Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Palladium-Catalyzed Stereoselective Construction of Chiral Allenes Bearing Nonadjacent Axial and Two Central Chirality

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1. General and Materials

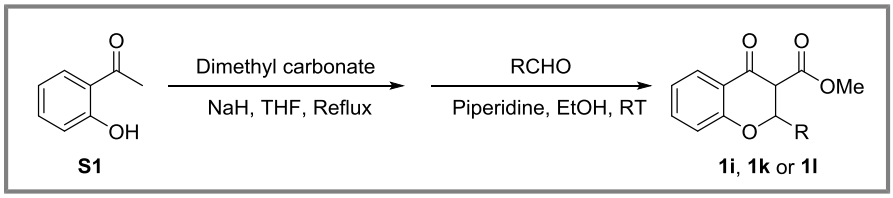
General: All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz instrument with TMS as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). The heat source for all heating reactions is the oil bath. High-resolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. All reactions were monitored by TLC analysis.

Materials: Commercially available reagents and solvents were used throughout without further purification.

2. Synthesis of Substrates

2.1. The Synthesis of Flavonoids

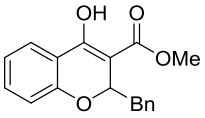
The flavonoids **1** were synthesized from (substituted) 2'-hydroxyacetophenones and carbonate esters through two steps according to the known procedure, in which **1a**-**h** and **1m**-**s** are the known compounds.[1-4] First, the methoxycarbonyl group was introduced to the known 2'-hydroxy-acetophenone **S1** under the basic condition to afford the intermediate β-keto ester. Then, β-keto ester underwent the base-catalyzed domino aldol-oxa-Michael reactions with aldehydes to provide the desired flavonoids **1**.



General procedure: To a solution of ketone (40 mmol) in THF (80 mL) was slowly added sodium hydride (4.800 g, 120 mmol, 60%) at the ambient temperature. Subsequently, the dimethyl carbonate (6.8 mL, 80 mmol) was added dropwise to the suspension. The reaction mixture was stirred at ambient temperature for about 5 minutes and then heated up to reflux for about 2 hours. The reaction was complete as monitored by TLC. After cooling to room temperature, the resulting mixture was acidified with aqueous HCl (3.0 M) to pH 4-5. After separation, the aqueous layer was extracted with ethyl acetate (50 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The combined organic layer was dried over sodium sulfate and evaporated under the reduced pressure. The crude residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (20/1-10/1) as eluent to give the intermediate ester.

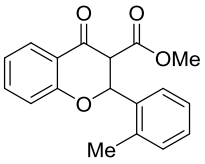
The ester intermediate (4.0 mmol) thus obtained was dissolved in ethanol (12 mL) followed by addition of aldehydes (4.0 mmol, 1.0 equiv.). After that, the piperidine (0.8 mmol, 0.2 equiv.) was added to the above ethanol solution. The resulting mixture was stirred at ambient temperature for about 12 h. After the completion of the reaction, the volatiles were removed under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the flavonoids **1**.

Methyl 2-Benzyl-4-hydroxy-2*H*-chromene-3-carboxylate (1i):



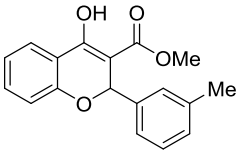
0.758 g, 64% yield (last step), white solid, mp 92-93 °C, new compound, R_f = 0.48 (hexanes/ethyl acetate 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (brs, 1H), 7.69 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.39-7.34 (m, 1H), 7.31-7.26 (m, 2H), 7.24-7.19 (m, 1H), 7.18-7.12 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.36 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.71 (s, 3H), 3.04 (dd, *J* = 13.8, 8.9 Hz, 1H), 2.82 (dd, *J* = 13.8, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 162.4, 155.6, 137.5, 133.5, 129.6, 128.3, 126.6, 124.7, 121.4, 117.9, 117.6, 95.6, 75.1, 51.8, 41.3. HRMS Calculated for $C_{18}H_{16}NaO_4$ $[M+Na]^+$ 319.0941, found: 319.0943.

Methyl 4-Oxo-2-(*o*-tolyl)chromane-3-carboxylate (1k):



0.730 g, 62% yield (last step), white solid, mp 121-122 °C, new compound, R_f = 0.40 (hexanes/ ethyl acetate 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.56-7.47 (m, 2H), 7.32-7.25 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.96 (d, *J* = 12.6 Hz, 1H), 4.29 (d, *J* = 12.6 Hz, 1H), 3.63 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 167.6, 161.3, 137.1, 136.8, 134.2, 131.2, 129.5, 127.6, 126.8, 126.5, 122.0, 119.9, 118.1, 77.5, 58.3, 52.5, 19.4. HRMS Calculated for $C_{18}H_{16}KO_4$ $[M+K]^+$ 335.0680, found: 335.0683.

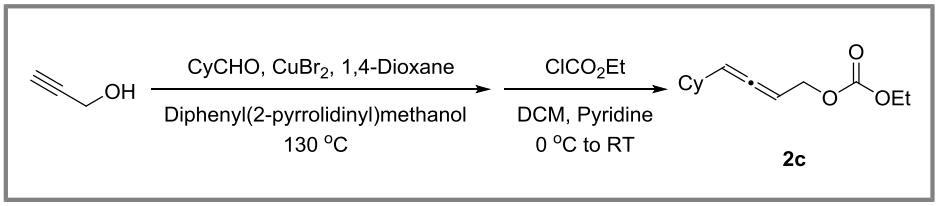
Methyl 4-Hydroxy-2-(*m*-tolyl)-2*H*-chromene-3-carboxylate (1l):



0.708 g, 60% yield (last step), white solid, mp 90-91 °C, new compound, R_f = 0.40 (hexanes/ethyl acetate 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.29 (brs, 1H), 7.68 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.28-7.26 (m 1H), 7.19-7.13 (m, 3H), 7.10-7.04 (m, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.22 (s, 1H), 3.76 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 163.1, 155.8, 140.0, 138.0, 133.4, 129.3, 128.3, 128.0, 124.5, 124.3, 121.3, 117.8, 117.3, 94.1, 74.7, 51.9, 21.5. HRMS Calculated for $C_{18}H_{17}O_4$ $[M+H]^+$ 297.1121, found: 297.1119.

2.2. The Synthesis of Allenylic Carbonates

The allenylic carbonates **2** could be conveniently synthesized from the commercially available propargyl alcohol and aldehydes through two steps according to the known procedure, all of which are the known compounds except for the **2c**.[5] First, the propargyl alcohol underwent the copper-catalyzed reaction with cyclohexanecarbaldehyde to provide the intermediate allenylic alcohol. Then, the allenylic carbonate **2c** could be prepared from the above allenylic alcohol intermediate and ethyl chloroformate under the basic condition.



Procedure: To a dried Schlenk flask were sequentially added copper dibromide (0.894 g, 4.0

mmol), diphenyl(2-pyrrolidinyl)methanol (5.067 g, 20 mmol), 1,4-dioxane (40 mL), cyclohexane carbaldehyde (3.365 g, 30 mmol), and propargyl alcohol (1.682 g, 30 mmol) under the nitrogen atmosphere. The mixture was stirred in an oil bath preheated at 130 ^{o}C for 12 h. After cooling to room temperature, the resulting mixture was diluted with diethyl ether (60 mL), which was washed with an aqueous solution of hydrochloric acid (HCl, 3.0 M, 60 mL). After separation, the aqueous layer was extracted with diethyl ether (60 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (20/1-10/1) as eluent to afford the intermediate allenylic alcohol.

A solution of the above allenylic alcohol (1.046 g, 6.9 mmol) and pyridine (1.67 mL, 20.7 mmol) in dichloromethane (18 mL) was cooled to 0 ℃. The ethyl chloroformate (1.31 mL, 13.8 mmol) was added dropwise over a period of 5 minutes. The reaction mixture was allowed to warm to room temperature. When the reaction was completed as monitored by TLC, the reaction mixture was acidified with the hydrogen chloride aqueous solution (HCl, 3.0 M) to pH 5-6 and extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the desirable allenylic carbonate **2c**.

4-Cyclohexylbuta-2,3-dien-1-yl Ethyl Carbonate (2c):

1.292 g, 29% yield (two steps), yellow liquid, new compound, R_f = 0.66 (hexanes/ethyl acetate 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40-5.21 (m, 2H), 4.64-4.55 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.07-1.94 (m, 1H), 1.80-1.67 (m, 4H), 1.67-1.58 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.29-1.01 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 155.2, 99.2, 87.5, 66.4, 64.1, 36.9, 33.0, 26.2, 26.1, 14.4. HRMS Calculated for $C_{13}H_{21}O_3$ $[M+H]^+$ 225.1485, found: 225.1484.

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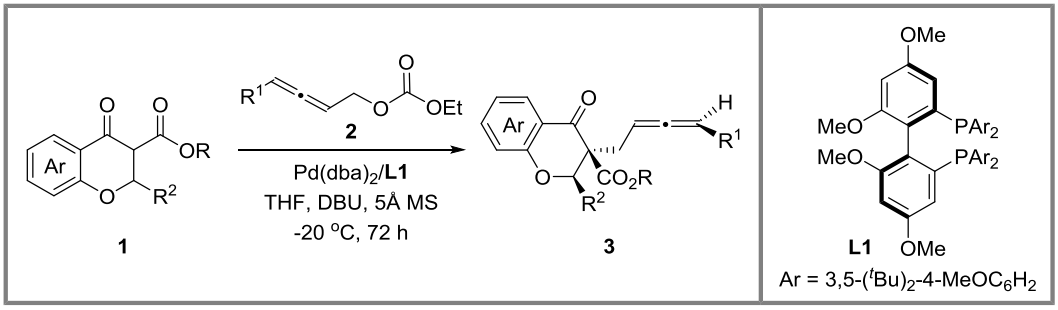
3. Pd-Catalyzed Asymmetric Allenylic Alkylation of Flavonoids

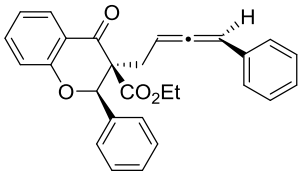


The metal precursor $Pd(dba)_2$ (0.02 mmol, 11.5 mg, 10 mol%), ligand (*R*)-DTBM-GARPHOS (**L1**) (0.022 mmol, 26.7 mg, 11 mol%) and tetrahydrofuran (1.5 mL) were placed in a dried Schlenk tube under nitrogen atmosphere. The mixture was stirred at 30 °C for 30 min. Then the mixture was cooled to -20 °C. Thereafter, the flavonoids **1** (0.20 mmol), 5Å MS (50.0 mg) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (35.9 μL, 0.24 mmol) were added, and the reaction mixture was stirred at -20 °C for 10 min. Sequentially, allenylic carbonates **2** (0.30 mmol) and tetrahydrofuran (0.5 mL) were added slowly. The mixture was stirred at -20 °C for 72 h. After the completion of the reaction, without any treatment, the residue was quickly purified by column chromatography on silica gel (hexanes/ethyl acetate/dichloromethane 100/1/2-100/3/6) to give the desirable chiral products **3**.

The racemates were prepared by running reactions with an achiral DPPP ligand at 30 °C. And two diastereoisomers were inseparable.

(-)-Ethyl 4-Oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)chromane-3-carboxylate (3aa):

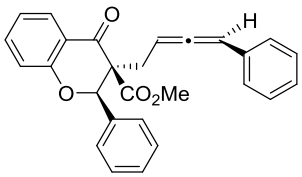
78.5 mg, 92% yield, pale yellow oil, new compound, R_f = 0.35 (hexanes/ethyl acetate 20/1), 16:1 dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -228.66 (*c* 0.98, $CHCl_3$). The major diastereoisomer:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55-7.43 (m, 3H), 7.42-7.35 (m, 3H), 7.28-7.15 (m, 5H), 7.13-7.06 (m, 1H), 7.04-6.99 (m, 1H), 6.24-6.17 (m, 1H), 5.71 (s, 1H), 5.62-5.48 (m, 1H), 4.11-3.95 (m, 2H), 3.34-3.24 (m, 1H), 2.57-2.40 (m, 1H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 190.0, 168.3, 161.6, 136.3, 135.6, 133.9, 129.2, 128.7, 128.4, 127.9, 127.4, 127.2, 126.9, 122.0, 121.2, 118.1, 95.8, 89.9, 82.5, 61.7, 61.3, 29.5, 13.8. HPLC: Chiralpak AD-3 column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 98/2, flow = 0.8 mL/min, retention time 17.1 min (major) and 18.0 min. HRMS Calculated for $C_{28}H_{25}O_4$ $[M+H]^+$ 425.1747, found: 425.1748.

(-)-Methyl 4-Oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)chromane-3-carboxylate (3ba):

77.7 mg, 95% yield, colorless oil, new compound, R_f = 0.28 (hexanes/ethyl acetate 20/1), 19:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -273.28 (*c* 1.03, $CHCl_3$). The major diastereoisomer:

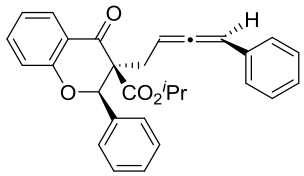


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.55-7.49 (m, 1H), 7.47-7.32 (m, 5H), 7.28-7.15 (m, 5H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.29-6.09 (m, 1H), 5.72 (s, 1H), 5.64-5.46 (m, 1H), 3.58 (s, 3H), 3.35-3.18 (m, 1H), 2.58-2.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.8, 168.9, 161.5, 136.3, 135.6, 133.8,

129.2, 128.7, 128.5, 127.9, 127.2, 126.9, 122.1, 121.2, 118.3, 95.9, 89.8, 82.5, 61.4, 52.6, 29.7. HPLC: Chiralpak AD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.8 mL/min, retention time 22.8 min (major) and 23.9 min. HRMS Calculated for $C_{27}H_{23}O_4$ $[M+H]^+$ 411.1591, found: 411.1589.

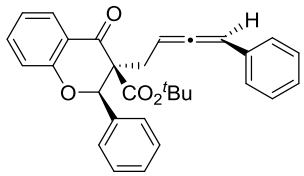
(-)-Isopropyl 4-Oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)chromane-3-carboxylate (3ca):

81.3 mg, 93% yield, colorless oil, new compound, R_f = 0.45 (hexanes/ethyl acetate 20/1), 12:1 dr, 97% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -220.58 (*c* 1.01, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.62-7.43 (m, 3H), 7.42-7.32 (m, 3H), 7.28-7.18 (m, 5H), 7.14-7.05 (m, 1H), 7.04-6.99 (m, 1H), 6.32-6.07 (m, 1H), 5.71 (s, 1H), 5.64-5.49 (m, 1H), 5.04-4.72 (m, 1H), 3.33-3.14 (m, 1H), 2.54-2.38 (m, 1H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.94 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 190.1, 167.8, 161.6, 136.2, 135.6, 133.9, 129.1, 128.7, 128.3, 127.8, 127.5, 127.2, 126.9, 121.9, 121.2, 118.0, 95.7, 90.0, 82.5, 69.8, 61.1, 29.4, 21.6, 21.3. HPLC: Chiralcel OD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.8 mL/min, retention time 9.9 min and 12.3 min (major). HRMS Calculated for $C_{29}H_{27}O_4$ $[M+H]^+$ 439.1904, found: 439.1902.



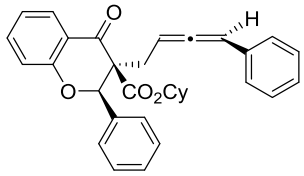
(-)-*tert*-Butyl 4-Oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)chromane-3-carboxylate (3da):

87.2 mg, 96% yield, colorless oil, new compound, R_f = 0.51 (hexanes/ethyl acetate 20/1), 12:1 dr, 95% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -201.54 (*c* 1.03, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.58-7.34 (m, 6H), 7.27-7.18 (m, 5H), 7.13-6.98 (m, 2H), 6.29-6.10 (m, 1H), 5.68 (s, 1H), 5.64-5.48 (m, 1H), 3.30-3.11 (m, 1H), 2.45-2.34 (m, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 190.3, 167.2, 161.5, 136.0, 135.6, 134.0, 129.1, 128.6, 128.2, 127.7, 127.6, 127.1, 126.9, 121.7, 121.3, 117.8, 95.6, 90.1, 83.0, 82.5, 61.6, 29.4, 27.7. HPLC: Chiralpak AD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 16.7 min and 21.0 min (major). HRMS Calculated for $C_{30}H_{29}O_4$ $[M+H]^+$ 453.2060, found: 453.2053.



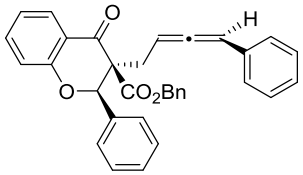
(-)-Cyclohexyl 4-Oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)chromane-3-carboxylate (3ea):

87.6 mg, 92% yield, colorless oil, new compound, R_f = 0.41 (hexanes/ethyl acetate 20/1), 12:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -175.04 (*c* 1.03, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.57-7.45 (m, 3H), 7.44-7.33 (m, 3H), 7.28-7.18 (m, 5H), 7.15-7.06 (m, 1H), 7.06-6.98 (m, 1H), 6.29-6.11 (m, 1H), 5.72 (s, 1H), 5.65-5.46 (m, 1H), 4.93-4.70 (m, 1H), 3.37-3.14 (m, 1H), 2.52-2.37 (m, 1H), 1.74-1.62 (m, 1H), 1.50-1.11 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 190.0, 167.6, 161.6, 136.1, 135.5, 133.9, 129.1, 128.6, 128.4, 127.8, 127.5, 127.1, 126.9, 121.9, 121.4, 118.0, 95.6, 90.0, 82.5, 73.6, 61.2, 31.0, 30.6, 29.3, 25.2, 22.5, 22.3. HPLC: Chiral-pak AD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 98/2, flow = 1.0 mL/min, retention time 21.1 min (major) and 23.1 min (minor). HRMS Calculated for $C_{32}H_{31}O_4$ $[M+H]^+$ 479.2217, found: 479.2214.



(-)-Benzyl 4-Oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)chromane-3-carboxylate (3fa):

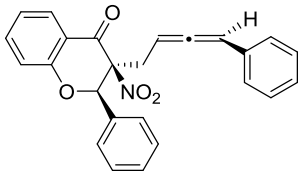
91.8 mg, 94% yield, pale yellow oil, new compound, R_f = 0.34 (hexanes/ethyl acetate 20/1), 16:1 dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -203.64 (*c* 1.04, $CHCl_3$). The major diastereoisomer:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.58-7.49 (m, 1H), 7.34-7.19 (m, 13H), 7.14-7.07 (m, 1H), 7.05-6.97 (m, 3H), 6.30-6.07 (m, 1H), 5.73 (s, 1H), 5.65-5.48 (m, 1H), 5.14 (d, *J* = 12.6 Hz, 1H), 4.93 (d, *J* = 12.6 Hz, 1H), 3.41-3.14 (m, 1H), 2.56-2.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.7, 168.1, 161.6, 136.3, 135.4, 134.9, 133.8, 129.1, 128.7, 128.4, 128.2, 128.0, 127.8, 127.4, 127.2, 126.9, 122.1, 121.3, 118.2, 95.8, 89.8, 82.6, 67.2, 61.3, 29.4. HPLC: Chiralpak AD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/min, retention time 27.0 min (major) and 31.8 min. HRMS Calculated for $C_{33}H_{27}O_4$ $[M+H]^+$ 487.1904, found: 487.1905.

(-)-3-Nitro-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)chroman-4-one (3ga):

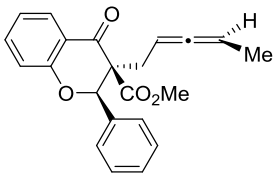
The reaction was conducted at -20 ^{o}C for 96 h. 58.8 mg, 74% yield, pale yellow oil, new compound, R_f = 0.37 (hexanes/ethyl acetate 20/1), 4:1 dr, 94% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -212.13 (*c* 0.98, $CHCl_3$). The major diastereoisomer:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.63-7.52 (m, 1H), 7.49-7.31 (m, 5H), 7.30-7.09 (m, 6H), 7.08-7.02 (m, 1H), 6.32-6.16 (m, 1H), 5.81 (s, 1H), 5.68-5.44 (m, 1H), 3.52-3.33 (m, 1H), 2.89-2.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 183.0, 161.3, 137.3, 133.0, 133.0, 130.1, 128.9, 128.9, 128.4, 127.7, 127.2, 127.0, 123.1, 120.7, 118.7, 97.0, 92.9, 88.2, 82.0, 30.3. HPLC: Chiralpak AD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 98/2, flow = 0.8 mL/min, retention time 15.7 min and 16.8 min (major). The HRMS Calculated for $C_{25}H_{19}NNaO_4$ $[M+Na]^+$ 420.1206, found: 420.1211.

(-)-Methyl 4-Oxo-3-(penta-2,3-dien-1-yl)-2-phenylchromane-3-carboxylate (3bb):

33.1 mg, 47% yield, pale yellow oil, new compound, R_f = 0.42 (hexanes/ethyl acetate 20/1), 5:1 dr, 95% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -189.18 (*c* 0.62, $CHCl_3$). The major diastereoisomer: ^{1}H

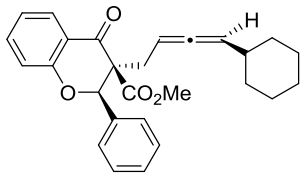


NMR (400 MHz, $CDCl_3$) δ 8.04-7.95 (m, 1H), 7.58-7.49 (m, 1H), 7.45-7.36 (m, 5H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 5.76 (s, 1H), 5.20-4.95 (m, 2H), 3.59 (s, 3H), 3.18-3.10 (m, 1H), 2.38-2.29 (m, 1H), 1.57 (dd, *J* = 7.0, 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 189.9, 169.0, 161.5, 136.2, 135.7, 129.1, 128.3, 127.8, 127.2, 122.0, 121.3, 118.2, 87.0, 85.0, 82.3, 61.6, 52.5, 29.7, 14.1. HPLC: Chiralpak IB column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 8.8 min and 15.9 min (major). HRMS Calculated for $C_{22}H_{21}O_4$ $[M+H]^+$ 349.1434, found: 349.1433.

(-)-Methyl 3-(4-Cyclohexylbuta-2,3-dien-1-yl)-4-oxo-2-phenylchromane-3-carboxylate (3bc):

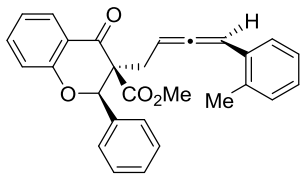
19.1 mg, 23% yield, pale yellow oil, new compound, R_f = 0.46 (hexanes/ethyl acetate 20/1), 10:1 dr, 87% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -137.94 (*c* 0.78, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.57-7.51 (m, 1H), 7.48-7.43 (m,

2H), 7.42-7.37 (m, 3H), 7.13-7.04 (m, 2H), 5.77 (s, 1H), 5.24-5.13 (m, 1H), 5.12-5.02 (m, 1H),



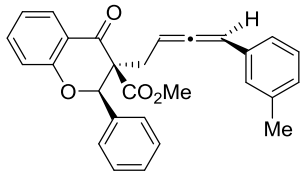
3.59 (s, 3H), 3.20-3.08 (m, 1H), 2.37-2.28 (m, 1H), 2.03-1.88 (m, 1H), 1.79-1.56 (m, 5H), 1.35-1.03 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 189.8, 169.1, 161.6, 136.2, 135.7, 129.1, 128.3, 127.9, 127.3, 122.0, 121.3, 118.2, 98.1, 86.3, 82.3, 61.5, 52.4, 37.1, 33.0, 32.7, 30.0, 26.1, 26.0, 25.9. HPLC: Chiralpak AD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.8 mL/min, retention time 11.3 min (minor) and 13.0 min (major). The HRMS Calculated for $C_{27}H_{29}O_4$ $[M+H]^+$ 417.2060, found: 417.2068.

(-)-Methyl 4-Oxo-2-phenyl-3-(4-(*o*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3bd):
75.7 mg, 89% yield, colorless oil, new compound, R_f = 0.28 (hexanes/ethyl acetate 20/1), 16:1 dr, 97% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -208.12 (*c* 1.02, $CHCl_3$). The major diastereoisomer: ^{1}H



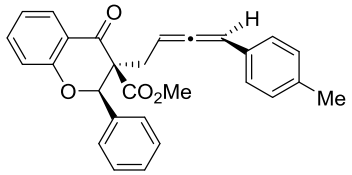
NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.56-7.49 (m, 1H), 7.48-7.41 (m, 2H), 7.42-7.33 (m, 3H), 7.32-7.28 (m, 1H), 7.17-7.05 (m, 4H), 7.04-6.99 (m, 1H), 6.50-6.26 (m, 1H), 5.73 (s, 1H), 5.59-5.45 (m, 1H), 3.58 (s, 3H), 3.34-3.15 (m, 1H), 2.54-2.42 (m, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 189.8, 168.9, 161.5, 136.3, 135.6, 135.1, 132.0, 130.5, 129.2, 128.4, 127.9, 127.4, 127.3, 127.2, 126.2, 122.1, 121.2, 118.2, 93.2, 88.8, 82.5, 61.4, 52.6, 29.7, 19.8. HPLC: Chiralcel OD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.8 mL/min, retention time 14.4 min and 29.7 min (major). HRMS Calculated for $C_{28}H_{25}O_4$ $[M+H]^+$ 425.1747, found: 425.1750.

(-)-Methyl 4-Oxo-2-phenyl-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3be):
76.9 mg, 91% yield, colorless oil, new compound, R_f = 0.28 (hexanes/ethyl acetate 20/1), 24:1 dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -224.23 (*c* 0.99, $CHCl_3$). The major diastereoisomer: ^{1}H



NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55-7.49 (m, 1H), 7.48-7.35 (m, 5H), 7.17-7.07 (m, 2H), 7.05-6.93 (m, 4H), 6.22-6.10 (m, 1H), 5.72 (s, 1H), 5.61-5.47 (m, 1H), 3.58 (s, 3H), 3.33-3.24 (m, 1H), 2.51-2.42 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.8, 168.9, 161.5, 138.2, 136.3, 135.6, 133.7, 129.2, 128.5, 128.4, 128.0, 127.9, 127.5, 127.2, 124.0, 122.1, 121.2, 118.2, 95.9, 89.6, 82.5, 61.4, 52.6, 29.7, 21.4. HPLC: Chiralcel OD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.8 mL/min, retention time 13.9 min (minor) and 21.4 min (major). HRMS Calculated for $C_{28}H_{28}NO_4$ $[M+NH_4]^+$ 442.2013, found: 442.2012.

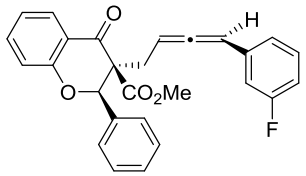
(-)-Methyl 4-Oxo-2-phenyl-3-(4-(*p*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3bf):
80.3 mg, 95% yield, colorless oil, new compound, R_f = 0.29 (hexanes/ethyl acetate 20/1), 19:1 dr,



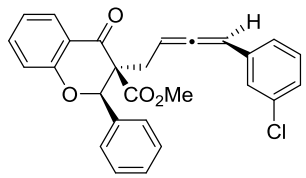
99% ee (the major diastereoisomer), $[\alpha]^{20}_D$ = -243.55 (*c* 1.15, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55-7.49 (m, 1H), 7.46-7.35 (m, 5H), 7.14-6.99 (m, 6H), 6.29-6.10 (m, 1H), 5.72 (s, 1H), 5.60-5.46 (m, 1H), 3.58 (s, 3H), 3.33-3.23 (m, 1H), 2.51-2.43 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 189.8, 168.9, 161.5, 137.0, 136.3, 135.6, 130.7, 129.4, 129.2, 128.4, 127.9, 127.2, 126.7, 122.1, 121.2, 118.2, 95.7, 89.7, 82.4, 61.4, 52.5, 29.8,

21.2. HPLC: Chiralcel OD-3 column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.8 mL/min, retention time 13.4 min and 19.4 min (major). HRMS Calculated for $C_{28}H_{28}NO_4$ $[M+NH_4]^+$ 442.2013, found: 442.2010.

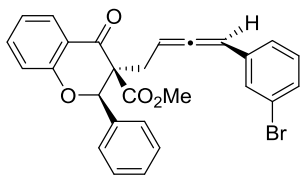
(-)-Methyl 3-(4-(3-Fluorophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylchromane-3-carboxylate (3bg): 52.4 mg, 61% yield, pale yellow oil, new compound, R_f = 0.21 (hexanes/ethyl acetate 20/1), 19:1 dr, 95% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -203.35 (*c* 1.01, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.56-7.51 (m, 1H), 7.45-7.36 (m, 5H), 7.25-7.18 (m, 1H), 7.14-7.08 (m, 1H), 7.05-6.96 (m, 2H), 6.94-6.82 (m, 2H), 6.21-6.08 (m, 1H), 5.68 (s, 1H), 5.65-5.54 (m, 1H), 3.60 (s, 3H), 3.32-3.18 (m, 1H), 2.52-2.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 189.7, 168.7, 163.1 (d, $^1J_{F\text{-}C}$ = 244.1 Hz), 161.5, 136.3 (d, $^3J_{F\text{-}C}$ = 8.7 Hz), 135.5, 130.0 (d, $^3J_{F\text{-}C}$ = 8.4 Hz), 129.3, 128.5, 127.9, 127.2, 122.6 (d, $^4J_{F\text{-}C}$ = 2.7 Hz), 122.1, 121.1, 118.2, 114.0 (d, $^2J_{F\text{-}C}$ = 21.4 Hz), 113.4 (d, $^2J_{F\text{-}C}$ = 22.1 Hz), 95.1 (d, $^4J_{F\text{-}C}$ = 2.7 Hz), 90.2, 82.6, 61.3, 52.6, 29.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.34. HPLC: Chiralpak IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 98/2, flow = 1.0 mL/min, retention time 25.6 min (major) and 32.0 min (minor). HRMS Calculated for $C_{27}H_{22}FO_4$ $[M+H]^+$ 429.1497, found: 429.1498.



(-)-Methyl 3-(4-(3-Chlorophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylchromane-3-carboxylate (3bh): 58.6 mg, 66% yield, pale yellow oil, new compound, R_f = 0.26 (hexanes/ethyl acetate 20/1), 19:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -189.99 (*c* 1.03, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.57-7.50 (m, 1H), 7.43-7.32 (m, 5H), 7.21-6.99 (m, 6H), 6.21-6.03 (m, 1H), 5.67 (s, 1H), 5.66-5.54 (m, 1H), 3.60 (s, 3H), 3.36-3.14 (m, 1H), 2.56-2.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 189.7, 168.7, 161.5, 136.4, 135.9, 135.5, 134.6, 129.8, 129.3, 128.5, 127.9, 127.2, 127.2, 126.8, 125.0, 122.2, 121.1, 118.2, 94.9, 90.3, 82.6, 61.3, 52.6, 29.6. HPLC: Chiralpak IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 96.5/3.5, flow = 1.0 mL/min, retention time 20.3 min (major) and 22.6 min (minor). HRMS Calculated for $C_{27}H_{22}ClO_4$ $[M+H]^+$ 445.1201 (^{35}Cl) and 447.1184 (^{37}Cl), found: 445.1204 (^{35}Cl) and 447.1181 (^{37}Cl).

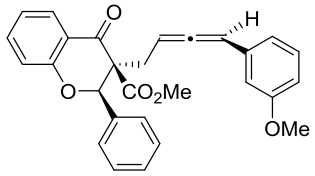


(-)-Methyl 3-(4-(3-Bromophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylchromane-3-carboxylate (3bi): 55.4 mg, 57% yield, pale yellow oil, new compound, R_f = 0.23 (hexanes/ethyl acetate 20/1), 19:1 dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -199.54 (*c* 0.89, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.57-7.51 (m, 1H), 7.45-7.37 (m, 5H), 7.35-7.28 (m, 2H), 7.16-7.09 (m, 3H), 7.04-6.99 (m, 1H), 6.17-6.05 (m, 1H), 5.67 (s, 1H), 5.65-5.56 (m, 1H), 3.60 (s, 3H), 3.31-3.18 (m, 1H), 2.52-2.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 189.7, 168.7, 161.5, 136.4, 136.1, 135.5, 130.1, 130.1, 129.7, 129.3, 128.5, 127.9, 127.2, 125.4, 122.8, 122.2, 121.1, 118.2, 94.8, 90.3, 82.6, 61.3, 52.6, 29.6. HPLC: Chiralpak AS-H + Chiralpak AS-H column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.7 mL/min, retention time 33.6 min (major) and 40.0 min (minor). HRMS Calculated for $C_{27}H_{22}BrO_4$ $[M+H]^+$ 489.0696 (^{79}Br) and 491.0680 (^{81}Br), found:

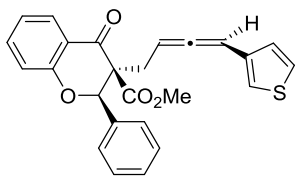


489.0699 (^{79}Br) and 491.0681 (^{81}Br).

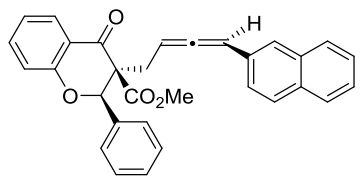
(-)-Methyl 3-(4-(3-Methoxyphenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylchromane-3-carboxylate (3bj): 74.6 mg, 85% yield, colorless oil, new compound, R_f = 0.17 (hexanes/ethyl acetate 20/1), 19:1 dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -229.98 (*c* 1.07, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.54-7.49 (m, 1H), 7.47-7.34 (m, 5H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.77-6.69 (m, 2H), 6.20-6.11 (m, 1H), 5.71 (s, 1H), 5.61-5.50 (m, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 3.35-3.16 (m, 1H), 2.56-2.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.8, 168.8, 161.5, 159.9, 136.3, 135.6, 135.2, 129.6, 129.2, 128.4, 127.9, 127.2, 122.1, 121.2, 119.5, 118.2, 113.2, 111.8, 95.9, 89.9, 82.5, 61.4, 55.2, 52.6, 29.7. HPLC: Chiralpak IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 90/10, flow = 1.0 mL /min, retention time 16.0 min (major) and 17.8 min. HRMS Calculated for $C_{28}H_{25}O_5$ $[M+H]^+$ 441.1697, found: 441.1700.



(-)-Methyl 4-Oxo-2-phenyl-3-(4-(thiophen-3-yl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3bk): 45.9 mg, 55% yield, colorless oil, new compound, R_f = 0.29 (hexanes/ethyl acetate 20/1), 19:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -215.09 (*c* 0.92, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.56-7.50 (m, 1H), 7.45-7.33 (m, 5H), 7.23-7.17 (m, 1H), 7.14-7.05 (m, 1H), 7.06-6.95 (m, 3H), 6.43-6.11 (m, 1H), 5.71 (s, 1H), 5.54-5.43 (m, 1H), 3.58 (s, 3H), 3.30-3.17 (m, 1H), 2.50-2.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 189.8, 168.8, 161.5, 136.3, 135.6, 135.0, 129.2, 128.4, 127.9, 127.2, 126.3, 126.0, 122.1, 121.2, 121.2, 118.2, 90.4, 89.0, 82.5, 61.4, 52.6, 29.8. HPLC: Chiralpak AD-3 column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 94/6, flow = 0.7 mL/min, retention time 23.7 min (major) and 24.7 min. HRMS Calculated for $C_{25}H_{21}O_4S$ $[M+H]^+$ 417.1155, found: 417.1151.

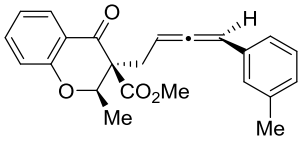


(-)-Methyl (2*R*,3*S*)-3-((*R*)-4-(Naphthalen-2-yl)buta-2,3-dien-1-yl)-4-oxo-2-phenylchromane-3-carboxylate (3bl): 68.5 mg, 74% yield, white solid, mp 69-70 °C, new compound, R_f = 0.24 (hexanes/ethyl acetate 20/1), 16:1 dr, 97% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -172.74 (*c* 0.98, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.81-7.69 (m, 3H), 7.60-7.54 (m, 1H), 7.53-7.31 (m, 9H), 7.14-7.06 (m, 1H), 6.99 (d, 1H), 6.46-6.28 (m, 1H), 5.75 (s, 1H), 5.71-5.57 (m, 1H), 3.58 (s, 3H), 3.38-3.18 (m, 1H), 2.59-2.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 189.8, 168.9, 161.5, 136.3, 135.6, 133.6, 132.7, 131.3, 129.2, 128.5, 128.3, 127.9, 127.8, 127.7, 127.2, 126.3, 125.8, 124.7, 122.1, 121.2, 118.2, 96.2, 90.0, 82.5, 61.5, 52.6, 29.8. HPLC: Chiralpak IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 90/10, flow = 1.0 mL/min, retention time 15.7 min (major) and 17.8 min (minor). HRMS Calculated for $C_{31}H_{25}O_4$ $[M+H]^+$ 461.1747, found: 461.1746.



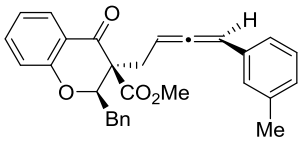
(-)-Methyl 2-Methyl-4-oxo-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3he):

59.7 mg, 82% yield, pale yellow oil, new compound, R_f = 0.35 (hexanes/ethyl acetate 20/1), 8:1 dr, 95% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -79.83 (*c* 1.19, $CHCl_3$). The major diastereoisomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.56-7.42 (m, 1H), 7.21-7.12 (m, 1H), 7.12-6.82 (m, 5H), 6.25-6.00 (m, 1H), 5.53-5.33 (m, 1H), 4.72 (q, *J* = 6.5 Hz, 1H), 3.62 (s, 3H), 3.39-3.23 (m, 1H), 2.75-2.61 (m, 1H), 2.30 (s, 3H), 1.59 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 189.9, 169.4, 161.4, 138.2, 135.9, 133.7, 128.5, 128.0, 127.9, 127.5, 124.1, 121.7, 121.3, 117.8, 95.0, 88.8, 78.2, 59.9, 52.7, 29.9, 21.4, 16.1. HPLC: Chiralpak ID column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 18.7 min (major) and 20.9 min (minor). HRMS Calculated for $C_{23}H_{23}O_4$ $[M+H]^+$ 363.1591, found: 363.1598.



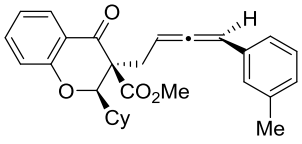
(-)-Methyl 2-Benzyl-4-oxo-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3ie):

The reaction was conducted at -20 °C for 96 h. 51.4 mg, 59% yield, pale yellow oil, new compound, R_f = 0.41 (hexanes/ethyl acetate 20/1), 7:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -220.59 (*c* 0.99, $CHCl_3$). The major diastereoisomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.45-7.40 (m, 1H), 7.37-7.30 (m, 4H), 7.29-7.24 (m, 1H), 7.17-7.13 (m, 1H), 7.07-6.97 (m, 4H), 6.90-6.83 (m, 1H), 6.16-6.02 (m, 1H), 5.54-5.37 (m, 1H), 4.79 (dd, *J* = 10.2, 1.9 Hz, 1H), 3.67 (s, 3H), 3.54-3.37 (m, 1H), 3.26 (dd, *J* = 14.8, 1.9 Hz, 1H), 3.20-3.09 (m, 1H), 2.91-2.78 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 189.7, 169.7, 161.2, 138.3, 138.0, 136.0, 133.7, 129.5, 128.6, 128.5, 128.1, 127.9, 127.6, 126.8, 124.2, 121.9, 121.4, 118.0, 95.4, 88.9, 82.7, 60.0, 52.9, 36.3, 30.4, 21.4. HPLC: Chiralpak AD-H + AD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 95/5, flow = 0.9 mL/min, retention time 18.2 min and 26.5 min (major). HRMS Calculated for $C_{29}H_{26}NaO_4$ $[M+Na]^+$ 461.1723, found: 461.1720.



(-)-Methyl 2-Cyclohexyl-4-oxo-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3je):

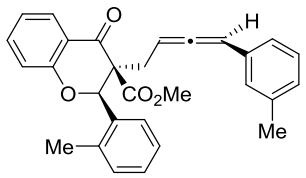
The reaction was conducted at -20 °C for 96 h. 24.3 mg, 28% yield, pale yellow oil, new compound, R_f = 0.46 (hexanes/ethyl acetate 20/1), 9:1 dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -112.94 (*c* 0.61, $CHCl_3$). The major diastereoisomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.0 Hz, 1H), 7.58-7.41 (m, 1H), 7.22-7.12 (m, 1H), 7.11-6.89 (m, 5H), 6.08-5.96 (m, 1H), 5.45-5.25 (m, 1H), 4.45 (s, 1H), 3.60 (s, 3H), 3.48-3.30 (m, 1H), 2.87-2.68 (m, 1H), 2.31 (s, 3H), 1.95-1.60 (m, 6H), 1.48-1.07 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 190.1, 170.2, 162.1, 138.2, 135.9, 133.8, 128.5, 128.0, 127.9, 127.5, 124.1, 121.4, 120.9, 117.8, 94.7, 89.1, 85.4, 58.6, 52.6, 38.0, 32.3, 30.3, 26.8, 26.3, 26.1, 25.8, 21.3. HPLC: Chiralcel OD-H + IC, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.8 mL/min, retention time 22.5 min and 32.6 min (major). HRMS Calculated for $C_{28}H_{30}NaO_4$ $[M+Na]^+$ 453.2036, found: 453.2041.



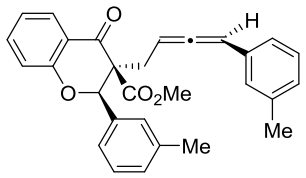
(-)-Methyl 4-Oxo-2-(*o*-tolyl)-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3ke):

81.2 mg, 93% yield, pale yellow oil, new compound, R_f = 0.26 (hexanes/ethyl acetate 20/1), 19:1

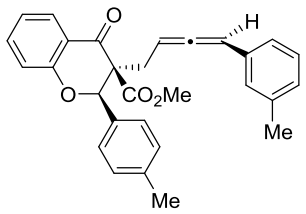
dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -178.35 (*c* 0.98, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52-7.43 (m, 1H), 7.42-7.37 (m, 1H), 7.29-7.19 (m, 3H), 7.14-7.06 (m, 2H), 7.00-6.86 (m, 4H), 6.01-5.88 (m, 1H), 5.84 (s, 1H), 5.67-5.49 (m, 1H), 3.62 (s, 3H), 3.25-3.08 (m, 1H), 2.55-2.46 (m, 1H), 2.45 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 190.3, 169.5, 161.3, 138.1, 136.7, 136.1, 133.9, 133.7, 131.0, 129.1, 128.4, 127.9, 127.9, 127.6, 127.5, 126.0, 124.1, 122.0, 121.3, 118.1, 96.4, 89.8, 79.7, 61.2, 52.6, 30.5, 21.3, 20.2. HPLC: Chiralpak AD-H column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/min, retention time 16.0 min (major) and 17.4 min. HRMS Calculated for $C_{29}H_{27}O_4$ $[M+H]^+$ 439.1904, found: 439.1901.



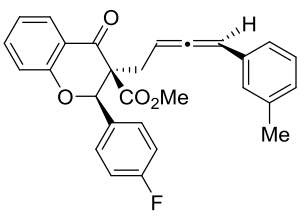
(-)-Methyl 4-Oxo-2-(*m*-tolyl)-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3le): 85.2 mg, 97% yield, pale yellow oil, new compound, R_f = 0.28 (hexanes/ethyl acetate 20/1), 24:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -217.08 (*c* 1.00, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.55-7.48 (m, 1H), 7.30-7.20 (m, 3H), 7.19-7.07 (m, 3H), 7.05-6.94 (m, 4H), 6.21-6.10 (m, 1H), 5.68 (s, 1H), 5.59-5.46 (m, 1H), 3.59 (s, 3H), 3.33-3.16 (m, 1H), 2.50-2.42 (m, 1H), 2.34 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 189.8, 168.9, 161.6, 138.2, 138.0, 136.3, 135.5, 133.7, 129.9, 128.6, 128.3, 128.0, 127.9, 127.5, 124.2, 124.0, 122.0, 121.2, 118.3, 95.8, 89.7, 82.6, 61.4, 52.5, 29.7, 21.6, 21.4. HPLC: Chiralpak AD-H column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/min, retention time 12.5 min and 14.1 min (major). HRMS Calculated for $C_{29}H_{27}O_4$ $[M+H]^+$ 439.1904, found: 439.1903.



(-)-Methyl 4-Oxo-2-(*p*-tolyl)-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3me): 81.3 mg, 93% yield, pale yellow oil, new compound, R_f = 0.28 (hexanes/ethyl acetate 20/1), 24:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -235.96 (*c* 1.02, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.54-7.47 (m, 1H), 7.35-7.28 (m, 2H), 7.22-7.05 (m, 4H), 7.05-6.92 (m, 4H), 6.25-6.04 (m, 1H), 5.68 (s, 1H), 5.59-5.40 (m, 1H), 3.59 (s, 3H), 3.35-3.21 (m, 1H), 2.49-2.41 (m, 1H), 2.35 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.9, 169.0, 161.6, 139.0, 138.2, 136.2, 133.7, 132.6, 129.1, 128.5, 128.0, 127.9, 127.5, 127.1, 124.0, 122.0, 121.2, 118.2, 95.8, 89.7, 82.5, 61.4, 52.6, 29.7, 21.4, 21.3. HPLC: Chiralpak AD-H column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/min, retention time 13.8 min and 22.4 min (major). HRMS Calculated for $C_{29}H_{27}O_4$ $[M+H]^+$ 439.1904, found: 439.1901.

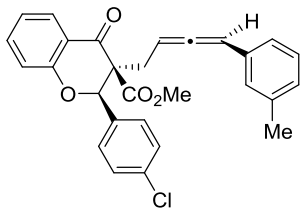


(-)-Methyl 2-(4-fluorophenyl)-4-oxo-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3ne): 79.4 mg, 90% yield, pale yellow oil, new compound, R_f = 0.30 (hexanes/ethyl acetate 20/1), 24:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -250.80 (*c* 0.98, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55-7.48 (m, 1H), 7.47-7.38 (m, 2H), 7.20-6.95 (m, 8H), 6.28-6.06

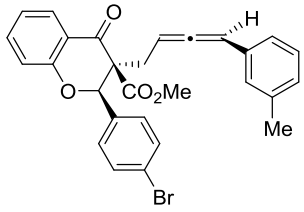


(m, 1H), 5.70 (s, 1H), 5.62-5.44 (m, 1H), 3.58 (s, 3H), 3.36-3.24 (m, 1H), 2.48-2.39 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.6, 168.8, 163.0 (d, $^1J_{F-C}$ = 246.7 Hz), 161.4, 138.3, 136.4, 133.5, 131.5 (d, $^4J_{F-C}$ = 3.4 Hz), 129.1 (d, $^3J_{F-C}$ = 8.1 Hz), 128.6, 128.1, 127.9, 127.5, 124.0, 122.2, 121.1, 118.2, 115.4 (d, $^2J_{F-C}$ = 21.4 Hz), 95.9, 89.6, 81.8, 61.4, 52.6, 29.7, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.10. HPLC: Chiralpak ID column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/ min, retention time 13.5 min (major) and 17.5 min. HRMS Calculated for $C_{28}H_{24}FO_4$ $[M+H]^+$ 443.1653, found: 443.1652.

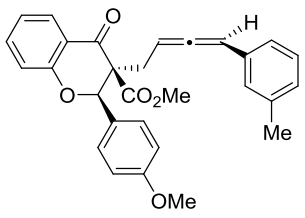
(-)-Methyl 2-(4-Chlorophenyl)-4-oxo-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3oe): 88.2 mg, 96% yield, pale yellow oil, new compound, R_f = 0.31 (hexanes/ethyl acetate 20/1), 24:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -233.51 (*c* 1.02, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55-7.48 (m, 1H), 7.44-7.30 (m, 4H), 7.18-7.07 (m, 2H), 7.04-6.95 (m, 4H), 6.23-6.07 (m, 1H), 5.69 (s, 1H), 5.60-5.45 (m, 1H), 3.58 (s, 3H), 3.34-3.25 (m, 1H), 2.48-2.40 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.4, 168.7, 161.3, 138.3, 136.4, 135.0, 134.1, 133.5, 128.6, 128.6, 128.6, 128.1, 127.9, 127.5, 124.0, 122.3, 121.1, 118.2, 96.0, 89.6, 81.8, 61.3, 52.7, 29.7, 21.4. HPLC: Chiralpak ID column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/min, retention time 13.6 min (major) and 17.6 min. HRMS Calculated for $C_{28}H_{24}ClO_4$ $[M+H]^+$ 459.1358 (^{35}Cl) and 461.1342 (^{37}Cl), found: 459.1360 (^{35}Cl) and 461.1334 (^{37}Cl).



(-)-Methyl 2-(4-Bromophenyl)-4-oxo-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3pe): 96.2 mg, 96% yield, pale yellow oil, new compound, R_f = 0.31 (hexanes/ethyl acetate 20/1), 24:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -208.29 (*c* 1.00, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.56-7.47 (m, 3H), 7.37-7.29 (m, 2H), 7.19-7.08 (m, 2H), 7.05-6.95 (m, 4H), 6.22-6.07 (m, 1H), 5.67 (s, 1H), 5.59-5.44 (m, 1H), 3.58 (s, 3H), 3.35-3.24 (m, 1H), 2.48-2.40 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 189.4, 168.7, 161.3, 138.3, 136.4, 134.6, 133.5, 131.6, 128.9, 128.6, 128.2, 127.9, 127.5, 124.0, 123.3, 122.3, 121.1, 118.2, 96.0, 89.6, 81.8, 61.3, 52.7, 29.7, 21.4. HPLC: Chiralpak IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/min, retention time 19.4 min (major) and 21.8 min. HRMS Calculated for $C_{28}H_{24}BrO_4$ $[M+H]^+$ 503.0852 (^{79}Br) and 505.0836 (^{81}Br), found: 503.0855 (^{79}Br) and 505.0831 (^{81}Br).

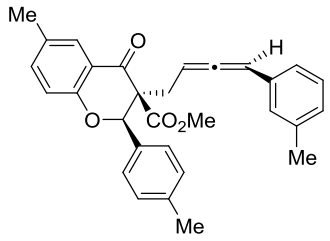


(-)-Methyl 2-(4-Methoxyphenyl)-4-oxo-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3qe): 85.7 mg, 94% yield, pale yellow oil, new compound, R_f = 0.15 (hexanes/ethyl acetate 20/1), 16:1 dr, 98% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -224.68 (*c* 0.98, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.54-7.48 (m, 1H), 7.39-7.31 (m, 2H), 7.19-7.06 (m, 2H), 7.06-6.96 (m, 4H), 6.94-6.87 (m, 2H), 6.24-6.07 (m, 1H), 5.66 (s, 1H), 5.60-5.46 (m, 1H), 3.80 (s, 3H), 3.60 (s, 3H), 3.36-3.22 (m, 1H), 2.49-2.39 (m, 1H), 2.29 (s, 3H). ^{13}C

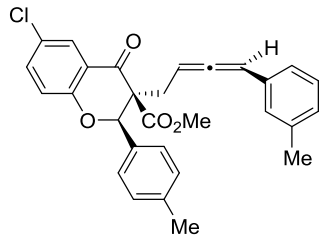


NMR (100 MHz, $CDCl_3$) δ 207.6, 190.0, 169.0, 161.7, 160.1, 138.2, 136.3, 133.7, 128.5, 128.0, 127.9, 127.6, 127.5, 124.0, 122.0, 121.2, 118.2, 113.8, 95.7, 89.7, 82.3, 61.5, 55.3, 52.6, 29.7, 21.4. HPLC: Chiralpak AD-H column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 90/10, flow = 1.0 mL/min, retention time 12.4 min and 13.2 min (major). HRMS Calculated for $C_{29}H_{27}O_5$ $[M+H]^+$ 455.1853, found: 455.1856.

(-)-Methyl 6-Methyl-4-oxo-2-(*p*-tolyl)-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3re): 85.7 mg, 95% yield, pale yellow oil, new compound, R_f = 0.34 (hexanes/ethyl acetate 20/1), 12:1 dr, 97% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -224.31 (*c* 0.97, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 1.4 Hz, 1H), 7.36-7.26 (m, 3H), 7.21-7.06 (m, 3H), 7.05-6.95 (m, 3H), 6.94-6.88 (m, 1H), 6.24-6.03 (m, 1H), 5.65 (s, 1H), 5.60-5.42 (m, 1H), 3.59 (s, 3H), 3.34-3.22 (m, 1H), 2.48-2.40 (m, 1H), 2.34 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 190.1, 169.1, 159.8, 139.0, 138.2, 137.4, 133.8, 132.7, 131.4, 129.1, 128.5, 128.0, 127.5, 127.4, 127.1, 124.1, 120.8, 118.0, 95.7, 89.7, 82.5, 61.4, 52.5, 29.7, 21.4, 21.3, 20.6. HPLC: Chiralpak IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 97/3, flow = 1.0 mL/ min, retention time 25.6 min (minor) and 28.1 min (major). The HRMS Calculated for $C_{30}H_{29}O_4$ $[M+H]^+$ 453.2060, found: 453.2060.



(-)-Methyl 6-Chloro-4-oxo-2-(*p*-tolyl)-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (3se): 87.6 mg, 93% yield, colorless oil, new compound, R_f = 0.42 (hexanes/ethyl acetate 20/1), 16:1 dr, 99% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -242.27 (*c* 1.05, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.6 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.33-7.26 (m, 2H), 7.23-7.16 (m, 2H), 7.16-7.11 (m, 1H), 7.03-6.86 (m, 4H), 6.23-6.06 (m, 1H), 5.66 (s, 1H), 5.59-5.45 (m, 1H), 3.60 (s, 3H), 3.30-3.15 (m, 1H), 2.47-2.40 (m, 1H), 2.36 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 189.0, 168.7, 160.0, 139.2, 138.3, 136.0, 133.5, 132.2, 129.2, 128.5, 128.1, 127.5, 127.5, 127.1, 127.1, 124.0, 122.0, 120.0, 96.2, 89.3, 82.6, 61.2, 52.7, 29.6, 21.4, 21.3. HPLC: Chiralpak IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 98/2, flow = 1.0 mL/min, retention time 17.0 min and 23.4 min (major). HRMS Calculated for $C_{29}H_{26}ClO_4$ $[M+H]^+$ 473.1514 (^{35}Cl) and 475.1499 (^{37}Cl), found: 473.1514 (^{35}Cl) and 475.1500 (^{37}Cl).



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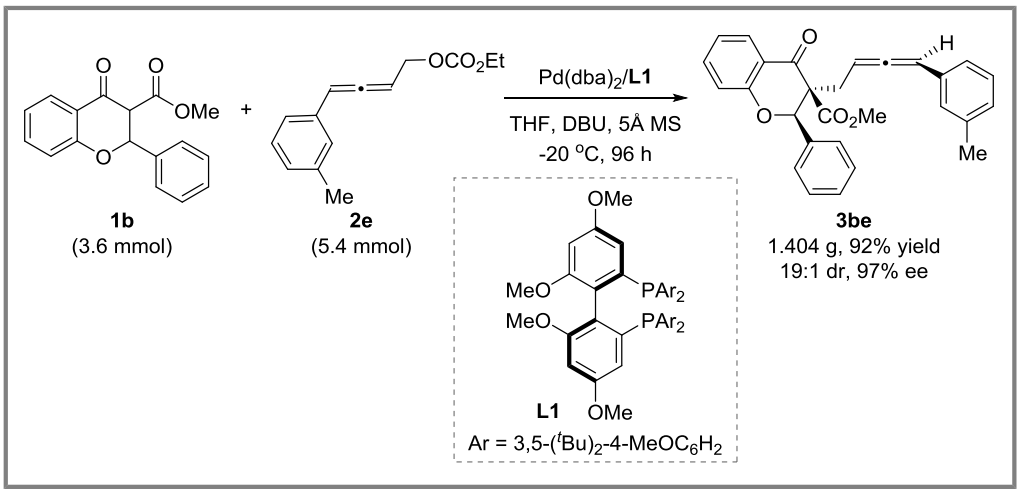
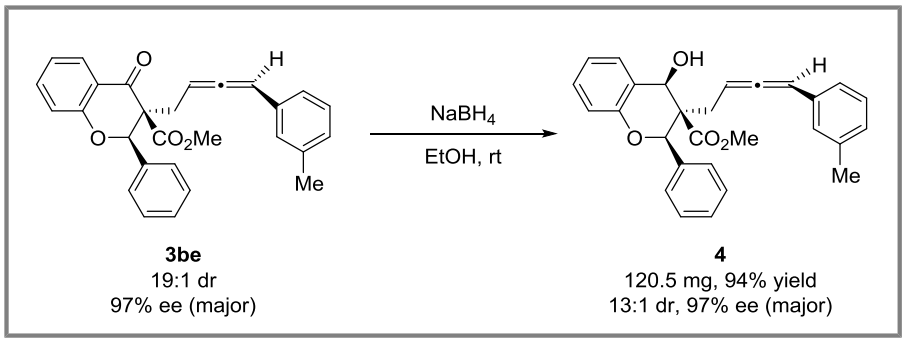
4. Experiment at Gram Scale



The metal precursor $Pd(dba)_2$ (0.36 mmol, 0.207 g), the chiral ligand (*R*)-DTBM-GARPHOS (**L1**) (0.396 mmol, 0.480 g) and tetrahydrofuran (34 mL) were placed in a dried Schlenk tube under nitrogen atmosphere. The mixture was stirred at 30 °C for 30 min. Then, the mixture was cooled to -20 °C. Subsequently, the substrate flavanone **1b** (3.6 mmol, 1.016 g), 5Å MS (0.900 g) and 1,8-dia-zabicyclo[5,4,0]undec-7-ene (DBU, 4.32 mmol, 0.65 mL) were added, and the reaction mixture was stirred at -20 °C for 10 minutes. Sequentially, allenylic carbonate **2e** (5.4 mmol, 1.254 g) and tetrahydrofuran (2.0 mL) were added slowly. The mixture was stirred at -20 °C for 96 hours. After the completion of the reaction, without any treatment, the residue was directly purified by column chromatography on silica gel (hexanes/ethyl acetate/dichloromethane 100/1/2-100/3/6) to give the chiral allenylic alkylation product **3be** 1.404 g with 92% isolated yield, 19:1 dr and 97% ee for the major diastereoisomer.

5. Product Elaboration

5.1. The Reduction of Carbonyl Functional Group



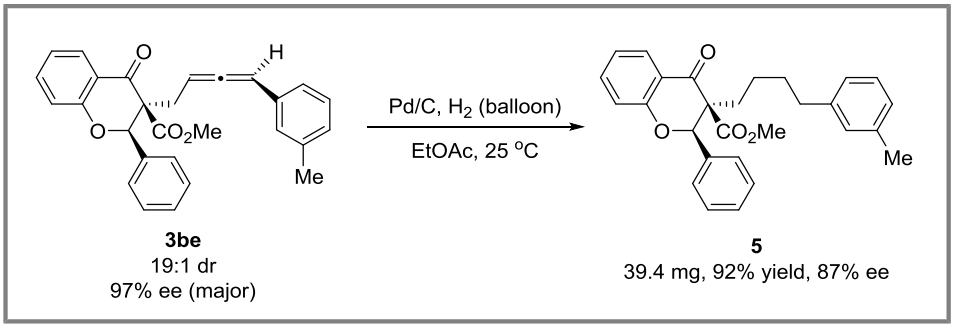
3be
19:1 dr
97% ee (major)

4
120.5 mg, 94% yield
13:1 dr, 97% ee (major)

To a solution of flavanone (-)-**3be** (127.4 mg, 0.3 mmol) in ethanol (15 mL) was added sodium borohydride (56.7 mg, 1.5 mmol) at ambient temperature. The reaction mixture was stirred for 12 h. The reaction was quenched with saturated ammonium chloride aqueous solution (10 mL). The aqueous layer was extracted with ethyl acetate (15 mL×3), dried over sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (20/1-10/1) as eluent to afford reductive product (-)-**4**.

