

Supporting Information

Enantio- and Regioselective CuH-Catalyzed Conjugate Reduction of Yne-Allenones

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Context

General Information.....	S2
X-Ray Absolute Configuration Structure of Product 3c	S2
Characterization Data of Compound 1p	S2
Copies of ¹ H and ¹³ C NMR Spectra for Compounds 1p	S3
General Procedure for the Synthesis of Product 4	S4
Characterization Data of Compound 4	S4
General Procedure for the Synthesis of Products 3	S4
Characterization Data of Compounds 3a-3dd	S4-S14
Copies of Chiral HPLC Analyses of Products 3a-3dd and 4	S15-S44
Copies of ¹ H and ¹³ C NMR Spectra for Compounds 3a-3dd and 4	S45-S104

Experimental

General Information

^1H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl_3 ($\text{DMSO}-d_6$) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

Yne-Allenones were prepared according to literature procedures (See *J. Org. Chem.* **2009**, *74*, 2224 and *Angew. Chem., Int. Ed.* **2017**, *56*, 15570). Dimethoxy(methyl)silane, chiral ligands (**L₁-L₈**) and other reagents, unless otherwise noted, were purchased from commercial vendors and used without further purification. The single-crystal of (*R*)-**3c** was grown from the mixed solution of ethanol and acetone (V/V = 3:1).

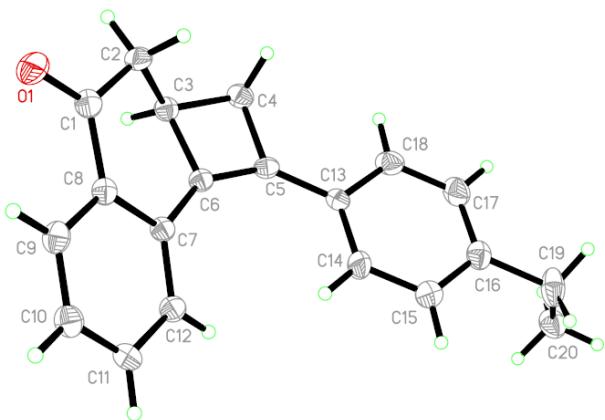
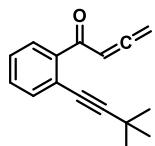
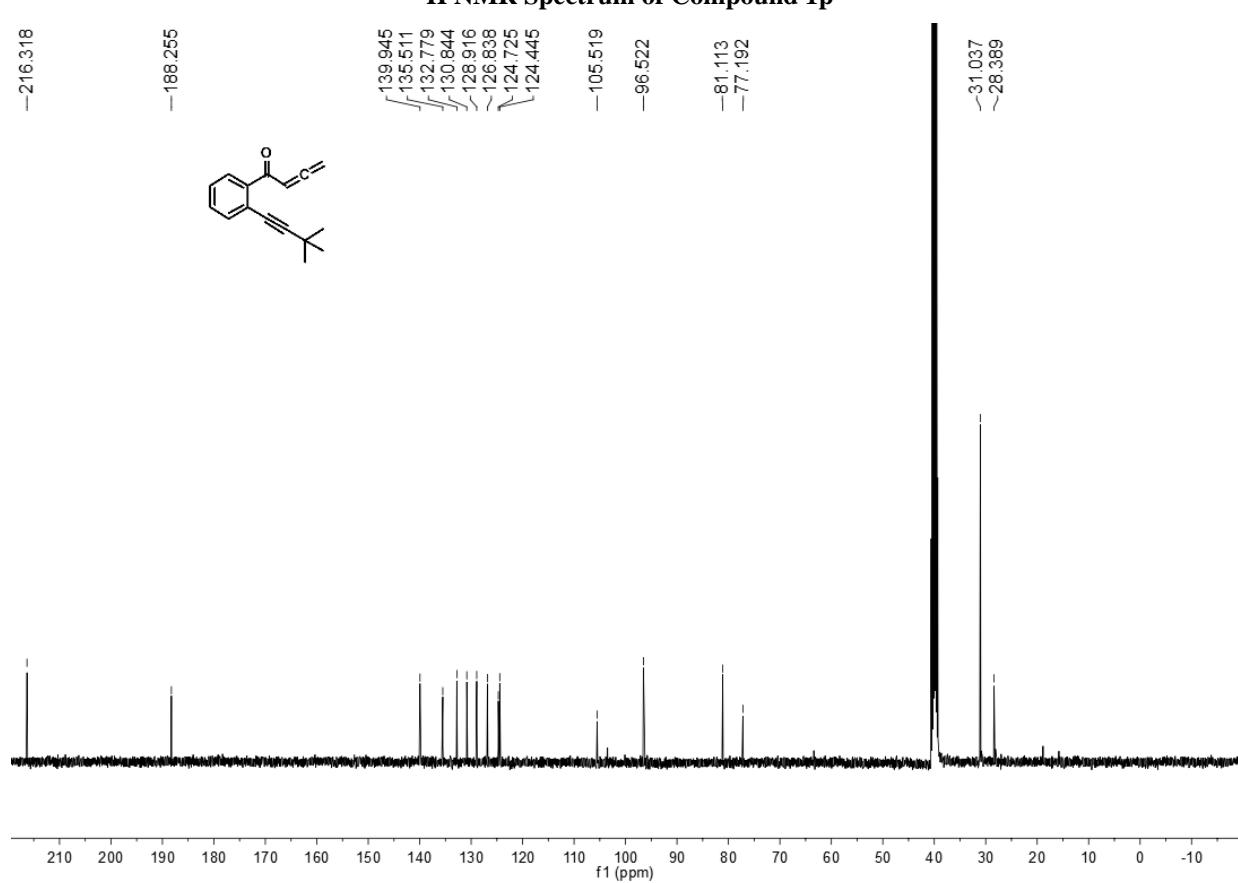
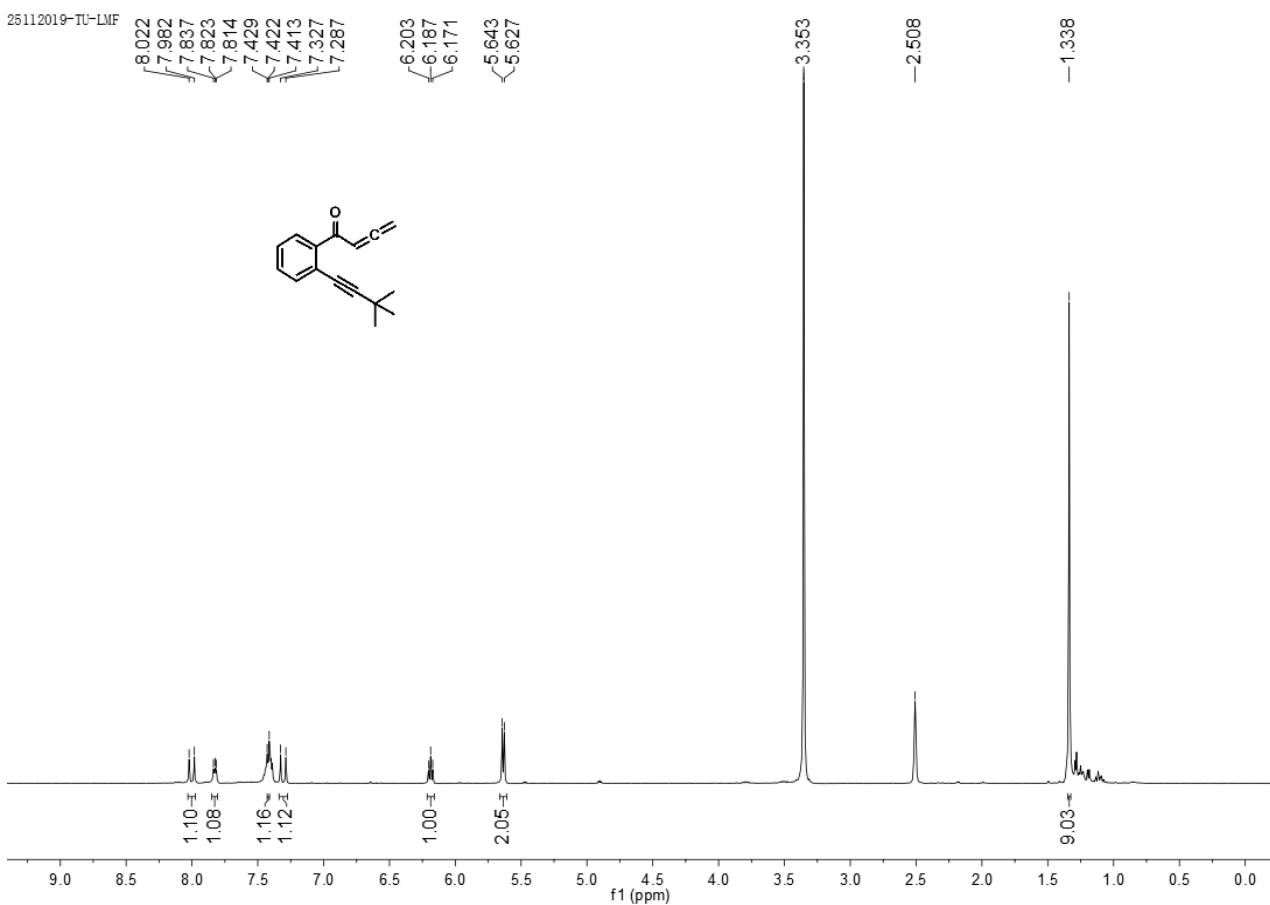


Figure S1. The ORTEP Drawing of Absolute Configuration of Product (*R*)-**3c**

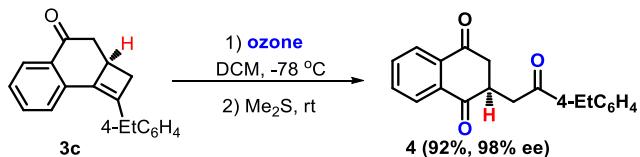
1-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)buta-2,3-dien-1-one (1p)



^1H NMR (400 MHz, DMSO) (δ , ppm): 8.00 (d, J = 16.0 Hz, 1H), 7.85-7.81 (m, 1H), 7.43-7.41 (m, 1H), 7.31 (d, J = 16.0 Hz, 1H), 6.20-6.17 (m, 1H), 5.64 (d, J = 6.4 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, DMSO) (δ , ppm): 216.3, 188.3, 139.9, 135.5, 132.8, 130.8, 128.9, 126.8, 124.7, 124.4, 105.5, 96.5, 81.1, 77.2, 31.0, 28.4.

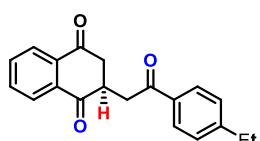


General procedure for the synthesis of compound 4



A solution of **3c** (0.1 mmol) in dry DCM was stirred at -78 °C, then the ozone generated by the ozone generator was passed into the solution until TLC (petroleum ether/ethyl acetate 10:1) revealed that conversion of the starting material **3c** was completed and the ozone was stopped. Next, the solution was quenched with dimethyl sulphide (6.0 mL) and the reaction mixture was adjusted to room temperature and stirred for 12 h. At last, the solvent was evaporated under reduced pressure, and the crude products were purified through preparative thin layer chromatography (petroleum ether/ethyl acetate 10:1) to get desired products **4** as white solid.

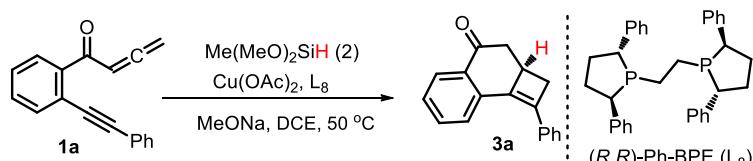
(*R*)-2-(2-(4-ethylphenyl)-2-oxoethyl)-2,3-dihydronaphthalene-1,4-dione (**4**)



White solid (instable); 56.3 mg, 92% yield; mp: 111-113 °C; $[\alpha]_D^{20} = -192.2$ (c = 0.116, acetone); ^1H NMR (400 MHz, CDCl₃) (δ , ppm): 8.11-8.08 (m, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.79-7.76 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.90-3.72 (m, 2H), 3.30-3.05 (m, 3H), 2.75 (q, J = 7.6 Hz, 2H), 1.28 (d, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl₃) (δ , ppm): 197.2, 196.7, 195.4, 150.5, 135.4, 135.3, 134.3, 134.1, 128.4, 128.2, 127.0, 126.6, 43.4, 43.0, 38.4, 29.0, 15.2. IR (KBr, ν , cm⁻¹): 2966, 2928, 1752, 1685, 1605, 1560, 1413, 828, 780; HRMS (ESI) m/z calcd for C₂₀H₁₈NaO₃ [M+Na]⁺ 329.1154, found 329.1156; HPLC: 98% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 70/30, flow rate: 0.6 mL/min, detector: 254 nm, t_R(major) = 12.515 min, t_R(minor) = 19.747 min.

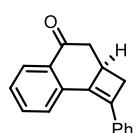
General procedure for the synthesis of compounds 3

Example for the synthesis of **3a**:



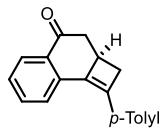
In an Ar-filled glove box, Cu(OAc)₂ (10 mol %), (*R,R*)-Ph-BPE (10 mol %), MeONa (1.5 equiv.), 1-(2-(phenylethyynyl)phenyl)buta-2,3-dien-1-one (**1a**, 0.2 mmol) and DCE (2.0 mL) were added to a Schlenk tube. The resulting mixture was stirred for 20 minutes at room temperature and then Me(MeO)₂SiH (0.6 mmol) were added successively. The Schlenk tube was removed from the dry box and the mixture was stirred in the oil bath at 50 °C for 12 hours. The mixture was concentrated under vacuum and the crude product was purified by column chromatography on silica with a mixture of ethyl acetate/petroleum ether (1:50) to get chiral desired products **3a**.

(*R*)-1-phenyl-2a,3-dihydrocyclobut[a]naphthalen-4(2H)-one (**3a**)



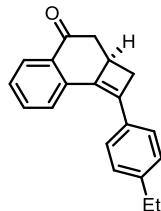
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 36.9 mg, 75% yield; $[\alpha]_D^{20} = +69.9$ ($c = 0.256$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.11-8.09 (m, 1H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.66-7.56 (m, 3H), 7.44-7.31 (m, 4H), 3.29-3.22 (m, 2H), 3.20-3.16 (m, 1H), 2.72-7.65 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 198.0, 137.5, 136.7, 136.4, 135.2, 133.6, 132.5, 128.7, 128.5, 128.2, 128.1, 126.0, 125.0, 46.1, 35.9, 35.8. IR (KBr, ν , cm^{-1}): 2949, 2922, 1685, 1602, 1529, 1451, 829, 728; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{NaO} [\text{M}+\text{Na}]^+$ 269.0942, found 269.0944; HPLC: >99% ee (Daicel Chiraldak OD-H, hexane/i-PrOH = 90/10, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (major) = 11.412 min.

(R)-1-(*p*-tolyl)-2a,3-dihydrocyclobuta[*a*]naphthalen-4(2H)-one (3b)



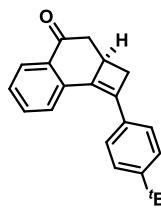
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 32.2 mg, 62% yield; $[\alpha]_D^{20} = +629.5$ ($c = 0.156$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.12-8.10 (m, 1H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.62-7.53 (m, 3H), 7.42-7.35 (m, 1H), 7.23 (d, $J = 7.6$ Hz, 2H), 3.33-3.14 (m, 3H), 2.73-2.66 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.9, 138.5, 137.5, 136.8, 135.1, 133.5, 132.4, 132.4, 129.3, 128.1, 127.8, 125.9, 124.9, 46.1, 35.8, 35.7, 21.4. IR (KBr, ν , cm^{-1}): 3005, 2909, 1683, 1592, 1510, 1461, 815, 750; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{NaO} [\text{M}+\text{Na}]^+$ 283.1099, found 283.1095; HPLC: >99% ee (Daicel Chiraldak IA, hexane/i-PrOH = 99/1, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 13.340 min, t_{R} (major) = 15.718 min.

(R)-1-(4-ethylphenyl)-2a,3-dihydrocyclobuta[*a*]naphthalen-4(2H)-one (3c)



White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 39.7 mg, 66% yield; mp: 140-142 °C; $[\alpha]_D^{20} = -1008.8$ ($c = 0.26$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.11-8.09 (m, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.65-7.54 (m, 3H), 7.42-7.36 (m, 1H), 7.26 (d, $J = 8.4$ Hz, 2H), 3.32-3.15 (m, 3H), 2.74-2.64 (m, 4H), 1.28 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.9, 144.9, 137.5, 136.8, 135.2, 133.4, 132.6, 132.4, 128.1, 128.0, 127.8, 126.0, 124.9, 46.1, 35.8, 35.7, 28.8, 15.5. IR (KBr, ν , cm^{-1}): 3005, 2965, 1683, 1594, 1507, 1462, 831, 765; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O} [\text{M}+\text{H}]^+$ 275.1436, found 275.1437; HPLC: >99% ee (Daicel Chiraldak AD-H, hexane/i-PrOH = 90/10, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 7.741 min, t_{R} (major) = 8.550 min.

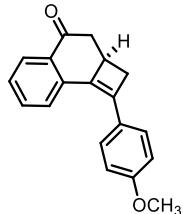
(R)-1-(4-(tert-butyl)phenyl)-2a,3-dihydrocyclobuta[*a*]naphthalen-4(2H)-one (3d)



White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 38.7 mg, 64% yield; mp: 118-120 °C; $[\alpha]_D^{20} = +632.1$ ($c = 0.468$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.10-8.08 (m, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.61-7.57 (m, 3H), 7.48-7.41 (m, 2H), 7.40-7.33 (m, 1H), 3.29-3.14 (m, 3H), 2.71-2.61 (m, 2H), 1.36 (s, 9H).

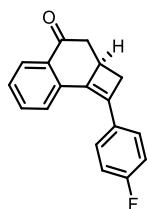
9H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.9, 151.7, 137.4, 136.8, 135.4, 133.4, 132.4, 128.0, 127.8, 125.8, 125.5, 124.9, 46.1, 35.8, 35.7, 34.8, 31.2. IR (KBr, ν , cm^{-1}): 3005, 2961, 1685, 1594, 1507, 1462, 3, 833, 750; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{O}$ [$\text{M}+\text{H}]^+$ 303.1749, found 303.1751; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH =99/1, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (major) = 17.509 min, t_{R} (minor) = 26.991 min.

(R)-1-(4-methoxyphenyl)-2a,3-di-hydrocyclobuta[a]naphthalen-4(2H)-one (3e)



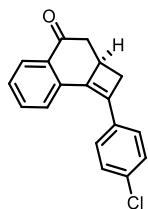
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 32.6 mg, 59% yield; $[\alpha]_D^{20} = +709.5$ ($c = 0.2$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.09-8.07 (m, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.64-7.49 (m, 3H), 7.42-7.31 (m, 1H), 7.01-6.86 (m, 2H), 3.85 (s, 3H), 3.30-3.12 (m, 3H), 2.72-2.58 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 198.0, 159.8, 137.2, 137.0, 133.7, 133.5, 132.3, 128.1, 127.6, 127.4, 124.7, 114.0, 55.3, 46.1, 35.7, 35.6. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2$ [$\text{M}+\text{H}]^+$ 277.1229, found 277.1231; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH =99/1, flow rate: 1.0 mL/min, detector: 254 nm, t_{R} (minor) = 13.628 min, t_{R} (major) = 18.175 min.

(R)-1-(4-fluorophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3f)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 36.6 mg, 69% yield; $[\alpha]_D^{20} = +201.6$ ($c = 0.127$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.11-8.09 (m, 1H), 7.75 (d, $J = 7.6$ Hz, 1H), 7.63-7.57 (m, 3H), 7.44-7.34 (m, 1H), 7.15-7.04 (m, 2H), 3.31-3.09 (m, 3H), 2.72-2.61 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.7, 163.9, 161.4 ($^1J_{\text{CF}} = 247.4$ Hz), 136.5, 136.2, 135.7(1), 135.7(9), 133.6, 132.4, 131.4(2), 131.4(8) ($^4J_{\text{CF}} = 3.7$ Hz), 128.2, 128.1, 127.8, 127.7 ($^3J_{\text{CF}} = 8.2$ Hz), 124.6, 115.7, 115.5 ($^2J_{\text{CF}} = 21.5$ Hz), 46.0, 35.8, 35.8. IR (KBr, ν , cm^{-1}): 2980, 2865, 1700, 1636, 1454, 823, 754; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{FO}$ [$\text{M}+\text{H}]^+$ 265.1029, found 265.1026; HPLC: >99% ee (Daicel Chiralpak IC, hexane/i-PrOH =70/30, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (major) = 11.156 min, t_{R} (minor) = 11.846 min.

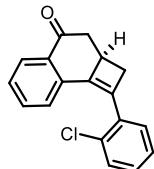
(R)-1-(4-chlorophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3g)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 45.7 mg, 72% yield; $[\alpha]_D^{20} = +540.8$ ($c = 0.279$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.11-8.09 (m, 1H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.66-7.56 (m, 3H), 7.44-7.31 (m, 4H), 3.29-3.22 (m, 2H), 3.26-3.16 (m, 1H), 2.71-2.63 (m, 2H). ^{13}C NMR (100 MHz,

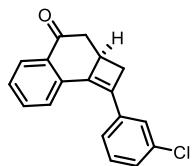
CDCl_3) (δ , ppm): 197.6, 137.0, 136.3, 136.1, 134.1, 133.6, 133.5, 132.5, 128.8, 128.2, 128.2, 127.2, 124.7, 45.9, 35.9, 35.1. IR (KBr, ν , cm^{-1}): 2940, 2911, 1683, 1591, 1477, 1407, 855, 763; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{ClO}$ [$\text{M}+\text{H}]^+$ 281.0733, found 281.0733; HPLC: 96% ee (Daicel Chiralpak IC, hexane/i-PrOH = 90/10, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (major) = 15.755 min, t_{R} (minor) = 17.453 min.

(R)-1-(2-chlorophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3h)



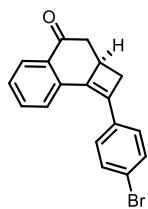
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 25.3 mg, 45% yield; $[\alpha]_D^{20} = +228.3$ ($c = 0.12$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.06 (d, $J = 7.6$ Hz, 1H), 7.68-7.61 (m, 1H), 7.49-7.47 (m, 2H), 7.44-7.33 (m, 2H), 7.27-7.21 (m, 2H), 3.50-3.45 (m, 1H), 3.33-3.24 (m, 1H), 3.20-3.15 (m, 1H), 2.90-2.86 (m, 1H), 2.75-2.68 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.7, 139.9, 135.9, 135.8, 133.9, 133.3, 132.8, 132.4, 130.4, 129.2(2), 129.2(0), 128.3, 127.9, 126.5, 124.8, 45.9, 39.7, 37.0. IR (KBr, ν , cm^{-1}): 3005, 2988, 1682, 1594, 1474, 1430, 896, 750; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{ClO}$ [$\text{M}+\text{H}]^+$ 281.0733, found 281.0732; HPLC: >99% ee (Daicel Chiralpak AS-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 9.556 min, t_{R} (major) = 10.219 min.

(R)-1-(3-chlorophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3i)



White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 38.6 mg, 63% yield; mp: 80-82 °C; $[\alpha]_D^{20} = +492.5$ ($c = 0.518$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.11-8.09 (m, 1H), 7.75 (d, $J = 7.6$ Hz, 1H), 7.63-7.59 (m, 1H), 7.57-7.56 (m, 1H), 7.53-7.51 (m, 1H), 7.42-7.38 (m, 1H), 7.36-7.27 (m, 2H), 3.27-3.15 (m, 3H), 2.71-2.61 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.4, 138.0, 136.8, 136.1, 135.8, 134.7, 133.6, 132.5, 129.8, 128.4, 128.3, 128.2, 126.0, 124.8, 124.0, 45.9, 36.0, 35.7. IR (KBr, ν , cm^{-1}): 2975, 2922, 1682, 1507, 1456, 1417, 762, 700; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{ClO}$ [$\text{M}+\text{H}]^+$ 281.0733, found 281.0725; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 11.725 min, t_{R} (major) = 13.959 min.

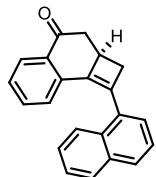
(R)-1-(4-bromophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3j)



White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 32.4 mg, 50% yield; mp: 95-97 °C; $[\alpha]_D^{20} = +520.5$ ($c = 0.336$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.11-8.08 (m, 1H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.61-7.57 (m, 1H), 7.56-7.45 (m, 4H), 7.43-7.36 (m, 1H), 3.25-3.15 (m, 3H), 2.72-2.61 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.5, 137.2, 136.3, 136.1, 133.9, 133.6, 132.5, 131.8, 128.3, 128.2, 127.4, 124.7, 122.3, 45.9, 35.9, 35.7. IR (KBr, ν , cm^{-1}): 3061, 2908, 1682, 1594, 1486, 1396, 820, 750; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{BrO}$

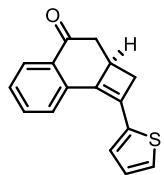
$[M+H]^+$ 325.0228, found 325.0221; HPLC: >99% ee (Daicel Chiralpak AS-H, hexane/i-PrOH =95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 11.319 min, t_R (major) = 13.121 min.

(R)-1-(naphthalen-1-yl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3k)



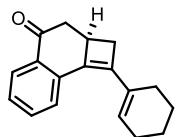
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 36.1 mg, 61% yield; $[\alpha]_D^{20} = +1094.3$ ($c = 0.12$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.14-8.12 (m, 1H), 7.96 (s, 1H), 7.92-7.80 (m, 5H), 7.65-7.60 (m, 1H), 7.55-7.47 (m, 2H), 7.43-7.39 (m, 1H), 3.38-3.18 (m, 3H), 2.79-2.66 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.8, 137.5, 136.8, 136.7, 133.6, 133.4, 133.2, 132.6, 132.5, 128.2, 128.2, 128.2, 128.1, 127.8, 126.5, 126.4, 125.2, 124.9, 123.7, 46.1, 36.0, 35.8. IR (KBr, ν , cm^{-1}): 3005, 2989, 1684, 1592, 1458, 1275, 817, 750; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{17}\text{O}$ $[M+H]^+$ 297.1279, found 297.1275; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH =95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 15.439 min, t_R (major) = 18.025 min.

(R)-1-(thiophen-2-yl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3l)



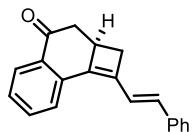
White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 40.1 mg, 70% yield; mp: 102-104 °C; $[\alpha]_D^{20} = +1886.5$ ($c = 0.200$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.07-8.06 (m, 1H), 7.88 (d, $J = 7.6$ Hz, 1H), 7.64-7.60 (m, 1H), 7.39-7.33 (m, 2H), 7.20 (d, $J = 3.5$ Hz, 1H), 7.08 (dd, $J = 5.0, 3.6$ Hz, 1H), 3.41-3.24 (m, 1H), 3.22-3.11 (m, 2H), 2.77-2.66 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.6, 138.0, 135.9, 133.6, 133.4, 132.2, 130.6, 128.0, 127.9, 127.5, 125.9(2), 125.9(9), 125.1, 45.8, 36.4, 36.2. IR (KBr, ν , cm^{-1}): 3059, 2911, 1680, 1591, 1560, 1463, 852, 709; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{OS}$ $[M+H]^+$ 253.0687, found 253.0694; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH =95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 12.618 min, t_R (major) = 13.255 min.

(R)-1-(cyclohex-1-en-1-yl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3m)



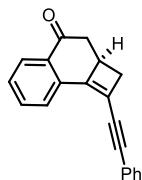
Colorless oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 27.5 mg, 55% yield; $[\alpha]_D^{20} = +43.9$ ($c = 0.13$, acetone); ^1H NMR (400 MHz, Acetone) (δ , ppm): 7.96 (d, $J = 7.6$ Hz, 1H), 7.74-7.55 (m, 2H), 7.39-7.36 (m, 1H), 6.00 (s, 1H), 3.13-2.96 (m, 2H), 2.67-2.52 (m, 2H), 2.46-2.34 (m, 2H), 2.21 (s, 2H), 1.82 (s, 1H), 1.65 (d, $J = 41.6$ Hz, 3H), 1.30 (s, 1H). ^{13}C NMR (100 MHz, Acetone) (δ , ppm): 196.6, 139.9, 136.8, 133.8, 133.2, 133.1, 132.2, 128.0, 127.3, 126.0, 45.7, 35.1, 34.2, 27.1, 25.5, 22.3, 21.7. IR (KBr, ν , cm^{-1}): 3051, 2949, 1676, 1592, 1509, 1445, 1423, 839, 760; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{NaO}$ $[M+\text{Na}]^+$ 273.1255, found 273.1245; HPLC: 98% ee (Daicel Chiralcel OJ-H, hexane/i-PrOH =70/30, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 8.186 min, t_R (major) = 8.642 min.

(R,E)-1-styryl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3n)



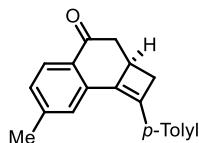
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 37.5 mg, 69% yield; $[\alpha]_D^{20} = +360.9$ ($c = 0.041$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.04 (d, $J = 8.0$ Hz, 1H), 7.59-7.50 (m, 4H), 7.41-7.34 (m, 3H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 16.0$ Hz, 1H), 6.72 (d, $J = 15.6$ Hz, 1H), 3.34-3.26 (m, 1H), 3.18-3.09 (m, 2H), 2.71-2.64 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.8, 137.7, 137.3, 136.8, 136.3, 133.6, 132.3, 132.0, 128.7, 128.2, 127.9, 127.7, 126.7, 124.9, 121.5, 45.8, 35.7, 34.7. IR (KBr, ν , cm^{-1}): 3035, 2957, 1678, 1623, 1567, 1409, 887, 798; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{O}$ [$\text{M}+\text{H}]^+$ 273.1279, found 273.1272; HPLC: >99% ee (Daicel Chiralpak IA, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 10.639 min, t_R (major) = 11.536 min.

(R)-1-(phenylethyynyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3o)



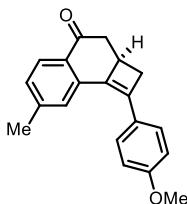
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 25.4 mg, 47% yield; $[\alpha]_D^{20} = +286.0$ ($c = 0.21$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.01 (d, $J = 7.2$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.61-7.57 (m, 1H), 7.54-7.49 (m, 2H), 7.41-7.34 (m, 4H), 3.34-3.25 (m, 1H), 3.16-3.06 (m, 2H), 2.77-2.65 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.2, 147.3, 135.1, 133.8, 132.1, 131.8, 128.7, 128.6, 128.4, 127.6, 126.7, 124.5, 122.8, 117.8, 93.9, 84.7, 45.3, 39.3, 36.9. IR (KBr, ν , cm^{-1}): 3065, 2936, 1640, 1609, 1554, 1439, 847, 754; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{NaO}$ [$\text{M}+\text{Na}]^+$ 293.0942, found 293.0934; HPLC: 72% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 99/1, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 22.919 min, t_R (major) = 27.665 min.

(R)-7-methyl-1-(p-tolyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3q)



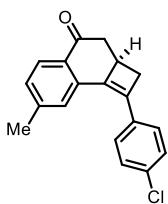
White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 41.8 mg, 76% yield; mp: 114-116 °C; $[\alpha]_D^{20} = +439.8$ ($c = 0.728$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.99 (d, $J = 8.0$ Hz, 1H), 7.60-7.51 (m, 3H), 7.26-7.14 (m, 3H), 3.24-3.09 (m, 3H), 2.67-2.60 (m, 2H), 2.45 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.7, 144.2, 138.4, 137.2, 136.9, 135.4, 132.5, 130.2, 129.3, 128.8, 128.1, 125.9, 125.2, 46.0, 35.9, 35.7, 22.0, 21.4. IR (KBr, ν , cm^{-1}): 2989, 2931, 1683, 1600, 1510, 1467, 829, 747; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}$ [$\text{M}+\text{H}]^+$ 275.1436, found 275.1432; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 99/1, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 13.817 min, t_R (major) = 18.564 min.

(R)-1-(4-methoxyphenyl)-7-methyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3r)



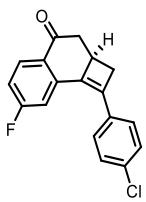
White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 32.0 mg, 55% yield; mp: 118-120 °C; $[\alpha]_D^{20} = +647.1$ (c = 0.384, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.98 (d, J = 8.0 Hz, 1H), 7.59-7.55 (m, 3H), 7.17-7.15 (m, 1H), 6.97-6.91 (m, 2H), 3.85 (s, 3H), 3.22-3.09 (m, 3H), 2.67-2.58 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.8, 159.7, 144.2, 137.0, 136.9, 133.9, 130.1, 128.6, 128.2, 128.2, 127.4, 125.0, 114.0, 55.3, 46.0, 35.7, 35.7, 22.0. IR (KBr, ν , cm^{-1}): 3004, 2907, 1675, 1606, 1510, 1463, 828, 764; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2$ [M+H]⁺ 291.1385, found 291.1381; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 12.597 min, t_{R} (major) = 15.511 min).

(R)-1-(4-chlorophenyl)-7-methyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3s)



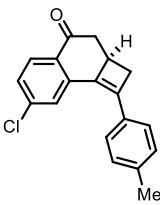
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 28.9 mg, 49% yield; $[\alpha]_D^{20} = +242.3$ (c = 0.104, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.00 (d, J = 8.0 Hz, 1H), 7.59-7.50 (m, 3H), 7.40-7.34 (m, 2H), 7.21 (d, J = 8.0 Hz, 1H), 3.23-3.12 (m, 3H), 2.69-2.59 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.4, 144.4, 137.2, 136.4, 135.8, 134.0, 133.6, 130.3, 129.3, 128.8, 128.3, 127.2, 125.0, 45.9, 36.0, 35.7, 22.0. IR (KBr, ν , cm^{-1}): 3005, 2922, 1682, 1602, 1490, 1401, 825, 746; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{ClO}$ [M+H]⁺ 295.0890, found 295.0885; HPLC: 99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 10.420 min, t_{R} (major) = 11.135 min).

(R)-1-(4-chlorophenyl)-7-fluoro-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3t)



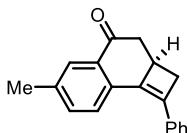
White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 23.8 mg, 40% yield; mp: 134-136 °C; $[\alpha]_D^{20} = +570.5$ (c = 0.200, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.14-8.10 (m, 1H), 7.54-7.50 (m, 2H), 7.41-7.34 (m, 3H), 7.09-7.04 (m, 1H), 3.26-3.12 (m, 3H), 2.69-2.60 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 196.1, 167.0, 164.5, 138.7, 138.6, 137.7, 135.8, 134.5, 133.1, 131.4, 131.3, 129.1, 129.0, 127.3, 115.7, 115.5, 111.3, 111.1, 45.6, 36.0, 35.9. IR (KBr, ν , cm^{-1}): 3005, 2989, 1684, 1600, 1491, 1401, 828, 763; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{13}\text{ClFO}$ [M+H]⁺ 299.0639, found 299.0640; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 11.232 min, t_{R} (major) = 12.095 min).

(R)-7-chloro-1-(*p*-tolyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3u)



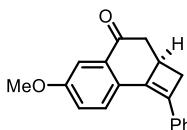
White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 35.3 mg, 60% yield; mp: 126-128 °C; $[\alpha]_D^{20} = +338.7$ (c = 0.194, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 8.01 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.32-7.30 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 3.25-3.12 (m, 3H), 2.68-2.60 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 196.9, 139.9, 139.2, 139.0, 138.0, 133.6, 132.0, 130.6, 129.7, 129.4, 128.0, 126.0, 124.6, 45.8, 35.9, 35.7, 21.5. IR (KBr, ν , cm^{-1}): 3005, 2985, 1685, 1586, 1511, 1416, 897, 764; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{ClO}$ [$\text{M}+\text{H}]^+$ 295.0890, found 295.0891; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 9.823 min, t_{R} (major) = 10.313 min.

(R)-6-methyl-1-phenyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3v)



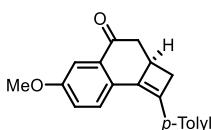
White solid after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 38.6 mg, 74% yield; mp: 72-74 °C; $[\alpha]_D^{20} = +444.2$ (c = 0.484, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.91 (d, J = 0.4 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.64-7.62 (m, 2H), 7.42-7.38 (m, 3H), 7.34-7.32 (m, 1H), 3.25-3.14 (m, 3H), 2.69-2.62 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 198.2, 138.1, 136.4, 136.4, 135.2, 134.3, 134.1, 132.3, 128.6, 128.3, 128.2, 125.9, 124.9, 46.1, 35.9, 35.6, 21.4. IR (KBr, ν , cm^{-1}): 3005, 2989, 1684, 1605, 1493, 1474, 825, 762; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{O}$ [$\text{M}+\text{H}]^+$ 261.1279, found 261.1278; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 9.906 min, t_{R} (major) = 12.111 min.

(R)-6-methoxy-1-phenyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3w)



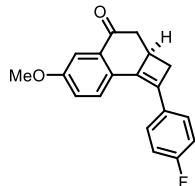
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 33.8 mg, 61% yield; $[\alpha]_D^{20} = -464.1$ (c = 0.128, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.75 (d, J = 8.4 Hz, 1H), 7.62-7.59 (m, 3H), 7.42-7.37 (m, 2H), 7.33-7.27 (m, 1H), 7.17-7.15 (m, 1H), 3.89 (s, 3H), 3.25-3.13 (m, 3H), 2.70-2.61 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.9, 159.4, 136.1, 135.3, 135.2, 133.8, 130.0, 128.6, 128.1, 126.5, 125.8, 121.4, 110.7, 55.6, 45.9, 35.9, 35.5. IR (KBr, ν , cm^{-1}): 3005, 1679, 1596, 1511, 1478, 828, 750; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2$ [$\text{M}+\text{H}]^+$ 277.1229, found 277.1231; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_{R} (minor) = 12.267 min, t_{R} (major) = 15.445 min.

(R)-6-methoxy-1-(*p*-tolyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3x)



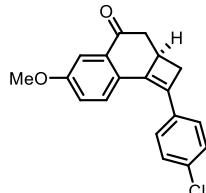
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 30.7 mg, 53% yield; $[\alpha]_D^{20} = -35.8$ ($c = 0.226$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.73 (d, $J = 8.4$ Hz, 1H), 7.58 (d, $J = 2.8$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.21-7.14 (m, 1H), 3.88 (s, 3H), 3.25-3.12 (m, 3H), 2.69-2.62 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 198.0, 159.2, 138.1, 135.2, 134.9, 133.7, 132.6, 130.2, 129.2, 126.4, 125.7, 121.4, 110.6, 55.6, 46.0, 35.8, 35.5, 21.4. IR (KBr, ν , cm^{-1}): 3005, 2989, 1680, 1599, 1511, 1478, 813, 750; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2$ [$\text{M}+\text{H}]^+$ 291.1385, found 291.1381; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 10.727 min, t_R (major) = 12.598 min.

(R)-1-(4-fluorophenyl)-6-methoxy-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3y)



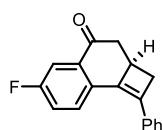
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 42.3 mg, 72% yield; $[\alpha]_D^{20} = -116.3$ ($c = 0.086$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.68 (d, $J = 8.8$ Hz, 1H), 7.61-7.54 (m, 3H), 7.17-7.14 (m, 1H), 7.09-7.05 (m, 2H), 3.89 (s, 3H), 3.23-3.12 (m, 3H), 2.68-2.62 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.7, 163.6, 161.2 ($^1J_{\text{CF}} = 246.8$ Hz), 159.4, 135.5(0), 135.5(8), 133.9(4), 133.9(5) ($^3J_{\text{CF}} = 8.6$ Hz), 131.7, 131.6 ($^4J_{\text{CF}} = 3.3$ Hz), 129.8, 127.5, 127.4, 126.2, 121.4, 115.7, 115.5 ($^2J_{\text{CF}} = 21.5$ Hz), 110.8, 55.6, 45.9, 35.8, 35.6. IR (KBr, ν , cm^{-1}): 3005, 2989, 1685, 1597, 1508, 1462, 830, 763; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{NaFO}_2$ [$\text{M}+\text{Na}]^+$ 317.0954, found 317.0957; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 11.816 min, t_R (major) = 12.692 min.

(R)-1-(4-chlorophenyl)-6-methoxy-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3z)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 54.6 mg, 88% yield; $[\alpha]_D^{20} = -38.4$ ($c = 0.700$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.68 (d, $J = 8.4$ Hz, 1H), 7.59 (d, $J = 2.8$ Hz, 1H), 7.54-7.50 (m, 2H), 7.38-7.33 (m, 2H), 7.18-7.15 (m, 1H), 3.89 (s, 3H), 3.24-3.14 (m, 3H), 2.70-2.62 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm): 197.6, 159.6, 136.8, 133.9, 133.8, 133.8, 133.7, 129.6, 128.8, 127.0, 126.3, 121.4, 110.8, 55.6, 45.8, 36.0, 35.4. IR (KBr, ν , cm^{-1}): 3005, 2989, 1685, 1598, 1492, 1474, 822, 766; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{ClNaO}_2$ [$\text{M}+\text{Na}]^+$ 333.0658, found 333.0656; HPLC: >99% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 12.583 min, t_R (major) = 13.148 min.

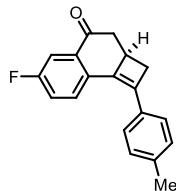
(R)-6-fluoro-1-phenyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (3aa)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 26.1 mg, 54% yield; $[\alpha]_D^{20} = +432.6$ ($c = 0.092$, acetone); ^1H NMR (400 MHz, CDCl_3) (δ , ppm): 7.84-7.76 (m, 2H), 7.62 (d, $J = 7.2$ Hz, 2H), 7.45-7.41 (m, 2H), 7.38-7.29 (m, 2H), 3.30-3.17 (m, 3H), 2.71-2.65 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm):

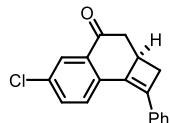
196.7, 163.4, 160.9 ($^1J_{CF} = 248.1$ Hz), 137.1, 135.1, 134.9, 134.5(2), 134.5(6), 133.0(2), 133.0(9) ($^4J_{CF} = 3.2$ Hz), 128.6, 128.5, 127.0, 126.9 ($^3J_{CF} = 7.2$ Hz), 125.9, 120.9, 120.7 ($^2J_{CF} = 22.4$ Hz), 114.6, 114.4, 45.7, 35.7, 35.7. IR (KBr, ν , cm $^{-1}$): 3005, 2988, 1686, 1603, 1521, 1445, 826, 750; HRMS (ESI) m/z calcd for C₁₈H₁₄FO [M+Na] $^{+}$ 265.1029, found 265.1028; HPLC: 97% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R(minor) = 10.487 min, t_R(major) = 13.519 min.

(R)-6-fluoro-1-(*p*-tolyl)-2*a*,3-dihydrocyclobuta[*a*]naphthalen-4(2*H*)-one (3bb)



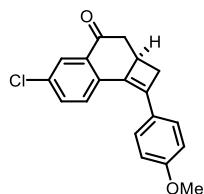
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 31.2 mg, 56% yield; $[\alpha]_D^{20} = +303.0$ (c = 0.462, acetone); ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 7.82-7.70 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.32-7.26 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 3.25-3.14 (m, 3H), 2.70-2.60 (m, 2H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 196.8, 160.0, 137.9, 135.2 ($^1J_{CF} = 269.9$ Hz), 133.6, 133.5, 133.4, 132.3, 128.1, 127.8, 127.4, 126.2, 114.1, 55.4, 45.8, 35.8, 35.4. IR (KBr, ν , cm $^{-1}$): 3025, 2914, 1686, 1603, 1511, 1417, 813, 749; HRMS (ESI) m/z calcd for C₁₉H₁₆FO [M+H] $^{+}$ 279.1185, found 279.1187; HPLC: >99% ee (Daicel Chiralpak IA, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R(minor) = 8.694 min, t_R(major) = 9.912 min.

(R)-6-chloro-1-phenyl-2*a*,3-dihydrocyclobuta[*a*]naphthalen-4(2*H*)-one (3cc)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 35.4 mg, 63% yield; $[\alpha]_D^{20} = +127.0$ (c = 0.126, acetone); ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 8.07 (d, J = 2.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.57-7.55 (m, 1H), 7.46-7.33 (m, 3H), 3.31-3.15 (m, 3H), 2.74-2.62 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 196.6, 138.2, 134.9, 134.9, 134.8, 134.1, 133.6, 133.4, 128.7, 128.1, 126.3, 126.0, 45.7, 35.9, 35.6. IR (KBr, ν , cm $^{-1}$): 3051, 2983, 1685, 1585, 1492, 1462, 825, 742; HRMS (ESI) m/z calcd for C₁₈H₁₄ClO [M+H] $^{+}$ 281.0733, found 281.0734; HPLC: 96% ee (Daicel Chiralcel OD-H, hexane/i-PrOH = 95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R(minor) = 9.772 min, t_R(major) = 12.988 min.

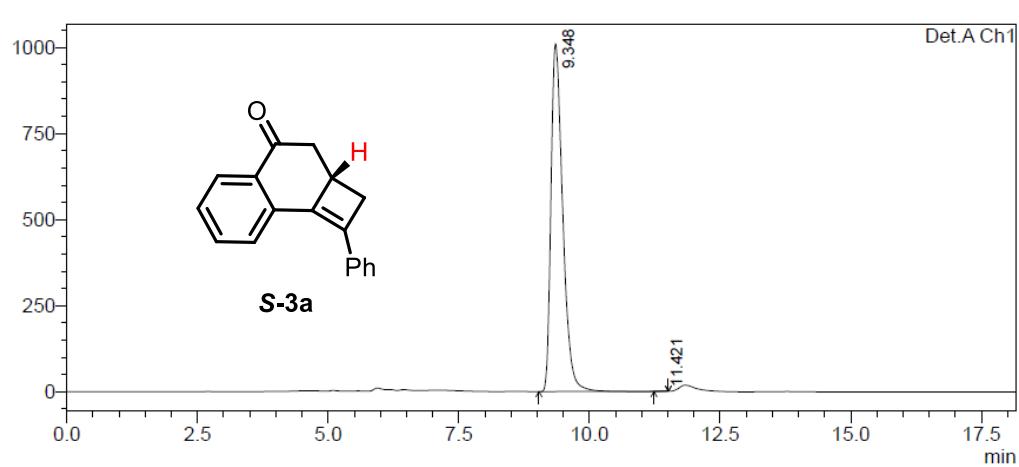
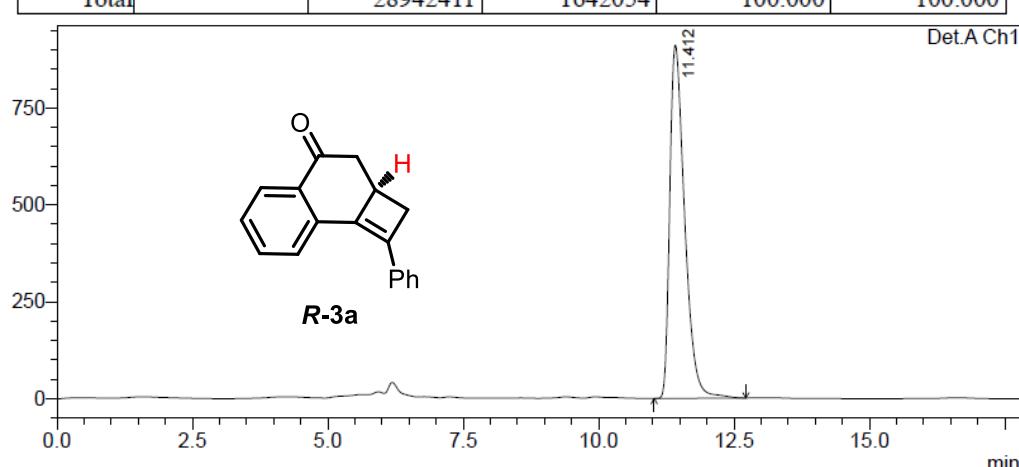
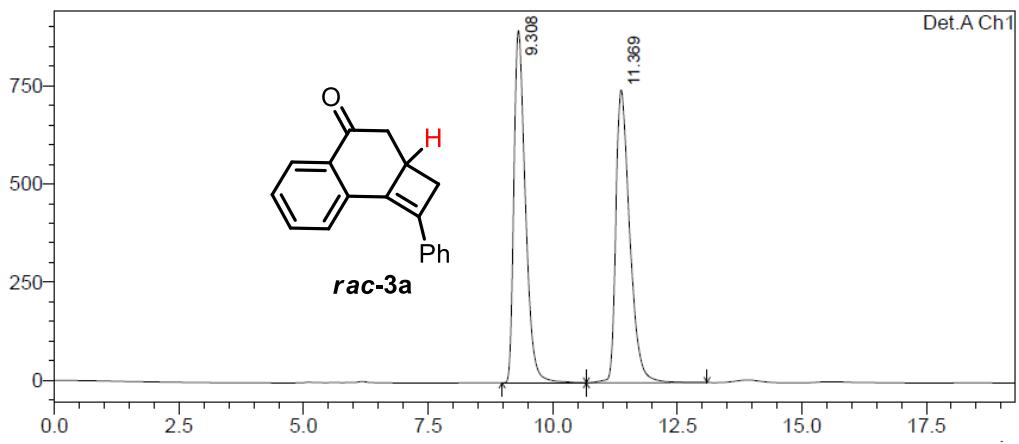
(R)-6-chloro-1-(4-methoxyphenyl)-2*a*,3-dihydrocyclobuta[*a*]naphthalen-4(2*H*)-one (3dd)

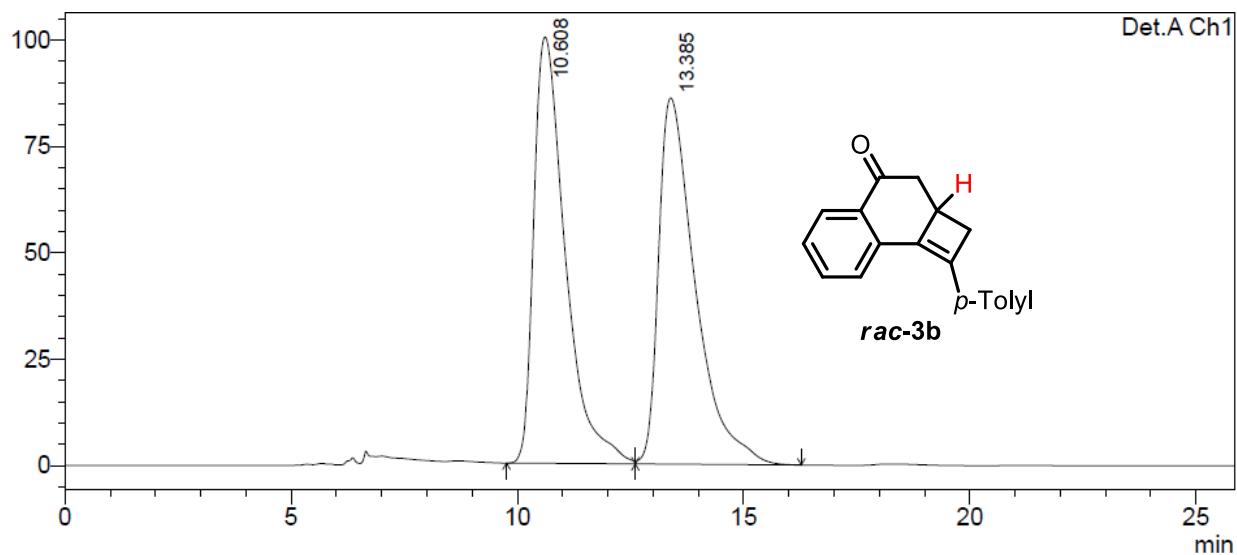


Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 50/1); 37.8 mg, 61% yield; $[\alpha]_D^{20} = +312.0$ (c = 0.150, acetone); ¹H NMR (400 MHz, CDCl₃) (δ , ppm): 8.03 (d, J = 2.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.59-7.47 (m, 3H), 6.96-6.90 (m, 2H), 3.85 (s, 3H), 3.26-3.12 (m, 3H), 2.70-2.59 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) (δ , ppm): 196.8, 160.0, 137.9, 135.2, 133.6, 133.5, 133.4, 132.3, 128.1, 127.8, 127.4, 126.2, 114.1, 55.4, 45.8, 35.8, 35.4. IR (KBr, ν , cm $^{-1}$): 3004, 2932, 1685, 1602, 1510, 1420, 826, 748; HRMS (ESI) m/z calcd for C₁₉H₁₅ClNaO₂

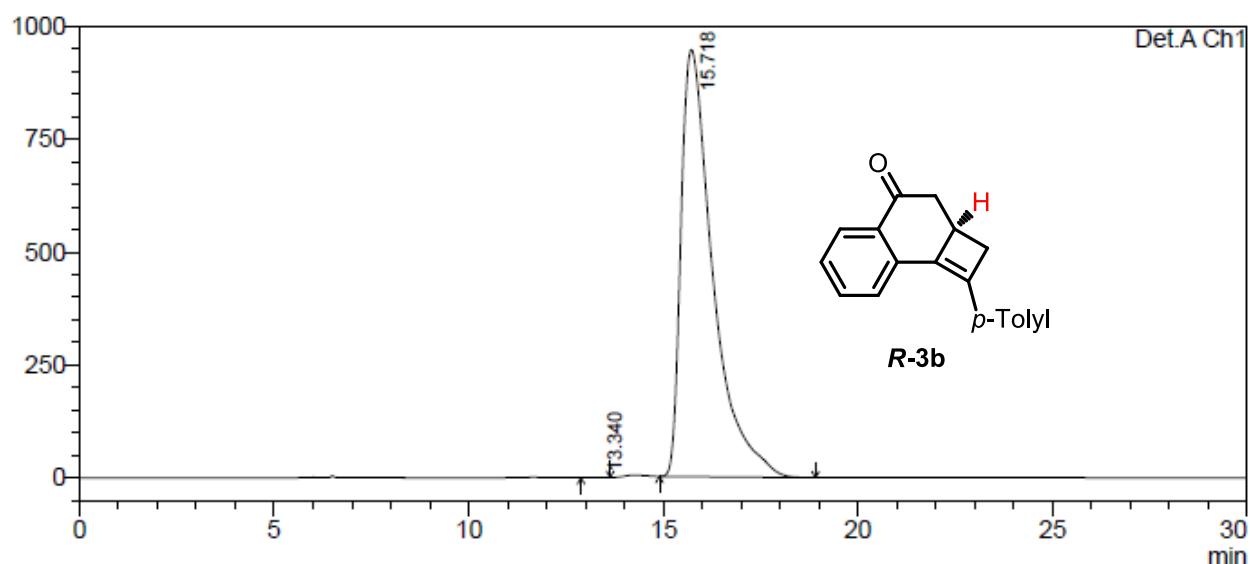
$[M+Na]^+$ 333.0658, found 333.0657; HPLC: 99% ee (Daicel Chiralpak IA, hexane/i-PrOH =95/5, flow rate: 0.6 mL/min, detector: 254 nm, t_R (minor) = 12.863 min, t_R (major) = 17.249 min.

