Supporting Information

Design and Synthesis of Chiral and Regenerable [2.2]Paracyclophane-Based NAD(P)H Models and Application in Biomimetic Reduction of Flavonoids

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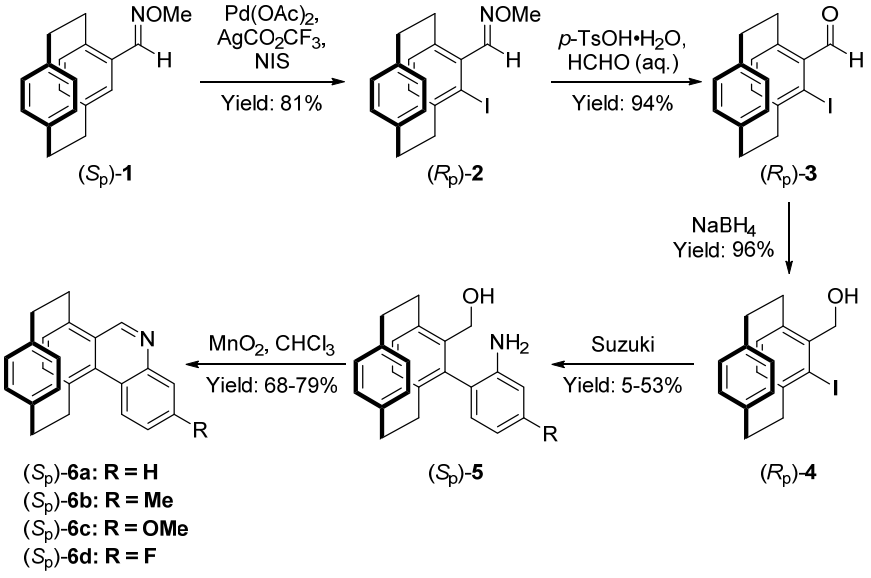
1. General

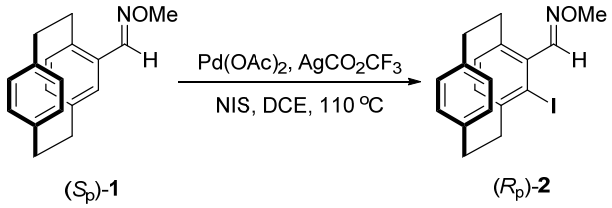
All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Brucker spectrometer. ^{19}F was recorded at 376 MHz with Brucker spectrometer. Chemical shifts are reported in ppm using tetramethylsilane (0) as internal standard when using $CDCl_3$ as solvent for ^{1}H NMR spectra. The following abbreviations were used to symbolize the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis. Optical rotations were measured by polarimeter. Enantiomeric excess was determined by HPLC analysis using chiral column described below in detail.

2. Procedures for Synthesis of NAD(P)H Model CYNAMs



A series of NAD(P)H models **6a-6d** with planar chirality could be synthesized in five steps from the known starting material oxime ether (S_p)-**1**. Compound (S_p)-**1** can be prepared according to the known literature procedure with some minor modifications.[1]

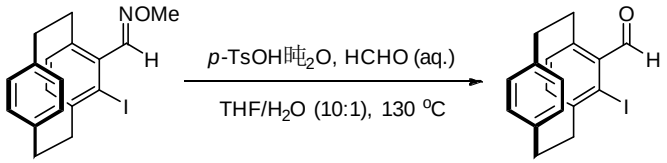
2.1. Synthesis of (R_p)-5-Formyl-4-iodo[2.2]paracyclophan-*O*-methylaldoxime (R_p)-2



To a solution of *N*-iodosuccinimide (1.981 g, 8.80 mmol), palladium(II) acetate (330 mg, 1.47 mmol) and silver trifluoroacetate (324 mg, 1.47 mmol) in anhydrous dichloroethane (120 mL) in a 250 mL Schlenk flask, (S_p)-4-formyl[2.2]paracyclophan-*O*-methylaldoxime (S_p)-**1** (1.947 g, 7.34 mmol) was added under nitrogen. The reaction mixture was stirred for 6 h at 110 ^{o}C. The mixture was cooled to ambient temperature and then filtered through celite. The solvent was evaporated in *vacuo*. The crude product was purified by flash chromatography to give the *O*-methylaldoxime

(R_p)-**2** (2.326 g, 81% yield, >99% ee). Yellow solid, new compound, m.p. = 98-99 °C, R_f = 0.60 (hexanes/dichloromethane 1/1), $[\alpha]^{20}_D$ = -147.03 (*c* 0.54, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.1 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.64-6.56 (m, 2H), 6.56-6.49 (m, 2H), 6.46 (d, *J* = 7.7 Hz, 1H), 4.03 (s, 3H), 3.83-3.73 (m, 1H), 3.46 (t, *J* = 10.6 Hz, 1H), 3.21-2.95 (m, 5H), 2.91-2.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 143.8, 140.7, 139.6, 138.8, 135.0, 134.3, 133.5, 133.2, 132.9, 130.0, 128.6, 110.1, 62.2, 40.0, 35.0, 34.7, 33.1. HRMS: Calculated for $C_{18}H_{19}INO$ $[M+H]^+$ 392.0506, found: 392.0507.

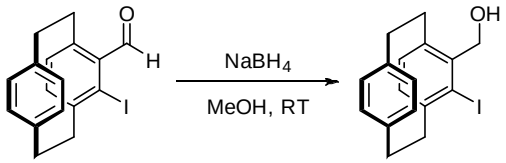
2.2. Synthesis of (R_p)-5-Formyl-4-iodo[2.2]paracyclophane (R_p)-3



(R_p)-**2** (R_p)-**3**

In a sealed tube, (R_p)-5-formyl-4-iodo[2.2]paracyclophan-*O*-methylaldoxime (R_p)-**2** (4.534 g, 11.59 mmol), formaldehyde (37% solution in water, 17.4 mL, 231.80 mmol) and *p*-toluene-sulfonic acid monohydrate (4.413 g, 23.18 mmol) were dissolved in tetrahydrofuran/water (44 mL, 10:1), and the reaction mixture was stirred for 72 h at 130 °C. The mixture was cooled to ambient temperature and extracted with dichloromethane (40 mL×3). Then the combined organic layer was dried over anhydrous sodium sulfate and concentrated in *vacuo*. The solid obtained was purified by flash column chromatography using hexanes/ethyl acetate as eluent to deliver the iodated aldehyde (R_p)-**3** (3.953 g, 94% yield, >99% ee). Yellow solid, new compound, m.p. = 83-84 °C, R_f = 0.80 (hexanes/ethyl acetate 30/1), $[\alpha]^{20}_D$ = -163.99 (*c* 0.40, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 6.98 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.69-6.54 (m, 3H), 6.49 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.38 (dd, *J* = 7.9, 1.8 Hz, 1H), 3.93-3.80 (m, 1H), 3.62-3.52 (m, 1H), 3.26-3.13 (m, 3H), 3.09-2.96 (m, 2H), 2.87-2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 144.6, 144.2, 139.8, 138.8, 137.0, 135.4, 135.3, 133.2, 132.8, 131.1, 128.8, 111.1, 39.2, 35.0, 34.3, 33.1. HRMS: Calculated for $C_{17}H_{16}IO$ $[M+H]^+$ 363.0240, found: 363.0244.

2.3. Synthesis of (R_p)-5-(Hydroxymethyl)-4-iodo[2.2]paracyclophane (R_p)-4

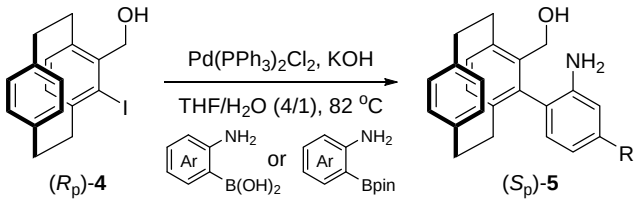


(R_p)-**3** (R_p)-**4**

To a solution of (R_p)-5-formyl-4-iodo[2.2]paracyclophane (R_p)-**3** (3.931 g, 10.90 mmol) in methanol (50 mL) under nitrogen was added sodium borohydride (455 mg, 12.00 mmol). The mixture was stirred for 6 h at ambient temperature. When TLC indicated that the reaction was finished, the reaction mixture was quenched with water (20 mL). After being extracted with dichloromethane and washed with water twice, the combined organic layer was dried over anhydrous sodium sulfate and concentrated in *vacuo*. A short silica gel column filtration of the crude mixture afforded the desired product (R_p)-5-(hydroxymethyl)-4-iodo[2.2]paracyclophane (R_p)-**4** (3.791 g, 96% yield, >99% ee). White solid, new compound, m.p. = 92-93 °C, R_f = 0.40 (hexanes/ethyl acetate 5/1), $[\alpha]^{20}_D$ = -90.19 (*c* 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01

(dd, J = 7.9, 1.9 Hz, 1H), 6.66-6.52 (m, 3H), 6.47 (d, J = 7.7 Hz, 2H), 4.61 (s, 2H), 3.57-3.45 (m, 2H), 3.24-3.13 (m, 2H), 3.11-2.97 (m, 4H), 1.80 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.5, 140.2, 139.1, 138.9, 134.5, 133.3, 133.2, 132.8, 130.7, 128.6, 111.3, 67.6, 40.2, 35.1, 34.0, 33.1. HRMS: Calculated for $C_{17}H_{17}INaO$ $[M+Na]^+$ 387.0216, found: 387.0215.

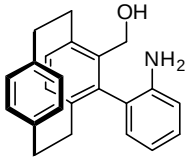
2.4. Suzuki Cross-Coupling



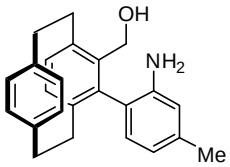
(R_p)-**4** (S_p)-**5**

Under nitrogen, a solution of the above alcohol (R_p)-**4** (911 mg, 2.50 mmol), bis(triphenylphosphine)palladium(II) chloride (351 mg, 20 mol%), potassium hydroxide (421 mg, 7.50 mmol) and the corresponding 2-aminoarylboronic acid or 2-aminoarylboronic acid pinacolate ester[2] (5.0 mmol) in tetrahydrofuran (36 mL) and water (9 mL) was heated at 82 °C for 24 h. The mixture was cooled to room temperature and extracted with ethyl acetate (20 mL×3). Then the combined organic layer was dried over anhydrous sodium sulfate and concentrated in *vacuo*. The residue was purified by flash column chromatography using hexanes and ethyl acetate as eluent to achieve the corresponding products (S_p)-**5a-c**.

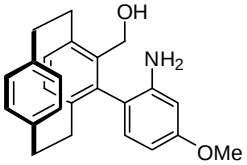
(S_p)-5-(Hydroxymethyl)-4-(2-aminophenyl)-[2.2]paracyclophane (5a): 0.274 g, 33% yield with 2-aminophenylboronic acid, brown foamy solid, new compound, m.p. = 145-146 °C, R_f = 0.20 (hexanes/ethyl acetate 5/1), >99% ee, $[\alpha]^{20}_D$ = +7.50 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.6, 1.3 Hz, 1H), 7.15-7.08(m, 1H), 6.94-6.87 (m, 1H), 6.67-6.58 (m, 4H), 6.50-6.41 (m, 3H), 4.23 (s, 2H), 3.54-3.43 (m, 1H), 3.14-3.06 (m, 1H), 3.05-2.98 (m, 1H), 2.98-2.88 (m, 3H), 2.87-2.76 (m, 4H), 2.75-2.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 140.3, 139.7, 139.5, 138.8, 137.4, 135.4, 134.7, 134.4, 133.3, 132.5, 130.8, 130.6, 129.4, 128.4, 125.5, 118.7, 116.1, 61.1, 35.3, 34.9, 33.0, 32.6. HRMS Calculated for $C_{23}H_{24}NO$ $[M+H]^+$ 330.1852, found: 330.1854.



(S_p)-5-(Hydroxymethyl)-4-(2-amino-4-methylphenyl)-[2.2]paracyclophane (5b): 0.277 g, 40% yield with 2-amino-4-methylphenylboronic acid, brown foamy solid, new compound, m.p. = 63-64 °C, R_f = 0.30 (hexanes/ethyl acetate 3/1), >99% ee, $[\alpha]^{20}_D$ = -2.38 (*c* 0.93, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.7 Hz, 1H), 6.79 (d, J = 7.2 Hz, 1H), 6.75-6.64 (m, 3H), 6.57-6.45 (m, 4H), 4.37-4.27 (m, 2H), 3.61-3.50 (m, 1H), 3.21-3.13 (m, 1H), 3.12-3.05 (m, 1H), 3.04-2.89 (m, 4H), 2.89-2.68 (m, 4H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.2, 139.7, 139.6, 139.0, 138.2, 137.5, 135.2, 134.9, 134.3, 133.3, 132.4, 130.9, 130.6, 129.2, 122.4, 119.4, 116.6, 61.2, 35.3, 34.9, 33.0, 32.6, 21.3. HRMS Calculated for $C_{24}H_{25}NONa$ $[M+Na]^+$ 366.1828, found: 366.1833.

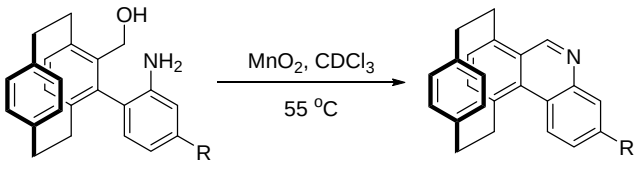


(S_p)-5-(Hydroxymethyl)-4-(2-amino-4-methoxyphenyl)-[2.2]paracyclophane (5c): 0.296 g, 53% yield with 2-amino-4-methoxyphenylboronic acid pinacolate ester, pale yellow foamy solid, new compound, m.p. = 69-70 °C, R_f = 0.20 (hexanes/ethyl acetate 5/1), >99% ee, $[\alpha]^{20}_D$ = +2.89 (*c* 0.90, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 1H), 6.74-6.63 (m, 3H), 6.58-6.46 (m, 4H), 6.27 (d, J = 2.4 Hz, 1H), 4.34 (dd, J = 28.7, 11.9 Hz, 2H), 3.83 (s, 3H),



3.59-3.51 (m, 1H), 3.21-3.14 (m, 1H), 3.12-3.05 (m, 1H), 3.05-2.86 (m, 5H), 2.86-2.79 (m, 1H), 2.61 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 145.7, 140.4, 139.7, 139.6, 139.3, 137.6, 135.1, 134.8, 134.3, 133.3, 132.4, 130.9, 130.5, 130.4, 117.8, 103.9, 101.2, 61.1, 55.2, 35.3, 35.0, 33.1, 32.7. HRMS: Calculated for $C_{24}H_{26}NO_2$ $[M+H]^+$ 360.1958, found: 360.1972.

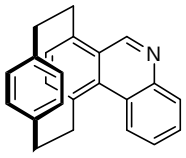
2.5. Synthesis of Chiral and Regenerable NAD(P)H Model CYNAMs (S_p)-6



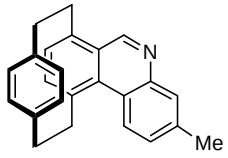
(S_p)-**5** (S_p)-**6**

To a solution of compound (S_p)-**5** (0.80 mmol) in chloroform (35 mL) was added manganese dioxide (1.251 g, 14.40 mmol). The resulted brown slurry was warmed to 55 °C for 72 h. When TLC indicated that the reaction was finished, the reaction mixture was directly purified by column chromatography on silica gel using hexanes and ethyl acetate to give products (S_p)-**6a-6c**.

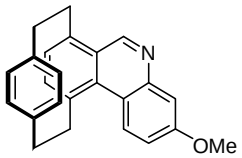
(S_p)-[2]Paracyclo[2](7,10)phenanthridinophane (6a): 0.190 g, 77% yield, yellow solid, new compound, mp = 142-143 °C, R_f = 0.60 (hexanes/ethyl acetate 3/1), >99% ee, $[\alpha]^{20}_D$ = +407.70 (*c* 0.22, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.52 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.74-7.67 (m, 1H), 7.65-7.56 (m, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.56-6.45 (m, 2H), 5.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.31 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.38-4.29 (m, 1H), 4.06-3.97 (m, 1H), 3.37-3.23 (m, 2H), 3.18-3.10 (m, 1H), 3.09-2.98 (m, 2H), 2.85-2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 144.6, 138.7, 138.3, 138.1, 137.9, 135.9, 134.8, 132.8, 132.4, 132.0, 130.4, 130.0, 128.6, 128.4, 128.1, 126.8, 126.4, 124.9, 38.3, 34.8, 34.2, 32.6. HRMS Calculated for $C_{23}H_{20}N$ $[M+H]^+$ 310.1590, found: 310.1593.



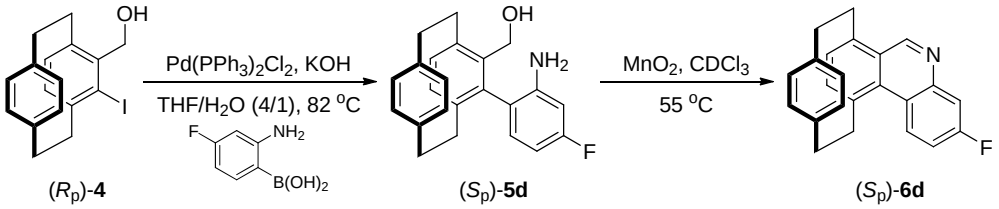
(S_p)-3-Methyl[2]paracyclo[2](7,10)phenanthridinophane (6b): 0.204 g, 79% yield, yellow solid, new compound, mp = 153-154 °C, R_f = 0.60 (hexanes/ethyl acetate 3/1), >99% ee, $[\alpha]^{20}_D$ = +253.48 (*c* 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 7.97 (s, 1H), 7.45 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.61-6.41 (m, 2H), 5.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.33 (dd, *J* = 7.8, 1.7 Hz, 1H), 4.39-4.30 (m, 1H), 4.06-3.97 (m, 1H), 3.36-3.24 (m, 2H), 3.19-3.11 (m, 1H), 3.10-3.00 (m, 2H), 2.86-2.77 (m, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 144.5, 138.6, 138.3, 138.3, 138.1, 137.9, 135.6, 134.9, 132.4, 132.4, 132.0, 130.3, 129.3, 128.4, 128.3, 128.2, 126.5, 122.7, 38.4, 34.8, 34.1, 32.5, 21.5. HRMS Calculated for $C_{24}H_{22}N$ $[M+H]^+$ 324.1747, found: 324.1752.



(S_p)-3-Methoxy[2]paracyclo[2](7,10)phenanthridinophane (6c): 0.191 g**,** 74% yield, yellow solid, new compound, mp = 181-182 °C, R_f = 0.50 (hexanes/ethyl acetate 3/1), >99% ee, $[\alpha]^{20}_D$ = +256.89 (*c* 0.42, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.44 (d, *J* = 9.2 Hz, 1H), 7.58 (d, *J* = 2.7 Hz, 1H), 7.26 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.55-6.43 (m, 2H), 5.80 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.34 (dd, *J* = 7.8, 1.7 Hz, 1H), 4.34-4.26 (m, 1H), 4.06-3.95 (m, 1H), 4.01 (s, 3H), 3.33-3.23 (m, 2H), 3.18-3.10 (m, 1H), 3.09-2.98 (m, 2H), 2.83-2.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 150.7, 146.3, 138.6, 138.3, 138.2, 137. 8,



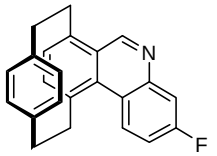
135.1, 132.3, 132.1, 131.9, 130.2, 128.1, 127.9, 127.8, 119.2, 117.5, 109.4, 55.5, 38.6, 34.8, 34.1, 32.5. HRMS Calculated for $C_{24}H_{22}NO$ $[M+H]^+$ 340.1696, found: 340.1697.



(R_p)-**4** (S_p)-**5d** (S_p)-**6d**

Under nitrogen, a solution of alcohol (R_p)-**4** (729 mg, 2.0 mmol), bis(triphenylphosphine)-palladium(II) chloride (421 mg, 30 mol%), potassium hydroxide (505 mg, 9.0 mmol) and (2-amino-4-fluorophenyl)boronic acid[2] (643 mg, 4.2 mmol) in tetrahydrofuran (30 mL) and water (7.5 mL) was heated at 82 °C for 24 h. The mixture was cooled to ambient temperature and extracted with ethyl acetate (20 mL×3). Then the combined organic layer was dried over anhydrous sodium sulfate and concentrated in *vacuo*. The oil obtained was simply purified by flash column chromatography to achieve the product (S_p)-**5d** (36 mg, 5% yield). Then to a solution of crude product (S_p)-**5d** (36 mg, 0.10 mmol) in chloroform (30 mL) was added manganese dioxide (162 mg, 1.80 mmol). The resulted brown slurry was warmed to 55 °C for 72 h. When TLC indicated that the reaction was finished, the reaction mixture was directly purified by column chromatography on silica gel using hexanes and ethyl acetate to give compound (S_p)-**6d**.

(S_p)-3-Fluoro[2]paracyclo[2](7,10)phenanthridinophane (6d): 23 mg, 68% yield, brown oil, new compound, R_f = 0.50 (hexanes/ethyl acetate 5/1), >99% ee, $[\alpha]^{20}_D$ = +254.57 (*c* 0.48, $CHCl_3$).

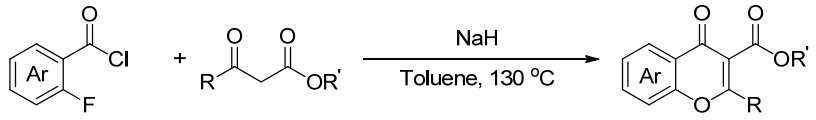


^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.51 (dd, *J* = 9.2, 6.0 Hz, 1H), 7.83 (dd, *J* = 9.7, 2.7 Hz, 1H), 7.44-7.34 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.59-6.43 (m, 2H), 5.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.33 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.33-4.22 (m, 1H), 4.01 (dd, *J* = 12.9, 11.0 Hz, 1H), 3.38-3.25 (m, 2H), 3.21-3.12 (m, 1H), 3.09-3.00 (m, 2H), 2.84-2.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, $^1J_{F\text{-}C}$ = 247.1 Hz), 151.4, 146.0, 145.9, 138.5, 138.5, 138.5, 137.9, 135.4, 134.7, 132.7, 132.5, 132.1, 130.4, 128.6 (d, $^3J_{F\text{-}C}$ = 9.1 Hz), 128.3, 121.7, 115.4 (d, $^2J_{F\text{-}C}$ = 23.3 Hz), 114.2 (d, $^2J_{F\text{-}C}$ = 20.1 Hz), 38.4, 34.8, 34.2, 32.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.49. HRMS Calculated for $C_{23}H_{19}FN$ $[M+H]^+$ 328.1496, found: 328.1498.

3. Lewis Acid-Promoted Biomimetic Asymmetric Reduction

3.1 Synthesis of Flavonoids

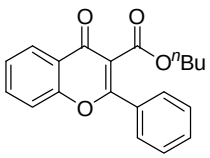
Flavonoids 7 could be prepared from readily available 2-fluoroaryl formyl chloride[3] and beta-ketoester[4-5] according to the known literature procedure with minor modification.[6] Among them, compounds **7a-b**,[7] 7**c**[8] and **7e-f**[8] are the known compounds.



7

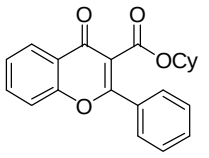
Under nitrogen, beta-ketoester (10 mmol) was dissolved in dry toluene (20 mL). Sodium hydride (11 mmol) was added and the mixture was stirred at room temperature for 30 min. Then the solution of 2-fluoroaryl formyl chloride (10 mmol) in dry toluene (20 mL) was added dropwise to the stirred mixture. After that the reaction was stirred under reflux overnight. The mixture was cooled to ambient temperature and quenched with water (20 mL). Then the mixture was extracted with ethyl acetate (40 mL×3). Then the combined organic layer was dried over anhydrous sodium sulfate and concentrated in *vacuo*. The products **7** were purified by flash column chromatography using hexanes/ethyl acetate as eluent. The solid products **7** could be obtained by recrystallization from dichloromethane/hexanes.

Butyl 4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (7d): 1.631 g, 56% yield, pale yellow oil, new compound, mp = 53-54 °C, R_f = 0.20 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$)



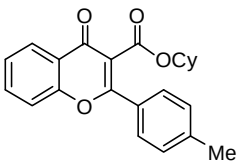
δ 8.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.80-7.70 (m, 3H), 7.60-7.50 (m, 4H), 7.49-7.43 (m, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 1.57-1.48 (m, 2H), 1.24-1.14 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 165.2, 163.1, 155.9, 134.3, 132.1, 131.6, 128.8, 128.1, 126.2, 125.7, 123.2, 118.5, 118.1, 65.8, 30.3, 18.9, 13.6. HRMS Calculated for $C_{20}H_{19}O_4$ $[M+H]^+$ 323.1278, found: 323.1276.

Cyclohexyl 4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (7g): 1.474 g, 43% yield, white solid, new compound, mp = 109-110 °C, R_f = 0.25 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400



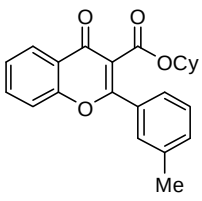
MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.82-7.68 (m, 3H), 7.58-7.41 (m, 5H), 5.02-4.91 (m, 1H), 1.84-1.74 (m, 2H), 1.66-1.56 (m, 2H), 1.52-1.44 (m, 1H), 1.39-1.26 (m, 4H), 1.24-1.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 164.5, 162.8, 155.9, 134.2, 132.1, 131.5, 128.7, 128.2, 126.1, 125.6, 123.3, 118.9, 118.1, 74.4, 31.2, 25.3, 23.6. HRMS Calculated for $C_{22}H_{21}O_4$ $[M+H]^+$ 349.1434, found: 349.1433.

Cyclohexyl 4-oxo-2-(*p*-tolyl)-4*H*-chromene-3-carboxylate (7h): 1.876 g, 59% yield, white solid, new compound, mp = 110-111 °C, R_f = 0.35 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400

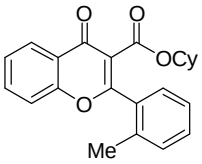


MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 1H), 7.78-7.64 (m, 3H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34-7.27 (m, 2H), 5.09-4.91 (m, 1H), 2.45 (s, 3H), 1.92-1.80 (m, 2H), 1.70-1.59 (m, 2H), 1.55-1.47 (m, 1H), 1.45-1.29 (m, 4H), 1.28-1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 164.8, 162.8, 155.9, 142.2, 134.2, 129.4, 129.2, 128.1, 126.1, 125.5, 123.3, 118.4, 118.0, 74.4, 31.2, 25.3, 23.6, 21.6. HRMS Calculated for $C_{23}H_{23}O_4$ $[M+H]^+$ 363.1591, found: 363.1593.

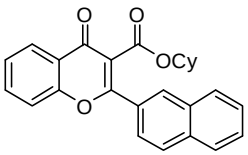
Cyclohexyl 4-oxo-2-(*m*-tolyl)-4*H*-chromene-3-carboxylate (7i): 0.806 g, 33% yield, white solid, new compound, mp = 119-120 °C, R_f = 0.30 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.76-7.69 (m, 1H), 7.63-7.51 (m, 3H), 7.48-7.35 (m, 3H), 5.05-4.94 (m, 1H), 2.44 (s, 3H), 1.89-1.78 (m, 2H), 1.68-1.57 (m, 2H), 1.54-1.46 (m, 1H), 1.43-1.29 (m, 4H), 1.27-1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 164.6, 163.0, 155.9, 138.6, 134.2, 132.3, 132.0, 128.7, 126.1, 125.6, 125.4, 123.3, 118.8, 118.1, 74.3, 31.2, 25.3, 23.6, 21.4. HRMS Calculated for $C_{23}H_{23}O_4$ $[M+H]^+$ 363.1591, found: 363.1597.



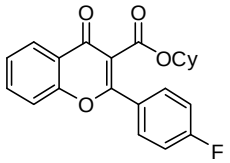
Cyclohexyl 4-oxo-2-(*o*-tolyl)-4*H*-chromene-3-carboxylate (7j): 0.492 g, 15% yield, white solid, new compound, mp = 130-131 °C, R_f = 0.30 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.28 (m, 1H), 7.78-7.68 (m, 1H), 7.51-7.40 (m, 4H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.31-7.25 (m, 1H), 4.84-4.73 (m, 1H), 2.41 (s, 3H), 1.65-1.39 (m, 5H), 1.30-1.07 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 165.2, 163.5, 156.0, 137.0, 134.2, 131.9, 130.9, 130.5, 129.0, 126.2, 125.8, 125.7, 123.6, 120.2, 118.1, 73.8, 31.0, 25.2, 23.5, 19.6. HRMS Calculated for $C_{23}H_{23}O_4$ $[M+H]^+$ 363.1591, found: 363.1593.



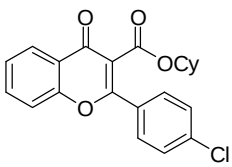
Cyclohexyl 2-(naphthalen-2-yl)-4-oxo-4*H*-chromene-3-carboxylate (7k): 1.021 g, 33% yield, white solid, new compound, mp = 120-121 °C, R_f = 0.50 (hexanes/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40-8.22 (m, 2H), 8.01-7.90 (m, 3H), 7.85 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.69-7.54 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 1H), 5.13-4.92 (m, 1H), 1.94-1.73 (m, 2H), 1.66-1.51 (m, 2H), 1.50-1.42 (m, 1H), 1.41-1.23 (m, 4H), 1.21-1.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 164.7, 162.6, 156.0, 134.5, 134.3, 132.6, 129.3, 129.1, 128.9, 128.7, 128.1, 127.9, 127.1, 126.2, 125.6, 124.3, 123.3, 119.1, 118.1, 74.5, 31.2, 25.2, 23.5. HRMS Calculated for $C_{26}H_{23}O_4$ $[M+H]^+$ 399.1591, found: 339.1595.



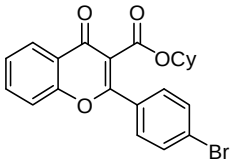
Cyclohexyl 2-(4-fluorophenyl)-4-oxo-4*H*-chromene-3-carboxylate (7l): 0.998 g, 36% yield, white solid, new compound, mp = 114-115 °C, R_f = 0.32 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.86-7.70 (m, 3H), 7.56-7.42 (m, 2H), 7.21 (t, *J* = 8.5 Hz, 2H), 5.06-4.91 (m, 1H), 1.90-1.78 (m, 2H), 1.70-1.60 (m, 2H), 1.55-1.47 (m, 1H), 1.43-1.30 (m, 4H), 1.27-1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 164.6 (d, $^1J_{F\text{-}C}$ = 251.8 Hz), 164.5, 161.5, 155.8, 134.3, 130.5 (d, $^3J_{F\text{-}C}$ = 8.8 Hz), 128.2 (d, $^4J_{F\text{-}C}$ = 3.2 Hz), 126.1, 125.71, 123.2, 118.8, 118.0, 116.0 (d, $^2J_{F\text{-}C}$ = 22.0 Hz), 74.6, 31.3, 25.2, 23.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.16. HRMS Calculated for $C_{22}H_{20}FO_4$ $[M+H]^+$ 367.1340, found: 367.1339.



Cyclohexyl 2-(4-chlorophenyl)-4-oxo-4*H*-chromene-3-carboxylate (7m): 1.245 g, 35% yield, white solid, new compound, mp = 148-149 °C, R_f = 0.30 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.80-7.70 (m, 3H), 7.58-7.44 (m, 4H), 5.07-4.93 (m, 1H), 1.94-1.77 (m, 2H), 1.70-1.60 (m, 2H), 1.57-1.49 (m, 1H), 1.44-1.31 (m, 4H), 1.28-1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 164.4, 161.3, 155.8, 137.9, 134.4, 130.4, 129.6, 129.1, 126.1, 125.8, 123.2, 119.0, 118.0, 74.7, 31.2, 25.2, 23.6. HRMS Calculated for $C_{22}H_{20}ClO_4$ $[M+H]^+$ 383.1045 and 385.1015, found: 383.1050 and 385.1023.

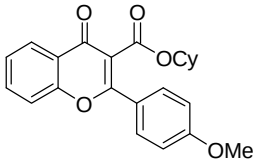


Cyclohexyl 2-(4-bromophenyl)-4-oxo-4*H*-chromene-3-carboxylate (7n): 2.709 g, 77% yield, white solid, new compound, mp = 149-150 °C, R_f = 0.30 (hexanes/ethyl acetate 10/1). ^{1}H NMR



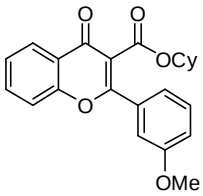
(400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.78-7.61 (m, 5H), 7.56-7.42 (m, 2H), 5.08-4.90 (m, 1H), 1.94-1.75 (m, 2H), 1.69-1.60 (m, 2H), 1.56-1.48 (m, 1H), 1.45-1.30 (m, 4H), 1.29-1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 164.4, 161.4, 155.8, 134.4, 132.1, 130.9, 129.7, 126.3, 126.1, 125.8, 123.2, 119.0, 118.1, 74.7, 31.2, 25.3, 23.6. HRMS Calculated for $C_{22}H_{20}BrO_4$ $[M+H]^+$ 427.0539 and 429.0519, found: 427.0536 and 429.0513.

Cyclohexyl 2-(4-methoxyphenyl)-4-oxo-4*H*-chromene-3-carboxylate (7o): 1.393 g, 42% yield, yellow solid, new compound, mp = 116-117 °C, R_f = 0.30 (hexanes/ethyl acetate 5/1). ^{1}H



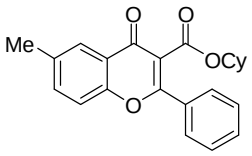
NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.74-7.67 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.09-4.95 (m, 1H), 3.89 (s, 3H), 1.97-1.76 (m, 2H), 1.70-1.62 (m, 2H), 1.57-1.48 (m, 1H), 1.47-1.31 (m, 4H), 1.28-1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 165.0, 162.4, 162.3, 155.8, 134.1, 130.0, 126.1, 125.4, 124.2, 123.2, 118.0, 117.9, 114.2, 74.4, 55.5, 31.3, 25.3, 23.6. HRMS Calculated for $C_{23}H_{23}O_5$ $[M+H]^+$ 379.1540, found: 379.1536.

Cyclohexyl 2-(3-methoxyphenyl)-4-oxo-4*H*-chromene-3-carboxylate (7p): 1.431 g, 47% yield, pale yellow solid, new compound, mp = 114-115 °C, R_f = 0.25 (hexanes/ethyl acetate



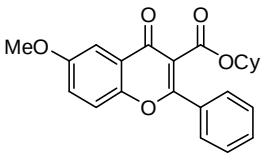
10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.48-7.34 (m, 3H), 7.31 (s, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 5.08-4.90 (m, 1H), 3.88 (s, 3H), 1.89-1.76 (m, 2H), 1.69-1.57 (m, 2H), 1.54-1.46 (m, 1H), 1.43-1.28 (m, 4H), 1.26-1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 164.5, 162.5, 159.7, 155.9, 134.3, 133.2, 129.9, 126.1, 125.6, 123.3, 120.6, 118.9, 118.1, 117.3, 113.5, 74.4, 55.5, 31.2, 25.3, 23.5. HRMS Calculated for $C_{23}H_{23}O_5$ $[M+H]^+$ 379.1540, found: 379.1536.

Cyclohexyl 6-methyl-4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (7q): 1.738 g, 60% yield, white solid, new compound, mp = 134-135 °C, R_f = 0.30 (hexanes/ethyl acetate 10/1). ^{1}H NMR



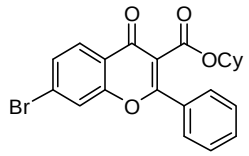
(400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.60-7.48 (m, 4H), 7.43 (d, *J* = 8.4 Hz, 1H), 5.05-4.89 (m, 1H), 2.49 (s, 3H), 1.88-1.73 (m, 2H), 1.65-1.60 (m, 2H), 1.53-1.45 (m, 1H), 1.40-1.28 (m, 4H), 1.25-1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 164.7, 162.6, 154.2, 135.7, 135.5, 132.2, 131.4, 128.7, 128.2, 125.4, 122.9, 118.7, 117.8, 74.3, 31.2, 25.3, 23.5, 21.0. HRMS Calculated for $C_{23}H_{23}O_4$ $[M+H]^+$ 363.1591, found: 363.1594.

Cyclohexyl 6-methoxy-4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (7r): 1.435 g, 38% yield, white solid, new compound, mp = 126-127 °C, R_f = 0.20 (hexanes/ethyl acetate 10/1). ^{1}H NMR



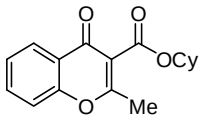
(400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 2.9 Hz, 1H), 7.59-7.45 (m, 4H), 7.34-7.29 (m, 1H), 5.05-4.92 (m, 1H), 3.92 (s, 3H), 1.88-1.76 (m, 2H), 1.68-1.58 (m, 2H), 1.54-1.46 (m, 1H), 1.41-1.28 (m, 4H), 1.26-1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 164.7, 162.5, 157.2, 150.7, 132.2, 131.4, 128.7, 128.2, 124.3, 123.9, 119.5, 118.1, 105.2, 74.3, 56.0, 31.2. 25.3, 23.6. HRMS Calculated for $C_{23}H_{23}O_5$ $[M+H]^+$ 379.1540, found: 379.1540.

Cyclohexyl 7-bromo-4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (7s): 2.721 g, 64% yield, white solid, new compound, mp = 124-125 °C, R_f = 0.40 (hexanes/ethyl acetate 10/1). ^{1}H NMR



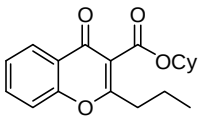
(400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.82-7.71 (m, 3H), 7.61-7.55 (m, 2H), 7.55-7.48 (m, 2H), 5.05-4.90 (m, 1H), 1.88-1.73 (m, 2H), 1.67-1.56 (m, 2H), 1.54-1.45 (m, 1H), 1.40-1.28 (m, 4H), 1.25-1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 164.1, 162.8, 155.9, 131.8, 131.6, 129.3, 128.8, 128.5, 128.2, 127.5, 122.2, 121.2, 119.1, 74.6, 31.2, 25.2, 23.5. HRMS Calculated for $C_{22}H_{20}BrO_4$ $[M+H]^+$ 427.0539 and 429.0519, found: 427.0541 and 429.0524.

Cyclohexyl 2-methyl-4-oxo-4*H*-chromene-3-carboxylate (7t): 0.404 g, 21% yield, pale yellow solid, new compound, mp = 122-123 °C, R_f = 0.40 (hexanes/ethyl acetate 10/1). ^{1}H NMR



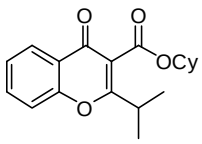
(400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.72-7.64 (m, 1H), 7.47-7.38 (m, 2H), 5.14-5.01 (m, 1H), 2.52 (s, 3H), 2.09-1.94 (m, 2H), 1.87-1.77 (m, 2H), 1.65-1.55 (m, 3H), 1.51-1.39 (m, 2H), 1.38-1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 166.0, 164.5, 155.6, 133.9, 126.1, 125.4, 123.4, 118.7, 117.7, 74.4, 31.6, 25.4, 23.8, 19.4. HRMS Calculated for $C_{17}H_{19}O_4$ $[M+H]^+$ 287.1278, found: 287.1277.

Cyclohexyl 4-oxo-2-propyl-4*H*-chromene-3-carboxylate (7u): 1.246 g, 28% yield, yellow oil, new compound, R_f = 0.30 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.71-7.63 (m, 1H), 7.47-7.37 (m, 2H), 5.13-5.01 (m, 1H),



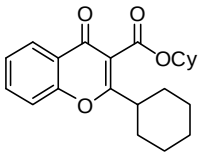
2.78-2.69 (m, 2H), 2.07-1.98 (m, 2H), 1.90-1.76 (m, 4H), 1.63-1.53 (m, 3H), 1.50-1.39 (m, 2H), 1.36-1.26 (m, 1H), 1.05 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 168.6, 164.5, 155.7, 133.8, 126.1, 125.4, 123.4, 118.7, 117.8, 74.4, 34.9, 31.6, 25.4, 23.8, 20.9, 13.8. HRMS Calculated for $C_{19}H_{23}O_4$ $[M+H]^+$ 315.1591, found: 315.1594.

Cyclohexyl 2-isopropyl-4-oxo-4*H*-chromene-3-carboxylate (7v): 1.506 g, 29% yield, white solid, new compound, mp = 87-88 °C, R_f = 0.30 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400 MHz,



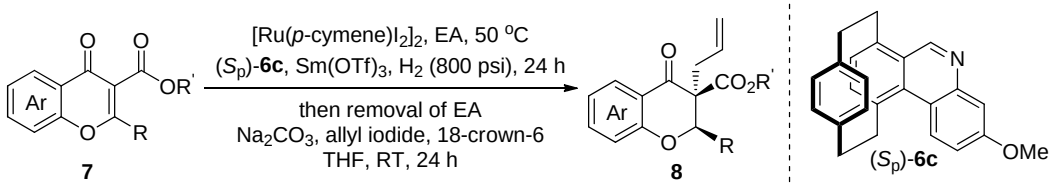
$CDCl_3$) δ 8.21 (d, *J* = 7.9 Hz, 1H), 7.72-7.64 (m, 1H), 7.50-7.37 (m, 2H), 5.14-5.02 (m, 1H), 3.22-3.08 (m, 1H), 2.08-1.94 (m, 2H), 1.86-1.74 (m, 2H), 1.66-1.53 (m, 3H), 1.50-1.26 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 171.5, 164.6, 155.8, 133.8, 126.0, 125.3, 123.5, 117.8, 117.5, 74.4, 32.3, 31.6, 25.4, 23.7, 19.9. HRMS Calculated for $C_{19}H_{23}O_4$ $[M+H]^+$ 315.1591, found: 315.1591.

Cyclohexyl 2-cyclohexyl-4-oxo-4*H*-chromene-3-carboxylate (7w): 2.659 g, 76% yield, yellow oil, new compound, R_f = 0.40 (hexanes/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ



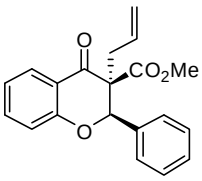
8.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71-7.63 (m, 1H), 7.49-7.35 (m, 2H), 5.15-5.03 (m, 1H), 2.86-2.71 (m, 1H), 2.07-1.85 (m, 6H), 1.84-1.67 (m, 5H), 1.64-1.53 (m, 3H), 1.50-1.26 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 171.0, 164.5, 155.8, 133.8, 126.0, 125.3, 123.5, 117.8, 117.6, 74.2, 42.3, 31.6, 29.8, 25.8, 25.6, 25.4, 23.7. HRMS Calculated for $C_{22}H_{27}O_4$ $[M+H]^+$ 355.1904, found: 355.1908.

3.2 Lewis Acid-Promoted Biomimetic Asymmetric Reduction of Flavonoids

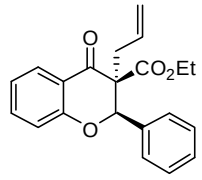


A mixture of [Ru(*p*-cymene)I_2]$_2$ (0.7 mg, 0.00075 mmol), samarium(III) trifluoromethanesulfonate (17.9 mg, 0.03 mmol), (S_p)-**6c** (5.1 mg, 0.015 mmol) and **7** (0.15 mmol) in ethyl acetate (3.0 mL) was stirred at room temperature for 5 min in glove box and then the mixture was transferred to an autoclave. The hydrogenation was performed at 50 °C under H_2 (800 psi) for 24 h. After carefully release of the hydrogen, the autoclave was opened and the reaction mixture was concentrated in *vacuo*. Then, sodium carbonate (63.6 mg, 0.60 mmol), allyl iodide (100.8 mg, 54.8 μL, 0.60 mmol), 18-crown-6 (11.8 mg, 10.2 μL, 0.045 mmol) and tetrahydrofuran (3.0 mL) were added to the mixture above. The new mixture was stirred at ambient temperature for 24 h. The reaction mixture was concentrated in *vacuo* and then purified by column chromatography on silica gel using hexanes and ethyl acetate to give **8**. The enantiomeric excesses were determined by chiral HPLC.

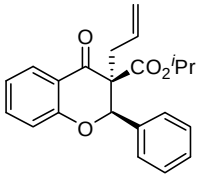
(-)-Methyl 3-allyl-4-oxo-2-phenylchromane-3-carboxylate (8a): 46 mg, 95% yield, pale yellow oil, new compound, R_f = 0.60 (hexanes/ethyl acetate 10/1), 93% ee, $[\alpha]^{20}_D$ = -251.61 (*c* 0.92, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.56-7.50 (m, 1H), 7.44-7.35 (m, 5H), 7.13-7.07 (m, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 5.83-5.68 (m, 1H), 5.51 (s, 1H), 5.29-5.16 (m, 2H), 3.60 (s, 3H), 3.22-3.11 (m, 1H), 2.41 (dd, *J* = 15.0, 9.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 168.9, 161.6, 136.3, 135.6, 132.8, 129.2, 128.4, 128.0, 127.4, 122.0, 121.1, 120.3, 118.2, 82.9, 61.3, 52.5, 34.5. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 0.7 mL/min, retention time 14.4 min and 17.3 min (major). HRMS Calculated for $C_{20}H_{19}O_4$ $[M+H]^+$ 323.1278, found: 323.1283.



(-)-Ethyl 3-allyl-4-oxo-2-phenylchromane-3-carboxylate (8b): 50 mg, 99% yield, pale yellow oil, new compound, R_f = 0.60 (hexanes/ethyl acetate 10/1), 95% ee, $[\alpha]^{20}_D$ = -255.18 (*c* 1.00, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.55-7.50 (m, 1H), 7.47-7.36 (m, 5H), 7.13-7.00 (m, 2H), 5.83-5.69 (m, 1H), 5.50 (s, 1H), 5.29-5.17 (m, 2H), 4.15-3.98 (m, 2H), 3.20-3.10 (m, 1H), 2.40 (dd, *J* = 15.0, 9.4 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 168.4, 161.6, 136.2, 135.6, 132.9, 129.2, 128.3, 127.9, 127.5, 121.9, 121.2, 120.2, 118.0, 82.9, 61.6, 61.1, 34.4, 13.8. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 0.7 mL/min, retention time 17.4 min and 20.4 min (major). HRMS Calculated for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found: 337.1433.

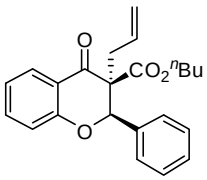


(-)-Isopropyl 3-allyl-4-oxo-2-phenylchromane-3-carboxylate (8c): 48 mg, 91% yield, colorless oil, new compound, R_f = 0.60 (hexanes/ethyl acetate 10/1), 97% ee, $[\alpha]^{20}_D$ = -244.36 (*c* 0.96, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.57-7.52 (m, 1H), 7.52-7.46 (m, 2H), 7.46-7.38 (m, 3H), 7.15-7.09 (m, 1H), 7.06 (dd, *J* = 8.3, 0.6 Hz, 1H), 5.90-5.71 (m, 1H), 5.52 (s, 1H), 5.30-5.18 (m, 2H), 5.02-4.87 (m, 1H), 3.21-3.07 (m, 1H), 2.41 (dd, *J* = 15.0, 9.3 Hz, 1H),

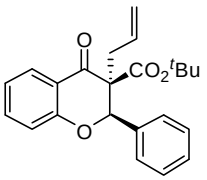


1.16 (d, J = 6.3 Hz, 3H), 1.00 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 167.9, 161.6, 136.1, 135.6, 133.0, 129.1, 128.2, 127.8, 127.7, 121.8, 121.2, 120.1, 117.9, 82.9, 69.6, 61.0, 34.3, 21.6, 21.3. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 0.7 mL/min, retention time 11.4 min and 12.9 min (major). HRMS Calculated for $C_{22}H_{23}O_4$ $[M+H]^+$ 351.1591, found: 351.1589.

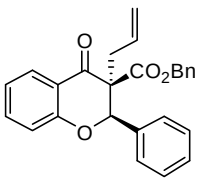
(-)-Butyl 3-allyl-4-oxo-2-phenylchromane-3-carboxylate (8d): 50 mg, 91% yield, colorless oil, new compound, R_f = 0.65 (hexanes/ethyl acetate 10/1), 97% ee, $[\alpha]^{20}_D$ = -235.38 (*c* 1.00, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 7.9, 1.7 Hz, 1H), 7.58-7.52 (m, 1H), 7.48-7.40 (m, 5H), 7.15-7.09 (m, 1H), 7.09-7.03 (m, 1H), 5.87-5.74 (m, 1H), 5.54 (s, 1H), 5.31-5.21 (m, 2H), 4.13-3.97 (m, 2H), 3.26-3.10 (m, 1H), 2.41 (dd, J = 15.0, 9.4 Hz, 1H), 1.48-1.37 (m, 2H), 1.16-1.04 (m, 2H), 0.78 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 168.4, 161.6, 136.1, 135.5, 132.9, 129.2, 128.3, 127.9, 127.5, 121.9, 121.2, 120.2, 118.0, 82.9, 65.4, 61.0, 34.2, 30.2, 18.8, 13.5. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 16.4 min (major) and 26.0 min. HRMS Calculated for $C_{23}H_{25}O_4$ $[M+H]^+$ 365.1747, found: 365.1745.



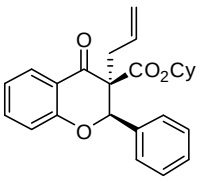
(-)-*tert*-Butyl 3-allyl-4-oxo-2-phenylchromane-3-carboxylate (8e): 52 mg, 95% yield, pale yellow solid, new compound, mp = 79-80 °C, R_f = 0.70 (hexanes/ethyl acetate 10/1), 98% ee, $[\alpha]^{20}_D$ = -224.50 (*c* 1.04, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.9, 1.6 Hz, 1H), 7.56-7.51 (m, 3H), 7.44-7.41 (m, 3H), 7.13-7.08 (m, 1H), 7.06 (dd, J = 8.3, 0.6 Hz, 1H), 5.88-5.77 (m, 1H), 5.49 (s, 1H), 5.26-5.20 (m, 2H), 3.14-3.07 (m, 1H), 2.36 (dd, J = 15.0, 9.2 Hz, 1H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 167.3, 161.5, 135.9, 135.5, 133.2, 129.1, 128.1, 127.8, 127.8, 121.7, 121.3, 119.9, 117.7, 83.1, 82.8, 61.4, 34.3, 27.7. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 0.5 mL/min, retention time 11.9 min and 16.6 min (major). HRMS Calculated for $C_{23}H_{24}NaO_4$ $[M+Na]^+$ 387.1567, found: 387.1569.



(-)-Benzyl 3-allyl-4-oxo-2-phenylchromane-3-carboxylate (8f): 50 mg, 84% yield, pale yellow solid, new compound, mp = 86-87 °C, R_f = 0.50 (hexanes/ethyl acetate 10/1), 98% ee, $[\alpha]^{20}_D$ = -230.98 (*c* 1.00, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.9, 1.5 Hz, 1H), 7.55-7.49 (m, 1H), 7.37-7.20 (m, 8H), 7.12-6.99 (m, 4H), 5.83-5.70 (m, 1H), 5.51 (s, 1H), 5.26-5.18 (m, 2H), 5.16 (d, J = 12.6 Hz, 1H), 4.94 (d, J = 12.6 Hz, 1H), 3.24-3.13 (m, 1H), 2.39 (dd, J = 15.0, 9.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 168.2, 161.6, 136.2, 135.3, 135.0, 132.8, 129.2, 128.4, 128.3, 128.1, 128.0, 127.8, 127.5, 122.0, 121.2, 120.3, 118.1, 83.0, 67.1, 61.1, 34.3. HPLC: Chiracel AD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 97/3, flow = 0.7 mL/min, retention time 16.6 min (major) and 20.0 min. HRMS Calculated for $C_{26}H_{23}O_4$ $[M+H]^+$ 399.1591, found: 399.1589.

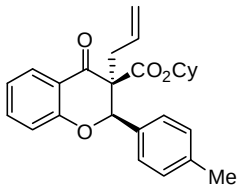


(-)-Cyclohexyl 3-allyl-4-oxo-2-phenylchromane-3-carboxylate (8g): 55 mg, 94% yield, pale yellow solid, new compound, mp = 59-60 °C, R_f = 0.60 (hexanes/ethyl acetate 10/1), 98% ee, $[\alpha]^{20}_D$ = -240.44 (*c* 1.10, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.9, 1.6 Hz, 1H), 7.57-7.52 (m, 1H), 7.51-7.46 (m, 2H), 7.45-7.39 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.3 Hz, 1H), 5.88-5.75 (m, 1H), 5.53 (s, 1H), 5.30-5.21 (m, 2H), 4.92-4.82 (m, 1H), 3.21-3.11 (m, 1H),



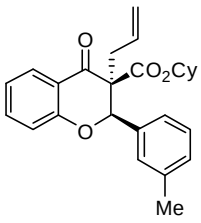
2.40 (dd, *J* = 15.1, 9.4 Hz, 1H), 1.72-1.64 (m, 1H), 1.55-1.46 (m, 2H), 1.40-1.14 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 167.7, 161.6, 136.0, 135.5, 133.0, 129.2, 128.2, 127.8, 127.7, 121.8, 121.4, 120.1, 117.9, 83.0, 73.5, 61.0, 34.1, 30.9, 30.6, 25.2, 22.4, 22.3. HPLC: Chiracel AD-H column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 0.5 mL/min, retention time 25.4 min and 27.5 min (major). HRMS Calculated for $C_{25}H_{27}O_4$ $[M+H]^+$ 391.1904, found: 391.1904.

(-)-Cyclohexyl 3-allyl-4-oxo-2-(*p*-tolyl)chromane-3-carboxylate (8h): 57 mg, 94% yield, pale yellow oil, new compound, R_f = 0.60 (hexanes/ethyl acetate 10/1), 97% ee, $[\alpha]^{20}_D$ = -203.58 (*c*



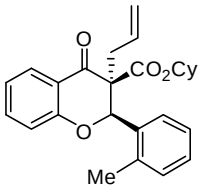
1.14, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.56-7.51 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13-7.04 (m, 2H), 5.87-5.75 (m, 1H), 5.49 (s, 1H), 5.28-5.20 (m, 2H), 4.93-4.84 (m, 1H), 3.21-3.10 (m, 1H), 2.44-2.35 (m, 1H), 2.41 (s, 3H), 1.72-1.65 (m, 1H), 1.56-1.47 (m, 2H), 1.42-1.29 (m, 4H), 1.25-1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 167.8, 161.7, 139.0, 135.9, 133.1, 132.5, 128.9, 127.8, 127.6, 121.7, 121.4, 120.0, 117.9, 83.0, 73.4, 61.0, 34.2, 30.9, 30.6, 25.2, 22.4, 22.3, 21.3. HPLC: Chiracel IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 10.7 min (major) and 18.6 min. HRMS Calculated for $C_{26}H_{29}O_4$ $[M+H]^+$ 405.2060, found: 405.2064.

(-)-Cyclohexyl 3-allyl-4-oxo-2-(*m*-tolyl)chromane-3-carboxylate (8i): 57 mg, 94% yield, white solid, new compound, mp = 59-60 ^{o}C, R_f = 0.60 (hexanes/ethyl acetate 10/1), 97% ee, $[\alpha]^{20}_D$



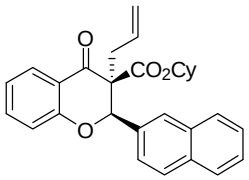
= -224.28 (*c* 1.14, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58-7.51 (m, 1H), 7.34-7.21 (m, 4H), 7.14-7.05 (m, 2H), 5.87-5.75 (m, 1H), 5.50 (s, 1H), 5.29-5.22 (m, 2H), 4.91-4.83 (m, 1H), 3.22-3.12 (m, 1H), 2.44-2.36 (m, 1H), 2.40 (s, 3H), 1.74-1.66 (m, 1H), 1.59-1.46 (m, 2H), 1.43-1.13 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 167.7, 161.7, 137.9, 136.0, 135.4, 133.1, 129.9, 128.2, 128.1, 127.8, 124.7, 121.7, 121.3, 120.1, 117.9, 82.9, 73.5, 61.0, 34.1, 30.9, 30.6, 25.2, 22.5, 22.3, 21.5. HPLC: Chiracel IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 10.7 min (major) and 16.8 min. HRMS Calculated for $C_{26}H_{29}O_4$ $[M+H]^+$ 405.2060, found: 405.2062.

(-)-Cyclohexyl 3-allyl-4-oxo-2-(*o*-tolyl)chromane-3-carboxylate (8j): 24 mg, 40% yield, colorless oil, new compound, R_f = 0.70 (hexanes/ethyl acetate 10/1), 92% ee, $[\alpha]^{20}_D$ = -58.54 (*c*

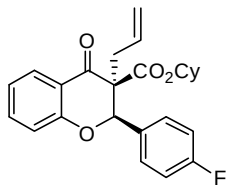


0.48, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55-7.48 (m, 2H), 7.34-7.21 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 5.88-5.76 (m, 1H), 5.70 (s, 1H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.98 (dd, *J* = 17.1, 1.3 Hz, 1H), 4.95-4.86 (m, 1H), 3.01 (dd, *J* = 14.6, 6.2 Hz, 1H), 2.54 (dd, *J* = 14.6, 7.8 Hz, 1H), 2.41 (s, 3H), 1.71-1.62 (m, 1H), 1.58-1.49 (m, 1H), 1.48-1.27 (m, 5H), 1.26-1.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 168.2, 161.5, 137.3, 135.8, 133.4, 132.8, 131.0, 129.1, 127.9, 126.0, 121.7, 121.3, 119.3, 117.7, 80.1, 73.6, 60.4, 34.9, 30.8, 30.6, 25.2, 22.5, 22.4, 20.0. HPLC: Chiracel IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 15.0 min (major) and 18.2 min. HRMS Calculated for $C_{26}H_{29}O_4$ $[M+H]^+$ 405.2060, found: 405.2061.

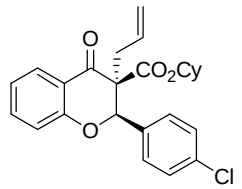
(2*R*,3*S*)-(-)-Cyclohexyl 3-allyl-2-(naphthalen-2-yl)-4-oxochromane-3-carboxylate (8k): 60 mg, 91% yield, pale yellow solid, new compound, mp = 107-108 °C, R_f = 0.60 (hexanes/ethyl acetate 10/1), 97% ee, $[\alpha]^{20}_D$ = -249.65 (*c* 1.20, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.98 (s, 1H), 7.94-7.83 (m, 3H), 7.63-7.52 (m, 4H), 7.19-7.07 (m, 2H), 5.97-5.80 (m, 1H), 5.70 (s, 1H), 5.36-5.24 (m, 2H), 4.97-4.82 (m, 1H), 3.30-3.10 (m, 1H), 2.45 (dd, *J* = 15.1, 9.5 Hz, 1H), 1.79-1.65 (m, 1H), 1.62-1.39 (m, 3H), 1.39-1.25 (m, 3H), 1.24-1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 167.8, 161.7, 136.1, 133.6, 133.2, 132.9, 132.8, 128.2, 128.0, 127.9, 127.8, 127.4, 126.6, 126.4, 124.9, 121.9, 121.4, 120.1, 117.9, 83.1, 73.6, 61.1, 34.2, 31.0, 30.6, 25.2, 22.5, 22.3. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 13.1 min (major) and 22.7 min. HRMS Calculated for $C_{29}H_{29}O_4$ $[M+H]^+$ 441.2060, found: 441.2057.



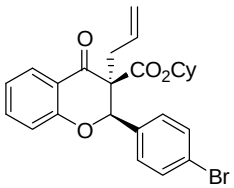
(-)-Cyclohexyl 3-allyl-2-(4-fluorophenyl)-4-oxochromane-3-carboxylate (8l): 58 mg, 95% yield, pale yellow solid, new compound, mp = 71-72 °C, R_f = 0.60 (hexanes/ethyl acetate 10/1), 99% ee, $[\alpha]^{20}_D$ = -210.76 (*c* 1.16, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58-7.52 (m, 1H), 7.50-7.43 (m, 2H), 7.15-7.03 (m, 4H), 5.86-5.74 (m, 1H), 5.50 (s, 1H), 5.27-5.18 (m, 2H), 4.91-4.81 (m, 1H), 3.22-3.09 (m, 1H), 2.36 (dd, *J* = 15.1, 9.5 Hz, 1H), 1.71-1.63 (m, 1H), 1.55-1.43 (m, 2H), 1.40-1.26 (m, 4H), 1.26-1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 167.6, 163.0 (d, $^1J_{F\text{-}C}$ = 246.6 Hz), 161.4, 136.0, 133.0, 131.4 (d, $^4J_{F\text{-}C}$ = 3.3 Hz), 129.5 (d, $^3J_{F\text{-}C}$ = 8.3 Hz), 127.8, 121.9, 121.3, 120.1, 117.8, 115.2 (d, $^2J_{F\text{-}C}$ = 21.5 Hz), 82.4, 73.6, 61.0, 34.1, 31.0, 30.6, 25.2, 22.4, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.23. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 8.8 min (major) and 13.4 min. HRMS Calculated for $C_{25}H_{26}FO_4$ $[M+H]^+$ 409.1810, found: 409.1808.



(-)-Cyclohexyl 3-allyl-2-(4-chlorophenyl)-4-oxochromane-3-carboxylate (8m): 58 mg, 91% yield, yellow oil, new compound, R_f = 0.65 (hexanes/ethyl acetate 10/1), 98% ee, $[\alpha]^{20}_D$ = -201.11 (*c* 1.16, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.58-7.51 (m, 1H), 7.45-7.37 (m, 4H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 5.85-5.72 (m, 1H), 5.49 (s, 1H), 5.28-5.18 (m, 2H), 4.90-4.80 (m, 1H), 3.24-3.09 (m, 1H), 2.37 (dd, *J* = 15.1, 9.4 Hz, 1H), 1.72-1.62 (m, 1H), 1.56-1.41 (m, 2H), 1.39-1.25 (m, 4H), 1.24-1.06 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 167.5, 161.4, 136.1, 135.0, 134.0, 132.9, 129.1, 128.4, 127.8, 122.0, 121.3, 120.2, 117.8, 82.3, 73.7, 60.9, 34.1, 31.0, 30.6, 25.2, 22.4, 22.3. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 8.9 min (major) and 13.9 min. HRMS Calculated for $C_{25}H_{26}ClO_4$ $[M+H]^+$ 425.1514 and 427.1485, found: 425.1515 and 427.1496.

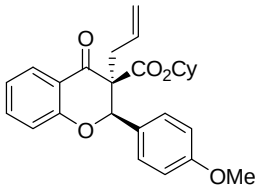


(-)-Cyclohexyl 3-allyl-2-(4-bromophenyl)-4-oxochromane-3-carboxylate (8n): 64 mg, 91% yield, pale yellow oil, new compound, R_f = 0.60 (hexanes/ethyl acetate 10/1), 99% ee, $[\alpha]^{20}_D$ = -187.49 (*c* 1.28, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.58-7.51 (m, 3H), 7.39-7.33 (m, 2H), 7.15-7.10 (m, 1H), 7.05 (dd, *J* = 8.3, 0.6 Hz, 1H), 5.85-5.72 (m, 1H), 5.48 (s, 1H), 5.28-5.17 (m, 2H), 4.90-4.79 (m, 1H), 3.26-3.04 (m, 1H), 2.37 (dd, *J* = 15.1, 9.4 Hz,

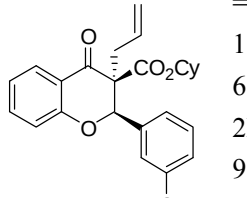


1H), 1.73-1.60 (m, 1H), 1.55-1.41 (m, 2H), 1.38-1.26 (m, 4H), 1.24-1.09 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 167.5, 161.3, 136.1, 134.5, 132.9, 131.4, 129.3, 127.8, 123.2, 122.0, 121.3, 120.2, 117.8, 82.3, 73.7, 60.8, 34.1, 31.0, 30.6, 25.2, 22.4, 22.3. HPLC: Chiracel IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 8.8 min (major) and 14.2 min. HRMS Calculated for $C_{25}H_{26}BrO_4$ $[M+H]^+$ 469.1009 and 471.0989, found: 469.1015 and 471.1002.

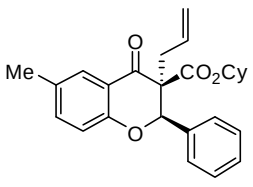
(-)-Cyclohexyl 3-allyl-2-(4-methoxyphenyl)-4-oxochromane-3-carboxylate (8o): 62 mg, 98% yield, pale yellow oil, new compound, R_f = 0.40 (hexanes/ethyl acetate 10/1), 90% ee, $[\alpha]^{20}_D$ = -209.99 (*c* 1.24, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.56-7.50 (m, 1H), 7.42-7.36 (m, 2H), 7.13-7.08 (m, 1H), 7.05 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.97-6.90 (m, 2H), 5.88-5.69 (m, 1H), 5.46 (s, 1H), 5.26-5.17 (m, 2H), 4.93-4.81 (m, 1H), 3.86 (s, 3H), 3.20-3.05 (m, 1H), 2.37 (dd, *J* = 15.0, 9.4 Hz, 1H), 1.72-1.63 (m, 1H), 1.56-1.44 (m, 2H), 1.37-1.25 (m, 4H), 1.24-1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 167.8, 161.7, 160.1, 135.9, 133.1, 129.0, 127.8, 127.6, 121.7, 121.4, 120.0, 117.9, 113.6, 82.8, 73.4, 61.0, 55.3, 34.2, 30.9, 30.6, 25.2, 22.4, 22.3. HPLC: Chiracel IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 13.0 min (major) and 22.8 min. HRMS Calculated for $C_{26}H_{29}O_5$ $[M+H]^+$ 421.2010, found: 421.2011.



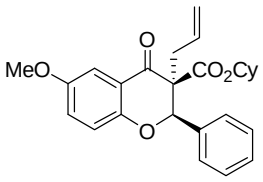
(-)-Cyclohexyl 3-allyl-2-(3-methoxyphenyl)-4-oxochromane-3-carboxylate (8p): 62 mg, 98% yield, pale yellow oil, new compound, R_f = 0.50 (hexanes/ethyl acetate 10/1), 98% ee, $[\alpha]^{20}_D$ = -230.06 (*c* 1.24, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.58-7.52 (m, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.14-7.03 (m, 4H), 6.95 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.86-5.75 (m, 1H), 5.50 (s, 1H), 5.31-5.22 (m, 2H), 4.91-4.82 (m, 1H), 3.83 (s, 3H), 3.24-3.14 (m, 1H), 2.43 (dd, *J* = 15.1, 9.5 Hz, 1H), 1.74-1.64 (m, 1H), 1.57-1.44 (m, 2H), 1.39-1.25 (m, 4H), 1.24-1.10 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 167.7, 161.6, 159.4, 136.9, 136.0, 133.1, 129.3, 127.8, 121.8, 121.3, 120.1, 119.9, 117.9, 114.5, 113.5, 82.8, 73.5, 61.0, 55.2, 34.1, 30.9, 30.5, 25.2, 22.4, 22.2. HPLC: Chiracel IC column, 254 nm, 30 ^{o}C, *n*-Hexane /*i*-PrOH = 98/2, flow = 0.8 mL/min, retention time 12.5 min (major) and 18.2 min. HRMS Calculated for $C_{26}H_{29}O_5$ $[M+H]^+$ 421.2010, found: 421.2015.



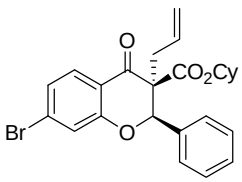
(-)-Cyclohexyl 3-allyl-6-methyl-4-oxo-2-phenylchromane-3-carboxylate (8q): 59 mg, 97% yield, pale yellow solid, new compound, mp = 104-105 ^{o}C, R_f = 0.60 (hexanes/ethyl acetate 10/1), 98% ee, $[\alpha]^{20}_D$ = -224.73 (*c* 1.18, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.7 Hz, 1H), 7.50-7.46 (m, 2H), 7.45-7.38 (m, 3H), 7.35 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.86-5.74 (m, 1H), 5.49 (s, 1H), 5.29-5.19 (m, 2H), 4.89-4.79 (m, 1H), 3.23-3.09 (m, 1H), 2.45-2.35 (m, 1H), 2.38 (s, 3H), 1.76-1.65 (m, 1H), 1.55-1.38 (m, 3H), 1.38-1.26 (m, 3H), 1.26-1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 167.8, 159.7, 137.1, 135.7, 133.1, 131.2, 129.1, 128.2, 127.6, 127.3, 121.0, 120.0, 117.7, 82.9, 73.5, 61.0, 34.2, 31.0, 30.7, 25.2, 22.6, 22.4, 20.5. HPLC: Chiracel IC column, 254 nm, 30 ^{o}C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 11.4 min (major) and 21.6 min. HRMS Calculated for $C_{26}H_{29}O_4$ $[M+H]^+$ 405.2060, found: 405.2060.



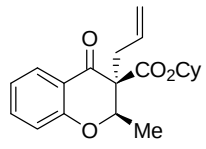
(-)-Cyclohexyl 3-allyl-6-methoxy-4-oxo-2-phenylchromane-3-carboxylate (8r): 59 mg, 94% yield, yellow solid, new compound, mp = 120-121 °C, R_f = 0.50 (hexanes/ethyl acetate 10/1), 98% ee, $[\alpha]^{20}_D$ = -209.22 (*c* 1.18, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 3H), 7.44-7.38 (m, 3H), 7.16 (dd, *J* = 9.0, 3.2 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.86-5.75 (m, 1H), 5.48 (s, 1H), 5.29-5.21 (m, 2H), 4.89-4.81 (m, 1H), 3.86 (s, 3H), 3.20-3.11 (m, 1H), 2.40 (dd, *J* = 15.0, 9.3 Hz, 1H), 1.75-1.67 (m, 1H), 1.55-1.46 (m, 2H), 1.45-1.38 (m, 1H), 1.37-1.27 (m, 3H), 1.26-1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 167.8, 156.4, 154.4, 135.6, 133.1, 129.1, 128.2, 127.6, 125.3, 121.2, 120.0, 119.2, 108.0, 83.1, 73.6, 60.9, 55.9, 34.2, 31.0, 30.7, 25.2, 22.6, 22.5. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 16.2 min (major) and 24.3 min. HRMS Calculated for $C_{26}H_{29}O_5$ $[M+H]^+$ 421.2010, found: 421.2015.



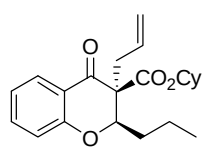
(-)-Cyclohexyl 3-allyl-7-bromo-4-oxo-2-phenylchromane-3-carboxylate (8s): 55 mg, 78% yield, pale yellow oil, new compound, R_f = 0.65 (hexanes/ethyl acetate 10/1), 67% ee, $[\alpha]^{20}_D$ = -131.17 (*c* 1.10, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.47-7.41 (m, 5H), 7.29-7.24 (m, 2H), 5.83-5.72 (m, 1H), 5.51 (s, 1H), 5.28-5.22 (m, 2H), 4.88-4.81 (m, 1H), 3.19-3.11 (m, 1H), 2.38 (dd, *J* = 15.1, 9.4 Hz, 1H), 1.77-1.65 (m, 1H), 1.58-1.45 (m, 2H), 1.43-1.31 (m, 3H), 1.29-1.20 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 167.4, 161.7, 135.0, 132.7, 130.5, 129.3, 129.0, 128.3, 127.6, 125.5, 121.1, 120.3, 120.3, 83.3, 73.8, 60.9, 34.0, 31.0, 30.6, 25.2, 22.6, 22.5. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 8.2 min (major) and 10.4 min. HRMS Calculated for $C_{25}H_{26}BrO_4$ $[M+H]^+$ 469.1009 and 471.0992, found: 469.1014 and 471.0997.



(-)-Cyclohexyl 3-allyl-2-methyl-4-oxochromane-3-carboxylate (8t): 49 mg, 99% yield, pale yellow oil, new compound, R_f = 0.70 (hexanes/ethyl acetate 10/1), 82% ee, $[\alpha]^{20}_D$ = -36.08 (*c* 0.92, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51-7.45 (m, 1H), 7.07-7.01 (m, 1H), 6.96 (dd, *J* = 8.3, 0.6 Hz, 1H), 5.73-5.62 (m, 1H), 5.24-5.17 (m, 1H), 5.13-5.07 (m, 1H), 4.88-4.79 (m, 1H), 4.52 (q, *J* = 6.5 Hz, 1H), 3.28-3.19 (m, 1H), 2.59 (dd, *J* = 14.4, 9.5 Hz, 1H), 1.61-1.51 (m, 5H), 1.39-1.24 (m, 5H), 1.24-1.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 168.3, 161.4, 135.6, 132.3, 127.7, 121.6, 121.4, 119.4, 117.5, 77.9, 73.4, 59.7, 34.0, 30.7, 30.7, 25.2, 22.3, 22.2, 15.7. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 6.8 min (major) and 9.1 min. HRMS Calculated for $C_{20}H_{25}O_4$ $[M+H]^+$ 329.1747, found: 329.1750.

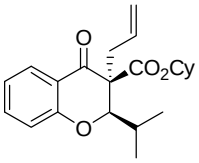


(-)-Cyclohexyl 3-allyl-4-oxo-2-propylchromane-3-carboxylate (8u): 53 mg, 99% yield, pale yellow oil, new compound, R_f = 0.60 (hexanes/ethyl acetate 10/1), 91% ee, $[\alpha]^{20}_D$ = -30.28 (*c* 1.06, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.52-7.44 (m, 1H), 7.07-7.01 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 5.73-5.59 (m, 1H), 5.19 (dd, *J* = 17.1, 0.6 Hz, 1H), 5.14-5.07 (m, 1H), 4.89-4.79 (m, 1H), 4.35 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.30-3.20 (m, 1H), 2.64 (dd, *J* = 14.4, 9.5 Hz, 1H), 1.93-1.80 (m, 2H), 1.79-1.71 (m, 1H), 1.59-1.42 (m, 3H), 1.39-1.18 (m, 8H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 168.5, 161.4, 135.6, 132.3, 127.7, 121.6, 121.3, 119.5, 117.5, 81.2, 73.3, 59.4, 34.1, 31.4, 30.7, 25.2, 22.3, 22.3, 19.2, 13.8. HPLC: Chiracel IC



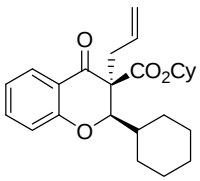
column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 6.8 min (major) and 10.9 min. HRMS Calculated for $C_{22}H_{29}O_4$ $[M+H]^+$ 357.2060, found: 357.2060.

(-)-Cyclohexyl 3-allyl-2-isopropyl-4-oxochromane-3-carboxylate (8v): 52 mg, 97% yield, colorless solid, new compound, mp = 45-46 °C, R_f = 0.60 (hexanes/ethyl acetate 10/1), 95% ee,



$[\alpha]^{20}_D$ = -111.43 (*c* 1.04, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.90 (m, 1H), 7.54-7.46 (m, 1H), 7.08-6.98 (m, 2H), 5.69-5.55 (m, 1H), 5.24-5.15 (m, 1H), 5.13-5.06 (m, 1H), 4.90-4.79 (m, 1H), 4.29 (d, *J* = 1.6 Hz, 1H), 3.37-3.26 (m, 1H), 2.71 (dd, *J* = 14.6, 9.8 Hz, 1H), 2.38-2.24 (m, 1H), 1.62-1.53 (m, 1H), 1.51-1.39 (m, 2H), 1.31-1.14 (m, 9H), 1.09-0.99 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 169.0, 162.2, 135.6, 132.7, 127.8, 121.2, 121.1, 119.4, 117.5, 84.7, 73.2, 58.9, 34.2, 30.6, 30.5, 27.9, 25.2, 22.2, 22.1, 22.0, 15.3. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 1.0 mL/min, retention time 7.2 min (major) and 10.5 min. HRMS Calculated for $C_{22}H_{29}O_4$ $[M+H]^+$ 357.2060, found: 357.2063.

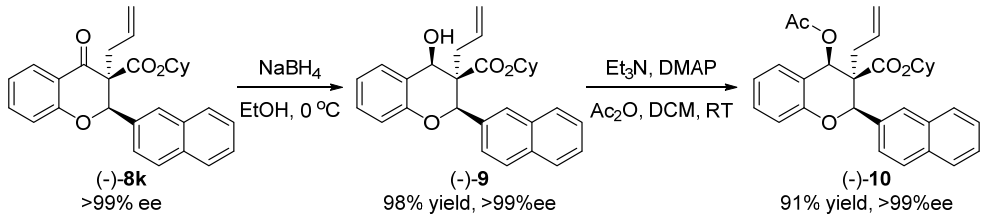
(-)-Cyclohexyl 3-allyl-2-cyclohexyl-4-oxochromane-3-carboxylate (8w): 56 mg, 94% yield, yellow oil, new compound, R_f = 0.60 (hexanes/ethyl acetate 10/1), 95% ee, $[\alpha]^{20}_D$ = -83.74 (*c* 1.12,



$CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.52-7.45 (m, 1H), 7.07-6.97 (m, 2H), 5.71-5.55 (m, 1H), 5.19 (d, *J* = 16.9 Hz, 1H), 5.13-5.06 (m, 1H), 4.90-4.77 (m, 1H), 4.23 (d, *J* = 1.3 Hz, 1H), 3.37-3.24 (m, 1H), 2.72 (dd, *J* = 14.6, 9.7 Hz, 1H), 1.99-1.89 (m, 1H), 1.84-1.67 (m, 4H), 1.66-1.53 (m, 3H), 1.52-1.32 (m, 4H), 1.32-1.15 (m, 8H), 1.12-1.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 169.1, 162.1, 135.6, 132.7, 127.8, 121.2, 121.1, 119.3, 117.5, 85.1, 73.1, 58.7, 37.9, 34.4, 32.1, 30.6, 30.5, 26.8, 26.3, 26.1, 25.8, 25.2, 22.2, 22.1. HPLC: Chiracel IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 99/1, flow = 0.7 mL/min, retention time 9.4 min (major) and 15.0 min. HRMS Calculated for $C_{25}H_{33}O_4$ $[M+H]^+$ 397.2373, found: 397.2376.

4. Transformations of the Products

Reduction of Product (-)-8k with Sodium Borohydride



(-)-**8k**
>99% ee

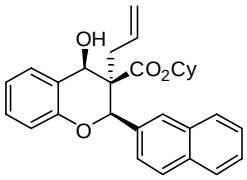
(-)-**9**
98% yield, >99%ee

(-)-**10**
91% yield, >99%ee

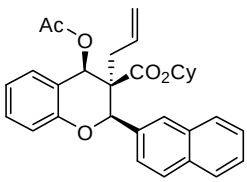
To a solution of flavanone (-)-**8k** (55 mg, 0.125 mmol) in ethanol (5.0 mL) was added sodium borohydride (24 mg, 0.624 mmol) at 0 °C. The reaction mixture was stirred for 32 h. The solution was quenched with saturated ammonium chloride aqueous solution (10 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3), washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford compound (-)-**9**.

To a solution of (-)-**9** (16 mg, 0.036 mmol) in dichloromethane (5.0 mL) was added triethylamine (23.3 mg, 32.0 μL, 0.230 mmol), 4-dimethylaminopyridine (1.4 mg, 0.011 mmol) and acetic anhydride (11.7 mg, 10.8 μL, 0.115 mmol) at ambient temperature. The reaction mixture was stirred overnight. The solution was quenched with saturated ammonium chloride aqueous solution (10 mL). The aqueous layer was extracted with dichloromethane (10 mL×3), washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford compound (-)-**10**.

(-)-(2*R*,3*R*,4*R*)-Cyclohexyl 3-allyl-4-hydroxy-2-(naphthalen-2-yl)chromane-3-carboxylate (9): 54 mg, 98% yield, colorless oil, new compound, R_f = 0.50 (hexanes/ethyl acetate 10/1), >99% ee, $[\alpha]^{20}_D$ = -25.67 (*c* 0.74, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.78 (m, 4H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.53-7.45 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.13-6.00 (m, 1H), 5.24-5.14 (m, 3H), 5.08 (d, *J* = 9.0 Hz, 1H), 4.93-4.84 (m, 1H), 2.86 (d, *J* = 9.3 Hz, 1H), 2.65 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.33 (dd, *J* = 14.2, 7.6 Hz, 1H), 1.75-1.64 (m, 2H), 1.53-1.45 (m, 1H), 1.43-1.27 (m, 4H), 1.25-1.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.4, 134.0, 133.6, 133.4, 132.7, 128.7, 128.1, 127.7, 127.6, 127.6, 127.5, 126.4, 126.2, 125.7, 125.7, 121.6, 119.4, 116.0, 82.3, 73.8, 70.6, 53.4, 39.2, 31.3, 31.3, 25.2, 23.2, 23.1. HPLC: Chiracel IC column, 230 nm, 30 °C, *n*-Hexane/*i*-PrOH = 98/2, flow = 1.0 mL/min, retention time 9.2 min (major) and 28.6 min. HRMS Calculated for $C_{29}H_{30}NaO_4$ $[M+Na]^+$ 465.2036, found: 465.2036.