(-)-Methyl 4-Hydroxy-2-phenyl-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)chromane-3-carboxylate (4): 120.5 mg, 94% yield, colorless liquid, new compound, R_f = 0.31 (hexanes/ethyl acetate 10/1), 13:1 dr, 97% ee (major diastereoisomer), $[\alpha]^{20}_D$ = -129.16 (*c* 1.21, $CHCl_3$). The major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.38-7.30 (m, 5H), 7.23-7.14 (m, 2H), 7.09-6.95 (m, 4H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.19-6.10 (m, 1H), 5.82-5.66 (m, 1H), 5.16 (d, *J* = 9.7 Hz, 1H), 5.08 (s, 1H), 3.54 (s, 3H), 2.96 (d, *J* = 9.8 Hz, 1H), 2.74-2.65 (m, 1H), 2.38-2.31 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 171.6, 154.3, 138.3, 136.5, 134.0, 128.9, 128.7, 128.6, 128.0, 127.9, 127.9, 127.5, 125.4, 124.1, 121.8, 116.2, 94.8, 90.0, 82.2, 70.6, 53.9, 51.8, 34.3, 21.4. HPLC: Chiralpak ID column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 90/10, flow = 1.0 mL/min, retention time 11.0 min (major) and 15.9 min (minor). HRMS Calculated for $C_{28}H_{26}NaO_4$ $[M+Na]^+$ 449.1723, found: 449.1723.

5.2. The Hydrogenation of Allenyl Functional Group



3be
19:1 dr
97% ee (major)

5
39.4 mg, 92% yield, 87% ee

To a solution of the chiral allenylic alkylation product (-)-**3be** (42.5 mg, 0.1 mmol) in ethyl acetate (1.0 mL) was added 10% Pd/C (5.3 mg, 0.005 mmol). The resulting mixture was degassed and stirred under hydrogen gas balloon pressure for about 5 hours at 25 °C. After the completion of hydrogenation, the volatiles were removed under the reduced pressure. The crude residue was

purified by flash column chromatography on silica gel using hexanes/ethyl acetate (30/1-20/1) as eluent to give the desirable allene hydrogenation product (2*R*,3*S*)-(-)-**5**.

(2*R*,3*S*)-(-)-Methyl 4-Oxo-2-phenyl-3-(4-(*m*-tolyl)butyl)chromane-3-carboxylate (5):

39.4 mg, 92% yield, colorless liquid, new compound, R_f = 0.28 (hexanes/ethyl acetate 20/1), 87% ee, $[\alpha]^{20}_D$ = -107.89 (*c* 0.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43-7.32 (m, 3H), 7.33-7.25 (m, 2H), 7.19-6.89 (m, 6H), 5.47 (s, 1H), 3.57 (s, 3H), 2.66-2.49 (m, 2H), 2.32 (s, 3H), 2.29-2.16 (m, 1H), 1.74-1.55 (m, 4H), 1.39-1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 169.4, 161.5, 142.2, 137.9, 136.1, 135.6, 129.2, 129.1, 128.3, 128.2, 128.0, 127.2, 126.5, 125.4, 122.0, 121.4, 118.1, 83.2, 61.6, 52.3, 35.3, 31.9, 30.1, 23.8, 21.5. HPLC: Chiralpak IA column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 16.6 min (minor) and 17.6 min (major). HRMS Calculated for $C_{28}H_{29}O_4$ $[M+H]^+$ 429.2060, found: 429.2066.

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6. Determination of Absolute Configuration

To determine the absolute configuration of (-)-methyl 3-(4-(naphthalen-2-yl)buta-2,3-dien-1-yl)-4-oxo-2-phenylchromane-3-carboxylate (**3bl**, 16:1 dr, 97% ee): first, (-)-**3bl** was upgraded to 32:1 dr and 98% ee for major diastereoisomer by recrystallization with *n*-hexane/dichloromethane. Then (-)-**3bl** was completely dissolved in dichloromethane (2.0 mL), and *n*-hexane (2.0 mL) was added slowly at room temperature. The solvent diffused slowly, and the single crystal was obtained after about two days. The structure in **Figure S1** showed the absolute configuration is (2*R*,3*S*,R_a). The CCDC number is 2226434. These details can be obtained free of charge via www.ccdc.com.ac.uk/data_request/cif from the Cambridge Crystallographic Data Centre.

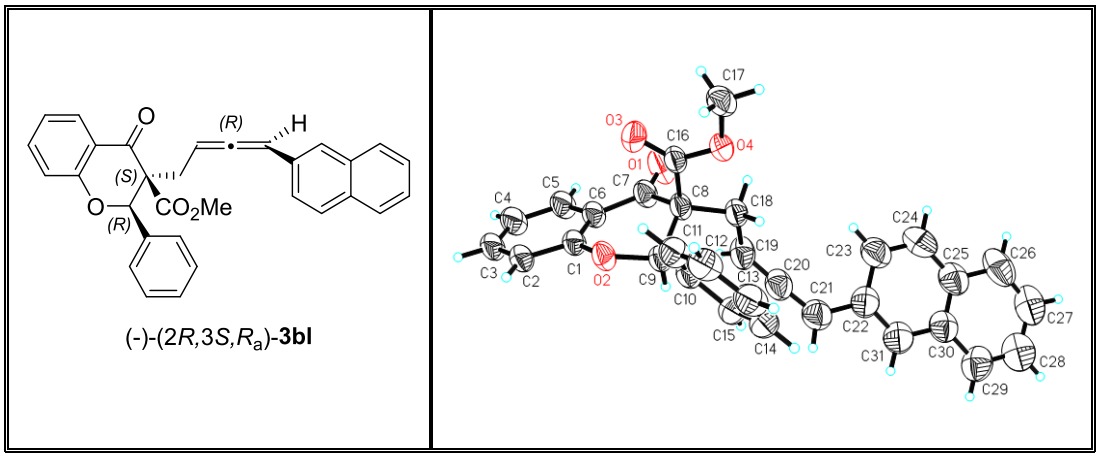
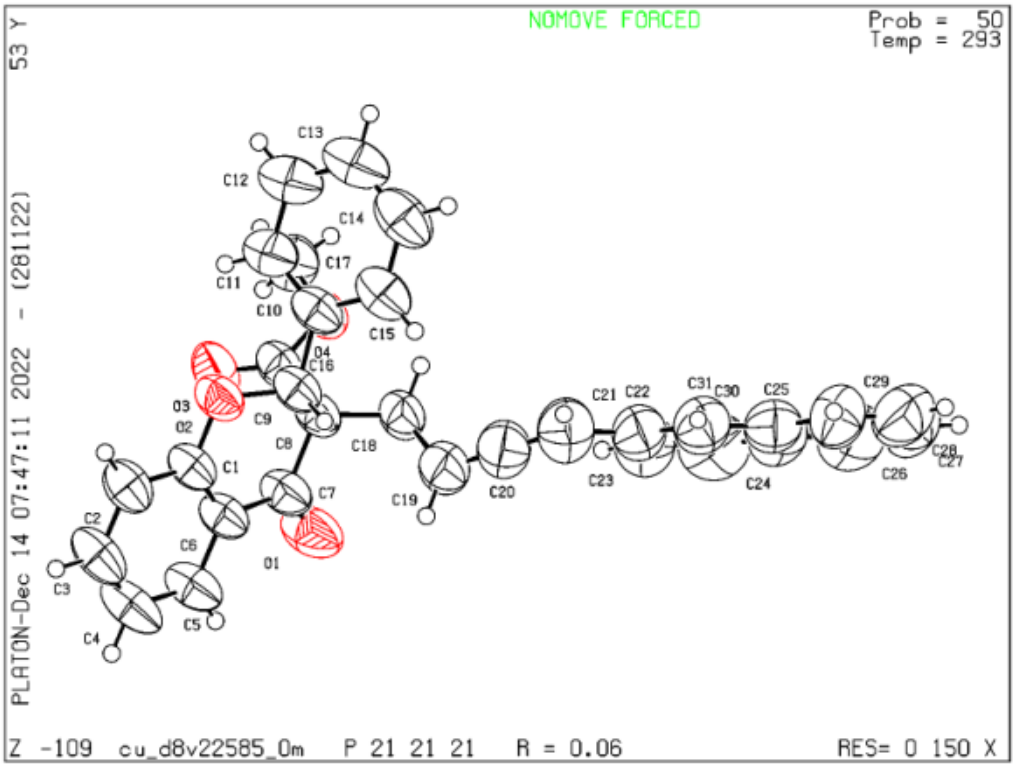


Figure S1. X-Ray Structure of (-)-(2*R*,3*S*,R_a)-**3bl**

Thermal Ellipsoid Plot for 3bl



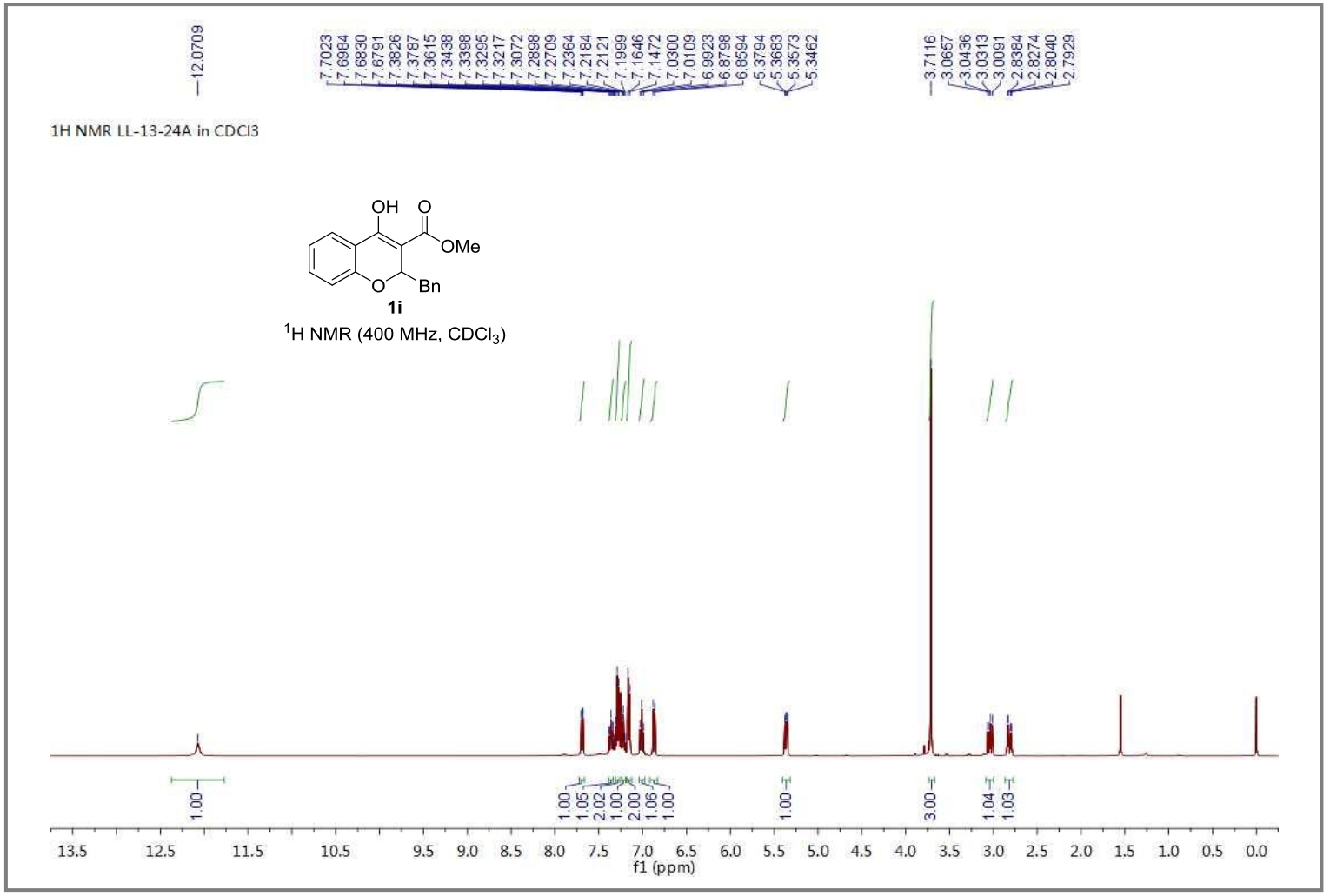
Crystal Data and Structure Refinement for cu_d8v22585_0m for (-)-(2*R*,3*S*,R_a)-**3bl**

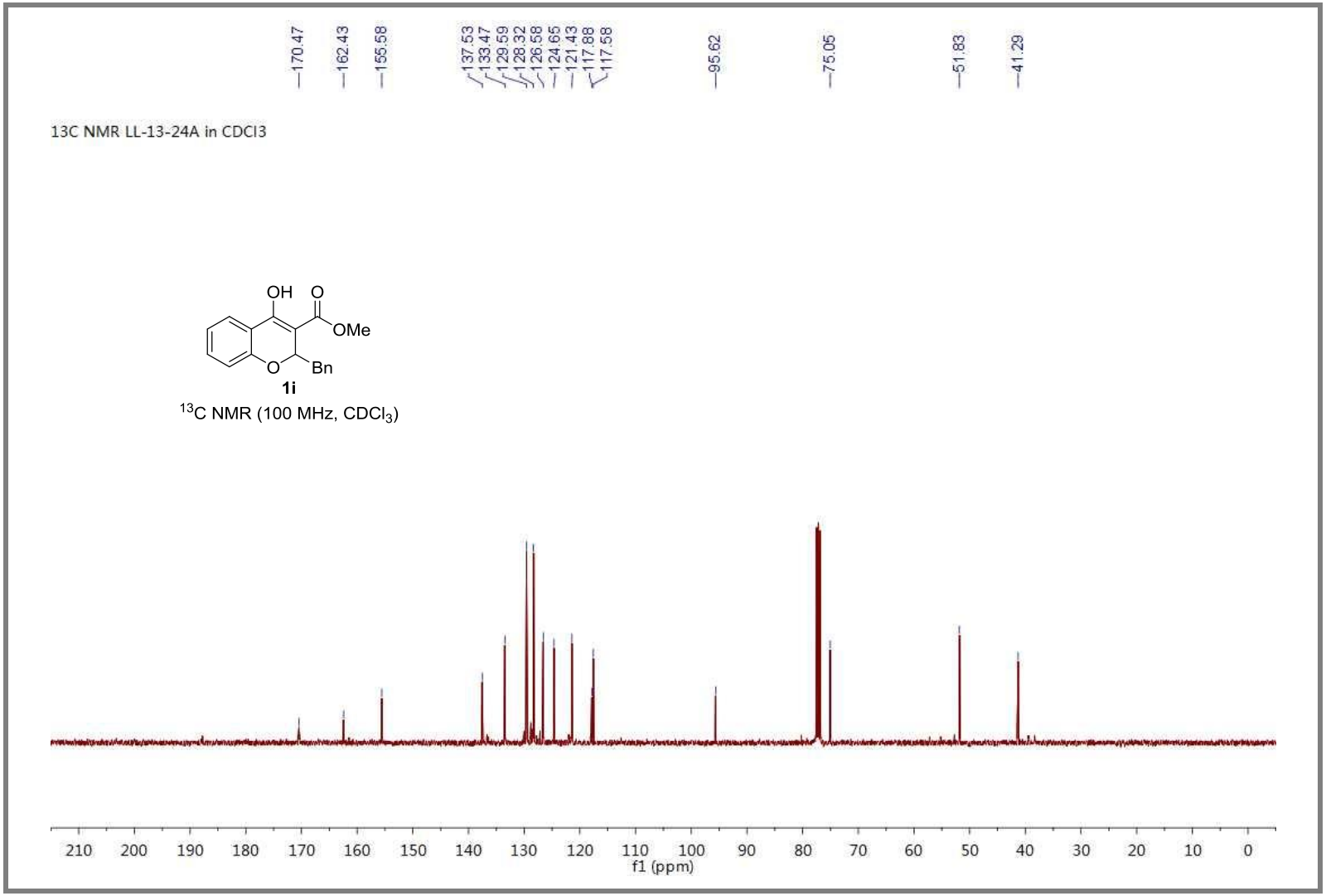
Identification code	cu_d8v22585_0m	
Empirical formula	C31 H24 O4	
Formula weight	460.50	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.6935(2) Å	α = 90 °
	b = 9.7330(2) Å	β = 90 °
	c = 33.1956(6) Å	γ = 90 °
Volume	2485.71(9) $Å^3$	
Z	4	
Density (calculated)	1.231 Mg/m^3	
Absorption coefficient	0.647 mm^{-1}	
F(000)	968	
Crystal size	0.180 x 0.140 x 0.090 mm^3	
Theta range for data collection	4.734 to 67.484 °.	
Index ranges	-9<=h<=8, -10<=k<=11, -35<=l<=39	
Reflections collected	15941	
Independent reflections	4440 [R(int) = 0.0541]	
Completeness to theta = 67.679 °	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5988	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4440 / 0 / 318	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1705	
R indices (all data)	R1 = 0.0729, wR2 = 0.1899	
Absolute structure parameter	0.01(16)	
Extinction coefficient	0.027(3)	
Largest diff. peak and hole	0.189 and -0.178 e.$Å^{-3}$	

7. References

1. Liu, L.-X.; Huang, W.-J.; Xie, Q.-X.; Wu, B.; Yu, C.-B.; Zhou, Y.-G. Dynamic Kinetic Resolution of Flavonoids via Asymmetric Allylic Alkylation: Construction of Two Contiguous Stereogenic Centers on Nucleophiles. *ACS Catal*. **2021**, *11*, 12859-12863.
2. Pechalrieu, D.; Dauzonne, D.; Arimond, P. B.; Lopez, M. Synthesis of Novel 3-Halo-3-nitroflavanones and Their Activities as DNA Methyltransferase Inhibitors in Cancer Cells. *Eur. J. Med. Chem.* **2020**, *186*, 111829.
3. Wang, N.; Cai, S.; Zhou, C.; Lu, X.; Wang, Y. One-Pot Synthesis of 2-Aryl-3-alkoxycarbonyl Chromones through a Cascade Lewis Acid-Catalyzed Aldehyde Olefination/Oxa-Michael Addition/Oxidation. *Tetrahedron* **2013**, *69*, 647-652.
4. Saengchantara, S. T.; Wallace, T. W. Conjugate Addition of Cuprate Reagents to Chromones: A Route to 2-Substituted Chroman-4-ones. *Tetrahedron* **1990**, *46*, 3029-3036.
5. Liu, L.-X.; Bai, Y.-Q.; Li, X.; Yu, C.-B.; Zhou, Y.-G. Palladium-Catalyzed Asymmetric Allenylic Alkylation: Construction of Multiple Chiral Thiochromanone Derivatives. *Chem. Sci*. **2023**, *14*, 5477-5482.

8. Copy of NMR and HPLC Spectra

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128.32
126.58
124.65
121.43
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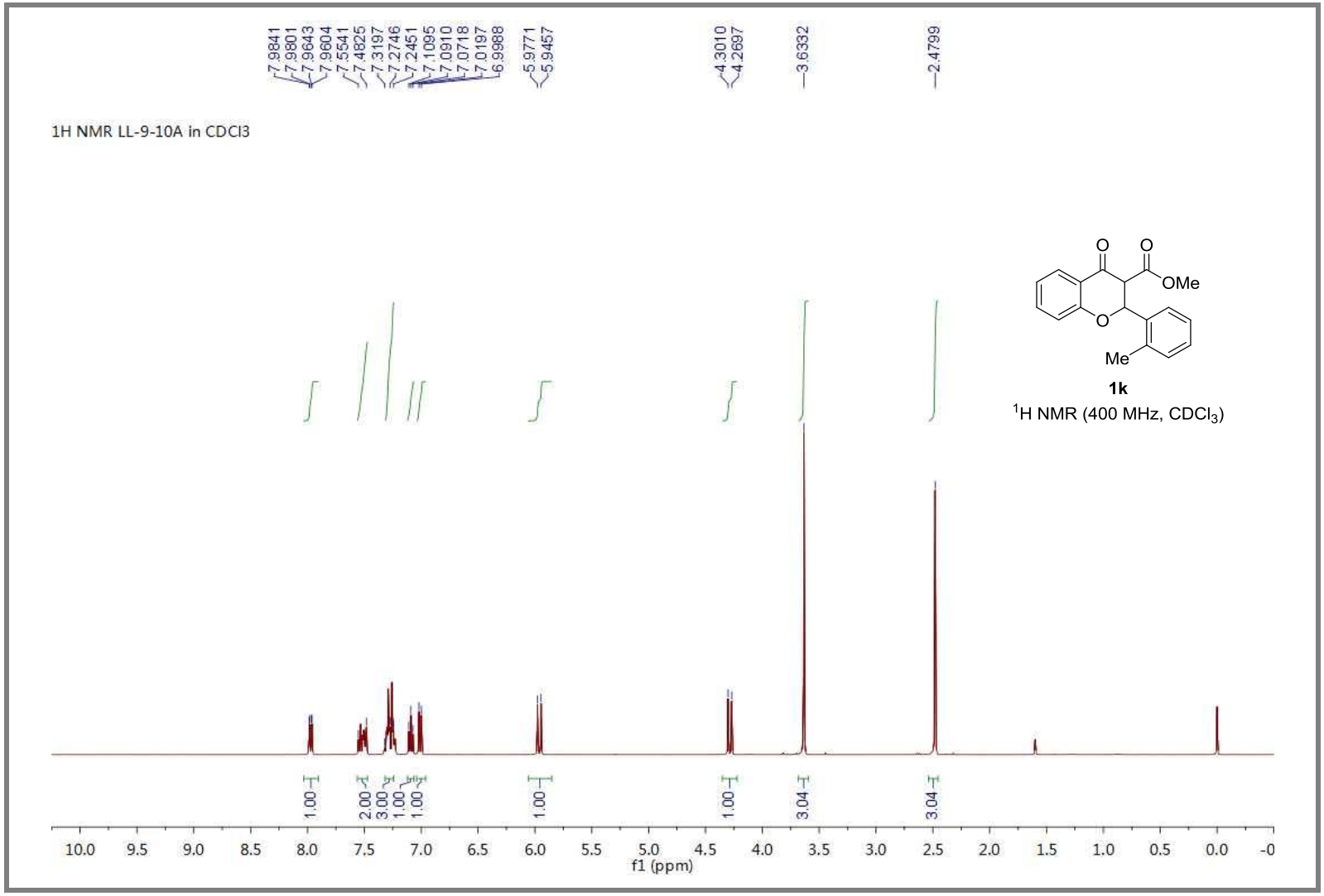
117.58
95.62
75.05
51.83
41.29
13C NMR LL-13-24A in CDCl3
OH
O
OMe
O
Bn
1i
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.3197
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7.1095
7.0910
7.0718
7.0197
6.9988
5.9771
5.9457
4.3010
4.2697
3.6332
2.4799
1H NMR LL-9-10A in CDCl3
O
O
OMe
O
Me
1k
1H NMR (400 MHz, CDCl3)
1.00
2.00
3.00
1.00
1.00
1.00
1.00
3.04
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
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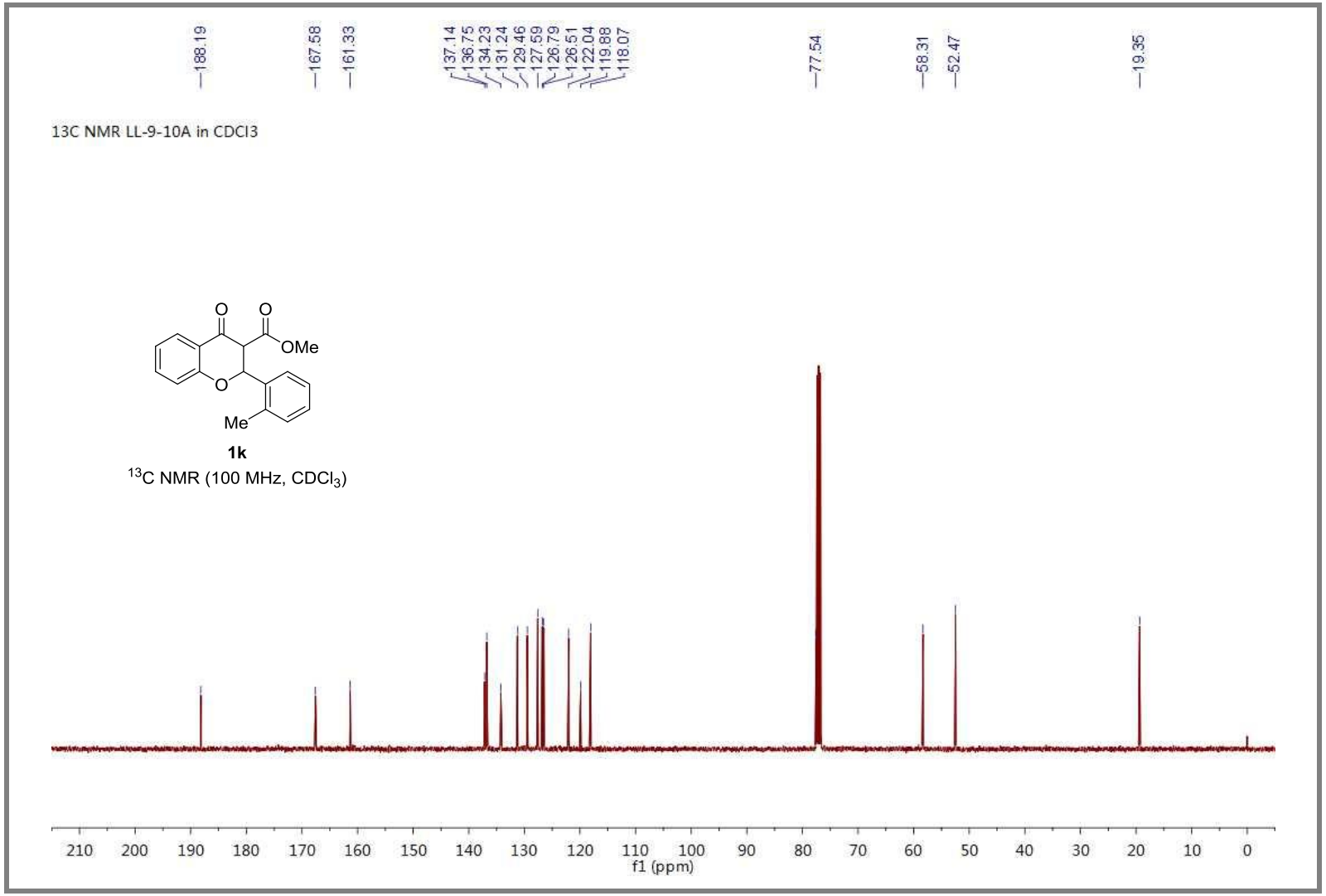
f1 (ppm)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119.88
118.07
77.54
58.31
52.47
19.35
13C NMR LL-9-10A in CDCl3
O
O
OMe
O
Me
1k
13C NMR (100 MHz, CDCl3)
210
200
190
180
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130
120
110
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90
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50
40
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20
10
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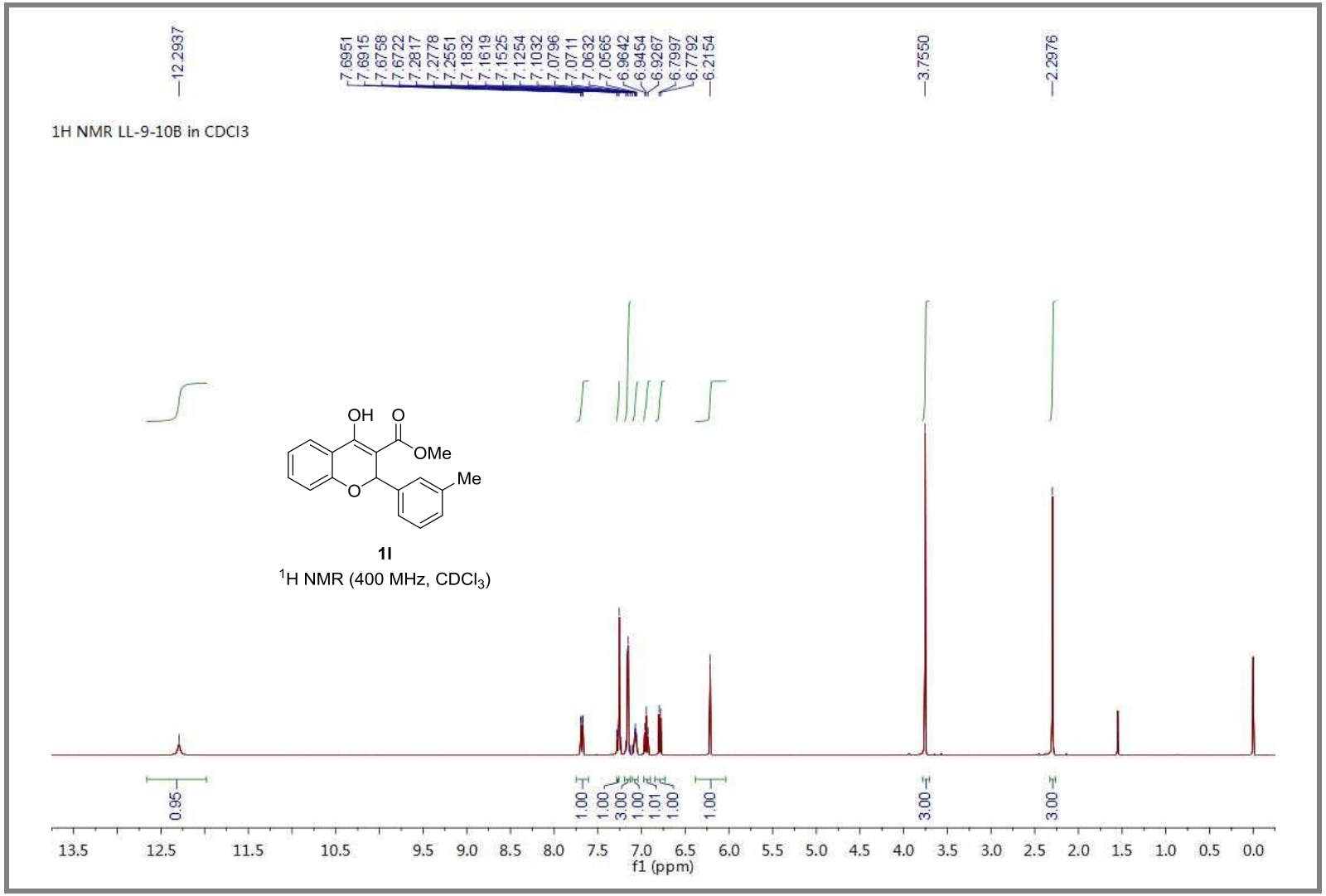
f1 (ppm)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7.1032
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7.0565
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6.7997
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3.7550
2.2976
1H NMR LL-9-10B in CDCl3
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O
OMe
Me
O
1I
1H NMR (400 MHz, CDCl3)
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1.00
3.00
1.00
1.01
1.00
1.00
3.00
3.00
13.5
12.5
11.5
10.5
9.5
9.0
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8.0
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7.0
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6.0
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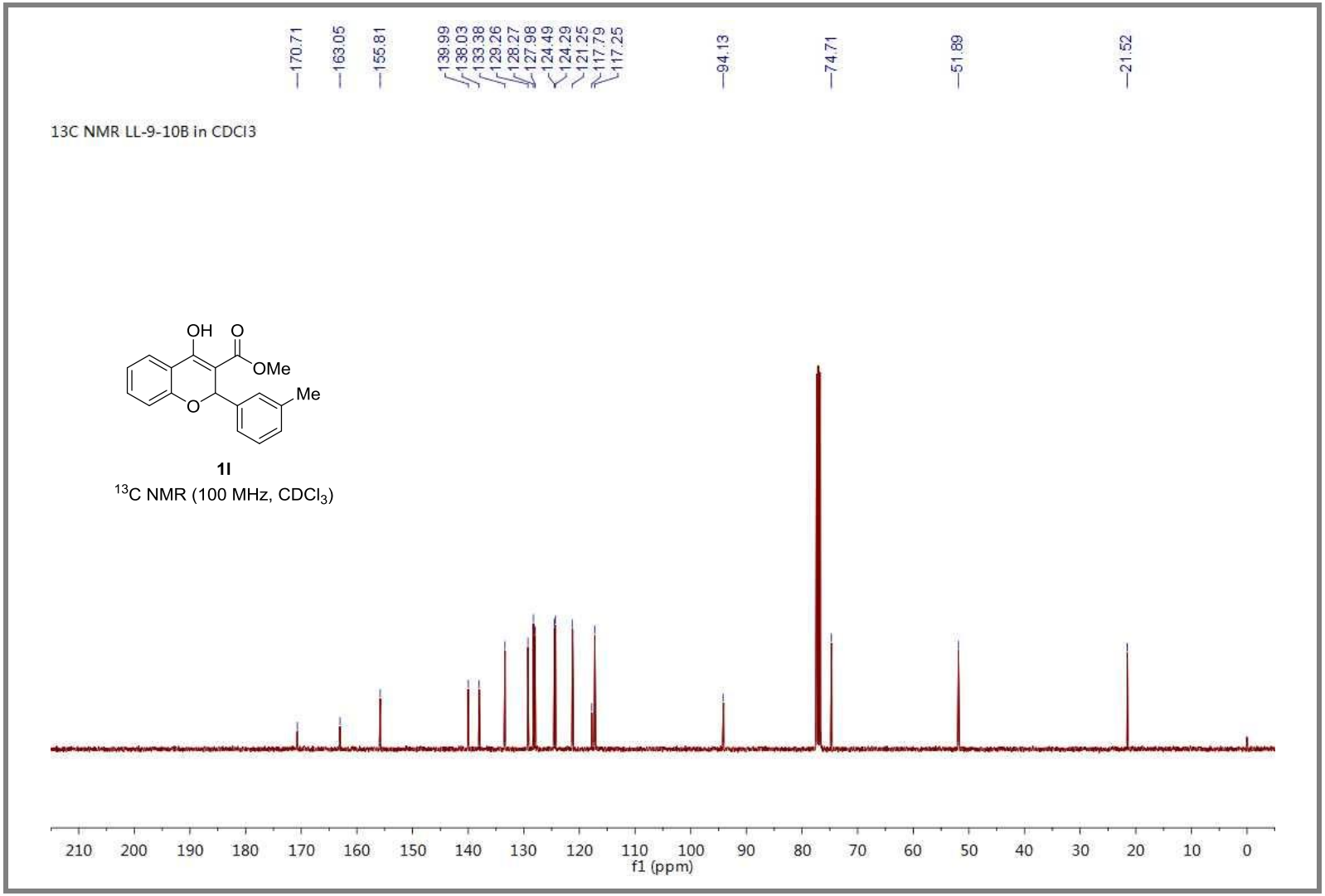
f1 (ppm)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139.99
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117.25
94.13
74.71
51.89
21.52
13C NMR LL-9-10B in CDCl3
OH
O
OMe
Me
O
1l
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
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130
120
110
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50
40
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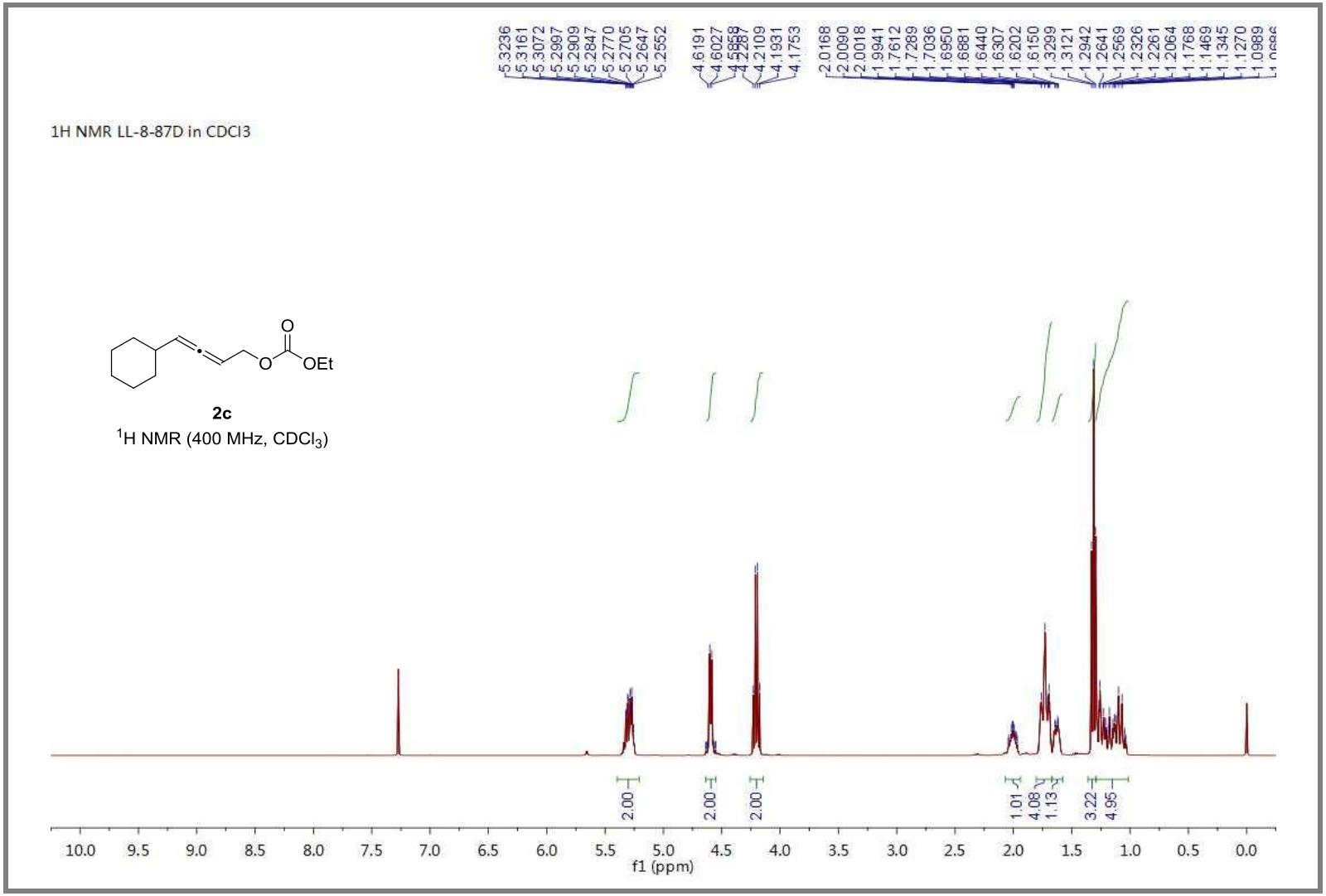
10
0
f1 (ppm)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2c
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1.13
3.22
4.95
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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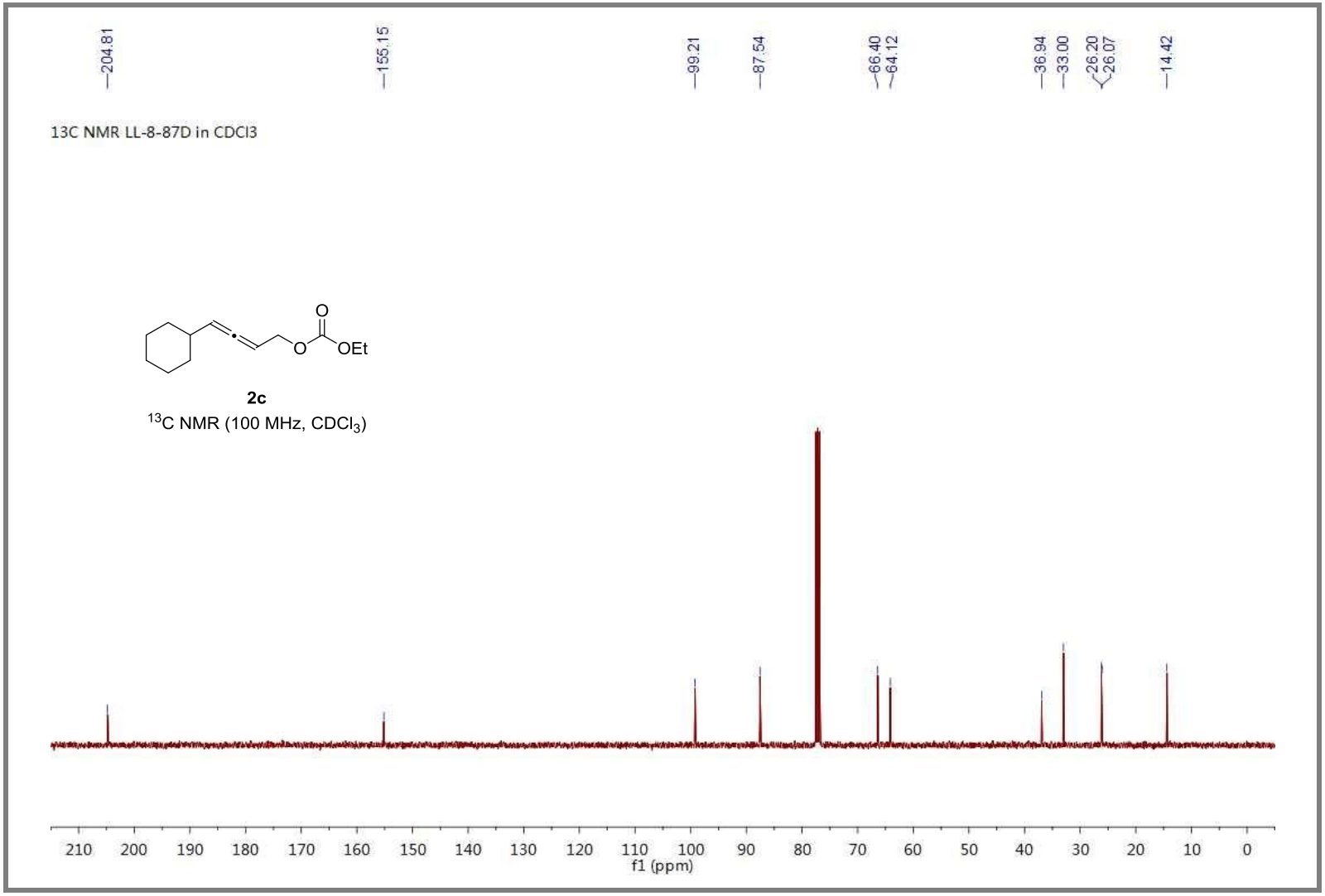
f1 (ppm)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O
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2c
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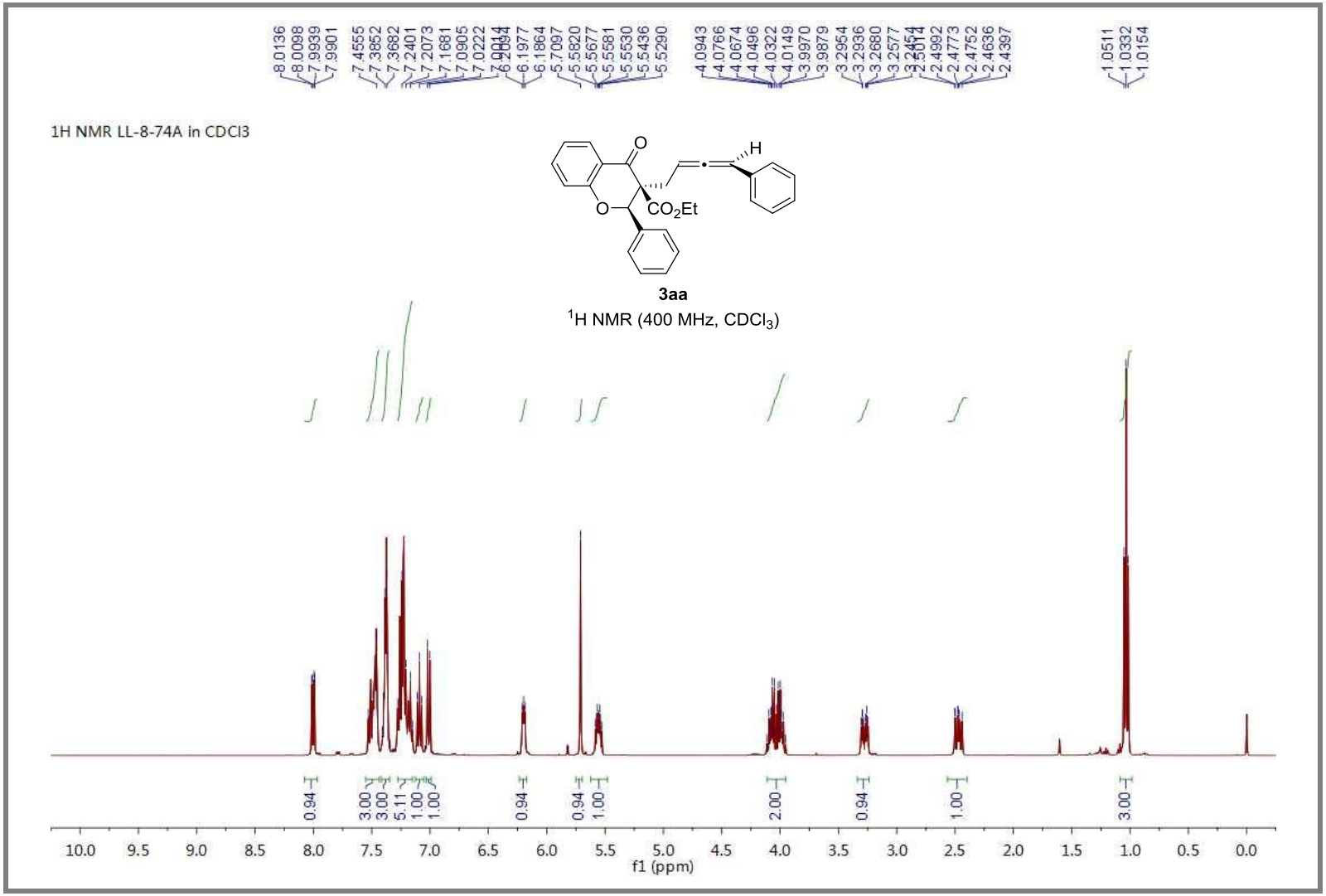
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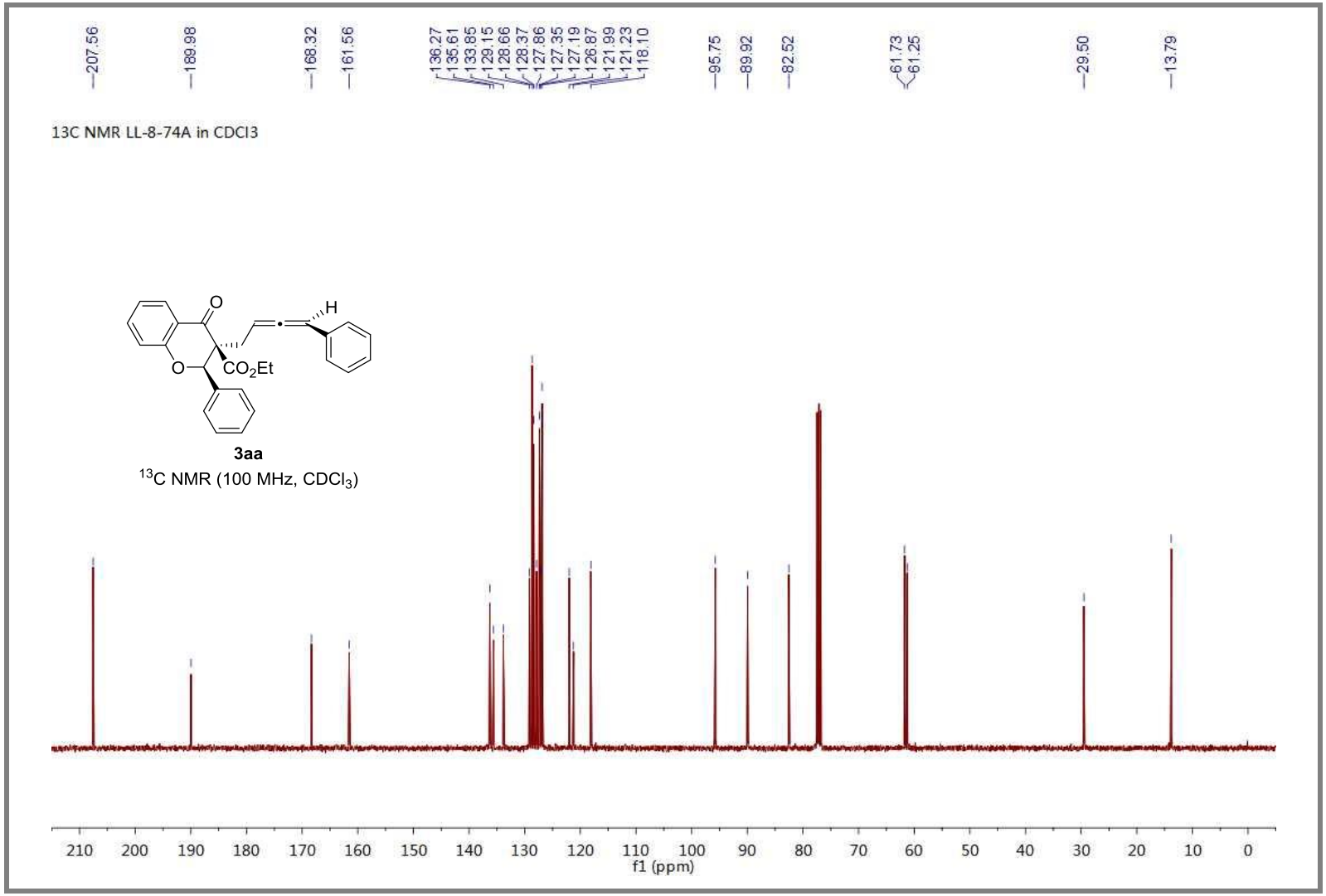
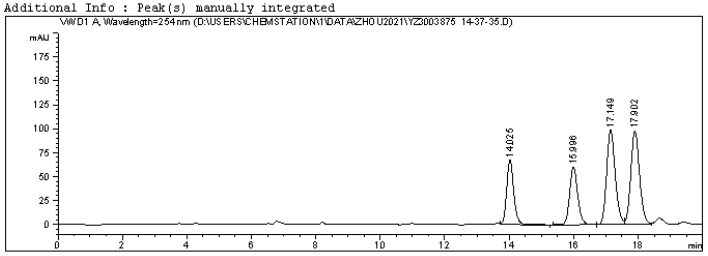
1.0511
1.0332
1.0154
O
H
O
CO2Et
3aa
1H NMR (400 MHz, CDCl3)
0.94
3.00
3.00
5.11
1.00
1.00
0.94
0.94
1.00
2.00
0.94
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.56
189.98
168.32
161.56
136.27
135.61
133.85
129.15
128.66
128.37
127.86
127.35
127.19
126.87
121.99
121.23
118.10
95.75
89.92
82.52
61.73
61.25
29.50
13.79
13C NMR LL-8-74A in CDCl3
O
H
O
CO2Et
3aa
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2021\YZ3003875 14-37-35.D
Sample Name: LL-8-68 A +/-

```
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                    Location :     -
Injection Date  : 12/23/2021 2:37:35 PM          Inj :   1
                                           Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 12/23/2021 1:26:23 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 6/20/2022 3:55:48 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 98/2, 0.8  mL/min, 30 oC, 254 nm
```

Additional Info : Peak(s) manually integrated

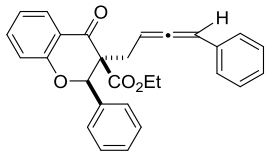


Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs
```

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.025	VB	0.2364	1036.10095	67.38773	18.0571
2	15.996	BB	0.2637	1030.33545	59.90638	17.9566
3	17.149	BV	0.2855	1826.95947	98.45656	31.8401
4	17.902	VV	0.2906	1844.52112	97.56199	32.1462
Totals :				5737.91699	323.31266	



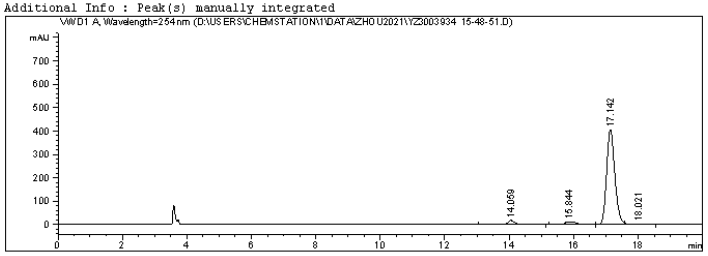
(+/-)-3aa

*** End of Report ***

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2021\YZ3003934 15-48-51.D
Sample Name: LL-8-74A

```
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                    Location :     -
Injection Date  : 12/31/2021 3:48:51 PM          Inj :   1
                                           Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 12/31/2021 2:23:41 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 6/20/2022 3:59:48 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 98/2, 0.8 mL/min, 30 oC, 254 nm
```

Additional Info : Peak(s) manually integrated

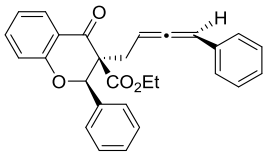


Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs
```

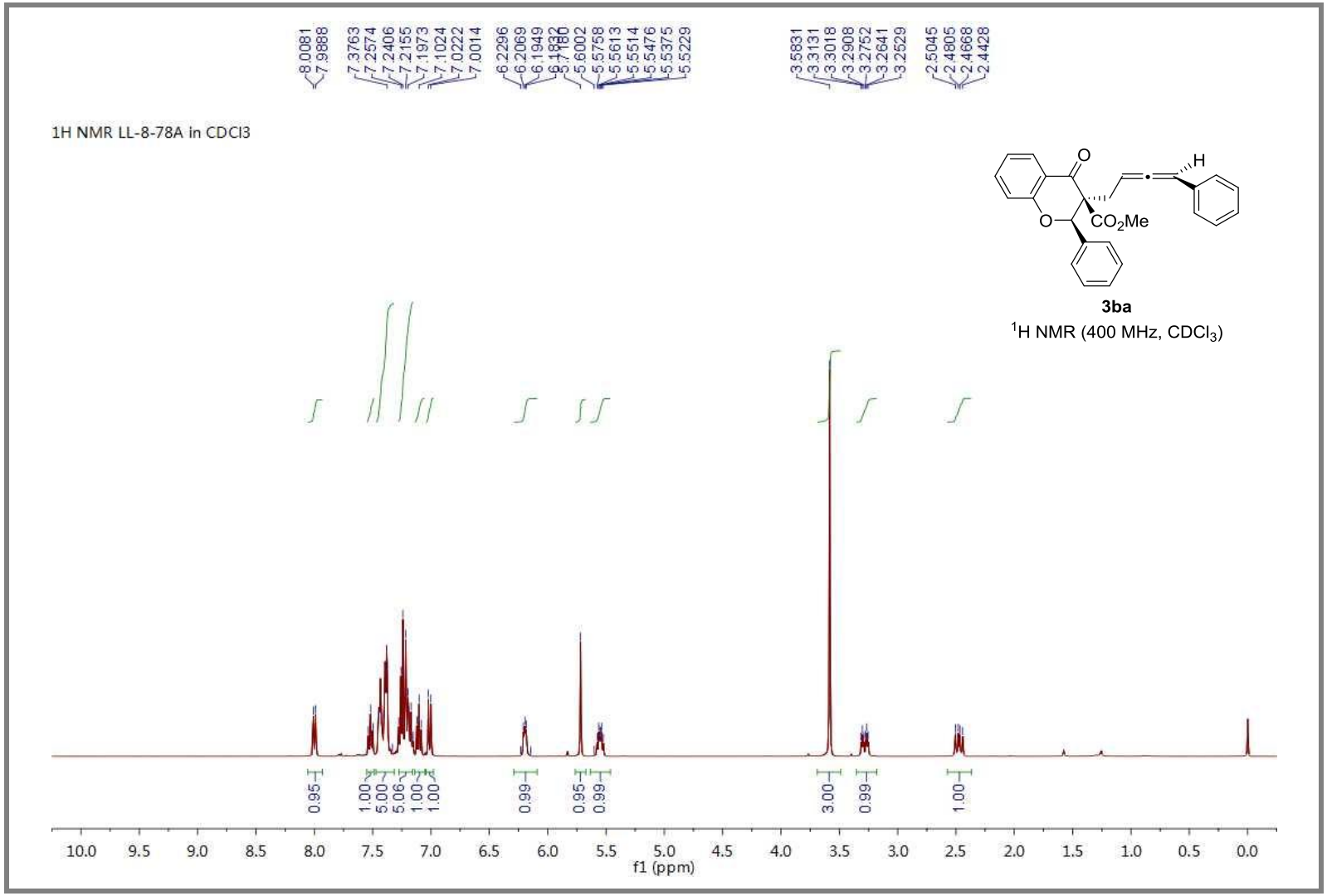
Signal 1: VWD1 A, Wavelength=254 nm

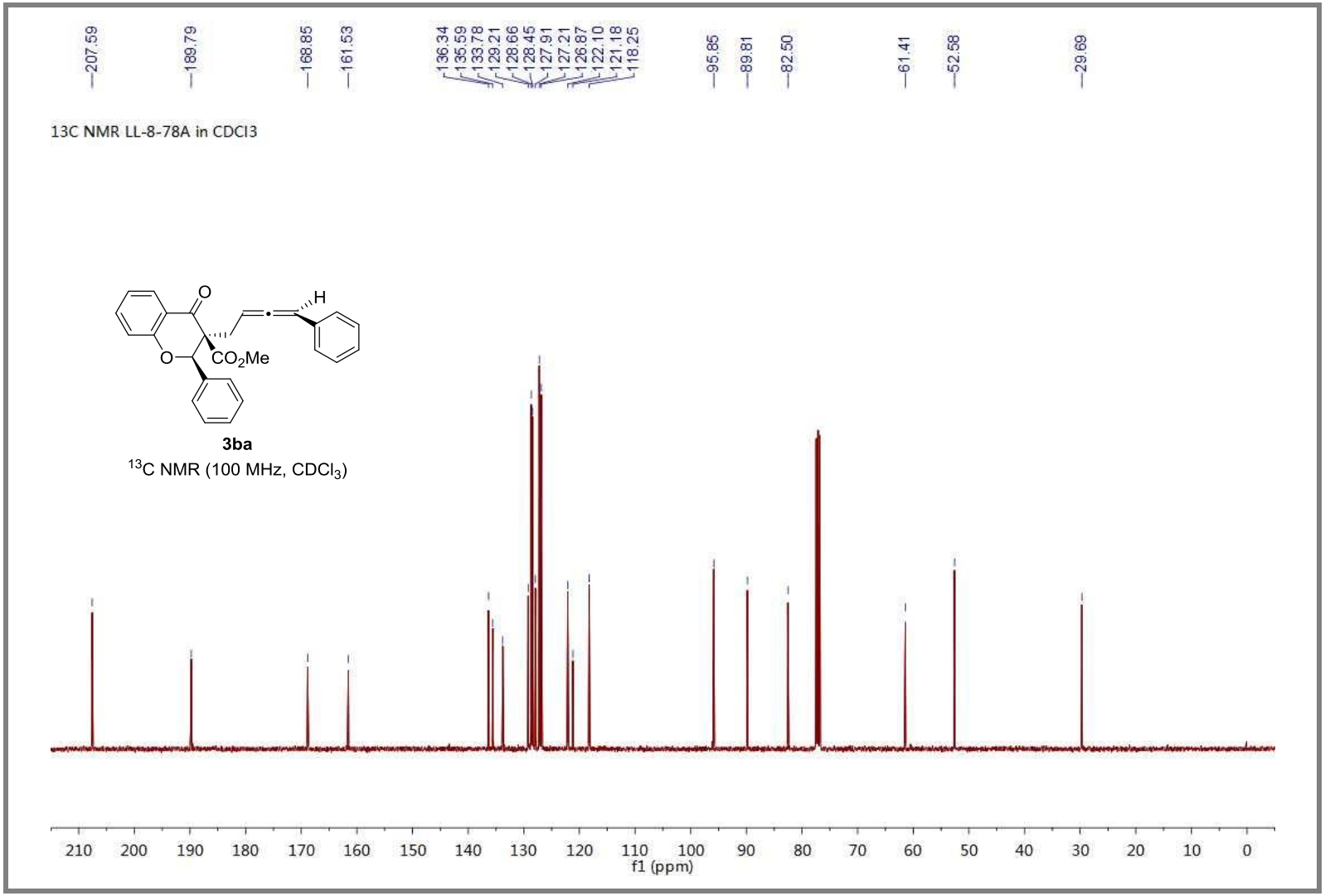
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.059	BB	0.2248	254.89165	17.31018	3.2716
2	15.844	BB	0.3116	287.61374	12.87648	3.6916
3	17.142	BV R	0.2726	7196.55566	406.36435	92.3701
4	18.021	VB E	0.3007	51.94418	2.59325	0.6667
Totals :				7791.00523	439.14426	