Chiral HPLC analyses of products 3

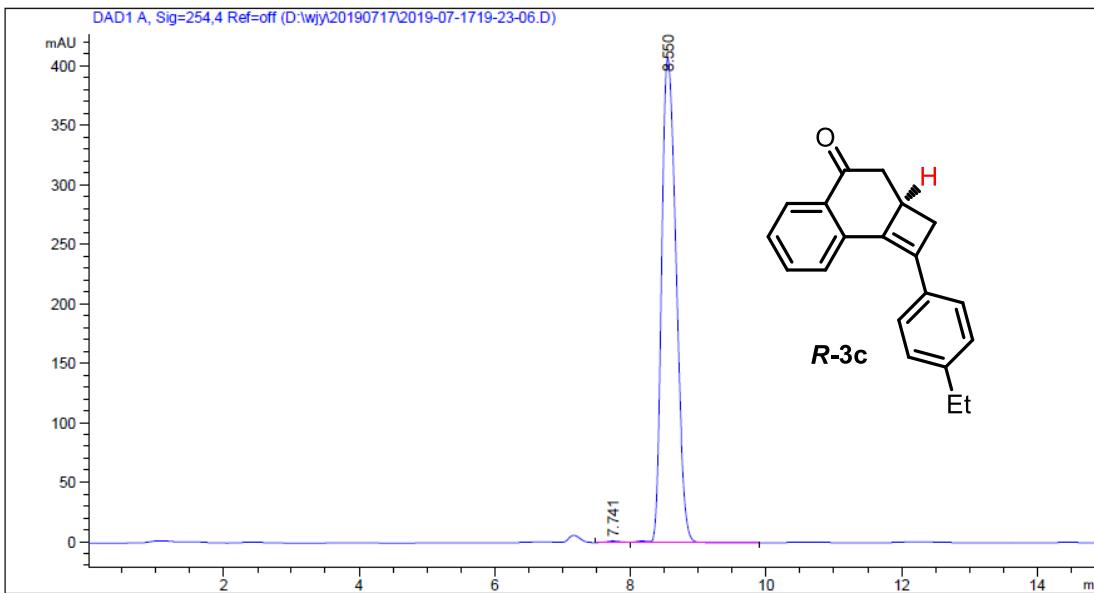
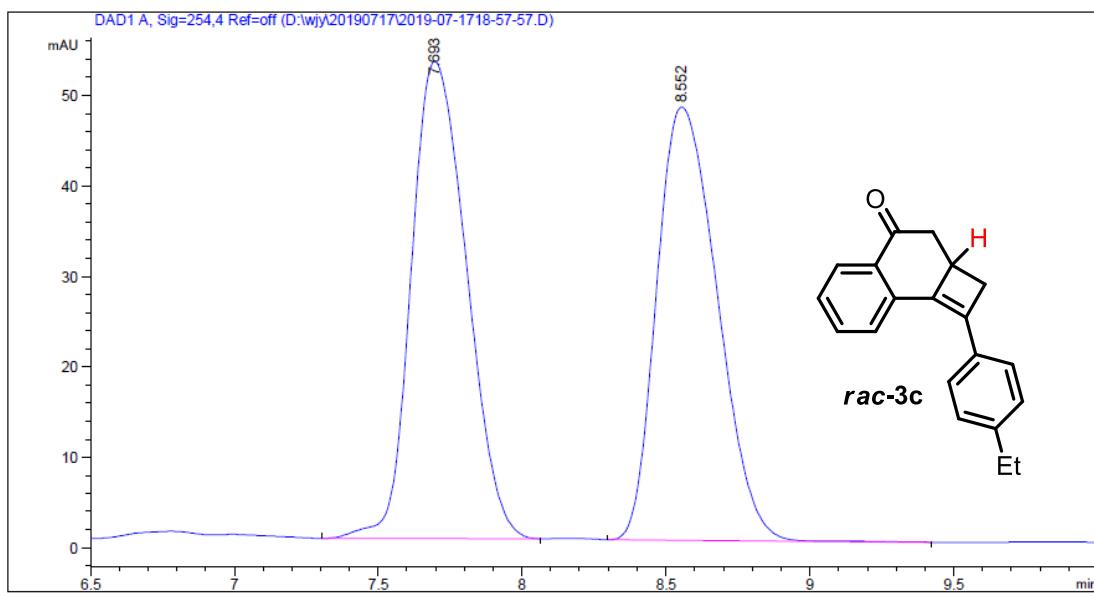




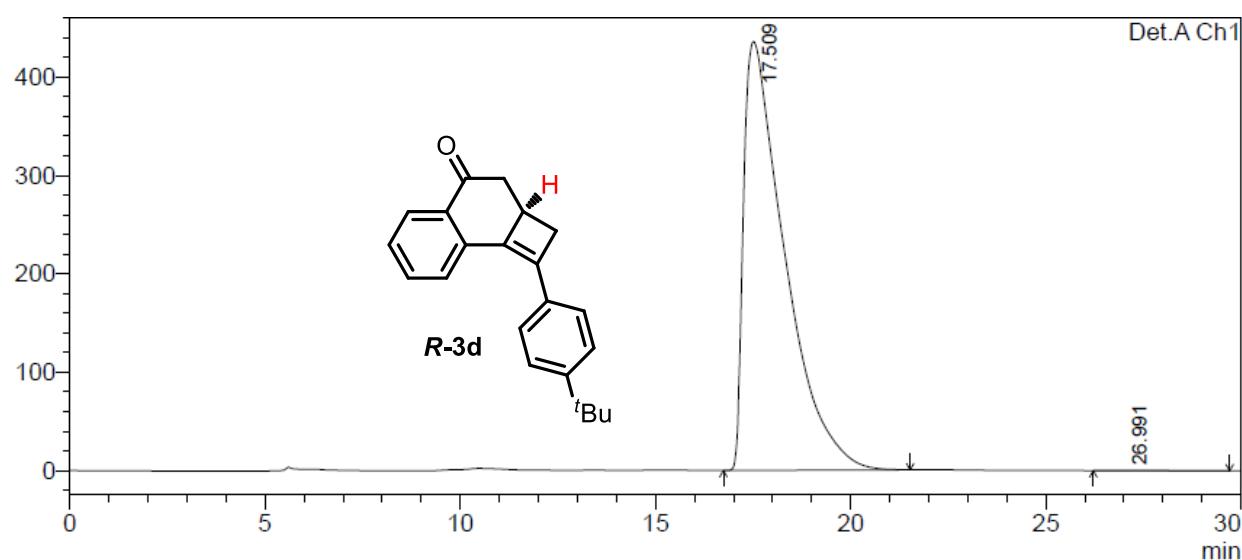
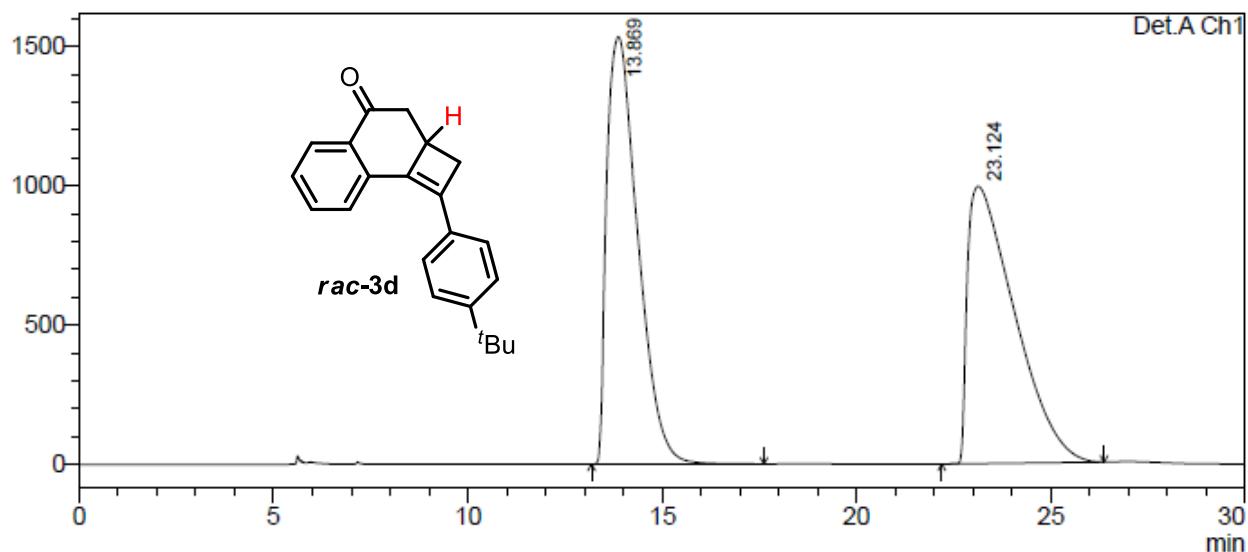
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.608	4855996	100131	50.041	53.794
2	13.385	4848102	86005	49.959	46.206
Total		9704098	186136	100.000	100.000

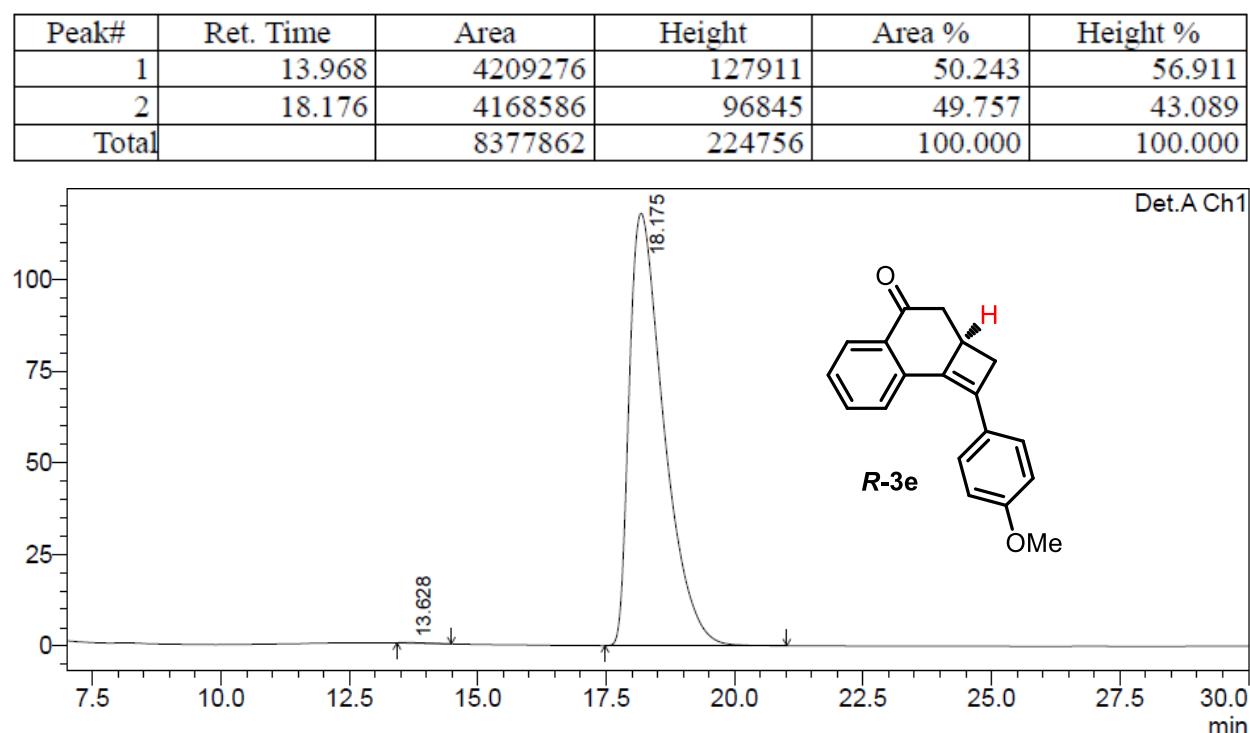
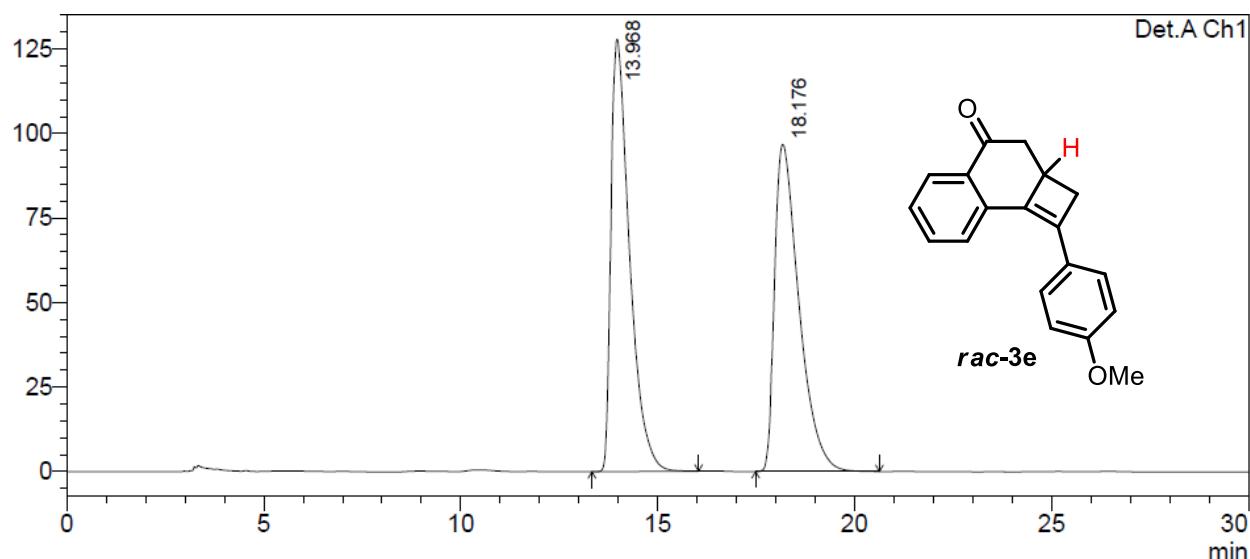


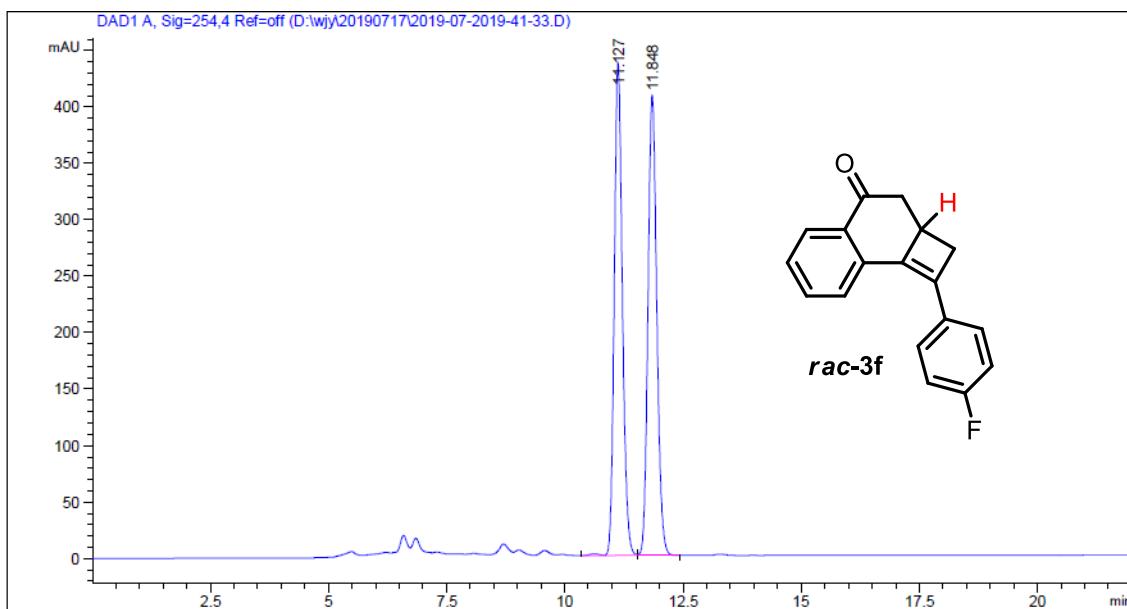
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.340	10841	434	0.020	0.046
2	15.718	53805793	945111	99.980	99.954
Total		53816634	945545	100.000	100.000



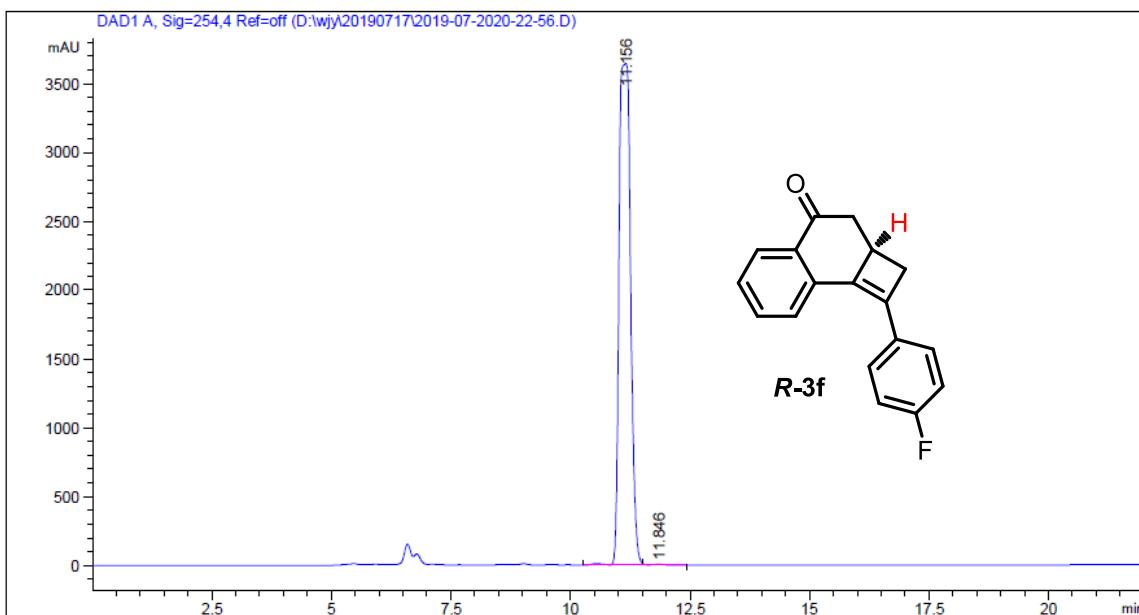
peak #	Retention time [min]	type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.741	BV E	0.2249	19.77050	1.30383	0.3287
2	8.550	VB R	0.2373	5995.68799	407.24240	99.6713



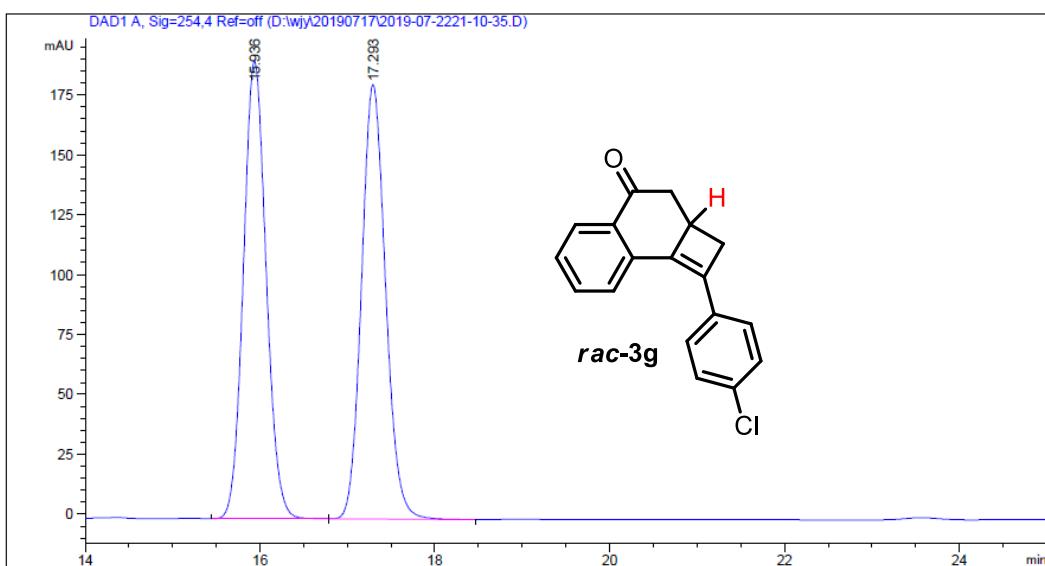




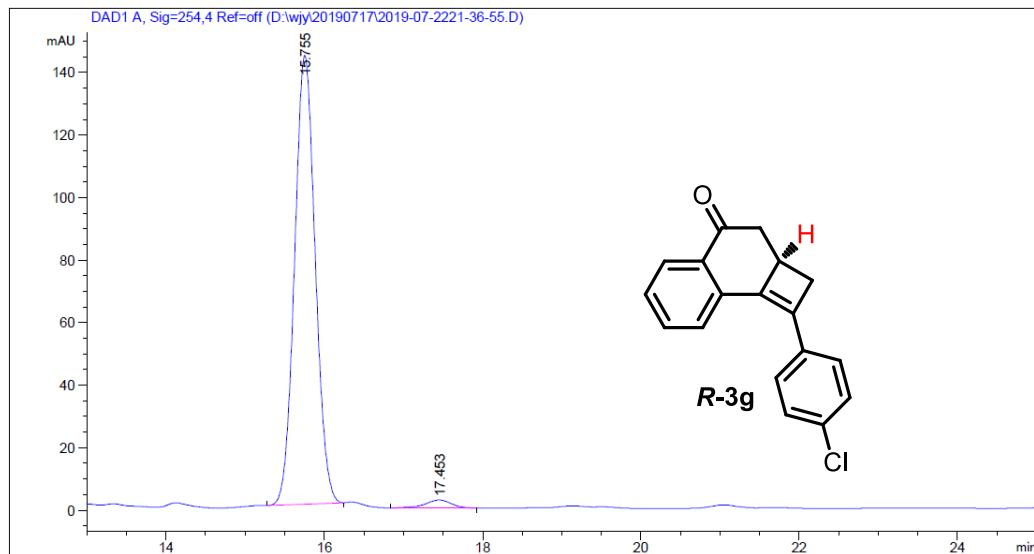
peak	Retention time	type	width	Area	Height	Area
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.127	VV R	0.1860	5259.14551	436.34793	50.0755
2	11.848	VB	0.1981	5243.29102	407.65311	49.9245



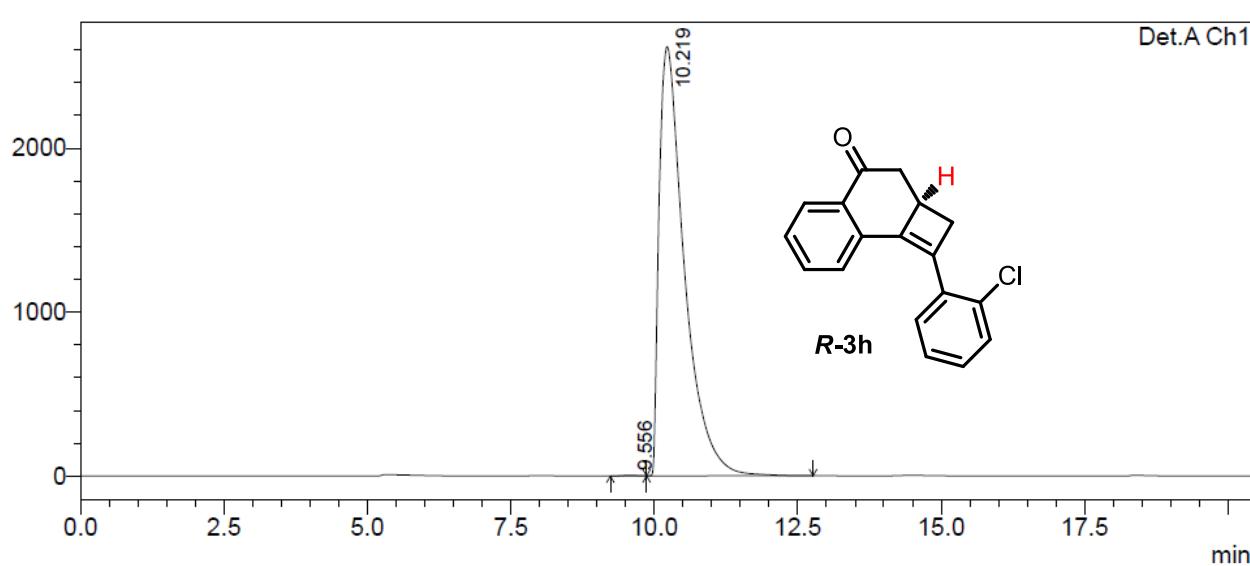
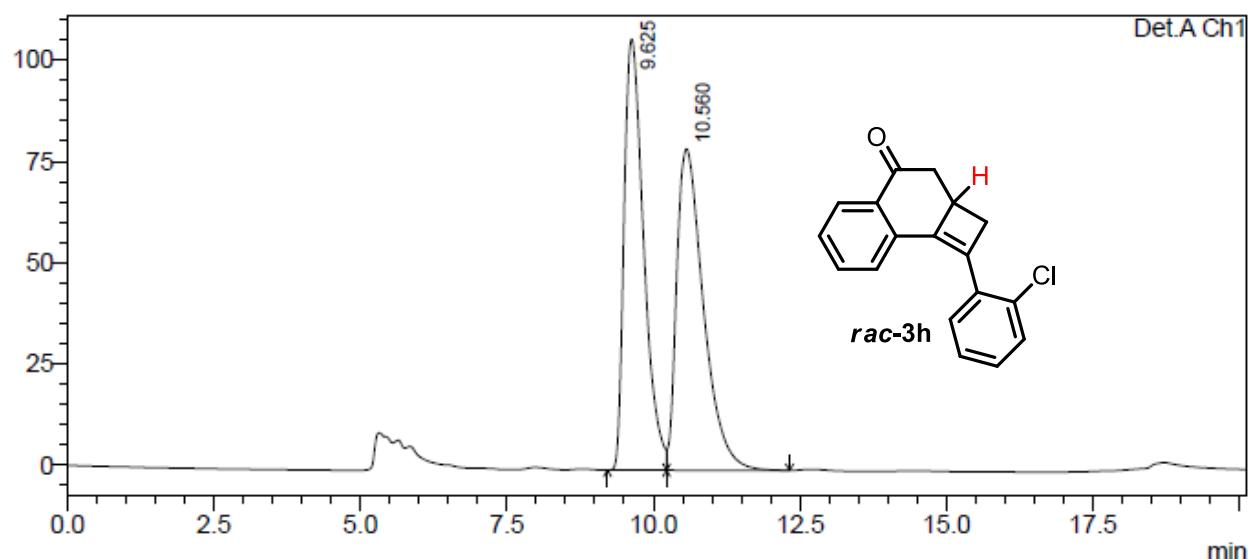
peak	Retention time	type	width	Area	Height	Area
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.156	VV R	0.2331	6.11520e4	3644.91211	99.8084
2	11.846	VB E	0.2433	117.42107	7.16215	0.1916

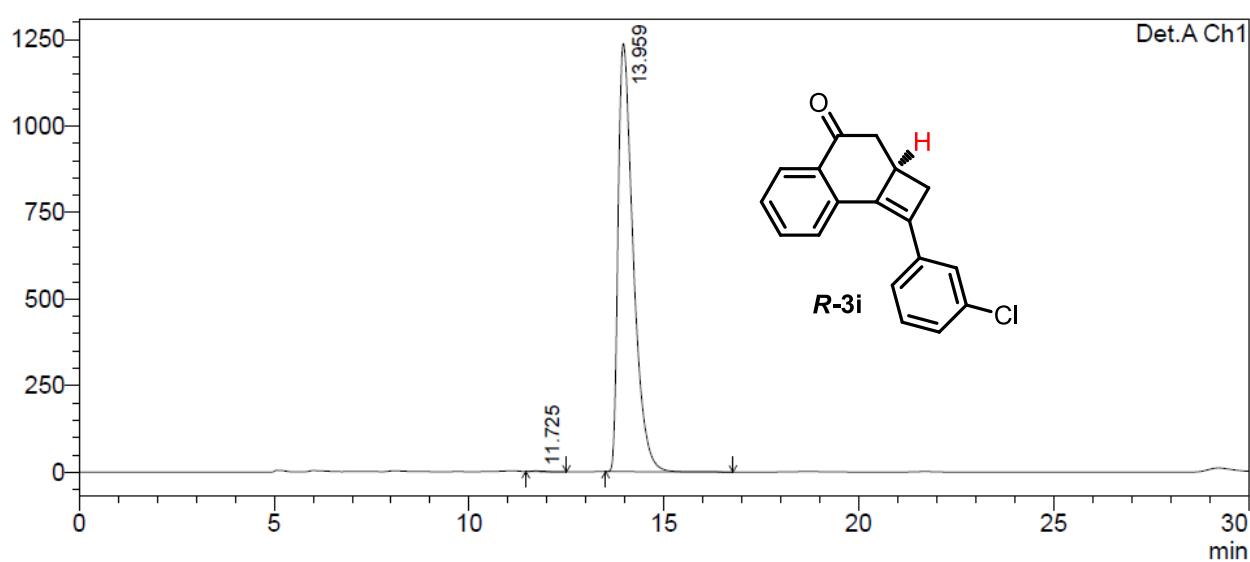
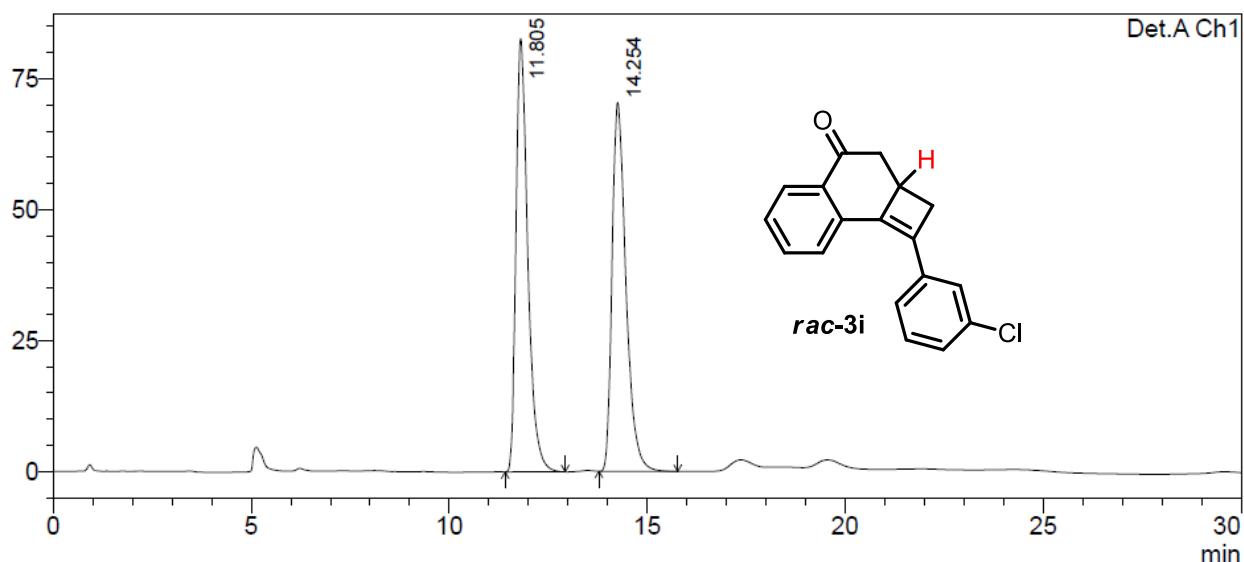


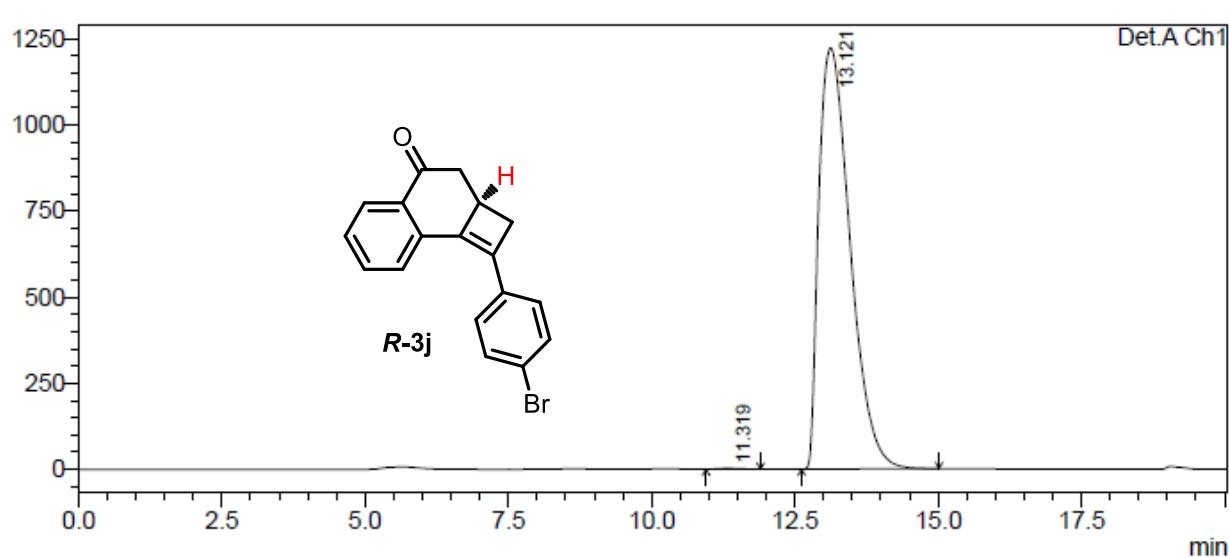
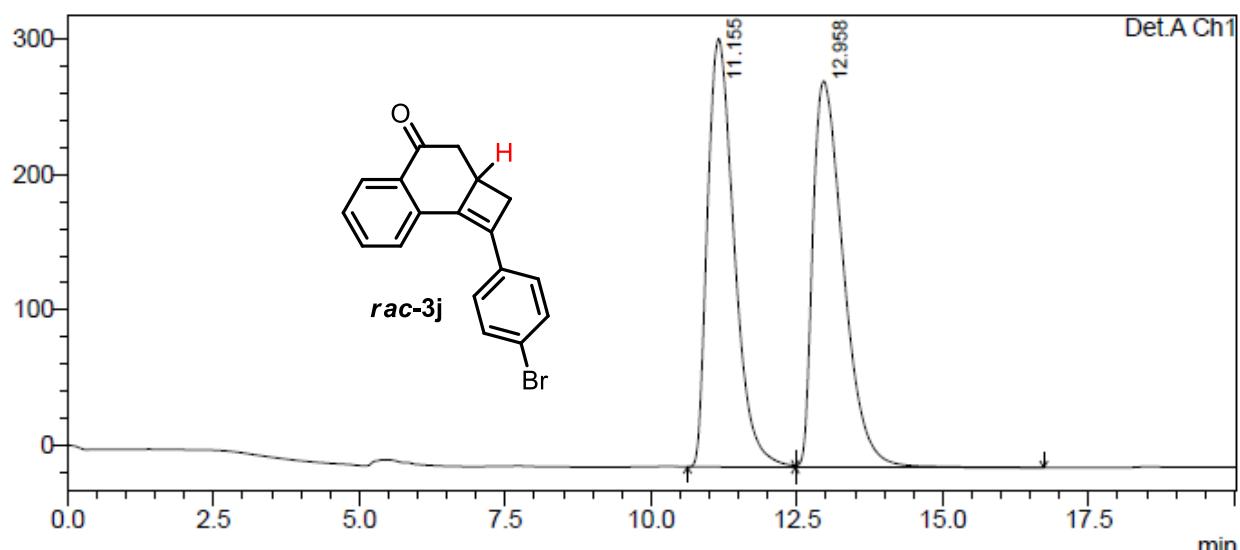
peak	Retention time	type	width	Area	Height	Area
峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.936	BB	0.2786	3451.18750	191.17418	49.9131
2	17.293	BB	0.2968	3463.20117	181.37451	50.0869

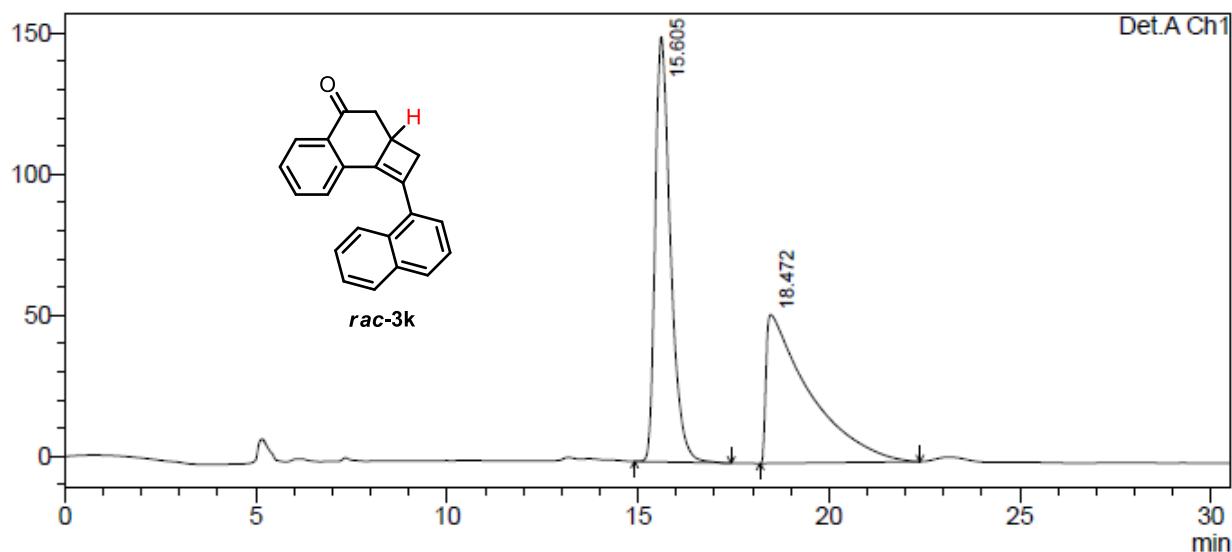


peak	Retention time	type	width	Area	Height	Area
峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.755	BB	0.2812	2599.72290	143.63481	97.8137
2	17.453	BB	0.3435	58.10947	2.57324	2.1863

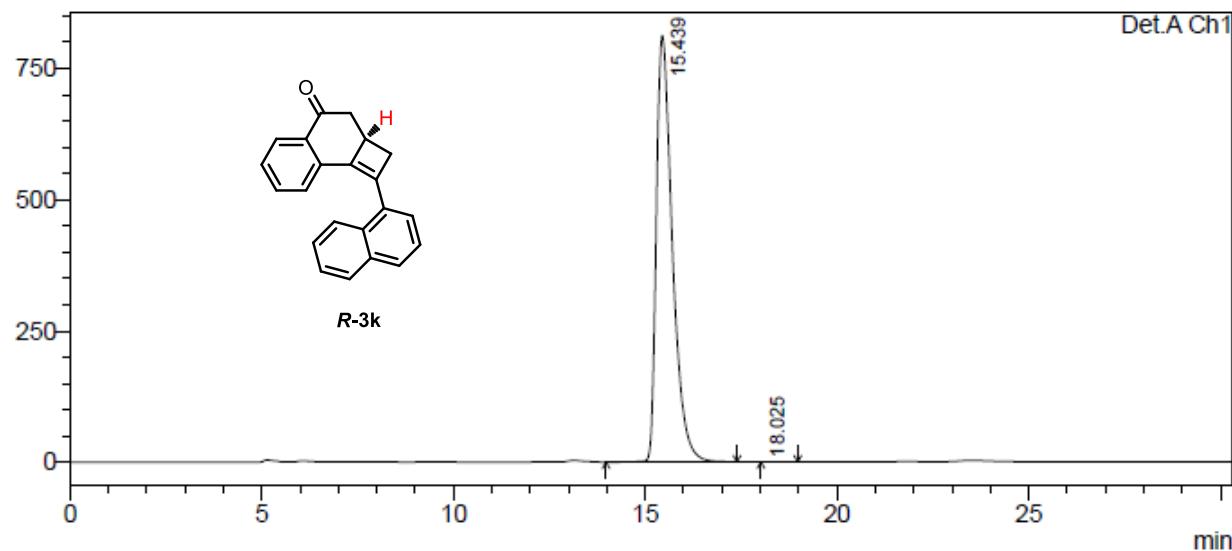




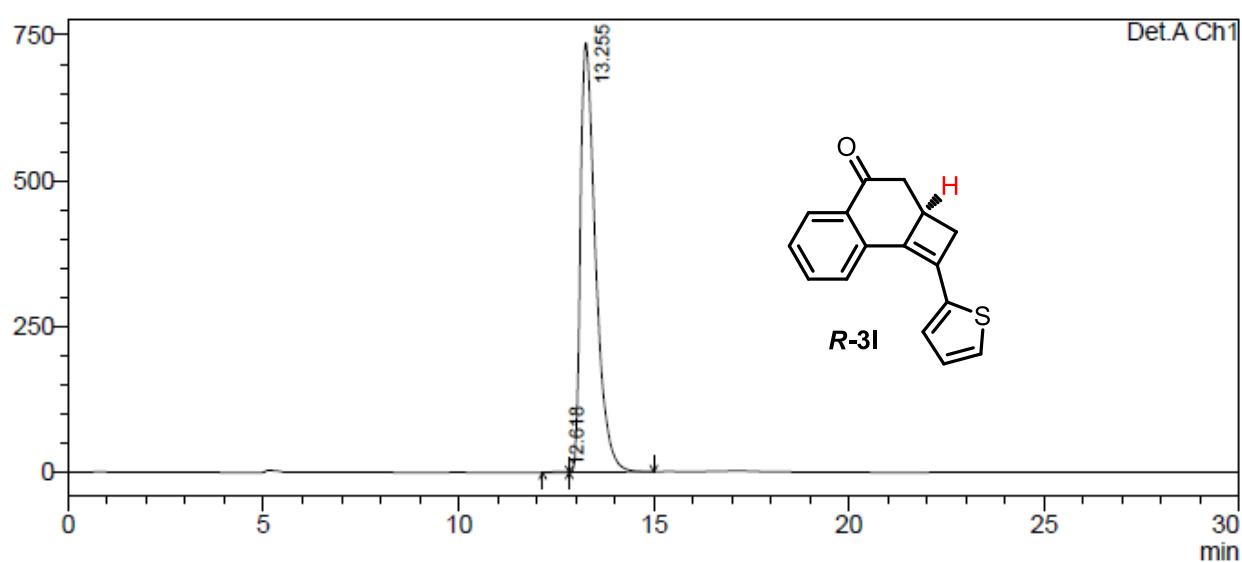
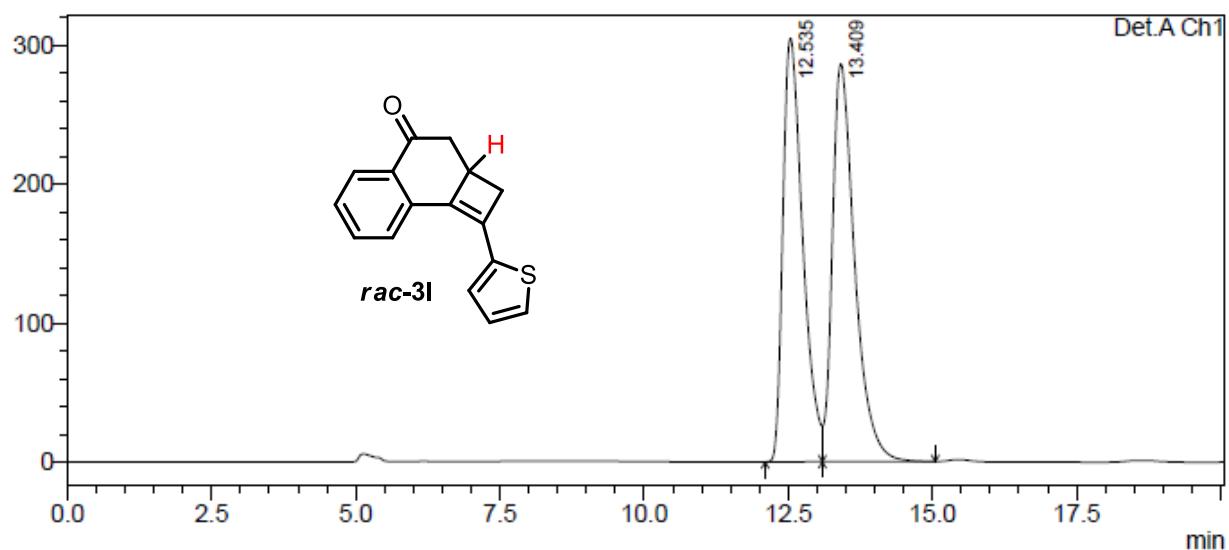


