Iodomethane in C1 chemistry: Application in palladium-catalyzed [2 + 2 + 1] annulation

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Electronic Supplementary Information

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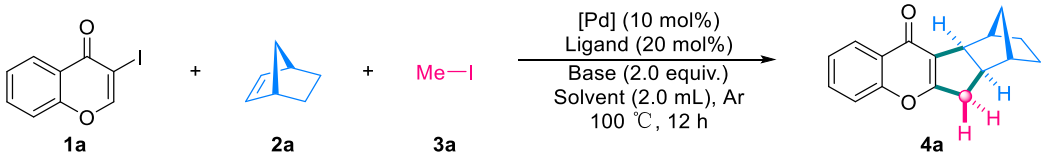
1. General experimental information

Unless otherwise noted, all commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H-NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer. Melting points were uncorrected.

3-Iodochromones (**1**) were prepared according to the reported procedures.[1] Bridged olefins **2a**-**c** were purchased from commercial suppliers. Bridged olefins **2d** and **2e** were prepared according to the reported procedures.[2,3] Iodomethane (**3**) and all ligands used in the optimization of reaction conditions were purchased from Bidepharm (China), Tansoole (China) or Innochem (China).

2. Optimization of the reaction conditions for the construction of 4a[a]



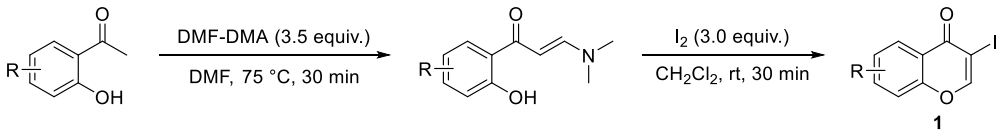
Entry	Catalyst	Ligand	Base	Solvent	Yield [b]
1	$Pd(OAc)_2$	$P(2,4,6\text{-}(CH_3)_3C_6H_3)_3$	Cs_2CO_3	Toluene	22
2	$Pd(OAc)_2$	Johnphos	Cs_2CO_3	Toluene	25
3	$Pd(OAc)_2$	Sphos	Cs_2CO_3	Toluene	33
4	$Pd(OAc)_2$	$P(2\text{-}OMe\text{-}C_6H_4)_3$	Cs_2CO_3	Toluene	35
5	$Pd(OAc)_2$	$P(4\text{-}Me\text{-}C_6H_4)_3$	Cs_2CO_3	Toluene	42
6	$Pd(OAc)_2$	$P(3,5\text{-}(CF_3)_2C_6H_4)_3$	Cs_2CO_3	Toluene	45
7	$Pd(OAc)_2$	$P(4\text{-}CF_3\text{-}C_6H_4)_3$	Cs_2CO_3	Toluene	77
8	$Pd(OAc)_2$	$P(3\text{-}FC_6H_4)$	Cs_2CO_3	Toluene	80
9	$Pd(OAc)_2$	TFP	Cs_2CO_3	Toluene	81
10	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Toluene	92
11	$Pd(PPh_3)_4$	PPh_3	Cs_2CO_3	Toluene	54
12	$Pd(dba)_2$	PPh_3	Cs_2CO_3	Toluene	66
13	$PdBr_2$	PPh_3	Cs_2CO_3	Toluene	70
14	$Pd(TFA)_2$	PPh_3	Cs_2CO_3	Toluene	87
15	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Mesitylene	89
16	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMSO	N.R.

17	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMF	trace
18	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	1,4-dioxane	90
19	$Pd(OAc)_2$	PPh_3	Na_2CO_3	Toluene	N.R.
20	$Pd(OAc)_2$	PPh_3	K_3PO_4	Toluene	22
21	$Pd(OAc)_2$	PPh_3	K_2CO_3	Toluene	25
22	$Pd(OAc)_2$	PPh_3	NaO^tBu	Toluene	17

[a] Unless otherwise noted, all reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), **3a** (0.3 mmol, 1.5 equiv.), Pd-catalyst (10 mol%), ligand (20 mol%), base (0.4 mmol, 2.0 equiv.) in 2.0 mL of solvent under Ar atmosphere at 100 °C for 12 h. [b] Isolated yields based on **1a** were given. N.R.: no reaction.

3. Synthetic methods of substrates

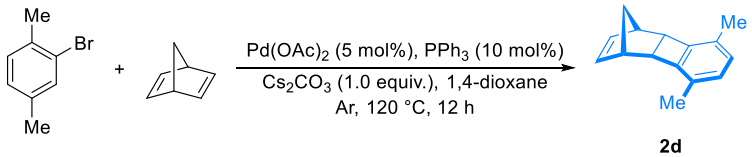
3.1 Synthesis of 3-iodochromones **1**



1

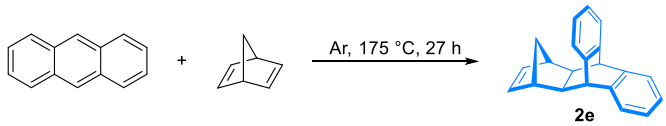
A solution of substituted 2-hydroxyacetophenones (10 mmol, 1.0 equiv.) and DMF-DMA (35 mmol, 3.5 equiv.) in *N,N* -dimethylformamide (DMF, 30 mL) was stirred at 75 °C (oil bath) for 30 min. After the mixture was cooled to room temperature, saturated brine (100 mL) was added and an orange precipitate appeared. The solid was separated to afford the substituted 3-(dimethylamino)-1-(2-hydroxyphenyl)propanones. 3-(Dimethylamino)-1-(2-hydroxyphenyl)propanones were dissolved in 30 mL of CH_2Cl_2 (DCM), added iodine (30.0 mmol, 3.0 equiv.), and the mixture was stirred at room temperature for 0.5 h. After completion of the reaction, the solution of 5% $NaHSO_3$ was added into the mixture. 5% $NaHCO_3$ (3 × 25 mL) was used to wash the organic phase and the solution was extracted three times with DCM (3 × 20 mL). The combined organic phase was concentrated and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give 3-iodochromones (**1**).[1]

3.2 Synthesis of bridged olefins **2**



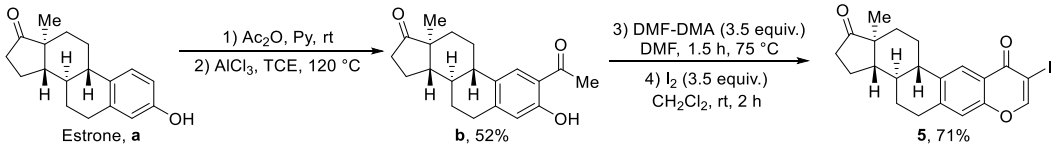
2d

PPh_3 (54 mg, 0.2 mmol, 10 mol%), $Pd(OAc)_2$ (22.6 mg, 0.1 mmol, 5 mol%), Cs_2CO_3 (752 mg, 2.0 mmol, 1.0 equiv.), 1,4-dioxane (3 mL), 2-bromo-*p*-xylene (290 mg, 2.0 mmol, 1.0 equiv.), and norbornadiene (NBDE, 553 mg, 6.0 mmol, 3.0 equiv.) were added into a 10 mL glass vial, which was evacuated and filled with argon three times. Then the reaction mixture was stirred at room temperature for 5 min, and then heated to 120 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature and passed through a thin layer of Celite bed and washed with ethyl acetate to remove inorganic salts. The filtrate was evaporated under reduced pressure and purified by silica gel chromatography (eluted with hexanes) to afford compound **2d** as a colorless oil (161 mg, 41% yield).[2]



Anthracene (891 mg, 5 mmol, 1.0 equiv.) and norbornadiene (NBDE, 2.3 g, 25 mmol, 5.0 equiv.) were added into a sealed glass tube under argon atmosphere. The mixture was stirred for 27 h at 175 °C in a heating module. After the completion of this reaction and cooling to room temperature, the mixture was purified by flash column chromatography on silica gel (petroleum ether) to afford the desired product **2e** as a white solid (1.08 g, 79% yield).[3]

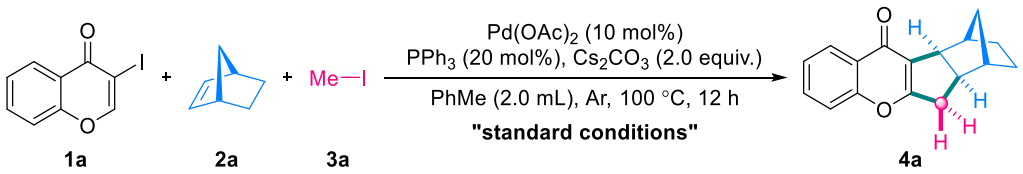
4. Synthesis of substrate 5



To a solution of estrone (**a**, 811 mg, 3.0 mmol, 1.0 equiv.) in pyridine (Py, 4 mL) was added acetic anhydride (Ac_2O, 1.99 g, 19.5 mmol, 6.5 equiv.) at ice-bath condition. After that, the reaction was stirred for 16 h at room temperature. To the tetrachloroethane (TCE, 30 mL, 0.1 M) was added $AlCl_3$ (1.00 g, 7.5 mmol, 2.5 equiv.) and the mixture was stirred at 90 °C in oil bath for 10 min, followed by the addition of a solution of estrone acetate (937 mg, 3 mmol, 1.0 equiv.) in DCM (3 mL, 1 M). The reaction was stirred at 120 °C (oil bath) for 8 h before poured into cold 2 M HCl (25 mL) and extracted with DCM (3 × 30 mL). The organic phase was washed with saturated $NaHCO_3$ solution (20 mL), brine (20 mL) and dried over Na_2SO_4. After the evaporation of solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give the product **b** as a yellow solid (487 mg, 52% yield).[4b]

A solution of **b** (487 mg, 1.56 mmol, 1.0 equiv.) and DMF-DMA (650 mg, 5.46 mmol, 3.5 equiv.) in DMF (30 mL) was stirred at 75 °C in oil bath for 1.5 h. After completion of the reaction, saturated brine (80 mL) was added to the mixture, and the resulting solid was filtrated. To a solution of the solid in DCM (30 mL) was added iodine (1381 mg, 5.46 mmol, 3.5 equiv.), and the mixture was stirred at room temperature for 2 h. After completion, the solution was quenched with 5% $NaHSO_3$ (60 mL), and was extracted with 50 mL DCM three times. The combined organic fractions were condensed and purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1 ~ 3:1) to give the product **5** as a white solid (496 mg, 71% yield).[4c] Characterization data of **1**, **2** and **5** can be found in previously reported.[4]

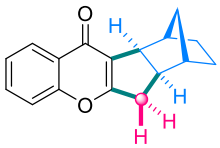
5. Representative procedure for the synthesis of compound 4a



1a (54.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (37.7 mg, 0.4 mmol, 2.0 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), PPh_3 (10.5 mg, 0.04 mmol, 20 mol%), Cs_2CO_3 (130.2 mg, 0.4 mmol, 2.0 equiv.) and toluene (2.0 mL) were added into a 4 mL flame-dried vial with a magnetic stir bar. The reaction vial was evacuated and backfilled with argon three times, then, **3a** (42.4mg, 0.3mmol, 1.5 equiv.) was added into flask, and the mixture was stirred at 100 °C (heating module) for 12 h. After completion of the reaction, it was concentrated to remove solvent and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the product **4a** (46.2 mg, 92% yield).

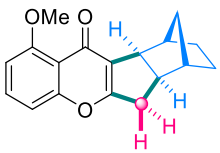
6. Characterization data of compounds 4a-6b

Scheme 2, 4a



Compound **4a**: yellow solid, 46.2 mg, 92% yield, m.p. 131.2 – 133.0 °C (lit.[4c] m.p. 134.4 – 135.6 °C); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.16 (dd, J = 8.0, 1.7 Hz, 1H), 7.53 (ddd, J = 8.6, 7.1, 1.7 Hz, 1H), 7.37 – 7.27 (m, 2H), 3.16 – 3.01 (m, 2H), 2.55 – 2.43 (m, 2H), 2.29 – 2.20 (m, 1H), 2.00 (d, J = 4.1 Hz, 1H), 1.60 – 1.41 (m, 2H), 1.39 – 1.30 (m, 1H), 1.24 – 1.12 (m, 2H), 1.04 (dt, J = 10.3, 1.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.2, 169.7, 156.8, 132.7, 125.7, 124.7, 124.3, 122.2, 117.9, 49.8, 42.8, 40.4, 39.2, 38.4, 32.3, 28.8, 28.5; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

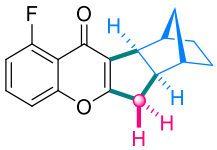
Scheme 2, 4b



Compound **4b**: yellow solid, 43.6 mg, 77% yield, m.p. 179.8 – 180.8 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.45 (t, J = 8.3 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 3.94 (s, 3H), 3.15 – 3.02 (m,

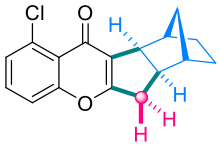
2H), 2.58 (d, *J* = 4.0 Hz, 1H), 2.53 – 2.41 (m, 1H), 2.30 – 2.21 (m, 1H), 2.03 (d, *J* = 4.1 Hz, 1H), 1.63 – 1.44 (m, 2H), 1.41 – 1.32 (m, 1H), 1.29 – 1.14 (m, 2H), 1.10 – 1.02 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.6, 167.2, 160.2, 159.3, 132.8, 123.6, 115.0, 110.3, 106.3, 56.5, 50.1, 42.9, 40.7, 39.1, 38.1, 32.4, 28.8, 28.7; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4c



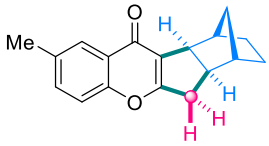
Compound **4c**: yellow solid, 44.9 mg, 83% yield, m.p. 146.2 – 148.3 °C (lit.[4c] m.p. 149.6 – 150.6 °C); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.49 (td, *J* = 8.3, 5.4 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 10.8, 8.2 Hz, 1H), 3.19 – 3.03 (m, 2H), 2.59 – 2.45 (m, 2H), 2.34 – 2.23 (m, 1H), 2.05 (d, *J* = 4.1 Hz, 1H), 1.63 – 1.45 (m, 2H), 1.41 – 1.33 (m, 1H), 1.27 – 1.17 (m, 2H), 1.09 (dt, *J* = 10.4, 1.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.9, 168.6, 161.2 (d, *J* = 263.8 Hz), 158.2 (d, *J* = 3.9 Hz), 132.7 (d, *J* = 10.9 Hz), 123.3, 114.9 (d, *J* = 10.0 Hz), 114.0 (d, *J* = 4.5 Hz), 111.9 (d, *J* = 21.2 Hz), 49.9, 42.9, 40.5, 39.1, 38.2, 32.4, 28.8, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4d



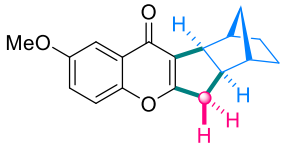
Compound **4d**: yellow solid, 48.1 mg, 84% yield, m.p. 174.0 – 175.1°C (lit.[4c] m.p. 172.3 – 174.0 °C); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.42 (t, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 3.19 – 2.99 (m, 2H), 2.61 – 2.44 (m, 2H), 2.29 (td, *J* = 9.9, 9.4, 3.8 Hz, 1H), 2.05 (d, *J* = 4.1 Hz, 1H), 1.62 – 1.47 (m, 2H), 1.39 – 1.32 (m, 1H), 1.27 – 1.17 (m, 2H), 1.09 (dt, *J* = 10.4, 1.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.3, 168.1, 158.7, 133.7, 131.9, 128.0, 123.5, 121.3, 117.4, 50.1, 42.9, 40.7, 39.1, 38.2, 32.4, 28.8, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4e



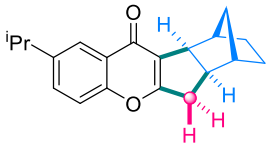
Compound **4e**: yellow solid, 46.2 mg, 87% yield, m.p. 136.6 – 137.4 °C (lit.[4c] m.p. 144.3 – 144.6 °C); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 2.3 Hz, 1H), 7.37 (dd, J = 8.5, 2.2 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 3.17 – 3.05 (m, 2H), 2.56 – 2.46 (m, 2H), 2.40 (s, 3H), 2.28 (td, J = 10.2, 9.8, 3.7 Hz, 1H), 2.03 (d, J = 4.1 Hz, 1H), 1.63 – 1.45 (m, 2H), 1.42 – 1.34 (m, 1H), 1.27 – 1.16 (m, 2H), 1.07 (d, J = 9.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.5, 169.7, 155.2, 134.6, 134.0, 125.3, 124.1, 122.2, 117.7, 49.9, 43.0, 40.6, 39.3, 38.5, 32.4, 28.9, 28.7, 21.0; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4f



Compound **4f**: yellow solid, 46.7 mg, 83% yield, m.p. 124.5 – 126.3 °C (lit.[4c] m.p. 127.1 – 128.8 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 3.1 Hz, 1H), 7.31 (d, J = 9.1 Hz, 1H), 7.16 (dd, J = 9.1, 2.9 Hz, 1H), 3.86 (s, 3H), 3.21 – 3.05 (m, 2H), 2.60 – 2.46 (m, 2H), 2.29 (td, J = 10.7, 9.8, 3.6 Hz, 1H), 2.04 (d, J = 4.1 Hz, 1H), 1.64 – 1.45 (m, 2H), 1.43 – 1.35 (m, 1H), 1.27 – 1.17 (m, 2H), 1.07 (d, J = 10.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.1, 169.7, 156.7, 151.8, 125.0, 122.6, 121.7, 119.3, 105.2, 55.9, 49.9, 43.0, 40.6, 39.3, 38.4, 32.4, 28.9, 28.7; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

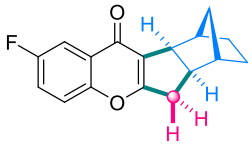
Scheme 2, 4g



Compound **4g**: yellow solid, 50.1 mg, 85% yield, m.p. 151.6 – 153.2 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 2.3 Hz, 1H), 7.45 (dd, J = 8.6, 2.3 Hz, 1H), 7.31 (d, J = 8.6 Hz, 1H), 3.29 – 3.06 (m, 2H), 3.01 (h, J = 6.9 Hz, 1H), 2.64 – 2.44 (m, 2H), 2.38 – 2.22 (m, 1H), 2.03 (d, J = 4.1 Hz, 1H), 1.69 – 1.44

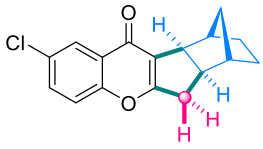
(m, 2H), 1.39 (td, *J* = 10.0, 8.3, 2.5 Hz, 1H), 1.32 – 1.14 (m, 8H), 1.12 – 1.00 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.6, 169.7, 155.4, 145.6, 131.6, 124.1, 122.6, 122.2, 117.8, 49.9, 43.0, 40.5, 39.3, 38.5, 33.8, 32.4, 28.9, 28.7, 24.1, 24.0; HRMS (ESI-TOF): calcd. for $[C_{20}H_{23}O_2]^+$ $[M + H]^+$ 295.1693; found 295.1692.

Scheme 2, 4h



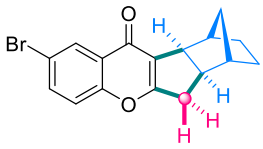
Compound **4h**: yellow solid, 44.6 mg, 83% yield, m.p. 157.6 – 159.8 °C (lit.[4c] m.p. 158.8 – 159.8 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.39 (dd, *J* = 9.1, 4.2 Hz, 1H), 7.33 – 7.27 (m, 1H), 3.21 – 3.05 (m, 2H), 2.58 – 2.48 (m, 2H), 2.37 – 2.26 (m, 1H), 2.06 (d, *J* = 4.1 Hz, 1H), 1.63 – 1.47 (m, 2H), 1.42 – 1.34 (m, 1H), 1.27 – 1.18 (m, 2H), 1.09 (d, *J* = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.5 (d, *J* = 2.1 Hz), 170.4, 159.7 (d, *J* = 245.7 Hz), 153.1 (d, *J* = 1.8 Hz), 125.7 (d, *J* = 7.1 Hz), 121.9, 120.9 (d, *J* = 25.5 Hz), 119.9 (d, *J* = 8.0 Hz), 110.8 (dd, *J* = 23.6, 2.1 Hz), 49.8, 43.0, 40.6, 39.3 (d, *J* = 1.6 Hz), 38.5, 32.4, 28.8, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4i



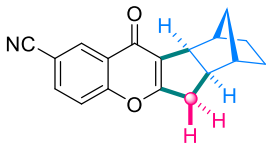
Compound **4i**: yellow solid, 44.5 mg, 78% yield, m.p. 181.5 – 183.0 °C (lit.[4c] m.p. 178.8 – 179.9 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.4 Hz, 1H), 7.52 (dt, *J* = 8.9, 1.9 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 3.23 – 3.06 (m, 2H), 2.60 – 2.48 (m, 2H), 2.36 – 2.25 (m, 1H), 2.07 (d, *J* = 4.1 Hz, 1H), 1.64 – 1.47 (m, 2H), 1.39 (td, *J* = 10.1, 8.7, 2.5 Hz, 1H), 1.28 – 1.18 (m, 2H), 1.13 – 1.06 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.1, 170.2, 155.3, 133.0, 130.8, 125.5, 125.4, 122.5, 119.7, 49.9, 43.0, 40.6, 39.3, 38.5, 32.5, 28.9, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4j



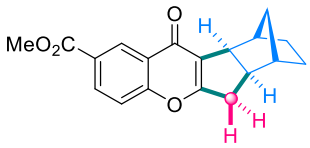
Compound **4j**: yellow solid, 49.2 mg, 74% yield, m.p. 202.0 – 203.9 °C (lit.[4c] m.p. 206.1 – 207.4 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 2.5 Hz, 1H), 7.66 (d, J = 6.3 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 3.24 – 3.04 (m, 2H), 2.62 – 2.47 (m, 2H), 2.37 – 2.27 (m, 1H), 2.08 (s, 1H), 1.66 – 1.47 (m, 2H), 1.39 (t, J = 9.8 Hz, 1H), 1.29 – 1.21 (m, 2H), 1.11 (d, J = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.0, 170.2, 155.8, 135.8, 128.6, 125.9, 122.6, 120.0, 118.3, 49.9, 43.0, 40.6, 39.3, 38.5, 32.5, 28.9, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4k



Compound **4k**: yellow solid, 22.6 mg, 41% yield, m.p. 180.6 – 182.2 °C (lit.[4c] m.p. 187.5 – 187.8 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.82 (dd, J = 8.7, 2.1 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 3.31 – 3.04 (m, 2H), 2.68 – 2.47 (m, 2H), 2.43 – 2.30 (m, 1H), 2.10 (d, J = 4.1 Hz, 1H), 1.66 – 1.49 (m, 2H), 1.40 (td, J = 11.4, 3.0 Hz, 1H), 1.28 – 1.20 (m, 2H), 1.13 (d, J = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.4, 170.5, 158.7, 135.3, 131.7, 125.0, 123.5, 119.7, 117.9, 109.0, 49.8, 42.9, 40.5, 39.3, 38.5, 32.5, 28.8, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

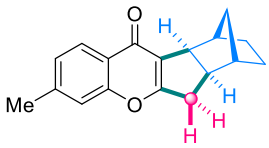
Scheme 2, 4l



Compound **4l**: yellow solid, 54.0 mg, 87% yield, m.p. 195.8 – 197.1 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.93 – 8.85 (m, 1H), 8.24 (dd, J = 8.8, 2.2 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H), 3.94 (s, 3H), 3.26 – 3.08 (m, 2H), 2.62 – 2.52 (m, 2H), 2.39 – 2.29 (m, 1H), 2.08 (d, J = 4.1 Hz, 1H), 1.65 – 1.49 (m, 2H), 1.44 – 1.37 (m, 1H), 1.26 – 1.21 (m, 2H), 1.15 – 1.09 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.7, 170.1,

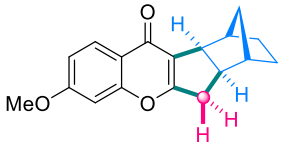
166.1, 159.5, 133.6, 128.5, 126.9, 124.2, 123.0, 118.5, 52.5, 49.9, 43.0, 40.6, 39.3, 38.5, 32.5, 28.9, 28.6; HRMS (ESI-TOF): calcd. for $[C_{19}H_{19}O_4]^+$ $[M + H]^+$ 311.1278; found 311.1277.

Scheme 2, 4m



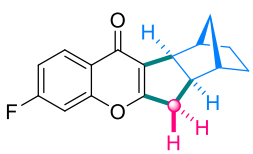
Compound **4m**: yellow solid, 46.5 mg, 87% yield, m.p. 144.6 – 146.4 °C (lit.[4c] m.p. 146.6 – 148.1 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 9.0 Hz, 2H), 3.20 – 3.00 (m, 2H), 2.60 – 2.47 (m, 2H), 2.43 (s, 3H), 2.33 – 2.22 (m, 1H), 2.04 (d, J = 4.1 Hz, 1H), 1.63 – 1.46 (m, 2H), 1.43 – 1.34 (m, 1H), 1.28 – 1.17 (m, 2H), 1.08 (d, J = 10.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.4, 169.5, 157.1, 144.0, 126.3, 125.6, 122.2, 122.1, 117.8, 49.9, 43.0, 40.5, 39.3, 38.5, 32.4, 28.9, 28.7, 21.8; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4n



Compound **4n**: yellow solid, 47.4 mg, 84% yield, m.p. 128.8 – 130.5 °C (lit.[4c] m.p. 130.2 – 132.3 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.8 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 6.77 (s, 1H), 3.84 (s, 3H), 3.16 – 3.00 (m, 2H), 2.58 – 2.41 (m, 2H), 2.32 – 2.22 (m, 1H), 2.03 (d, J = 4.1 Hz, 1H), 1.61 – 1.44 (m, 2H), 1.37 (t, J = 10.4 Hz, 1H), 1.28 – 1.15 (m, 2H), 1.06 (d, J = 10.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.0, 169.2, 163.4, 158.7, 127.1, 122.1, 118.3, 113.7, 100.5, 55.8, 49.8, 43.0, 40.6, 39.3, 38.4, 32.4, 28.9, 28.7; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

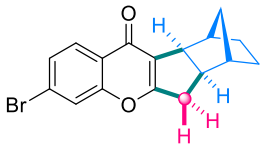
Scheme 2, 4o



Compound **4o**: yellow solid, 45.2 mg, 84% yield, m.p. 125.5 – 126.7 °C (lit.[4c] m.p. 124.6 – 126.1 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 9.2, 6.4 Hz, 1H), 7.13 – 6.99 (m, 2H), 3.21 – 3.05 (m, 2H),

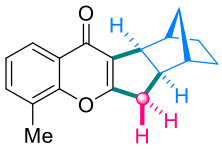
2.60 – 2.47 (m, 2H), 2.37 – 2.26 (m, 1H), 2.06 (d, *J* = 4.1 Hz, 1H), 1.65 – 1.45 (m, 2H), 1.44 – 1.33 (m, 1H), 1.29 – 1.16 (m, 2H), 1.10 (d, *J* = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.5, 170.0, 165.1 (d, *J* = 253.4 Hz), 157.9 (d, *J* = 13.0 Hz), 128.2 (d, *J* = 10.6 Hz), 122.5, 121.3 (d, *J* = 2.4 Hz), 113.4 (d, *J* = 22.6 Hz), 104.7 (d, *J* = 25.4 Hz), 49.8, 42.9, 40.6, 39.3, 38.4, 32.4, 28.9, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4p



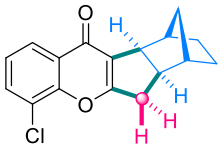
Compound **4p**: yellow solid, 51.6 mg, 78% yield, m.p. 180.7 – 182.0 °C (lit.[4c] m.p. 182.4 – 183.8 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 3.21 – 2.96 (m, 2H), 2.59 – 2.45 (m, 2H), 2.36 – 2.24 (m, 1H), 2.05 (d, *J* = 4.1 Hz, 1H), 1.64 – 1.44 (m, 2H), 1.37 (t, *J* = 10.7 Hz, 1H), 1.27 – 1.15 (m, 2H), 1.09 (d, *J* = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.6, 169.9, 157.0, 128.4, 127.3, 126.9, 123.4, 122.7, 121.1, 49.8, 42.9, 40.5, 39.3, 38.4, 32.4, 28.8, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4q



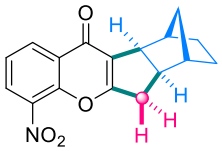
Compound **4q**: yellow solid, 48.9 mg, 92% yield, m.p. 126.3 – 128.0 °C (lit.[4c] m.p. 125.1 – 127.2 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 3.21 – 3.06 (m, 2H), 2.59 – 2.50 (m, 2H), 2.42 (s, 3H), 2.33 – 2.23 (m, 1H), 2.05 (d, *J* = 4.0 Hz, 1H), 1.61 – 1.46 (m, 2H), 1.42 – 1.34 (m, 1H), 1.29 – 1.18 (m, 2H), 1.07 (d, *J* = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.7, 169.7, 155.5, 133.8, 127.3, 124.3, 124.2, 123.4, 122.1, 49.9, 43.0, 40.5, 39.3, 38.5, 32.4, 28.8, 28.6, 15.7; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4r



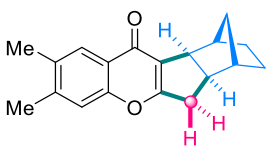
Compound **4r**: yellow solid, 49.0 mg, 86% yield, m.p. 142.9 – 144.1 °C (lit.[4c] m.p. 142.4 – 144.5 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 3.22 (dd, J = 18.9, 10.3 Hz, 1H), 3.11 (d, J = 7.7 Hz, 1H), 2.67 – 2.51 (m, 2H), 2.39 – 2.28 (m, 1H), 2.08 (d, J = 4.1 Hz, 1H), 1.65 – 1.47 (m, 2H), 1.44 – 1.35 (m, 1H), 1.30 – 1.19 (m, 2H), 1.11 (d, J = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.5, 169.9, 152.6, 133.2, 125.9, 124.9, 124.6, 122.9, 122.7, 49.8, 43.0, 40.6, 39.2, 38.5, 32.4, 28.8, 28.6.; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4s



Compound **4s**: yellow solid, 29.8 mg, 50% yield, m.p. 158.9 – 160.3 °C (lit.[4c] m.p. 160.4 – 161.4 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 7.9, 1.8 Hz, 1H), 8.22 (dd, J = 7.9, 1.7 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 3.24 (dd, J = 19.1, 10.2 Hz, 1H), 3.13 (d, J = 7.7 Hz, 1H), 2.70 – 2.53 (m, 2H), 2.40 – 2.33 (m, 1H), 1.67 – 1.50 (m, 2H), 1.45 – 1.37 (m, 1H), 1.29 – 1.22 (m, 2H), 1.14 (dt, J = 10.4, 1.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.2, 170.2, 149.1, 139.2, 131.8, 128.9, 126.4, 124.1, 123.5, 49.8, 43.0, 40.6, 39.3, 38.5, 32.5, 28.9, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

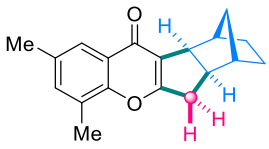
Scheme 2, 4t



Compound **4t**: yellow solid, 47.5 mg, 85% yield, m.p. 168.0 – 169.2 °C (lit.[4c] m.p. 167.0 – 169.0 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.12 (s, 1H), 3.16 – 3.03 (m, 2H), 2.56 – 2.45 (m, 2H), 2.31 (d, J = 7.7 Hz, 7H), 2.03 (d, J = 4.1 Hz, 1H), 1.62 – 1.45 (m, 2H), 1.42 – 1.34 (m, 1H), 1.27 – 1.17 (m,

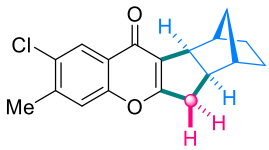
2H), 1.06 (d, *J* = 10.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ* 176.4, 169.3, 155.5, 143.0, 133.9, 125.5, 122.2, 122.0, 118.1, 49.9, 43.0, 40.5, 39.3, 38.4, 32.4, 28.9, 28.7, 20.4, 19.3; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4u



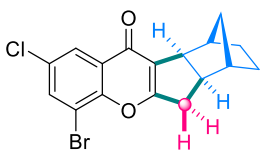
Compound **4u**: yellow solid, 44.6 mg, 80% yield, m.p. 214.8 – 215.5 °C (lit.[4c] m.p. 212.1 – 213.6 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) *δ* 7.82 (s, 1H), 7.21 (s, 1H), 3.20 – 3.04 (m, 2H), 2.57 – 2.48 (m, 2H), 2.37 (d, *J* = 7.5 Hz, 6H), 2.31 – 2.24 (m, 1H), 2.04 (d, *J* = 3.9 Hz, 1H), 1.62 – 1.45 (m, 2H), 1.42 – 1.34 (m, 1H), 1.27 – 1.17 (m, 2H), 1.06 (d, *J* = 10.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ* 176.7, 169.4, 153.8, 135.1, 134.0, 126.9, 123.9, 122.8, 121.9, 49.9, 43.0, 40.6, 39.3, 38.5, 32.4, 28.9, 28.6, 20.9, 15.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4v



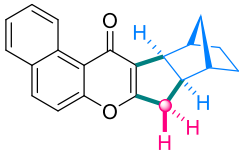
Compound **4v**: yellow solid, 45.8 mg, 76% yield, m.p. 184.3 – 185.8 °C (lit.[4c] m.p. 184.5 – 186.3 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) *δ* 8.12 (s, 1H), 7.25 (s, 1H), 3.23 – 3.01 (m, 2H), 2.61 – 2.39 (m, 5H), 2.30 (d, *J* = 9.2 Hz, 1H), 2.05 (s, 1H), 1.63 – 1.46 (m, 2H), 1.37 (t, *J* = 10.5 Hz, 1H), 1.23 (d, *J* = 10.5 Hz, 2H), 1.08 (d, *J* = 10.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ* 175.2, 169.9, 155.2, 141.8, 131.4, 125.6, 123.6, 122.3, 119.8, 49.9, 43.0, 40.6, 39.3, 38.5, 32.4, 28.9, 28.6, 20.8; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4w



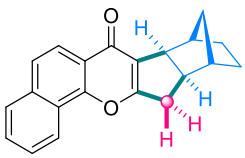
Compound **4w**: yellow solid, 53.9 mg, 74% yield, m.p. 143.4 – 145.1 °C (lit.[4c] m.p. 144.0 – 146.3 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 2.5 Hz, 1H), 7.78 (d, J = 2.4 Hz, 1H), 3.22 (dd, J = 19.0, 10.1 Hz, 1H), 3.10 (d, J = 7.7 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.39 – 2.30 (m, 1H), 2.09 (d, J = 4.1 Hz, 1H), 1.65 – 1.48 (m, 2H), 1.39 (t, J = 9.9 Hz, 1H), 1.29 – 1.19 (m, 2H), 1.12 (d, J = 10.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 174.3, 170.4, 152.2, 136.0, 130.9, 126.3, 124.9, 122.7, 112.5, 49.8, 43.0, 40.6, 39.3, 38.5, 32.5, 28.8, 28.6; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4x



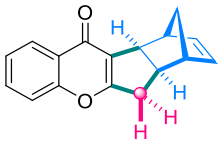
Compound **4x**: yellow solid, 35.5 mg, 55% yield, m.p. 205.2 – 206.2 °C (lit.[4c] m.p. 202.1 – 203.3 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.14 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 8.0 Hz 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 9.0 Hz, 1H), 3.21 – 3.10 (m, 2H), 2.68 – 2.50 (m, 2H), 2.37 – 2.27 (m, 1H), 2.07 (d, J = 4.1 Hz, 1H), 1.68 – 1.47 (m, 2H), 1.48 – 1.38 (m, 1H), 1.29 – 1.18 (m, 2H), 1.14 – 1.07 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 178.7, 166.9, 158.1, 134.5, 131.1, 130.7, 128.9, 128.1, 127.2, 126.3, 125.1, 117.8, 117.4, 50.2, 43.0, 41.0, 39.3, 38.0, 32.5, 28.9, 28.7; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 2, 4y



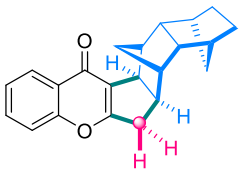
Compound **4y**: yellow solid, 50.5 mg, 84% yield, m.p. 181.9 – 183.7 °C (lit.[4c] m.p. 188.4 – 190.1 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 8.9 Hz, 1H), 8.17 (d, J = 8.7 Hz, 1H), 7.88 (dd, J = 7.5, 1.8 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.62 (pd, J = 7.1, 1.5 Hz, 2H), 3.26 (dd, J = 18.4, 10.1 Hz, 1H), 3.17 (d, J = 7.7 Hz, 1H), 2.73 – 2.57 (m, 2H), 2.41 – 2.30 (m, 1H), 2.10 (d, J = 4.2 Hz, 1H), 1.68 – 1.50 (m, 2H), 1.47 – 1.39 (m, 1H), 1.31 – 1.21 (m, 2H), 1.12 (d, J = 10.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.4, 168.9, 154.2, 135.6, 128.9, 128.1, 126.9, 124.9, 124.2, 123.7, 122.2, 121.2, 120.6, 50.0, 43.0, 40.8, 39.3, 38.4, 32.5, 28.9, 28.7; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Fig. 1, 4z



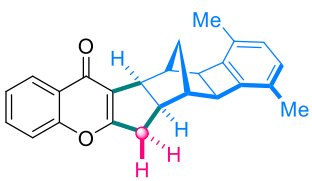
Compound **4z**: yellow solid, 30.1 mg, 60% yield, m.p. 140.0 – 142.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.0, 1.8 Hz, 1H), 7.59 (ddd, J = 8.7, 7.1, 1.8 Hz, 1H), 7.43 – 7.33 (m, 2H), 6.24 (dd, J = 5.8, 3.0 Hz, 1H), 6.08 (dd, J = 5.8, 3.0 Hz, 1H), 3.22 – 3.00 (m, 3H), 2.66 (s, 1H), 2.54 (ddd, J = 18.8, 3.8, 2.3 Hz, 1H), 2.37 – 2.27 (m, 1H), 1.39 (dt, J = 9.2, 1.7 Hz, 1H), 1.31 (d, J = 8.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.2, 170.2, 157.0, 138.2, 136.4, 132.9, 125.9, 124.9, 124.5, 122.4, 118.0, 47.7, 47.1, 44.4, 41.8, 37.6, 36.4; HRMS (ESI-TOF): calcd. for $[C_{17}H_{15}O_2]^+$ $[M + H]^+$ 251.1067; found 251.1064.

