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Electronic Supporting Information

Indium-Catalyzed Synthesis of Benzannulated Spiroketals by Intramolecular Double Hydroalkoxylation of *o*-(Hydroxyalkynyl)benzyl Alcohols

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General methods

All reactions were carried out in flame-dried glassware, under argon atmosphere, using standard gas-tight syringes, cannulae and septa. Reaction temperatures refer to external bath temperatures. Toluene was distilled from sodium/benzophenone. THF and dichloromethane were dried via MBraun MB-SPS 800 Solvent Purification System. Dry piperidine, MeOH, Et_3N, DCE and other available reagents were used as received. Indium(III) iodide (99.998%), indium(III) bromide (99.999%), silver hexafluoroantimonate(V) (98%) were used as received. Indium triiodide was stored and weight inside of the globebox and all of the indium-catalyzed cycloisomerization reactions were performed under argon atmosphere to prevent its hydrolysis. Butyllithium (2.5 M in hexane, Aldrich) was titrated prior to use. Completion of the reactions and reaction times were estimated by thin layer chromatography (TLC), pre-coated silica gel foils with fluorescent indicator 254 nm (Alugram® Xtra SIL G/UV_{254}, 0.20 mm thick), UV light as the visualizing agent, and ethanolic phosphomolybdic acid as the developing agent. Flash column chromatography was performed using 230-400 mesh silica gel. ^1H NMR and $^{13}C\{H\}$ NMR spectra were recorded at room temperature in $CDCl_3$ using a 300 and 400 MHz Bruker Advance 300 MHz, 400 Mz or a Bruker Advance 500 MHz spectrometer and calibrated to the solvent peak. DEPT data were used to assign carbon types. Chemical shifts are reported in ppm (δ) relative to the solvent $CDCl_3$ (δ_H 7.26 ppm and δ_C 77.1 ppm) and toluene-d8 (δ_H 2.09 ppm and δ_C 20.4 ppm). Etylenglicol (80%) in DMSO-d6 was used for calibration in the ^1H NMR measuraments at 60 ºC. Mass spectra were obtained with a MAT 95XP Magnetic Sector EI spectrometer or with a QSTAR Elite hybrid quadrupole time-of-flight (TOF) ESI mass spectrometer, both operating in the positive ionization mode.

General procedure for the synthesis of (*o*-hydroxyalkynyl)phenyl alcohols

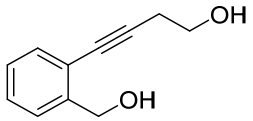
(*o*-Hydroxyalkynyl)phenyl alcohols **1a–1m** (Table 2, Scheme 1 and Scheme 2) and protected alcohols **16** and **17** (Scheme 4) were prepared by using a Sonogashira protocol or by two-step procedure Sonogashira/reduction of the corresponding ketone or aldehyde.

General procedure for Sonogashira reaction. In a round-bottom flask equipped with a stirring bar (2-iodophenyl)methanol or 2-(2-iodophenyl)ethan-1-ol (1.0 equiv.), $Pd(OAc)_2$ (1-2 mol%) and PPh_3 (2-4 mol%) or $PdCl_2(PPh_3)_2$ (2 mol%), Et_3N (7-15 mL), the corresponding alkynol (1.5 equiv.) and CuI (1-5 mol%) were added at room temperature. The mixture was stirred at room temperature or heating at 60–90 ºC until completion of the reaction (5–24 h), indicated by TLC. The reaction was quenched with saturated aqueous NH_4Cl (10 mL). The resulting mixture was extracted with dichloromethane (2 x 20 mL), and the organic layer was washed with H_2O (15 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and concentrated under

reduced pressure. Purification of the crude product by flash column chromatography on silica gel afford the corresponding pure compounds.

General procedure for reduction of benzyl aldehydes and ketones. To a solution of ketone **S1–S3** or aldehyde **S4–S6** (1.0 equiv.) in MeOH (0.16 M) $NaBH_4$ (2.2 equiv.) was added at room temperature. The reaction mixture was stirred at room temperature until TLC showed that the reaction was completed. The solvent was removed under reduced pressure and the residue redisolved in EtOAc (20 mL). The resulting organic extract was washed with saturated aqueous NH_4Cl (10 mL), H_2O (10 mL) and brine (10 mL), dried ($MgSO_4$) filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

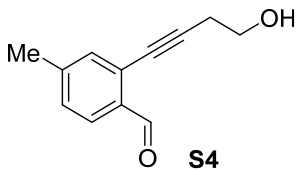
4-(2-(Hydroxymethyl)phenyl)but-3-yn-1-ol (1a).[1]



1a

Following the general procedure, the reaction of but-3-yn-1ol (1.19 g, 17.0 mmol) with (2-iodophenyl)methanol (2.66 g, 11.4 mmol), $PdCl_2(PPh_3)_2$ (159 mg, 0.22 mmol), Et_3N (15 mL, 107 mmol) and CuI (22 mg, 0.11 mmol) was stirred at rt for 24 h. After purification by column chromatography (40-80% EtOAc/hexanes) **1a** (1.79 g, 89%) was obtained as an orange solid. R_f = 0.13 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.38-7.23 (m, 3H), 4.79 (s, 2H), 3.85 (t, *J* = 6.0 Hz, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.48 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5 (C), 131.9 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 122.3 (C), 92.3 (C), 80.2 (C), 64.2 (CH_2), 61.1 (CH_2), 23.8 (CH_2). MS (EI) *m/z* (%) 176 $[M]^+$ (2), 145 $[M - CH_3O]^+$ (52). HRMS (EI) m/z calcd for $C_{11}H_{12}O_2$ $[M]^+$ 176.0832; found 176.0827.

2-(4-Hydroxybut-1-yn-1-yl)-4-methylbenzaldehyde (S4).[2]



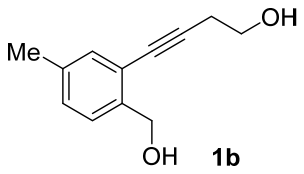
S4

1 X. Li, A. R. Chianese, T. Vogel, and R. H. Crabtree, Intramolecular Alkyne Hydroalkoxylation and Hydroamination Catalyzed by Iridium Hydrides, *Org. Lett*., 2005, **5**, 5437–5440.

2 P. Vinoth, T. Vivekanand, P. A. Suryavanshi, J. C. Menéndez, H. Sasaic and V. Sridharan, Palladium(II)-Catalyzed Intramolecular Carboxypalladation-Olefin Insertion Cascade: Direct Access to Indeno[1,2-*b*]furan-2-ones, *Org. Biomol. Chem*., 2015, **13**, 5175–5181.

Following the general procedure, the reaction of *o*-bromo-*p*-methylbenzaldehyde (418 mg, 2.10 mmol) with but-3-yn-1-ol (163 mg, 2.3 mmol), $Pd(OAc)_2$ (4.77 mg, 0.02 mmol), PPh_3 (11.2 mg, 0.04 mmol), CuI (7.62 mg, 0.04 mmol) and Et_3N (10 mL, 72 mmol) was heated at 90 ºC for 4 h. After purification by column chromatography (70% EtOAc/hexanes) **S4** (288 mg, 73%) was obtained as a yellow oil. R_f = 0.46 (50% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 3.77 (t, *J* = 6.3 Hz, 2H), 2.66 (t, *J* = 6.2 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7 (CHO), 144.8 (C), 133.9 (C), 133.8 (CH), 129.2 (CH), 128.5 (CH), 126.5 (C), 93.8 (C), 78.6 (C), 61.0 (CH_2), 24.0 (CH_2), 21.6 (CH_3). MS (EI) *m/z* (%) 189 $[M]^{2+}$ (59), 172 $[M - H_2O]^+$ (100). HRMS (EI) m/z calcd for $C_{12}H_{12}O_2$ $[M]^+$ 188.0832; found 188.0827.

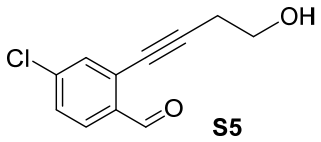
4-(2-(Hydroxymethyl)-5-methylphenyl)but-3-yn-1-ol (1b).



1b

Following the general procedure, the reaction of 2-(4-hydroxybut-1-yn-1-yl)-4-methylbenzaldehyde (**S4**) (150 mg, 0.80 mmol) with with $NaBH_4$ (66.3 mg, 1.75 mmol) in MeOH (7 mL) was stirred at rt for 1 h. After purification by column chromatography (50% EtOAc/hexanes) **1b** (97 mg, 65%) was obtained as a yellow oil. R_f = 0.19 (50% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.28-7.14 (m, 2H), 7.13 (dd, *J* = 6.9 Hz, 1.4 Hz, 1H), 4.77 (s, 2H), 3.87 (t, *J* = 5.9 Hz, 2H), 2.73 (t, *J* = 6.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7 (C), 137.6 (C), 132.7 (CH), 129.0 (CH), 128.0 (CH), 122.2 (C), 91.6 (C), 80.5 (C), 64.4 (CH_2), 61.3 (CH_2), 24.0 (CH_2), 20.9 (CH_3). MS (EI) *m/z* (%) 190 $[M]^+$ (7), 62 $[M - C_8H_9O]^+$ (100). HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ $[M]^+$ 190.0777; found 190.0787.

4-Chloro-2-(4-hydroxybut-1-yn-1-yl)benzaldehyde (S5).[2]

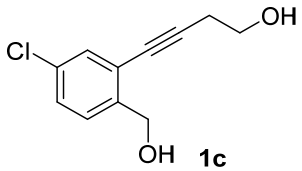


S5

Following the general procedure, the reaction of *o*-bromo-*p*-chlorobenzaldehyde (500 mg, 2.28 mmol) with but-3-yn-1-ol (175mg, 2.50 mmol), $Pd(OAc)_2$ (5.12 mg, 0.02 mmol), PPh_3 (13.1 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and Et_3N (9.50 mL, 68.4 mmol) was heated at 90 ºC for 24 h. After purification by column chromatography (70% EtOAc/hexanes) **S5** (171.3 mg, 36%) was obtained as a yellow oil. R_f = 0.37 (50% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.0

Hz, 1 H), 3.82−3.93 (m, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.12 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6 (CHO), 140.2 (C), 134.5 (2 x C), 133.2 (CH), 129.6 (CH), 128.8 (CH), 127.9 (C), 95.7 (C), 60.9 (CH_2), 24.0 (CH_2).

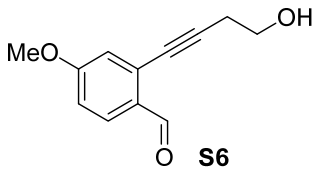
4-(5-Chloro-2-(hydroxymethyl)phenyl)but-3-yn-1-ol (1c).



1c

Following the general procedure, the reaction of 4-chloro-2-(4-hydroxybut-1-yn-1-yl)benzaldehyde (**S5**) (150 mg, 0.72 mmol) with with $NaBH_4$ (59.7 mg, 1.58 mmol) in MeOH (10 mL) was stirred at rt for 30 min. After purification by column chromatography (60% EtOAc/hexanes) **1c** (99 mg, 65%) was obtained as a yellow solid. R_f = 0.27 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.30 (m, 3H), 4.75 (s, 2H), 3.86 (t, *J* = 6.1 Hz, 2H), 2.72 (t, *J* = 6.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1 (C), 133.3 (C), 131.7 (CH), 129.1 (CH), 128.3 (CH), 123.9 (CH), 93.6 (C), 79.1 (C), 63.6 (CH_2), 61.1 (CH_2), 23.8 (CH_2). MS (EI) *m/z* 210 [M, ^{35}Cl]$^+$ (8), 212 [M, ^{37}Cl]$^+$ (2), 179 [M, ^{35}Cl – CH_3O]$^+$ (32), 181 [M, ^{37}Cl – CH_3O]$^+$ (11), 162 [M, ^{35}Cl – CH_4O_2]$^+$ (100), 164 [M, ^{37}Cl – CH_4O_2]$^+$ (67). HRMS (EI) m/z calcd for $C_{11}H_{11}O_2Cl$ [M]$^+$ 210.0442; found 210.0442.

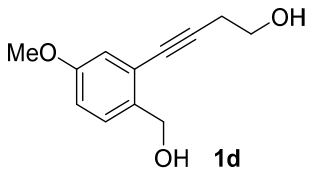
2-(4-Hydroxybut-1-yn-1-yl)-4-methoxybenzaldehyde (S6).



S6

Following the general procedure, the reaction of *o*-bromo-*p*-methoxybenzaldehyde (417 mg, 1.96 mmol) with but-3-yn-1-ol (179 mg, 2.50 mmol), $PdCl_2(PPh_3)_2$ (68.8 mg, 0.10 mmol), CuI (18.7 mg, 0.10 mmol) and Et_3N (10 mL, 72 mmol) was heated at 85 ºC for 6 h. After purification by column chromatography (50% EtOAc/hexanes) **S6** (313 mg, 80%) was obtained as a yellow solid. R_f = 0.40 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.3 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 6.88-7.11 (m, 2H), 3.82-3.96 (m, 5H), 2.77 (t, *J* = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5 (CHO), 163.7 (C), 130.9 (CH), 129.9 (C), 128.4 (C), 117.6 (CH), 115.0 (CH), 94.1 (C), 78.6 (C), 61.0 (CH_2), 55.7 (CH_3), 24.0 (CH_2). MS (EI) *m/z* (%) 204 [M]$^+$ (6), 187 [M – HO]$^+$ (100). HRMS (EI) m/z calcd for $C_{12}H_{12}O_3$ [M]$^+$ 204.0781; found 204.0766.

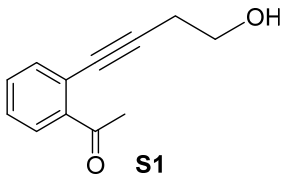
4-(2-(Hydroxymethyl)-5-methoxyphenyl)but-3-yn-1-ol (1d).



1d

Following the general procedure, the reaction of 2-(4-hydroxybut-1-yn-1-yl)-4-methoxybenzaldehyde (**S6**) (150 mg, 0.73 mmol) with with $NaBH_4$ (60.5 mg, 1.60 mmol) in MeOH (15 mL) was stirred at rt for 1 h. After purification by column chromatography (40% EtOAc/hexanes) **1d** (80 mg, 53%) was obtained as a yellow oil. R_f = 0.27 (70% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.97 (d, *J* = 2.7 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.71 (s, 2H), 3.85 (t, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 2.71 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9 (C), 135.1 (C), 129.6 (CH), 123.7 (C), 116.9 (CH), 114.2 (CH), 92.1 (C), 80.2 (C), 63.7 (CH_2), 61.1 (CH_2), 55.4 (CH_3), 23.8 (CH_2). MS (EI) *m/z* (%) 206 $[M]^+$ (6), 69 $[M - C_8H_9O_2]^+$ (92). HRMS (EI) m/z calcd for $C_{12}H_{14}O_3$ $[M]^+$ 206.0937; found 206.0937.

1-(2-(4-Hydroxybut-1-yn-1-yl)phenyl)ethan-1-one (S1).[3]

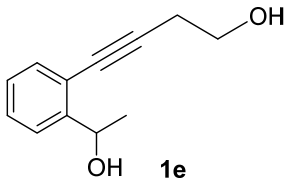


S1

Following the general procedure, the reaction of but-3-yn-1-ol (0.905 g, 12.8 mmol) with *orto*-bromoacetophenone (2.12 g, 10.7 mmol), Et_3N (15.0 mL, 108 mmol), $PdCl_2(PPh_3)_2$ (147 mg, 0.21 mmol), PPh_3 (280 mg, 1.06 mmol) and CuI (101 mg, 0.53 mmol) was heated at 85 ºC for 5 h. After purification by column chromatography (20% EtOAc/hexanes) **S1** (0.922 g, 46%) was obtained as a yellow oil. R_f = 0.28 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.77 (m, 1H), 7.49-7.54 (m, 1H), 7.40-7.48 (m, 1H), 7.32-7.39 (m, 1H), 3.86 (t, *J* = 5.9 Hz, 2H), 2.70 (t, *J* = 5.8 Hz, 2H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8 (C), 139.9 (C), 134.0 (CH), 131.6 (CH), 129.2 (CH), 127.7 (CH), 122.1 (C), 92.7 (C), 82.1 (C), 61.1 (CH_2), 29.2 (CH_3), 24.3 (CH_2).

3 M. Feuerstein, F. Berthiol, H. Doucet and M. Santelli, Palladium-Tetraphosphine Complex: An efficient Catalyst for the Alkynylation of *ortho*-Substituted Aryl Bromides, *Synthesis* 2004, 1281–1289.

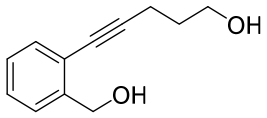
4-(2-(1-Hydroxyethyl)phenyl)but-3-yn-1-ol (1e).



1e

Following the general procedure, the reaction of 1-(2-(4-hydroxybut-1-yn-1-yl)phenyl)ethan-1-one (**S1**) (450 mg, 2.39 mmol) with $NaBH_4$ (199 mg, 5.26 mg) in MeOH (15 mL) was stirred at rt for 1 h. After purification by column chromatography (40% EtOAc/hexanes) **1e** (386 mg, 85%) was obtained as a yellow oil. R_f = 0.30 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.40 (m, 2H), 7.35-7.30 (m, 1H), 7.27-7.19 (m, 1H), 5.28 (q, *J* = 6.5 Hz, 1H), 3.86 (t, *J* = 6.1 Hz, 2H), 2.74 (t, *J* = 6.1 Hz, 2H), 1.56 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2 (C), 132.4 (CH), 128.3 (CH), 127.1 (CH), 125.1 (CH), 120.9 (C), 92.1 (C), 80.2 (C), 68.6 (CH_2), 61.0 (CH_2), 23.8 (CH), 23.4 (CH_3). MS (EI) *m/z* (%) 190 $[M]^+$ (15), 175 $[M - CH_3]^+$ (30), 159 $[M - CH_3O]^+$ (70). HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ $[M]^+$ 190.0988; found 190.0999.

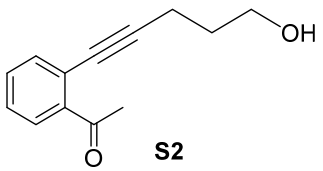
5-(2-(Hydroxymethyl)phenyl)pent-4-yn-1-ol (1f).[1]



1f

Following the general procedure, the reaction of pent-4-yn-1-ol (0.647 g, 7.69 mmol) with (2-iodophenyl)methanol (1.20 g, 5.13 mmol), $PdCl_2(PPh_3)_2$ (72 mg, 0.103 mmol), Et_3N (7 mL, 50.2 mmol) and CuI (9.8 mg, 0.05 mmol) was stirred at rt for 7 h. After purification by column chromatography (20% EtOAc/hexanes) **1f** (855 mg, 88%) was obtained as a yellow oil. R_f = 0.12 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (dt, *J* = 7.2, 1.3 Hz, 2H), 7.29-7.22 (m, 3H), 4.78 (s, 2H), 3.84 (t, *J* = 6.9 Hz, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 1.92-1.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4 (C), 132.2 (CH), 128.1 (CH), 127.49 (CH), 127.46 (CH), 122.2 (C), 94.4 (C), 78.7 (C), 64.1 (CH_2), 61.6 (CH_2), 31.2 (CH_2), 16.2 (CH_2). MS (EI) *m/z* (%) 190.1 $[M]^+$ (23), 172 $[M - H_2O]^+$ (100). HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ $[M]^+$ 190.0988; found 190.0987.

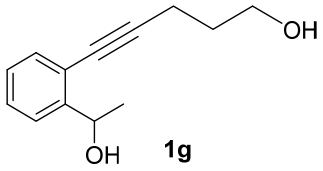
1-(2-(5-Hydroxypent-1-yn-1-yl)phenyl)ethan-1-one (S2).[4]



S2

Following the general procedure, the reaction of pent-4-yn-1-ol (499 mg, 5.96 mmol) with *orto*-bromoacetophenone (983 mg, 4.94 mmol), Et_3N (15.0 mL, 108 mmol), $PdCl_2(PPh_3)_2$ (69 mg, 0.09 mmol), PPh_3 (129 mg, 0.49 mmol) and CuI (47.1 mg, 0.25 mmol) was heated at 85 ºC for 3 h. After purification by column chromatography (50% EtOAc/hexanes) **S2** (290 mg, 54%) was obtained as an orange solid. R_f = 0.25 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.50 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45-7.31 (m, 2H), 3.85 (t, *J* = 7.7 Hz, 1H), 2.70 (s, 3 H), 2.61 (t, *J* = 6.9 Hz, 2H), 1.89 (quint, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6 (C), 140.6 (C), 134.1 (CH), 131.2 (CH), 128.6 (CH), 127.6 (CH), 122.2 (C), 95.5 (C), 80.2 (C), 61.7 (CH_2), 31.0 (CH_2), 29.7 (CH_3), 16.4 (CH_2). MS (EI) m/z (%) 202 $[M]^+$ (100). HRMS (EI) m/z calcd for $C_{13}H_{14}O_2$ $[M]^+$ 202.0988; found 202.0991.

5-(2-(1-Hydroxyethyl)phenyl)pent-4-yn-1-ol (1g).

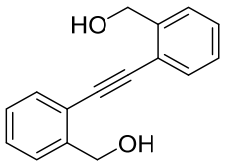


1g

Following the general procedure, the reaction of 1-(2-(5-hydroxypent-1-yn-1-yl)phenyl)ethan-1-one **(S2)** (300 mg, 1.48 mmol) with $NaBH_4$ (123 mg, 3.26 mmol) in MeOH (15 mL) was stirred at rt for 3 h. After purification by column chromatography (50% EtOAc/hexanes) **1g** (278 mg, 92%) was obtained as a brown oil. R_f = 0.33 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.32 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.21 (dt, *J* = 7.5, 1.3 Hz, 1H), 5.29 (q, *J* = 6.5 Hz, 1H), 3.84 (t, *J* = 6.2 Hz, 2H), 2.60 (t, *J* = 6.2 Hz, 2H), 1.92-1.87 (m, 4H), 1.53 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2 (C), 132.4 (CH), 128.3 (CH), 127.0 (CH), 124.7 (CH), 121.0 (C), 94.6 (C), 78.9 (C), 68.5 (CH_2), 61.8 (CH_2), 31.4 (CH), 23.7 (CH_2), 16.2 (CH_3). MS (EI) *m/z* (%) 204 $[M]^+$ (11), 186 $[M - H_2O]^+$ (100), 186 $[M - C_3H_7O]^+$ (52). HRMS (EI) m/z calcd for $C_{13}H_{16}O_2$ $[M]^+$ 204.1145; found 204.1147.

4 B. Akkachairin, J. Tummatorn, N. Supantanapong, P. Nimnual, C. Thongsornkleeb and S. Ruchirawat, Silver-Catalyzed Cyclization of *ortho*-Carbonylacetylenols for the Synthesis of Dihydronaphthofurans, *J. Org. Chem*. 2017, **82**, 3727–3740.

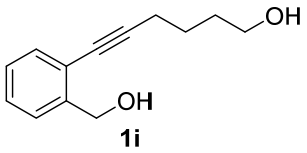
(Ethyne-1,2-diylbis(2,1-phenylene))dimethanol (1h).[5]



1h

Following the general procedure, the reaction of (2-iodophenyl)methanol (683 mg, 2.75 mmol), $PdCl_2(PPh_3)_2$ (38.6 mg, 0.055 mmol), Et_3N (10 mL, 71.7 mmol), (2-ethynylphenyl)methanol (400 g, 3.03 mmol)[6] and CuI (10.5 mg, 0.055 mmol) was heated at 60 ºC for 15 h. After purification by column chromatography (50% EtOAc/hexanes) **1h** (290 mg, 45%) was obtained as an orange solid. R_f = 0.23 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.46 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.40-7.32 (m, 4H), 4.89 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4 (2 x C), 132.5 (2 x CH), 128.9 (2 x CH), 128.2 (2 x CH), 127.9 (2 x CH), 122.1 (2 x C), 91.6 (2 x C), 64.5 (2 x CH_2). MS (EI) *m/z* (%) 238 $[M]^+$ (3). 220 $[M - H_2O]^+$ (100). HRMS (EI) m/z calcd for for $C_{16}H_{14}O_2$ $[M]^+$ 238.0992; found 238.0988.

6-(2-(Hydroxymethyl)phenyl)hex-5-yn-1-ol (1i).[1]



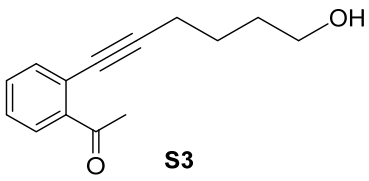
1i

Following the general procedure, the reaction of hex-5-yn-1-ol (1.081 g, 11.0 mmol) with (2-iodophenyl)methanol (1.72 g, 7.34 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.150 mmol), Et_3N (8.5 mL, 61 mmol) and CuI (13.3 mg, 0.07 mmol) was stirred at room temperature for 48 h. After purification by column chromatography (80% EtOAc/hexanes) **1i** (1.5 g, 99%) was obtained as an orange solid. R_f = 0.44 (80% EtOAc/Hex). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.27-7.19 (m, 2H), 4.76 (s, 2H), 3.64 (t, *J* = 6.2 Hz, 2H), 2.46 (t, *J* = 6.4 Hz, 2H), 1.70-1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4 (C), 132.1 (CH), 128.0 (CH), 127.31 (CH), 127.29 (CH), 122.1 (C), 94.9 (C), 78.6 (C), 63.8 (CH_2), 62.1 (CH_2), 31.8 (CH_2), 25.0 (CH_2), 19.3 (CH_2). MS (EI) m/z (%) 204 $[M]^+$ (27), 115 $[M - C_4H_{10}O_2]^+$ (100). HRMS (EI) m/z calcd for $C_{13}H_{16}O_2$ $[M]^+$ 204.1145; found 204.1148.

5 B. A. Messerle and K. Q. Vuong, Rhodium- and Iridium-Catalyzed Double Hydroalkoxylation of Alkynes, an Efficient Method for the Synthesis of *O,O*-Acetals: Catalytic and Mechanistic Studies, *Organometallics* 2007, **26**, 3031–3040.

6 H. Wu, Y.-P. He and L.-Z. Gong, Direct Access to Enantioenriched Spiroacetls Through Asymmetric Relay Catalytic Three-Component Reaction, *Org. Lett*., 2013, **14**, 460–463.

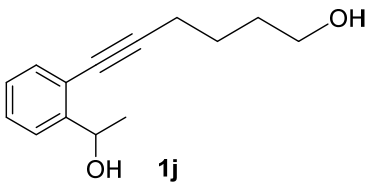
1-(2-(6-Hydroxyhex-1-yn-1-yl)phenyl)ethan-1-one (S3).[4]



S3

Following the general procedure, the reaction of hex-5-yn-1-ol (800 mg, 3.7 mmol) with *orto*-bromoacetophenone (736mg, 3.70 mmol), Et_3N (15 mL, 108 mmol), $PdCl_2(PPh_3)_2$ (52 mg, 0.074 mmol), PPh_3 (97 mg, 0.37 mmol) and CuI (35 mg, 0.19 mmol) was heated at 85 ºC for 8 h. affording **S3** as a purple oil which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.63 (m, 1H), 7.51-7.45 (m, 1H), 7.44-7.37 (m, 1H), 7.34-7.32 (m, 1H), 3.72 (t, *J* = 6.0 Hz, 2H), 2.70 (s, 3H), 2.51 (t, *J* = 6.6 Hz, 2H), 1.98 (br s, 1H), 1.81-1.69 (m, 4H).

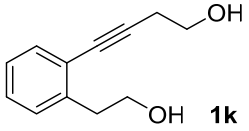
6-(2-(1-Hydroxyethyl)phenyl)hex-5-yn-1-ol (1j).



1j

Following the general procedure, the reaction of 1-(2-(6-hydroxyhex-1-yn-1-yl)phenyl)ethan-1-one (**S3**) (800 mg, 3.70 mmol) with $NaBH_4$ (308 mg, 8.14 mmol) in MeOH (15 mL) was stirred at rt for 3 h. After purification by column chromatography (40% EtOAc/hexanes) **1j** (389 mg, 48%) was obtained as a yellow oil. R_f = 0.23 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.30 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.19 (dt, *J* = 7.5, 1.4 Hz, 1H), 5.30 (q, *J* = 6.5 Hz, 1H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.50 (t, *J* = 6.8 Hz, 2H), 1.77-1.69 (m, 4H), 1.51 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 (C), 132.1 (CH), 128.1 (CH), 126.8(CH), 124.6 (CH), 121.0 (C), 95.0 (C), 78.7 (C), 68.1 (CH), 62.0 (CH_2), 31.7 (CH_2), 25.0 (CH_2), 24.0 (CH_3), 19.3 (CH_2). MS (EI) m/z (%) 218 $[M]^+$ (9). HRMS (EI) m/z calcd for $C_{14}H_{18}O_2$ $[M]^+$ 218.1272; found 218.1301.

5-(2-(2-Hydroxyethyl)phenyl)pent-4-yn-1-ol (1k).[7]

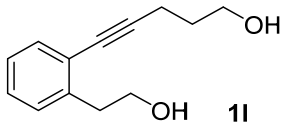


1k

7 A. Zhdanko and M. E. Maier, Gold(I)-, Palladium(II)-, Platinum(II)-, and Mercury(II)-Catalyzed Spirocyclization of 1,3-Enyediols: Reaction Scope, *Eur. J. Org. Chem*., 2014, 3411–3422.

Following the general procedure, the reaction of but-3-yn-1-ol (124 mg, 1.77 mmol) with 2-(2-iodophenyl)ethan-1-ol (400 mg, 1.61 mmol),[8] $PdCl_2(PPh_3)_2$ (21.1 mg, 0.03 mmol), Et_3N (6.70 mL, 48.3 mmol) and CuI (5.7 mg, 0.03 mmol) was heated at 60 ºC for 24 h. After purification by column chromatography (EtOAc) **1k** (264 mg, 86%) was obtained as a brown paste. R_f = 0.33 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.25-7.21 (m, 3H), 3.91 (t, *J* = 6.7 Hz, 2H), 3.85 (t, *J* = 5.9 Hz, 2H), 3.08 (t, *J* = 6.8 Hz, 2H), 2.72 (t, *J* = 6.8 Hz, 2H), 1.95 (br s, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7 (C), 132.1 (CH), 129.4 (CH), 128.2 (CH), 126.4 (CH), 123.6 (C), 91.1 (C), 81.1 (C), 63.6 (CH_2), 61.3 (CH_2), 38.1 (CH_2), 24.1 (CH_2). MS (EI) *m/z* (%) 190 $[M]^+$ (11). 128 $[M - C_2H_6O_2]^+$ (100). HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ $[M]^+$ 190.0988; found 190.0993.

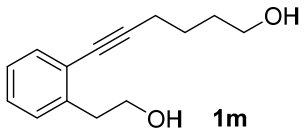
5-(2-(2-Hydroxyethyl)phenyl)pent-4-yn-1-ol (1l).



1l

Following the general procedure, the reaction of pent-4-yl-1-ol (261 mg, 3.10 mmol) with - 2-(2-iodophenyl)ethan-1-ol (700 mg, 2.82), $PdCl_2(PPh_3)_2$ (42.1 mg, 0.06 mmol), Et_3N (10 mL, 71.7 mmol) and CuI (5.7 mg, 0.03 mmol) in THF (10 mL) was heated at 60 ºC for 41 h. After purification by column chromatography (80% EtOAc/hexanes-EtOAc). compound **1l** (521 mg, 90%) was obtained as a yellow oil. R_f = 0.28 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.1, 1H), 7.23−7.15 (m, 3H), 3.89 (q, *J* = 8.4 Hz, 4H), 3.07 (t, *J* = 8.4 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 1.93-1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2 (C), 132.2 (CH), 129.5 (CH), 127.8 (CH), 126.3 (CH), 123.7 (C), 93.3 (C), 79.5 (C), 62.7 (CH_2), 61.0 (CH_2), 38.1 (CH_2), 31.3 (CH_2), 16.0 (CH_2). MS (EI) *m/z* (%) 204 $[M]^+$ (7). 128 $[M - C_3H_8O_2]^+$ (100). HRMS (EI) m/z calcd for $C_{13}H_{16}O_2$ $[M]^+$ 204.1145; found 204.1149.

6-(2-(2-Hydroxyethyl)phenyl)hex-5-yn-1-ol (1m).



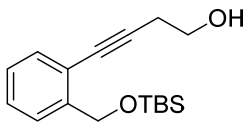
1m

Following the general procedure, the reaction of hex-5-yl-1-ol (174 mg, 1.77 mmol) with 2-(2-iodophenyl)ethan-1-ol (400 mg, 1.61 mmol), $PdCl_2(PPh_3)_2$ (22.6 mg, 0.03 mmol), Et_3N (7 mL 48.3 mmol) and CuI (6.1 mg, 0.03 mmol) was heated at 60 ºC for 15 h. After purification by

8 A. Minatti and S. L. Buchwald, Synthesis of Indolines via a Domino Cu-Catalyzed Amidation/Cyclization, *Org. Lett.*, 2008, **10**, 2721–2724.

column chromatography (EtOAc) **1m** (318 mg, 90%) was obtained as a brown paste. R_f = 0.37 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 6.9 Hz, 0.8 Hz, 1H), 7.25-7.16 (m, 3H), 3.89 (t, *J* = 8.4 Hz, 2H), 3.75 (t, *J* = 8.4 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 1.83-1.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0 (C), 132.3 (CH), 129.5 (CH), 127.9 (CH), 126.4 (CH), 123.8 (C), 93.7 (C), 79.6 (C), 63.1 (CH_2), 62.4 (CH_2), 38.3 (CH_2), 31.8 (CH_2), 25.0 (CH_2), 19.3 (CH_2). MS (EI) *m/z* (%) 218 $[M]^+$ (3). 128 $[M - C_4H_{10}O_2]^+$ (100). HRMS (EI) m/z calcd for $C_{14}H_{18}O_2$ $[M]^+$ 218.1301; found 218.1298.

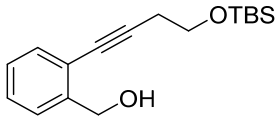
4-(2-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl)but-3-yn-1-ol (16).[9]



16

Following the general procedure, the reaction of *tert*-butyl((2-iodobenzyl)oxy)dimethylsilane.[10] (300 mg, 0.86 mmol), $PdCl_2(PPh_3)_2$ (12.1 mg, 0.02 mmol), Et_3N (4 mL, 28.7 mmol), but-3-yn-1-ol (90.5 mg, 1.29 mmol) and CuI (3.3 mg, 0.02 mmol) was heated at 60 ºC for 18 h. After purification by column chromatography (20% EtOAc/hexanes) **16** (208 mg, 83%) was obtaibed as an orange oil. R_f = 0.43 (20% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.40-7.20 (m,3H), 4.87 (s, 2H), 3.84 (t, *J* = 6.1 Hz, 2H), 2.73 (t, *J* = 6.2 Hz, 2H), 0.95 (s, 9H), -0.11 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0 (C), 131.7 (CH), 128.1 (CH), 126.6 (CH), 126.3 (CH), 120.7 (C), 91.4 (C), 80.1 (C), 63.7 (CH_2), 61.3 (CH_2), 26.0 (3 x CH_3), 24.0 (CH_2), 18.4 (C), -5.3 (2 x CH_3). HRMS (ESI) m/z calcd for $C_{17}H_{26}O_2SiNa$ $[M+Na]^+$ 313.1600; found 313.2728.

(2-(4-((*tert*-Butyldimethylsilyl)oxy)but-1-yn-1-yl)phenyl)methanol (18).[11]



18

Following the general procedure, the reaction of (2-iodophenyl)methanol (1.00 g, 4.27 mmol), $PdCl_2(PPh_3)_2$ (60 mg, 0.09 mmol), Et_3N (7 mL, 50.2 mmol), (but-3-yn-1-yloxy)(*tert*-

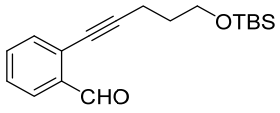
9 K. Lio, S. Sachimori, T. Watanabe and H. Fuwa, Ruthenium-Catalyzed Intramolecular Double Hydroalkoxylation of Internal Alkynes, *Org. Lett*., 2018, **20**, 7851−7855.

10 C. R. Mir and T. Dudding, Phase-Transfer Catalyzed O-Silyl Ether Deprotection Mediated by Cyclopropenium Cation, *J. Org. Chem*., 2017, **82**, 709–714.

11 K. Nishimura, R. Hanzawa, T. Sugai and H. Fuwa, Ruthenium-Catalyzed Intramolecular Double Hydrofunctionalization of Alkynes. Synthesis of Spirocyclic Hemiaminal Ethers and their Acid-Mediated Cleavage/Nuclophilic Addition, *J. Org. Chem*., 2021, **86**, 6674–6697.

butyl)dimethylsilane.[12] (1181 mg, 6.4 mmol) and CuI (8.1 mg, 0.04 mmol) was heated at 60 ºC for 24 h. After purification by column chromatography (15% EtOAc/hexanes) **18** (1.15 g, 93%) was as an orange oil. R_f = 0.38 (10% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.20-7.11 (m, 2H), 4.67 (s, 2H), 3.73 (t, *J* = 6.7 Hz, 2H), 2.56 (t, *J* = 6.7 Hz, 2H), 0.81 (s, 9H), -0.00 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8(C), 132.1 (CH), 128.1 (CH), 127.44 (CH), 127.41 (CH), 122.1 (C), 92.4 (C), 79.3 (C), 64.3 (CH_2), 62.0 (CH_2), 25.9 (3 x CH_3), 24.0 (CH_2), 18.4 (C), -5.3 (2 x CH_3). MS (EI) *m/z* (%) 291 $[M]^+$ (3). 233 $[M - C_3H_5O]^+$ (100). HRMS (EI) m/z calcd for for $C_{17}H_{27}O_2Si$ $[M+H]^+$ 291.1775; found 291.1765.