(-)-(2*R*,3*S*,4*R*)-Cyclohexyl 4-acetoxy-3-allyl-2-(naphthalen-2-yl)chromane-3-carboxylate (10): 16 mg, 91% yield, colorless oil, new compound, R_f = 0.55 (hexanes/ethyl acetate 10/1), >99% ee, $[\alpha]^{20}_D$ = -61.25 (*c* 0.32, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.87-7.80 (m, 3H), 7.53-7.48 (m, 3H), 7.30-7.25 (m, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.02-6.96 (m, 2H), 6.42 (s, 1H), 6.00-5.89 (m, 1H), 5.44 (s, 1H), 5.20-5.12 (m, 2H), 5.03-4.95 (m, 1H), 2.58 (dd, *J* = 14.5, 6.2 Hz, 1H), 2.28 (dd, *J* = 14.5, 8.5 Hz, 1H), 1.93 (s, 3H), 1.79-1.72 (m, 1H), 1.68-1.61 (m, 1H), 1.51-1.32 (m, 6H), 1.28-1.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 169.3, 154.7, 134.2, 133.4, 132.8, 132.1, 129.4, 128.1, 128.0, 127.8, 127.6,



127.6, 126.4, 126.2, 125.4, 121.4, 121.2, 119.6, 116.3, 81.0, 73.1, 69.6, 51.7, 39.0, 31.3, 30.9, 25.3, 22.8, 22.6, 21.1. HPLC: Chiracel IA column, 230 nm, 30 °C, *n*-Hexane/*i*-PrOH = 95/5, flow = 1.0 mL/min, retention time 13.1 min (major). HRMS Calculated for $C_{31}H_{32}NaO_5$ $[M+Na]^+$ 507.2142, found: 507.2144.

The NOE result of **(-)-10** (Figure S1)

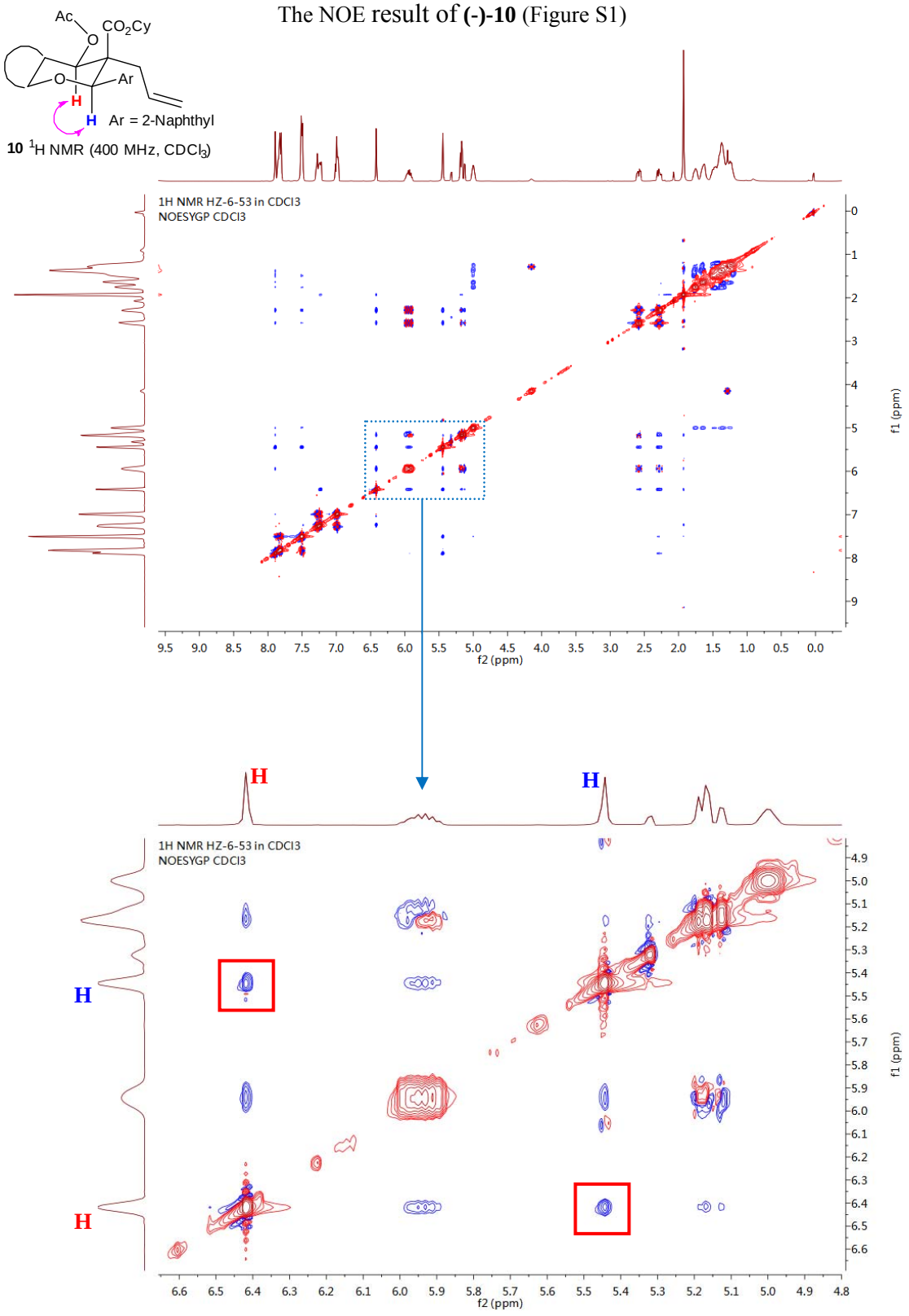
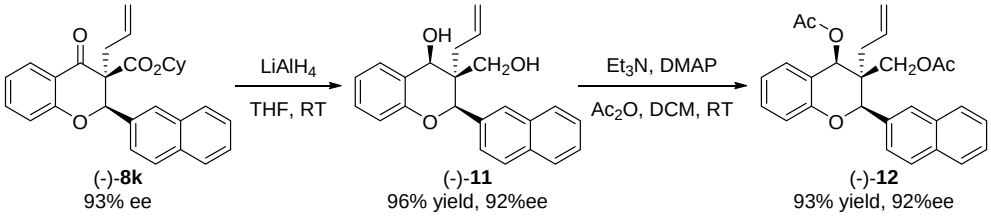


Figure S1. NOE spectrum of (-)-**10**

Reduction of Product (-)-8k with Lithium Aluminium Tetrahydride



(-)-**8k**
93% ee

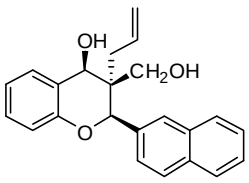
(-)-**11**
96% yield, 92%ee

(-)-**12**
93% yield, 92%ee

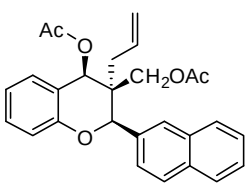
To a solution of (-)-**8k** (90 mg, 0.204 mmol) in tetrahydrofuran (5.0 mL) was added lithium aluminium tetrahydride (23 mg, 0.612 mmol) at ambient temperature. The reaction mixture was stirred for 18.5 h. The solution was quenched with saturated ammonium chloride aqueous solution (10 mL). The aqueous layer was extracted with ethyl acetate (10 mL×3), washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford compound (-)-**11**.

To a solution of (-)-**11** (30 mg, 0.087 mmol) in dichloromethane (5.0 mL) was added triethylamine (87.6 mg, 0.12 mL, 0.866 mmol), 4-dimethylaminopyridine (5.3 mg, 0.043 mmol) and acetic anhydride (44.2 mg, 40.9 μL, 0.433 mmol) at ambient temperature. The reaction mixture was stirred overnight. The solution was quenched with saturated ammonium chloride aqueous solution (10 mL). The aqueous layer was extracted with dichloromethane (10 mL×3), washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford compound (-)-**12**.

(-)-(2*R*,3*R*,4*S*)-3-allyl-3-(hydroxymethyl)-2-(naphthalen-2-yl)chroman-4-ol (11): 68 mg, 96% yield, colorless oil, new compound, R_f = 0.28 (hexanes/ethyl acetate 10/1), 92% ee, $[\alpha]^{20}_D$ = -45.62 (*c* 0.48, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 4H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.53-7.45 (m, 3H), 7.24-7.18 (m, 1H), 7.04-6.98 (m, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 5.98-5.82 (m, 1H), 5.26-5.13 (m, 2H), 5.19 (s, 1H), 5.04 (d, *J* = 8.3 Hz, 1H), 4.23 (d, *J* = 11.0 Hz, 1H), 3.83 (d, *J* = 8.8 Hz, 1H), 3.73 (dd, *J* = 10.9, 2.1 Hz, 1H), 2.60 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.36 (brs, 1H), 2.15 (dd, *J* = 14.6, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 134.4, 133.7, 133.3, 132.9, 128.9, 128.2, 127.9, 127.7, 127.7, 127.2, 126.5, 125.5, 125.4, 121.5, 119.7, 115.8, 82.8, 72.3, 63.1, 42.2, 35.9. HPLC: Chiracel IC column, 230 nm, 30 °C, *n*-Hexane/*i*-PrOH = 95/5, flow = 0.8 mL/min, retention time 18.1 min and 26.2 min (major). HRMS Calculated for $C_{23}H_{22}NaO_3$ $[M+Na]^+$ 369.1461, found: 369.1465.



(-)-((2*R*,3*S*,4*S*)-4-acetoxy-3-allyl-2-(naphthalen-2-yl)chroman-3-yl)methyl acetate (12): 35 mg, 93% yield, colorless oil, new compound, R_f = 0.45 (hexanes/ethyl acetate 10/1), 92% ee, $[\alpha]^{20}_D$ = -7.57 (*c* 0.70, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.78 (m, 4H), 7.54-7.46 (m, 3H), 7.35-7.30 (m, 1H), 7.28-7.23 (m, 1H), 7.05-6.97 (m, 2H), 6.20 (s, 1H), 5.99-5.86 (m, 1H), 5.41 (s, 1H), 5.27-5.13 (m, 2H), 4.32 (d, *J* = 11.6 Hz, 1H), 4.14 (d, *J* = 11.6 Hz, 1H), 2.38-2.26 (m, 2H), 1.89 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170. 6, 170.6, 154.2, 134.9, 133.1, 132.6, 131.9, 130.1, 129.2, 128.1, 127.6, 127.3, 127.1, 126.3, 126.2, 125.8, 121.2, 120.1, 119.9, 116.4, 80.7, 69.4, 62.1, 42.4, 37.2, 20.9, 20.7. HPLC: Chiracel IA column, 230 nm, 30 °C, *n*-Hexane/*i*-PrOH = 95/5, flow = 1.0 mL/min, retention time 14.2 min (major) and 20.0 min. HRMS Calculated for $C_{27}H_{26}NaO_5$ $[M+Na]^+$ 453.1672, found: 453.1673.



The NOE result of **(-)-12** (Figure S2)

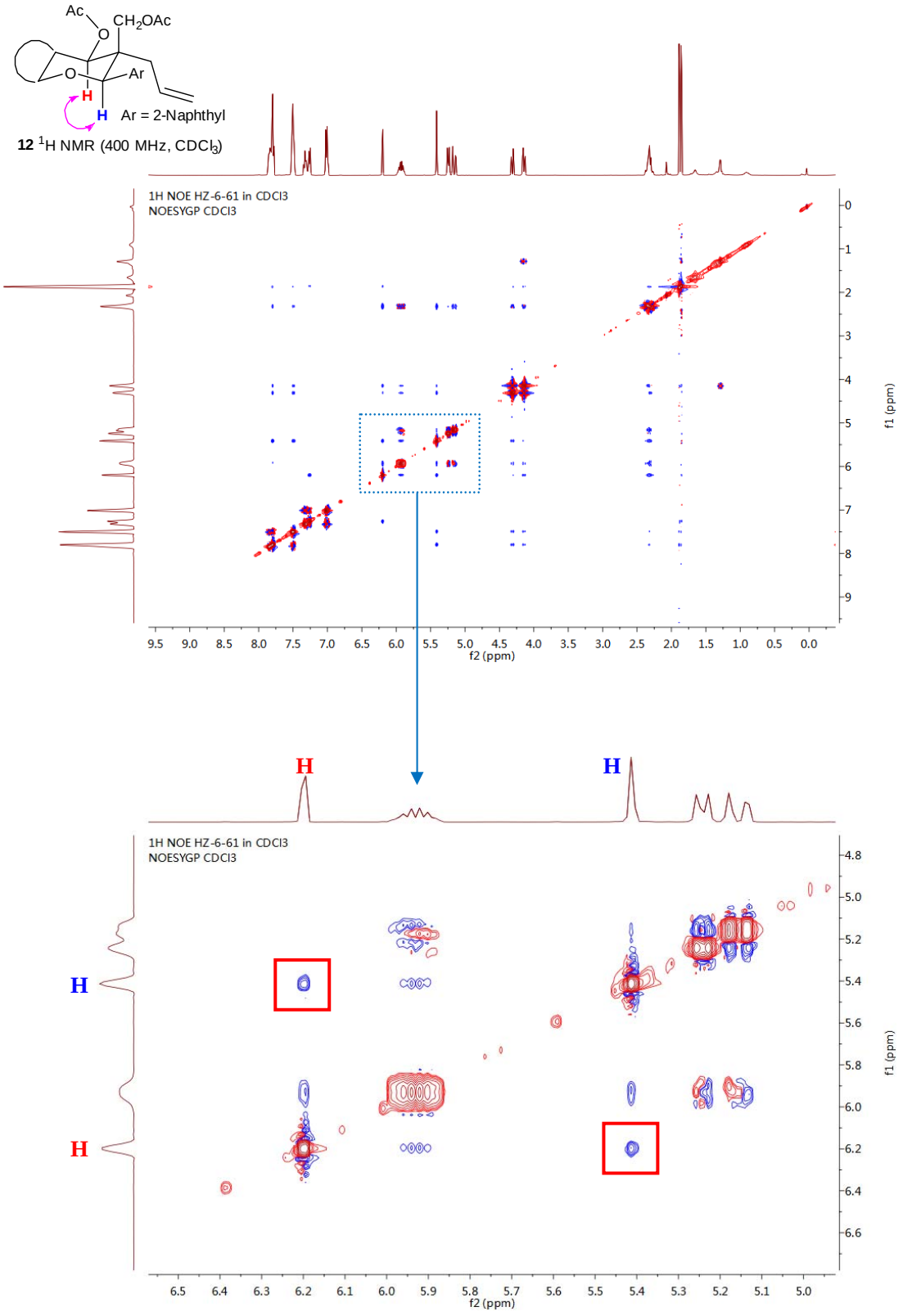
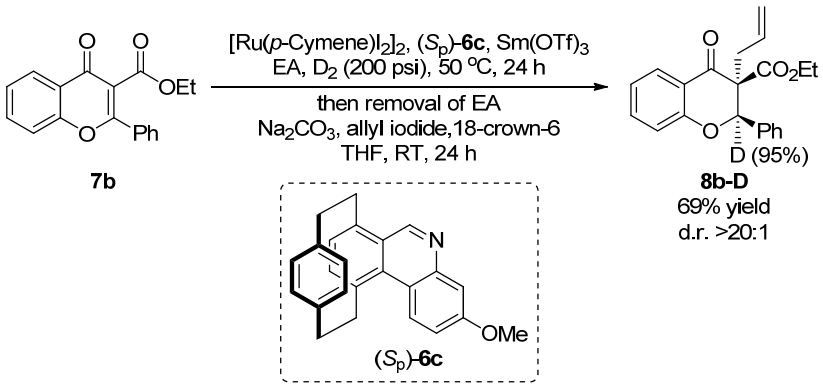


Figure S2. NOE spectrum of (-)-**12**

5. Mechanistic Investigation

5.1 Biomimetic Asymmetric Reduction of Flavonoid with D_2



A mixture of [Ru(*p*-cymene)I_2]$_2$ (0.5 mg, 0.0005 mmol), samarium(III) trifluoromethanesulfonate (12.0 mg, 0.02 mmol), (S_p)-**6c** (3.4 mg, 0.01 mmol) and **7b** (0.10 mmol) in ethyl acetate (2.0 mL) was stirred at room temperature for 5 min in glove box and then the mixture was transferred to an autoclave. The hydrogenation was performed at 50 °C under D_2 (200 psi) for 24 h. After carefully release of the hydrogen, the autoclave was opened and the reaction mixture was concentrated in *vacuo*. Then, sodium carbonate (21.2 mg, 0.20 mmol), allyl iodide (33.6 mg, 18.3 μL, 0.20 mmol), 18-crown-6 (4.0 mg, 3.4 μL, 0.015 mmol) and tetrahydrofuran (2.0 mL) were added to the mixture above. The new mixture was stirred at ambient temperature for 24 h. The final reaction mixture was concentrated in *vacuo* and then purified by column chromatography on silica gel using hexanes and ethyl acetate to give **8b-D** with 69% yield (**Figure S3-S4**). The result indicated that substrate **7b** could be reduced under D_2 atmosphere, affording the deuterium product **8b-D**, and D_2 was the terminal reductant in the reaction.

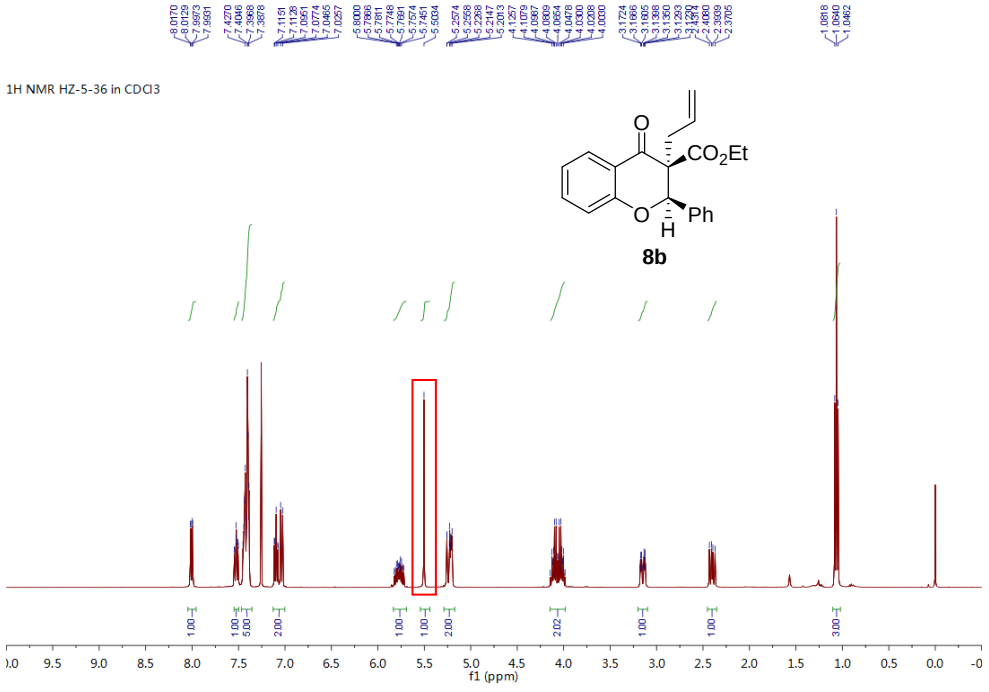


Figure S3

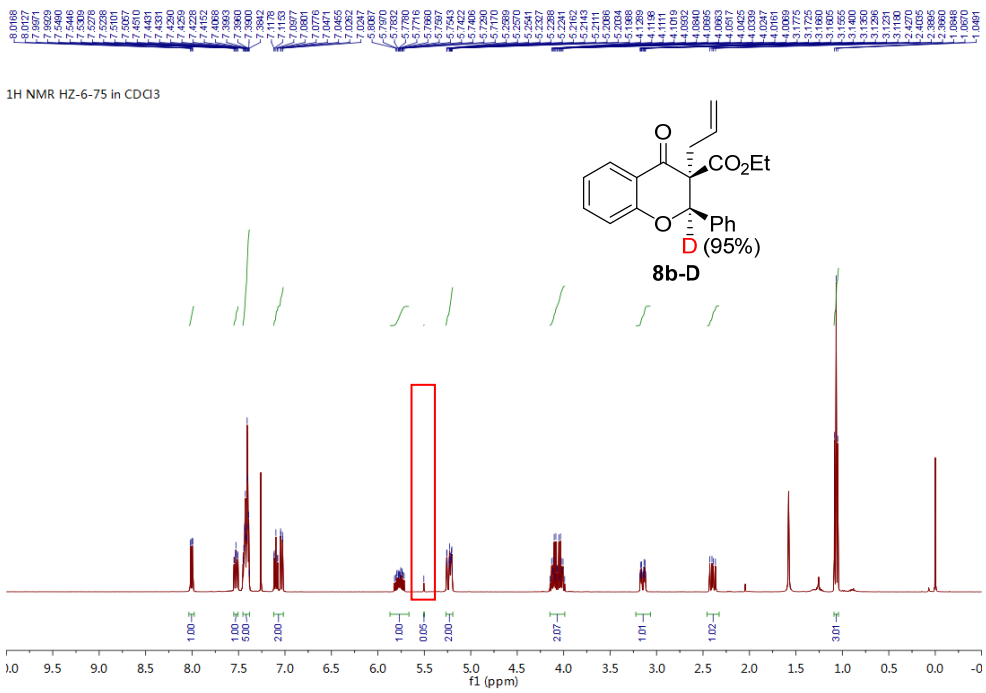
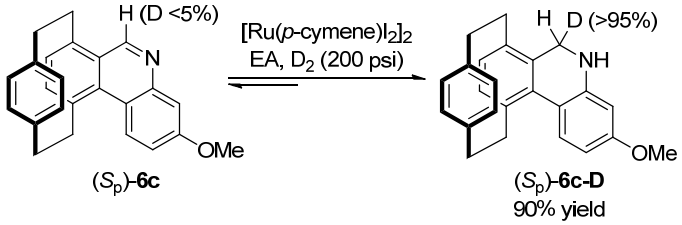


Figure S4

5.2 The Reduction of NAD(P)H Model (S_p)-6c with D_2



(S_p)-**6c** (S_p)-**6c-D** 90% yield

A mixture of [Ru(*p*-cymene)I_2]$_2$ (4.9 mg, 0.005 mmol), (S_p)-**6c** (33.9 mg, 0.10 mmol) in ethyl acetate (2 mL) was stirred at room temperature for 5 min in glove box and then the mixture was transferred to an autoclave. The hydrogenation was performed at 50 ^oC under D_2 (200 psi) for 24 h. After careful release of the gas, the autoclave was opened, and it gave the (S_p)-**6c-D** with 90% yield. The result showed that the chiral regenerable NAD(P)H model (S_p)-**6c** could be regenerated in the presence of D_2, and deuterium atom was added to the less steric face. No deuterium atom incorporation was observed in the recovered NAD(P)H model (S_p)-**6c** (**Figure S5-S8**).

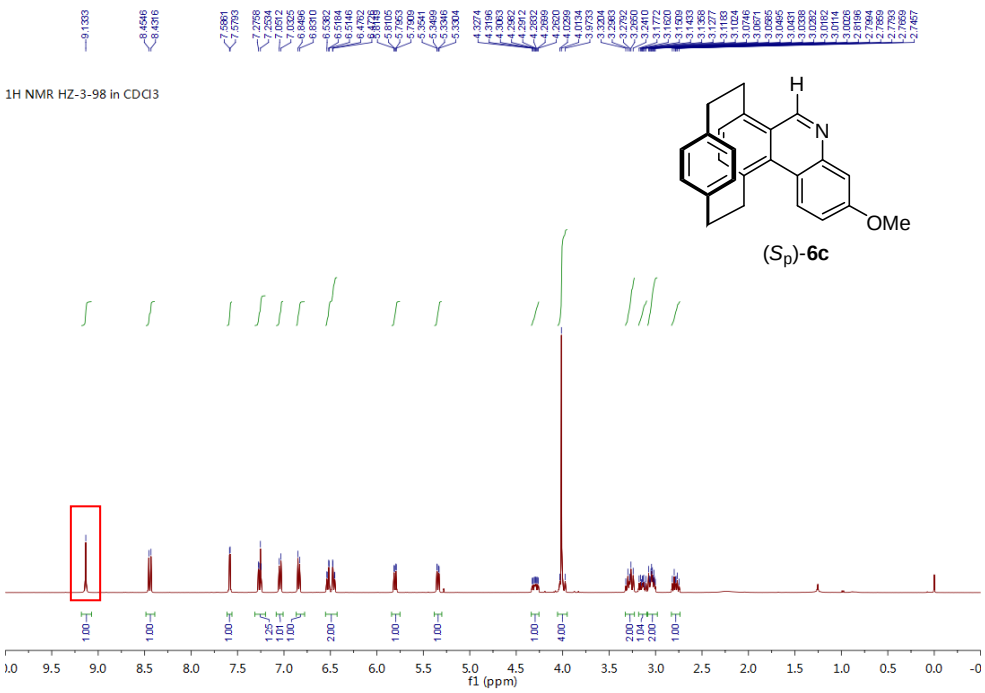


Figure S5

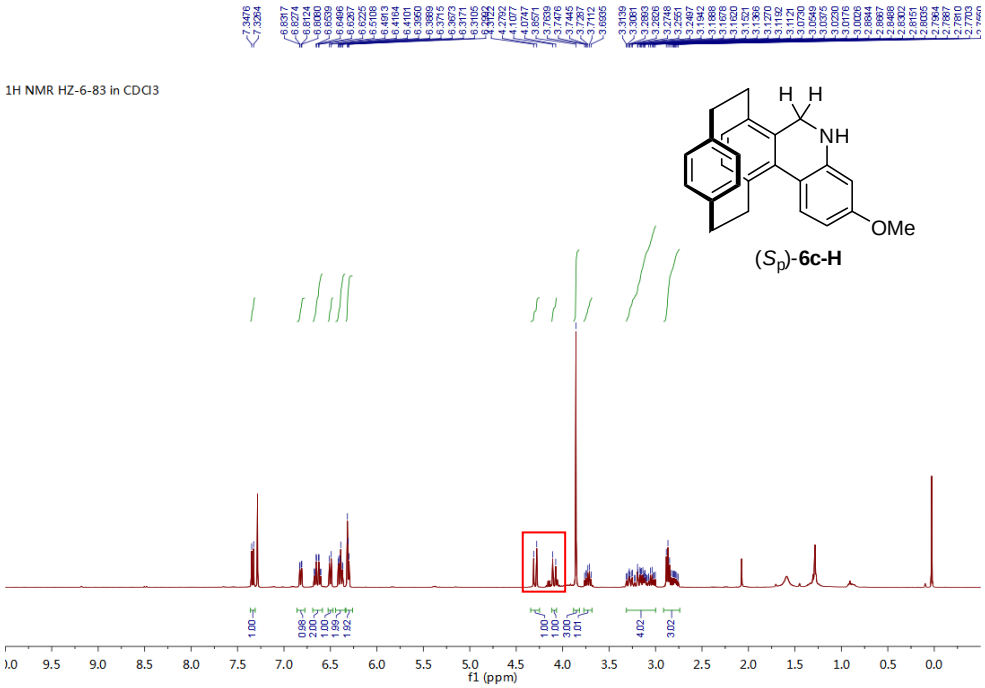


Figure S6-a

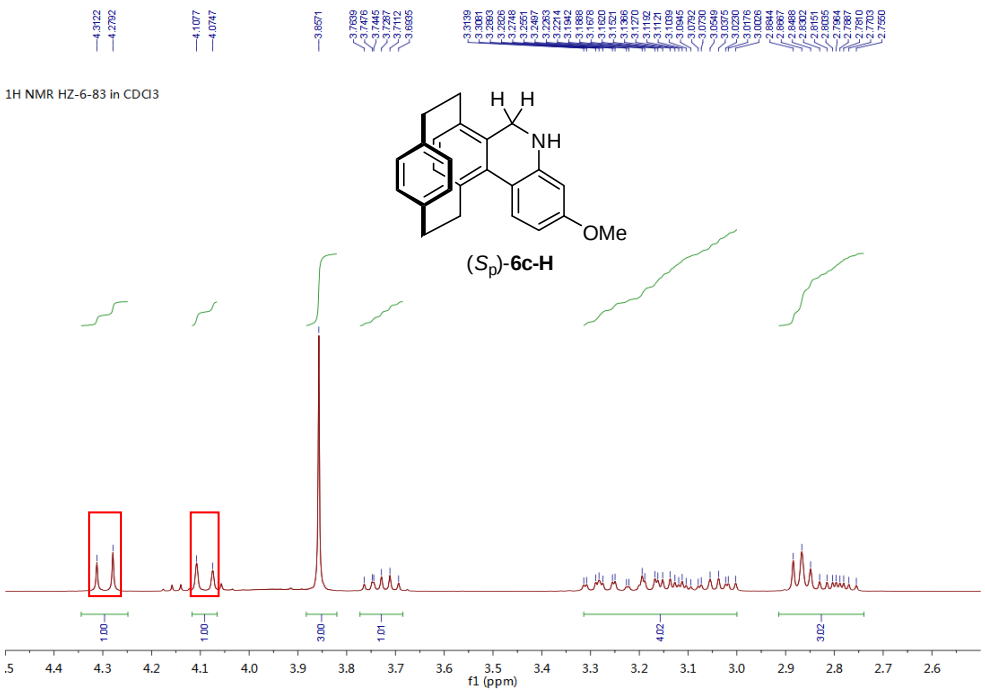


Figure S6-b

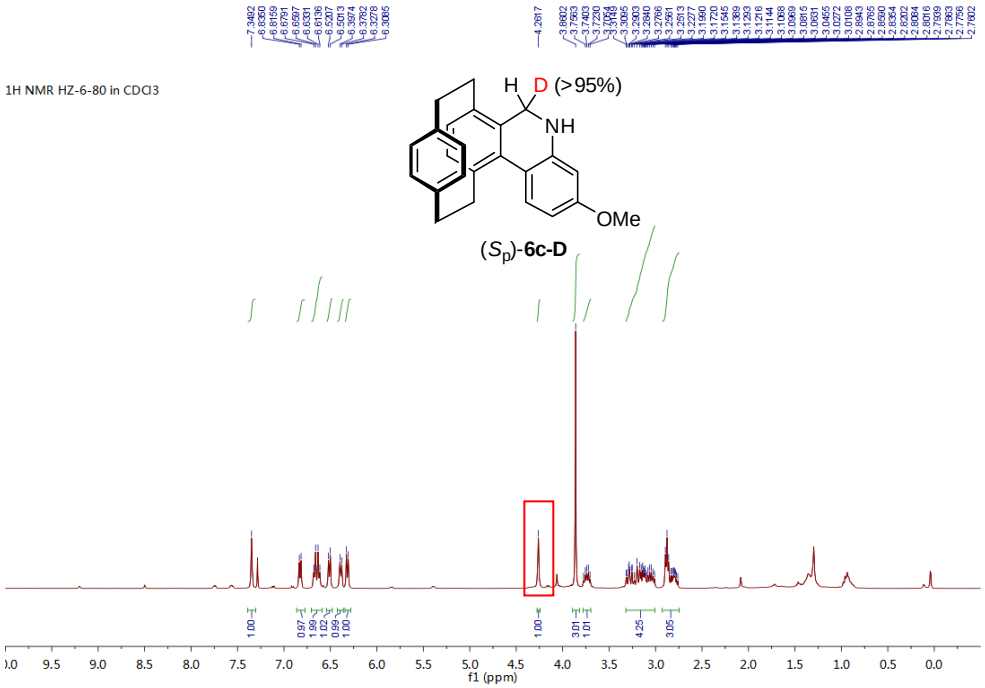


Figure S7

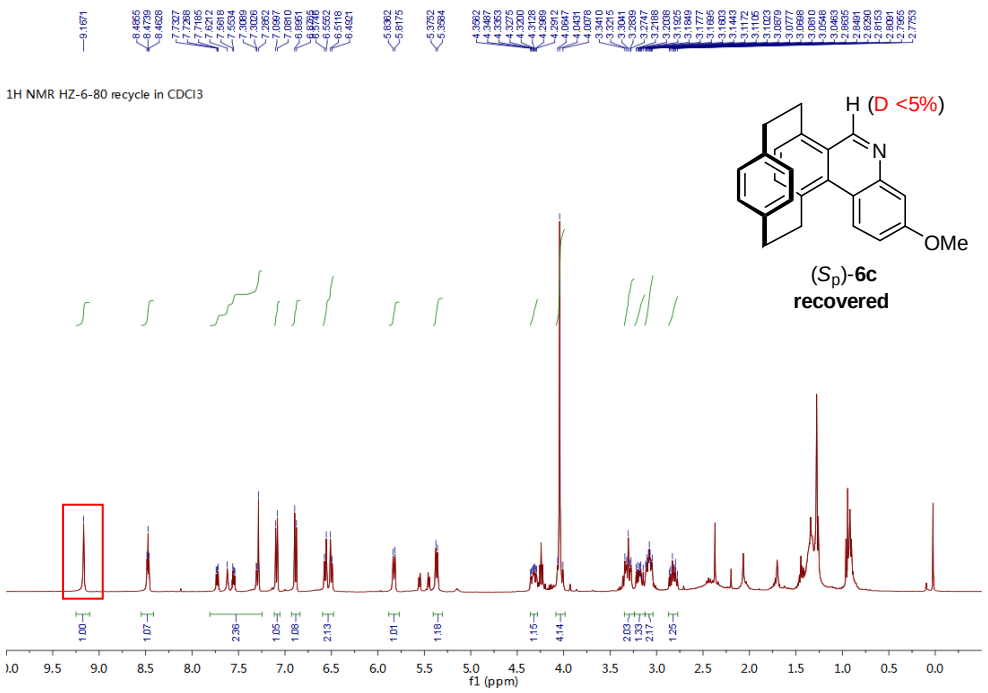
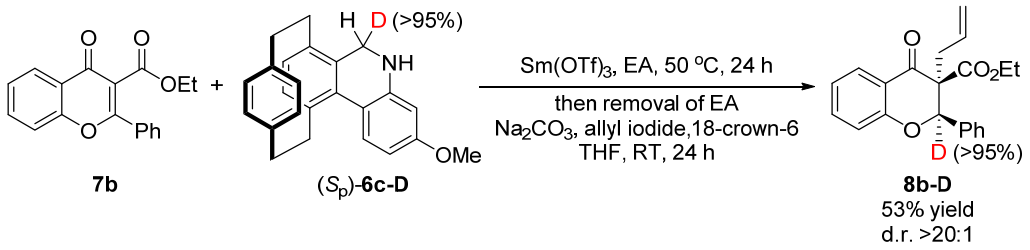


Figure S8

5.3 Biomimetic Asymmetric Reduction of Flavonoids with (S_p)-6c-D



In a 10 mL sealed tube, a mixture of (S_p)-**6c-D** (31.1 mg, 0.091 mmol), samarium(III) trifluoromethanesulfonate (10.9 mg, 0.018 mmol), and flavonoid **7b** (26.6, 0.091 mmol) in ethyl acetate (2.0 mL) was stirred at 50 °C for 24 h. Then the reaction mixture was concentrated in *vacuo*. Sodium carbonate (19.3 mg, 0.182 mmol), allyl iodide (30.6 mg, 16.6 µL, 0.182 mmol), 18-crown-6 (3.7 mg, 3.2 µL, 0.014 mmol) and tetrahydrofuran (2.0 mL) were added to the mixture above. The new mixture was stirred at ambient temperature for 24 h. The final reaction mixture was concentrated in *vacuo* and then purified by column chromatography on silica gel using hexanes and ethyl acetate to give **8b-D** with 53% yield. The product was determined by NMR spectra (**Figure S9**). The result showed that the deuterium chiral NAD(P)H model (S_p)-**6c-D** could transfer deuterium to the flavonoid **7b** in the presence of Lewis acid and deuterium atom on the less steric face was selectively transferred, leading to the good enantioselectivity.

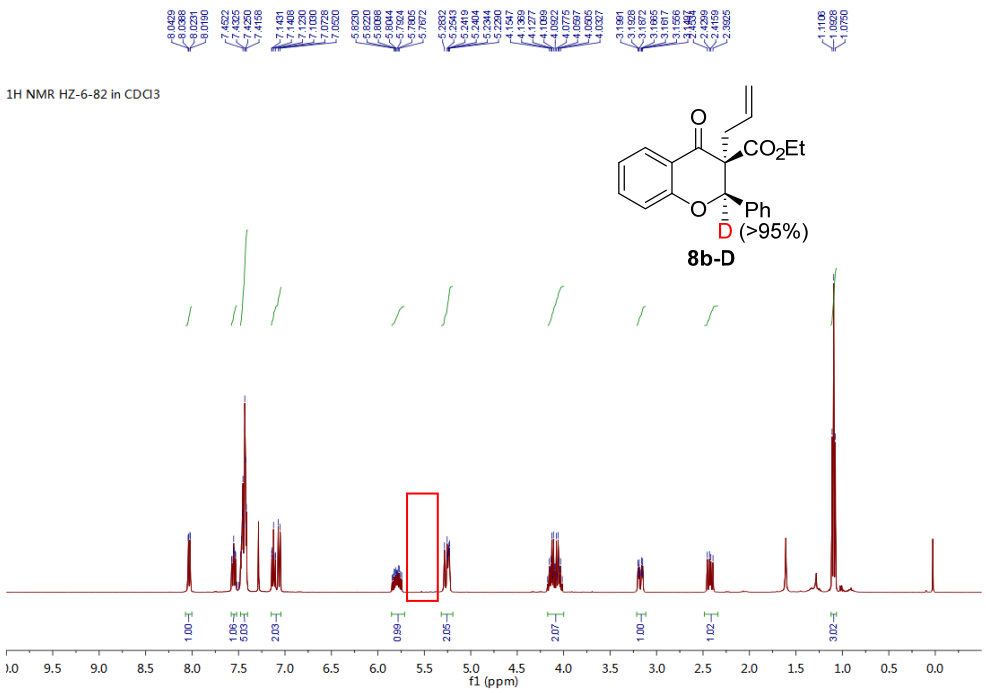

1H NMR HZ-6-82 in CDCl3
O
CO2Et
O
Ph
D (>95%)
8b-D
1.00
1.08
5.03
2.03
0.99
2.05
2.07
1.00
1.02
3.02
f1 (ppm)

Figure S9

6. Determination of the Absolute Configuration

To determine the absolute configuration of (-)-cyclohexyl 3-allyl-2-(naphthalen-2-yl)-4-oxo-chromane-3-carboxylate (-)-**8k** (97% ee)**:** firstly, (-)-**8k** was upgraded to >99% ee by recrystallization with *n*-hexane/dichloromethane and completely dissolved in dichloromethane (2 mL). Then part of dichloromethane was evaporated and *n*-hexane (2 mL) was added slowly at ambient temperature. The solvent was slowly evaporated and the single crystal of was obtained after one day. The structure in **Figure S10** showed the absolute configuration of (-)-**8k** is (2*R*,3*S*). The CCDC number is 1918727. These details can be obtained free of charge *via* www.ccdc.com.ac.uk/data_request /cif from the Cambridge Crystallographic Data Centre.

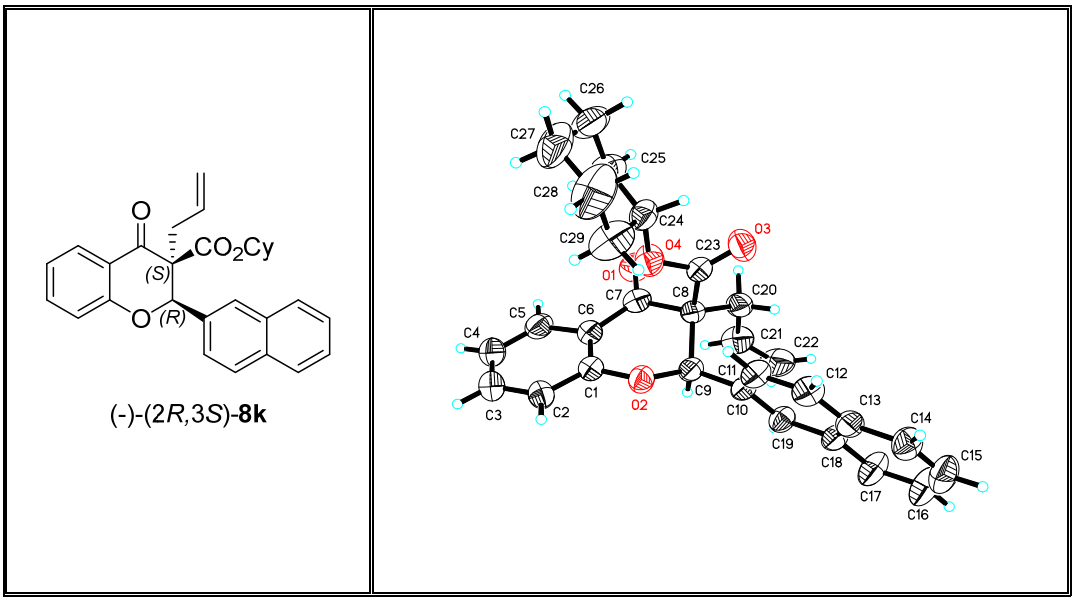


Figure S10. X-ray crystallographic analysis of (-)-(2*R*,3*S*)-**8k**

7. References

1) Kramer, J. J. P.; Yildiz, C.; Nieger, M.; Bräse, S. Direct Access to 4,5-Disubstituted [2.2]Paracyclophanes by Selective *ortho*-Halogenation with Palladium-Catalyzed C–H Activation. *Eur. J. Org. Chem.* **2014**, *2014*, 1287-1295.

2) Zhou, F.; Driver, T. G. Efficient Synthesis of 3*H*-Indoles Enabled by the Lead-Mediated *α*-Arylation of *β*-Ketoesters or *γ*-Lactams Using Aryl Azides. *Org. Lett*. **2014**, *16*, 2916-2919.

3) Lin, J.-P.; Long, Y.-Q. Transition Metal-Free One-Pot Synthesis of 2-Substituted 3-Carboxy-4-Quinolone and Chromone Derivatives. *Chem. Commun.* **2013**, *49*, 5313-5315.

4) Lv, X.-J.; Chen, Y.-H.; Liu, Y.-K. Two Competitive but Switchable Organocatalytic Cascade Reaction Pathways: The Diversified Synthesis of Chiral Acetal-Containing Bridged Cyclic Compounds. *Org. Lett.* **2019**, *21*, 190-195.

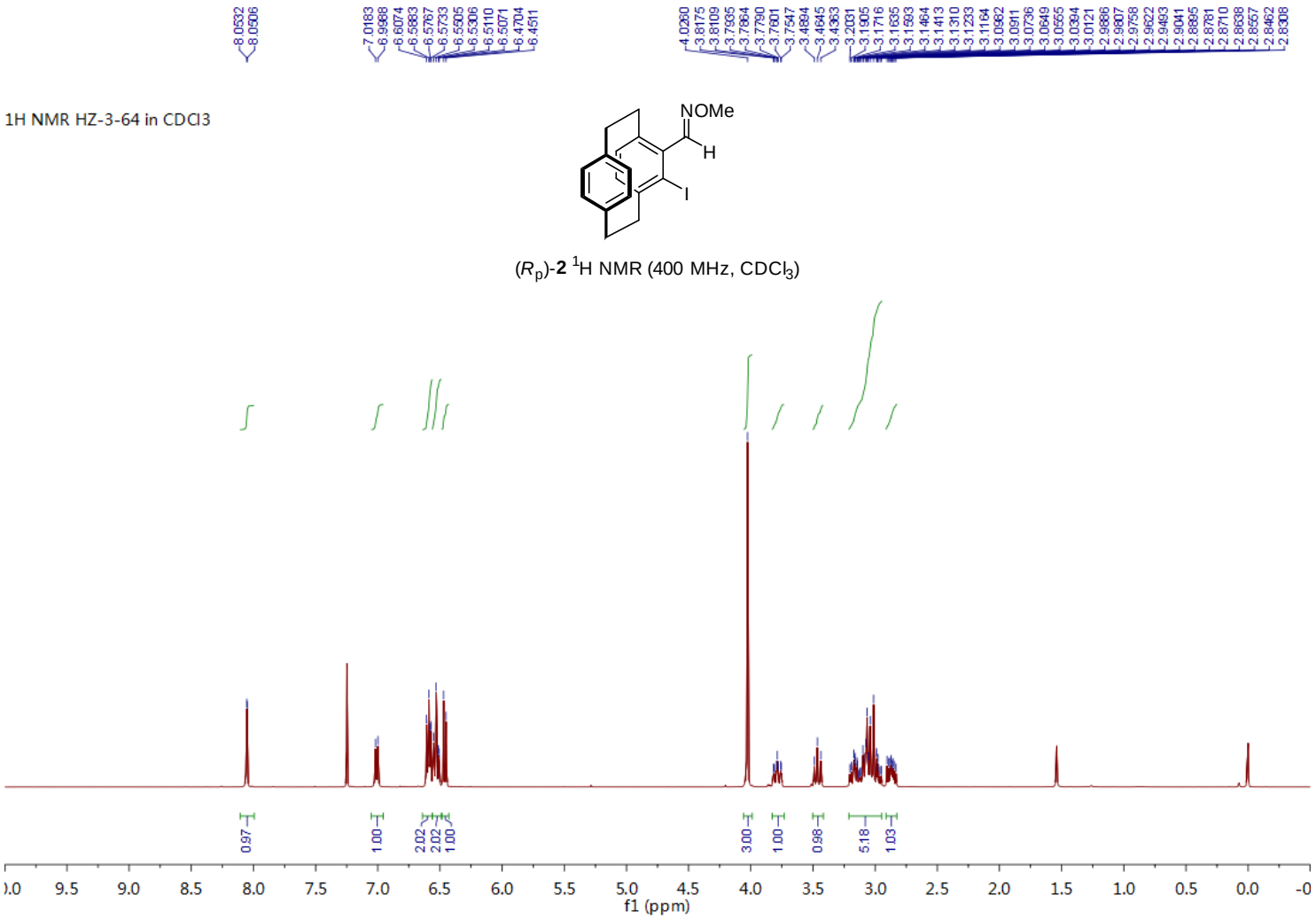
5) Ko, T. Y.; Youn, S. W. Cooperative Indium(III)/Silver(I) System for Oxidative Coupling/ Annulation of 1,3-Dicarbonyls and Styrenes: Construction of Five-Membered Heterocycles. *Adv. Synth. Catal.* **2016**, *358*, 1934-1941.

6) Suljić, S.; Mortzfeld, F. B.; Gunne, M.; Urlacher, V. B.; Pietruszka, J. Enhanced Biocatalytic Performance of Bacterial Laccase from *Streptomyces sviceus*: Application in the Michael Addition Sequence Towards 3-Arylated 4-Oxochromanes. *ChemCatChem* **2015**, *7*, 1380-1385.

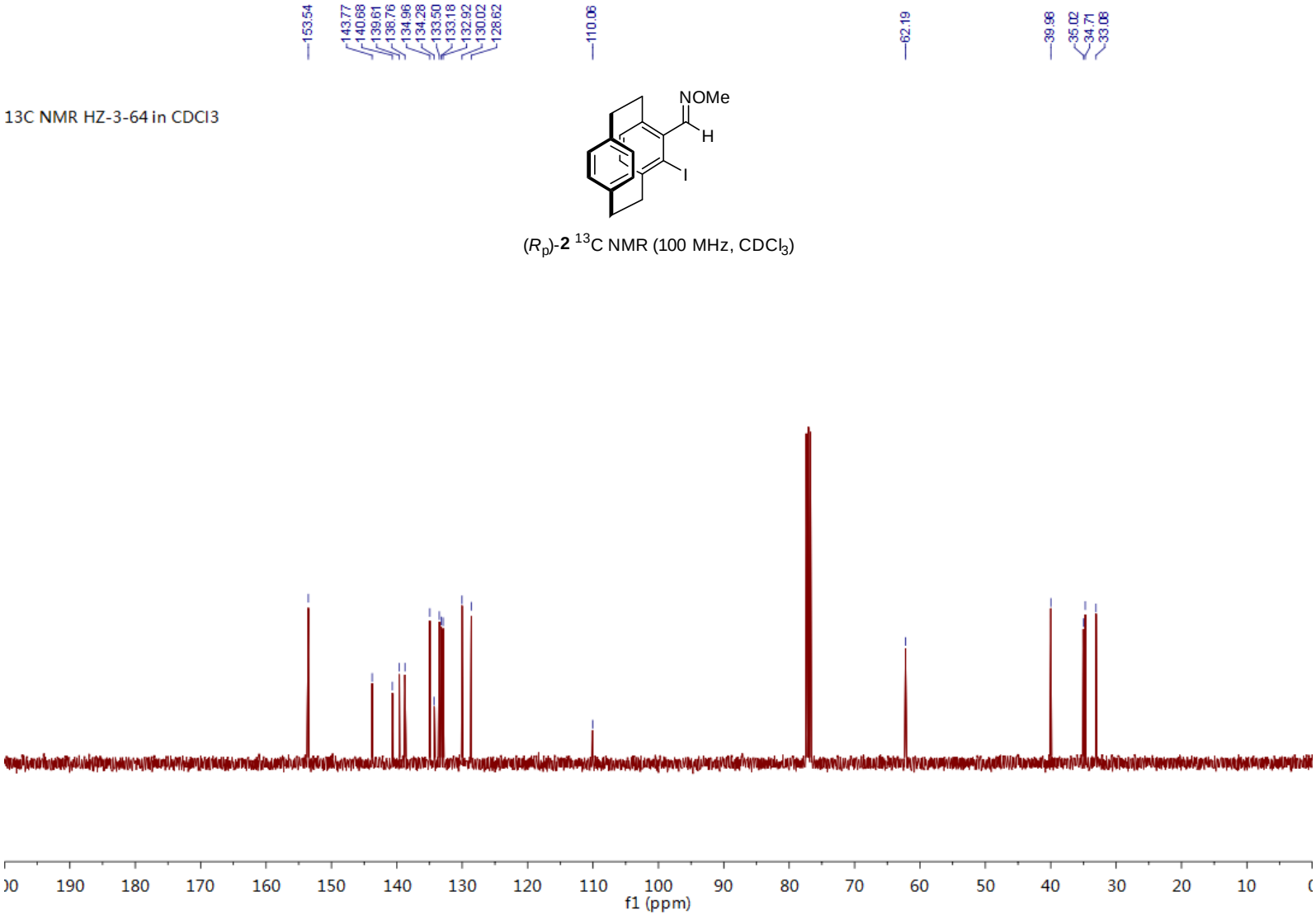
7) Zanwar, M. R.; Raihan, M. J.; Gawande, S. D.; Kavala, V.; Janreddy, D.; Kuo, C.-W.; Ambre, R.; Yao, C.-F. Alcohol Mediated Synthesis of 4-Oxo-2-aryl-4*H*-chromene-3-carboxylate Derivatives from 4-Hydroxycoumarins. *J. Org. Chem.* **2012**, *77*, 6495-6504.

8) Yoshida, M.; Saito, K.; Fujino, Y.; Doi, T. A Concise Total Synthesis of Biologically Active Frutinones via Tributylphosphine-Catalyzed Tandem Acyl Transfer Cyclization. *Tetrahedron* **2014**, *70*, 3452-3458.

8. Copy of NMR and HPLC Spectra

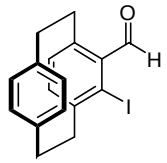


(R_p)-**2** ^{1}H NMR (400 MHz, $CDCl_3$)

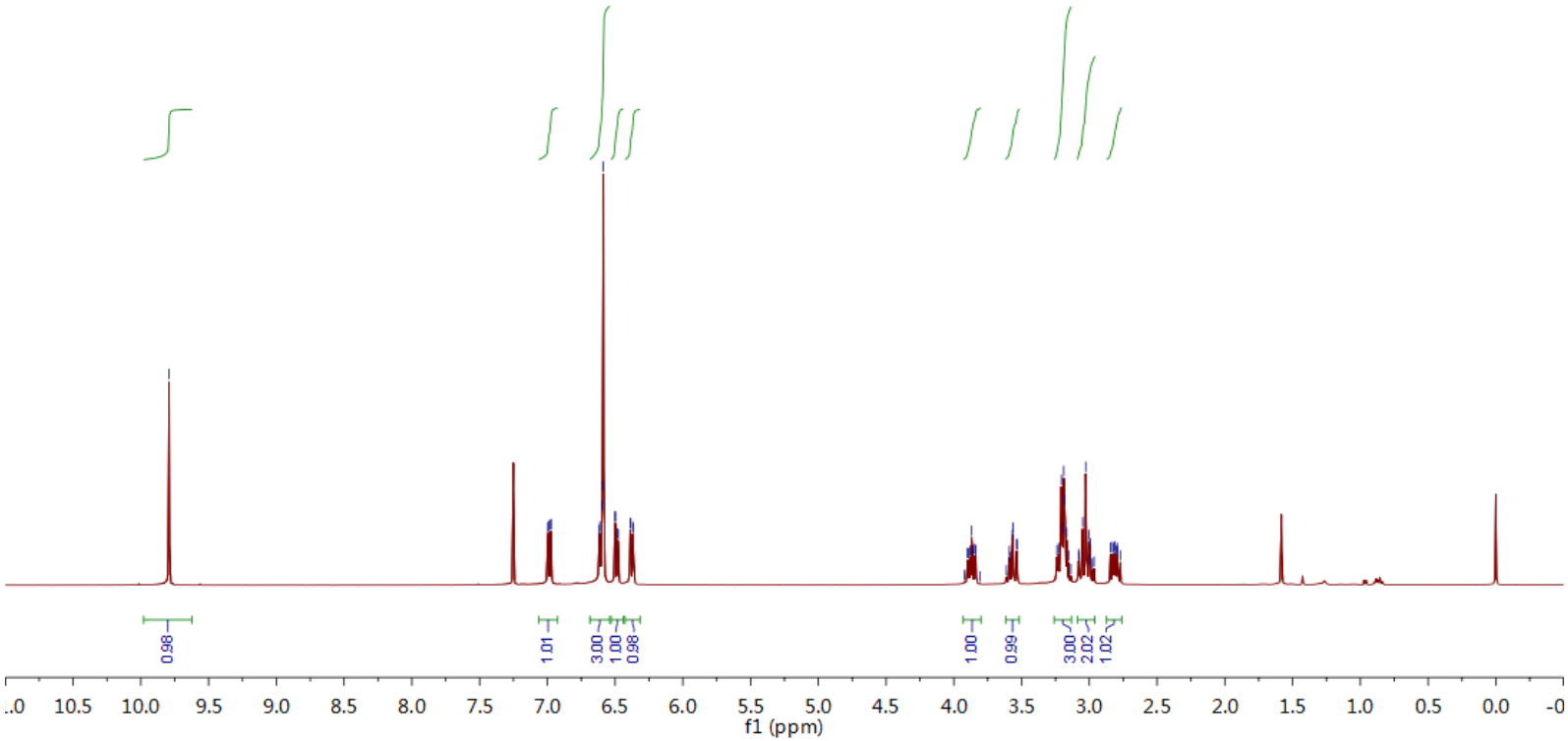


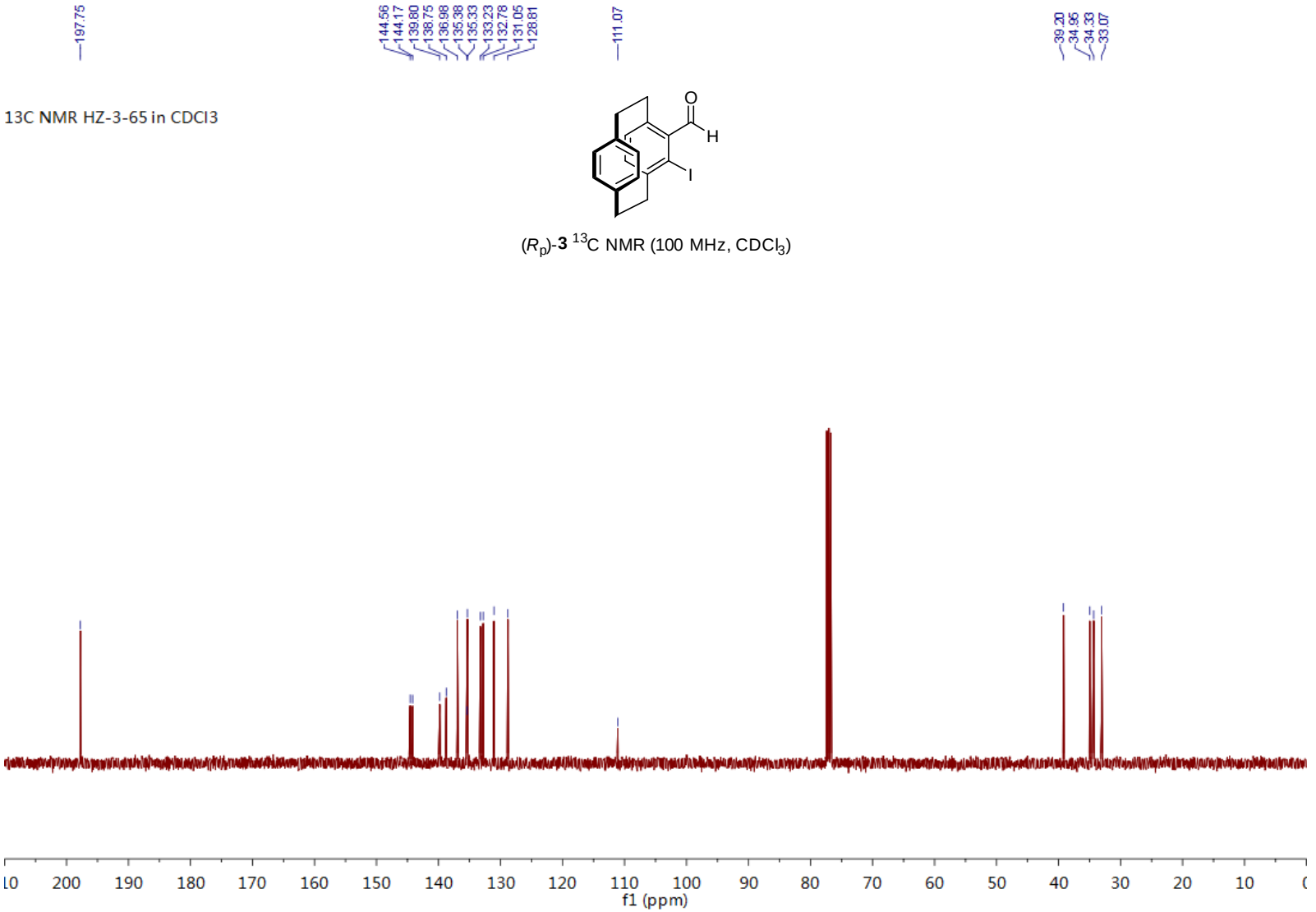
(R_p)-**2** ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-3-65 in CDCl3



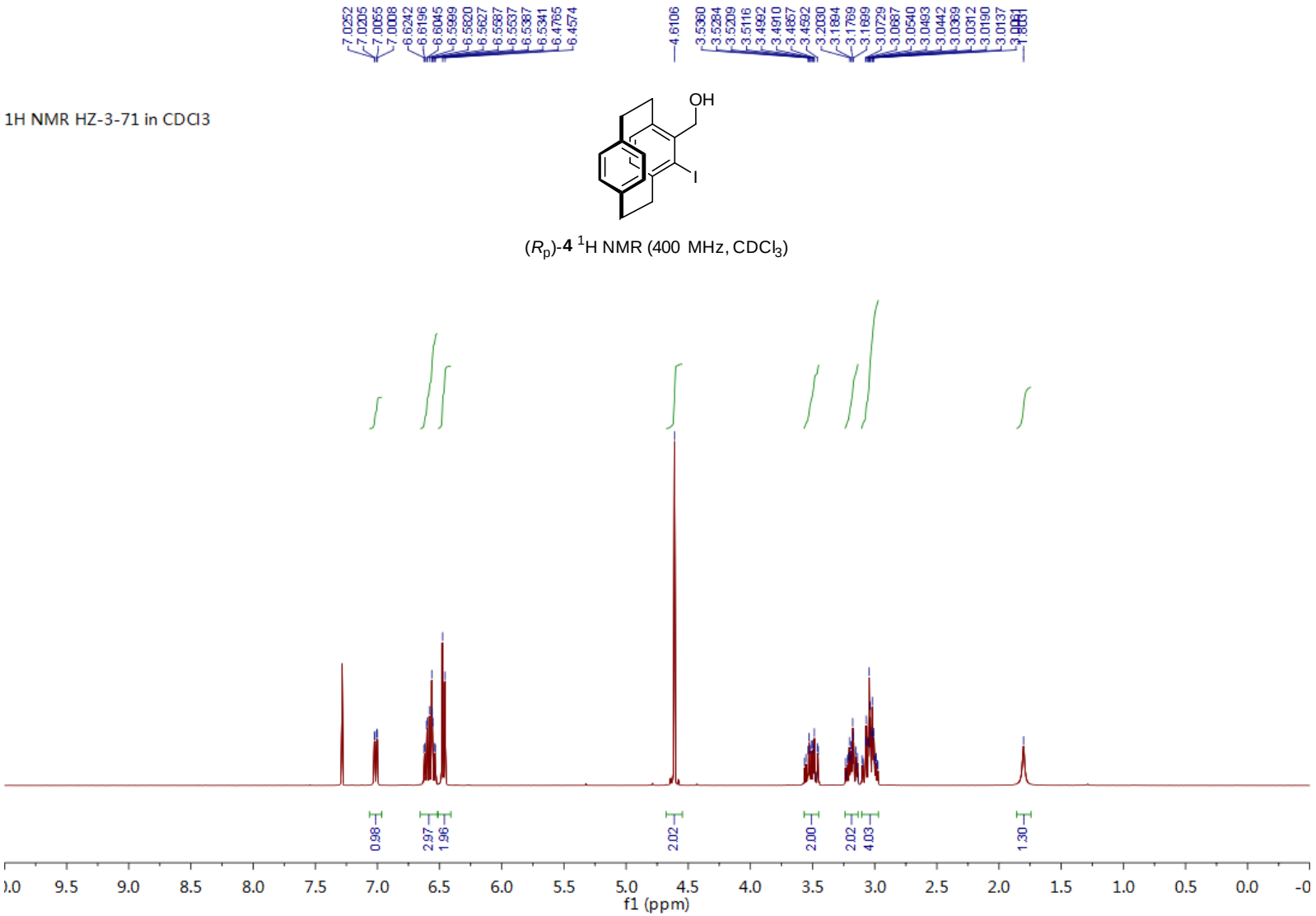
(R_p)-**3** ^{1}H NMR (400 MHz, $CDCl_3$)



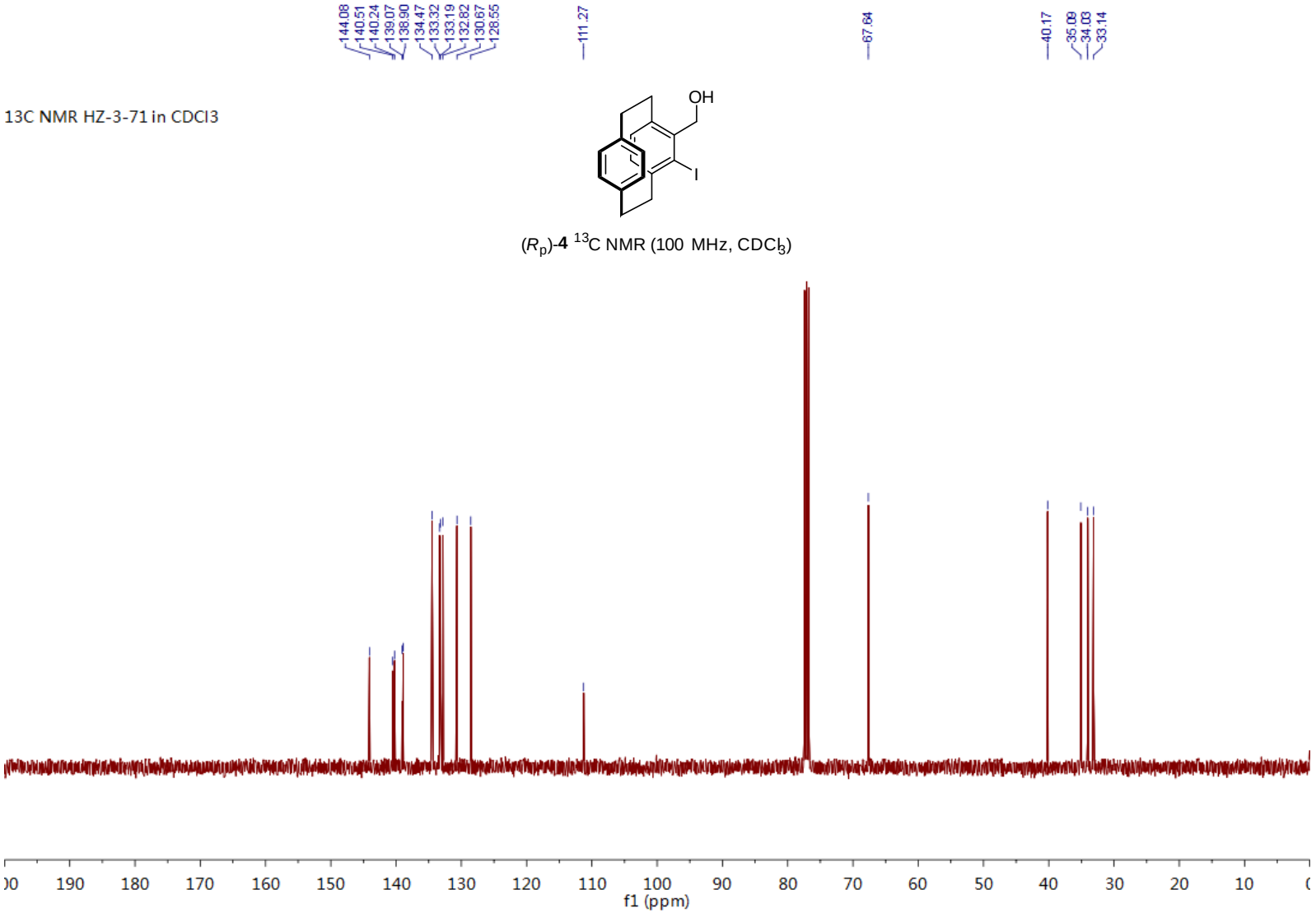


(R_p)-**3** ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-3-71 in CDCl3

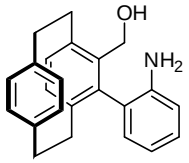


(R_p)-**4** ^{1}H NMR (400 MHz, $CDCl_3$)

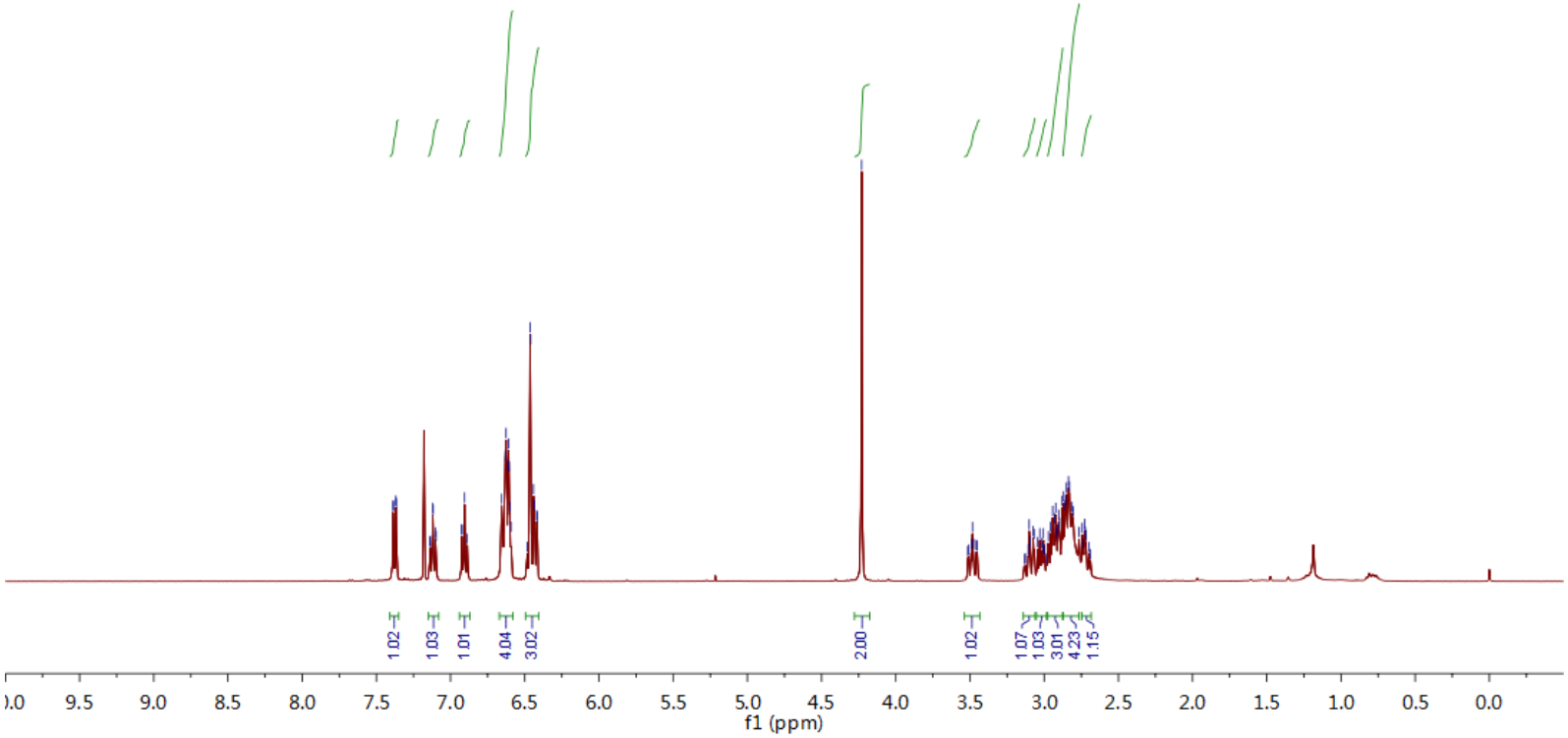


(R_p)-**4** ^{13}C NMR (100 MHz, $CDCl_3$)

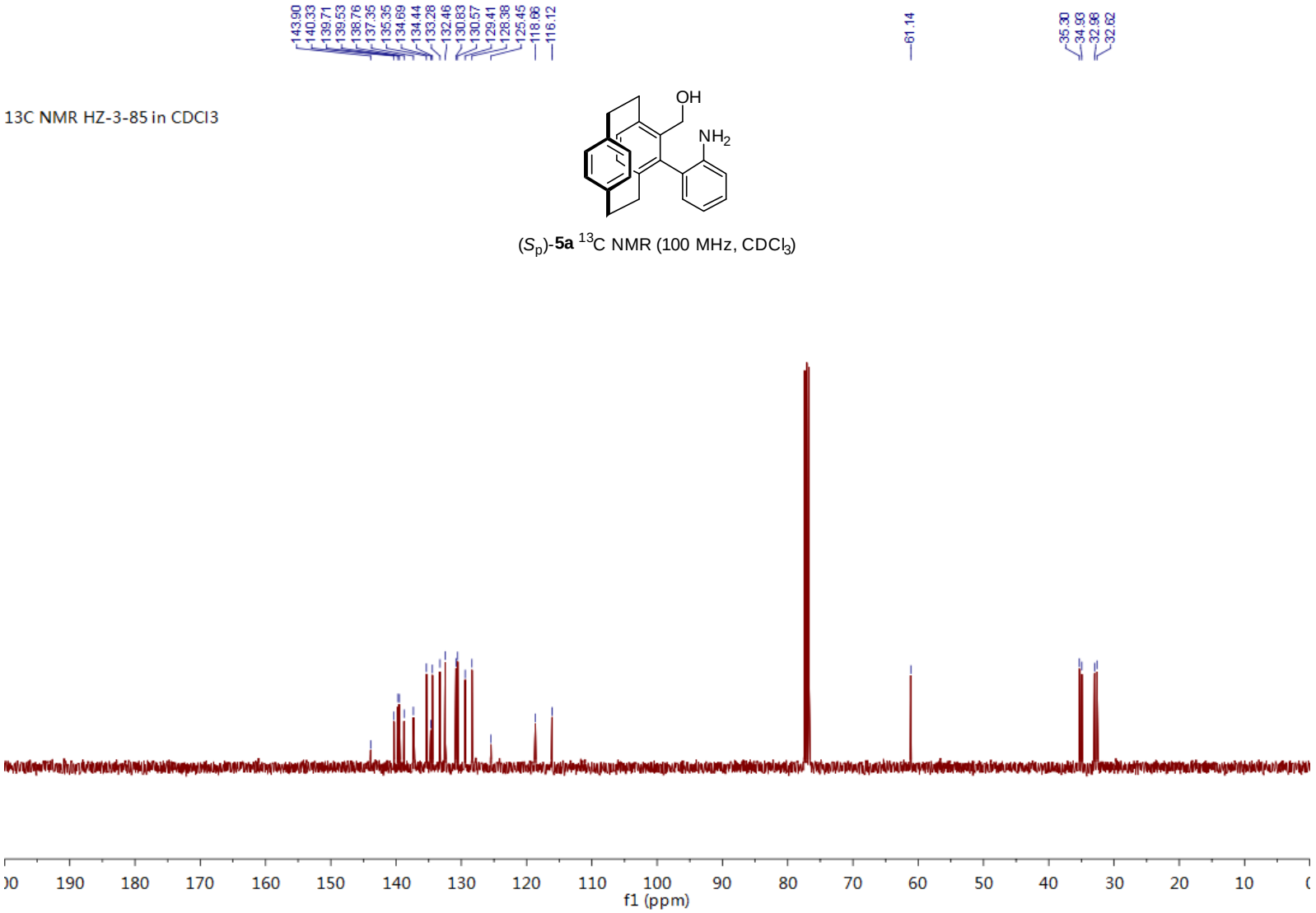
1H NMR HZ-3-85 in CDCl3



(S_p)-**5a** ^{1}H NMR (400 MHz, $CDCl_3$)

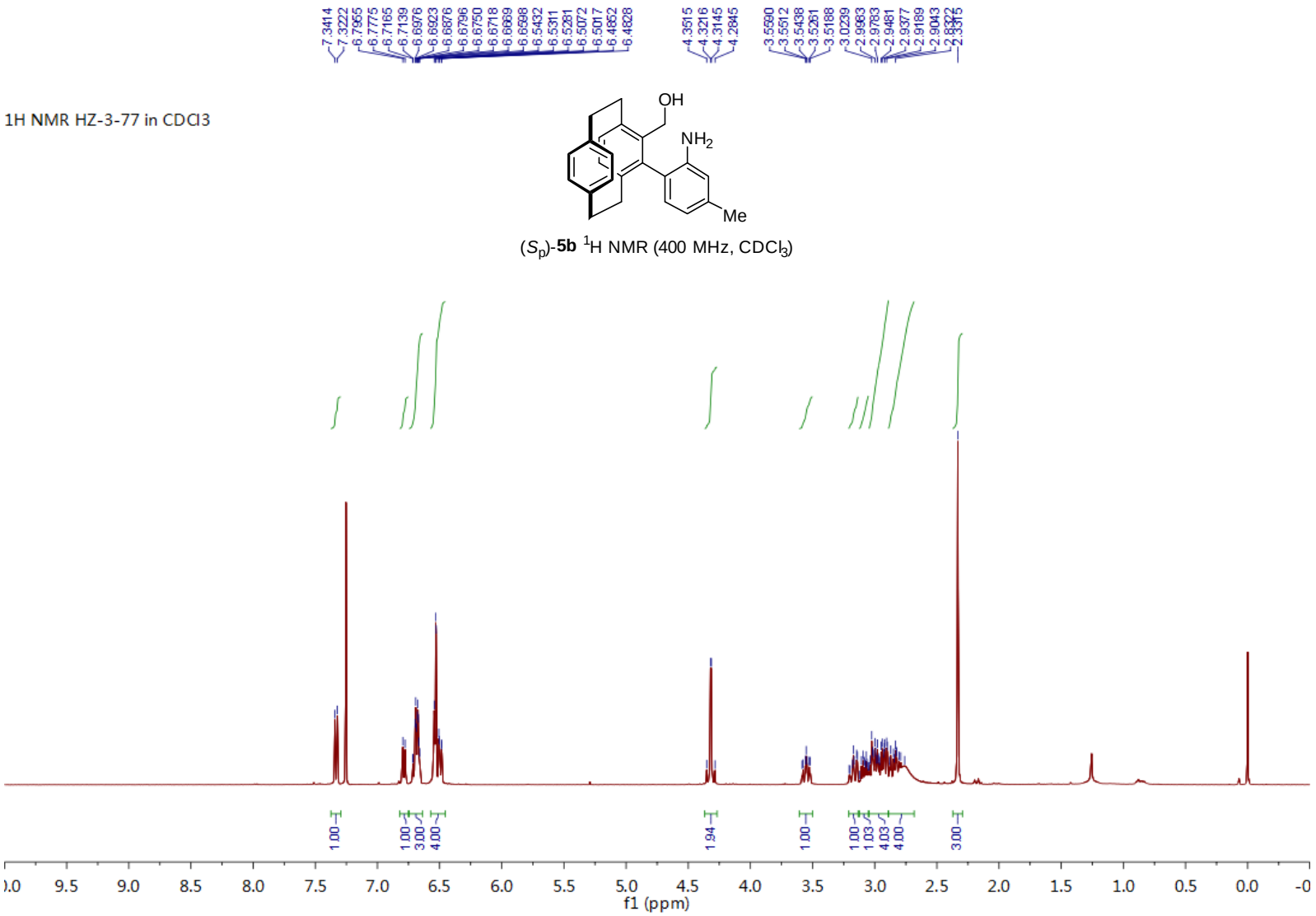


13C NMR HZ-3-85 in CDCl3

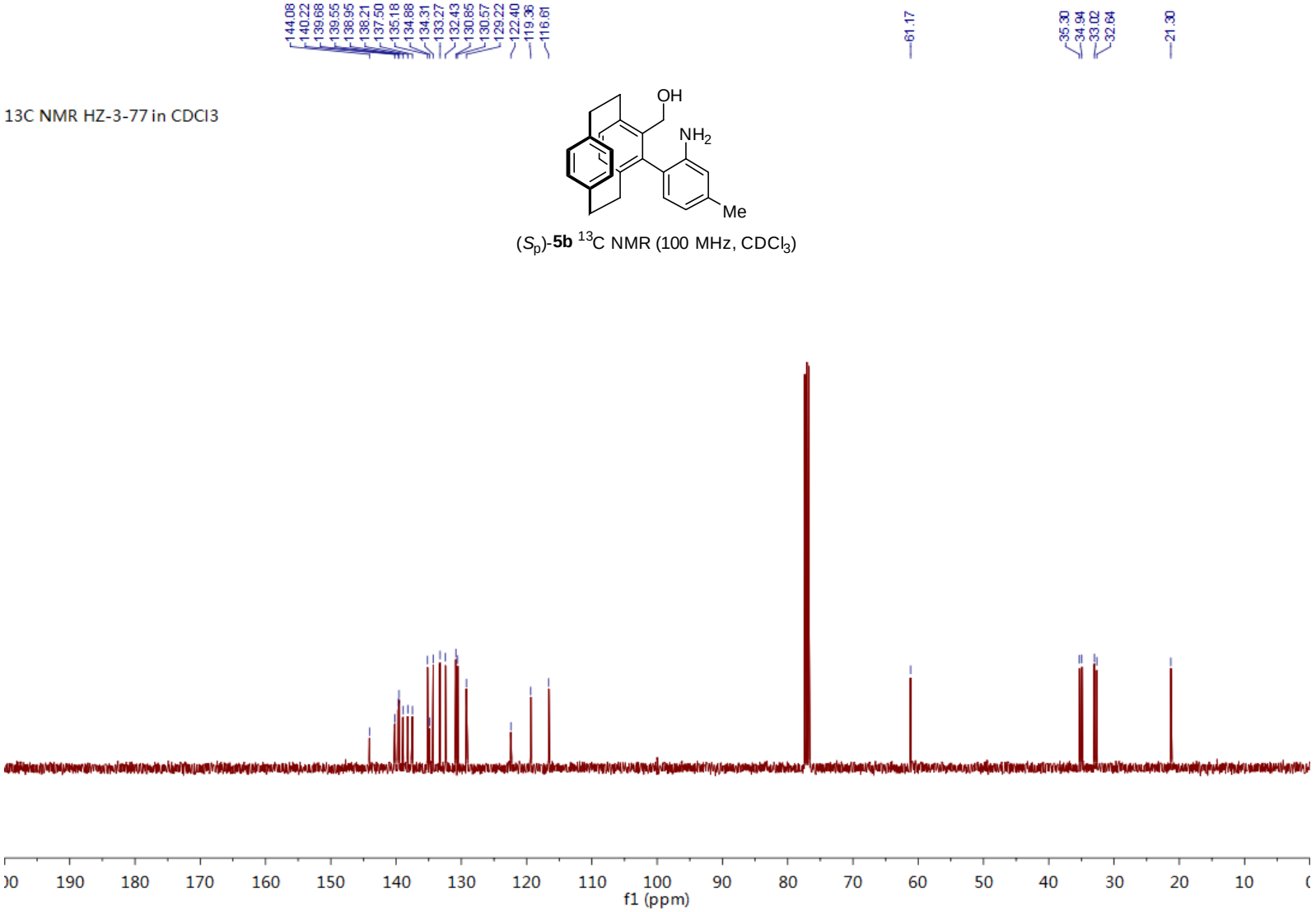


(S_p)-**5a** ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-3-77 in CDCl3

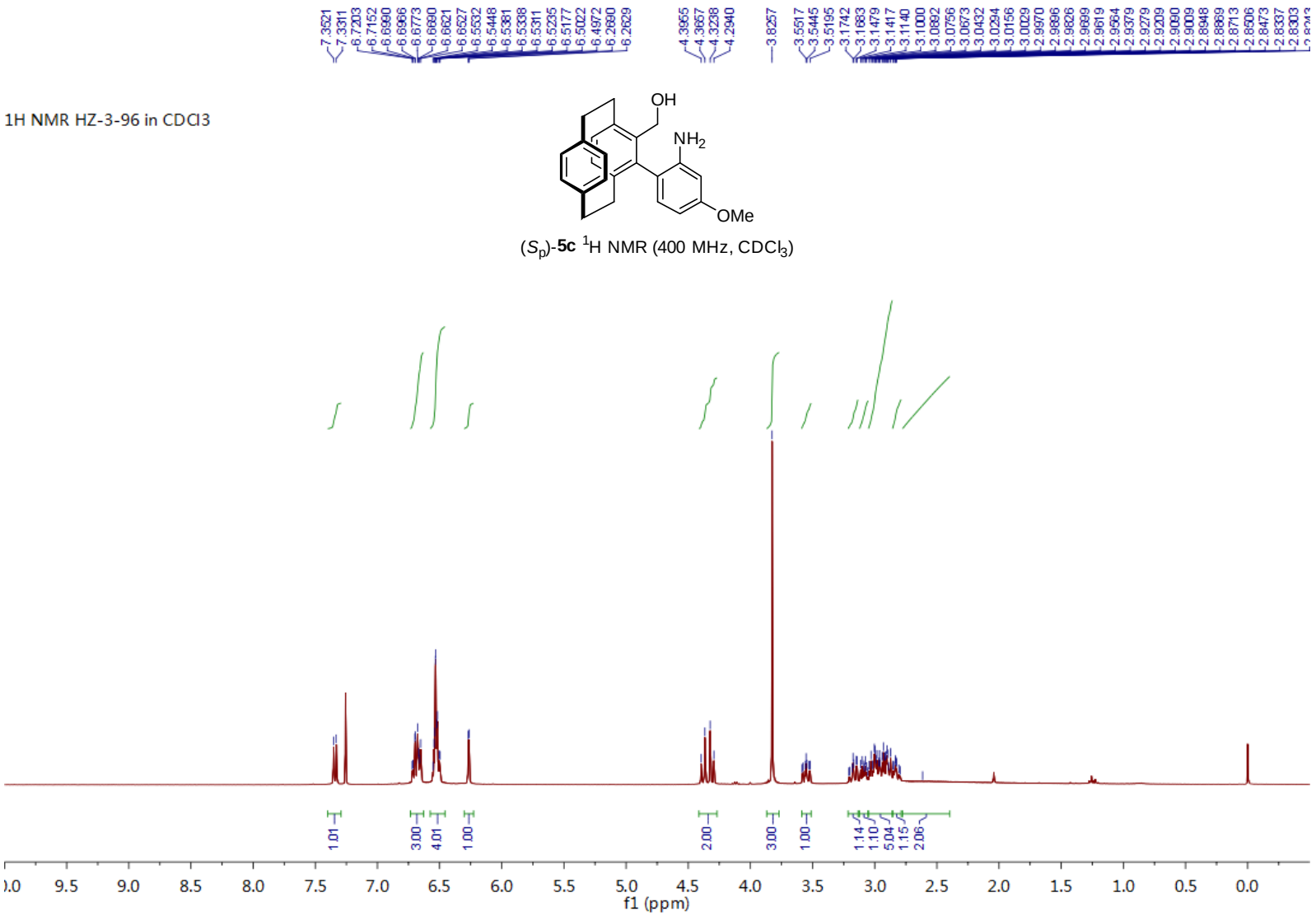


(S_p)-**5b** ^{1}H NMR (400 MHz, $CDCl_3$)