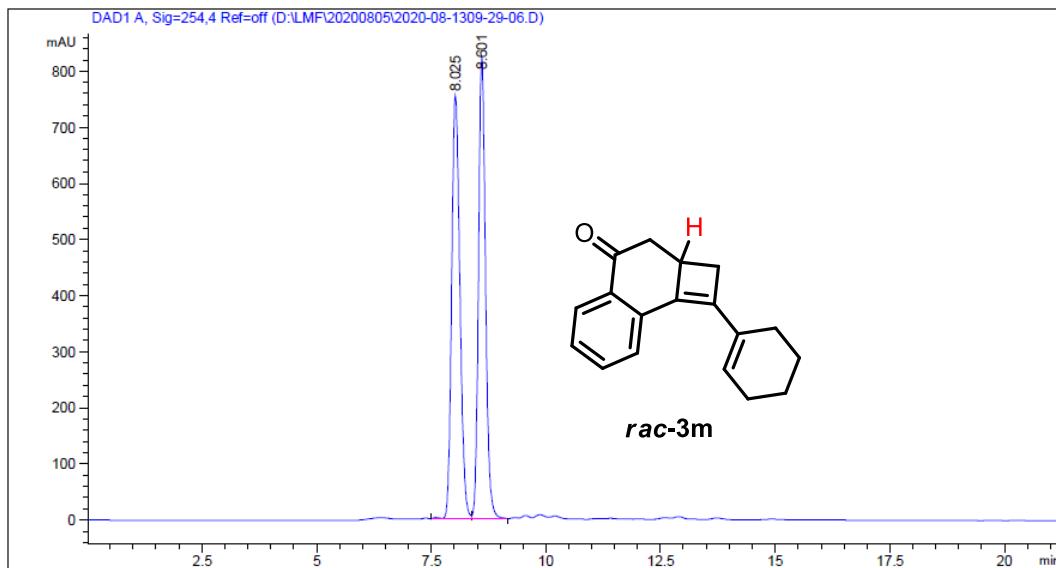


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.605	4223254	150689	50.437	74.114
2	18.472	4150120	52632	49.563	25.886
Total		8373374	203321	100.000	100.000

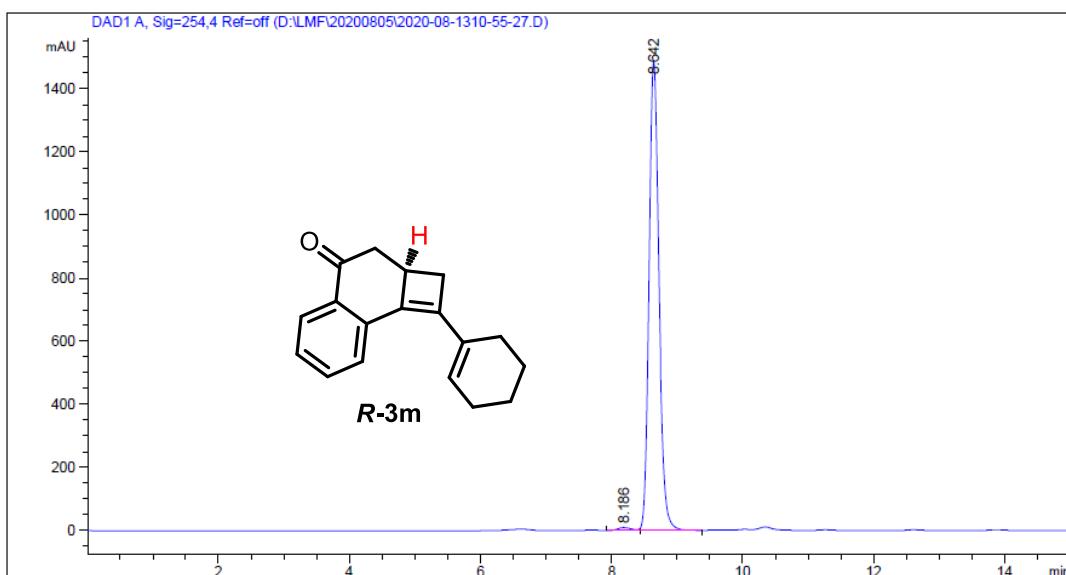


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.439	23619560	812183	100.002	100.000
2	18.025	-543	-0	-0.002	-0.000
Total		23619016	812182	100.000	100.000

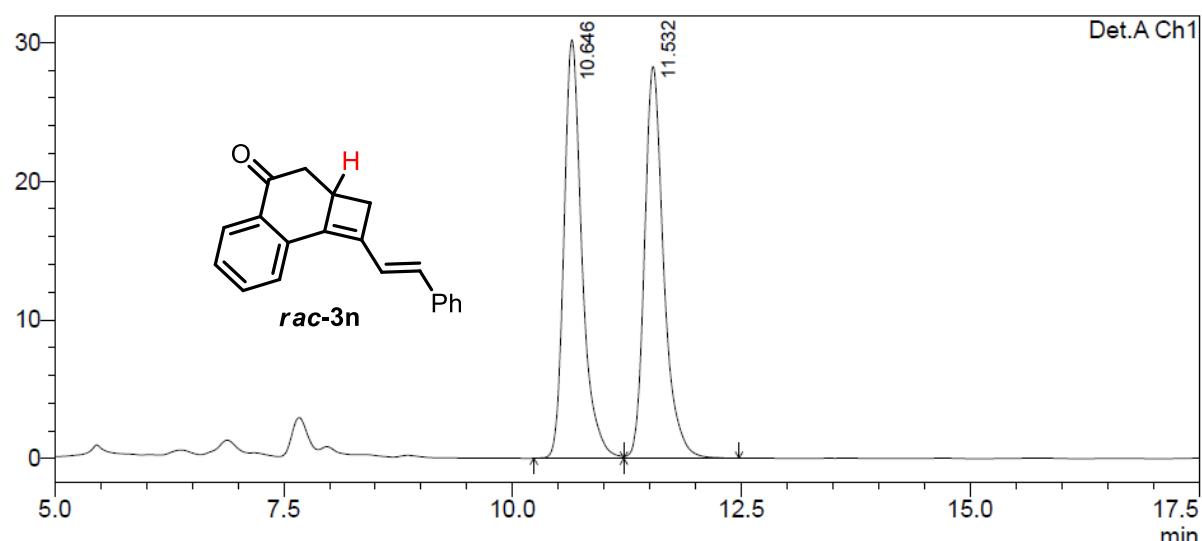




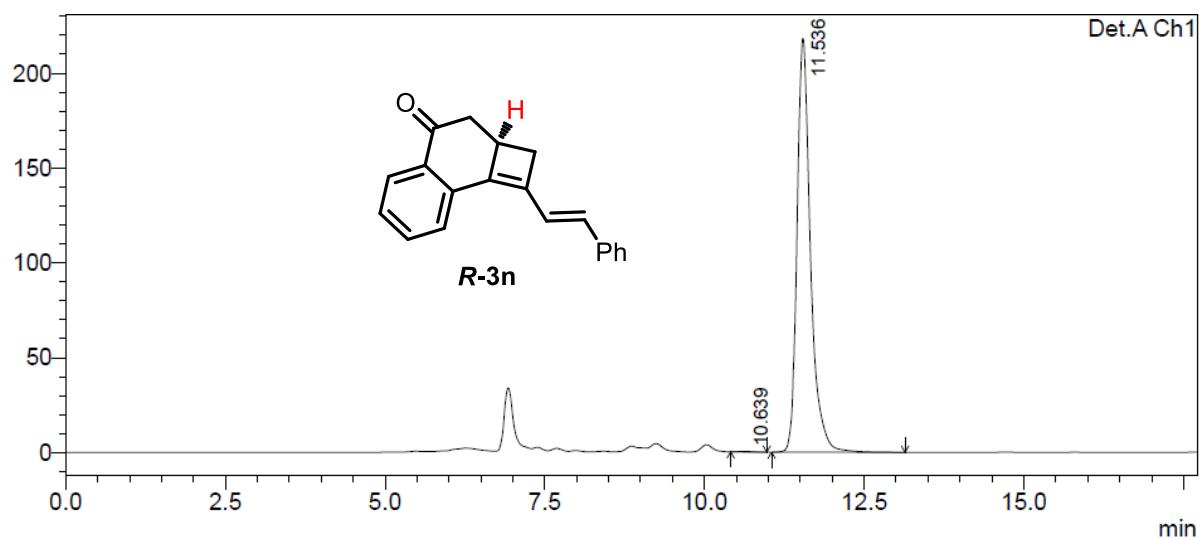
peak	Retention time	type	width	Area	Height	Area
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.025	VV R	0.1960	9464.05176	754.56012	51.8693
2	8.601	VB	0.1645	8781.89355	822.93097	48.1307



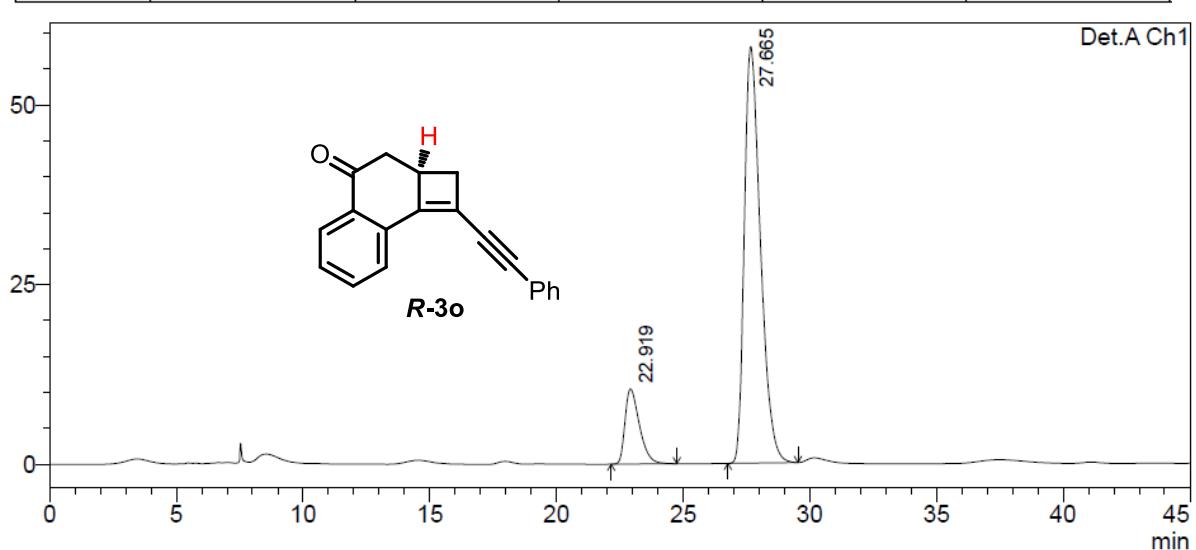
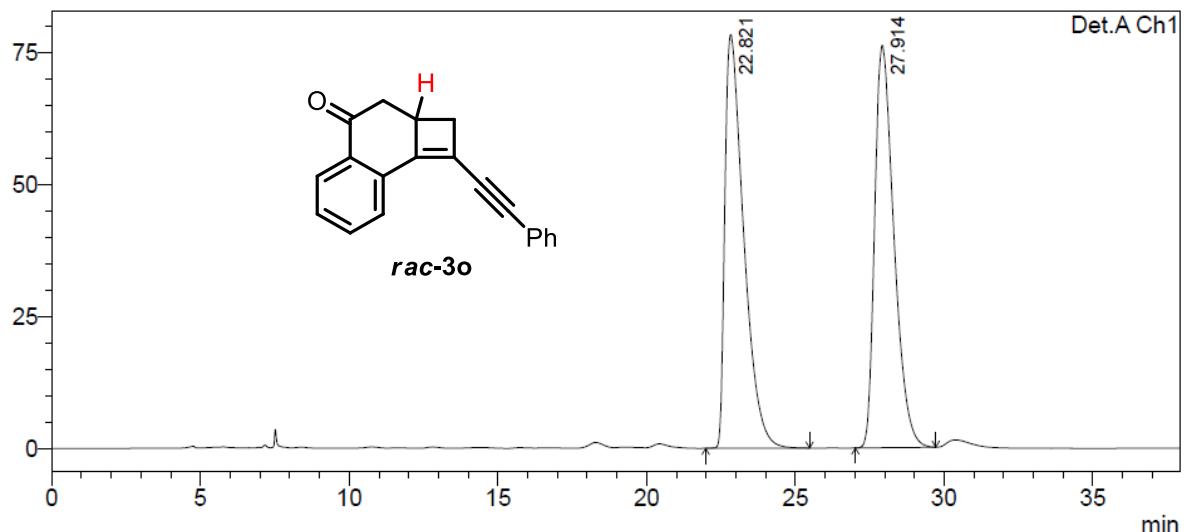
peak	Retention time	type	width	Area	Height	Area
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.186	BV E	0.2115	127.96854	9.24203	0.8129
2	8.642	VB R	0.1625	1.56137e4	1486.80530	99.1871

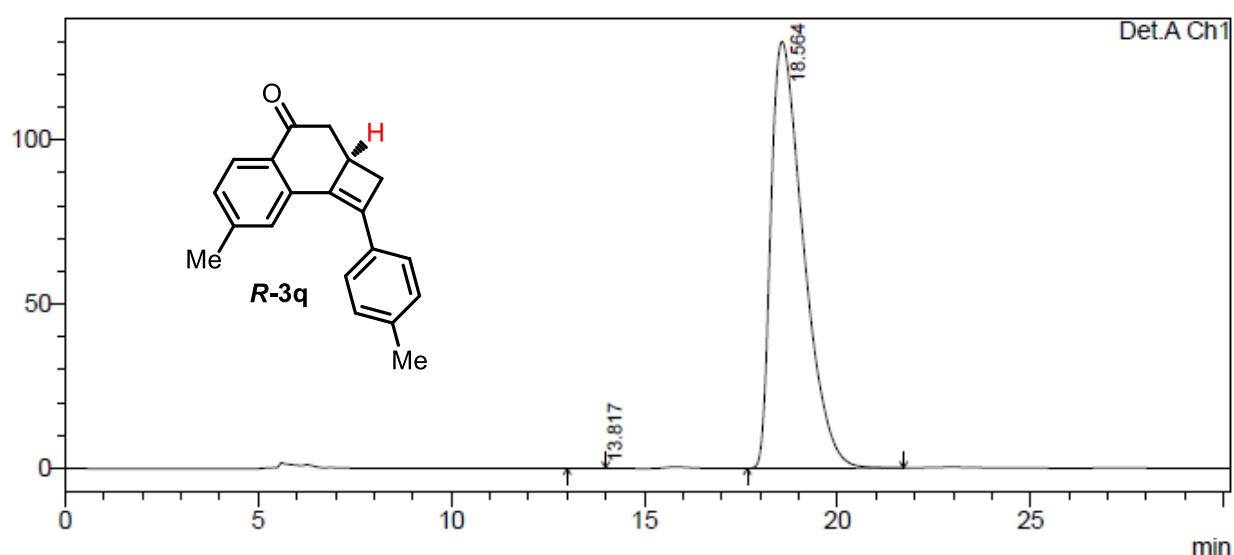
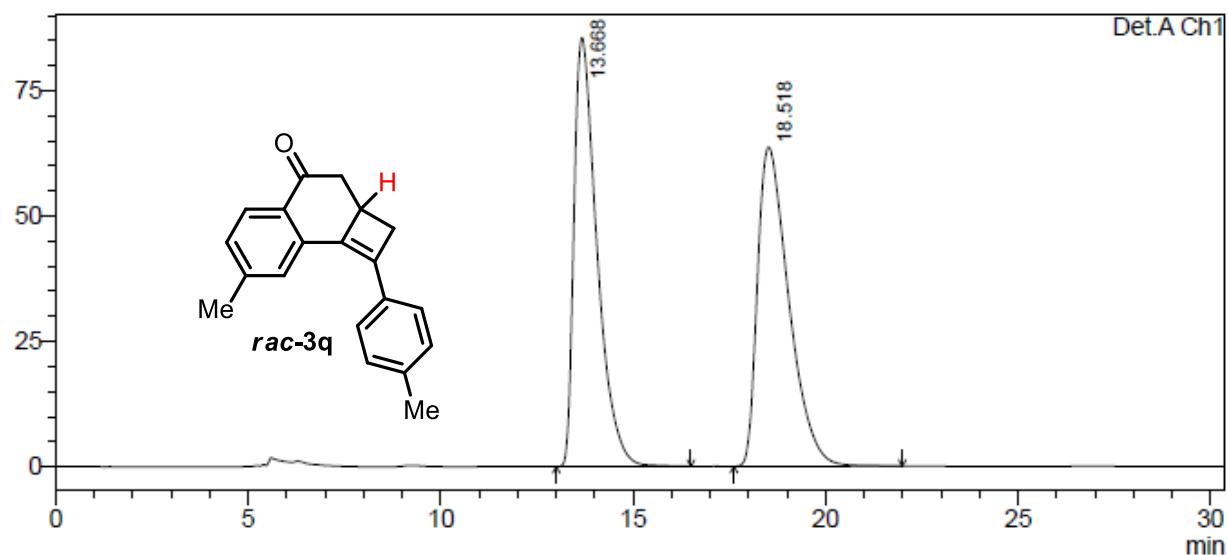


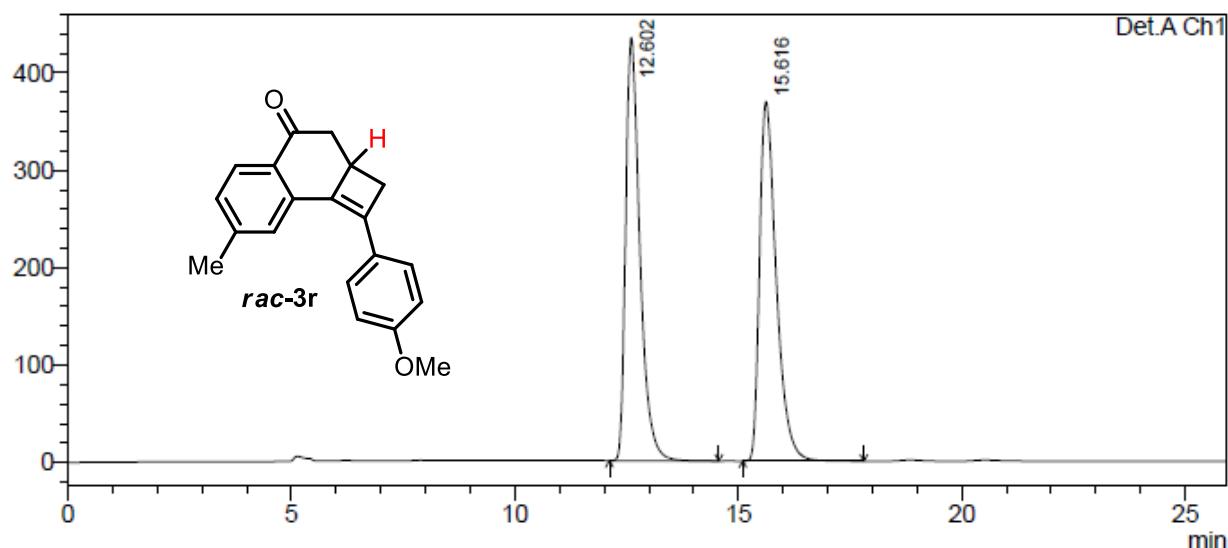
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.646	412663	30169	50.059	51.662
2	11.532	411687	28228	49.941	48.338
Total		824350	58396	100.000	100.000



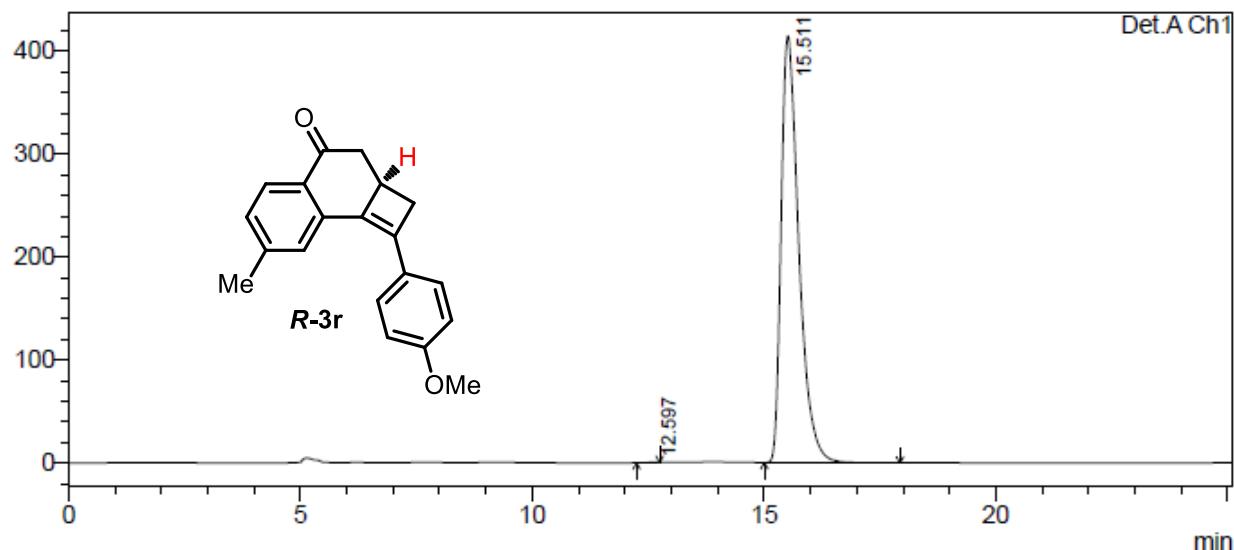
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.639	3595	263	0.112	0.120
2	11.536	3198923	218363	99.888	99.880
Total		3202517	218626	100.000	100.000



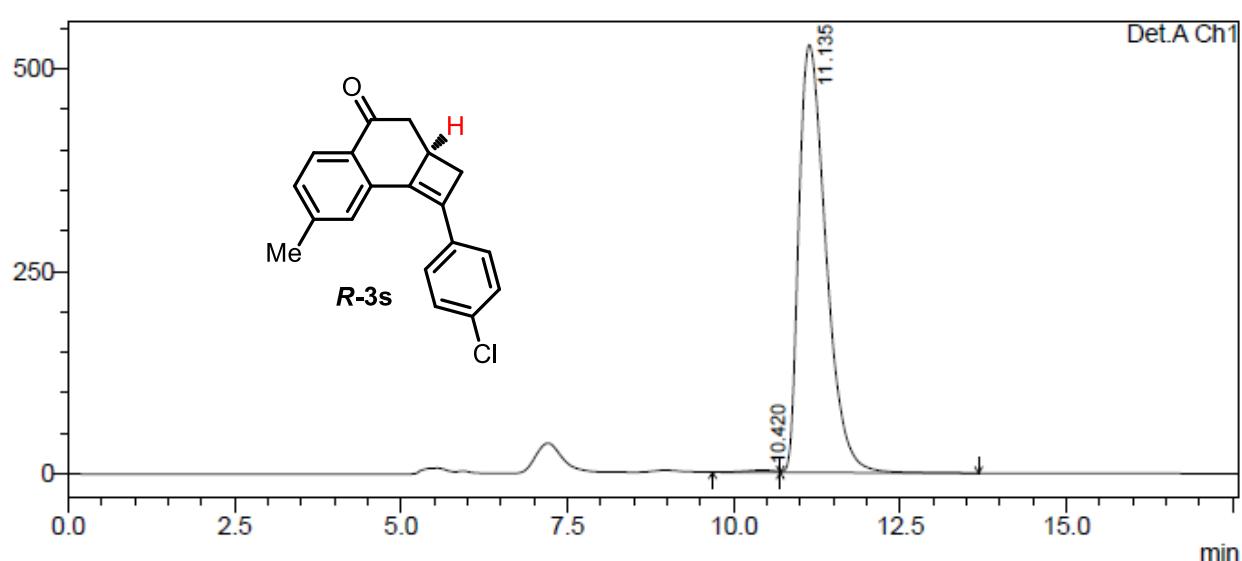
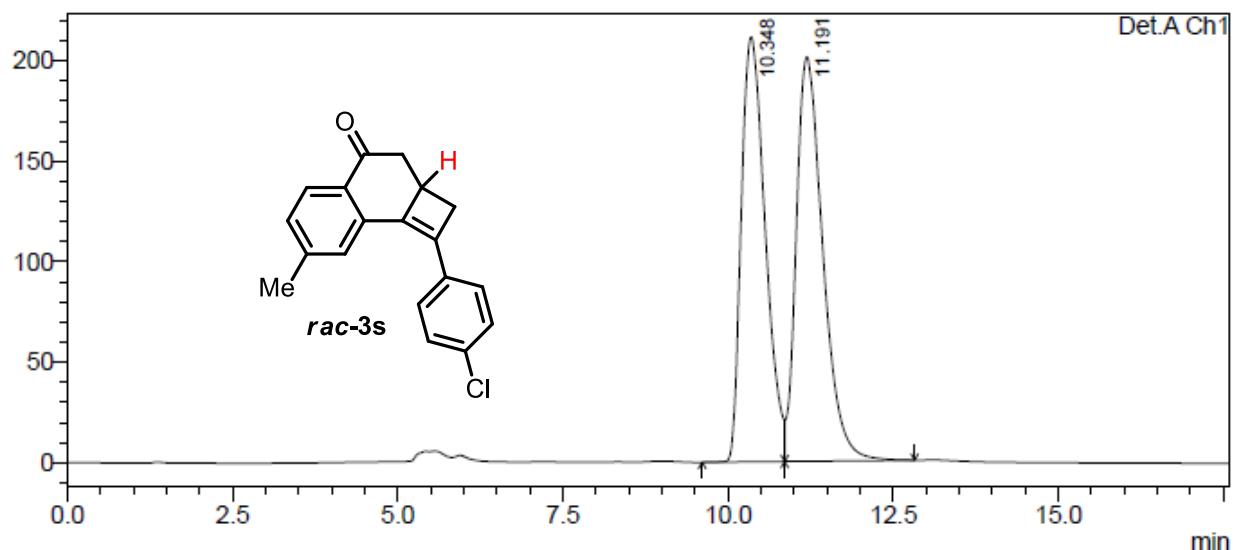


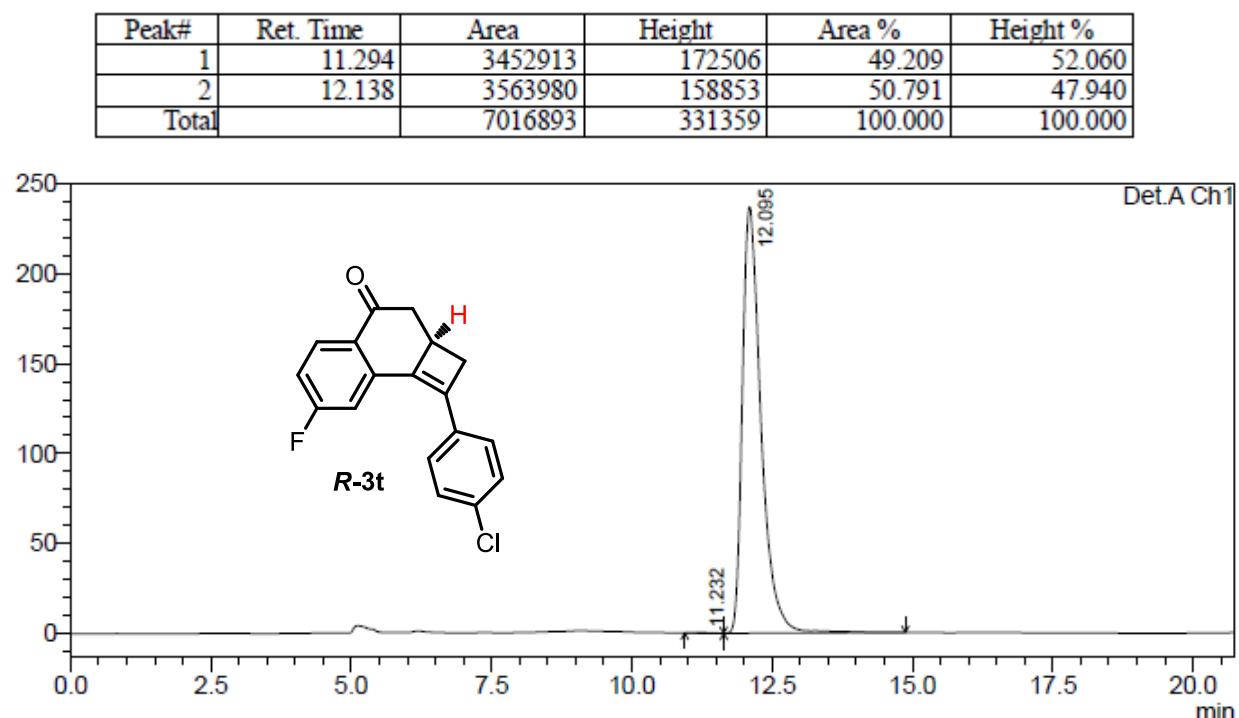
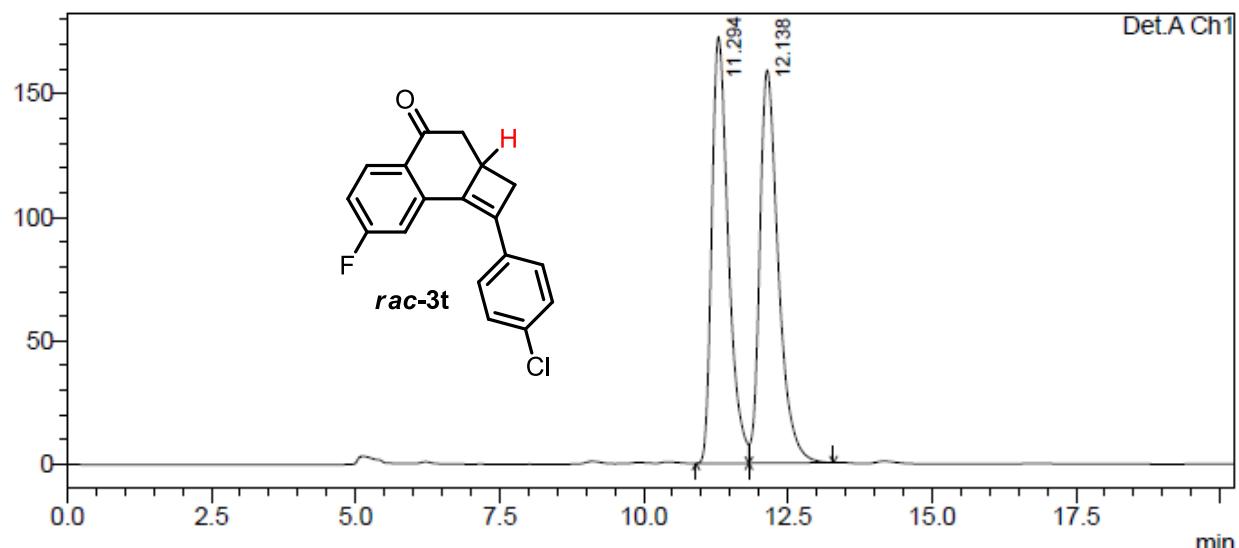


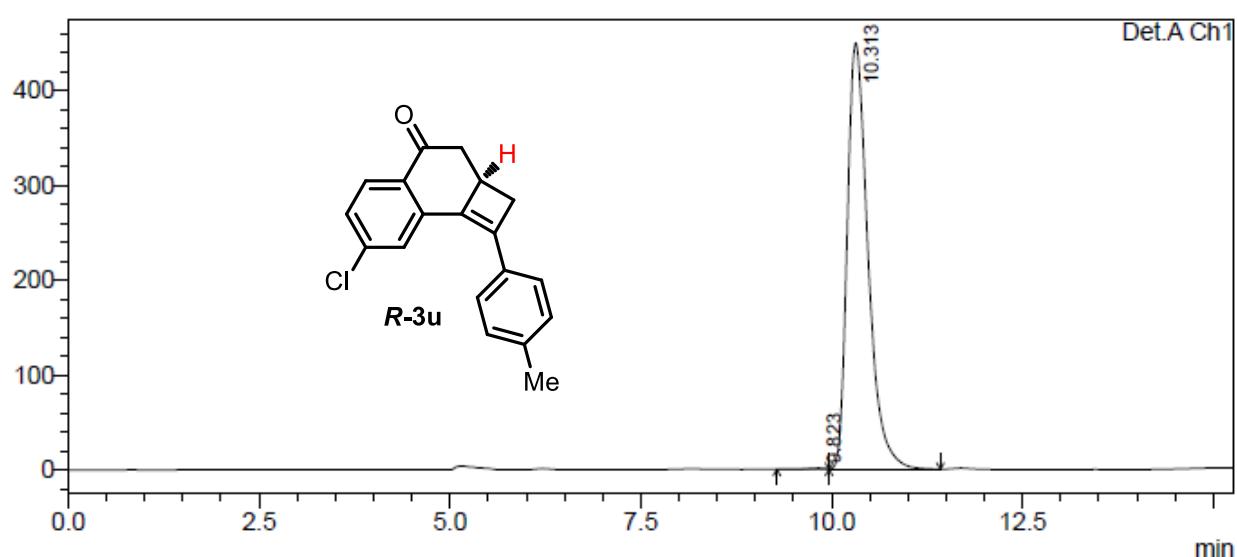
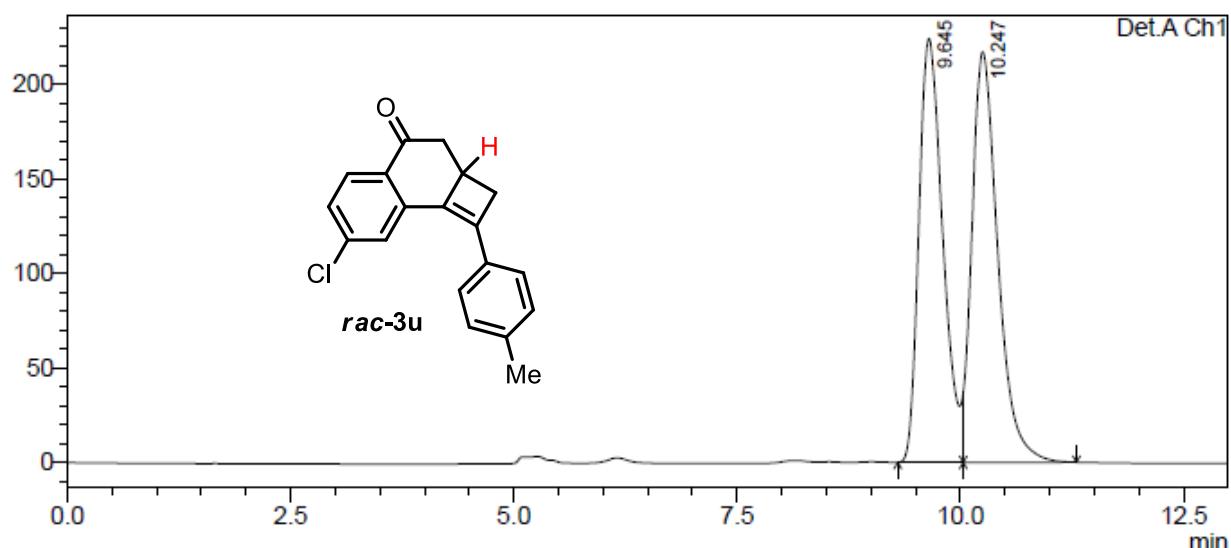
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.602	9616317	434413	50.039	54.074
2	15.616	9601176	368948	49.961	45.926
Total		19217492	803361	100.000	100.000

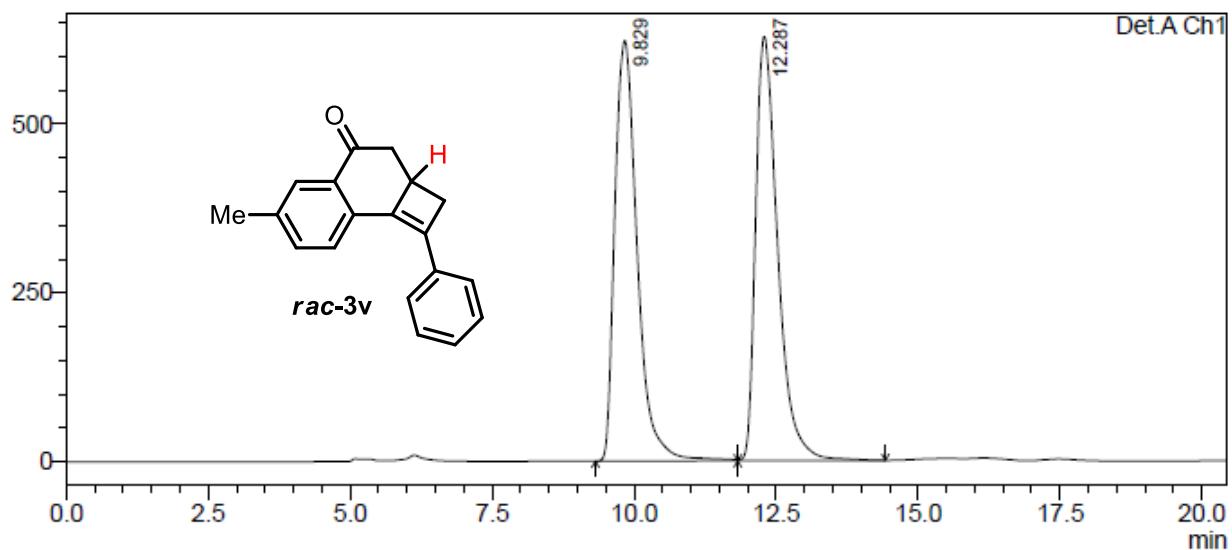


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.597	2545	156	0.023	0.038
2	15.511	11015633	414672	99.977	99.962
Total		11018179	414828	100.000	100.000

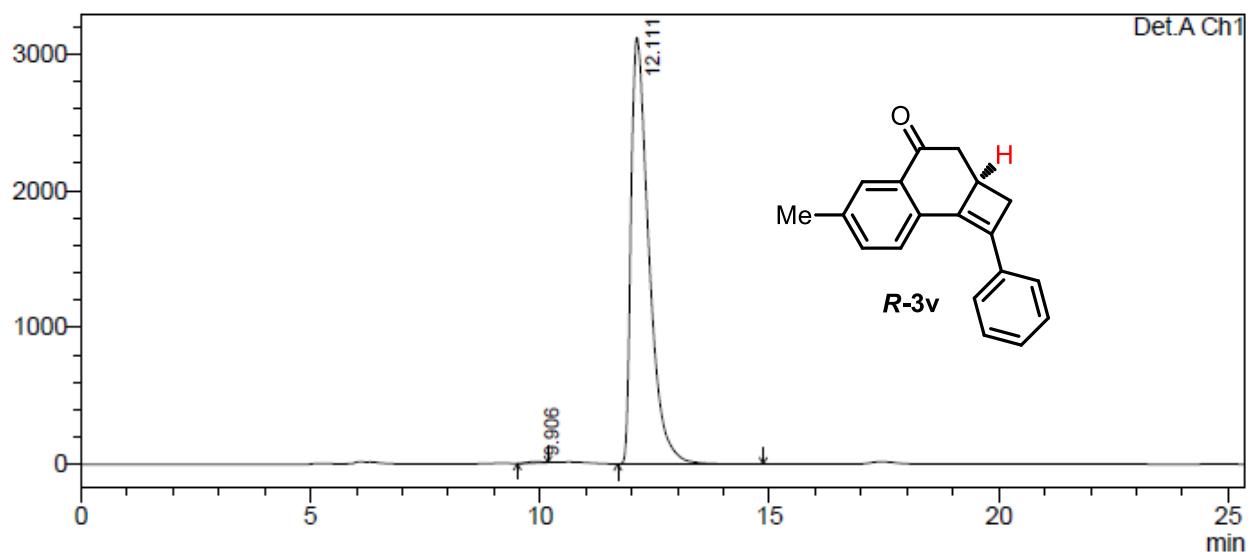




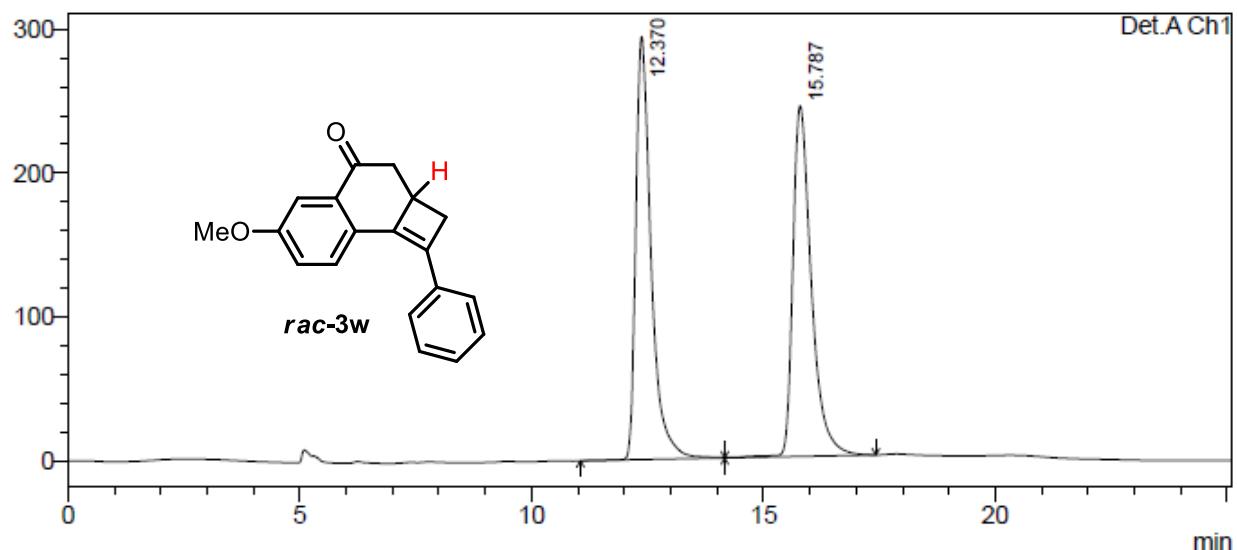




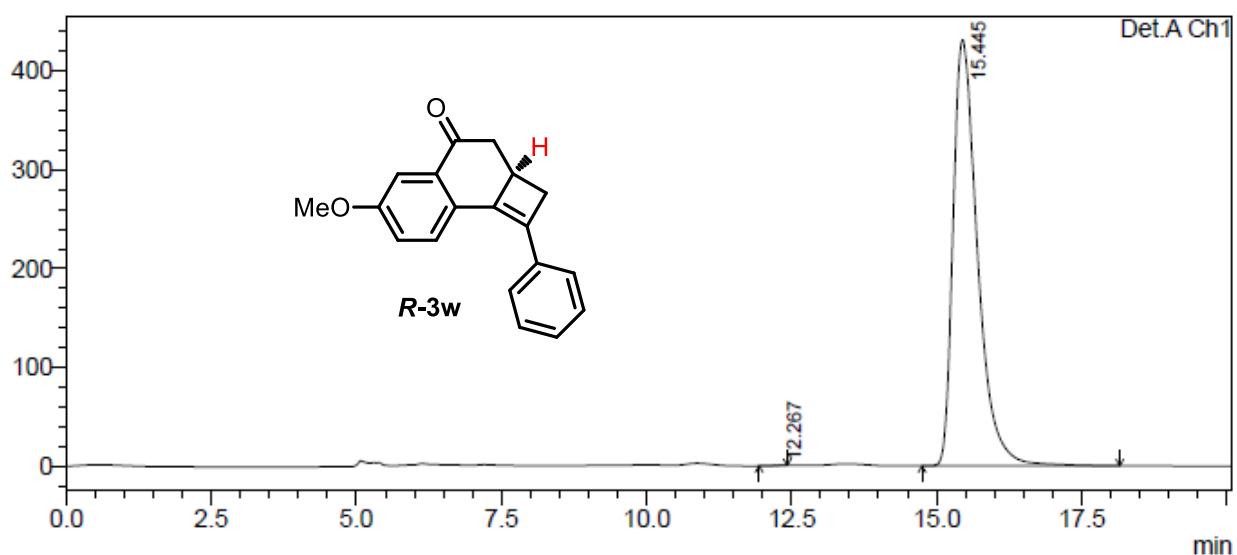
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.829	17100649	622467	50.164	49.786
2	12.287	16988919	627812	49.836	50.214
Total		34089568	1250278	100.000	100.000



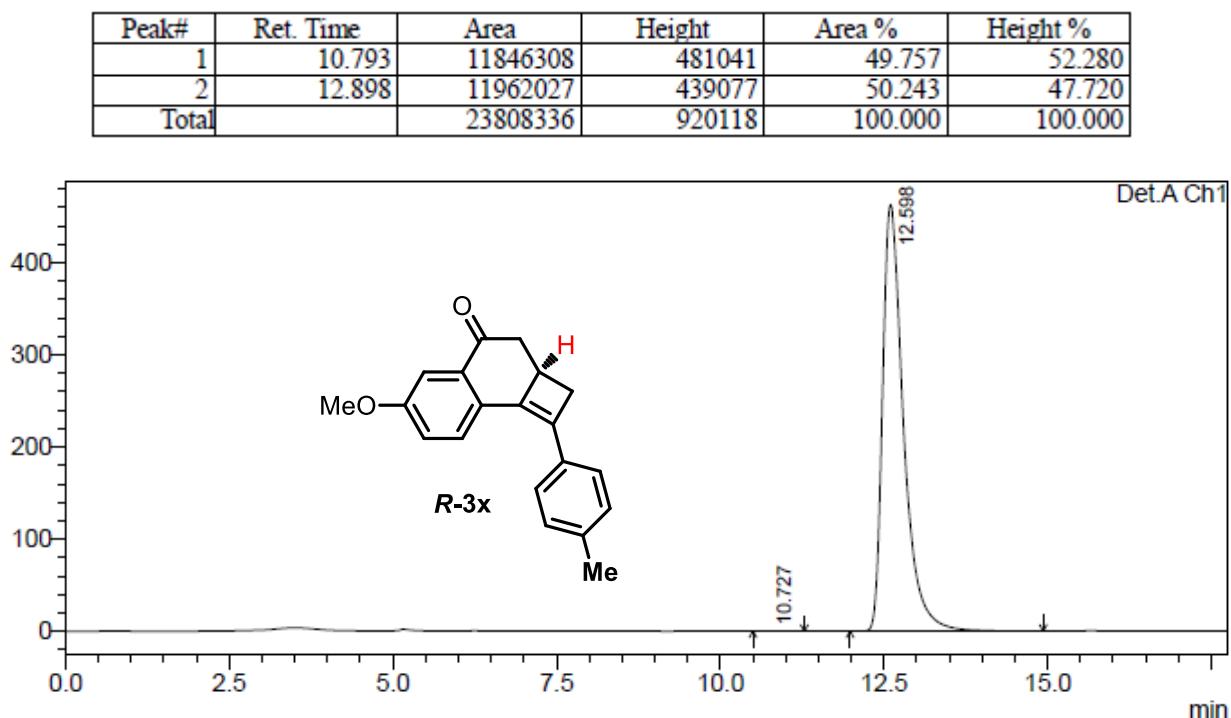
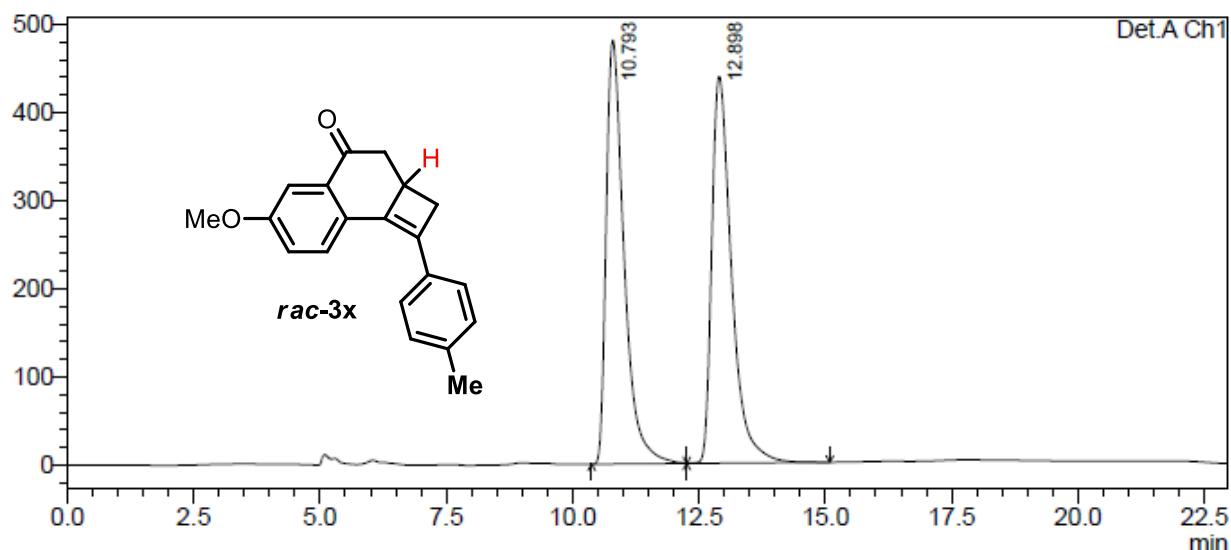
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.906	195221	9812	0.232	0.314
2	12.111	83993708	3114908	99.768	99.686
Total		84188929	3124720	100.000	100.000

