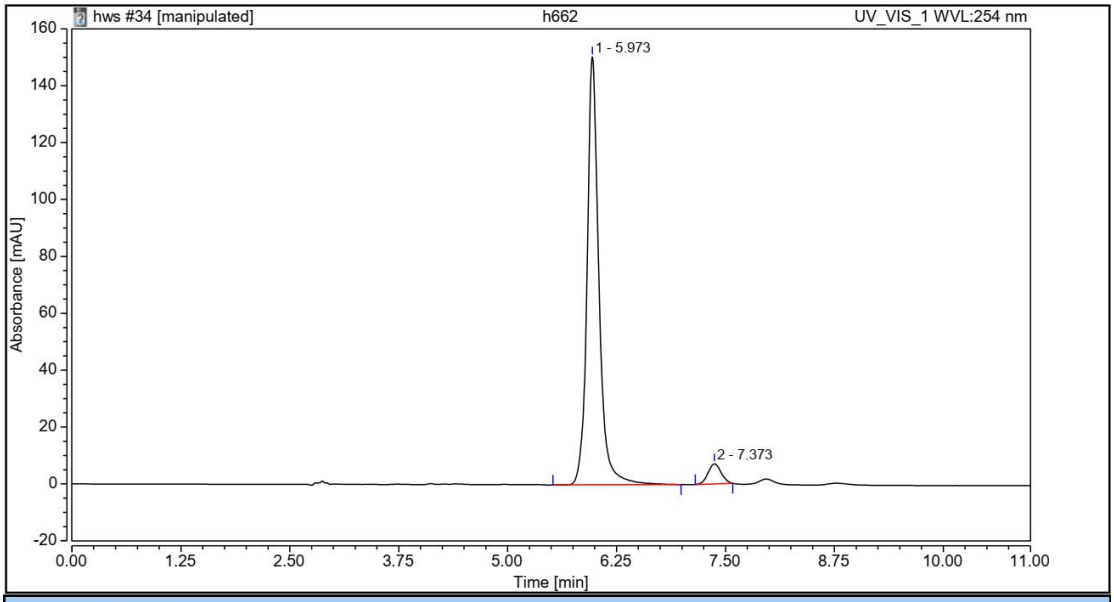
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.563	52.057	442.652	96.07	96.06	n.a.
2		5.773	2.127	18.149	3.93	3.94	n.a.
Total:			**54.184**	**460.801**	**100.00**	**100.00**	

8



Integration Results

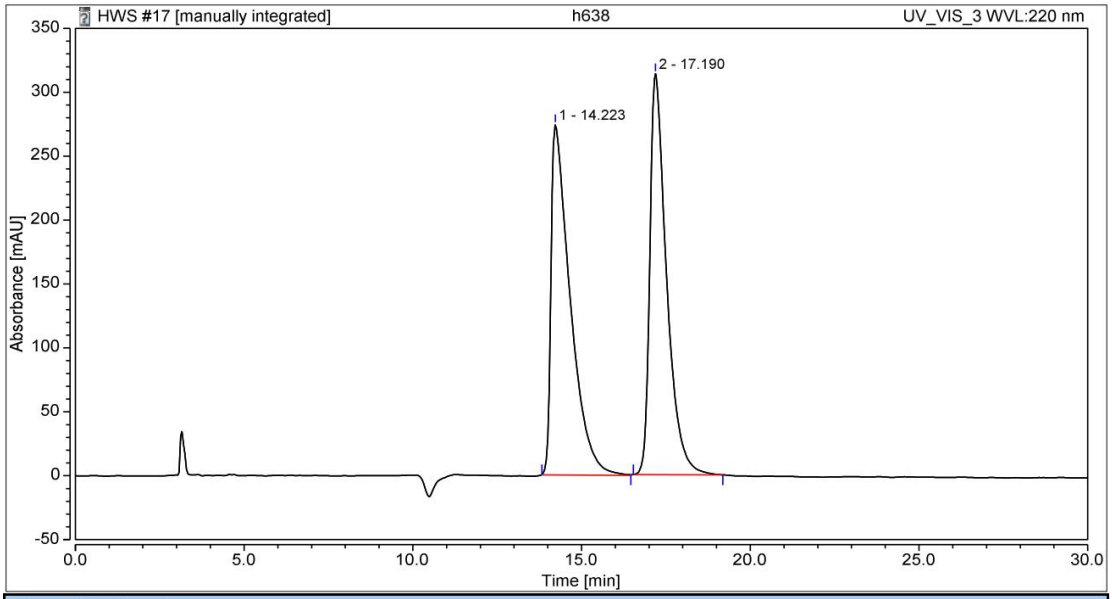
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.000	32.579	199.205	50.15	55.50	n.a.
2		7.370	32.382	159.752	49.85	44.50	n.a.
Total:			**64.961**	**358.957**	**100.00**	**100.00**	