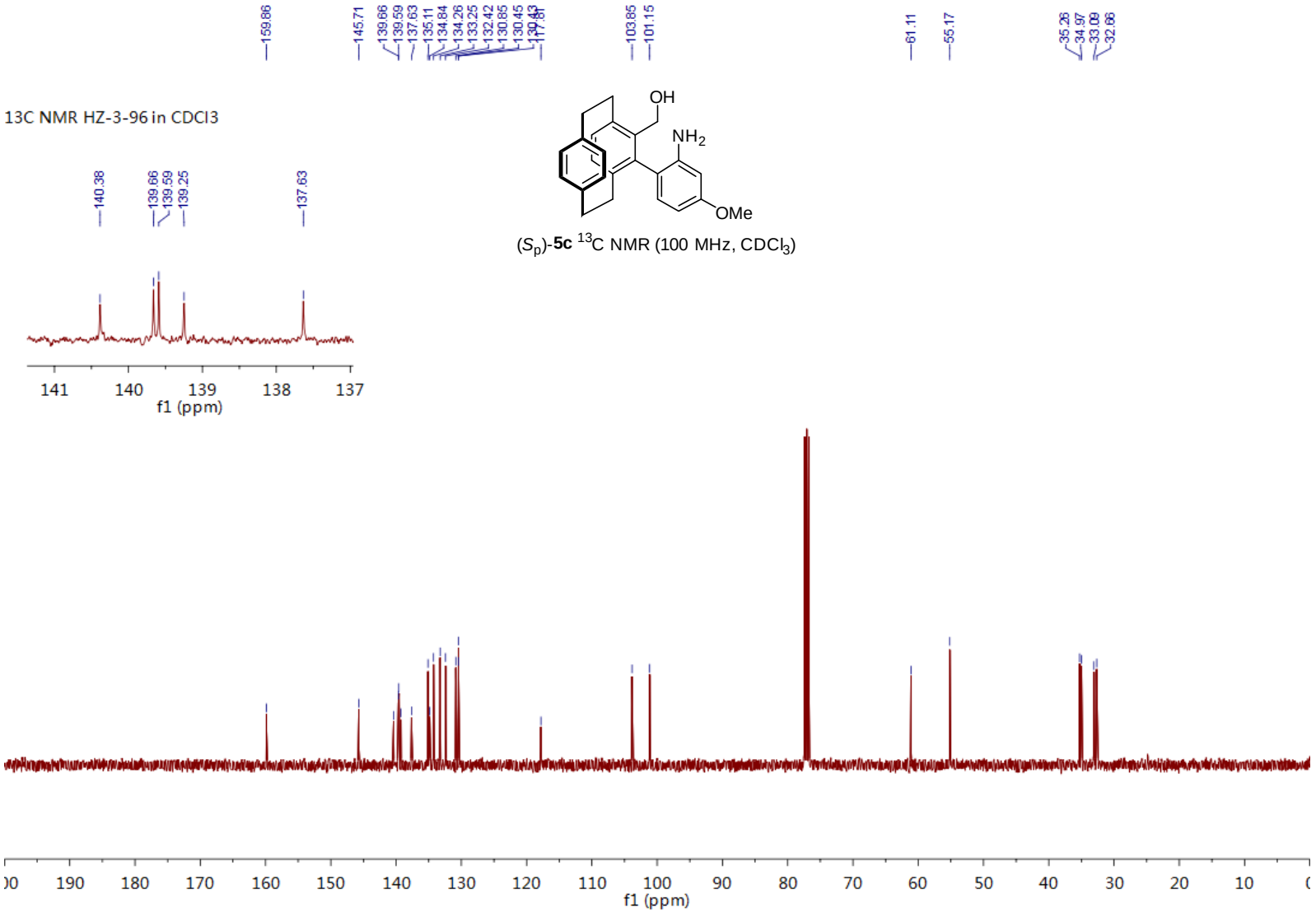


(S_p)-**5b** ^{13}C NMR (100 MHz, $CDCl_3$)

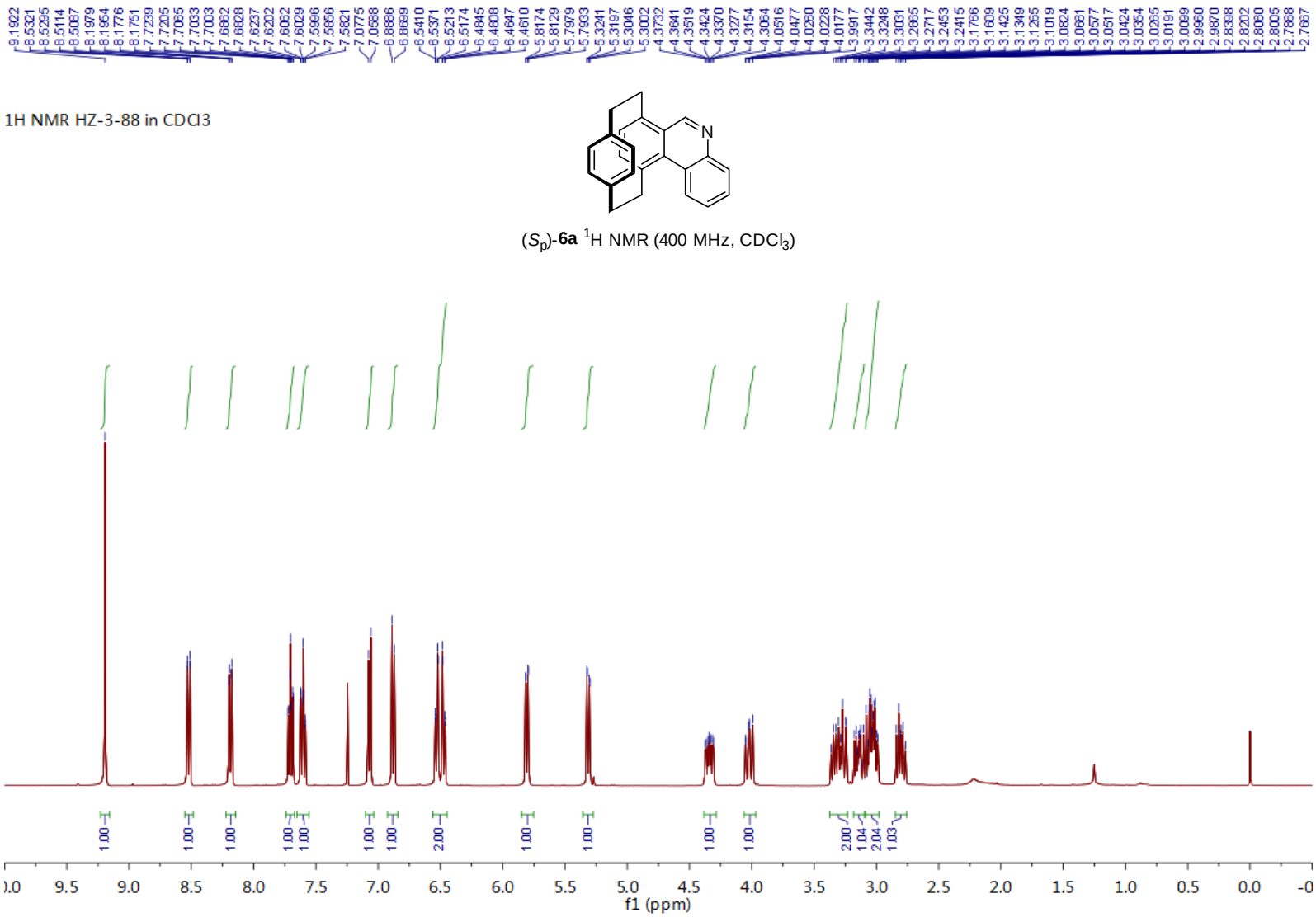
1H NMR HZ-3-96 in CDCl3



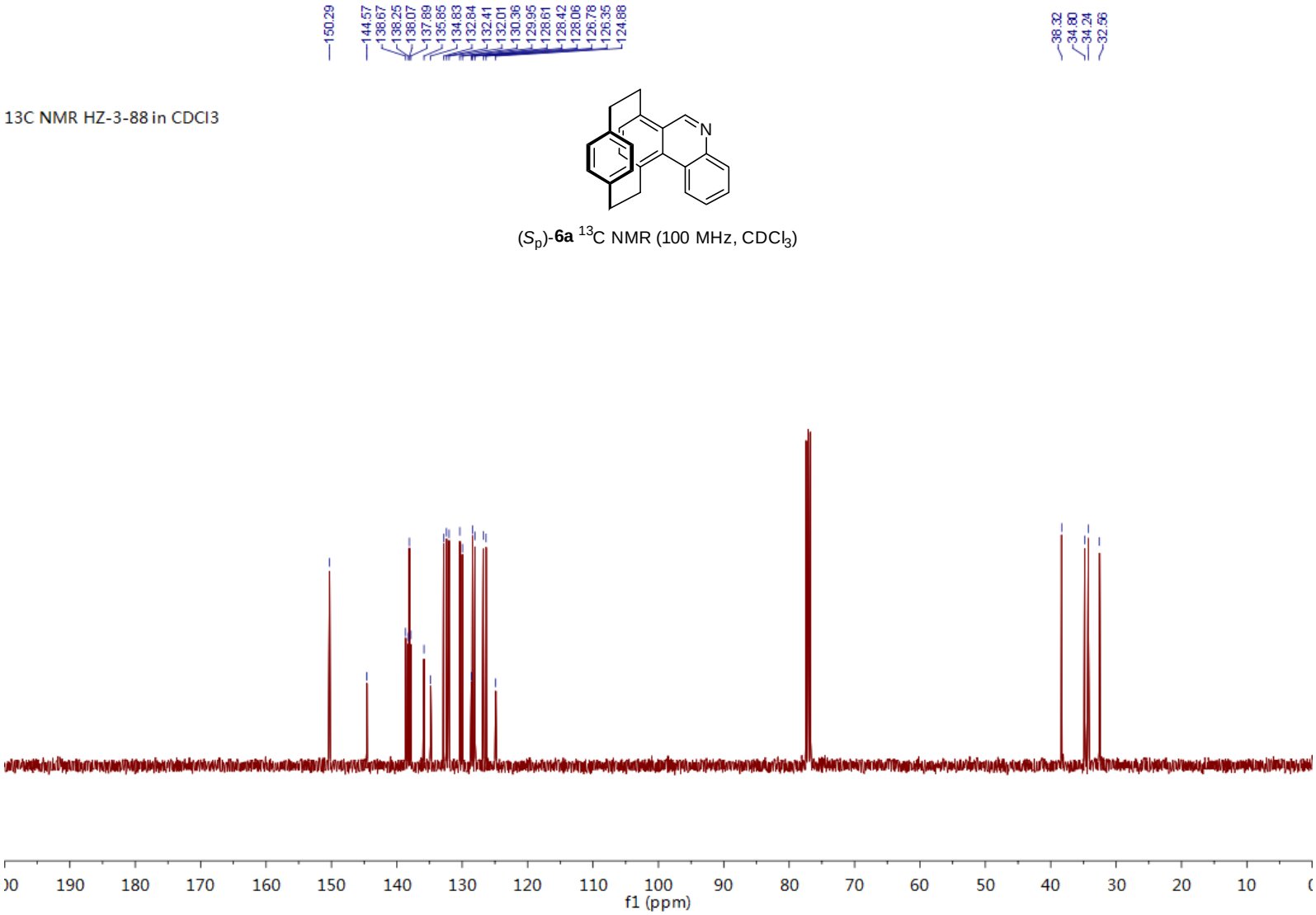
(S_p)-**5c** ^{1}H NMR (400 MHz, $CDCl_3$)



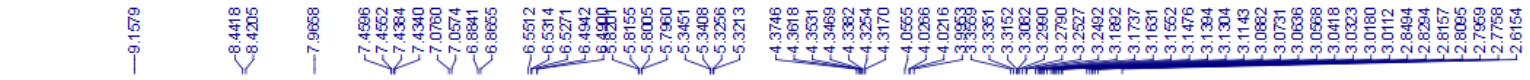
(S_p)-**5c** ^{13}C NMR (100 MHz, $CDCl_3$)



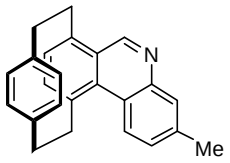
(S_p)-**6a** ^{1}H NMR (400 MHz, $CDCl_3$)



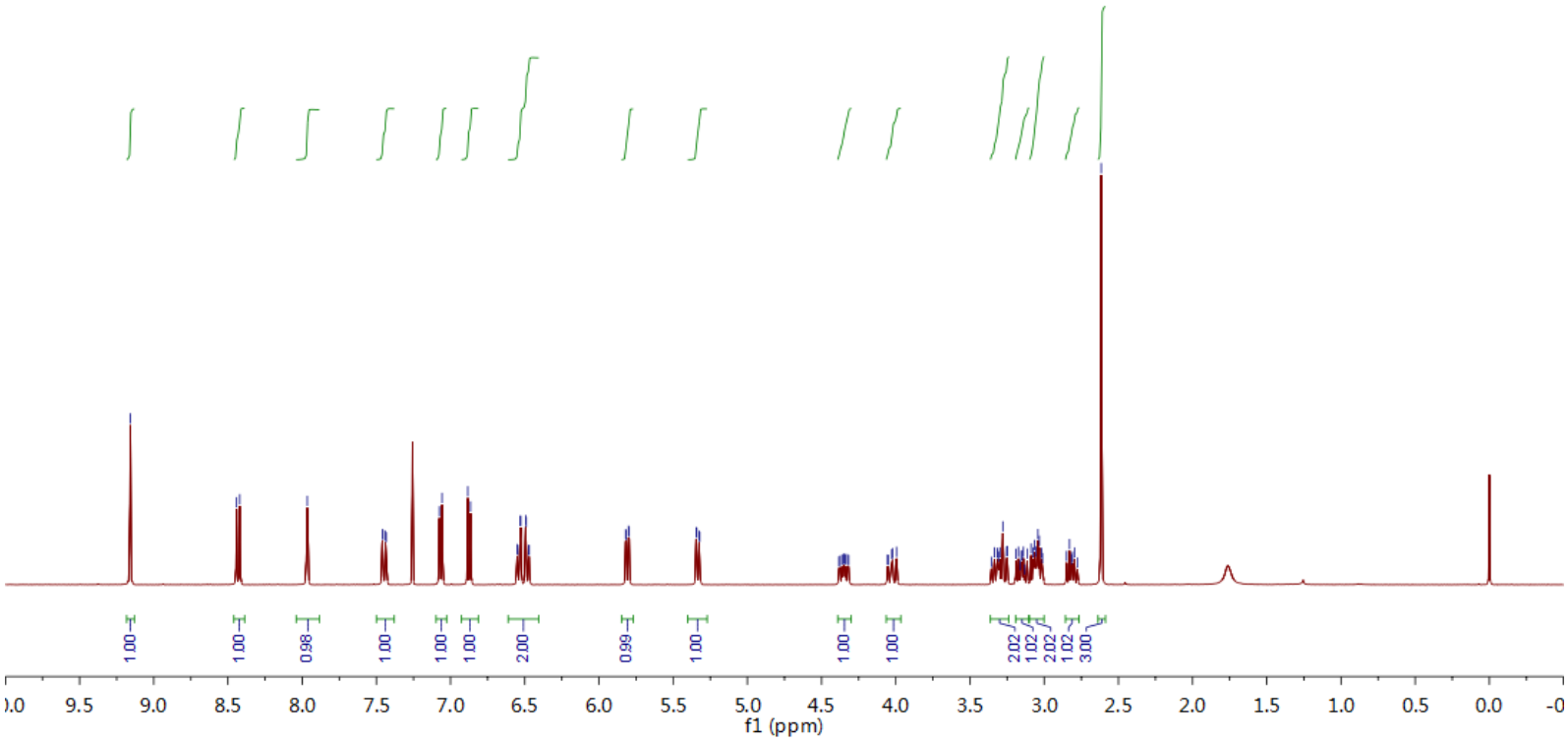
(S_p)-**6a** ^{13}C NMR (100 MHz, $CDCl_3$)

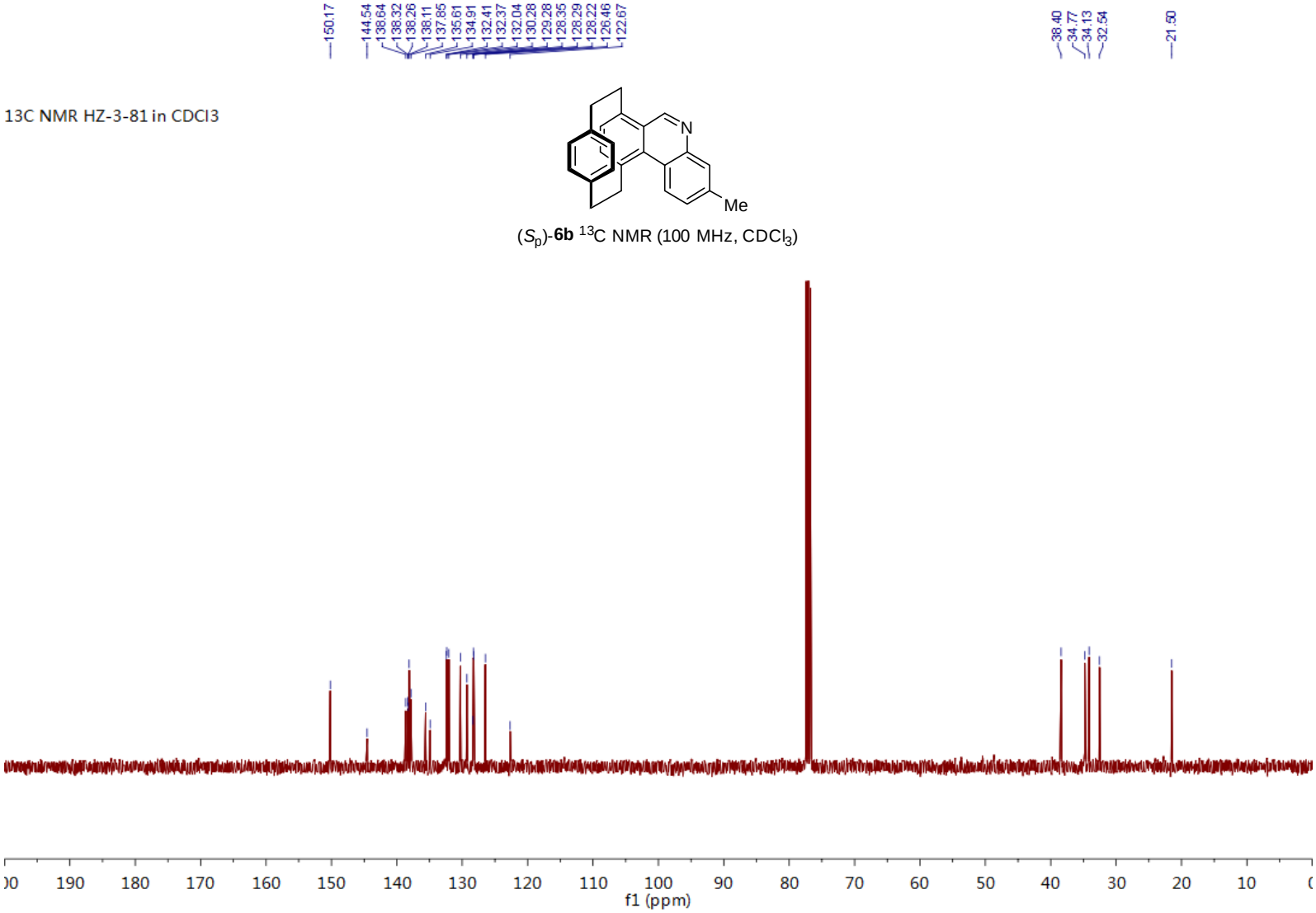


1H NMR HZ-3-81 in CDCl3



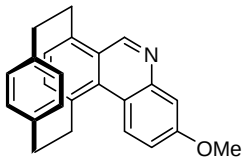
(S_p)-**6b** ^{1}H NMR (400 MHz, $CDCl_3$)



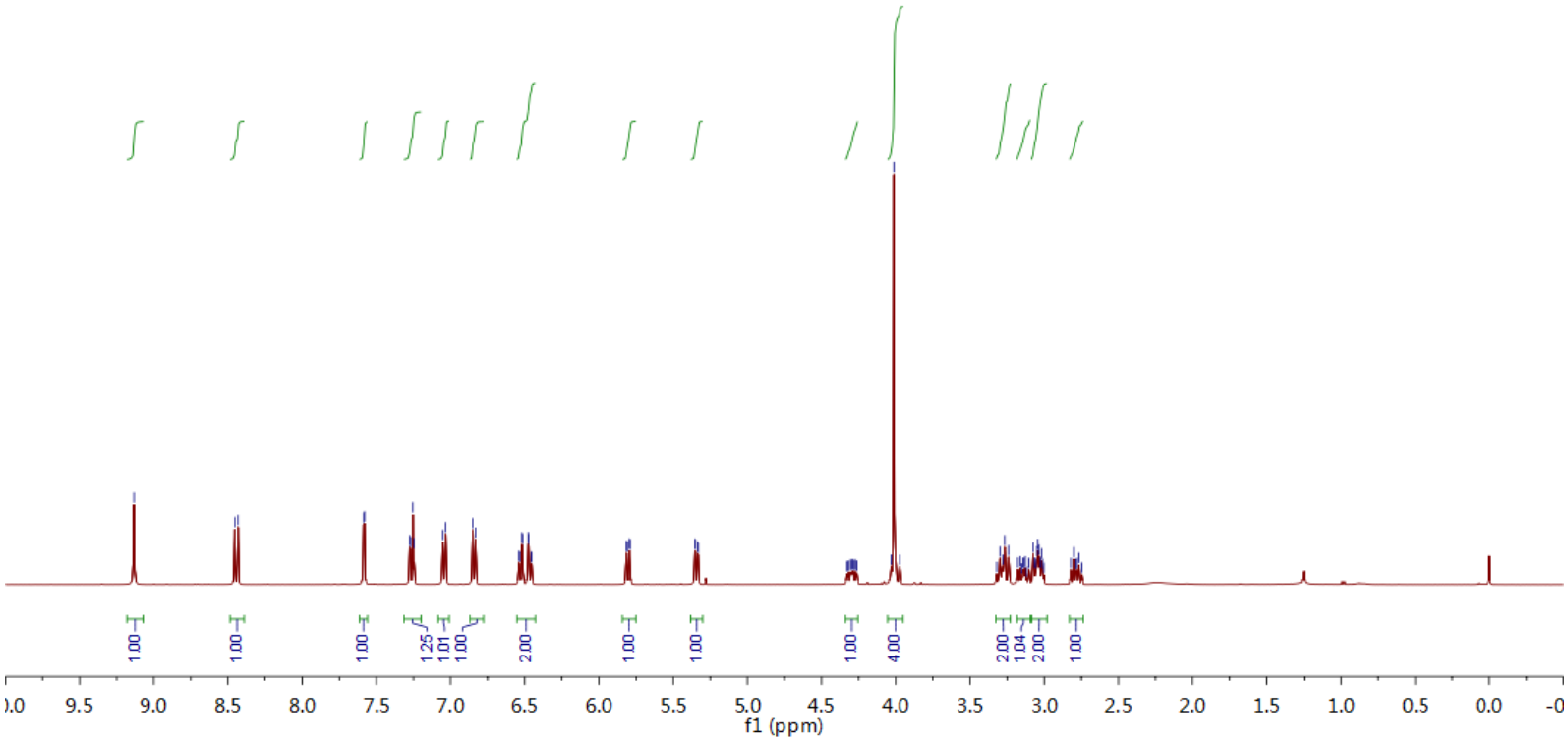


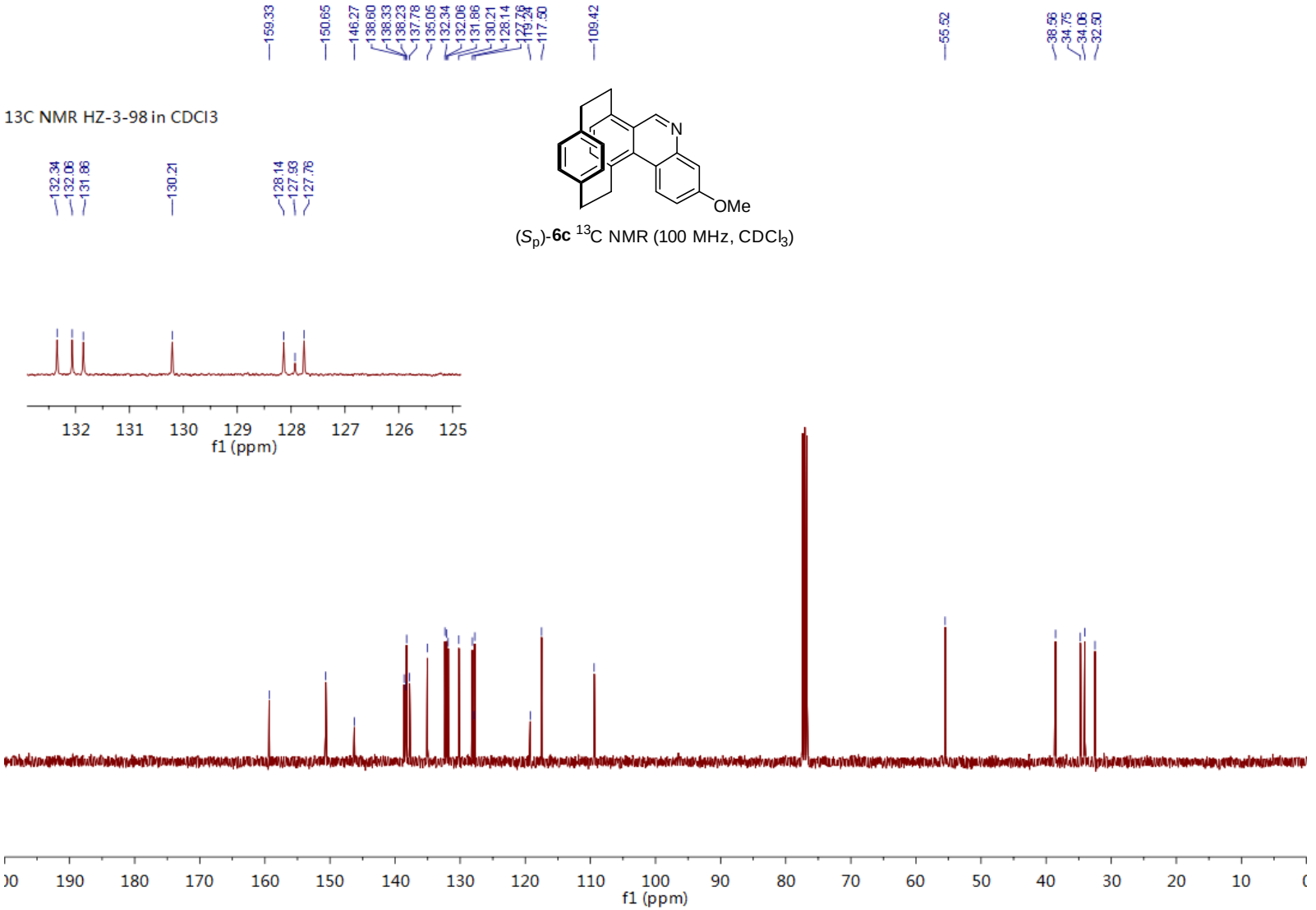
(S_p)-**6b** ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-3-98 in CDCl3



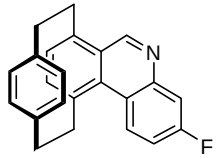
(S_p)-**6c** ^{1}H NMR (400 MHz, $CDCl_3$)



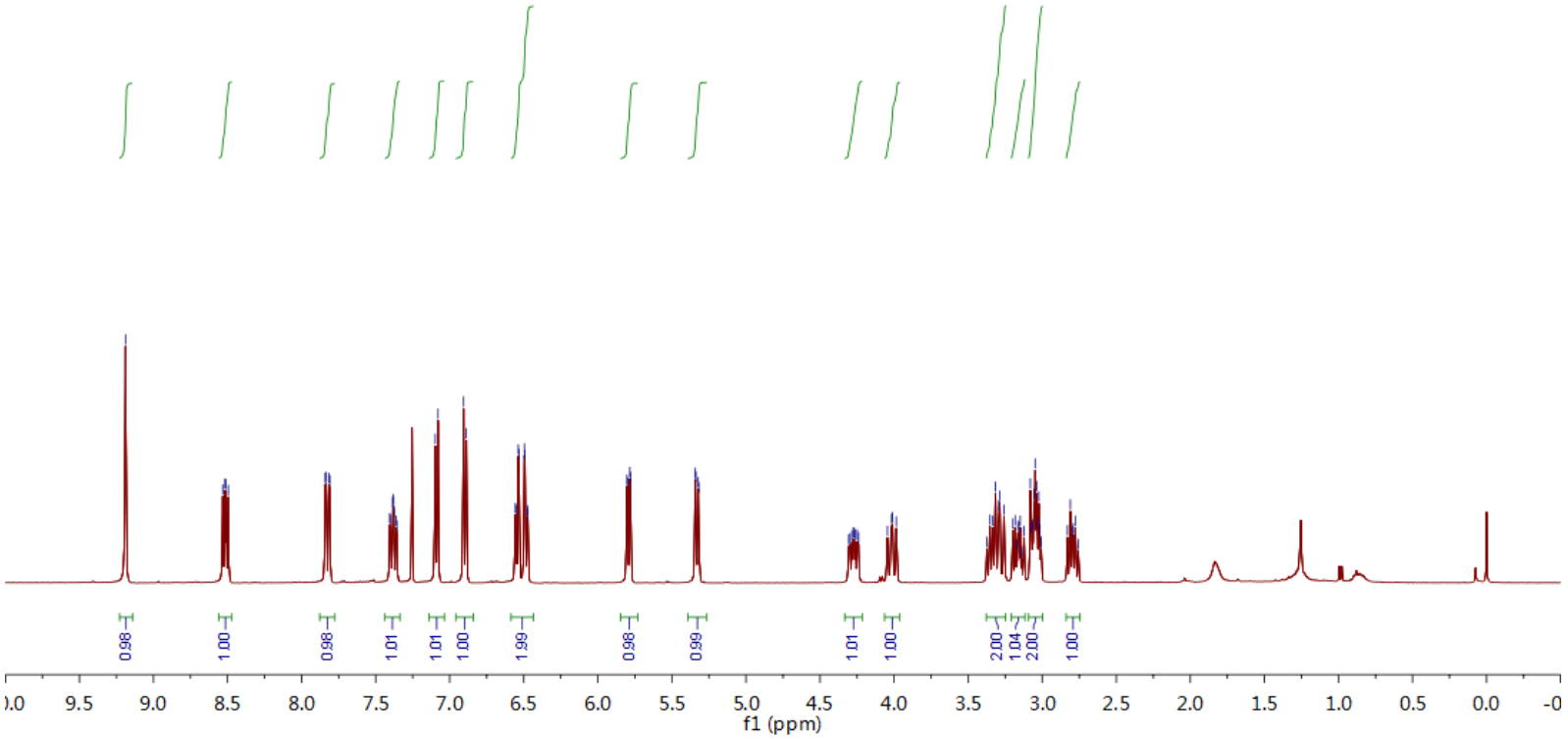


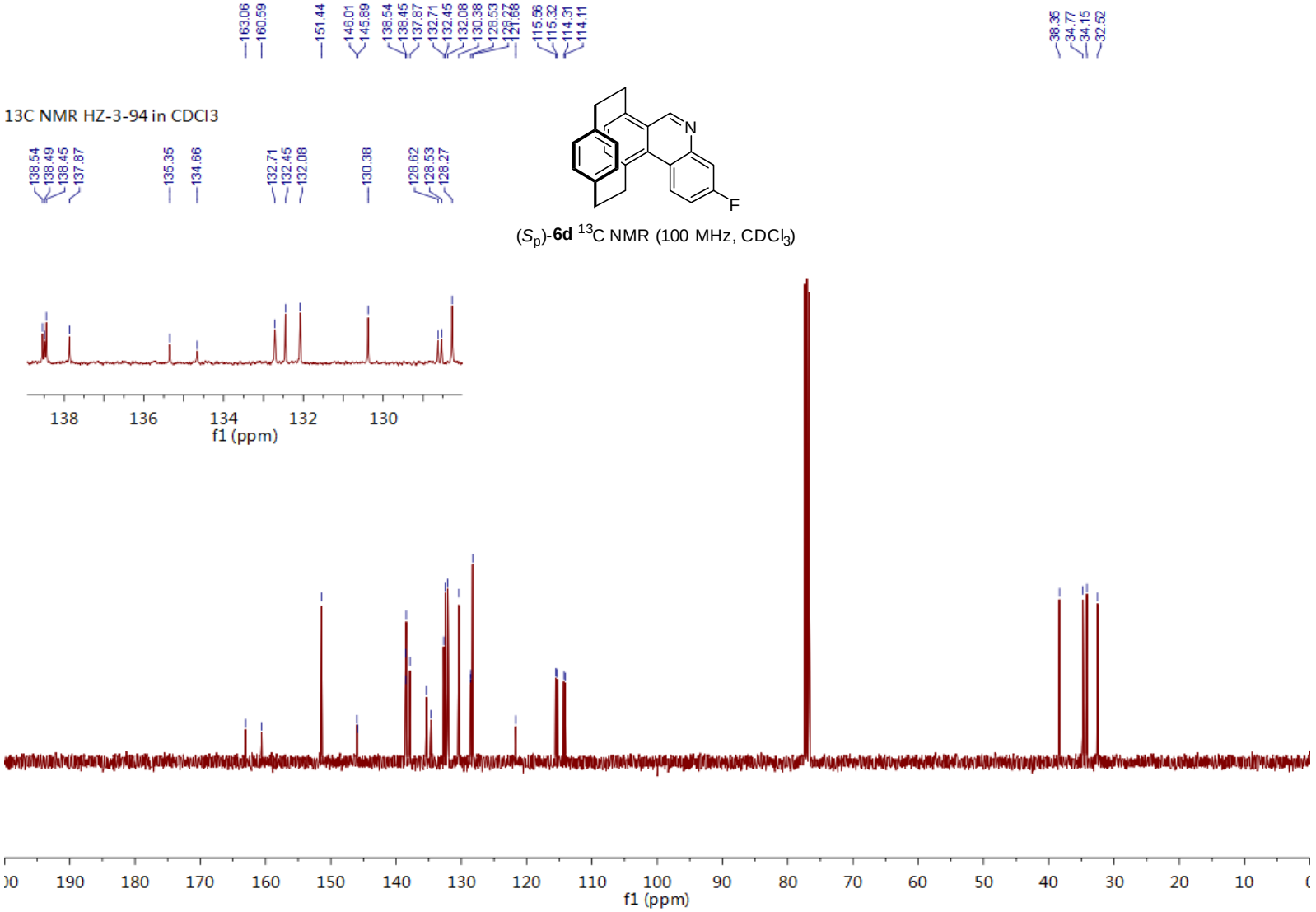
(S_p)-**6c** ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-3-94 in CDCl3



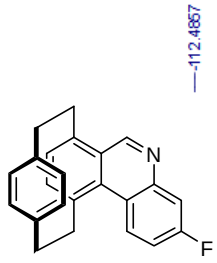
(S_p)-**6d** ^{1}H NMR (400 MHz, $CDCl_3$)



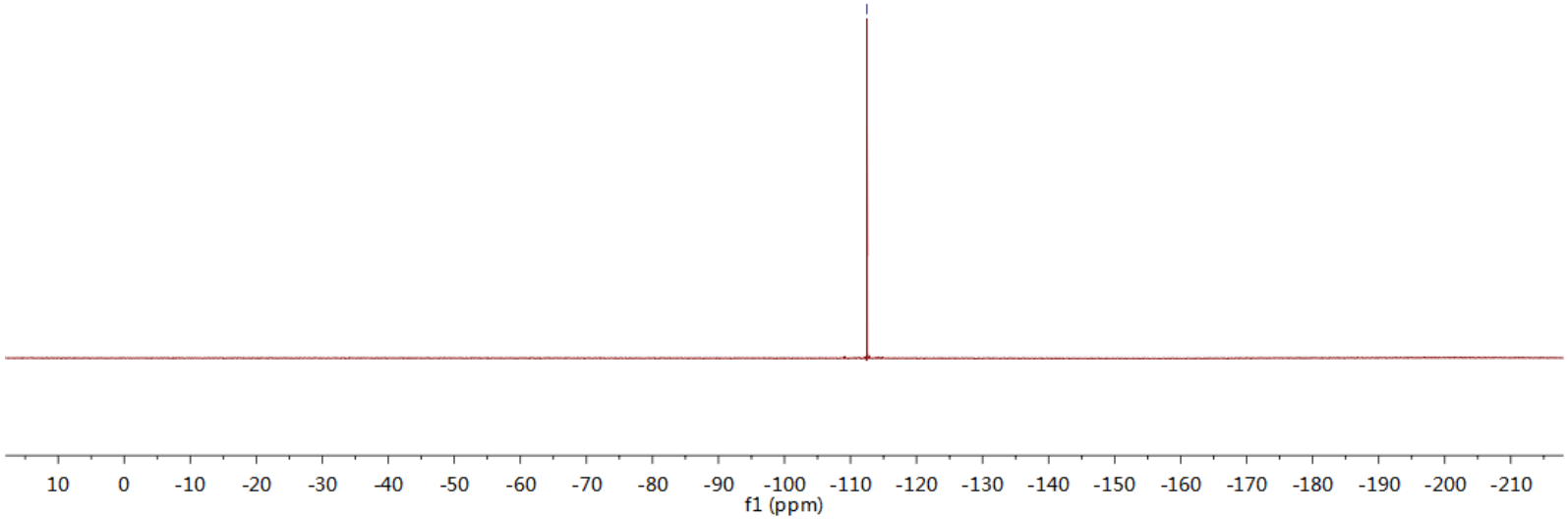


(S_p)-**6d** ^{13}C NMR (100 MHz, $CDCl_3$)

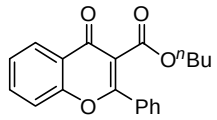
19F NMR HZ-3-94 in CDCl3



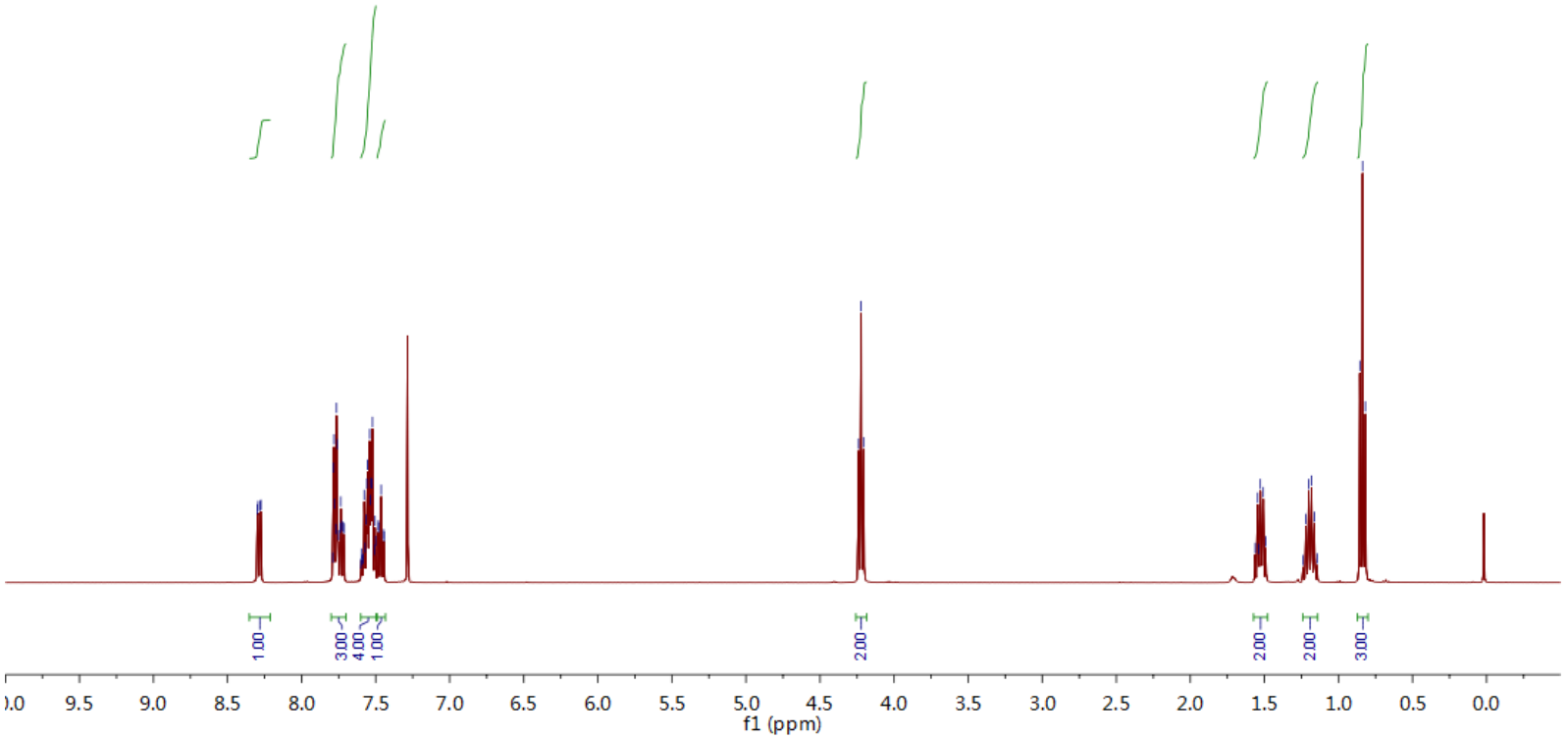
(S_p)-**6d** ^{19}F NMR (376 MHz, $CDCl_3$)

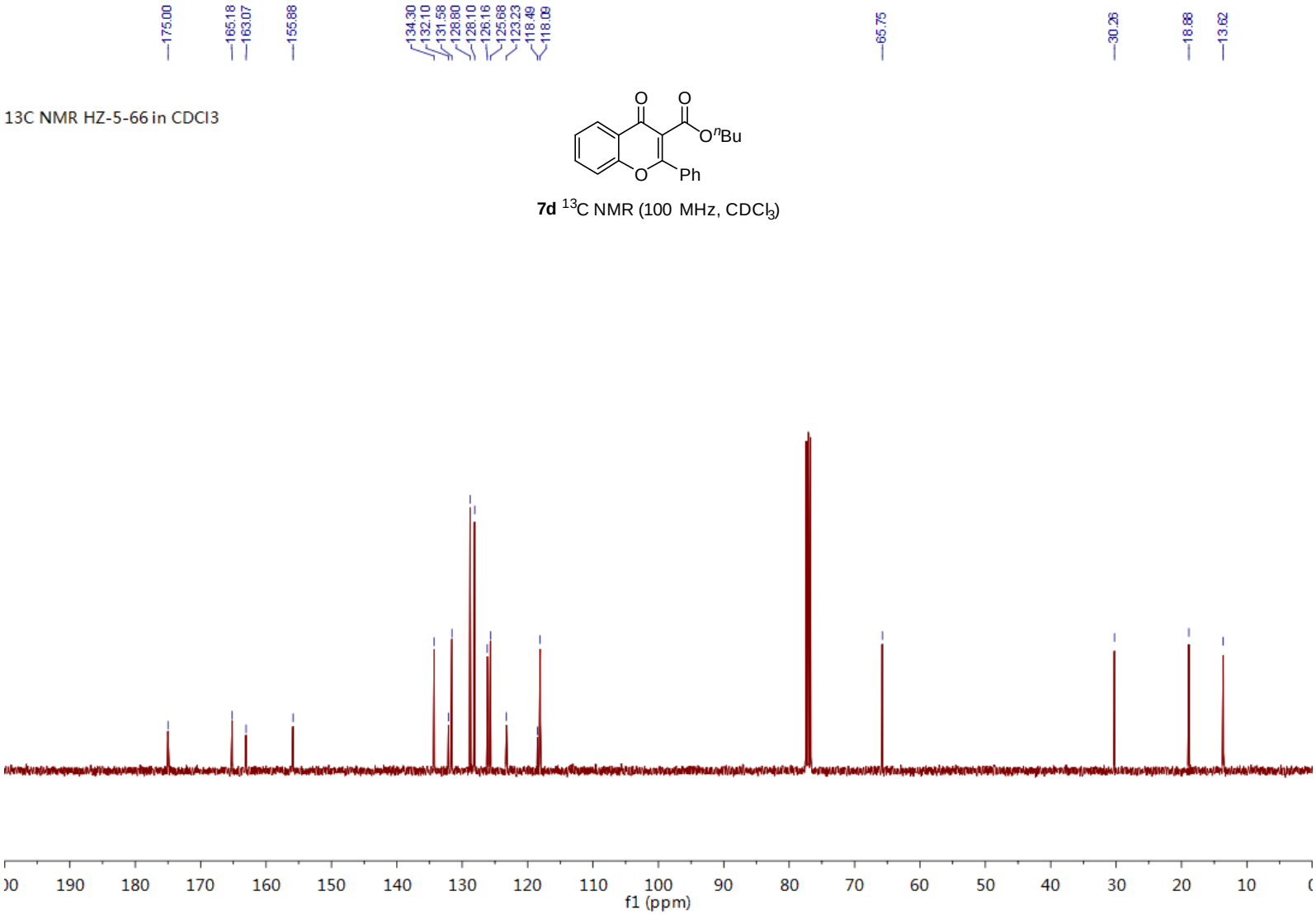


1H NMR HZ-5-66 in CDCl3



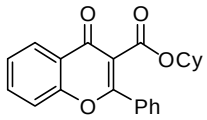
7d ^{1}H NMR (400 MHz, $CDCl_3$)



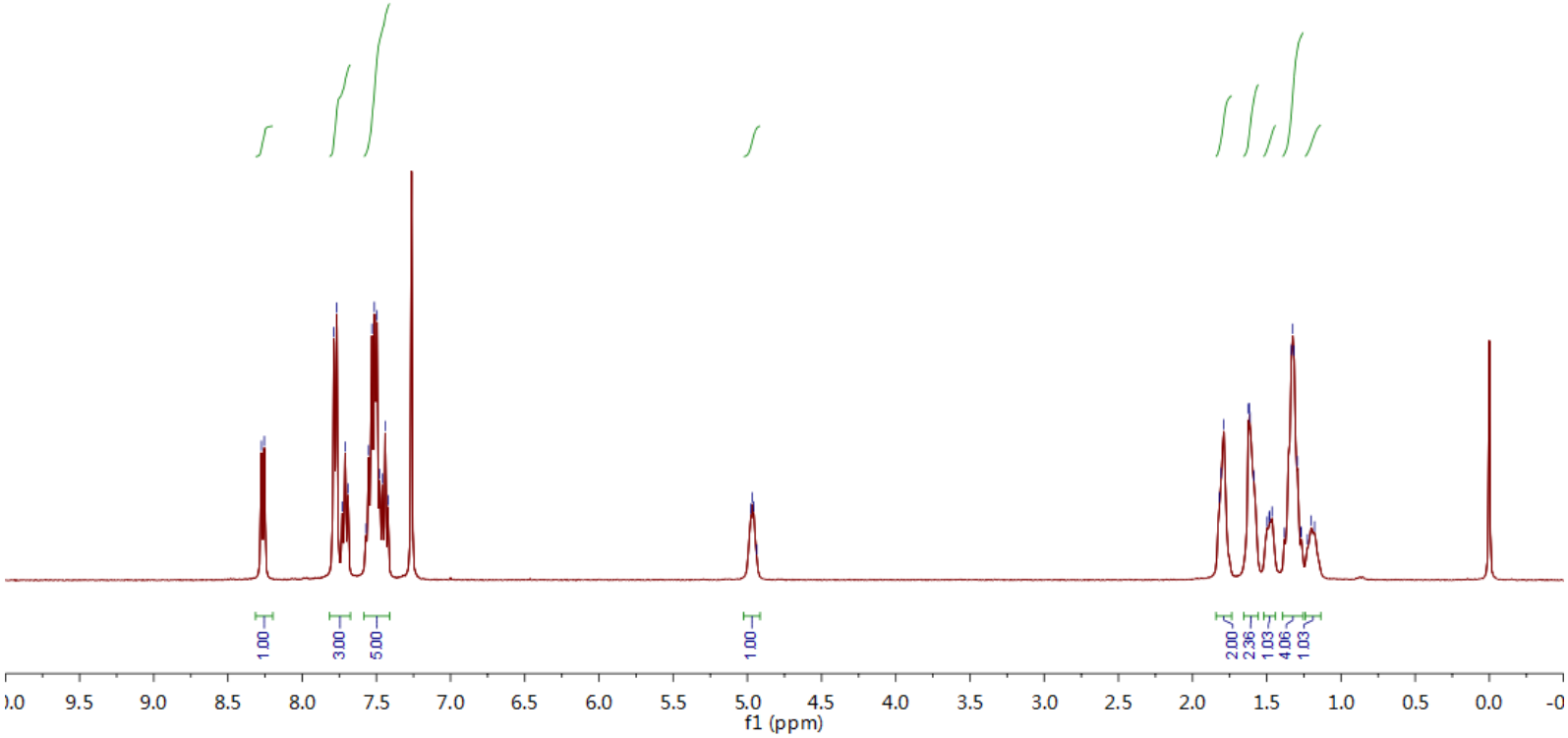


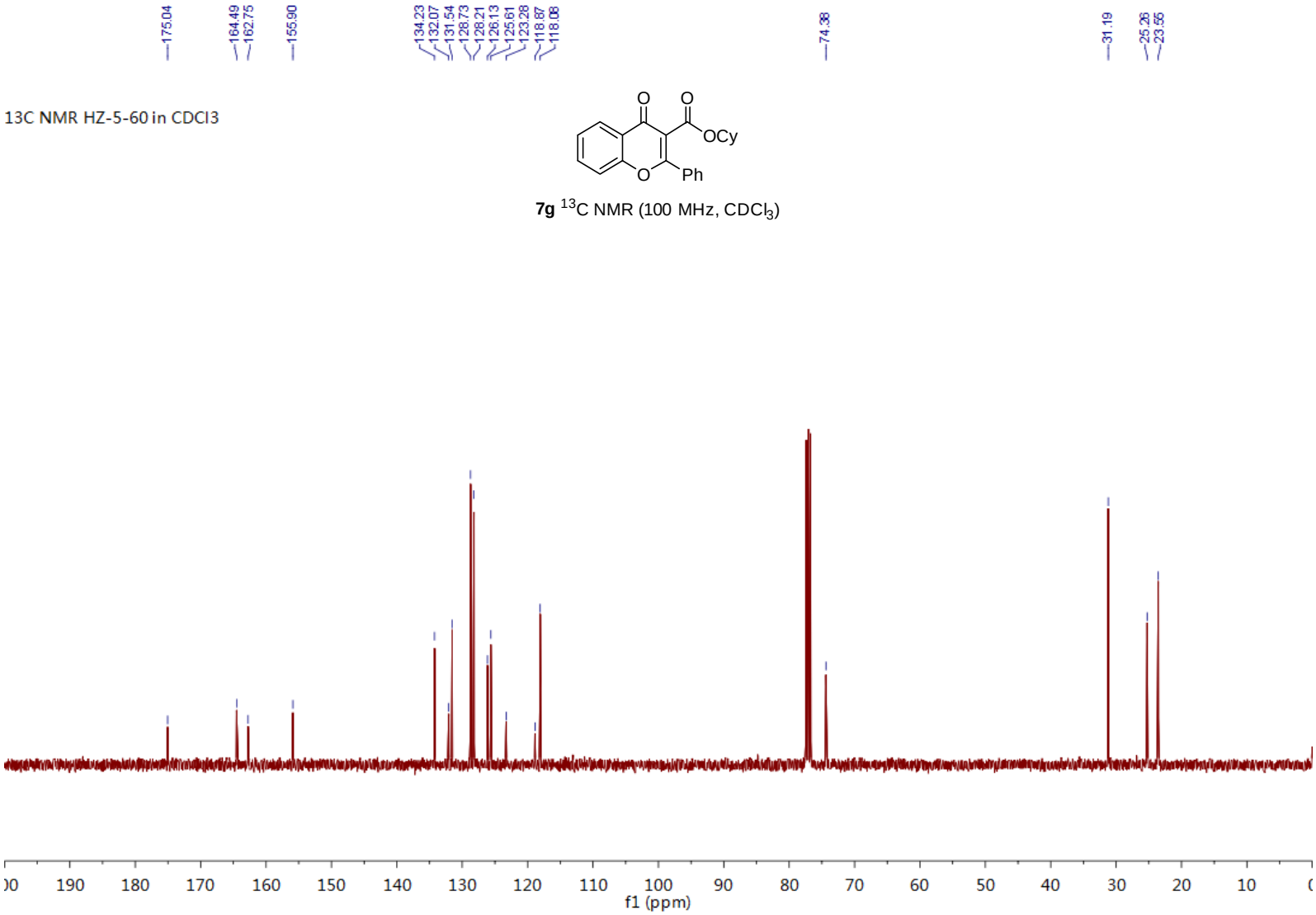
7d ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-60 in CDCl3



7g ^{1}H NMR (400 MHz, $CDCl_3$)





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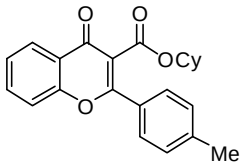
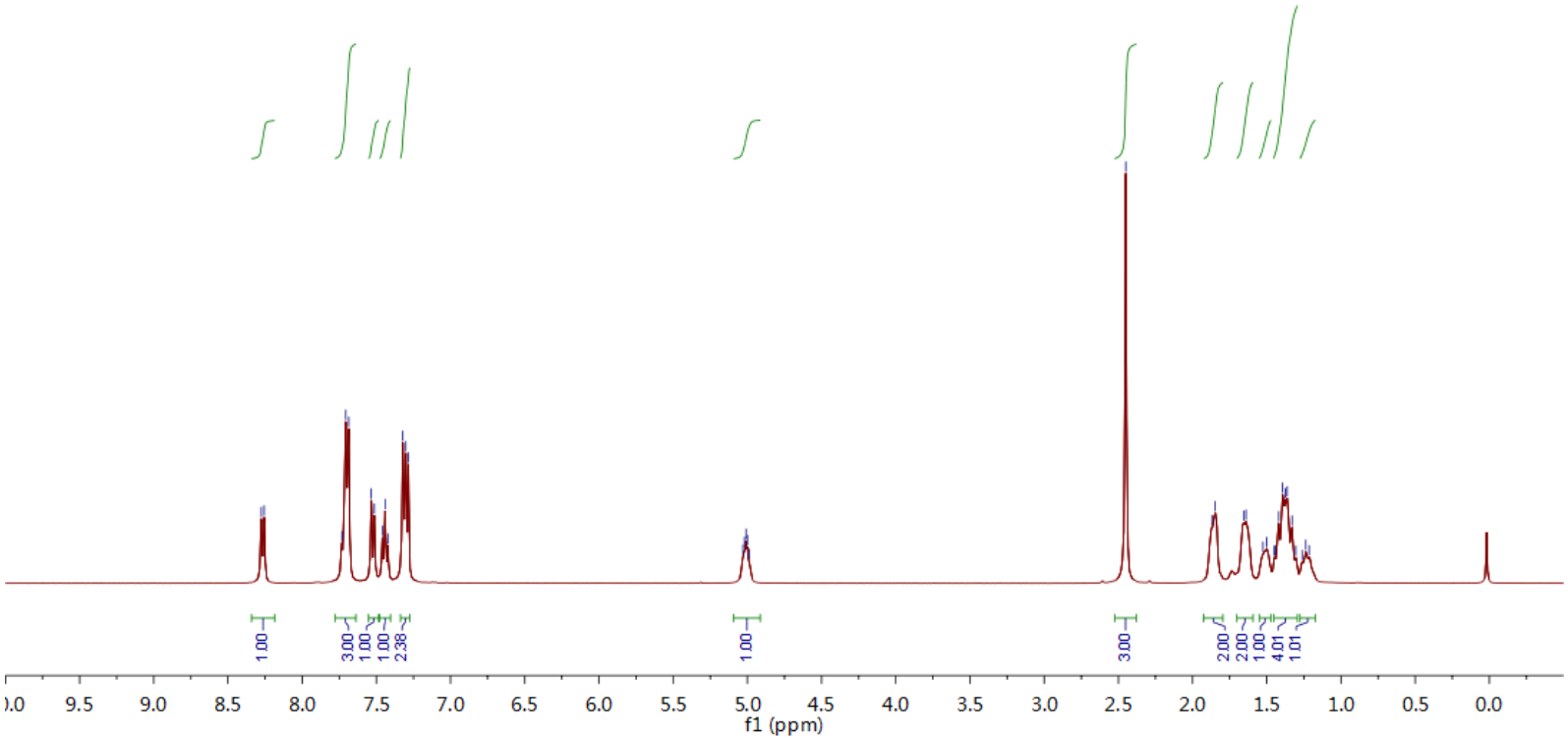
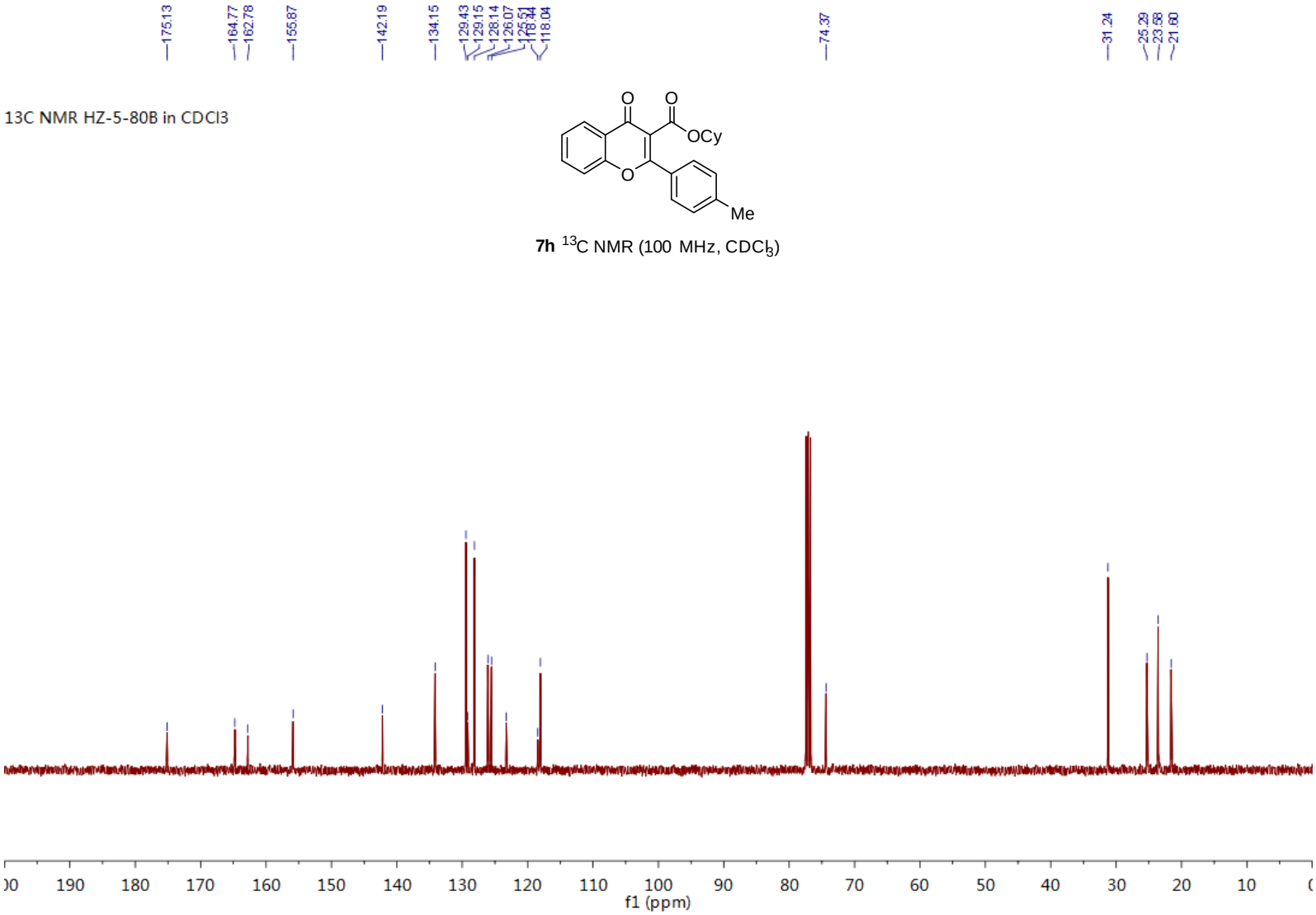
1H NMR HZ-5-80B in CDCl3



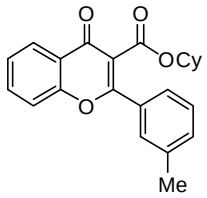
7h ^{1}H NMR (400 MHz, $CDCl_3$)



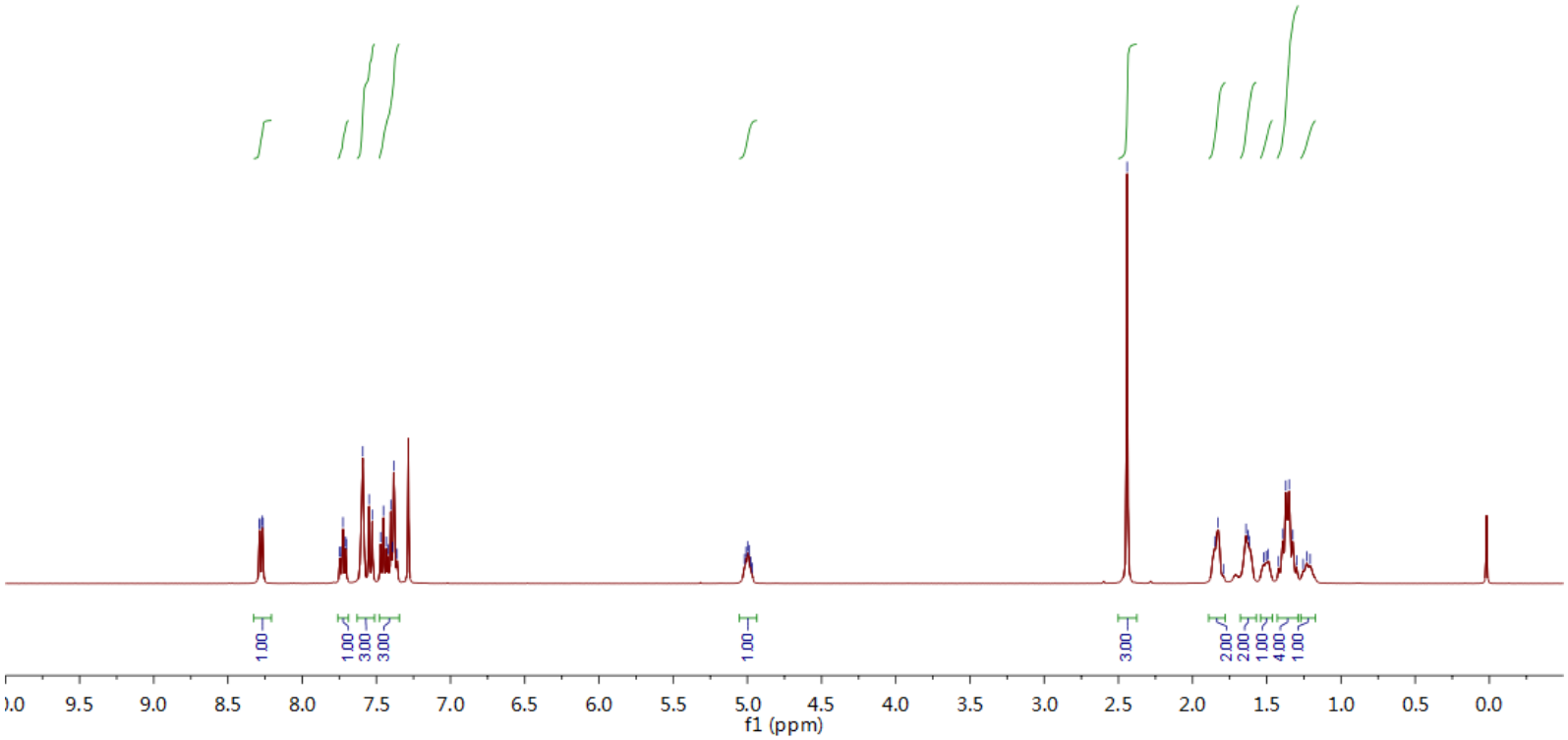


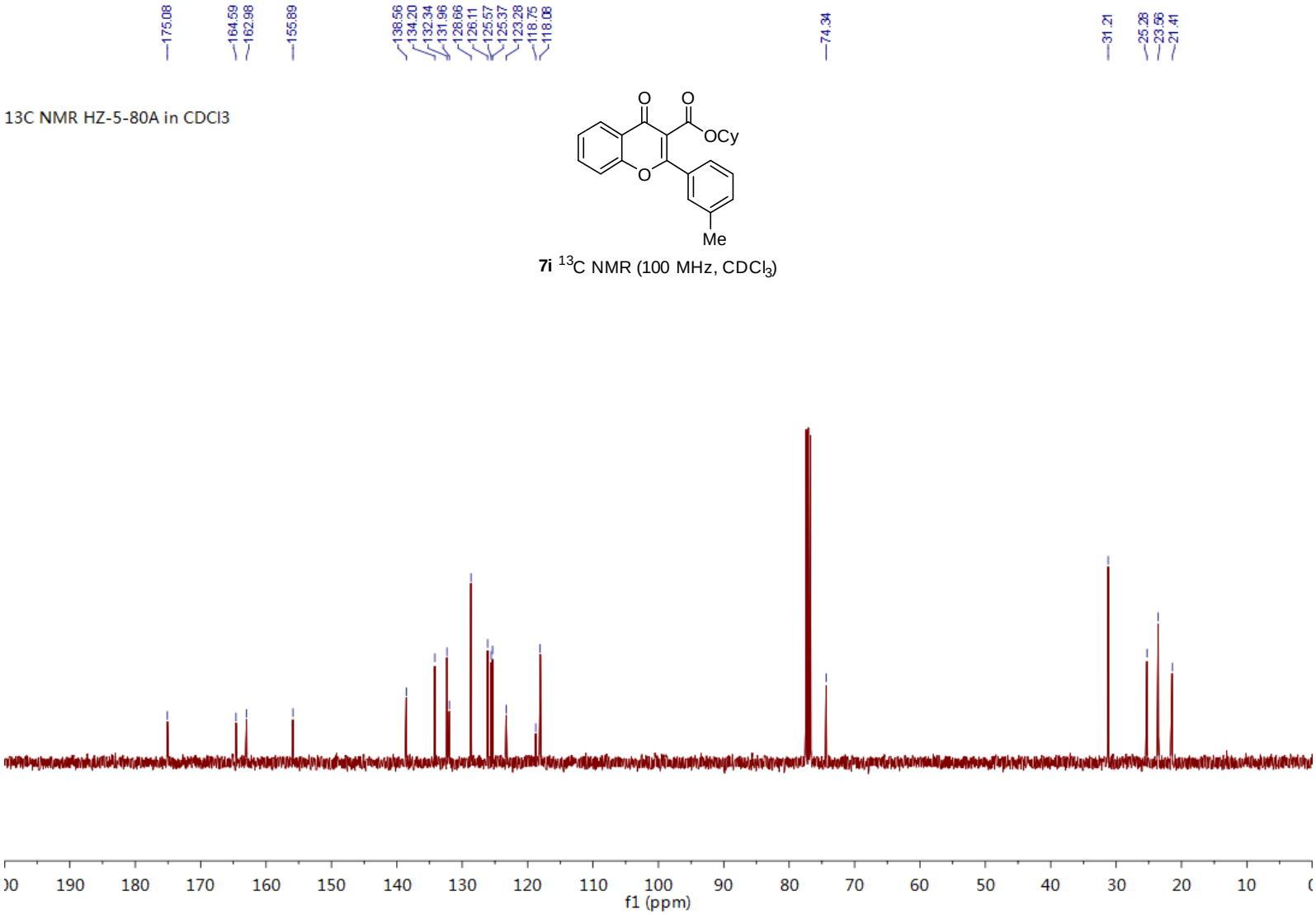
7h ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-80A in CDCl3



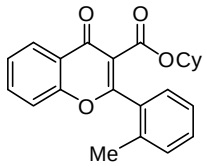
7i ^{1}H NMR (400 MHz, $CDCl_3$)



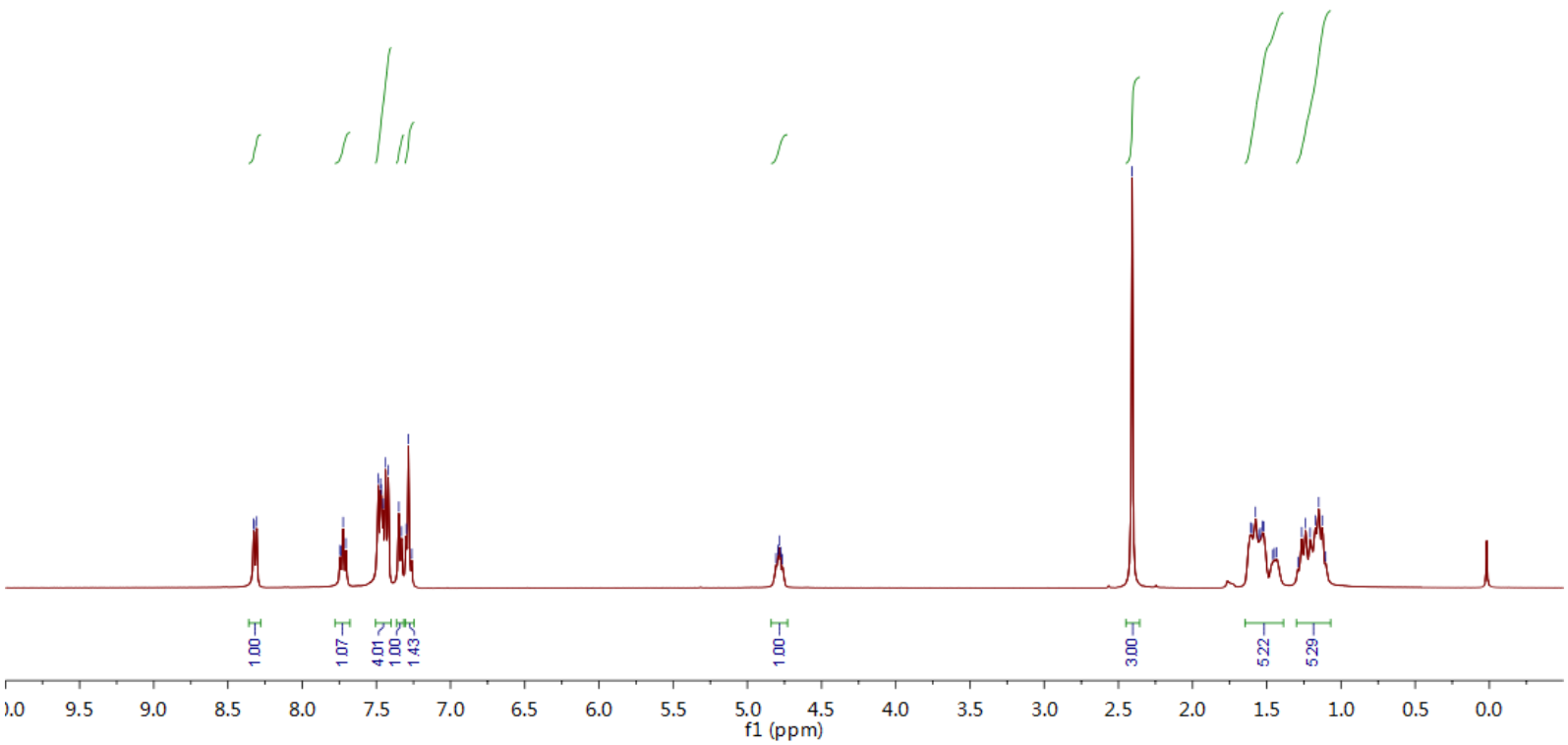


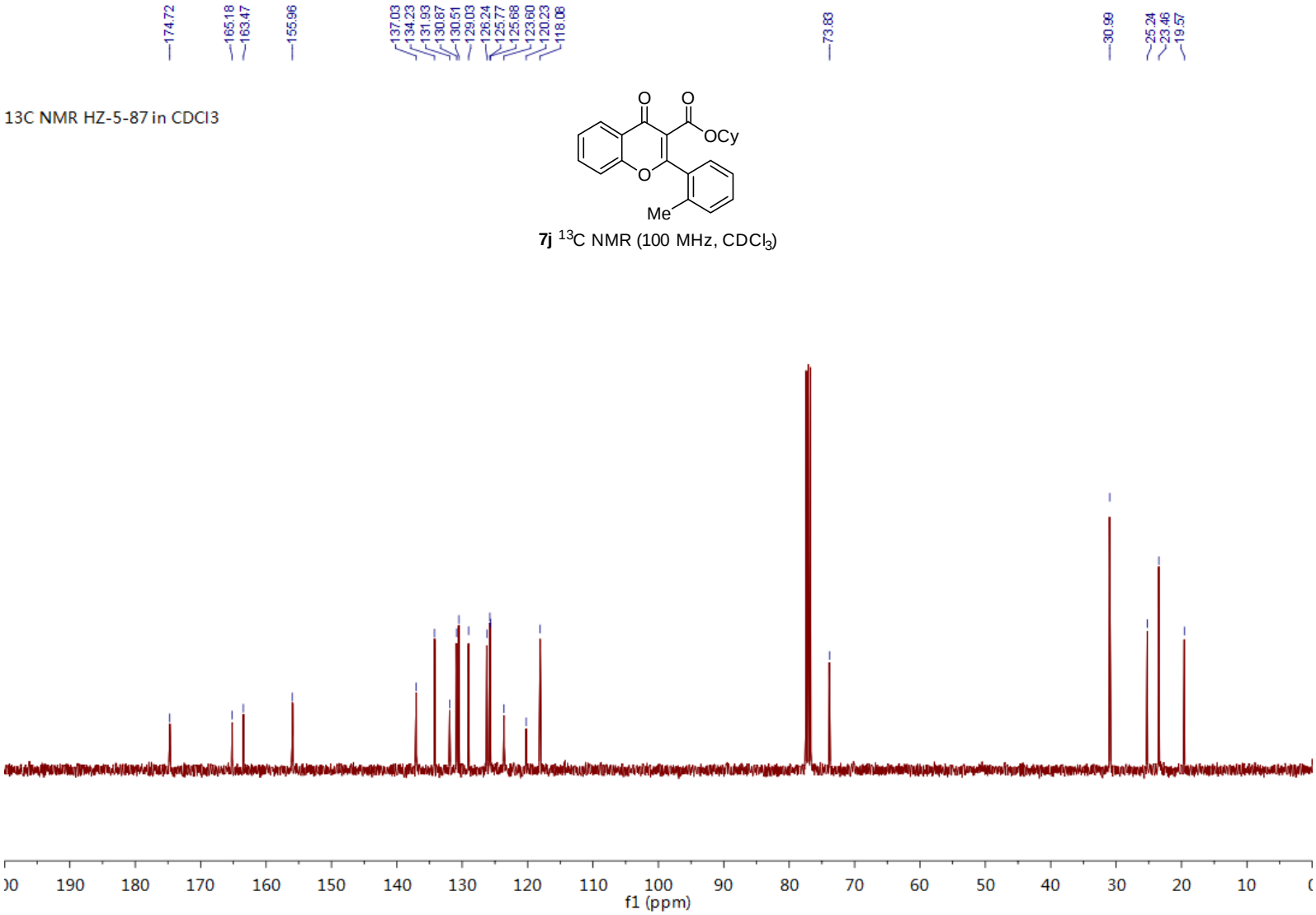
7i ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-87 in CDCl3



7j ^{1}H NMR (400 MHz, $CDCl_3$)