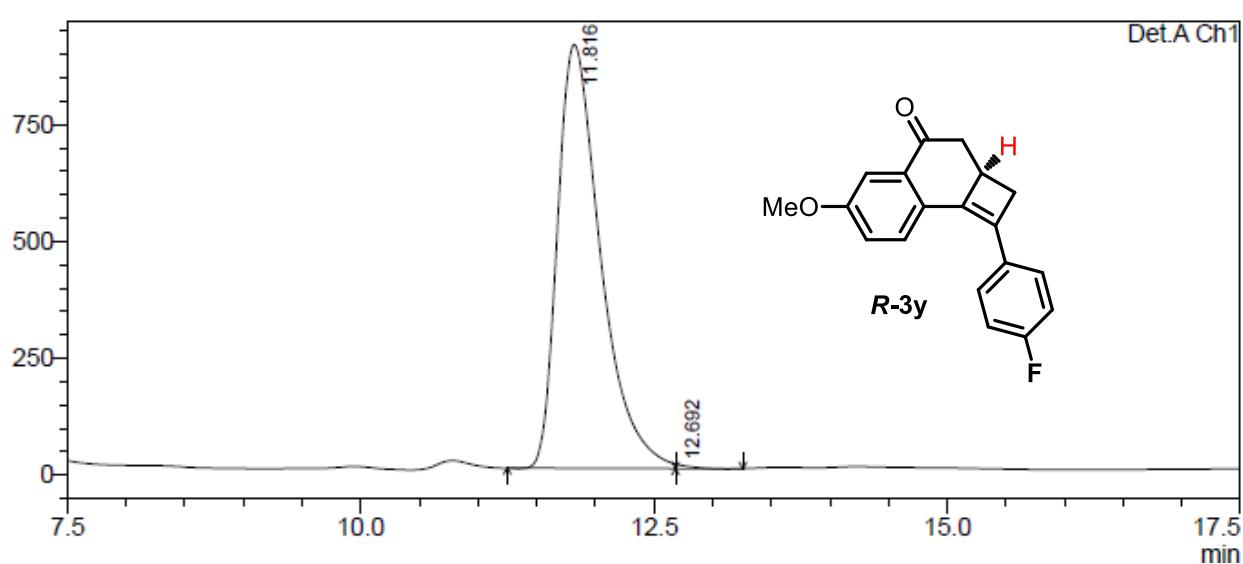
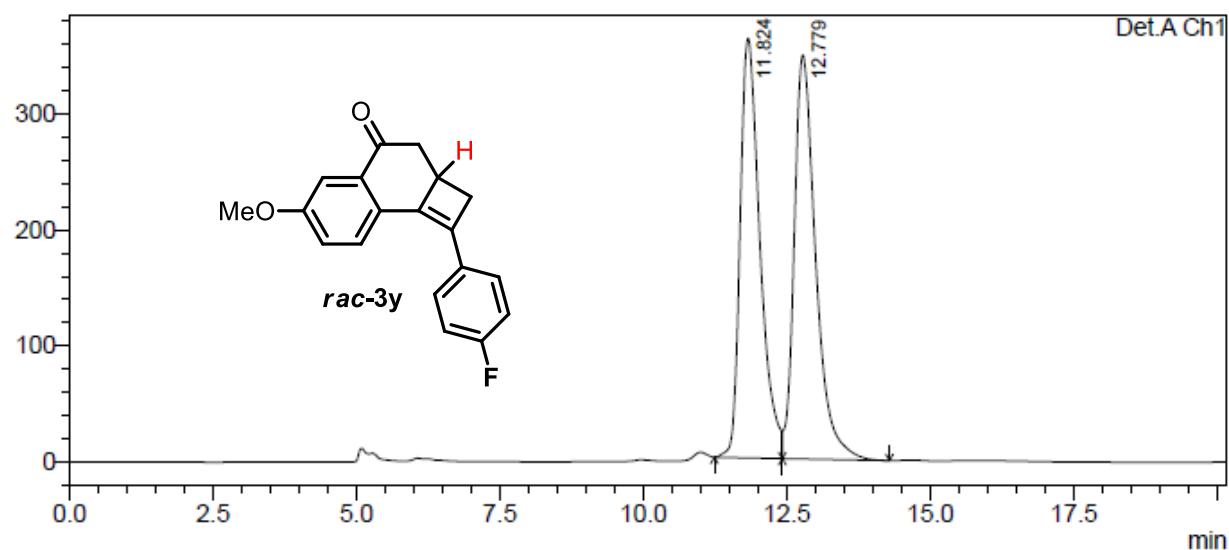


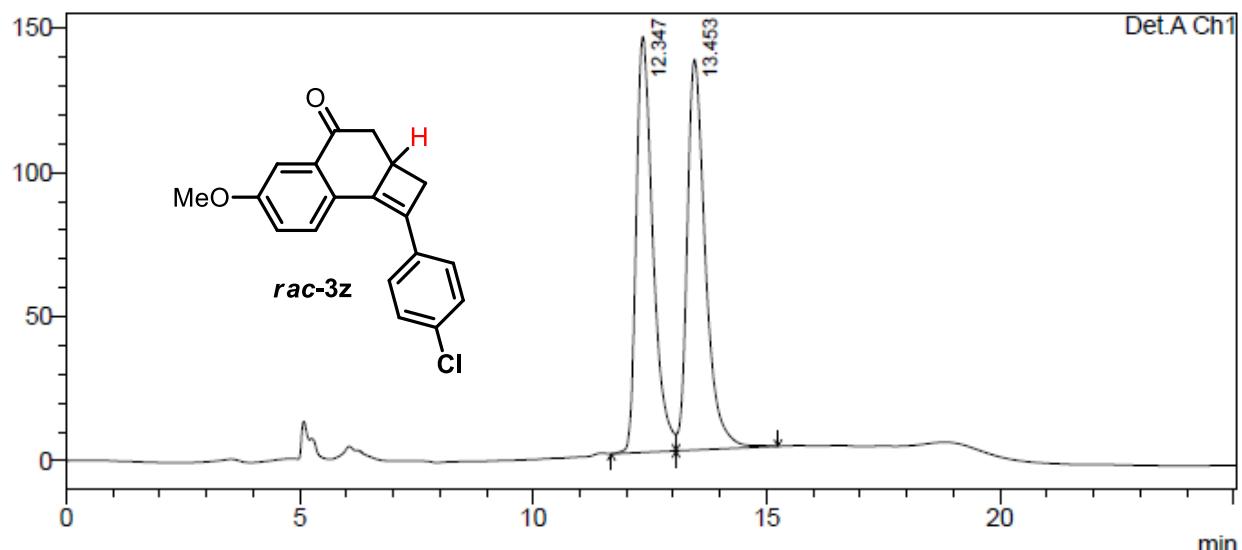
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.370	6754627	293750	49.970	54.672
2	15.787	6762643	243544	50.030	45.328
Total		13517271	537294	100.000	100.000



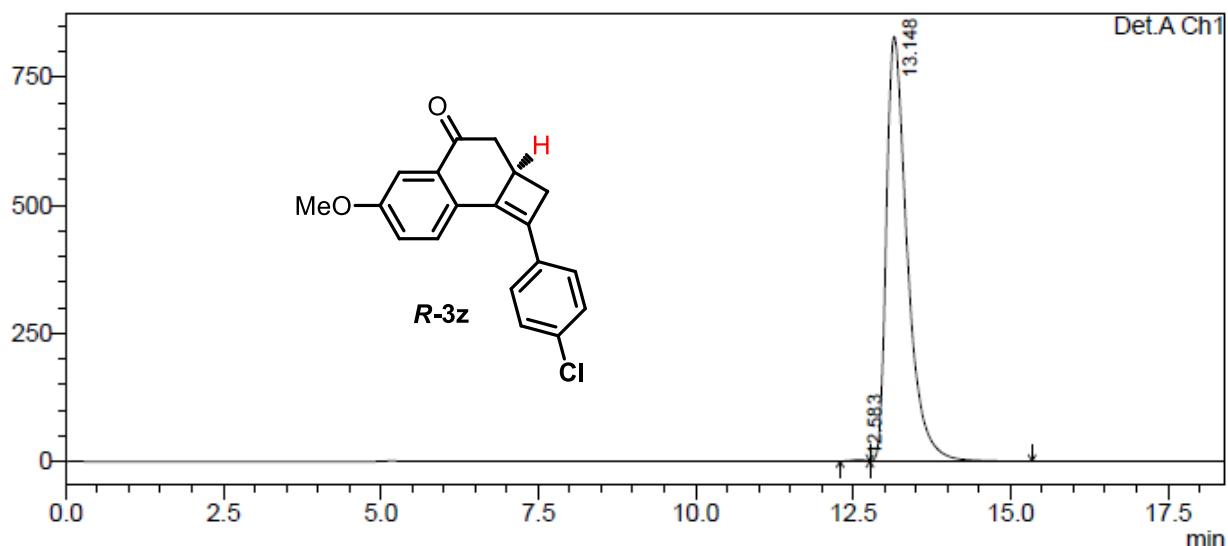
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.267	2882	155	0.023	0.036
2	15.445	12651652	431285	99.977	99.964
Total		12654533	431439	100.000	100.000



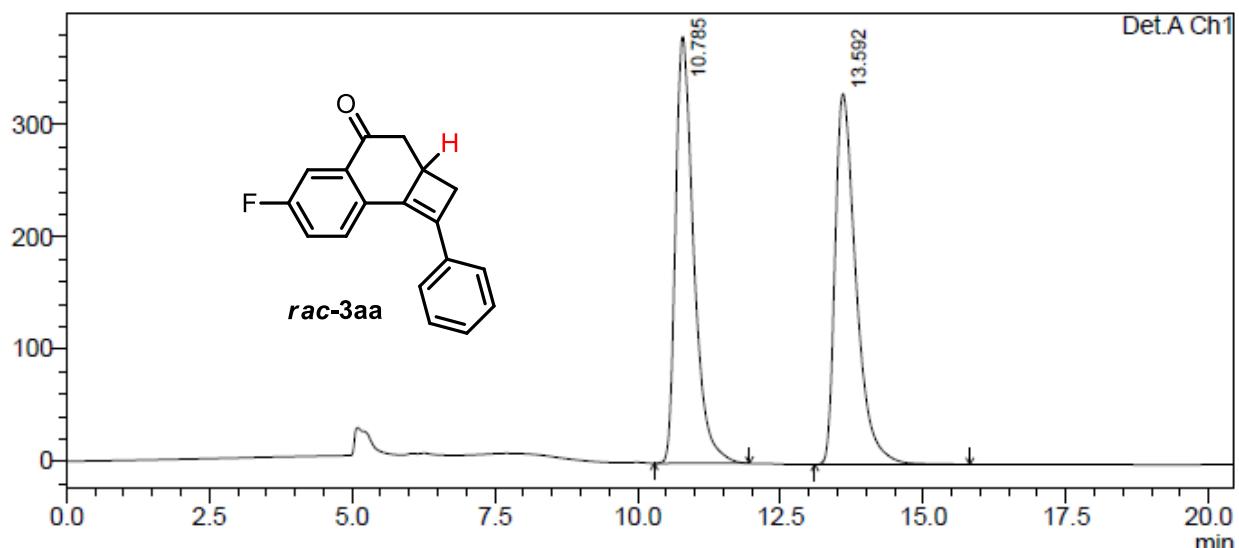




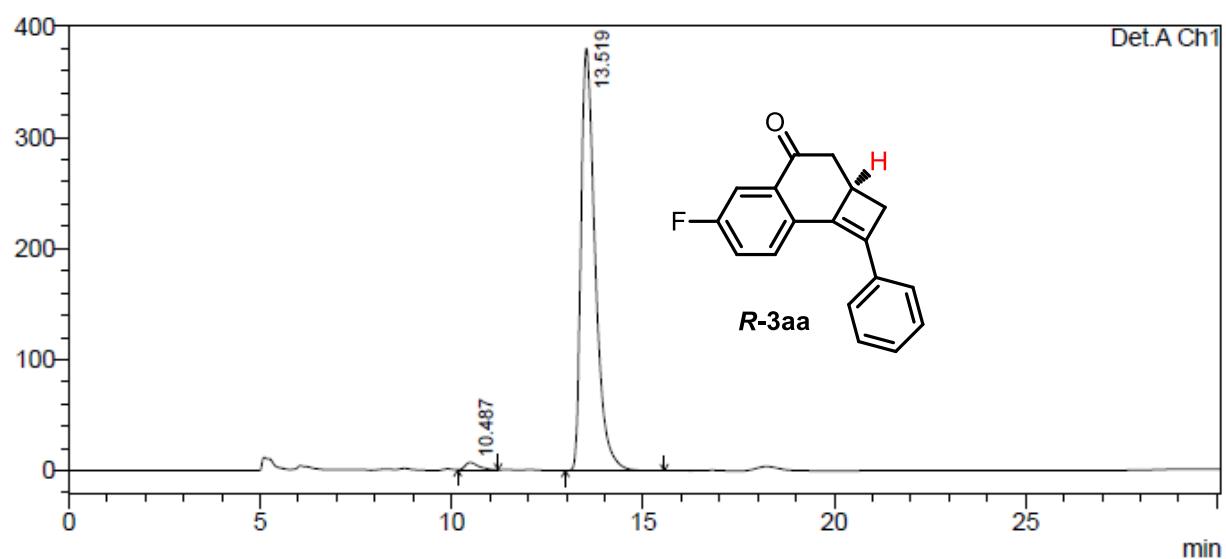
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.347	3584112	144231	49.403	51.567
2	13.453	3670675	135465	50.597	48.433
Total		7254787	279696	100.000	100.000



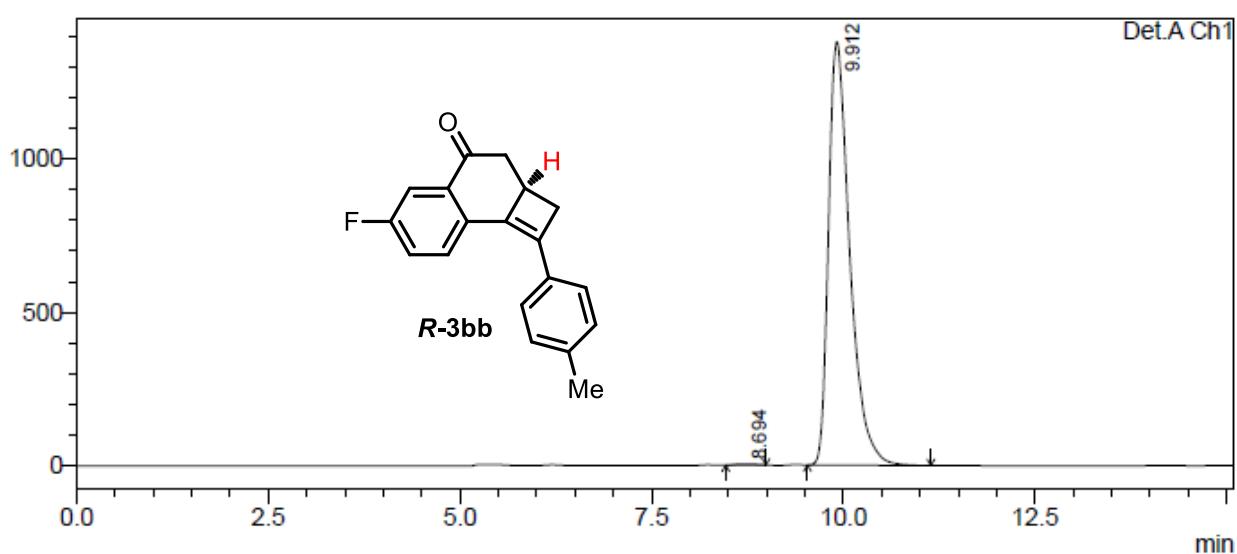
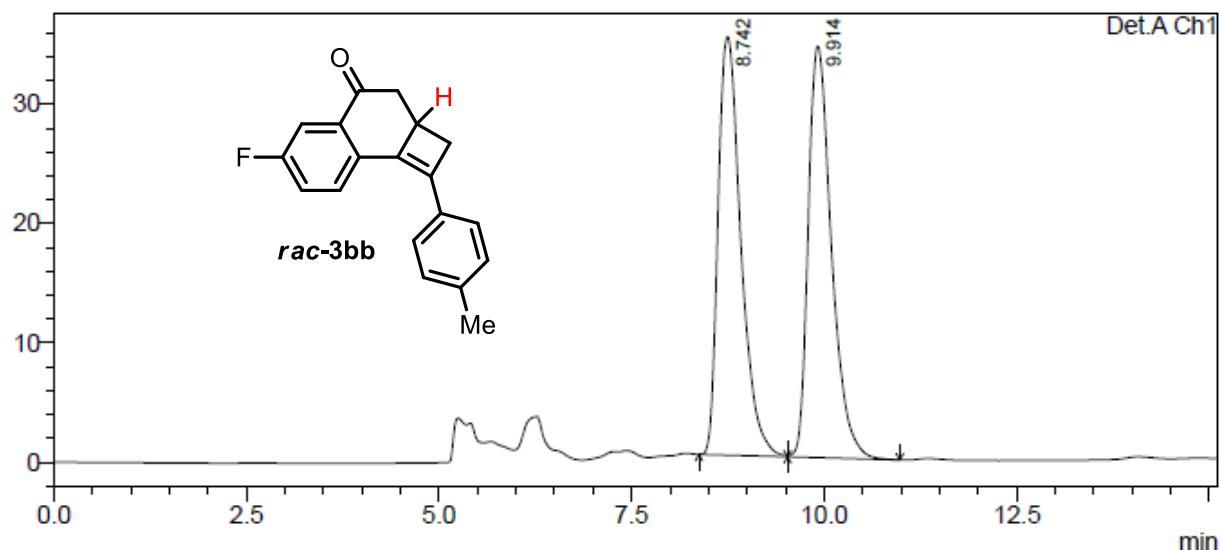
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.583	40252	2531	0.210	0.305
2	13.148	19108550	828174	99.790	99.695
Total		19148803	830705	100.000	100.000

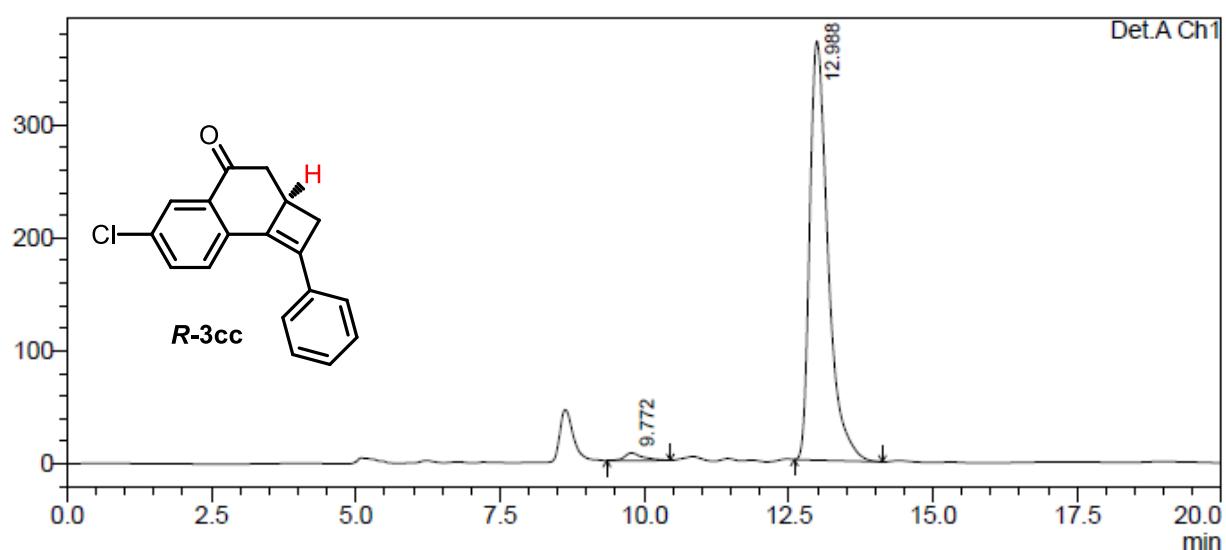
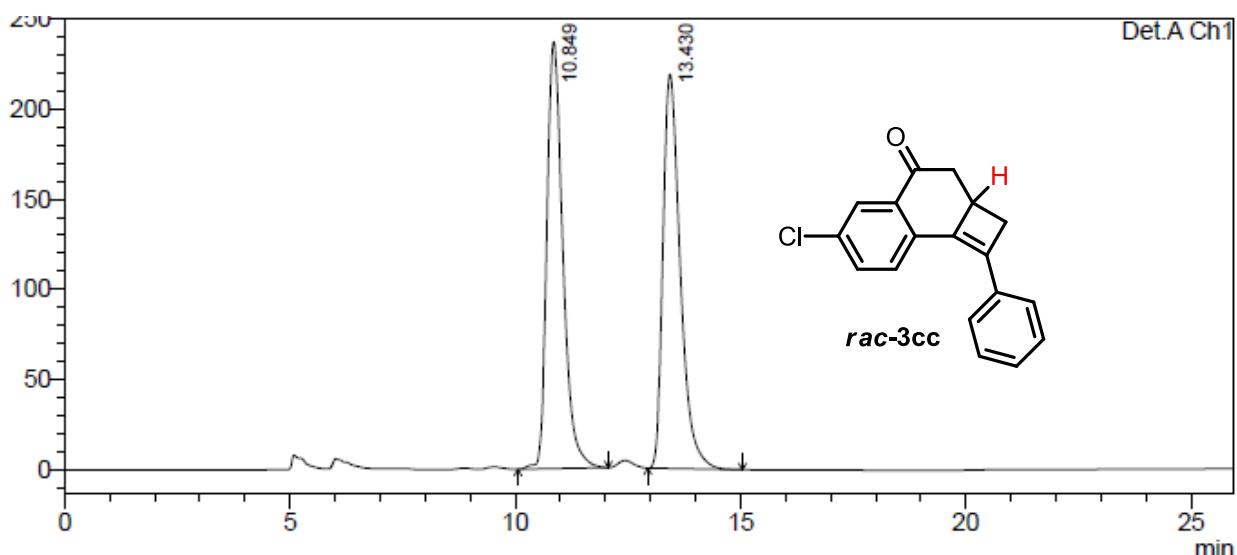


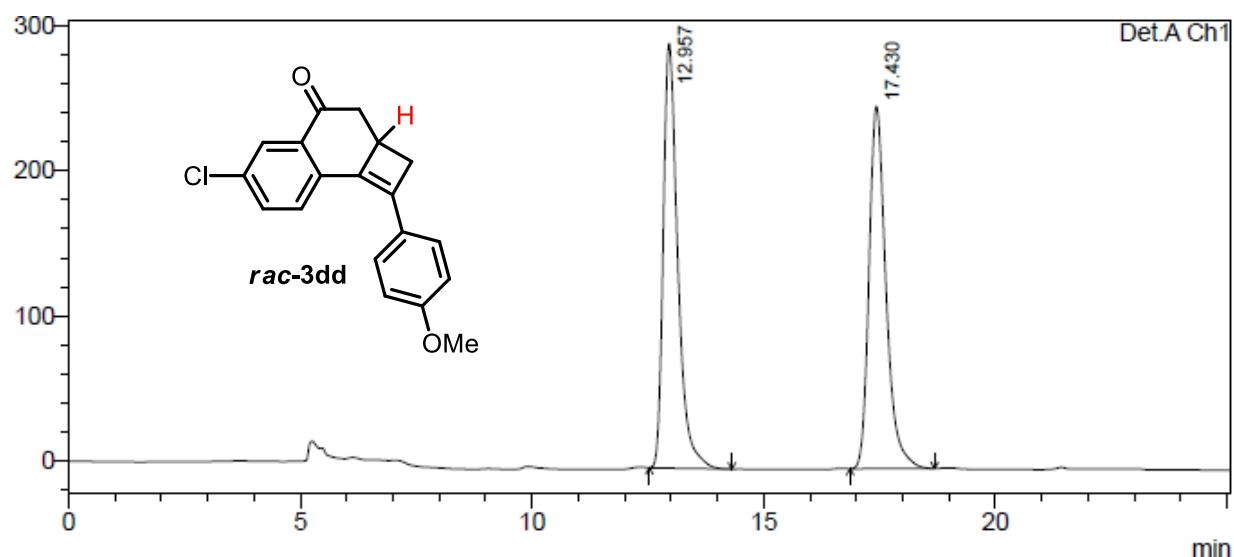
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.785	8425380	380304	49.968	53.535
2	13.592	8436075	330075	50.032	46.465
Total		16861455	710379	100.000	100.000



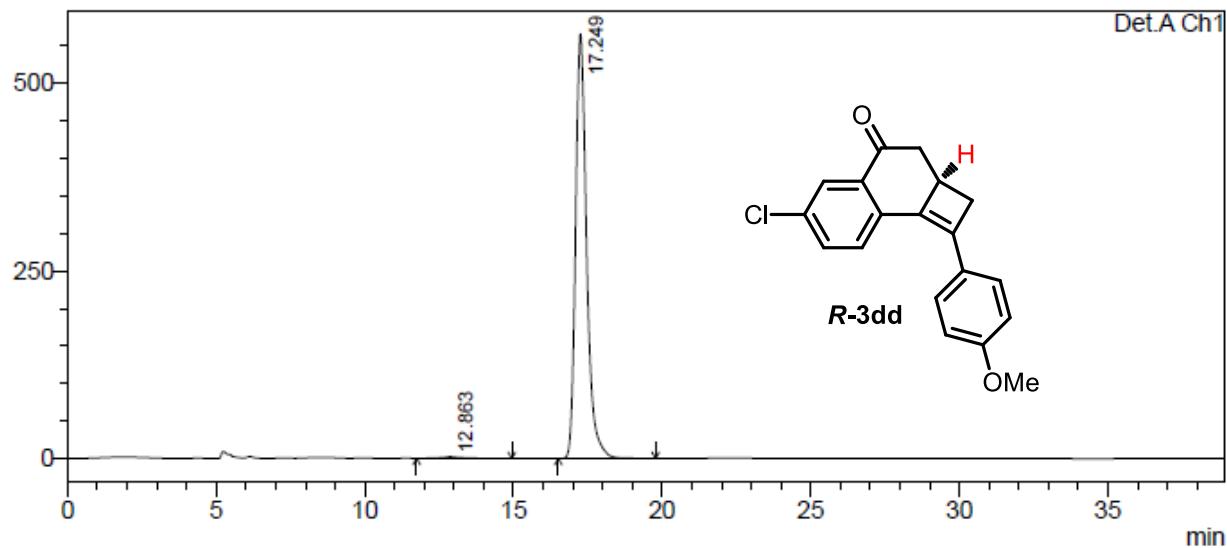
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.487	162129	6839	1.625	1.768
2	13.519	9814496	380013	98.375	98.232
Total		9976625	386852	100.000	100.000



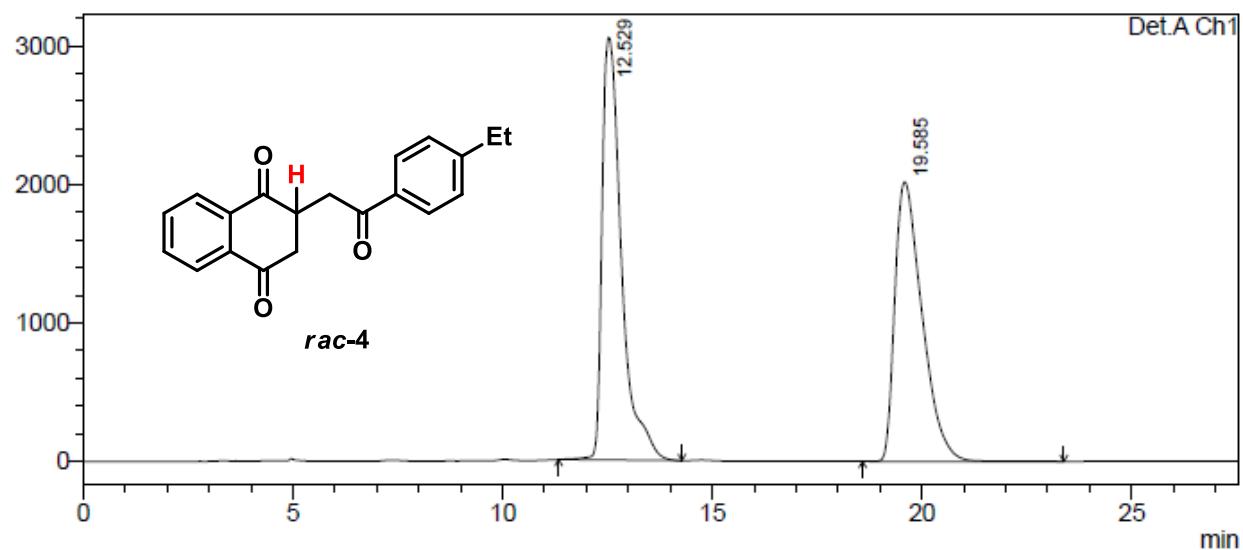




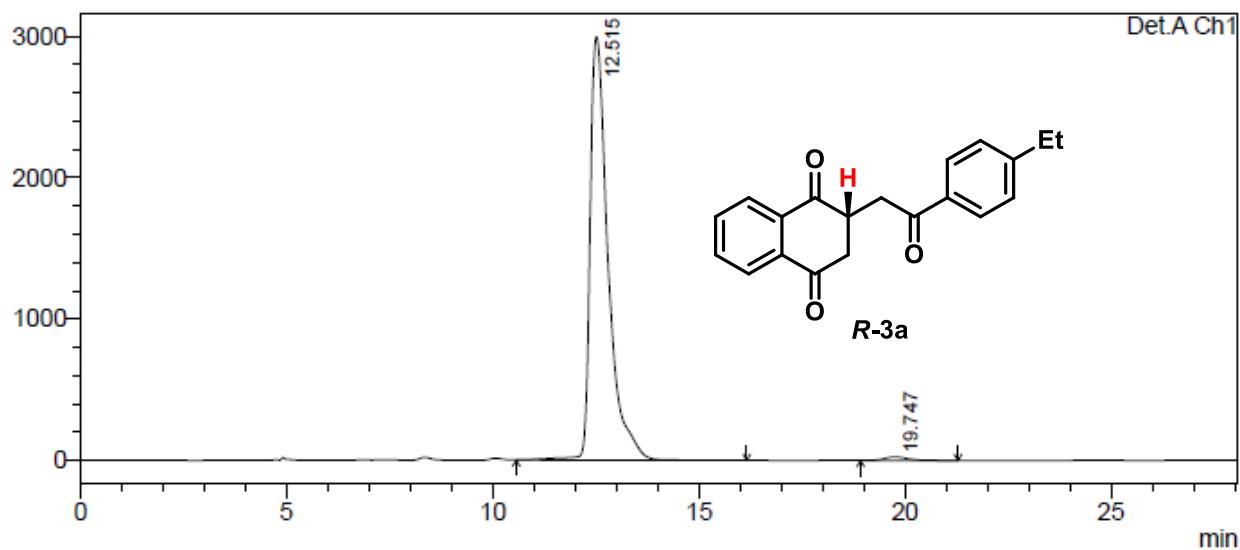
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.957	6356037	292026	50.103	53.955
2	17.430	6329849	249214	49.897	46.045
Total		12685886	541240	100.000	100.000



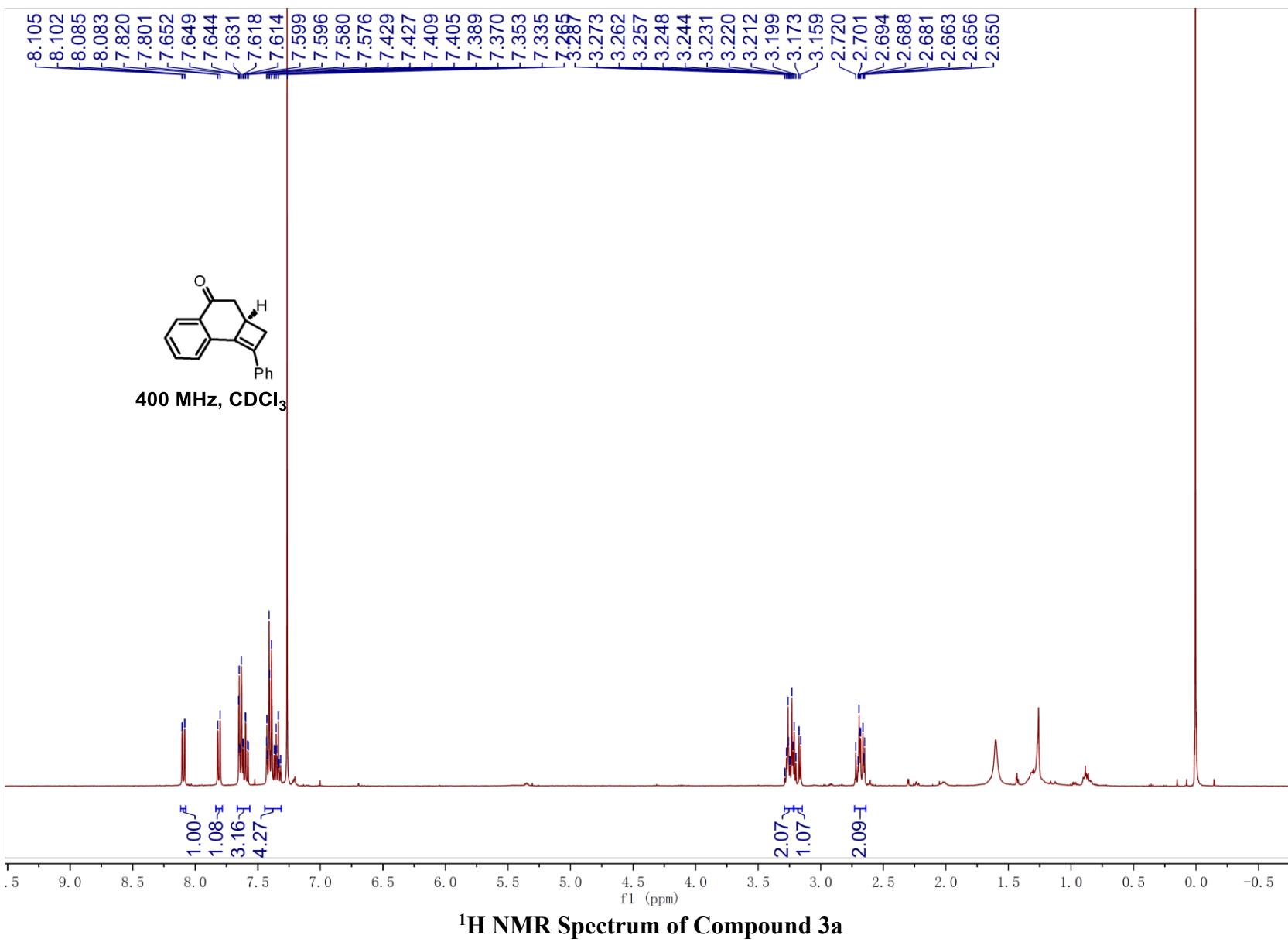
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.863	101034	2046	0.683	0.360
2	17.249	14684832	565823	99.317	99.640
Total		14785867	567869	100.000	100.000



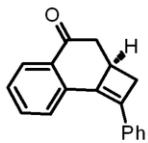
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.529	98420795	3049844	51.941	60.207
2	19.585	91065333	2015747	48.059	39.793
Total		189486127	5065592	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.515	91040680	2995994	98.902	99.162
2	19.747	1010821	25326	1.098	0.838
Total		92051501	3021320	100.000	100.000



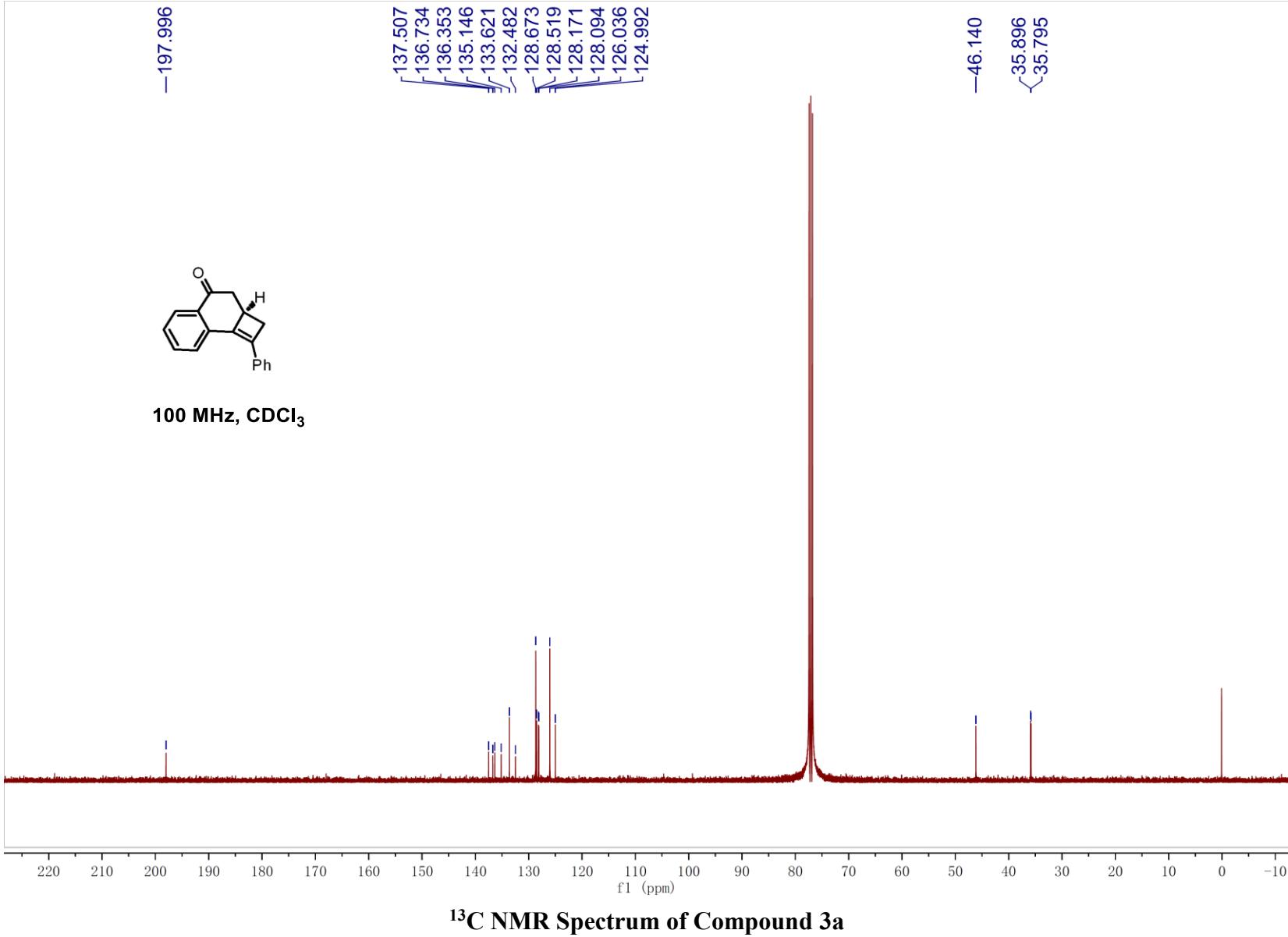
-197.996



100 MHz, CDCl₃

137.507
136.734
136.353
135.146
133.621
132.482
128.673
128.519
128.171
128.094
126.036
124.992

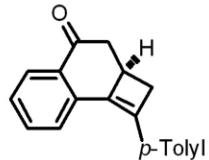
-46.140
35.896
35.795



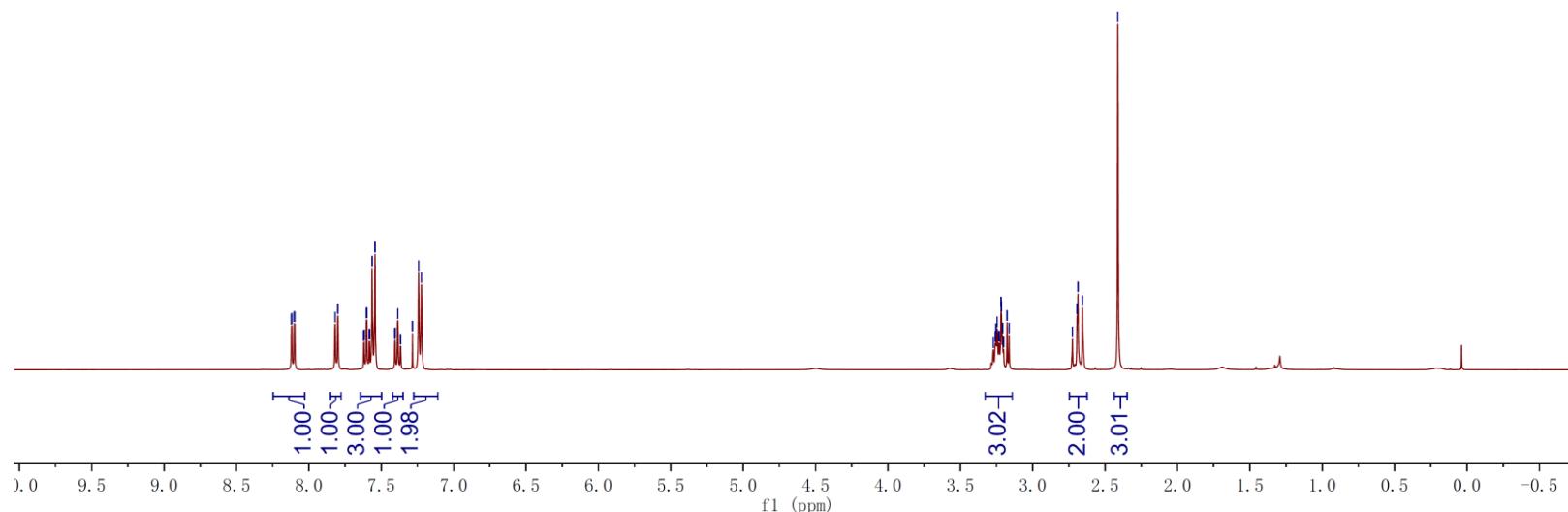
¹³C NMR Spectrum of Compound 3a

8.120
8.117
8.100
8.098
7.819
7.800
7.621
7.618
7.602
7.599
7.584
7.580
7.563
7.543
7.406
7.404
7.385
7.368
7.366
7.284
7.241
7.222

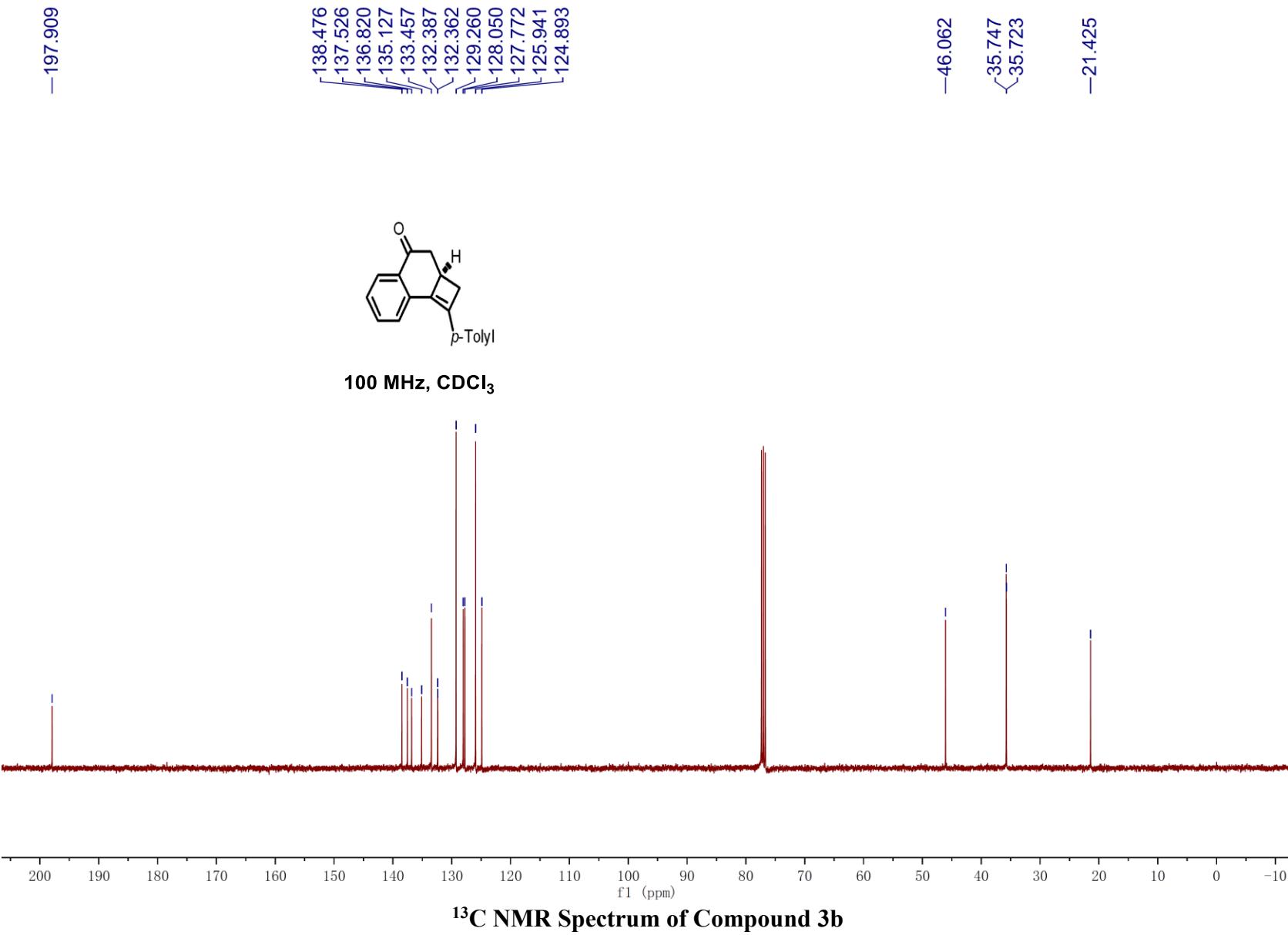
3.272
3.258
3.253
3.245
3.233
3.230
3.218
3.216
3.208
3.201
3.177
3.163
2.725
2.693
2.687
2.656
2.411