Integration Results

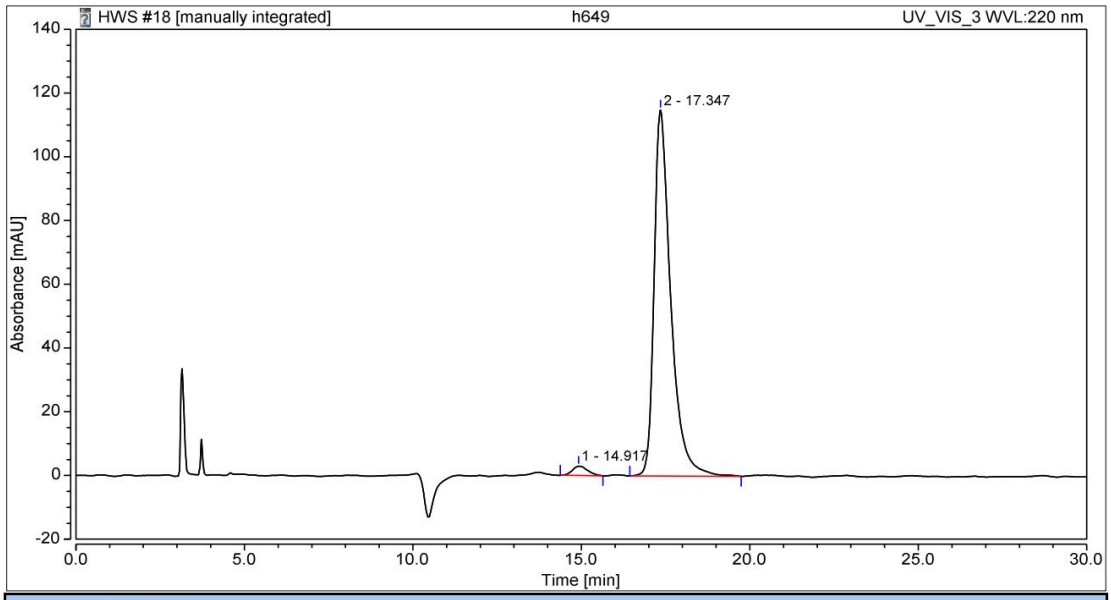
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.973	23.730	150.489	95.08	95.51	n.a.
2		7.373	1.227	7.066	4.92	4.49	n.a.
Total:			**24.957**	**157.555**	**100.00**	**100.00**	

9



Integration Results

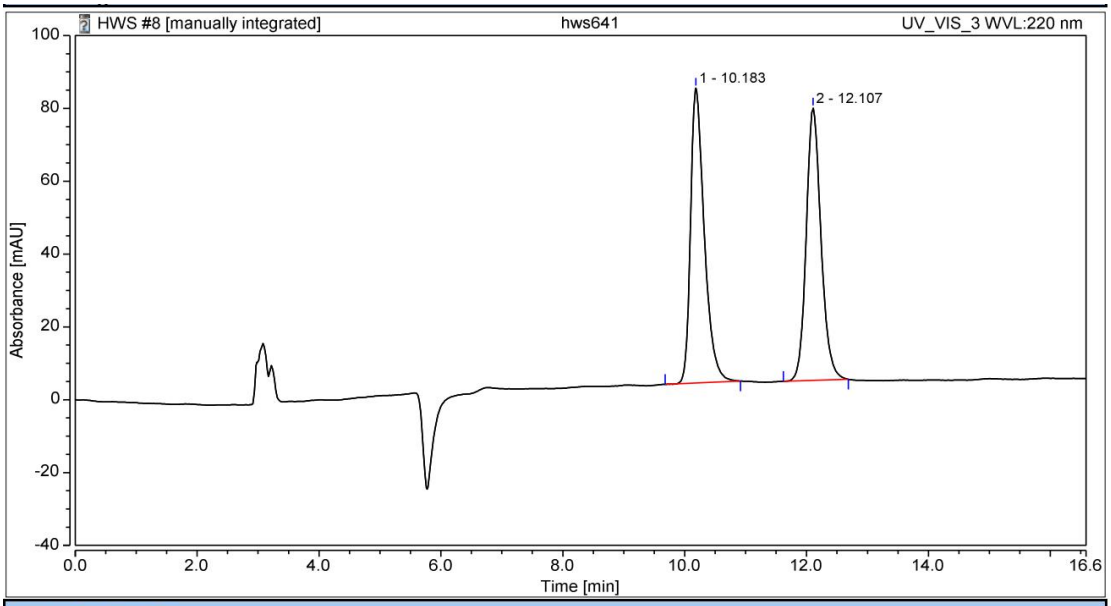
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.223	180.592	274.049	50.09	46.63	n.a.
2		17.190	179.952	313.676	49.91	53.37	n.a.
Total:			**360.544**	**587.725**	**100.00**	**100.00**	