Fig. 1, 4aa



Compound **4aa**: yellow solid, 57.0 mg, 90% yield, m.p. 183.0 – 184.0 °C (lit.[4c] m.p. 180.2 – 182.1 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 8.0, 1.7 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.36 (dd, J = 16.8, 8.2 Hz, 2H), 3.49 (d, J = 7.3 Hz, 1H), 3.14 (dd, J = 18.5, 10.1 Hz, 1H), 2.70 – 2.59 (m, 2H), 2.44 (dt, J = 18.6, 3.0 Hz, 1H), 2.38 (d, J = 3.0 Hz, 1H), 2.17 (d, J = 3.1 Hz, 1H), 2.09 (d, J = 4.8 Hz, 1H), 1.79 (dd, J = 10.0, 4.7 Hz, 1H), 1.72 – 1.64 (m, 2H), 1.52 – 1.42 (m, 2H), 1.28 (d, J = 10.2 Hz, 1H), 1.10 (d, J = 10.3 Hz, 1H), 0.99 (t, J = 8.6 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.1, 169.5, 156.9, 132.8, 125.8, 124.8, 124.4, 122.4, 117.9, 50.1, 50.1, 48.2, 44.8, 44.0, 38.9, 36.4, 35.6, 35.4, 35.2, 31.4, 31.4; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

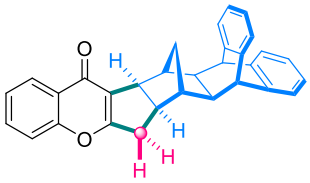
Fig. 1, 4ab



Compound **4ab**: yellow solid, 64.4 mg, 91% yield, m.p. 233.6 – 234.4 °C (lit.[4c] m.p. 235.0 – 236.1 °C); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 8.0, 1.7 Hz, 1H), 7.61 (ddd, J = 8.7, 7.0, 1.7 Hz, 1H), 7.47 –

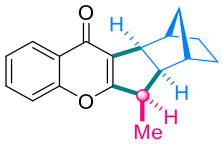
7.32 (m, 2H), 6.90 (s, 2H), 3.40 (d, *J* = 3.8 Hz, 1H), 3.31 – 3.14 (m, 3H), 2.75 – 2.58 (m, 2H), 2.41 – 2.33 (m, 1H), 2.25 – 2.10 (m, 7H), 1.03 (d, *J* = 11.7 Hz, 1H), 0.80 (d, *J* = 11.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ* 176.4, 169.6, 157.0, 144.0, 143.3, 133.0, 129.7, 129.1, 128.7, 128.5, 125.9, 125.0, 124.4, 122.1, 118.0, 48.6, 48.6, 47.8, 42.4, 39.2, 38.9, 38.2, 26.7, 16.4, 16.3; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Fig. 1, 4ac



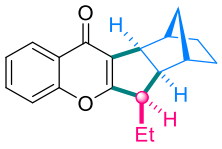
Compound **4ac**: white solid, 66.1 mg, 77% yield, m.p. 294.6 – 295.2 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ* 8.21 (d, *J* = 7.5 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.20 – 7.13 (m, 2H), 7.13 – 7.04 (m, 4H), 4.37 (d, *J* = 2.8 Hz, 1H), 4.27 (d, *J* = 2.8 Hz, 1H), 3.13 – 2.96 (m, 2H), 2.47 – 2.32 (m, 2H), 2.22 – 2.11 (m, 2H), 1.99 – 1.93 (m, 1H), 1.88 (s, 1H), 0.45 (d, *J* = 11.6 Hz, 1H), -0.48 (d, *J* = 11.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ* 176.3, 170.0, 156.9, 144.7, 144.5, 142.3, 142.0, 132.9, 126.2, 126.0, 125.8, 125.8, 125.6, 124.9, 124.5, 124.3, 124.2, 123.5, 123.2, 121.4, 117.9, 51.2, 49.1, 48.5, 48.4, 48.2, 46.2, 42.5, 41.6, 37.7, 27.1; ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

Scheme 3, 4ad



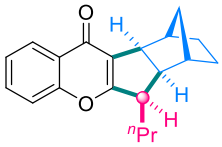
Compound **4ad**: yellow solid, 32.9 mg, 62% yield, m.p. 142.6 – 144.3 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ* 8.22 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 7.43 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.36 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 3.42 (dq, *J* = 10.1, 7.5 Hz, 1H), 3.18 (d, *J* = 7.7 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.33 – 2.19 (m, 2H), 1.66 – 1.49 (m, 2H), 1.42 – 1.35 (m, 1H), 1.31 (d, *J* = 7.5 Hz, 3H), 1.19 – 1.12 (m, 2H), 1.07 (dt, *J* = 10.0, 1.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ* 176.6, 172.5, 157.0, 132.8, 125.9, 124.8, 124.6, 120.8, 118.1, 49.7, 44.4, 40.9, 37.6, 37.1, 34.0, 29.4, 28.6, 12.0; HRMS (ESI-TOF): calcd. for $[C_{18}H_{19}O_2]^+$ $[M + H]^+$ 267.1380; found 267.1377.

Scheme 3, 4ae



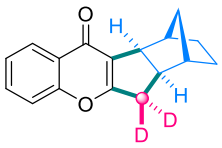
Compound **4ae**: yellow solid, 35.0 mg, 62% yield, m.p. 99.8 – 101.6 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.9, 1.7 Hz, 1H), 7.59 (ddd, J = 8.7, 7.1, 1.8 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.40 – 7.32 (m, 1H), 3.25 – 3.10 (m, 2H), 2.60 (d, J = 3.8 Hz, 1H), 2.36 – 2.26 (m, 2H), 1.99 – 1.89 (m, 1H), 1.70 – 1.53 (m, 3H), 1.43 – 1.35 (m, 1H), 1.18 (t, J = 7.4 Hz, 5H), 1.09 – 1.03 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.6, 172.0, 157.0, 132.8, 125.9, 124.9, 124.6, 121.0, 118.1, 49.4, 48.5, 43.7, 37.8, 36.9, 34.0, 29.6, 28.5, 20.3, 13.9; HRMS (ESI-TOF): calcd. for $[C_{19}H_{21}O_2]^+$ [M + H]$^+$ 281.1536; found 281.1537.

Scheme 3, 4af



Compound **4af**: yellow solid, 18.0 mg, 31% yield, m.p. 115.3 – 116.8 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.9, 1.8 Hz, 1H), 7.59 (ddd, J = 8.7, 7.0, 1.8 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 3.26 (td, J = 9.4, 4.4 Hz, 1H), 3.18 (d, J = 7.6 Hz, 1H), 2.61 (d, J = 3.9 Hz, 1H), 2.33 – 2.22 (m, 2H), 1.70 – 1.47 (m, 5H), 1.44 – 1.35 (m, 1H), 1.21 – 1.13 (m, 2H), 1.10 – 1.00 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.5, 172.0, 157.0, 132.8, 125.9, 124.8, 124.6, 121.0, 118.1, 49.5, 46.5, 43.8, 37.7, 37.0, 34.0, 29.6, 29.3, 28.5, 22.4, 14.5; HRMS (ESI-TOF): calcd. for $[C_{20}H_{23}O_2]^+$ [M + H]$^+$ 295.1693; found 295.1692.

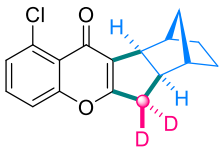
Scheme 3, 4ag



Compound **4ag**: yellow solid, 45.8 mg, 90% yield, 92% D, m.p. 139.7 – 141.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.0, 1.8 Hz, 1H), 7.59 (ddd, J = 8.6, 7.1, 1.8 Hz, 1H), 7.43 – 7.30 (m, 2H), 3.11

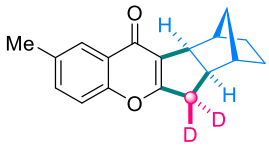
(d, *J* = 7.8 Hz, 1H), 2.56 (d, *J* = 4.1 Hz, 1H), 2.29 (d, *J* = 7.7 Hz, 1H), 2.06 (d, *J* = 4.2 Hz, 1H), 1.64 – 1.47 (m, 2H), 1.44 – 1.36 (m, 1H), 1.28 – 1.19 (m, 2H), 1.09 (dt, *J* = 10.3, 1.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.4, 169.8, 157.0, 132.8, 125.9, 124.8, 124.4, 122.5, 118.0, 49.9, 42.9, 40.4, 39.3, 38.6 – 36.9 (m), 32.4, 28.9, 28.7; HRMS (ESI-TOF): calcd. for $[C_{17}H_{15}D_2O_2]^+$ $[M + H]^+$ 255.1349; found 255.1345.

Scheme 3, 4ah



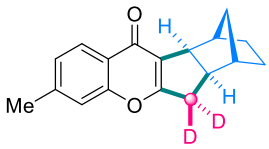
Compound **4ah**: yellow solid, 40.4 mg, 70% yield, 76% D, m.p. 173.0 – 174.2 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 8.1 Hz, 1H), 7.31 (td, *J* = 7.8, 1.3 Hz, 2H), 3.06 (d, *J* = 7.7 Hz, 1H), 2.62 – 2.47 (m, 1H), 2.28 (d, *J* = 7.7 Hz, 1H), 2.05 (d, *J* = 4.0 Hz, 1H), 1.65 – 1.45 (m, 2H), 1.41 – 1.32 (m, 1H), 1.27 – 1.17 (m, 2H), 1.09 (dt, *J* = 10.3, 1.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 175.4, 168.1, 158.8, 133.8, 131.9, 128.1, 123.6, 121.4, 117.4, 50.1, 42.8, 40.5, 39.2, 38.4 – 37.3 (m), 32.5, 28.8, 28.6; HRMS (ESI-TOF): calcd. for $[C_{17}H_{14}D_2ClO_2]^+$ $[M + H]^+$ 289.0959; found 289.0957.

Scheme 3, 4ai



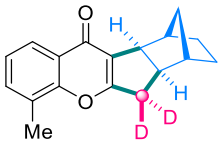
Compound **4ai**: yellow solid, 42.0 mg, 78% yield, 86% D, m.p. 142.1 – 144.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.6 Hz, 1H), 7.39 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 3.10 (d, *J* = 7.6 Hz, 1H), 2.56 (d, *J* = 4.1 Hz, 1H), 2.42 (s, 3H), 2.28 (d, *J* = 7.7 Hz, 1H), 2.05 (d, *J* = 4.1 Hz, 1H), 1.64 – 1.47 (m, 2H), 1.43 – 1.36 (m, 1H), 1.26 – 1.15 (m, 2H), 1.08 (dt, *J* = 10.3, 1.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.5, 169.7, 155.3, 134.7, 134.0, 125.3, 124.1, 122.3, 117.7, 49.9, 42.9, 40.4, 39.3, 38.7 – 37.2 (m), 32.4, 28.9, 28.7, 21.0; HRMS (ESI-TOF): calcd. for $[C_{18}H_{17}D_2O_2]^+$ $[M + H]^+$ 269.1505; found 269.1503.

Scheme 3, 4aj



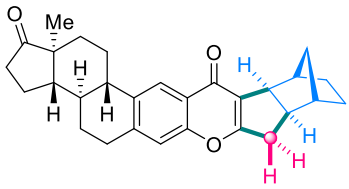
Compound **4aj**: yellow solid, 44.9 mg, 84% yield, 89% D, m.p. 147.3 – 148.4 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.7 Hz, 2H), 3.09 (d, J = 7.6 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.44 (s, 3H), 2.27 (d, J = 7.7 Hz, 1H), 2.05 (d, J = 4.1 Hz, 1H), 1.63 – 1.47 (m, 2H), 1.43 – 1.35 (m, 1H), 1.26 – 1.17 (m, 2H), 1.08 (dt, J = 10.3, 1.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.4, 169.5, 157.2, 144.0, 126.3, 125.7, 122.3, 122.2, 117.8, 49.9, 42.9, 40.6, 39.3, 38.7 – 36.8 (m), 32.4, 28.9, 28.7, 21.8; HRMS (ESI-TOF): calcd. for $[C_{18}H_{17}D_2O_2]^+$ $[M + H]^+$ 269.1505; found 269.1505.

Scheme 3, 4ak



Compound **4ak**: yellow solid, 43.5 mg, 81% yield, 90% D, m.p. 121.9 – 123.8 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.0, 1.8 Hz, 1H), 7.55 – 7.38 (m, 1H), 7.31 – 7.27 (m, 1H), 3.15 (d, J = 7.7 Hz, 1H), 2.61 (d, J = 4.1 Hz, 1H), 2.48 (s, 3H), 2.34 (d, J = 7.7 Hz, 1H), 2.11 (d, J = 4.1 Hz, 1H), 1.69 – 1.52 (m, 2H), 1.48 – 1.40 (m, 1H), 1.32 – 1.23 (m, 2H), 1.14 (dd, J = 10.3, 1.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 176.7, 169.5, 155.5, 133.9, 127.3, 124.3, 124.3, 123.5, 122.2, 49.9, 42.9, 40.4, 39.3, 38.8 – 37.0 (m), 32.4, 28.9, 28.7, 15.8; HRMS (ESI-TOF): calcd. for $[C_{18}H_{17}D_2O_2]^+$ $[M + H]^+$ 269.1505; found 269.1503.

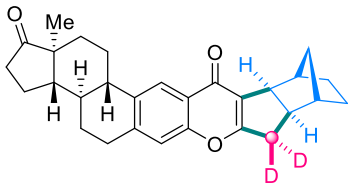
Scheme 4, 6a



Compound **6a**: white solid, 80.0 mg, 93% yield, m.p. 274.6 – 275.7 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 4.2 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 3.19 – 3.07 (m, 2H), 3.05 – 2.91 (m, 2H), 2.64 – 2.44 (m, 4H), 2.36 – 2.24 (m, 2H), 2.20 – 1.96 (m, 5H), 1.68 – 1.44 (m, 8H), 1.39 (td, J = 9.9, 8.3, 2.6 Hz, 1H), 1.28 – 1.17 (m, 2H), 1.07 (d, J = 9.7 Hz, 1H), 0.89 (d, J = 3.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz)

δ 220.7, 176.4, 169.5 (d, J = 3.4 Hz), 155.3, 143.0 (d, J = 1.5 Hz), 137.4 (d, J = 4.6 Hz), 122.2, 122.1 (d, J = 1.8 Hz), 121.9, 117.2 (d, J = 2.4 Hz), 50.6 (d, J = 1.5 Hz), 49.9, 48.0 (d, J = 1.2 Hz), 44.2 (d, J = 1.5 Hz), 43.0, 40.5 (d, J = 2.3 Hz), 39.3 (d, J = 3.1 Hz), 38.5, 38.0 (d, J = 3.0 Hz), 35.9, 32.4 (d, J = 1.5 Hz), 31.5, 29.7 (d, J = 1.6 Hz), 28.9 (d, J = 2.4 Hz), 28.7, 26.2 (d, J = 3.4 Hz), 25.9 (d, J = 4.4 Hz), 21.7, 13.9 (d, J = 1.8 Hz); ^{1}H and ^{13}C NMR data are consistent with previously reported.[4c]

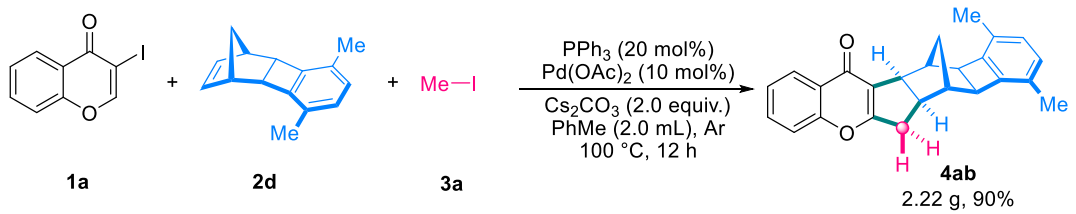
Scheme 4, 6b



Compound **6b**: white solid, 73.6 mg, 85% yield, 80% D, m.p. 275.9 – 277.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 4.3 Hz, 1H), 7.11 (d, J = 2.4 Hz, 1H), 3.09 (d, J = 7.5 Hz, 1H), 3.05 – 2.91 (m, 2H), 2.63 – 2.45 (m, 3H), 2.36 – 2.24 (m, 2H), 2.17 – 1.95 (m, 5H), 1.70 – 1.45 (m, 8H), 1.40 (t, J = 5.7 Hz, 1H), 1.28 – 1.24 (m, 1H), 1.22 – 1.17 (m, 1H), 1.07 (d, J = 10.4 Hz, 1H), 0.89 (d, J = 3.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 220.6 (d, J = 1.5 Hz), 176.4, 169.3 (d, J = 3.4 Hz), 155.2, 142.9 (d, J = 1.4 Hz), 137.3 (d, J = 4.7 Hz), 122.1, 122.0 (d, J = 1.6 Hz), 121.9, 117.1 (d, J = 2.4 Hz), 50.5 (d, J = 1.5 Hz), 49.8, 47.9 (d, J = 1.4 Hz), 44.1 (d, J = 1.5 Hz), 42.8, 40.3 (d, J = 2.3 Hz), 40.2 (d, J = 2.2 Hz), 39.2 (d, J = 3.2 Hz), 37.9 (d, J = 3.0 Hz), 35.8, 32.3, 31.4, 29.6 (d, J = 1.6 Hz), 28.8 (d, J = 2.5 Hz), 28.6, 26.1 (d, J = 3.4 Hz), 25.8 (d, J = 4.4 Hz), 21.6, 13.8 (d, J = 1.8 Hz); HRMS (ESI-TOF): calcd. for $[C_{29}H_{31}D_2O_3]^+$ $[M + H]^+$ 431.2550; found 431.2548.

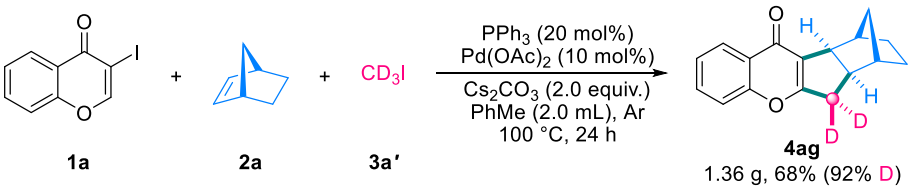
7. Preparative-scale experiments

7.1 Synthesis of **4ab** on a gram-scale

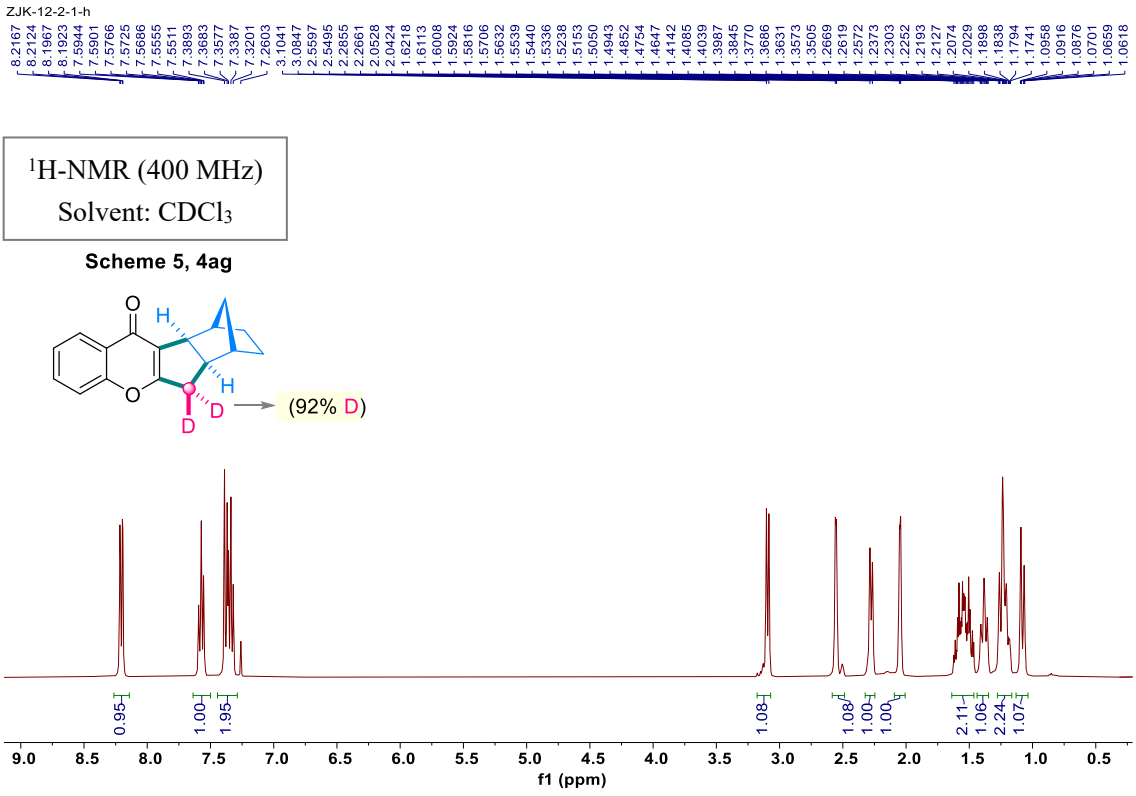


To a 250 mL flame-dried round bottom flask with a stir bar, **1a** (1.90 g, 7.0 mmol, 1.0 equiv.), **2d** (1.32 g, 14 mmol, 2.0 equiv.), $Pd(OAc)_2$ (157.2 mg, 0.7 mmol, 10 mol%), PPh_3 (367.2 mg, 1.4 mmol, 20 mol%), Cs_2CO_3 (4.56 g, 14.0 mmol, 2.0 equiv.), and toluene (70.0 mL) were added. The reaction flask was evacuated and backfilled with argon three times, then, **3a** (1.55 g, 10.5 mmol, 1.5 equiv.) was added into flask. The mixture was stirred at 100 °C in a heating module for 12 h. After completion of the reaction, it was concentrated to remove solvent and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 ~ 5:1) to afford the product **4ab** (2.22 g, 90% yield).

7.2 Synthesis of **4ag** on a gram-scale



To a 250 mL flame-dried round bottom flask with a stir bar, **1a** (2.18 g, 8.0 mmol, 1.0 equiv.), **2a** (1.51 g, 16 mmol, 2.0 equiv.), $Pd(OAc)_2$ (180 mg, 0.8 mmol, 10 mol%), PPh_3 (420.0 mg, 1.6 mmol, 20 mol%), Cs_2CO_3 (5.208 g, 16.0 mmol, 2.0 equiv.), and toluene (80.0 mL) were added. The reaction flask was evacuated and backfilled with argon three times, then, **3a'** (1.74 g, 12 mmol, 1.5 equiv.) was added into flask, the mixture was stirred at 100 °C in a heating module for 12 h. After completion of the reaction, it was concentrated to remove solvent and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 ~ 5:1) to afford the product **4ag** (1.36 g, 68% yield).


ZJK-12-2-1-h
8.2167 8.2124 8.1967 8.1923 7.5944 7.5901 7.5766 7.5725 7.5686 7.5555 7.5511 7.3893 7.3683 7.3577 7.3387 7.3201 7.2603 3.1041 3.0847 2.5597 2.5495 2.2855 2.2661 2.0528 2.0424 1.6218 1.6113 1.6008 1.5924 1.5816 1.5706 1.5632 1.5539 1.5440 1.5336 1.5238 1.5153 1.5050 1.4943 1.4852 1.4754 1.4647 1.4142 1.4085 1.4039 1.3987 1.3845 1.3770 1.3686 1.3631 1.3573 1.3505 1.2669 1.2619 1.2572 1.2373 1.2303 1.2252 1.2193 1.2127 1.2074 1.2029 1.1898 1.1838 1.1794 1.1741 1.0958 1.0916 1.0876 1.0701 1.0659 1.0618
^{1}H-NMR (400 MHz)
Solvent: CDCl$_3$
Scheme 5, 4ag
O
H
H
D
D
(92% D)
0.95
1.00
1.95
1.08
1.08
1.00
1.00
2.11
1.06
2.24
1.07
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
f1 (ppm)

8. Reference

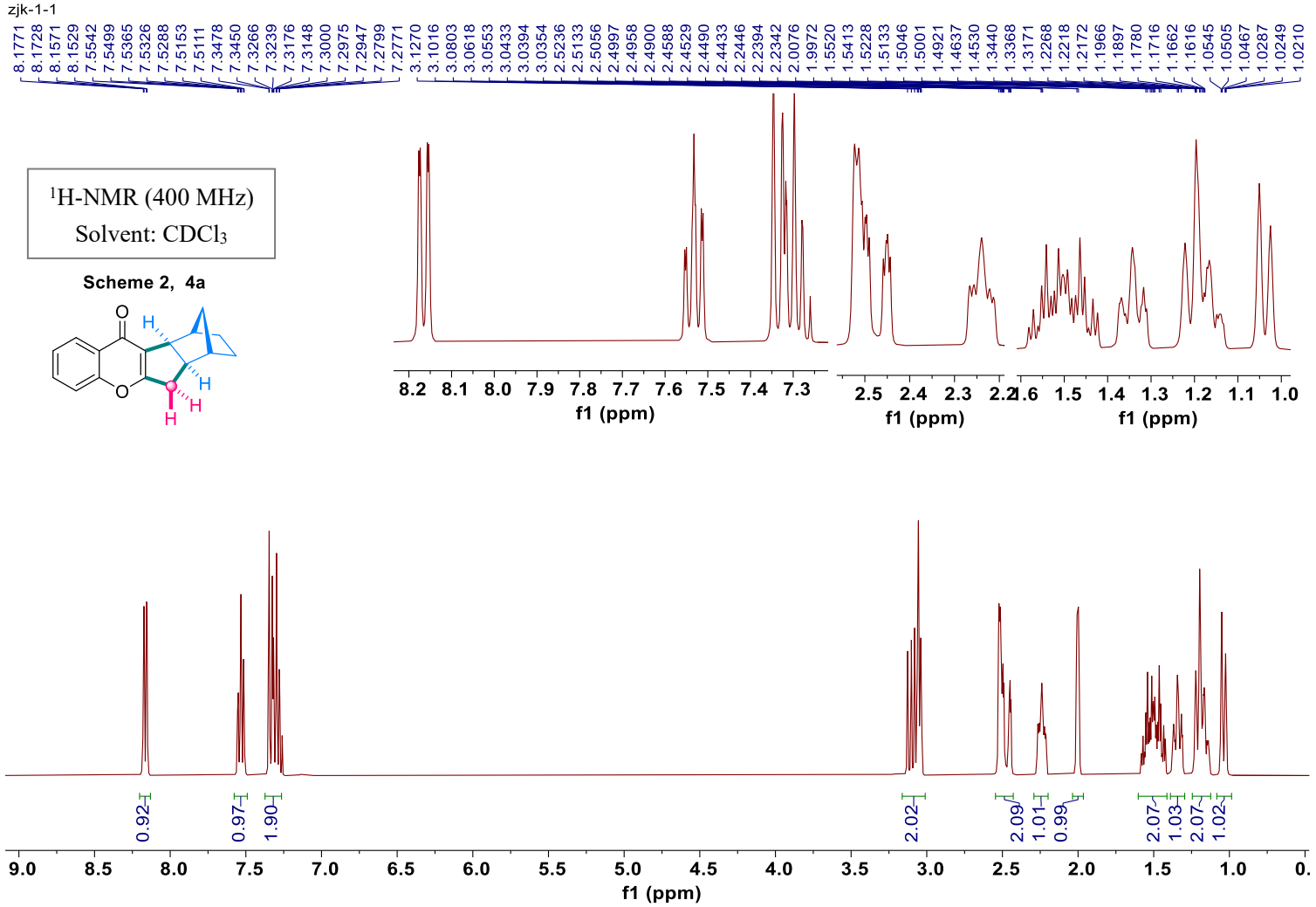
(1) D. A. Vasselin, A. D. Westwell, C. S. Matthews, T. D. Bradshaw and M. F. G. Stevens, *J. Med. Chem.*, 2006, **49**, 3973−3981.

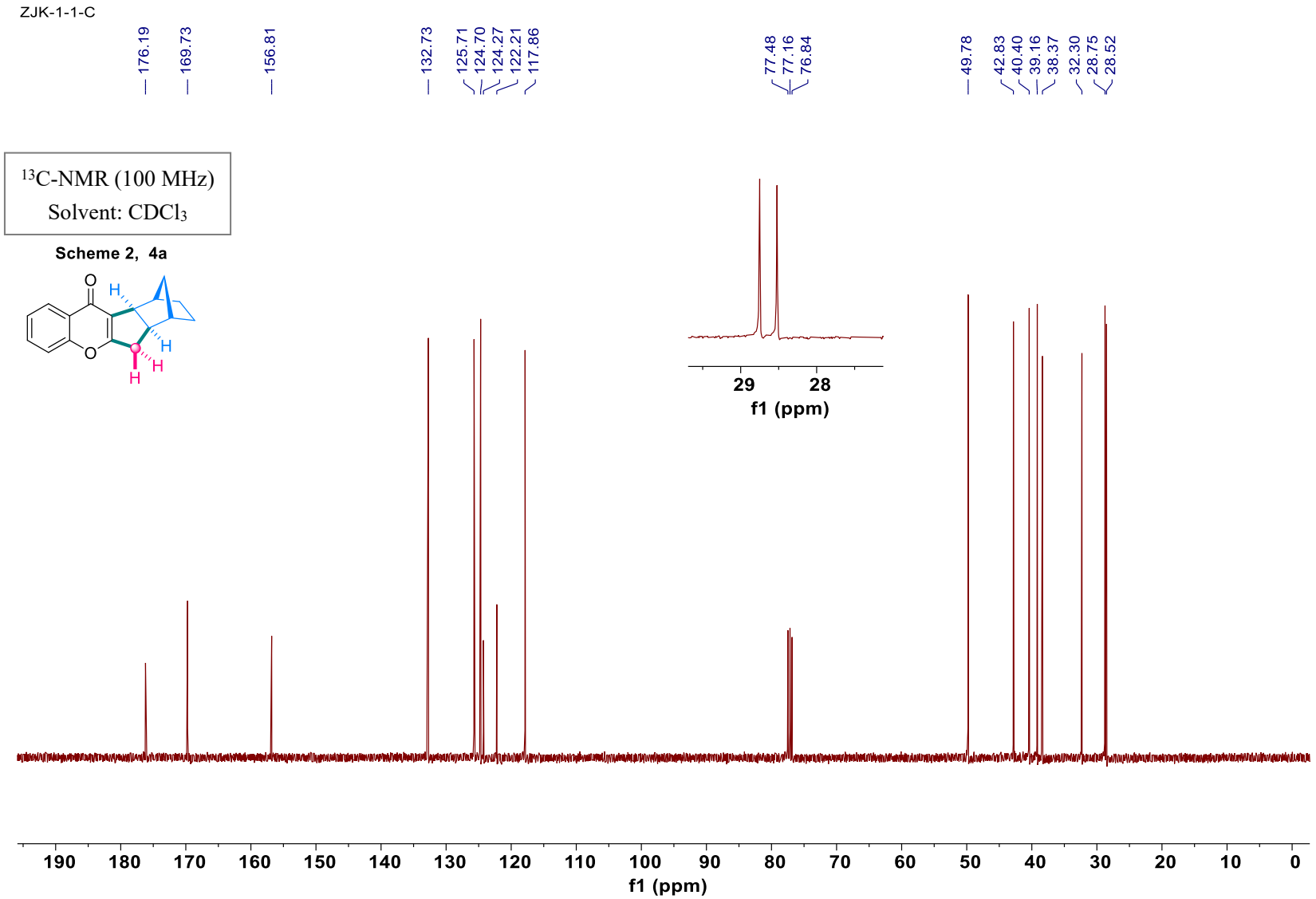
(2) S. Liu, Z. Jin, Y. C. Teo and Y. Xia, *J. Am. Chem. Soc.*, 2014, **136**, 17434−17437.

(3) M. N. Paddon-Row and R. Hartcher, *J. Am. Chem. Soc.*, 1980, **102**, 671−678.

(4) (*a*) W.-Q. Zhu, Y.-C. Fang, W.-Y. Han, F. Li, M.-G. Yang and Y.-Z. Chen, *Org. Chem. Front.*, 2021, **8**, 3082−3090; (*b*) J. Huang, R. Zhang, X. Wu, G. Dong and Y. Xia, *Org. Lett.*, 2022, **24**, 2436−2440; (*c*) F. Li, H.-M. Li, R.-F. Xiu, J.-K. Zhang, B.-D. Cui, N.-W. Wan, Y.-Z. Chen and W.-Y. Han, *Org. Lett.*, 2022, **24**, 9392−9397.