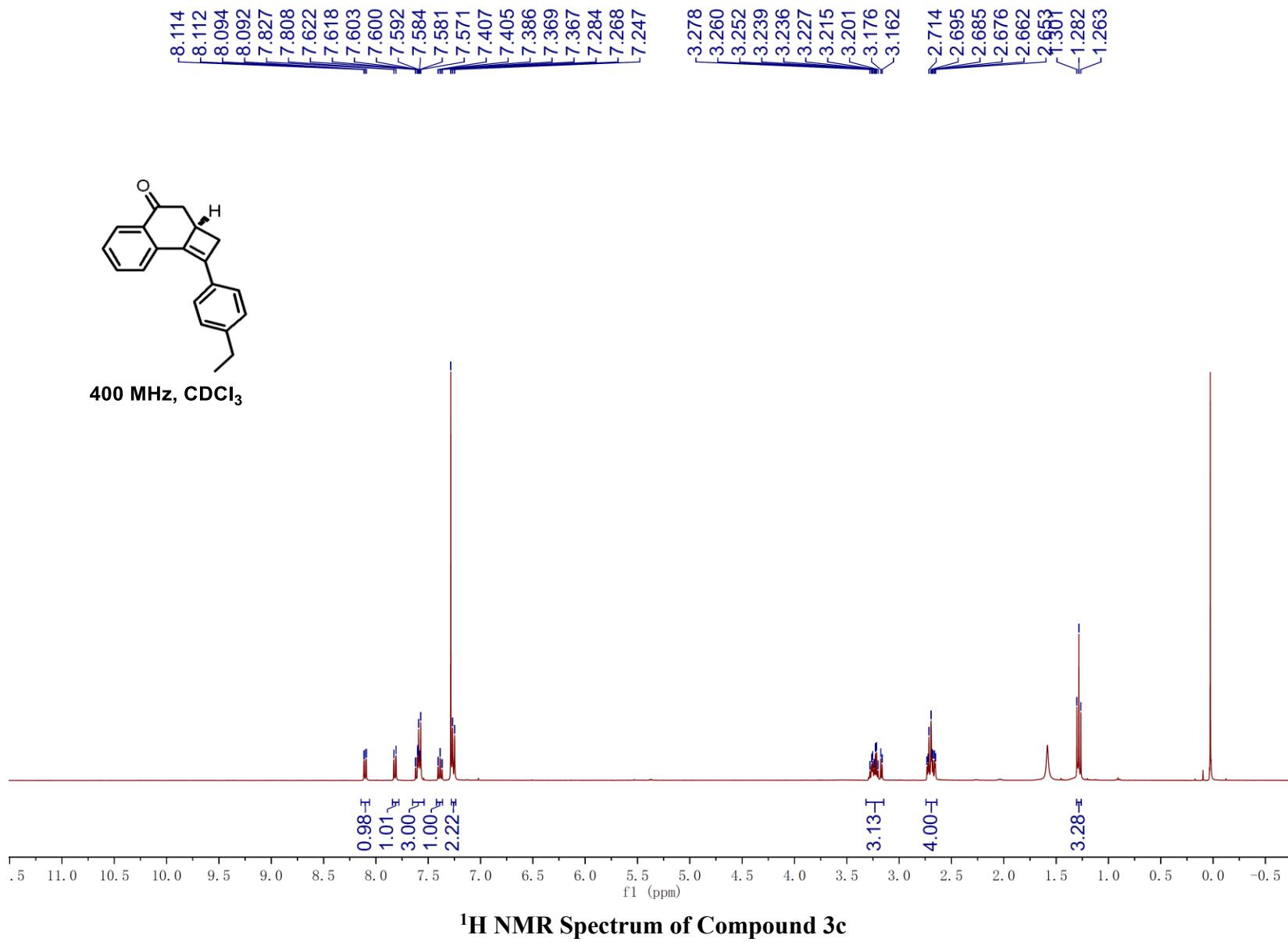


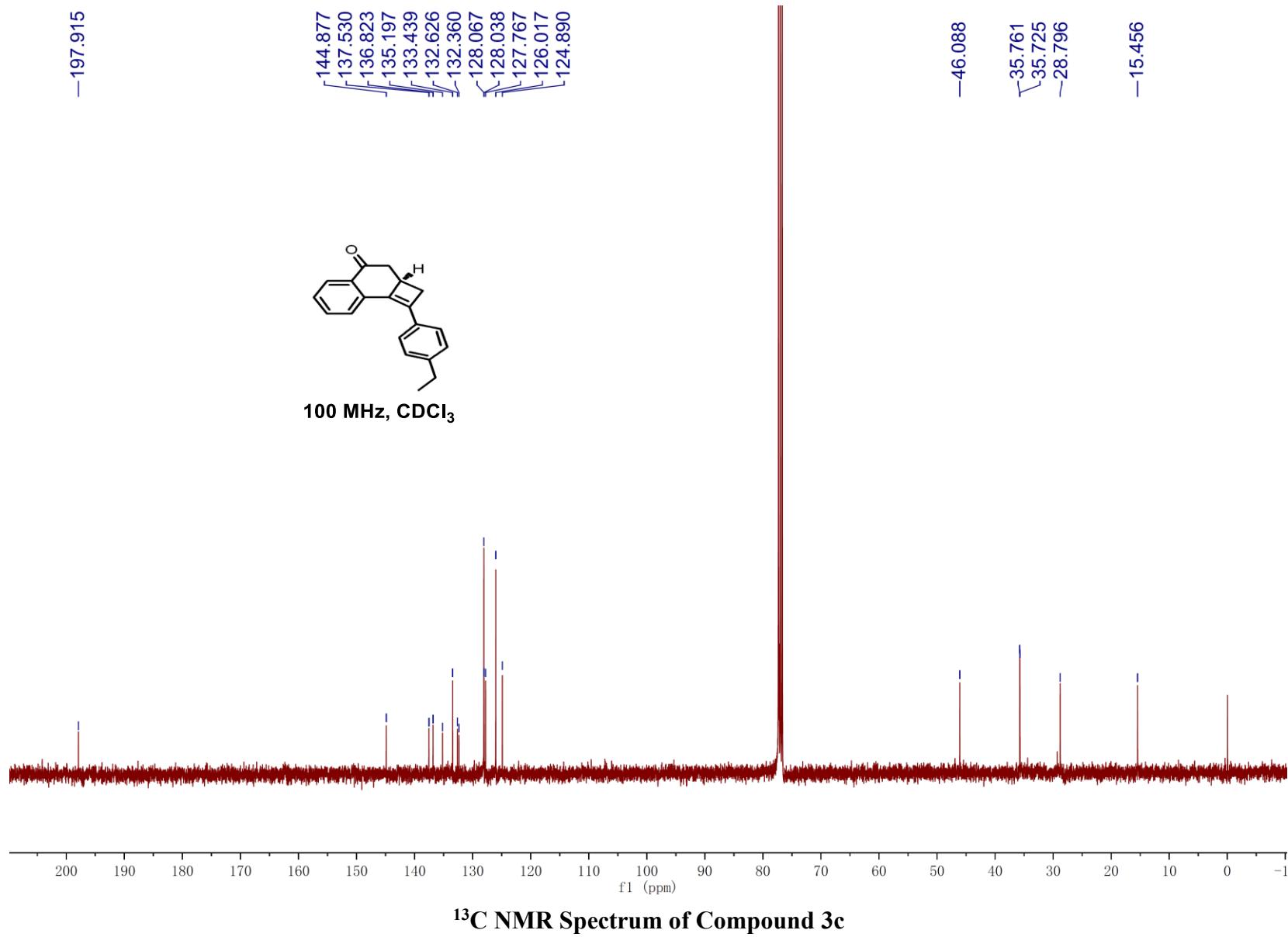
400 MHz, CDCl₃

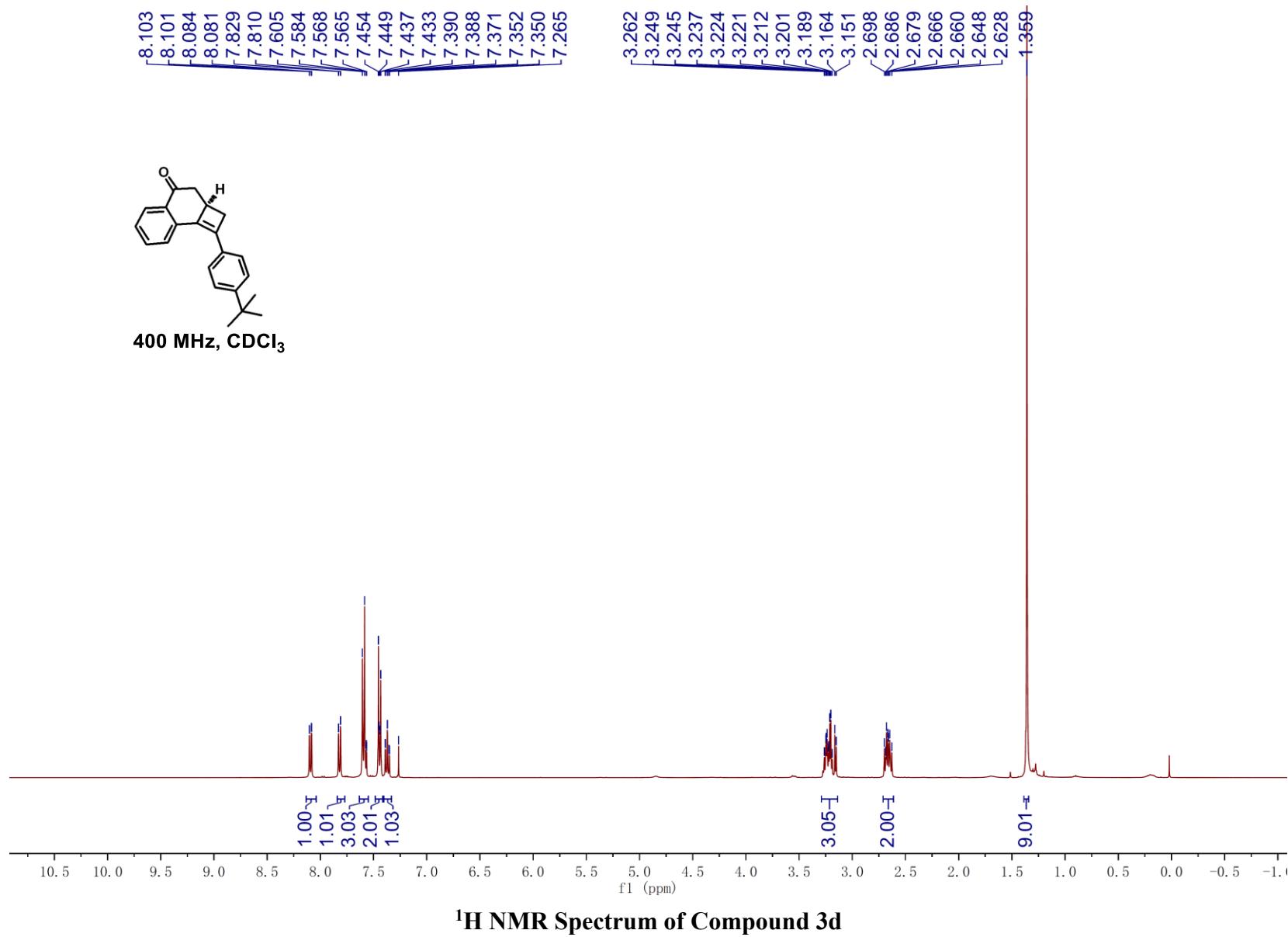


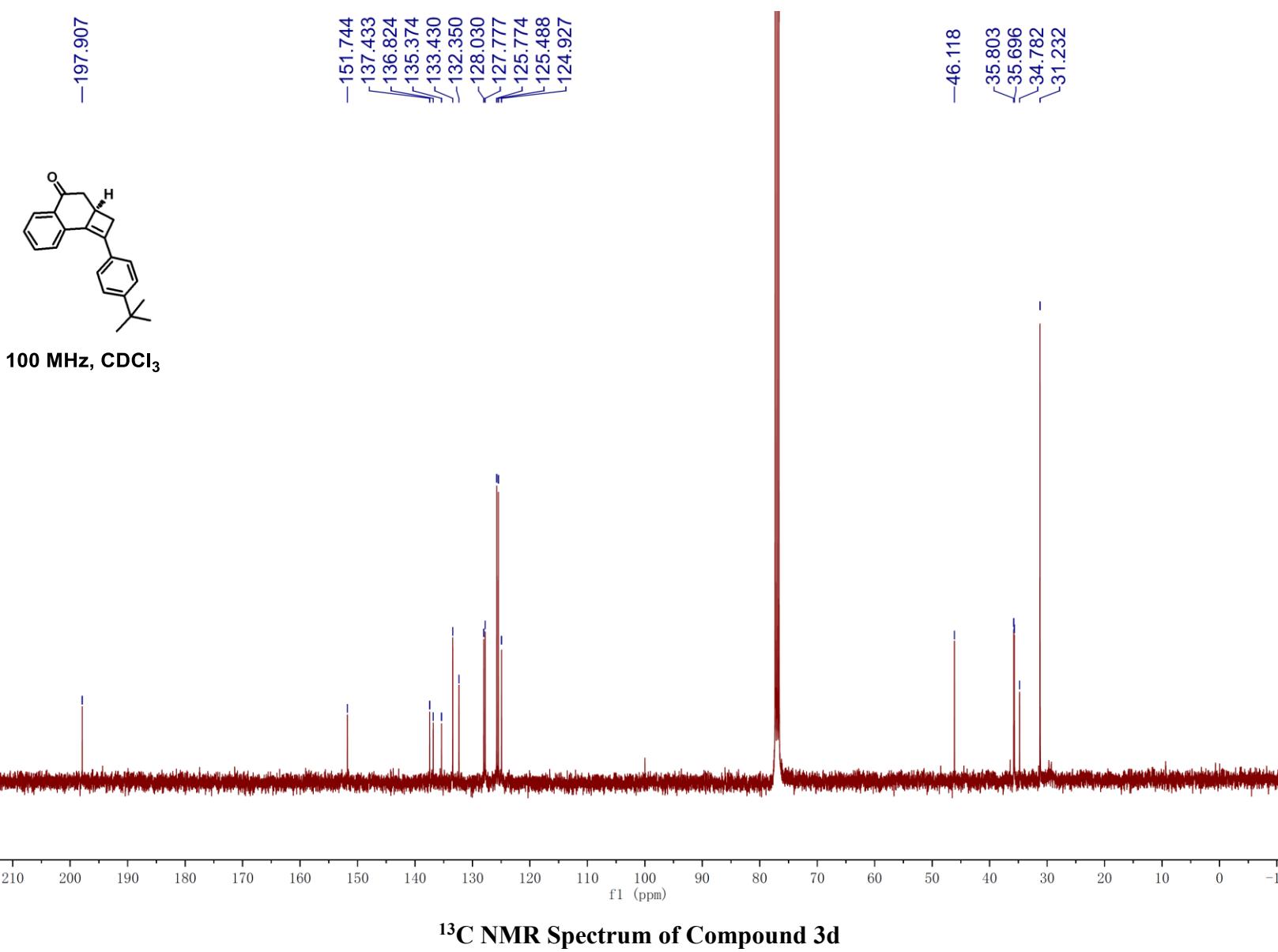
¹H NMR Spectrum of Compound 3b

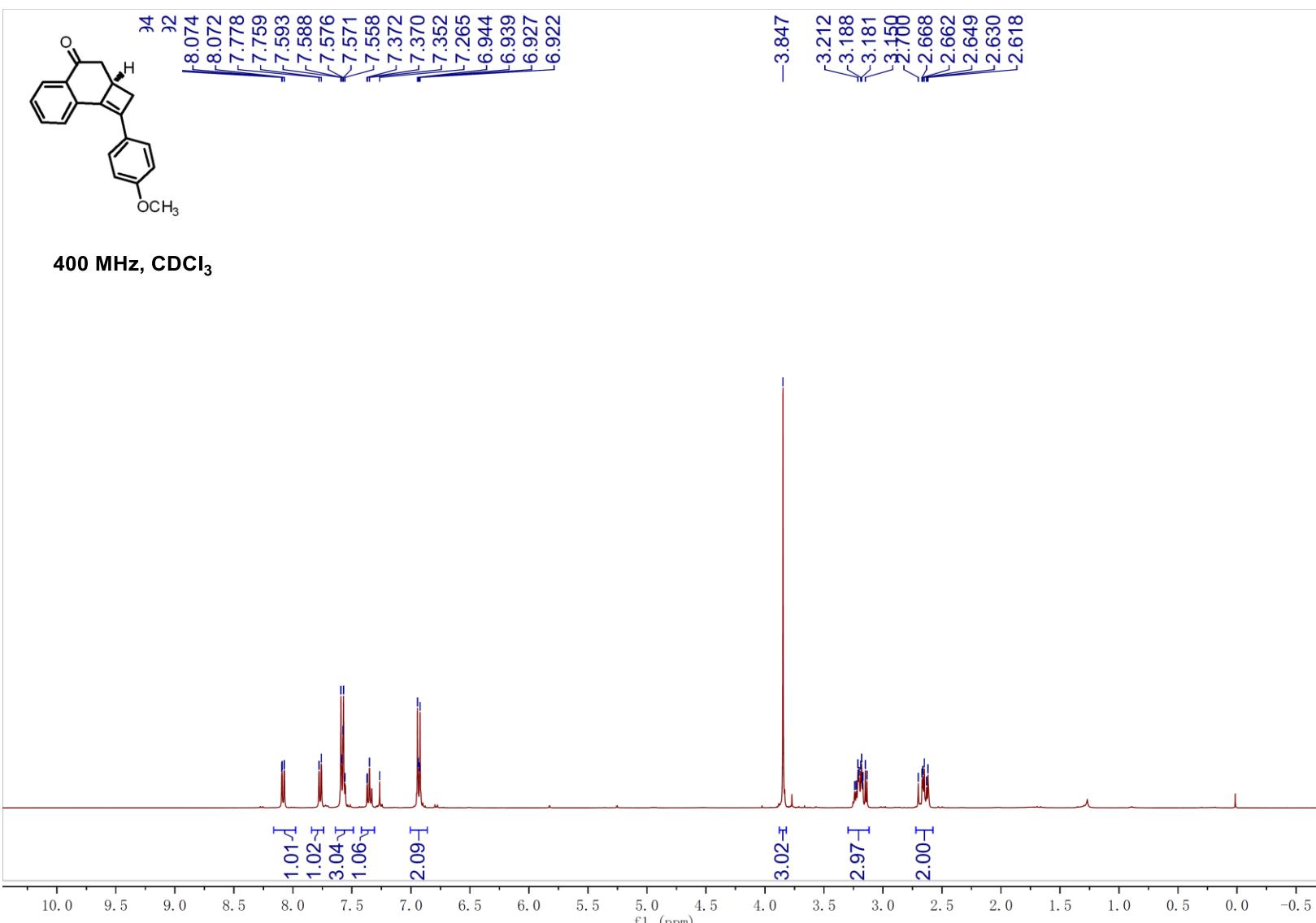




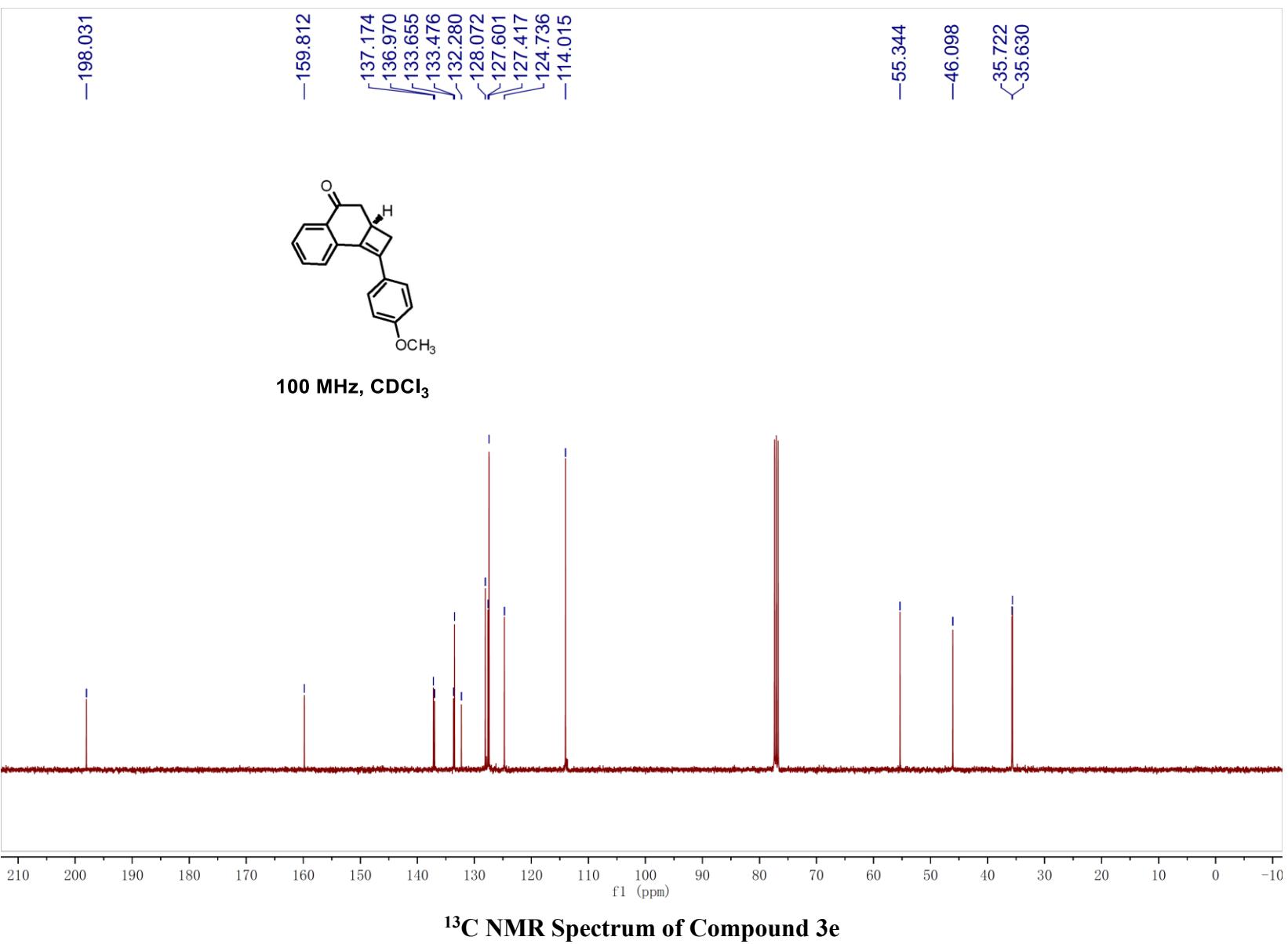


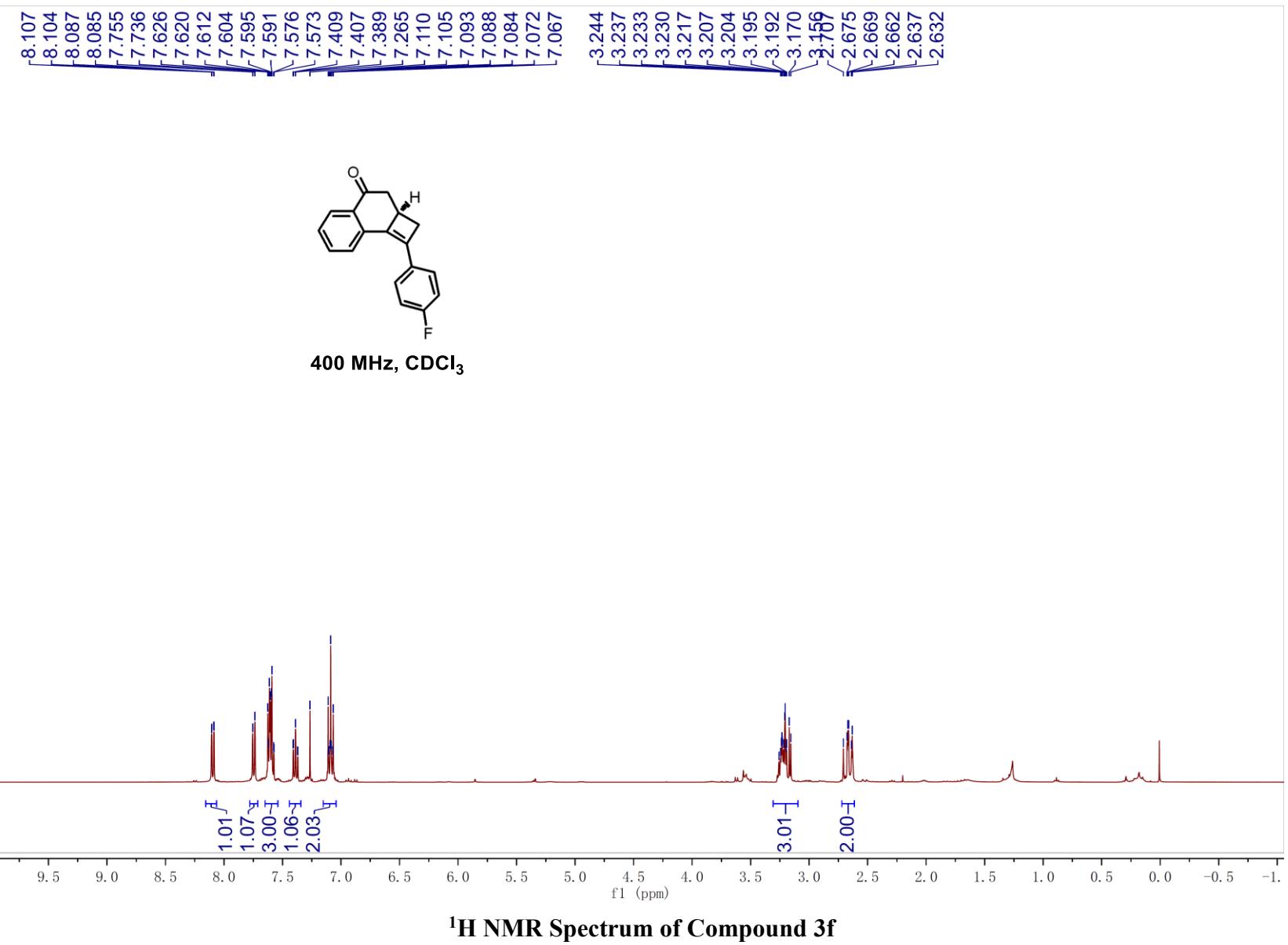


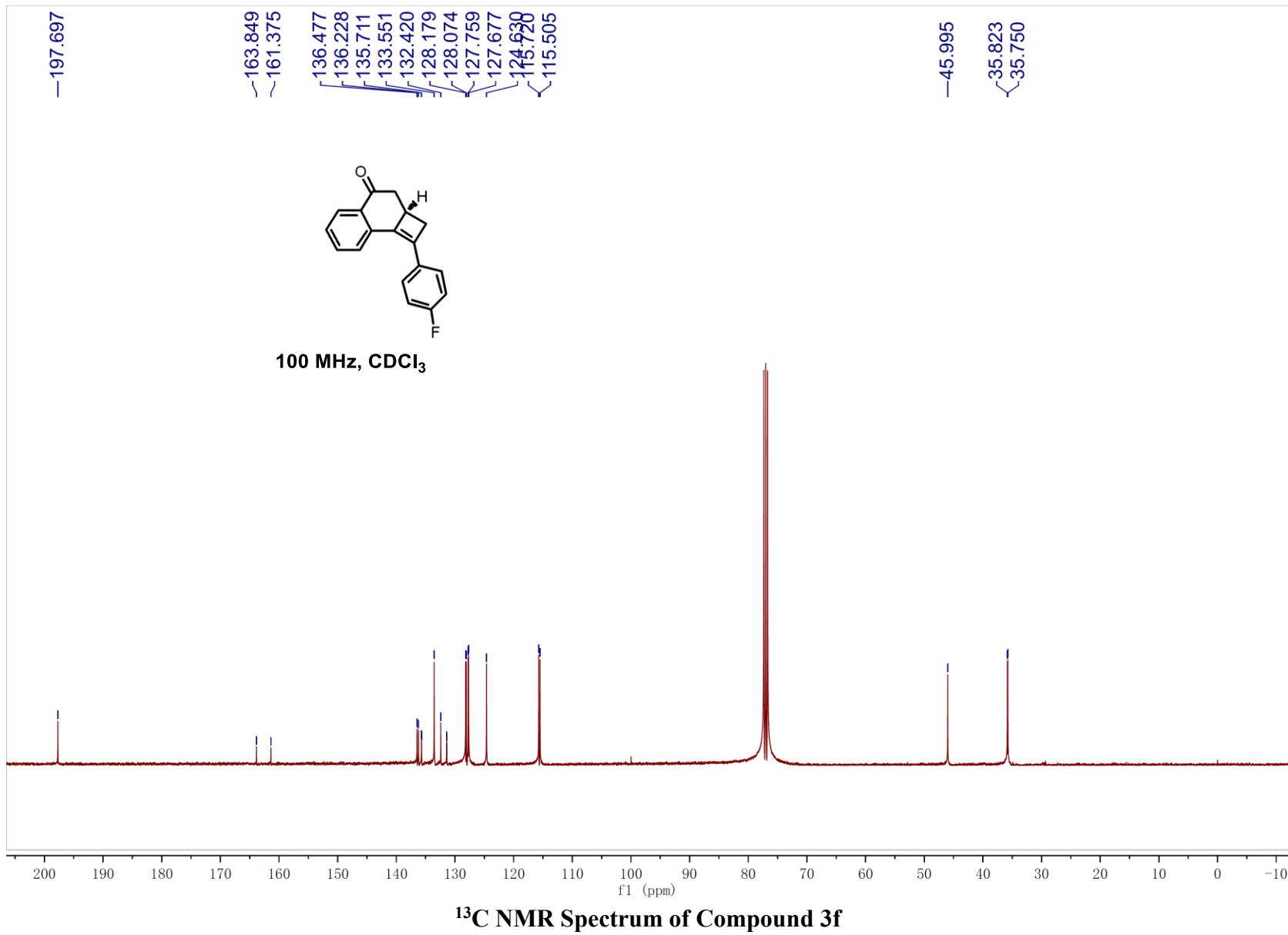


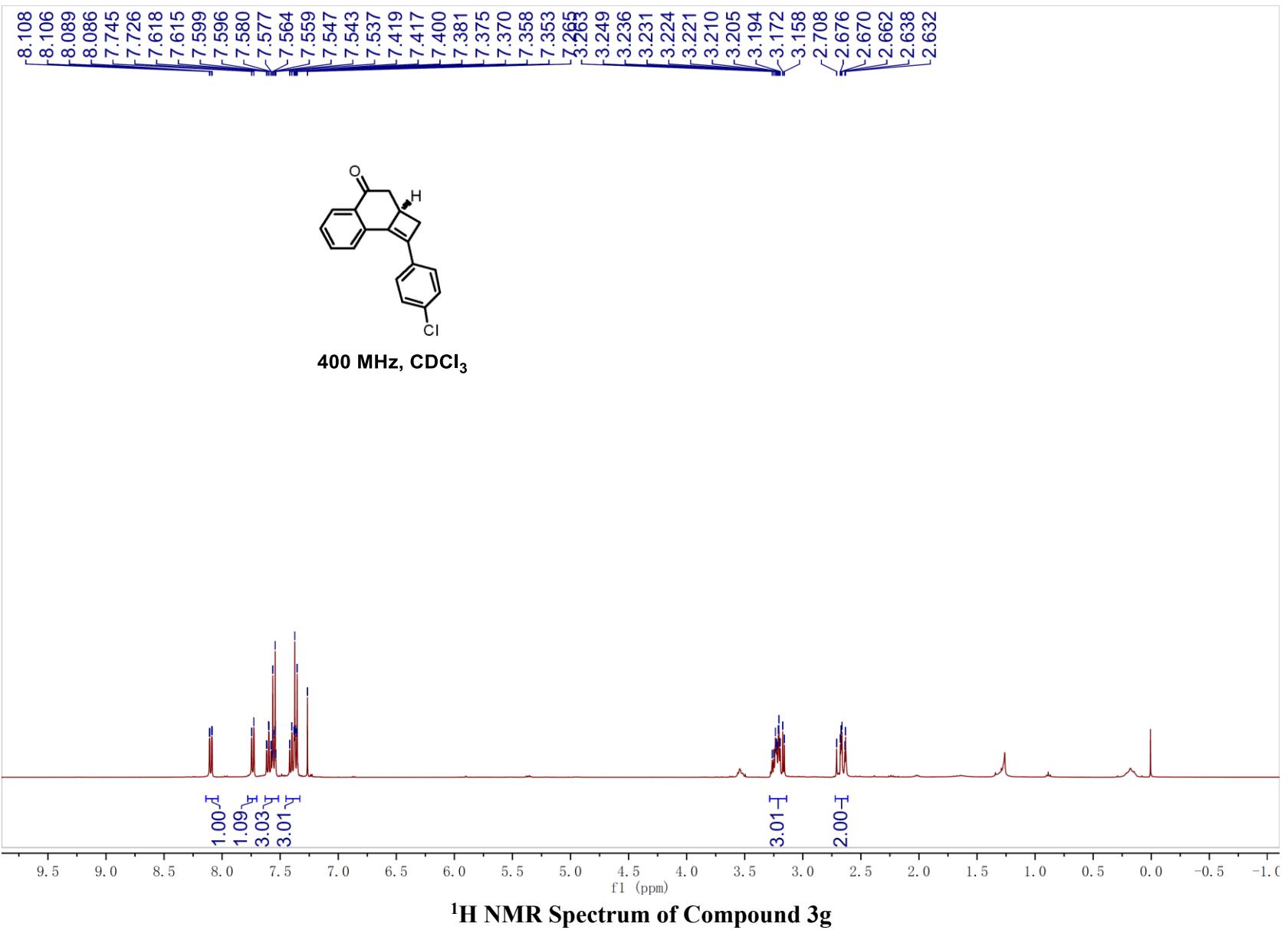


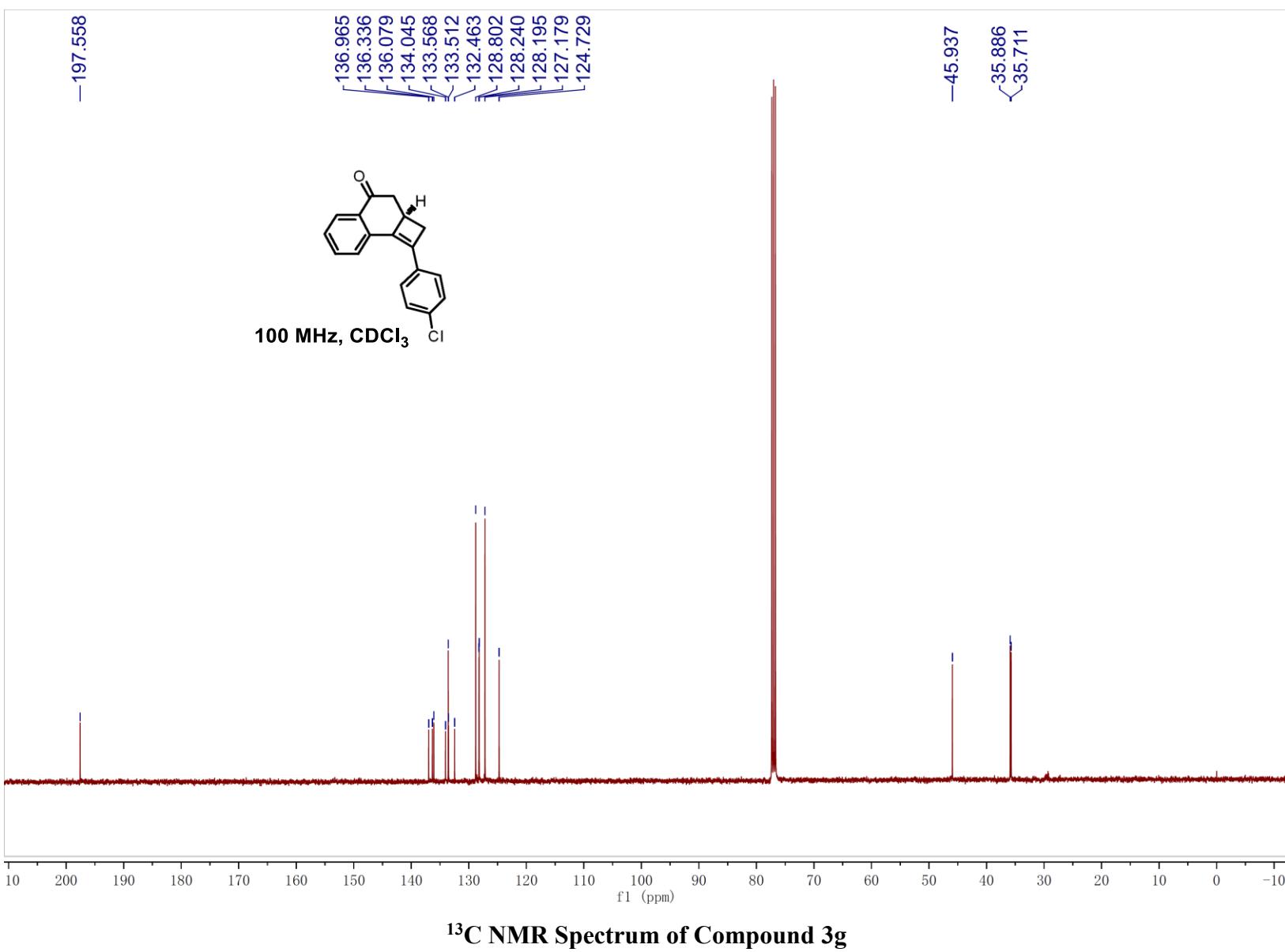
¹H NMR Spectrum of Compound 3e

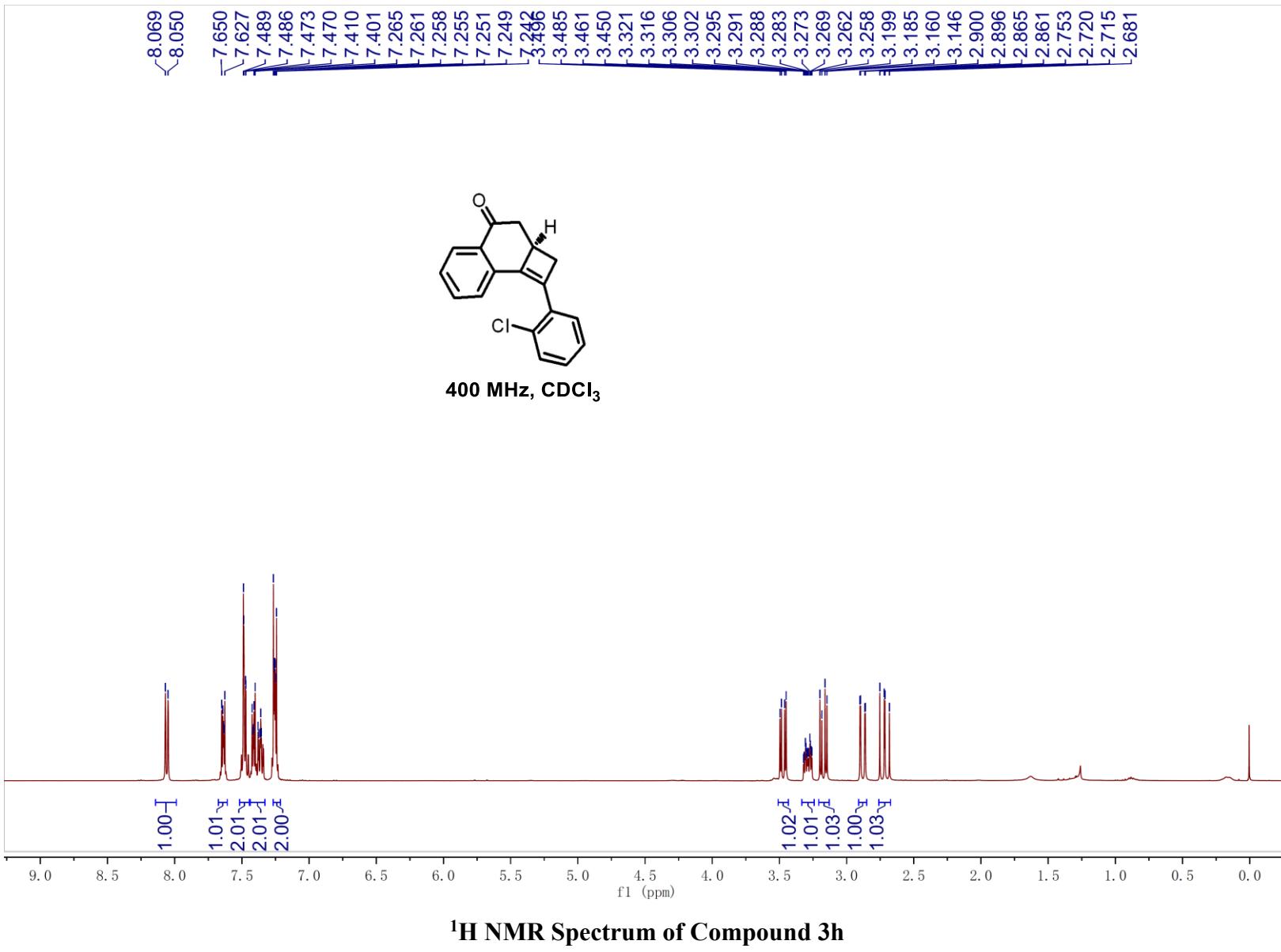


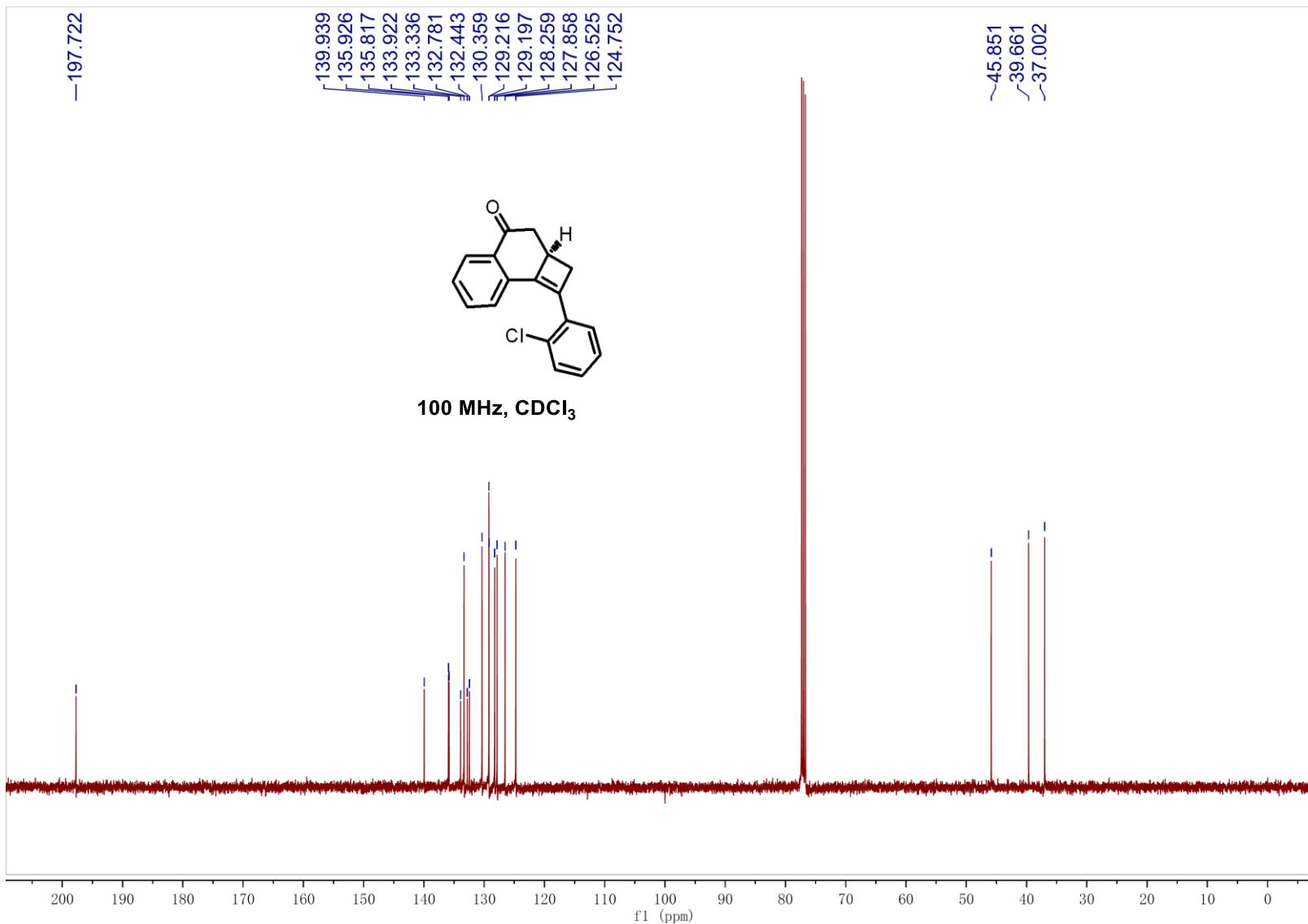




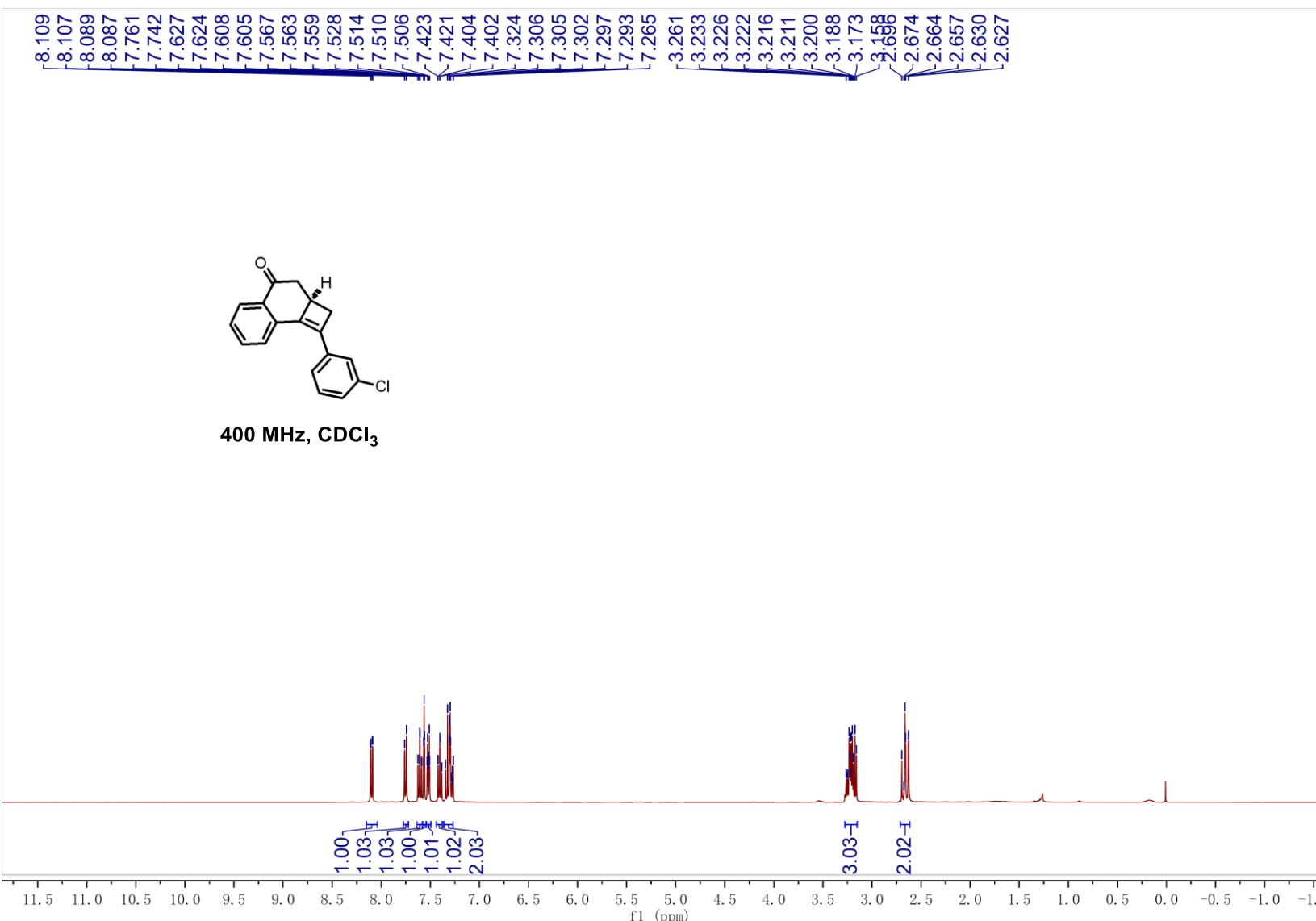




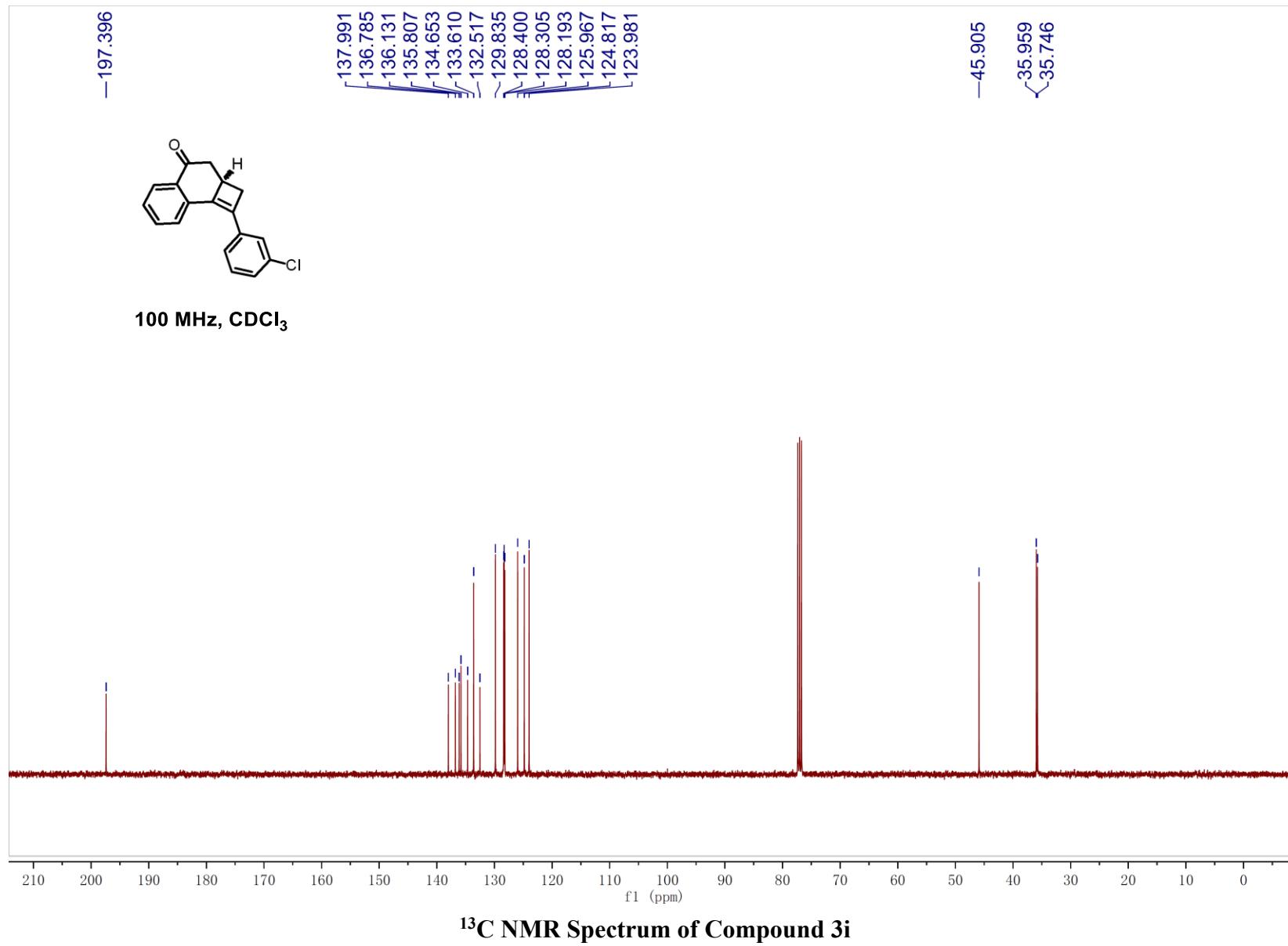


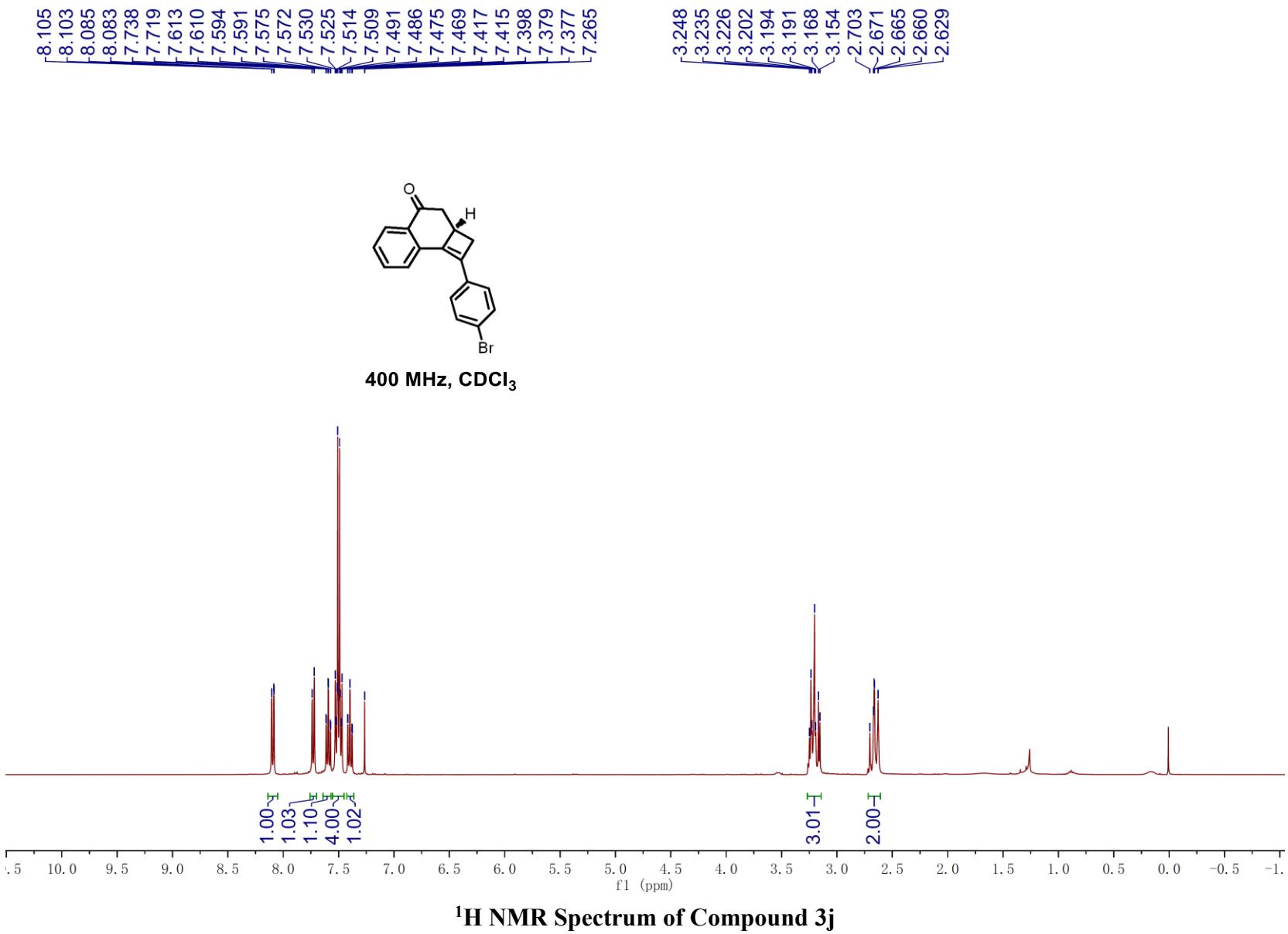


