

Supporting Information

Gold-catalyzed (4+2)-Annulations between α -Alkyl alkenylgold Carbenes and Benzisoxazoles with Reactive Alkyl Groups

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(1) Representative synthetic procedures

(A) General experimental:

Unless otherwise noted, all reactions were carried out under a N₂ atmosphere in reaction tube. Tetrahydrofuran was dried with sodium benzophenone and distilled before use. Dichloromethane were dried over CaH₂ and distilled before use. The triethylamine (Et₃N) were stored over 4 Å molecular sieves prior to use. Reagents were purchased from commercial sources and used without purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin layer chromatography carried out on 0.25 mm E. Merck silica gel plate (60f- 254) using UV light as visualizing agents and/or potassium permanganate (KMnO₄). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400, Varian 400, 500, and 600 MHz spectrometers using chloroform-*d* (CDCl₃) and *d*-acetone (CD₃)₂CO as the internal standard. Chemical shifts are reported in parts per million (ppm). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants *J* are reported in Hertz (Hz). The substrates **1a** and **1b** were prepared by using literature procedure.^{S1} The vinylallene substrates^{S2-S4} **4a-4t** and benzisoxazole substrates^{S5} **2a-2j** were prepared according to literature procedures.

(S1) Z. Liu, Q. Li, P. Liao and X. Bi, *Chem. Eur. J.*, 2017, **23**, 4756.

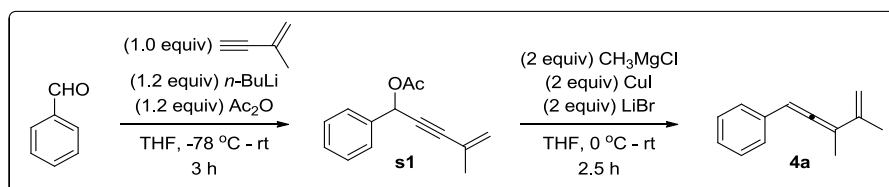
(S2) S. Bhunia and R.-S. Liu, *J. Am. Chem. Soc.*, 2008, **130**, 16488.

(S3) T. M. Macdonald and D. R. Reagan, *J. Org. Chem.*, 1980, **45**, 4740.

(S4) R. Chaudhari, H.-Y. Liao and R.-S. Liu, *Chem. Eur. J.*, 2009, **15**, 8895.

(S5) (a) J. Chauhan and S. Fletcher, *Tetrahedron Lett.*, 2012, **53**, 4951; (b) H. Jin, L. Huang, J. Xie, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2016, **55**, 794; (c) H. Jin, B. Tian, X. Song, J. Xie, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2016, **55**, 12688; (d) R. L. Sahani and R.-S. Liu, *Angew. Chem. Int. Ed.*, 2017, **56**, 12736.

(B) Synthesis of the substrate (3,4-dimethylpenta-1,2,4-trien-1-yl)benzene (**4a**):



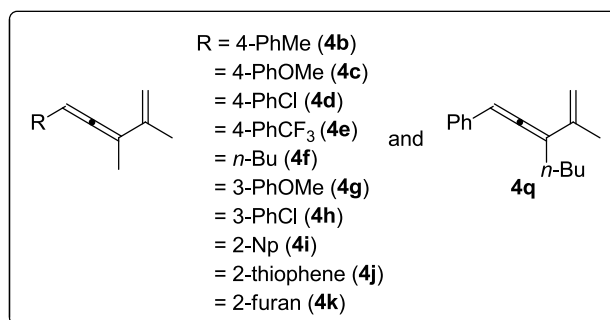
(a) Synthesis of 4-methyl-1-phenylpent-4-en-2-yn-1-yl acetate (**s1**):

To a THF (10 mL) solution of 2-methylbut-1-en-3-yne (1.0 g, 15.13 mmol) was added *n*-BuLi (2.5 M in hexane, 7.3 mL, 18.15 mmol) at -78 °C and stirred at this temperature for 0.5 h. The THF (10 mL) solution of PhCHO (1.61 g, 15.13 mmol) was added and the reaction mixture was stirred at rt for additional 1.5 h. The resulting mixture was quenched by acetic anhydride (1.86 g, 18.15 mmol) and stirred for next 1 h. After completion of reaction, saturated NH₄Cl was added and extracted with diethyl ether (2 x 50 mL). The combined organic layer were dried over MgSO₄ and concentrated under reduced pressure. The crude reaction mass was purified by silica column eluting with hexane/ethyl acetate (5:1) to afford 4-methyl-1-phenylpent-4-en-2-yn-1-ol **s1** (3.1 g, 14.48 mmol, 96%) as pale yellow oil.

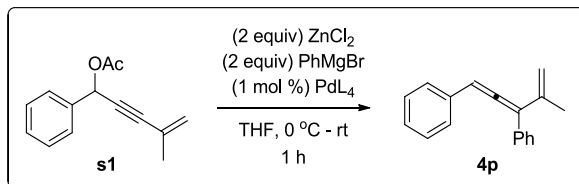
(b) Synthesis of (3,4-dimethylpenta-1,2,4-trien-1-yl)benzene (4a):

To a dry 250-mL flask were added LiBr (0.81 g, 9.33 mmol) and CuI (1.78 g, 9.33 mmol), evacuated and backfilled with N₂ balloon before dried THF (25 mL) was added. The reaction mixture was cooled to 0 °C, CH₃MgCl (3.0 M in THF, 2.1 mL, 9.33 mmol) was added. The resulting solution was stirred reaction mixture at 0 °C for additional 0.5 h. To this solution was added propargylic acetate (**s1**) (1 g, 4.67 mmol), and the mixture was stirred for 2 h. The resulting mixture was quenched by a saturated NH₄Cl, filtrated, and extracted with diethyl ether (2 x 50 mL). The extract was dried over MgSO₄, concentrated in vacuo and purified by a silica column to afford (3,4-dimethylpenta-1,2,4-trien-1-yl)benzene **4a** (0.600 g, 3.52 mmol, 76%) as colorless oil.

Substrates **4b-4k** and **4q** were synthesized using same as above procedure.



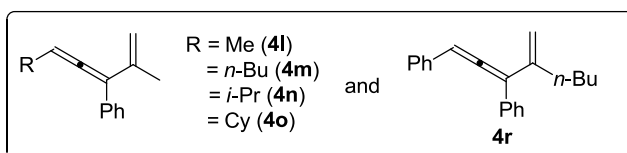
(C) Synthesis of the substrate (4-methylpenta-1,2,4-triene-1,3-diyl)dibenzene (4p):



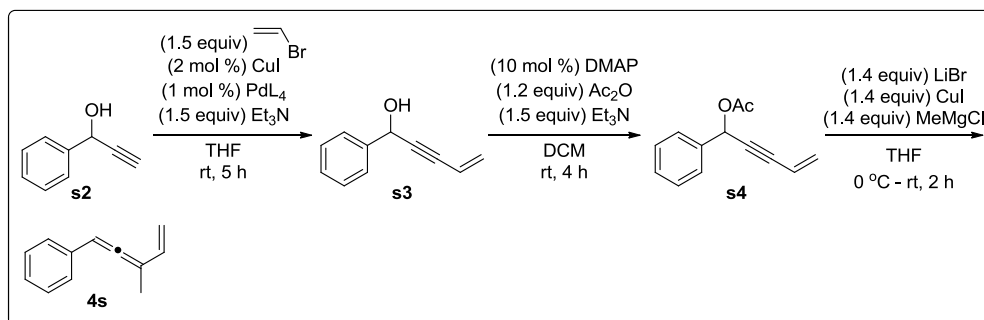
Synthesis of (4-methylpenta-1,2,4-triene-1,3-diyl)dibenzene (**4p**):

To a dry 250-mL flask was added ZnCl_2 (1.27 g, 9.93 mmol), dried in vacuo and refilled with N_2 balloon. To this flask were added dry THF (25 mL) and then PhMgBr (1.69 g, 9.93 mmol); the mixture was stirred at 25 °C for 0.5 h. The $[\text{Pd}(\text{PPh}_3)_4]$ (54.0 mg, 0.047 mmol) and compound **s1** (1 g, 4.67 mmol) were added to this reaction mixture; the resulting solution was stirred for 1 h before quenching with water. The organic layer was extracted with diethyl ether (2 x 25 mL), dried over MgSO_4 and concentrated under reduced pressure. The residue was eluted through a silica column to afford (4-methylpenta-1,2,4-triene-1,3-diyl)dibenzene **4p** (0.800 g, 3.44 mmol, 74%) as colorless liquid.

Substrates **4l-4o** and **4r** were synthesized using same as above procedure.



(D) Synthesis of the substrate (3-methylpenta-1,2,4-trien-1-yl)benzene (**4s**):



(a) Synthesis of 1-phenylpent-4-en-2-yn-1-ol (**s3**):

Copper (I) iodide (0.029 g, 0.15 mmol) and tetrakis(triphenylphosphin)palladium (0.087 g, 0.076 mmol) were dissolved in anhydrous and degassed Et_3N (3.2 mL, 22.7 mmol), and the mixture was cooled to 0 °C. To this solution was added alkyne **s2** (1 g, 7.57 mmol) and

vinyl bromide (1 M in THF, 1.21 g, 11.35 mmol), and the mixture was stirred at room temperature until a complete consumption of starting material. The reaction solution was filtered through a celite pad, concentrated and eluted through a silica column to give 1-phenylpent-4-en-2-yn-1-ol **s3** (0.550 g, 2.75 mmol, 46%) as colorless oil.

(b) Synthesis of 1-phenylpent-4-en-2-yn-1-yl acetate (s4**):**

To a DCM solution of 1-phenylpent-4-en-2-yn-1-ol (1.0 g, 6.33 mmol) were added DMAP (77 mg, 0.63 mmol), Et₃N (0.96 g, 9.49 mmol) and the mixtures were stirred at 0 °C for 15 min. To this solution was added Ac₂O (0.78 g, 7.59 mmol), and the mixture was slowly warmed to room temperature for a stirring of 4 h. The solution was quenched by water and extracted with DCM (2 x 25 mL). The combined organic layer was dried over MgSO₄, concentrated in vacuo, and further purified by a silica column to afford 1-phenylpent-4-en-2-yn-1-yl acetate **s4** (1.19 g, 7.52 mmol, 94%) as pale yellow oil.

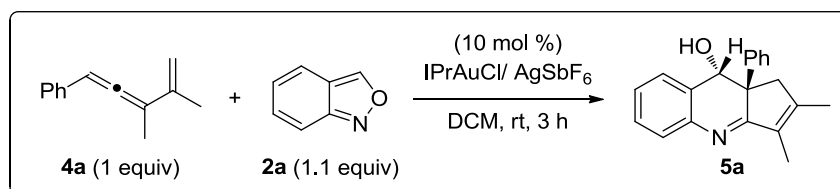
(c) Synthesis of (3-methylpenta-1,2,4-trien-1-yl)benzene (4s**):**

The substrate **1s** was synthesized using similar synthetic procedure of substrate **4a** from **s1**.

Substrate **4t** was prepared using same as above procedure of **4s**.

(2) Standard procedures for catalytic operation.

(a) Standard procedure for the synthesis of (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (5a**):**

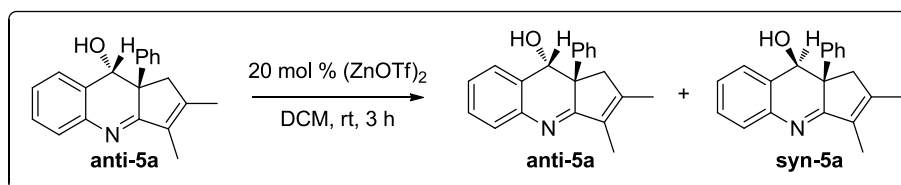


A catalytic tube was charged with IPrAuCl (0.036 g, 0.059 mmol) and AgNTf₂ (0.020 g, 0.059 mmol), and to this mixture was added dry DCM (0.5 mL). The resulting mixture was stirred at room temperature for 10 min. To this mixture was added a dry DCM solution (0.5 mL) of benzisoxazole (**2a**) (0.077 g, 0.646 mmol) followed by dropwise addition of (3,4-dimethylpenta-1,2,4-trien-1-yl)benzene (**4a**) (0.100 g, 0.587 mmol) in 1 mL DCM. After stirring at room temperature for 3 h, the reaction mixture was filtered over a short celite bed, concentrated, and eluted through a silica column (EA/hexane = 30/70) to give the desired

(9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (**5a**) (0.144 g, 0.498 mmol, 85%) as white solid.

The compounds **3**, **7**, **8**, and **9** were synthesized using same as above catalytic procedure.

(b) Standard procedure for the synthesis of (9*R*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (syn-5a**):**



To a DCM (4 mL) solution of (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (**5a**) (0.200 g, 0.69 mmol) was added Zn(OTf)₂ (0.050 g, 0.13 mmol), and refluxed for 48 hours. The reaction mixture was then filtered over a short celite bed, concentrated and eluted through a silica column (EA/hexane = 2/5) to give isomers dr ratio 4:1 the (**syn-5a**, 0.048 g, 0.13 mmol, 19%) and (**anti-5a**, 0.152 g, 0.52 mmol, 76%).

(3) Synthetic procedures for chemical functionalizations:

(i) Synthesis of (3*aR*,9*R*,9*aS*)-2,3-dimethyl-9*a*-phenyl-3*a*,4,9,9*a*-tetrahydro-1*H*-cyclopenta[*b*]quinolin-9-ol (5a-H**):**

To a CH₃OH (7 mL) solution of corresponding imine (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (**5a**) (0.100 g, 0.34 mmol) was added NaBH₄ (0.019 g, 0.50 mmol) and the resulting mixture was stirred at the 50 °C for 48 h. After completion, the reaction was quenched with saturated ammonium chloride solution and extracted with dichloromethane (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, and concentrated. The residue was purified via column chromatography (30% EtOAc/hexanes) to give **5a-H** (0.090 g, 0.30 mmol, 90%) as colorless liquid.

(ii) Synthesis of (1*aR*,7*S*,7*aS*,8*aS*)-1*a*,8*a*-dimethyl-7*a*-phenyl-7,7*a*,8,8*a*-tetrahydro-1*aH*-oxireno[2',3':4,5]cyclopenta[1,2-*b*]quinolin-7-ol (5a-O**):**

To a DCM (5 mL) solution of the (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-

cyclopenta[*b*]quinolin-9-ol (**5a**) (0.200 g, 0.69 mmol) was added *m*-CPBA (0.119 g, 0.69 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was then quenched with saturated NaHCO₃ solution and extracted with DCM (2 x 10 mL). The combined organic layer were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified via column chromatography (25% EtOAc/Hexanes) to afford compound **5a-O** (0.160 g, 0.52 mmol, 76%) as Colorless liquid.

(iii) Synthesis of (1*R*,4*S*,5*aS*,6*S*)-1,4-dimethyl-5*a*-phenyl-4,5,5*a*,6-tetrahydro-1*H*-1,4-epoxy[1,2]dioxepino[4,5-*b*]quinolin-6-yl acetate (5a-O₃**):**

(a) Synthesis of (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-yl acetate (5a-OAc**):**

To a DCM (10 mL) solution of (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (**5a**) (0.500 g, 1.72 mmol) was added Et₃N (0.364 mL, 2.59 mmol) and acetic anhydride (0.196 mL, 2.06 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. The saturated NaHCO₃ solution was added in to the reaction mixture and extracted with DCM (2 x 20 mL). The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (20% EtOAc/hexanes) to give **5a-OAc** (0.503 g, 1.52 mmol, 80%) as white solid.

(b) Synthesis of (1*R*,4*S*,5*aS*,6*S*)-1,4-dimethyl-5*a*-phenyl-4,5,5*a*,6-tetrahydro-1*H*-1,4-epoxy[1,2]dioxepino[4,5-*b*]quinolin-6-yl acetate (5a-O₃**):**

To a DCM (10 mL) solution of (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-yl acetate (**5a-OAc**) (0.333 g, 1 mmol) at -60 °C, a stream of O₃/O₂ (~ 1 mmol/min of O₃) was introduced through a disposable pipet for a period with the amount of alkene 4 min. Once complete, the reaction was sparged with O₂ and then N₂. The crude reaction mixture was concentrated and purified by flash chromatography with (25% EtOAc/Hexanes) to furnish the **5a-O₃** (0.323 g, 0.85 mmol, 85%) as white solid.

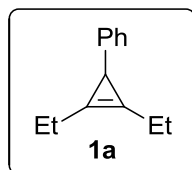
(iv) Synthesis of (9*S*,9*aS*)-2-methyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinoline-3,9-diol (7a'**):**

To a THF (10 mL) and MeOH (5 mL) solution of (9*S*,9*aS*)-9-hydroxy-2-methyl-9*a*-phenyl-

9,9a-dihydro-1*H*-cyclopenta[*b*]quinolin-3-yl acetate (**7a**) (0.170 g, 0.50 mmol) was added 4M aqueous NaOH (4 mL) solution at 0 °C. The reaction mixture was stirred at this temperature for 2 h. The solution was concentrated, then diluted with DCM and quenched with 1N HCl. The aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with saturated NaHCO₃, dried over MgSO₄, and concentrated. The residue was purified by column chromatography (25% EtOAc/hexanes) to give compound **7a'** (0.113 g, 0.38 mmol, 80%) as brown solid.

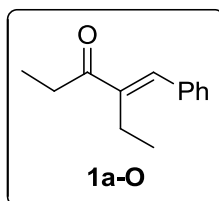
(4) Spectral data of key compounds

Spectral data for (2,3-diethylcycloprop-2-en-1-yl)benzene (**1a**):



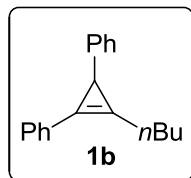
Colorless oil (0.079 g, 0.459 mmol, 70%); ¹H NMR (400 MHz, CDCl₃): δ 7.26 ~ 7.22 (m, 2H), 7.12 ~ 7.07 (m, 3H), 2.50 (s, 1H), 2.48 ~ 2.44 (m, 4H), 1.20 ~ 1.60 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 127.9, 125.3, 124.4, 111.3, 25.2, 17.9, 12.4.

Spectral data for (*E*)-4-benzylidenehexan-3-one (**1a-O**):



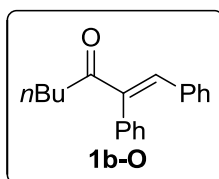
Colorless oil (0.021 g, 0.11 mmol, 19%); ¹H NMR (400 MHz, CDCl₃): δ 7.44 (s, 1H), 7.41 ~ 7.30 (m, 5H), 2.81 (q, *J* = 7.3 Hz, 2H), 2.53 (q, *J* = 7.4 Hz, 2H), 1.49 (t, *J* = 7.3 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 202.9, 143.6, 137.8, 135.9, 129.2, 128.5, 128.4, 31.0, 19.8, 13.8, 8.8; HRMS (ESI⁺, *m/z*) calcd for C₁₃H₁₇O [M+H]⁺: 189.1279, found: 189.1279.

Spectral data for (3-butylcycloprop-2-ene-1,2-diyl)dibenzene (**1b**):



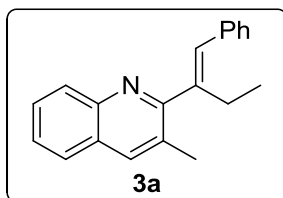
Colorless oil (0.124 g, 0.499 mmol, 76%); ^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, J = 6.8 Hz, 2H), 7.38 ~ 7.32 (m, 2H), 7.28 ~ 7.20 (m, 3H), 7.15 ~ 7.09 (m, 3H), 2.86 (s, 1H), 2.73 ~ 2.63 (m, 2H), 1.72 (p, J = 7.6 Hz, 2H), 1.49 ~ 1.41 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.1, 129.2, 128.6, 128.0, 127.8, 126.5, 125.6, 125.0, 116.6, 108.5, 30.0, 25.0, 24.9, 22.6, 13.8; HRMS (ESI+, m/z) calcd for $\text{C}_{19}\text{H}_{21}\text{Na}$ [$\text{M}+\text{H}$]: 272.1541, found: 272.1534.

Spectral data for (*E*)-1,2-diphenylhept-1-en-3-one (1b-O):



Colorless oil (0.018 g, 0.068 mmol, 17%); ^1H NMR (400 MHz, CDCl_3): δ 7.60 (s, 1H), 7.41 ~ 7.33 (m, 3H), 7.20 ~ 7.11 (m, 5H), 7.00 (d, J = 8.0 Hz, 2H), 2.54 (t, J = 7.2 Hz, 2H), 1.62 ~ 1.55 (m, 2H), 1.31 ~ 1.24 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 201.8, 140.8, 137.7, 137.1, 134.8, 130.8, 129.6, 129.0, 129.0, 128.2, 127.8, 39.7, 26.5, 22.3, 13.9; HRMS (ESI+, m/z) calcd for $\text{C}_{19}\text{H}_{21}\text{O}$ [$\text{M}+\text{H}$]: 265.1592, found: 265.1595.

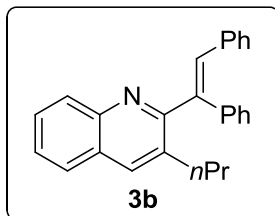
Spectral data for (*E*)-3-methyl-2-(1-phenylbut-1-en-2-yl)quinoline (3a):



Pale yellow viscous oil (0.119 g, 0.435 mmol, 75%); ^1H NMR (400 MHz, CDCl_3): δ 8.10 (d, J = 8.4 Hz, 1H), 7.97 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.63 (td, J = 8.0, 1.2 Hz, 1H), 7.48 (td, J = 8.0, 0.8 Hz, 1H), 7.42 ~ 7.35 (m, 4H), 7.27 (d, J = 6.8 Hz, 1H), 6.51 (s, 1H), 2.89 (q, J = 7.6 Hz, 2H), 2.54 (s, 3H), 1.01 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.7, 146.3, 143.7, 137.4, 136.5, 130.0, 129.5, 129.0, 128.8, 128.6, 128.2, 127.4, 126.8, 126.7,

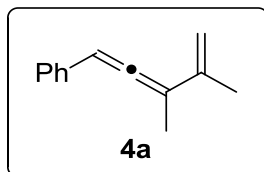
126.2, 25.1, 20.1, 12.7; HRMS (ESI+, m/z) calcd for $C_{20}H_{20}N$ $[M+H]$: 274.1596, found: 274.1607.

Spectral data for (*E*)-2-(1,2-diphenylvinyl)-3-propylquinoline (3b):



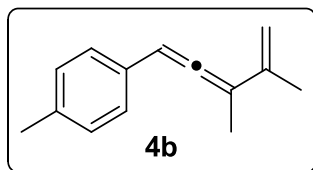
Pale yellow viscous oil (0.102 g, 0.292 mmol, 72%); 1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, $J = 8.4$ Hz, 1H), 7.89 (s, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.66 (td, $J = 8.4, 1.2$ Hz, 1H), 7.50 (td, $J = 8.0, 1.2$ Hz, 1H), 7.27 ~ 7.25 (m, 3H), 7.23 ~ 7.18 (m, 7H), 6.88 (s, 1H), 2.49 (t, $J = 8.0$ Hz, 2H), 1.51 ~ 1.41 (m, 2H), 0.80 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 146.3, 142.0, 138.4, 136.7, 136.1, 134.5, 131.8, 129.8, 129.7, 129.3, 128.7, 128.3, 127.9, 127.8, 127.5, 127.2, 126.9, 126.3, 34.7, 23.5, 14.0; HRMS (ESI+, m/z) calcd for $C_{26}H_{24}N$ $[M+H]$: 350.1909, found: 350.1920.

Spectral data for (3,4-dimethylpenta-1,2,4-trien-1-yl)benzene (4a):



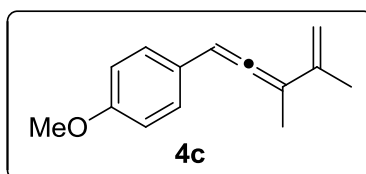
Pale yellow oil (0.600 g, 3.52 mmol, 76%); 1H NMR (600 MHz, $CDCl_3$): δ 7.30 ~ 7.24 (m, 4H), 7.19 ~ 7.16 (m, 1H), 6.28 (s, 1H), 5.00 (s, 1H), 4.96 (d, $J = 1.4$ Hz, 1H), 1.97 (d, $J = 2.6$ Hz, 3H), 1.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.6, 140.5, 134.9, 128.6, 126.8, 126.7, 111.5, 106.5, 95.4, 21.5, 16.3; HRMS (EI+, m/z) calcd for $C_{13}H_{14}$ $[M^+]$: 170.1096, found: 170.1091.

Spectral data for 1-(3,4-dimethylpenta-1,2,4-trien-1-yl)-4-methylbenzene (4b):



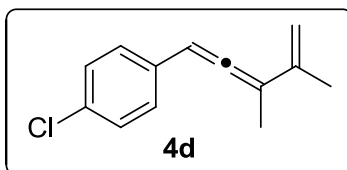
Pale yellow oil (0.282 g, 1.53 mmol, 70%); ^1H NMR (600 MHz, CDCl_3): δ 7.16 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.25 (s, 1H), 4.99 (s, 1H), 4.95 (d, J = 1.4 Hz, 1H), 2.31 (s, 3H), 1.96 (d, J = 2.6 Hz, 3H), 1.85 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 207.3, 140.7, 136.5, 131.9, 129.3, 126.6, 111.3, 106.4, 95.2, 21.4, 21.1, 16.3; HRMS (EI⁺, m/z) calcd for $\text{C}_{14}\text{H}_{16}$ [M^+]: 184.1253, found: 184.1253.

Spectral data for 1-(3,4-dimethylpenta-1,2,4-trien-1-yl)-4-methoxybenzene (4c):



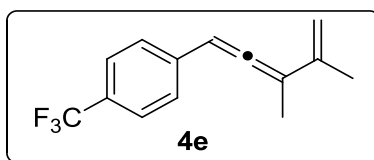
Pale yellow oil (0.260 g, 1.30 mmol, 63%); ^1H NMR (600 MHz, CDCl_3): δ 7.20 ~ 7.17 (m, 2H), 6.84 ~ 6.82 (m, 2H), 6.24 (s, 1H), 4.98 (s, 1H), 4.95 (d, J = 1.3 Hz, 1H), 3.78 (s, 3H), 1.95 (d, J = 2.7 Hz, 3H), 1.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 207.0, 158.7, 140.9, 127.8, 127.2, 114.1, 111.2, 106.4, 94.7, 55.3, 21.5, 16.5; HRMS (ESI, m/z) calcd for $\text{C}_{14}\text{H}_{17}\text{O}$ [$\text{M}+\text{H}$]: 201.1279, found: 201.1271.

Spectral data for 1-chloro-4-(3,4-dimethylpenta-1,2,4-trien-1-yl)benzene (4d):



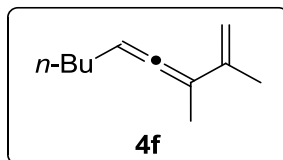
Pale yellow oil (0.340 g, 1.66 mmol, 82%); ^1H NMR (600 MHz, CDCl_3): δ 7.26 ~ 7.25 (m, 2H), 7.20 ~ 7.18 (m, 2H), 6.25 (s, 1H), 5.03 (s, 1H), 4.99 (d, J = 1.4 Hz, 1H), 1.98 (d, J = 2.6 Hz, 3H), 1.85 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 207.7, 140.2, 133.5, 132.4, 128.7, 127.9, 111.9, 107.0, 94.5, 21.4, 16.2; HRMS (EI⁺, m/z) calcd for $\text{C}_{13}\text{H}_{13}\text{Cl}$ [M^+]: 204.0706, found: 204.0705.

Spectral data for 1-(3,4-dimethylpenta-1,2,4-trien-1-yl)-4-(trifluoromethyl)benzene (4e):



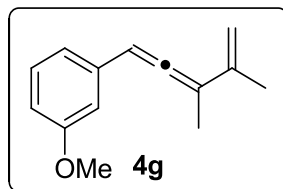
Pale yellow oil (0.360 g, 1.51 mmol, 85%); ^1H NMR (600 MHz, CDCl_3): δ 7.52 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.3$ Hz, 2H), 6.31 (s, 1H), 5.05 (s, 1H), 5.00 (d, $J = 1.3$ Hz, 1H), 1.99 (d, $J = 2.6$ Hz, 3H), 1.89 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 208.6, 139.9, 139.0, 129.9 ($J_{\text{C-F}} = 283.8$), 128.2 ($J_{\text{C-F}} = 32.0$), 126.8, 125.6, 125.5, 112.3, 107.2, 94.7, 29.7, 21.4, 16.1; HRMS (EI+, m/z) calcd for $\text{C}_{14}\text{H}_{13}\text{F}_3$ [M^+]: 238.0969, found: 238.0966.

Spectral data for 2,3-dimethylnona-1,3,4-triene (4f):



Colorless liquid (0.386 g, 2.59 mmol, 85%); ^1H NMR (400 MHz, CDCl_3): δ 5.22 (s, 1H), 4.84 (d, $J = 2.8$ Hz, 2H), 2.03 ~ 1.97 (m, 2H), 1.83 (d, $J = 5.6$ Hz, 3H), 1.81 (s, 3H), 1.39 ~ 1.33 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 205.4, 141.5, 110.0, 102.4, 91.7, 31.4, 28.8, 22.2, 21.6, 16.8, 13.9; HRMS (EI+, m/z) calcd for $\text{C}_{11}\text{H}_{18}$ [M^+]: 150.1409, found: 150.1406.

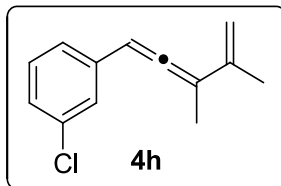
Spectral data for 1-(3,4-dimethylpenta-1,2,4-trien-1-yl)-3-methoxybenzene (4g):



Pale yellow oil (0.295 g, 1.47 mmol, 72%); ^1H NMR (600 MHz, CDCl_3): δ 7.22 (t, $J = 7.9$ Hz, 1H), 6.89 (dd, $J = 7.6, 1.0$ Hz, 1H), 6.84 ~ 6.83 (m, 1H), 6.76 (dt, $J = 8.3, 1.5$ Hz, 1H), 6.27 (s, 1H), 5.03 (s, 1H), 4.99 (d, $J = 1.3$ Hz, 1H), 3.80 (s, 3H), 1.99 (d, $J = 2.6$ Hz, 3H), 1.88 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 207.7, 159.9, 140.5, 136.5, 129.5, 119.4, 112.3, 112.2, 111.5, 106.6, 95.3, 55.1, 21.5, 16.3; HRMS (EI+, m/z) calcd for $\text{C}_{14}\text{H}_{16}\text{O}$ [M^+]:

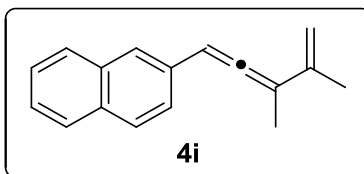
200.1201, found: 200.1203.

Spectral data for 1-chloro-3-(3,4-dimethylpenta-1,2,4-trien-1-yl)benzene (4h):



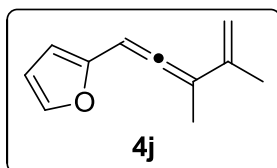
Pale yellow oil (0.330 g, 1.33 mmol, 80%); ^1H NMR (600 MHz, CDCl_3): δ 7.26 (s, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.17 ~ 7.13 (m, 2H), 6.24 (s, 1H), 5.05 (s, 1H), 5.01 (s, 1H), 1.99 (d, $J = 2.7$ Hz, 3H), 1.86 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 207.9, 140.1, 137.0, 134.6, 129.8, 126.8, 126.5, 124.9, 112.1, 107.1, 94.5, 21.4, 16.2; HRMS (EI $^+$, m/z) calcd for $\text{C}_{13}\text{H}_{13}\text{Cl}$ [M^+]: 204.0706, found: 204.0703.

Spectral data for 2-(3,4-dimethylpenta-1,2,4-trien-1-yl)naphthalene (4i):



Pale yellow solid, mp: 77-78 °C (0.650 g, 2.95 mmol, 78%); ^1H NMR (600 MHz, CDCl_3): δ 7.79 ~ 7.75 (m, 3H), 7.66 (s, 1H), 7.47 ~ 7.41 (m, 3H), 6.49 (s, 1H), 5.07 (s, 1H), 5.02 (s, 1H), 2.05 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 208.2, 140.6, 133.7, 132.6, 132.5, 128.2, 127.7, 127.6, 126.2, 125.5, 125.4, 124.7, 111.6, 106.7, 95.8, 21.5, 16.4; HRMS (ESI, m/z) calcd for $\text{C}_{17}\text{H}_{17}$ [$\text{M}+\text{H}$]: 221.1330, found: 221.1324.

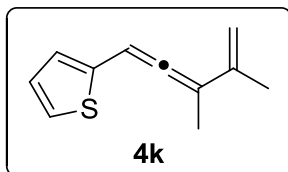
Spectral data for 2-(3,4-dimethylpenta-1,2,4-trien-1-yl)furan (4j):



Colorless oil (0.340 g, 2.12 mmol, 72%); ^1H NMR (400 MHz, CDCl_3): δ 7.34 (dd, $J = 2, 0.8$, Hz, 1H), 6.36 (dd, $J = 3.2, 1.6$ Hz, 1H), 6.26 (d, $J = 1.2$ Hz, 1H), 6.19 (d, $J = 3.2$ Hz, 1H), 5.01 (d, $J = 0.8$ Hz, 1H), 5.00 (dd, $J = 2.8, 1.2$ Hz, 1H), 1.97 (d, $J = 2.8$ Hz, 3H), 1.86 (s, 3H);

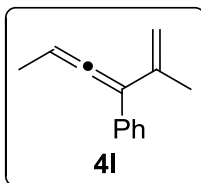
^{13}C NMR (100 MHz, CDCl_3): δ 206.9, 148.7, 141.9, 140.3, 111.9, 111.3, 107.0, 106.8, 86.2, 21.5, 16.5; HRMS (EI $^+$, m/z) calcd for $\text{C}_{11}\text{H}_{12}\text{O}$ [M^+]: 160.0888, found: 160.0883.

Spectral data for 2-(3,4-dimethylpenta-1,2,4-trien-1-yl)thiophene (4k):



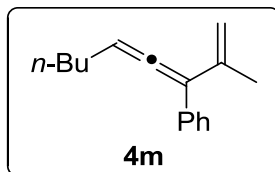
Colorless oil (0.376 g, 2.13 mmol, 78%); ^1H NMR (400 MHz, CDCl_3): δ 7.13 (d, J = 5.1, Hz, 1H), 6.94 (t, J = 4.3 Hz, 1H), 6.89 (t, J = 1.7 Hz, 1H), 6.50 (s, 1H), 5.02 (s, 1H), 4.99 (d, J = 1.3 Hz, 1H), 1.96 (d, J = 2.6 Hz, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 207.0, 140.3, 139.5, 127.3, 124.4, 124.3, 112.0, 106.7, 89.7, 21.4, 16.3; HRMS (EI $^+$, m/z) calcd for $\text{C}_{11}\text{H}_{12}\text{S}$ [M^+]: 176.0660, found: 176.0657.

Spectral data for (2-methylhexa-1,3,4-trien-3-yl)benzene (4l):



Pale yellow oil (0.700 g, 4.11 mmol, 62%); ^1H NMR (600 MHz, CDCl_3): δ 7.32 ~ 7.31 (m, 4H), 7.25 ~ 7.23 (m, 1H), 5.48 (q, J = 7.1 Hz, 1H), 5.03 ~ 5.02 (m, 1H), 4.82 (d, J = 0.6 Hz, 1H), 1.95 (s, 3H), 1.76 (dd, J = 7.1, 0.8 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 206.2, 140.5, 137.3, 129.1, 128.1, 126.8, 114.2, 110.8, 88.0, 22.1, 14.5; HRMS (EI $^+$, m/z) calcd for $\text{C}_{13}\text{H}_{14}$ [M^+]: 170.1096, found: 170.1089.

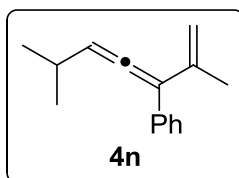
Spectral data for (2-methylnona-1,3,4-trien-3-yl)benzene (4m):



Pale yellow oil (0.486 g, 2.29 mmol, 89%); ^1H NMR (400 MHz, CDCl_3): δ 7.33 ~ 7.30 (m,

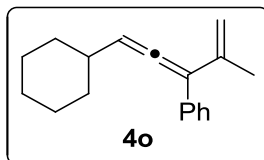
4H), 7.28 ~ 7.21 (m, 1H), 5.52 (t, $J = 6.4$ Hz, 1H), 5.03 (d, $J = 1.6$ Hz, 1H), 4.83 (d, $J = 0.4$ Hz, 1H), 2.15 ~ 1.98 (m, 2H), 1.98 (s, 3H), 1.51 ~ 1.43 (m, 2H), 1.47 ~ 1.32 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 205.3, 140.4, 137.4, 129.0, 128.0, 126.7, 114.1, 111.4, 93.4, 31.3, 28.8, 22.3, 22.1, 13.9; HRMS (EI^+ , m/z) calcd for $\text{C}_{16}\text{H}_{20}$ [M^+]: 212.1565, found: 212.1564.

Spectral data for (2,6-dimethylhepta-1,3,4-trien-3-yl)benzene (4n):



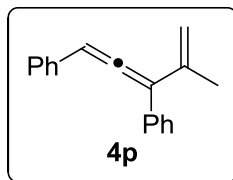
Pale yellow oil (0.725 g, 3.66 mmol, 66%); ^1H NMR (400 MHz, CDCl_3): δ 7.32 ~ 7.30 (m, 4H), 7.25 ~ 7.21 (m, 1H), 5.52 (d, $J = 5.6$ Hz, 1H), 5.02 ~ 5.00 (m, 1H), 4.80 (d, $J = 0.4$ Hz, 1H), 2.43 ~ 2.38 (m, 1H), 1.96 (s, 3H), 1.08 (d, $J = 3.2$, 3H), 1.06 (d, $J = 3.2$, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.8, 140.5, 137.4, 129.0, 128.1, 126.8, 114.1, 112.4, 100.7, 28.5, 22.5, 22.4, 22.1; HRMS (EI^+ , m/z) calcd for $\text{C}_{15}\text{H}_{18}$ [M^+]: 198.1409, found: 198.1407.

Spectral data for (1-cyclohexyl-4-methylpenta-1,2,4-trien-3-yl)benzene (4o):



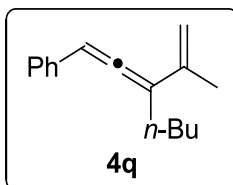
Pale yellow oil (0.350 g, 1.47 mmol, 65%); ^1H NMR (400 MHz, CDCl_3): δ 7.35 ~ 7.30 (m, 4H), 7.28 ~ 7.22 (m, 1H), 5.51 (d, $J = 5.6$ Hz, 1H), 5.03 ~ 5.01 (m, 1H), 4.82 (s, 1H), 2.18 ~ 2.05 (m, 1H), 1.97 (s, 3H), 1.83 (d, $J = 12.0$ Hz, 2H), 1.75 ~ 1.72 (m, 2H), 1.68 ~ 1.63 (m, 1H), 1.35 ~ 1.12 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 204.2, 140.5, 137.4, 129.0, 128.0, 126.7, 114.0, 112.1, 99.3, 37.8, 33.2, 33.0, 26.1, 22.2; HRMS (EI^+ , m/z) calcd for $\text{C}_{18}\text{H}_{22}$ [M^+]: 238.1722, found: 238.1725.

Spectral data for (4-methylpenta-1,2,4-triene-1,3-diyl)dibenzene (4p):



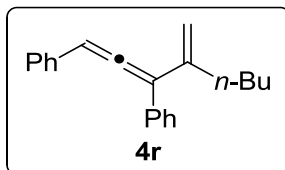
Orange yellow oil (0.800 g, 3.44 mmol, 74%); ^1H NMR (600 MHz, CDCl_3): δ 7.44 ~ 7.42 (m, 2H), 7.40 ~ 7.33 (m, 6H), 7.31 ~ 7.30 (m, 1H), 7.25 ~ 7.22 (m, 1H), 6.56 (s, 1H), 5.17 ~ 5.16 (m, 1H), 5.00 ~ 5.00 (m, 1H), 2.04 (t, J = 0.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 207.7, 139.8, 136.2, 134.3, 129.0, 128.7, 128.3, 127.3, 127.2, 126.8, 115.5, 96.9, 22.0; HRMS (EI⁺, m/z) calcd for $\text{C}_{18}\text{H}_{16}$ [M^+]: 232.1252, found: 232.1253.

Spectral data for (3-(prop-1-en-2-yl)hepta-1,2-dien-1-yl)benzene (4q):



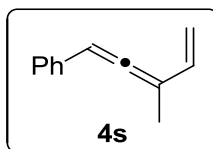
Colorless liquid (0.495 g, 2.33 mmol, 90%); ^1H NMR (400 MHz, CDCl_3): δ 7.29 ~ 7.24 (m, 4H), 7.20 ~ 7.16 (m, 1H), 6.36 (s, 1H), 5.05 (s, 1H), 4.96 (s, 1H), 2.32 ~ 2.29 (m, 2H), 1.85 (s, 3H), 1.52 ~ 1.48 (m, 2H), 1.40 ~ 1.34 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 207.2, 140.0, 135.1, 128.6, 126.7, 126.6, 111.7, 110.9, 97.1, 30.2, 29.1, 22.7, 21.9, 13.9; HRMS (EI⁺, m/z) calcd for $\text{C}_{16}\text{H}_{20}$ [M^+]: 212.1595, found: 212.1557.

Spectral data for (4-methyleneocta-1,2-diene-1,3-diyl)dibenzene (4r):



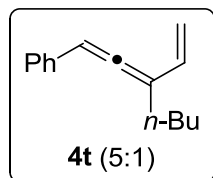
Pale yellow oil (0.750 g, 2.73 mmol, 70%); ^1H NMR (400 MHz, CDCl_3): δ 7.40 ~ 7.30 (m, 8H), 7.27 ~ 7.19 (m, 2H), 6.53 (s, 1H), 5.13 (s, 1H), 5.00 (s, 1H), 2.34 ~ 2.29 (m, 2H), 1.56 ~ 1.49 (m, 2H), 1.37 ~ 1.28 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 207.3, 144.5, 136.5, 134.3, 128.7, 128.7, 128.3, 127.3, 127.1, 126.9, 114.8, 114.4, 96.9, 35.1, 30.8, 22.4, 13.9; HRMS (EI⁺, m/z) calcd for $\text{C}_{21}\text{H}_{22}$ [M^+]: 274.1722, found: 274.1726.

Spectral data for (3-methylpenta-1,2,4-trien-1-yl)benzene (4s):



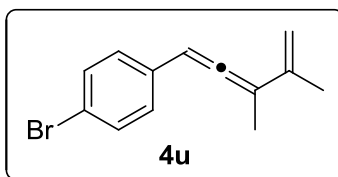
Pale yellow oil (0.450 g, 2.88 mmol, 58%); ^1H NMR (400 MHz, CDCl_3): δ 7.39 ~ 7.34 (m, 4H), 7.28 ~ 7.24 (m, 1H), 6.50 (dd, J = 17.6, 10.8 Hz, 1H), 6.33 (s, 1H), 5.30 (dd, J = 17.6, 1.2 Hz, 1H), 5.19 (dd, J = 10.4, 0.8 Hz, 1H), 2.03 (d, J = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 209.1, 134.8, 134.6, 128.6, 126.9, 126.9, 113.4, 104.1, 94.2, 14.5; HRMS (EI⁺, m/z) calcd for $\text{C}_{12}\text{H}_{12}$ [M^+]: 156.0939, found: 156.0933.

Spectral data for (3-vinylhepta-1,2-dien-1-yl)benzene (4t):



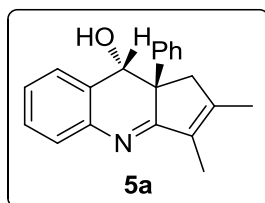
Colorless liquid (0.446 g, 2.25 mmol, 90%); ^1H NMR (400 MHz, CDCl_3); dr = 5:1; (*Major isomer*); δ 7.32 ~ 7.22 (m, 4H), 7.20 ~ 7.17 (m, 1H), 6.37 ~ 6.29 (m, 2H), 5.27 (dd, J = 16.7, 0.8 Hz, 1H), 5.09 (d, J = 10.7 Hz, 1H), 2.32 ~ 2.24 (m, 2H), 1.55 ~ 1.49 (m, 2H), 1.42 ~ 1.35 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3); δ 208.6, 134.7, 134.3, 128.6, 126.8, 126.8, 113.1, 109.2, 95.8, 29.8, 28.0, 22.6, 13.9; ^1H NMR (400 MHz, CDCl_3); (*Minor isomer*); δ 7.24 ~ 7.21 (m, 5H), 6.26 ~ 6.21 (m, 2H), 5.18 (d, J = 17.6 Hz, 1H), 5.04 (d, J = 10.8 Hz, 1H), 2.18 ~ 2.15 (m, 2H), 1.49 ~ 1.46 (m, 2H), 1.42 ~ 1.35 (m, 2H), 0.94 ~ 0.92 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3); δ 212.2, 126.8, 112.9, 105.6, 90.8, 30.9, 30.3, 22.4, 13.6 other carbons are merged or not clearly visible; HRMS (EI⁺, m/z) calcd for $\text{C}_{15}\text{H}_{18}$ [M^+]: 198.1409, found: 198.1390.

Spectral data for 1-bromo-4-(3,4-dimethylpenta-1,2,4-trien-1-yl)benzene (4u):



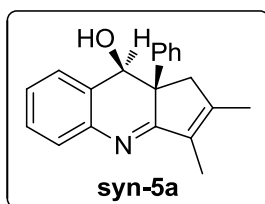
Pale yellow oil (0.410 g, 1.65 mmol, 80%); ^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.24 (s, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 1.98 (d, J = 2.8 Hz, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 207.7, 140.2, 131.7, 128.2, 120.4, 111.9, 107.0, 94.6, 21.4, 16.2.

Spectral data for (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (5a):



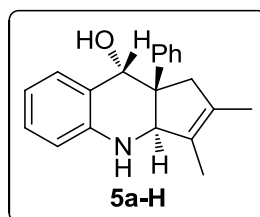
Pale yellow solid, mp: 207-208 °C (0.144 g, 0.498 mmol, 85%); ^1H NMR (400 MHz, CDCl_3): δ 7.06 ~ 6.95 (m, 8H), 6.85 ~ 6.81 (m, 1H), 4.97 (bs, 1H), 4.73 (s, 1H), 3.68 (d, J = 16.8 Hz, 1H), 2.53 (d, J = 16.8 Hz, 1H), 1.83 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.3, 158.7, 143.4, 141.6, 133.8, 129.1, 129.1, 128.2, 126.7, 126.7, 126.5, 125.7, 125.4, 73.1, 54.9, 45.3, 16.3, 8.9; HRMS (EI⁺, m/z) calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$ [M^+]: 289.1467, found: 289.1469.

Spectral data for (9*R*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (syn-5a):



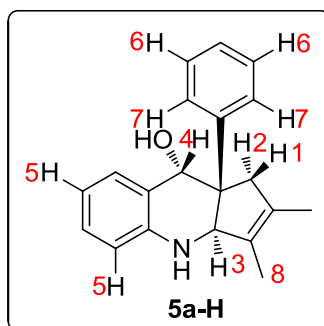
White solid, mp: 141-142 °C (0.048 g, 0.13 mmol, 19%); ^1H NMR (600 MHz, CDCl_3): δ 7.43 (d, J = 7.8 Hz, 1H), 7.26 ~ 7.24 (m, 1H), 7.21 (dd, J = 6.45, 1.0 Hz, 1H), 7.13 ~ 7.07 (m, 5H), 7.04 (t, J = 7.5 Hz, 1H), 4.82 (d, J = 10.5 Hz, 1H), 3.08 (d, J = 17.1 Hz, 1H), 2.99 (d, J = 17.1 Hz, 1H), 1.98 (s, 3H), 1.96 (s, 3H), 1.75 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 181.2, 157.0, 145.3, 135.5, 133.9, 130.5, 128.6, 128.3, 128.2, 127.2, 126.2, 125.8, 123.2, 75.5, 50.8, 50.0, 16.3, 9.3; HRMS (EI⁺, m/z) calcd for $\text{C}_{20}\text{H}_{20}\text{NO}$ [$\text{M}+\text{H}$]: 290.1545, found: 290.1537.

Spectral data for (3a*R*,9*R*,9a*S*)-2,3-dimethyl-9a-phenyl-3a,4,9,9a-tetrahydro-1*H*-cyclopenta[*b*]quinolin-9-ol (5a-*H*):



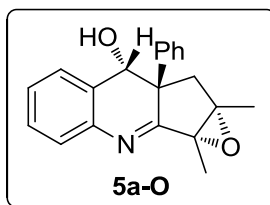
White solid, mp: 151-152 °C (0.090 g, 0.30 mmol, 90%); ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 ~ 6.99 (m, 4H), 6.61 (dd, *J* = 9.2, 7.2 Hz, 2H), 5.07 (s, 1H), 4.44 (s, 1H), 4.30 (s, 1H), 3.03 (d, *J* = 13.6 Hz, 1H), 2.10 (d, *J* = 14.8 Hz, 1H), 2.02 (s, 1H), 1.89 (s, 3H), 1.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 145.2, 143.3, 131.9, 129.1, 128.9, 128.6, 128.0, 127.0, 125.8, 125.3, 118.3, 116.4, 72.8, 60.8, 54.5, 44.4, 14.2, 10.5; HRMS (EI⁺, *m/z*) calcd for C₂₀H₂₂NO [M+H]⁺: 292.1701, found: 292.1689.

¹H NOE of Compound (3a*R*,9*R*,9a*S*)-2,3-dimethyl-9a-phenyl-3a,4,9,9a-tetrahydro-1*H*-cyclopenta[*b*]quinolin-9-ol (5a-*H*):



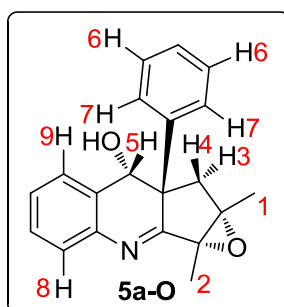
Sr. No.	Irradiation	Intensity Increase % (Key peaks)
1	H1 (δ 2.10)	H2 (δ 3.03, 24.69%), H4 (δ 5.07, 1.70%), H5 (δ 6.61, 4.78%), H7 (δ 7.49, 5.13%)
2	H2 (δ 3.03)	H1 (δ 2.10, 27.76%), H3 (δ 4.82, 4.44%), H4 (δ 5.07, 1.71%)
3	H3 (δ 4.82)	H2 (δ 3.03, 2.31%), H4 (δ 5.07, 1.68%), H5 (δ 6.61, 3.66%), CH ₃ 8 (δ 1.89, 3.40%)
4	H4 (δ 5.07)	H6 (δ 7.09 ~ 6.99, 10.41%), H7 (δ 7.49, 18.61%)
5	H7 (δ 7.49)	H1 (δ 2.10, 1.94%), H4 (δ 5.07, 7.77%), H6 (δ 7.09 ~ 6.99, 10.55%), CH ₃ 8 (δ 1.89, 1.35%)

Spectral data for (1a*R*,7*S*,7a*S*,8a*S*)-1a,8a-dimethyl-7a-phenyl-7,7a,8,8a-tetrahydro-1a*H*-oxireno[2',3':4,5]cyclopenta[1,2-*b*]quinolin-7-ol (5a-*O*):



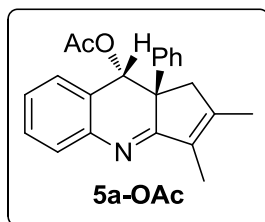
Colorless liquid (0.160 g, 0.52 mmol, 76%); ^1H NMR (400 MHz, CDCl_3): δ 7.37 (d, J = 7.7 Hz, 1H), 7.24 ~ 7.21 (m, 1H), 7.14 ~ 7.08 (m, 2H), 7.06 ~ 6.98 (m, 5H), 4.52 (d, J = 7.4 Hz, 1H), 3.21 (d, J = 14.4 Hz, 1H), 2.30 (s, 1H), 2.26 (d, J = 14.4 Hz, 1H), 1.76 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.1, 142.8, 140.9, 129.6, 129.0, 128.8, 128.1, 127.7, 127.1, 126.5, 126.2, 72.7, 68.9, 68.4, 55.1, 42.6, 15.8, 10.4; HRMS (EI+, m/z) calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_2$ [$\text{M}+\text{H}$]: 306.1494, found: 306.1503.

^1H NOE of Compound (1*aR*,7*S*,7*aS*,8*aS*)-1*a*,8*a*-dimethyl-7*a*-phenyl-7,7*a*,8,8*a*-tetrahydro-1*aH*-oxireno[2',3':4,5]cyclopenta[1,2-*b*]quinolin-7-ol (5*a*-O):



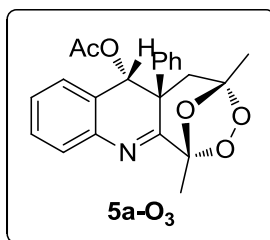
Sr. No.	Irradiation	Intensity Increase % (Key peaks)
1	CH_3 1 (δ 1.47)	CH_3 2 (δ 1.76, 1.01%), H3 (δ 2.26, 0.61%), H4 (δ 2.30, 0.27%)
2	CH_3 2 (δ 1.76)	CH_3 1 (δ 1.47, 1.76%), H8 (δ 7.06 ~ 6.98, 0.62%)
3	H3 (δ 2.26)	CH_3 1 (δ 1.47, 0.41%), H4 (δ 2.30, 21.03%), H5 (δ 4.52, 0.32%), H6,7 (δ 7.06 ~ 6.98, 4.42%)
4	H4 (δ 2.30)	CH_3 1 (δ 1.47, 1.39%), H3 (δ 2.26, 27.70%), H5 (δ 4.52, 3.02%), H9 (δ 7.37, 0.94%)
5	H5 (δ 4.52)	H3 (δ 2.26, 0.69%), H4 (δ 2.30, 1.63%), H6 (δ 7.06 ~ 6.98, 11.36%), H7 (δ 7.14 ~ 7.08, 9.75%)

Spectral data for (9*S*,9*aS*)-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-yl acetate (5*a*-OAc):



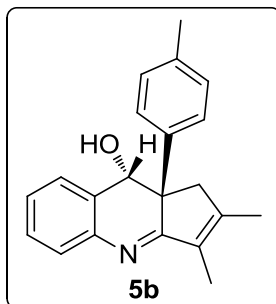
White solid, mp: 188-189 °C (0.503 g, 1.52 mmol, 80%); ^1H NMR (400 MHz, CDCl_3): δ 7.36 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.12 ~ 7.09 (m, 5H), 7.07 ~ 7.05 (m, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.18 (s, 1H), 3.07 (d, J = 16.8 Hz, 1H), 2.60 (d, J = 16.8 Hz, 1H), 2.03 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.3, 170.7, 156.9, 145.0, 140.5, 133.9, 130.1, 130.0, 128.4, 127.1, 126.8, 126.0, 125.7, 122.8, 73.2, 50.9, 46.0, 21.1, 16.2, 9.1; HRMS (EI⁺, m/z) calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2$ [$\text{M}+\text{H}$]: 332.1651, found: 332.1637.

Spectral data for (1*R*,4*S*,5a*S*,6*S*)-1,4-dimethyl-5a-phenyl-4,5,5a,6-tetrahydro-1*H*-1,4-epoxy[1,2]dioxepino[4,5-*b*]quinolin-6-yl acetate (5a-O₃):



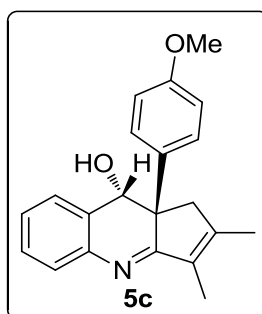
White solid, mp: 195-196 °C (0.323 g, 0.85 mmol, 85%); ^1H NMR (600 MHz, CDCl_3): δ 7.37 (d, J = 7.8 Hz, 1H), 7.26 ~ 7.24 (m, 1H), 7.16 (t, J = 7.5 Hz, 2H), 7.11 ~ 7.01 (m, 5H), 5.89 (s, 1H), 2.68 (d, J = 14.7 Hz, 1H), 2.59 (d, J = 14.7 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 167.1, 142.6, 140.1, 130.1, 129.3, 128.9, 128.3, 127.5, 127.3, 126.4, 123.7, 108.2, 106.5, 72.6, 44.6, 40.9, 22.1, 21.2, 17.2; HRMS (EI⁺, m/z) calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_5$ [$\text{M}+\text{H}$]: 380.1498, found: 380.1495.

Spectral data for (9*S*,9a*S*)-2,3-dimethyl-9a-(*p*-tolyl)-9,9a-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (5b):



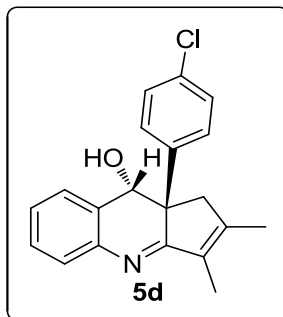
Pale yellow solid, mp: 223-224 °C (0.135 g, 0.445 mmol, 82%); ^1H NMR (400 MHz, CDCl_3): δ 6.99 ~ 6.96 (m, 3H), 6.89 ~ 6.83 (m, 5H), 4.72 (s, 1H), 3.66 (dd, J = 16.8, 1.2 Hz, 1H), 2.52 (d, J = 16.8 Hz, 1H), 2.13 (s, 3H), 1.83 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.5, 158.7, 143.5, 138.6, 136.1, 133.8, 129.2, 129.1, 128.9, 126.8, 126.6, 125.7, 125.4, 73.2, 54.5, 45.3, 20.8, 16.3, 8.9; HRMS (EI+, m/z) calcd for $\text{C}_{21}\text{H}_{21}\text{NO}$ [M^+]: 303.1623, found: 303.1620.

Spectral data for (9S,9aS)-9a-(4-methoxyphenyl)-2,3-dimethyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5c):



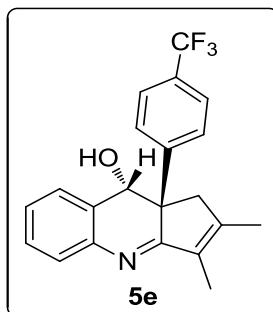
Pale yellow solid, mp: 168-169 °C (0.124 g, 0.388 mmol, 78%); ^1H NMR (400 MHz, CDCl_3): δ 6.99 ~ 6.95 (m, 3H), 6.90 ~ 6.83 (m, 3H), 6.57 (d, J = 8.4 Hz, 2H), 4.68 (s, 1H), 3.64 (d, J = 16.4 Hz, 1H), 3.60 (s, 3H), 2.49 (d, J = 16.4 Hz, 1H), 1.83 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.6, 158.7, 157.9, 143.4, 133.8, 133.4, 129.2, 129.1, 127.7, 126.8, 125.7, 125.4, 113.5, 73.2, 54.9, 54.1, 45.3, 16.3, 8.9; HRMS (EI+, m/z) calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2$ [M^+]: 319.1572, found: 319.1574.

Spectral data for (9S,9aS)-9a-(4-chlorophenyl)-2,3-dimethyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5d):



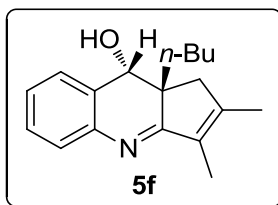
White solid, mp: 208-209 °C (0.139 g, 0.429 mmol, 88%); ^1H NMR (400 MHz, CDCl_3): δ 7.01 ~ 6.94 (m, 5H), 6.90 ~ 6.84 (m, 3H), 4.66 (s, 1H), 3.64 (d, J = 16.4 Hz, 1H), 2.45 (d, J = 16.8 Hz, 1H), 1.83 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 181.9, 158.9, 143.3, 140.1, 133.8, 132.3, 129.4, 129.2, 128.4, 128.1, 126.4, 125.9, 125.5, 73.0, 54.3, 45.2, 16.3, 8.9; HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{19}\text{ClNO}$ [$\text{M}+\text{H}$]: 324.1155, found: 324.1134.

Spectral data for (9S,9aS)-2,3-dimethyl-9a-(4-(trifluoromethyl)phenyl)-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5e):



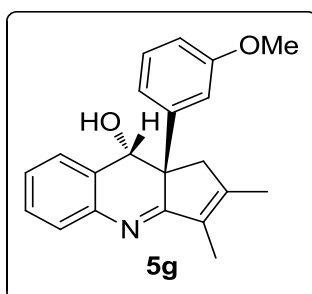
White solid, mp: 231-232 °C (0.128 g, 0.358 mmol, 85%); ^1H NMR (400 MHz, CDCl_3): δ 7.32 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.07 ~ 7.05 (m, 2H), 6.97 (d, J = 7.2 Hz, 1H), 6.92 ~ 6.87 (m, 1H), 4.74 (s, 1H), 3.95 (bs, 1H), 3.67 (d, J = 16.8 Hz, 1H), 2.50 (d, J = 16.8 Hz, 1H), 1.87 (s, 3H), 1.74 (s, 3H); ^{19}F NMR (500 MHz, CDCl_3): δ -62.6; ^{13}C NMR (100 MHz, CDCl_3): δ 181.4, 158.9, 145.7, 143.5, 134.0, 129.8, 129.1, 127.2, 126.2, 126.1, 125.9, 125.3, 125.3, 72.9, 54.4, 45.2, 16.3, 9.0; HRMS (ESI, m/z) calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{NO}$ [$\text{M}+\text{H}$]: 358.1419, found: 358.1413.

Spectral data for (9S,9aR)-9a-butyl-2,3-dimethyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5f):



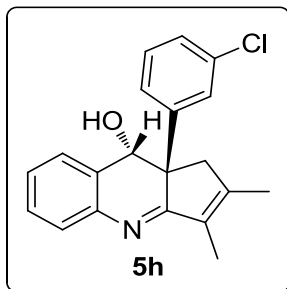
White solid, mp: 139-140 °C (0.15 g, 0.557 mmol, 84%); ^1H NMR (400 MHz, CDCl_3): δ 7.14 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 6.4 Hz, 1H), 7.01 (t, J = 8.0 Hz, 2H), 4.33 (s, 1H), 3.13 (d, J = 16.8 Hz, 1H), 2.16 (d, J = 17.2 Hz, 1H), 1.93 (s, 3H), 1.63 (s, 3H), 1.05 ~ 1.0 (m, 6H), 0.69 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 185.4, 159.1, 142.7, 133.5, 129.2, 129.1, 127.1, 125.7, 125.5, 70.8, 49.0, 40.0, 34.3, 26.9, 23.0, 16.2, 13.7, 8.6; HRMS (EI+, m/z) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}$ [$\text{M}+\text{H}$]: 270.1858, found: 270.1963.

Spectral data for (9S,9aS)-9a-(3-methoxyphenyl)-2,3-dimethyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5g):



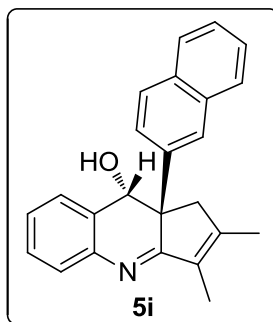
Yellow solid, mp: 180-181 °C (0.134 g, 0.420 mmol, 84%); ^1H NMR (400 MHz, CDCl_3): δ 7.07 ~ 6.96 (m, 4H), 6.86 (t, J = 6.88 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.55 ~ 6.54 (m, 2H), 4.73 (s, 1H), 3.64 ~ 3.60 (m, 4H), 2.54 (d, J = 16.8 Hz, 1H), 1.86 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.2, 159.2, 158.8, 143.5, 143.2, 133.8, 129.3, 129.1, 129.1, 126.7, 125.7, 125.5, 119.3, 113.1, 111.5, 73.1, 54.9, 54.7, 45.3, 16.3, 8.9; HRMS (ESI, m/z) calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_2$ [$\text{M}+\text{H}$]: 320.1651, found: 320.1641.

Spectral data for (9S,9aS)-9a-(3-chlorophenyl)-2,3-dimethyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5h):



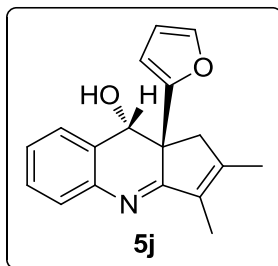
White solid, mp: 216-217 °C (0.138 g, 0.426 mmol, 87%); ^1H NMR (400 MHz, CDCl_3): δ 7.03 (d, J = 3.2 Hz, 2H), 6.99 ~ 6.94 (m, 4H), 6.90 ~ 6.86 (m, 1H), 6.86 ~ 6.82 (m, 1H), 4.69 (s, 1H), 3.63 (d, J = 16.8, 1H), 2.48 (d, J = 16.8, 1H), 1.86 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 181.5, 158.9, 143.7, 143.4, 134.1, 134.0, 129.6, 129.5, 129.1, 127.1, 127.0, 126.3, 126.0, 125.7, 124.9, 72.9, 54.3, 45.2, 16.3, 9.0; HRMS (ESI, m/z) calcd for $\text{C}_{20}\text{H}_{19}\text{ClNO}$ [$\text{M}+\text{H}$]: 324.1155, found: 324.1190.

Spectral data for (9S,9aS)-2,3-dimethyl-9a-(naphthalen-2-yl)-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5i):



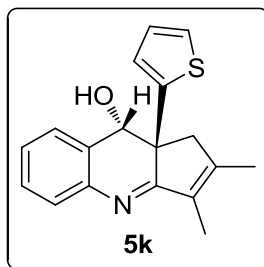
Pale yellow solid, mp: 240-241 °C (0.126 g, 0.371 mmol, 82%); ^1H NMR (400 MHz, CDCl_3): δ 7.66 ~ 7.57 (m, 3H), 7.33 ~ 7.29 (m, 4H), 7.09 (d, J = 7.6 Hz, 1H), 7.01 ~ 6.95 (m, 2H), 6.81 (t, J = 7.4 Hz, 1H), 4.91 (s, 1H), 4.26 (bs, 1H), 3.74 (d, J = 16.8 Hz, 1H), 2.63 (d, J = 17.2 Hz, 1H), 1.86 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.2, 158.7, 143.6, 138.8, 134.0, 133.0, 132.1, 129.4, 129.1, 128.1, 127.9, 127.2, 126.6, 125.8, 125.7, 125.6, 125.3, 125.1, 73.0, 54.8, 45.2, 16.3, 9.0; HRMS (EI+, m/z) calcd for $\text{C}_{24}\text{H}_{21}\text{NO}$ [M^+]: 339.1623, found: 339.1629.

Spectral data for (9S,9aS)-9a-(furan-2-yl)-2,3-dimethyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5j):



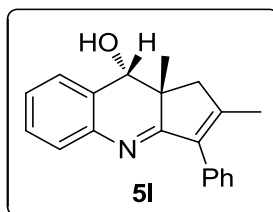
Brown solid, mp: 204-205 °C (0.146 g, 0.522 mmol, 83%); ^1H NMR (400 MHz, CDCl_3): δ 7.15 ~ 7.10 (m, 4H), 7.0 ~ 6.96 (m, 1H), 5.97 ~ 5.95 (m, 1H), 5.55 (d, J = 2.8 Hz, 1H), 4.83 (s, 1H), 3.39 (d, J = 17.2 Hz, 1H), 2.68 (d, J = 17.2 Hz, 1H), 1.94 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 179.9, 159.3, 153.3, 143.4, 141.5, 133.5, 129.7, 129.1, 126.8, 126.0, 109.8, 105.8, 69.9, 50.0, 41.2, 16.4, 9.1; HRMS (ESI, m/z) calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_2$ [$\text{M}+\text{H}$]: 280.1338, found: 280.1337.

Spectral data for (9S,9aS)-2,3-dimethyl-9a-(thiophen-2-yl)-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5k):



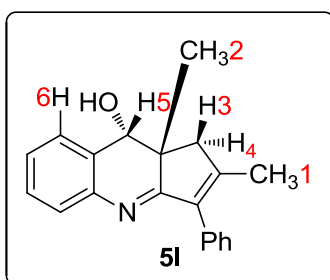
Brown solid, mp: 213-214 °C (0.141 g, 0.477 mmol, 84%); ^1H NMR (400 MHz, CDCl_3): δ 7.13 ~ 7.10 (m, 3H), 6.99 ~ 6.93 (m, 2H), 6.61 (t, J = 4.4 Hz, 1H), 6.47 (d, J = 3.6 Hz, 1H), 4.80 (s, 1H), 3.60 (d, J = 16.8 Hz, 1H), 3.45 (bs, 1H), 2.58 (d, J = 16.8 Hz, 1H), 1.93 (s, 3H), 1.76 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3): δ 181.3, 158.9, 145.3, 143.3, 133.4, 129.6, 129.4, 126.8, 126.1, 126.0, 124.1, 123.5, 72.7, 51.0, 45.8, 16.4, 9.1; HRMS (ESI, m/z) calcd for $\text{C}_{18}\text{H}_{18}\text{NOS}$ [$\text{M}+\text{H}$]: 296.1109, found: 296.1101.

Spectral data for (9S,9aR)-2,9a-dimethyl-3-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5l):



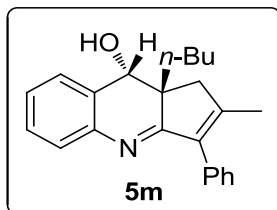
Pale yellow solid, mp: 191-192 °C (0.142 g, 0.491 mmol, 84%); ^1H NMR (400 MHz, CDCl_3): δ 7.44 ~ 7.40 (m, 4H), 7.34 ~ 7.22 (m, 4H), 7.15 ~ 7.09 (m, 1H), 4.39 (s, 1H), 3.36 (d, J = 17.2 Hz, 1H), 2.26 (d, J = 17.6 Hz, 1H), 2.13 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.3, 160.7, 143.2, 137.0, 133.0, 129.9, 129.8, 129.1, 128.1, 127.4, 127.1, 126.7, 126.1, 72.3, 44.7, 43.3, 22.4, 17.7; HRMS (EI⁺, m/z) calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$ [M^+]: 289.1467, found: 289.1466.

^1H NOE of Compound (9S,9aR)-2,9a-dimethyl-3-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5l):



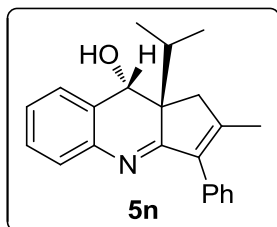
Sr. No.	Irradiation	Intensity Increase % (Key peaks)
1	$\text{CH}_3\text{2}$ (δ 0.98)	H3 (δ 2.26, 1.86%), H5 (δ 4.36, 3.19%)
2	OH (δ 1.76)	H4 (δ 3.33, 0.74%), H5 (δ 4.36, 0.89%)
3	H3 (δ 2.26)	$\text{CH}_3\text{2}$ (δ 0.98, 4.05%), H4 (δ 3.33, 30.53%)
4	H4 (δ 3.33)	OH (δ 1.76, 0.61%), $\text{CH}_3\text{1}$ (δ 2.13, 0.26%), H3 (δ 2.26, 26.20%), H5 (δ 4.36, 2.36%)
5	H5 (δ 4.36)	$\text{CH}_3\text{2}$ (δ 0.98, 3.72%), OH (δ 1.76, 1.67%), H4 (δ 3.33, 1.62%), H6 (δ 7.08 ~ 7.01, 1.51%)

Spectral data for (9S,9aR)-9a-butyl-2-methyl-3-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5m):



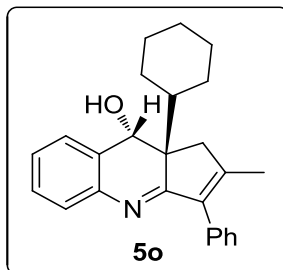
White solid, mp: 170-171 °C (0.133 g, 0.401 mmol, 85%); ^1H NMR (600 MHz, CDCl_3): δ 7.45 ~ 7.40 (m, 4H), 7.33 ~ 7.25 (m, 3H), 7.20 (dd, J = 6.1, 1.2 Hz, 1H), 7.10 ~ 7.08 (m, 1H), 4.43 (s, 1H), 3.29 (dd, J = 16.1, 1.3 Hz, 1H), 2.36 (dd, J = 16.7, 0.7 Hz, 1H), 2.12 (s, 3H), 1.66 (s, 1H), 1.33 ~ 1.30 (m, 1H), 1.23 ~ 1.17 (m, 3H), 1.13 ~ 1.08 (m, 2H), 0.76 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.2, 161.1, 143.4, 138.2, 133.0, 129.8, 129.8, 128.9, 128.1, 127.4, 126.9, 126.7, 126.0, 71.2, 48.4, 40.7, 34.5, 27.0, 23.2, 17.5, 13.9; HRMS (ESI, m/z) calcd for $\text{C}_{23}\text{H}_{26}\text{NO}$ [$\text{M}+\text{H}$]: 332.2014, found: 332.2022.

Spectral data for (9S,9aS)-9a-isopropyl-2-methyl-3-phenyl-9,9a-dihydro-1H-cyclopenta[*b*]quinolin-9-ol (5n):



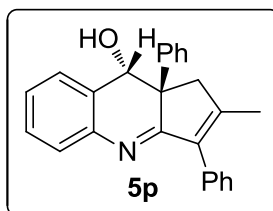
Pale yellow solid, mp: 192-193 °C (0.136 g, 0.428 mmol, 85%); ^1H NMR (400 MHz, CDCl_3): δ 7.44 ~ 7.40 (m, 4H), 7.34 ~ 7.31 (m, 1H), 7.27 ~ 7.26 (m, 2H), 7.17 (d, J = 6.8 Hz, 1H), 7.09 ~ 7.05 (m, 1H), 4.53 (s, 1H), 3.09 (d, J = 18.0 Hz, 1H), 2.40 (d, J = 17.6 Hz, 1H), 2.11 (s, 3H), 1.87 (bs, 1H), 1.78 ~ 1.77 (m, 1H), 0.83 (d, J = 6.4 Hz, 3H), 0.78 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.9, 162.2, 143.7, 139.3, 133.0, 129.8, 129.7, 128.6, 128.1, 127.4, 126.6, 126.4, 125.8, 70.7, 51.6, 36.1, 29.3, 19.1, 17.3, 17.2; HRMS (EI+, m/z) calcd for $\text{C}_{22}\text{H}_{23}\text{NO}$ [M^+]: 317.1780, found: 317.1785.

Spectral data for (9S,9aS)-9a-cyclohexyl-2-methyl-3-phenyl-9,9a-dihydro-1H-cyclopenta[*b*]quinolin-9-ol (5o):



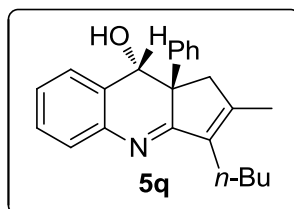
Pale yellow solid, mp: 151-152 °C (0.123 g, 0.344 mmol, 82%); ^1H NMR (400 MHz, CDCl_3): δ 7.45 ~ 7.39 (m, 4H), 7.34 ~ 7.29 (m, 1H), 7.27 ~ 7.26 (m, 2H), 7.15 ~ 7.13 (m, 1H), 7.09 ~ 7.05 (m, 1H), 4.55 (d, J = 2.8 Hz, 1H), 3.12 (d, J = 18.0 Hz, 1H), 2.47 (d, J = 17.6 Hz, 1H), 2.11 (s, 3H), 1.67 ~ 1.52 (m, 5H), 1.42 ~ 1.39 (m, 1H), 1.05 ~ 0.94 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.9, 161.9, 143.6, 139.2, 133.0, 129.8, 129.7, 128.5, 128.0, 127.4, 126.6, 126.5, 125.8, 70.1, 51.6, 39.9, 37.4, 29.1, 26.8, 26.4, 26.3, 26.2, 17.2; HRMS (EI+, m/z) calcd for $\text{C}_{25}\text{H}_{27}\text{NO}$ [M^+]: 357.2093, found: 357.2095.

Spectral data for (9S,9aS)-2-methyl-3,9a-diphenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5p):



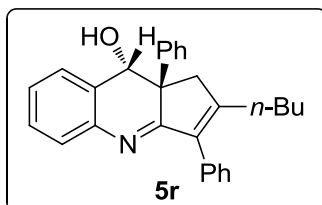
Pale yellow solid, mp: 177-178 °C (0.121 g, 0.344 mmol, 80%); ^1H NMR (400 MHz, CDCl_3): δ 7.53 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.28 ~ 7.07 (m, 7H), 7.98 (d, J = 7.2 Hz, 1H), 6.91 (t, J = 7.2 Hz, 1H), 4.80 (s, 1H), 3.76 (d, J = 17.2 Hz, 1H), 2.73 (d, J = 17.2 Hz, 1H), 2.16 (bs, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.3, 160.8, 143.9, 141.3, 138.4, 133.0, 129.9, 129.8, 128.7, 128.5, 128.2, 127.6, 126.9, 126.8, 126.5, 126.3, 126.2, 73.2, 54.0, 45.8, 17.6; HRMS (EI+, m/z) calcd for $\text{C}_{25}\text{H}_{21}\text{NO}$ [M^+]: 351.1623, found: 351.1622.

Spectral data for (9S,9aS)-3-butyl-2-methyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5q):



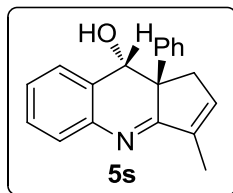
White solid, mp: 187-188 °C (0.134 g, 0.404 mmol, 86%); ^1H NMR (400 MHz, CDCl_3): δ 7.19 (d, $J = 7.6$ Hz, 1H), 7.12 ~ 7.03 (m, 6H), 6.96 ~ 6.94 (m, 1H), 6.89 ~ 6.85 (m, 1H), 4.75 (s, 1H), 3.61 (d, $J = 16.8$ Hz, 1H), 2.57 (d, $J = 16.9$ Hz, 1H), 2.53 ~ 2.48 (m, 1H), 2.23 ~ 2.15 (m, 1H), 1.90 (s, 3H), 1.66 ~ 1.55 (m, 2H), 1.36 ~ 1.30 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 181.6, 158.4, 143.5, 141.7, 138.6, 129.1, 129.0, 128.2, 126.8, 126.5, 126.5, 125.6, 125.5, 73.3, 54.6, 45.3, 30.4, 23.3, 22.6, 16.3, 13.9; HRMS (ESI, m/z) calcd for $\text{C}_{23}\text{H}_{26}\text{NO}$ [$\text{M}+\text{H}$]: 332.2014, found: 332.1997.

Spectral data for (9S,9aS)-2-butyl-3,9a-diphenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5r):



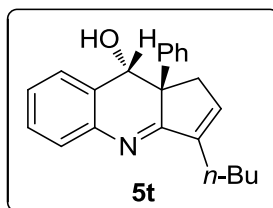
Pale yellow solid, mp: 159-160 °C (0.115 g, 0.292 mmol, 80%); ^1H NMR (400 MHz, CDCl_3): δ 7.49 ~ 7.46 (m, 4H), 7.39 ~ 7.34 (m, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.22 ~ 7.06 (m, 6H), 6.99 (dd, $J = 7.2, 1.2$ Hz, 1H), 6.92 (td, $J = 7.2, 1.2$ Hz, 1H), 4.82 (s, 1H), 3.76 (d, $J = 17.2$ Hz, 1H), 2.75 (d, $J = 17.2$ Hz, 1H), 2.53 ~ 2.45 (m, 1H), 2.36 ~ 2.28 (m, 1H), 2.15 (bs, 1H), 1.46 ~ 1.41 (m, 2H), 1.25 ~ 1.15 (m, 2H), 0.79 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.6, 165.1, 144.1, 141.3, 138.5, 133.3, 129.9, 129.8, 128.8, 128.4, 128.2, 127.6, 126.9, 126.7, 126.7, 126.4, 126.2, 73.2, 53.8, 43.2, 30.7, 29.9, 22.5, 13.7; HRMS (EI+, m/z) calcd for $\text{C}_{28}\text{H}_{27}\text{NO}$ [M^+]: 393.2093, found: 393.2099.

Spectral data for (9S,9aS)-3-methyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5s):



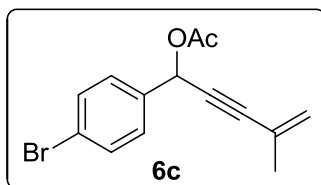
White solid, mp: 189-190 °C (0.144 g, 0.523 mmol, 82%); ^1H NMR (400 MHz, CDCl_3): δ 7.22 ~ 7.20 (m, 1H), 7.13 ~ 7.03 (m, 6H), 6.98 (d, J = 7.3 Hz, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.64 (s, 1H), 4.81 (s, 1H), 3.64 (dd, J = 17.3, 1.5 Hz, 1H), 2.84 (bs, 1H), 2.63 (d, J = 17.3, Hz, 1H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 181.5, 147.9, 143.6, 141.2, 140.2, 129.7, 128.9, 128.3, 126.8, 126.7, 126.4, 126.4, 126.2, 73.2, 54.8, 40.5, 11.6; HRMS (ESI, m/z) calcd for $\text{C}_{19}\text{H}_{18}\text{NO}$ [$\text{M}+\text{H}$]: 276.1388, found: 276.1379.

Spectral data for (9S,9aS)-3-butyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (5t):



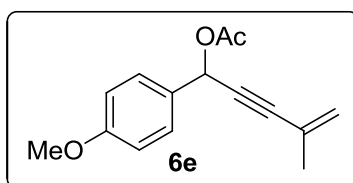
White solid, mp: 161-162 °C (0.133 g, 0.419 mmol, 83%); ^1H NMR (400 MHz, CDCl_3): δ 7.18 ~ 7.10 (m, 7 H), 7.05 (d, J = 7.2 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.67 (s, 1H), 4.87 (s, 1H), 3.76 (dd, J = 15.2, 2.4 Hz, 1H), 2.73 (d, J = 17.6 Hz, 1H), 2.50 (d, J = 7.2 Hz, 1H), 2.36 (d, J = 6.4 Hz, 1H), 1.74 ~ 1.64 (m, 1H), 1.62 ~ 1.56 (m, 1H), 1.49 ~ 1.41 (m, 2H), 1.02 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 181.2, 146.4, 144.7, 143.3, 141.4, 129.5, 128.9, 128.2, 126.7, 126.4, 126.2, 125.8, 124.2, 73.2, 55.4, 40.5, 29.5, 25.6, 25.5, 14.0; HRMS (ESI, m/z) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}$ [$\text{M}+\text{H}$]: 318.1858, found: 318.1850.

Spectral data for 1-(4-bromophenyl)-4-methylpent-4-en-2-yn-1-yl acetate (6c):



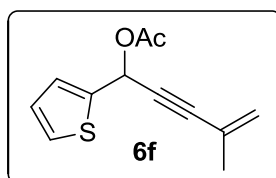
Colorless liquid (0.537 g, 1.8317 mmol, 92%); ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 5.35 (s, 1H), 5.28 (s, 1H), 2.08 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 136.3, 131.8, 129.4, 125.7, 123.5, 123.0, 88.5, 83.9, 65.3, 23.1, 21.0; HRMS (EI $^+$, m/z) calcd for $\text{C}_{14}\text{H}_{13}\text{BrO}_2$ [M^+]: 292.0099, found: 292.0093.

Spectral data for 1-(4-methoxyphenyl)-4-methylpent-4-en-2-yn-1-yl acetate (6e):



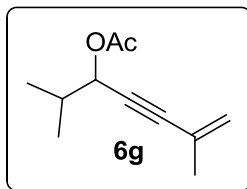
Colorless liquid (0.549 g, 2.25 mmol, 91%); ^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.52 (s, 1H), 5.35 (s, 1H), 5.26 (s, 1H), 3.79 (s, 3H), 2.06 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 160.0, 129.3, 128.1, 126.0, 123.0, 113.9, 87.9, 84.7, 65.7, 55.3, 23.2, 21.1; HRMS (ESI, m/z) calcd for $\text{C}_{15}\text{H}_{16}\text{NaO}_3$ [$\text{M}+\text{Na}$]: 267.0997, found: 267.1013.

Spectral data for 4-methyl-1-(thiophen-2-yl)pent-4-en-2-yn-1-yl acetate (6f):



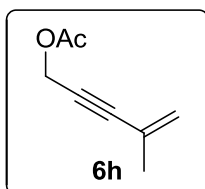
Colorless liquid (0.556 g, 2.52 mmol, 90%); ^1H NMR (400 MHz, CDCl_3): δ 7.30 (d, J = 5.2 Hz, 1H), 7.22 ~ 7.21 (m, 1H), 6.96 ~ 6.94 (m, 1H), 6.79 (s, 1H), 5.38 (s, 1H), 5.29 (s, 1H), 2.06 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.4, 140.0, 127.5, 126.8, 126.5, 125.5, 123.4, 87.5, 83.8, 60.8, 22.9, 20.8; HRMS (ESI, m/z) calcd for $\text{C}_{12}\text{H}_{12}\text{NaO}_2\text{S}$ [$\text{M}+\text{Na}$]: 243.0456, found: 243.0430.

Spectral data for 2,6-dimethylhept-6-en-4-yn-3-yl acetate (6g):



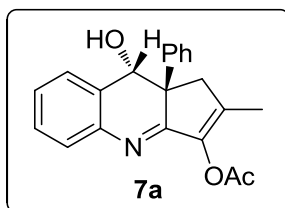
Colorless liquid (0.586 g, 3.2559 mmol, 90%); ^1H NMR (400 MHz, CDCl_3): δ 5.30 (d, J = 5.6 Hz, 1H), 5.26 (s, 1H), 5.19 (t, J = 1.6 Hz, 1H), 2.04 (s, 3H), 1.98 ~ 1.93 (m, 1H), 1.83 (s, 3H), 0.97 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.0, 126.0, 122.5, 86.9, 84.2, 69.2, 32.5, 23.2, 20.9, 18.2, 17.4; HRMS (ESI, m/z) calcd for $\text{C}_{11}\text{H}_{16}\text{NaO}_2$ [$\text{M}+\text{Na}$]: 203.1048, found: 203.1026.

Spectral data for 4-methylpent-4-en-2-yn-1-yl acetate (6h):



Colorless liquid (0.895 g, 6.48 mmol, 85%); ^1H NMR (400 MHz, CDCl_3): δ 5.31 (s, 1H), 5.24 (d, J = 1.6 Hz, 1H), 4.76 (s, 2H), 2.07 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.3, 125.9, 123.0, 87.6, 81.8, 52.7, 23.1, 20.7; HRMS (ESI+, m/z) calcd for $\text{C}_8\text{H}_{10}\text{NaO}_2$ [$\text{M}+\text{Na}$]: 161.0578, found: 161.0579.

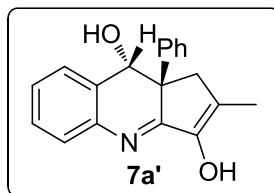
Spectral data for (9S,9aS)-9-hydroxy-2-methyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-3-yl acetate (7a):



White solid, mp: 208-209 °C (0.115 g, 0.345 mmol, 74%); ^1H NMR (400 MHz, CDCl_3): δ 7.17 ~ 7.16 (m, 2H), 7.09 ~ 7.07 (m, 2H), 7.02 ~ 7.0 (m, 1H), 6.96 ~ 6.95 (m, 1H), 6.85 ~ 6.80 (m, 2H), 6.65 ~ 6.64 (m, 1H), 4.71 (s, 1H), 3.78 (dd, J = 15.2, 1.1 Hz, 1H), 2.59 (dd, J = 15.6, 0.8 Hz, 1H), 2.36 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.2, 167.9,

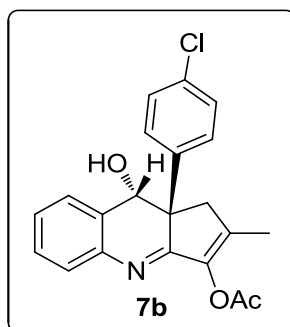
150.0, 143.0, 141.9, 140.8, 129.1, 129.0, 128.3, 126.8, 126.7, 126.5, 126.1, 124.9, 72.9, 53.1, 42.0, 20.5, 14.4; HRMS (EI⁺, m/z) calcd for C₂₁H₂₀NO₃ [M+H]: 334.1443, found: 334.1437.

Spectral data for (9*S*,9*aS*)-2-methyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinoline-3,9-diol (7*a'*):



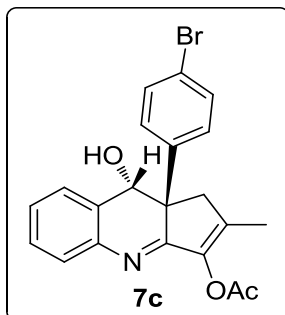
Brown solid, mp: 163-164 °C (0.113 g, 0.38 mmol, 80%); ¹H NMR (400 MHz, (CD₃)₂CO): δ 7.24 ~ 7.21 (m, 2H), 7.14 ~ 7.07 (m, 2H), 7.03 ~ 7.0 (m, 4H), 6.92 ~ 6.88 (m, 1H), 4.93 (s, 1H), 3.61 (dd, *J* = 14.4, 1.7 Hz, 1H), 2.90 (bs, 2H), 2.46 (d, *J* = 16.2 Hz, 1H), 1.92 (s, 3H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ 176.5, 149.0, 144.4, 143.1, 136.1, 130.1, 129.8, 129.1, 129.0, 127.7, 127.5, 126.7, 126.0, 73.1, 52.2, 42.2, 13.7; HRMS (EI⁺, m/z) calcd for C₁₉H₁₈NO₂ [M+H]: 292.1338, found: 292.1331.

Spectral data for (9*S*,9*aS*)-9*a*-(4-chlorophenyl)-9-hydroxy-2-methyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-3-yl acetate (7*b*):



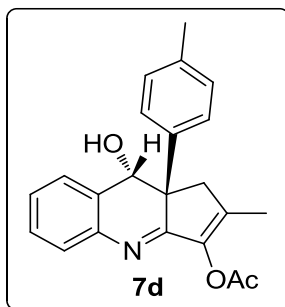
White solid, mp: 216-217 °C (0.099 g, 0.269 mmol, 67%); ¹H NMR (400 MHz, CDCl₃): δ 7.12 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.94 ~ 6.86 (m, 2H), 6.83 (d, *J* = 7.4 Hz, 1H), 4.68 (s, 1H), 4.48 (bs, 1H), 3.73 (d, *J* = 16.8 Hz, 1H), 2.53 (d, *J* = 16.6 Hz, 1H), 2.36 (s, 3H), 1.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.8, 168.0, 150.3, 143.1, 142.0, 139.2, 132.7, 129.6, 129.1, 128.6, 128.3, 126.6, 126.2, 125.4, 72.8, 52.4, 42.0, 20.6, 14.5; HRMS (EI⁺, m/z) calcd for C₂₁H₁₈ClNO₃ [M+H]: 368.1053, found: 368.1058.

Spectral data for (9S,9aS)-9a-(4-bromophenyl)-9-hydroxy-2-methyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-3-yl acetate (7c):



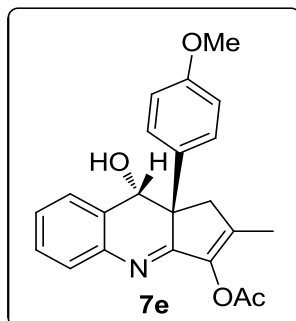
Yellow solid, mp: 189-190 °C (0.093 g, 0.226 mmol, 66%); ^1H NMR (400 MHz, CDCl_3): δ 7.21 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.97 ~ 6.96 (m, 1H), 6.91 ~ 6.85 (m, 2H), 6.75 (d, J = 6.2 Hz, 1H), 4.88 (bs, 1H), 4.66 (s, 1H), 3.74 (d, J = 16.4 Hz, 1H), 2.52 (d, J = 16.8 Hz, 1H), 2.35 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.8, 168.0, 150.2, 143.0, 141.9, 139.9, 131.5, 129.5, 129.2, 128.7, 126.5, 126.2, 125.3, 120.8, 72.8, 52.6, 41.9, 20.5, 14.5; HRMS (EI⁺, m/z) calcd for $\text{C}_{21}\text{H}_{19}\text{BrNO}_3$ [$\text{M}+\text{H}$]: 412.0548, found: 412.0541.

Spectral data for (9S,9aS)-9-hydroxy-2-methyl-9a-(*p*-tolyl)-9,9a-dihydro-1H-cyclopenta[b]quinolin-3-yl acetate (7d):



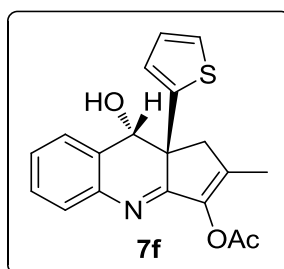
White solid, mp: 211-212 °C (0.108 g, 0.311 mmol, 71%); ^1H NMR (400 MHz, CDCl_3): δ 7.05 (d, J = 8.0 Hz, 2H), 6.96 (t, J = 8.4 Hz, 1H), 6.89 (d, J = 7.9 Hz, 2H), 6.83 (t, J = 3.6 Hz, 2H), 6.71 (t, J = 2.9 Hz, 1H), 4.69 (s, 1H), 3.75 (d, J = 16.4 Hz, 1H), 2.57 (d, J = 16.4 Hz, 1H), 2.35 (s, 3H), 2.12 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.5, 168.0, 150.1, 143.1, 142.2, 137.7, 136.4, 129.3, 129.1, 126.7, 126.6, 126.2, 125.3, 73.0, 52.7, 42.1, 20.8, 20.6, 14.5; HRMS (EI⁺, m/z) calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_3$ [$\text{M}+\text{H}$]: 348.1600, found: 348.1597.

Spectral data for (9*S*,9*aS*)-9-hydroxy-9*a*-(4-methoxyphenyl)-2-methyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-3-yl acetate (7e):



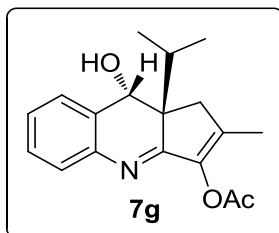
White solid, mp: 204-205 °C (0.109 g, 0.300 mmol, 73%); ¹H NMR (400 MHz, CDCl₃): δ 7.07 (d, *J* = 8.8 Hz, 2H), 6.98 ~ 6.96 (m, 1H), 6.85 (t, *J* = 3.8 Hz, 2H), 6.73 ~ 6.71 (m, 1H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.68 (s, 1H), 3.73 (d, *J* = 16.5 Hz, 1H), 3.60 (s, 3H), 2.55 (d, *J* = 16.5 Hz, 1H), 2.35 (s, 3H), 1.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.6, 168.1, 158.2, 150.5, 143.0, 141.9, 132.5, 129.3, 129.1, 127.9, 126.6, 126.3, 125.2, 113.8, 73.0, 55.0, 52.4, 42.1, 20.6, 14.6; HRMS (EI⁺, *m/z*) calcd for C₂₂H₂₂NO₄ [M+H]: 364.1549, found: 364.1545.

Spectral data for (9*S*,9*aS*)-9-hydroxy-2-methyl-9*a*-(thiophen-2-yl)-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-3-yl acetate (7f):



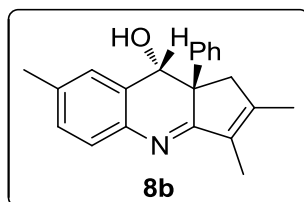
White solid, mp: 198-199 °C (0.114 g, 0.336 mmol, 74%); ¹H NMR (600 MHz, CDCl₃): δ 7.09 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 5.0 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 3.2 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.60 (t, *J* = 4.2 Hz, 1H), 5.19 (s, 1H), 4.76 (s, 1H), 3.71 (d, *J* = 16.4 Hz, 1H), 2.59 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H), 1.88 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 172.3, 168.0, 150.3, 144.4, 142.8, 141.6, 129.4, 129.4, 126.6, 126.5, 126.3, 125.5, 125.0, 124.0, 72.7, 49.8, 42.5, 20.6, 14.6; HRMS (EI⁺, *m/z*) calcd for C₁₉H₁₈NO₃S [M+H]: 340.1007, found: 340.1003.

Spectral data for (9*S*,9*aS*)-9-hydroxy-9*a*-isopropyl-2-methyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-3-yl acetate (7g):



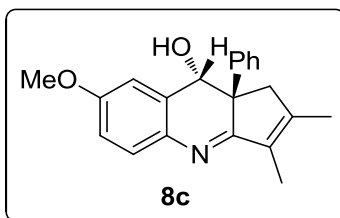
White solid, mp: 194-195 °C (0.102 g, 0.341 mmol, 61%); ¹H NMR (400 MHz, CDCl₃): δ 7.15 (d, *J* = 6.8 Hz, 1H), 7.07 (t, *J* = 6.9 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 4.44 (s, 1H), 3.0 (d, *J* = 17.2 Hz, 1H), 2.32 (d, *J* = 12.4 Hz, 4H), 1.91 (s, 3H), 1.63 ~ 1.59 (m, 1H), 0.81 (d, *J* = 6.4 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 176.8, 168.1, 152.2, 144.2, 142.0, 129.7, 128.9, 126.6, 126.1, 125.7, 70.2, 50.7, 32.0, 28.8, 20.5, 18.8, 17.2, 14.4; HRMS (EI⁺, *m/z*) calcd for C₁₈H₂₂NO₃ [M+H]⁺: 300.1600, found: 300.1591.

Spectral data for (9*S*,9*aS*)-2,3,7-trimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (8b):



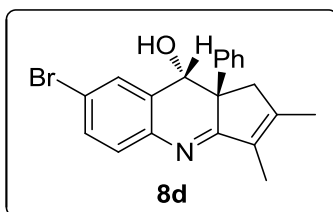
Pale yellow solid, mp: 199-200 °C (0.150 g, 0.494 mmol, 84%); ¹H NMR (400 MHz, CDCl₃): δ 7.09 ~ 6.99 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 4.68 (s, 1H), 3.64 (d, *J* = 16.8 Hz, 1H), 2.52 (d, *J* = 16.8 Hz, 1H), 2.15 (s, 3H), 1.84 (s, 3H), 1.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 181.3, 157.8, 141.9, 141.2, 135.4, 133.8, 129.9, 129.6, 128.2, 126.8, 126.5, 126.4, 125.5, 73.3, 54.7, 45.3, 20.9, 16.2, 8.9; HRMS (EI⁺, *m/z*) calcd for C₂₁H₂₁NO [M⁺]: 303.1623, found: 303.1621.

Spectral data for (9*S*,9*aS*)-7-methoxy-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (8c):



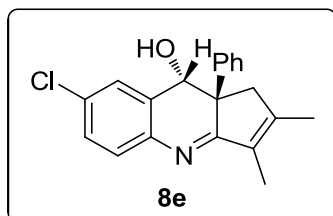
White solid, mp: 193-194 °C (0.157 g, 0.49 mmol, 84%); ^1H NMR (400 MHz, CDCl_3): δ 7.08 ~ 6.93 (m, 5H), 6.94 (d, J = 9.1 Hz, 1H), 6.51 ~ 6.50 (m, 2H), 4.76 (s, 1H), 3.69 ~ 3.61 (m, 4H), 2.52 (d, J = 16.7 Hz, 1H), 1.86 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.3, 157.3, 141.8, 137.1, 133.7, 128.3, 127.9, 126.9, 126.6, 126.5, 114.9, 113.6, 73.5, 55.2, 54.7, 45.3, 16.2, 8.9; HRMS (EI⁺, m/z) calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_2$ [$\text{M}+\text{H}$]: 320.1651, found: 320.1648.