9. ^{1}H and ^{13}C NMR spectra of 4a-ak and 6a-b



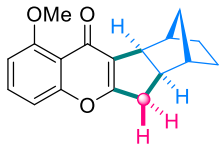

ZJK-1-1-C
176.19
169.73
156.81
132.73
125.71
124.70
124.27
122.21
117.86
77.48
77.16
76.84
49.78
42.83
40.40
39.16
38.37
32.30
28.75
28.52
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 2, 4a
O
H
H
H
H
O
29
28
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

ZJK-24-1-h

7.4716 7.4508 7.4299 7.2606 6.9602 6.9392 6.7634 6.7428 3.9370 3.1249 3.0997 3.0788 3.0550 3.0374 2.5885 2.5784 2.4979 2.4919 2.4875 2.4825 2.4518 2.4458 2.4416 2.4365 2.2872 2.2785 2.2613 2.2422 2.2337 2.0311 2.0209 1.5933 1.5746 1.5635 1.5514 1.5452 1.5356 1.5264 1.5184 1.5090 1.5008 1.4904 1.4795 1.4610 1.4504 1.3934 1.3869 1.3626 1.3419 1.3363 1.3302 1.2661 1.2607 1.2378 1.2310 1.2180 1.2124 1.2055 1.1941 1.1872 1.1677 1.1603 1.1549 1.0779 1.0736 1.0703 1.0515 1.0478 1.0442

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4b

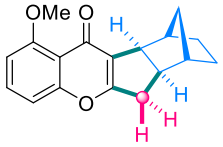


ZJK-24-1-C

176.57
167.23
160.24
159.29
132.81
123.55
115.03
110.25
106.27
77.48
77.16
76.84
56.46
50.07
42.93
40.66
39.09
38.11
32.40
28.82
28.66

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4b

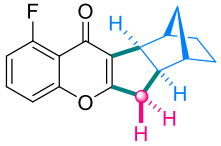


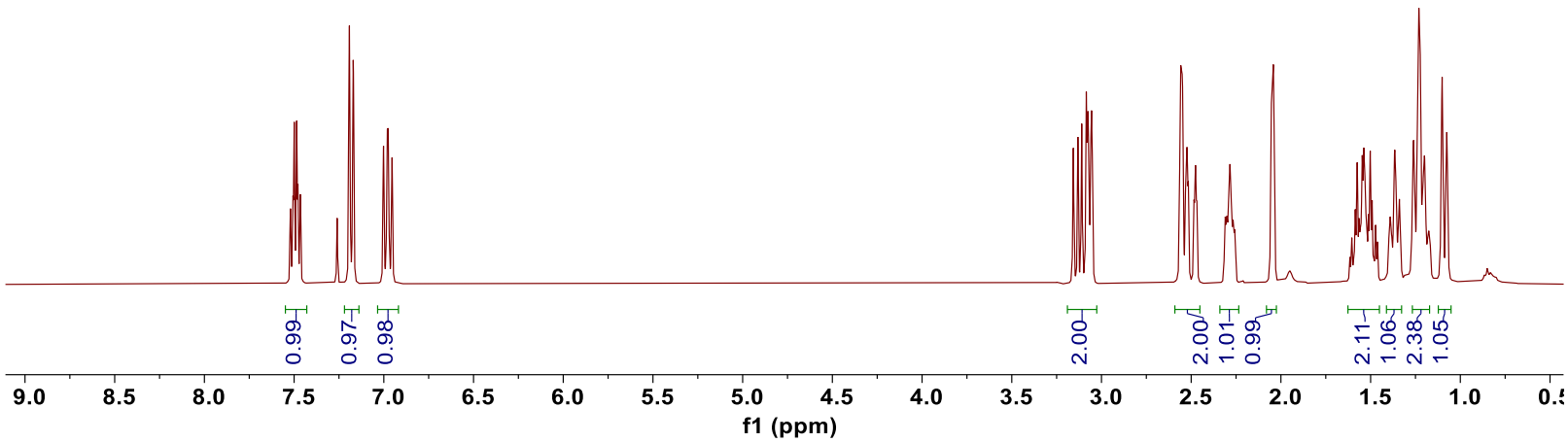
ZJK-23-2-h

7.5203 7.5065 7.4994 7.4857 7.4784 7.4650 7.2601 7.1918 7.1705 7.0016 6.9809 6.9744 6.9542 3.1571 3.1316 3.1102 3.0846 3.0742 3.0552 2.5592 2.5491 2.5311 2.5251 2.5213 2.5153 2.4842 2.4781 2.4743 2.4685 2.3107 2.3014 2.2840 2.2657 2.2562 2.0511 2.0409 1.5857 1.5748 1.5639 1.5565 1.5471 1.5382 1.5301 1.5209 1.5121 1.5020 1.4914 1.4722 1.3964 1.3899 1.3660 1.3590 1.3452 1.3394 1.2654 1.2605 1.2557 1.2385 1.2341 1.2304 1.2242 1.2117 1.2054 1.1996 1.1952 1.1761 1.1051 1.1010 1.0969 1.0794 1.0751 1.0709

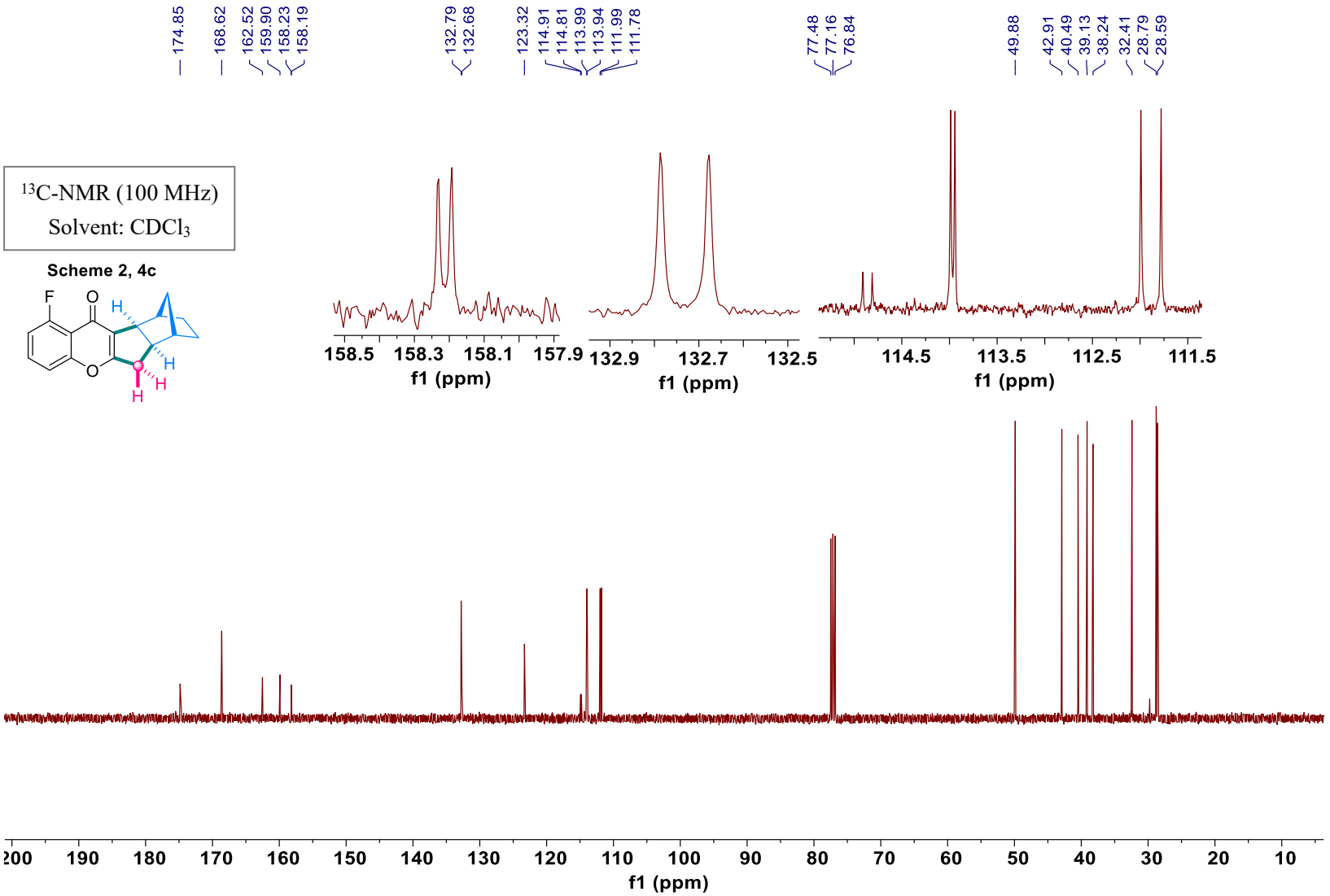
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4c





ZJK-23-2-C



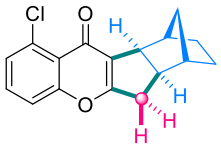
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

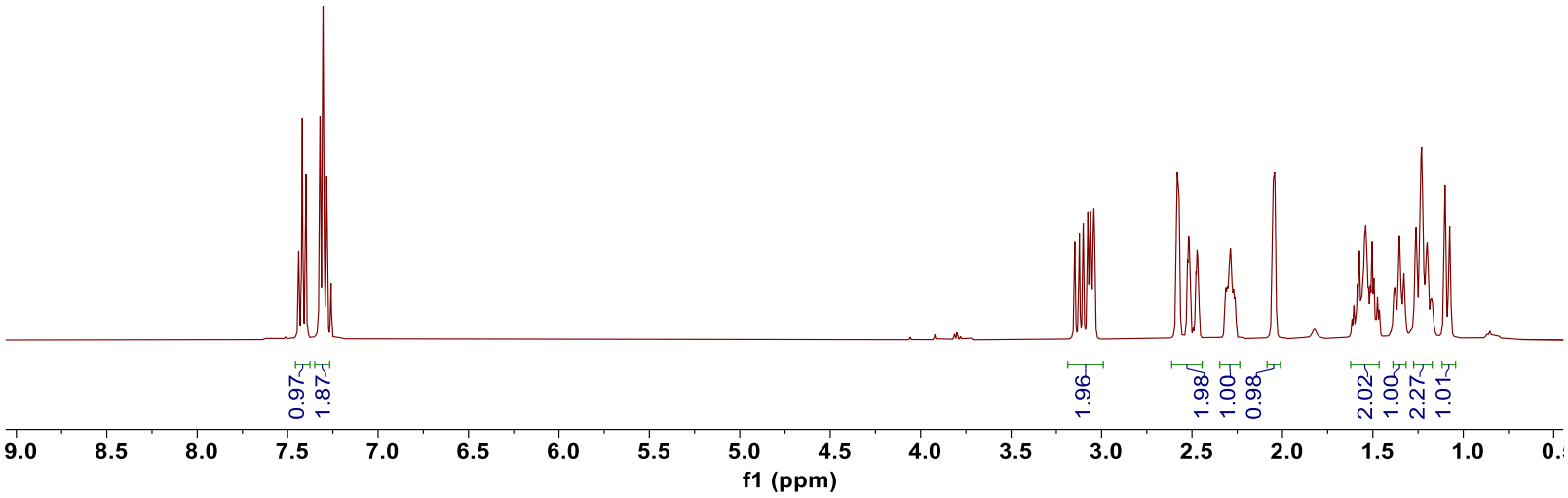
Scheme 2, 4c

ZJK-23-1-h

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4d



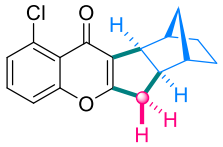


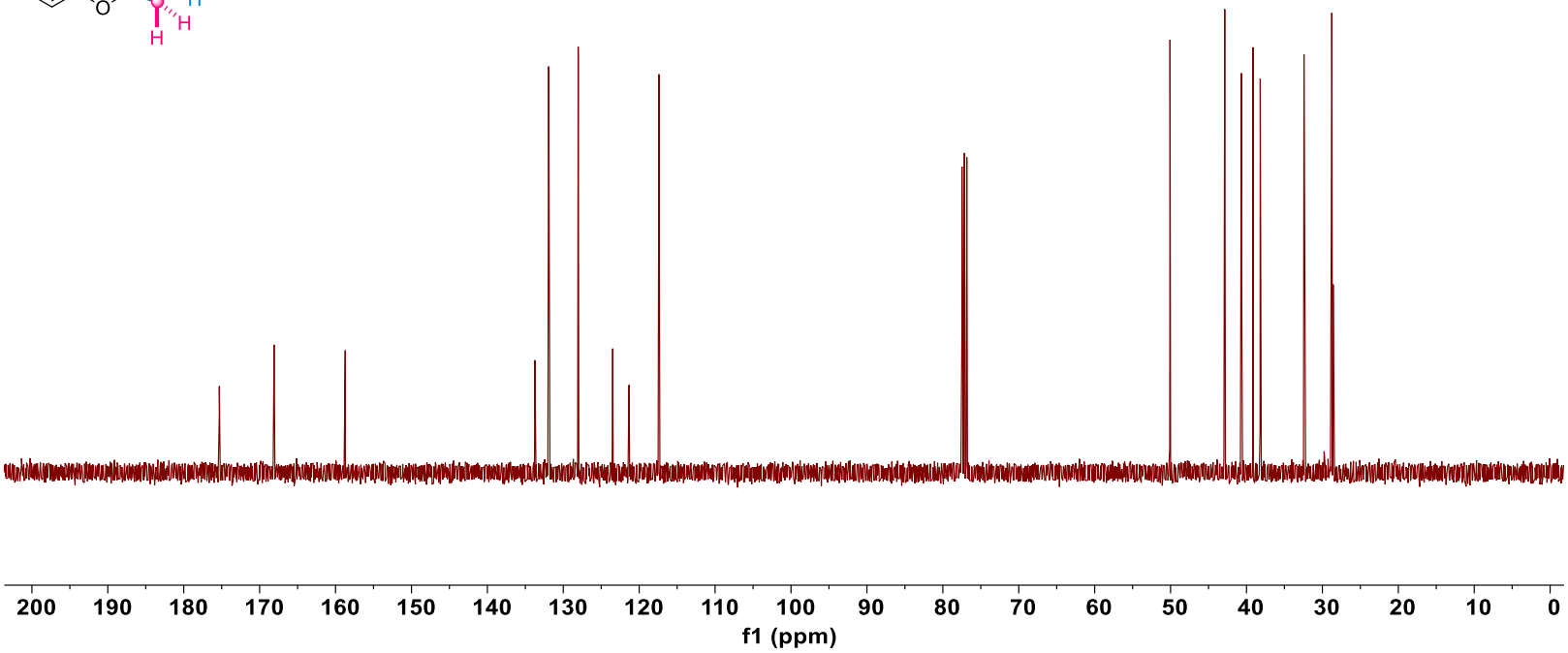
ZJK-23-1-C

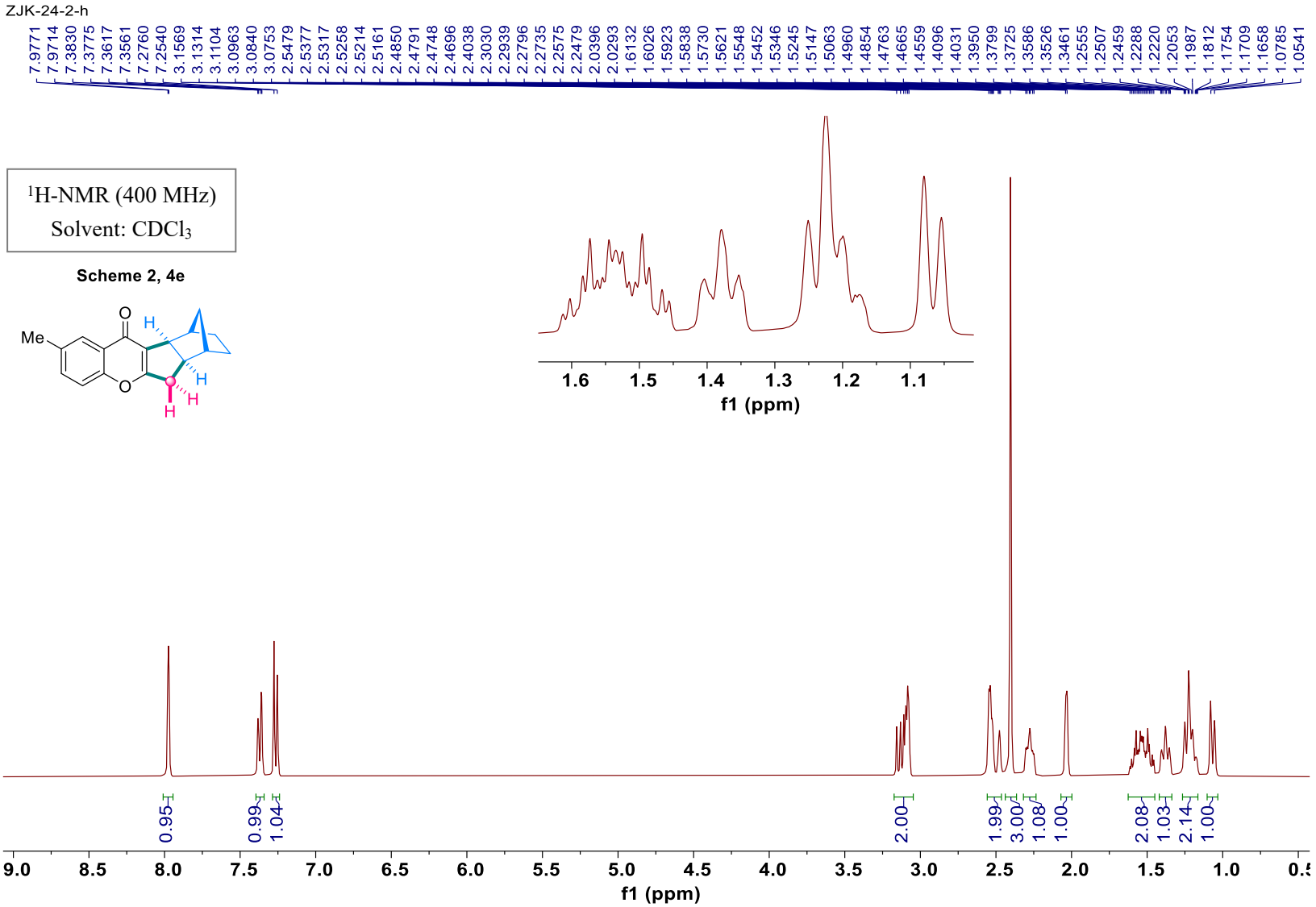
175.31
168.10
158.72
133.74
131.93
128.03
123.50
121.34
117.40
77.48
77.16
76.84
50.08
42.87
40.67
39.13
38.19
32.42
28.76
28.58

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

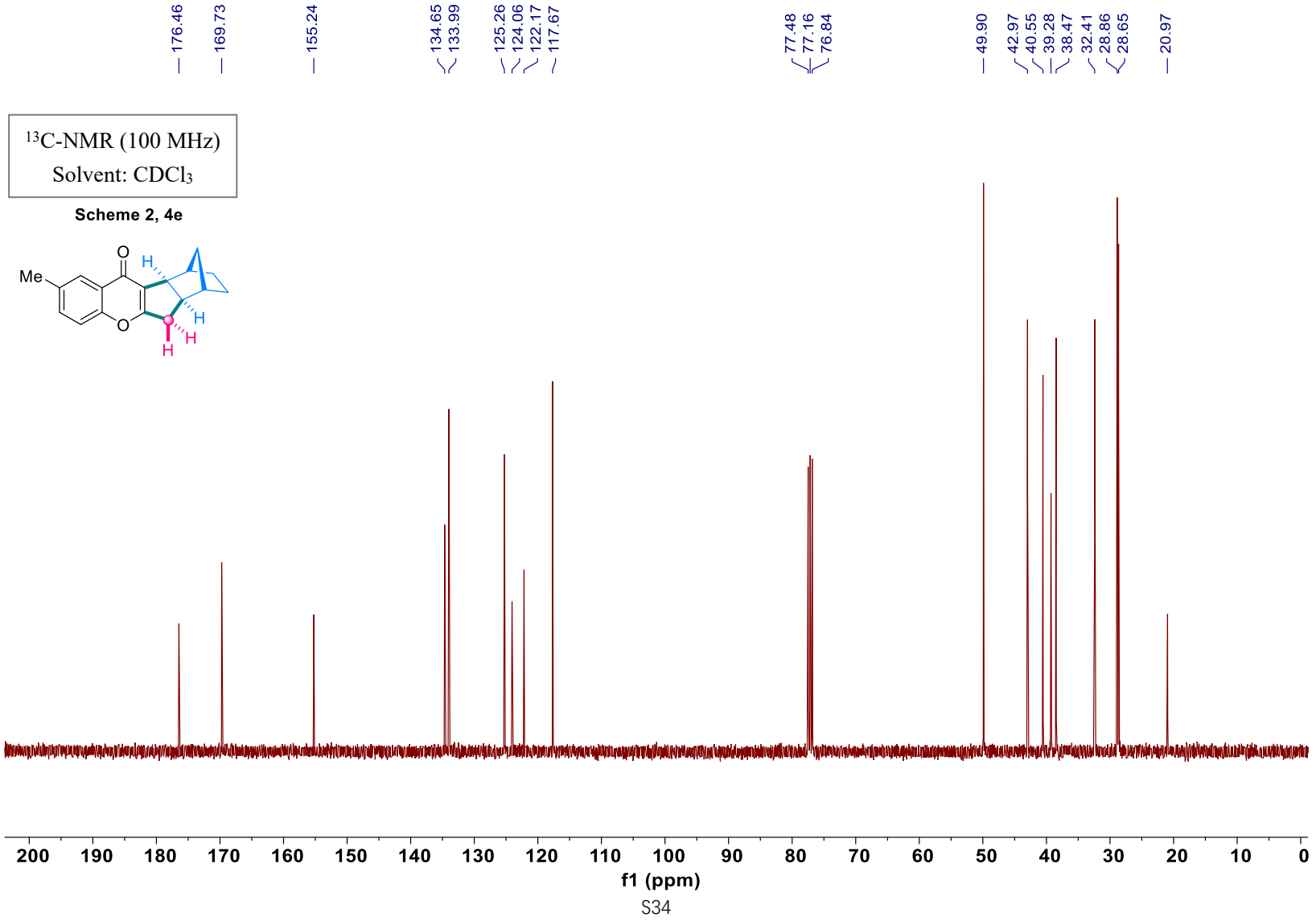
Scheme 2, 4d






ZJK-24-2-h
7.9771 7.9714 7.3830 7.3775 7.3617 7.3561 7.2760 7.2540 3.1569 3.1314 3.1104 3.0963 3.0840 3.0753 2.5479 2.5377 2.5317 2.5258 2.5214 2.5161 2.4850 2.4791 2.4748 2.4696 2.4038 2.3030 2.2939 2.2796 2.2735 2.2575 2.2479 2.0396 2.0293 1.6132 1.6026 1.5923 1.5838 1.5730 1.5621 1.5548 1.5452 1.5346 1.5245 1.5147 1.5063 1.4960 1.4854 1.4763 1.4665 1.4559 1.4096 1.4031 1.3950 1.3799 1.3725 1.3586 1.3526 1.3461 1.2555 1.2507 1.2459 1.2288 1.2220 1.2053 1.1987 1.1812 1.1754 1.1709 1.1658 1.0785 1.0541
1H-NMR (400 MHz)
Solvent: CDCl3
Scheme 2, 4e
Me
O
H
H
H
H
O
1.6 1.5 1.4 1.3 1.2 1.1
f1 (ppm)
0.95 0.99 1.04 2.00 1.99 3.00 1.08 1.00 2.08 1.03 2.14 1.00
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
f1 (ppm)

ZJK-24-2-c

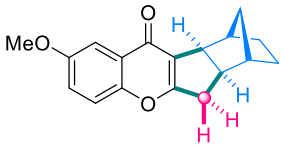

176.46
169.73
155.24
134.65
133.99
125.26
124.06
122.17
117.67
77.48
77.16
76.84
49.90
42.97
40.55
39.28
38.47
32.41
28.86
28.65
20.97
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Scheme 2, 4e
Me
O
H
H
H
H
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

ZJK-25-1-h

7.5725 7.5647 7.3186 7.2959 7.2600 7.1708 7.1636 7.1482 7.1408 3.8769 3.8615 3.1646 3.1392 3.1181 3.1114 3.1067 3.0921 3.0856 2.5574 2.5475 2.5391 2.5322 2.5279 2.5232 2.4919 2.4856 2.4815 2.4766 2.3143 2.3058 2.2921 2.2869 2.2799 2.2696 2.2600 2.0462 2.0360 1.6130 1.5945 1.5836 1.5726 1.5651 1.5554 1.5460 1.5403 1.5318 1.5219 1.5130 1.5029 1.4924 1.4842 1.4736 1.4630 1.4202 1.4136 1.4052 1.3910 1.3833 1.3692 1.3630 1.3564 1.2548 1.2286 1.2120 1.2067 1.2026 1.1890 1.1826 1.1787 1.1738 1.0864 1.0609

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4f

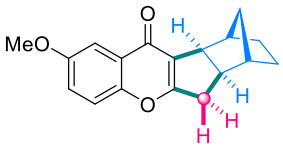


ZJK-25-1-C

176.14
169.74
156.67
151.75
125.02
122.59
121.70
119.25
105.19
77.48
77.16
76.84
55.92
49.88
42.99
40.61
39.26
38.42
32.41
28.86
28.65

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4f

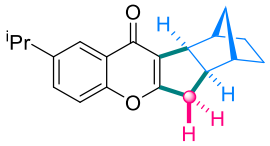


ZJK-2-10-1-1-h

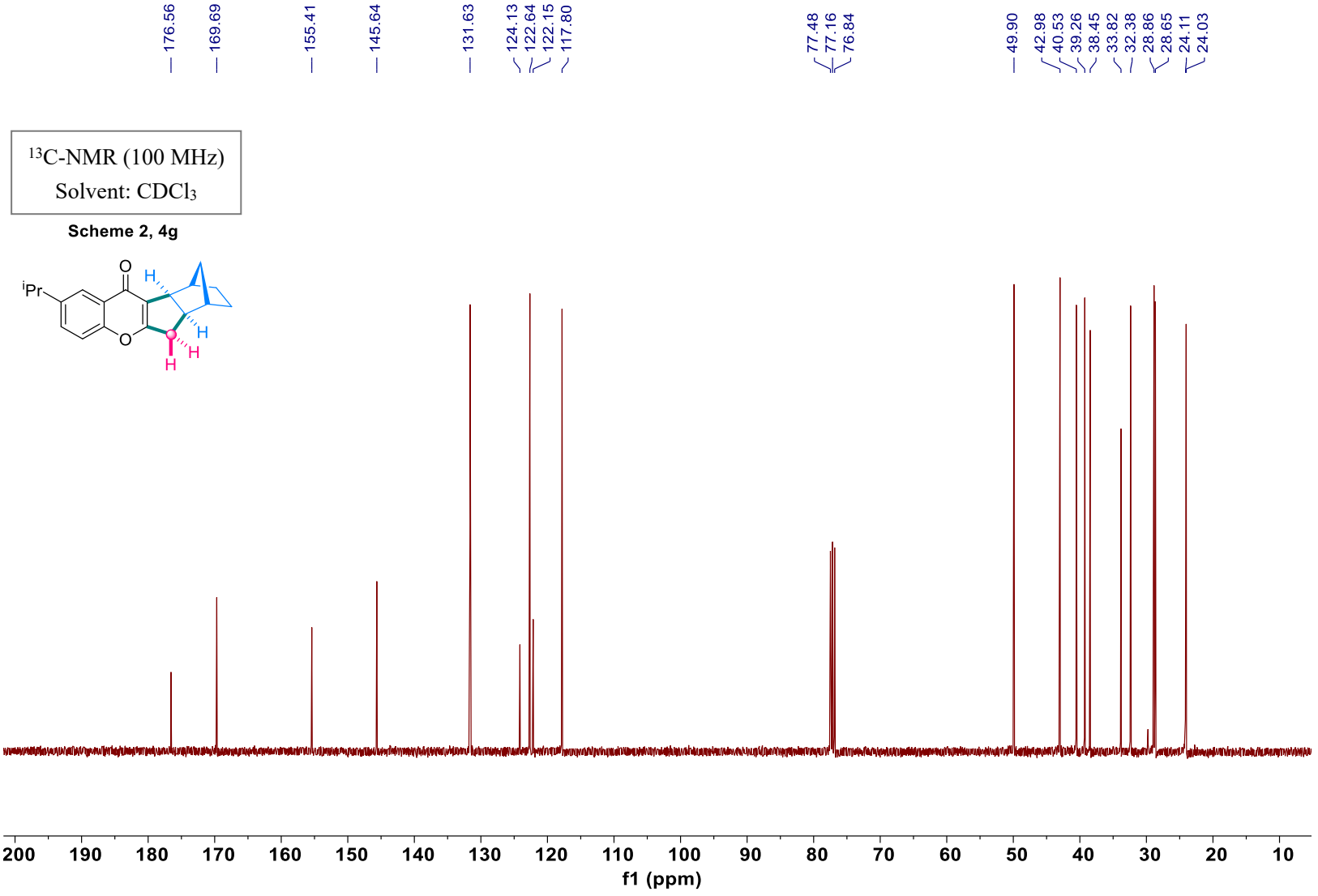
8.0480 8.0423 7.4624 7.4566 7.4410 7.4351 7.3217 7.3003 7.2604 3.1617 3.1362 3.1145 3.1061 3.0890 3.0310 3.0138 2.9966 2.9792 2.9620 2.5562 2.5461 2.5340 2.5284 2.5242 2.4874 2.4817 2.4774 2.4719 2.3059 2.3023 2.2948 2.2778 2.2594 2.2500 2.0393 2.0289 1.5897 1.5792 1.5683 1.5607 1.5508 1.5416 1.5359 1.5272 1.5173 1.5086 1.4985 1.4879 1.4692 1.4197 1.4137 1.4080 1.3904 1.3826 1.3682 1.3617 1.3551 1.2696 1.2521 1.2260 1.2206 1.2153 1.2075 1.2027 1.1986 1.1845 1.1761 1.0813 1.0766 1.0550 1.0512 1.0473

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4g



ZJK-2-10-1-C

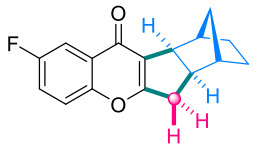

176.56
169.69
155.41
145.64
131.63
124.13
122.64
122.15
117.80
77.48
77.16
76.84
49.90
42.98
40.53
39.26
38.45
33.82
32.38
28.86
28.65
24.11
24.03
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 2, 4g
iPr
O
H
H
H
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

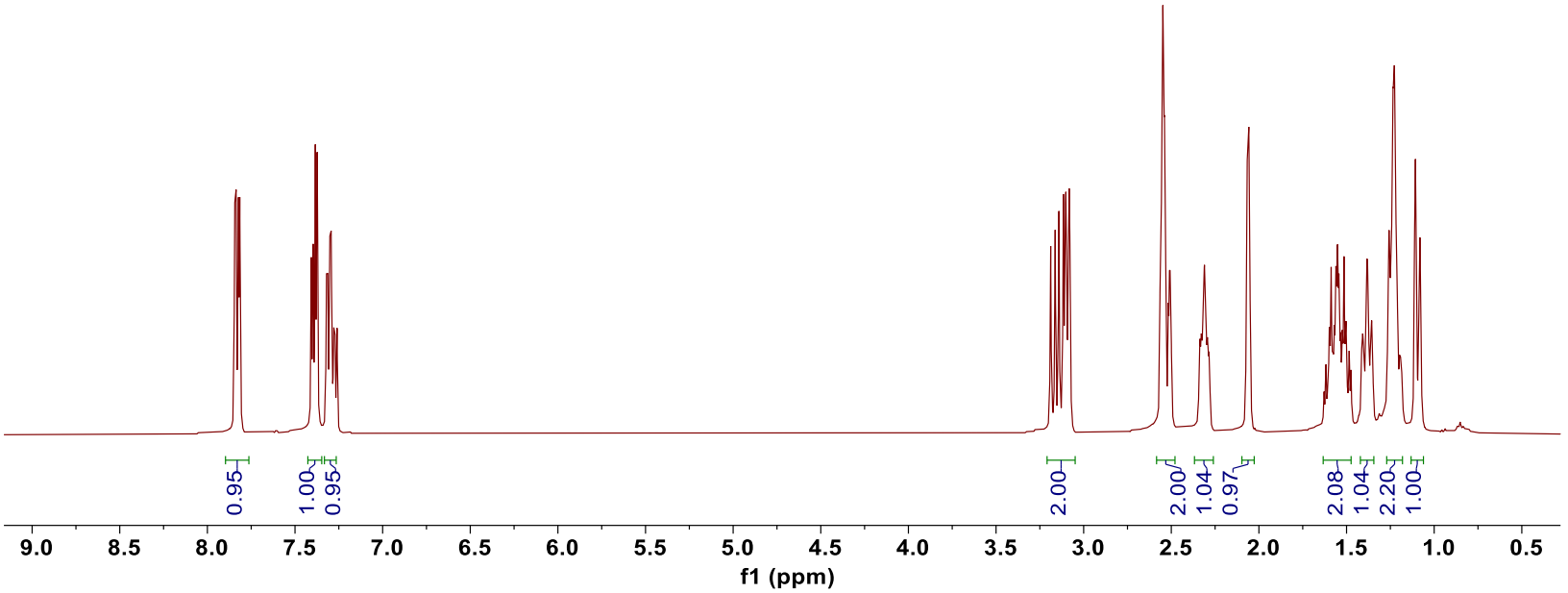
ZJK-25-2-h

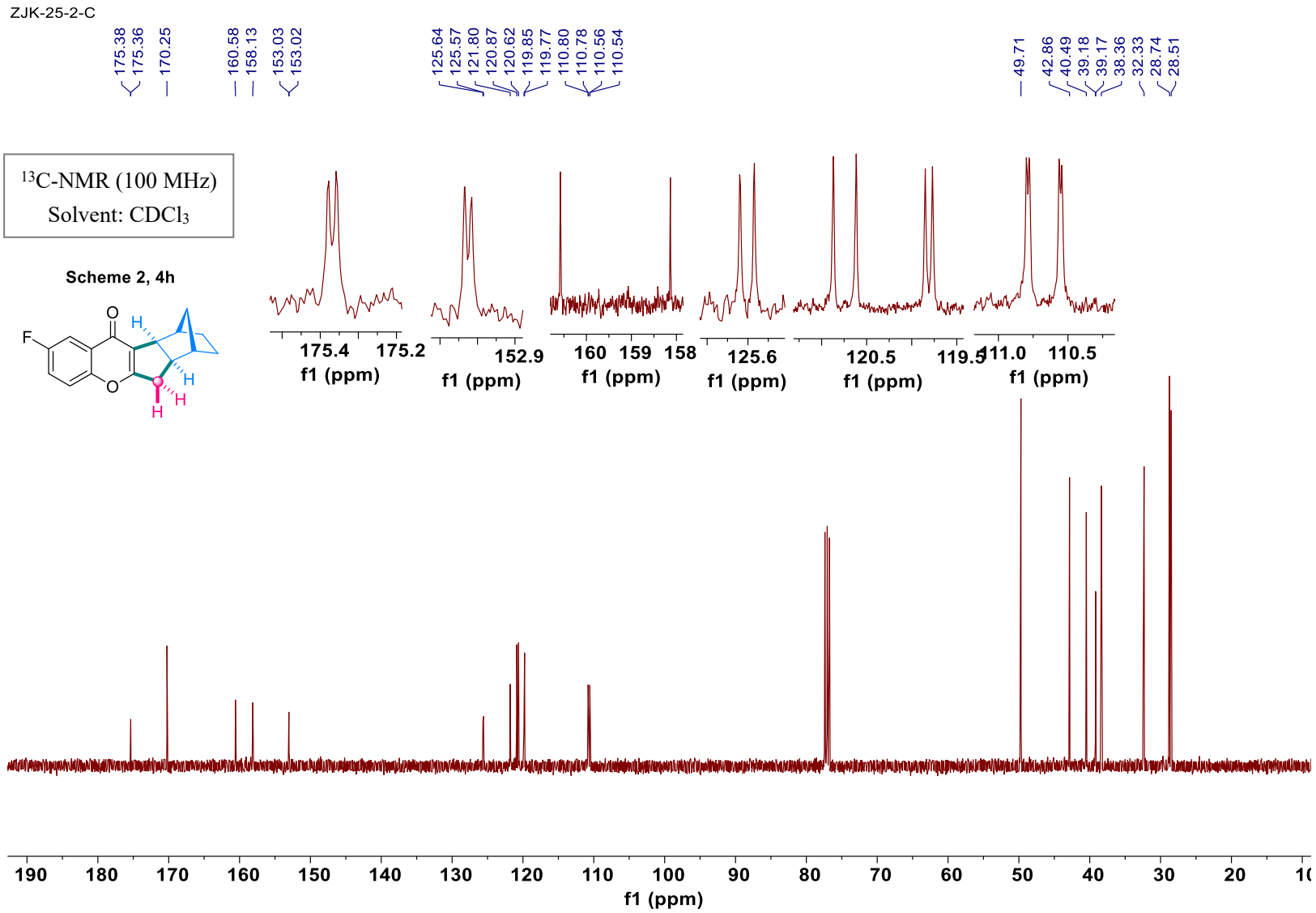
7.8440 7.8364 7.8228 7.8151 7.4072 7.3967 7.3844 7.3739 7.3205 7.3129 7.3015 7.2971 7.2936 7.2894 7.2789 7.2711 7.2602 3.1882 3.1628 3.1413 3.1159 3.1016 3.0822 2.5638 2.5580 2.5534 2.5478 2.5376 2.5167 2.5109 2.5066 2.5012 2.3387 2.3296 2.3196 2.3157 2.3107 2.3050 2.2934 2.0664 2.0562 1.5986 1.5878 1.5770 1.5693 1.5600 1.5514 1.5428 1.5335 1.5245 1.5145 1.5040 1.4139 1.4079 1.4033 1.3846 1.3769 1.3629 1.3568 1.2624 1.2577 1.2528 1.2477 1.2416 1.2363 1.2314 1.2265 1.2206 1.2154 1.2109 1.1069 1.0810