(-)-3aa

*** End of Report ***

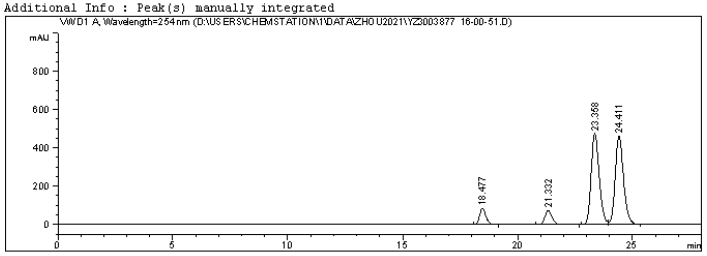

1H NMR LL-8-78A in CDCl3
8.0081
7.9888
7.3763
7.2574
7.2406
7.2155
7.1973
7.1024
7.0222
7.0014
6.2296
6.2069
6.1949
5.6002
5.5758
5.5613
5.5514
5.5476
5.5375
5.5229
3.5831
3.3131
3.3018
3.2908
3.2752
3.2641
3.2529
2.5045
2.4805
2.4668
2.4428
O
H
O
CO2Me
3ba
1H NMR (400 MHz, CDCl3)
0.95
1.00
5.00
5.06
1.00
1.00
0.99
0.95
0.99
3.00
0.99
1.00
10.0
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)


207.59
189.79
168.85
161.53
136.34
135.59
133.78
129.21
128.66
128.45
127.91
127.21
126.87
122.10
121.18
118.25
95.85
89.81
82.50
61.41
52.58
29.69
13C NMR LL-8-78A in CDCl3
O
H
O
CO2Me
3ba
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2021\YZ3003877 16-00-51.D
Sample Name: LL-8-68 B +/-

```
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                    Location :     -
Injection Date  : 12/23/2021 4:00:51 PM          Inj :    1
                                           Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 12/23/2021 2:58:36 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 12/23/2021 4:39:02 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 97/3, 0.8  mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
                        Area Percent Report

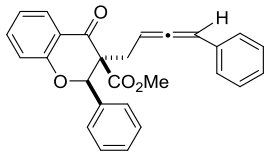
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.477 BB    0.2868 1558.24158   83.86393   5.9223
   2  21.332 BB    0.3352 1604.02991   73.91971   6.0964
   3  23.358 BV    0.3763 1.15468e4   473.89447  43.8853
   4  24.411 VB    0.3865 1.16022e4   462.79044  44.0960

Totals :                  2.63112e4  1094.46854

                        *** End of Report ***
```

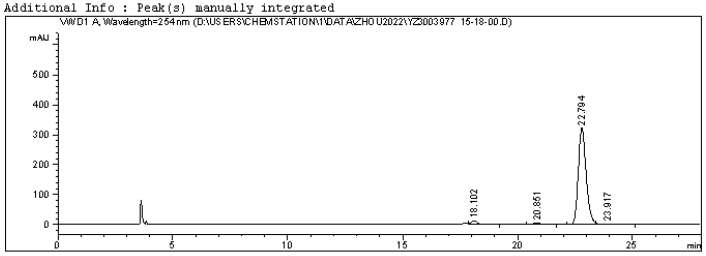


(+/-)-3ba

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2022\YZ3003977 15-18-00.D
Sample Name: LL-8-78A

```
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                    Location :     -
Injection Date  : 1/7/2022 3:18:00 PM            Inj :    1
                                           Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 1/7/2022 1:40:20 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 6/14/2022 8:29:40 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
                        Area Percent Report

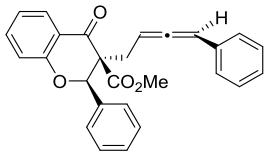
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

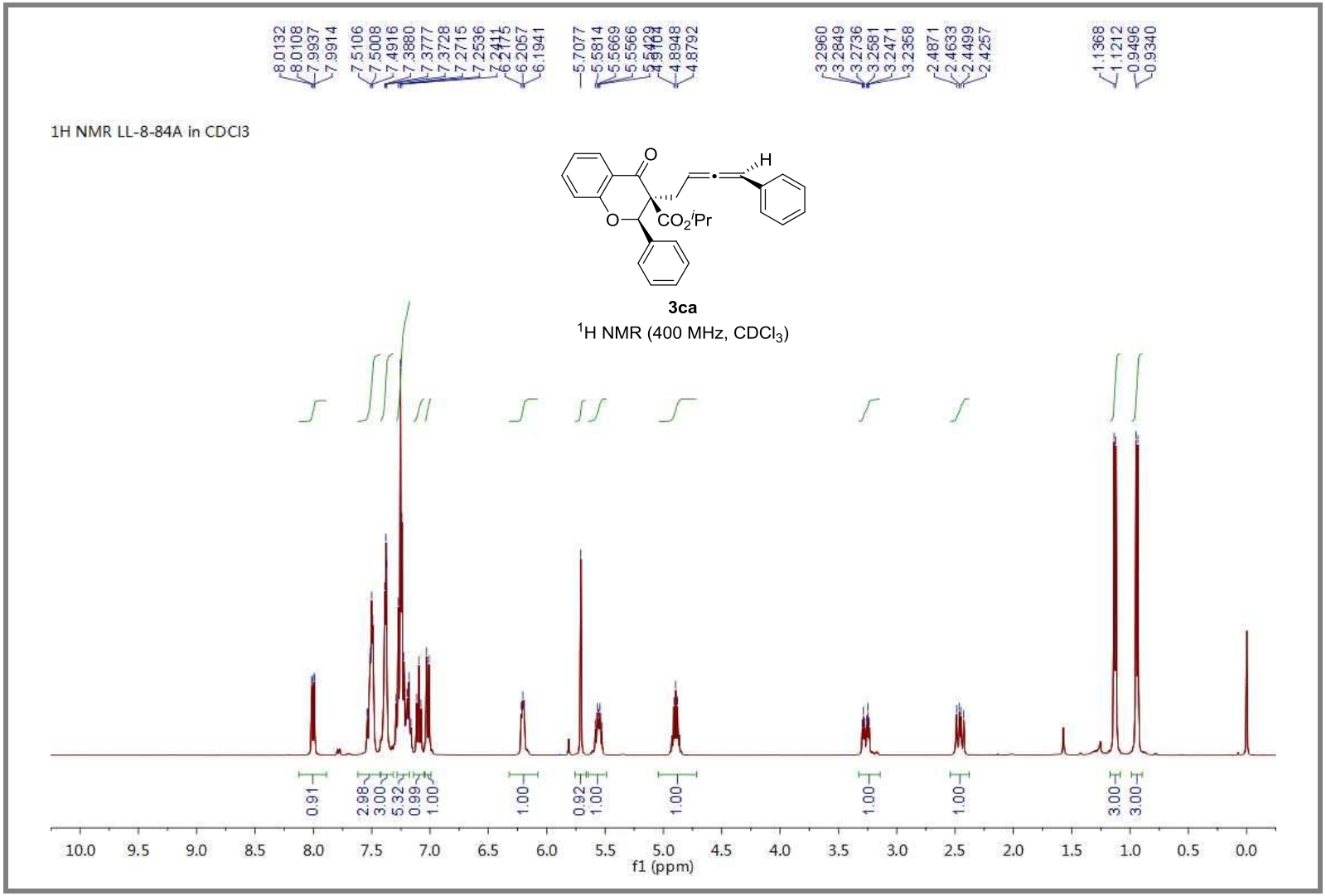
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.102 VB    0.2912  246.32407   12.76291   3.0138
   2  20.851 BB    0.3255  129.07010    6.10963   1.5792
   3  22.794 BV R  0.3678 7730.21631  322.29019  94.5791
   4  23.917 VB E  0.4038   67.67116    2.46122   0.8280

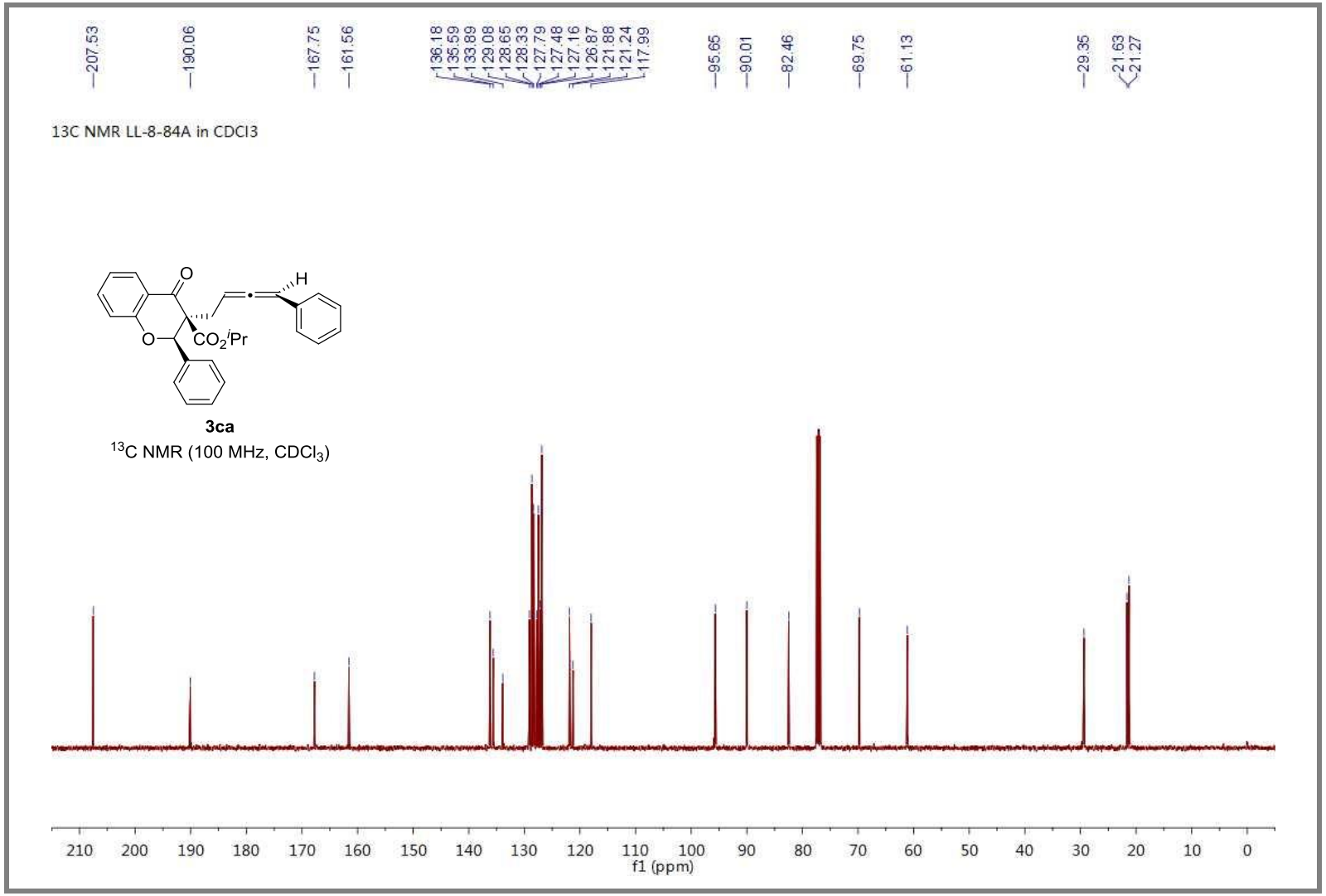
Totals :                  8173.28163  343.62395

                        *** End of Report ***
```



(-)-3ba

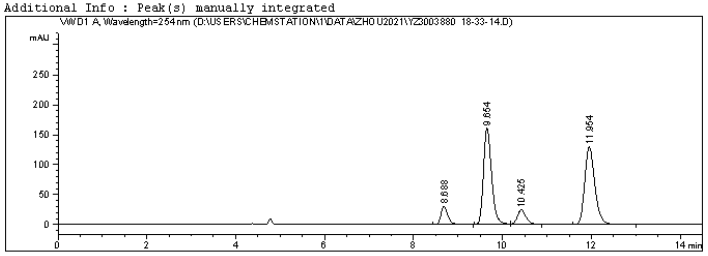

1H NMR LL-8-84A in CDCl3
O
H
O
CO2iPr
3ca
1H NMR (400 MHz, CDCl3)
f1 (ppm)


207.53
190.06
167.75
161.56
136.18
135.59
133.89
129.08
128.65
128.33
127.79
127.48
127.16
126.87
121.88
121.24
117.99
95.65
90.01
82.46
69.75
61.13
29.35
21.63
21.27
13C NMR LL-8-84A in CDCl3
O
H
O
CO2iPr
3ca
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2021\YZ3003880 18-33-14.D
Sample Name: LL-8-68 C +/- 3

```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :     -
Injection Date  : 12/23/2021 6:33:14 PM              Inj :   1
                                               Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 12/23/2021 6:16:06 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 12/23/2021 6:52:15 PM by SYSTEM
                  (modified after loading)
Sample Info     : OD-3, n-Hexane/i-PrOH = 97/3, 0.8  mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

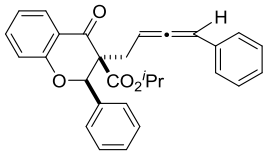
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.688 BB    0.1692  337.20175   30.45543   7.0671
   2   9.654 BV    0.1970 2054.58472  160.89732  43.0600
   3  10.425 VB    0.2101  331.29941   24.14574   6.9434
   4  11.954 BB    0.2447 2048.35547  129.37819  42.9295

Totals :                  4771.44135  344.87668

==========================================================================
                        *** End of Report ***
```

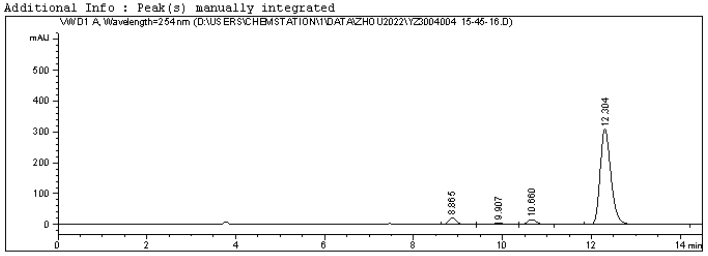


(+/-)-3ca

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2022\YZ3004004 15-45-16.D
Sample Name: LL-8--84A

```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :     -
Injection Date  : 1/14/2022 3:45:16 PM               Inj :   1
                                               Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 1/14/2022 3:00:41 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 6/14/2022 8:33:33 PM by SYSTEM
                  (modified after loading)
Sample Info     : OD-3, n-Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

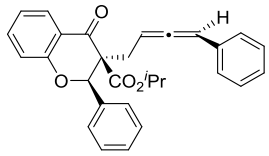
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

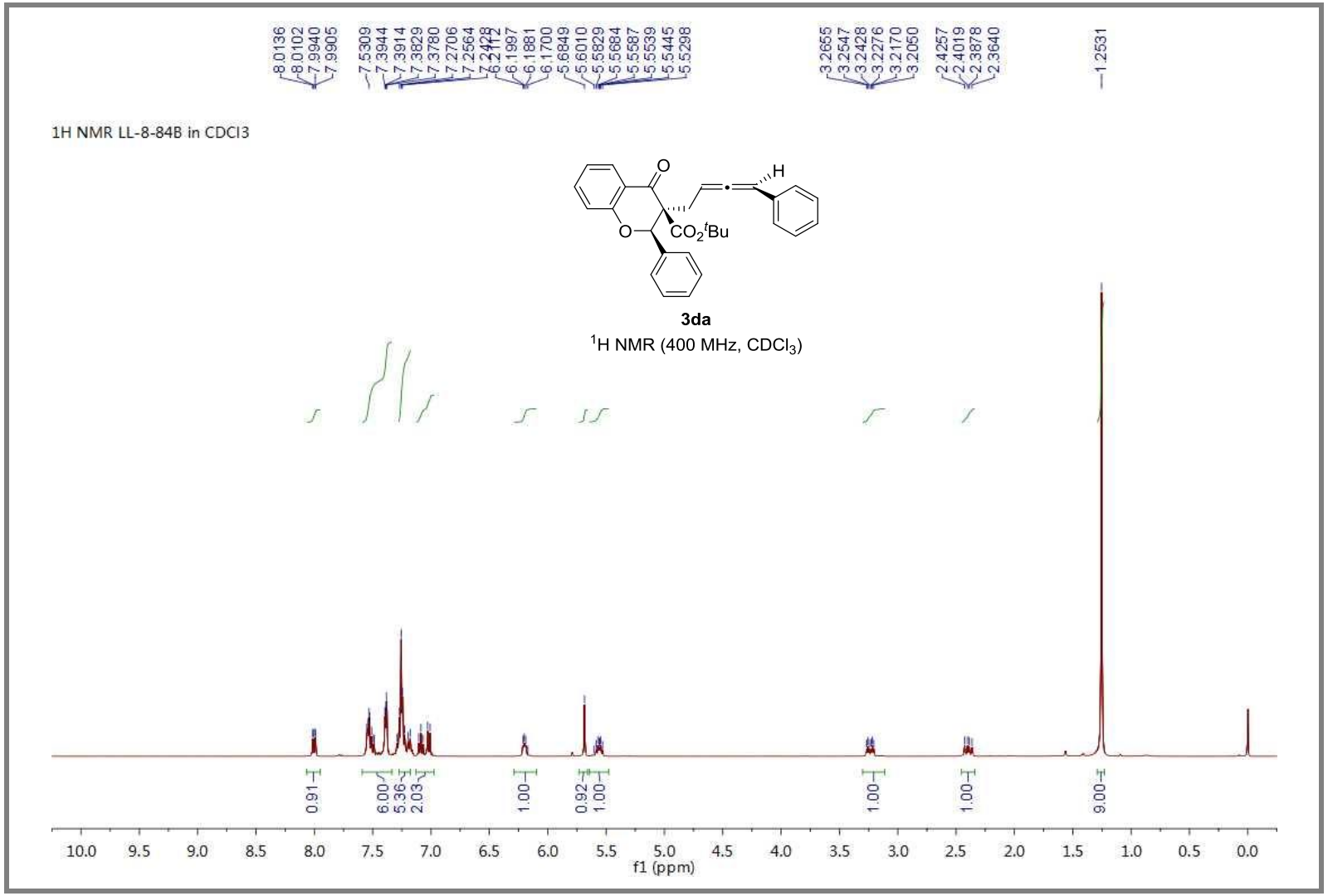
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.865 BB    0.1820  262.53870   22.04147   4.5513
   2   9.907 VB R  0.2183   71.21669    4.93606   1.2346
   3  10.660 BB    0.2204  228.42139   16.01500   3.9598
   4  12.304 BB    0.2589 5206.26318  308.55396  90.2543

Totals :                  5768.43996  351.54649

==========================================================================
                        *** End of Report ***
```

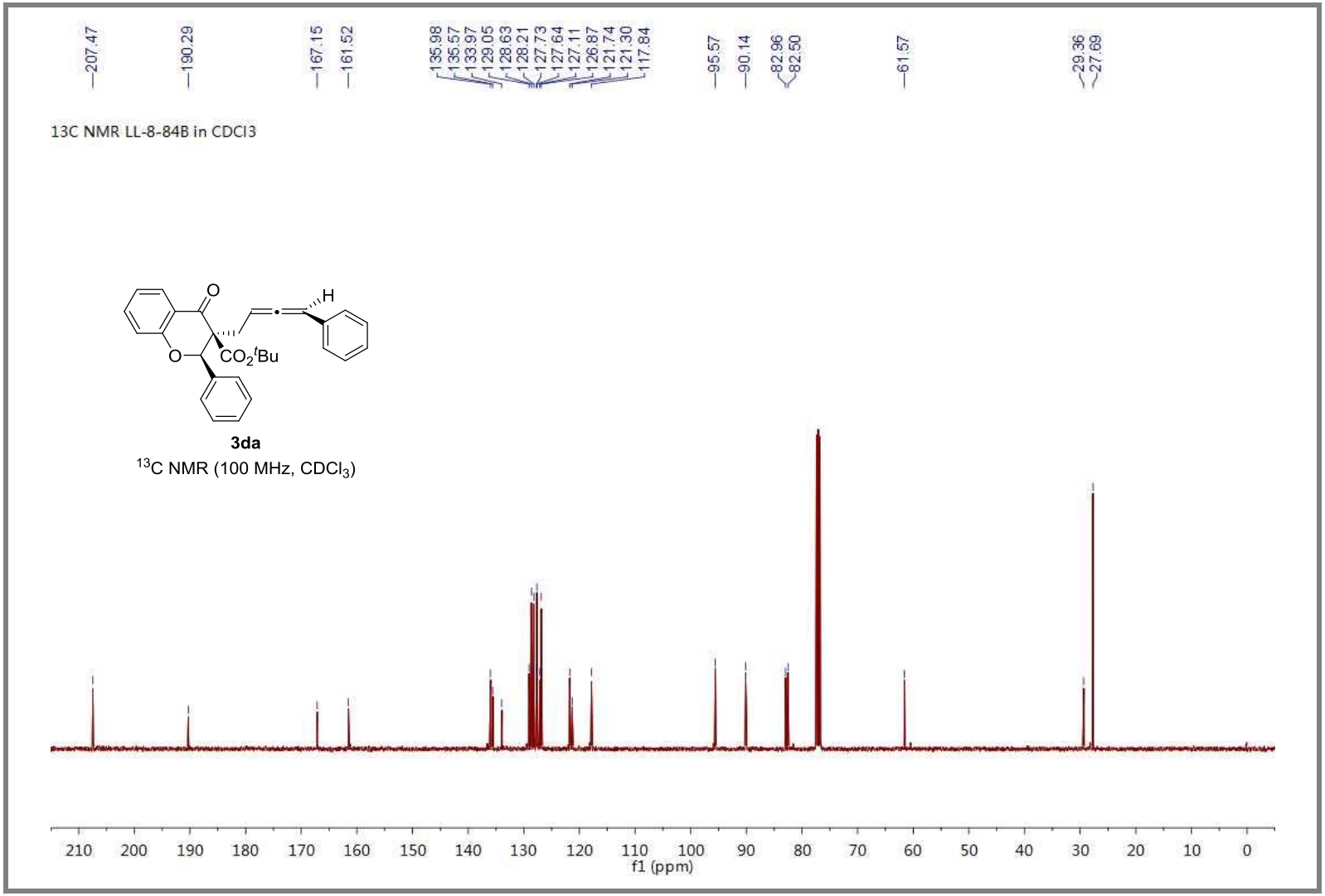


(-)-3ca



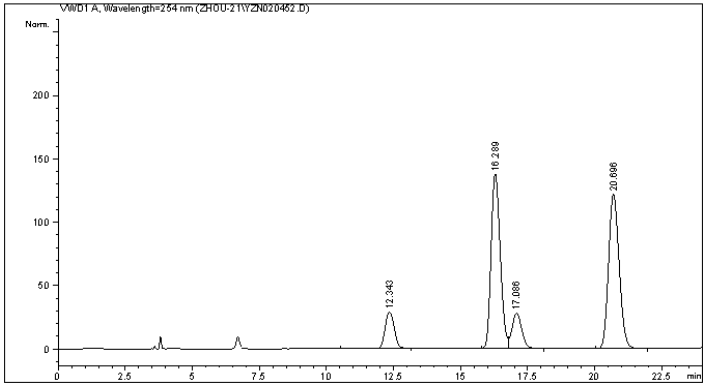
3da

^{1}H NMR (400 MHz, $CDCl_3$)


207.47
190.29
167.15
161.52
135.98
135.57
133.97
129.05
128.63
128.21
127.73
127.64
127.11
126.87
121.74
121.30
117.84
95.57
90.14
82.96
82.50
61.57
29.36
27.69
13C NMR LL-8-84B in CDCl3
O
H
O
CO2tBu
3da
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-21\YZN020452.D
Sample Name: LL-8-84B +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/16/2022 2:40:59 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/16/2022 2:37:00 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/16/2022 3:11:59 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



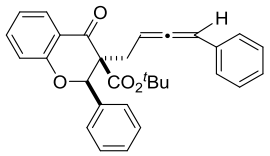

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|---------|--------|
   1  12.343 VB    0.3787  679.84802   28.65406   8.5002
   2  16.289 BV    0.3699 3266.26392  137.69011  40.8386
   3  17.086 VB    0.3915  707.85175   27.95877   8.8504
   4  20.696 BB    0.4303 3344.02783  122.05649  41.8108

Totals :                  7997.99152  316.35943
```



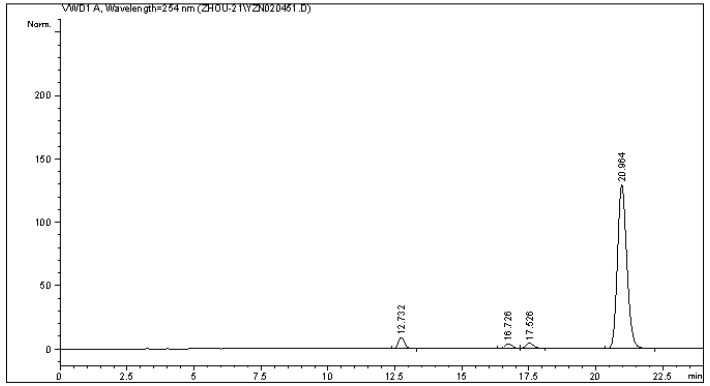
(+/-)-3da

*** End of Report ***

Instrument 1 1/16/2022 3:12:04 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-21\YZN020451.D
Sample Name: LL-8-84 B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/16/2022 2:11:58 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/16/2022 1:42:40 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 8:04:22 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



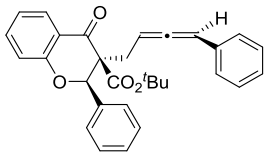

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|---------|--------|
   1  12.732 BB    0.2540  142.20184    8.73670   4.1266
   2  16.726 BV    0.3096   79.56863    3.96833   2.3090
   3  17.526 VV    0.3259   90.82600    4.23491   2.6357
   4  20.964 VB    0.3733 3133.42603  129.15248  90.9288

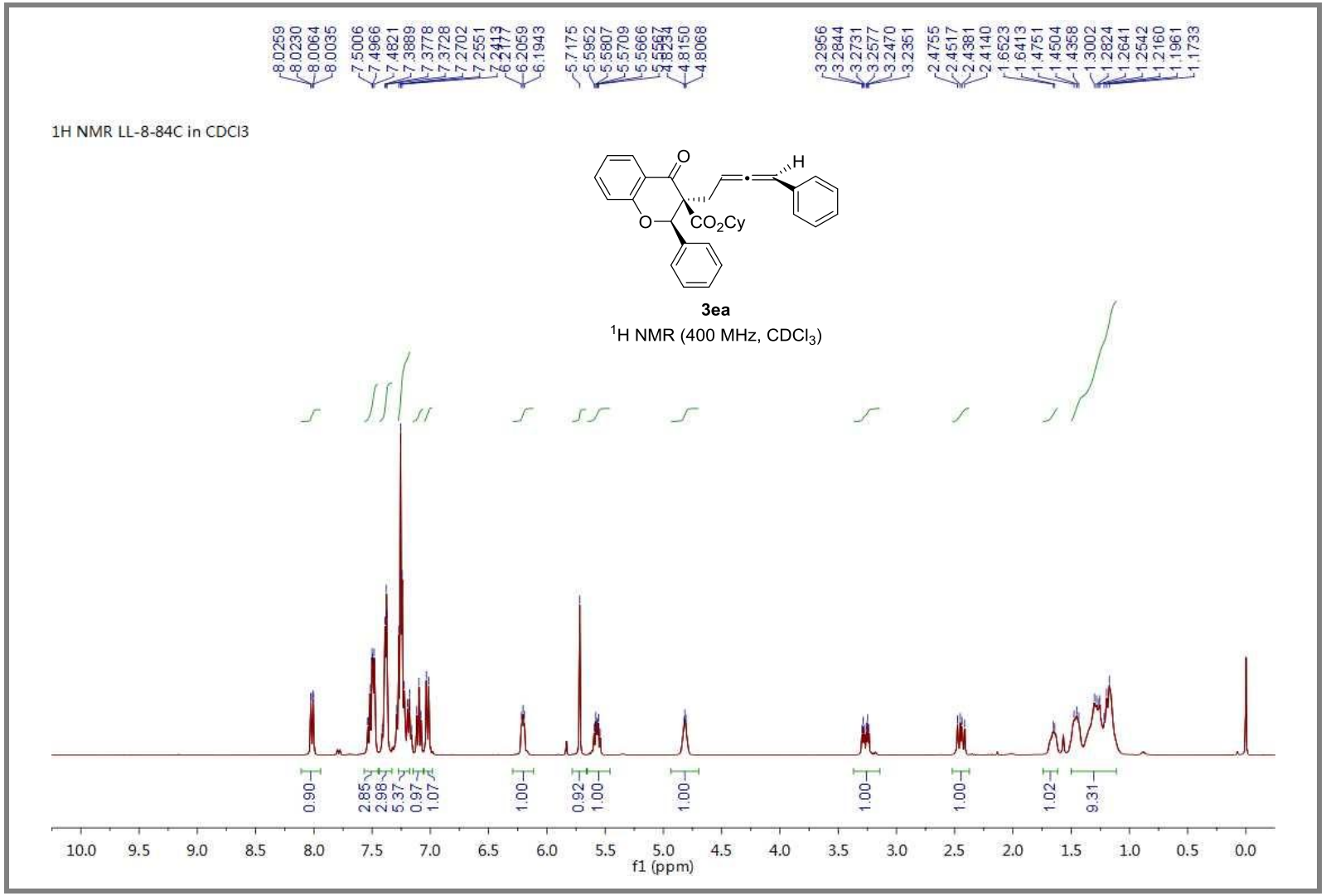
Totals :                  3446.02250  146.09242
```

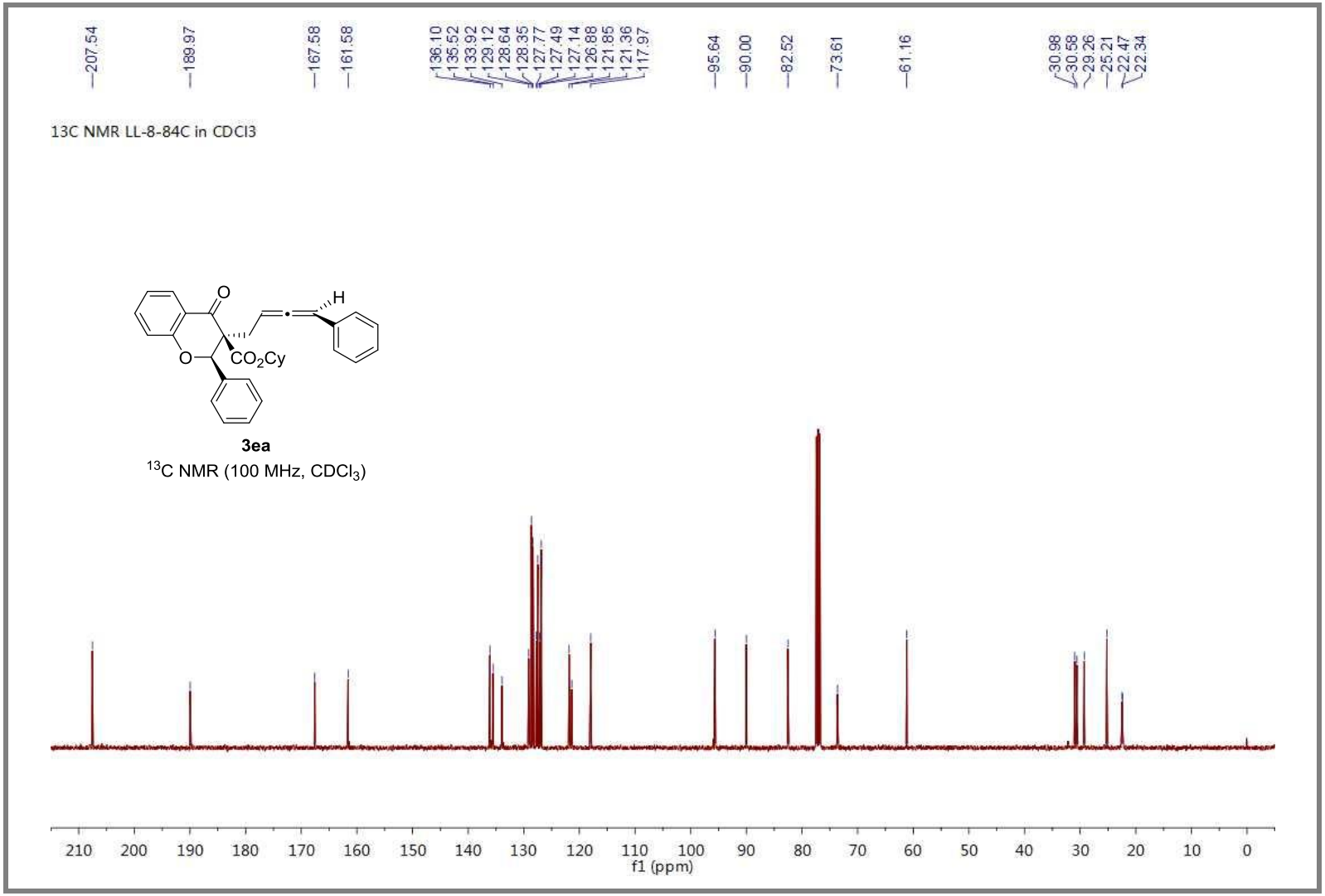


(-)-3da

*** End of Report ***

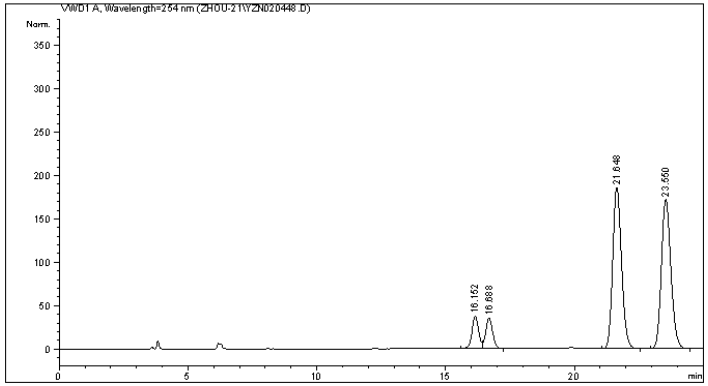
Instrument 1 6/15/2022 8:04:26 AM Page 1 of 1


8.0259
8.0230
8.0064
8.0035
7.5006
7.4966
7.4821
7.3889
7.3778
7.3728
7.2702
7.2551
6.2059
6.1943
5.7175
5.5952
5.5807
5.5709
5.5666
4.8150
4.8068
3.2956
3.2844
3.2731
3.2577
3.2470
3.2351
2.4755
2.4517
2.4381
2.4140
1.6523
1.6413
1.4751
1.4504
1.4358
1.3002
1.2824
1.2641
1.2542
1.2160
1.1961
1.1733
1H NMR LL-8-84C in CDCl3
O
H
O
CO2Cy
3ea
1H NMR (400 MHz, CDCl3)
0.90
2.85
2.98
5.37
0.97
1.07
1.00
0.92
1.00
1.00
1.00
1.00
1.02
9.31
10.0
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)


207.54
189.97
167.58
161.58
136.10
135.52
133.92
129.12
128.64
128.35
127.77
127.49
127.14
126.88
121.85
121.36
117.97
95.64
90.00
82.52
73.61
61.16
30.98
30.58
29.26
25.21
22.47
22.34
13C NMR LL-8-84C in CDCl3
O
H
O
CO2Cy
3ea
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-21\YZN020448.D
Sample Name: LL-8-84C +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/15/2022 8:17:36 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/15/2022 7:49:40 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/16/2022 3:00:38 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 98/2, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

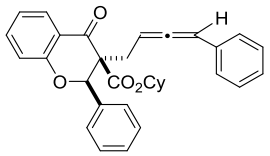
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.152 BV    0.2740  671.10840   37.55547   6.5966
   2  16.688 VB    0.2867  666.36212   35.62247   6.5500
   3  21.648 BB    0.3681 4428.58887  185.99136  43.5307
   4  23.550 BB    0.3952 4407.42920  171.90681  43.3227

Totals :                  1.01735e4   431.07611

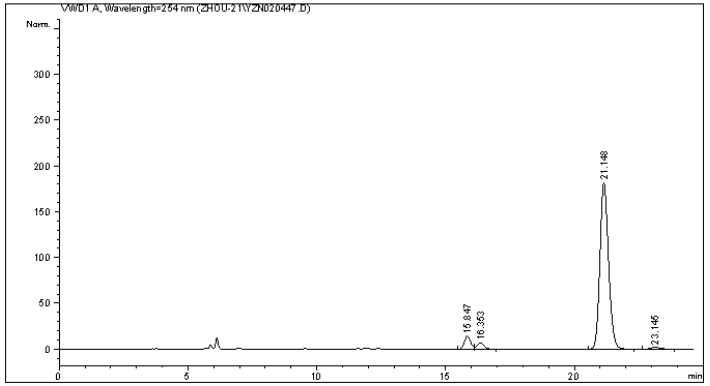
                          *** End of Report ***
```



(+/-)-3ea

Data File C:\CHEM32\1\DATA\ZHOU-21\YZN020447.D
Sample Name: LL-8-84C

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/15/2022 4:48:56 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/15/2022 4:36:08 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 8:09:31 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 98/2, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

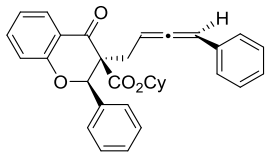
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

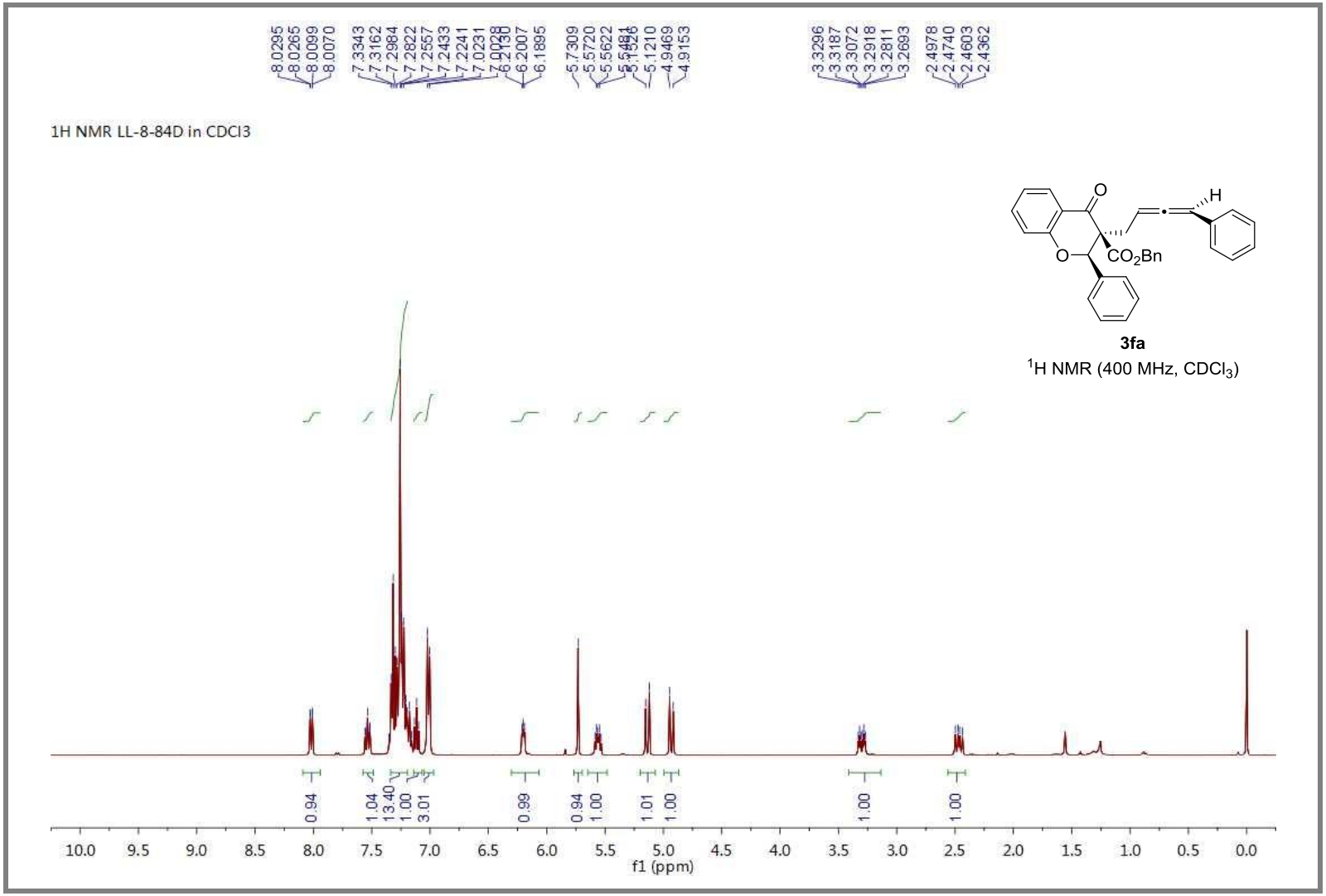
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.847 BV    0.2608  236.18698   14.00446   5.1294
   2  16.353 VB    0.2801  124.84607    6.83315   2.7113
   3  21.148 BB    0.3571 4199.25146  181.64714  91.1969
   4  23.145 BB    0.3869   44.31448    1.76028   0.9624

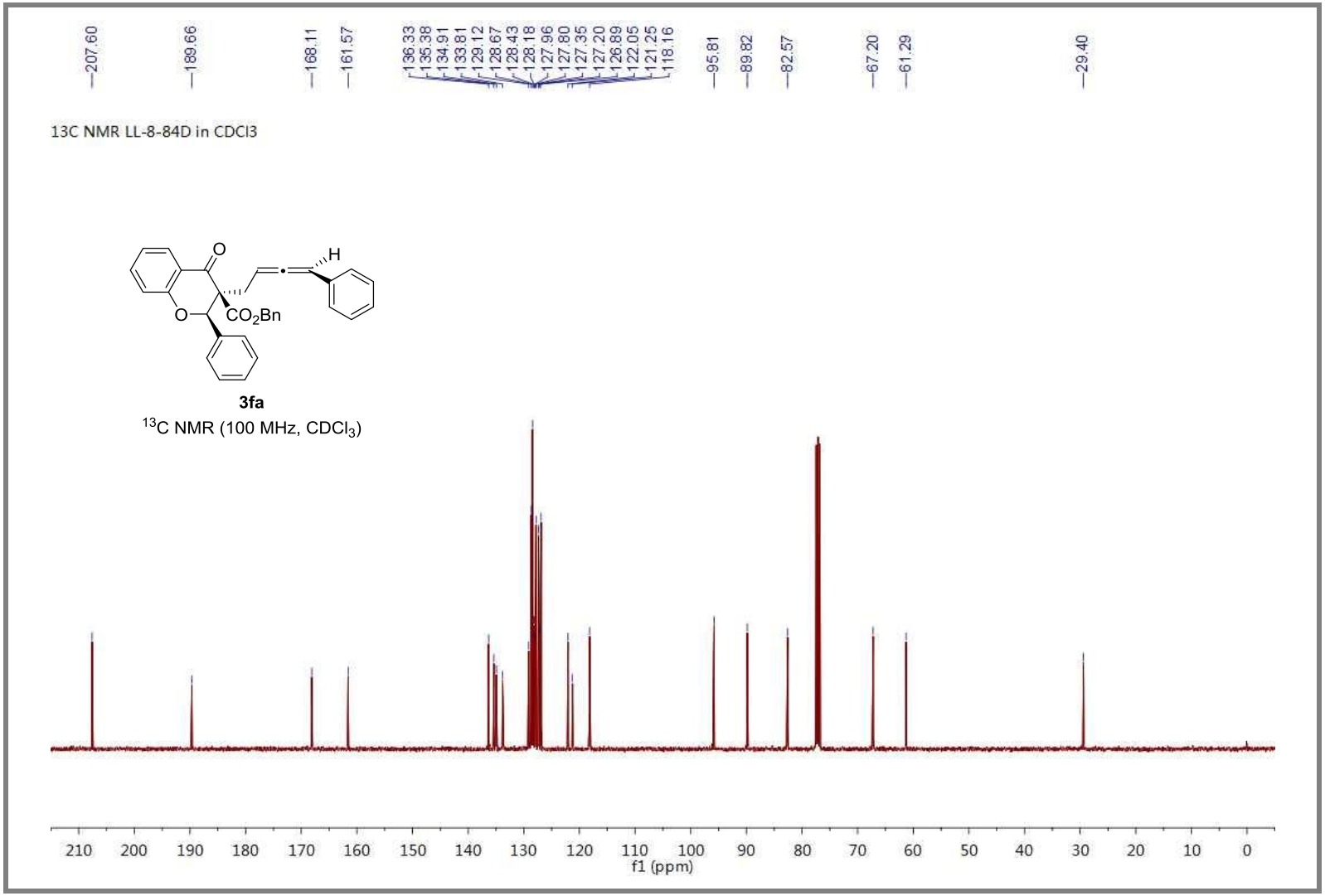
Totals :                  4604.59899  204.24503

                          *** End of Report ***
```



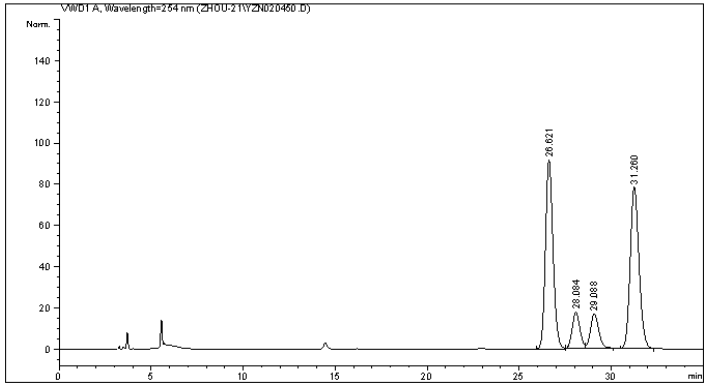
(-)-3ea


1H NMR LL-8-84D in CDCl3
8.0295
8.0265
8.0099
8.0070
7.3343
7.3162
7.2984
7.2822
7.2557
7.2433
7.2241
7.0231
6.2130
6.2007
6.1895
5.7309
5.5720
5.5622
5.1210
4.9469
4.9153
3.3296
3.3187
3.3072
3.2918
3.2811
3.2693
2.4978
2.4740
2.4603
2.4362
O
H
O
CO2Bn
3fa
1H NMR (400 MHz, CDCl3)
0.94
1.04
13.40
1.00
3.01
0.99
0.94
1.00
1.01
1.00
1.00
1.00
10.0
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)


207.60
189.66
168.11
161.57
136.33
135.38
134.91
133.81
129.12
128.67
128.43
128.18
127.96
127.80
127.35
127.20
126.89
122.05
121.25
118.16
95.81
89.82
82.57
67.20
61.29
29.40
13C NMR LL-8-84D in CDCl3
O
H
O
CO2Bn
3fa
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-21\YZN020450.D
Sample Name: LL-8-84D +/-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/15/2022 9:29:38 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/15/2022 9:27:29 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/16/2022 3:04:48 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

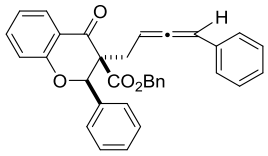
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  26.621 BV    0.4401 2627.69873   91.82907   41.7876
   2  28.084 VV    0.4507  520.09857   17.84485    8.2710
   3  29.088 VB    0.4814  529.96985   16.94309    8.4280
   4  31.260 BB    0.5124 2610.45972   78.36729   41.5134

Totals :                  6288.22687  204.98429

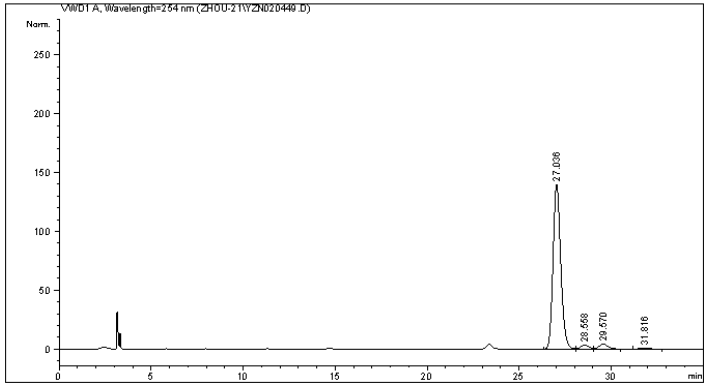
==========================================================================
                        *** End of Report ***
```



(+/-)-3fa

Data File C:\CHEM32\1\DATA\ZHOU-21\YZN020449.D
Sample Name: LL-8-84D

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/15/2022 8:50:05 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/15/2022 8:43:22 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 8:12:57 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

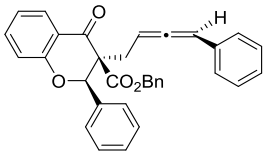
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

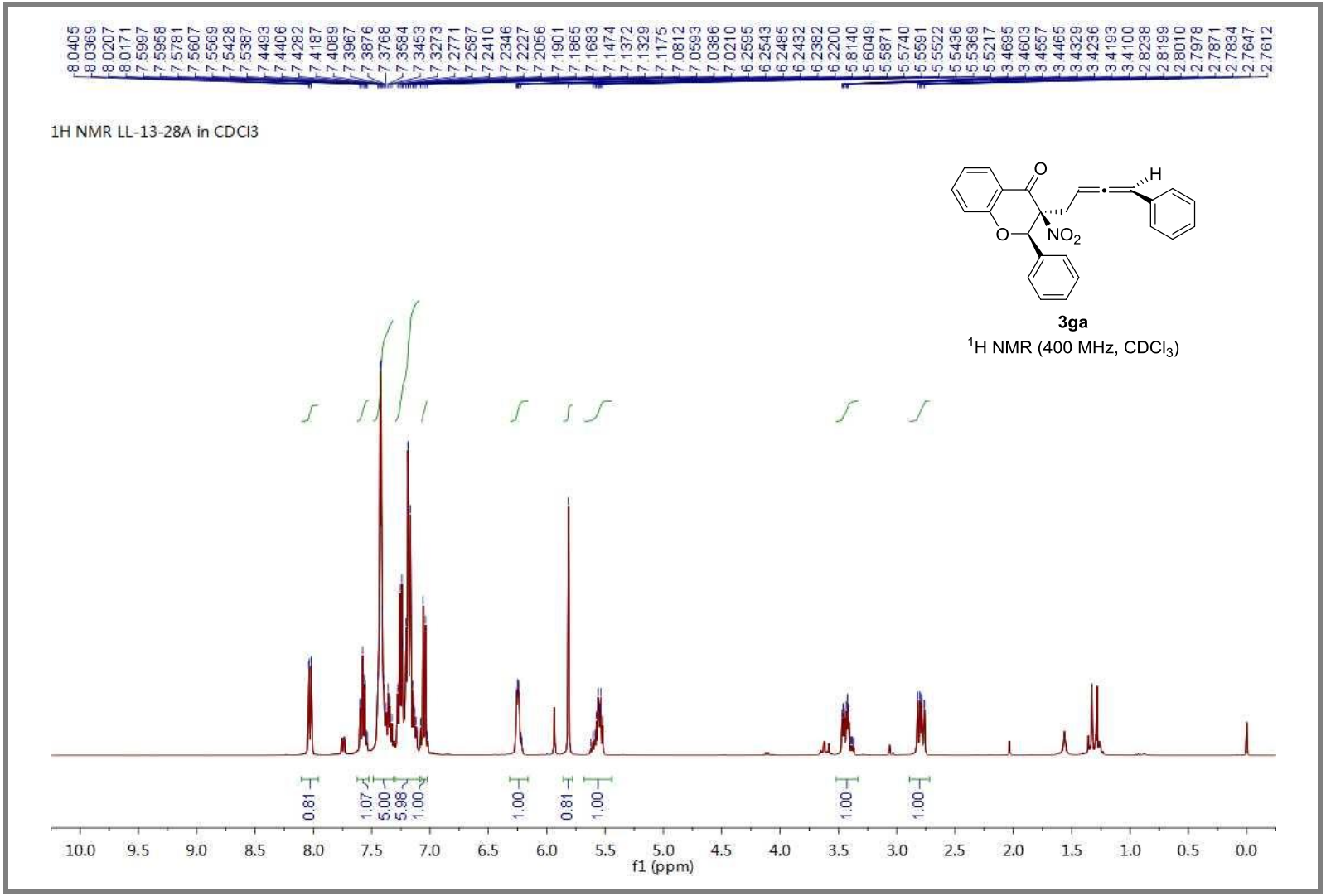
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  27.036 BV    0.4466 4072.18286  140.19965   94.1272
   2  28.558 VV    0.4691   97.39050    3.19550    2.2511
   3  29.570 VB    0.4894  134.01563    4.19242    3.0977
   4  31.816 BB    0.5066   22.66817 6.93395e-1    0.5240

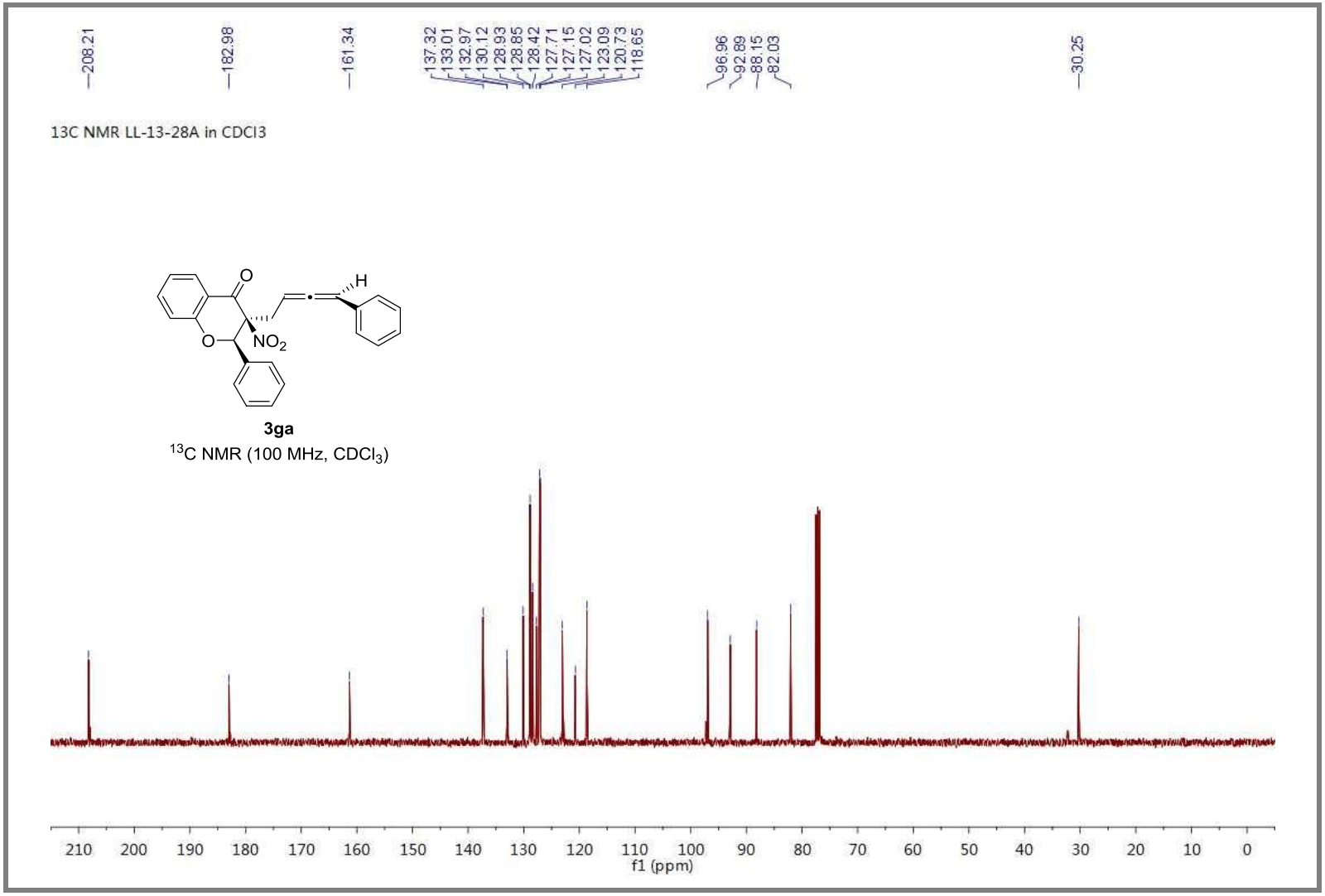
Totals :                  4326.25716  148.28096

==========================================================================
                        *** End of Report ***
```



(-)-3fa

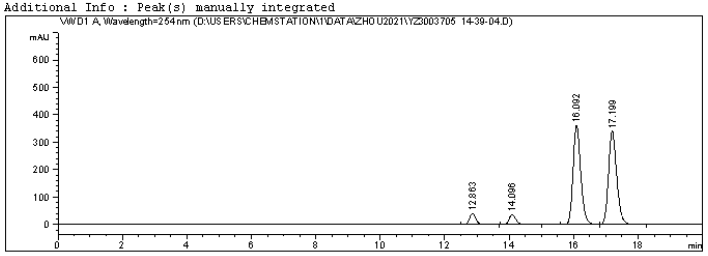

1H NMR LL-13-28A in CDCl3
O
H
O
NO2
3ga
1H NMR (400 MHz, CDCl3)
0.81
1.07
5.00
5.98
1.00
1.00
0.81
1.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