Integration Results

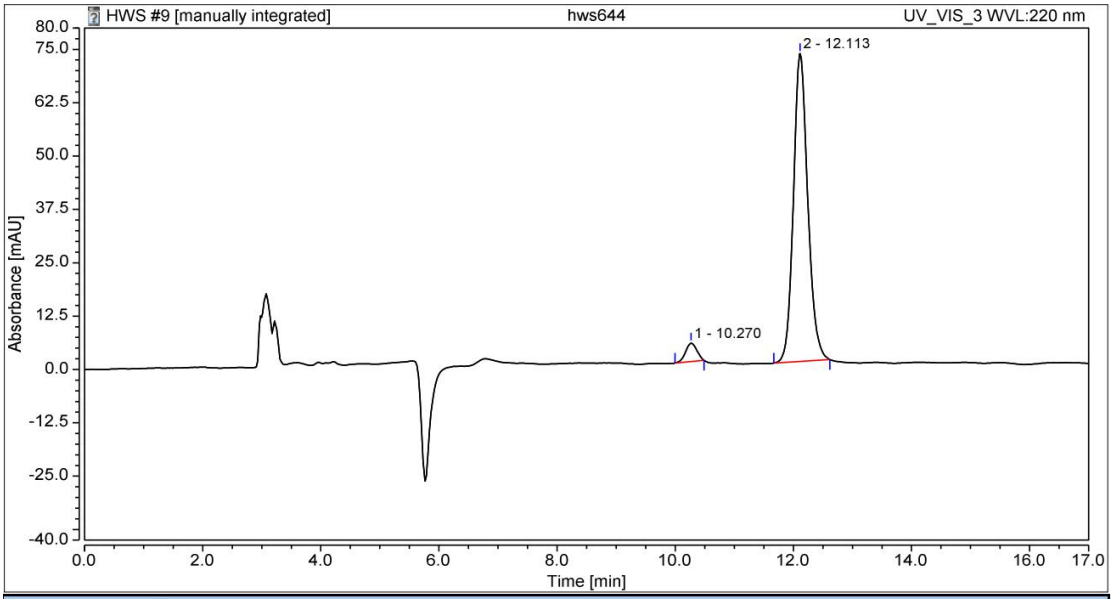
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.917	1.536	2.928	2.28	2.49	n.a.
2		17.347	65.917	114.827	97.72	97.51	n.a.
Total:			**67.453**	**117.754**	**100.00**	**100.00**	

10



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.183	21.152	80.978	50.08	51.97	n.a.
2		12.107	21.080	74.846	49.92	48.03	n.a.
Total:			**42.232**	**155.825**	**100.00**	**100.00**	

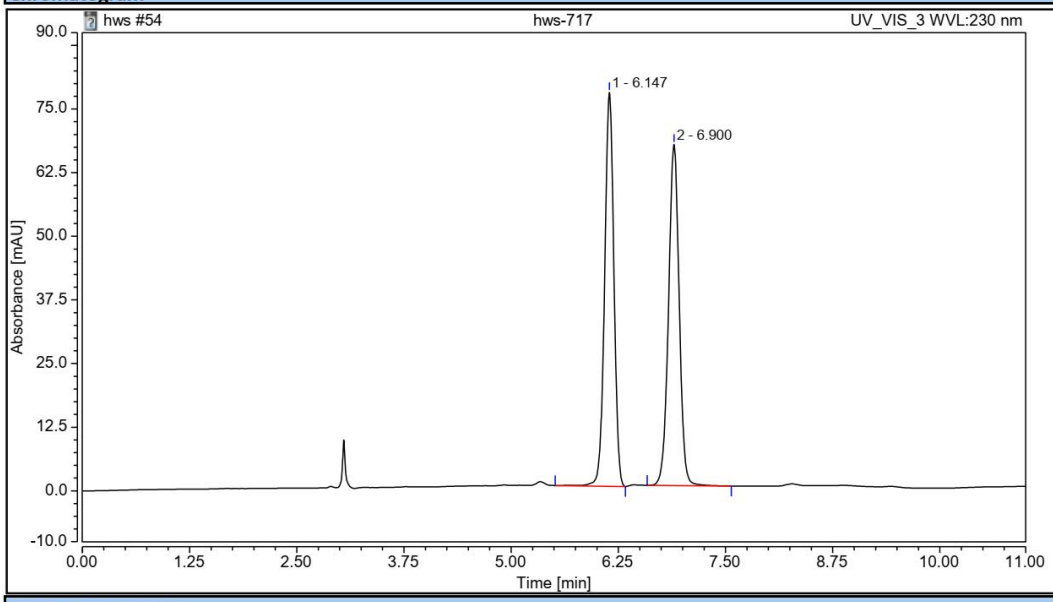


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.270	0.951	4.328	4.49	5.66	n.a.
2		12.113	20.252	72.158	95.51	94.34	n.a.
Total:			**21.203**	**76.486**	**100.00**	**100.00**	

