Generation and Trapping of Electron-Deficient 1,2-Cyclohexadienes. Unexpected Hetero-Diels-Alder Reactivity

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Electronic Supplementary Information, Part 1 (Experimental Details and Characterization Data)

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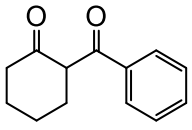
General Information. Reactions were carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise stated. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes. Solvents were purified by usual methods before use. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F254 (Merck). Flash chromatography columns were packed with 230-400 mesh silica gel (Silicycle). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 500 MHz and coupling constants (*J*) are reported in Hertz (Hz). Standard notation is used to describe the multiplicity of signals observed in ^{1}H NMR spectra: broad (br), multiplet (m), singlet (s), doublet (d), triplet (t), quartet (q), etc. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz. The chemical shifts are reported on the δ scale (ppm) and referenced to the residual solvent peaks: $CDCl_3$ (7.26 ppm, ^{1}H; 77.06 ppm, ^{13}C) as internal standards. Infrared (IR) spectra were measured with a Mattson Galaxy Series FT-IR 3000 spectrophotometer. High-resolution mass spectrometry (HRMS) data (APPI/APCI/ESI technique) were recorded using an Agilent Technologies 6220 oaTOF instrument. HRMS data (EI technique) were recorded using a Kratos MS50 instrument.

Experimental Section

General Procedure for the Synthesis of Intermediates

General procedure for the preparation of the 2-arylacylhexanones A-C (1,3-diketones)

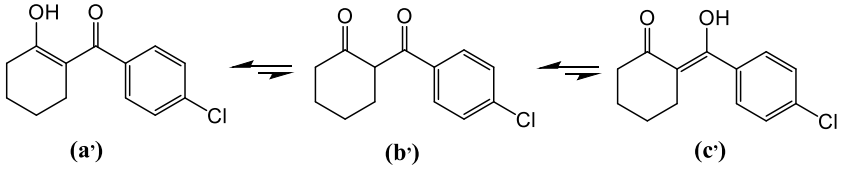
This procedure was based on that of Fos *et al.*[1] To an ice-water cooled solution of 1-morpholino-1-cyclohexene (typically 40 mmol, 1 equiv.) and triethylamine (41 mmol, 1.03 equiv.) in chloroform (25 mL), arylacyl chloride (40 mmol, 1 equiv.) in 15 mL of chloroform was added dropwise with temperature below 15 °C (20 min). After that, the mixture was stirred at room temperature for 20 h. Then, 15 mL of 4 N hydrochloric acid were added and the mixture was refluxed for 5 h. The organic layer was separated, the aqueous layer was extracted with DCM (2 × 15 mL). The extract was combined with the organic layer separated and washed with water (2 × 15 mL). Following drying over $MgSO_4$, the solvents were removed under reduced pressure. The residue can be used directly, or washed with mixture solvents of hexanes and DCM, or purified further using flash chromatography to afford intermediates **A-C**.



A

Using the general procedure, 1-morpholino-1-cyclohexene with benzoyl chloride gave **A** as a yellow viscous liquid, yield 80%, which is pure enough to undergo further reaction. To treat the liquid with DCM and hexanes (placed in a fridge), light yellow solid can be obtained, totally in diketone form by ^{1}H NMR; mp 81-83 °C (lit.[1] mp 76-78 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.89 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 4.38 (t, *J* = 7.0 Hz, 1H), 2.61-2.55 (m, 1H), 2.52-2.46 (m, 1H), 2.35-2.28 (m, 1H), 2.14-2.07 (m, 1H), 2.04-1.90 (m, 3H), 1.78-1.72 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 197.5, 136.6, 133.3, 128.7, 128.5, 58.9, 42.3, 30.0, 27.3, 23.1.



(a') **(b')** **(c')**

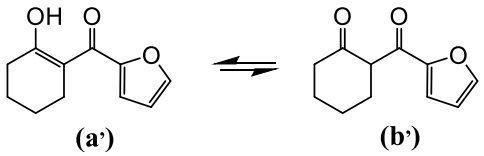
B [**a'**/**b'**/**c'** = 1/0.65/0.21]

Using the general procedure and flash chromatography (12:1 hexane:EtOAc), 1-morpholino-1-cyclohexene with 4-chlorobenzoyl chloride gave **B** as a red viscous liquid, yield 85%, 1:0.65:0.21 enol/keto mixture of **a'**, **b'** and **c'** by ^{1}H NMR; IR (cast film) 3414, 3093, 2945, 2848, 1712, 1683, 1589, 1574, 1488, 1450, 1275, 1092 cm^{-1}; HRMS (EI, M^+) for $C_{13}H_{13}O_2{}^{35}Cl$ calcd. 236.0604, found: m/z 236.0602.

B(a'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 2.48 (t, *J* = 6.5 Hz, 2H), 2.38 (t, *J* = 6.5 Hz, 2H), 1.78-1.74 (m, 2H), 1.64-1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.0, 189.9, 136.6, 135.8, 129.2, 128.4, 107.1, 32.7, 26.5, 23.4, 21.8.

B(b'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.31 (dd, *J* = 3.0, 1.0 Hz, 1H), 2.58-2.49 (m, 2H), 2.35-2.26 (m, 1H), 2.15-2.05 (m, 1H), 2.04-1.96 (m, 1H), 1.95-1.84 (m, 1H), 1.80-1.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 196.3, 139.8, 135.0, 129.9, 129.0, 58.9, 42.3, 29.9, 27.3, 23.1.

B(c'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 2.49-2.46 (m, 3H), 2.05-1.96 (m, 3H), 1.94-1.85 (m, 1H), 1.62-1.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 165.8, 139.2, 135.7, 130.9, 128.7, 27.5, 26.3, 23.5, 22.4.



(a') **(b')**

C [**a'**/**b'** = 1.07/1]

Using the general procedure, 1-morpholino-1-cyclohexene with 2-furoyl chloride gave **C** as light yellow solid, yield 78%, 1.07:1 enol/keto mixture of **a'** and **b'** by ^{1}H NMR; mp 104-107 °C; IR (cast film) 3394, 3131, 3117, 2938, 2861, 1700, 1661, 1566, 1468, 1445, 1271, 1254, 1029 cm^{-1}; HRMS (EI, M^+) for $C_{11}H_{12}O_3$ calcd. 192.0786, found: m/z 192.0788.

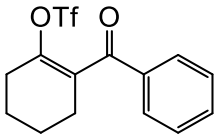
C(a'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 1.5, 0.5 Hz, 1H), 7.16 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.55 (dd, *J* = 4.0, 2.0 Hz, 1H), 2.69 (t, *J* = 5.5 Hz, 2H), 2.46 (t, *J* = 3.5 Hz, 2H), 1.77-1.72 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.1, 177.0, 150.9, 145.9, 118.2, 112.0, 105.9, 33.0, 24.7, 23.3, 21.4.

C(b'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 1.5, 0.5 Hz, 1H), 7.22 (dd, *J* = 3.5, 0.5 Hz,

1H), 6.53 (dd, *J* = 4.0, 2.0 Hz, 1H), 4.17 (ddd, *J* = 9.5, 6.0, 1.0 Hz, 1H), 2.57-2.53 (m, 1H), 2.50-2.46 (m, 1H), 2.29-2.23 (m, 1H), 2.13-2.08 (m, 1H), 2.02-1.97 (m, 2H), 1.90-1.86 (m, 1H), 1.74-1.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 189.5, 152.5, 146.6, 117.7, 112.5, 59.1, 42.3, 29.3, 27.2, 23.1.

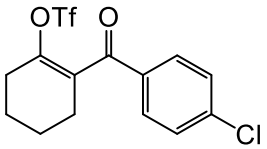
General procedure for the preparation of the arylacylhexenyl triflate intermediates 5a-5c

A solution of diketone **A** (or **B**, **C**) (typically 10 mmol, 1.0 equiv.) in THF (10 mL) was added dropwise to a stirred suspension of NaH (60% in mineral oil, 12 mmol, 1.2 equiv.) in THF (45 mL) at -10 ºC-0 ºC. After 45 min, a solution of $PhNTf_2$ (13 mmol, 1.3 equiv.) in THF (15 mL) was added and the resulting mixture was reacted at -10 ºC-0 ºC for 15 h. The reaction was diluted with H_2O (50 mL) and extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography to yield the triflate intermediate **5(a-c)**.



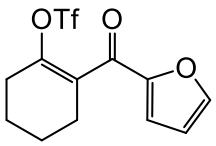
5a

Using the general procedure and flash chromatography (18:1 hexane:Et_2O) provided **5a** as a colorless oil, yield 73%; R*f* 0.37 (hexanes/Et_2O 5:1); IR (cast film) 3064, 2947, 2867, 1669, 1598, 1582, 1450, 1418, 1247, 1212, 1139, 1031 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.62-7.58 (m, 1H), 7.51-7.47 (m, 2H), 2.56-2.52 (m, 2H), 2.50-2.46 (m, 2H), 1.95-1.90 (m, 2H), 1.81-1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 146.1, 135.5, 134.0, 130.2, 129.4, 128.8, 118.0 (q, *J* = 318.4 Hz, CF_3), 27.6, 27.5, 22.7, 21.1; HRMS (ESI) for $C_{14}H_{13}F_3O_4S$ calcd. 357.0379 ([M+Na]$^+$) and 335.0559 ([M+H]$^+$), found: m/z 357.0372 ([M+Na]$^+$) and 335.0560 ([M+H]$^+$).



5b

Using the general procedure and flash chromatography (20:1 hexane:Et_2O) provided **5b** as white solid, yield 72%; R*f* 0.46 (hexanes/Et_2OAc 6:1); mp 61-63 °C; IR (cast film) 3093, 2959, 2869, 1660, 1584, 1484, 1450, 1413, 1248, 1201, 1011 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 2.55-2.51 (m, 2H), 2.49-2.45 (m, 2H), 1.95-1.90 (m, 2H), 1.81-1.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 146.5, 140.6, 133.8, 130.7, 129.8, 129.2, 118.0 (q, *J* = 318.1 Hz, CF_3), 27.6, 27.4, 22.6, 21.1; HRMS (EI, M$^+$) for $C_{14}H_{12}O_4S^{35}ClF_3$ calcd. 368.0097, found: m/z 368.0095.

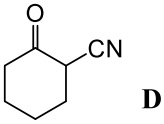


5c

Using the general procedure and flash chromatography (6:1 to 3:1 hexane:Et_2O) provided **5c** as white solid, yield 56%; R*f* 0.28 (hexanes/Et_2O 5:1); mp 98-99 °C; IR (cast film) 3270, 3125, 3095, 2938, 2871, 1698, 1641, 1561, 1466, 1413, 1207, 1134, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.0 Hz, 1H), 7.25 (dd, *J* = 5.0, 0.5 Hz, 1H), 6.58 (dd, *J* = 3.5, 1.5 Hz, 1H), 2.54-2.48 (m, 4H), 1.92-1.86 (m, 2H), 1.78-1.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.4, 151.5, 147.7, 147.0, 129.2, 120.2, 118.1 (q, *J* = 318.1 Hz, CF_3), 112.7, 27.7, 26.9, 22.6, 21.1; HRMS (ESI) for $C_{12}H_{11}F_3O_5S$ calcd. 347.0171 ($[M+Na]^+$) and 325.0352 ($[M+H]^+$), found: m/z 347.0168 ($[M+Na]^+$) and 325.0353 ($[M+H]^+$).

Procedure for the preparation of the 2-cyanohexanone D

This procedure was based on that of Vallribera and Shafir *et al.*[2] NaH (60% in mineral oil, 6.96 g, 174 mmol, 3.0 equiv.) and a stir bar were placed in an an oven-dried 3-neck 250 mL flask under nitrogen. Dry hexane (80 mL) was added and the mixture was stirred for 15 min, then decanted the liquid via cannula to remove the protecting oil in NaH. Dry THF (80 mL) and *N*-methylaniline (18.62 g, 174 mmol, 3.0 equiv.) were added. The flask was then fitted with a reflux condenser and a solution of pimelonitrile (7.08 g, 58 mmol, 1.0 equiv.) in THF (40 mL) was added to the flask though an addition funnel (10 min). After that, the reaction mixture was brought to reflux for 2.5 h, leading to the formation of a thick paste. This mixture was cooled to 0 °C and was quenched with H_2O (30 mL). The mixture was further acidified to a pH of 1 using 4 N HCl for the complete hydrolysis of the intermediate imine. The resulting yellow solution was extracted with Et_2O (3 × 25 mL) and the organic layer combined was dried over $MgSO_4$. The solvents were removed under reduced pressure and the residue was purified by column chromatography.



D

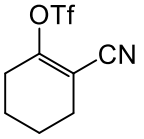
Flash chromatography (3:1 hexane:EtOAc) gave **D** (5.94 g, yield 83 %) as yellow oil (lit.[2] yield 73% (using distillation)).

D: R*f* 0.35 (hexanes/EtOAc 2:1); ^1H NMR (500 MHz, $CDCl_3$) δ 3.50 (dd, *J* = 11.0, 5.5 Hz, 1H), 2.62-2.58 (m, 1H), 2.43-2.32 (m, 2H), 2.08-1.96 (m, 3H), 1.84-1.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5, 116.7, 43.4, 40.7, 32.1, 26.8, 23.7; HRMS (EI, M^+) for C_7H_9NO calcd. 123.0684, found: m/z 123.0681.

Procedure for the preparation of the cyanohexenyl triflate intermediate 5d

This procedure was based on that of Lin and Boyd *et al.*[3] To a stirred, ice-cold solution of 2-cyanocyclohexanone (**D**, 1.80 g, 14.6 mmol, 1.0 equiv.) and diisopropylethylamine (3.06 mL,

17.6 mmol, 1.21 equiv.) in 18 mL of dry 1,2-dichloroethane, triflic anhydride (2.95 mL, 17.5 mmol, 1.2 equiv.) was added. The mixture was stirred at 0 ºC for 2 h. Ethyl acetate (20 mL) was added to the mixture, and the resulting suspension was filtered through a short plug of silica gel and rinsed with excess EtOAc. The filtrate was concentrated under reduced pressure to give an oily residue which was made further purification by column chromatography.



5d

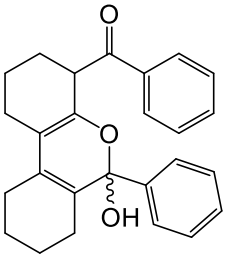
Flash chromatography (5:1 hexane:EtOAc) gave **5d** (2.87 g, yield 77 %) as yellow oil (lit.[3] yield 75%).

5d: R*f* 0.71 (hexanes/EtOAc 2:1); IR (cast film) 2953, 2873, 2227, 1668, 1426, 1218, 1139, 1054 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.54-2.50 (m, 2H), 2.45-2.41 (m, 2H), 1.86-1.81 (m, 2H), 1.73-1.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 118.3 (q, J = 318.6 Hz, CF_3), 114.0, 105.1, 28.5, 26.8, 21.7, 20.4; HRMS (EI, M^+) for $C_8H_8NO_3F_3S$ calcd. 255.0177, found: m/z 255.0181.

General Synthetic Procedure for the Dimerization and Furan Trapping Products

General synthetic procedure for the dimerization products 6a-6c of 1-arylacyl-1,2-cyclohexadienes *via* the hetero-Diels-Alder reaction

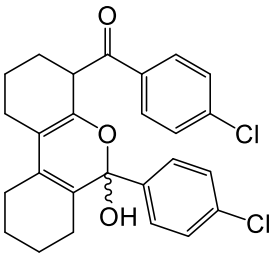
To a stirred solution of intermediate **5** (0.4 mmol, 1.0 equiv.) in anhydrous THF (1.0 mL) was added dropwise a solution of KO^{t}Bu (0.48 mmol, 1.2 equiv.) in anhydrous THF (1.5 mL) at room temperature in 20 min. After being stirred over night, the reaction mixture was quenched with H_2O (10 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was further purified by column chromatography to afford the new dimerization product **6**.



6a

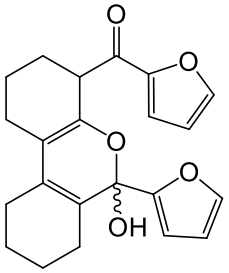
134 mg of starting material **5a** was used. Flash chromatography (7:1 hexane:EtOAc) gave **6a** (20 mg, 26 %) as yellow sticky oil (starting material **5a** recovered 7 mg, 5%); R*f* 0.42 (hexanes/EtOAc 4:1); IR (cast film) 3398, 3062, 2940, 2868, 1672, 1597, 1580, 1449, 1267 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.59-7.54 (m, 1H), 7.50-7.45 (m, 4H), 7.40-7.33 (m, 3H), 3.03 (br s, 1H), 2.60-2.51 (m, 2H), 2.47 (dd, J = 12.0, 4.0 Hz, 1H), 2.46-2.32

(m, 2H), 2.60-2.00 (m, 1H), 1.86-1.80 (m, 1H), 1.81-1.71 (m, 2H), 1.64-1.56 (m, 2H), 1.58-1.55 (m, 1H), 1.55-1.50 (m, 1H), 1.49-1.42 (m, 1H), 1.44-1.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 145.9, 137.3, 135.7, 134.1, 133.4, 133.0, 129.3, 129.1, 128.6, 128.4, 127.9, 106.0, 97.3, 42.7, 37.0, 31.2, 28.8, 26.3, 24.5, 23.1(2), 23.1(1); HRMS (ESI, $[M+Na]^+$) for $C_{26}H_{26}O_3$ calcd. 409.1774, found: m/z 409.1770.



6b

73.7 mg of starting material **5b** was used. Flash chromatography (18:1 to 12:1 hexane:EtOAc) gave **6b** (5 mg, 11 %) as yellow sticky oil (starting material **5b** recovered 20 mg, 27%), there were little impurities in the product (very difficult to be removed); R*f* 0.34 (hexanes/EtOAc 6:1); IR (cast film) 3405, 2937, 2869, 1666, 1587, 1488, 1446, 1263, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 2.90 (br s, 1H), 2.55-2.48 (m, 2H), 2.42 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.36-2.27 (m, 2H), 2.24-1.98 (m, 1H), 1.88-1.73 (m, 2H), 1.76-1.71 (m, 1H), 1.64-1.57 (m, 2H), 1.58-1.52 (m, 2H), 1.50-1.45 (m, 1H), 1.44-1.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 144.9, 139.5, 135.4, 134.3, 134.2, 134.0, 133.0, 130.7, 130.4, 128.8, 128.1, 106.3, 97.3, 42.6, 37.2, 31.2, 28.6, 26.2, 24.4, 23.1, 23.0; HRMS (EI, M^+) for $C_{26}H_{24}O_3{}^{35}Cl_2$ calcd. 454.1103, found: m/z 454.1102.

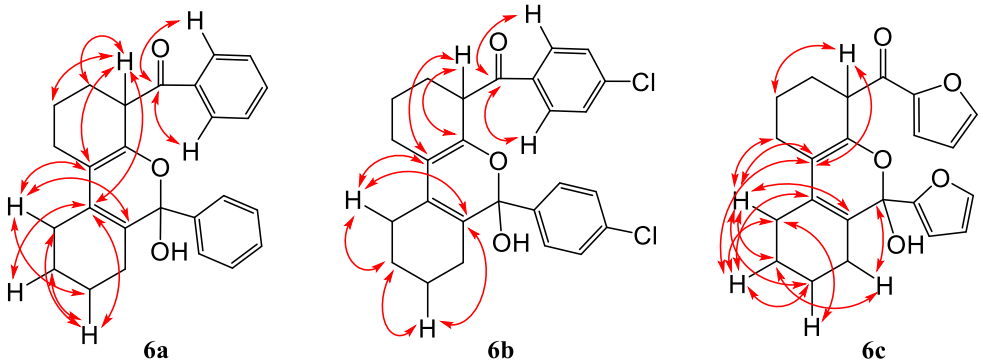


6c

130 mg of starting material **5c** was used. Flash chromatography (3:2 hexane:Et_2O) gave **6c** (31 mg, 42 %) as yellow sticky oil (starting material **5c** recovered 12 mg, 10%); R*f* 0.28 (hexanes/Et_2O 1:1); IR (cast film) 3408, 2930, 2855, 1647, 1562, 1462, 1164, 1083, 1020 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.48 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.22 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.64 (d, *J* = 3.5 Hz, 1H), 6.54 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.46 (dd, *J* = 3.5, 2.0 Hz, 1H), 2.95 (br s, 1H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.61 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.52-2.49 (m, 2H), 2.11-2.05 (m, 1H), 1.94-1.78 (m, 2H), 1.80-1.74 (m, 1H), 1.66-1.58 (m, 2H), 1.60-1.52 (m, 2H), 1.51-1.44 (m, 1H), 1.39-1.30 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.9, 152.8, 150.2, 146.7, 142.7, 137.3, 135.6, 133.3, 119.2, 112.3, 111.2, 111.1, 106.9, 97.1, 42.5, 37.1, 31.4, 28.3, 24.7, 24.4, 23.1, 22.7; HRMS (ESI, $[M+Na]^+$) for $C_{22}H_{22}O_5$ calcd. 389.1359,

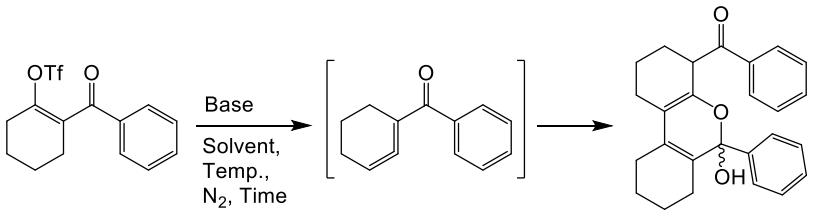
found: m/z 389.1358.

HMBC correlations for the dimerization products **6a-6c**:



6a **6b** **6c**

Table S1 Optimization of the dimerization reaction conditions of 1,2-cyclohexadiene bearing arylacyl group [a]



5a **7a** **6a**

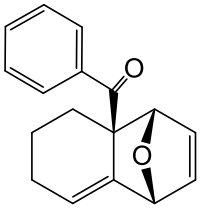
Entry	Base (equiv.)	Solvent	Temp.	Time	Yield **6a** (%)[b]
1	Et_3N (1.5)	THF	rt	12 h	0 [c]
2	DBU (1.05)	THF	rt	12 h	0
3	NaOH (1.05)	THF	rt	12 h	Trace [d]
4	KOH (1.05)	DMSO	rt	12 h	Trace
5	NaH (1.6)	THF	rt	12 h	0
6	KO^{t}Bu (1.75)	THF	rt	12 h	5%
7	KO^{t}Bu (1.2)	THF	- 78 to 0 °C	12 h	- [e]
8	KO^{t}Bu (1.75)	THF	0 °C to rt	12 h	Trace
9	KO^{t}Bu (1.75)	DMSO	40	12 h	-
10	KO^{t}Bu (1.2)	THF	45	3 h	12% [f]
11	KO^{t}Bu (1.75)	Dioxane	100	2 h	0
12	KO^{t}Bu (1.75)	DMF	120	2 h	-
13	KO^{t}Bu (1.75)	DMSO	120	2 h	-
14	KO^{t}Bu (1.02)	THF	rt	1.5 h	6% [f]
15	KO^{t}Bu (2.1)	THF	rt	40 min	8% [f]
16	KO^{t}Bu (2.1)	THF	45-50	30 min	Trace
17	KO^{t}Bu (4.0)	THF	rt	2 h	-
18	KO^{t}Bu (1.2)	THF	rt	3 h	20% [f]
19	KO^{t}Bu (1.2)	THF	rt	12 h	26% [f]

[a] Reaction conditions: in general, **5a** (0.4 mmol) and base (0.42 ~ 1.6 mmol) in anhydrous solvent (~ 2.5 mL)

at different temperature under nitrogen for different time as mentioned in the table. [b] Isolated yield. [c] Almost no reaction underwent. [d] With little hydrolysis product **A**. [e] Messy mixture. [f] **5a** recovered 5%-8%, with little hydrolysis product **A**.

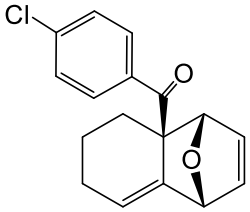
General procedure for the regioselective synthesis of the furan (or 2,5-dimethylfuran) trapping-[4+2] cycloadducts 10a-10d and 11d

To a stirred solution of intermediate **5** (0.2 mmol, 1.0 equiv.) and furan (2.0 mL, 137 equiv.) in anhydrous THF (0.5 mL) was added dropwise a solution of KO^{t}Bu (0.4 mmol, 2.0 equiv.) in anhydrous THF (1.5 mL) at room temperature in 20 min. After being further stirred for 2 h, the reaction mixture was quenched with H_2O (10 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was further purified by column chromatography to afford the cycloadduct **10**.



10a

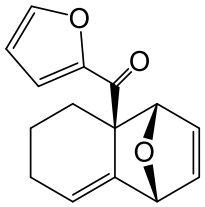
67 mg of starting material **5a** was used. Flash chromatography (12:1 hexane:EtOAc) gave **10a** (25 mg, 50 %) as white solid (**5a** recovered 3 mg, 5%); R*f* 0.30 (hexanes/EtOAc 6:1); mp 85-87 °C; IR (cast film) 3067, 3005, 2932, 2866, 1674, 1596, 1578, 1446, 1225, 1172, 1010 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.49-7.46 (m, 1H), 7.42-7.38 (m, 2H), 6.52 (dd, *J* = 5.5, 2.0 Hz, 1H), 6.25 (dd, *J* = 5.5, 1.5 Hz, 1H), 5.79 (t, *J* = 3.5 Hz, 1H), 5.43 (t, *J* = 1.0 Hz, 1H), 5.22 (br s, 1H), 2.61 (dt, *J* = 12.0, 3.5 Hz, 1H), 2.13-2.07 (m, 1H), 2.00-1.89 (m, 1H), 1.71-1.64 (m, 1H), 1.50-1.38 (m, 1H), 0.75 (ddd, *J* = 14.5, 12.0, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 139.4, 138.7, 138.1, 131.7, 129.7, 128.9, 128.0, 121.5, 85.9, 80.0, 59.0, 32.9, 24.1, 19.8; HRMS (EI, M^+) for $C_{17}H_{16}O_2$ calcd. 252.1150, found: m/z 252.1151.



10b

73.7 mg of starting material **5b** was used. Flash chromatography (15:1 to 12:1 hexane:EtOAc) gave **10b** (47 mg, 82 %) as light yellow solid (**5b** recovered 1.4 mg, 2%); R*f* 0.32 (hexanes/EtOAc 7:1); mp 87-89 °C; IR (cast film) 3090, 3015, 2936, 2867, 1674, 1587, 1486, 1445, 1225, 1094 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 6.52 (dd, *J* = 5.5, 2.0 Hz, 1H), 6.24 (dd, *J* = 5.5, 2.0 Hz, 1H), 5.79 (t, *J* = 3.5 Hz, 1H), 5.35 (br s, 1H), 5.23 (br s, 1H), 2.57 (dt, *J* = 12.0, 3.5 Hz, 1H), 2.11-2.04 (m, 1H), 1.99-1.91 (m,

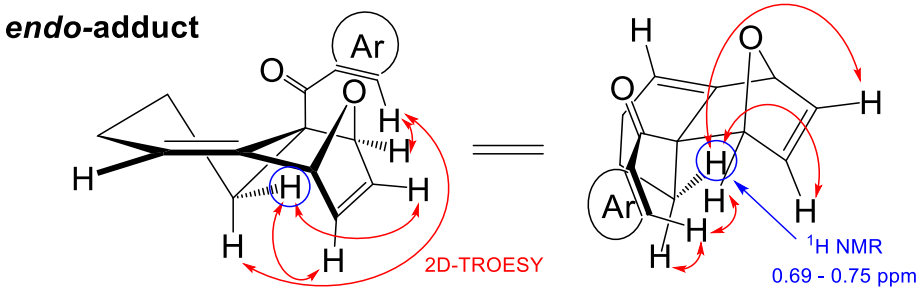
1H), 1.71-1.65 (m, 1H), 1.43-1.35 (m, 1H), 0.70 (ddd, *J* = 13.3, 12.5, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 139.3, 138.6, 138.0, 136.8, 130.4, 129.8, 128.3, 121.9, 86.1, 80.0, 59.0, 33.0, 24.2, 19.8; HRMS (EI, M^+) for $C_{17}H_{15}O_2{}^{35}Cl$ calcd. 286.0761, found: m/z 286.0755.

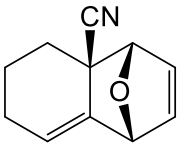


10c

65 mg of starting material **5c** was used. Flash chromatography (8:1 to 5:1 hexane:EtOAc) gave **10c** (29 mg, 60 %) as white solid (**5c** recovered 1 mg, 2%); R*f* 0.29 (hexanes/EtOAc 4:1); mp 105-107 °C; IR (cast film) 3131, 3008, 2934, 2867, 2835, 1666, 1645, 1562, 1464, 1285, 1010 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.32 (dd, *J* = 3.5, 0.5 Hz, 1H), 6.52 (dd, *J* = 5.5, 2.0 Hz, 1H), 6.50 (dd, *J* = 3.5, 2.0 Hz, 1H), 6.22 (dd, *J* = 5.5, 2.0 Hz, 1H), 5.86 (t, *J* = 3.5 Hz, 1H), 5.44 (t, *J* = 1.0 Hz, 1H), 5.21 (br s, 1H), 2.61 (dt, *J* = 12.5, 3.5 Hz, 1H), 2.21-2.15 (m, 1H), 2.00-1.92 (m, 1H), 1.70-1.64 (m, 1H), 1.43-1.33 (m, 1H), 0.69 (ddd, *J* = 13.5, 12.5, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 152.6, 145.7, 138.8, 138.7, 129.6, 121.9, 119.6, 112.1, 85.1, 80.0, 58.2, 31.1, 24.3, 19.7; HRMS (EI, M^+) for $C_{15}H_{14}O_3$ calcd. 242.0943, found: m/z 242.0939.

Pertinent ROESY correlations for stereochemistry of above fuan trapping products containing arylacyl group:



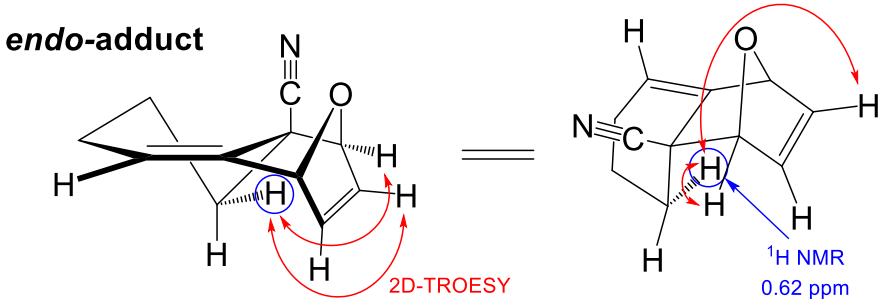


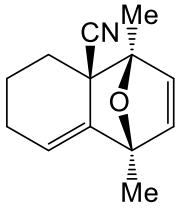
10d

153 mg (0.6 mmol, 1.0 equiv.) of starting material **5d**, 4.0 mL (92 equiv.) of furan and KO^{t}Bu (1.2 mmol, 2.0 equiv.) were used to carry out the reaction for 45 min at room temperature. Flash chromatography (9:1 to 6:1 hexane:EtOAc) gave **10d** (47 mg, 45 %) as colorless oil; R*f* 0.25 (hexanes/EtOAc 4:1); IR (cast film) 3084, 3011, 2928, 2855, 2231, 1563, 1459, 1305, 1021 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47 (dd, *J* = 5.5, 2.0 Hz, 1H), 6.07 (dd, *J* = 5.5, 1.5 Hz, 1H), 5.79

(t, *J* = 3.5 Hz, 1H), 5.27 (br s, 1H), 5.23 (br s, 1H), 2.38-2.28 (m, 1H), 2.22 (dt, *J* = 12.0, 3.5 Hz, 1H), 2.06-1.96 (m, 2H), 1.90-1.84 (m, 1H), 0.62 (ddd, *J* = 12.5, 12.0, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 136.0, 127.9, 122.4, 122.3, 84.5, 79.7, 42.5, 30.4, 24.0, 19.6; HRMS (EI, M^+) for $C_{11}H_{11}NO$ calcd. 173.0841, found: m/z 173.0839.

Pertinent ROESY correlations for stereochemistry:

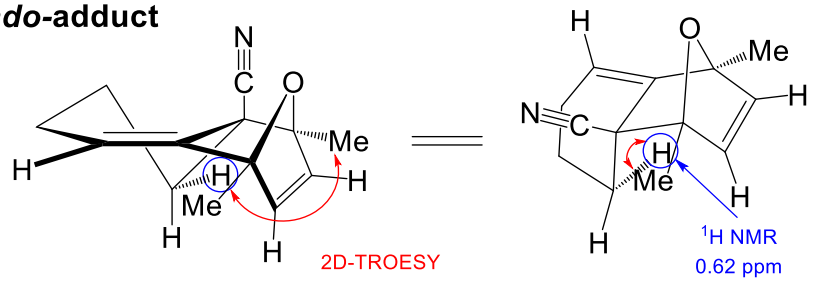




11d

102 mg (0.4 mmol, 1.0 equiv.) of starting material **5d**, 2.8 mL (65 equiv.) of 2,5-dimethylfuran and KO^{t}Bu (0.8 mmol, 2.0 equiv.) were used to carry out the reaction for 45 min at room temperature. Flash chromatography (9:1 hexane:EtOAc) gave **11d** (16 mg, yield 20 %) as yellow oil (**5d** recovered 10 mg, 10%); R*f* 0.67 (hexanes/EtOAc 2:1); IR (cast film) 3079, 2977, 2933, 2872, 2229, 1573, 1446, 1383, 1316, 1138 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.20 (d, *J* = 5.5 Hz, 1H), 5.83 (d, *J* = 5.0 Hz, 1H), 5.67 (dd, *J* = 4.0, 3.0 Hz, 1H), 2.35-2.30 (m, 1H), 2.12 (dt, *J* = 12.0, 3.5 Hz, 1H), 2.04-1.96 (m, 2H), 1.90-1.85 (m, 1H), 1.81 (s, 3H), 1.65 (s, 3H), 0.62 (ddd, *J* = 12.8, 12.0, 4.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 142.2, 131.8, 121.4, 120.2, 89.3, 87.1, 48.3, 30.0, 23.5, 19.5, 15.6, 14.8; HRMS (EI, M^+) for $C_{13}H_{15}NO$ calcd. 201.1154, found: m/z 201.1154.

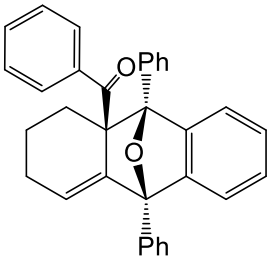
Pertinent ROESY correlations for stereochemistry:



General procedure for the regioselective synthesis of the DPIBF trapping-[4+2]

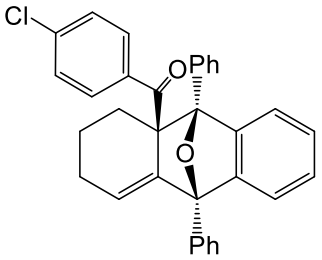
cycloadducts 12a-12d and 13d

To a stirred solution of intermediate **5** (0.2 mmol, 1.0 equiv.) and 1,3-diphenylisobenzofuran (DPIBF) (0.4 mmol, 2.0 equiv.) in anhydrous THF (2.0 mL) was added dropwise a solution of KO^{t}Bu (0.4 mmol, 2.0 equiv.) in anhydrous THF (1.5 mL) at room temperature in 20 min. After being stirred for 2 h, the reaction mixture was quenched with H_2O (10 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was further purified by column chromatography to afford the cycloadduct **12**.



12a

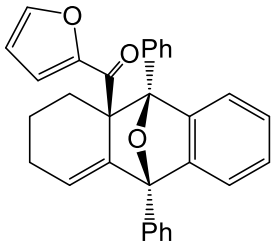
67 mg of starting material **5a** was used. Flash chromatography (30:1 hexane:EtOAc) gave **12a** (18 mg, 20 %) as white solid (**5a** recovered 22 mg, 33%; **6a** can also be isolated, 5%); R*f* 0.41 (hexanes/EtOAc 10:1); mp 124-126 °C; IR (cast film) 3060, 3035, 2932, 2853, 1668, 1598, 1578, 1497, 1458, 1448, 1238 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.60 (m, 4H), 7.47-7.41 (m, 5H), 7.38-7.34 (m, 1H), 7.30-7.26 (m, 4H), 7.23-7.18 (m, 2H), 7.15-7.08 (m, 3H), 6.01 (dd, *J* = 5.0, 2.5 Hz, 1H), 3.04 (ddd, *J* = 11.5, 4.0, 3.0 Hz, 1H), 2.13-2.07 (m, 1H), 2.03-1.95 (m, 1H), 1.69-1.60 (m, 2H), 0.56 (ddd, *J* = 12.3, 12.0, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.9, 149.3, 144.7, 144.6, 143.1, 136.3, 134.8, 130.0, 128.4, 128.3, 128.0(8), 128.0(6), 128.0(0), 127.8, 127.6, 127.2, 126.0, 125.7, 124.4, 121.6, 117.5, 93.0, 89.4, 65.3, 32.2, 24.3, 19.6; HRMS (EI, M^+) for $C_{33}H_{26}O_2$ calcd. 454.1933, found: m/z 454.1928.



12b

73.7 mg of starting material **5b** was used. Flash chromatography (20:1 hexane:EtOAc) gave **12b** (22 mg, 23 %) as light yellow solid (**5b** recovered 5 mg, 7%); R*f* 0.58 (hexanes/EtOAc 6:1); mp 159-161 °C; IR (cast film) 3062, 3040, 2937, 1668, 1590, 1497, 1485, 1458, 1448, 1244, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.5 Hz, 2H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.53-7.45 (m, 3H), 7.44-7.41 (m, 2H), 7.38-7.35 (m, 1H), 7.29-7.18 (m, 5H), 7.16-7.12 (m, 1H), 7.07-7.04 (m, 2H), 6.06 (dd, *J* = 5.0, 3.0 Hz, 1H), 3.03 (ddd, *J* = 11.5, 4.5, 3.0 Hz, 1H), 2.07-2.00 (m, 2H), 1.68-1.59 (m, 2H), 0.55 (ddd, *J* = 12.8, 12.0, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$)

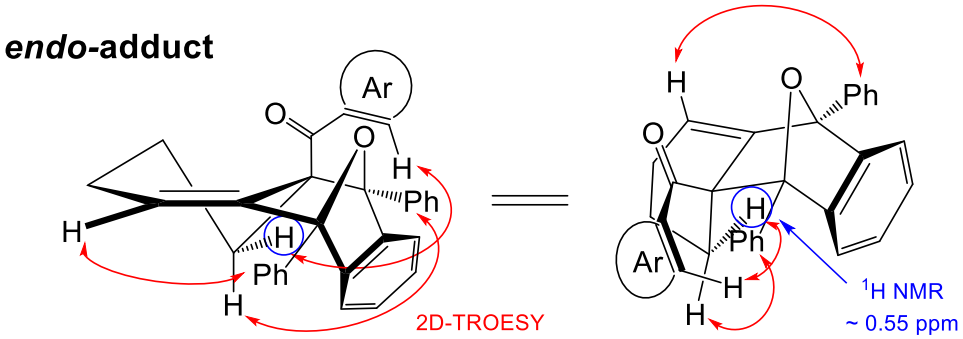
δ 203.5, 149.1, 144.5, 144.4, 141.1 136.4, 136.0, 134.7, 129.9, 128.5, 128.4, 128.1, 127.9, 127.7, 127.6, 127.4, 126.1, 125.6, 124.7, 121.6, 117.5, 92.9, 89.3, 65.3, 32.1, 24.2, 19.6; HRMS (EI, M^+) for $C_{33}H_{25}O_2{}^{35}Cl$ calcd. 488.1543, found: m/z 488.1542.

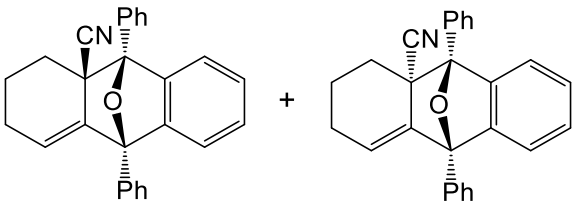


12c

65 mg of starting material **5c** was used. Flash chromatography (18:1 to 3:1 hexane:EtOAc) gave **12c** (26 mg, 29 %) as colorless sticky oil (**5c** recovered 8 mg, 12%; **6c** can also be isolated, 8%); R*f* 0.24 (hexanes/EtOAc 10:1); IR (cast film) 3061, 3039, 2938, 2869, 1649, 1601, 1556, 1497, 1458, 1270 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.58-7.49 (m, 5H), 7.39-7.28 (m, 4H), 7.23-7.14 (m, 4H), 6.97 (d, *J* = 3.5 Hz, 1H), 6.23 (dd, *J* = 3.5, 2.0 Hz, 1H), 6.07 (dd, *J* = 5.0, 2.5 Hz, 1H), 3.08 (ddd, *J* = 12.0, 4.5, 3.0 Hz, 1H), 2.07-2.02 (m, 1H), 1.99-1.90 (m, 1H), 1.66-1.59 (m, 1H), 1.53-1.46 (m, 1H), 0.55 (ddd, *J* = 13.0, 12.0, 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.1, 153.6, 149.7, 145.4, 144.7, 144.4, 136.0, 135.4, 128.5, 128.4, 128.2, 128.0, 127.7, 127.6, 126.0, 125.5, 123.7, 121.6, 119.5, 117.6, 111.4, 92.7, 89.5, 63.8, 31.3, 24.3, 19.5; HRMS (EI, M^+) for $C_{31}H_{24}O_3$ calcd. 444.1726, found: m/z 444.1730.

Pertinent ROESY correlations for stereochemistry of above DPIBF trapping products containing arylacyl group:





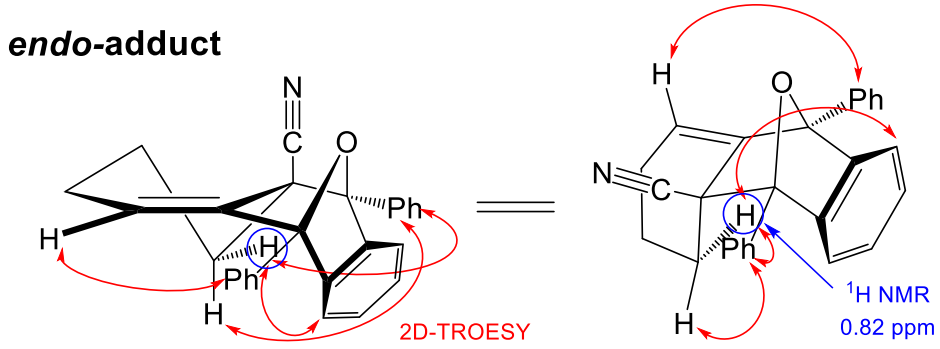
12d **13d**

76.5 mg (0.3 mmol, 1.0 equiv.) of starting material **5d**, 0.9 mmol (3.0 equiv.) of DPIBF and

KO^{t}Bu (0.6 mmol, 2.0 equiv.) were used to carry out the reaction for 30 min at room temperature. Flash chromatography (45:1 to 18:1 hexane:EtOAc) gave **12d** (40 mg, 36 %) and **13d** (13 mg, 12 %) as white solids.

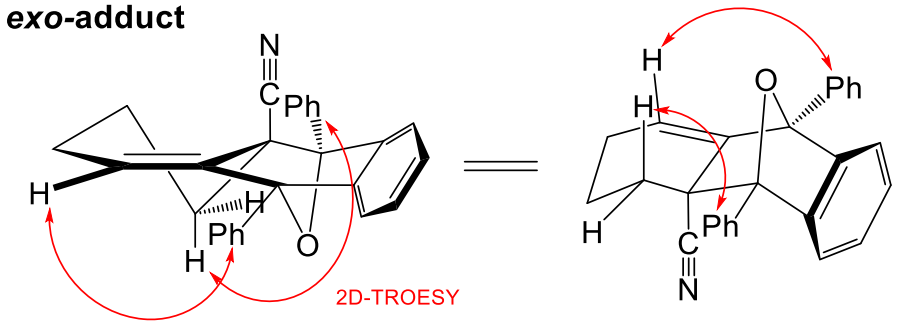
12d: R*f* 0.25 (hexanes/EtOAc 10:1); mp 195-196 °C; IR (cast film) 3061, 3033, 2954, 2869, 2235, 1599, 1498, 1457, 1448, 1306, 1005 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 6.5 Hz, 2H), 7.75 (d, *J* = 7.0 Hz, 2H), 7.56-7.50 (m, 5H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.32-7.17 (m, 4H), 5.86 (dd, *J* = 4.0, 3.0 Hz, 1H), 2.51 (dt, *J* = 12.0, 3.5 Hz, 1H), 2.38-2.32 (m, 1H), 2.06-2.02 (m, 1H), 1.96-1.82 (m, 2H), 0.82 (ddd, *J* = 13.5, 12.0, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 142.1, 141.7, 135.4, 133.2, 129.1, 128.8, 128.6, 128.5(8), 128.5(6), 128.5(2), 126.6, 125.8, 125.2, 122.2, 120.6, 118.4, 91.7, 90.1, 51.1, 30.1, 24.0, 19.1; HRMS (EI, M$^+$) for $C_{27}H_{21}NO$ calcd. 375.1623, found: m/z 375.1621.

Pertinent ROESY correlations for stereochemistry:



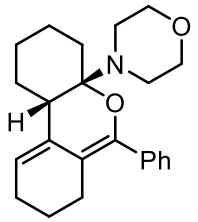
13d: R*f* 0.45 (hexanes/EtOAc 10:1); mp 198-199 °C; IR (cast film) 3059, 3032, 2940, 2871, 2230, 1602, 1499, 1459, 1448, 1310, 1010 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.58-7.54 (m, 4H), 7.48-7.43 (m, 3H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.31-7.24 (m, 2H), 5.85 (dd, *J* = 6.0, 2.5 Hz, 1H), 2.32-2.25 (m, 1H), 2.12-2.04 (m, 1H), 1.99-1.91 (m, 2H), 1.77-1.70 (m, 1H), 1.17 (dt, *J* = 6.0, 12.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 143.9, 140.7, 134.8, 134.7, 128.8, 128.7, 128.3, 128.1, 128.0, 127.6, 125.6, 125.5, 122.2, 121.2, 121.0, 120.2, 90.5, 90.2, 47.8, 29.8, 22.0, 17.8; HRMS (EI, M$^+$) for $C_{27}H_{21}NO$ calcd. 375.1623, found: m/z 375.1623.

Pertinent ROESY correlations for stereochemistry:



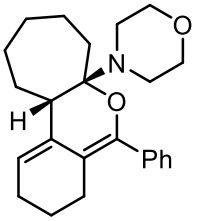
General procedure for the synthesis of the cycloadducts 16a-16h through Hetero-Diels-Alder trapping of cyclic allenes derived from 5a,b with electron-rich heterodienophiles

To a stirred solution of starting material **5** (0.3 mmol, 1.0 equiv.) and enamine **15** (3 mmol, 10 equiv.) in anhydrous THF (3 mL) under nitrogen atmosphere was added dropwise a solution of KO^{t}Bu (0.45 mmol, 1.5 equiv.) in anhydrous THF (1.5 mL) at room temperature over 30 minutes. The reaction mixture was stirred for 3 h at room temperature and then it was quenched with NH_4Cl sat. solution (10 mL) and extracted with Et_2O (5 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude was further purified by column chromatography on Al_2O_3 (neutral, Brockmann I, 40-160 μm) to afford the cycloadduct **16**. The column chromatography can be performed on silica as well, but for a slightly cleaner product we recommend the use of neutral alumina. When required HSQC was used for ^{13}C NMR assignments. Enamine **15** was either readily available or synthesized according with the literature.[4-6]



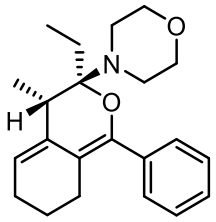
16a

110 mg of starting material **5a** was used. Flash chromatography (99:1 to 20:1 hexane:Et_2O) on neutral alumina gave **16a** (76 mg, 65 %) as light yellow solid; R*f* 0.38 (hexanes/EtOAc 9:1); mp 94-96 °C; IR (cast film) cm^{-1} 3083, 3054, 3034, 2933, 2851, 1684, 1598, 1492, 1446, 1263, 1118; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.25 (m, 1H), 5.34 (t, *J* = 4.2 Hz, 1H), 3.61 (t, *J* = 4.6 Hz, 4H), 2.80 – 2.68 (m, 4H), 2.48 (ddd, *J* = 14.5, 6.0, 3.9 Hz, 1H), 2.39 (ddd, *J* = 14.6, 10.8, 4.0 Hz, 1H), 2.32 (dd, *J* = 10.1, 4.7 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.99 (dtd, *J* = 13.5, 3.9, 1.3 Hz, 1H), 1.74 – 1.55 (m, 7H), 1.34 (ddd, *J* = 13.6, 11.7, 4.6 Hz, 1H), 1.25 – 1.17 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 136.8, 134.7, 128.8, 127.8, 127.4, 120.3, 108.8, 90.3, 67.9, 44.9, 42.0, 30.6, 27.9, 26.7, 26.0, 24.4, 24.1, 22.7; HRMS (ESI, $[M+H]^+$) for $C_{23}H_{29}NO_2$ calcd. 352.2271, found: m/z 352.2275.

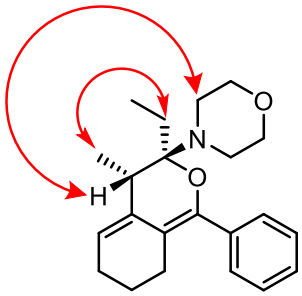


16b

104 mg of starting material **5a** was used. Flash chromatography (99:1 to 20:1 hexane: Et_2O) on neutral alumina gave **16b** (28 mg, 24 %) as light yellow oil; R*f* 0.45 (hexanes/EtOAc 10:1); IR (cast film) cm^{-1} 3057, 3023, 2925, 2853, 1663, 1597, 1449, 1276, 1119; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (dt, *J* = 6.3, 1.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 5.41 (td, *J* = 4.3, 1.2 Hz, 1H), 3.63 (t, *J* = 4.7 Hz, 4H), 2.78 (q, *J* = 4.7 Hz, 4H), 2.62 (d, *J* = 7.7 Hz, 1H), 2.52 – 2.36 (m, 2H), 2.18 (ddt, *J* = 8.1, 5.7, 3.1 Hz, 2H), 2.09 – 1.92 (m, 2H), 1.87 (ddd, *J* = 14.9, 7.2, 3.5 Hz, 1H), 1.80 – 1.39 (m, 7H), 1.36 – 1.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 136.4, 135.7, 128.8, 127.7, 127.5, 119.6, 108.7, 93.8, 67.9, 45.6, 44.1, 31.1, 28.5, 28.1, 26.8, 26.1, 26.0, 23.8, 21.7; HRMS (ESI, $[M+H]^+$) for $C_{24}H_{31}NO_2$ calcd. 366.2428, found: m/z 366.2417.



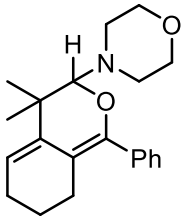
16c



16c

Relevant 2D-TROESY for **16c**

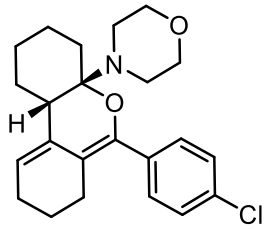
94 mg of starting material **5a** was used. Flash chromatography (99:1 to 20:1 hexane: Et_2O) on neutral alumina gave **16c** (28 mg, 29 %) as light yellow oil; R*f* 0.42 (hexanes/EtOAc 10:1); IR (cast film) cm^{-1} 3053, 3019, 2970, 2919, 2885, 2851, 1664, 1634, 1615, 1597, 1491, 1446, 1271, 1175, 1120, 1070; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.23 (m, 1H), 5.46 (td, *J* = 4.2, 1.3 Hz, 1H), 3.67 – 3.59 (m, 4H), 3.00 – 2.88 (m, 4H), 2.76 – 2.69 (m, 1H), 2.50 – 2.40 (m, 2H), 2.22 – 2.14 (m, 2H), 1.93 – 1.81 (m, 2H), 1.72 – 1.60 (m, 2H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 136.4, 136.0, 128.8, 127.7, 127.6, 119.8, 108.1, 94.3, 68.0, 45.8, 36.7, 26.7, 26.1, 25.5, 23.8, 14.4, 8.9; HRMS (ESI, $[M+H]^+$) for $C_{22}H_{29}NO_2$ calcd. 340.2271, found: m/z 340.2271.



16d

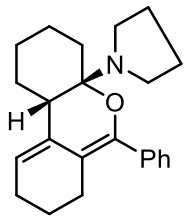
96 mg of starting material **5a** was used. Flash chromatography (99:1 to 20:1 hexane: Et_2O) on neutral alumina gave **16d** (9 mg, 9 %) as light yellow oil; R*f* 0.40 (hexanes/EtOAc 10:1); IR (cast film) cm^{-1} 3057, 3034, 2957, 2930, 2855, 1667, 1597, 1491, 1448, 1254, 1119, 1066; ^1H

NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 5.58 (t, *J* = 4.3 Hz, 1H), 4.26 (s, 1H), 3.72 – 3.56 (m, 4H), 3.24 – 3.17 (m, 2H), 2.75 – 2.68 (m, 2H), 2.46 – 2.32 (m, 2H), 2.22 – 2.10 (m, 2H), 1.72 – 1.63 (m, 1H), 1.52 – 1.44 (m, 1H), 1.21 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 139.1, 136.1, 128.8, 128.0, 127.9, 115.5, 106.7, 98.3, 67.5, 49.4, 36.5, 30.4, 26.8, 26.0, 23.2, 23.2; HRMS (ESI, $[M+H]^+$) for $C_{21}H_{27}NO_2$ calcd. 326.2115, found: m/z 326.2113.



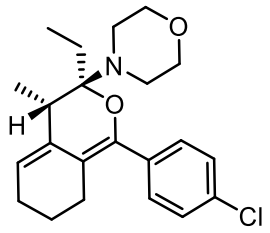
16e

112 mg of starting material **5b** was used. Flash chromatography (99:1 to 20:1 hexane: Et_2O) on neutral alumina gave **16e** (54 mg, 46 %) as light yellow oil; R*f* 0.28 (hexanes/EtOAc 10:1); IR (cast film) cm^{-1} 3034, 2931, 2854, 1680, 1592, 1489, 1448, 1279, 1118, 1094; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 5.36 (t, *J* = 4.2 Hz, 1H), 3.59 (t, *J* = 4.6 Hz, 4H), 2.79 – 2.64 (m, 4H), 2.45 (ddd, *J* = 14.5, 6.0, 4.0 Hz, 1H), 2.38 (dd, *J* = 10.6, 4.0 Hz, 1H), 2.34 – 2.28 (m, 1H), 2.20 – 2.08 (m, 2H), 2.01 – 1.93 (m, 1H), 1.75 – 1.46 (m, 7H), 1.38 – 1.29 (m, 1H), 1.25 – 1.16 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.5, 135.2, 134.5, 133.1, 130.1, 128.0, 120.9, 109.3, 90.4, 67.9, 44.9, 41.9, 30.6, 27.9, 26.7, 25.9, 24.3, 24.0, 22.7; HRMS (ESI, $[M+H]^+$) for $C_{23}H_{28}ClNO_2$ calcd. 386.1881, found: m/z 386.1872.



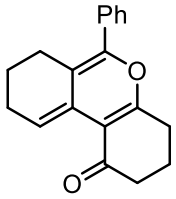
16f

104 mg of starting material **5a** was used. Flash chromatography (99:1 to 20:1 hexane: Et_2O) on neutral alumina gave **16f** (53 mg, 51 %) as light yellow oil; R*f* 0.30 (hexanes/EtOAc 10:1); IR (cast film) cm^{-1} 3054, 3034, 2929, 2856, 1673, 1597, 1447, 1270, 1113; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 5.54 (t, *J* = 4.6 Hz, 1H), 2.98 – 2.87 (m, 4H), 2.67 (s, 1H), 2.44 (t, *J* = 6.2 Hz, 2H), 2.25 – 2.14 (m, 2H), 2.10 – 2.00 (m, 1H), 1.90 – 1.52 (m, 10H), 1.35 – 1.24 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 137.1, 133.3, 128.9, 127.6, 127.3, 119.4, 106.8, 91.4, 44.1, 41.3, 29.7, 28.3, 26.8, 26.1, 24.6, 23.5, 23.5, 21.5; HRMS (ESI, $[M+H]^+$) for $C_{23}H_{29}NO$ calcd. 336.2322, found: m/z 336.2325.