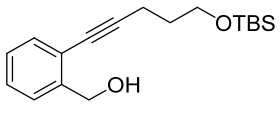
(2-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)benzaldehyde (S7).



S7

Following the general procedure, the reaction of *o*-bromobenzaldehyde (424 mg, 2.29 mmol) with ter-butyldimethyl(pent-4-yn-1-yloxy)silane[13] (500 mg, 2.52 mmol), $Pd(OAc)_2$ (40.4 mg, 0.0.18 mmol), PPh_3 (97 mg, 0.37 mmol), CuI (43.6 mg, 0.23 mmol) and Et_3N (15 mL, 108 mmol) was heated at 90 ºC for 4 h. After purification by column chromatography (20-40% EtOAc/hexanes) **S7** (492 mg, 71%) was obtained as a yellow oil. R_f = 0.39 (20% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.52-7.50 (m, 2H), 7.41-7.36 (m, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.58 (t, *J* = 6.0 Hz, 2H), 1.89-1.82 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2 (C), 135.0 (C), 133.7 (CH), 133.3 (CH), 127.9 (CH), 127.87 (C), 126.9 (CH), 97.7 (C), 76.4 (C), 61.5 (CH_2), 31.6 (CH_2), 25.9 (3 x CH_3), 18.4 (C), 16.1 (CH_2), -5.3 (2 x CH_3). HRMS (ESI) m/z calcd for for $C_{18}H_{26}O_2SiNa$ $[M+Na]^+$ 325.1600; found 325.1594.

(2-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenyl)methanol (19).[11]



19

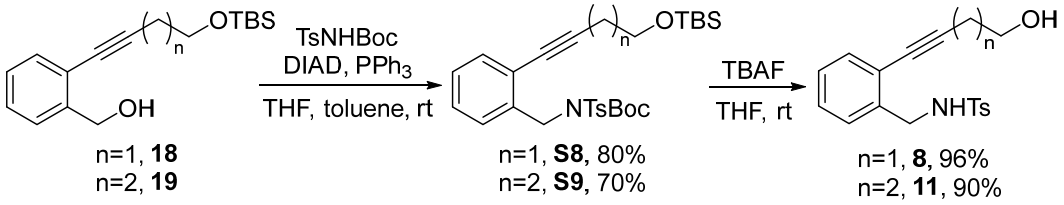
In a round-bottom flask equipped with a stirring bar (2-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)benzaldehyde (**S7**) (480 mg, 1.59 mmol) and MeOH (15 mL) were added. $NaBH_4$

12 H. F. Sneddon, M. J. Gaunt and S. V. Ley, Addition of Dithiols to Bis-Ynones: Development of a Versatile Platform for the Synthesis of Polyketide Natural Products, *Org. Lett*., 2003, **5**, 1147–1150.

13 H. G. Gudmundsson, C. J. Kuper, D. Cornut, F. Urbitsch, B. L. Elbert and E. A. Anderson, Synthesis of Cyclic Alkenyl Dimethylsiloxanes from Alkynyl Benzyldimethylsilanes and Application in Polyene Synthesis, *J. Org. Chem*., 2019, **84**, 14868–14882.

(37.8 mg, 1.91 mmol) was added at 0 ºC in portions and the reaction mixture was left to stirring at rt until completion of the reaction (30 min), indicated by TLC. The solvent was removed under reduced pressure and the residue redisolved in Et_2O (15 mL). The resulting organic extract was washed with saturated aqueous NH_4Cl, H_2O and brine, dried ($MgSO_4$) filtered and the solvent was removed under reduced pressure. After purification by column chromatography (20-40% EtOAc/hexanes) **19** (430 mg, 89%) was obtained as a yellow oil. R_f = 0.53 (20% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.29-7.22 (m, 2H), 4.79 (s, 2H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.55 (t, *J* = 6.0 Hz, 2H), 1.85-1.80 (m, 2H), 0.91 (s, 9H), -0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4 (C), 132.2 (CH), 128.0 (CH), 127.4 (CH), 127.3 (CH), 122.2 (C), 95.0 (C), 78.2 (C), 64.3 (CH_2), 61.6 (CH_2), 31.8 (C), 25.9 (3 x CH_3), 18.4 (C), 16.0 (CH_2), -5.3 (2 x CH_3). HRMS (ESI) m/z calcd for for $C_{18}H_{28}O_2SiNa$ $[M+Na]^+$ 327.1756; found 327.1749.

General procedure for the synthesis of *N*-tosyl (*o*-hydroxyalkynyl)benzyl amines 8 and 11.



n=1, **18**
n=2, **19**

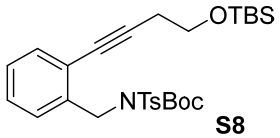
n=1, **S8**, 80%
n=2, **S9**, 70%

n=1, **8**, 96%
n=2, **11**, 90%

A solution of DIAD (1.3 equiv.) and PPh_3 (1.3 equiv.) in THF (0.2 M) was stirred at 0 ºC for 30 min. Then, a solution of the corresponding protected diols **18-19** (1 equiv.) and TsNHBoc (1 equiv.) in toluene (0.2 M) was added dropwise. Reaction mixture was stirred at rt until completion of the reaction, indicated by TLC. The solvent was evaporated under vacuo and the crude product was purified by column chromatography.

TBAF (1.5 equiv. 1M in THF) was added dopwise over a solution of the protected alcohols **S8-9** (1.0 equiv.) in THF (2 mL) and left stirring overnight at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL) at 0 ºC and the aqueous layer was extracted with EtOAc (3 x 10mL). The combined organic layer was washed with H_2O (15 mL), brine (15 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography.

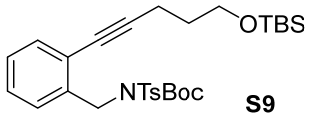
***tert*-Butyl (2-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)benzyl)(tosyl)-carbamate (S8).[11]**



S8

Following the general procedure, the reaction of **18** (200 mg, 0.70 mmol), TsNHBoc (190 mg, 0.70 mmol), DIAD (184 mg, 0.91 mmol) and PPh_3 (239 mg, 0.91 mmol) in THF (3.5 mL) and toluene (3.5 mL) was stirred at rt for 15 h afforded. After purification by column chromatography (4% EtOAc/hexanes) **S8** (293 mg, 80%) was obtained as a yellow oil. R_f = 0.8 (5% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.37-7.44 (m, 1H), 7.27.7.33 (m, 2H), 7.13-7.25 (m, 3H), 5.21 (s, 2H), 3.84 (t, *J* = 7.0 Hz, 2H), 2.68 (t, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 1.29 (s, 9 H), 0.92 (s, 9 H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0 (CO), 144.0 (C), 138.9 (C), 137.0 (C), 132.2 (CH), 129.2 (2 x CH), 128.3 (2 x CH), 128.0 (CH), 126.7 (CH), 125.3 (CH), 121.6 (C), 92.8 (C), 84.3 (C), 79.0 (C), 61.9 (CH_2), 49.1 (CH_2), 27.8 (3 x CH_3), 25.9 (3 x CH_3), 24.0 (CH_2), 21.6 (CH_3),18.3 (C), -5.2 (2 x CH_3). HRMS (ESI) m/z calcd for $C_{29}H_{41}NO_5SSiNa$ $[M+Na]^+$ 566.2372; found 566.2376.

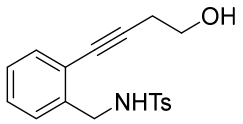
***tert*-Butyl (2-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)benzyl)(tosyl)-carbamate (S9).[11]**



S9

Following the general procedure, the reaction of **19** (250 mg, 0.82 mmol), TsNHBoc (223 mg, 0.82 mmol), DIAD (215.6 mg, 1.07 mmol) and PPh_3 (281 mg, 1.07 mmol) in THF (4 mL) and toluene (4 mL) was stirred at rt for 15 h. After purification by column chromatography (20% EtOAc/hexanes) **S9** (313 mg, 70%) was obtained as a yellow oil. R_f = 0.53 (30% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.15-7.25 (m, 3H), 5.21 (s, 2H), 3.77 (t, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.84 (quint, *J* = 6.6 Hz, 2H), 1.29 (s, 9 H), 0.91 (s, 9 H), 0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0 (CO), 144.3 (C), 139.1 (C), 137.3 (C), 132.2 (CH), 129.2 (2 x CH), 128.3 (2 x CH), 128.0 (CH), 126.7 (CH), 125.3 (CH), 121.6 (C), 92.8 (C), 84.3 (C), 79.0 (C), 62.0 (CH_2), 49.1 (CH_2), 31.8 (CH_2), 27.8 (3 x CH_3), 25.9 (3 x CH_3), 21.6 (CH_3), 18.3 (C), 16.1 (CH_2), -5.2 (2 x CH_3). HRMS (ESI) m/z calcd for $C_{30}H_{43}NO_5SSiNa$ $[M+Na]^+$ 580.2529; found 580.2507.

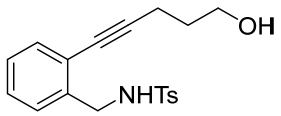
***N*-(2-(4-Hydroxybut-1-yn-1-yl)benzyl)-4-methylbenzenesulfonamide (8).[11]**



8

Following the general procedure, the reaction of **S8** (140 mg, 0.320 mmol) with TBAF (0.48 mL, 0.48 mmol) was stirred at rt for 15 h. After purification by column chromatography (40% EtOAc/hexanes) **8** (100 mg, 96%) was obtained as a white solid. R_f = 0.18 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.30-7.26 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.16-7.10 (m, 2H), 4.26 (s, 2H), 3.87 (t, *J* = 5.9 Hz, 2H), 2.68 (t, *J* = 5.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0 (C), 138.3 (C), 137.4 (C), 132.0 (CH), 129.4 (2 x CH), 129.2 (CH), 128.0 (CH), 127.7 (CH), 127.0 (2 x CH), 122.9(C), 93.1 (C), 80.0 (C), 61.1 (CH_2), 46.6 (CH_2), 23.5 (CH_2), 21.5 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NO_3SNa$, 352.0983; found 352.0987.

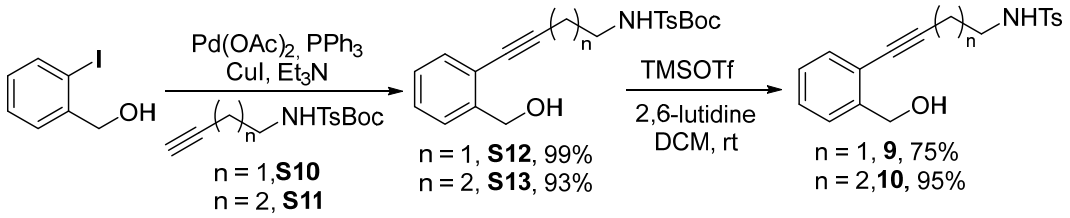
***N*-(2-(5-Hydroxypent-1-yn-1-yl)benzyl)-4-methylbenzenesulfonamide (11).[11]**



11

Following the general procedure, the reaction of **S9** (150 mg, 0.330 mmol) with TBAF (0.5 mL, 0.5 mmol) was stirred at rt for 16 h. After purification by column chromatography (50% EtOAc/hexanes) **11** (100 mg, 90%) was obtained as a white solid. R_f = 0.31 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.42-7.36 (m, 2H), 7.33-7.22 (m, 4H), 5.21 (br s, 1H), 4.77 (s, 2H), 3.15 (q, *J* = 6.5 Hz, 2H), 2.50 (t, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 1.79 (quint, *J* = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4 (C), 142.3 (C), 136.9 (C), 132.2 (CH), 129.7 (2 x CH), 128.2 (CH), 127.6 (CH), 127.5 (CH), 127.1 (2 x CH), 122.0 (C), 93.3 (C), 789.4 (C), 64.0 (CH_2), 42.3 (CH_2), 28.3 (CH_2), 21.5 (CH_3), 16.9 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{21}NO_3SNa$, 366.1140; found 366.1141.

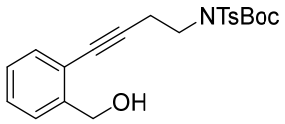
General procedure for the synthesis of *o*-(*N*-tosylaminoalkynyl)benzyl alcohols 9 and 10.



Alkynyl amine **S10-11** (1.1 equiv.) was added over a suspension of iodobenzylalcohol (1.0 equiv.), $Pd(OAc)_2$ (0.05 equiv.), PPh_3 (0.1 equiv.) and CuI (0.1 equiv.) in Et_3N (10 mL). The reaction mixture was stirred at rt until completion of the reaction, indicated by TLC. Then, reaction mixture was filtered through a celite pad and washed with EtOAc (20 mL). The filtrate was washed with H_2O (15 mL) and brine (15 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography.

TMSOTf (4 equiv.) was added dropwise over a solution of the alkynyl benzenesulphonamide **S12-13** (1.0 equiv.) and 2,6-lutidine (5 equiv.) in DCM (0.2 M) at 0 ºC. The reaction mixture was stirred at rt until completion of the reaction, indicated by TLC. Then, the reaction mixture was quenched with HCl (10 mL, 1M) and diluted with EtOAc (15 mL). The organic layer was washed with HCl (10 mL, 1M), saturated aqueous $NaHCO_3$ (10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by column chromatography.

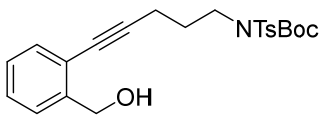
***tert*-Butyl (4-(2-(hydroxymethyl)phenyl)but-3-yn-1-yl)(tosyl)carbamate (S12).[11]**



S12

Following the general procedure, the reaction of (2-iodophenyl)methanol (152 mg, 0.65 mmol) with **S10** (230 mg, 0.71 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), PPh_3 (17 mg, 0.07 mmol) and CuI (12.4 mg, 0.07) in Et_3N (10 mL, 70.1 mmol) was stirred at rt for 4 h. After purification by column chromatography (40-50% EtOAc/hexanes) **S12** (275 mg, 99%) was obtained as a yellow syrup. R_f = 0.60 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32-7.17 (m, 4H), 4.76 (s, 2H), 4.11 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9 (CO), 144.3 (C), 142.7 (C), 137.2 (C), 132.4 (CH), 129.3 (2 x CH), 128.3 (CH), 127.9 (2 x CH), 127.6 (CH), 127.3 (CH), 121. 8 (C), 90.8 (C), 84.8 (C), 63.9 (CH_2), 45.3 (CH_2), 27.8 (3 x CH_3), 21.6 (CH_3), 21.1 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{27}NO_5SNa$, 452.1508; found 452.1506.

***tert*-Butyl (5-(2-(hydroxymethyl)phenyl)pent-4-yn-1-yl)(tosyl)carbamate (S13).[11]**

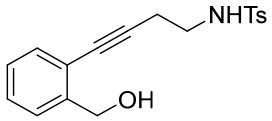


S13

Following the general procedure, the reaction of (2-iodophenyl)methanol (328 mg, 1.4 mmol) with **S11** (500 mg, 1.54 mmol), $Pd(OAc)_2$ (15.7 mg, 0.07 mmol), PPh_3 (37 mg, 0.17 mmol) and

CuI (26.7 mg, 0.14 mmol) in Et_3N (10 mL, 70.1 mmol) was stirred at rt for 3 h. After purification by column chromatography (40-50% EtOAc/hexanes) **S13** (580 mg, 93%) was obtained as a brown oil. R_f = 0.62 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.38 (td, *J* = 7.4, 1.3 Hz, 2H), 7.31-7.14 (m, 4H), 4.79 (s, 2H), 4.12-3.86 (m, 2H), 2.53 (t, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 2.06 (quint, *J* = 7.2 Hz, 2H), 1.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0 (CO), 144.3 (C), 142.5 (C), 137.3 (C), 132.3 (CH), 129.3 (2 x CH), 128.1 (CH), 127.8 (2 x CH), 127.6 (CH), 127.3 (CH), 122.1 (C), 93.5 (C), 84.5 (C), 79.0 (C), 64.3 (CH_2), 46.4 (CH_2), 29.2 (CH_2), 27.9 (3 x CH_3), 21.6 (CH_3), 17.1 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{29}NO_5SNa$, 466.1664; found 466.1668.

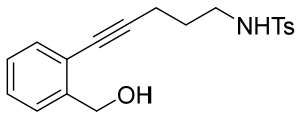
***N*-(4-(2-(Hydroxymethyl)phenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (9).[11]**



9

Following the general procedure, the reaction of **S12** (270 mg, 0.630 mmol) with TMSOTf (0.46 mL, 2.51 mmol) and 2,6-lutidine (0.36 mL, 3.13 mmol) in DCM (4.0 mL) was stirred at rt for 24 h. After purification by column chromatography (40% EtOAc/hexanes) **9** (155 mg, 75%) was obtained as a beige solid. R_f = 0.19 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.37 (dt, J = 7.2,1.7 Hz, 2H), 7.31-7.25 (m, 4H), 4.76 (s, 2H), 3.21 (t, *J* = 6.1 Hz, 2H), 2.61 (t, *J* = 6.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4 (C), 142.3 (C), 137.2 (C), 132.0 (CH), 129.7 (2 x CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 127.1 (2 x CH), 122.2 (C), 91.1 (C), 80.9 (C), 64.2 (CH_2), 42.1 (CH_2), 21.5 (CH_3), 20.9 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NO_3SNa$, 352.0983; found 352.0988.

***N*-(5-(2-(Hydroxymethyl)phenyl)pent-4-yn-1-yl)-4-methylbenzenesulfona-mide (10).[11]**

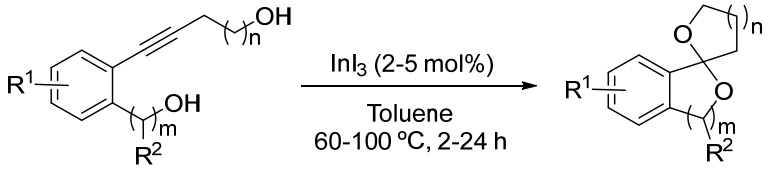


10

Following the general procedure, the reaction of **S13** (450 mg, 1.01 mmol) with TMSOTf (0.73 mL, 4.04 mmol) and 2,6-lutidine (0.59 mL, 5.05 mmol) in DCM (5 mL) was stirred at rt for 24 h. After purification by column chromatography (40% EtOAc/hexanes) **10** (330 mg, 95%) was obtained as a yellow solid. R_f = 0.77 (40% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 6.4, 1.8 Hz, 2H), 7.29 (dd, *J* = 6.3, 2.6 Hz, 1H), 7.21 (dd, *J* = 8.6, 0.7 Hz, 2H), 7.16-7.08 (m, 3H), 5.47 (t, *J* = 6.5 Hz, 1H), 4.25 (d, *J* = 6.5 Hz, 2H), 3.83 (t, *J* = 5.9 Hz, 2H), 2.55 (t, *J* = 5.9 Hz, 2H), 2.38 (s, 3H), 1.83 (quint, *J* = 5.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)

δ 143.2 (C), 137.8 (C), 137.2 (C), 132.3 (CH), 129.5(2 x CH), 128.9 (CH), 127.9 (CH), 127.7 (CH), 127.1 (2 x CH), 123.0 (CH), 95.2 (C), 78.6 (C), 61.7 (CH_2), 46.5 (CH_2), 30.8 (CH_2), 21.5 (CH_3), 16.3 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{21}NO_3SNa$, 366.1140; found 366.1144.

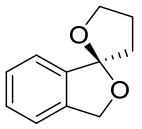
General procedure for the Indium-catalyzed synthesis of benzannulated spiroketals and spiroaminals.



n, m = 1, 2, 3
R^1 = H, OMe, Cl, Me
R^2 = H, Me

A Schlenk tube was charged with InI_3 (2-5 mol%) inside of a glovebox and a solution of the corresponding (*o*-hydroxyalkynyl)benzyl alcohol (100 mg, 0.6 mmol) in toluene (0.035 M) was added dropwise. The reaction mixture was then heated in an oil bath at the corresponding temperature (60–100 °C) and monitored by TLC until the starting alkyne diol was consumed. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with Et_2O (2 x 30 mL). The combined organic layer dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (EtOAc/hexanes) to give the corresponding pure spiroketal.

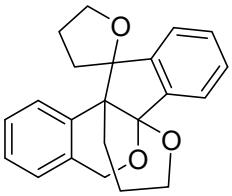
4,5-Dihydro-3*H*,3'*H*-spiro[furan-2,1'-isobenzofuran] (2a).[1,5]



2a

Following the general procedure, the reaction of **1a** (100 mg, 0.567 mmol) with InI_3 (5.6 mg, 0.011 mmol, 2 mol%) in toluene (17 mL) was heated at 60 ºC for 45 h. After purification by column chromatography (10% EtOAc/hexanes neutralized with 2% of Et_3N) **2a** (74 mg, 74%) was obtained as a colourless oil. R_f = 0.31 (10% EtOAc/hexanes) ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.33 (m, 3H), 7.28-7.25 (m, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.20-4.13 (m, 2H), 4.10-4.03 (m, 2H), 2.32-2.41 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2 (C), 139.1 (C), 128.9 (CH), 127.7 (CH), 122.0 (CH), 121.0 (CH), 117.0 (C), 70.8 (CH_2), 68.5 (CH_2), 37.1 (CH_2), 25.2 (CH_2). MS (EI) *m/z* (%) 176 [M^+] (22). HRMS (EI) m/z calcd $C_{11}H_{12}O_2$ $[M]^+$ 176.0832; found 176.0828.

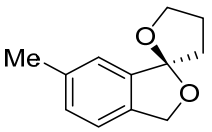
Characterization data of 4,5'-dihydro-3'H,5H-spiro[6a,11a-epoxy-propano)indeno[1,2-c]isochromene-11,2'-furan] (3a, Table 1).[14]



3a

R_f = 0.14 (10% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.42-7.33 (m, 3H), 7.31-7.23 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 5.36 (d, *J* = 14.9 Hz, 1H), 4.73 (d, *J* = 14.9 Hz, 1H), 4.14-4.12 (m, 1H), 4.04-3.98 (m, 1H), 3.96-3.90 (m, 1H), 3.53-3.46 (m, 1H), 2.61 (dd, *J* = 14.2 Hz, 2.7 Hz, 1H), 1.93-1.83 (m, 1H), 1.80-1.68 (m, 2H), 1.63-1.58 (m, 1H), 1.53-1.42 (m, 1H), 1.31-1.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5 (C), 137.2 (C), 135.0 (C), 134.6 (C), 130.0 (CH), 127.9 (CH), 127.0 (CH), 126.8 (CH), 126.2 (CH), 123.7 (CH), 123.4 (CH), 122.7 (CH), 102.7 (C), 93.9 (C), 70.0 (CH_2), 65.1 (CH_2), 63.2 (CH_2), 52.4 (CH_2), 37.3 (CH_2), 30.8 (CH_2), 29.7 (C), 25.9 (CH_2). MS (EI) *m/z* (%) 334 [M^+] (70). HRMS (EI) m/z calcd $C_{22}H_{22}O_3$ $[M]^+$ 334.1563; found 334.1572.

6'-Methyl-4,5-dihydro-3*H*,3'*H*-spiro[furan-2,1'-isobenzofuran] (2b).



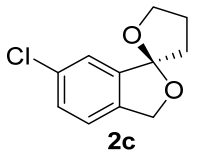
2b

Following the general procedure, the reaction of **1b** (100 mg, 0.500 mmol) with InI_3 (4.9 mg, 0.01 mmol, 2 mol%) in toluene (14 mL) was heated at 60 ºC for 6 h. After purification by column chromatography (40% EtOAc/hexanes neutralized with 2% of Et_3N) **2b** (65 mg, 65%) was obtained as a yellow solid. R_f = 0.67 (30% EtOAc/hexanes).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.3 Hz, 1H), 6.91 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 5.10 (d, *J* = 12.1 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.15-4.12 (m, 1H), 4.06-4.04 (m, 1H), 3.82 (s, 3H), 2.29-2.13 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (C), 140.6 (C), 132.1 (C), 121.8 (CH), 116.9 (C), 116.0 (CH), 106.6 (CH), 70.5 (CH_2), 68.5 (CH_2), 55.6 (CH_2), 37.0 (CH_2), 25.2 (CH_3).

14 M. G. Timerbulatova, M. R. D. Gatus, K. Q. Vuong, M. Bhadbhade, A. G. Algarra, S. A. Macgregor and B. A. Messerle in Bimetallic Complexes for Enhancing Catalyst Efficiency: Probing the Relationship between Activity and Intermetallic Distance, *Organometallics*, 2013, **32**, 5071–5081.

MS (EI) *m/z* (%) 190 $[M]^+$ (84). HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ $[M]^+$ 190.0988; found 190.0990.

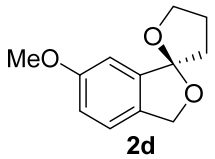
6'-Chloro-4,5-dihydro-3*H*,3'*H*-spiro[furan-2,1'-isobenzofuran] (2c).



2c

Following the general procedure, the reaction of **1c** (100 mg, 0.430 mmol) with InI_3 (4.23 mg, 0.009 mmol, 2 mol%) in toluene (12 mL) was heated at 80 ºC for 24 h. After purification by column chromatography (15% EtOAc/hexanes neutralized with 2% of Et_3N) **2c** (59 mg, 59%) was obtained as a yellow oil. R_f = 0.33 (20% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 5.00 (d, *J* = 12.8 Hz, 1H), 4.10 (d, *J* = 12.9 Hz, 1H), 4.17-4.12 (m, 1H), 4.09-4-01 (m, 1H), 2.30-2.14 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3 (C), 138.7 (C), 133.6 (C), 129.2 (CH), 122.5 (CH), 122.3 (CH), 116.5 (C), 70.4 (CH_2), 68.7 (CH_2), 37.1 (CH_2), 25.2 (CH_2). MS (EI) *m/z* (%) 210 $[M]^+$ (28), 169 $[M - C_3H_6]^+$ (47). HRMS (EI) m/z calcd for $C_{11}H_{11}ClO_2$ $[M]^+$, 210.0442; found 210.0441.

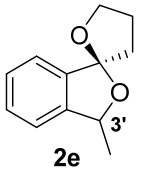
6'-Methoxy-4,5-dihydro-3*H*,3'*H*-spiro[furan-2,1'-isobenzofuran] (2d).



2d

Following the general procedure, the reaction of **1d** (100 mg, 0.360 mmol) with InI_3 (3.60 mg, 0.007 mmol, 5 mol%) in toluene (10 mL) was heated at 80 ºC for 3 h. After purification by column chromatography (10% EtOAc/hexanes neutralized with 2% of Et_3N) **2d** (61 mg, 61%) was obtained as a yellow oil. R_f = 0.39 (20% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.2 Hz, 1H), 6.90 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.15-4.12 (m, 1H), 4.08-4.02 (m, 1H), 3.82 (s, 3H), 2.29-2.13 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9 (C), 140.6 (C), 132.1 (C), 121.8 (CH), 116.9 (C), 116.0 (CH), 106.5 (CH), 70.5 (CH_2), 68.5 (CH_2), 55.6 (CH_3), 37.0 (CH_2), 25.2 (CH_2). MS (EI) *m/z* (%) 206 $[M]^+$ (64). HRMS (EI) m/z calcd for $C_{12}H_{14}O_3$ $[M]^+$ 206.0937; found 206.0945.

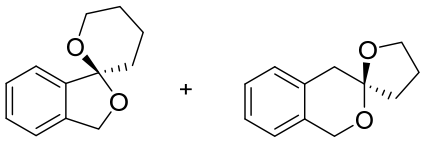
3'-Methyl-4,5-dihydro-3*H*,3'*H*-spiro[furan-2,1'-isobenzofuran] (2e).



2e

Following the general procedure, the reaction of **1h** (100 mg, 0.530 mmol) with InI_3 (5.21 mg, 0.01 mmol, 2 mol%) in toluene (14 mL) in toluene was heated at 60 ºC for 24 h. After purification by column chromatography (10% EtOAc/hexanes neutralized with 2% of Et_3N) a non-separable mixture of isomers of **2e** (72 mg, 72%) were obtained as a yellow oil, in a ratio 60:40 determined by ^1H NMR of the crude. R_f = 0.45 (20% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.17 (m, 4H), 5.40 (q, *J* = 6.7 Hz, 0.60H, $H_{3'}$ major isomer), 5.22 (q, *J* = 6.6 Hz, 0.40H, $H_{3'}$ minor isomer), 4.07-4.04 (m, 2H), 2.34-2.25 (m, 4H), 1.57 (d, *J* = 6.4 Hz, 1.2H minor isomer), 1.51 (d, *J* = 6.4 Hz, 1.8H major isomer).^{13}C NMR (75 MHz, $CDCl_3$) δ mixture of major and minor isomers 144.7 (C), 144.5 (C), 139.39 (C), 139.38 (C), 128.99 (CH), 128.93 (CH), 127.88 (CH), 127.83 (CH), 122.03 (CH), 121.84 (CH), 120.87 (CH), 120.80 (CH), 78.1 (C), 77.3 (C), 68.6 (CH), 68.3 (CH), 37.67 (CH_2), 37.63 (CH_3), 29.78 (CH_2), 29.70 (CH_2), 25.29 (CH_3), 25.21 (CH_2) 23.3 (CH_2), 21.3 (CH_2). MS (EI) m/z (%) 190 $[M]^+$ (6), 104 $[M - C_4H_6O_2]^+$ (100). HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ $[M]^+$ 190.0988; found 190.0999.

3',4',5',6'-Tetrahydro-3*H*-spiro[isobenzofuran-1,2'-pyran] and 4,5-dihydro-3H-spiro[furan-2,3'-isochromane] (4a and 5a).[1,5,15]



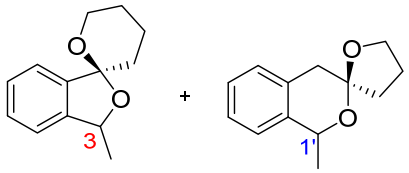
4a **5a**

Following the general procedure, the reaction of **1f** (100 mg, 0.500 mmol) with InI_3 (5.20 mg, 0.01 mmol, 2 mol%) in toluene (15 mL) was heated at 60 ºC for 17 h. After purification by column chromatography (10% EtOAc/hexanes neutralized with 2% of Et_3N) a non-separable mixture of **4a** and **5a** (90 mg, 90%) were obtained as a yellow solid, in a ratio **4a**:**5a** of 1:3.5 (determined by ^1H NMR of the crude). For compound **4a**: R_f = 0.41 (20% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.32 (m, 3H), 7.26 (m, 1H), 5.18 (d, *J* = 12.6 Hz, 1H), 5.00 (d, *J* = 12.6 Hz, 1H), 4.12-4.04 (m, 1H), 3.82-3.78 (m, 1H), 2.15-1.84 (m, 4H), 1.79-1.63 (m, 2H). For compound **5a**: R_f = 0.41 (20% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 7.11-7.07 (m, 1H), 4.92 (d, *J* = 14.9 Hz, 1H), 4.68 (d, *J* = 14.8 Hz, 1H), 4.00 (apparent

15 J. H. H. Ho, R. Hodgson, J¨org Wagler and B. A. Messerle. Highly Efficient Rh(I) and Ir(I) single and Dual Metal Catalysed Dihydroalkoxylation Reactions, *Dalton Trans.*, 2010, **39**, 4062–4069.

t, J = 7.3 Hz, 2H), 3.23 (d, J = 16.4 Hz, 1H), 2.83 (d, J = 16.4 Hz, 1H), 2.20-1.88 (m, 4H). Mixture of compounds **4a:5a** ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7 (C), 139.9 (C), 133.7 (CH), 131.9 (CH), 128.8 (CH), 128.7 (CH), 127.5 (C), 126.4 (CH), 126.0 (CH), 123.9 (CH), 121.7 (C), 121.2 (C), 108.0 (C), 105.2 (CH), 71.0 (CH_2), 67.9 (CH_2), 63.3 (CH_2), 62.5 (CH_2), 37.2 (CH_2), 36.0 (CH_2), 33.8 (CH_2), 25.2 (CH_2), 23.8 (CH_2), 19.6 (CH_2). HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{12}H_{14}O_2Na$ 213.0988; found 213.0885.

3-Methyl-3',4',5',6'-tetrahydro-3*H*-spiro[isobenzofuran-1,2'-pyran] (4b)[16] and 1'-Methyl-4,5-dihydro-3*H*-spiro[furan-2,3-isochromane (5b).

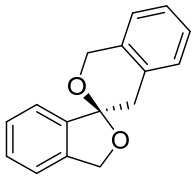


4b **5b**

Following the general procedure, the reaction of **1g** (100 mg, 0.49 mmol) with InI_3 (12.1 mg, 0.024 mmol, 5 mol%) in toluene (14 mL) was heated at 80 ºC for 15 h. After purification by column chromatography (95% EtOAc/hexanes neutralized with 2% of Et_3N) a mixture of **4b** and **5b** (91 mg, 91%) were obtained as a colorless oil, in a ratio of 1.9:1 (determined by ^{1}H NMR). For compound **4b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.29 (m, 3H), 7.17-7.15 (m, 1H), 5.37 (q, J = 6.6 Hz, 0.6H, H_3 major isomer), 5.28 (q, J = 6.6 Hz, 0.4H, H_3 minor isomer), 4.14-4.09 (m, 2H), 3.81-3.76 (m, 1H), 2.22-2.03 (m, 2H), 1.86-1.71 (m, 3H), 1.65-1.63 (m, 1H), 1.56 (d, J = 6.6 Hz, 1.2H, CH_3 minor isomer), 1.51 (d, J = 6.6 Hz, 1.8H, CH_3 major isomer). For compound **5b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.14 (m, 2H), 7.12-7.06 (m, 1H), 4.98 (q, J = 6.6 Hz, 1H), 4.01-3.94 (m, 2H), 3.27 (d, J = 15.4 Hz, 1H), 2.80 (d, J = 15.4 Hz, 1H), 2.22-2.03 (m, 2H), 1.91-1.71 (m, 2H), 1.54 (d, J = 6.6 Hz, 3H, CH_3). Mixture of **4b** and **5b**: ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.44 (C), 144.27 (C), 141.94 (C), 141.56 (C), 138.58 (C), 131.94 (C), 128.94 (2 x CH), 128.61 (CH), 127.69 (CH), 127.64 (CH), 126.39 (CH), 126.20 (CH), 124.08 (CH), 121.77 (CH), 121.55 (CH), 121.09 (CH), 120.98 (CH), 107.33 (C), 106.72 (C), 105.14 (C), 79.02 (CH), 77.03 (CH), 67.78 (CH_2), 67.07 (CH), 63.23 (CH_2), 62.70 (CH_2), 37.58 (CH_2), 36.78 (CH_2), 34.58 (CH_2), 34.26 (CH_2), 25.27 (CH_2), 25.19 (CH_2), 23.91 (CH_2), 23.60(CH_3), 21.38 (CH_3), 21.22 (CH_3), 19.68 (CH_2), 19.52 (CH_2). HRMS (EI) m/z calcd for $C_{13}H_{15}O_2Na[M]^+$ 227.1048; found 227.1043.

16 A. N. Butkevich, A. Corbu, L. Meerpoel, I. Stansfield, P. Angibaud, P. Bonnet and J. Cossy, Two-Step One-Pot Synthesis of Benzoannulated Spiroacetals by Suzuki-Miyaura Coupling/Acid-Catalyzed Spiroacetalization, *Org. Lett*., 2012, **14**, 4998–5001.

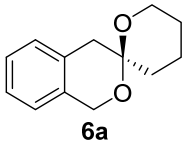
3*H*-Spiro[isobenzofuran-1,3'-isochromane] (4c).[5,15]



4c

Following the general procedure, the reaction of **1h** (100 mg, 0.42 mmol) with InI_3 (10.4 mg, 0.021 mmol, 5 mol%) in toluene (12 mL) was heated at 60 ºC for 18 h. After purification by column chromatography (5% EtOAc/hexanes neutralized with 2% of Et_3N) **4c** (68 mg, 68%) was obtained as a yellow oil. R_f = 0.59 (10% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.46-7.32 (m, 4H), 7.28-7.20 (m, 3H), 7.14-7.11 (m, 1H), 5.29 (d, *J* = 12.6 Hz, 1H), 5.20 (d, *J* = 15.3 Hz, 1H), 5.11 (d, *J* = 12.7 Hz, 1H), 4.91 (d, *J* = 15.0 Hz, 1H), 3.61 (d, *J* = 16.3 Hz, 1H), 3.11 (d, *J* = 16.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6 (C), 140.1 (C), 133.8 (C), 131.6 (C), 129.2 (CH), 128.9 (CH), 127.8 (CH), 126.8 (CH), 126.3 (CH), 124.0 (CH), 122.0 (CH), 121.3 (CH), 107.6 (C), 71.6 (CH_2), 64.5 (CH_2), 36.9 (CH_2). MS (EI) *m/z* (%) 238 $[M]^+$ (1), 104 $[M - C_8H_6O_2]^+$ (100). HRMS (EI) m/z calcd for $C_{16}H_{14}O_2$ $[M]^+$ 238.0988; found 238.0951.

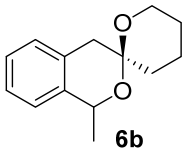
3',4',5',6'-Tetrahydrospiro[isochromane-3,2'-pyran] (6a).[15]



6a

Following the general procedure, the reaction of **1i** (100 mg, 0.490 mmol) with InI_3 (12.1 mg, 0.02 mmol, 5 mol%) in toluene (14 mL) was heated at 80 ºC for 24 h. After purification by column chromatography (10% EtOAc/hexanes neutralized with 2% of Et_3N) **6a** (70 mg, 70%) was obtained as a colorless oil. R_f = 0.37 (10% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 7.09-7.07 (m, 1H), 7.03-7.01 (m, 1H), 4.76 (d, *J* = 14.9 Hz, 1H), 4.70 (d, *J* = 14.8 Hz, 1H), 3.80 (dt, *J* = 11.1, 3.7 Hz, 1H), 3.71-3.65 (m, 1H), 2.90 (d, *J* = 16.6 Hz, 1H), 2.77 (d, *J* = 16.6 Hz, 1H), 2.04-1.90 (m, 1H), 1.86-1.80 (m, 1H), 1.74-1.55 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.6 (C), 131.2 (C), 128.9 (CH), 126.5 (CH), 125.8 (CH), 123.8 (CH), 95.3 (C), 61.7 (CH_2), 38.9 (CH_2), 34.8 (CH_2), 25.0 (CH_2), 18.8 (CH_2). MS (EI) *m/z* (%) 204 $[M]^+$ (3), 204 $[M - C_8H_8]^+$ (100). HRMS (EI) m/z calcd for $C_{13}H_{16}O_2$ $[M]^+$ 204.1145; found 204.1148.