^{13}C NMR Spectrum of Compound 3h

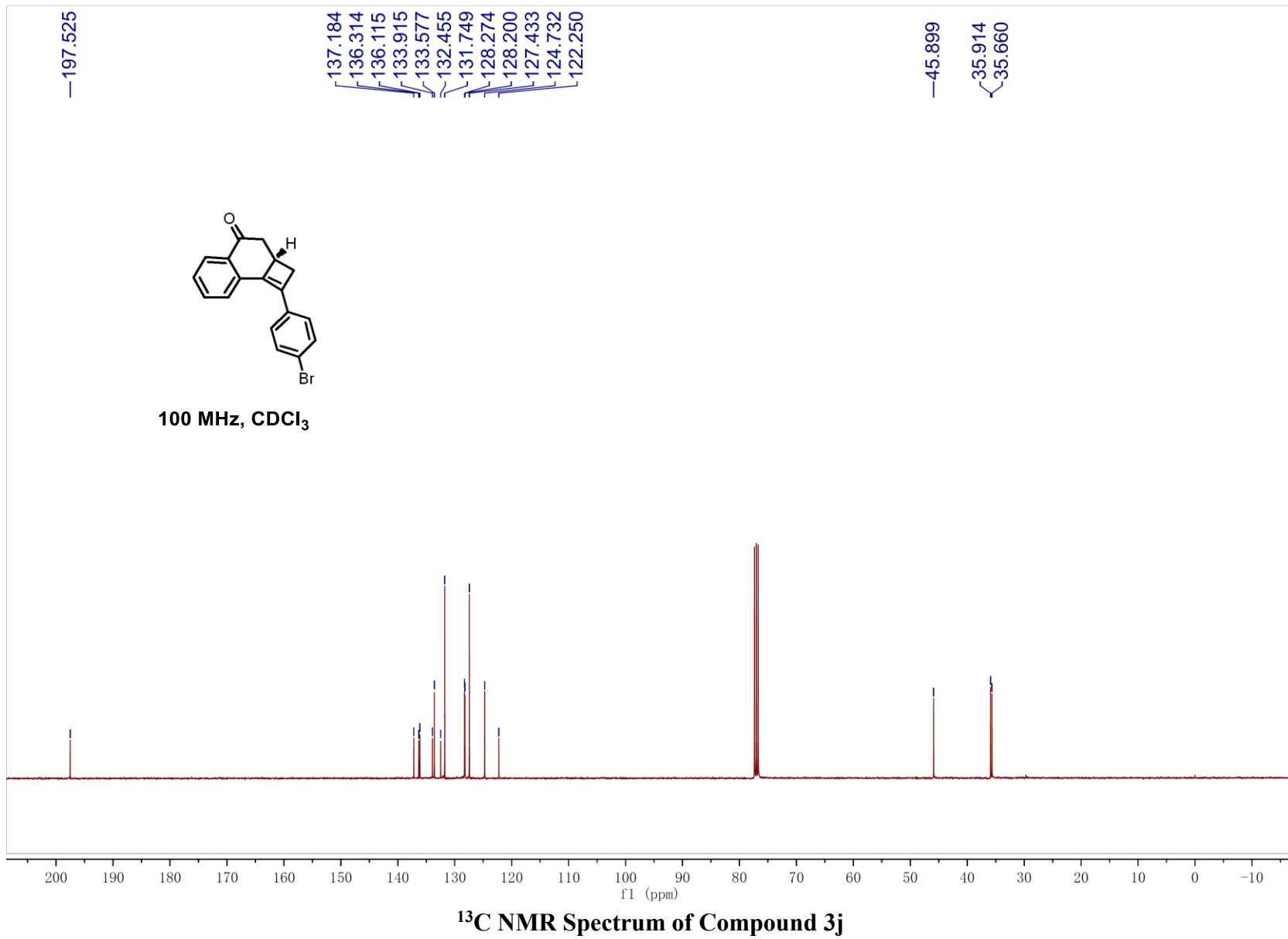


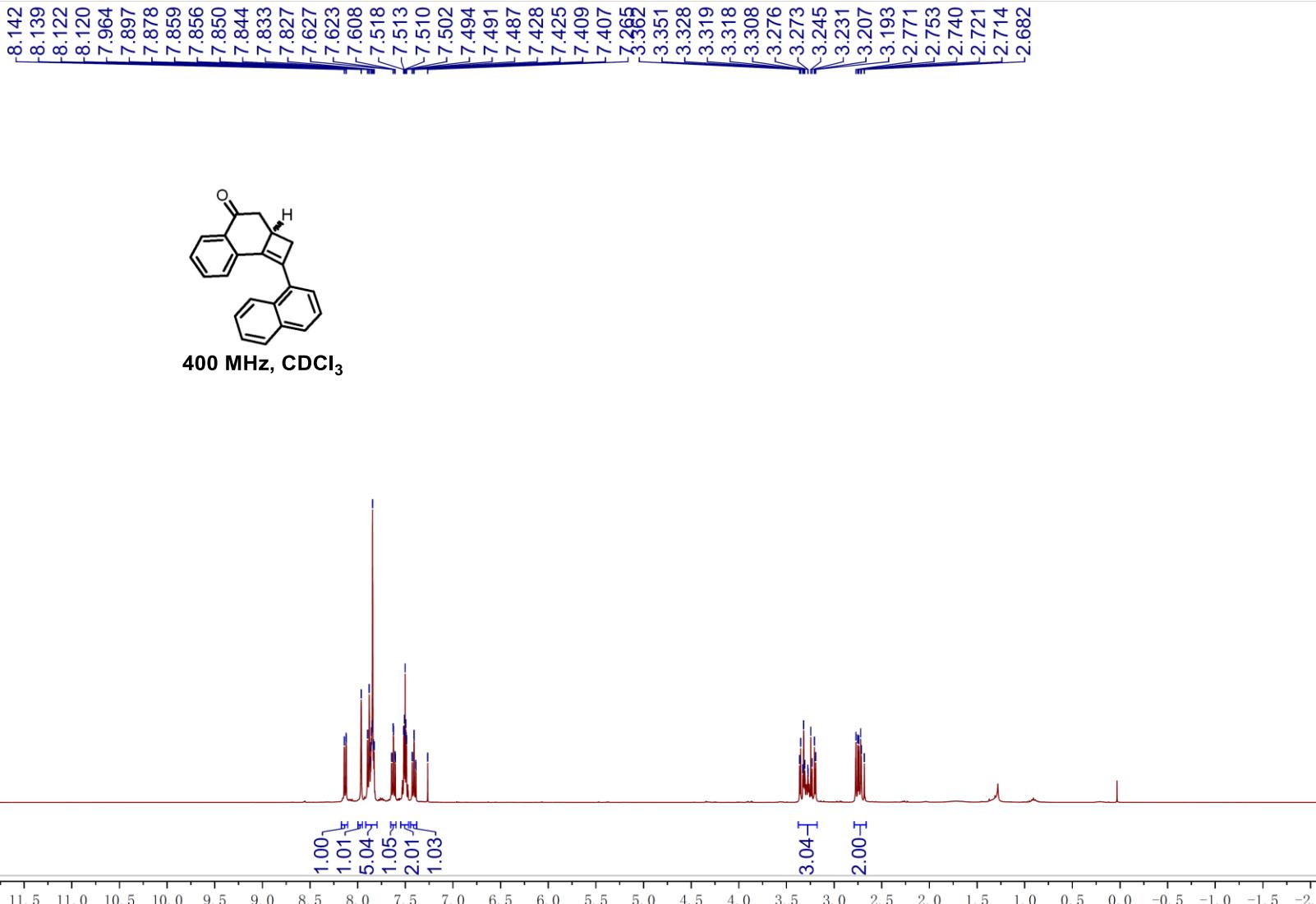
¹H NMR Spectrum of Compound 3i



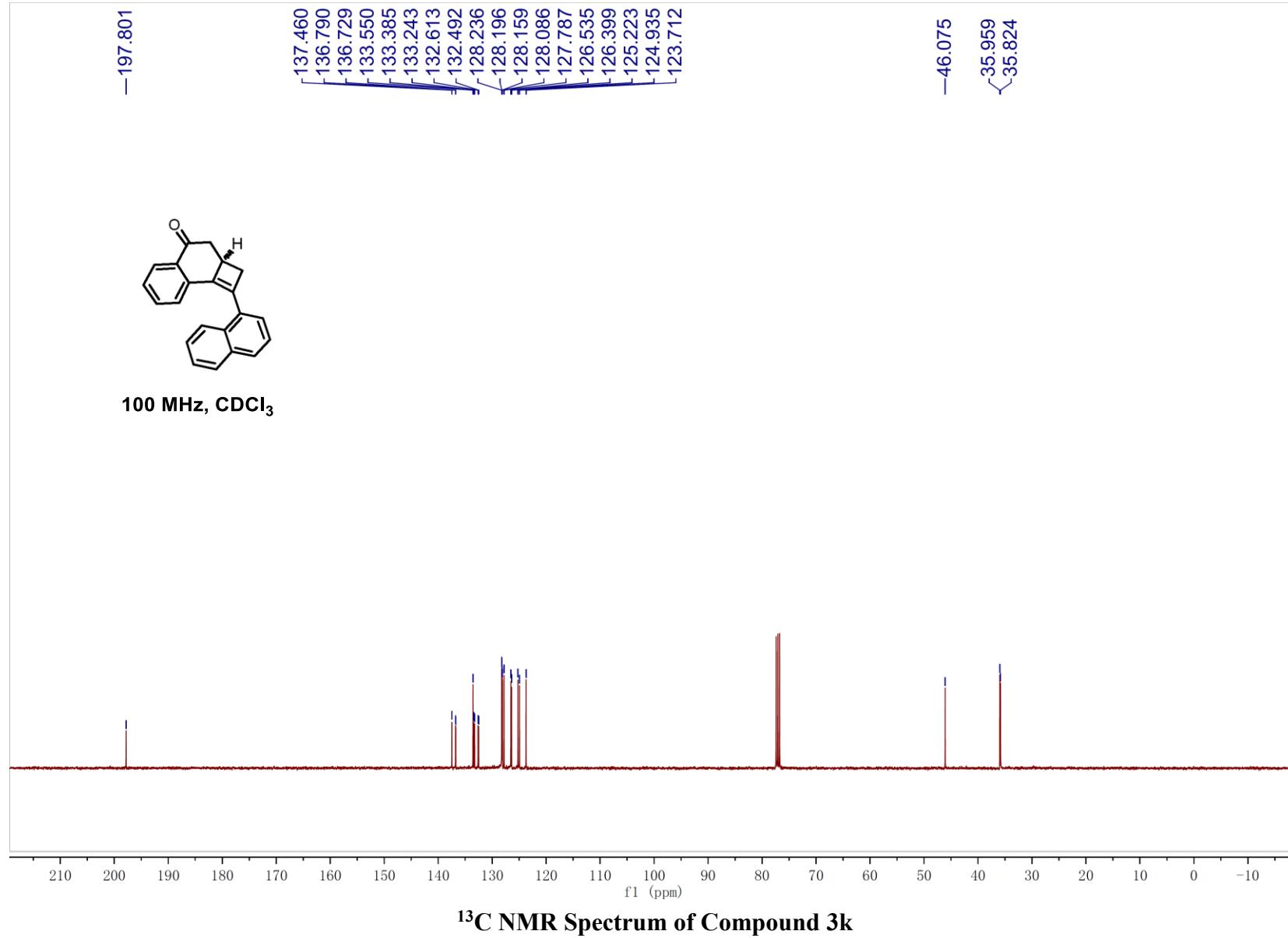


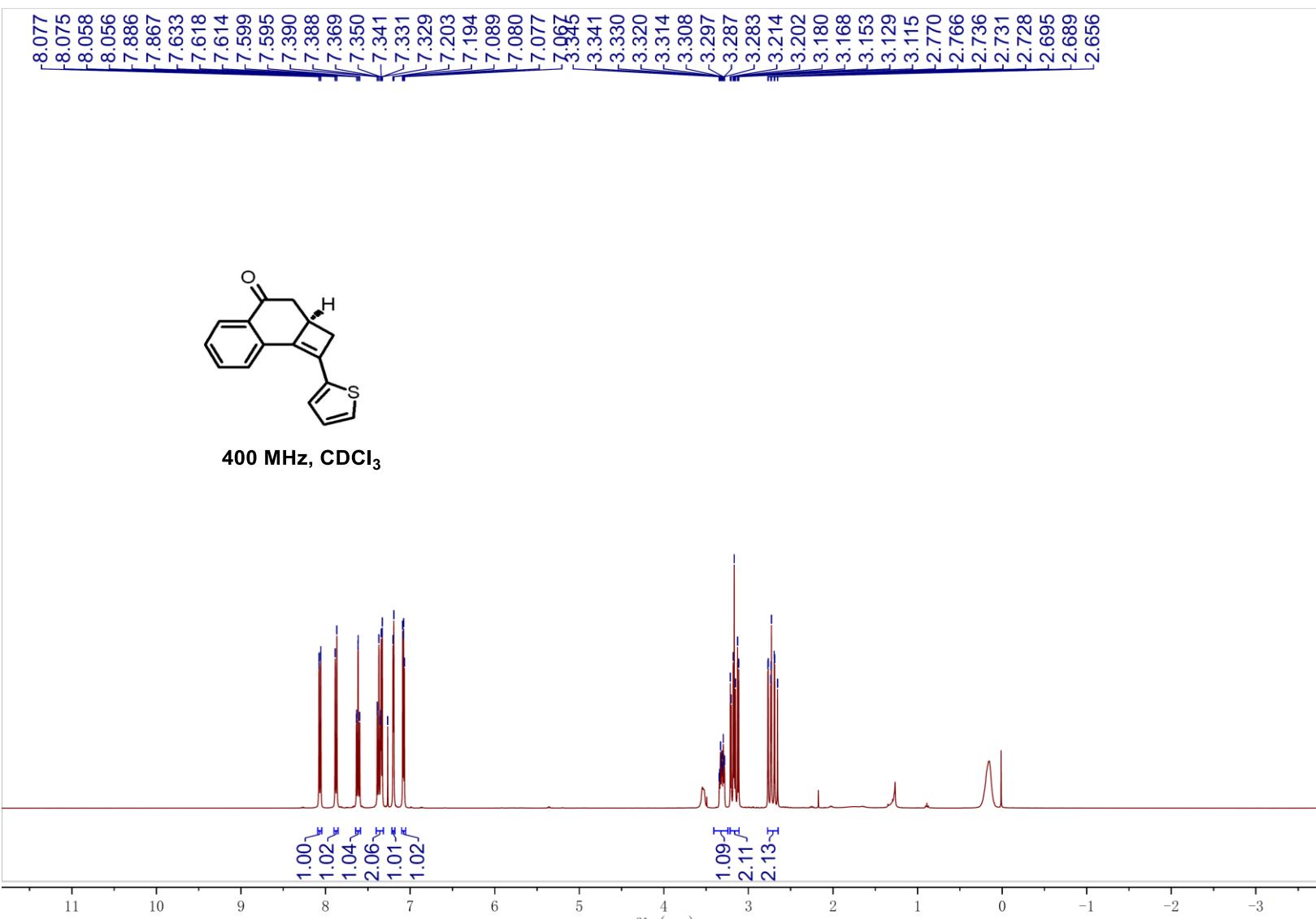
¹H NMR Spectrum of Compound 3j



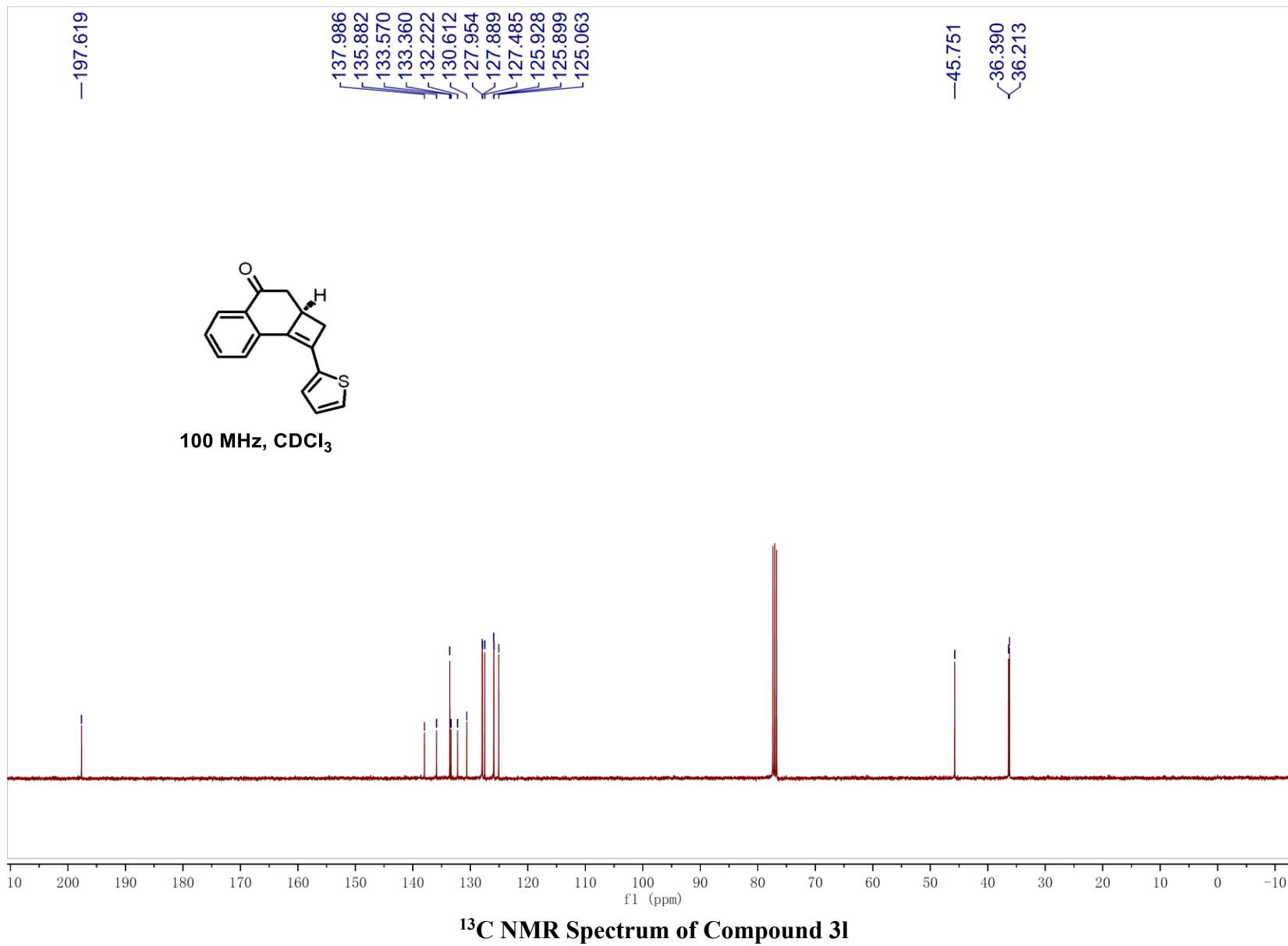


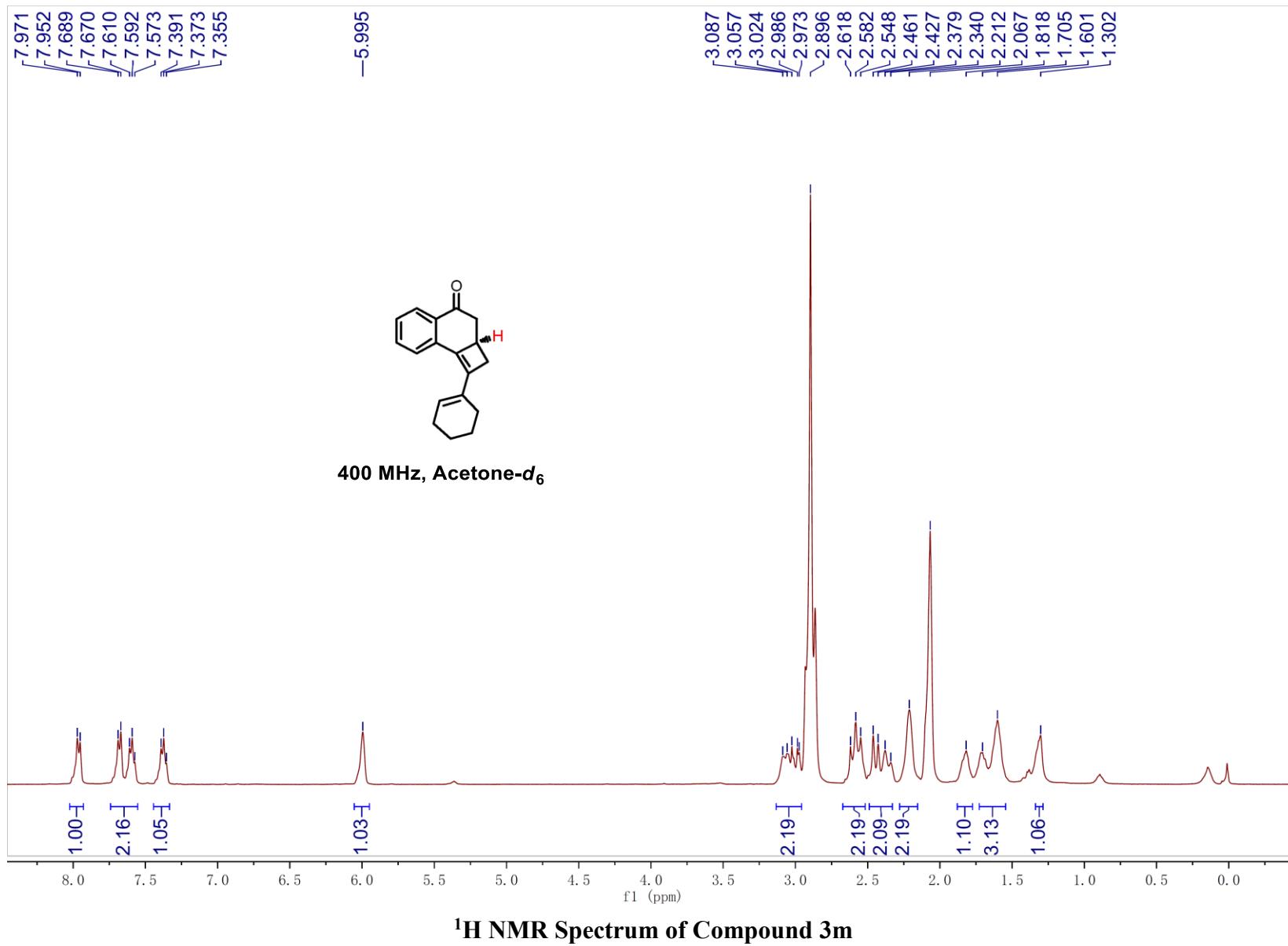
¹H NMR Spectrum of Compound 3k

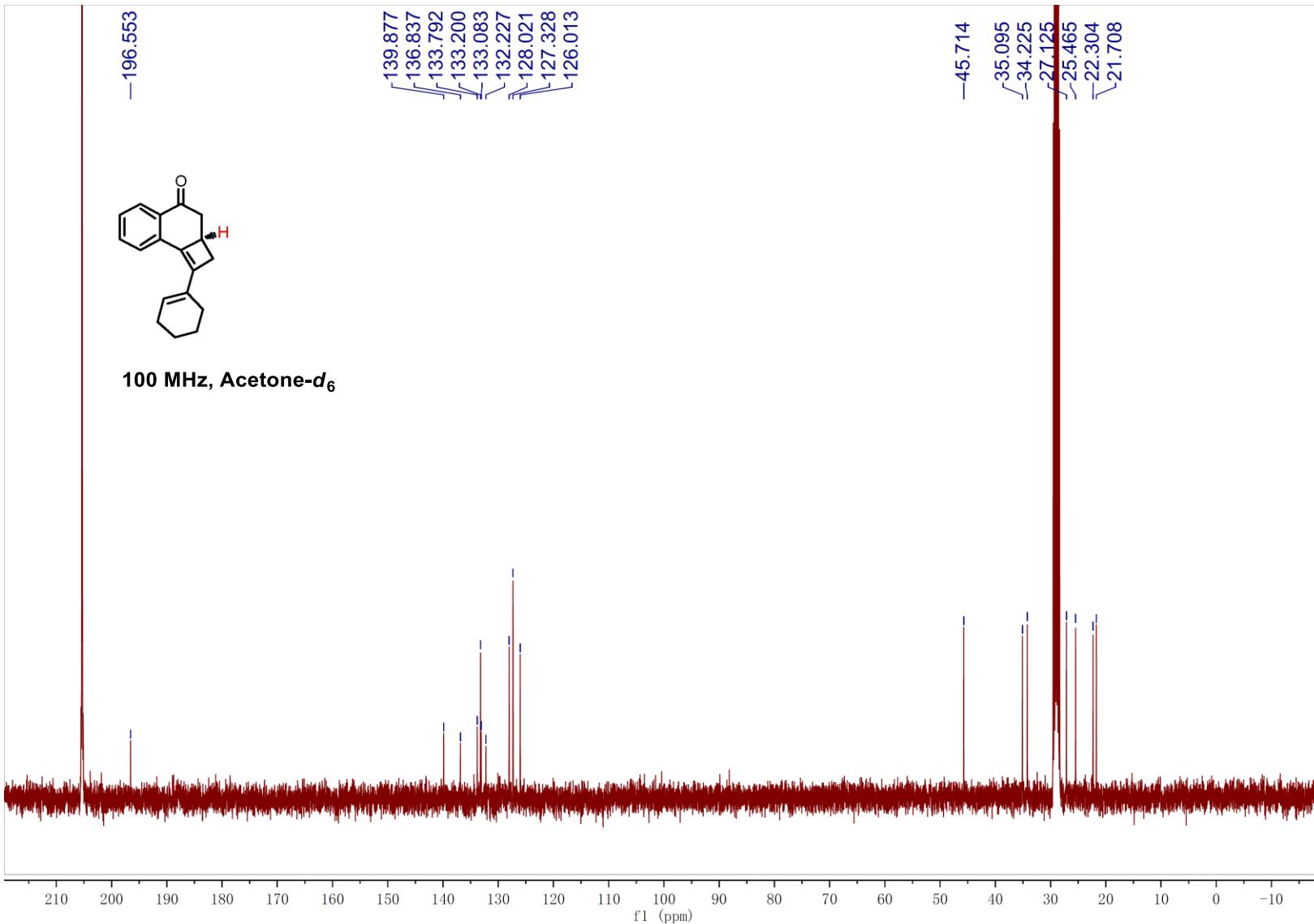




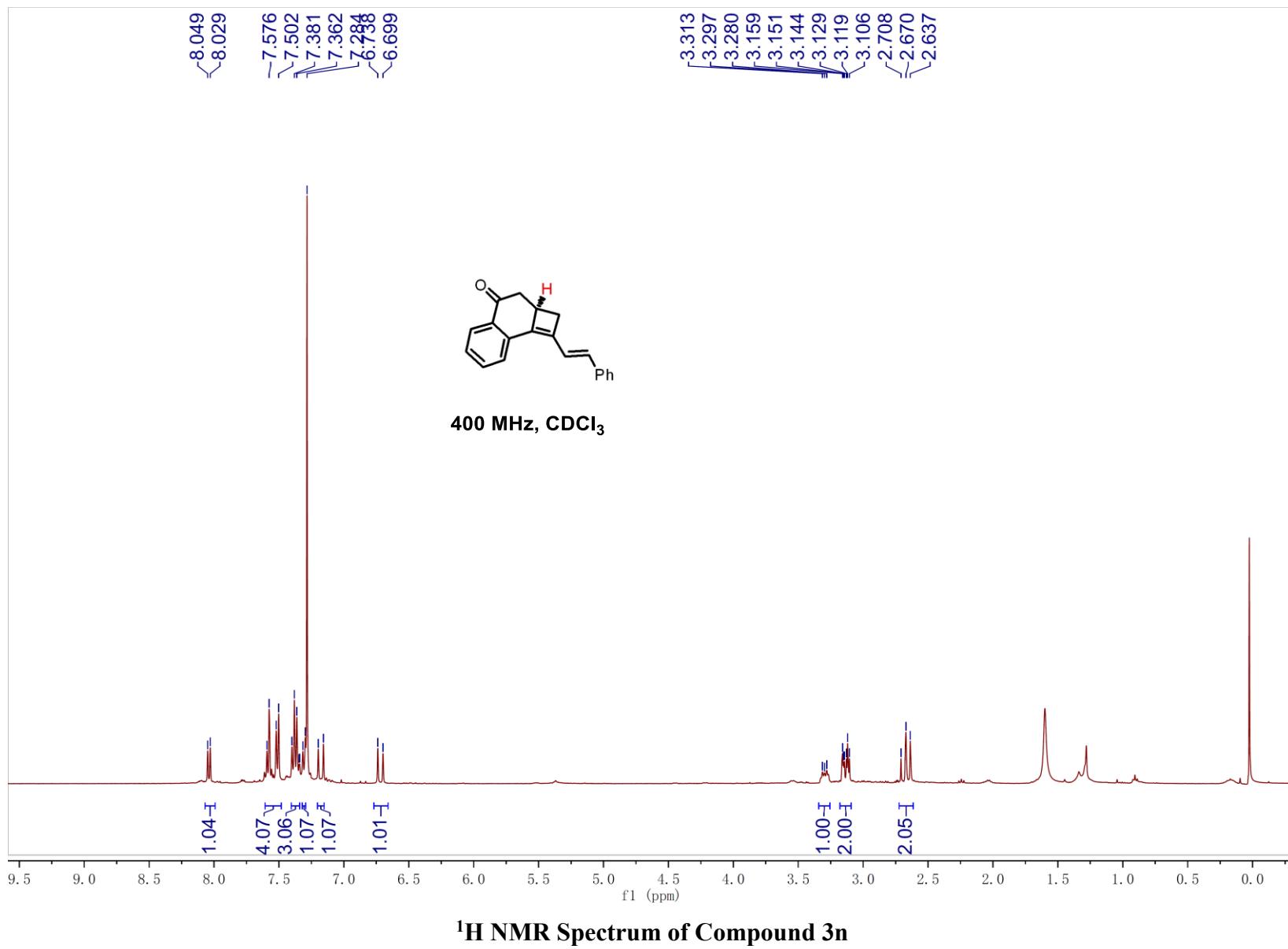
^1H NMR Spectrum of Compound 3I

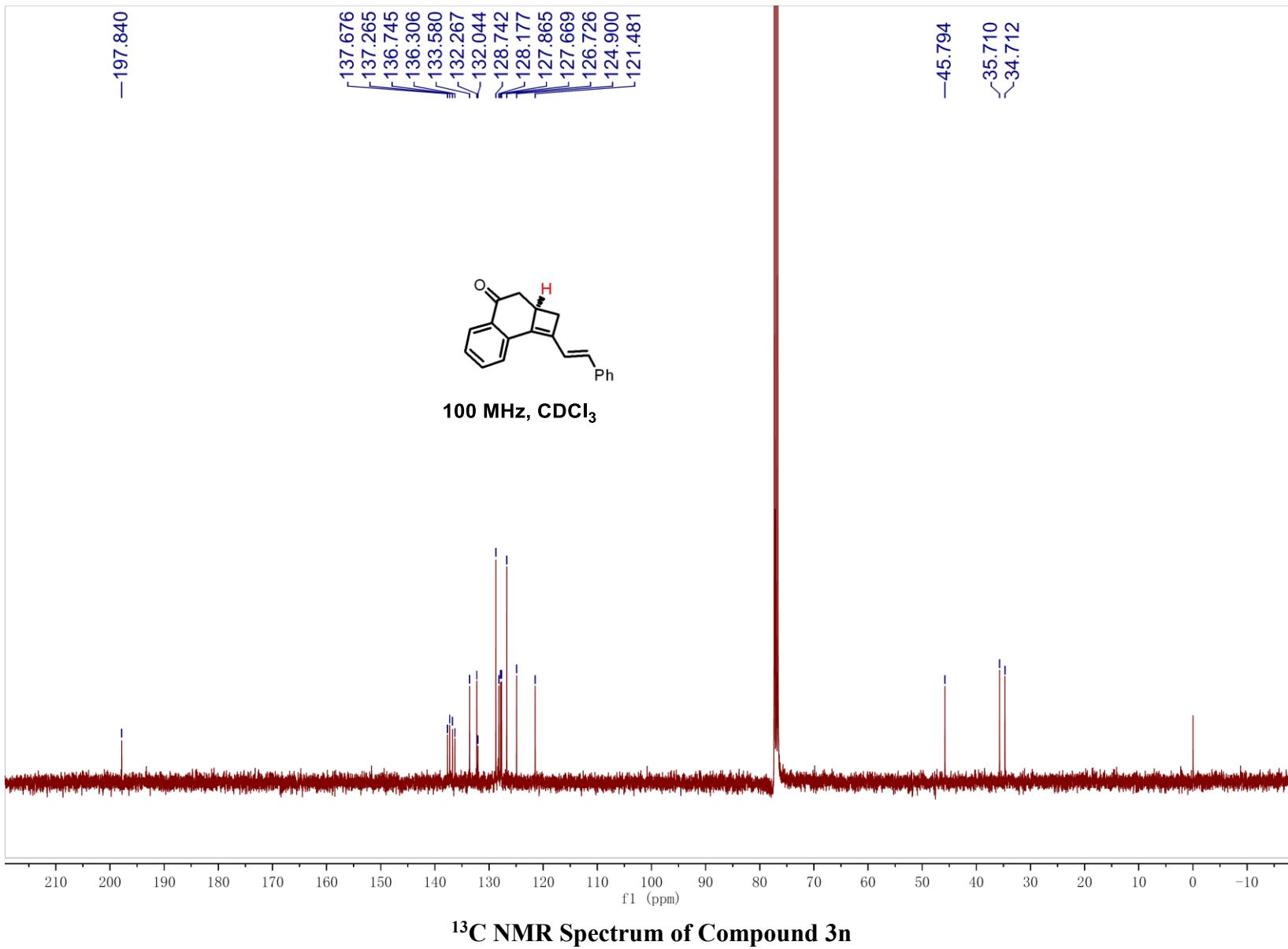


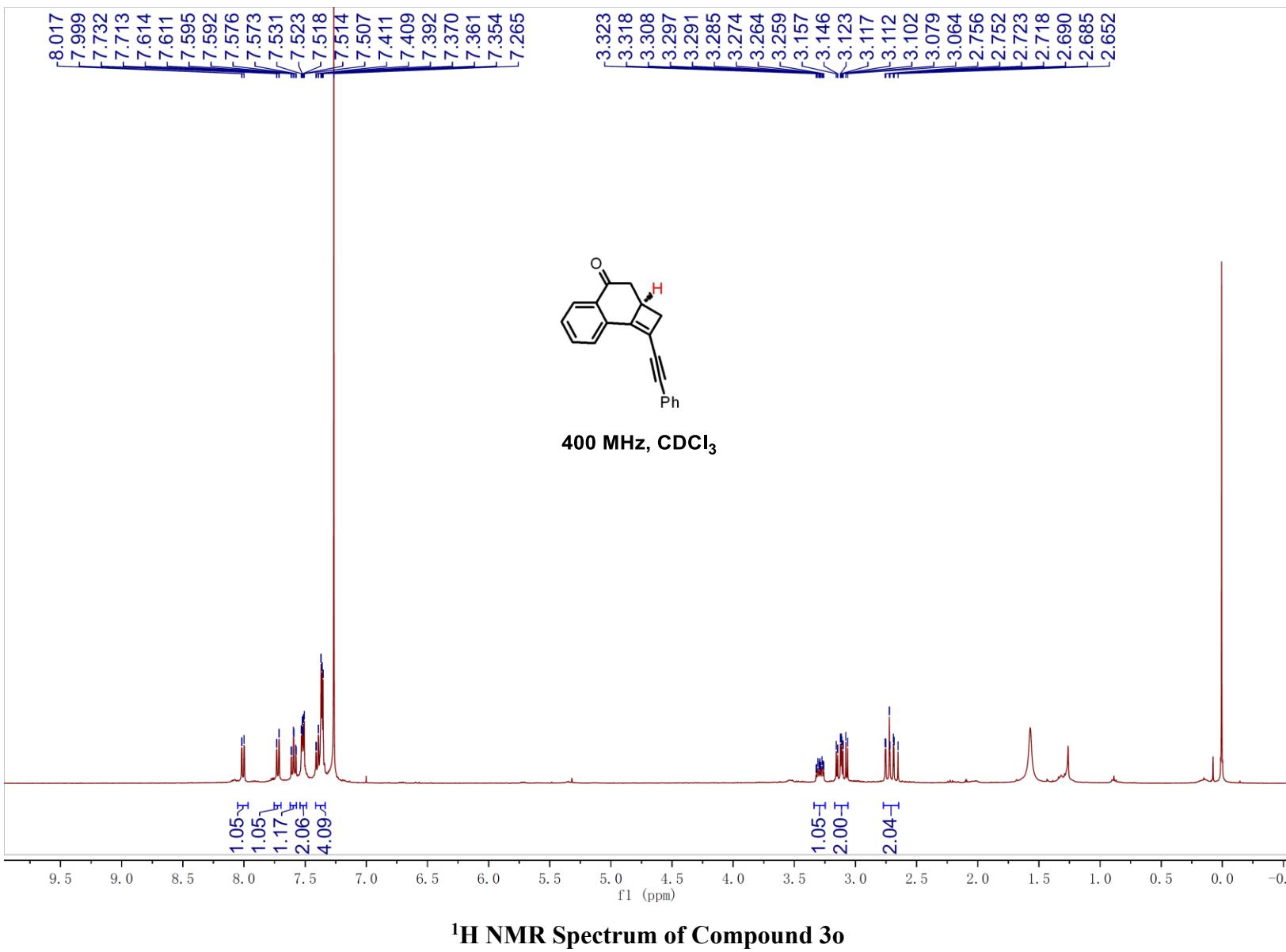




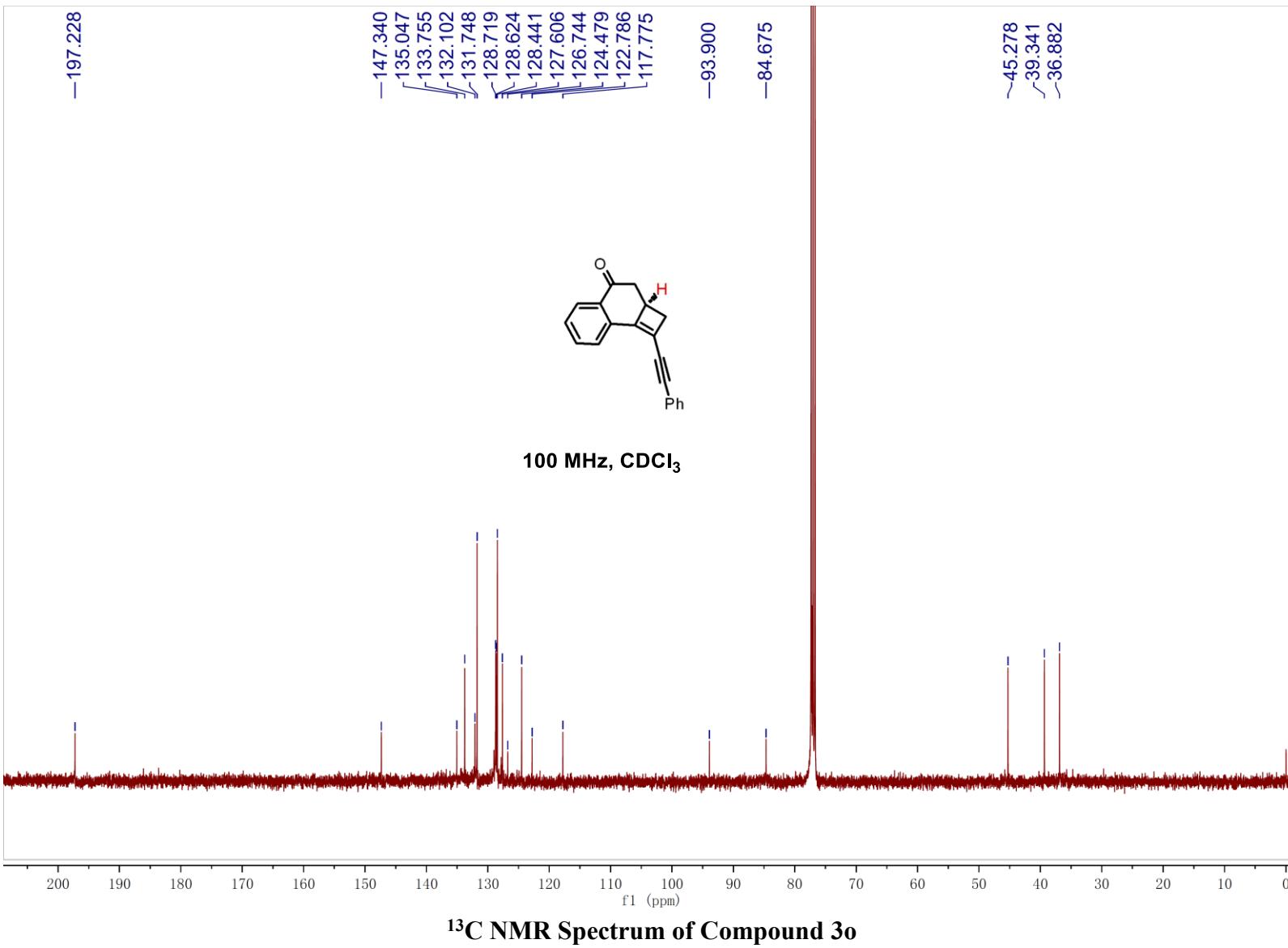
^{13}C NMR Spectrum of Compound 3m

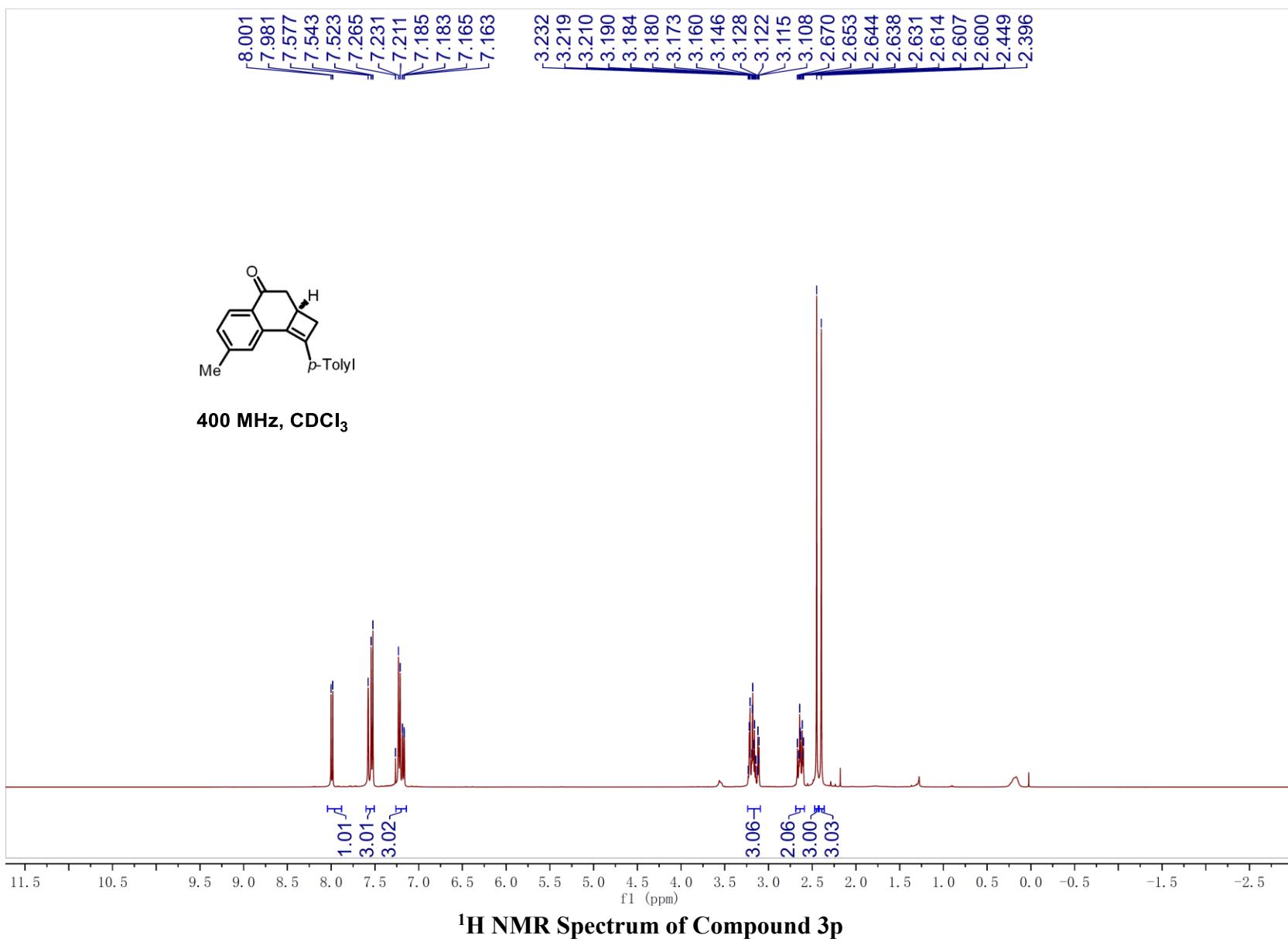


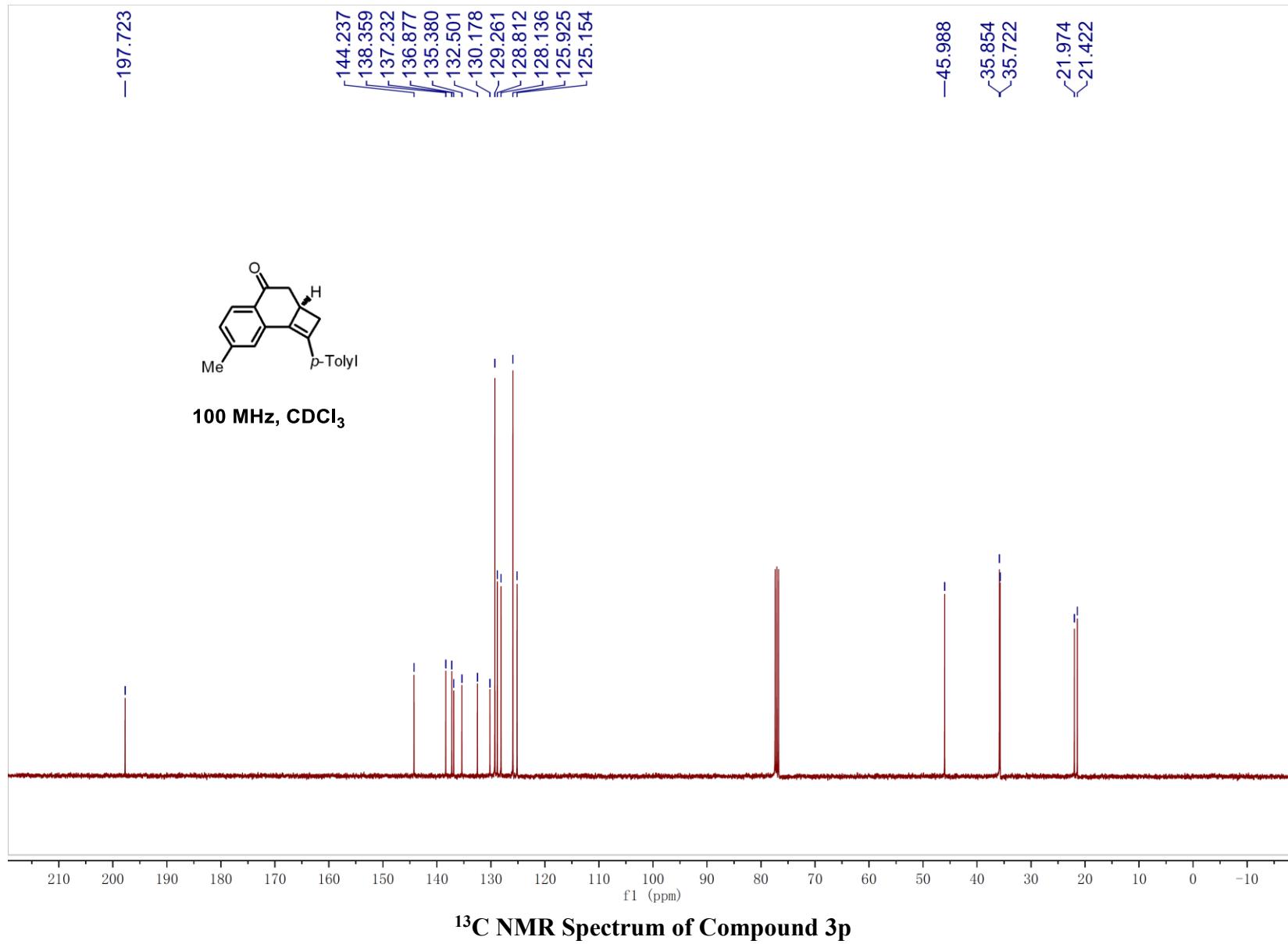