16g

103 mg of starting material **5b** was used. Flash chromatography (99:1 to 20:1 hexane: Et_2O) on neutral alumina gave **16g** (20 mg, 19 %) as light yellow oil; R*f* 0.47 (hexanes/EtOAc 10:1); IR (cast film) cm^{-1} 3042, 2971, 2932, 2886, 2851, 1672, 1613, 1591, 1489, 1450, 1270, 1120; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.49 (dt, *J* = 5.2, 2.5 Hz, 1H), 3.63 (t, *J* = 4.6 Hz, 4H), 2.91 (t, *J* = 4.7 Hz, 4H), 2.76 – 2.67 (m, 1H), 2.48 – 2.34 (m, 2H), 2.25 – 2.11 (m, 2H), 1.94 – 1.78 (m, 2H), 1.75 – 1.54 (m, 2H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 135.7, 134.9, 133.3, 130.1, 127.9, 120.4, 108.6, 94.5, 67.9, 45.8, 36.7, 26.7, 26.0, 25.4, 23.7, 14.3, 8.9; HRMS (ESI, $[M+H]^+$) for $C_{22}H_{28}ClNO_2$ calcd. 374.1881, found: m/z 374.1881.



16h

116 mg of starting material **5a** was used. Flash chromatography (99:1 to 20:1 hexane:EtOAc) on silica gave **16h** (6 mg, 6 %) as light yellow oil, which in contact with the air becomes dark red; R*f* 0.30 (hexanes/EtOAc 20:1); IR (cast film) cm^{-1} 3057, 2929, 2851, 1716, 1660, 1597, 1581, 1448, 1393, 1278; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 5H), 6.94 (t, *J* = 4.6 Hz, 1H), 2.57 – 2.49 (m, 4H), 2.47 – 2.41 (m, 2H), 2.31 – 2.26 (m, 2H), 2.03 (p, *J* = 6.4 Hz, 2H), 1.64 (p, *J* = 6.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 168.4, 142.3, 133.4, 128.8, 128.6, 128.2, 122.4, 117.3, 117.0, 112.4, 39.1, 28.8, 26.4, 25.5, 21.1, 20.3; HRMS (EI, M^+) for $C_{19}H_{18}O_2$ calcd. 278.1307, found: m/z 278.1300.

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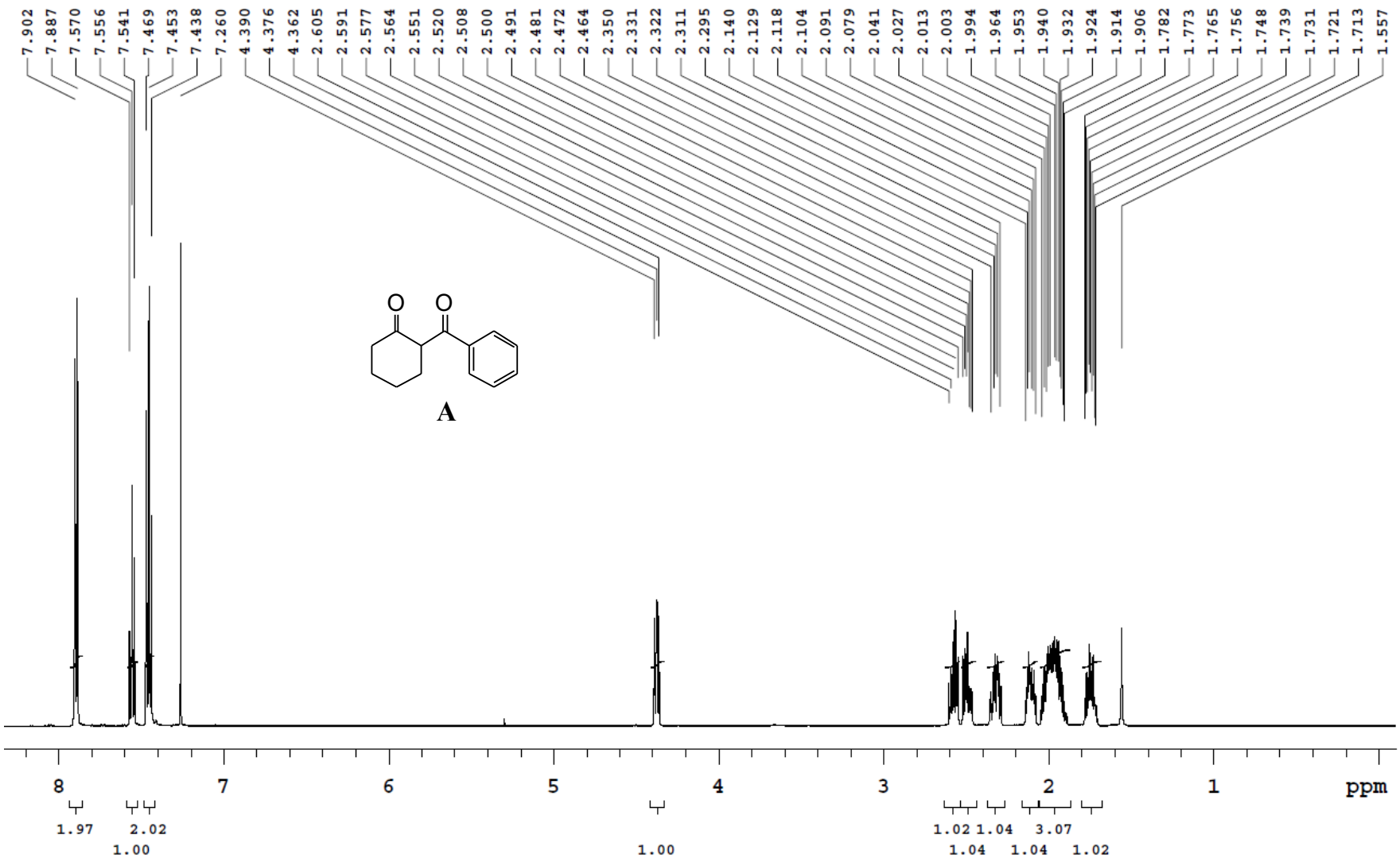
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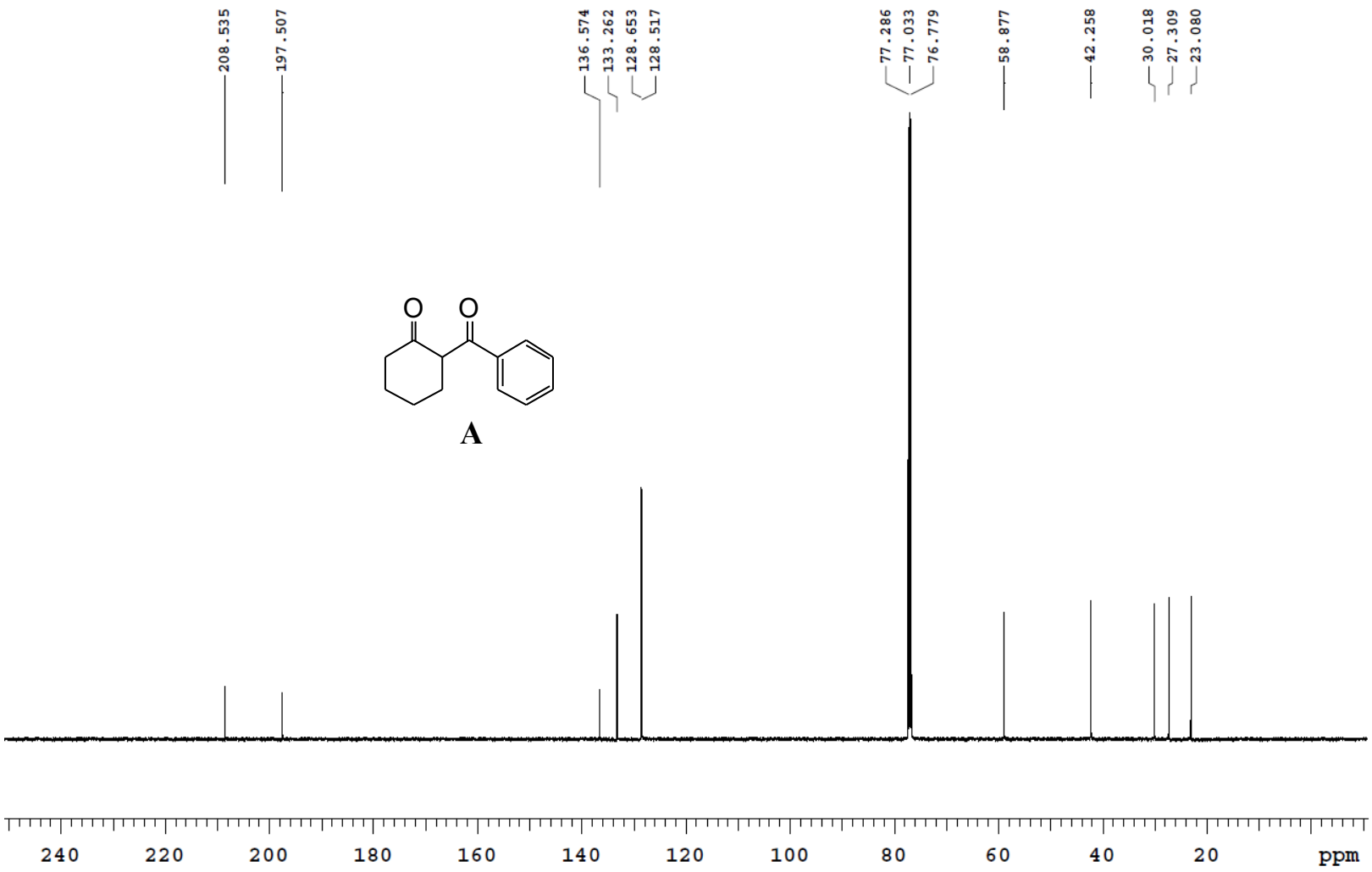
1.02
1.04
1.04
3.07
1.04
1.02

Baolei, BLW-1-4-a
125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



A

Baolei, BLW-I-7_2_
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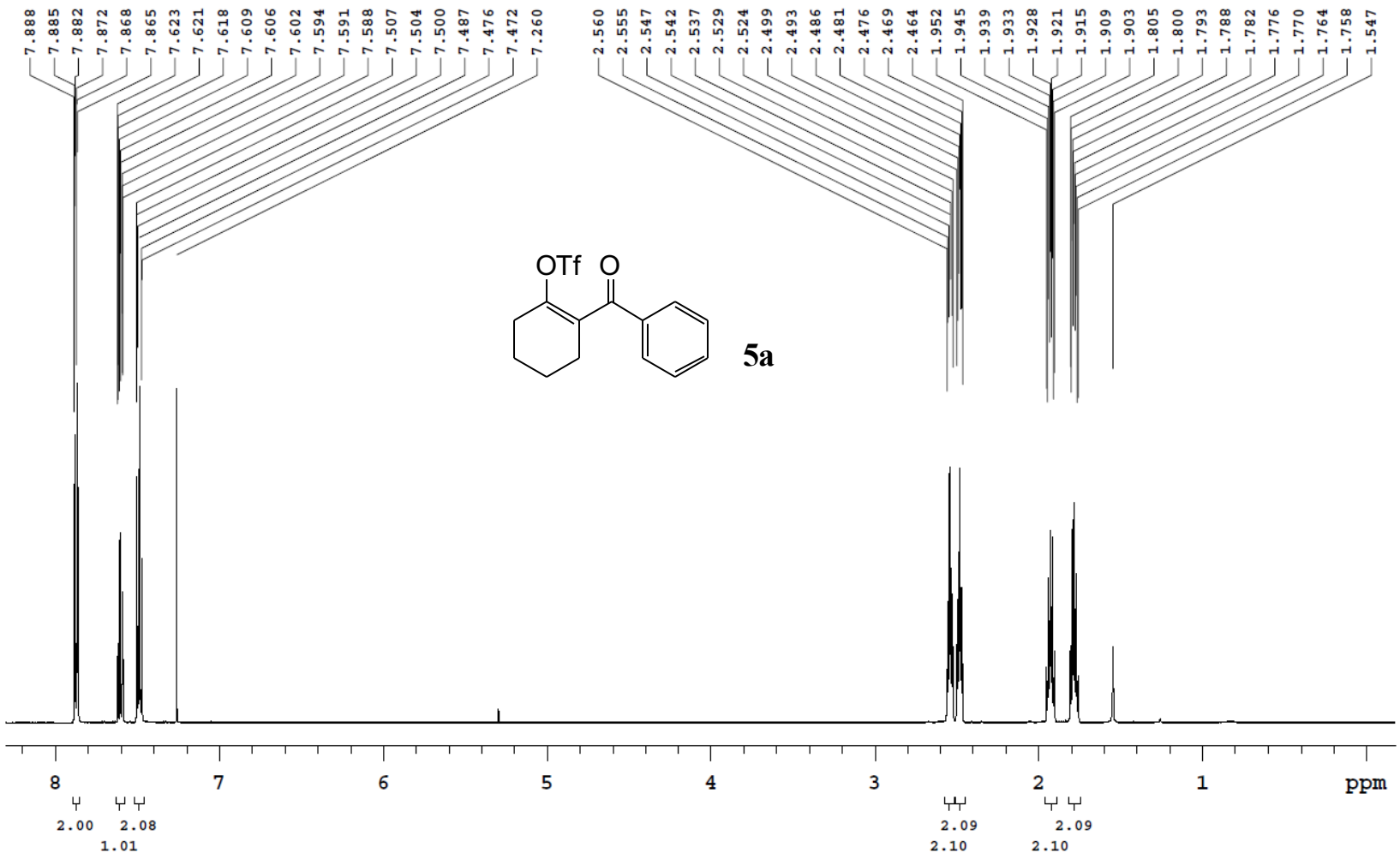

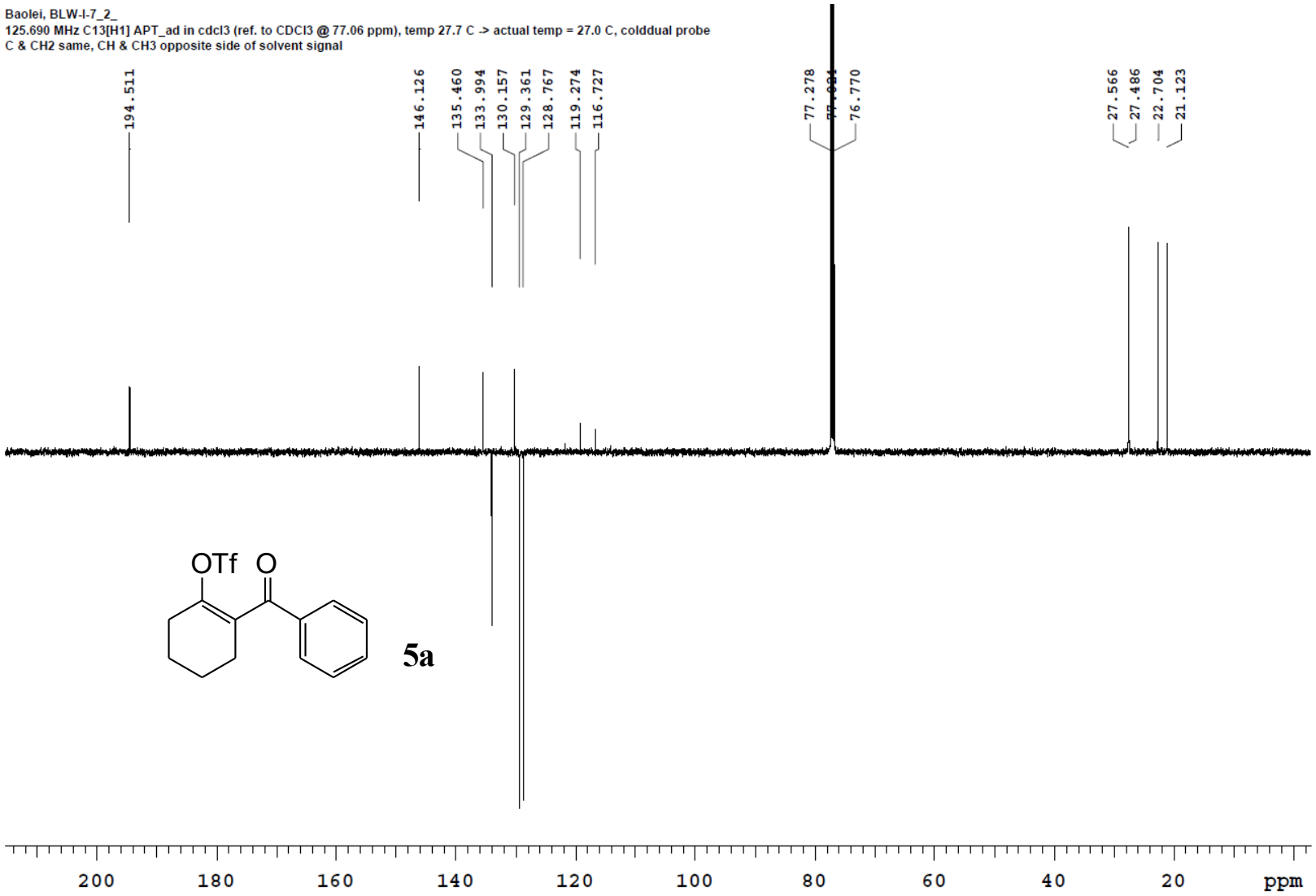
Baolei, BLW-I-7_2_
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146.126
135.460
133.994
130.157
129.361
128.767
119.274
116.727
77.278
76.770
27.566
27.486
22.704
21.123
OTf
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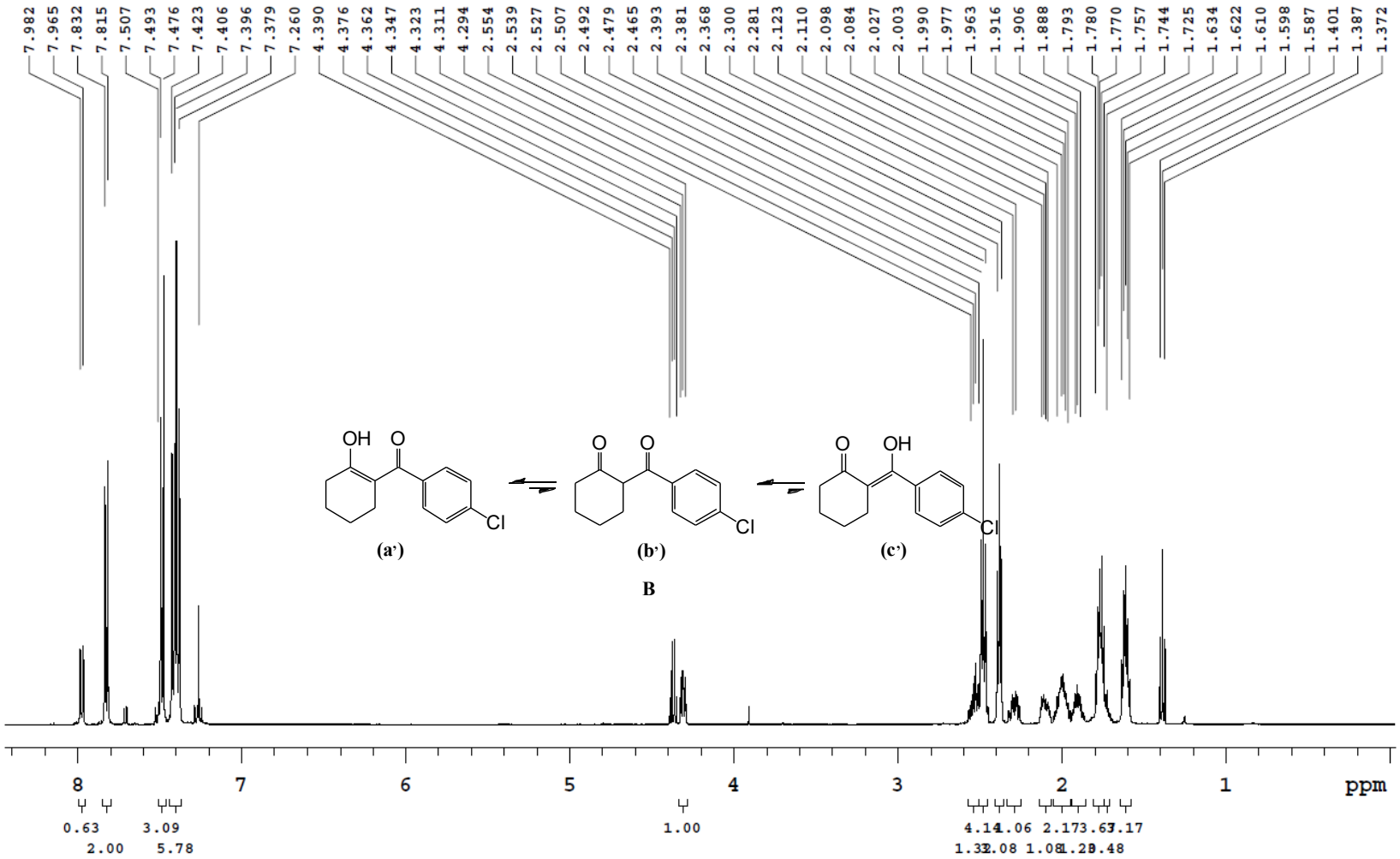
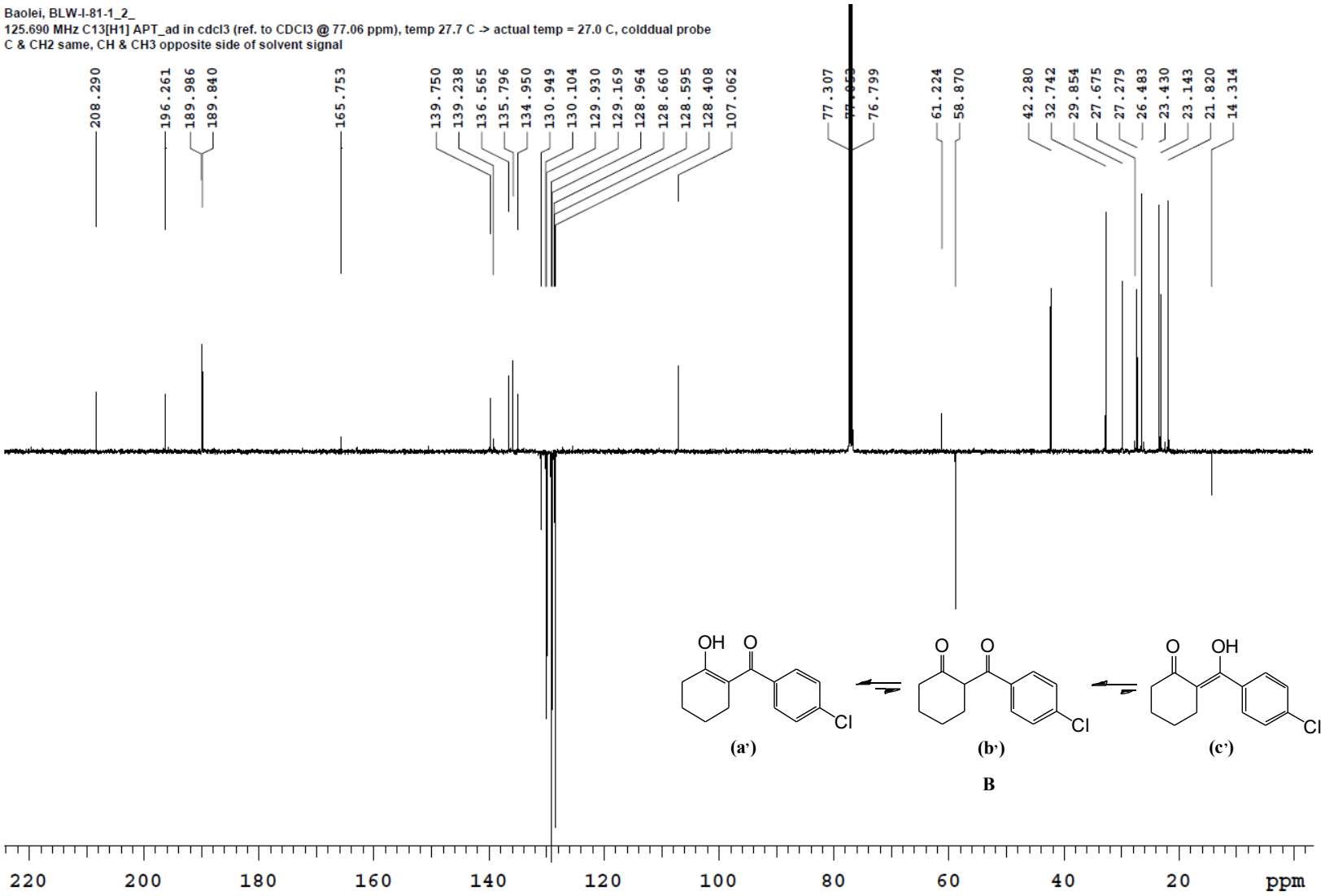
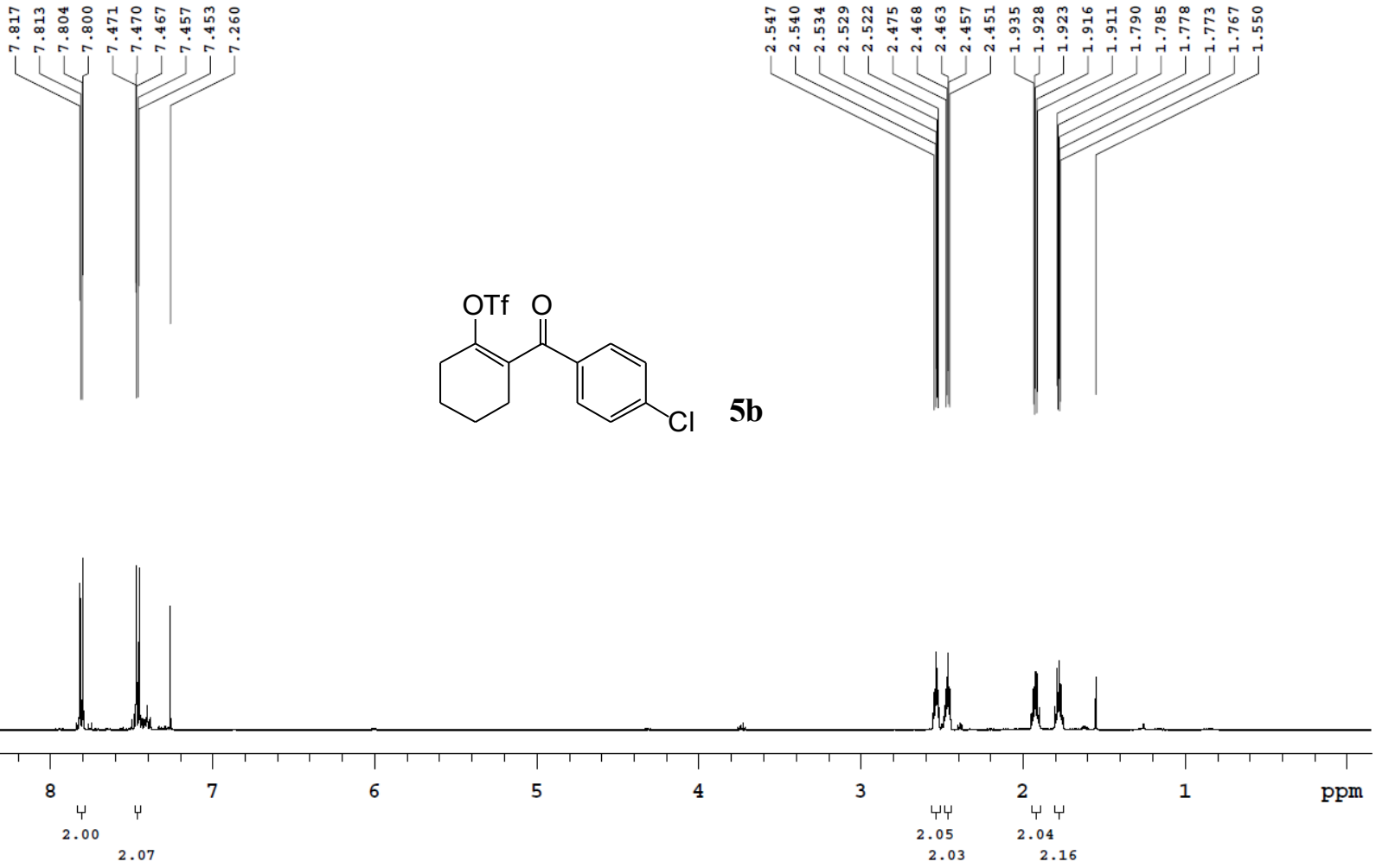
200
180
160
140
120
100
80
60
40
20
ppm

Baolei, BLW-I-81-1_2_
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

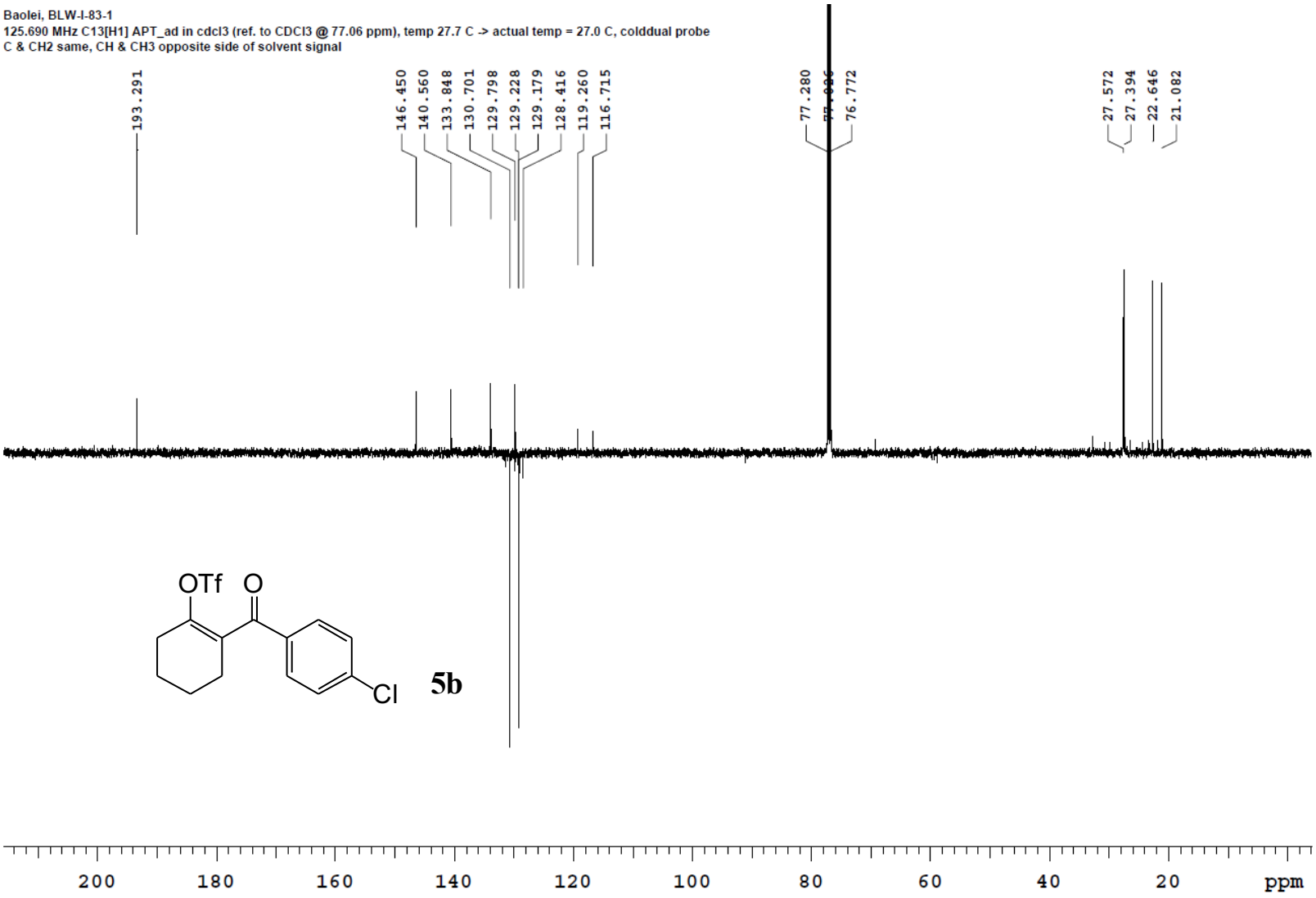



Baolei, BLW-I-81-1_2_
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
208.290
196.261
189.986
189.840
165.753
139.750
139.238
136.565
135.796
134.950
130.949
130.104
129.930
129.169
128.964
128.660
128.595
128.408
107.062
77.307
77.053
76.799
61.224
58.870
42.280
32.742
29.854
27.675
27.279
26.483
23.430
23.143
21.820
14.314
220
200
180
160
140
120
100
80
60
40
20
ppm
OH
O
Cl
(a')
O
O
Cl
(b')
O
OH
Cl
(c')
B

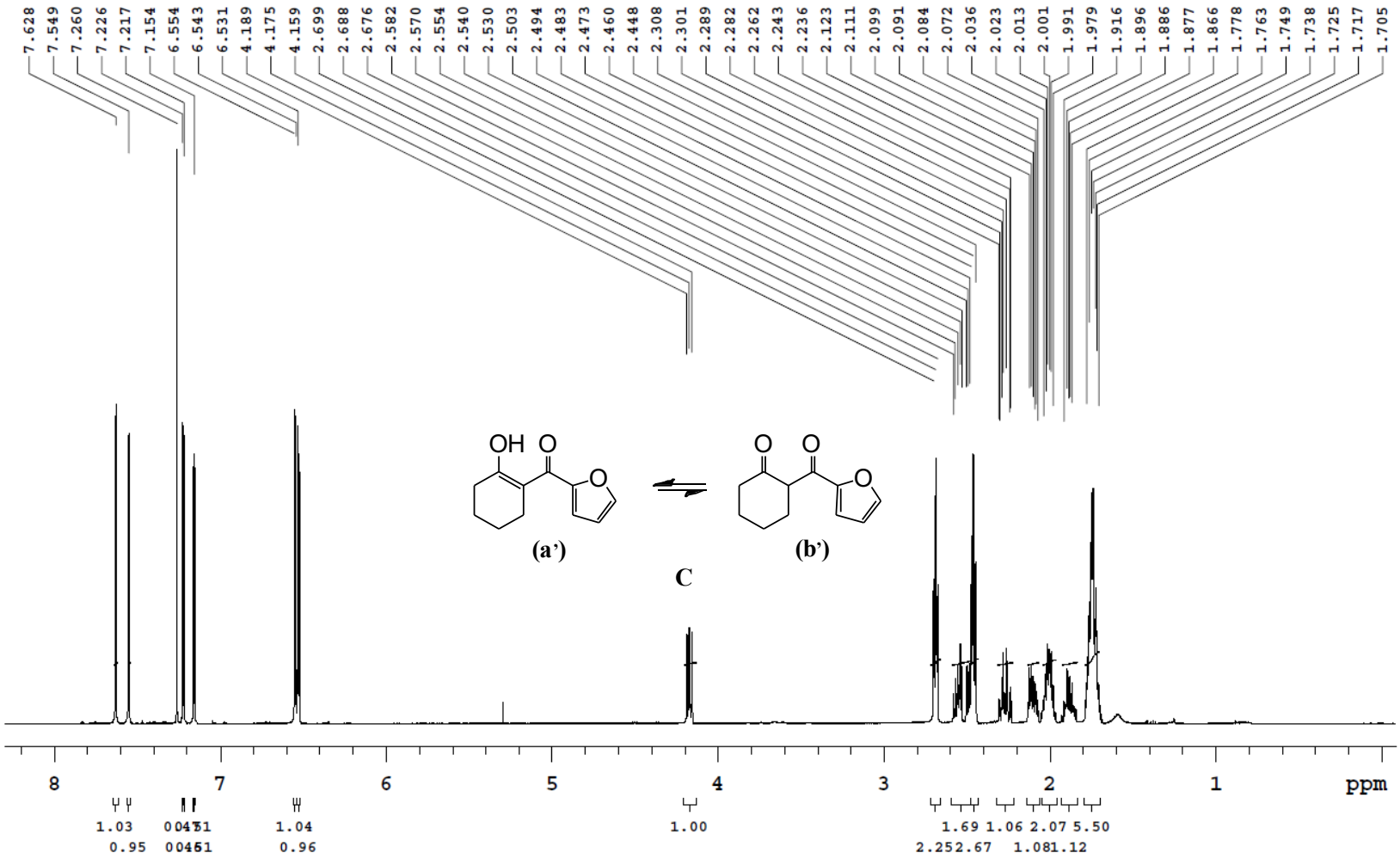
Baolei, BLW-I-83-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

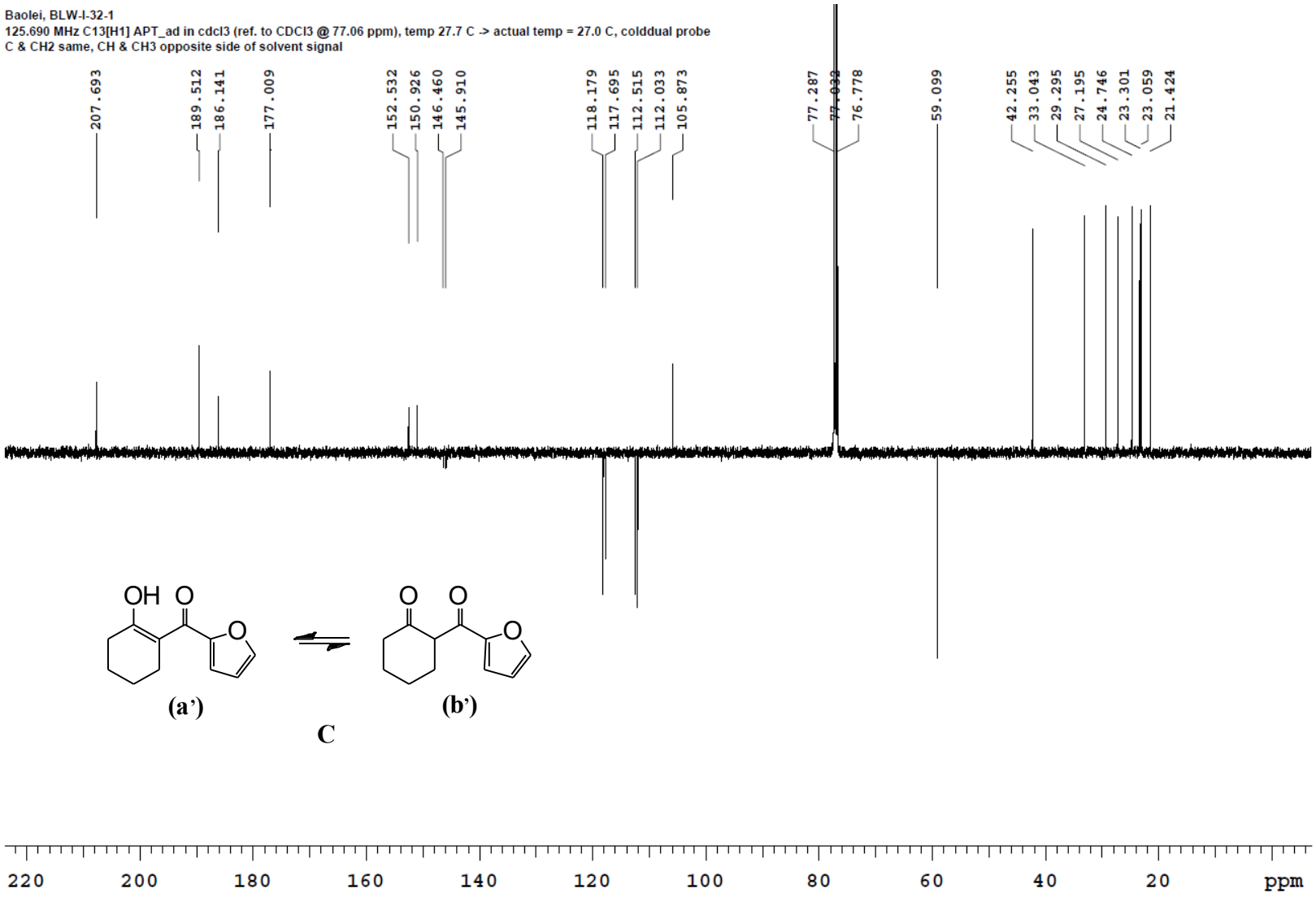


5b

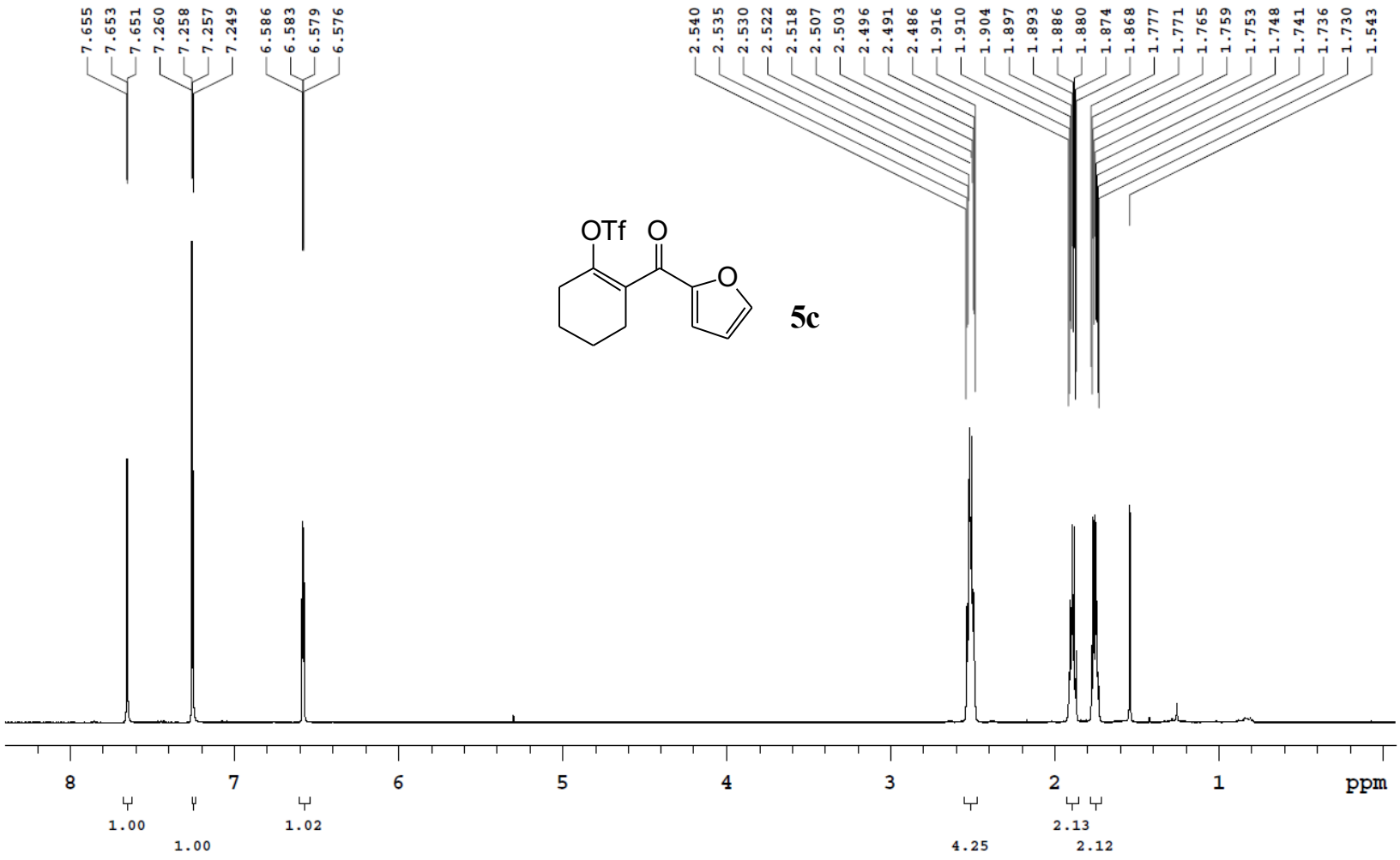

Baolei, BLW-I-83-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
193.291
146.450
140.560
133.848
130.701
129.798
129.228
129.179
128.416
119.260
116.715
77.280
76.772
27.572
27.394
22.646
21.082
OTf
O
Cl
5b
200
180
160
140
120
100
80
60
40
20
ppm

Baolei, BLW-I-32-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

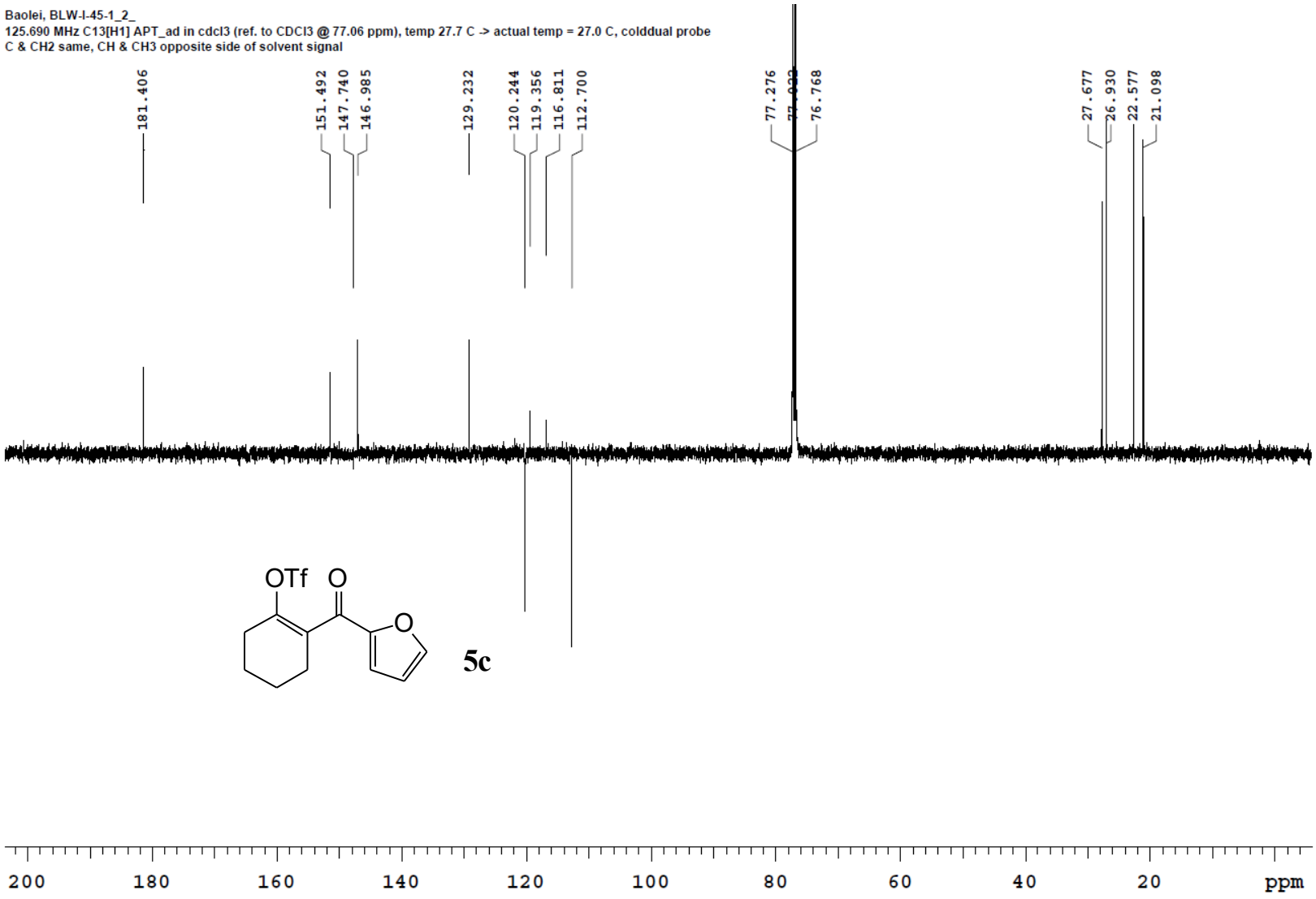



Baolei, BLW-I-32-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
207.693
189.512
186.141
177.009
152.532
150.926
146.460
145.910
118.179
117.695
112.515
112.033
105.873
77.287
77.033
76.778
59.099
42.255
33.043
29.295
27.195
24.746
23.301
23.059
21.424
OH
O
O
O
O
(a')
(b')
C
220
200
180
160
140
120
100
80
60
40
20
ppm

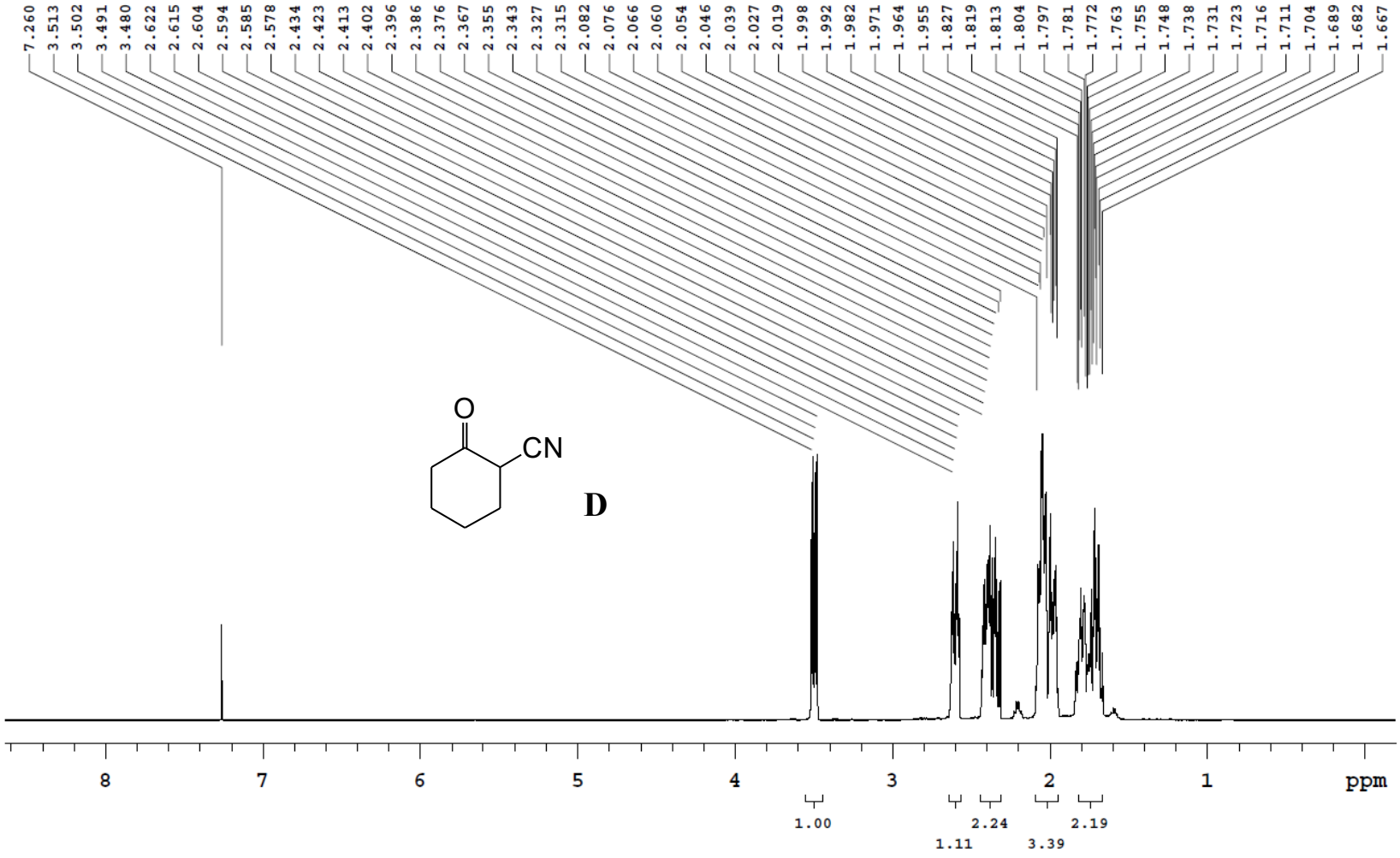
Baolei, BLW-I-45-1_2_
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



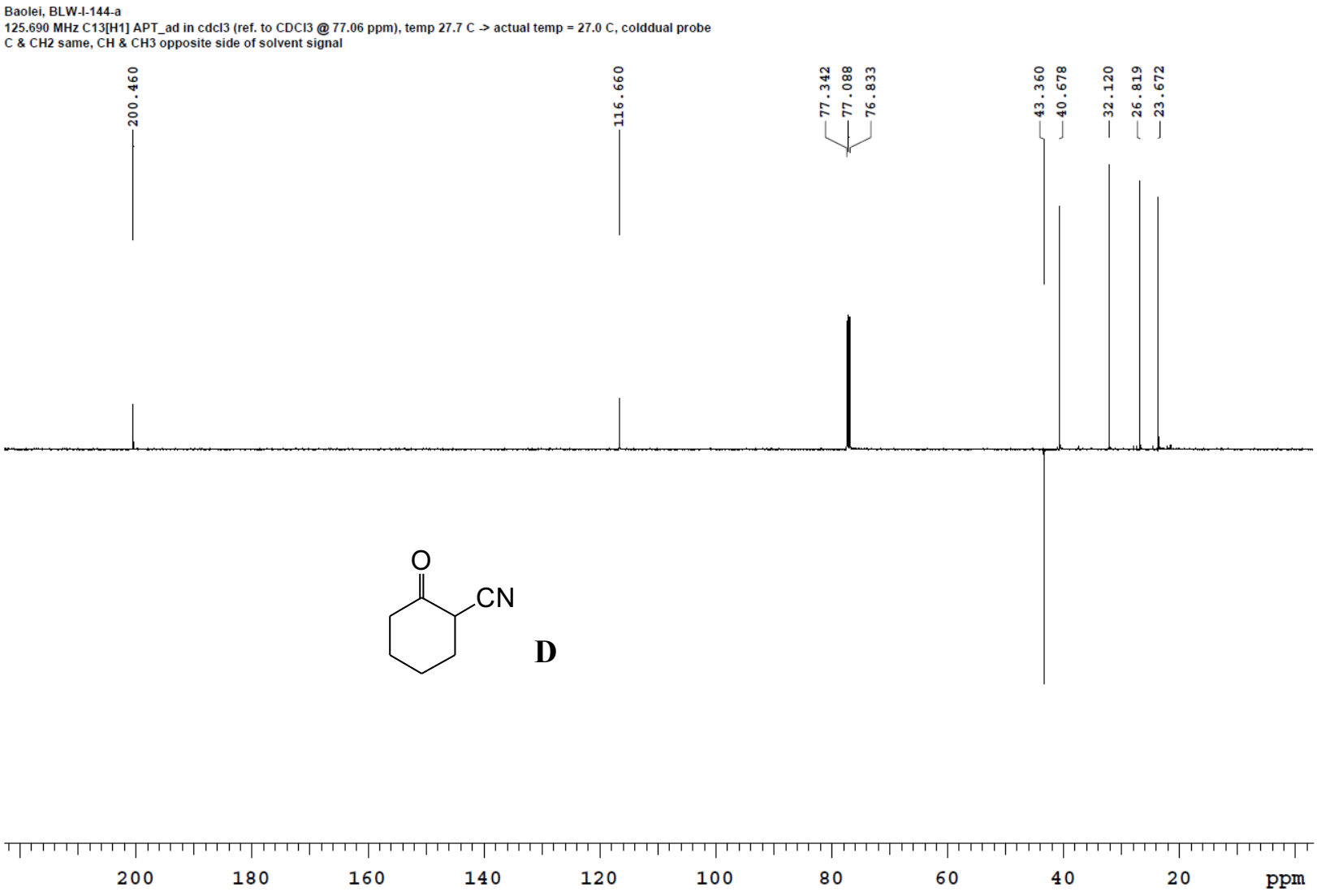
5c


Baolei, BLW-I-45-1_2_
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
181.406
151.492
147.740
146.985
129.232
120.244
119.356
116.811
112.700
77.276
77.023
76.768
27.677
26.930
22.577
21.098
OTf
O
O
5c
200
180
160
140
120
100
80
60
40
20
ppm

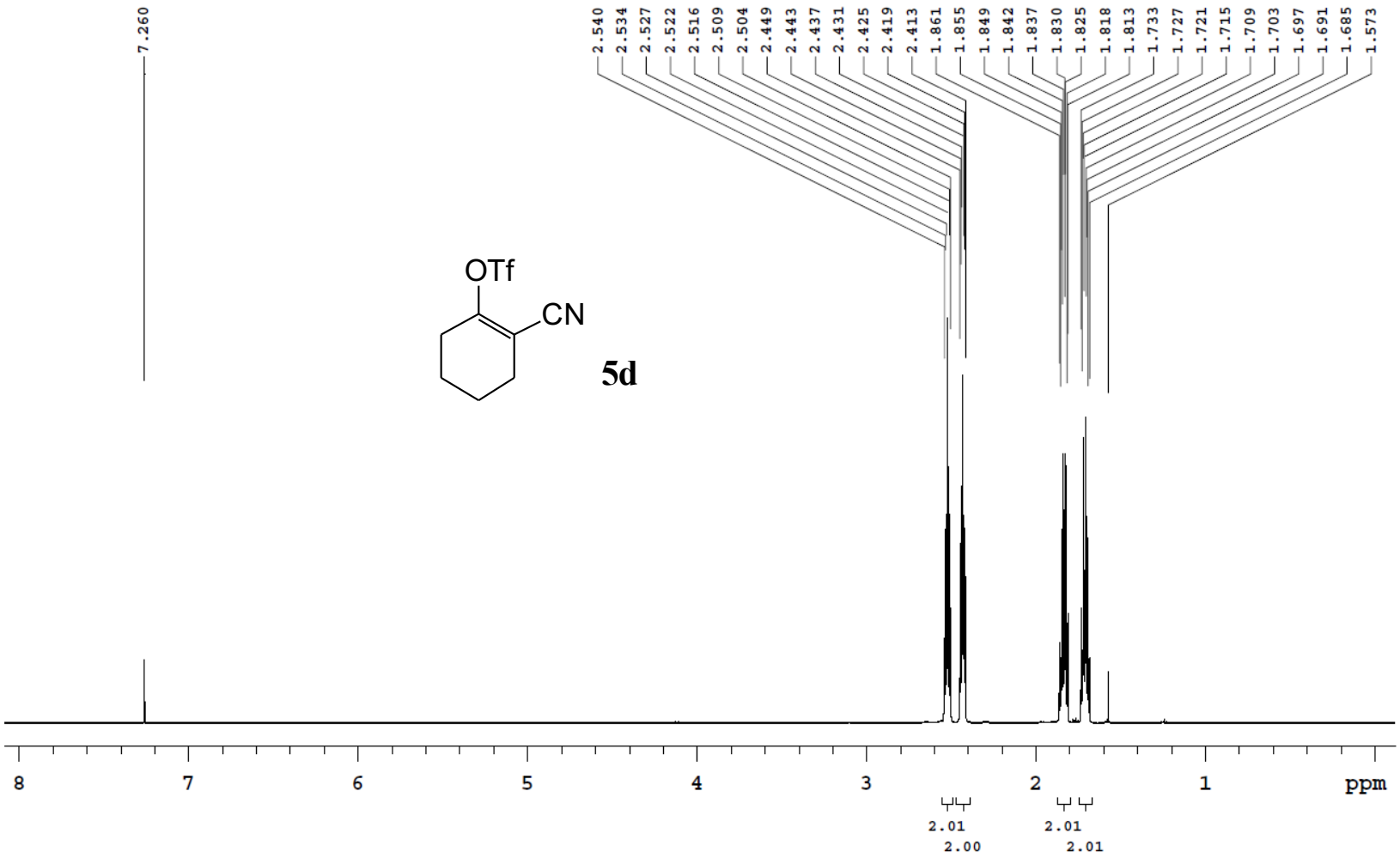
Baolei, BLW-I-144-a
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



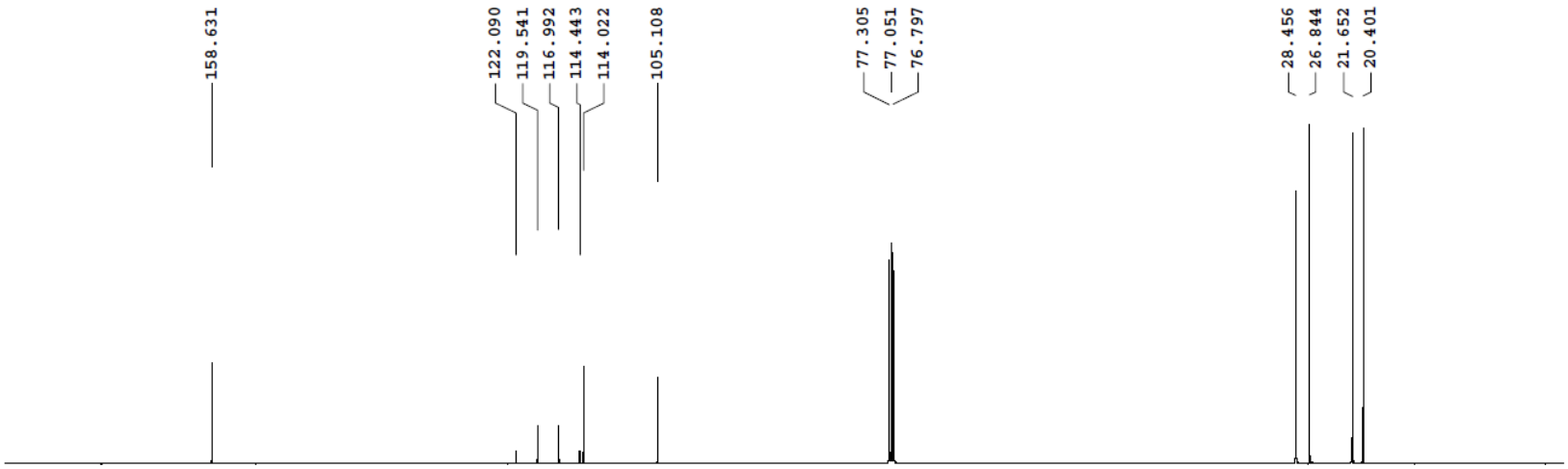
D

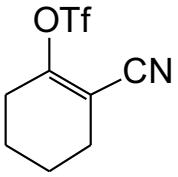

Baolei, BLW-I-144-a
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
200.460
116.660
77.342
77.088
76.833
43.360
40.678
32.120
26.819
23.672
O
CN
D
200
180
160
140
120
100
80
60
40
20
ppm

Baolei, BLW-I-145-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

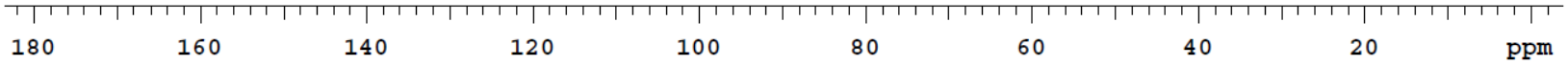


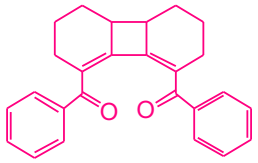
Baolei, BLW-I-145-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal





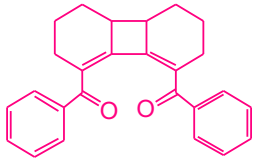
5d





$C_{26}H_{24}O_2$
M+H = 369.1855 (calcd.)