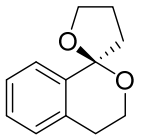
1-Methyl-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran] (6b).



6b

Following the general procedure, the reaction of **1j** (100 mg, 0.46 mmol) with InI_3 (11.4 mg, 0.23 mmol, 5 mol%) in toluene (14 mL) was heated at 80 ºC for 17 h. After purification by column chromatography (5% EtOAc/hexanes neutralized with 2% of Et_3N) **6b** (36 mg, 36%) was obtained as a pale yellow oil. R_f = 0.58 (20% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.16 (m, 2H), 7.13-7.11 (m, 1H), 7.08-7.05 (m, 1H), 4.88 (q, *J* = 6.5 Hz, 1H), 3.80 (dd, *J* = 11.3, 3.2 Hz, 1H), 3.67-3.64 (m, 1H), 2.80 (d, *J* = 16.5 Hz, 1H), 2.76 (d, *J* = 16.3 Hz, 1H), 2.05-1.96 (m, 1H), 1.85-1.79 (m, 1H), 1.71-1.62 (m, 3H), 1.59 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5 (C), 131.4 (C), 128.8 (CH), 126.5 (CH), 126.0 (CH), 123.9 (CH), 95.3 (C), 66.1 (CH), 61.8 (CH_2), 39.6 (CH_2) 35.2 (CH_2), 25.2 (CH_2), 21.2 (CH_3), 18.9 (CH_2). HRMS (EI) m/z calcd for $C_{14}H_{18}O_2$ $[M]^+$ 218.1301; found 218.1287.

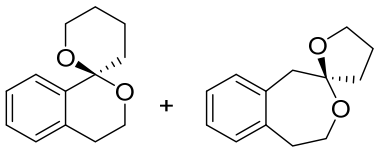
4,5-Dihydro-3*H*-spiro[furan-2,1'-isochromane] (5c).[16]



5c

Following the general procedure, the reaction of **1k** (100 mg, 0.530 mmol) with InI_3 (13 mg, 0.03 mmol, 5 mol%) in toluene (13 mL) was heated at 100 ºC for 1 h. After purification by column chromatography (10% EtOAc/hexanes neutralized with 2% of Et_3N) **5c** (85 mg, 85%) was obtained as a white solid. R_f = 0.35 (20% EtOAc/Hex). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.22 (m, 3H), 7.14-7.12 (m, 1H), 4.15-3.95 (m, 3H), 3.95 (ddd, *J* = 11.2, 5.8, 1.8 Hz, 1H), 3.10-3.02 (m, 1H), 2.64 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.34-2.24 (m, 3H), 2.19-2.12 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3 (C), 135.2 (C), 128.4 (CH), 127.7 (CH), 126.6 (CH), 126.5 (CH), 105.6 (C), 68.0 (CH_2), 59.5 (CH_2), 39.6 (CH_2), 28.8 (CH_2), 25.2 (CH_2). MS (EI) *m/z* (%) 190 $[M]^+$ (21), 86 $[M - C_8H_8]^+$ (100). HRMS (EI) m/z calcd for for $C_{12}H_{14}O_2$ $[M]^+$ 190.0988; found 190.0983.

3',4',5',6'-Tetrahydrospiro[isochromane-1,2'-pyran] (6c)[16] and 4,4',5,5'-tetrahydro-1*H*,3'*H*-spiro[benzo[d]oxepine-2,2'-furan] (7a).



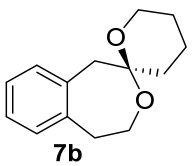
6c **7a**

Following the General procedure, the reaction of **1l** (100 mg, 0.490 mmol) with InI_3 (12.1 mg, 0.02 mmol, 5 mol%) in toluene (14 mL) was heated at 100 ºC for 5 h. After purification by column chromatography (2% EtOAc/hexanes neutralized with 2% of Et_3N) **6c** (79 mg, 79%) and **7a** (15 mg, 15%) were obtained as yellow oils.

For compound **6c:** R_f = 0.28 (10% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.32 (m, 1H), 7.18-7.13 (m, 2H), 7.04-7.01 (m, 1H), 3.39-3.84 (m, 3H), 3.63 (dd, *J* = 5.0, 3.2 Hz, 1H), 3.03-2.94 (m, 1H), 2.50 (dd, *J* = 16.3, 3.3 Hz, 1H), 2.04 (td, *J* = 12.7, 4.0 Hz, 1H), 1.75-1.62 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3 (C), 134.2 (C), 128.5 (CH), 127.6 (CH), 126.5 (CH), 126.4 (CH), 96.2 (C), 61.5 (CH_2), 58.1 (CH_2), 35.4 (CH_2), 28.9 (CH_2), 25.2 (CH_2), 19.1 (CH_2). MS (EI) *m/z* (%) 204 $[M]^+$ (50). HRMS (EI) m/z calcd for $C_{13}H_{16}O_2$ $[M]^+$ 204.1145; found 204.1152.

For compound **7a:** R_f = 0.17 (10% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15-7.05 (m, 4H), 3.96-3.89 (m, 2H), 3.85-3.81 (m, 1H), 3.76-3.71 (m, 1H), 3.42 (d, *J* = 14.4 Hz, 1H), 3.21-3.14 (m, 1H), 3.01 (d, *J* = 14.5 Hz, 1H), 2.79 (dd, *J* = 5.5,1.79 Hz, 1H), 2.11-2.01 (m, 2H), 1.96-1.88 (m, 1H), 1.85-1.78 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6 (C), 137.1 (C), 130.3 (CH), 128.8 (CH), 126.7 (CH), 126.4 (CH), 106.2 (C), 67.6 (CH_2), 61.3 (CH_2), 46.2(CH_2), 38.7 (CH_2), 38.4 (CH_2), 24.0 (CH_2). HRMS (EI) m/z calcd for $C_{13}H_{16}O_2$ $[M]^+$ 204.1145; found 204.1152.

3',4',5',5',6'-Hexahydro-1*H*-spiro[benzo[*d*]oxepine-2,2'-pyran] (7b).

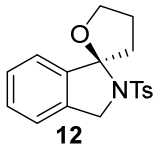


7b

Following the general procedure, the reaction of **1m** (100 mg, 0.460 mmol) with InI_3 (11.3 mg, 0.02 mmol, 5 mol%) in toluene (14 mL) was heated at 100 ºC for 48 h. After purification by column chromatography (10% EtOAc/hexanes neutralized with 2% of Et_3N) **7b** (71 mg, 71%) was obtained as a colourless oil. R_f = 0.40 (10% EtOAc/Hex). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.07 (m, 4H), 3.93-3.78 (m, 2H), 3.66-3.57 (m, 2H), 3.23-3.13 (m, 2H), 2.97 (d, *J* = 14.6

Hz, 1H), 2.86-2.79 (m, 1H), 1.87-1.74 (m, 2H), 1.65-1.47 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5 (C), 136.7 (C), 130.5 (CH), 128.6 (CH), 126.6 CH), 126.4 (CH), 96.2 (C), 61.3 (CH_2), 60.4 (CH_2), 48.4 (CH_2), 38.0 (CH_2), 35.8 (CH_2), 25.1(CH_2), 18.9 (CH_2). MS (EI) *m/z* (%) 218 $[M]^+$ (16), 118 $[M - C_5H_8O_2]^+$ (100). HRMS (EI) m/z calcd for $C_{14}H_{18}O_2$ $[M]^+$ 218.1301; found 218.1302.

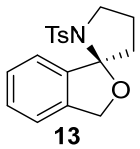
2'-Tosyl-4,5-dihydro-3*H*-spiro[furan-2,1'-isoindoline] (12).[11]



12

Following the general procedure, the reaction of **8** (80 mg, 0.24 mmol) with InI_3 (6 mg, 0.01 mmol) in toluene (7.5 mL) was heated at 80 ºC for 3 h. After purification by column chromatography (15% EtOAc/hexanes) **12** (48 mg, 60%) was obtained as a colorless oil. R_f = 0.54 (30% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.4, 1.9 Hz, 2H), 7.34-7.27 (m, 5H), 7.19-7.16 (m, 1H), 4.65 (d, *J* = 13.3 Hz, 1H), 4.50-4.43 (m, 2H), 4.15-4.09 (m, 1H), 3.26-3.18 (m, 1H), 2.61-2.45 (m, 2H), 2.41 (s, 3H), 2.33-2.21 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4 (C), 143.3 (C), 136.9 (C), 133.9 (C), 129.3 (2 x CH), 128.9 (CH), 128.4 (CH), 127.9 (2 xCH), 122.2 (CH), 122.0 (CH), 105.9 (C), 70.0 (CH_2), 52.7 (CH_2), 39.6 (CH_2), 26.6 (CH_2), 21.5 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NO_3SNa$, 352.0983; found 352.0988.

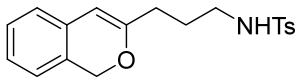
1'-Tosyl-3*H*-spiro[isobenzofuran-1,2'-pyrrolidine] (13).[11]



13

Following the general procedure, the reaction of **9** (100 mg, 0.30 mmol) with InI_3 (7.5 mg, 0.015 mmol) in toluene (9.5 mL) was heated at 80 ºC for 3 h. After purification by column chromatography (15-25% EtOAc/hexanes) **13** (49 mg, 49%) was obtained as a colorless oil. R_f = 0.41 (30% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.5 Hz, 2H), 7.34 (t, *J* = 6.1 Hz, 1H), 7.26-7.19 (m, 4H), 7.09 (d, *J* = 8.3 Hz, 1H), 5.32 (d, *J* =12.1 Hz, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 3.69-3.64 (m, 1H), 3.57-3.52 (m, 1H), 2.42 (s, 3H), 2.27-2.24 (m, 1H), 2.10-2.05 (m, 1H), 2.01-1.97 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9 (C), 139.8 (C), 139.4 (C), 137.6 (C), 129.1 (2 x CH), 128.7 (CH), 127.4 (2 x CH), 122.2 (CH), 120.9 (CH), 105.4 (C), 72.0 (CH_2), 49.3 (CH_2), 43.0 (CH_2), 22.5 (CH_2), 21.5 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NO_3SNa$, 352.0983; found 352.0978.

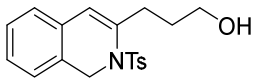
***N*-(3-(1*H*-Isochromen-3-yl)propyl)-4-methylbenzenesulfonamide (14).[11]**



14

Following the general procedure, the reaction of **10** (95 mg, 0.28 mmol) with InI_3 (6.9 mg, 0.014 mmol) in toluene (9 mL) was heated at 80 ºC for 2 h. After purification by column chromatography (20% EtOAc/hexanes) **14** (53 mg, 53%) was obtained as an organge oil. R_f = 0.15 (30% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.4, 1H), 7.23 (t, *J* = 7.3 Hz, 1 H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 5.70 (s, 1H), 5.11 (s, 2H), 4.98 (t, *J* = 6.3 Hz, 2H), 3.13 (q, *J* = 6.5 Hz, 2H), 2.54 (s, 3H), 2.33 (t, *J* = 7.3 Hz, 2H), 1.87 (quint, *J* = 7.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9 (C), 143.4 (C), 137.0 (C), 131.5 (C), 129.7 (2 x CH), 129.1 (CH), 128.1 (CH), 127.1 (2 x CH),126.0 (CH), 123.7 (CH), 122.5 (CH), 101.9 (CH), 68.7 (CH_2), 42.5 (CH_2), 30.5 (CH_2), 27.0 (CH_2), 21.5 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{21}NO_3SNa$, 366.1140; found 366.1136.

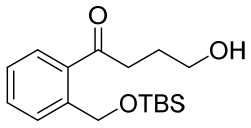
3-(2-Tosyl-1,2-dihydroisoquinolin-3-yl)propan-1-ol (15).[11]



15

Following the general procedure, the reaction of **11** (100 mg, 0.29 mmol) with InI_3 (7.2 mg, 0.014 mmol) in toluene (9.0 mL) was heated at 80 ºC for 3 h. After purification by column chromatography (15-25% EtOAc/hexanes) **15** (58 mg, 58%) was obtained as a yellow oil. R_f = 0.39 (30% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.04-6.93 (m, 3H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 7.3, 1H), 6.19 (s, 1H), 4.71 (s, 2H), 3.75 (t, *J* = 6.3 Hz, 2H), 2.80 (t, *J* = 6.0 Hz, 2H), 2.18 (s, 3H), 1.98 (quint, *J* = 7.0 Hz, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2 (C), 141.1 (C), 134.7 (C), 131.0 (C), 129.2 (CH), 128.5 (2 x CH), 127.3 (2 x CH), 127.1 (2 x CH), 125.0 (CH), 124.1 (CH) 120.2 (CH), 62.1 (CH_2), 50.8 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 21.3 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{21}NO_3SiNa$, 366.1140; found 366.1141.

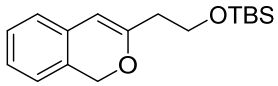
(2-(1*H*-Isochromen-3-yl)ethoxy)(*tert*-butyl)dimethylsilane (17).



17

Following the general procedure, the reaction of **16** (100 mg, 0.340 mmol) with InI_3 (8.5 mg, 0.175 mmol, 5 mol%) in toluene (10 mL) was heated at 60 ºC for 2 days. After purification by column chromatography (5-20% EtOAc/hexanes neutralized with 2% of Et_3N) **17** (38 mg, 38%) was obtained as a yellow oil. R_f = 0.15 (20% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (t, *J* = 8.8 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.1 Hz, 1H), 5.02 (s, 2H), 3.73 (t, *J* = 6.2 Hz, 2H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.14 (quint, *J* = 6.6 Hz, 2H), 0.96 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4 (C), 143.2 (2 x C), 132.2 (CH), 128.9 (CH), 126.9 (CH), 126.4 (CH), 63.5 (CH_2), 62.4 (CH_2), 37.4 (CH_2), 27.1 (CH_2), 26.0 (2 x CH_3), 5.3 (CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{28}O_3SiNa$, 331.1705; found 331.1699.

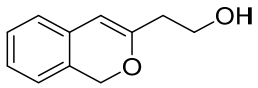
(2-(1*H*-Isochromen-3-yl)ethoxy)(*tert*-butyl)dimethylsilane (20).



20

Following the general procedure, the reaction of **17** (100 mg, 0.340 mmol) with InI_3 (8.4 mg, 0.017 mmol, 5 mol%) in toluene (10 mL) was heated at 60 ºC for 3 h. After purification by column chromatography (2% EtOAc/hexanes neutralized with 2% of Et_3N) 1**9** (55 mg, 55%) was obtained as a yellow oil. R_f = 0.53 (10% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.22-7.06 (m, 2H), 7.10 (dt, *J* = 7.4,1.4 Hz, 1H), 6.95 (dd, *J* = 7.2, 1.3 Hz, 1H), 5.71 (s, 1H), 5.04 (s, 2H), 3.83 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 6.8 Hz, 2H), -0.90 (s, 9 H), -0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7 (C), 131.9 (C), 128.1 (CH), 127.2 (C), 125.8 (CH), 123.7 (CH), 122.4 (CH), 102.5 (CH), 68.7 (CH_2), 60.9 (CH_2), 37.5 (CH_2), 25.9 (3 x CH_3), 18.3 (C), -5.3 (2 x CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{26}O_2SiNa$ 313.1600; found 313.1595.

(2-(1*H*-Isochromen-3-yl)ethan-1-ol (3b).[5]

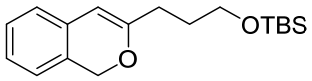


3b

TBAF (0.62 mL, 0.62 mmol, 1M in THF) was added dropwise over a solution of isochromene **20** (180 mg, 0.62 mmol) in THF (15 mL) was stirred at 0 ºC and left stirring overnight at rt. Then, reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL) at 0 ºC and the aqueous layer was extracted with Et_2O (3 x 10mL). The combined organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. After purification by column chromatography (25% EtOAc/hexanes neutralized with 2% of Et_3N) **3b** (67 mg, 61%) was obtained as a colorless oil. R_f = 0.53 (10% EtOAc/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.25-7.09 (m, 2H), 7.00 (dd, *J* = 7.4 y 1.4 Hz, 1H), 6.94 (dd, *J* = 7.2, 1.3 Hz,

1H), 5.73 (s, 1H), 5.07 (s, 2H), 3.83 (t, *J* = 6.8 Hz, 2H), 2.47 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4 (C), 131.4 (C), 128.2 (CH), 127.1 (C), 126.1 (CH), 123.7 (CH), 122.6 (CH), 102.9 (CH), 68.8 (CH_2), 60.5 (CH_2), 37.0 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}O_2Na$ 199.0735; found 199.0718.

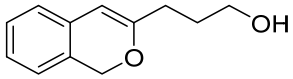
(3-(1*H*-Isochromen-3-yl)propoxy)(*tert*-butyl)dimethylsilane (21).



21

Following the general procedure, the reaction of **19** (100 mg, 0.330 mmol) with InI_3 (8.1 mg, 0.016 mmol, 5 mol%) in toluene (9 mL) was heated at 80 ºC for 2 h. After purification by column chromatography (2% EtOAc/hexanes) **21** (49 mg, 49%) was obtained as a light yellow solid. R_f = 0.77 (10% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.18 (m, 1H), 7.17-7.16 (m, 1H), 7.10 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.00-6.97 (m, 1H), 6.92 (dd, *J* = 7.4, 1.4 Hz, 1H), 5.62 (s, 1H), 5.05 (s, 2H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.27 (t, *J* = 6.3 Hz, 2H), 1.84-1.75 (m, 2H), 1.05 (s, 9H), -0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5 (C), 132.0 (C), 128.1 (CH), 127.2 (C), 125.7 (CH), 123.7 (CH), 122.4 (CH), 101.1 (C), 68.8 (CH_2), 62.4 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 26.0 (3 x CH_3), 18.4 (C), -5.3 (2 x CH_3). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{28}O_2SiNa$ 327.1756; found 327.1753.

(3-(1*H*-Isochromen-3-yl)propan-1-ol (22).[17]



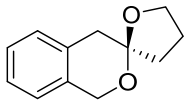
22

TBAF (0.16 mL, 0.16 mmol, 1M in THF) was added dropwise over a solution of isochromene **21** (48 mg, 0.16 mmol) in THF (5 mL) was stirred at 0 ºC and left stirring 1 h at rt. Then, reaction mixture was quenched with saturated aqueous NH_4Cl (3 mL) at 0 ºC and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layer was washed with brine (5 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. After purification by column chromatography (30% EtOAc/hexanes neutralized with 2% of Et_3N) **22** (30 mg, 99%) was obtained as a white solid. R_f = 0.14 (10% EtOAc/hexanes). ^{1}H NMR (300 MHz, Toluene-d8) δ 7.09-7.01 (m, 1H), 6.94 (dt, *J* = 7.5, 1.4 Hz, 1H), 6.81 (d, *J* = 7.5Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 5.54 (s, 1H), 4.82 (s, 2H), 3.42 (t, *J* = 6.3 Hz, 2H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.72-1.63

17 R. Visbal, R. P. Herrera and M. C. Gimeno, Thiolate Bridged Gold(I)–NHC Catalysts: New Approach for Catalyst Design and its Application to Trapping Catalytic Intermediates**,** *Chem. Eur. J.*, 2019, **25**, 15837–15845; (b) Y. Y. Khomutnyk, A. J. Argüelles, G. A. Winschel, Z. Sun, P. M. Zimmerman, P. Nagorny, Studies of the Mechanism and Origins of Enantioselectivity for the Chiral Phosphoric Acid-Catalyzed Stereoselective Spiroketalization Reactions, *J. Am. Chem. Soc.*, 2016, **138**, 444–456.

(m, 2H). ^{13}C NMR (75 MHz, Toluene-d8) δ 158.2 (C), 137.1 (CH), 128.0 (CH), 125.5 (CH), 123.5 (CH), 122.4 (CH), 122.4 (CH), 101.2 (CH), 68.5 (CH_2), 61.5 (CH_2), 30.2 (CH_2), 30.0 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{14}O_2Na$ 213.0891; found 213.0885.

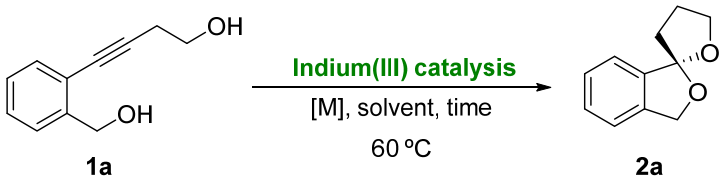
4,5(Dihydro-3*H*-spiro[furan-2,3'-isochromane] (5a).[1,5,15]



5a

Following the general procedure, the reaction of **22** (15 mg, 0.08 mmol) with InI_3 (2.0 mg, 0.004 mmol, 5 mol%) in toluene (2.3 mL) was stirred at rt for 2 h. Then the solvent was concentrated under reduced pressure and **5a** (15 mg, 99%) was obtained as a light yellow oil. R_f = 0.60 (30% EtOAc/hexanes). ^{1}H NMR (300 MHz, Toluene-d_8) δ 7.14-7.01 (m, 2H), 6.91 (d, *J* = 6.5 Hz, 1H), 6.73 (d, *J* = 6.5 Hz, 1H), 4.91 (d, *J* = 14.4 Hz, 1H), 4.55 (d, *J* = 14.7 Hz, 1H), 3.88-3.73 (m, 2H), 3.00 (d, *J* = 17.0 Hz, 1H), 2.66 (d, *J* = 16.6 Hz, 1H), 2.03-1.97 (m, 2 H), 1.63-1.50 (m, 2H). ^{13}C NMR (75 MHz, Toluene-d_8) δ 134.1 (C), 132.3 (C), 128.5 (CH), 126.1 (CH), 125.6 (CH), 123.8 (CH), 67.3 (CH_2), 62.1 (CH_2), 37.2 (CH_2), 35.8 (CH_2), 23.7 (CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{14}O_2Na$ 213.0891; found 213.0886.

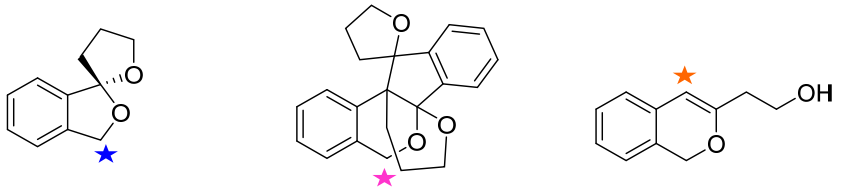
Table 1. In(III)-catalyzed intramolecular double dihydroalkoxylation reaction of 2-(4-hydroxybutynyl)benzyl alcohol (**1a**).[a]



1a **2a**

Entry	InX_3 (mol%)	[M][a]	t (h)[b]	Solvent	**2a**:**3a**:**3b**[c]	**2a** (%)[d]
1	InI_3 (5%)	0.10	1.5	DCE	69:29:2	46
2	InI_3 (5%)	0.07	1.5	DCE	95:4:1	64
3	InI_3 (2%)	0.07	3	DCE	83:14:3	52
4	InI_3 (2%)	0.035	21	DCE	95:5:0	61
5	$InBr_3$ (2%)	0.07	24	DCE	85:11:3	64
6	$InBr_3$ (2%)	0.035	21	DCE	92:7:1	53
7	InI_3 (2%)[e]	0.035	6	DCE	60:40:0	34
8	InI_3 (2 %)	0.035	45	Toluene	92:0:8	74
9	InI_3 (5 %)	0.035	21	Toluene	95:0:5	66

[a][0.035 M] corresponds with 0.6 mmol of **1a** in 15 mL of solvent (approx); [b] Estimated by TLC; [c] Ratio measured by ^{1}H NMR; [d] Isolated yield; [e] $AgSbF_6$ (2 mol%) was added.



2a **3a** **3b**

Table 1, entry 1. Ratio of **2a:3a:3b (69:29:2).**

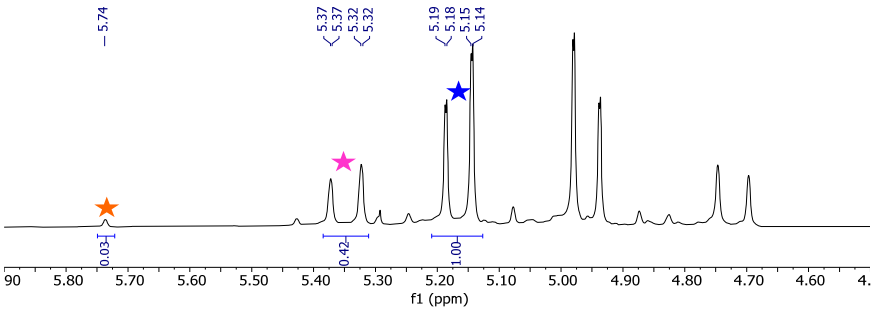


Table 1, entry 2. Ratio of **2a:3a:3b (95:4:1).**

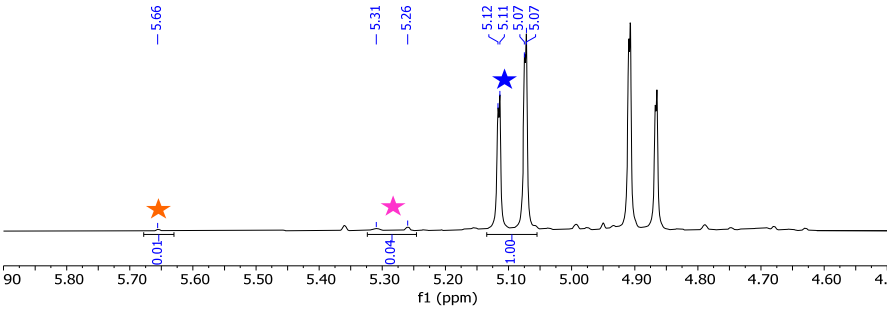


Table 1, entry 3. Ratio of **2a:3a:3b (83:14:3).**

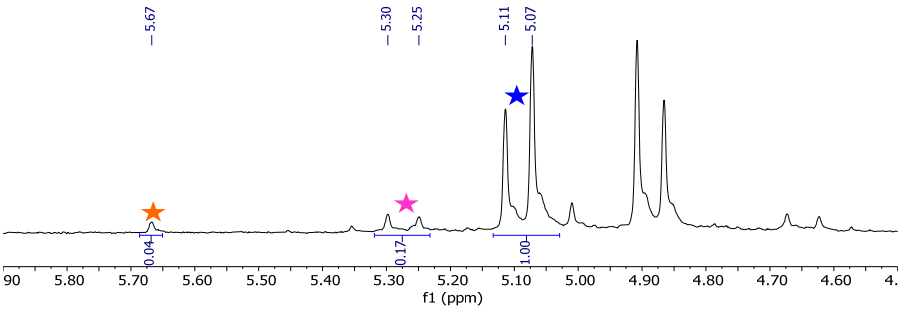


Table 1, entry 4. Ratio of **2a:3a:3b (85:11:3).**

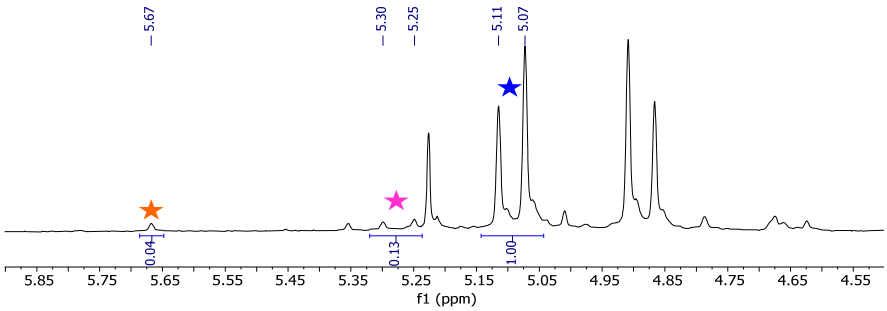


Table 1, entry 5. Ratio of **2a:3a:3b (92:7:1).**

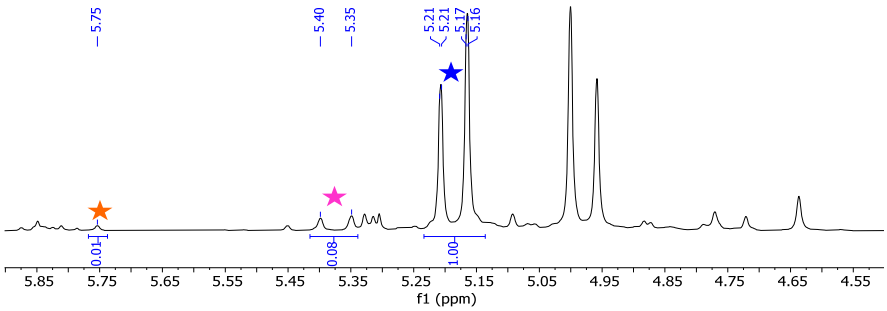


Table 1, entry 6. Ratio of **2a:3a:3b (95:5:0).**

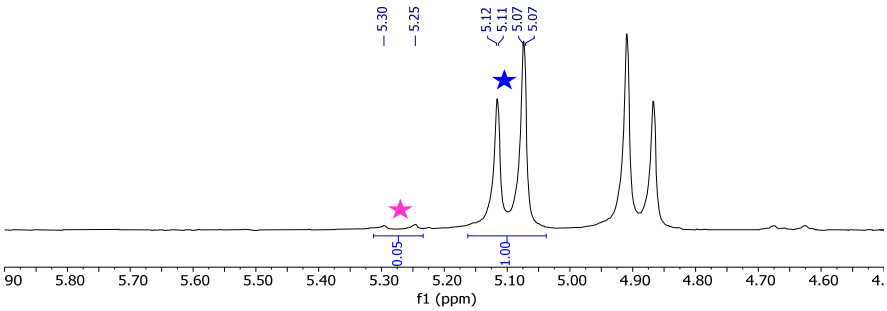


Table 1, entry 7. Ratio of **2a:3a:3b (60:40:0).**

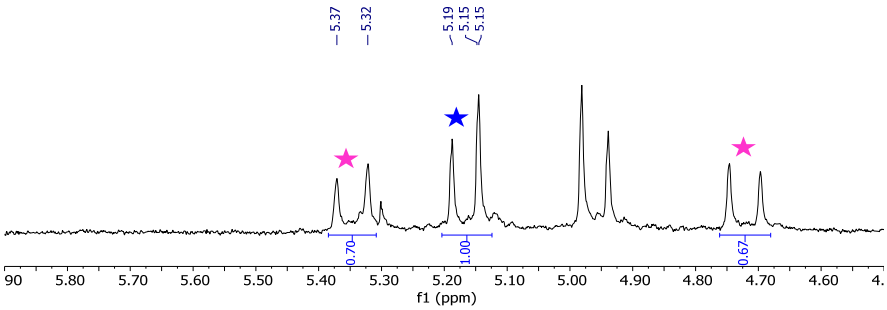


Table 1, entry 8. Ratio of **2a:3a:3b (93:0:7).**

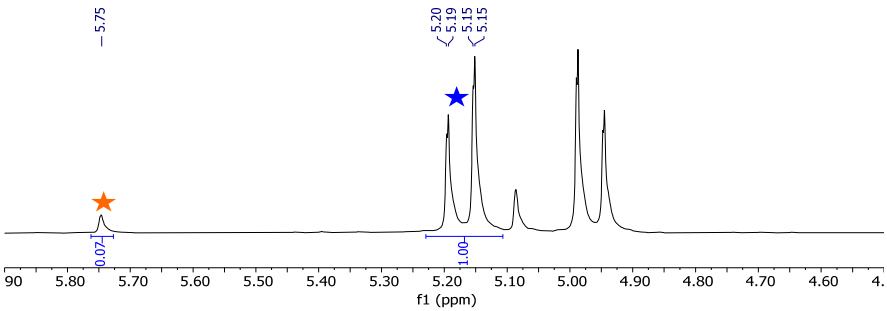
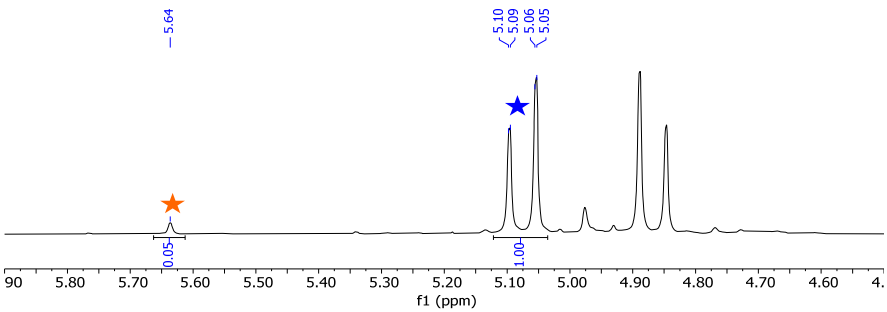
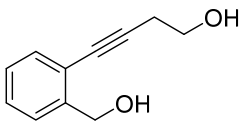


Table 1, entry 9. Ratio of **2a:3a:3b (95:0:5).**

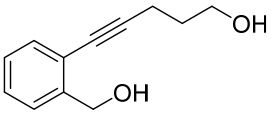


Experimental procedure for the reaction of 1a, 1f, 16, and 17 with InI_3 in the NMR magnet.

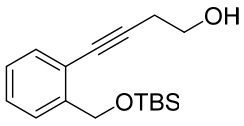
In a NMR tube a solution of **1a**, **1f**, **16** and **17** (20 mg) and InI_3 (5 mol%) in toluene-d_8 (0.75 mL) was prepared. The mixture was heated at 60 ºC in the NMR magnet and the reaction progress was monitored by ^1H NMR analysis at regular intervals.



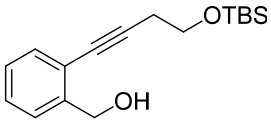
1a



1f



16



17

Figure 1. Reaction of **1a** with InI_3 (5 mol%) monitored by ^1H NMR (Toluene-d_8, 400 MHz) at 60 ºC.

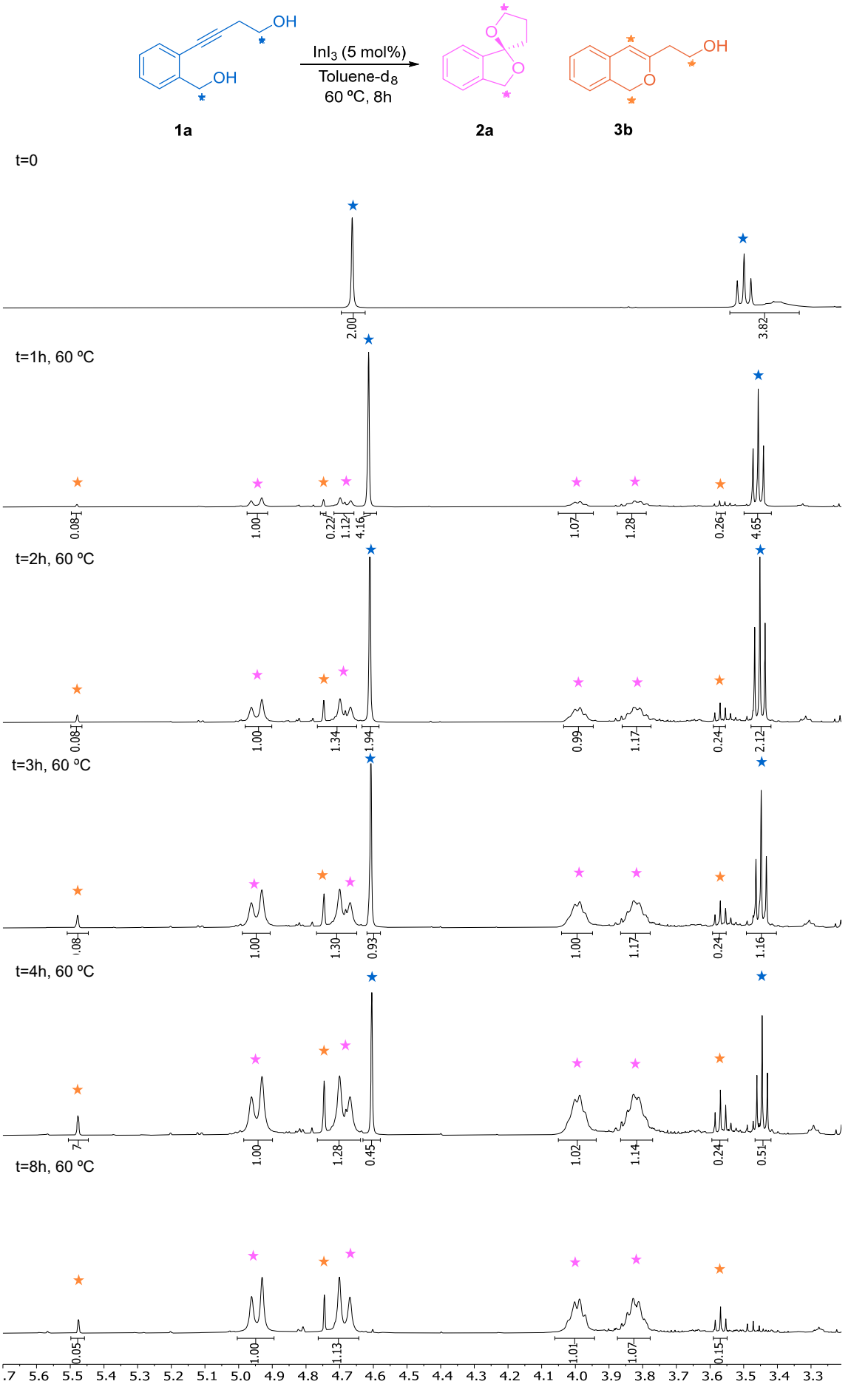
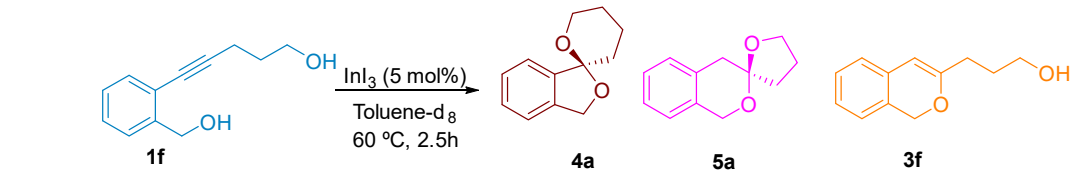


Figure 2. Reaction of **1f** with InI_3 (5 mol%) monitored by ^1H NMR (Toluene-d_8, 400 MHz) at 60 ºC.