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4h





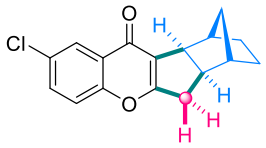

ZJK-25-2-C
175.38
175.36
170.25
160.58
158.13
153.03
153.02
125.64
125.57
121.80
120.87
120.62
119.85
119.77
110.80
110.78
110.56
110.54
49.71
42.86
40.49
39.18
39.17
38.36
32.33
28.74
28.51
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 2, 4h
F
O
H
O
H
H
H
175.4
175.2
f1 (ppm)
152.9
f1 (ppm)
160
159
158
f1 (ppm)
125.6
f1 (ppm)
120.5
119.5
f1 (ppm)
111.0
110.5
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

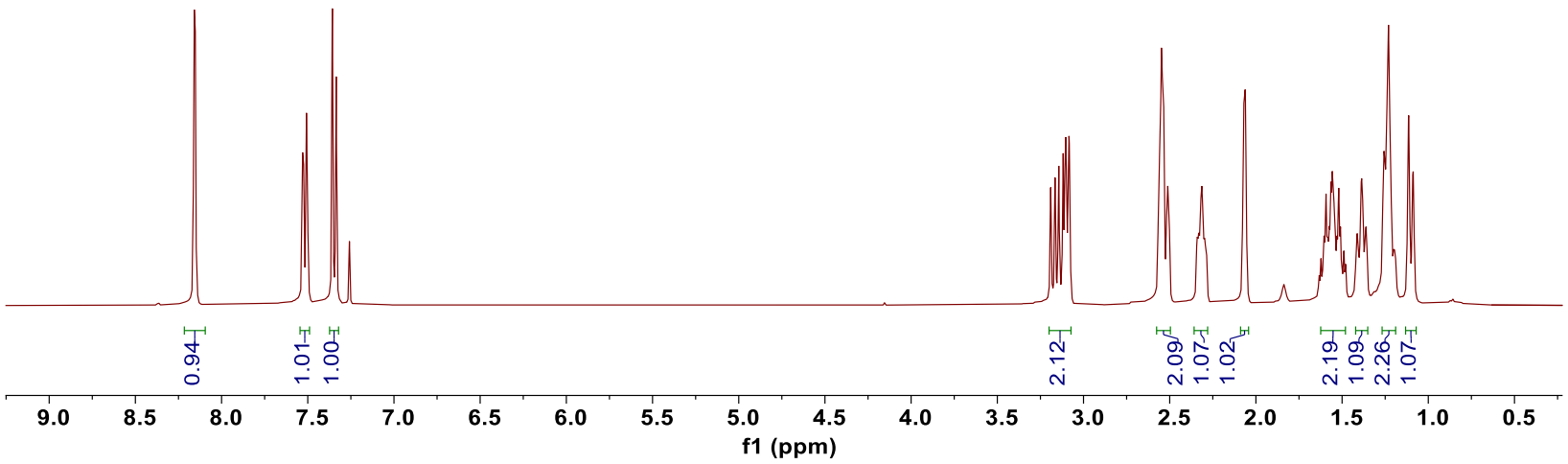
ZJK-26-1-h

8.1581 8.1522 7.5338 7.5301 7.5241 7.5116 7.5077 7.5018 7.3581 7.3359 7.2617 7.2584 3.1909 3.1656 3.1439 3.1184 3.1034 3.0840 2.5646 2.5581 2.5489 2.5432 2.5358 2.5173 2.5113 2.5069 2.5021 2.3417 2.3322 2.3224 2.3177 2.3128 2.3075 2.2965 2.2867 2.0711 2.0609 1.6228 1.6040 1.5930 1.5816 1.5746 1.5654 1.5562 1.5478 1.5383 1.5294 1.5194 1.5086 1.4898 1.4791 1.4178 1.4108 1.3891 1.3824 1.3661 1.3606 1.3547 1.2624 1.2571 1.2514 1.2387 1.2293 1.2012 1.1955 1.1908 1.1168 1.1125 1.1090 1.0908 1.0864 1.0828

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4i



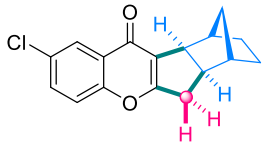


ZJK-26-1-C

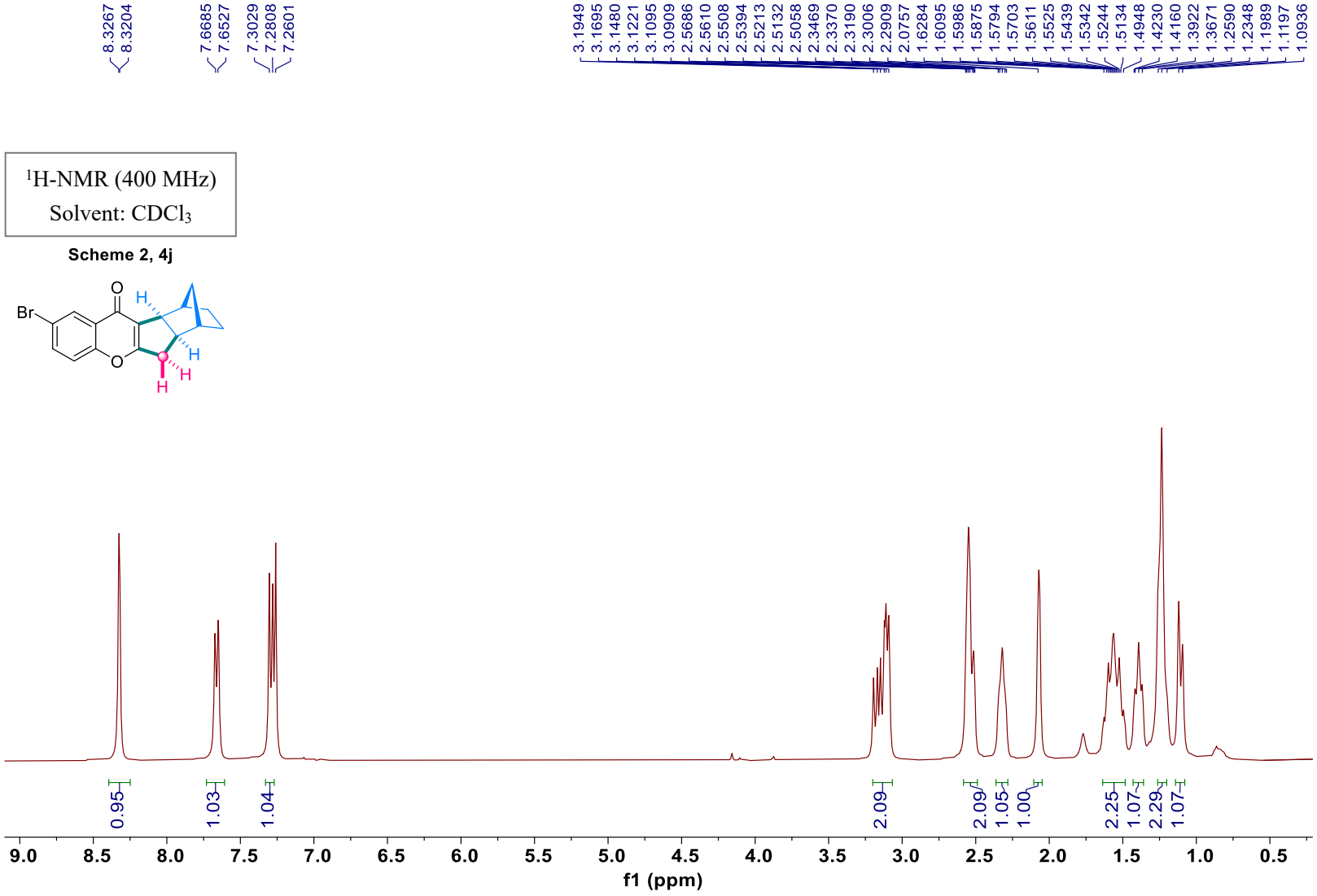
175.09
170.23
155.29
132.97
130.75
125.49
125.36
122.53
119.68
77.48
77.16
76.84
49.86
42.97
40.57
39.28
38.48
32.45
28.85
28.61

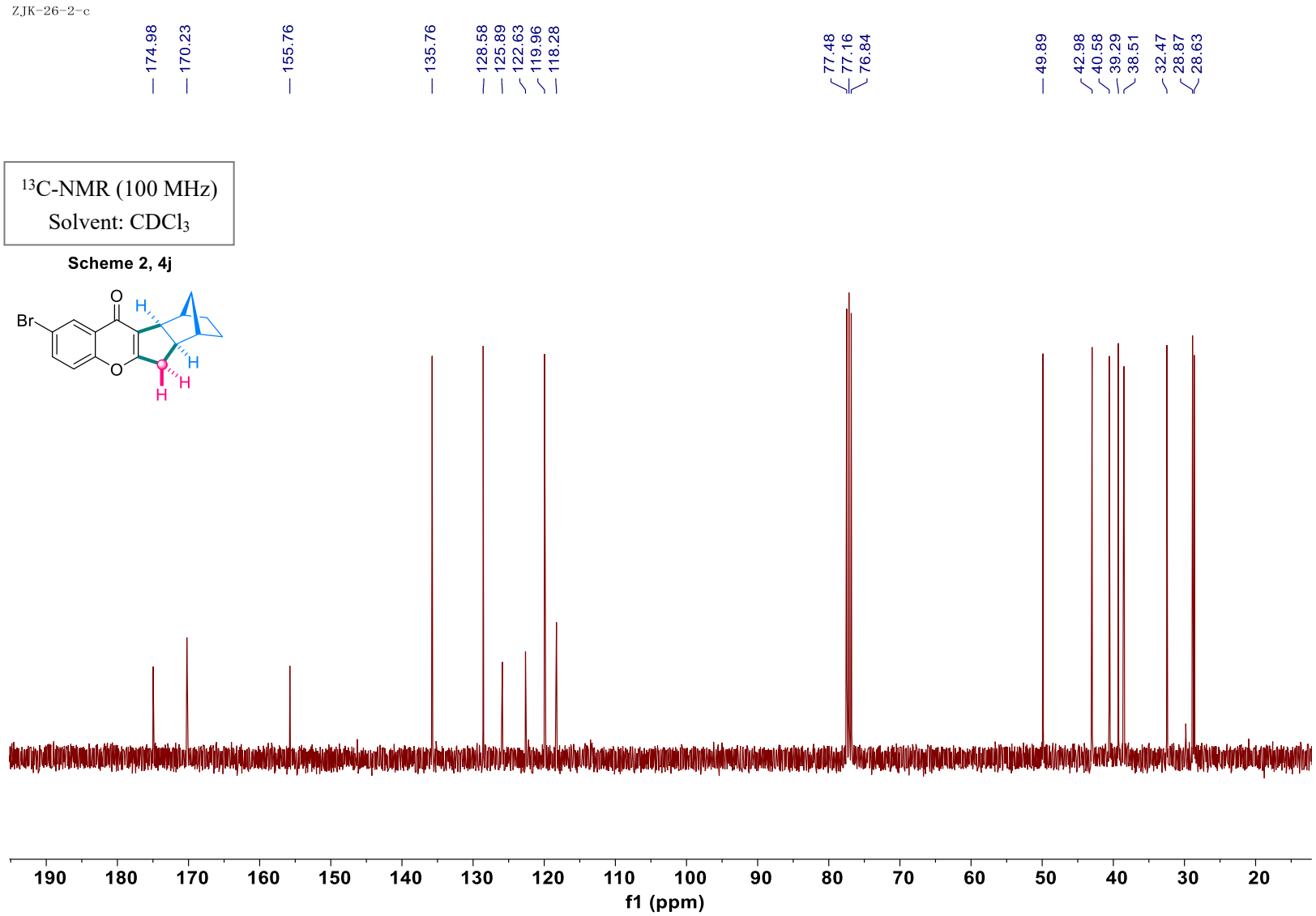
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4i



ZJK-26-2-h

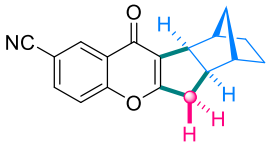

8.3267
8.3204
7.6685
7.6527
7.3029
7.2808
7.2601
3.1949
3.1695
3.1480
3.1221
3.1095
3.0909
2.5686
2.5610
2.5508
2.5394
2.5213
2.5132
2.5058
2.3469
2.3370
2.3190
2.3006
2.2909
2.0757
1.6284
1.6095
1.5986
1.5875
1.5794
1.5703
1.5611
1.5525
1.5439
1.5342
1.5244
1.5134
1.4948
1.4230
1.4160
1.3922
1.3671
1.2590
1.2348
1.1989
1.1197
1.0936
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
Scheme 2, 4j
Br
O
H
H
H
H
O
0.95
1.03
1.04
2.09
2.09
1.05
1.00
2.25
1.07
2.29
1.07
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
f1 (ppm)

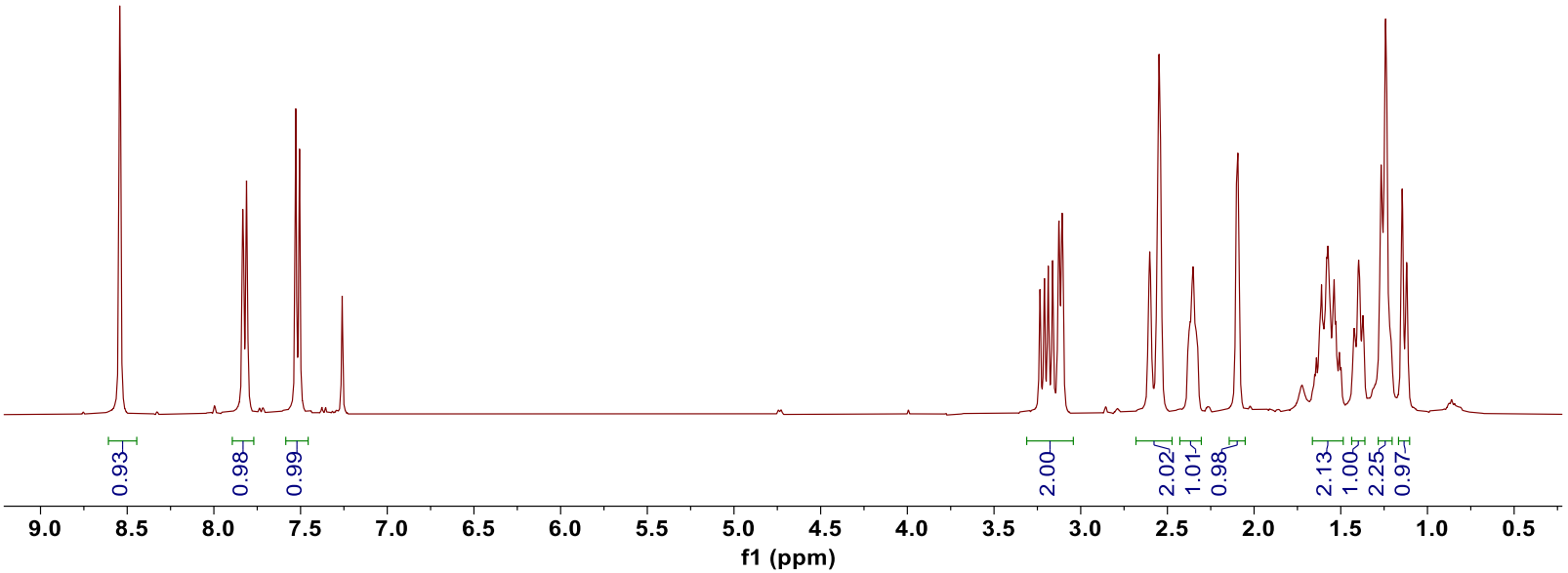

ZJK-26-2-c
174.98
170.23
155.76
135.76
128.58
125.89
122.63
119.96
118.28
77.48
77.16
76.84
49.89
42.98
40.58
39.29
38.51
32.47
28.87
28.63
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 2, 4j
Br
O
H
H
H
H
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

ZJK-27-1-h

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4k



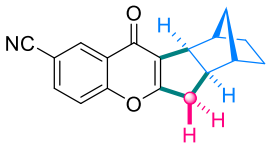


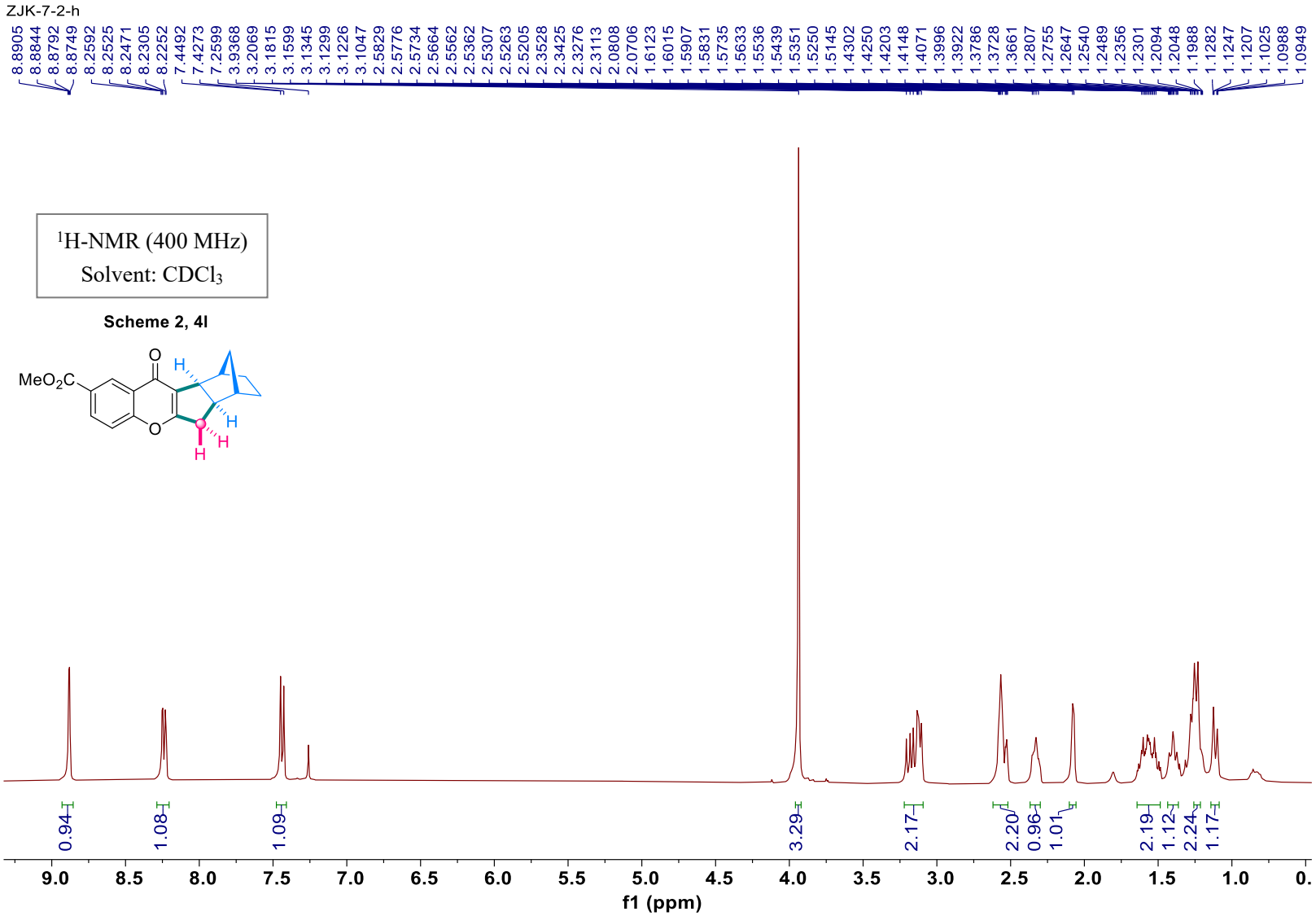
ZJK-27-1-c

174.38
170.53
158.72
135.27
131.67
124.97
123.49
119.74
117.89
109.04
77.48
77.16
76.84
49.82
42.94
40.52
39.27
38.49
32.49
28.84
28.56

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4k



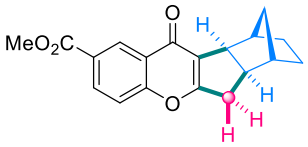

ZJK-7-2-h
8.8905 8.8844 8.8792 8.8749 8.2592 8.2525 8.2471 8.2305 8.2252 7.4492 7.4273 7.2599 3.9368 3.2069 3.1815 3.1599 3.1345 3.1299 3.1226 3.1047 2.5829 2.5776 2.5734 2.5664 2.5562 2.5362 2.5307 2.5263 2.5205 2.3528 2.3425 2.3276 2.3113 2.0808 2.0706 1.6123 1.6015 1.5907 1.5831 1.5735 1.5633 1.5536 1.5439 1.5351 1.5250 1.5145 1.4302 1.4250 1.4203 1.4148 1.4071 1.3996 1.3922 1.3786 1.3728 1.3661 1.2807 1.2755 1.2647 1.2540 1.2489 1.2356 1.2301 1.2094 1.2048 1.1988 1.1282 1.1247 1.1207 1.1025 1.0988 1.0949
¹H-NMR (400 MHz)
Solvent: CDCl₃
Scheme 2, 4l
MeO2C
O
H
H
H
O
H
0.94
1.08
1.09
3.29
2.17
2.20
0.96
1.01
2.19
1.12
2.24
1.17
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.
f1 (ppm)

ZJK-7-2-C

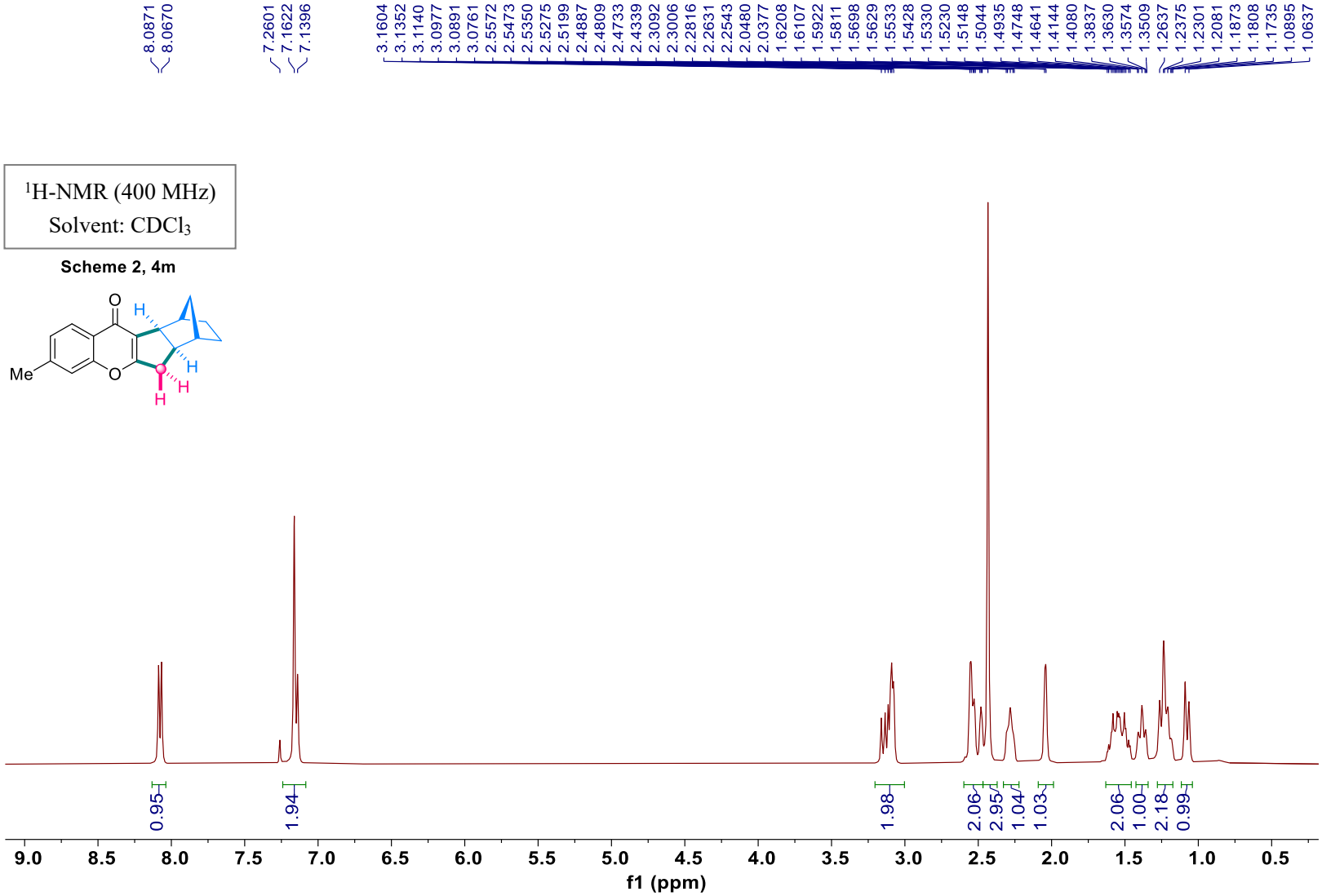
175.69
170.07
166.08
159.46
133.59
128.48
126.93
124.21
123.03
118.47
77.48
77.16
76.84
52.50
49.86
42.99
40.58
39.29
38.47
32.48
28.88
28.62

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4l



ZJK-27-2-h



^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

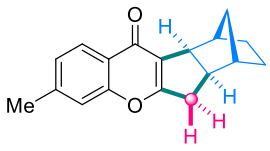
Scheme 2, 4m

ZJK-27-2-C

176.37
169.51
157.12
143.98
126.26
125.59
122.17
122.15
117.76
77.48
77.16
76.84
49.88
42.96
40.54
39.29
38.46
32.41
28.86
28.65
21.77

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4m

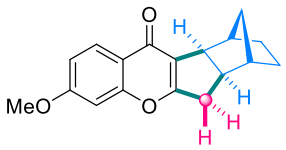


ZJK-28-1-h

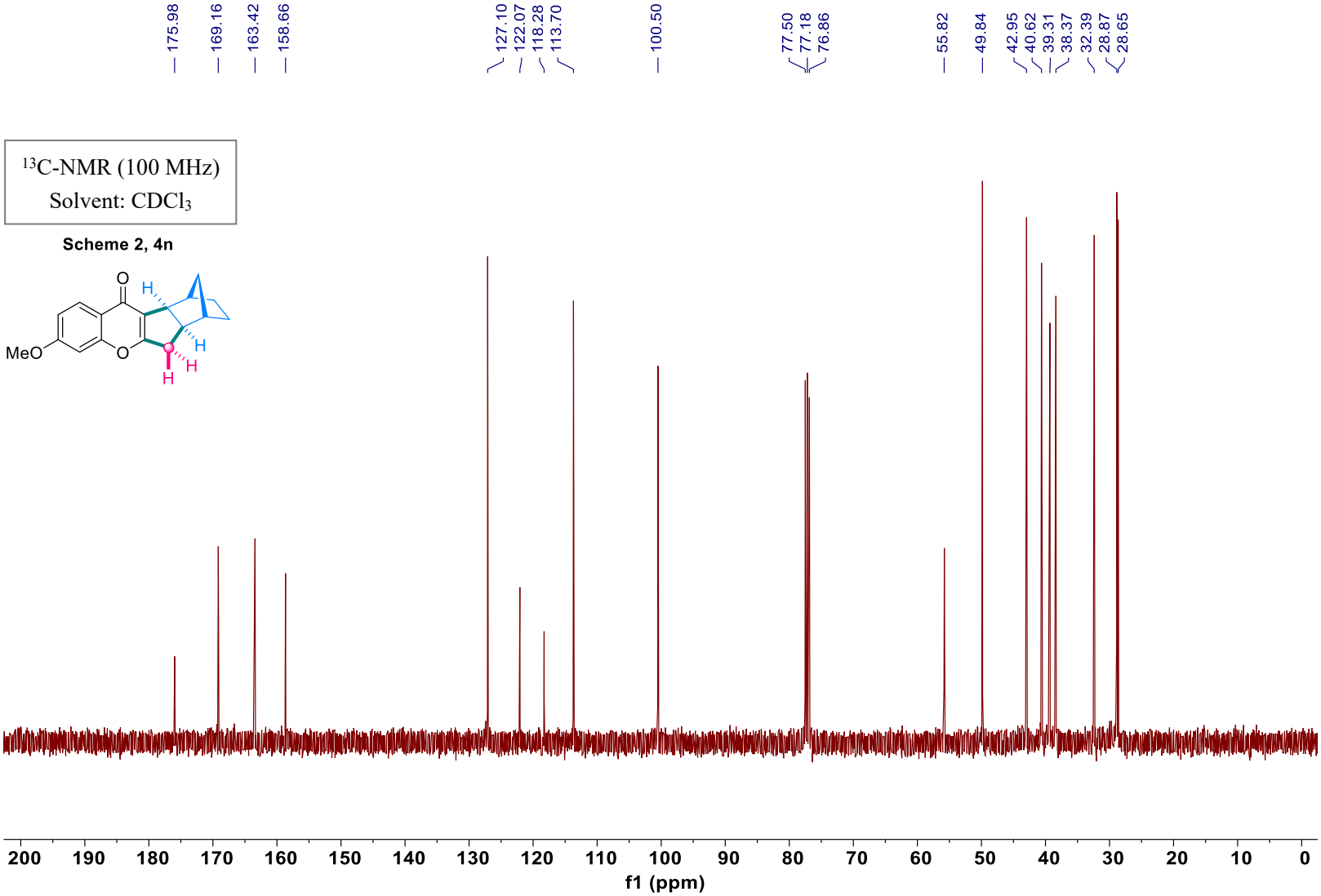
8.0951
8.0731
7.2610
6.9089
6.9020
6.8804
6.7694
3.8403
3.1336
3.1086
3.0879
3.0642
3.0478
2.5386
2.5289
2.5032
2.4947
2.4630
2.4563
2.4486
2.2920
2.2842
2.2653
2.2477
2.2391
2.0321
2.0219
1.6079
1.5976
1.5888
1.5791
1.5681
1.5588
1.5508
1.5397
1.5300
1.5203
1.5118
1.5027
1.4914
1.4812
1.4619
1.4518
1.3928
1.3660
1.3407
1.2591
1.2322
1.2198
1.1916
1.1650
1.0778
1.0521

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4n



ZJK-28-1-C

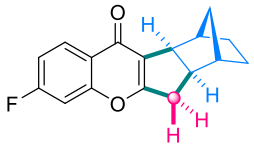

175.98
169.16
163.42
158.66
127.10
122.07
118.28
113.70
100.50
77.50
77.18
76.86
55.82
49.84
42.95
40.62
39.31
38.37
32.39
28.87
28.65
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 2, 4n
MeO
O
H
H
H
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

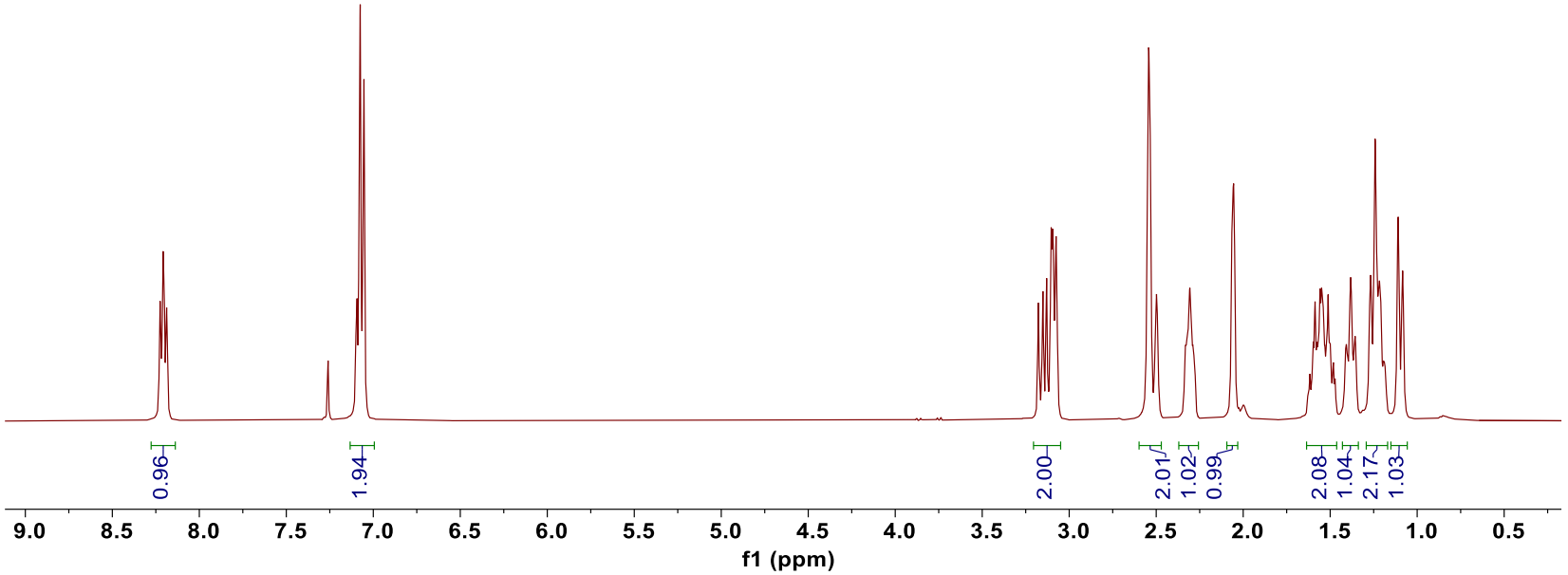
ZJK-28-2-h

8.2256 8.2084 8.2014 8.1866 7.2605 7.0988 7.0932 7.0792 7.0744 7.0541 3.1770 3.1516 3.1302 3.1040 3.0937 3.0751 2.5516 2.5449 2.5363 2.5050 2.4974 2.4899 2.3334 2.3239 2.3062 2.2876 2.2784 2.0630 2.0527 1.6271 1.6167 1.6037 1.5975 1.5867 1.5752 1.5681 1.5589 1.5491 1.5401 1.5302 1.5219 1.5116 1.5008 1.4919 1.4819 1.4712 1.4107 1.4057 1.3830 1.3617 1.3560 1.3502 1.2723 1.2668 1.2417 1.2242 1.2172 1.2106 1.1943 1.1882 1.1835 1.1785 1.1094 1.0834