Spectral data for (9S,9aS)-7-bromo-2,3-dimethyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (8d):



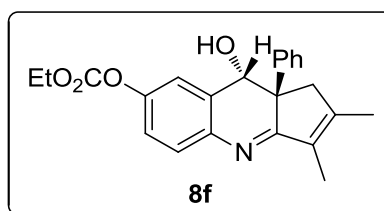
Pale yellow solid, mp: 215-216 °C (0.195 g, 0.529 mmol, 90%); ^1H NMR (400 MHz, CDCl_3): δ 7.08 ~ 7.01 (m, 5H), 6.94 (d, J = 6.8, Hz, 2H), 6.68 (d, J = 8.4 Hz, 1H), 5.32 (bs, 1H), 4.68 (s, 1H), 3.68 (d, J = 16.8 Hz, 1H), 2.54 (d, J = 17.2 Hz, 1H), 1.87 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.1, 160.1, 142.1, 141.0, 133.8, 131.9, 131.9, 128.6, 128.4, 126.9, 126.8, 126.7, 118.6, 72.6, 55.0, 45.4, 16.4, 8.8; HRMS (EI⁺, m/z) calcd for $\text{C}_{20}\text{H}_{18}\text{BrNO}$ [M^+]: 367.0572, found: 367.0574.

Spectral data for (9S,9aS)-7-chloro-2,3-dimethyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[b]quinolin-9-ol (8e):



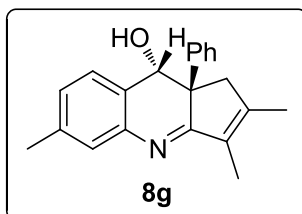
Pale yellow solid, mp: 198-199 °C (0.162 g, 0.500 mmol, 85%); ^1H NMR (400 MHz, CDCl_3): δ 7.09 ~ 7.01 (m, 3H), 6.96 ~ 6.93 (m, 3H), 6.90 (dd, J = 8.4, 2.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 5.19 (bs, 1H), 4.68 (s, 1H), 3.68 (d, J = 16.8 Hz, 1H), 2.54 (d, J = 16.8 Hz, 1H), 1.88 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.0, 159.9, 141.7, 141.1, 133.8, 130.6, 129.1, 128.9, 128.4, 128.3, 126.9, 126.7, 126.5, 72.7, 54.9, 45.4, 16.3, 8.8; HRMS (EI+, m/z) calcd for $\text{C}_{20}\text{H}_{18}\text{ClNO}$ [M^+]: 323.1077, found: 323.1073.

Spectral data for ethyl ((9*S*,9*aS*)-9-hydroxy-2,3-dimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-7-yl) carbonate (8f):



White solid, mp: 195-196 °C (0.177 g, 0.47 mmol, 80%); ^1H NMR (400 MHz, CDCl_3): δ 7.13 (d, J = 8.6 Hz, 1H), 7.10 ~ 7.0 (m, 5H), 6.91 (dd, J = 5.9, 2.6 Hz, 1H), 6.81 (d, J = 2.6 Hz, 1H), 4.74 (s, 1H), 4.25 ~ 4.20 (q, 2H), 3.62 (d, J = 16.9 Hz, 1H), 2.55 (d, J = 16.9 Hz, 1H), 1.90 (s, 3H), 1.86 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.2, 159.1, 153.4, 148.4, 141.7, 141.1, 134.0, 128.4, 127.7, 126.9, 126.8, 126.7, 121.8, 121.3, 73.0, 64.7, 53.8, 45.3, 16.4, 14.2, 9.0; HRMS (EI+, m/z) calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_4$ [$\text{M}+\text{H}$]: 378.1705, found: 378.1709.

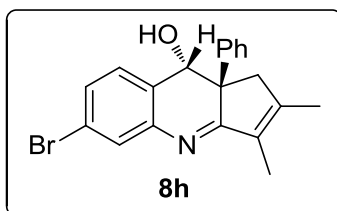
Spectral data for ((9*S*,9*aS*)-2,3,6-trimethyl-9*a*-phenyl-9,9*a*-dihydro-1*H*-cyclopenta[*b*]quinolin-9-ol (8g):



Pale yellow solid, mp: 192-193 °C (0.158 g, 0.521 mmol, 88%); ^1H NMR (400 MHz, CDCl_3): δ 7.06 ~ 6.96 (m, 5H), 6.81 (d, J = 7.6 Hz, 1H), 6.60 (d, J = 6.4 Hz, 2H), 5.01 (bs, 1H), 4.70 (s, 1H), 3.71 (dd, J = 16.8, 1.6 Hz, 1H), 2.54 (d, J = 16.8 Hz, 1H), 2.05 (s, 3H), 1.87 (s, 3H),

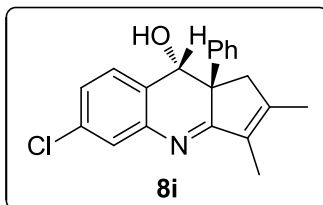
1.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.2, 158.4, 143.0, 141.9, 138.5, 133.9, 128.5, 128.2, 126.7, 126.5, 126.4, 126.1, 123.9, 72.9, 55.1, 45.5, 21.1, 16.3, 8.9; HRMS (EI+, m/z) calcd for $\text{C}_{21}\text{H}_{21}\text{NO}$ [M^+]: 303.1623, found: 303.1625.

Spectral data for (9S,9aS)-6-bromo-2,3-dimethyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[*b*]quinolin-9-ol (8h):



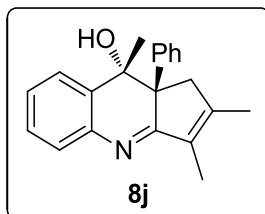
Yellow solid, mp: 200-201 °C (0.159 g, 0.43 mmol, 86%); ^1H NMR (400 MHz, CDCl_3): δ 7.09 ~ 7.01 (m, 5H), 6.97 ~ 6.95 (m, 2H), 6.84 (d, J = 7.9 Hz, 1H), 4.73 (s, 1H), 3.68 (d, J = 16.9 Hz, 1H), 2.56 (d, J = 16.9 Hz, 1H), 1.92 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.8, 160.7, 144.6, 141.1, 133.8, 130.1, 129.1, 128.4, 128.3, 126.8, 126.6, 125.8, 122.6, 72.6, 55.0, 45.5, 16.5, 8.9; HRMS (EI+, m/z) calcd for $\text{C}_{20}\text{H}_{19}\text{BrNO}$ [$\text{M}+\text{H}$]: 368.0650, found: 368.0658.

Spectral data for (9S,9aS)-6-chloro-2,3-dimethyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[*b*]quinolin-9-ol (8i):



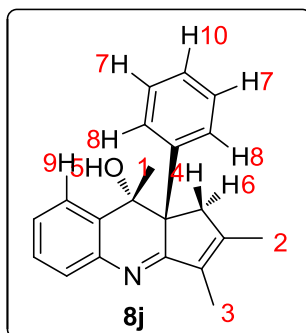
Pale yellow solid, mp: 231-232 °C (0.175 g, 0.54 mmol, 92%); ^1H NMR (400 MHz, CDCl_3): δ 7.08 ~ 7.00 (m, 3H), 6.95 ~ 6.83 (m, 4H), 6.78 (d, J = 1.6 Hz, 1H), 5.09 (bs, 1H), 4.72 (s, 1H), 3.72 (d, J = 17.2 Hz, 1H), 2.56 (d, J = 17.2 Hz, 1H), 1.91 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.9, 160.8, 144.2, 141.2, 134.2, 133.8, 129.8, 128.4, 126.8, 126.6, 126.1, 125.4, 125.3, 72.6, 55.3, 45.5, 16.5, 8.9; HRMS (EI+, m/z) calcd for $\text{C}_{20}\text{H}_{18}\text{ClNO}$ [M^+]: 323.1077, found: 323.1072.

Spectral data for (9S,9aS)-2,3,9-trimethyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[*b*]quinolin-9-ol (8j):



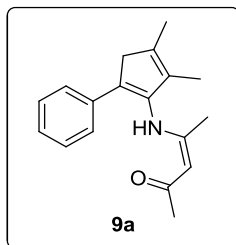
White solid, mp: 179-180 °C (0.156 g, 0.52 mmol, 82%); ^1H NMR (400 MHz, CDCl_3): δ 7.25 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 7.07 ~ 7.06 (m, 3H), 7.05 ~ 7.03 (m, 3H), 6.94 (t, J = 7.2 Hz, 1H), 3.56 (d, J = 16.4 Hz, 1H), 3.15 (s, 1H), 2.85 (d, J = 16.5 Hz, 1H), 1.90 (s, 3H), 1.75 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.5, 158.6, 144.2, 138.4, 133.8, 130.8, 128.8, 128.8, 127.5, 126.7, 125.9, 125.8, 124.0, 72.1, 57.4, 43.5, 22.1, 16.3, 8.8; HRMS (EI⁺, m/z) calcd for $\text{C}_{21}\text{H}_{22}\text{NO}$ [$\text{M}+\text{H}$]: 304.1701, found: 304.1715.

^1H NOE of Compound (9S,9aS)-2,3,9-trimethyl-9a-phenyl-9,9a-dihydro-1H-cyclopenta[*b*]quinolin-9-ol (8j):



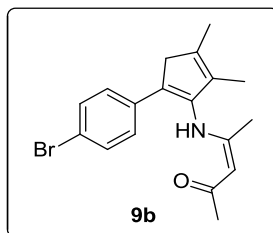
Sr. No.	Irradiation	Intensity Increase % (Key peaks)
1	$\text{CH}_3\mathbf{1}$ (δ 1.67)	$\text{H}\mathbf{6}$ (δ 3.56, 1.79%), $\text{H}\mathbf{7}\mathbf{8}$ (δ 7.07 ~ 7.06, 8.71%), $\text{H}\mathbf{9}$ (δ 7.25, 0.90%)
2	$\text{H}\mathbf{4}$ (δ 2.85)	$\text{H}\mathbf{6}$ (δ 3.56, 28.16%), $\text{H}\mathbf{7}$ (δ 7.05 ~ 7.03, 16.77%)
3	$\text{OH}\mathbf{5}$ (δ 3.15)	$\text{H}\mathbf{6}$ (δ 3.56, 2.07%), $\text{H}\mathbf{8}$ (δ 7.07 ~ 7.06, 2.55%), $\text{H}\mathbf{9}$ (δ 7.25, 3.68%)
4	$\text{H}\mathbf{6}$ (δ 3.56)	$\text{H}\mathbf{4}$ (δ 2.85, 22.63%), $\text{H}\mathbf{9}$ (δ 7.25, 0.94%)
5	$\text{H}\mathbf{8}$ (δ 7.07 ~ 7.06)	$\text{CH}_3\mathbf{1}$ (δ 1.67, 3.06%), $\text{H}\mathbf{4}$ (δ 2.85, 2.76%), $\text{H}\mathbf{10}$ (δ 6.94, 2.66%)

Spectral data for (Z)-4-((4,5-dimethyl-2-phenylcyclopenta-1,4-dien-1-yl)amino)pent-3-en-2-one (9a):



Brown oil (0.113 g, 0.423 mmol, 72%); ^1H NMR (400 MHz, CDCl_3): δ 11.99 (bs, 1H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.26 (t, $J = 7.6$ Hz, 2H), 7.12 (t, $J = 7.2$ Hz, 1H), 5.14 (s, 1H), 3.27 (s, 2H), 2.10 (s, 3H), 1.98 (s, 3H), 1.76 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 196.1, 162.0, 137.9, 135.7, 135.4, 134.9, 132.4, 128.6, 126.3, 125.9, 96.8, 44.4, 29.1, 19.0, 13.9, 10.1; HRMS (ESI, m/z) calcd for $\text{C}_{18}\text{H}_{21}\text{NaNO}$ [M^+]: 290.1521, found: 290.1526.

Spectral data for (Z)-4-((2-(4-bromophenyl)-4,5-dimethylcyclopenta-1,4-dien-1-yl)amino)pent-3-en-2-one (9b):



Pale yellow solid, mp: 146-147 °C (0.089 g, 0.26 mmol, 64%); ^1H NMR (400 MHz, CDCl_3): δ 11.96 (bs, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.8$ Hz, 2H), 5.15 (s, 1H), 3.22 (s, 2H), 2.1 (s, 3H), 1.96 (s, 3H), 1.74 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 196.4, 161.7, 138.8, 136.2, 135.1, 134.3, 131.7, 131.2, 127.4, 119.9, 97.1, 44.2, 29.1, 19.1, 14.0, 10.1; HRMS (EI $^+$, m/z) calcd for $\text{C}_{18}\text{H}_{20}\text{BrNO}$ [M^+]: 345.0728, found: 345.0724.

(5) (a) X-ray crystallographic structure and data for compound (5a)

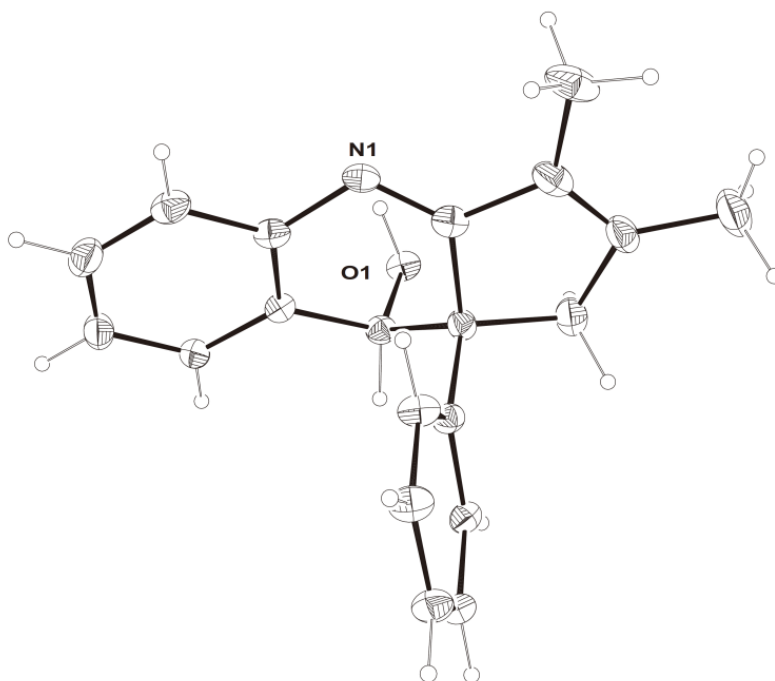
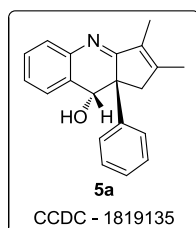


Table S1. Crystal data and structure refinement for d19364.

Identification code	d19364	
Empirical formula	C ₂₀ H ₁₉ N O	
Formula weight	289.36	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 9.5578(12) Å	α = 90°.
	b = 20.653(2) Å	β = 108.514(6)°.
	c = 8.4644(10) Å	γ = 90°.
Volume	1584.4(3) Å ³	
Z	4	
Density (calculated)	1.213 Mg/m ³	
Absorption coefficient	0.074 mm ⁻¹	
F(000)	616	
Crystal size	0.22 x 0.21 x 0.08 mm ³	
Theta range for data collection	2.25 to 25.04°.	
Index ranges	-11 ≤ h ≤ 10, -24 ≤ k ≤ 24, -9 ≤ l ≤ 10	
Reflections collected	21837	
Independent reflections	2789 [R(int) = 0.0500]	
Completeness to theta = 25.04°	99.5 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9941 and 0.9839	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2789 / 0 / 202	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R ₁ = 0.0687, wR ₂ = 0.1679	
R indices (all data)	R ₁ = 0.0953, wR ₂ = 0.1948	
Extinction coefficient	0.016(5)	
Largest diff. peak and hole	0.525 and -0.196 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d19364. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	1904(3)	5191(1)	4632(4)	39(1)
C(2)	2152(3)	5011(1)	3025(3)	39(1)
C(3)	1218(3)	4609(1)	1866(4)	45(1)
C(4)	1478(4)	4432(2)	418(4)	59(1)
C(5)	2726(4)	4671(2)	110(4)	63(1)
C(6)	3678(4)	5068(2)	1230(4)	54(1)
C(7)	3404(3)	5252(1)	2715(4)	43(1)
C(8)	3975(3)	5954(1)	4948(4)	44(1)
C(9)	4825(4)	6374(2)	6264(5)	57(1)
C(10)	6289(4)	6633(2)	6327(6)	77(1)
C(11)	4077(4)	6456(2)	7389(4)	60(1)
C(12)	4600(5)	6821(2)	8961(6)	95(2)
C(13)	2641(4)	6107(2)	6863(4)	54(1)
C(14)	2416(3)	5893(1)	5049(3)	39(1)
C(15)	1346(3)	6347(1)	3783(4)	40(1)
C(16)	1756(3)	6714(1)	2635(4)	48(1)
C(17)	784(3)	7138(2)	1576(4)	54(1)
C(18)	-639(4)	7197(2)	1624(4)	55(1)
C(19)	-1085(3)	6825(2)	2720(4)	49(1)
C(20)	-110(3)	6399(1)	3787(4)	42(1)
N(1)	4436(2)	5662(1)	3868(3)	41(1)
O(1)	2626(2)	4757(1)	5970(2)	43(1)

Table S3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for d19364.

C(1)-O(1)	1.438(3)
C(1)-C(2)	1.500(4)
C(1)-C(14)	1.534(4)
C(1)-H(1)	1.0000
C(2)-C(3)	1.376(4)
C(2)-C(7)	1.395(4)
C(3)-C(4)	1.376(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.390(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.361(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.415(4)
C(6)-H(6)	0.9500
C(7)-N(1)	1.425(4)
C(8)-N(1)	1.285(4)
C(8)-C(9)	1.441(4)
C(8)-C(14)	1.525(4)
C(9)-C(11)	1.371(5)
C(9)-C(10)	1.484(5)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.472(5)
C(11)-C(13)	1.487(5)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.546(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.542(4)
C(15)-C(16)	1.383(4)
C(15)-C(20)	1.398(4)

C(16)-C(17)	1.380(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.380(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.372(5)
C(18)-H(18)	0.9500
C(19)-C(20)	1.387(4)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
O(1)-H(1')	0.8885

O(1)-C(1)-C(2)	112.6(2)
O(1)-C(1)-C(14)	111.7(2)
C(2)-C(1)-C(14)	108.2(2)
O(1)-C(1)-H(1)	108.1
C(2)-C(1)-H(1)	108.1
C(14)-C(1)-H(1)	108.1
C(3)-C(2)-C(7)	118.8(3)
C(3)-C(2)-C(1)	122.8(3)
C(7)-C(2)-C(1)	118.3(3)
C(4)-C(3)-C(2)	122.4(3)
C(4)-C(3)-H(3)	118.8
C(2)-C(3)-H(3)	118.8
C(3)-C(4)-C(5)	118.8(3)
C(3)-C(4)-H(4)	120.6
C(5)-C(4)-H(4)	120.6
C(6)-C(5)-C(4)	120.5(3)
C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(7)	120.6(3)
C(5)-C(6)-H(6)	119.7
C(7)-C(6)-H(6)	119.7
C(2)-C(7)-C(6)	118.9(3)
C(2)-C(7)-N(1)	122.1(3)
C(6)-C(7)-N(1)	119.0(3)
N(1)-C(8)-C(9)	126.7(3)

N(1)-C(8)-C(14)	124.2(3)
C(9)-C(8)-C(14)	109.1(3)
C(11)-C(9)-C(8)	108.7(3)
C(11)-C(9)-C(10)	128.7(3)
C(8)-C(9)-C(10)	122.6(4)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-C(12)	126.0(4)
C(9)-C(11)-C(13)	111.6(3)
C(12)-C(11)-C(13)	122.3(4)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-C(14)	105.1(3)
C(11)-C(13)-H(13A)	110.7
C(14)-C(13)-H(13A)	110.7
C(11)-C(13)-H(13B)	110.7
C(14)-C(13)-H(13B)	110.7
H(13A)-C(13)-H(13B)	108.8
C(8)-C(14)-C(1)	108.2(2)
C(8)-C(14)-C(15)	110.7(2)
C(1)-C(14)-C(15)	108.8(2)
C(8)-C(14)-C(13)	101.6(2)
C(1)-C(14)-C(13)	115.7(2)
C(15)-C(14)-C(13)	111.6(2)
C(16)-C(15)-C(20)	117.6(3)
C(16)-C(15)-C(14)	123.3(2)
C(20)-C(15)-C(14)	119.1(2)
C(17)-C(16)-C(15)	121.5(3)

C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(18)-C(17)-C(16)	120.2(3)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(19)-C(18)-C(17)	119.4(3)
C(19)-C(18)-H(18)	120.3
C(17)-C(18)-H(18)	120.3
C(18)-C(19)-C(20)	120.5(3)
C(18)-C(19)-H(19)	119.8
C(20)-C(19)-H(19)	119.8
C(19)-C(20)-C(15)	120.7(3)
C(19)-C(20)-H(20)	119.6
C(15)-C(20)-H(20)	119.6
C(8)-N(1)-C(7)	116.6(2)
C(1)-O(1)-H(1')	105.6

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d19364. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	35(1)	40(2)	44(2)	0(1)	15(1)	-3(1)
C(2)	39(1)	37(1)	42(2)	1(1)	15(1)	2(1)
C(3)	40(2)	46(2)	44(2)	-5(1)	8(1)	4(1)
C(4)	69(2)	57(2)	44(2)	-9(2)	6(2)	17(2)
C(5)	73(2)	72(2)	46(2)	2(2)	24(2)	23(2)
C(6)	52(2)	65(2)	51(2)	16(2)	26(2)	14(2)
C(7)	38(2)	46(2)	46(2)	13(1)	16(1)	5(1)
C(8)	42(2)	34(1)	54(2)	10(1)	13(1)	-1(1)
C(9)	48(2)	39(2)	68(2)	7(2)	-4(2)	-2(1)
C(10)	47(2)	46(2)	115(3)	19(2)	-8(2)	-7(2)
C(11)	61(2)	39(2)	60(2)	-9(2)	-10(2)	5(2)
C(12)	101(3)	65(3)	84(3)	-28(2)	-23(3)	8(2)
C(13)	65(2)	47(2)	46(2)	-2(1)	12(2)	1(2)
C(14)	39(2)	38(2)	40(2)	-4(1)	11(1)	-4(1)
C(15)	38(1)	34(1)	49(2)	0(1)	14(1)	1(1)
C(16)	40(2)	45(2)	62(2)	14(2)	19(1)	3(1)
C(17)	51(2)	47(2)	67(2)	18(2)	21(2)	5(1)
C(18)	51(2)	51(2)	61(2)	10(2)	14(2)	15(2)
C(19)	41(2)	53(2)	54(2)	-5(2)	14(1)	10(1)
C(20)	41(2)	39(2)	49(2)	-2(1)	20(1)	1(1)
N(1)	32(1)	41(1)	49(1)	12(1)	12(1)	-1(1)
O(1)	44(1)	44(1)	46(1)	14(1)	21(1)	3(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d19364.

	x	y	z	U(eq)
H(1)	819	5173	4455	47
H(3)	361	4448	2074	53
H(4)	817	4151	-358	71
H(5)	2916	4556	-889	75
H(6)	4535	5223	1013	64
H(10A)	7027	6288	6652	116
H(10B)	6565	6985	7143	116
H(10C)	6241	6799	5225	116
H(12A)	5522	7044	9026	143
H(12B)	4774	6522	9903	143
H(12C)	3854	7140	9000	143
H(13A)	1832	6397	6917	65
H(13B)	2674	5727	7587	65
H(16)	2728	6673	2575	58
H(17)	1097	7390	811	65
H(18)	-1305	7493	906	66
H(19)	-2068	6859	2746	59
H(20)	-436	6141	4531	50
H(1')	3476	4653	5817	51

(b) X-ray crystallographic structure and data for compound (5a-O₃)

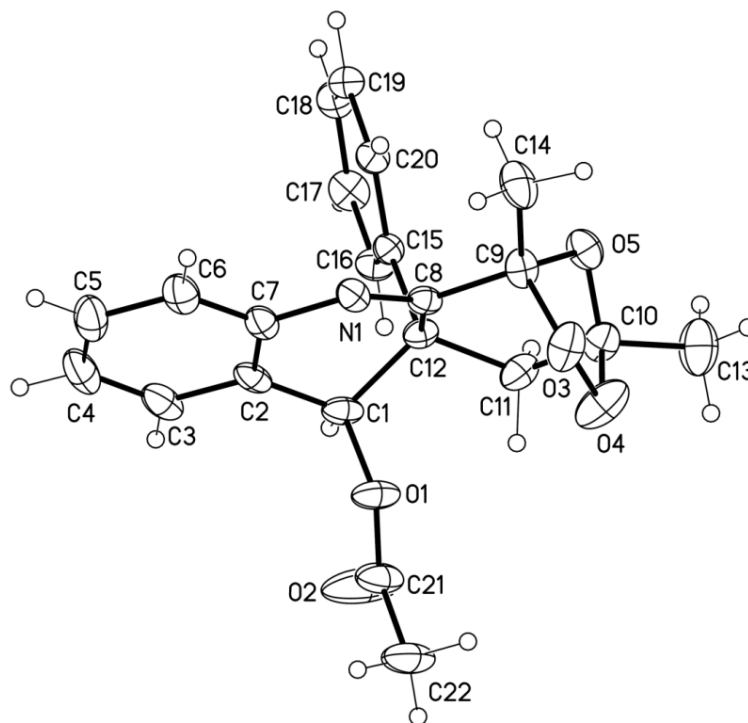
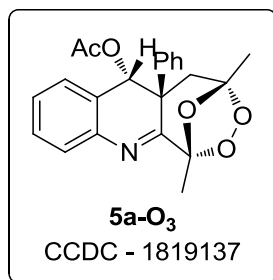


Table S6. Crystal data and structure refinement for 180108LT_0M_A_SQ.

Identification code	180108lt_0m_a_sq	
Empirical formula	C ₂₂ H ₂₁ N O ₅	
Formula weight	379.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 11.8837(10) Å	α = 90°.
	b = 10.0611(7) Å	β = 107.518(3)°.
	c = 19.6889(16) Å	γ = 90°.
Volume	2244.9(3) Å ³	
Z	4	
Density (calculated)	1.123 Mg/m ³	
Absorption coefficient	0.080 mm ⁻¹	
F(000)	800	
Crystal size	0.20 x 0.15 x 0.15 mm ³	
Theta range for data collection	2.169 to 26.414°.	
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 12, -22 ≤ l ≤ 24	
Reflections collected	19526	
Independent reflections	4606 [R(int) = 0.0304]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.8566	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4606 / 0 / 256	
Goodness-of-fit on F ²	1.064	
Final R indices [I > 2σ(I)]	R ₁ = 0.0513, wR ₂ = 0.1177	
R indices (all data)	R ₁ = 0.0637, wR ₂ = 0.1254	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.409 and -0.392 e.Å ⁻³	

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 180108LT_0M_A_SQ. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6145(2)	4106(2)	2494(1)	24(1)
C(2)	4877(2)	4300(2)	2084(1)	24(1)
C(3)	3971(2)	3633(2)	2247(1)	31(1)
C(4)	2811(2)	3881(2)	1862(1)	38(1)
C(5)	2547(2)	4810(2)	1322(1)	36(1)
C(6)	3445(2)	5496(2)	1155(1)	30(1)
C(7)	4608(2)	5230(2)	1530(1)	23(1)
C(8)	6554(2)	5466(2)	1552(1)	20(1)
C(9)	7501(2)	6209(2)	1324(1)	24(1)
C(10)	8951(2)	5245(2)	2152(1)	27(1)
C(11)	8258(2)	4230(2)	2428(1)	29(1)
C(12)	6924(2)	4207(2)	1998(1)	21(1)
C(13)	10256(2)	5001(3)	2368(2)	47(1)
C(14)	7102(2)	6802(2)	591(1)	35(1)
C(15)	6652(2)	2980(2)	1505(1)	19(1)
C(16)	6866(2)	1714(2)	1806(1)	24(1)
C(17)	6668(2)	586(2)	1385(1)	28(1)
C(18)	6247(2)	697(2)	654(1)	28(1)
C(19)	6008(2)	1944(2)	341(1)	25(1)
C(20)	6208(2)	3074(2)	768(1)	21(1)
C(21)	6796(2)	4882(2)	3697(1)	36(1)
C(22)	7020(3)	6092(2)	4157(1)	43(1)
N(1)	5509(1)	5927(2)	1337(1)	22(1)
O(1)	6468(2)	5192(1)	3009(1)	30(1)
O(2)	6915(3)	3760(2)	3909(1)	76(1)
O(3)	7963(1)	7259(1)	1818(1)	34(1)
O(4)	8747(2)	6551(2)	2419(1)	44(1)
O(5)	8482(1)	5372(1)	1404(1)	28(1)

Table S8. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for 180108LT_0M_A_SQ.

C(1)-O(1)	1.462(2)
C(1)-C(2)	1.492(3)
C(1)-C(12)	1.538(3)
C(1)-H(1)	1.0000
C(2)-C(3)	1.385(3)
C(2)-C(7)	1.400(3)
C(3)-C(4)	1.381(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.380(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.391(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.382(3)
C(6)-H(6)	0.9500
C(7)-N(1)	1.424(2)
C(8)-N(1)	1.273(3)
C(8)-C(9)	1.527(3)
C(8)-C(12)	1.529(3)
C(9)-O(5)	1.408(2)
C(9)-O(3)	1.428(2)
C(9)-C(14)	1.500(3)
C(10)-O(5)	1.416(3)
C(10)-O(4)	1.462(2)
C(10)-C(13)	1.499(3)
C(10)-C(11)	1.513(3)
C(11)-C(12)	1.556(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(15)	1.542(3)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800

C(14)-H(14C)	0.9800
C(15)-C(20)	1.390(3)
C(15)-C(16)	1.396(3)
C(16)-C(17)	1.382(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.379(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.389(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.391(3)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-O(2)	1.196(3)
C(21)-O(1)	1.329(3)
C(21)-C(22)	1.492(3)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
O(3)-O(4)	1.453(2)
O(1)-C(1)-C(2)	106.80(16)
O(1)-C(1)-C(12)	107.99(15)
C(2)-C(1)-C(12)	110.51(16)
O(1)-C(1)-H(1)	110.5
C(2)-C(1)-H(1)	110.5
C(12)-C(1)-H(1)	110.5
C(3)-C(2)-C(7)	119.5(2)
C(3)-C(2)-C(1)	122.72(19)
C(7)-C(2)-C(1)	117.78(17)
C(4)-C(3)-C(2)	120.2(2)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	120.2(2)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(4)-C(5)-C(6)	120.4(2)

C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(7)-C(6)-C(5)	119.4(2)
C(7)-C(6)-H(6)	120.3
C(5)-C(6)-H(6)	120.3
C(6)-C(7)-C(2)	120.26(19)
C(6)-C(7)-N(1)	118.22(18)
C(2)-C(7)-N(1)	121.52(18)
N(1)-C(8)-C(9)	117.16(17)
N(1)-C(8)-C(12)	125.10(17)
C(9)-C(8)-C(12)	117.71(16)
O(5)-C(9)-O(3)	103.35(15)
O(5)-C(9)-C(14)	110.88(17)
O(3)-C(9)-C(14)	107.83(17)
O(5)-C(9)-C(8)	109.47(15)
O(3)-C(9)-C(8)	109.17(16)
C(14)-C(9)-C(8)	115.42(17)
O(5)-C(10)-O(4)	103.71(16)
O(5)-C(10)-C(13)	111.06(19)
O(4)-C(10)-C(13)	108.32(19)
O(5)-C(10)-C(11)	110.41(17)
O(4)-C(10)-C(11)	108.07(18)
C(13)-C(10)-C(11)	114.62(19)
C(10)-C(11)-C(12)	112.98(17)
C(10)-C(11)-H(11A)	109.0
C(12)-C(11)-H(11A)	109.0
C(10)-C(11)-H(11B)	109.0
C(12)-C(11)-H(11B)	109.0
H(11A)-C(11)-H(11B)	107.8
C(8)-C(12)-C(1)	107.23(16)
C(8)-C(12)-C(15)	109.37(15)
C(1)-C(12)-C(15)	107.14(15)
C(8)-C(12)-C(11)	111.69(16)
C(1)-C(12)-C(11)	111.35(16)
C(15)-C(12)-C(11)	109.92(16)
C(10)-C(13)-H(13A)	109.5

C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(9)-C(14)-H(14A)	109.5
C(9)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(9)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(20)-C(15)-C(16)	117.92(17)
C(20)-C(15)-C(12)	122.96(17)
C(16)-C(15)-C(12)	119.11(17)
C(17)-C(16)-C(15)	121.25(18)
C(17)-C(16)-H(16)	119.4
C(15)-C(16)-H(16)	119.4
C(18)-C(17)-C(16)	120.15(19)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	119.80(19)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	119.72(18)
C(18)-C(19)-H(19)	120.1
C(20)-C(19)-H(19)	120.1
C(15)-C(20)-C(19)	121.14(18)
C(15)-C(20)-H(20)	119.4
C(19)-C(20)-H(20)	119.4
O(2)-C(21)-O(1)	123.0(2)
O(2)-C(21)-C(22)	125.3(2)
O(1)-C(21)-C(22)	111.72(19)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5

H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(8)-N(1)-C(7)	118.01(16)
C(21)-O(1)-C(1)	117.81(16)
C(9)-O(3)-O(4)	102.28(13)
O(3)-O(4)-C(10)	106.44(15)
C(9)-O(5)-C(10)	102.88(15)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 180108LT_0M_A_SQ. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	40(1)	15(1)	18(1)	-3(1)	12(1)	-5(1)
C(2)	36(1)	17(1)	26(1)	-6(1)	19(1)	-3(1)
C(3)	45(1)	22(1)	36(1)	-6(1)	27(1)	-6(1)
C(4)	42(1)	28(1)	56(2)	-13(1)	35(1)	-12(1)
C(5)	26(1)	33(1)	52(2)	-11(1)	18(1)	-3(1)
C(6)	30(1)	24(1)	39(1)	-5(1)	16(1)	1(1)
C(7)	27(1)	18(1)	28(1)	-6(1)	14(1)	-3(1)
C(8)	26(1)	16(1)	18(1)	-2(1)	9(1)	-1(1)
C(9)	24(1)	17(1)	33(1)	2(1)	10(1)	1(1)
C(10)	25(1)	22(1)	33(1)	-4(1)	6(1)	1(1)
C(11)	28(1)	30(1)	24(1)	0(1)	0(1)	-2(1)
C(12)	26(1)	17(1)	18(1)	0(1)	5(1)	-1(1)
C(13)	25(1)	50(2)	62(2)	7(1)	8(1)	8(1)
C(14)	32(1)	37(1)	41(1)	17(1)	17(1)	1(1)
C(15)	19(1)	19(1)	20(1)	0(1)	7(1)	1(1)
C(16)	30(1)	22(1)	21(1)	2(1)	7(1)	4(1)
C(17)	35(1)	18(1)	34(1)	3(1)	14(1)	4(1)
C(18)	30(1)	21(1)	34(1)	-7(1)	13(1)	-1(1)
C(19)	26(1)	28(1)	21(1)	-3(1)	7(1)	-2(1)
C(20)	24(1)	20(1)	21(1)	3(1)	8(1)	1(1)
C(21)	60(2)	31(1)	22(1)	-4(1)	20(1)	-17(1)
C(22)	72(2)	36(1)	26(1)	-12(1)	22(1)	-19(1)
N(1)	26(1)	17(1)	25(1)	-1(1)	12(1)	-2(1)
O(1)	53(1)	20(1)	19(1)	-4(1)	12(1)	-5(1)
O(2)	166(3)	35(1)	24(1)	-1(1)	22(1)	-33(1)
O(3)	27(1)	18(1)	50(1)	-2(1)	5(1)	0(1)
O(4)	48(1)	24(1)	46(1)	-7(1)	-9(1)	5(1)
O(5)	28(1)	24(1)	35(1)	3(1)	15(1)	4(1)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 180108LT_0M_A_SQ.

	x	y	z	U(eq)
H(1)	6262	3228	2744	29
H(3)	4148	3003	2624	37
H(4)	2193	3411	1971	45
H(5)	1747	4982	1062	43
H(6)	3261	6142	786	35
H(11A)	8339	4429	2933	35
H(11B)	8597	3337	2408	35
H(13A)	10411	4139	2183	70
H(13B)	10571	5000	2889	70
H(13C)	10639	5706	2174	70
H(14A)	7760	7279	499	53
H(14B)	6451	7422	557	53
H(14C)	6834	6093	239	53
H(16)	7152	1625	2309	29
H(17)	6822	-266	1601	34
H(18)	6120	-78	365	33
H(19)	5710	2025	-162	30
H(20)	6039	3925	552	26
H(22A)	7355	5829	4657	65
H(22B)	6277	6567	4095	65
H(22C)	7577	6674	4020	65

(c) X-ray crystallographic structure and data for compound (7a)

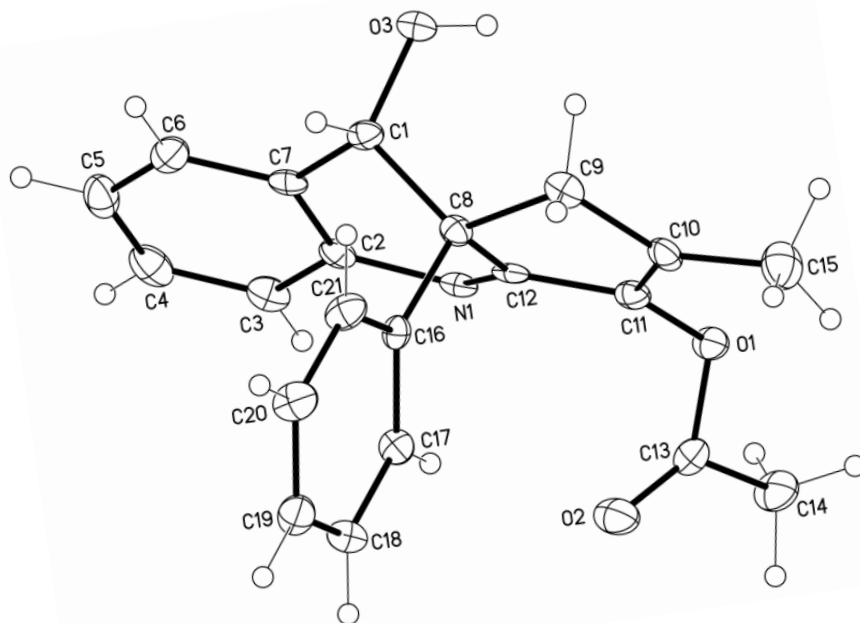
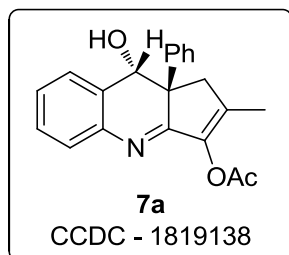


Table S11. Crystal data and structure refinement for TWIN5.

Identification code	TWIN5	
Empirical formula	C ₄₃ H ₃₉ Cl ₃ N ₂ O ₆	
Formula weight	786.11	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.282(7) Å	α = 84.071(19)°.
	b = 11.457(7) Å	β = 88.539(15)°.
	c = 14.934(9) Å	γ = 84.074(13)°.
Volume	1909(2) Å ³	
Z	2	
Density (calculated)	1.367 Mg/m ³	
Absorption coefficient	0.292 mm ⁻¹	
F(000)	820	
Crystal size	0.18 x 0.15 x 0.04 mm ³	
Theta range for data collection	1.371 to 24.997°.	
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, 0 ≤ l ≤ 17	
Reflections collected	6443	
Independent reflections	6443 [R(int) = 0.0495]	
Completeness to theta = 25.000°	95.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9484 and 0.8556	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6443 / 0 / 494	
Goodness-of-fit on F ²	1.028	
Final R indices [I > 2σ(I)]	R ₁ = 0.0451, wR ₂ = 0.0929	
R indices (all data)	R ₁ = 0.0704, wR ₂ = 0.1031	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.302 and -0.328 e.Å ⁻³	

Table S12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for TWIN5. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	8091(3)	4161(2)	6166(2)	15(1)
C(2)	10340(3)	3893(2)	6227(2)	15(1)
C(3)	11420(3)	3181(3)	6334(2)	18(1)
C(4)	11426(3)	1976(3)	6554(2)	24(1)
C(5)	10366(3)	1463(3)	6660(2)	24(1)
C(6)	9286(3)	2164(3)	6543(2)	20(1)
C(7)	9253(3)	3383(2)	6326(2)	15(1)
C(8)	8239(2)	5360(2)	6517(2)	14(1)
C(9)	7305(3)	6404(2)	6192(2)	18(1)
C(10)	8032(3)	7440(2)	6000(2)	16(1)
C(11)	9185(3)	7053(2)	5938(2)	16(1)
C(12)	9402(2)	5786(2)	6133(2)	14(1)
C(13)	10952(3)	7868(2)	6226(2)	19(1)
C(14)	11874(3)	8595(3)	5768(2)	26(1)
C(15)	7494(3)	8689(3)	5881(2)	27(1)
C(16)	8248(2)	5219(2)	7555(2)	13(1)
C(17)	9217(3)	5472(2)	8043(2)	16(1)
C(18)	9153(3)	5394(3)	8977(2)	20(1)
C(19)	8147(3)	5057(2)	9444(2)	21(1)
C(20)	7188(3)	4793(3)	8965(2)	22(1)
C(21)	7236(3)	4888(3)	8034(2)	20(1)
C(22)	5704(3)	2013(2)	8814(2)	16(1)
C(23)	6533(3)	905(3)	8721(2)	18(1)
C(24)	7742(3)	932(3)	8528(2)	23(1)
C(25)	8475(3)	-103(3)	8453(2)	28(1)
C(26)	8010(3)	-1188(3)	8576(2)	26(1)
C(27)	6802(3)	-1232(3)	8779(2)	20(1)
C(28)	4120(2)	670(2)	8816(2)	13(1)
C(29)	2844(3)	843(2)	8970(2)	14(1)
C(30)	2410(3)	1975(3)	8842(2)	17(1)
C(31)	3415(3)	2731(2)	8605(2)	17(1)

C(32)	4503(3)	1851(2)	8389(2)	15(1)
C(33)	1145(3)	2474(3)	8955(2)	25(1)
O(6)	2183(2)	-78(2)	9304(1)	17(1)
C(35)	2042(2)	-905(2)	8727(2)	15(1)
C(36)	4696(2)	1847(2)	7369(2)	13(1)
C(37)	4974(3)	2884(3)	6861(2)	18(1)
C(38)	5183(3)	2915(3)	5938(2)	23(1)
C(39)	5102(3)	1921(3)	5504(2)	22(1)
C(40)	4804(3)	896(3)	6001(2)	20(1)
C(41)	4604(3)	859(2)	6923(2)	16(1)
C(42)	6058(2)	-191(2)	8836(2)	15(1)
C(43)	3645(3)	6718(2)	7504(2)	21(1)
Cl(1)	3697(1)	5908(1)	6562(1)	38(1)
Cl(2)	3862(1)	5771(1)	8510(1)	39(1)
Cl(3)	4755(1)	7703(1)	7392(1)	37(1)
N(1)	10375(2)	5136(2)	5996(1)	14(1)
N(2)	4816(2)	-276(2)	9026(1)	14(1)
O(1)	10070(2)	7779(2)	5635(1)	17(1)
O(2)	10959(2)	7417(2)	6987(1)	26(1)
O(3)	7745(2)	4276(2)	5248(1)	18(1)
O(4)	5578(2)	2292(2)	9727(1)	21(1)
O(5)	2349(2)	-790(2)	7955(1)	21(1)
C(34)	1463(3)	-1920(3)	9203(2)	23(1)

Table S13. Bond lengths [Å] and angles [°] for TWIN5.

C(1)-O(3)	1.423(3)
C(1)-C(7)	1.517(4)
C(1)-C(8)	1.546(4)
C(1)-H(1)	1.0000
C(2)-C(3)	1.398(4)
C(2)-C(7)	1.411(4)
C(2)-N(1)	1.434(4)
C(3)-C(4)	1.384(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.384(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.392(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.397(4)
C(6)-H(6)	0.9500
C(8)-C(12)	1.524(4)
C(8)-C(16)	1.542(4)
C(8)-C(9)	1.556(4)
C(9)-C(10)	1.511(4)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.335(4)
C(10)-C(15)	1.490(4)
C(11)-O(1)	1.402(3)
C(11)-C(12)	1.447(4)
C(12)-N(1)	1.286(4)
C(13)-O(2)	1.199(3)
C(13)-O(1)	1.365(3)
C(13)-C(14)	1.506(4)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800

C(15)-H(15C)	0.9800
C(16)-C(21)	1.397(4)
C(16)-C(17)	1.400(4)
C(17)-C(18)	1.389(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.384(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.388(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.383(4)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(22)-O(4)	1.432(3)
C(22)-C(23)	1.513(4)
C(22)-C(32)	1.546(4)
C(22)-H(22)	1.0000
C(23)-C(24)	1.390(4)
C(23)-C(42)	1.408(4)
C(24)-C(25)	1.387(5)
C(24)-H(24)	0.9500
C(25)-C(26)	1.392(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.394(4)
C(26)-H(26)	0.9500
C(27)-C(42)	1.395(4)
C(27)-H(27)	0.9500
C(28)-N(2)	1.287(4)
C(28)-C(29)	1.449(4)
C(28)-C(32)	1.533(4)
C(29)-C(30)	1.335(4)
C(29)-O(6)	1.398(3)
C(30)-C(33)	1.494(4)
C(30)-C(31)	1.510(4)
C(31)-C(32)	1.556(4)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900

C(32)-C(36)	1.534(4)
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
O(6)-C(35)	1.368(3)
C(35)-O(5)	1.194(3)
C(35)-C(34)	1.498(4)
C(36)-C(41)	1.386(4)
C(36)-C(37)	1.401(4)
C(37)-C(38)	1.391(4)
C(37)-H(37)	0.9500
C(38)-C(39)	1.379(4)
C(38)-H(38)	0.9500
C(39)-C(40)	1.389(4)
C(39)-H(39)	0.9500
C(40)-C(41)	1.386(4)
C(40)-H(40)	0.9500
C(41)-H(41)	0.9500
C(42)-N(2)	1.433(4)
C(43)-Cl(1)	1.760(3)
C(43)-Cl(3)	1.764(3)
C(43)-Cl(2)	1.766(3)
C(43)-H(43)	1.0000
O(3)-H(3A)	0.8400
O(4)-H(4A)	0.8400
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
O(3)-C(1)-C(7)	112.4(2)
O(3)-C(1)-C(8)	112.9(2)
C(7)-C(1)-C(8)	107.5(2)
O(3)-C(1)-H(1)	108.0
C(7)-C(1)-H(1)	108.0
C(8)-C(1)-H(1)	108.0
C(3)-C(2)-C(7)	120.0(3)

C(3)-C(2)-N(1)	118.4(3)
C(7)-C(2)-N(1)	121.6(2)
C(4)-C(3)-C(2)	120.2(3)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	120.5(3)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	119.7(3)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(5)-C(6)-C(7)	121.0(3)
C(5)-C(6)-H(6)	119.5
C(7)-C(6)-H(6)	119.5
C(6)-C(7)-C(2)	118.5(3)
C(6)-C(7)-C(1)	122.1(3)
C(2)-C(7)-C(1)	119.3(2)
C(12)-C(8)-C(16)	110.8(2)
C(12)-C(8)-C(1)	108.4(2)
C(16)-C(8)-C(1)	109.9(2)
C(12)-C(8)-C(9)	102.4(2)
C(16)-C(8)-C(9)	108.9(2)
C(1)-C(8)-C(9)	116.2(2)
C(10)-C(9)-C(8)	104.1(2)
C(10)-C(9)-H(9A)	110.9
C(8)-C(9)-H(9A)	110.9
C(10)-C(9)-H(9B)	110.9
C(8)-C(9)-H(9B)	110.9
H(9A)-C(9)-H(9B)	109.0
C(11)-C(10)-C(15)	127.0(3)
C(11)-C(10)-C(9)	109.6(2)
C(15)-C(10)-C(9)	123.3(3)
C(10)-C(11)-O(1)	123.5(2)
C(10)-C(11)-C(12)	112.5(2)
O(1)-C(11)-C(12)	123.8(3)
N(1)-C(12)-C(11)	127.1(2)

N(1)-C(12)-C(8)	126.3(2)
C(11)-C(12)-C(8)	106.7(2)
O(2)-C(13)-O(1)	123.3(3)
O(2)-C(13)-C(14)	127.2(3)
O(1)-C(13)-C(14)	109.5(2)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(10)-C(15)-H(15A)	109.5
C(10)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(10)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(21)-C(16)-C(17)	118.1(2)
C(21)-C(16)-C(8)	119.5(2)
C(17)-C(16)-C(8)	122.3(2)
C(18)-C(17)-C(16)	120.0(3)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	121.3(3)
C(19)-C(18)-H(18)	119.3
C(17)-C(18)-H(18)	119.3
C(18)-C(19)-C(20)	119.0(3)
C(18)-C(19)-H(19)	120.5
C(20)-C(19)-H(19)	120.5
C(21)-C(20)-C(19)	120.1(3)
C(21)-C(20)-H(20)	119.9
C(19)-C(20)-H(20)	119.9
C(20)-C(21)-C(16)	121.4(3)
C(20)-C(21)-H(21)	119.3
C(16)-C(21)-H(21)	119.3
O(4)-C(22)-C(23)	112.5(2)

O(4)-C(22)-C(32)	113.0(2)
C(23)-C(22)-C(32)	107.6(2)
O(4)-C(22)-H(22)	107.8
C(23)-C(22)-H(22)	107.8
C(32)-C(22)-H(22)	107.8
C(24)-C(23)-C(42)	119.1(3)
C(24)-C(23)-C(22)	122.4(3)
C(42)-C(23)-C(22)	118.5(3)
C(25)-C(24)-C(23)	120.7(3)
C(25)-C(24)-H(24)	119.6
C(23)-C(24)-H(24)	119.6
C(24)-C(25)-C(26)	120.3(3)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(25)-C(26)-C(27)	119.7(3)
C(25)-C(26)-H(26)	120.1
C(27)-C(26)-H(26)	120.1
C(26)-C(27)-C(42)	120.1(3)
C(26)-C(27)-H(27)	120.0
C(42)-C(27)-H(27)	120.0
N(2)-C(28)-C(29)	127.0(2)
N(2)-C(28)-C(32)	126.0(3)
C(29)-C(28)-C(32)	107.0(2)
C(30)-C(29)-O(6)	124.6(3)
C(30)-C(29)-C(28)	112.7(2)
O(6)-C(29)-C(28)	122.3(2)
C(29)-C(30)-C(33)	127.2(3)
C(29)-C(30)-C(31)	109.6(3)
C(33)-C(30)-C(31)	123.1(2)
C(30)-C(31)-C(32)	105.1(2)
C(30)-C(31)-H(31A)	110.7
C(32)-C(31)-H(31A)	110.7
C(30)-C(31)-H(31B)	110.7
C(32)-C(31)-H(31B)	110.7
H(31A)-C(31)-H(31B)	108.8
C(28)-C(32)-C(36)	111.4(2)

C(28)-C(32)-C(22)	107.0(2)
C(36)-C(32)-C(22)	108.4(2)
C(28)-C(32)-C(31)	102.2(2)
C(36)-C(32)-C(31)	110.8(2)
C(22)-C(32)-C(31)	116.9(2)
C(30)-C(33)-H(33A)	109.5
C(30)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(30)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(35)-O(6)-C(29)	116.0(2)
O(5)-C(35)-O(6)	122.4(2)
O(5)-C(35)-C(34)	127.0(3)
O(6)-C(35)-C(34)	110.6(2)
C(41)-C(36)-C(37)	118.2(3)
C(41)-C(36)-C(32)	122.8(2)
C(37)-C(36)-C(32)	119.0(2)
C(38)-C(37)-C(36)	121.0(3)
C(38)-C(37)-H(37)	119.5
C(36)-C(37)-H(37)	119.5
C(39)-C(38)-C(37)	120.1(3)
C(39)-C(38)-H(38)	120.0
C(37)-C(38)-H(38)	120.0
C(38)-C(39)-C(40)	119.2(3)
C(38)-C(39)-H(39)	120.4
C(40)-C(39)-H(39)	120.4
C(41)-C(40)-C(39)	120.9(3)
C(41)-C(40)-H(40)	119.5
C(39)-C(40)-H(40)	119.5
C(36)-C(41)-C(40)	120.6(3)
C(36)-C(41)-H(41)	119.7
C(40)-C(41)-H(41)	119.7
C(27)-C(42)-C(23)	120.1(3)
C(27)-C(42)-N(2)	118.2(2)
C(23)-C(42)-N(2)	121.7(3)

Cl(1)-C(43)-Cl(3)	109.66(16)
Cl(1)-C(43)-Cl(2)	110.99(16)
Cl(3)-C(43)-Cl(2)	109.49(16)
Cl(1)-C(43)-H(43)	108.9
Cl(3)-C(43)-H(43)	108.9
Cl(2)-C(43)-H(43)	108.9
C(12)-N(1)-C(2)	115.8(2)
C(28)-N(2)-C(42)	115.6(2)
C(13)-O(1)-C(11)	116.6(2)
C(1)-O(3)-H(3A)	109.5
C(22)-O(4)-H(4A)	109.5
C(35)-C(34)-H(34A)	109.5
C(35)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(35)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for TWIN5. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	17(2)	19(2)	9(1)	-3(1)	2(1)	-6(1)
C(2)	18(2)	20(2)	7(1)	-3(1)	0(1)	0(1)
C(3)	15(2)	25(2)	15(2)	-4(1)	1(1)	0(1)
C(4)	26(2)	29(2)	15(2)	-4(1)	0(1)	7(1)
C(5)	35(2)	18(2)	16(2)	0(1)	0(1)	3(1)
C(6)	26(2)	21(2)	13(2)	-4(1)	4(1)	-7(1)
C(7)	17(2)	21(2)	7(1)	-5(1)	0(1)	-2(1)
C(8)	10(2)	16(2)	14(2)	0(1)	-2(1)	-1(1)
C(9)	15(2)	23(2)	16(2)	-1(1)	0(1)	-1(1)
C(10)	20(2)	18(2)	10(1)	0(1)	-1(1)	0(1)
C(11)	19(2)	21(2)	9(1)	0(1)	-1(1)	-8(1)
C(12)	13(2)	22(2)	7(1)	-3(1)	-3(1)	-6(1)
C(13)	19(2)	16(2)	22(2)	-3(1)	0(1)	-4(1)
C(14)	26(2)	28(2)	25(2)	-1(1)	2(1)	-14(2)
C(15)	22(2)	25(2)	33(2)	1(1)	-2(1)	1(1)
C(16)	14(2)	10(1)	15(2)	-2(1)	1(1)	1(1)
C(17)	14(2)	17(2)	17(2)	-1(1)	1(1)	-3(1)
C(18)	21(2)	23(2)	16(2)	-3(1)	-4(1)	-3(1)
C(19)	29(2)	19(2)	15(2)	-4(1)	5(1)	-4(1)
C(20)	21(2)	28(2)	18(2)	-5(1)	7(1)	-9(1)
C(21)	18(2)	22(2)	21(2)	-6(1)	4(1)	-7(1)
C(22)	24(2)	16(2)	10(1)	0(1)	-1(1)	-10(1)
C(23)	21(2)	25(2)	9(1)	-1(1)	-5(1)	-4(1)
C(24)	21(2)	32(2)	17(2)	6(1)	-3(1)	-11(2)
C(25)	16(2)	44(2)	22(2)	4(2)	0(1)	-6(2)
C(26)	20(2)	34(2)	21(2)	-1(1)	-2(1)	7(1)
C(27)	23(2)	21(2)	15(2)	0(1)	-3(1)	-2(1)
C(28)	20(2)	14(2)	6(1)	-4(1)	-1(1)	-5(1)
C(29)	18(2)	16(2)	10(1)	-2(1)	1(1)	-6(1)
C(30)	20(2)	22(2)	10(1)	-5(1)	-1(1)	-1(1)
C(31)	24(2)	12(1)	16(2)	-4(1)	1(1)	-1(1)

C(32)	20(2)	12(1)	13(2)	-1(1)	-1(1)	-4(1)
C(33)	24(2)	25(2)	23(2)	-5(1)	3(1)	4(1)
O(6)	19(1)	18(1)	15(1)	-3(1)	3(1)	-7(1)
C(35)	14(2)	14(2)	17(2)	-4(1)	-3(1)	0(1)
C(36)	11(2)	13(1)	14(1)	-1(1)	-1(1)	0(1)
C(37)	21(2)	19(2)	16(2)	-1(1)	-5(1)	-7(1)
C(38)	22(2)	27(2)	19(2)	5(1)	-6(1)	-10(1)
C(39)	18(2)	34(2)	14(2)	-1(1)	1(1)	-1(1)
C(40)	23(2)	23(2)	15(2)	-6(1)	0(1)	2(1)
C(41)	17(2)	14(2)	17(2)	-1(1)	-1(1)	0(1)
C(42)	16(2)	20(2)	8(1)	2(1)	-2(1)	-4(1)
C(43)	20(2)	18(2)	24(2)	-4(1)	-1(1)	-4(1)
Cl(1)	53(1)	31(1)	31(1)	-17(1)	-7(1)	0(1)
Cl(2)	49(1)	38(1)	27(1)	6(1)	2(1)	2(1)
Cl(3)	26(1)	21(1)	68(1)	-16(1)	14(1)	-9(1)
N(1)	12(1)	21(1)	10(1)	-3(1)	-3(1)	-3(1)
N(2)	15(1)	15(1)	12(1)	-3(1)	-2(1)	-2(1)
O(1)	18(1)	20(1)	15(1)	1(1)	0(1)	-9(1)
O(2)	28(1)	35(1)	19(1)	3(1)	-3(1)	-17(1)
O(3)	14(1)	30(1)	11(1)	-4(1)	2(1)	-6(1)
O(4)	35(1)	16(1)	12(1)	0(1)	-3(1)	-11(1)
O(5)	25(1)	22(1)	17(1)	-6(1)	2(1)	-8(1)
C(34)	23(2)	21(2)	27(2)	-2(1)	2(1)	-9(1)

Table S15. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for TWIN5.

	x	y	z	U(eq)
H(1)	7454	3789	6536	18
H(3)	12152	3523	6256	22
H(4)	12162	1498	6634	29
H(5)	10375	637	6811	28
H(6)	8561	1808	6612	23
H(9A)	6905	6241	5643	22
H(9B)	6695	6552	6667	22
H(14A)	12401	8816	6220	39
H(14B)	11476	9310	5443	39
H(14C)	12345	8133	5342	39
H(15A)	8128	9216	5846	40
H(15B)	6964	8847	6394	40
H(15C)	7036	8824	5324	40
H(17)	9919	5696	7736	19
H(18)	9812	5575	9302	24
H(19)	8114	5007	10083	25
H(20)	6498	4547	9277	26
H(21)	6565	4724	7714	24
H(22)	6051	2683	8453	19
H(24)	8070	1668	8446	28
H(25)	9299	-71	8316	33
H(26)	8514	-1895	8523	31
H(27)	6485	-1971	8878	24
H(31A)	3587	3168	9117	20
H(31B)	3211	3304	8076	20
H(33A)	639	1829	9081	37
H(33B)	883	2956	8401	37
H(33C)	1082	2965	9458	37
H(37)	5021	3576	7153	22
H(38)	5382	3623	5605	27

H(39)	5248	1936	4874	26
H(40)	4737	211	5705	24
H(41)	4402	150	7251	19
H(43)	2846	7182	7535	25
H(3A)	8332	4427	4915	27
H(4A)	5566	1666	10073	31
H(34A)	1192	-2402	8758	35
H(34B)	778	-1618	9559	35
H(34C)	2039	-2402	9602	35

(d) X-ray crystallographic structure and data for compound (9b)

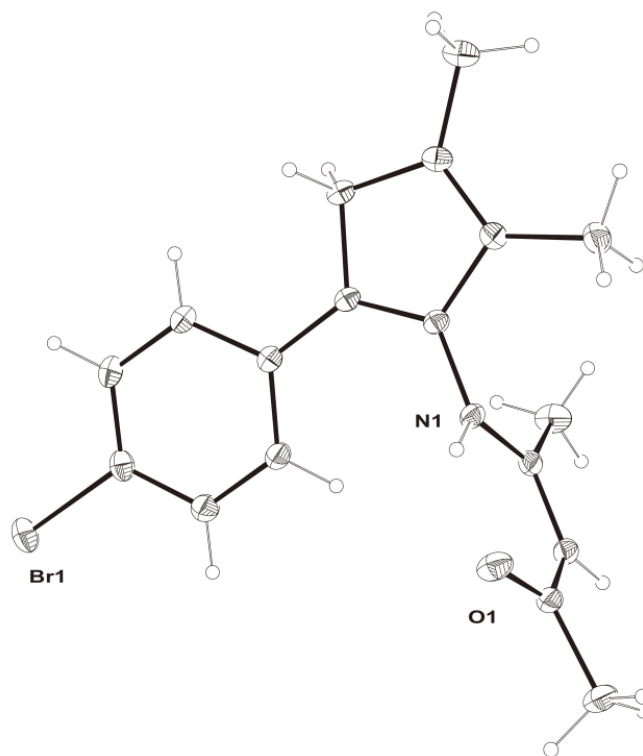
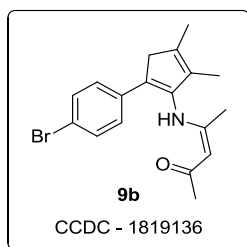


Table S16. Crystal data and structure refinement for d19332.

Identification code	d19332	
Empirical formula	C ₁₈ H ₂₀ Br N O	
Formula weight	346.26	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6388(10) Å	α = 116.079(3)°.
	b = 11.2206(13) Å	β = 109.218(4)°.
	c = 11.3511(13) Å	γ = 91.505(4)°.
Volume	808.23(17) Å ³	
Z	2	
Density (calculated)	1.423 Mg/m ³	
Absorption coefficient	2.542 mm ⁻¹	
F(000)	356	
Crystal size	0.43 x 0.31 x 0.15 mm ³	
Theta range for data collection	2.87 to 25.07°.	
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13	
Reflections collected	26621	
Independent reflections	2830 [R(int) = 0.0345]	
Completeness to theta = 25.07°	98.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7017 and 0.4078	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2830 / 0 / 192	
Goodness-of-fit on F ²	1.060	
Final R indices [I > 2σ(I)]	R ₁ = 0.0237, wR ₂ = 0.0630	
R indices (all data)	R ₁ = 0.0258, wR ₂ = 0.0643	
Largest diff. peak and hole	0.228 and -0.318 e.Å ⁻³	

Table S17. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d19332. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	4367(3)	8155(2)	7066(2)	39(1)
C(2)	3160(3)	7474(2)	5659(2)	41(1)
C(3)	2584(3)	6087(2)	5005(2)	37(1)
C(4)	3178(2)	5336(2)	5724(2)	31(1)
C(5)	4390(3)	6070(2)	7156(2)	40(1)
C(6)	4982(3)	7458(2)	7822(2)	44(1)
C(7)	2509(2)	3872(2)	4993(2)	30(1)
C(8)	1050(2)	3113(2)	3503(2)	34(1)
C(9)	797(2)	1663(2)	3184(2)	36(1)
C(10)	-481(3)	543(2)	1771(2)	50(1)
C(11)	1944(2)	1566(2)	4312(2)	34(1)
C(12)	2222(3)	320(2)	4467(2)	45(1)
C(13)	3002(2)	2930(2)	5414(2)	30(1)
C(14)	4258(2)	3204(2)	7831(2)	31(1)
C(15)	2314(3)	3133(3)	7840(2)	52(1)
C(16)	5801(3)	3330(2)	8962(2)	35(1)
C(17)	7660(3)	3336(2)	8970(2)	37(1)
C(18)	9204(3)	3379(2)	10236(2)	54(1)
Br(1)	5171(1)	10062(1)	7971(1)	51(1)
N(1)	4473(2)	3152(2)	6689(2)	31(1)
O(1)	8081(2)	3301(2)	7987(1)	47(1)

Table S18. Bond lengths [Å] and angles [°] for d19332.

C(1)-C(2)	1.381(3)
C(1)-C(6)	1.382(3)
C(1)-Br(1)	1.8961(19)
C(2)-C(3)	1.379(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.402(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.403(3)
C(4)-C(7)	1.458(3)
C(5)-C(6)	1.380(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(13)	1.354(2)
C(7)-C(8)	1.507(2)
C(8)-C(9)	1.495(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(11)	1.345(3)
C(9)-C(10)	1.496(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(13)	1.465(2)
C(11)-C(12)	1.496(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-N(1)	1.421(2)
C(14)-N(1)	1.336(2)
C(14)-C(16)	1.376(2)
C(14)-C(15)	1.489(3)
C(15)-H(15A)	0.9549
C(15)-H(15B)	0.8910
C(15)-H(15C)	0.9907

C(16)-C(17)	1.417(3)
C(16)-H(16)	0.9500
C(17)-O(1)	1.244(2)
C(17)-C(18)	1.509(3)
C(18)-H(18A)	0.9645
C(18)-H(18B)	1.0108
C(18)-H(18C)	0.9528
N(1)-H(1')	0.9247

C(2)-C(1)-C(6)	120.53(18)
C(2)-C(1)-Br(1)	119.63(14)
C(6)-C(1)-Br(1)	119.83(15)
C(3)-C(2)-C(1)	119.40(17)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	122.14(17)
C(2)-C(3)-H(3)	118.9
C(4)-C(3)-H(3)	118.9
C(3)-C(4)-C(5)	116.50(17)
C(3)-C(4)-C(7)	120.12(16)
C(5)-C(4)-C(7)	123.37(15)
C(6)-C(5)-C(4)	121.94(17)
C(6)-C(5)-H(5)	119.0
C(4)-C(5)-H(5)	119.0
C(5)-C(6)-C(1)	119.49(18)
C(5)-C(6)-H(6)	120.3
C(1)-C(6)-H(6)	120.3
C(13)-C(7)-C(4)	130.85(16)
C(13)-C(7)-C(8)	106.27(15)
C(4)-C(7)-C(8)	122.87(15)
C(9)-C(8)-C(7)	104.79(14)
C(9)-C(8)-H(8A)	110.8
C(7)-C(8)-H(8A)	110.8
C(9)-C(8)-H(8B)	110.8
C(7)-C(8)-H(8B)	110.8
H(8A)-C(8)-H(8B)	108.9

C(11)-C(9)-C(10)	128.15(18)
C(11)-C(9)-C(8)	109.32(15)
C(10)-C(9)-C(8)	122.44(17)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-C(13)	107.95(16)
C(9)-C(11)-C(12)	128.44(17)
C(13)-C(11)-C(12)	123.56(16)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(7)-C(13)-N(1)	126.50(16)
C(7)-C(13)-C(11)	111.65(15)
N(1)-C(13)-C(11)	121.59(15)
N(1)-C(14)-C(16)	120.42(16)
N(1)-C(14)-C(15)	118.03(16)
C(16)-C(14)-C(15)	121.55(16)
C(14)-C(15)-H(15A)	107.3
C(14)-C(15)-H(15B)	112.4
H(15A)-C(15)-H(15B)	108.9
C(14)-C(15)-H(15C)	112.9
H(15A)-C(15)-H(15C)	104.3
H(15B)-C(15)-H(15C)	110.7
C(14)-C(16)-C(17)	123.39(16)
C(14)-C(16)-H(16)	118.3
C(17)-C(16)-H(16)	118.3
O(1)-C(17)-C(16)	123.46(16)
O(1)-C(17)-C(18)	118.45(18)
C(16)-C(17)-C(18)	118.09(18)

C(17)-C(18)-H(18A)	107.9
C(17)-C(18)-H(18B)	108.3
H(18A)-C(18)-H(18B)	117.6
C(17)-C(18)-H(18C)	110.7
H(18A)-C(18)-H(18C)	104.5
H(18B)-C(18)-H(18C)	107.8
C(14)-N(1)-C(13)	126.37(14)
C(14)-N(1)-H(1')	114.2
C(13)-N(1)-H(1')	119.4

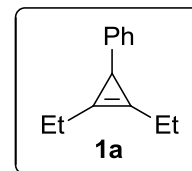
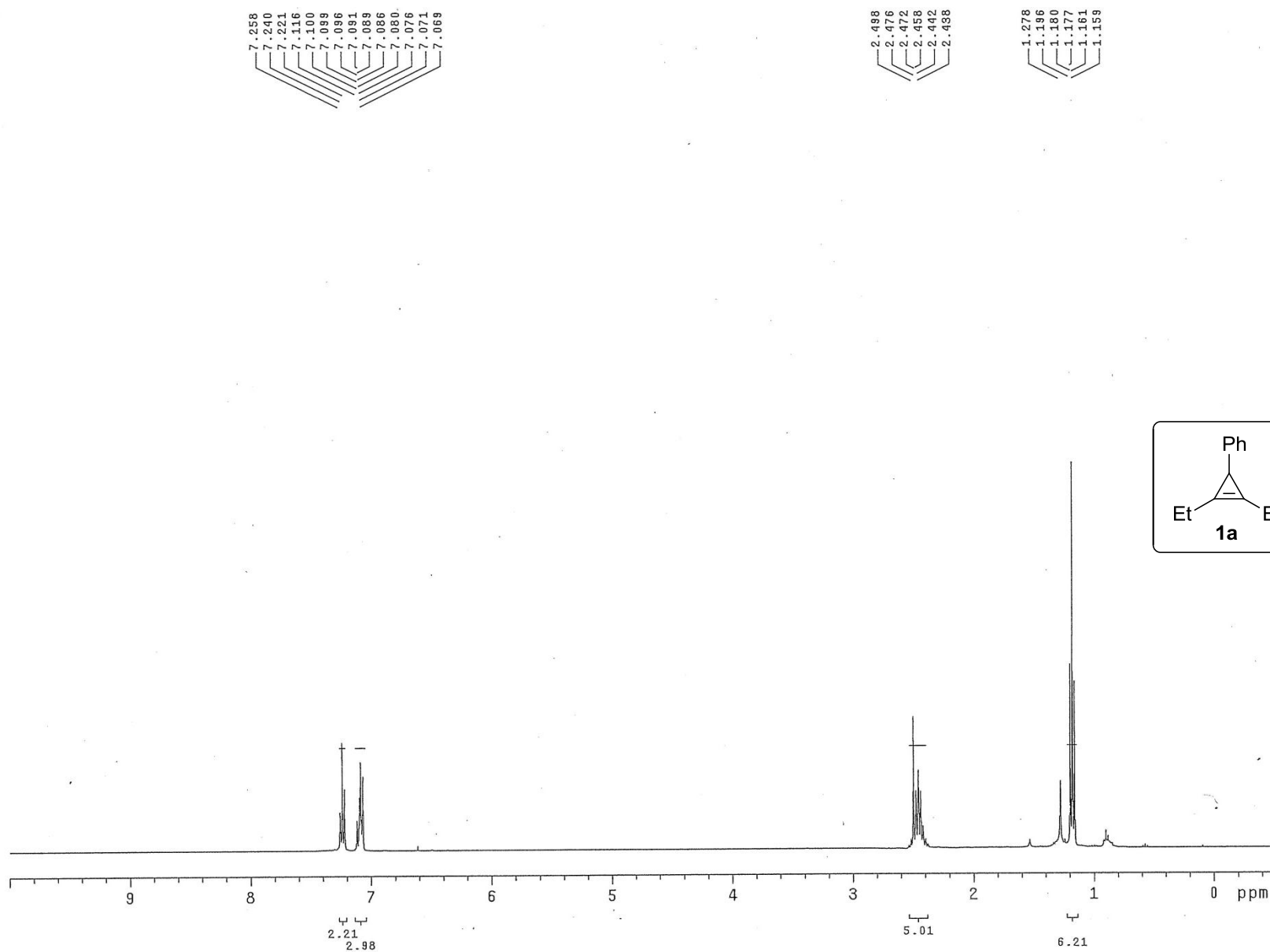
Symmetry transformations used to generate equivalent atoms:

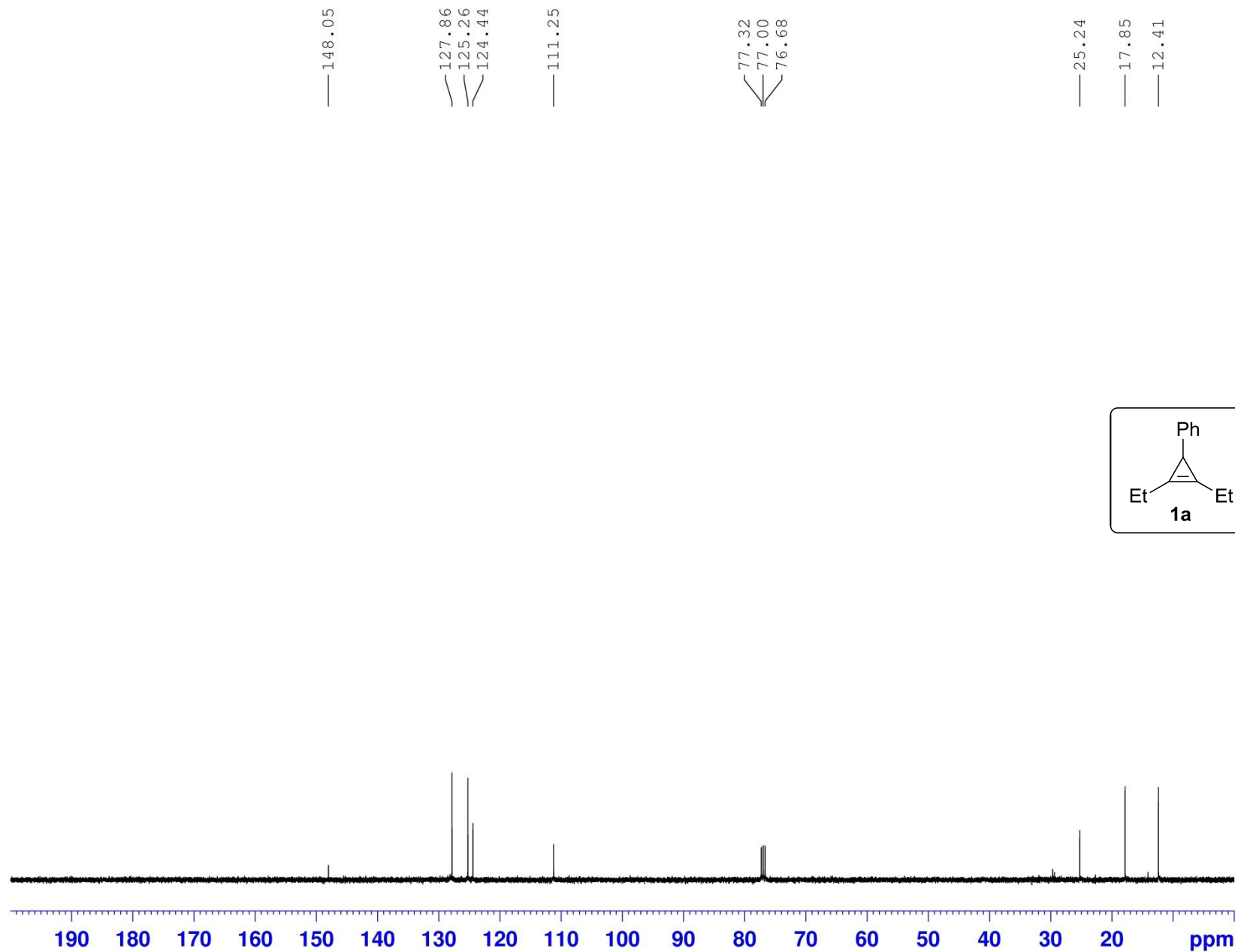
Table S19. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d19332. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

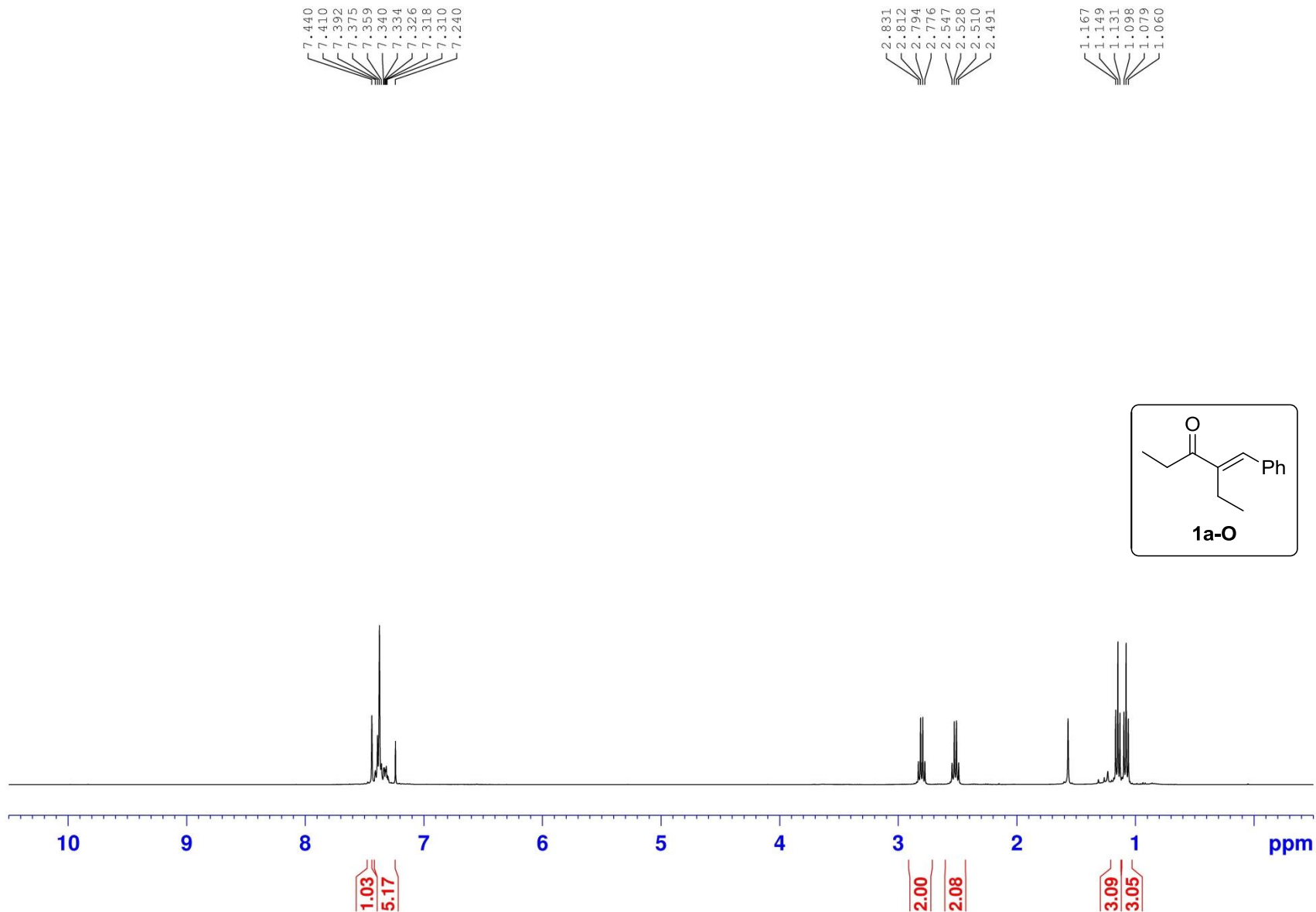
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	45(1)	32(1)	47(1)	20(1)	25(1)	11(1)
C(2)	50(1)	41(1)	47(1)	29(1)	23(1)	16(1)
C(3)	40(1)	41(1)	34(1)	22(1)	14(1)	12(1)
C(4)	31(1)	36(1)	32(1)	19(1)	15(1)	11(1)
C(5)	50(1)	36(1)	35(1)	20(1)	10(1)	9(1)
C(6)	51(1)	37(1)	37(1)	16(1)	12(1)	7(1)
C(7)	28(1)	36(1)	28(1)	16(1)	11(1)	9(1)
C(8)	30(1)	43(1)	28(1)	18(1)	10(1)	10(1)
C(9)	30(1)	39(1)	32(1)	12(1)	12(1)	6(1)
C(10)	46(1)	50(1)	36(1)	9(1)	9(1)	1(1)
C(11)	31(1)	33(1)	36(1)	15(1)	14(1)	7(1)
C(12)	48(1)	35(1)	49(1)	20(1)	16(1)	7(1)
C(13)	27(1)	35(1)	29(1)	16(1)	10(1)	7(1)
C(14)	37(1)	26(1)	30(1)	12(1)	12(1)	6(1)
C(15)	41(1)	68(2)	42(1)	19(1)	19(1)	6(1)
C(16)	45(1)	32(1)	27(1)	14(1)	12(1)	5(1)
C(17)	42(1)	29(1)	32(1)	14(1)	5(1)	6(1)
C(18)	52(1)	57(1)	41(1)	26(1)	0(1)	10(1)
Br(1)	62(1)	33(1)	62(1)	21(1)	30(1)	7(1)
N(1)	28(1)	36(1)	33(1)	20(1)	9(1)	7(1)
O(1)	34(1)	68(1)	40(1)	28(1)	10(1)	10(1)

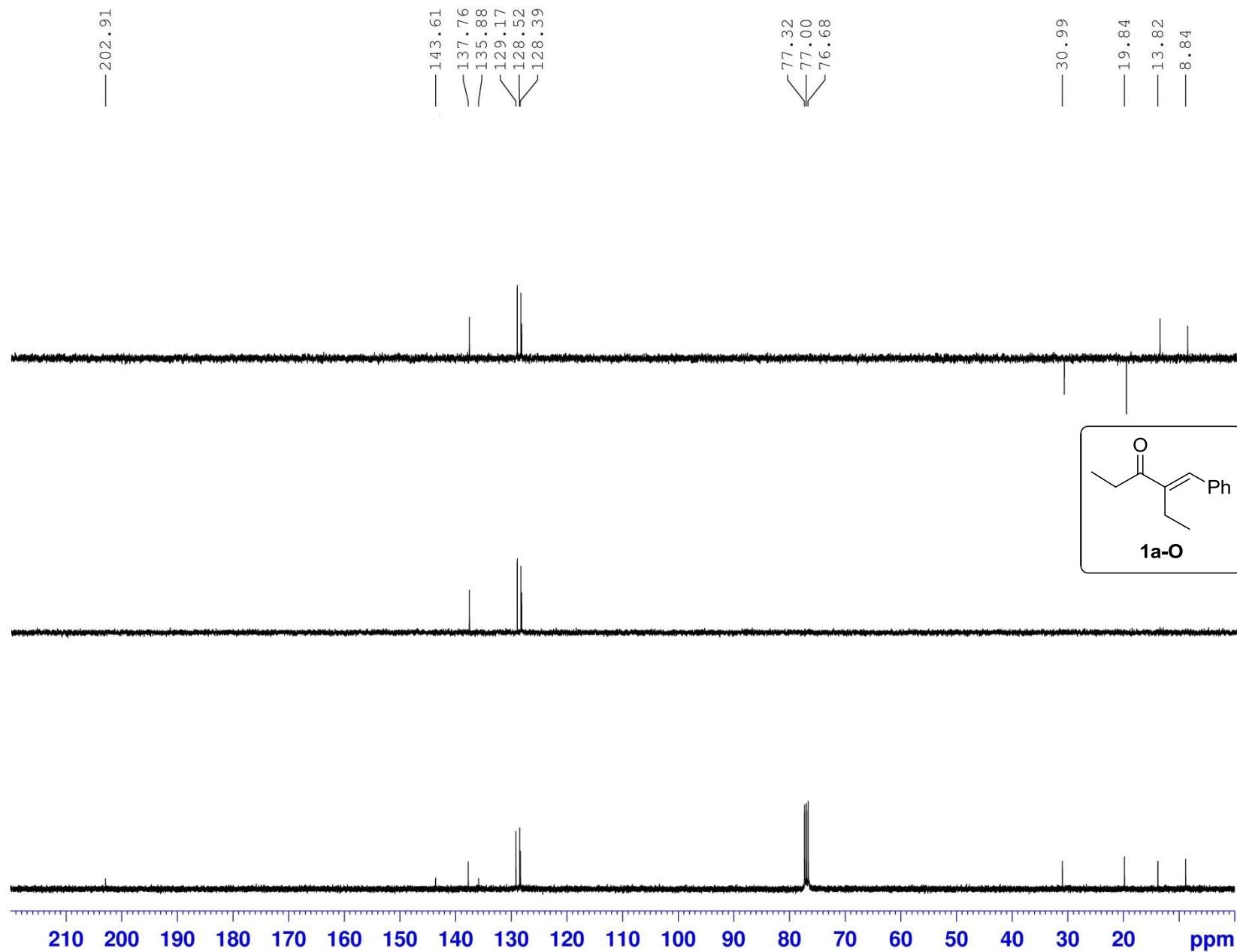
Table S20. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d19332.