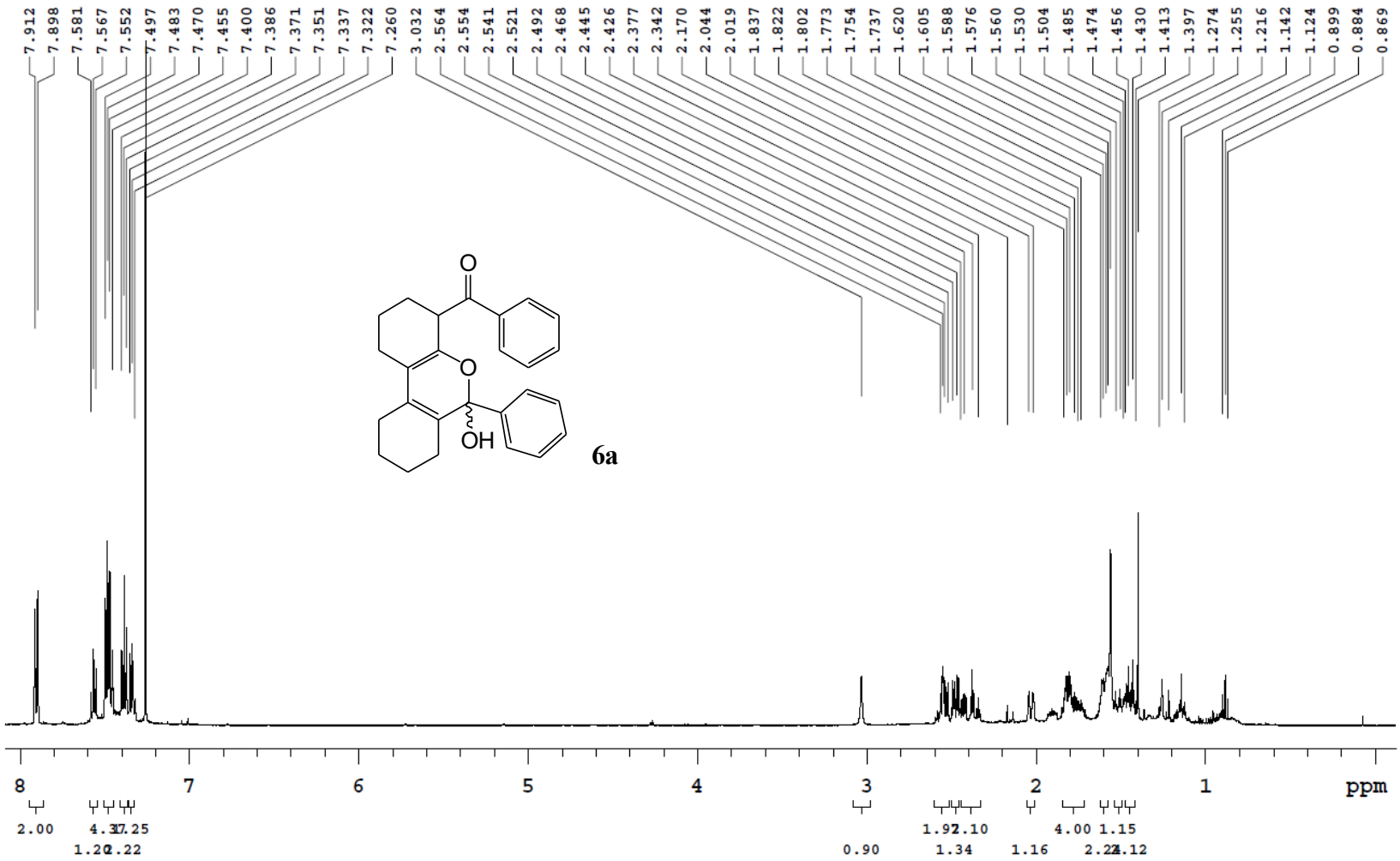
Mass spectrum (APPI) proof for the possible dimerization product of 1-benzoyl-1,2-cyclohexadiene **7a**, which was isolated as an impure mixture from column chromatography after stirring the precursor **5a** and KO^{t}Bu in THF at room temperature for 3 h.



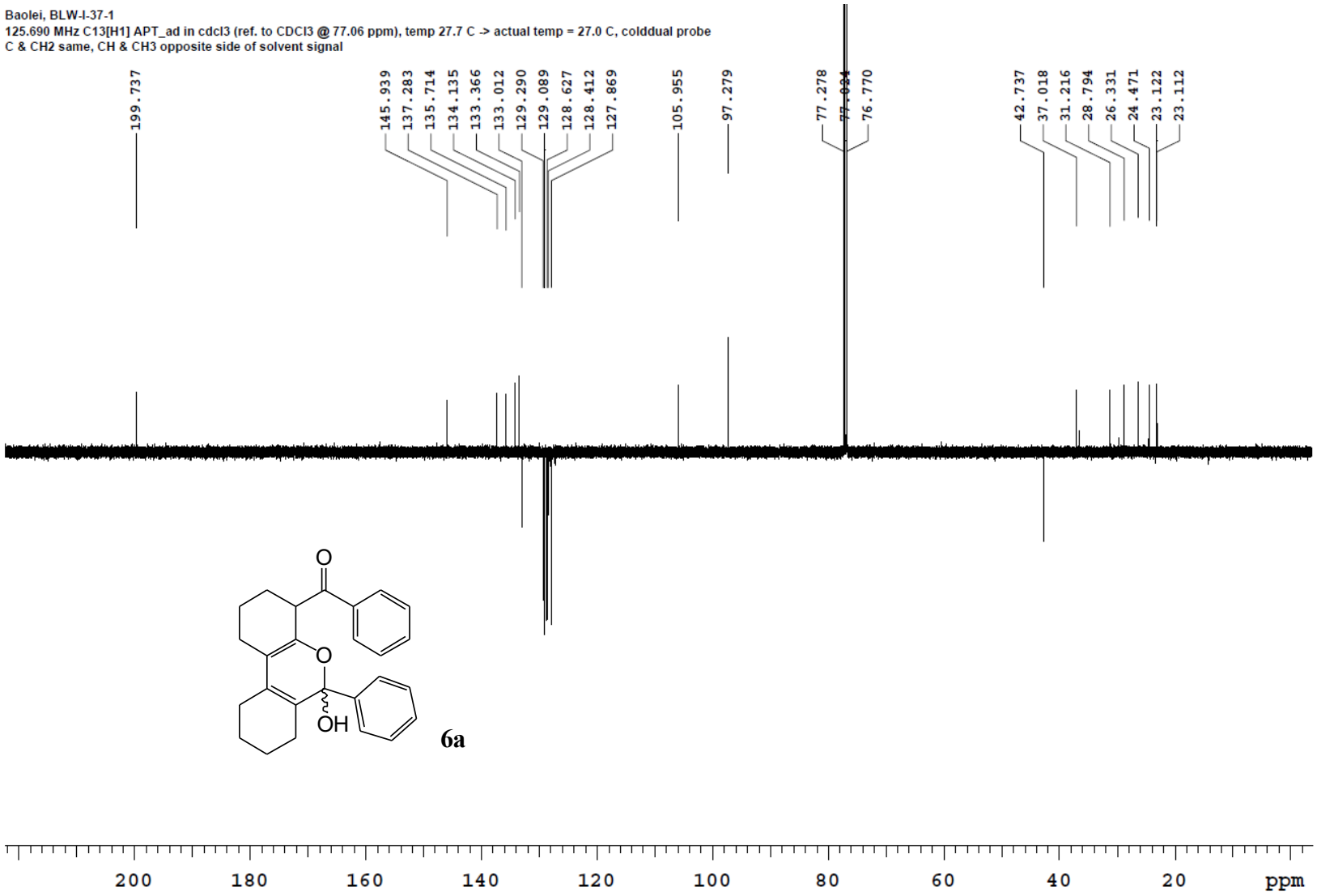
$C_{26}H_{24}O_2$
M+H = 369.1855 (calcd.)

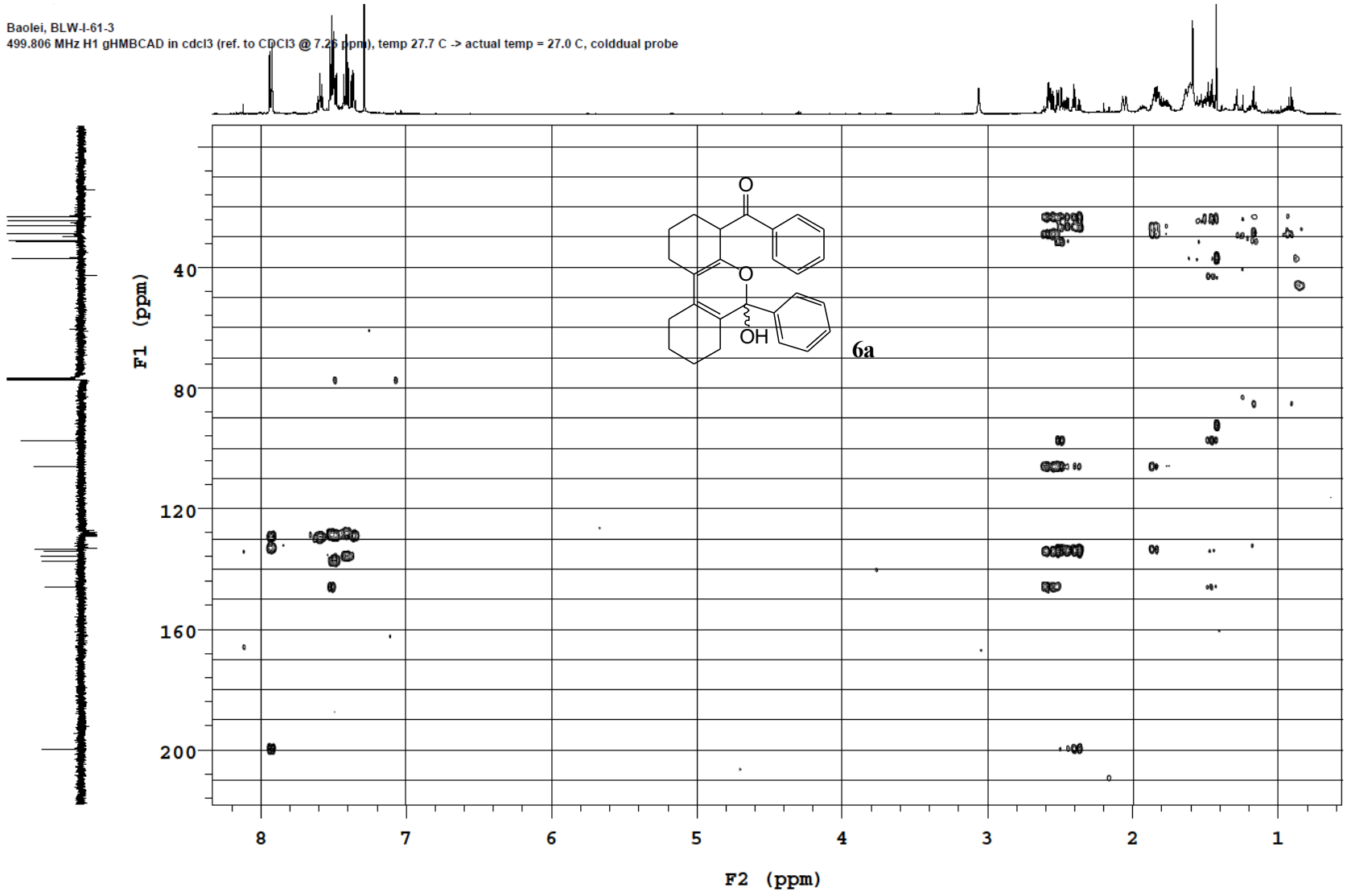
Mass spectrum (APPI) proof for the possible dimerization product of 1-benzoyl-1,2-cyclohexadiene **7a**, which was isolated as an impure mixture from column chromatography after stirring the precursor **5a** and KO^{t}Bu in THF at room temperature over night.

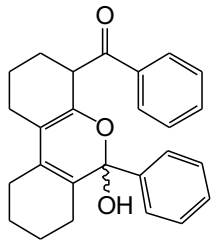
Baolei, BLW-I-61-3
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



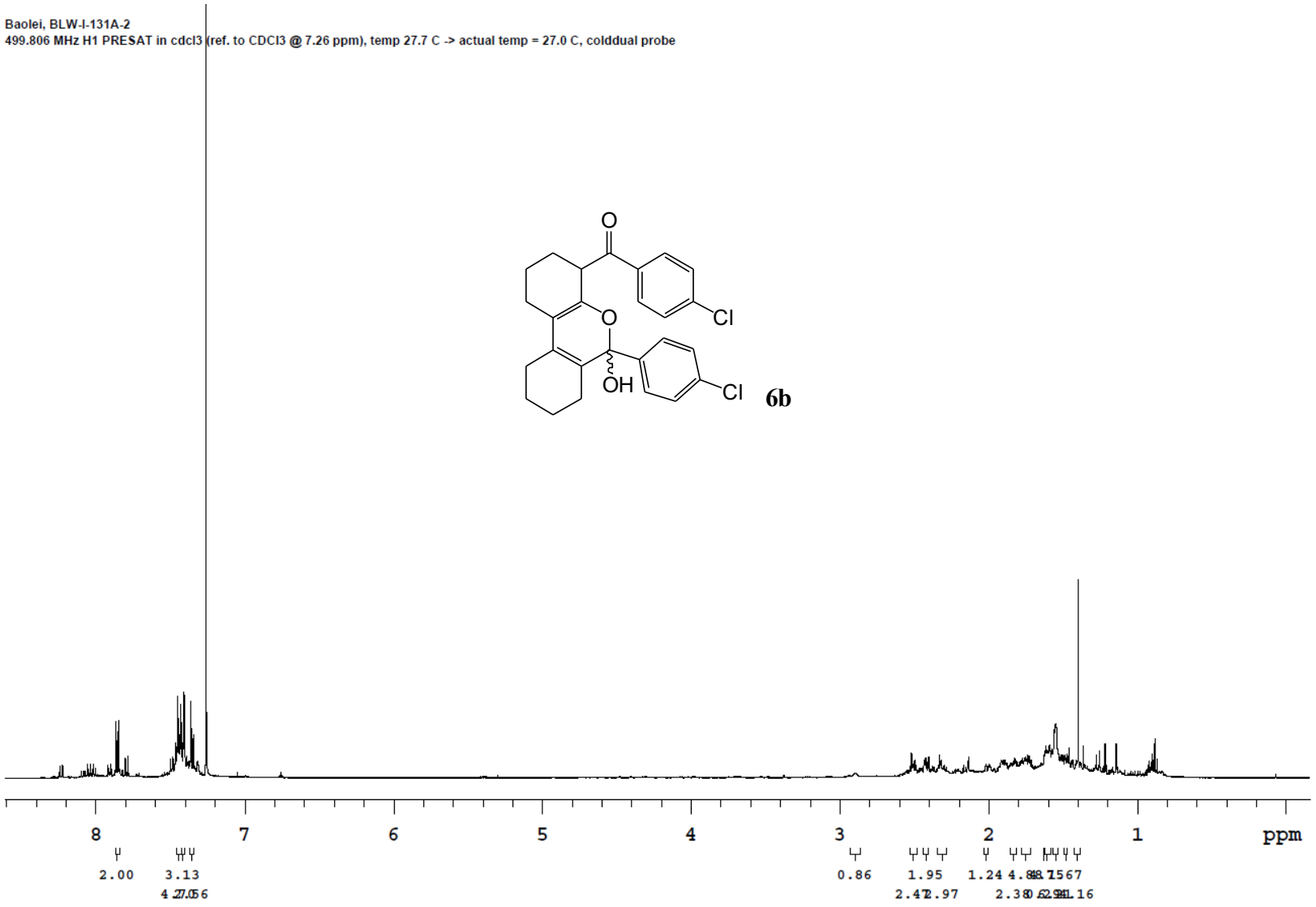
6a


Baolei, BLW-I-37-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
199.737
145.939
137.283
135.714
134.135
133.366
133.012
129.290
129.089
128.627
128.412
127.869
105.955
97.279
77.278
77.034
76.770
42.737
37.018
31.216
28.794
26.331
24.471
23.122
23.112
O
O
OH
6a
200
180
160
140
120
100
80
60
40
20
ppm

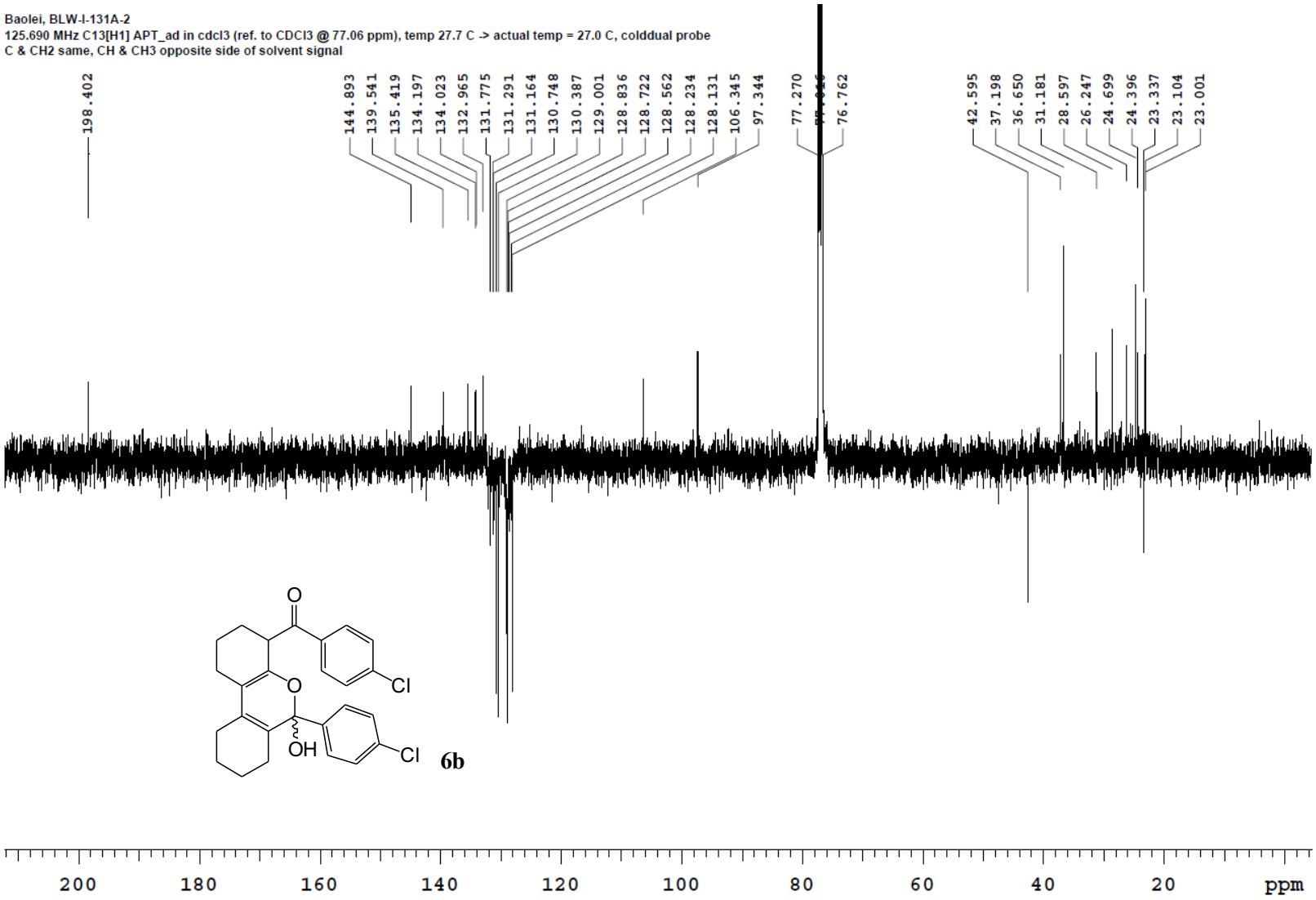

Baolei, BLW-I-61-3
499.806 MHz H1 gHMBCAD in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
O
O
OH
6a
F1 (ppm)
40
80
120
160
200
8
7
6
5
4
3
2
1
F2 (ppm)

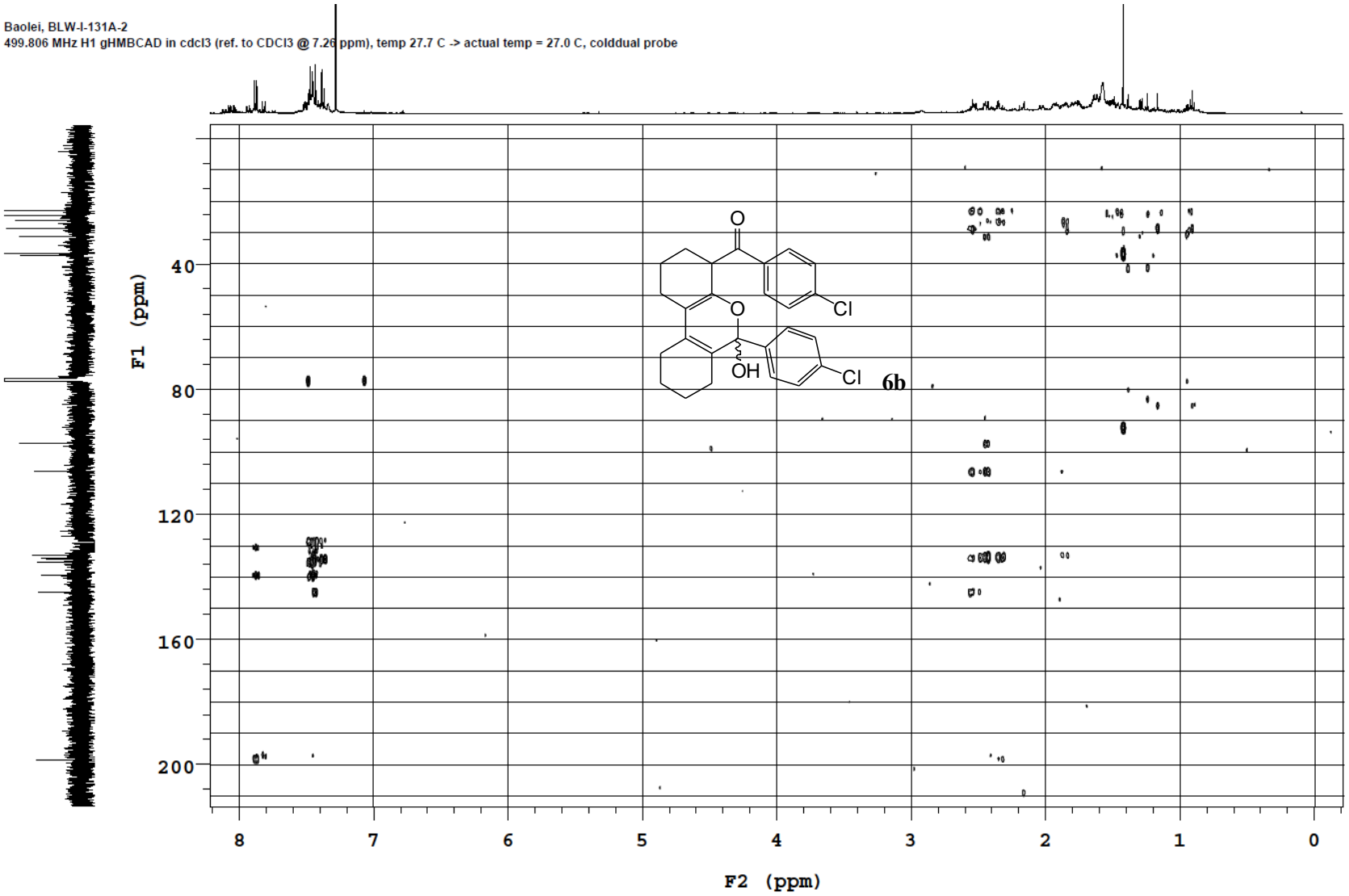


6a


Baolei, BLW-I-131A-2
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
O
O
Cl
OH
Cl
8
7
6
5
4
3
2
1
ppm
2.00
3.13
0.86
1.95
1.24

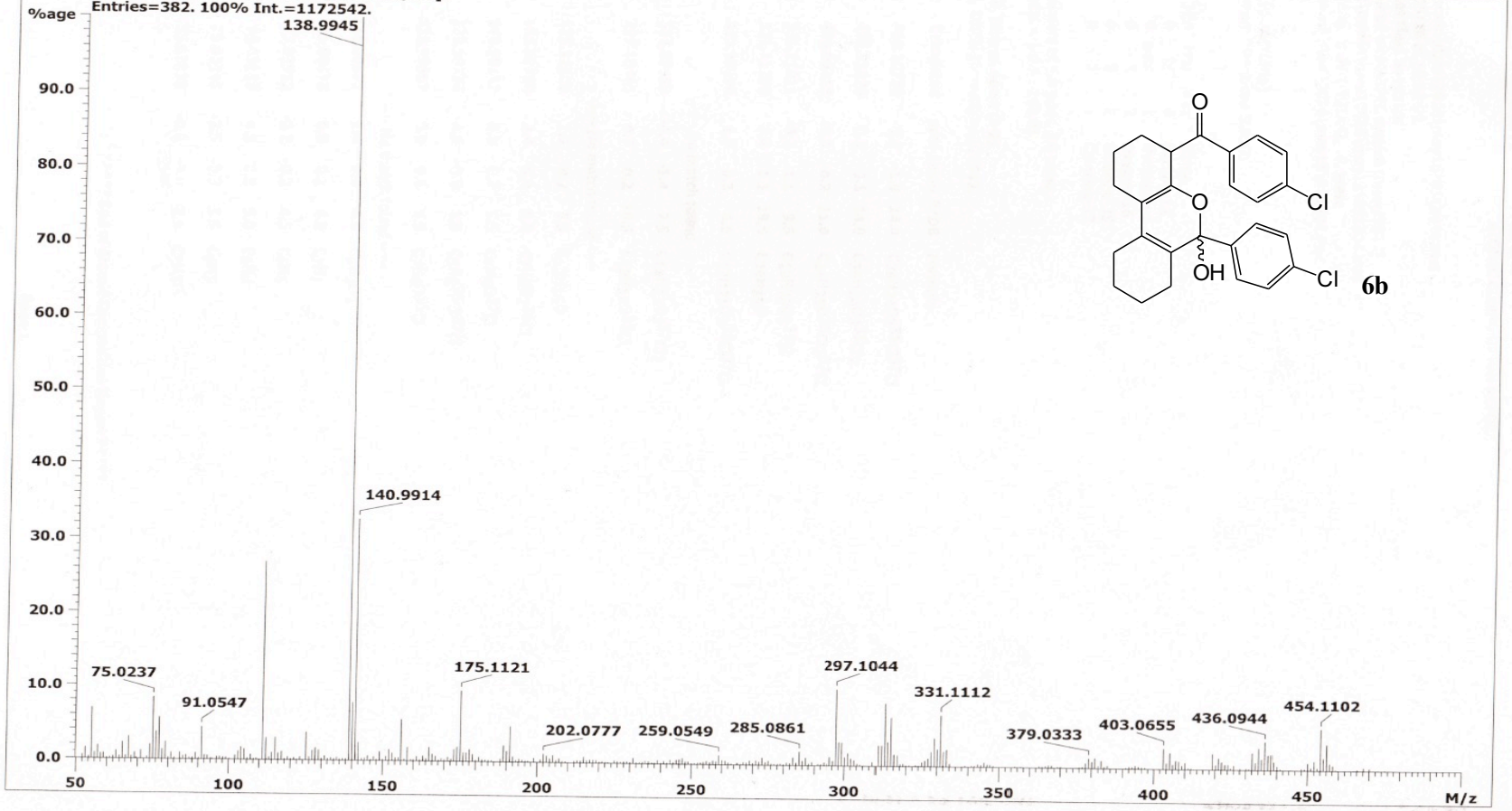
6b


Baolei, BLW-I-131A-2
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
198.402
144.893
139.541
135.419
134.197
134.023
132.965
131.775
131.291
131.164
130.748
130.387
129.001
128.836
128.722
128.562
128.234
128.131
106.345
97.344
77.270
76.762
42.595
37.198
36.650
31.181
28.597
26.247
24.699
24.396
23.337
23.104
23.001
O
O
Cl
OH
Cl
6b
200
180
160
140
120
100
80
60
40
20
ppm


Baolei, BLW-I-131A-2
499.806 MHz H1 gHMBCAD in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
F1 (ppm)
40
80
120
160
200
F2 (ppm)
8
7
6
5
4
3
2
1
0
O
O
OH
Cl
Cl
6b

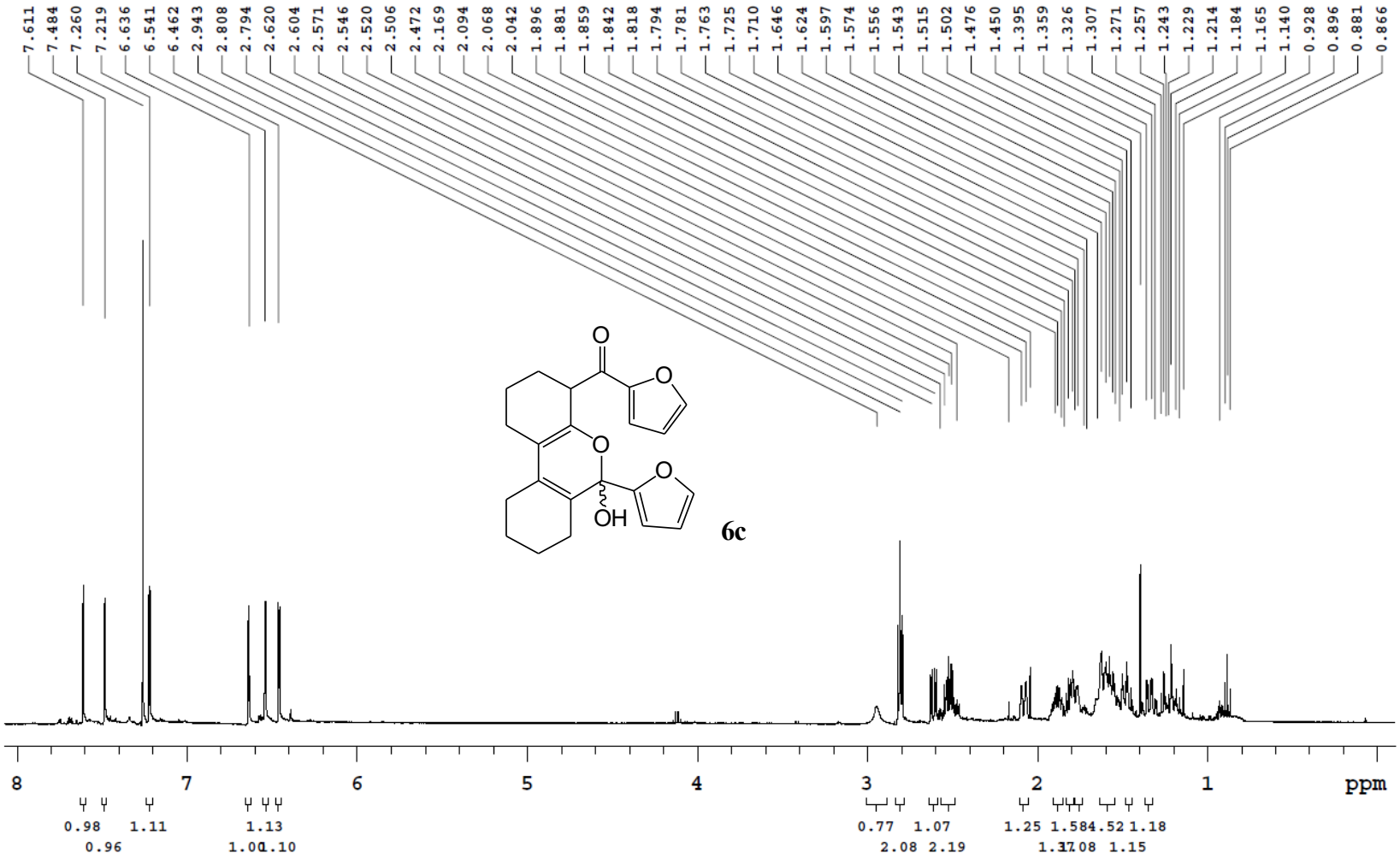
File Name : c:\mswin\data\2016\may16\051304a.mss
Creation Date/Time : 13/05/16 at 10:12:22
File Type : Hi-Res Mass Spectrum
File Source : Acquired on MASPEC system [msw/9849]
as c:\mswin\data\2016\may16\051304.mss
File Title : B. Wang, BLW-I-131A-2, F. West
Source File : c:\mswin\data\2016\may16\051304.mss
Source Scan(s) : 9:18

SCAN GRAPH. Flagging=M/z. Filter=[Excl: Ref/Ex.].
Entries=382. 100% Int.=1172542.

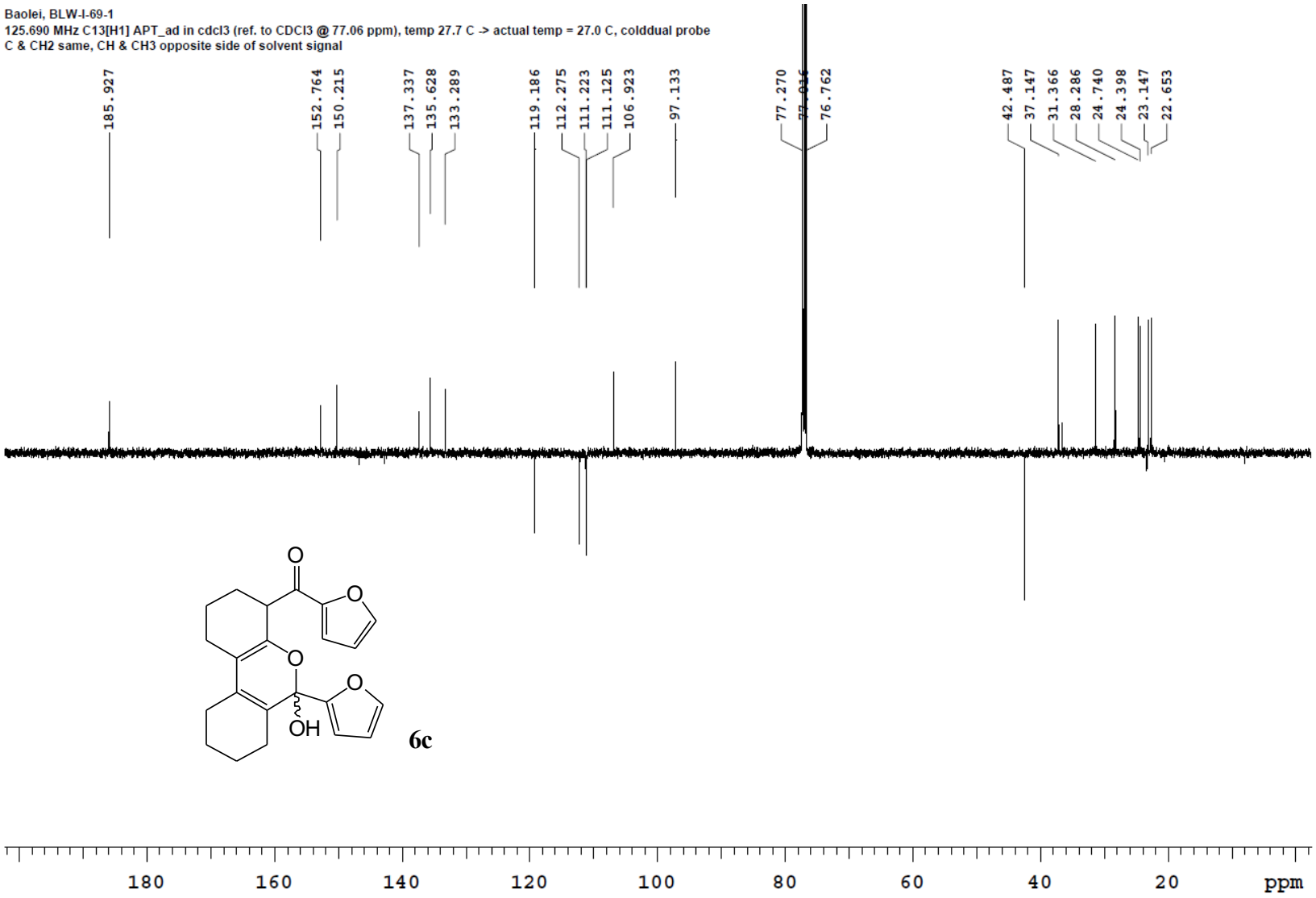


6b

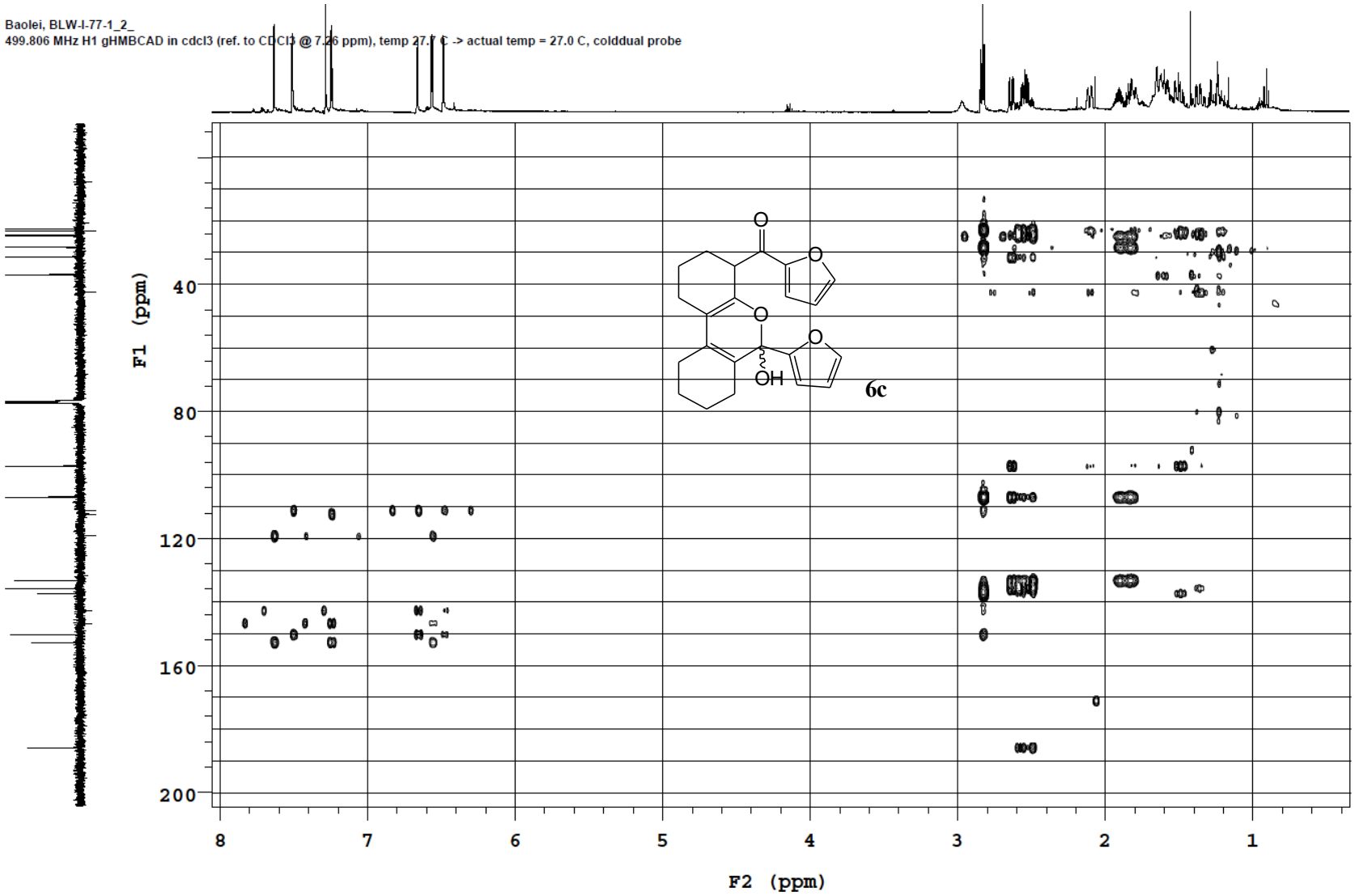
Baolei, BLW-I-69-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

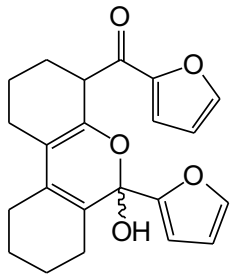


6c


Baolei, BLW-I-69-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
185.927
152.764
150.215
137.337
135.628
133.289
119.186
112.275
111.223
111.125
106.923
97.133
77.270
76.762
42.487
37.147
31.366
28.286
24.740
24.398
23.147
22.653
O
O
O
O
OH
180
160
140
120
100
80
60
40
20
ppm

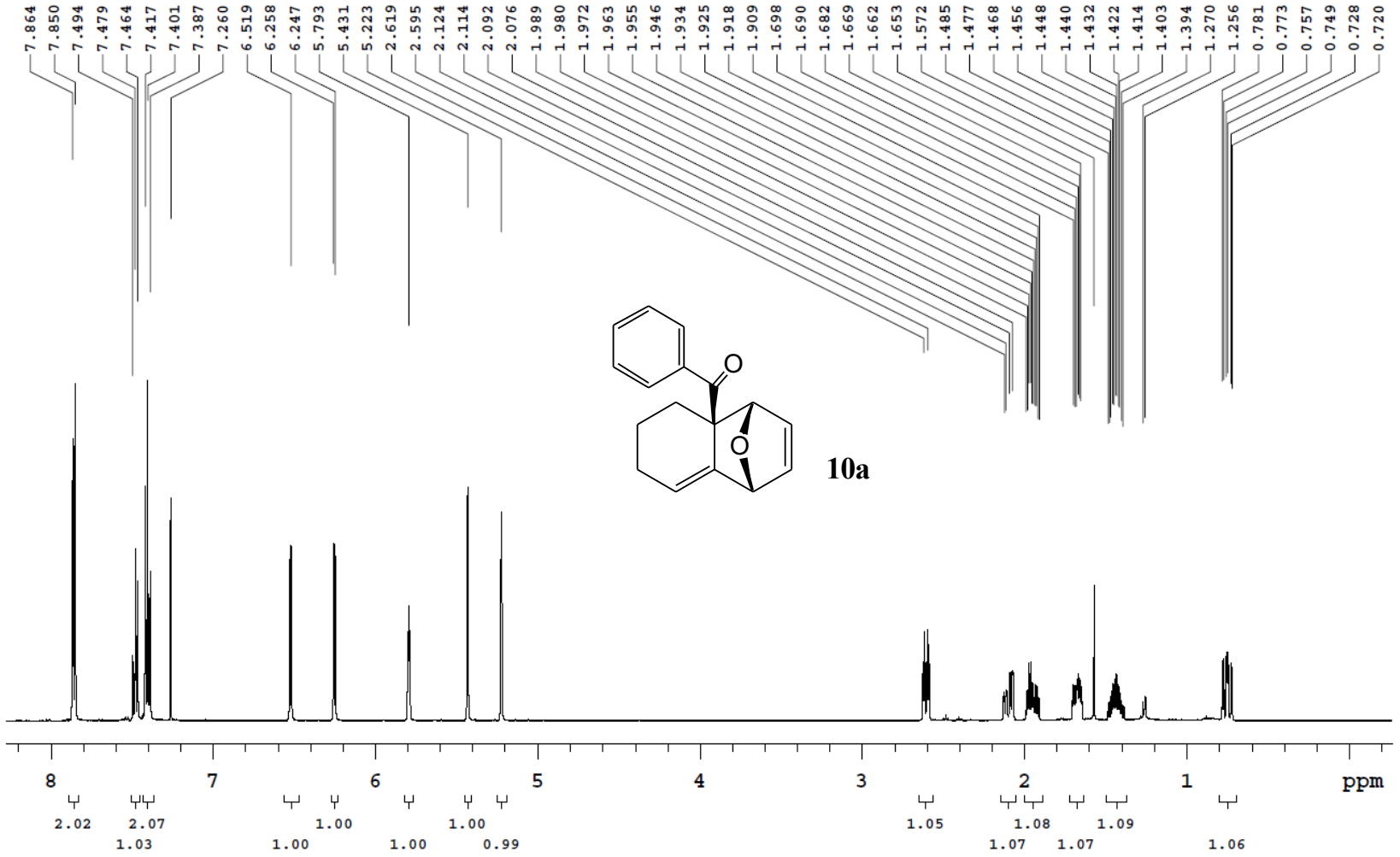
6c


Baolei, BLW-I-77-1_2_
499.806 MHz H1 gHMBCAD in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.0 C -> actual temp = 27.0 C, colddual probe
F1 (ppm)
40
80
120
160
200
F2 (ppm)
8
7
6
5
4
3
2
1
O
O
O
O
OH
6c