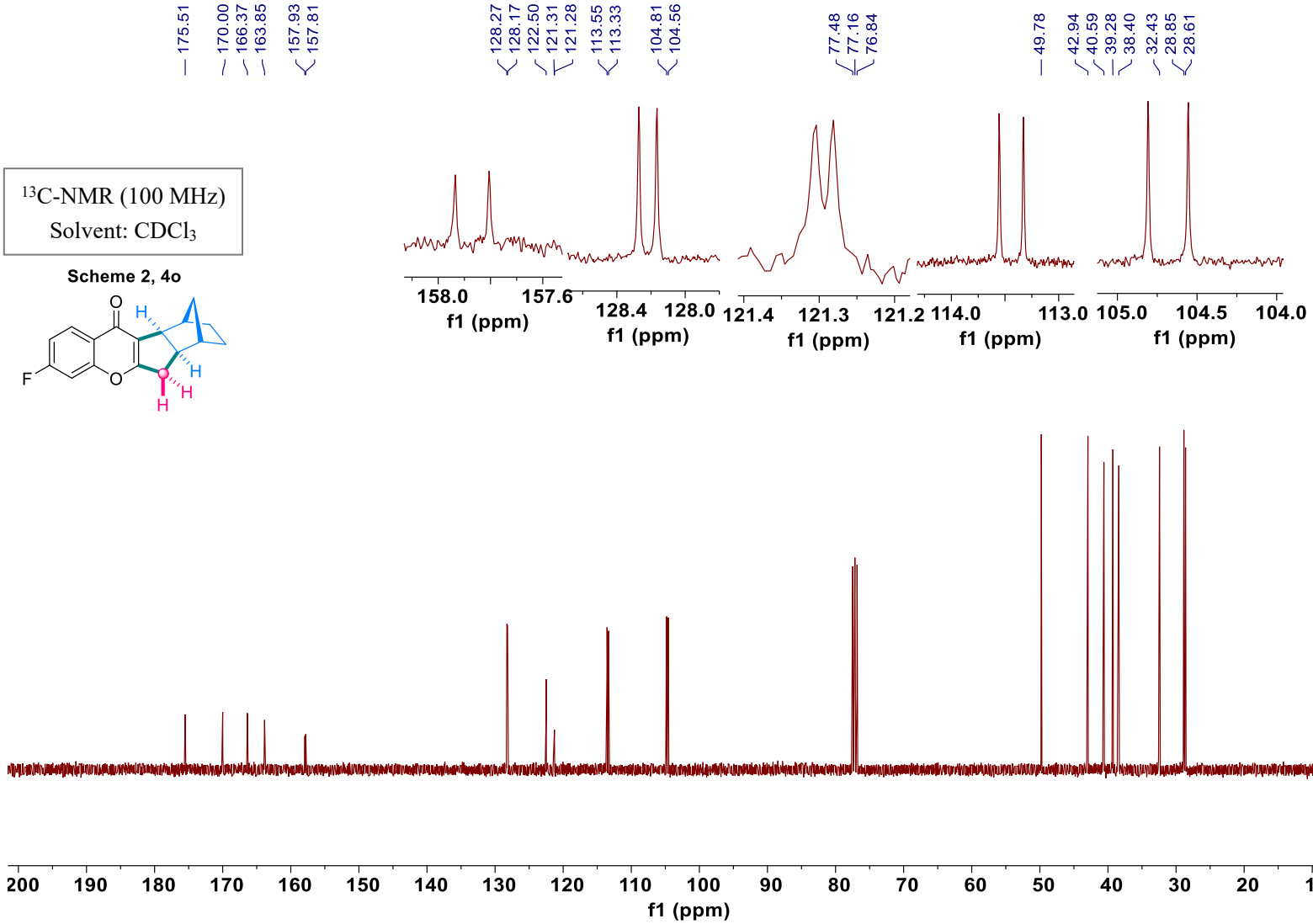
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4o





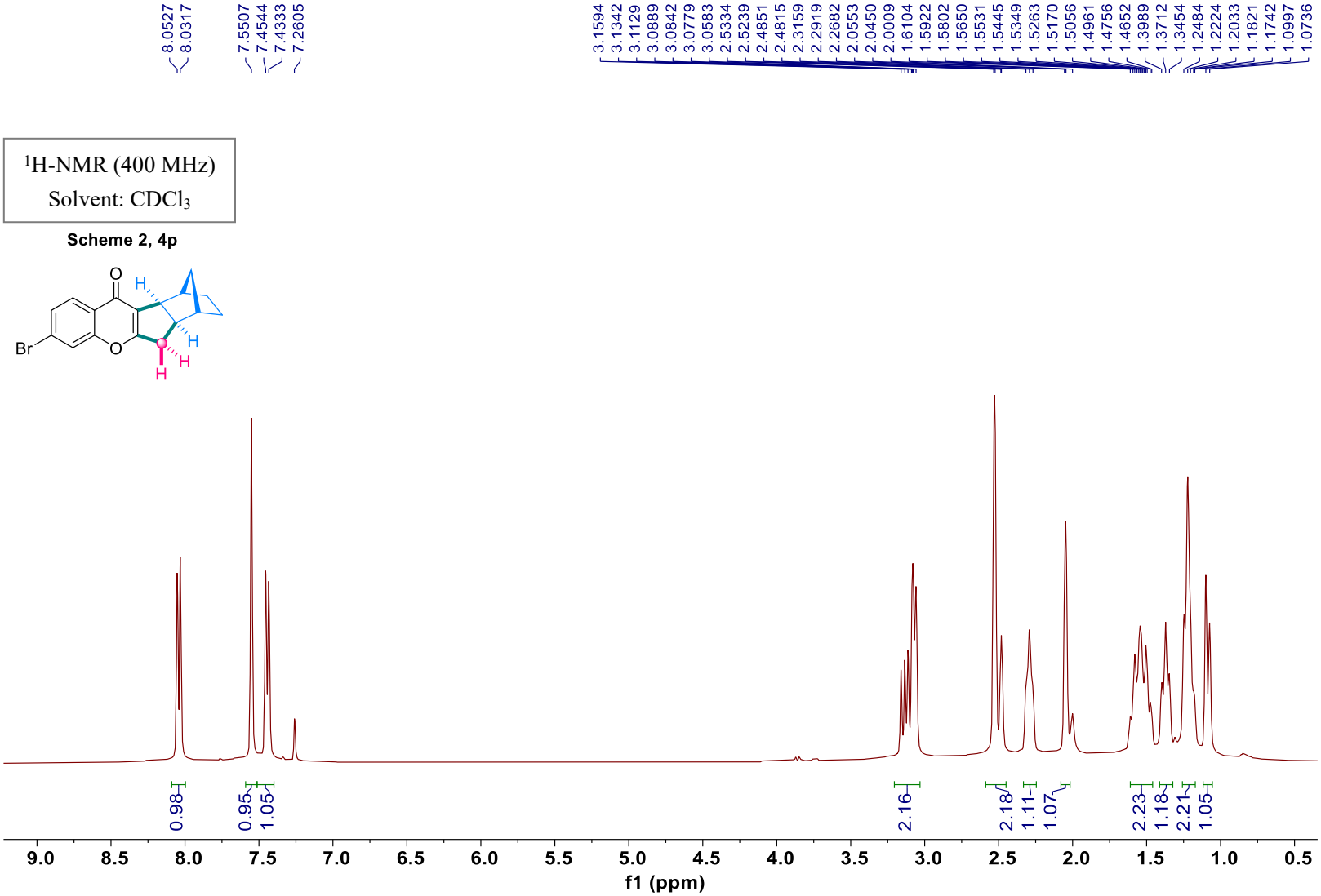
ZJK-28-2-C



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4o

ZJK-29-1-h

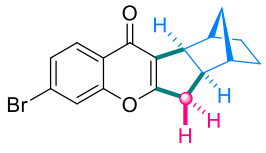

8.0527
8.0317
7.5507
7.4544
7.4333
7.2605
3.1594
3.1342
3.1129
3.0889
3.0842
3.0779
3.0583
2.5334
2.5239
2.4851
2.4815
2.3159
2.2919
2.2682
2.0553
2.0450
2.0009
1.6104
1.5922
1.5802
1.5650
1.5531
1.5445
1.5349
1.5263
1.5170
1.5056
1.4961
1.4756
1.4652
1.3989
1.3712
1.3454
1.2484
1.2224
1.2033
1.1821
1.1742
1.0997
1.0736
1H-NMR (400 MHz)
Solvent: CDCl3
Scheme 2, 4p
O
H
Br
O
H
H
H
0.98
0.95
1.05
2.16
2.18
1.11
1.07
2.23
1.18
2.21
1.05
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
f1 (ppm)

ZJK-29-1-C

175.55
169.87
156.99
128.38
127.29
126.86
123.37
122.74
121.08
77.48
77.16
76.84
49.84
42.93
40.53
39.25
38.43
32.42
28.83
28.59

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4p



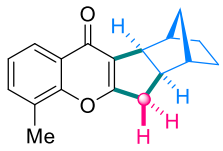
ZJK-29-2-h

8.0494 8.0296 7.4034 7.3853 7.2592 7.2341 7.2150 7.1958

3.1885 3.1633 3.1421 3.1171 3.0998 3.0799 2.5712 2.5628 2.5571 2.5520 2.5254 2.5216 2.5167 2.5096 2.4158 2.3120 2.3040 2.2864 2.2682 2.2588 2.0515 2.0413 1.6195 1.6091 1.6002 1.5906 1.5794 1.5695 1.5623 1.5515 1.5416 1.5320 1.5232 1.5145 1.5035 1.4934 1.4737 1.4641 1.4081 1.3810 1.3580 1.3513 1.2688 1.2629 1.2371 1.2078 1.1834 1.1765 1.0865 1.0606

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4q

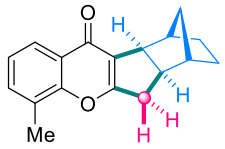


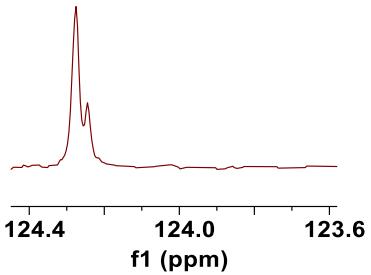
ZJK-29-2-C

176.65 169.56 155.45 133.80 127.28 124.28 124.24 123.44 122.07 77.48 77.16 76.84 49.89 42.96 40.53 39.25 38.54 32.39 28.84 28.64 15.73

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4q

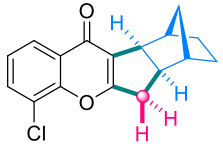


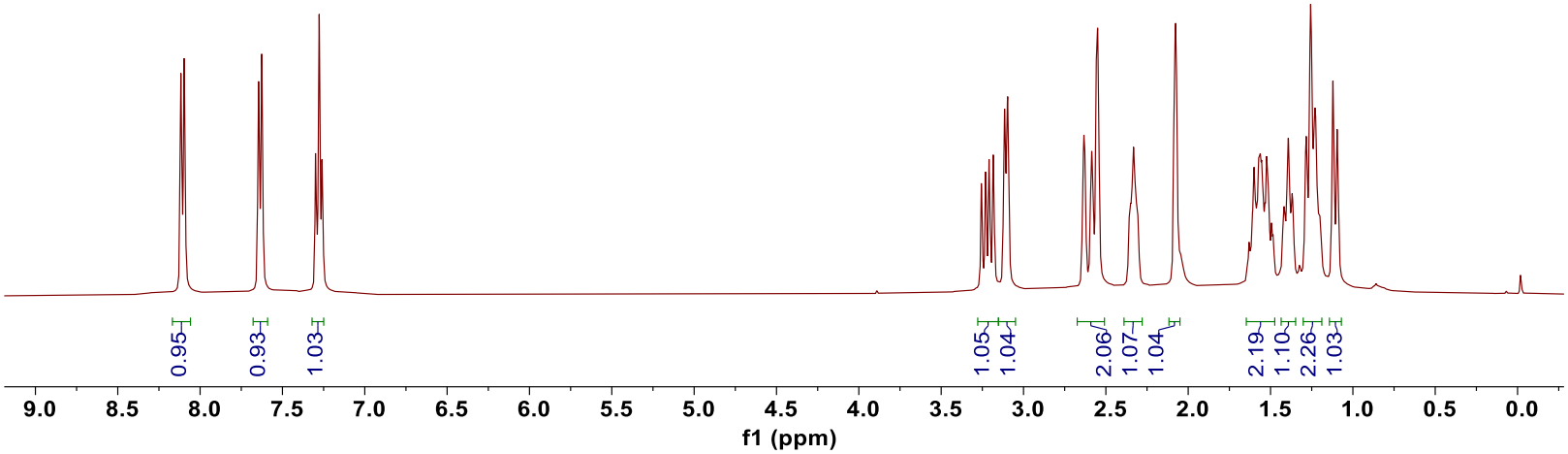


ZJK-30-1-h

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4r



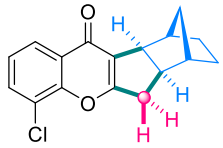


ZJK-30-1-C

175.54
169.87
152.59
133.18
125.89
124.87
124.55
122.94
122.68
77.48
77.16
76.84
49.82
42.95
40.55
39.23
38.46
32.42
28.84
28.59

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4r

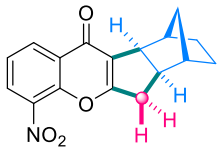


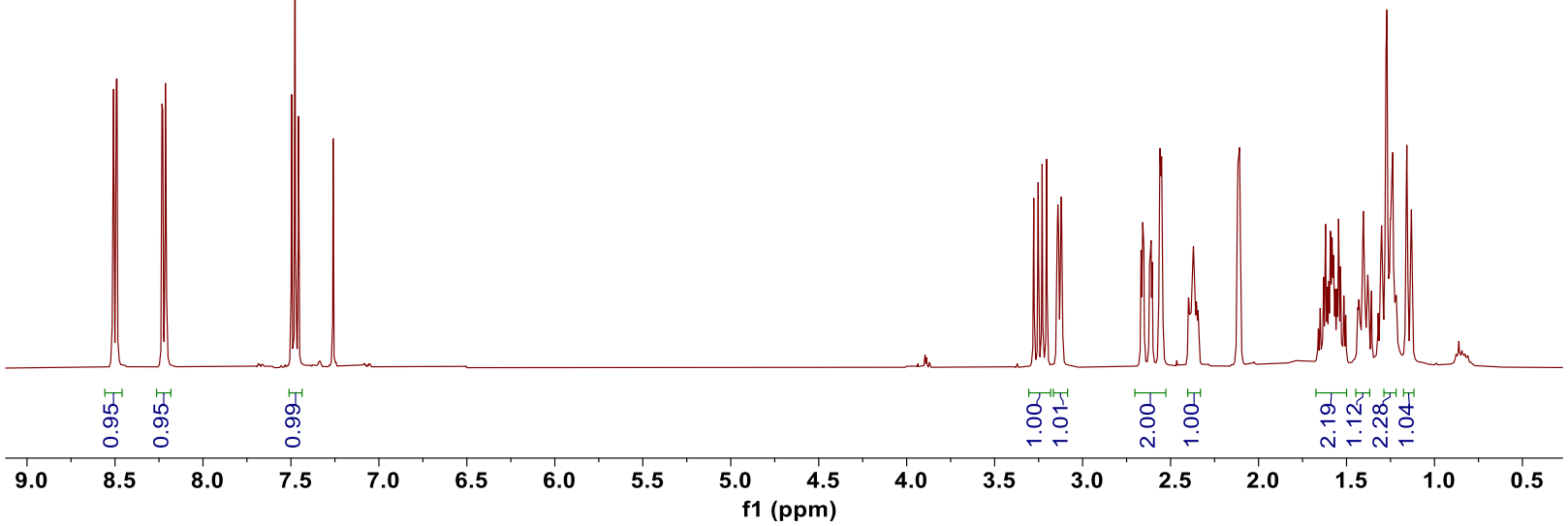
ZJK-34-1-h

8.5126 8.5082 8.4928 8.4884 8.2331 8.2287 8.2133 8.2090 7.4965 7.4766 7.4569 7.2600 3.2778 3.2523 3.2299 3.2045 3.1405 3.1211 2.6679 2.6617 2.6580 2.6520 2.6199 2.6139 2.6102 2.6042 2.5605 2.5503 2.3990 2.3798 2.3751 2.3699 2.3649 2.1176 2.1073 1.6301 1.6194 1.6086 1.6008 1.5915 1.5841 1.5816 1.5744 1.5712 1.5639 1.5552 1.5450 1.5343 1.5150 1.4119 1.4076 1.4042 1.3981 1.3787 1.2848 1.2760 1.2699 1.2641 1.2578 1.2514 1.2464 1.2410 1.2363 1.2286 1.2228 1.2172 1.1610 1.1572 1.1534 1.1350 1.1311 1.1273

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4s



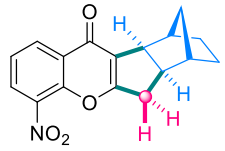


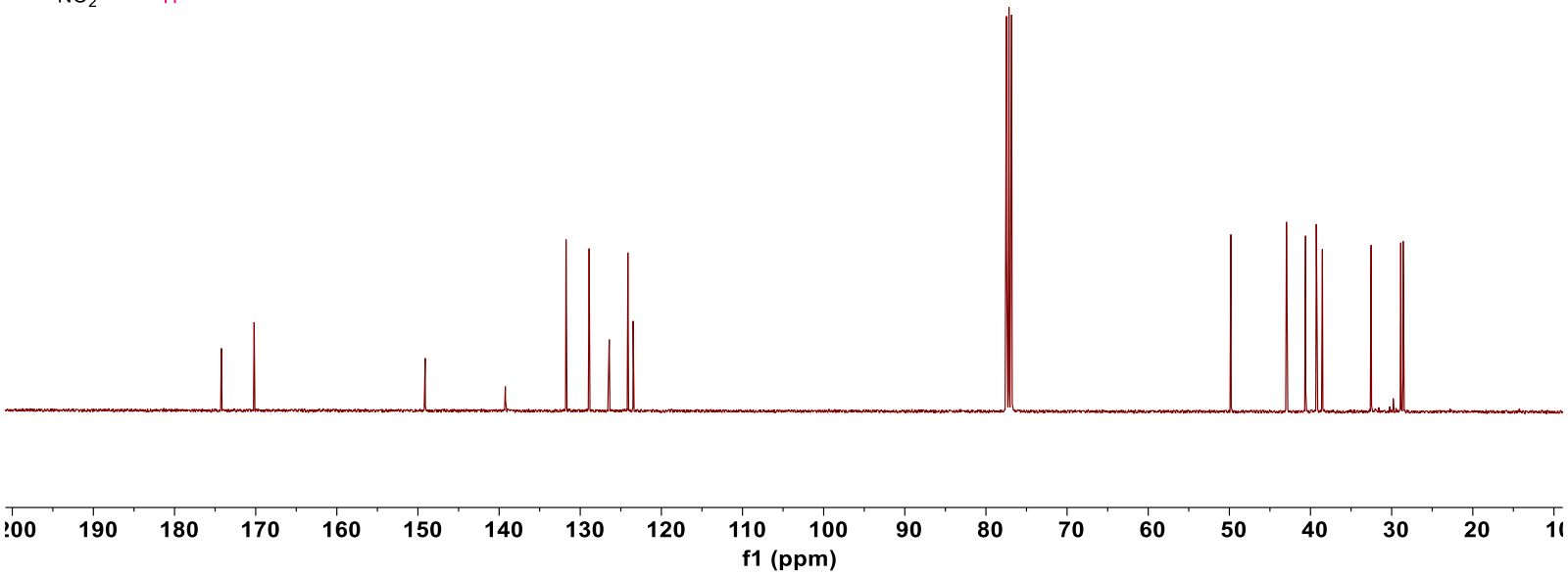
ZJK-34-1-C

174.23
170.19
149.11
139.23
131.75
128.90
126.42
124.13
123.48
77.48
77.16
76.84
49.81
42.96
40.61
39.29
38.53
32.53
28.88
28.58

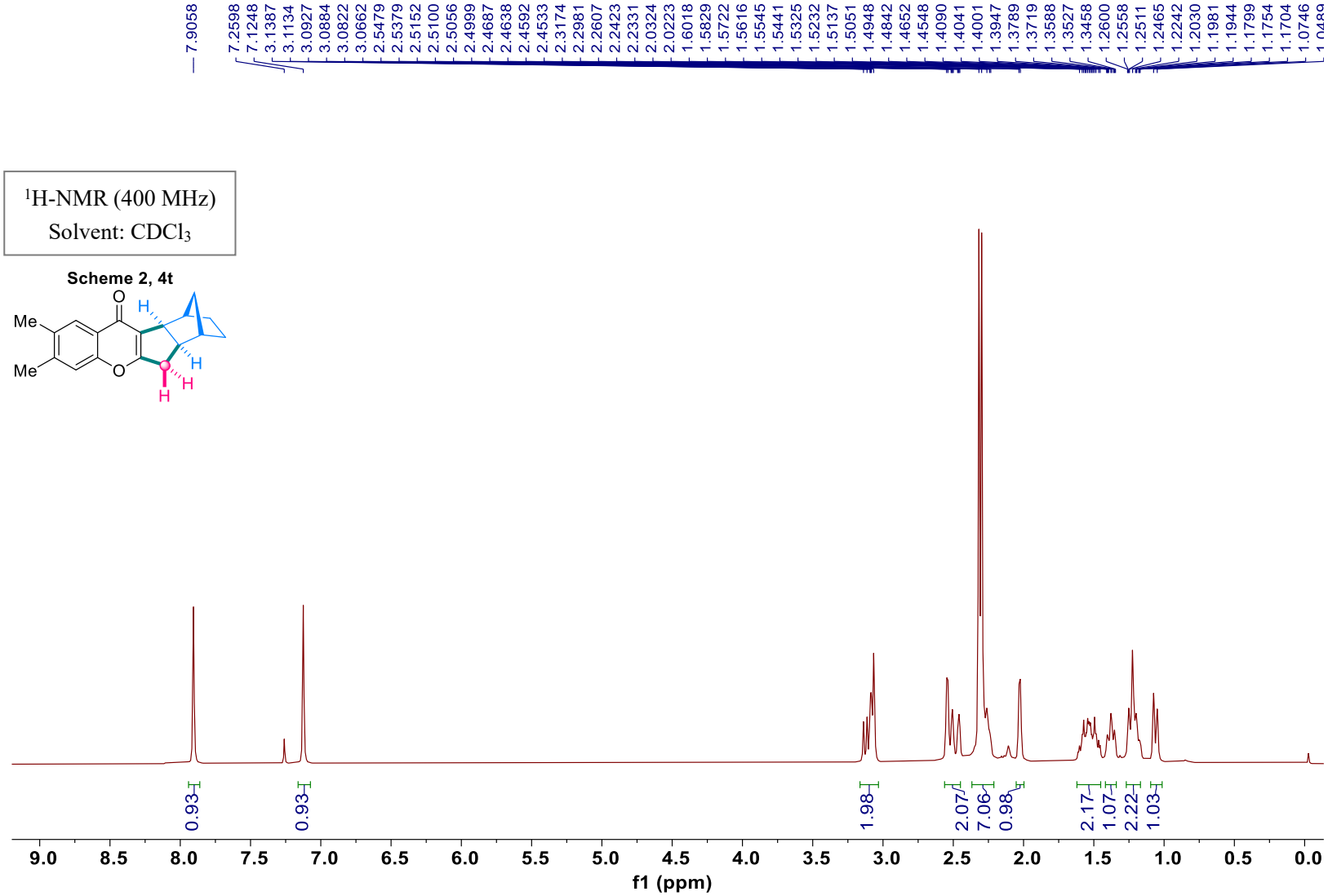
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4s



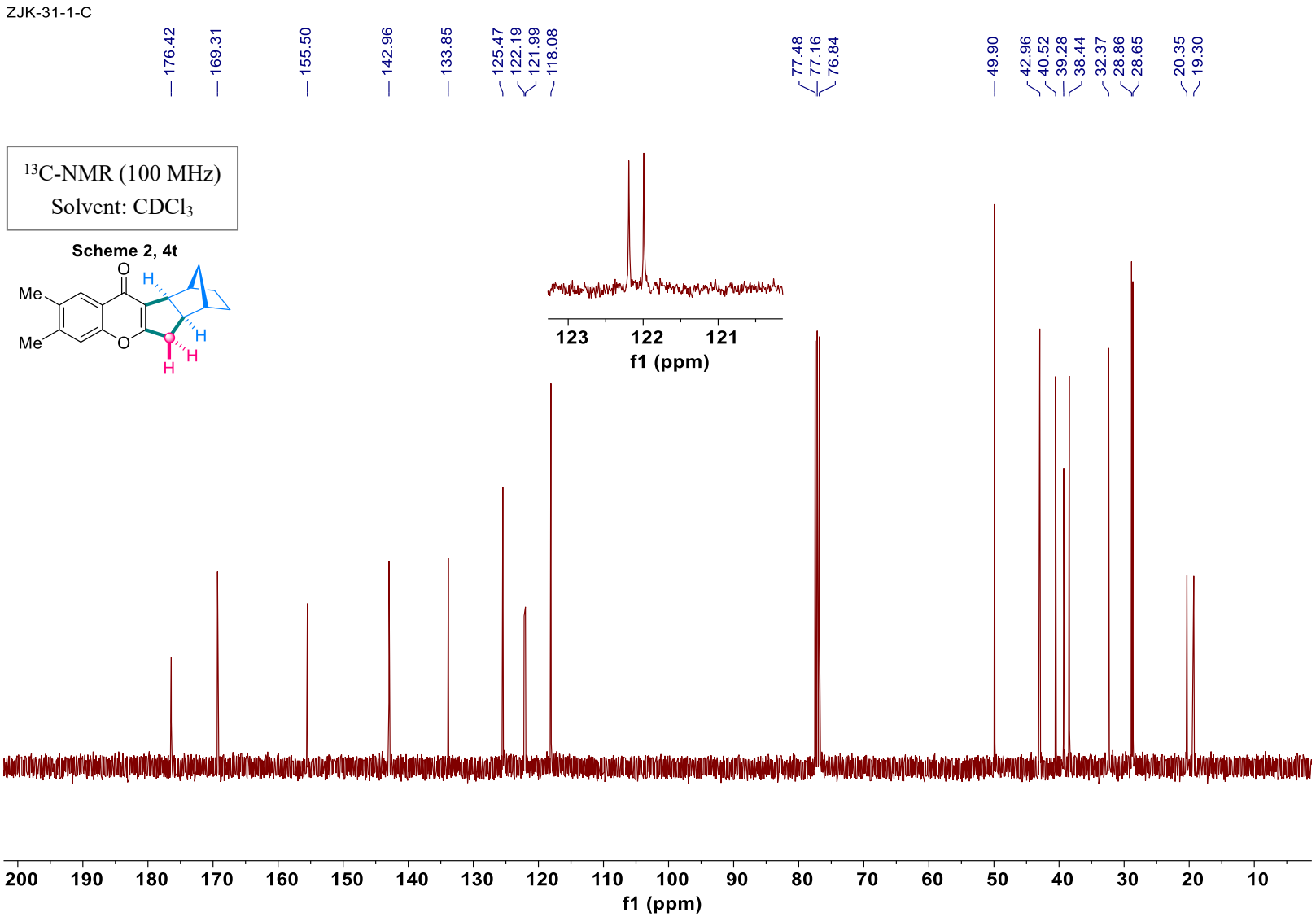


ZJK-31-1-h

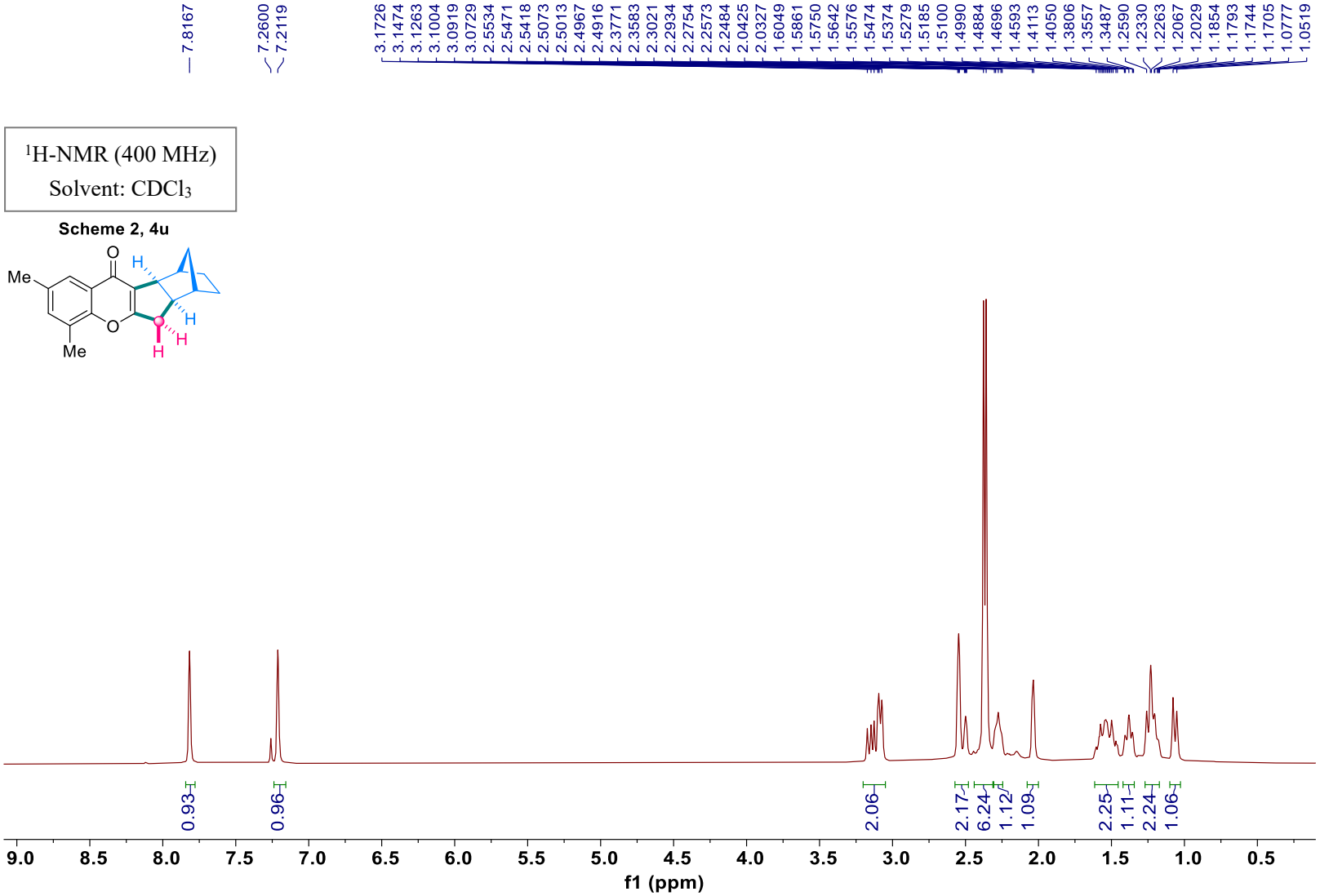


^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4t


ZJK-31-1-C
176.42
169.31
155.50
142.96
133.85
125.47
122.19
121.99
118.08
77.48
77.16
76.84
49.90
42.96
40.52
39.28
38.44
32.37
28.86
28.65
20.35
19.30
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 2, 4t
Me
Me
O
O
H
H
H
H
123
122
121
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

ZJK-31-2-h



^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

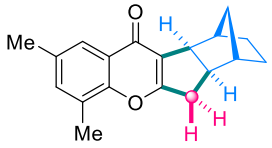
Scheme 2, 4u

ZJK-31-2-C

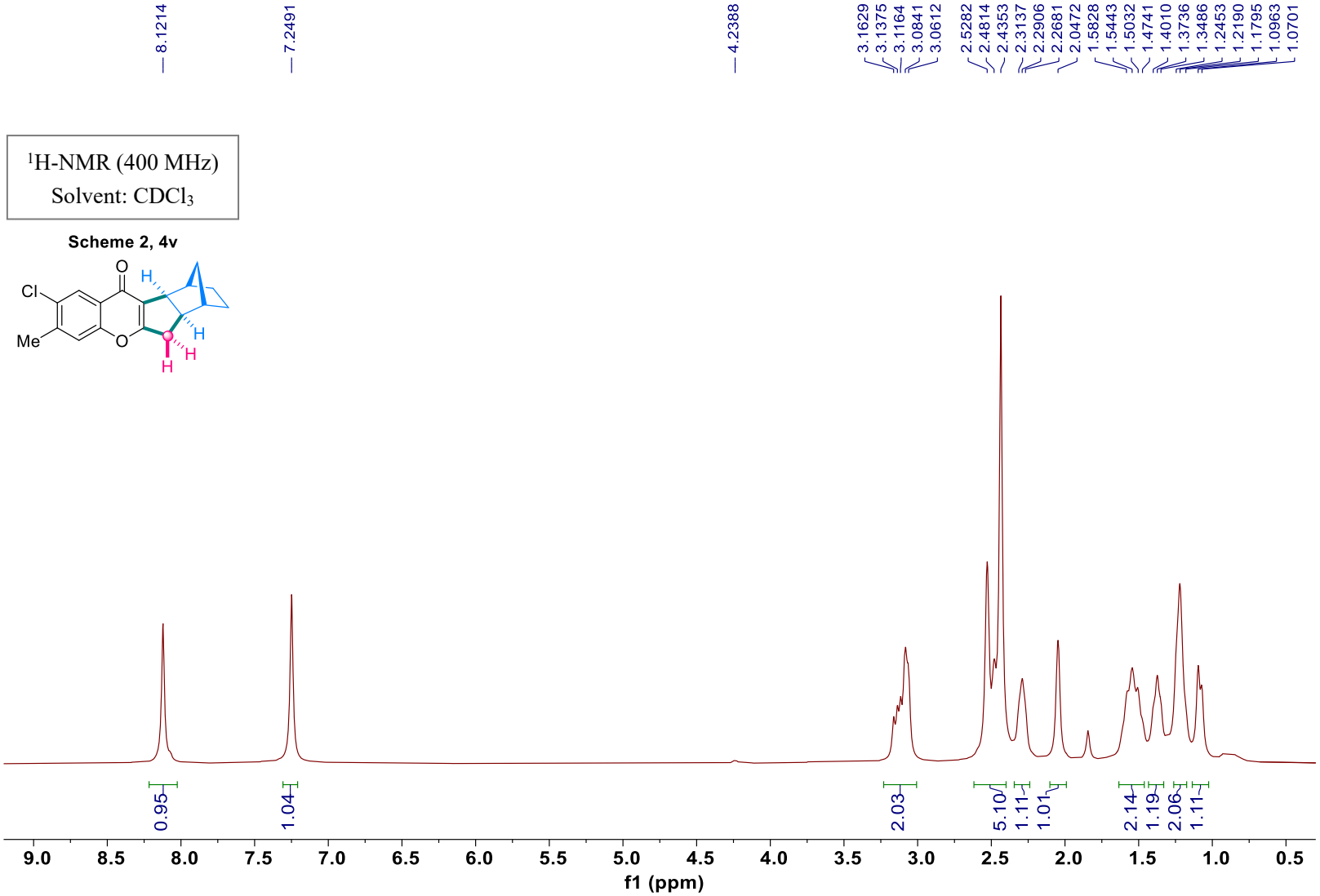
176.72
169.44
153.76
135.07
133.98
126.90
123.94
122.82
121.89
77.48
77.16
76.84
49.87
42.97
40.55
39.25
38.51
32.37
28.85
28.64
20.85
15.63