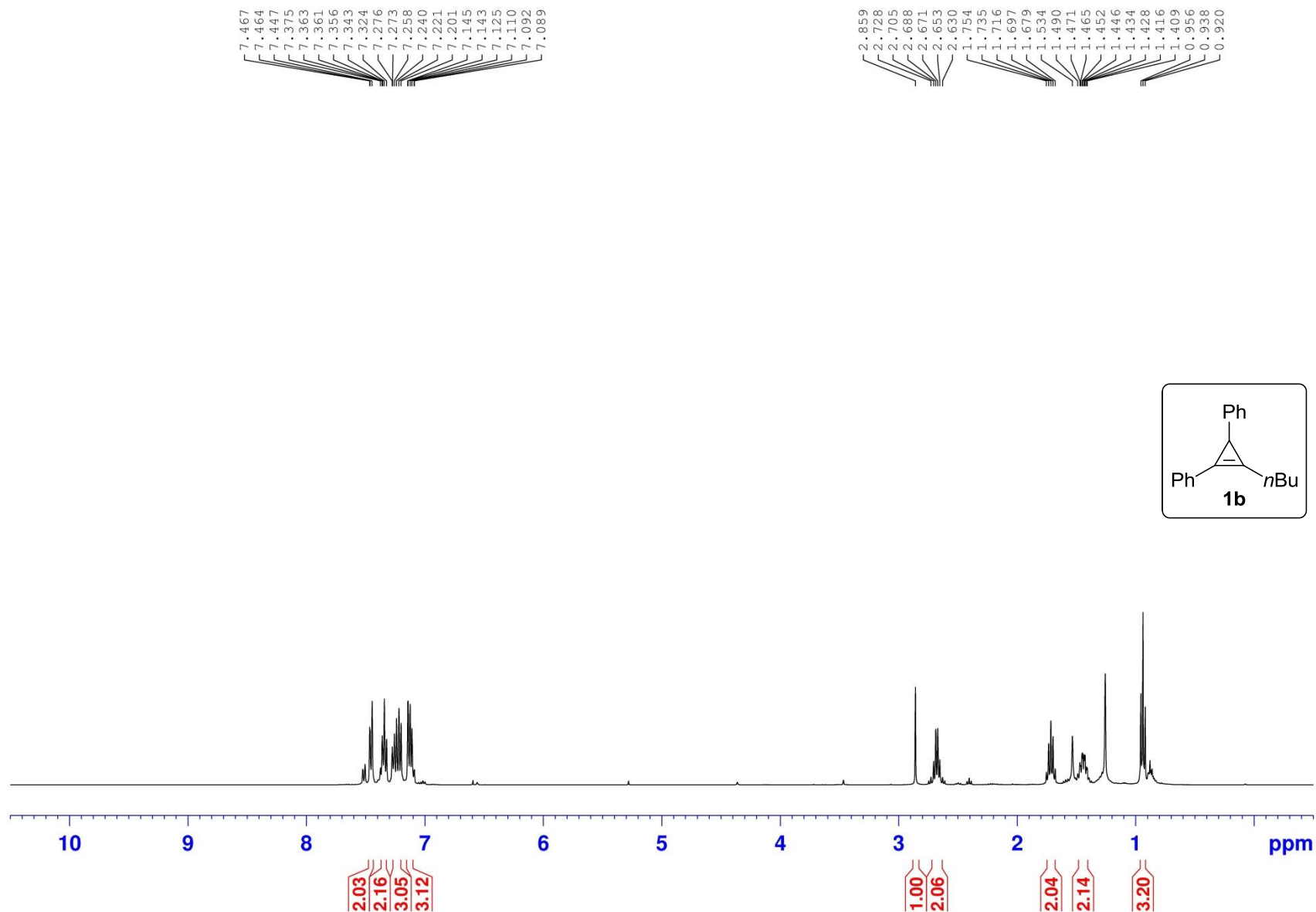
	x	y	z	U(eq)
H(2)	2729	7958	5146	50
H(3)	1758	5625	4035	44
H(5)	4816	5598	7682	49
H(6)	5805	7931	8792	53
H(8A)	-156	3434	3443	40
H(8B)	1501	3232	2830	40
H(10A)	132	344	1089	76
H(10B)	-1674	820	1440	76
H(10C)	-738	-269	1857	76
H(12A)	1798	353	5206	67
H(12B)	3566	275	4732	67
H(12C)	1482	-483	3566	67
H(16)	5610	3418	9780	42
H(1')	5715	3242	6760	57
H(15A)	1793	3808	7619	57
H(15B)	1564	2327	7203	57
H(15C)	2305	3391	8792	57
H(18A)	10006	4269	10773	57
H(18B)	9818	2575	9887	57
H(18C)	8691	3308	10867	57

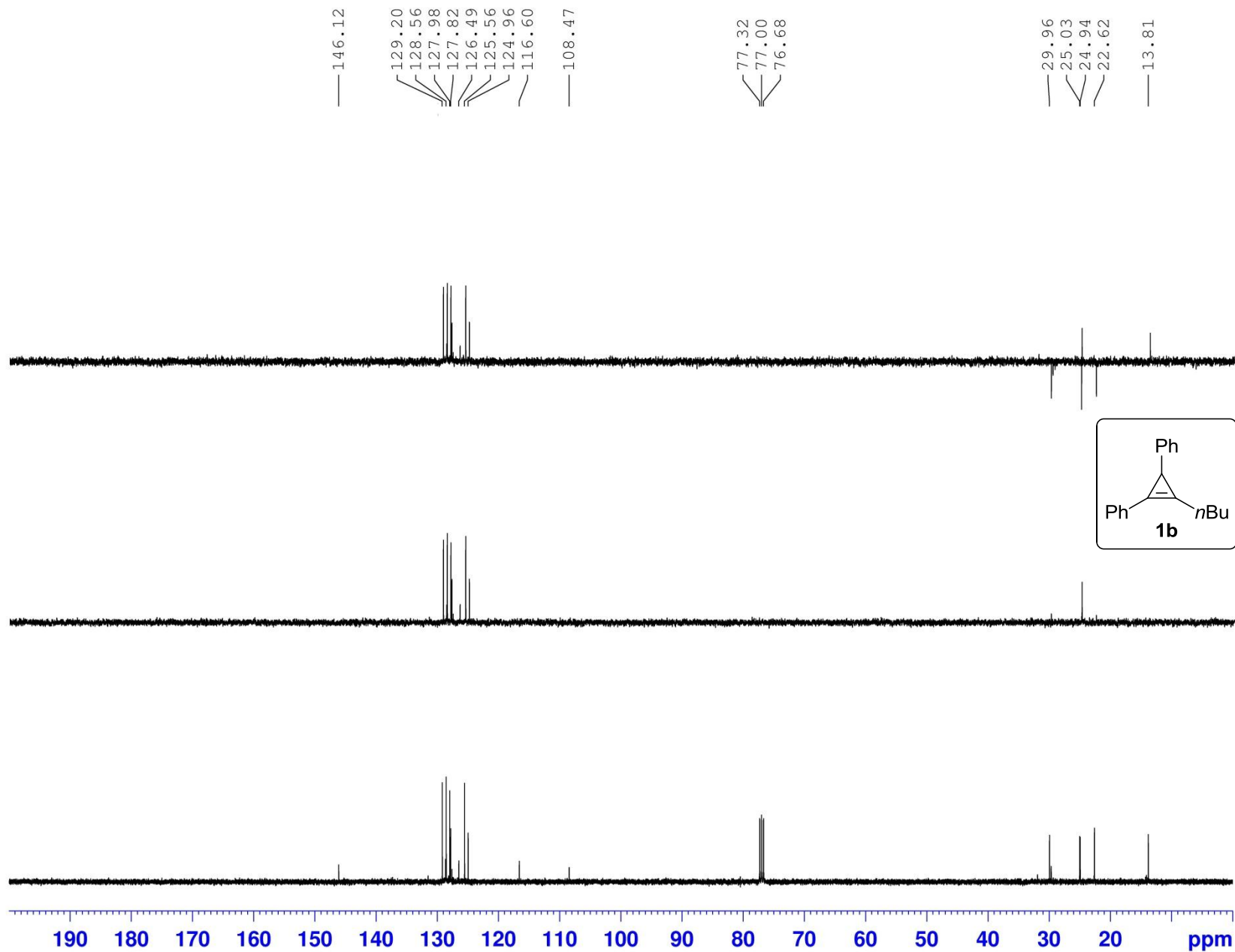


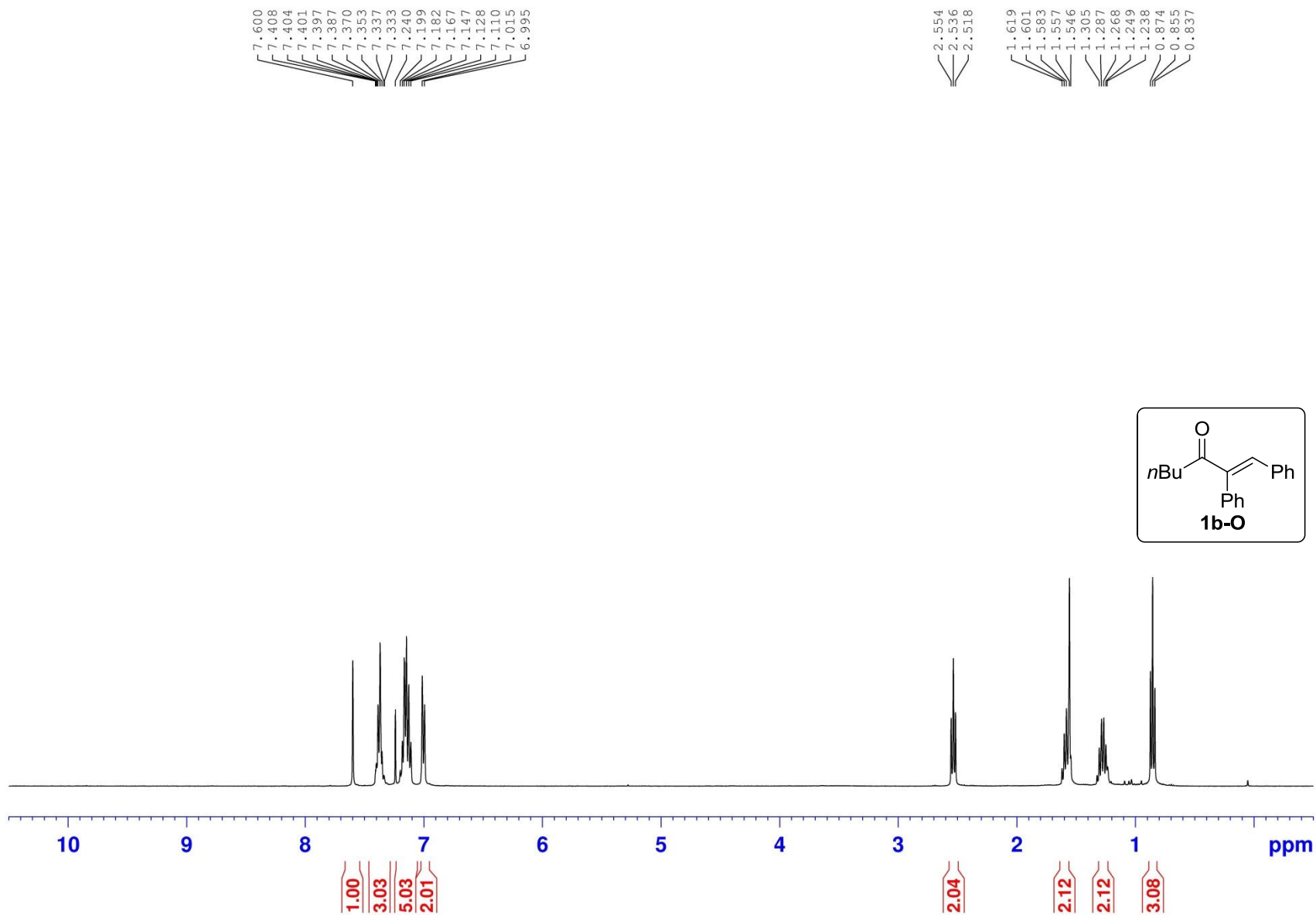


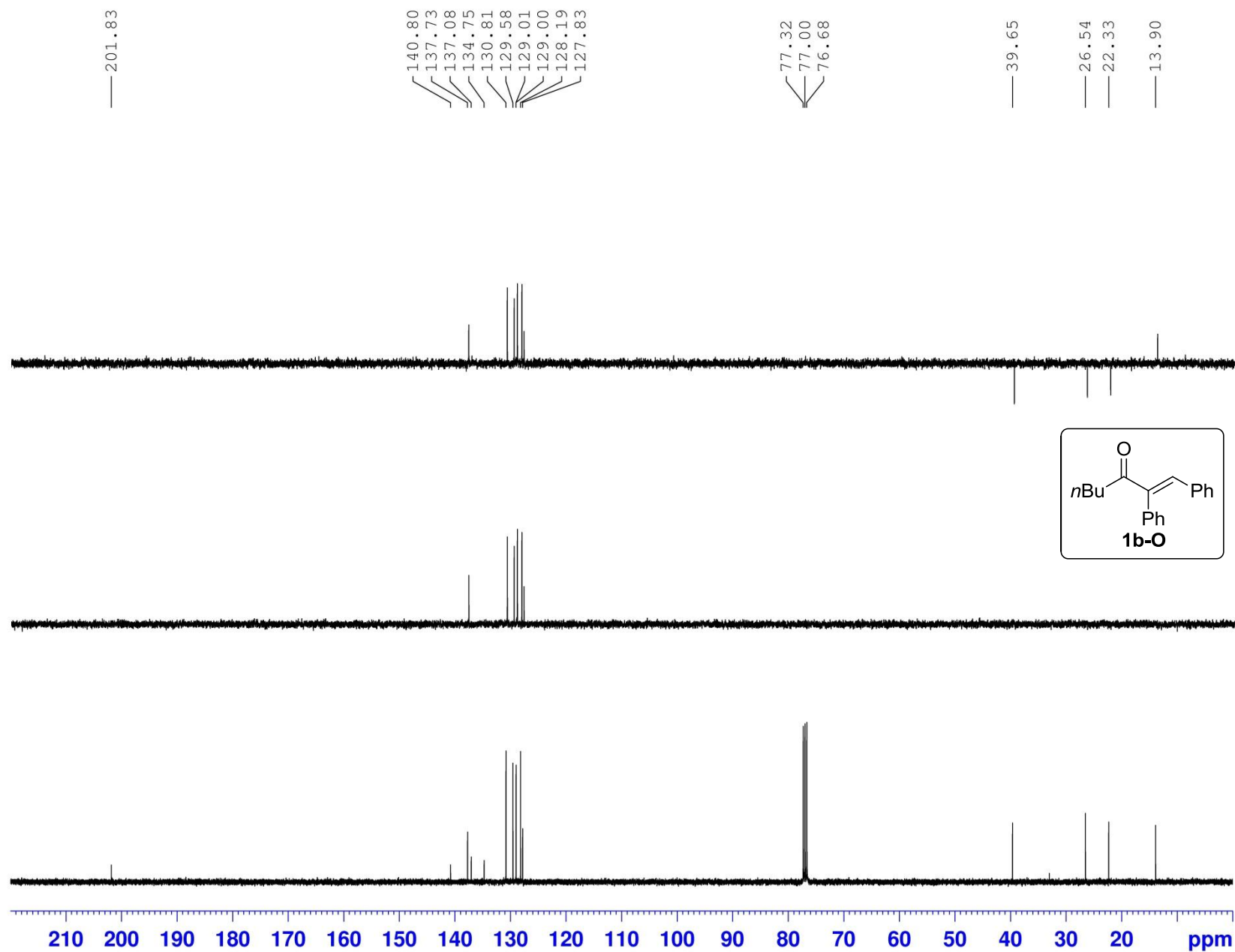


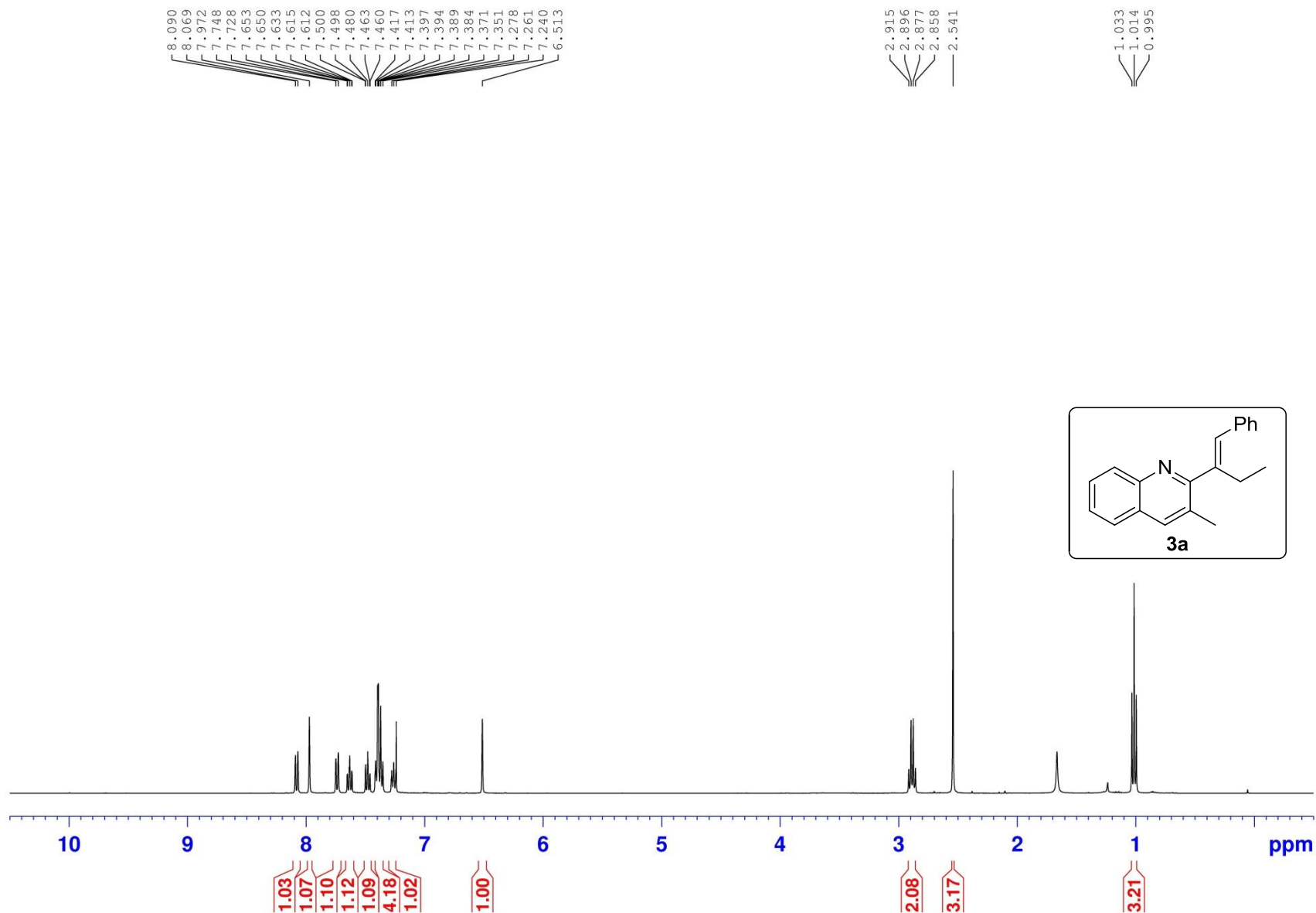


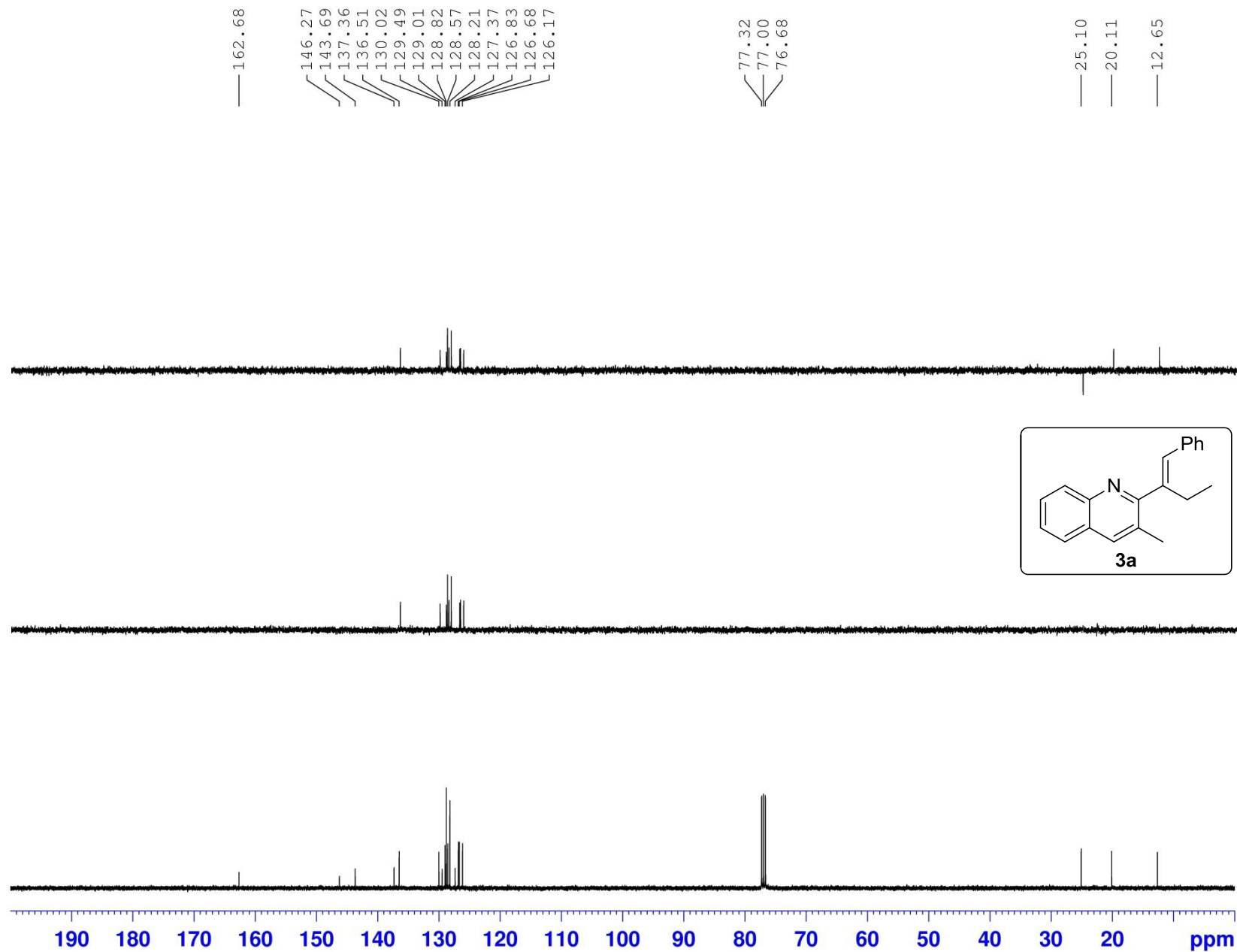


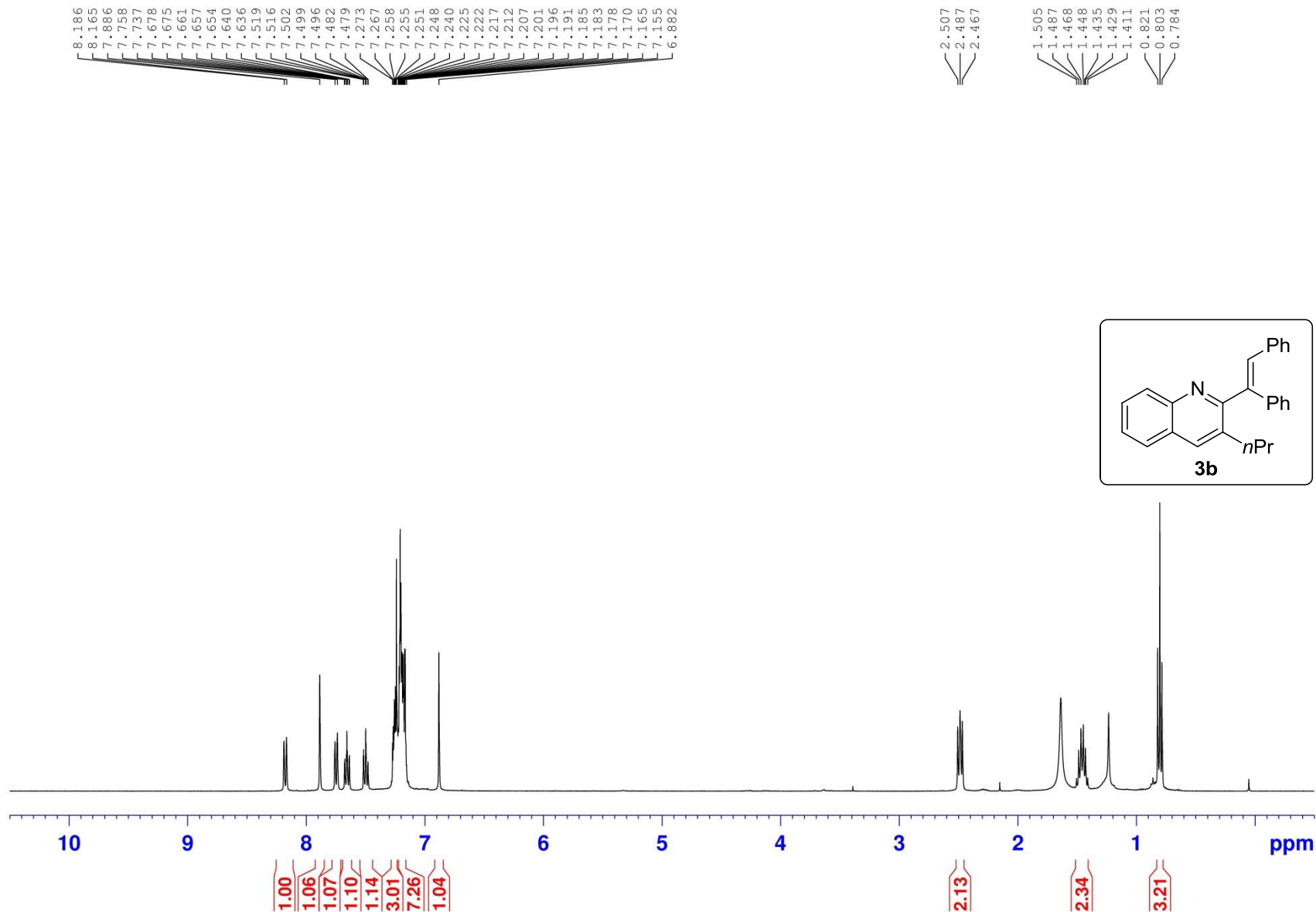


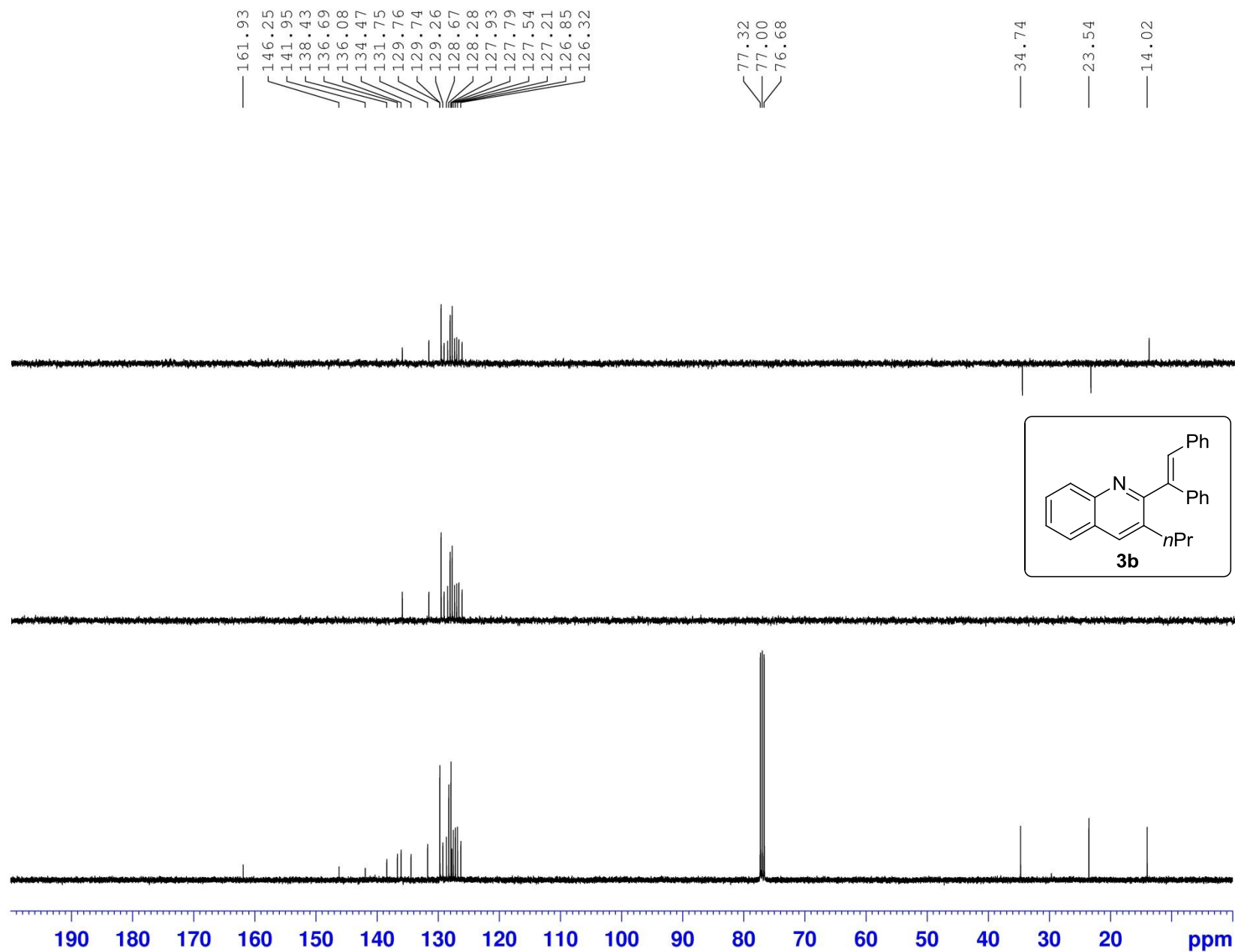


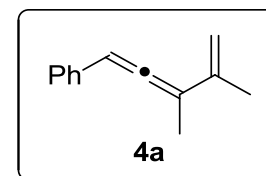
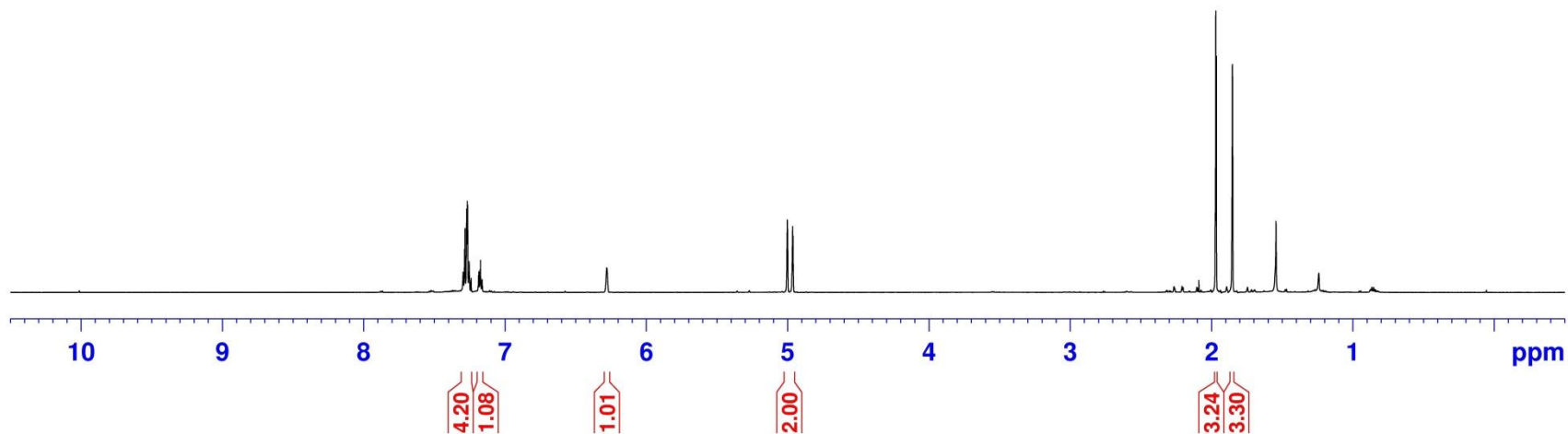