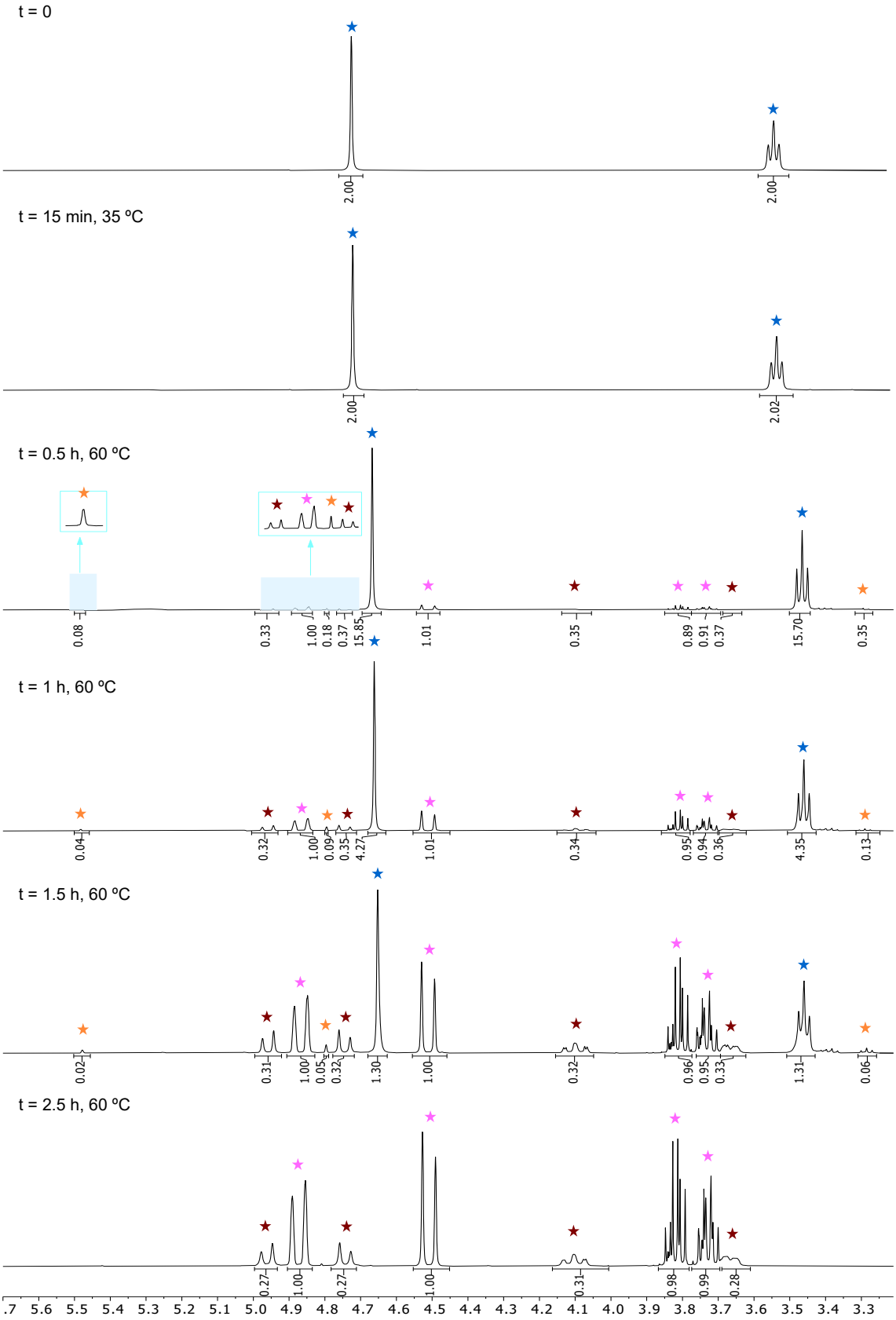
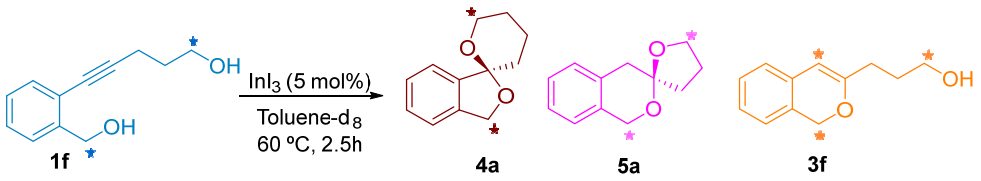


Figure 3. Ampliation of the reaction of **1f** with InI_3 (5 mol%) monitored by ^1H NMR (Toluene-d_8, 400 MHz) at 35 ºC (15 min) and 60 ºC (0.5 h).



t = 0.5 h, 60 ºC

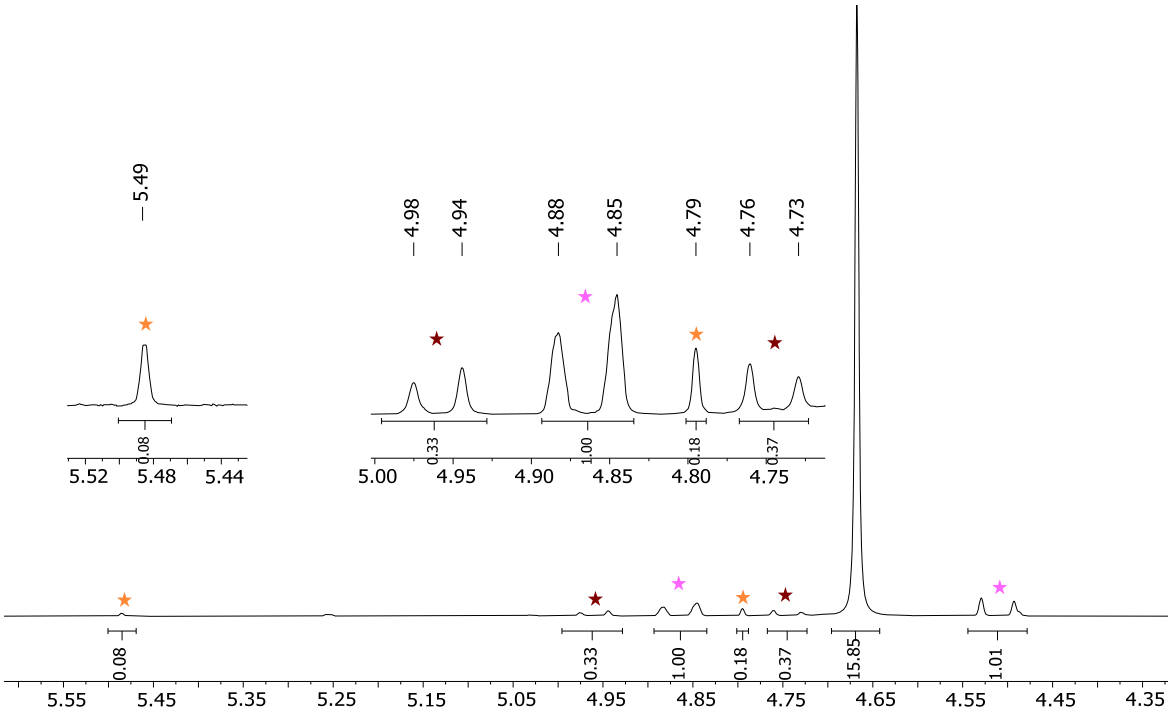


Figure 4. Reaction of **16** with InI_3 (5 mol%) monitored by ^1H NMR (Toluene-d_8, 400 MHz) at 60 ºC.

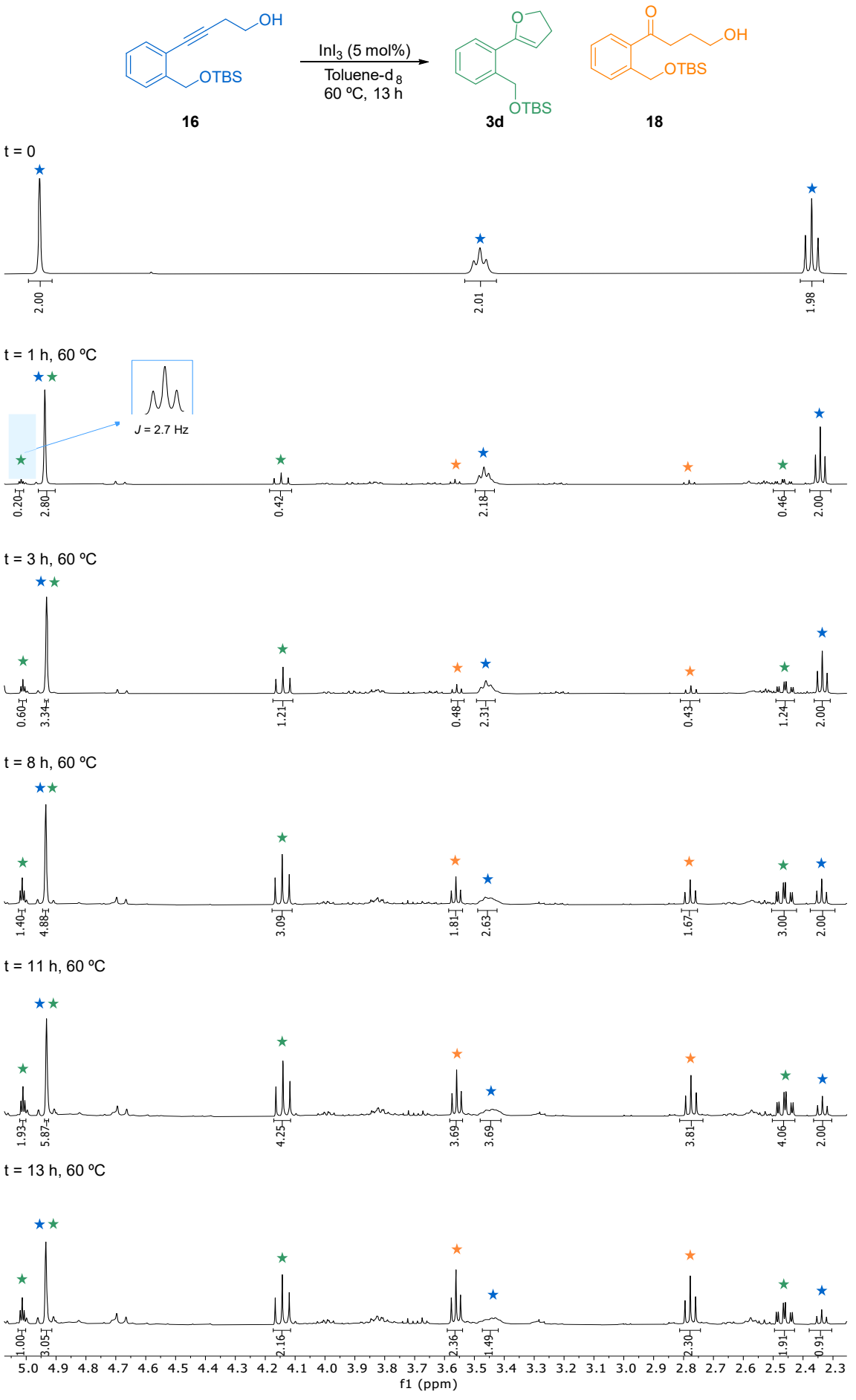
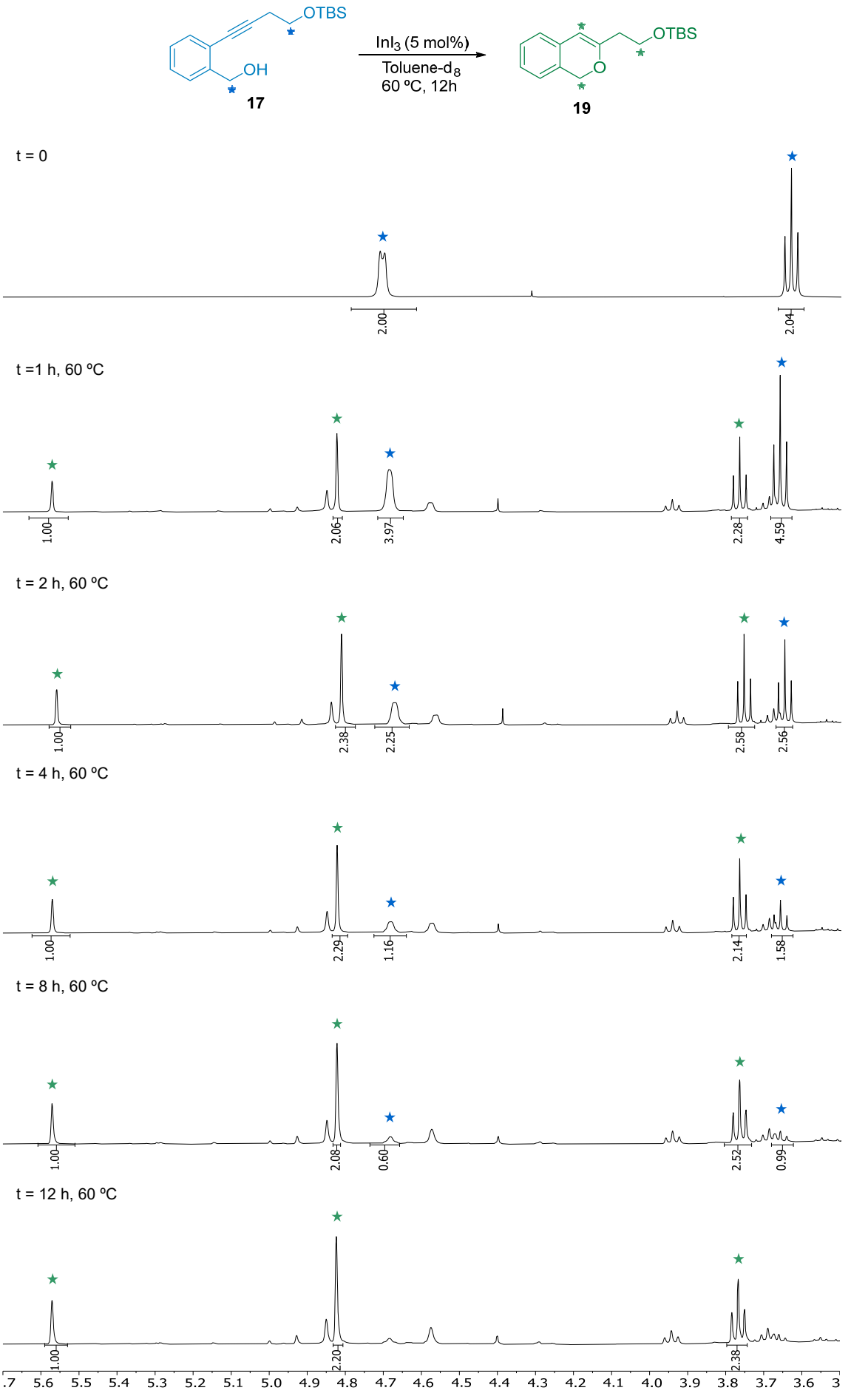
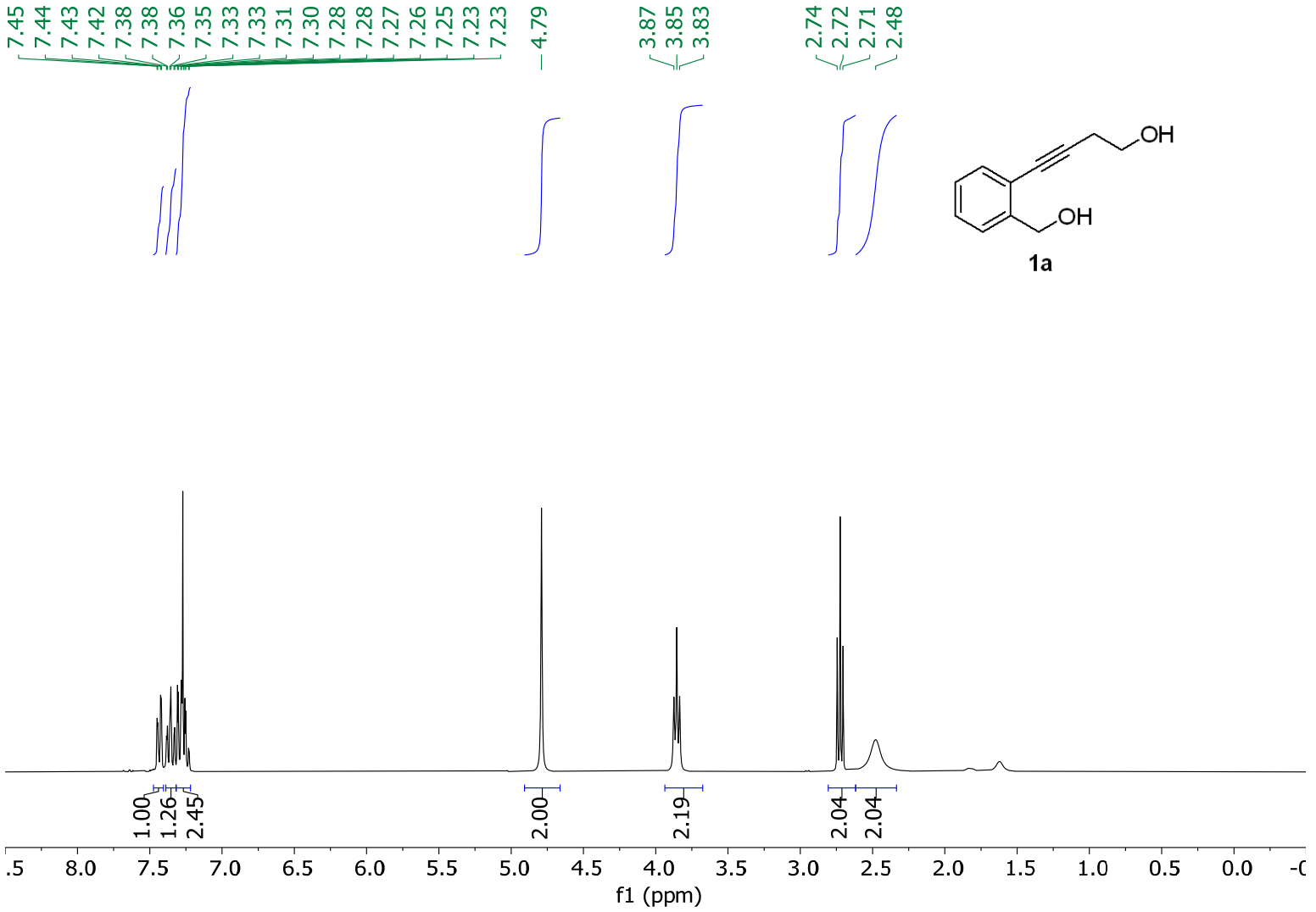


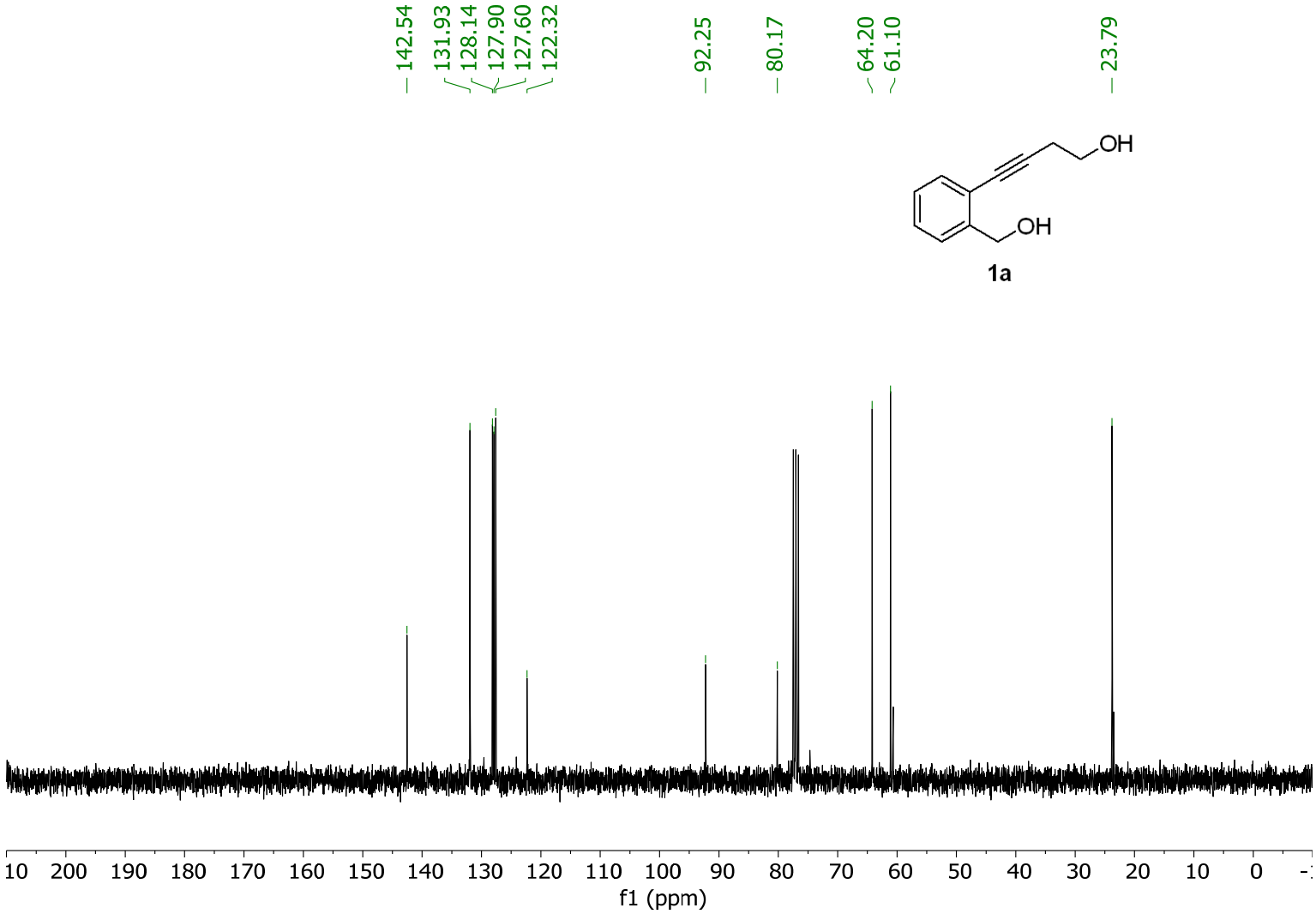
Figure 5. Reaction of **17** with InI_3 (5 mol%) monitored by ^1H NMR (Toluene-d_8, 400 MHz) at 60 ºC.



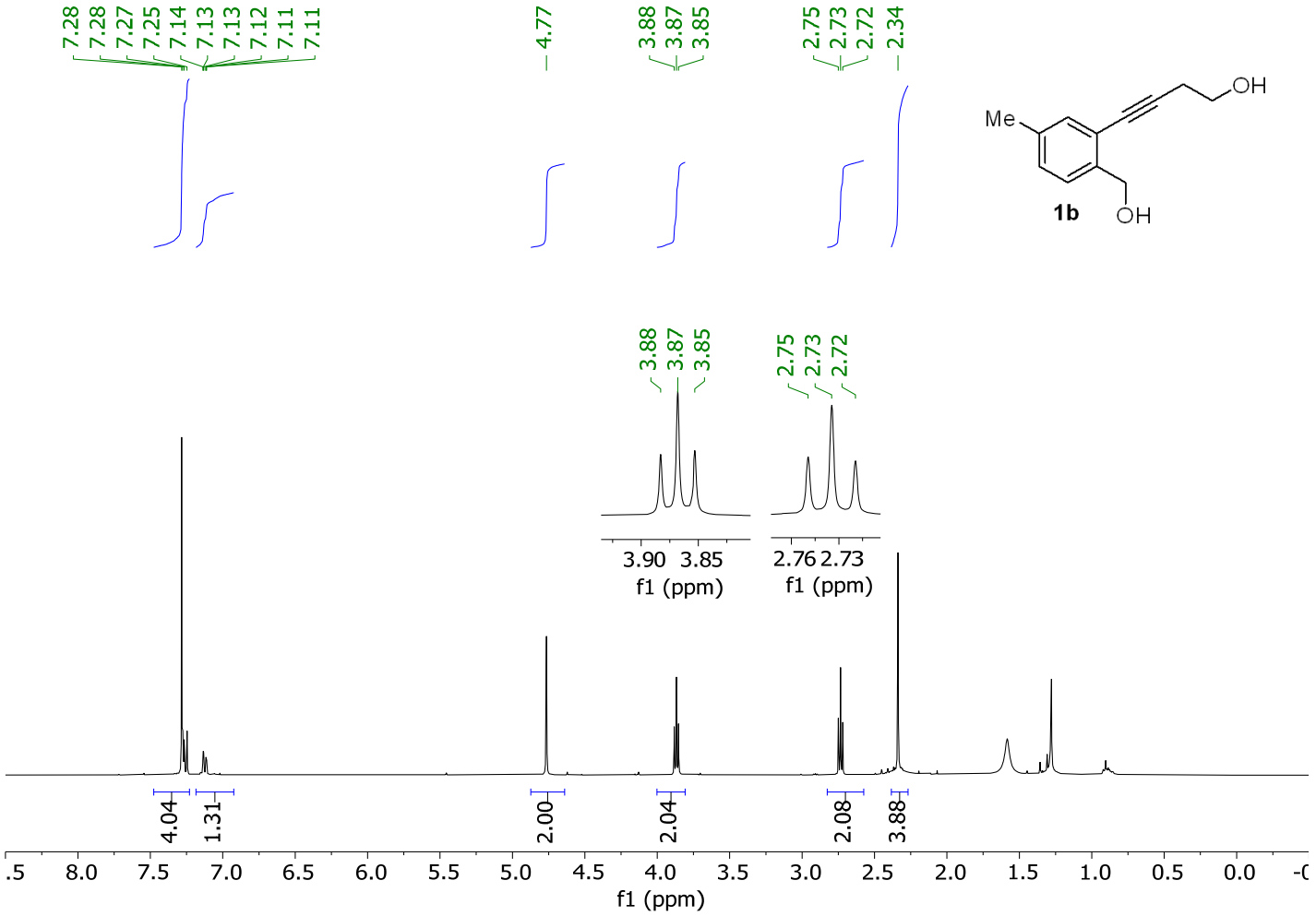
300 MHz ^{1}H-NMR Spectrum of compound **1a** ($CDCl_3$, 300 K)



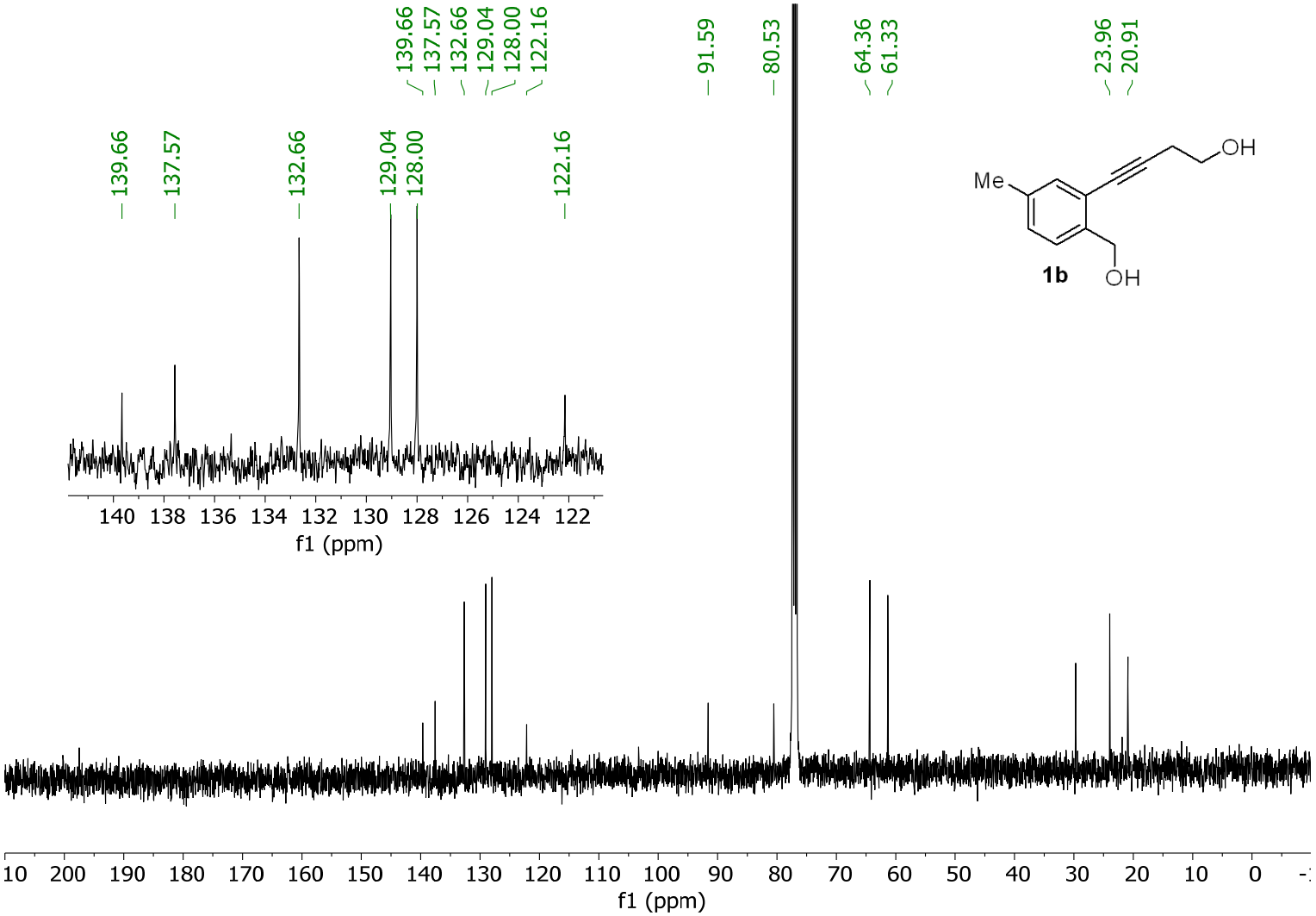
100 MHz ^{13}C-NMR Spectrum of compound **1a** ($CDCl_3$, 300 K)



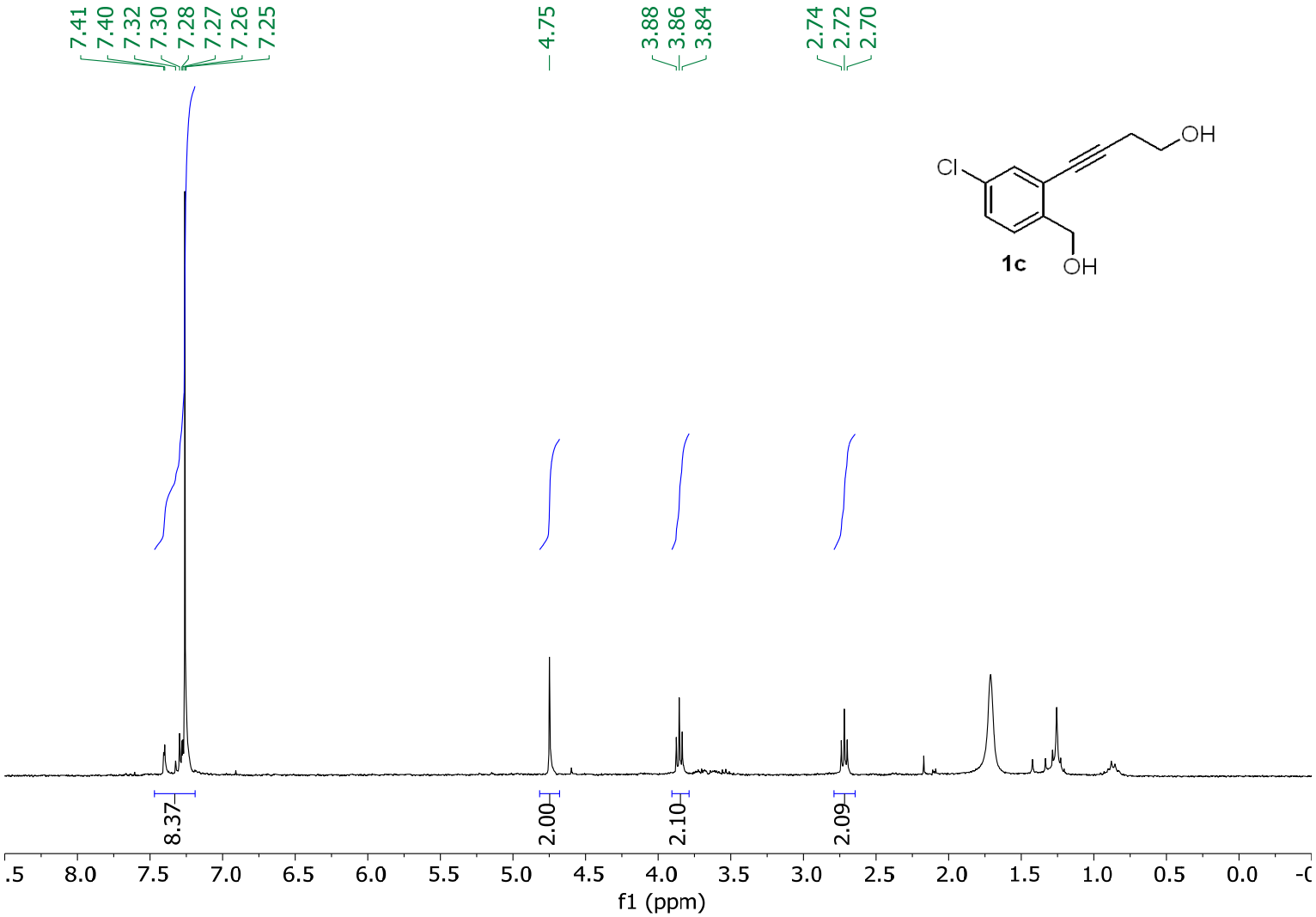
300 MHz ^{1}H-NMR Spectrum of compound **1b** ($CDCl_3$, 300 K)



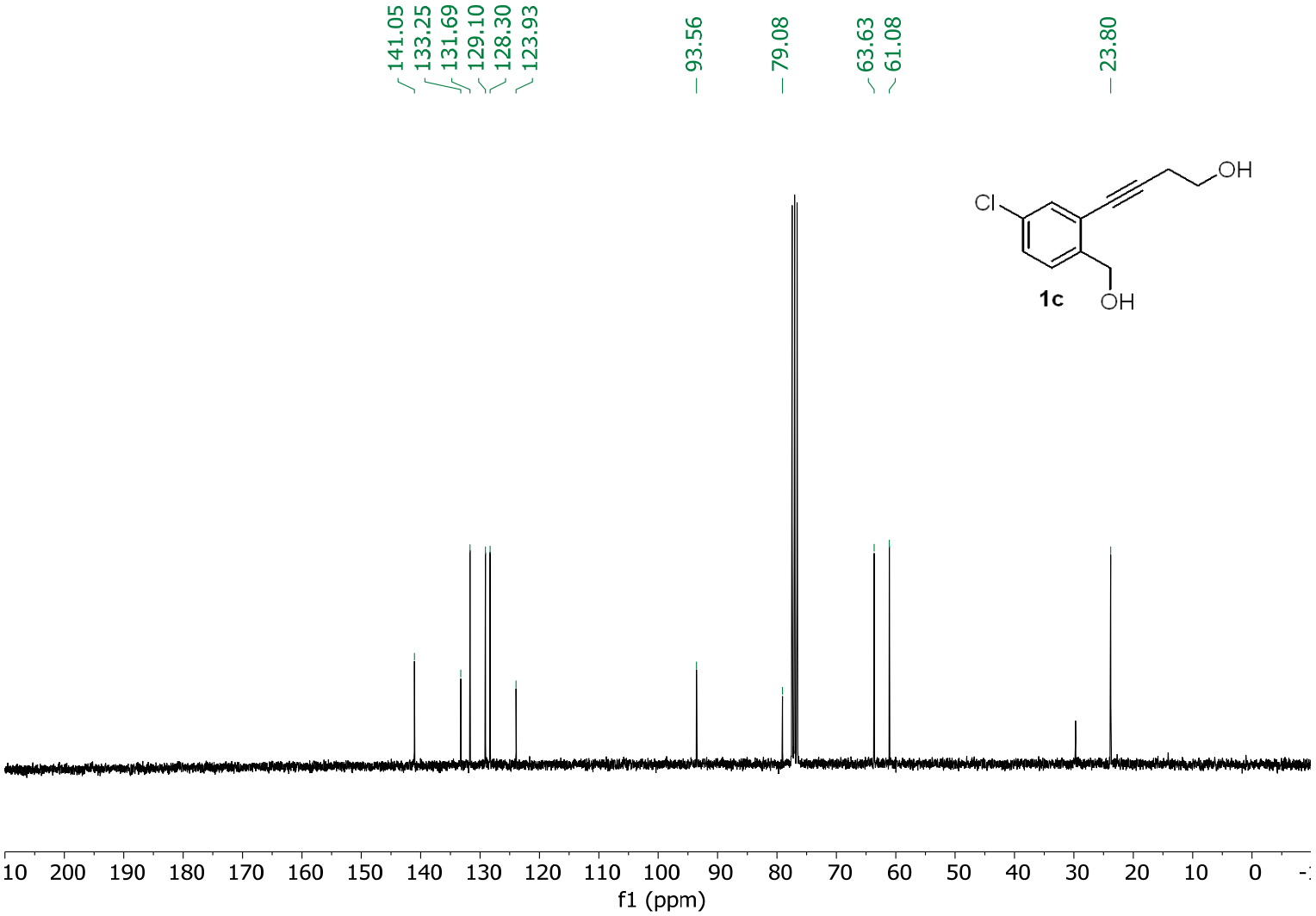
75 MHz ^{13}C-NMR Spectrum of compound **1b** ($CDCl_3$, 300 K)