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4u



ZJK-32-1-h



^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

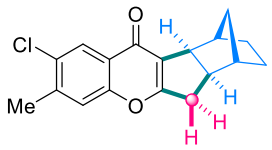
Scheme 2, 4v

ZJK-32-1-C

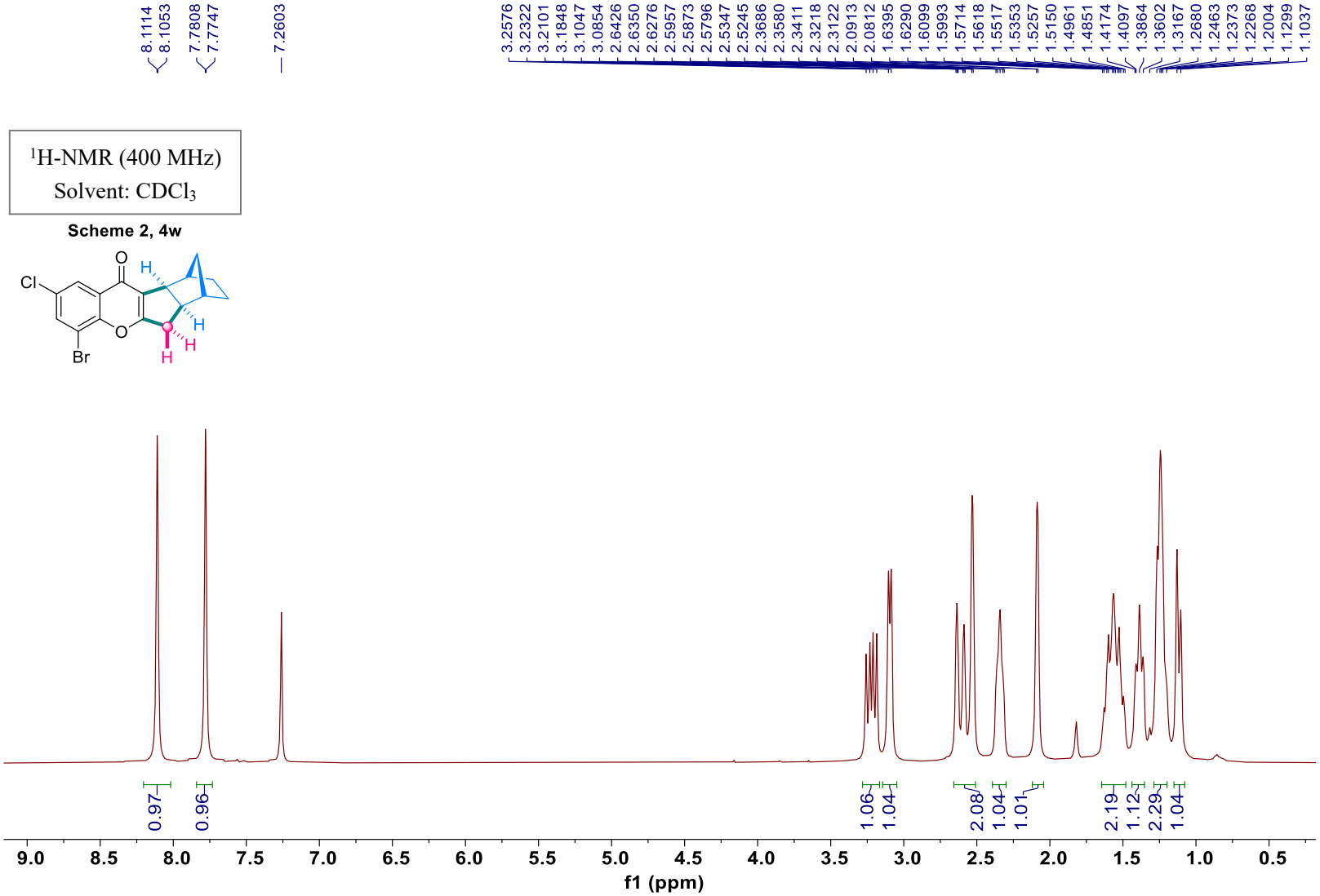
175.21
169.92
155.23
141.81
131.43
125.55
123.56
122.25
119.81
77.48
77.16
76.84
49.86
42.97
40.56
39.30
38.48
32.44
28.86
28.63
20.81

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

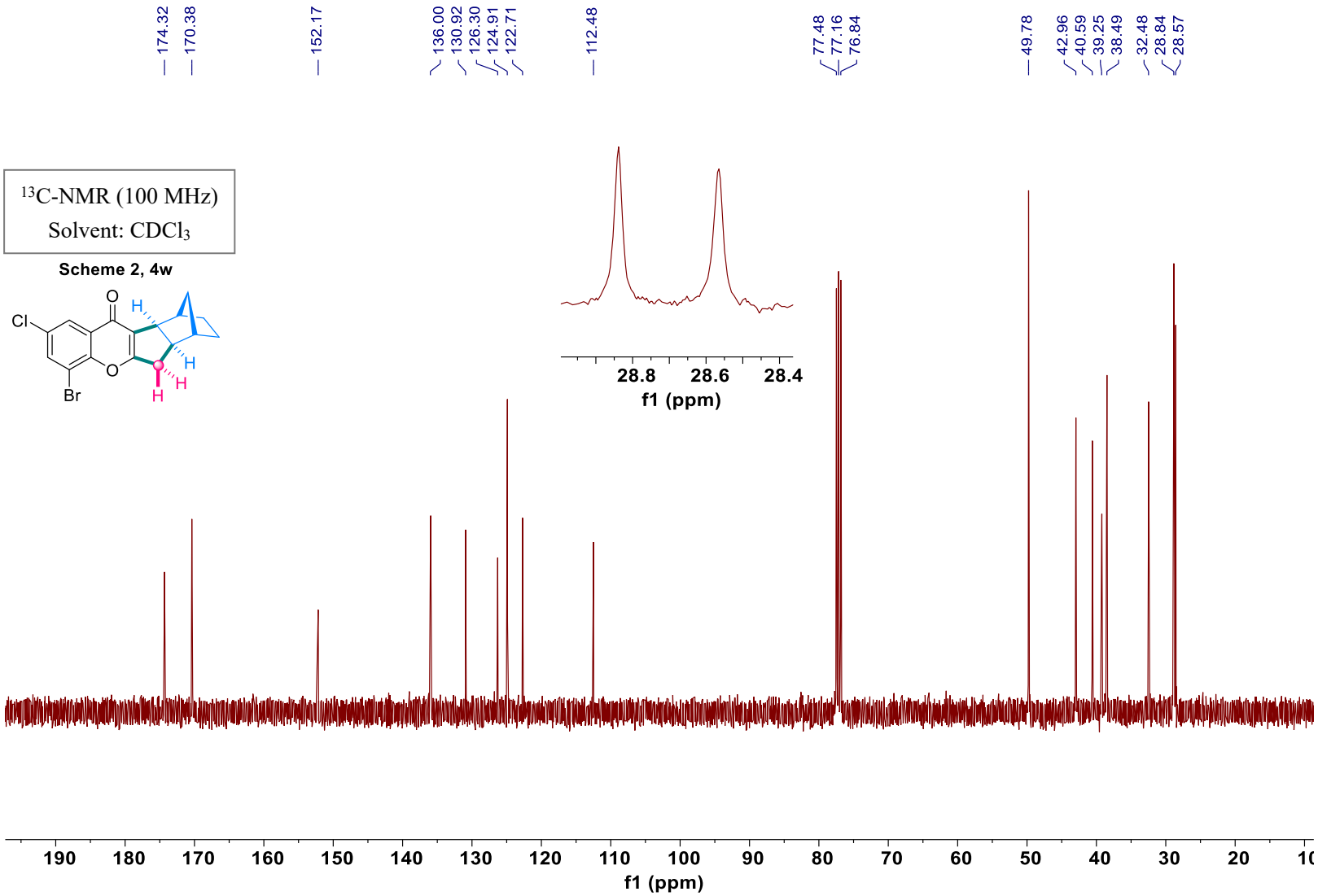
Scheme 2, 4v

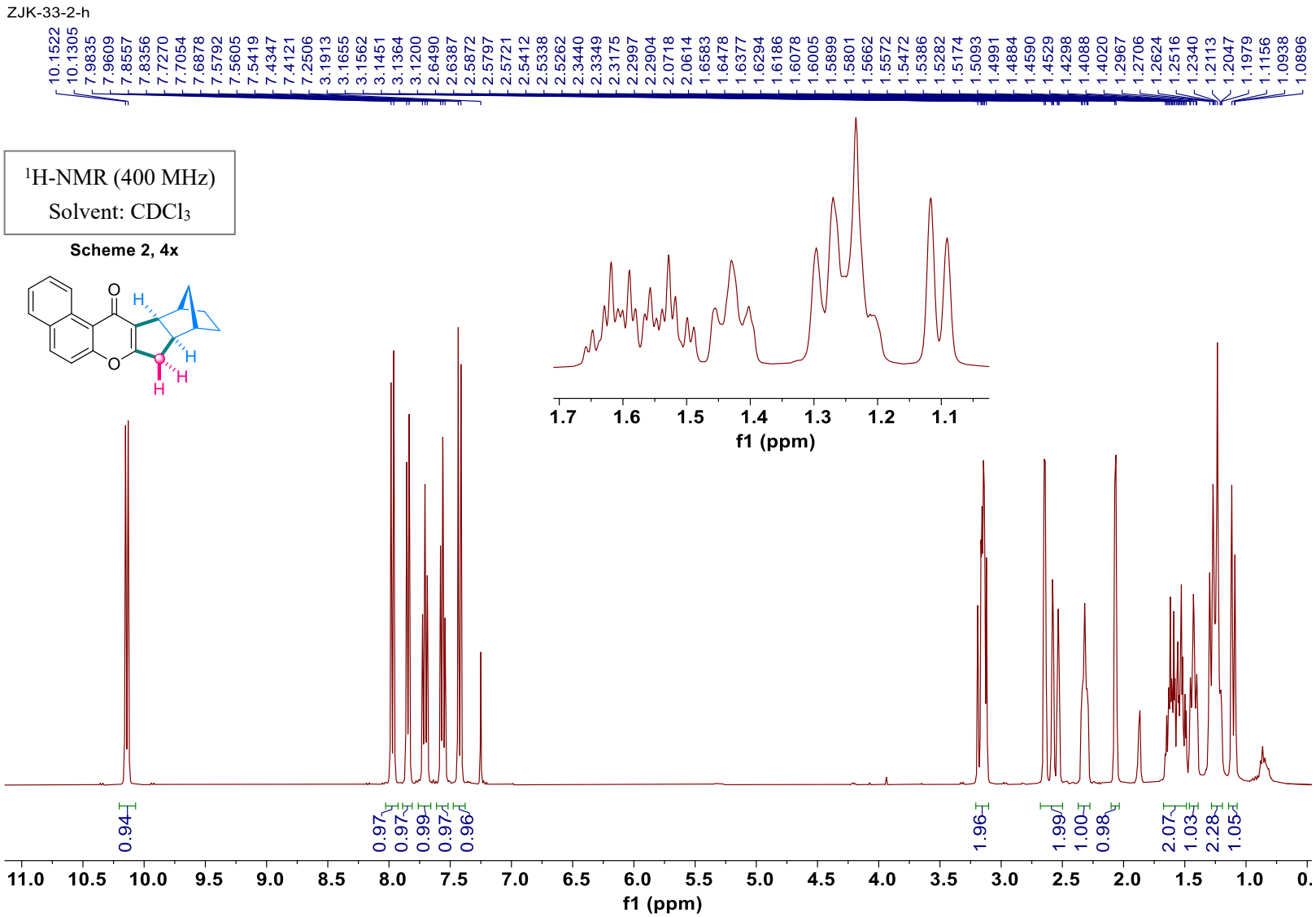


ZJK-32-2-h


8.1114
8.1053
7.7808
7.7747
7.2603
3.2576
3.2322
3.2101
3.1848
3.1047
3.0854
2.6426
2.6350
2.6276
2.5957
2.5873
2.5796
2.5347
2.5245
2.3686
2.3580
2.3411
2.3218
2.3122
2.0913
2.0812
1.6395
1.6290
1.6099
1.5993
1.5714
1.5618
1.5517
1.5353
1.5257
1.5150
1.4961
1.4851
1.4174
1.4097
1.3864
1.3602
1.3167
1.2680
1.2463
1.2373
1.2268
1.2004
1.1299
1.1037
1H-NMR (400 MHz)
Solvent: CDCl3
Scheme 2, 4w
Cl
O
H
H
H
H
O
Br
0.97
0.96
1.06
1.04
2.08
1.04
1.01
2.19
1.12
2.29
1.04
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
f1 (ppm)

ZJK-32-2-c


174.32
170.38
152.17
136.00
130.92
126.30
124.91
122.71
112.48
77.48
77.16
76.84
49.78
42.96
40.59
39.25
38.49
32.48
28.84
28.57
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Scheme 2, 4w
Cl
O
O
Br
H
H
H
28.8
28.6
28.4
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

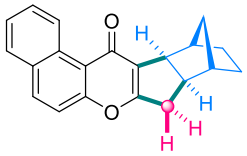

ZJK-33-2-h
10.1522 10.1305 7.9835 7.9609 7.8557 7.8356 7.7270 7.7054 7.6878 7.5792 7.5605 7.5419 7.4347 7.4121 7.2506 3.1913 3.1655 3.1562 3.1451 3.1364 3.1200 2.6490 2.6387 2.5872 2.5797 2.5721 2.5412 2.5338 2.5262 2.3440 2.3349 2.3175 2.2997 2.2904 2.0718 2.0614 1.6583 1.6478 1.6377 1.6294 1.6186 1.6078 1.6005 1.5899 1.5801 1.5662 1.5572 1.5472 1.5386 1.5282 1.5174 1.5093 1.4991 1.4884 1.4590 1.4529 1.4298 1.4088 1.4020 1.2967 1.2706 1.2624 1.2516 1.2340 1.2113 1.2047 1.1979 1.1156 1.0938 1.0896
1H-NMR (400 MHz)
Solvent: CDCl3
Scheme 2, 4x
O
H
H
H
O
1.7 1.6 1.5 1.4 1.3 1.2 1.1
f1 (ppm)
0.94 0.97 0.97 0.99 0.97 0.96 1.96 1.99 1.00 0.98 2.07 1.03 2.28 1.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.
f1 (ppm)

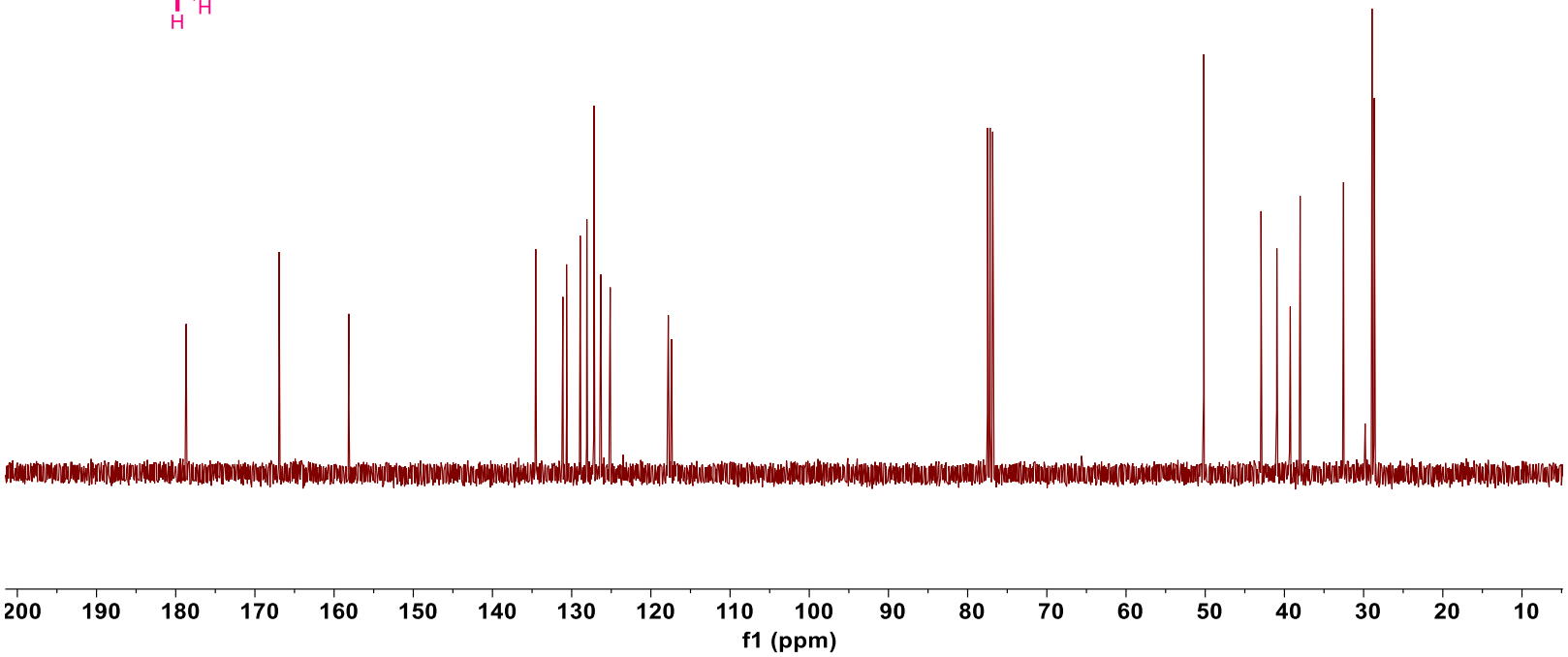
ZJK-33-2-C

178.68
166.94
158.14
134.53
131.11
130.65
128.92
128.08
127.19
126.32
125.13
117.81
117.38
77.48
77.16
76.84
50.18
42.95
40.96
39.29
38.01
32.54
28.93
28.66

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4x



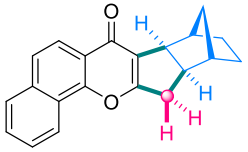


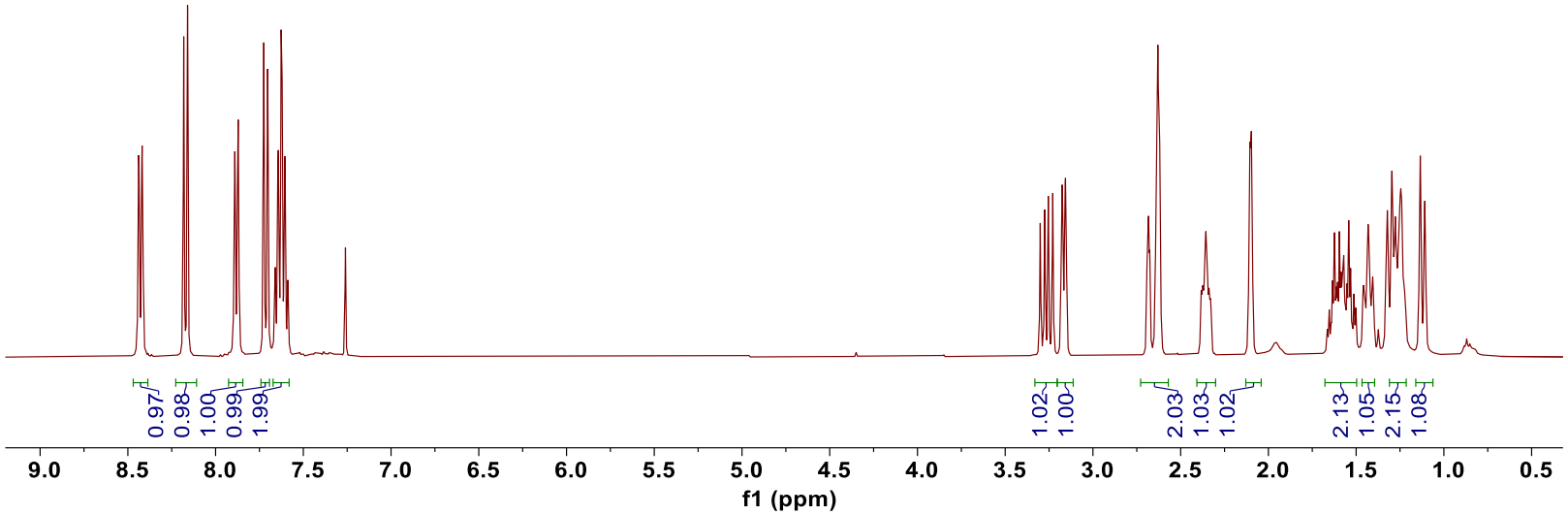
ZJK-33-1-h

8.4382 8.4159 8.1815 8.1597 7.8939 7.8896 7.8754 7.8707 7.7253 7.7034 7.6631 7.6591 7.6452 7.6411 7.6270 7.6221 7.6074 7.6035 7.5895 7.5859 7.2602 3.3003 3.2750 3.2542 3.2289 3.1756 3.1563 2.6917 2.6859 2.6822 2.6760 2.6455 2.6359 2.6294 2.6200 2.3739 2.3562 2.3377 2.1063 2.0959 1.6347 1.6238 1.6129 1.6058 1.5956 1.5864 1.5790 1.5705 1.5523 1.5420 1.5313 1.4571 1.4329 1.4253 1.4055 1.3272 1.3220 1.3173 1.3006 1.2960 1.2915 1.2831 1.2767 1.2681 1.2623 1.2556 1.2506 1.2459 1.2405 1.2315 1.1345 1.1085

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 2, 4y



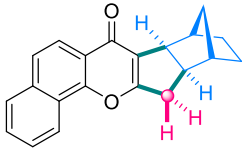


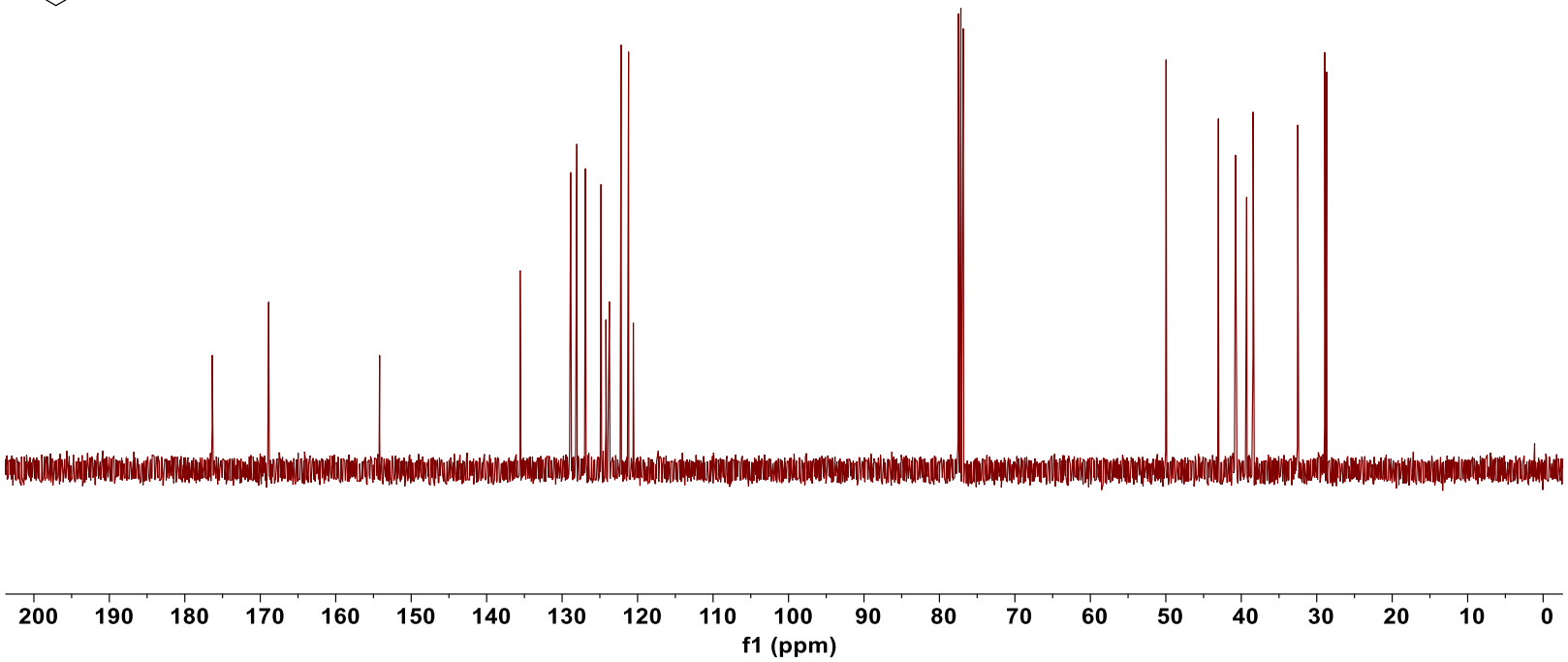
ZJK-33-1-C

176.37
168.89
154.18
135.56
128.87
128.05
126.91
124.85
124.19
123.73
122.19
121.19
120.56
77.48
77.16
76.84
49.96
43.04
40.76
39.29
38.43
32.52
28.93
28.68

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4y

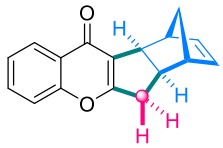


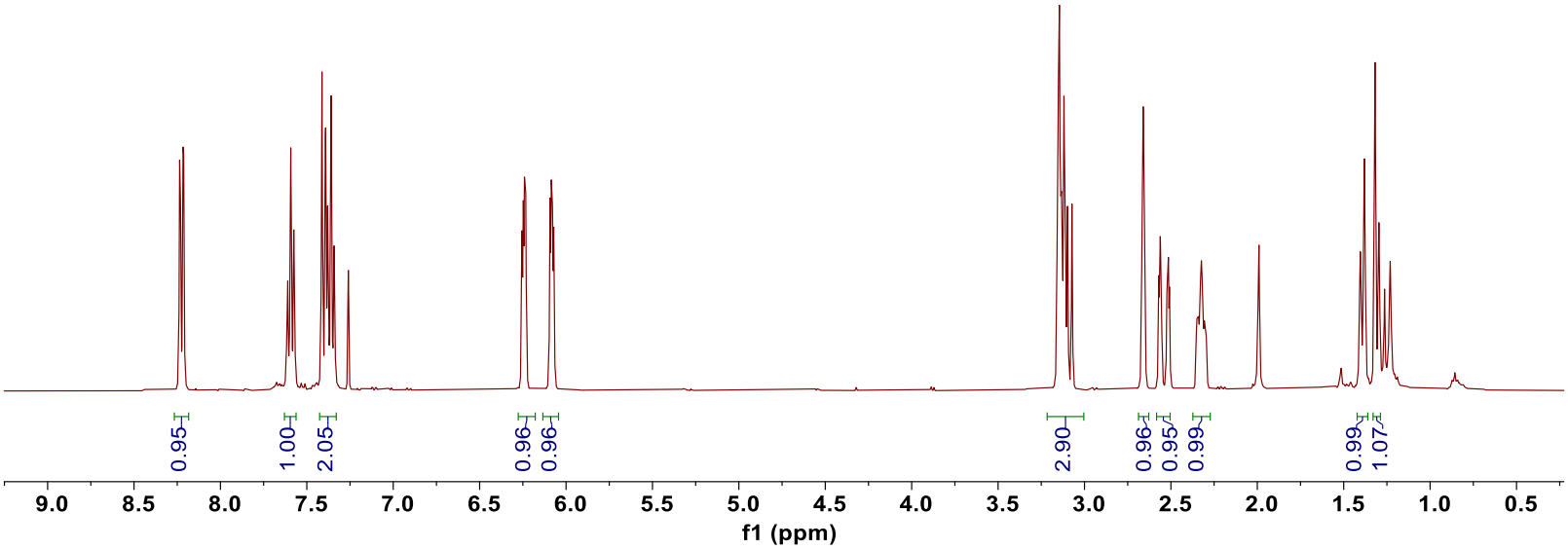


ZJK-40-1-h

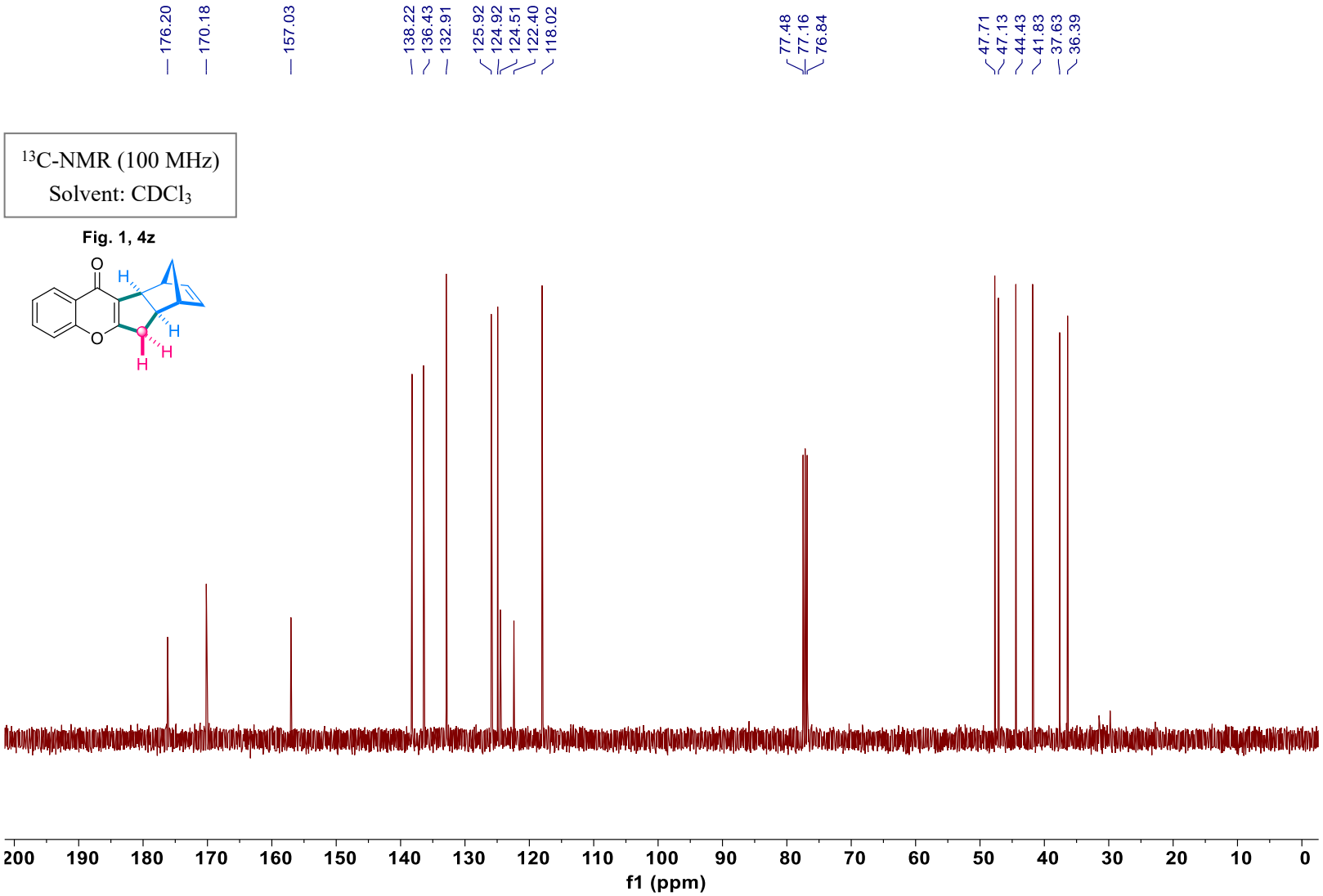
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Fig. 1, 4z





ZJK-40-1-C


176.20
170.18
157.03
138.22
136.43
132.91
125.92
124.92
124.51
122.40
118.02
77.48
77.16
76.84
47.71
47.13
44.43
41.83
37.63
36.39
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Fig. 1, 4z
O
H
H
H
O
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

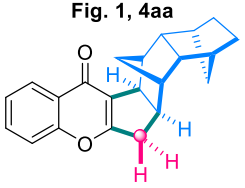
ZJK-36-1-h

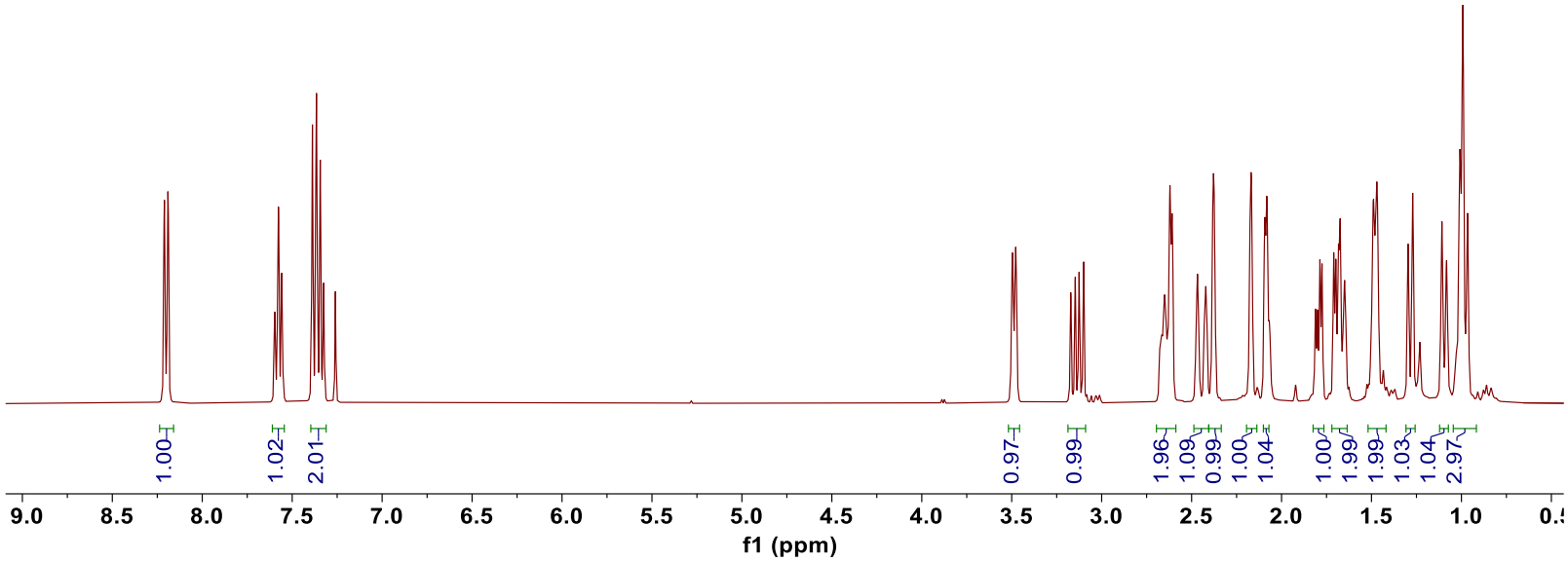
8.2118 8.2076 8.1919 8.1877 7.5975 7.5933 7.5769 7.5590 7.5548 7.3876 7.3652 7.3438 7.3250 7.2599

3.4958 3.4776 3.1720 3.1467 3.1256 3.1004 2.6769 2.6676 2.6497 2.6203 2.6076 2.4745 2.4670 2.4591 2.4279 2.4202 2.4127 2.3810 2.3733 2.1743 2.1664 2.0935 2.0816 2.0662 1.8118 1.8001 1.7868 1.7748 1.7101 1.6984 1.6841 1.6740 1.6492 1.5035 1.4929 1.4859 1.4693 1.4571 1.2963 1.2708 1.2314 1.1084 1.0826 1.0280 1.0090 0.9923 0.9658

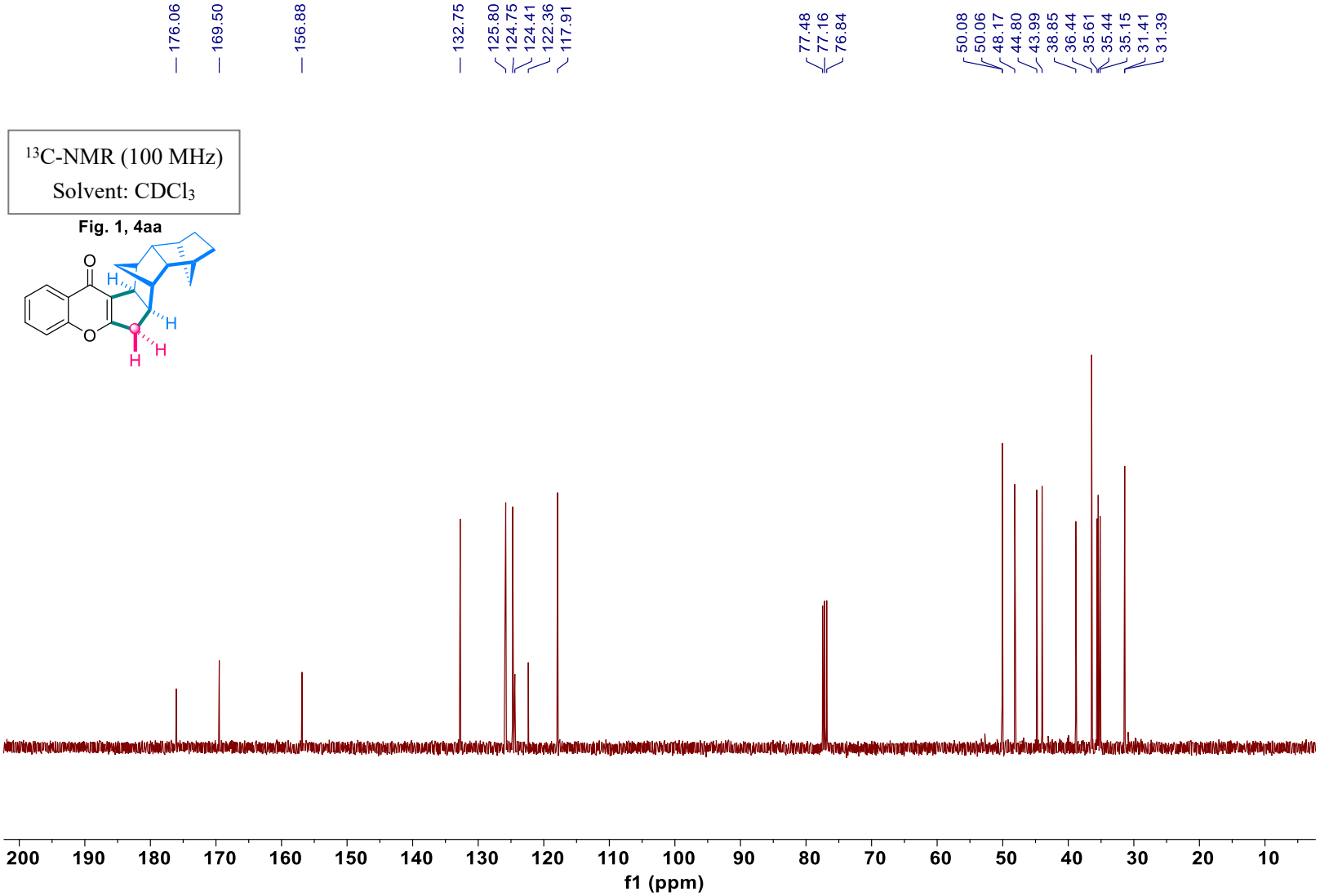
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Fig. 1, 4aa