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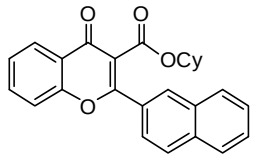
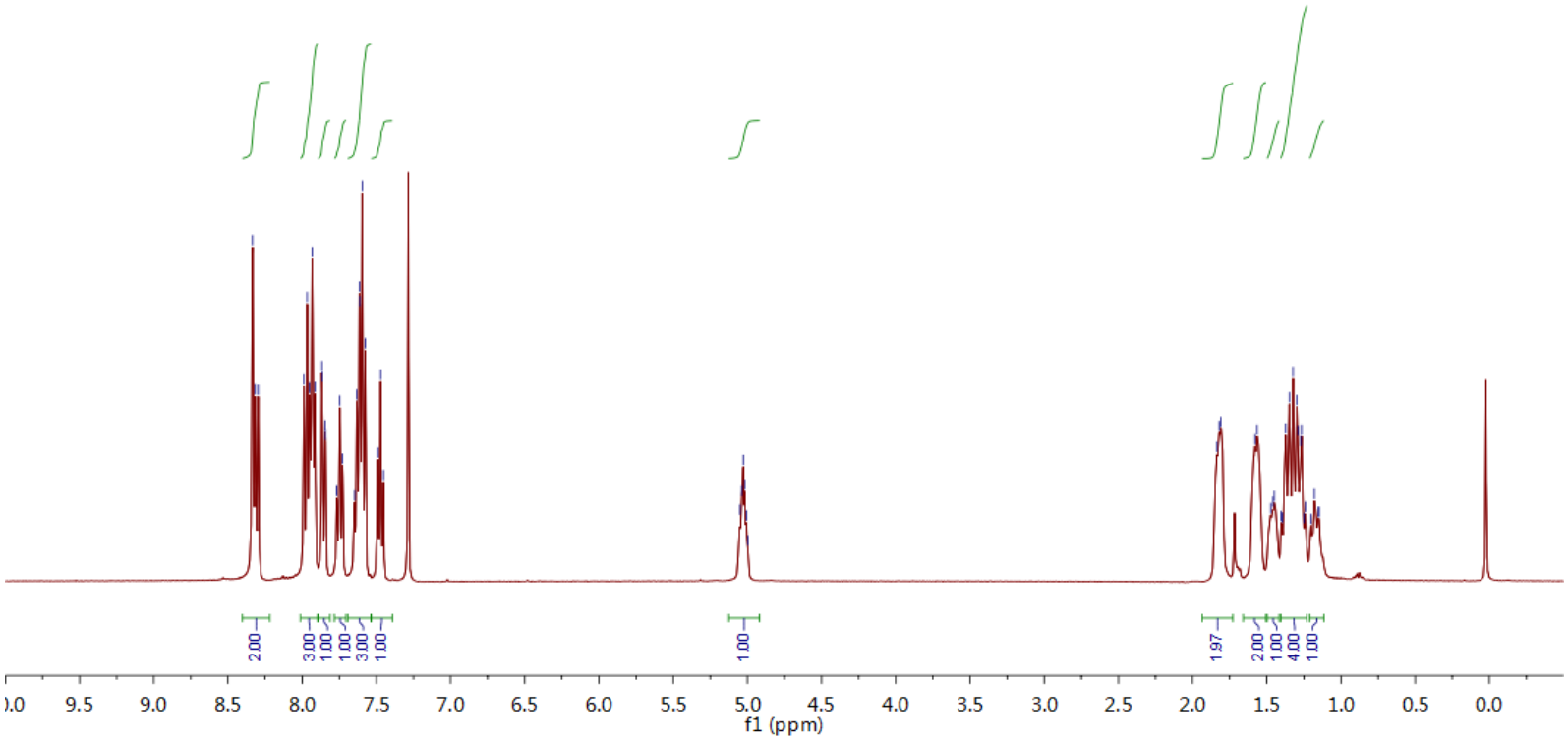
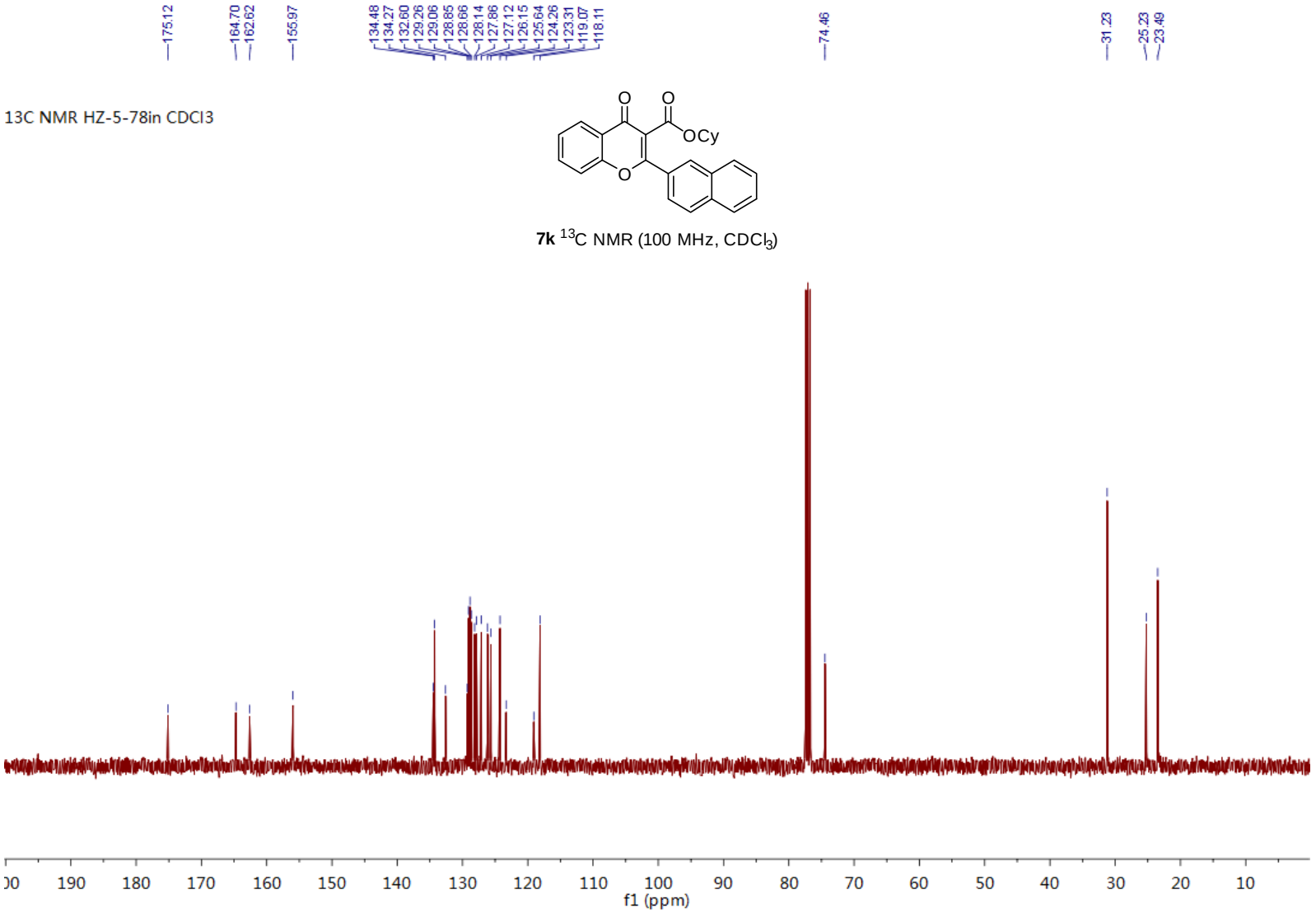
1H NMR HZ-5-78 in CDCl3



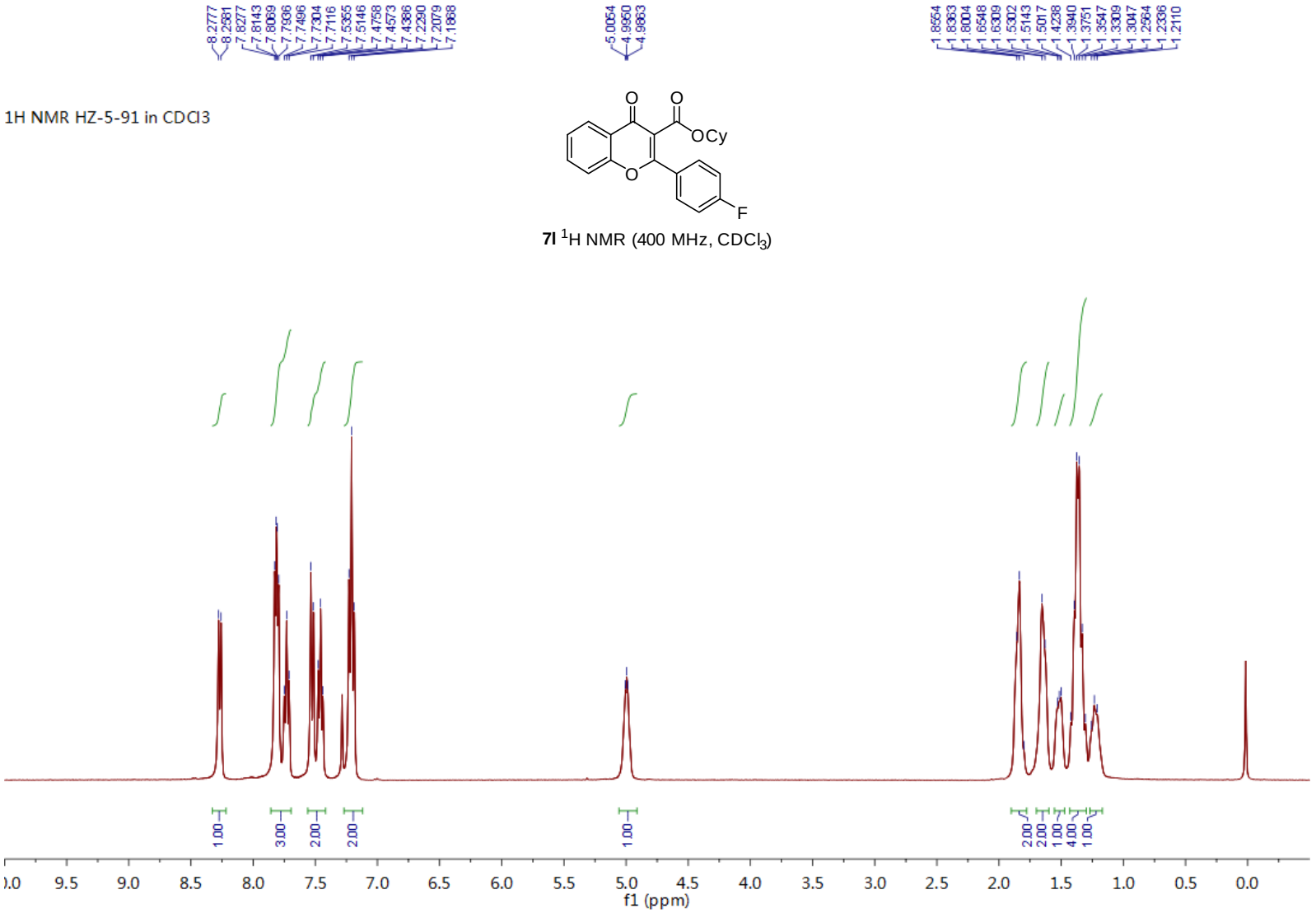
7k ^{1}H NMR (400 MHz, $CDCl_3$)



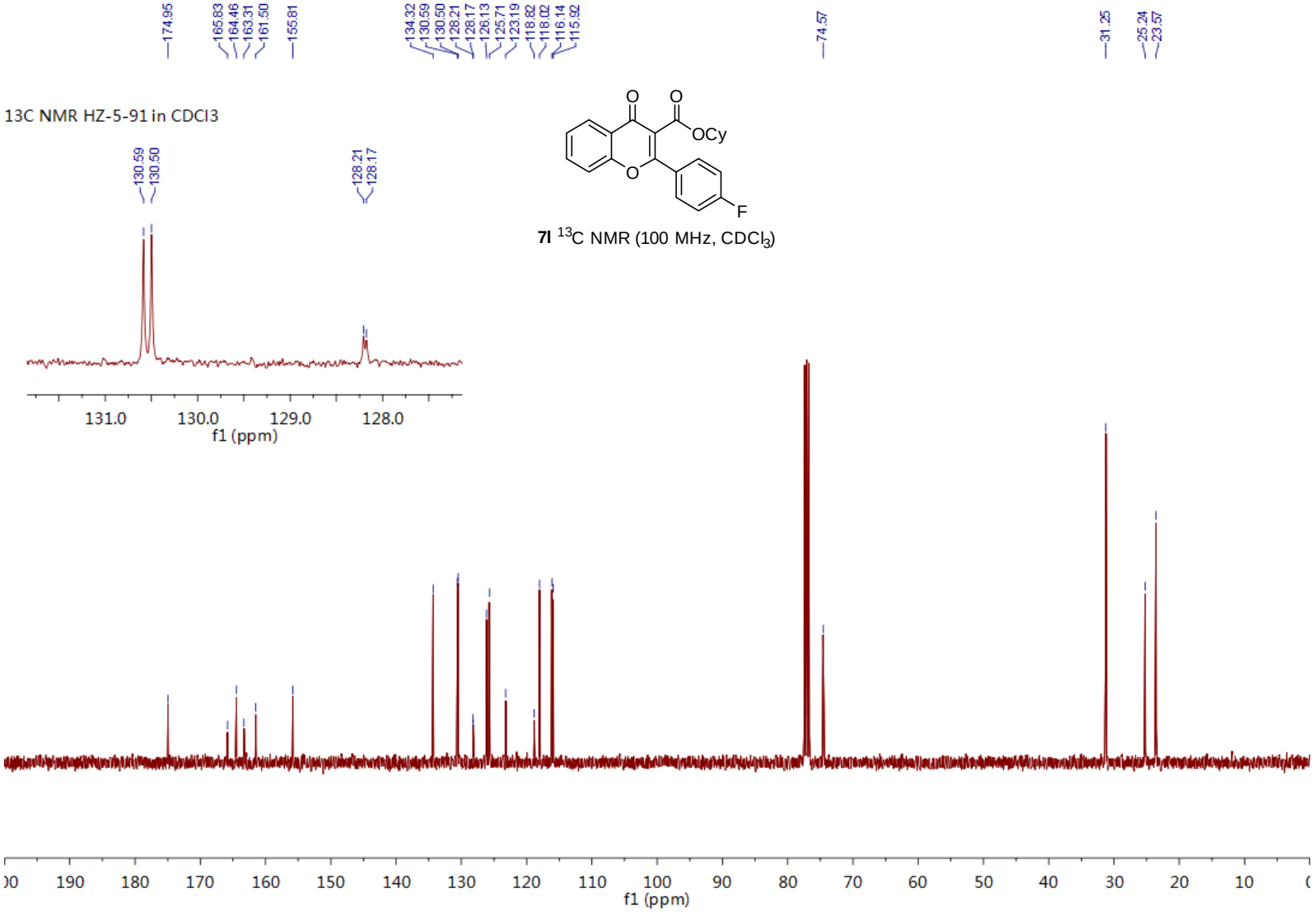


7k ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-91 in CDCl3

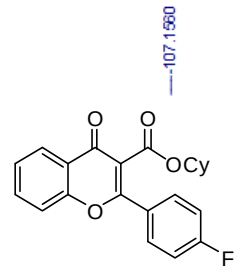


7l ^{1}H NMR (400 MHz, $CDCl_3$)

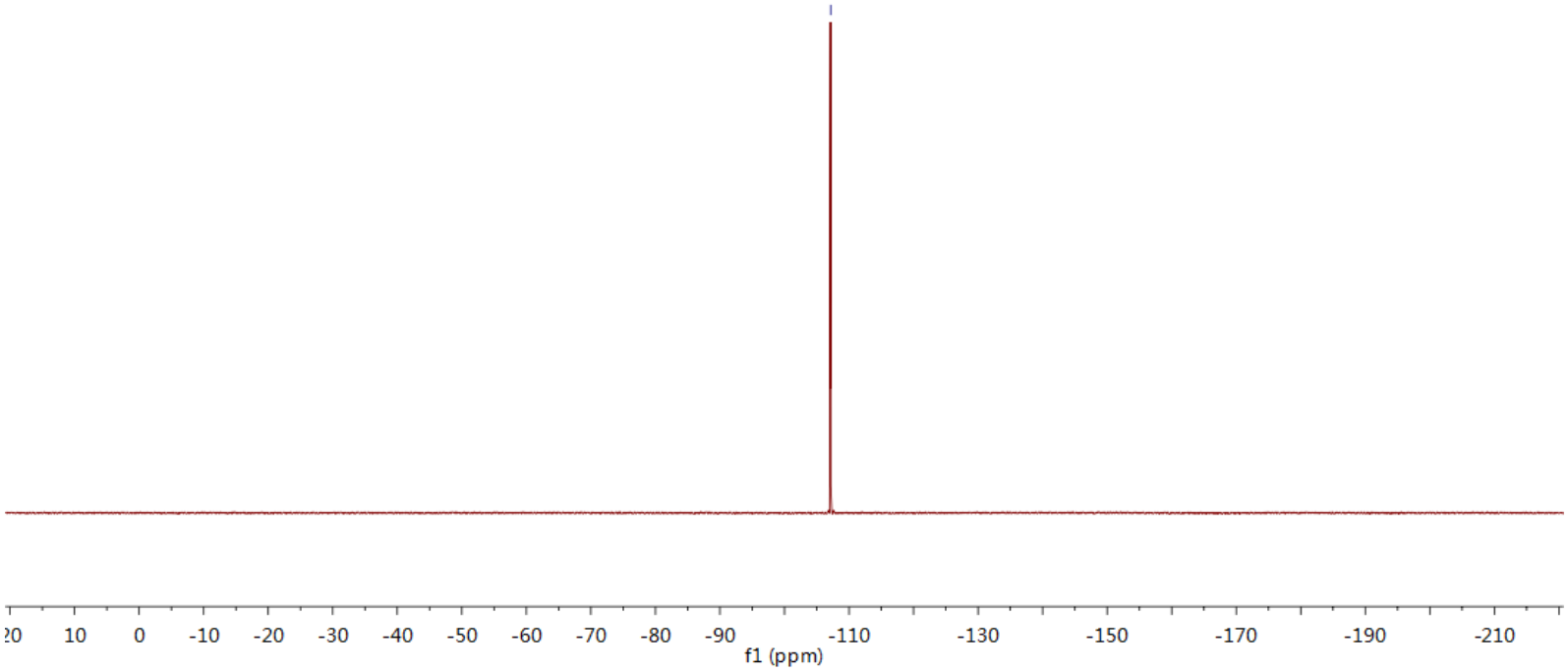


7l ^{13}C NMR (100 MHz, $CDCl_3$)

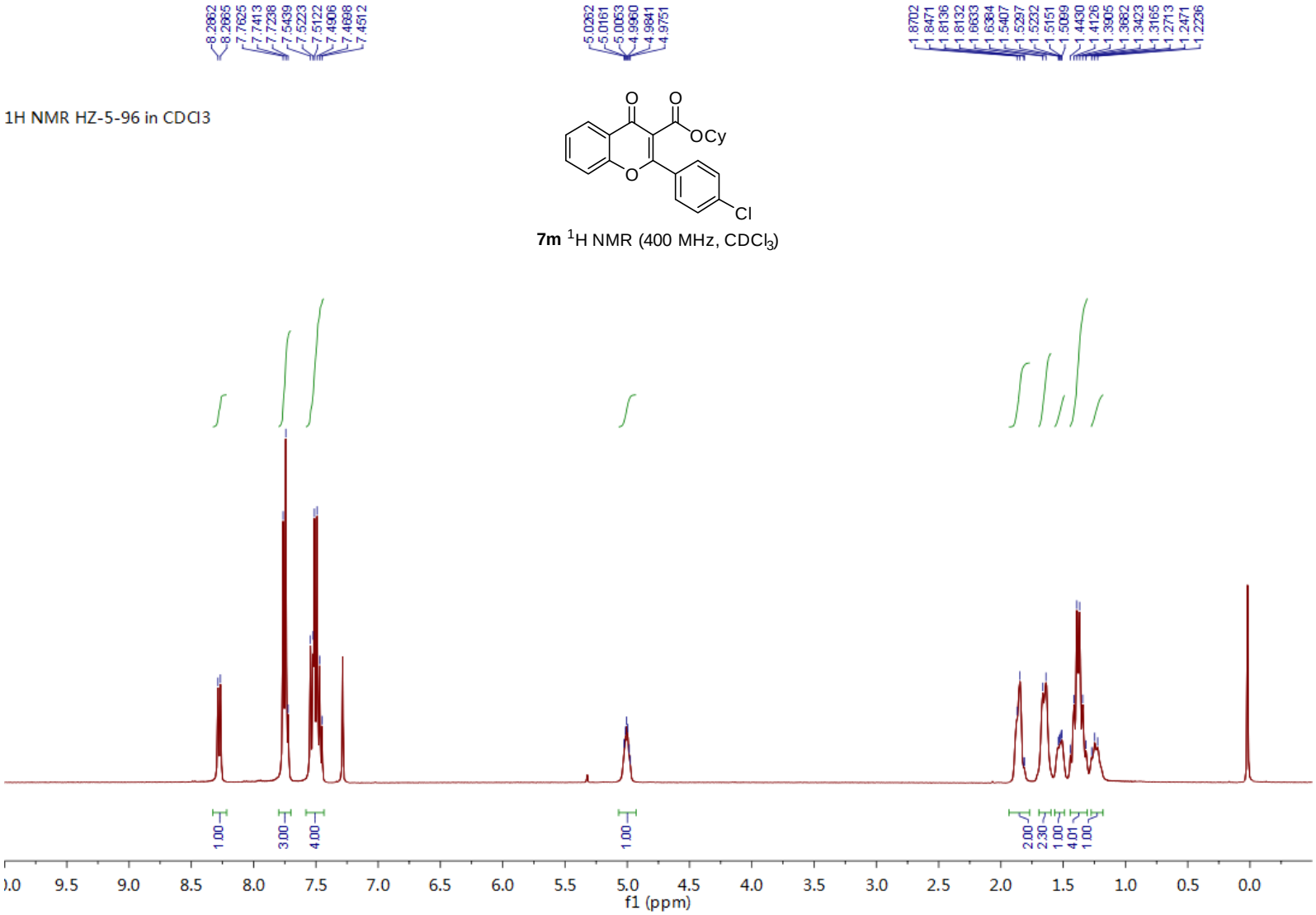
19F NMR HZ-5-91 in CDCl3



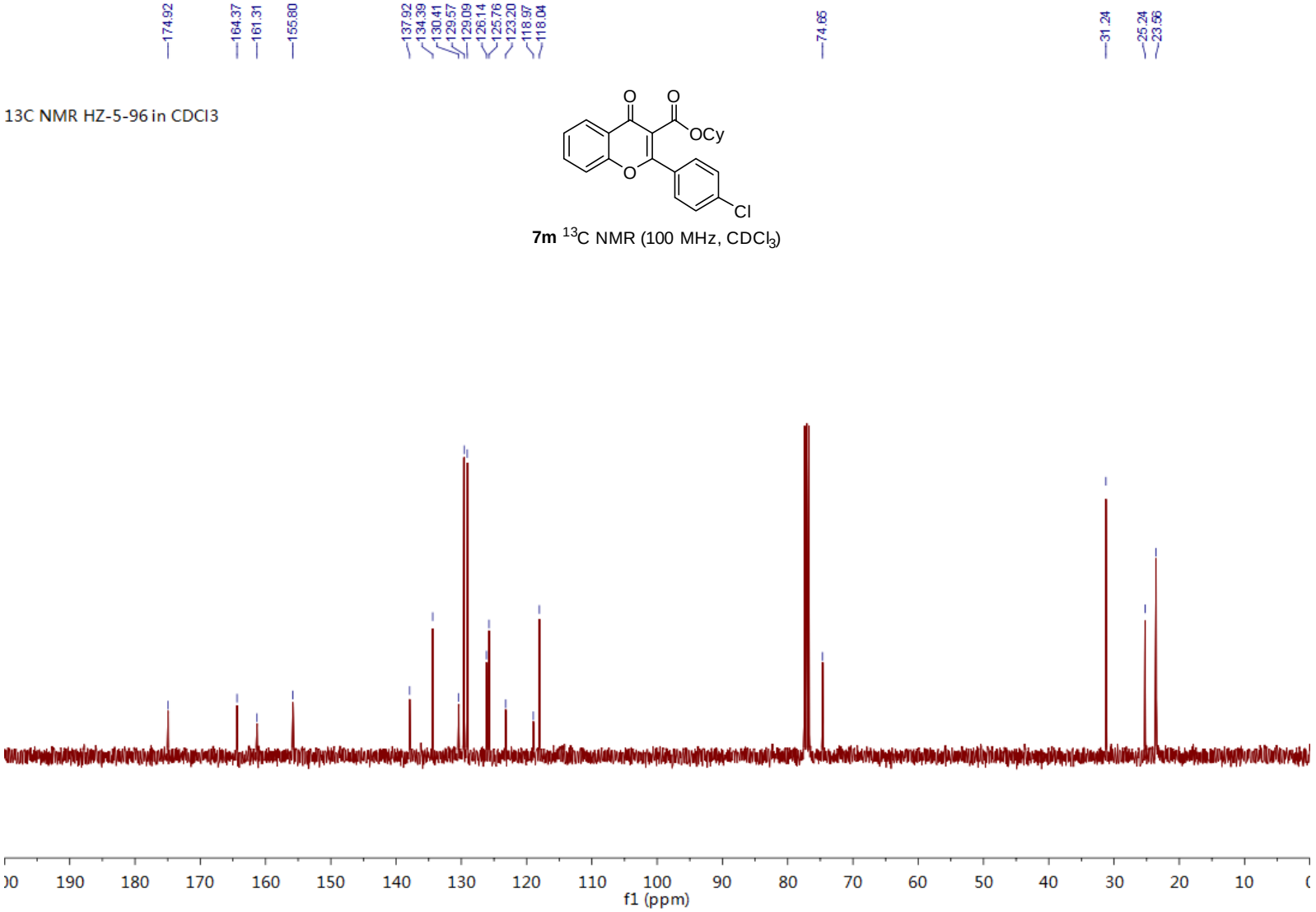
7l ^{19}F NMR (376 MHz, $CDCl_3$)



1H NMR HZ-5-96 in CDCl3

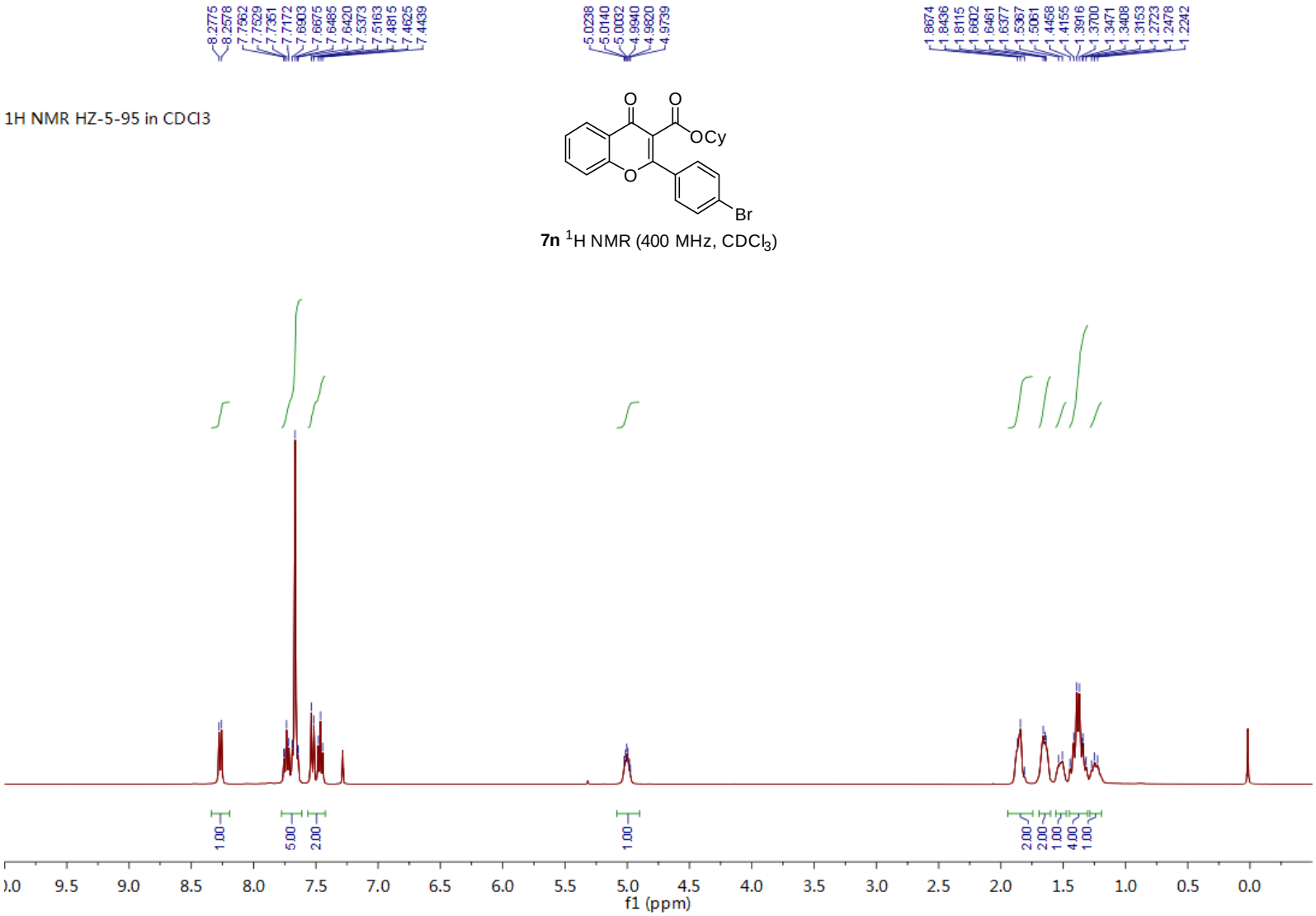


7m ^{1}H NMR (400 MHz, $CDCl_3$)

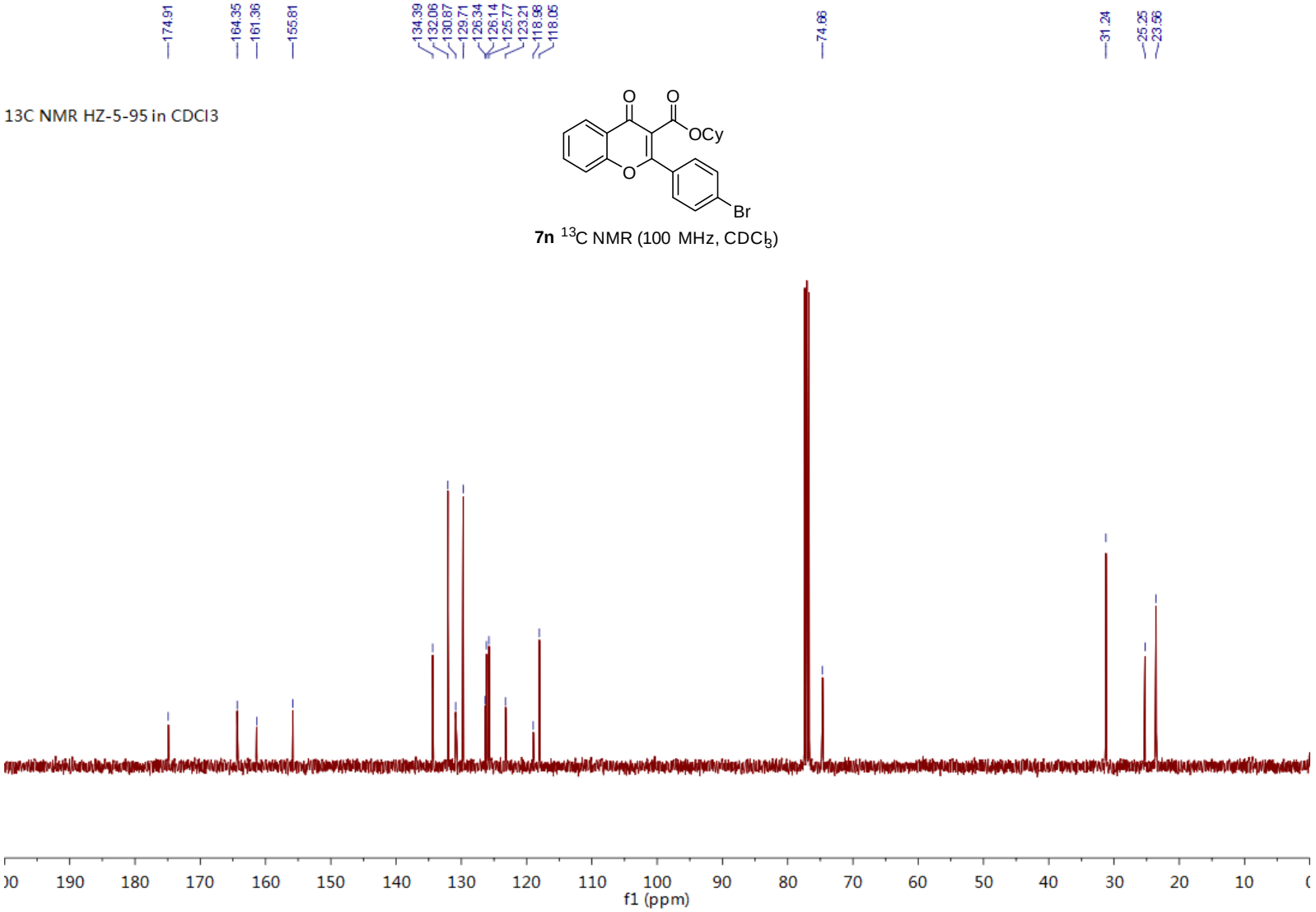


7m ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-95 in CDCl3

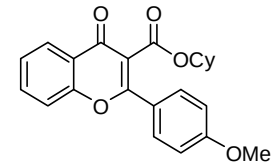


7n ^{1}H NMR (400 MHz, $CDCl_3$)

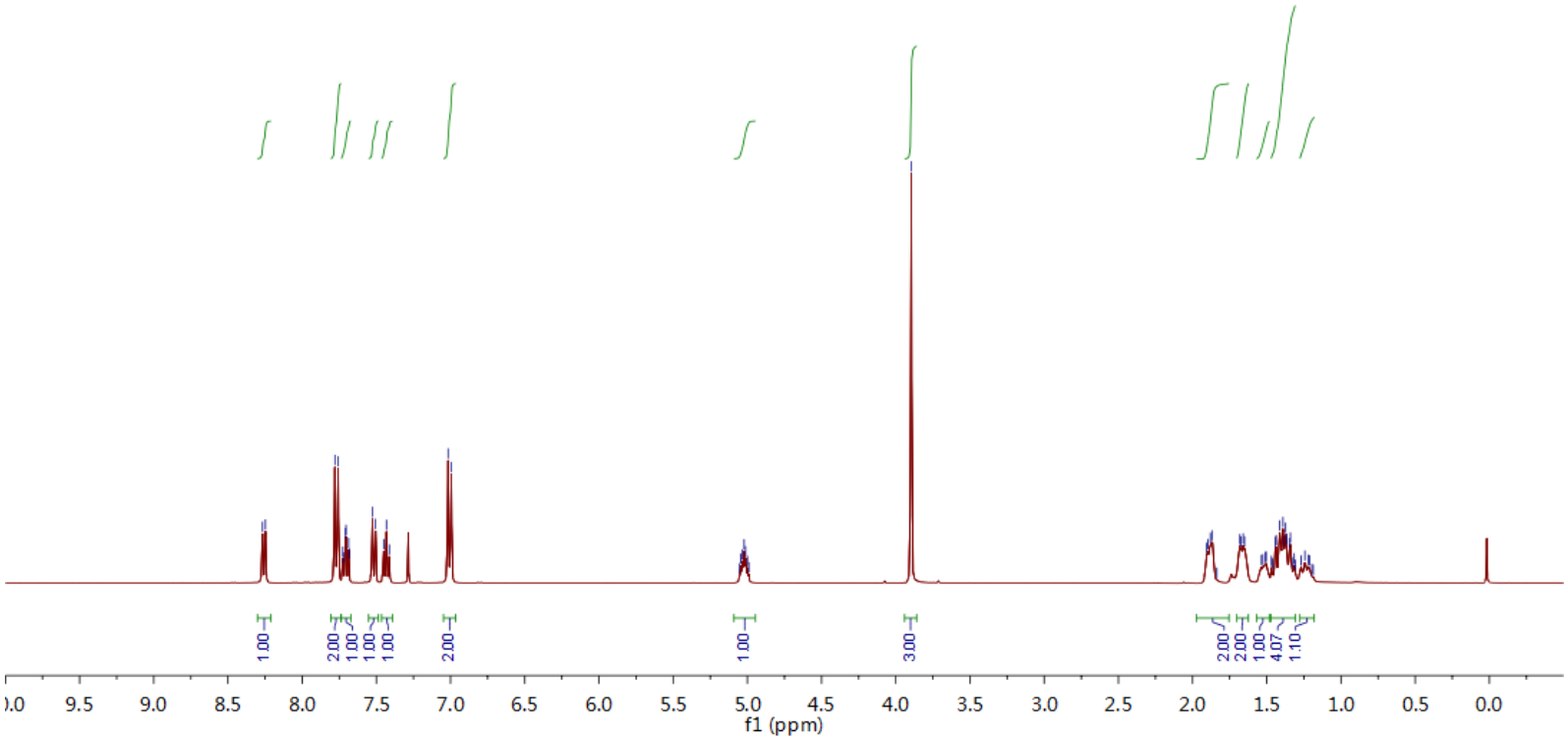


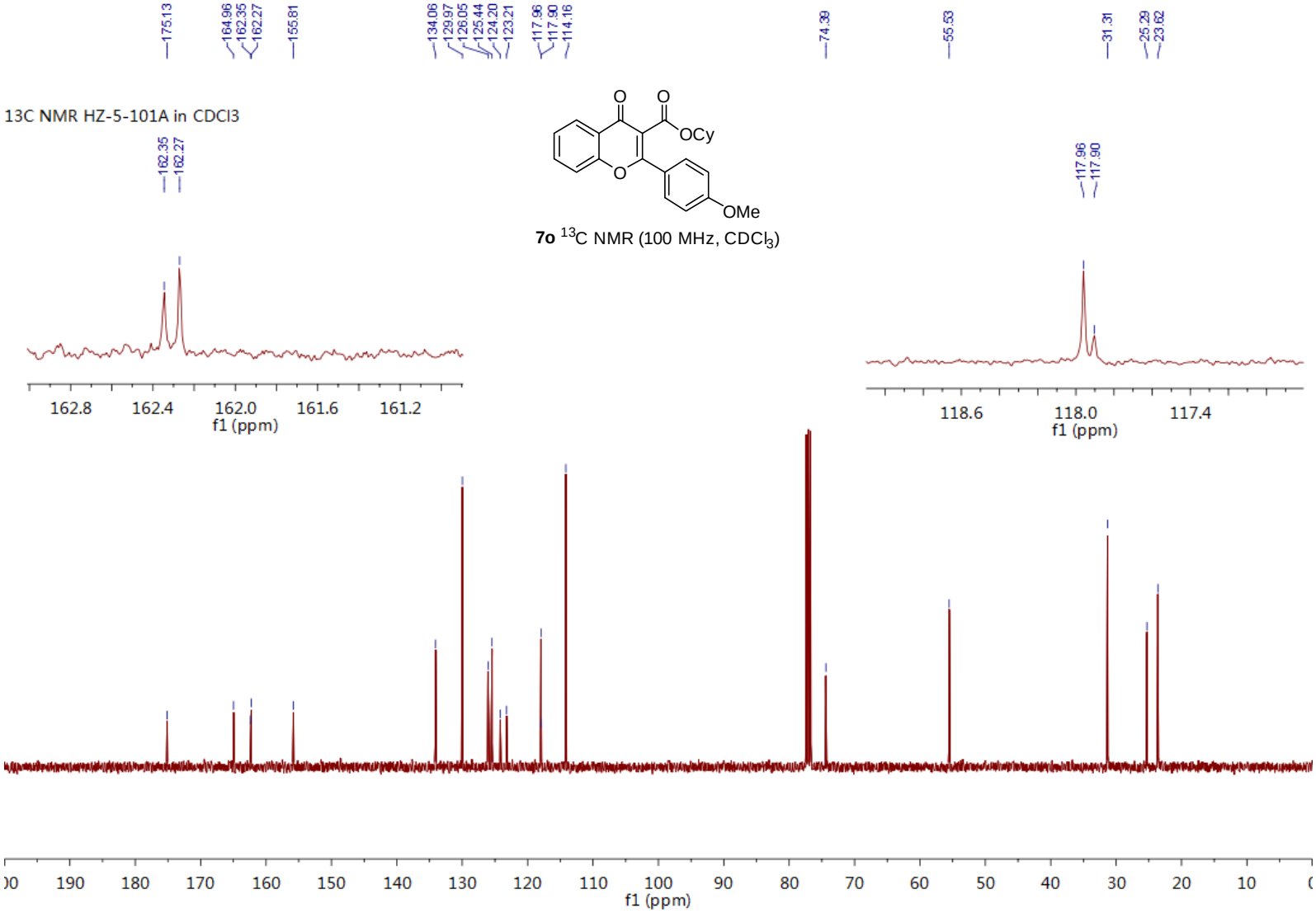
7n ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-101A in CDCl3



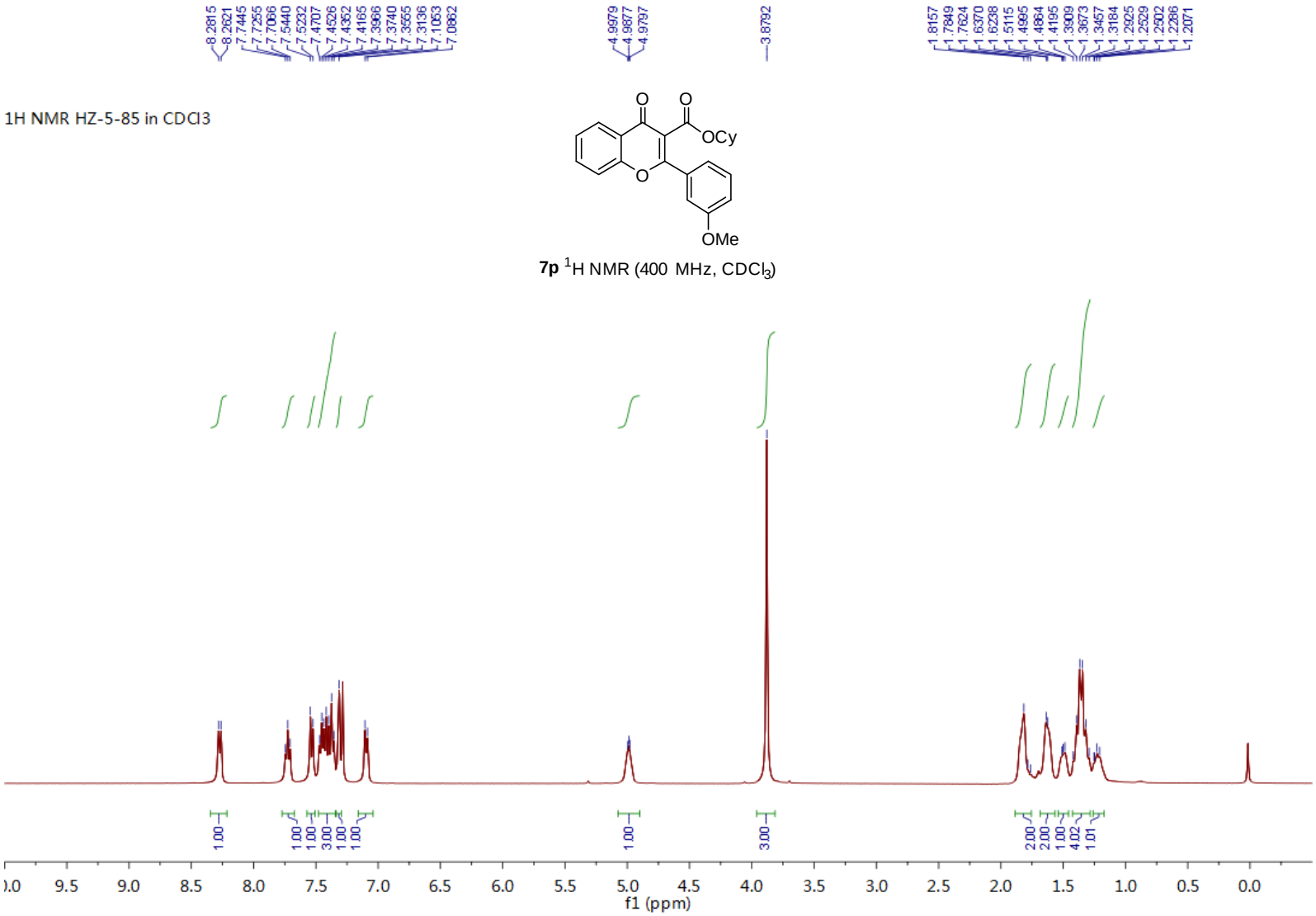
7o ^{1}H NMR (400 MHz, $CDCl_3$)



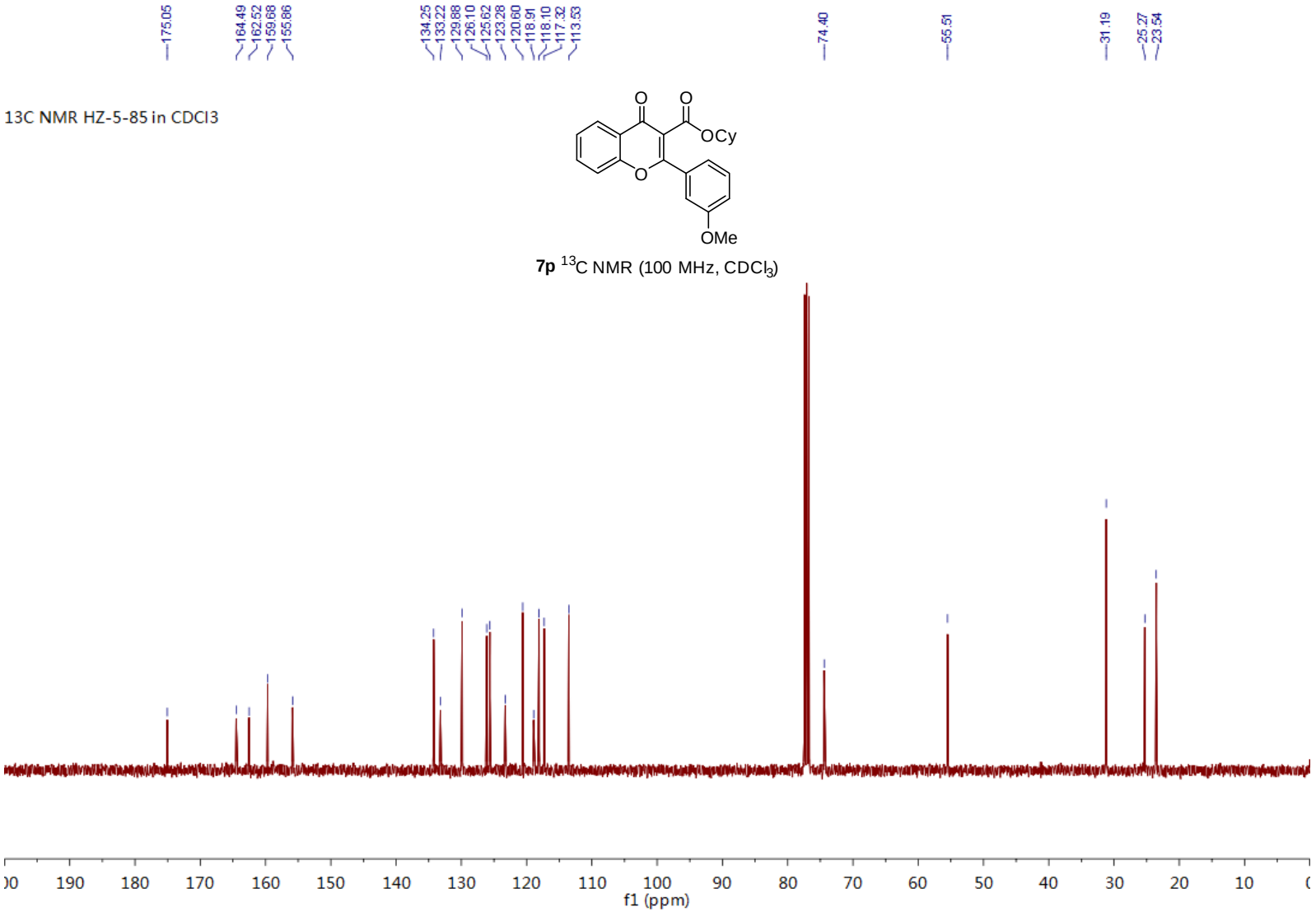


7o ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-85 in CDCl3

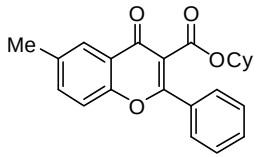


7p ^{1}H NMR (400 MHz, $CDCl_3$)

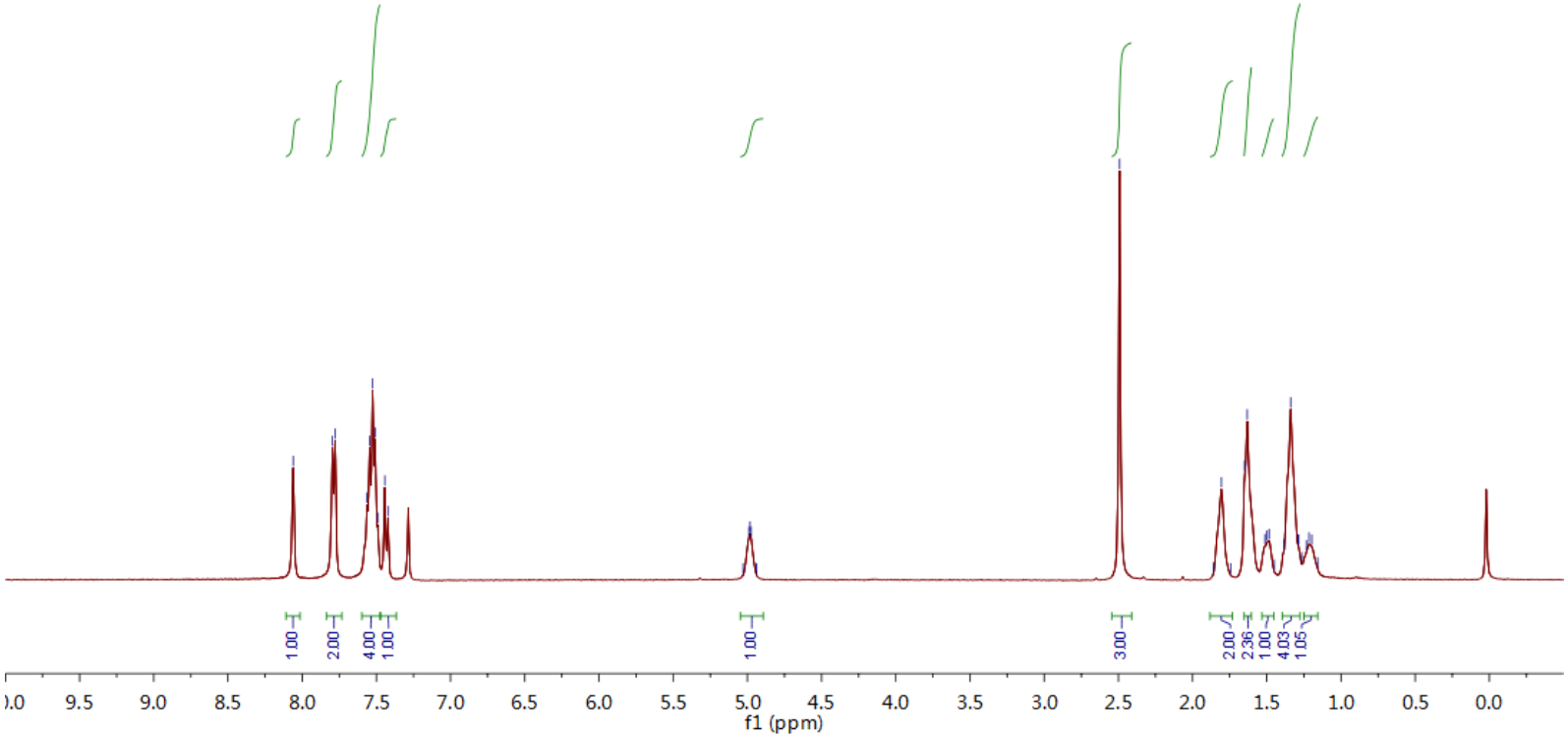


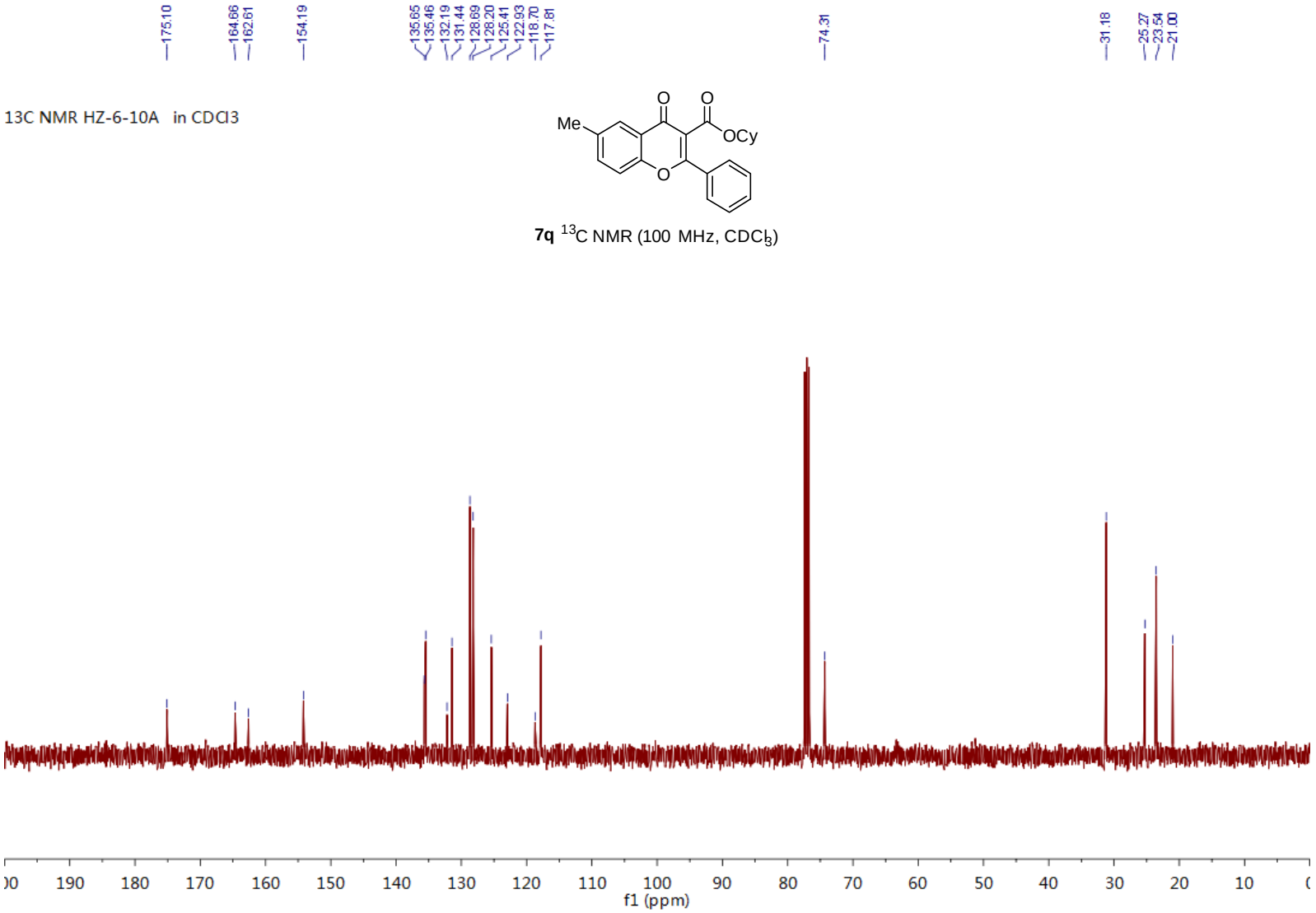
7p ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-10A in CDCl3

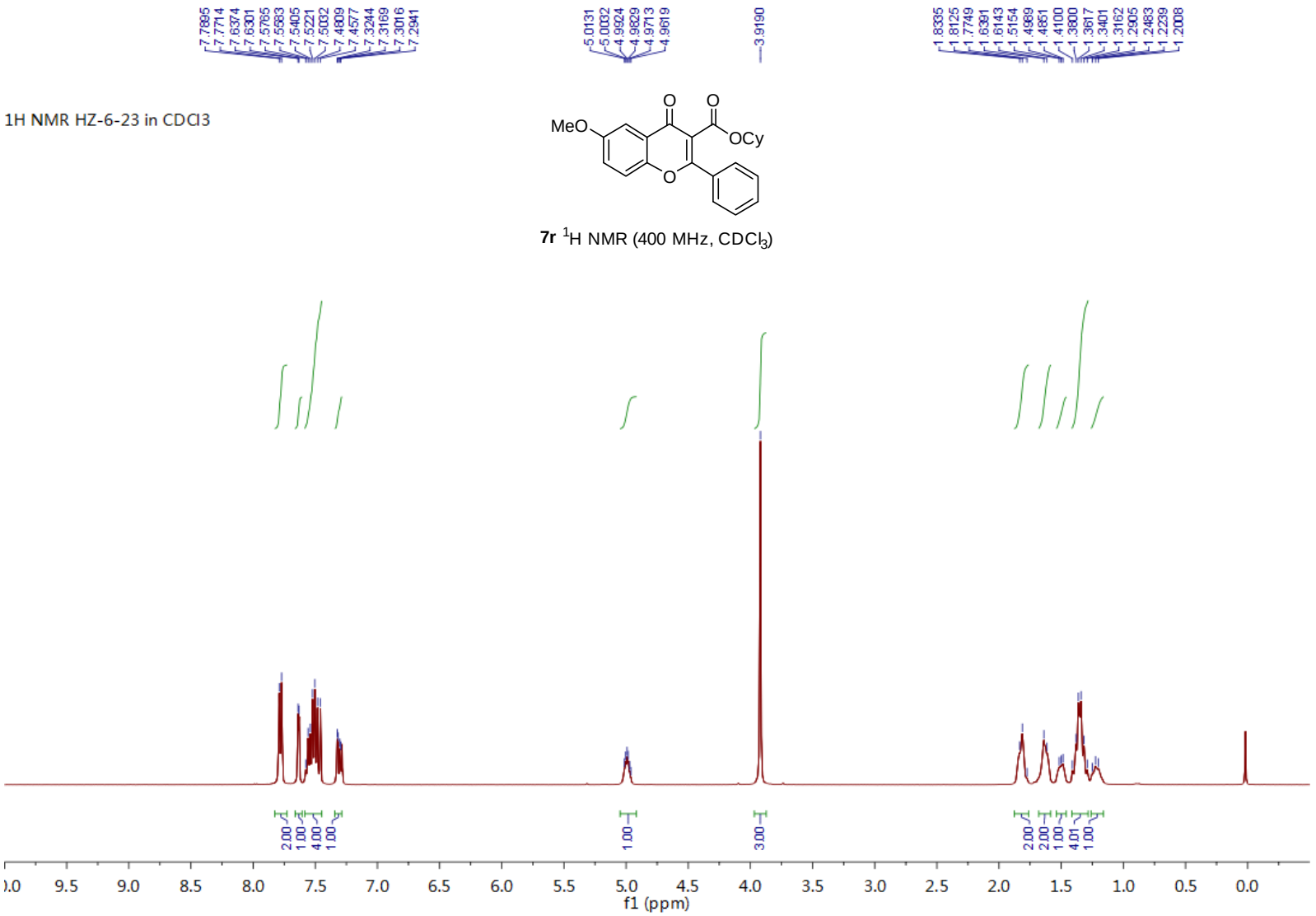


7q ^{1}H NMR (400 MHz, $CDCl_3$)

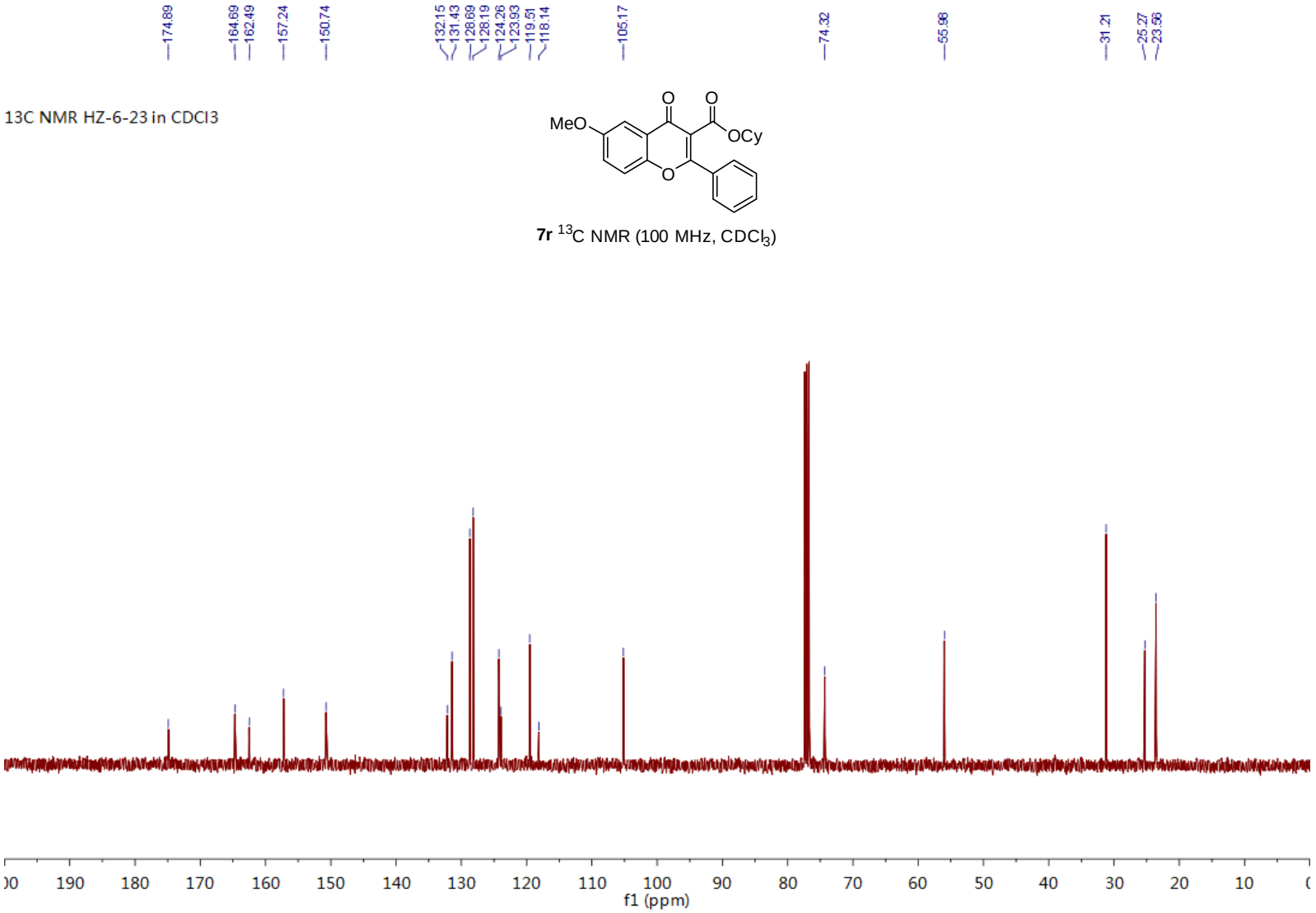




7q ^{13}C NMR (100 MHz, $CDCl_3$)

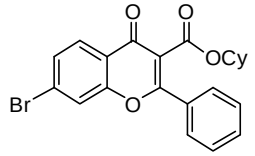


7r ^{1}H NMR (400 MHz, $CDCl_3$)

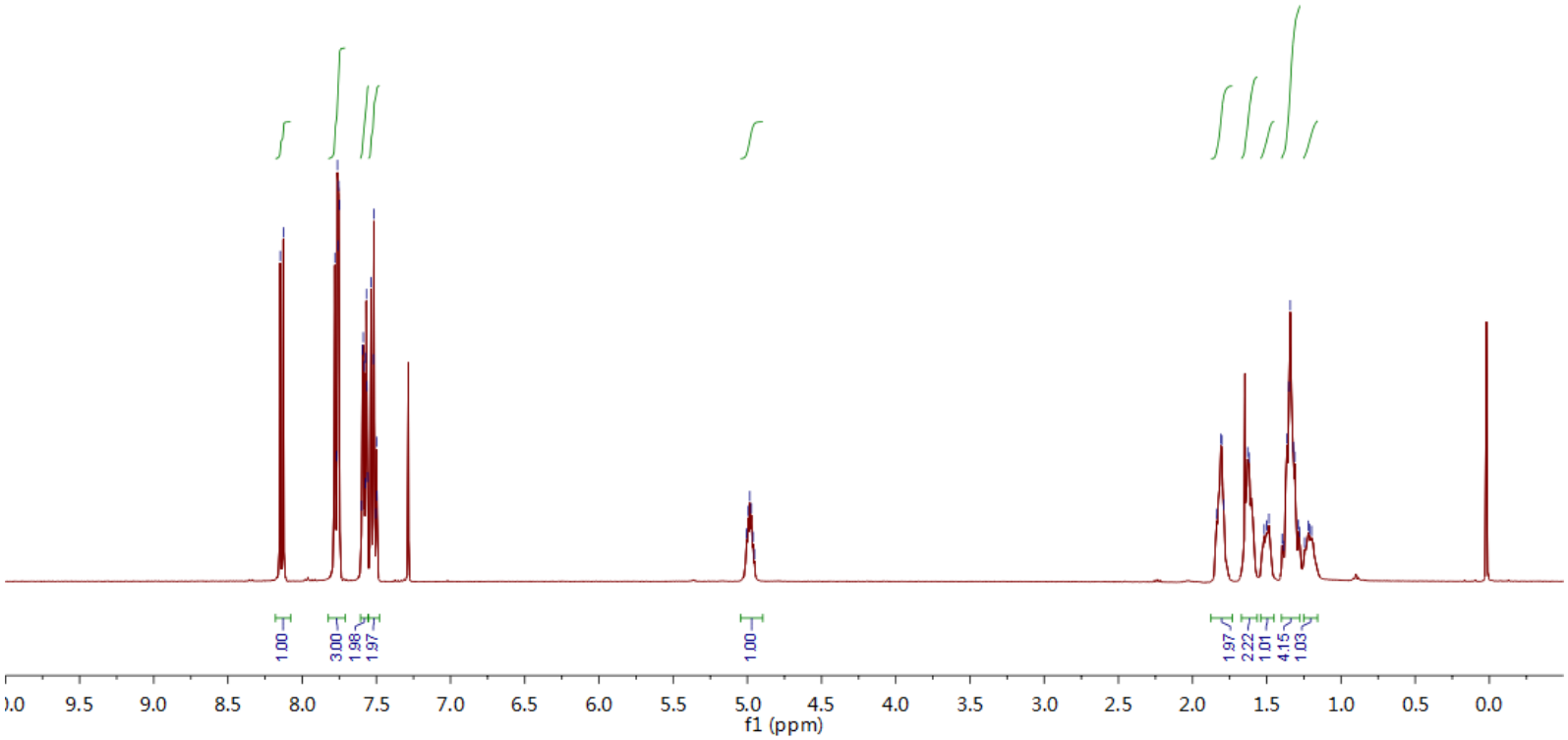


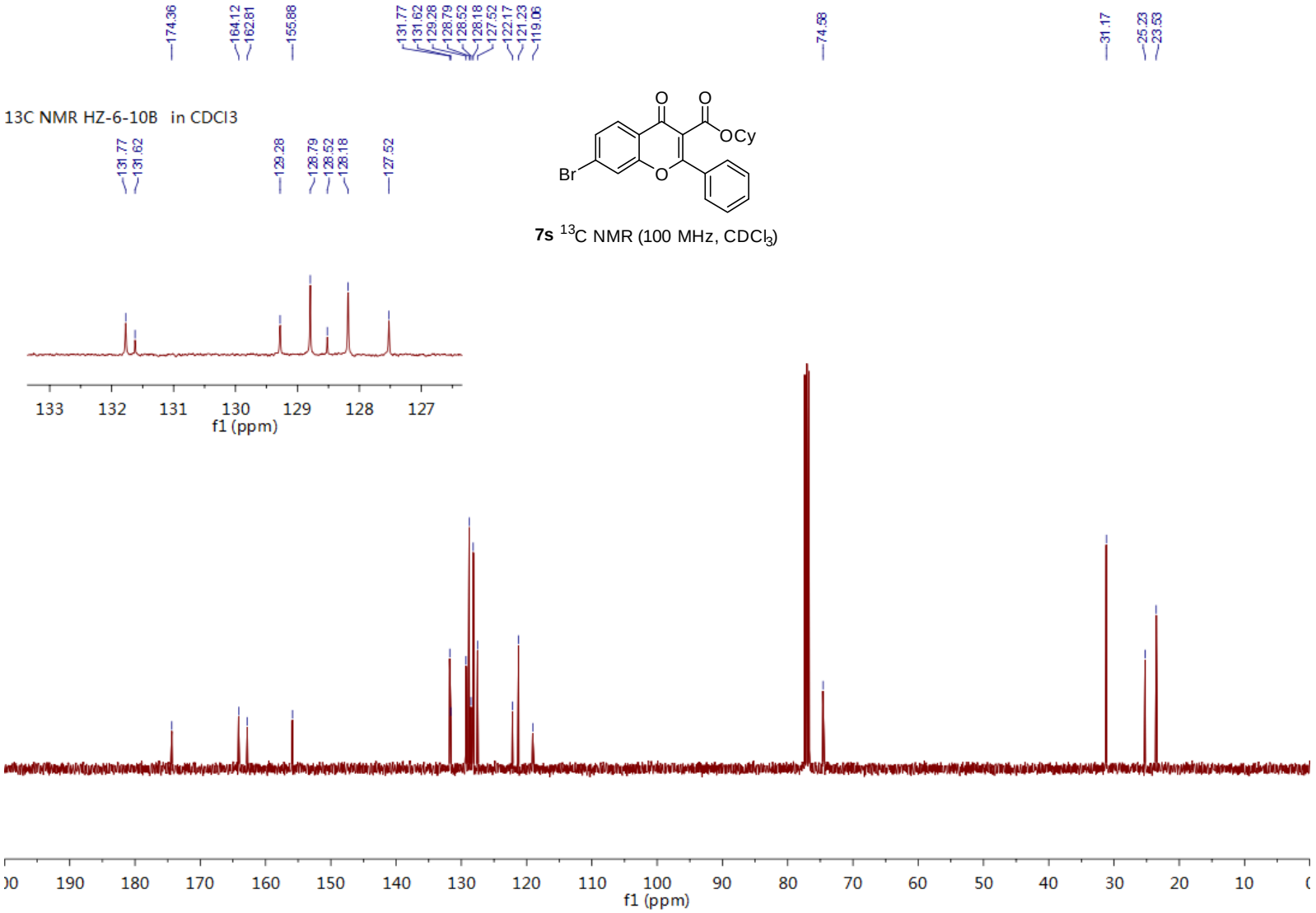
7r ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-10B in CDCl3



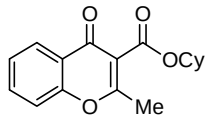
7s ^{1}H NMR (400 MHz, $CDCl_3$)



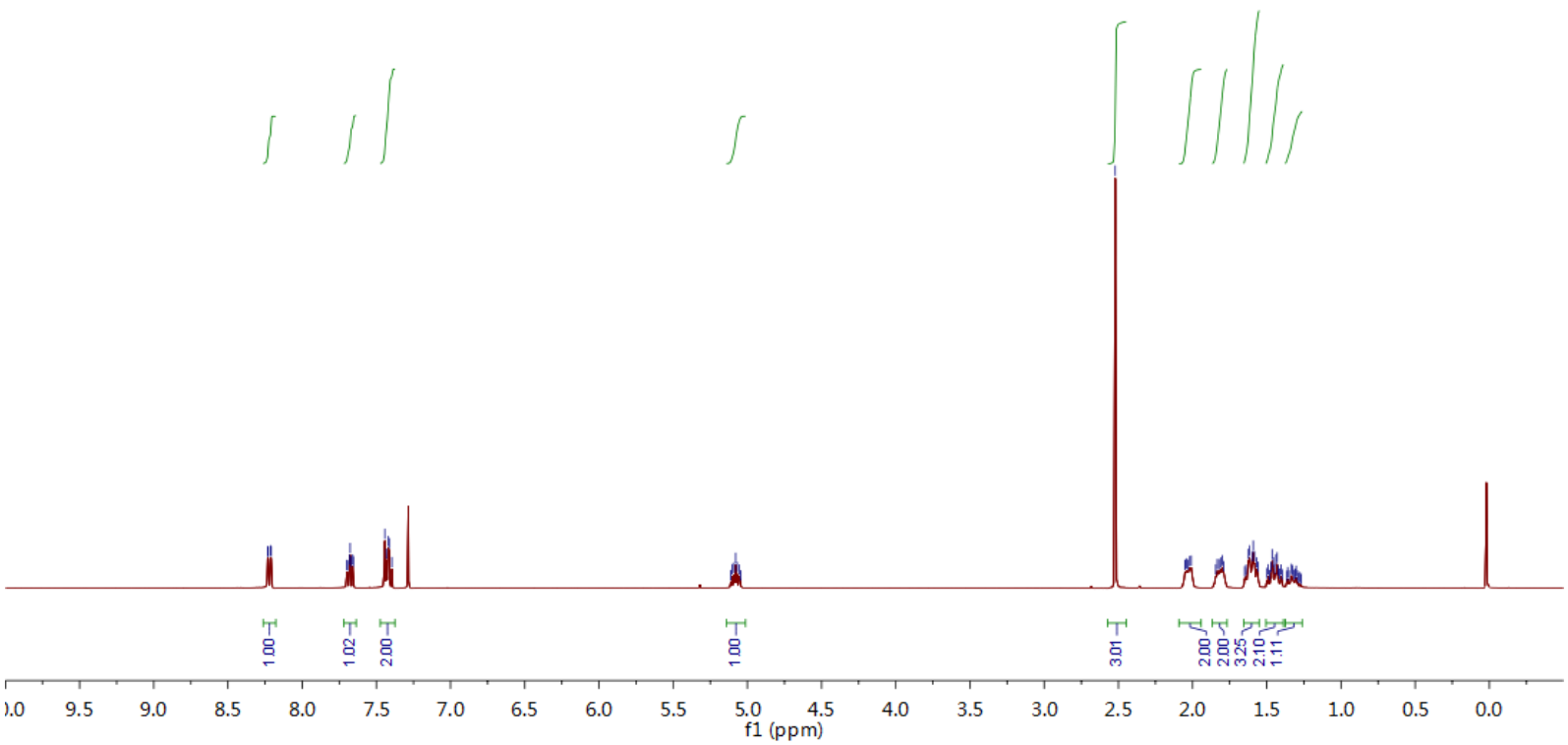


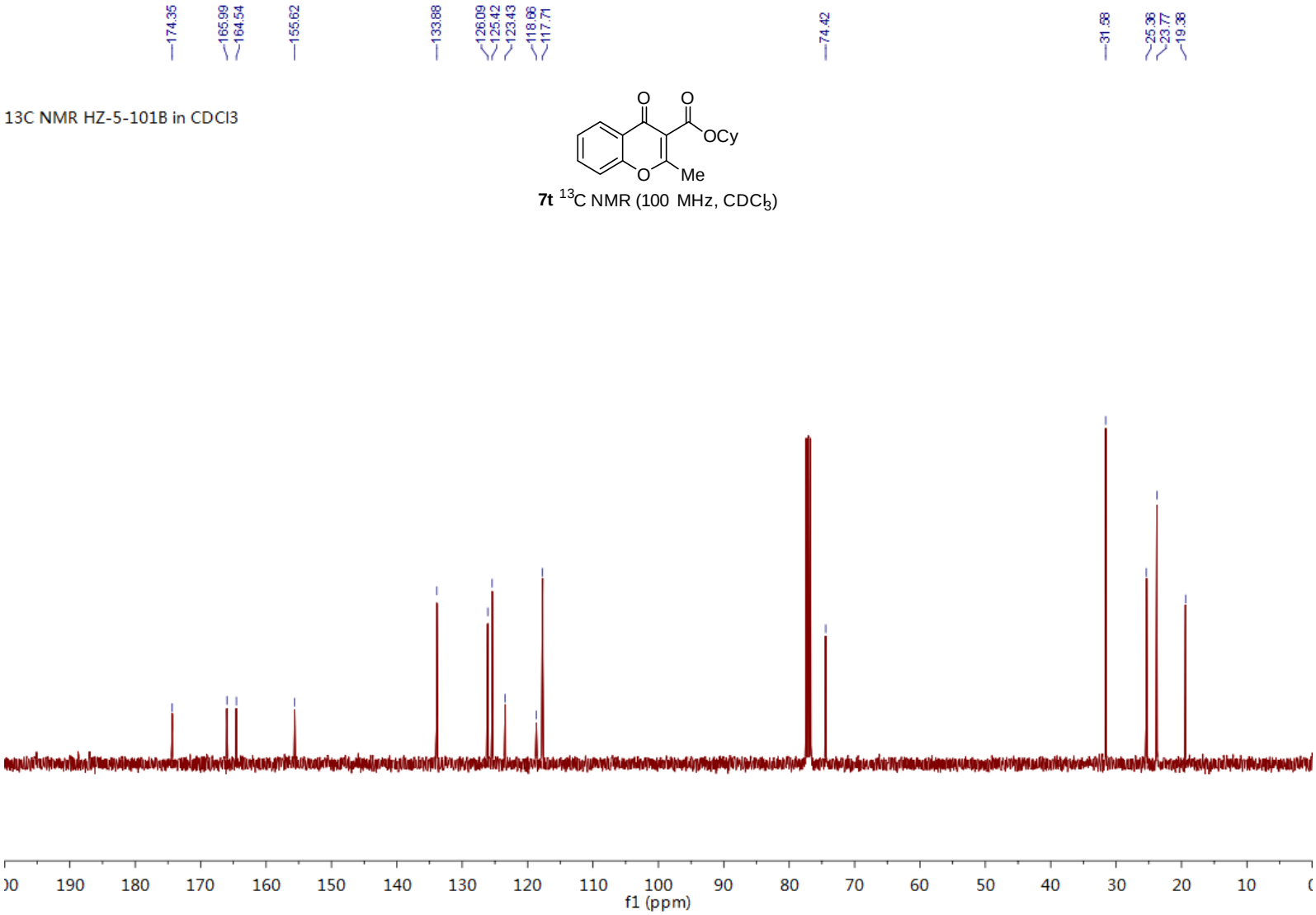
7s ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-101B in CDCl3



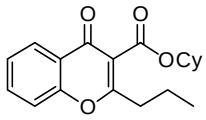
7t ^{1}H NMR (400 MHz, $CDCl_3$)