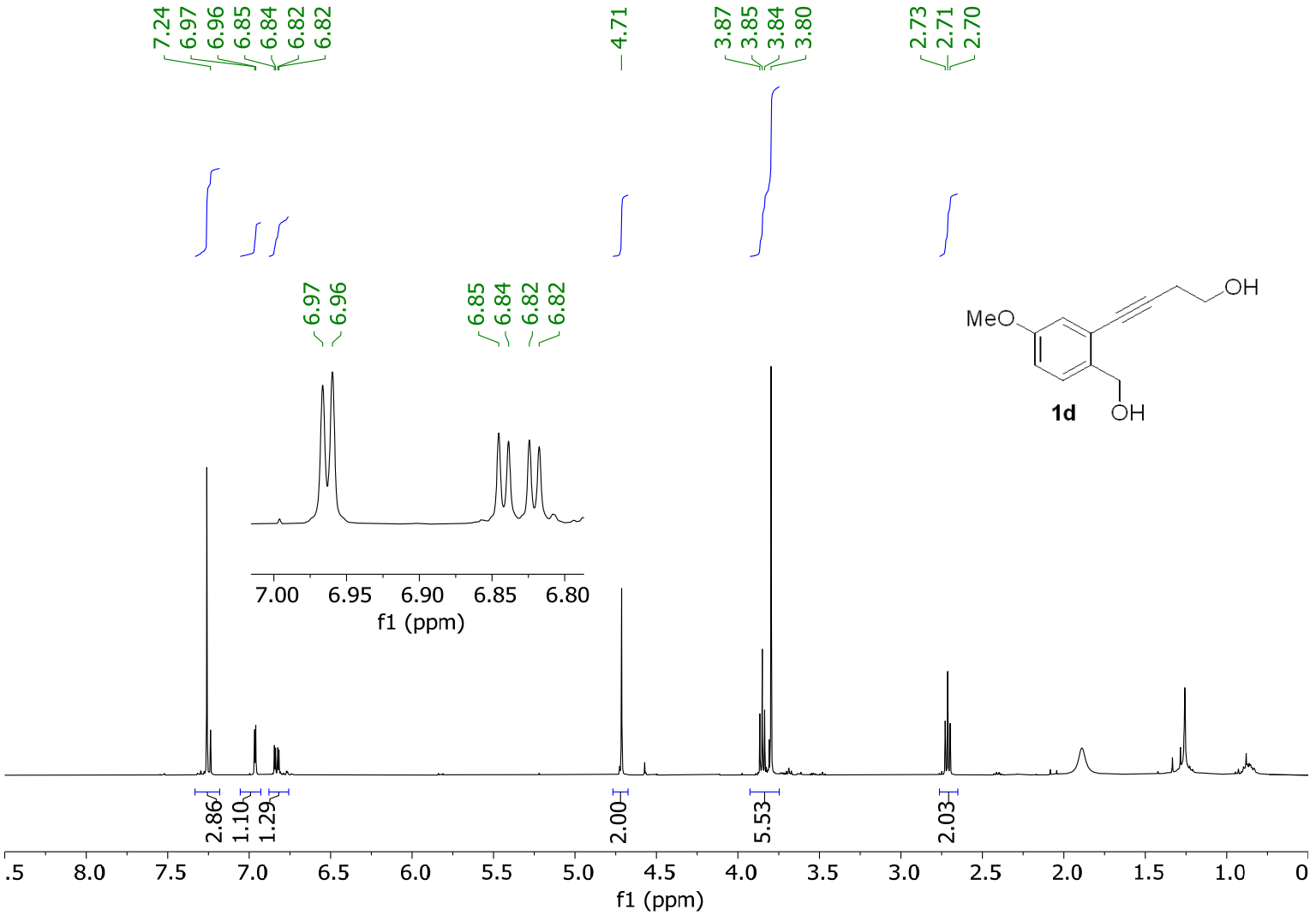
300 MHz ^{1}H-NMR Spectrum of compound **1c** ($CDCl_3$, 300 K)



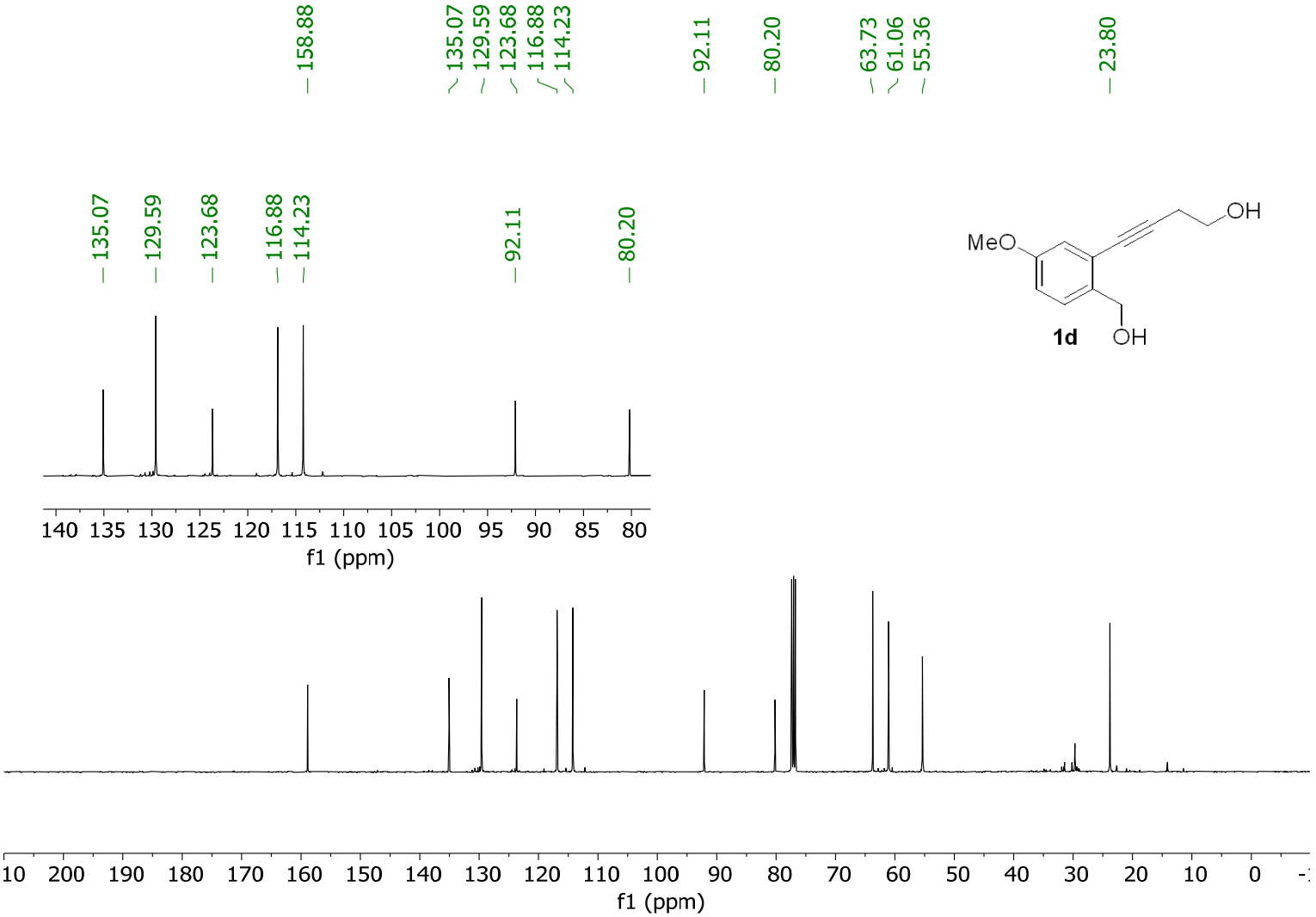
75 MHz ^{13}C-NMR Spectrum of compound **1c** ($CDCl_3$, 300 K)



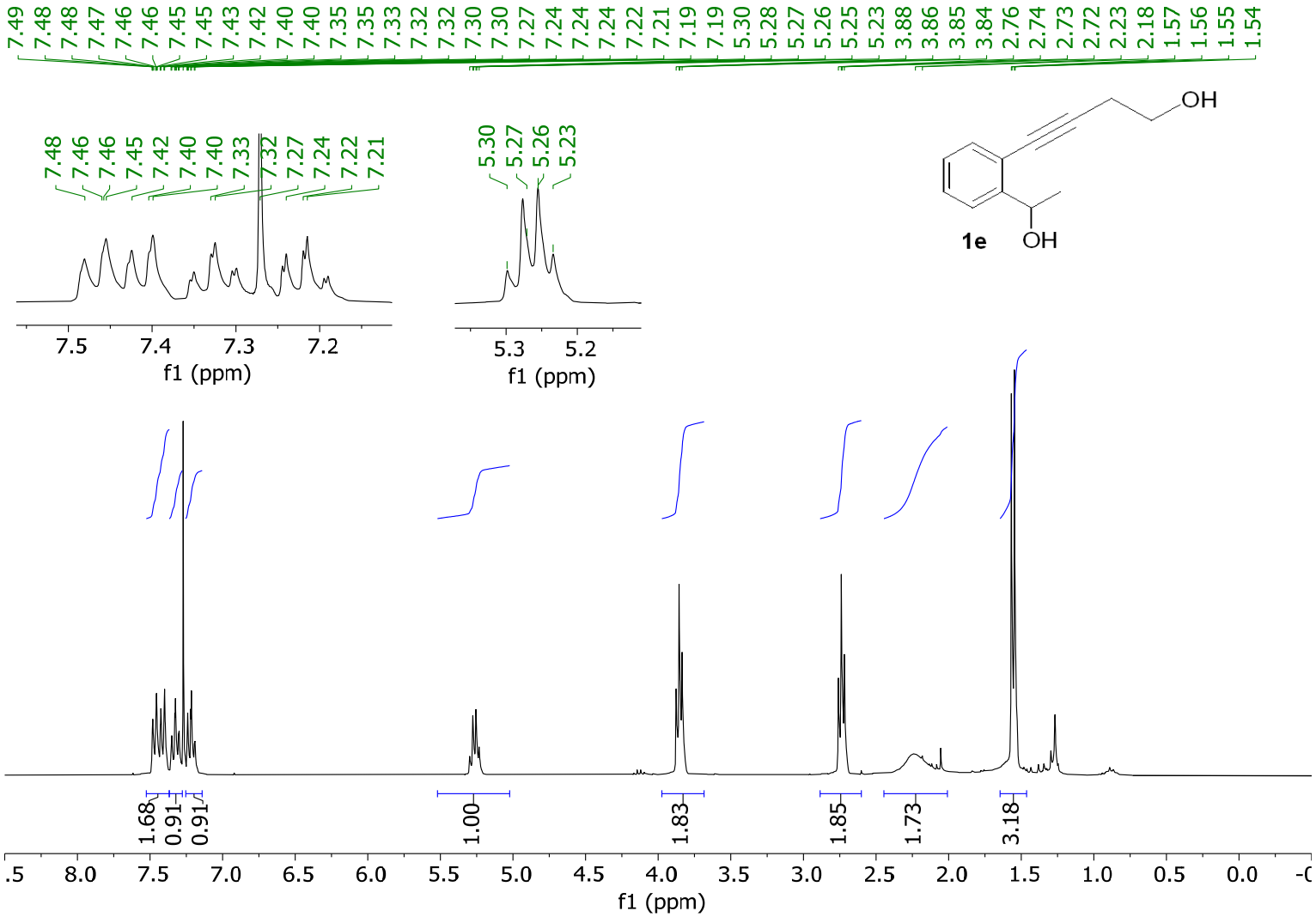
300 MHz ^{1}H-NMR Spectrum of compound **1d** ($CDCl_3$, 300 K)



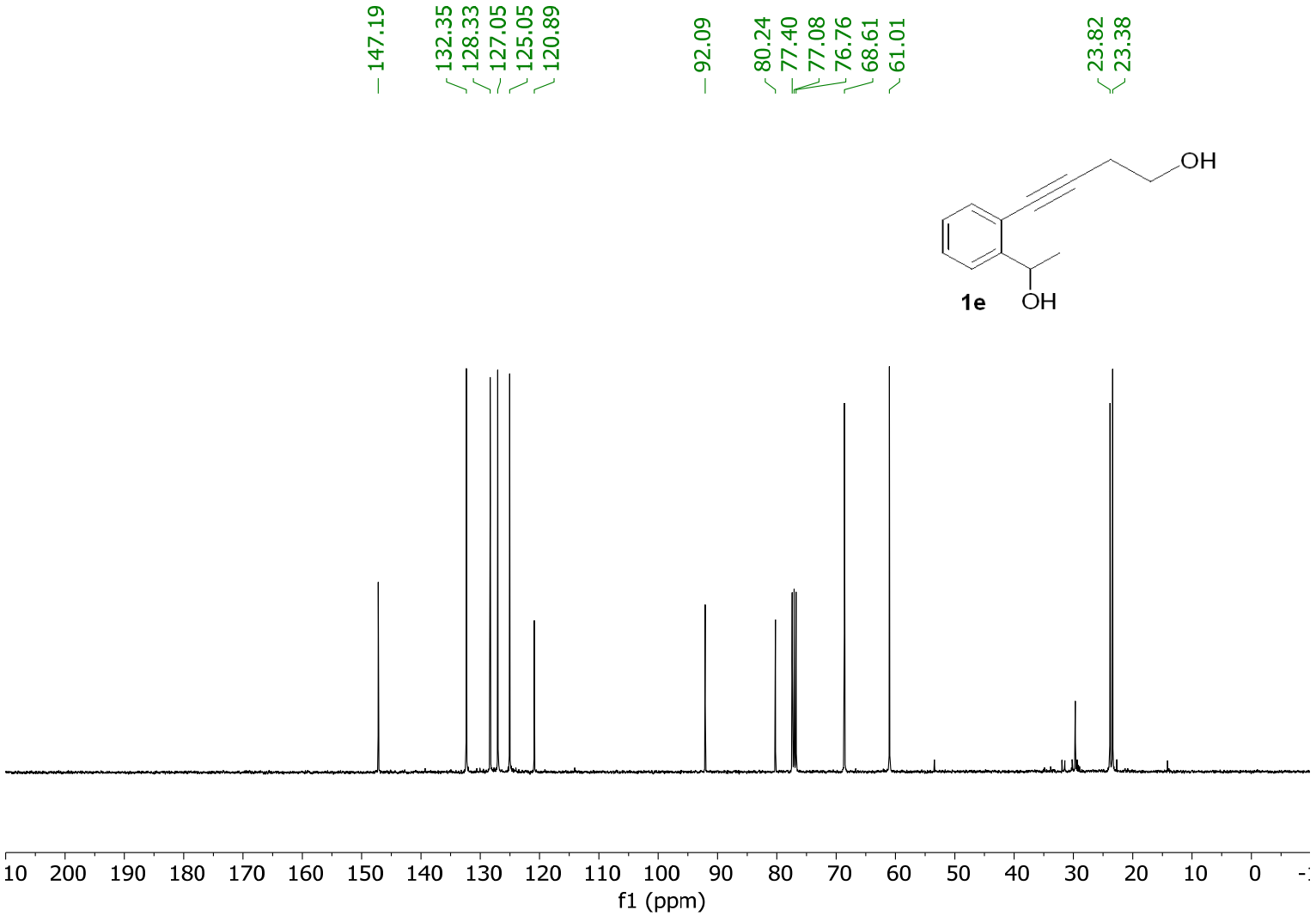
75 MHz ^{13}C-NMR Spectrum of compound **1d** ($CDCl_3$, 300 K)



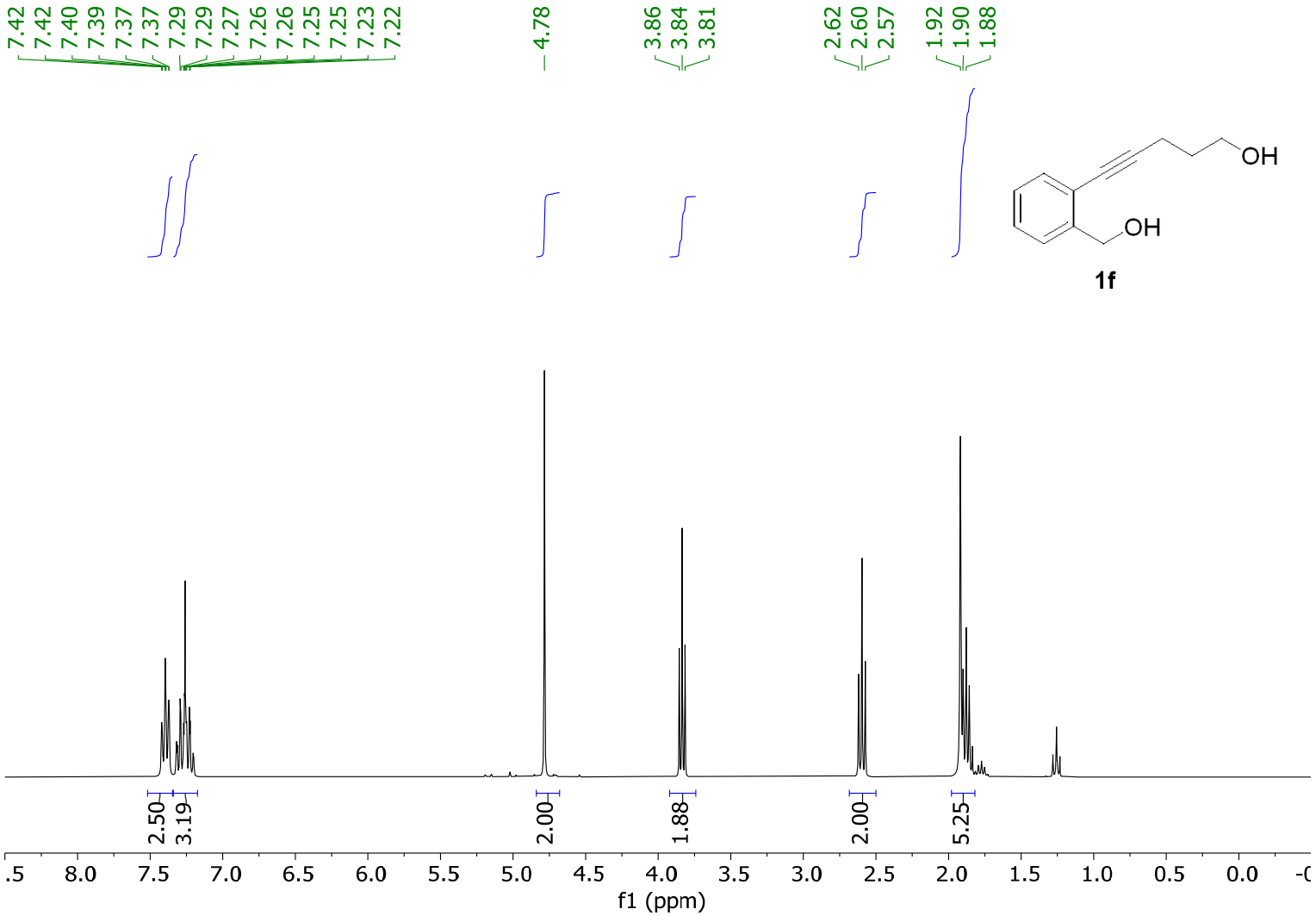
300 MHz ^{1}H-NMR Spectrum of compound **1e** ($CDCl_3$, 300 K)



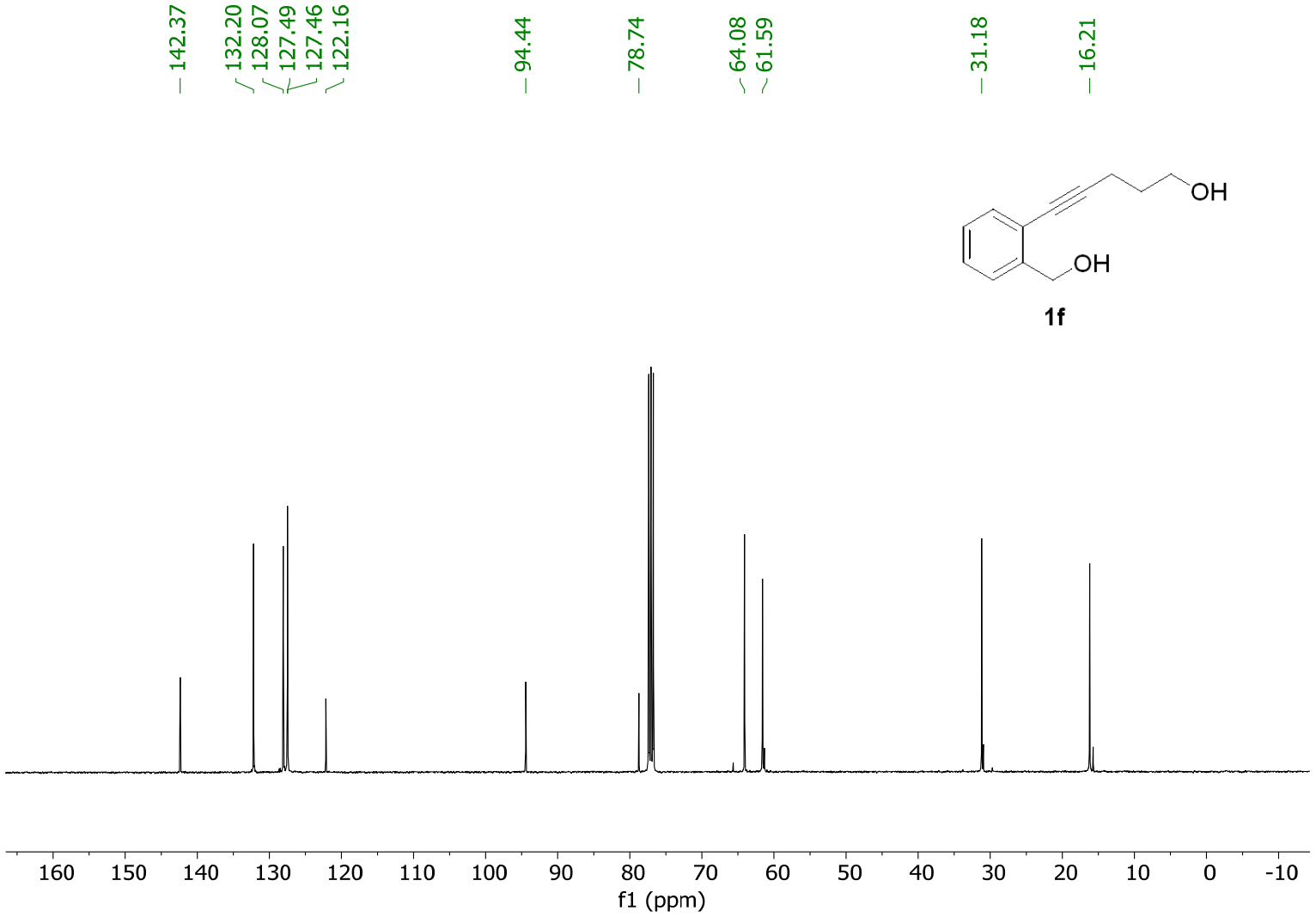
100 MHz ^{13}C-NMR Spectrum of compound **1e** ($CDCl_3$, 300 K)



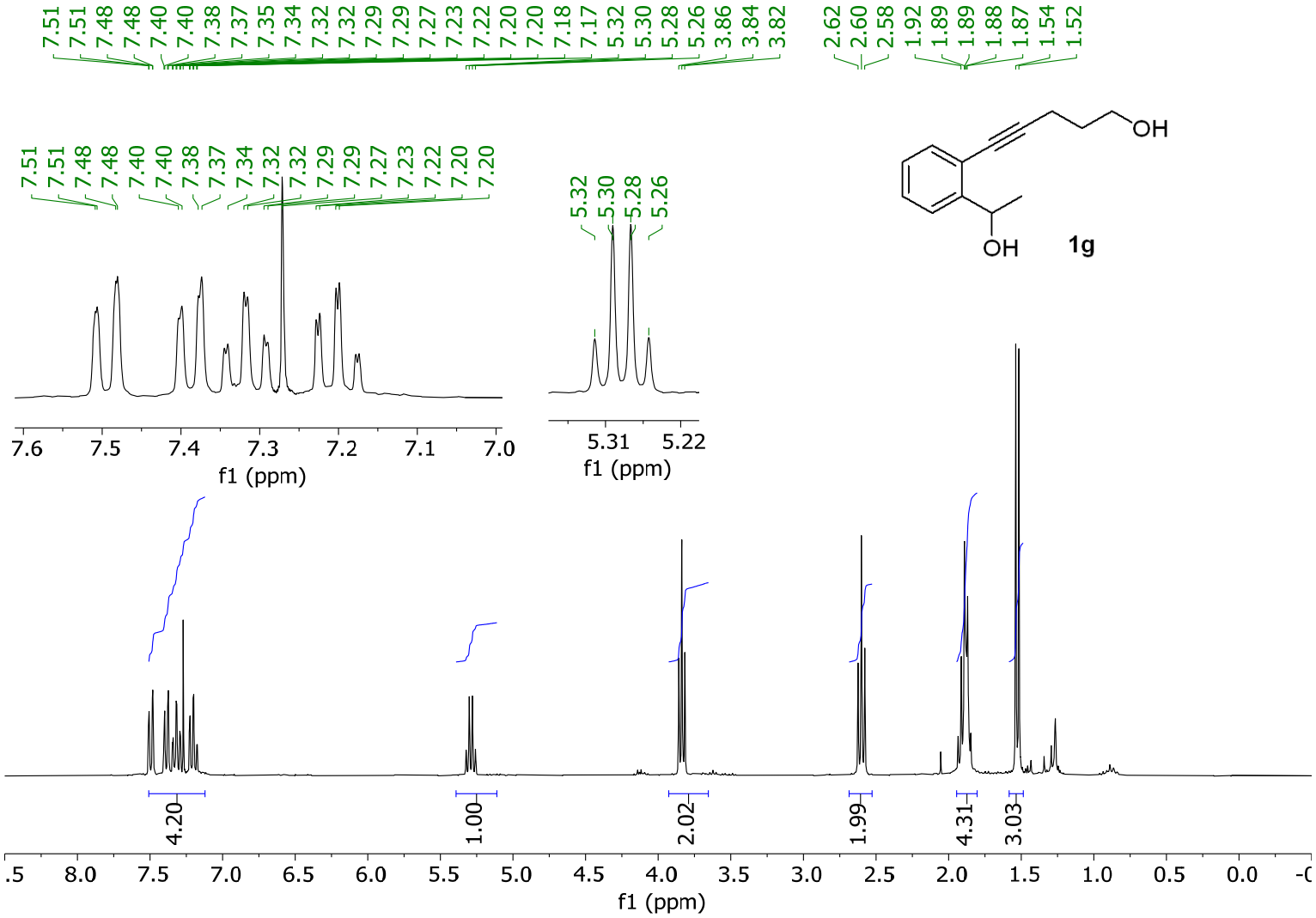
300 MHz ^{1}H-NMR Spectrum of compound **1f** ($CDCl_3$, 300 K)



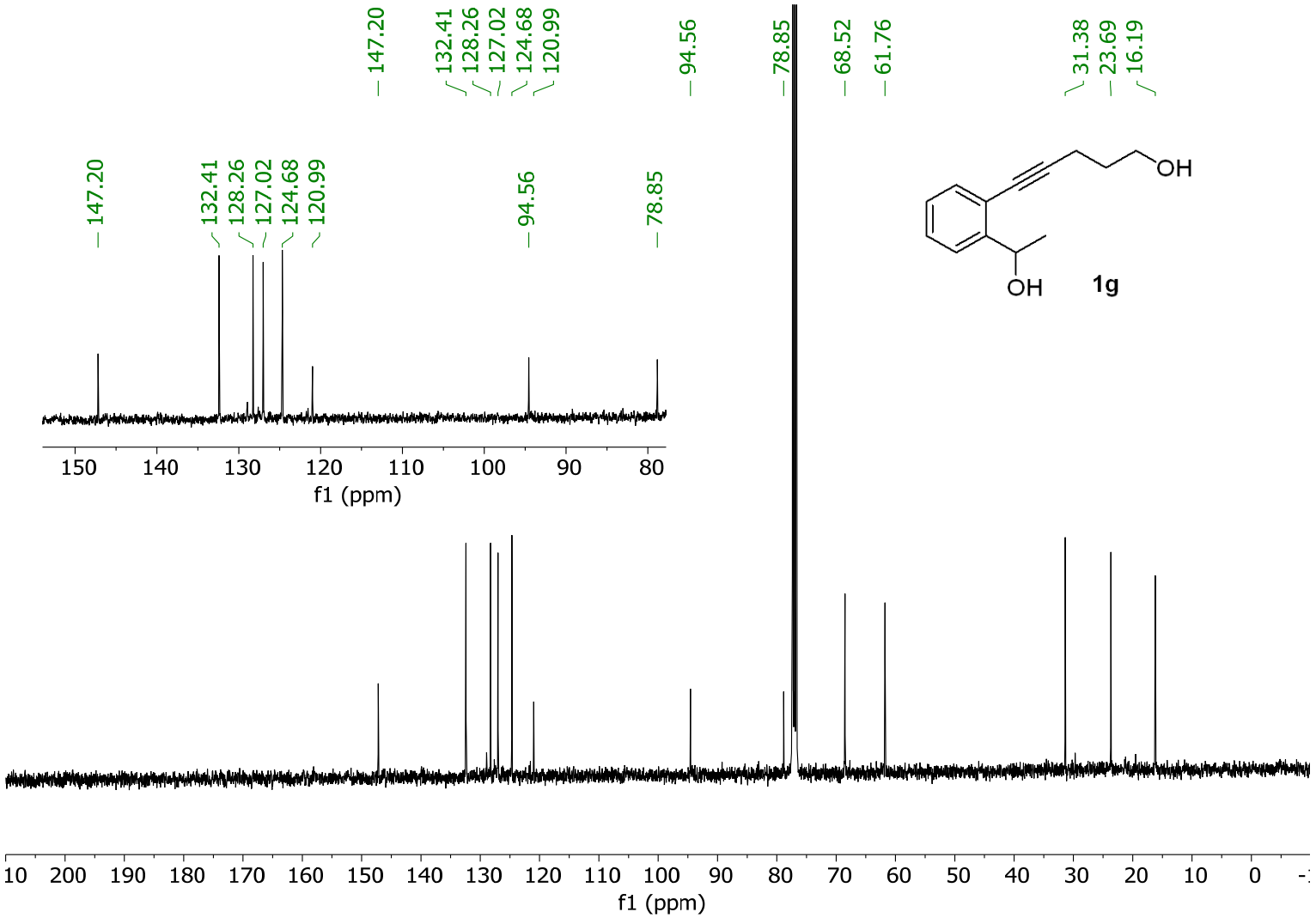
100 MHz ^{13}C-NMR Spectrum of compound **1f** ($CDCl_3$, 300 K)



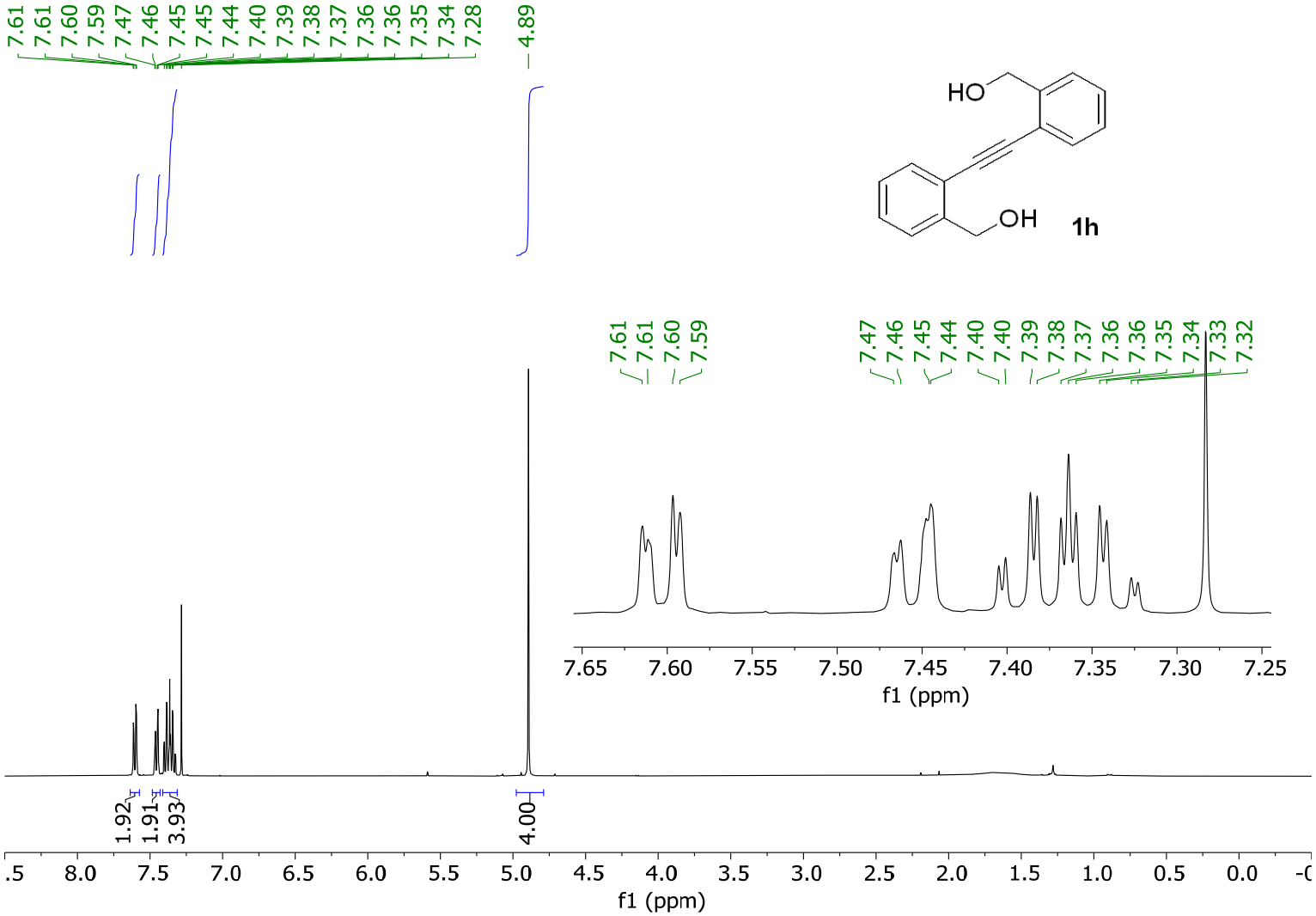
300 MHz ^{1}H-NMR Spectrum compound **1g** ($CDCl_3$, 300 K)



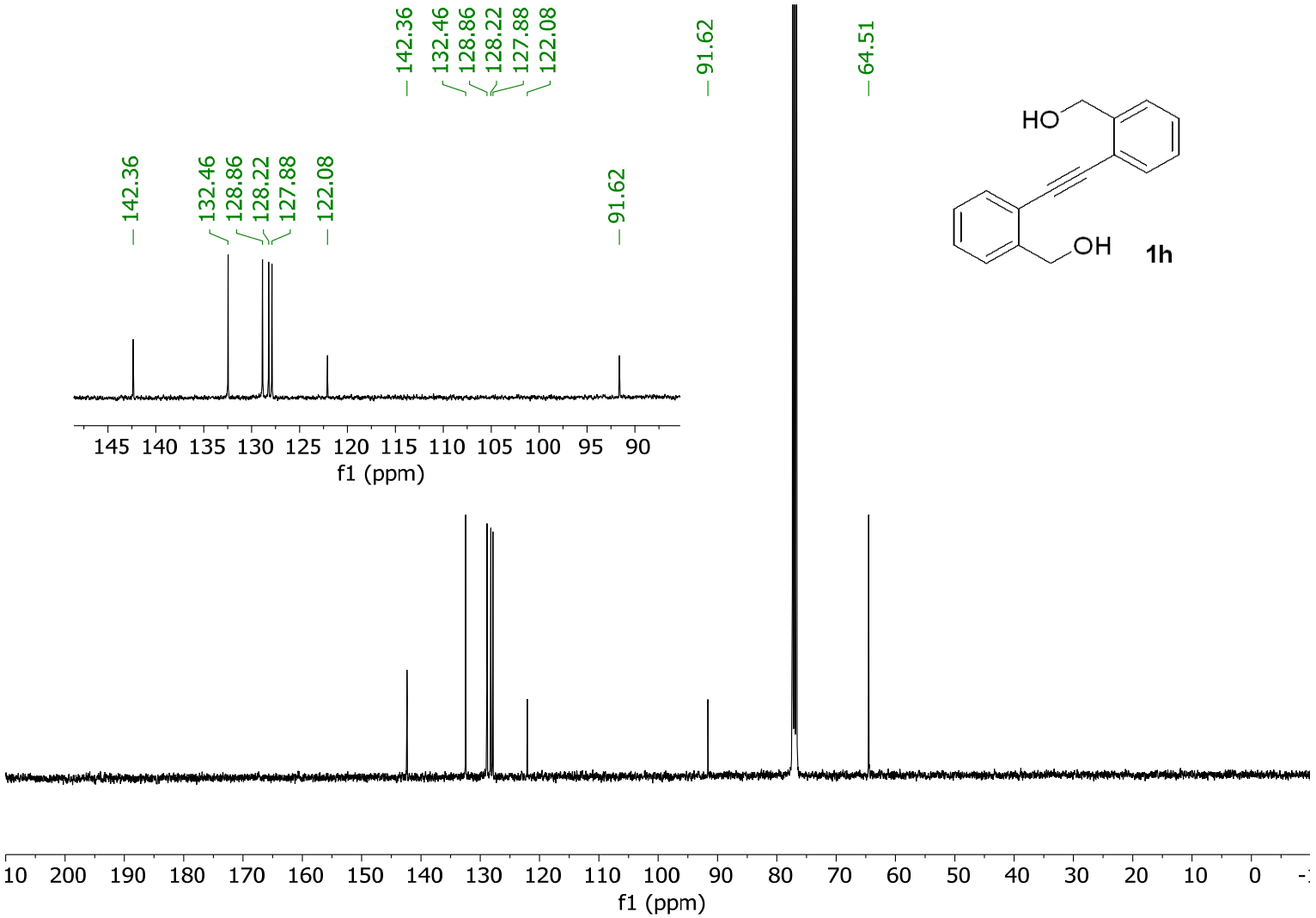
75 MHz ^{13}C-NMR Spectrum of compound **1g** ($CDCl_3$, 300 K)