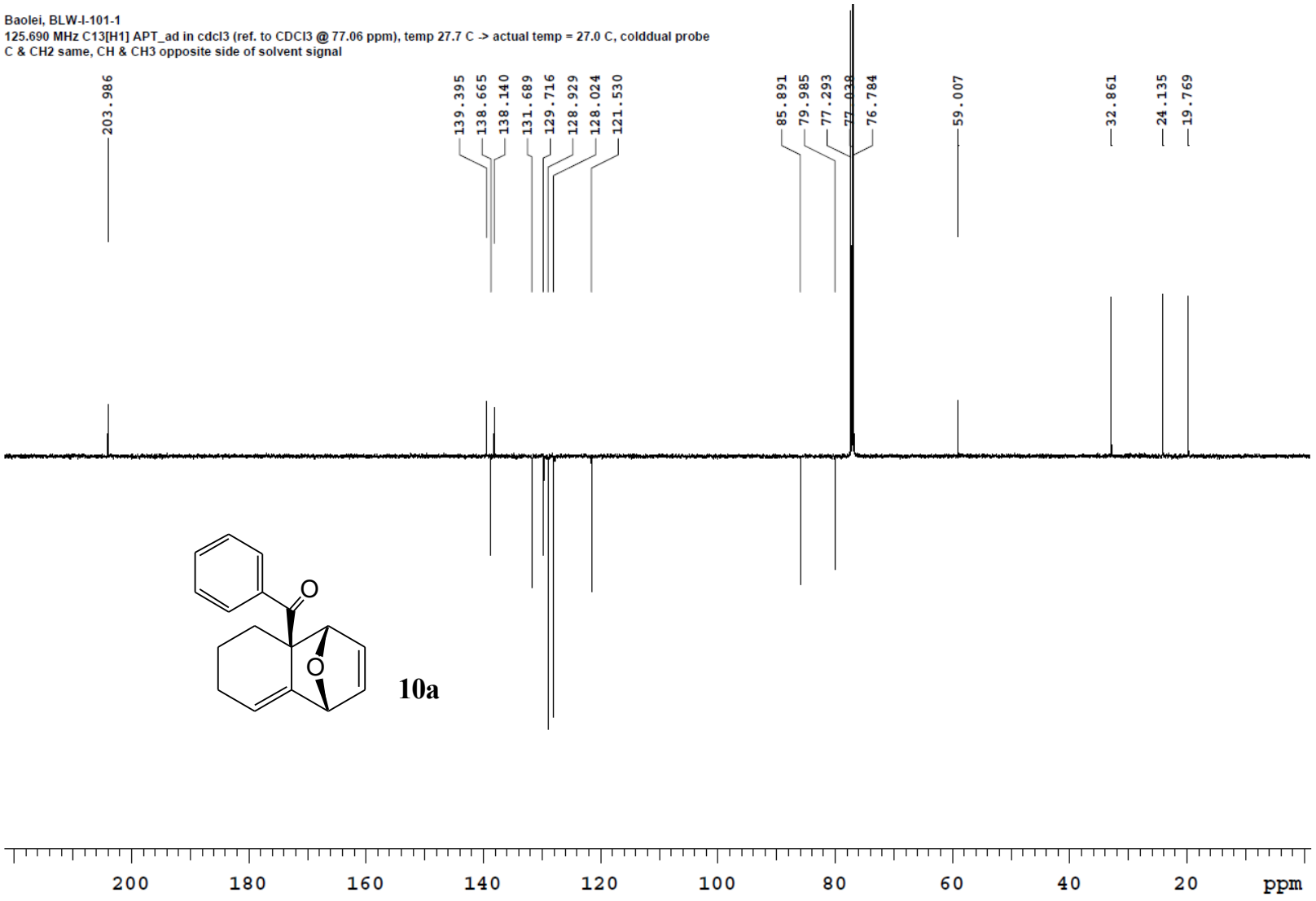


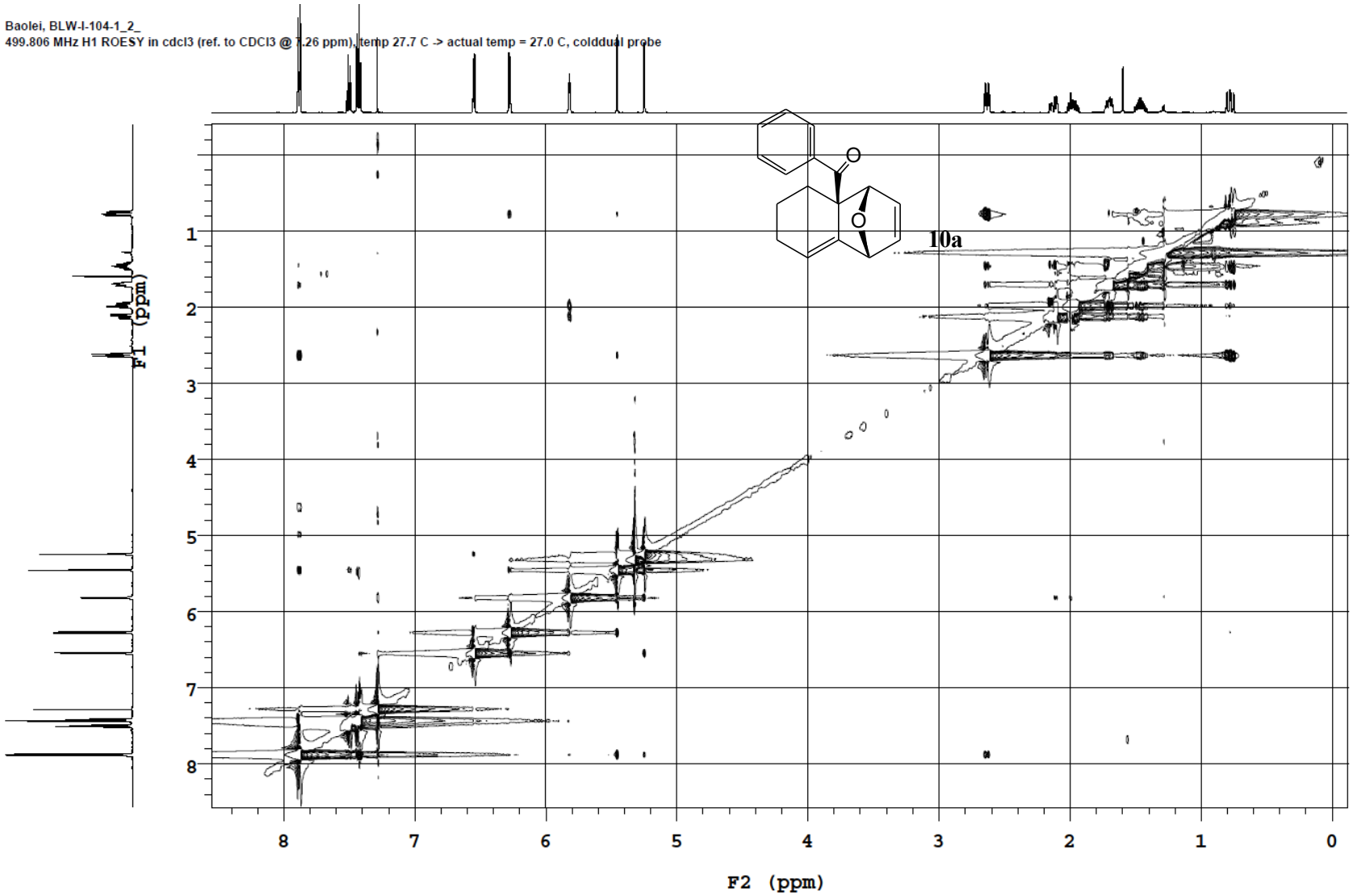
6c

Baolei, BLW-I-101-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

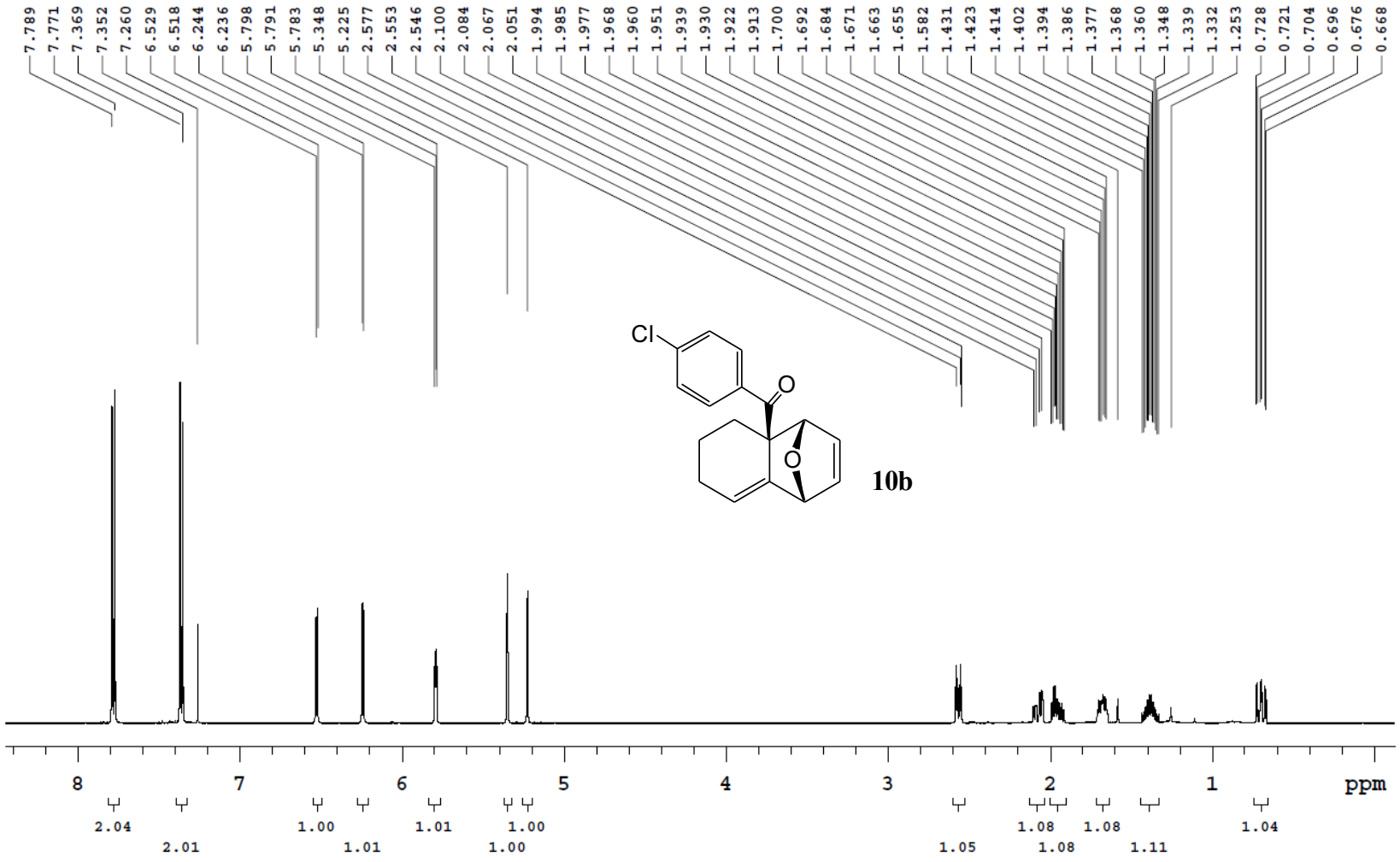


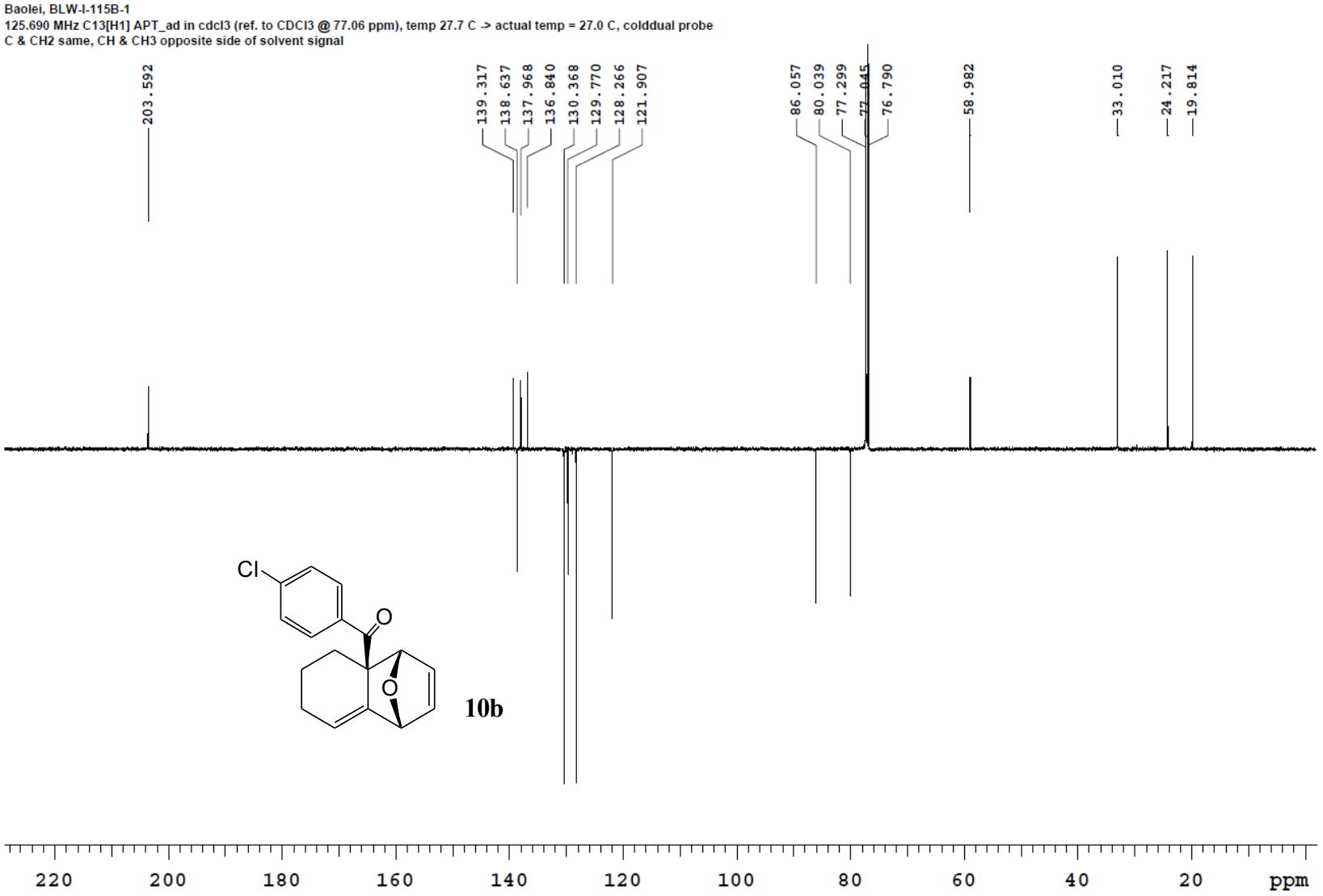
10a

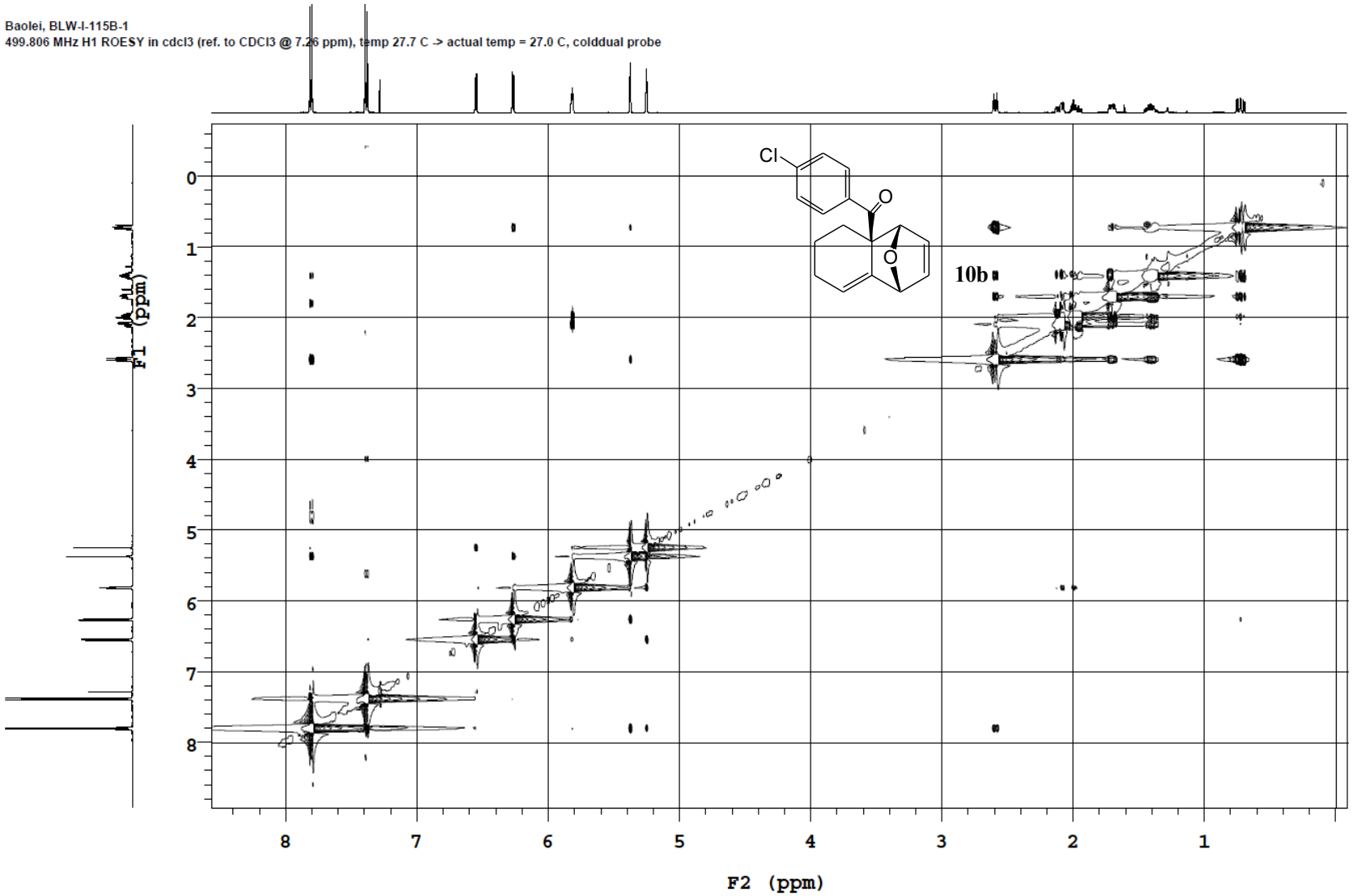

Baolei, BLW-I-101-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
203.986
139.395
138.665
138.140
131.689
129.716
128.929
128.024
121.530
85.891
79.985
77.293
77.038
76.784
59.007
32.861
24.135
19.769
O
O
10a
200
180
160
140
120
100
80
60
40
20
ppm


Baolei, BLW-I-104-1_2_
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
10a
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8
0

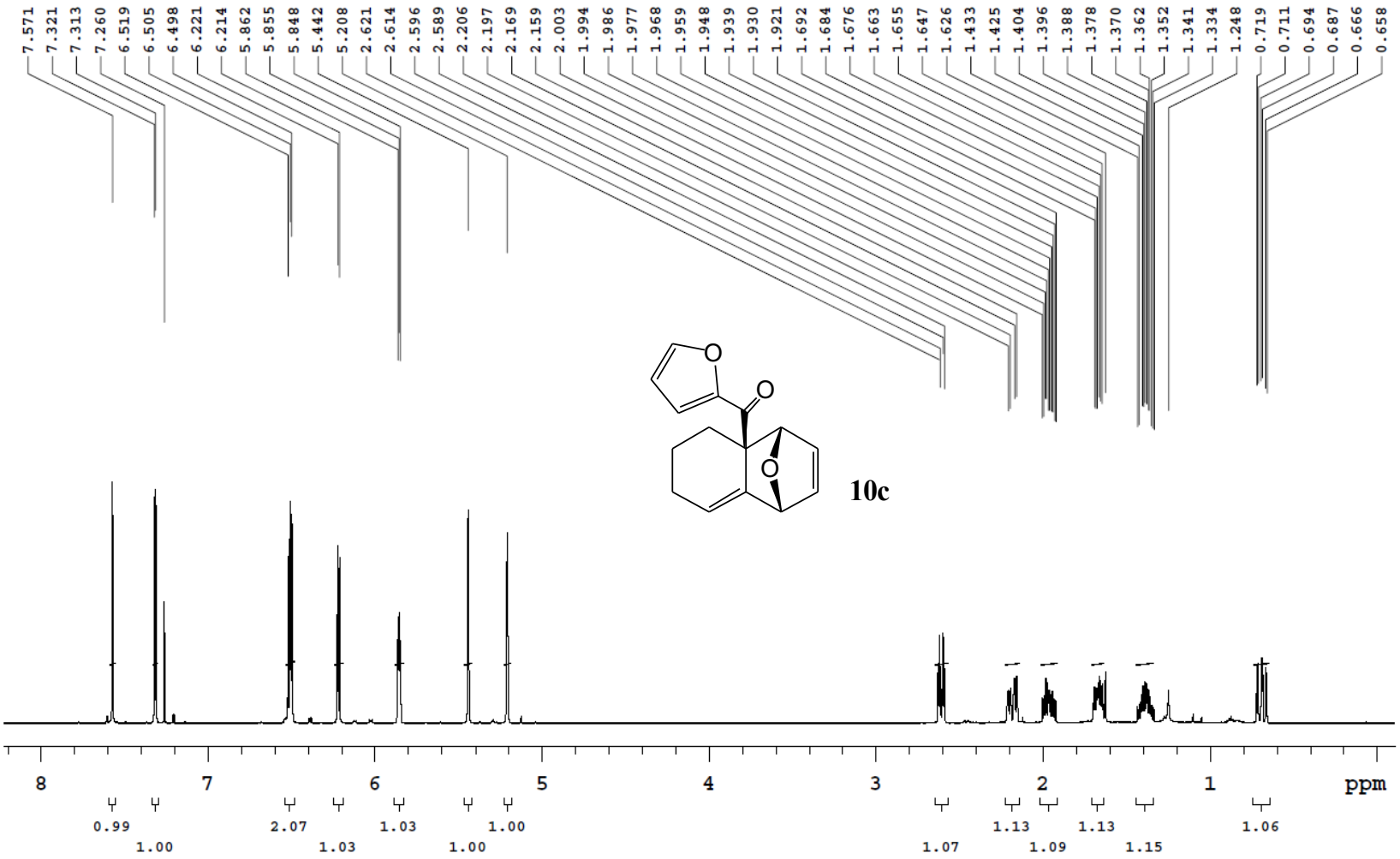
Baolei, BLW-I-115B-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



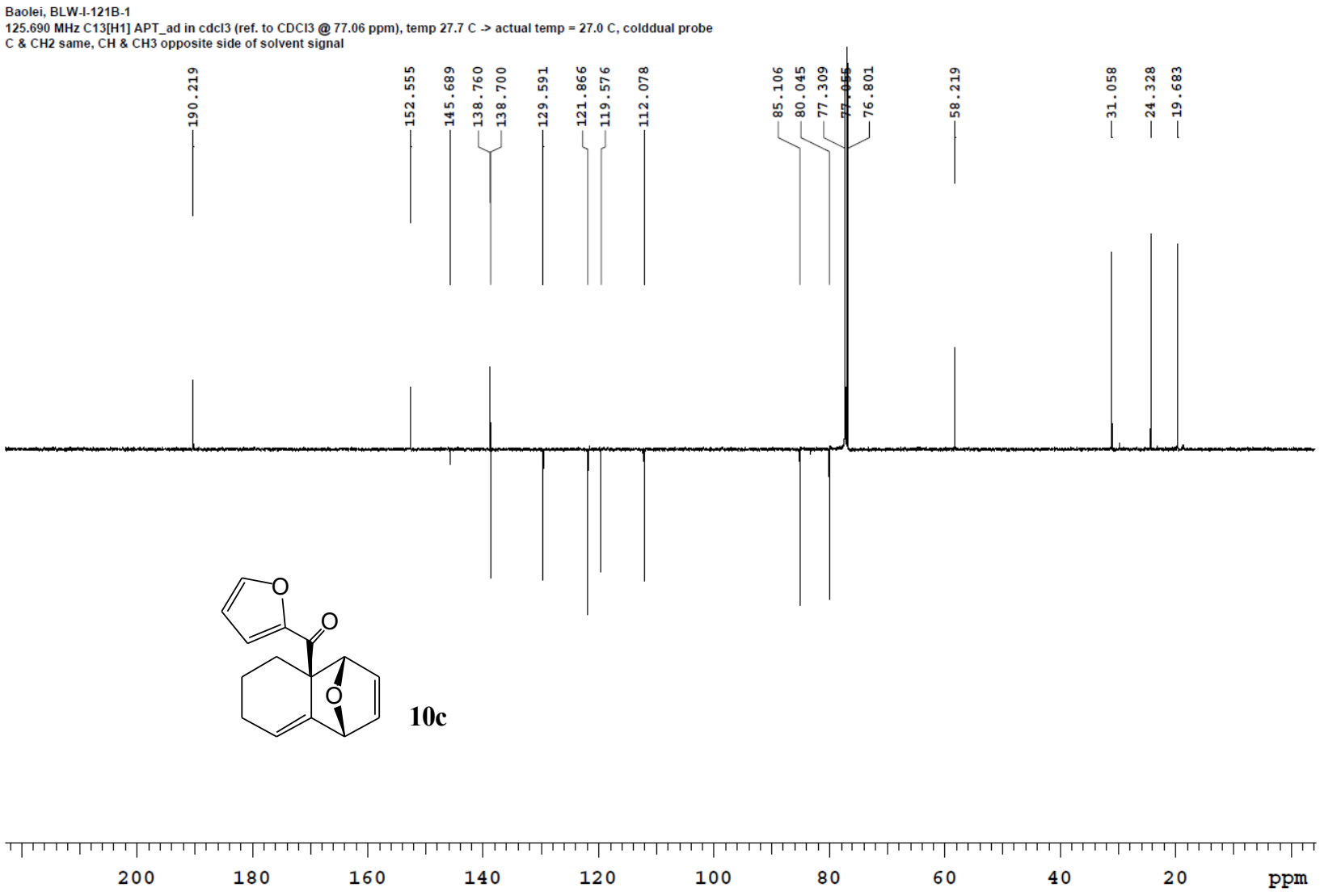

Baolei, BLW-I-115B-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
203.592
139.317
138.637
137.968
136.840
130.368
129.770
128.266
121.907
86.057
80.039
77.299
77.045
76.790
58.982
33.010
24.217
19.814
Cl
O
O
10b
220
200
180
160
140
120
100
80
60
40
20
ppm

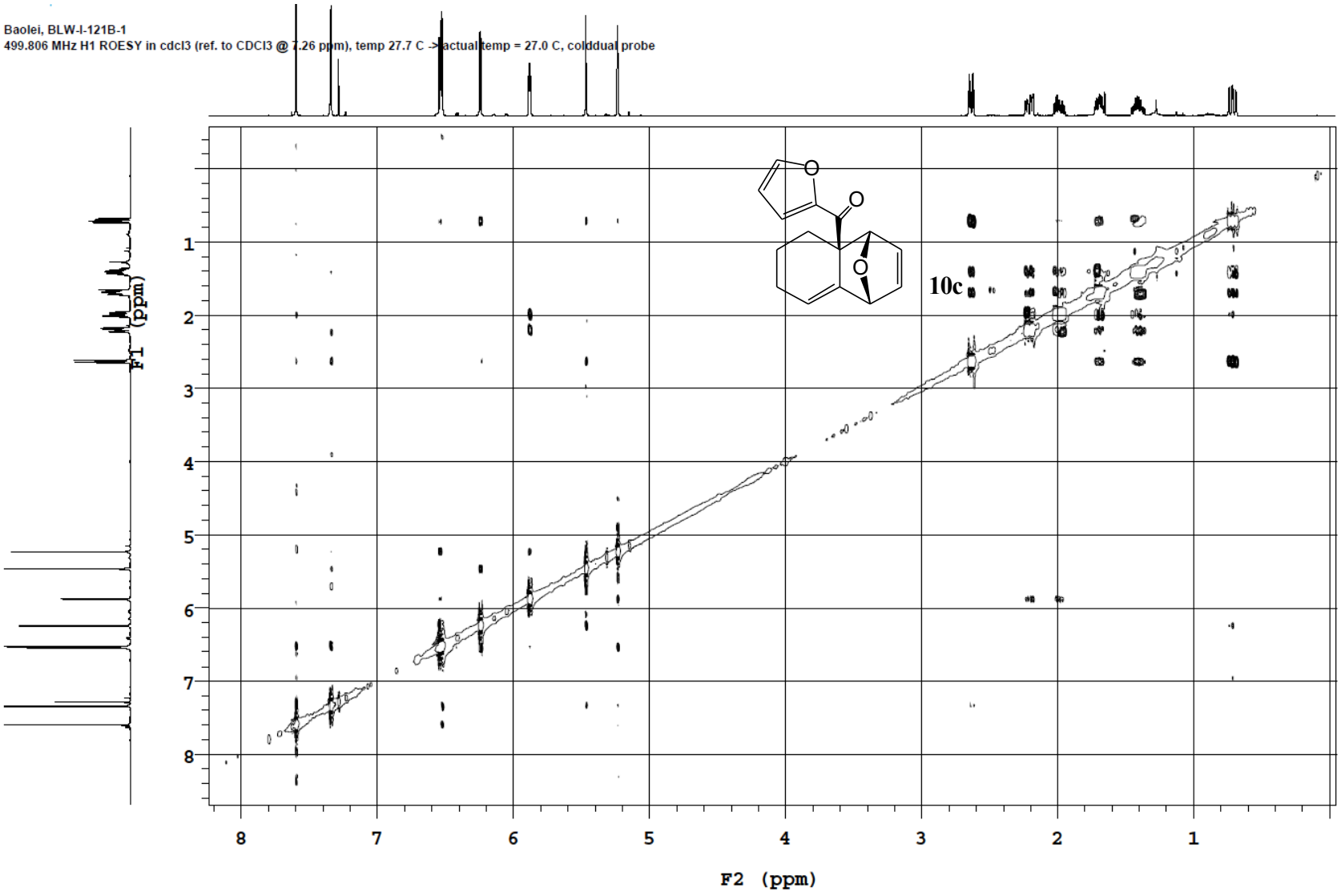

Baolei, BLW-I-115B-1
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
Cl
O
O
10b
F1 (ppm)
F2 (ppm)
0
1
2
3
4
5
6
7
8

Baolei, BLW-I-121B-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

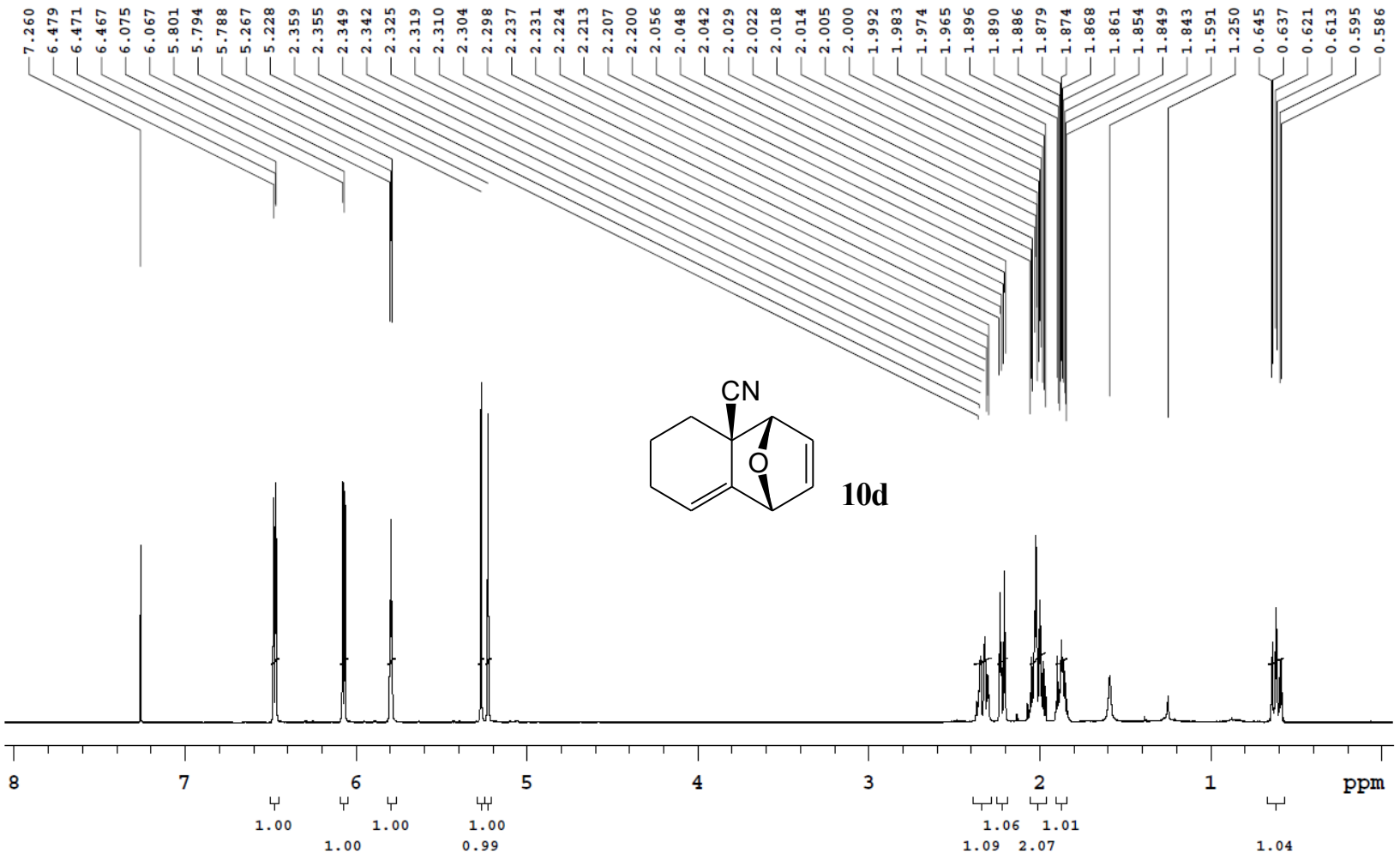


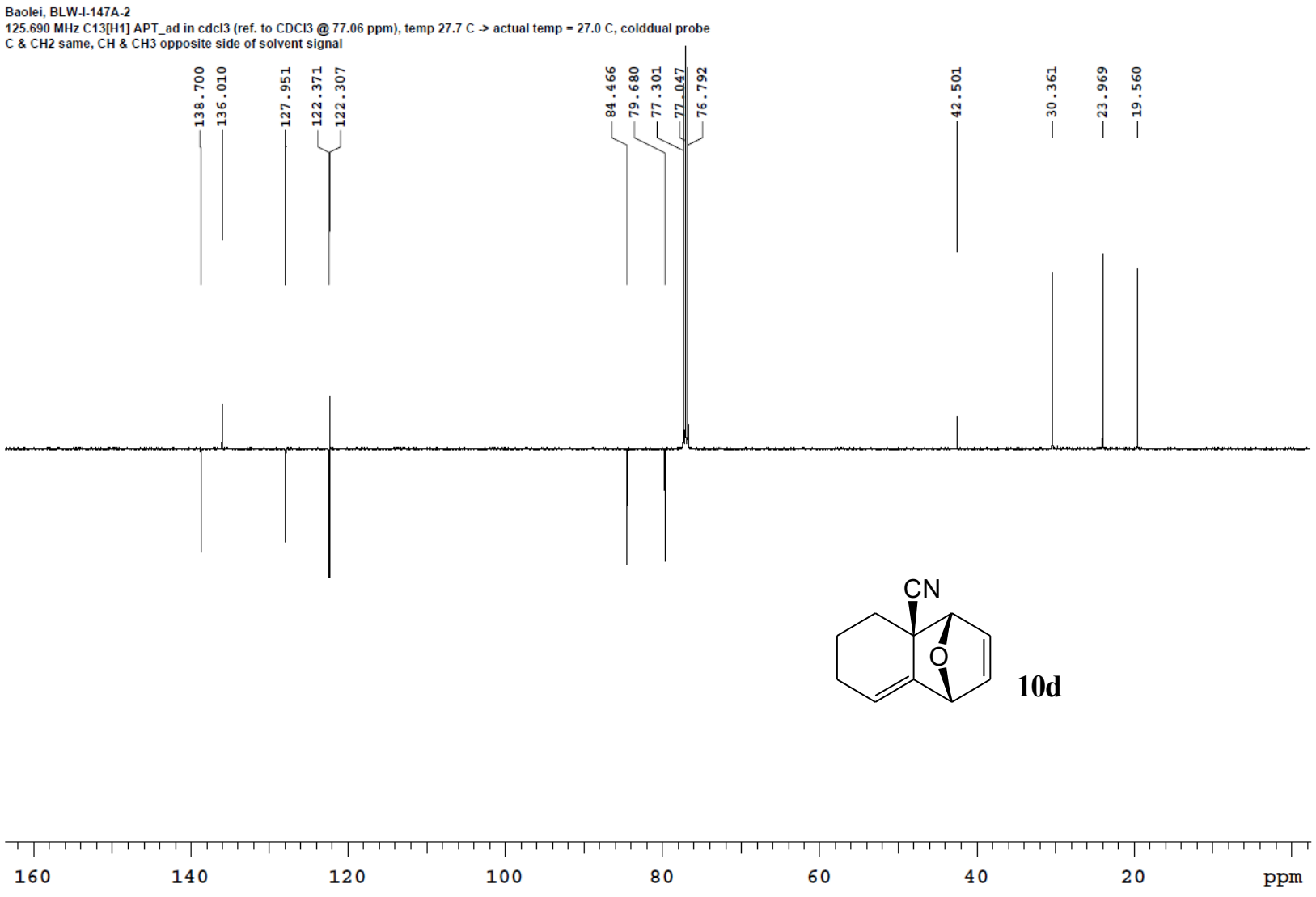
10c

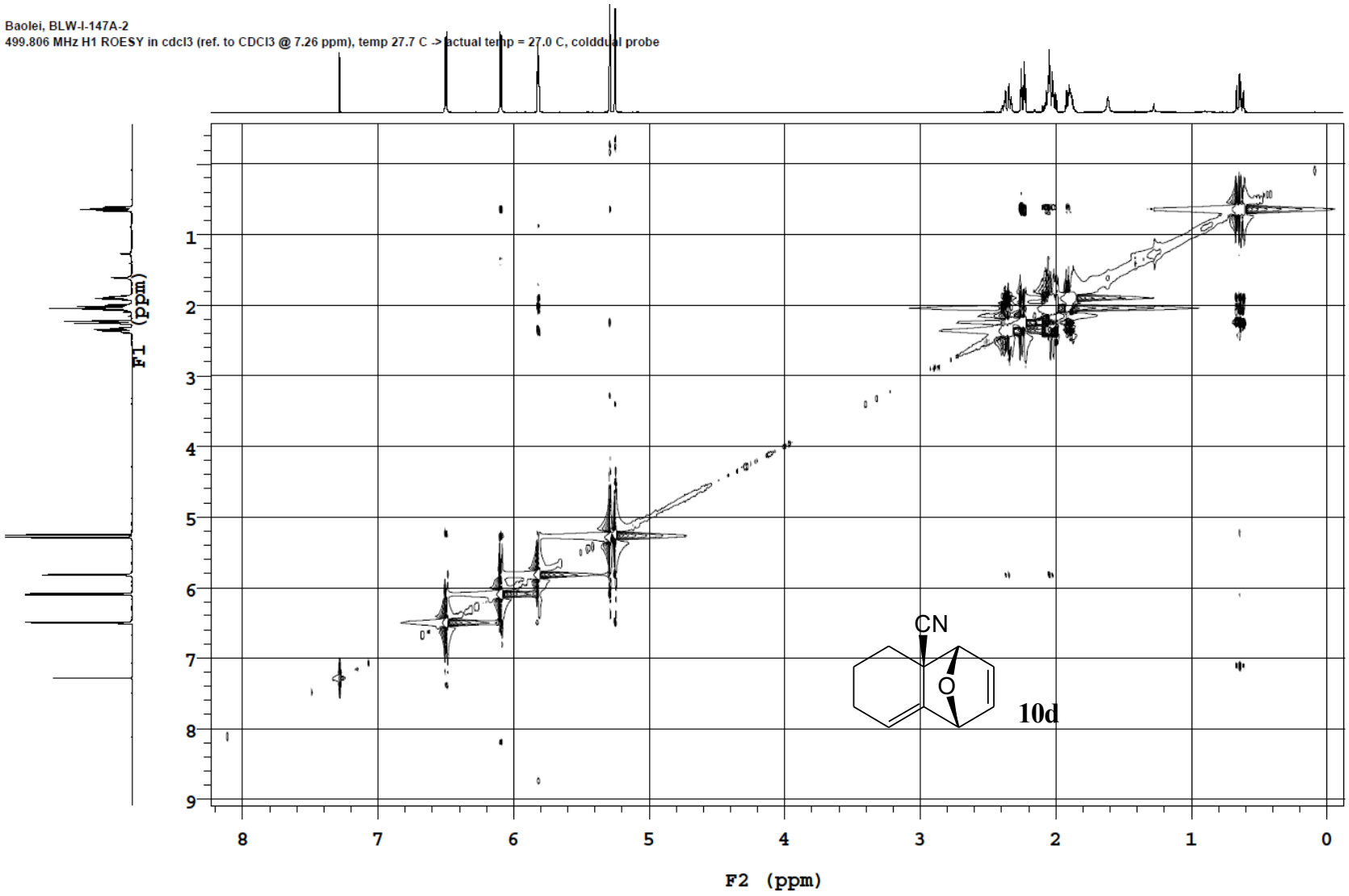

Baolei, BLW-I-121B-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
190.219
152.555
145.689
138.760
138.700
129.591
121.866
119.576
112.078
85.106
80.045
77.309
77.055
76.801
58.219
31.058
24.328
19.683
O
O
O
10c
200
180
160
140
120
100
80
60
40
20
ppm


Baolei, BLW-I-121B-1
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
10c
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8

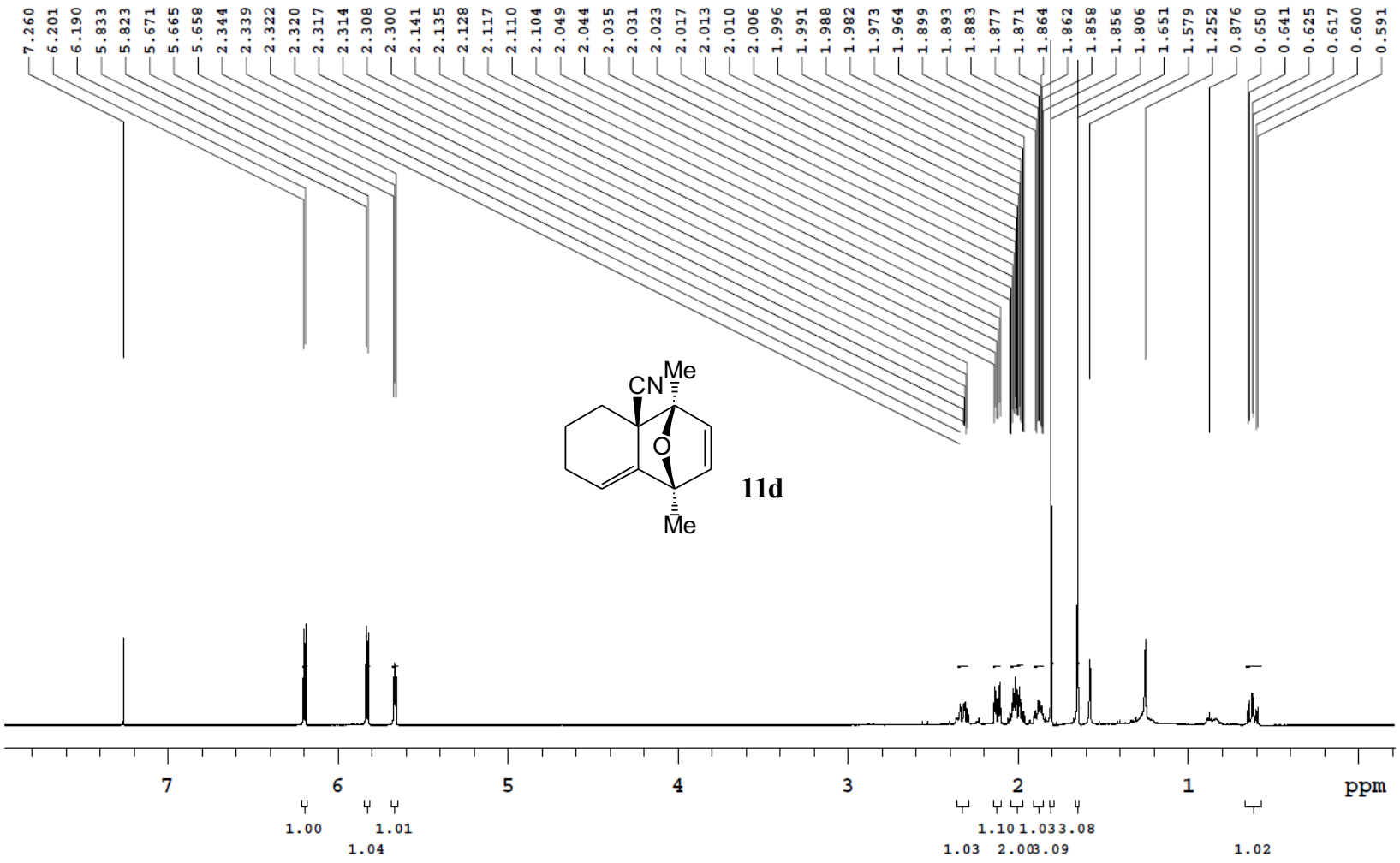
Baolei, BLW-I-147A-2
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

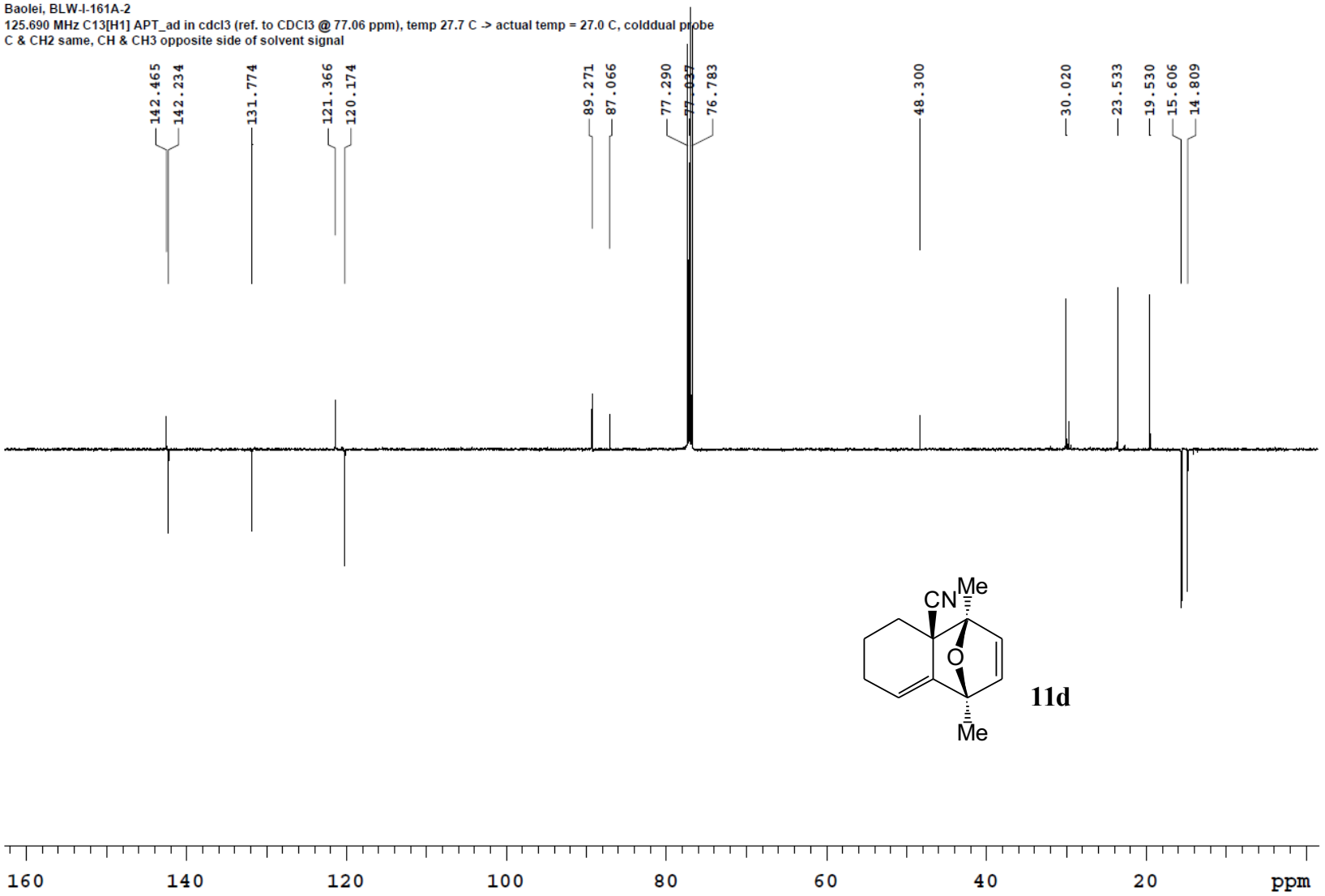



Baolei, BLW-I-147A-2
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
138.700
136.010
127.951
122.371
122.307
84.466
79.680
77.301
77.047
76.792
42.501
30.361
23.969
19.560
CN
O
10d
160
140
120
100
80
60
40
20
ppm

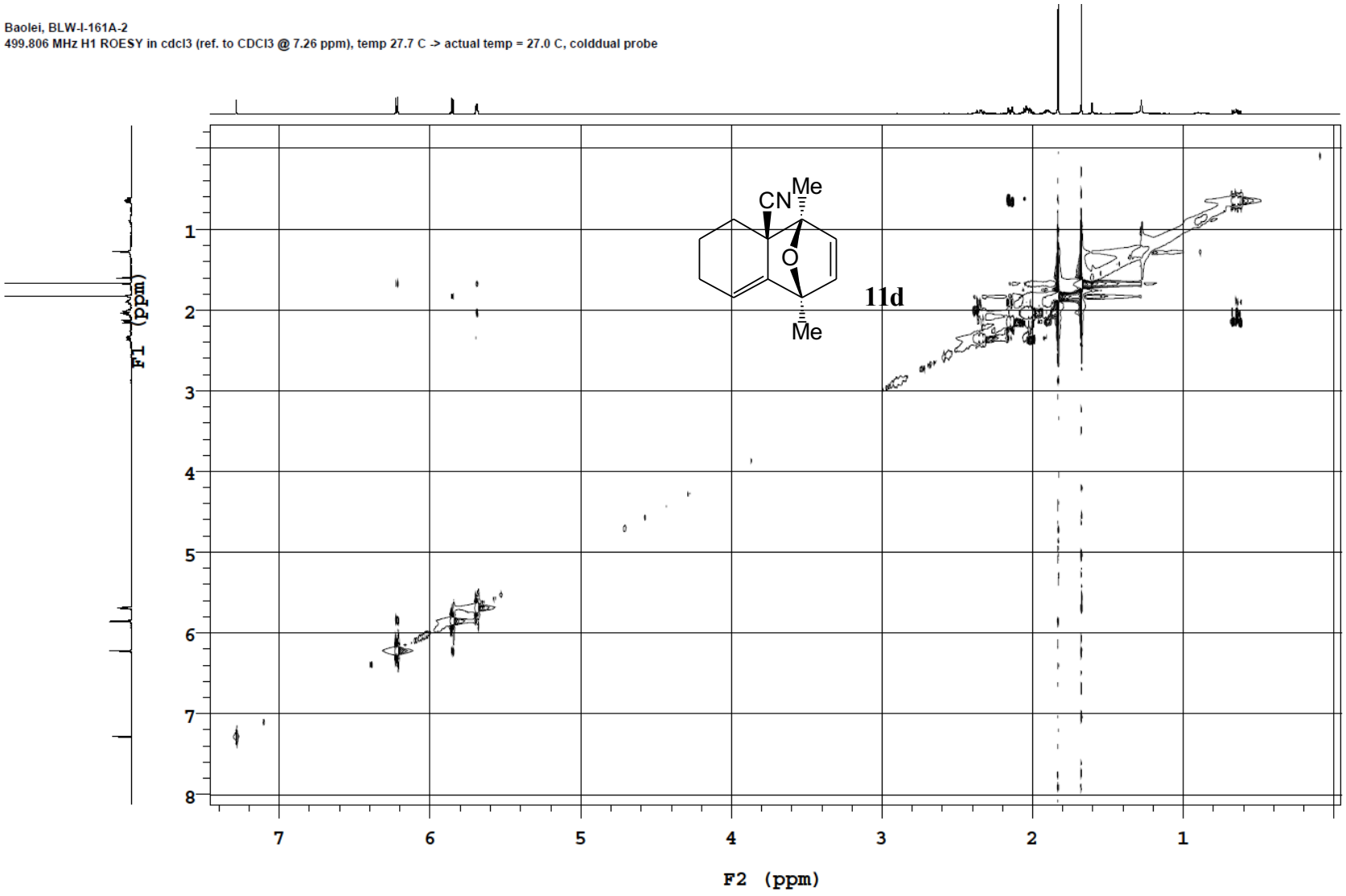

Baolei, BLW-I-147A-2
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
F1 (ppm)
F2 (ppm)
CN
O
10d

Baolei, BLW-I-161A-2
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

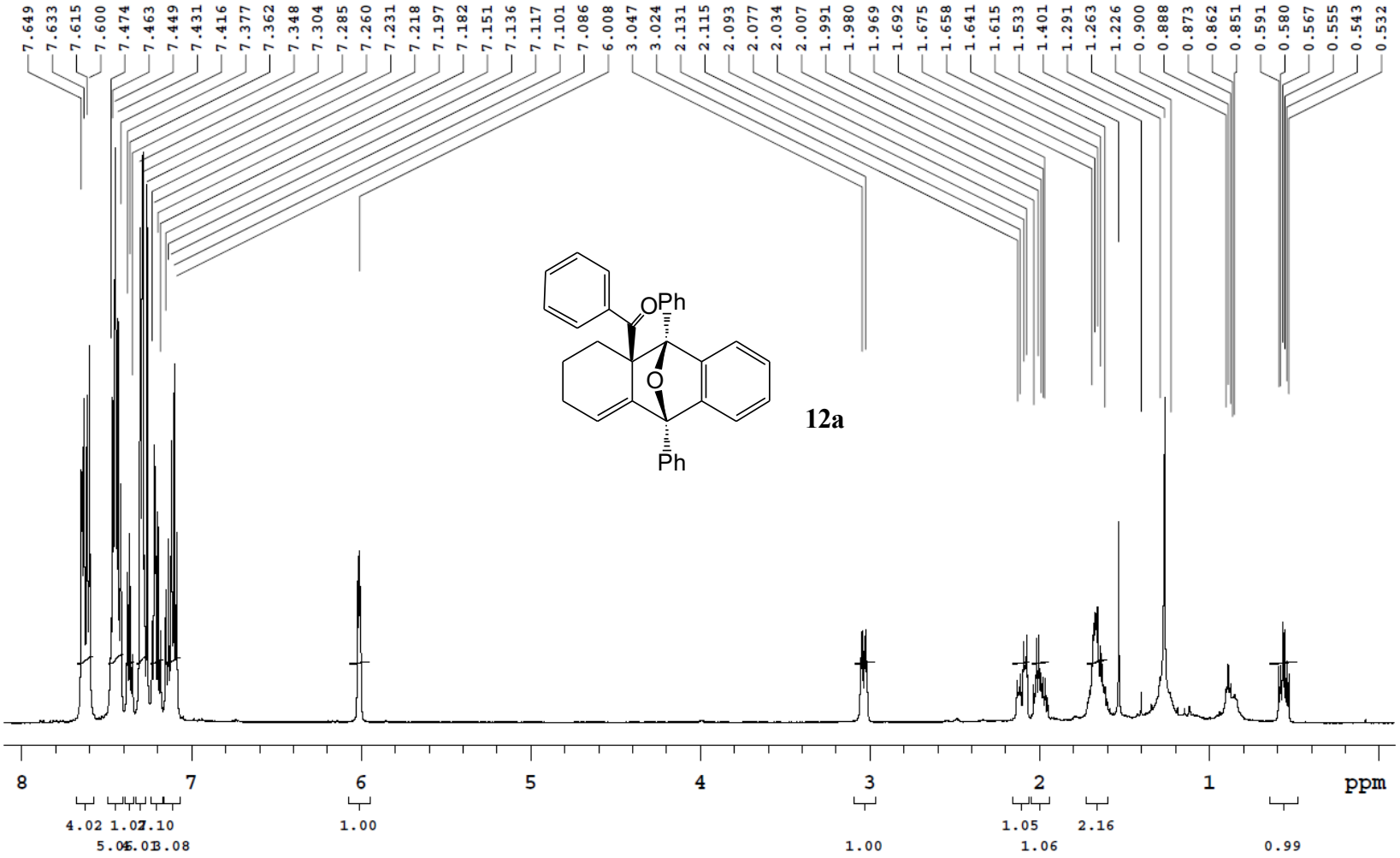


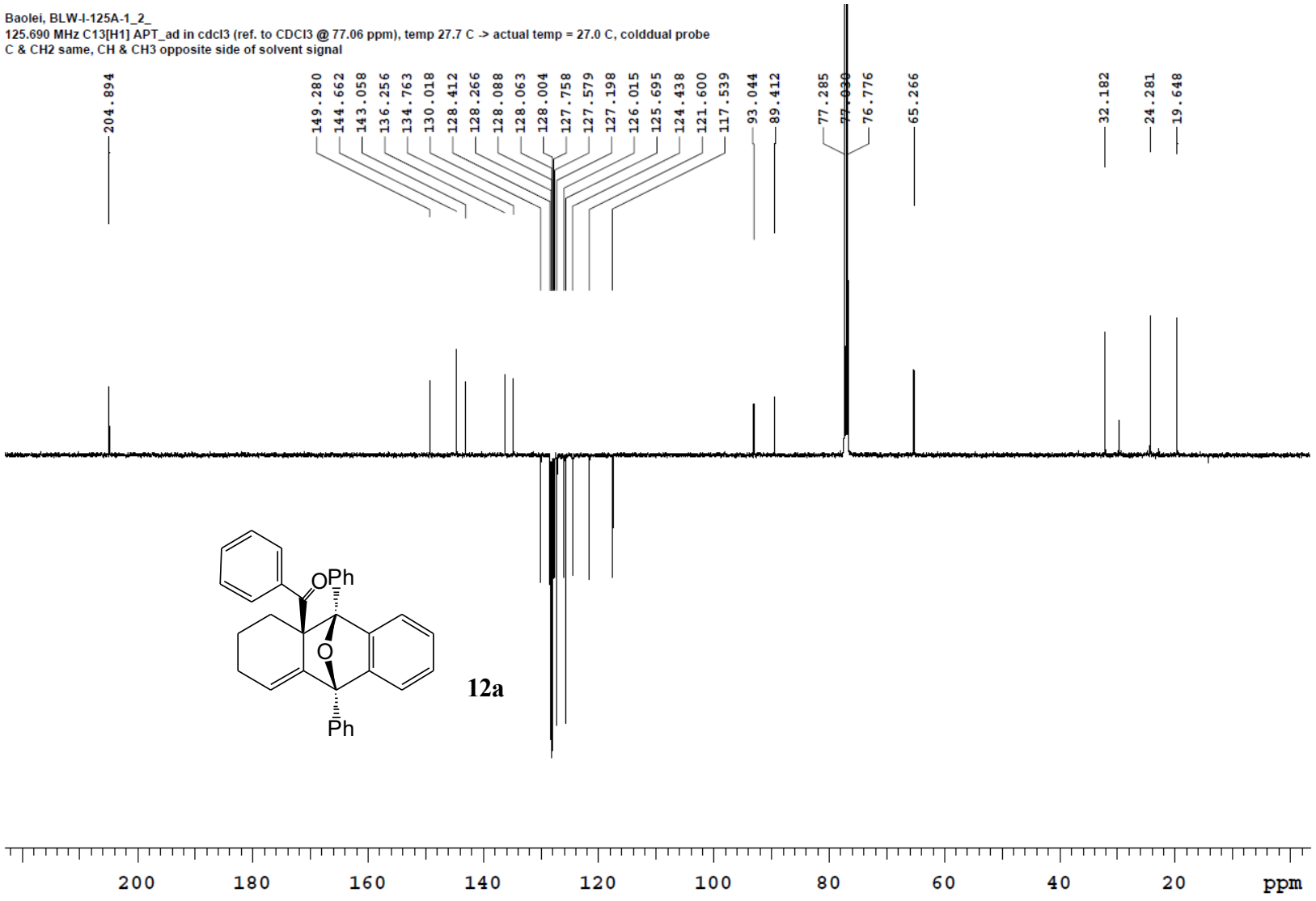

Baolei, BLW-I-161A-2
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
142.465
142.234
131.774
121.366
120.174
89.271
87.066
77.290
77.037
76.783
48.300
30.020
23.533
19.530
15.606
14.809
CN
Me
O
Me
160
140
120
100
80
60
40
20
ppm