ZJK-36-1-c



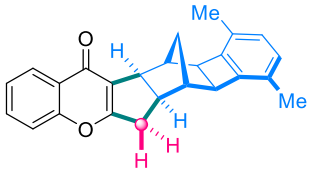
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Fig. 1, 4aa

ZJK-35-1-h

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Fig. 1, 4ab

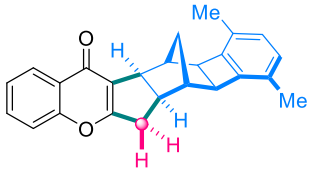


ZJK-35-1-c

176.38
169.64
156.98
143.98
143.32
132.97
129.66
129.07
128.68
128.50
125.89
124.95
124.40
122.11
118.01
77.48
77.16
76.85
48.64
48.60
47.81
42.39
39.19
38.93
38.19
26.70
16.44
16.27

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Fig. 1, 4ab

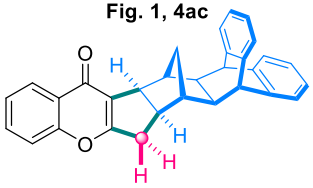


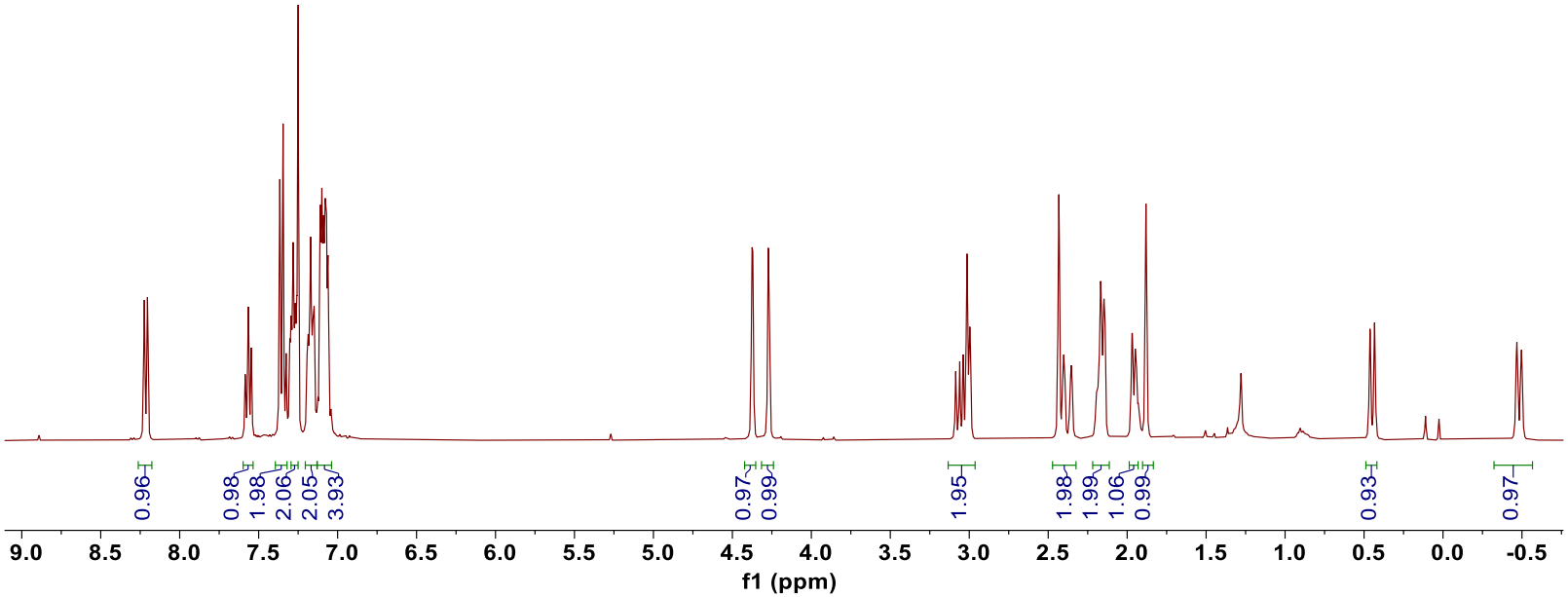
ZJK-35-2-h

8.2240 8.2052 7.5894 7.5855 7.5816 7.5681 7.5640 7.5468 7.5422 7.3661 7.3454 7.3259 7.3031 7.2944 7.2811 7.2675 7.2578 7.2504 7.1919 7.1858 7.1708 7.1546 7.1478 7.1260 7.1101 7.1003 7.0902 7.0780 7.0699 7.0608 7.0561 7.0420 7.0370 4.3763 4.3693 4.2738 4.2667 3.0859 3.0605 3.0391 3.0143 2.9959 2.4327 2.4086 2.4011 2.3937 2.3619 2.3542 2.1960 2.1873 2.1694 2.1620 2.1480 1.9715 1.9642 1.9500 1.9429 1.9276 1.8809 0.4623 0.4332 -0.4678 -0.4968

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Fig. 1, 4ac



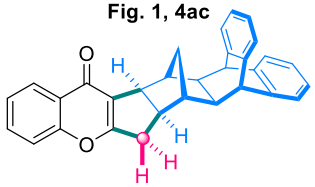


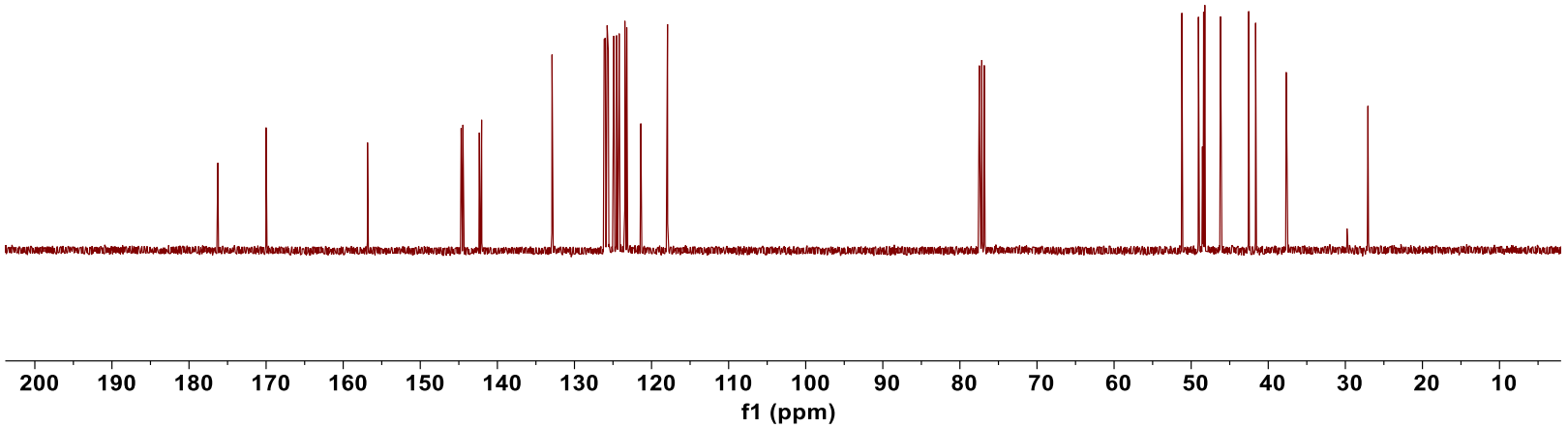
ZJK-35-2-c

176.26
170.01
156.85
144.70
144.47
142.34
142.04
132.91
126.15
125.99
125.83
125.76
125.61
124.89
124.53
124.28
124.20
123.46
123.22
121.39
117.93
77.48
77.16
76.84
51.20
49.06
48.53
48.38
48.23
46.20
42.53
41.64
37.67
27.07

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Fig. 1, 4ac



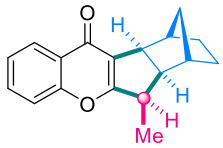


ZJK-37-2-h

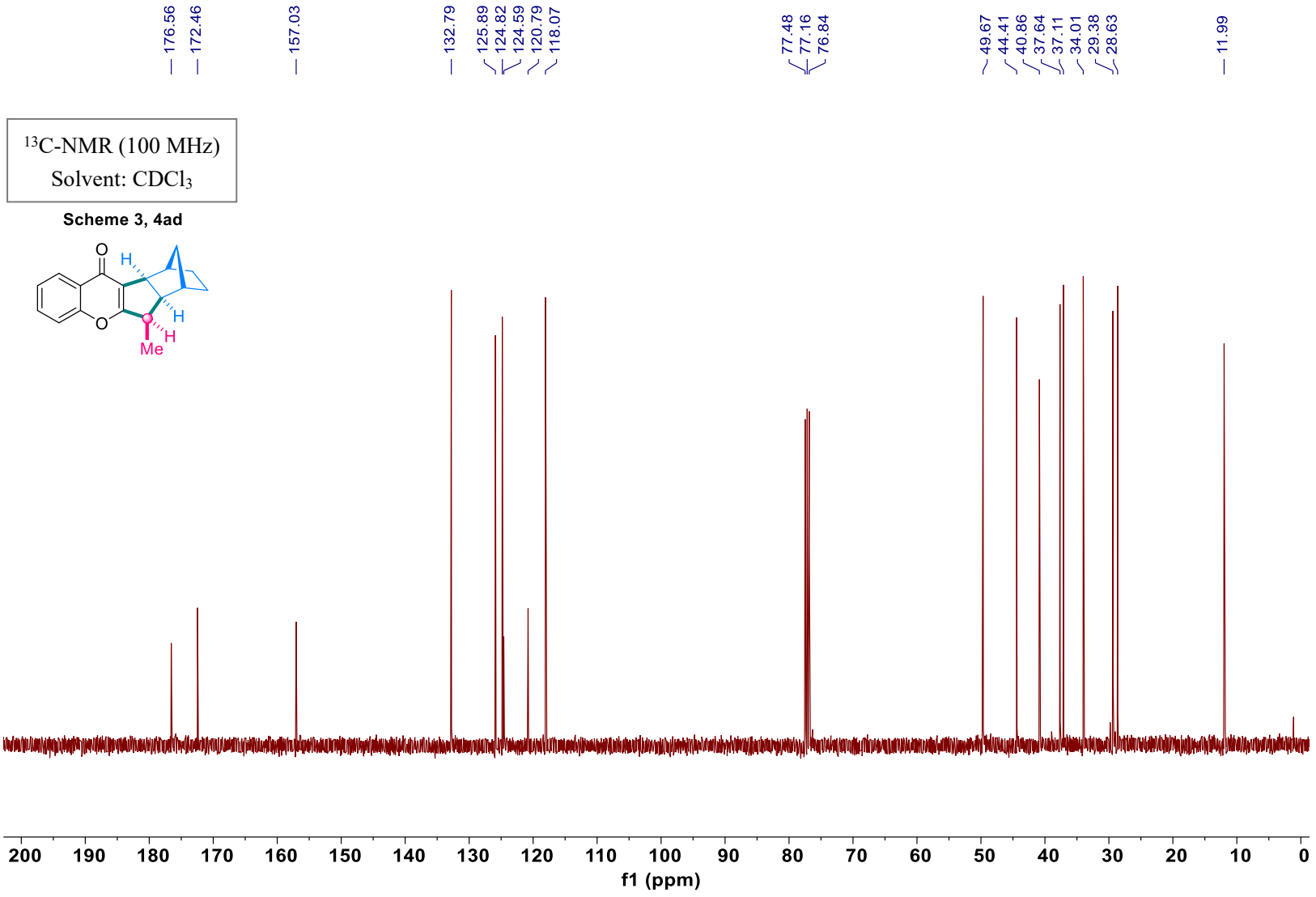
7.6149 7.6104 7.5972 7.5931 7.5892 7.5760 7.5716 7.4373 7.4344 7.4161 7.4131 7.3753 7.3724 7.3577 7.3551 7.3525 7.3376 7.3347 7.2599 3.4376 3.4188 3.4122 3.3936 3.1902 3.1710 2.5959 2.5908 2.5838 2.3033 2.2994 2.2840 2.2790 2.2738 2.2587 2.2549 2.2402 2.2303 1.5996 1.5810 1.5764 1.5712 1.5662 1.5603 1.5515 1.5415 1.5308 1.3897 1.3852 1.3804 1.3611 1.3218 1.3162 1.2975 1.2693 1.2368 1.1802 1.1761 1.1715 1.1668 1.1619 1.1575 1.1545 1.1508 1.1459 1.1409 1.1375 1.0890 1.0848 1.0805 1.0634 1.0597 1.0555

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 3, 4ad



ZJK-37-2-c



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

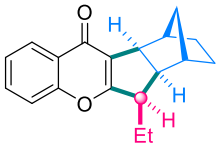
Scheme 3, 4ad

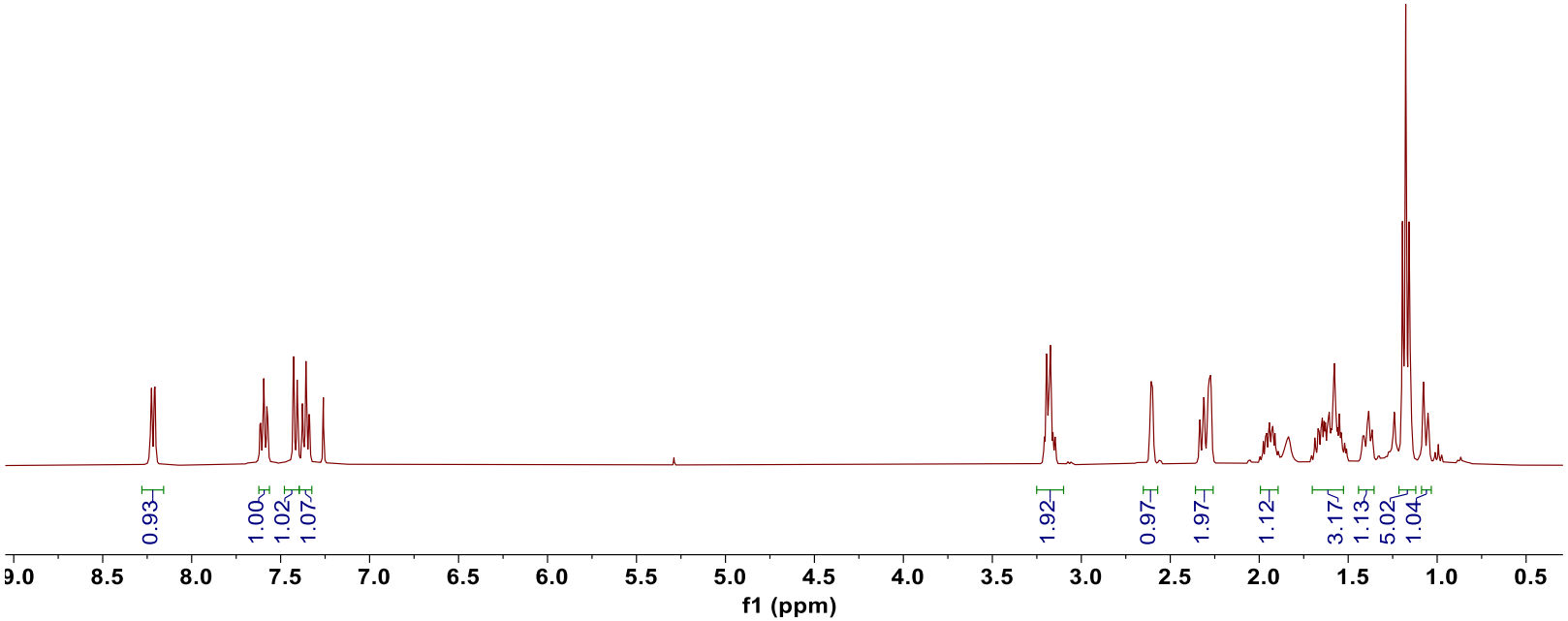
ZJK-39-1-h

8.2297 8.2253 8.2098 8.2055 7.6165 7.6121 7.5989 7.5949 7.5909 7.5777 7.5732 7.4288 7.4262 7.4077 7.4051 7.3780 7.3750 7.3604 7.3578 7.3550 7.3403 7.3374 7.2599 3.1954 3.1834 3.1766 3.1725 2.6097 2.6001 2.3356 2.3318 2.3164 2.3116 2.3067 2.2915 2.2875 2.2817 2.2723 1.9462 1.9424 1.9303 1.9237 1.6699 1.6633 1.6530 1.6456 1.6357 1.6283 1.6161 1.6104 1.6057 1.5963 1.5859 1.5781 1.5730 1.5686 1.5598 1.5495 1.5388 1.3928 1.3875 1.3836 1.3655 1.1949 1.1766 1.1581 1.0804 1.0767 1.0727 1.0550 1.0512 1.0474

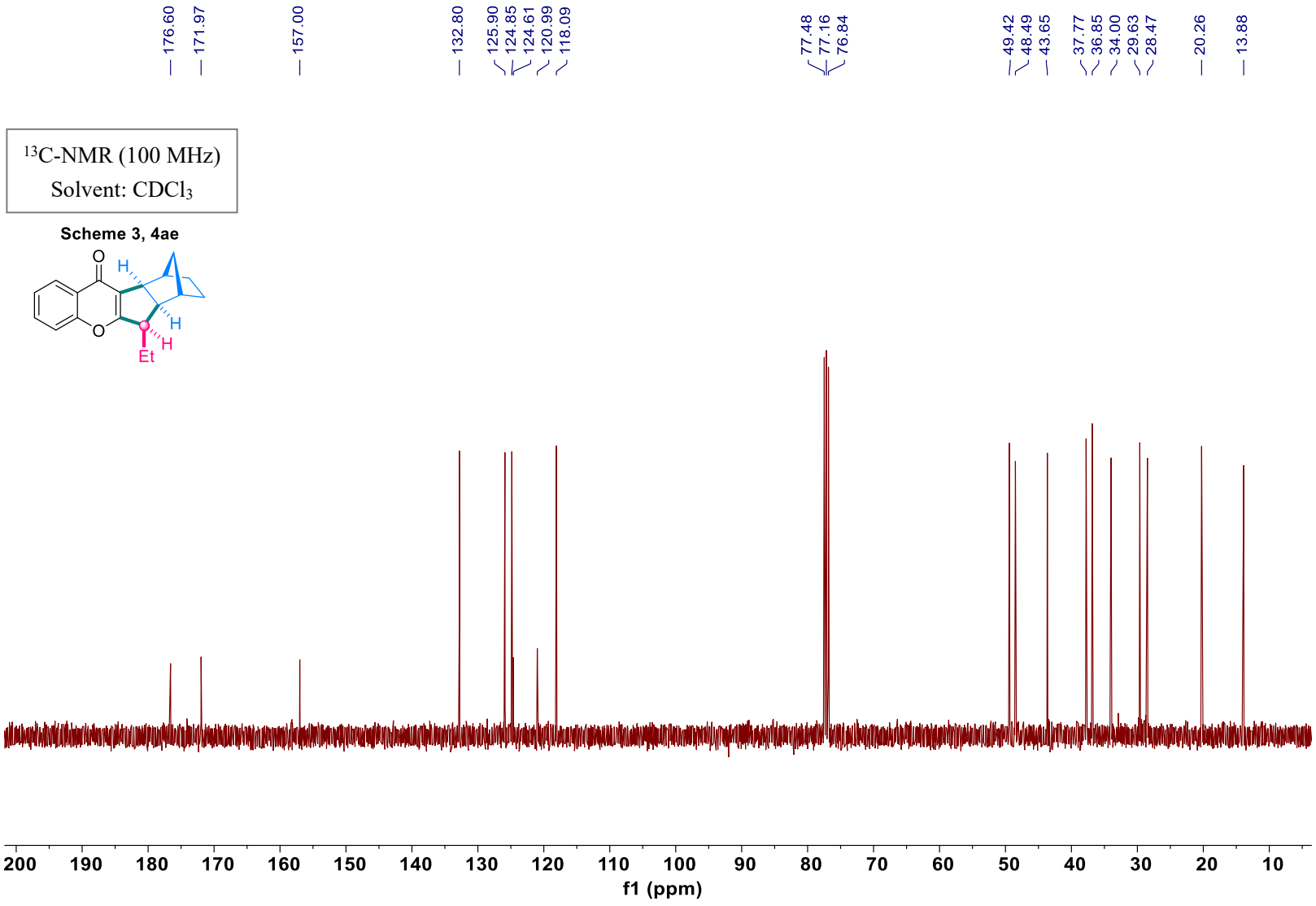
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 3, 4ae





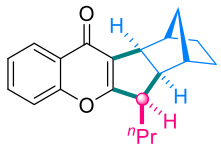
ZJK-39-1-c

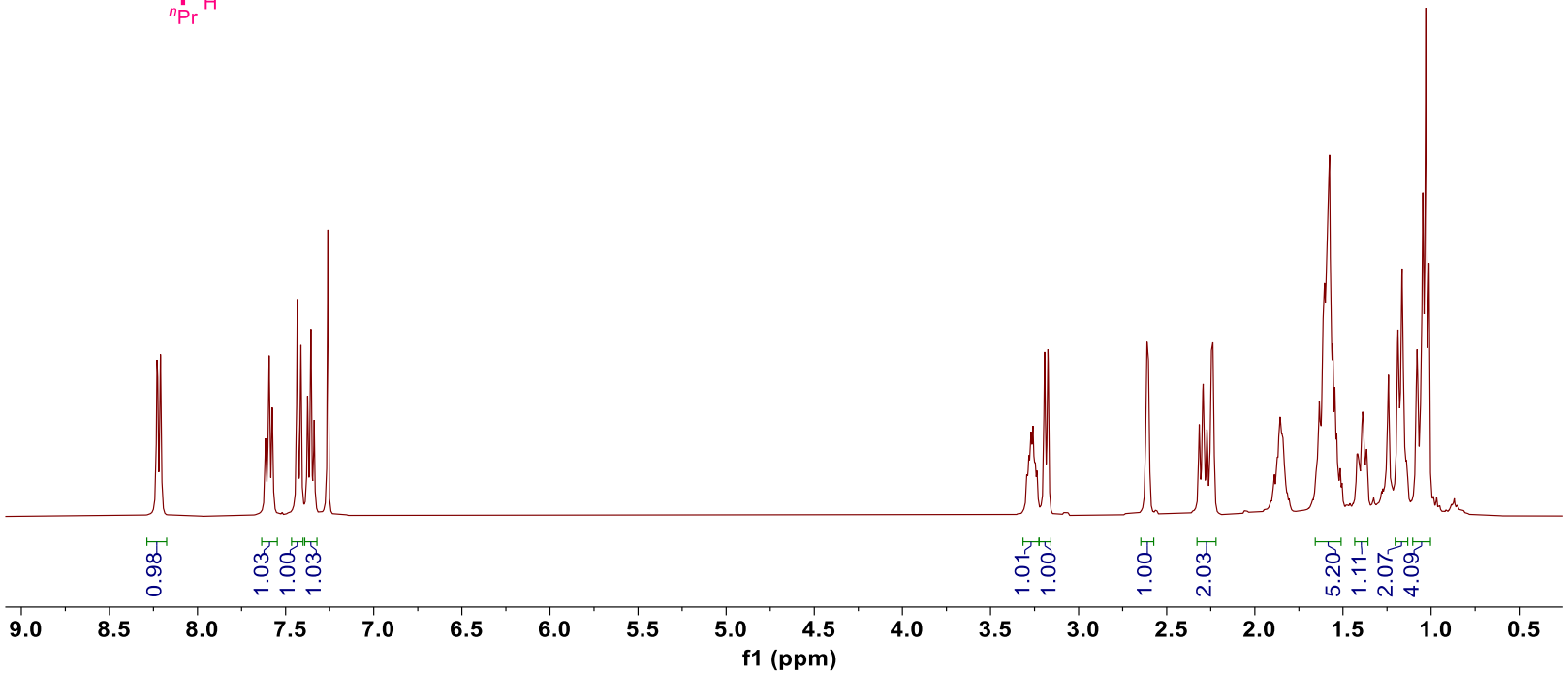

176.60
171.97
157.00
132.80
125.90
124.85
124.61
120.99
118.09
77.48
77.16
76.84
49.42
48.49
43.65
37.77
36.85
34.00
29.63
28.47
20.26
13.88
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Scheme 3, 4ae
O
H
H
H
O
Et
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

ZJK-40-2-h

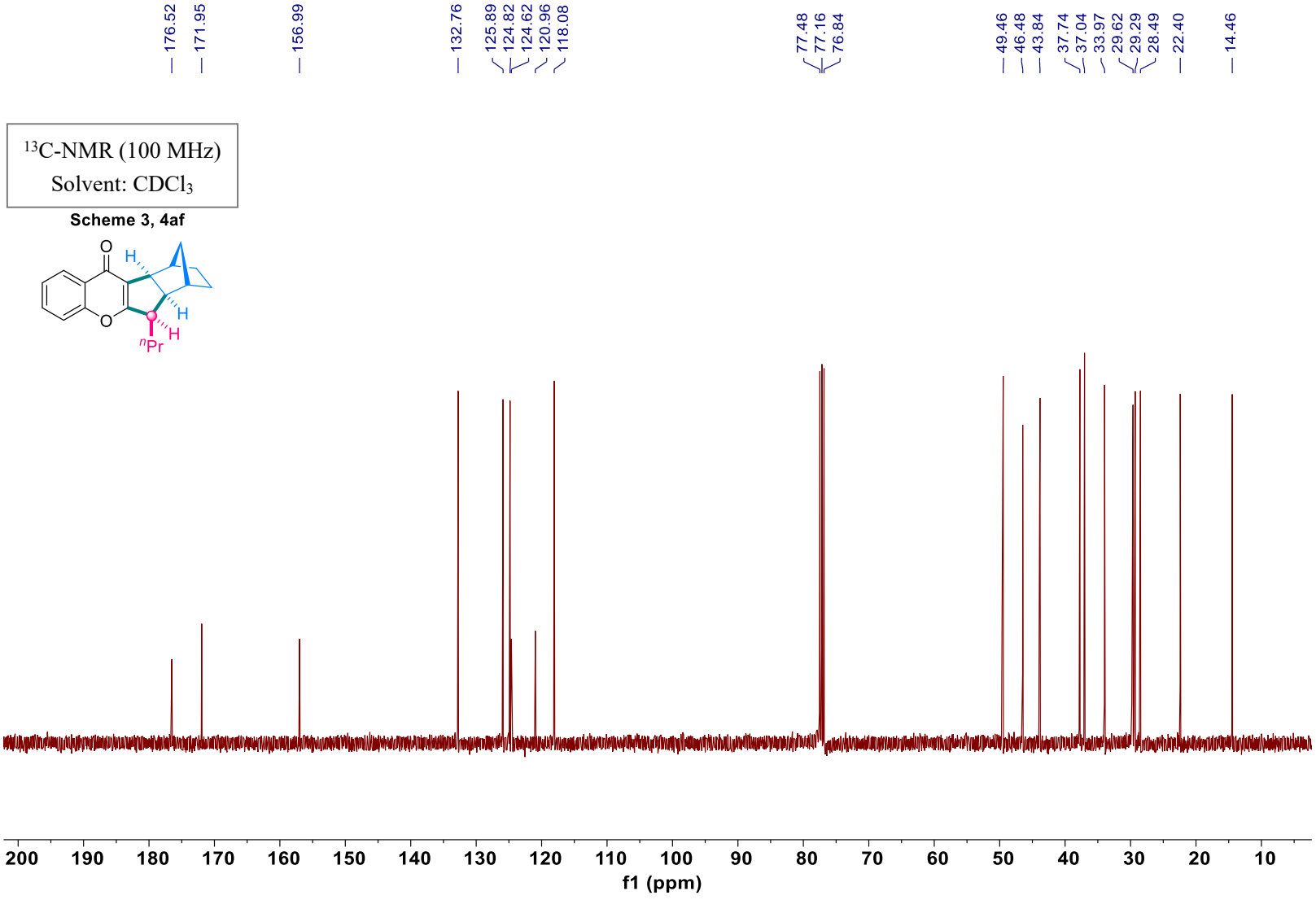
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 3, 4af





ZJK-40-2-c

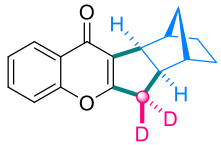

176.52
171.95
156.99
132.76
125.89
124.82
124.62
120.96
118.08
77.48
77.16
76.84
49.46
46.48
43.84
37.74
37.04
33.97
29.62
29.29
28.49
22.40
14.46
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Scheme 3, 4af
O
H
H
H
^{n}Pr
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

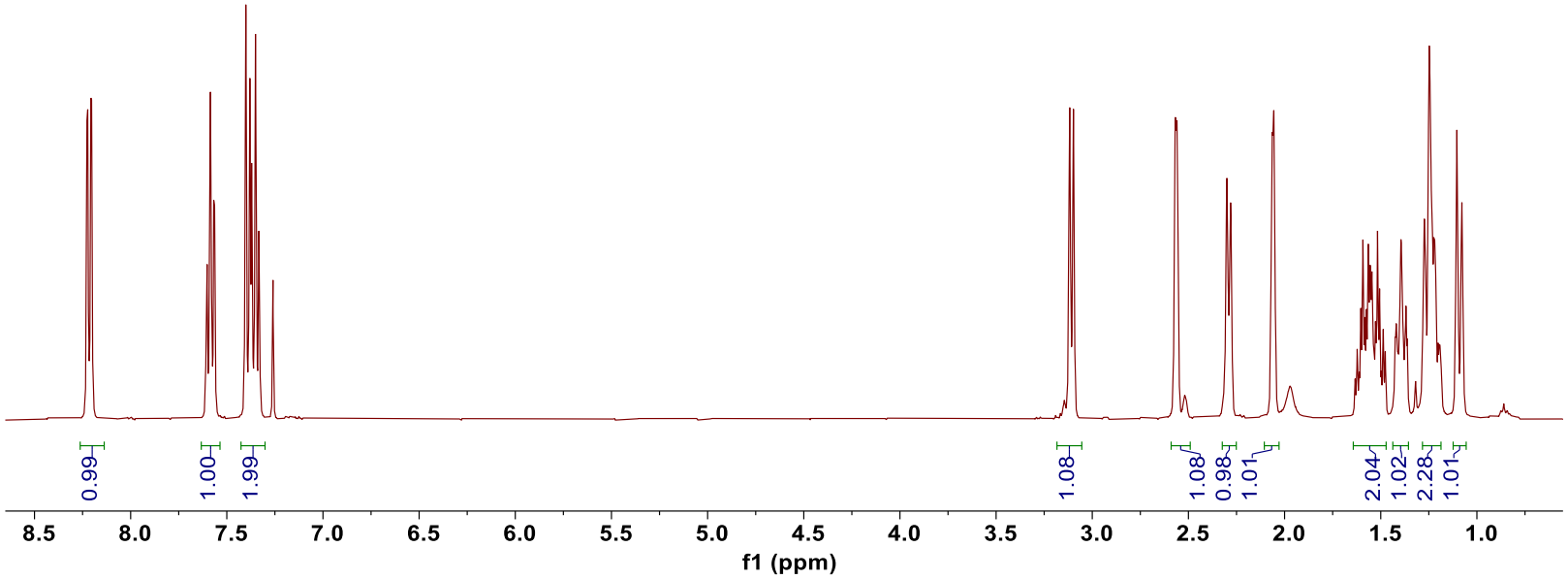
ZJK-41-1

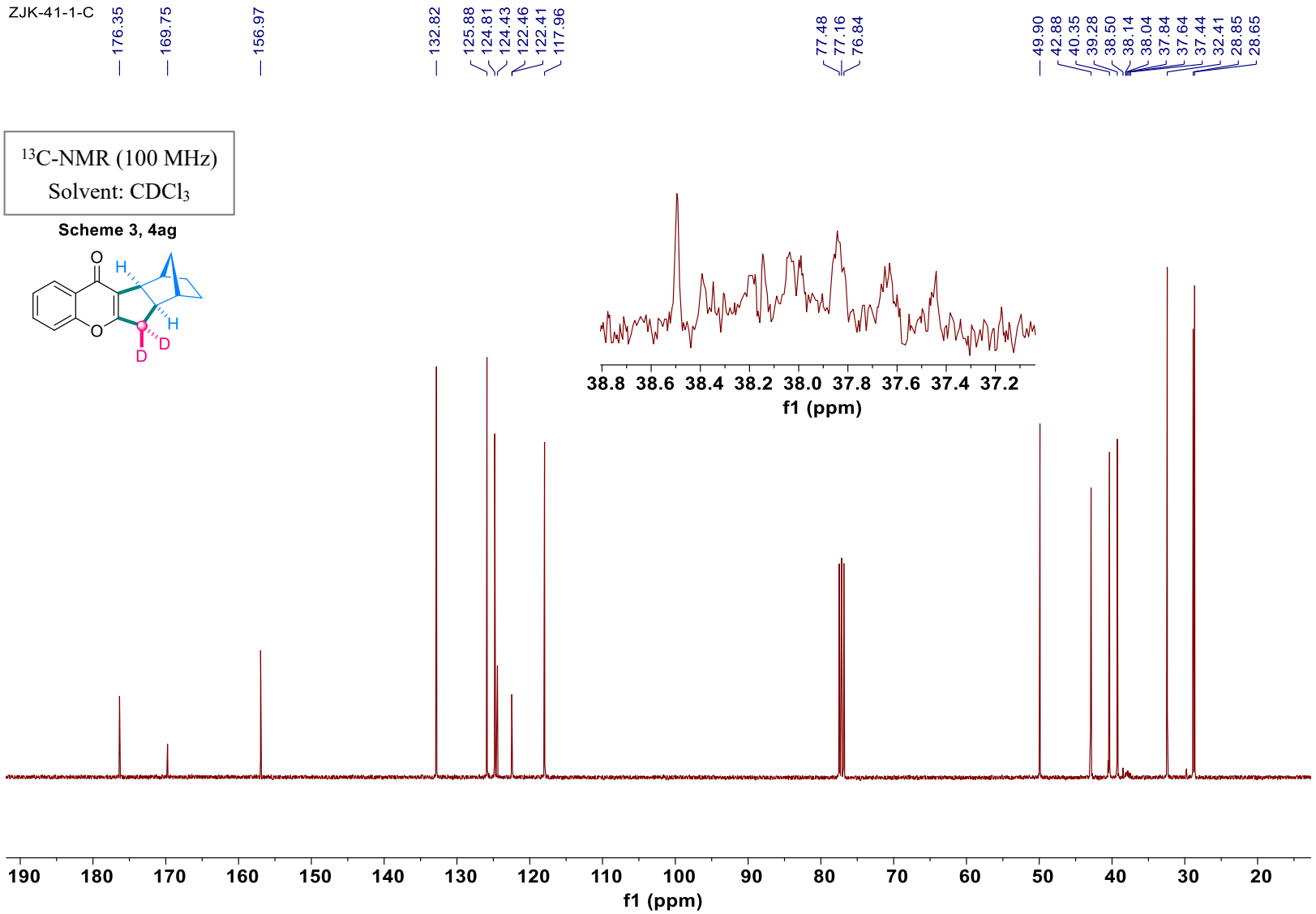
8.2273 8.2229 8.2073 8.2029 7.6069 7.6025 7.5891 7.5851 7.5812 7.5680 7.5636 7.4033 7.4005 7.3823 7.3793 7.3712 7.3683 7.3538 7.3511 7.3484 7.3335 7.3306 7.2599 3.1175 3.0980 2.5686 2.5583 2.2999 2.2806 2.0655 2.0551 1.6036 1.5927 1.5818 1.5745 1.5648 1.5578 1.5546 1.5517 1.5460 1.5429 1.5354 1.5268 1.5166 1.5060 1.4869 1.4255 1.4199 1.4024 1.3954 1.3882 1.3747 1.3686 1.2784 1.2736 1.2689 1.2659 1.2518 1.2481 1.2423 1.2367 1.2318 1.2247 1.2193 1.2148 1.2097 1.1079 1.1040 1.1001 1.0820 1.0782 1.0742