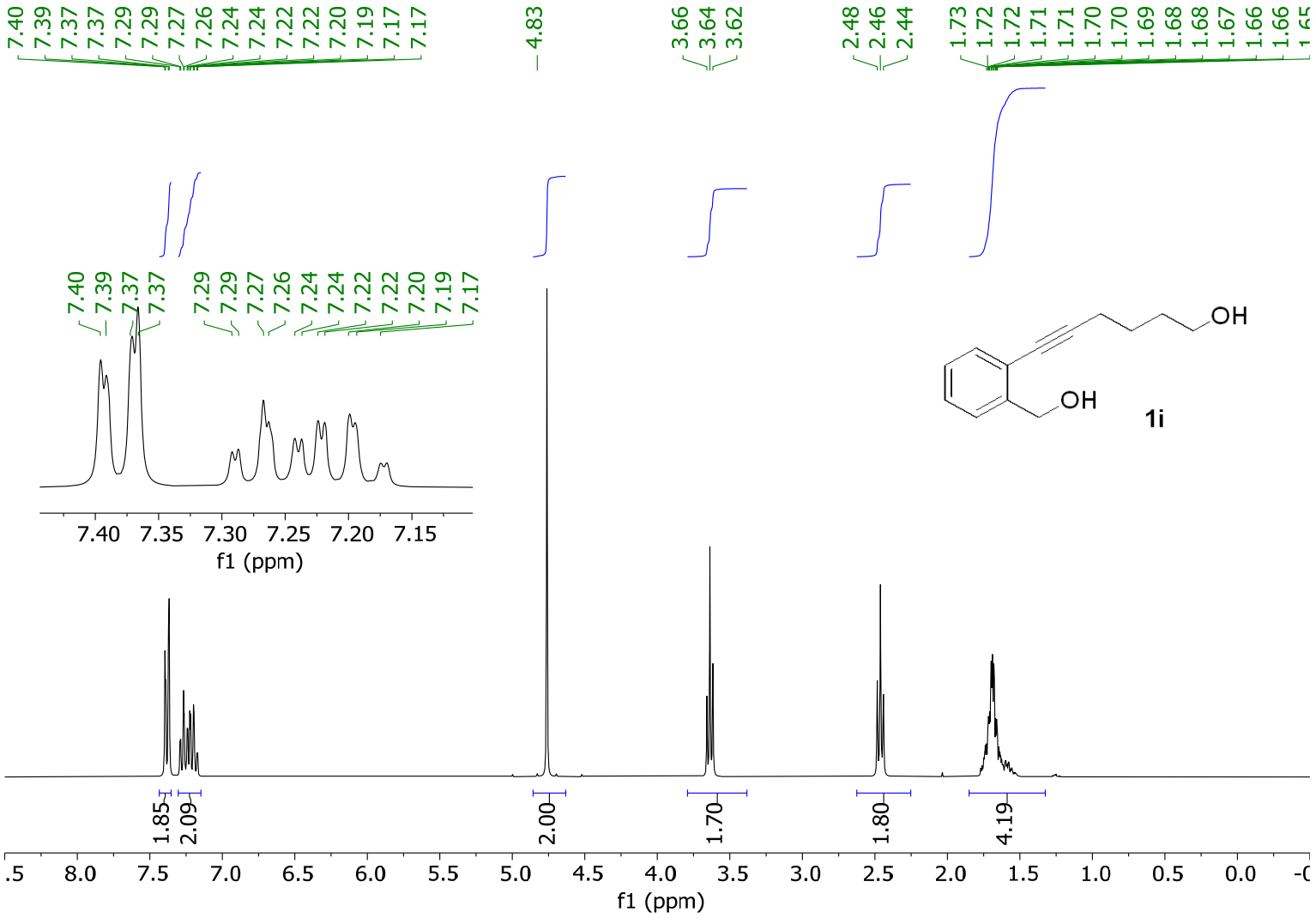
300 MHz ^{1}H-NMR Spectrum compound **1h** ($CDCl_3$, 300 K)



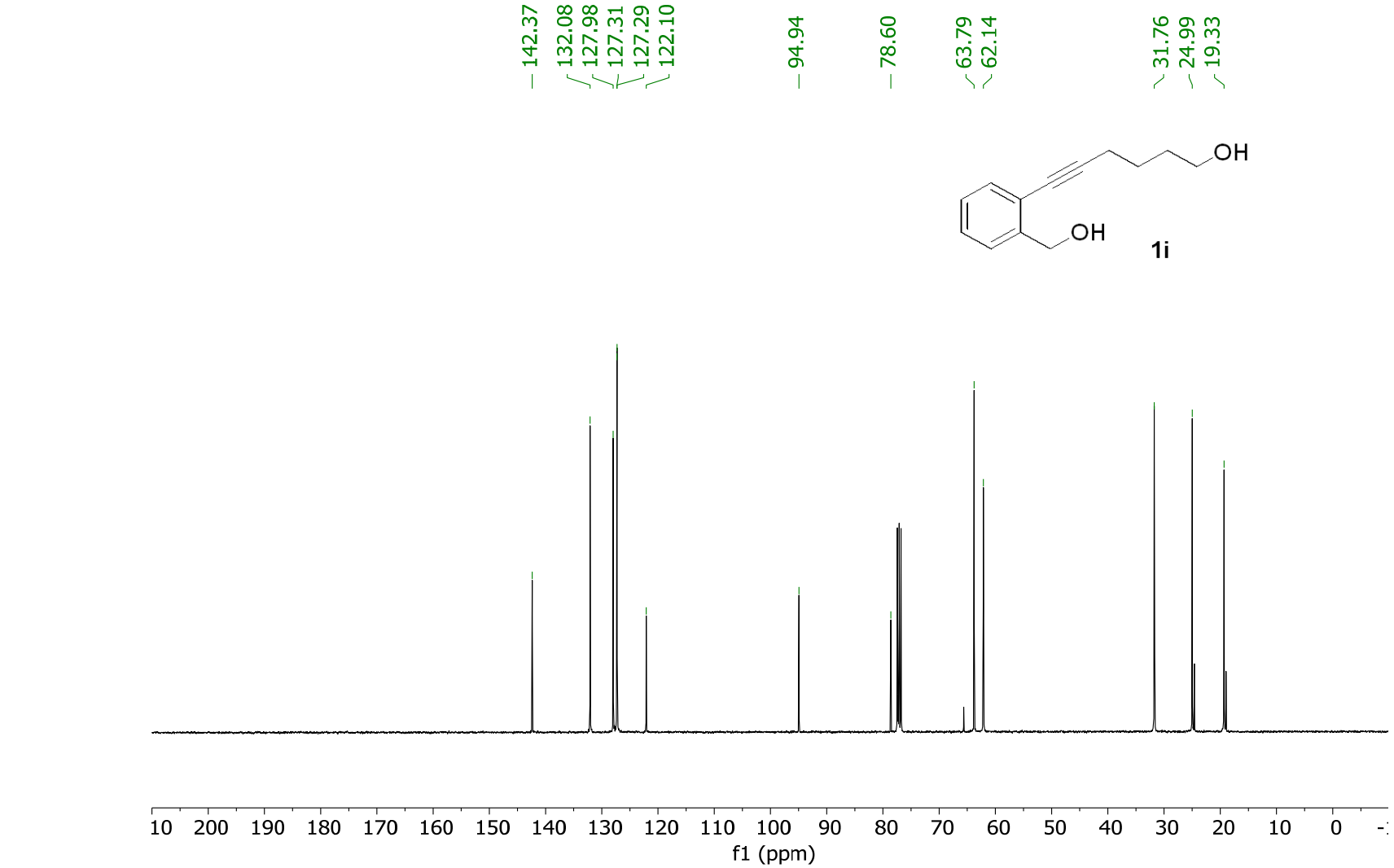
100 MHz ^{13}C-NMR Spectrum of compound **1h** ($CDCl_3$, 300 K)



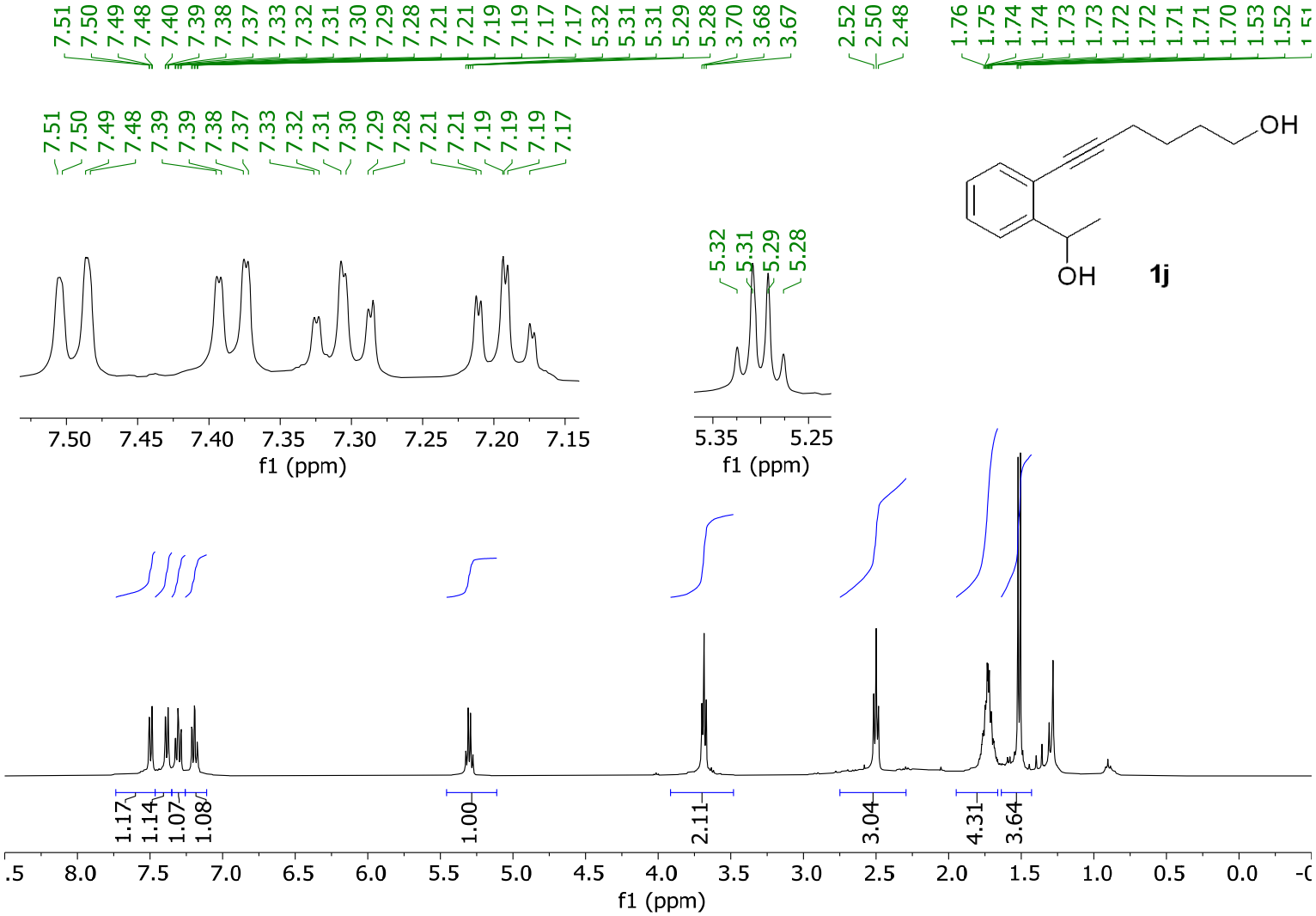
300 MHz ^{1}H-NMR Spectrum of compound **1i** ($CDCl_3$, 300 K)



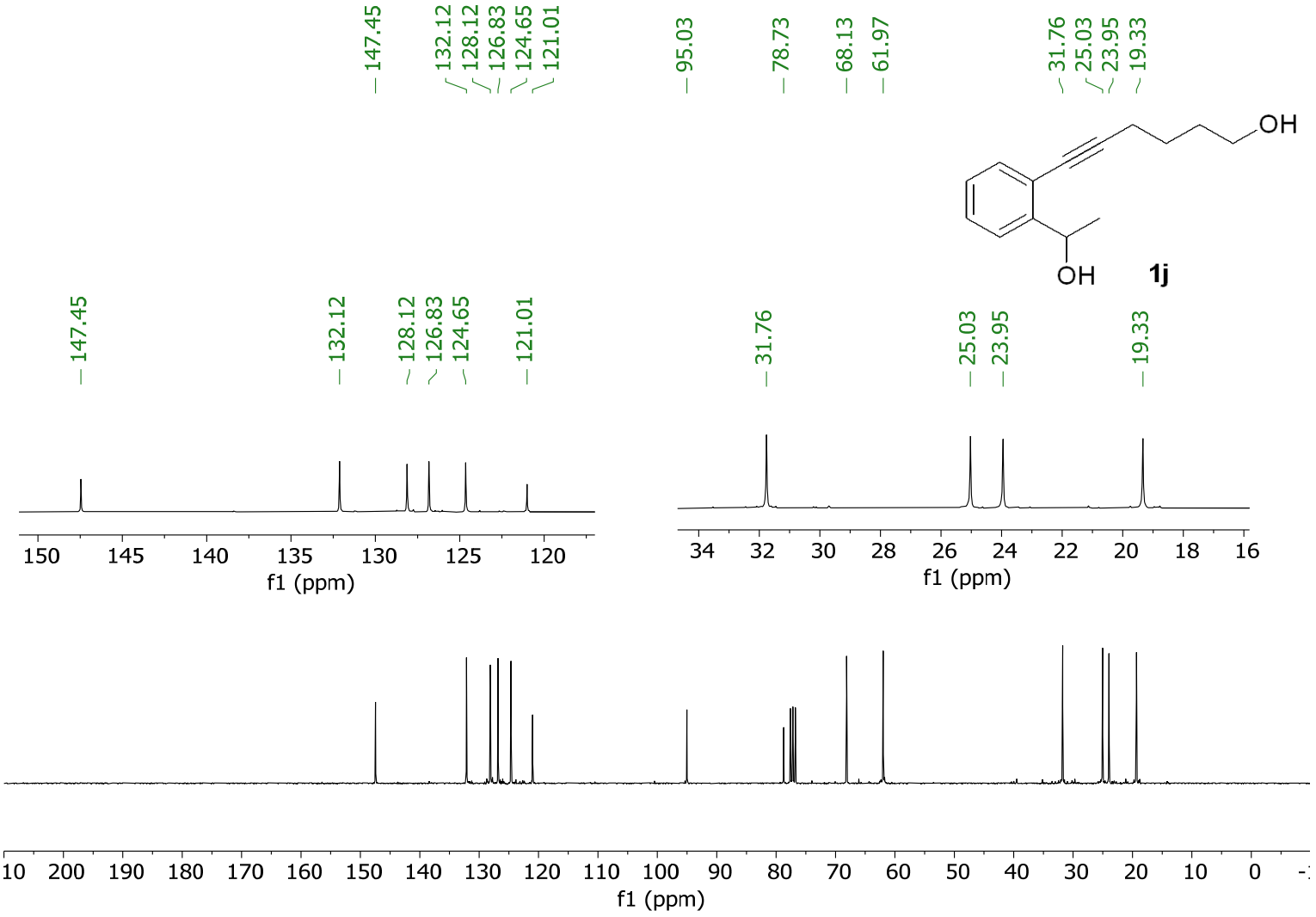
100 MHz ^{13}C-NMR Spectrum of compound **1i** ($CDCl_3$, 300 K)



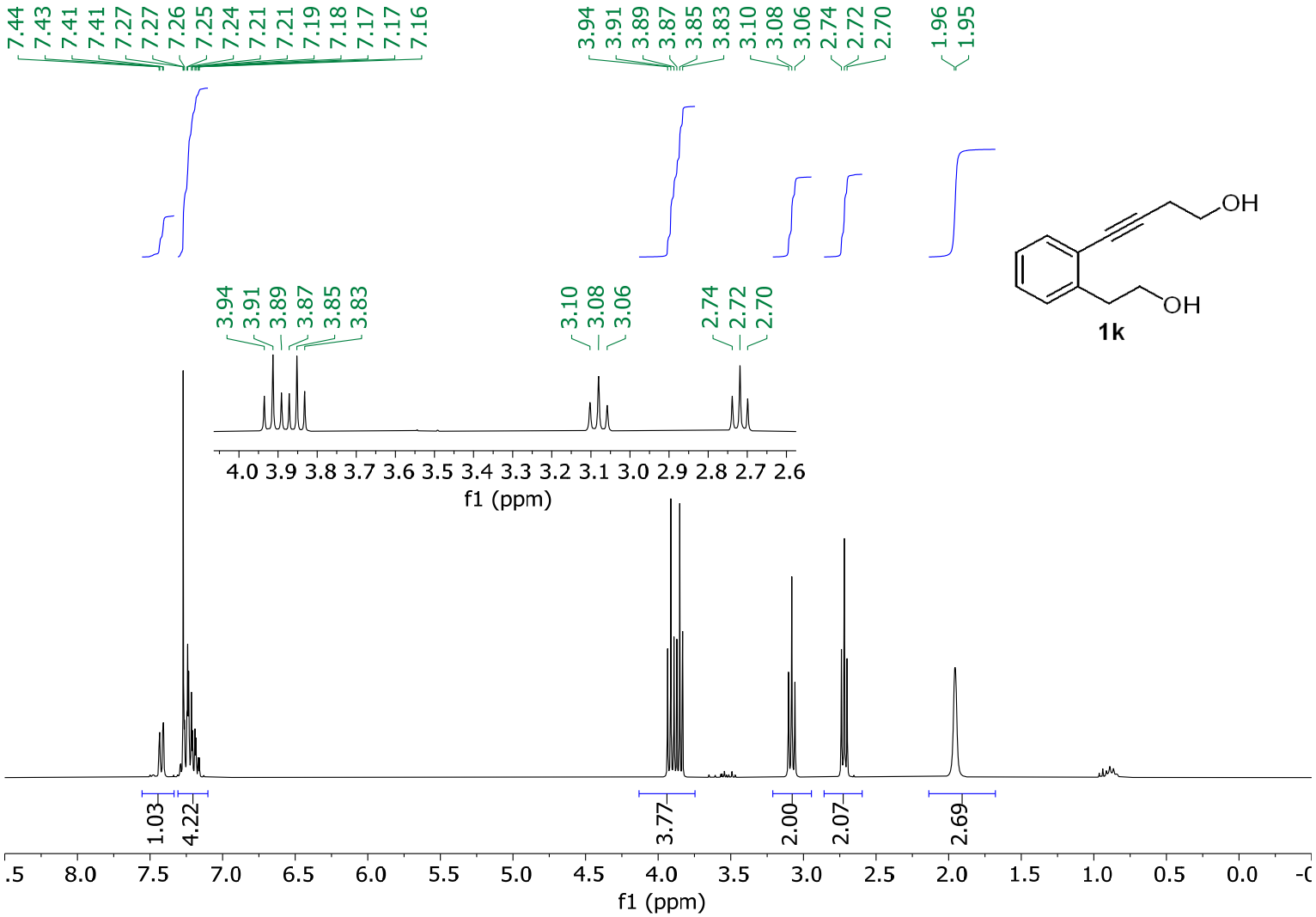
300 MHz ^{1}H-NMR Spectrum compound **1j** ($CDCl_3$, 300 K)



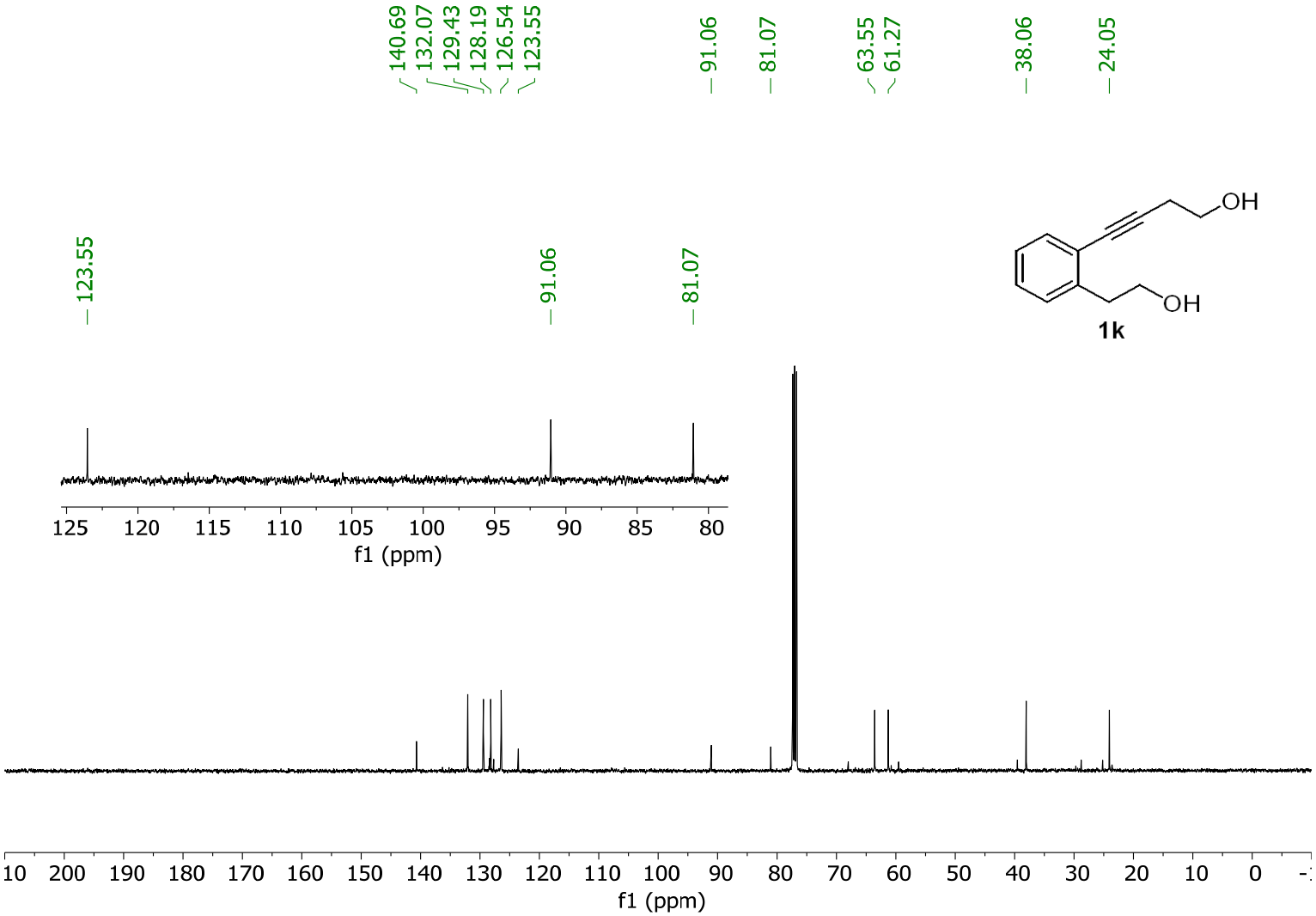
100 MHz ^{13}C-NMR Spectrum of compound **1j** ($CDCl_3$, 300 K)



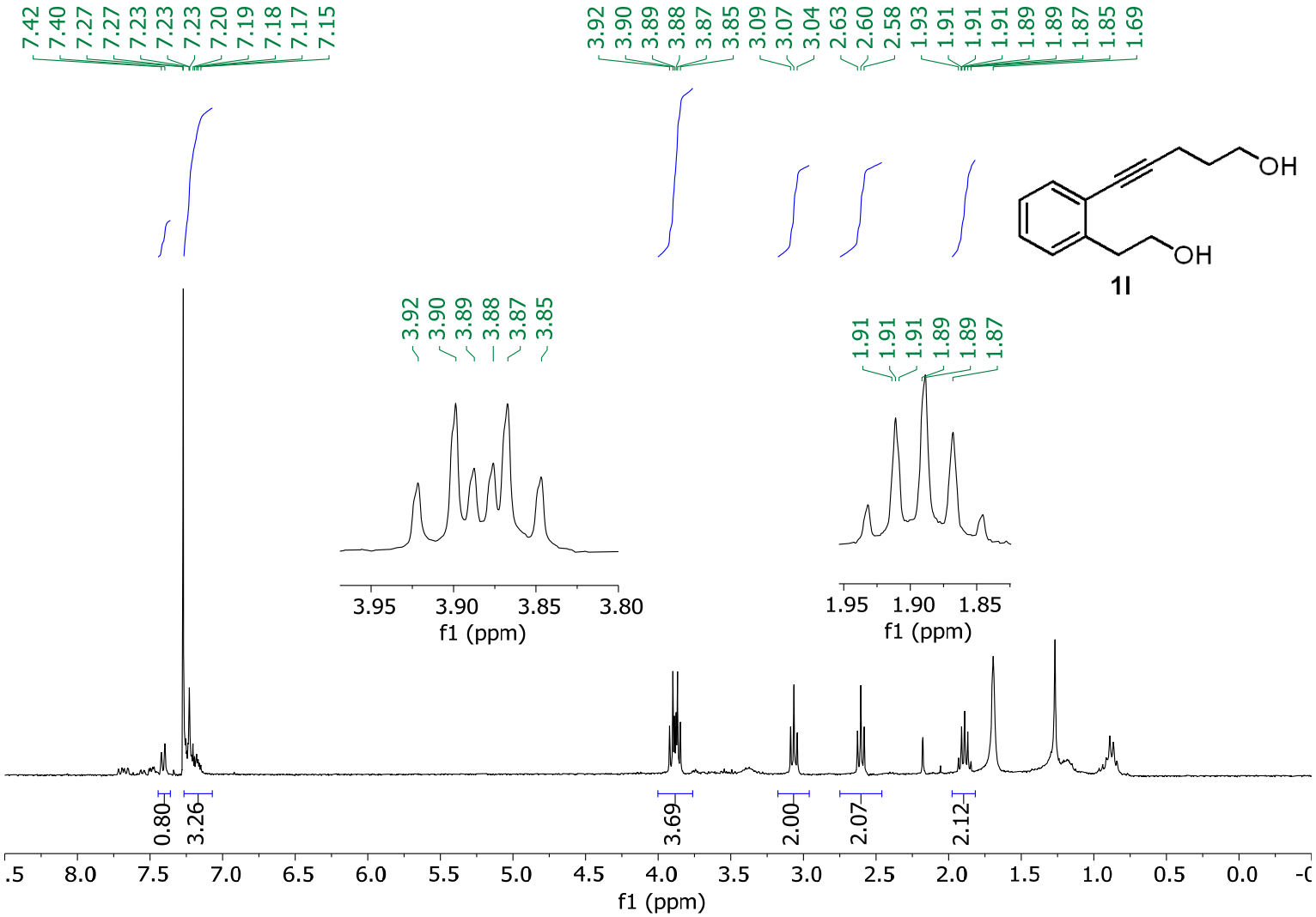
300 MHz ^{1}H-NMR Spectrum of compound **1k** ($CDCl_3$, 300 K)



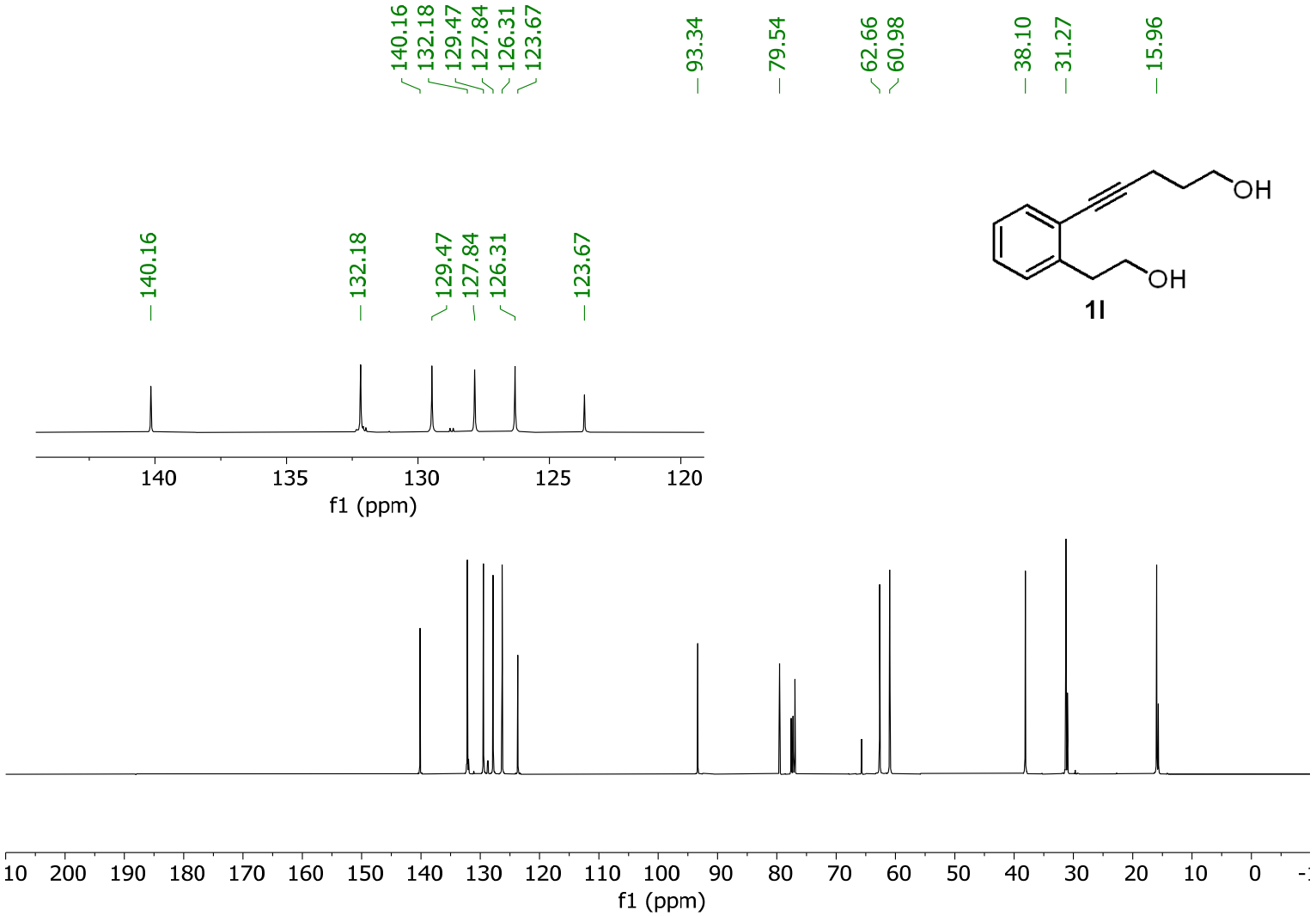
75 MHz ^{13}C-NMR Spectrum of compound **1k** ($CDCl_3$, 300 K)



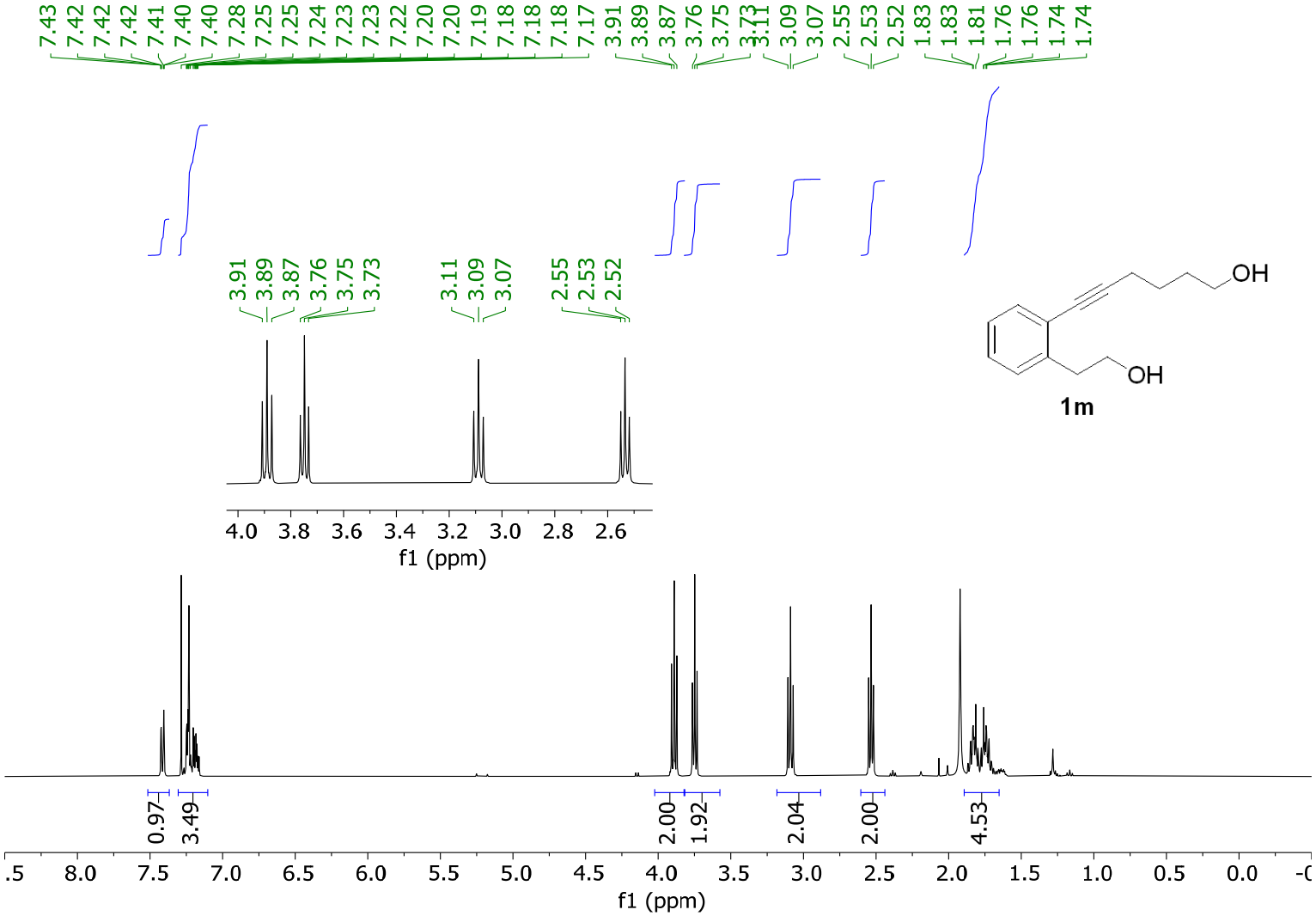
300 MHz ^{1}H-NMR Spectrum of compound **1l** ($CDCl_3$, 300 K)