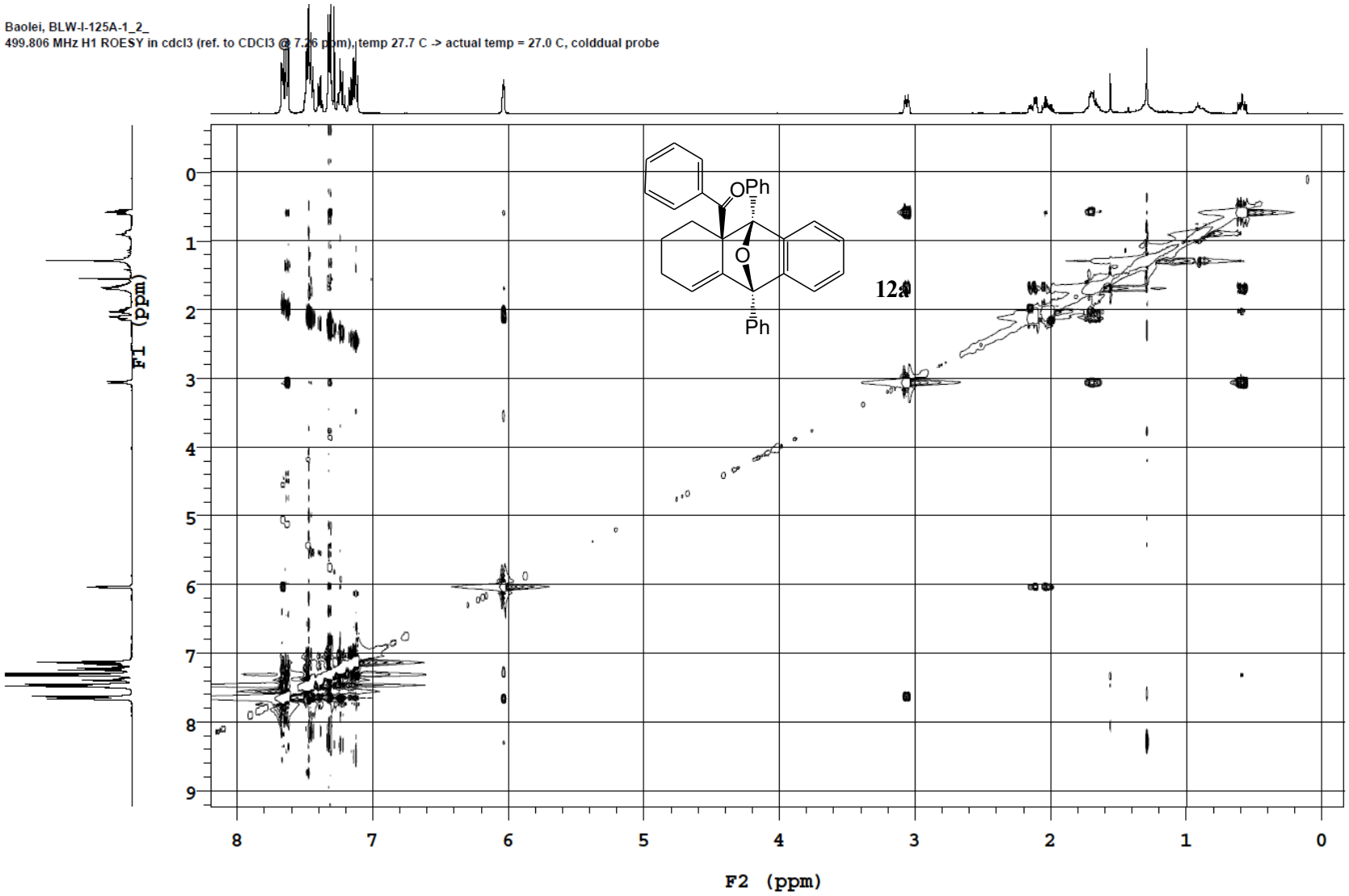
11d


Baolei, BLW-I-161A-2
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
CN
Me
O
Me
11d
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8
7
6
5
4
3
2
1

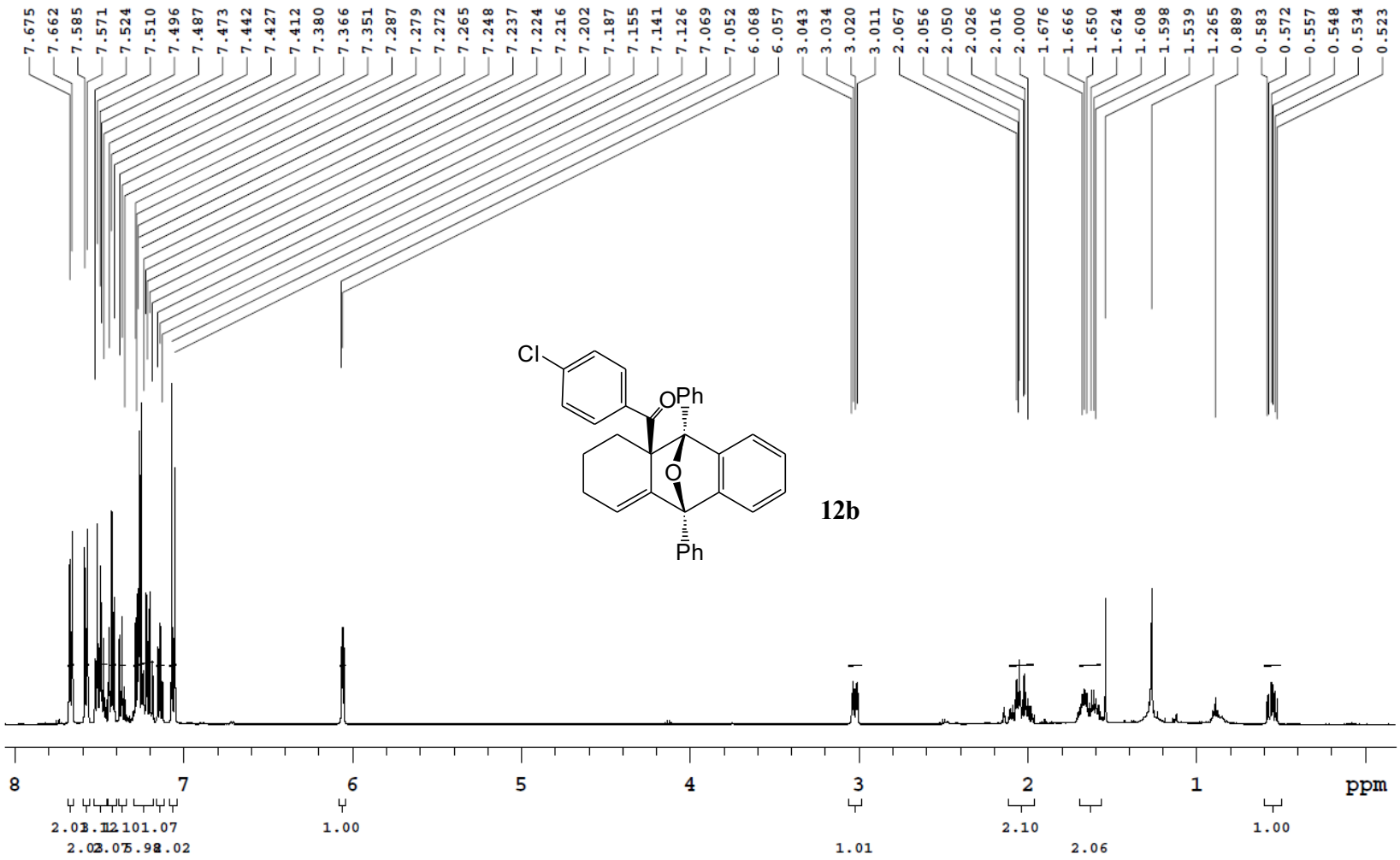
Baolei, BLW-I-125A-1_2_
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

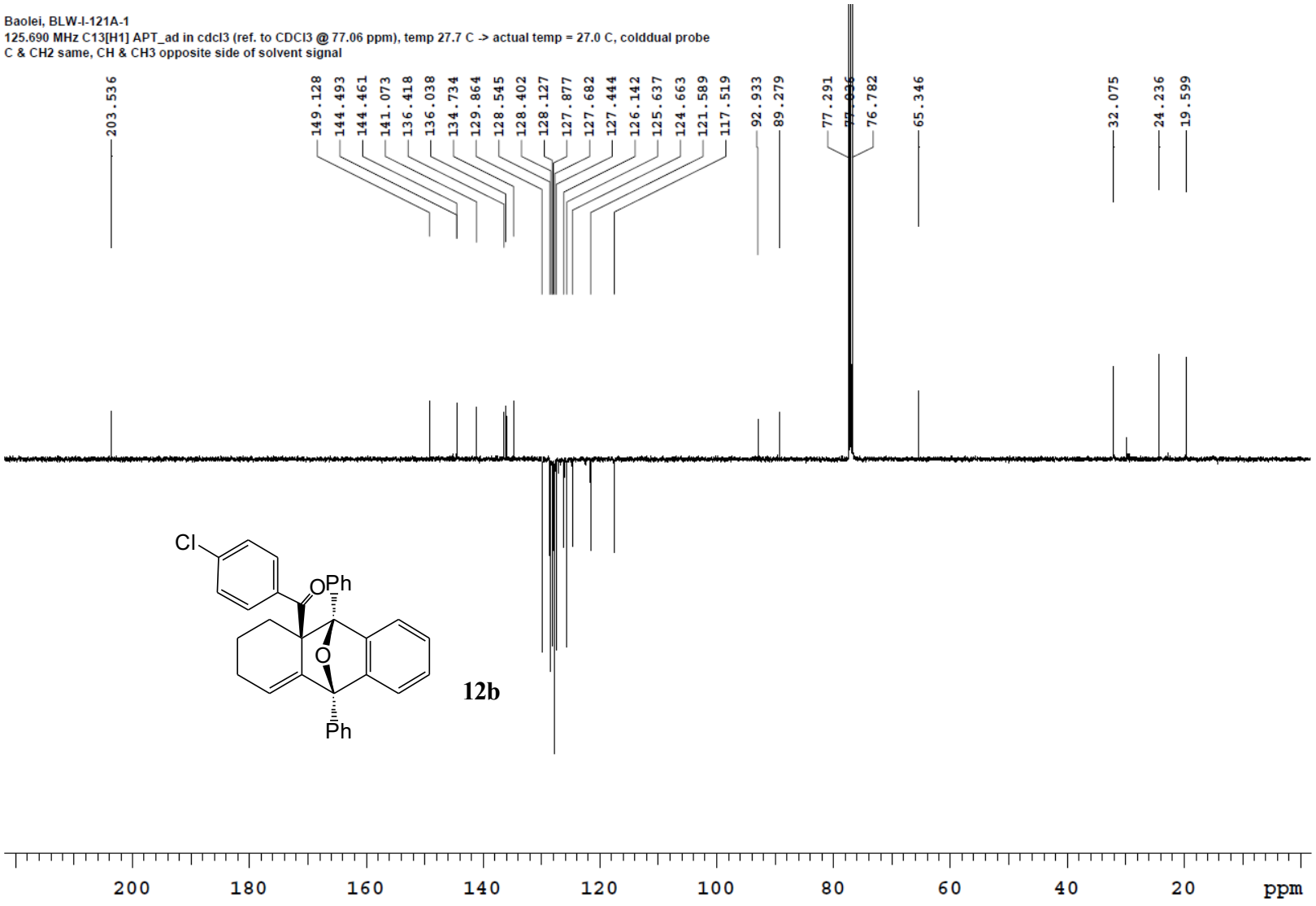


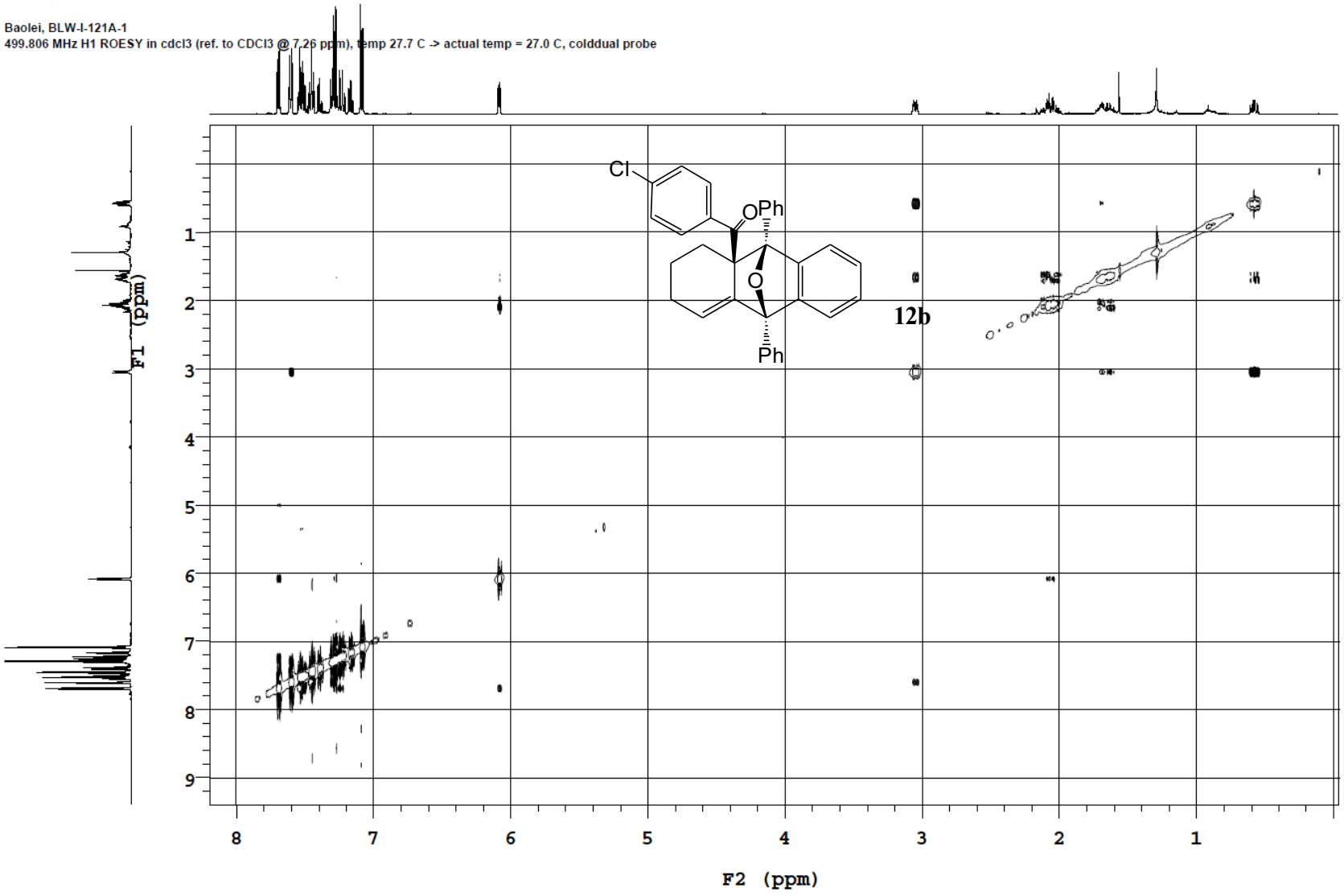

Baolei, BLW-I-125A-1_2_
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
204.894
149.280
144.662
143.058
136.256
134.763
130.018
128.412
128.266
128.088
128.063
128.004
127.758
127.579
127.198
126.015
125.695
124.438
121.600
117.539
93.044
89.412
77.285
77.030
76.776
65.266
32.182
24.281
19.648
OPh
O
Ph
12a
200
180
160
140
120
100
80
60
40
20
ppm


Baolei, BLW-I-125A-1_2_
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
OPh
O
Ph
12a
F1 (ppm)
F2 (ppm)
0
1
2
3
4
5
6
7
8
9
8
7
6
5
4
3
2
1
0

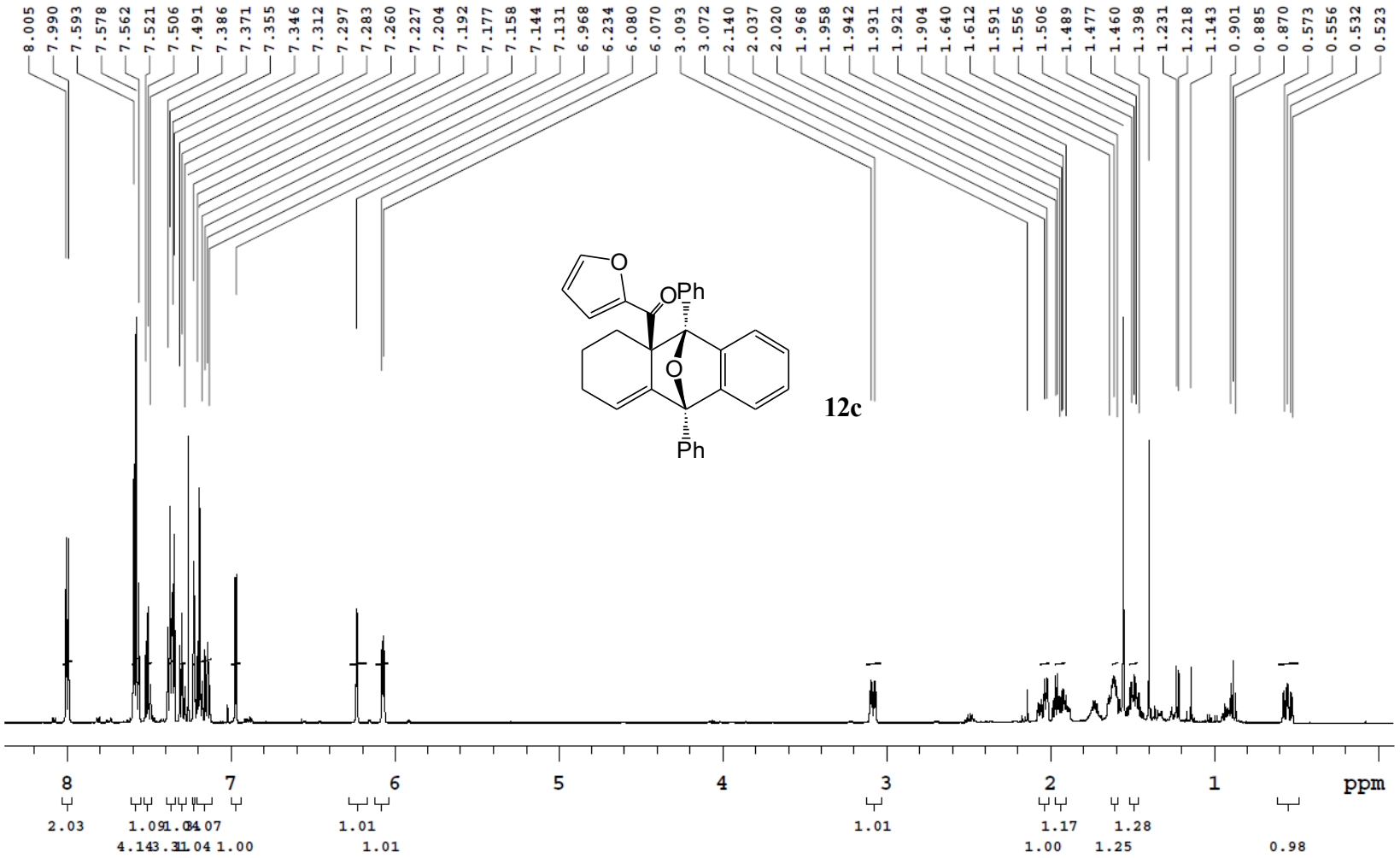
Baolei, BLW-I-121A-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

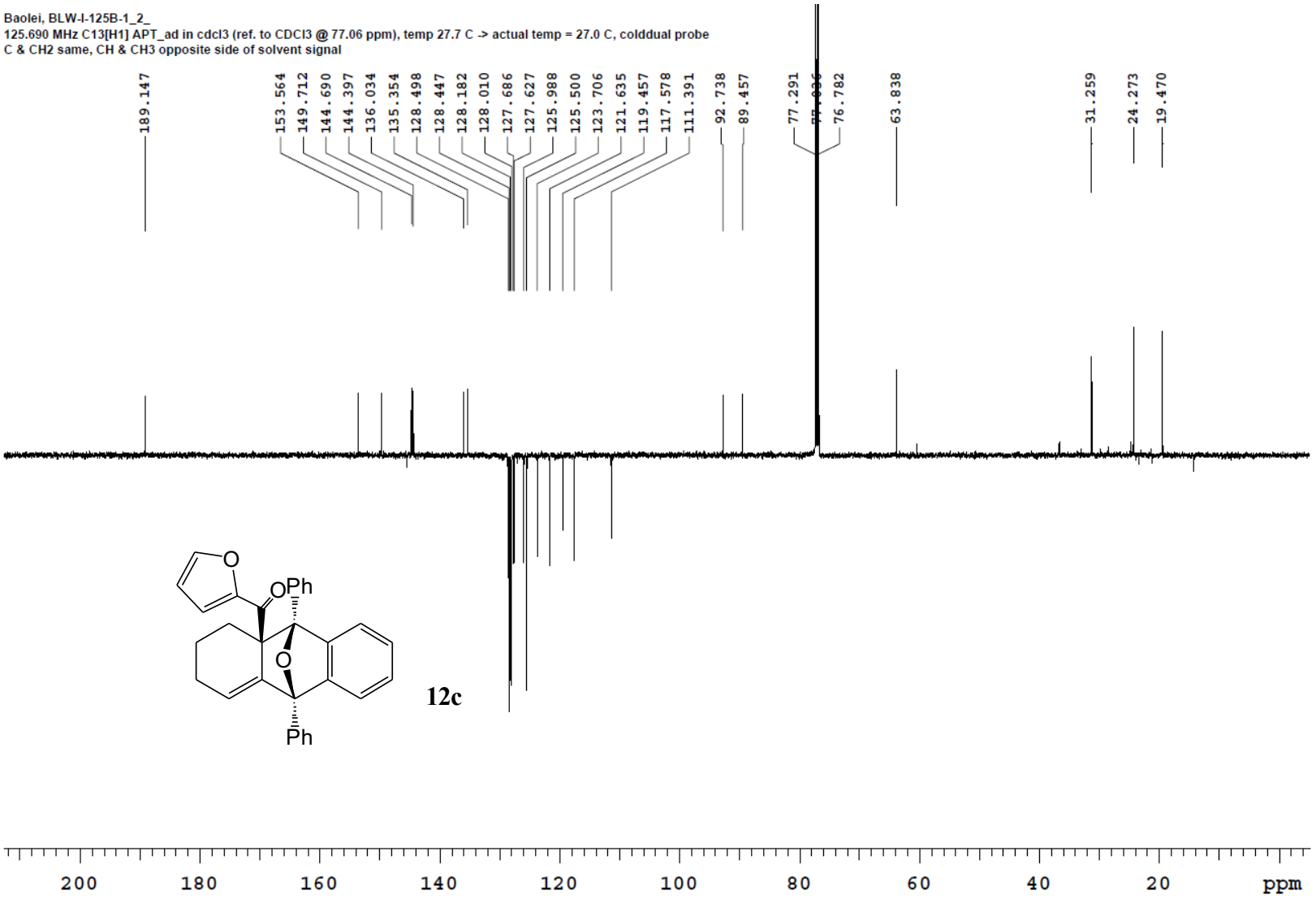


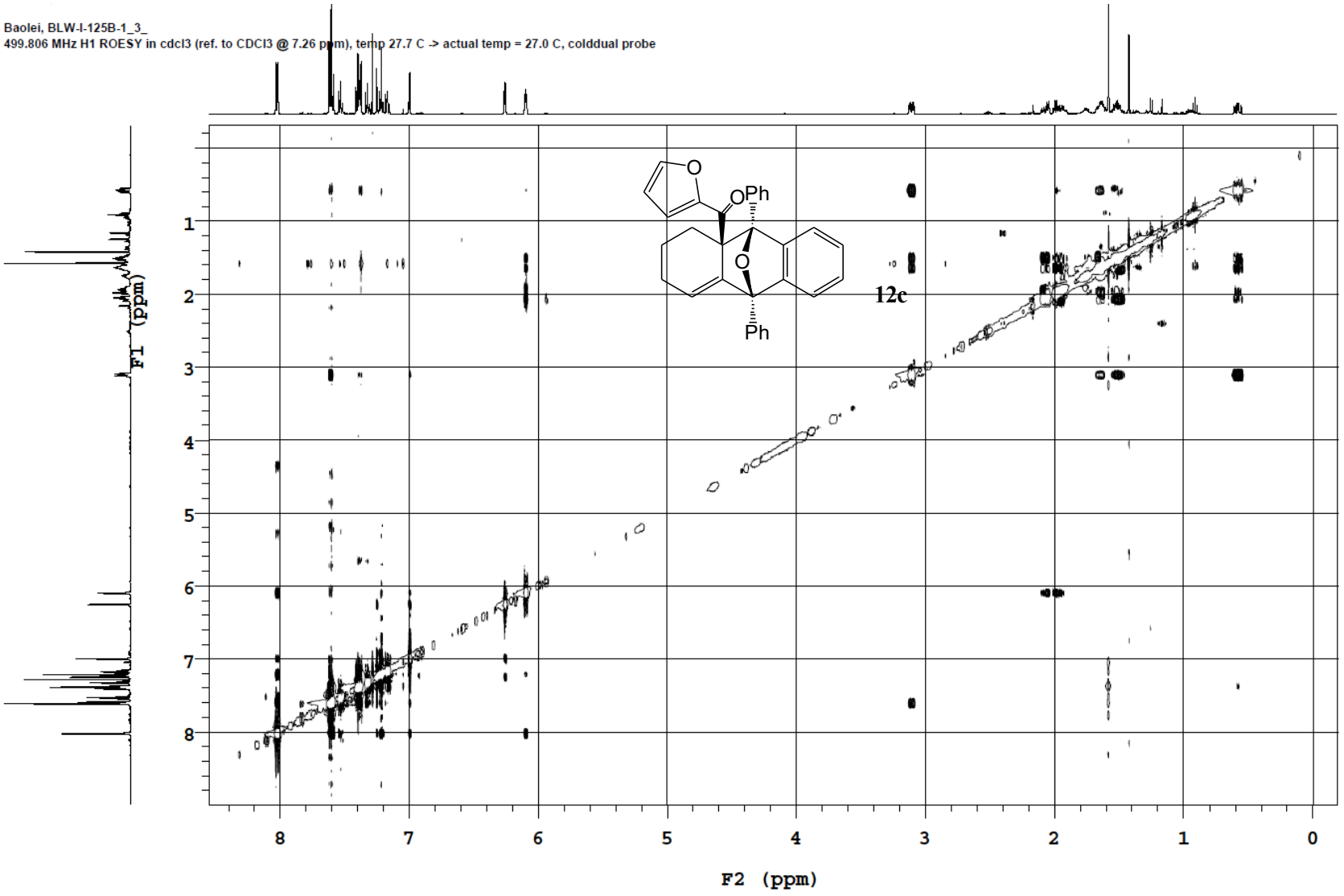

Baolei, BLW-I-121A-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
203.536
149.128
144.493
144.461
141.073
136.418
136.038
134.734
129.864
128.545
128.402
128.127
127.877
127.682
127.444
126.142
125.637
124.663
121.589
117.519
92.933
89.279
77.291
77.036
76.782
65.346
32.075
24.236
19.599
Cl
O
Ph
O
Ph
12b
200
180
160
140
120
100
80
60
40
20
ppm


Baolei, BLW-I-121A-1
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
Cl
OPh
O
Ph
12b
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8
9

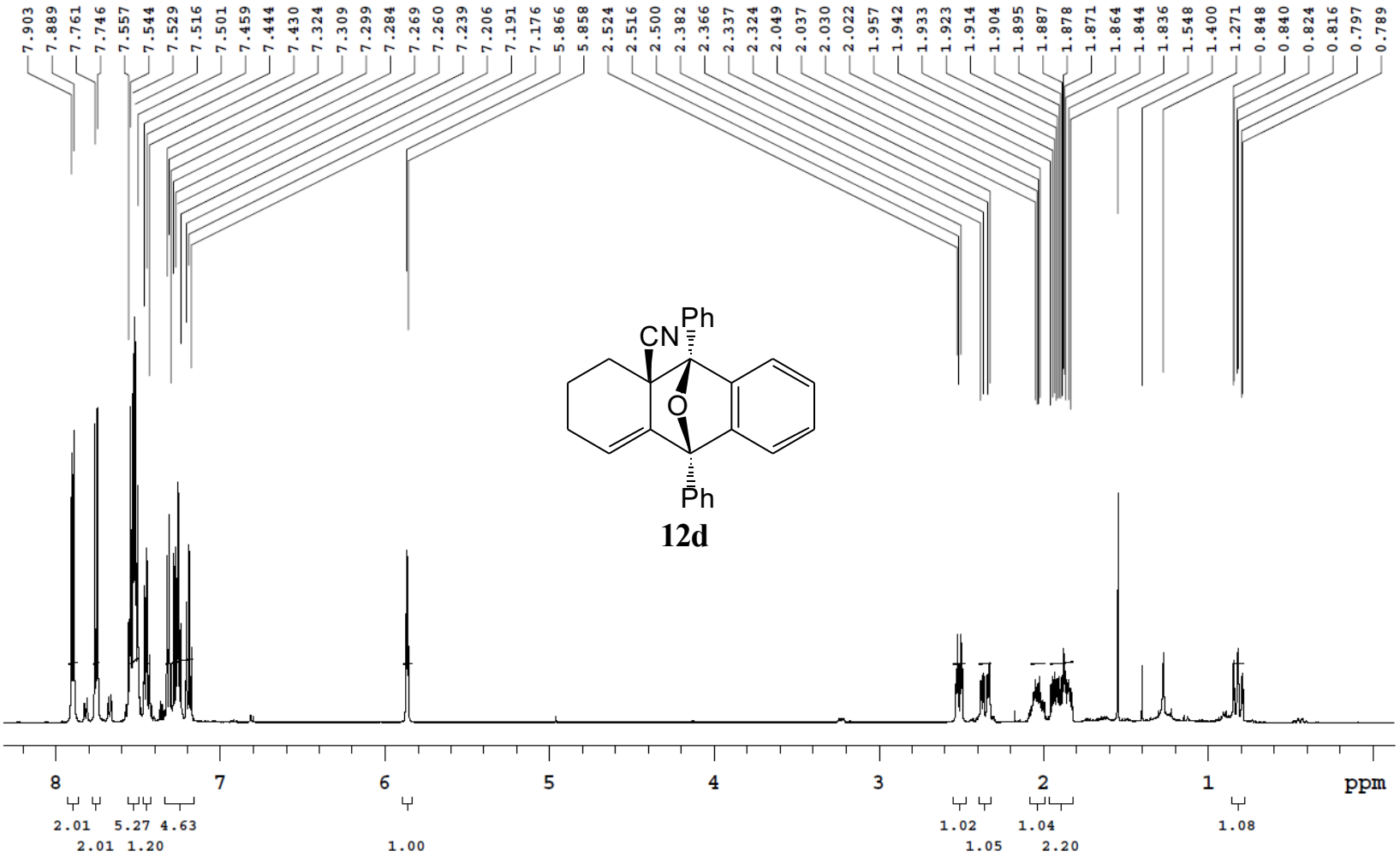
Baolei, BLW-I-125B-1_3_
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



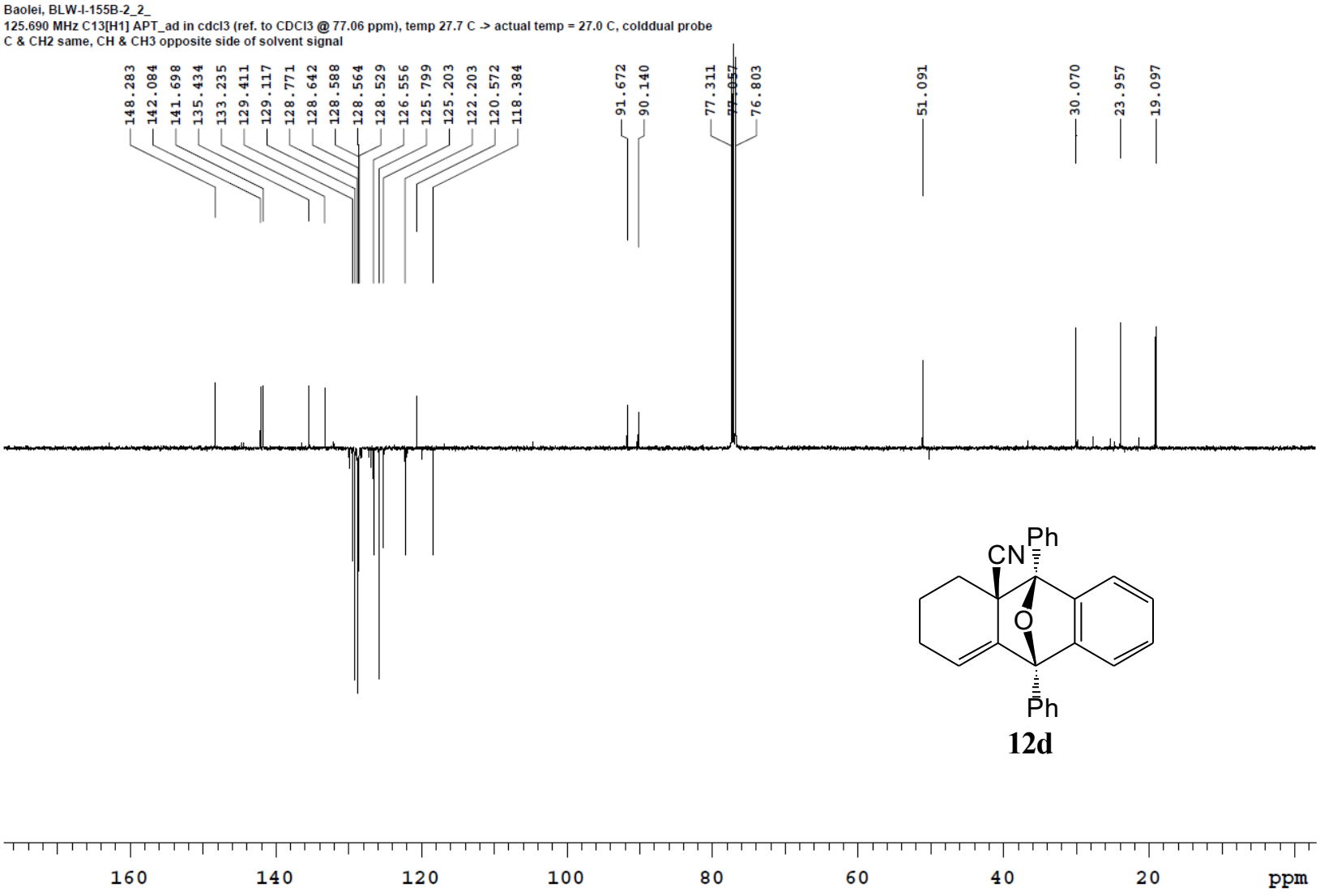

Baolei, BLW-I-125B-1_2_
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
189.147
153.564
149.712
144.690
144.397
136.034
135.354
128.498
128.447
128.182
128.010
127.686
127.627
125.988
125.500
123.706
121.635
119.457
117.578
111.391
92.738
89.457
77.291
76.782
63.838
31.259
24.273
19.470
O
OPh
O
Ph
12c
200
180
160
140
120
100
80
60
40
20
ppm


Baolei, BLW-I-125B-1_3_
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
O
OPh
O
Ph
12c
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8
0

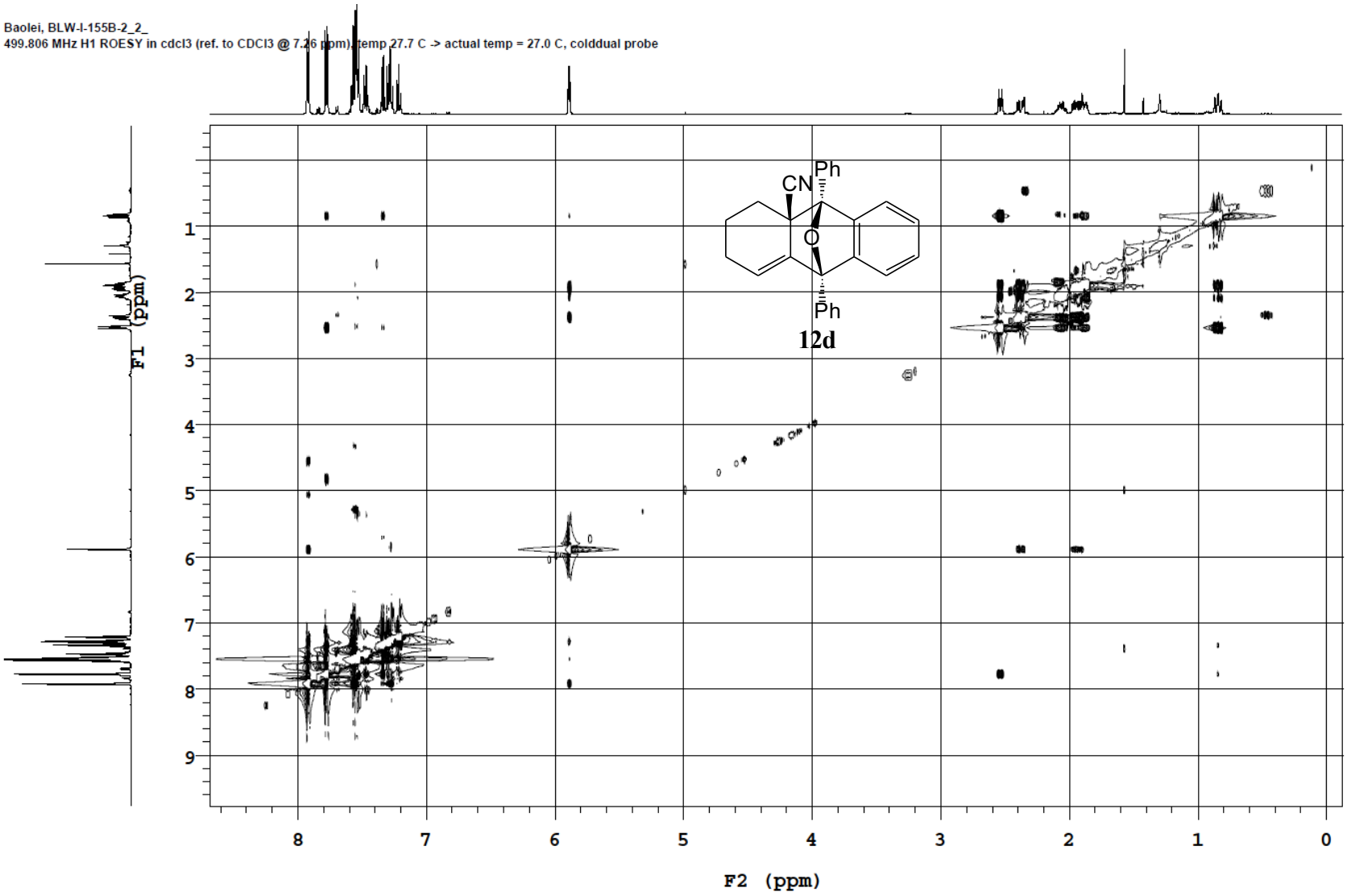
Baolei, BLW-I-155B-2_2_
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



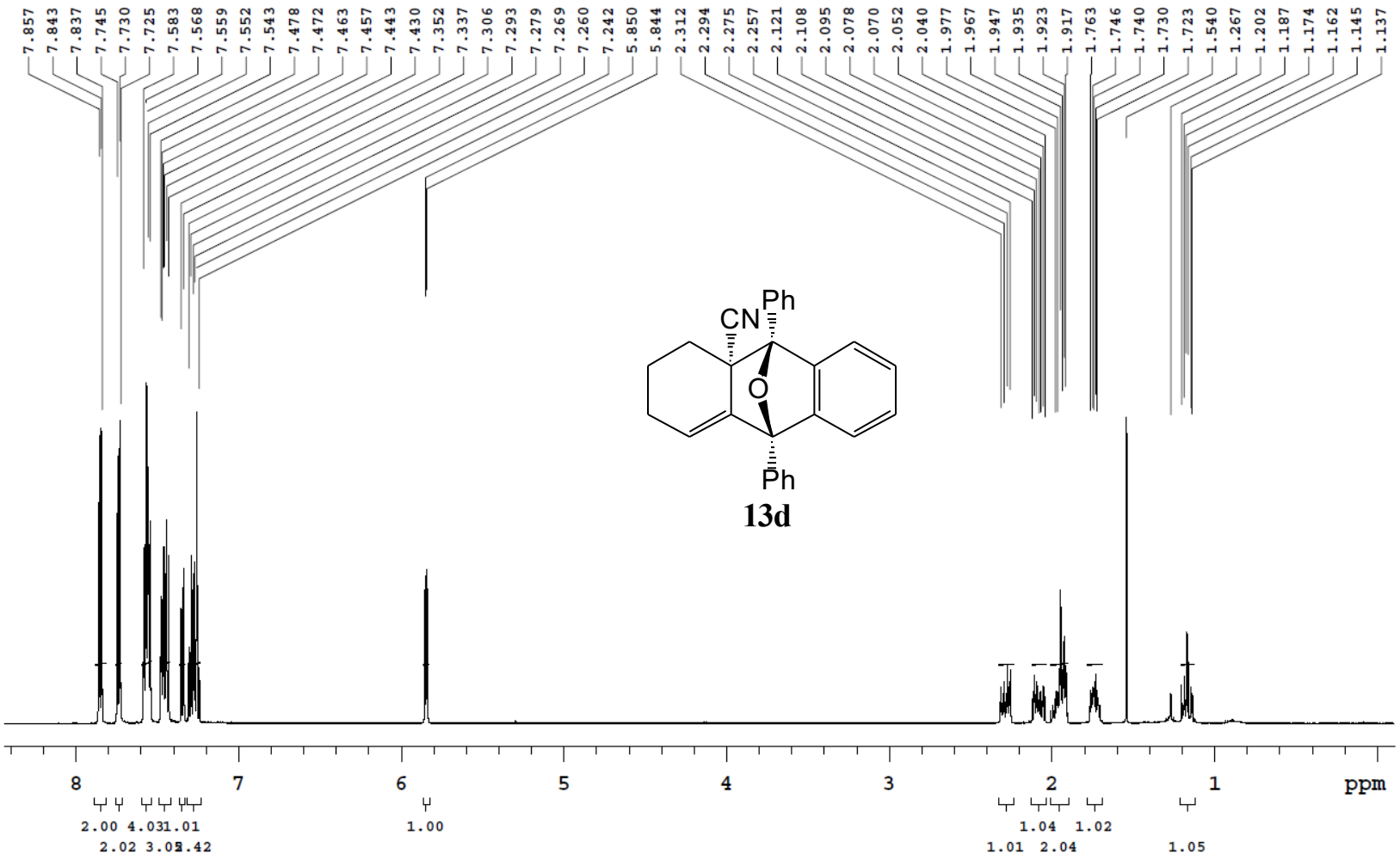
12d


Baolei, BLW-I-155B-2_2_
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
148.283
142.084
141.698
135.434
133.235
129.411
129.117
128.771
128.642
128.588
128.564
128.529
126.556
125.799
125.203
122.203
120.572
118.384
91.672
90.140
77.311
77.057
76.803
51.091
30.070
23.957
19.097
CN
Ph
O
Ph
160
140
120
100
80
60
40
20
ppm

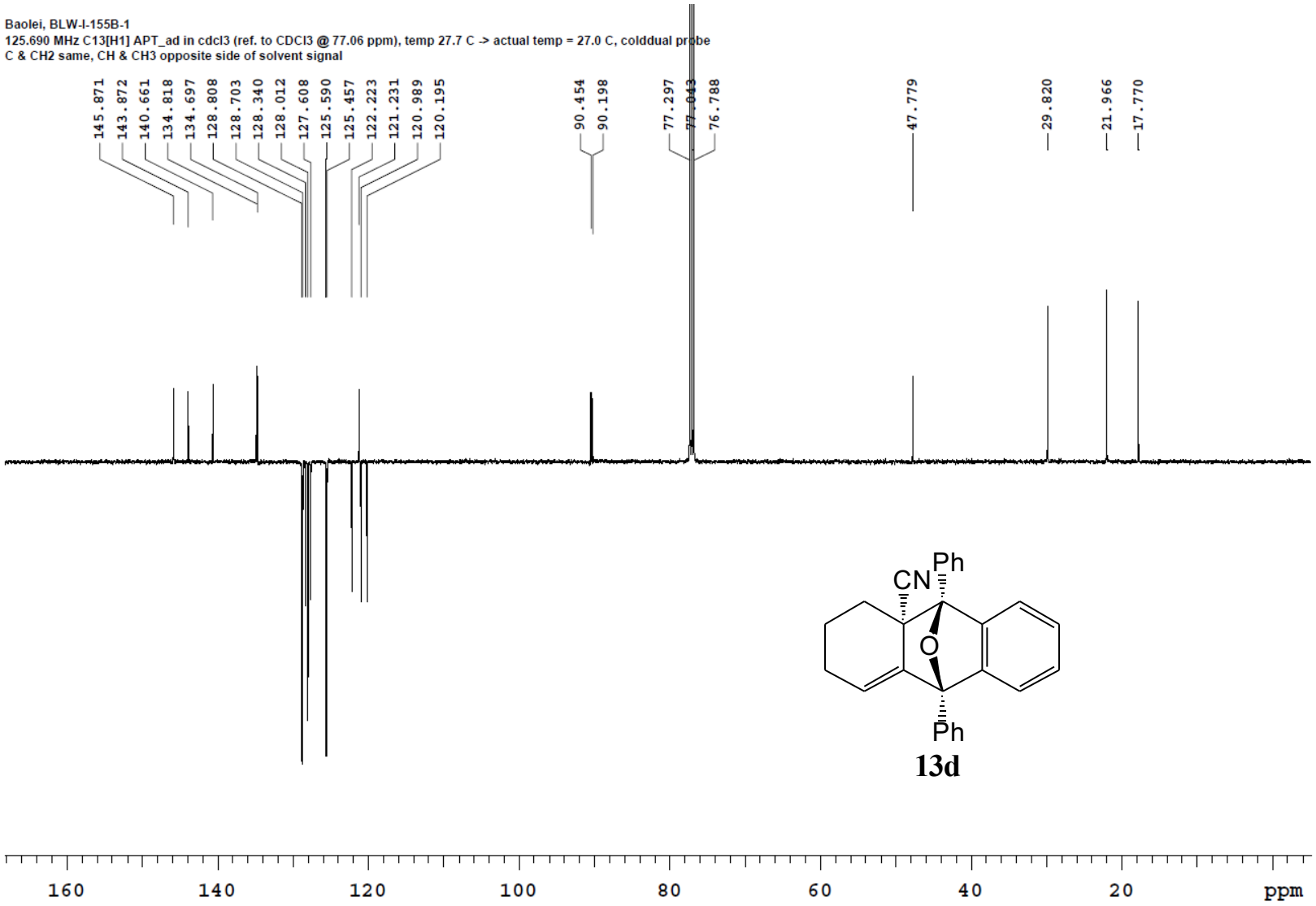
12d


Baolei, BLW-I-155B-2_2_
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
CN
Ph
O
Ph
12d
F1 (ppm)
F2 (ppm)
1
2
3
4
5
6
7
8
9
0

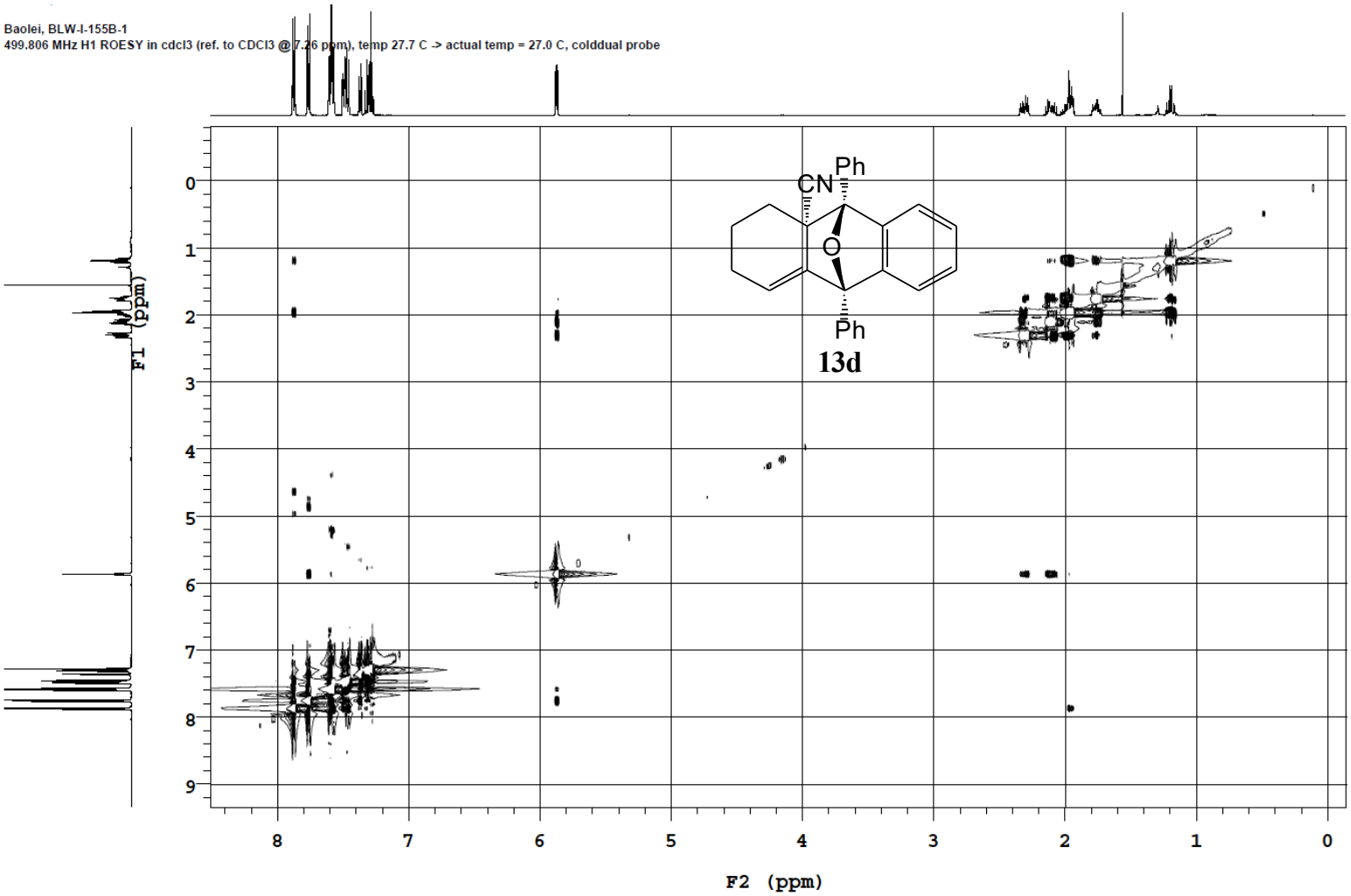
Baolei, BLW-I-155B-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