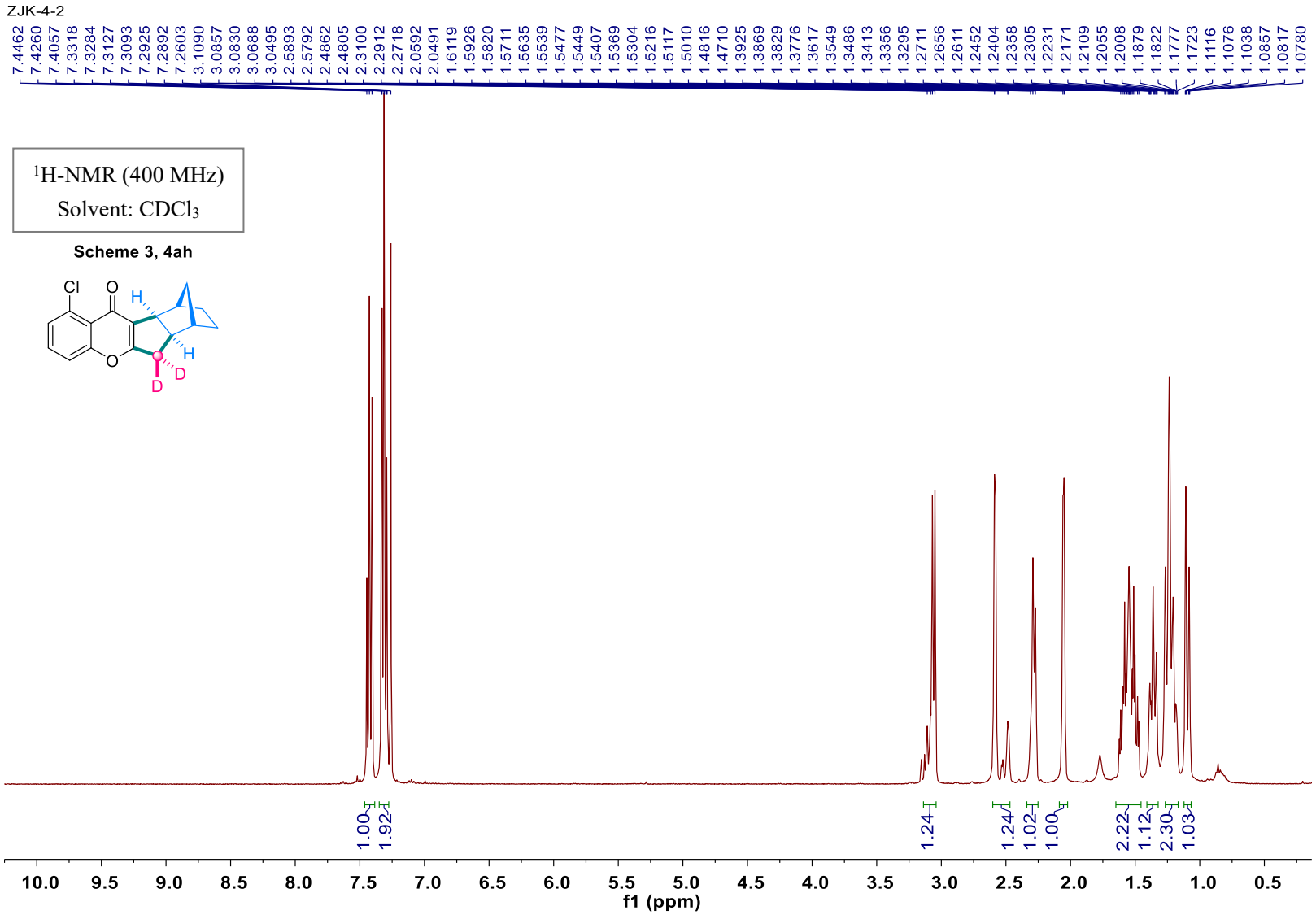
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 3, 4ag

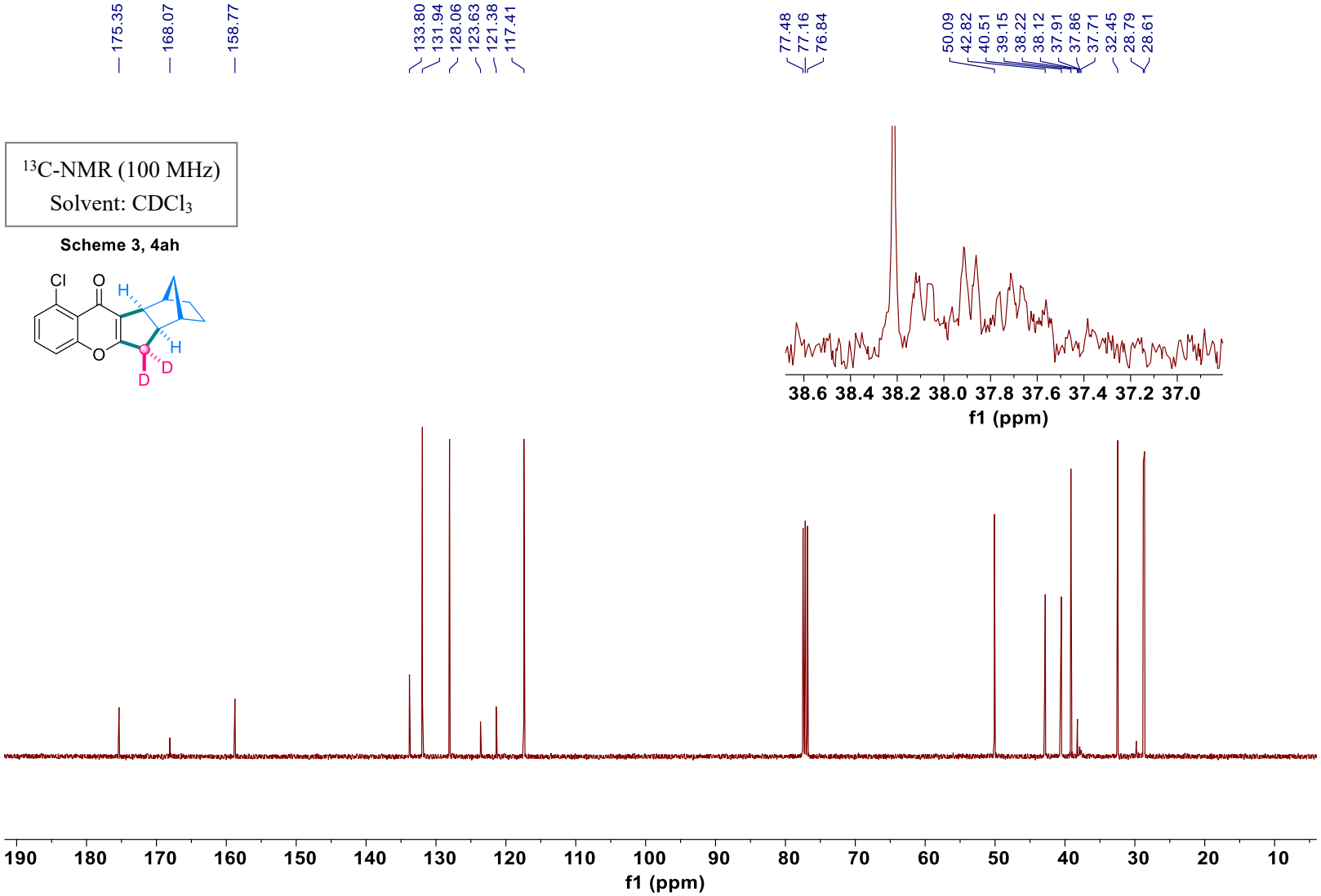





ZJK-41-1-C
176.35
169.75
156.97
132.82
125.88
124.81
124.43
122.46
122.41
117.96
77.48
77.16
76.84
49.90
42.88
40.35
39.28
38.50
38.14
38.04
37.84
37.64
37.44
32.41
28.85
28.65
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 3, 4ag
O
H
H
D
D
O
38.8 38.6 38.4 38.2 38.0 37.8 37.6 37.4 37.2
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


ZJK-4-2
7.4462 7.4260 7.4057 7.3318 7.3284 7.3127 7.3093 7.2925 7.2892 7.2603 3.1090 3.0857 3.0830 3.0688 3.0495 2.5893 2.5792 2.4862 2.4805 2.3100 2.2912 2.2718 2.0592 2.0491 1.6119 1.5926 1.5820 1.5711 1.5635 1.5539 1.5477 1.5449 1.5407 1.5369 1.5304 1.5216 1.5117 1.5010 1.4816 1.4710 1.3925 1.3869 1.3829 1.3776 1.3617 1.3549 1.3486 1.3413 1.3356 1.3295 1.2711 1.2656 1.2611 1.2452 1.2404 1.2358 1.2305 1.2231 1.2171 1.2109 1.2055 1.2008 1.1879 1.1822 1.1777 1.1723 1.1116 1.1076 1.1038 1.0857 1.0817 1.0780
1H-NMR (400 MHz)
Solvent: CDCl3
Scheme 3, 4ah
Cl
O
H
H
O
D
D
1.00
1.92
1.24
1.24
1.02
1.00
2.22
1.12
2.30
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

ZJK-4-2-c

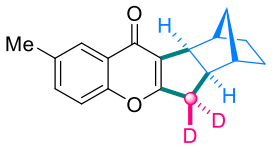

175.35
168.07
158.77
133.80
131.94
128.06
123.63
121.38
117.41
77.48
77.16
76.84
50.09
42.82
40.51
39.15
38.22
38.12
37.91
37.86
37.71
32.45
28.79
28.61
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Scheme 3, 4ah
Cl
O
H
H
D
D
38.6 38.4 38.2 38.0 37.8 37.6 37.4 37.2 37.0
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

ZJK-1-1-h

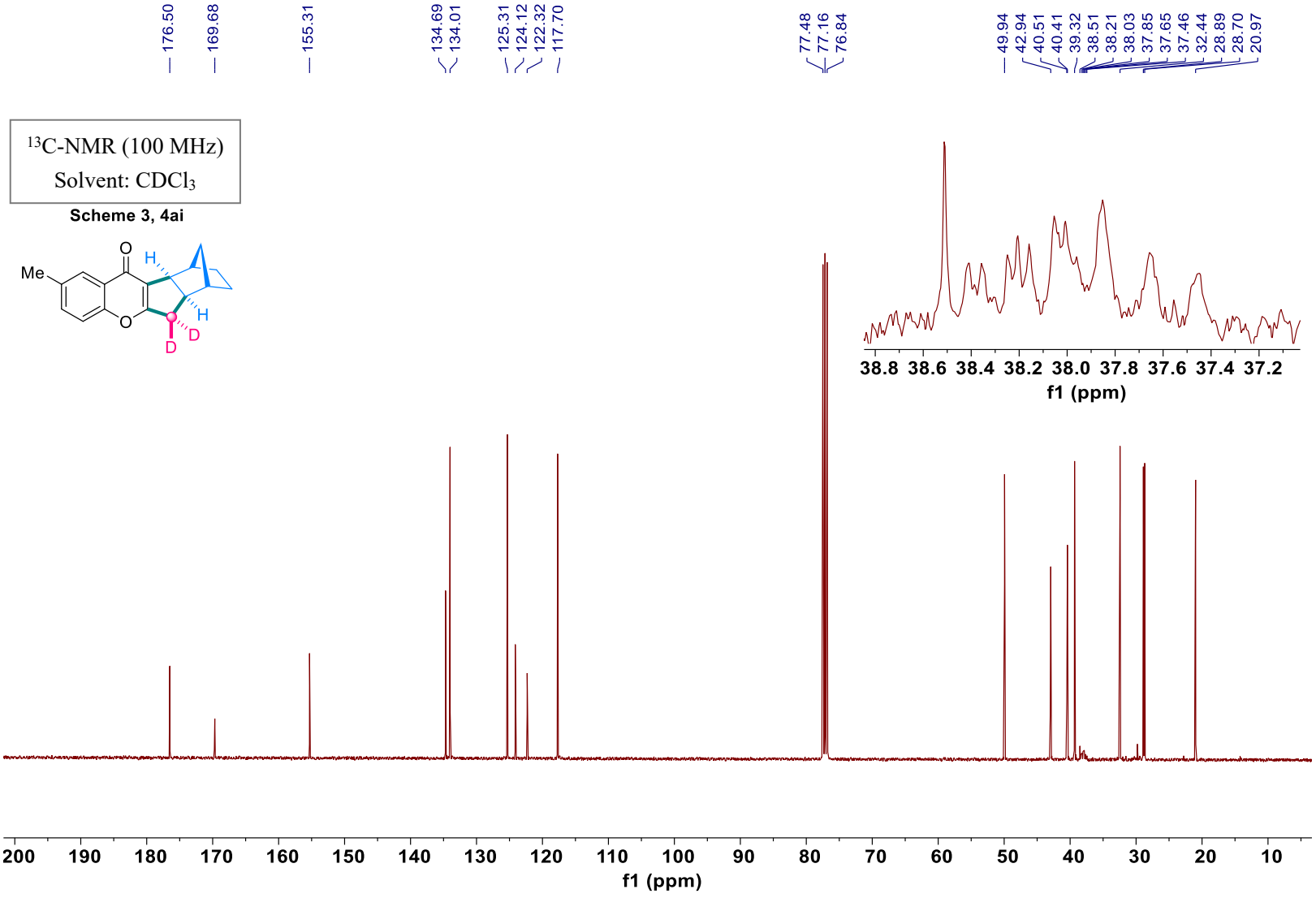
7.9920 7.9881 7.3989 7.3932 7.3776 7.3720 7.2921 7.2708 7.2600 3.1114 3.0924 2.5643 2.5541 2.4203 2.2901 2.2707 2.0574 2.0472 1.6202 1.6013 1.5906 1.5797 1.5722 1.5627 1.5553 1.5520 1.5494 1.5426 1.5328 1.5241 1.5140 1.5034 1.4845 1.4739 1.4264 1.4207 1.4163 1.4106 1.4029 1.3963 1.3889 1.3755 1.3694 1.3628 1.3592 1.3211 1.2768 1.2726 1.2684 1.2627 1.2459 1.2404 1.2356 1.2284 1.2220 1.2167 1.2121 1.2069 1.1993 1.1934 1.1890 1.1834 1.1042 1.1002 1.0964 1.0925 1.0885 1.0784 1.0746 1.0706 1.0668 1.0629

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 3, 4ai



ZJK-1-1-c

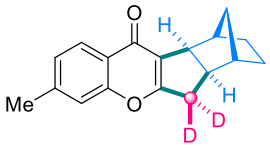

176.50
169.68
155.31
134.69
134.01
125.31
124.12
122.32
117.70
77.48
77.16
76.84
49.94
42.94
40.51
40.41
39.32
38.51
38.21
38.03
37.85
37.65
37.46
32.44
28.89
28.70
20.97
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 3, 4ai
Me
O
H
H
D
D
38.8 38.6 38.4 38.2 38.0 37.8 37.6 37.4 37.2
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

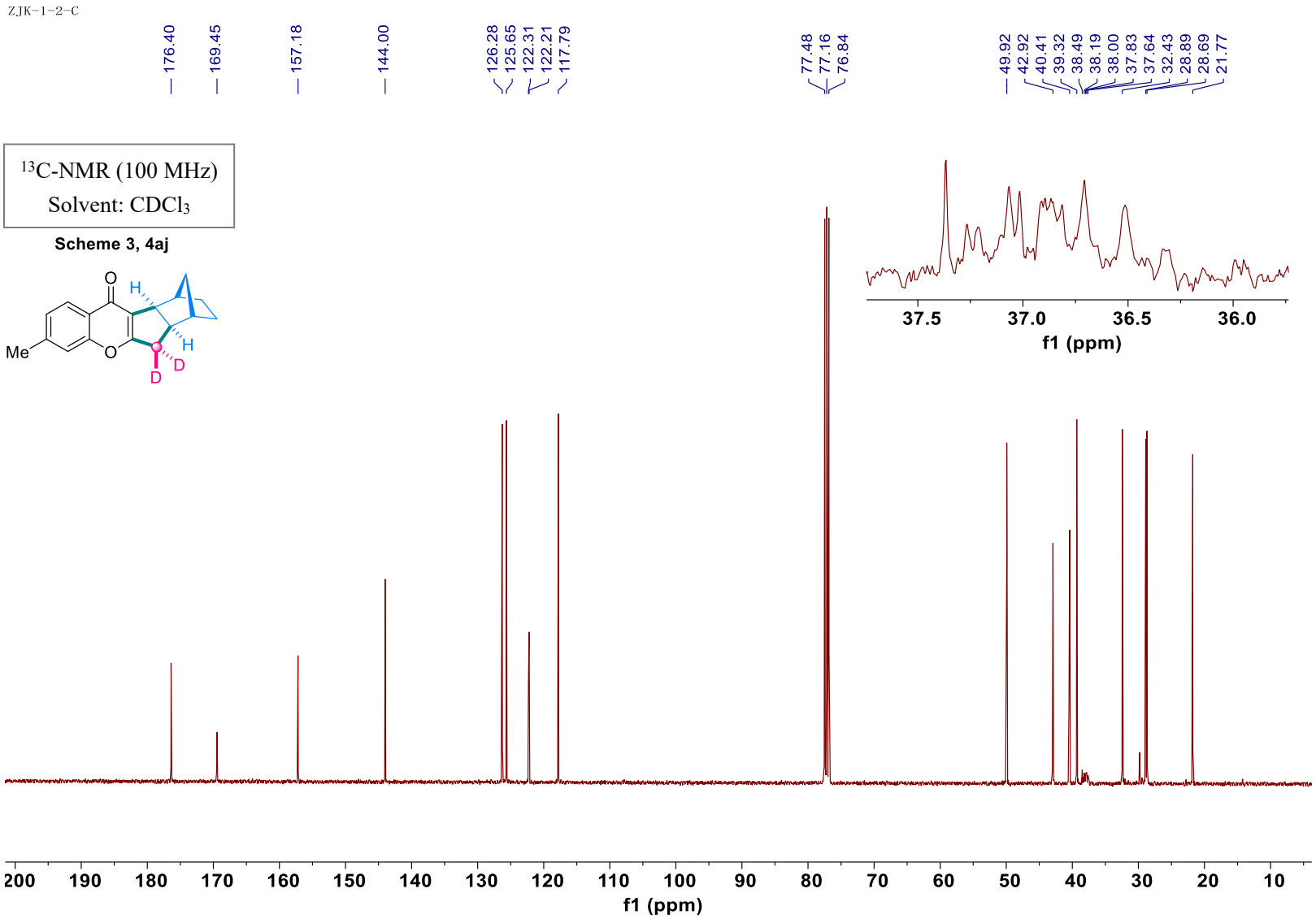
ZJK-1-2-h

8.0925 8.0725 7.2601 7.1680 7.1461 7.1421 3.1205 3.1001 3.0811 2.5962 2.5623 2.5522 2.5017 2.4954 2.4903 2.4391 2.3039 2.2842 2.2651 2.0542 2.0439 1.6277 1.6172 1.6069 1.5983 1.5874 1.5766 1.5692 1.5597 1.5521 1.5487 1.5399 1.5300 1.5215 1.5112 1.5006 1.4915 1.4816 1.4710 1.4208 1.4152 1.4104 1.4053 1.3972 1.3908 1.3836 1.3700 1.3641 1.3572 1.2431 1.2356 1.2253 1.2189 1.2136 1.2090 1.1957 1.1890 1.1856 1.1801 1.0988 1.0949 1.0908 1.0731 1.0693 1.0652

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 3, 4aj



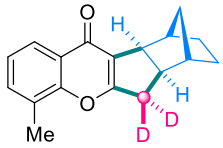

ZJK-1-2-C
176.40
169.45
157.18
144.00
126.28
125.65
122.31
122.21
117.79
77.48
77.16
76.84
49.92
42.92
40.41
39.32
38.49
38.19
38.00
37.83
37.64
32.43
28.89
28.69
21.77
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 3, 4aj
Me
O
H
H
D
D
37.5
37.0
36.5
36.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

ZJK-2-1-h

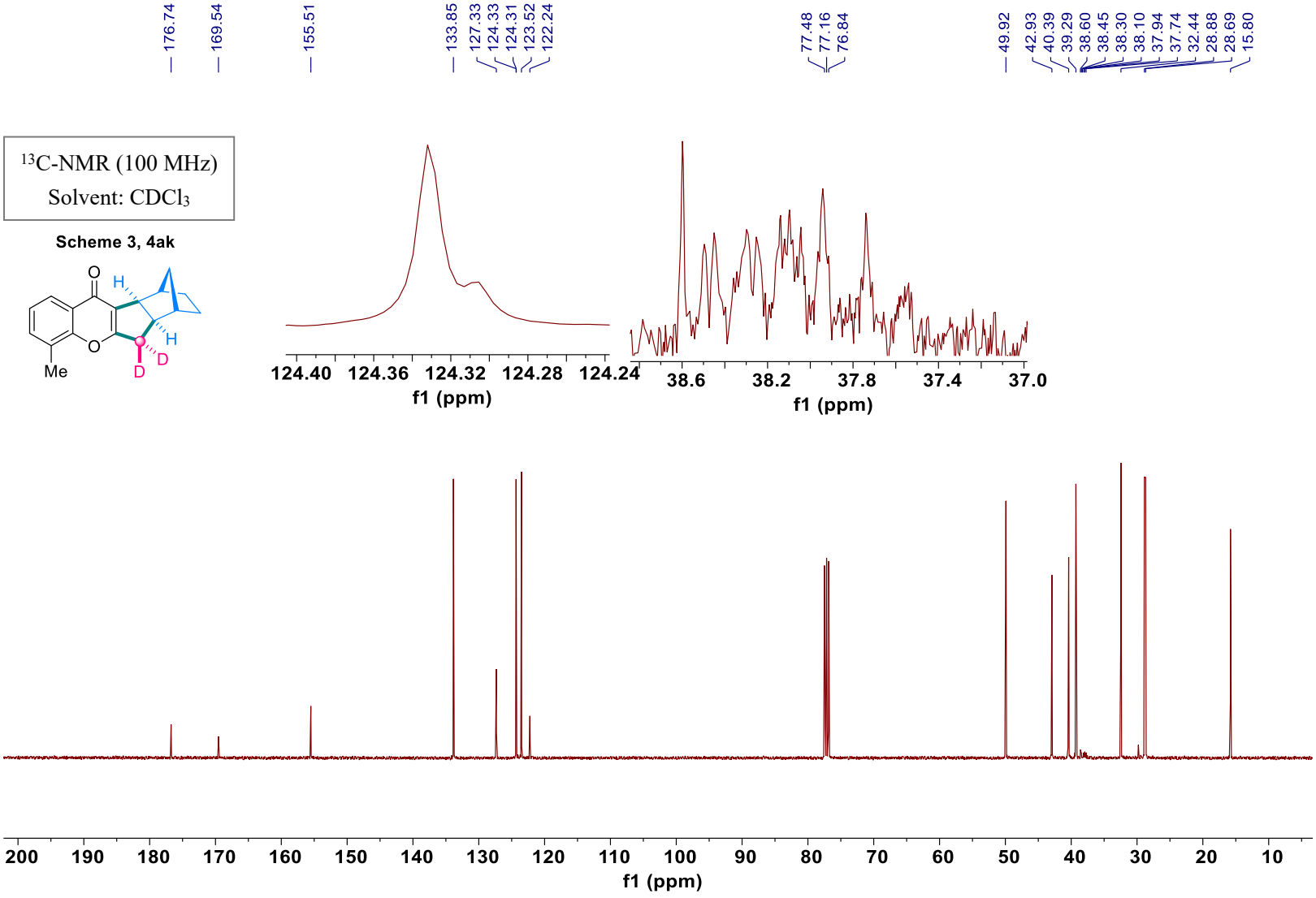
8.1142 8.1098 8.0943 8.0898 7.4712 7.4696 7.4683 7.4654 7.4533 7.4516 7.3014 7.2975 7.2791 7.2602 5.3249 3.2103 3.1853 3.1637 3.1444 2.6187 2.6086 2.5870 2.4788 2.3484 2.3291 2.1139 2.1037 1.6779 1.6675 1.6571 1.6485 1.6377 1.6266 1.6195 1.6100 1.6002 1.5909 1.5811 1.5727 1.5625 1.5518 1.5426 1.5328 1.5222 1.4725 1.4656 1.4569 1.4486 1.4428 1.4357 1.4216 1.4157 1.4090 1.3283 1.3238 1.3193 1.2991 1.2926 1.2780 1.2711 1.2679 1.2631 1.2500 1.2451 1.2407 1.2340 1.1504 1.1466 1.1246 1.1208

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 3, 4ak



ZJK-2-1-C

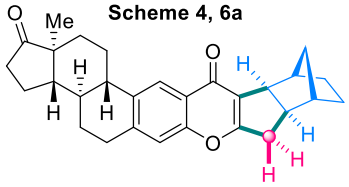

176.74
169.54
155.51
133.85
127.33
124.33
124.31
123.52
122.24
77.48
77.16
76.84
49.92
42.93
40.39
39.29
38.60
38.45
38.30
38.10
37.94
37.74
32.44
28.88
28.69
15.80
13C-NMR (100 MHz)
Solvent: CDCl3
Scheme 3, 4ak
O
H
H
O
D
D
Me
124.40 124.36 124.32 124.28 124.24
f1 (ppm)
38.6 38.2 37.8 37.4 37.0
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

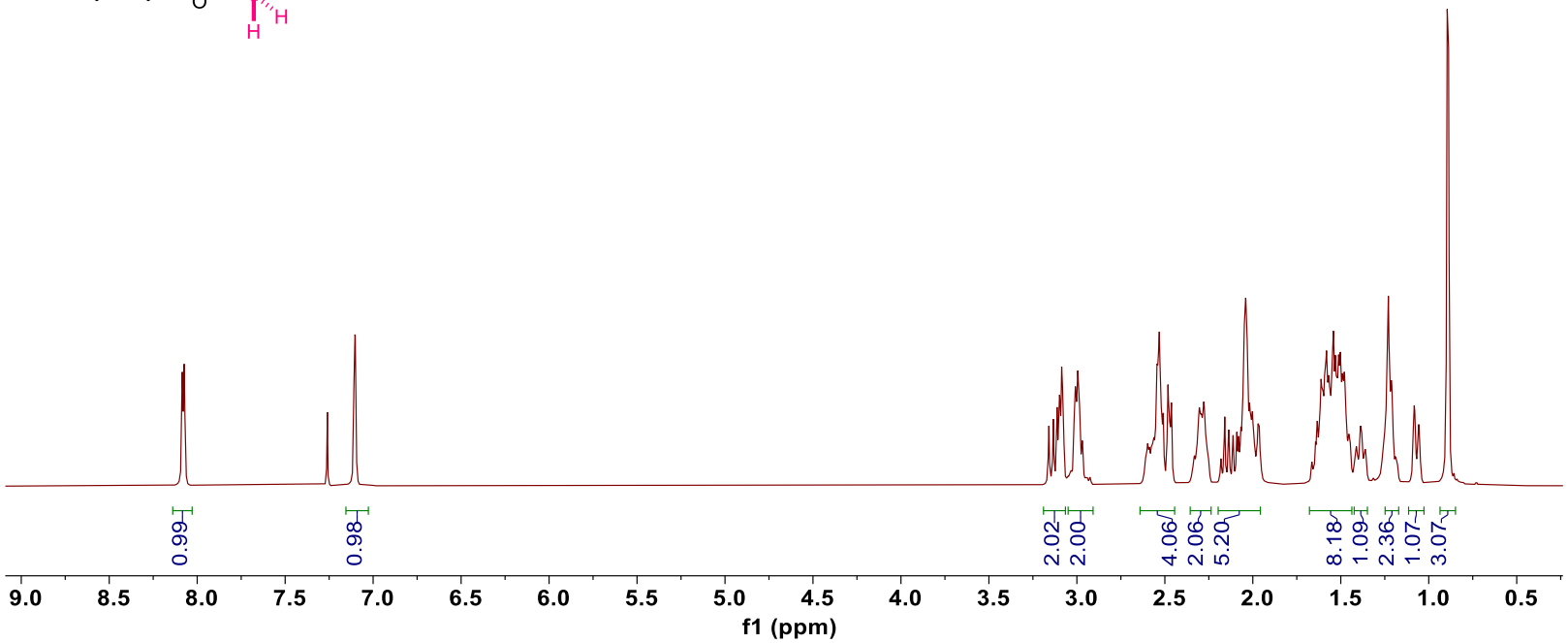
ZJK-7-1-h

8.0848 8.0742 7.2606 7.1070 7.1009 3.1593 3.1338 3.1128 3.0994 3.0864 3.0785 3.0138 3.0080 2.9947 2.9852 2.5447 2.5315 2.5208 2.5163 2.5088 2.4823 2.4745 2.4695 2.4621 2.3052 2.2934 2.2781 2.1597 2.1367 2.1124 2.0911 2.0683 2.0572 2.0491 2.0407 2.0326 2.0179 2.0105 2.0022 1.9945 1.9708 1.9629 1.6340 1.6208 1.6123 1.6056 1.6008 1.5900 1.5824 1.5785 1.5687 1.5608 1.5505 1.5419 1.5305 1.5217 1.5126 1.5031 1.4906 1.4802 1.4747 1.4551 1.3883 1.3809 1.2381 1.2298 1.2111 1.0825 1.0582 1.0527 0.8951 0.8871

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 4, 6a



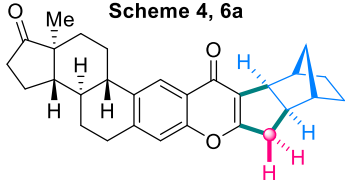


ZJK-7-1-c

220.69
176.44
169.47
169.43
155.26
142.99
142.98
137.41
137.37
122.20
122.09
122.07
121.93
117.24
117.22
77.48
77.16
76.84
50.57
50.56
49.92
47.99
47.97
44.17
43.01
40.53
40.51
39.31
39.28
38.49
38.00
37.97
35.91
32.40
32.39
31.46
29.67
29.65
28.89
28.86
28.68
26.22
26.19
25.89
25.84
21.68
13.87
13.85

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 4, 6a

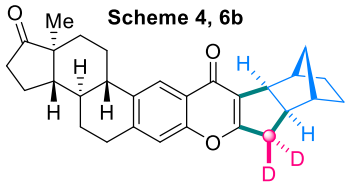


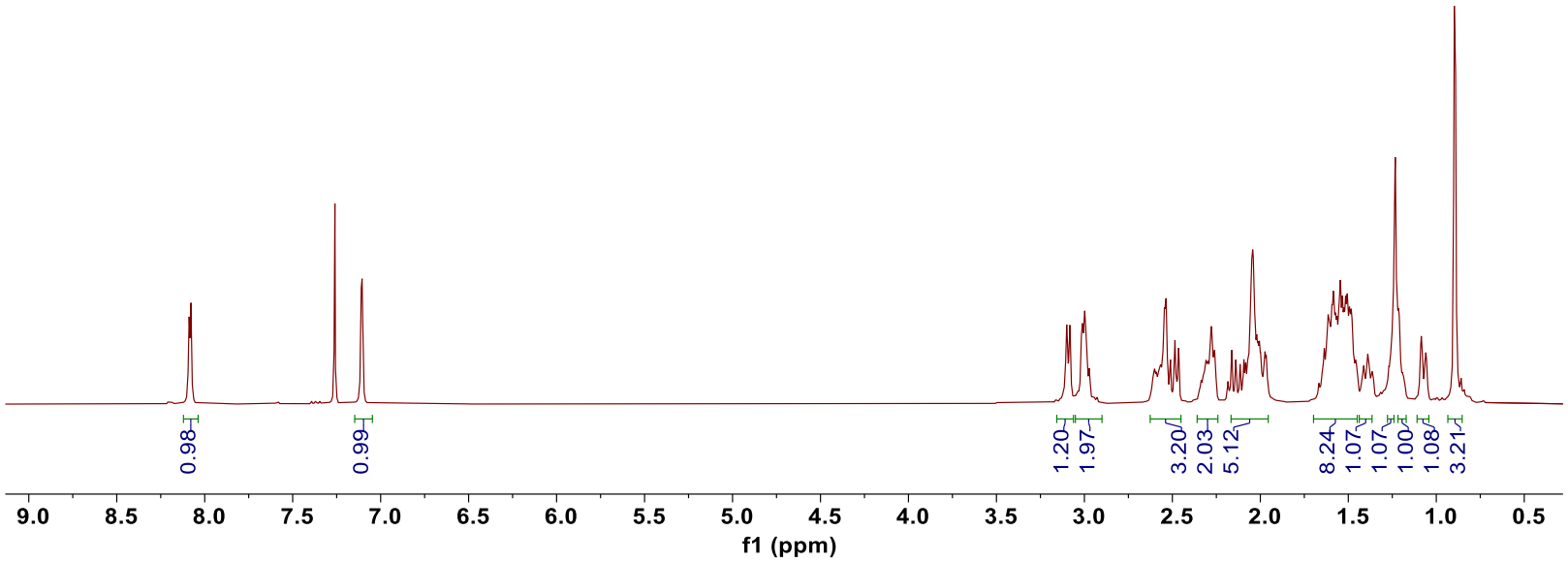
ZJK-8-1-h

8.0890 8.0783 7.2606 7.1104 7.1044 3.1007 3.0820 3.0140 2.9982 2.9880 2.9718 2.5757 2.5669 2.5442 2.5336 2.5111 2.4852 2.4647 2.3094 2.2969 2.2790 2.2596 2.1626 2.1395 2.1152 2.0938 2.0834 2.0707 2.0515 2.0427 2.0356 2.0205 2.0125 2.0050 1.9974 1.9816 1.9736 1.9658 1.6462 1.6367 1.6235 1.6148 1.6079 1.6040 1.5925 1.5851 1.5812 1.5716 1.5638 1.5528 1.5452 1.5337 1.5246 1.5156 1.5059 1.4932 1.4834 1.4785 1.4585 1.4526 1.4114 1.3908 1.3832 1.2696 1.2660 1.2537 1.2334 1.2118 1.0849 1.0590 0.8977 0.8897

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

Scheme 4, 6b





ZJK-8-1-C

220.70
220.68
176.46
169.41
169.37
155.28
143.00
142.98
137.42
137.37
122.21
122.10
122.08
122.03
117.25
117.23
77.48
77.16
76.84
50.57
50.56
49.91
47.99
47.98
44.18
44.16
43.02
42.94
40.44
40.42
40.35
40.33
39.31
39.28
38.01
37.98
35.91
32.41
31.46
29.79
29.67
29.66
28.89
28.86
28.68
26.23
26.20
25.89
25.85
21.68
13.87

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 4, 6b