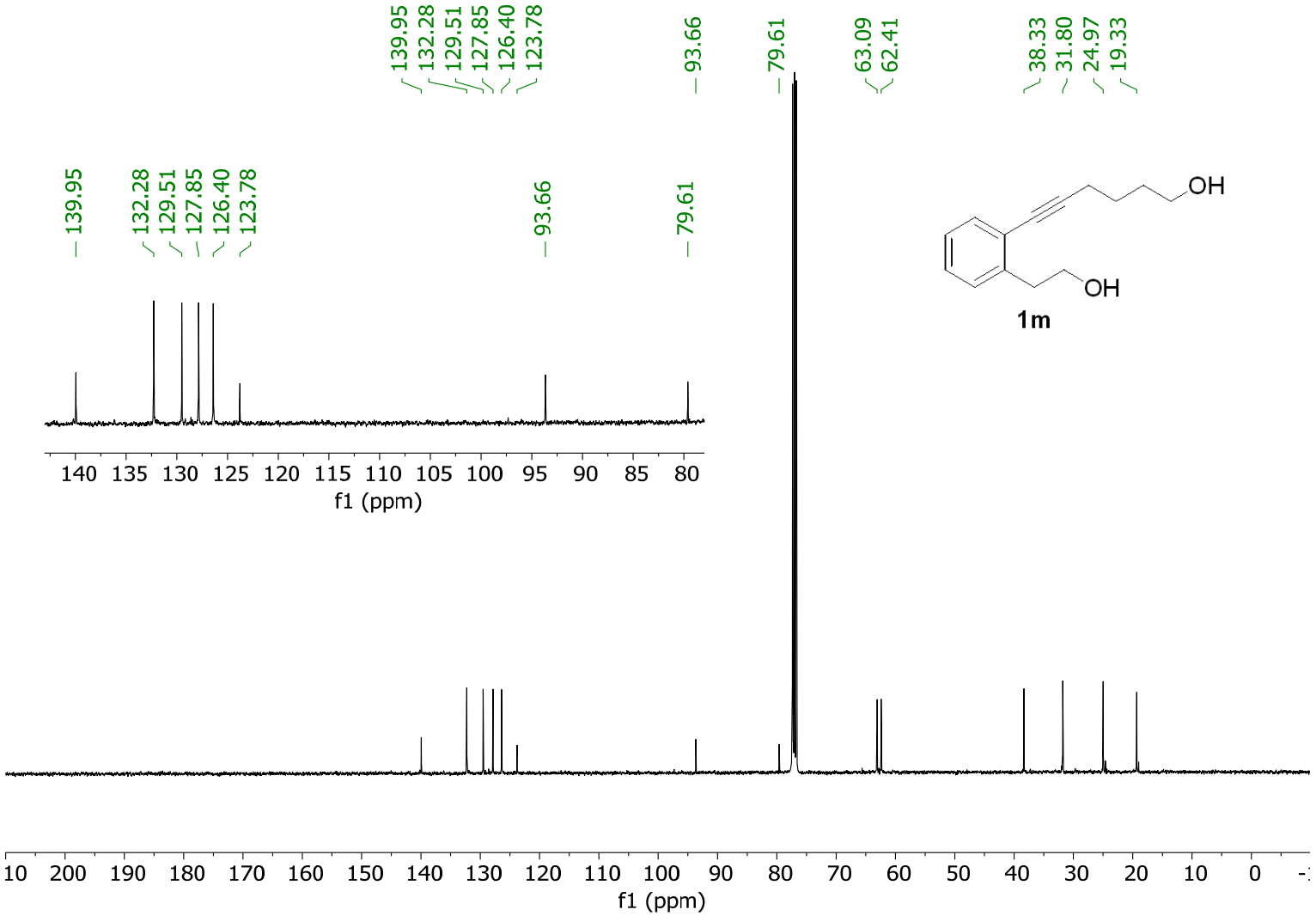
100 MHz ^{13}C-NMR Spectrum of compound **1l** ($CDCl_3$, 300 K)



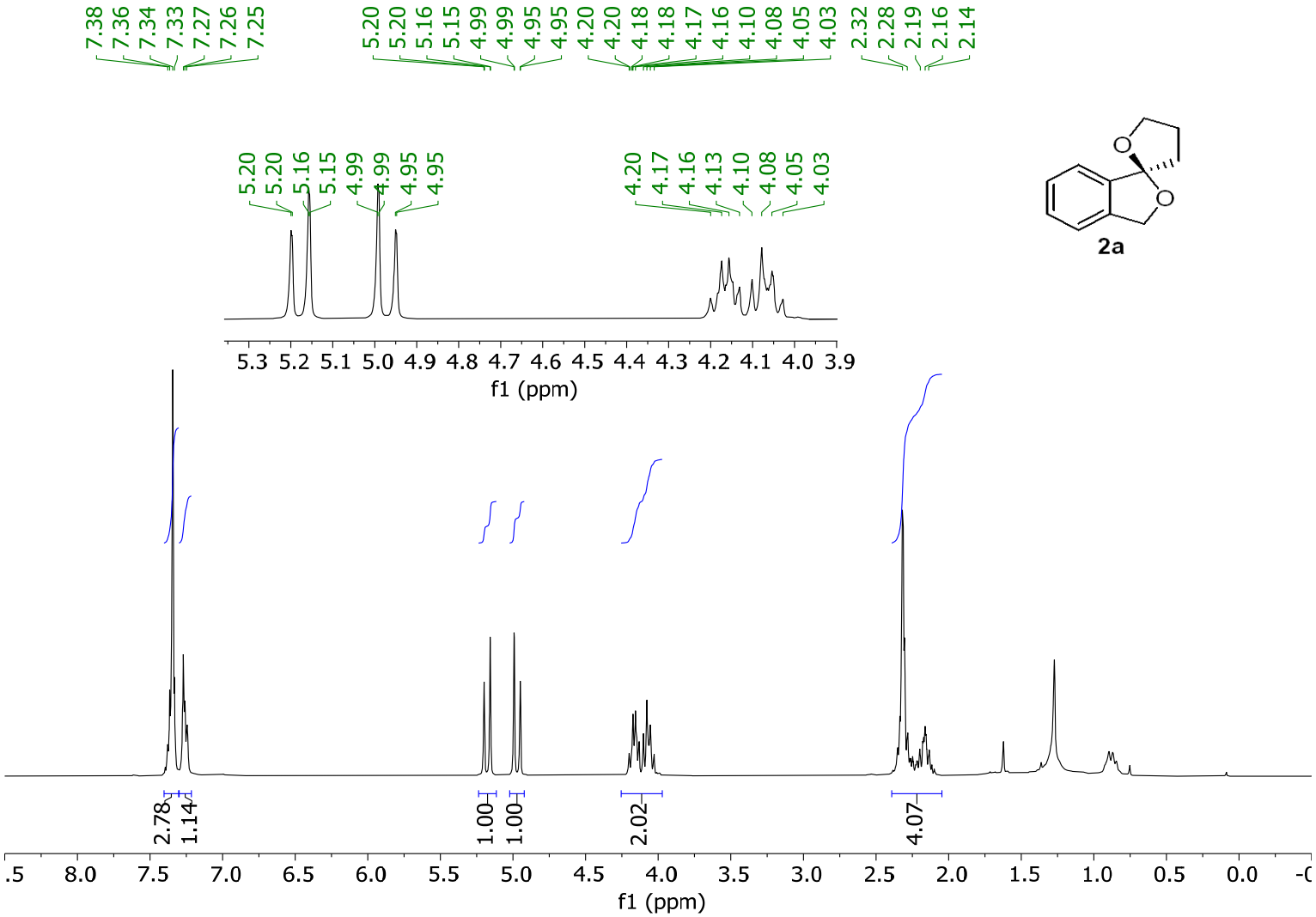
300 MHz ^{1}H-NMR Spectrum of compound **1m** ($CDCl_3$, 300 K)



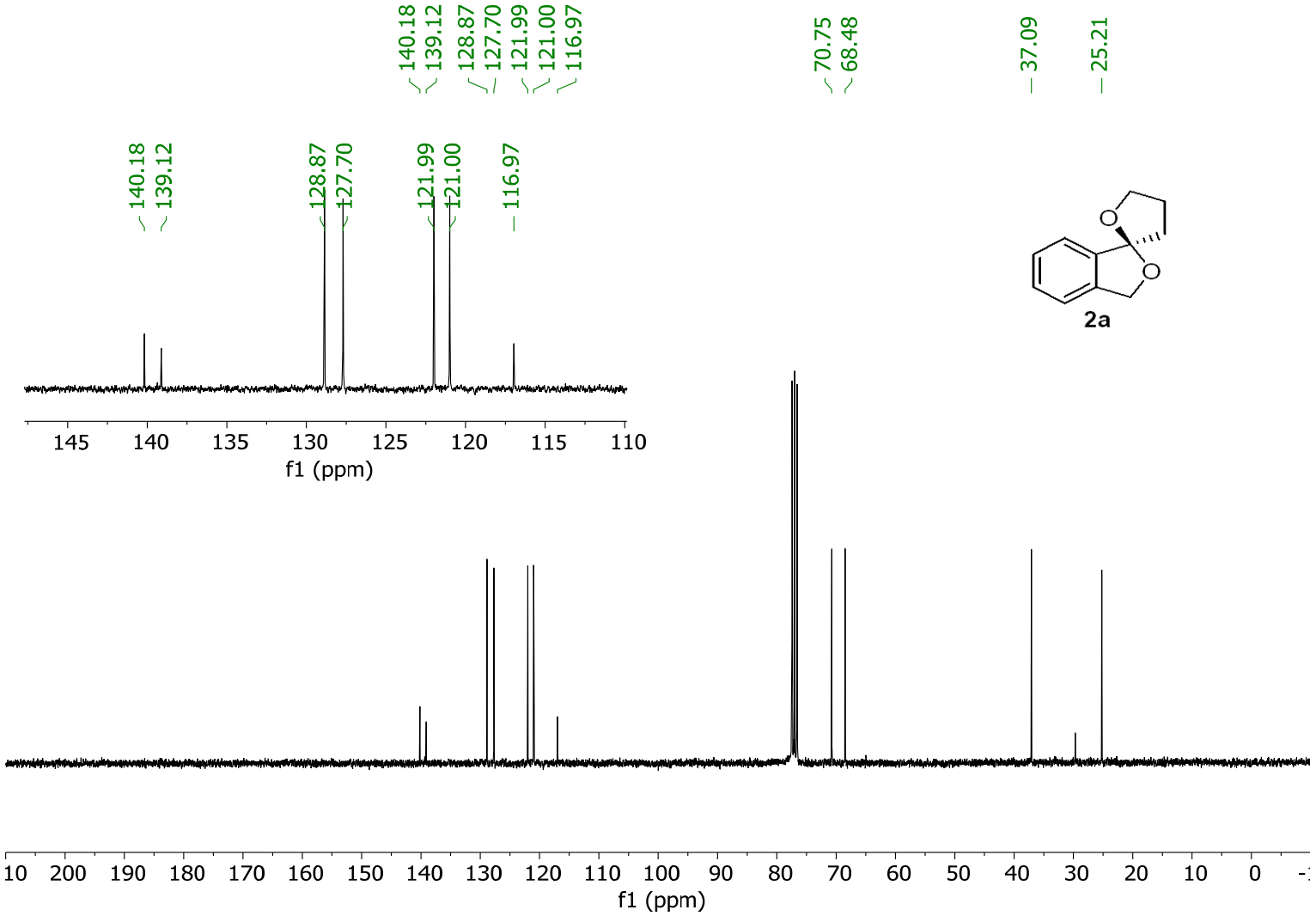
100 MHz ^{13}C-NMR Spectrum of compound **1m** ($CDCl_3$, 300 K)



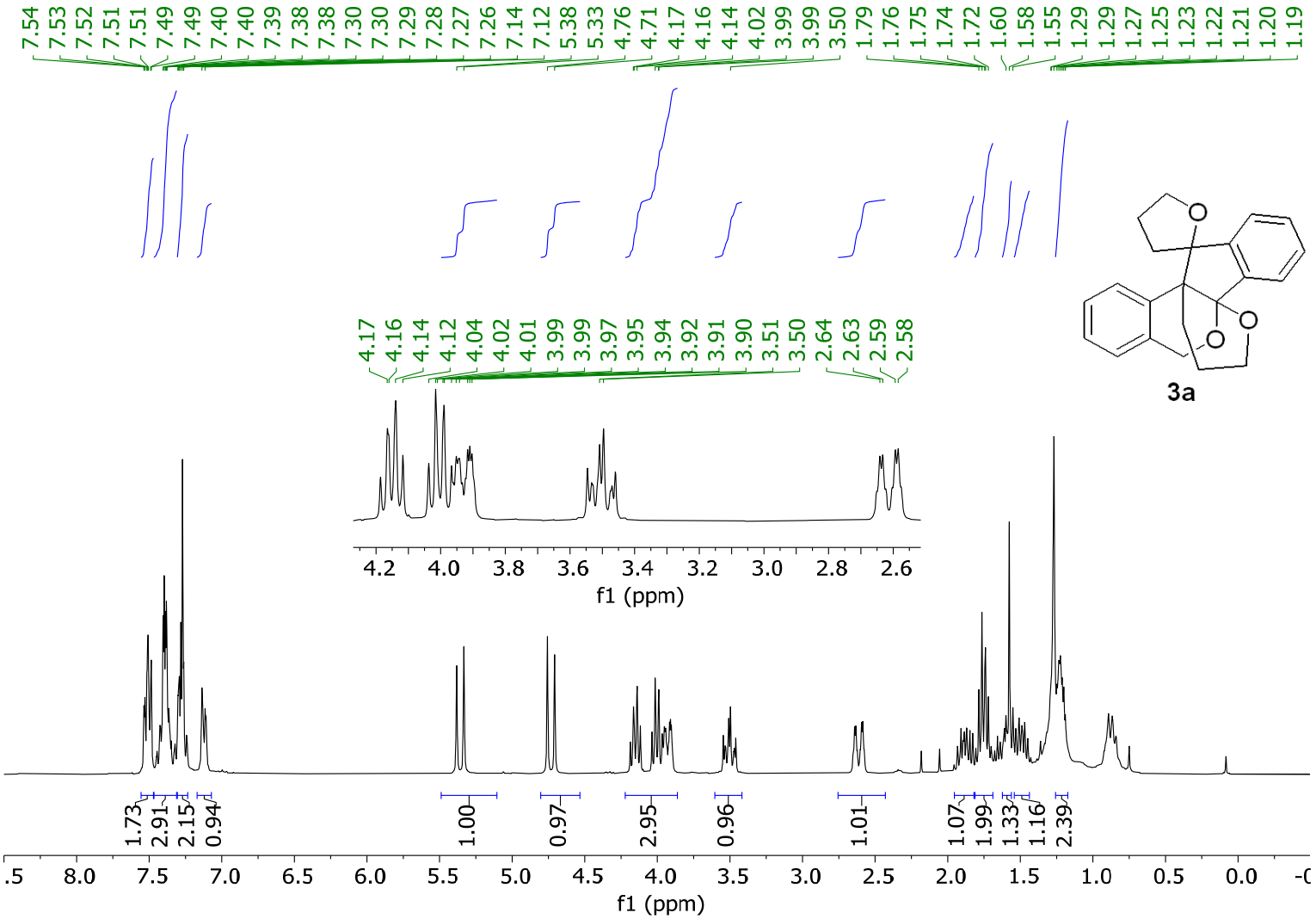
300 MHz ^{1}H-NMR Spectrum compound **2a** ($CDCl_3$, 300 K)



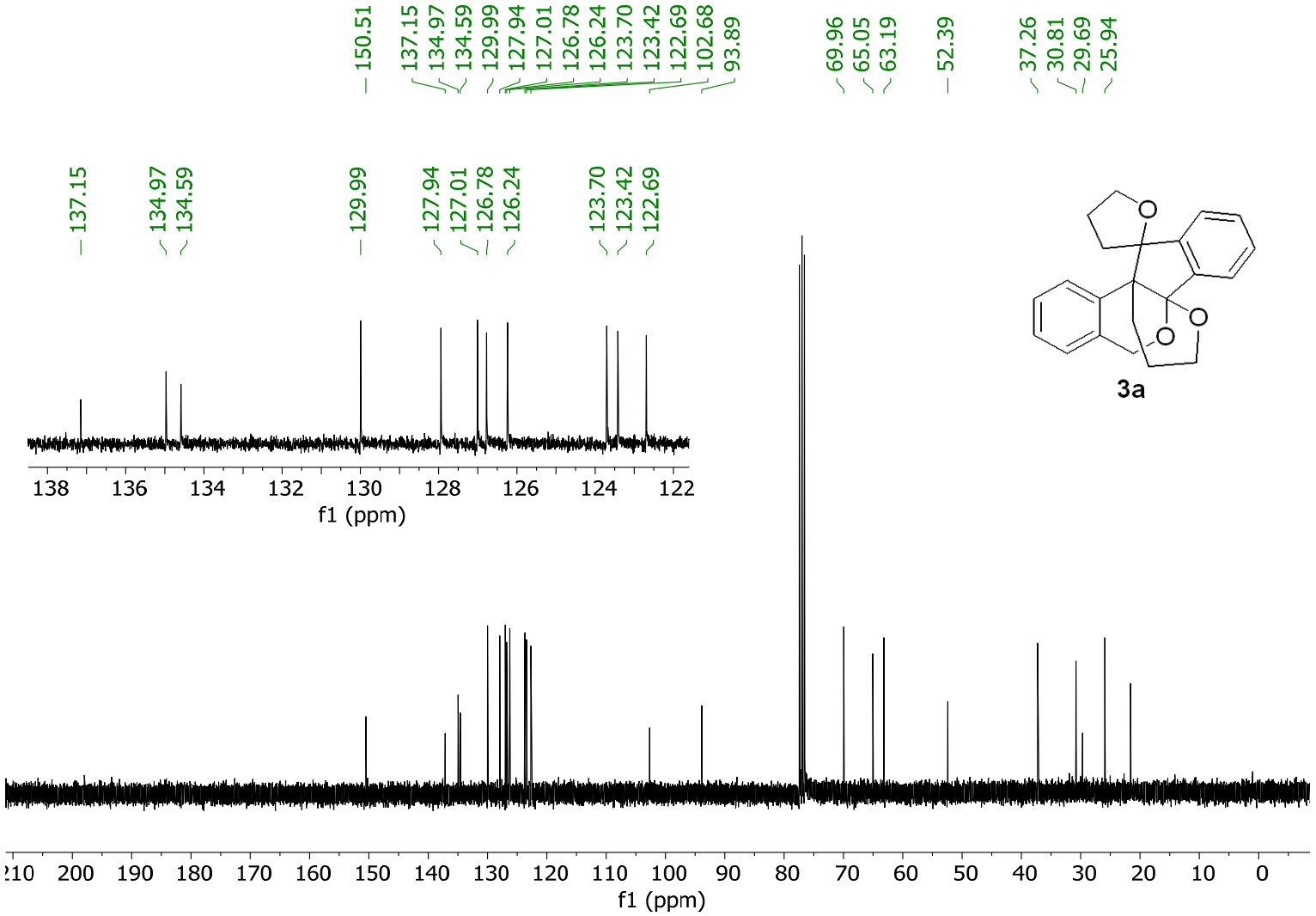
75 MHz ^{13}C-NMR Spectrum of compound **2a** ($CDCl_3$, 300 K)



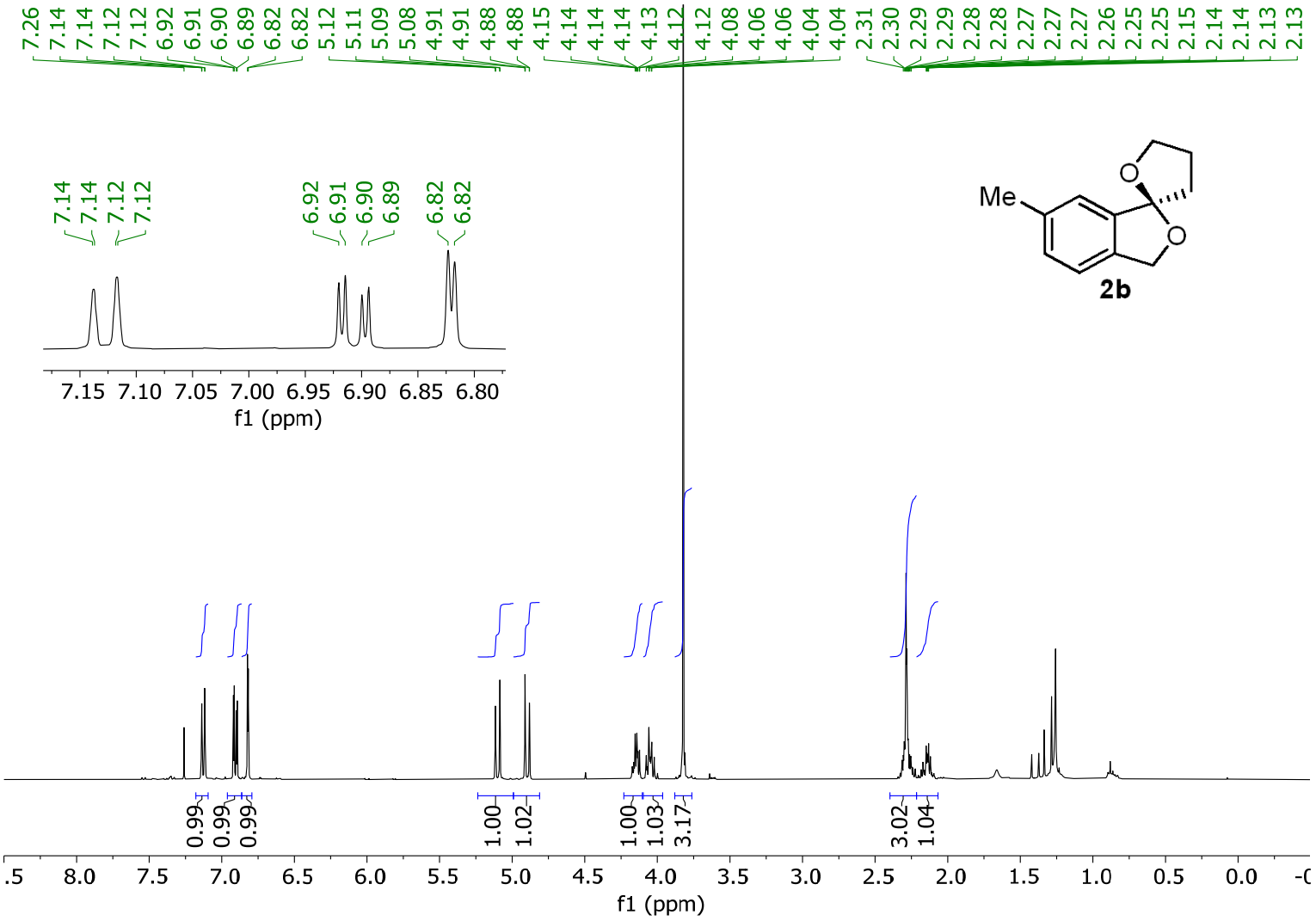
300 MHz ^{1}H-NMR Spectrum compound **3a** ($CDCl_3$, 300 K)



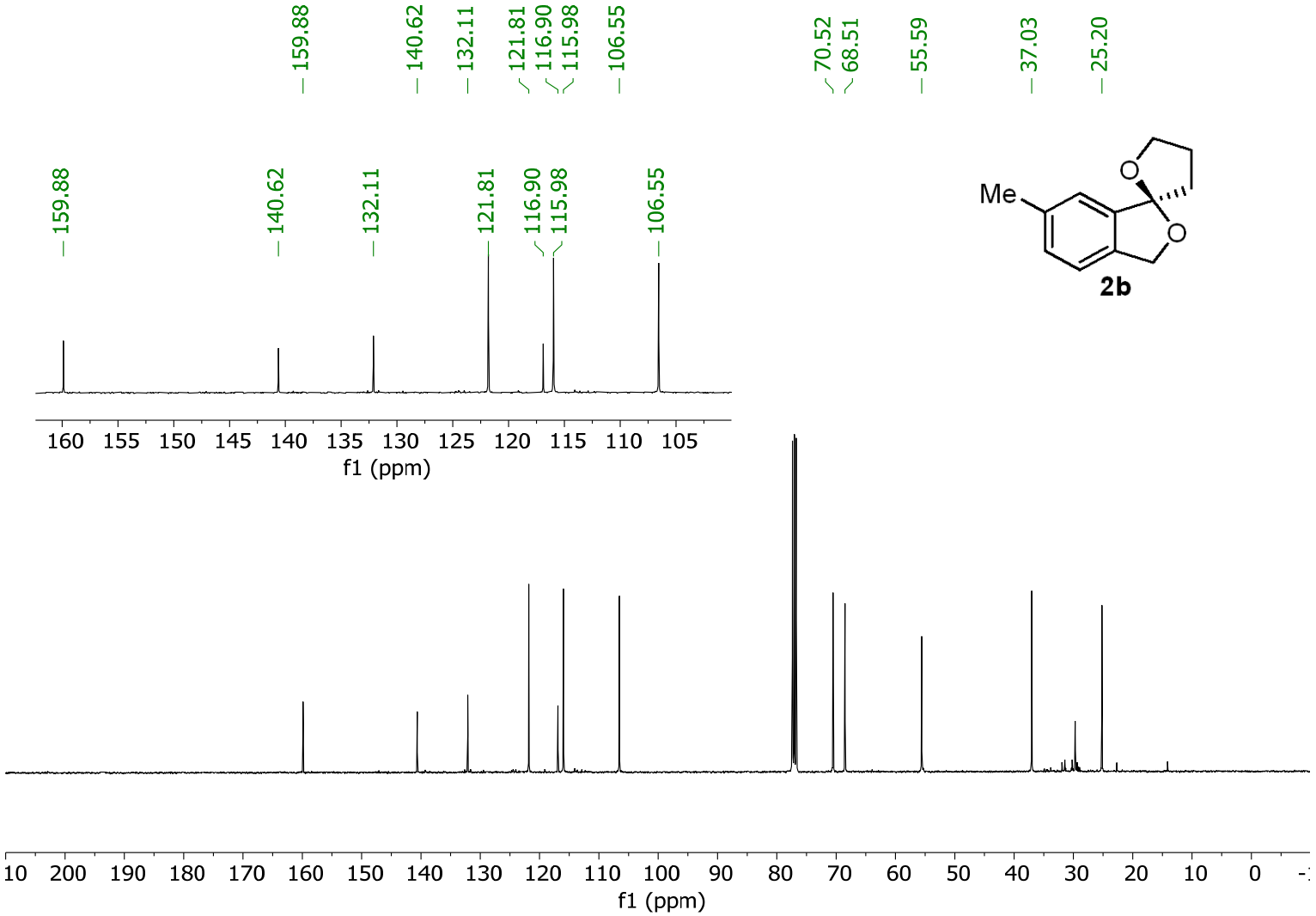
75 MHz ^{13}C-NMR Spectrum of compound **3a** ($CDCl_3$, 300 K)



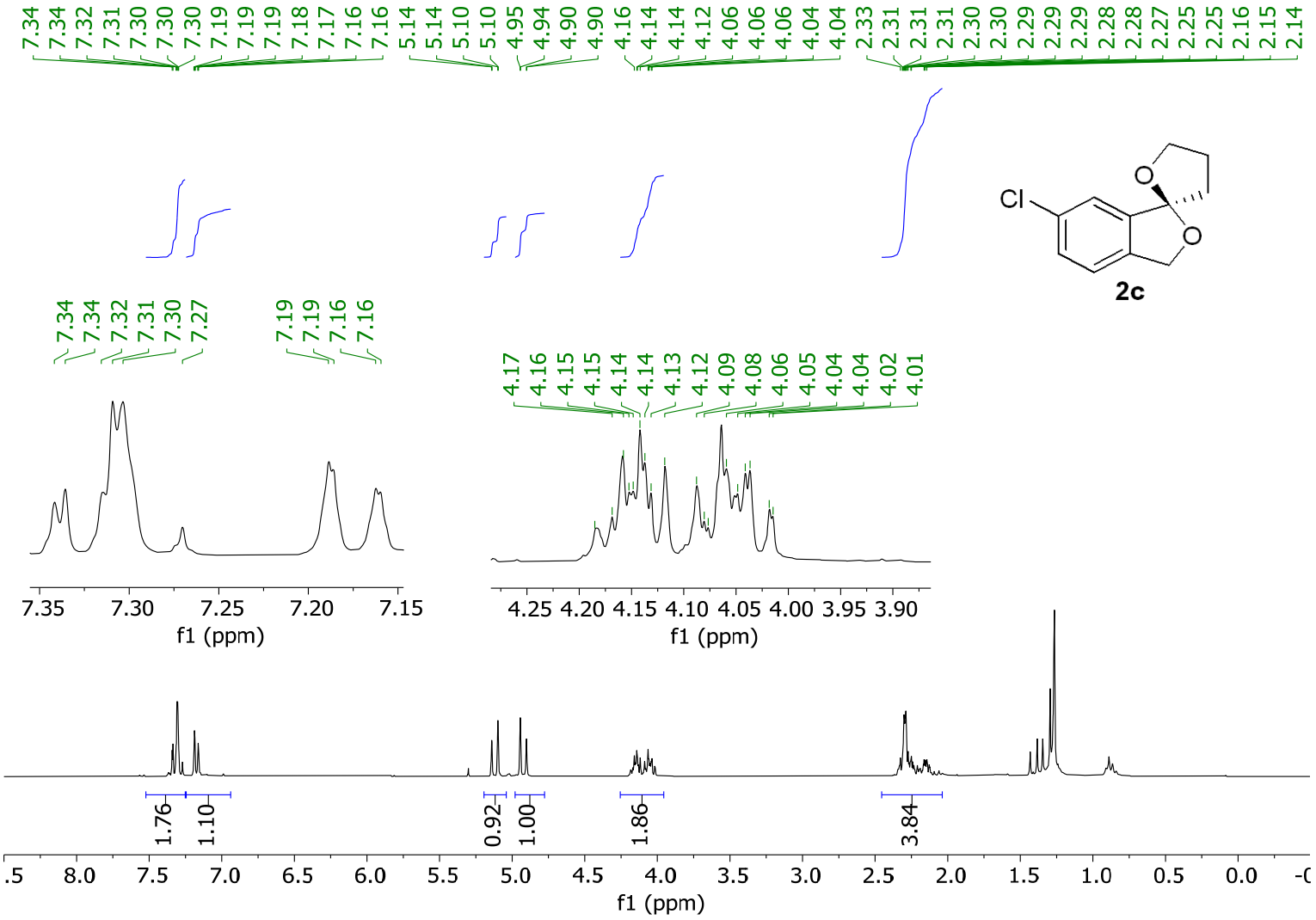
300 MHz ^{1}H-NMR Spectrum compound **2b** ($CDCl_3$, 300 K)



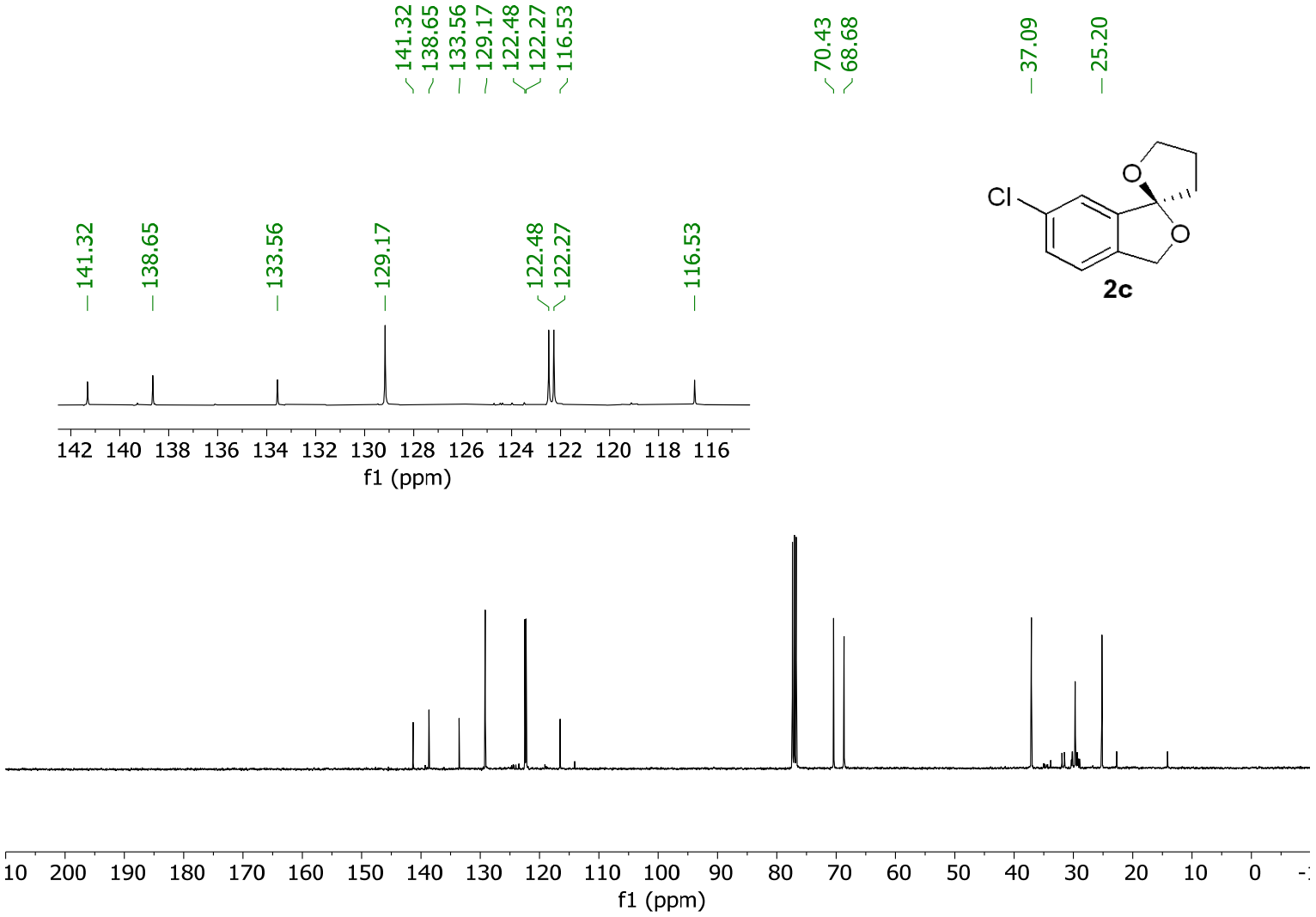
100 MHz ^{13}C-NMR Spectrum of compound **2b** ($CDCl_3$, 300 K)



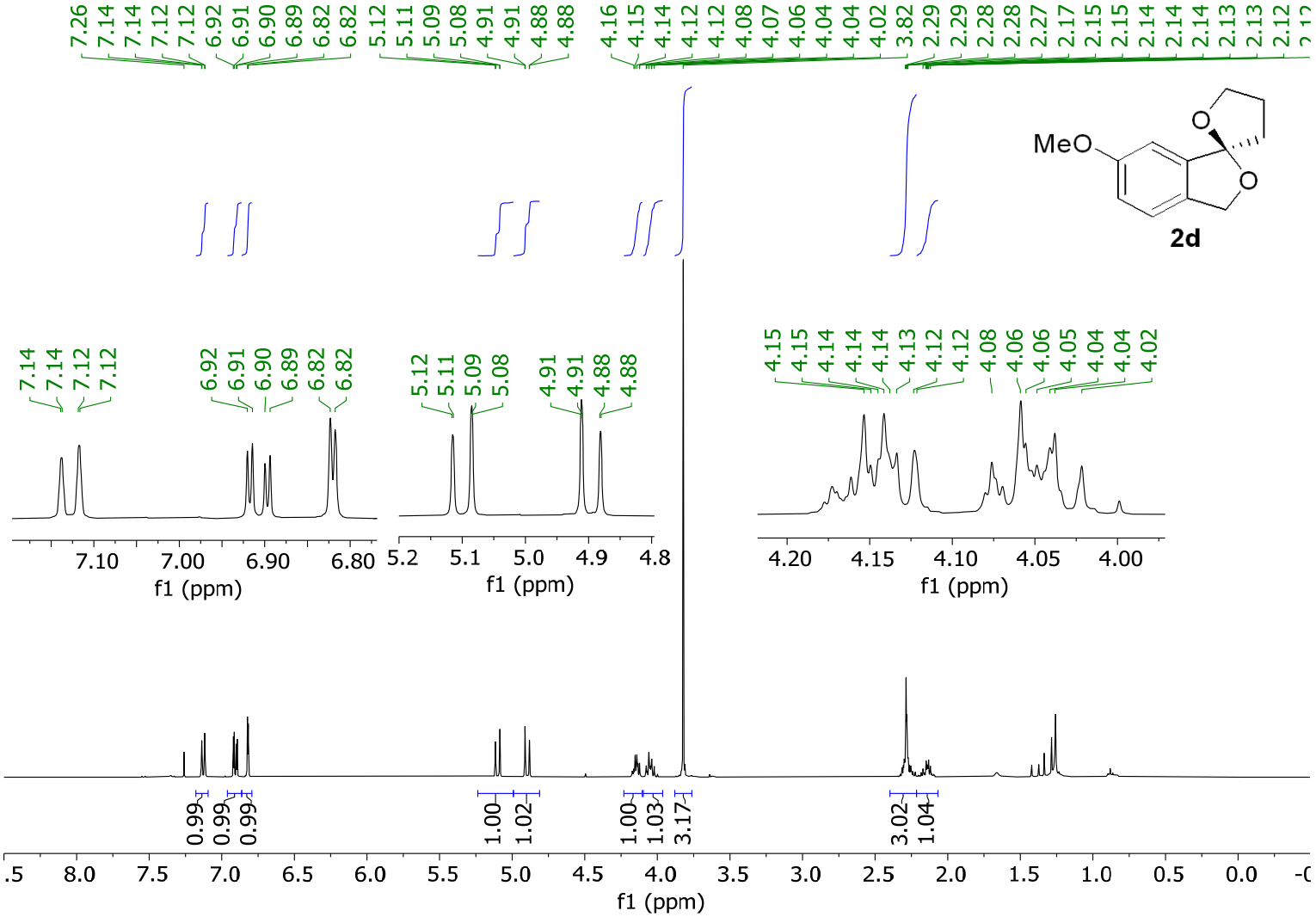
300 MHz ^{1}H-NMR Spectrum compound **2c** ($CDCl_3$, 300 K)