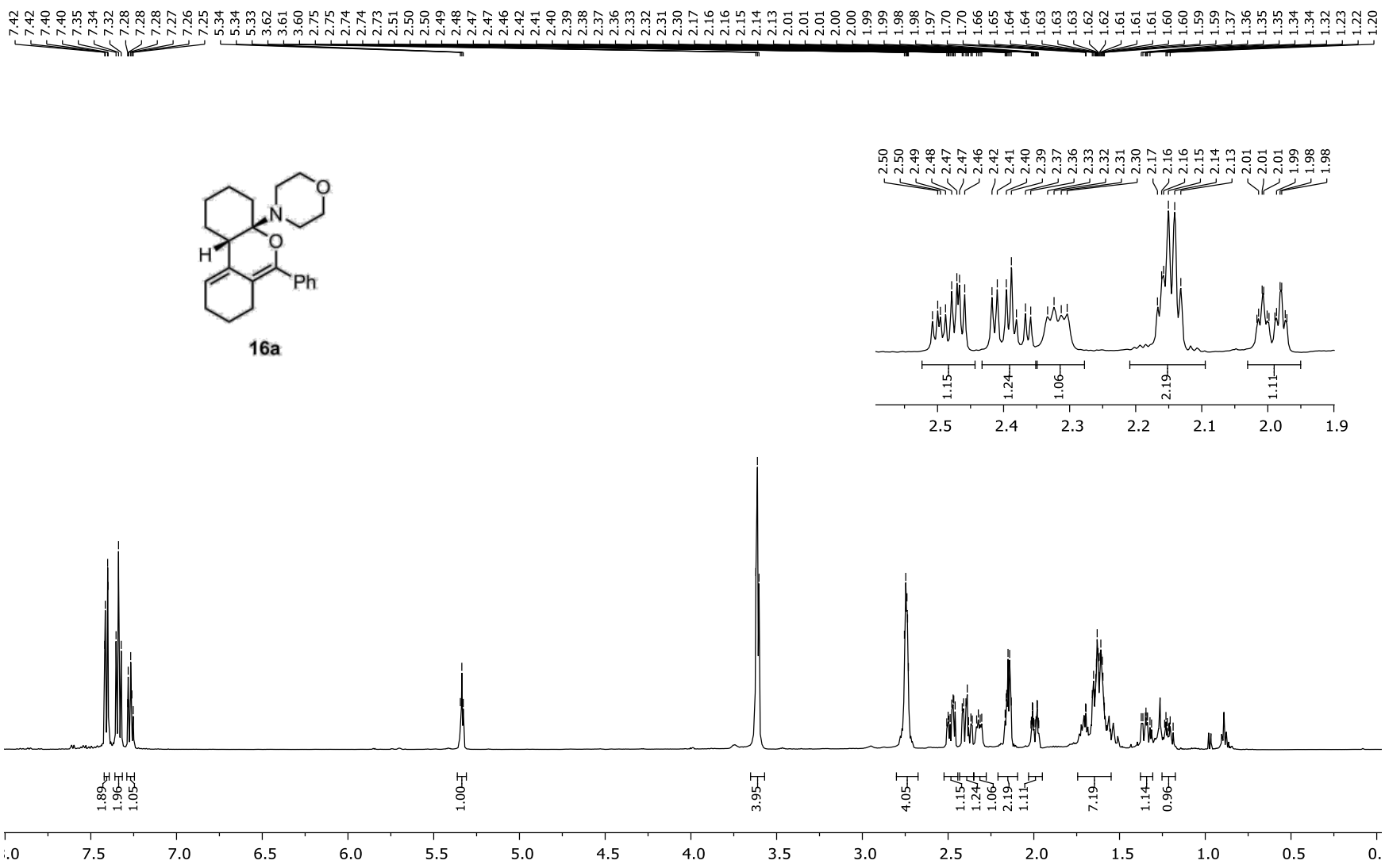


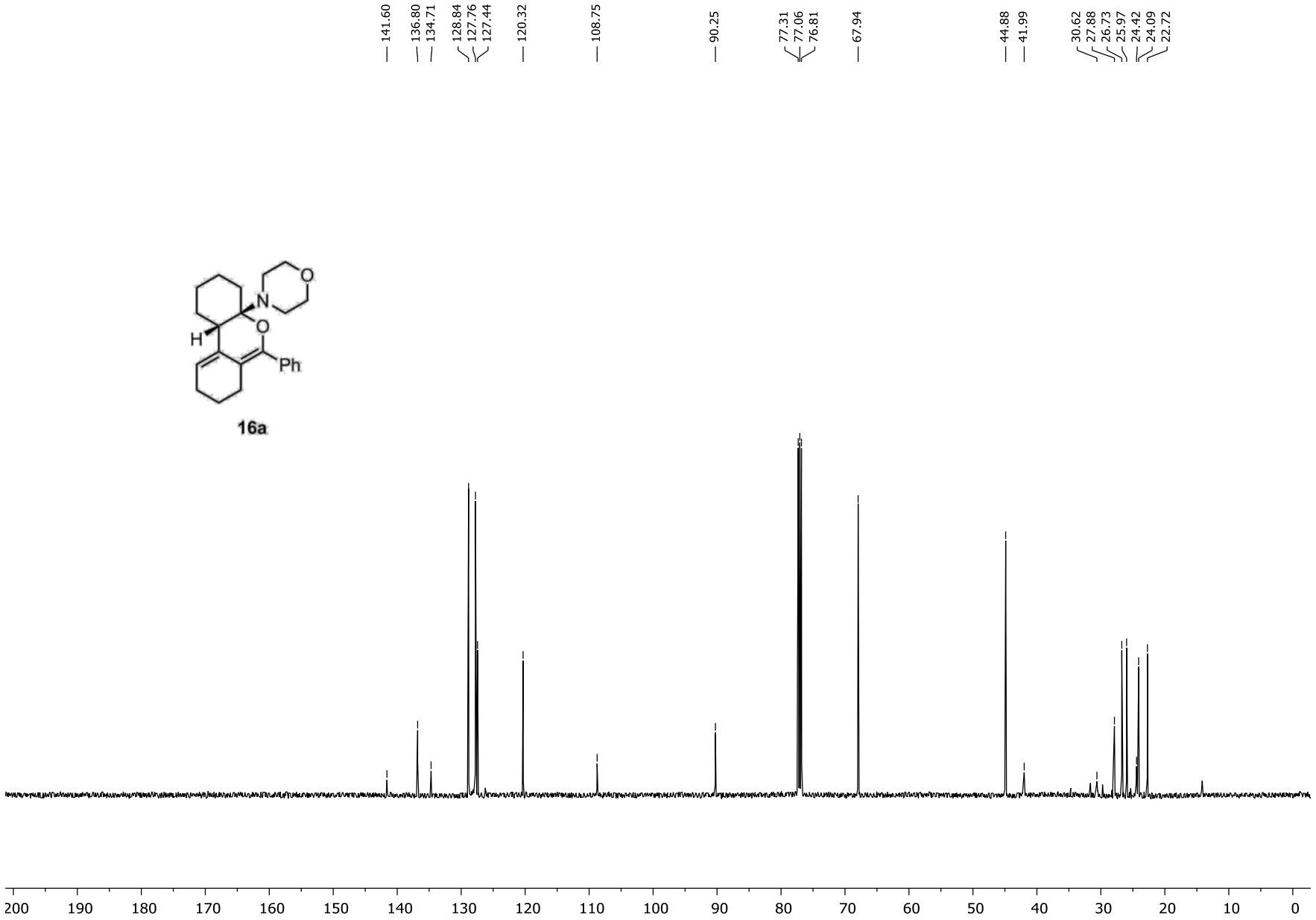
13d

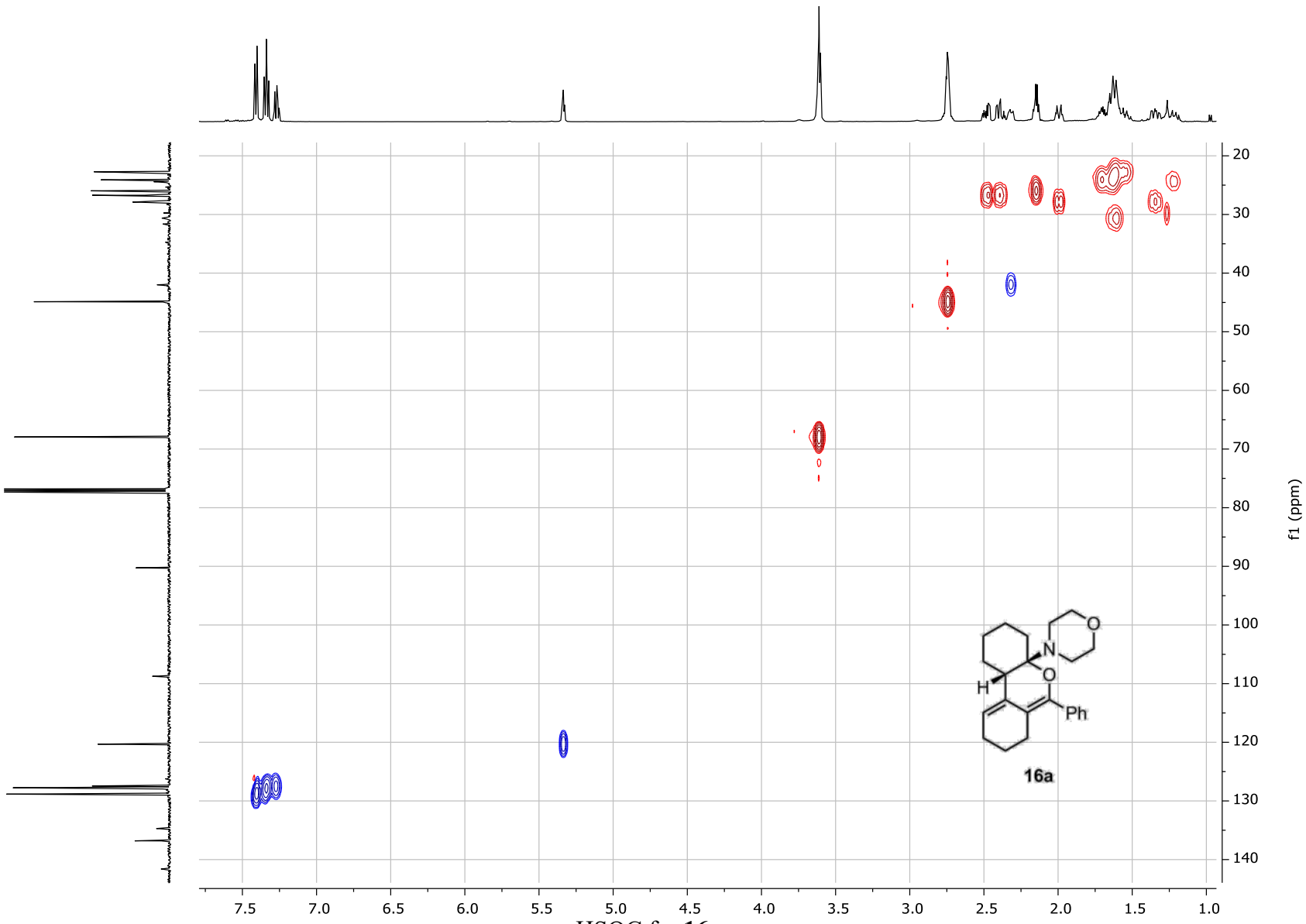

Baolei, BLW-I-155B-1
125.690 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
145.871
143.872
140.661
134.818
134.697
128.808
128.703
128.340
128.012
127.608
125.590
125.457
122.223
121.231
120.989
120.195
90.454
90.198
77.297
77.043
76.788
47.779
29.820
21.966
17.770
CN
Ph
O
Ph
160
140
120
100
80
60
40
20
ppm

13d


Baolei, BLW-I-155B-1
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
CN
Ph
O
Ph
13d
F1 (ppm)
F2 (ppm)
0
1
2
3
4
5
6
7
8
9
8
7
6
5
4
3
2
1
0


7.42 7.42 7.40 7.40 7.35 7.34 7.32 7.28 7.28 7.28 7.27 7.26 7.25
5.34 5.34 5.33 3.62 3.61 3.60 2.75 2.75 2.74 2.74 2.73 2.51 2.50 2.50 2.49 2.48 2.47 2.47 2.46 2.42 2.41 2.40 2.39 2.38 2.37 2.36 2.33 2.32 2.31 2.30 2.17 2.16 2.16 2.15 2.14 2.13 2.01 2.01 2.01 2.00 2.00 1.99 1.99 1.98 1.98 1.97 1.70 1.70 1.66 1.65 1.64 1.64 1.63 1.63 1.63 1.62 1.62 1.61 1.61 1.61 1.60 1.60 1.59 1.59 1.37 1.36 1.35 1.35 1.34 1.34 1.32 1.23 1.22 1.20
O
N
H
O
Ph
16a
2.50 2.50 2.49 2.48 2.47 2.47 2.46 2.42 2.41 2.40 2.39 2.37 2.36 2.33 2.32 2.31 2.30 2.17 2.16 2.16 2.15 2.14 2.13 2.01 2.01 2.01 1.99 1.98 1.98
1.15 1.24 1.06 2.19 1.11
2.5 2.4 2.3 2.2 2.1 2.0 1.9
1.89 1.96 1.05 1.00 3.95 4.05 1.15 1.24 1.06 2.19 1.11 7.19 1.14 0.96
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


141.60
136.80
134.71
128.84
127.76
127.44
120.32
108.75
90.25
77.31
77.06
76.81
67.94
44.88
41.99
30.62
27.88
26.73
25.97
24.42
24.09
22.72
O
N
H
O
Ph
16a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
N
O
O
H
Ph
16a

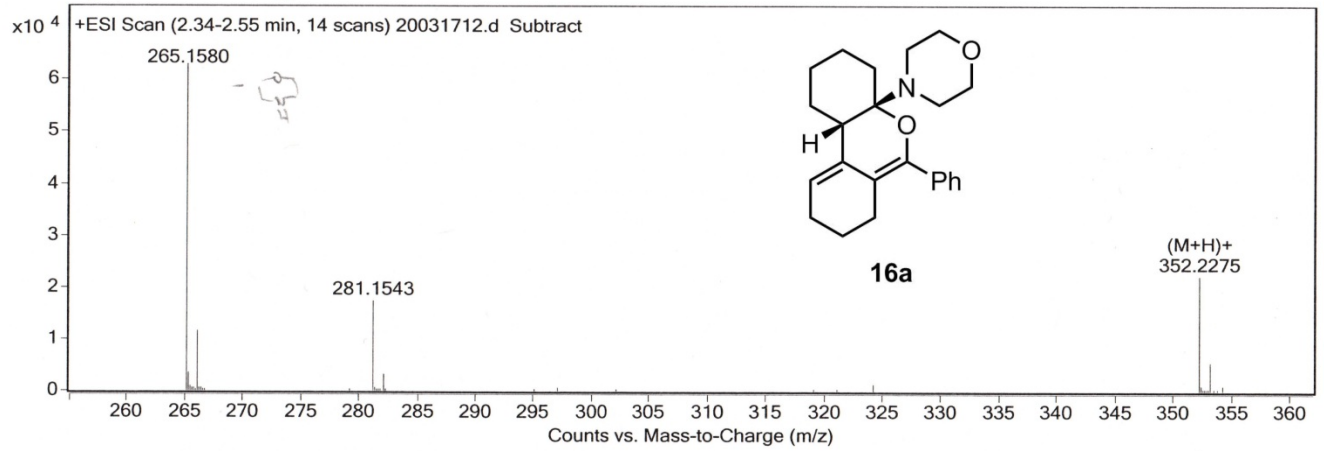
HSQC for **16a**

Department of Chemistry Mass Spectrometry Laboratory

Name	M. Constantin, West	**Sample Name**	cmi e1
Data Filename	20031712.d	**Instrument Name**	oaTOF6220
Position	-1	**Operator**	ami
Acq Method		**DA Method**	da ami low mass.m

User Spectra

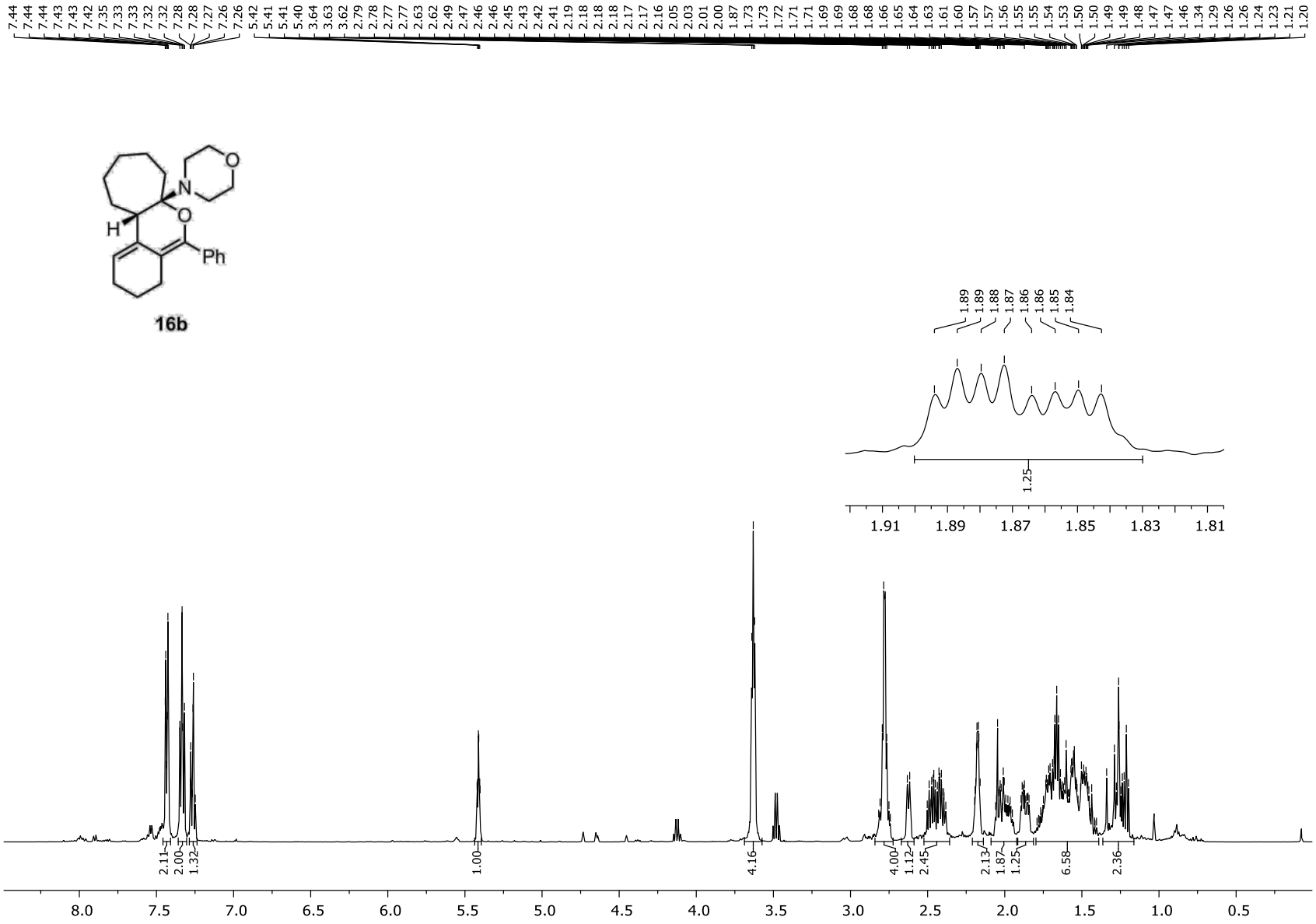
Fragmentor Voltage 0 **Source Type** Esi

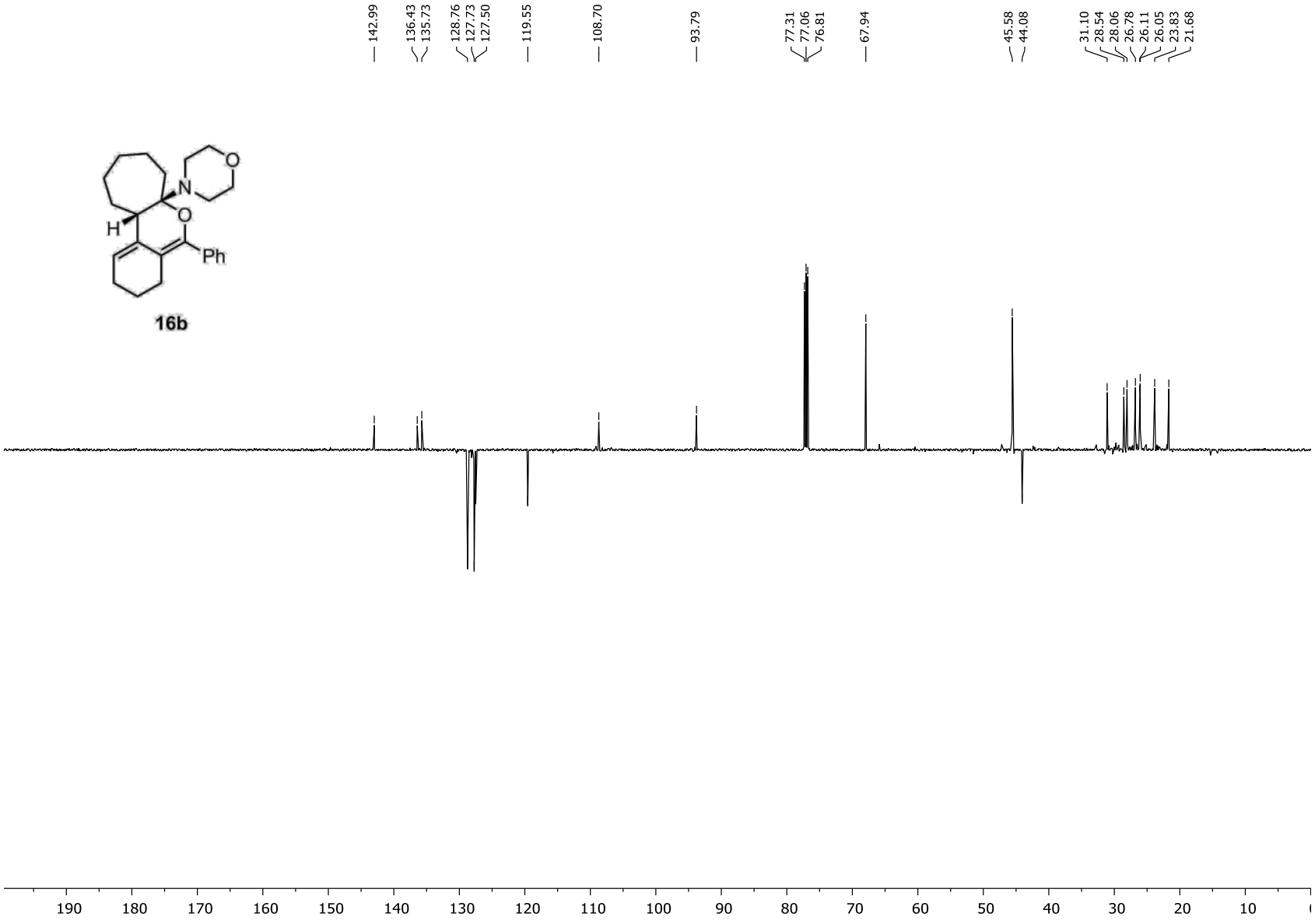


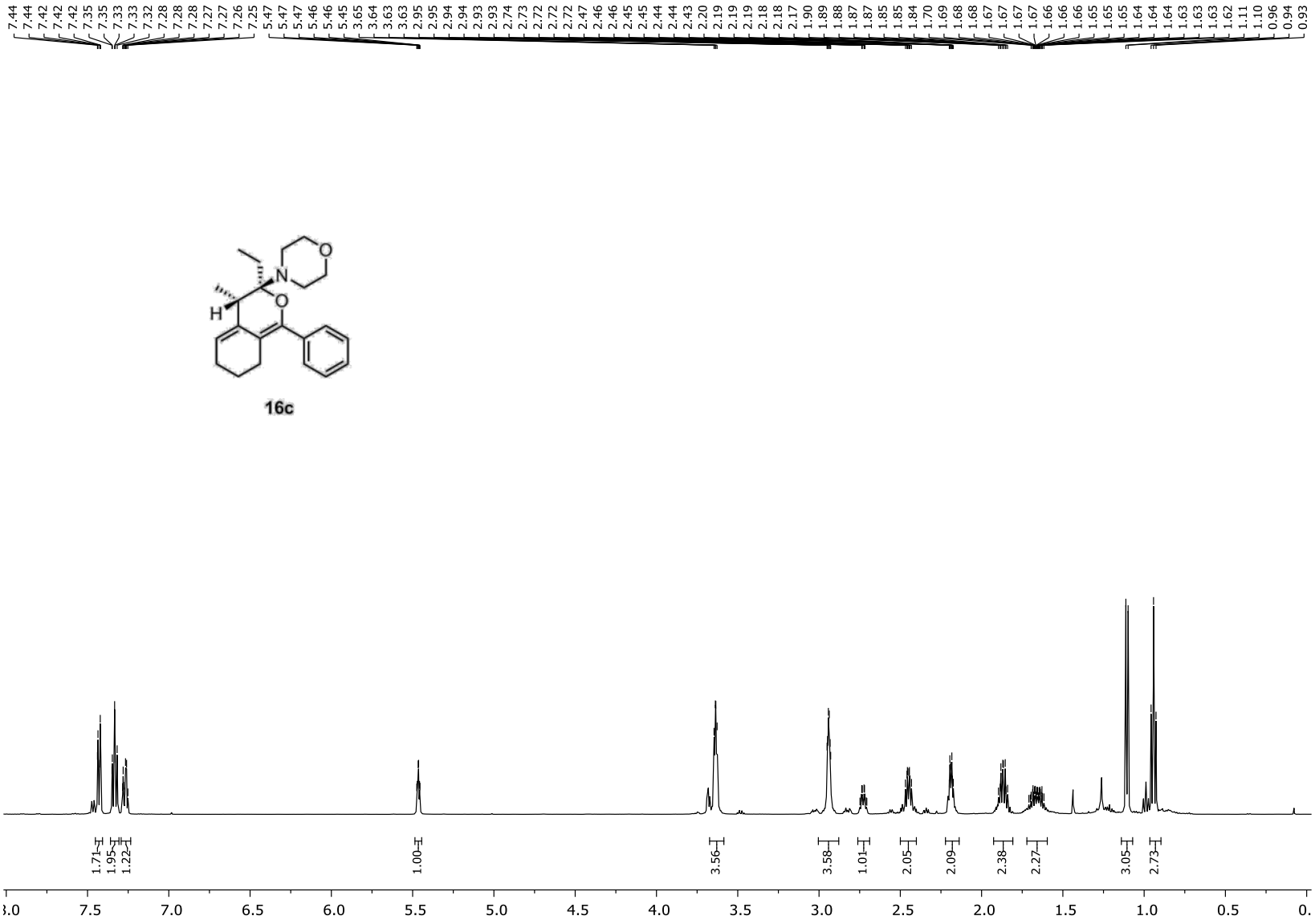
Formula Calculator Results

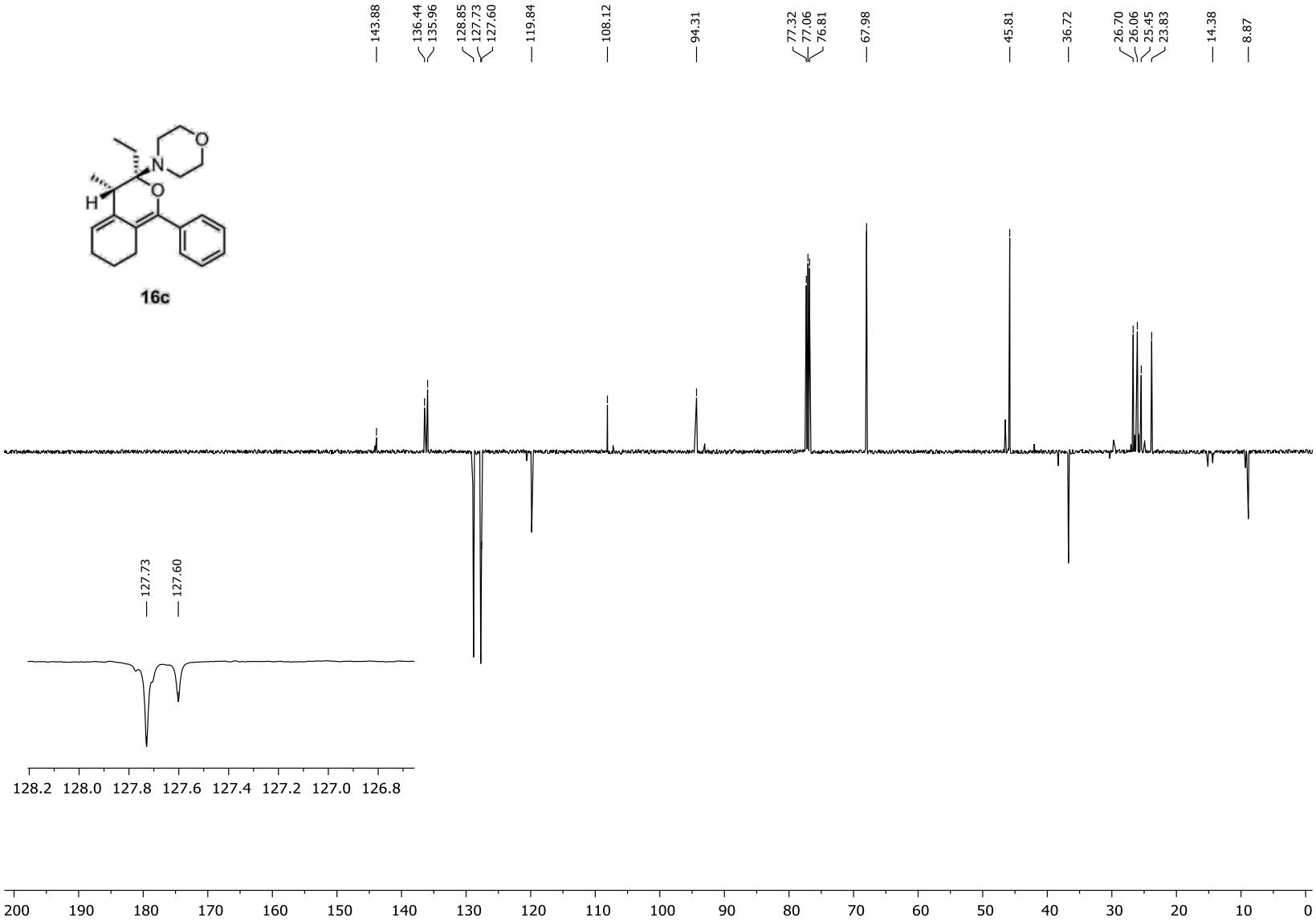
Formula	Ion Species	Mass	Calc. Mass	m/z	Calc. m/z	Diff (mDa)	Diff (ppm)	DBE	Ion	Score
C23 H29 N O2	C23 H30 N O2	351.2202	351.2198	352.2275	352.2271	-0.38	-1.08	10	(M+H)+	97.8

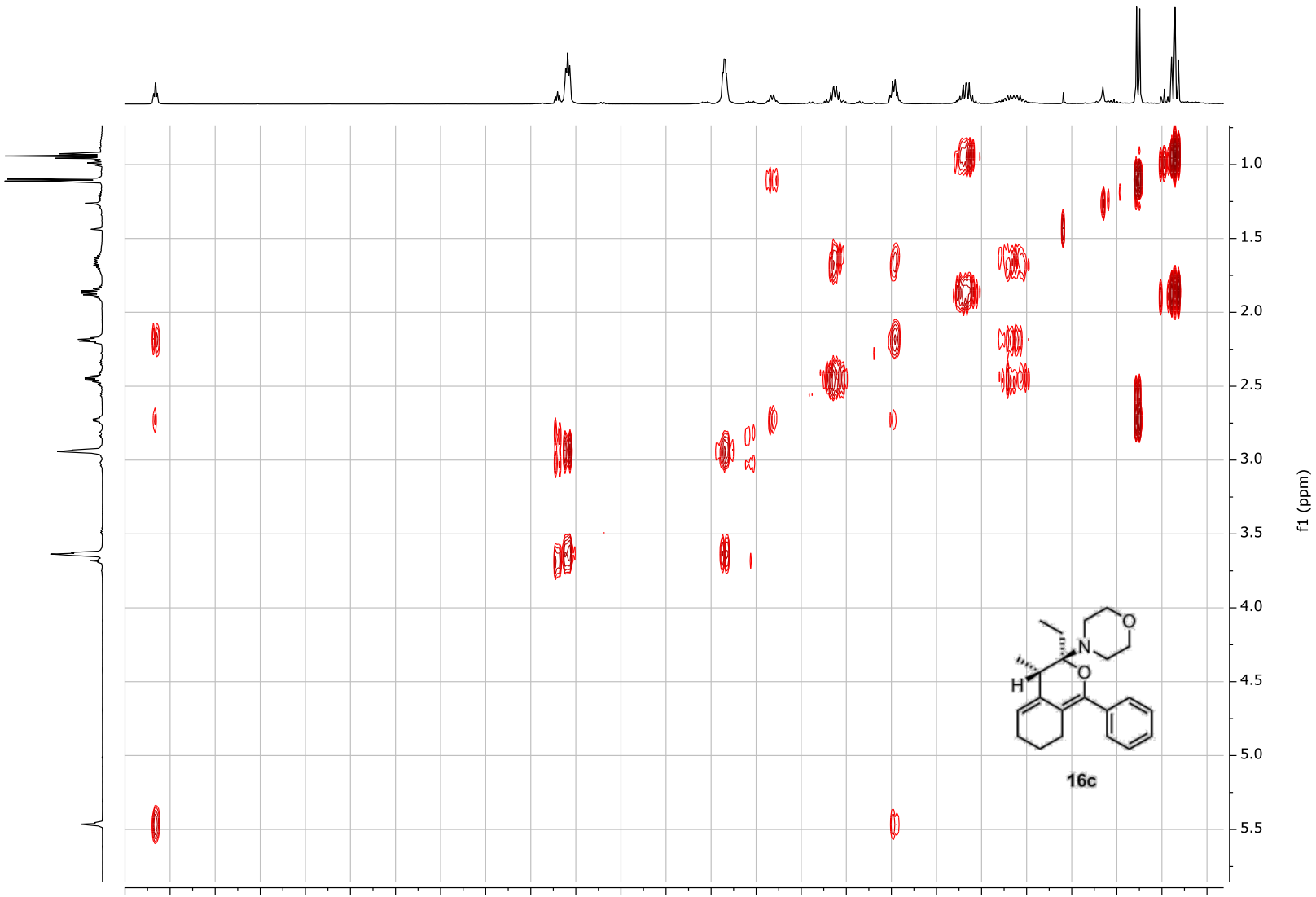
--- End Of Report ---


7.44 7.44 7.44 7.43 7.43 7.42 7.35 7.33 7.33 7.32 7.32 7.28 7.28 7.27 7.26 7.26 5.42 5.41 5.41 5.40 3.64 3.63 3.62 2.79 2.78 2.77 2.77 2.63 2.62 2.49 2.47 2.46 2.46 2.45 2.43 2.42 2.41 2.19 2.18 2.18 2.18 2.17 2.16 2.05 2.03 2.01 2.00 1.87 1.73 1.73 1.72 1.71 1.71 1.69 1.69 1.68 1.68 1.66 1.65 1.64 1.63 1.61 1.60 1.57 1.57 1.56 1.55 1.55 1.54 1.53 1.50 1.50 1.49 1.49 1.48 1.47 1.47 1.46 1.34 1.29 1.26 1.26 1.24 1.23 1.21 1.20
O
N
O
H
Ph
16b
1.89 1.89 1.88 1.87 1.86 1.86 1.85 1.84
1.25
1.91 1.89 1.87 1.85 1.83 1.81
2.11 2.00 1.32 1.00 4.16 4.00 1.12 2.45 2.13 1.87 1.25 6.58 2.36
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

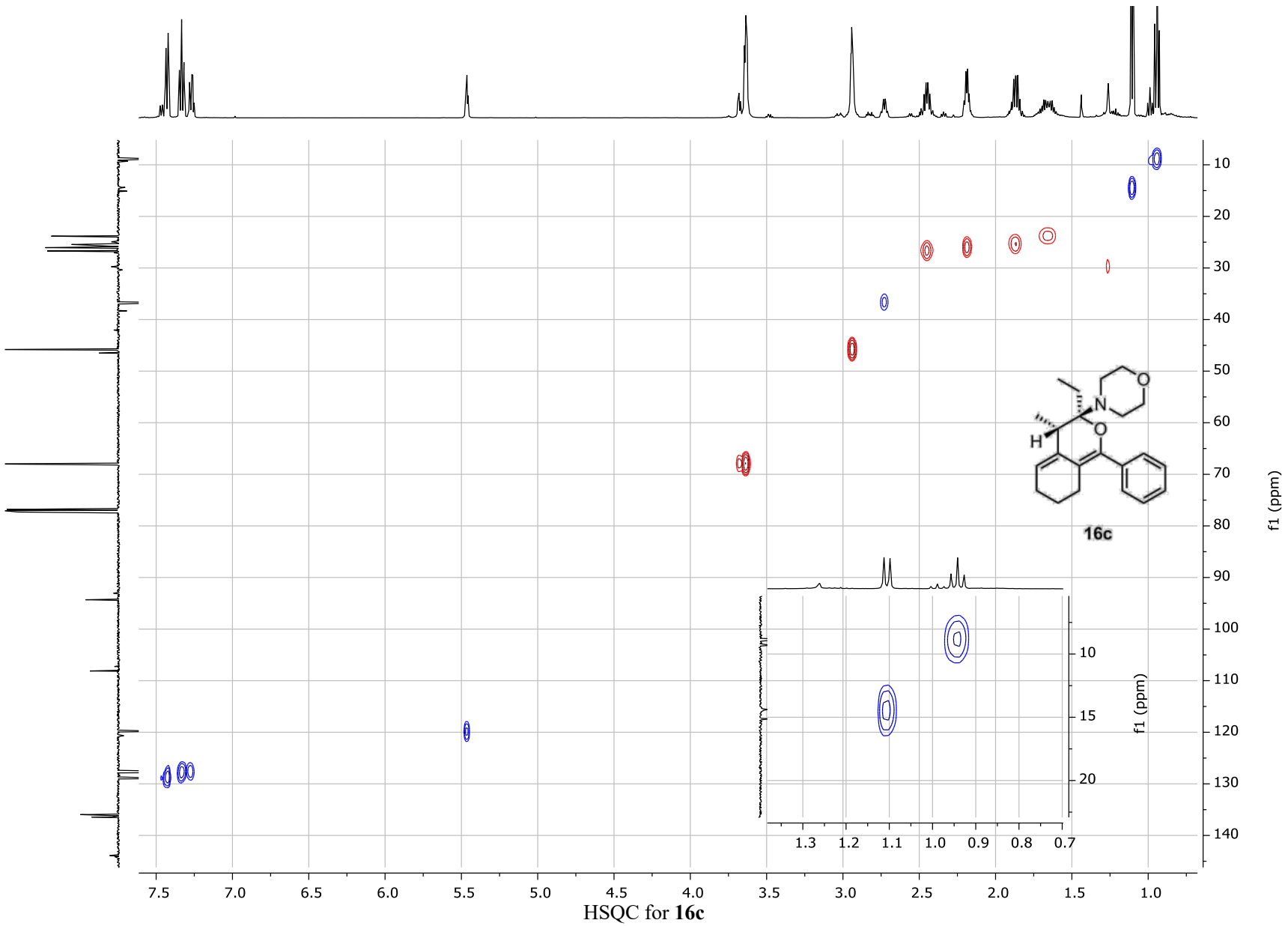

142.99
136.43
135.73
128.76
127.73
127.50
119.55
108.70
93.79
77.31
77.06
76.81
67.94
45.58
44.08
31.10
28.54
28.06
26.78
26.11
26.05
23.83
21.68
O
N
O
H
Ph
16b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.44 7.44 7.42 7.42 7.42 7.35 7.35 7.33 7.33 7.32 7.28 7.28 7.28 7.27 7.27 7.26 7.25 5.47 5.47 5.46 5.46 5.45 3.65 3.64 3.63 3.63 2.95 2.95 2.94 2.93 2.93 2.74 2.73 2.72 2.72 2.47 2.46 2.46 2.45 2.44 2.44 2.43 2.20 2.19 2.19 2.18 2.17 1.90 1.89 1.88 1.87 1.87 1.85 1.85 1.84 1.70 1.69 1.68 1.68 1.67 1.67 1.67 1.67 1.66 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.64 1.63 1.63 1.63 1.62 1.11 1.10 0.96 0.94 0.93
O
N
O
H
16c
1.71
1.95
1.22
1.00
3.56
3.58
1.01
2.05
2.09
2.38
2.27
3.05
2.73
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

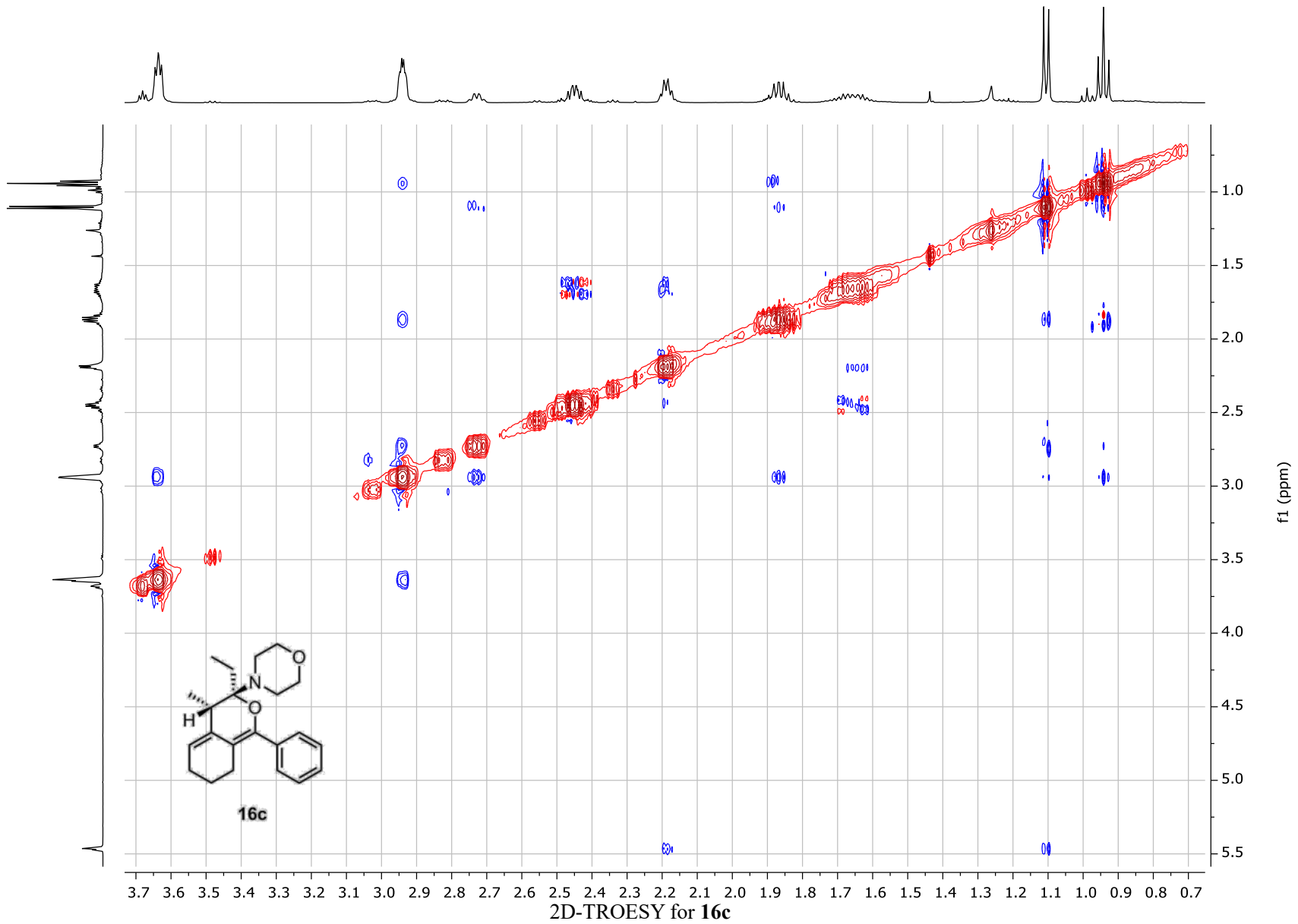

143.88
136.44
135.96
128.85
127.73
127.60
119.84
108.12
94.31
77.32
77.06
76.81
67.98
45.81
36.72
26.70
26.06
25.45
23.83
14.38
8.87
16c
127.73
127.60
128.2 128.0 127.8 127.6 127.4 127.2 127.0 126.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)
O
N
O
H
16c

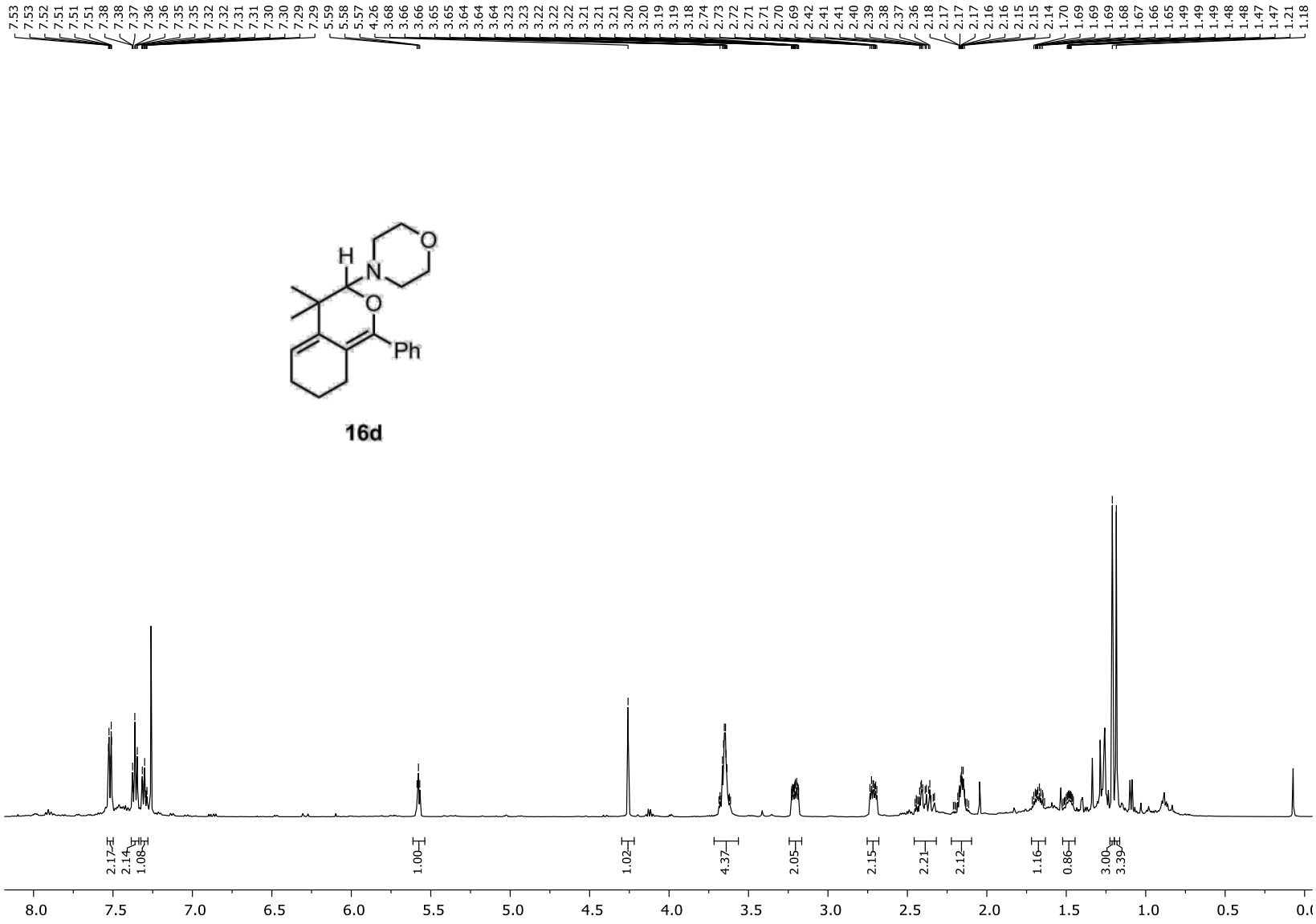
COSY for **16c**

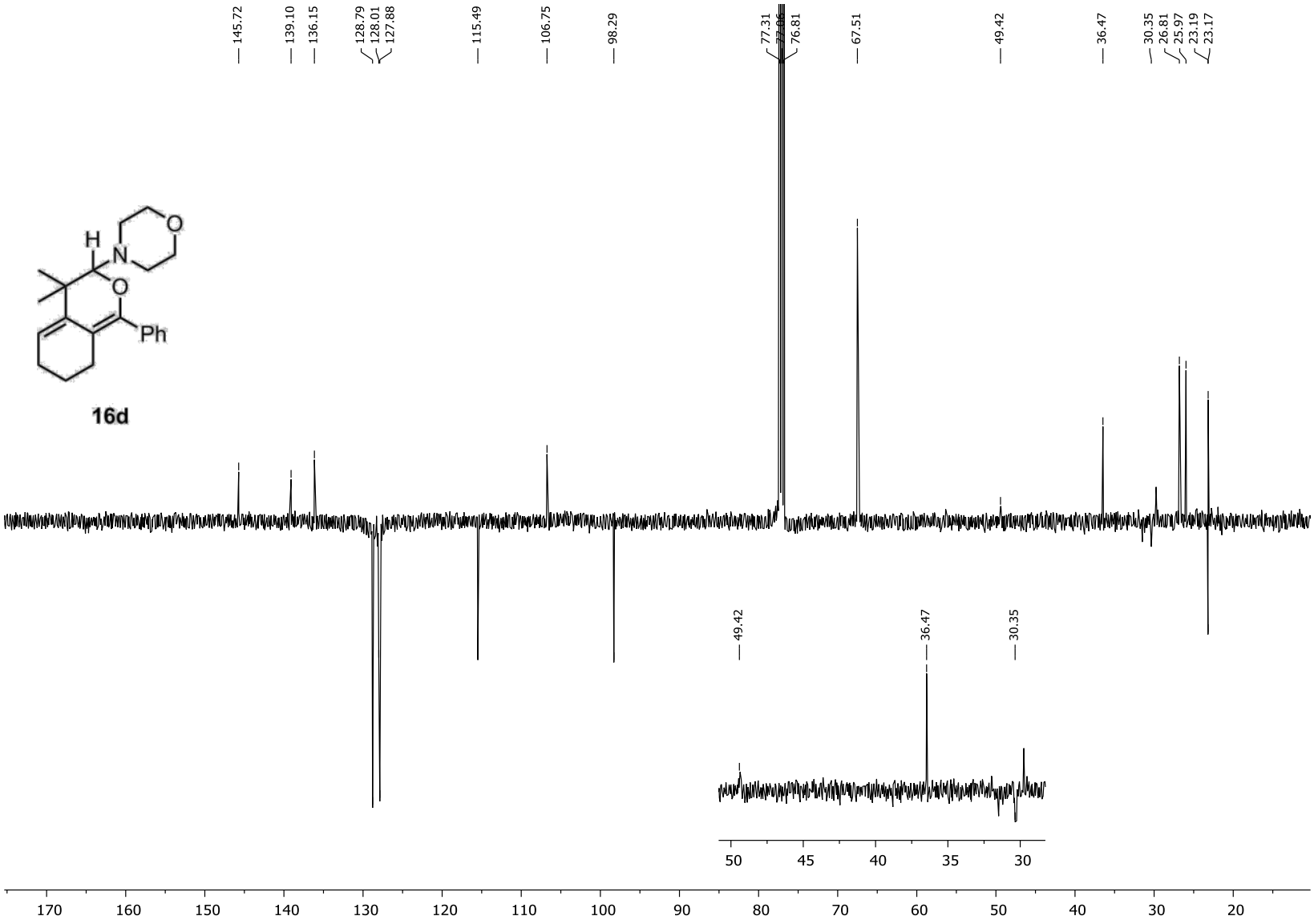


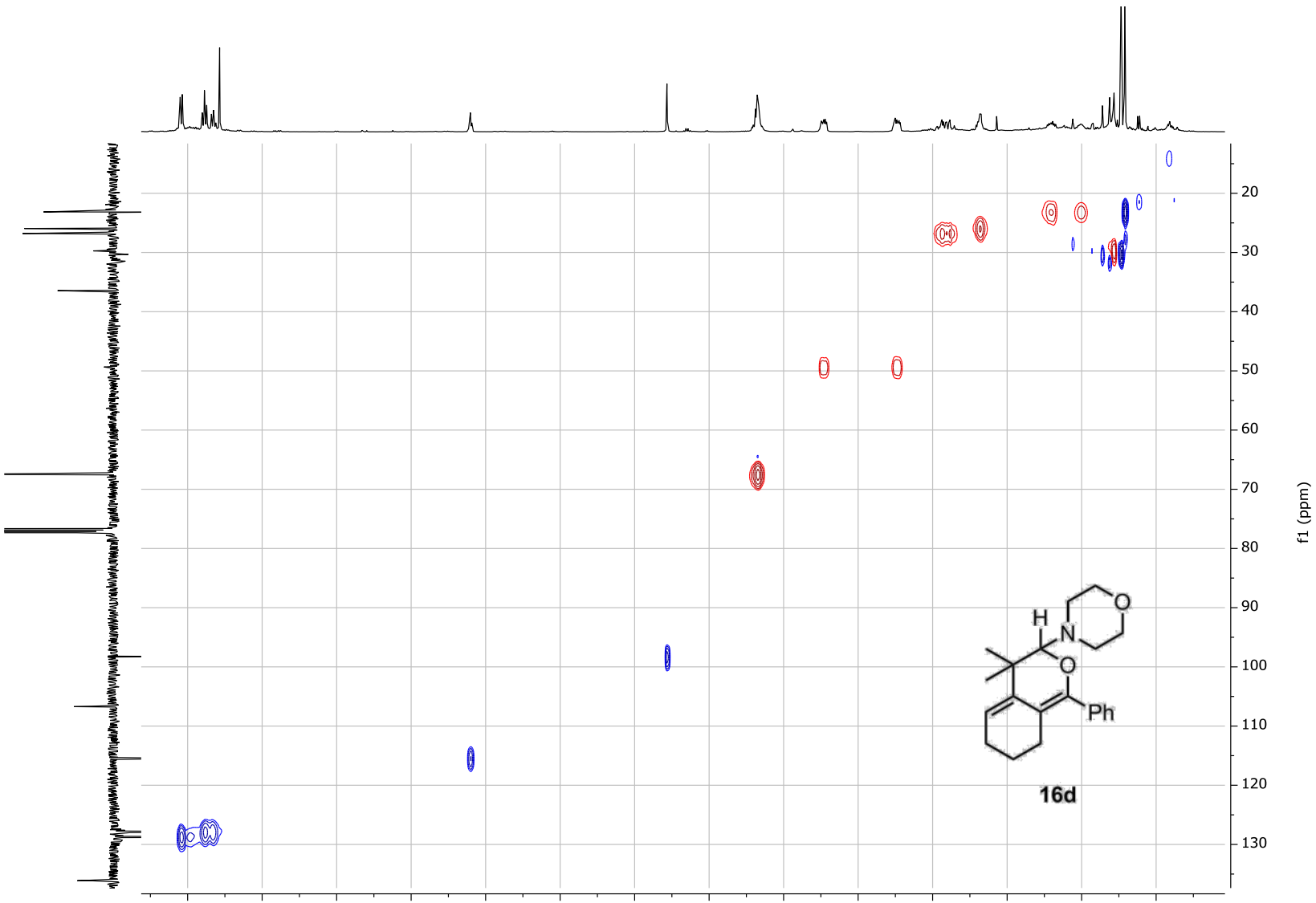
HSQC for **16c**



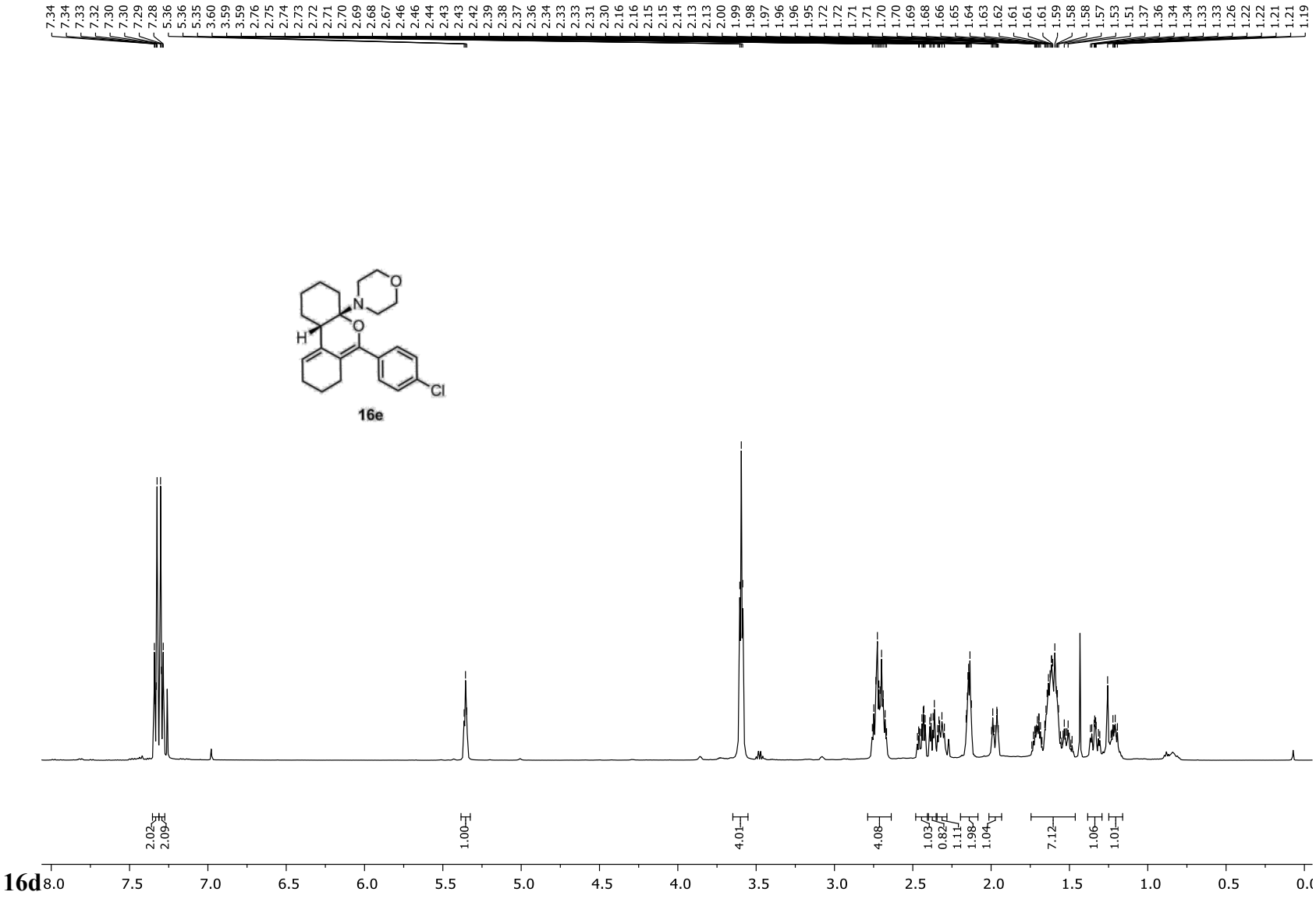
2D-TROESY for **16c**


7.53 7.53 7.52 7.51 7.51 7.51 7.51 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29
5.59 5.58 5.57 4.26 3.68 3.66 3.66 3.65 3.65 3.64 3.64 3.64 3.23 3.23 3.22 3.22 3.22 3.21 3.21 3.21 3.20 3.20 3.19 3.19 3.18 2.74 2.73 2.72 2.71 2.71 2.70 2.69 2.42 2.41 2.41 2.40 2.39 2.38 2.37 2.36 2.18 2.17 2.17 2.17 2.16 2.16 2.15 2.15 2.14 1.70 1.69 1.69 1.69 1.68 1.67 1.66 1.65 1.49 1.49 1.49 1.48 1.48 1.47 1.47 1.21 1.18
H
N
O
O
Ph
16d
2.17
2.14
1.08
1.00
1.02
4.37
2.05
2.15
2.21
2.12
1.16
0.86
3.00
3.39
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