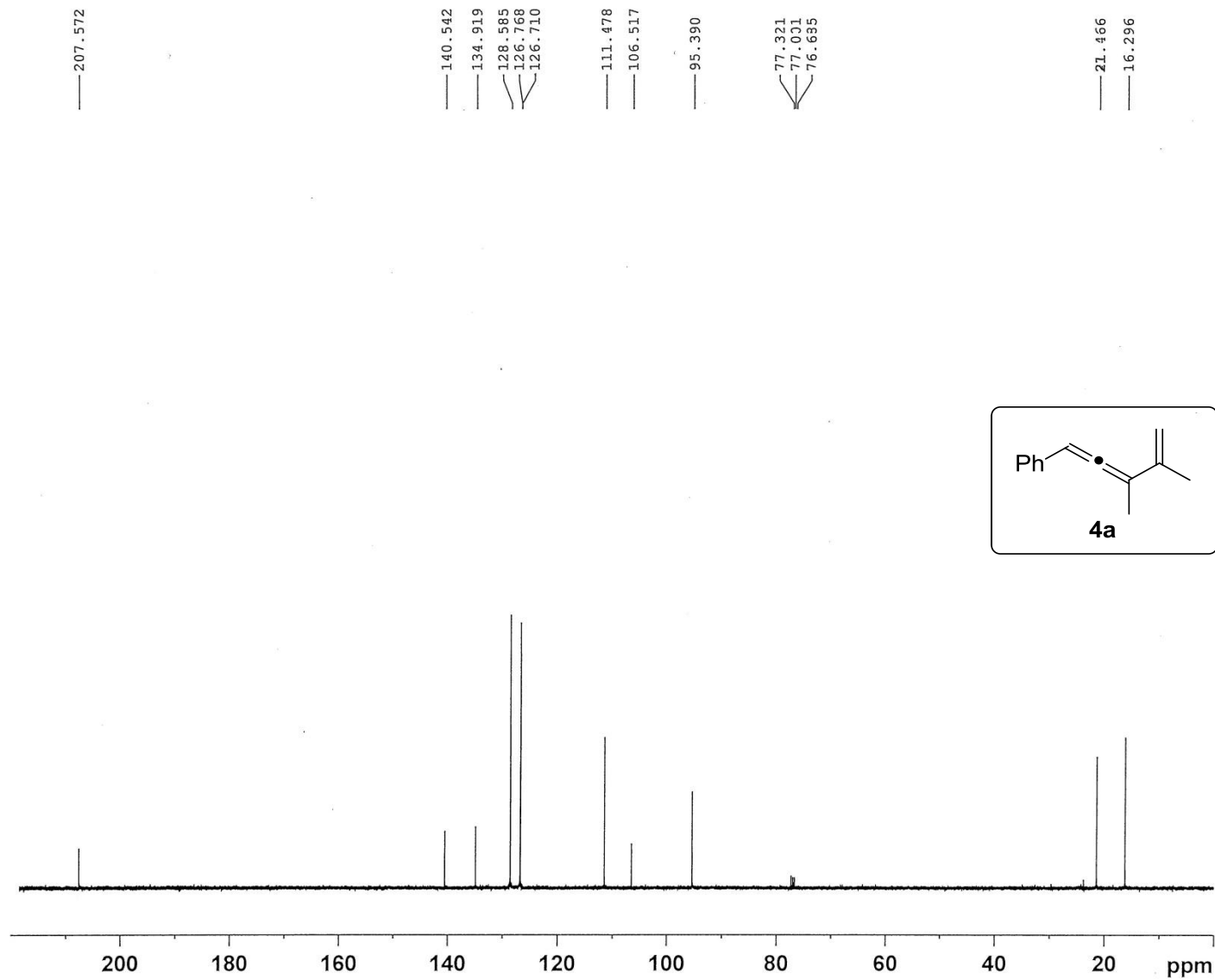


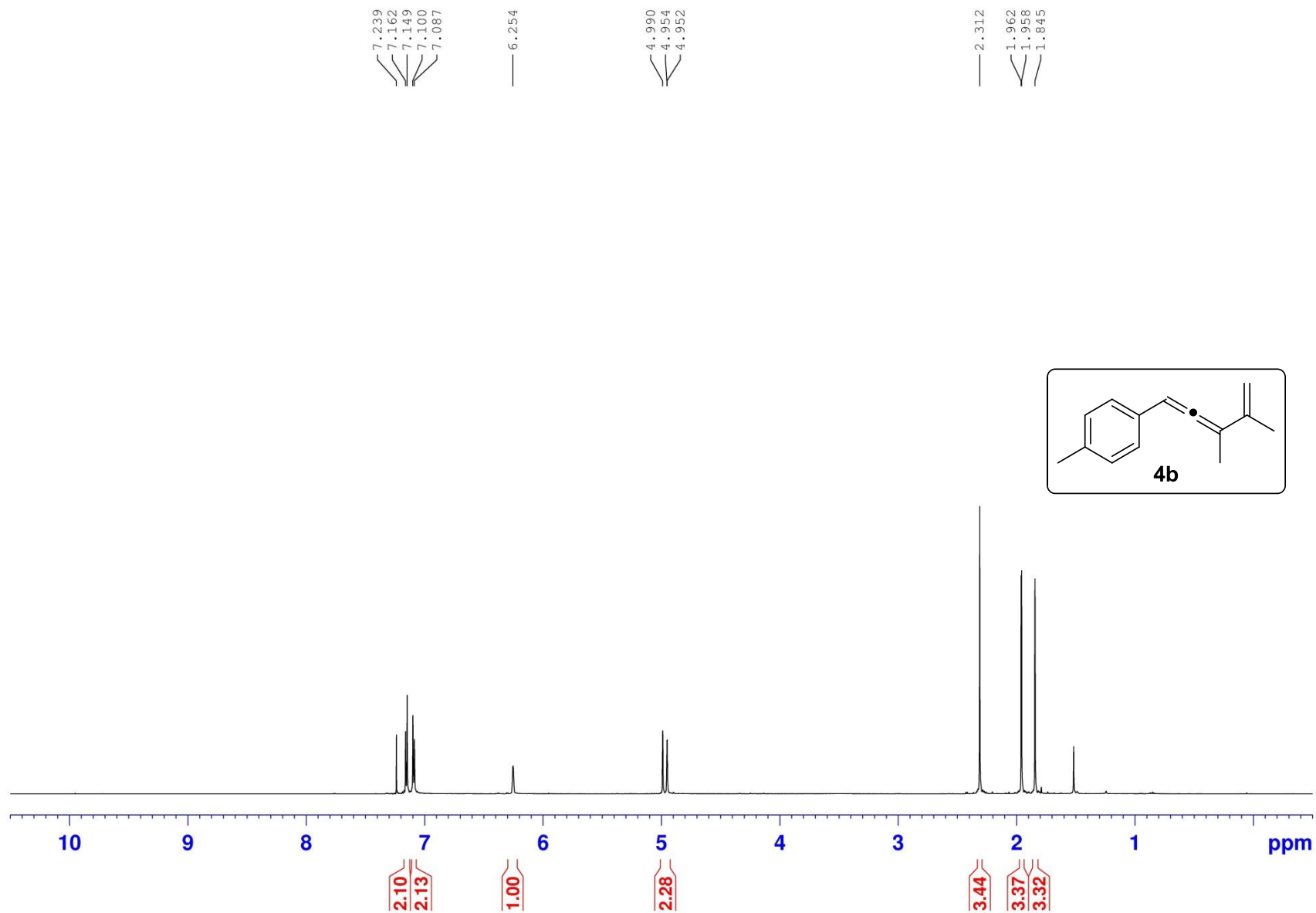


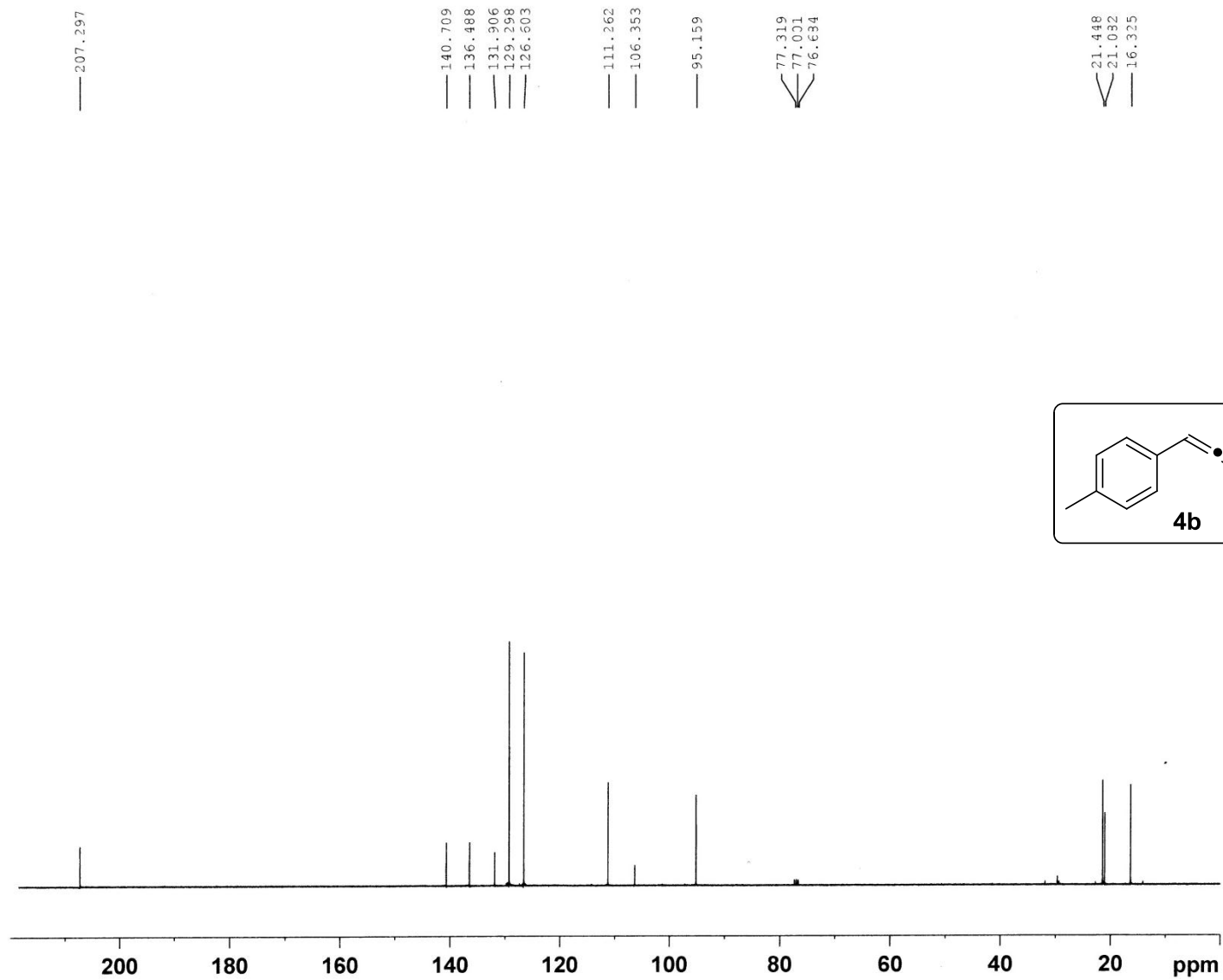


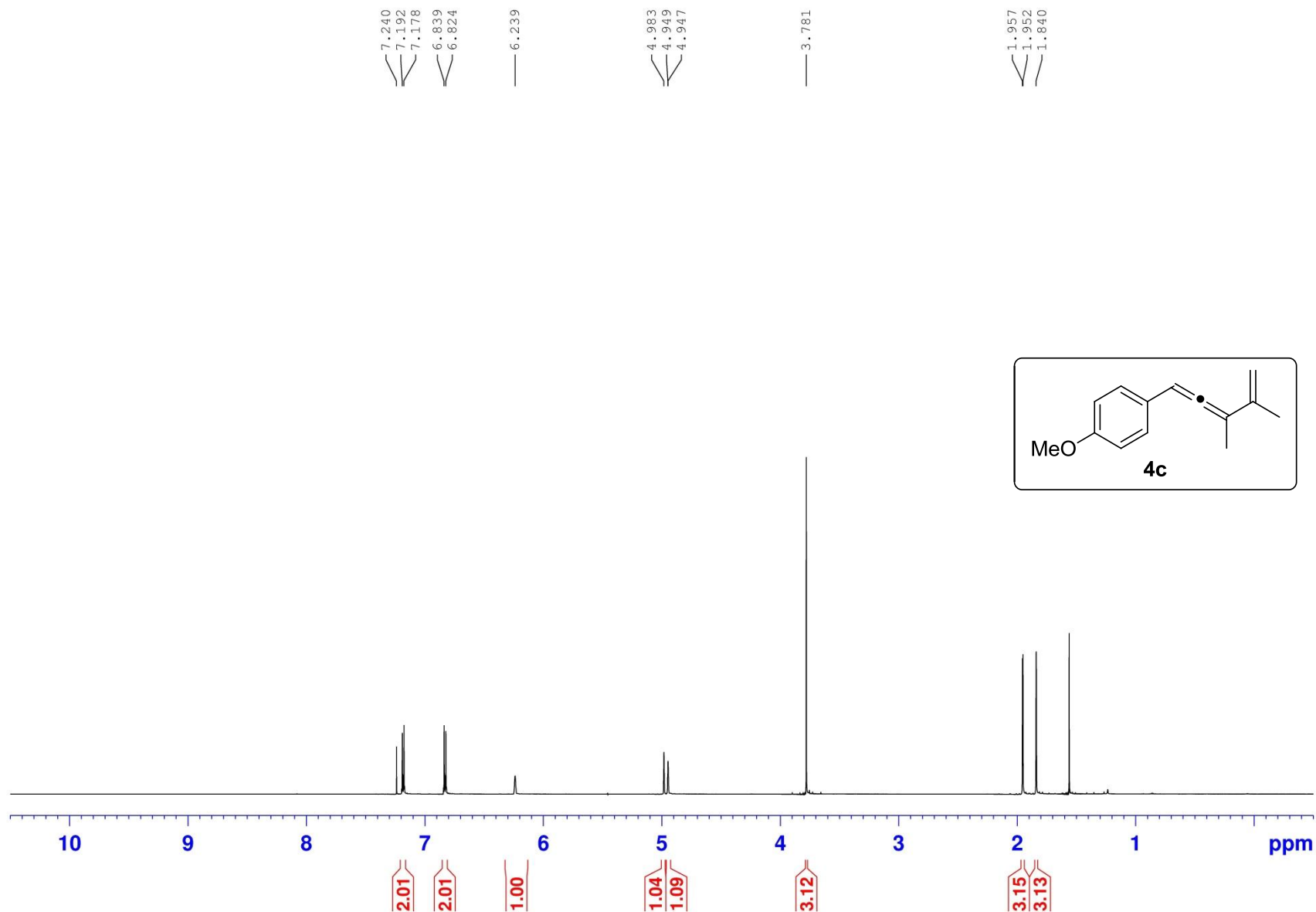


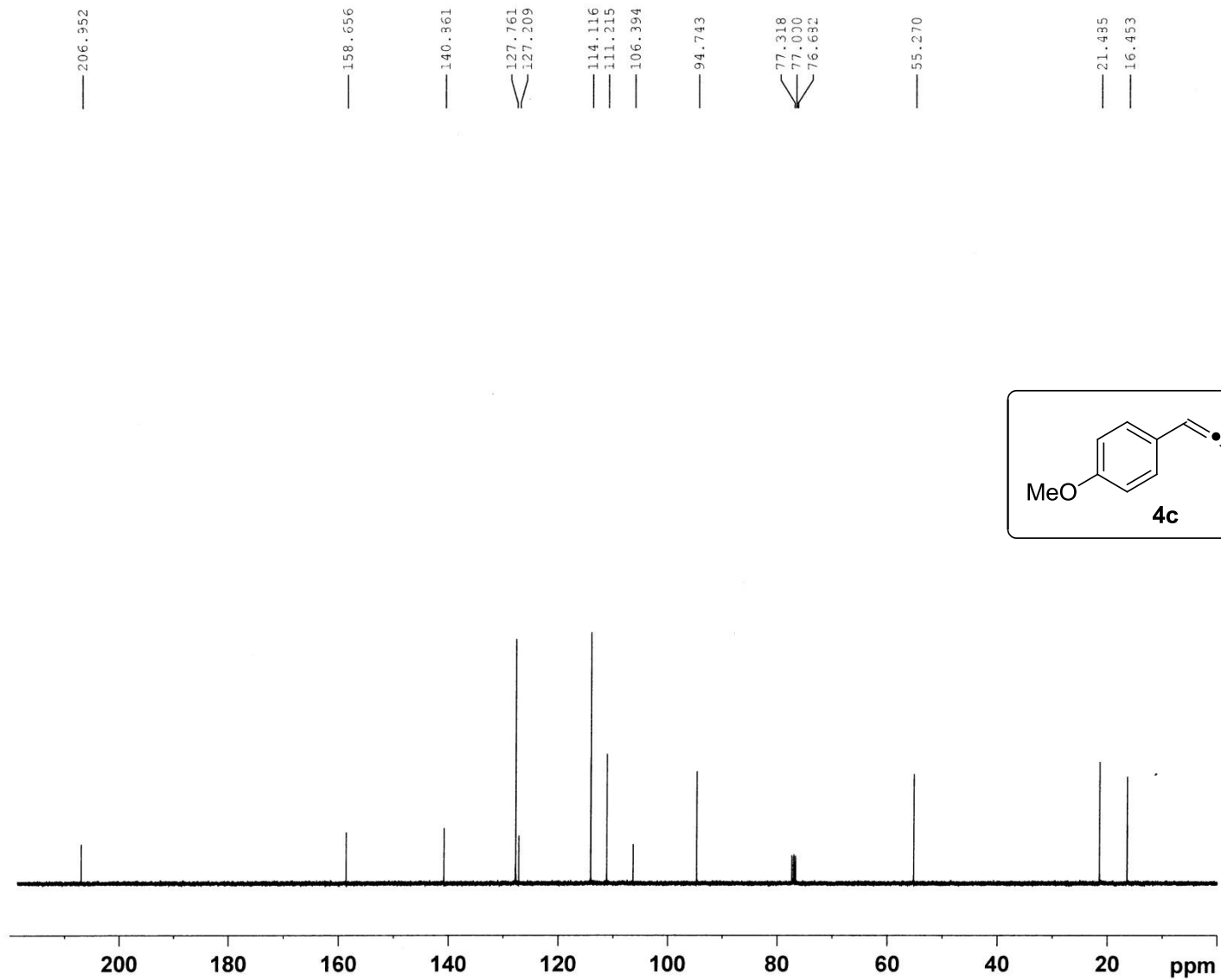


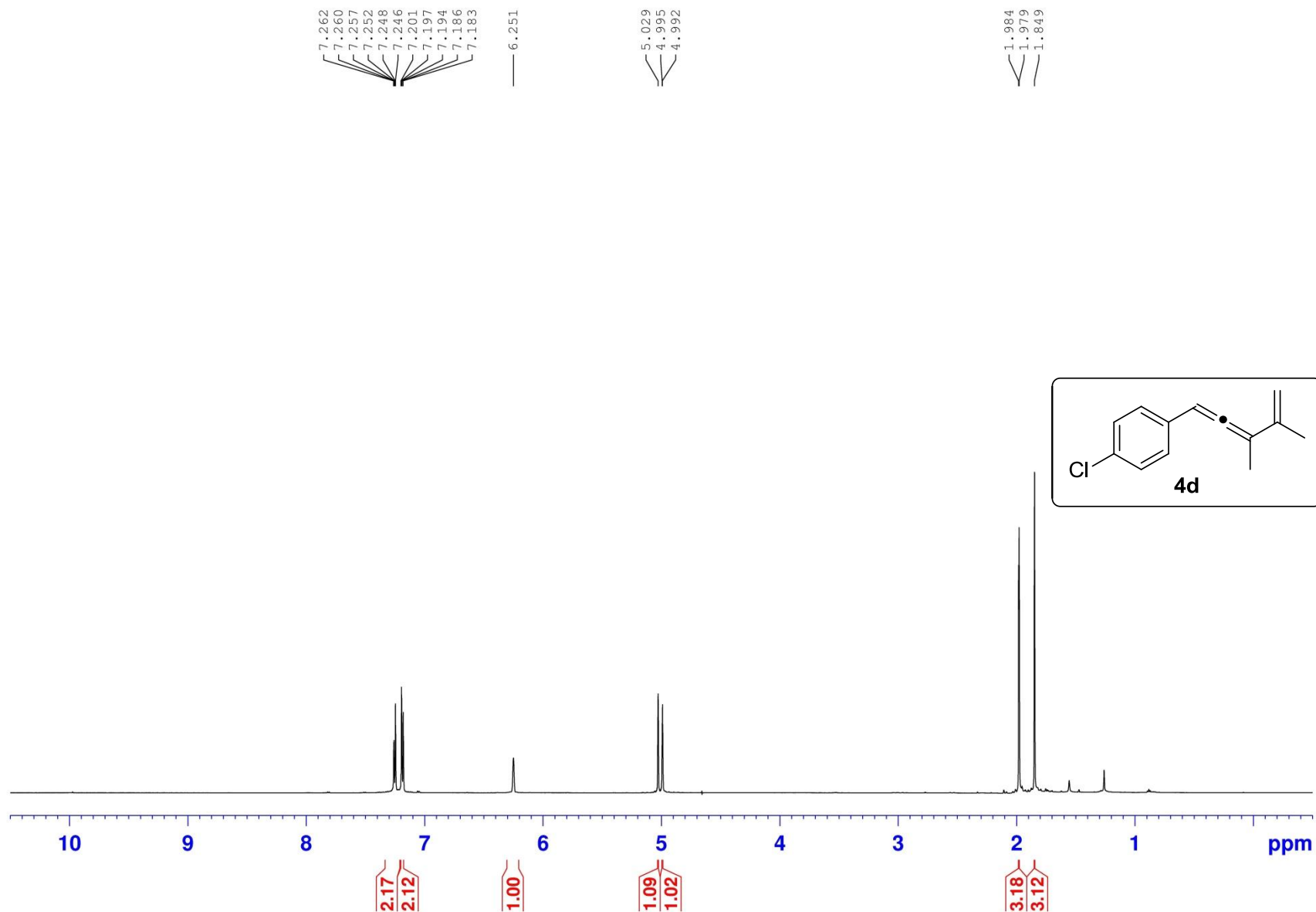


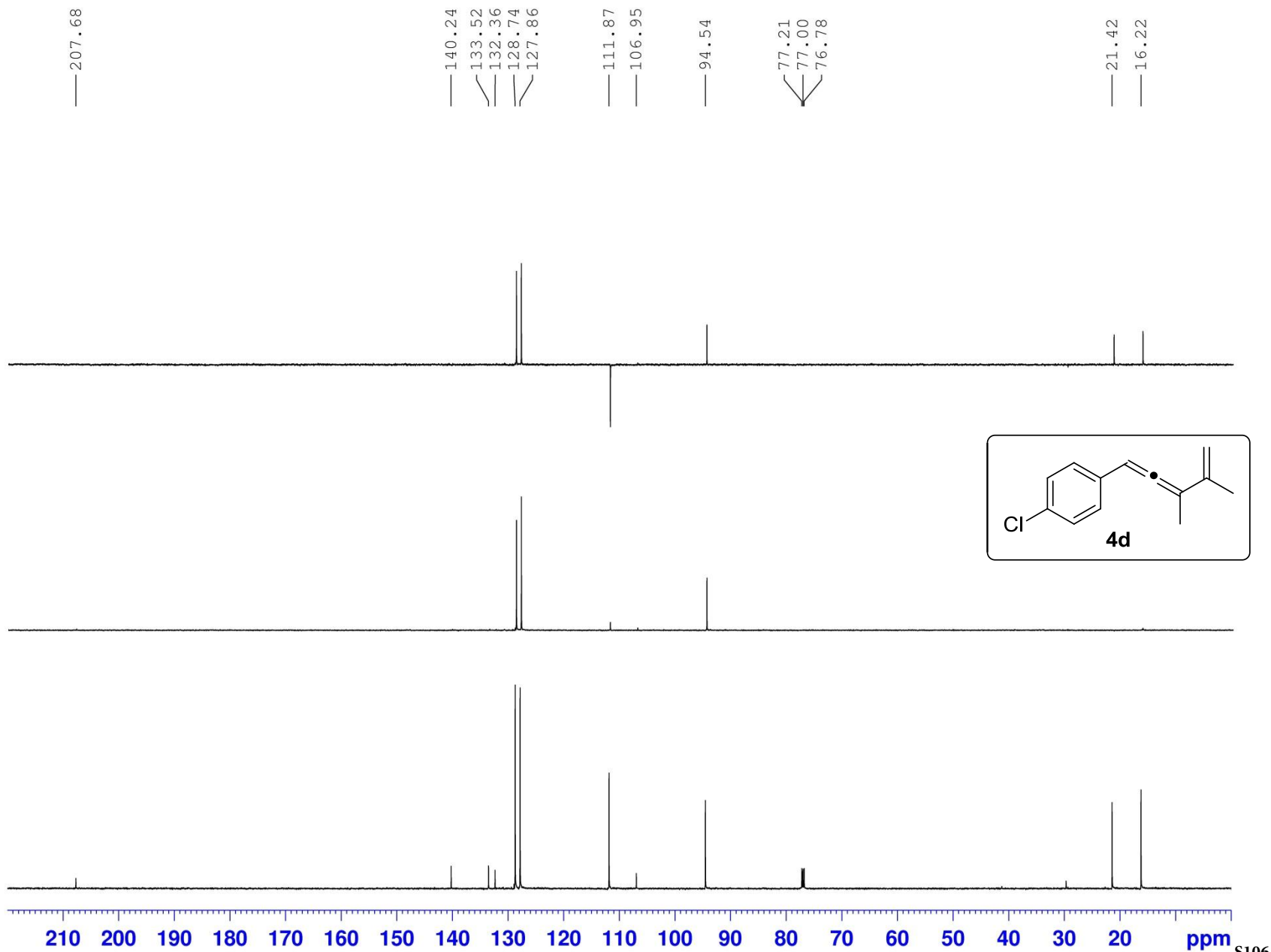


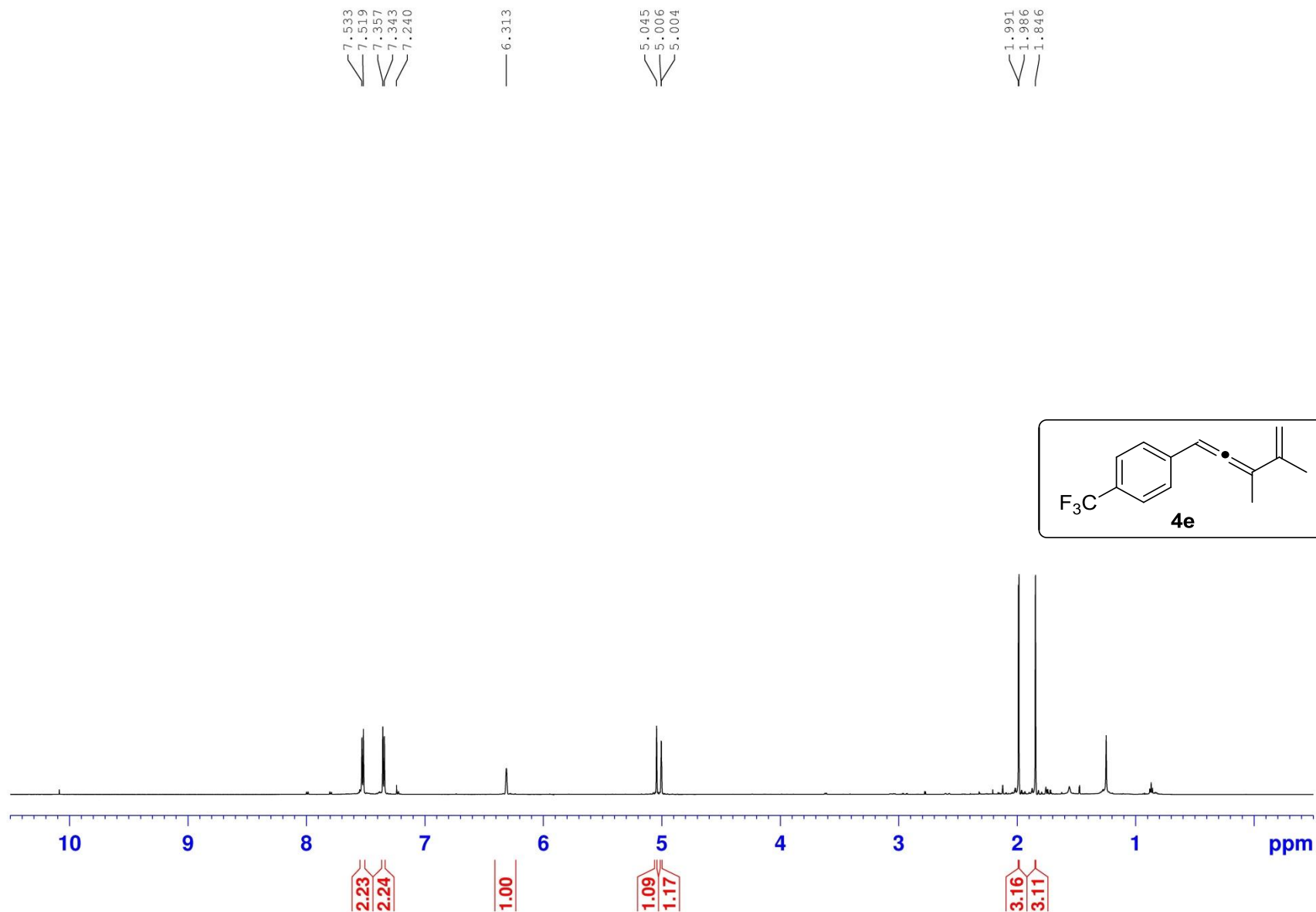


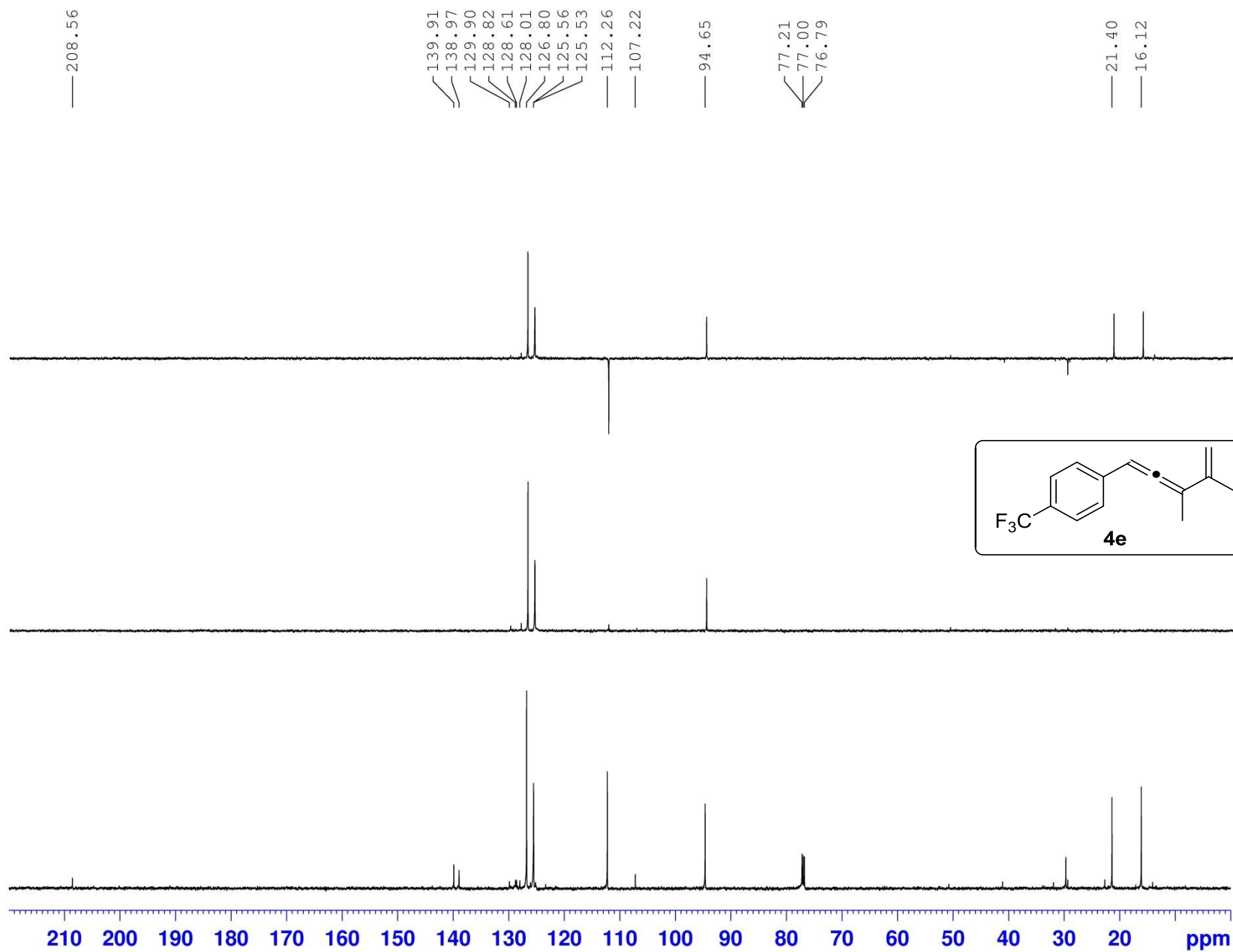


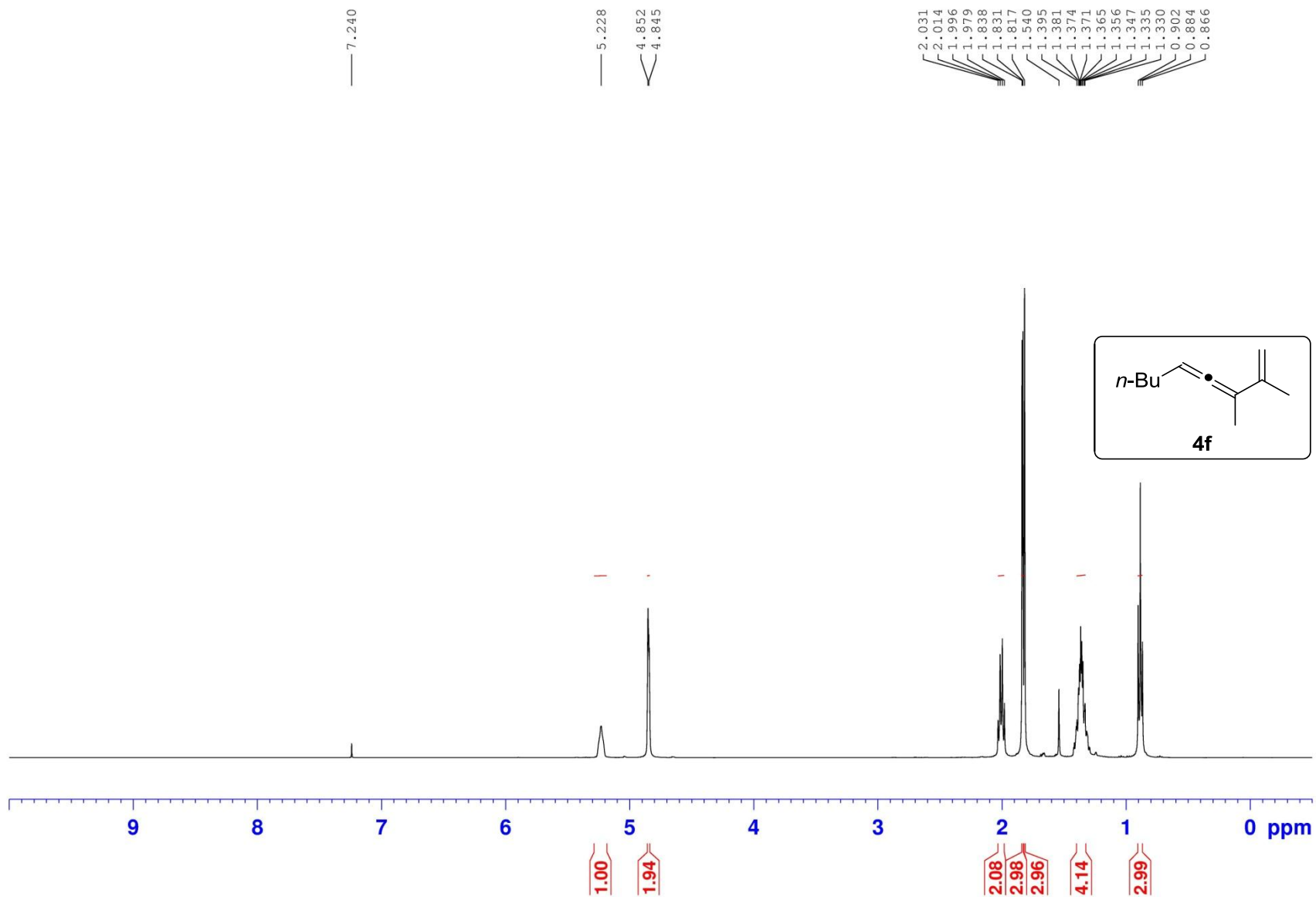


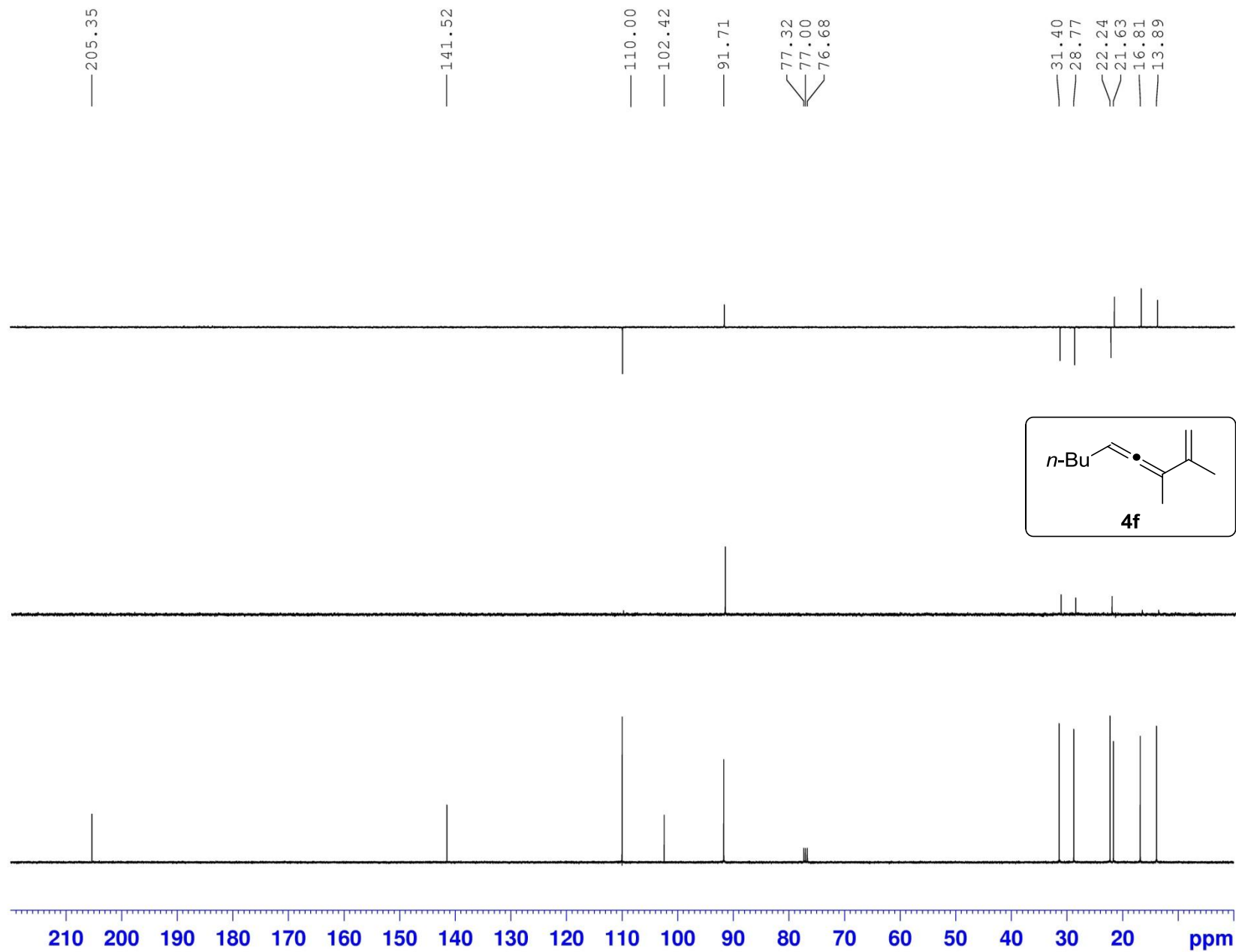


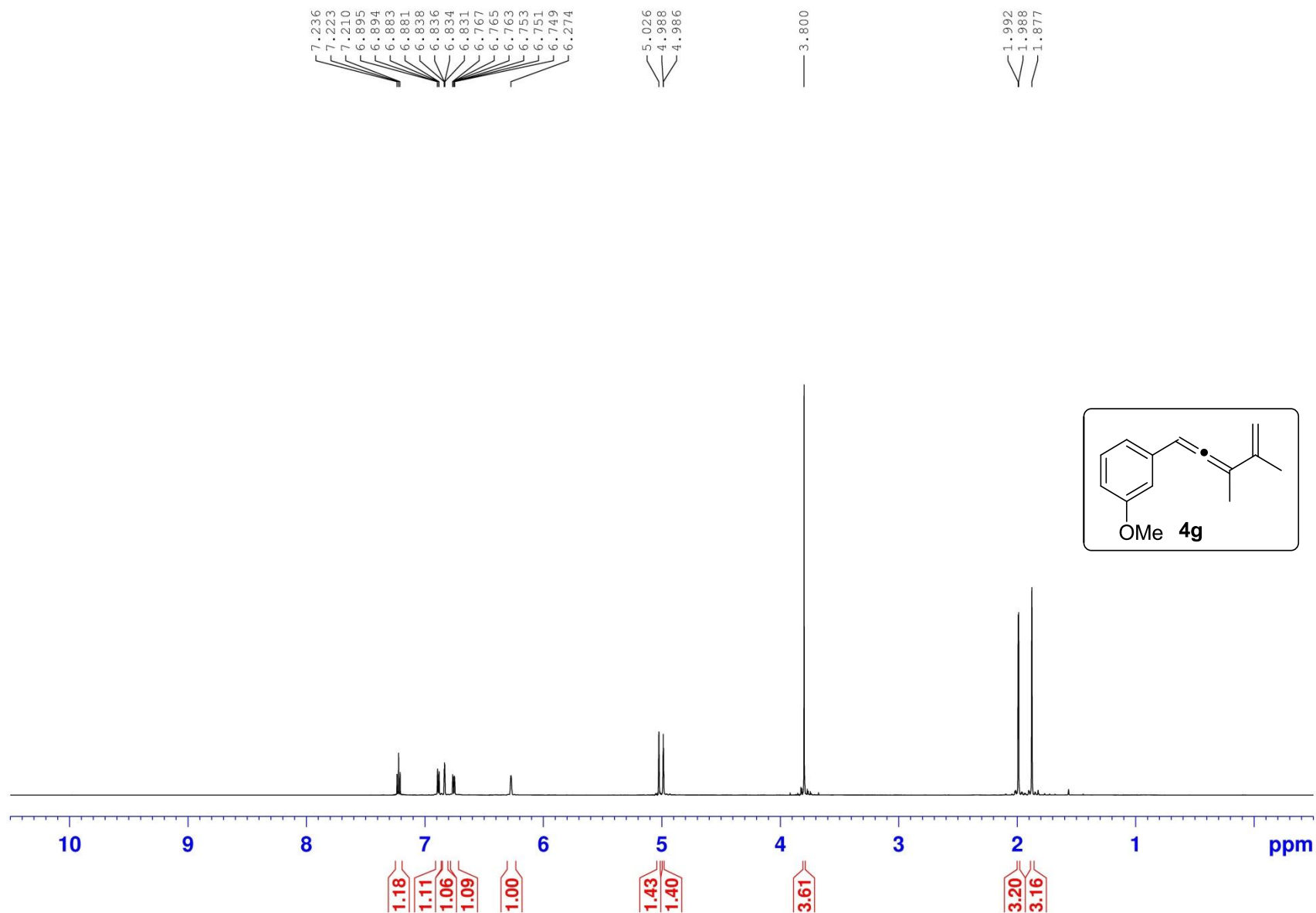


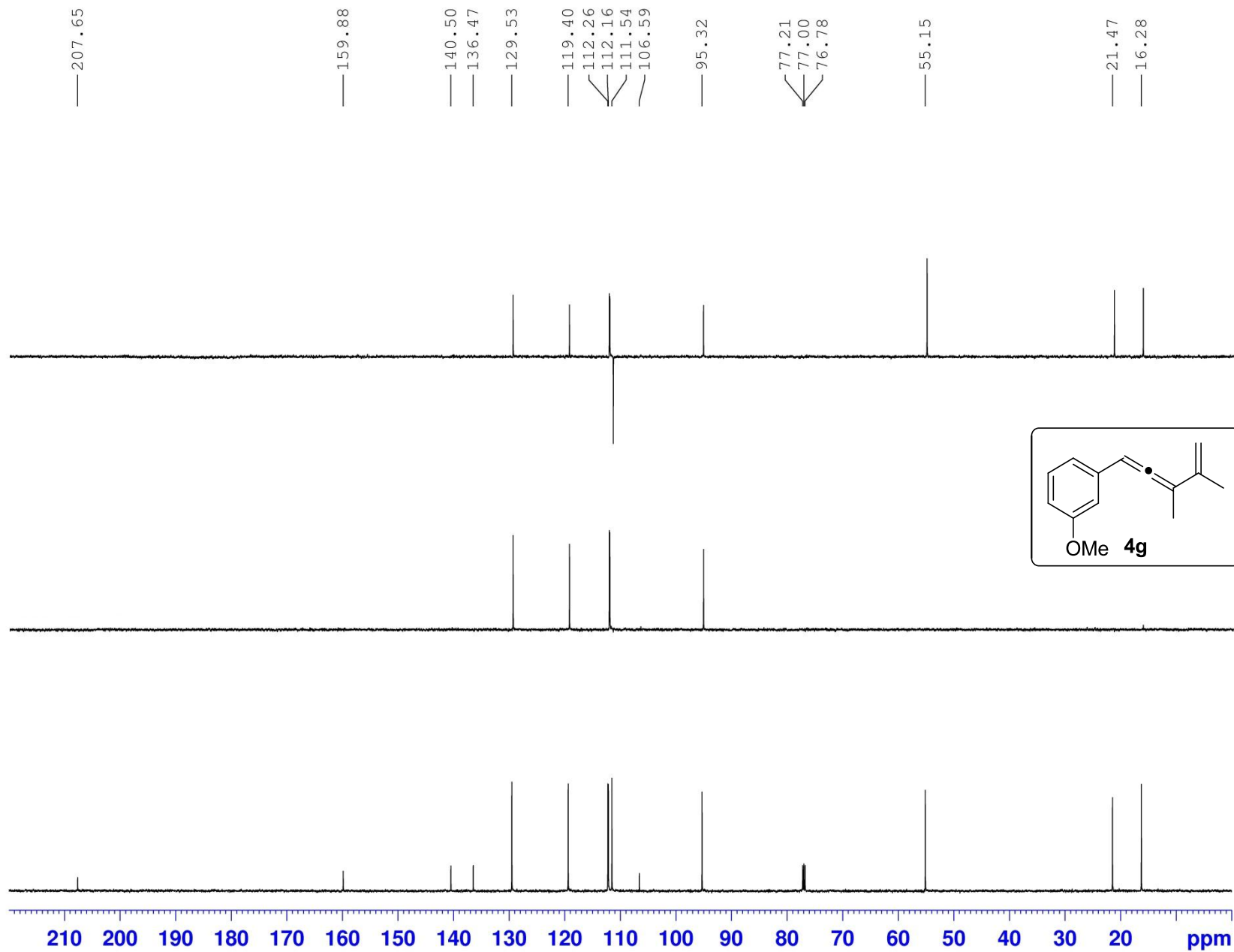


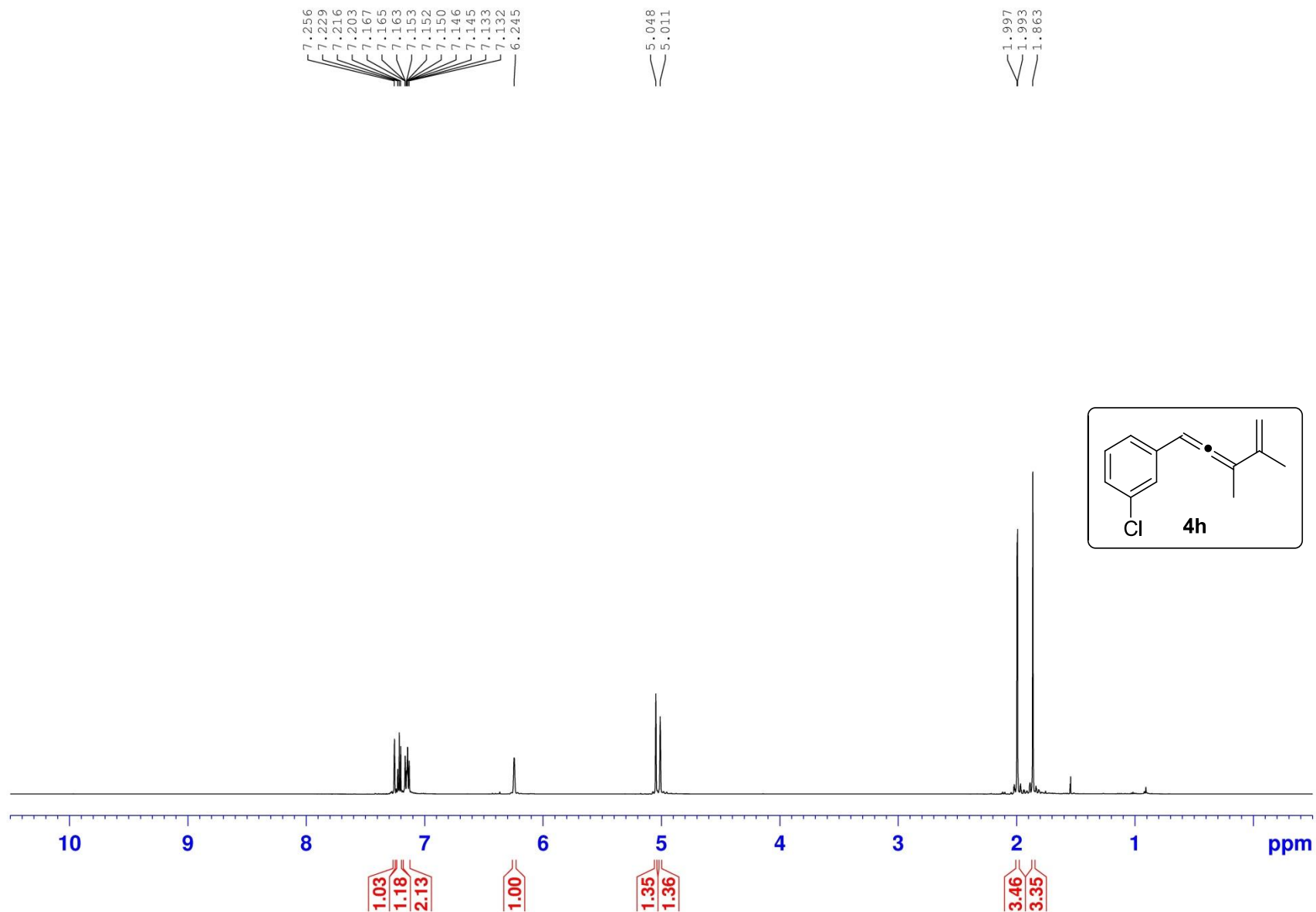


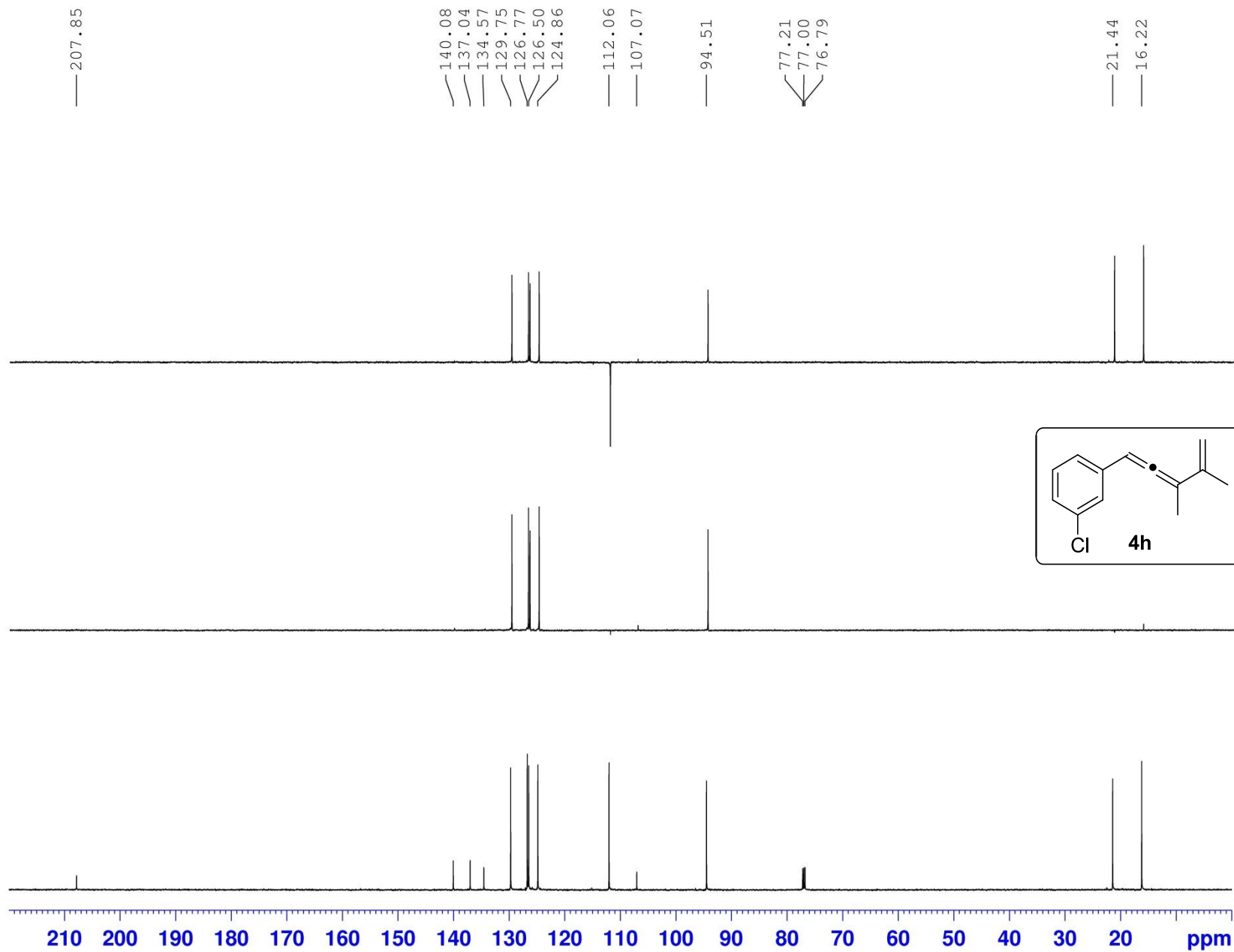


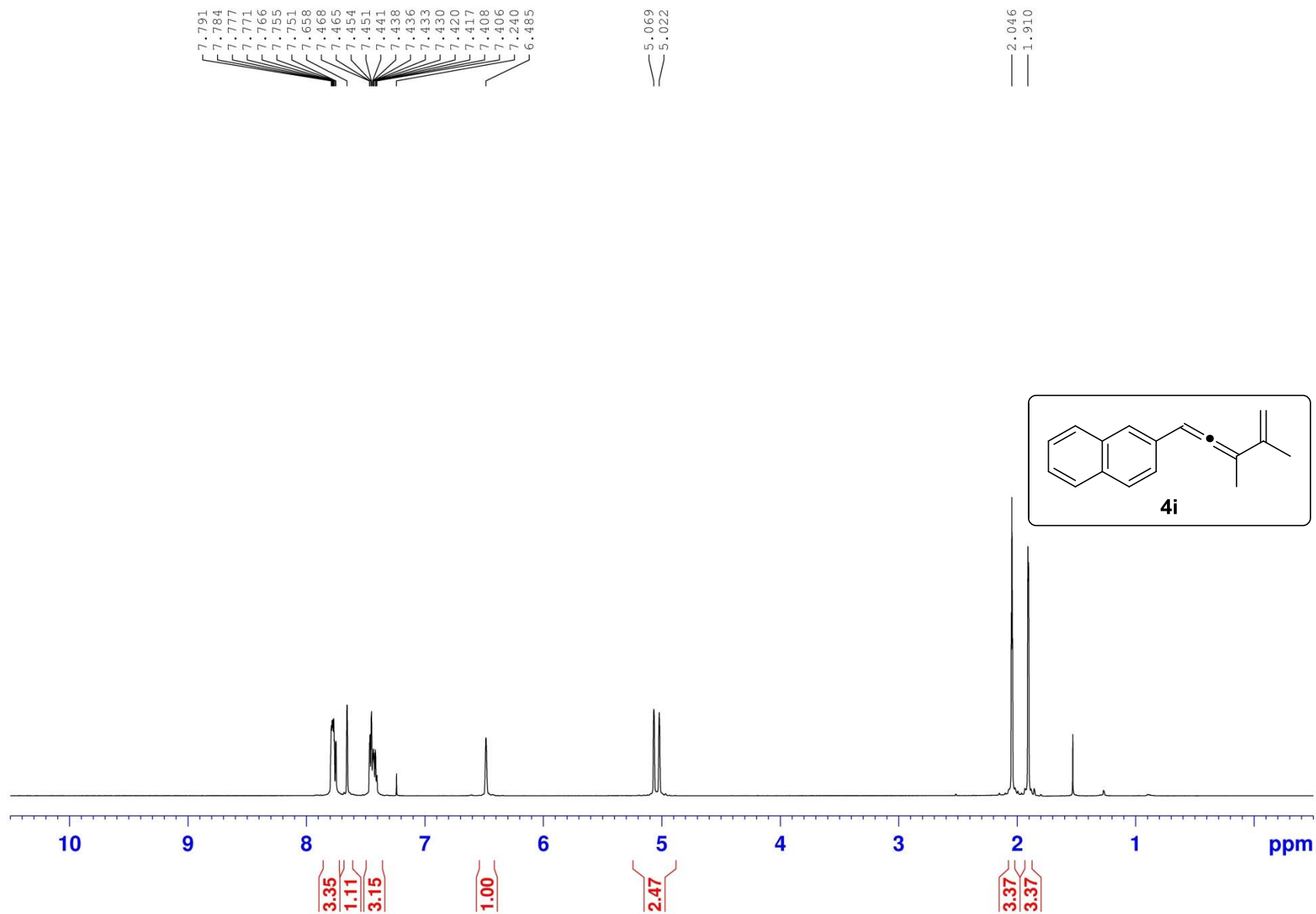


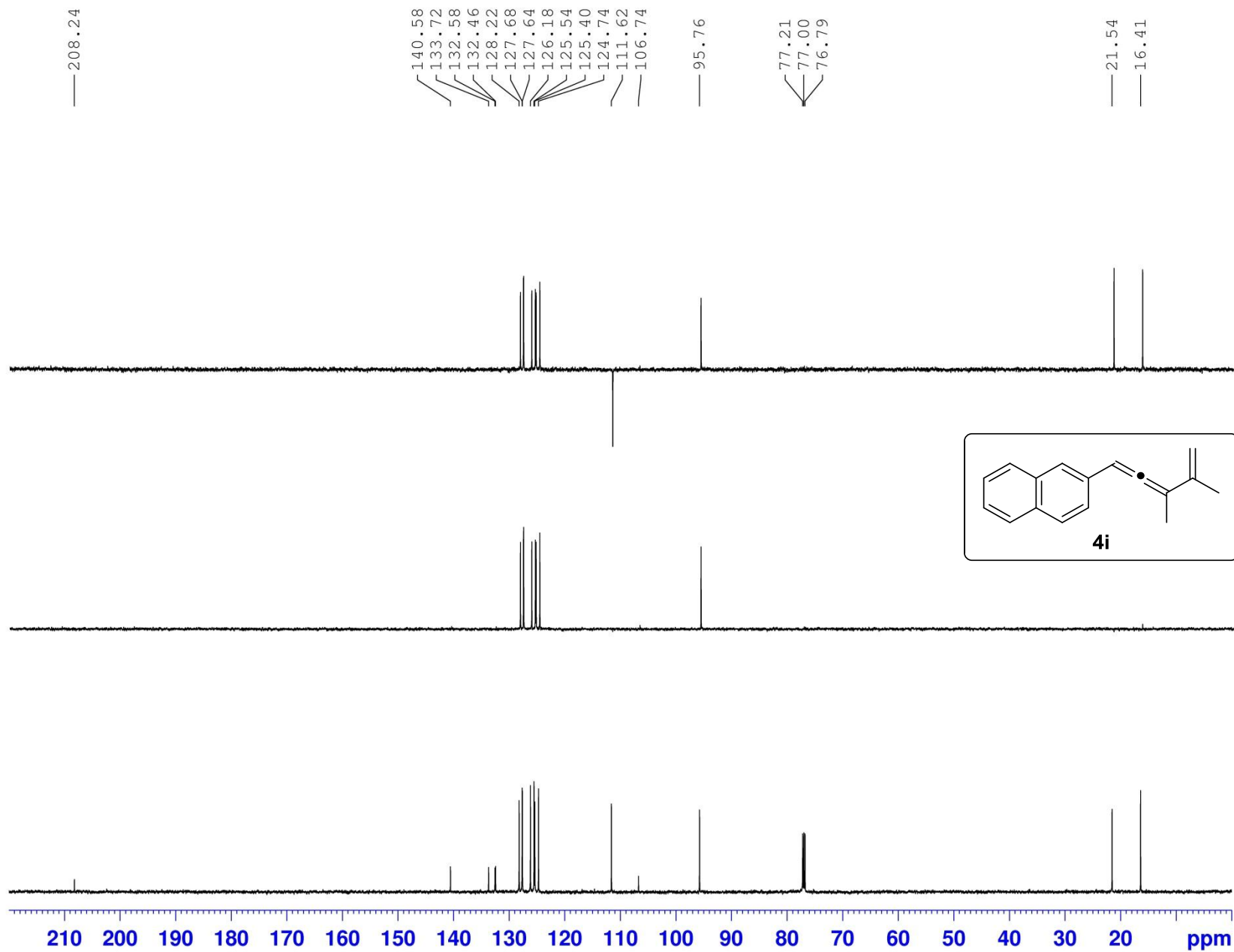


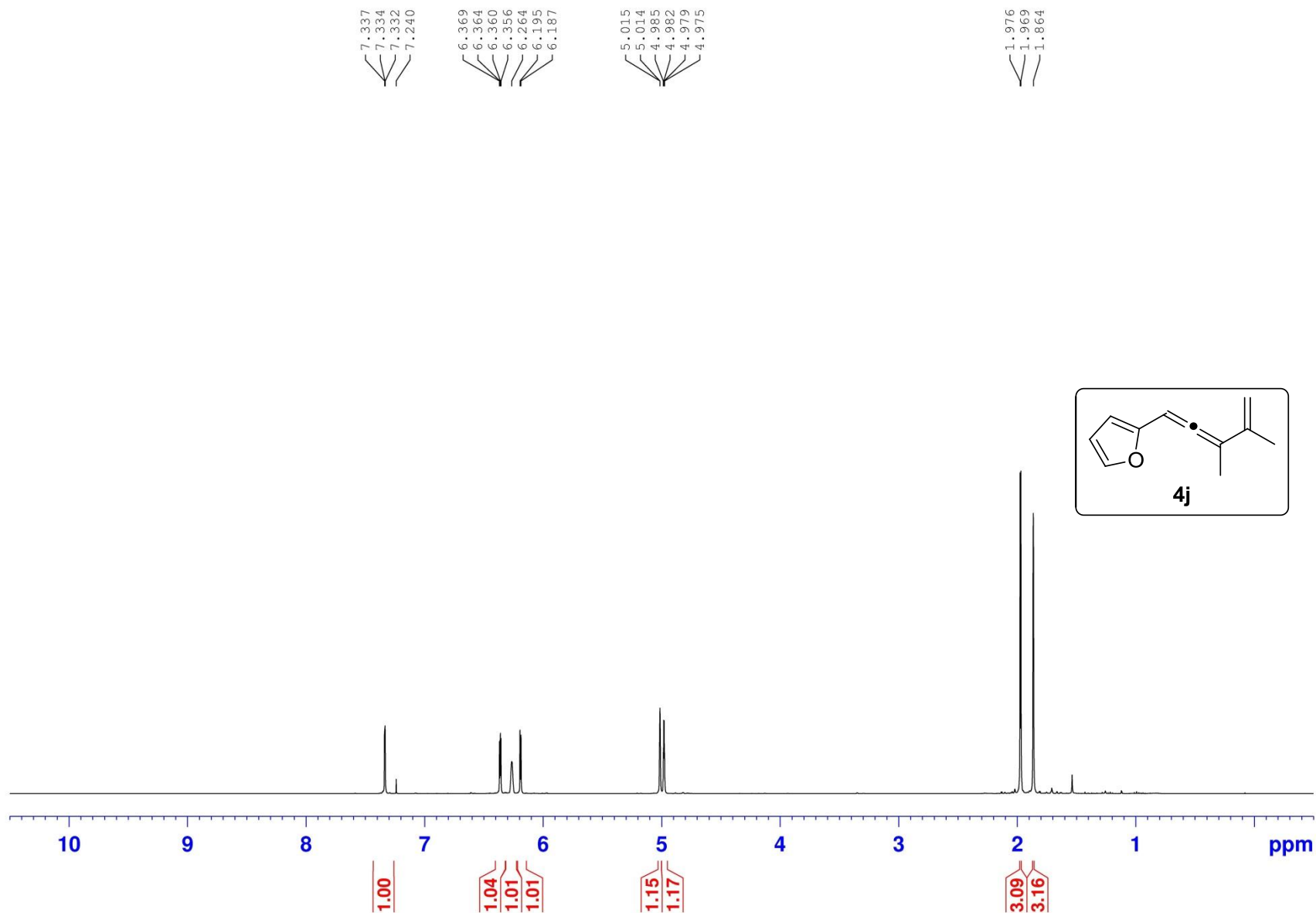


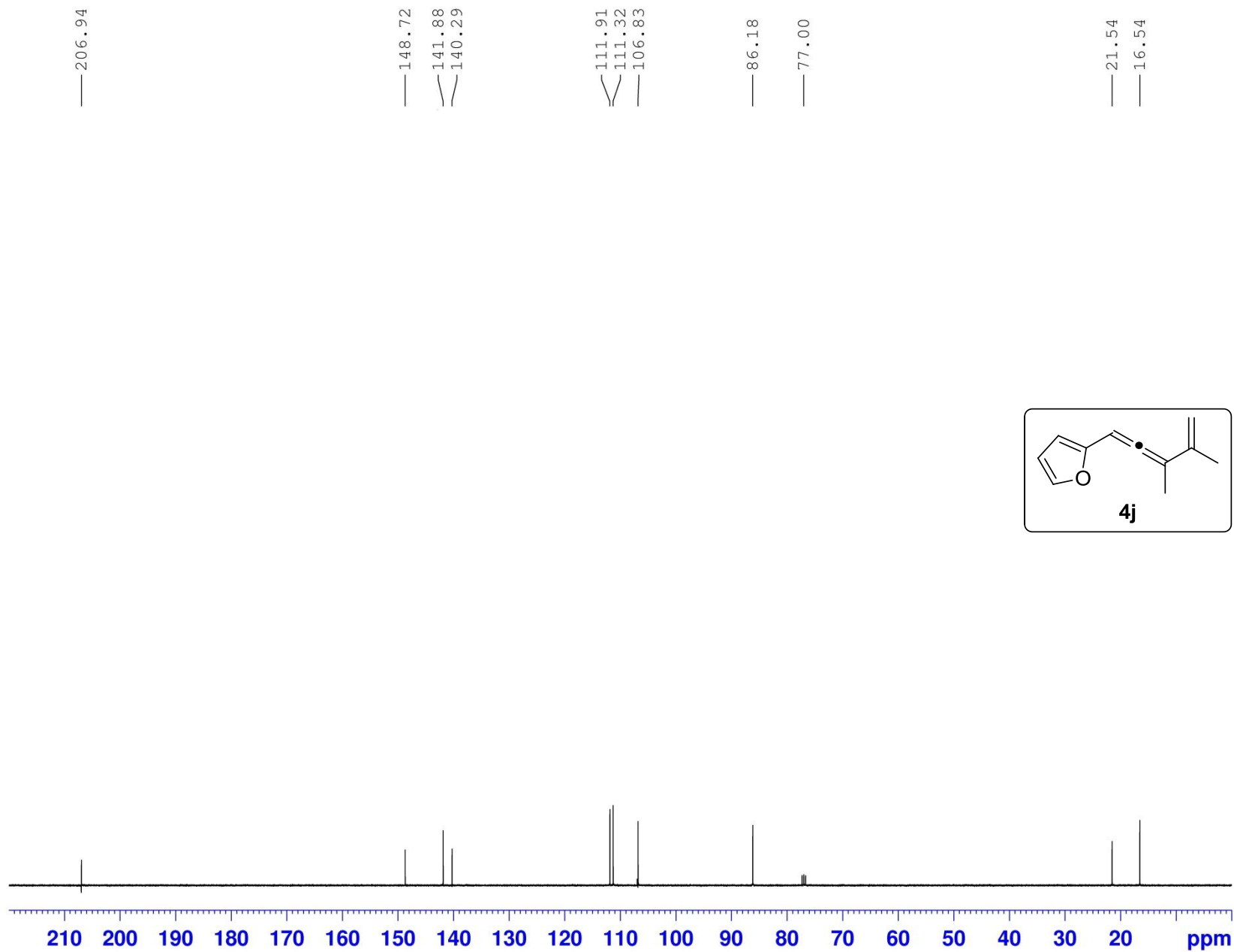


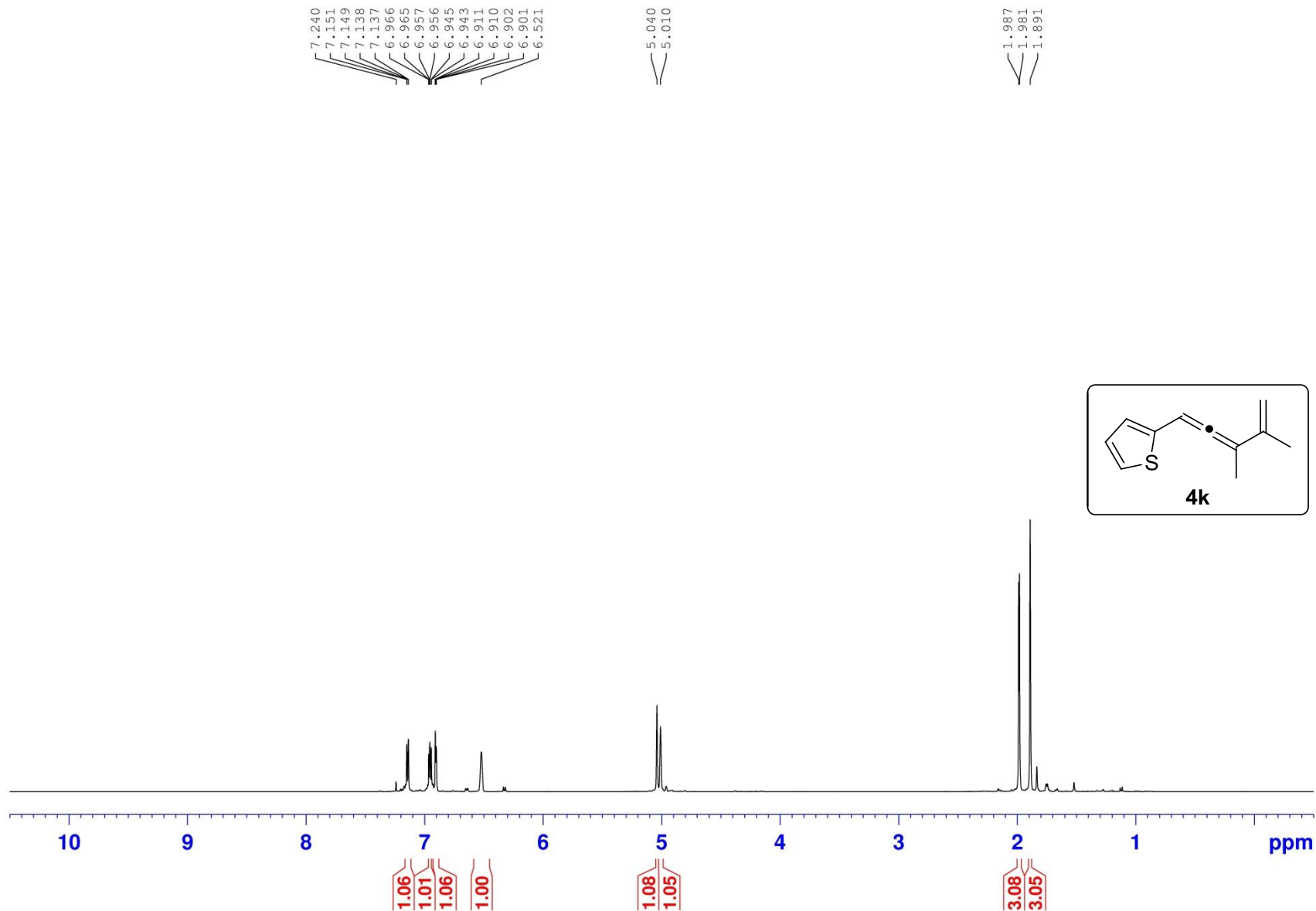


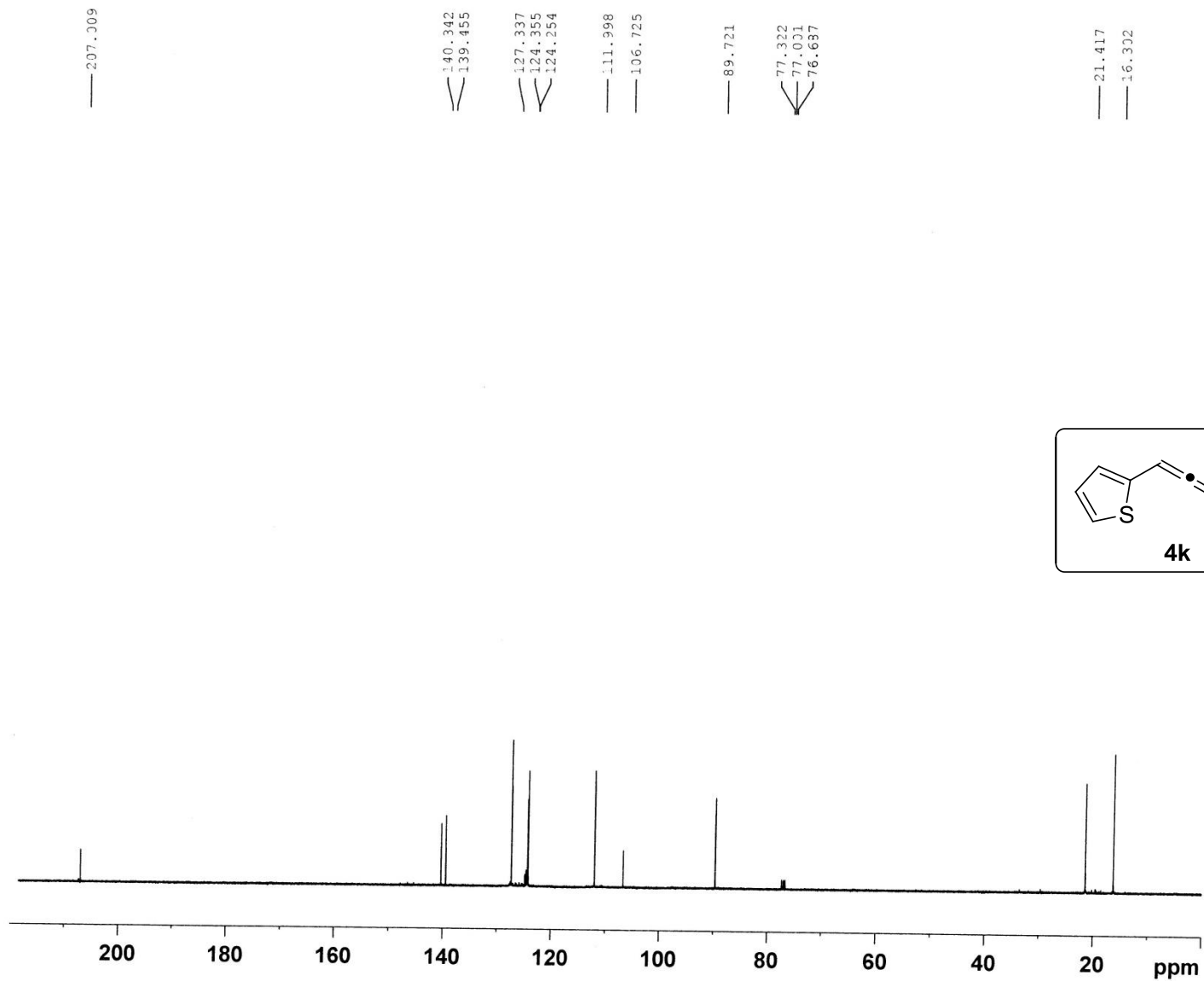


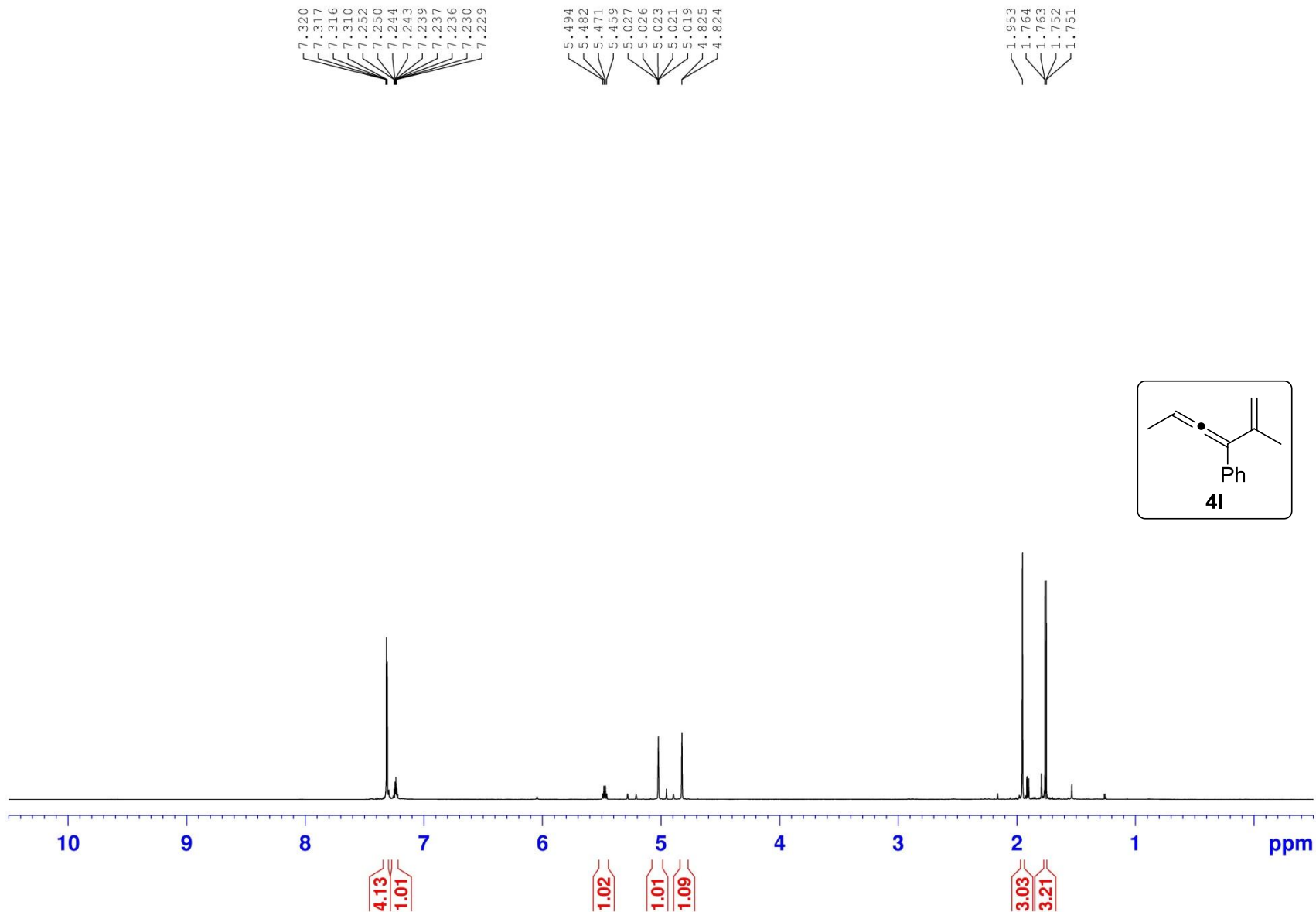


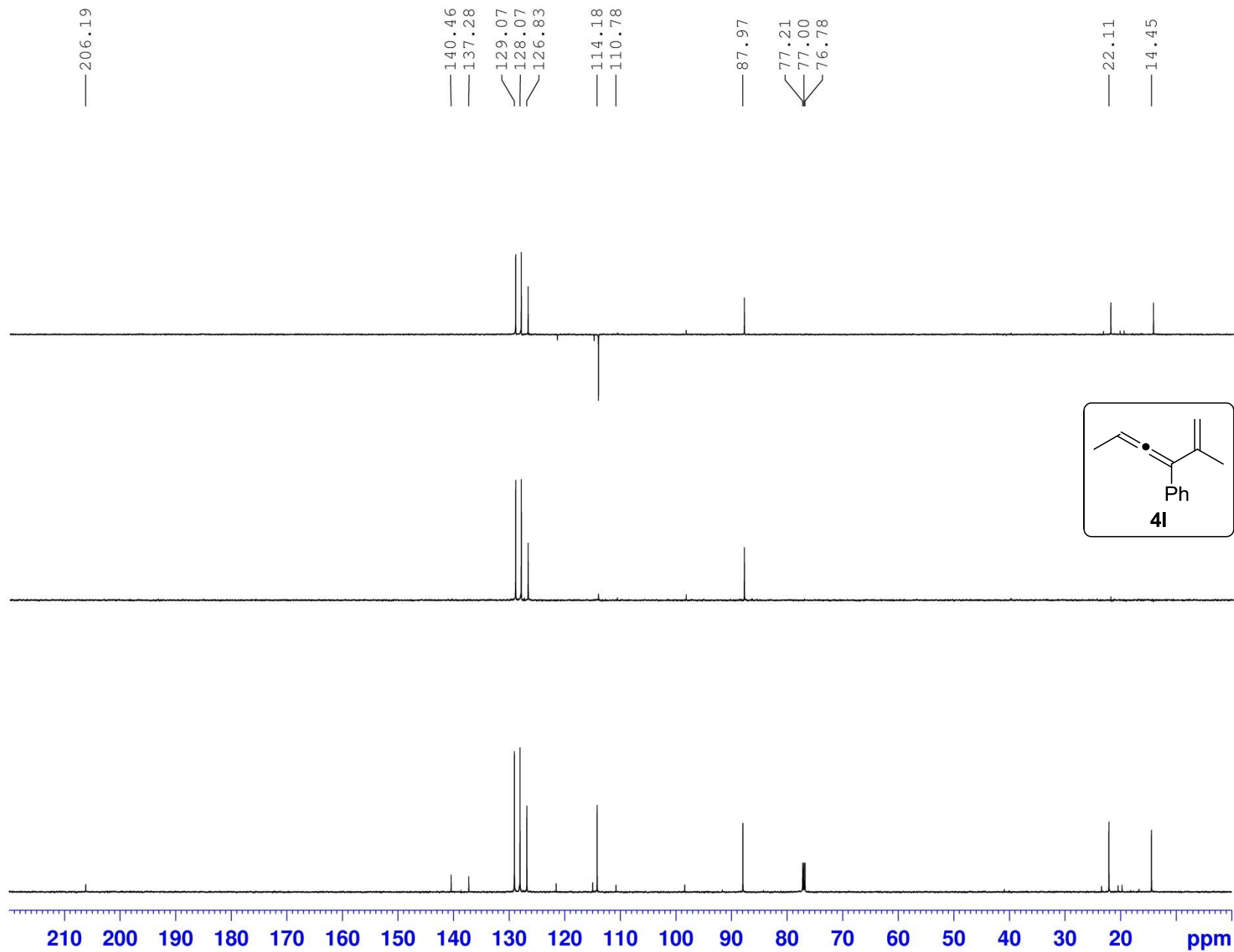


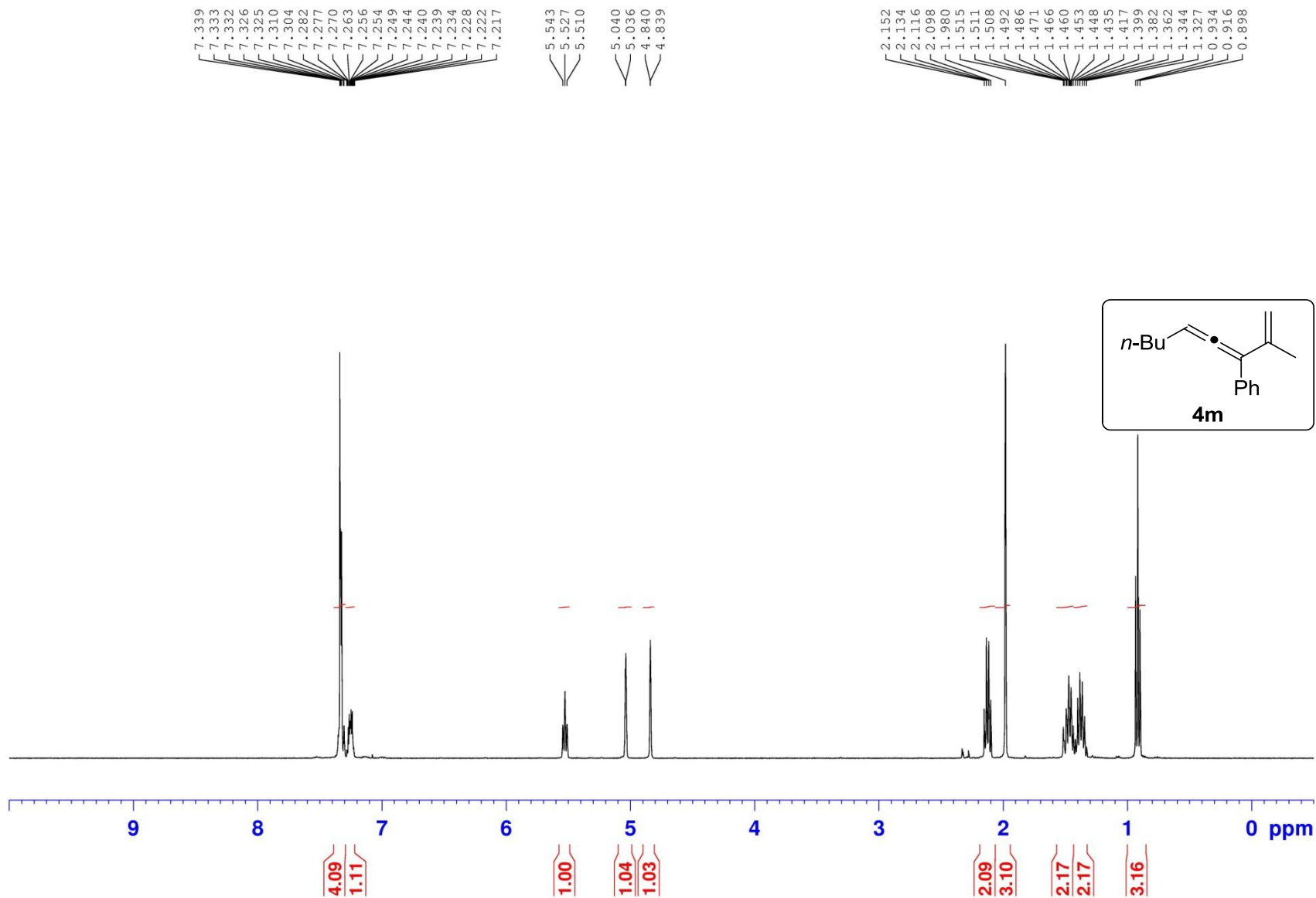


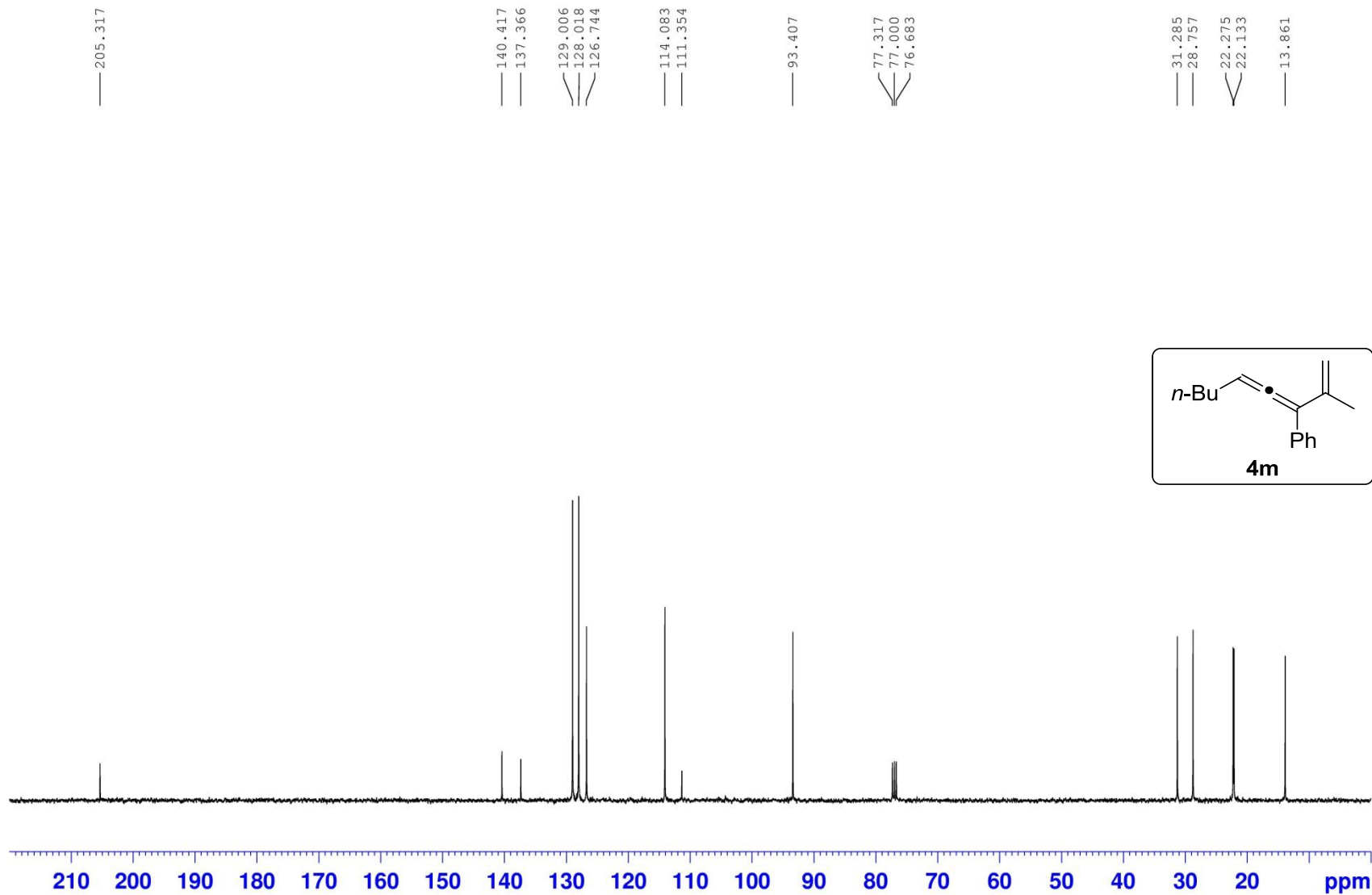


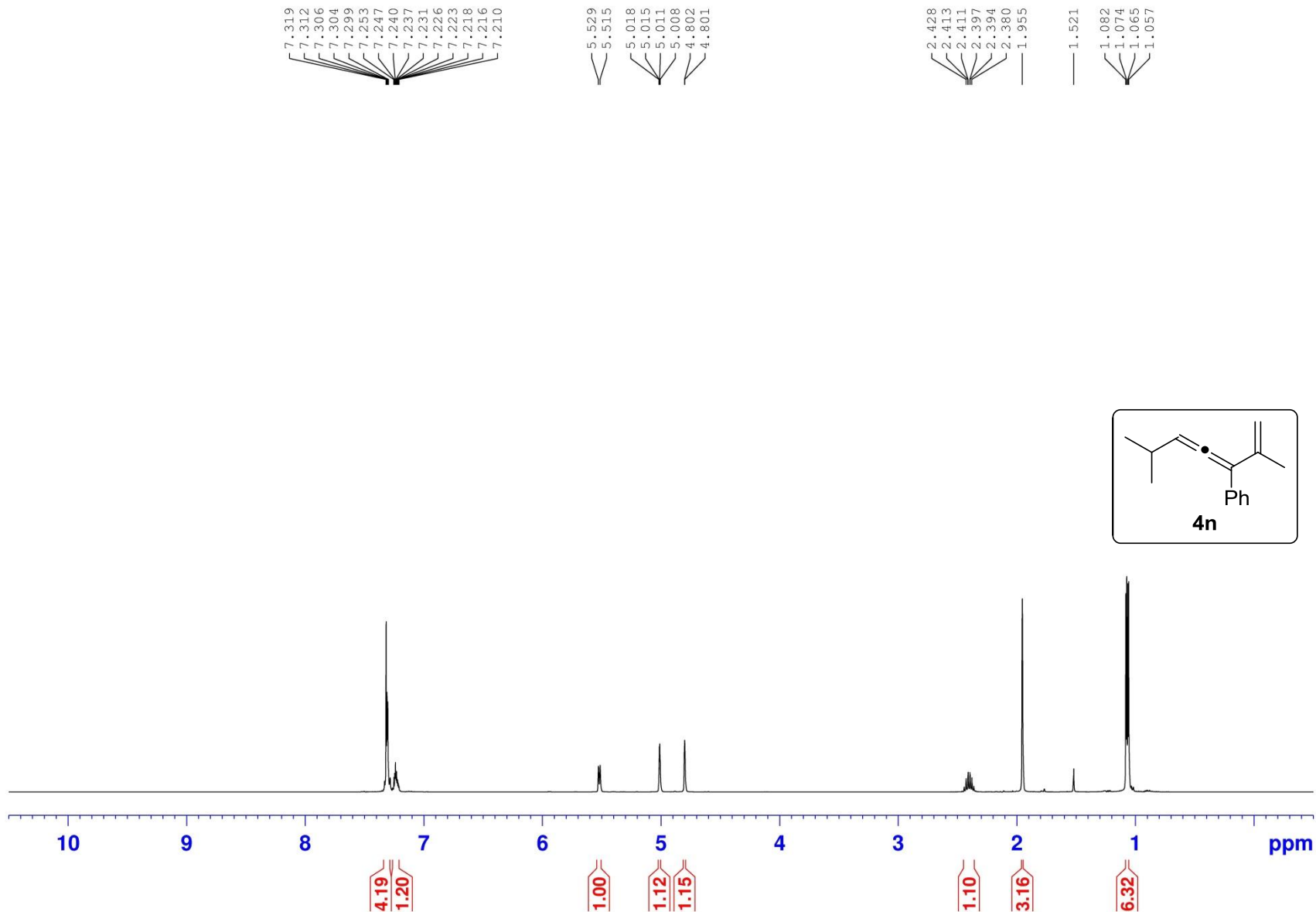


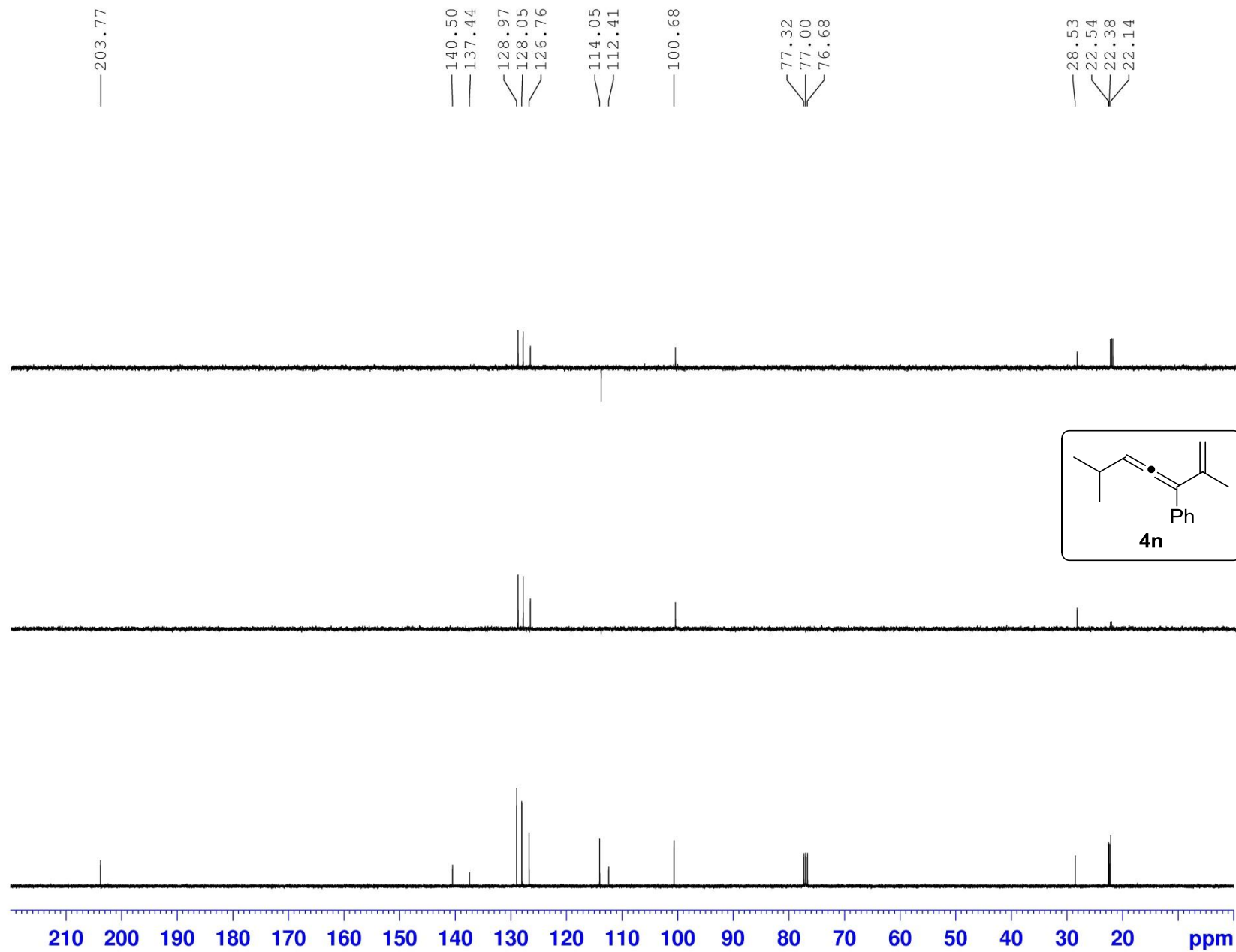


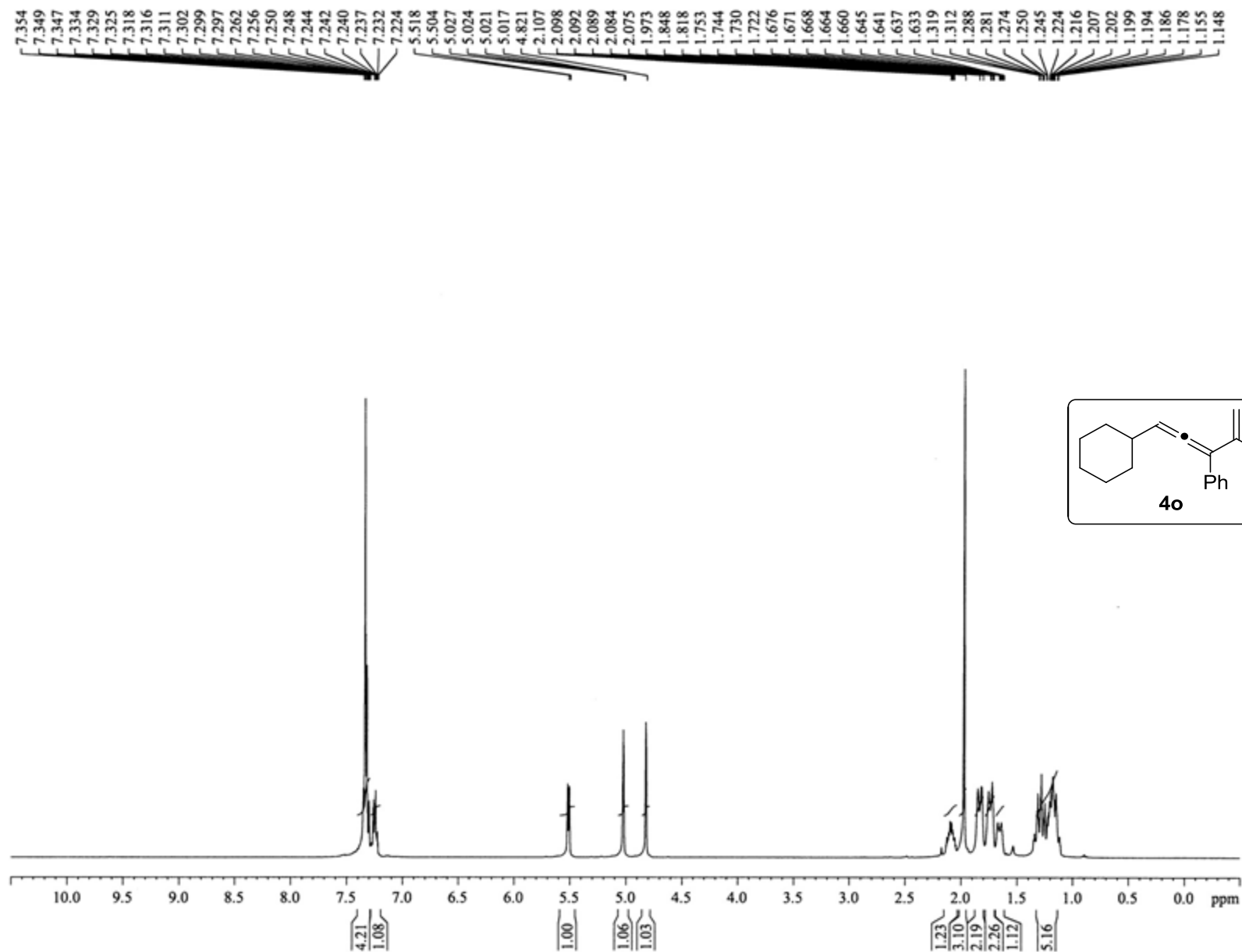


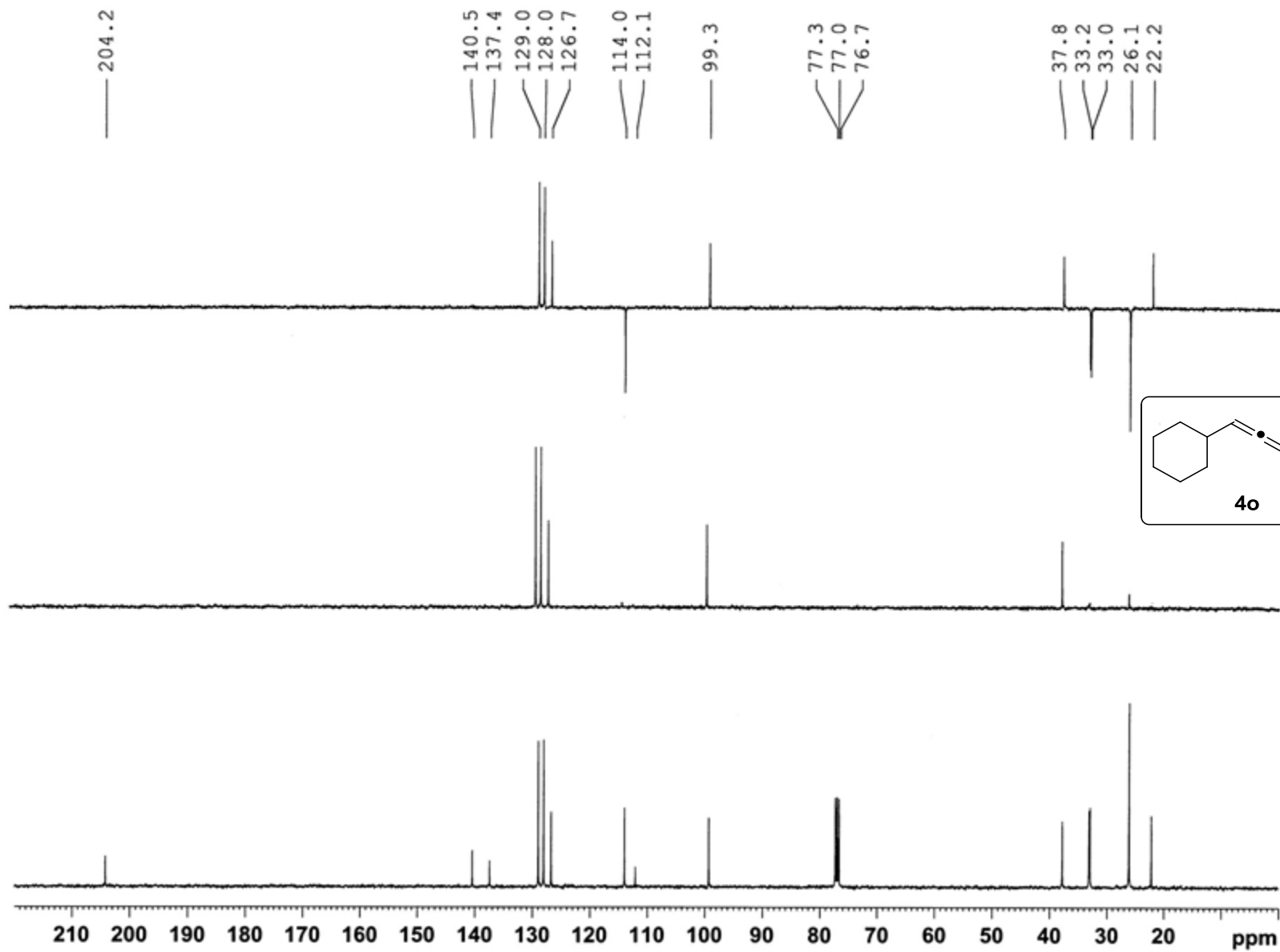


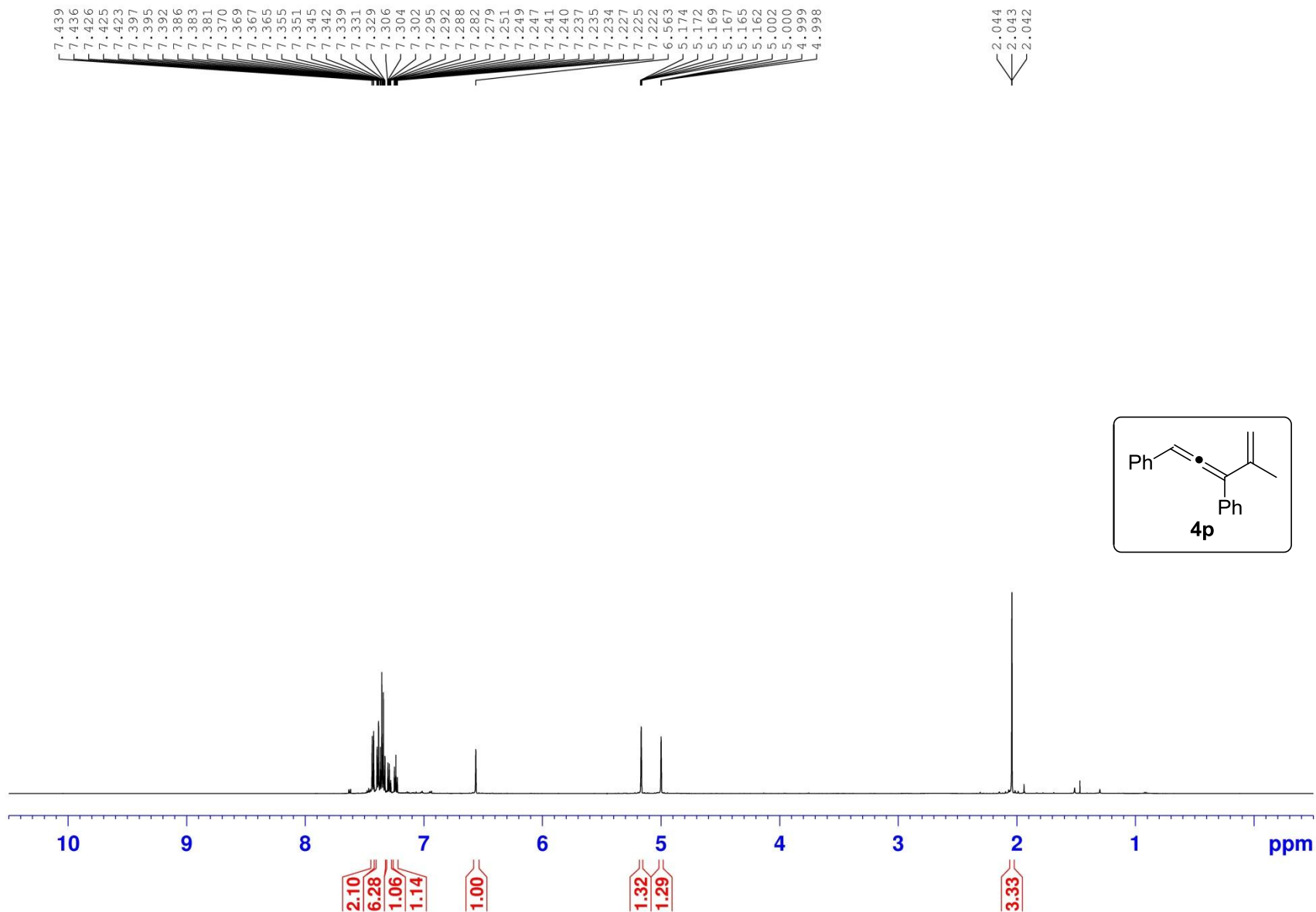


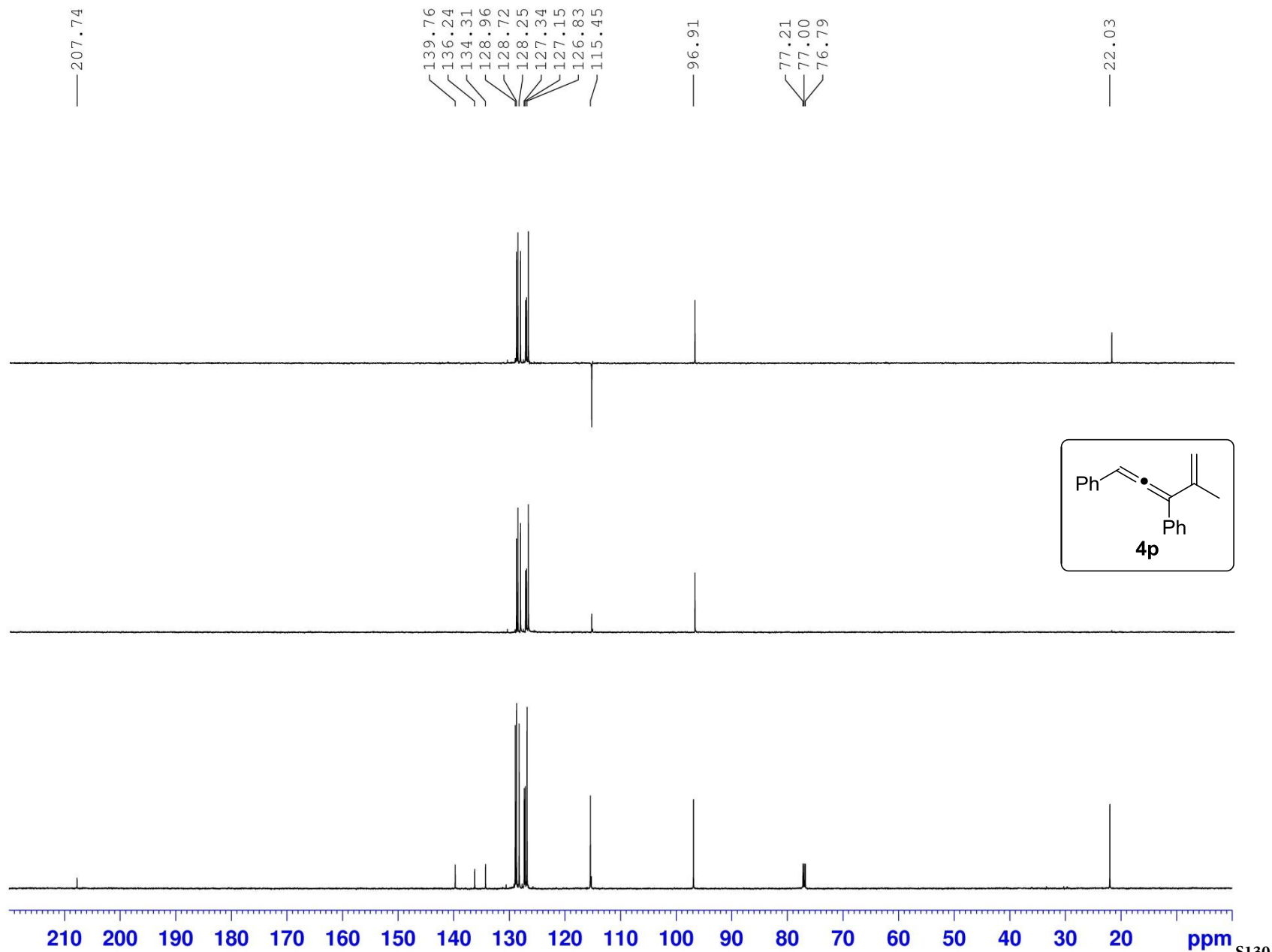


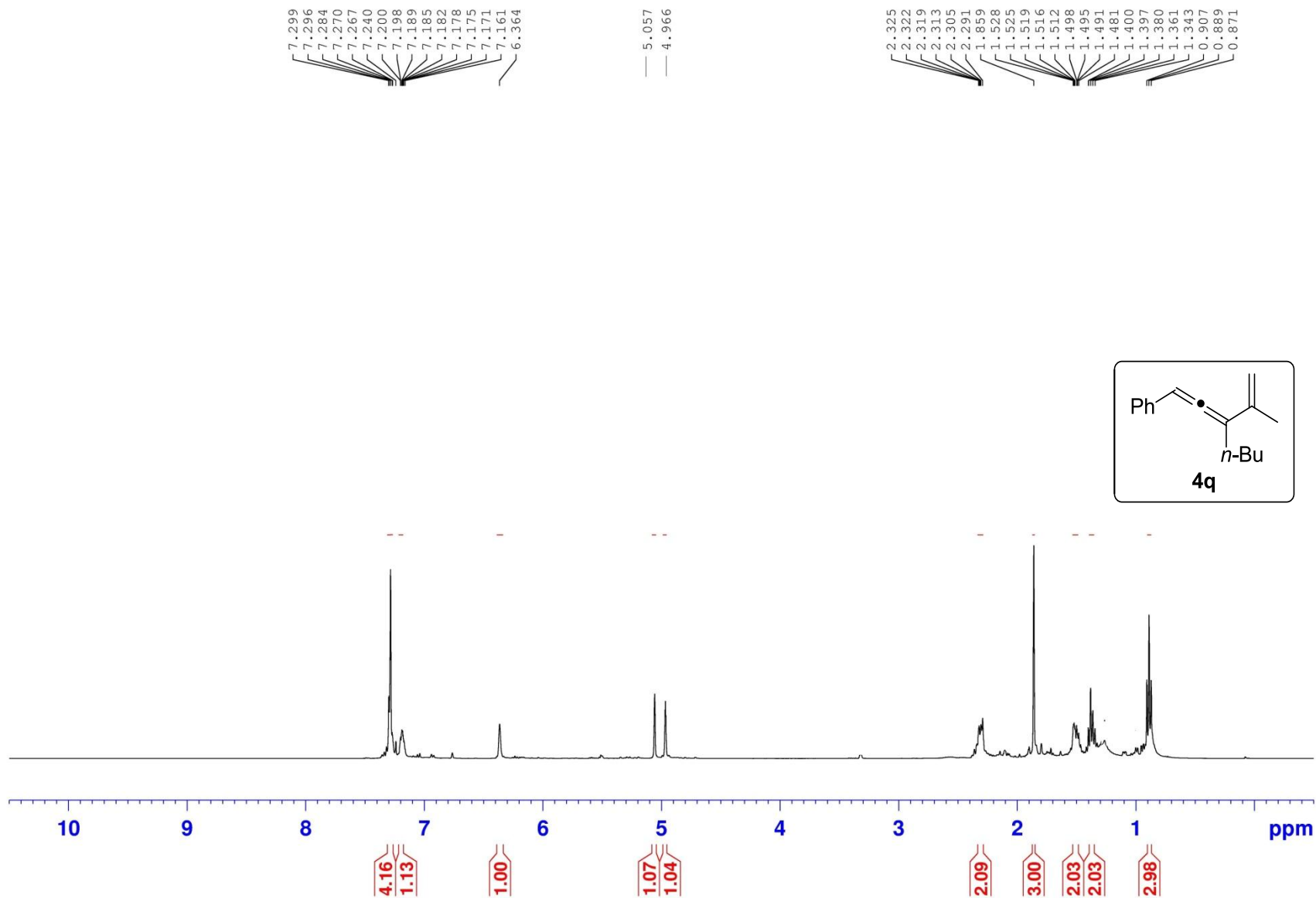


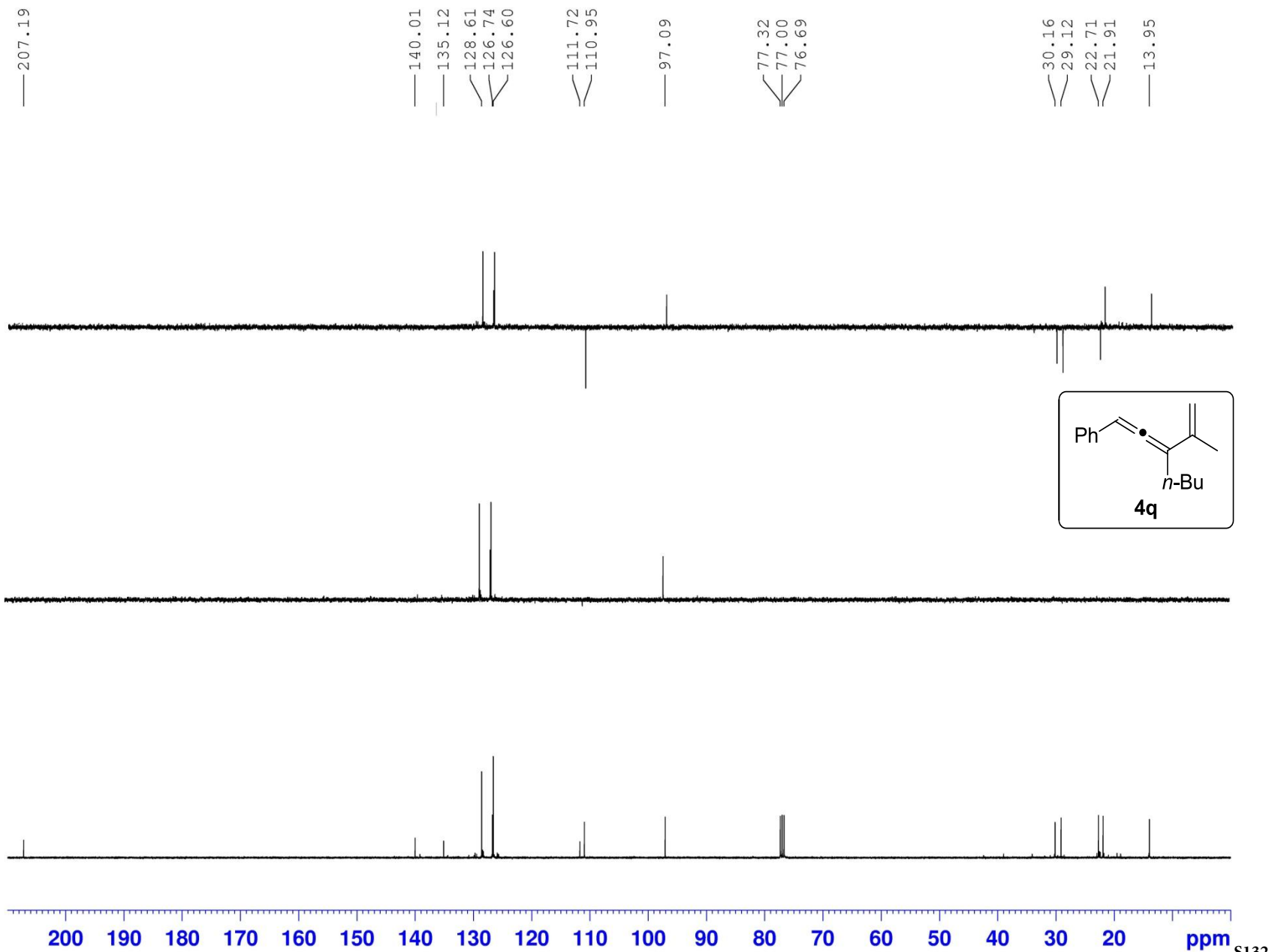


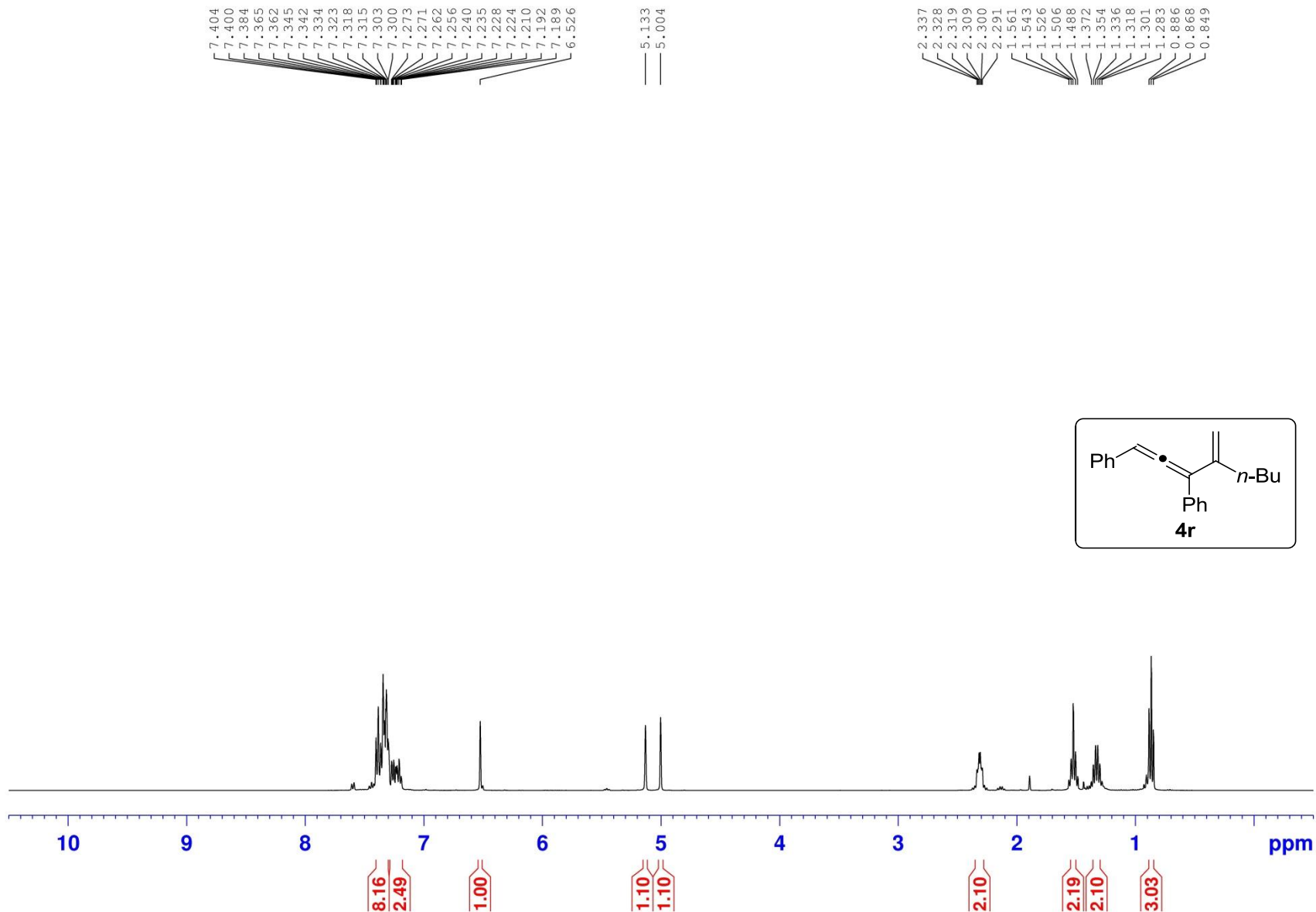


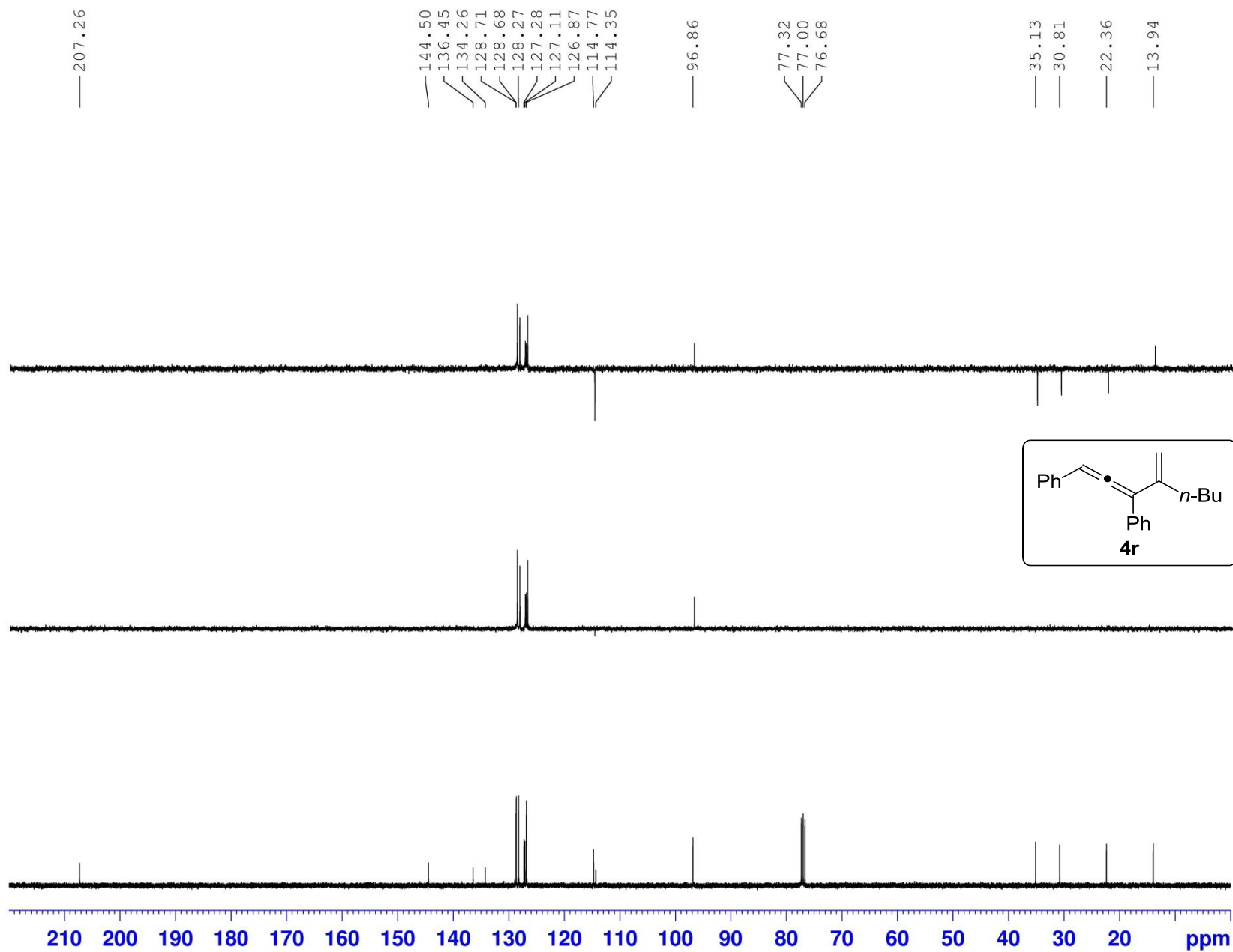


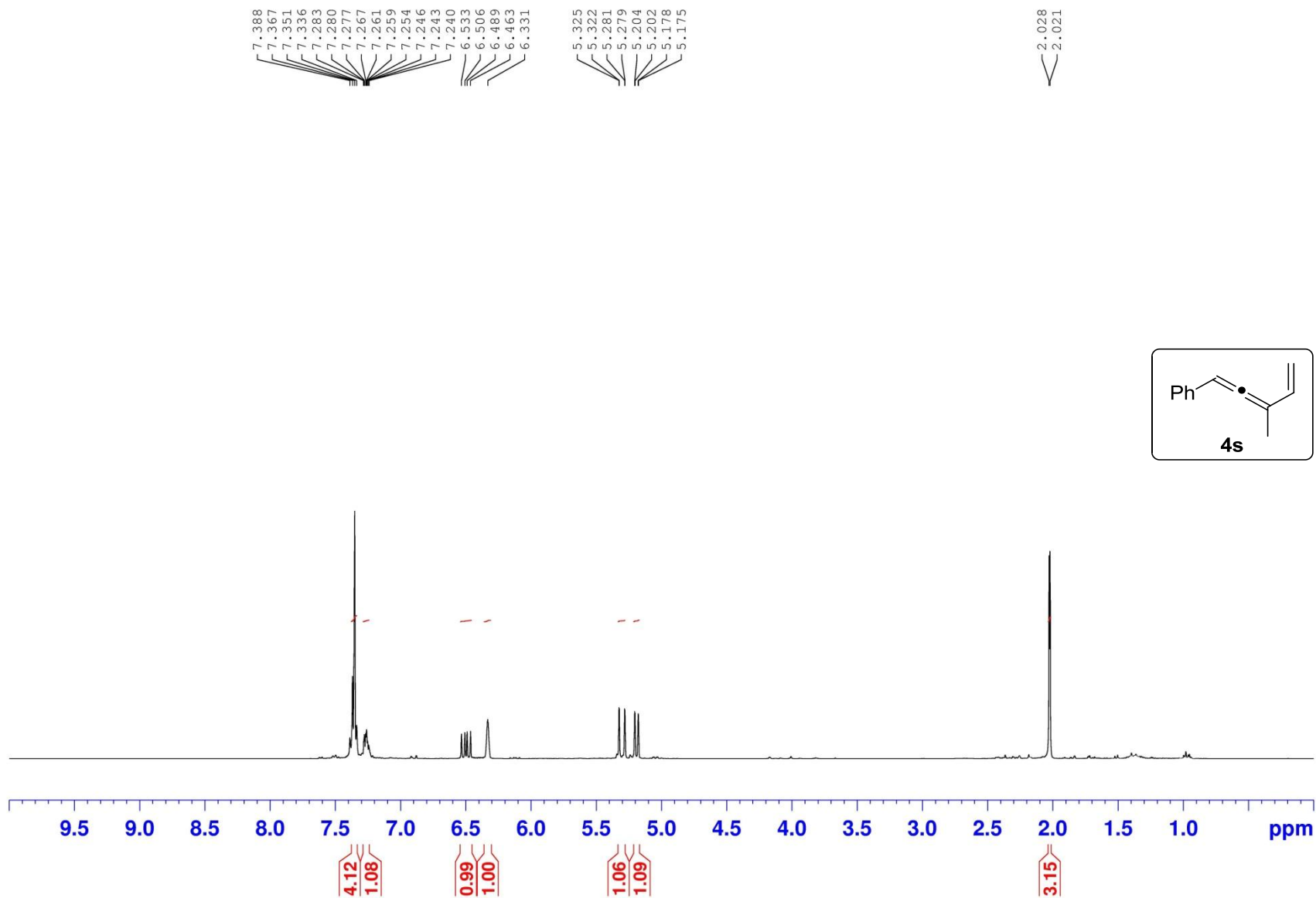


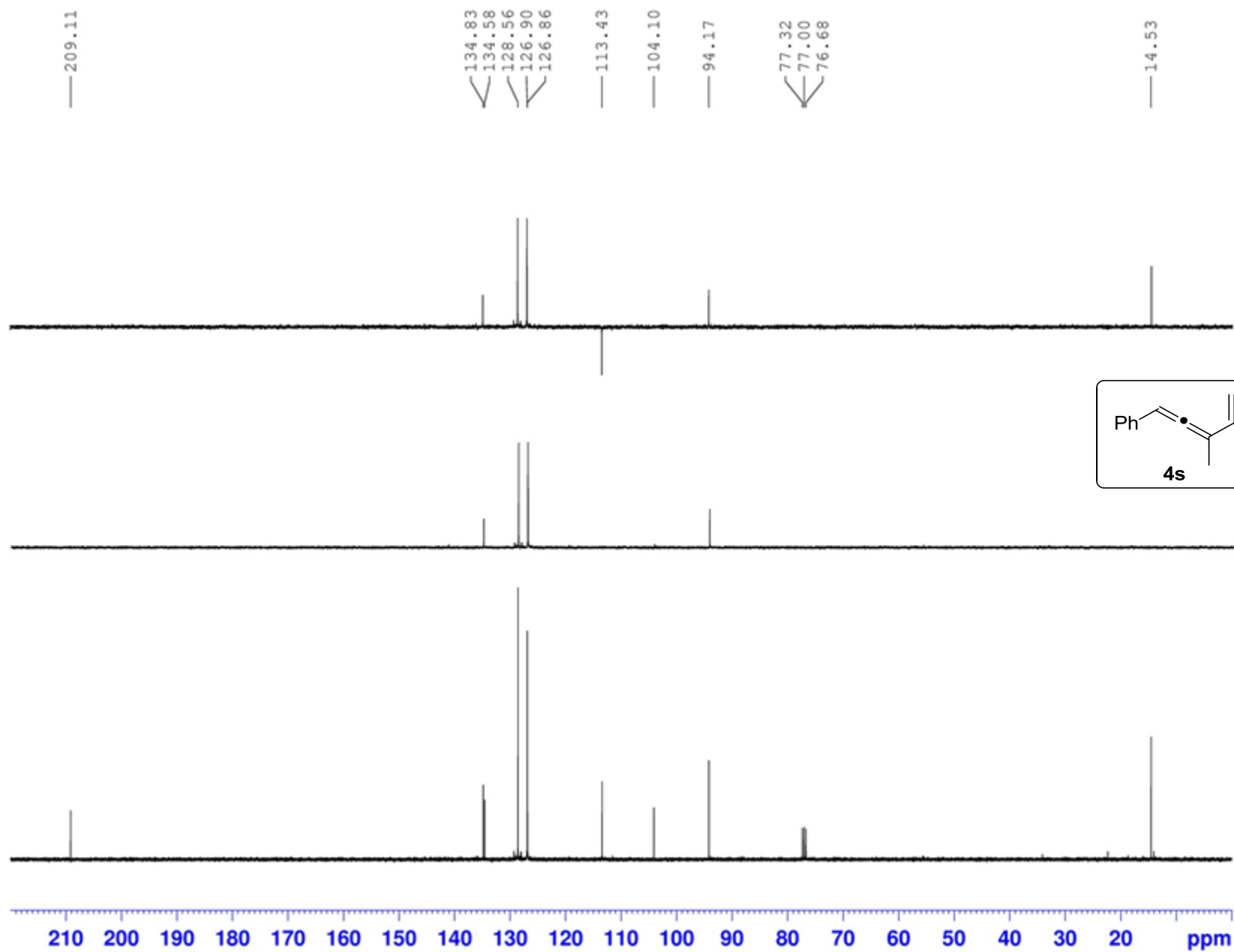


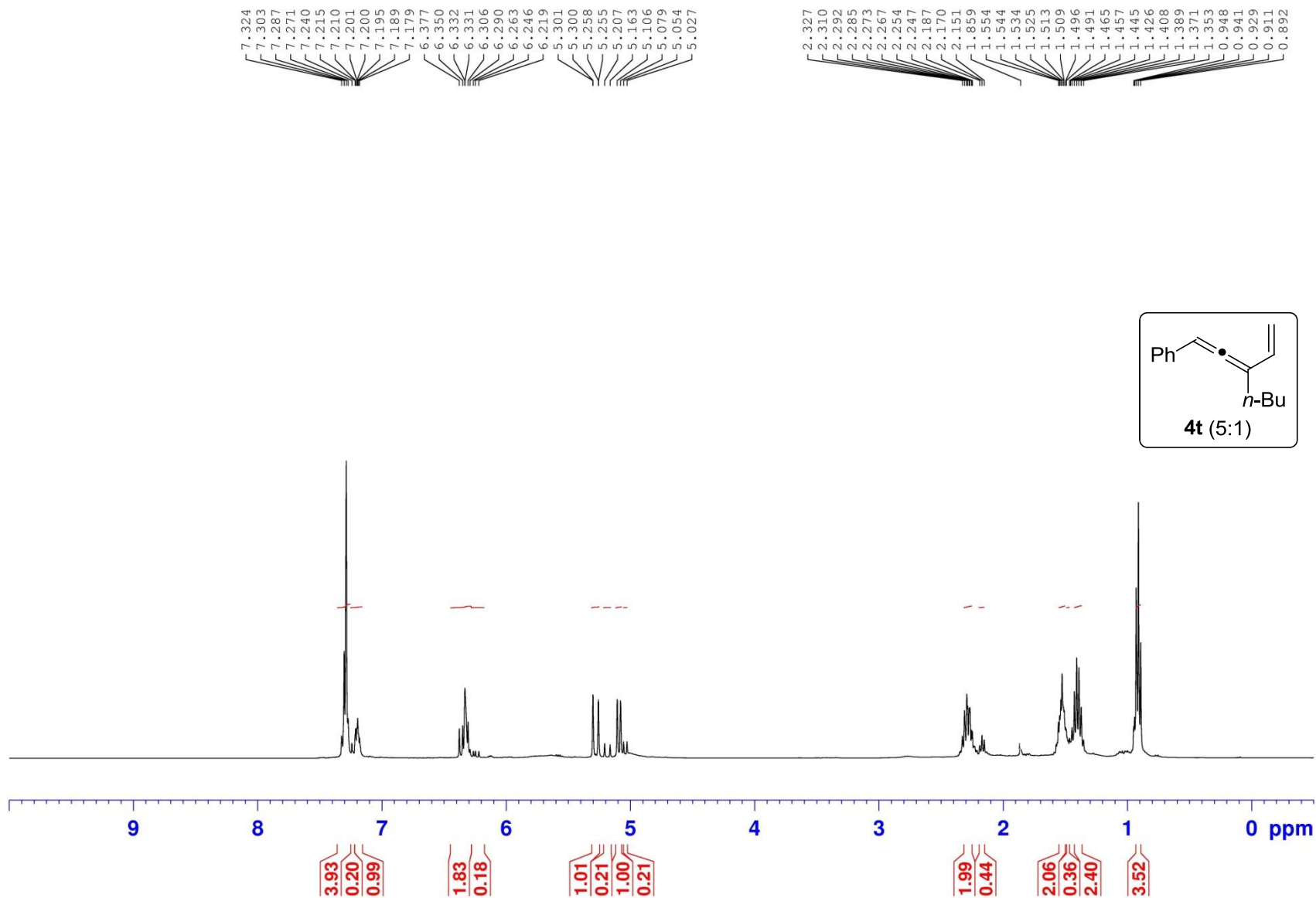


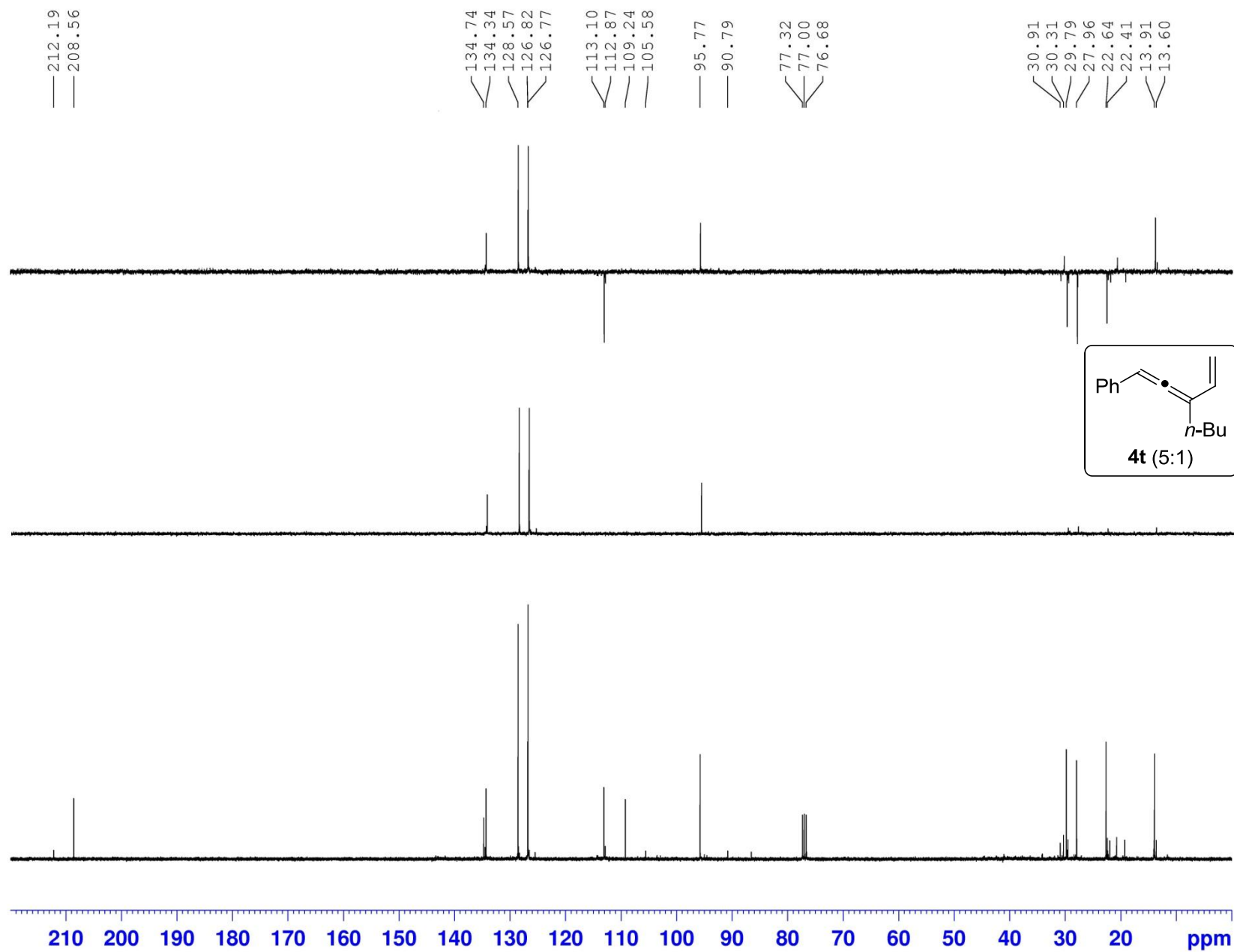


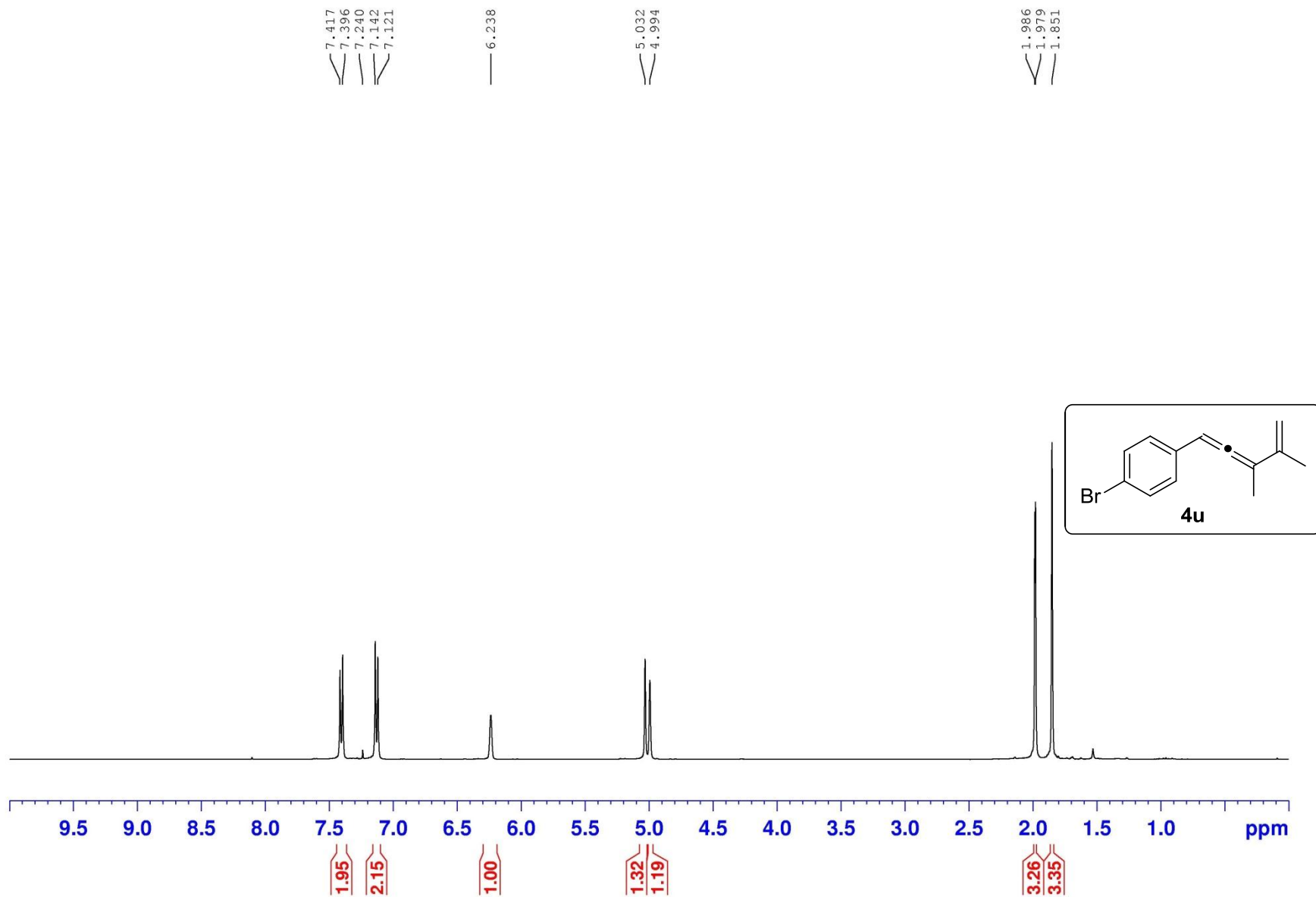


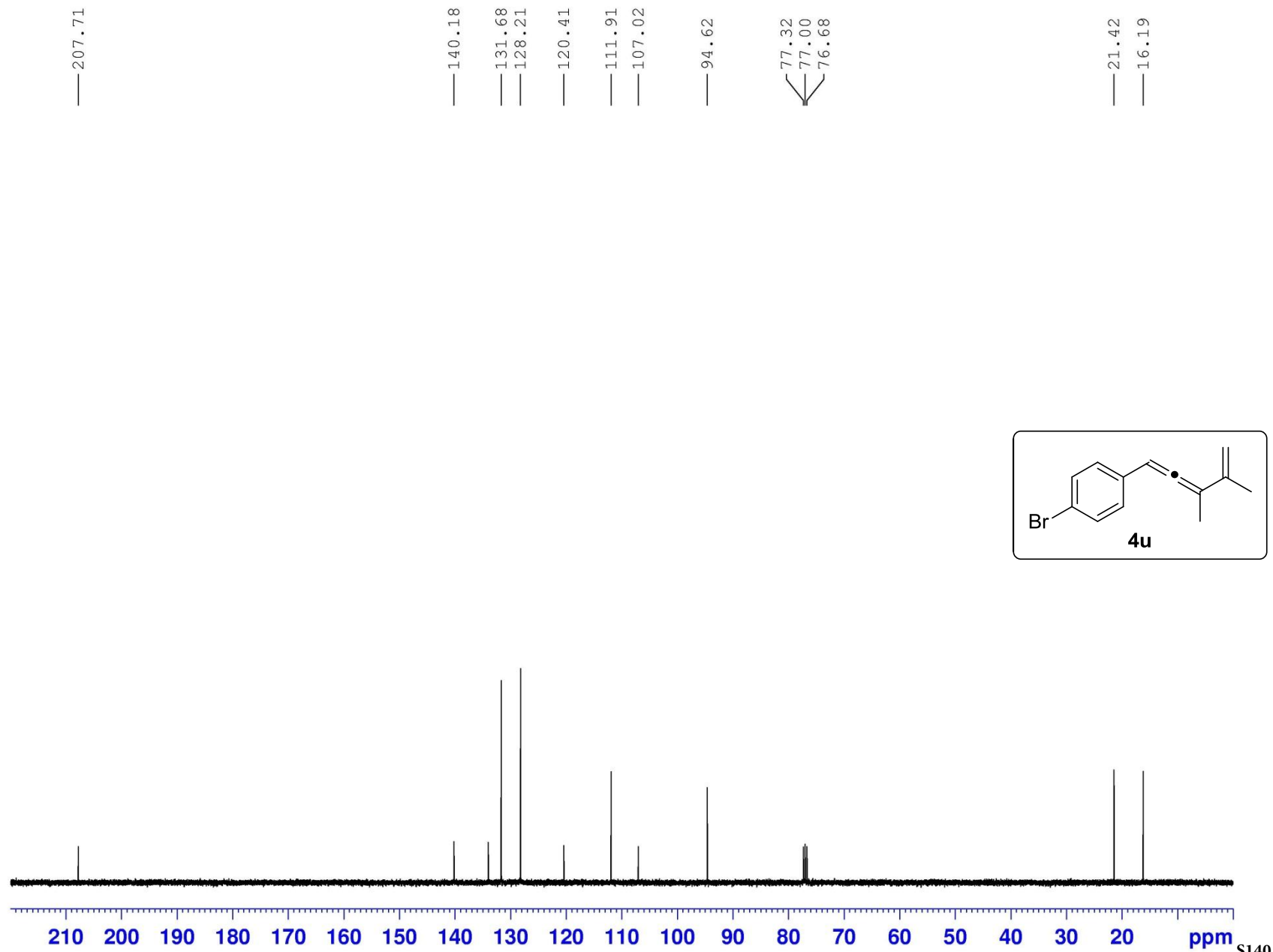


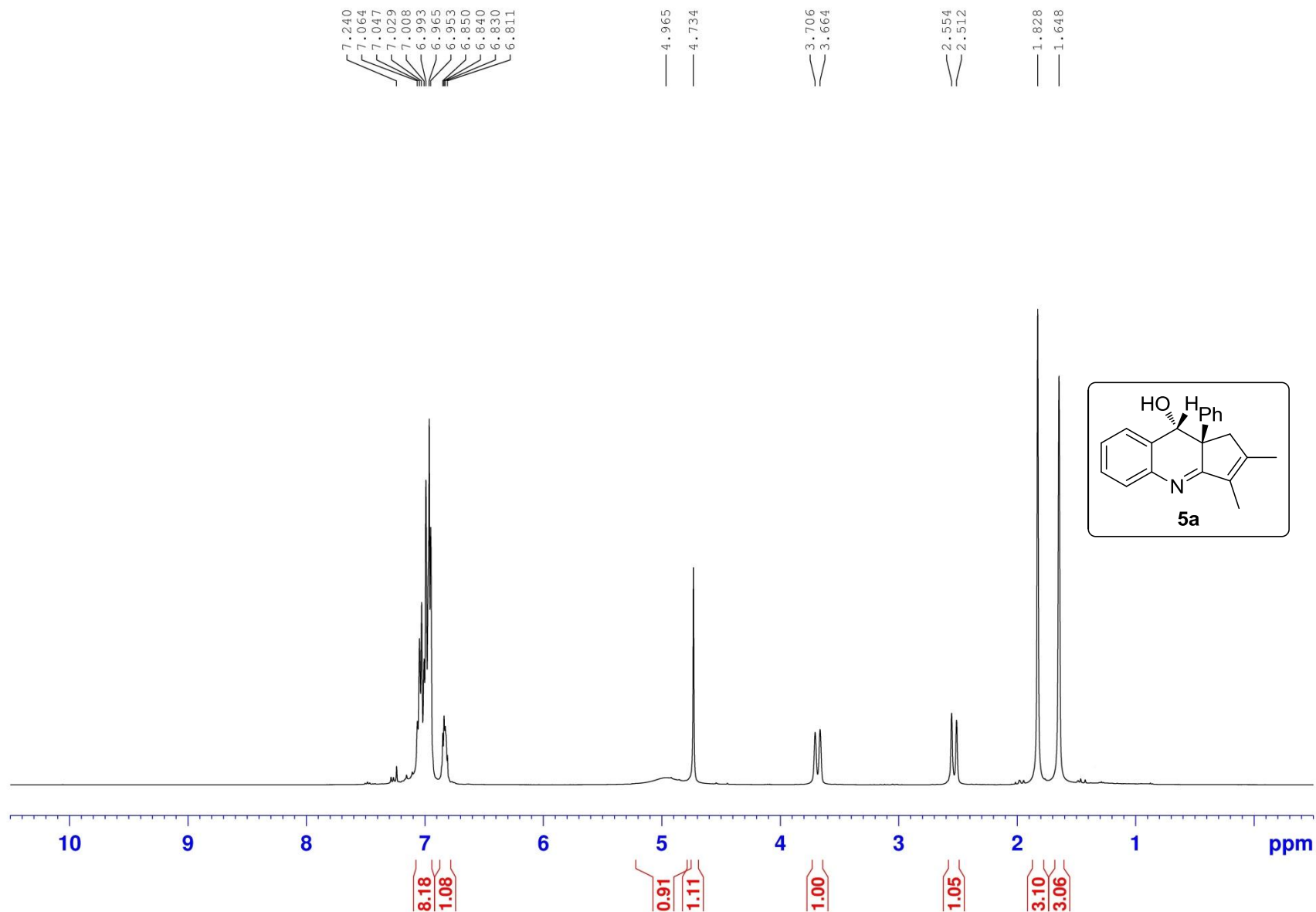


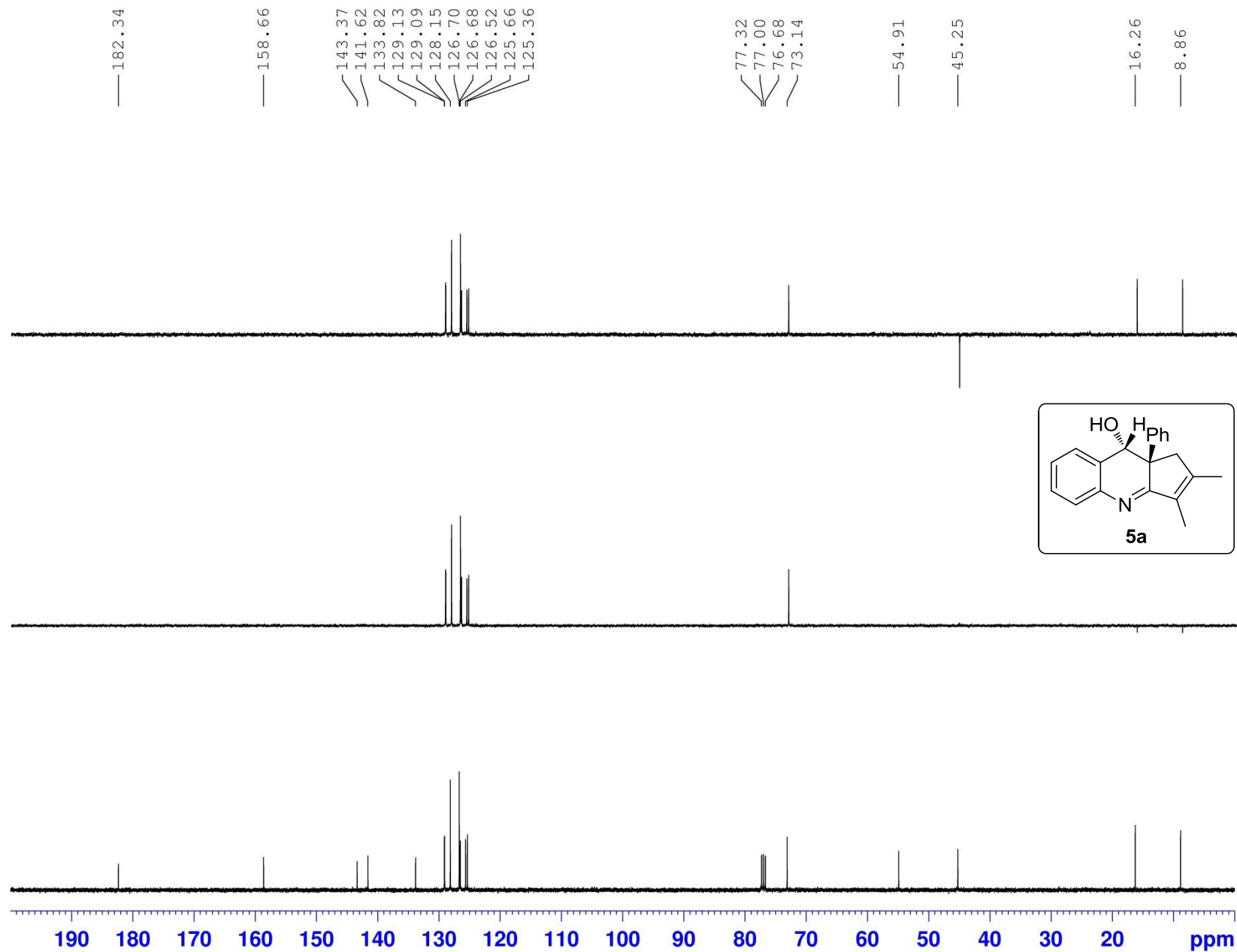


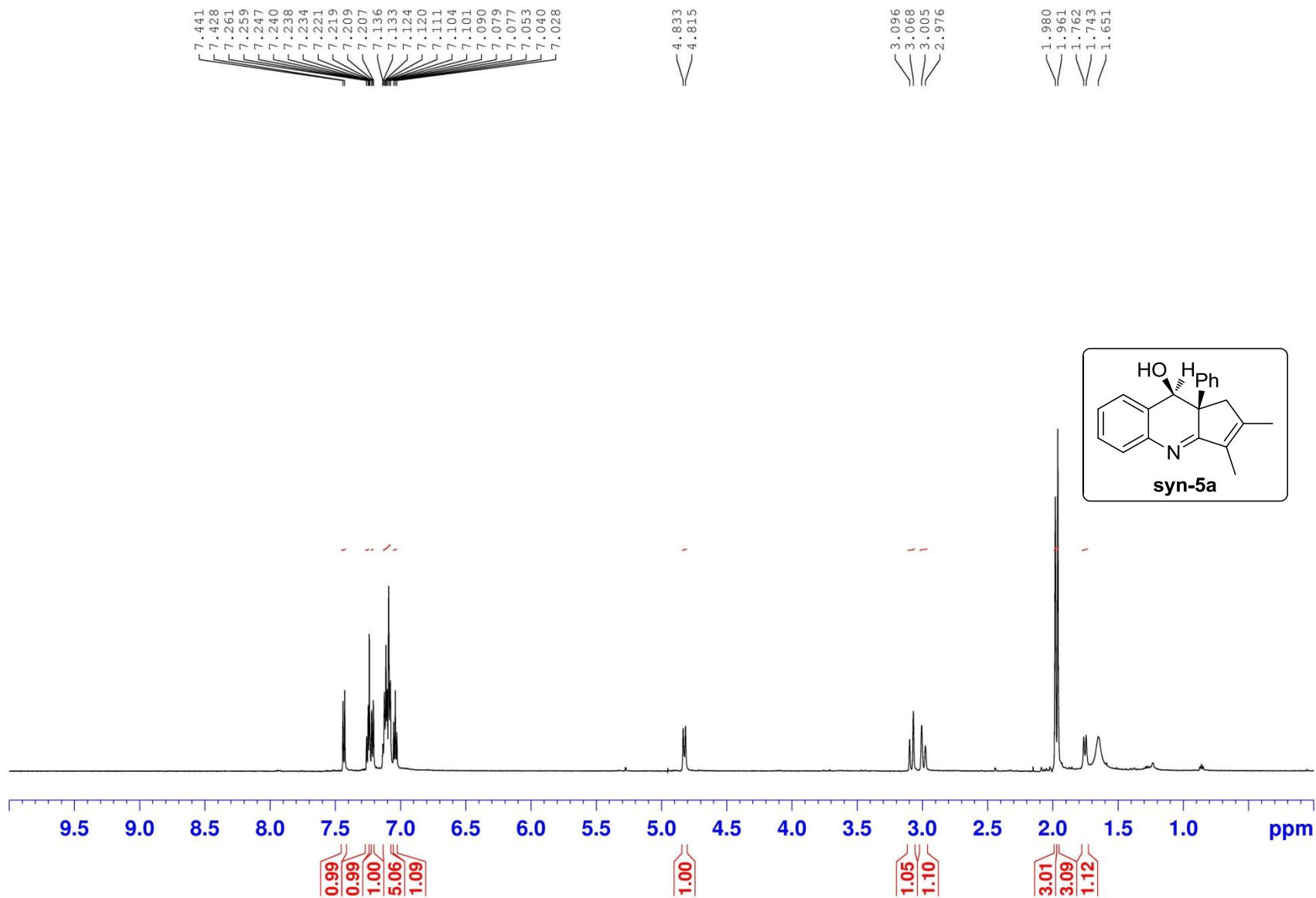