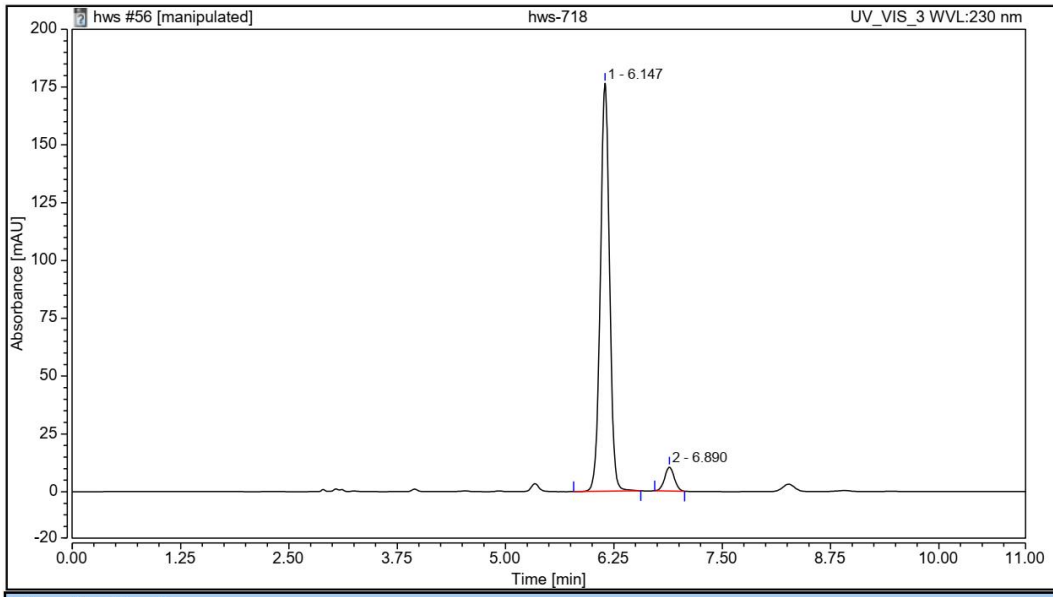
11

Chromatogram



Integration Results

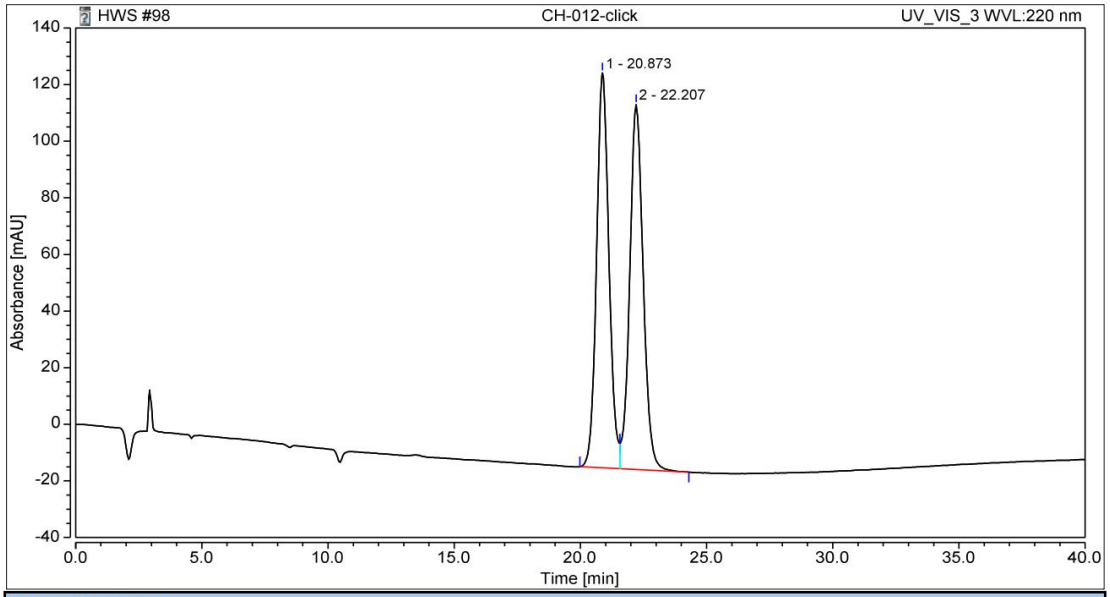
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.147	9.652	77.402	49.93	53.61	n.a.
2		6.900	9.679	66.988	50.07	46.39	n.a.
Total:			**19.331**	**144.390**	**100.00**	**100.00**	



Integration Results

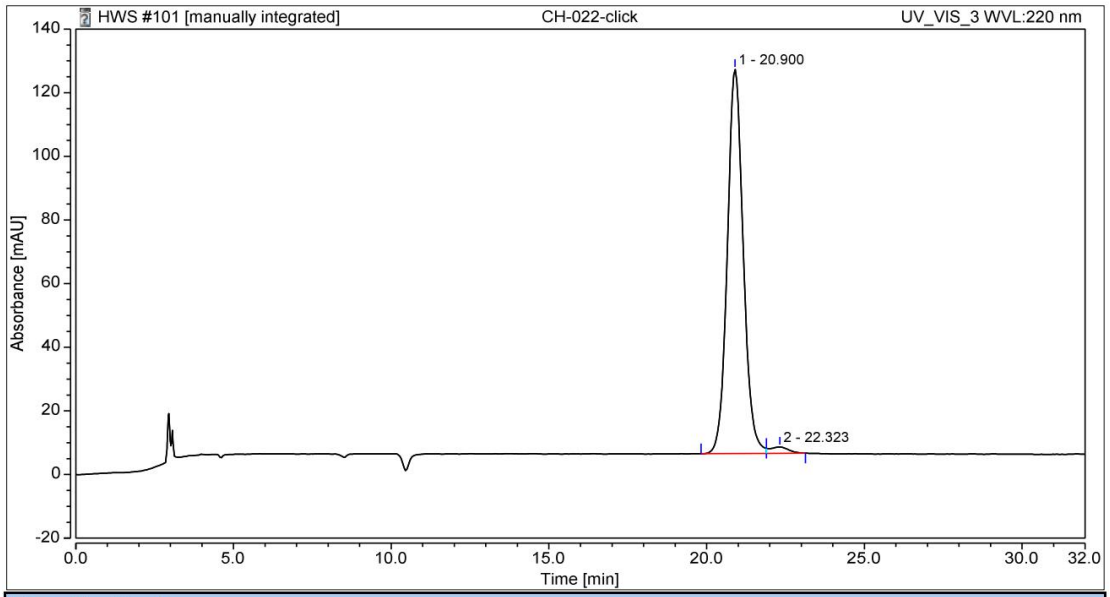
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.147	21.649	176.419	94.18	94.43	n.a.
2		6.890	1.339	10.413	5.82	5.57	n.a.
Total:			**22.988**	**186.832**	**100.00**	**100.00**	