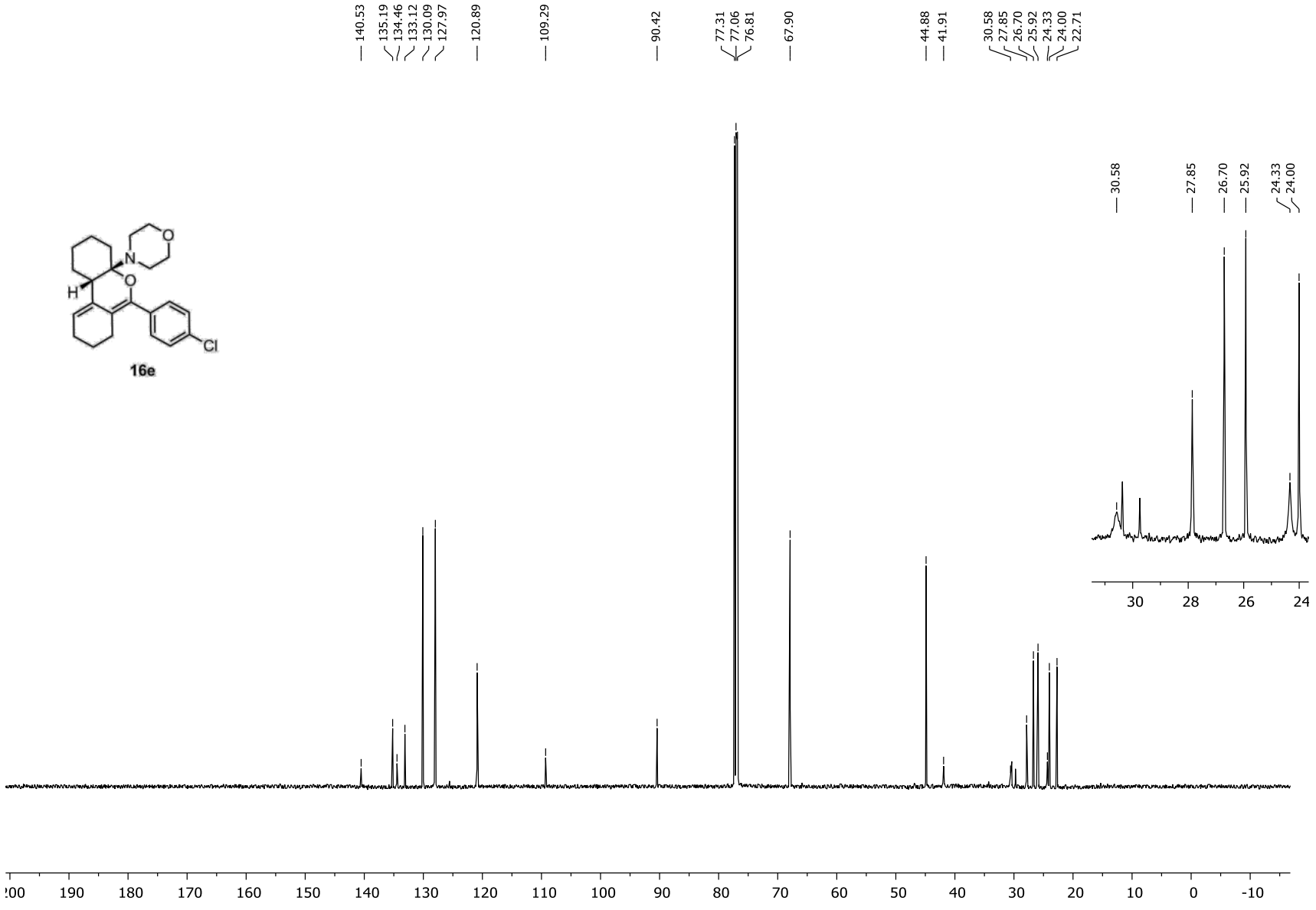

145.72
139.10
136.15
128.79
128.01
127.88
115.49
106.75
98.29
77.31
77.06
76.81
67.51
49.42
36.47
30.35
26.81
25.97
23.19
23.17
H
N
O
O
Ph
16d
49.42
36.47
30.35
50
45
40
35
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

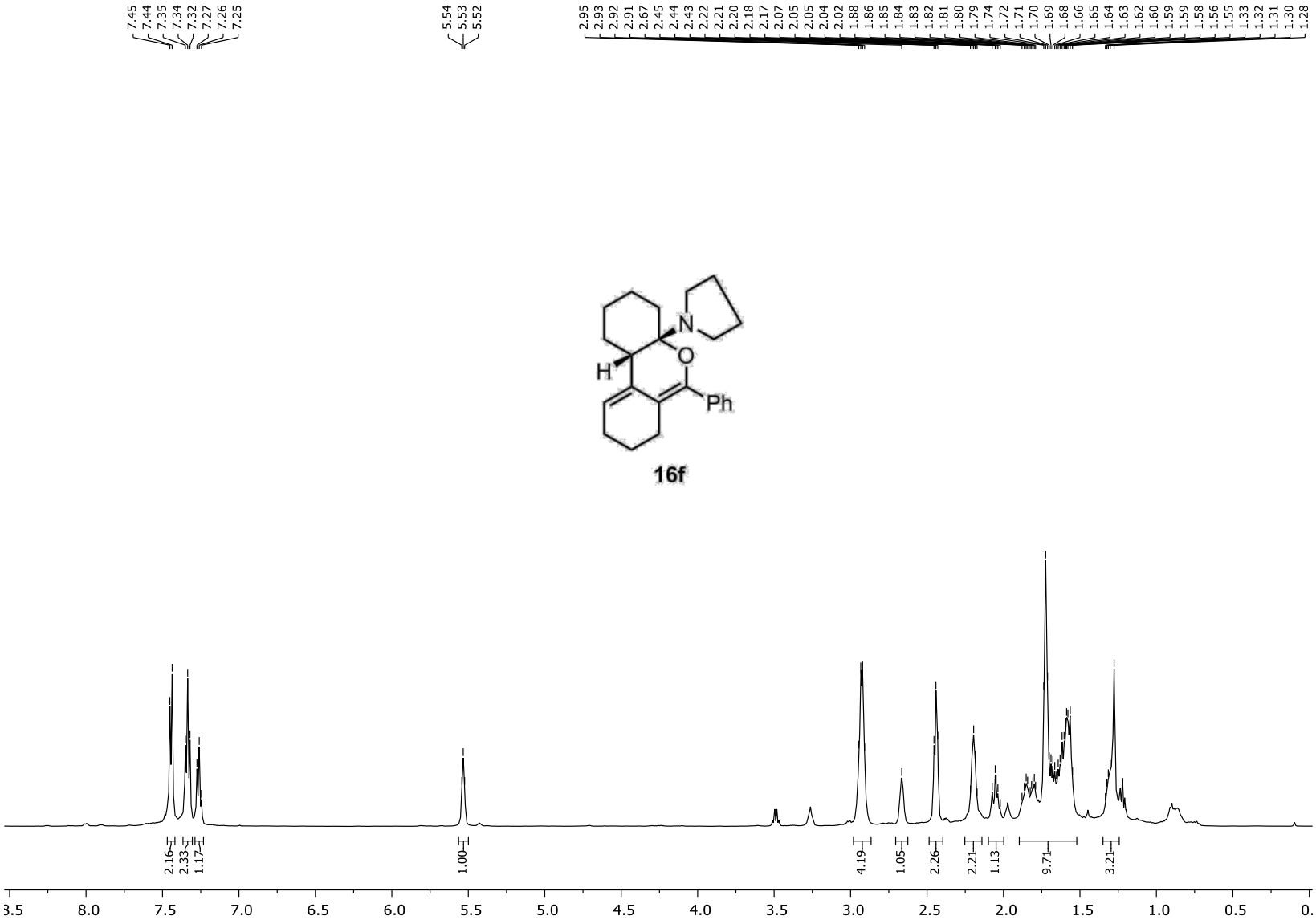

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)
H
N
O
O
Ph
16d

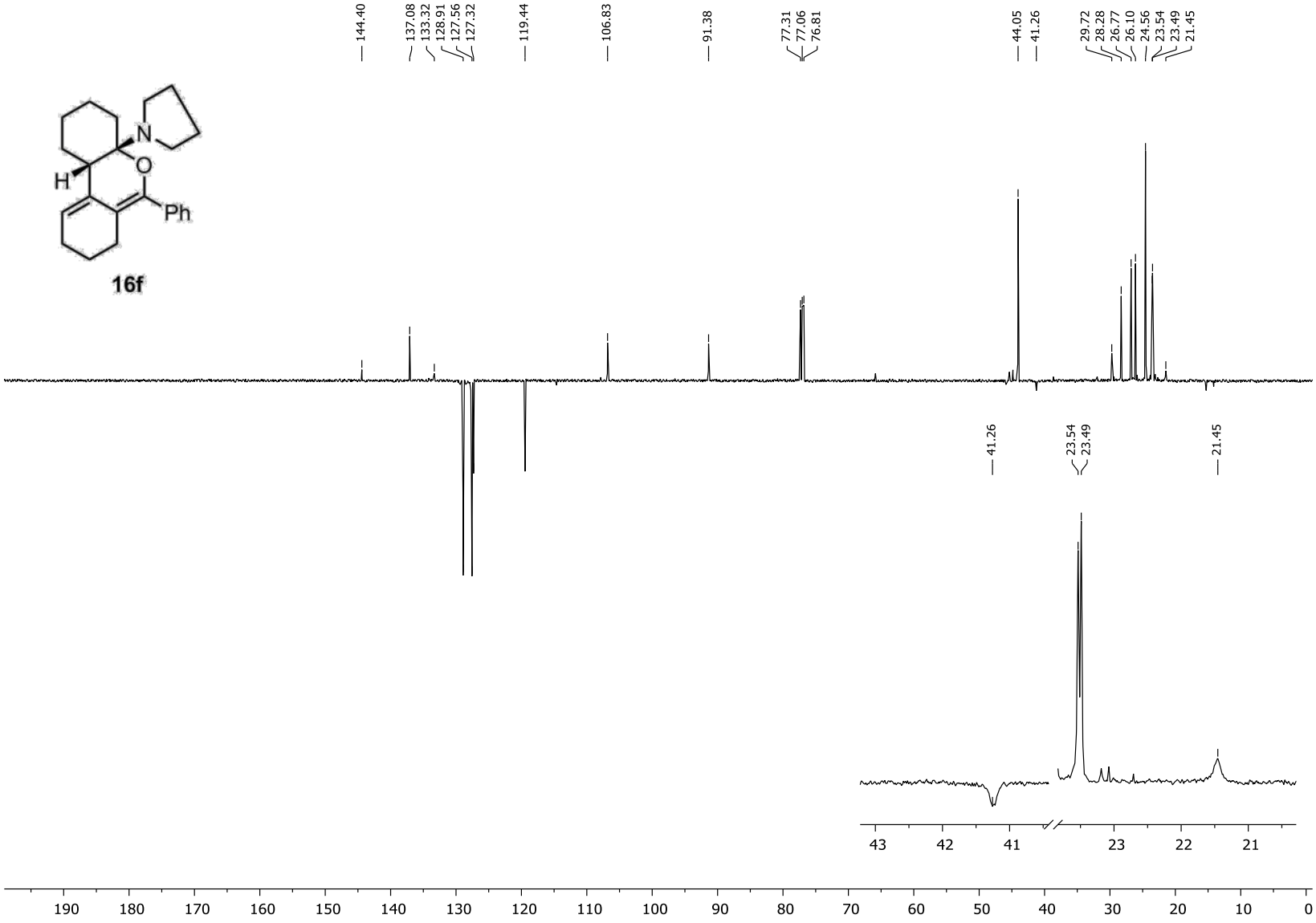
HSQC for

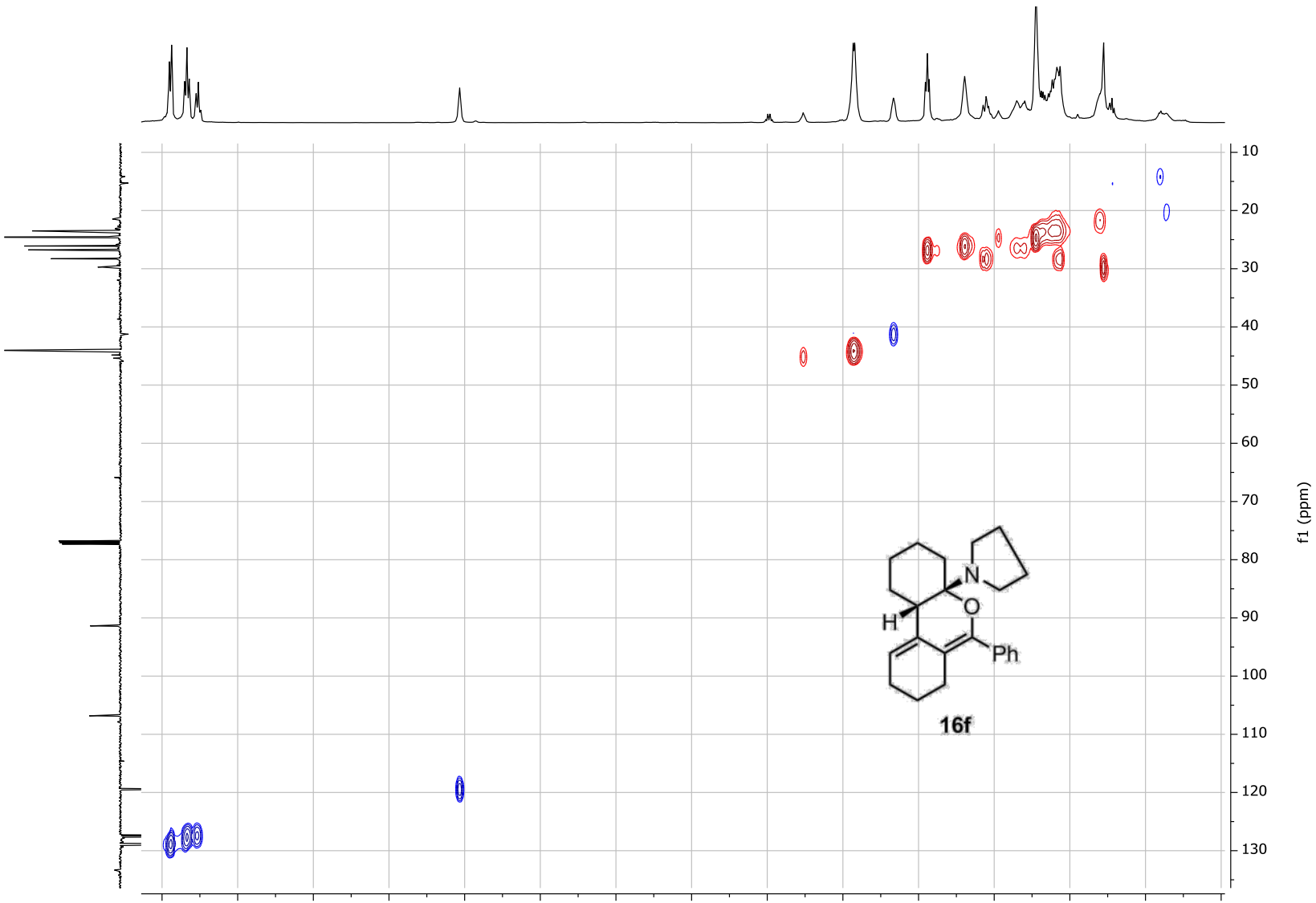

7.34 7.34 7.33 7.32 7.30 7.30 7.29 7.28 5.36 5.36 5.35 3.60 3.59 3.59 2.76 2.75 2.74 2.73 2.72 2.71 2.70 2.69 2.68 2.67 2.46 2.46 2.44 2.43 2.43 2.42 2.39 2.38 2.37 2.36 2.34 2.33 2.33 2.31 2.30 2.16 2.16 2.15 2.15 2.14 2.13 2.13 2.00 1.99 1.98 1.97 1.96 1.96 1.95 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.68 1.66 1.65 1.64 1.63 1.62 1.61 1.61 1.61 1.59 1.58 1.58 1.57 1.53 1.51 1.37 1.36 1.34 1.34 1.33 1.33 1.26 1.22 1.22 1.21 1.21 1.19
O
N
O
H
Cl
16e
2.02
2.09
1.00
4.01
4.08
1.03
0.82
1.11
1.98
1.04
7.12
1.06
1.01
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

16d

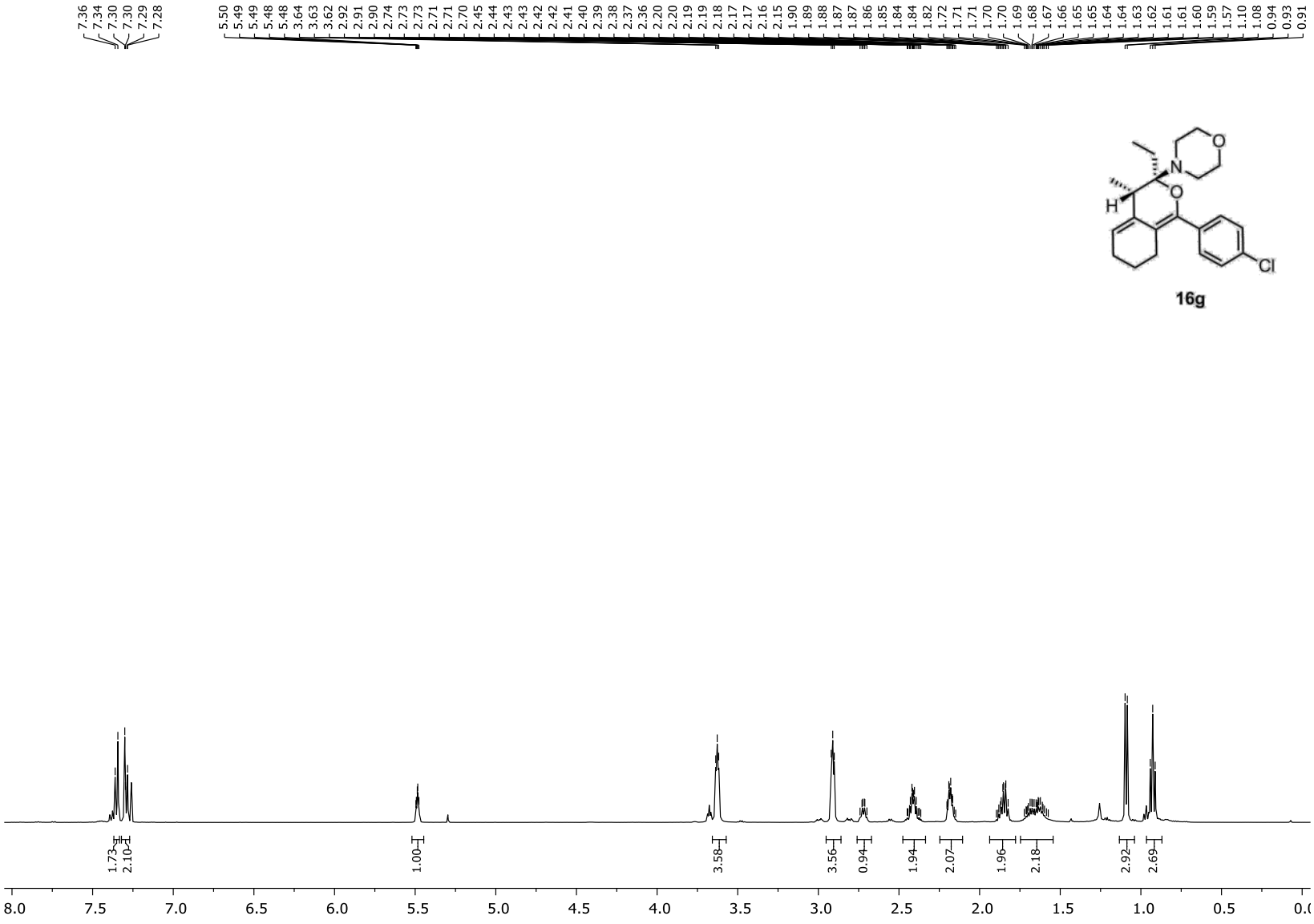

140.53
135.19
134.46
133.12
130.09
127.97
120.89
109.29
90.42
77.31
77.06
76.81
67.90
44.88
41.91
30.58
27.85
26.70
25.92
24.33
24.00
22.71
O
N
O
H
Cl
16e
30
28
26
24
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

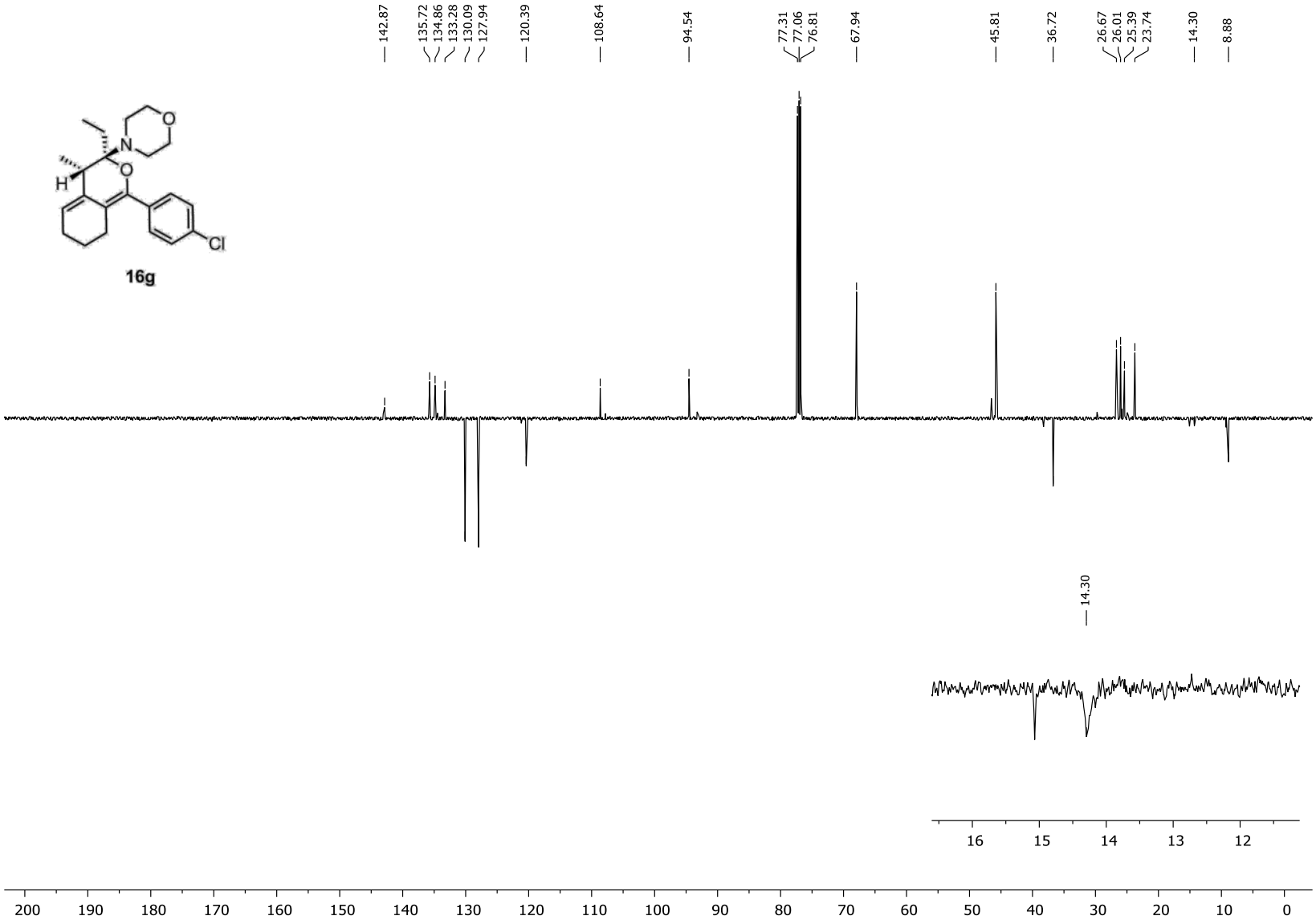

7.45
7.44
7.35
7.34
7.32
7.27
7.26
7.25
5.54
5.53
5.52
2.95
2.93
2.92
2.91
2.67
2.45
2.44
2.43
2.22
2.21
2.20
2.18
2.17
2.07
2.05
2.05
2.04
2.02
1.88
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.74
1.72
1.71
1.70
1.69
1.68
1.66
1.65
1.64
1.63
1.62
1.60
1.59
1.59
1.58
1.56
1.55
1.33
1.32
1.31
1.30
1.28
N
O
H
Ph
16f
2.16
2.33
1.17
1.00
4.19
1.05
2.26
2.21
1.13
9.71
3.21
3.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.


144.40
137.08
133.32
128.91
127.56
127.32
119.44
106.83
91.38
77.31
77.06
76.81
44.05
41.26
29.72
28.28
26.77
26.10
24.56
23.54
23.49
21.45
N
O
H
Ph
16f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
43
42
41
23
22
21


10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)
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
N
O
H
Ph
16f

HSQC for **16f**


7.36 7.34 7.30 7.30 7.29 7.28
5.50 5.49 5.49 5.48 5.48 3.64 3.63 3.62 2.92 2.91 2.90 2.74 2.73 2.71 2.71 2.70 2.45 2.44 2.43 2.43 2.42 2.42 2.41 2.40 2.39 2.38 2.37 2.36 2.20 2.20 2.19 2.19 2.18 2.17 2.17 2.16 2.15 1.90 1.89 1.88 1.87 1.87 1.86 1.85 1.84 1.84 1.82 1.72 1.71 1.71 1.70 1.70 1.69 1.68 1.67 1.66 1.65 1.65 1.64 1.64 1.63 1.62 1.61 1.61 1.60 1.59 1.57 1.10 1.08 0.94 0.93 0.91
O
N
O
H
Cl
16g
1.73
2.10
1.00
3.58
3.56
0.94
1.94
2.07
1.96
2.18
2.92
2.69
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


142.87
135.72
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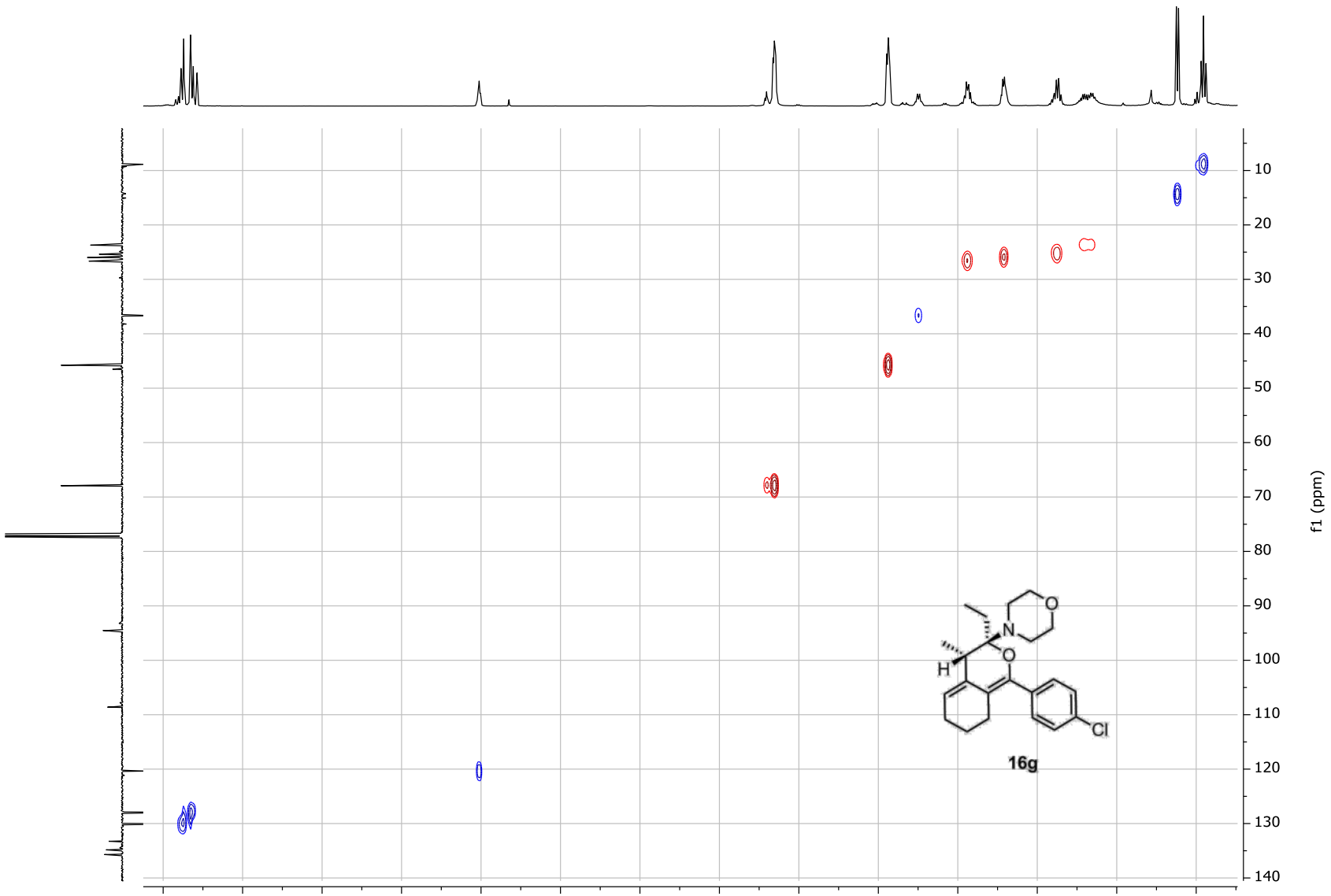
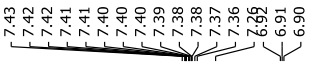
133.28
130.09
127.94
120.39
108.64
94.54
77.31
77.06
76.81
67.94
45.81
36.72
26.67
26.01
25.39
23.74
14.30
8.88
O
N
O
H
Cl
16g
14.30
16
15
14
13
12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


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
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
O
N
O
H
Cl
16g

HSQC for **16g**


7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.37
7.36
6.92
6.91
6.90


2.54
2.52
2.51
2.51
2.49
2.48
2.43
2.42
2.42
2.41
2.40
2.27
2.26
2.25
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2.02
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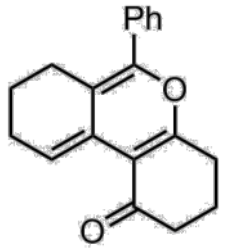
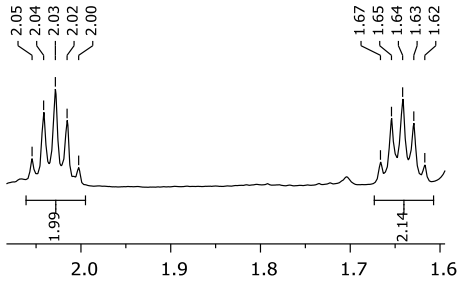
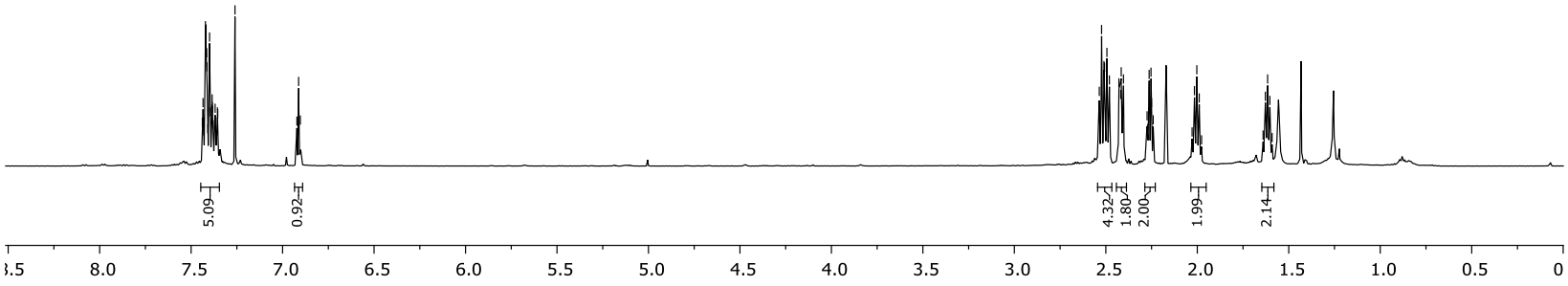
1.98
1.64
1.63
1.62
1.60
1.59


Ph
O
O

16h


2.05
2.04
2.03
2.02
2.00
1.67
1.65
1.64
1.63
1.62
1.99
2.14
2.0
1.9
1.8
1.7
1.6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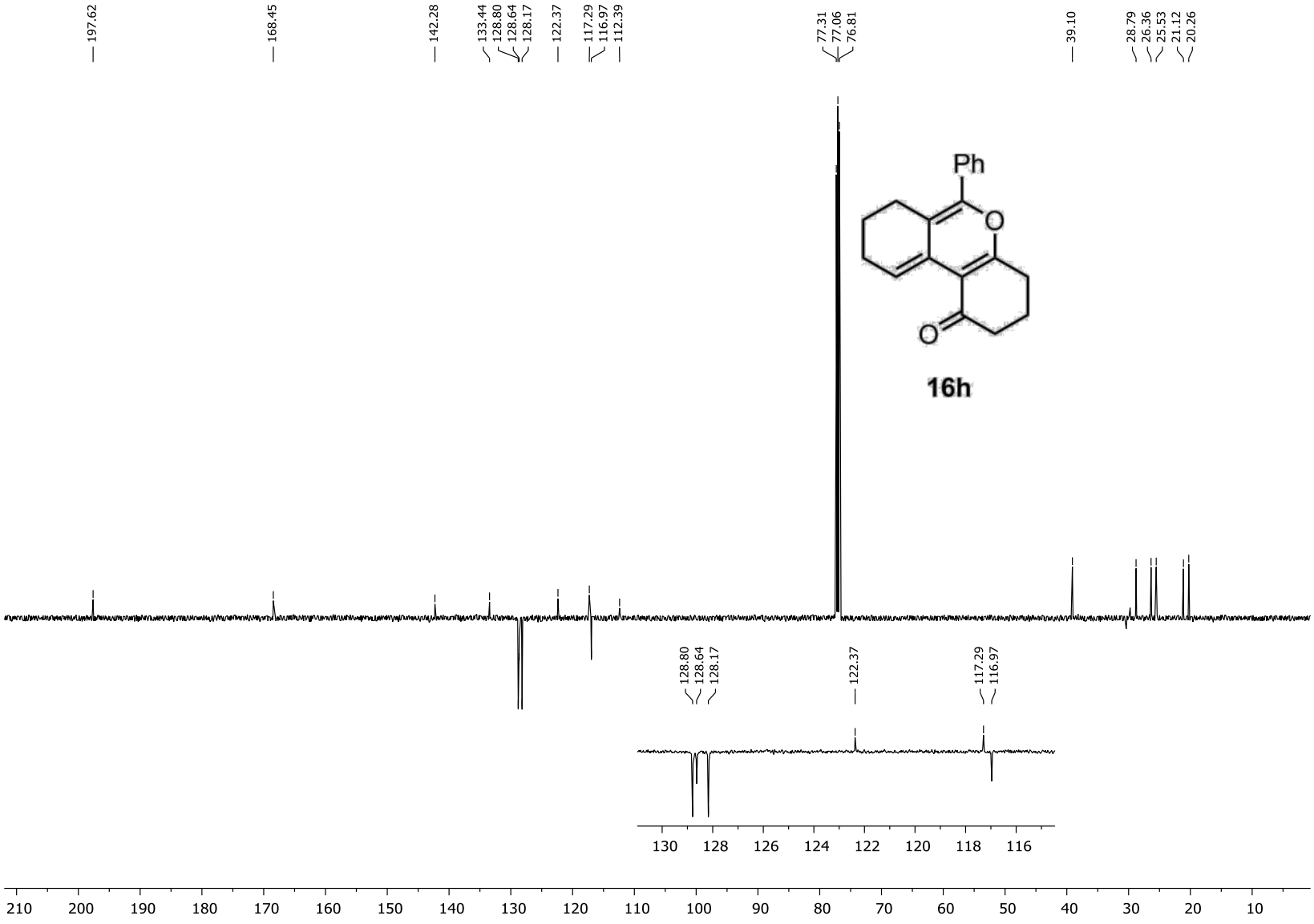
0.92
4.32
1.80
2.00
1.99
2.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0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168.45
142.28
133.44
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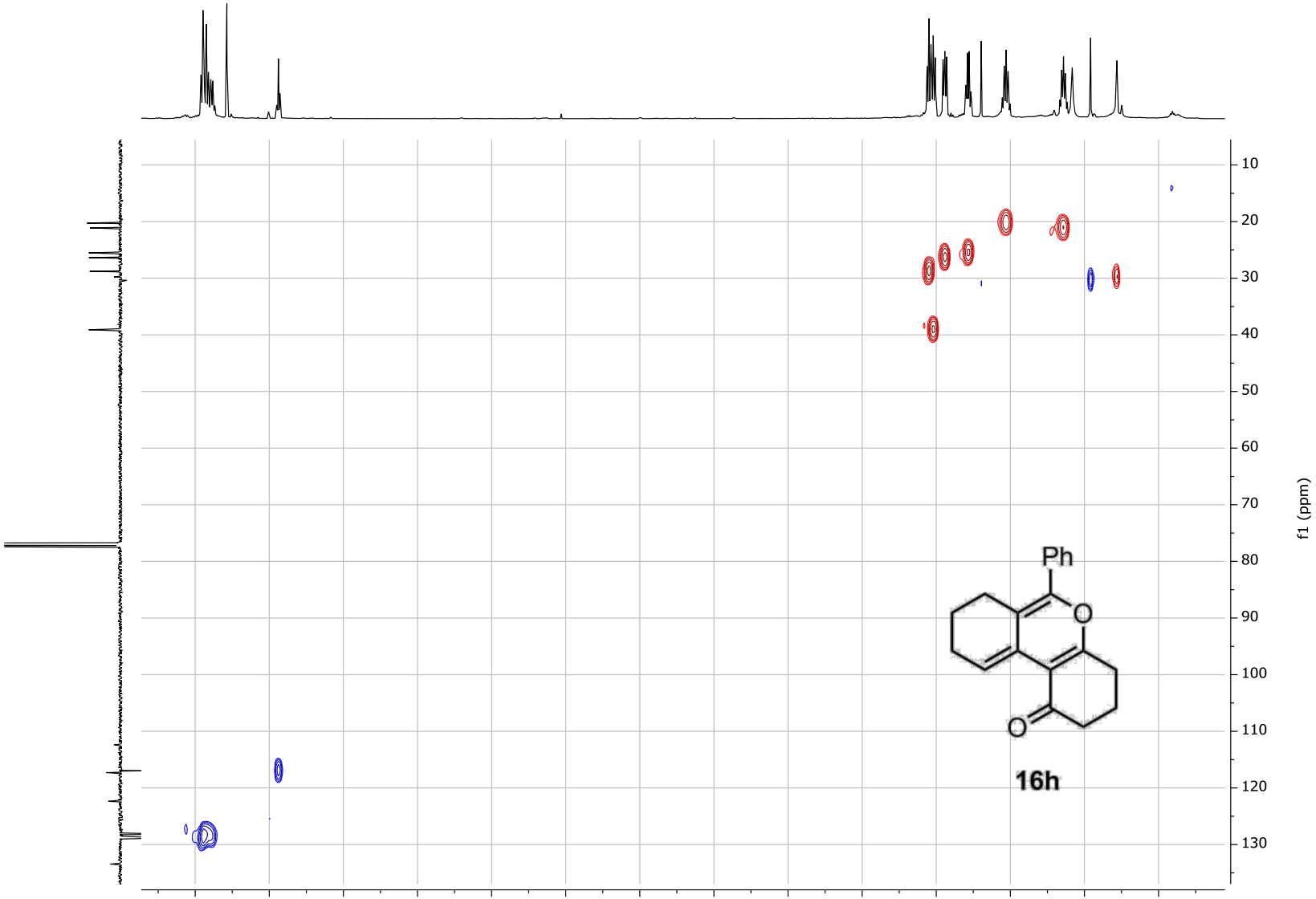
128.64
128.17
122.37
117.29
116.97
112.39
77.31
77.06
76.81
39.10
28.79
26.36
25.53
21.12
20.26
Ph
O
O
16h
128.80
128.64
128.17
122.37
117.29
116.97
130
128
126
124
122
120
118
116
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Ph
O
O
16h
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
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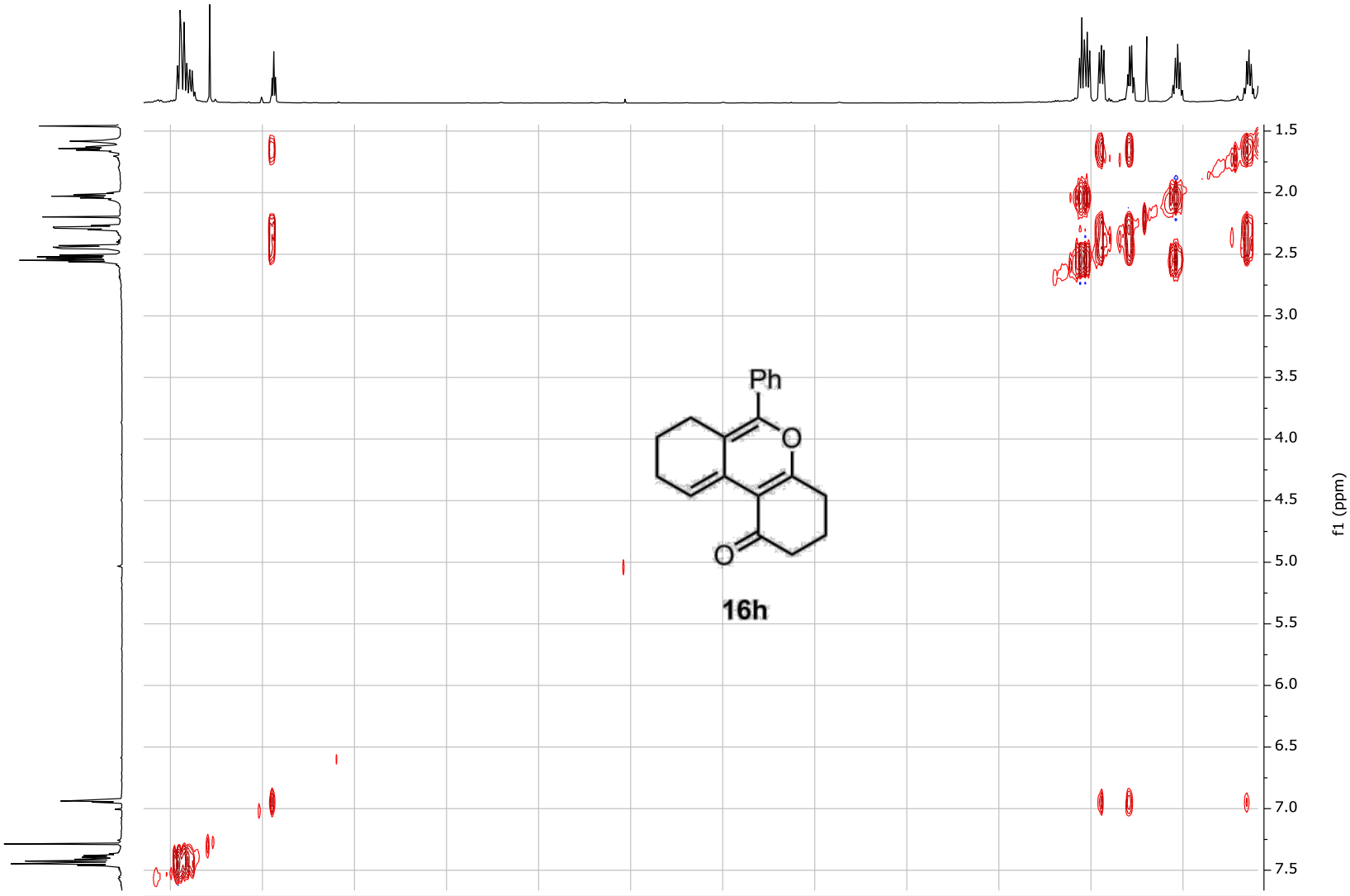
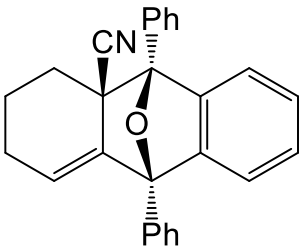
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

HSQC for **16h**



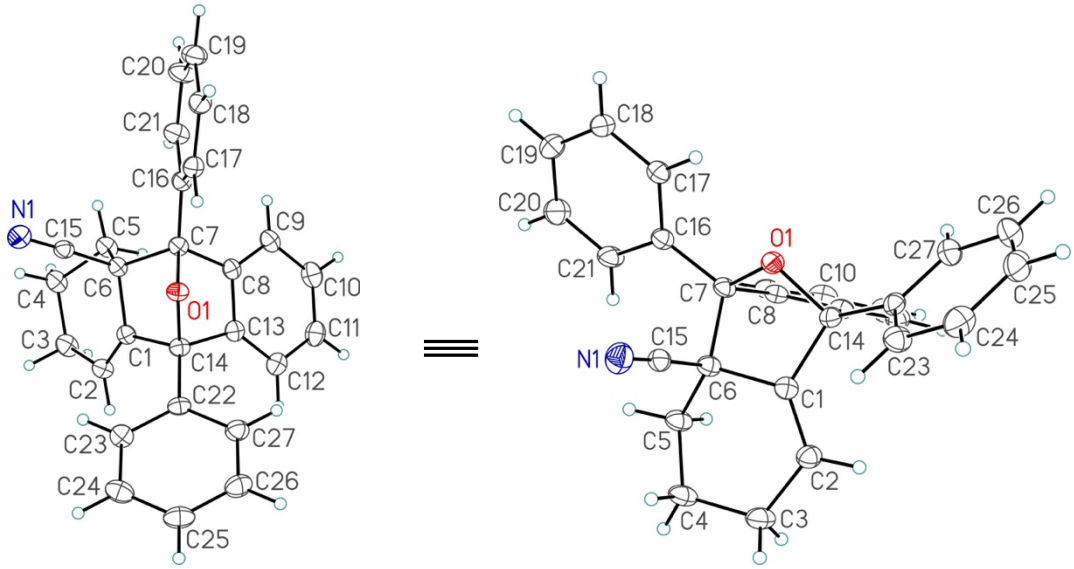
TOCSY for **16h**

X-ray Data for Product 12d



12d

Molecule A



Molecule B

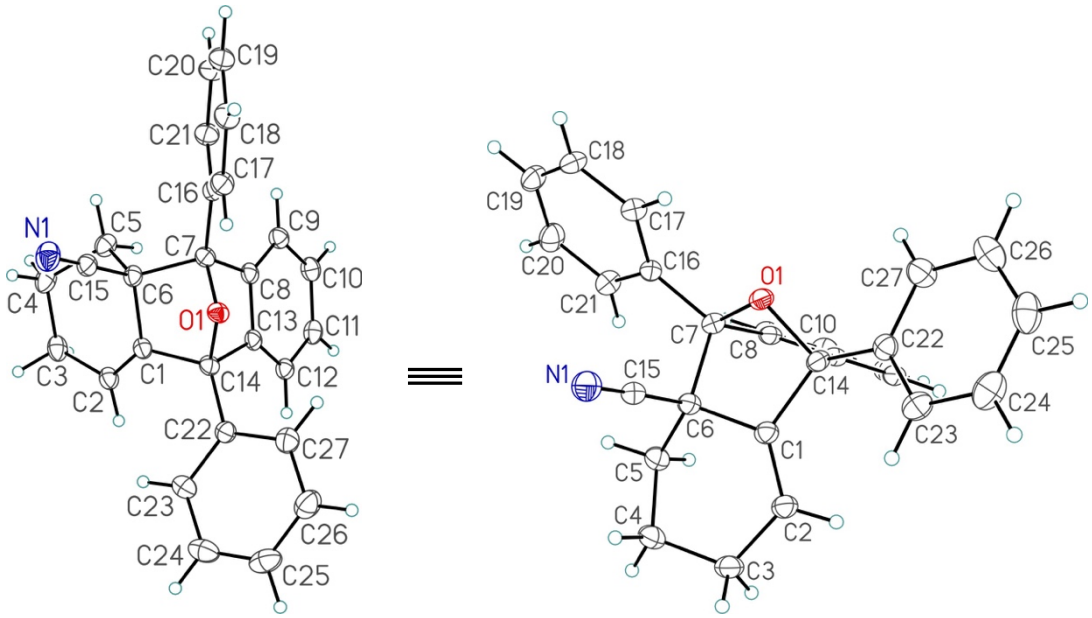


Table 1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_{27}H_{21}NO$
formula weight	375.45
crystal dimensions (mm)	0.31 × 0.23 × 0.06
crystal system	triclinic
space group	*P* (No. 2)
unit cell parameters[a]	
a (Å)	10.4535 (9)
b (Å)	11.5142 (10)
c (Å)	17.3923 (14)
α (deg)	71.1047 (11)
β (deg)	87.8758 (11)
γ (deg)	89.5875 (11)
V (Å^3)	1979.2 (3)
Z	4
ρ_{calcd} (g cm^{-3})	1.260
μ (mm^{-1})	0.076
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.99
total data collected	15431 (-13 ≤ *h* ≤ 12, -14 ≤ *k* ≤ 14, -21 ≤ *l* ≤ 21)
independent reflections	8136 (R_{int} = 0.0361)
number of observed reflections (*NO*)	5553 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods/dual space (*SHELXD*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	1.0000–0.8231
data/restraints/parameters	8136 / 0 / 523
goodness-of-fit (*S*)[e] [all data]	1.023
final *R* indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0521
wR_2 [all data]	0.1518
largest difference peak and hole	0.321 and –0.221 e Å^{-3}

[a]Obtained from least-squares refinement of 5641 reflections with 4.54° < 2θ < 52.48°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Schneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, *D58*, 1772-1779.