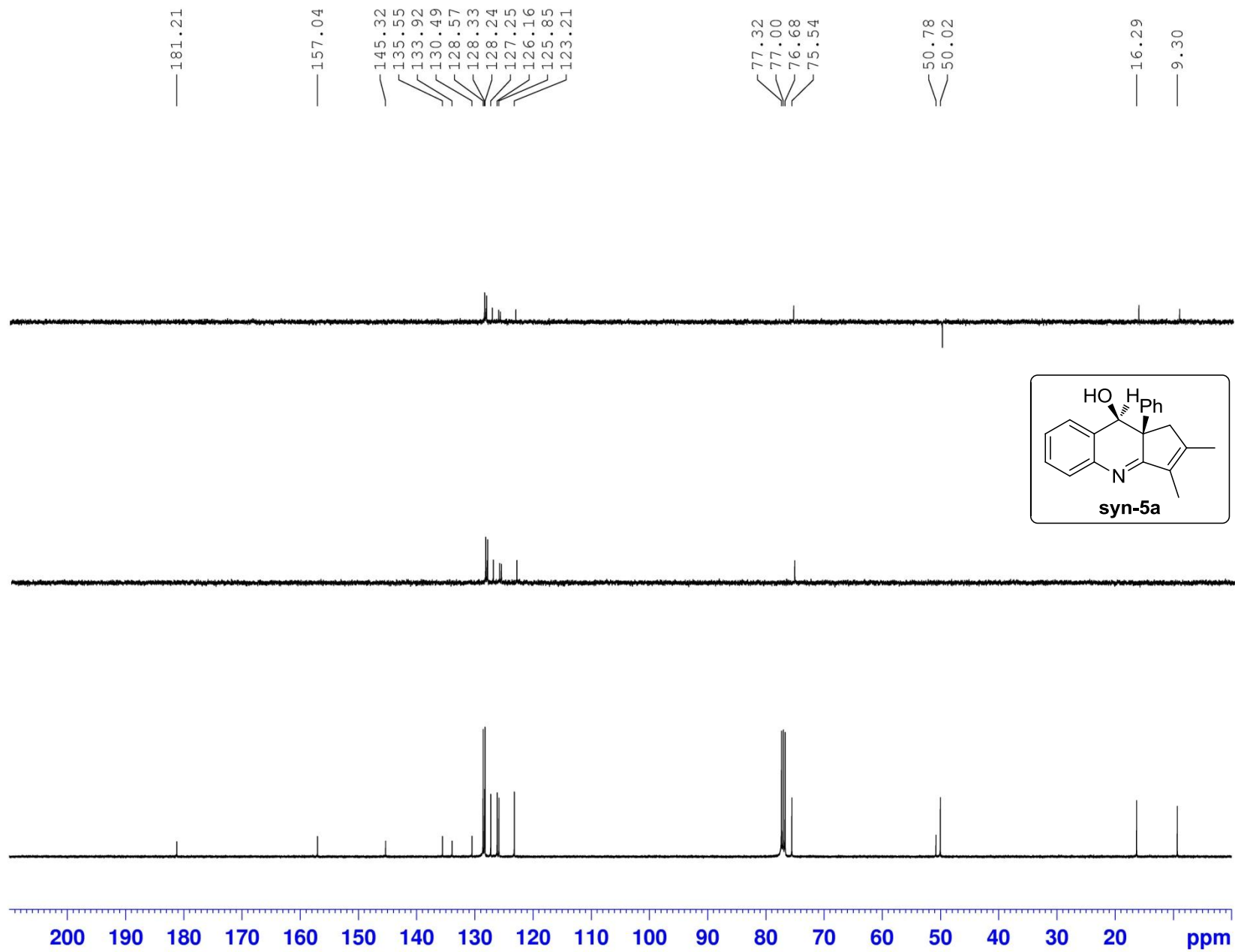


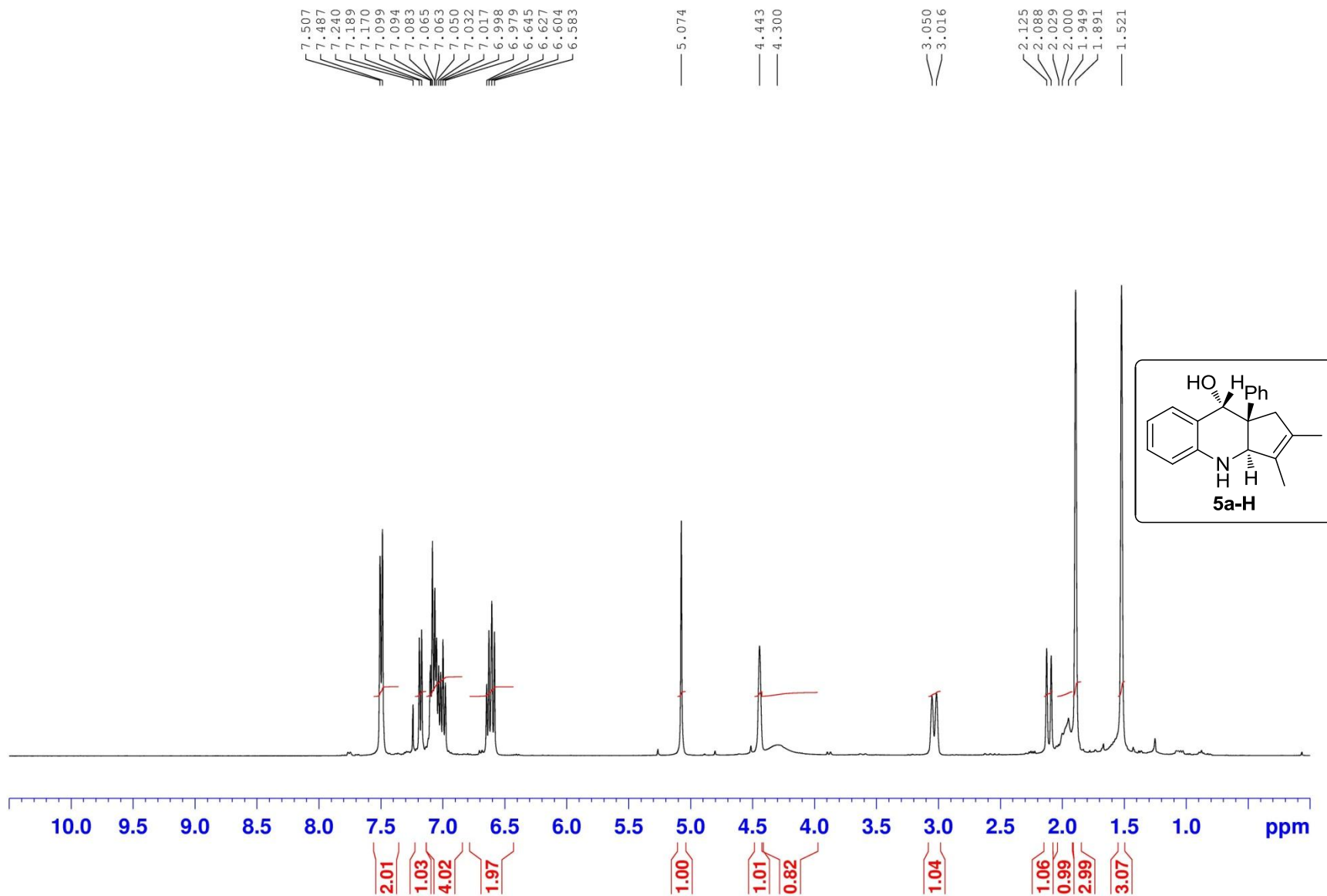


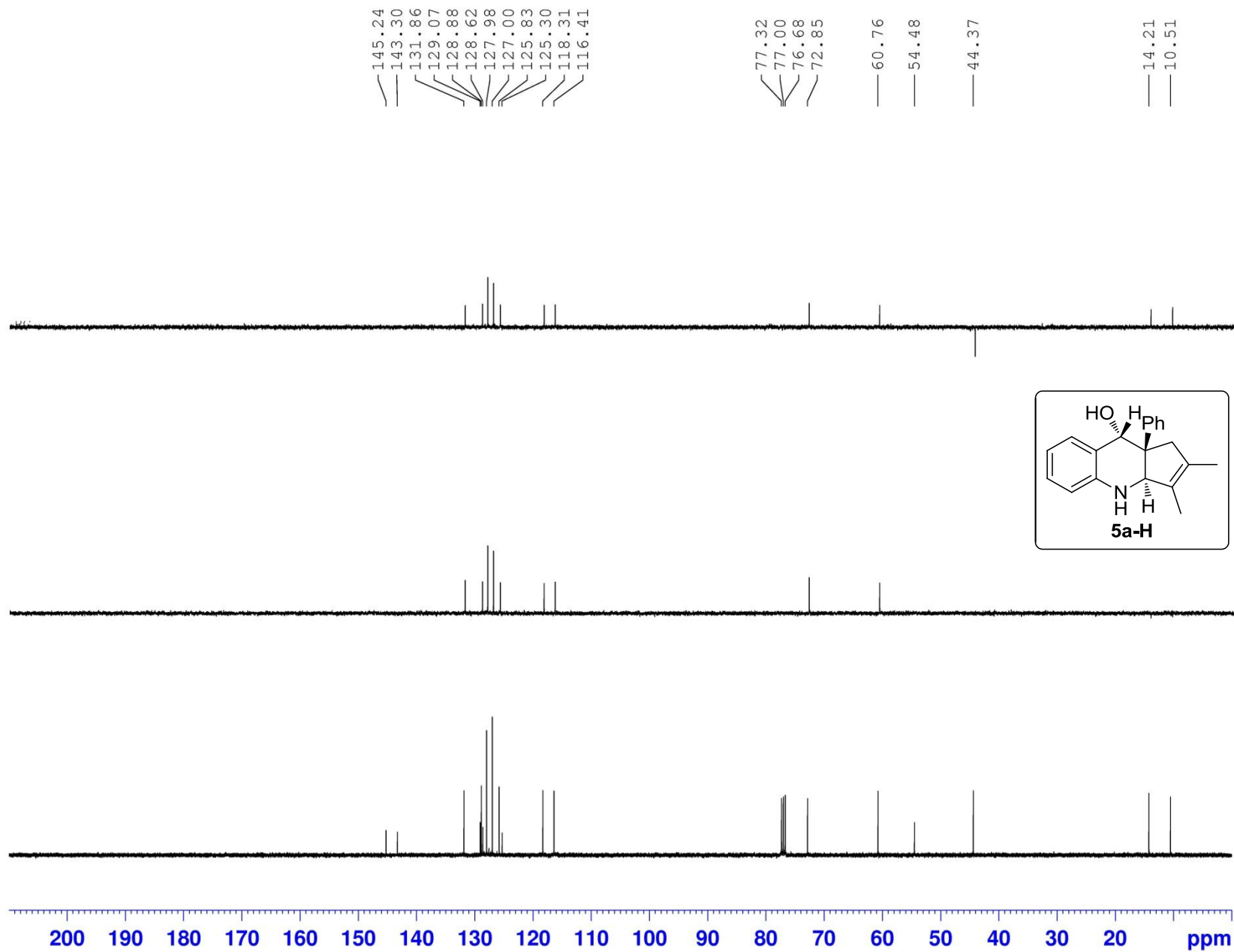


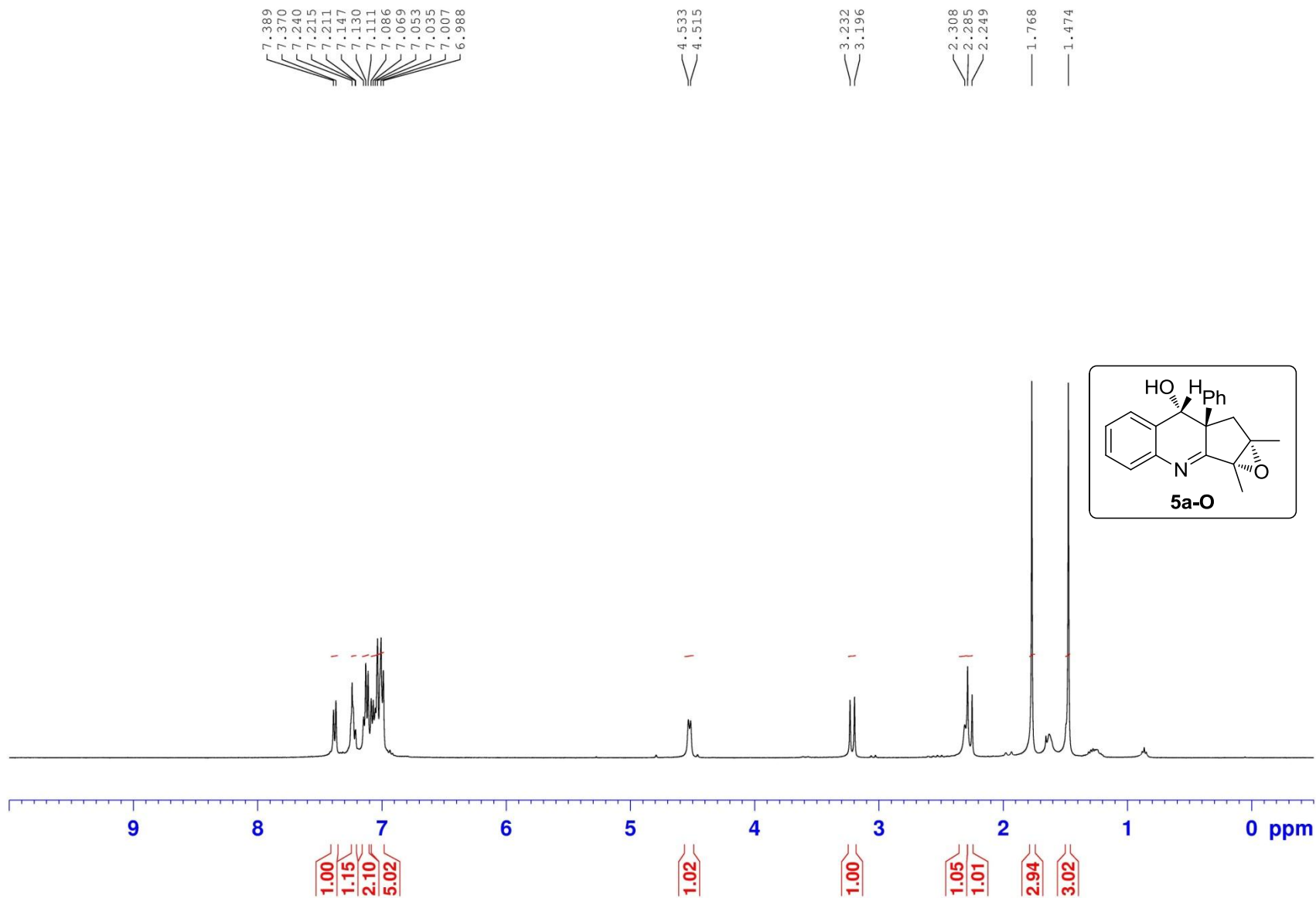


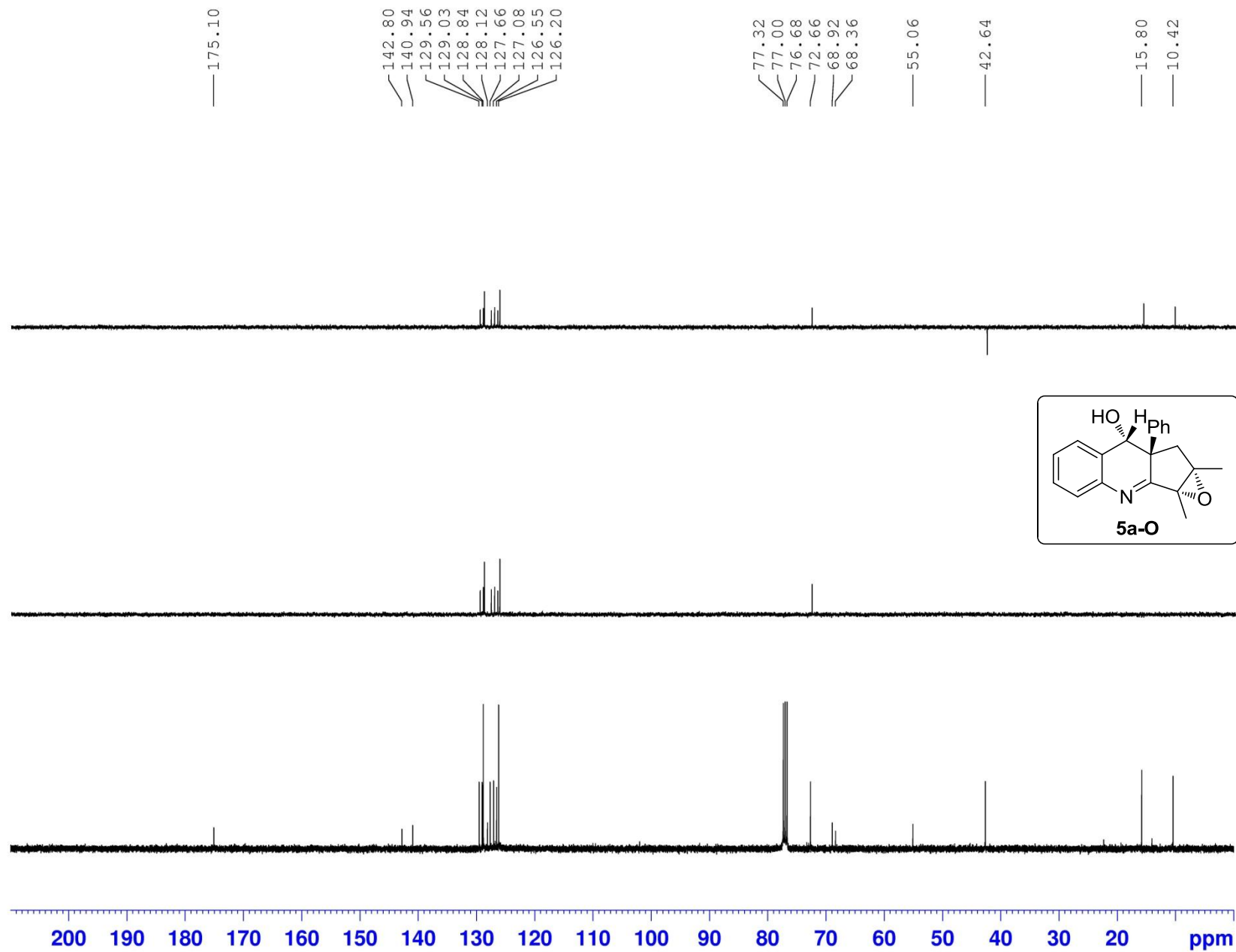


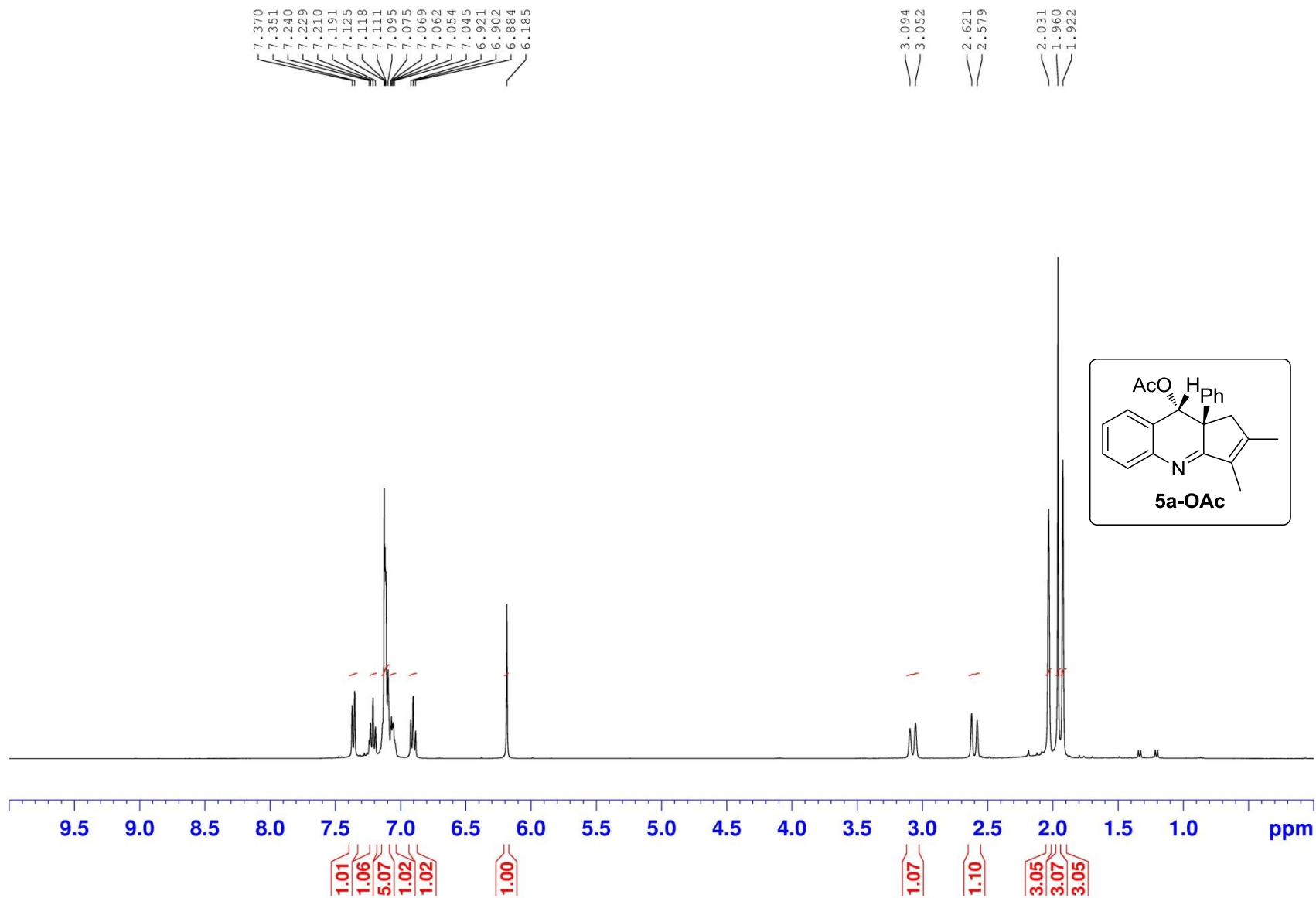


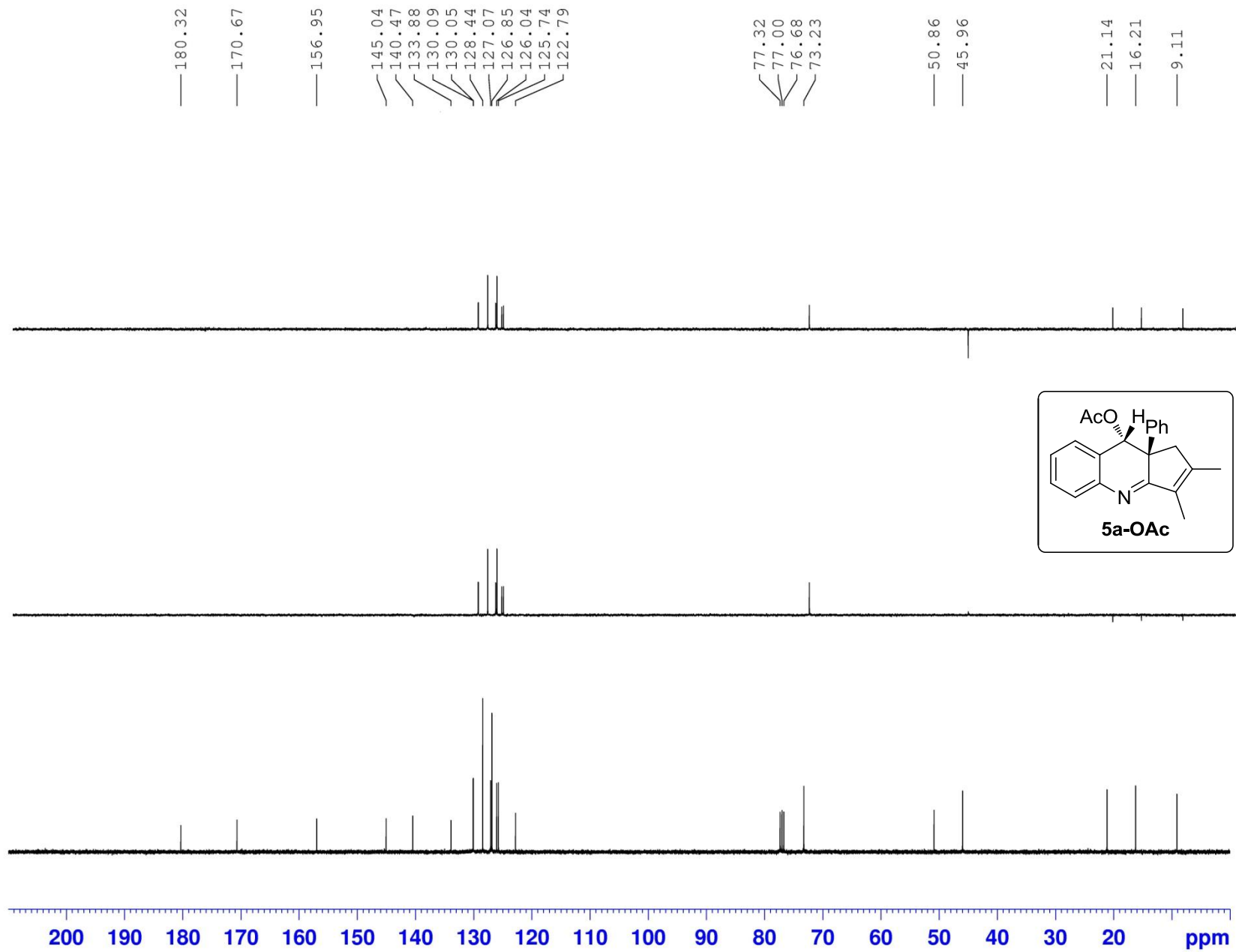


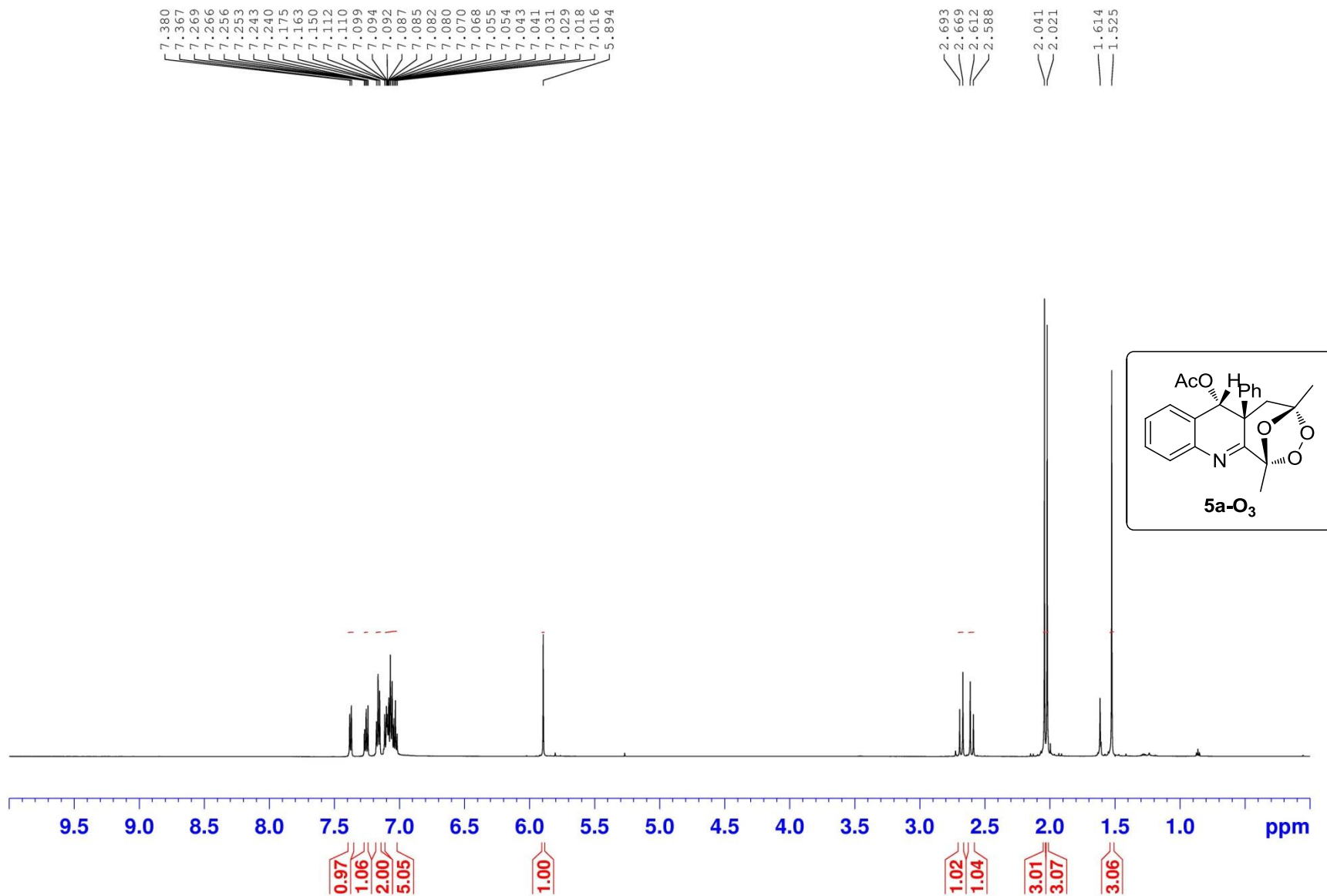


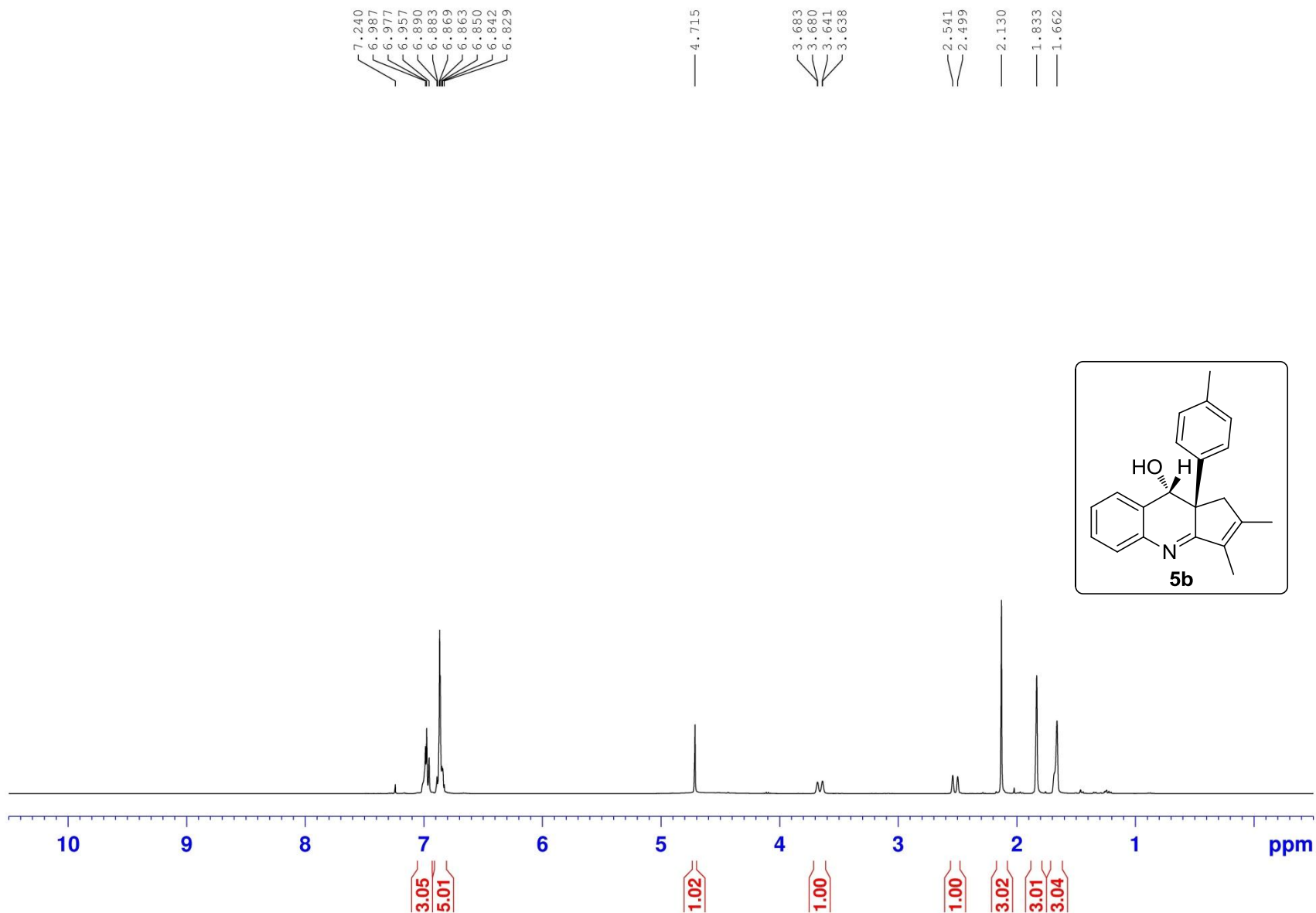


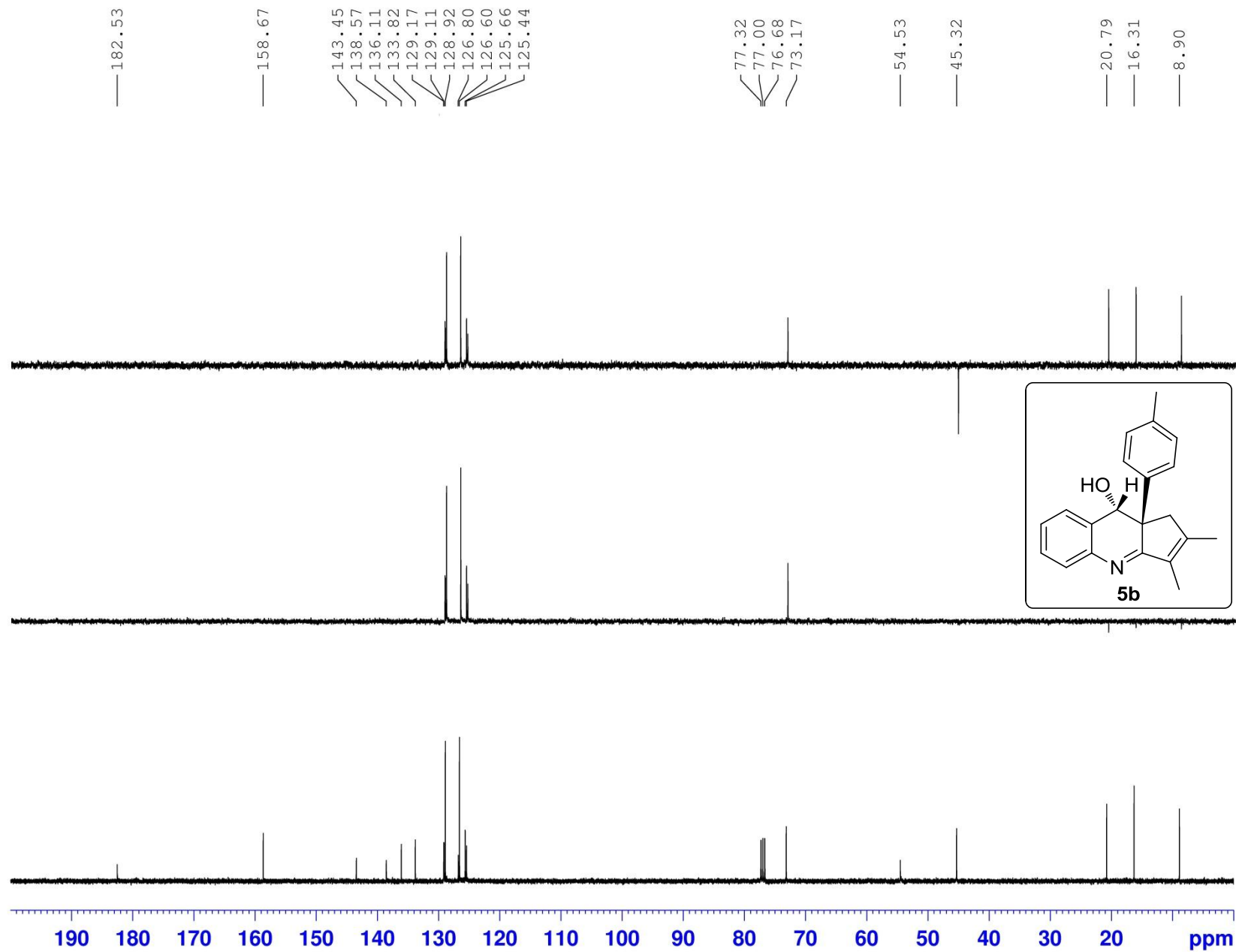


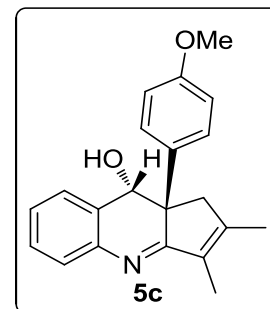
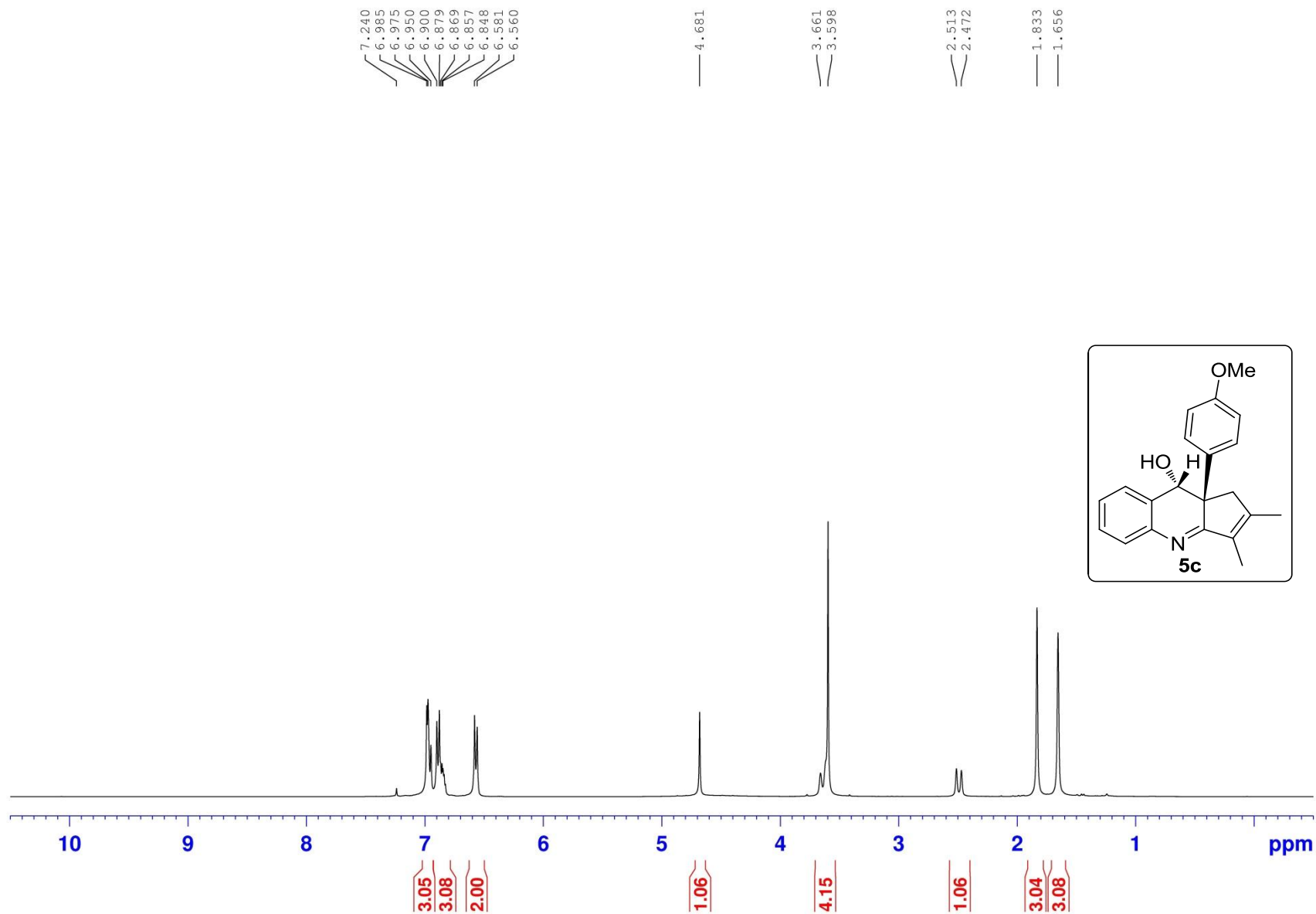


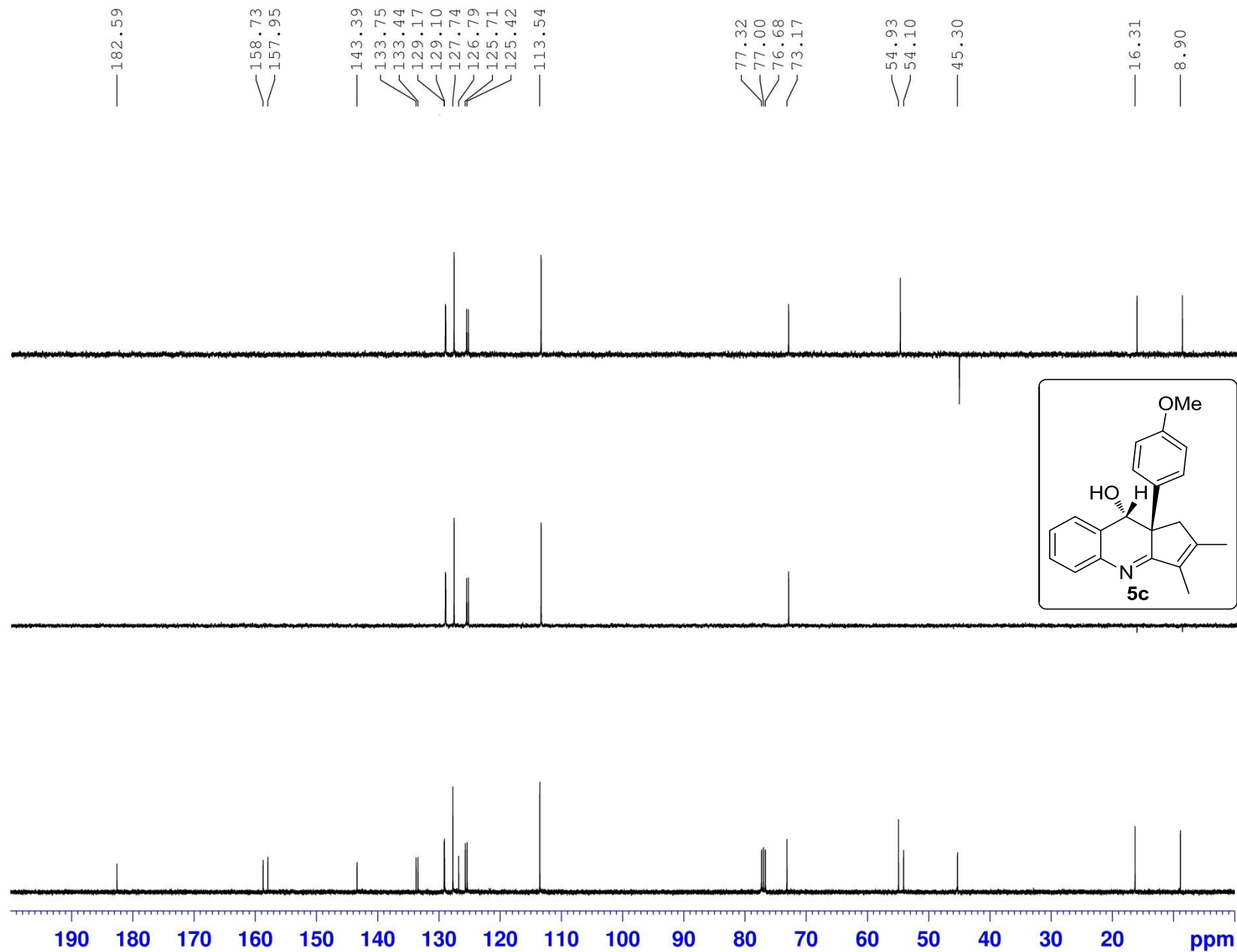


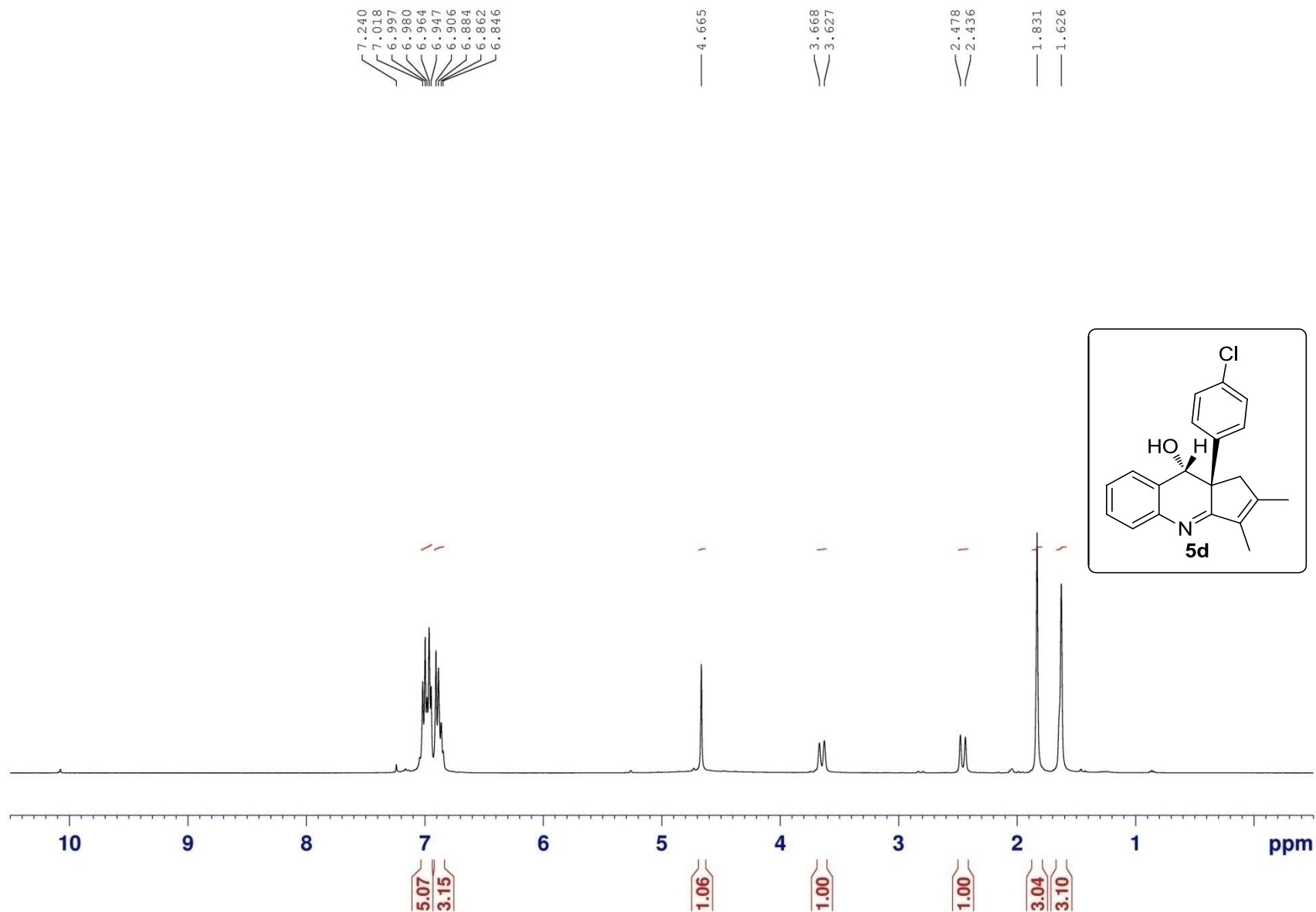


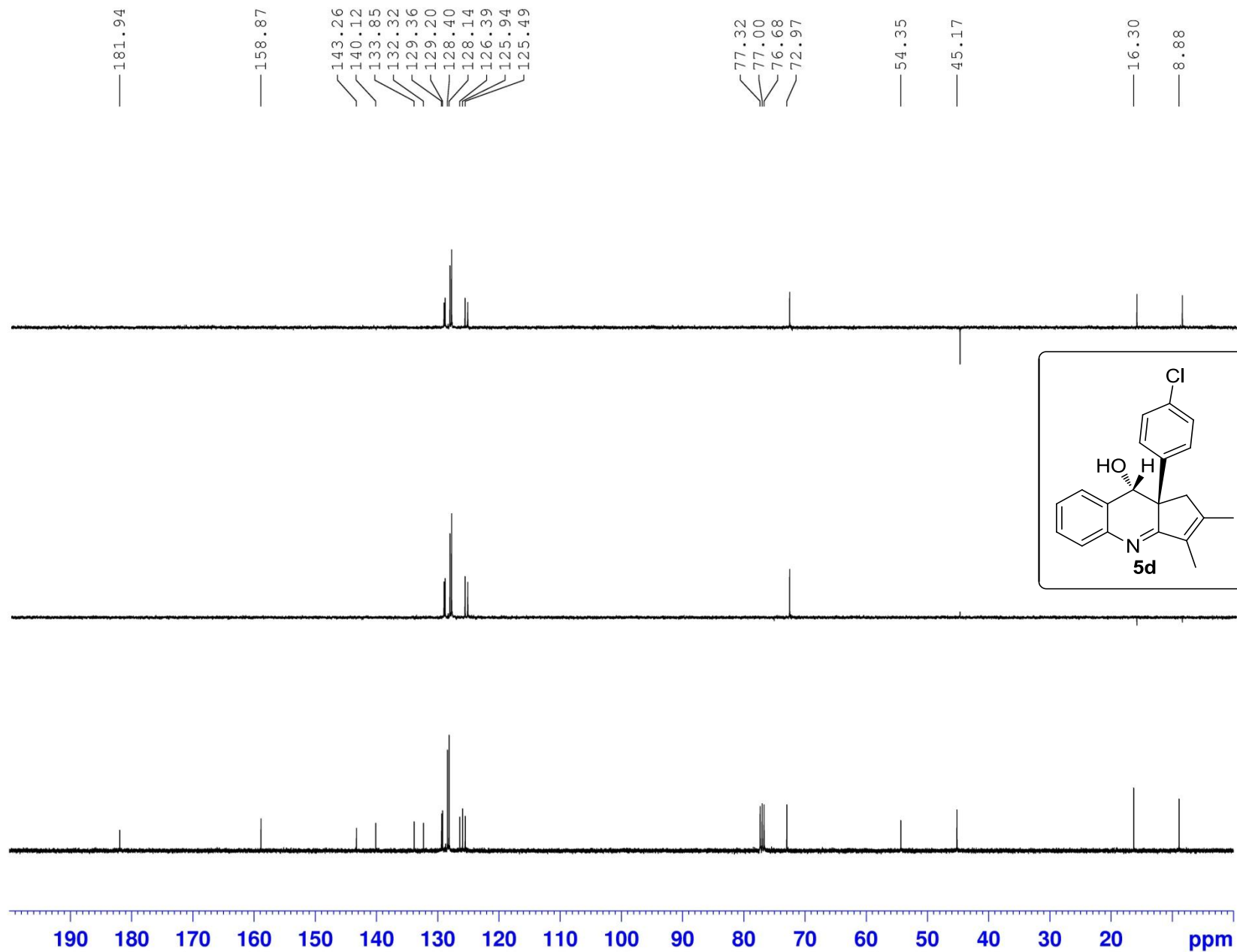


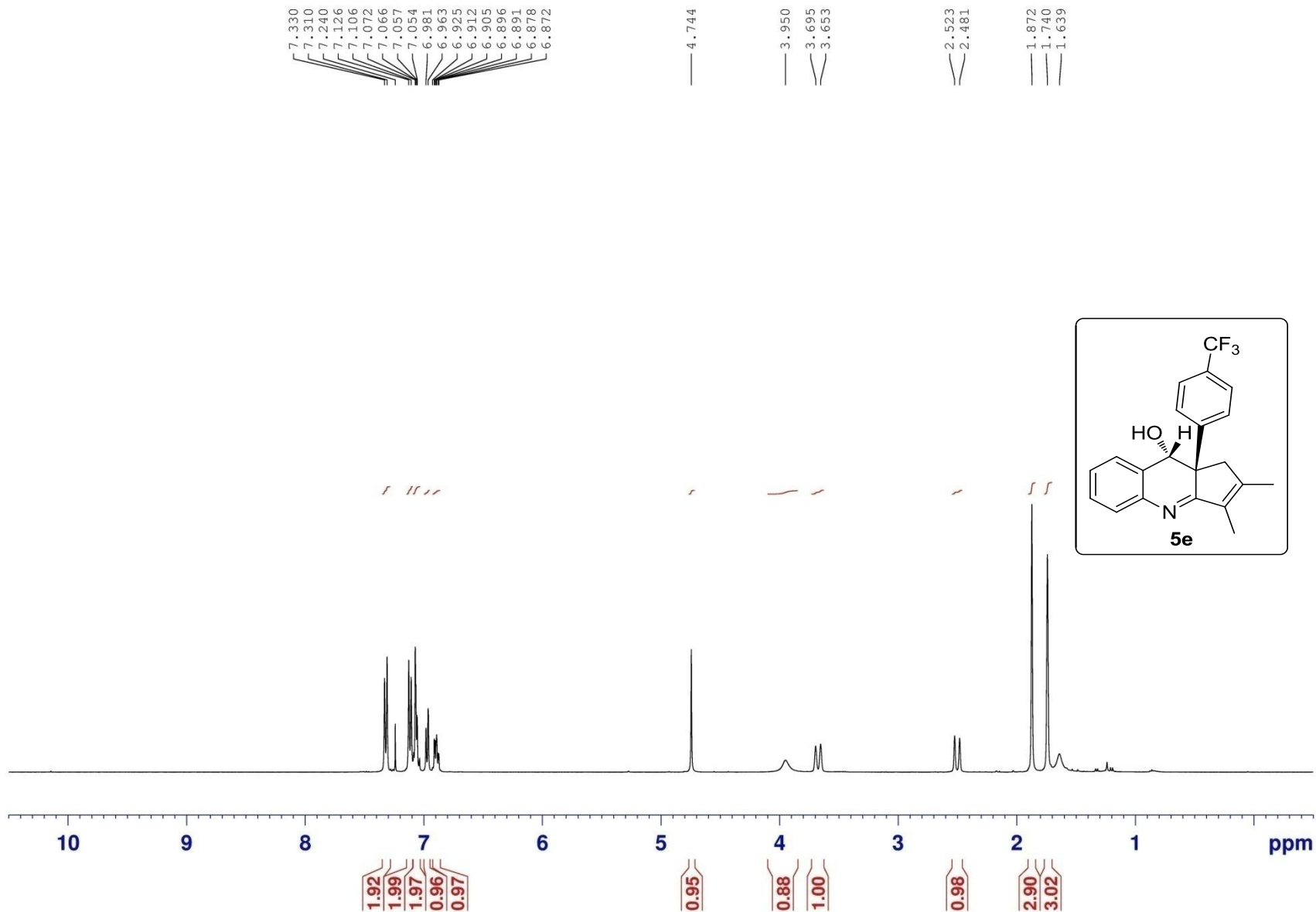


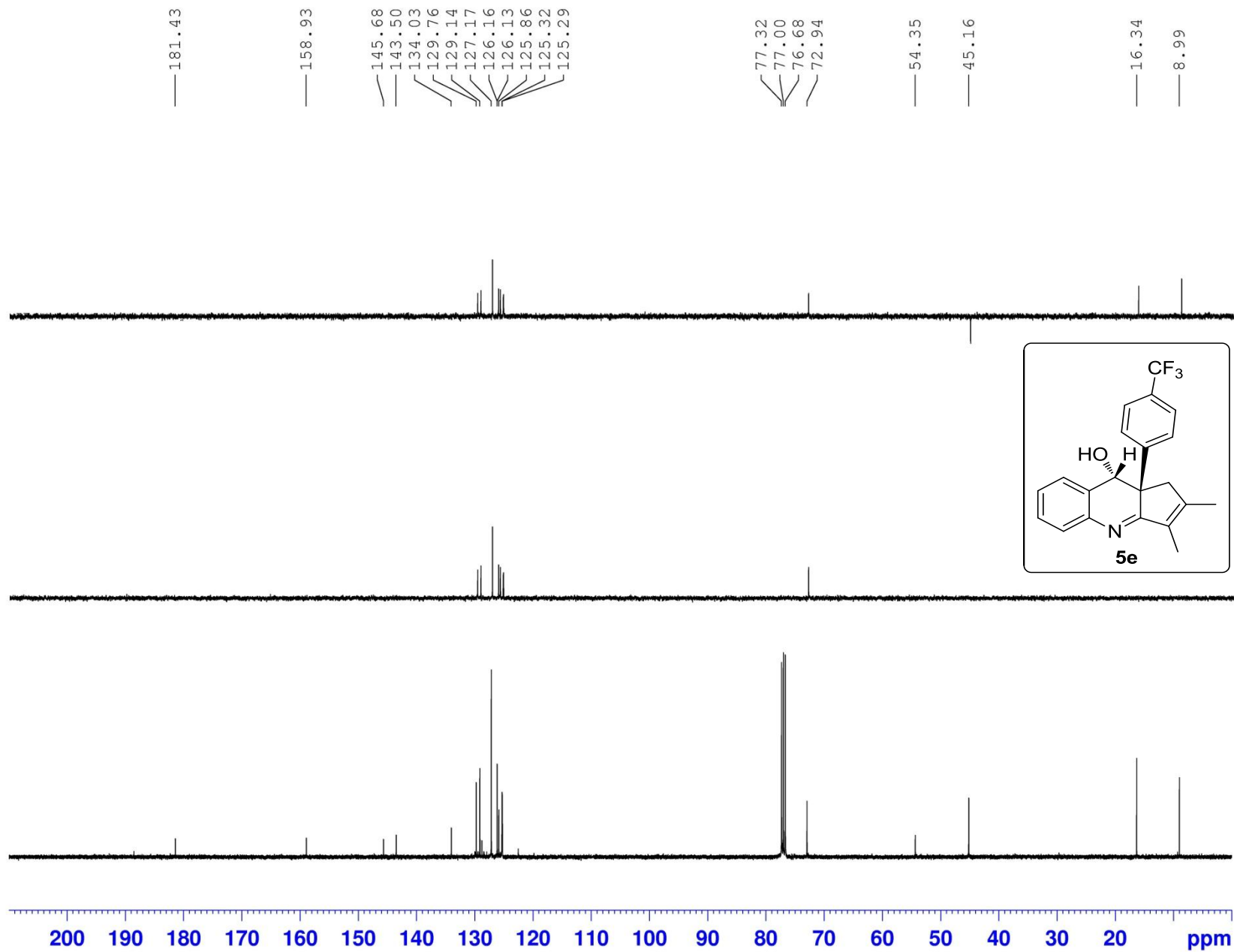












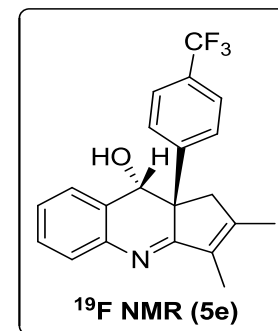
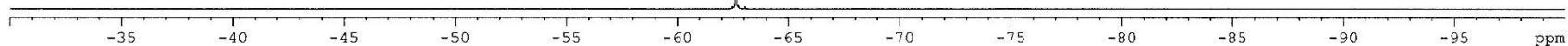
PDJ-C33

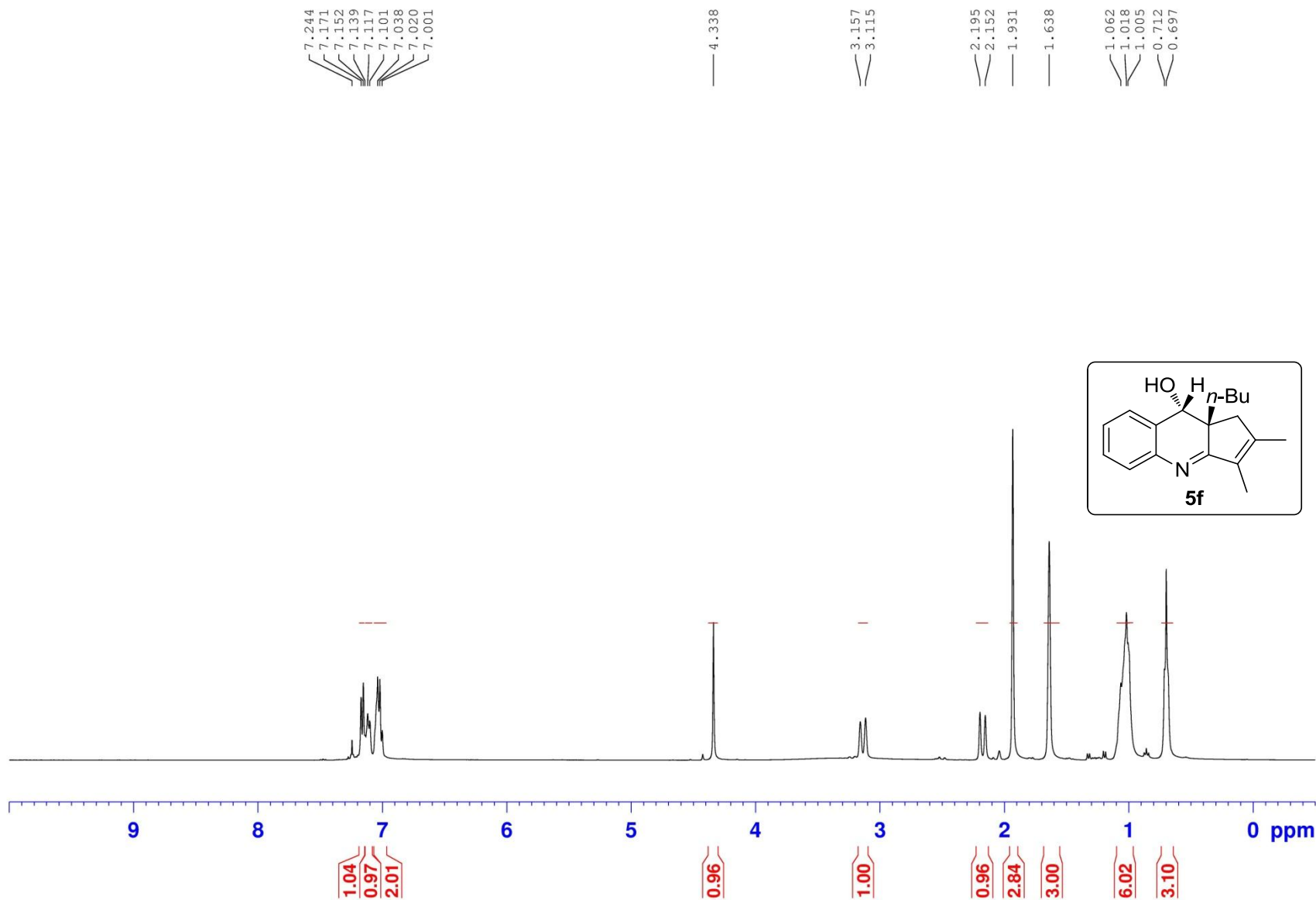
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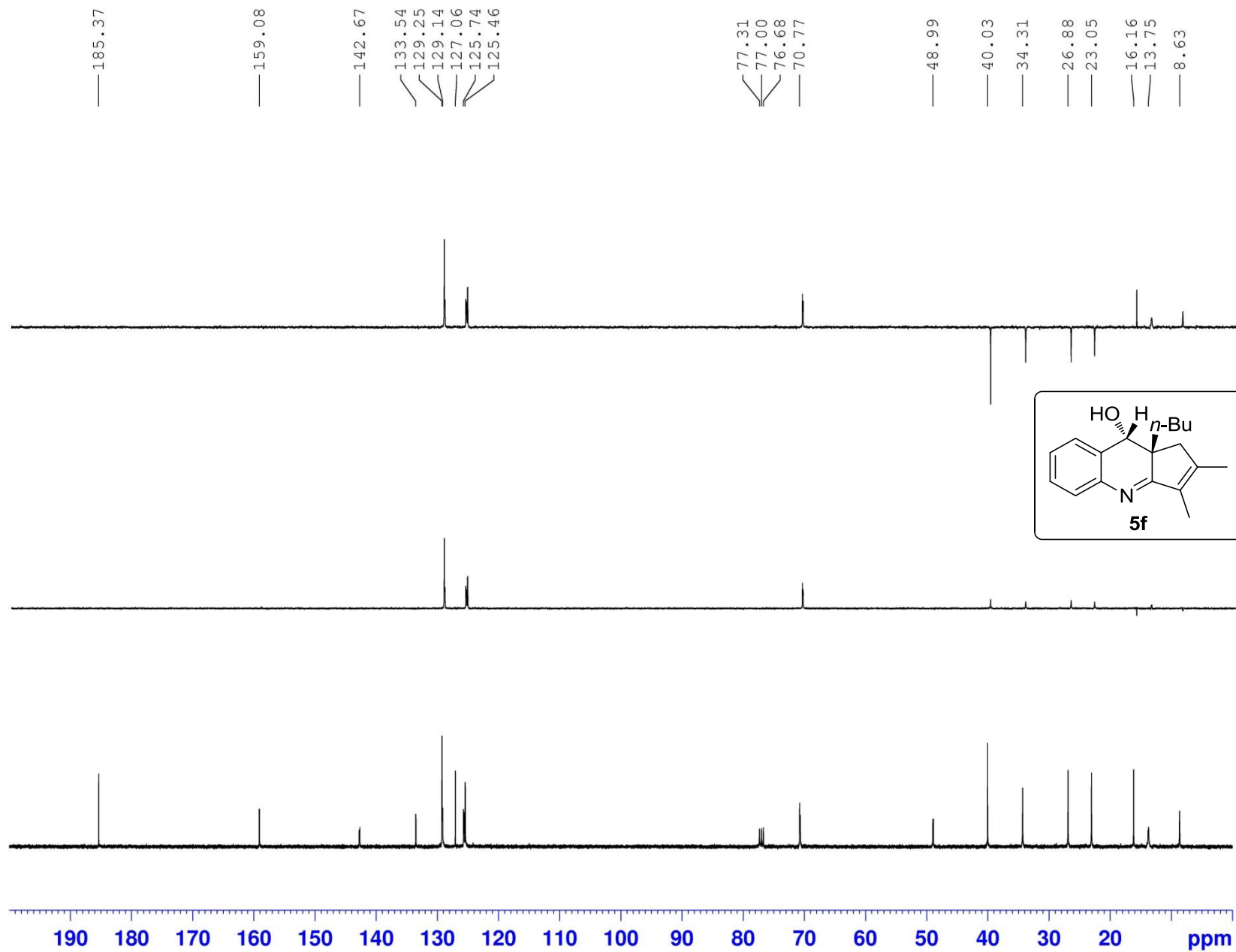
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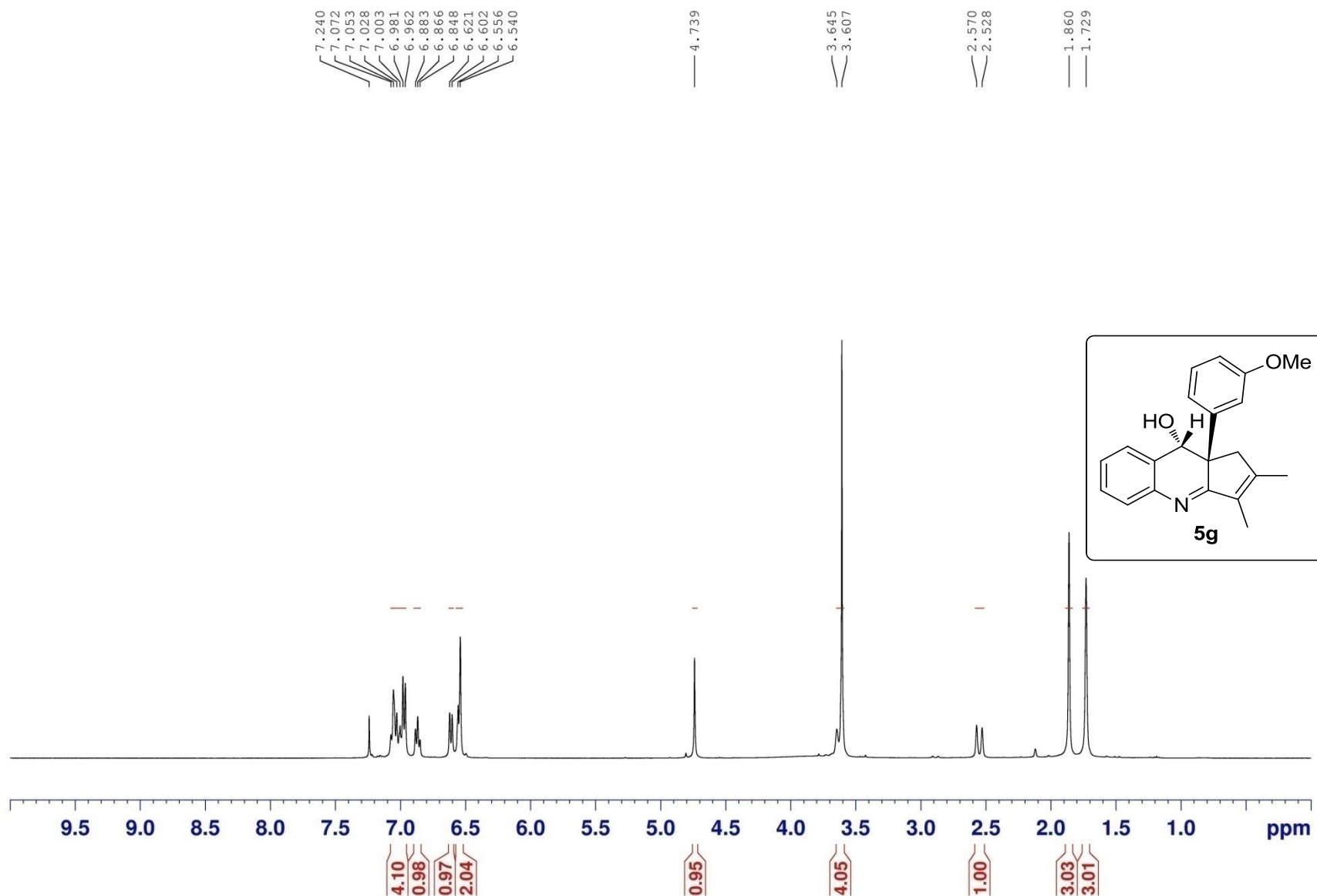
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PLW2 26.0000000 W
PLW12 0.40625000 W

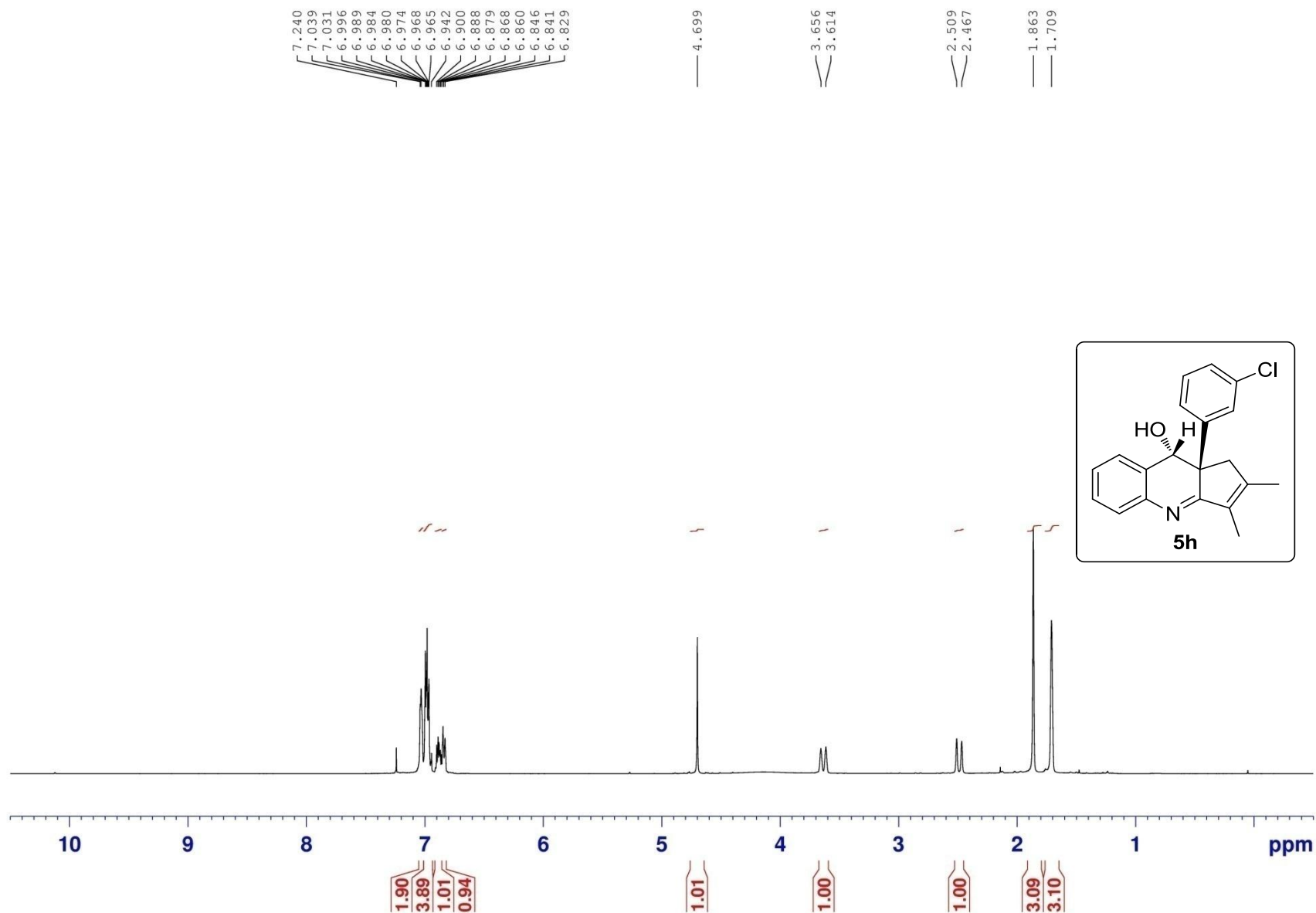
F2 - Processing parameters
SI 65536
SF 470.6206054 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

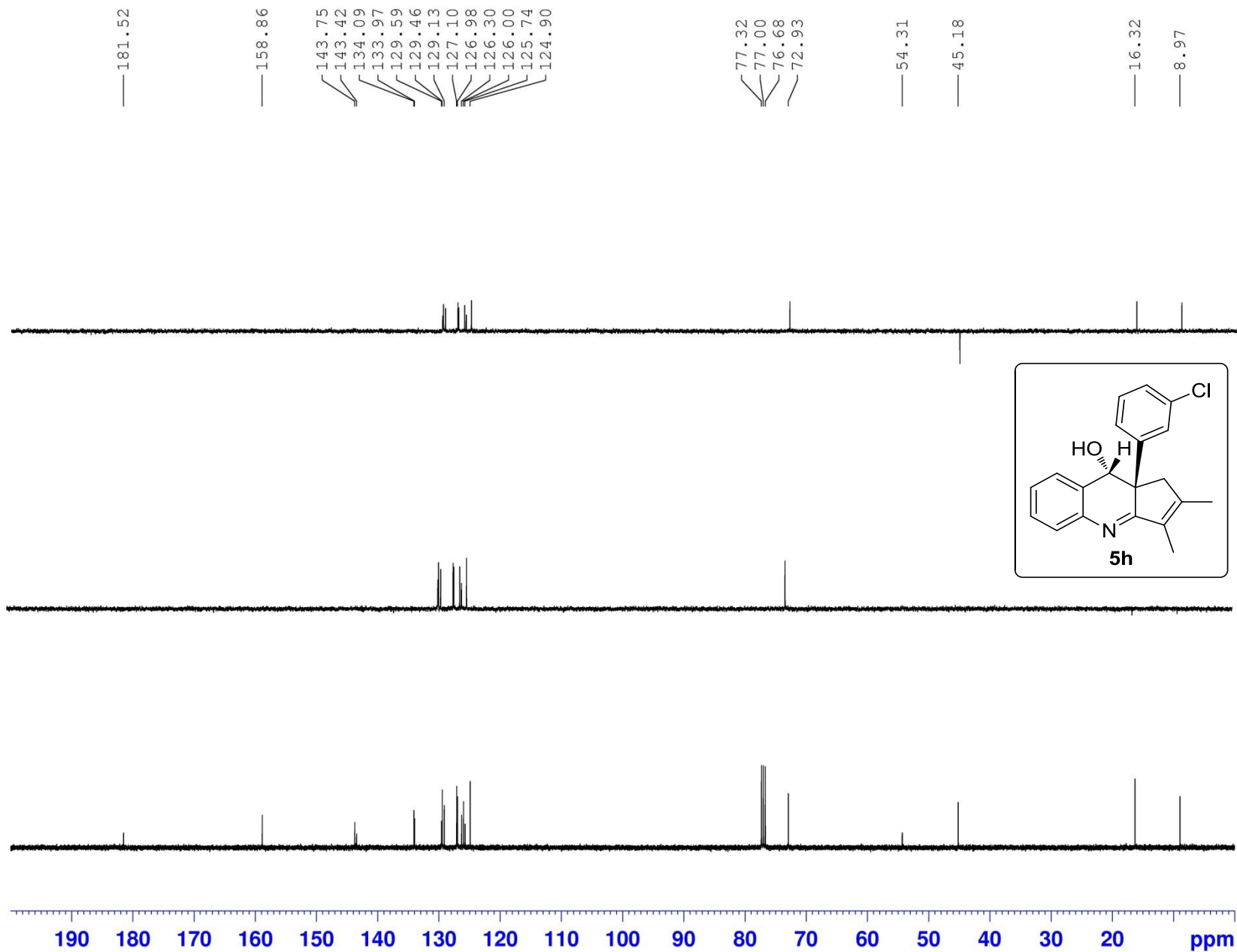


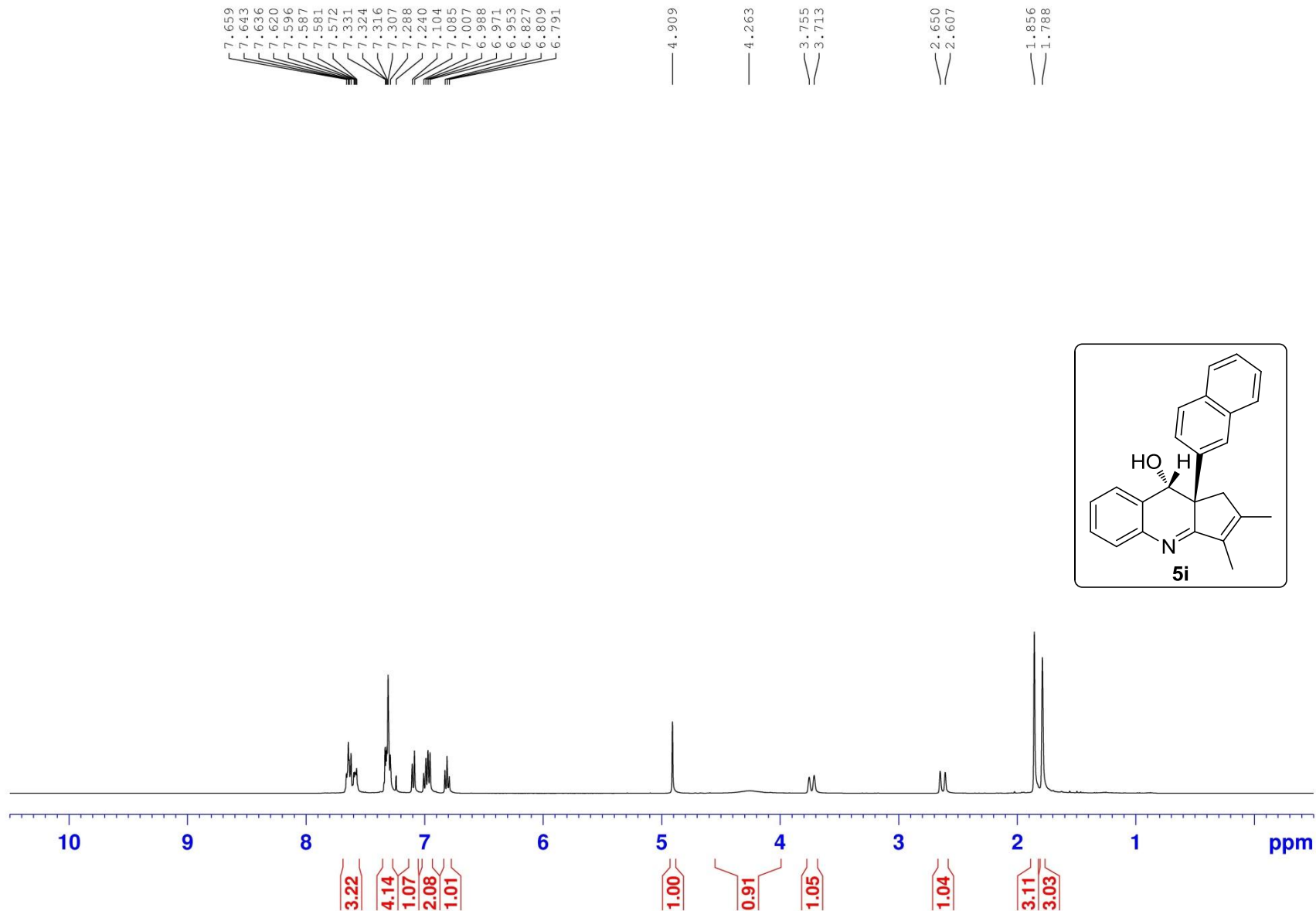


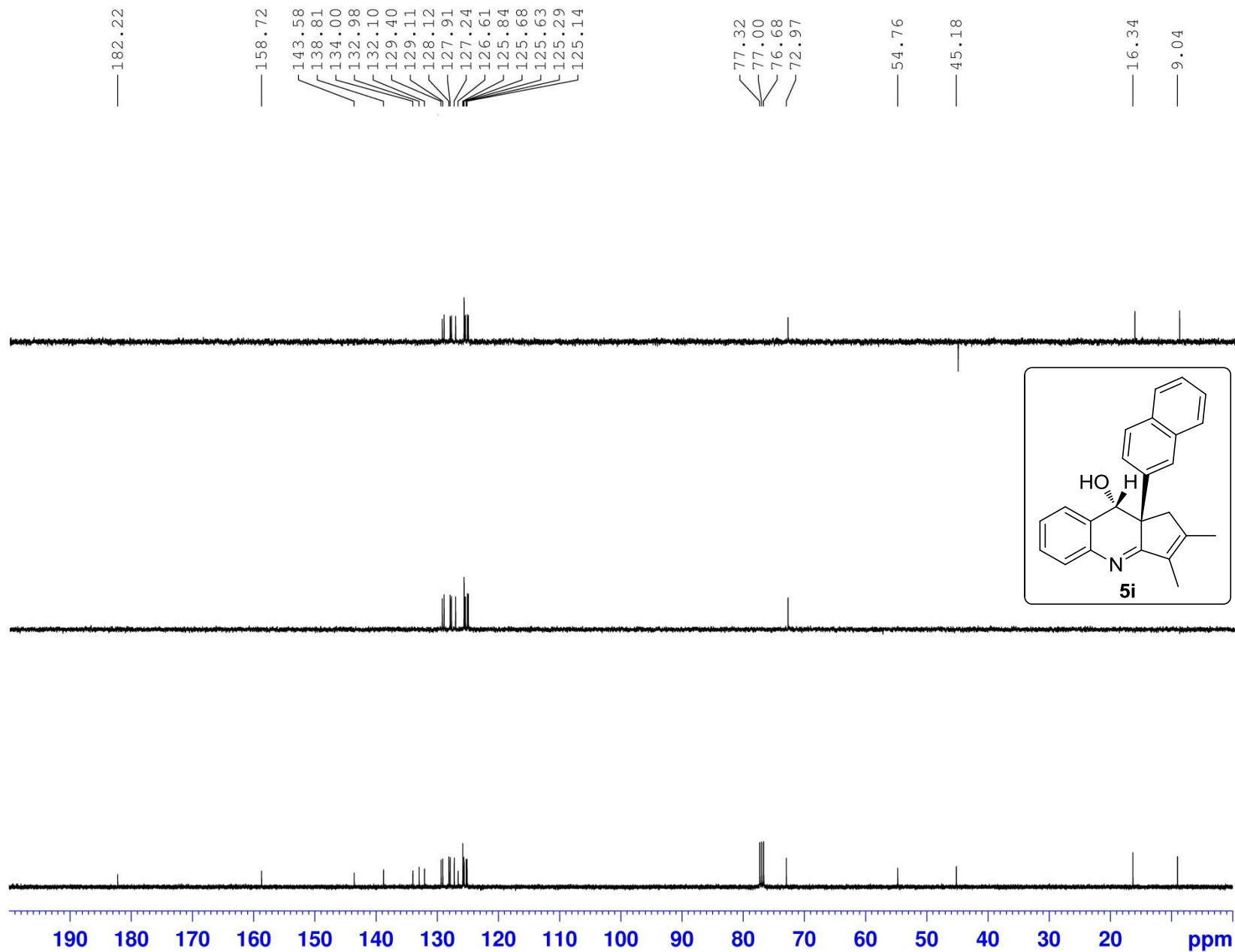


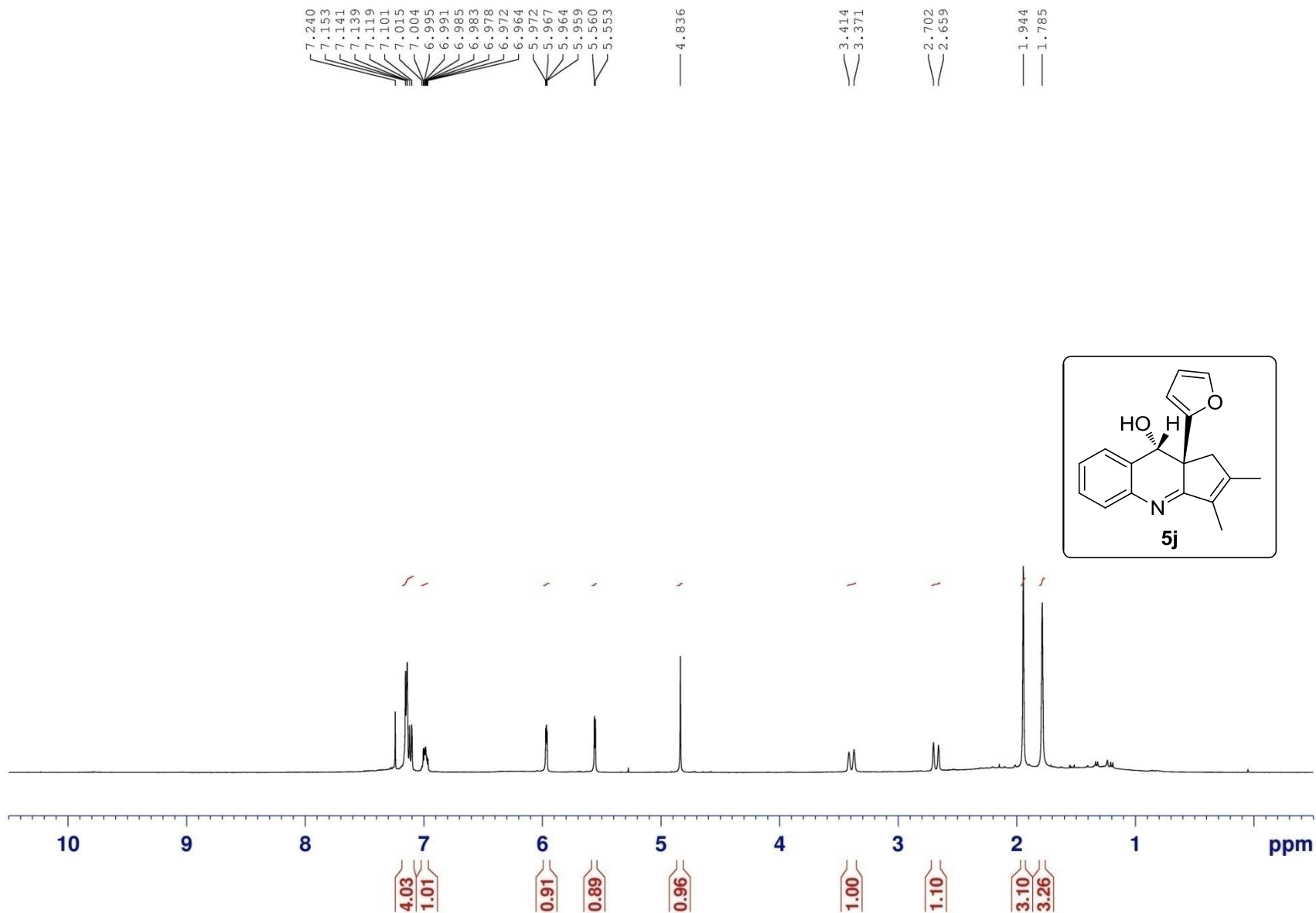


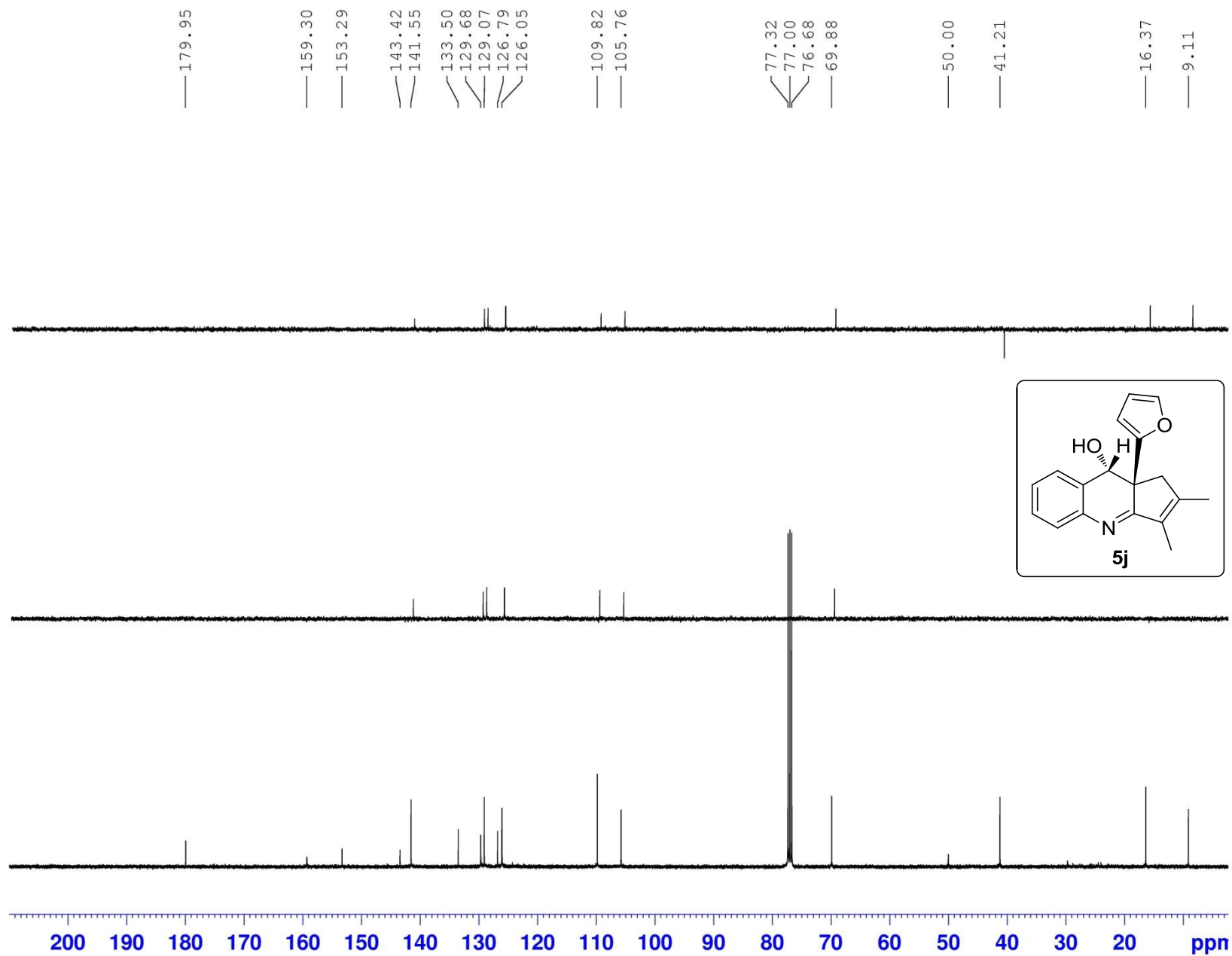


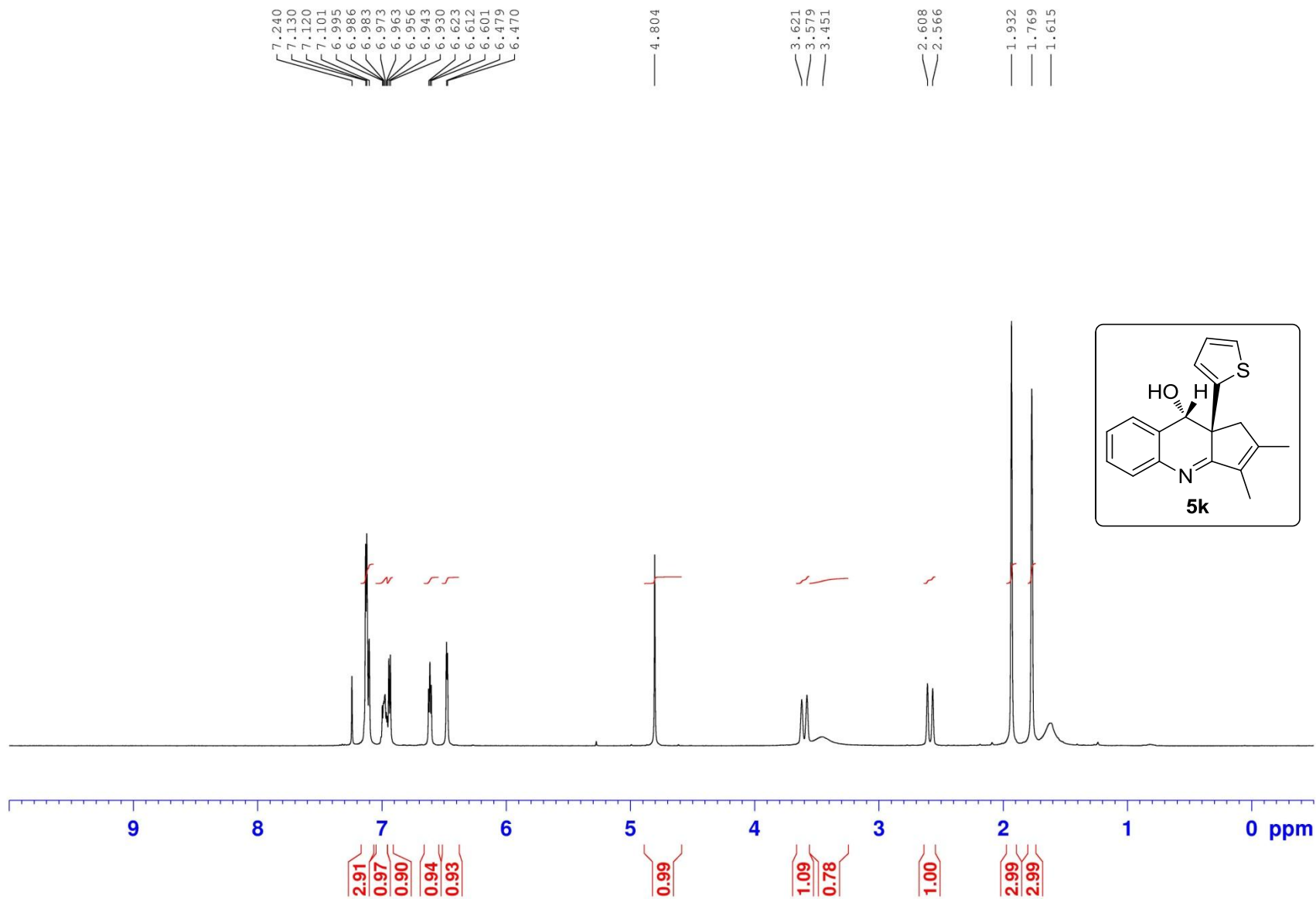


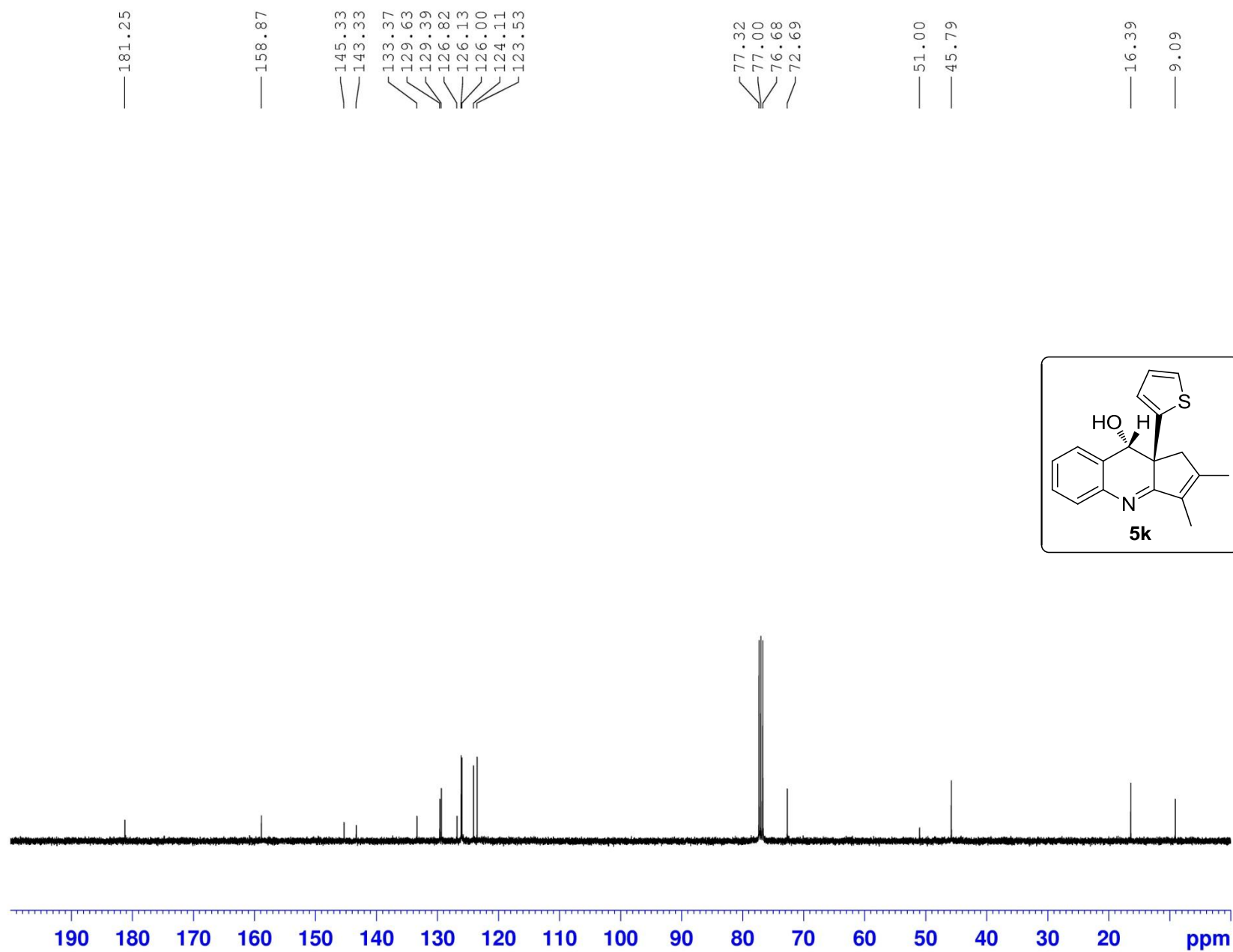


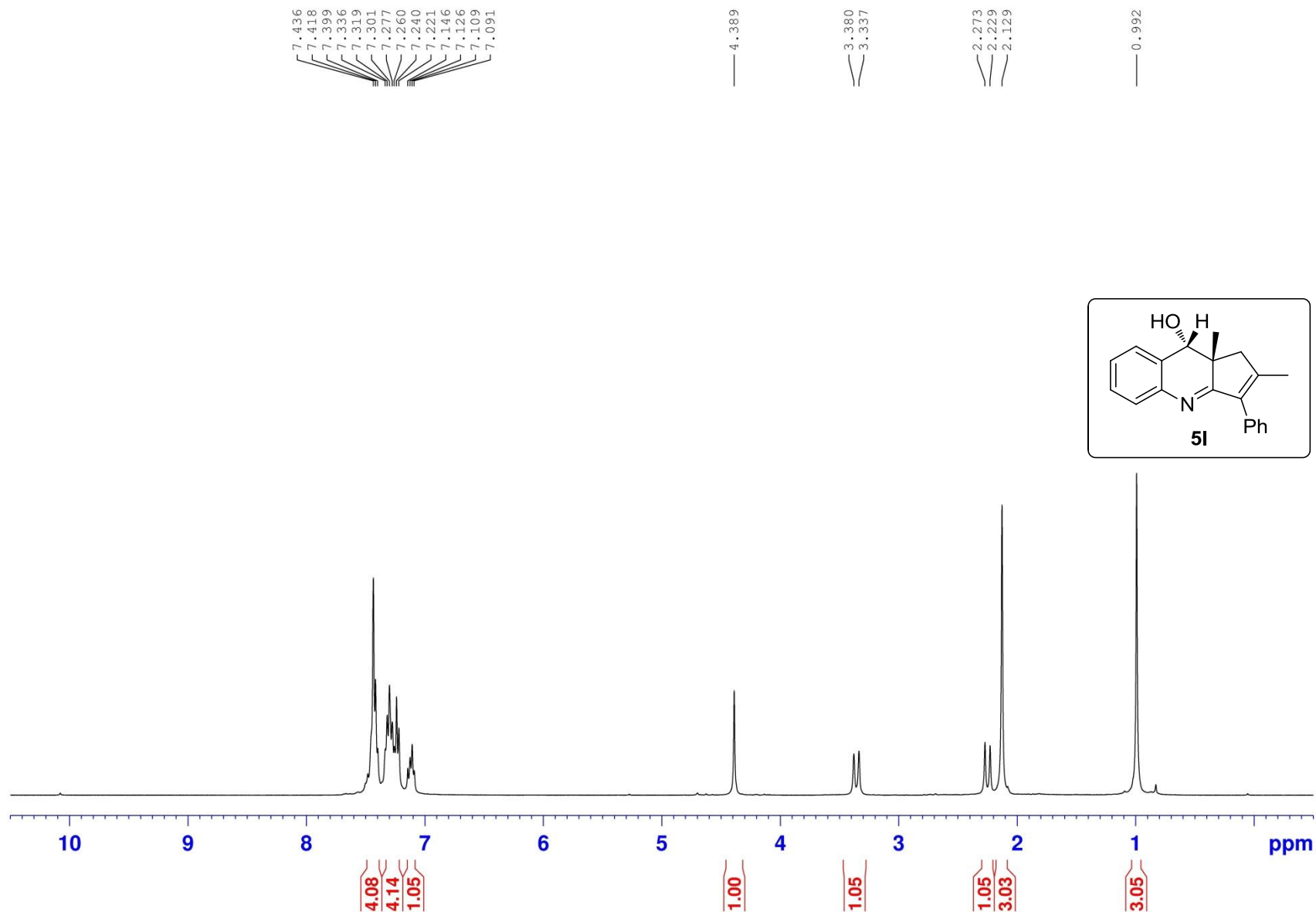


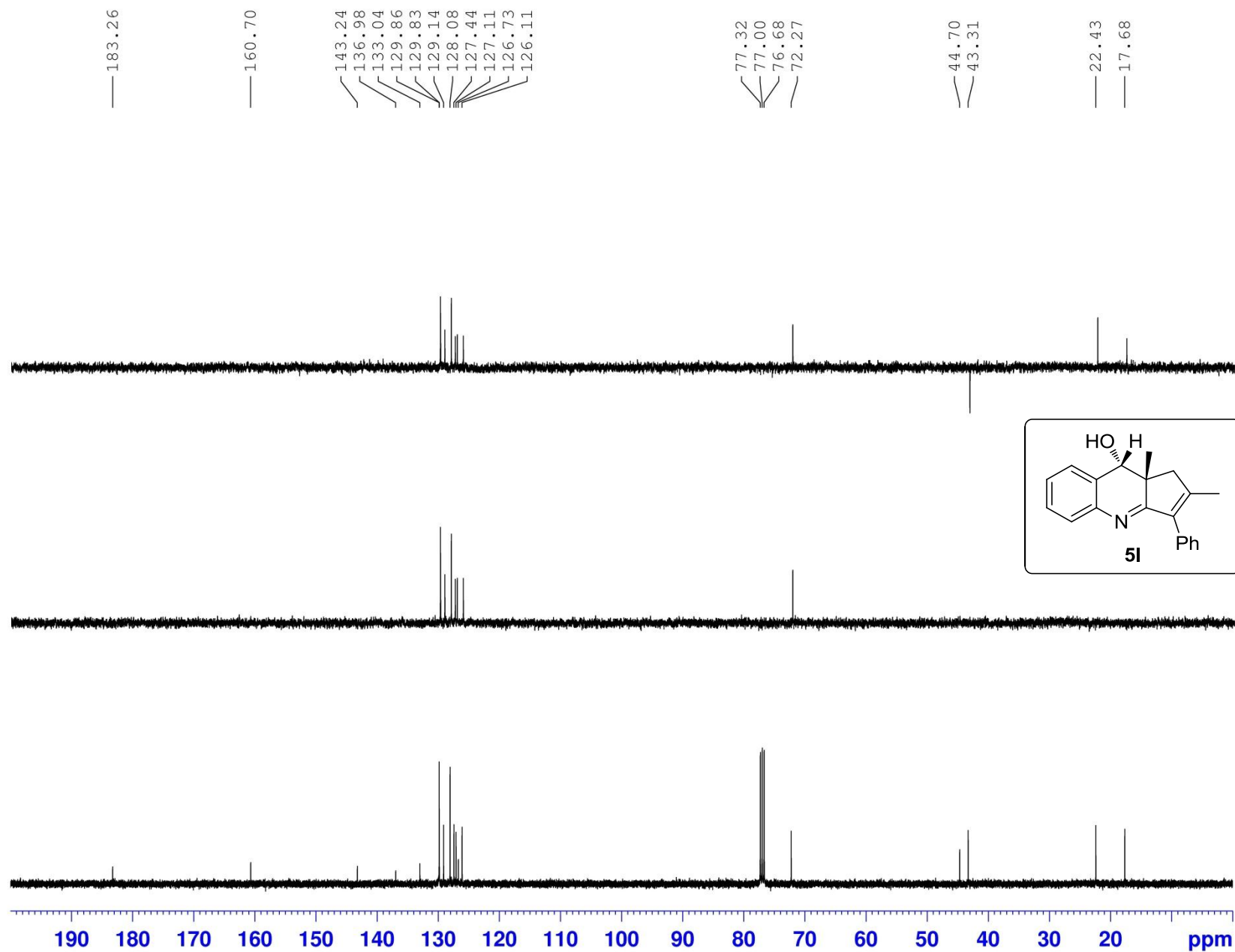


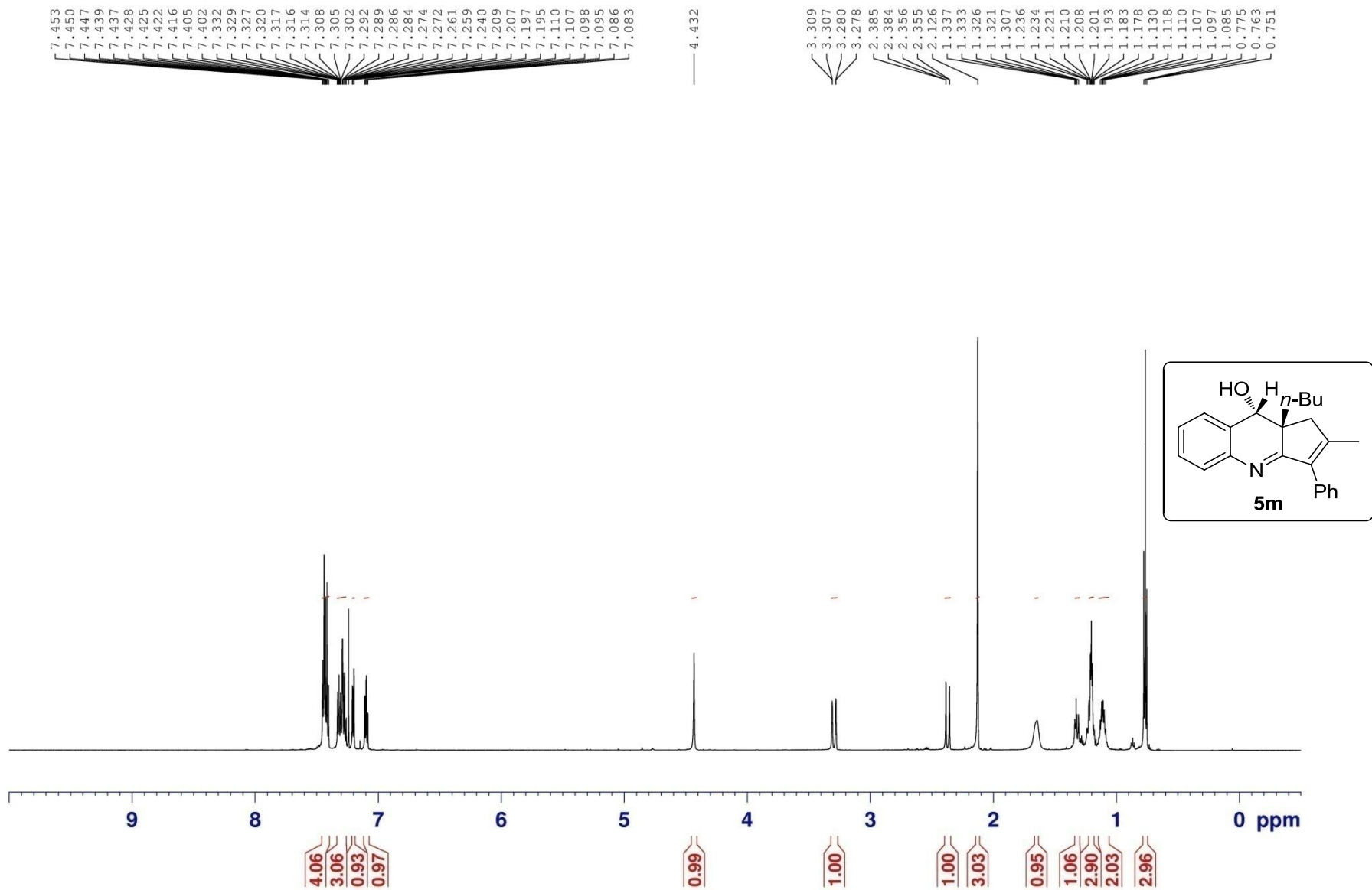


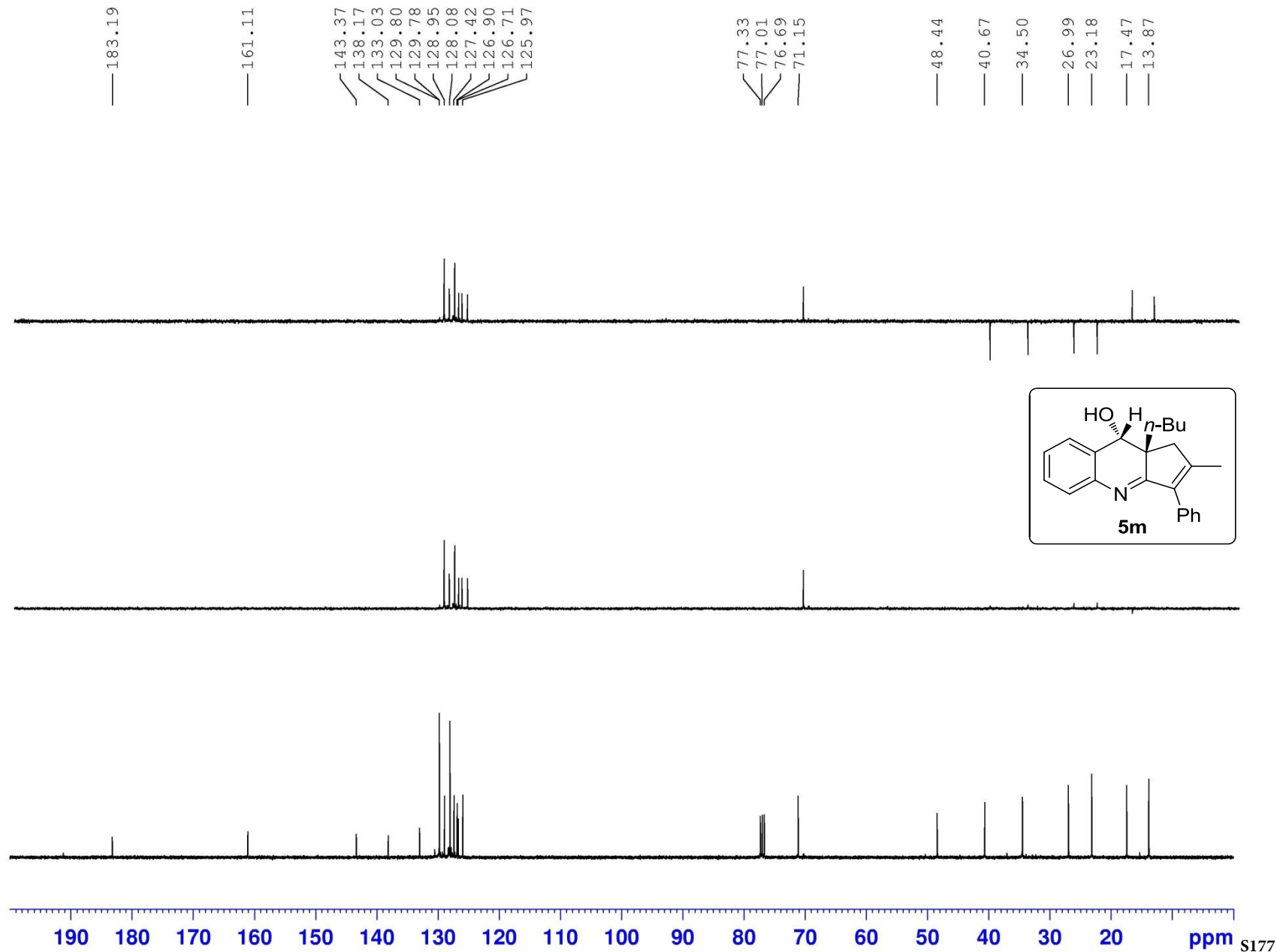


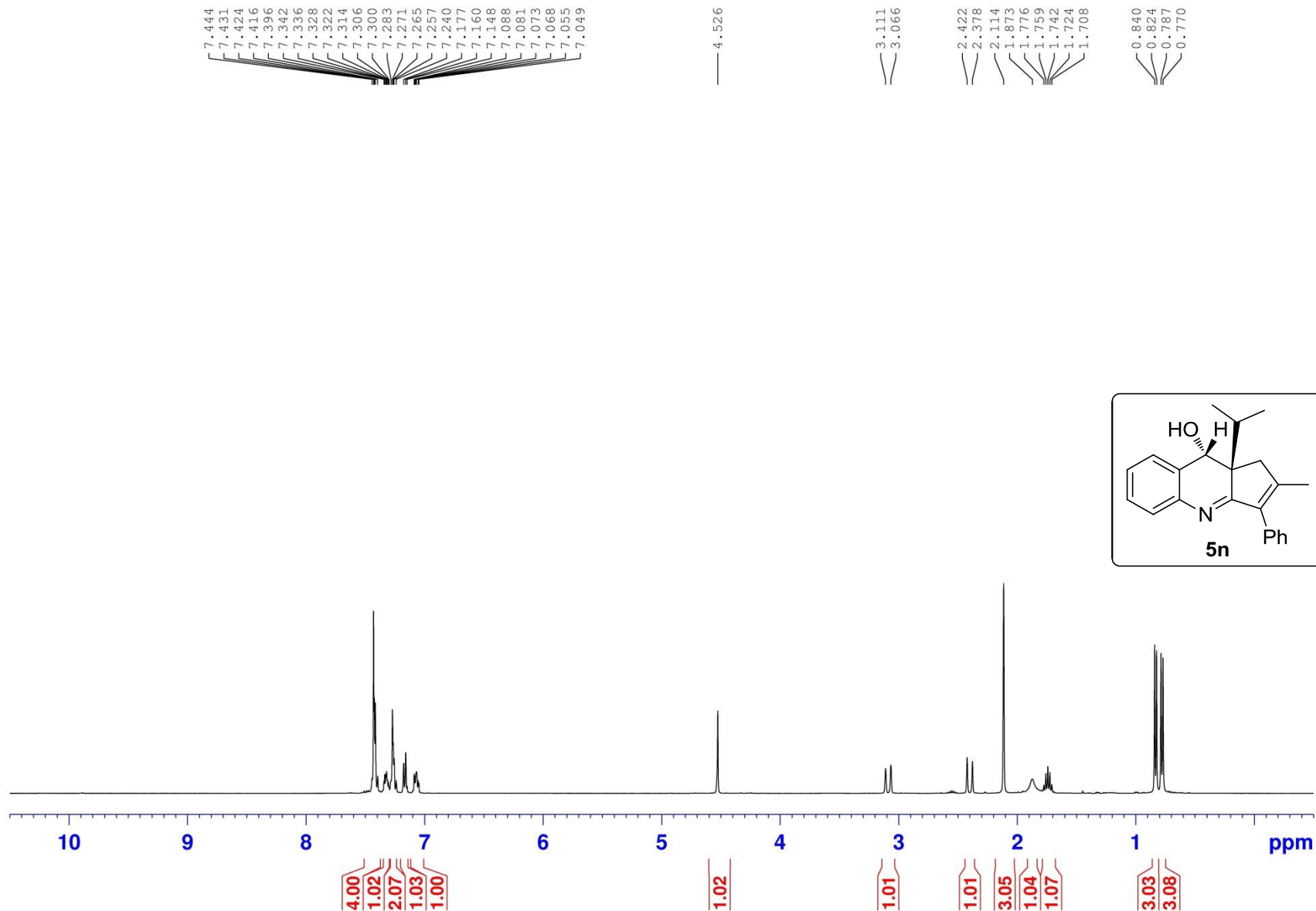


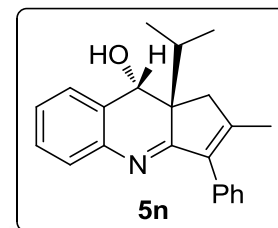
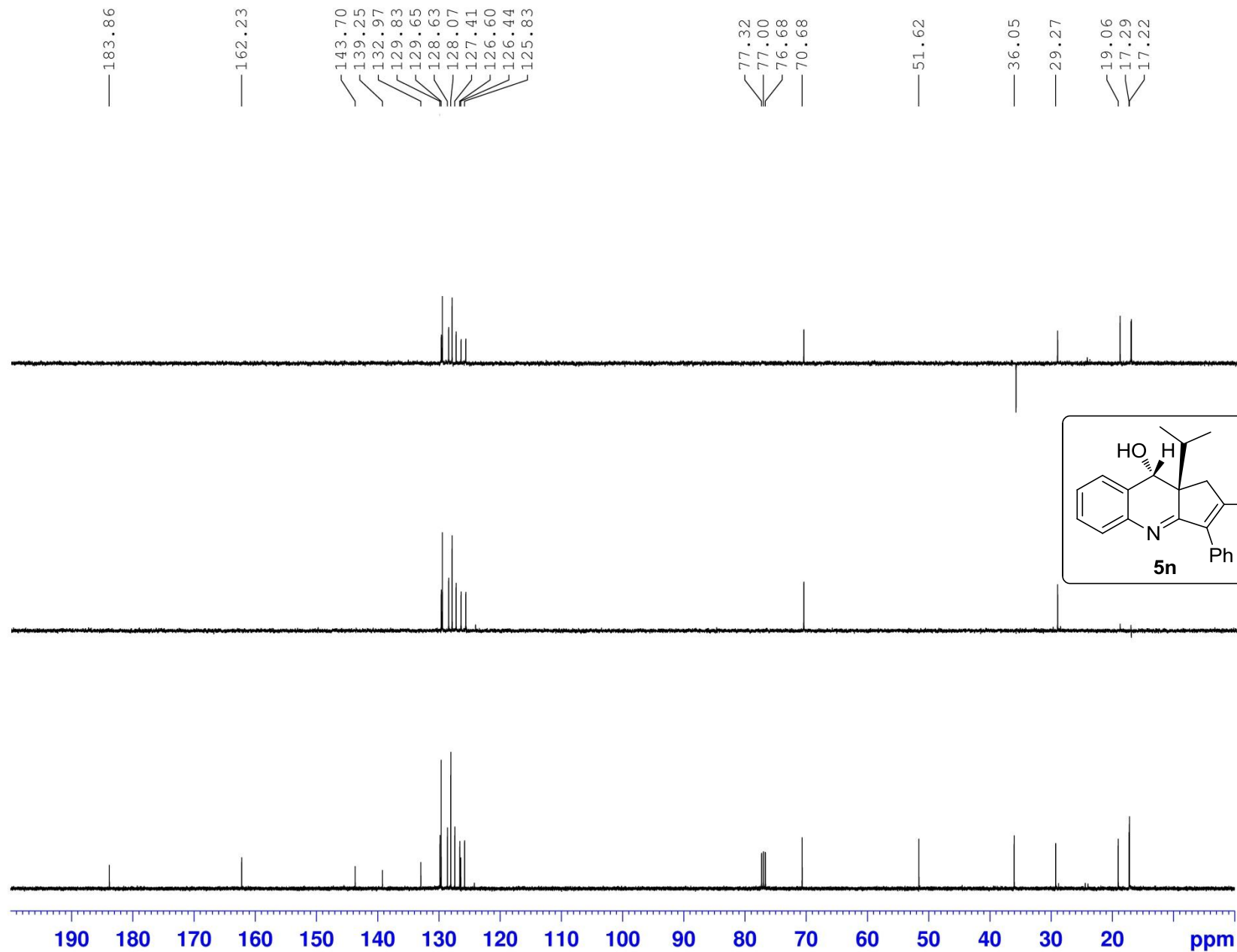