208.21
182.98
161.34
137.32
133.01
132.97
130.12
128.93
128.85
128.42
127.71
127.15
127.02
123.09
120.73
118.65
96.96
92.89
88.15
82.03
30.25
13C NMR LL-13-28A in CDCl3
O
H
O
NO2
3ga
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2021\YZ3003705 14-39-04.D
Sample Name: LL-8-31 +/- 1

```
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :     -
Injection Date  : 11/24/2021 2:39:05 PM              Inj :   1
                                               Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 11/24/2021 2:05:23 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 9/27/2023 9:09:36 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 98/2, 0.8 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
                          Area Percent Report

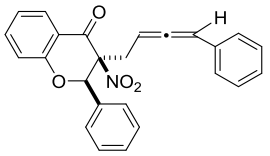
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1  12.863 BB    0.2096  553.90057   40.49520   4.2227
   2  14.096 BB    0.2267  552.29535   37.31293   4.2104
   3  16.092 BB    0.2546 5999.64648  361.53226  45.7385
   4  17.199 BB    0.2725 6011.43799  339.63300  45.8284

Totals :                  1.31173e4   778.97338


                          *** End of Report ***
```

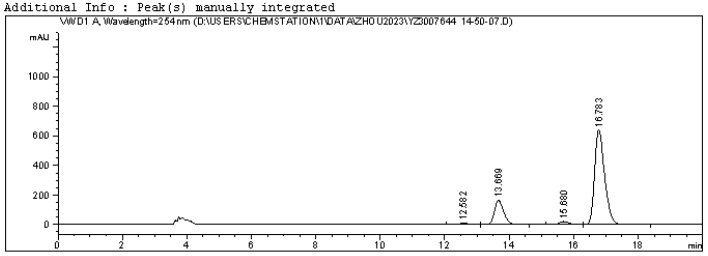


(+/-)-3ga

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2023\YZ3007644 14-50-07.D
Sample Name: LL-13-28A-1

```
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :     -
Injection Date  : 9/20/2023 2:50:07 PM               Inj :   1
                                               Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 9/20/2023 1:38:07 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 9/27/2023 9:11:50 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 98/2, 0.8 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
                          Area Percent Report

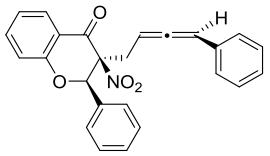
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

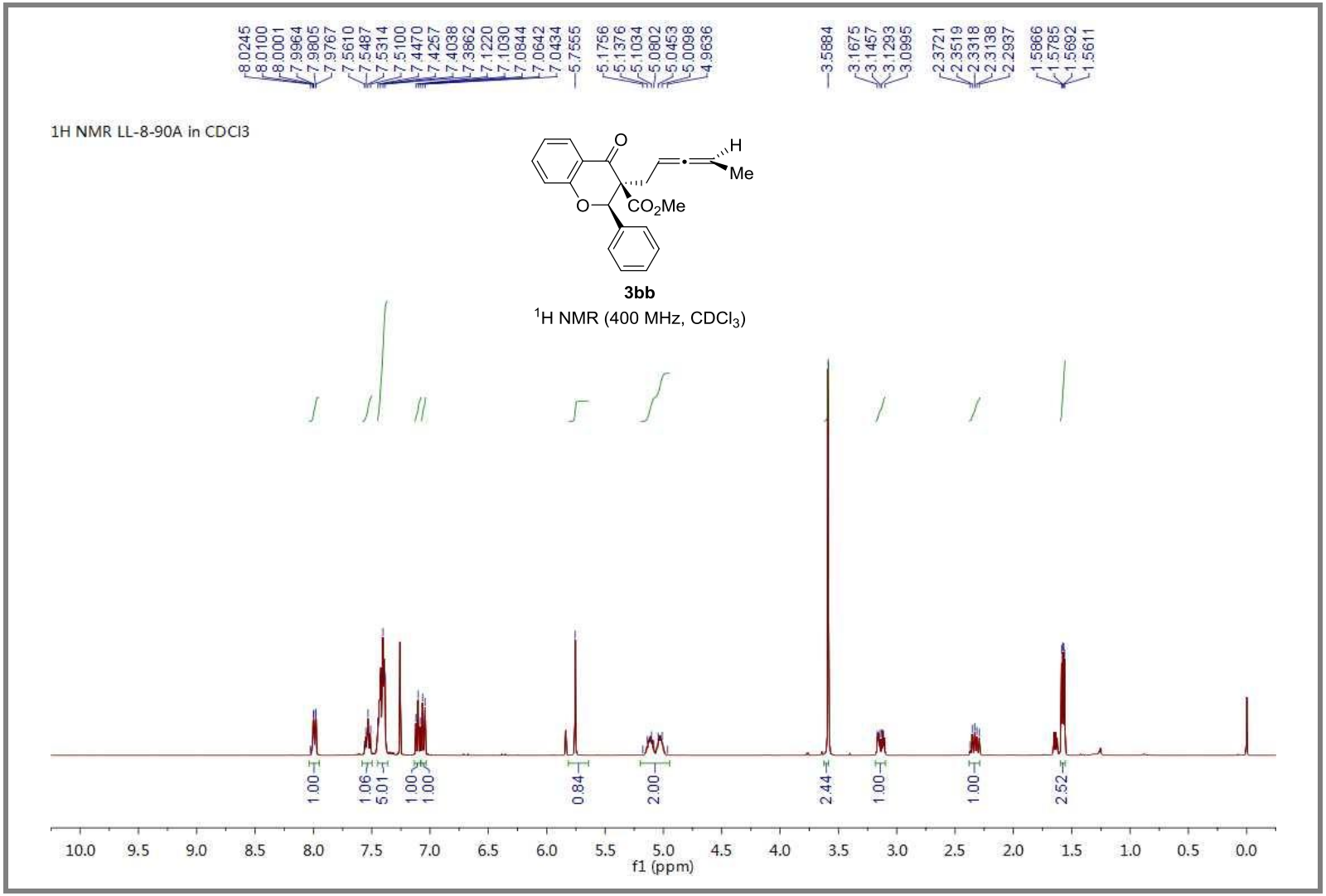
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1  12.582 BB    0.3108  187.08337    9.29691   1.0599
   2  13.669 BB    0.3019 3276.88501  164.83392  18.5640
   3  15.680 BV    0.3083  425.16043   20.90683   2.4086
   4  16.783 VB    0.3265 1.37627e4   641.01404  77.9675

Totals :                  1.76518e4   836.05170


                          *** End of Report ***
```

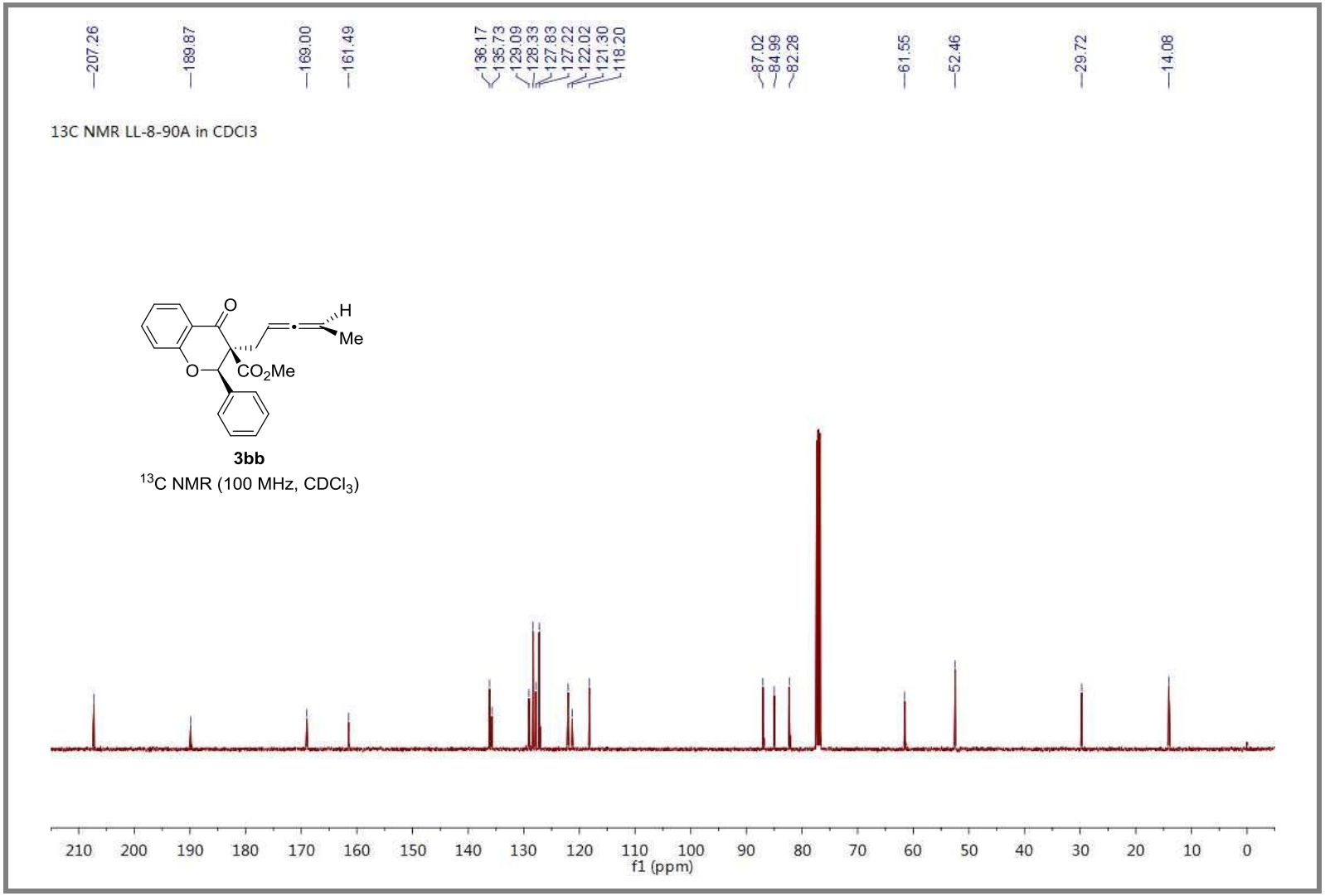


(-)-3ga



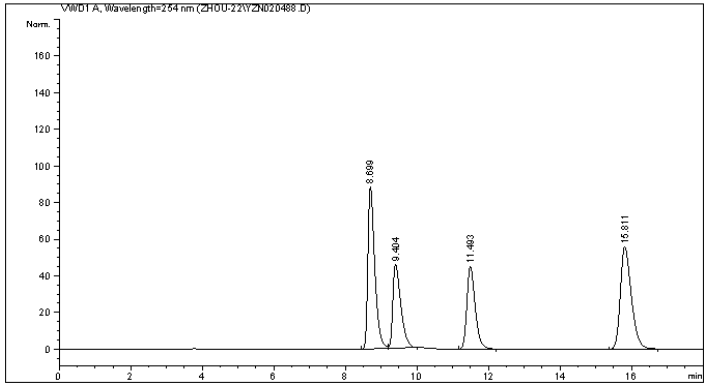
3bb

^{1}H NMR (400 MHz, $CDCl_3$)


207.26
189.87
169.00
161.49
136.17
135.73
129.09
128.33
127.83
127.22
122.02
121.30
118.20
87.02
84.99
82.28
61.55
52.46
29.72
14.08
13C NMR LL-8-90A in CDCl3
O
H
Me
O
CO2Me
3bb
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020488.D
Sample Name: LL-8-90A +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/19/2022 2:24:16 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/19/2022 2:23:11 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/19/2022 2:56:17 AM
                  (modified after loading)
Sample Info     : IB, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

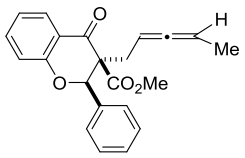
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.699 BV    0.2000 1177.30811   88.68472  30.8241
   2   9.404 VB    0.2338  711.30988   45.75225  18.6234
   3  11.493 BB    0.2476  733.77289   45.20787  19.2115
   4  15.811 BB    0.3255 1197.04639   55.90168  31.3409

Totals :                  3819.43726  235.54651

                          *** End of Report ***
```

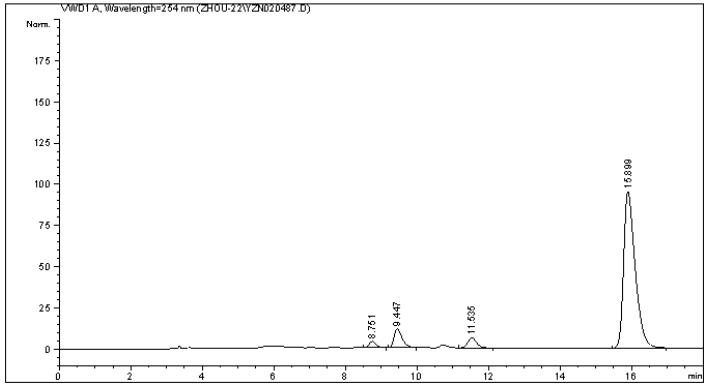


(+/-)-3bb

Instrument 1 1/19/2022 2:56:20 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020487.D
Sample Name: LL-8-90A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 1/19/2022 2:05:09 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 1/19/2022 1:45:26 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 7:58:29 AM
                  (modified after loading)
Sample Info     : IB, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

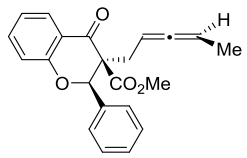
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.751 BB    0.2101   51.58413    3.81583   2.0912
   2   9.447 BB    0.2400  181.70757   11.48165   7.3664
   3  11.535 VB    0.2605  107.80194    6.30854   4.3702
   4  15.899 BB    0.3365 2125.62988   95.10351  86.1722

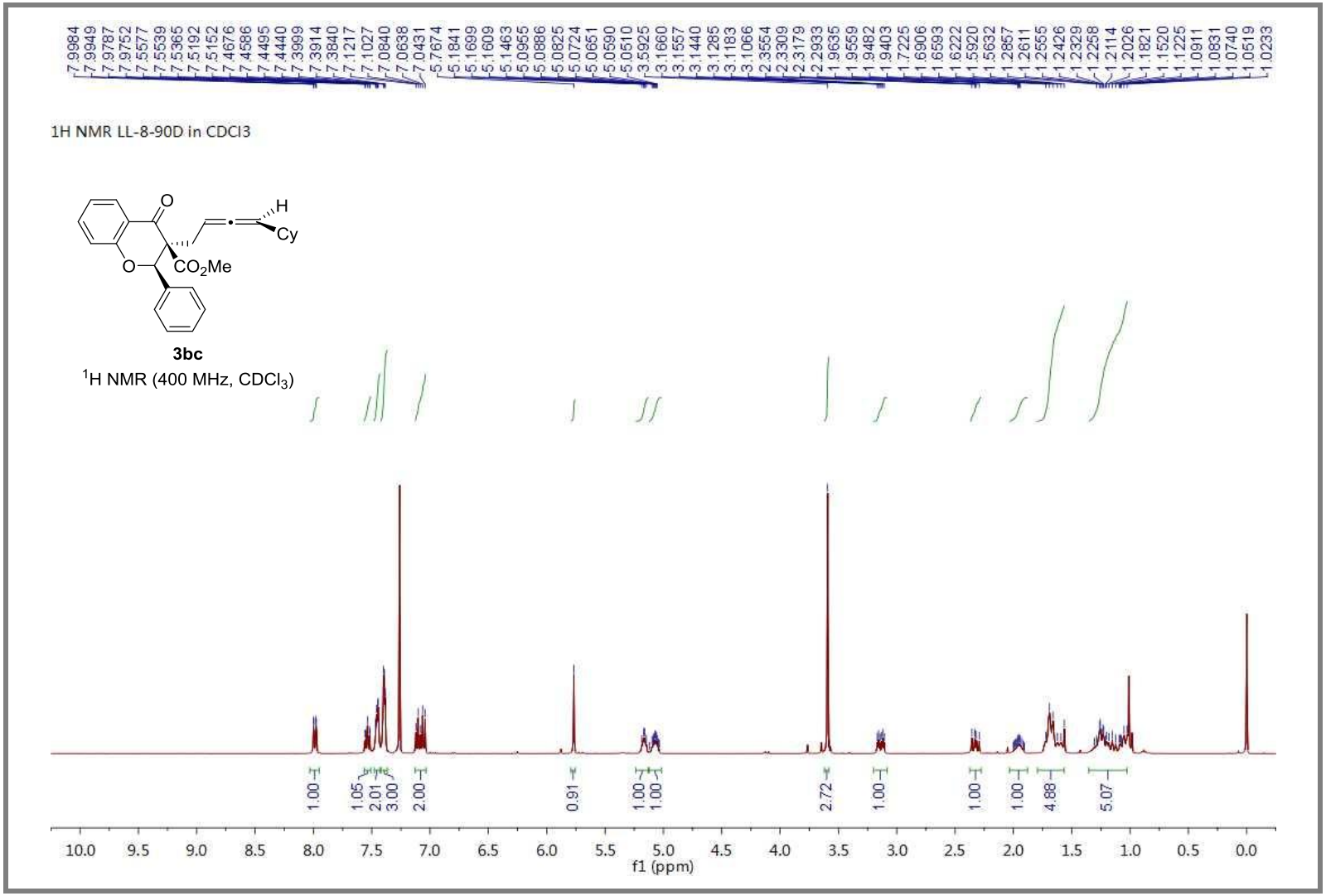
Totals :                  2466.72351  116.70953

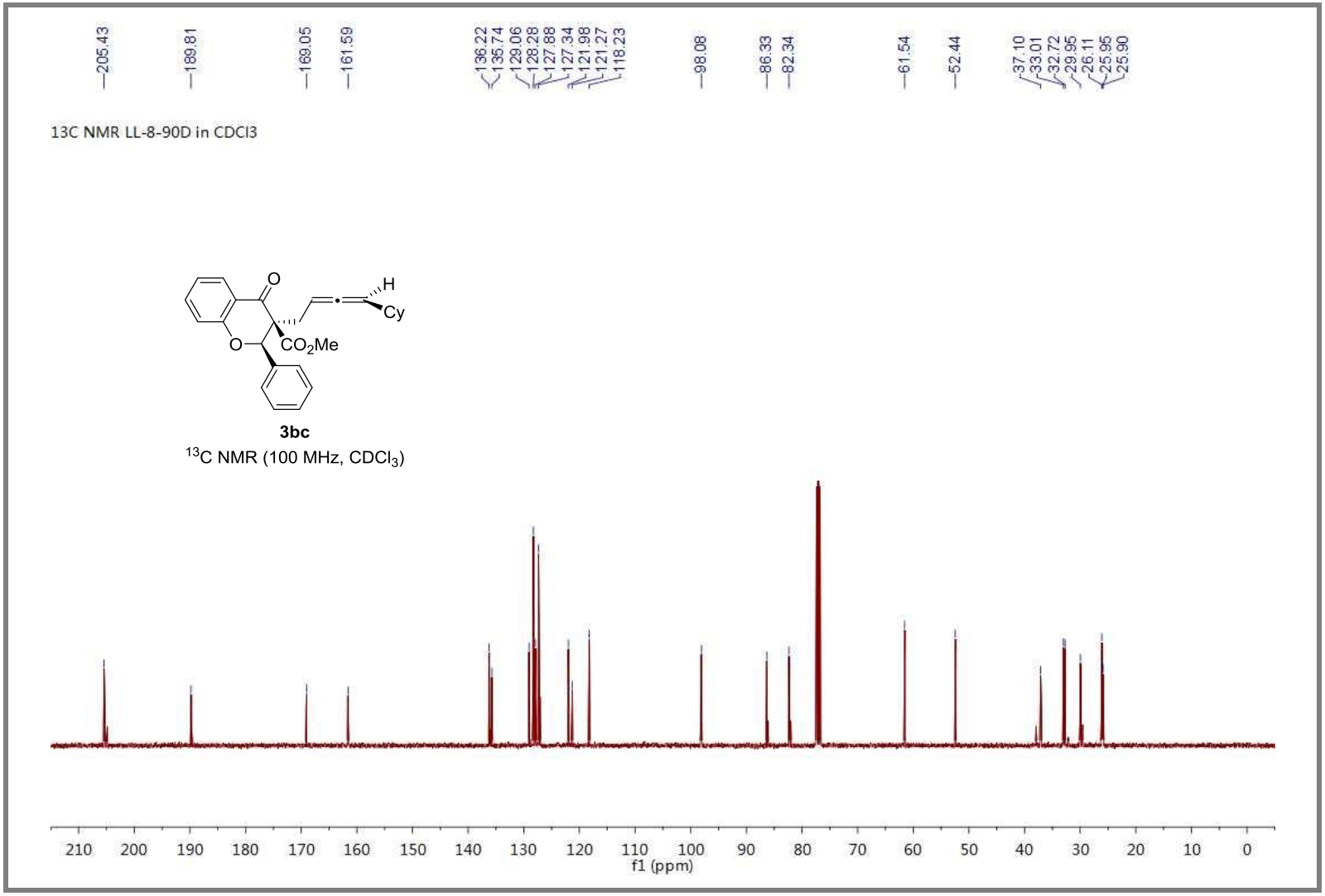
                          *** End of Report ***
```



(-)-3bb

Instrument 1 6/15/2022 7:58:41 AM Page 1 of 1

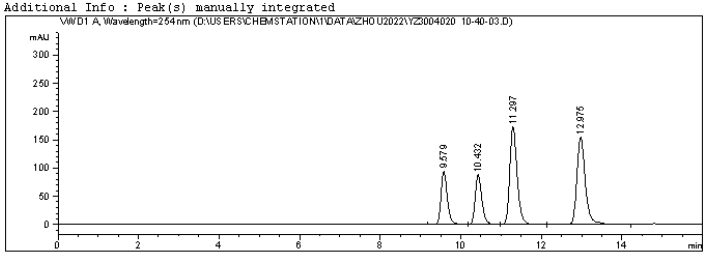

1H NMR LL-8-90D in CDCl3
O
H
Cy
O
CO2Me
3bc
1H NMR (400 MHz, CDCl3)
1.00
1.05
2.01
3.00
2.00
0.91
1.00
1.00
2.72
1.00
1.00
1.00
4.88
5.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


205.43
189.81
169.05
161.59
136.22
135.74
129.06
128.28
127.88
127.34
121.98
121.27
118.23
98.08
86.33
82.34
61.54
52.44
37.10
33.01
32.72
29.95
26.11
25.95
25.90
13C NMR LL-8-90D in CDCl3
O
H
Cy
O
CO2Me
3bc
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2022\YZ3004020 10-40-03.D
Sample Name: LL-8-90D +/- (1)

```
==================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                    Location :     -
Injection Date  : 1/17/2022 10:40:03 AM          Inj :    1
                                           Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 1/17/2022 9:10:08 AM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 9/27/2023 9:15:16 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
==================================================================
                      Area Percent Report
==================================================================

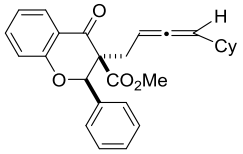
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   9.579 BV    0.1674 1036.89233   94.19881  15.9424
   2  10.432 VB    0.1757 1014.32281   87.85240  15.5954
   3  11.297 BB    0.1946 2197.13647  172.51257  33.7814
   4  12.975 VB R  0.2213 2255.62329  154.56055  34.6807

Totals :                  6503.97491  509.12433


==================================================================
                      *** End of Report ***
```

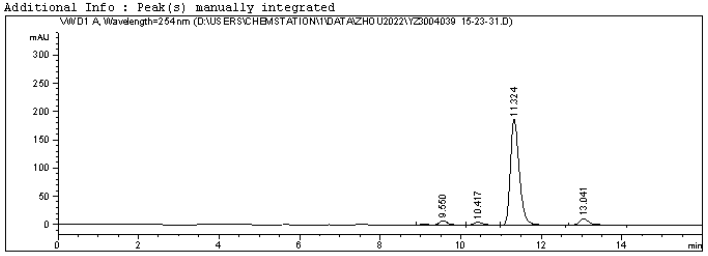


(+/-)-3bc

Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2022\YZ3004039 15-23-31.D
Sample Name: LL-8-90 D

```
==================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                    Location :     -
Injection Date  : 1/20/2022 3:23:31 PM           Inj :    1
                                           Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 1/20/2022 3:02:28 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 9/27/2023 9:15:16 PM by SYSTEM
                  (modified after loading)
Sample Info     : AD-3, n-Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm

Additional Info : Peak(s) manually integrated
```




```
==================================================================
                      Area Percent Report
==================================================================

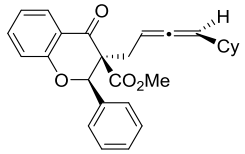
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

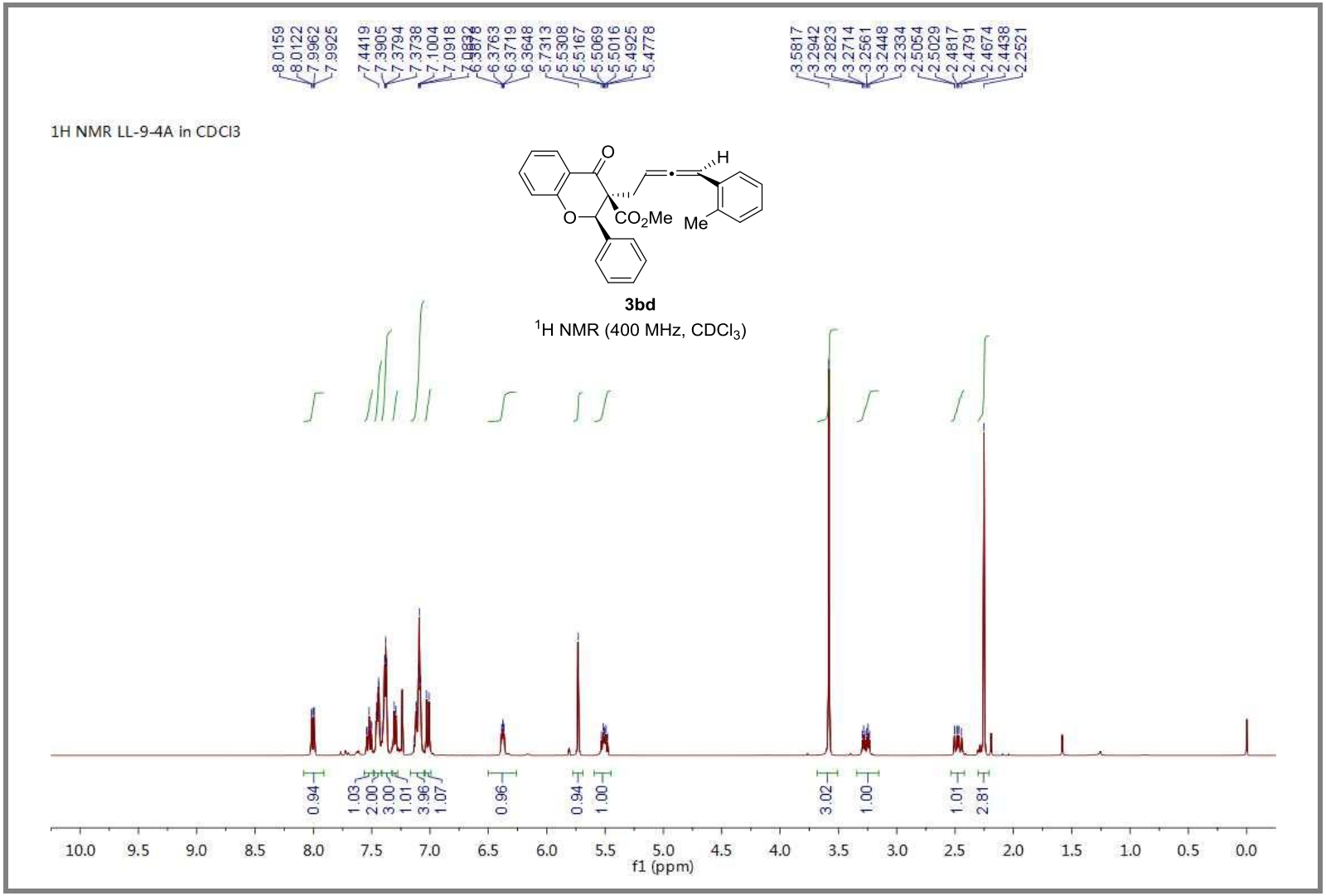
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   9.550 VB R  0.2480  122.43332    7.44029   3.7532
   2  10.417 BV    0.2238   73.90514    5.07692   2.2656
   3  11.324 VB    0.2364 2868.95532  186.58206  87.9482
   4  13.041 BB    0.2622  196.80342   11.29893   6.0330

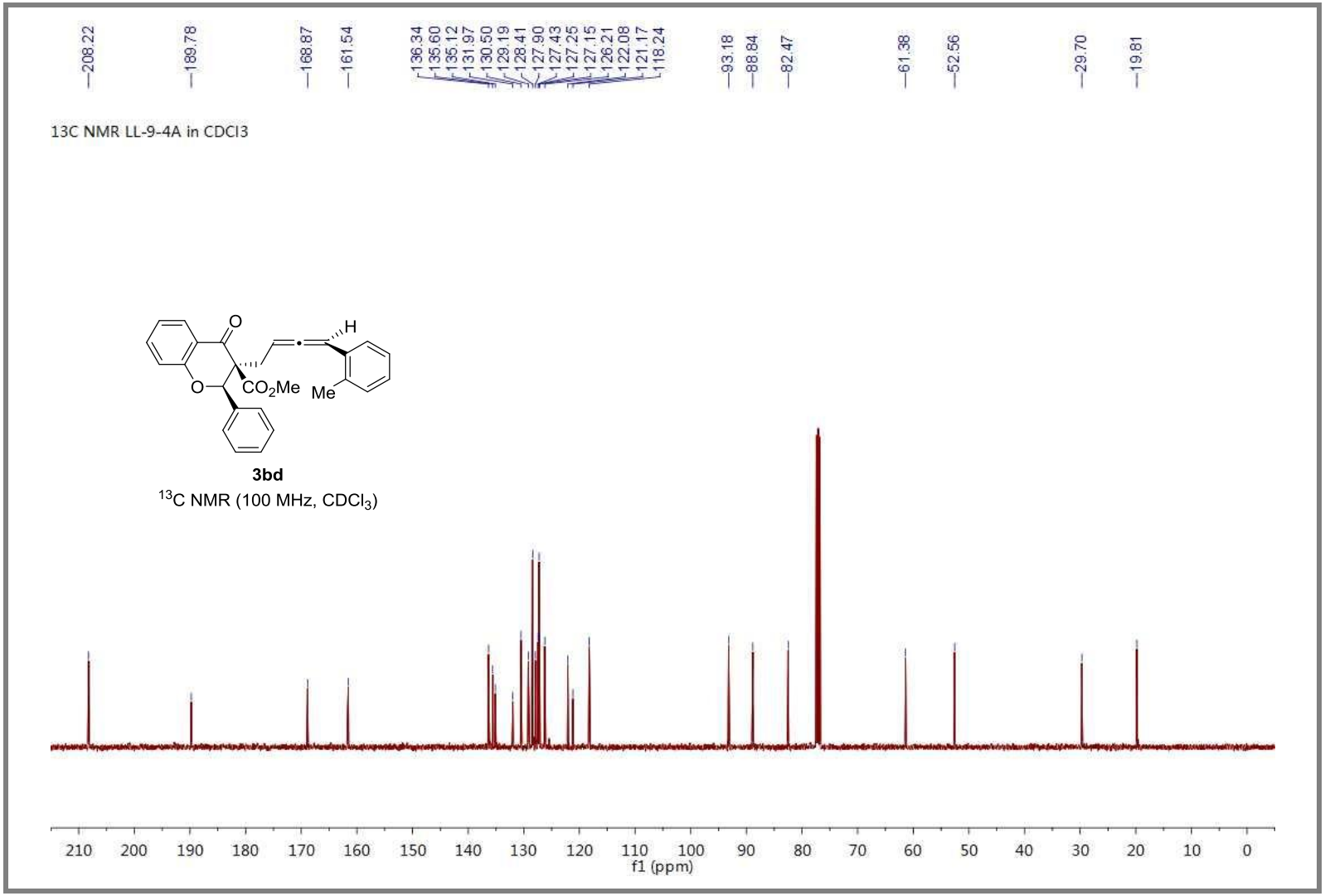
Totals :                  3262.09720  210.39821


==================================================================
                      *** End of Report ***
```



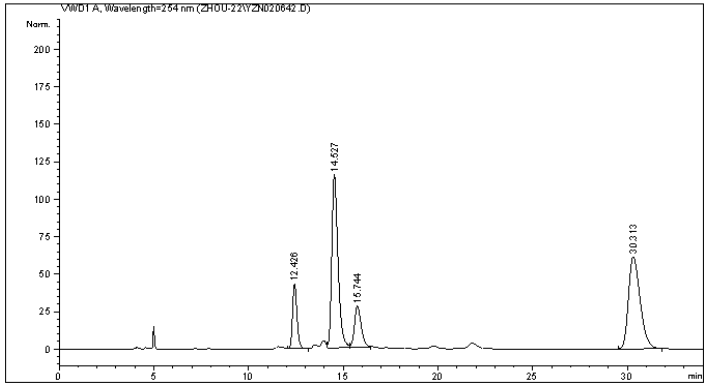
(-)-3bc


8.0159
8.0122
7.9962
7.9925
7.4419
7.3905
7.3794
7.3738
7.1004
7.0918
6.3763
6.3719
6.3648
5.7313
5.5308
5.5167
5.5069
5.5016
5.4925
5.4778
3.5817
3.2942
3.2823
3.2714
3.2561
3.2448
3.2334
2.5054
2.5029
2.4817
2.4791
2.4674
2.4438
2.2521
1H NMR LL-9-4A in CDCl3
O
H
O
CO2Me
Me
3bd
1H NMR (400 MHz, CDCl3)
0.94
1.03
2.00
3.00
1.01
3.96
1.07
0.96
0.94
1.00
3.02
1.00
1.01
2.81
10.0
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)


208.22
189.78
168.87
161.54
136.34
135.60
135.12
131.97
130.50
129.19
128.41
127.90
127.43
127.25
127.15
126.21
122.08
121.17
118.24
93.18
88.84
82.47
61.38
52.56
29.70
19.81
13C NMR LL-9-4A in CDCl3
O
H
O
CO2Me
Me
3bd
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020642.D
Sample Name: LL-9-4A +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2/26/2022 2:50:12 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 2/26/2022 2:48:31 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 2/26/2022 3:53:51 AM
                  (modified after loading)
Sample Info     : OD-3, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm
```



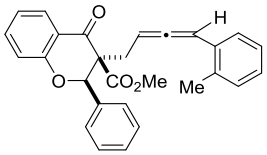

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  12.426 VB    0.2495  705.01190   43.33867  10.5804
   2  14.527 VV    0.3485 2645.67480  115.62691  39.7048
   3  15.744 VB    0.3760  675.83881   27.45697  10.1426
   4  30.313 BB    0.6572 2636.83643   61.71507  39.5722

Totals :                  6663.36194  248.13762
```

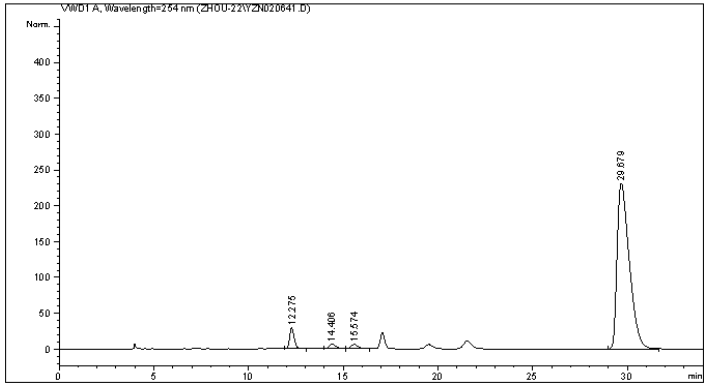


(+/-)-3bd

```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020641.D
Sample Name: LL-9-4A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2/26/2022 2:11:58 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 2/26/2022 1:41:52 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 7:47:10 AM
                  (modified after loading)
Sample Info     : OD-3, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm
```



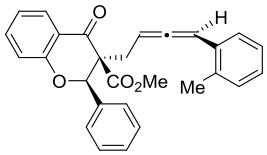

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

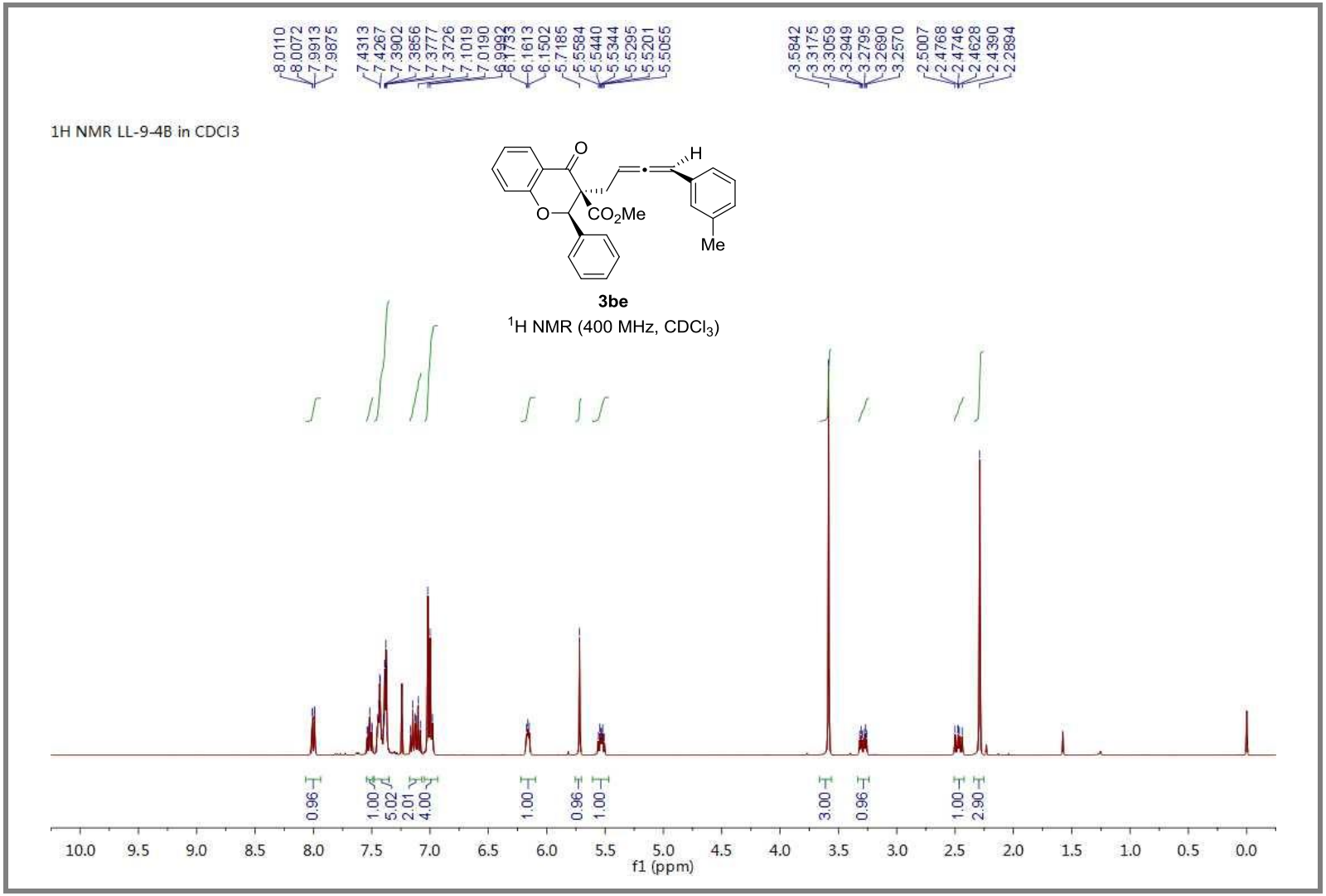
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  12.275 VB    0.2529  480.19705   29.21026   4.3250
   2  14.406 BB    0.3711  154.46072    6.28627   1.3912
   3  15.574 BB    0.3937  154.72795    6.03518   1.3936
   4  29.679 BB    0.6775 1.03133e4   231.28595  92.8902

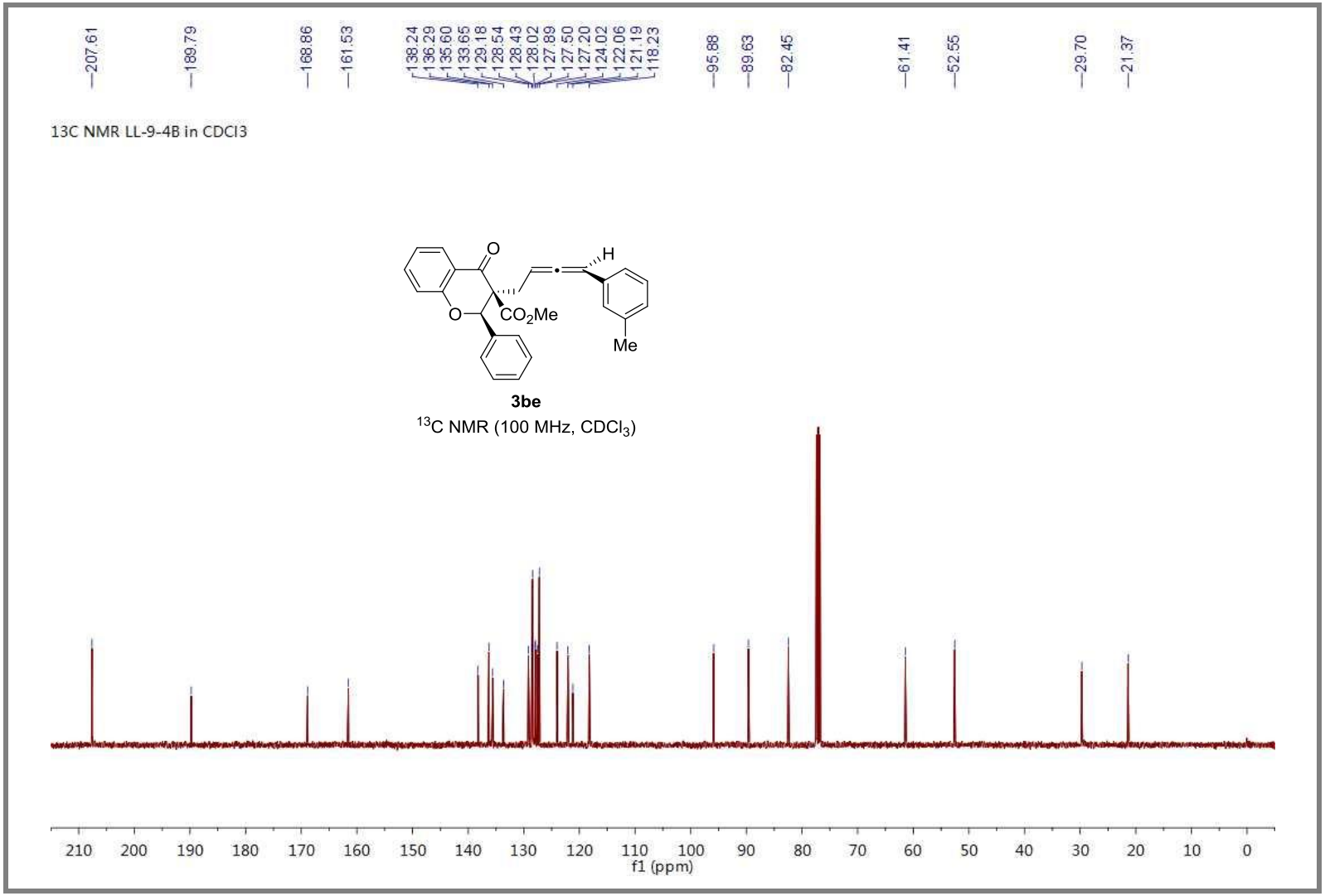
Totals :                  1.11027e4   272.81765
```



(-)-3bd

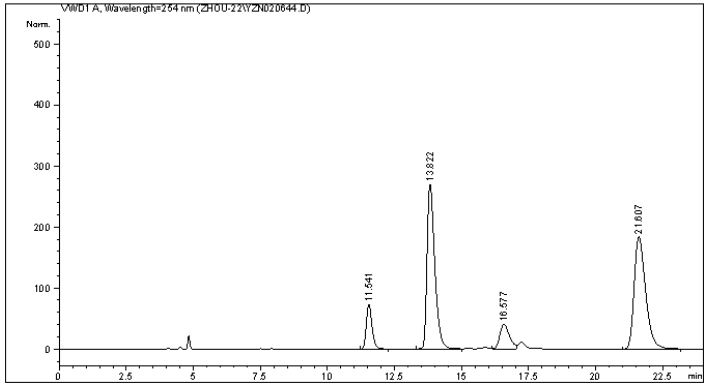
```
                          *** End of Report ***
```


1H NMR LL-9-4B in CDCl3
O
H
O
CO2Me
Me
3be
1H NMR (400 MHz, CDCl3)
f1 (ppm)


207.61
189.79
168.86
161.53
138.24
136.29
135.60
133.65
129.18
128.54
128.43
128.02
127.89
127.50
127.20
124.02
122.06
121.19
118.23
95.88
89.63
82.45
61.41
52.55
29.70
21.37
13C NMR LL-9-4B in CDCl3
O
H
O
CO2Me
Me
3be
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020644.D
Sample Name: LL-9-4B +/-

```
    ======================================================================
    Acq. Operator   :
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 2/26/2022 3:52:29 AM
    Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 2/26/2022 3:50:34 AM
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 2/26/2022 4:25:39 AM
                      (modified after loading)
    Sample Info     : OD-3, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

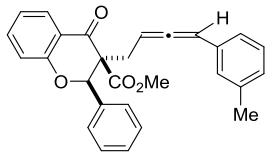
    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1  11.541 BB    0.2279 1087.85034   72.92671   8.3751
       2  13.822 BB    0.3068 5418.80371  270.20404  41.7179
       3  16.577 VV    0.3780 1001.24353   40.60318   7.7083
       4  21.607 BB    0.4571 5481.26563  183.79692  42.1988

    Totals :                  1.29892e4   567.53085

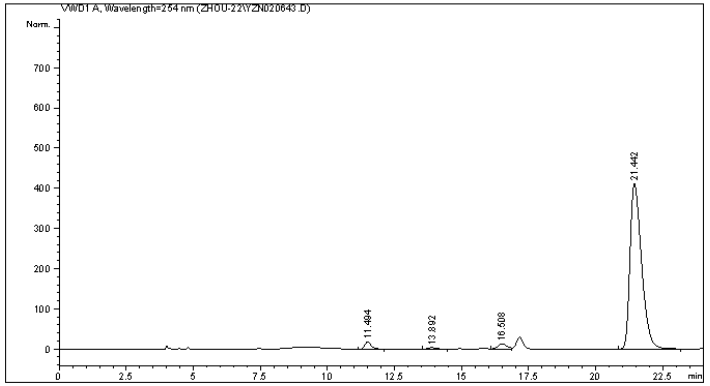
    ======================================================================
                              *** End of Report ***
```



(+/-)-3be

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020643.D
Sample Name: LL-9-4B

```
    ======================================================================
    Acq. Operator   :
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 2/26/2022 3:25:59 AM
    Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 2/26/2022 3:24:54 AM
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 6/15/2022 7:50:32 AM
                      (modified after loading)
    Sample Info     : OD-3, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

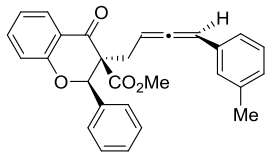
    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

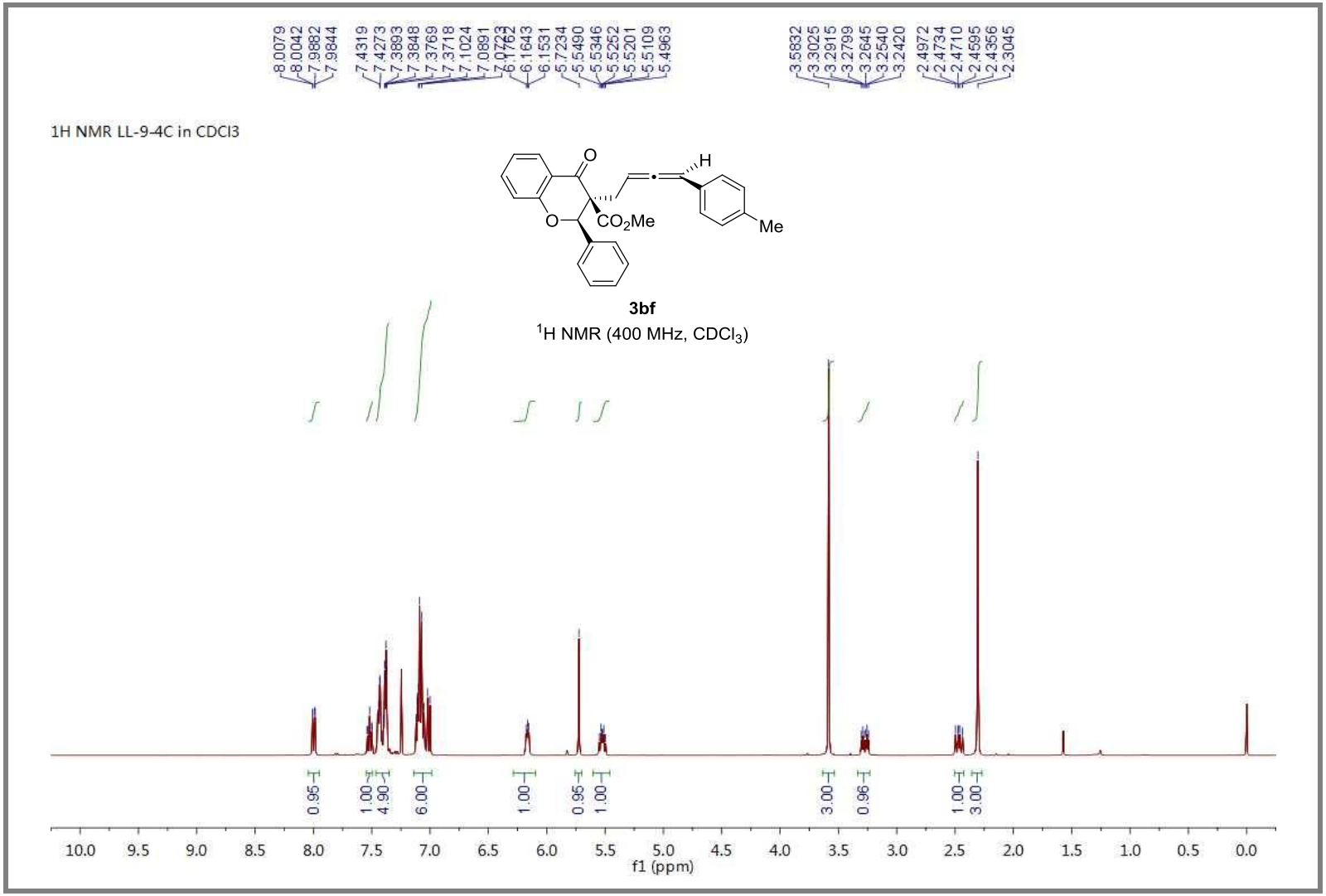
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1  11.494 VB    0.2387  281.79428   18.07372   2.1713
       2  13.892 BB    0.3105   70.44738    3.47928   0.5428
       3  16.508 VV    0.3752  298.75476   12.29424   2.3020
       4  21.442 BB    0.4605 1.23272e4   411.14001  94.9839

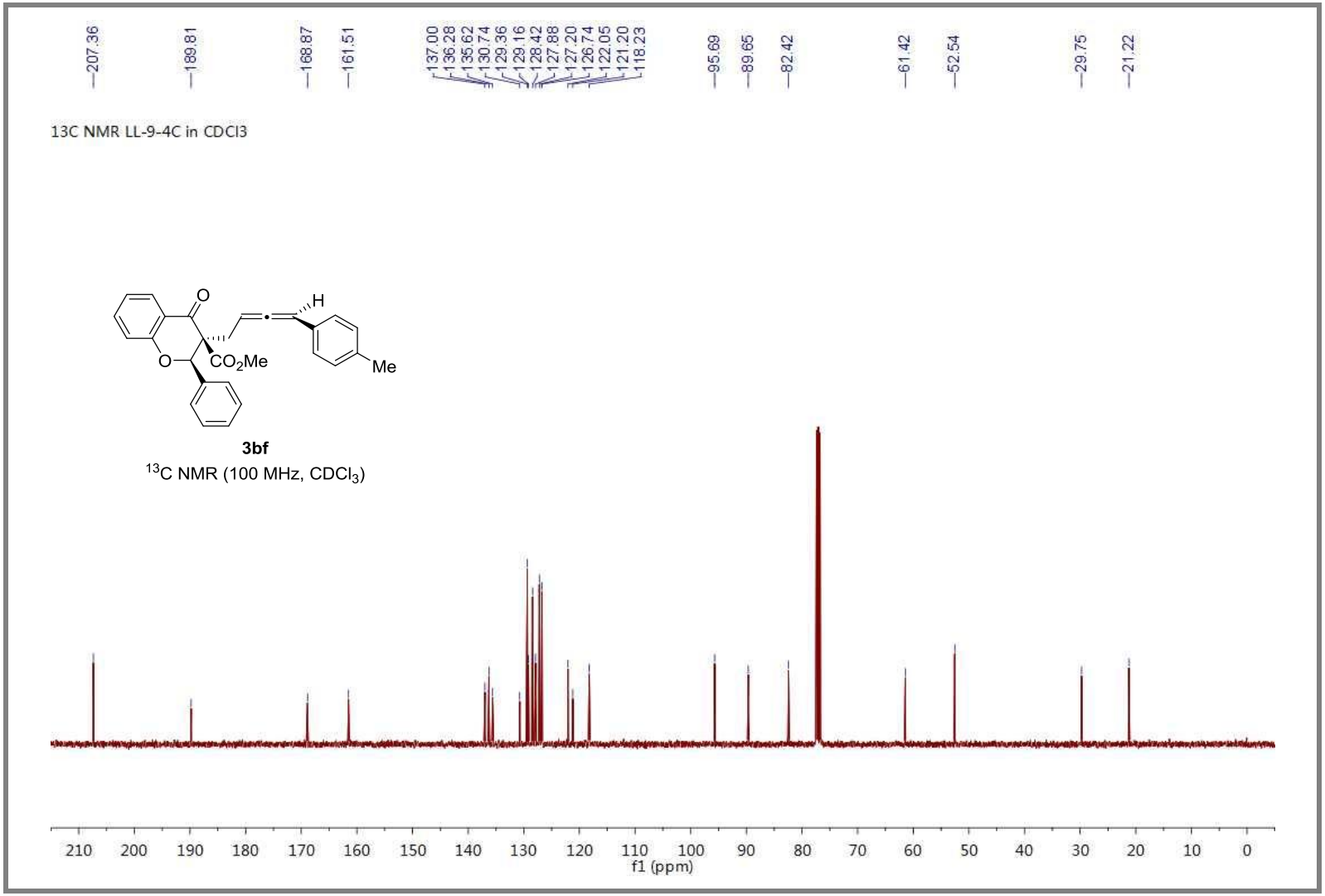
    Totals :                  1.29782e4   444.98725

    ======================================================================
                              *** End of Report ***
```



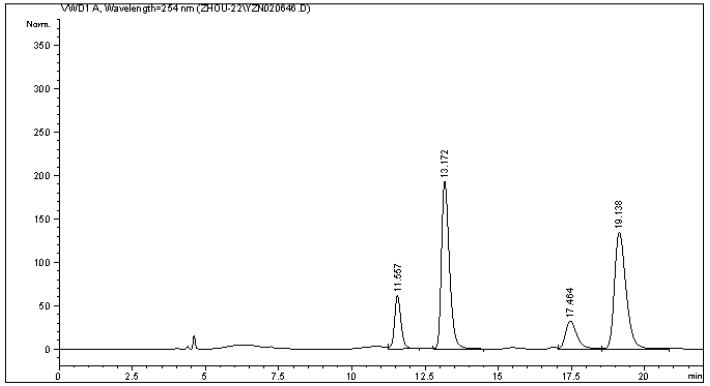
(-)-3be


8.0079
8.0042
7.9882
7.9844
7.4319
7.4273
7.3893
7.3848
7.3769
7.3718
7.1024
7.0891
7.0723
6.1762
6.1643
6.1531
5.7234
5.5490
5.5346
5.5252
5.5201
5.5109
5.4963
3.5832
3.3025
3.2915
3.2799
3.2645
3.2540
3.2420
2.4972
2.4734
2.4710
2.4595
2.4356
2.3045
1H NMR LL-9-4C in CDCl3
O
H
O
CO2Me
Me
3bf
1H NMR (400 MHz, CDCl3)
0.95
1.00
4.90
6.00
1.00
0.95
1.00
3.00
0.96
1.00
3.00
10.0
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)


207.36
189.81
168.87
161.51
137.00
136.28
135.62
130.74
129.36
129.16
128.42
127.88
127.20
126.74
122.05
121.20
118.23
95.69
89.65
82.42
61.42
52.54
29.75
21.22
13C NMR LL-9-4C in CDCl3
O
H
O
CO2Me
Me
3bf
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020646.D
Sample Name: LL-9-4C +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2/26/2022 4:41:28 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 2/26/2022 4:40:22 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 2/26/2022 5:04:41 AM
                  (modified after loading)
Sample Info     : OD-3, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm
```



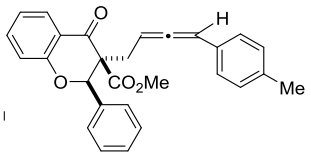

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  11.557 VB    0.2326  941.12762   61.42798  10.3031
   2  13.172 BB    0.2898 3635.43457  192.83620  39.7995
   3  17.464 VV    0.4106  874.47797   32.44318   9.5735
   4  19.138 VB    0.4216 3683.33350  134.44211  40.3239

Totals :                  9134.37366  421.14947
```



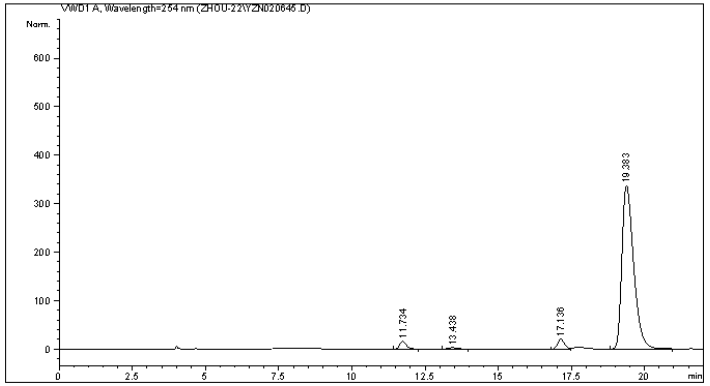
(+/-)-3bf