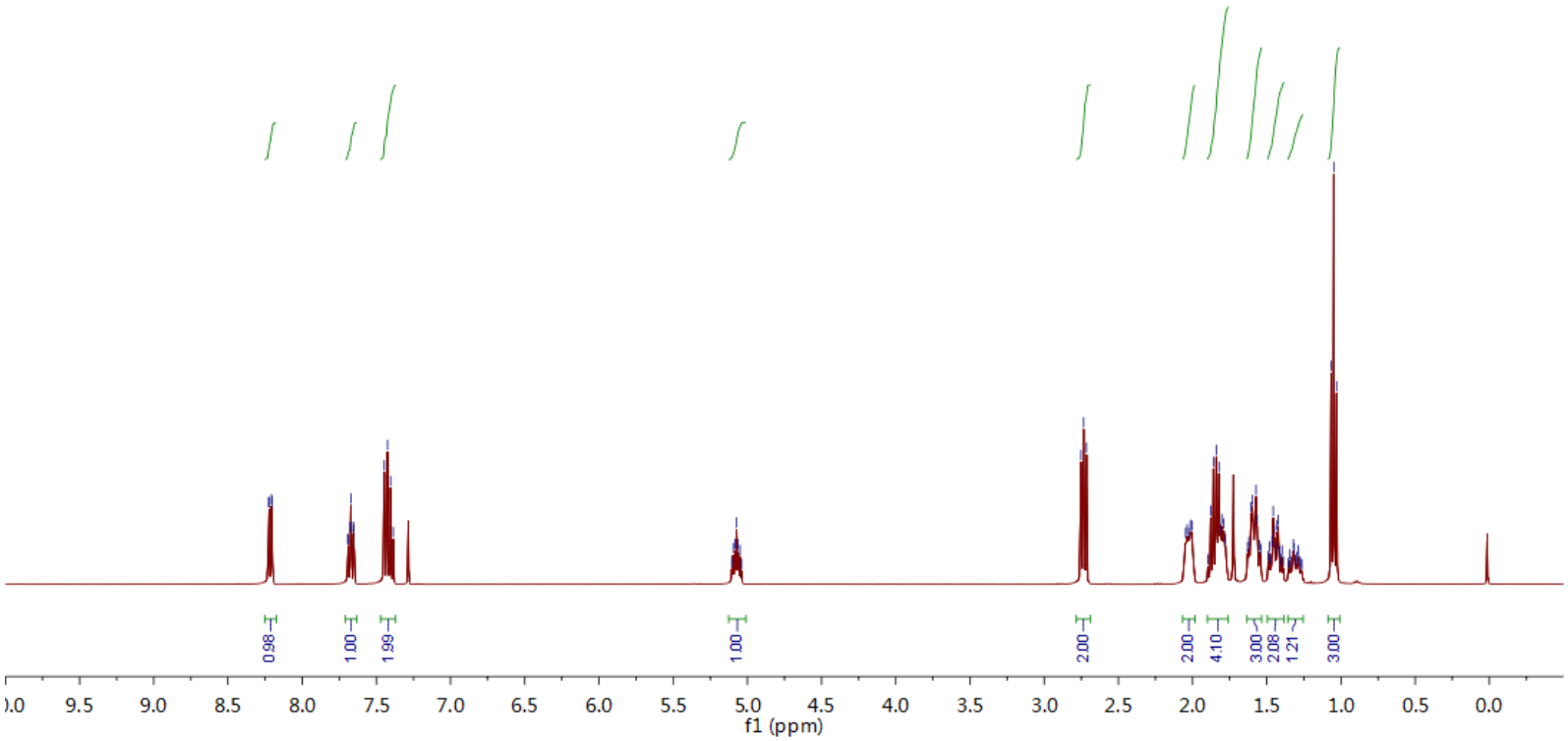


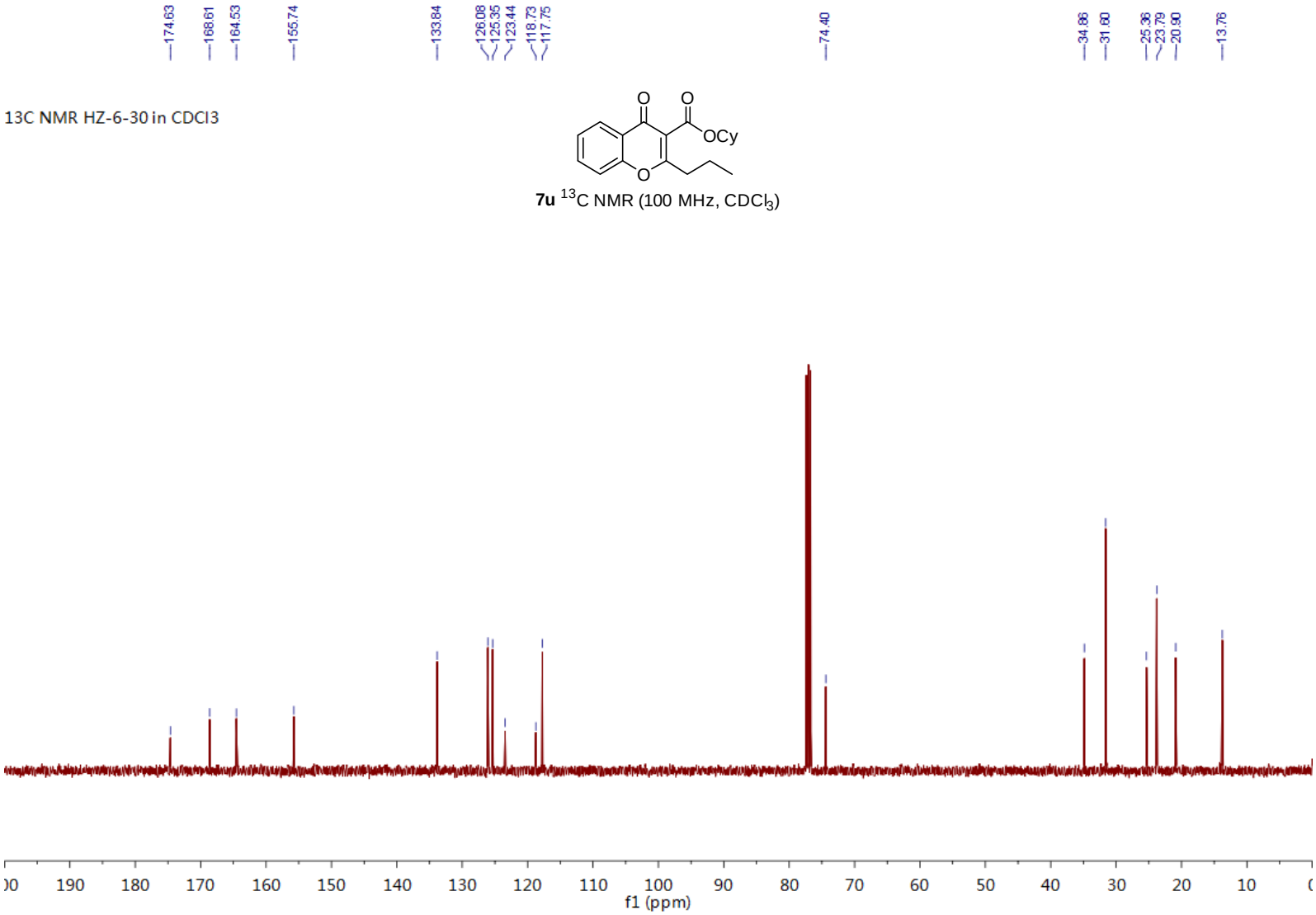
7t ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-30 in CDCl3



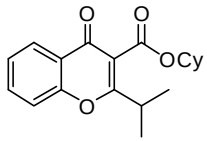
7u ^{1}H NMR (400 MHz, $CDCl_3$)



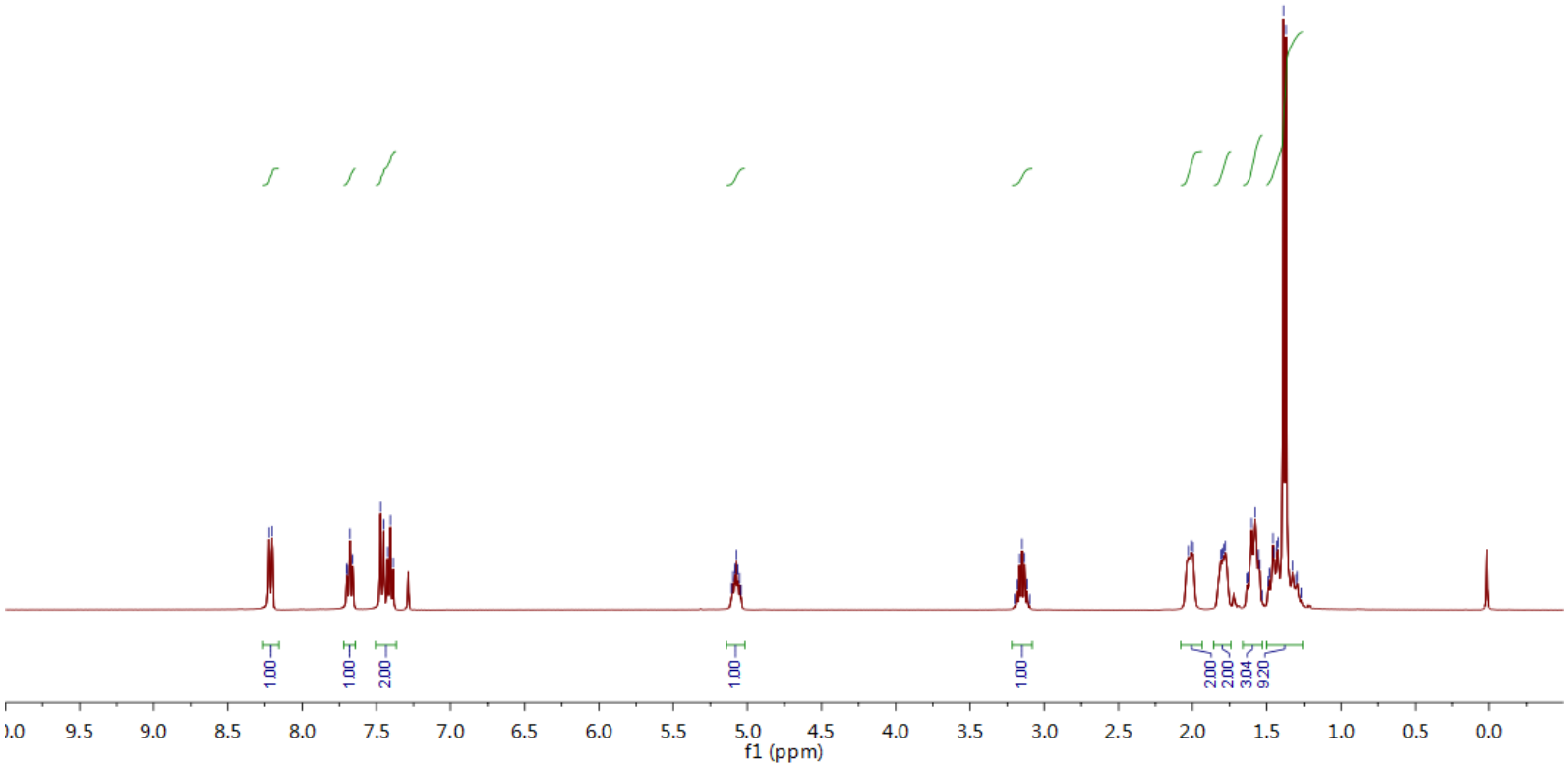


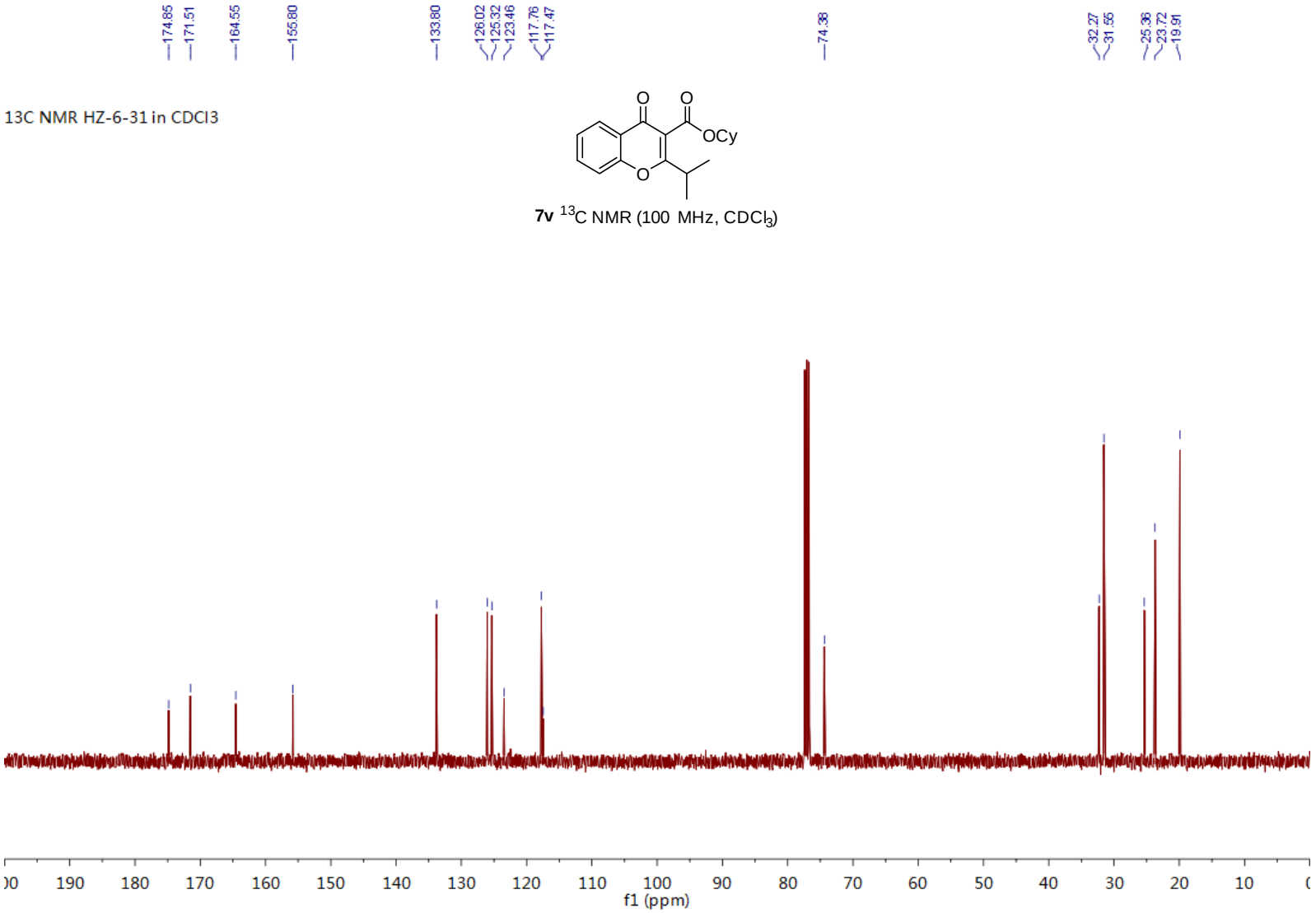
7u ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-31 in CDCl3



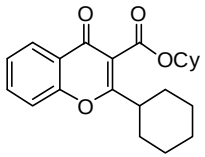
7v ^{1}H NMR (400 MHz, $CDCl_3$)



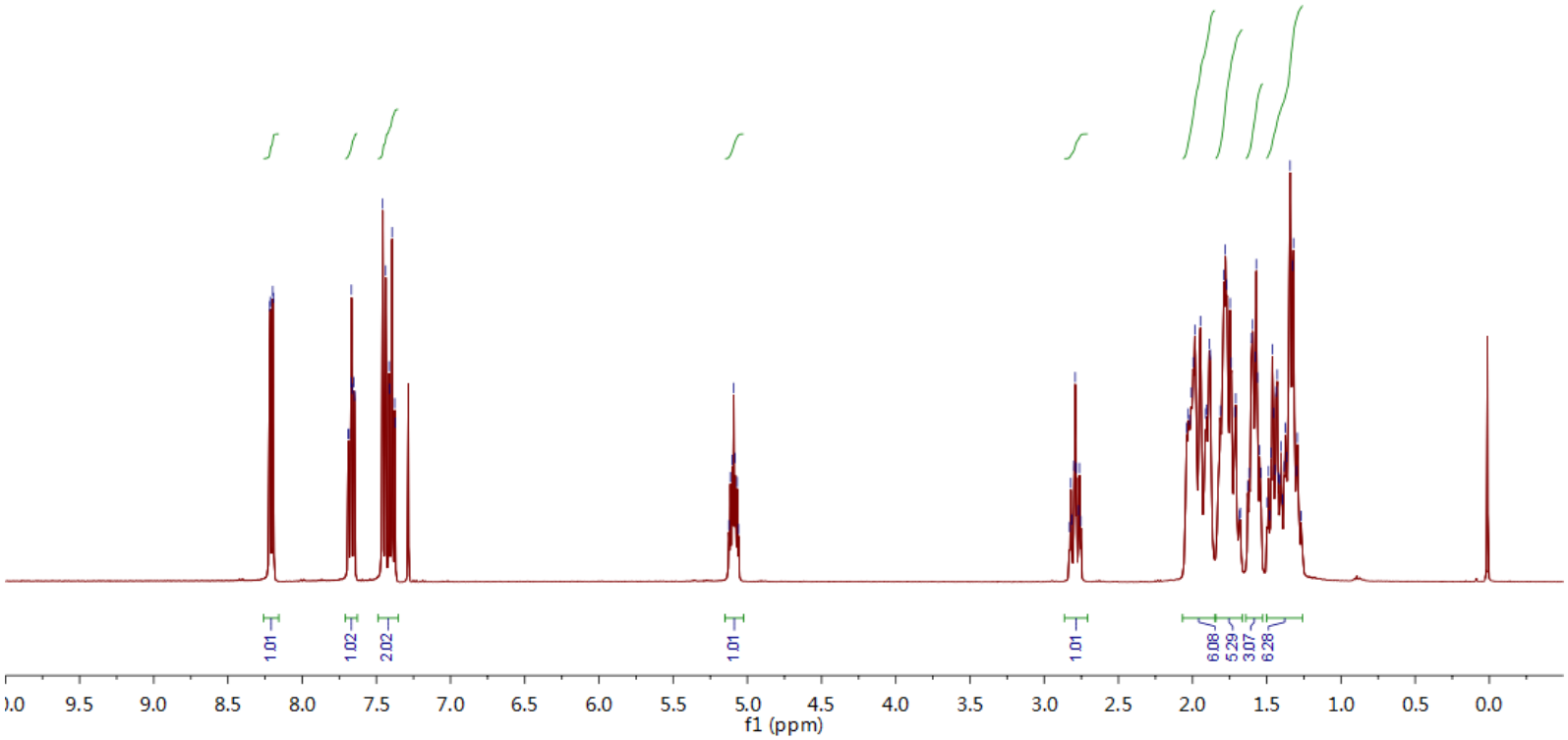


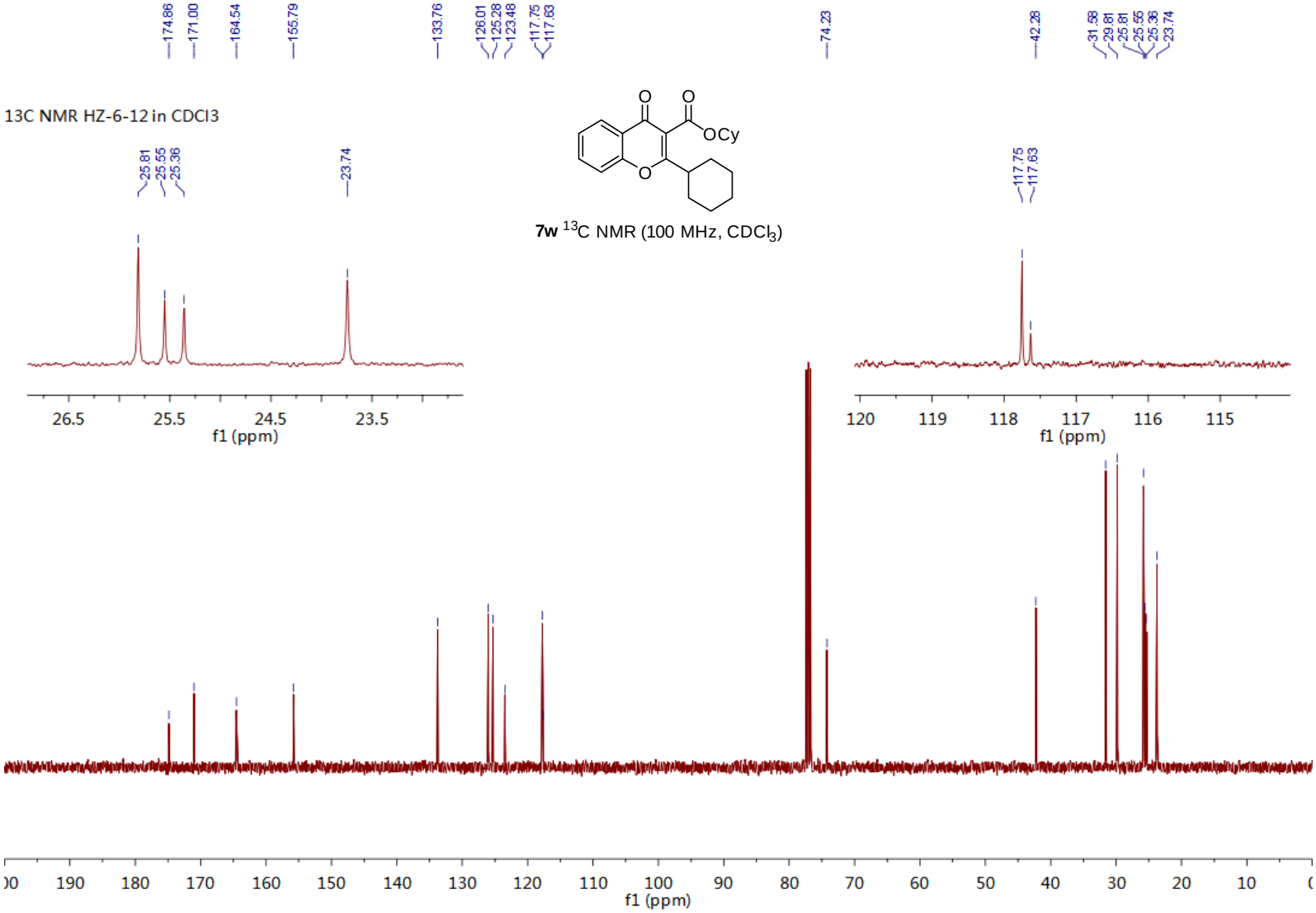
7v ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-12 in CDCl3

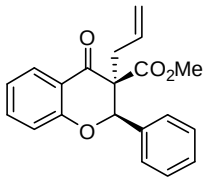


7w ^{1}H NMR (400 MHz, $CDCl_3$)

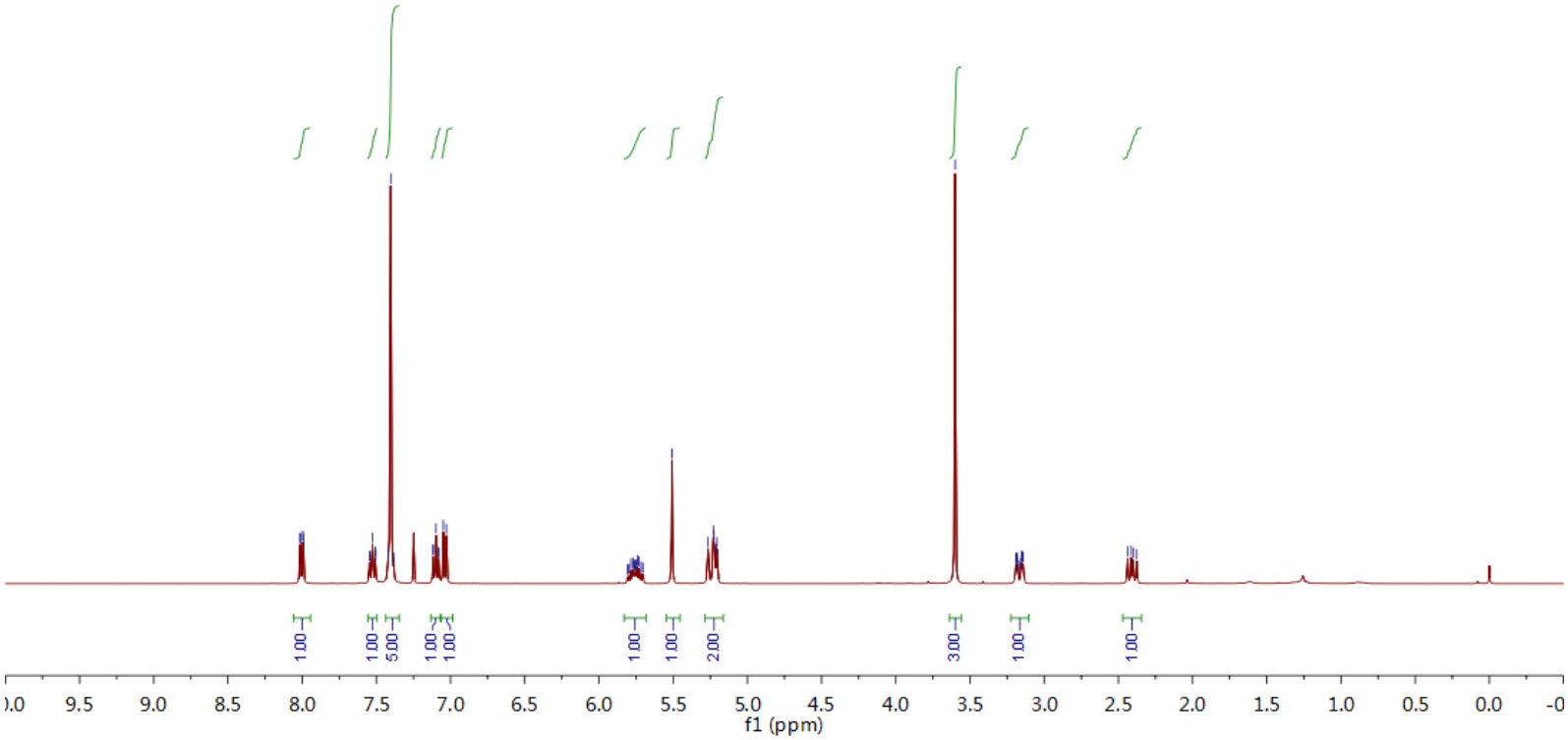


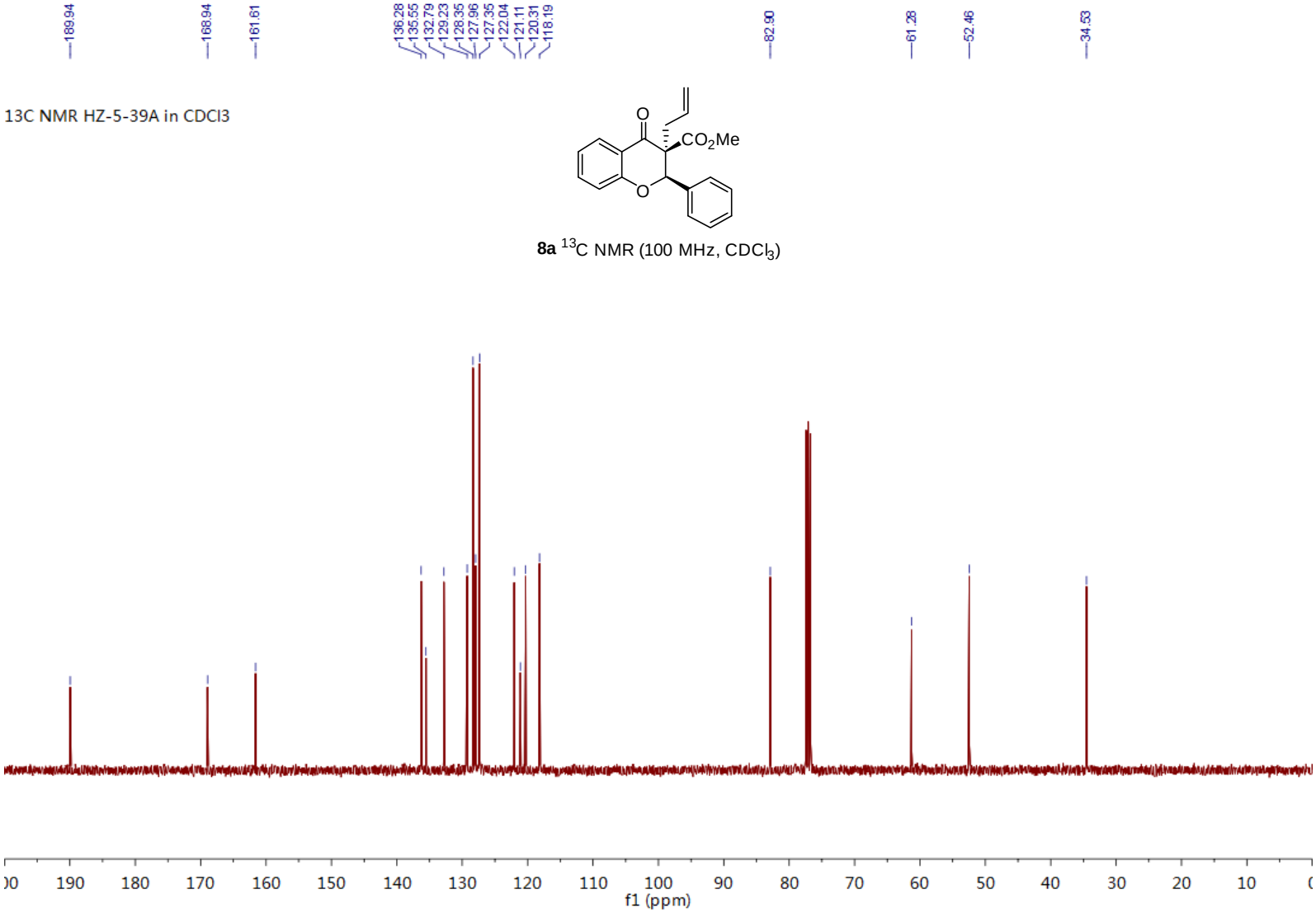

174.86
171.00
164.54
155.79
133.76
126.01
125.28
123.48
117.75
117.63
74.23
42.28
31.68
29.81
25.81
25.55
25.36
23.74
13C NMR HZ-6-12 in CDCl3
O
O
OCy
O
7w 13C NMR (100 MHz, CDCl3)
25.81
25.55
25.36
23.74
117.75
117.63
26.5
25.5
24.5
23.5
f1 (ppm)
120
119
118
117
116
115
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1H NMR HZ-5-39A in CDCl3



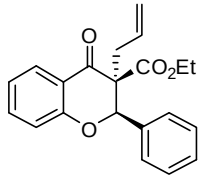
8a ^{1}H NMR (400 MHz, $CDCl_3$)



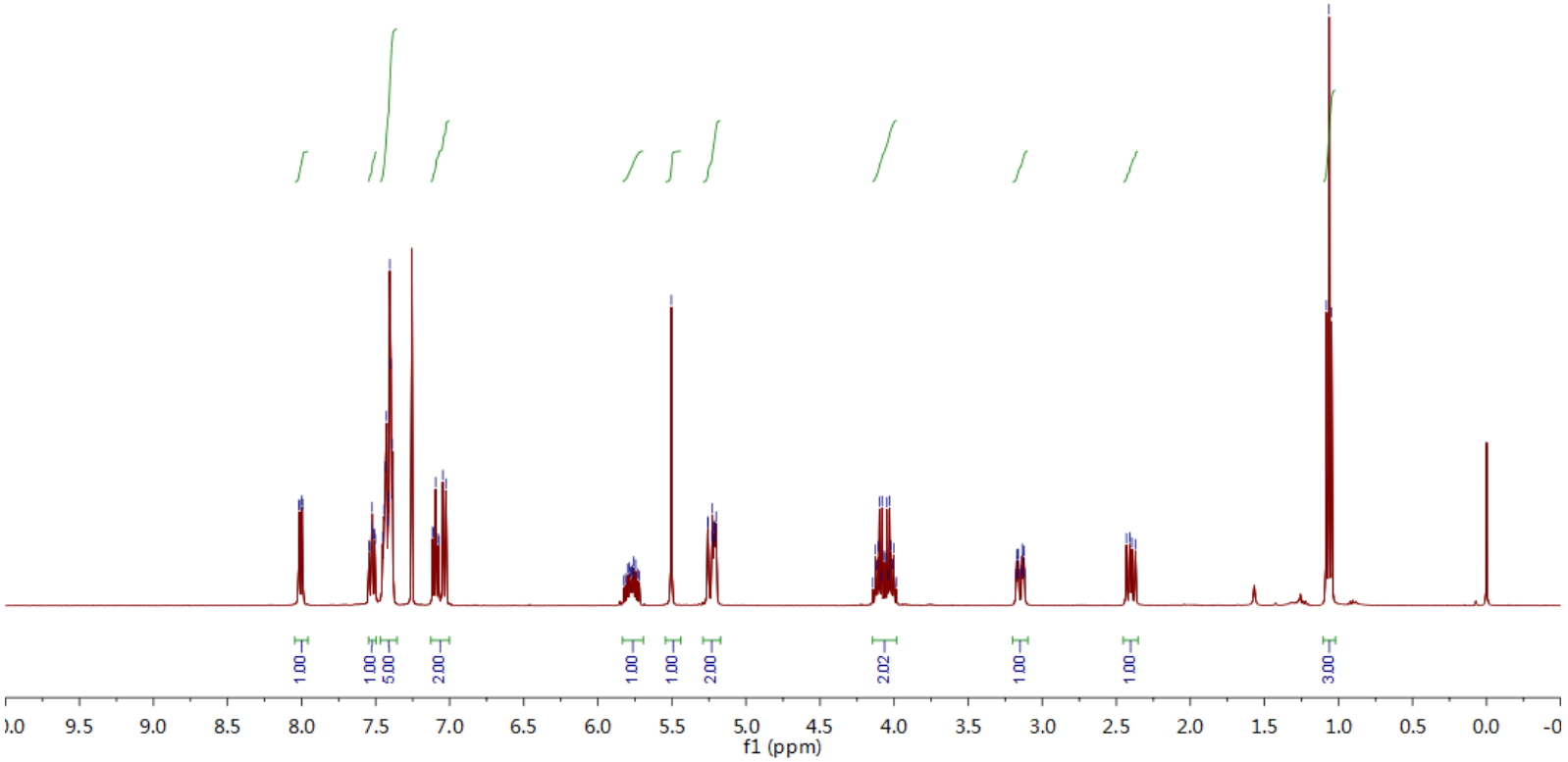


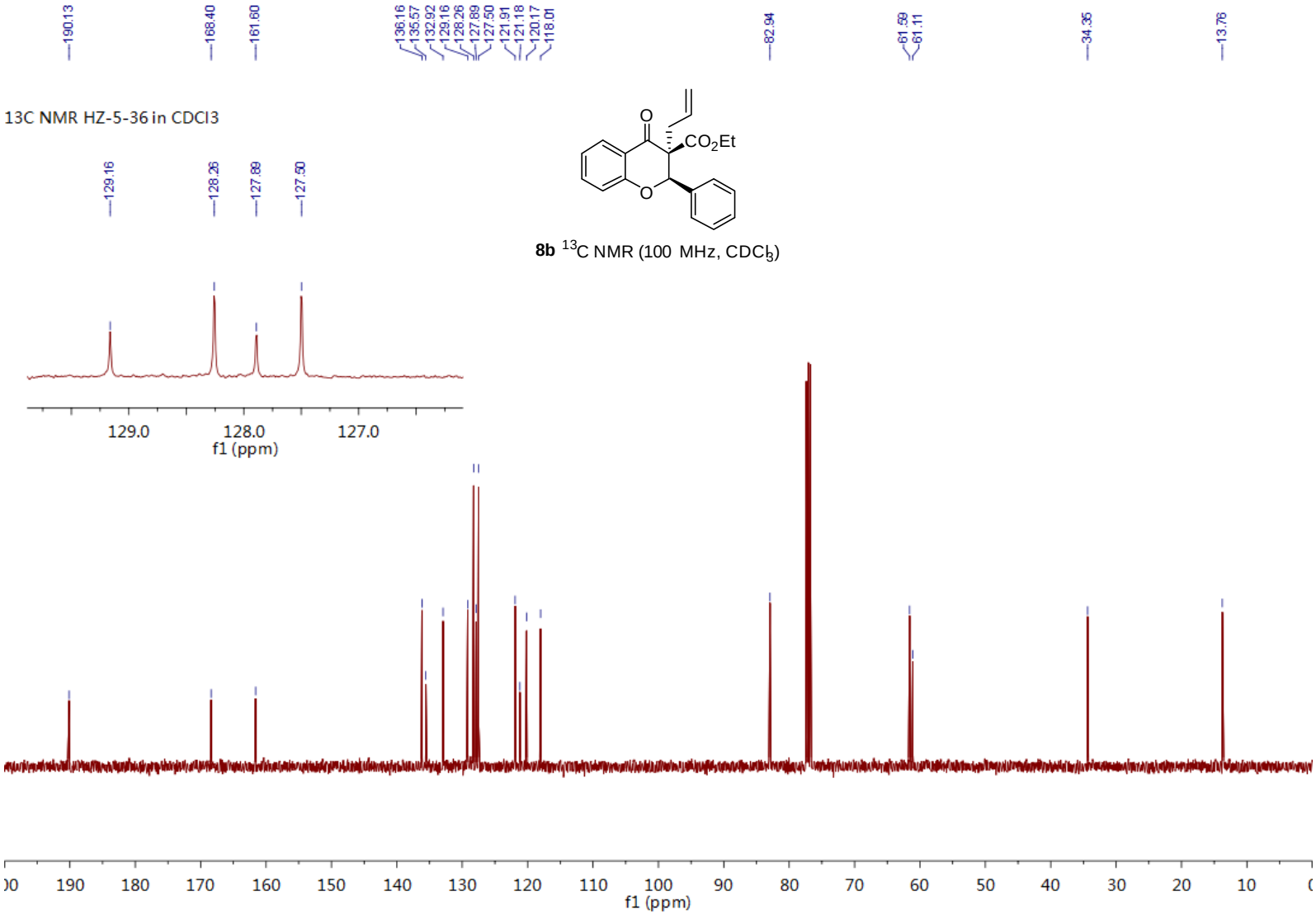
8a ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-36 in CDCl3

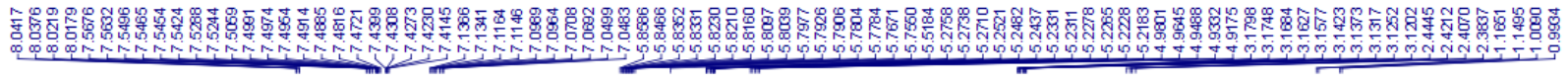


8b ^{1}H NMR (400 MHz, $CDCl_3$)

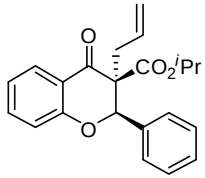




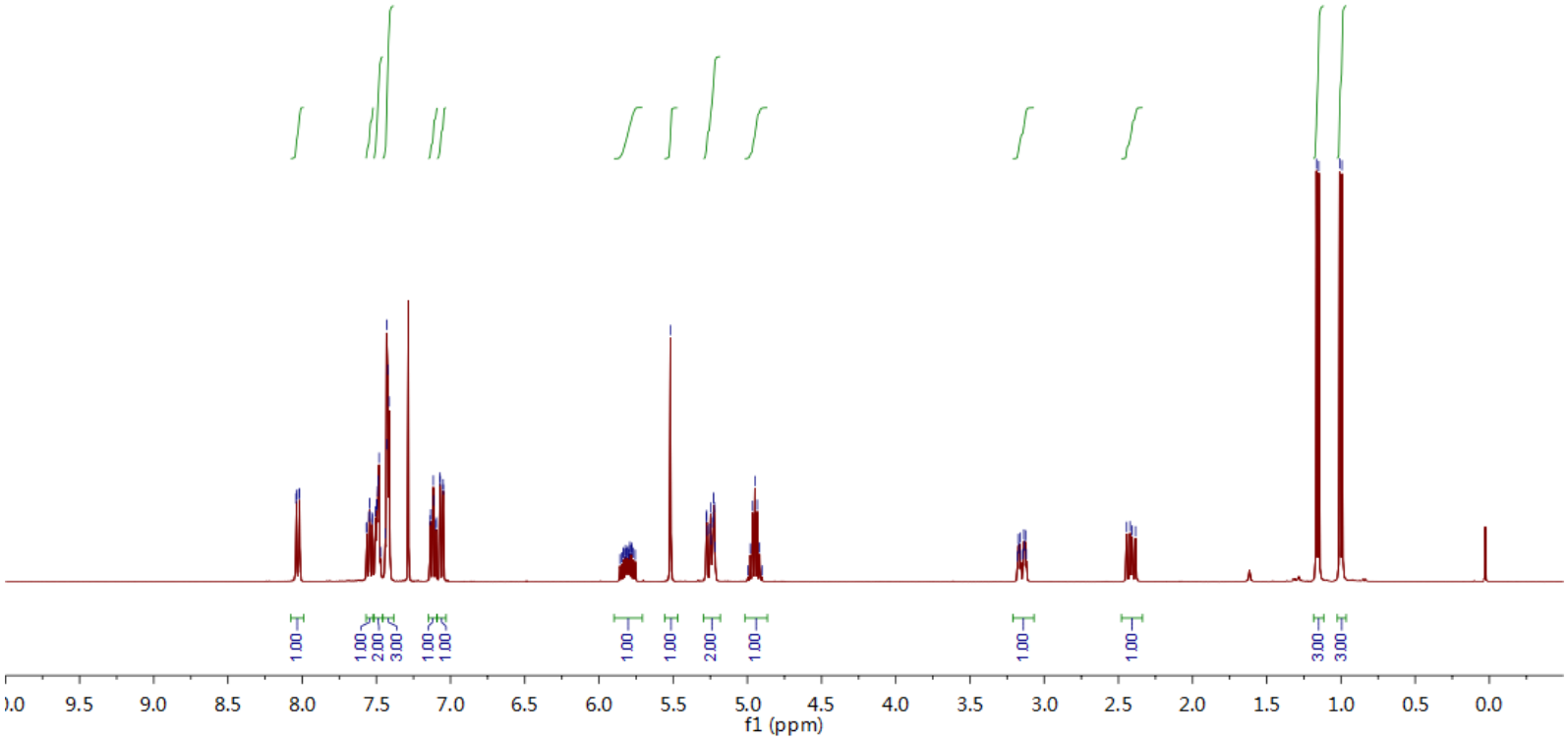
8b ^{13}C NMR (100 MHz, $CDCl_3$)

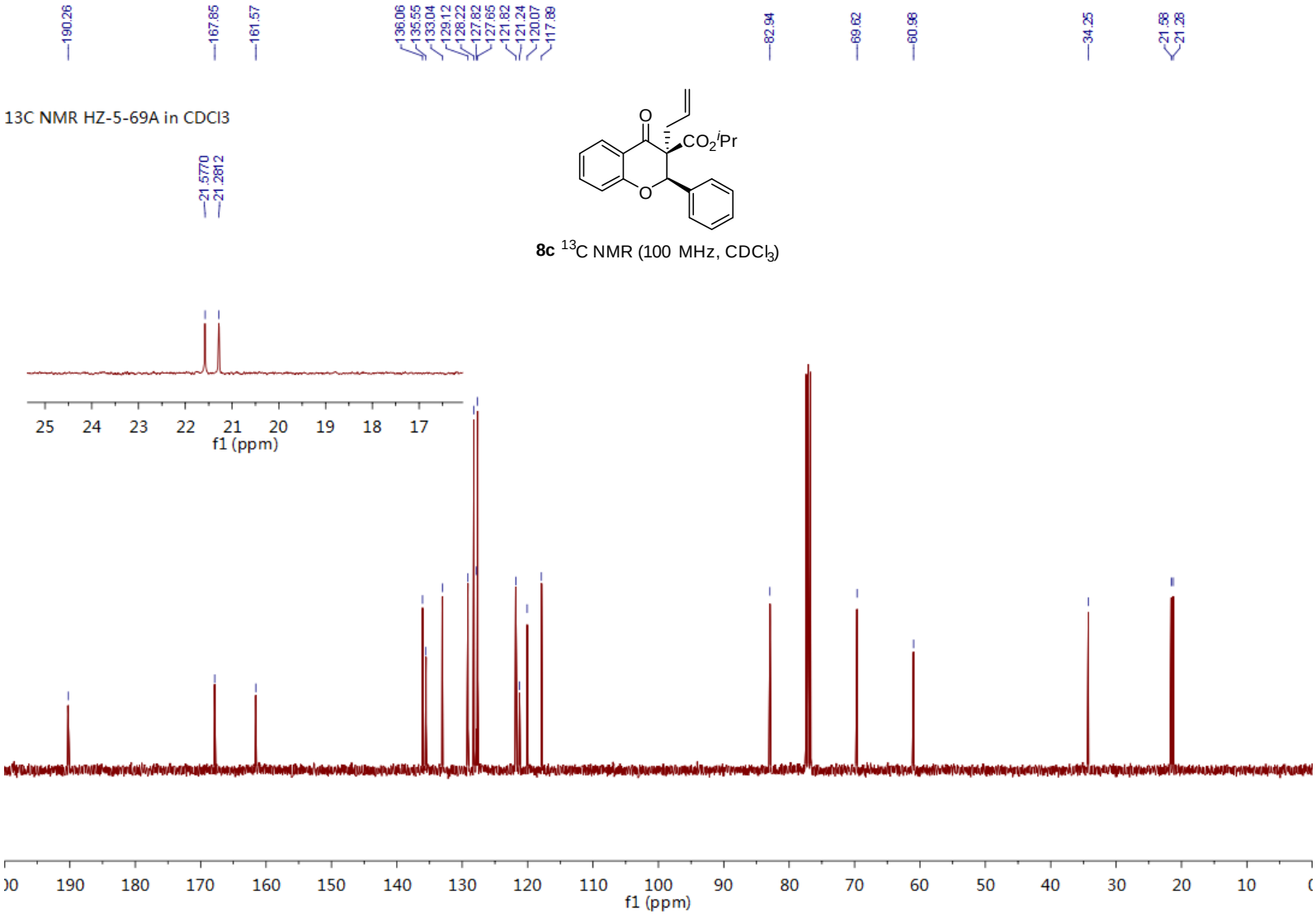


1H NMR HZ-5-69A in CDCL3

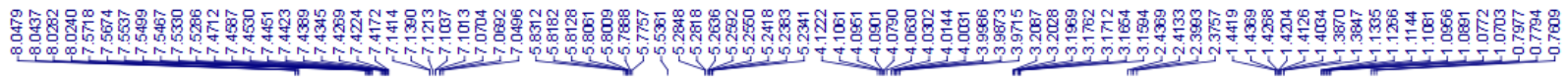


8c ^{1}H NMR (400 MHz, $CDCl_3$)

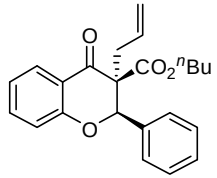




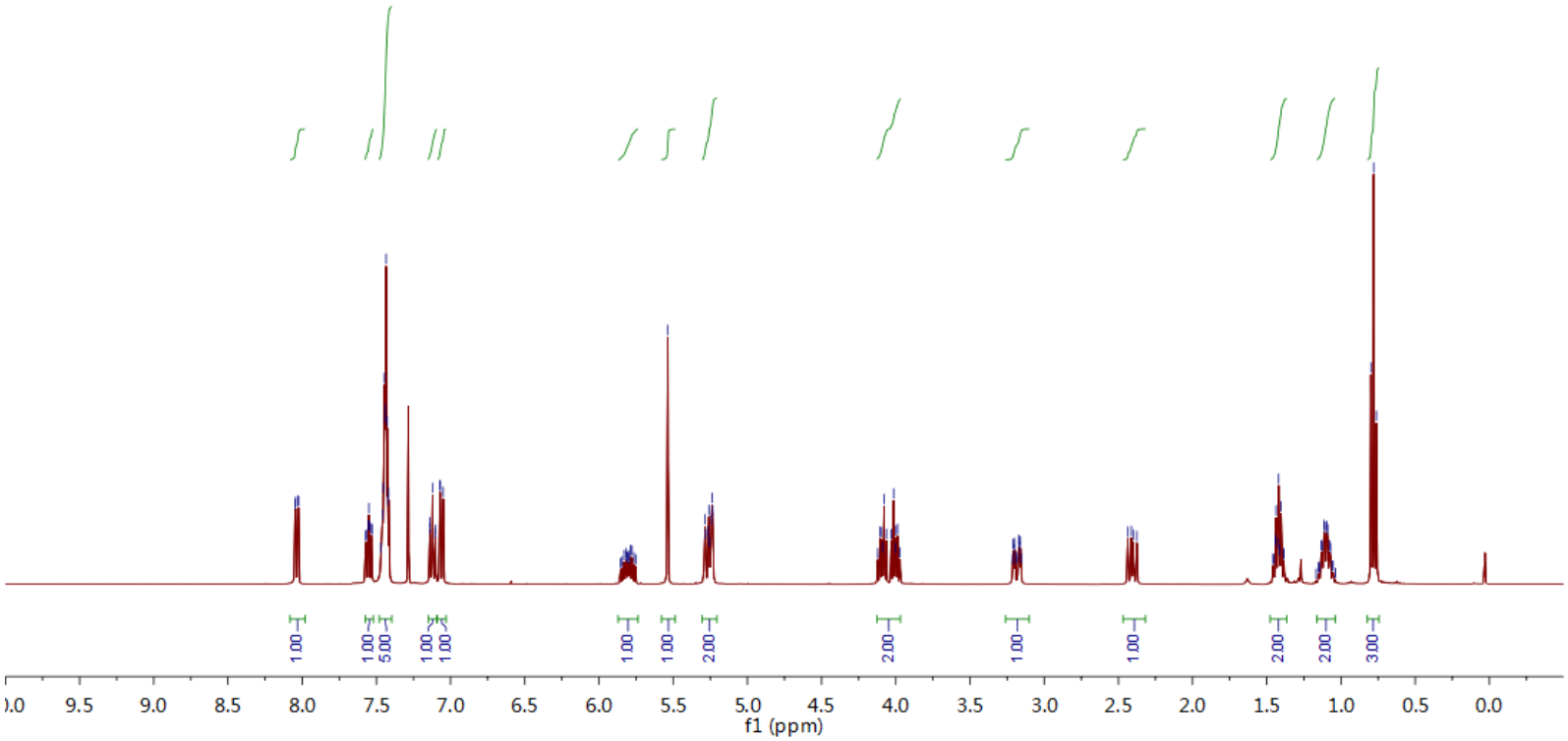
8c ^{13}C NMR (100 MHz, $CDCl_3$)

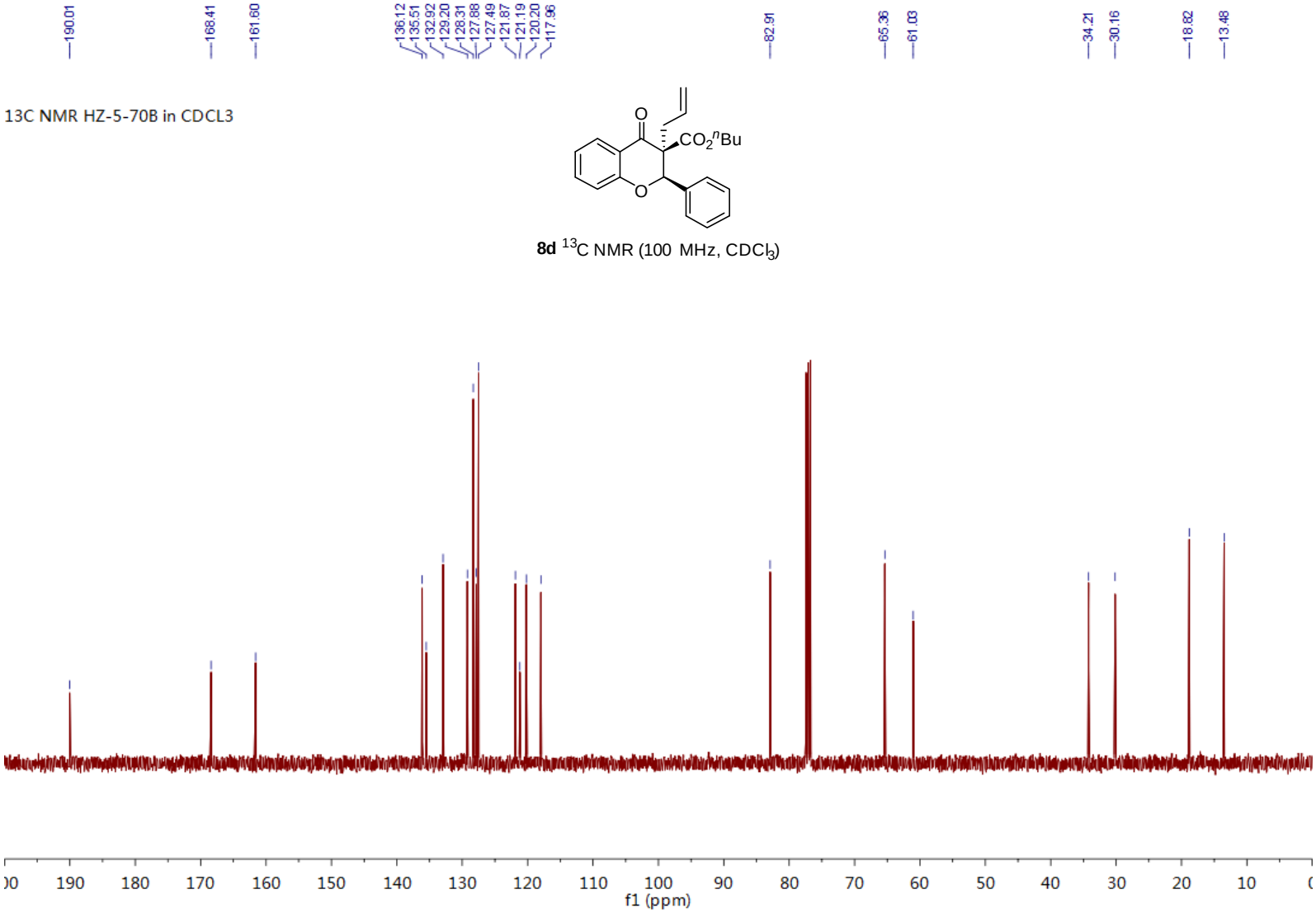


1H NMR HZ-5-70B in CDCL3

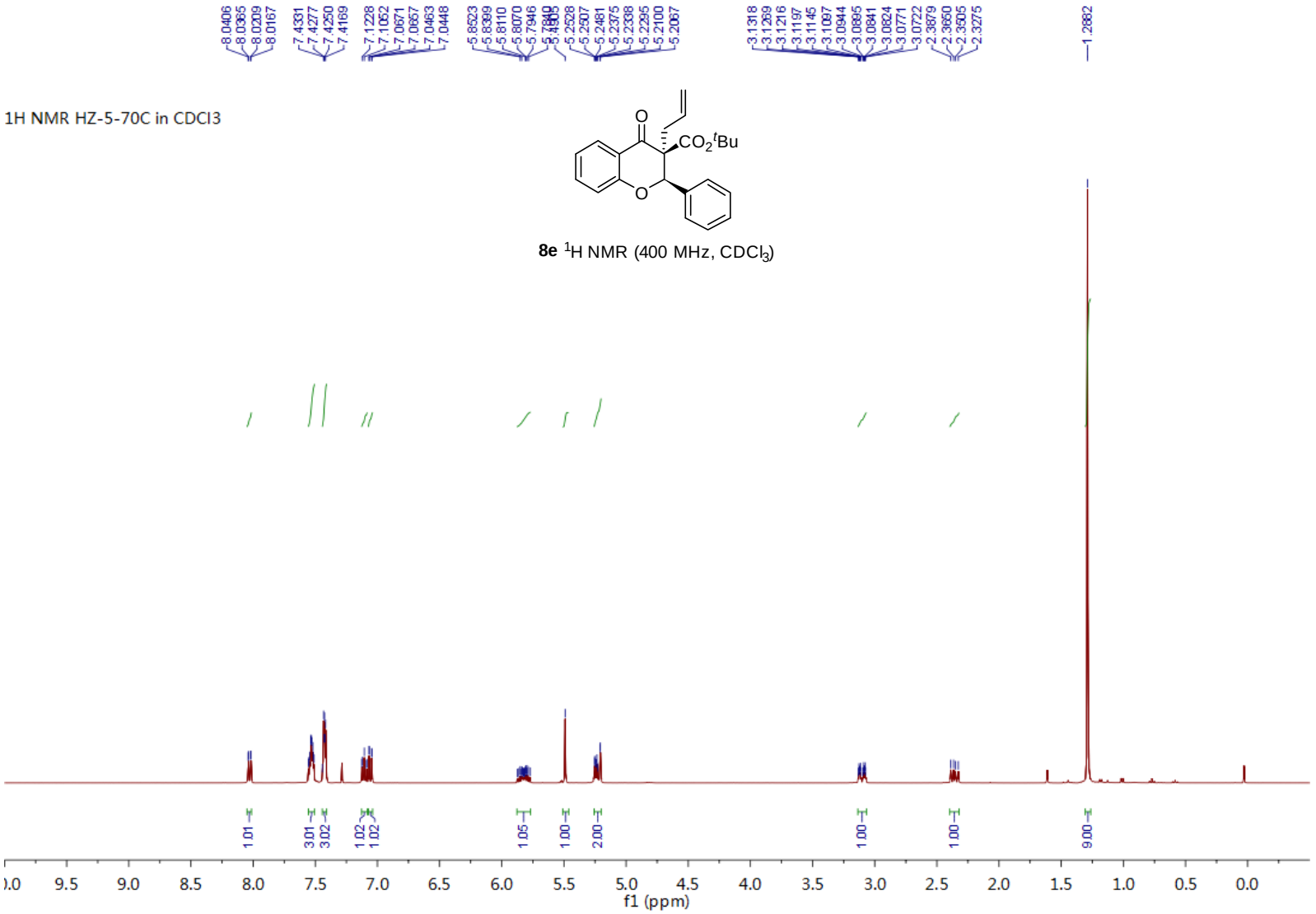


8d ^{1}H NMR (400 MHz, $CDCl_3$)

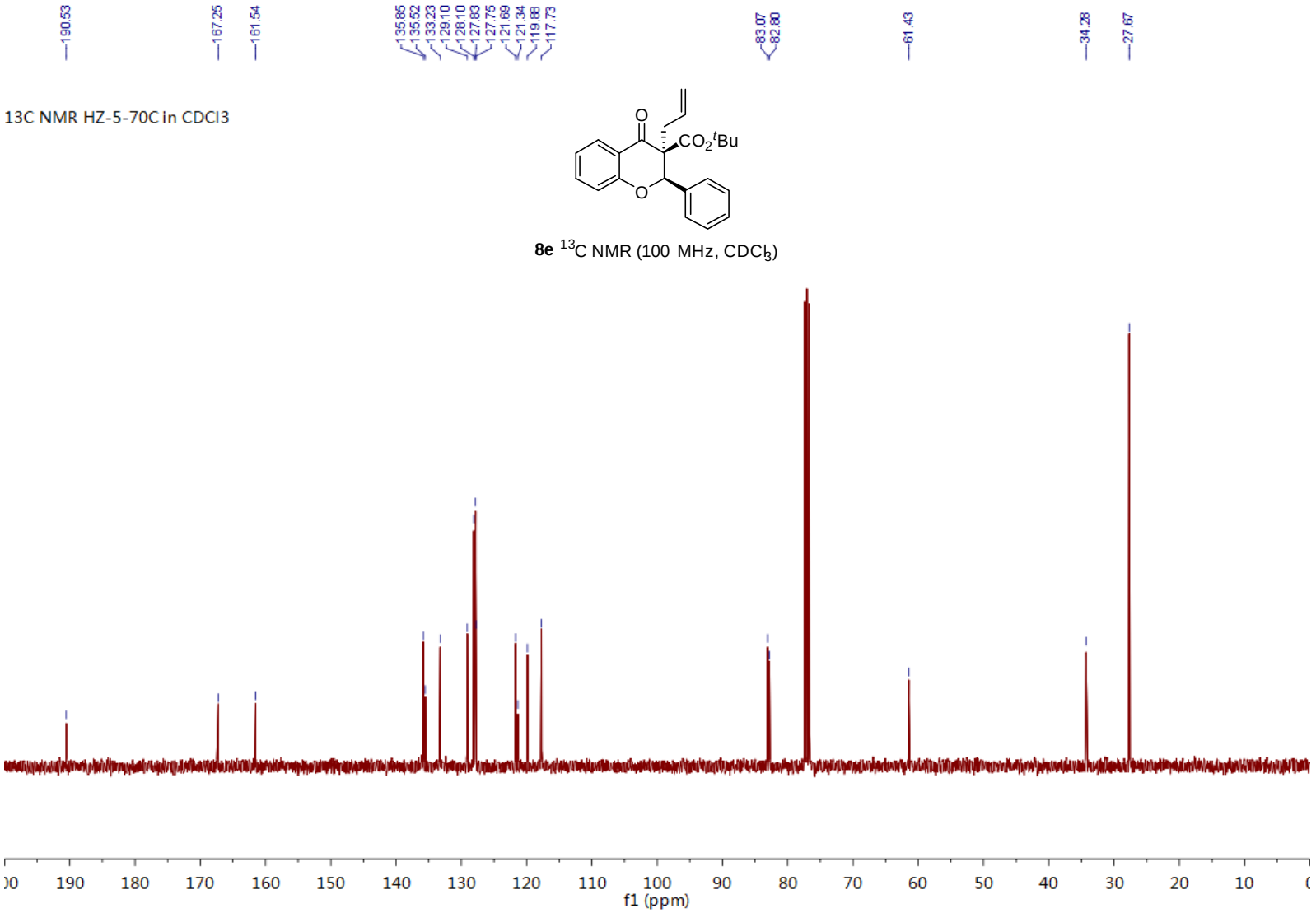




8d ^{13}C NMR (100 MHz, $CDCl_3$)

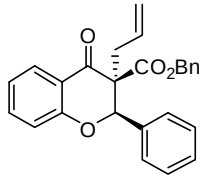


8e ^{1}H NMR (400 MHz, $CDCl_3$)

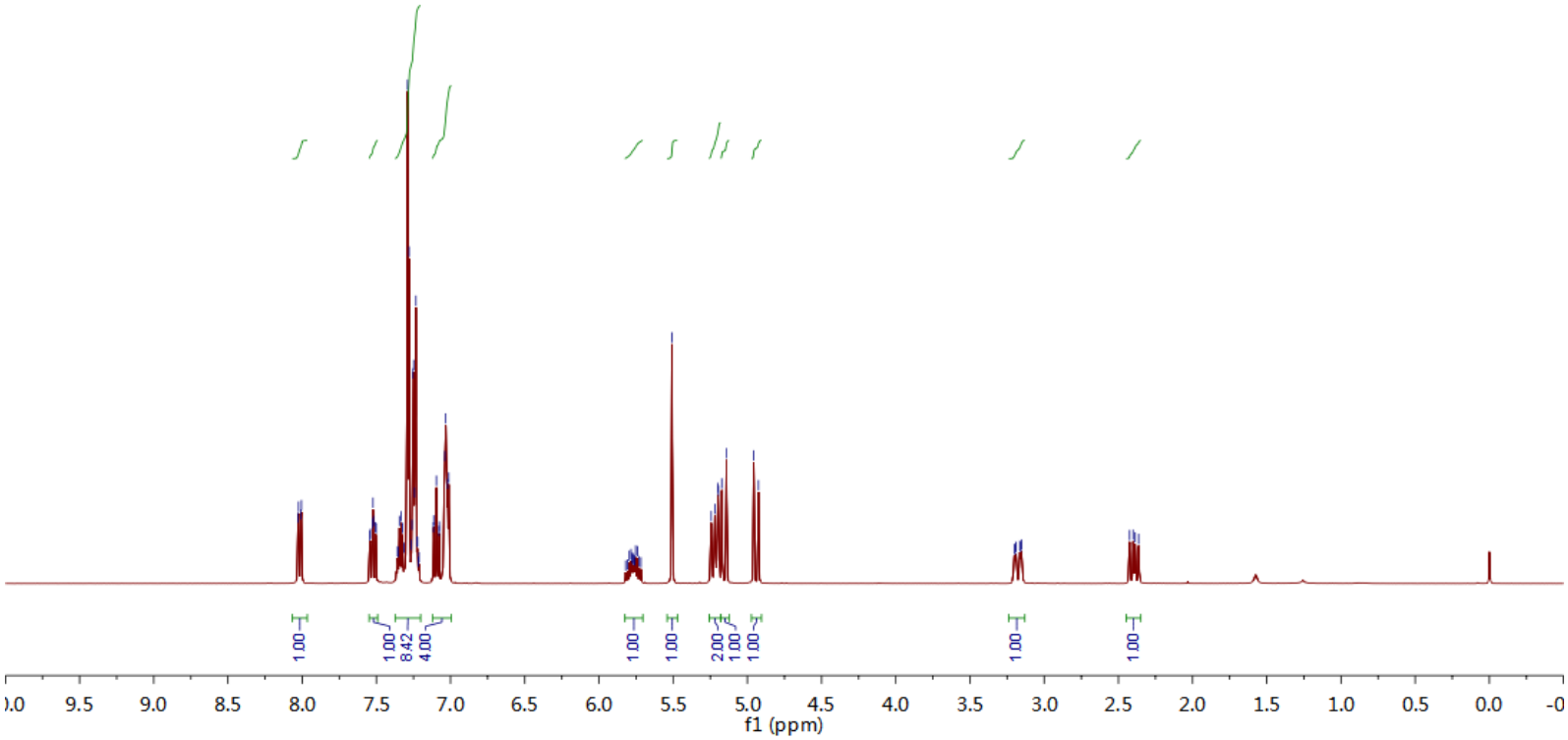


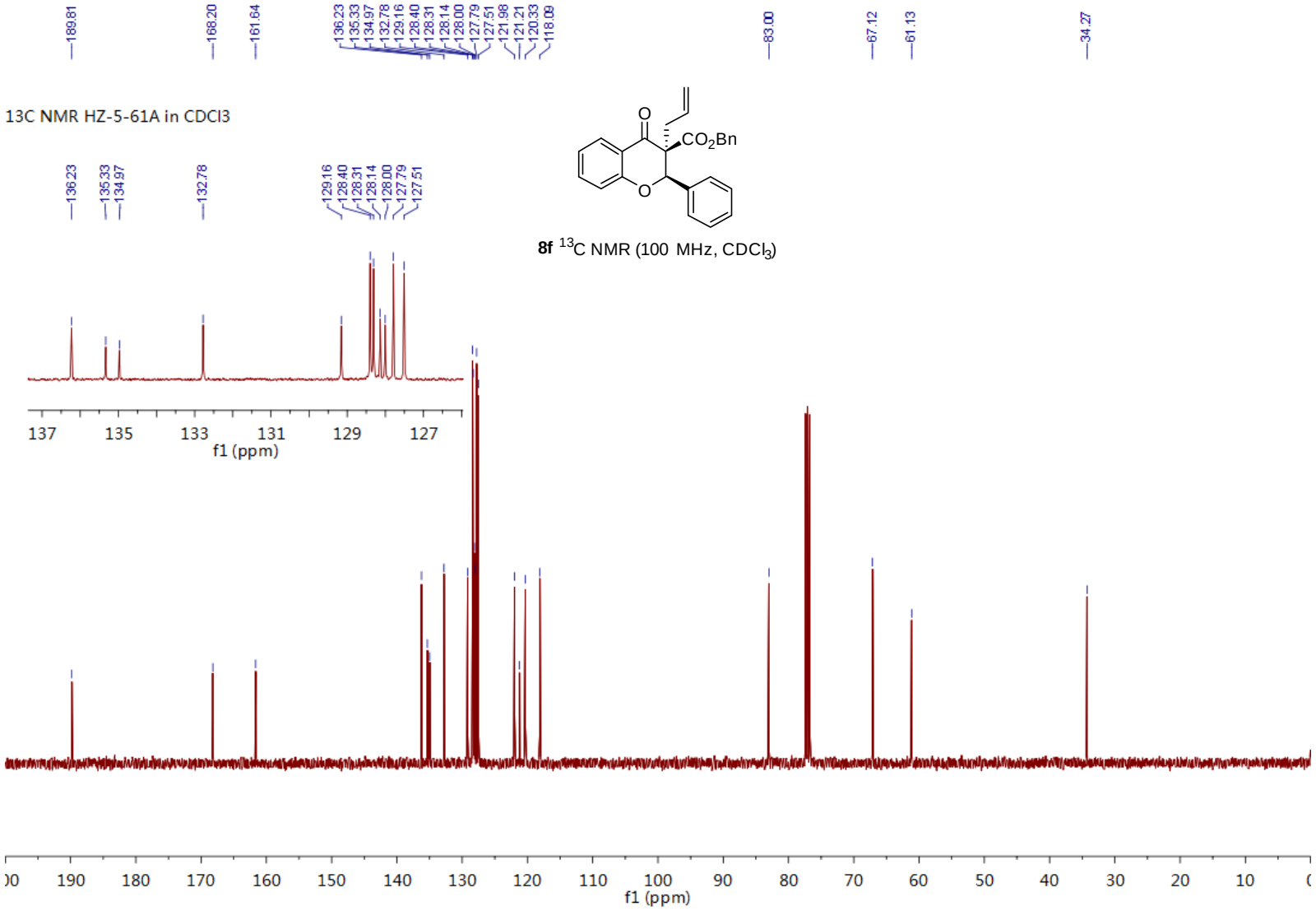
8e ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-61A in CDCl3



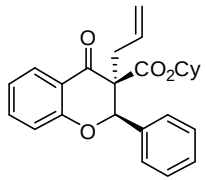
8f ^{1}H NMR (400 MHz, $CDCl_3$)



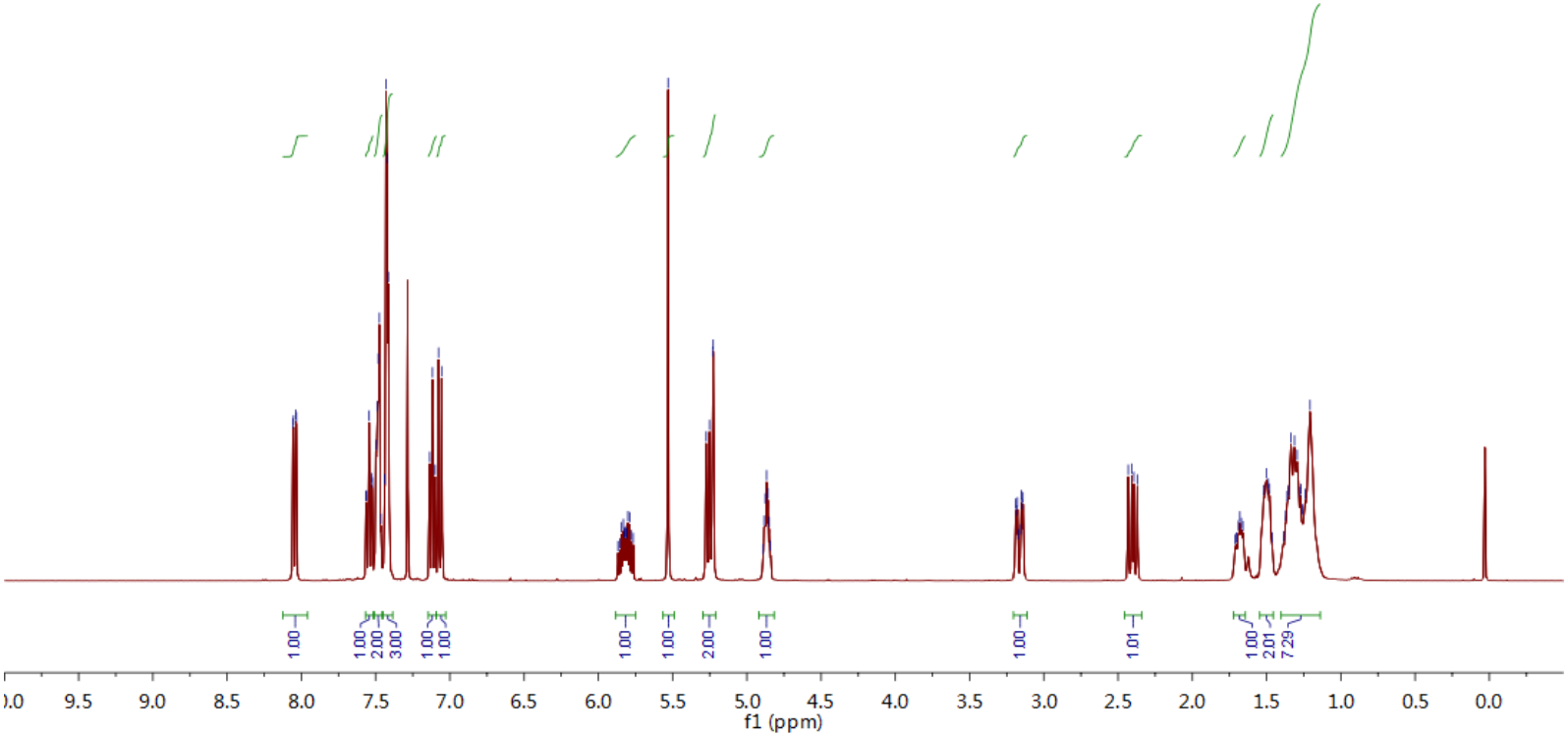


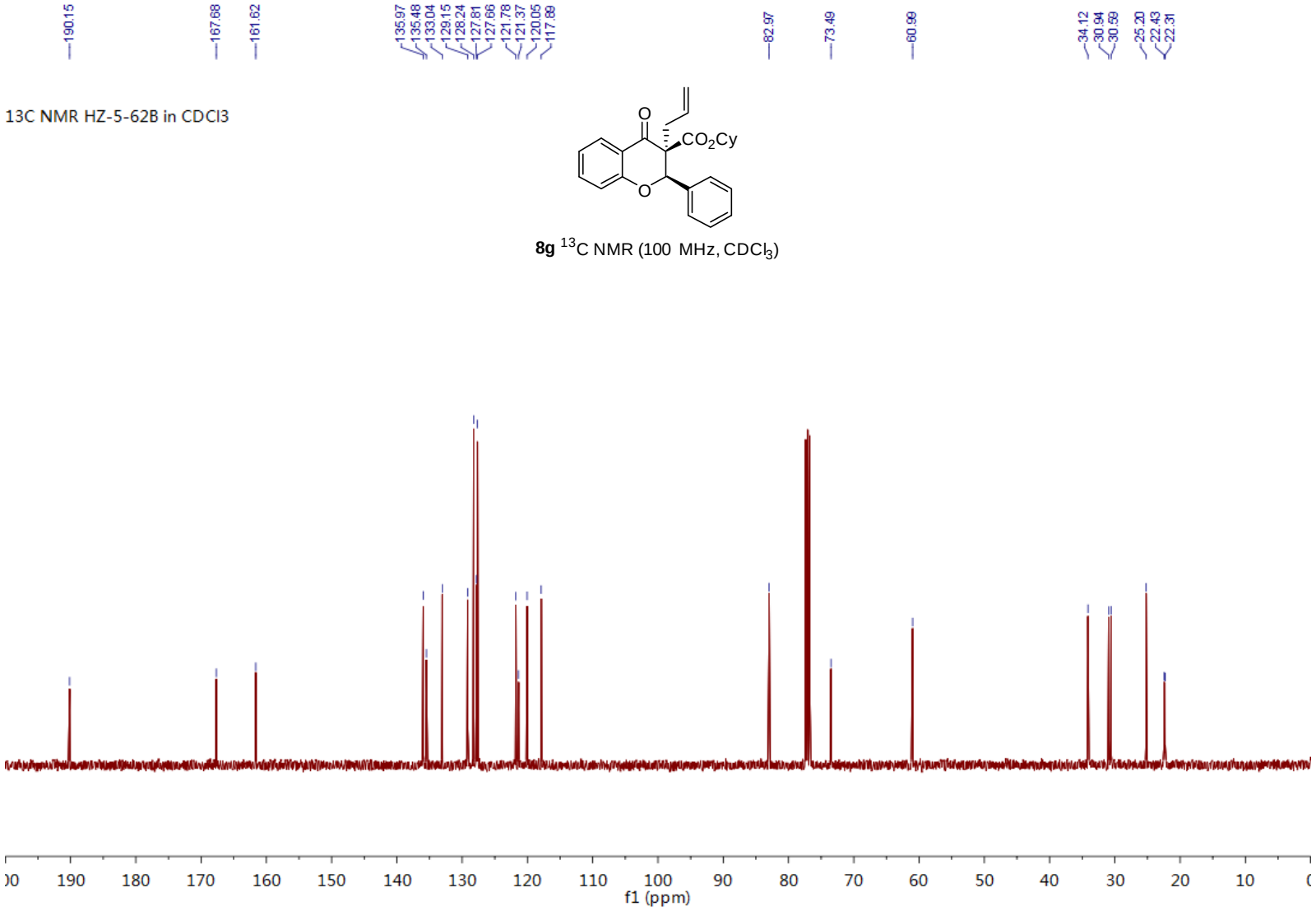
8f ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-62B in CDCl3



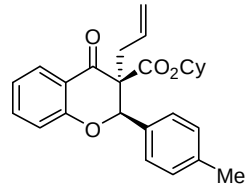
8g ^{1}H NMR (400 MHz, $CDCl_3$)



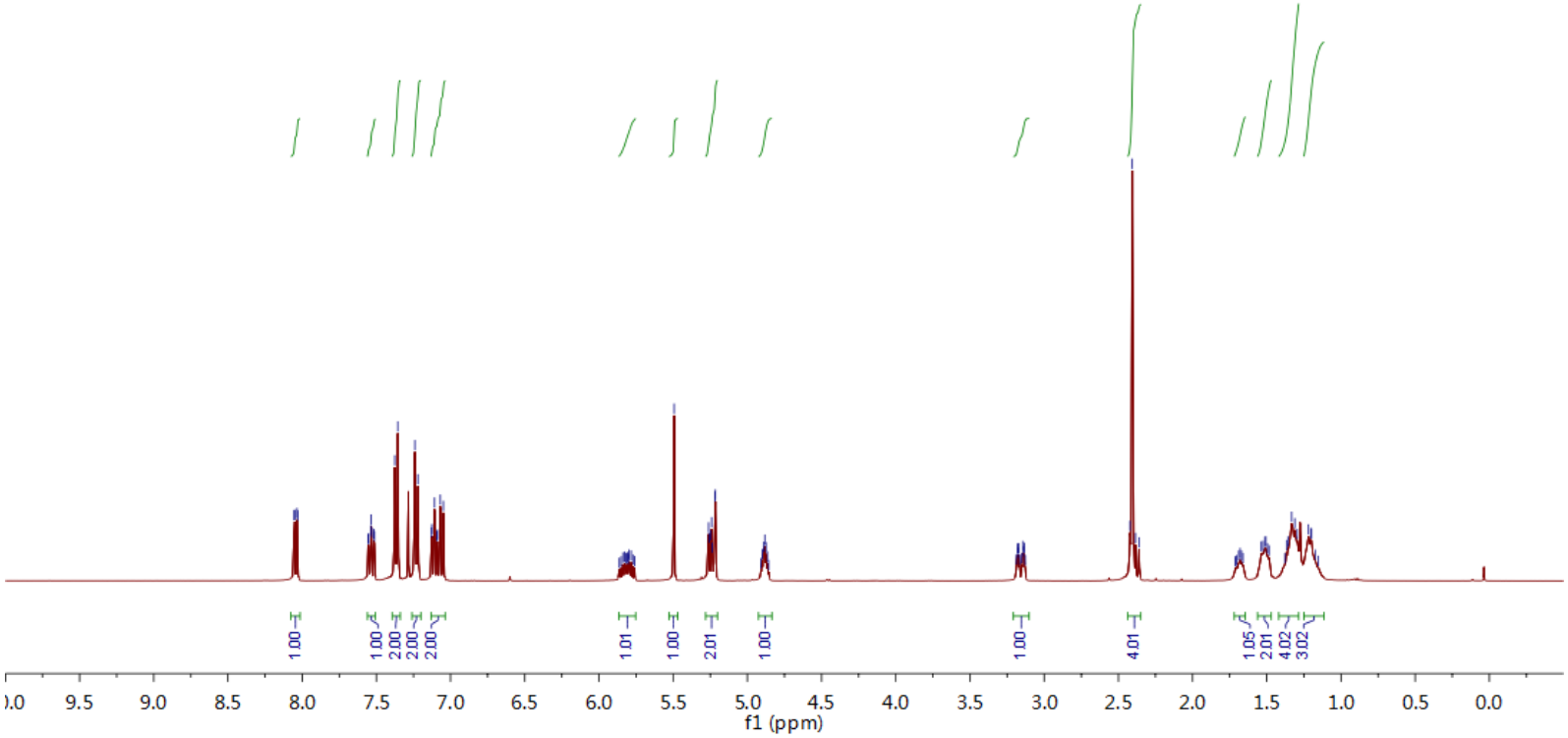


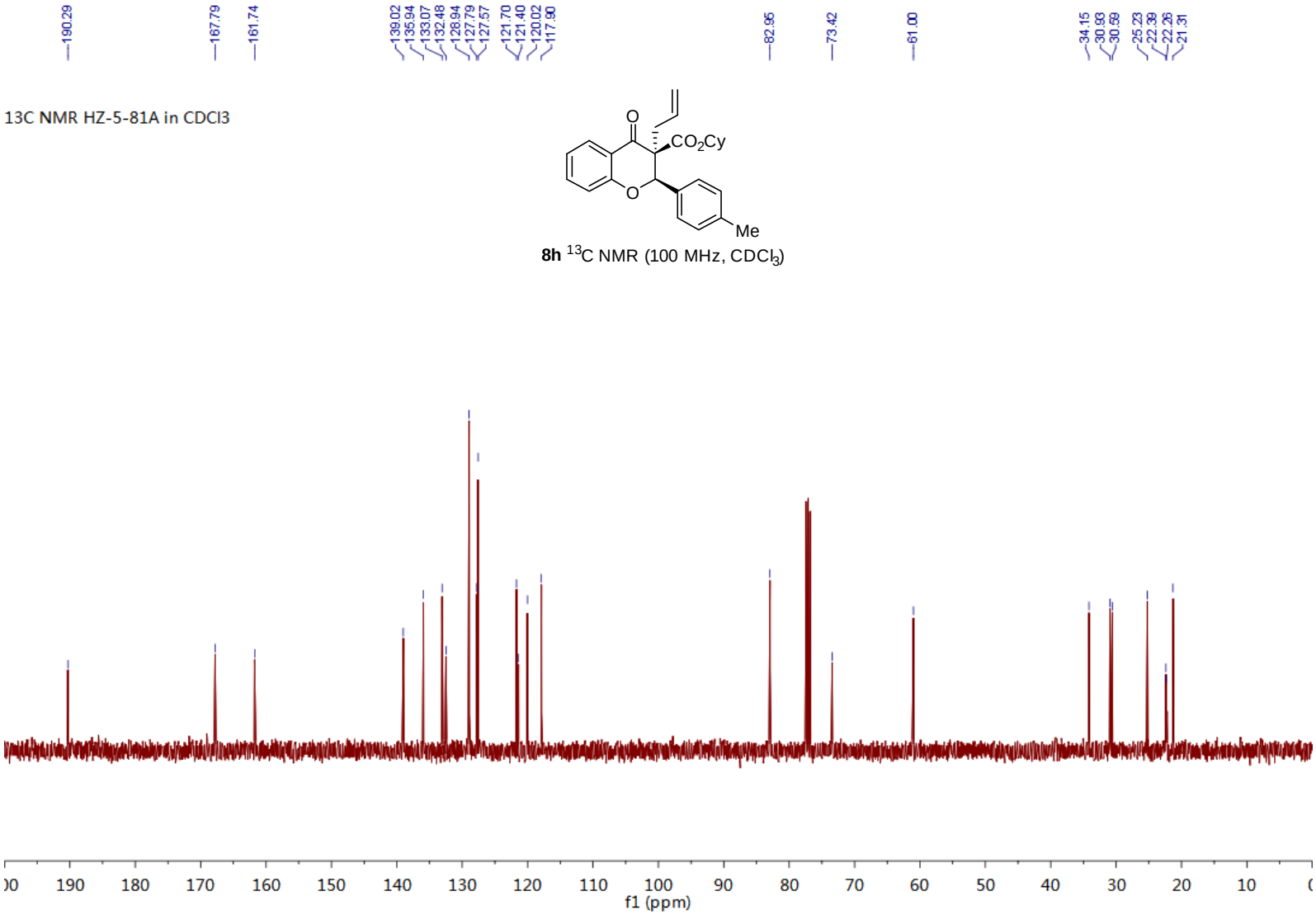
8g ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-81A in CDCl3