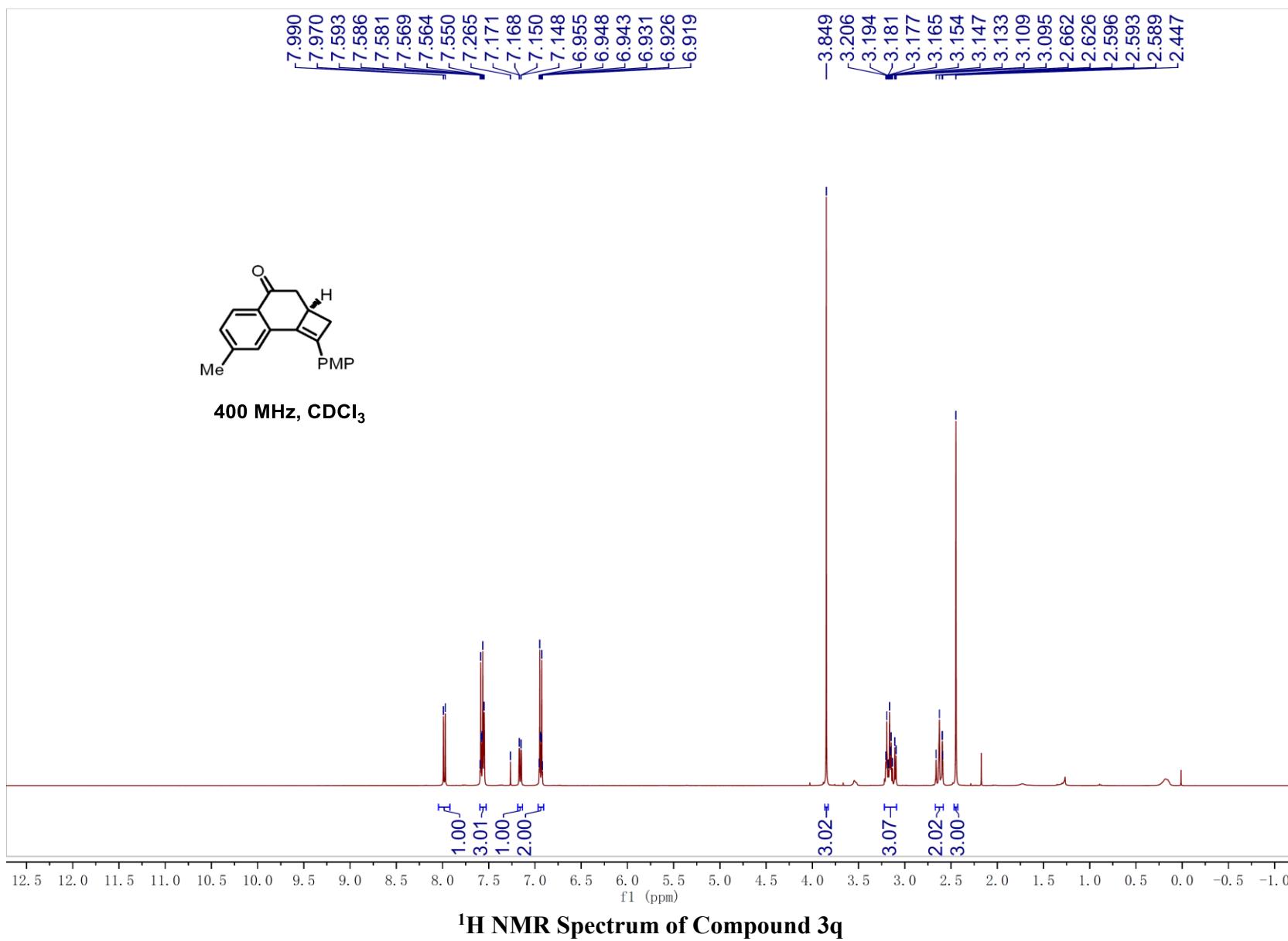


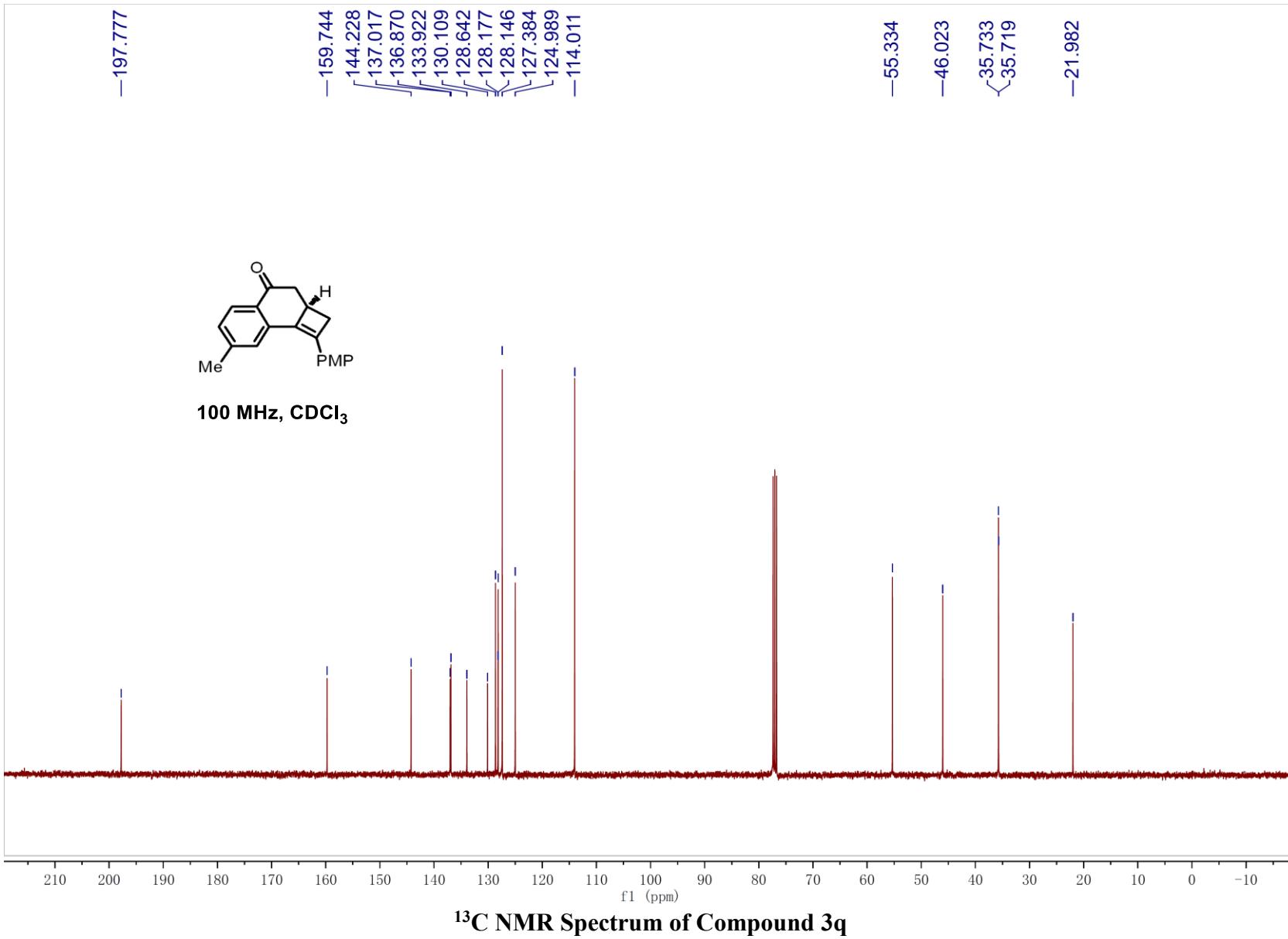
^1H NMR Spectrum of Compound 3o

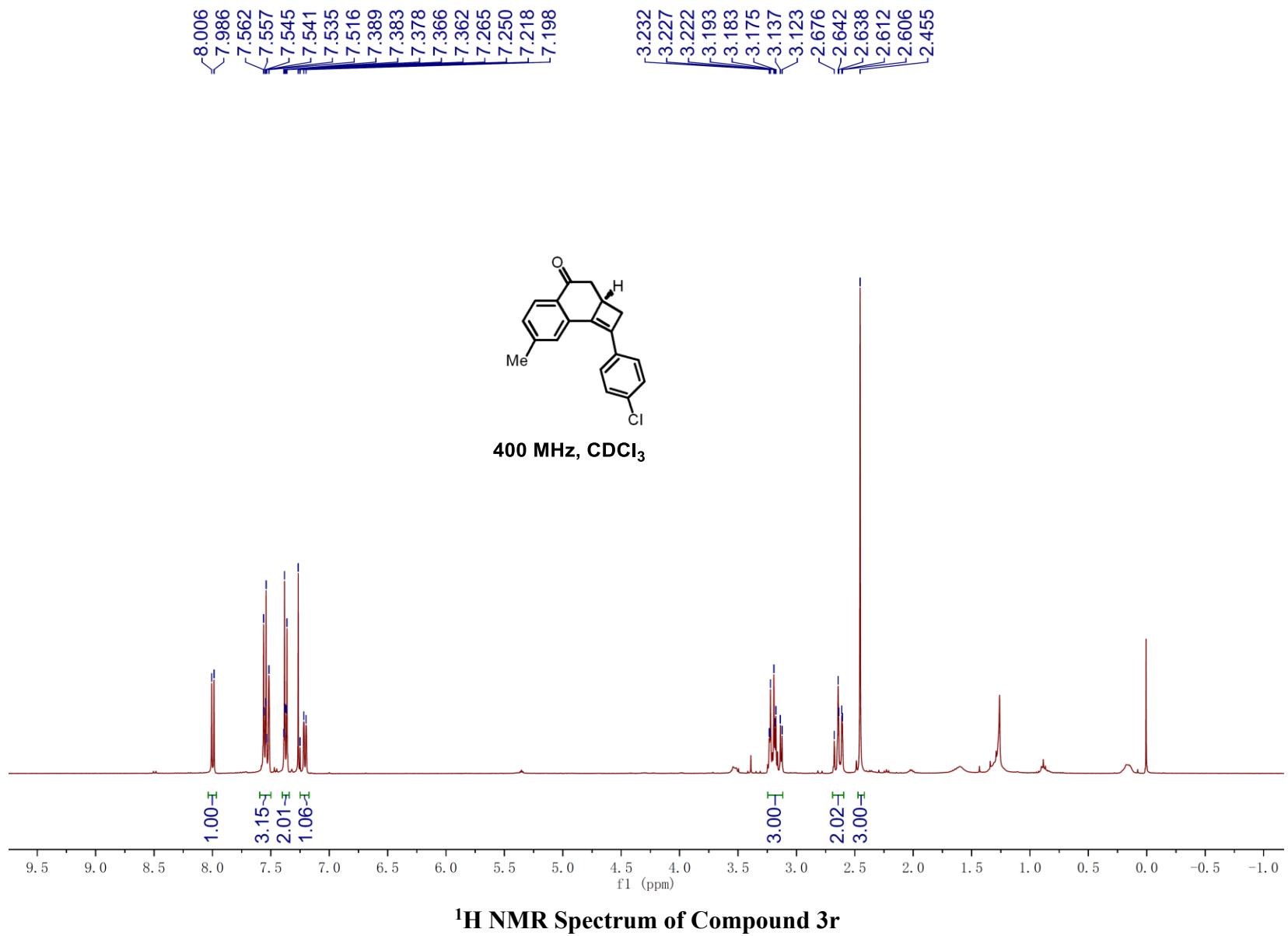


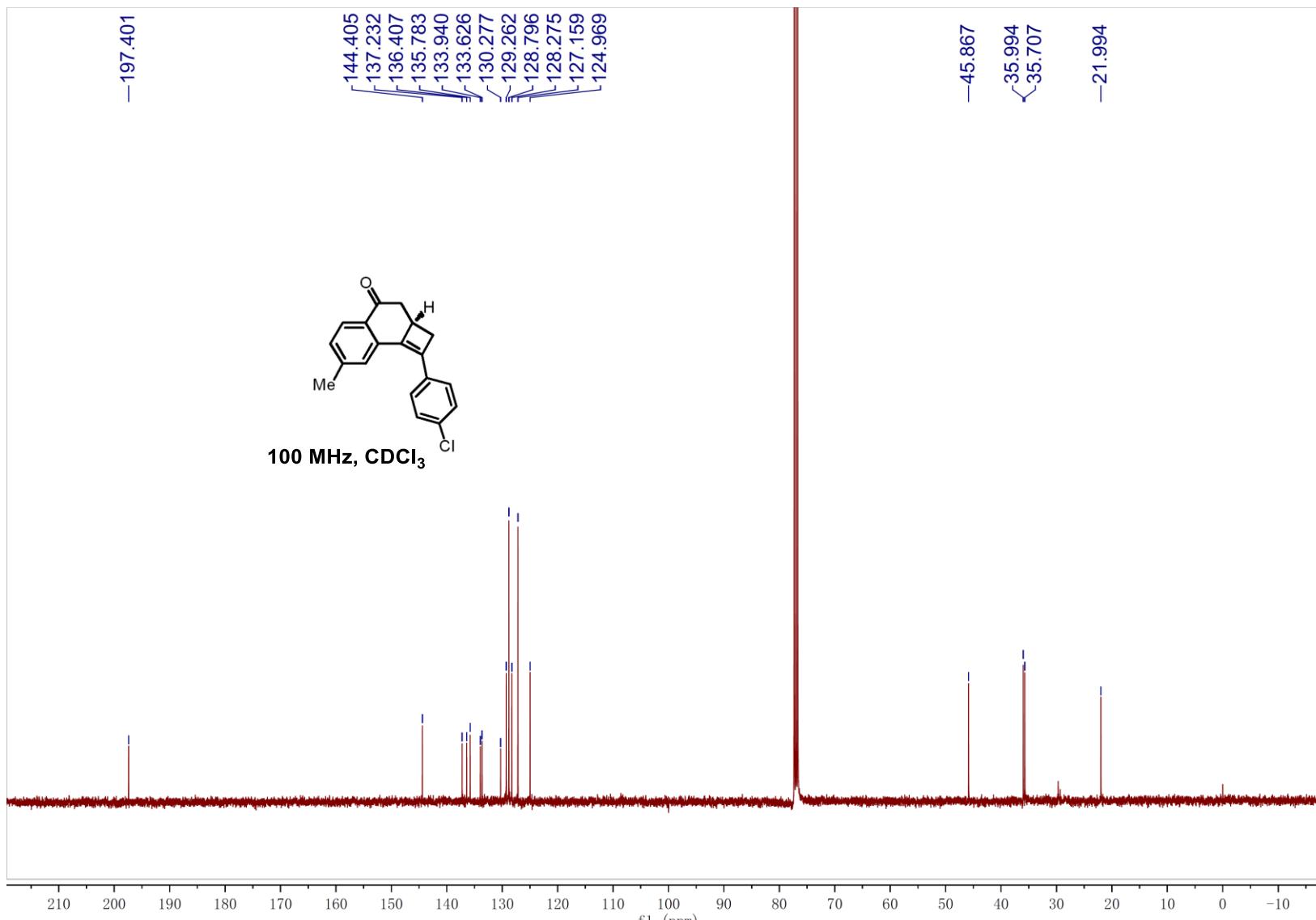




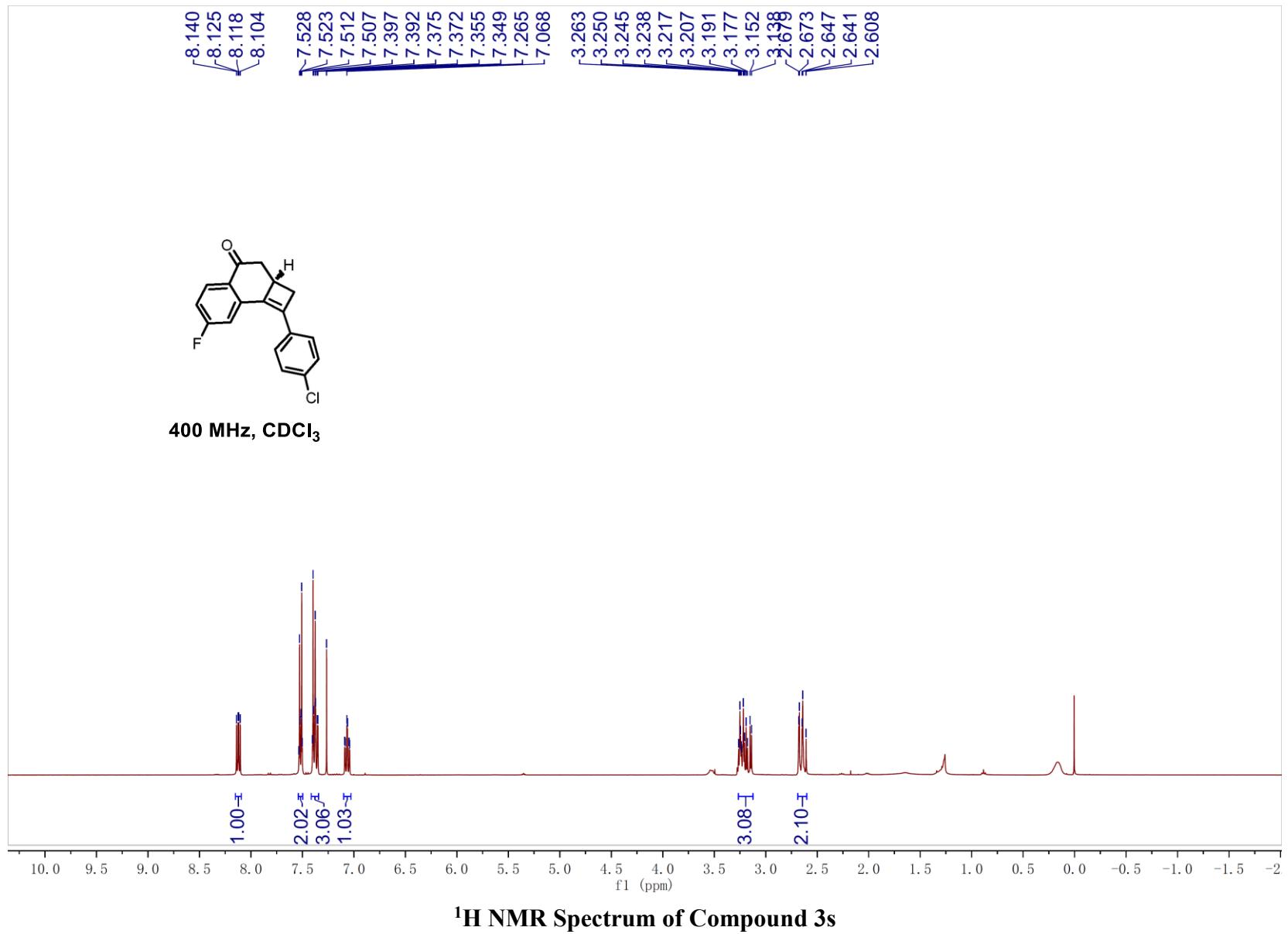


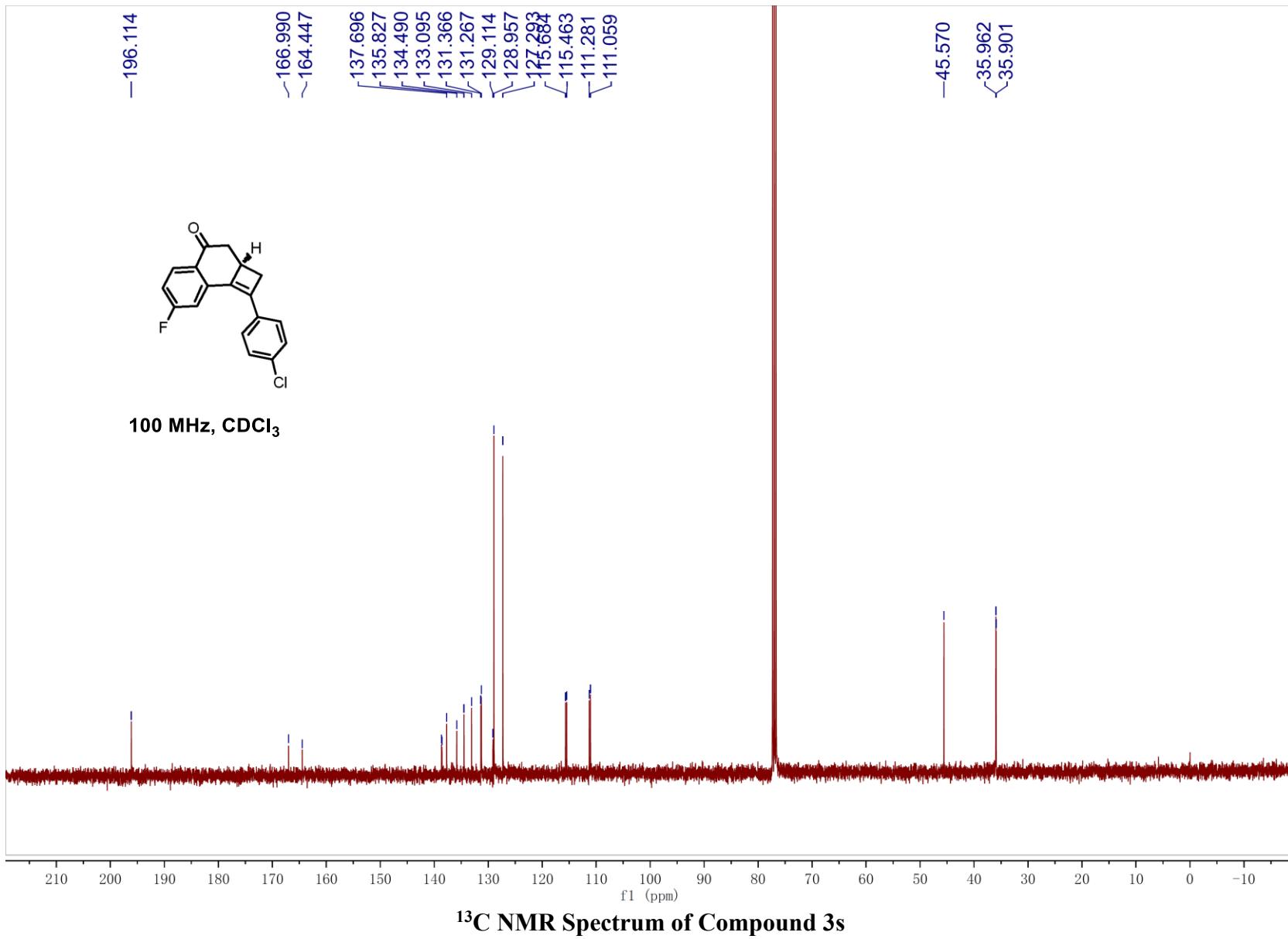




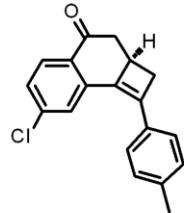


^{13}C NMR Spectrum of Compound 3r



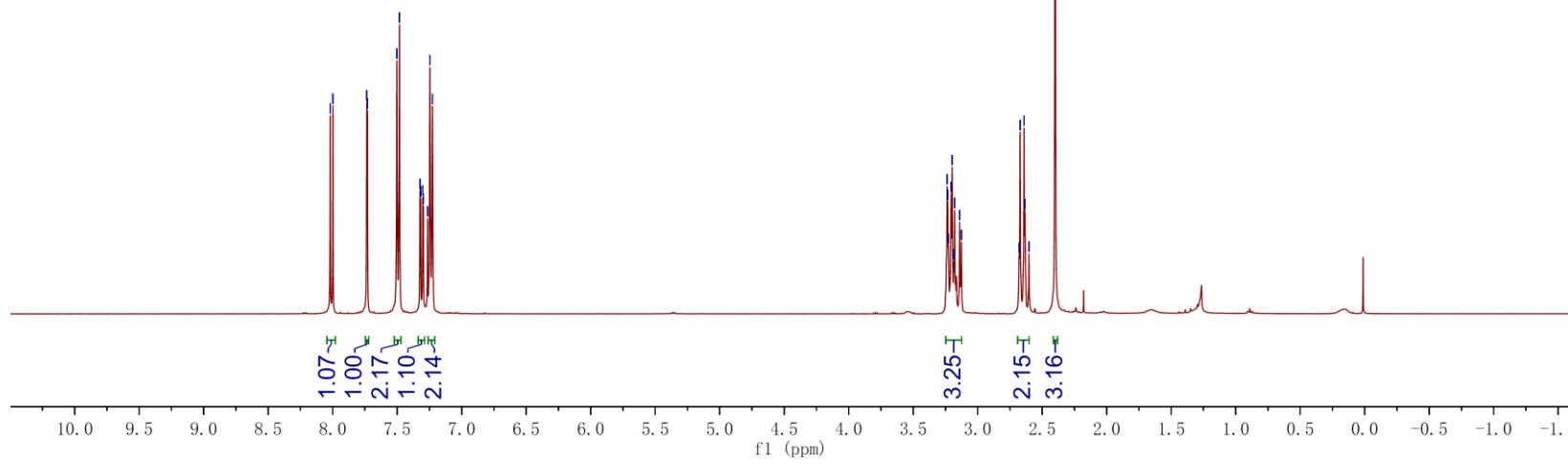


8.019
7.998
7.735
7.730
7.503
7.482
7.323
7.318
7.302
7.297
7.265
7.246
7.226

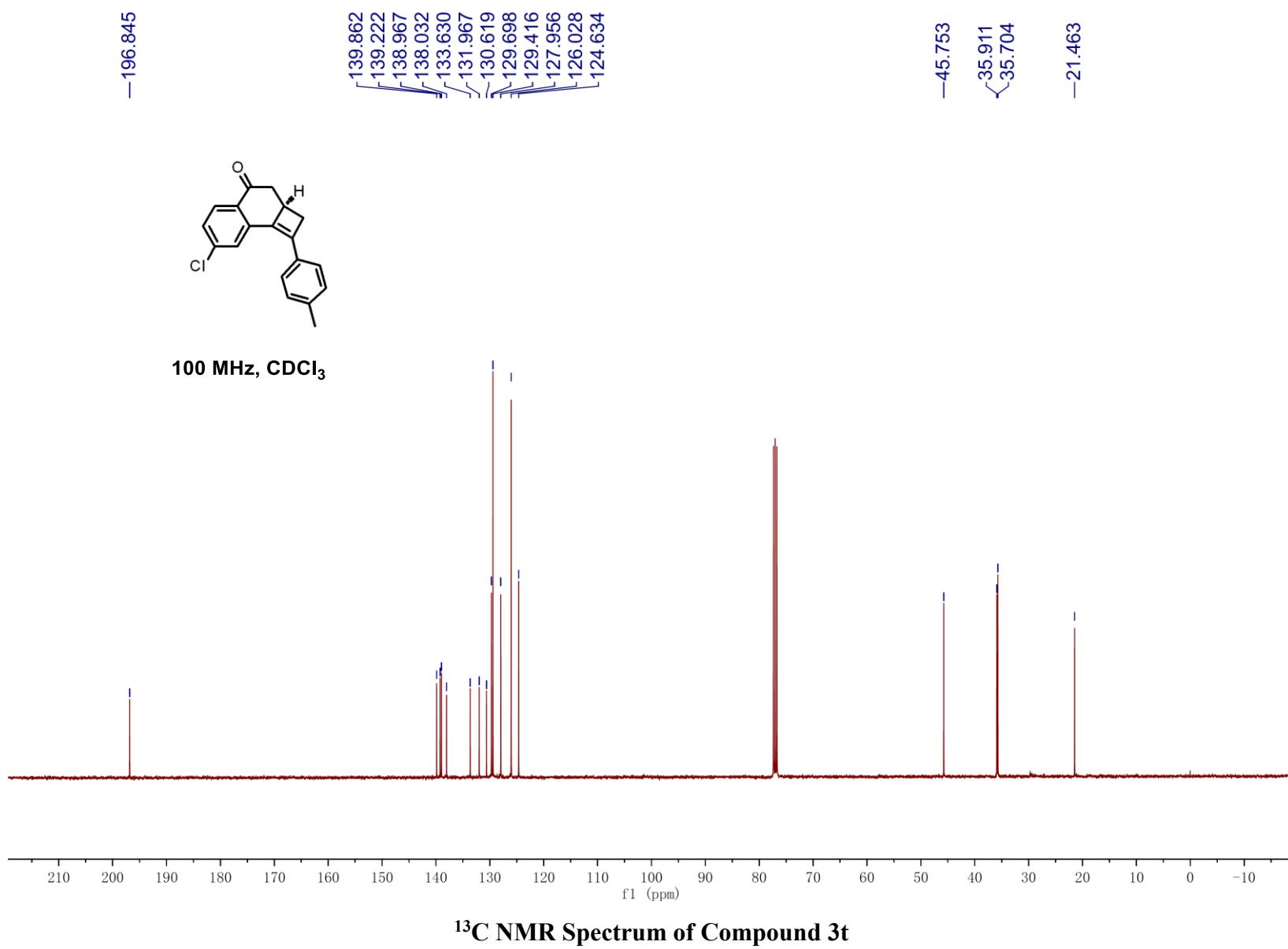


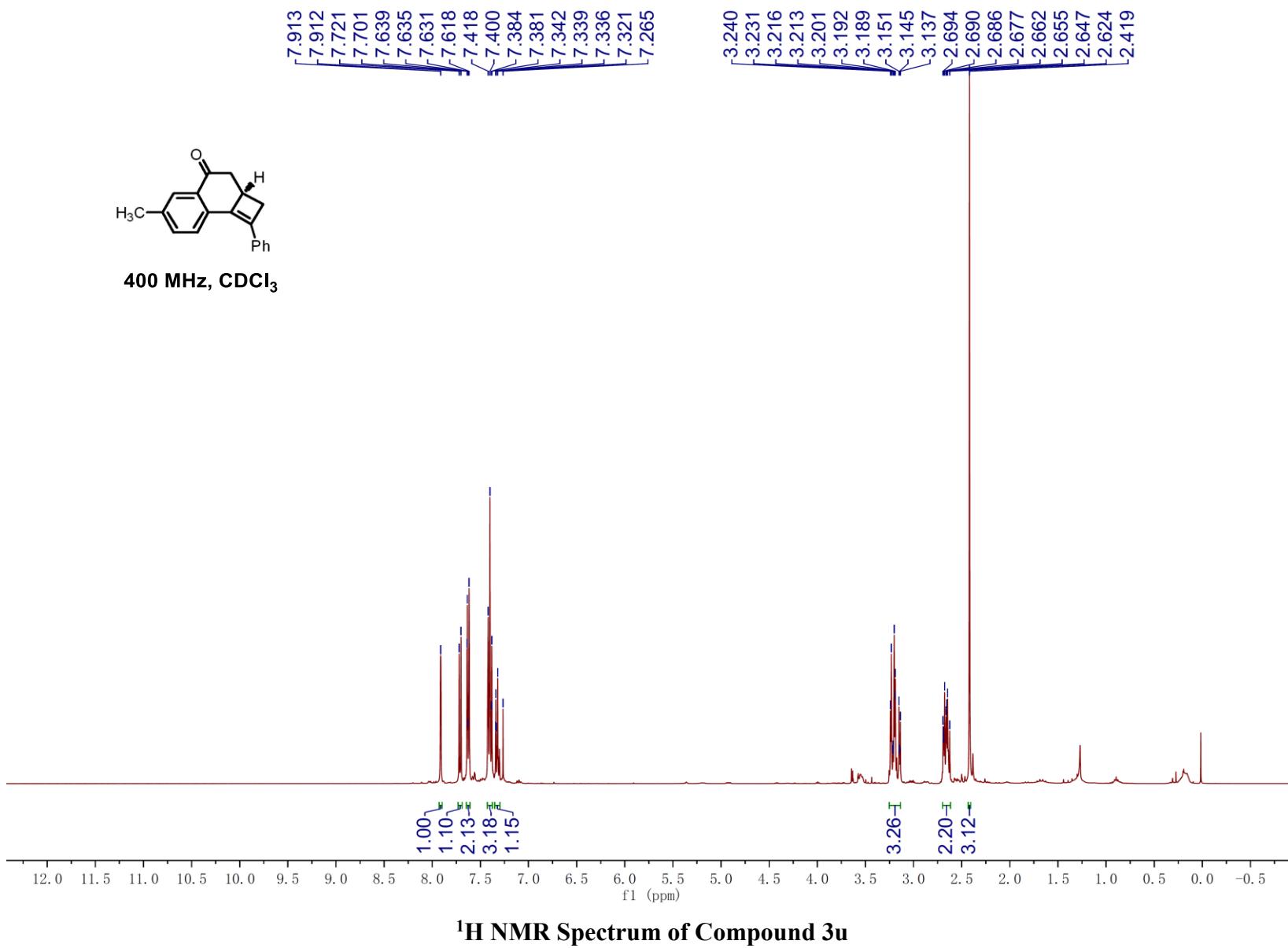
400 MHz, CDCl_3

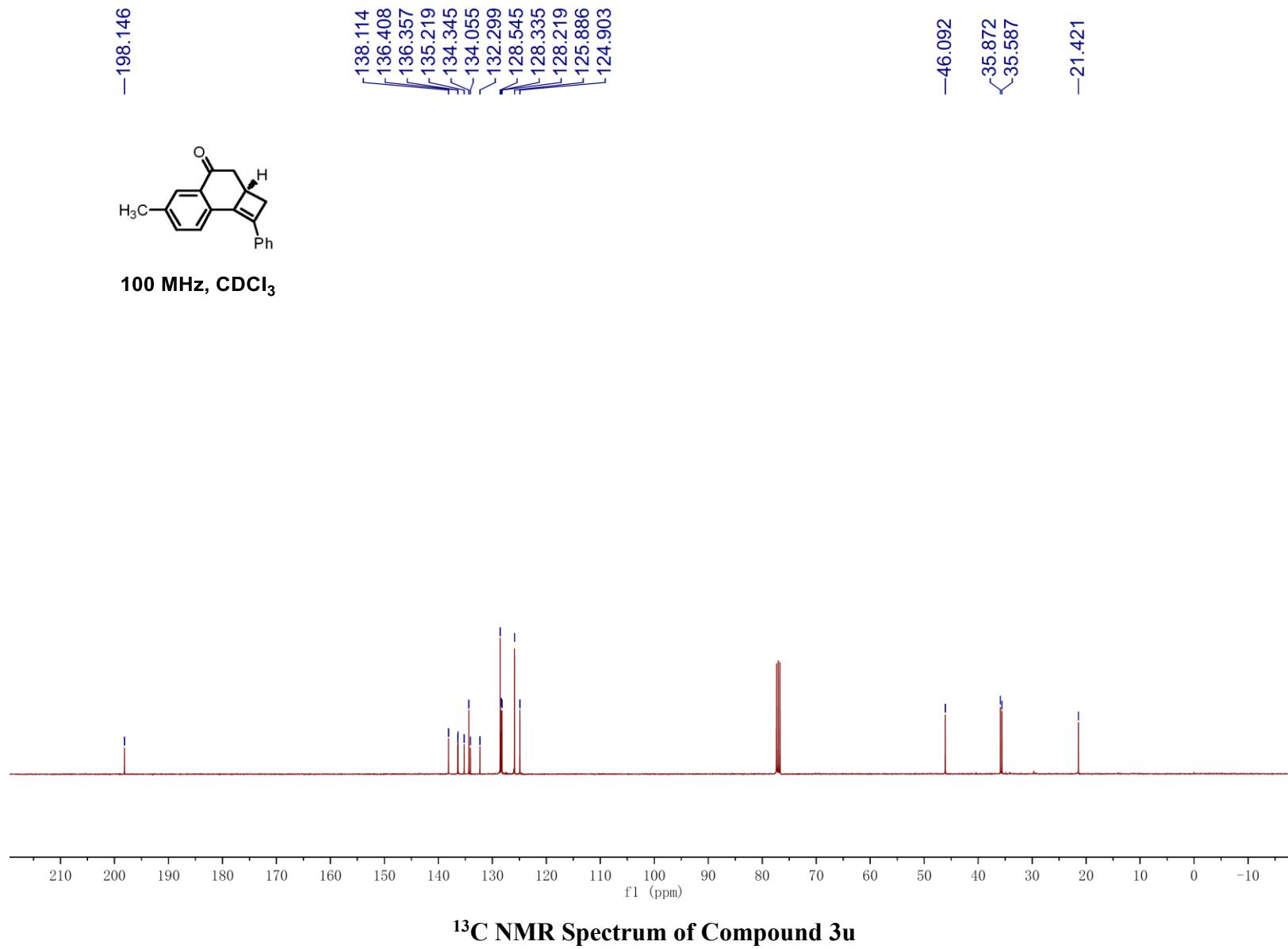
3.237
3.232
3.227
3.205
3.198
3.186
3.178
3.140
3.126
2.678
2.671
2.640
2.634
2.603
2.399