```
                        *** End of Report ***
```

Instrument 1 2/26/2022 5:04:43 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020645.D
Sample Name: LL-9-4C

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2/26/2022 4:17:56 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 2/26/2022 4:17:13 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 7:54:09 AM
                  (modified after loading)
Sample Info     : OD-3, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 nm
```



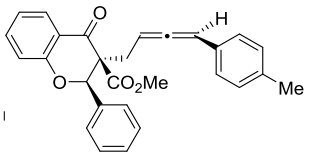

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  11.734 BB    0.2321  245.99806   16.23227   2.4633
   2  13.438 BB    0.2959   57.65097    2.97564   0.5773
   3  17.136 BV    0.2537  330.85602   20.20274   3.3130
   4  19.383 BB    0.4253 9352.09570  337.43399  93.6464

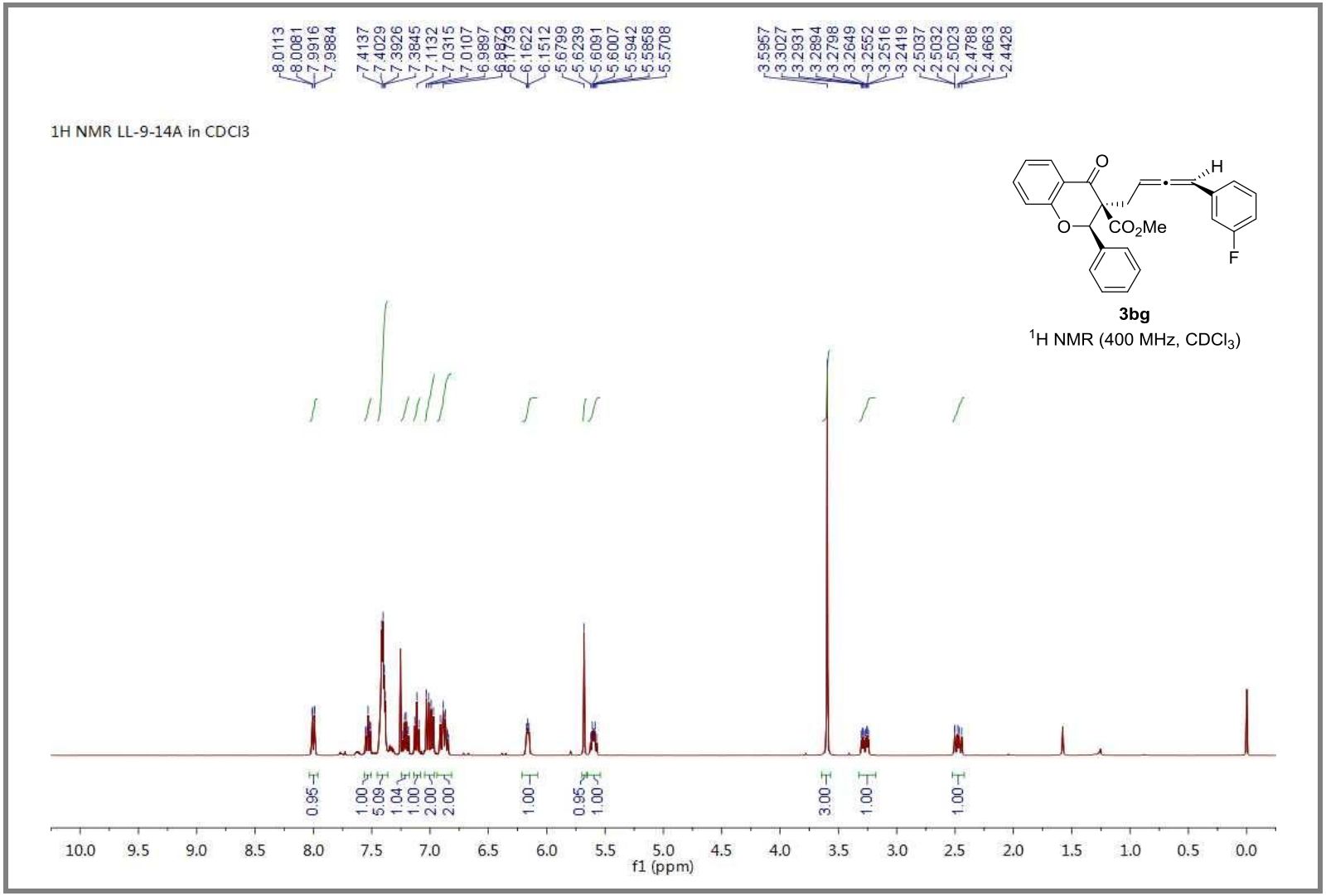
Totals :                  9986.60075  376.84464
```



(-)-3bf

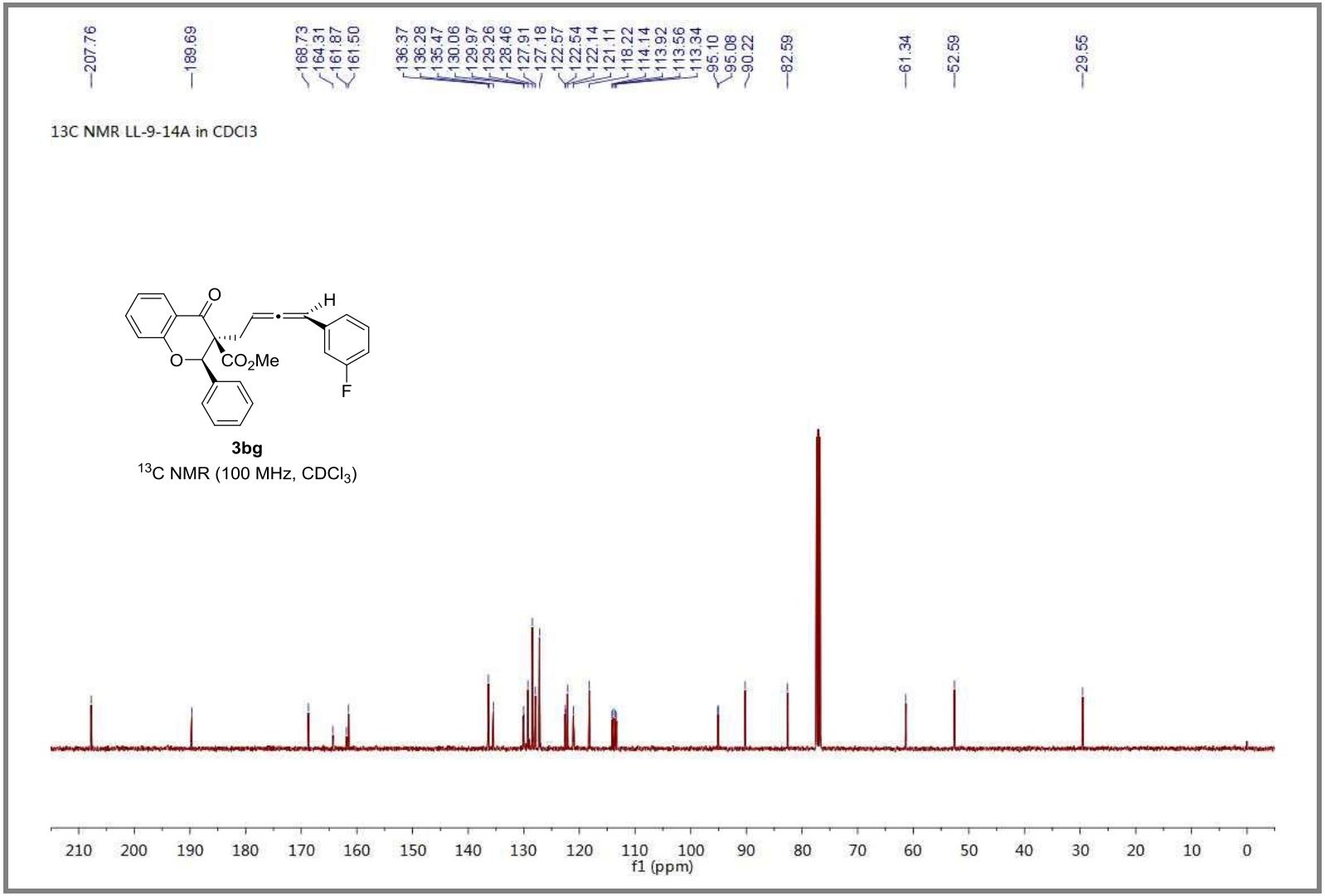
```
                        *** End of Report ***
```

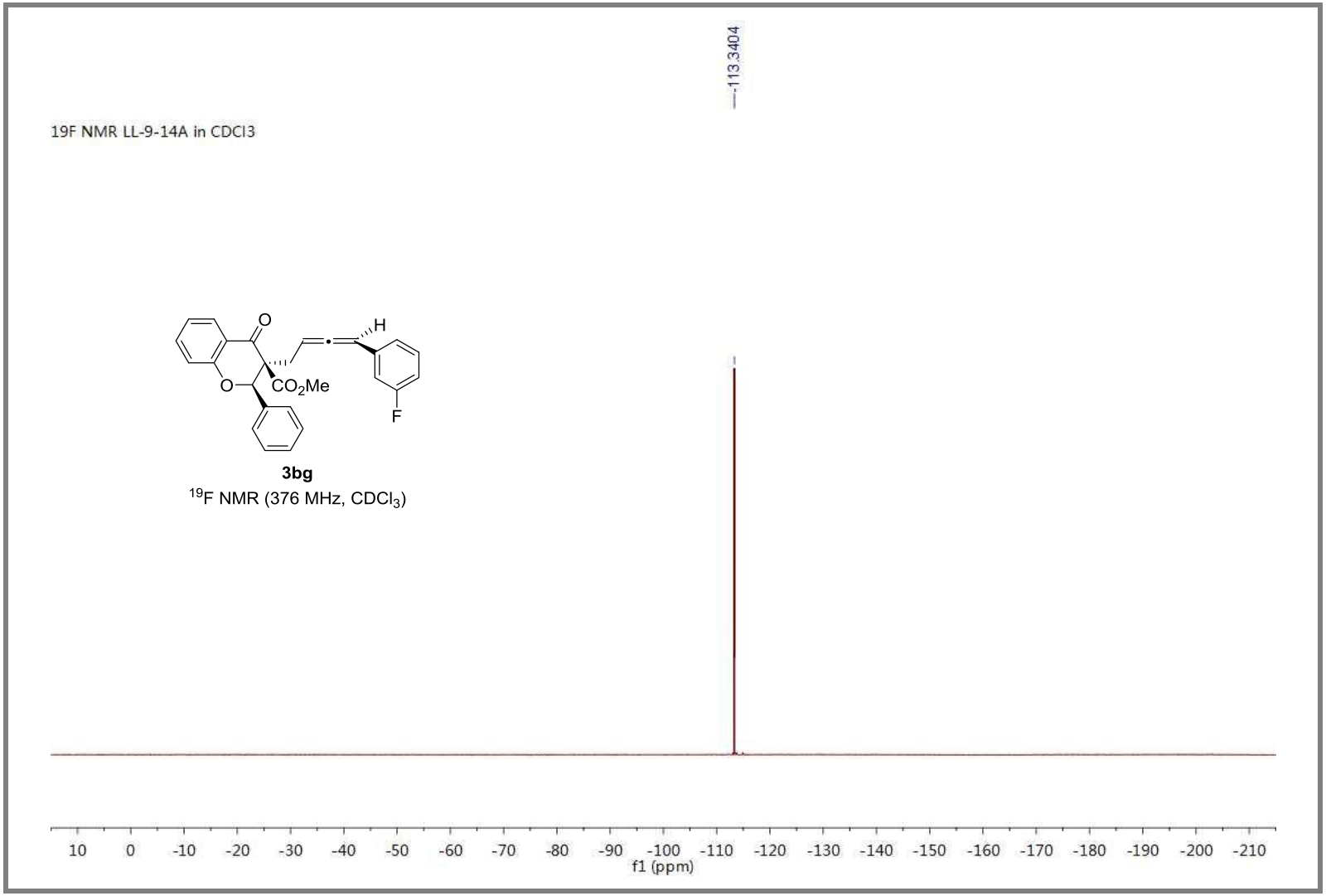
Instrument 1 6/15/2022 7:54:12 AM Page 1 of 1



3bg

^{1}H NMR (400 MHz, $CDCl_3$)


207.76
189.69
168.73
164.31
161.87
161.50
136.37
136.28
135.47
130.06
129.97
129.26
128.46
127.91
127.18
122.57
122.54
122.14
121.11
118.22
114.14
113.92
113.56
113.34
95.10
95.08
90.22
82.59
61.34
52.59
29.55
13C NMR LL-9-14A in CDCl3
O
H
O
CO2Me
F
3bg
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

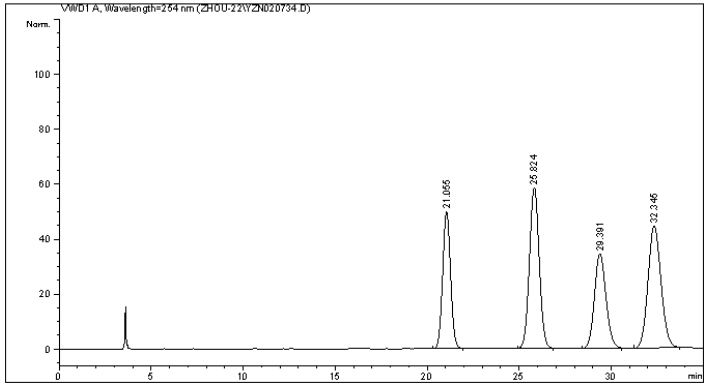


3bg

^{19}F NMR (376 MHz, $CDCl_3$)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020734.D
Sample Name: LL-9-14A +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/10/2022 9:39:24 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/10/2022 9:20:39 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/10/2022 10:45:50 PM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 98/2, 1.0 mL/min, 30 oC, 254 nm
```



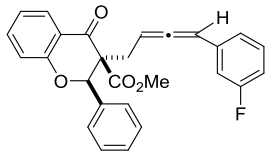

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  21.055 BB    0.4605 1489.24036   49.87651  20.2912
   2  25.824 BB    0.5754 2167.15796   58.62949  29.5280
   3  29.391 BB    0.6744 1502.19189   34.37493  20.4677
   4  32.345 BB    0.7521 2180.73877   44.51692  29.7131

Totals :                  7339.32898  187.39785
```

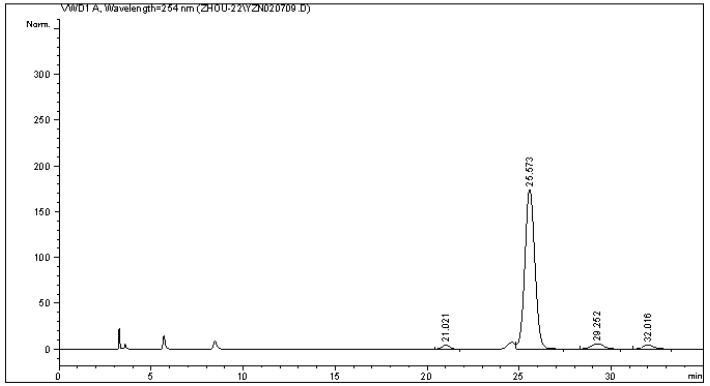


(+/-)-3bg

```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020709.D
Sample Name: LL-9-14 A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/9/2022 4:27:35 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/9/2022 4:24:51 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 4:58:16 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 98/2, 1.0 mL/min, 30 oC, 254 nm
```



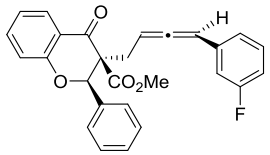

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

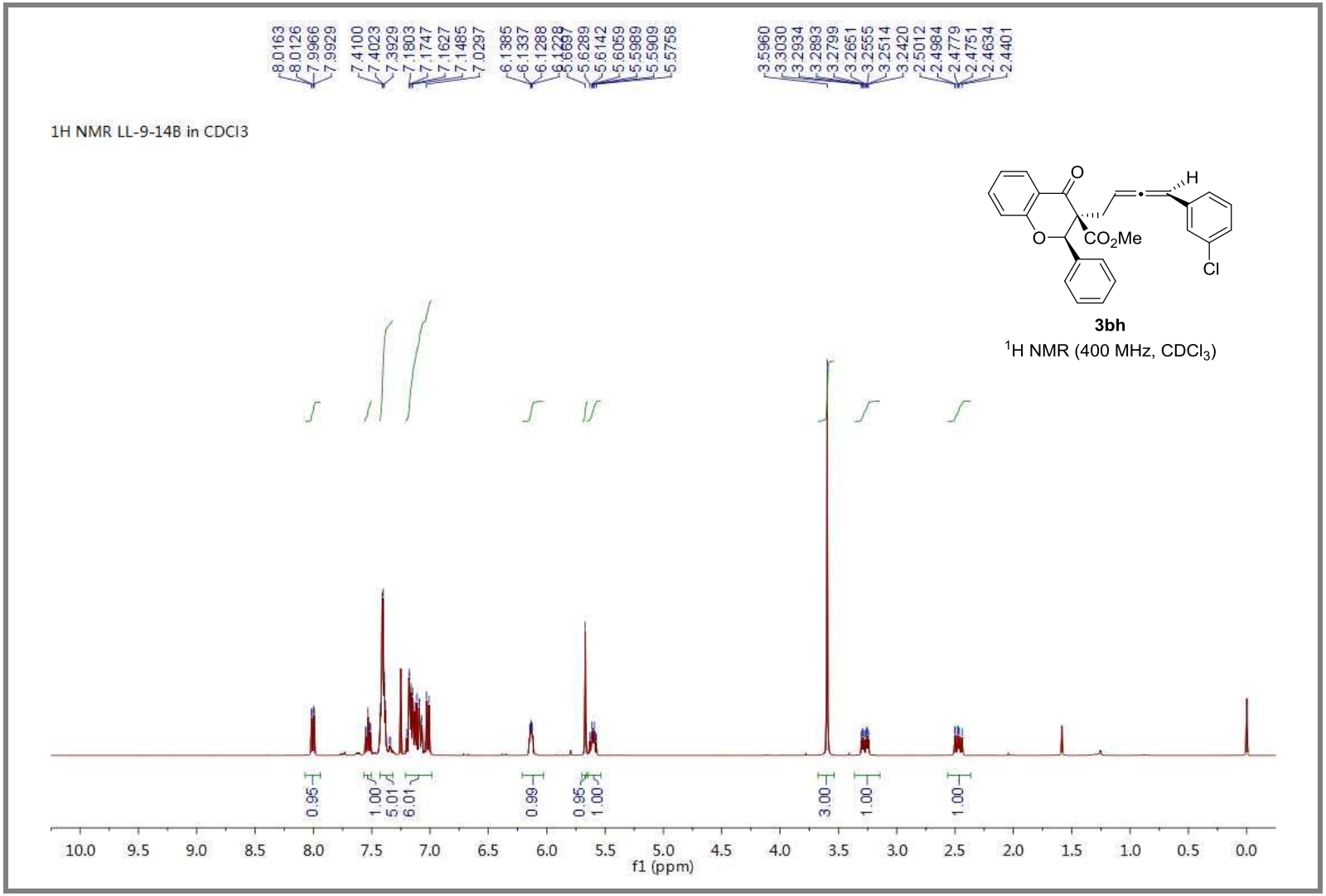
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  21.021 BB    0.4359  126.30781    4.53140   1.7663
   2  25.573 VB    0.5850 6576.21143  174.61166  91.9627
   3  29.252 BB    0.7254  267.64407    5.79272   3.7428
   4  32.016 BB    0.6045  180.79289    4.53857   2.5282

Totals :                  7150.95620  189.47435
```



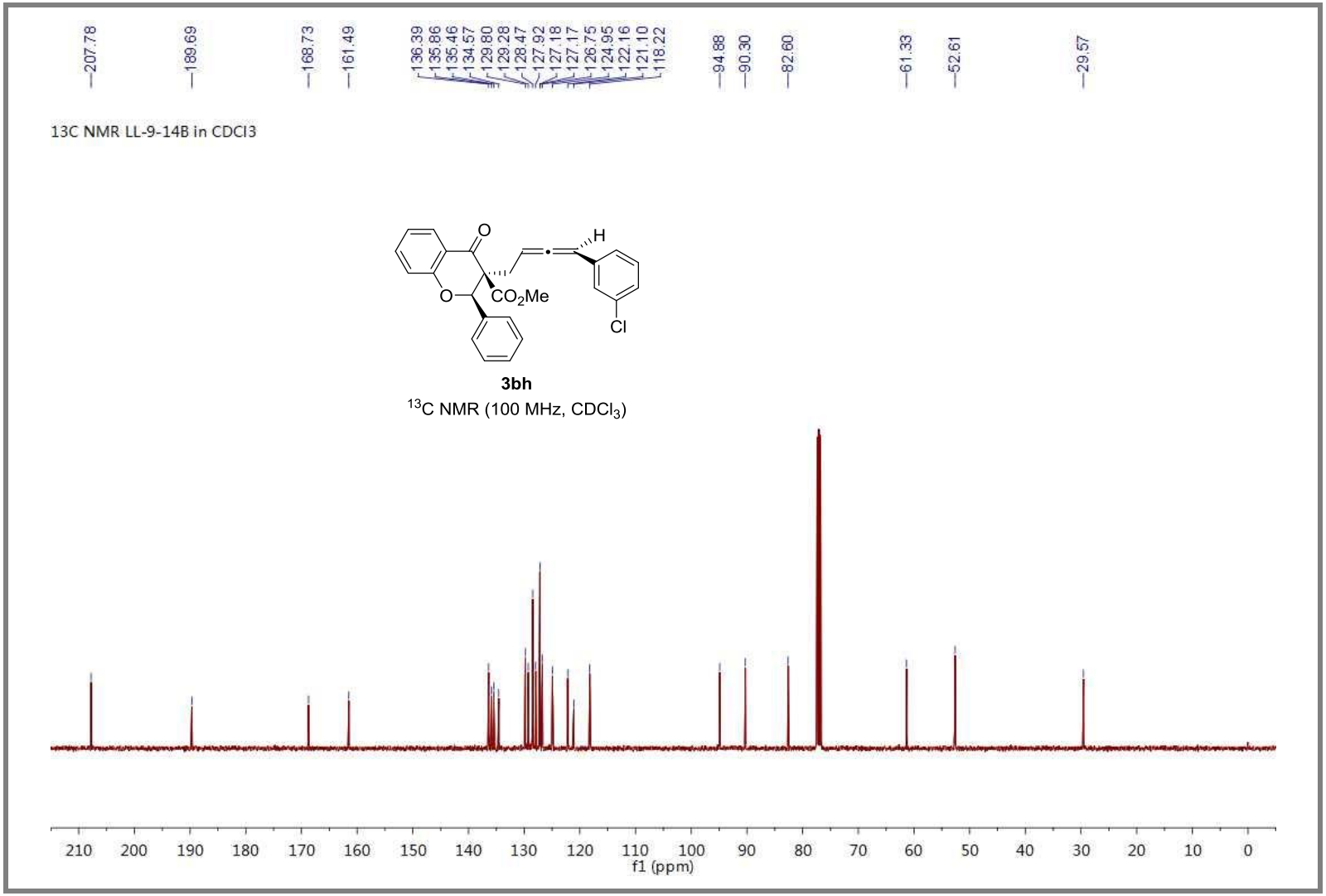
(-)-3bg

```
                          *** End of Report ***
```



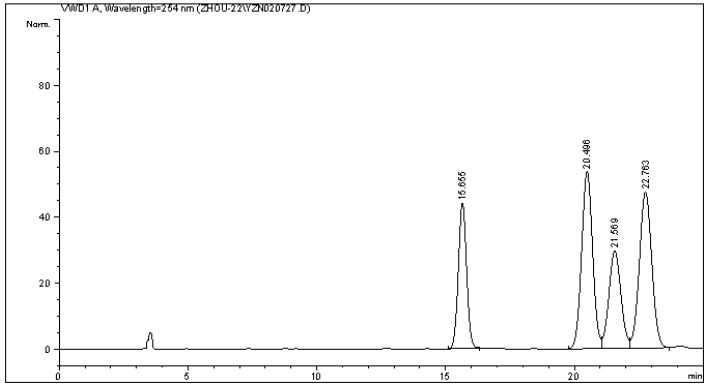
3bh

^{1}H NMR (400 MHz, $CDCl_3$)


207.78
189.69
168.73
161.49
136.39
135.86
135.46
134.57
129.80
129.28
128.47
127.92
127.18
127.17
126.75
124.95
122.16
121.10
118.22
94.88
90.30
82.60
61.33
52.61
29.57
13C NMR LL-9-14B in CDCl3
O
H
O
CO2Me
Cl
3bh
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020727.D
Sample Name: LL-9-14B +/- (11)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/10/2022 4:12:39 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/10/2022 3:54:50 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/10/2022 8:41:23 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 96.5/3.5, 1.0 mL/min, 30 oC, 254 nm
```



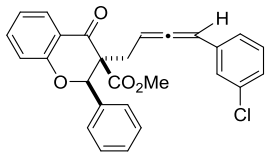
Area Percent Report

```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  15.655 BB    0.3470  980.72534   44.06423  19.0929
   2  20.496 BV    0.4622 1599.76135   53.76189  31.1444
   3  21.569 VV    0.5027  963.63342   29.66976  18.7601
   4  22.763 VB    0.5233 1592.47852   47.36810  31.0026

Totals :                  5136.59863  174.86398
```

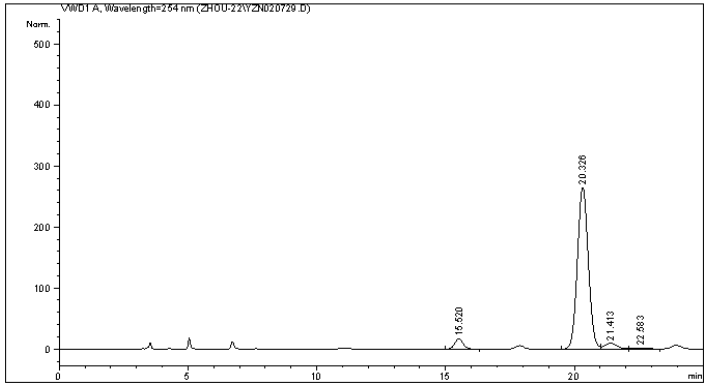


(+/-)-3bh

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020729.D
Sample Name: LL-9-14B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/10/2022 7:24:27 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/10/2022 7:23:31 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 5:01:41 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 96.5/3.5, 1.0 mL/min, 30 oC, 254 nm
```



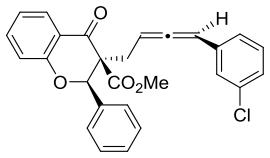
Area Percent Report

```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

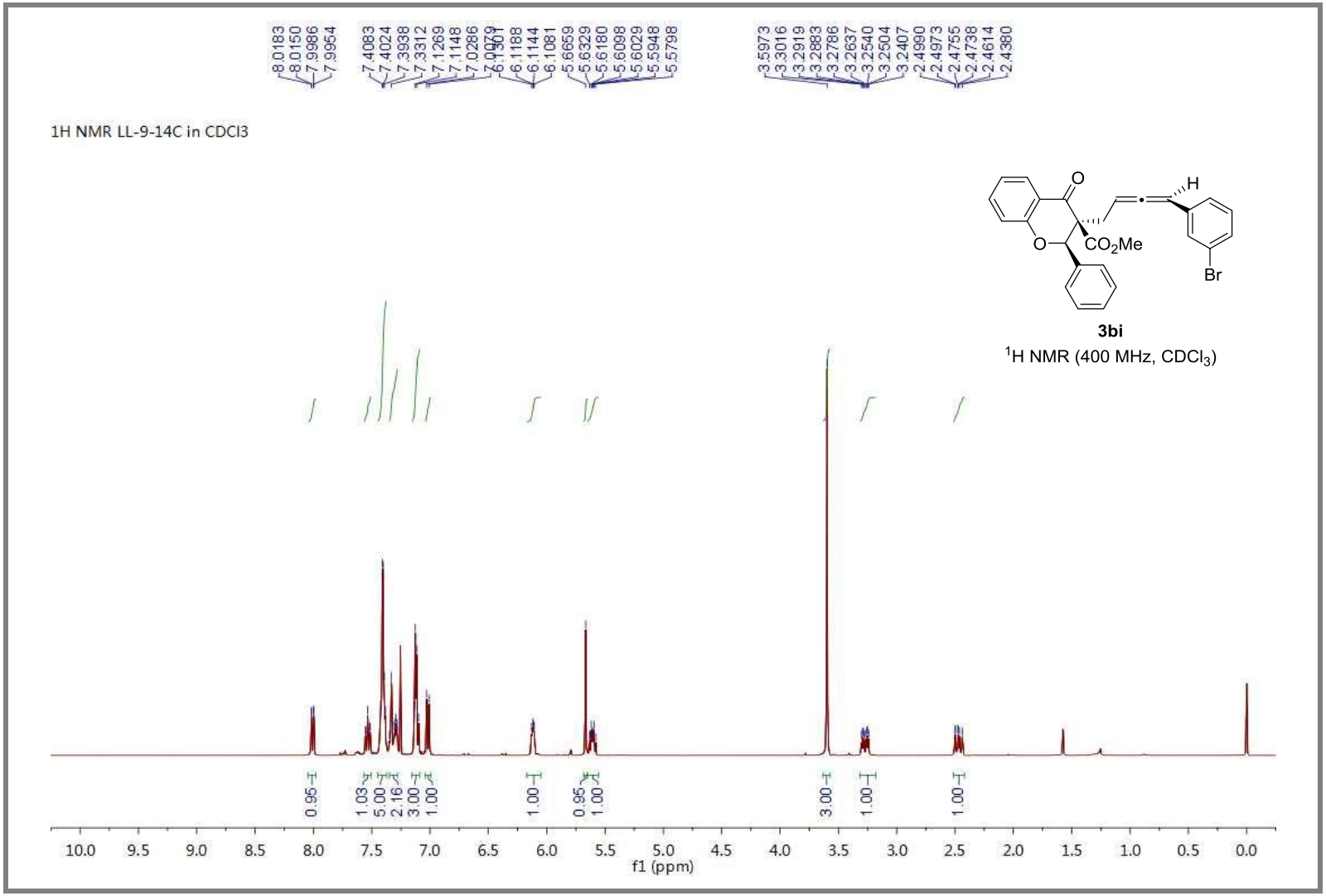
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  15.520 BB    0.3452  369.87930   16.73534   4.3393
   2  20.326 BV    0.4562 7788.28125  265.19955  91.3689
   3  21.413 VV    0.5009  303.66852    9.28656   3.5625
   4  22.583 VV    0.5328   62.16397    1.81847   0.7293

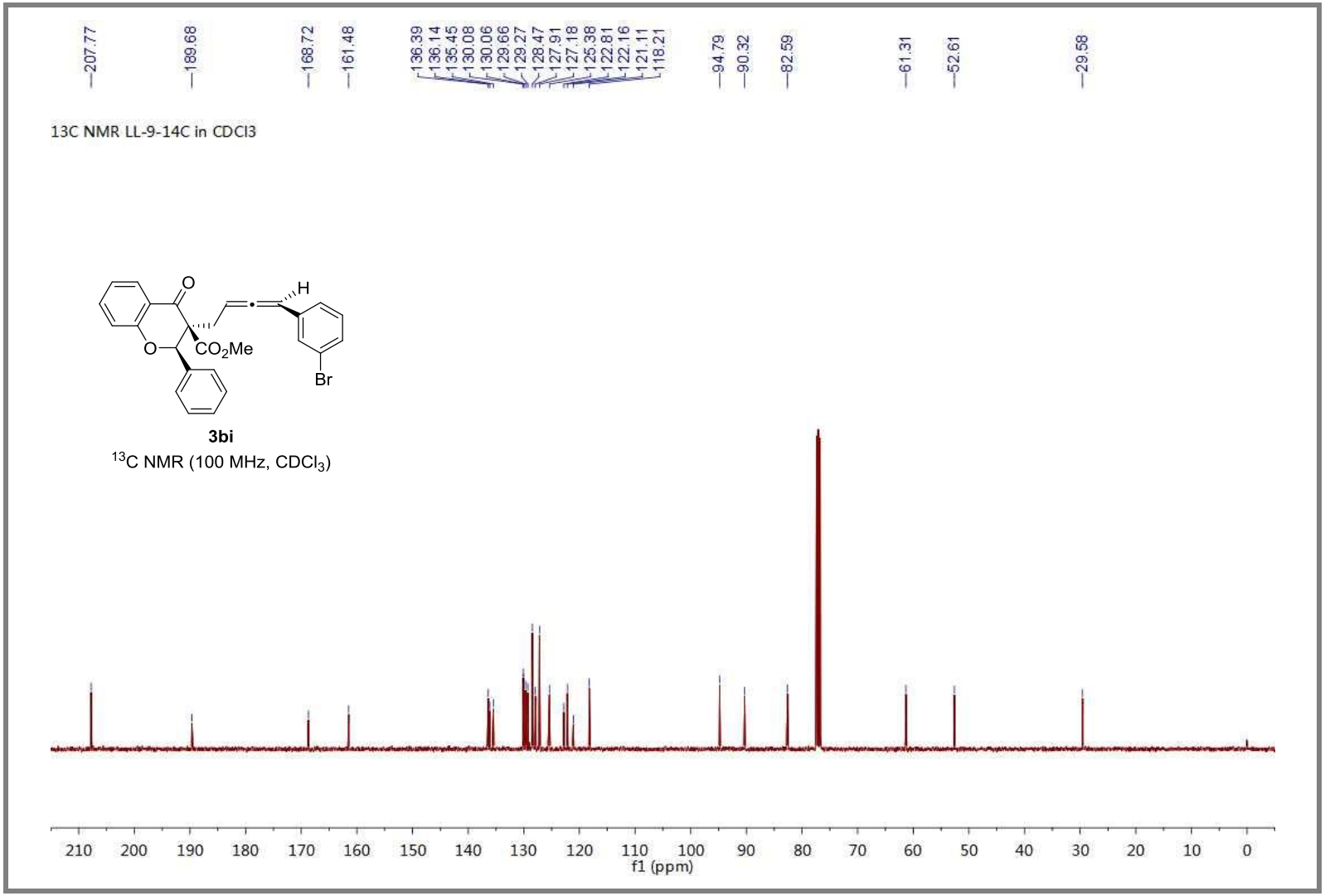
Totals :                  8523.99304  293.03992
```



(-)-3bh

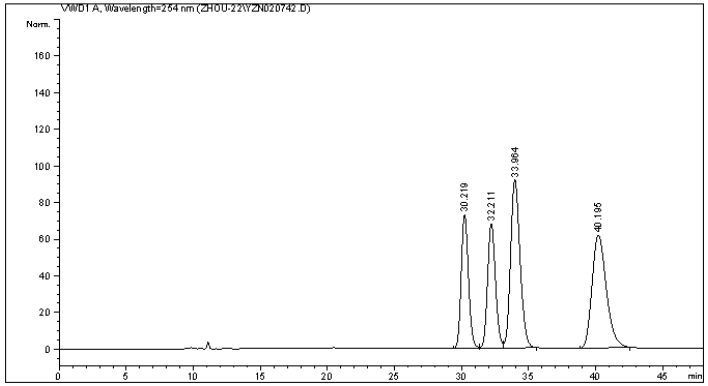
*** End of Report ***


1H NMR LL-9-14C in CDCl3
8.0183
8.0150
7.9986
7.9954
7.4083
7.4024
7.3938
7.3312
7.1269
7.1148
7.0286
6.1188
6.1144
6.1081
5.6659
5.6329
5.6180
5.6098
5.6029
5.5948
5.5798
3.5973
3.3016
3.2919
3.2883
3.2786
3.2637
3.2540
3.2504
3.2407
2.4990
2.4973
2.4755
2.4738
2.4614
2.4380
O
H
CO2Me
O
Br
3bi
1H NMR (400 MHz, CDCl3)
0.95
1.03
5.00
2.16
3.00
1.00
1.00
0.95
1.00
3.00
1.00
1.00
10.0
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)


207.77
189.68
168.72
161.48
136.39
136.14
135.45
130.08
130.06
129.66
129.27
128.47
127.91
127.18
125.38
122.81
122.16
121.11
118.21
94.79
90.32
82.59
61.31
52.61
29.58
13C NMR LL-9-14C in CDCl3
O
H
O
CO2Me
Br
3bi
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020742.D
Sample Name: LL-9-14C +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/11/2022 10:15:34 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/11/2022 9:38:00 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/12/2022 3:01:50 AM
                  (modified after loading)
Sample Info     : AS-H*2, Hexane/i-PrOH = 97/3, 0.7 mL/min, 30 oC, 254 nm
```



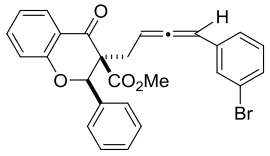
Area Percent Report

```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  30.219 BB    0.5790 2731.96191   72.80563  18.7275
   2  32.211 BV    0.6321 2785.74146   68.03014  19.0961
   3  33.964 VB    0.7554 4497.72119   91.73990  30.8317
   4  40.195 BB    1.1143 4572.56738   61.75148  31.3447

Totals :                  1.45880e4   294.32714
```

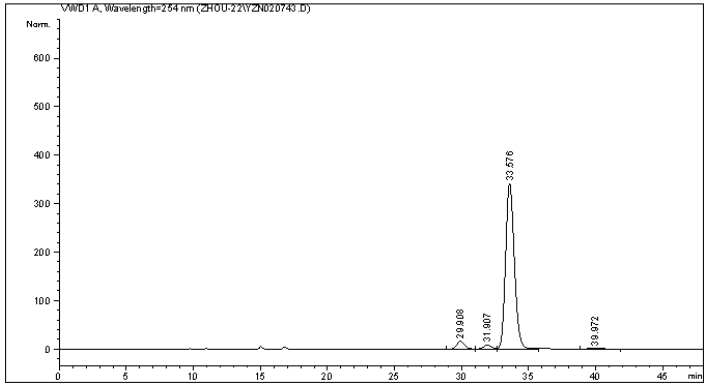


(+/-)-3bi

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020743.D
Sample Name: LL-9-14C

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/11/2022 11:30:09 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/11/2022 11:04:16 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 5:04:47 AM
                  (modified after loading)
Sample Info     : AS-H*2, Hexane/i-PrOH = 97/3, 0.7 mL/min, 30 oC, 254 nm
```



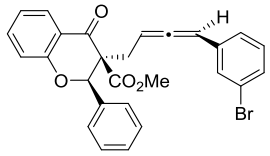
Area Percent Report

```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

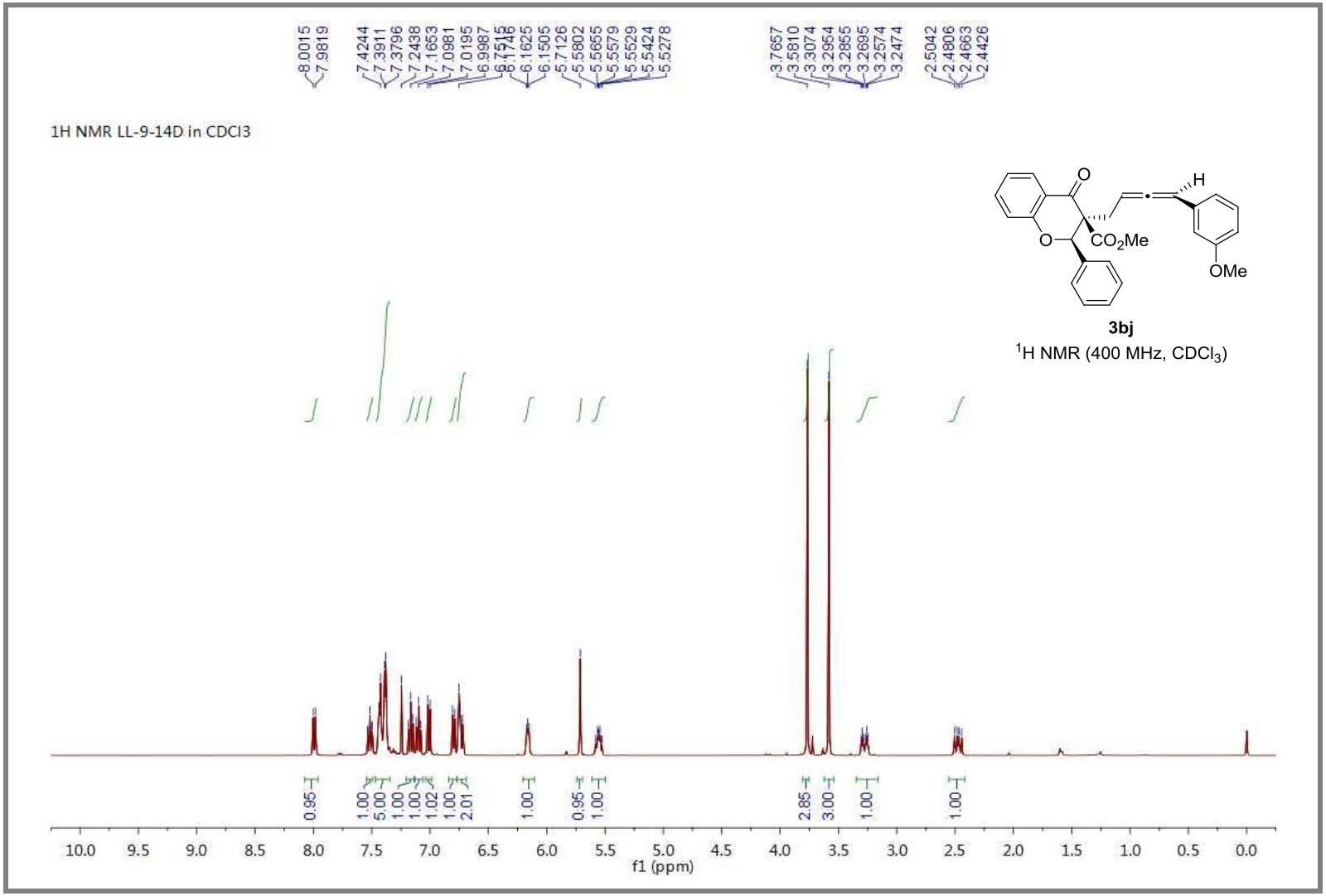
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  29.908 BV    0.6071  623.25531   15.95604   3.7716
   2  31.907 VV    0.6471  328.42636    7.82199   1.9875
   3  33.576 VV    0.7003 1.54821e4   341.74258  93.6888
   4  39.972 BB    0.9205   91.24649    1.26014   0.5522

Totals :                  1.65250e4   366.78075
```



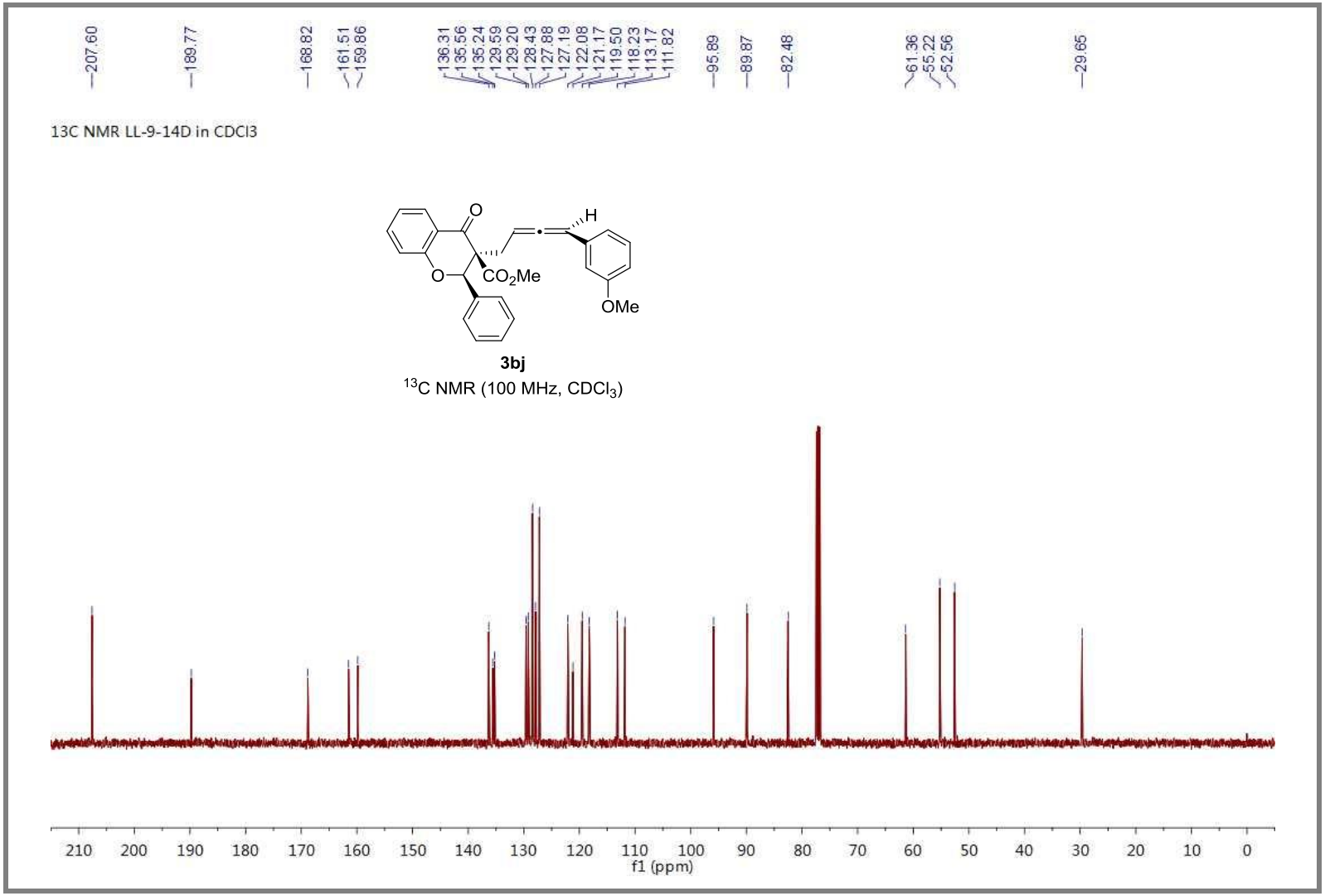
(-)-3bi

*** End of Report ***



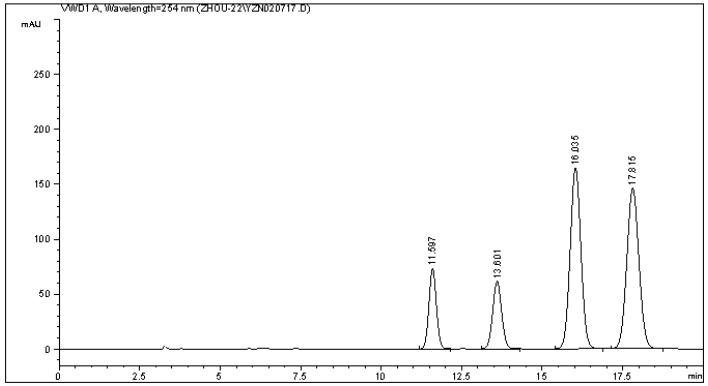
3bj

^{1}H NMR (400 MHz, $CDCl_3$)


207.60
189.77
168.82
161.51
159.86
136.31
135.56
135.24
129.59
129.20
128.43
127.88
127.19
122.08
121.17
119.50
118.23
113.17
111.82
95.89
89.87
82.48
61.36
55.22
52.56
29.65
13C NMR LL-9-14D in CDCl3
O
H
O
CO2Me
OMe
3bj
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020717.D
Sample Name: LL-9-14D +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/9/2022 10:04:02 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/9/2022 9:26:59 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/9/2022 11:07:55 PM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```



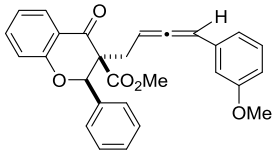

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  11.597 BB    0.2538 1187.90027   73.03640  11.8266
   2  13.601 BB    0.3030 1194.94287   61.33486  11.8967
   3  16.035 BB    0.3623 3821.21606  164.78664  38.0436
   4  17.815 BB    0.4085 3840.24072  146.11418  38.2330

Totals :                  1.00443e4   445.27208
```

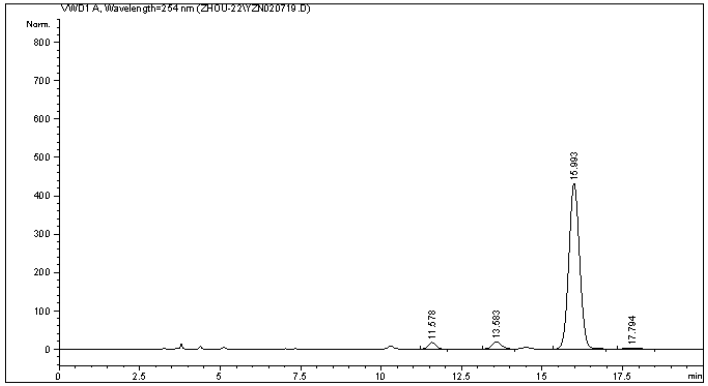


(+/-)-3bj

```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020719.D
Sample Name: LL-9-14D

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/9/2022 10:48:21 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/9/2022 10:47:15 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 7:42:54 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```



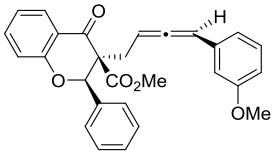

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

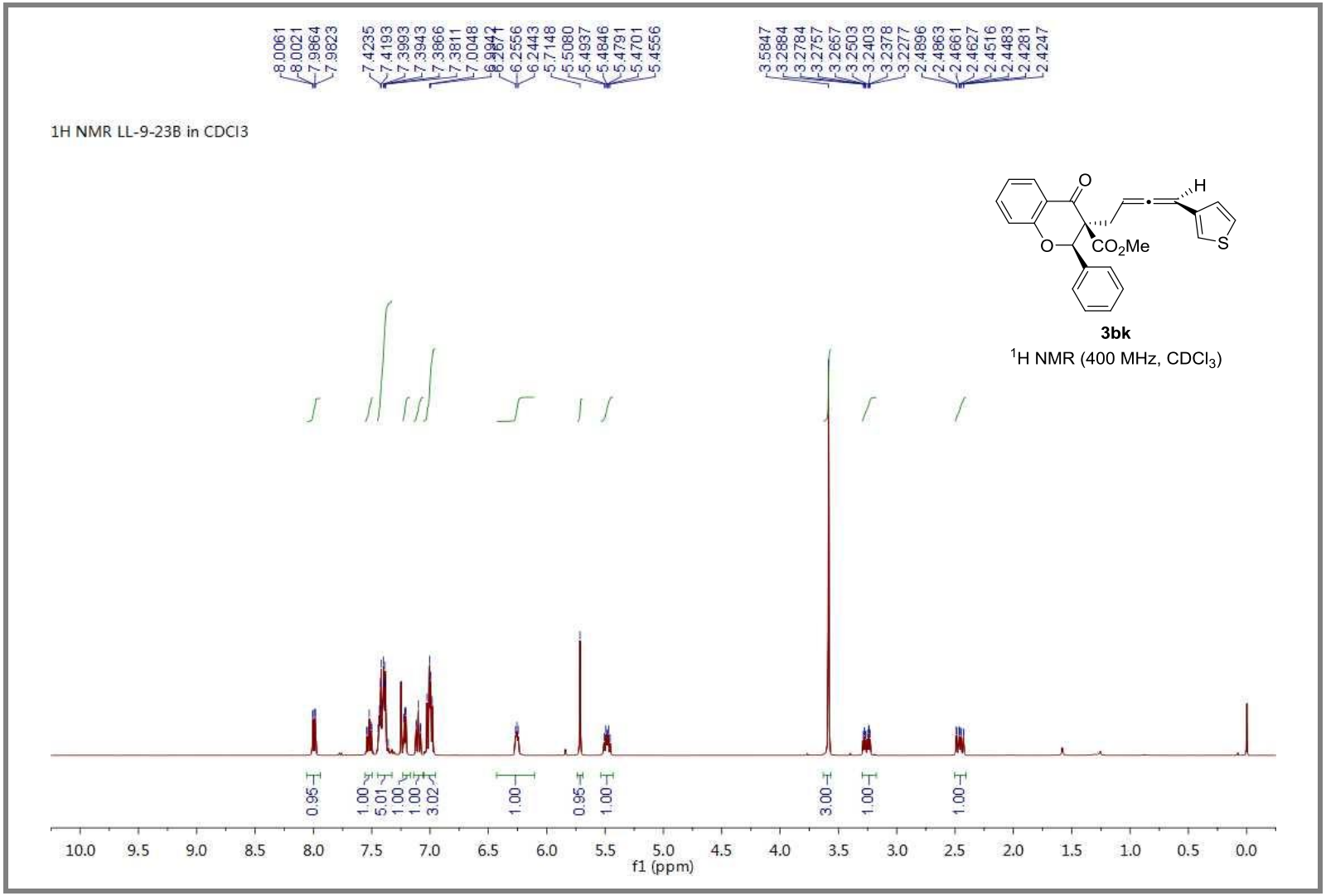
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  11.578 BB    0.2544  278.29999   17.05905   2.6014
   2  13.583 BB    0.3163  378.79193   18.59351   3.5407
   3  15.993 BB    0.3601 9988.02344  431.86627  93.3622
   4  17.794 BB    0.4003   53.03202    2.06328   0.4957

Totals :                  1.06981e4   469.58212
```



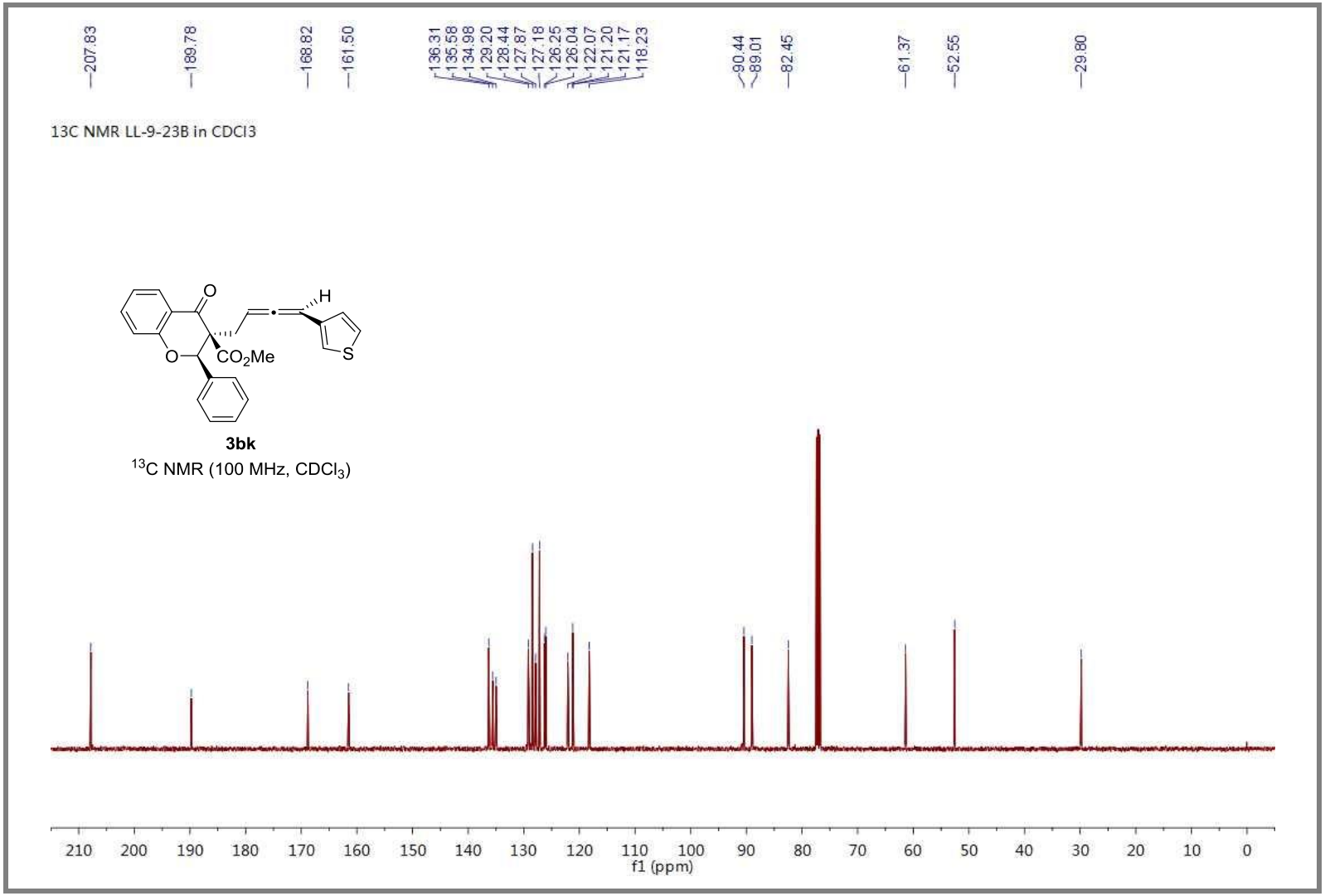
(-)-3bj

```
                          *** End of Report ***
```



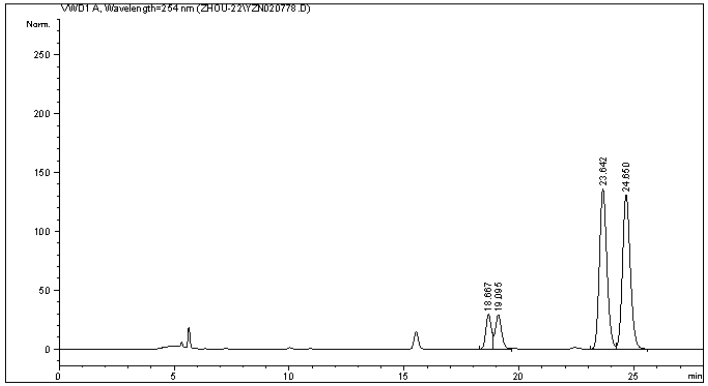
3bk

^{1}H NMR (400 MHz, $CDCl_3$)


207.83
189.78
168.82
161.50
136.31
135.58
134.98
129.20
128.44
127.87
127.18
126.25
126.04
122.07
121.20
121.17
118.23
90.44
89.01
82.45
61.37
52.55
29.80
13C NMR LL-9-23B in CDCl3
O
H
O
CO2Me
S
3bk
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020778.D
Sample Name: LL-9-23B +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/17/2022 9:14:09 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/17/2022 9:06:21 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/17/2022 9:46:38 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 94/6, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

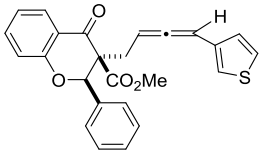
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.667 BV    0.2585  494.46790   29.45338   6.8550
   2  19.095 VB    0.2783  533.12946   29.03381   7.3909
   3  23.642 BV    0.3487 3085.68091  136.25540  42.7777
   4  24.650 VB    0.3648 3100.00732  131.04520  42.9764

Totals :                  7213.28558  325.78779

                        *** End of Report ***
```