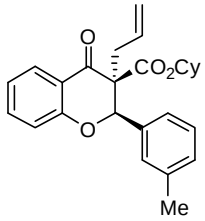
8h ^{1}H NMR (400 MHz, $CDCl_3$)



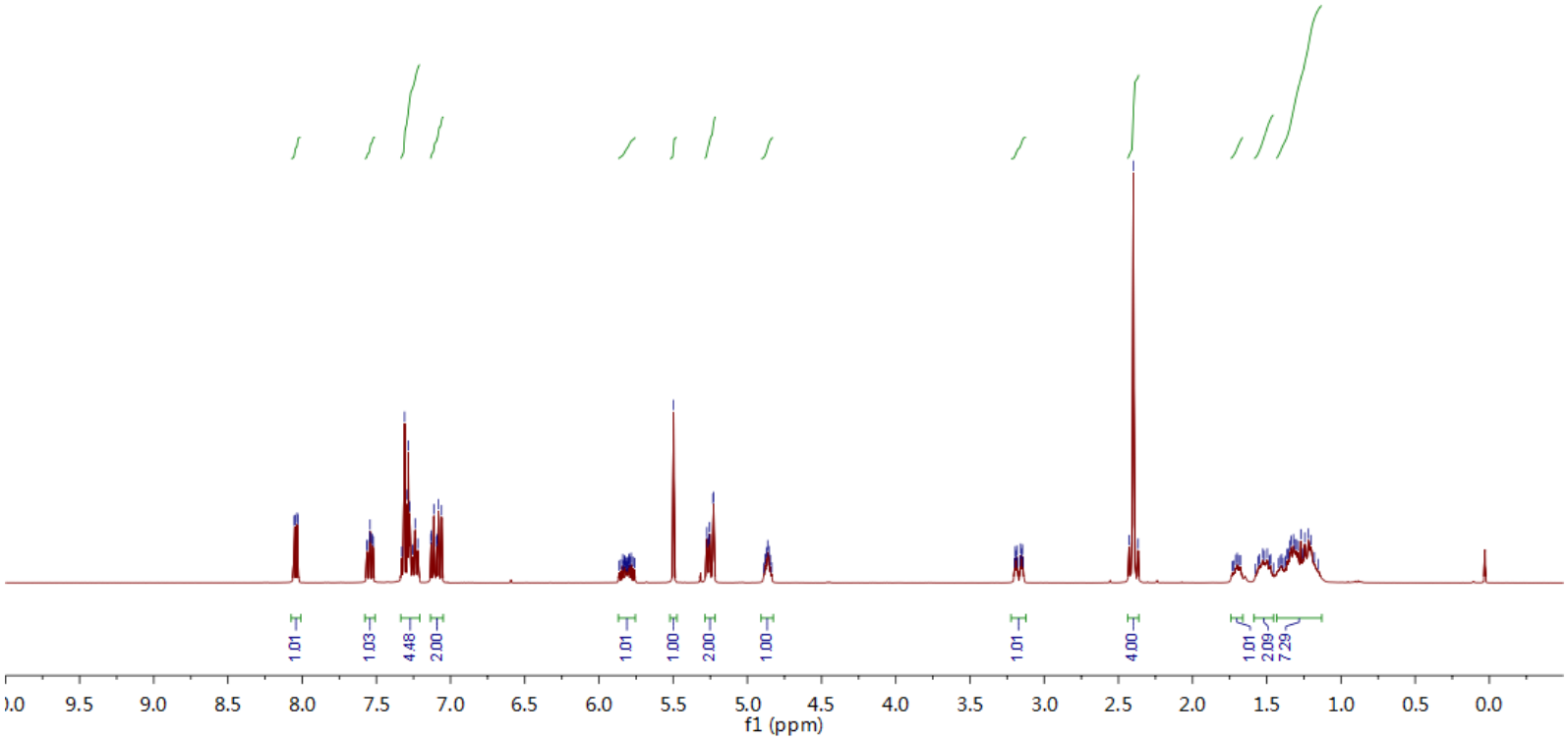


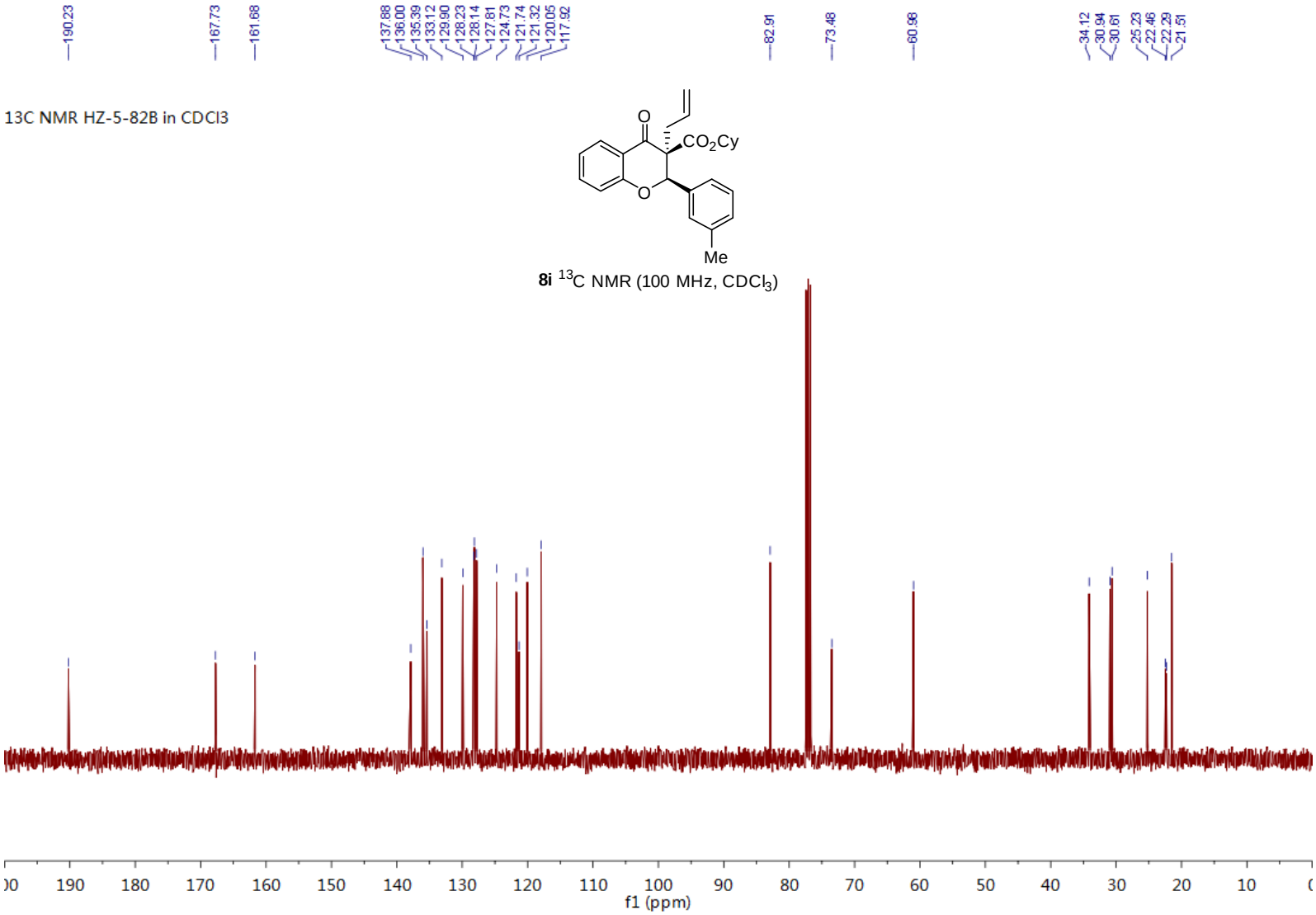
8h ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-82B in CDCl3



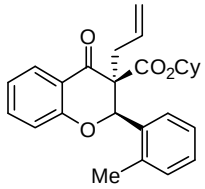
8i ^{1}H NMR (400 MHz, $CDCl_3$)



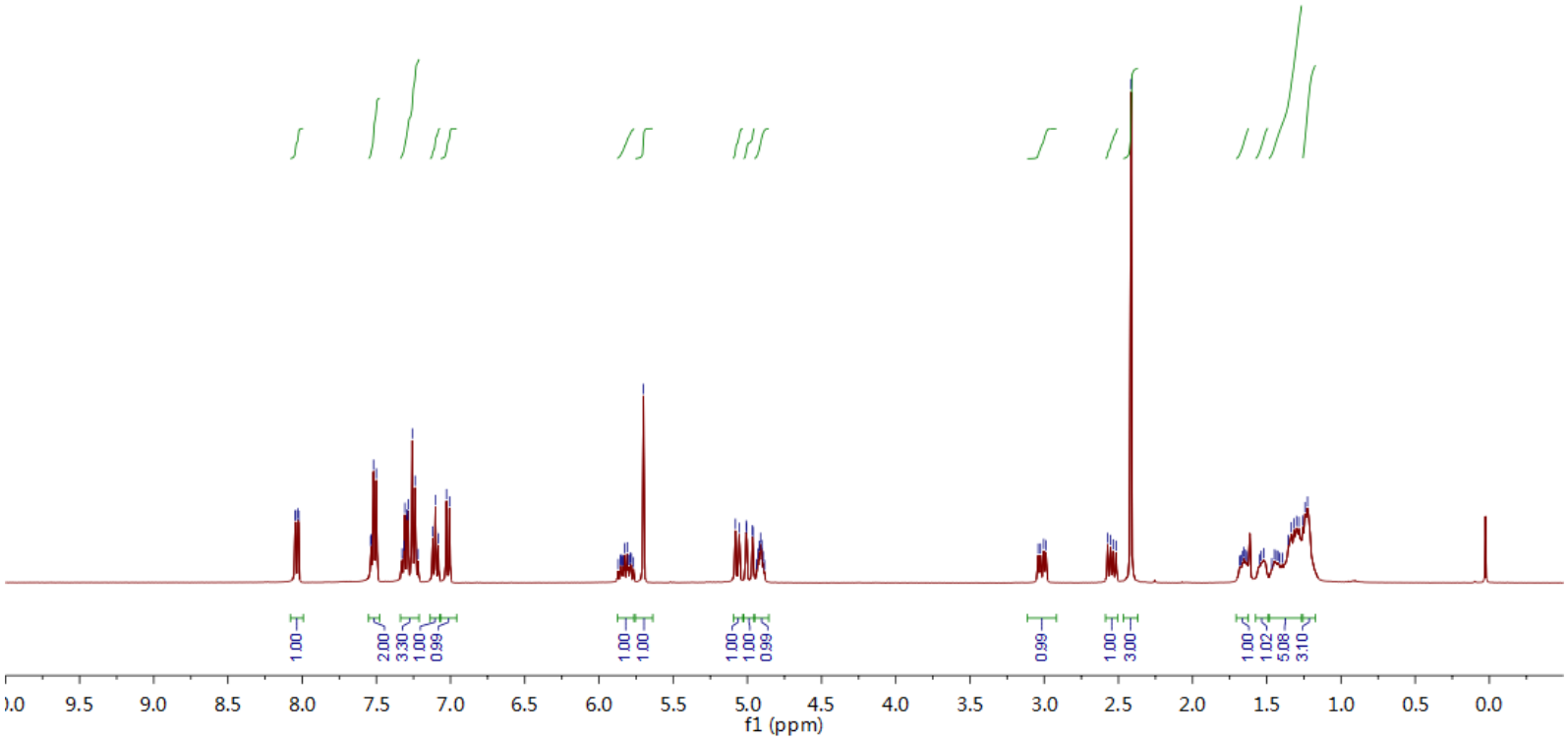


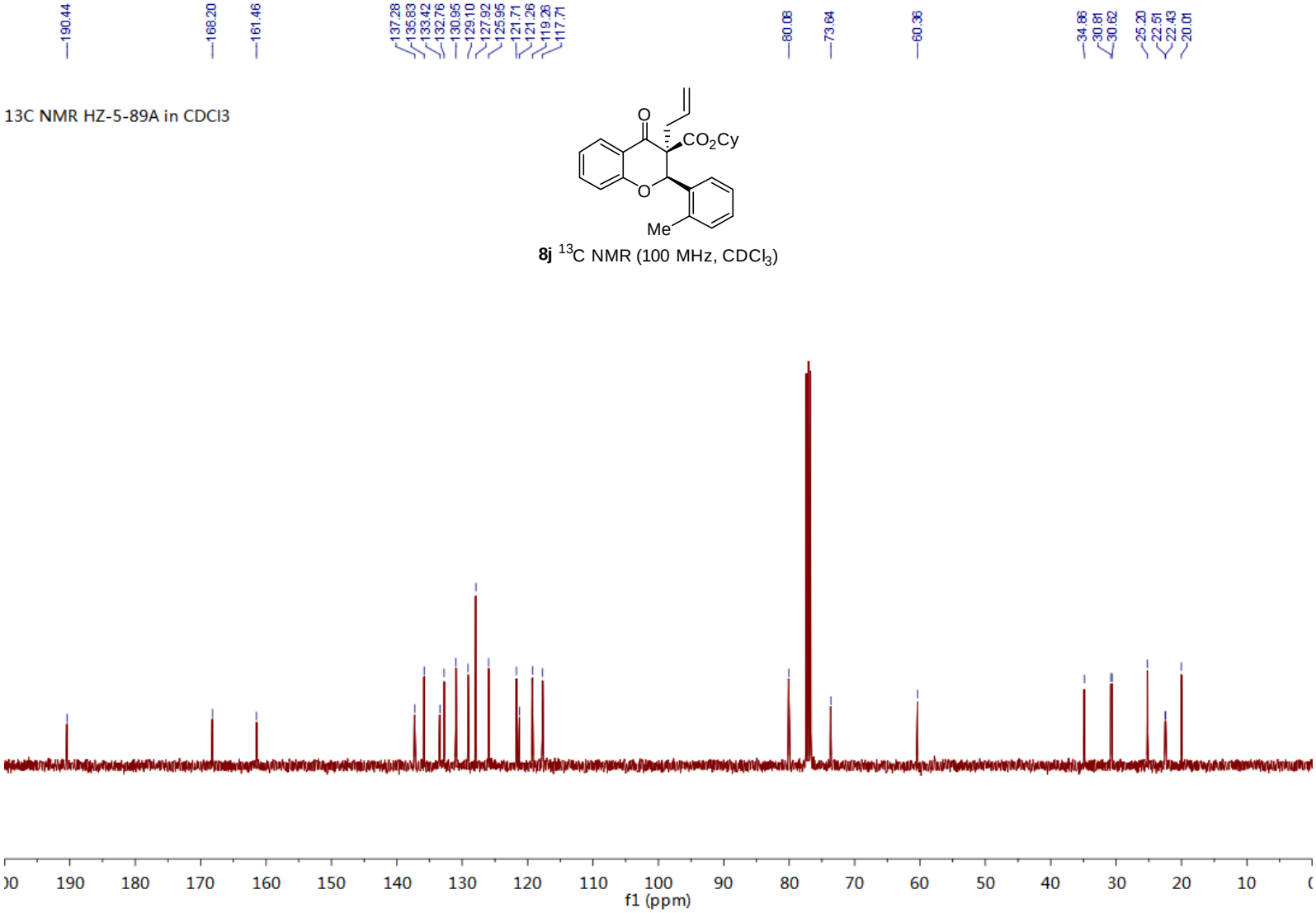
8i ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-5-89A in CDCl3

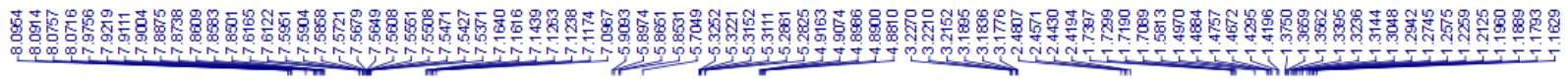


8j ^{1}H NMR (400 MHz, $CDCl_3$)

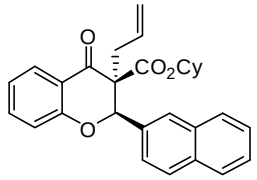




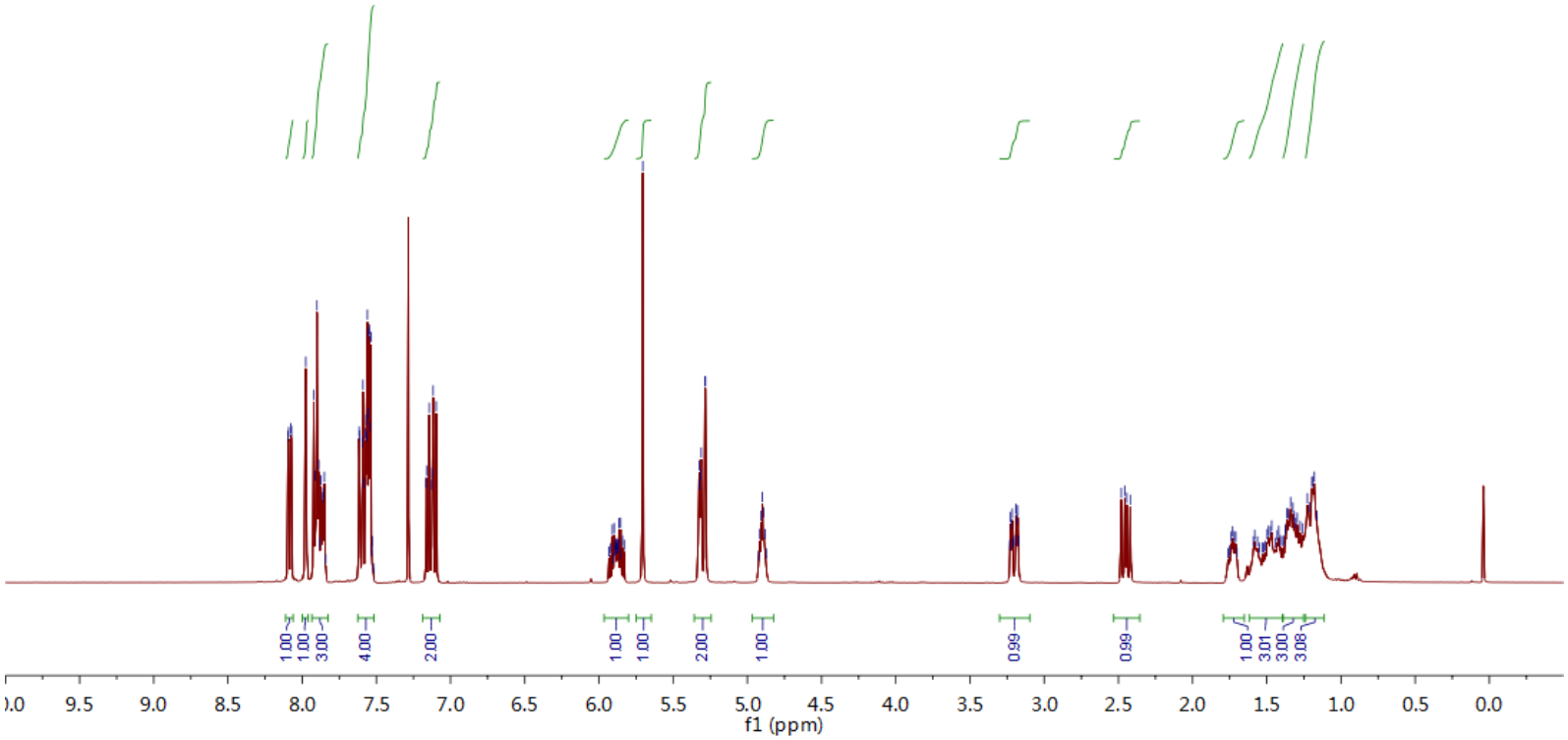
8j ^{13}C NMR (100 MHz, $CDCl_3$)



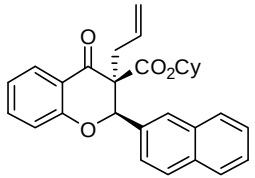
1H NMR HZ-5-82C in CDCl3



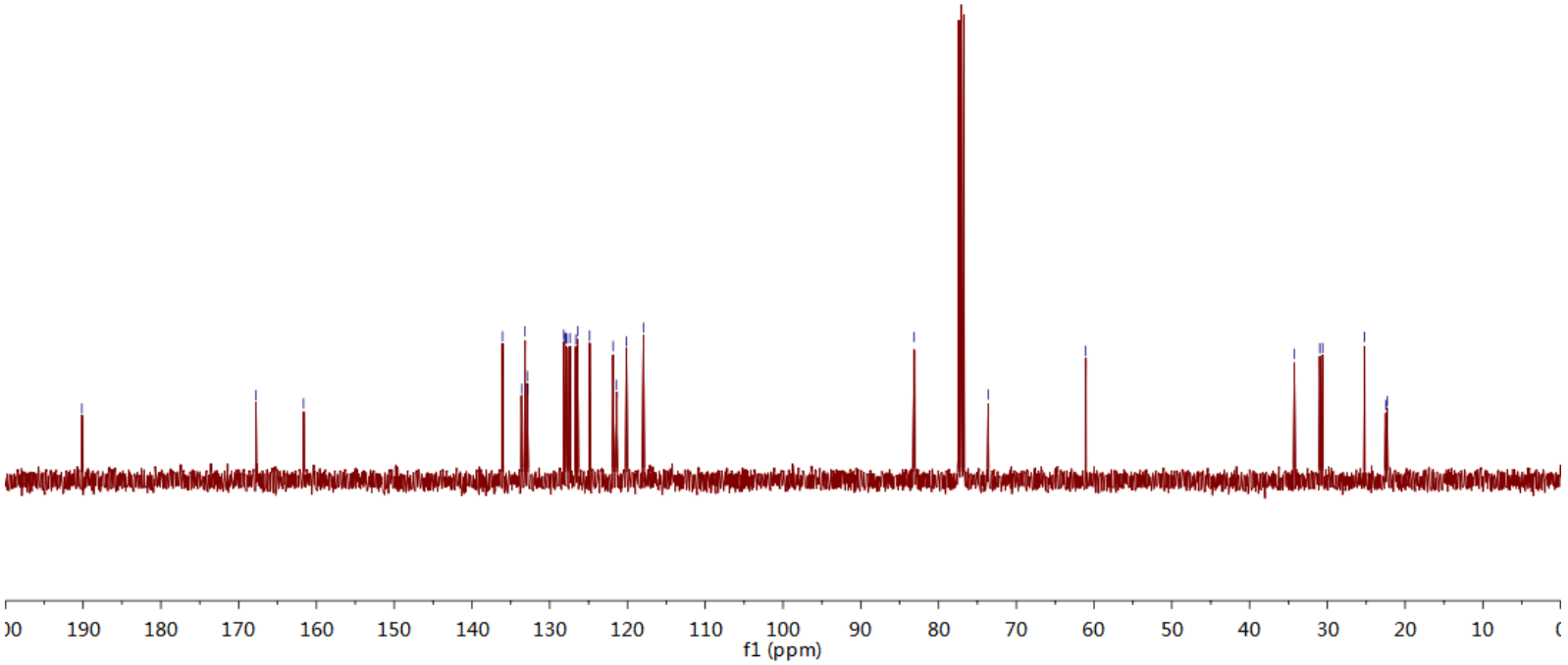
8k ^{1}H NMR (400 MHz, $CDCl_3$)

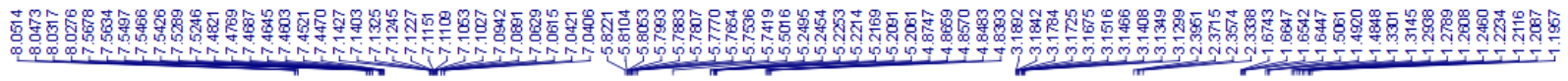


13C NMR HZ-5-82C in CDCl3

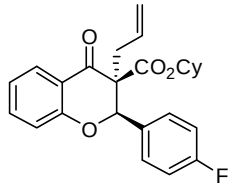


8k ^{13}C NMR (100 MHz, $CDCl_3$)

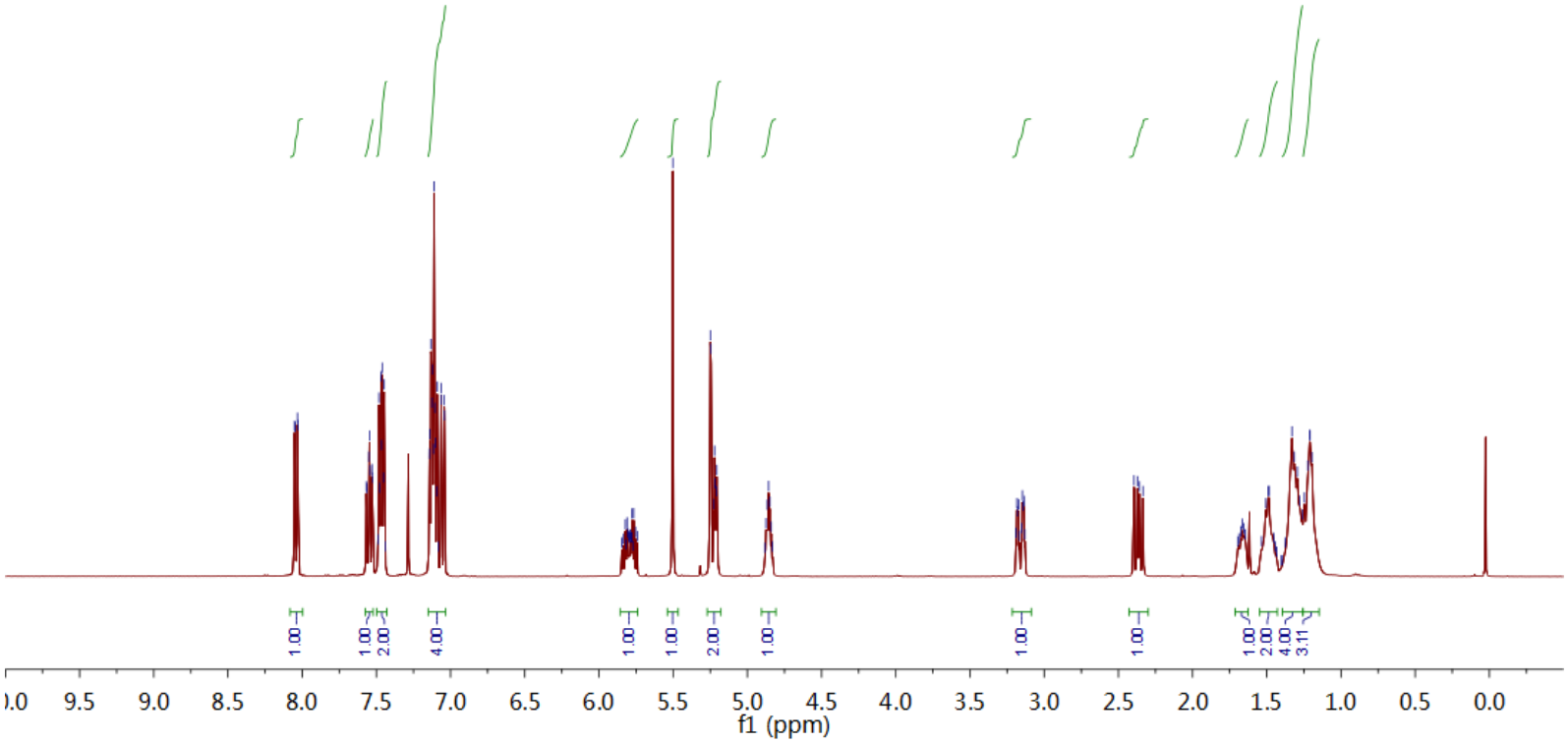


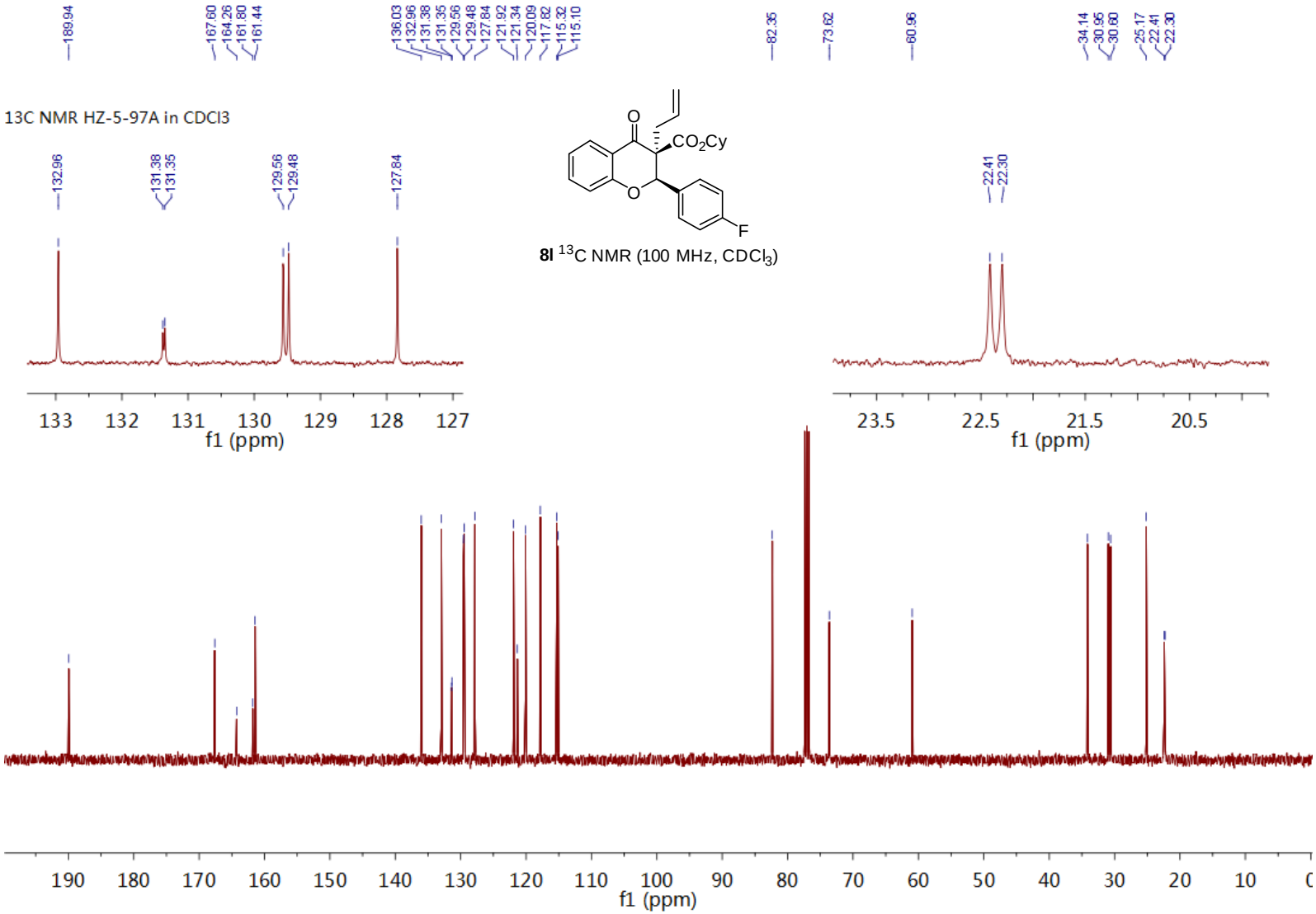


1H NMR HZ-5-97A in CDCl3



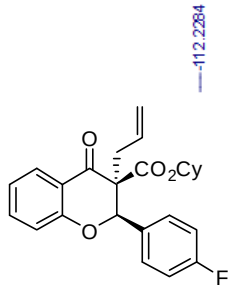
8l ^{1}H NMR (400 MHz, $CDCl_3$)



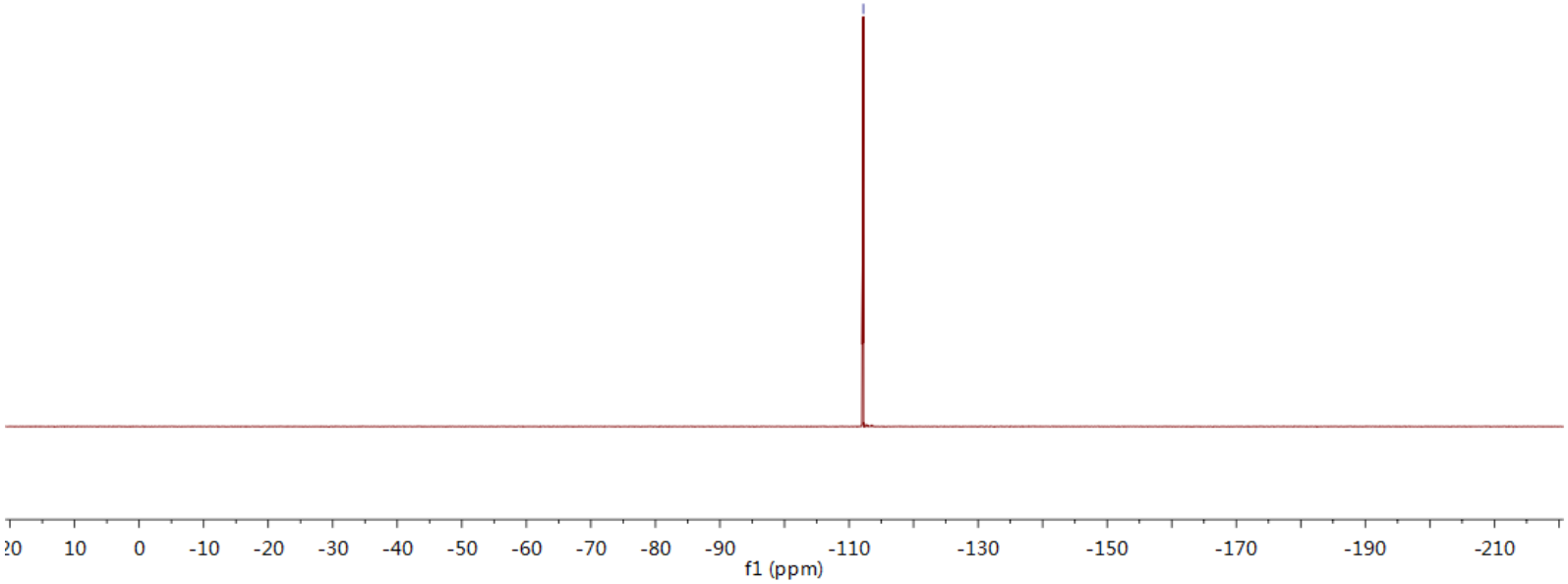


8l ^{13}C NMR (100 MHz, $CDCl_3$)

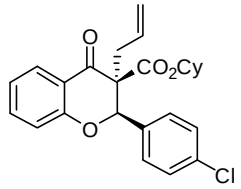
19F NMR HZ-5-97A in CDCl3



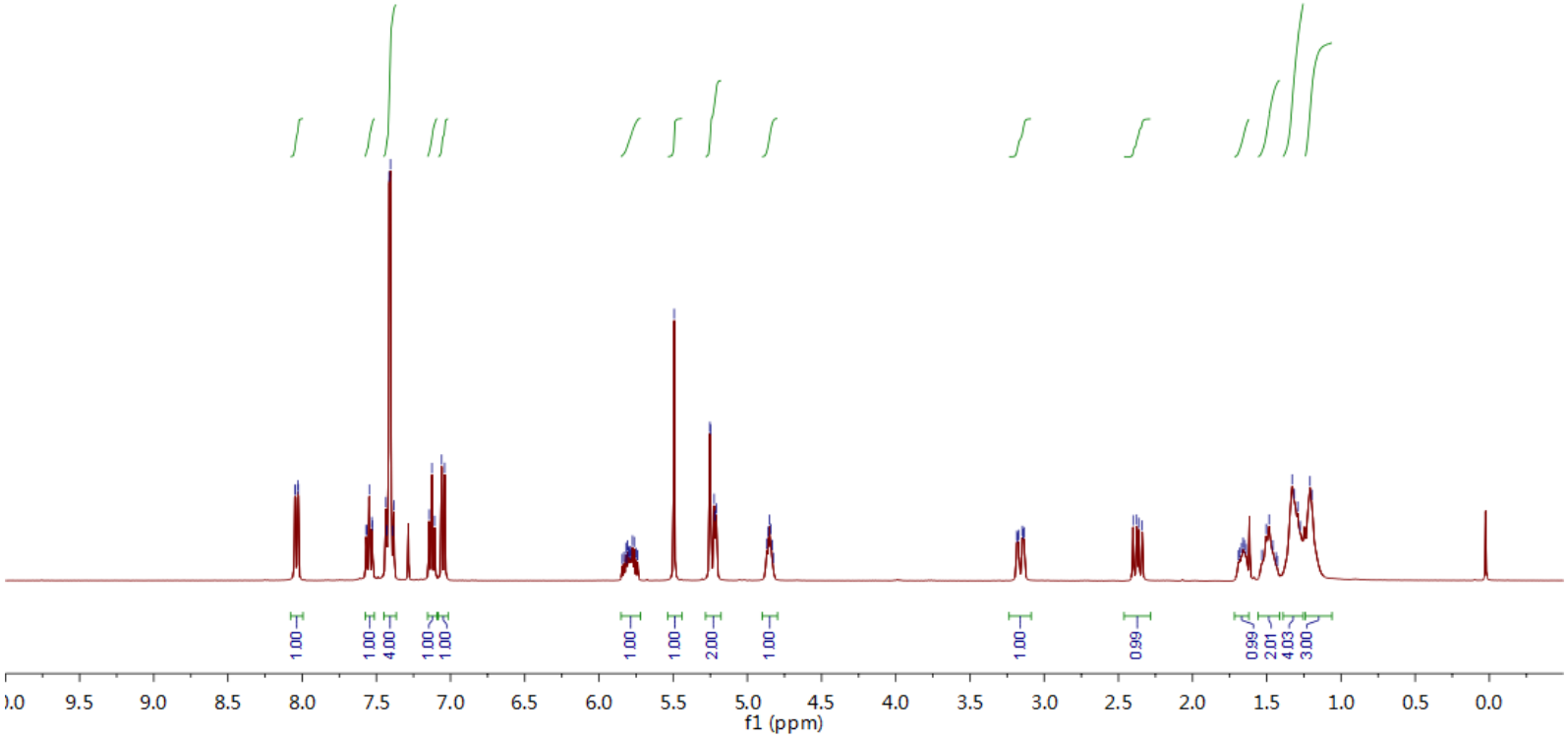
8l ^{19}F NMR (376 MHz, $CDCl_3$)



1H NMR HZ-6-4 in CDCl3

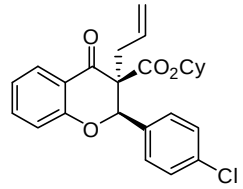


8m ^{1}H NMR (400 MHz, $CDCl_3$)

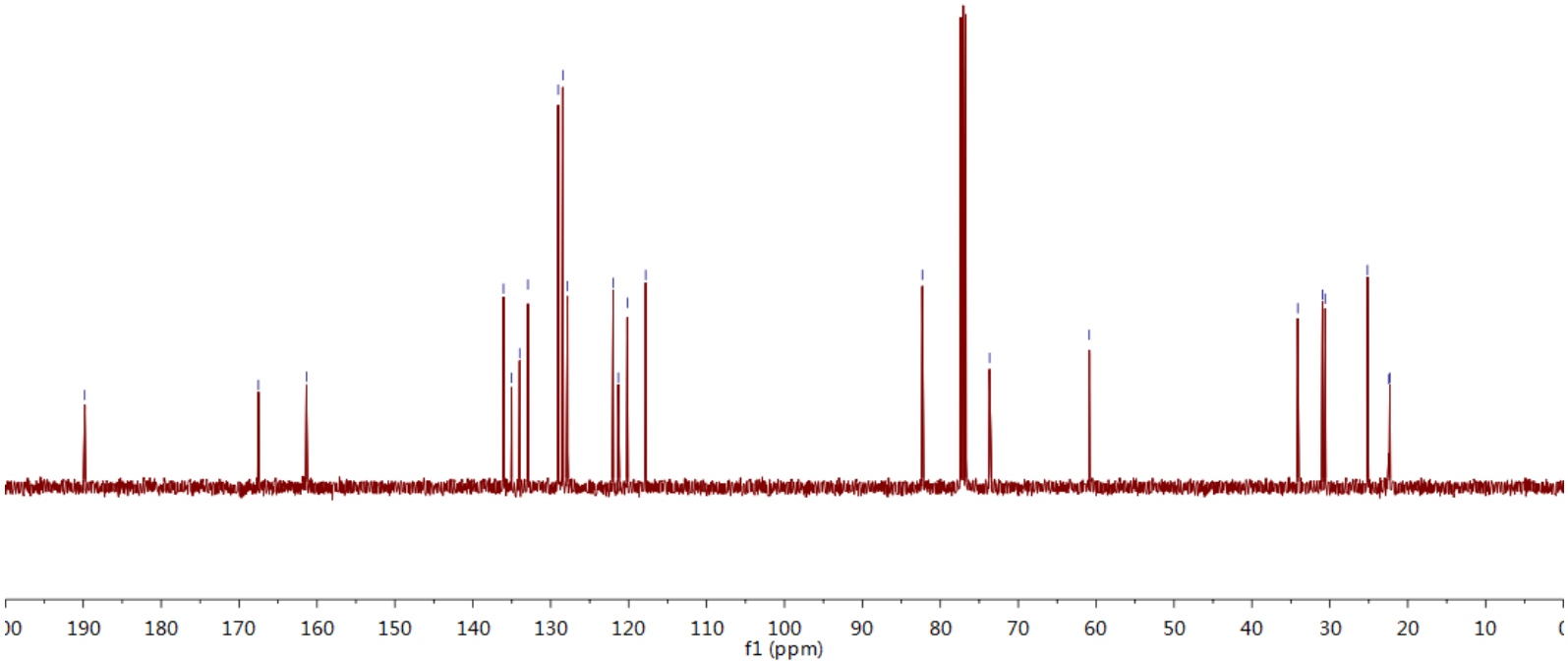


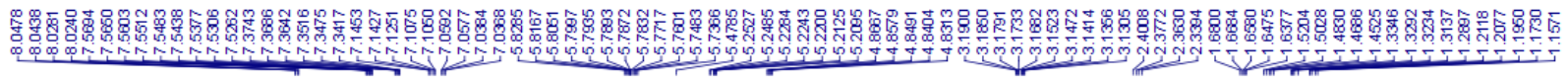
189.81
167.52
161.36
136.06
135.02
133.98
132.92
129.05
128.44
127.84
121.98
121.32
120.17
117.82
82.30
73.67
60.88
34.12
30.95
30.60
25.16
22.42
22.30

13C NMR HZ-6-4 in CDCl3

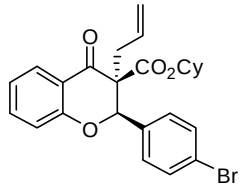


8m ^{13}C NMR (100 MHz, $CDCl_3$)

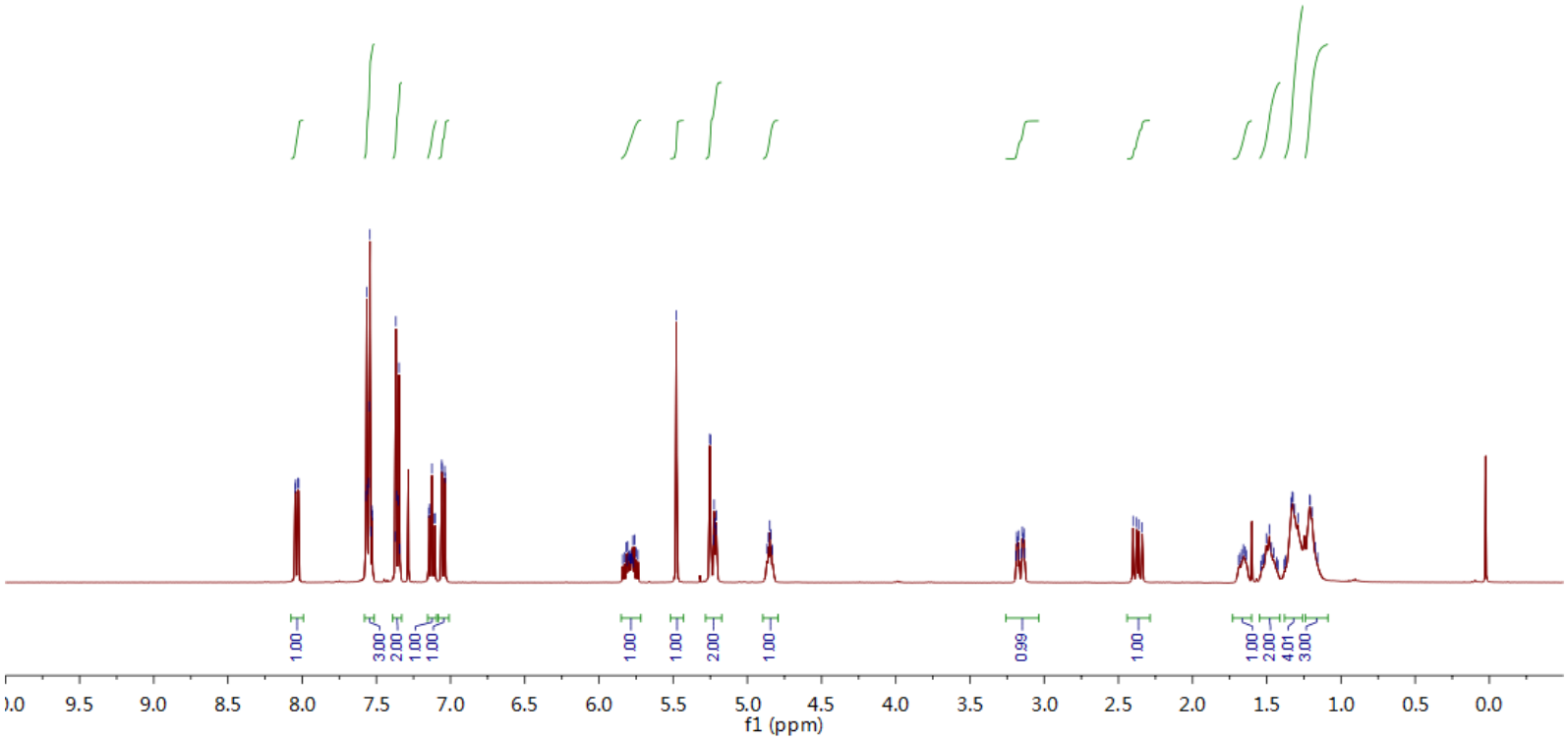


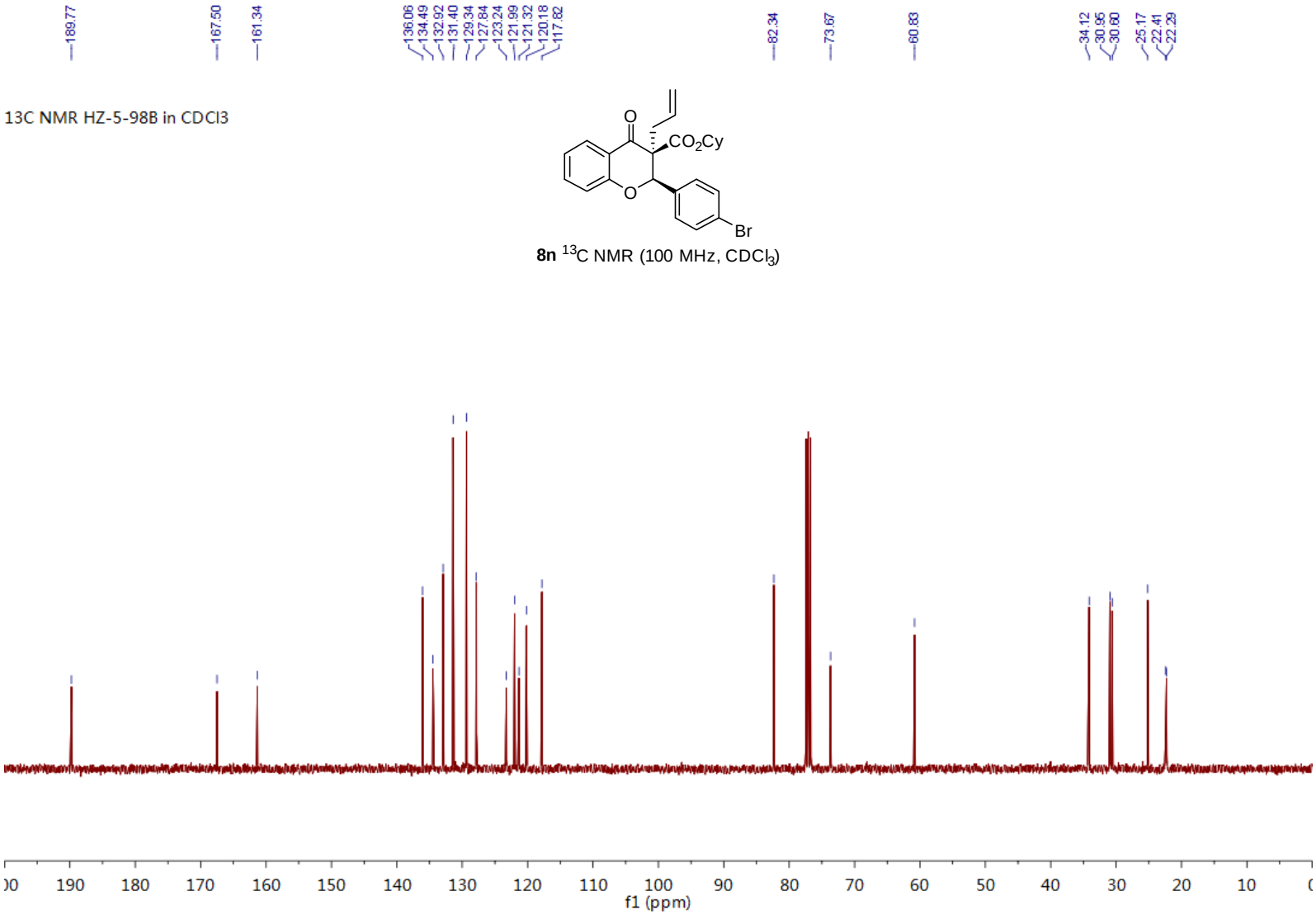


1H NMR HZ-5-98B in CDCl3



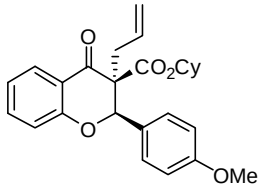
8n ^{1}H NMR (400 MHz, $CDCl_3$)



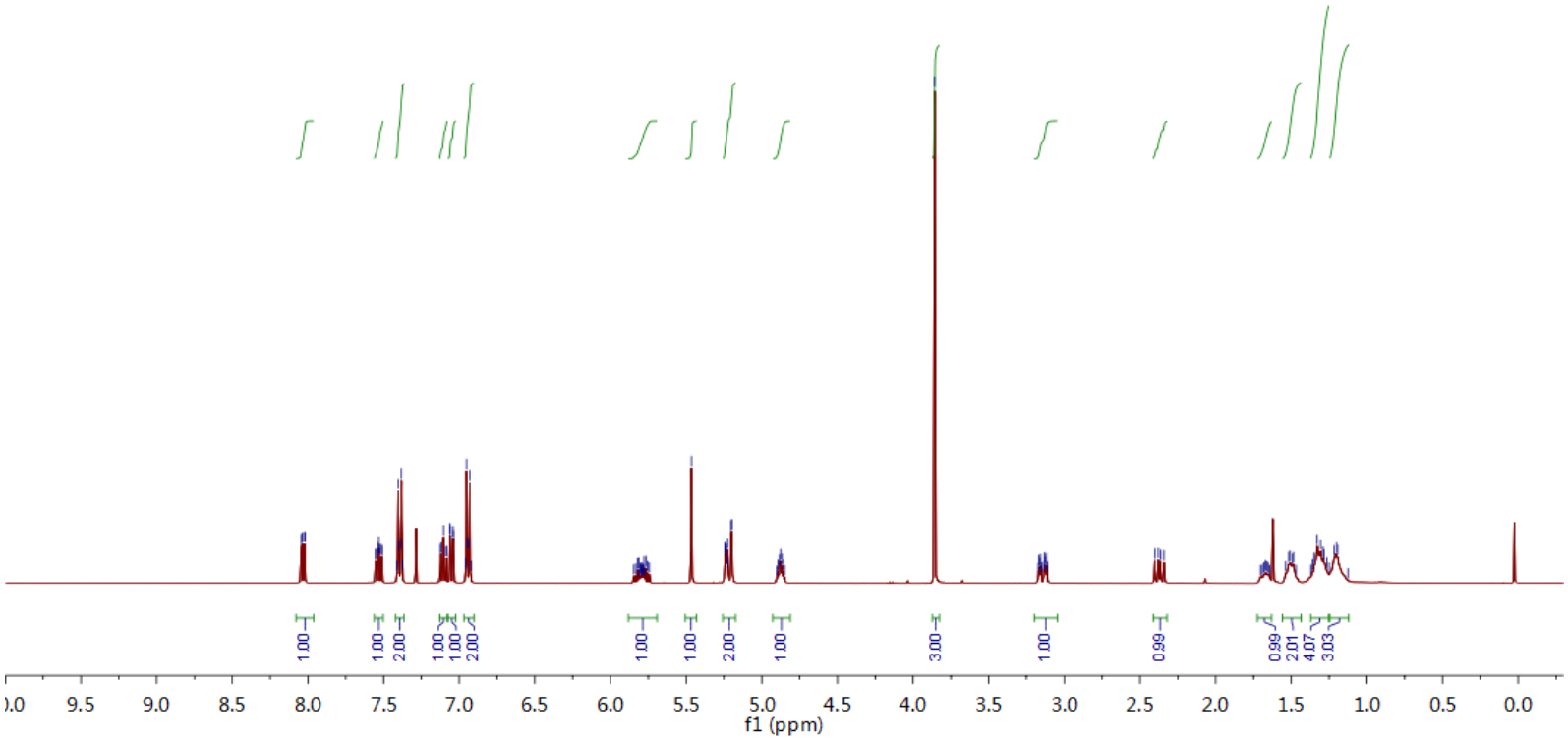


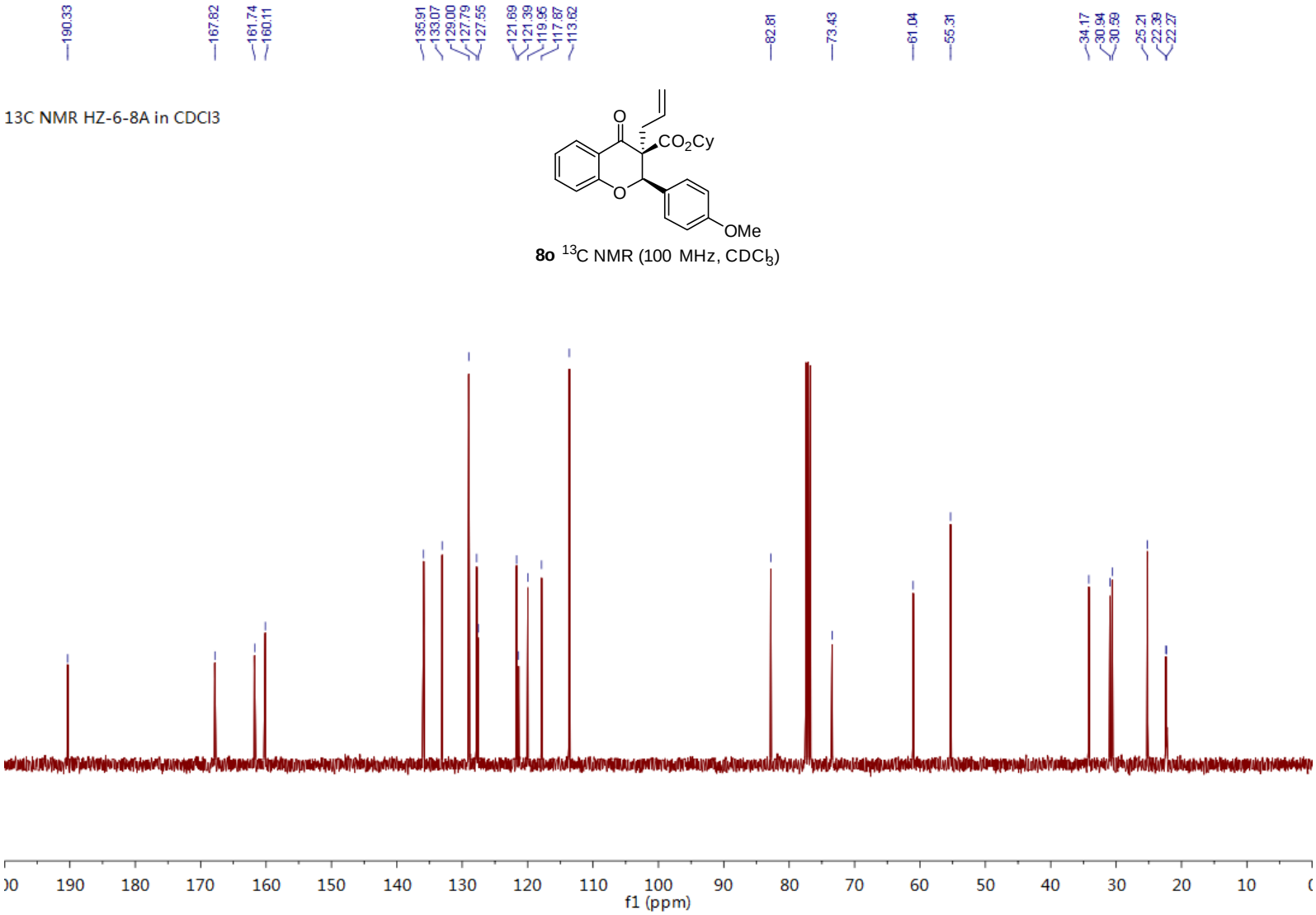
8n ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-8A in CDCl3

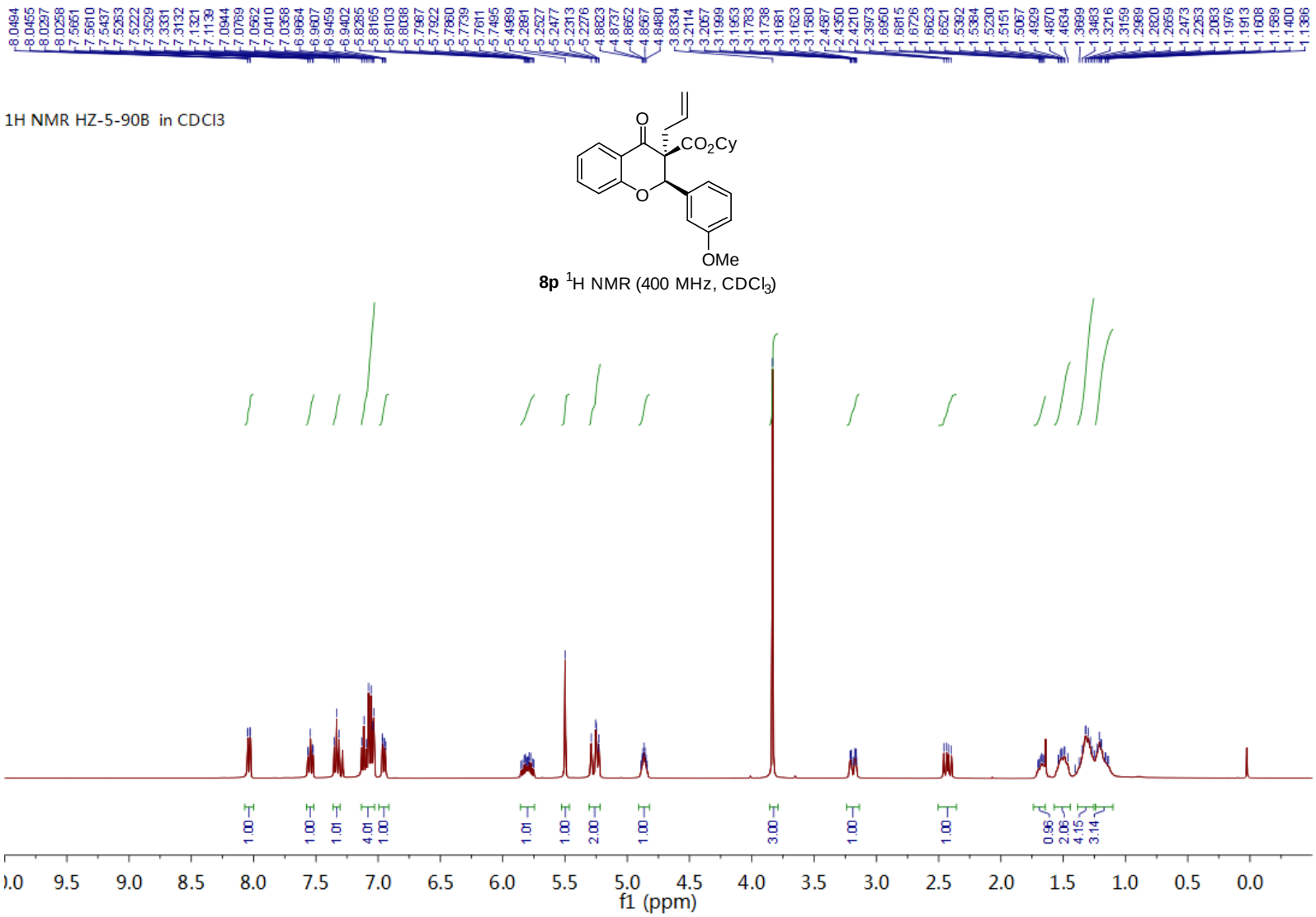


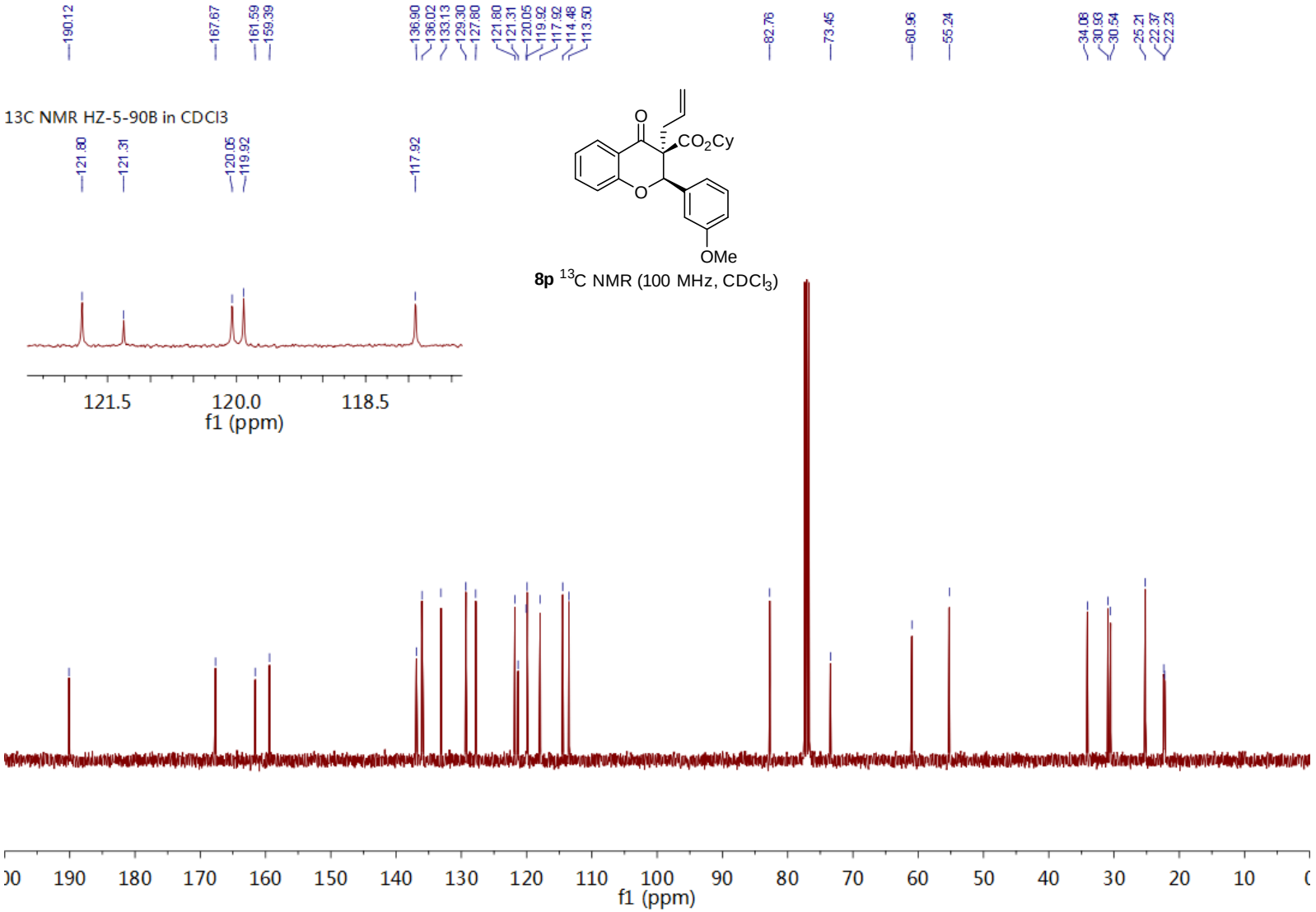
8o ^{1}H NMR (400 MHz, $CDCl_3$)



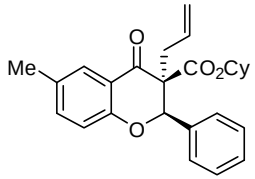


8o ^{13}C NMR (100 MHz, $CDCl_3$)

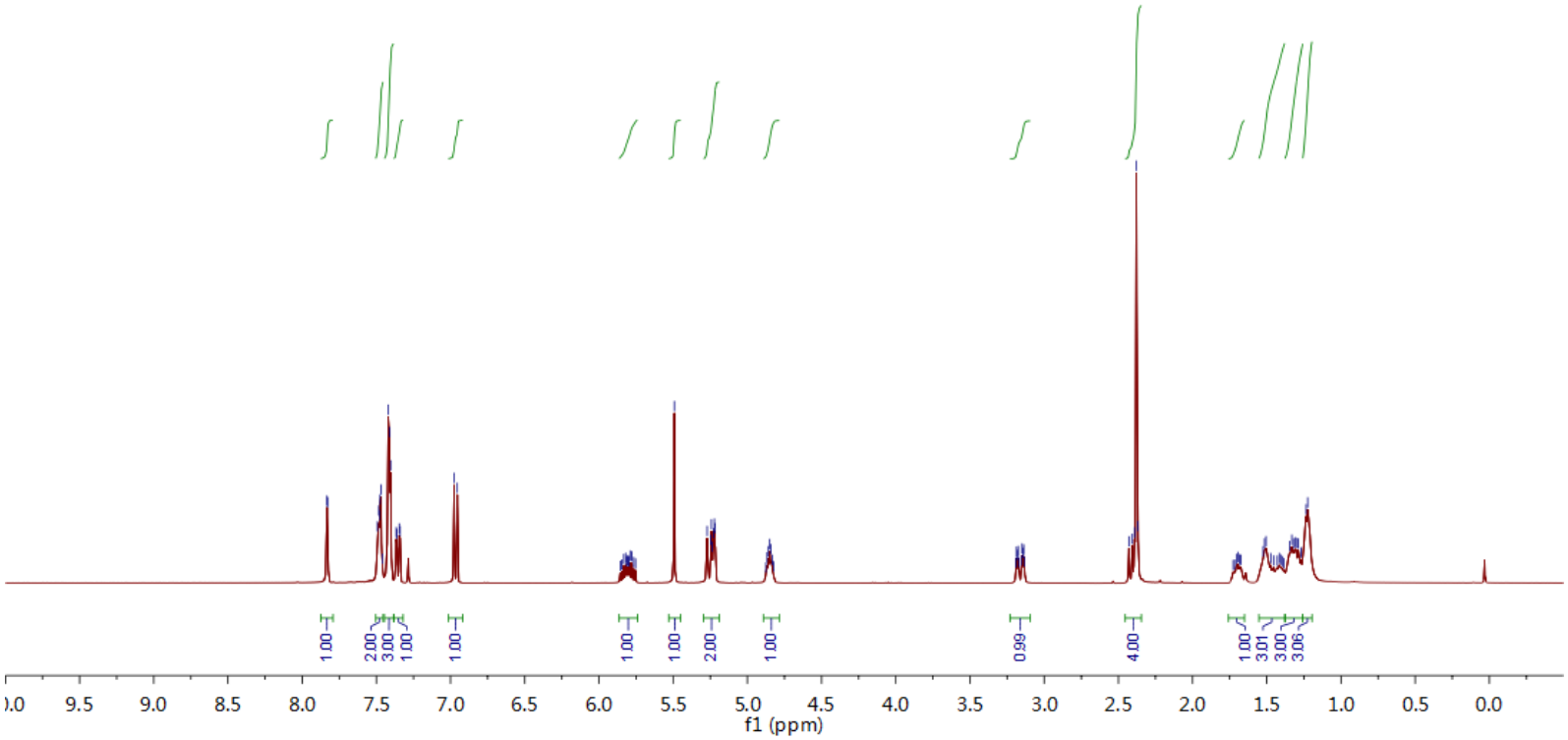

1H NMR HZ-5-90B in CDCl3
O
CO2Cy
O
OMe
8p 1H NMR (400 MHz, CDCl3)
f1 (ppm)

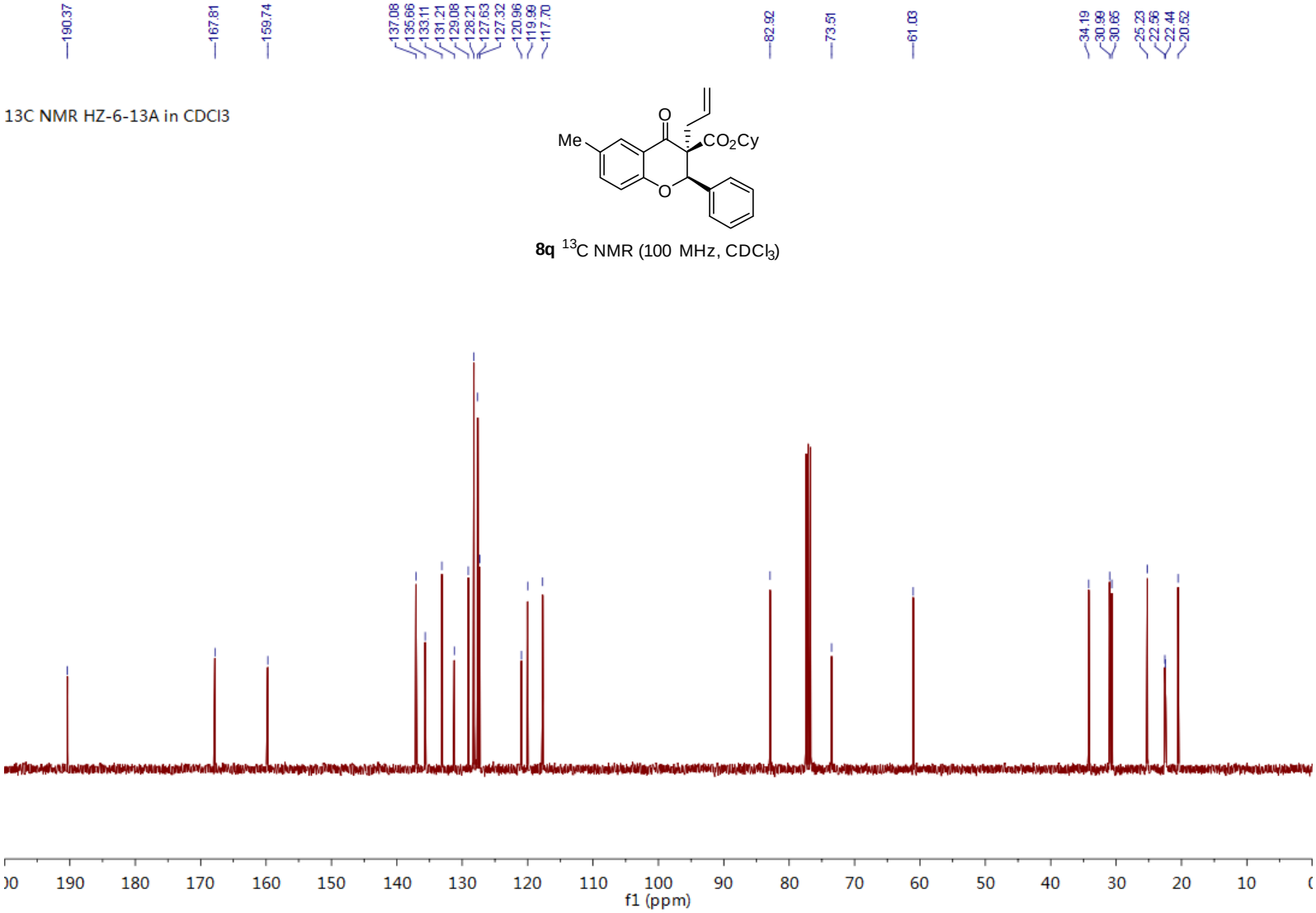

190.12
167.67
161.59
159.39
136.90
136.02
133.13
129.30
127.80
121.80
121.31
120.05
119.92
117.92
114.48
113.50
82.76
73.45
60.96
55.24
34.08
30.93
30.54
25.21
22.37
22.23
13C NMR HZ-5-90B in CDCl3
121.80
121.31
120.05
119.92
117.92
O
CO2Cy
O
OMe
8p 13C NMR (100 MHz, CDCl3)
121.5
120.0
118.5
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1H NMR HZ-6-13A in CDCl3



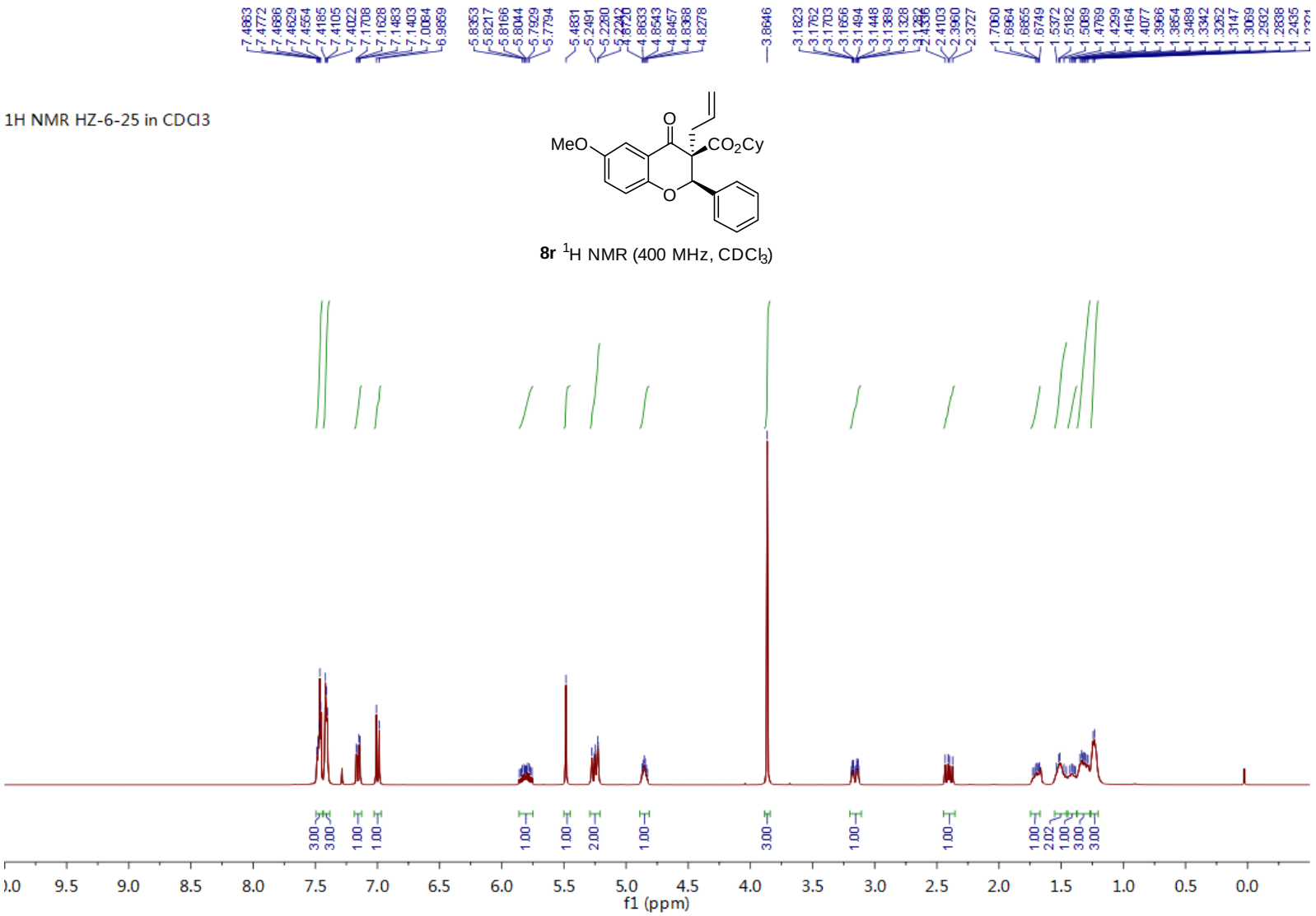
8q ^{1}H NMR (400 MHz, $CDCl_3$)





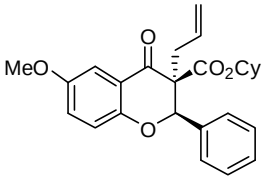
8q ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-25 in CDCl3