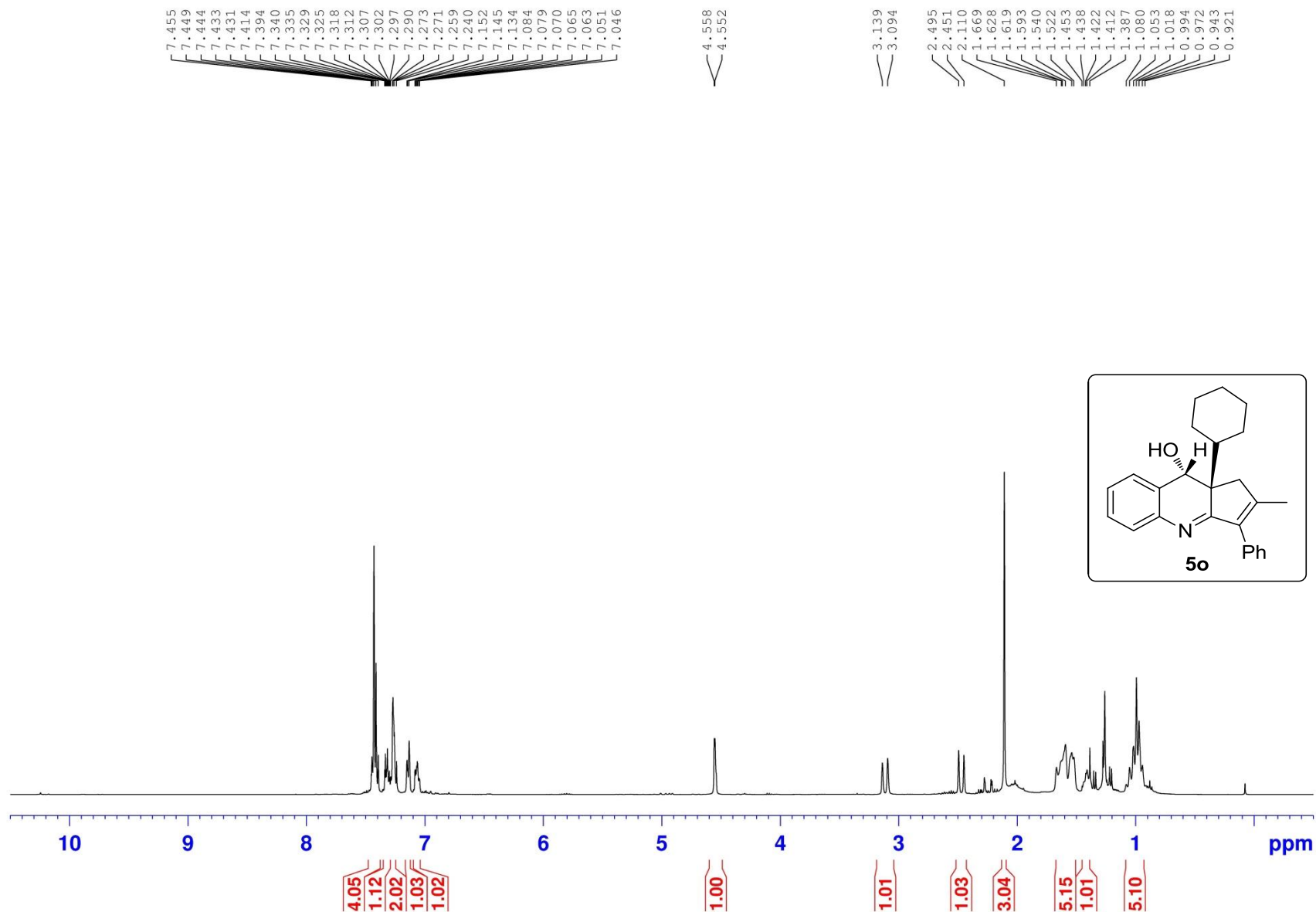


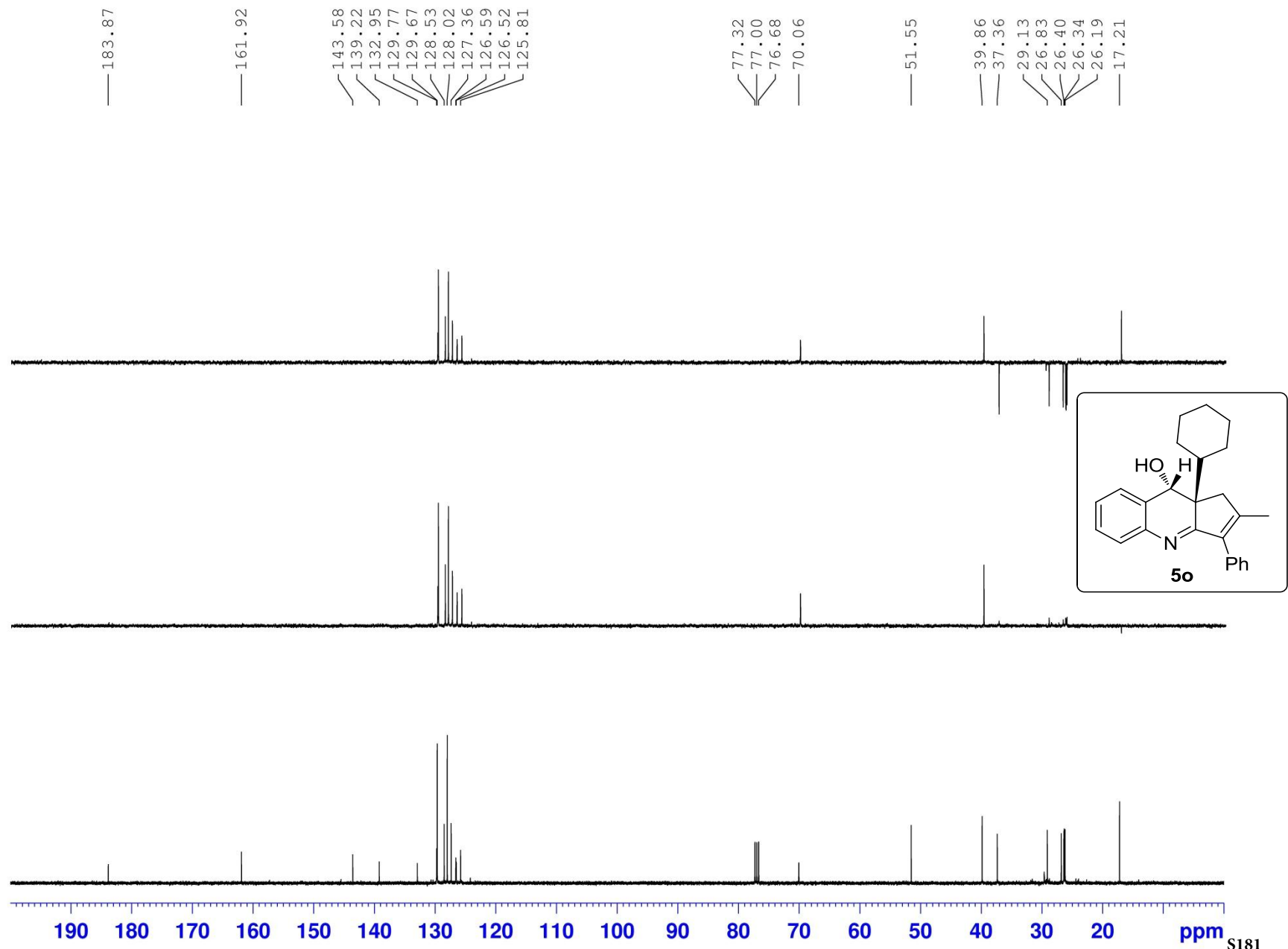


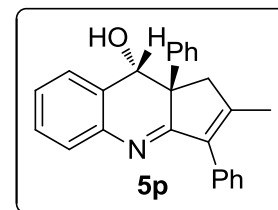
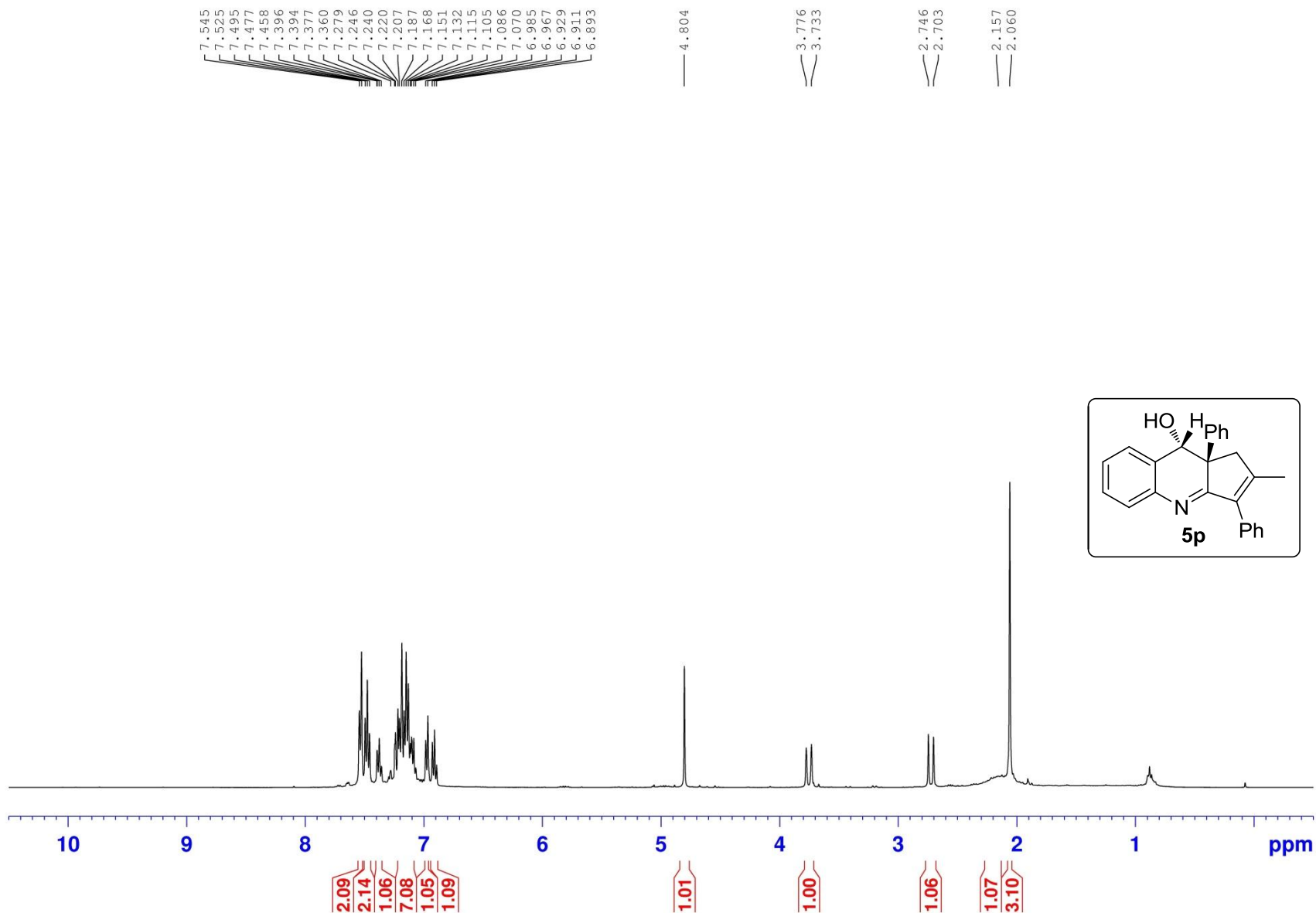


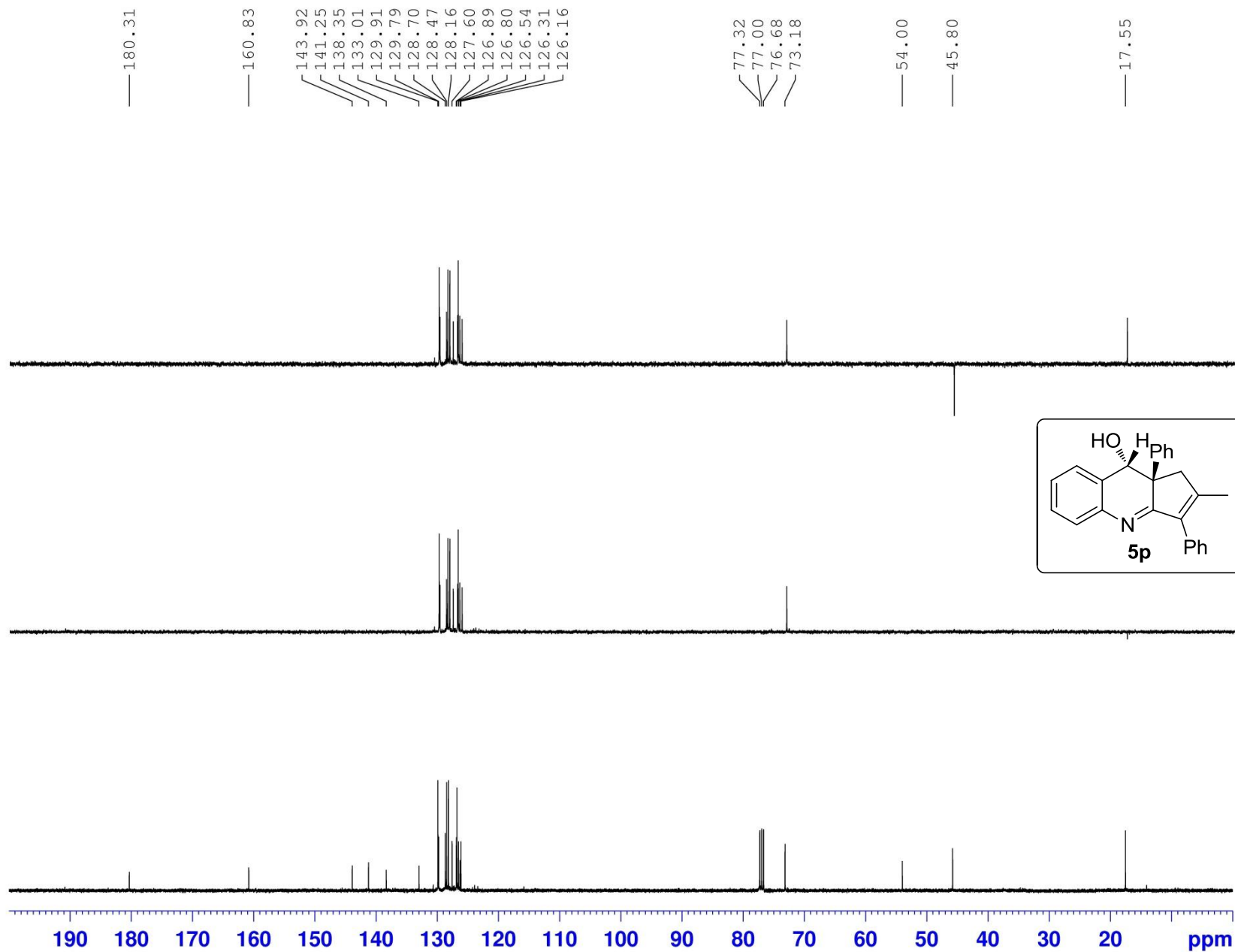


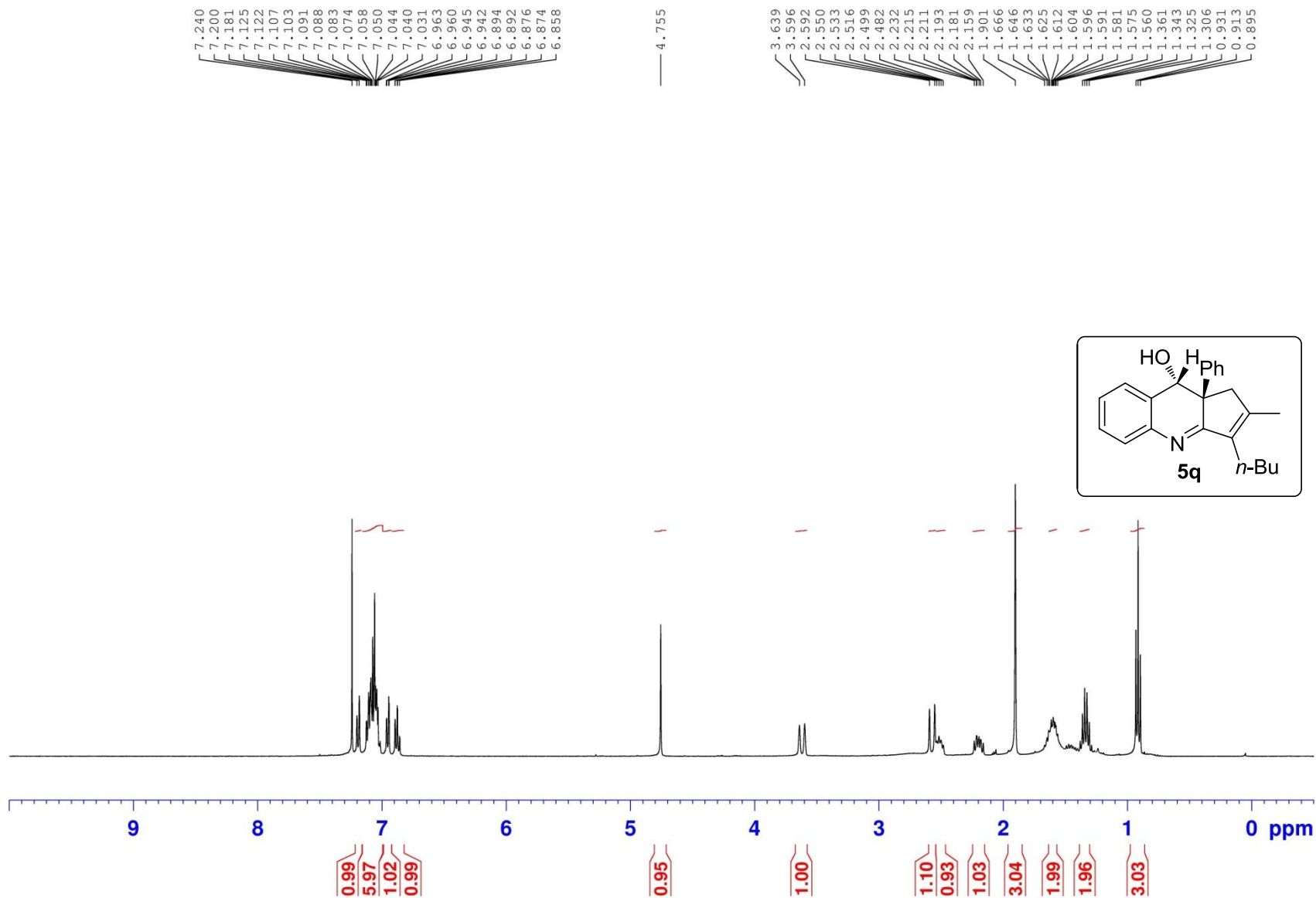


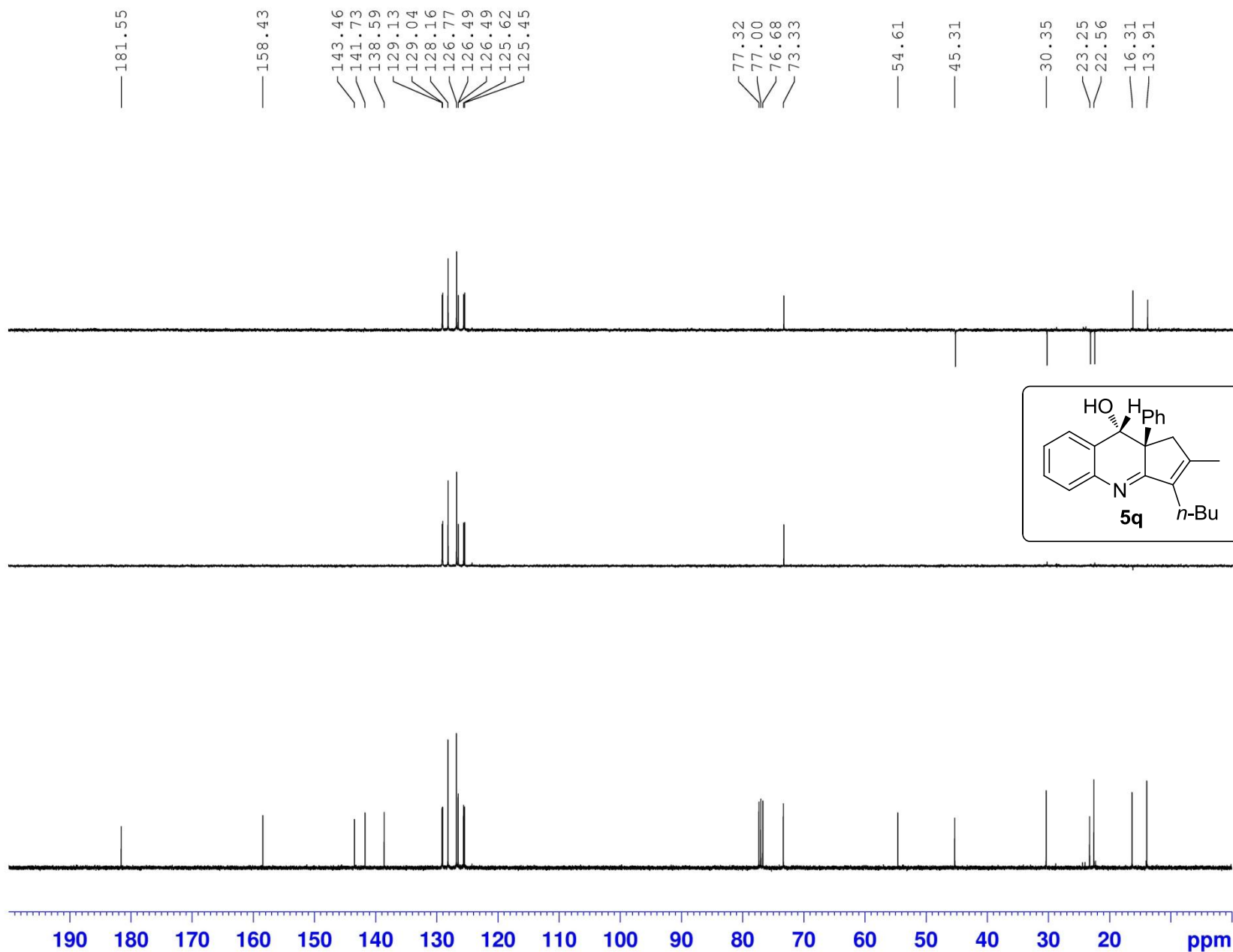


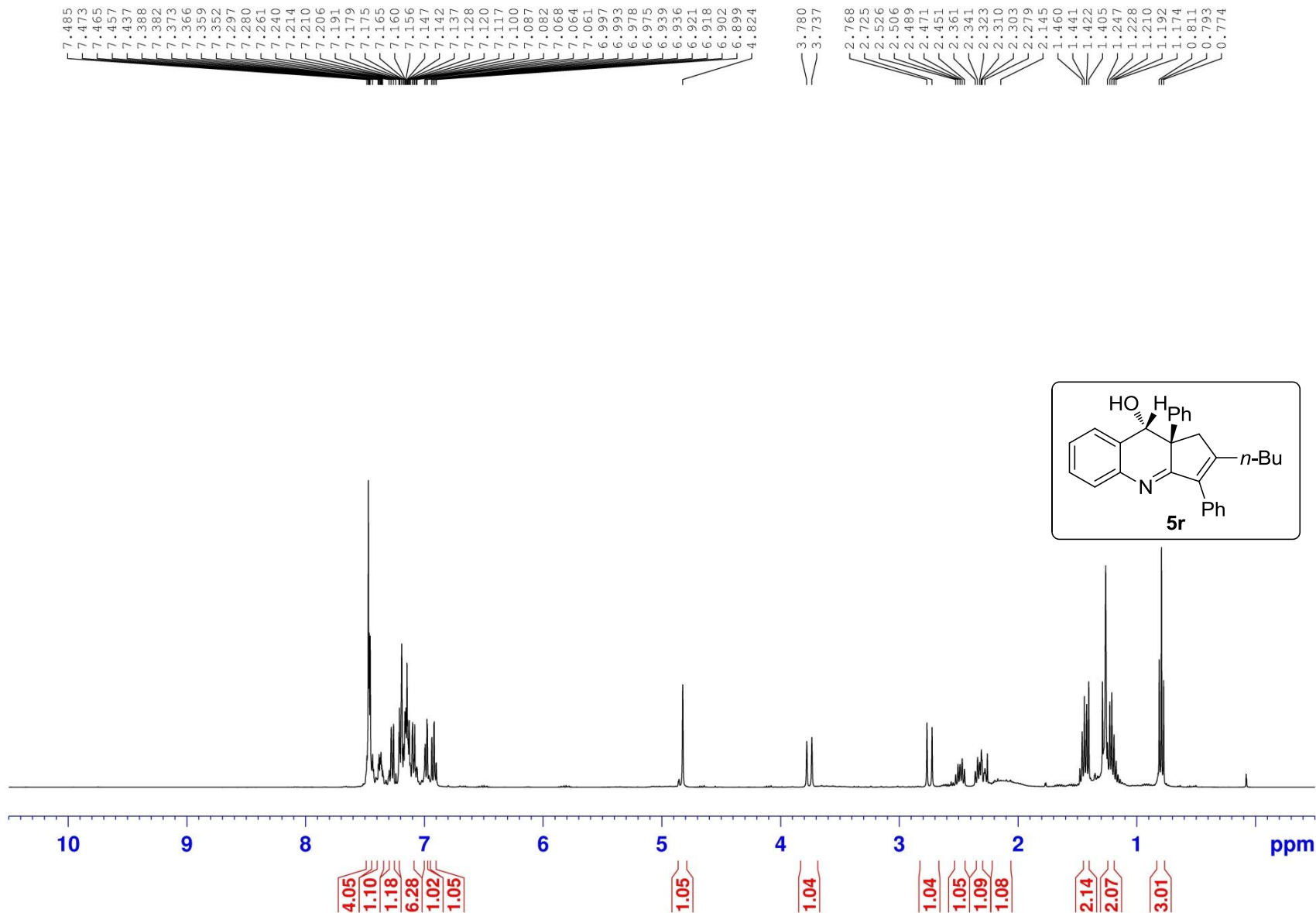


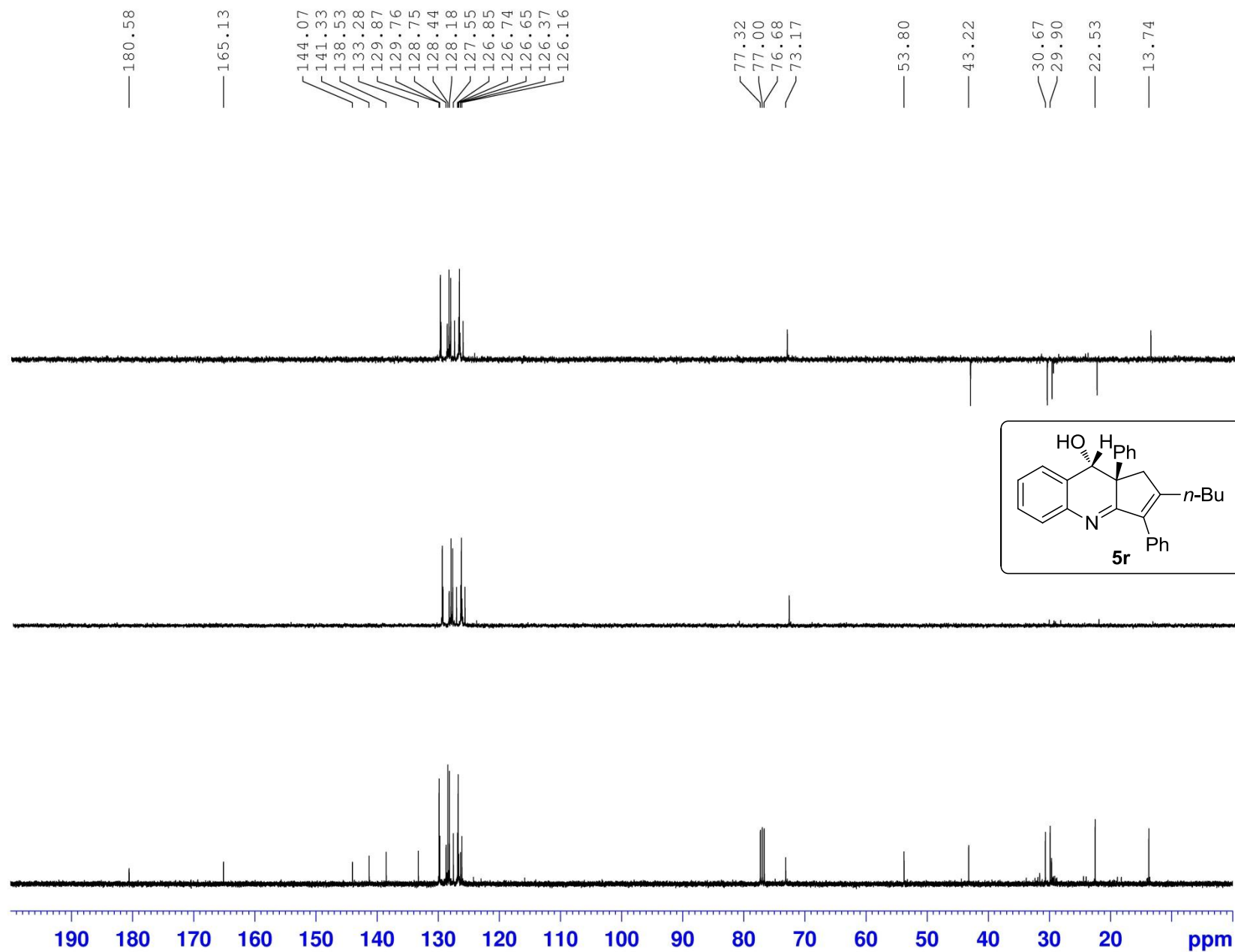


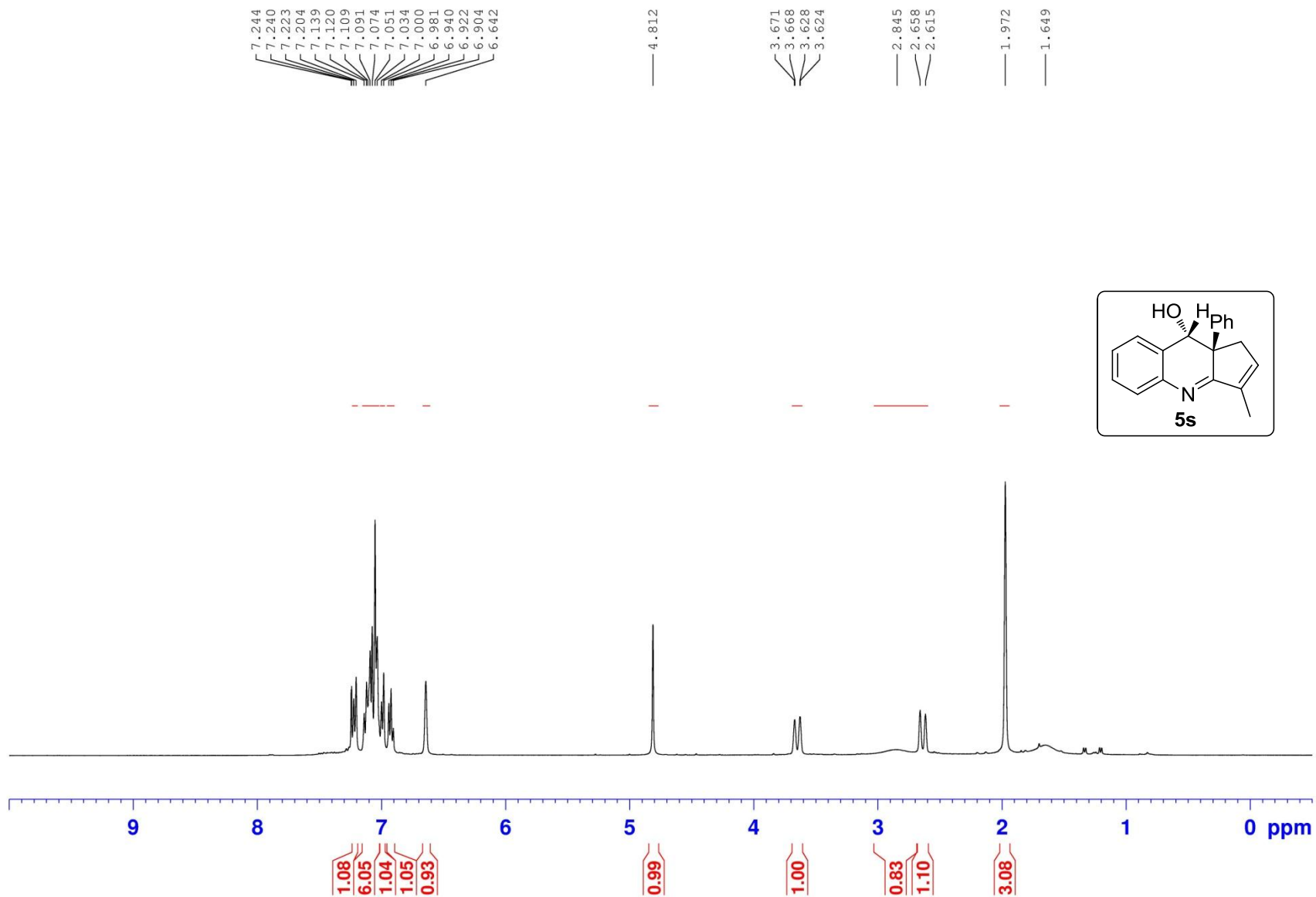


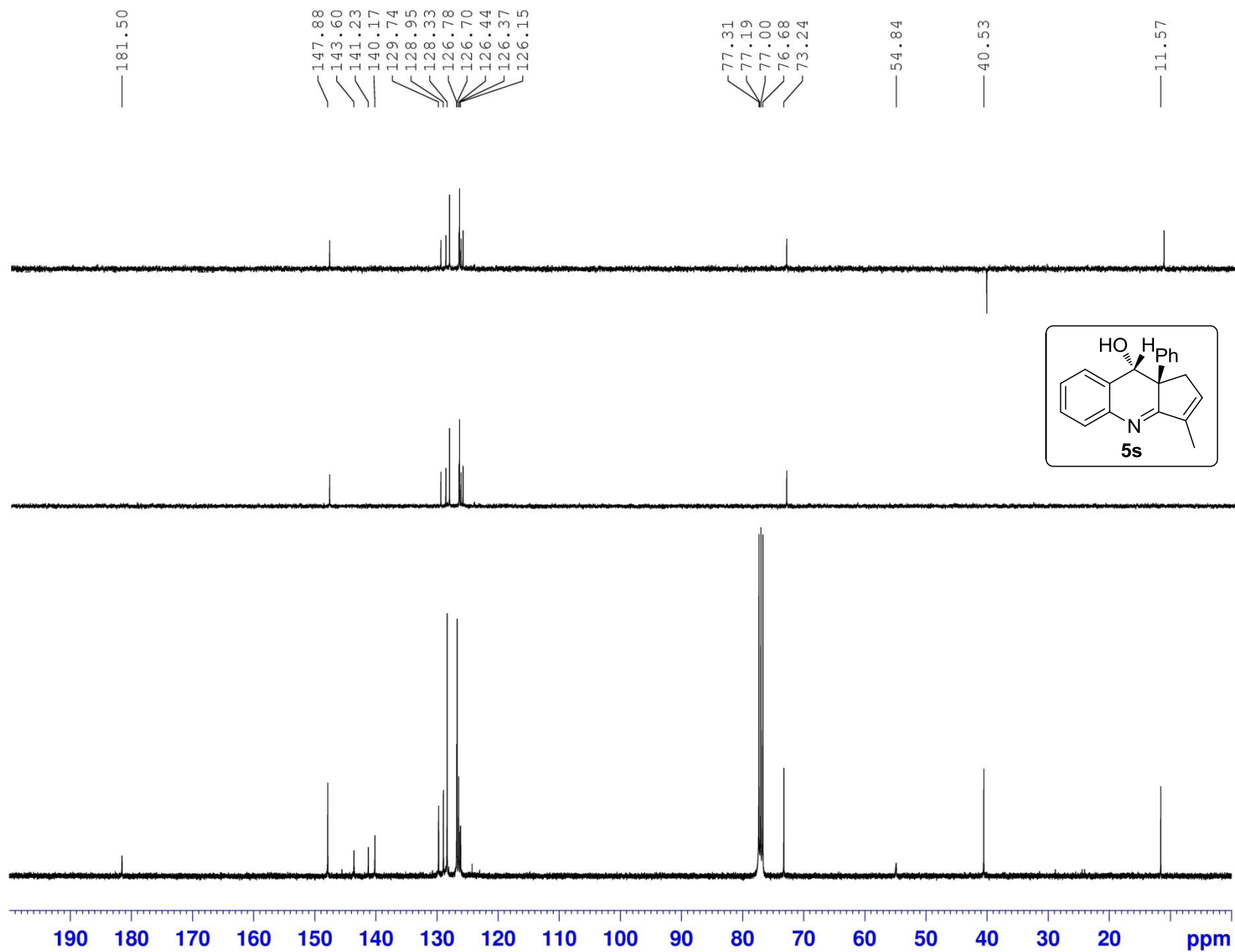


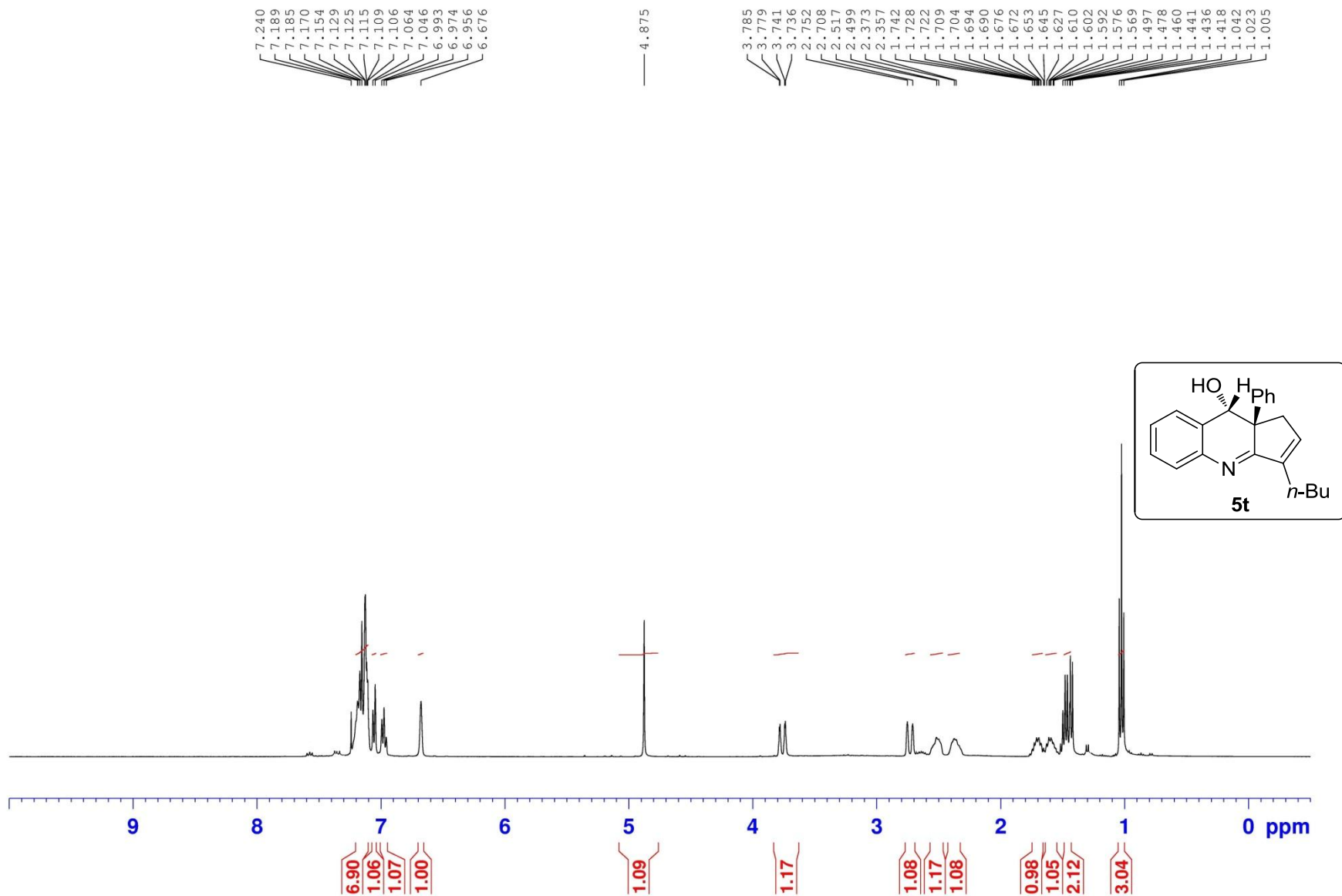


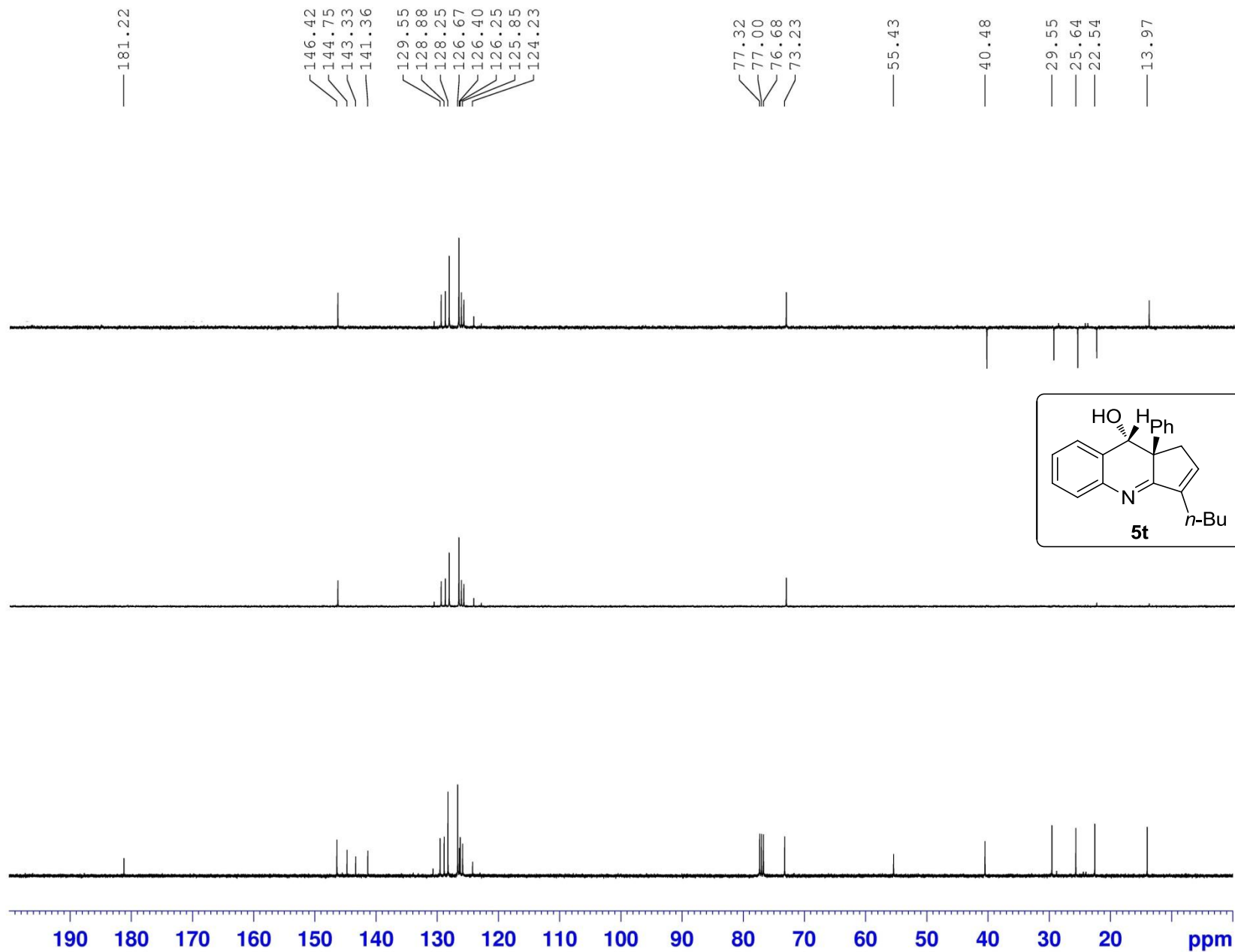


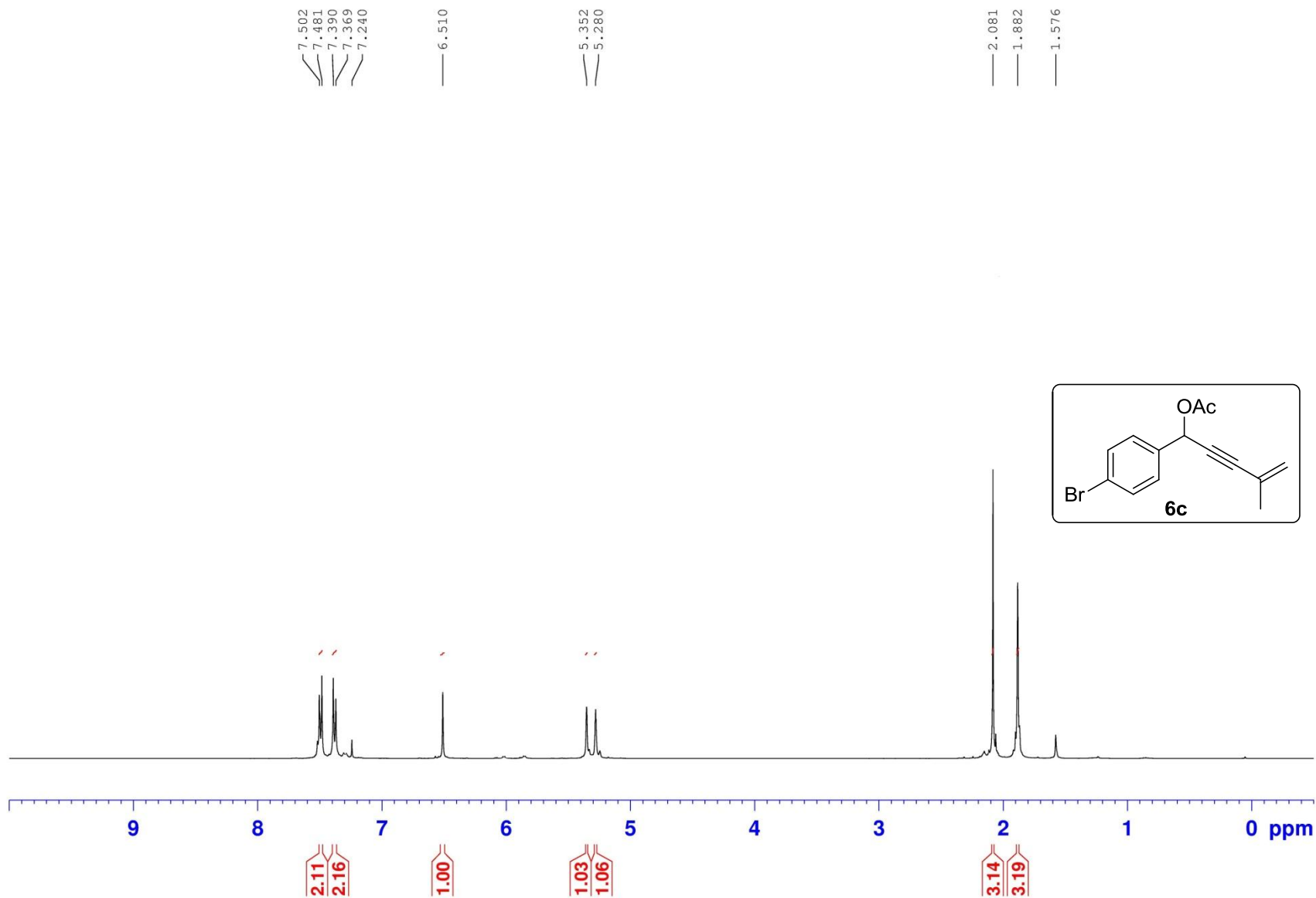


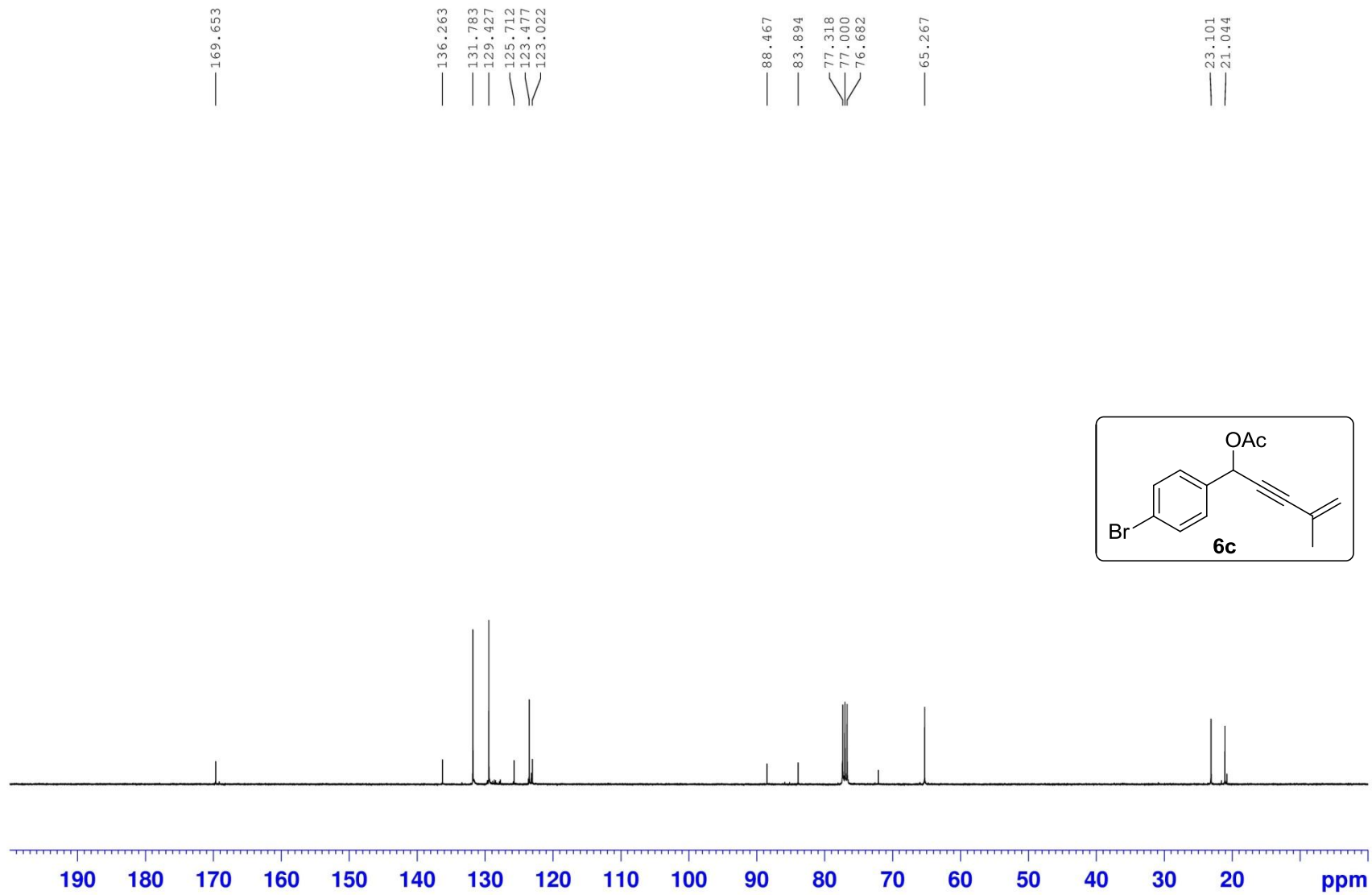


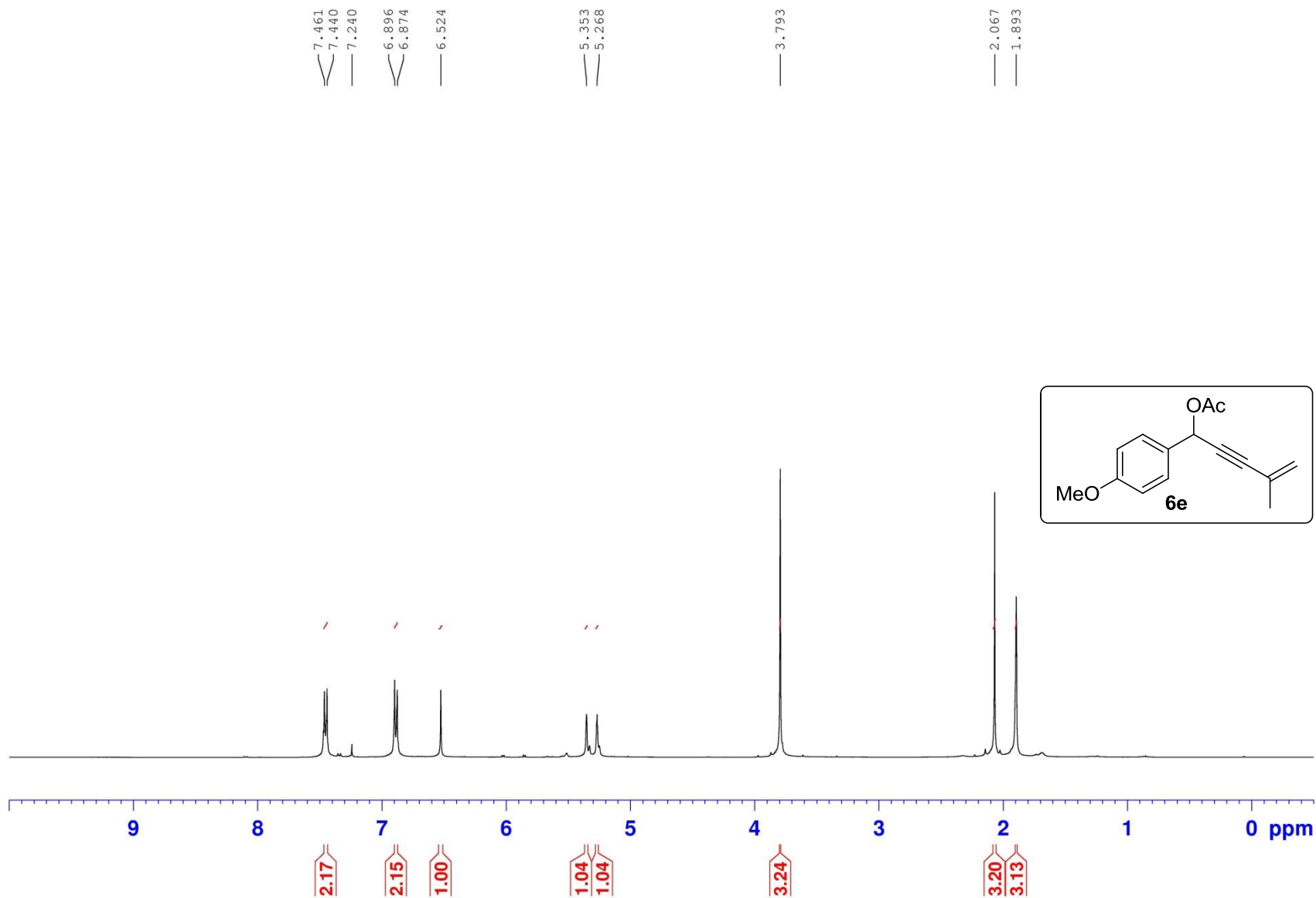


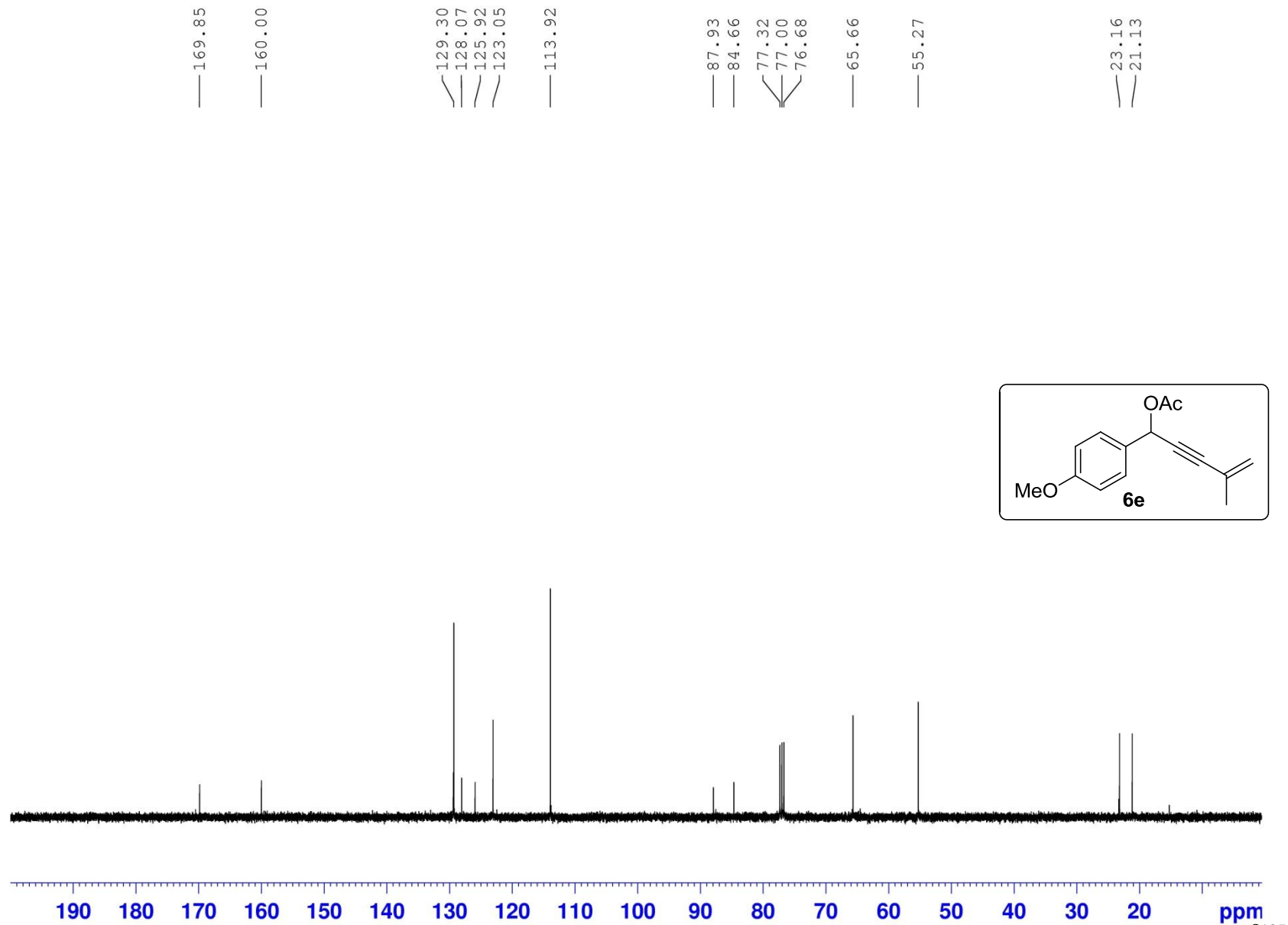


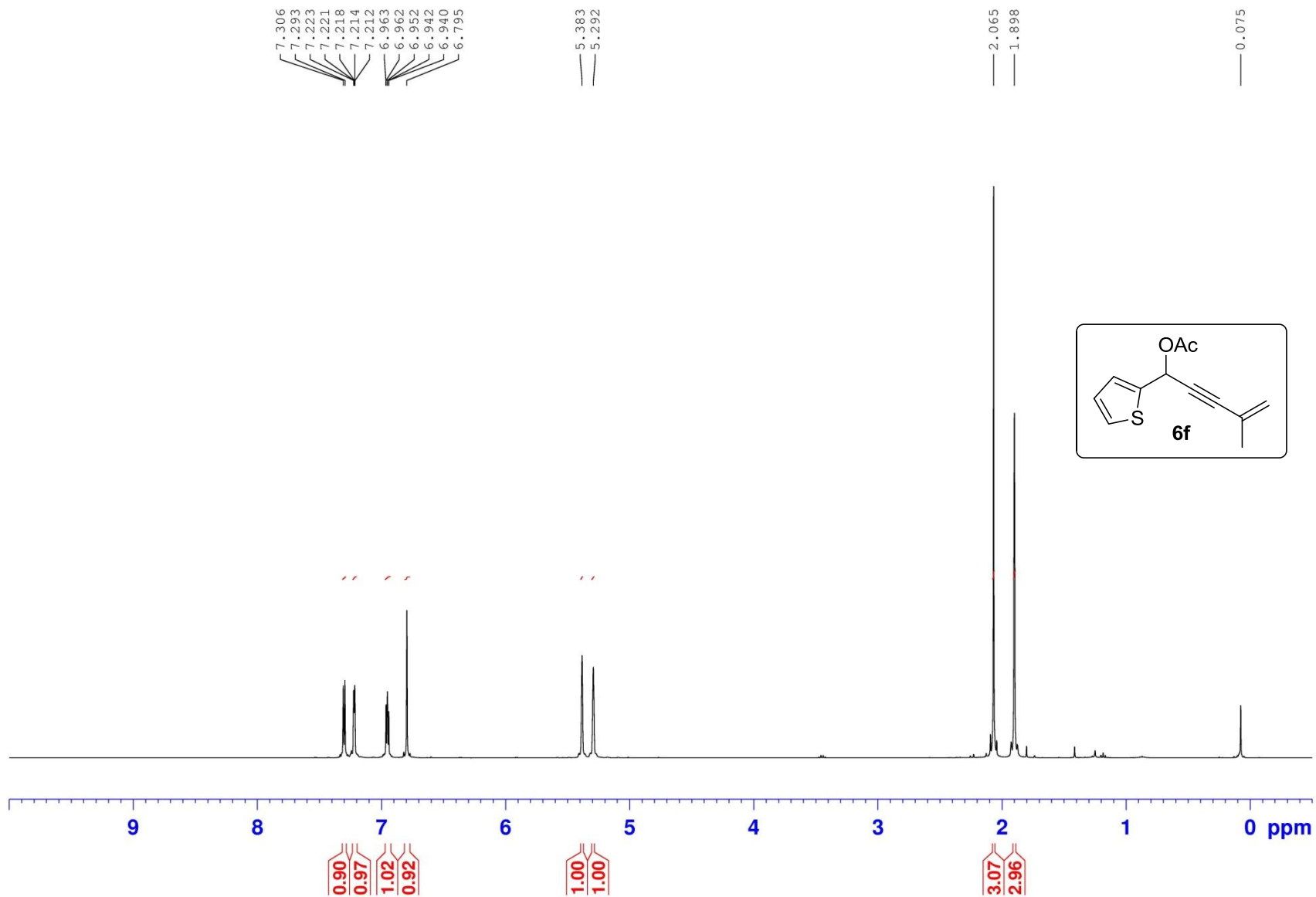


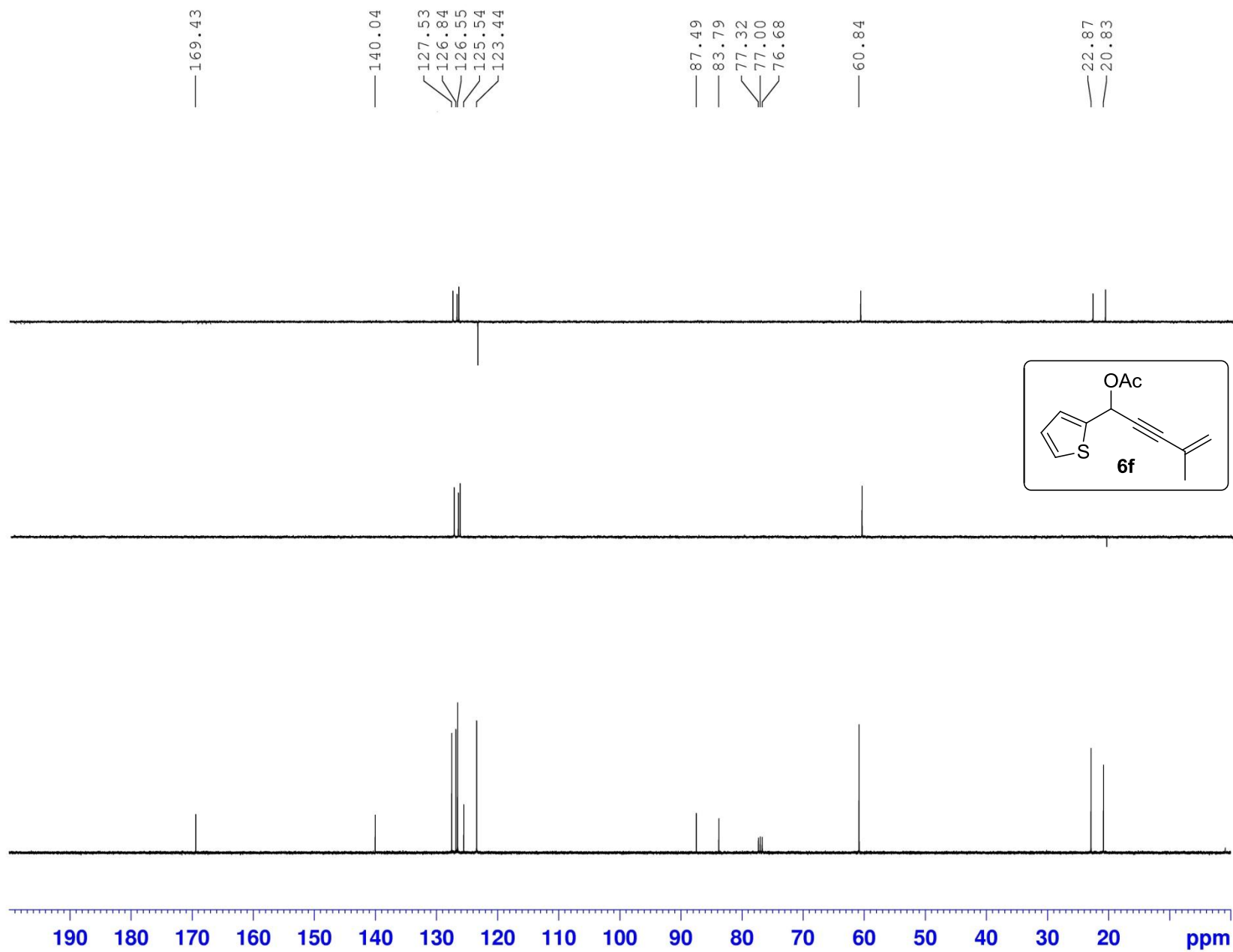


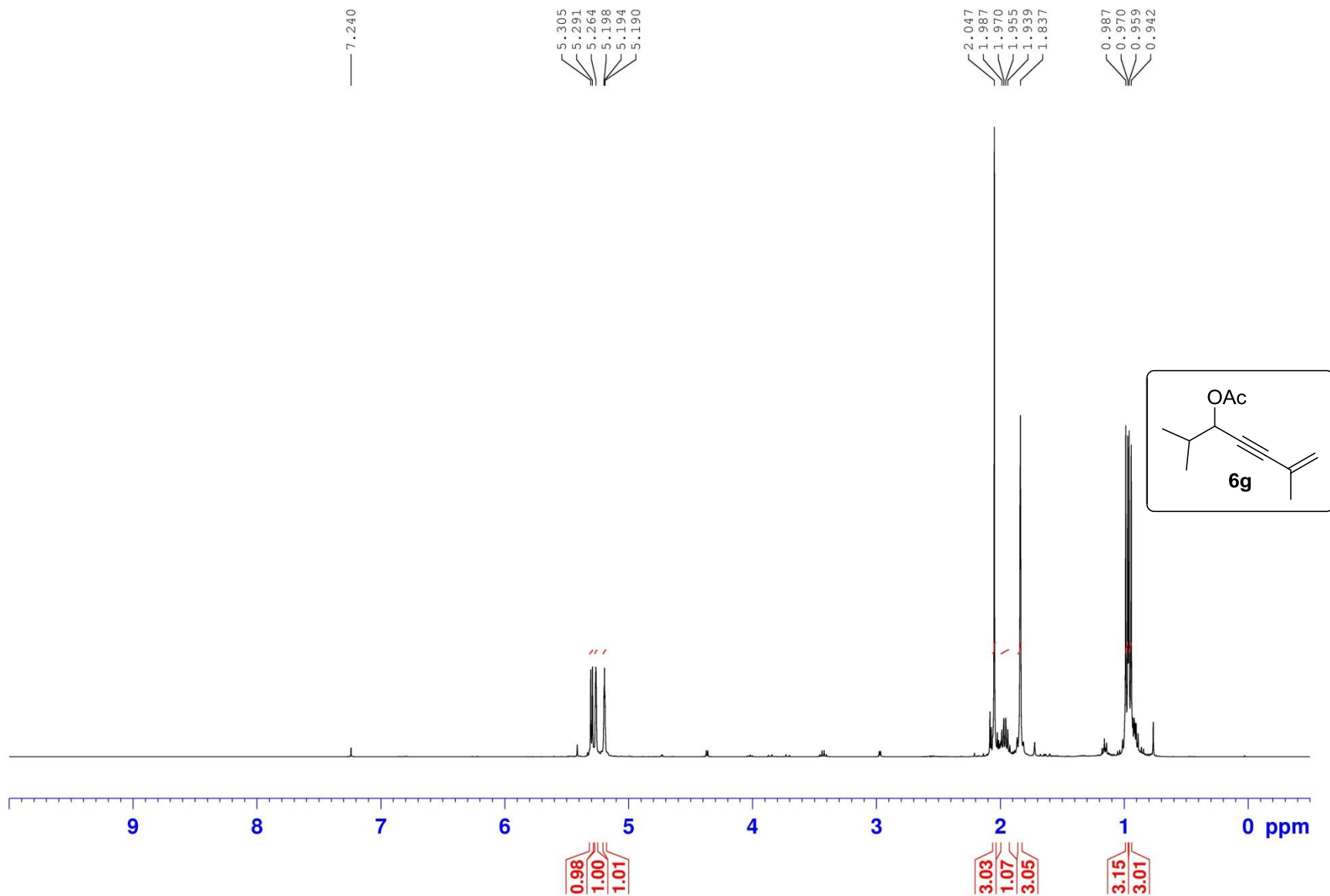


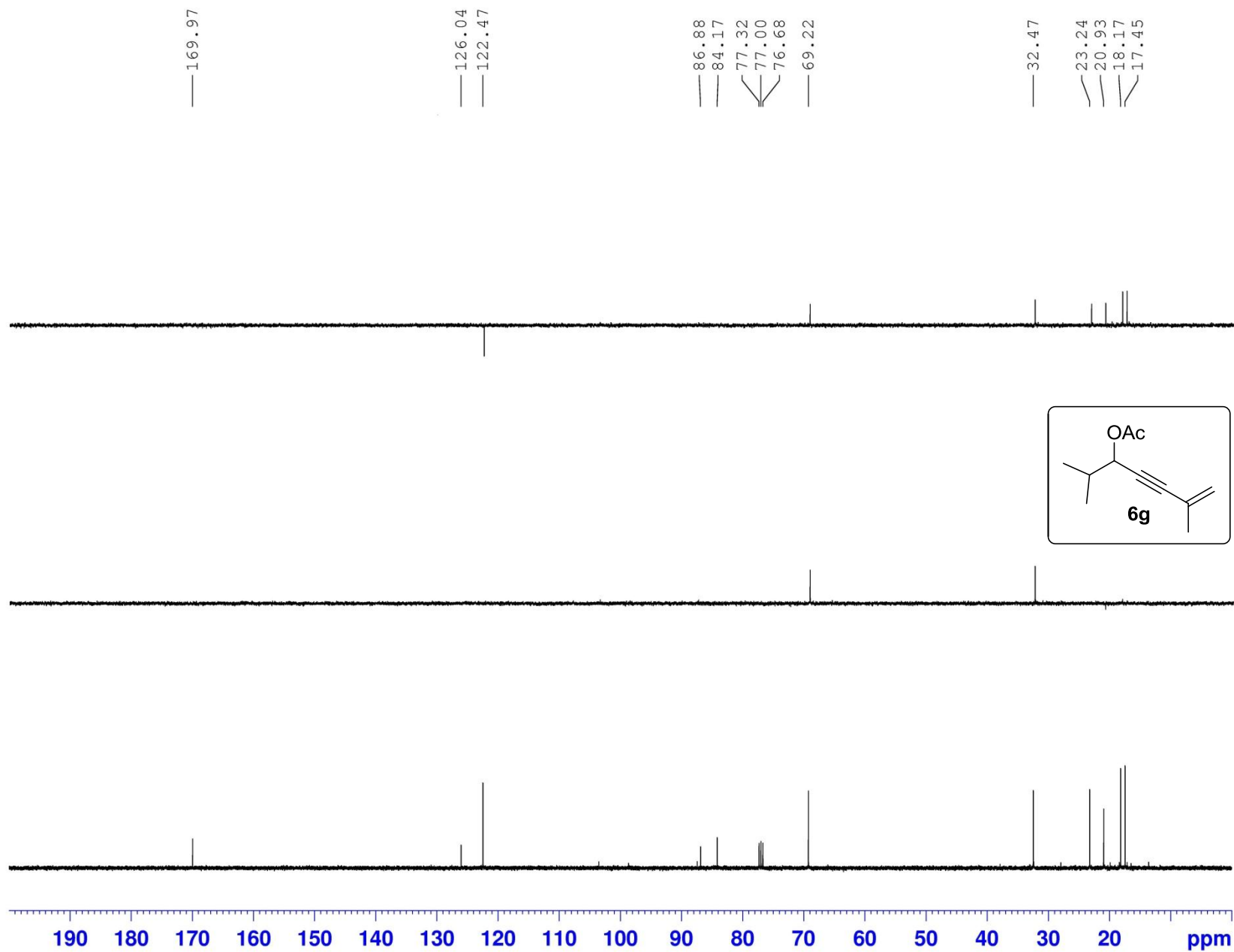












BM-07-89

Current Data Parameters
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PROCNO 1

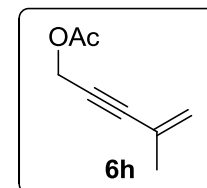
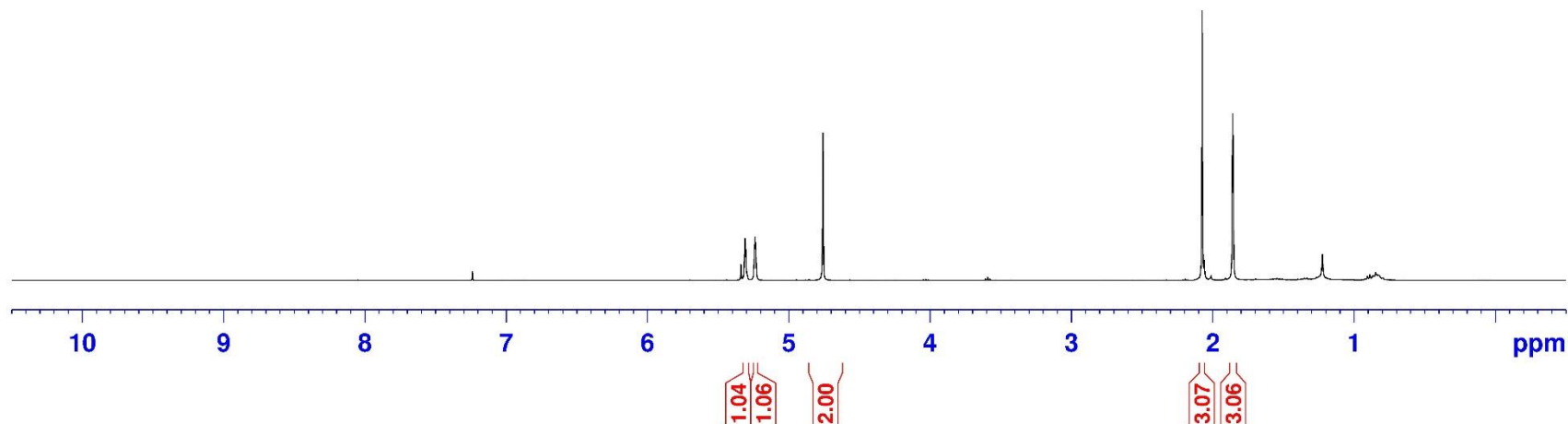
F2 - Processing parameters
SI 32768
SF 399.7611797 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

7.240

5.309
5.239
5.235

4.759

2.074
1.857



Current Data Parameters
 NAME BM-07-89-13C.fid
 EXPNO 1
 PROCNO 1

F2 - Processing parameters
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 SF 100.5214586 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

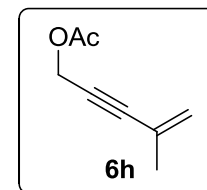
— 170.257

— 125.882
 — 123.024

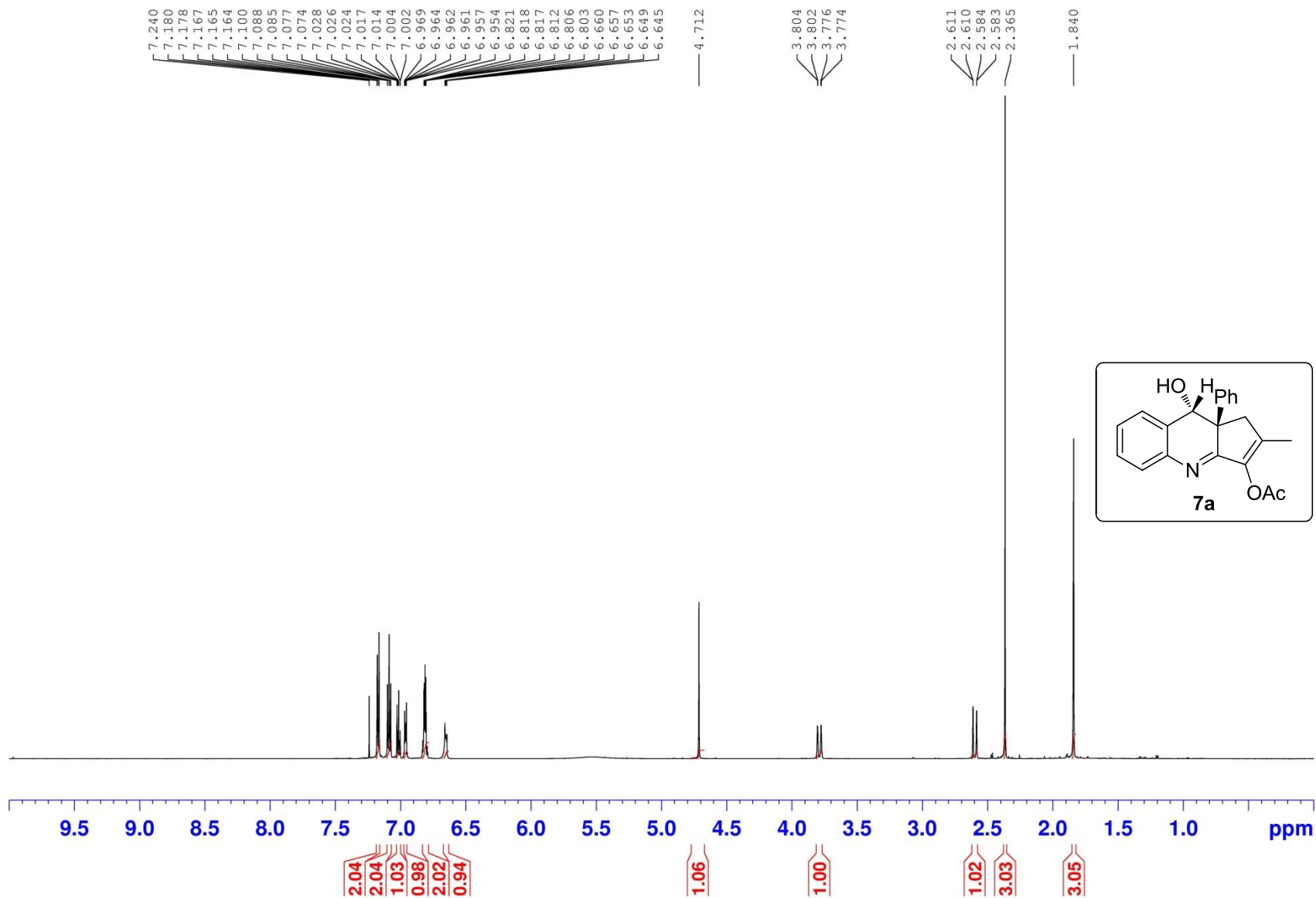
— 87.602
 — 81.798
 — 77.318
 — 77.000
 — 76.682

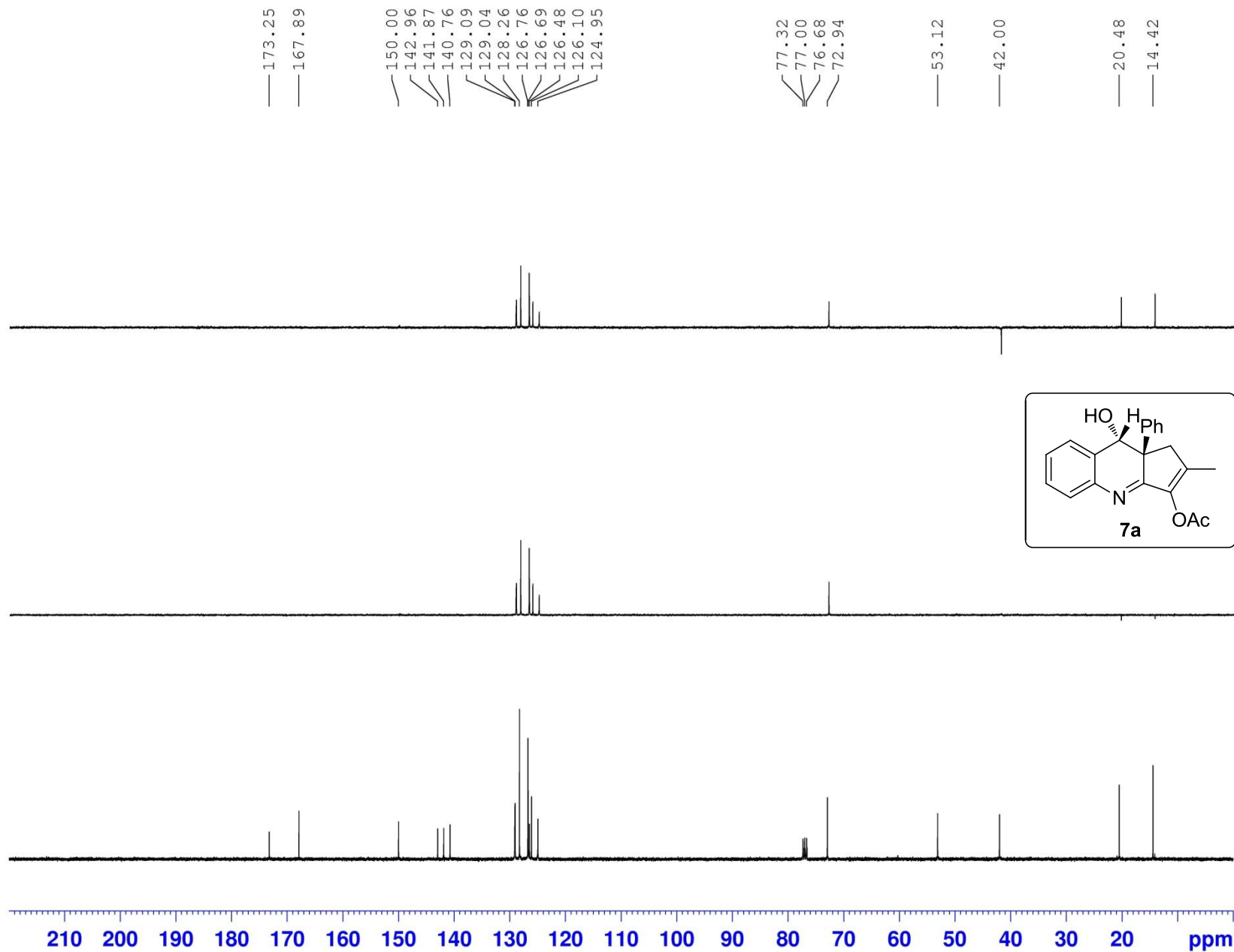
— 52.696

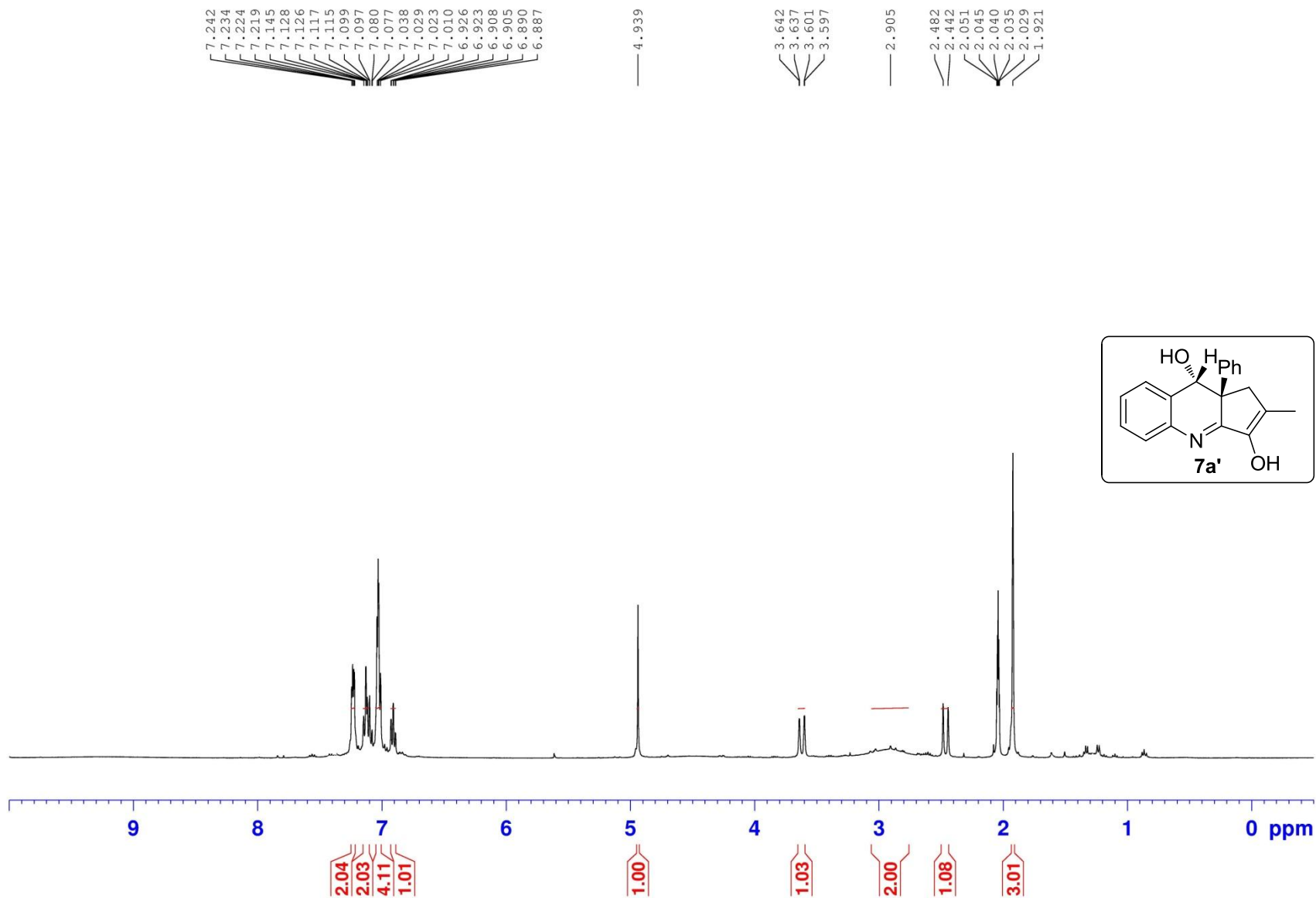
— 23.105
 — 20.737

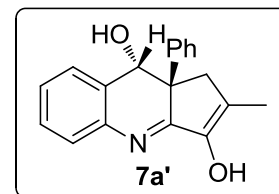
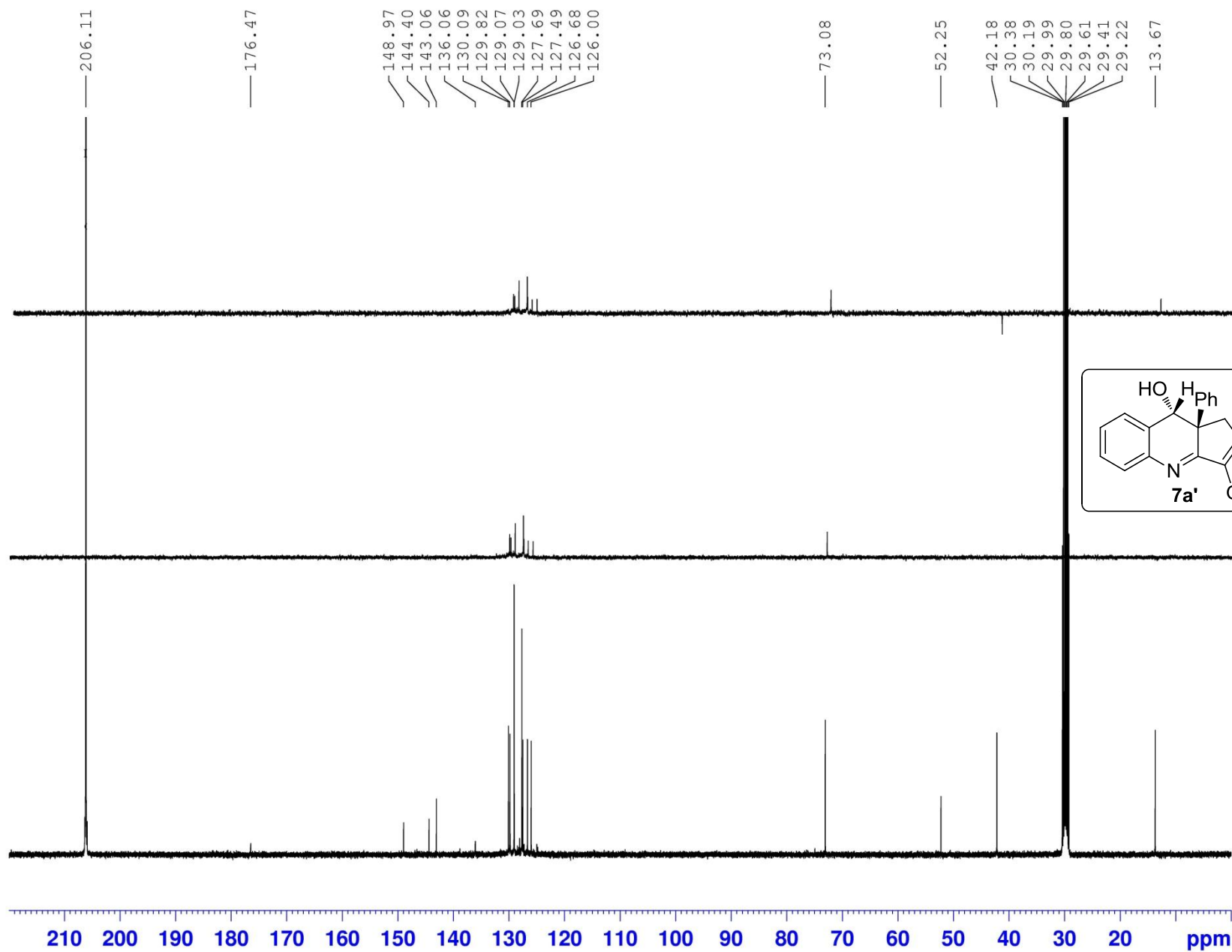