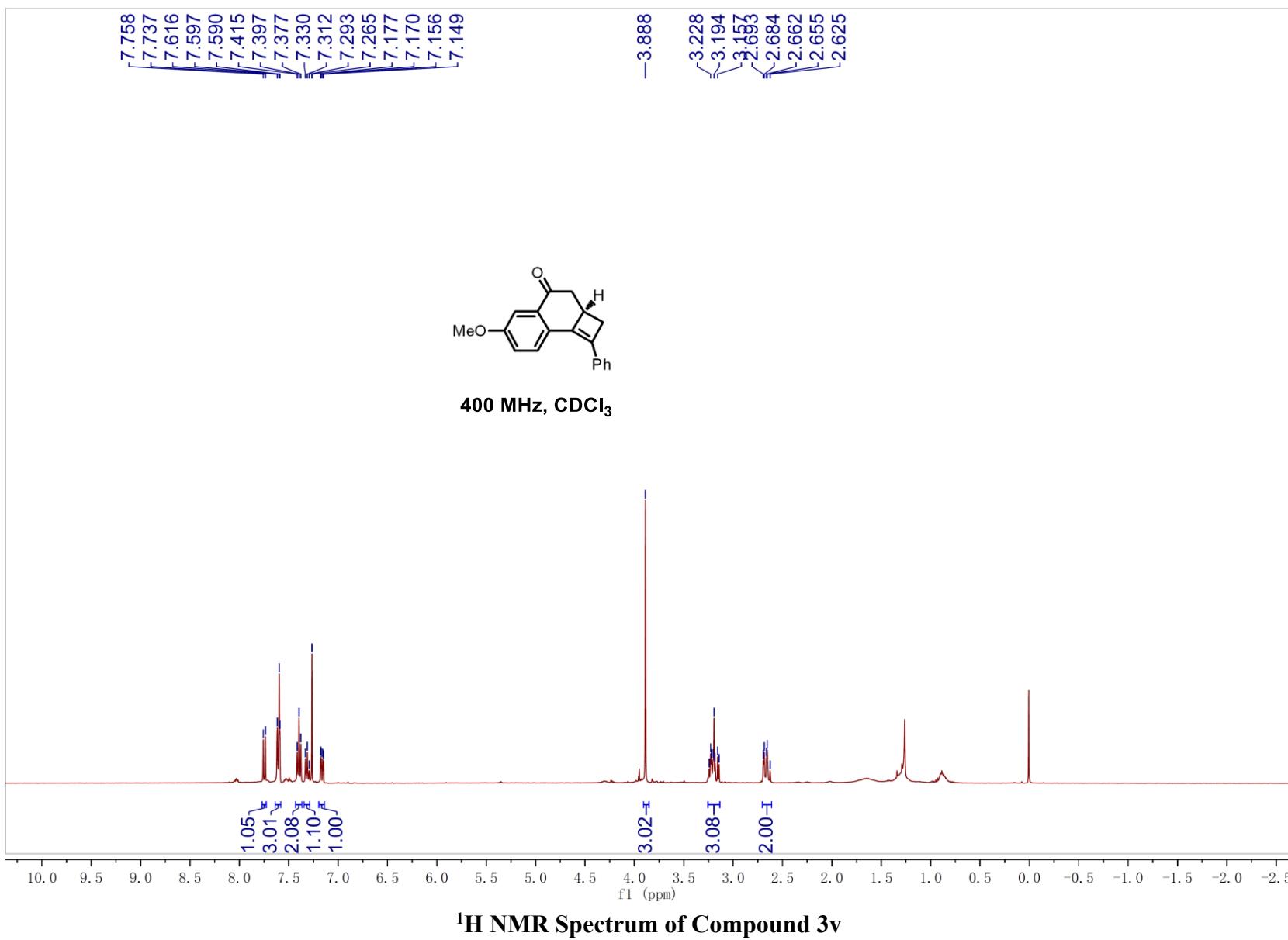


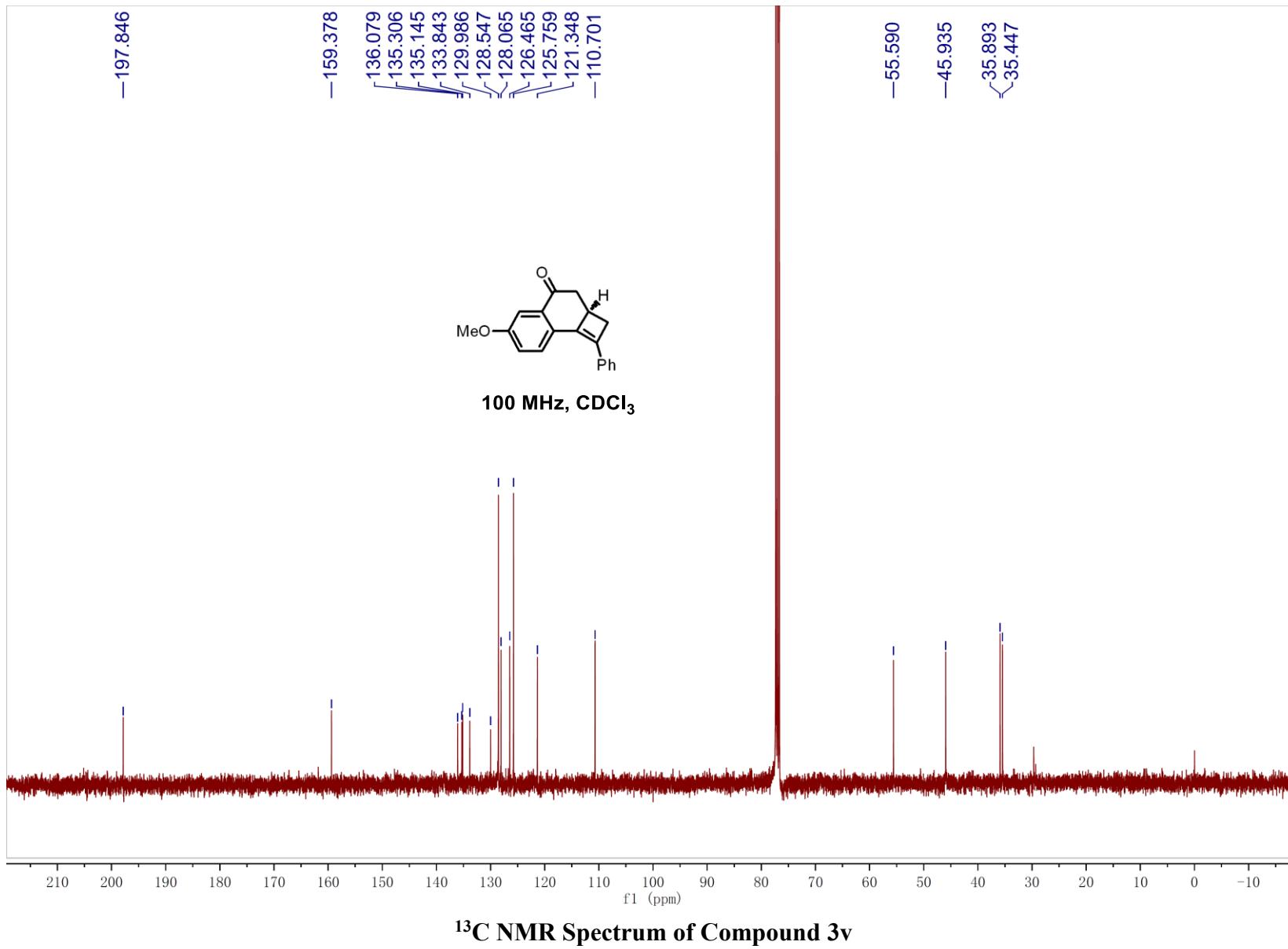
^1H NMR Spectrum of Compound 3t

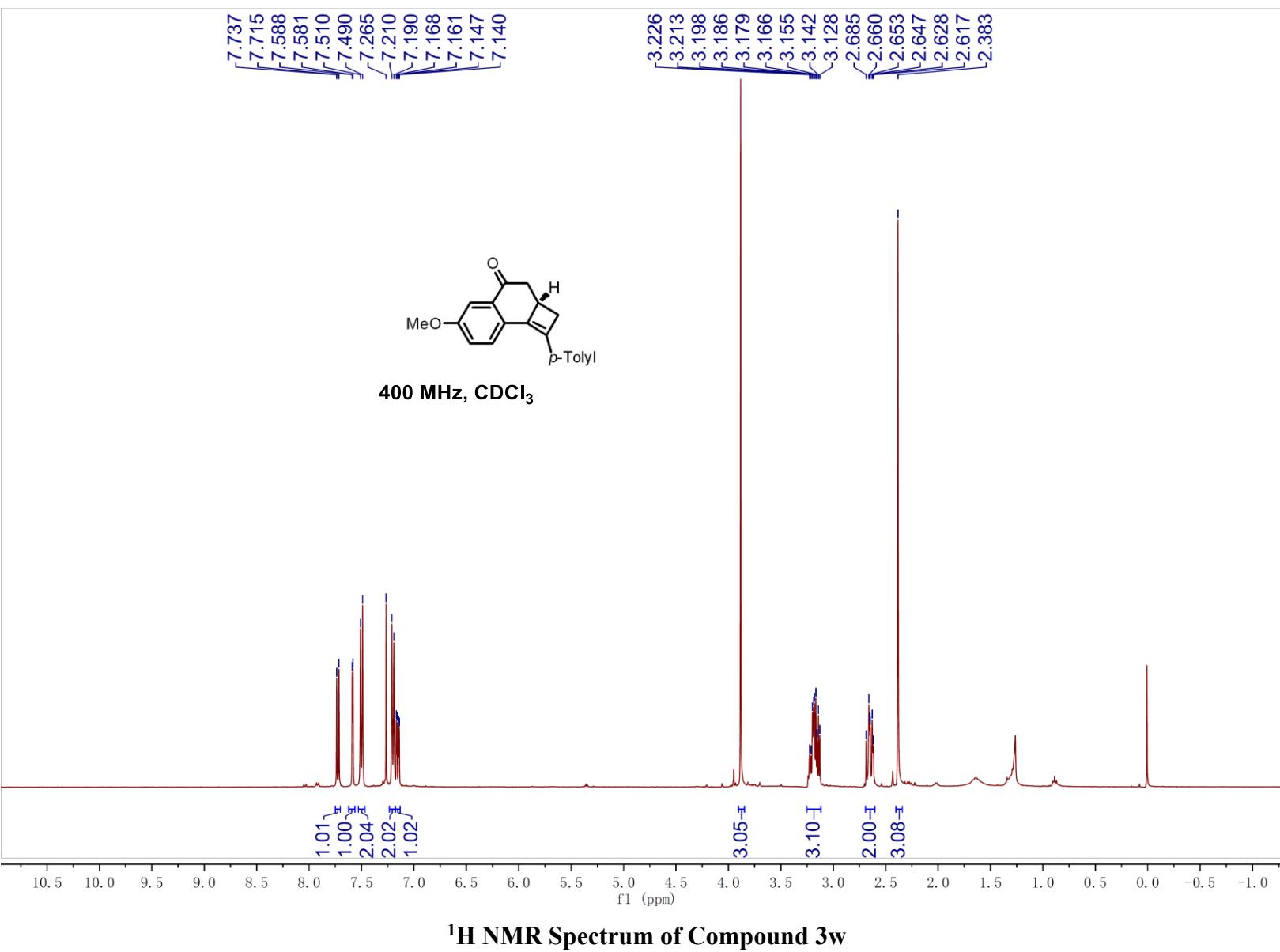


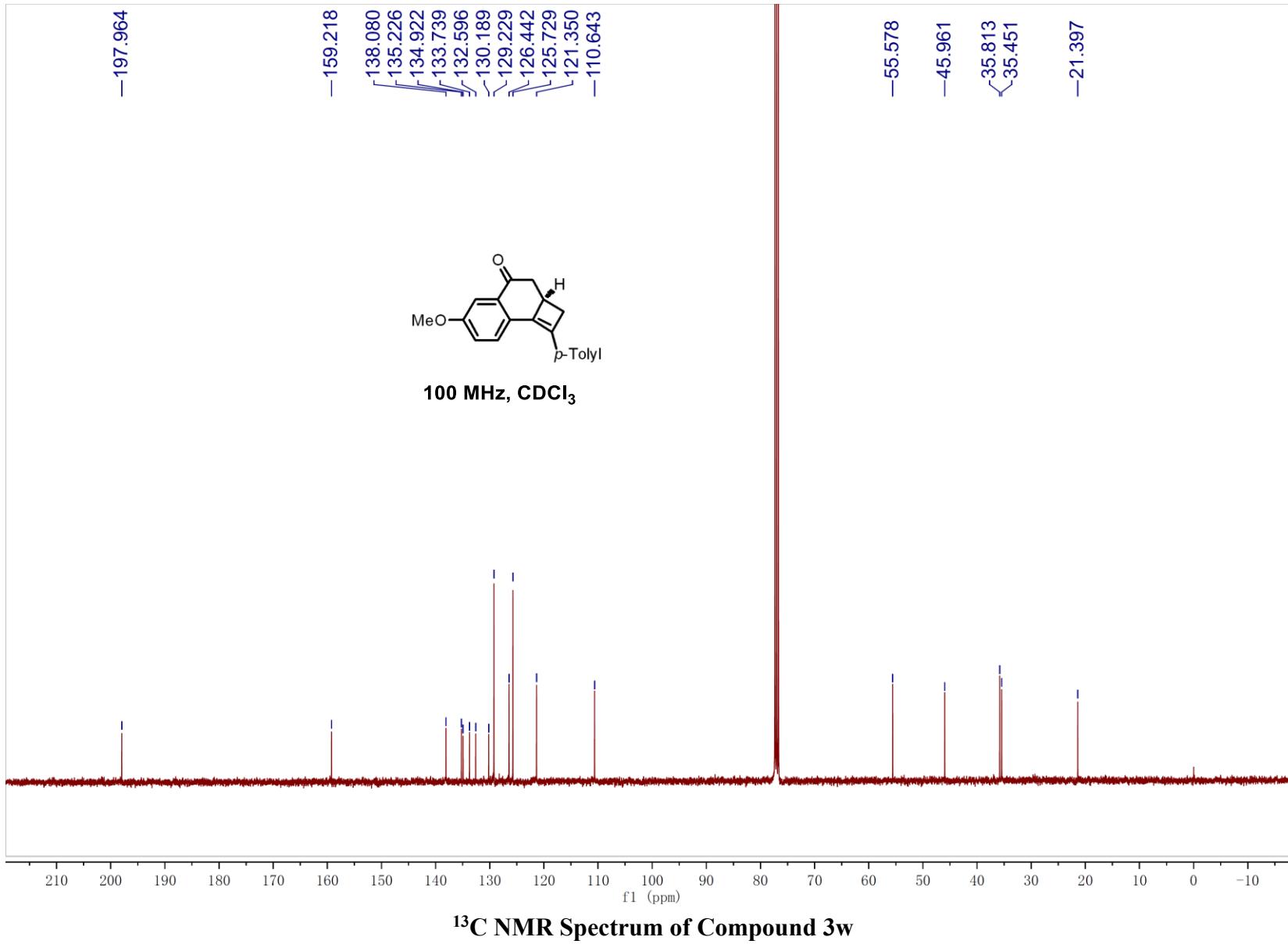


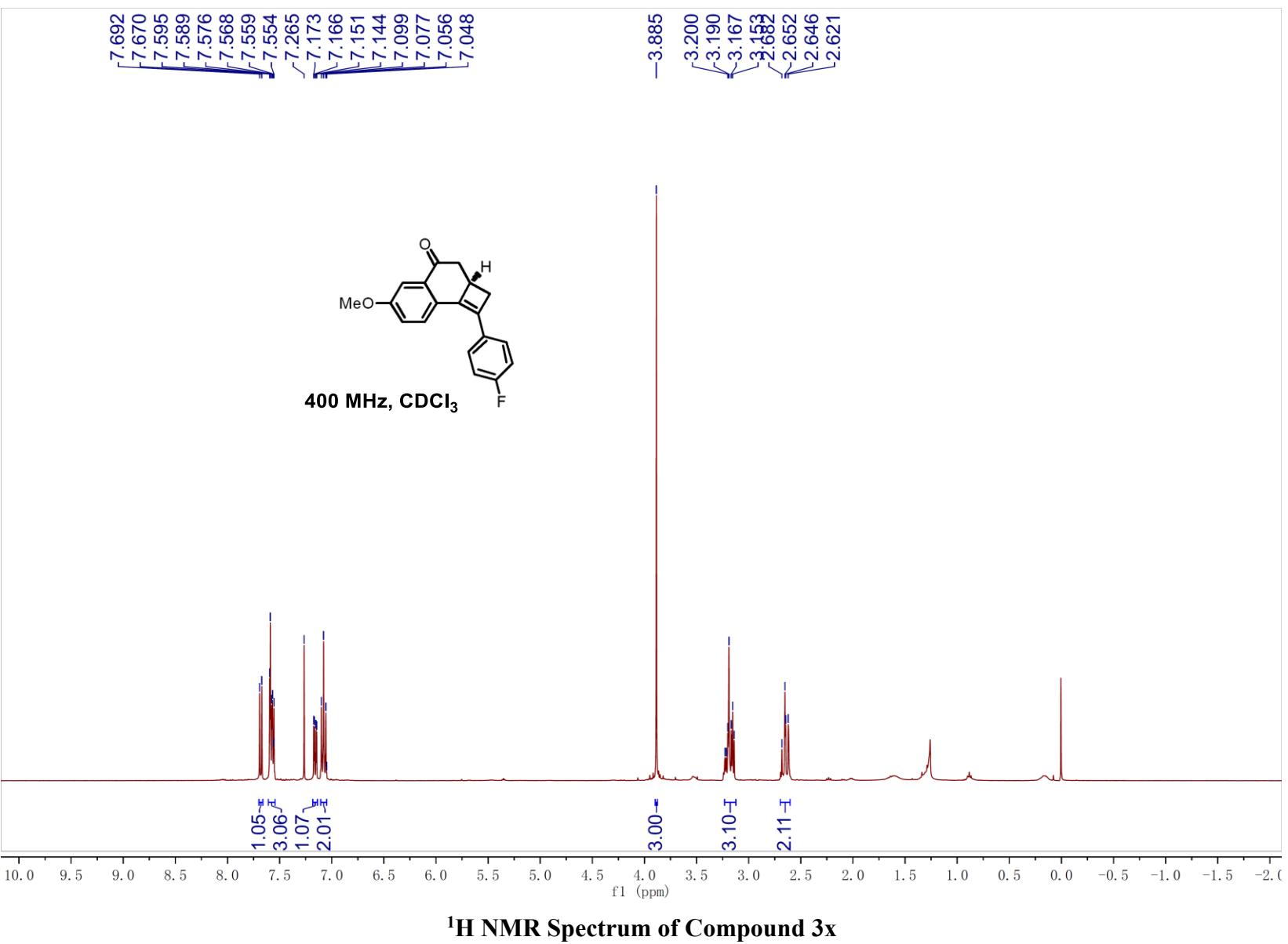


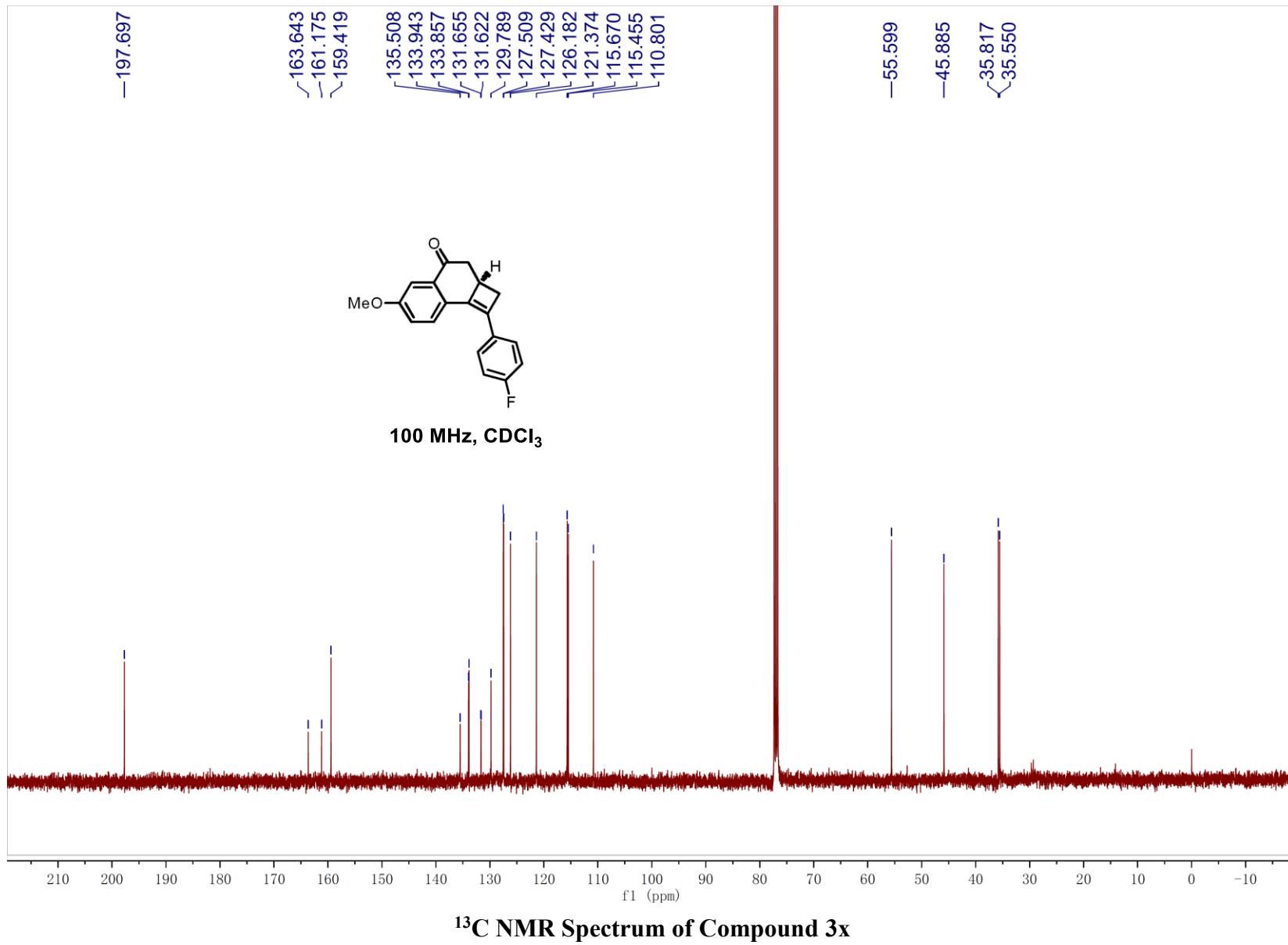


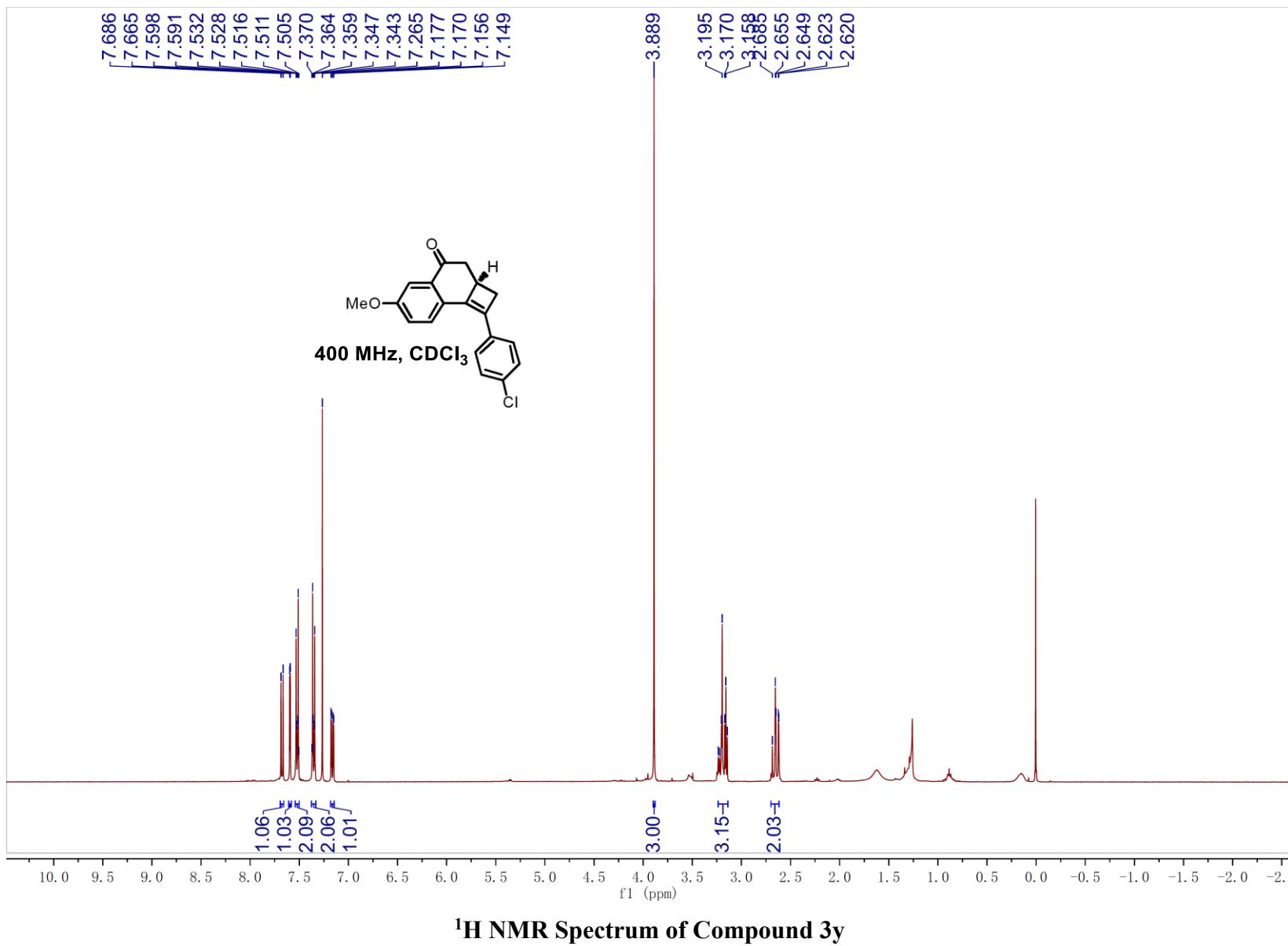


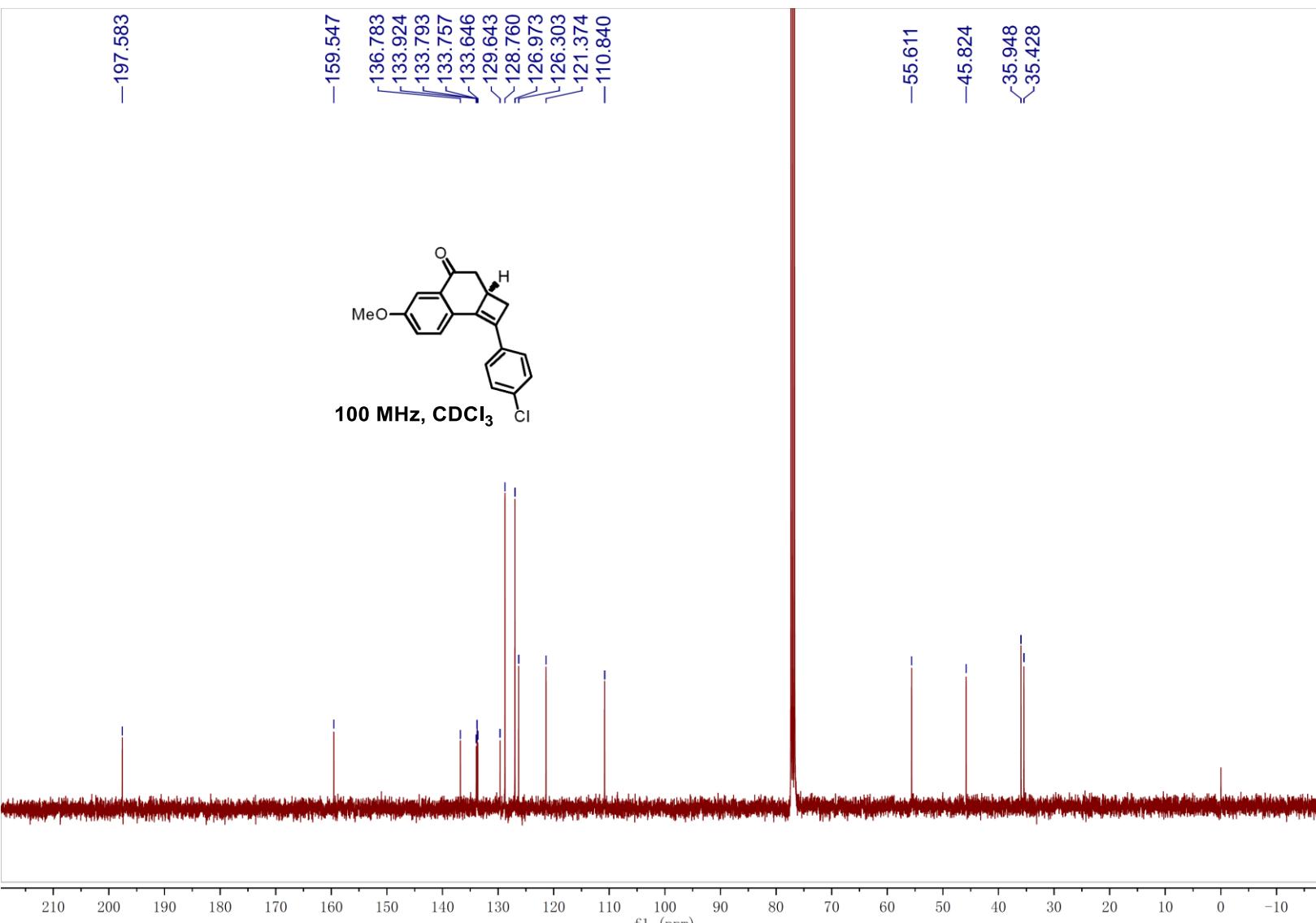






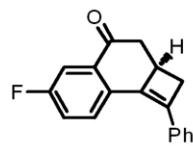




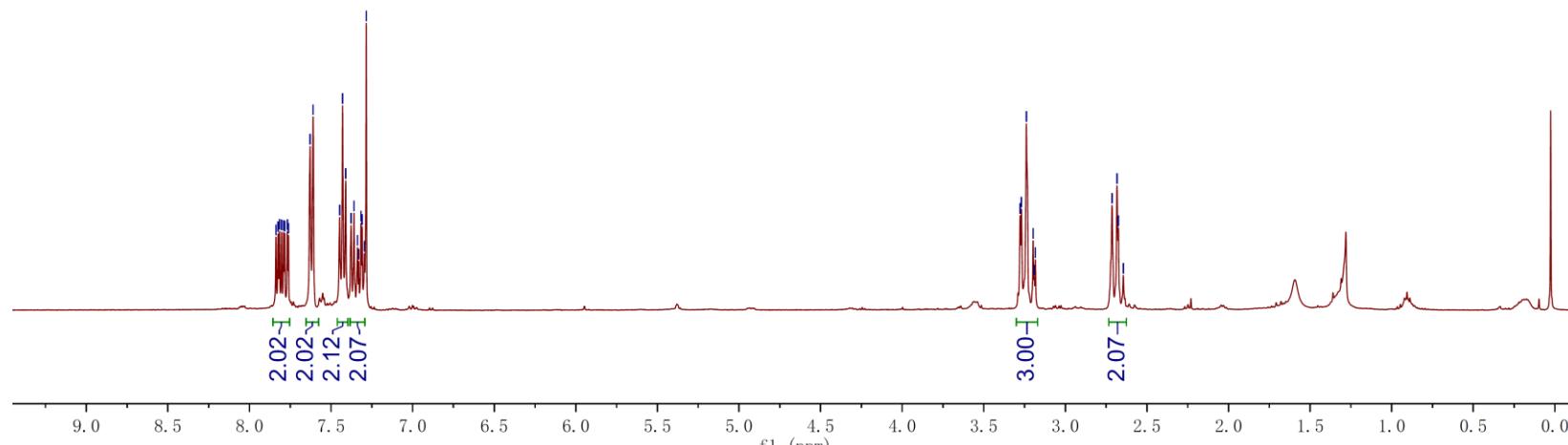


^{13}C NMR Spectrum of Compound 3y

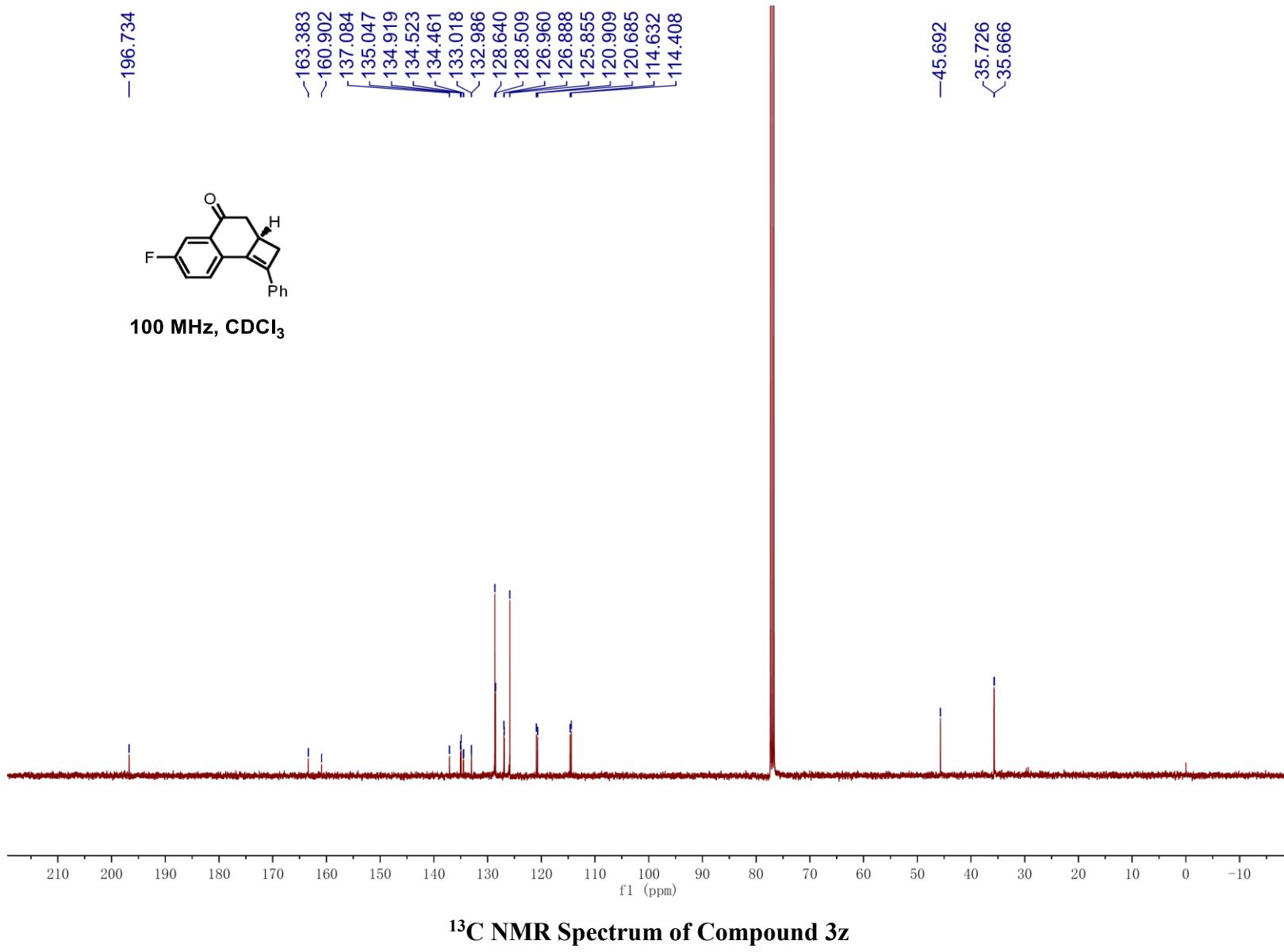
7.838
7.825
7.816
7.804
7.791
7.784
7.768
7.761
7.628
7.610
7.447
7.429
7.410
7.377
7.359
7.338
7.330
7.317
7.310
7.296
7.284

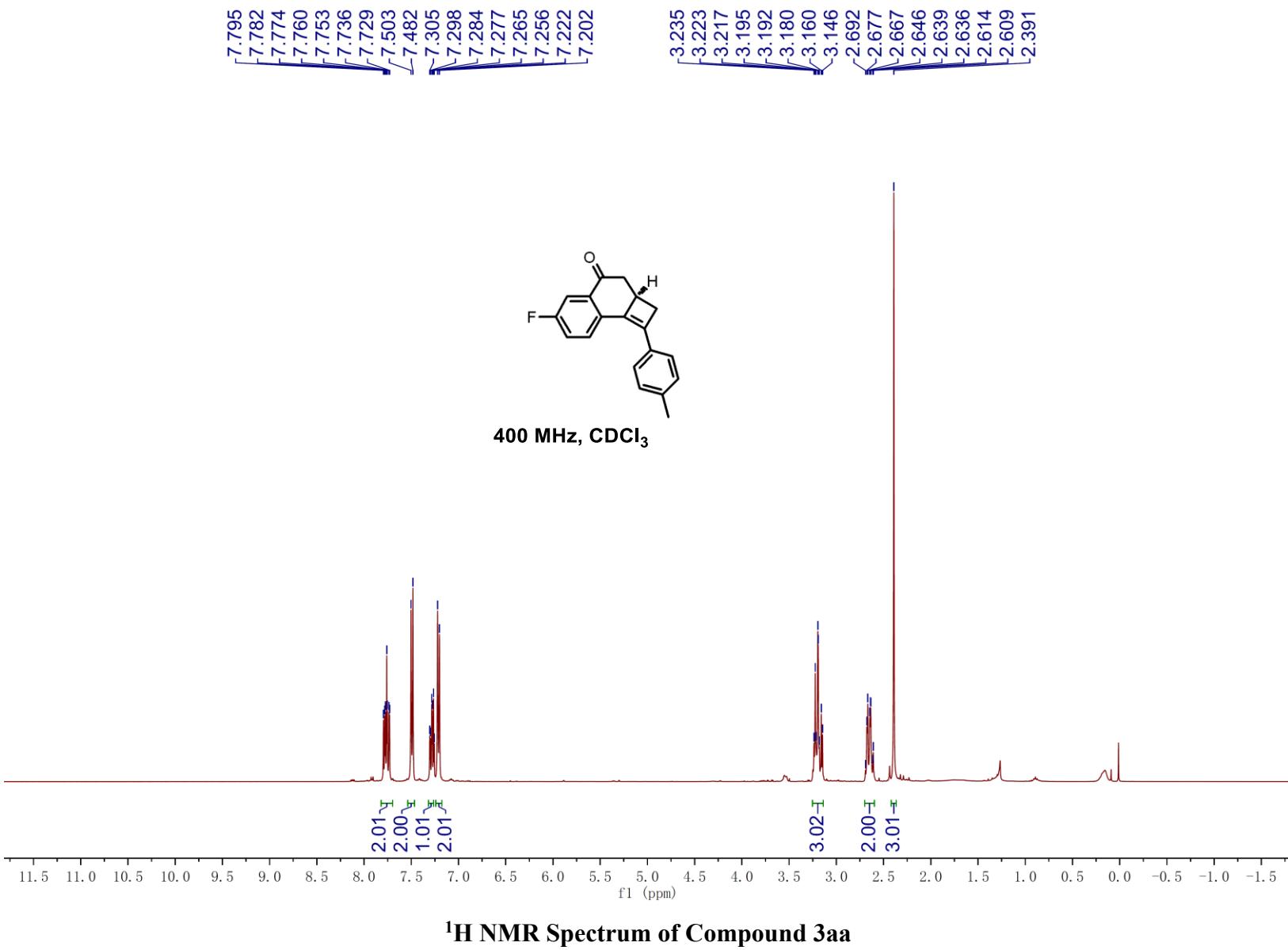


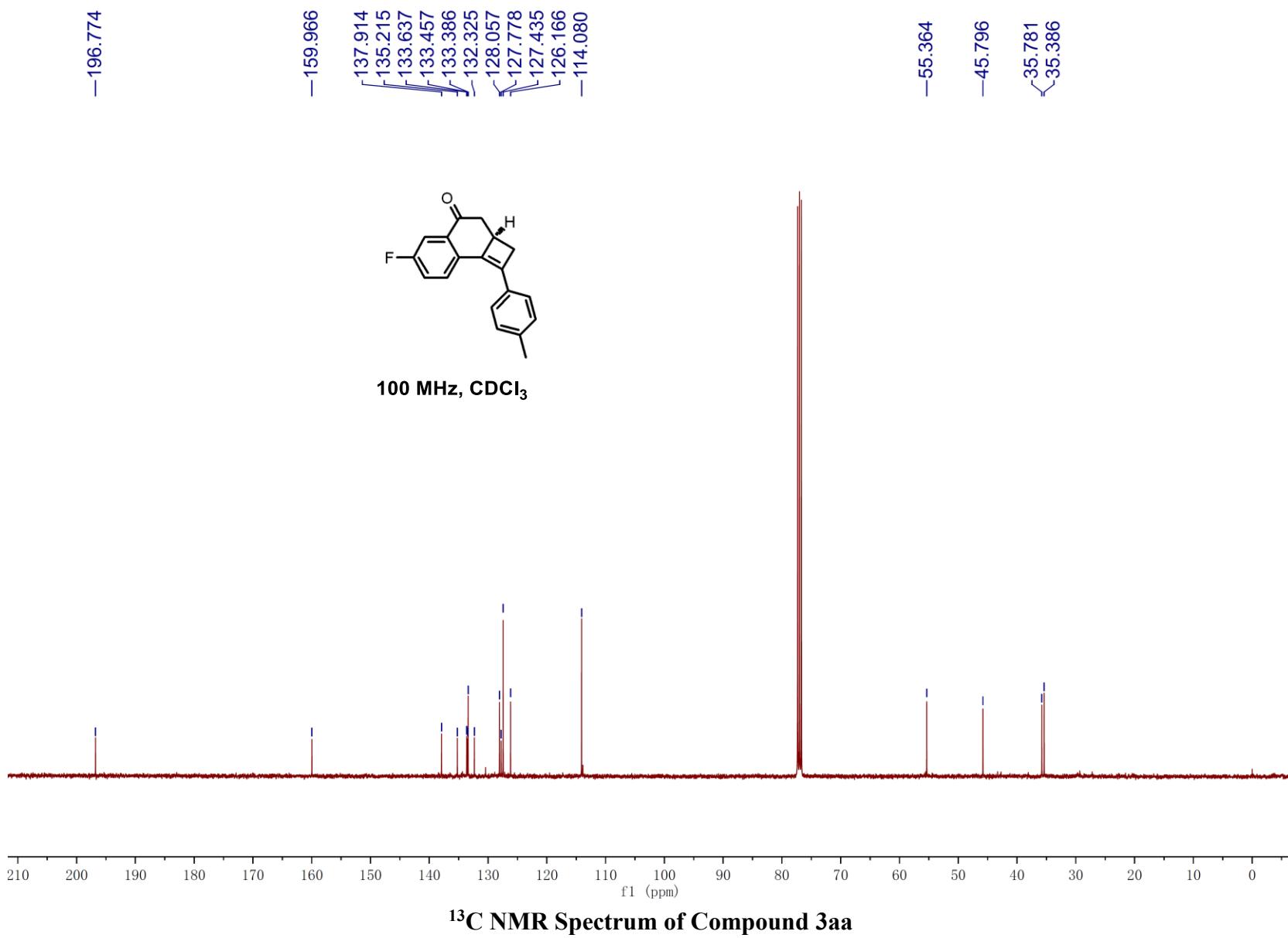
400 MHz, CDCl₃



¹H NMR Spectrum of Compound 3z

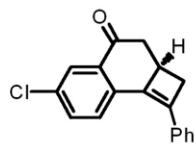




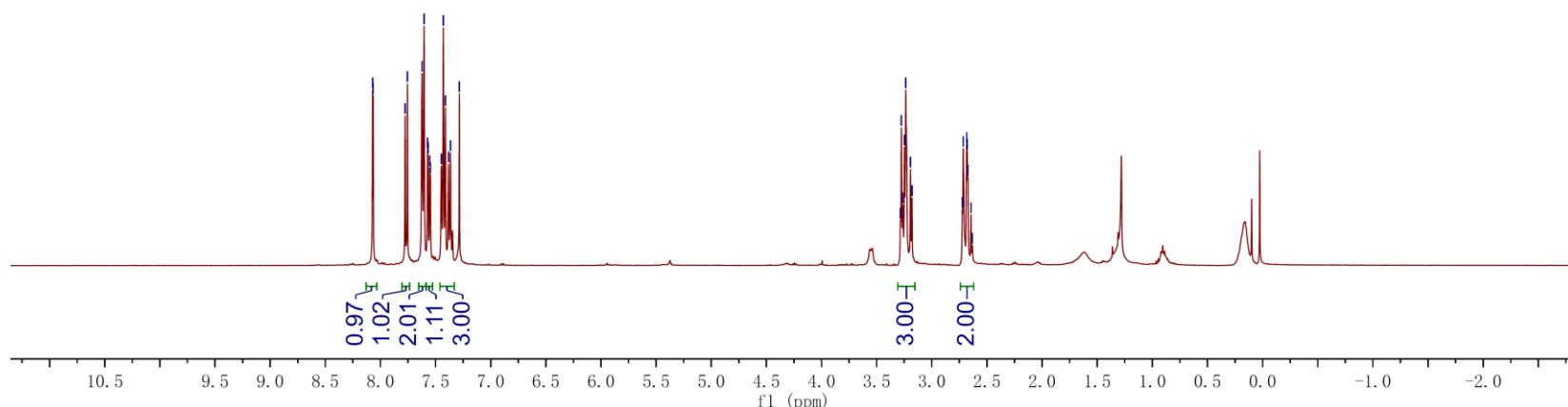


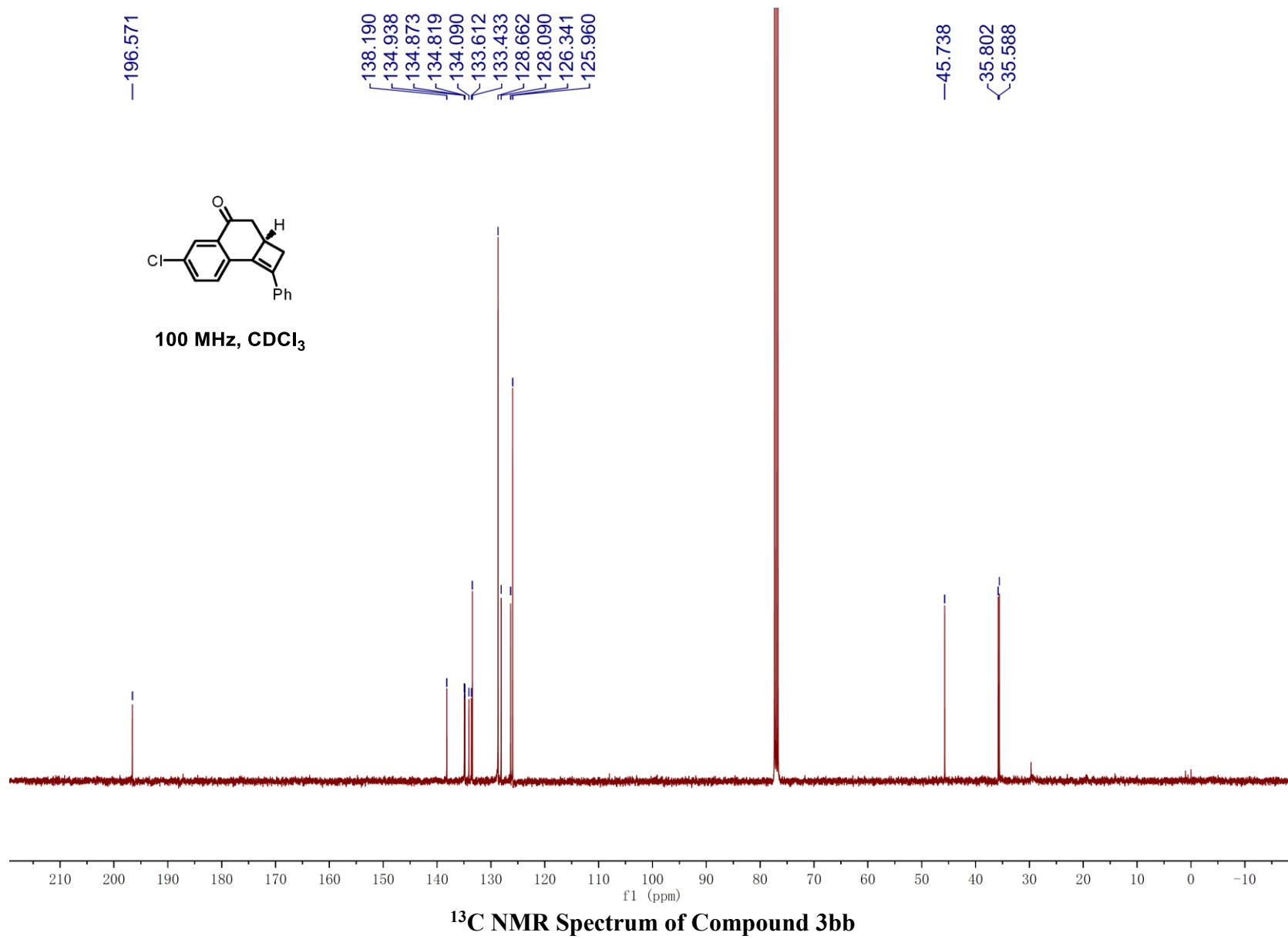
8.071
8.065
7.776
7.755
7.623
7.605
7.572
7.567
7.552
7.546
7.448
7.430
7.411
7.382
7.364
7.284

3.284
3.275
3.264
3.247
3.235
3.193
3.180
2.723
2.715
2.684
2.679
2.672
2.644
2.632



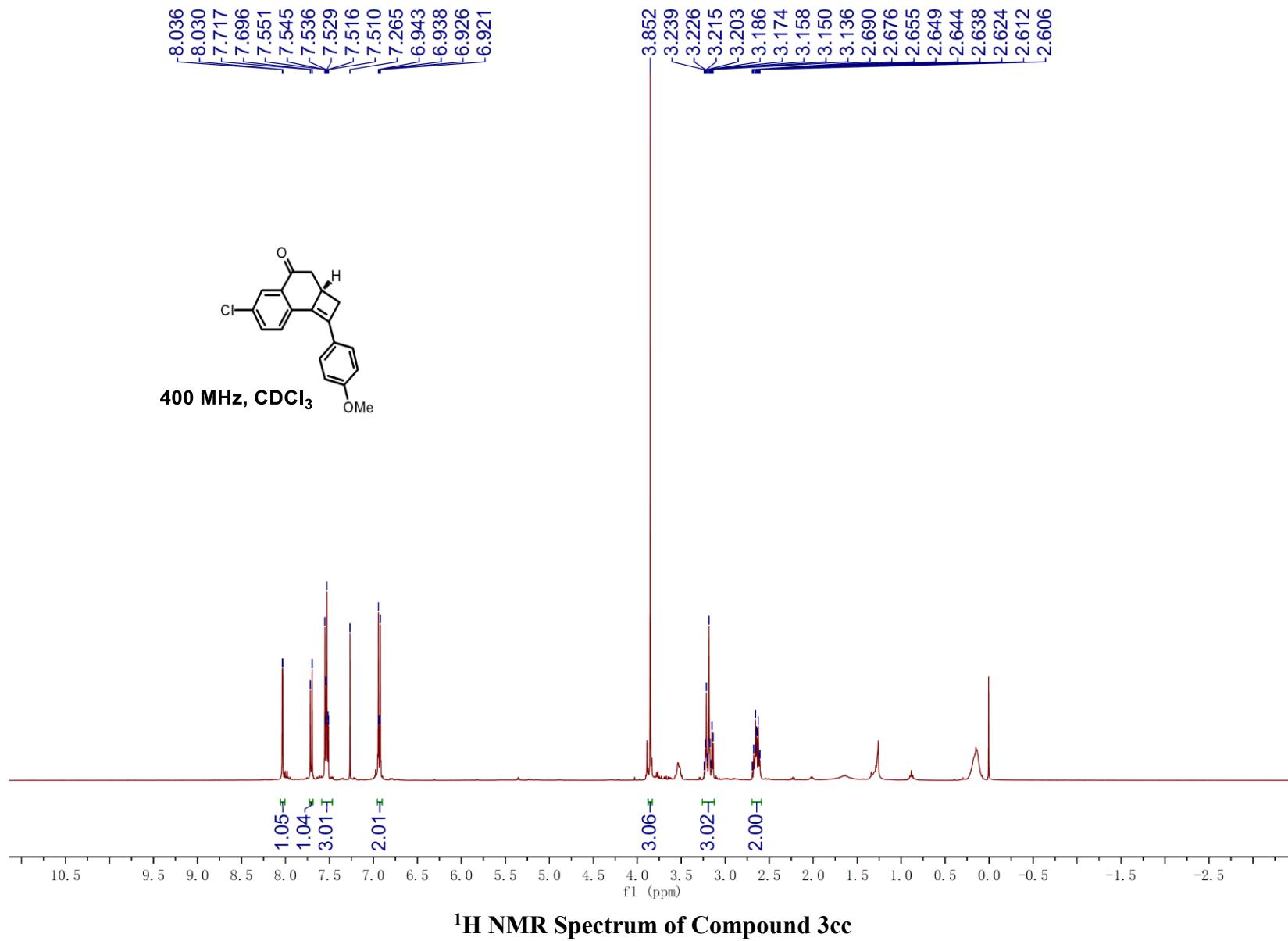
400 MHz, CDCl₃

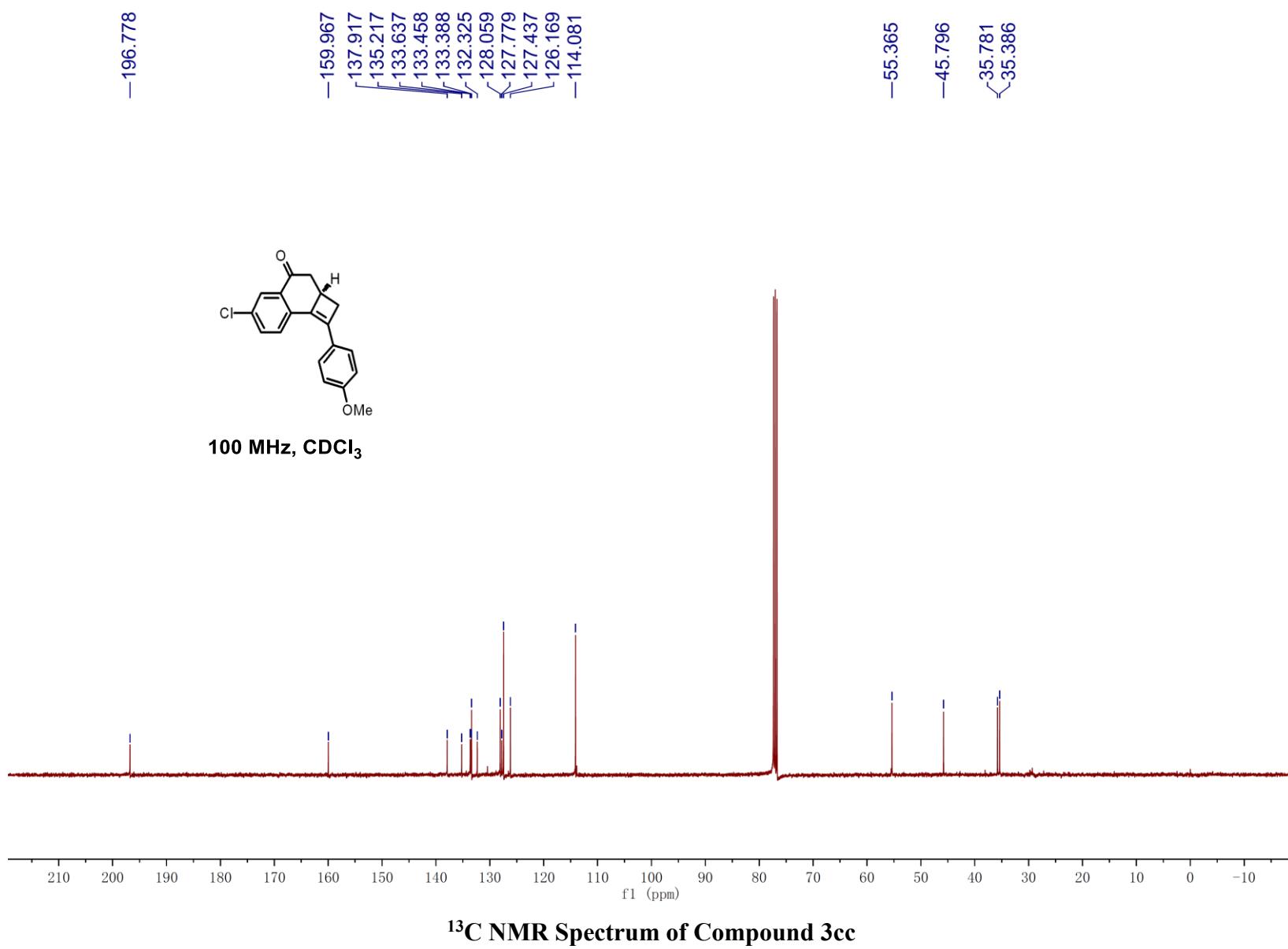




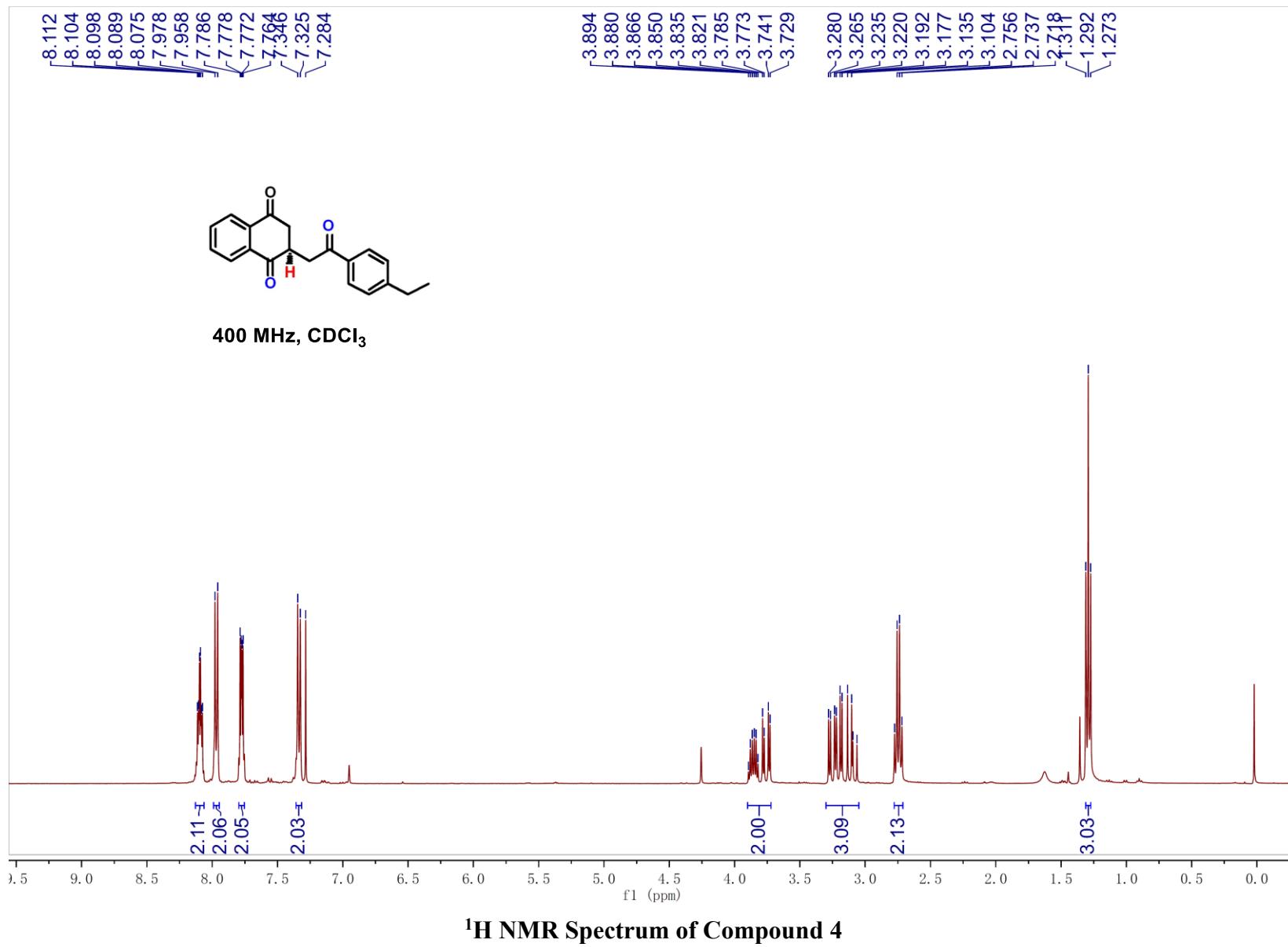


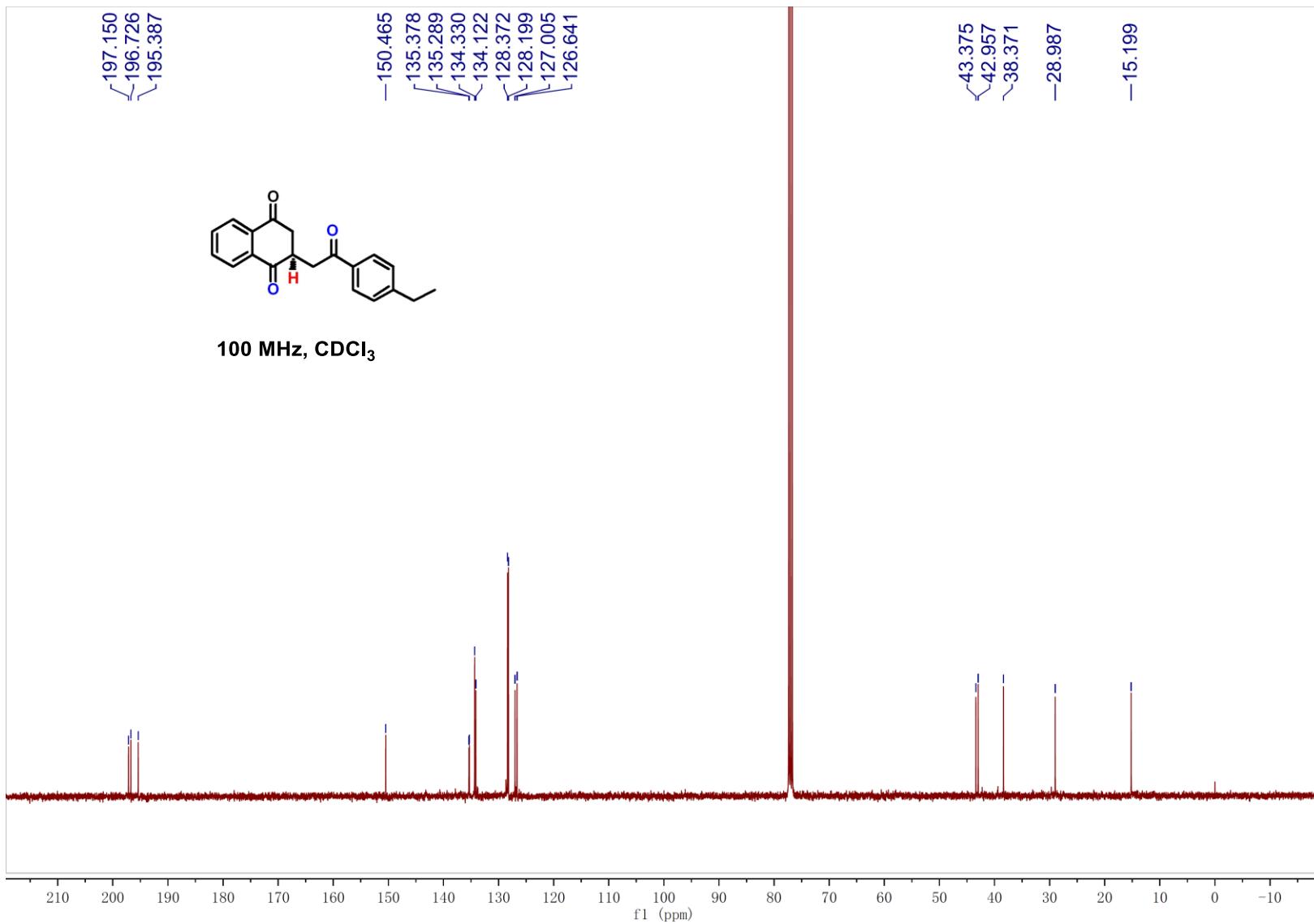
400 MHz, CDCl₃ OM





¹³C NMR Spectrum of Compound 3cc





^{13}C NMR Spectrum of Compound 4