12



Integration Results

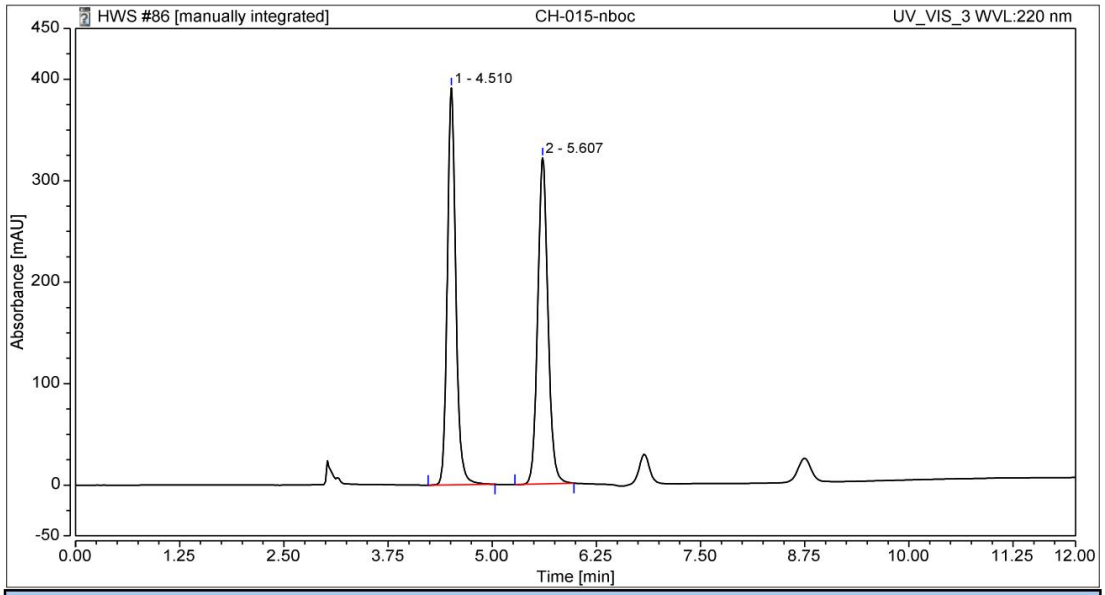
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.873	78.853	139.497	49.65	51.97	n.a.
2		22.207	79.972	128.918	50.35	48.03	n.a.
Total:			**158.825**	**268.414**	**100.00**	**100.00**	



Integration Results

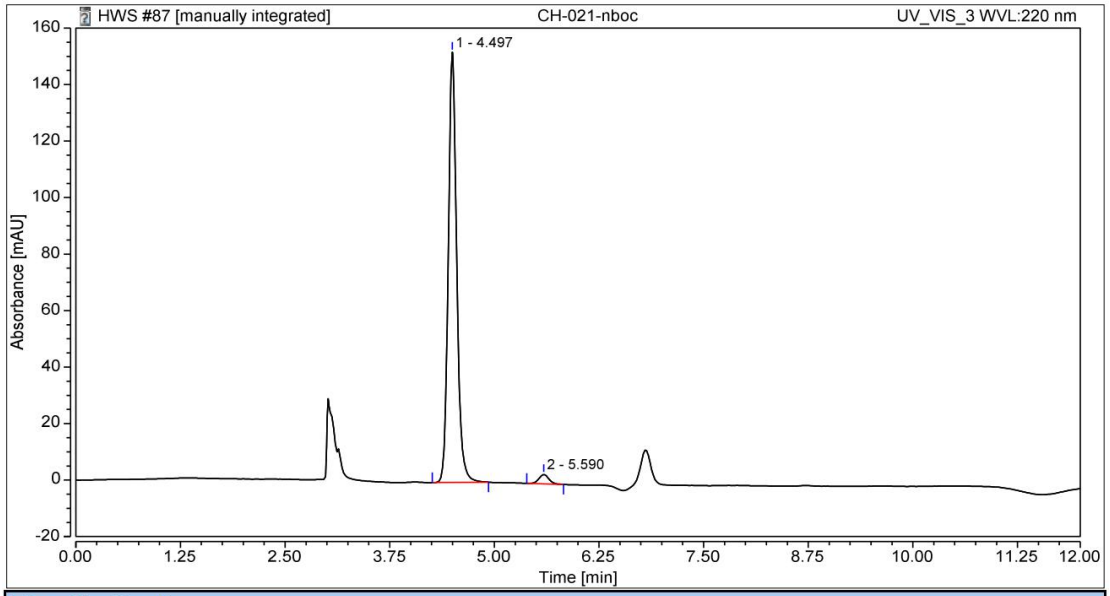
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.900	70.657	120.766	98.15	98.40	n.a.
2		22.323	1.334	1.958	1.85	1.60	n.a.
Total:			**71.991**	**122.724**	**100.00**	**100.00**	