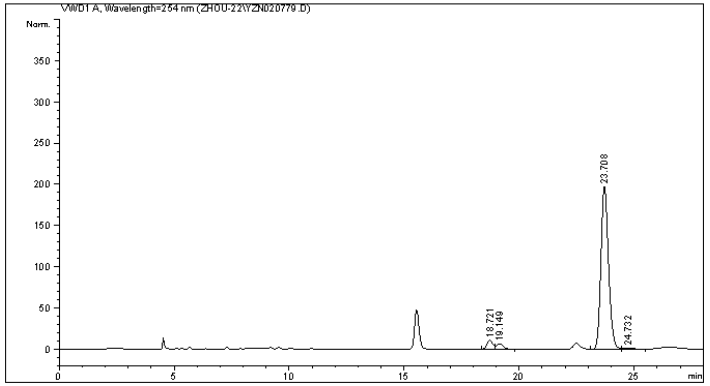


(+/-)-3bk

Instrument 1 3/17/2022 9:46:47 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020779.D
Sample Name: LL-9-23B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/17/2022 9:45:37 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/17/2022 9:42:44 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 4:53:16 AM
                  (modified after loading)
Sample Info     : AD-3, Hexane/i-PrOH = 94/6, 0.7 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

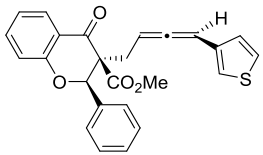
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.721 BV    0.2694  187.69525   10.81949   3.8552
   2  19.149 VB    0.2803  119.87869    6.46915   2.4623
   3  23.708 VV    0.3519 4523.33008  197.32307  92.9075
   4  24.732 VB    0.3947   37.73370    1.44586   0.7750

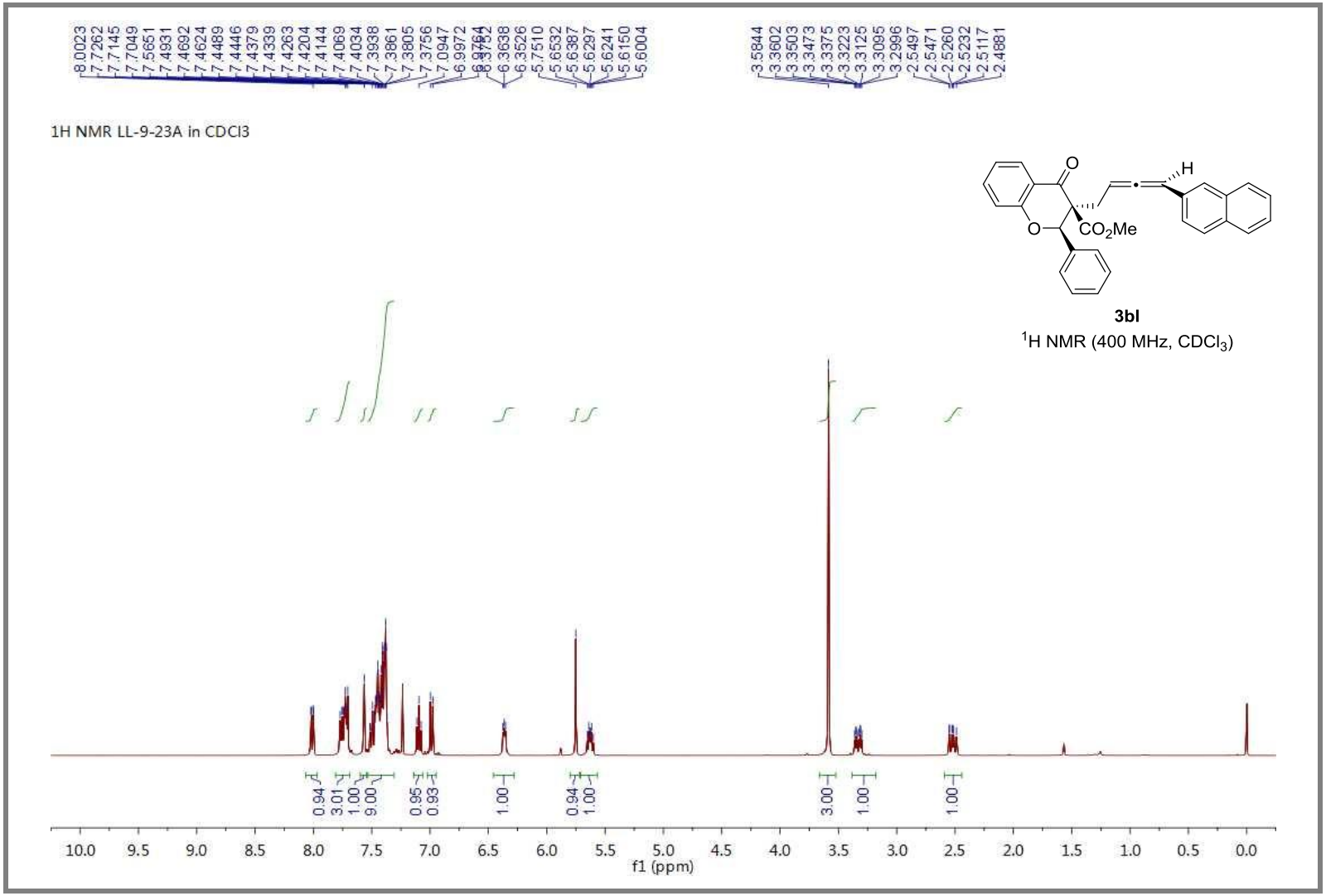
Totals :                  4868.63772  216.05758

                        *** End of Report ***
```



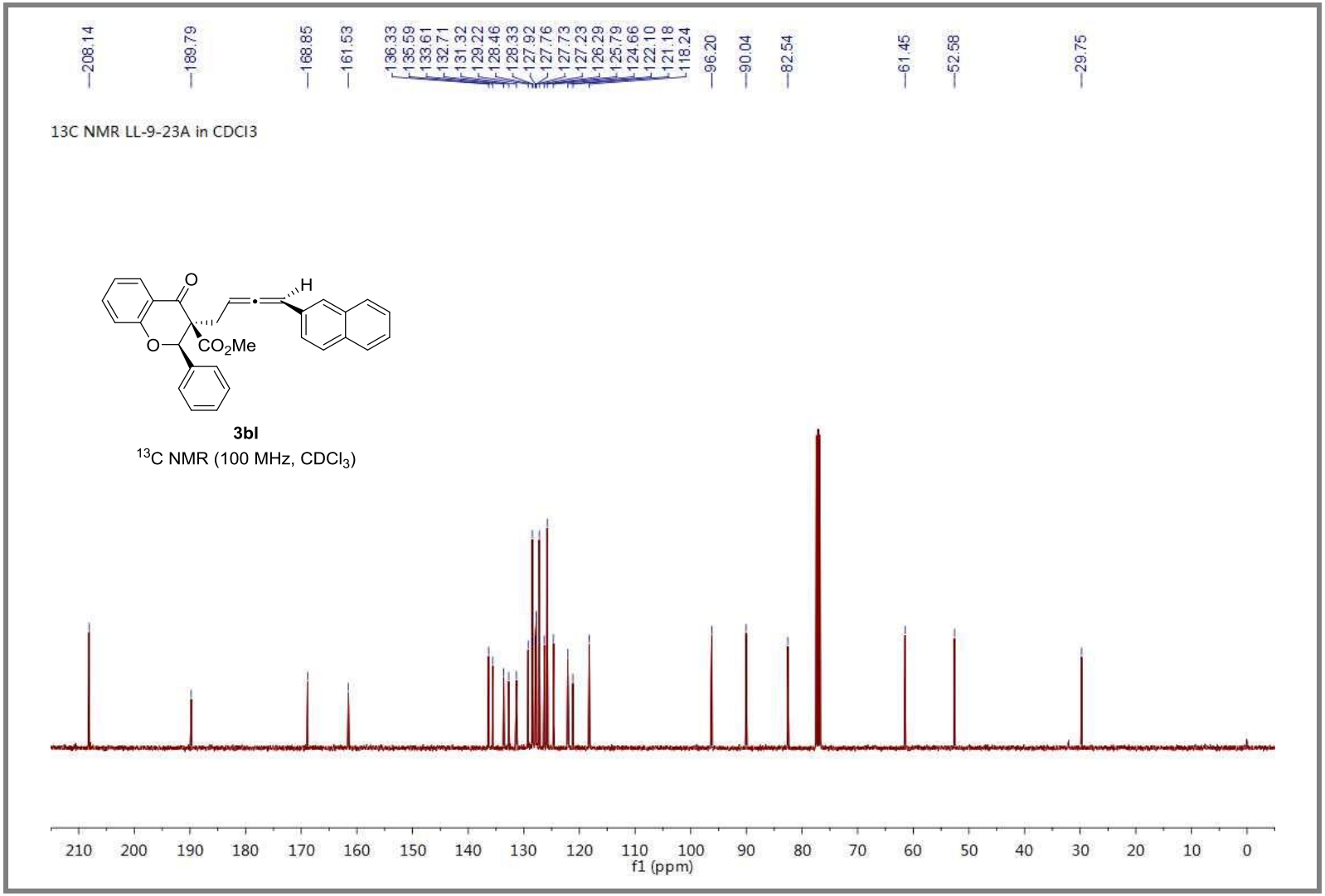
(-)-3bk

Instrument 1 6/15/2022 4:53:23 AM Page 1 of 1



3bl

^{1}H NMR (400 MHz, $CDCl_3$)

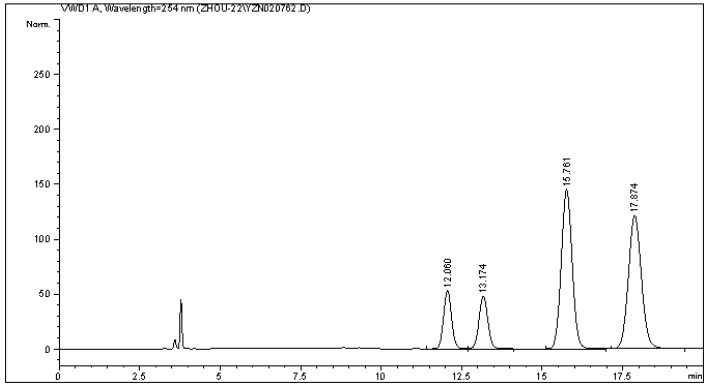


3bl

^{13}C NMR (100 MHz, $CDCl_3$)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020762.D
Sample Name: LL-9-23A +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/16/2022 7:43:07 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/16/2022 7:41:24 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 4:44:50 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

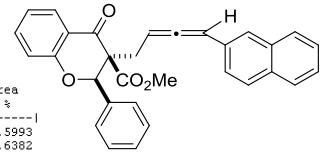
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|-------|
   1  12.060 VV    0.2685  919.55884   53.22244  10.5993
   2  13.174 VB    0.3008  922.93939   47.83205  10.6382
   3  15.761 BB    0.3673 3409.43750  145.10915  39.2988
   4  17.874 BB    0.4372 3423.75244  121.25208  39.4638

Totals :                  8675.68817  367.41571

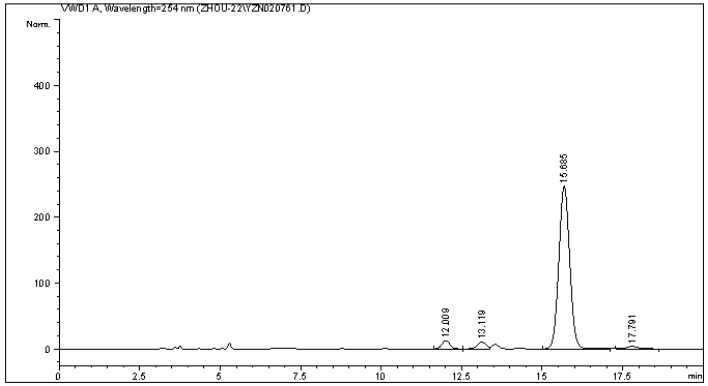
                          *** End of Report ***
```



(+/-)-3bl

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020761.D
Sample Name: LL-9-23A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/16/2022 7:21:04 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/16/2022 6:39:23 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 4:43:35 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

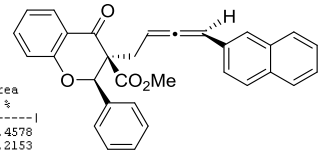
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

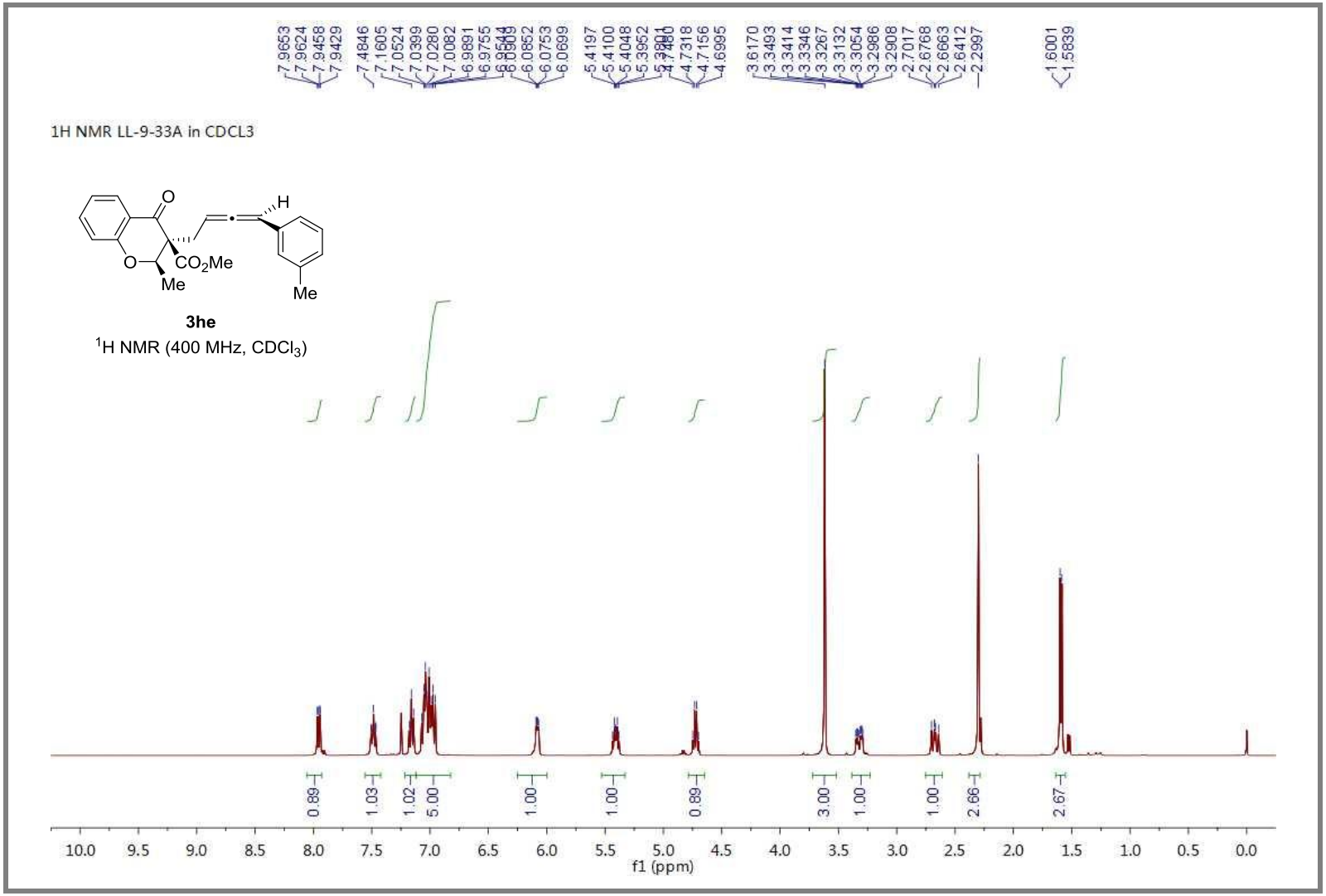
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|-------|
   1  12.009 BV    0.2665  217.30882   12.70723   3.4578
   2  13.119 VV    0.2936  202.06879   10.67644   3.2153
   3  15.685 BB    0.3659 5772.92822  246.96793  91.8572
   4  17.791 BB    0.3742   92.37219    3.75670   1.4698

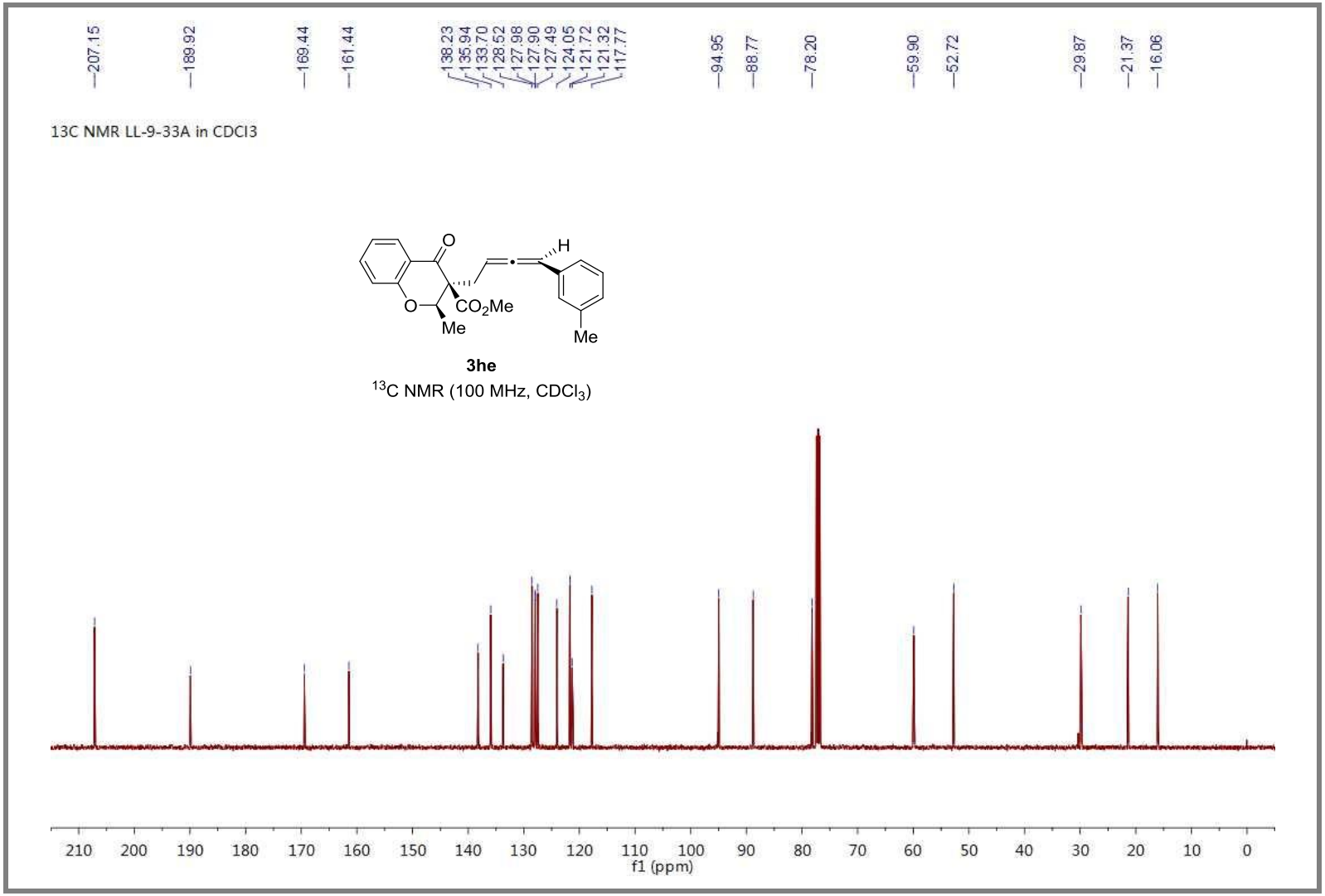
Totals :                  6284.67802  274.10829

                          *** End of Report ***
```



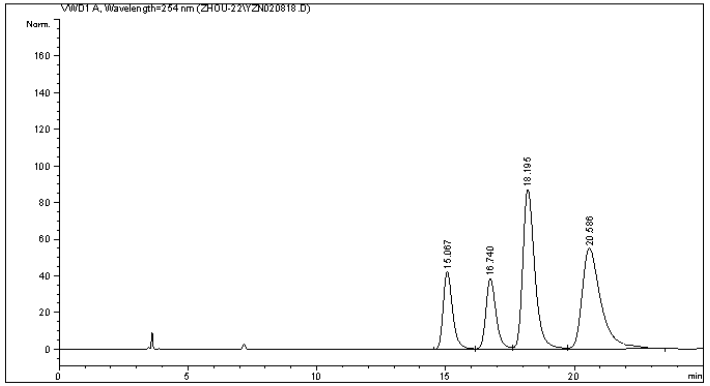
(-)-3bl


7.9653
7.9624
7.9458
7.9429
7.4846
7.1605
7.0524
7.0399
7.0280
7.0082
6.9891
6.9755
6.0909
6.0852
6.0753
6.0699
5.4197
5.4100
5.4048
5.3952
4.7318
4.7156
4.6995
3.6170
3.3493
3.3414
3.3346
3.3267
3.3132
3.3054
3.2986
3.2908
2.7017
2.6768
2.6663
2.6412
2.2997
1.6001
1.5839
1H NMR LL-9-33A in CDCL3
O
H
O
CO2Me
Me
Me
3he
1H NMR (400 MHz, CDCl3)
0.89
1.03
1.02
5.00
1.00
1.00
0.89
3.00
1.00
1.00
2.66
2.67
10.0
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)


207.15
189.92
169.44
161.44
138.23
135.94
133.70
128.52
127.98
127.90
127.49
124.05
121.72
121.32
117.77
94.95
88.77
78.20
59.90
52.72
29.87
21.37
16.06
13C NMR LL-9-33A in CDCl3
O
H
O
CO2Me
Me
Me
3he
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020818.D
Sample Name: LL-9-33A +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/23/2022 5:07:09 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 5:05:33 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 8:37:37 AM
                  (modified after loading)
Sample Info     : ID, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



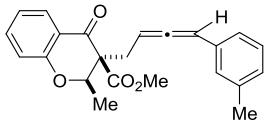

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  15.067 BV    0.3869 1076.42566   42.34293  13.9090
   2  16.740 VV    0.4183 1056.60730   38.60597  13.6529
   3  18.195 VV    0.4912 2811.66382   87.19404  36.3309
   4  20.586 VB    0.7624 2794.34814   54.92817  36.1071

Totals :                  7739.04492  223.07110
```

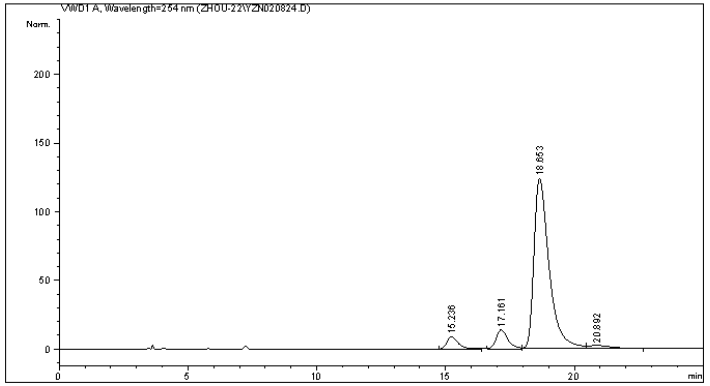


(+/-)-3he

```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020824.D
Sample Name: LL-9-33A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/23/2022 8:26:43 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 8:06:34 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 3:07:38 AM
                  (modified after loading)
Sample Info     : ID, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



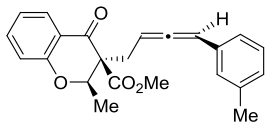

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

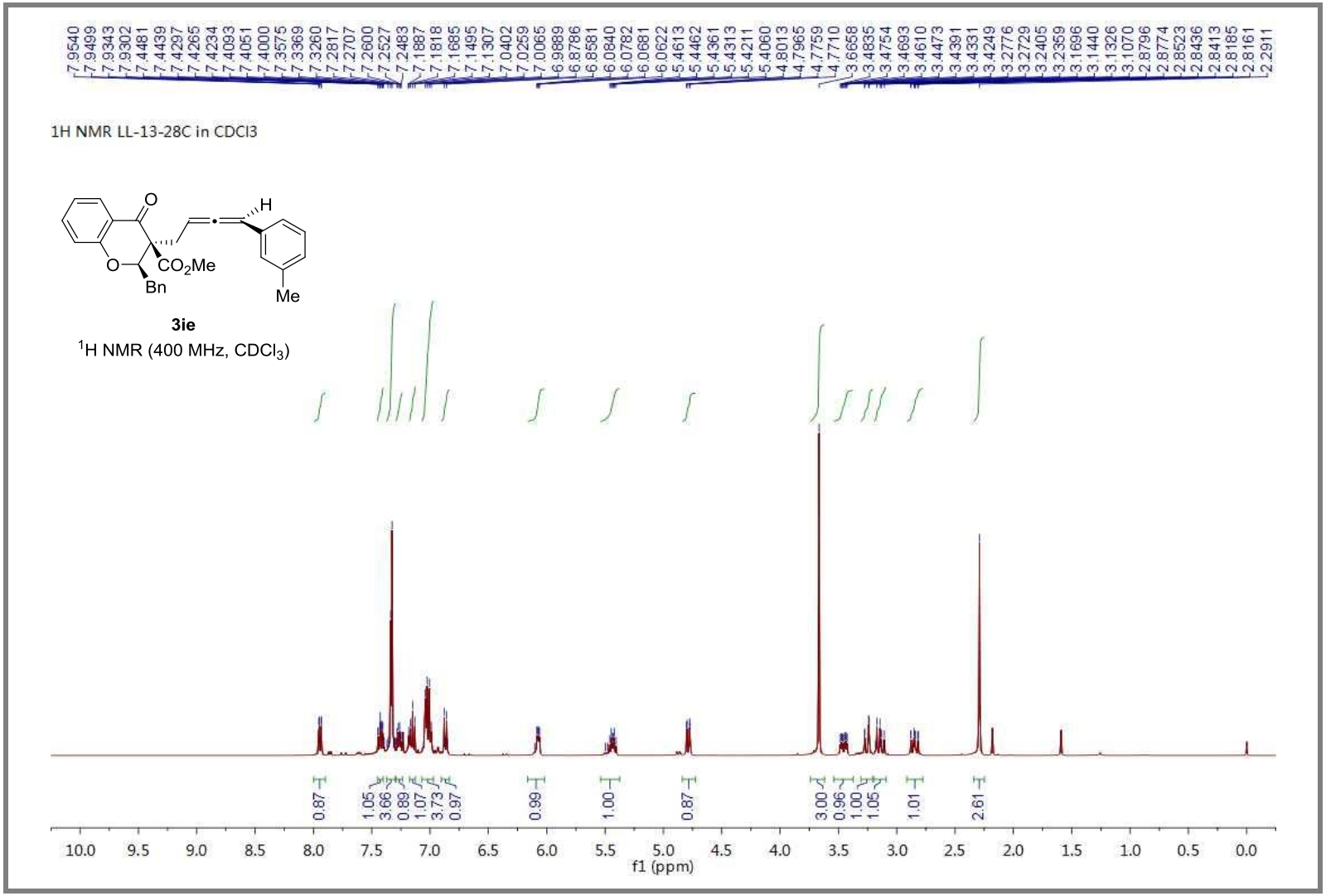
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  15.236 BB    0.4487  266.65994    8.97192   4.4915
   2  17.161 BV    0.4802  437.92758   13.82677   7.3762
   3  18.653 VV    0.6141 5081.28662  124.22329  85.5865
   4  20.892 VB    0.9457  151.14662    2.34036   2.5458

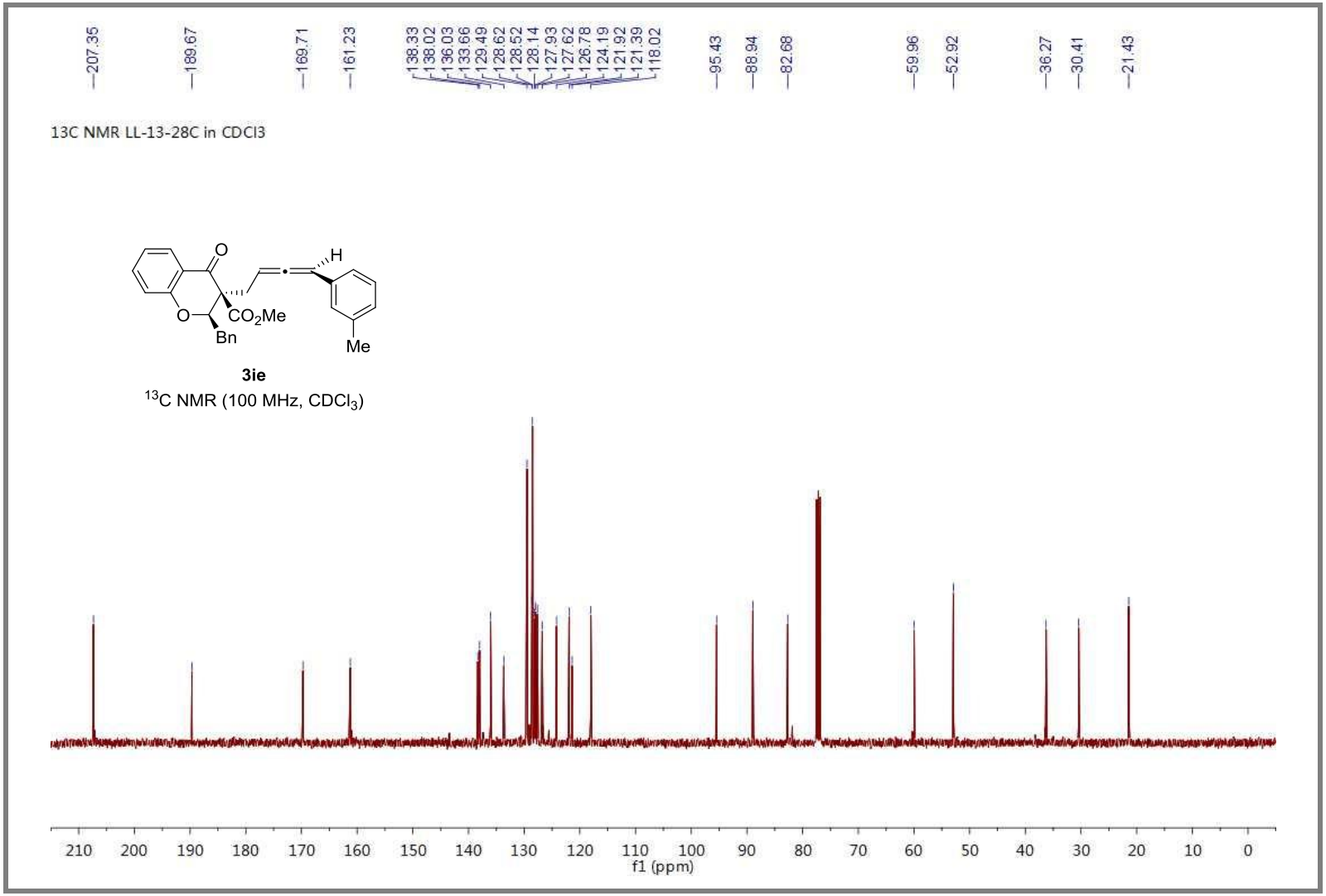
Totals :                  5937.02077  149.36235
```



(-)-3he

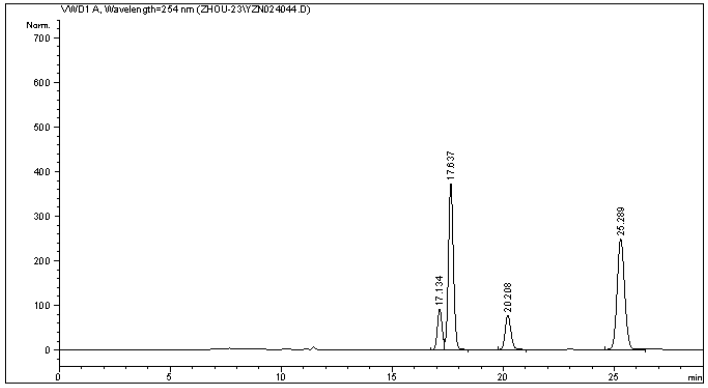
```
                          *** End of Report ***
```


1H NMR LL-13-28C in CDCl3
O
H
O
CO2Me
Bn
Me
3ie
1H NMR (400 MHz, CDCl3)
f1 (ppm)


207.35
189.67
169.71
161.23
138.33
138.02
136.03
133.66
129.49
128.62
128.52
128.14
127.93
127.62
126.78
124.19
121.92
121.39
118.02
95.43
88.94
82.68
59.96
52.92
36.27
30.41
21.43
13C NMR LL-13-28C in CDCl3
O
H
O
CO2Me
Bn
Me
3ie
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-23\YZN024044.D
Sample Name: LL-13-28C +/-

```
    ======================================================================
    Acq. Operator   :
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 9/19/2023 10:43:19 PM
    Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/19/2023 10:38:08 PM
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/21/2023 9:24:15 PM
                      (modified after loading)
    Sample Info     : AD-H+AD-H, Hexane/i-PrOH = 95/5, 0.9 mL/min, 30 oC, 254
                      nm
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

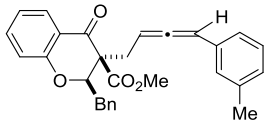
    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #  [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1  17.134 VV    0.2300 1342.38940   91.20565   9.3562
       2  17.637 VB    0.2410 5789.79736  372.53113  40.3537
       3  20.208 BB    0.2780 1394.49280   77.64726   9.7193
       4  25.289 VB    0.3624 5820.95996  248.25450  40.5709

    Totals :                  1.43476e4   789.63854

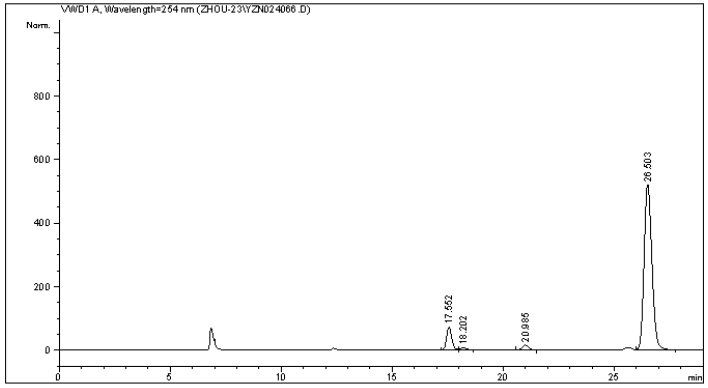

    ======================================================================
                               *** End of Report ***
```



(+/-)-3ie

Data File C:\CHEM32\1\DATA\ZHOU-23\YZN024066.D
Sample Name: LL-13-28C

```
    ======================================================================
    Acq. Operator   :
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 9/21/2023 6:43:02 AM
    Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/21/2023 6:13:05 AM
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/21/2023 9:23:50 PM
                      (modified after loading)
    Sample Info     : AD-H+AD-H, Hexane/i-PrOH = 95/5, 0.9 mL/min, 30 oC, 254
                      nm
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

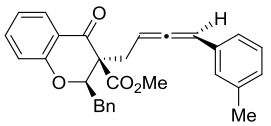
    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

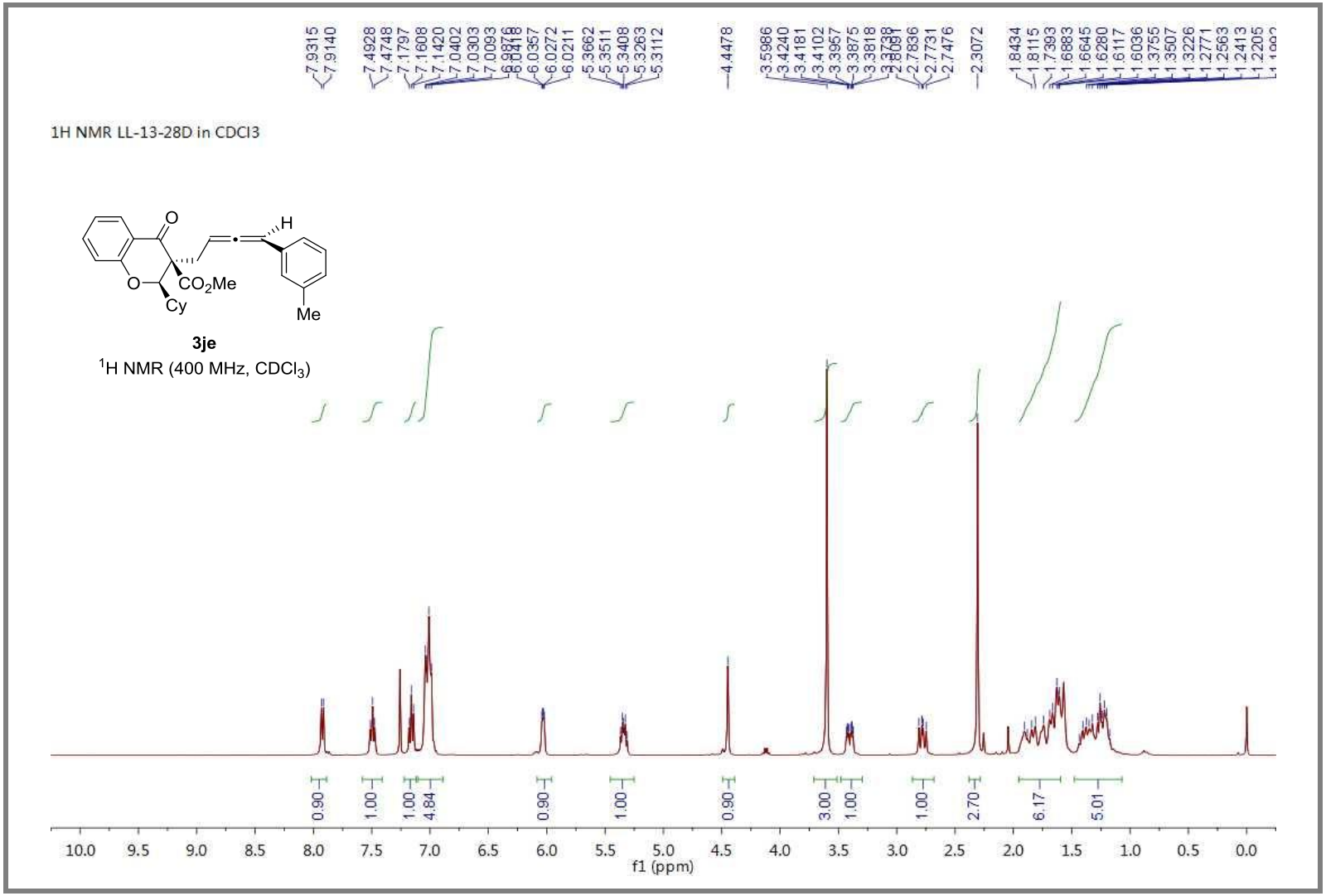
    Peak RetTime Type  Width     Area      Height     Area
      #  [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1  17.552 BV    0.2471 1139.35913   71.46947   7.9879
       2  18.202 VB    0.2570  115.74724    6.89500   0.8115
       3  20.985 BB    0.2890  289.00583   15.38932   2.0262
       4  26.503 VB    0.3780 1.27194e4   520.98602  89.1744

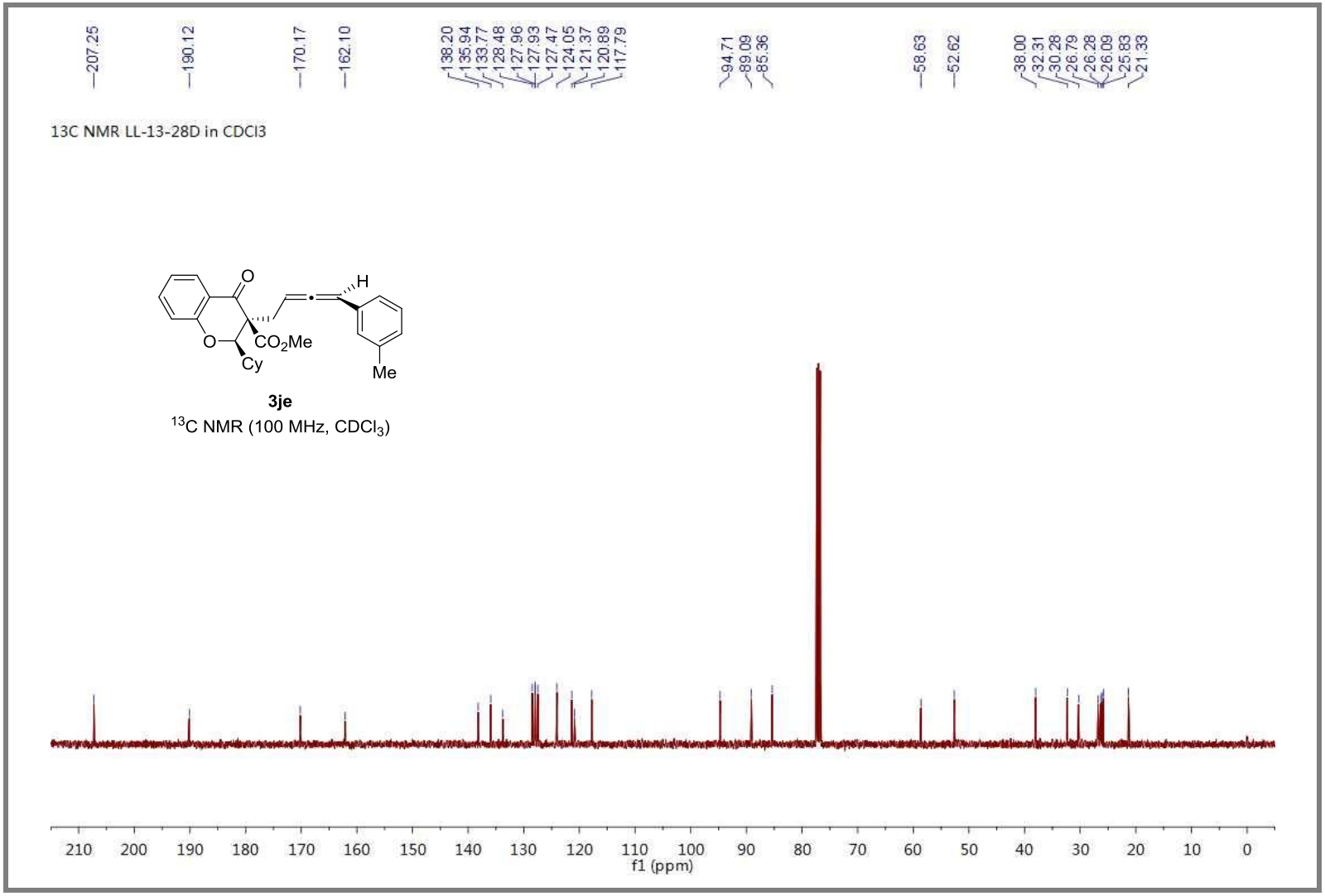
    Totals :                  1.42635e4   614.73982


    ======================================================================
                               *** End of Report ***
```



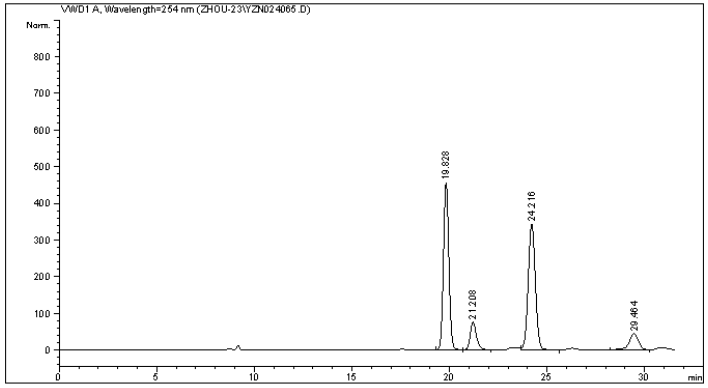
(-)-3ie


1H NMR LL-13-28D in CDCl3
O
H
O
CO2Me
Cy
Me
3je
1H NMR (400 MHz, CDCl3)
f1 (ppm)


207.25
190.12
170.17
162.10
138.20
135.94
133.77
128.48
127.96
127.93
127.47
124.05
121.37
120.89
117.79
94.71
89.09
85.36
58.63
52.62
38.00
32.31
30.28
26.79
26.28
26.09
25.83
21.33
13C NMR LL-13-28D in CDCl3
O
H
O
CO2Me
Cy
Me
3je
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-23\YZN024065.D
Sample Name: LL-13-28D +/-

```
    ======================================================================
    Acq. Operator   :
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 9/21/2023 4:46:20 AM
    Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/21/2023 4:44:14 AM
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/21/2023 9:32:06 PM
                      (modified after loading)
    Sample Info     : OD-H+IC, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 n
                      m
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

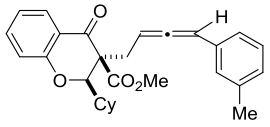
    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #  [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|---------|---------|--------|
       1  19.828 VV    0.2995 8726.39648  454.84616  42.2623
       2  21.208 VV    0.3446 1705.59131   75.62910   8.2603
       3  24.216 VB    0.3957 8728.98437  343.23184  42.2749
       4  29.464 VV    0.5188 1487.19116   43.76091   7.2025

    Totals :                  2.06482e4   917.46801

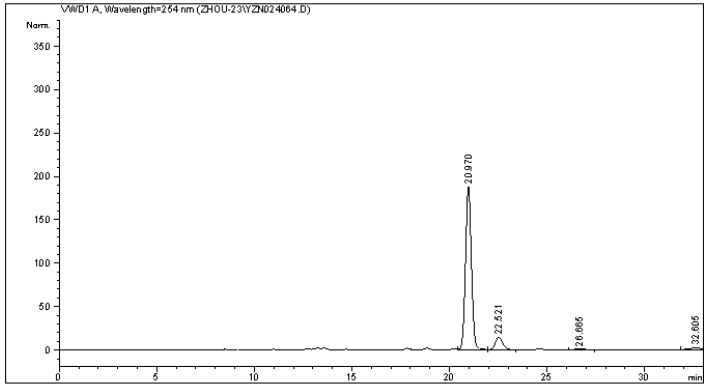

    ======================================================================
                              *** End of Report ***
```



(+/-)-3je

Data File C:\CHEM32\1\DATA\ZHOU-23\YZN024064.D
Sample Name: LL-13-28D

```
    ======================================================================
    Acq. Operator   :
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 9/21/2023 4:03:42 AM
    Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/21/2023 3:40:41 AM
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 9/21/2023 9:29:16 PM
                      (modified after loading)
    Sample Info     : OD-H+IC, Hexane/i-PrOH = 97/3, 0.8 mL/min, 30 oC, 254 n
                      m
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

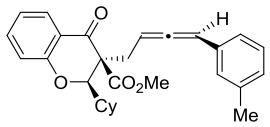
    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

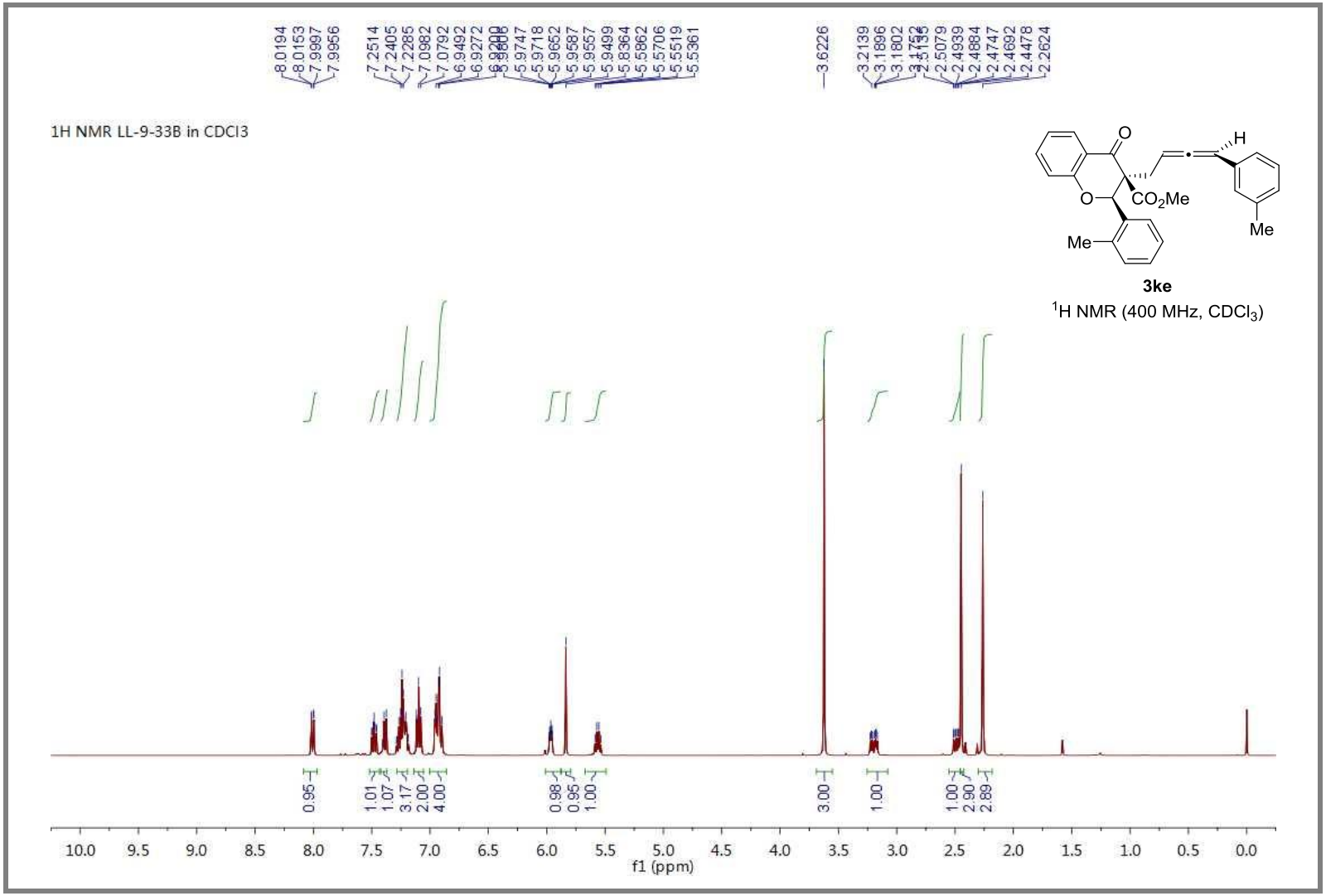
    Peak RetTime Type  Width     Area      Height     Area
      #  [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|---------|---------|--------|
       1  20.970 VV    0.3273 3958.90942  187.91132  89.2798
       2  22.521 VB    0.3844  371.30734   14.72752   8.3736
       3  26.665 BB    0.4477   24.16426 8.29179e-1   0.5449
       4  32.605 BV    0.5840   79.88892    2.07104   1.8016

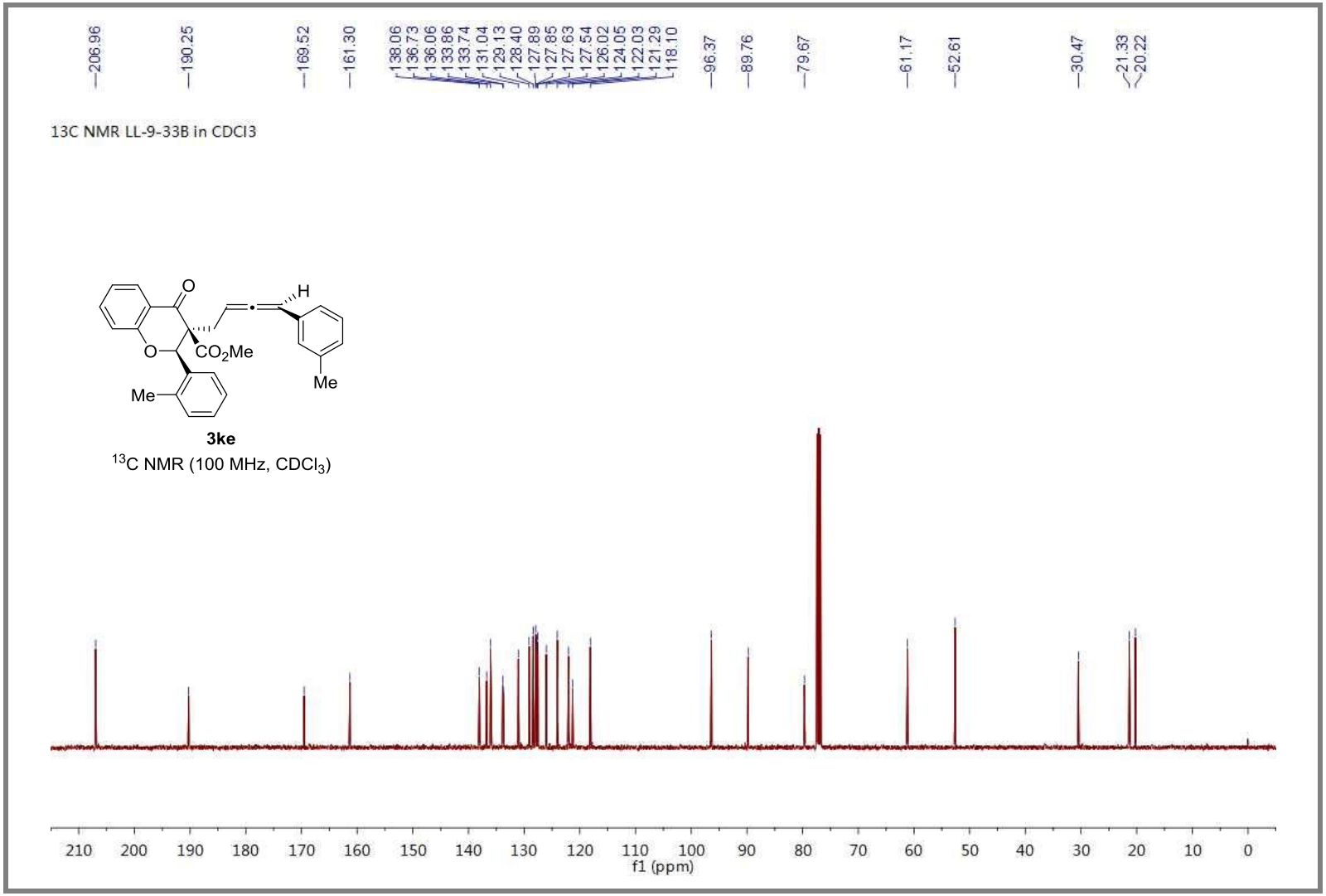
    Totals :                  4434.26995  205.53906


    ======================================================================
                              *** End of Report ***
```



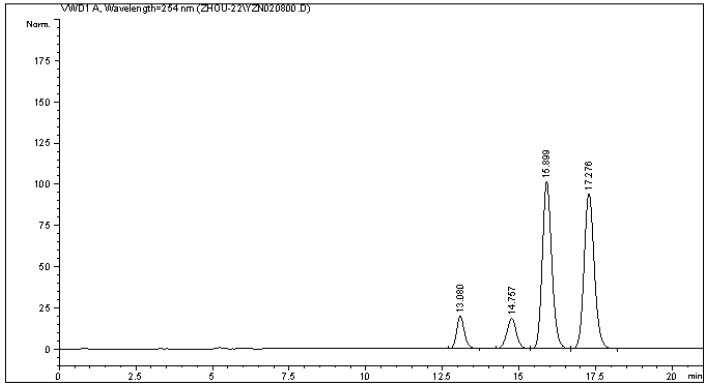
(-)-3je


1H NMR LL-9-33B in CDCl3
8.0194
8.0153
7.9997
7.9956
7.2514
7.2405
7.2285
7.0982
7.0792
6.9492
6.9272
5.9747
5.9718
5.9652
5.9587
5.9557
5.9499
5.8364
5.5862
5.5706
5.5519
5.5361
3.6226
3.2139
3.1896
3.1802
2.5079
2.4939
2.4884
2.4747
2.4692
2.4478
2.2624
O
H
O
CO2Me
Me
Me
3ke
1H NMR (400 MHz, CDCl3)
0.95
1.01
1.07
3.17
2.00
4.00
0.98
0.95
1.00
3.00
1.00
1.00
2.90
2.89
10.0
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)


206.96
190.25
169.52
161.30
138.06
136.73
136.06
133.86
133.74
131.04
129.13
128.40
127.89
127.85
127.63
127.54
126.02
124.05
122.03
121.29
118.10
96.37
89.76
79.67
61.17
52.61
30.47
21.33
20.22
13C NMR LL-9-33B in CDCl3
O
H
O
CO2Me
Me
Me
3ke
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020800.D
Sample Name: LL-9-33B +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/21/2022 9:16:41 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/21/2022 9:14:25 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 2:31:43 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```



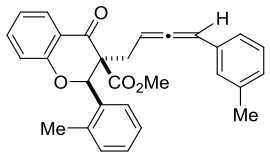

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|-------|
   1  13.080 VV    0.2688  349.19962   19.90305   6.8548
   2  14.757 VV    0.3283  400.72632   18.51077   7.8663
   3  15.899 VV    0.3288 2171.24585  101.26318  42.6215
   4  17.276 VB    0.3564 2173.07373   94.22297  42.6574

Totals :                  5094.24551  233.89997
```

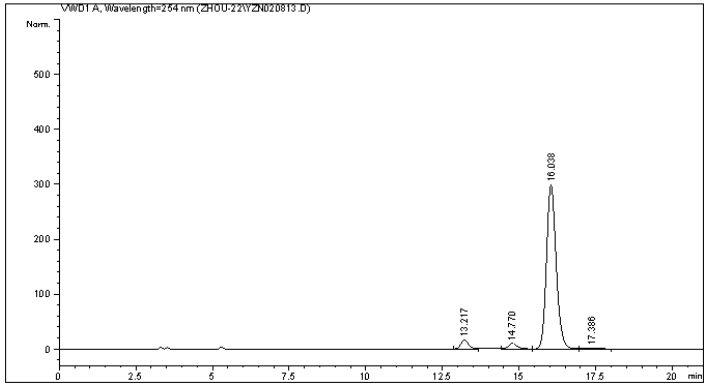


(+/-)-3ke

```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020813.D
Sample Name: LL-9-33B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/23/2022 2:02:39 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 2:01:05 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 3:12:17 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```