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0798P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

(a) Molecule A

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O1	0.32084(11)	0.30007(11)	0.34947(7)	0.0294(3)*
N1	0.14271(18)	0.24811(16)	0.53516(11)	0.0465(5)*
C1	0.15280(17)	0.16363(16)	0.36272(11)	0.0293(4)*
C2	0.07751(18)	0.06953(17)	0.36727(12)	0.0349(4)*
C3	-0.06261(18)	0.06473(18)	0.39148(14)	0.0428(5)*
C4	-0.10861(18)	0.17559(17)	0.41441(13)	0.0399(5)*
C5	-0.03807(17)	0.29470(17)	0.36646(13)	0.0365(5)*
C6	0.10551(17)	0.27742(16)	0.38186(11)	0.0295(4)*
C7	0.20669(16)	0.37536(16)	0.32844(11)	0.0279(4)*
C8	0.19400(17)	0.38232(16)	0.24007(11)	0.0302(4)*
C9	0.14056(18)	0.46925(18)	0.17421(12)	0.0367(5)*
C10	0.1468(2)	0.4470(2)	0.09978(13)	0.0452(5)*
C11	0.2002(2)	0.3407(2)	0.09294(13)	0.0443(5)*
C12	0.25033(18)	0.25121(19)	0.16012(12)	0.0379(5)*
C13	0.24788(17)	0.27472(17)	0.23338(11)	0.0314(4)*
C14	0.28438(17)	0.20005(16)	0.31981(11)	0.0295(4)*
C15	0.12782(17)	0.26300(16)	0.46790(12)	0.0314(4)*
C16	0.22020(17)	0.49341(16)	0.34635(11)	0.0301(4)*
C17	0.33755(17)	0.52796(17)	0.36751(11)	0.0317(4)*
C18	0.35167(19)	0.64011(17)	0.37996(12)	0.0367(5)*
C19	0.2491(2)	0.71869(19)	0.37199(13)	0.0443(5)*
C20	0.1313(2)	0.68469(19)	0.35149(14)	0.0484(6)*
C21	0.11679(19)	0.57307(18)	0.33858(13)	0.0409(5)*
C22	0.38996(17)	0.10639(16)	0.33479(11)	0.0302(4)*
C23	0.39171(19)	0.00826(18)	0.40625(12)	0.0379(5)*
C24	0.4940(2)	-0.07237(19)	0.42244(14)	0.0459(5)*
C25	0.5966(2)	-0.0541(2)	0.36665(14)	0.0469(5)*
C26	0.5958(2)	0.0433(2)	0.29533(14)	0.0456(5)*
C27	0.49321(19)	0.12336(18)	0.27920(13)	0.0389(5)*

(b) Molecule B

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O1	0.20567(11)	0.38816(11)	0.86935(7)	0.0291(3)*
N1	0.32261(17)	0.11407(16)	1.01204(11)	0.0471(5)*
C1	0.42747(17)	0.37202(16)	0.85732(11)	0.0293(4)*
C2	0.55337(17)	0.38714(18)	0.84885(11)	0.0344(4)*
C3	0.64413(18)	0.28669(18)	0.84779(12)	0.0407(5)*
C4	0.58052(19)	0.16471(18)	0.85434(13)	0.0438(5)*
C5	0.44825(18)	0.18203(18)	0.81699(12)	0.0375(5)*
C6	0.36313(17)	0.25167(16)	0.86021(11)	0.0297(4)*
C7	0.22849(17)	0.30301(16)	0.82448(11)	0.0292(4)*
C8	0.25341(16)	0.39146(16)	0.73835(11)	0.0288(4)*
C9	0.23818(18)	0.38329(18)	0.66181(11)	0.0335(4)*
C10	0.27860(19)	0.48249(18)	0.59470(12)	0.0375(5)*
C11	0.33440(18)	0.58554(18)	0.60508(12)	0.0362(5)*
C12	0.34992(17)	0.59328(17)	0.68252(11)	0.0315(4)*
C13	0.30802(16)	0.49604(16)	0.74836(11)	0.0284(4)*
C14	0.31861(17)	0.46663(16)	0.84033(11)	0.0291(4)*
C15	0.33875(17)	0.17473(17)	0.94560(12)	0.0331(4)*
C16	0.12356(17)	0.20890(16)	0.83995(11)	0.0295(4)*
C17	0.02732(18)	0.20032(17)	0.89854(12)	0.0359(5)*
C18	-0.06671(18)	0.10969(18)	0.91364(13)	0.0420(5)*
C19	-0.0653(2)	0.02888(19)	0.87017(13)	0.0452(5)*
C20	0.0300(2)	0.03684(19)	0.81178(13)	0.0442(5)*
C21	0.12480(19)	0.12615(17)	0.79695(12)	0.0382(5)*
C22	0.31384(18)	0.57187(16)	0.87313(11)	0.0314(4)*
C23	0.4156(2)	0.60579(19)	0.91068(12)	0.0401(5)*
C24	0.4063(2)	0.7078(2)	0.93638(13)	0.0512(6)*
C25	0.2958(3)	0.7754(2)	0.92697(13)	0.0527(6)*
C26	0.1917(2)	0.7396(2)	0.89249(14)	0.0519(6)*
C27	0.2015(2)	0.64016(19)	0.86471(13)	0.0432(5)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

(a) Molecule A

Atom1	Atom2	Distance
O1	C7	1.456(2)
O1	C14	1.464(2)
N1	C15	1.142(2)
C1	C2	1.323(2)
C1	C6	1.527(2)
C1	C14	1.534(2)
C2	C3	1.505(3)
C3	C4	1.525(3)
C4	C5	1.533(2)
C5	C6	1.535(2)
C6	C7	1.587(2)
C6	C15	1.478(3)
C7	C8	1.523(3)
C7	C16	1.498(2)
C8	C9	1.387(3)
C8	C13	1.394(3)
C9	C10	1.398(3)
C10	C11	1.379(3)
C11	C12	1.400(3)
C12	C13	1.385(3)
C13	C14	1.531(3)
C14	C22	1.507(2)
C16	C17	1.391(3)
C16	C21	1.394(3)
C17	C18	1.387(3)
C18	C19	1.380(3)
C19	C20	1.388(3)
C20	C21	1.385(3)
C22	C23	1.383(3)
C22	C27	1.393(3)
C23	C24	1.387(3)
C24	C25	1.389(3)
C25	C26	1.377(3)
C26	C27	1.385(3)

(b) Molecule B

Atom1	Atom2	Distance
O1	C7	1.451(2)
O1	C14	1.463(2)
N1	C15	1.147(2)
C1	C2	1.325(2)
C1	C6	1.530(2)
C1	C14	1.539(2)
C2	C3	1.495(3)
C3	C4	1.527(3)
C4	C5	1.534(3)
C5	C6	1.527(3)
C6	C7	1.591(3)
C6	C15	1.476(3)
C7	C8	1.528(2)
C7	C16	1.502(2)
C8	C9	1.379(3)
C8	C13	1.400(2)
C9	C10	1.397(3)
C10	C11	1.392(3)
C11	C12	1.394(3)
C12	C13	1.377(2)
C13	C14	1.532(2)
C14	C22	1.497(3)
C16	C17	1.386(3)
C16	C21	1.388(3)
C17	C18	1.394(3)
C18	C19	1.376(3)
C19	C20	1.378(3)
C20	C21	1.389(3)
C22	C23	1.391(3)
C22	C27	1.394(3)
C23	C24	1.387(3)
C24	C25	1.374(3)
C25	C26	1.389(3)
C26	C27	1.381(3)

Table 4. Selected Interatomic Angles (deg)

(a) Molecule A				*(b) Molecule B*			
Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C7	O1	C14	98.84(12)	C7	O1	C14	98.77(12)
C2	C1	C6	123.04(17)	C2	C1	C6	121.94(17)
C2	C1	C14	130.20(17)	C2	C1	C14	130.80(17)
C6	C1	C14	105.04(14)	C6	C1	C14	104.70(14)
C1	C2	C3	123.24(18)	C1	C2	C3	123.32(18)
C2	C3	C4	113.79(16)	C2	C3	C4	114.80(16)
C3	C4	C5	113.27(16)	C3	C4	C5	112.37(16)
C4	C5	C6	108.80(15)	C4	C5	C6	108.83(17)
C1	C6	C5	109.77(15)	C1	C6	C5	110.41(15)
C1	C6	C7	99.71(13)	C1	C6	C7	99.67(13)
C1	C6	C15	109.69(15)	C1	C6	C15	109.72(15)
C5	C6	C7	120.64(15)	C5	C6	C7	119.91(16)
C5	C6	C15	109.48(15)	C5	C6	C15	109.46(15)
C7	C6	C15	106.93(14)	C7	C6	C15	107.07(14)
O1	C7	C6	97.84(13)	O1	C7	C6	98.37(13)
O1	C7	C8	100.84(13)	O1	C7	C8	101.18(13)
O1	C7	C16	111.39(14)	O1	C7	C16	112.07(14)
C6	C7	C8	107.73(14)	C6	C7	C8	107.66(13)
C6	C7	C16	118.00(14)	C6	C7	C16	115.35(14)
C8	C7	C16	117.89(15)	C8	C7	C16	119.34(15)
C7	C8	C9	132.35(17)	C7	C8	C9	133.75(17)
C7	C8	C13	106.08(15)	C7	C8	C13	105.28(15)
C9	C8	C13	121.55(18)	C9	C8	C13	120.89(17)
C8	C9	C10	117.36(19)	C8	C9	C10	118.06(18)
C9	C10	C11	121.2(2)	C9	C10	C11	120.78(18)
C10	C11	C12	121.3(2)	C10	C11	C12	120.97(17)
C11	C12	C13	117.61(19)	C11	C12	C13	117.95(17)
C8	C13	C12	120.89(18)	C8	C13	C12	121.34(17)
C8	C13	C14	105.12(15)	C8	C13	C14	105.49(15)
C12	C13	C14	133.77(18)	C12	C13	C14	132.88(16)
O1	C14	C1	101.36(13)	O1	C14	C1	101.90(13)
O1	C14	C13	99.68(13)	O1	C14	C13	100.11(13)
O1	C14	C22	109.57(14)	O1	C14	C22	110.10(14)
C1	C14	C13	101.96(14)	C1	C14	C13	100.65(14)
C1	C14	C22	119.62(15)	C1	C14	C22	123.15(16)
C13	C14	C22	121.26(15)	C13	C14	C22	117.59(15)
N1	C15	C6	177.6(2)	N1	C15	C6	178.5(2)
C7	C16	C17	120.55(16)	C7	C16	C17	121.12(16)
C7	C16	C21	120.57(17)	C7	C16	C21	119.73(16)

C17	C16	C21	118.82(17)	C17	C16	C21	119.11(16)
C16	C17	C18	120.55(18)	C16	C17	C18	120.09(19)
C17	C18	C19	120.37(19)	C17	C18	C19	120.35(19)
C18	C19	C20	119.54(19)	C18	C19	C20	119.92(18)
C19	C20	C21	120.3(2)	C19	C20	C21	120.1(2)
C16	C21	C20	120.37(19)	C16	C21	C20	120.46(19)
C14	C22	C23	121.04(17)	C14	C22	C23	123.58(17)
C14	C22	C27	119.90(17)	C14	C22	C27	118.03(17)
C23	C22	C27	118.85(18)	C23	C22	C27	118.39(18)
C22	C23	C24	120.80(19)	C22	C23	C24	120.4(2)
C23	C24	C25	119.8(2)	C23	C24	C25	120.8(2)
C24	C25	C26	119.8(2)	C24	C25	C26	119.3(2)
C25	C26	C27	120.2(2)	C25	C26	C27	120.2(2)
C22	C27	C26	120.50(19)	C22	C27	C26	120.9(2)

Table 5. Torsional Angles (deg)

(a) Molecule A

Atom1	Atom2	Atom3	Atom4	Angle
C14	O1	C7	C6	60.15(14)
C14	O1	C7	C8	-49.69(14)
C14	O1	C7	C16	-175.60(14)
C7	O1	C14	C1	-52.69(15)
C7	O1	C14	C13	51.71(14)
C7	O1	C14	C22	179.98(14)
C6	C1	C2	C3	0.2(3)
C14	C1	C2	C3	-162.52(19)
C2	C1	C6	C5	-26.7(2)
C2	C1	C6	C7	-154.31(18)
C2	C1	C6	C15	93.7(2)
C14	C1	C6	C5	139.77(15)
C14	C1	C6	C7	12.11(17)
C14	C1	C6	C15	-99.91(16)
C2	C1	C14	O1	-171.62(19)
C2	C1	C14	C13	85.8(2)
C2	C1	C14	C22	-51.1(3)
C6	C1	C14	O1	23.31(17)
C6	C1	C14	C13	-79.27(16)
C6	C1	C14	C22	143.79(16)
C1	C2	C3	C4	-2.9(3)
C2	C3	C4	C5	32.8(3)
C3	C4	C5	C6	-58.9(2)
C4	C5	C6	C1	53.8(2)
C4	C5	C6	C7	168.75(17)
C4	C5	C6	C15	-66.6(2)
C1	C6	C7	O1	-43.68(15)
C1	C6	C7	C8	60.40(17)
C1	C6	C7	C16	-163.03(15)
C5	C6	C7	O1	-163.69(16)
C5	C6	C7	C8	-59.6(2)
C5	C6	C7	C16	77.0(2)
C15	C6	C7	O1	70.48(15)
C15	C6	C7	C8	174.56(14)
C15	C6	C7	C16	-48.9(2)
O1	C7	C8	C9	-152.76(19)
O1	C7	C8	C13	28.54(16)
C6	C7	C8	C9	105.3(2)
C6	C7	C8	C13	-73.41(17)

(b) Molecule B

Atom1	Atom2	Atom3	Atom4	Angle
C14	O1	C7	C6	59.68(14)
C14	O1	C7	C8	-50.29(15)
C14	O1	C7	C16	-178.54(14)
C7	O1	C14	C1	-52.30(15)
C7	O1	C14	C13	50.96(15)
C7	O1	C14	C22	175.45(14)
C6	C1	C2	C3	-4.8(3)
C14	C1	C2	C3	-163.77(18)
C2	C1	C6	C5	-24.6(2)
C2	C1	C6	C7	-151.66(17)
C2	C1	C6	C15	96.2(2)
C14	C1	C6	C5	139.09(15)
C14	C1	C6	C7	11.99(16)
C14	C1	C6	C15	-100.18(16)
C2	C1	C14	O1	-175.28(19)
C2	C1	C14	C13	81.9(2)
C2	C1	C14	C22	-51.4(3)
C6	C1	C14	O1	23.11(17)
C6	C1	C14	C13	-79.73(15)
C6	C1	C14	C22	146.97(16)
C1	C2	C3	C4	2.0(3)
C2	C3	C4	C5	30.2(2)
C3	C4	C5	C6	-58.6(2)
C4	C5	C6	C1	54.59(19)
C4	C5	C6	C7	169.47(15)
C4	C5	C6	C15	-66.31(19)
C1	C6	C7	O1	-43.54(14)
C1	C6	C7	C8	61.09(16)
C1	C6	C7	C16	-162.88(15)
C5	C6	C7	O1	-163.94(15)
C5	C6	C7	C8	-59.3(2)
C5	C6	C7	C16	76.7(2)
C15	C6	C7	O1	70.69(16)
C15	C6	C7	C8	175.32(14)
C15	C6	C7	C16	-48.6(2)
O1	C7	C8	C9	-153.08(19)
O1	C7	C8	C13	30.23(17)
C6	C7	C8	C9	104.3(2)
C6	C7	C8	C13	-72.39(17)

C16	C7	C8	C9	-31.3(3)	C16	C7	C8	C9	-29.7(3)
C16	C7	C8	C13	149.98(15)	C16	C7	C8	C13	153.64(16)
O1	C7	C16	C17	9.5(2)	O1	C7	C16	C17	-7.3(2)
O1	C7	C16	C21	-173.32(16)	O1	C7	C16	C21	174.91(16)
C6	C7	C16	C17	121.52(18)	C6	C7	C16	C17	104.2(2)
C6	C7	C16	C21	-61.3(2)	C6	C7	C16	C21	-73.6(2)
C8	C7	C16	C17	-106.3(2)	C8	C7	C16	C17	-125.17(19)
C8	C7	C16	C21	70.8(2)	C8	C7	C16	C21	57.0(2)
C7	C8	C9	C10	179.26(18)	C7	C8	C9	C10	-176.40(18)
C13	C8	C9	C10	-2.2(3)	C13	C8	C9	C10	-0.1(3)
C7	C8	C13	C12	179.17(16)	C7	C8	C13	C12	176.29(16)
C7	C8	C13	C14	3.72(18)	C7	C8	C13	C14	1.70(17)
C9	C8	C13	C12	0.3(3)	C9	C8	C13	C12	-0.9(3)
C9	C8	C13	C14	-175.15(16)	C9	C8	C13	C14	-175.51(16)
C8	C9	C10	C11	2.1(3)	C8	C9	C10	C11	1.0(3)
C9	C10	C11	C12	0.0(3)	C9	C10	C11	C12	-0.9(3)
C10	C11	C12	C13	-1.9(3)	C10	C11	C12	C13	-0.2(3)
C11	C12	C13	C8	1.8(3)	C11	C12	C13	C8	1.1(3)
C11	C12	C13	C14	175.68(19)	C11	C12	C13	C14	173.94(18)
C8	C13	C14	O1	-34.46(16)	C8	C13	C14	O1	-32.69(17)
C8	C13	C14	C1	69.45(16)	C8	C13	C14	C1	71.59(16)
C8	C13	C14	C22	-154.53(15)	C8	C13	C14	C22	-151.84(16)
C12	C13	C14	O1	150.95(19)	C12	C13	C14	O1	153.62(19)
C12	C13	C14	C1	-105.1(2)	C12	C13	C14	C1	-102.1(2)
C12	C13	C14	C22	30.9(3)	C12	C13	C14	C22	34.5(3)
O1	C14	C22	C23	90.48(19)	O1	C14	C22	C23	130.74(18)
O1	C14	C22	C27	-84.3(2)	O1	C14	C22	C27	-49.9(2)
C1	C14	C22	C23	-25.8(2)	C1	C14	C22	C23	10.6(3)
C1	C14	C22	C27	159.48(17)	C1	C14	C22	C27	-170.04(16)
C13	C14	C22	C23	-154.40(17)	C13	C14	C22	C23	-115.5(2)
C13	C14	C22	C27	30.9(2)	C13	C14	C22	C27	63.8(2)
C7	C16	C17	C18	176.63(16)	C7	C16	C17	C18	-177.92(18)
C21	C16	C17	C18	-0.6(3)	C21	C16	C17	C18	-0.1(3)
C7	C16	C21	C20	-176.96(18)	C7	C16	C21	C20	178.61(18)
C17	C16	C21	C20	0.2(3)	C17	C16	C21	C20	0.7(3)
C16	C17	C18	C19	0.4(3)	C16	C17	C18	C19	-0.5(3)
C17	C18	C19	C20	0.1(3)	C17	C18	C19	C20	0.5(3)
C18	C19	C20	C21	-0.4(3)	C18	C19	C20	C21	0.2(3)
C19	C20	C21	C16	0.3(3)	C19	C20	C21	C16	-0.8(3)

Table 5. Torsional Angles (continued)

(a) Molecule A

Atom1	Atom2	Atom3	Atom4	Angle
C14	C22	C23	C24	-175.01(18)
C27	C22	C23	C24	-0.2(3)
C14	C22	C27	C26	174.81(18)
C23	C22	C27	C26	0.0(3)
C22	C23	C24	C25	0.5(3)
C23	C24	C25	C26	-0.5(3)
C24	C25	C26	C27	0.2(3)
C25	C26	C27	C22	0.0(3)

(b) Molecule B

Atom1	Atom2	Atom3	Atom4	Angle
C14	C22	C23	C24	177.11(18)
C27	C22	C23	C24	-2.2(3)
C14	C22	C27	C26	-178.94(18)
C23	C22	C27	C26	0.4(3)
C22	C23	C24	C25	1.5(3)
C23	C24	C25	C26	1.1(3)
C24	C25	C26	C27	-2.9(3)
C25	C26	C27	C22	2.1(3)

Table 6. Anisotropic Displacement Parameters (U_{ij}, Å^2)

(a) Molecule A

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0230(7)	0.0294(6)	0.0371(7)	-0.0123(6)	-0.0046(5)	0.0028(5)
N1	0.0554(12)	0.0446(10)	0.0413(11)	-0.0166(9)	-0.0004(9)	0.0005(9)
C1	0.0267(10)	0.0304(9)	0.0293(10)	-0.0075(8)	-0.0044(7)	0.0017(7)
C2	0.0304(11)	0.0319(10)	0.0419(11)	-0.0111(9)	-0.0034(8)	0.0000(8)
C3	0.0302(11)	0.0400(11)	0.0548(13)	-0.0108(10)	-0.0004(9)	-0.0072(9)
C4	0.0235(10)	0.0393(11)	0.0508(13)	-0.0064(10)	0.0014(9)	-0.0035(8)
C5	0.0221(10)	0.0347(10)	0.0479(12)	-0.0067(9)	-0.0029(8)	0.0007(8)
C6	0.0244(10)	0.0291(9)	0.0325(10)	-0.0066(8)	-0.0013(7)	-0.0003(7)
C7	0.0185(9)	0.0286(9)	0.0350(10)	-0.0081(8)	-0.0020(7)	0.0023(7)
C8	0.0226(9)	0.0326(10)	0.0332(10)	-0.0076(8)	-0.0002(7)	-0.0046(7)
C9	0.0269(10)	0.0361(10)	0.0416(12)	-0.0047(9)	-0.0030(8)	-0.0033(8)
C10	0.0401(13)	0.0517(13)	0.0373(12)	-0.0045(10)	-0.0094(9)	-0.0034(10)
C11	0.0416(13)	0.0577(14)	0.0334(11)	-0.0142(10)	-0.0025(9)	-0.0056(10)
C12	0.0329(11)	0.0455(12)	0.0374(11)	-0.0162(9)	-0.0006(8)	-0.0050(9)
C13	0.0230(10)	0.0358(10)	0.0347(10)	-0.0104(8)	-0.0013(7)	-0.0036(8)
C14	0.0252(10)	0.0293(9)	0.0363(10)	-0.0136(8)	-0.0020(8)	-0.0020(7)
C15	0.0279(10)	0.0271(9)	0.0391(12)	-0.0111(8)	0.0031(8)	0.0004(7)
C16	0.0258(10)	0.0297(9)	0.0331(10)	-0.0080(8)	0.0004(7)	0.0005(7)
C17	0.0260(10)	0.0355(10)	0.0331(10)	-0.0106(8)	-0.0009(8)	0.0012(8)
C18	0.0346(11)	0.0389(11)	0.0383(11)	-0.0152(9)	0.0005(8)	-0.0056(9)
C19	0.0482(14)	0.0322(11)	0.0551(14)	-0.0180(10)	0.0037(10)	-0.0042(9)
C20	0.0384(13)	0.0359(11)	0.0718(16)	-0.0190(11)	-0.0003(11)	0.0083(9)
C21	0.0232(10)	0.0363(11)	0.0625(14)	-0.0150(10)	-0.0014(9)	0.0013(8)
C22	0.0255(10)	0.0302(9)	0.0401(11)	-0.0180(8)	-0.0051(8)	0.0015(7)
C23	0.0322(11)	0.0393(11)	0.0414(12)	-0.0118(9)	-0.0044(9)	0.0010(9)
C24	0.0449(13)	0.0366(11)	0.0551(14)	-0.0121(10)	-0.0145(10)	0.0071(9)
C25	0.0355(12)	0.0448(12)	0.0660(16)	-0.0251(12)	-0.0101(10)	0.0114(9)
C26	0.0340(12)	0.0500(13)	0.0561(14)	-0.0221(11)	0.0015(10)	0.0078(10)
C27	0.0342(11)	0.0378(11)	0.0455(12)	-0.0148(9)	0.0005(9)	0.0046(9)

(b) Molecule B

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0222(7)	0.0319(7)	0.0336(7)	-0.0112(6)	0.0009(5)	-0.0028(5)
N1	0.0432(11)	0.0459(10)	0.0427(11)	-0.0012(9)	0.0004(8)	0.0003(8)
C1	0.0255(10)	0.0314(9)	0.0280(10)	-0.0052(8)	-0.0026(7)	-0.0009(7)
C2	0.0277(10)	0.0366(10)	0.0347(11)	-0.0054(8)	-0.0035(8)	-0.0014(8)
C3	0.0267(11)	0.0473(12)	0.0404(12)	-0.0035(9)	-0.0004(8)	0.0020(9)
C4	0.0325(12)	0.0401(11)	0.0521(13)	-0.0062(10)	0.0034(9)	0.0085(9)
C5	0.0334(11)	0.0347(10)	0.0435(12)	-0.0121(9)	0.0032(9)	0.0043(8)

Table 6. Anisotropic Displacement Parameters (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	0.0247(10)	0.0298(9)	0.0319(10)	-0.0060(8)	-0.0018(7)	0.0016(7)
C7	0.0238(10)	0.0312(9)	0.0323(10)	-0.0099(8)	-0.0001(7)	-0.0019(7)
C8	0.0201(9)	0.0319(9)	0.0327(10)	-0.0081(8)	-0.0019(7)	0.0024(7)
C9	0.0300(10)	0.0372(10)	0.0347(11)	-0.0133(8)	-0.0022(8)	0.0024(8)
C10	0.0354(11)	0.0464(12)	0.0290(10)	-0.0099(9)	-0.0017(8)	0.0052(9)
C11	0.0313(11)	0.0379(11)	0.0323(11)	-0.0021(8)	0.0021(8)	0.0037(8)
C12	0.0246(10)	0.0317(10)	0.0360(11)	-0.0078(8)	-0.0017(8)	0.0017(8)
C13	0.0197(9)	0.0308(9)	0.0337(10)	-0.0089(8)	-0.0032(7)	0.0040(7)
C14	0.0226(9)	0.0298(9)	0.0327(10)	-0.0071(8)	-0.0008(7)	-0.0038(7)
C15	0.0248(10)	0.0311(10)	0.0408(12)	-0.0077(9)	-0.0031(8)	0.0002(8)
C16	0.0241(10)	0.0273(9)	0.0344(10)	-0.0061(8)	-0.0037(7)	0.0001(7)
C17	0.0273(10)	0.0365(10)	0.0422(11)	-0.0106(9)	0.0006(8)	-0.0007(8)
C18	0.0245(11)	0.0429(12)	0.0524(13)	-0.0074(10)	0.0042(9)	-0.0046(9)
C19	0.0327(12)	0.0395(11)	0.0574(14)	-0.0069(10)	-0.0053(10)	-0.0096(9)
C20	0.0473(13)	0.0392(11)	0.0486(13)	-0.0170(10)	-0.0074(10)	-0.0079(10)
C21	0.0355(11)	0.0395(11)	0.0392(11)	-0.0124(9)	0.0014(9)	-0.0044(9)
C22	0.0336(11)	0.0304(9)	0.0280(10)	-0.0065(8)	-0.0013(8)	-0.0012(8)
C23	0.0369(12)	0.0452(12)	0.0398(12)	-0.0155(10)	-0.0041(9)	-0.0053(9)
C24	0.0610(16)	0.0559(14)	0.0410(13)	-0.0214(11)	-0.0025(11)	-0.0153(12)
C25	0.0787(18)	0.0402(12)	0.0428(13)	-0.0191(10)	0.0061(12)	-0.0060(12)
C26	0.0623(16)	0.0448(13)	0.0509(14)	-0.0186(11)	-0.0024(11)	0.0132(11)
C27	0.0422(12)	0.0430(12)	0.0455(13)	-0.0157(10)	-0.0058(9)	0.0062(9)

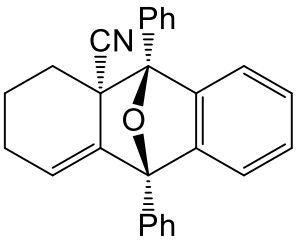
The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H2A	0.1137	0.0017	0.3546	0.042
H3A	-0.0796	-0.0105	0.4383	0.051
H3B	-0.1129	0.0588	0.3458	0.051
H4A	-0.0968	0.1591	0.4732	0.048
H4B	-0.2013	0.1867	0.4048	0.048
H5A	-0.0709	0.3633	0.3841	0.044
H5B	-0.0526	0.3147	0.3077	0.044
H9A	0.1013	0.5411	0.1795	0.044
H10A	0.1136	0.5060	0.0531	0.054
H11A	0.2031	0.3280	0.0416	0.053
H12A	0.2848	0.1770	0.1556	0.045
H17A	0.4086	0.4743	0.3735	0.038
H18A	0.4324	0.6630	0.3941	0.044
H19A	0.2590	0.7955	0.3805	0.053
H20A	0.0603	0.7383	0.3463	0.058
H21A	0.0359	0.5506	0.3244	0.049
H23A	0.3220	-0.0041	0.4447	0.045
H24A	0.4940	-0.1398	0.4715	0.055
H25A	0.6672	-0.1088	0.3777	0.056
H26A	0.6658	0.0557	0.2571	0.055
H27A	0.4933	0.1903	0.2299	0.047
H2B	0.5877	0.4658	0.8432	0.041
H3C	0.7024	0.2729	0.8935	0.049
H3D	0.6970	0.3142	0.7967	0.049
H4C	0.5715	0.1140	0.9124	0.053
H4D	0.6362	0.1199	0.8263	0.053
H5C	0.4565	0.2288	0.7582	0.045
H5D	0.4096	0.1011	0.8233	0.045
H9B	0.2013	0.3123	0.6549	0.040
H10B	0.2679	0.4796	0.5414	0.045
H11B	0.3623	0.6516	0.5587	0.043
H12B	0.3882	0.6635	0.6897	0.038
H17B	0.0254	0.2563	0.9284	0.043
H18B	-0.1321	0.1037	0.9542	0.050
H19B	-0.1300	-0.0323	0.8804	0.054
H20B	0.0309	-0.0188	0.7816	0.053
H21B	0.1909	0.1306	0.7571	0.046
H23B	0.4920	0.5588	0.9188	0.048
H24B	0.4772	0.7311	0.9608	0.061
H25B	0.2906	0.8460	0.9439	0.063
H26B	0.1136	0.7836	0.8880	0.062
H27B	0.1308	0.6180	0.8395	0.052

X-ray Data for Product 13d



13d

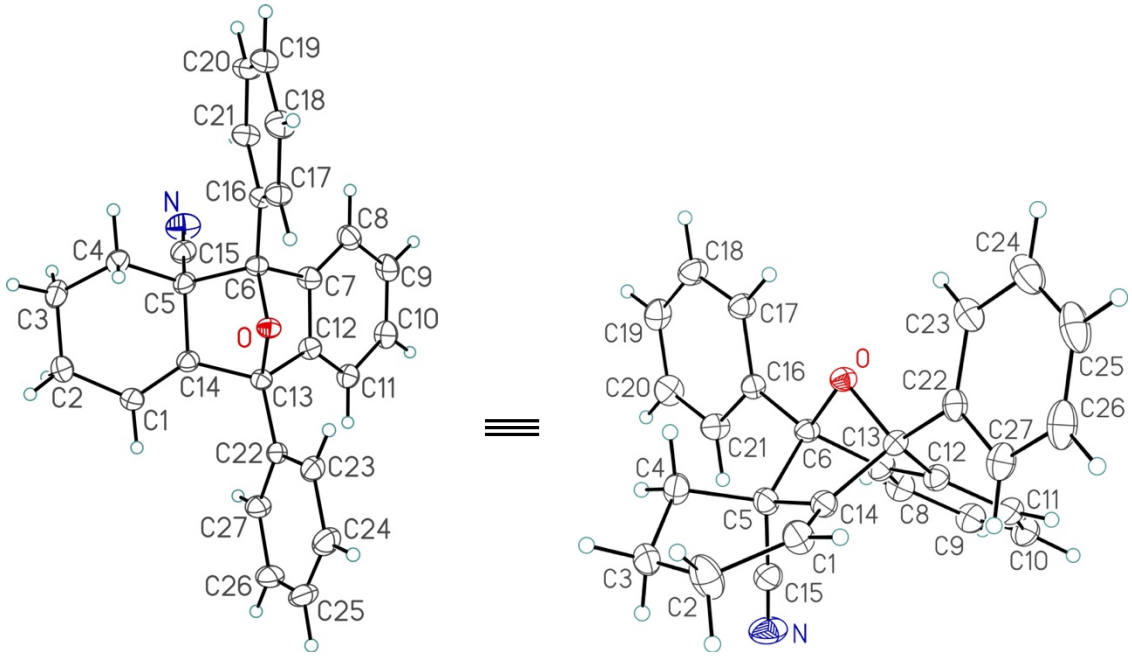


Table 1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_{27}H_{21}NO$
formula weight	375.45
crystal dimensions (mm)	0.34 × 0.21 × 0.06
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	14.8685 (8)
b (Å)	8.0336 (4)
c (Å)	16.4560 (9)
β (deg)	93.1431 (7)
V (Å^3)	1962.67 (18)
Z	4

ρ_{calcd} (g cm^{-3})	1.271
μ (mm^{-1})	0.077

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	52.89
total data collected	14714 ($-18 \le h \le 18$, $-10 \le k \le 10$, $-20 \le l \le 20$)
independent reflections	4038 (R_{int} = 0.0358)
number of observed reflections (*NO*)	3140 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods/dual space (*SHELXD*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	1.0000–0.9012
data/restraints/parameters	4038 / 0 / 262
goodness-of-fit (S)[e] [all data]	1.078
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0562
wR_2 [all data]	0.1652
largest difference peak and hole	0.779 and –0.282 e Å^{-3}

[a]Obtained from least-squares refinement of 5004 reflections with $4.96° < 2\theta < 51.46°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Schneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, *D58*, 1772-1779.

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0809P)^2 + 0.8151P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O	0.12733(8)	0.16615(15)	0.48272(7)	0.0285(3)*
N	0.39612(14)	-0.1294(3)	0.52544(13)	0.0578(6)*
C1	0.30903(14)	0.2916(3)	0.38548(12)	0.0396(5)*
C2	0.39145(17)	0.3671(4)	0.42596(15)	0.0568(7)*
C3	0.40635(14)	0.3337(3)	0.51482(13)	0.0430(5)*
C4	0.32413(14)	0.2703(3)	0.55586(12)	0.0377(5)*
C5	0.28197(13)	0.1245(3)	0.50916(11)	0.0345(4)*
C6	0.18588(12)	0.0624(2)	0.53356(11)	0.0283(4)*
C7	0.17075(14)	-0.1058(2)	0.49067(12)	0.0353(4)*
C8	0.16660(15)	-0.2675(3)	0.51641(14)	0.0425(5)*
C9	0.15235(15)	-0.3918(3)	0.45727(14)	0.0437(5)*
C10	0.14280(15)	-0.3515(3)	0.37498(14)	0.0428(5)*
C11	0.14471(13)	-0.1846(2)	0.34977(13)	0.0358(4)*
C12	0.15831(13)	-0.0651(2)	0.40817(11)	0.0330(4)*
C13	0.16217(12)	0.1243(2)	0.40351(10)	0.0276(4)*
C14	0.25940(12)	0.1805(2)	0.42192(11)	0.0319(4)*
C15	0.34703(14)	-0.0185(3)	0.51652(12)	0.0406(5)*
C16	0.16781(12)	0.0759(2)	0.62189(11)	0.0297(4)*
C17	0.09843(13)	0.1729(3)	0.64883(12)	0.0359(4)*
C18	0.08543(15)	0.1849(3)	0.73168(13)	0.0441(5)*
C19	0.14030(15)	0.1001(3)	0.78776(13)	0.0444(5)*
C20	0.20952(16)	0.0020(3)	0.76106(13)	0.0448(5)*
C21	0.22303(14)	-0.0100(3)	0.67895(12)	0.0393(5)*
C22	0.10887(13)	0.2045(2)	0.33437(11)	0.0311(4)*
C23	0.02467(14)	0.2724(3)	0.34571(13)	0.0402(5)*
C24	-0.02312(16)	0.3499(3)	0.28124(16)	0.0528(6)*
C25	0.01247(19)	0.3604(3)	0.20600(15)	0.0569(7)*
C26	0.09520(19)	0.2892(3)	0.19322(14)	0.0532(6)*
C27	0.14311(16)	0.2091(3)	0.25732(12)	0.0417(5)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
O	C6	1.440(2)	C10	C11	1.405(3)
O	C13	1.468(2)	C11	C12	1.366(3)
N	C15	1.156(3)	C12	C13	1.525(3)
C1	C2	1.491(3)	C13	C14	1.529(3)
C1	C14	1.323(3)	C13	C22	1.496(2)
C2	C3	1.491(3)	C16	C17	1.385(3)
C3	C4	1.517(3)	C16	C21	1.395(3)
C4	C5	1.518(3)	C17	C18	1.391(3)
C5	C6	1.585(3)	C18	C19	1.378(3)
C5	C14	1.524(3)	C19	C20	1.386(3)
C5	C15	1.502(3)	C20	C21	1.380(3)
C6	C7	1.535(3)	C22	C23	1.388(3)
C6	C16	1.496(2)	C22	C27	1.392(3)
C7	C8	1.369(3)	C23	C24	1.391(3)
C7	C12	1.399(3)	C24	C25	1.375(4)
C8	C9	1.402(3)	C25	C26	1.383(4)
C9	C10	1.392(3)	C26	C27	1.397(3)

Table 4. Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C6	O	C13	98.74(12)	O	C13	C12	99.65(13)
C2	C1	C14	122.50(19)	O	C13	C14	97.61(13)
C1	C2	C3	116.04(18)	O	C13	C22	112.27(14)
C2	C3	C4	114.65(18)	C12	C13	C14	108.79(15)
C3	C4	C5	110.76(16)	C12	C13	C22	116.60(15)
C4	C5	C6	117.87(16)	C14	C13	C22	118.66(15)
C4	C5	C14	108.22(16)	C1	C14	C5	121.78(17)
C4	C5	C15	107.64(16)	C1	C14	C13	130.86(18)
C6	C5	C14	100.16(14)	C5	C14	C13	104.87(15)
C6	C5	C15	108.93(16)	N	C15	C5	177.2(2)
C14	C5	C15	114.15(16)	C6	C16	C17	121.88(17)
O	C6	C5	101.27(14)	C6	C16	C21	119.18(16)
O	C6	C7	100.00(14)	C17	C16	C21	118.93(18)
O	C6	C16	112.81(14)	C16	C17	C18	119.92(19)
C5	C6	C7	105.77(15)	C17	C18	C19	120.9(2)
C5	C6	C16	115.82(15)	C18	C19	C20	119.41(19)
C7	C6	C16	118.71(15)	C19	C20	C21	120.0(2)
C6	C7	C8	134.51(19)	C16	C21	C20	120.82(19)
C6	C7	C12	104.39(15)	C13	C22	C23	120.73(17)
C8	C7	C12	121.09(19)	C13	C22	C27	119.94(18)
C7	C8	C9	118.0(2)	C23	C22	C27	119.32(18)
C8	C9	C10	120.87(19)	C22	C23	C24	120.0(2)
C9	C10	C11	120.44(19)	C23	C24	C25	120.6(2)
C10	C11	C12	117.90(19)	C24	C25	C26	120.1(2)
C7	C12	C11	121.69(18)	C25	C26	C27	119.8(2)
C7	C12	C13	106.19(16)	C22	C27	C26	120.2(2)
C11	C12	C13	132.12(18)				

Table 5. Torsional Angles (deg)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C13	O	C6	C5	55.47(15)	C7	C6	C16	C21	67.4(2)
C13	O	C6	C7	-52.98(15)	C6	C7	C8	C9	-179.2(2)
C13	O	C6	C16	179.91(14)	C12	C7	C8	C9	2.0(3)
C6	O	C13	C12	51.30(15)	C6	C7	C12	C11	178.55(17)
C6	O	C13	C14	-59.33(15)	C6	C7	C12	C13	-2.3(2)
C6	O	C13	C22	175.38(14)	C8	C7	C12	C11	-2.3(3)
C14	C1	C2	C3	-10.4(4)	C8	C7	C12	C13	176.82(19)
C2	C1	C14	C5	1.5(3)	C7	C8	C9	C10	0.0(3)
C2	C1	C14	C13	160.7(2)	C8	C9	C10	C11	-1.8(3)
C1	C2	C3	C4	-16.4(3)	C9	C10	C11	C12	1.5(3)
C2	C3	C4	C5	50.5(3)	C10	C11	C12	C7	0.5(3)
C3	C4	C5	C6	-169.25(17)	C10	C11	C12	C13	-178.40(19)
C3	C4	C5	C14	-56.7(2)	C7	C12	C13	O	-29.89(18)
C3	C4	C5	C15	67.2(2)	C7	C12	C13	C14	71.63(19)
C4	C5	C6	O	88.40(19)	C7	C12	C13	C22	-150.89(17)
C4	C5	C6	C7	-167.69(16)	C11	C12	C13	O	149.1(2)
C4	C5	C6	C16	-34.0(2)	C11	C12	C13	C14	-109.3(2)
C14	C5	C6	O	-28.59(17)	C11	C12	C13	C22	28.1(3)
C14	C5	C6	C7	75.31(17)	O	C13	C14	C1	-121.7(2)
C14	C5	C6	C16	-150.97(16)	O	C13	C14	C5	40.11(17)
C15	C5	C6	O	-148.65(15)	C12	C13	C14	C1	135.3(2)
C15	C5	C6	C7	-44.75(19)	C12	C13	C14	C5	-62.84(18)
C15	C5	C6	C16	88.97(19)	C22	C13	C14	C1	-1.1(3)
C4	C5	C14	C1	32.5(3)	C22	C13	C14	C5	160.69(16)
C4	C5	C14	C13	-131.44(16)	O	C13	C22	C23	-15.1(2)
C6	C5	C14	C1	156.43(19)	O	C13	C22	C27	165.94(16)
C6	C5	C14	C13	-7.47(18)	C12	C13	C22	C23	99.0(2)
C15	C5	C14	C1	-87.4(2)	C12	C13	C22	C27	-80.0(2)
C15	C5	C14	C13	108.73(18)	C14	C13	C22	C23	-127.84(19)
O	C6	C7	C8	-144.4(2)	C14	C13	C22	C27	53.2(2)
O	C6	C7	C12	34.50(18)	C6	C16	C17	C18	-178.48(19)
C5	C6	C7	C8	110.7(3)	C21	C16	C17	C18	0.7(3)
C5	C6	C7	C12	-70.33(18)	C6	C16	C21	C20	178.72(19)
C16	C6	C7	C8	-21.4(3)	C17	C16	C21	C20	-0.5(3)
C16	C6	C7	C12	157.55(16)	C16	C17	C18	C19	-0.6(3)
O	C6	C16	C17	3.0(2)	C17	C18	C19	C20	0.2(3)
O	C6	C16	C21	-176.13(16)	C18	C19	C20	C21	0.0(3)
C5	C6	C16	C17	119.1(2)	C19	C20	C21	C16	0.1(3)
C5	C6	C16	C21	-60.1(2)	C13	C22	C23	C24	178.48(19)
C7	C6	C16	C17	-113.4(2)	C27	C22	C23	C24	-2.5(3)

Table 5. Torsional Angles (continued)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C13	C22	C27	C26	-177.57(19)	C23	C24	C25	C26	1.9(4)
C23	C22	C27	C26	3.4(3)	C24	C25	C26	C27	-1.0(4)
C22	C23	C24	C25	-0.1(3)	C25	C26	C27	C22	-1.7(3)

Table 6. Anisotropic Displacement Parameters (U_{ij}, Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O	0.0301(7)	0.0298(7)	0.0256(7)	0.0026(5)	0.0023(5)	0.0055(5)
N	0.0525(12)	0.0685(14)	0.0526(12)	0.0030(10)	0.0043(9)	0.0301(11)
C1	0.0389(11)	0.0471(12)	0.0327(10)	0.0052(9)	0.0018(8)	-0.0050(9)
C2	0.0483(13)	0.0734(18)	0.0483(14)	0.0130(12)	-0.0008(11)	-0.0271(12)
C3	0.0353(11)	0.0512(13)	0.0425(12)	-0.0106(10)	0.0023(9)	-0.0094(9)
C4	0.0405(11)	0.0391(11)	0.0331(10)	-0.0047(8)	-0.0005(8)	-0.0044(9)
C5	0.0297(10)	0.0460(12)	0.0280(10)	-0.0019(8)	0.0018(7)	-0.0034(8)
C6	0.0284(9)	0.0292(9)	0.0272(9)	0.0019(7)	0.0013(7)	0.0052(7)
C7	0.0431(11)	0.0285(10)	0.0345(10)	-0.0004(8)	0.0028(8)	0.0033(8)
C8	0.0465(12)	0.0362(11)	0.0451(12)	0.0050(9)	0.0041(9)	-0.0035(9)
C9	0.0490(12)	0.0237(10)	0.0583(14)	0.0008(9)	0.0026(10)	-0.0003(9)
C10	0.0459(12)	0.0297(10)	0.0527(13)	-0.0087(9)	0.0035(10)	-0.0004(9)
C11	0.0360(10)	0.0349(10)	0.0367(11)	-0.0053(8)	0.0024(8)	0.0000(8)
C12	0.0356(10)	0.0296(10)	0.0335(10)	-0.0013(8)	0.0009(8)	0.0028(8)
C13	0.0308(9)	0.0272(9)	0.0250(9)	-0.0017(7)	0.0031(7)	0.0009(7)
C14	0.0303(9)	0.0383(10)	0.0272(9)	-0.0009(8)	0.0022(7)	0.0009(8)
C15	0.0386(11)	0.0489(13)	0.0344(11)	-0.0028(9)	0.0028(8)	0.0031(10)
C16	0.0309(9)	0.0318(9)	0.0267(9)	0.0014(7)	0.0033(7)	-0.0015(8)
C17	0.0372(10)	0.0392(11)	0.0317(10)	0.0002(8)	0.0047(8)	0.0042(8)
C18	0.0455(12)	0.0505(13)	0.0376(11)	-0.0050(9)	0.0135(9)	0.0021(10)
C19	0.0523(13)	0.0536(13)	0.0281(10)	-0.0001(9)	0.0090(9)	-0.0100(10)
C20	0.0510(12)	0.0525(13)	0.0308(10)	0.0105(9)	0.0018(9)	-0.0001(10)
C21	0.0413(11)	0.0435(12)	0.0332(10)	0.0060(9)	0.0038(8)	0.0070(9)
C22	0.0367(10)	0.0263(9)	0.0297(9)	0.0009(7)	-0.0041(7)	-0.0059(8)
C23	0.0362(11)	0.0391(11)	0.0442(11)	0.0042(9)	-0.0066(9)	-0.0026(9)
C24	0.0460(13)	0.0485(13)	0.0617(16)	0.0068(11)	-0.0181(11)	0.0008(10)
C25	0.0695(17)	0.0483(14)	0.0493(14)	0.0121(11)	-0.0296(12)	-0.0081(12)
C26	0.0749(17)	0.0532(14)	0.0300(11)	0.0048(10)	-0.0102(11)	-0.0141(12)
C27	0.0526(13)	0.0426(12)	0.0295(10)	0.0000(9)	-0.0015(9)	-0.0044(10)

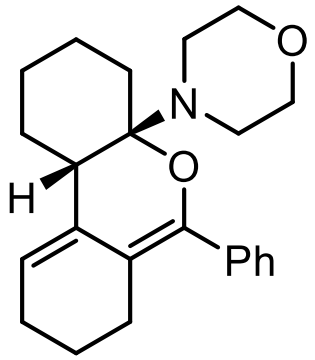
The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H1	0.2915	0.3246	0.3315	0.047
H2A	0.3885	0.4891	0.4178	0.068
H2B	0.4445	0.3259	0.3982	0.068
H3A	0.4270	0.4377	0.5421	0.052
H3B	0.4552	0.2506	0.5227	0.052
H4A	0.2794	0.3611	0.5588	0.045
H4B	0.3418	0.2350	0.6121	0.045
H8	0.1732	-0.2947	0.5726	0.051
H9	0.1492	-0.5050	0.4736	0.052
H10	0.1349	-0.4375	0.3356	0.051
H11	0.1368	-0.1557	0.2939	0.043
H17	0.0598	0.2312	0.6108	0.043
H18	0.0381	0.2524	0.7498	0.053
H19	0.1308	0.1087	0.8442	0.053
H20	0.2477	-0.0569	0.7993	0.054
H21	0.2705	-0.0775	0.6611	0.047
H23	-0.0004	0.2659	0.3975	0.048
H24	-0.0808	0.3960	0.2892	0.063
H25	-0.0198	0.4165	0.1628	0.068
H26	0.1194	0.2949	0.1410	0.064
H27	0.1992	0.1576	0.2483	0.050

X-ray Data for Product 16a



16a

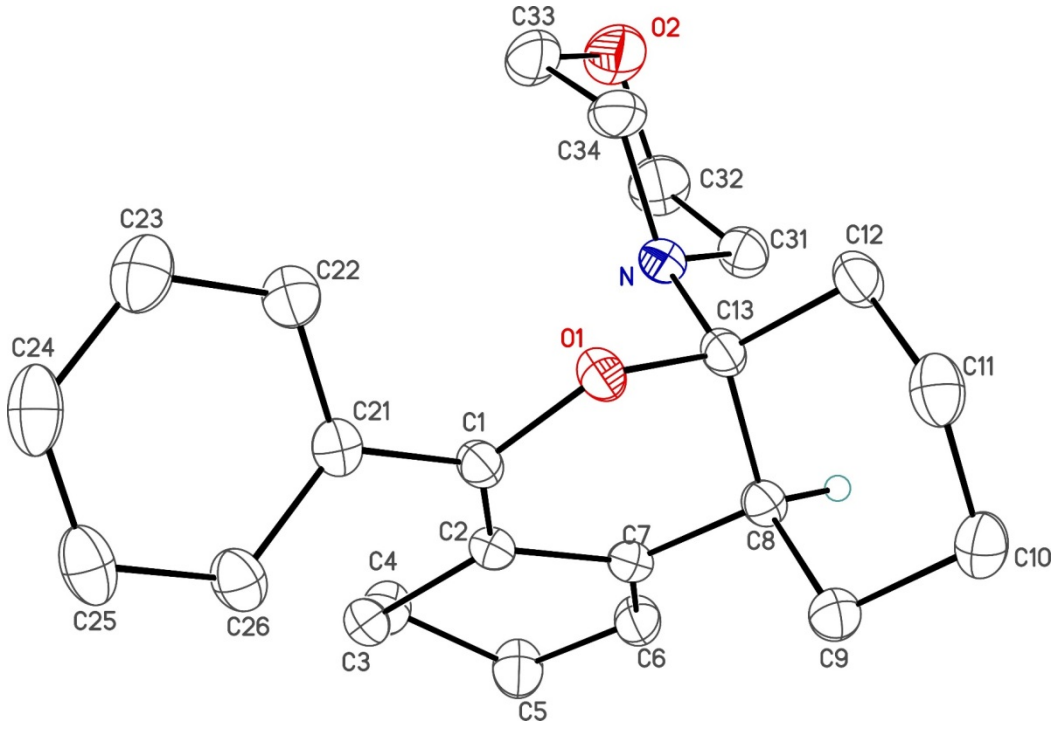


Table 1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_{23}H_{29}NO_2$
formula weight	351.47
crystal dimensions (mm)	0.36 × 0.27 × 0.26
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	15.4338(3)
b (Å)	8.3344(2)
c (Å)	16.0463(3)
β (deg)	110.5183(8)
V (Å^3)	1933.12(7)
Z	4
ρ_{calcd} (g cm^{-3})	1.208
μ (mm^{-1})	0.593
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–80
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	149.93
total data collected	66578 (-19 ≤ h ≤ 19, -9 ≤ k ≤ 10, -19 ≤ l ≤ 19)
independent reflections	3902 (R_{int} = 0.0480)
number of observed reflections (*NO*)	3560 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2017*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9621–0.7950
data/restraints/parameters	3902 / 0 / 239
goodness-of-fit (S)[e] [all data]	1.103
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0430
wR_2 [all data]	0.1286
largest difference peak and hole	0.183 and –0.213 e Å^{-3}

[a]Obtained from least-squares refinement of 9802 reflections with 6.12° < 2θ < 148.34°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

(continued)

Table 1. Crystallographic Experimental Details (continued)

[c]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2017*)

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0673P)^2 + 0.4530P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O1	0.71104(5)	0.37267(10)	0.68193(5)	0.0344(2)*
O2	0.53163(9)	-0.12043(17)	0.69359(9)	0.0693(4)*
N	0.64683(7)	0.11503(13)	0.65666(7)	0.0359(3)*
C1	0.78813(8)	0.34536(14)	0.75709(7)	0.0313(3)*
C2	0.84835(8)	0.22543(14)	0.76283(7)	0.0309(3)*
C3	0.92586(8)	0.18042(16)	0.84794(8)	0.0359(3)*
C4	0.93700(10)	-0.00132(17)	0.85492(9)	0.0436(3)*
C5	0.95663(11)	-0.0698(2)	0.77551(9)	0.0513(4)*
C6	0.88951(9)	-0.00518(17)	0.68988(9)	0.0410(3)*
C7	0.83861(8)	0.12677(15)	0.68487(8)	0.0322(3)*
C8	0.76949(8)	0.18703(14)	0.59835(8)	0.0322(3)*
H8	0.7525(9)	0.0988(17)	0.5553(9)	0.032(3)
C9	0.80872(9)	0.32148(17)	0.55623(8)	0.0397(3)*
C10	0.73538(10)	0.38577(17)	0.47183(9)	0.0443(3)*
C11	0.65370(11)	0.45178(17)	0.49318(9)	0.0472(3)*
C12	0.61212(9)	0.32224(17)	0.53497(8)	0.0408(3)*
C13	0.68338(8)	0.24444(14)	0.61675(8)	0.0325(3)*
C21	0.79393(8)	0.46500(14)	0.82682(8)	0.0335(3)*
C22	0.71454(10)	0.51525(16)	0.84195(9)	0.0411(3)*
C23	0.71993(12)	0.62699(18)	0.90769(10)	0.0509(4)*
C24	0.80441(12)	0.68916(16)	0.95970(9)	0.0516(4)*
C25	0.88332(12)	0.64203(17)	0.94491(9)	0.0500(4)*
C26	0.87858(10)	0.53197(16)	0.87855(9)	0.0423(3)*
C31	0.63129(10)	-0.04054(16)	0.61192(9)	0.0424(3)*
C32	0.60945(13)	-0.1643(2)	0.67040(13)	0.0620(4)*
C33	0.54912(12)	0.0305(3)	0.73736(11)	0.0661(5)*
C34	0.56526(10)	0.1582(2)	0.67802(10)	0.0510(4)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
O1	C1	1.3842(14)	C8	C9	1.5381(17)
O1	C13	1.4510(14)	C8	C13	1.5354(16)
O2	C32	1.424(2)	C8	H8	0.980(14)
O2	C33	1.420(2)	C9	C10	1.5258(18)
N	C13	1.4646(16)	C10	C11	1.521(2)
N	C31	1.4606(17)	C11	C12	1.526(2)
N	C34	1.4608(17)	C12	C13	1.5299(16)
C1	C2	1.3458(17)	C21	C22	1.3944(18)
C1	C21	1.4778(16)	C21	C26	1.3954(18)
C2	C3	1.5139(15)	C22	C23	1.3876(19)
C2	C7	1.4601(16)	C23	C24	1.379(2)
C3	C4	1.5241(19)	C24	C25	1.377(2)
C4	C5	1.5203(19)	C25	C26	1.3878(19)
C5	C6	1.5011(19)	C31	C32	1.510(2)
C6	C7	1.3375(18)	C33	C34	1.506(2)
C7	C8	1.5097(16)			

Table 4. Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	O1	C13	116.92(9)	C8	C9	C10	111.23(10)
C32	O2	C33	108.97(12)	C9	C10	C11	110.04(11)
C13	N	C31	117.44(10)	C10	C11	C12	110.65(11)
C13	N	C34	114.65(11)	C11	C12	C13	112.96(11)
C31	N	C34	109.11(10)	O1	C13	N	106.75(9)
O1	C1	C2	122.94(10)	O1	C13	C8	108.20(9)
O1	C1	C21	110.74(10)	O1	C13	C12	104.33(9)
C2	C1	C21	126.32(11)	N	C13	C8	110.28(10)
C1	C2	C3	123.65(11)	N	C13	C12	114.57(10)
C1	C2	C7	119.90(10)	C8	C13	C12	112.19(10)
C3	C2	C7	116.41(10)	C1	C21	C22	120.72(11)
C2	C3	C4	110.22(10)	C1	C21	C26	121.06(11)
C3	C4	C5	111.21(12)	C22	C21	C26	118.22(12)
C4	C5	C6	110.88(11)	C21	C22	C23	120.78(13)
C5	C6	C7	123.52(12)	C22	C23	C24	120.28(14)
C2	C7	C6	121.99(11)	C23	C24	C25	119.62(13)
C2	C7	C8	115.33(10)	C24	C25	C26	120.58(14)
C6	C7	C8	122.65(11)	C21	C26	C25	120.49(14)
C7	C8	C9	112.73(10)	N	C31	C32	109.56(12)
C7	C8	C13	107.88(9)	O2	C32	C31	112.31(14)
C7	C8	H8	109.1(8)	O2	C33	C34	110.99(13)
C9	C8	C13	110.98(10)	N	C34	C33	108.76(14)
C9	C8	H8	106.6(8)				

Table 5. Torsional Angles (deg)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C13	O1	C1	C2	15.13(16)	C3	C4	C5	C6	-48.56(17)
C13	O1	C1	C21	-165.38(9)	C4	C5	C6	C7	18.1(2)
C1	O1	C13	N	70.33(12)	C5	C6	C7	C2	3.7(2)
C1	O1	C13	C8	-48.36(13)	C5	C6	C7	C8	-178.21(13)
C1	O1	C13	C12	-167.99(10)	C2	C7	C8	C9	80.52(13)
C33	O2	C32	C31	-57.80(19)	C2	C7	C8	C13	-42.37(13)
C32	O2	C33	C34	59.97(19)	C6	C7	C8	C9	-97.66(14)
C31	N	C13	O1	-168.06(10)	C6	C7	C8	C13	139.45(12)
C31	N	C13	C8	-50.74(13)	C7	C8	C9	C10	-176.78(10)
C31	N	C13	C12	76.98(14)	C13	C8	C9	C10	-55.64(13)
C34	N	C13	O1	61.84(12)	C7	C8	C13	O1	60.27(12)
C34	N	C13	C8	179.17(10)	C7	C8	C13	N	-56.15(12)
C34	N	C13	C12	-53.12(14)	C7	C8	C13	C12	174.83(10)
C13	N	C31	C32	170.44(12)	C9	C8	C13	O1	-63.68(12)
C34	N	C31	C32	-56.93(15)	C9	C8	C13	N	179.89(9)
C13	N	C34	C33	-166.63(11)	C9	C8	C13	C12	50.87(13)
C31	N	C34	C33	59.30(14)	C8	C9	C10	C11	59.48(15)
O1	C1	C2	C3	-171.87(10)	C9	C10	C11	C12	-58.15(15)
O1	C1	C2	C7	5.80(18)	C10	C11	C12	C13	54.43(15)
C21	C1	C2	C3	8.72(19)	C11	C12	C13	O1	65.94(13)
C21	C1	C2	C7	-173.61(11)	C11	C12	C13	N	-177.70(10)
O1	C1	C21	C22	39.77(15)	C11	C12	C13	C8	-50.96(14)
O1	C1	C21	C26	-139.53(12)	C1	C21	C22	C23	179.68(12)
C2	C1	C21	C22	-140.76(13)	C26	C21	C22	C23	-1.00(19)
C2	C1	C21	C26	39.94(18)	C1	C21	C26	C25	-178.82(12)
C1	C2	C3	C4	141.23(12)	C22	C21	C26	C25	1.86(19)
C7	C2	C3	C4	-36.51(14)	C21	C22	C23	C24	-0.5(2)
C1	C2	C7	C6	-171.78(12)	C22	C23	C24	C25	1.2(2)
C1	C2	C7	C8	10.02(16)	C23	C24	C25	C26	-0.4(2)
C3	C2	C7	C6	6.05(17)	C24	C25	C26	C21	-1.2(2)
C3	C2	C7	C8	-172.15(10)	N	C31	C32	O2	56.98(17)
C2	C3	C4	C5	58.16(15)	O2	C33	C34	N	-61.69(17)

Table 6. Anisotropic Displacement Parameters (U_{ij}, Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13} U_{12}
O1	0.0314(4)	0.0355(4)	0.0313(4)	-0.0040(3)	0.0049(3)0.0027(3)
O2	0.0673(7)	0.0807(9)	0.0687(8)	-0.0103(6)	0.0346(6) -0.0364(7)
N	0.0288(5)	0.0434(6)	0.0340(5)	-0.0046(4)	0.0092(4) -0.0064(4)
C1	0.0291(5)	0.0332(6)	0.0289(6)	-0.0008(4)	0.0067(4) -0.0038(4)
C2	0.0265(5)	0.0340(6)	0.0310(6)	-0.0012(4)	0.0086(4) -0.0033(4)
C3	0.0307(6)	0.0429(7)	0.0308(6)	0.0007(5)	0.0067(5)0.0003(5)
C4	0.0443(7)	0.0460(7)	0.0384(7)	0.0057(5)	0.0120(6)0.0129(6)
C5	0.0493(8)	0.0573(9)	0.0437(8)	0.0001(6)	0.0120(6)0.0222(7)
C6	0.0374(6)	0.0482(7)	0.0363(6)	-0.0051(5)	0.0115(5)0.0087(5)
C7	0.0260(5)	0.0378(6)	0.0322(6)	-0.0026(5)	0.0095(4) -0.0019(4)
C8	0.0301(6)	0.0342(6)	0.0305(6)	-0.0034(5)	0.0084(4) -0.0025(4)
C9	0.0395(6)	0.0438(7)	0.0361(6)	-0.0012(5)	0.0138(5) -0.0062(5)
C10	0.0560(8)	0.0405(7)	0.0356(7)	0.0015(5)	0.0152(6) -0.0033(6)
C11	0.0573(8)	0.0428(7)	0.0357(7)	0.0040(6)	0.0091(6)0.0082(6)
C12	0.0345(6)	0.0489(7)	0.0323(6)	-0.0003(5)	0.0033(5)0.0054(5)
C13	0.0292(5)	0.0357(6)	0.0286(6)	-0.0036(5)	0.0053(4) -0.0010(5)
C21	0.0399(6)	0.0275(5)	0.0310(6)	0.0021(4)	0.0097(5) -0.0003(5)
C22	0.0435(7)	0.0366(6)	0.0413(7)	-0.0013(5)	0.0125(5)0.0059(5)
C23	0.0669(9)	0.0414(7)	0.0458(8)	-0.0001(6)	0.0214(7)0.0162(7)
C24	0.0842(11)	0.0301(6)	0.0347(7)	-0.0021(5)	0.0137(7)0.0084(7)
C25	0.0647(9)	0.0356(7)	0.0390(7)	-0.0046(5)	0.0048(6) -0.0077(6)
C26	0.0458(7)	0.0365(7)	0.0402(7)	-0.0046(5)	0.0096(6) -0.0070(5)
C31	0.0426(7)	0.0415(7)	0.0419(7)	-0.0040(6)	0.0132(5) -0.0080(6)
C32	0.0672(10)	0.0554(9)	0.0659(10)	0.0055(8)	0.0263(8)

	-0.0161(8)				
C33	0.0552(9)	0.0973(14)	0.0539(9)	-0.0205(9)	0.0295(8)
	-0.0341(9)				
C34	0.0368(7)	0.0663(9)	0.0536(8)	-0.0184(7)	0.0206(6)
	-0.0129(6)				

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H3A	0.911935	0.221683	0.899722	0.043
H3B	0.984375	0.230072	0.848608	0.043
H4A	0.988509	-0.029007	0.910321	0.052
H4B	0.879726	-0.050090	0.858032	0.052
H5A	1.020473	-0.041585	0.780163	0.062
H5B	0.951860	-0.188206	0.775799	0.062
H6	0.882825	-0.061025	0.636365	0.049
H9A	0.831494	0.410015	0.599556	0.048
H9B	0.861746	0.279582	0.541682	0.048
H10A	0.762351	0.471730	0.445949	0.053
H10B	0.714138	0.298513	0.427430	0.053
H11A	0.605976	0.491397	0.437913	0.057
H11B	0.674382	0.543267	0.534817	0.057
H12A	0.583924	0.238216	0.490014	0.049
H12B	0.562306	0.370314	0.552375	0.049
H22	0.656065	0.472472	0.806844	0.049
H23	0.665197	0.660810	0.916915	0.061
H24	0.808146	0.764063	1.005457	0.062
H25	0.941520	0.685228	0.980449	0.060
H26	0.933365	0.501997	0.868263	0.051
H31A	0.687249	-0.073151	0.599509	0.051
H31B	0.579176	-0.032634	0.554524	0.051
H32A	0.596963	-0.268553	0.638876	0.074
H32B	0.663981	-0.177973	0.725425	0.074
H33A	0.604215	0.022045	0.792324	0.079
H33B	0.495682	0.061024	0.754519	0.079
H34A	0.510609	0.166859	0.622690	0.061
H34B	0.575020	0.263268	0.708693	0.061