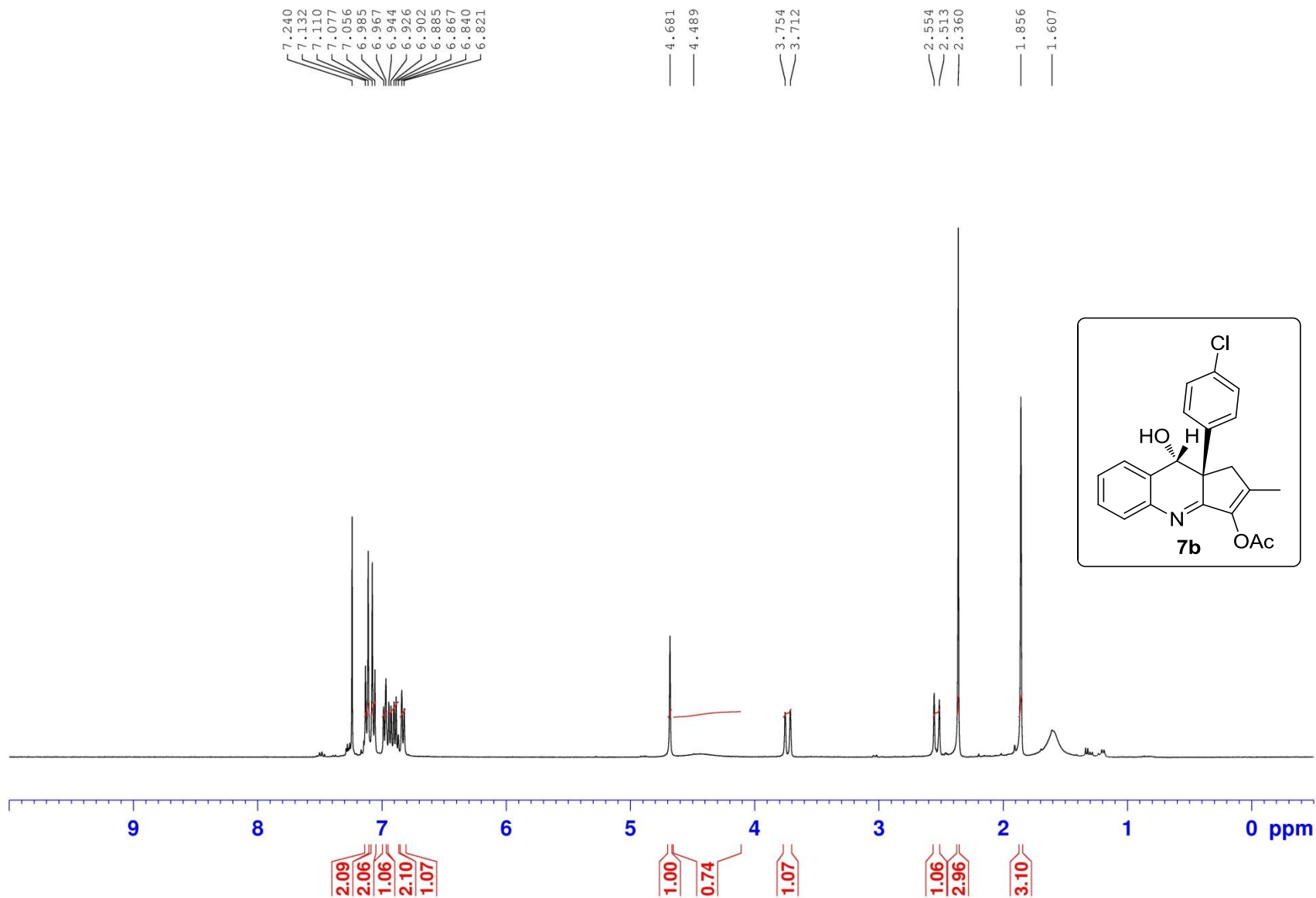
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