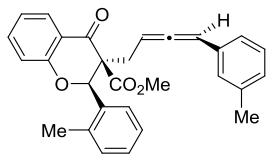

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

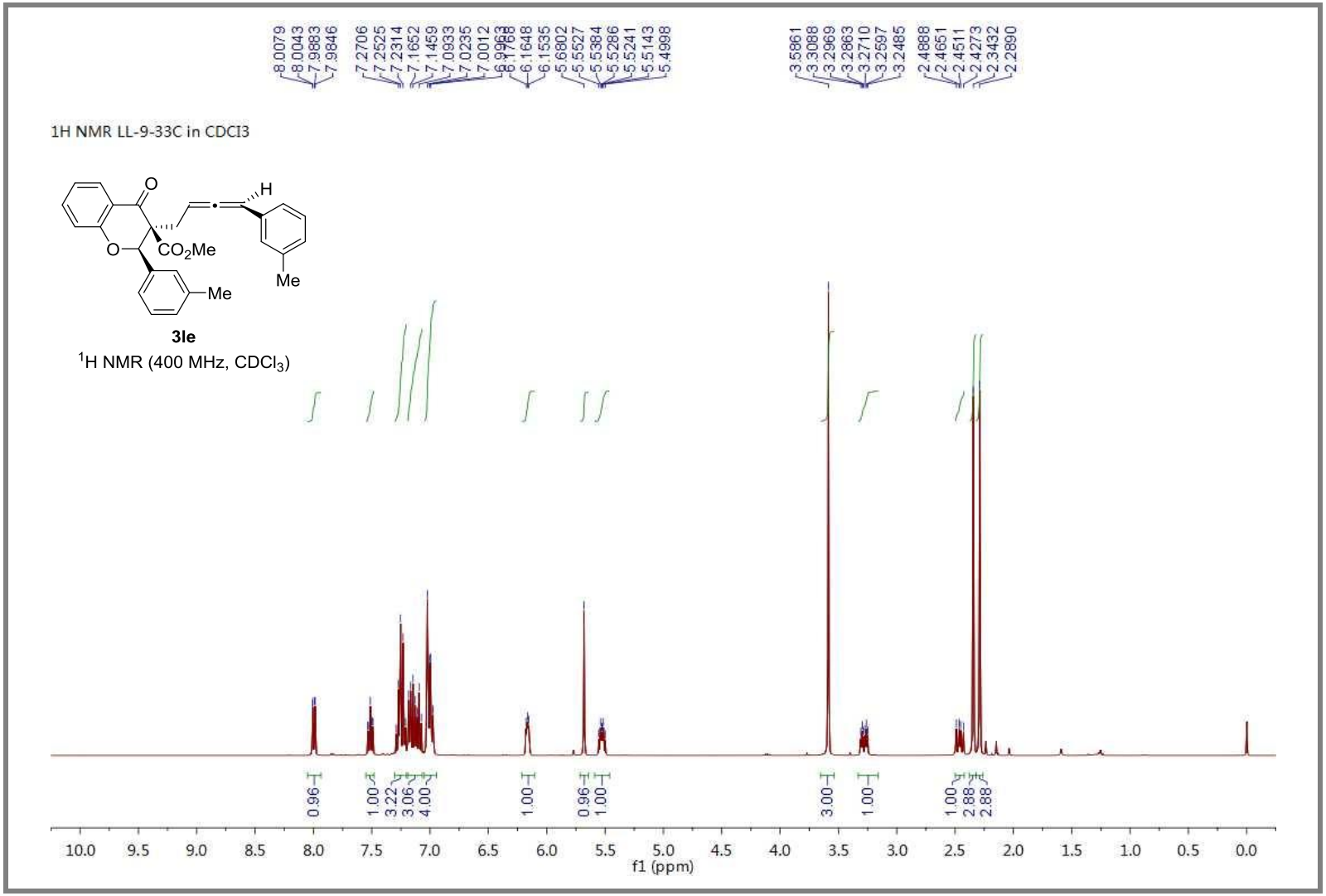
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|-------|
   1  13.217 BV    0.2721  283.35965   16.11409   4.0129
   2  14.770 VV    0.3024  196.67789    9.86794   2.7853
   3  16.038 VV    0.3399 6539.77539  298.73343  92.6143
   4  17.386 VB    0.3877   41.48568    1.61131   0.5875

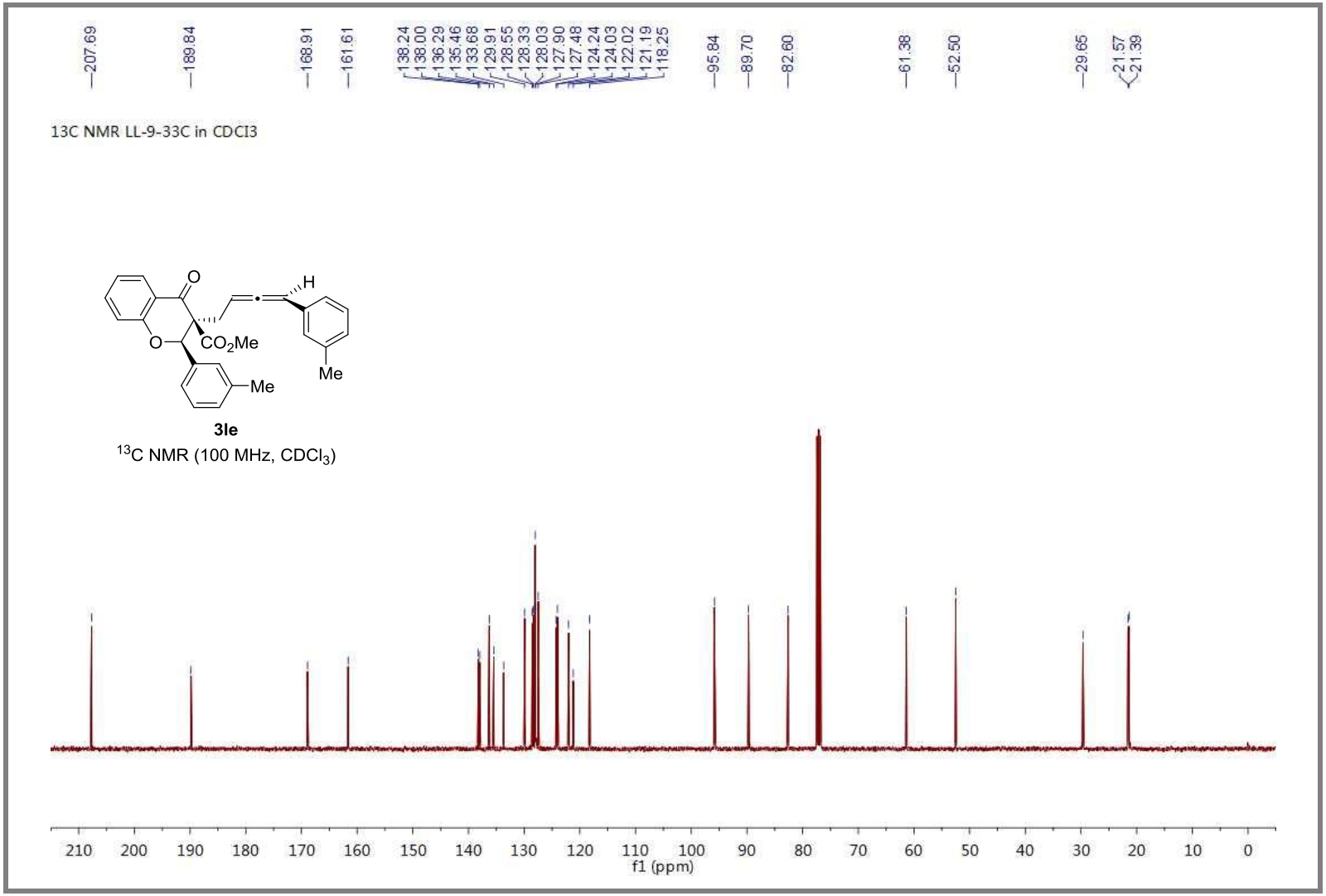
Totals :                  7061.29861  326.32676
```



(-)-3ke

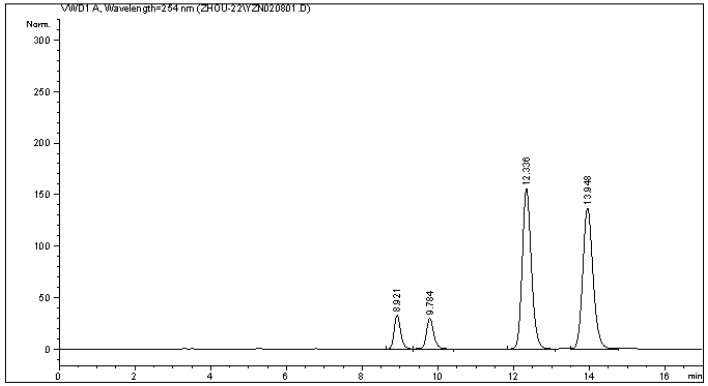
```
                          *** End of Report ***
```


8.0079
8.0043
7.9883
7.9846
7.2706
7.2525
7.2314
7.1652
7.1459
7.0933
7.0235
7.0012
6.1648
6.1535
5.6802
5.5527
5.5384
5.5286
5.5241
5.5143
5.4998
3.5861
3.3088
3.2969
3.2863
3.2710
3.2597
3.2485
2.4888
2.4651
2.4511
2.4273
2.3432
2.2890
1H NMR LL-9-33C in CDCl3
O
H
CO2Me
O
Me
Me
3Ie
1H NMR (400 MHz, CDCl3)
0.96
1.00
3.22
3.06
4.00
1.00
0.96
1.00
3.00
1.00
1.00
2.88
2.88
10.0
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)


207.69
189.84
168.91
161.61
138.24
138.00
136.29
135.46
133.68
129.91
128.55
128.33
128.03
127.90
127.48
124.24
124.03
122.02
121.19
118.25
95.84
89.70
82.60
61.38
52.50
29.65
21.57
21.39
13C NMR LL-9-33C in CDCl3
O
H
O
CO2Me
Me
Me
3Ie
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020801.D
Sample Name: LL-9-33C +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/21/2022 9:46:05 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/21/2022 9:43:18 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 2:52:19 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

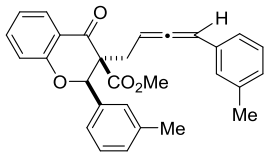
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   8.921 BV    0.1816  388.22244   32.83931   6.5050
   2   9.784 VB    0.2028  397.62344   29.97575   6.6626
   3  12.336 BV    0.2583 2589.84790  155.56494  43.3953
   4  13.948 VV    0.2909 2592.34204  136.83603  43.4371

Totals :                  5968.03583  355.21602

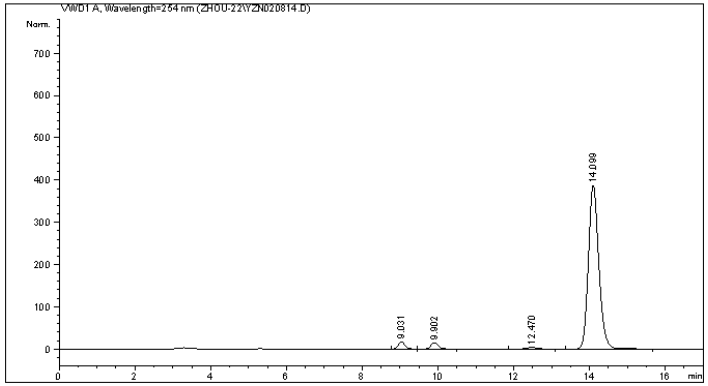
                          *** End of Report ***
```



(+/-)-3le

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020814.D
Sample Name: LL-9-33C

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/23/2022 2:34:22 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 2:29:56 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 4:32:15 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

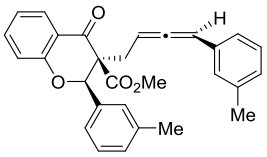
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

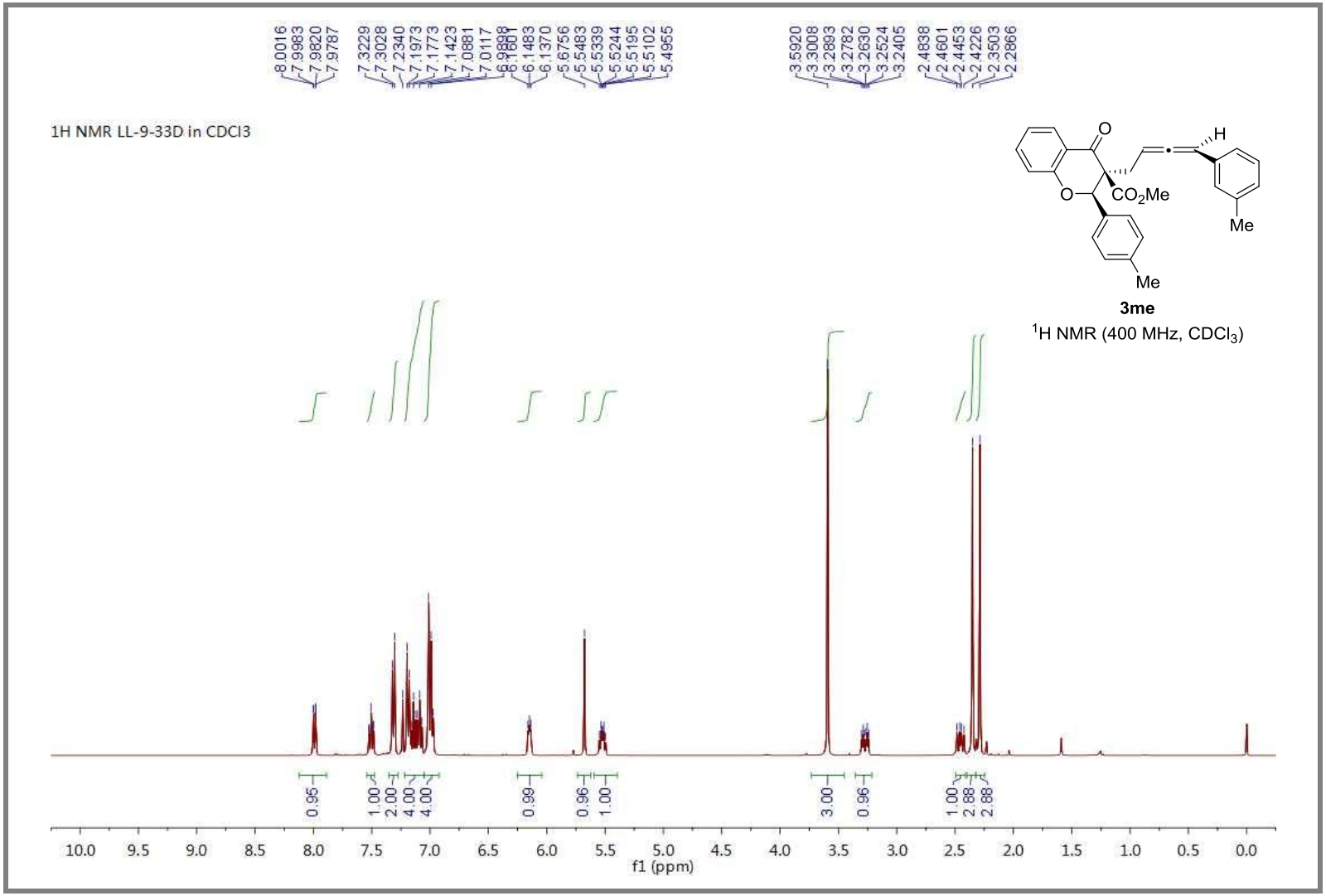
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   9.031 BV    0.1839  208.25015   17.33076   2.6406
   2   9.902 VB    0.2099  202.37326   14.72315   2.5660
   3  12.470 BB    0.2745   69.80332    3.86965   0.8851
   4  14.099 BB    0.2929 7406.14648  387.51746  93.9083

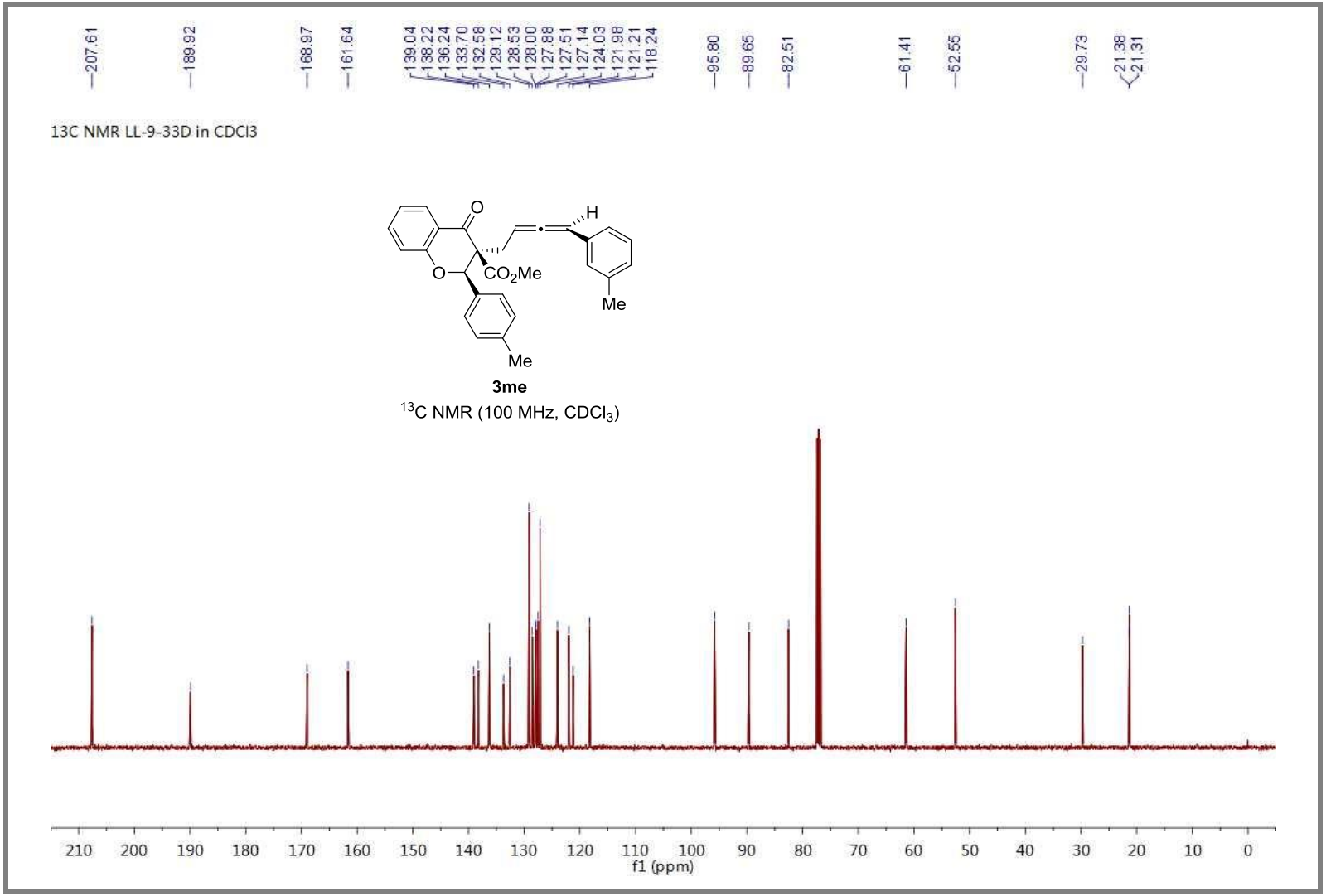
Totals :                  7886.57322  423.44101

                          *** End of Report ***
```



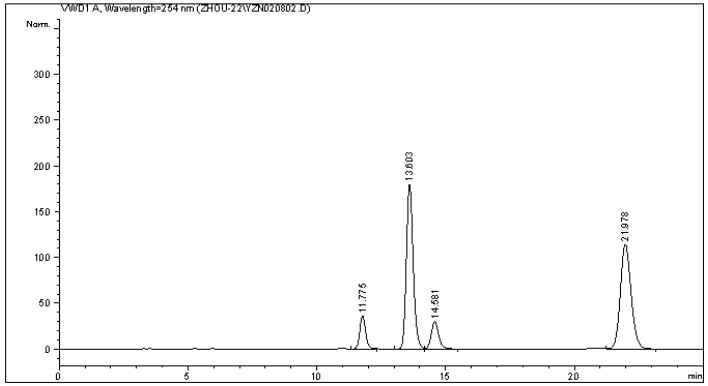
(-)-3le


1H NMR LL-9-33D in CDCl3
8.0016
7.9983
7.9820
7.9787
7.3229
7.3028
7.2340
7.1973
7.1773
7.1423
7.0881
7.0117
6.9898
6.9801
6.1483
6.1370
5.6756
5.5483
5.5339
5.5244
5.5195
5.5102
5.4955
3.5920
3.3008
3.2893
3.2782
3.2630
3.2524
3.2405
2.4838
2.4601
2.4453
2.4226
2.3503
2.2866
O
H
O
CO2Me
Me
Me
3me
1H NMR (400 MHz, CDCl3)
0.95
1.00
2.00
4.00
4.00
0.99
0.96
1.00
3.00
0.96
1.00
2.88
2.88
10.0
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)


207.61
189.92
168.97
161.64
139.04
138.22
136.24
133.70
132.58
129.12
128.53
128.00
127.88
127.51
127.14
124.03
121.98
121.21
118.24
95.80
89.65
82.51
61.41
52.55
29.73
21.38
21.31
13C NMR LL-9-33D in CDCl3
O
H
O
CO2Me
Me
Me
3me
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020802.D
Sample Name: LL-9-33D +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/21/2022 10:05:06 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/21/2022 10:03:11 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 3:23:06 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```



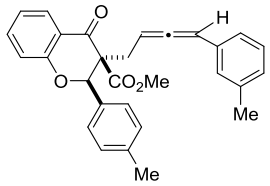

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  11.775 VB    0.2399  563.10925   36.16396   7.2382
   2  13.603 BV    0.2831 3315.15112  180.14198  42.6129
   3  14.581 VB    0.3028  588.46716   29.85586   7.5641
   4  21.978 VB    0.4451 3312.97021  114.57842  42.5848

Totals :                  7779.69775  360.74022
```

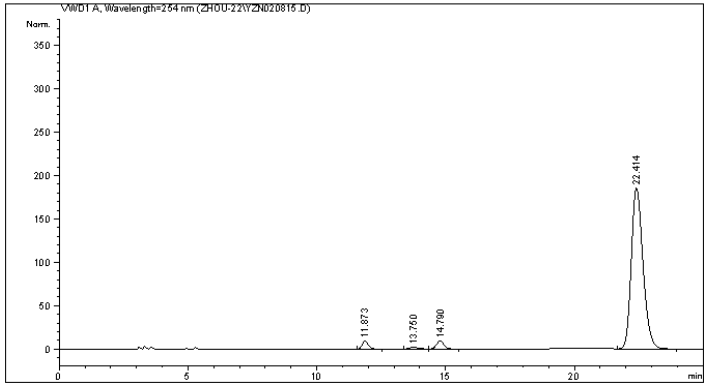


(+/-)-3me

```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020815.D
Sample Name: LL-9-33D

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/23/2022 2:56:01 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/23/2022 2:52:50 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/15/2022 4:36:51 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```



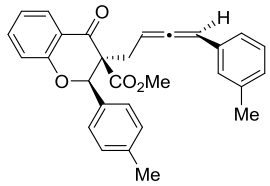

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

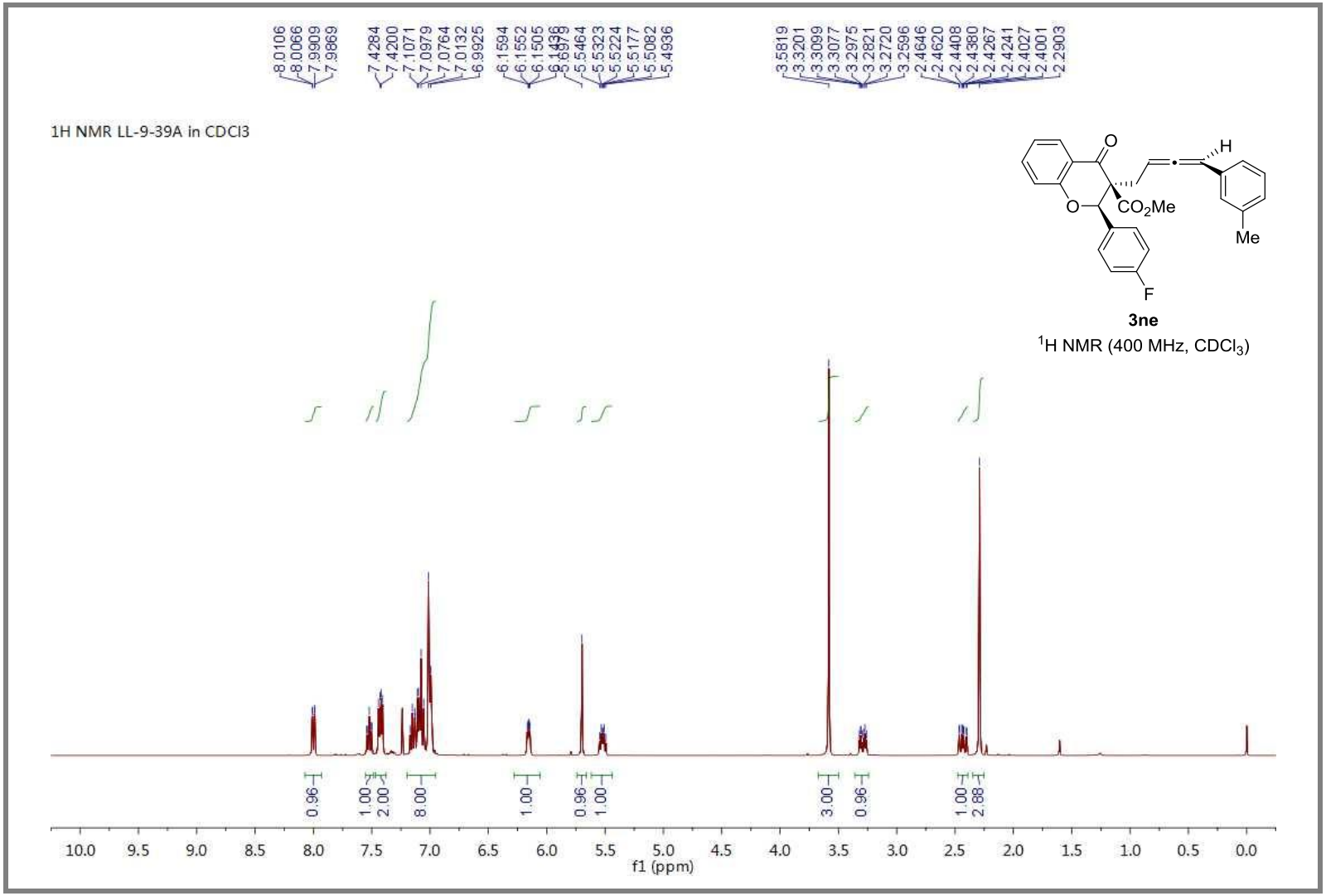
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  11.873 BB    0.2422  151.93513    9.63317   2.4237
   2  13.750 BV    0.3152   51.64087    2.45618   0.8238
   3  14.790 VB    0.3130  184.72479    9.19614   2.9468
   4  22.414 VB    0.4891 5880.36475  185.57999  93.8057

Totals :                  6268.66554  206.86547
```



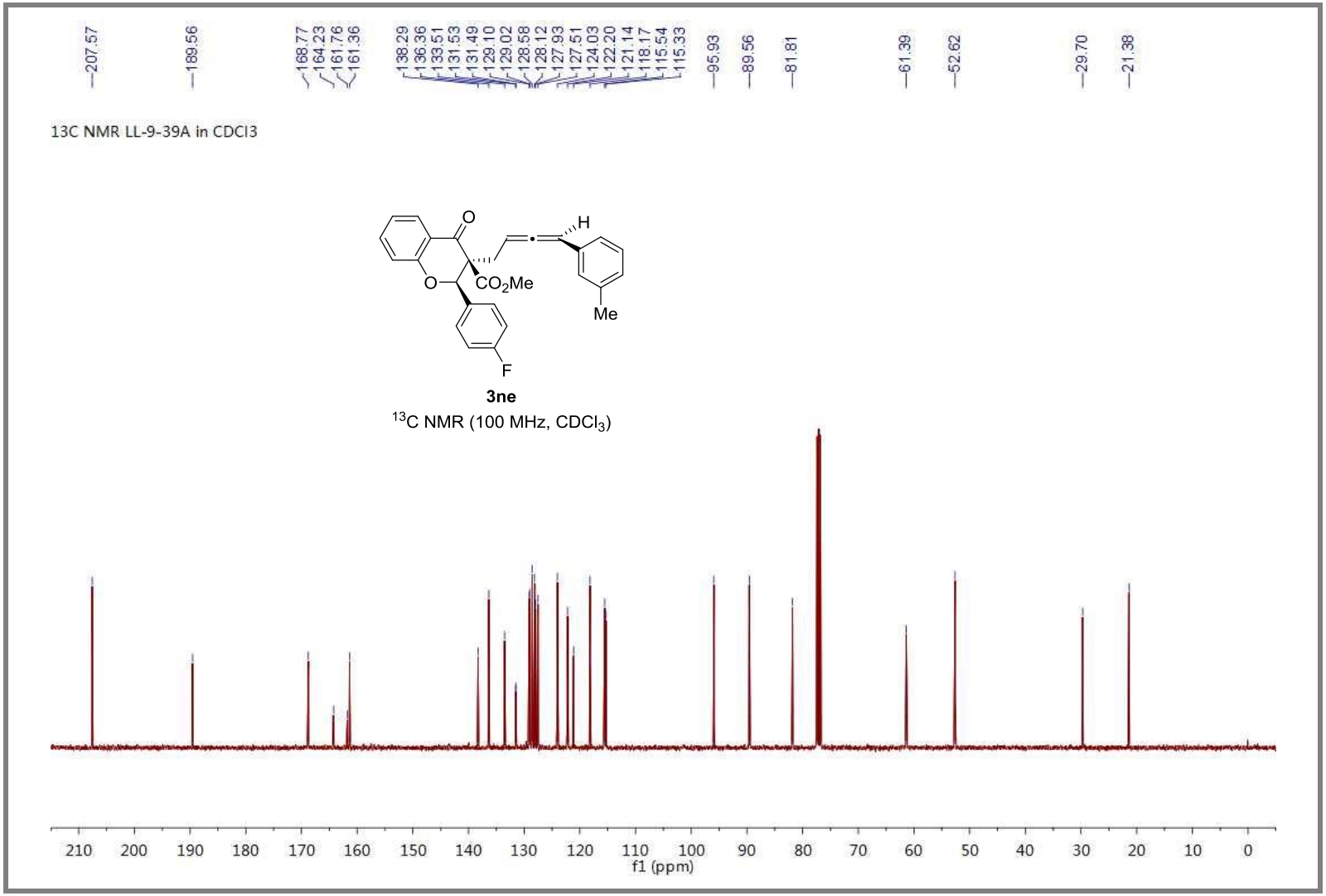
(-)-3me

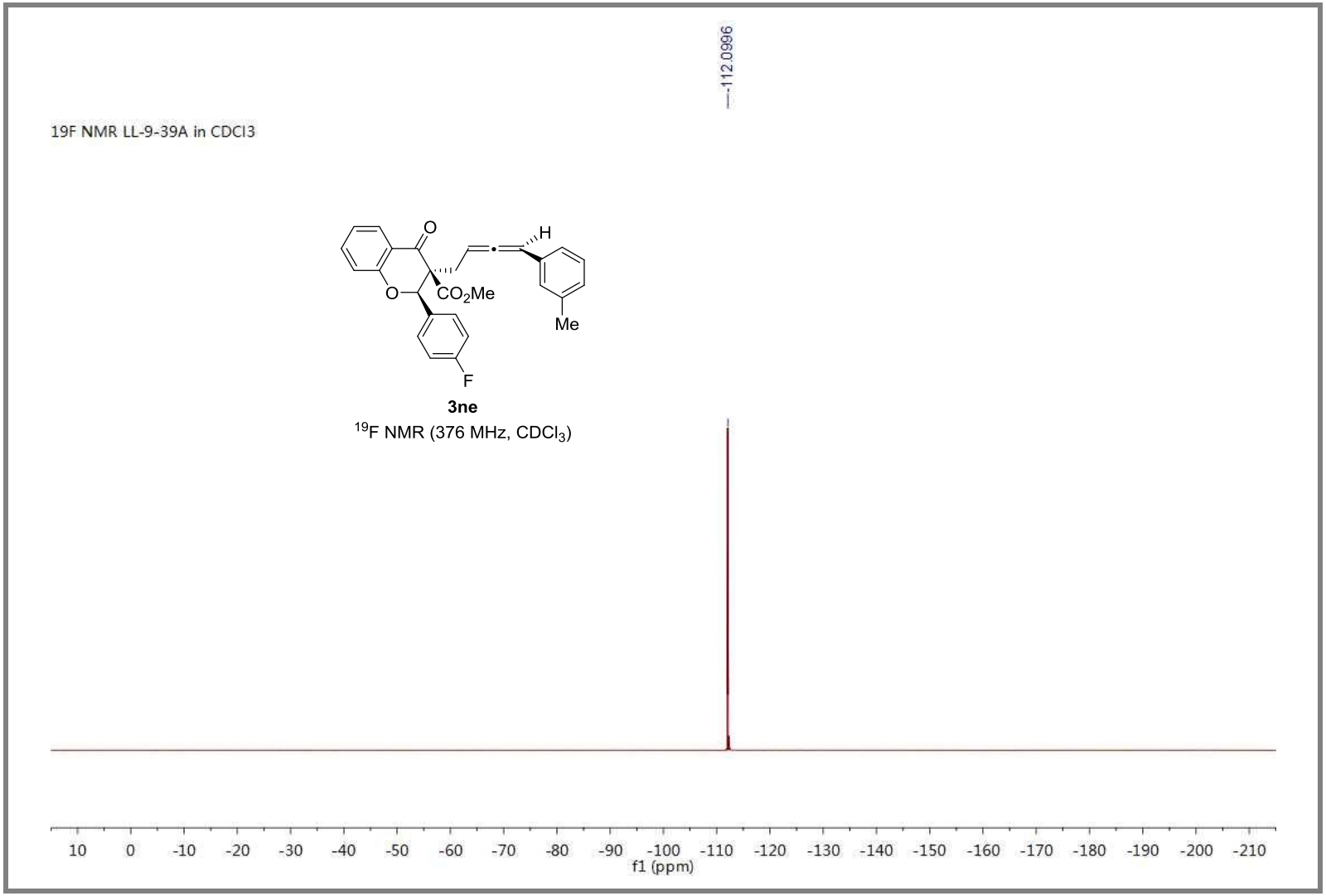
```
                          *** End of Report ***
```



3ne

^{1}H NMR (400 MHz, $CDCl_3$)


207.57
189.56
168.77
164.23
161.76
161.36
138.29
136.36
133.51
131.53
131.49
129.10
129.02
128.58
128.12
127.93
127.51
124.03
122.20
121.14
118.17
115.54
115.33
95.93
89.56
81.81
61.39
52.62
29.70
21.38
13C NMR LL-9-39A in CDCl3
O
H
O
CO2Me
Me
F
3ne
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

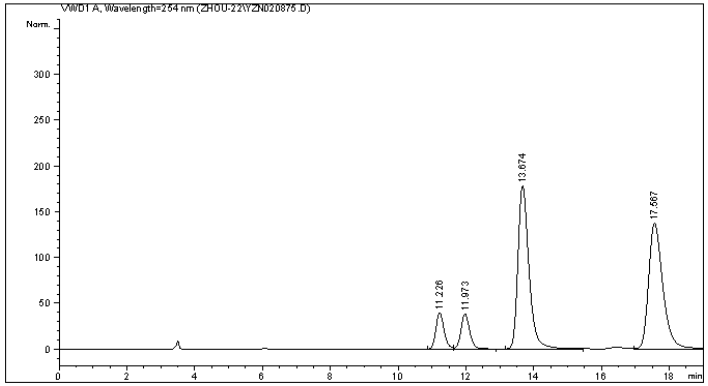


3ne

^{19}F NMR (376 MHz, $CDCl_3$)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020875.D
Sample Name: LL-9-39A +/-

Acq. Operator :
Acq. Instrument : Instrument 1 Location : -
Injection Date : 3/30/2022 3:37:44 AM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 3:35:57 AM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 4:22:58 AM
(modified after loading)
Sample Info : ID, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm

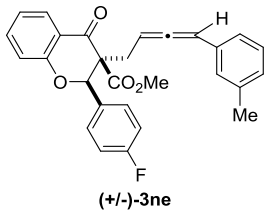


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.226	BV	0.2543	659.95746	39.86446	7.0423
2	11.973	VB	0.2749	685.86603	38.49050	7.3187
3	13.674	BB	0.3450	4022.82959	178.11646	42.9267
4	17.567	VB	0.4419	4002.73682	137.34512	42.7123
Totals :				9371.38989	393.81653	



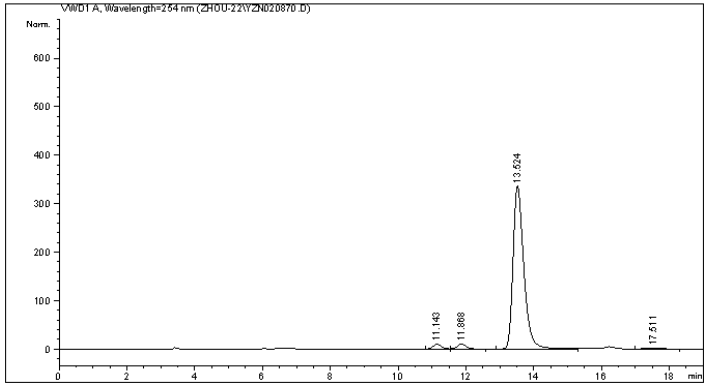
(+/-)-3ne

*** End of Report ***

Instrument 1 3/30/2022 4:23:08 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020870.D
Sample Name: LL-9-39A

Acq. Operator :
Acq. Instrument : Instrument 1 Location : -
Injection Date : 3/30/2022 2:10:48 AM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 2:09:10 AM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 4:23:50 AM
(modified after loading)
Sample Info : ID, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm

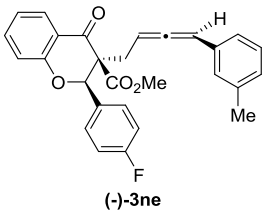


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

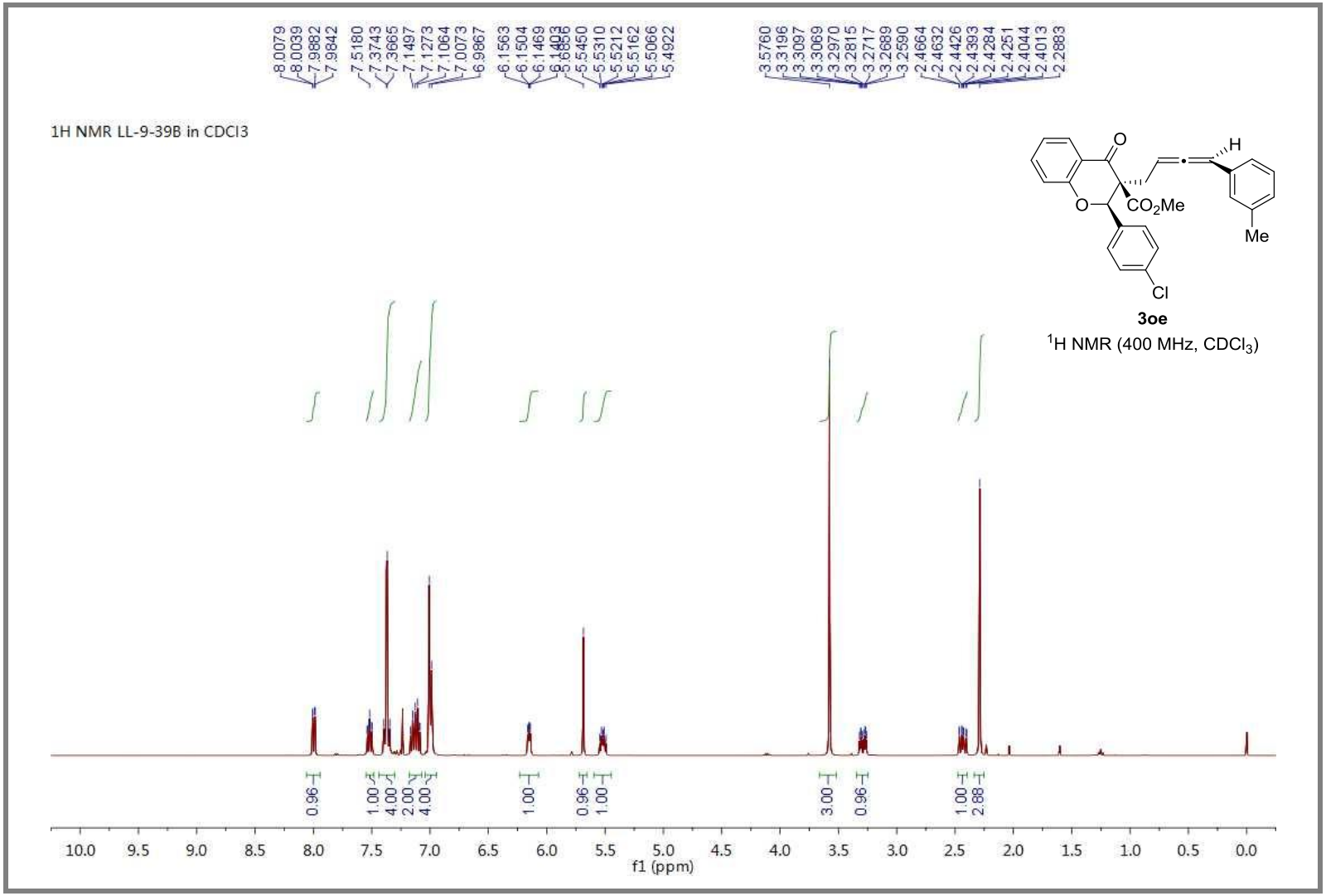
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.143	BV	0.2503	162.96674	10.04978	2.0748
2	11.868	VB	0.2712	192.18999	10.82592	2.4468
3	13.524	BB	0.3364	7429.46289	336.24368	94.5867
4	17.511	BB	0.4513	70.03980	2.35823	0.8917
Totals :				7854.65942	359.47761	



(-)-3ne

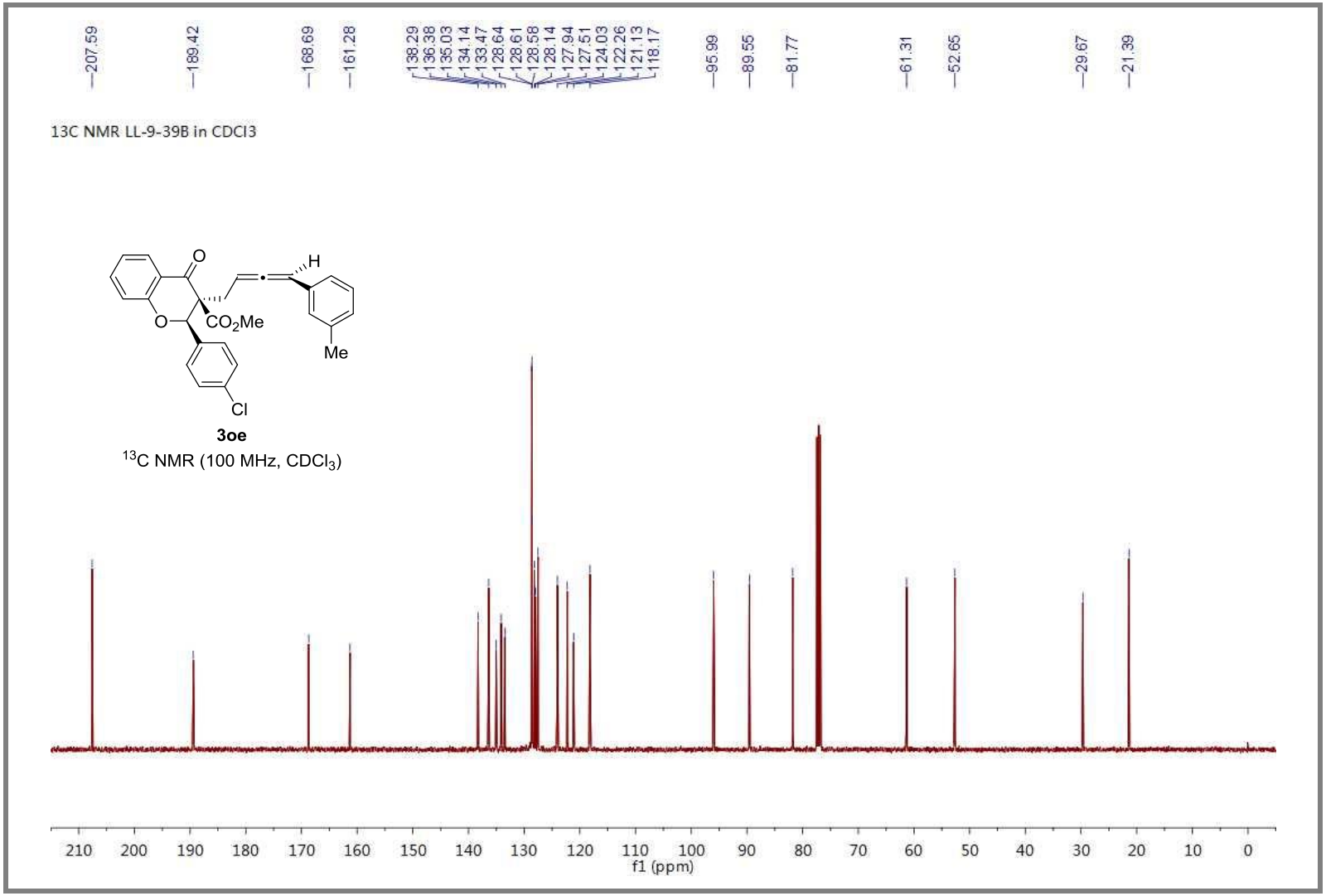
*** End of Report ***

Instrument 1 3/30/2022 4:23:55 AM Page 1 of 1



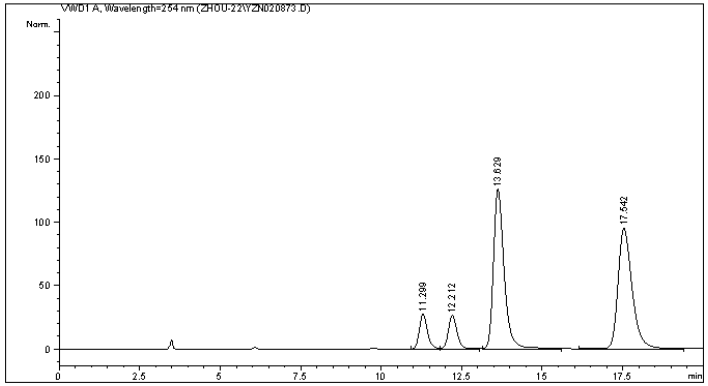
3oe

^{1}H NMR (400 MHz, $CDCl_3$)


207.59
189.42
168.69
161.28
138.29
136.38
135.03
134.14
133.47
128.64
128.61
128.58
128.14
127.94
127.51
124.03
122.26
121.13
118.17
95.99
89.55
81.77
61.31
52.65
29.67
21.39
13C NMR LL-9-39B in CDCl3
O
H
O
CO2Me
Me
Cl
3oe
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020873.D
Sample Name: LL-9-39B +/-

Acq. Operator :
Acq. Instrument : Instrument 1 Location : -
Injection Date : 3/30/2022 2:52:41 AM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 2:51:20 AM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 4:29:05 AM
(modified after loading)
Sample Info : ID, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm

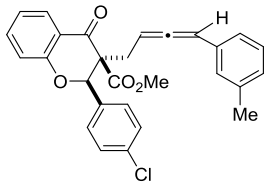


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.299	BV	0.2701	484.30914	27.42727	7.0920
2	12.212	VB	0.2909	499.88123	26.39233	7.3200
3	13.629	BB	0.3519	2918.70996	125.94702	42.7402
4	17.542	BB	0.4661	2926.05200	95.25815	42.8477
Totals :				6828.95233	275.02478	

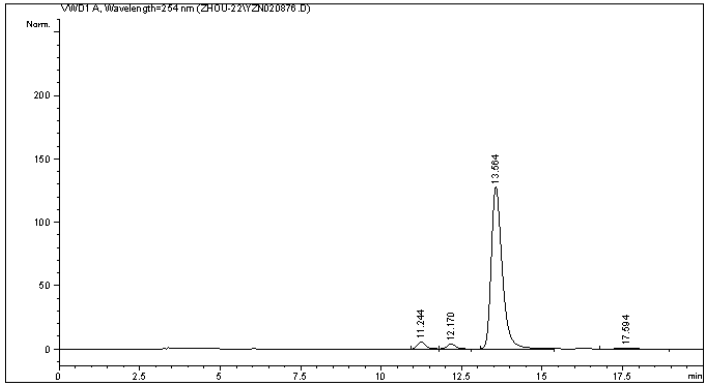


(+/-)-3oe

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020876.D
Sample Name: LL-9-39B

Acq. Operator :
Acq. Instrument : Instrument 1 Location : -
Injection Date : 3/30/2022 4:04:35 AM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 3:58:40 AM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 3/30/2022 4:29:05 AM
(modified after loading)
Sample Info : ID, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm

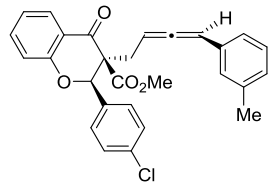


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

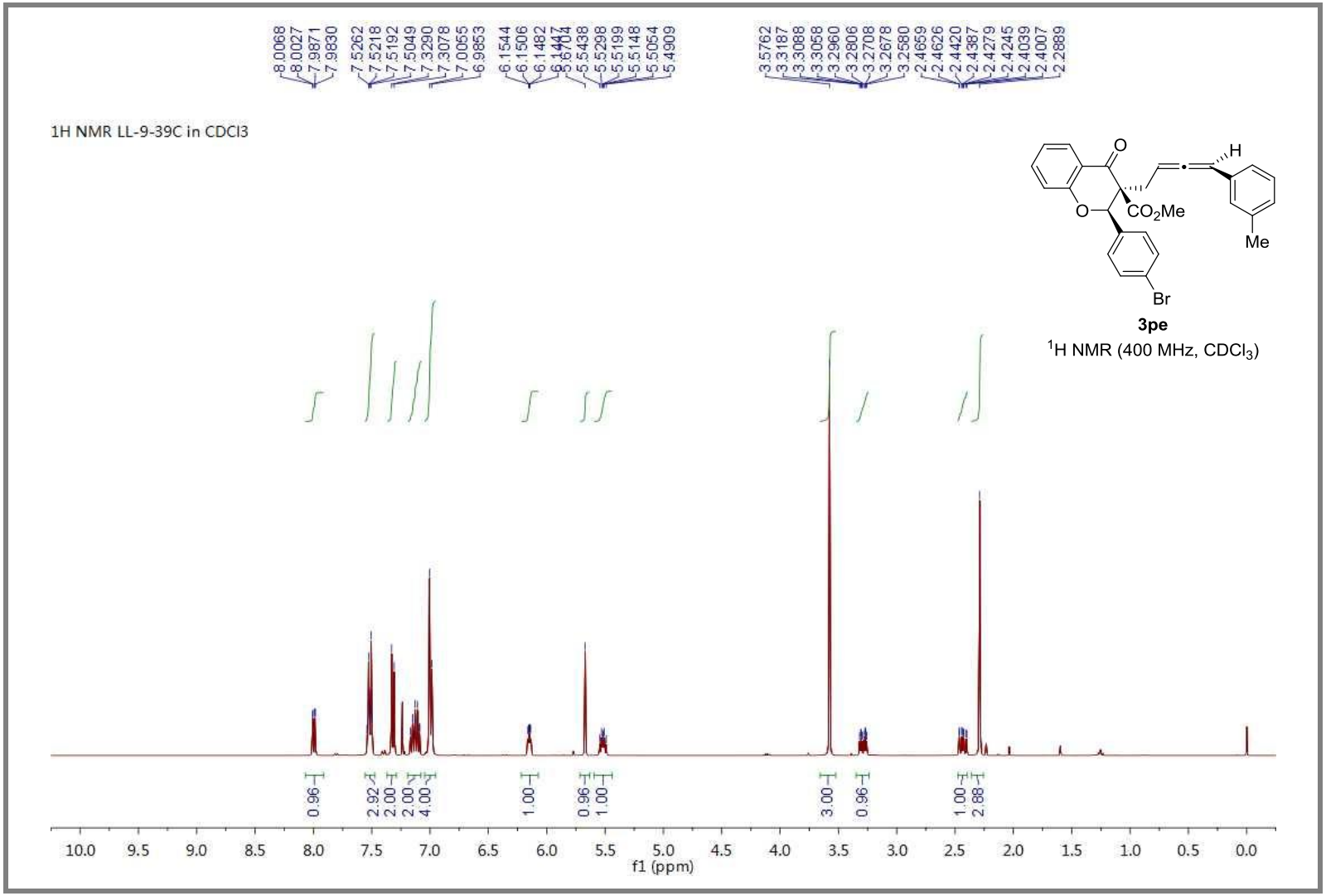
Signal 1: VWD1 A, Wavelength=254 nm

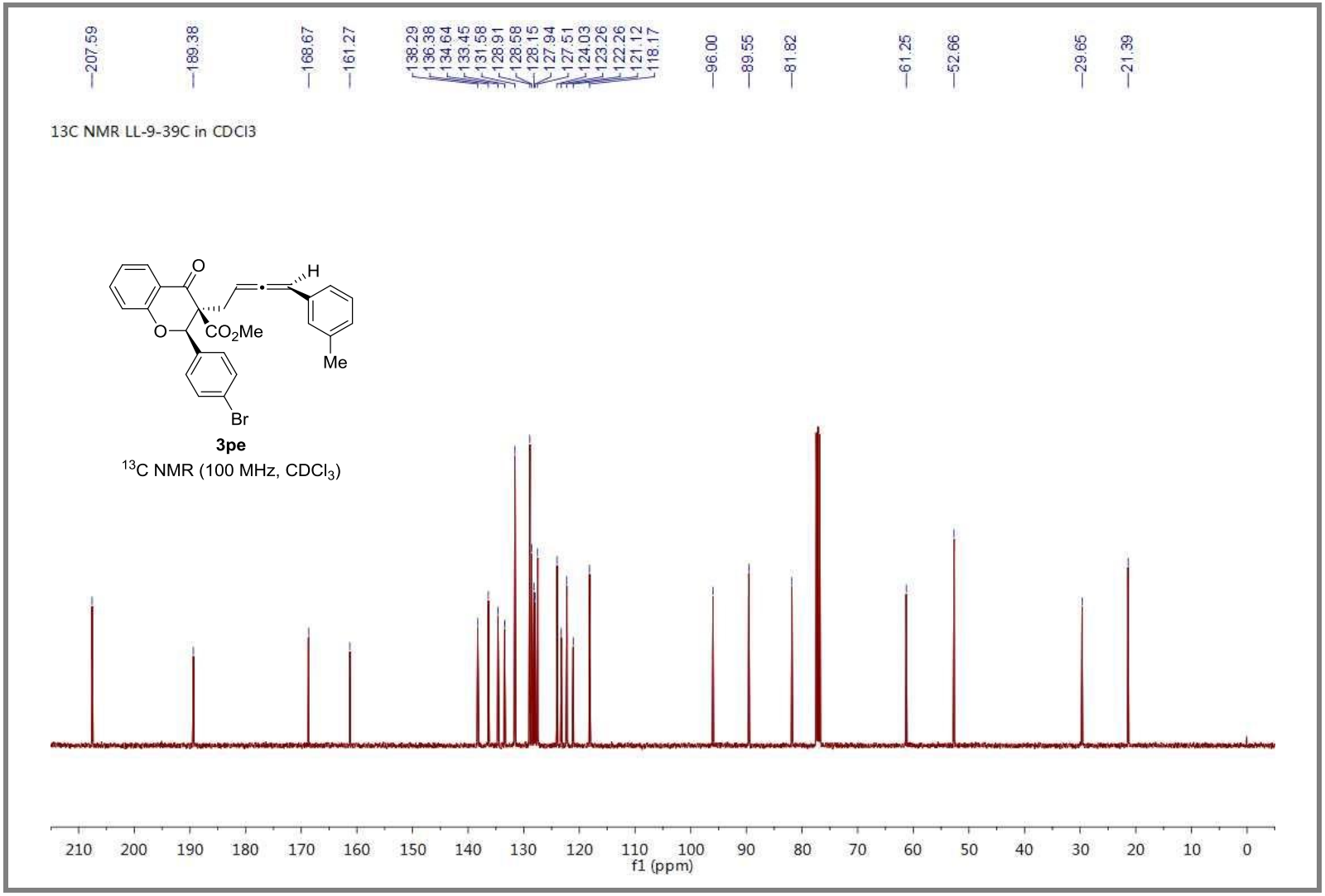
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.244	BV	0.2763	99.79084	5.56123	3.0790
2	12.170	VB	0.2960	72.66874	3.79805	2.2421
3	13.564	BB	0.3621	3039.11841	127.68930	93.7697
4	17.594	VB	0.5155	29.46769	8.74243e-1	0.9092
Totals :				3241.04567	137.92283	



(-)-3oe

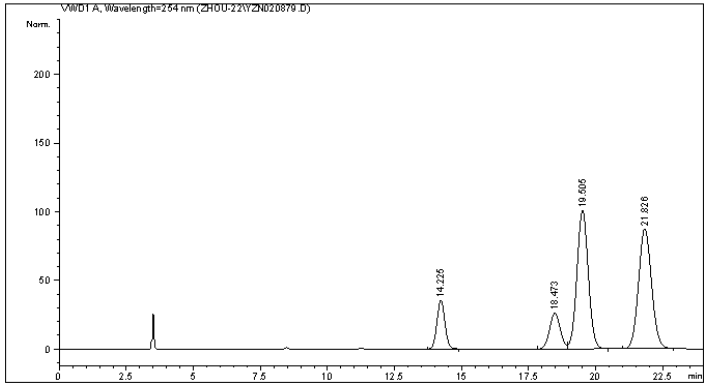
*** End of Report ***


1H NMR LL-9-39C in CDCl3
8.0068
8.0027
7.9871
7.9830
7.5262
7.5218
7.5192
7.5049
7.3290
7.3078
7.0055
6.9853
6.1544
6.1506
6.1482
6.1447
6.1404
5.5438
5.5298
5.5199
5.5148
5.5054
5.4909
3.5762
3.3187
3.3088
3.3058
3.2960
3.2806
3.2708
3.2678
3.2580
2.4659
2.4626
2.4420
2.4387
2.4279
2.4245
2.4039
2.4007
2.2889
0.96
2.92
2.00
2.00
4.00
1.00
0.96
1.00
3.00
0.96
1.00
2.88
10.0
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)
O
H
O
CO2Me
Me
Br
3pe
1H NMR (400 MHz, CDCl3)


207.59
189.38
168.67
161.27
138.29
136.38
134.64
133.45
131.58
128.91
128.58
128.15
127.94
127.51
124.03
123.26
122.26
121.12
118.17
96.00
89.55
81.82
61.25
52.66
29.65
21.39
13C NMR LL-9-39C in CDCl3
O
H
O
CO2Me
Me
Br
3pe
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020879.D
Sample Name: LL-9-39C +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/30/2022 7:28:45 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 7:27:14 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 8:00:24 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```



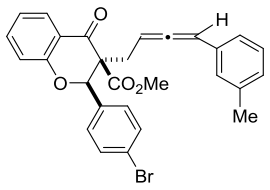
Area Percent Report

```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  14.225 BB    0.3216  733.11090   35.40981   9.9532
   2  18.473 BV    0.4315  724.22681   26.09992   9.8325
   3  19.505 VB    0.4584 2968.50244  100.86356  40.3022
   4  21.826 BB    0.5232 2939.77002   87.14444  39.9121

Totals :                  7365.61017  249.51773
```