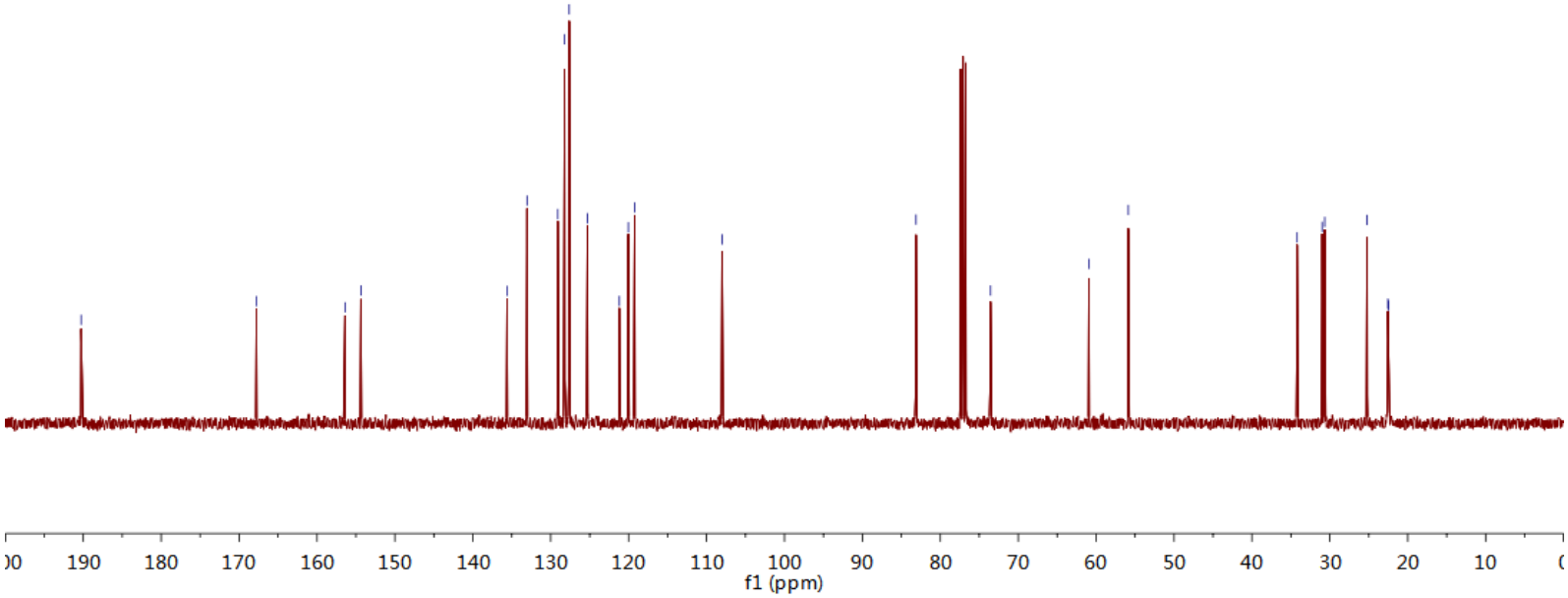


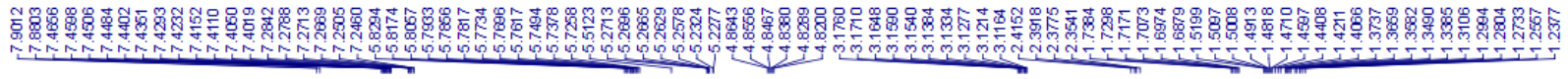
8r ^{1}H NMR (400 MHz, $CDCl_3$)

13C NMR HZ-6-25 in CDCl3

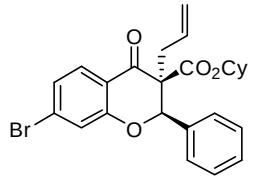


8r ^{13}C NMR (100 MHz, $CDCl_3$)

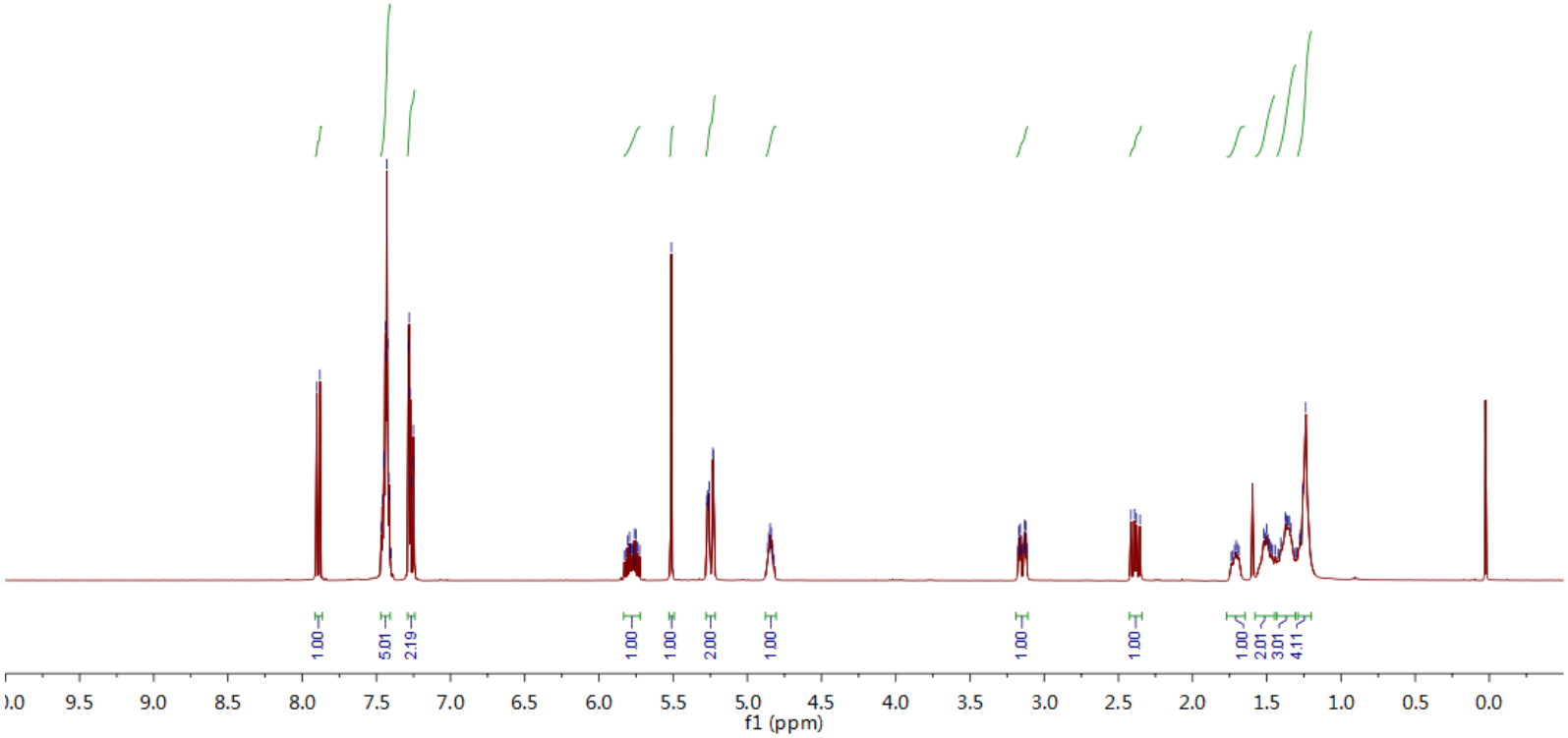




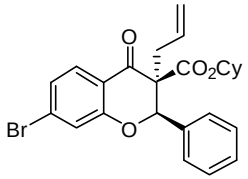
1H NMR HZ-6-14B in CDCl3



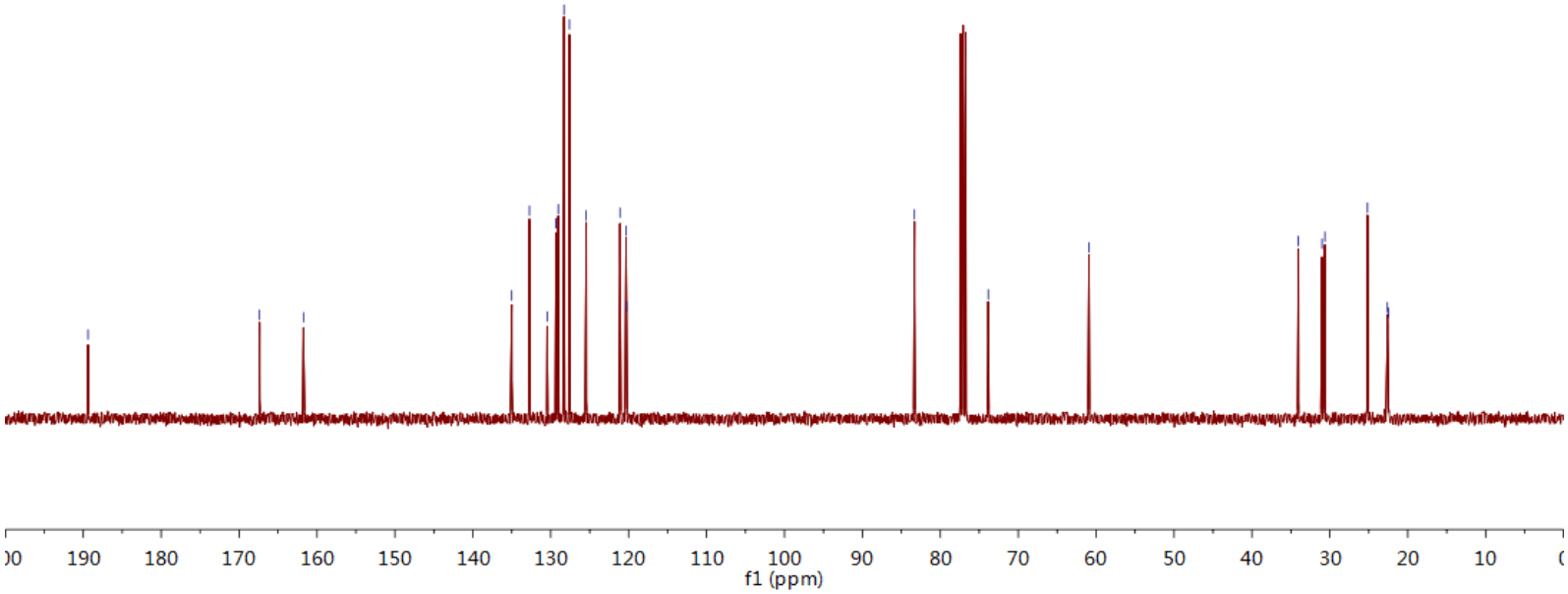
8s ^{1}H NMR (400 MHz, $CDCl_3$)



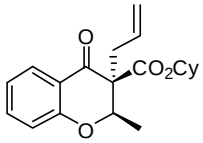
13C NMR HZ-6-14B in CDCl3



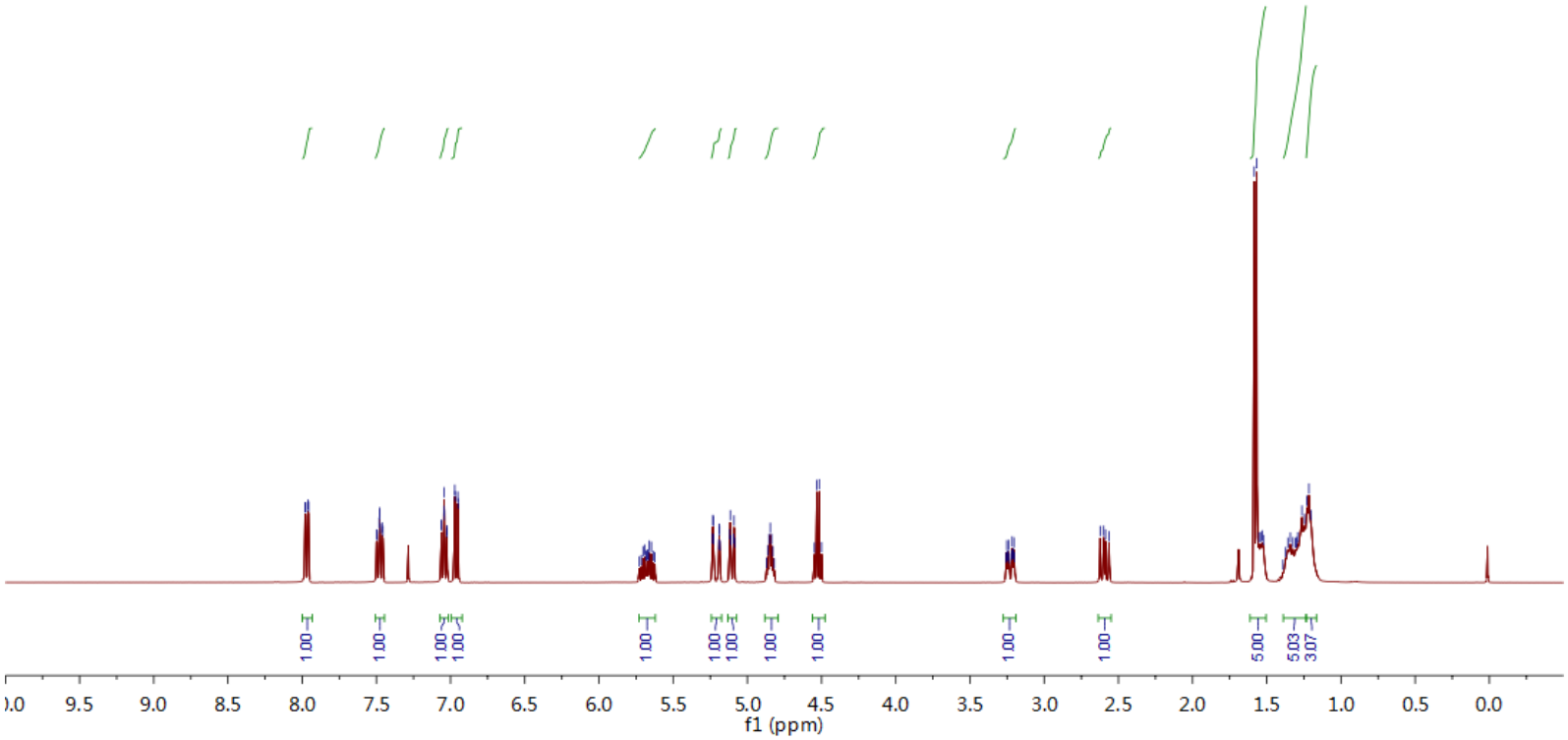
8s ^{13}C NMR (100 MHz, $CDCl_3$)

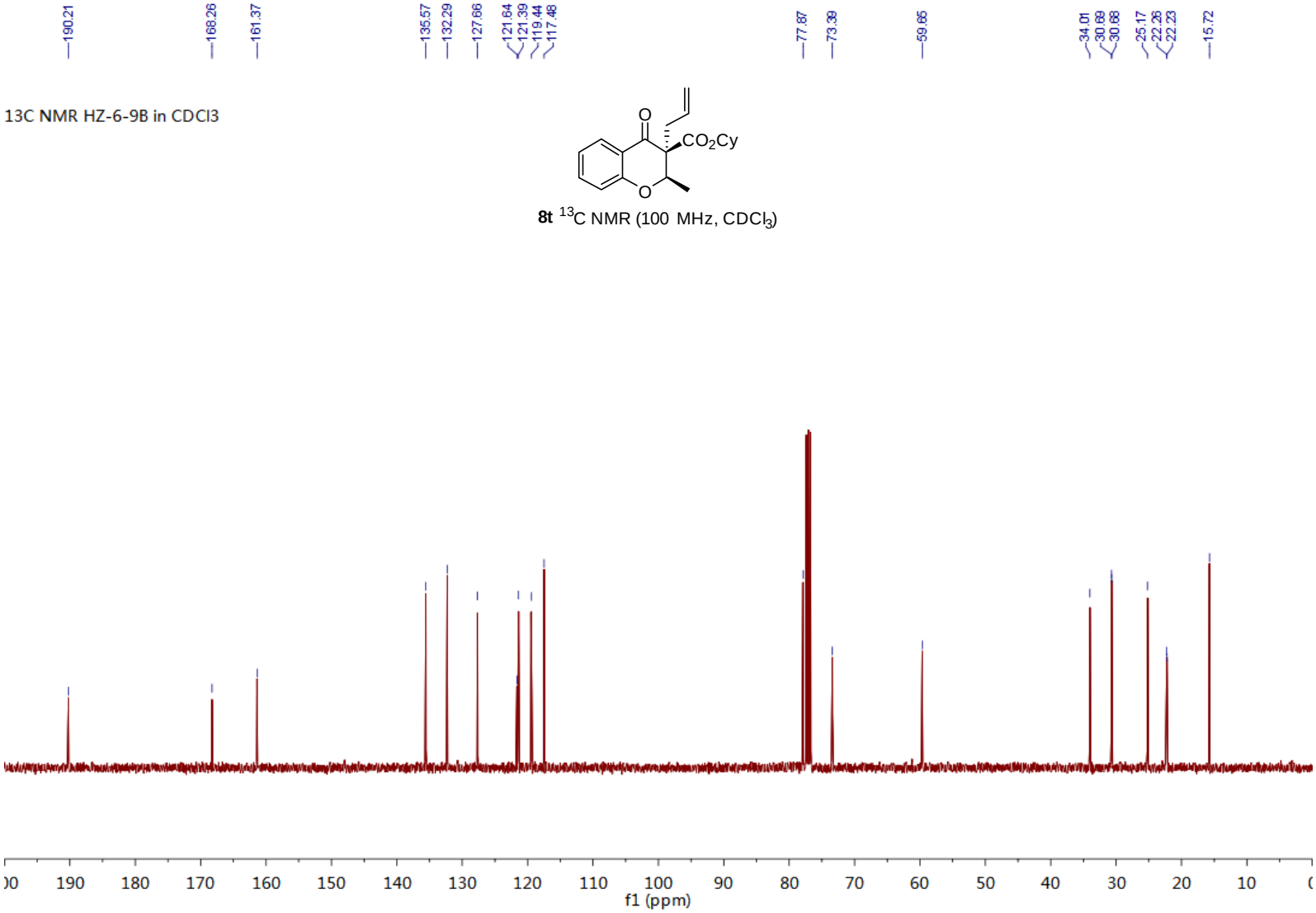


1H NMR HZ-6-9B in CDCl3



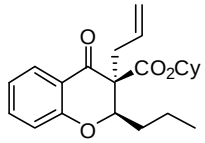
8t ^{1}H NMR (400 MHz, $CDCl_3$)



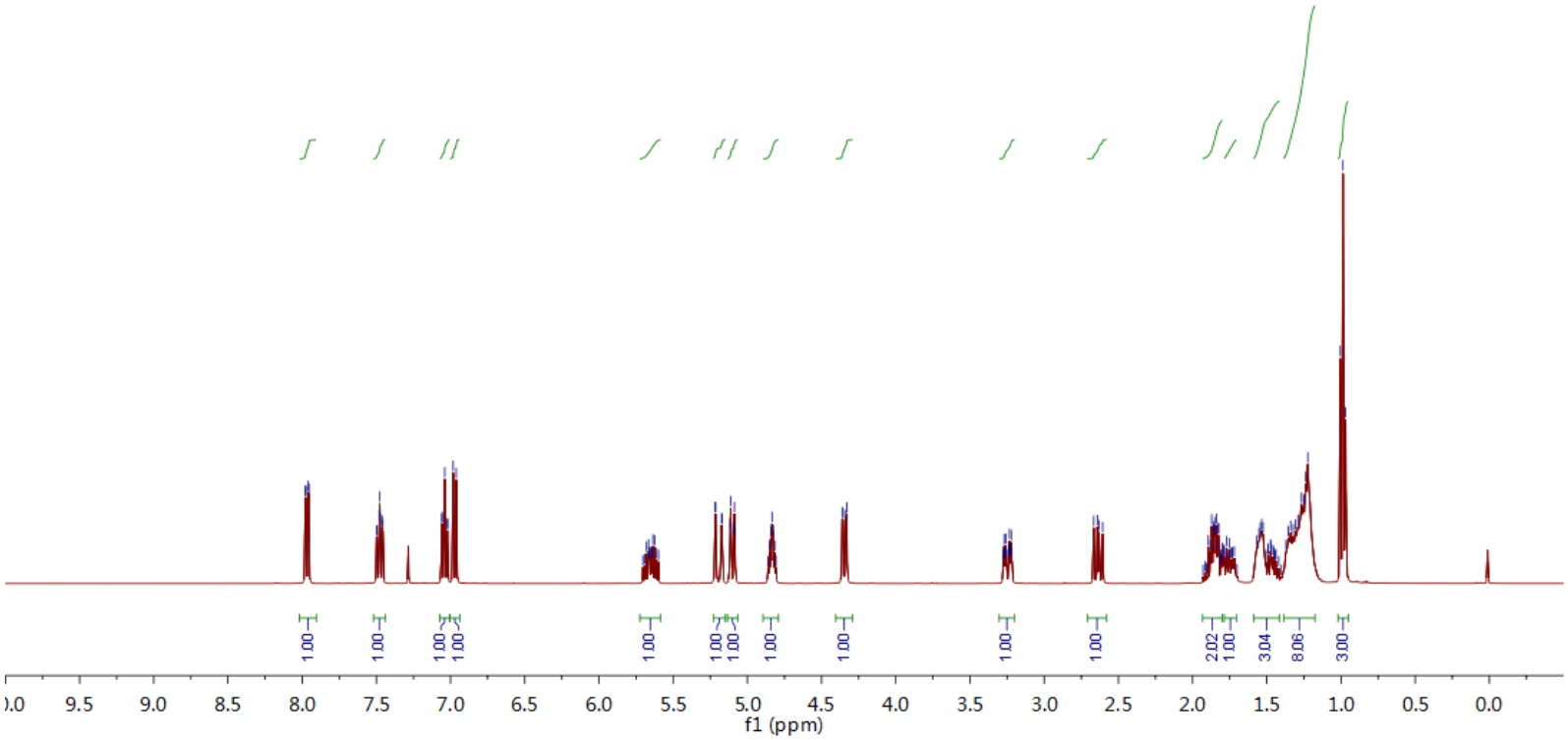


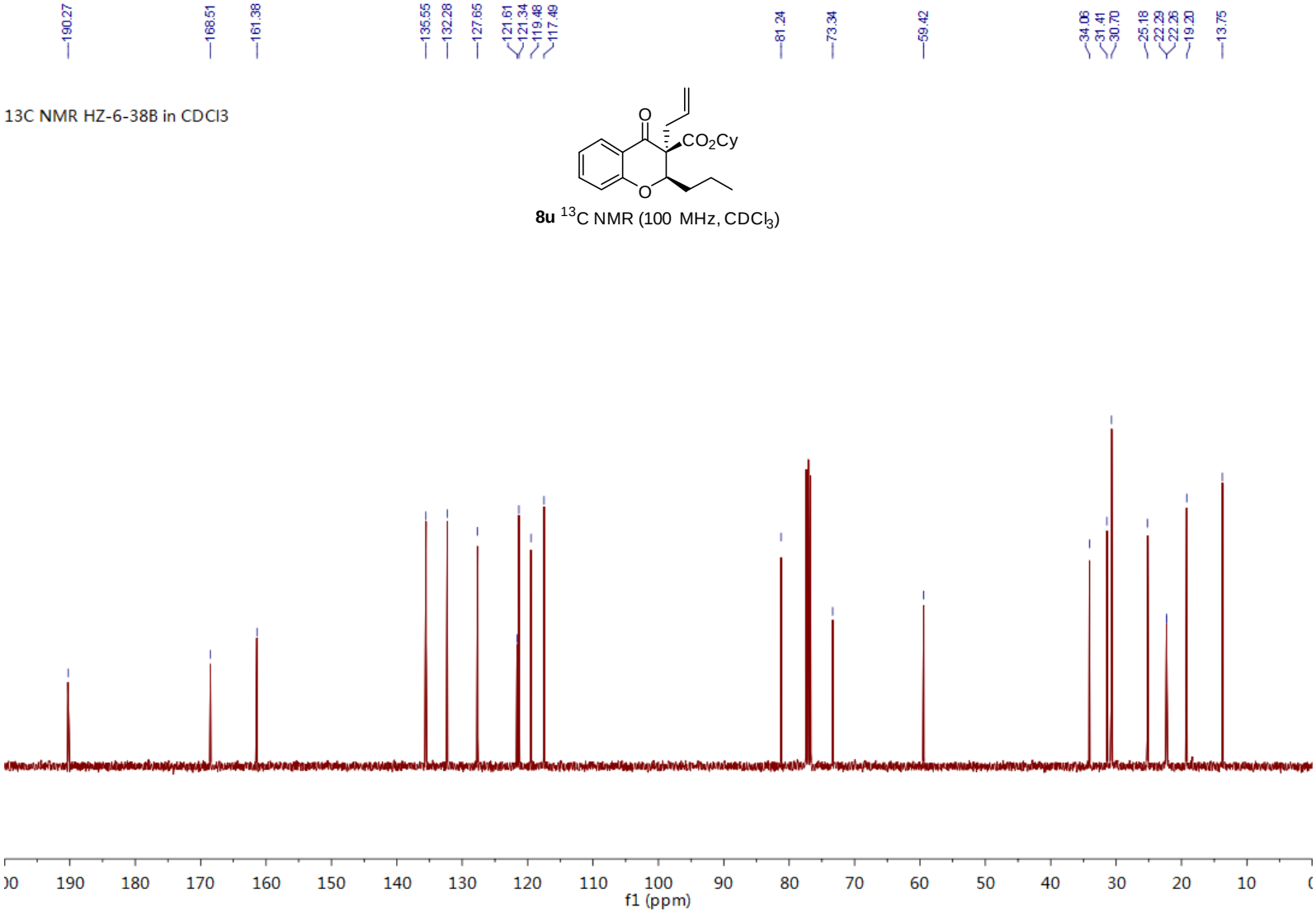
8t ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-38B in CDCl3

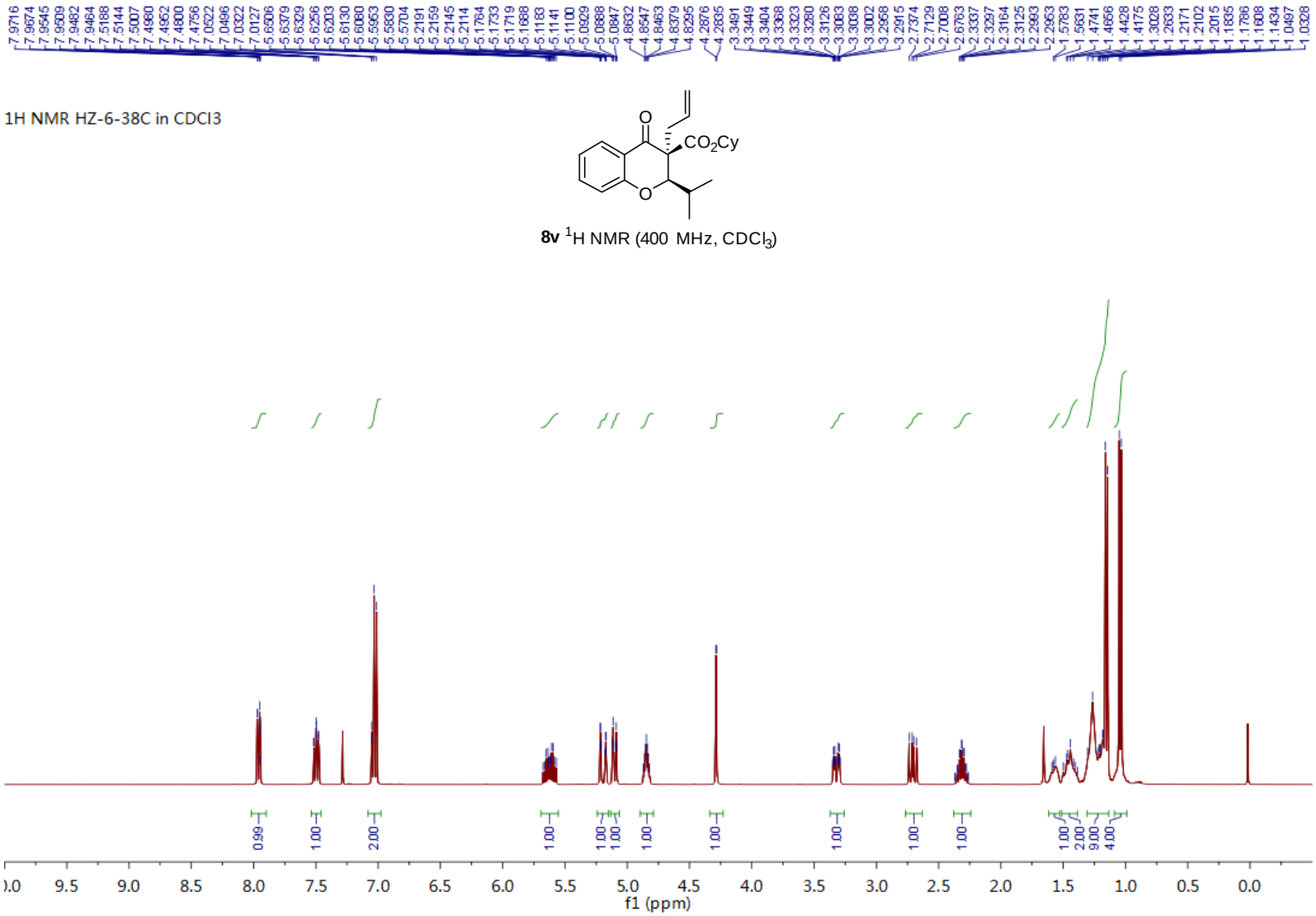


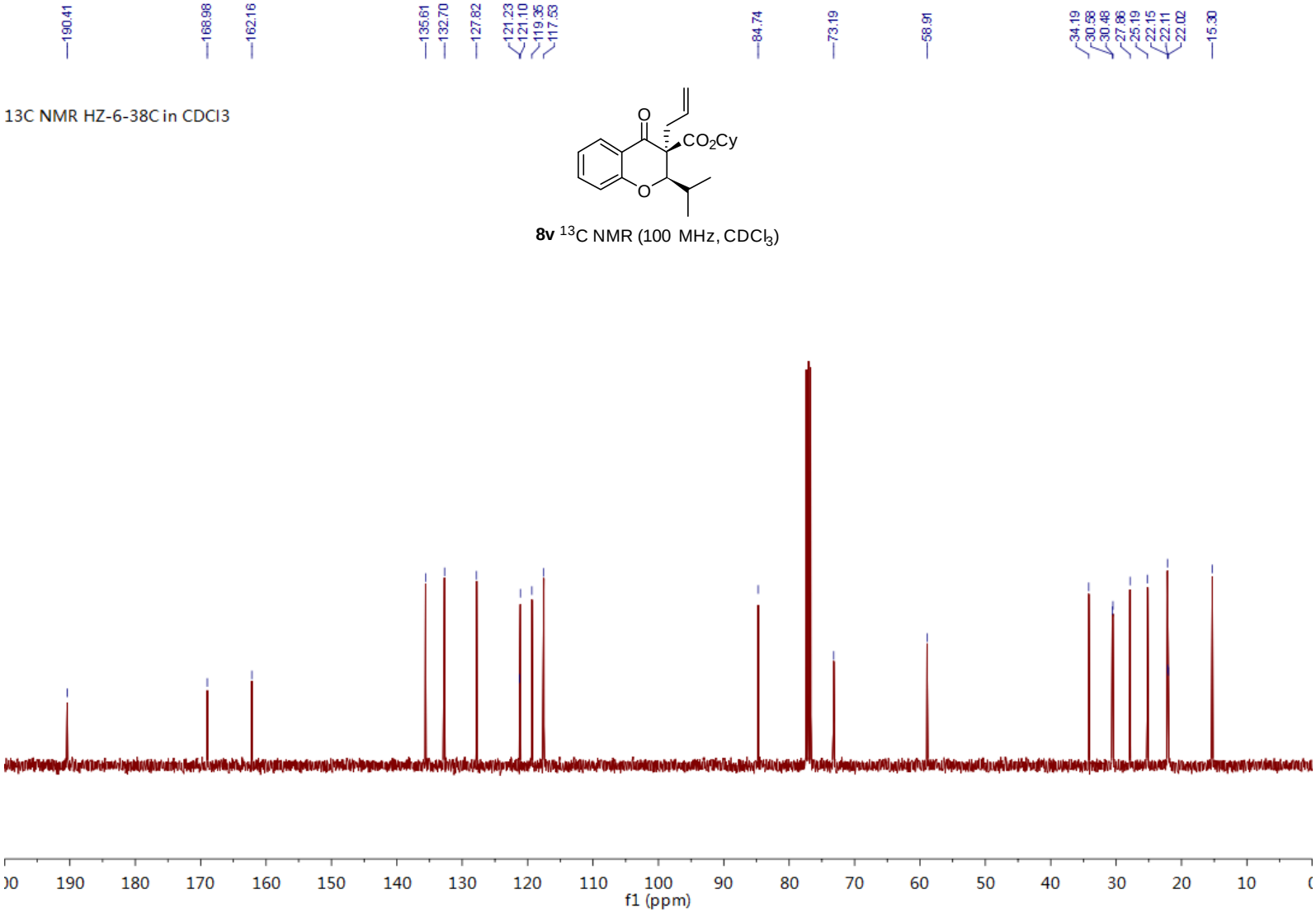
8u ^{1}H NMR (400 MHz, $CDCl_3$)





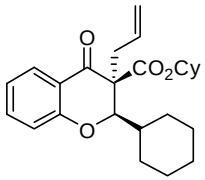
8u ^{13}C NMR (100 MHz, $CDCl_3$)


7.9716
7.9674
7.9645
7.9509
7.9482
7.9464
7.5188
7.5144
7.5007
7.4960
7.4952
7.4800
7.4756
7.0522
7.0496
7.0322
7.0127
5.6506
5.6379
5.6329
5.6256
5.6203
5.6130
5.6080
5.5953
5.5830
5.5704
5.2191
5.2159
5.2145
5.2114
5.1764
5.1733
5.1719
5.1688
5.1183
5.1141
5.1100
5.0929
5.0888
5.0847
4.8632
4.8547
4.8463
4.8379
4.8295
4.2876
4.2835
3.3491
3.3449
3.3404
3.3368
3.3323
3.3280
3.3126
3.3063
3.3038
3.3002
3.2968
3.2915
2.7374
2.7129
2.7008
2.6763
2.3337
2.3297
2.3164
2.3125
2.2993
2.2953
1.5783
1.5631
1.4741
1.4656
1.4428
1.4175
1.3028
1.2633
1.2171
1.2102
1.2015
1.1835
1.1786
1.1608
1.1434
1.0497
1.0328
1H NMR HZ-6-38C in CDCl3
O
CO2Cy
O
8v 1H NMR (400 MHz, CDCl3)
0.99
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
9.00
4.00
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)

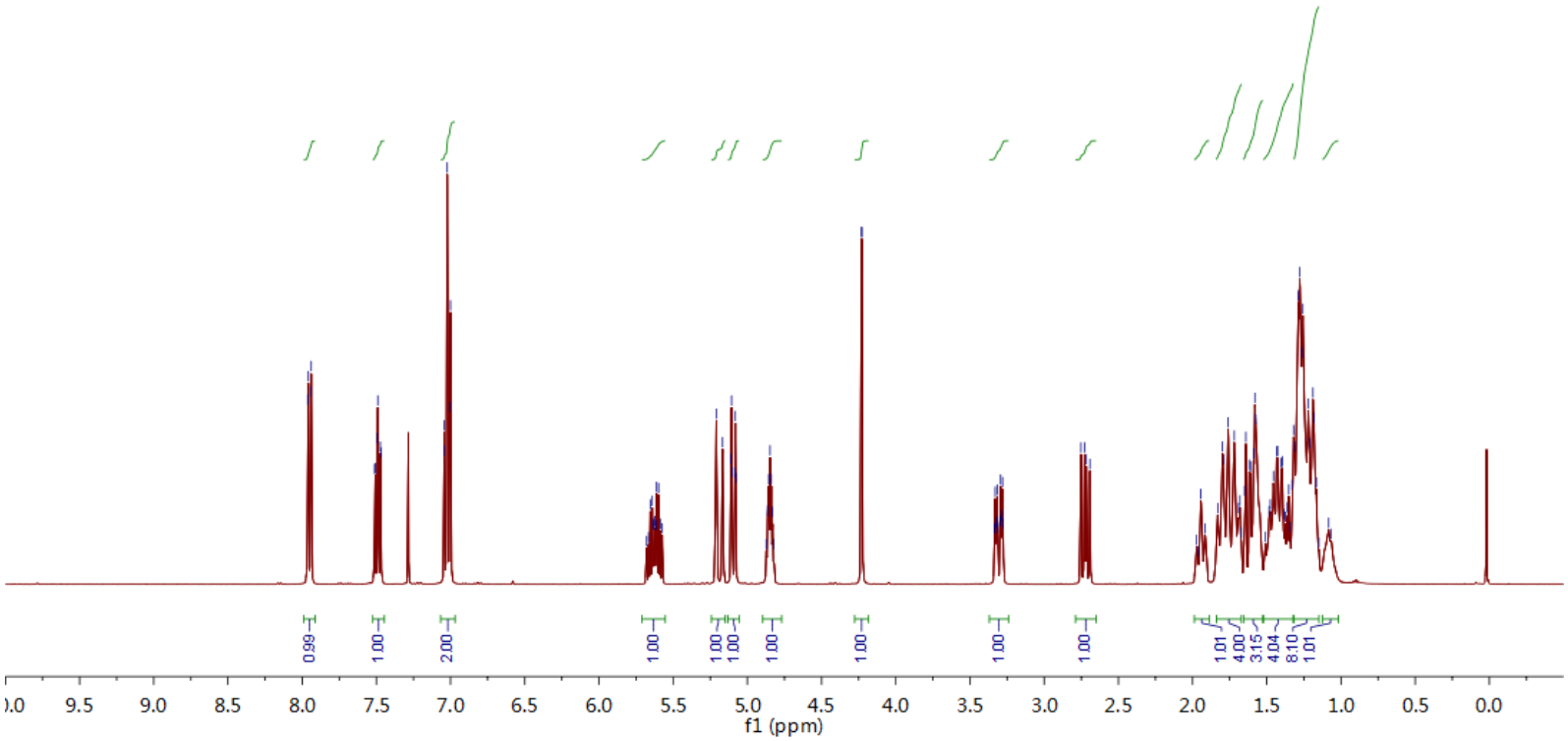


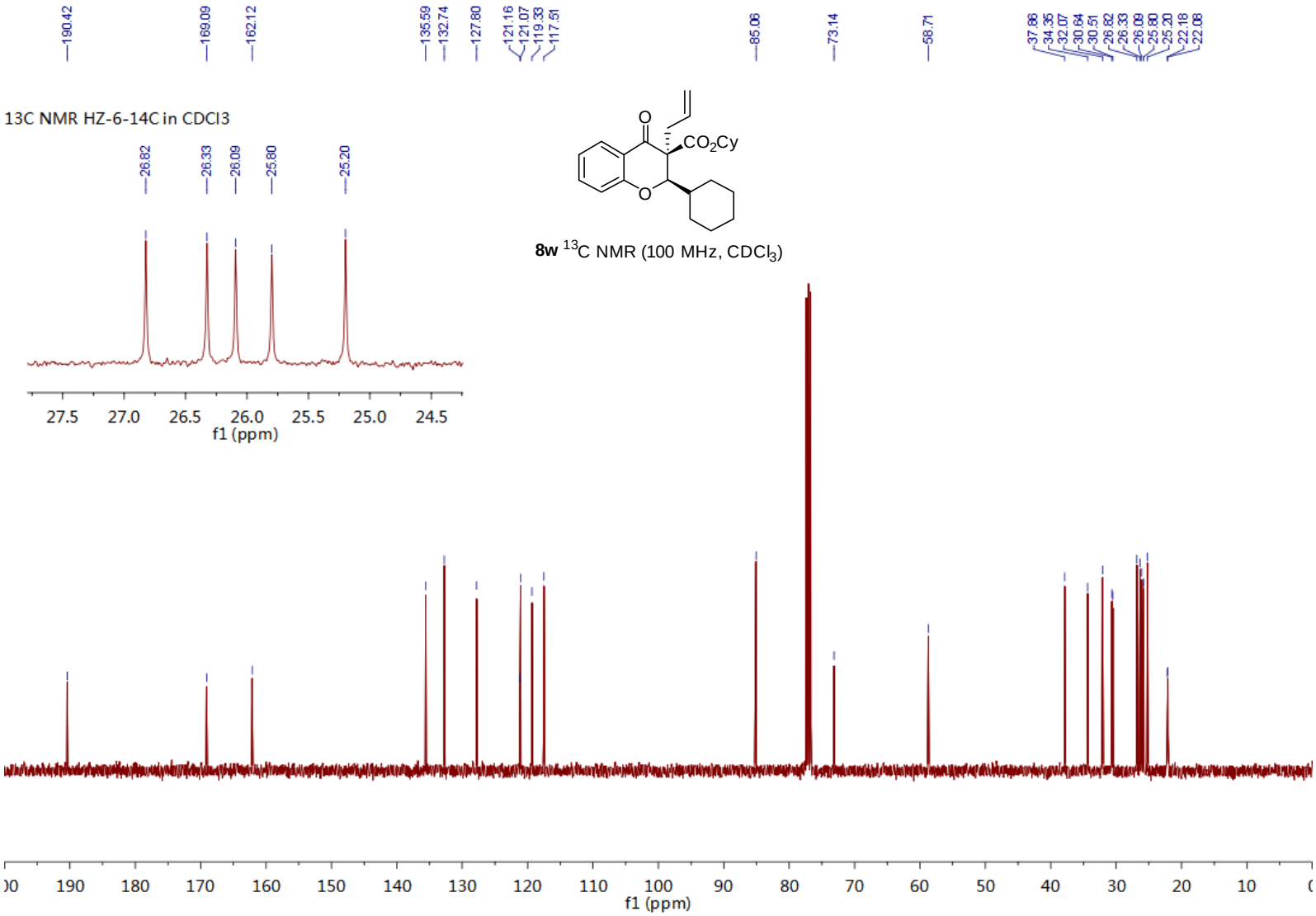
8v ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-14C in CDCl3

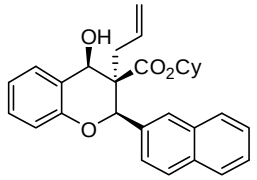


8w ^{1}H NMR (400 MHz, $CDCl_3$)

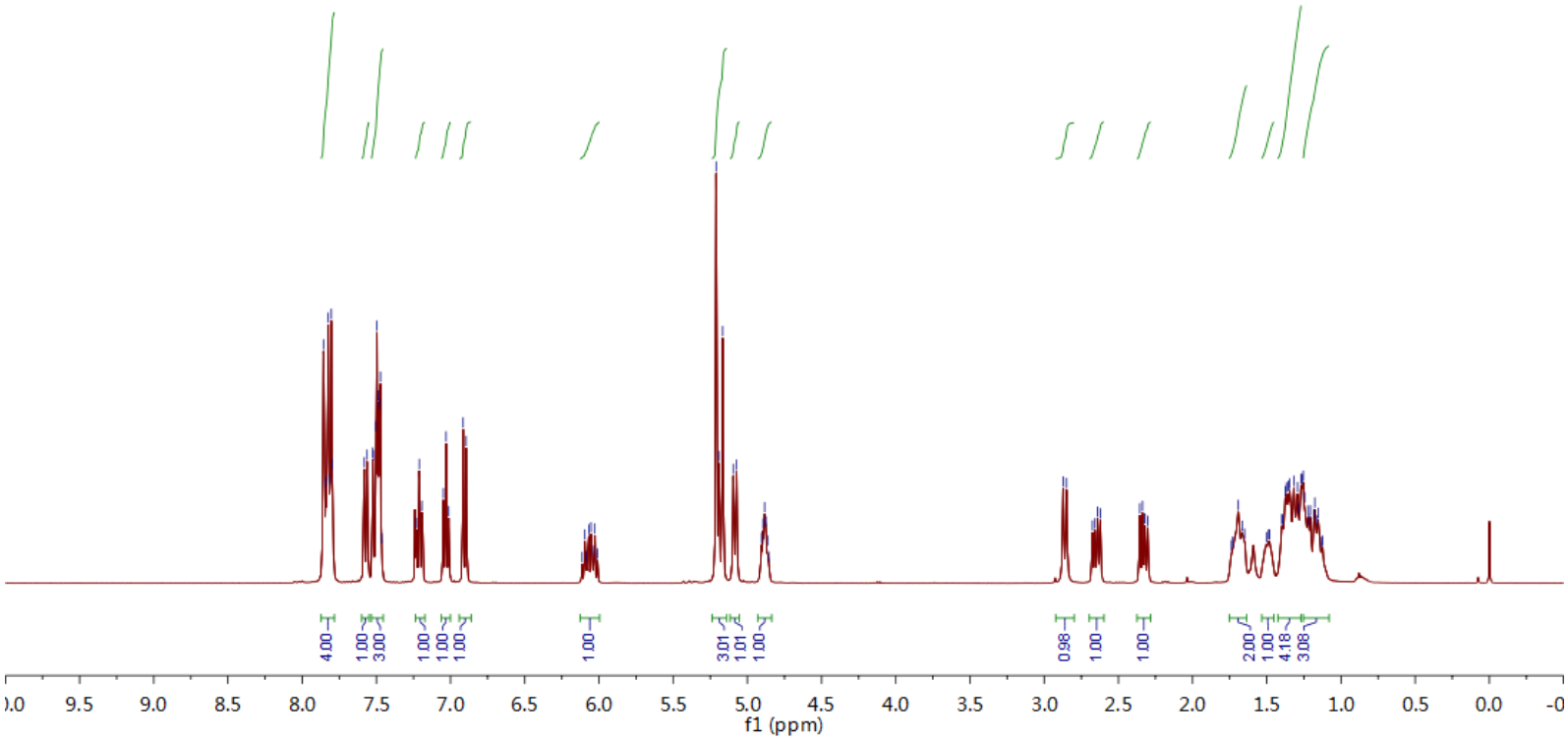


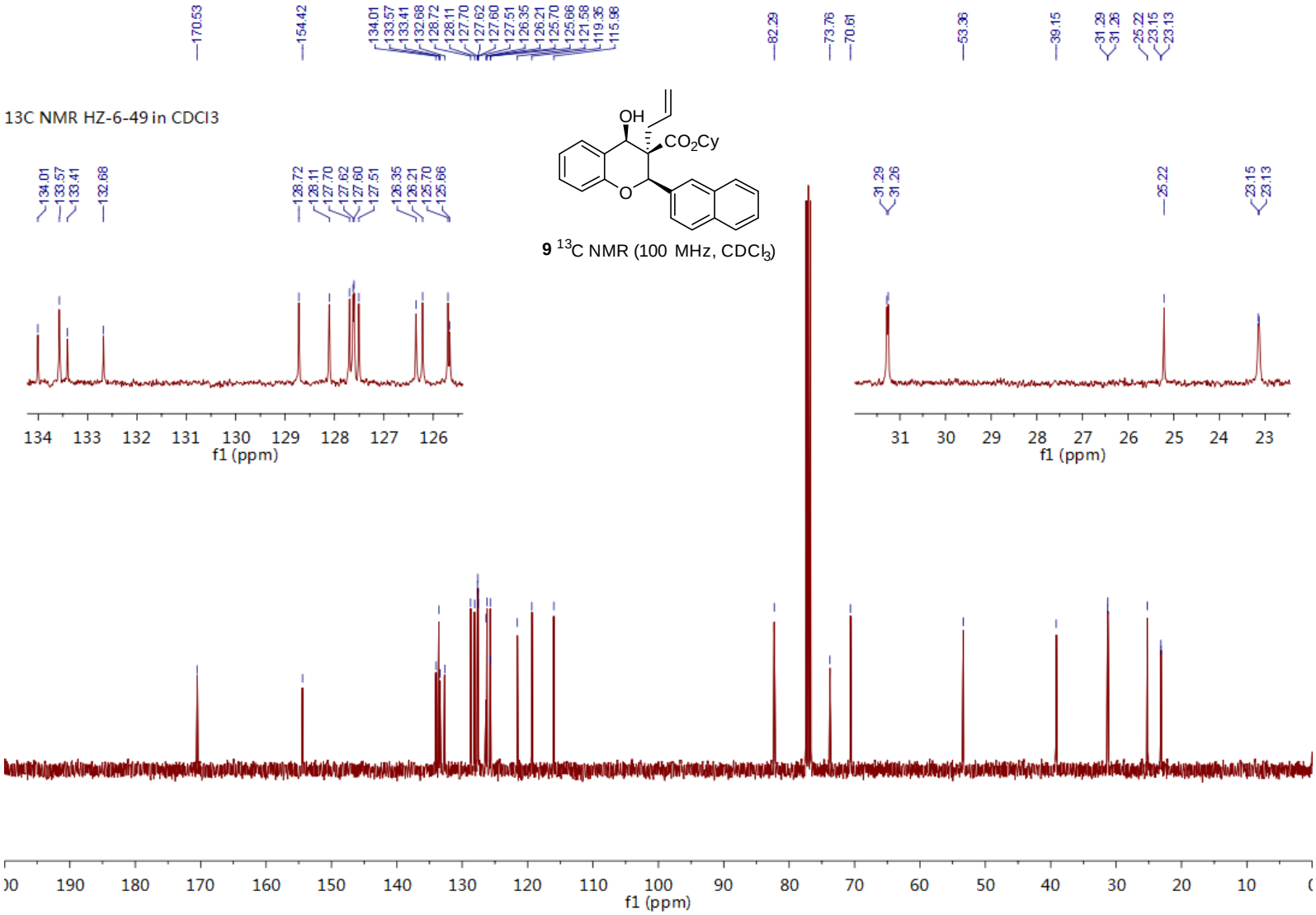

190.42
169.09
162.12
135.59
132.74
127.80
121.16
121.07
119.33
117.51
85.06
73.14
58.71
37.86
34.36
32.07
30.64
30.51
26.82
26.33
26.09
25.80
25.20
22.18
22.08
13C NMR HZ-6-14C in CDCl3
26.82
26.33
26.09
25.80
25.20
27.5
27.0
26.5
26.0
25.5
25.0
24.5
f1 (ppm)
O
CO2Cy
O
8w 13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1H NMR HZ-6-49 in CDCl3



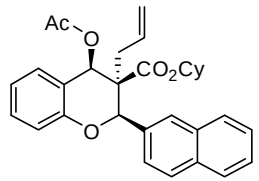
9 ^{1}H NMR (400 MHz, $CDCl_3$)



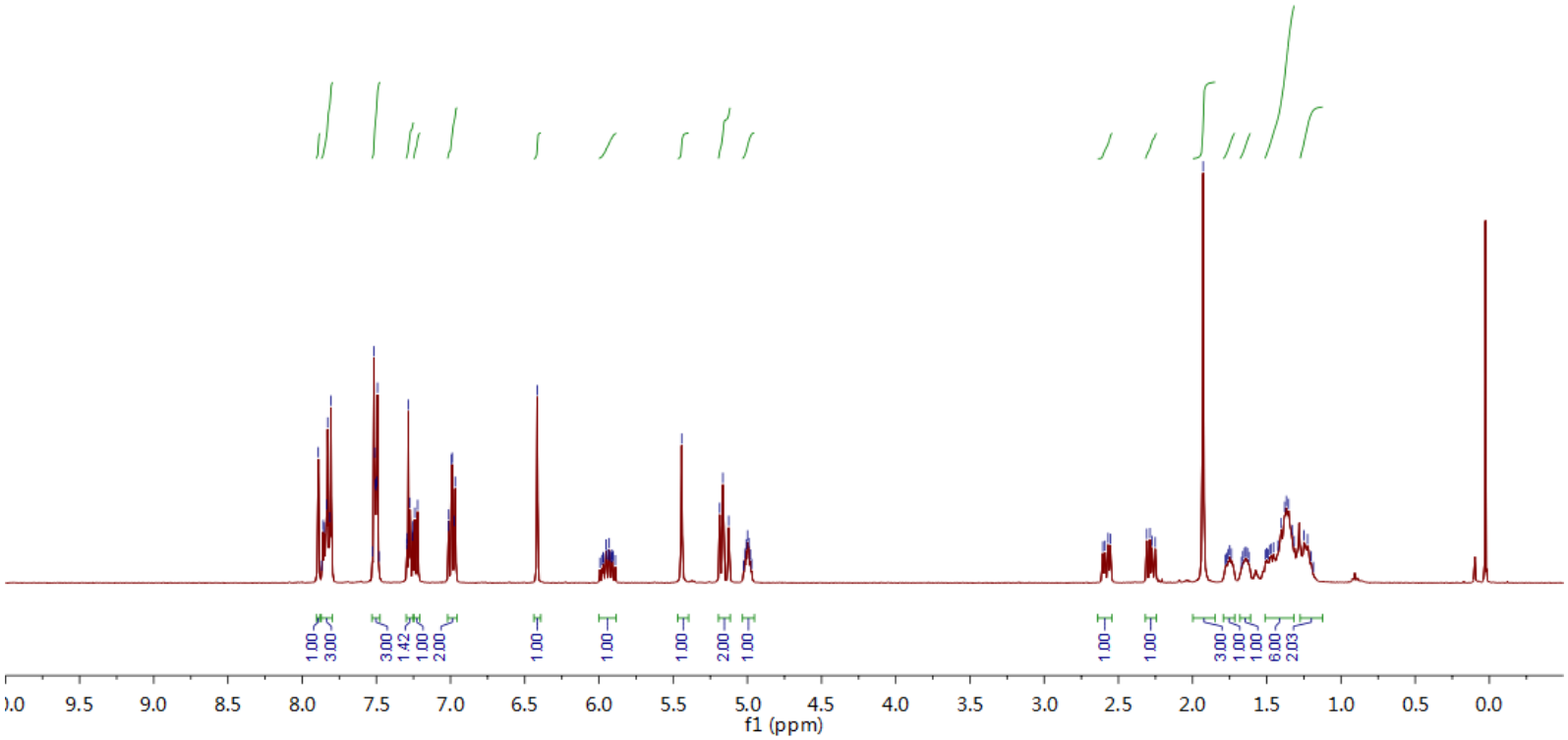


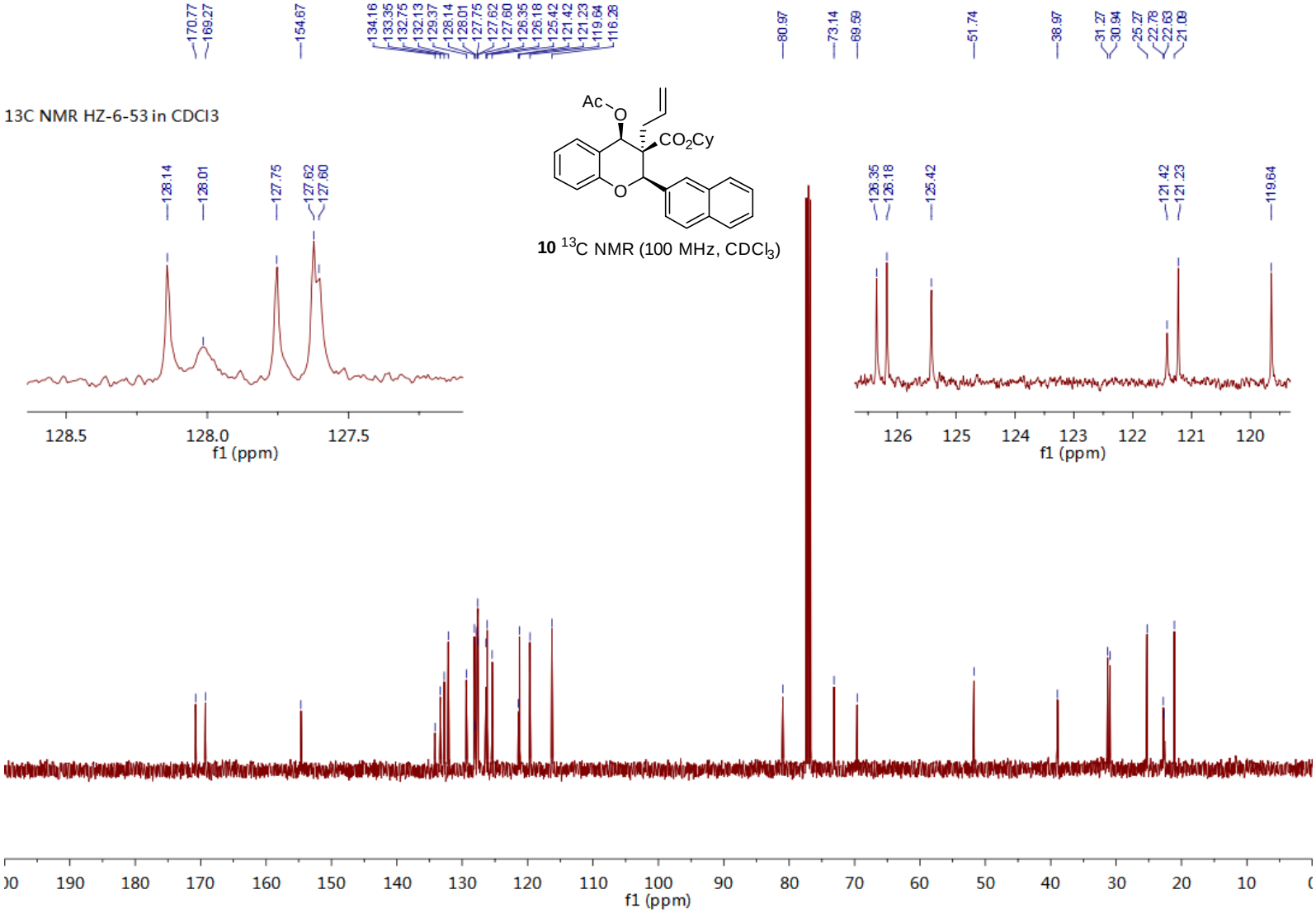
9 ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-53 in CDCl3



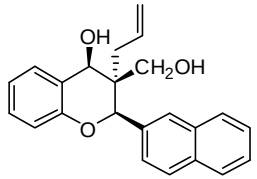
10 ^{1}H NMR (400 MHz, $CDCl_3$)



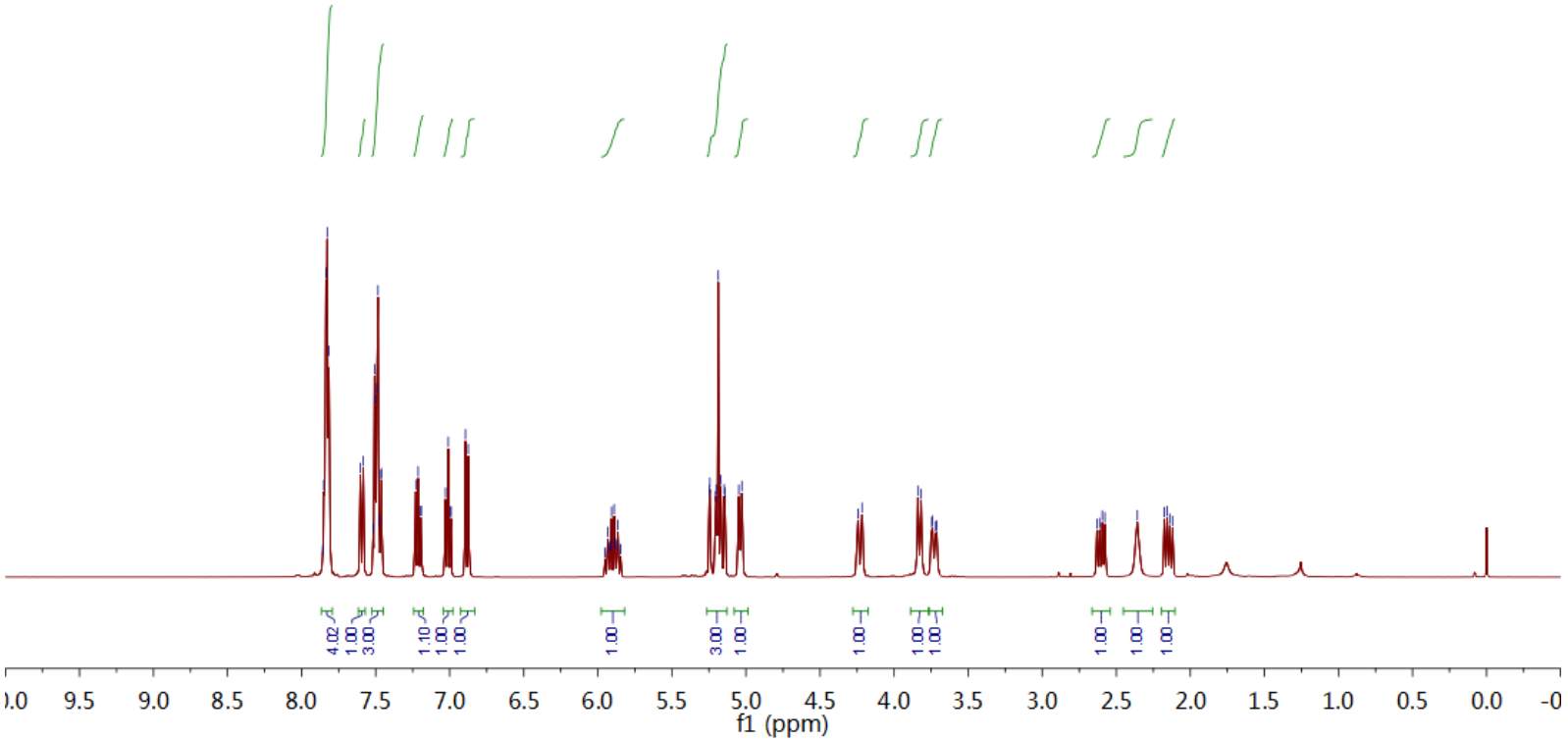


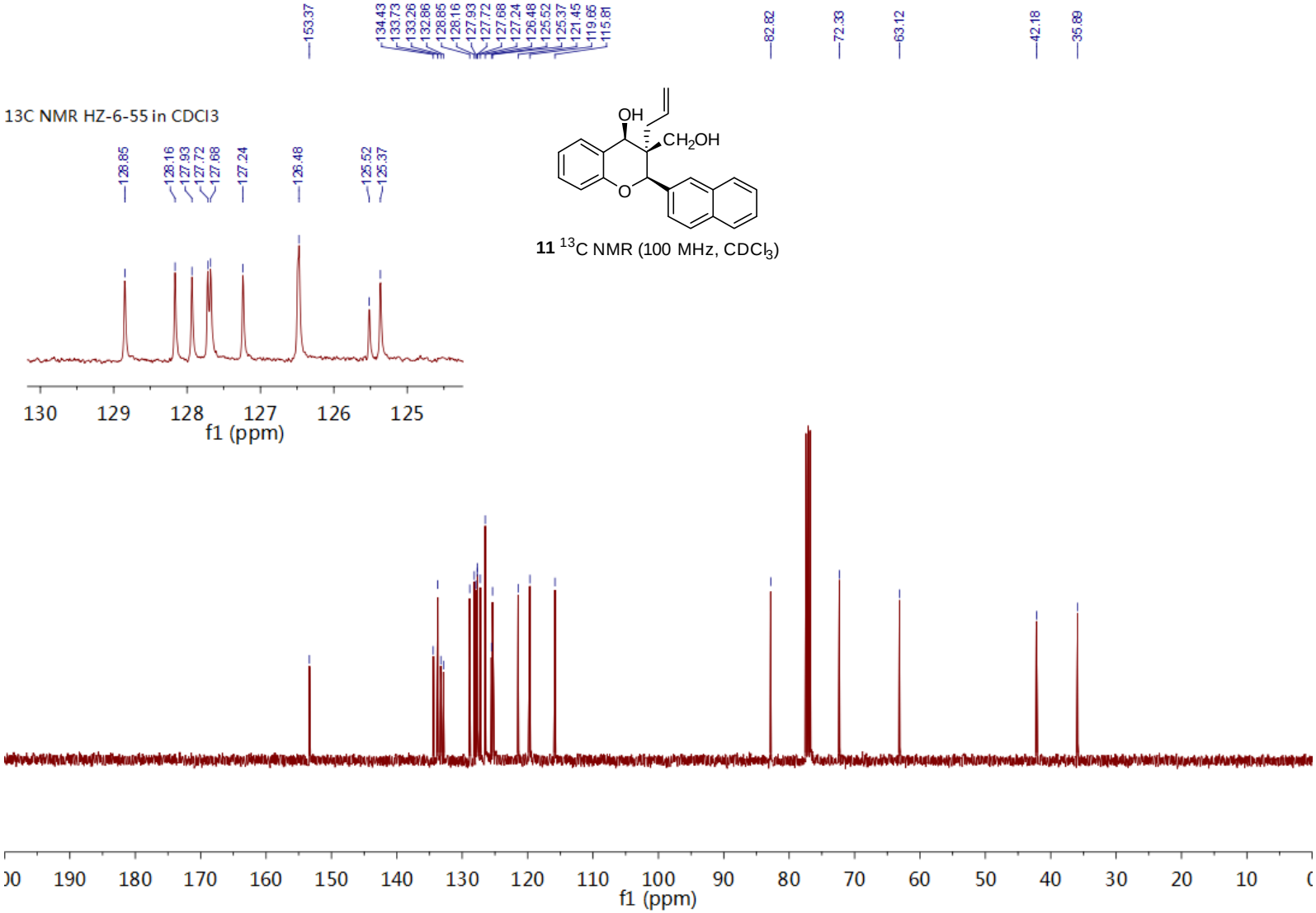
10 ^{13}C NMR (100 MHz, $CDCl_3$)

1H NMR HZ-6-55 in CDCl3

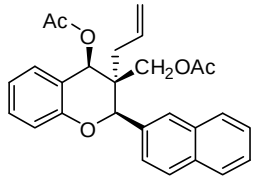


11 ^{1}H NMR (400 MHz, $CDCl_3$)

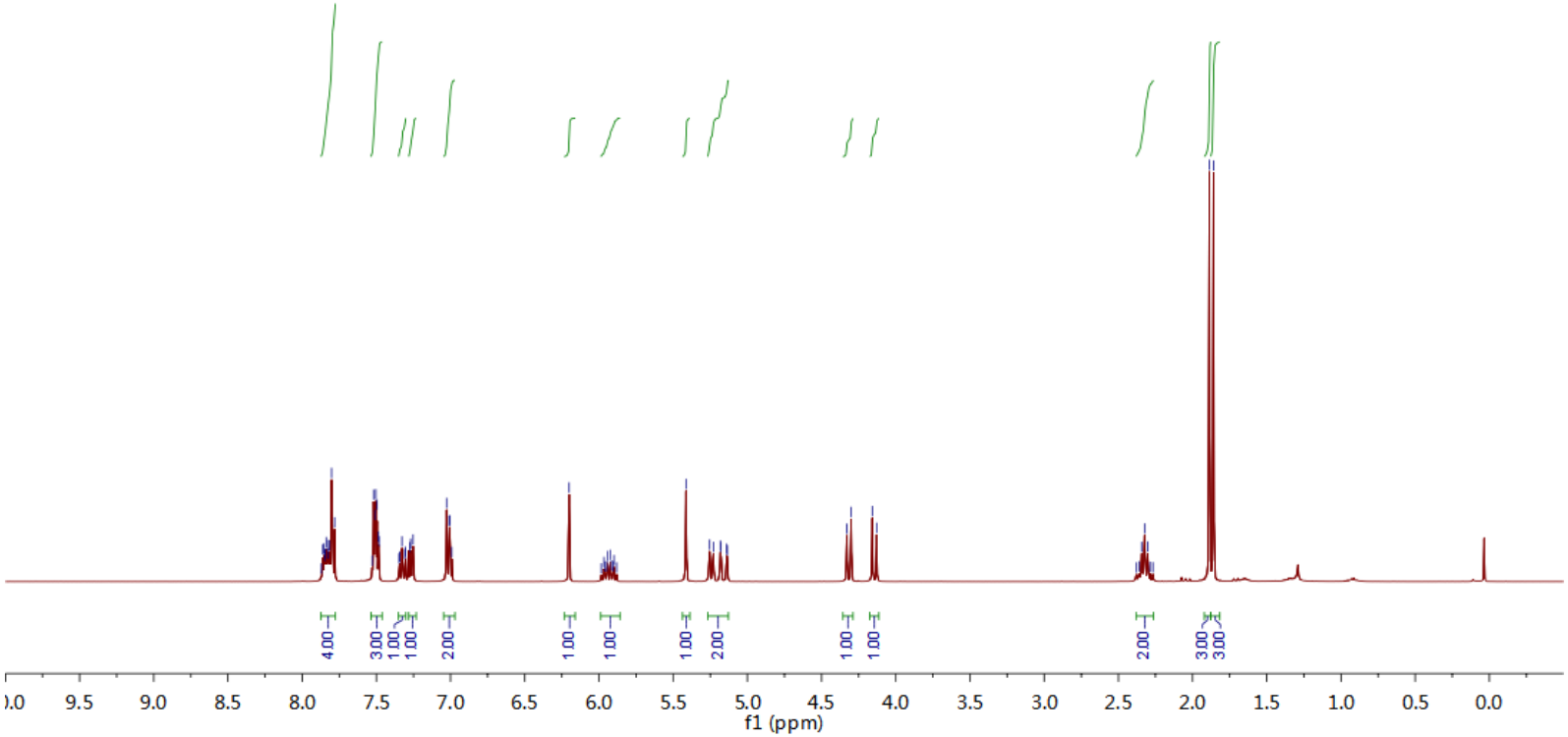


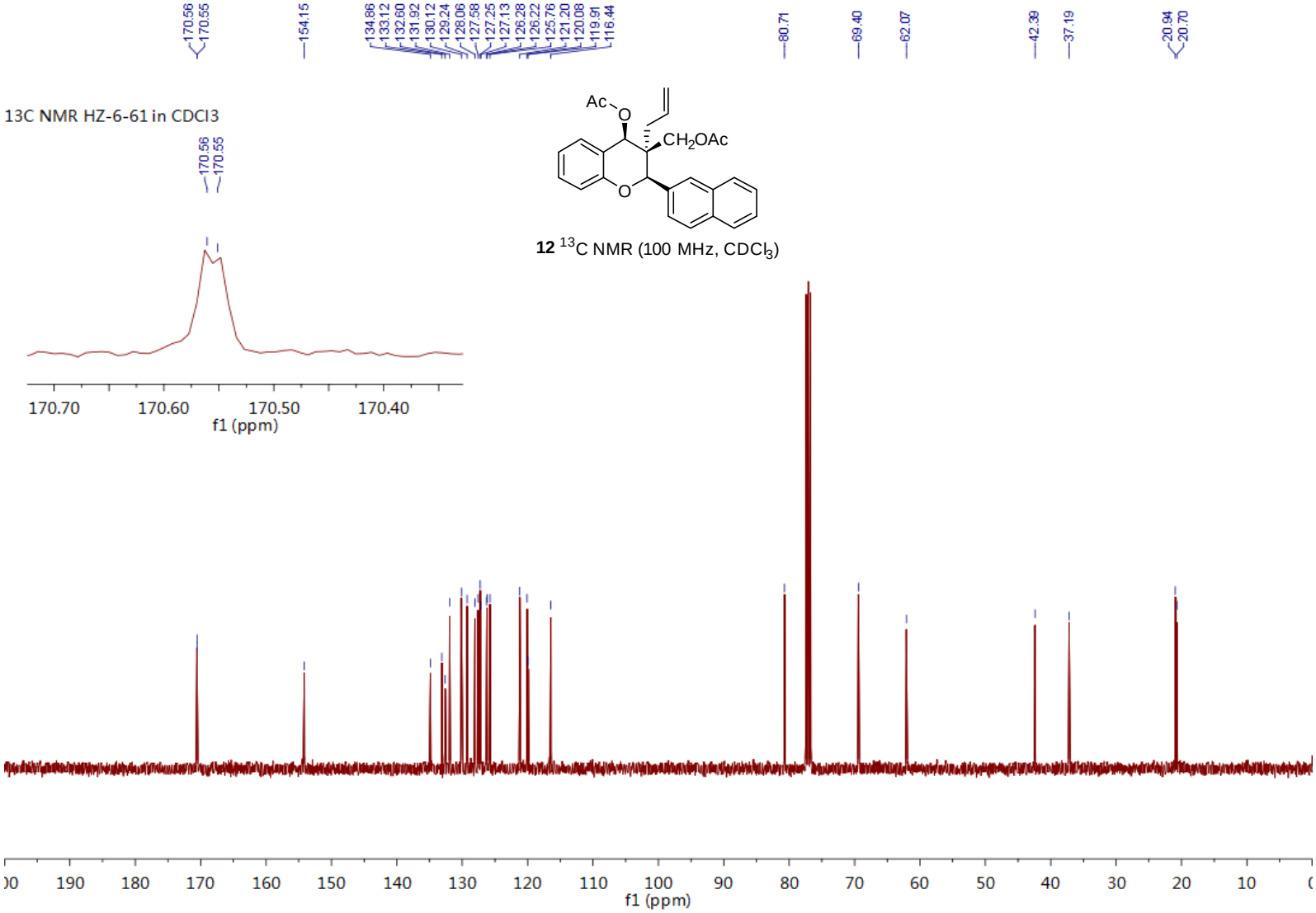

153.37
134.43
133.73
133.26
132.86
128.85
128.16
127.93
127.72
127.68
127.24
126.48
125.52
125.37
121.45
119.65
115.81
82.82
72.33
63.12
42.18
35.89
13C NMR HZ-6-55 in CDCl3
128.85
128.16
127.93
127.72
127.68
127.24
126.48
125.52
125.37
130
129
128
127
126
125
f1 (ppm)
OH
CH2OH
O
11 13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1H NMR HZ-6-61 in CDCl3



12 ^{1}H NMR (400 MHz, $CDCl_3$)

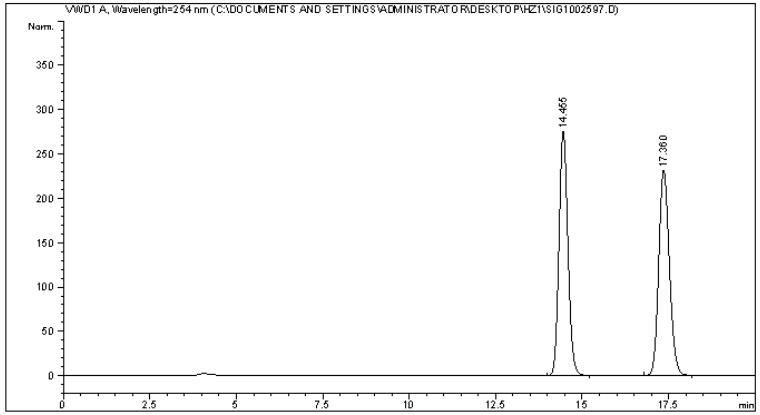




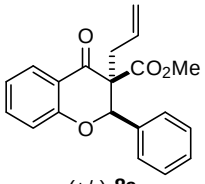
12 ^{13}C NMR (100 MHz, $CDCl_3$)

Data File C:\DOCUMENTS AND SETTINGS\ADMINISTRATOR\DESKTOP\HZ1\SIG1002597.D
Sample Name: HZ-5-37A(+-)

```
Acq. Operator   :
Acq. Instrument : 仪器 1                          Location : Vial 1
Injection Date  : 2/28/2019 3:04:25 PM
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 2/28/2019 1:53:34 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:12:15 AM
                  (modified after loading)
Sample Info     : AD-H, n-hexane/i-PrOH =99/1, 0.7 mL/min, 30 oC, 254 nm
```



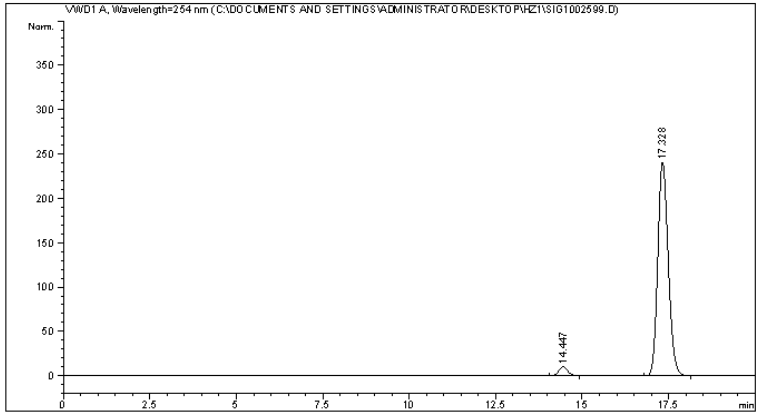

```
                          Area Percent Report

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  14.455 BB    0.2773 4933.59668  274.98660  49.9969
   2  17.360 VB    0.3308 4934.21094  231.37503  50.0031

Totals :                  9867.80762  506.36163

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



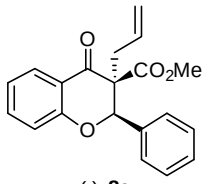
(+/-)-**8a**

Data File C:\DOCUMENTS AND SETTINGS\ADMINISTRATOR\DESKTOP\HZ1\SIG1002599.D
Sample Name: HZ-5-39A

```
Acq. Operator   :
Acq. Instrument : 仪器 1                          Location : Vial 1
Injection Date  : 2/28/2019 7:53:54 PM
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 2/28/2019 7:17:11 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:12:15 AM
                  (modified after loading)
Sample Info     : AD-H, n-hexane/i-PrOH =99/1, 0.7 mL/min, 30 oC, 254 nm
```



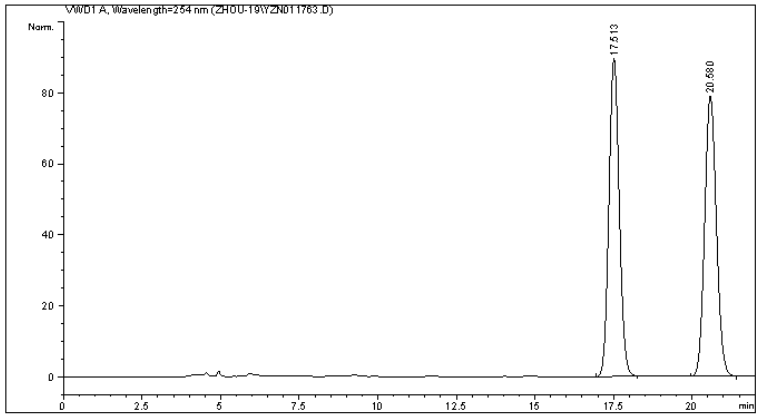

```
                          Area Percent Report

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  14.447 BB    0.2784  185.19722   10.31643   3.5243
   2  17.328 BB    0.3267 5069.73975  240.73480  96.4757

Totals :                  5254.93697  251.05124

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



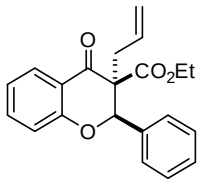
(-)-**8a**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN011763.D
Sample Name: HZ-5-36(+-)

```
==================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2/25/2019 2:45:20 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 2/25/2019 2:40:09 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:03:12 AM
                  (modified after loading)
Sample Info     : AD-H,  Hexane/i-PrOH = 99/1, 0.7 mL/min, 30 oC, 254 nm
```



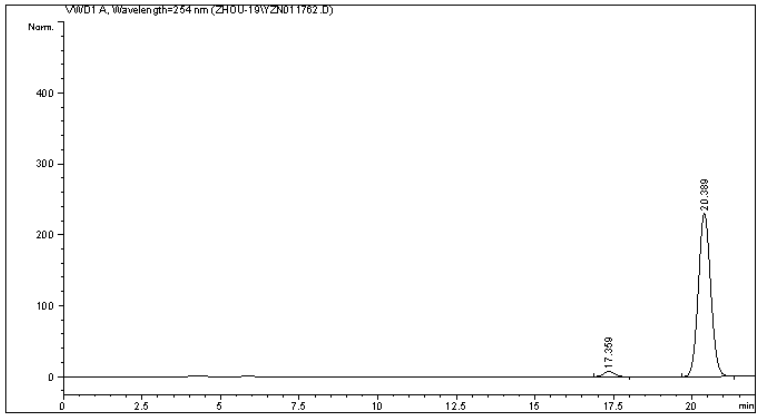

```
==================================================================
                      Area Percent Report
==================================================================

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  17.513 BB    0.3555 2046.39795   89.52306  50.0331
   2  20.580 BB    0.4024 2043.68945   78.96239  49.9669

Totals :                  4090.08740  168.48546

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



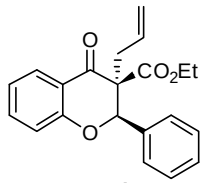
(+/-)-**8b**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN011762.D
Sample Name: HZ-5-36

```
==================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2/25/2019 2:15:01 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 2/25/2019 1:38:10 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:01:48 AM
                  (modified after loading)
Sample Info     : AD-H,  Hexane/i-PrOH = 99/1, 0.7 mL/min, 30 oC, 254 nm
```



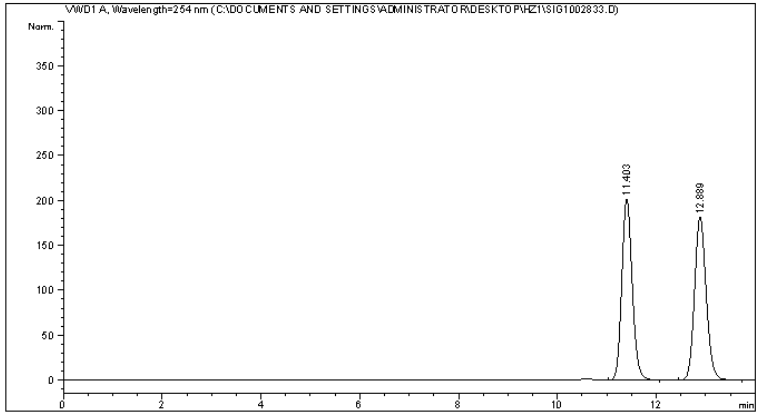

```
==================================================================
                      Area Percent Report
==================================================================

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  17.359 BB    0.3774  173.96945    7.17867   2.6987
   2  20.389 BB    0.4247 6272.43555  229.80196  97.3013