13



Integration Results

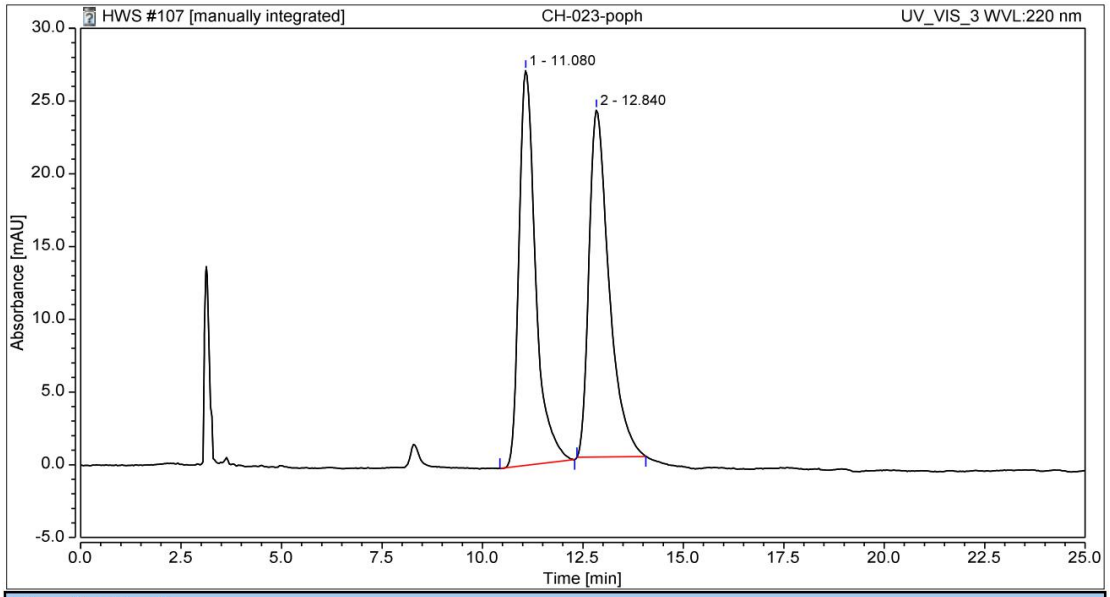
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.510	46.261	391.261	50.27	54.90	n.a.
2		5.607	45.761	321.367	49.73	45.10	n.a.
Total:			**92.021**	**712.628**	**100.00**	**100.00**	



Integration Results

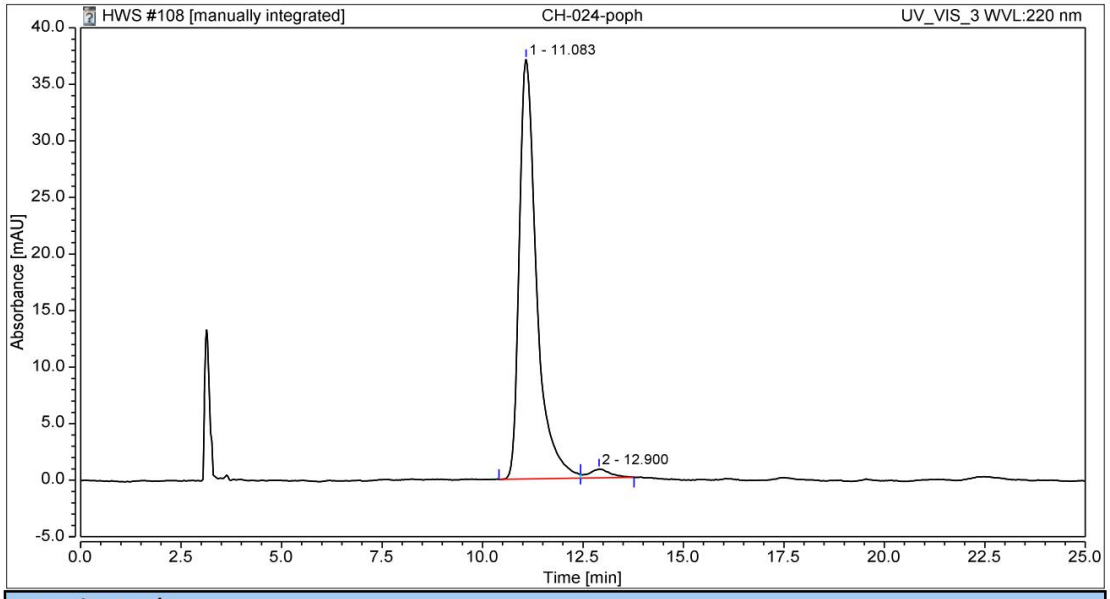
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.497	17.853	152.353	97.49	97.86	n.a.
2		5.590	0.460	3.329	2.51	2.14	n.a.
Total:			**18.312**	**155.682**	**100.00**	**100.00**	

14



Integration Results

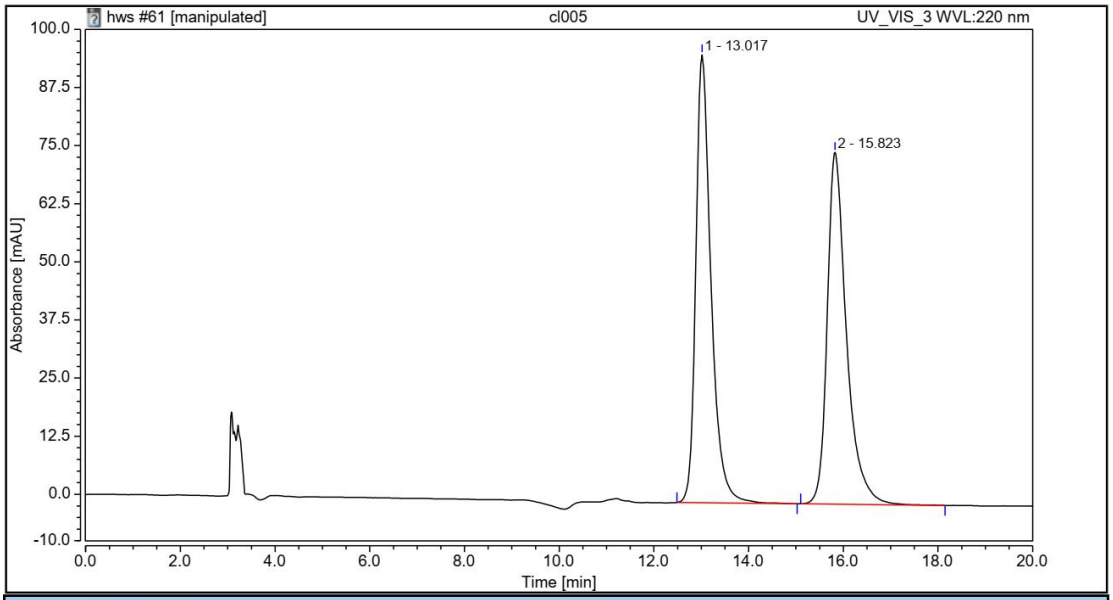
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.080	13.010	27.158	48.46	53.22	n.a.
2		12.840	13.837	23.876	51.54	46.78	n.a.
Total:			**26.848**	**51.034**	**100.00**	**100.00**	