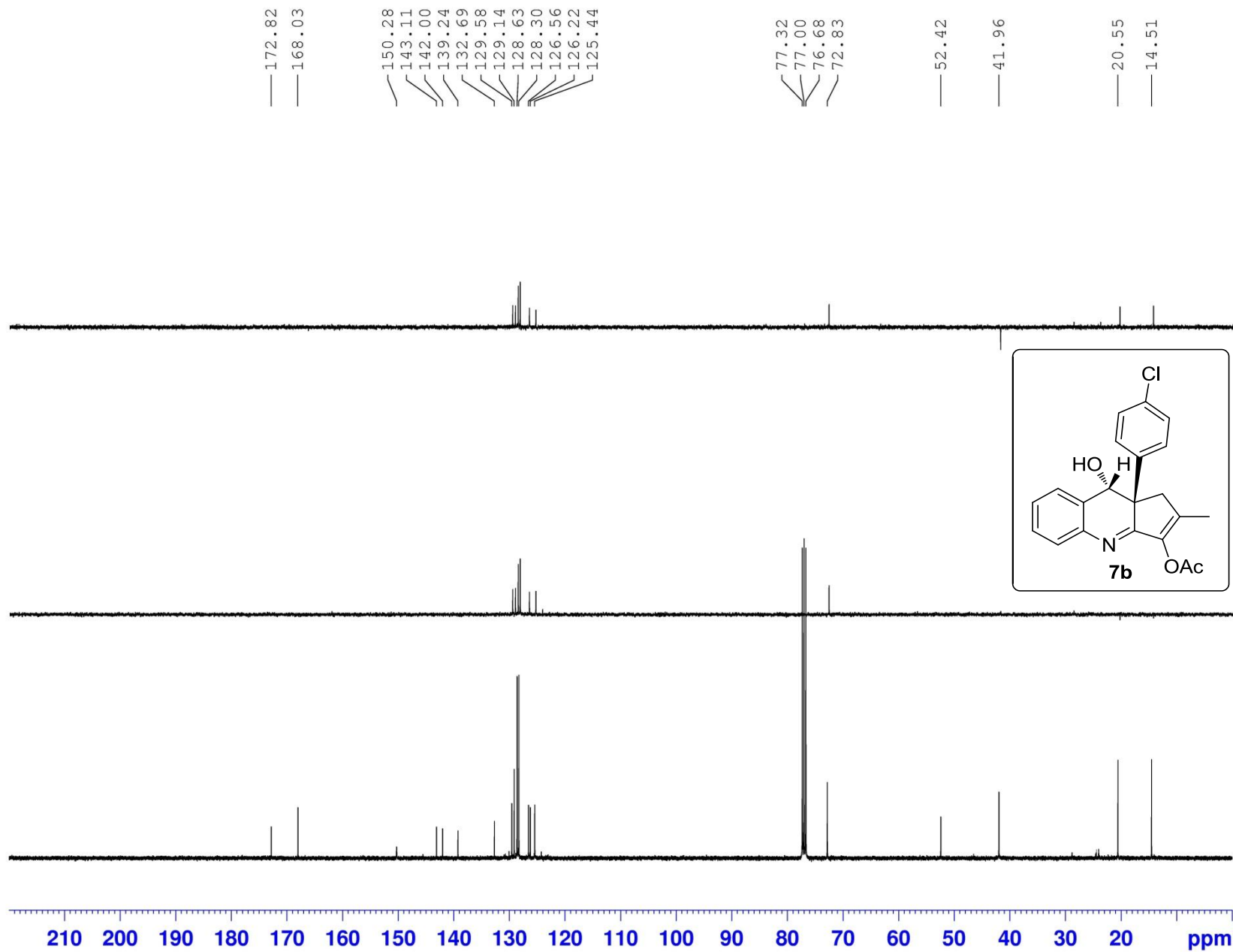


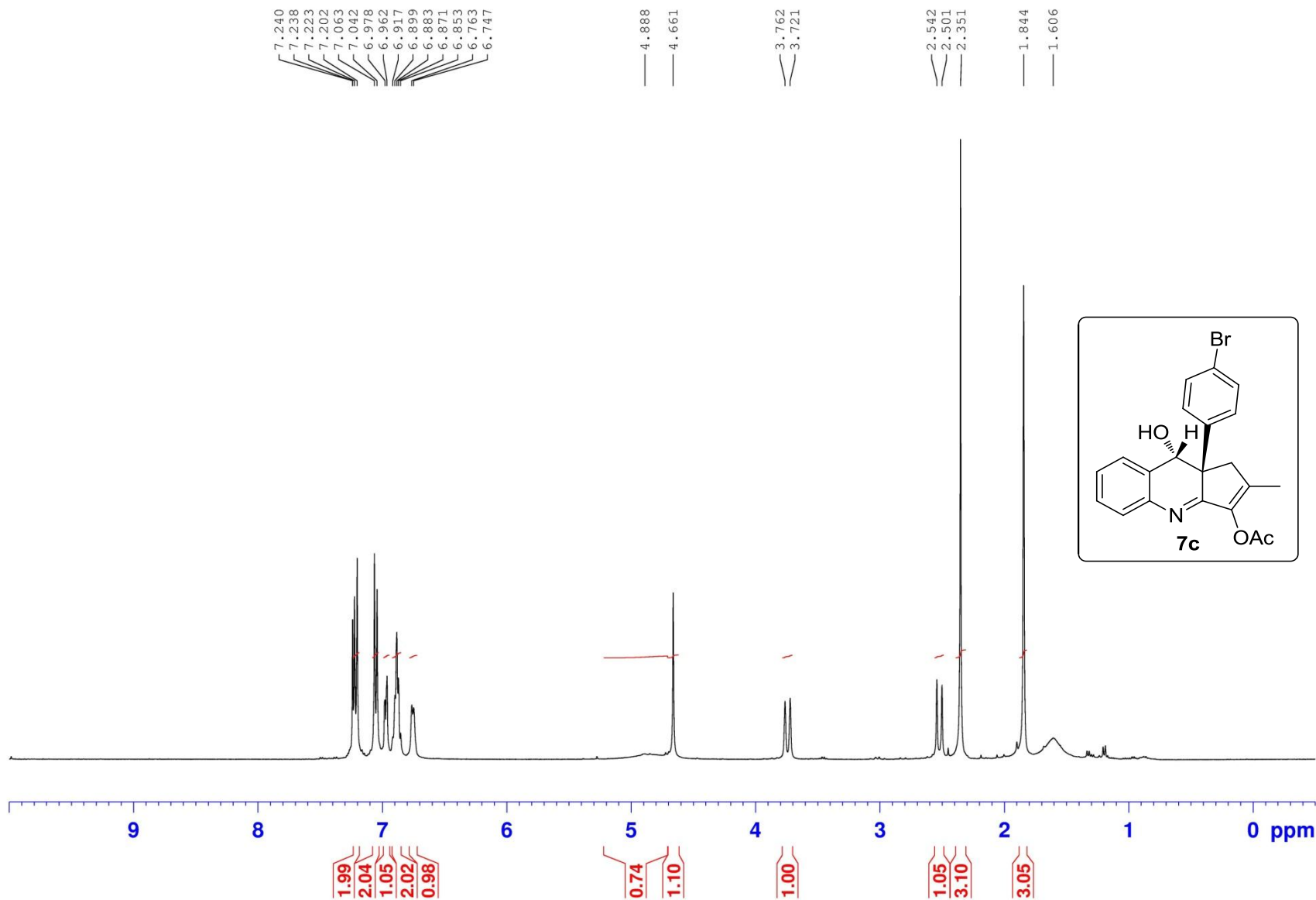


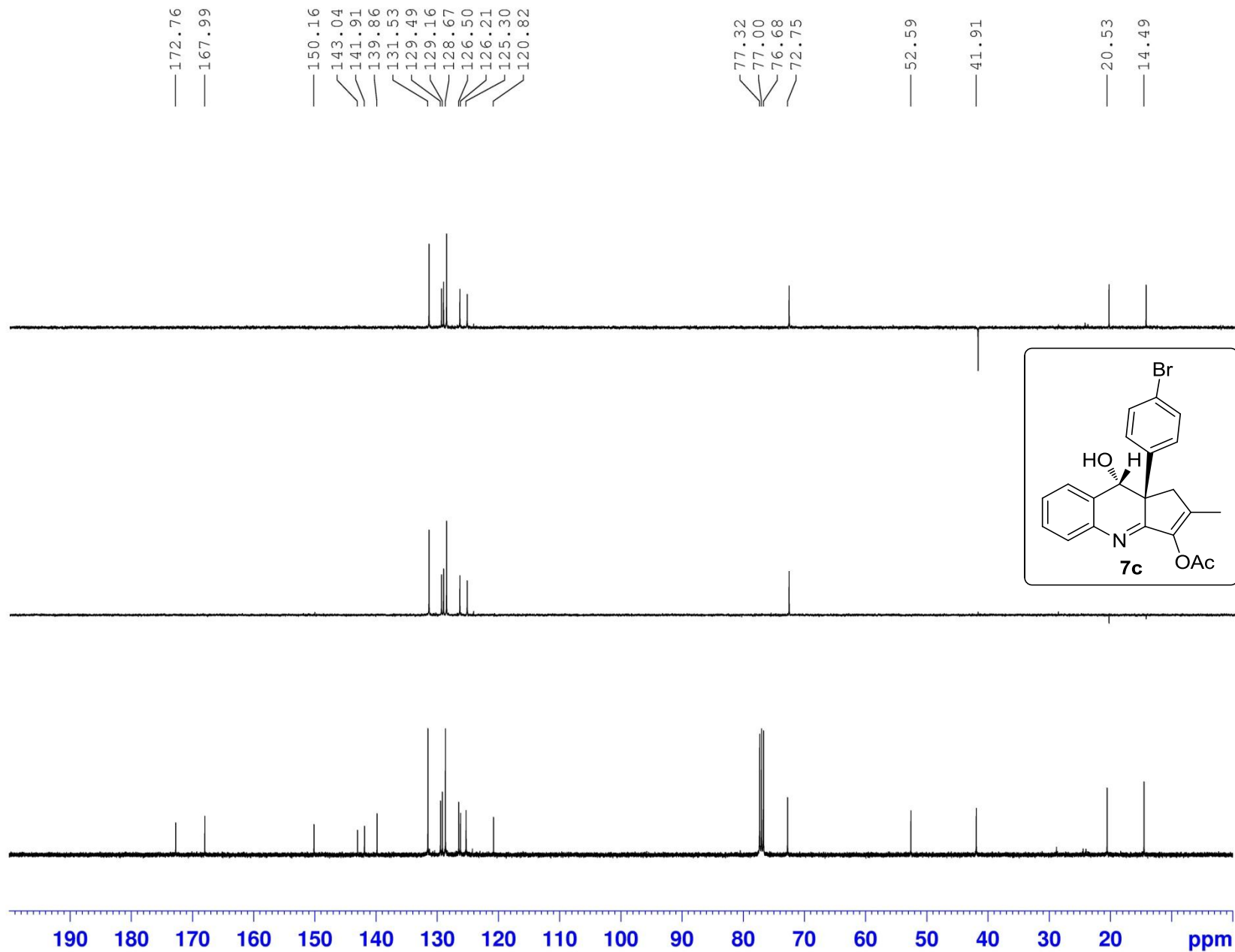


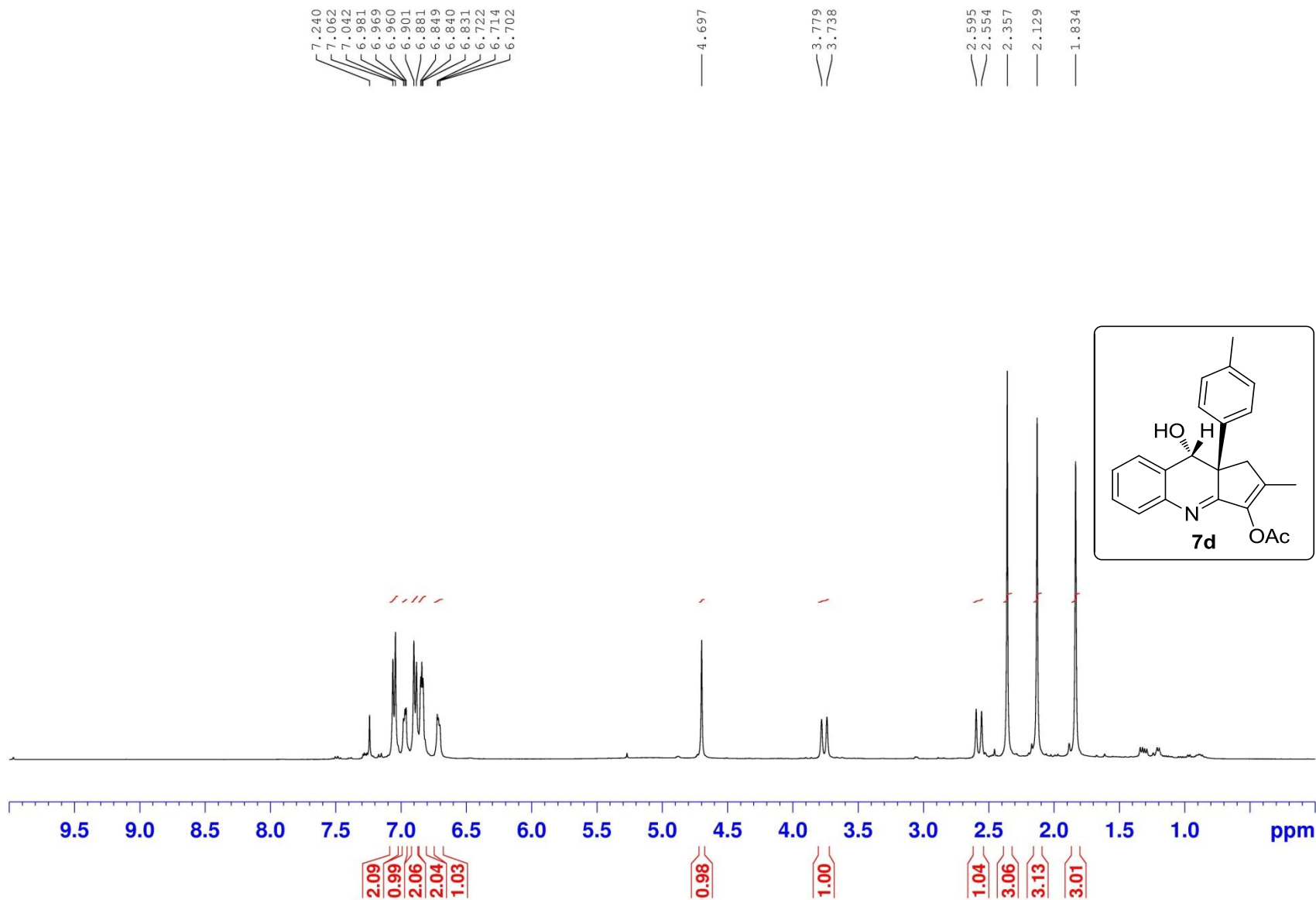


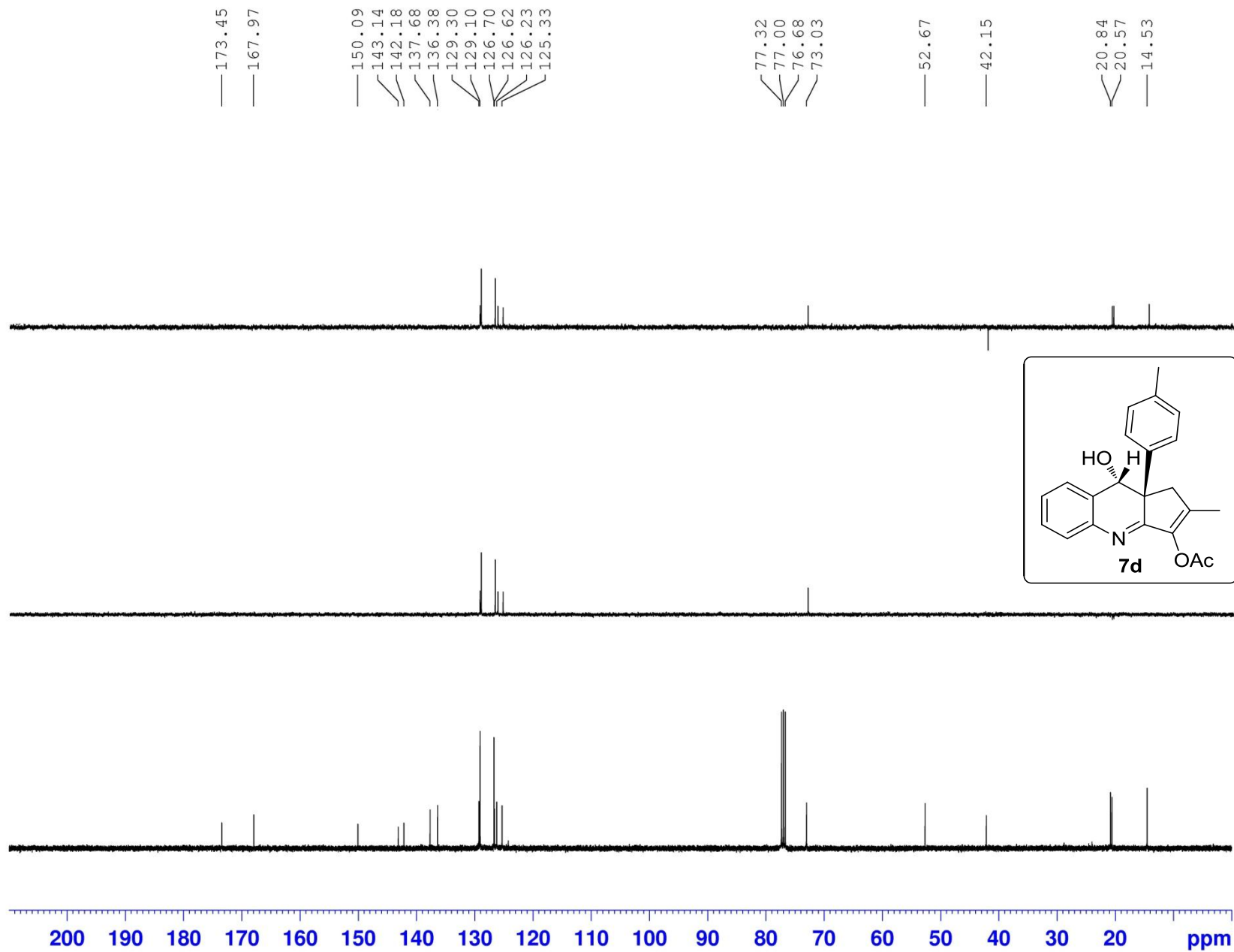


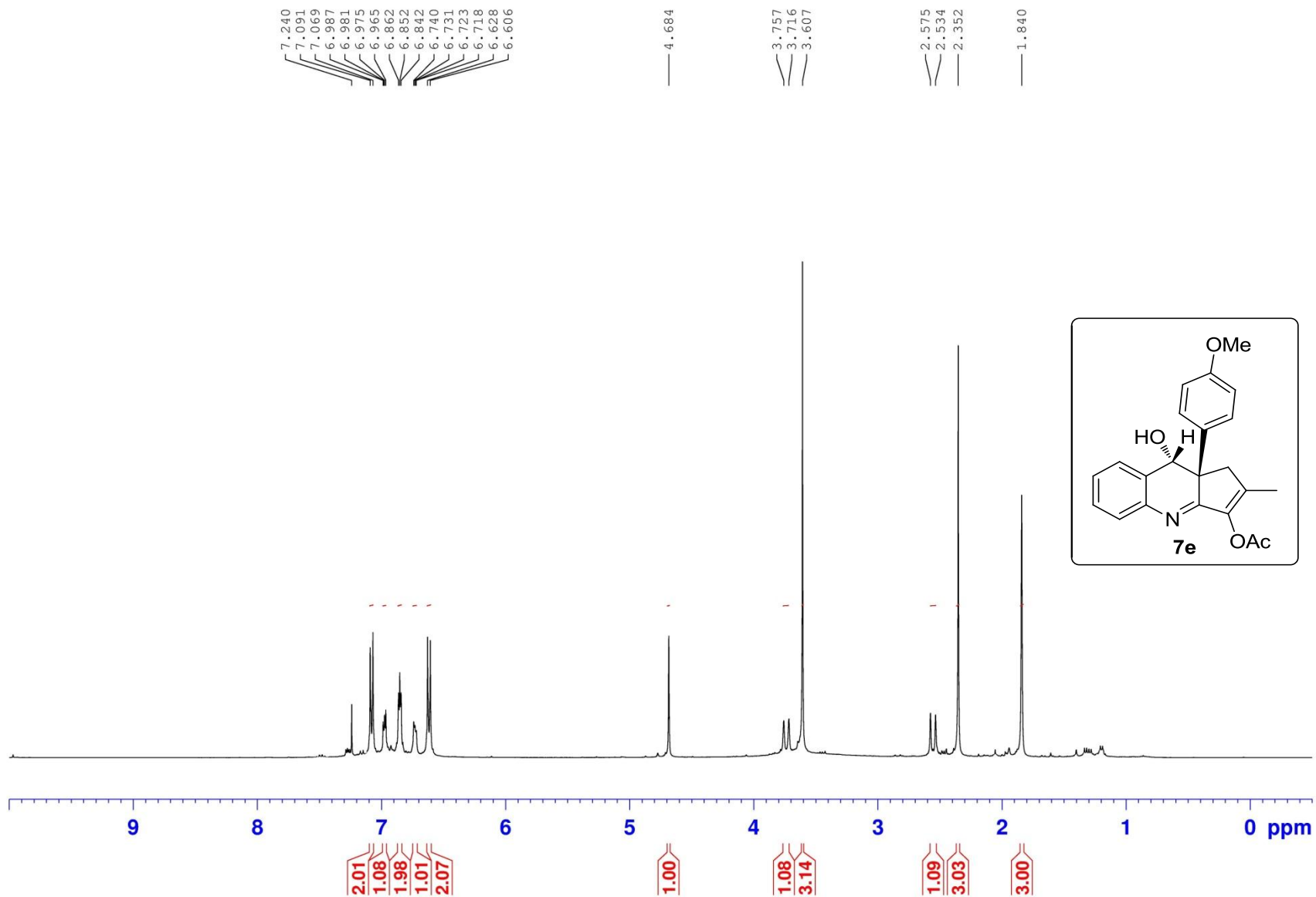


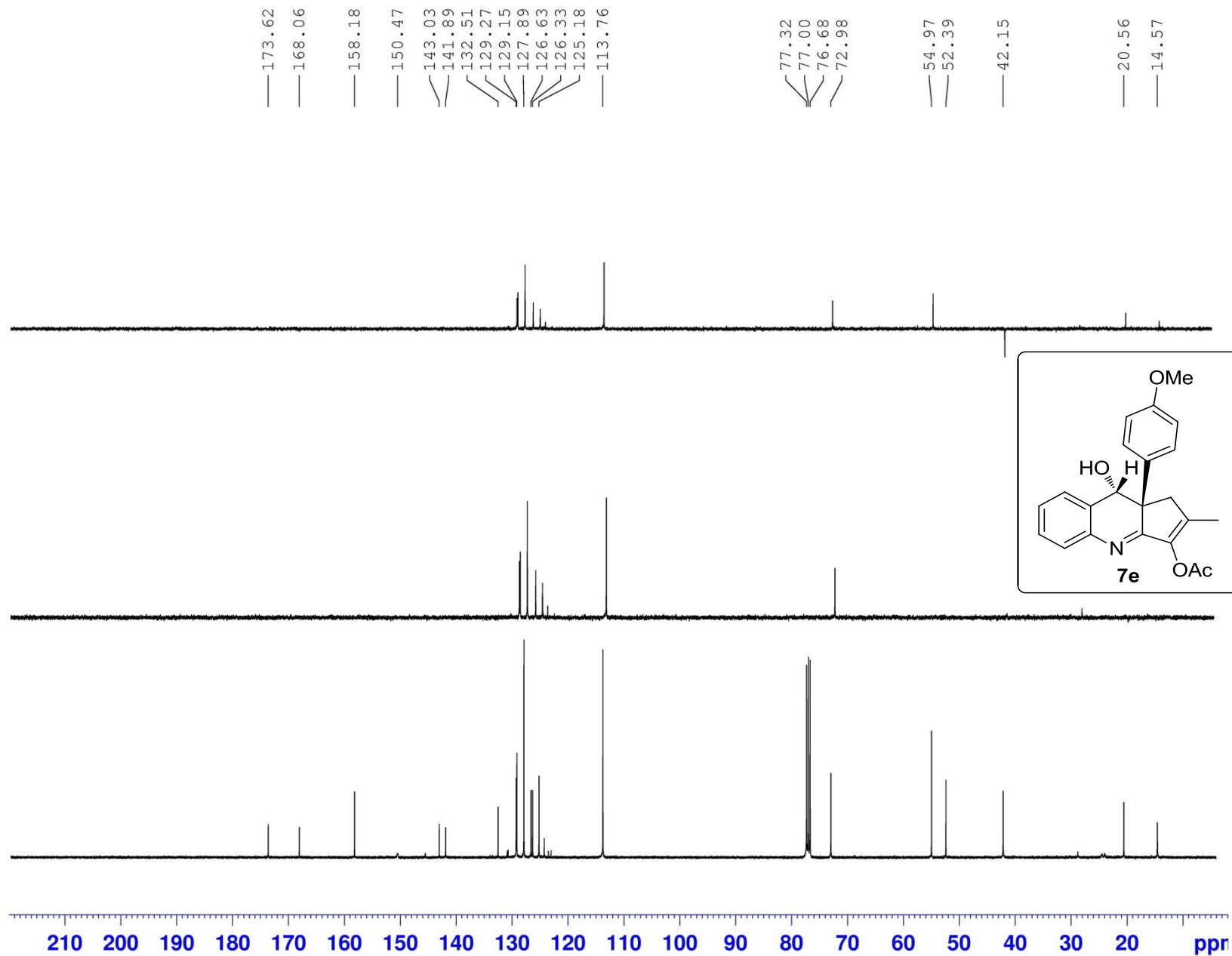


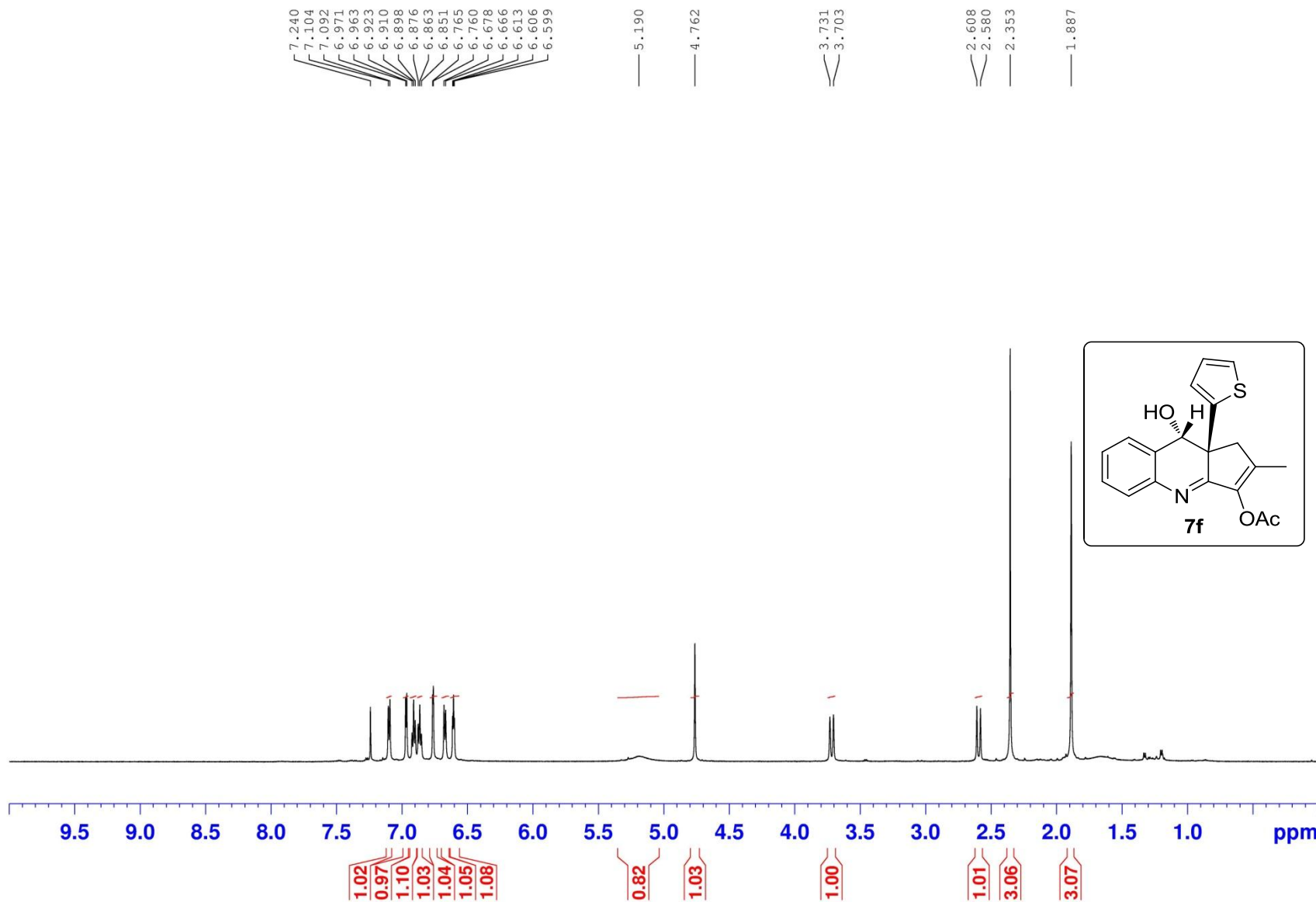


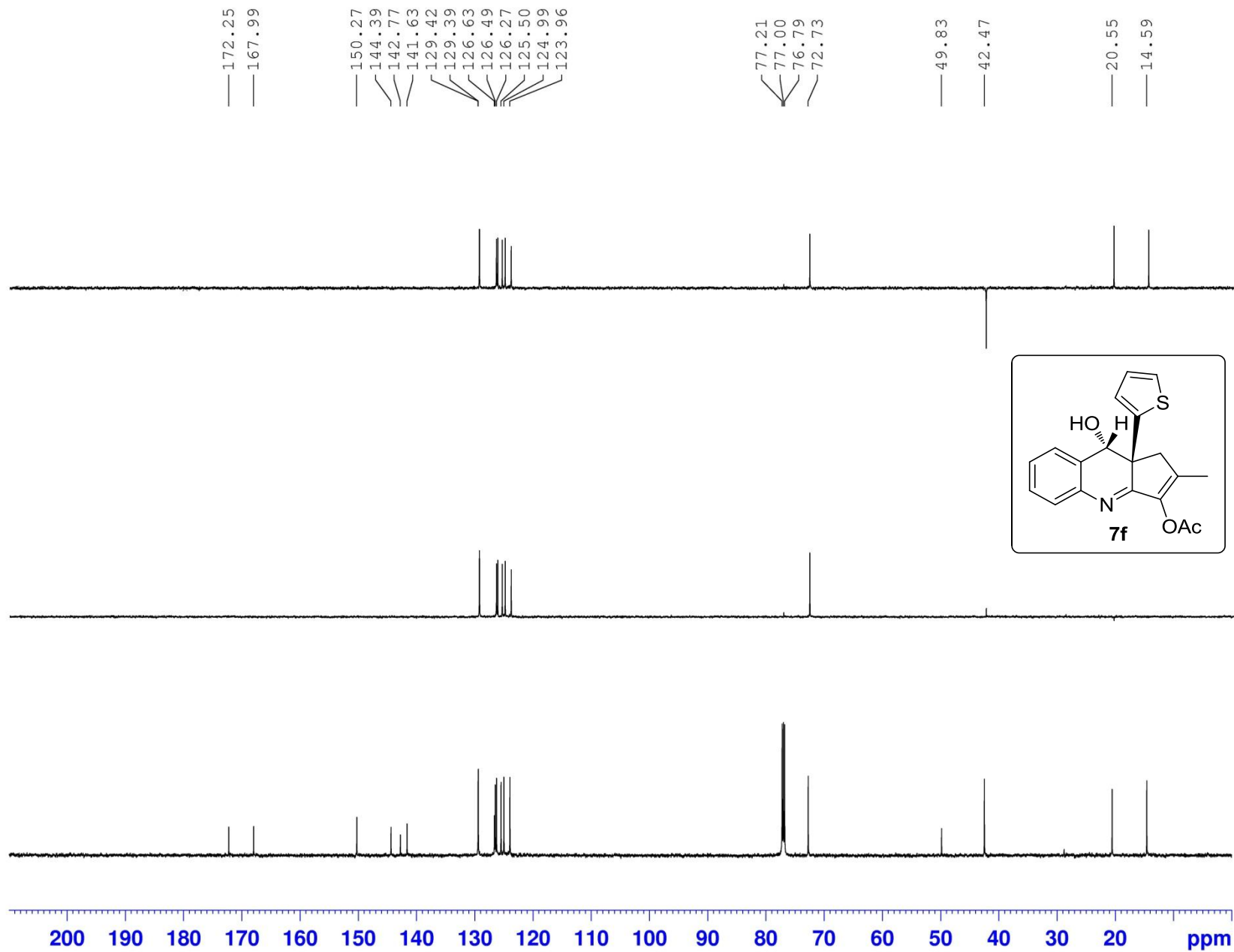


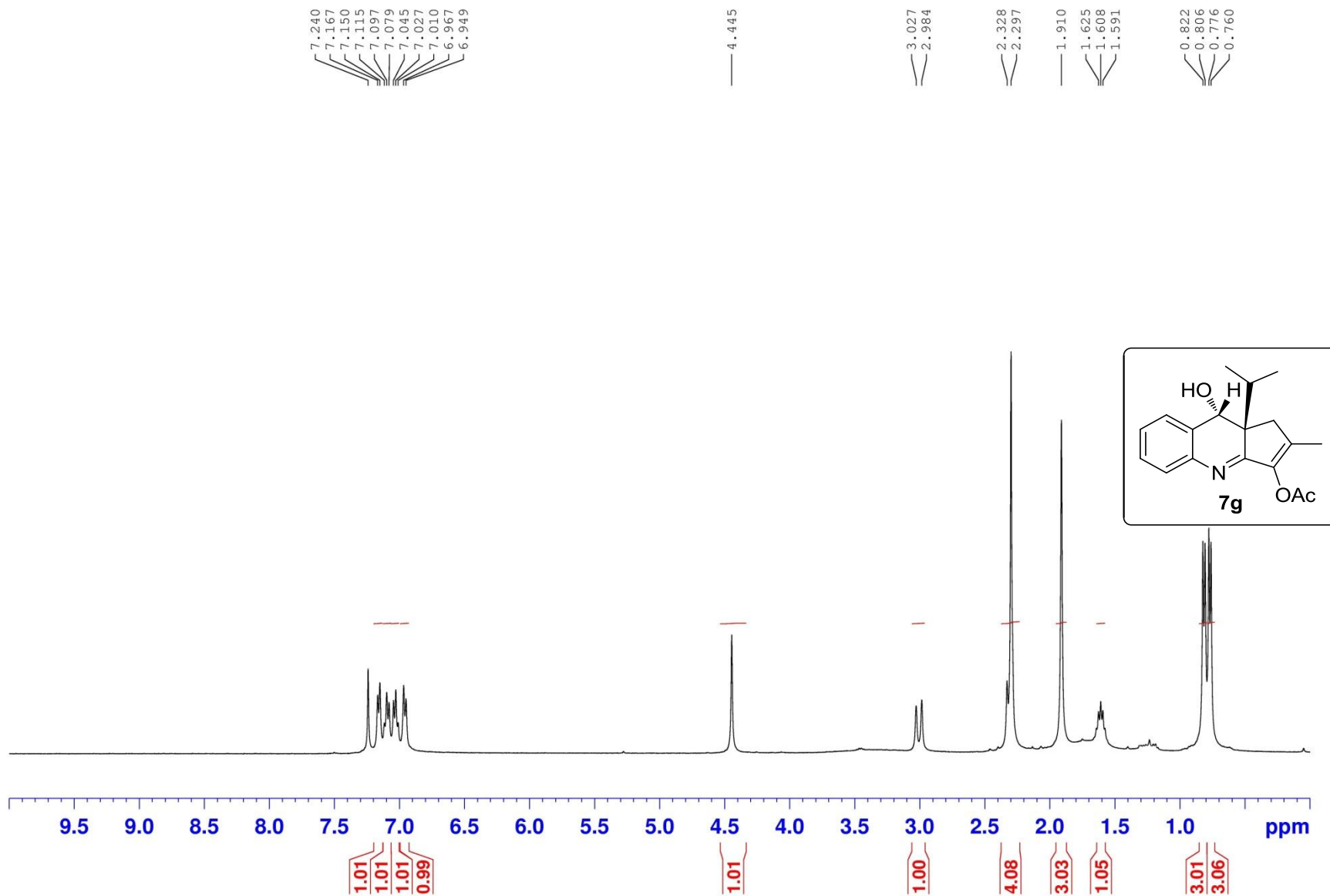


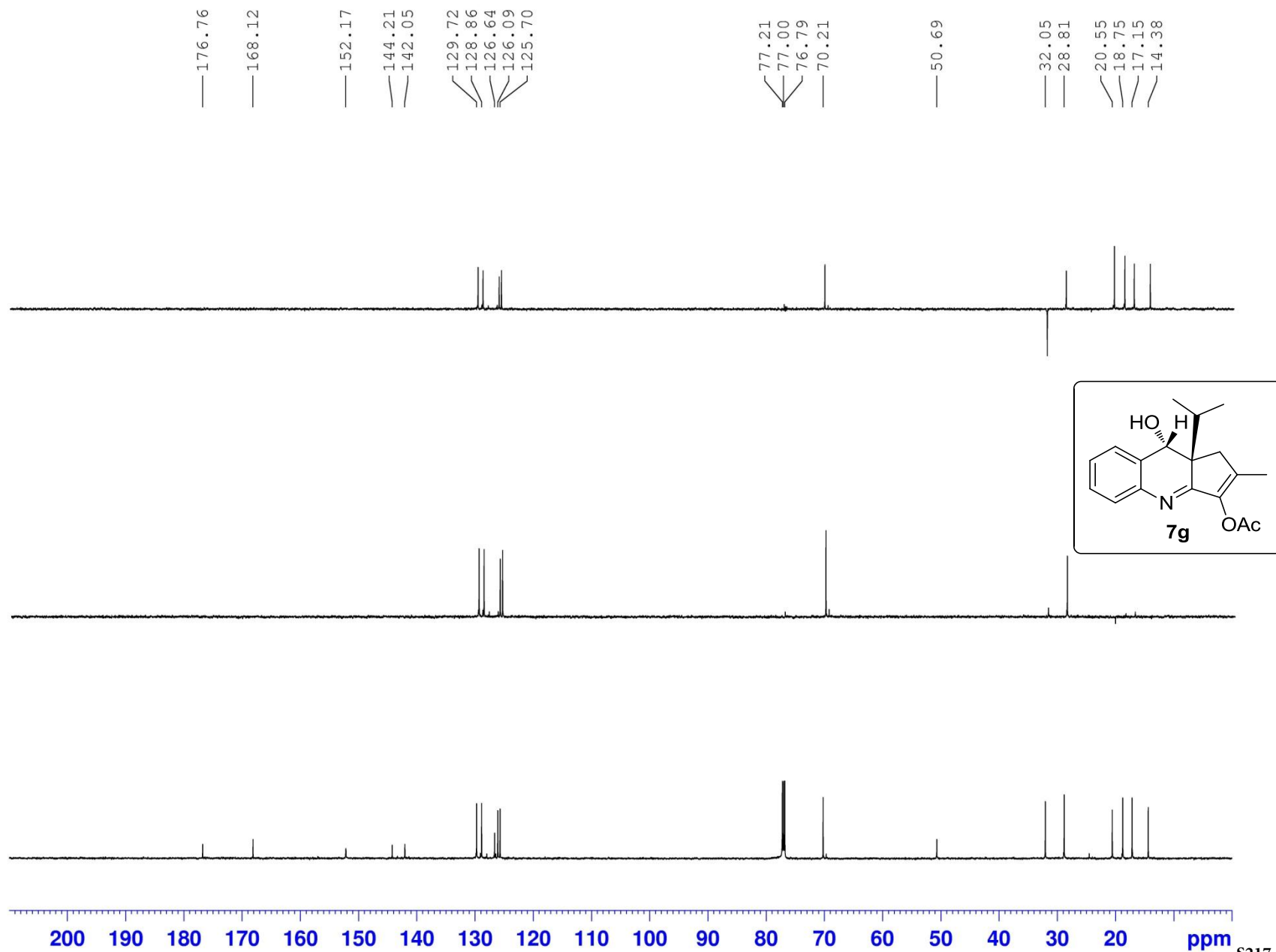


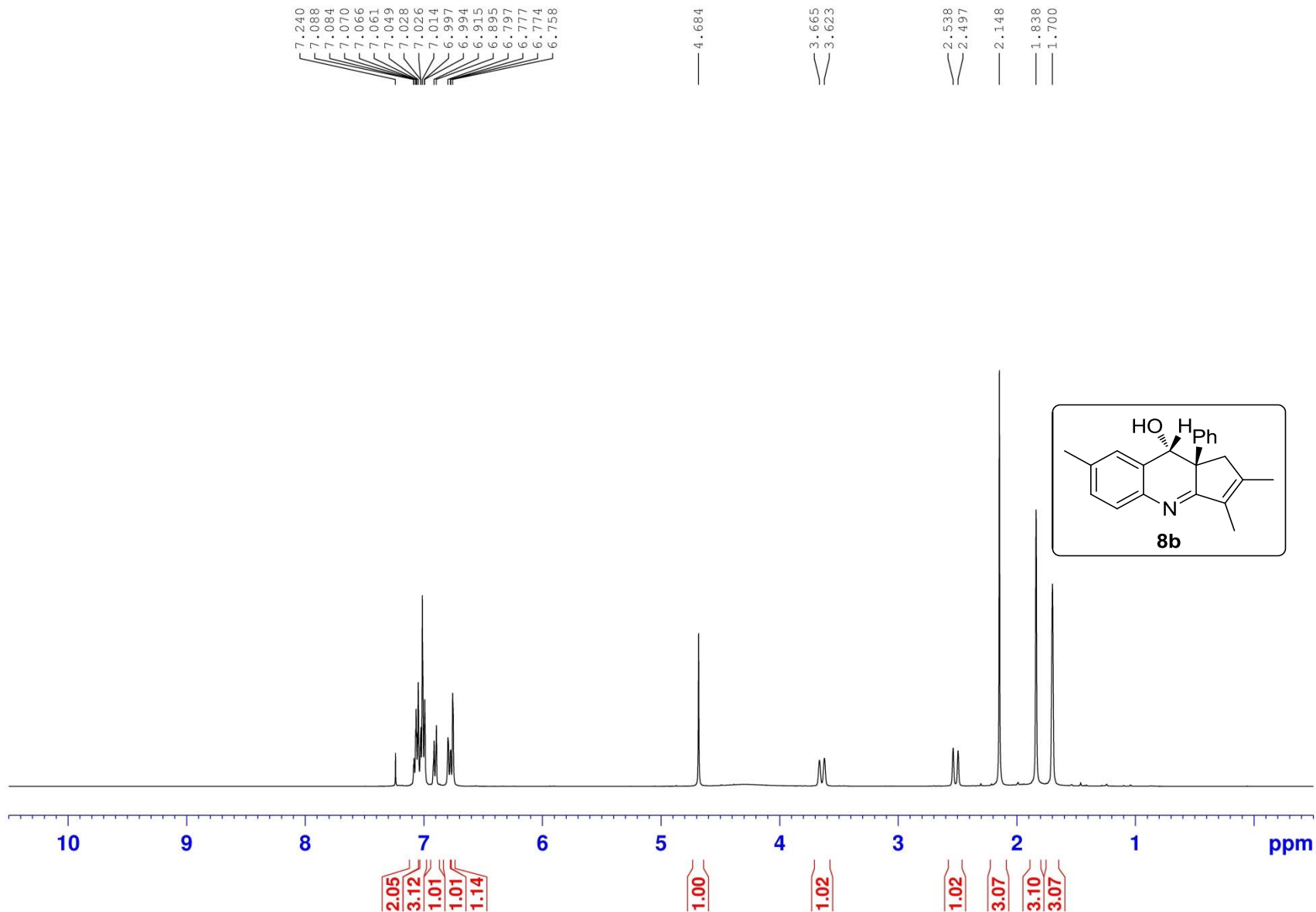


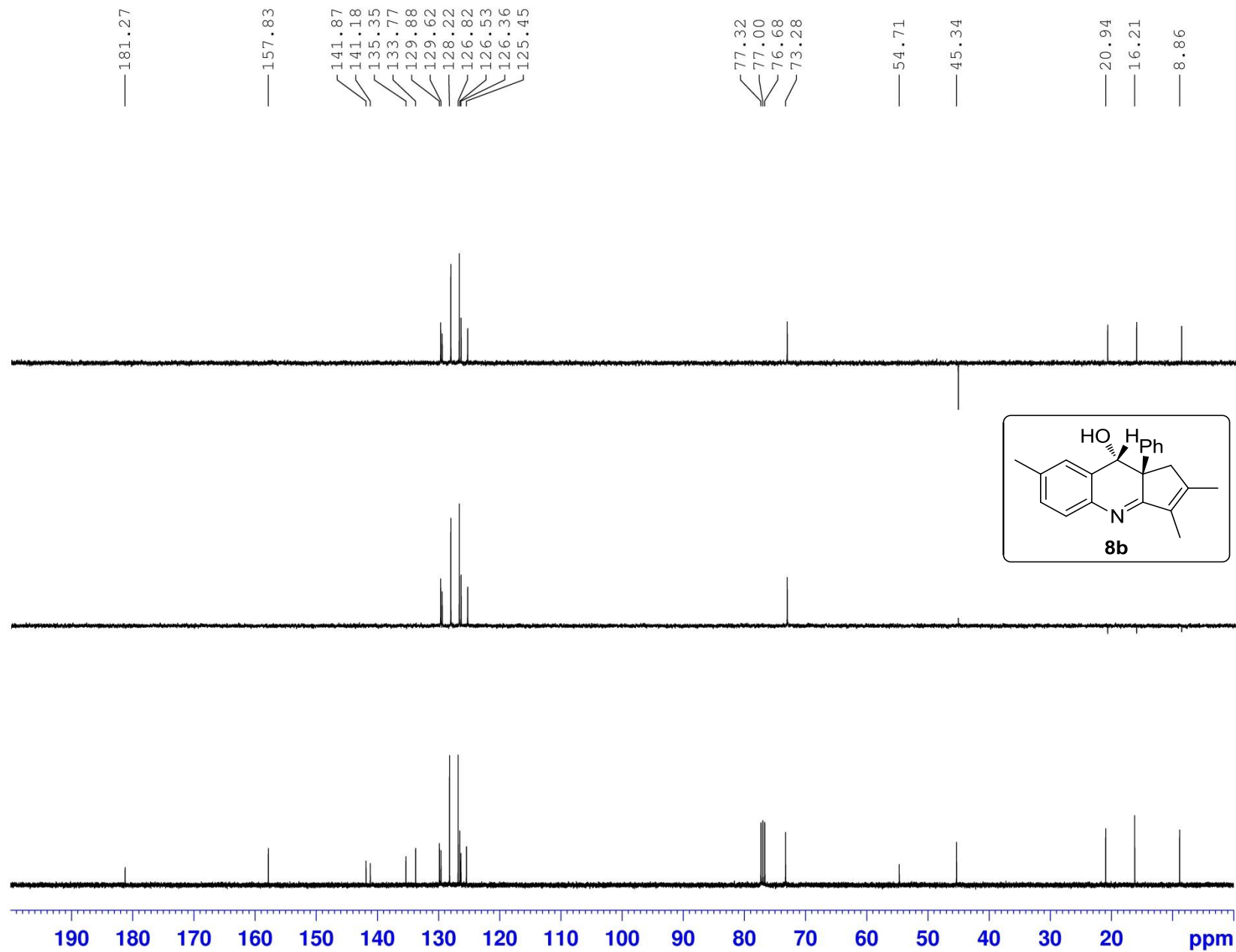


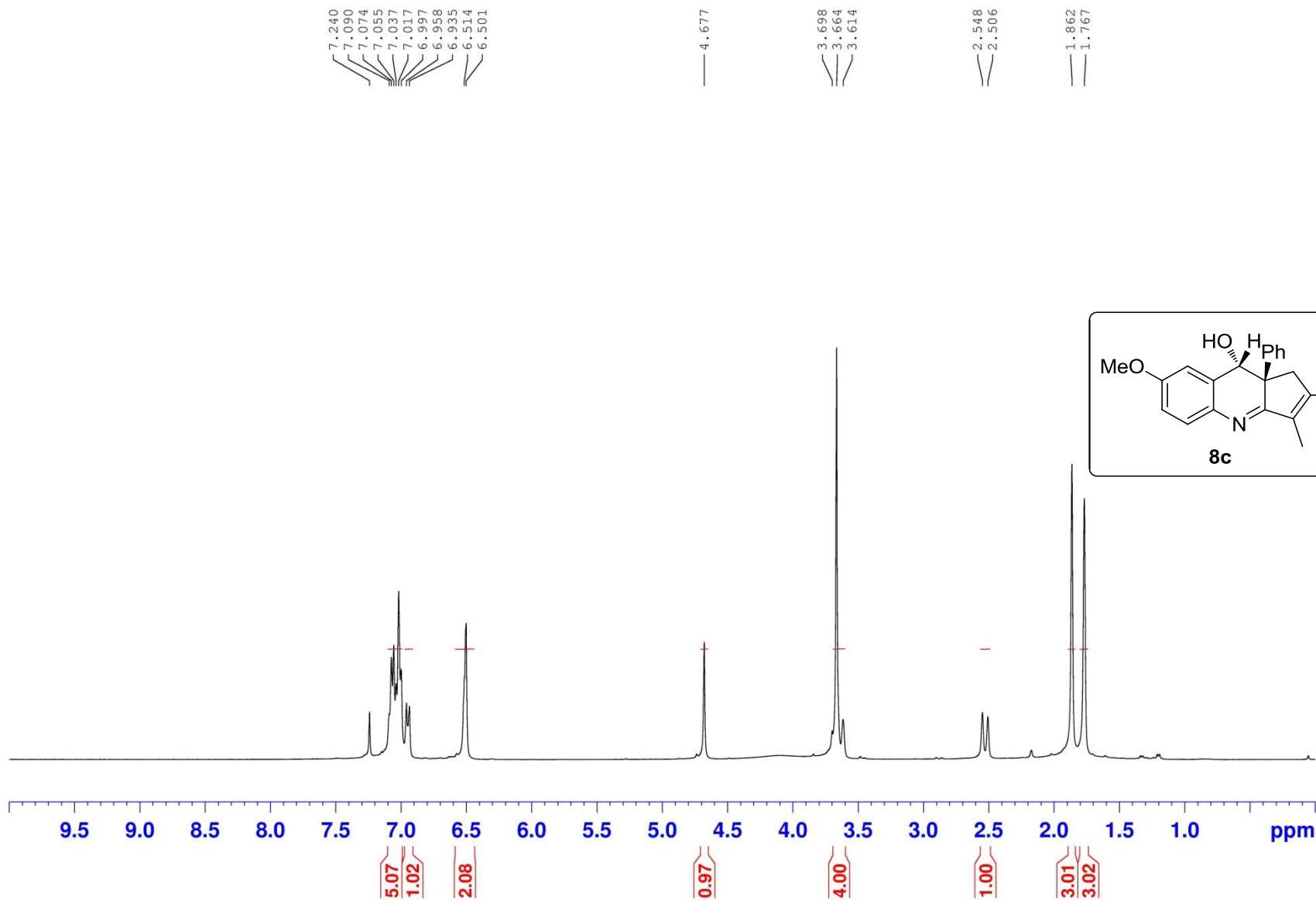


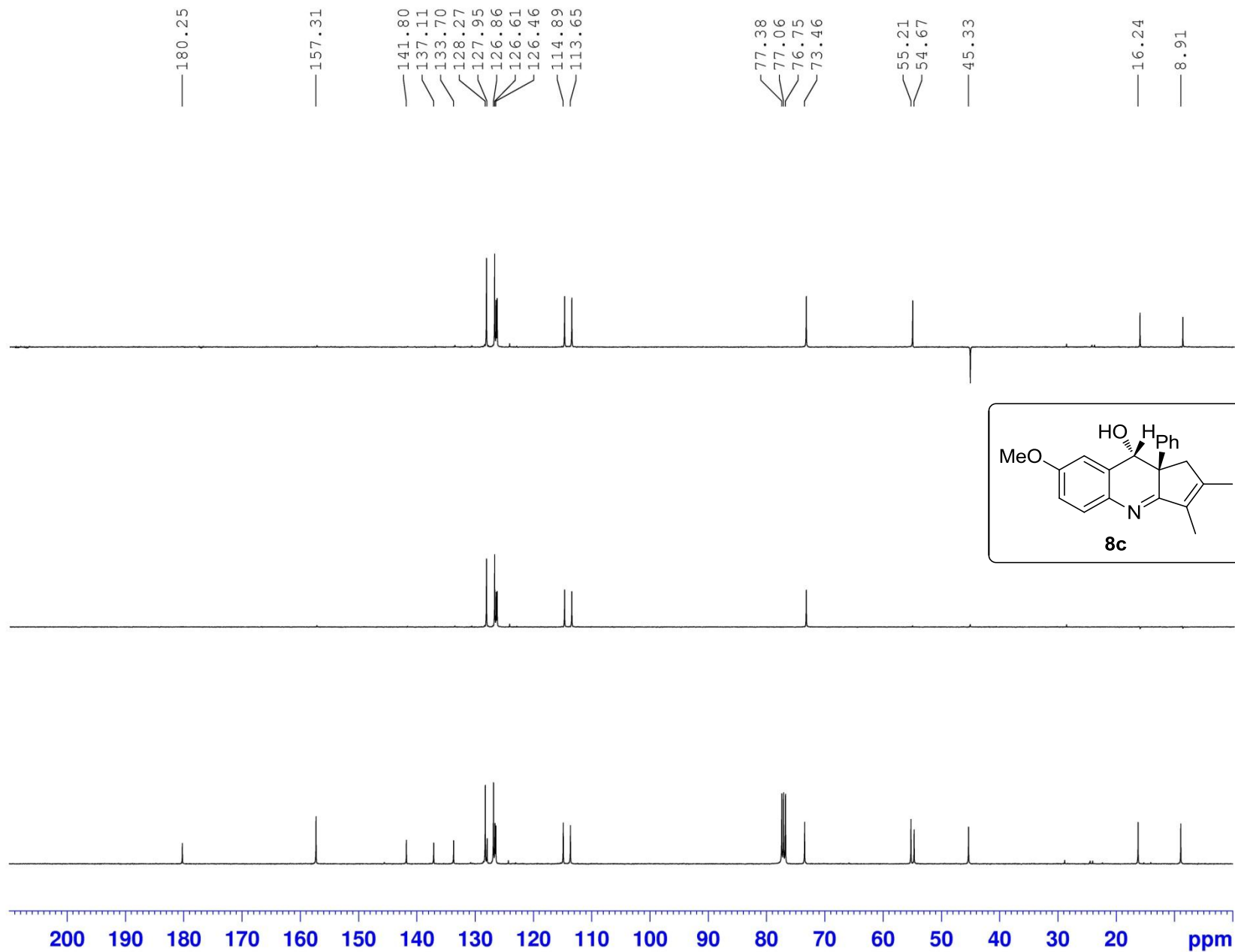


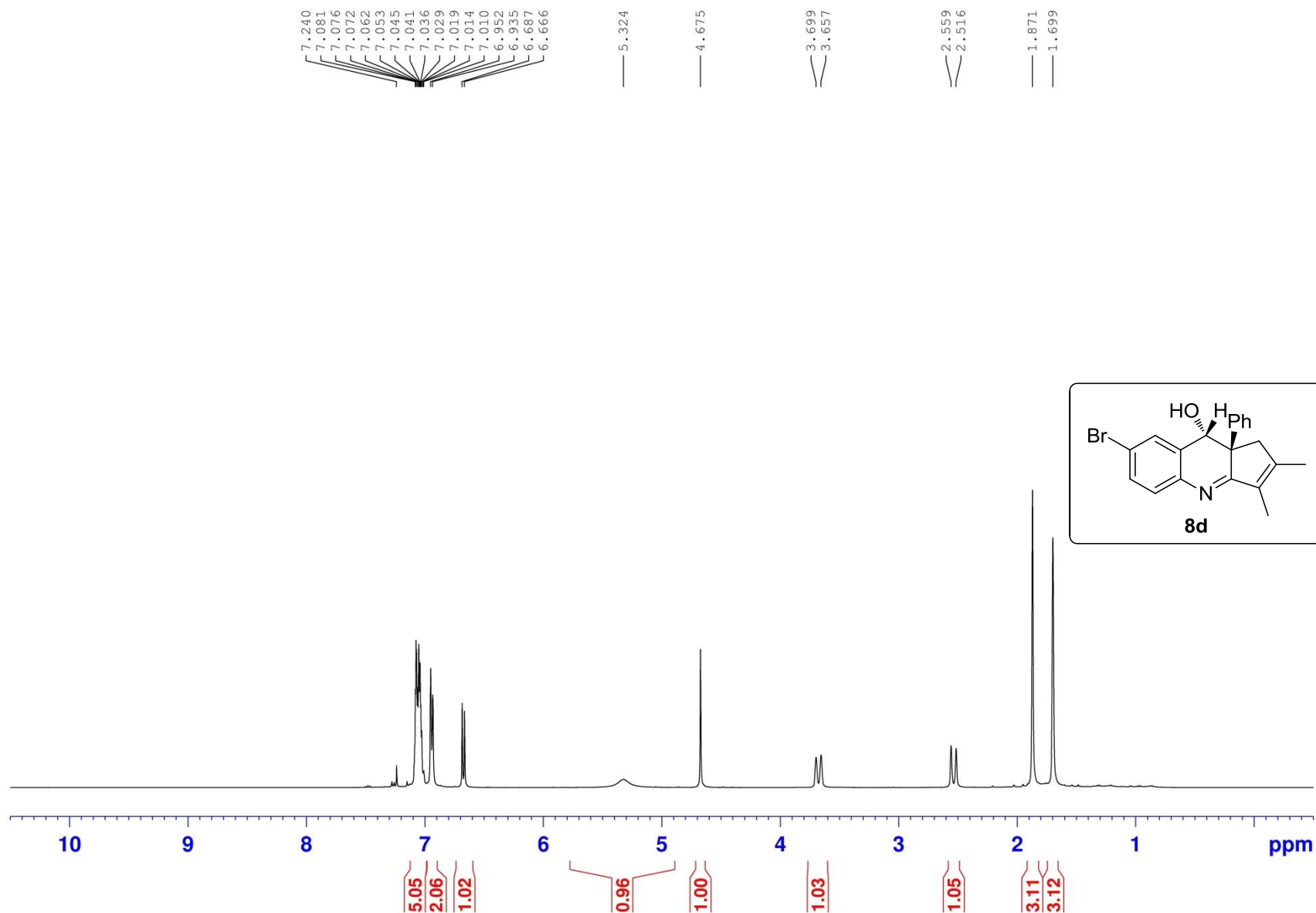


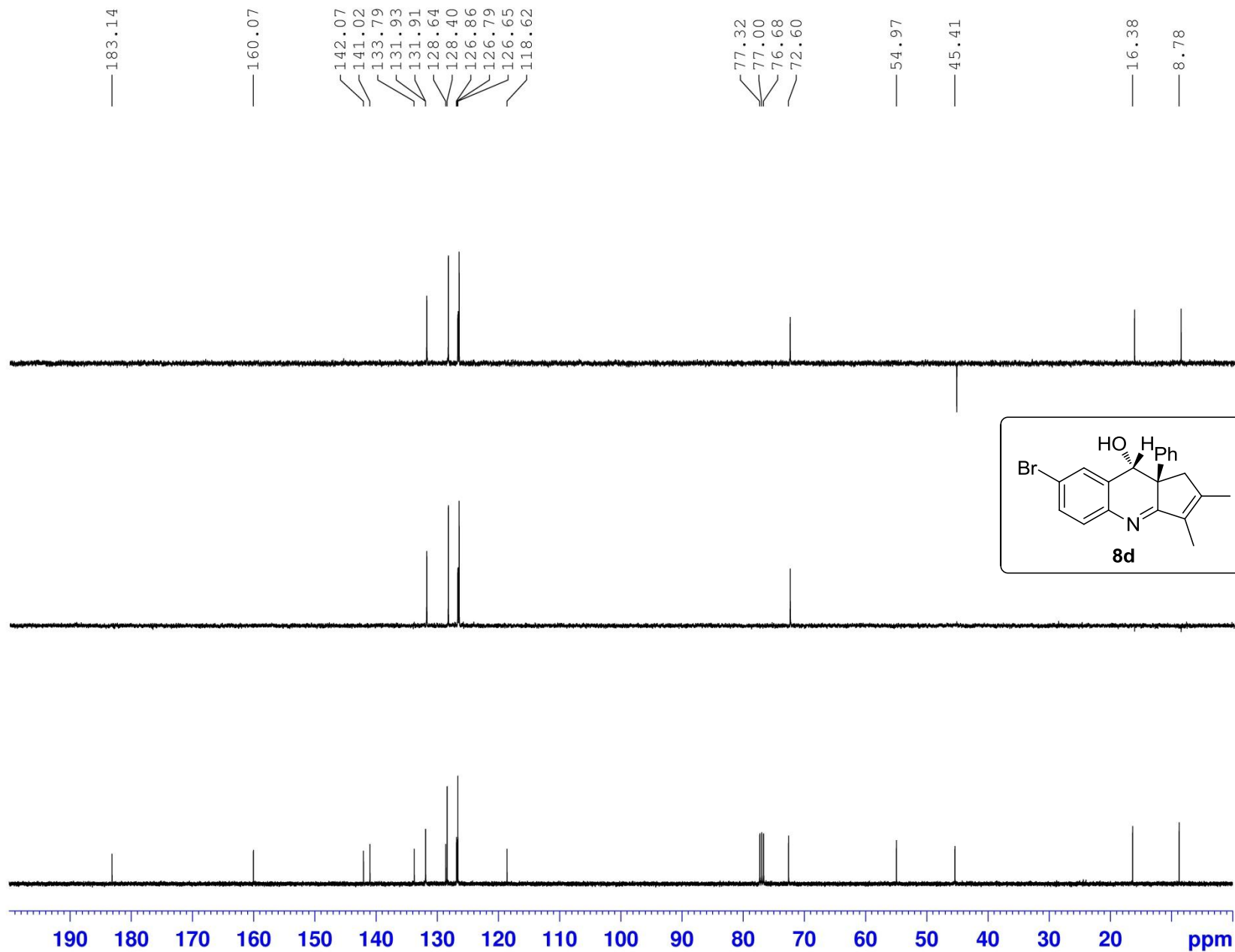


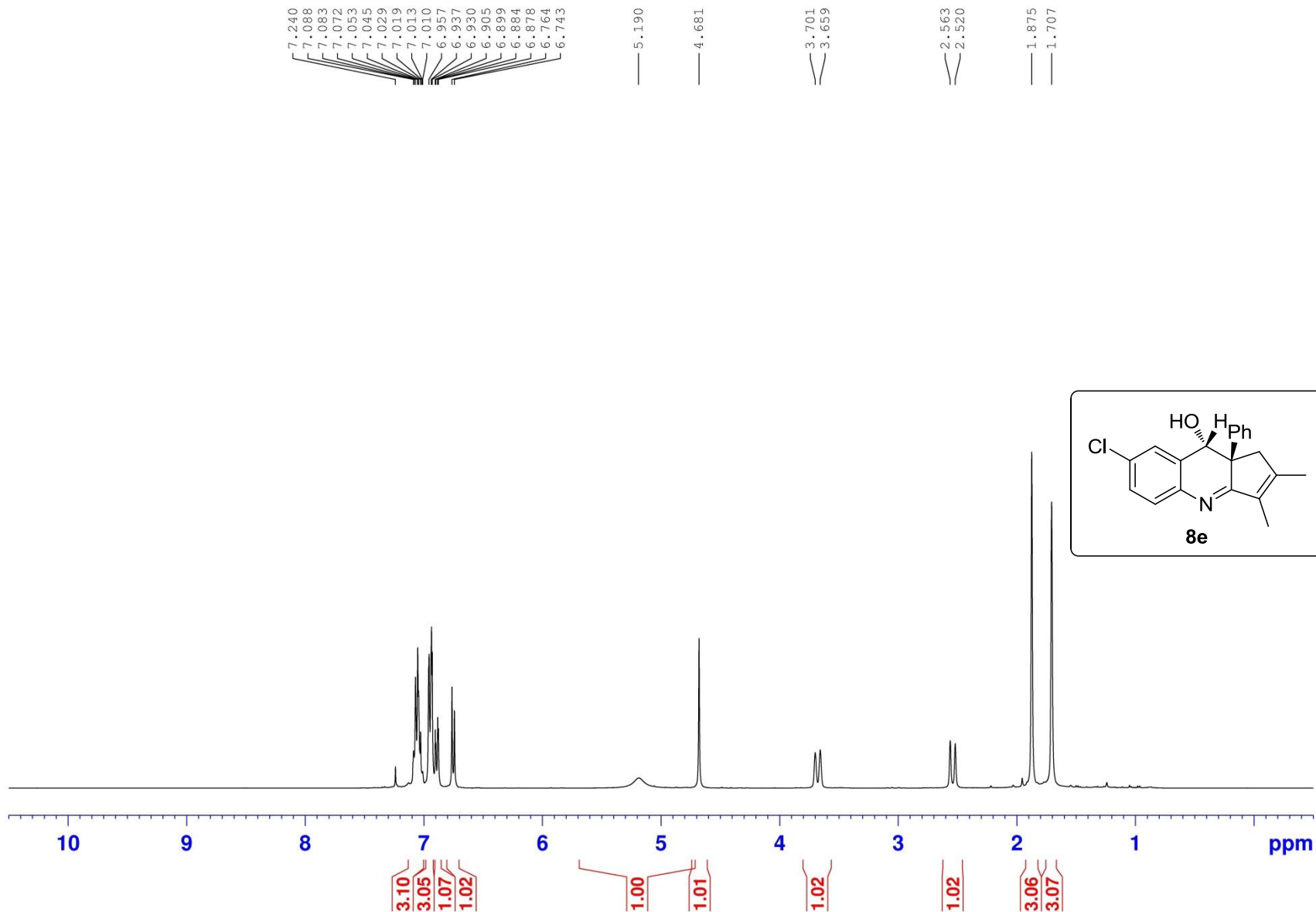


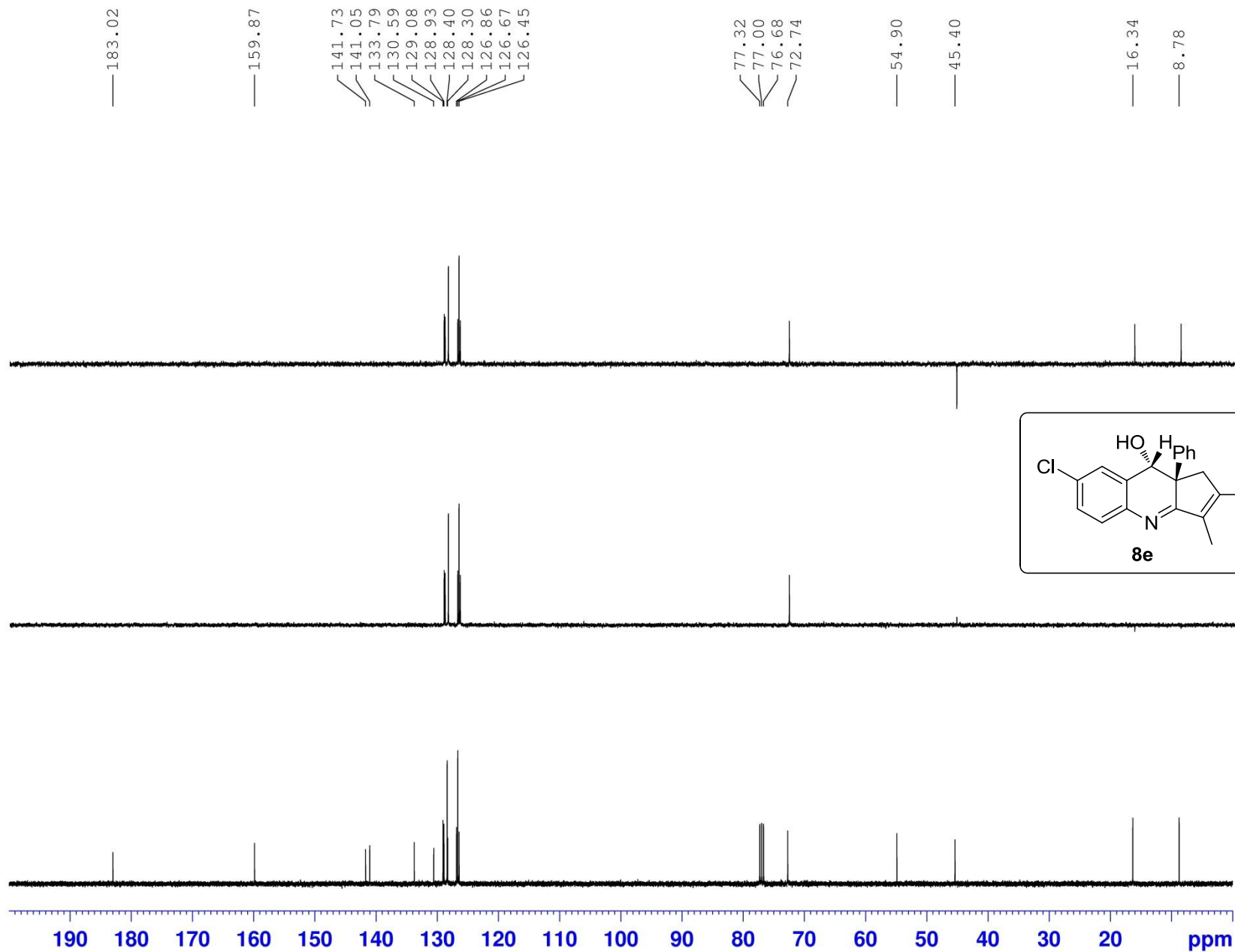


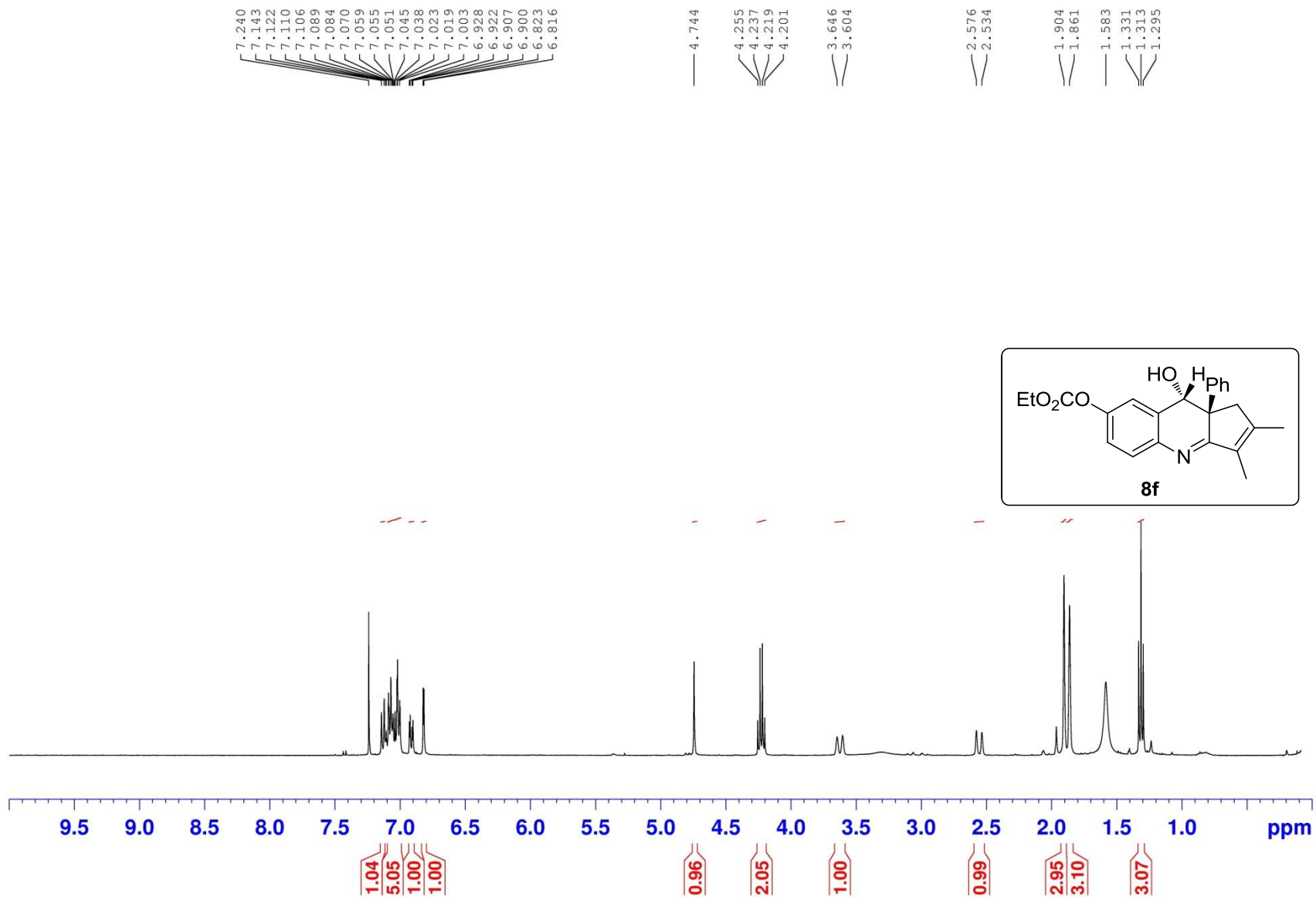


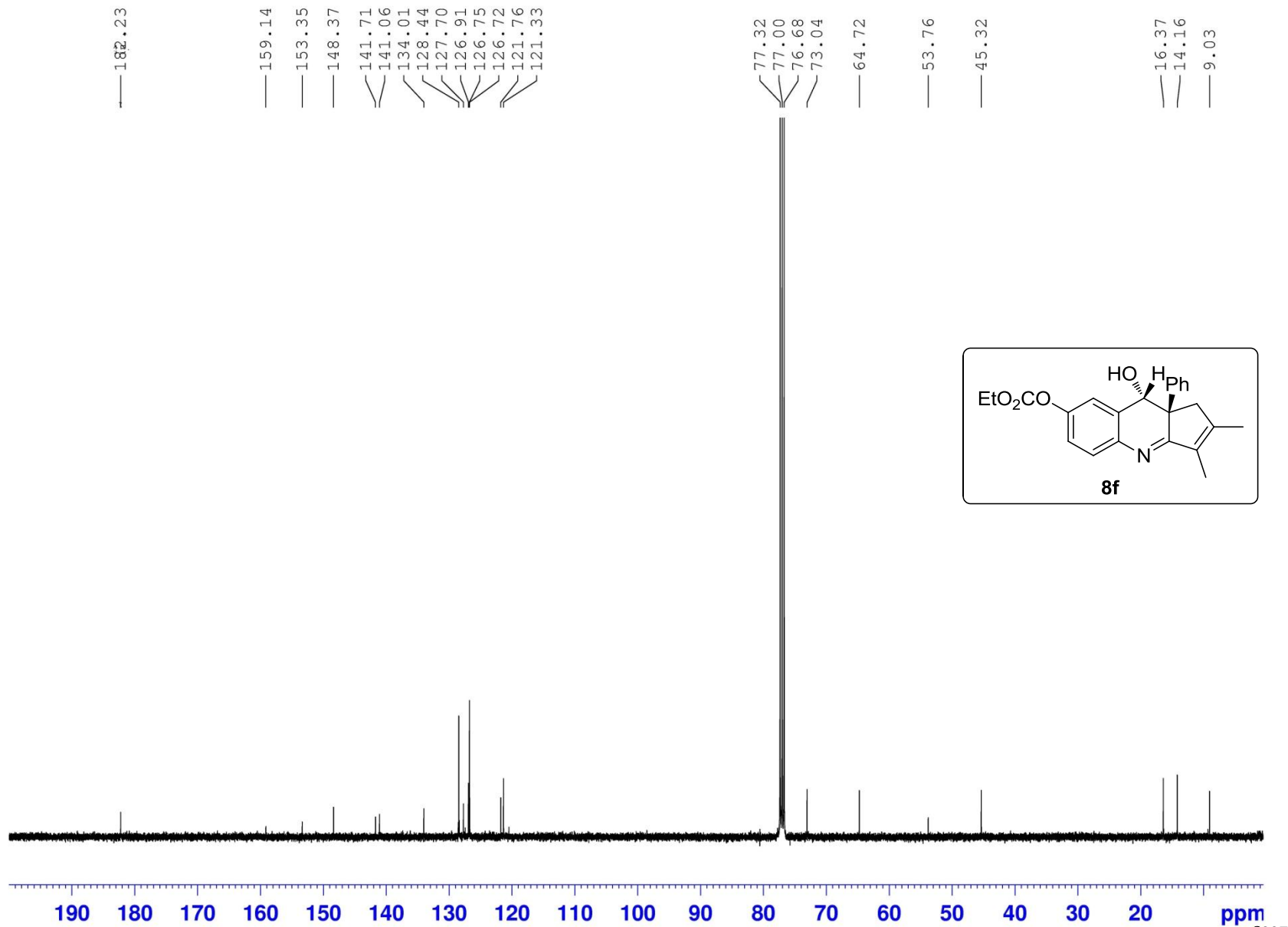


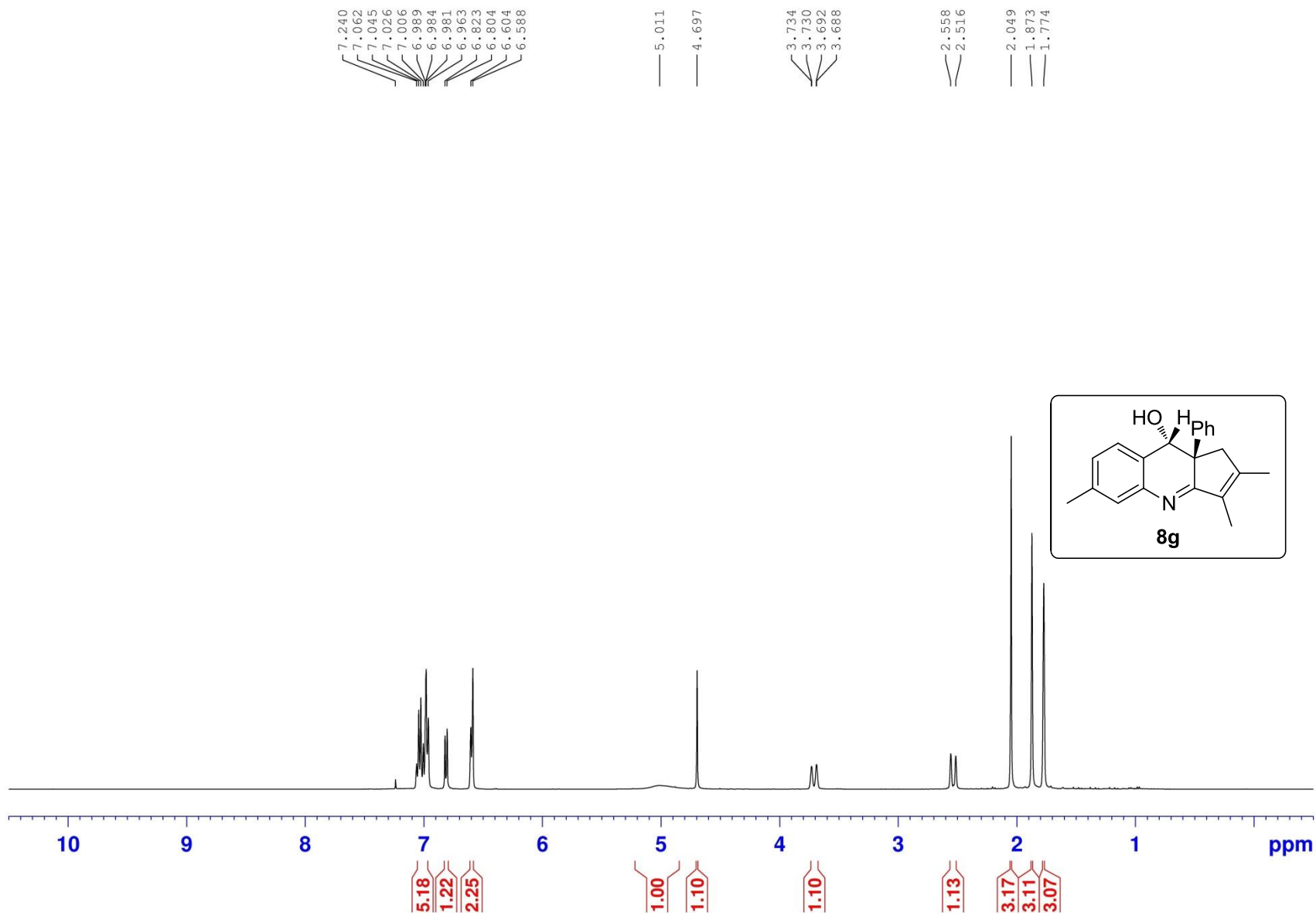


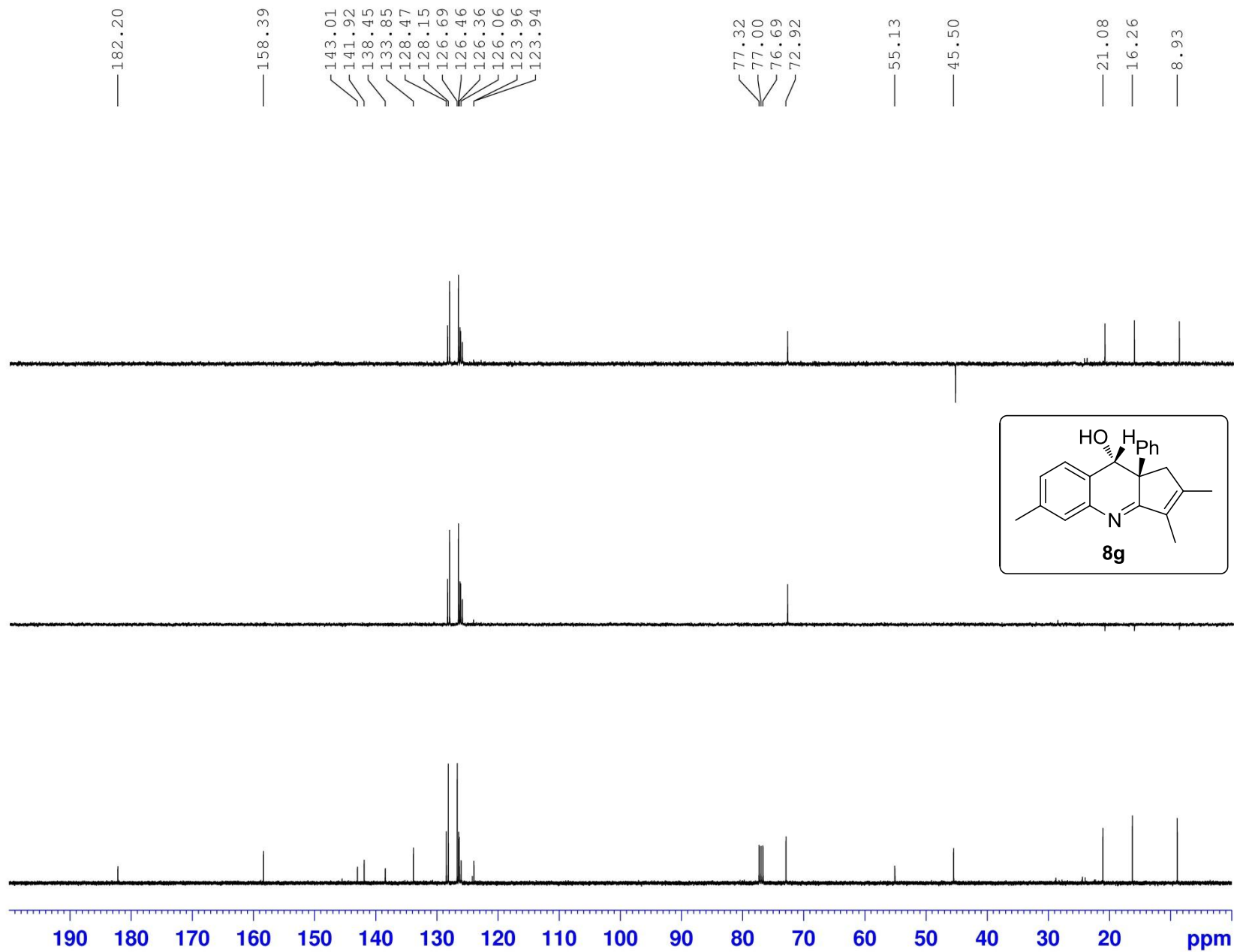


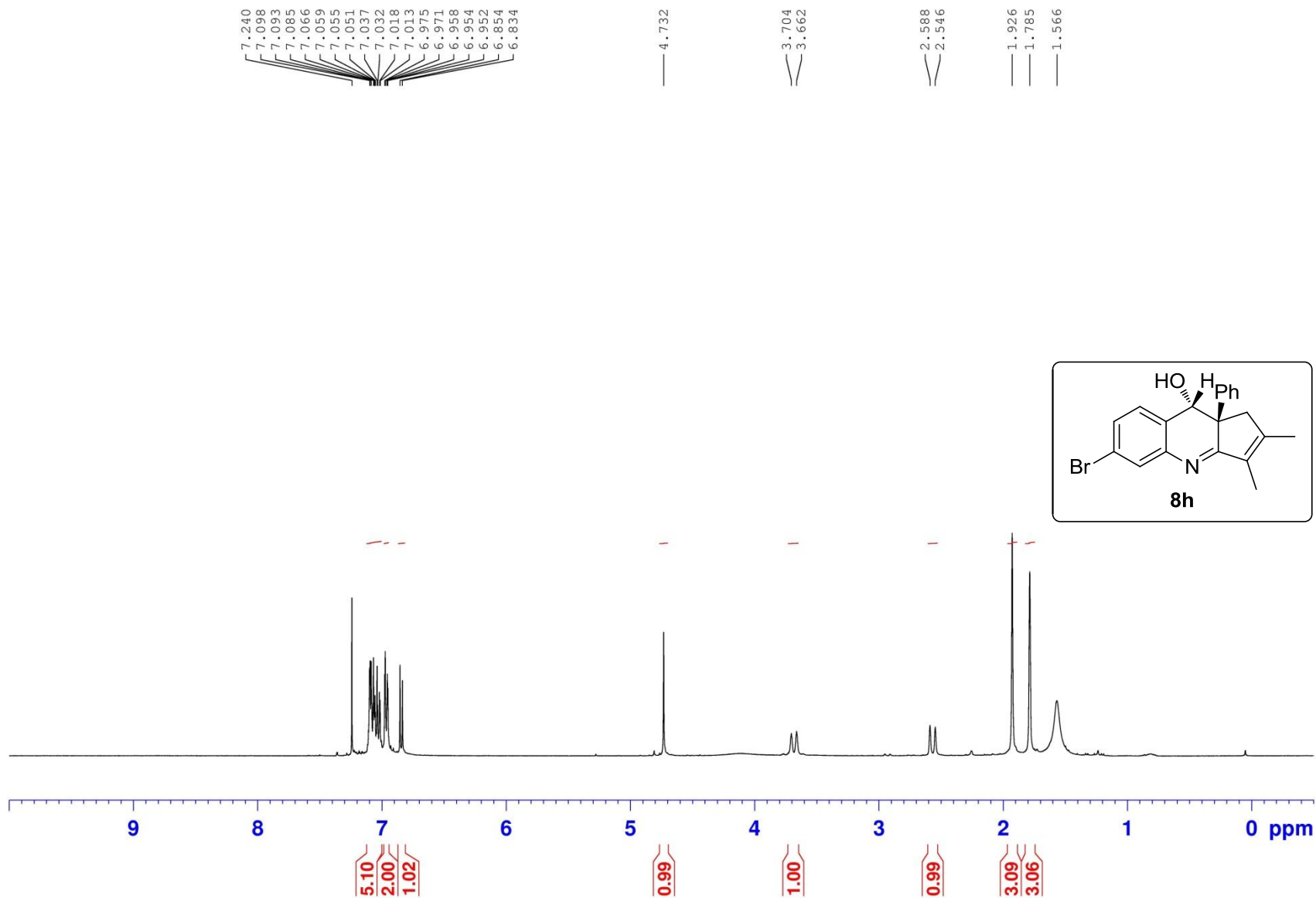


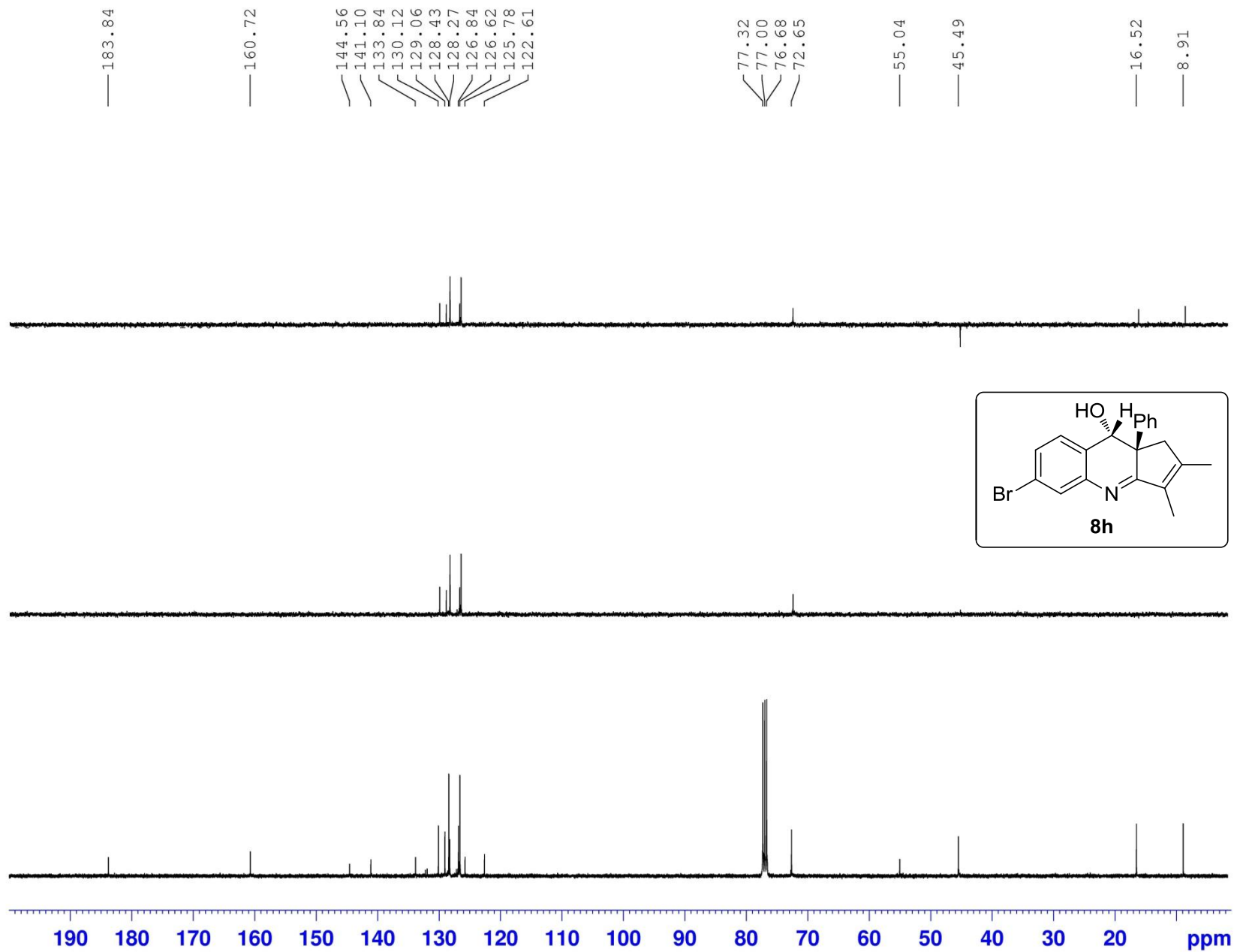


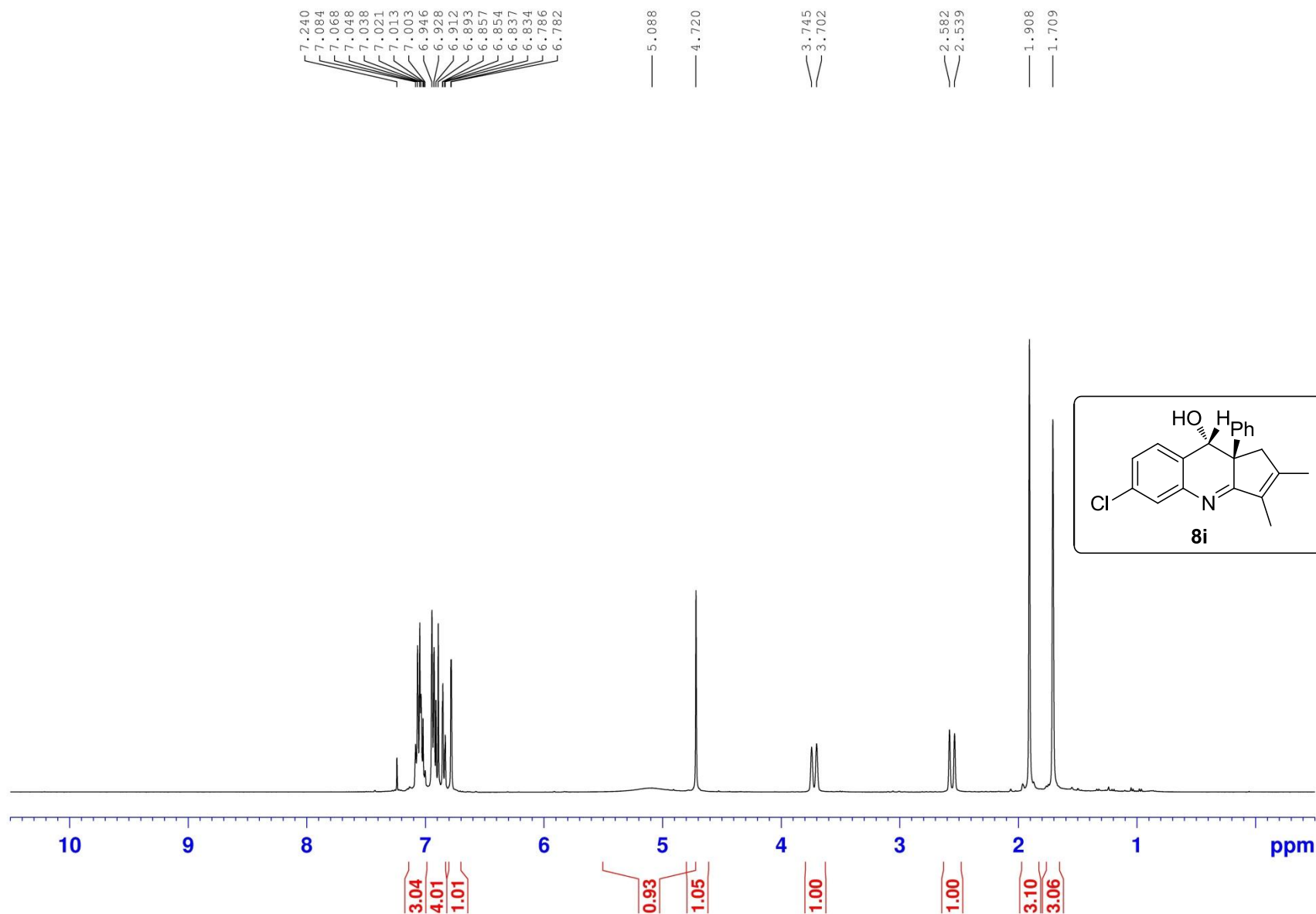


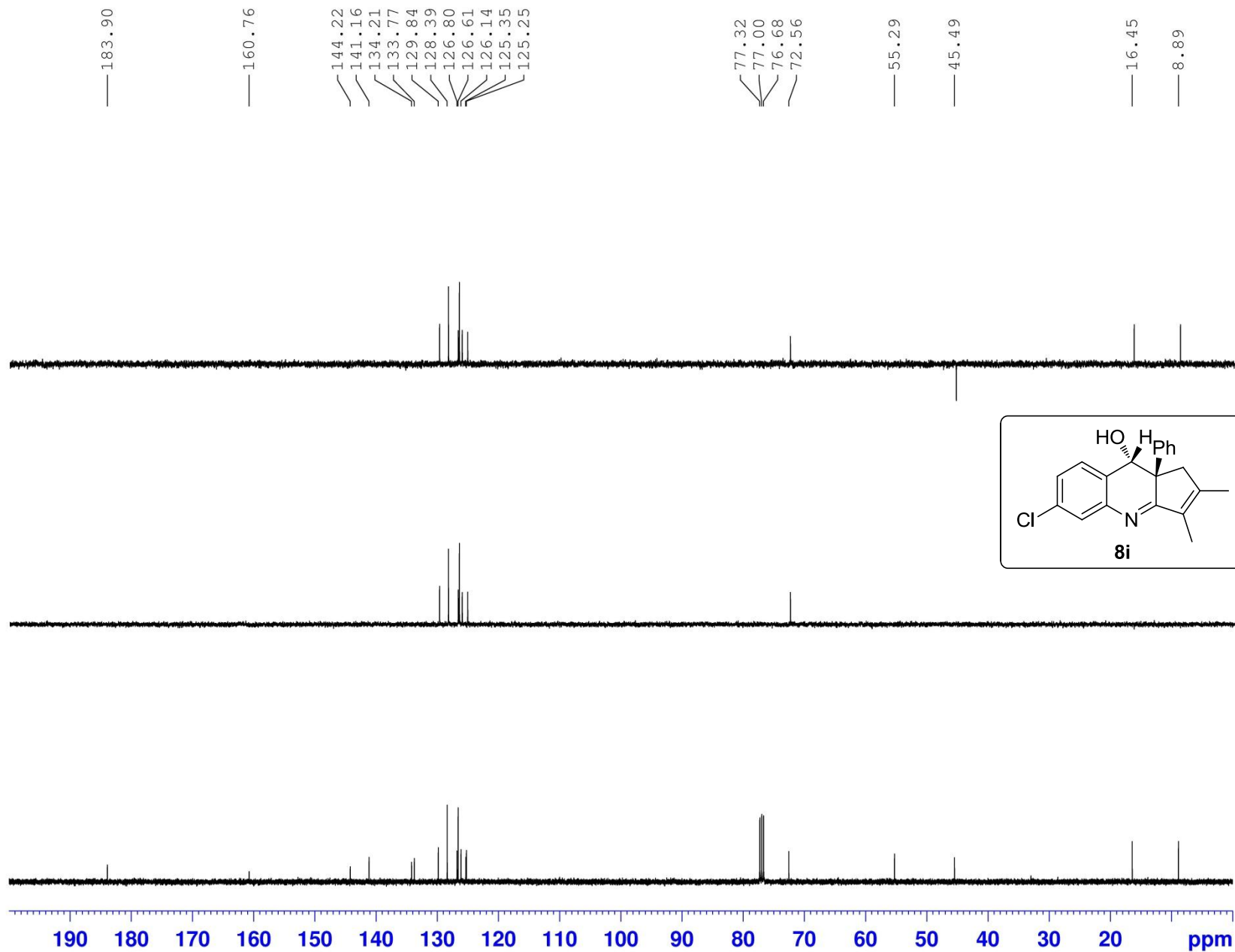


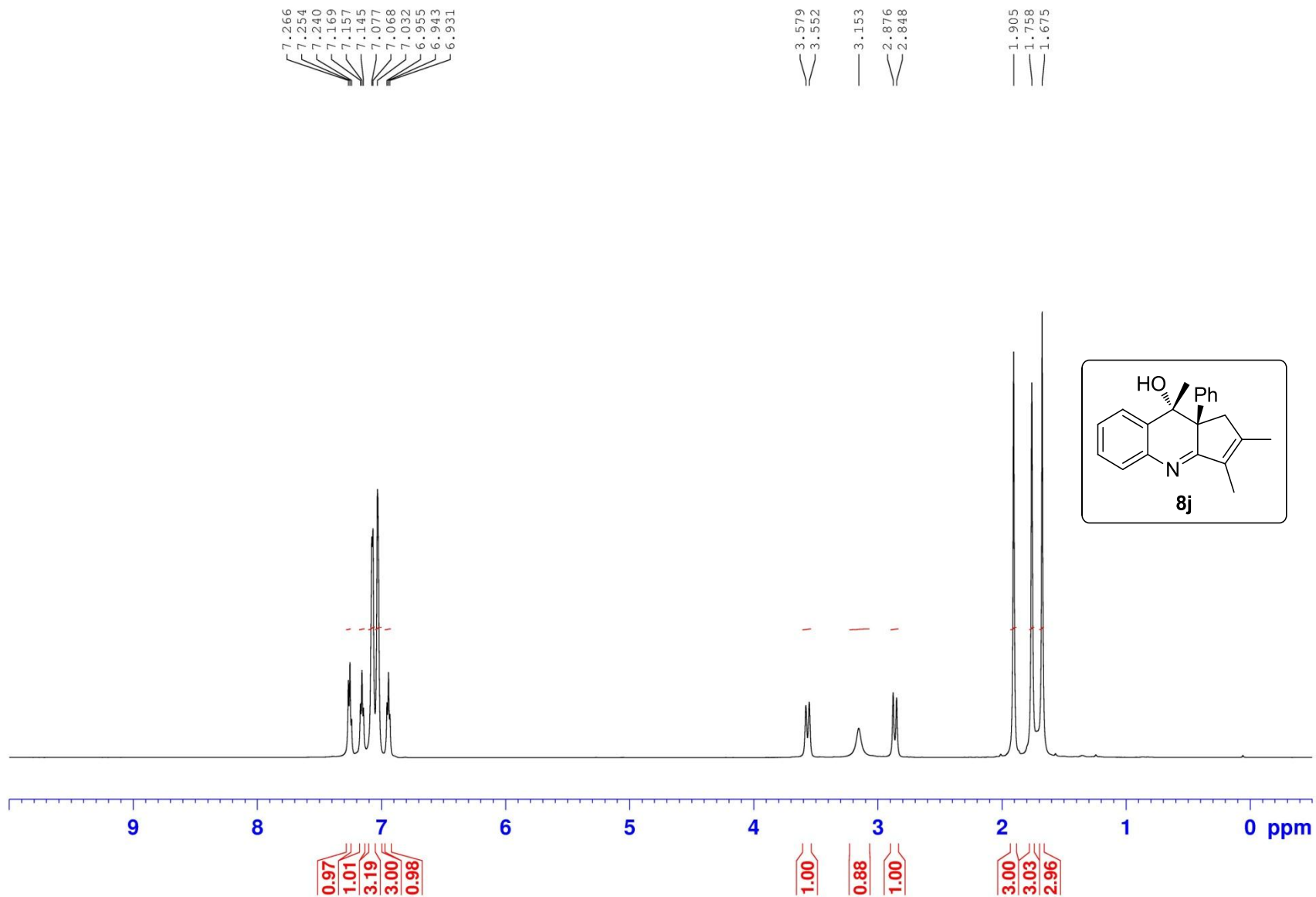


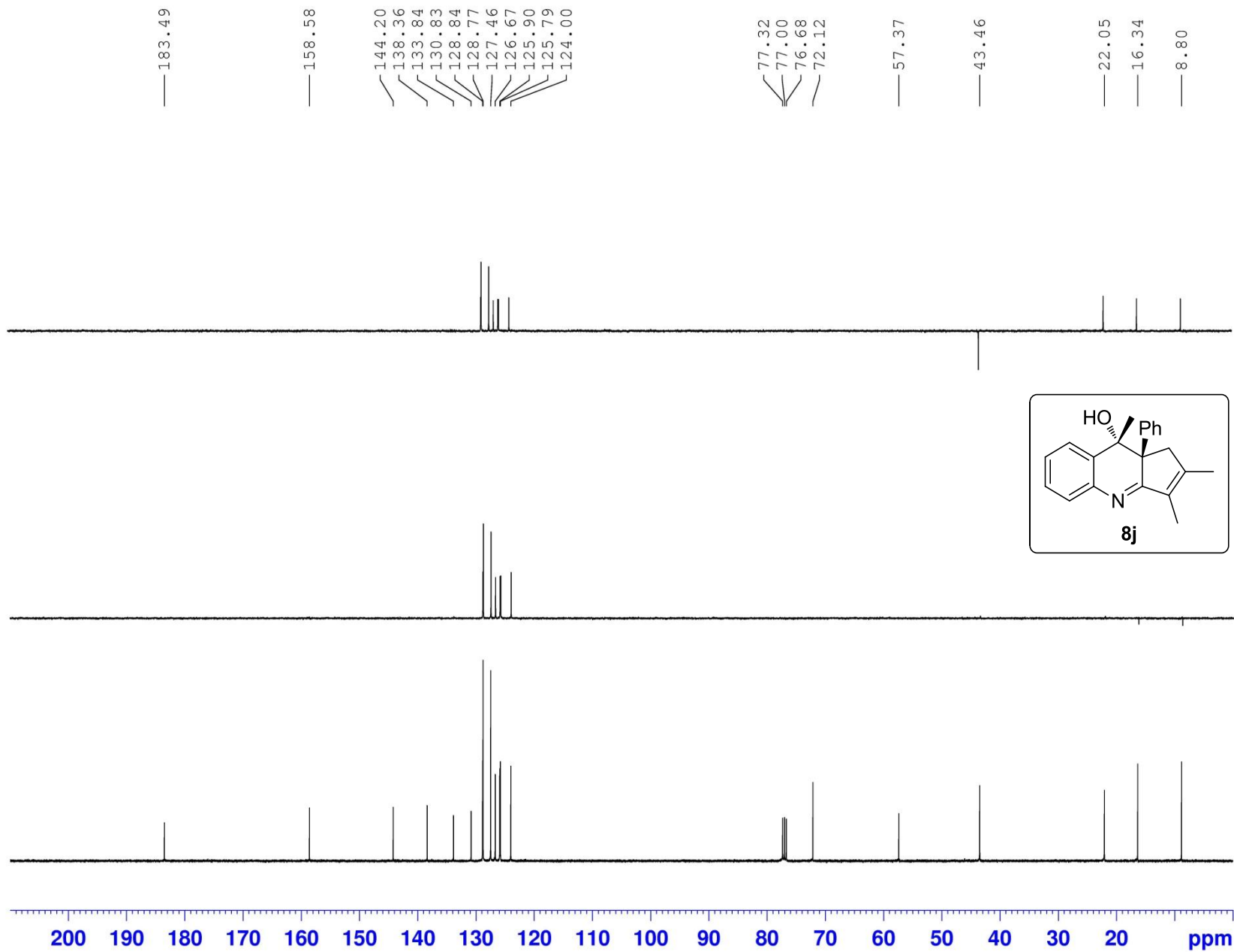


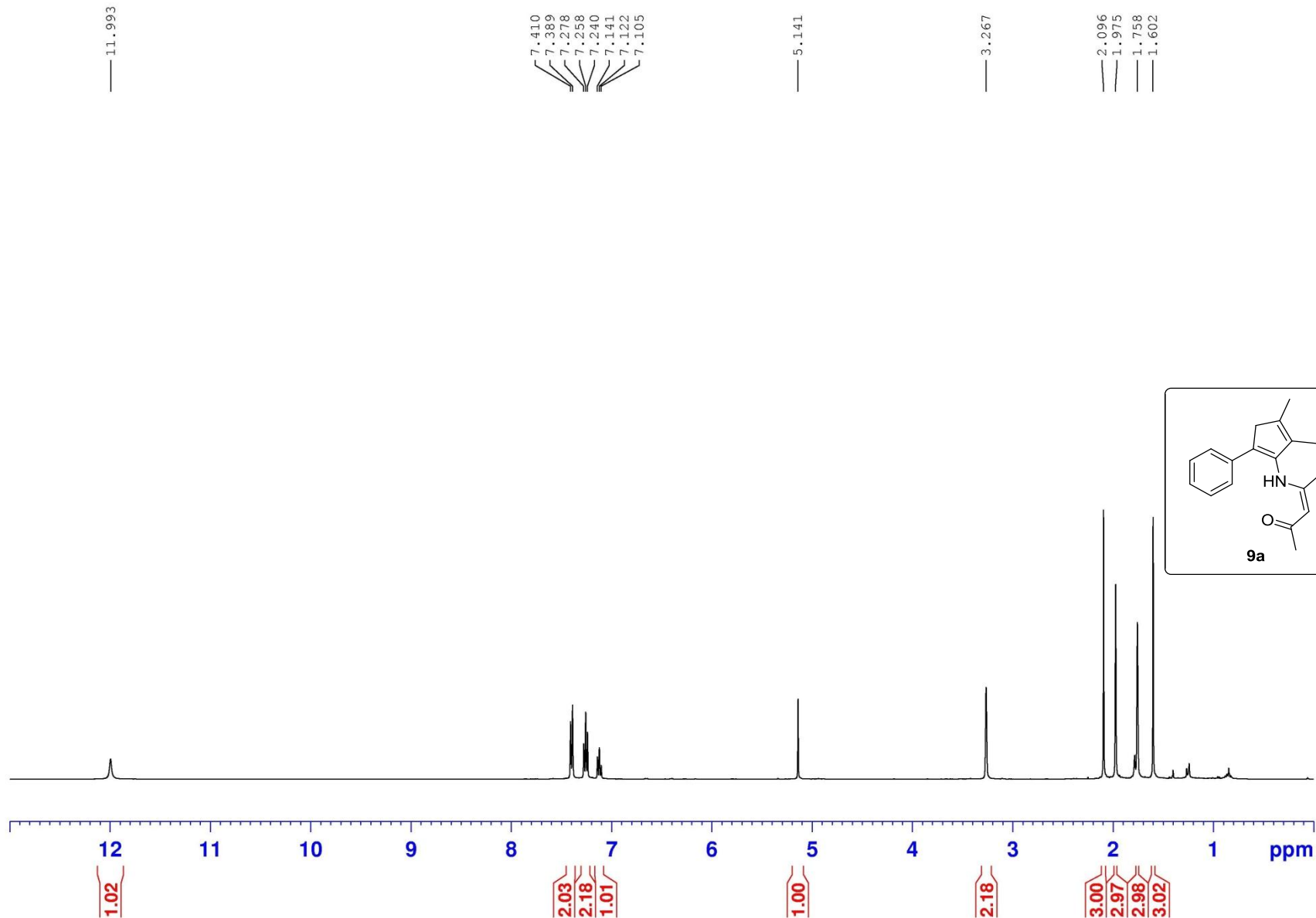


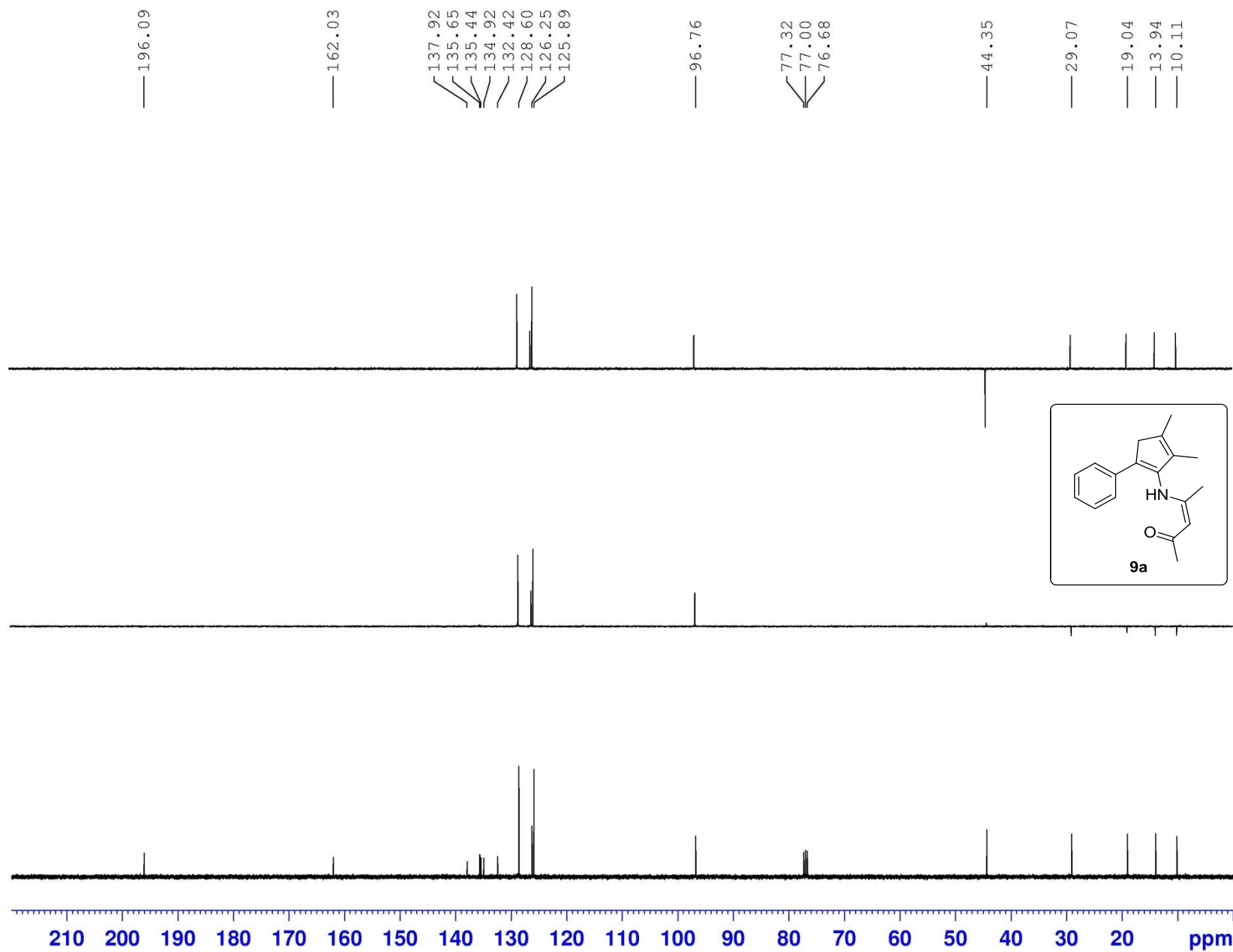


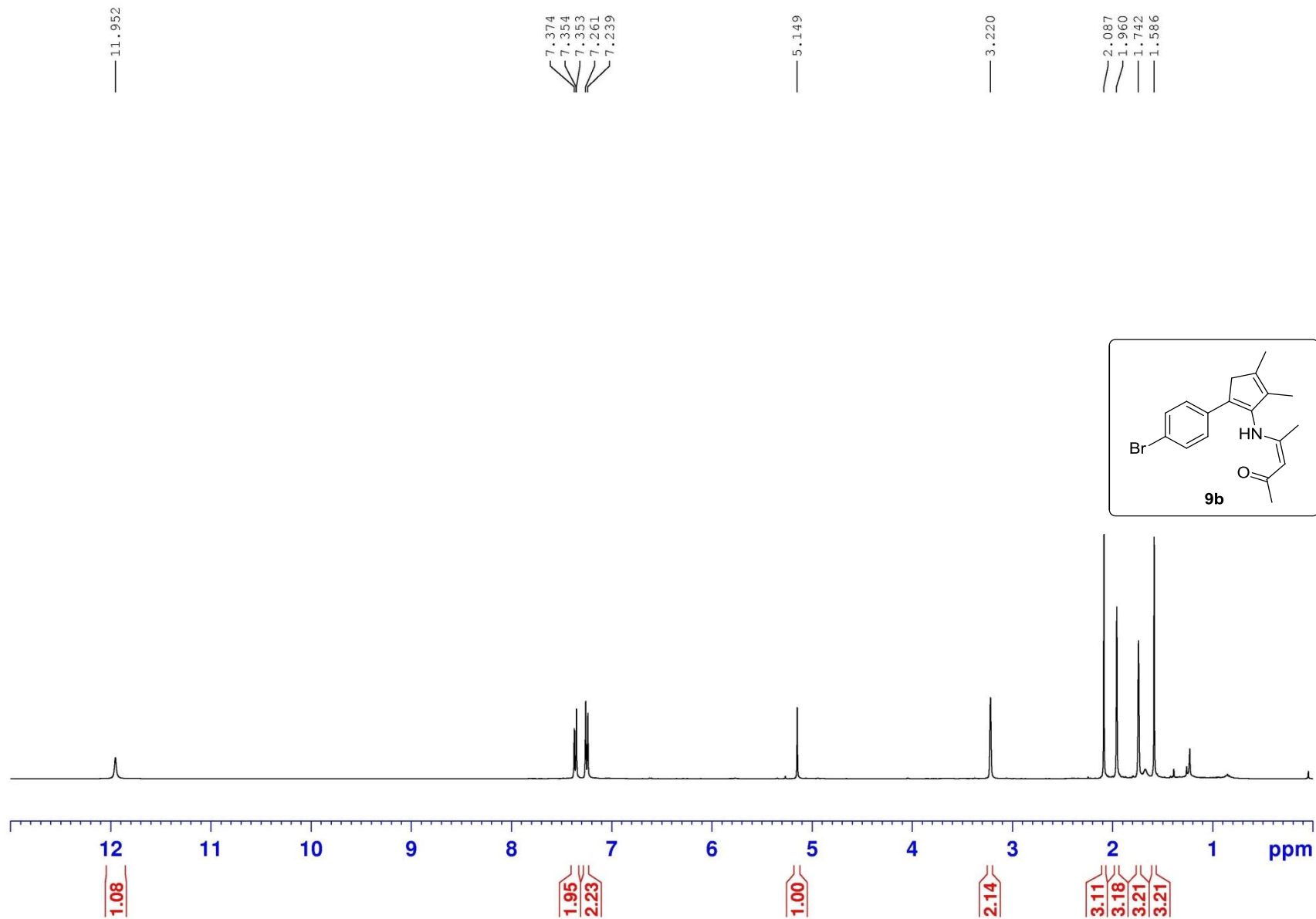


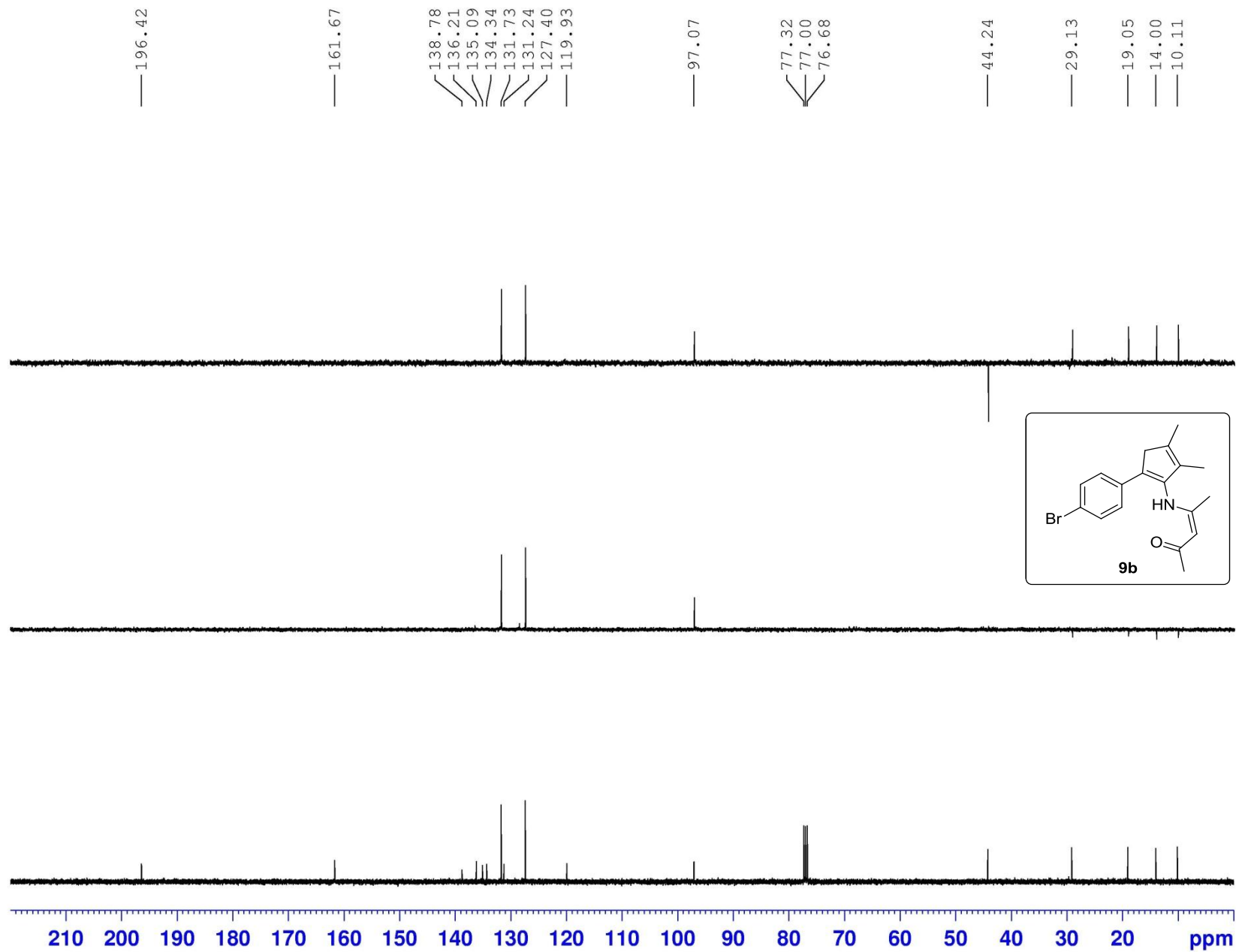




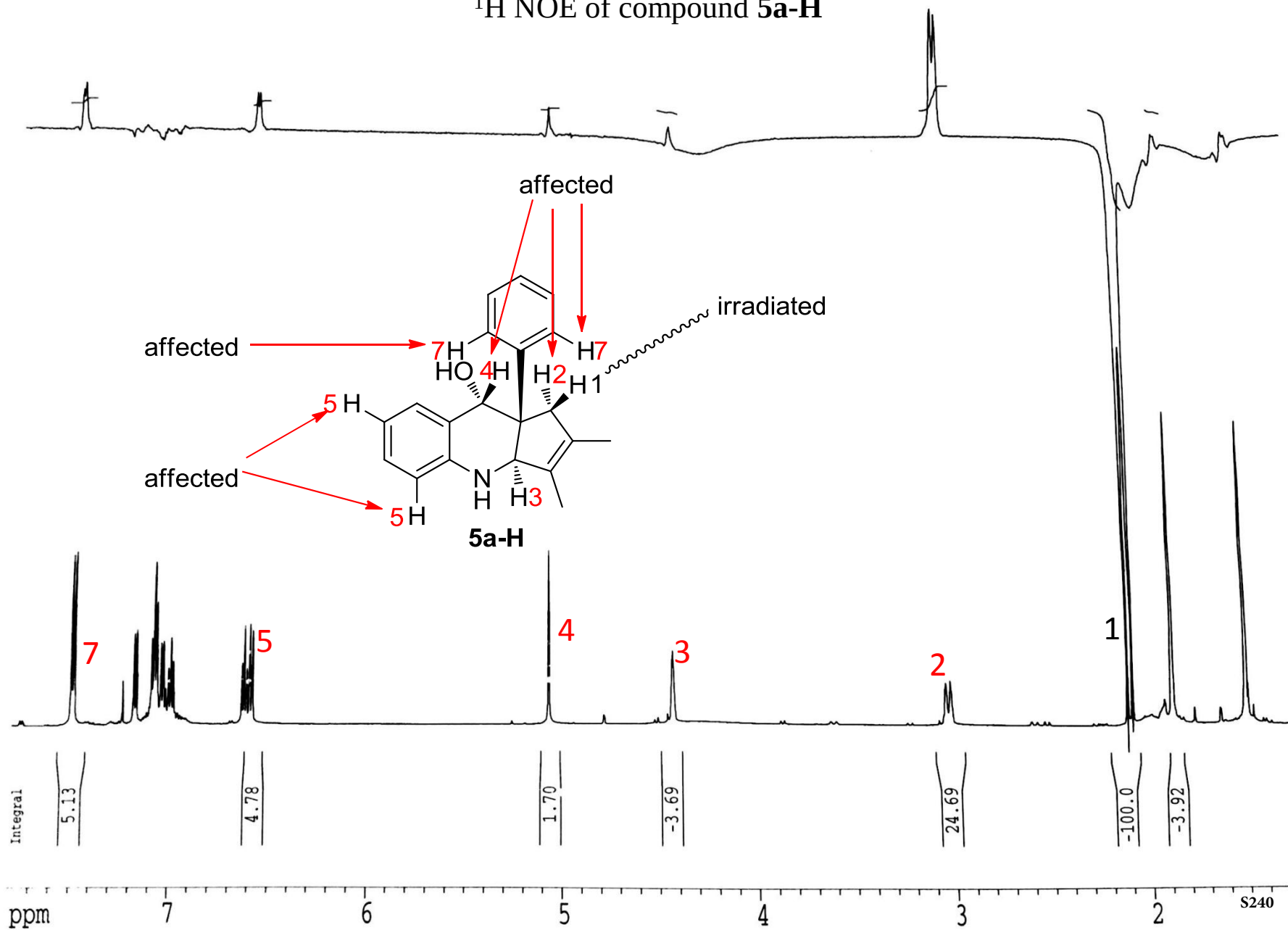




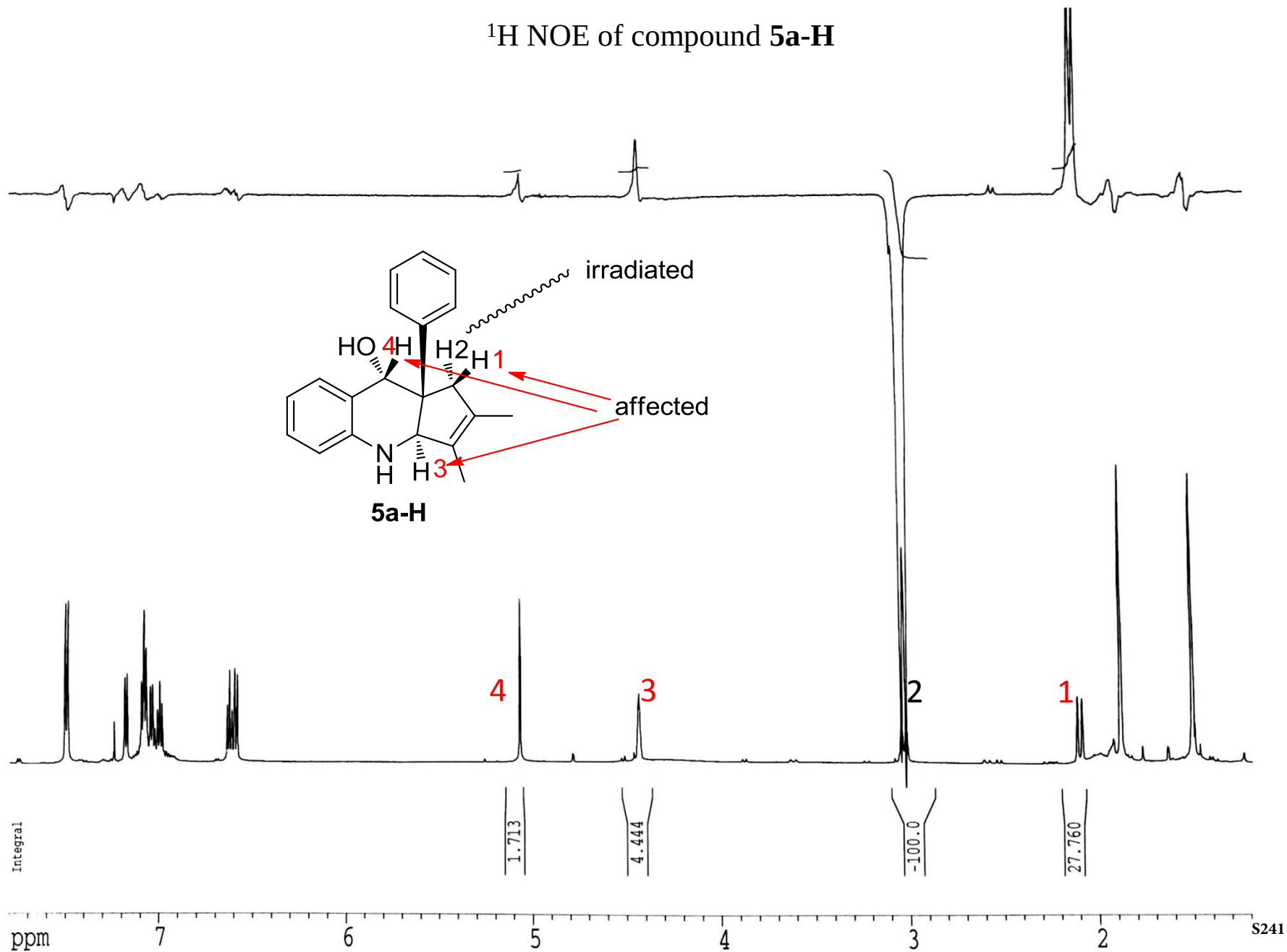




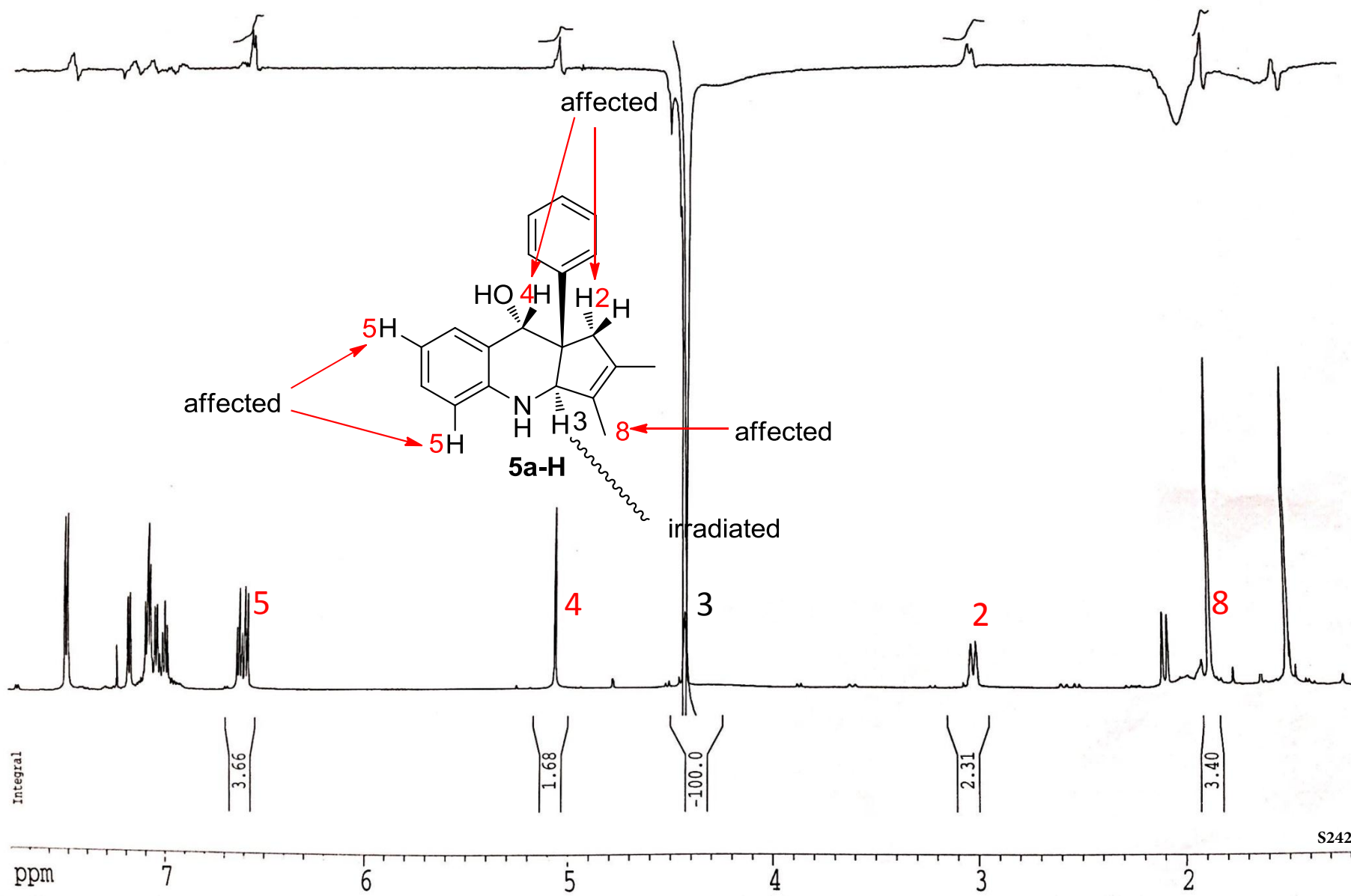
^1H NOE of compound **5a-H**



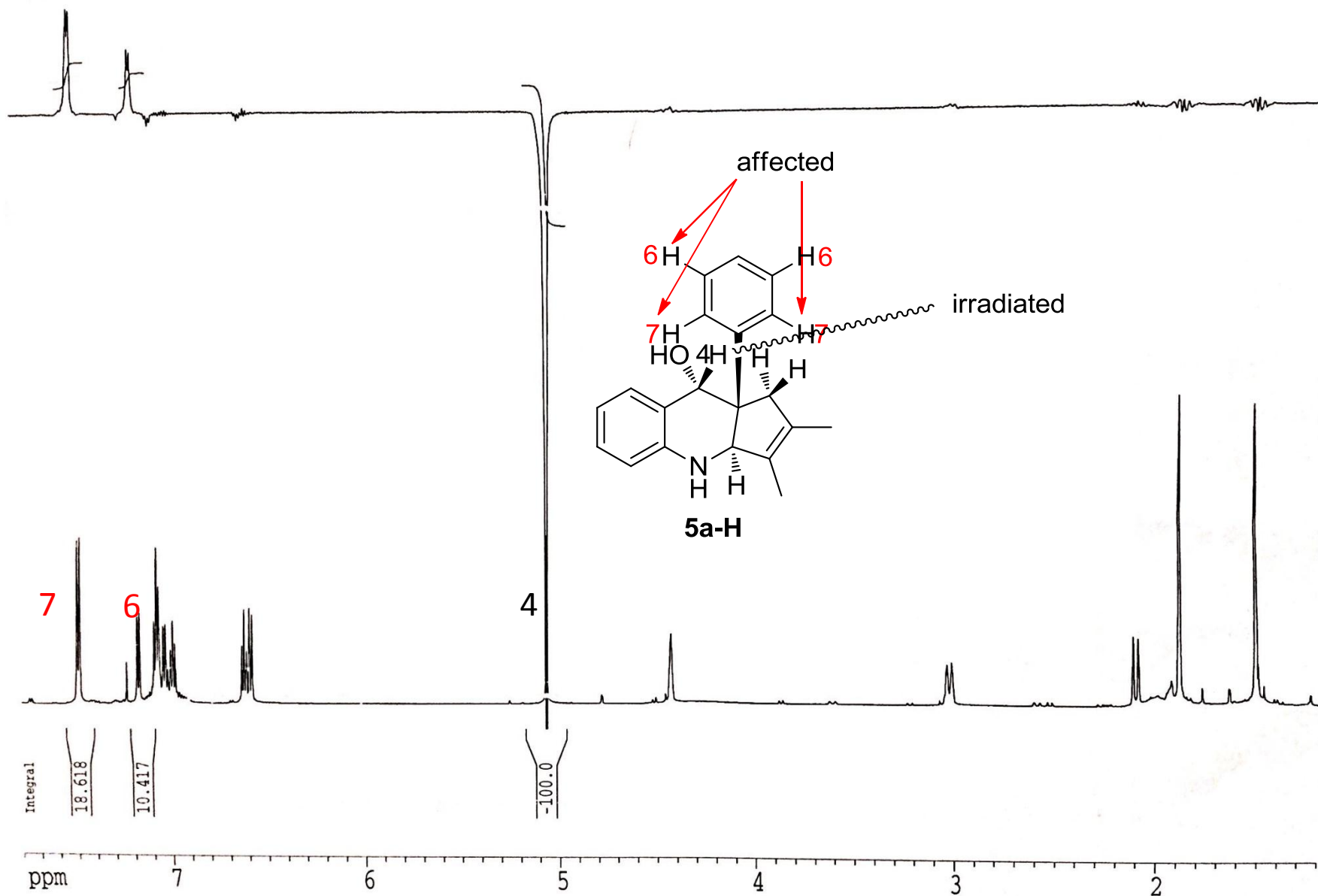
^1H NOE of compound **5a-H**



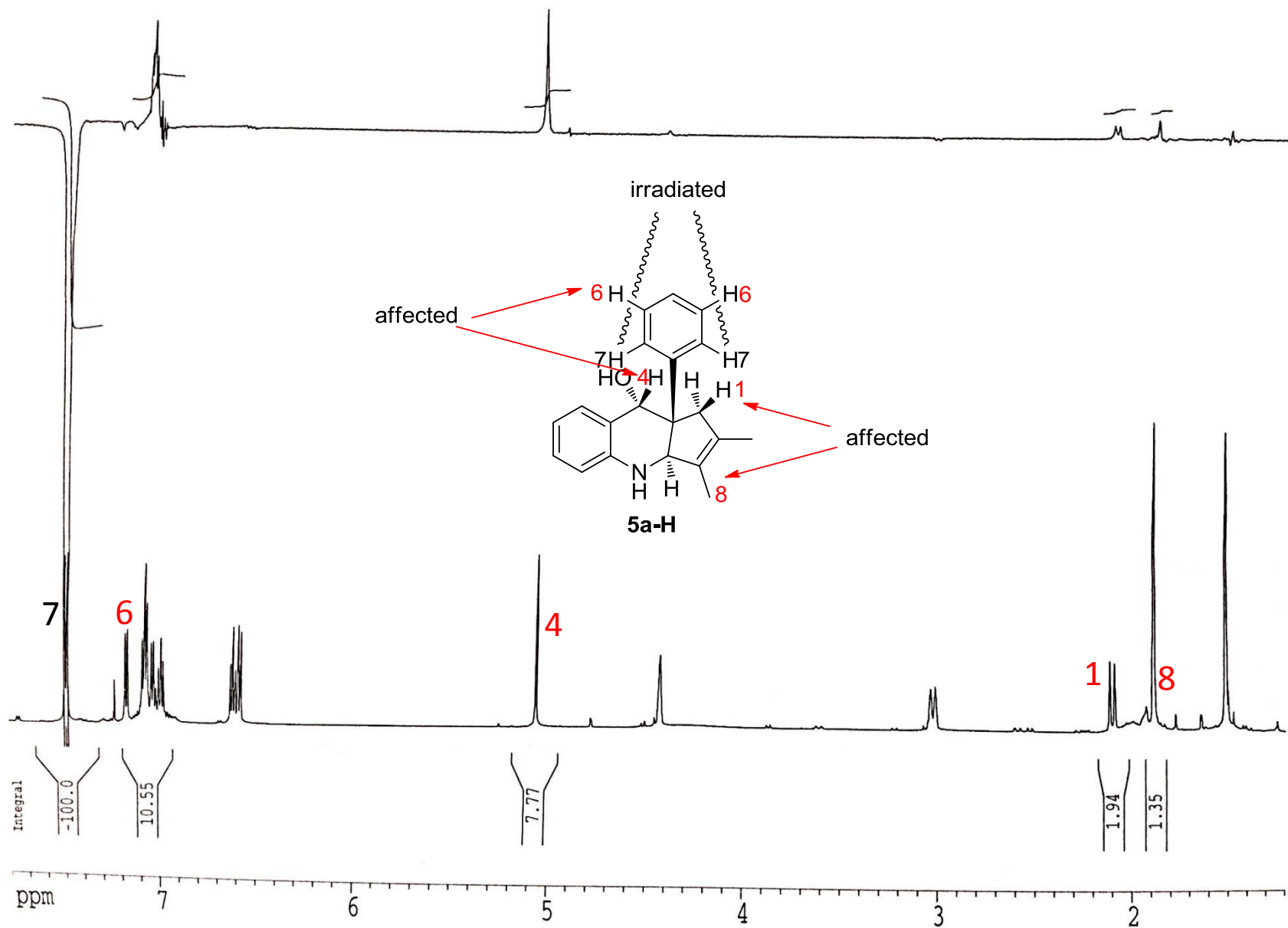
^1H NOE of compound **5a-H**



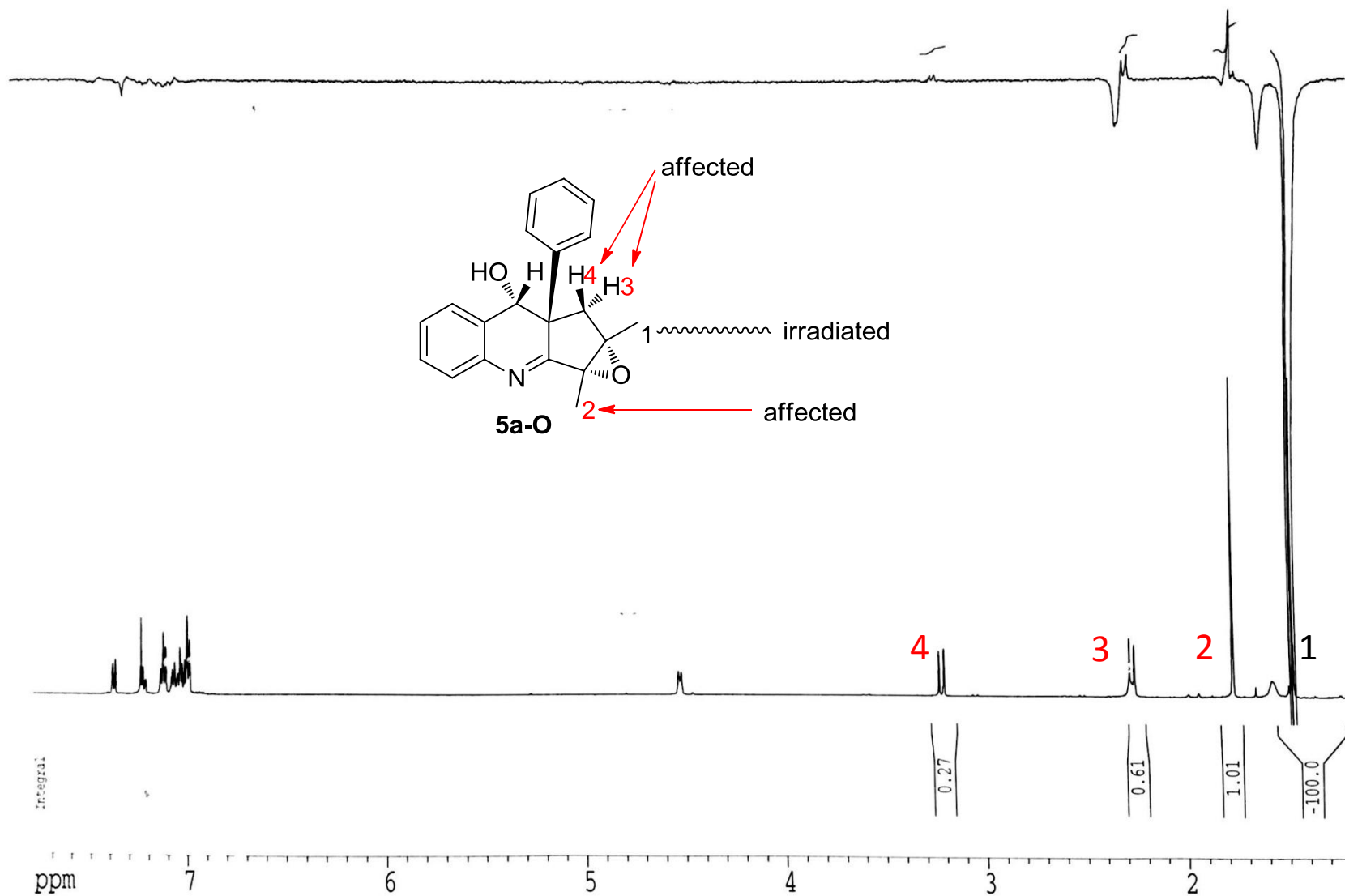
^1H NOE of compound **5a-H**



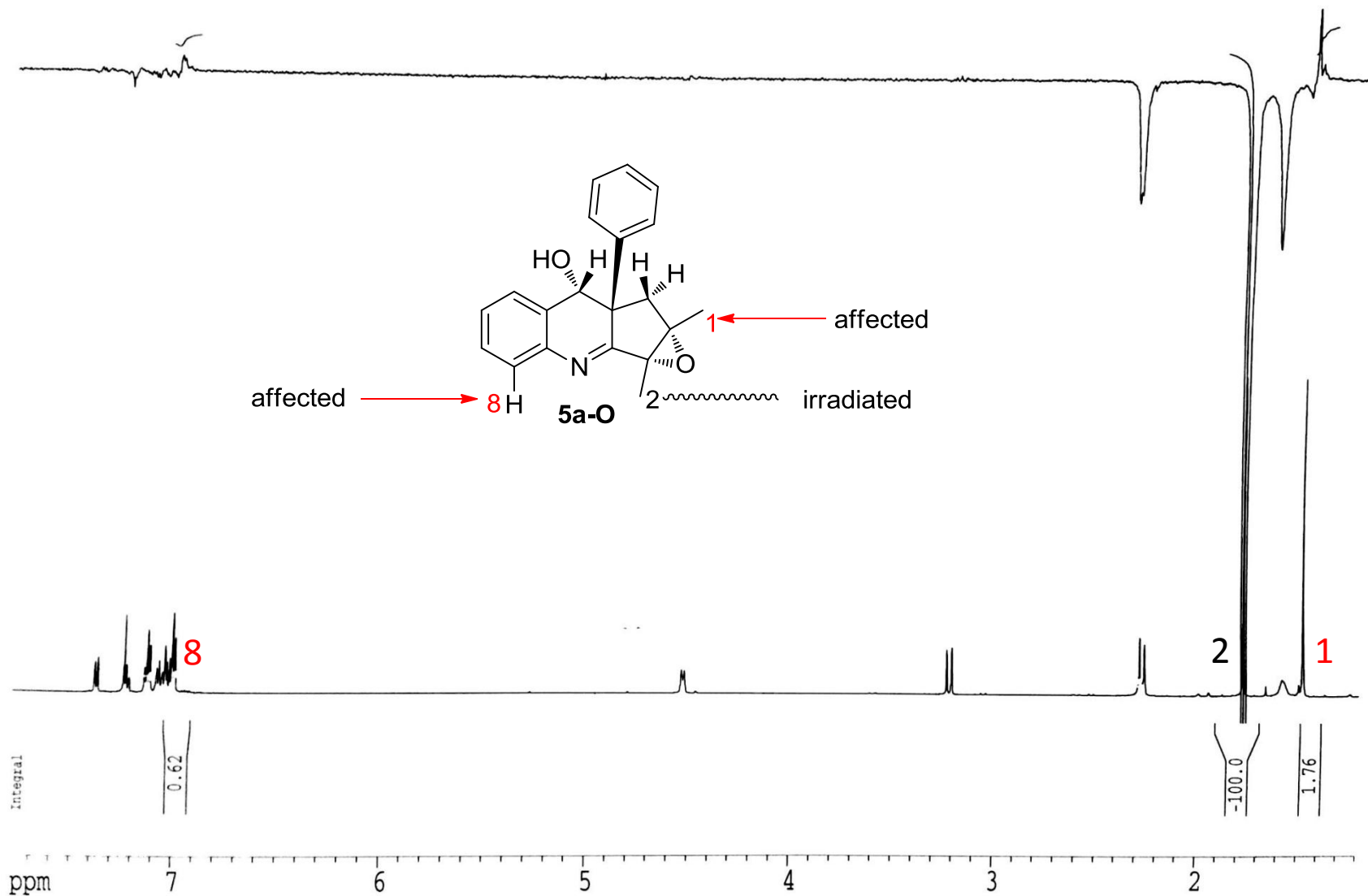
^1H NOE of compound 5a-H



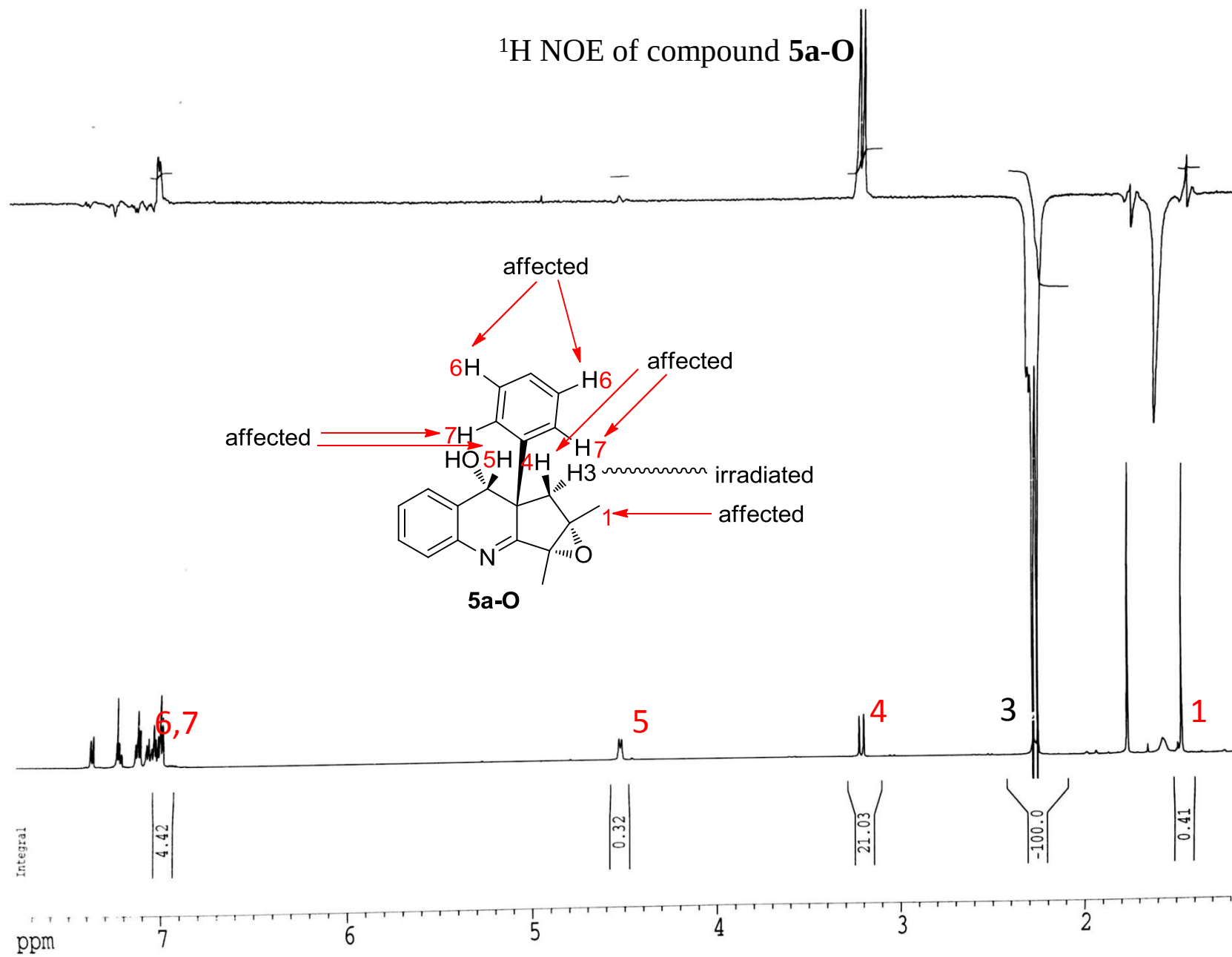
^1H NOE of compound 5a-O



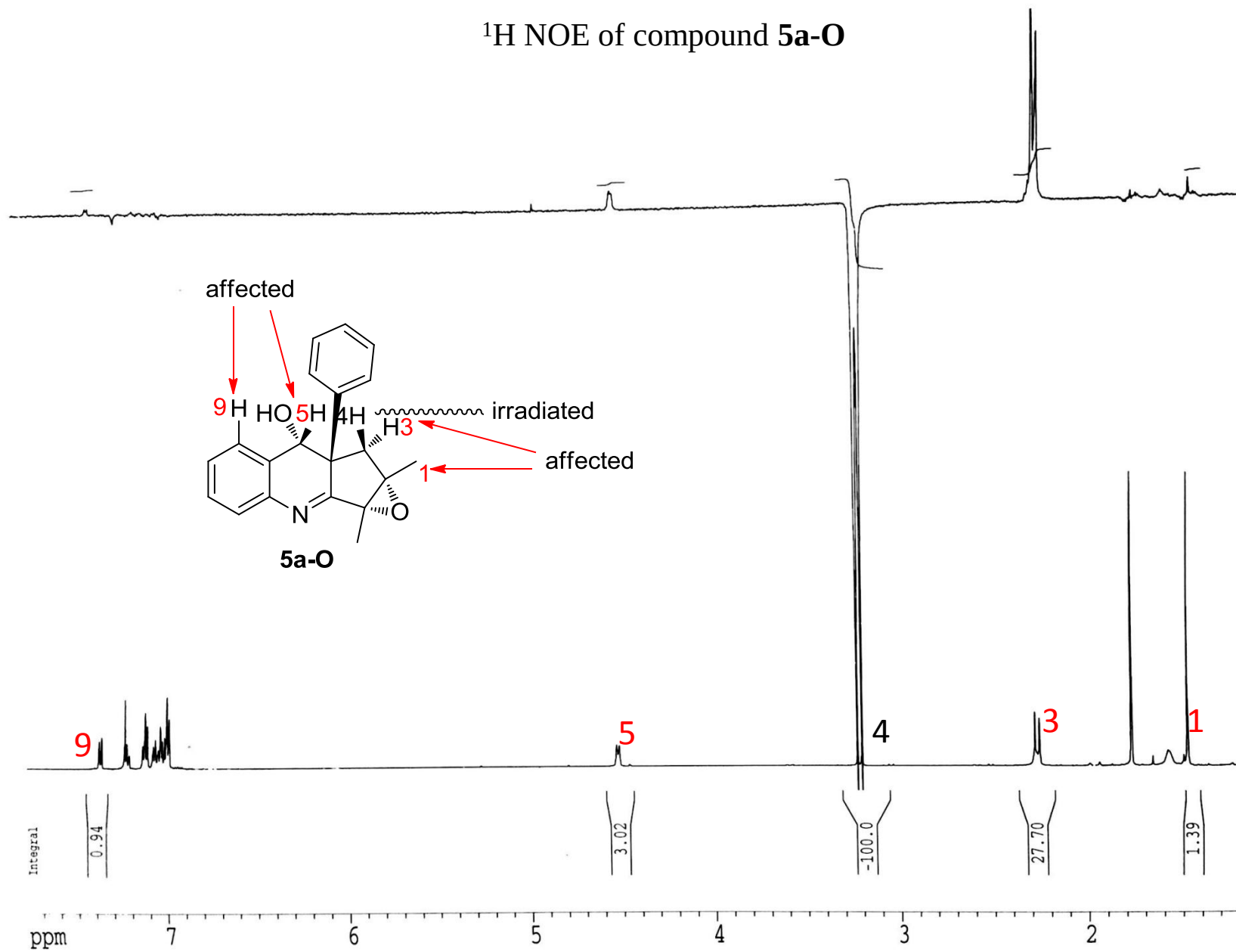
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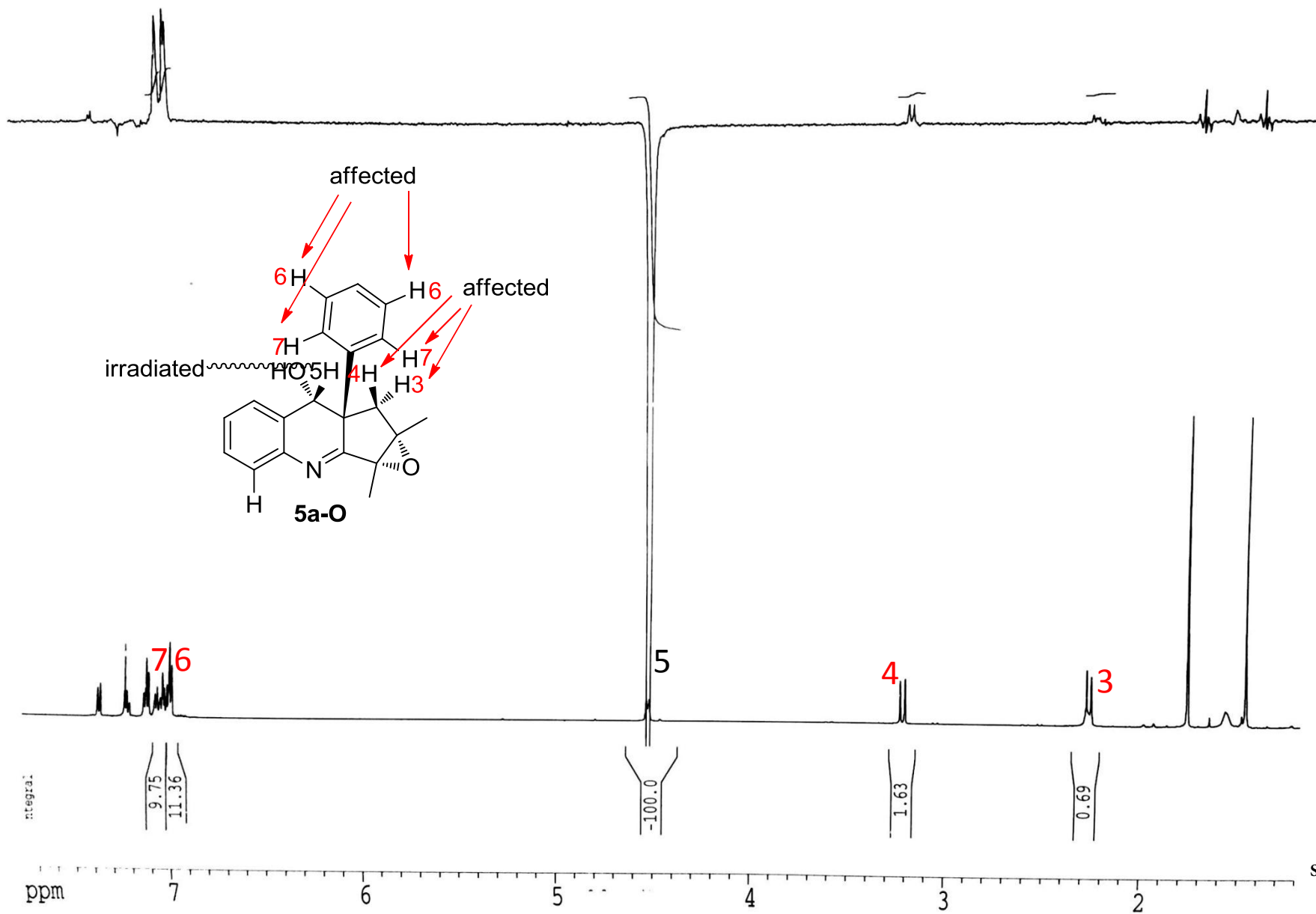
^1H NOE of compound 5a-O



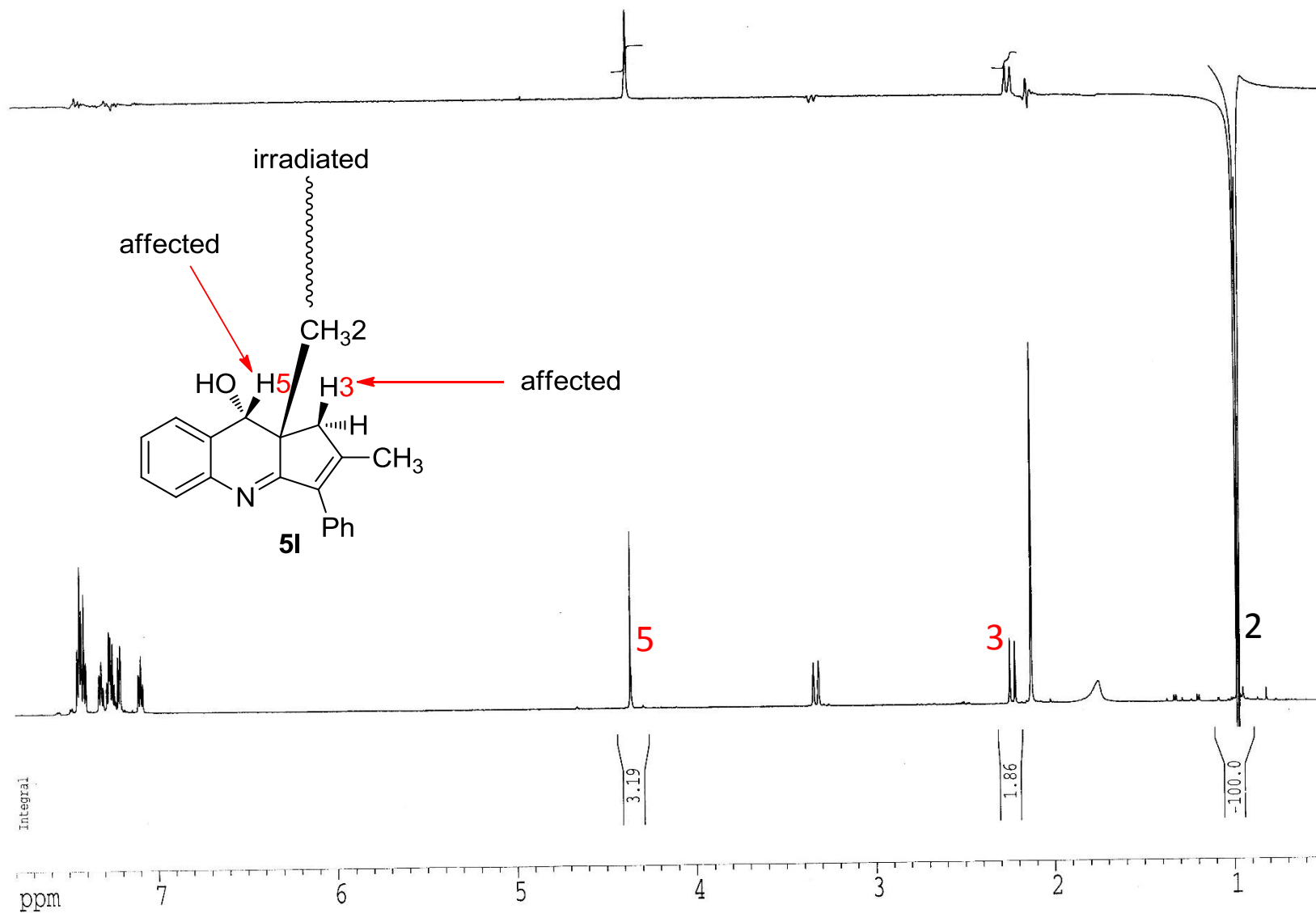
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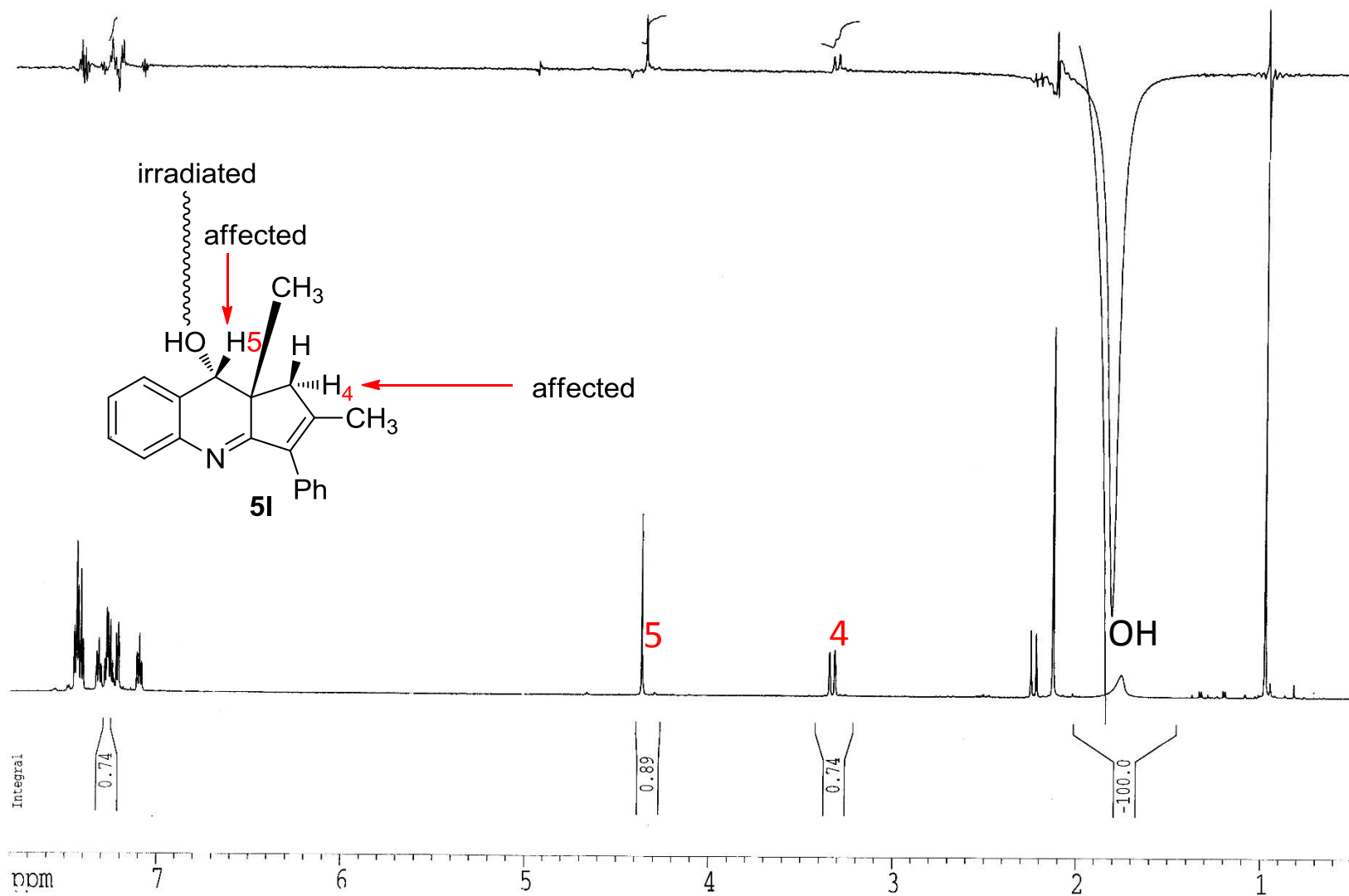
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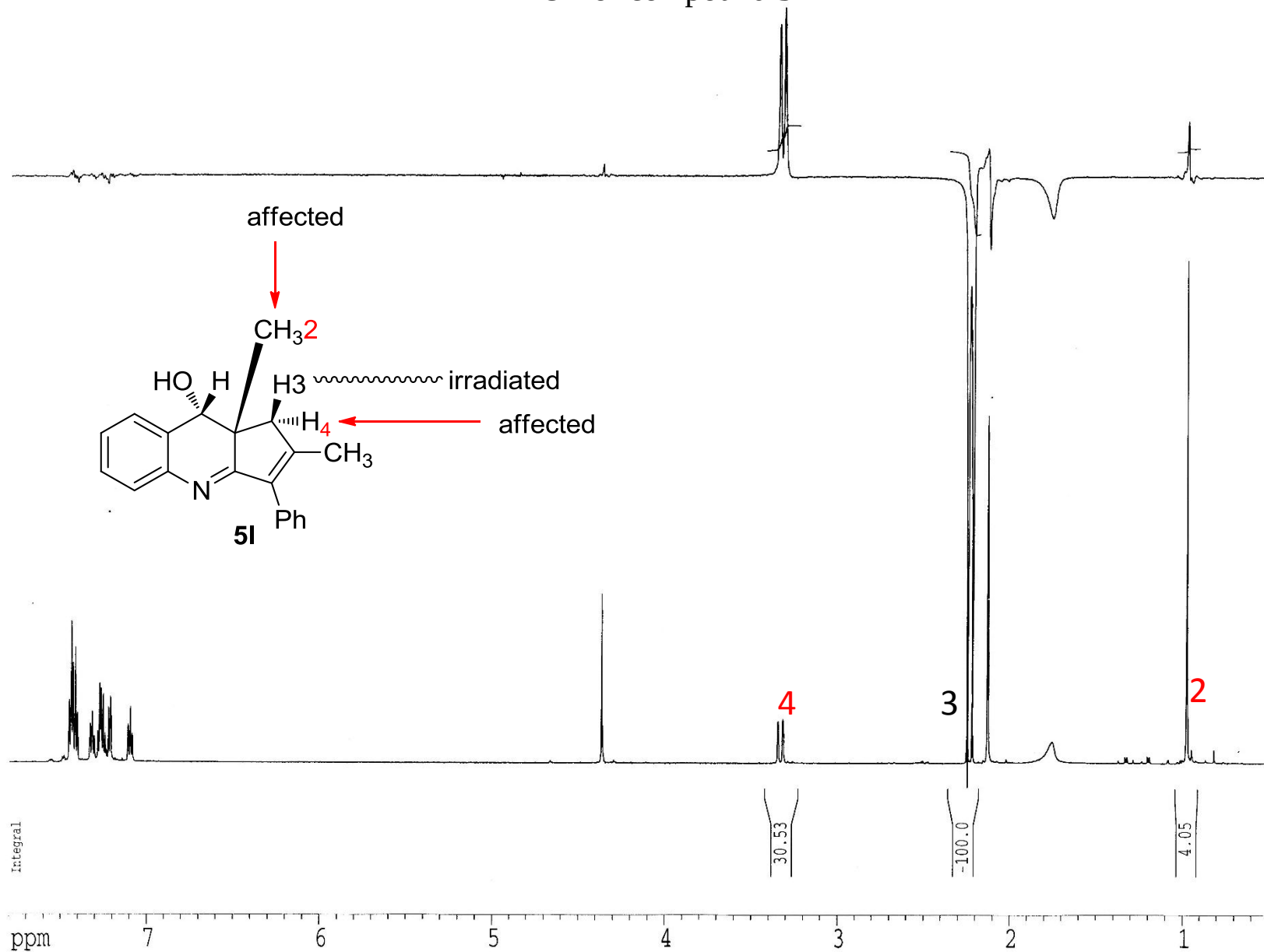
^1H NOE of compound **5l**



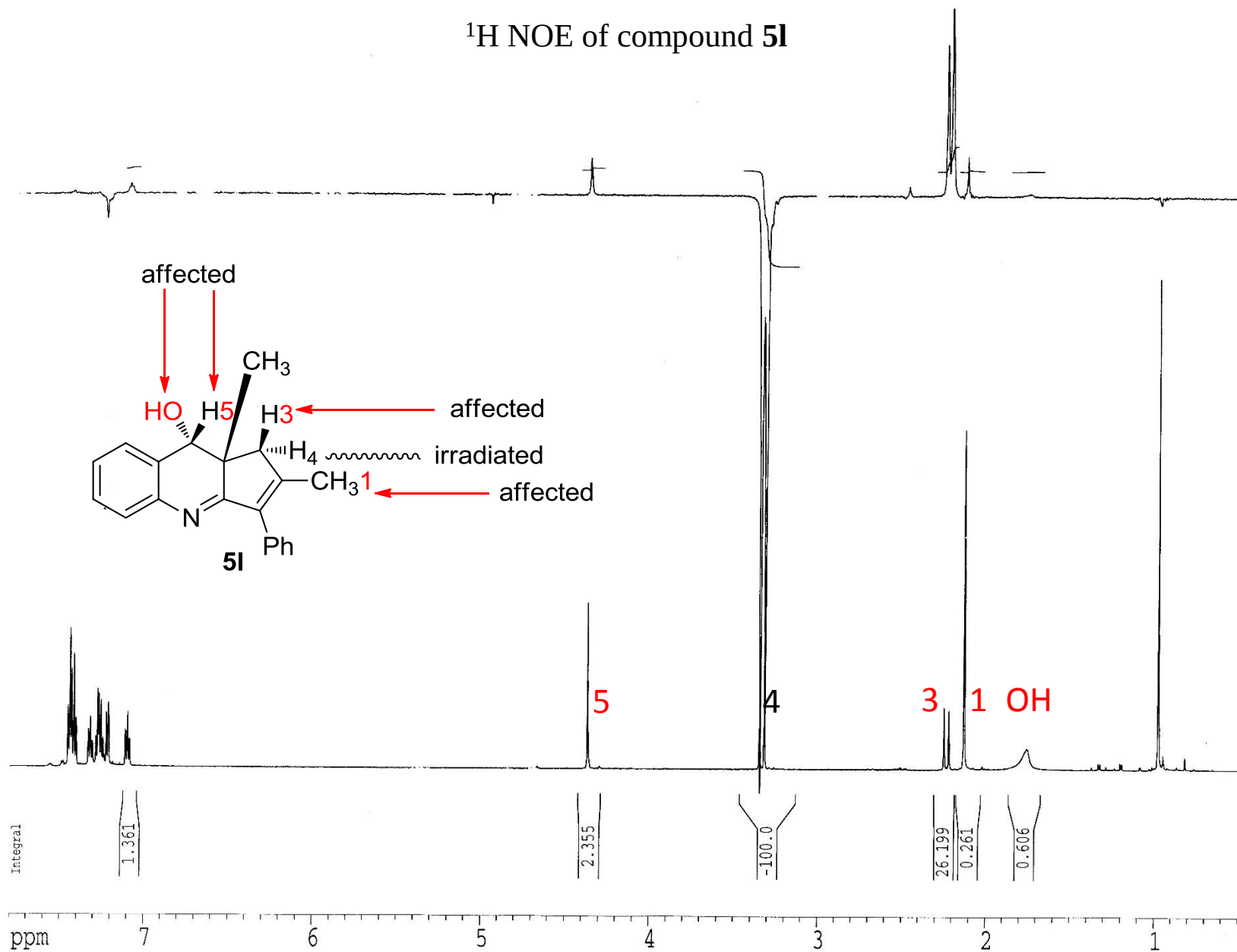
^1H NOE of compound **5l**



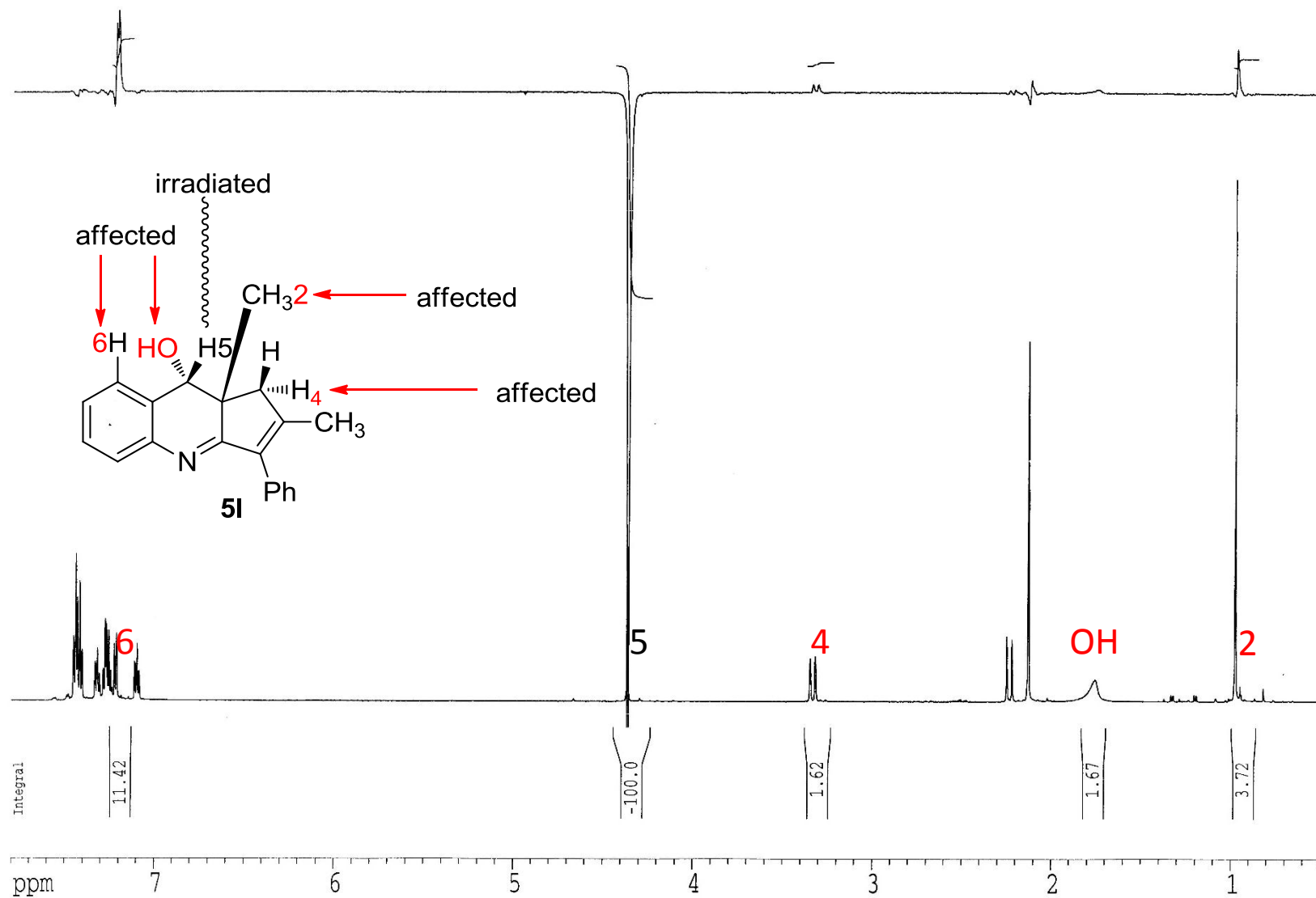
^1H NOE of compound **5l**



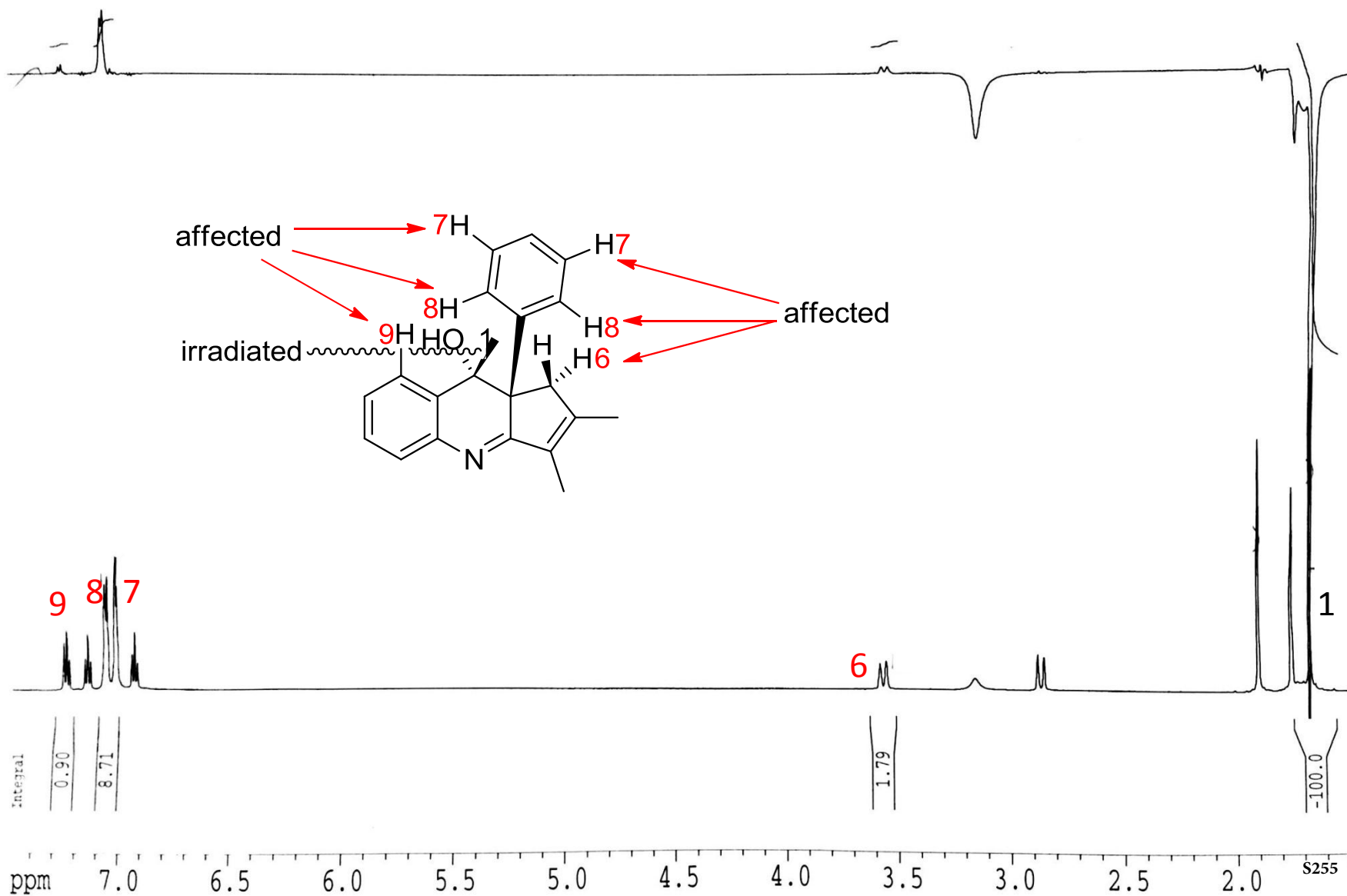
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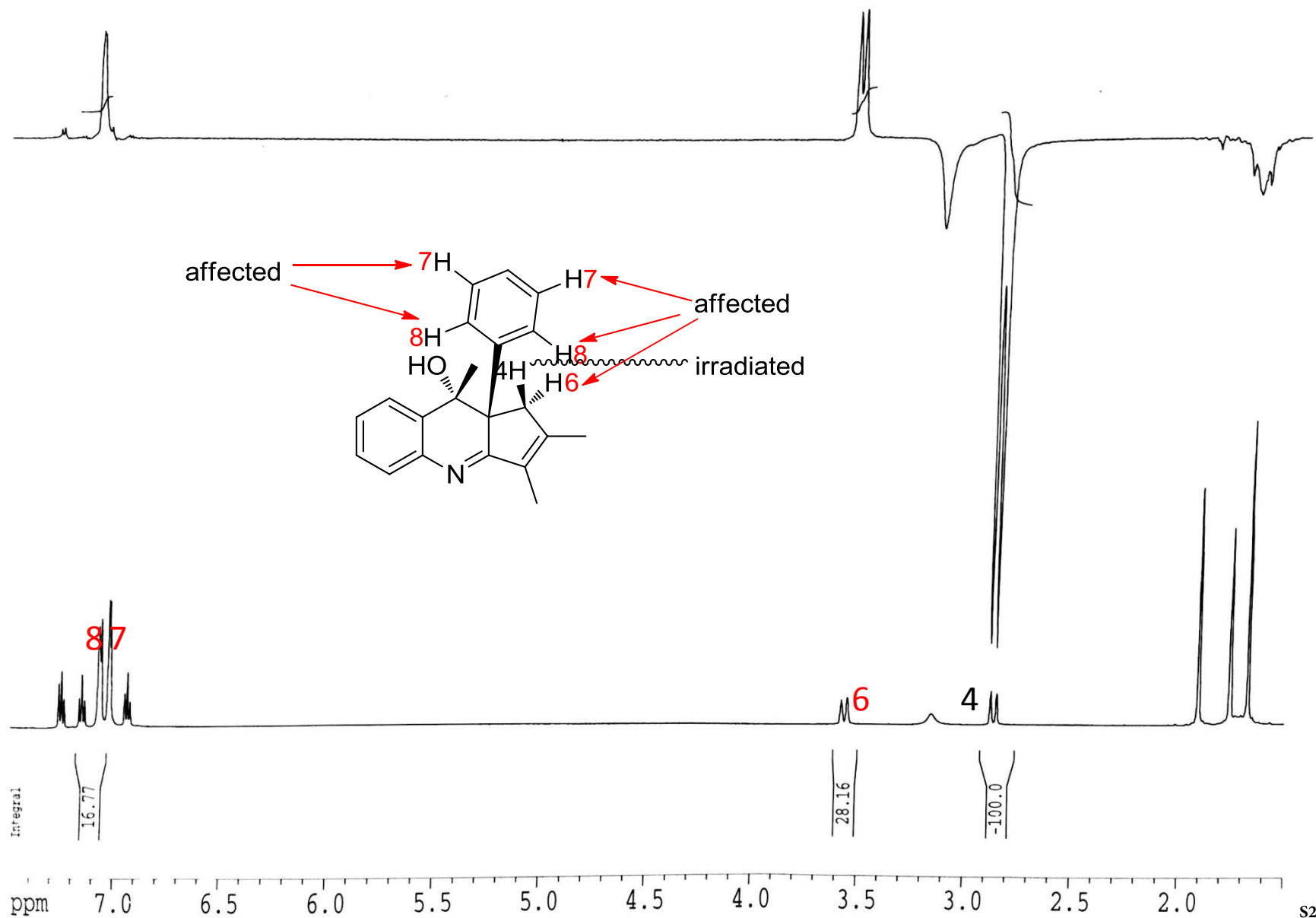
^1H NOE of compound **5I**



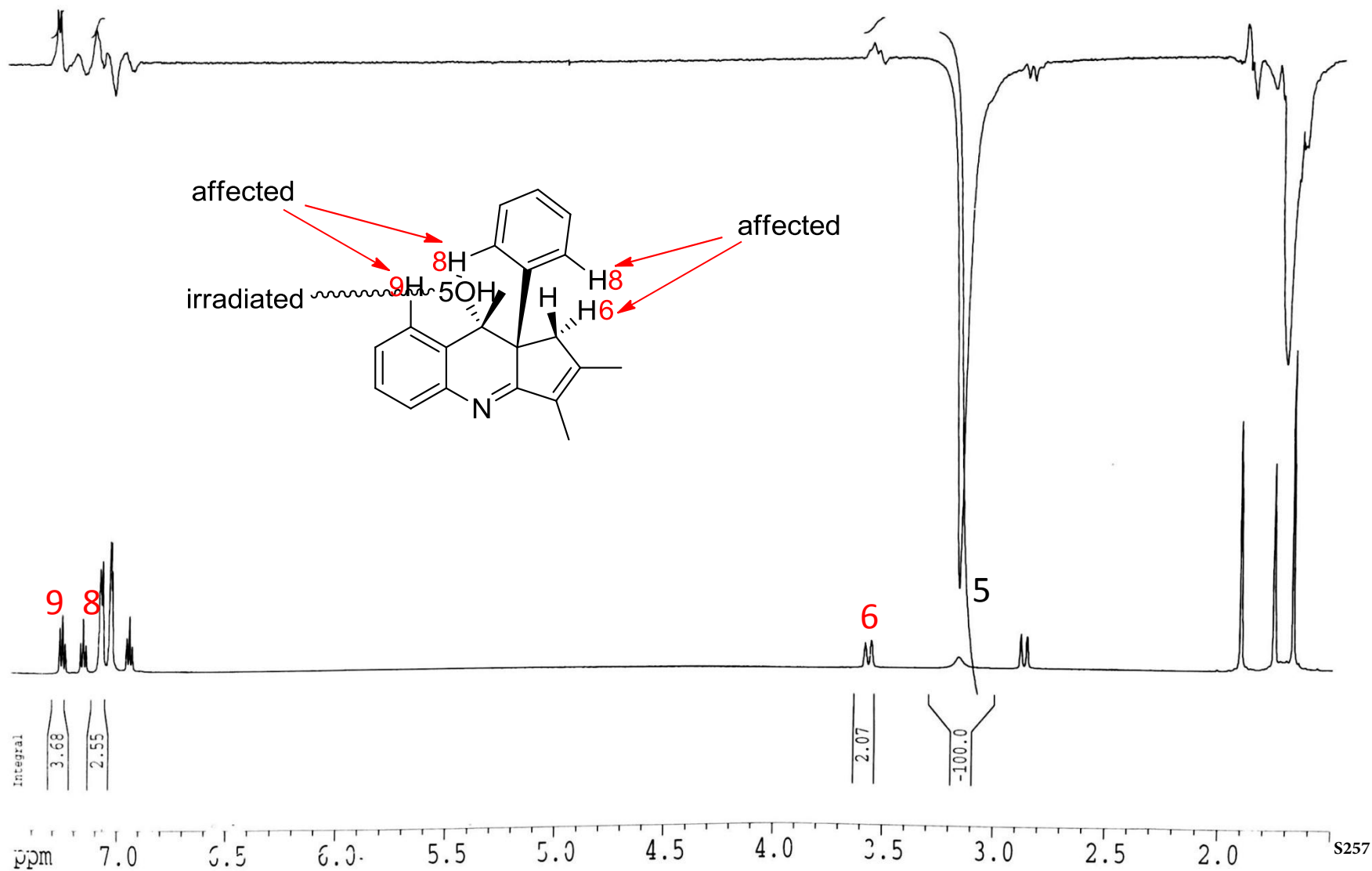
^1H NOE of compound **8j**



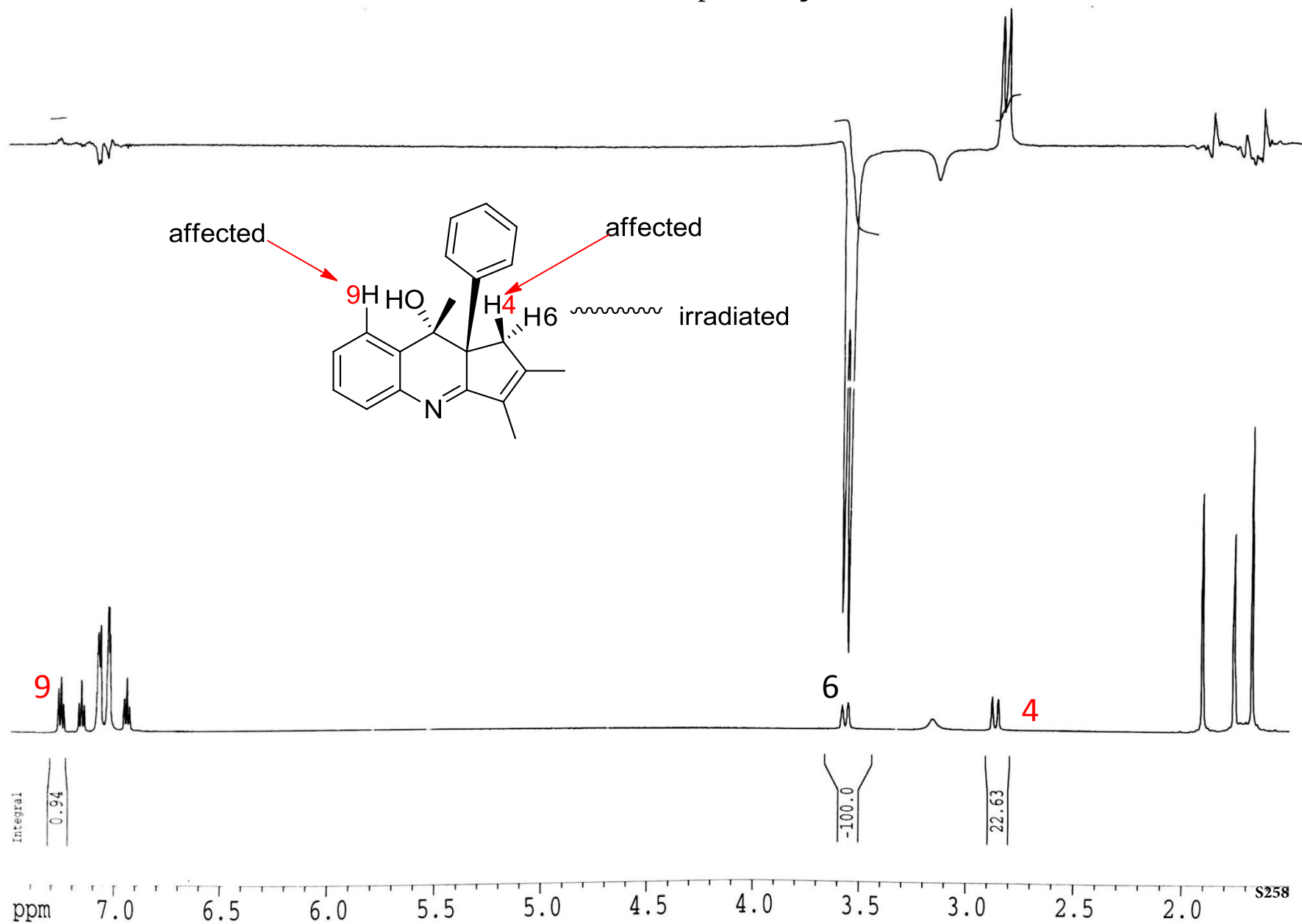
^1H NOE of compound **8j**



^1H NOE of compound **8j**



^1H NOE of compound **8j**



^1H NOE of compound **8j**