Totals :                  6446.40500  236.98063

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



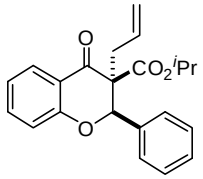
(-)-**8b**

Data File C:\DOCUMENTS AND SETTINGS\ADMINISTRATOR\DESKTOP\HZ1\SIG1002833.D
Sample Name: HZ-5-69A+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : 仪器 1                          Location : Vial 1
Injection Date  : 3/31/2019 5:20:11 PM
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/31/2019 5:17:33 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:18:10 AM
                  (modified after loading)
Sample Info     : AD-H, n-hexane/i-PrOH = 99/1, 0.7 mL/min, 30 oC, 254 nm
```



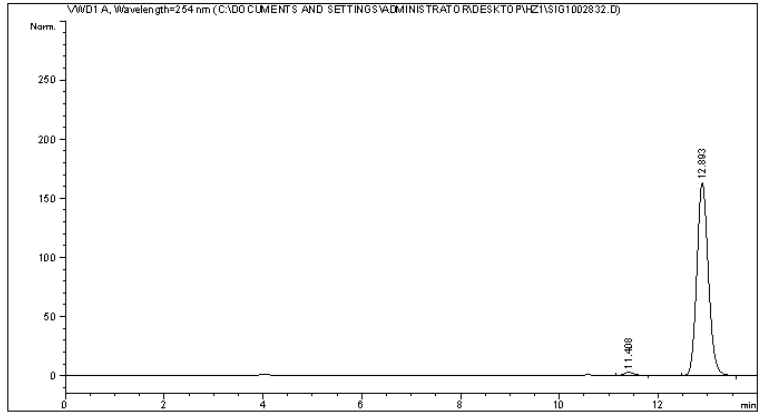

```
==========================================================================
                        Area Percent Report
==========================================================================

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  11.403 BB    0.2257 2953.02173  201.81802  49.8932
   2  12.889 BB    0.2528 2965.66919  181.30154  50.1068

Totals :                  5918.69092  383.11957

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



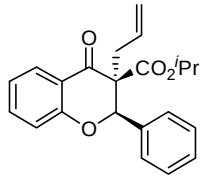
(+/-)-**8c**

Data File C:\DOCUMENTS AND SETTINGS\ADMINISTRATOR\DESKTOP\HZ1\SIG1002832.D
Sample Name: HZ-5-71A

```
==========================================================================
Acq. Operator   :
Acq. Instrument : 仪器 1                          Location : Vial 1
Injection Date  : 3/31/2019 5:02:35 PM
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/31/2019 4:54:16 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:17:44 AM
                  (modified after loading)
Sample Info     : AD-H, n-hexane/i-PrOH = 99/1, 0.7 mL/min, 30 oC, 254 nm
```



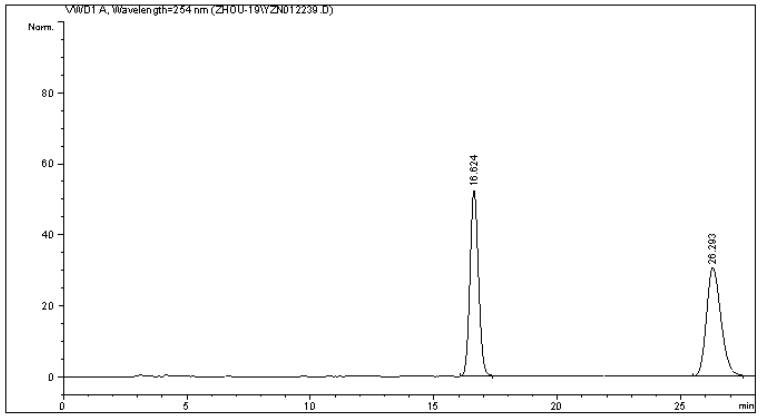

```
==========================================================================
                        Area Percent Report
==========================================================================

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  11.408 BB    0.2246   39.59365    2.72323   1.4833
   2  12.893 BB    0.2492 2629.76392  162.99953  98.5167

Totals :                  2669.35757  165.72275

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



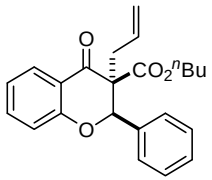
(-)-**8c**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012239.D
Sample Name: HZ-5-70B+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/30/2019 10:12:45 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/30/2019 10:11:26 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:24:28 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



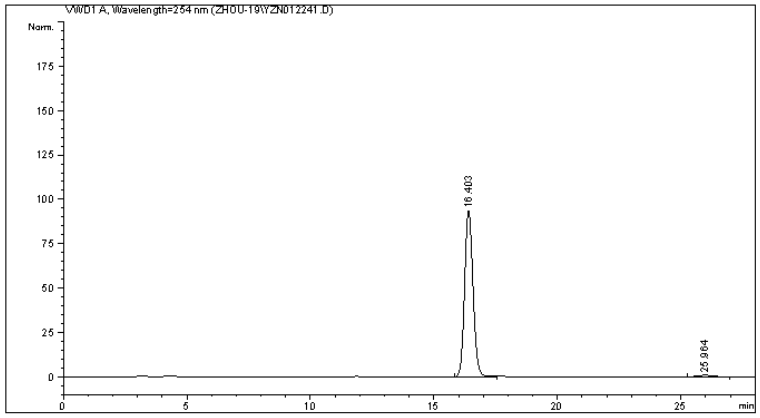

```
==========================================================================
                        Area Percent Report
==========================================================================

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  16.624 BB    0.3715 1251.18738   52.45699  50.2891
   2  26.293 BB    0.6236 1236.80322   30.56243  49.7109

Totals :                  2487.99060   83.01942

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



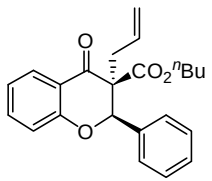
(+/-)-**8d**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012241.D
Sample Name: HZ-5-72B

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/30/2019 10:45:45 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/30/2019 10:43:55 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:25:50 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



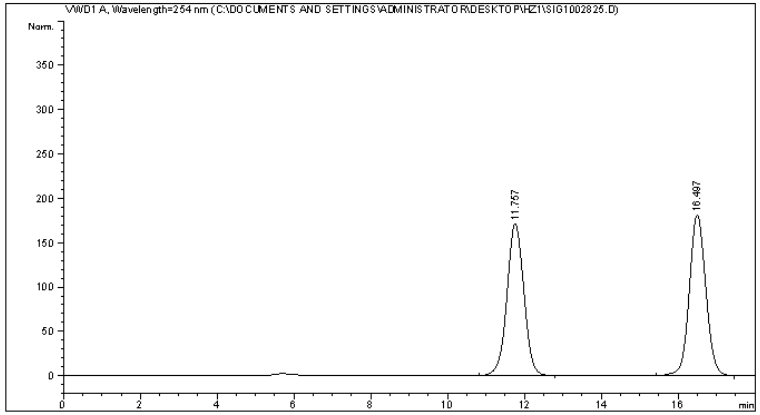

```
==========================================================================
                        Area Percent Report
==========================================================================

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  16.403 BV    0.3657 2212.51123   93.71712  98.5297
   2  25.964 BB    0.6083   33.01616 8.43179e-1   1.4703

Totals :                  2245.52739   94.56030

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



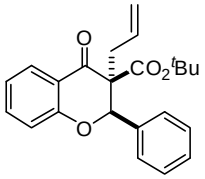
(-)-**8d**

Data File C:\DOCUMENTS AND SETTINGS\ADMINISTRATOR\DESKTOP\HZ1\SIG1002825.D
Sample Name: HZ-5-70C+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : 仪器 1                          Location : Vial 1
Injection Date  : 3/30/2019 11:48:38 PM
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/30/2019 11:45:33 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:22:59 AM
                  (modified after loading)
Sample Info     : AD-H, n-hexane/i-PrOH = 99/1, 0.5 mL/min, 30 oC, 254 nm
```



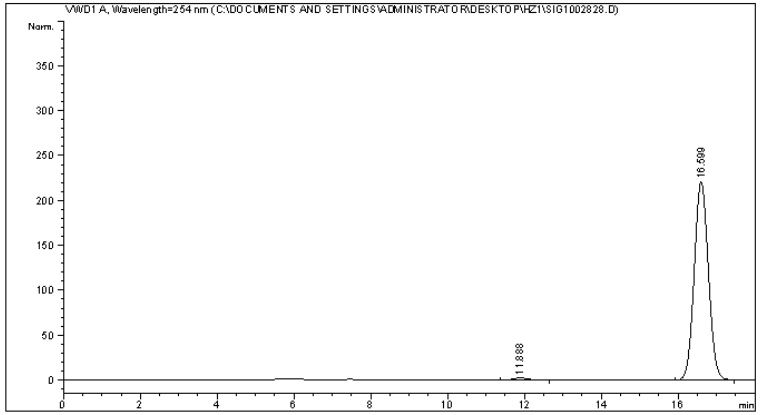

```
==========================================================================
                        Area Percent Report
==========================================================================

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  11.757 BB    0.4803 5243.48047  171.19159  49.3074
   2  16.497 BB    0.4632 5390.77832  181.16483  50.6926

Totals :                  1.06343e4   352.35641

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



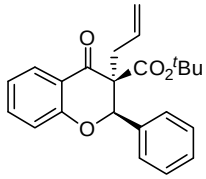
(+/-)-**8e**

Data File C:\DOCUMENTS AND SETTINGS\ADMINISTRATOR\DESKTOP\HZ1\SIG1002828.D
Sample Name: HZ-5-72C

```
==========================================================================
Acq. Operator   :
Acq. Instrument : 仪器 1                          Location : Vial 1
Injection Date  : 3/31/2019 12:59:34 AM
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/31/2019 12:55:35 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:20:38 AM
                  (modified after loading)
Sample Info     : AD-H, n-hexane/i-PrOH = 99/1, 0.5 mL/min, 30 oC, 254 nm
```



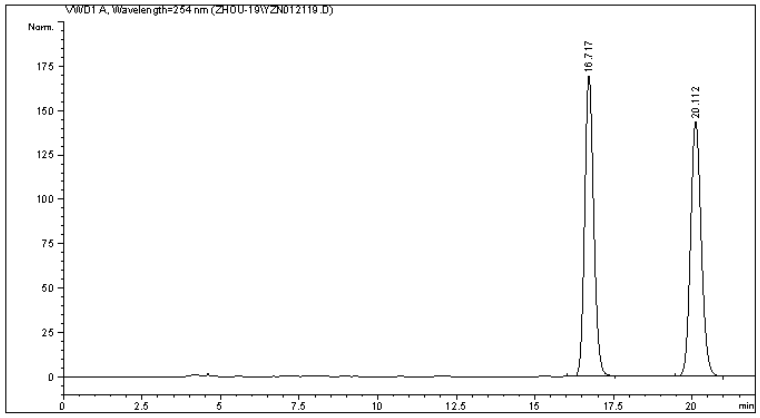

```
==========================================================================
                        Area Percent Report
==========================================================================

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  11.888 VB    0.4139   57.64151    2.24970   1.0132
   2  16.599 BB    0.3997 5631.38818  220.68689  98.9868

Totals :                  5689.02970  222.93659

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



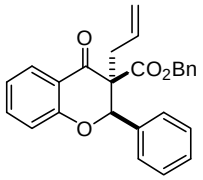
(-)-**8e**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012119.D
Sample Name: HZ-5-61A+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/23/2019 9:22:54 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/23/2019 9:19:22 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:06:11 AM
                  (modified after loading)
Sample Info     : AD-H,  Hexane/i-PrOH = 97/3, 0.7 mL/min, 30 oC, 254 nm
```



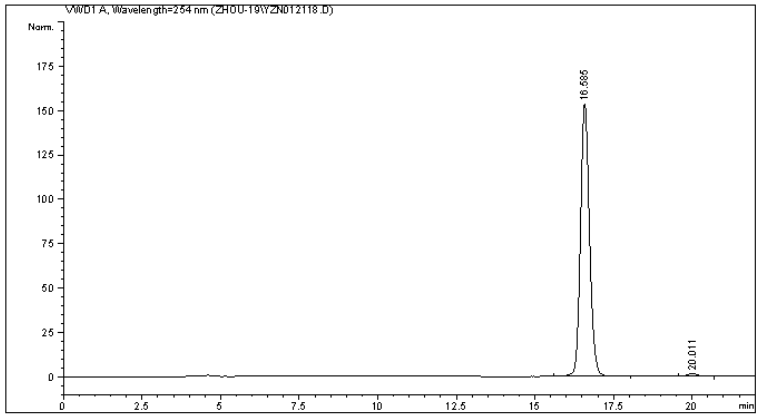

```
==========================================================================
                        Area Percent Report
==========================================================================

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  16.717 BB    0.3070 3379.20703  169.42137  49.9382
   2  20.112 BB    0.3655 3387.56885  143.57513  50.0618

Totals :                  6766.77588  312.99651

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



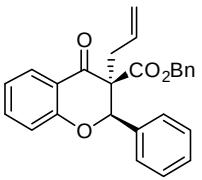
(+/-)-**8f**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012118.D
Sample Name: HZ-5-64A

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/23/2019 8:50:18 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/23/2019 8:47:30 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:06:46 AM
                  (modified after loading)
Sample Info     : AD-H,  Hexane/i-PrOH = 97/3, 0.7 mL/min, 30 oC, 254 nm
```



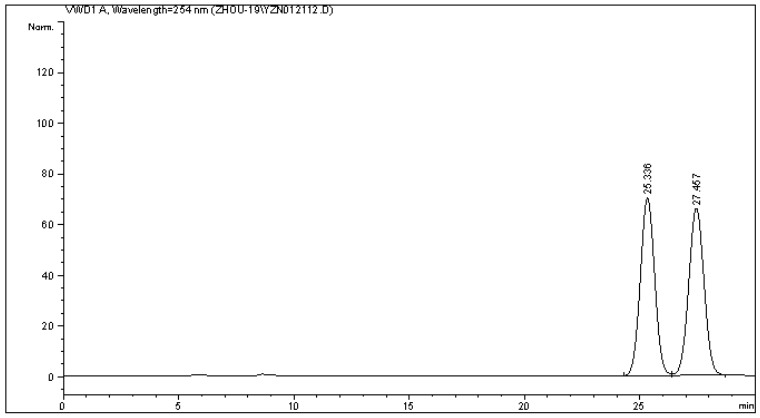

```
==========================================================================
                        Area Percent Report
==========================================================================

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  16.585 BB    0.3089 3069.94922  153.56570  98.9530
   2  20.011 BB    0.3609   32.48267    1.41576   1.0470

Totals :                  3102.43189  154.98147

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



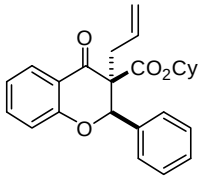
(-)-**8f**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012112.D
Sample Name: HZ-5-62B+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/22/2019 9:04:57 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/22/2019 8:52:36 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:08:17 AM
                  (modified after loading)
Sample Info     : AD-H,  Hexane/i-PrOH = 99/1, 0.5 mL/min, 30 oC, 254 nm
```



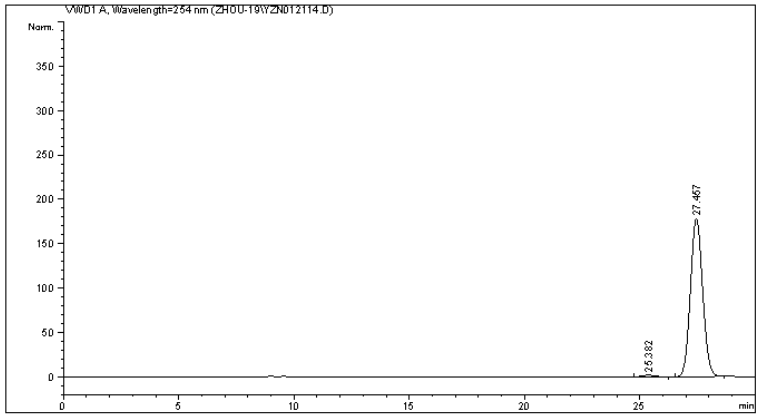

```
==========================================================================
                        Area Percent Report
==========================================================================

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  25.336 BV    0.6766 3036.05371   70.16979  49.9876
   2  27.457 VB    0.7275 3037.56519   65.84913  50.0124

Totals :                  6073.61890  136.01892

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



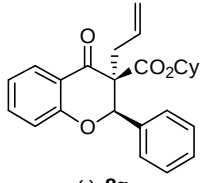
(+/-)-**8g**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012114.D
Sample Name: HZ-5-65B

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 3/22/2019 10:31:24 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 3/22/2019 10:21:17 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:08:55 AM
                  (modified after loading)
Sample Info     : AD-H,  Hexane/i-PrOH = 99/1, 0.5 mL/min, 30 oC, 254 nm
```



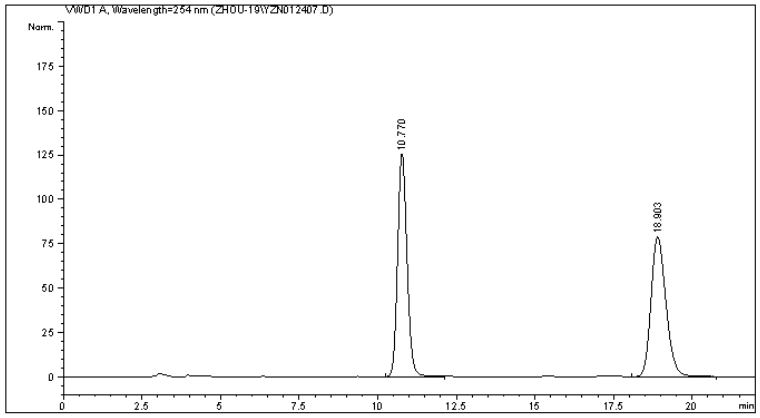

```
==========================================================================
                        Area Percent Report
==========================================================================

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  25.382 BB    0.4805   64.36123    1.89603   0.9707
   2  27.457 BB    0.5753 6565.90039  177.68295  99.0293

Totals :                  6630.26162  179.57899

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



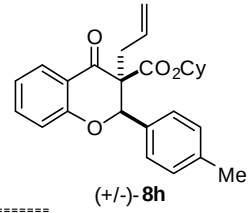
(-)-**8g**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012407.D
Sample Name: HZ-5-81A(+-)

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/17/2019 8:04:40 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/17/2019 8:02:48 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:54:08 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm
```



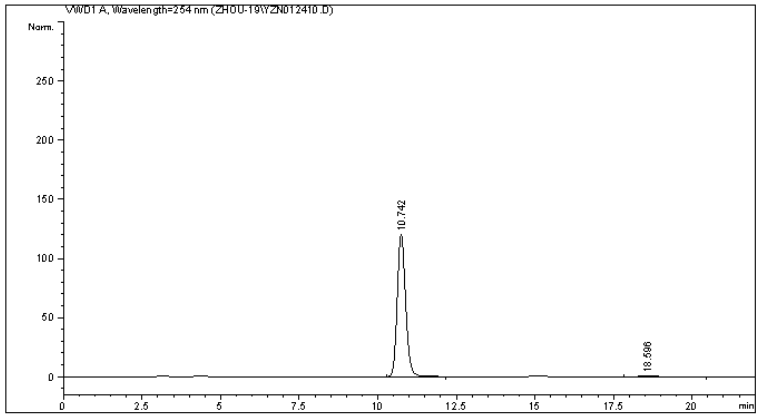

```
==========================================================================
                        Area Percent Report
==========================================================================

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  10.770 BB    0.3241 2615.15234  125.80367  50.0999
   2  18.903 VB    0.5103 2604.72168   78.91474  49.9001

Totals :                  5219.87402  204.71841

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



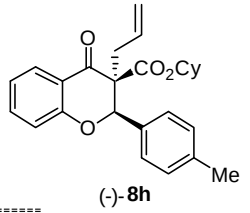
(+/-)-**8h**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012410.D
Sample Name: HZ-5-83A

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/17/2019 9:34:48 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/17/2019 9:32:55 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:52:49 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm
```



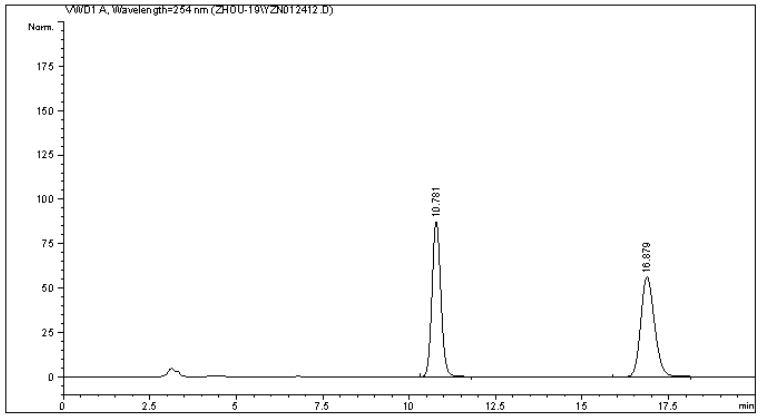

```
==========================================================================
                        Area Percent Report
==========================================================================

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  10.742 BB    0.2862 2232.10352  120.37609  98.6494
   2  18.596 VB    0.4881   30.55843 9.44536e-1   1.3506

Totals :                  2262.66195  121.32063

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



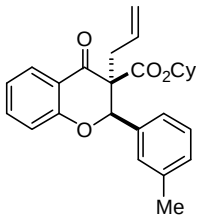
(-)-**8h**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012412.D
Sample Name: HZ-5-82B+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/17/2019 10:23:51 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/17/2019 10:22:35 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:56:21 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm
```



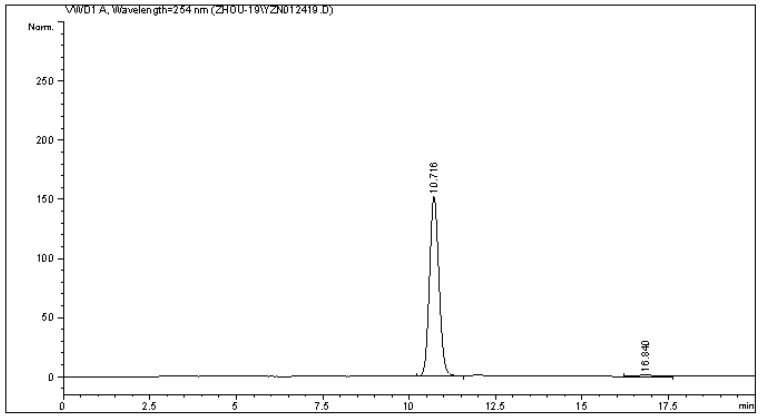

```
==========================================================================
                        Area Percent Report
==========================================================================

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  10.781 BB    0.2769 1555.35498   87.66850  49.9401
   2  16.879 VB    0.4245 1559.08545   56.39009  50.0599

Totals :                  3114.44043  144.05859

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



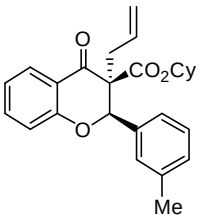
(+/-)-**8i**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012419.D
Sample Name: HZ-5-84B

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/18/2019 9:29:10 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/18/2019 9:24:48 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:55:29 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm
```



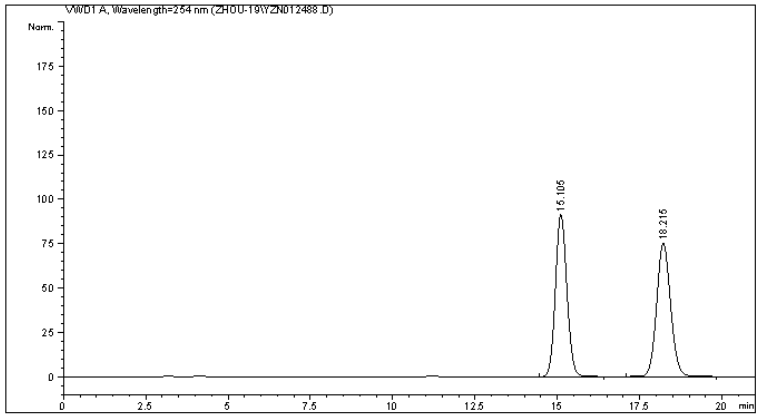

```
==========================================================================
                        Area Percent Report
==========================================================================

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  10.716 BV    0.2961 2909.43652  152.01653  98.6682
   2  16.840 BB    0.4592   39.27236    1.30353   1.3318

Totals :                  2948.70888  153.32005

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



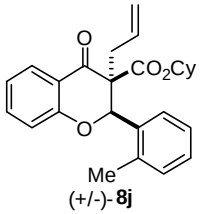
(-)-**8i**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012488.D
Sample Name: HZ-5-89A+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/25/2019 8:16:12 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/25/2019 8:14:51 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 9:00:52 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



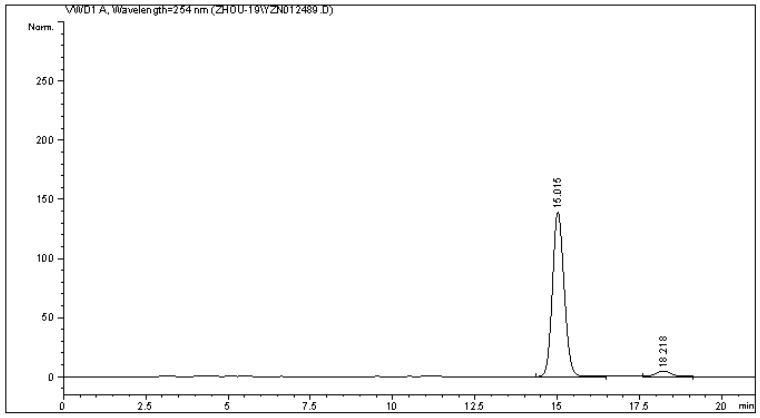

```
==========================================================================
                        Area Percent Report
==========================================================================

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  15.105 BB    0.3758 2213.73779   91.38393  49.9088
   2  18.215 BB    0.4586 2221.82739   75.13814  50.0912

Totals :                  4435.56519  166.52206

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



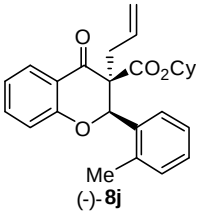
(+/-)-**8j**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012489.D
Sample Name: HZ-5-92A

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/25/2019 8:38:35 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/25/2019 8:38:00 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 9:03:58 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



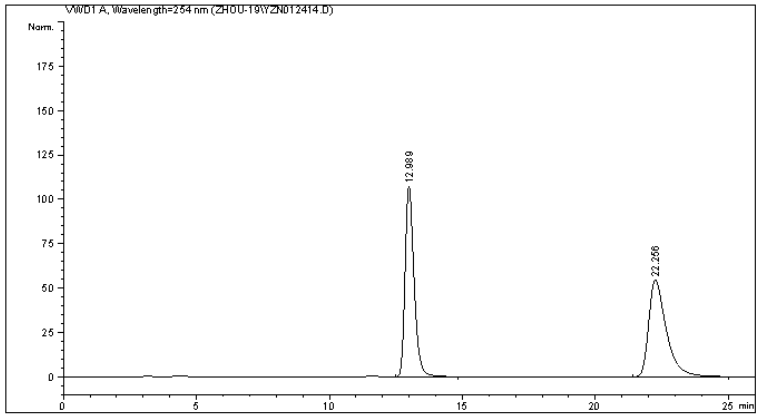

```
==========================================================================
                        Area Percent Report
==========================================================================

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  15.015 BB    0.3837 3426.23169  138.96808  95.9993
   2  18.218 BB    0.4740  142.78436    4.69715   4.0007

Totals :                  3569.01605  143.66523

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



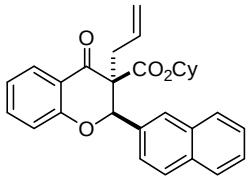
(-)-**8j**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012414.D
Sample Name: HZ-5-82C+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/17/2019 11:15:59 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/17/2019 11:14:27 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:57:17 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm
```



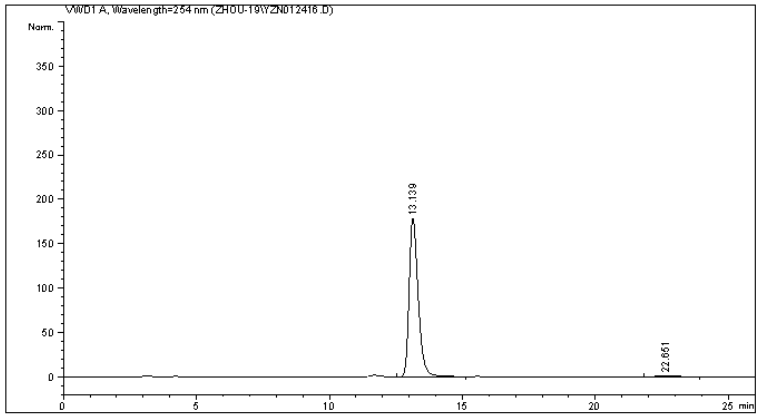

```
==========================================================================
                        Area Percent Report
==========================================================================

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  12.989 BB    0.3582 2522.35864  107.48181  50.0378
   2  22.256 BB    0.6859 2518.54785   54.68048  49.9622

Totals :                  5040.90649  162.16229

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



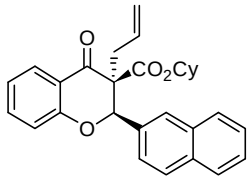
(+/-)-**8k**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012416.D
Sample Name: HZ-5-84C

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/18/2019 12:16:08 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/18/2019 12:13:07 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:59:42 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH =99/1, 1.0 mL/min, 30 oC, 254 nm
```



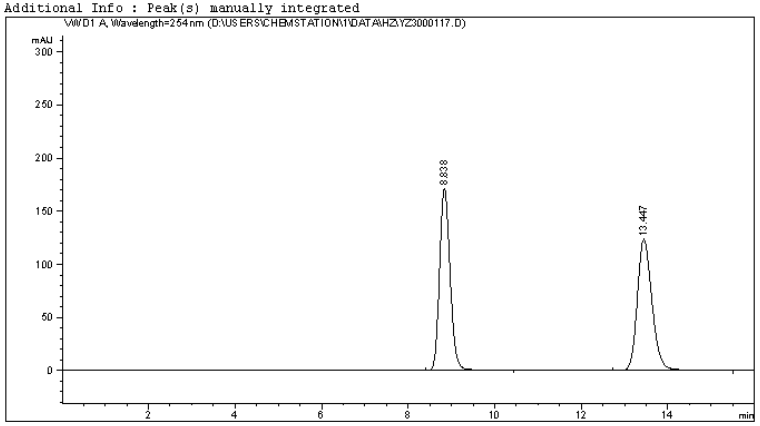

```
==========================================================================
                        Area Percent Report
==========================================================================

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  13.139 VB    0.3636 4226.47412  178.52505  98.7389
   2  22.651 BB    0.7410   53.98066    1.09522   1.2611

Totals :                  4280.45478  179.62027

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



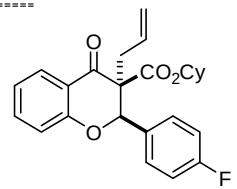
(-)-**8k**

Data File D:\USERS\CHEMSTATION\1\DATA\HZ\YZ3000117.D
Sample Name: HZ-5-97A+-

```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :   1
Injection Date  : 4/30/2019 4:49:24 PM             Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 4/30/2019 3:21:41 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 7/11/2019 11:58:30 PM by SYSTEM
                  (modified after loading)
Sample Info     : IC, n-Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm

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



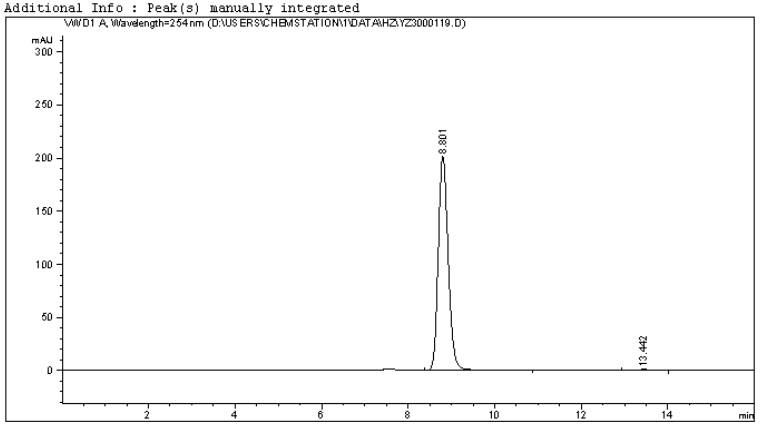

```
==========================================================================
                        Area Percent Report
==========================================================================

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   8.838 VB    0.2632 2891.92334  171.12738  49.9343
   2  13.447 BB    0.3620 2899.53442  123.44003  50.0657
```



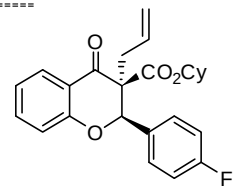
(+/-)-**8l**

Data File D:\USERS\CHEMSTATION\1\DATA\HZ\YZ3000119.D
Sample Name: HZ-5-99A

```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :   1
Injection Date  : 4/30/2019 5:23:41 PM             Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 4/30/2019 3:21:41 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 7/11/2019 9:33:23 PM by SYSTEM
                  (modified after loading)
Sample Info     : IC, n-Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm

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



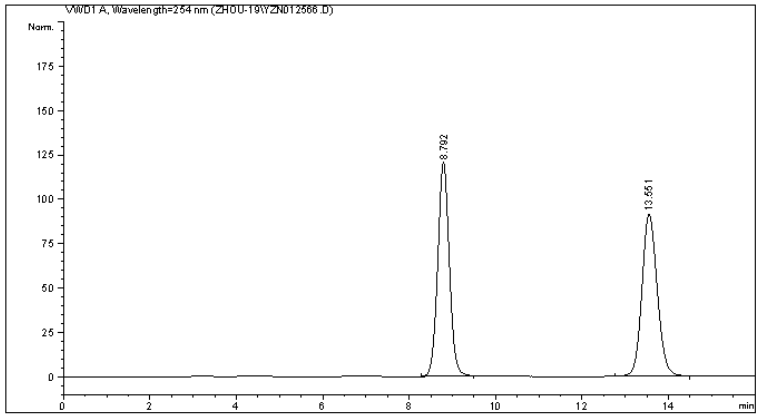

```
==========================================================================
                        Area Percent Report
==========================================================================

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   8.801 VB    0.2485 3216.52051  201.22316  99.3524
   2  13.442 BB    0.3473   20.96466 9.43304e-1   0.6476
```



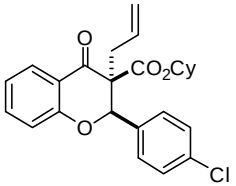
(-)-**8l**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012566.D
Sample Name: HZ-6-4+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/8/2019 10:42:29 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/8/2019 10:39:41 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:03:42 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254nm
```



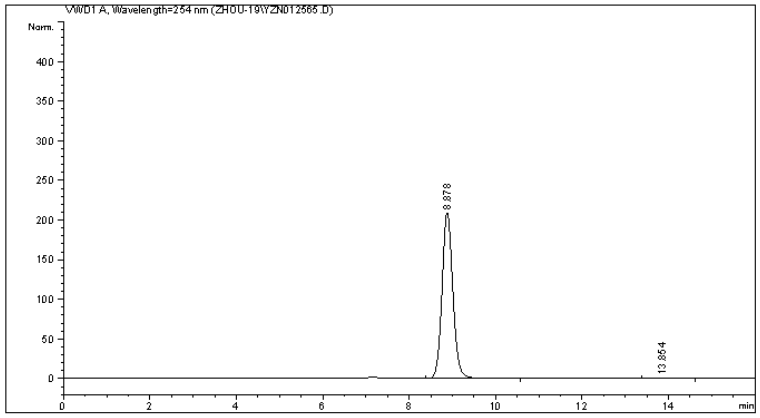

```
==========================================================================
                        Area Percent Report
==========================================================================

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   8.792 BB    0.2844 2228.45142  120.36389  49.7765
   2  13.551 BB    0.3786 2248.46362   91.43044  50.2235

Totals :                  4476.91504  211.79433

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



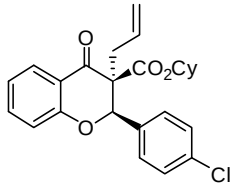
(+/-)-**8m**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012565.D
Sample Name: HZ-6-4

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/8/2019 10:16:03 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/8/2019 10:13:10 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:10:16 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254nm
```



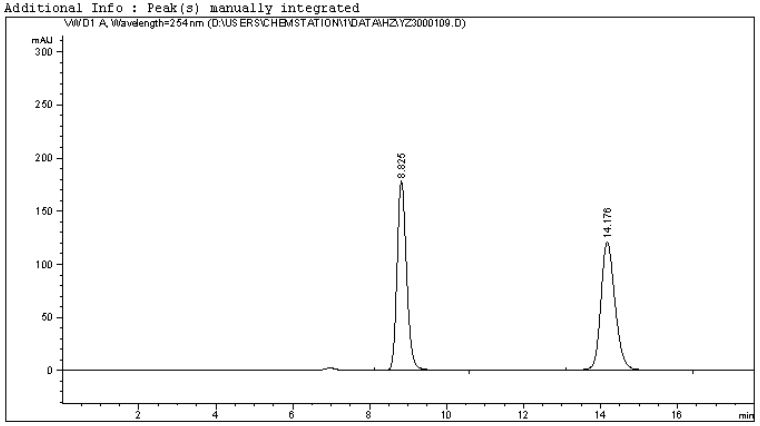

```
==========================================================================
                        Area Percent Report
==========================================================================

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   8.878 BB    0.2677 3654.65991  209.41612  99.1768
   2  13.854 BB    0.3642   30.33416    1.26511   0.8232

Totals :                  3684.99407  210.68123

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



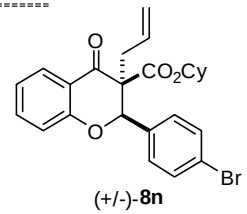
(-)-**8m**

Data File D:\USERS\CHEMSTATION\1\DATA\HZ\YZ3000109.D
Sample Name: HZ-5-98B+-

```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :   1
Injection Date  : 4/30/2019 10:42:04 AM             Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 4/30/2019 8:15:06 AM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 7/11/2019 11:57:00 PM by SYSTEM
                  (modified after loading)
Sample Info     : IC, n-Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm

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



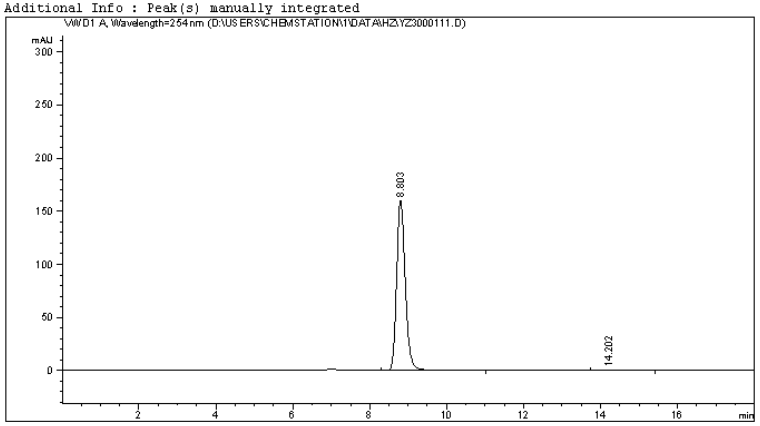

```
==========================================================================
                        Area Percent Report
==========================================================================

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   8.825 BB    0.2649 3068.51440  178.19858  49.6171
   2  14.176 BB    0.3964 3115.87427  121.02505  50.3829
```



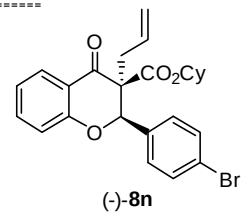
(+/-)-**8n**

Data File D:\USERS\CHEMSTATION\1\DATA\HZ\YZ3000111.D
Sample Name: HZ-5-100B

```
==========================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : 1260II                        Location :   1
Injection Date  : 4/30/2019 11:28:31 AM             Inj :   1
                                                Inj Volume : No inj
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 4/30/2019 8:15:06 AM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\def_LC.M
Last changed    : 7/11/2019 11:55:04 PM by SYSTEM
                  (modified after loading)
Sample Info     : IC, n-Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm

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



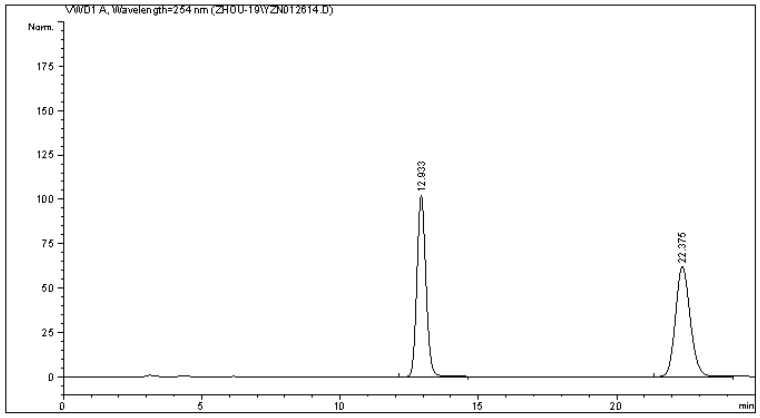

```
==========================================================================
                        Area Percent Report
==========================================================================

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   8.803 BB    0.2409 2506.81030  159.88077  99.3593
   2  14.202 BB    0.3853   16.16588 6.56519e-1   0.6407
```



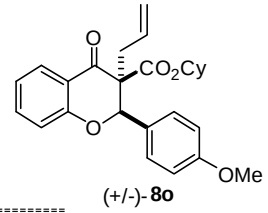
(-)-**8n**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012614.D
Sample Name: HZ-6-8A+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/14/2019 11:36:49 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/14/2019 11:35:45 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:13:39 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



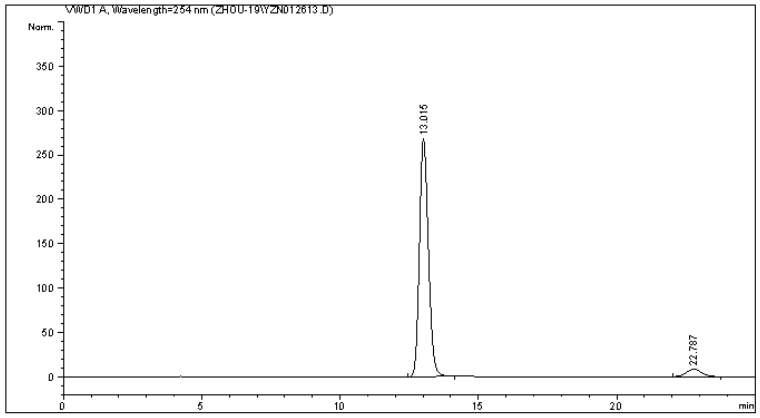

```
==========================================================================
                        Area Percent Report
==========================================================================

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  12.933 BB    0.3501 2299.66626  102.11424  50.0695
   2  22.375 BB    0.5737 2293.27881   62.07491  49.9305

Totals :                  4592.94507  164.18915

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



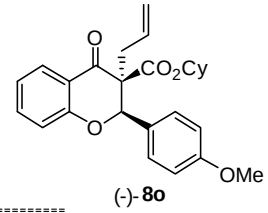
(+/-)-**8o**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012613.D
Sample Name: HZ-6-8A

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/14/2019 11:08:48 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/14/2019 10:37:18 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:16:59 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



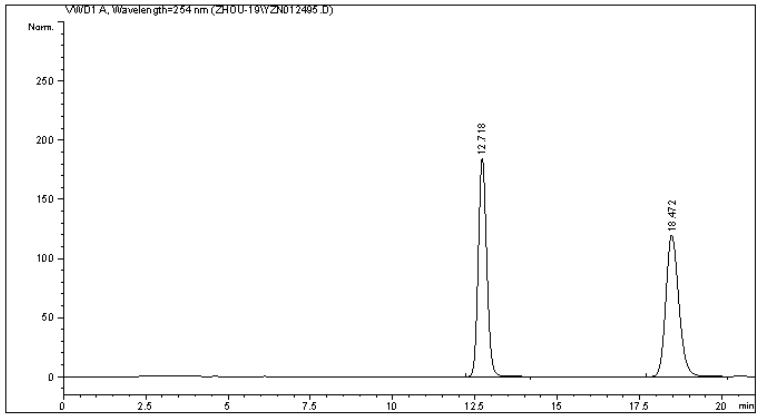

```
==========================================================================
                        Area Percent Report
==========================================================================

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  13.015 BB    0.3494 6026.62988  268.27670  94.8859
   2  22.787 BB    0.5884  324.81699    8.52953   5.1141

Totals :                  6351.44687  276.80623

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



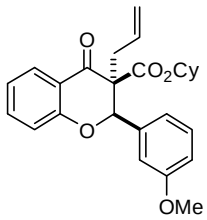
(-)-**8o**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012495.D
Sample Name: HZ-5-90B+-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/26/2019 10:07:28 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/26/2019 10:04:30 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 9:01:30 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH = 98/2, 0.8 mL/min, 30 oC, 254 nm
```



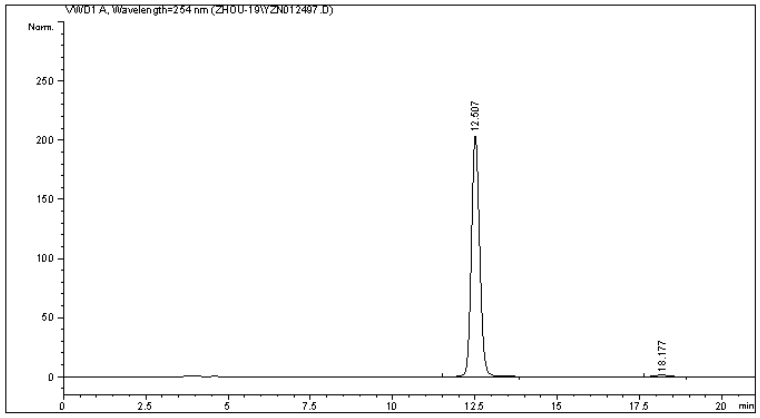

```
                          Area Percent Report

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  12.718 BB    0.2750 3297.26880  184.88219  50.0874
   2  18.472 BB    0.4221 3285.76343  119.71832  49.9126

Totals :                  6583.03223  304.60050

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



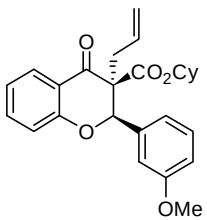
(+/-)-**8p**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012497.D
Sample Name: HZ-5-93B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 4/26/2019 11:05:50 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 4/26/2019 11:04:25 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 9:03:58 AM
                  (modified after loading)
Sample Info     : IC,  Hexane/i-PrOH = 98/2, 0.8 mL/min, 30 oC, 254 nm
```



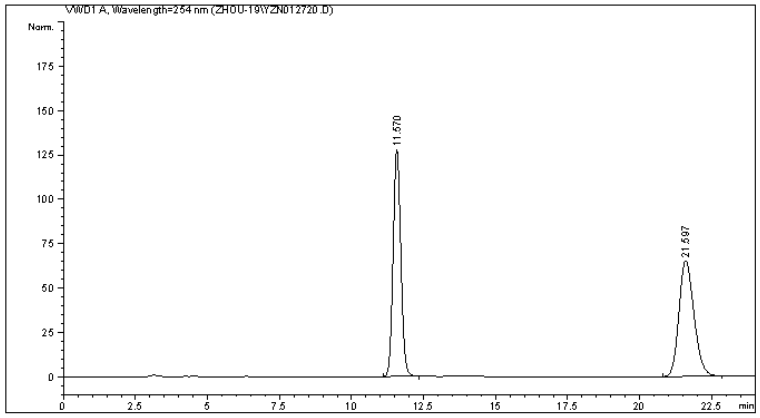

```
                          Area Percent Report

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  12.507 BB    0.2704 3555.88794  203.96745  98.9343
   2  18.177 BB    0.4274   38.30169    1.39785   1.0657

Totals :                  3594.18963  205.36530

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



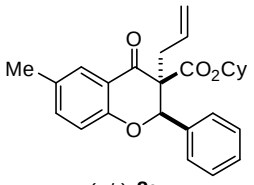
(-)-**8p**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012720.D
Sample Name: HZ-6-13A+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/23/2019 11:13:16 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/23/2019 11:10:55 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:25:44 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



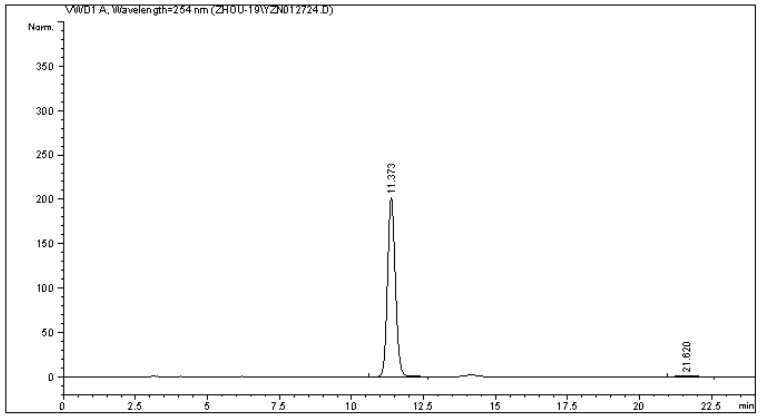

```
==========================================================================
                        Area Percent Report
==========================================================================

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  11.570 BB    0.2884 2379.09741  127.86348  50.0762
   2  21.597 BB    0.5617 2371.85791   65.35931  49.9238

Totals :                  4750.95532  193.22279

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



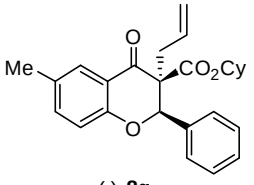
(+/-)-**8q**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012724.D
Sample Name: HZ-6-15A

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/23/2019 1:22:54 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/23/2019 1:21:48 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:27:02 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



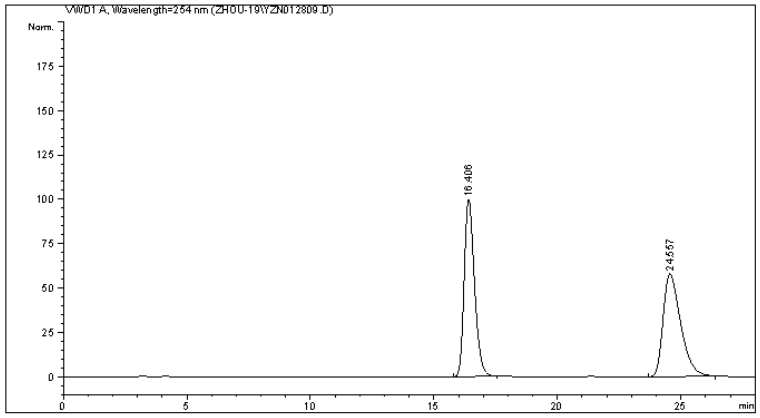

```
==========================================================================
                        Area Percent Report
==========================================================================

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  11.373 BB    0.2934 3813.63843  201.73183  98.9318
   2  21.620 BB    0.5686   41.17778    1.09063   1.0682

Totals :                  3854.81620  202.82246

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



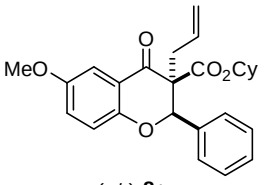
(-)-**8q**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012809.D
Sample Name: HZ-6-25+-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/6/2019 7:34:07 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/6/2019 7:32:10 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:33:45 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254nm
```




```
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  16.406 BB    0.4455 2892.05713   99.90707  50.1896
   2  24.557 BB    0.7534 2870.20605   58.01248  49.8104

Totals :                  5762.26318  157.91956
```

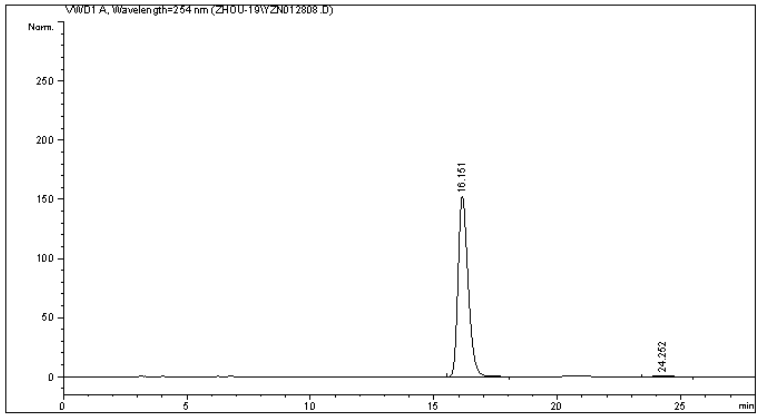


(+/-)-**8r**

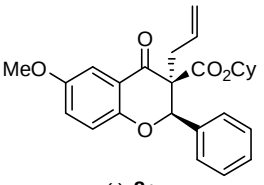
Instrument 1 7/12/2019 7:33:58 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012808.D
Sample Name: HZ-6-28

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/6/2019 6:54:12 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/6/2019 6:52:23 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:34:35 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254nm
```




```
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  16.151 BB    0.4339 4305.24219  152.64198  99.0482
   2  24.252 BB    0.7059   41.37173 8.70460e-1   0.9518

Totals :                  4346.61392  153.51244
```

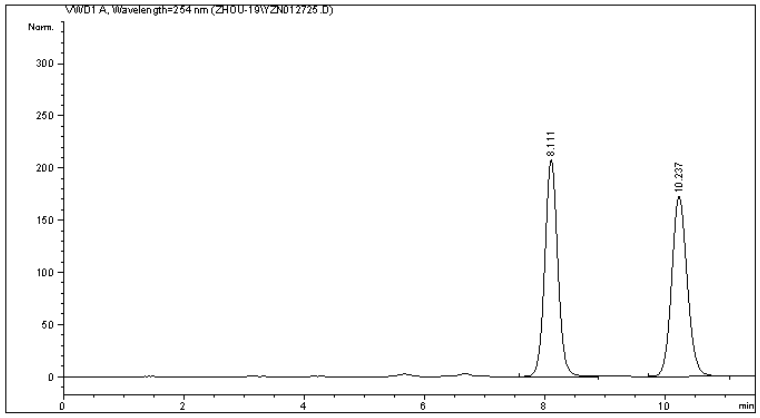


(-)-**8r**

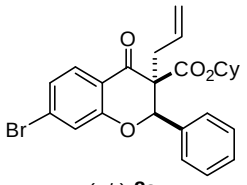
Instrument 1 7/12/2019 7:34:40 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012725.D
Sample Name: HZ-6-14B+-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/23/2019 1:52:58 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/23/2019 1:49:04 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:28:44 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



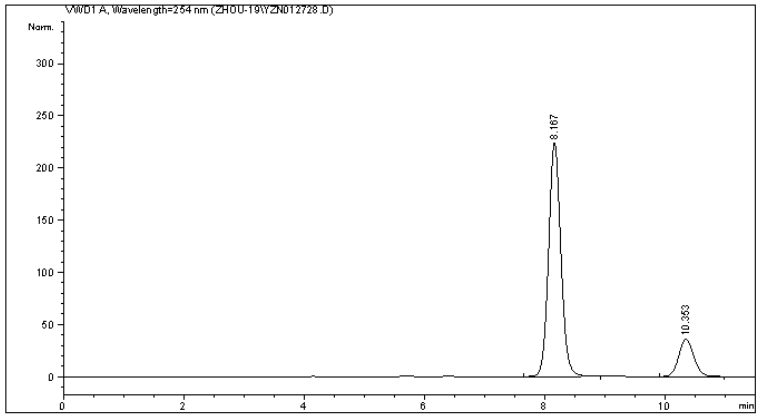

```
                          Area Percent Report

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   8.111 BB    0.2294 3098.75928  207.66937  49.9645
   2  10.237 BB    0.2770 3103.15991  172.36786  50.0355

Totals :                  6201.91919  380.03723

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



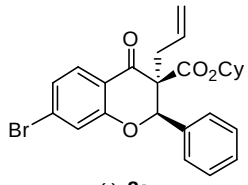
(+/-)-**8s**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012728.D
Sample Name: HZ-6-16B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/23/2019 2:44:34 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/23/2019 2:42:13 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:28:44 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



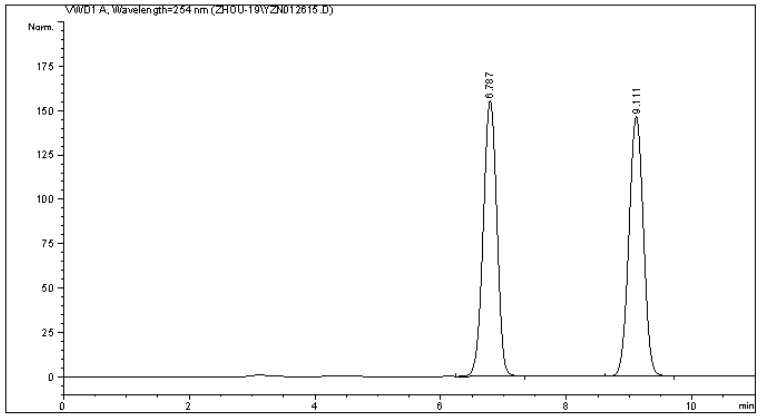

```
                          Area Percent Report

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   8.167 BB    0.2184 3187.21680  224.07458  83.4842
   2  10.353 BB    0.2696  630.53333   36.05210  16.5158

Totals :                  3817.75012  260.12669

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



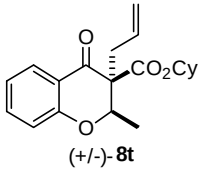
(-)-**8s**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012615.D
Sample Name: HZ-6-9B+-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/14/2019 2:16:32 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/14/2019 1:45:51 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:22:37 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



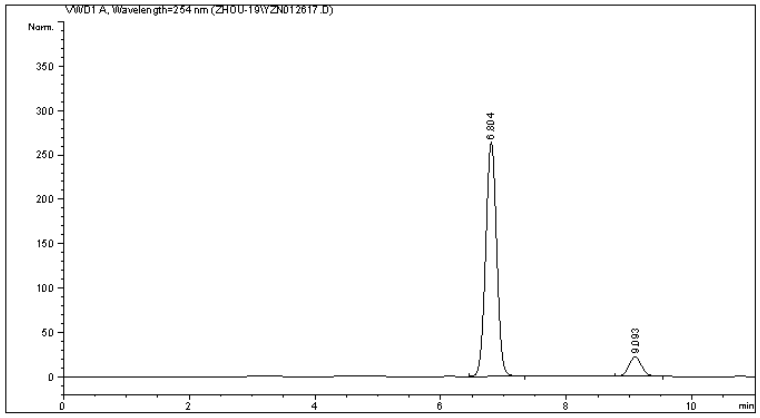

```
Area Percent Report

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   6.787 VB    0.2381 2334.02466  155.16696  49.8979
   2   9.111 BB    0.2523 2343.57910  146.38698  50.1021

Totals :                  4677.60376  301.55394

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



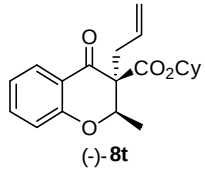
(+/-)-**8t**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012617.D
Sample Name: HZ-6-9B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/14/2019 3:06:42 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/14/2019 3:05:04 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:23:32 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



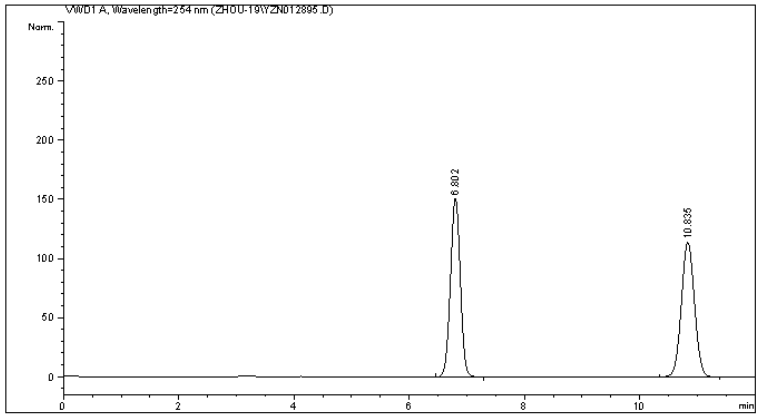

```
Area Percent Report

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   6.804 BB    0.1891 3189.43066  263.81479  91.0900
   2   9.093 BB    0.2214  311.97650   21.91809   8.9100

Totals :                  3501.40717  285.73288

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



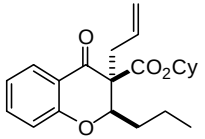
(-)-**8t**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012895.D
Sample Name: HZ-6-32A+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/18/2019 3:47:26 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/18/2019 3:45:19 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:36:30 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



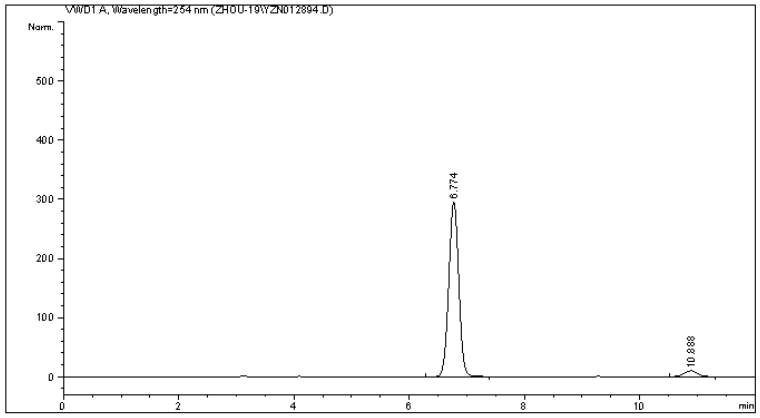

```
==========================================================================
                        Area Percent Report
==========================================================================

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   6.802 VB    0.1849 1793.43872  151.29637  49.8426
   2  10.835 BB    0.2475 1804.76294  113.89653  50.1574

Totals :                  3598.20166  265.19290

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



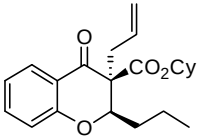
(+/-)-**8u**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012894.D
Sample Name: HZ-6-38B

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/18/2019 3:28:28 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/18/2019 3:14:53 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:36:55 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
```



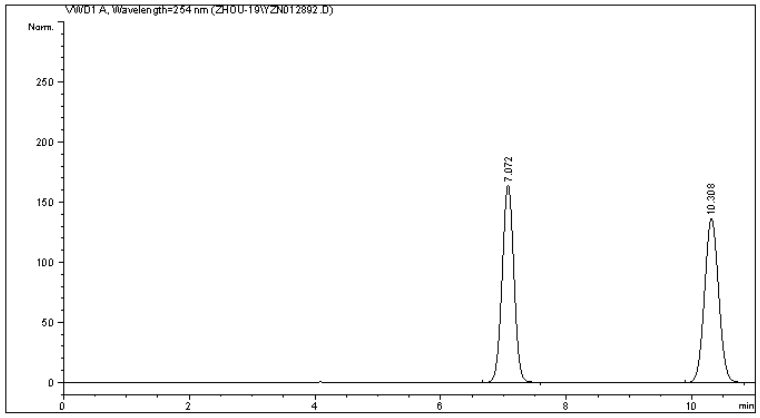

```
==========================================================================
                        Area Percent Report
==========================================================================

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   6.774 BB    0.1877 3538.31787  295.53546  95.6065
   2  10.888 BB    0.2538  162.59843    9.99957   4.3935

Totals :                  3700.91631  305.53503

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



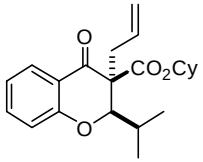
(-)-**8u**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012892.D
Sample Name: HZ-6-33B+-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/18/2019 2:17:51 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/18/2019 2:07:51 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:45:11 AM
                  (modified after loading)
Sample Info     : IC, 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   7.072 BB    0.2035 2126.85376  164.21469  50.0675
   2  10.308 BB    0.2425 2121.11694  136.48390  49.9325

Totals :                  4247.97070  300.69859

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

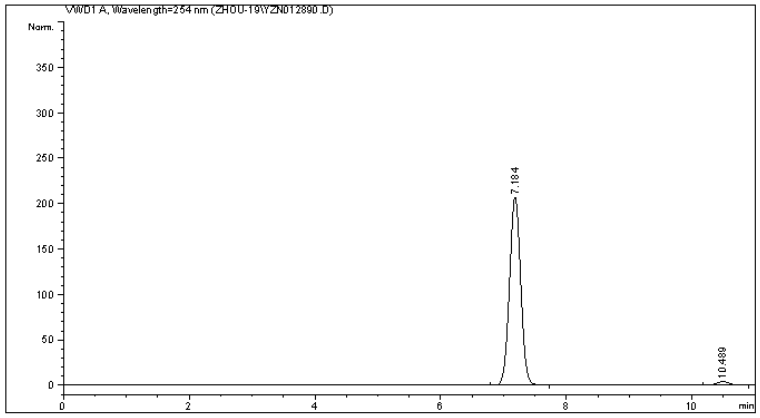


(+/-)-**8v**

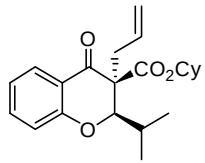
Instrument 1 7/12/2019 7:45:14 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012890.D
Sample Name: HZ-6-38C

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/18/2019 1:37:16 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/18/2019 1:36:10 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:43:59 AM
                  (modified after loading)
Sample Info     : IC, 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   7.184 VB    0.1940 2566.23267  207.14871  97.7005
   2  10.489 BB    0.2374   60.39883    3.96568   2.2995

Totals :                  2626.63150  211.11439

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

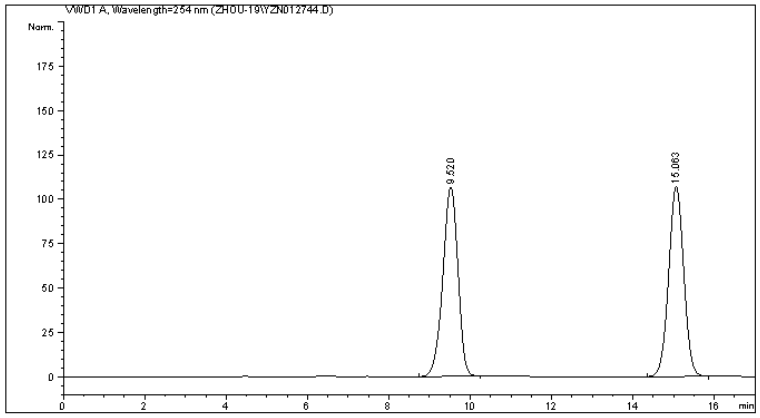


(-)-**8v**

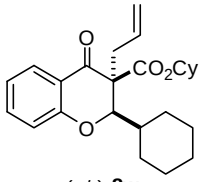
Instrument 1 7/12/2019 7:44:15 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012744.D
Sample Name: HZ-6-14C+-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/24/2019 1:58:19 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/24/2019 1:41:23 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:30:54 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 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   9.520 BB    0.4011 2752.42163  106.80527  49.9998
   2  15.063 BB    0.3991 2752.44312  106.99122  50.0002

Totals :                  5504.86475  213.79649

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

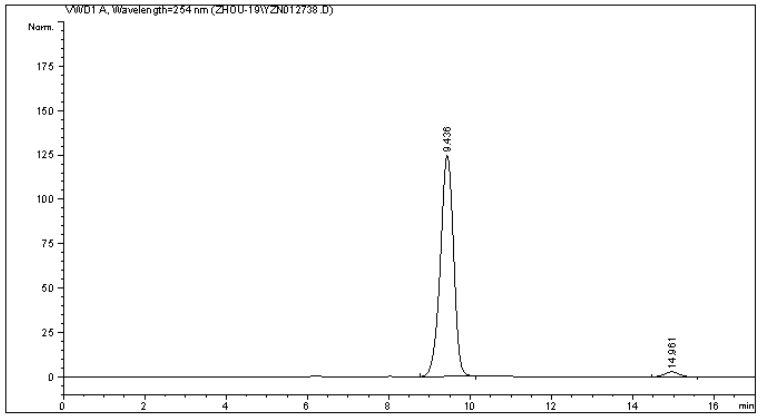


(+/-)-**8w**

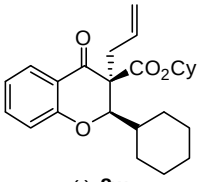
Instrument 1 7/12/2019 7:30:58 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN012738.D
Sample Name: HZ-6-16C

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/24/2019 11:01:39 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 5/24/2019 11:00:02 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:30:54 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 99/1, 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   9.436 BB    0.3503 2808.21704  124.61282  97.6537
   2  14.961 BB    0.3749   67.47202    2.77970   2.3463

Totals :                  2875.68906  127.39252

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

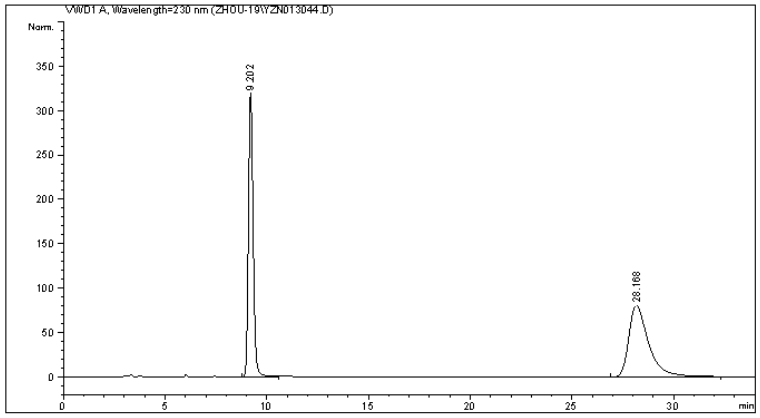


(-)-**8w**

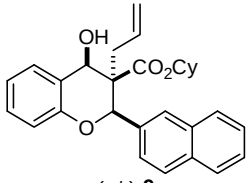
Instrument 1 7/12/2019 7:31:34 AM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013044.D
Sample Name: HZ-6-49+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/30/2019 10:48:17 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/30/2019 10:46:47 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:51:05 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 98/2, 1.0 mL/min, 30 oC, 230 nm
```



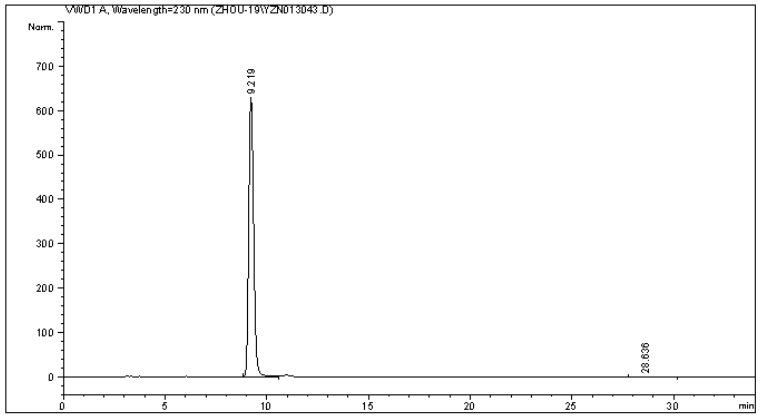

```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.202 BV    0.2496 5161.31494  319.48514  48.7492
   2  28.168 BB    1.0141 5426.16504   80.14133  51.2508

Totals :                  1.05875e4   399.62646

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



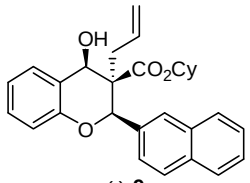
(+/-)-**9**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013043.D
Sample Name: HZ-6-49

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 6/30/2019 10:09:52 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 6/30/2019 10:09:15 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:51:38 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 98/2, 1.0 mL/min, 30 oC, 230 nm
```



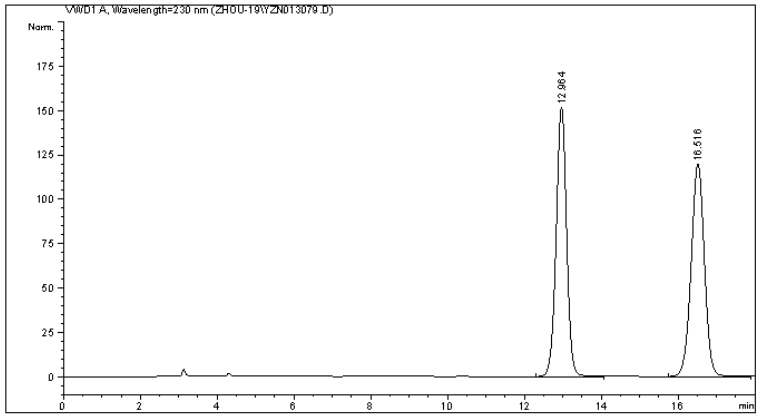

```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.219 BV    0.2629 1.05737e4   629.63544  99.7380
   2  28.636 BB    0.8190   27.77522 4.05735e-1   0.2620

Totals :                  1.06014e4   630.04117

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



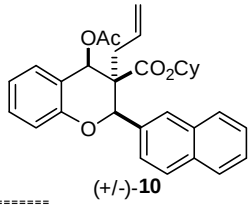
(-)-**9**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013079.D
Sample Name: HZ-6-59+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/5/2019 3:46:44 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/5/2019 3:42:04 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:53:00 AM
                  (modified after loading)
Sample Info     : IA, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 230 nm
```



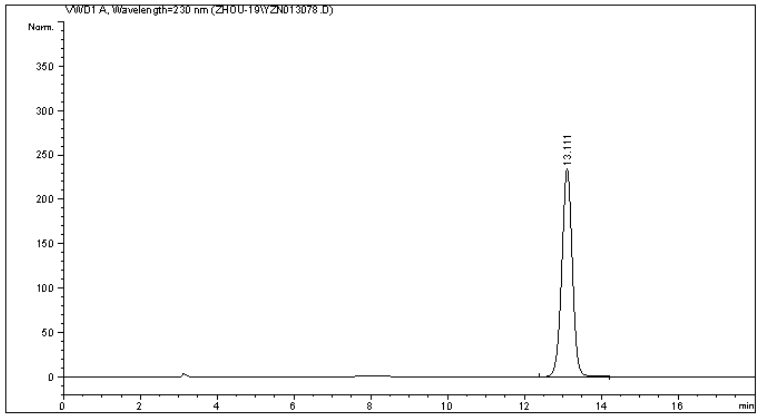

```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.964 BB    0.2897 2862.83130  151.93648  49.9196
   2  16.516 BB    0.3728 2872.05151  119.83685  50.0804

Totals :                  5734.88281  271.77333

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



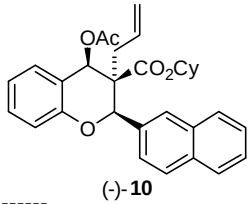
(+/-)-**10**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013078.D
Sample Name: HZ-6-53

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/5/2019 3:21:50 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/5/2019 3:18:37 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:55:39 AM
                  (modified after loading)
Sample Info     : IA, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 230 nm
```



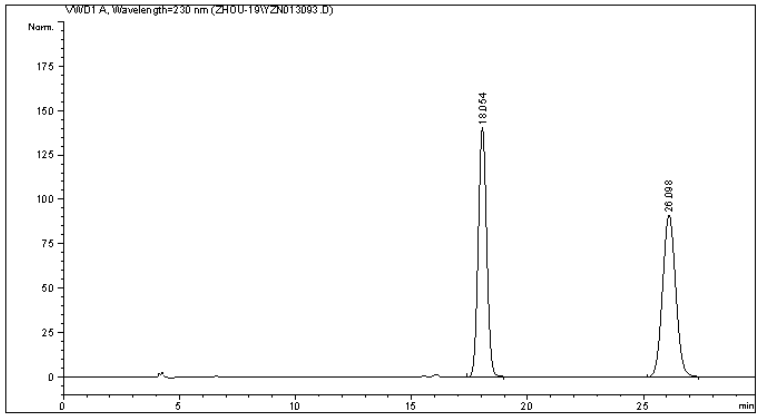

```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.111 BB    0.2929 4446.59863  234.11324 100.0000

Totals :                  4446.59863  234.11324

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



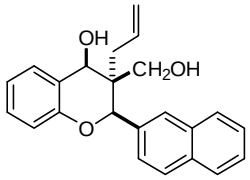
(-)-**10**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013093.D
Sample Name: HZ-6-60+-

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/8/2019 11:16:10 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/8/2019 11:15:52 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:58:33 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 95/5, 0.8 mL/min, 30 oC, 230nm
```



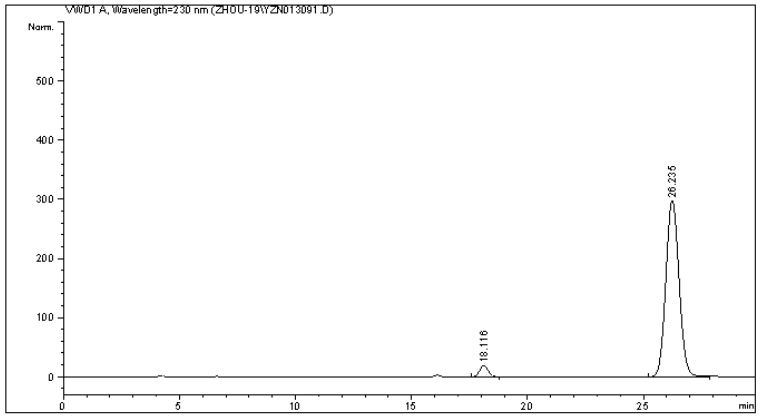

```
                          Area Percent Report

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.054 BB    0.3942 3535.55273  140.41505  49.6575
   2  26.098 BB    0.6123 3584.32813   91.31763  50.3425

Totals :                  7119.88086  231.73269

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



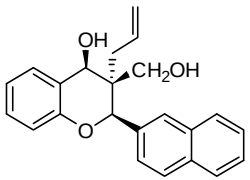
(+/-)-**11**

Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013091.D
Sample Name: HZ-6-55

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/8/2019 10:14:42 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/8/2019 10:13:28 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:57:37 AM
                  (modified after loading)
Sample Info     : IC, Hexane/i-PrOH = 95/5, 0.8 mL/min, 30 oC, 230nm
```




```
                          Area Percent Report

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.116 BB    0.3912  477.47681   19.06427   3.8962
   2  26.235 BB    0.6205 1.17773e4   297.52084  96.1038

Totals :                  1.22548e4   316.58512

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



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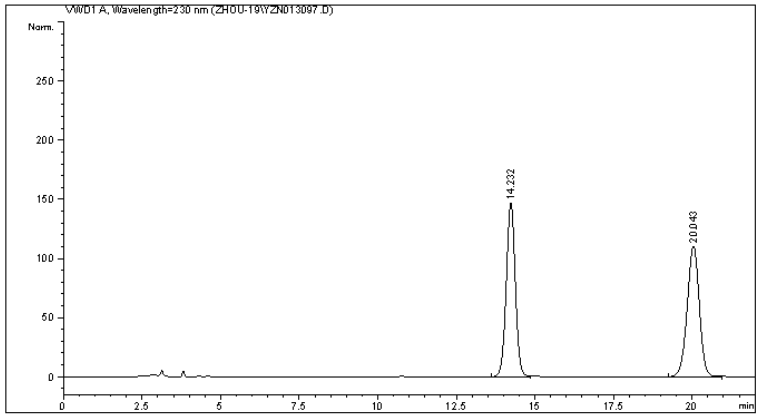
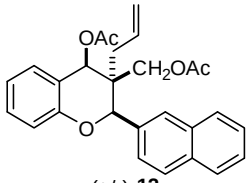
Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013097.D
Sample Name: HZ-6-62+-

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/8/2019 10:41:07 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/8/2019 10:38:06 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 8:00:25 AM
                  (modified after loading)
Sample Info     : IA, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 230nm
```




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

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.232 BB    0.3091 2936.47437  146.76790  49.8710
   2  20.043 BB    0.4137 2951.66016  110.46583  50.1290

Totals :                  5888.13452  257.23373

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



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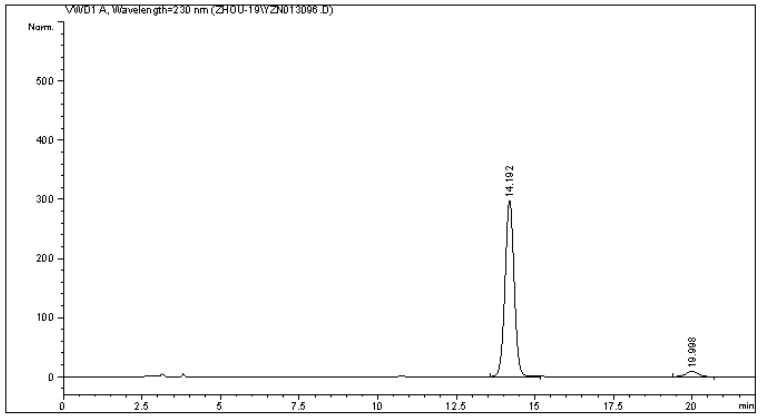
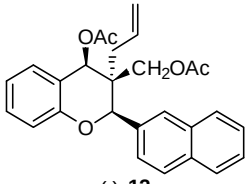
Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013096.D
Sample Name: HZ-6-61

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/8/2019 10:12:40 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/8/2019 10:11:31 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/12/2019 7:59:40 AM
                  (modified after loading)
Sample Info     : IA, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 230nm
```




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

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


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.192 BB    0.3111 6003.69434  297.58200  96.2212
   2  19.998 BB    0.4099  235.77727    8.88931   3.7788

Totals :                  6239.47160  306.47131

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



(-)-**12**