Integration Results

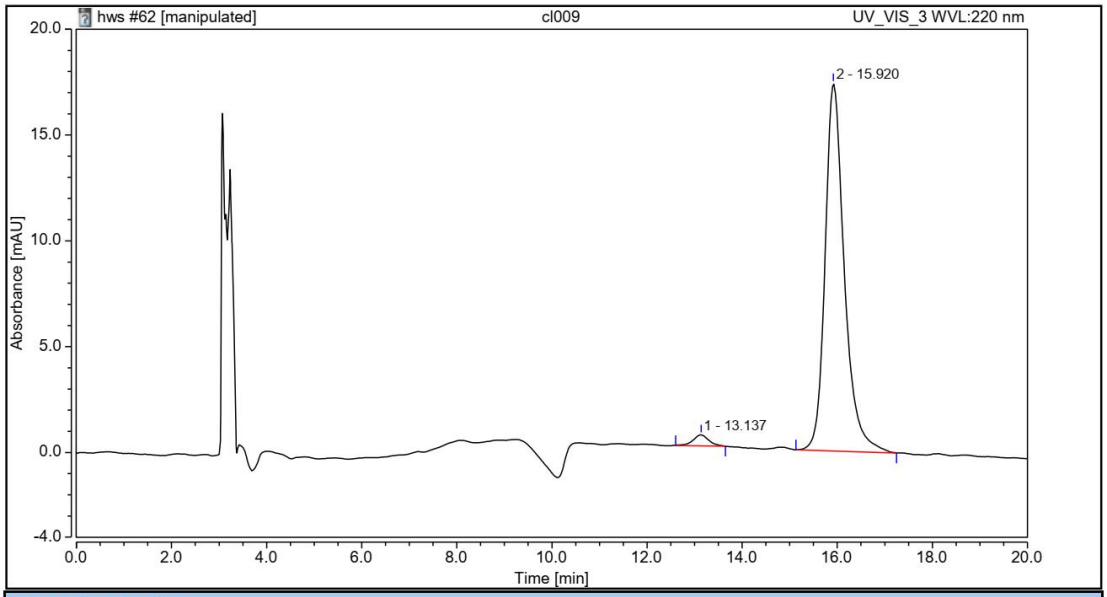
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.083	18.530	37.087	97.52	97.96	n.a.
2		12.900	0.471	0.772	2.48	2.04	n.a.
Total:			**19.001**	**37.859**	**100.00**	**100.00**	

15



Integration Results

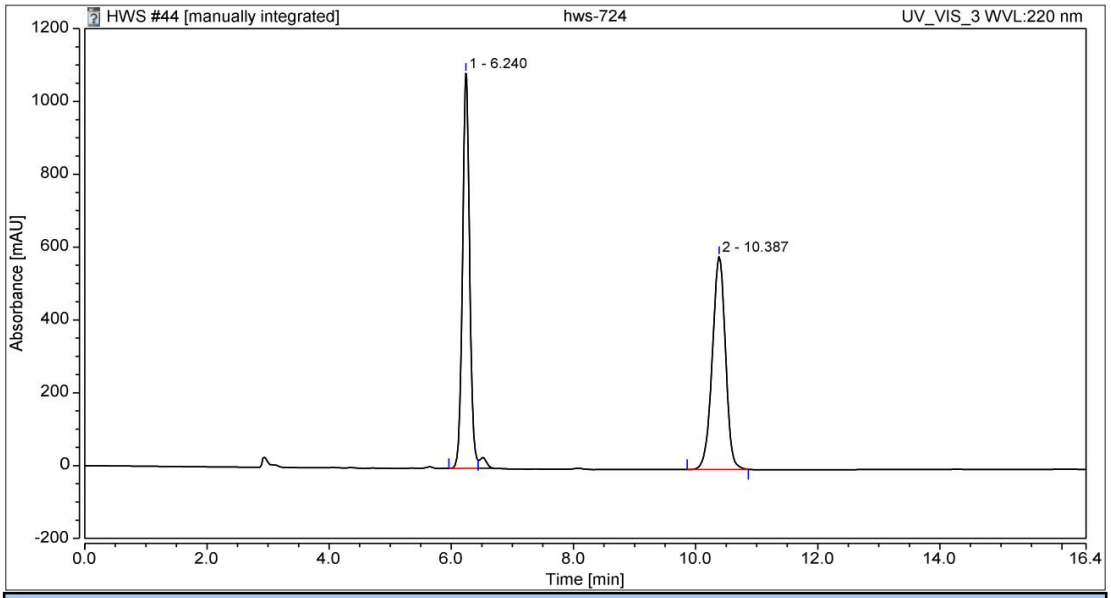
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.017	35.748	96.375	50.05	56.02	n.a.
2		15.823	35.675	75.675	49.95	43.98	n.a.
Total:			**71.423**	**172.050**	**100.00**	**100.00**	