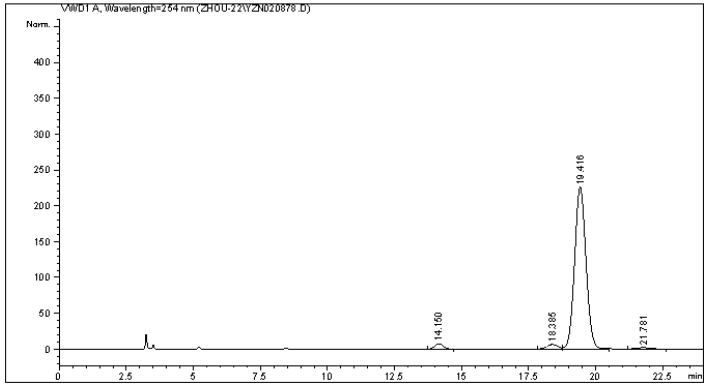


(+/-)-3pe

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020878.D
Sample Name: LL-9-39C

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/30/2022 7:02:04 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 5:52:07 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 8:01:01 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm
```



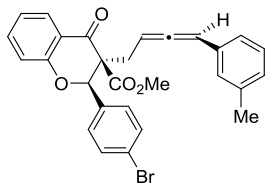
Area Percent Report

```
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

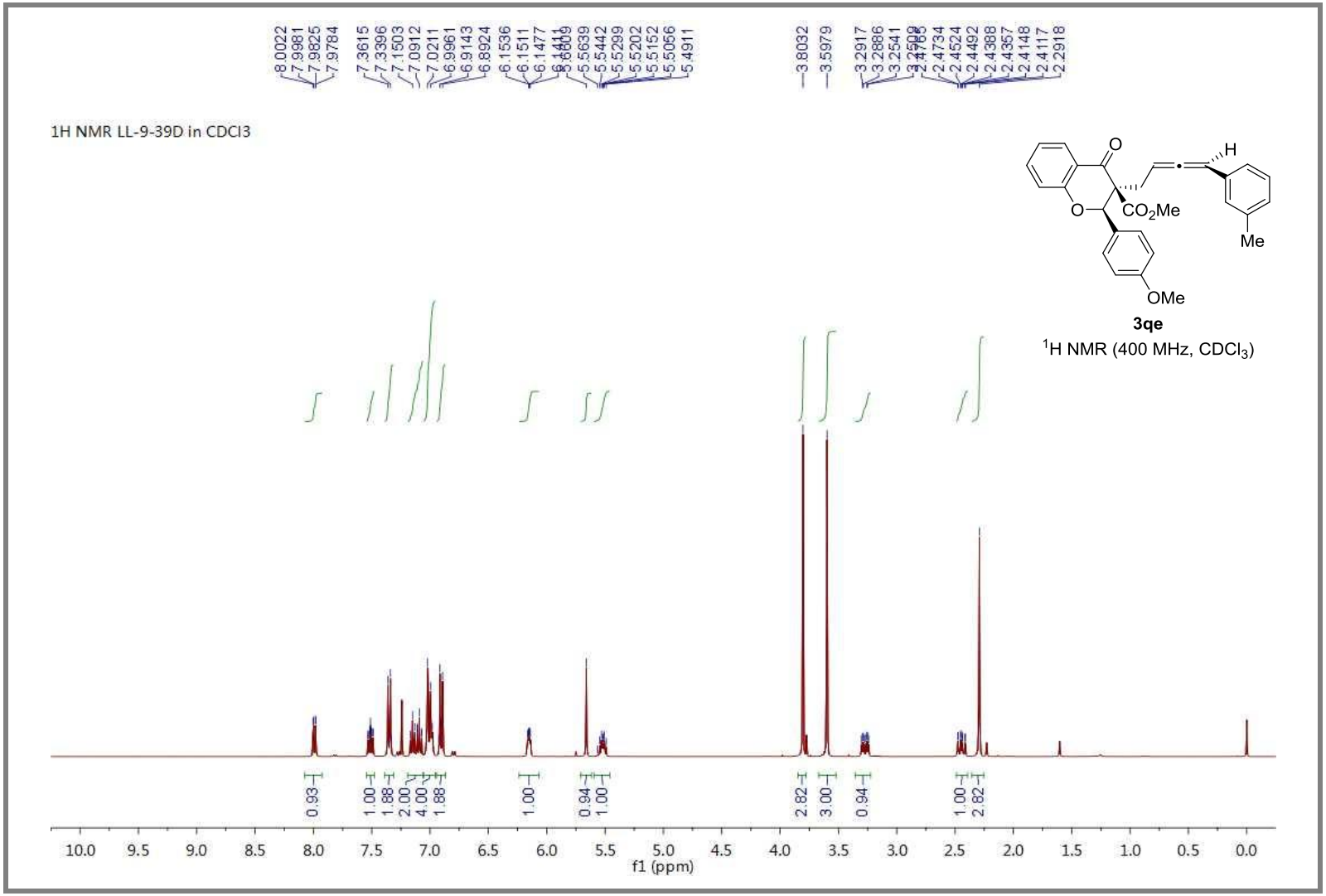
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  14.150 BB    0.3268  153.28743    7.29247   2.1775
   2  18.385 BV    0.4152  171.09190    6.28301   2.4304
   3  19.416 VB    0.4610 6658.12012  225.47424  94.5816
   4  21.781 BB    0.4914   57.04807    1.78218   0.8104

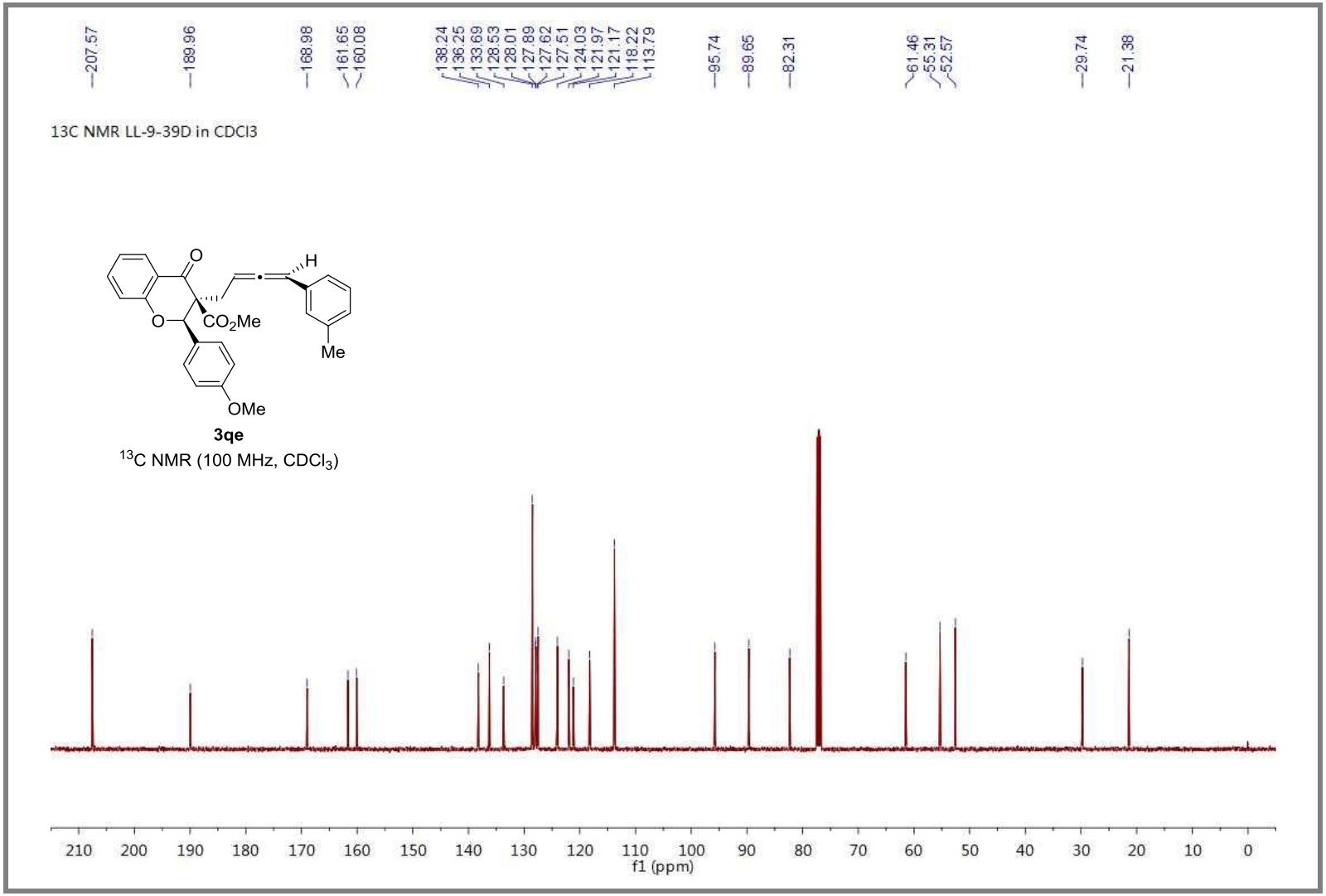
Totals :                  7039.54752  240.83190
```



(-)-3pe

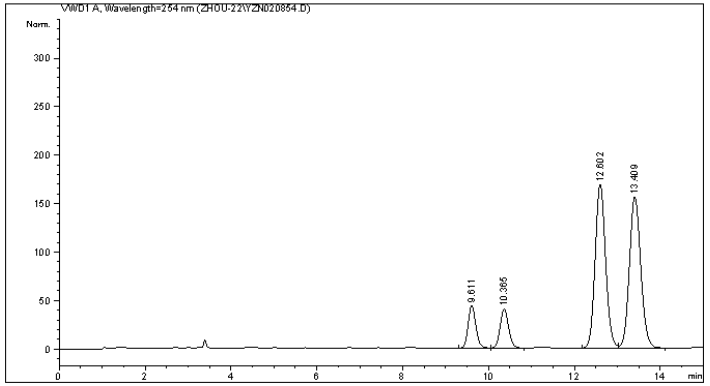
*** End of Report ***


1H NMR LL-9-39D in CDCl3
8.0022
7.9981
7.9825
7.9784
7.3615
7.3396
7.1503
7.0912
7.0211
6.9961
6.9143
6.8924
6.1536
6.1511
6.1477
5.5639
5.5442
5.5299
5.5202
5.5152
5.5056
5.4911
3.8032
3.5979
3.2917
3.2886
3.2541
2.4734
2.4524
2.4492
2.4388
2.4357
2.4148
2.4117
2.2918
O
H
O
CO2Me
Me
OMe
3qe
1H NMR (400 MHz, CDCl3)
0.93
1.00
1.88
2.00
4.00
1.88
1.00
0.94
1.00
2.82
3.00
0.94
1.00
2.82
10.0
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)


207.57
189.96
168.98
161.65
160.08
138.24
136.25
133.69
128.53
128.01
127.89
127.62
127.51
124.03
121.97
121.17
118.22
113.79
95.74
89.65
82.31
61.46
55.31
52.57
29.74
21.38
13C NMR LL-9-39D in CDCl3
O
H
O
CO2Me
Me
OMe
3qe
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020854.D
Sample Name: LL-9-39D +/-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/29/2022 2:06:43 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/29/2022 2:03:51 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 8:59:36 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

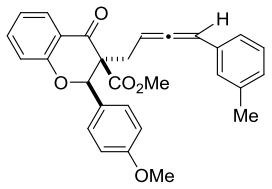
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.611 BV    0.1941  547.21344   43.71530   8.0220
   2  10.365 VB    0.2105  547.29370   40.40053   8.0232
   3  12.602 BV    0.2633 2859.57886  168.69302  41.9208
   4  13.409 VB    0.2843 2867.30200  156.01204  42.0340

Totals :                  6821.38800  408.82089

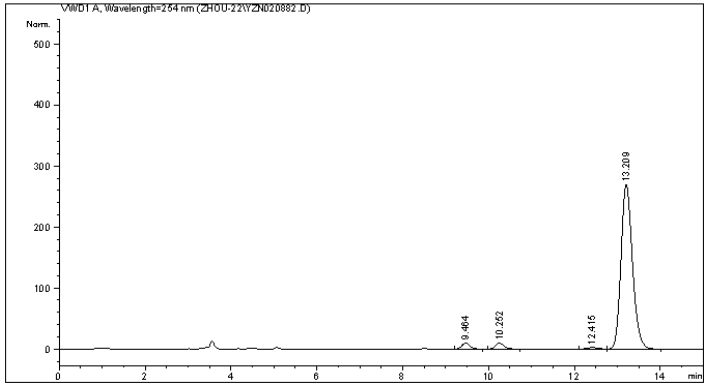
==========================================================================
                        *** End of Report ***
```



(+/-)-3qe

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020882.D
Sample Name: LL-9-39D

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/30/2022 9:02:40 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 9:01:22 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 3/30/2022 9:23:04 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

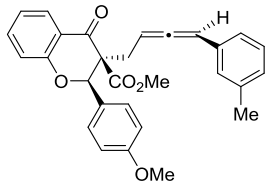
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

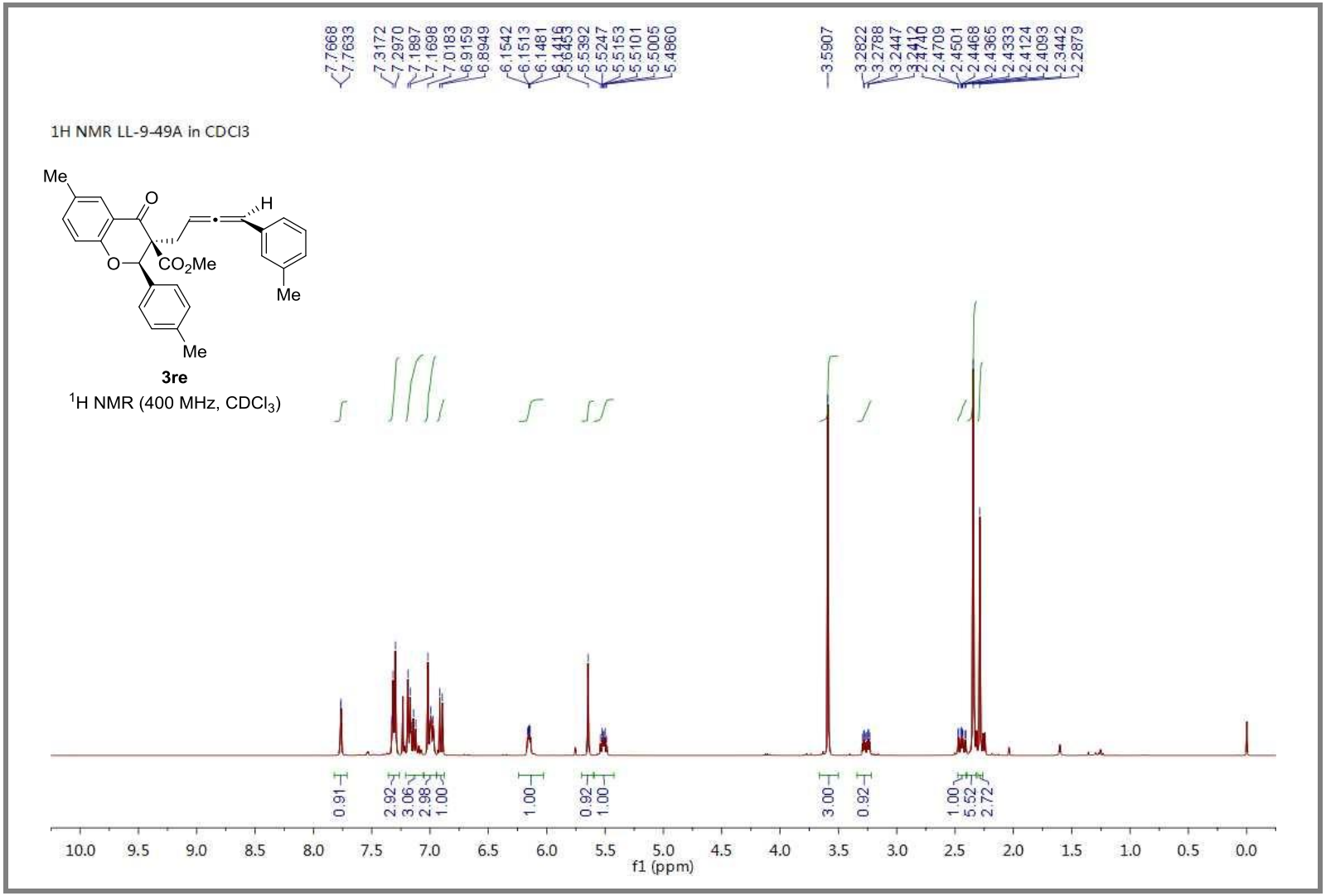
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.464 BB    0.1953  125.08141    9.81078   2.3634
   2  10.252 BB    0.2123  139.69920   10.09933   2.6397
   3  12.415 BV    0.2567   39.72606    2.40534   0.7506
   4  13.209 VB    0.2843 4987.81689  269.61588  94.2463

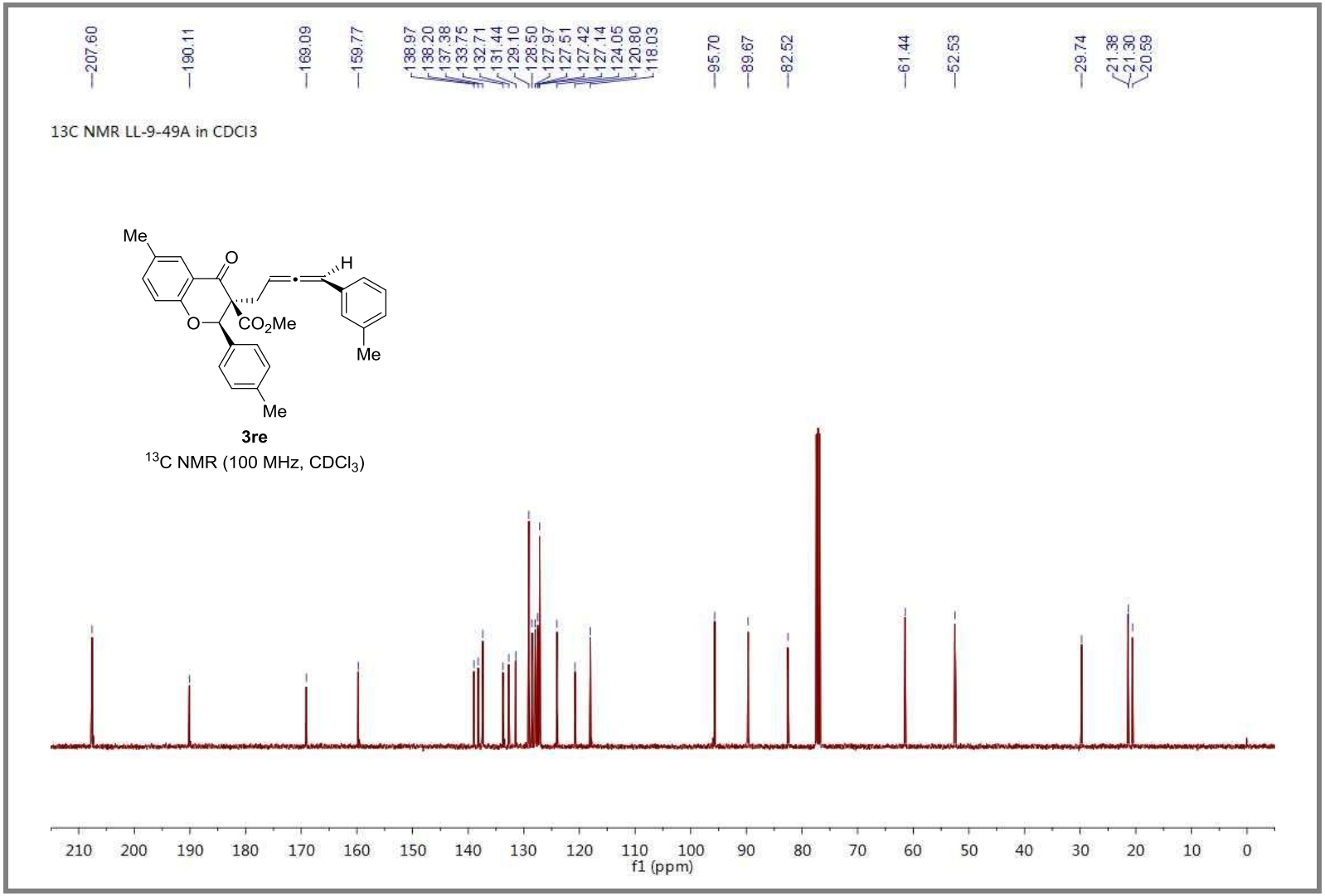
Totals :                  5292.32357  291.93133

==========================================================================
                        *** End of Report ***
```



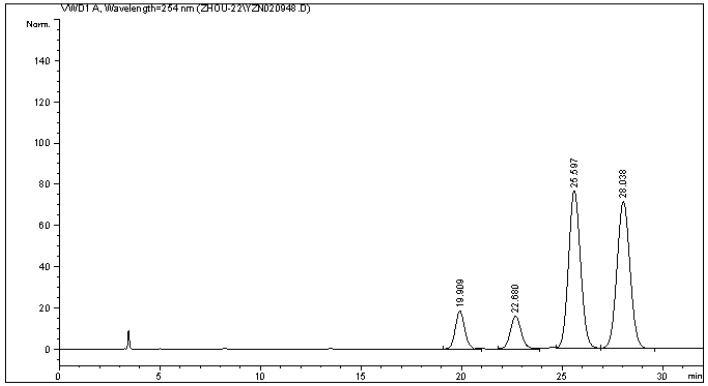
(-)-3qe


1H NMR LL-9-49A in CDCl3
Me
O
H
O
CO2Me
Me
Me
3re
1H NMR (400 MHz, CDCl3)
7.7668
7.7633
7.3172
7.2970
7.1897
7.1698
7.0183
6.9159
6.8949
6.1542
6.1513
6.1481
5.5392
5.5247
5.5153
5.5101
5.5005
5.4860
3.5907
3.2822
3.2788
3.2447
2.4709
2.4501
2.4468
2.4365
2.4333
2.4124
2.4093
2.3442
2.2879
0.91
2.92
3.06
2.98
1.00
1.00
0.92
1.00
3.00
0.92
1.00
5.52
2.72
10.0
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)


207.60
190.11
169.09
159.77
138.97
138.20
137.38
133.75
132.71
131.44
129.10
128.50
127.97
127.51
127.42
127.14
124.05
120.80
118.03
95.70
89.67
82.52
61.44
52.53
29.74
21.38
21.30
20.59
13C NMR LL-9-49A in CDCl3
Me
O
H
O
CO2Me
Me
Me
3re
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020948.D
Sample Name: LL-9-49A (+/-)

Acq. Operator :
Acq. Instrument : Instrument 1 Location : -
Injection Date : 4/12/2022 10:19:06 PM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 4/12/2022 10:16:55 PM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 4/12/2022 10:52:51 PM
(modified after loading)
Sample Info : IC, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm

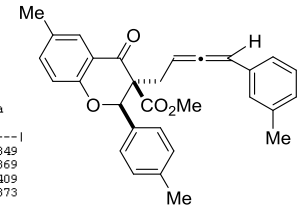


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.909	BB	0.4943	591.56036	18.47964	7.7849
2	22.680	BB	0.5743	587.91638	15.89114	7.7369
3	25.597	VV	0.6478	3202.21997	76.83402	42.1409
4	28.038	VB	0.7013	3217.14160	71.47879	42.3373
Totals :				7598.83832	182.68359	



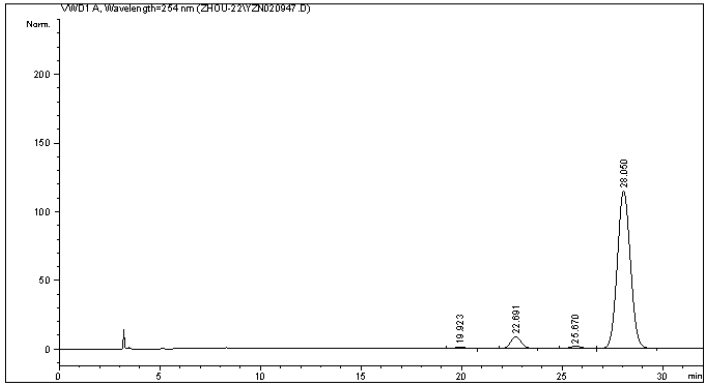
(+/-)-3re

*** End of Report ***

Instrument 1 4/12/2022 10:52:55 PM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020947.D
Sample Name: LL-9-49A

Acq. Operator :
Acq. Instrument : Instrument 1 Location : -
Injection Date : 4/12/2022 9:42:24 PM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 4/12/2022 9:28:32 PM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 4/12/2022 10:50:29 PM
(modified after loading)
Sample Info : IC, Hexane/i-PrOH = 97/3, 1.0 mL/min, 30 oC, 254 nm

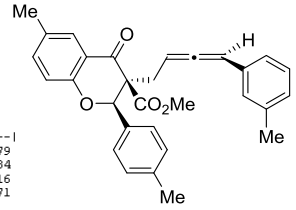


Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

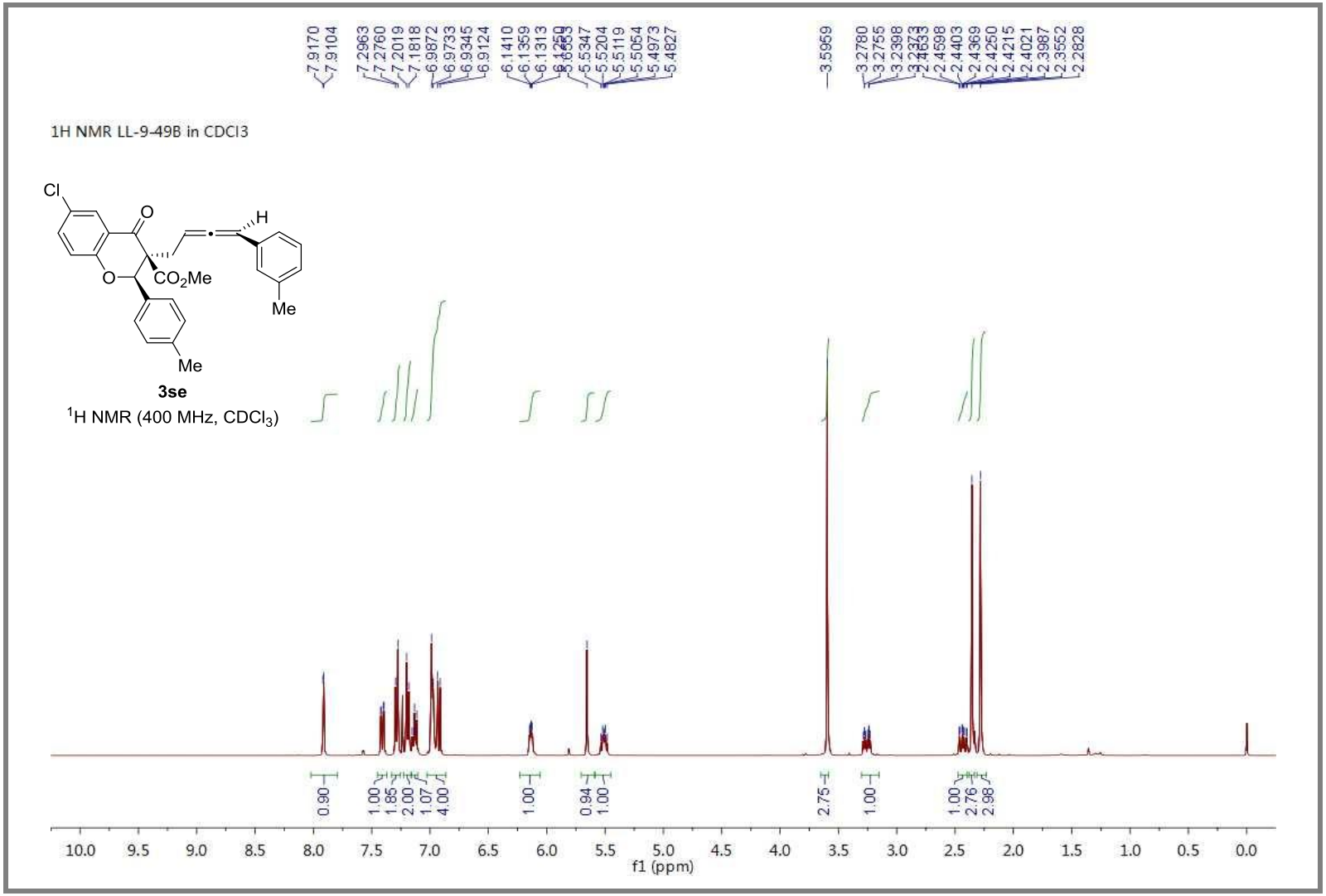
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.923	BB	0.4965	43.03652	1.31603	0.7679
2	22.691	BB	0.5731	317.96243	8.58951	5.6734
3	25.670	BV	0.6103	66.22372	1.59264	1.1816
4	28.050	VB	0.7022	5177.21680	114.83069	92.3771
Totals :				5604.43947	126.32886	

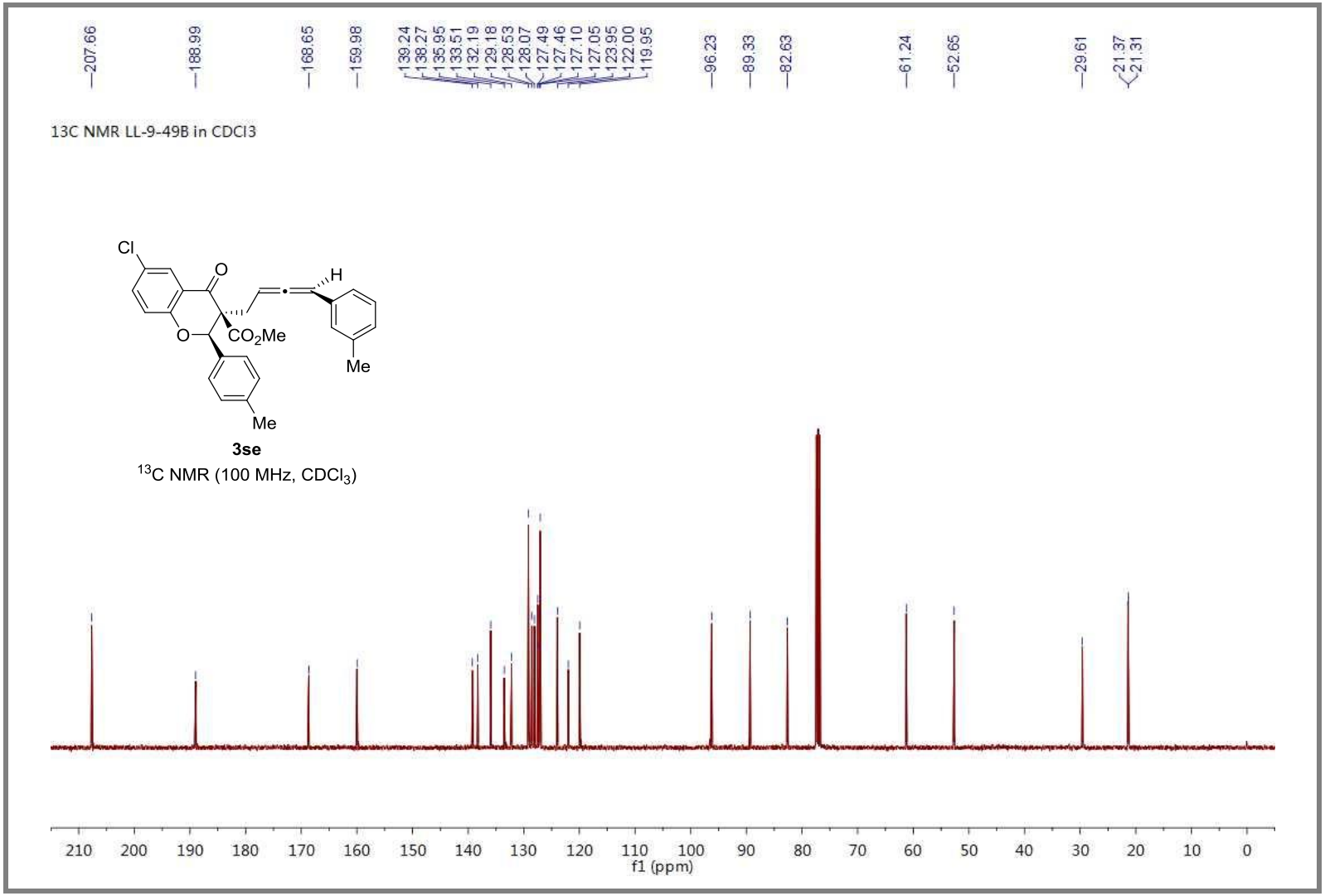


(-)-3re

*** End of Report ***

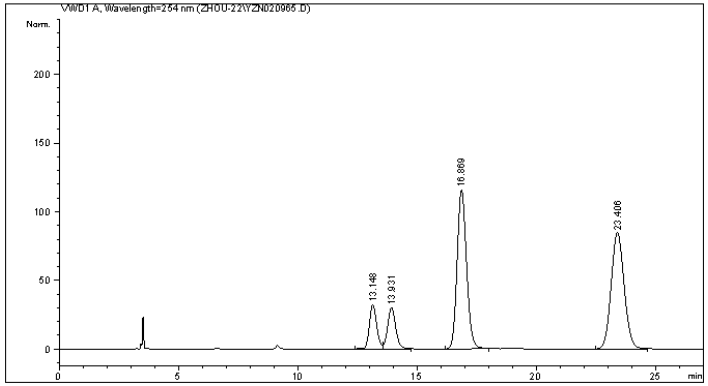
Instrument 1 4/12/2022 10:50:38 PM Page 1 of 1


1H NMR LL-9-49B in CDCl3
Cl
O
H
O
CO2Me
Me
Me
3se
1H NMR (400 MHz, CDCl3)
f1 (ppm)


207.66
188.99
168.65
159.98
139.24
138.27
135.95
133.51
132.19
129.18
128.53
128.07
127.49
127.46
127.10
127.05
123.95
122.00
119.95
96.23
89.33
82.63
61.24
52.65
29.61
21.37
21.31
13C NMR LL-9-49B in CDCl3
Cl
O
H
O
CO2Me
Me
Me
3se
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020965.D
Sample Name: LL-9-49B +/-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/13/2022 8:30:06 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 4/13/2022 8:28:06 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 4/13/2022 9:04:03 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 98/2,1.0 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

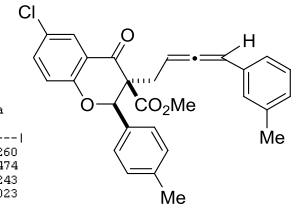
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.148 BV    0.3286  687.04541   32.25151   8.8260
   2  13.931 VB    0.3596  704.27374   30.18419   9.0474
   3  16.869 BB    0.4272 3185.66895  115.82655  40.9243
   4  23.406 BB    0.5896 3207.30396   84.54397  41.2023

Totals :                  7784.29205  262.80622

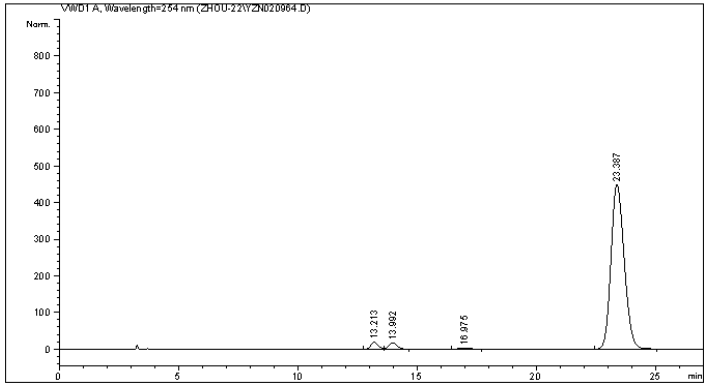
==========================================================================
                        *** End of Report ***
```



(+/-)-3se

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN020964.D
Sample Name: LL-9-49B

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/13/2022 8:00:27 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 4/13/2022 7:21:48 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 4/13/2022 9:06:04 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 98/2,1.0 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

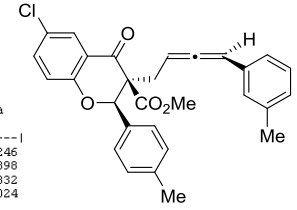
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

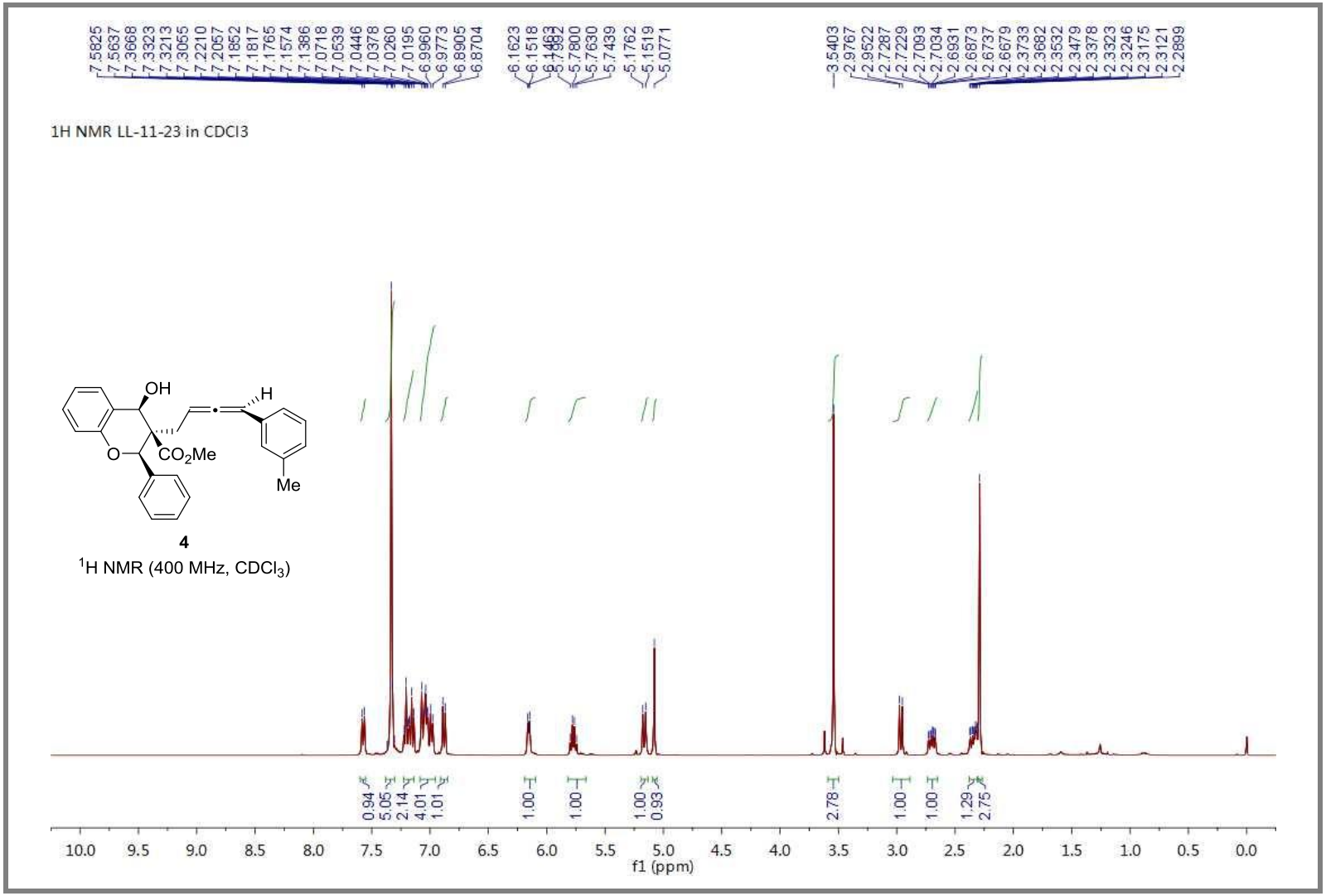
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.213 BV    0.3268  403.63647   18.97101   2.2246
   2  13.992 VB    0.3558  388.24243   16.78070   2.1398
   3  16.975 BB    0.4170   96.74460    3.50108   0.5332
   4  23.387 BB    0.5985 1.72556e4   448.82495  95.1024

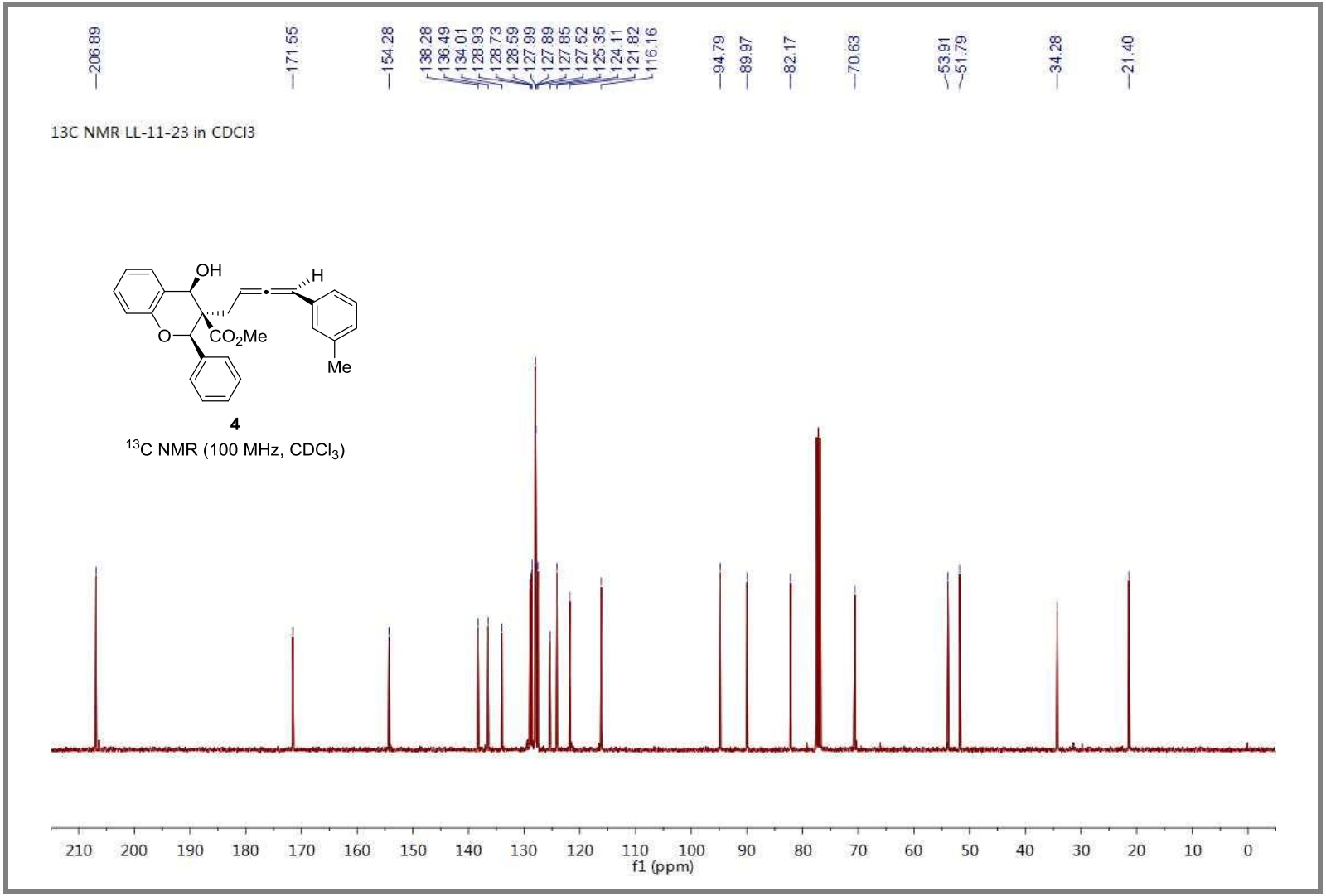
Totals :                  1.81442e4   488.07774

==========================================================================
                        *** End of Report ***
```



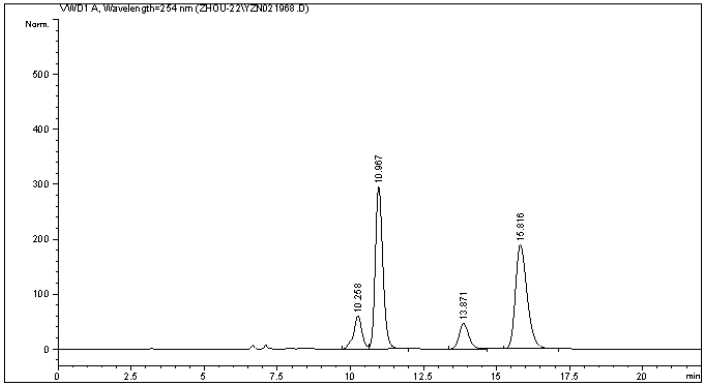
(-)-3se


1H NMR LL-11-23 in CDCl3
OH
H
O
CO2Me
Me
4
1H NMR (400 MHz, CDCl3)
f1 (ppm)


206.89
171.55
154.28
138.28
136.49
134.01
128.93
128.73
128.59
127.99
127.89
127.85
127.52
125.35
124.11
121.82
116.16
94.79
89.97
82.17
70.63
53.91
51.79
34.28
21.40
13C NMR LL-11-23 in CDCl3
OH
H
O
CO2Me
Me
4
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN021968.D
Sample Name: LL-11-23 +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 11/4/2022 10:29:51 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/4/2022 10:13:16 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/5/2022 7:36:04 AM
                  (modified after loading)
Sample Info     : ID, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```



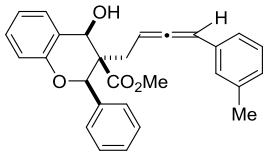

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  10.258 BV    0.2947 1194.14185   60.40765   9.3277
   2  10.967 VB    0.2770 5304.89404  294.68143  41.4377
   3  13.871 BB    0.3519 1052.33911   46.16315   8.2201
   4  15.816 BB    0.4273 5250.72168  189.13594  41.0145

Totals :                  1.28021e4   590.38817
```

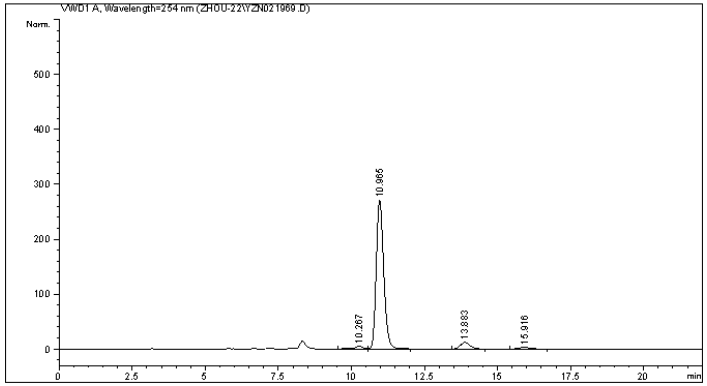


(+/-)-4

```
                          *** End of Report ***
```


Data File C:\CHEM32\1\DATA\ZHOU-22\YZN021969.D
Sample Name: LL-11-23

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 11/4/2022 10:54:23 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/4/2022 10:52:49 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 11/5/2022 7:36:04 AM
                  (modified after loading)
Sample Info     : ID, Hexane/i-PrOH = 90/10, 1.0 mL/min, 30 oC, 254 nm
```



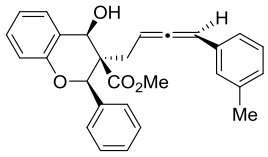

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  10.267 BV    0.3174  105.68909    4.78379   2.0084
   2  10.965 VB    0.2740 4805.31104  270.75851  91.3166
   3  13.883 BB    0.3511  270.88757   11.91542   5.1477
   4  15.916 BB    0.4418   80.36528    2.88241   1.5272

Totals :                  5262.25298  290.34014
```



(-)-4

```
                          *** End of Report ***
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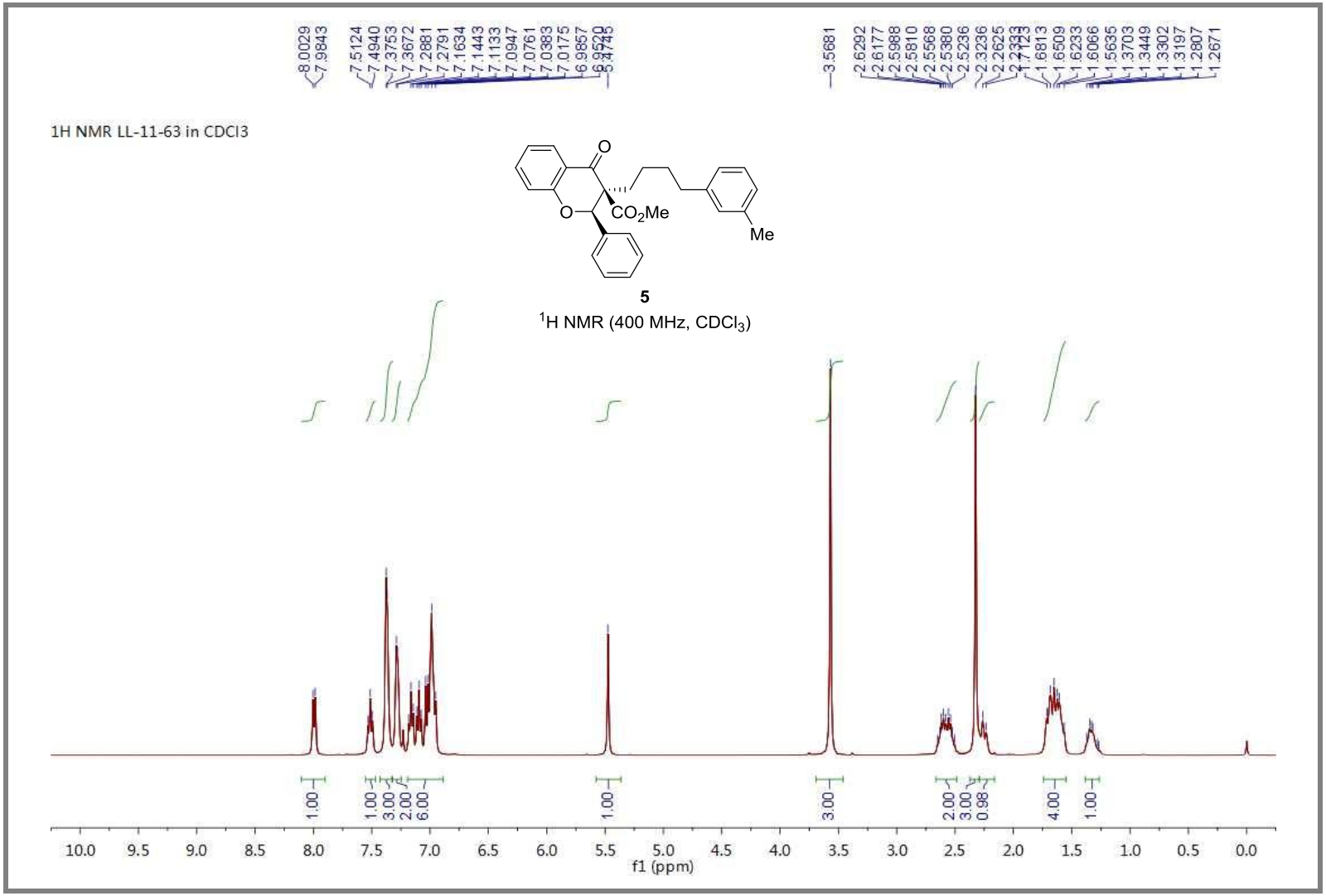
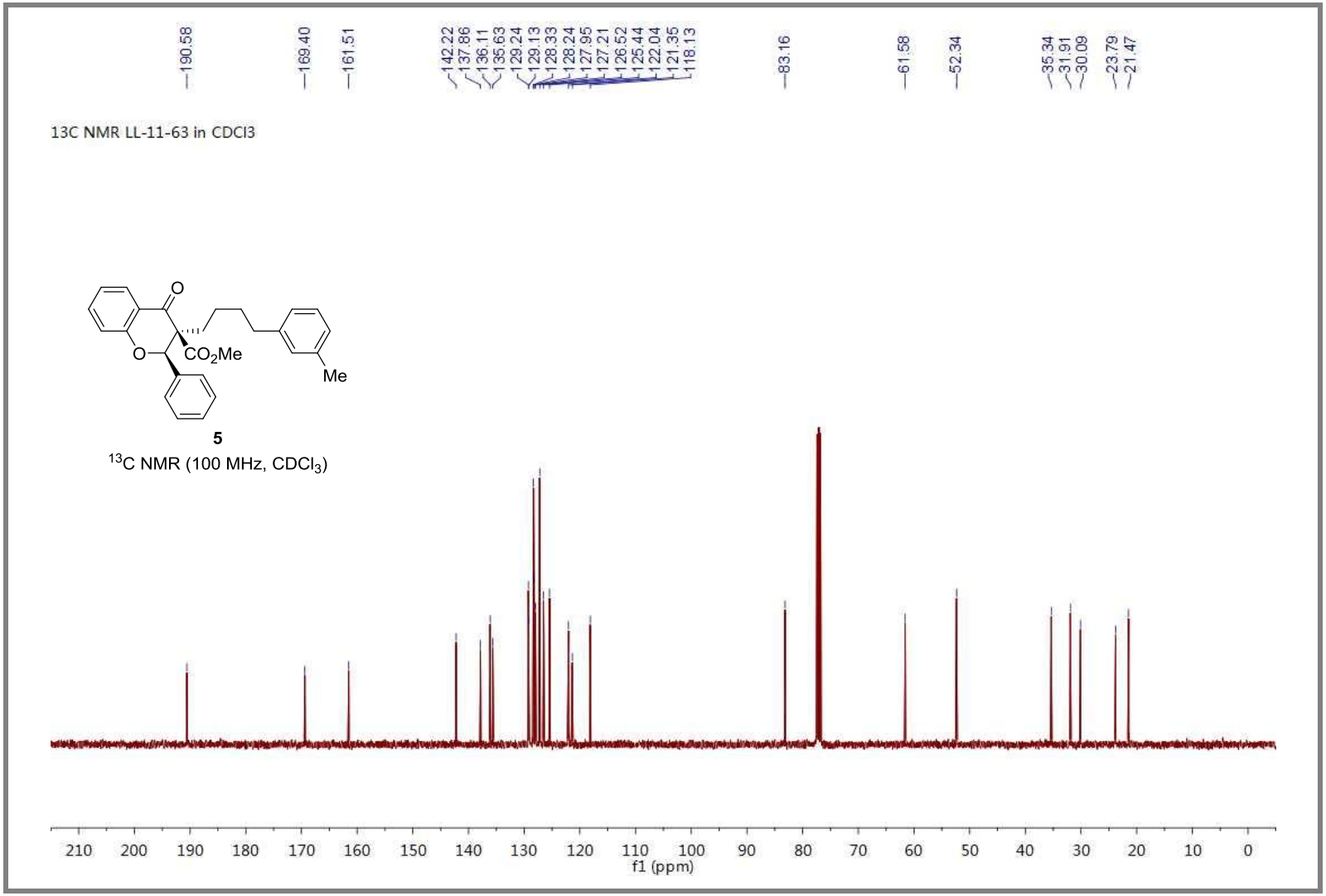
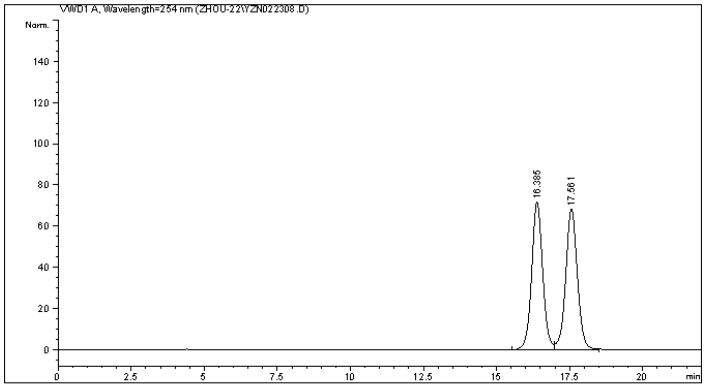

1H NMR LL-11-63 in CDCl3
8.0029
7.9843
7.5124
7.4940
7.3753
7.3672
7.2881
7.2791
7.1634
7.1443
7.1133
7.0947
7.0761
7.0383
7.0175
6.9857
6.9520
3.5681
2.6292
2.6177
2.5988
2.5810
2.5568
2.5380
2.5236
2.3236
2.2625
2.2333
2.2123
1.6813
1.6509
1.6233
1.6066
1.5635
1.3703
1.3449
1.3302
1.3197
1.2807
1.2671
O
O
CO2Me
Me
5
1H NMR (400 MHz, CDCl3)
1.00
1.00
3.00
2.00
6.00
1.00
3.00
2.00
3.00
0.98
4.00
1.00
10.0
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)


190.58
169.40
161.51
142.22
137.86
136.11
135.63
129.24
129.13
128.33
128.24
127.95
127.21
126.52
125.44
122.04
121.35
118.13
83.16
61.58
52.34
35.34
31.91
30.09
23.79
21.47
13C NMR LL-11-63 in CDCl3
O
O
CO2Me
Me
5
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN022308.D
Sample Name: LL-11-63 +/-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 12/31/2022 3:39:18 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 12/31/2022 3:33:27 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 12/31/2022 4:31:43 AM
                  (modified after loading)
Sample Info     : IA, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

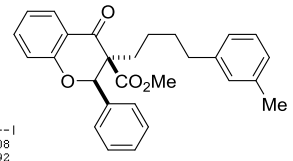
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.385 BV    0.4003 1878.85657   71.71486  49.8908
   2  17.561 VB    0.4227 1887.08228   68.32843  50.1092

Totals :                  3765.93884  140.04329

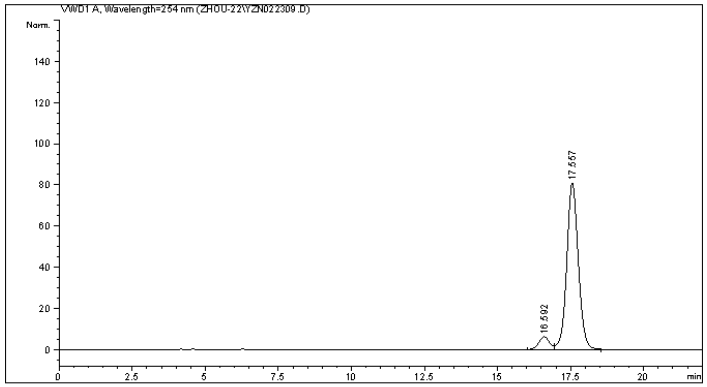
                          *** End of Report ***
```



(+/-)-5

Data File C:\CHEM32\1\DATA\ZHOU-22\YZN022309.D
Sample Name: LL-11-63

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 12/31/2022 4:02:32 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 12/31/2022 4:01:40 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 12/31/2022 4:31:43 AM
                  (modified after loading)
Sample Info     : IA, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

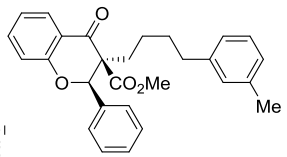
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.592 BV    0.3872  159.30807    6.22962   6.6852
   2  17.557 VB    0.4209 2223.68799   80.96862  93.3148

Totals :                  2382.99606   87.19824

                          *** End of Report ***
```



(-)-5