Integration Results

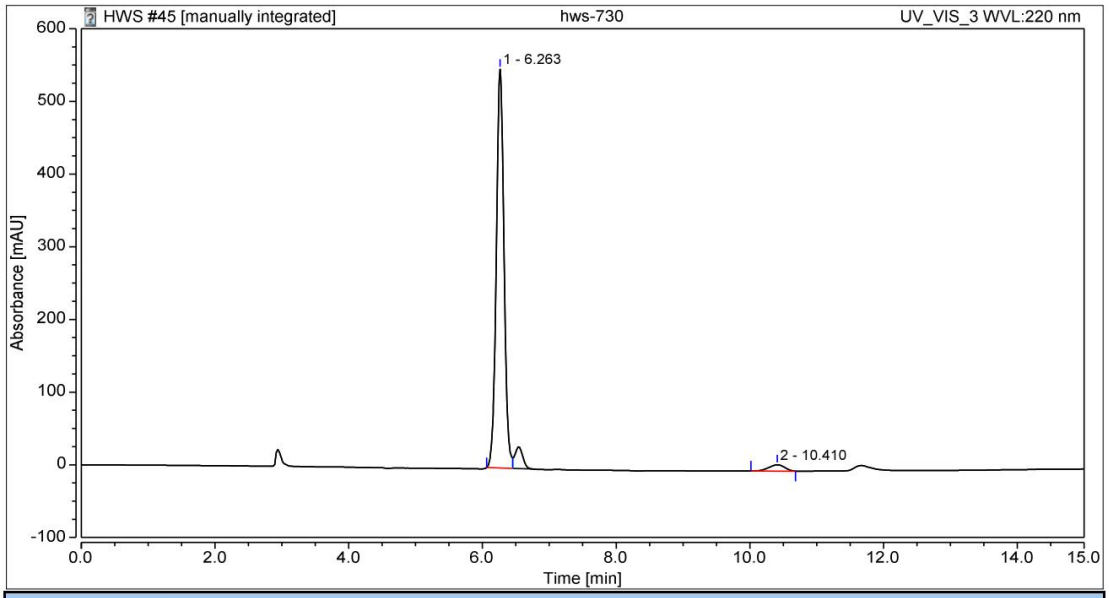
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.137	0.197	0.514	2.36	2.88	n.a.
2		15.920	8.144	17.363	97.64	97.12	n.a.
Total:			**8.341**	**17.877**	**100.00**	**100.00**	

16



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.240	146.565	1085.194	50.01	64.98	n.a.
2		10.387	146.533	584.875	49.99	35.02	n.a.
Total:			**293.098**	**1670.069**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.263	72.811	548.783	96.82	98.46	n.a.
2		10.410	2.388	8.592	3.18	1.54	n.a.
Total:			**75.199**	**557.375**	**100.00**	**100.00**	

Crystallographic data of 3d

Chemical Formula	**C19 H18 Cl F O2**
Molecular Weight / *g.mol*$^{-1}$	332.78
Crystal System	Monoclinic
Space Group	$P2_1$ (n°4)
Z , Z' (asymmetric units per unit cell)	4,2
a / *Å*	8.179(1)
b / *Å*	22.368(4)
c / *Å*	9.641(1)
α / °	90
β / °	90.631(3)
γ / °	90
V / *Å*^{3}	1763.7(5)
d_{calc} / *g.cm*$^{-3}$	1.253
F(000) / *e*$^-$	696
Absorption coefficient μ (MoKα_1) / *mm*$^{-1}$	0.232
Absolute structure parameter	-0.05(10)

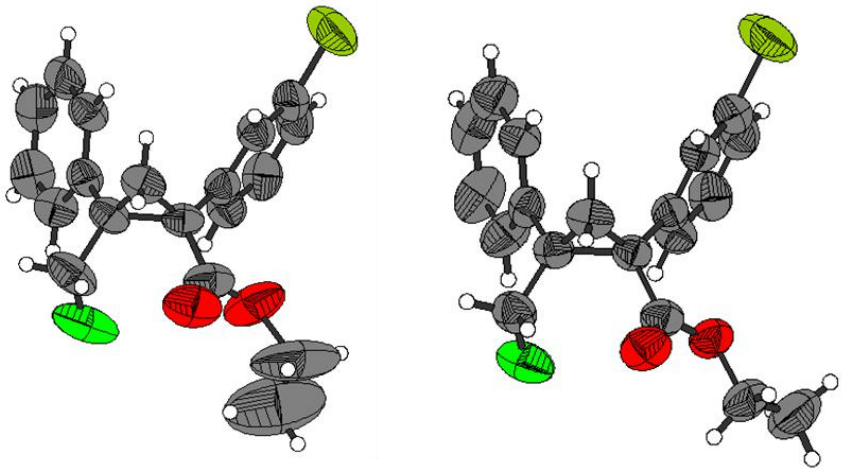


Figure 1: Asymmetric unit in thermal ellipsoidal represantion . (on the left molA, on the right MOL0)