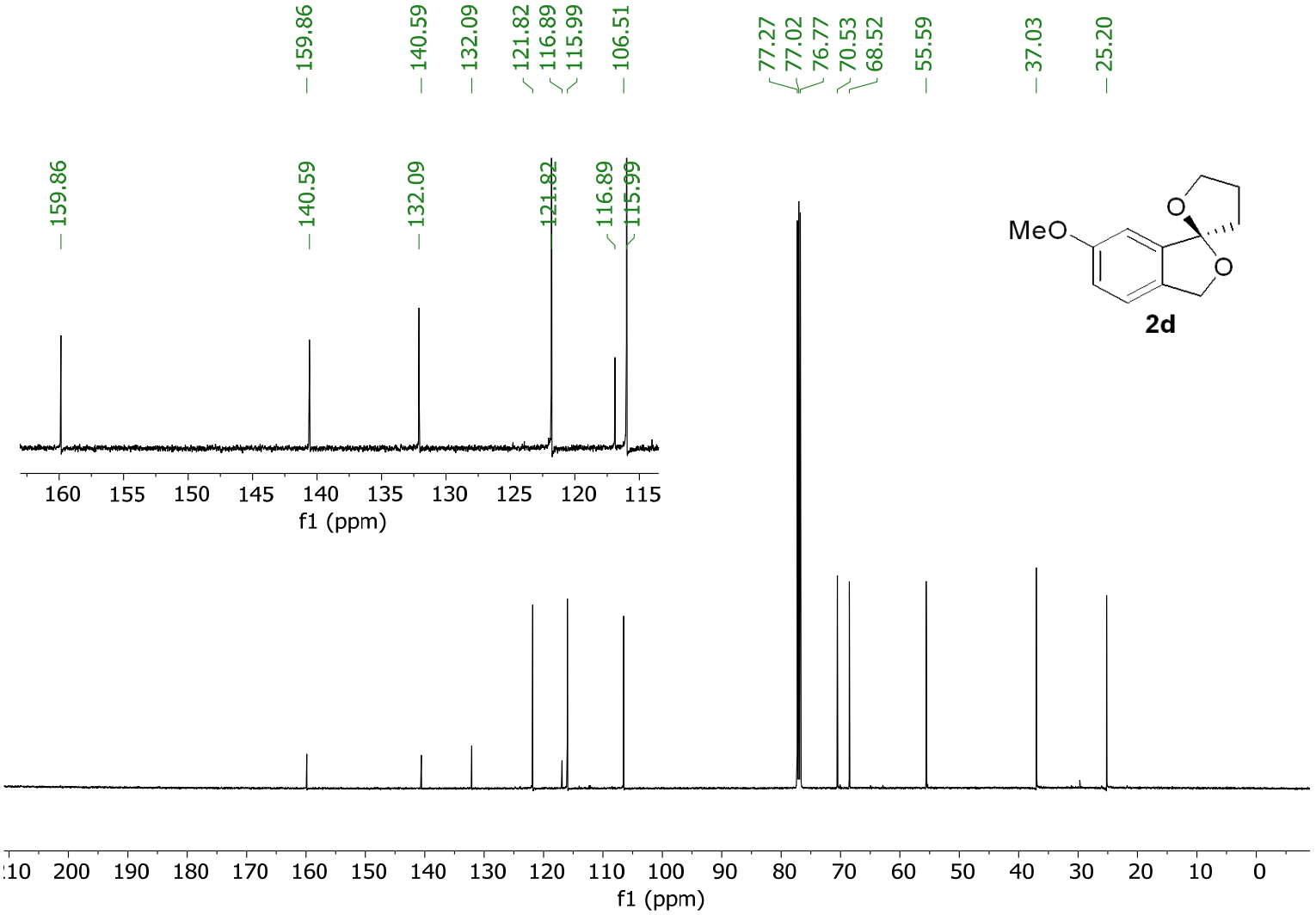
75 MHz ^{13}C-NMR Spectrum of compound **2c** ($CDCl_3$, 300 K)



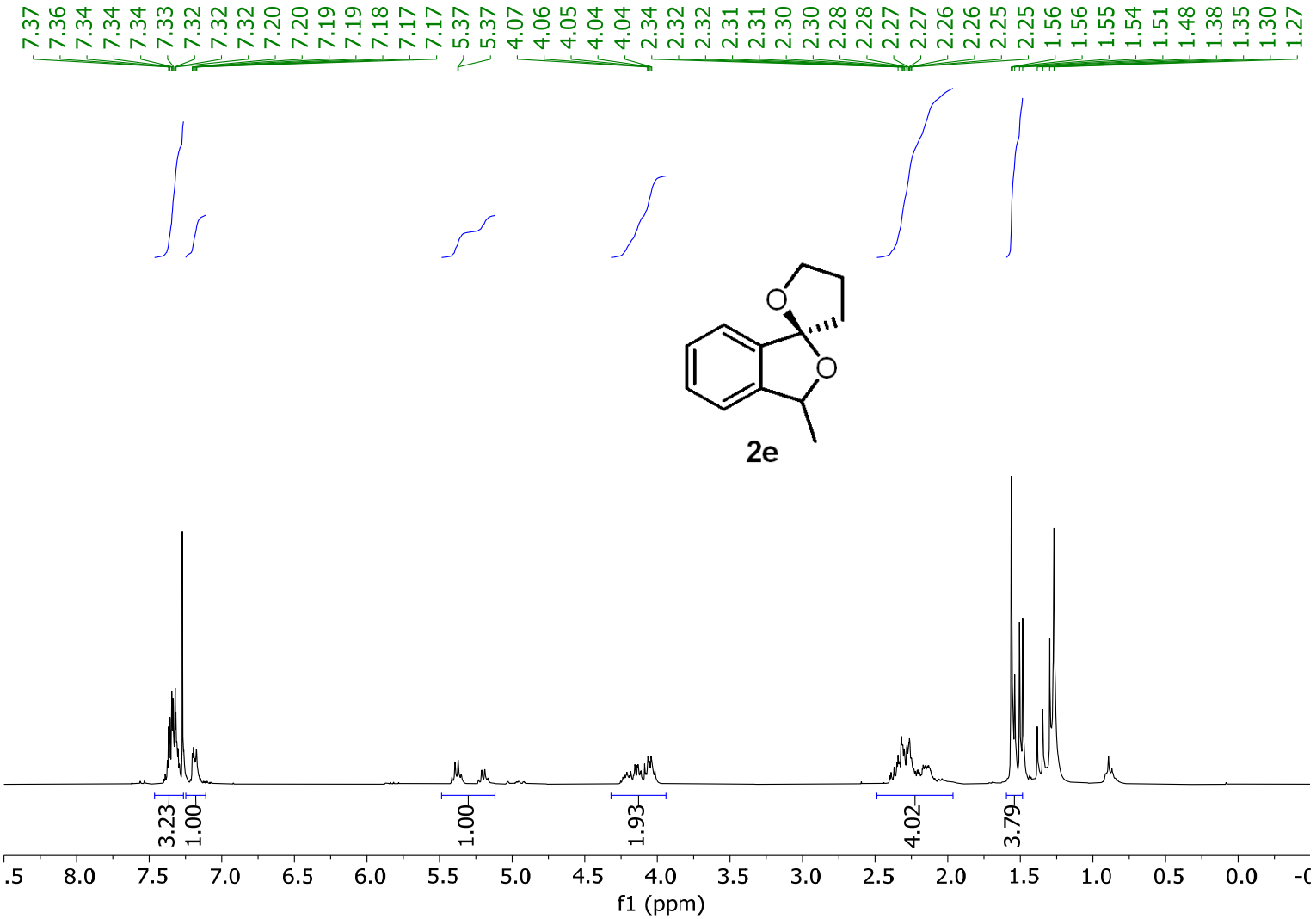
300 MHz ^{1}H-NMR Spectrum compound **2d** ($CDCl_3$, 300 K)



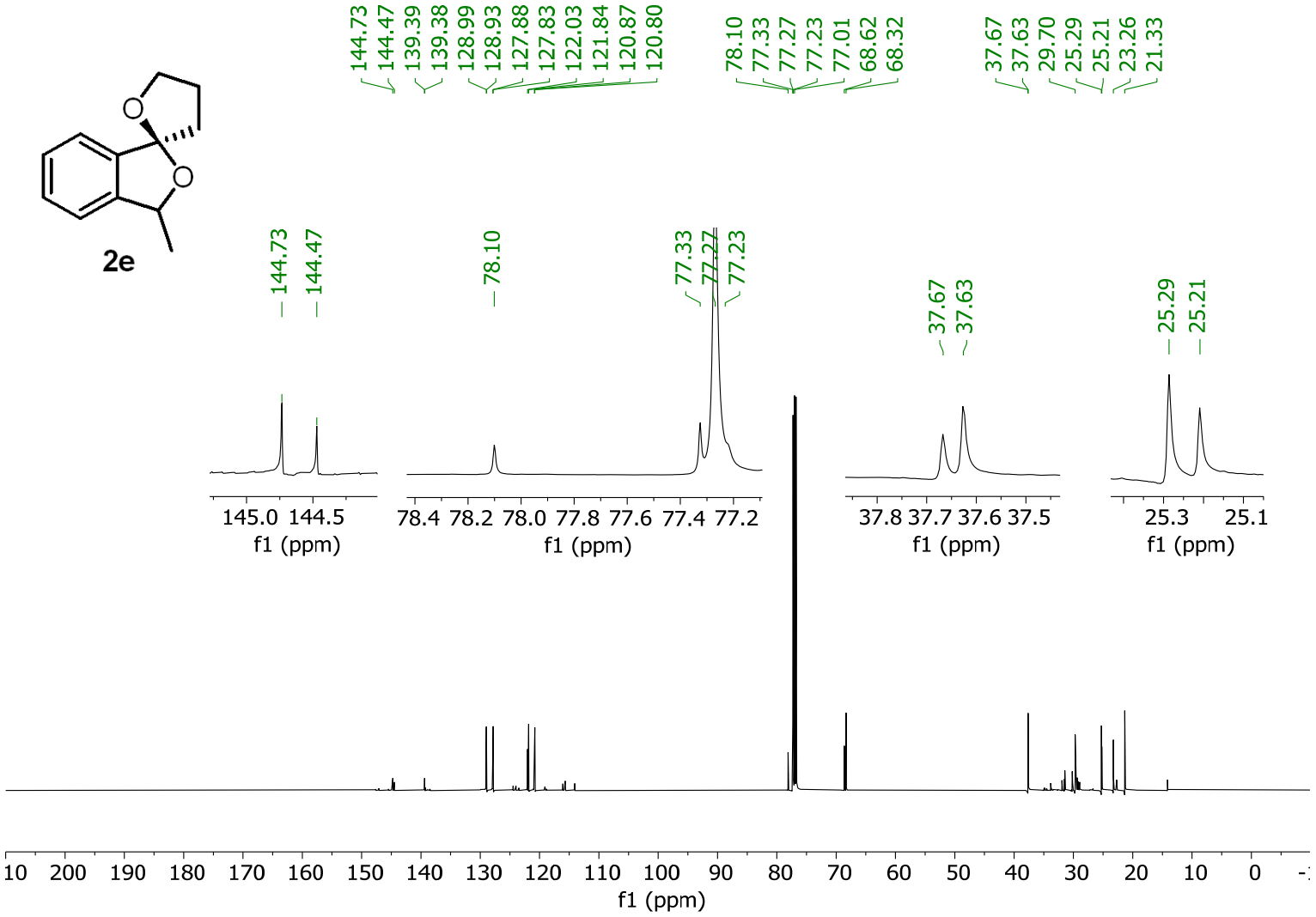
75 MHz ^{13}C-NMR Spectrum of compound **2d** ($CDCl_3$, 300 K)



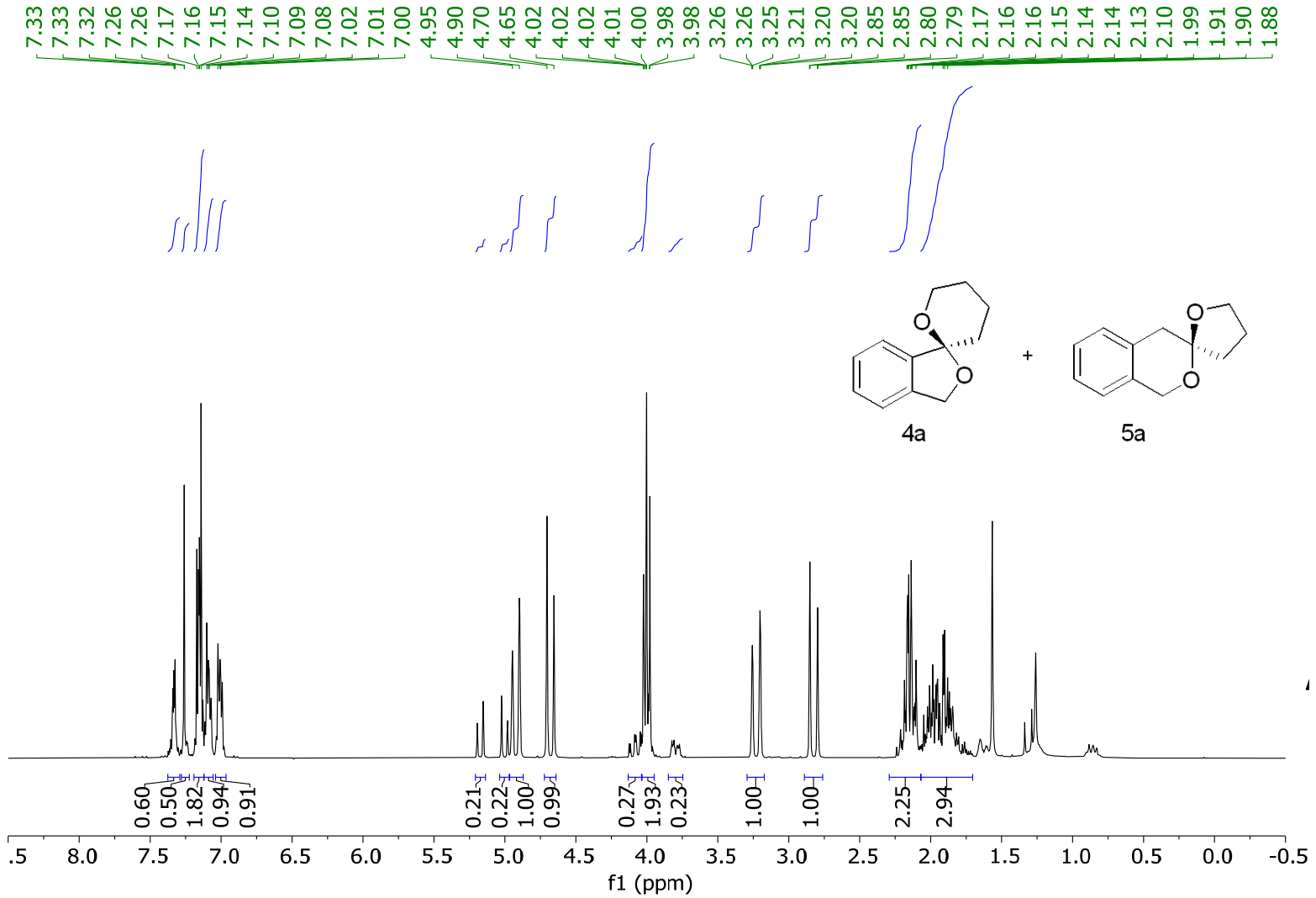
300 MHz ^{1}H-NMR Spectrum compound **2e** ($CDCl_3$, 300 K)



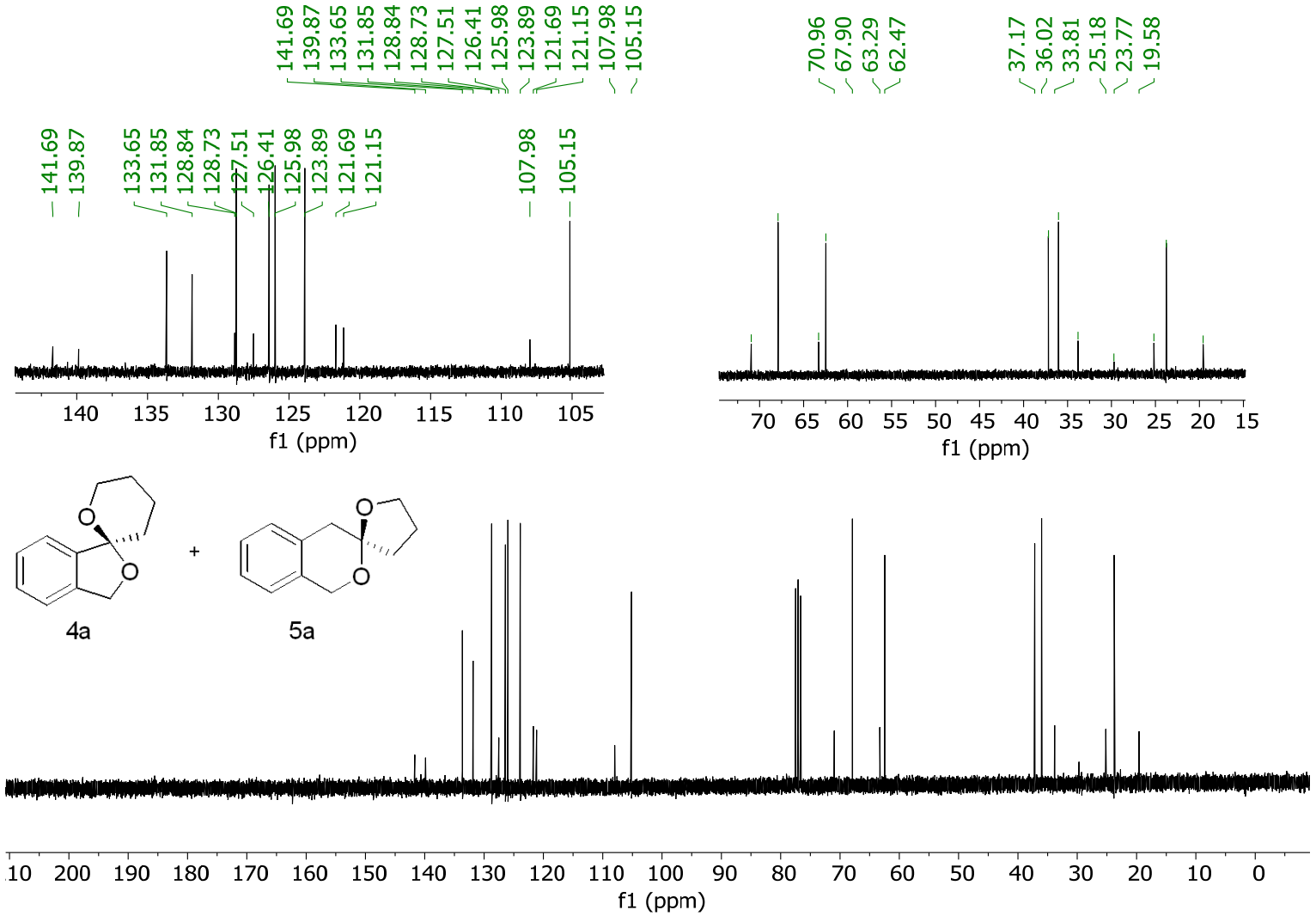
75 MHz ^{13}C-NMR Spectrum of compound **2e** ($CDCl_3$, 300 K)



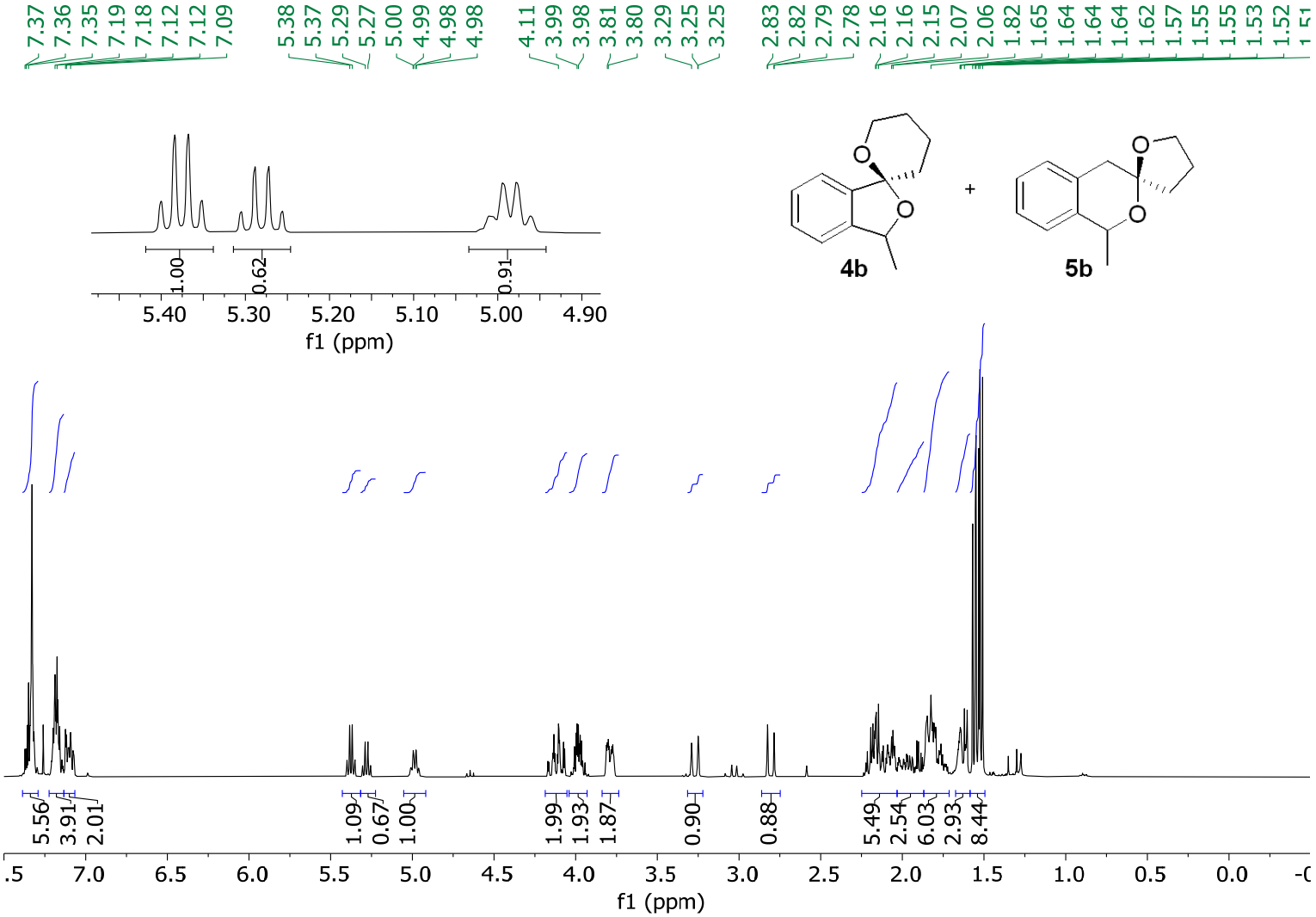
300 MHz ^{1}H-NMR Spectrum compound **4a:5a** ($CDCl_3$, 300 K)



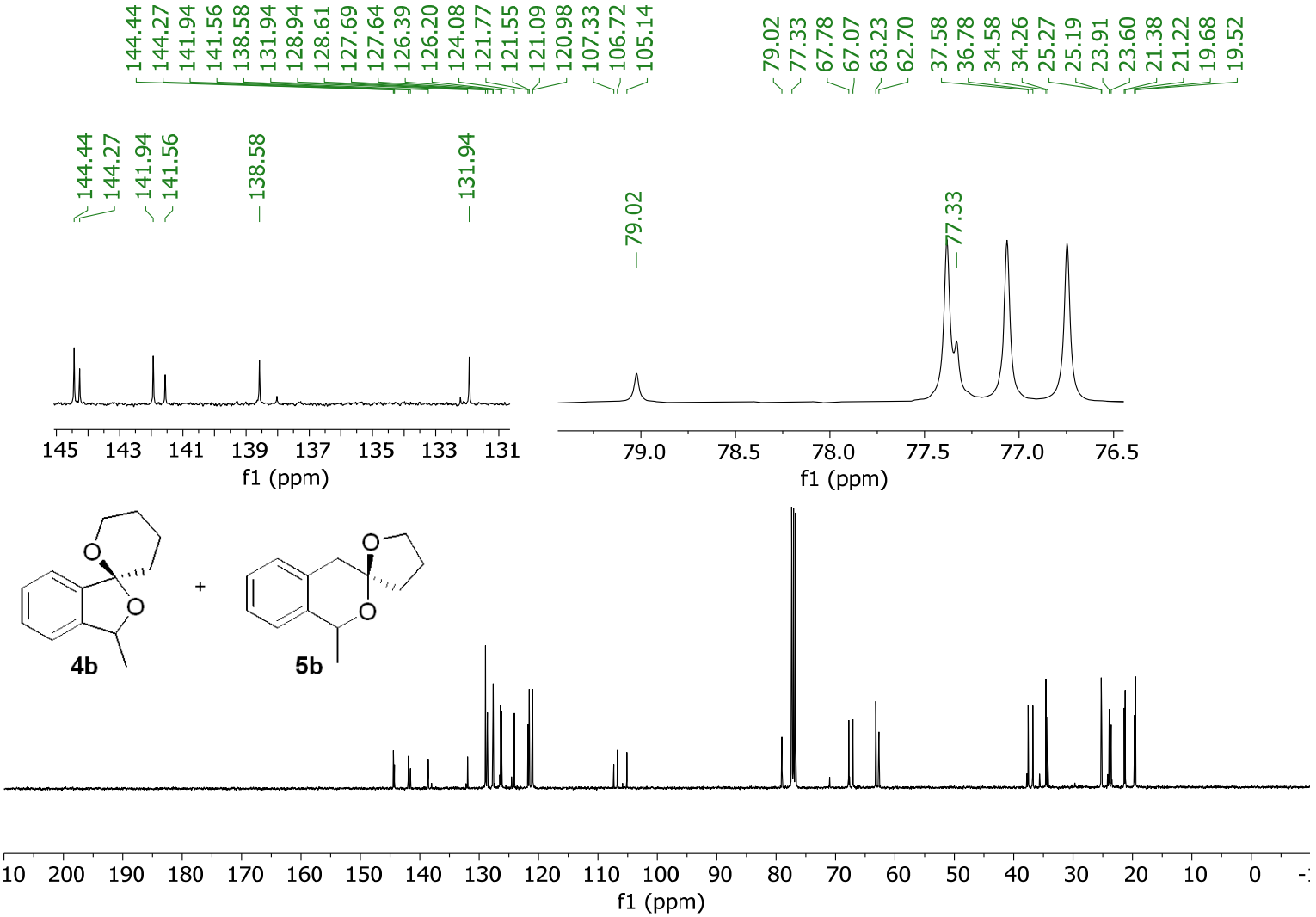
75 MHz ^{13}C-NMR Spectrum of compound **4a:5a** ($CDCl_3$, 300 K)



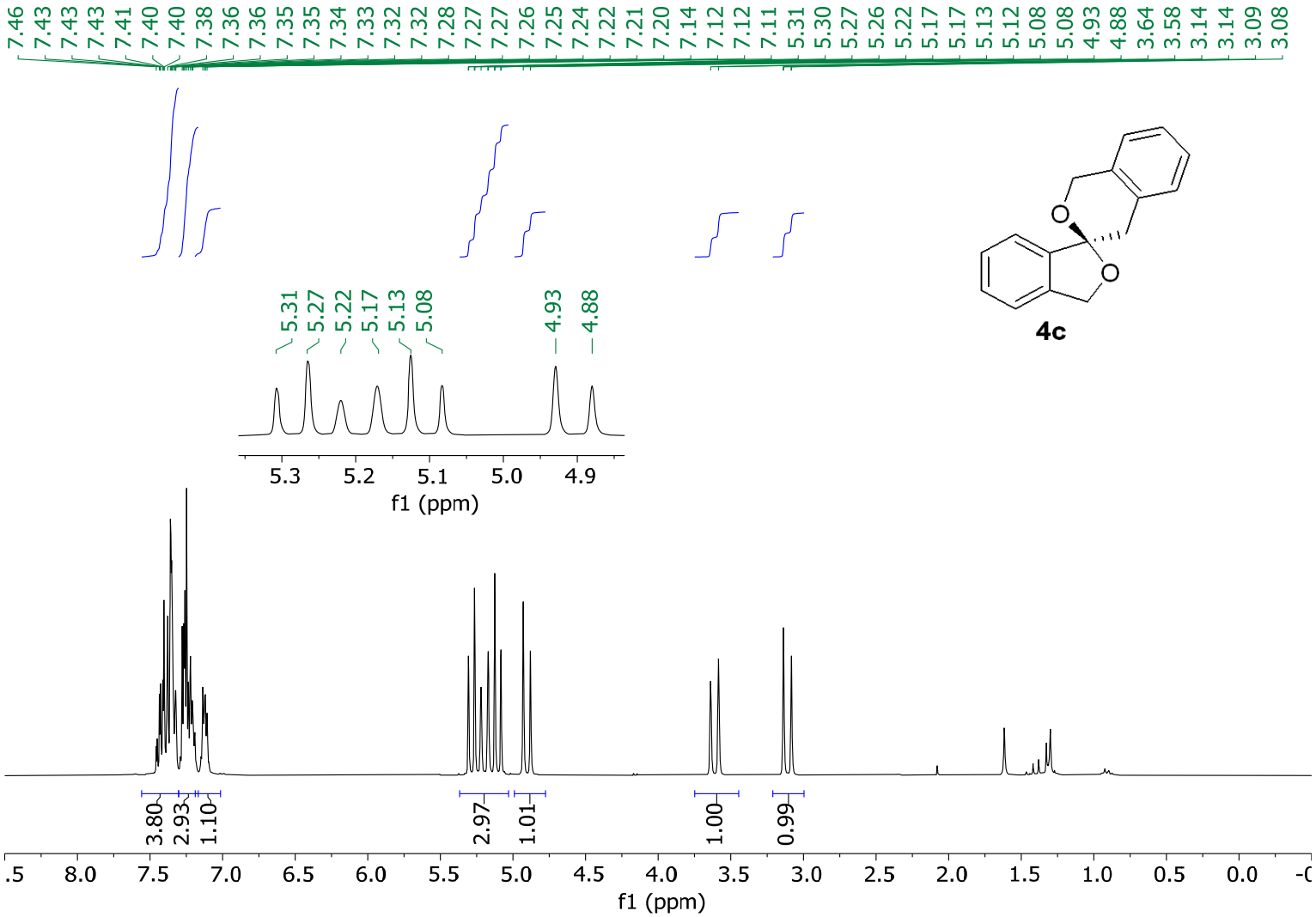
300 MHz ^{1}H-NMR Spectrum compound **4b:5b** ($CDCl_3$, 300 K)



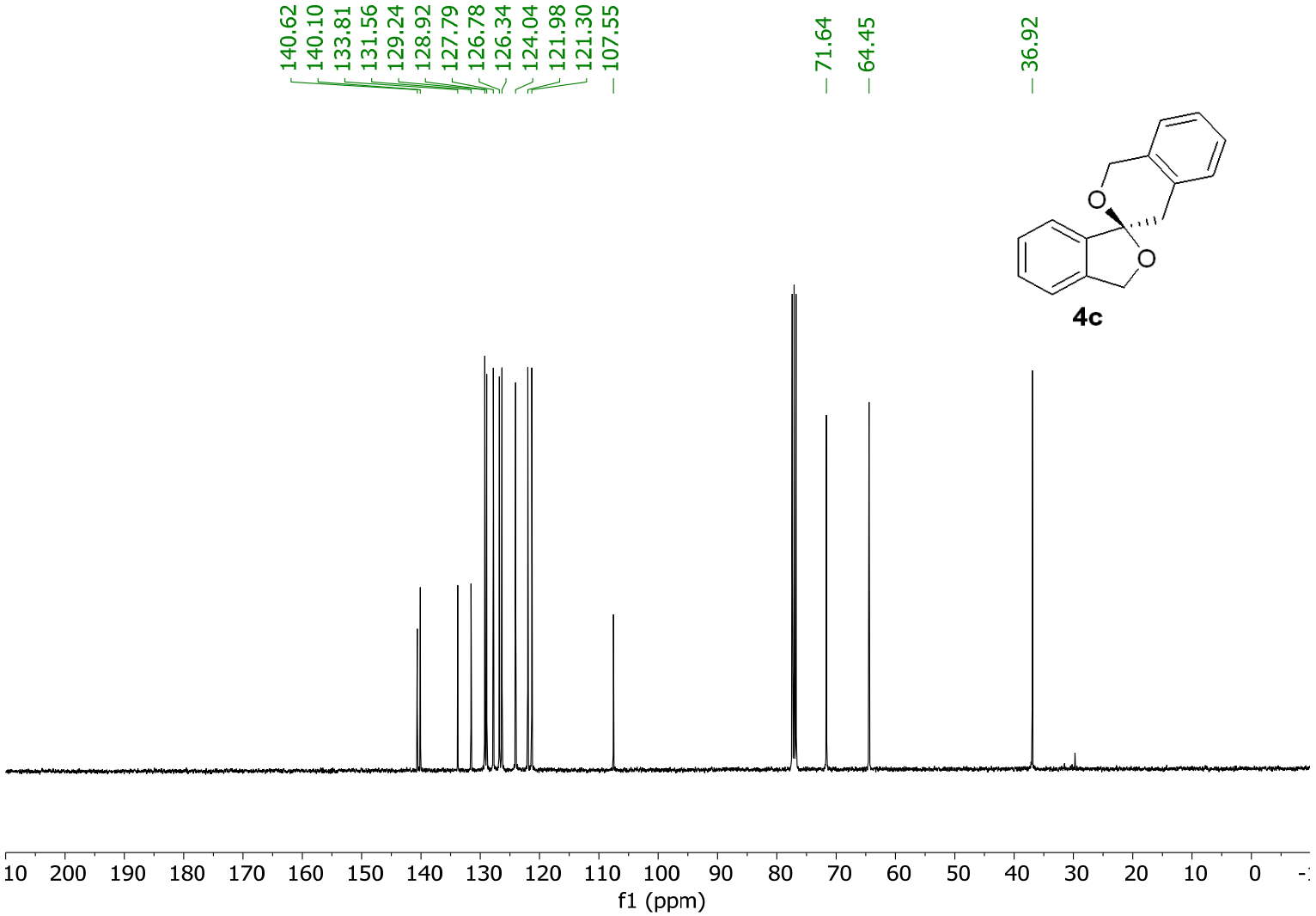
75 MHz ^{13}C-NMR Spectrum of compound **4b:5b** ($CDCl_3$, 300 K)



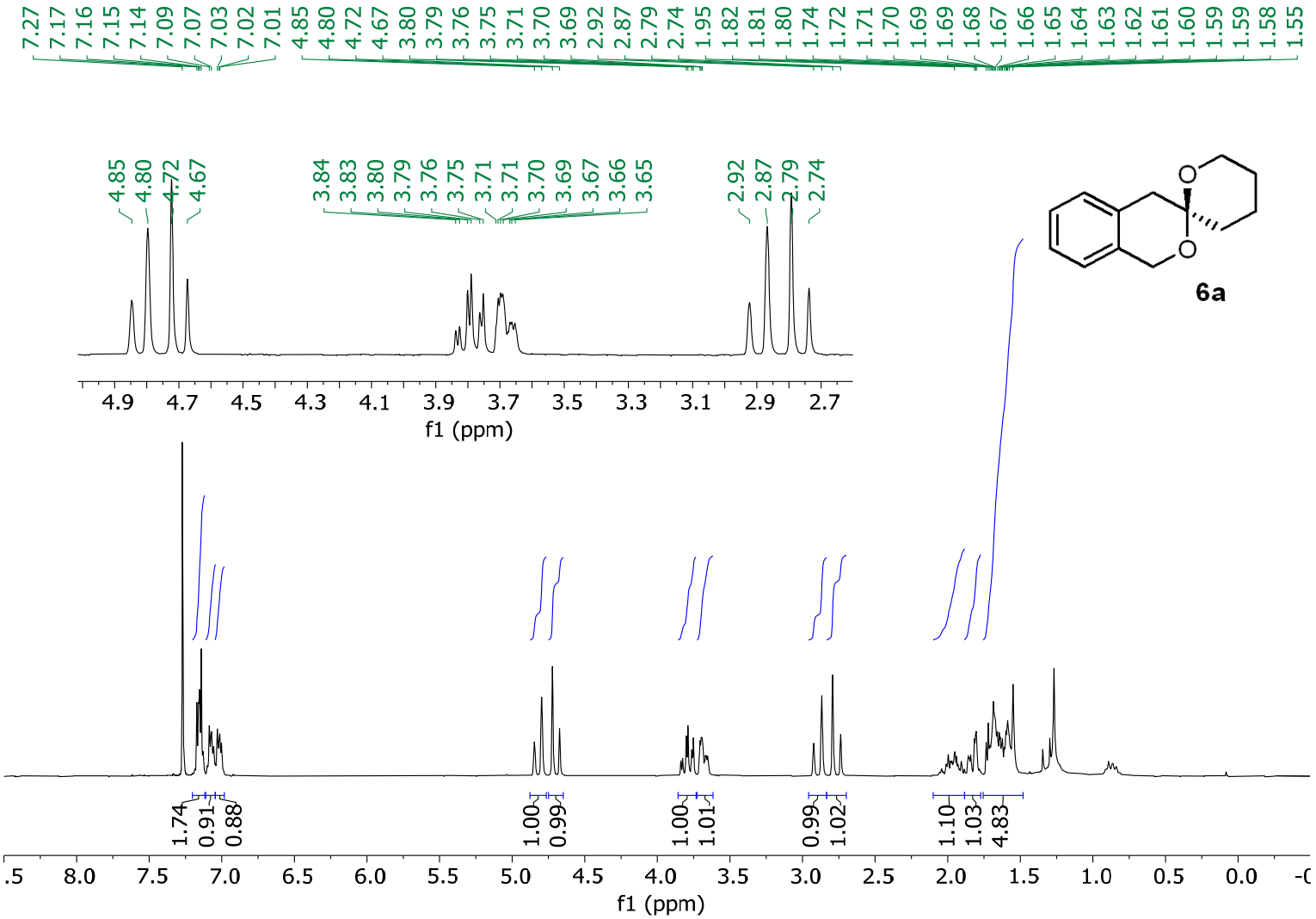
300 MHz ^{1}H-NMR Spectrum compound **4c** ($CDCl_3$, 300 K)



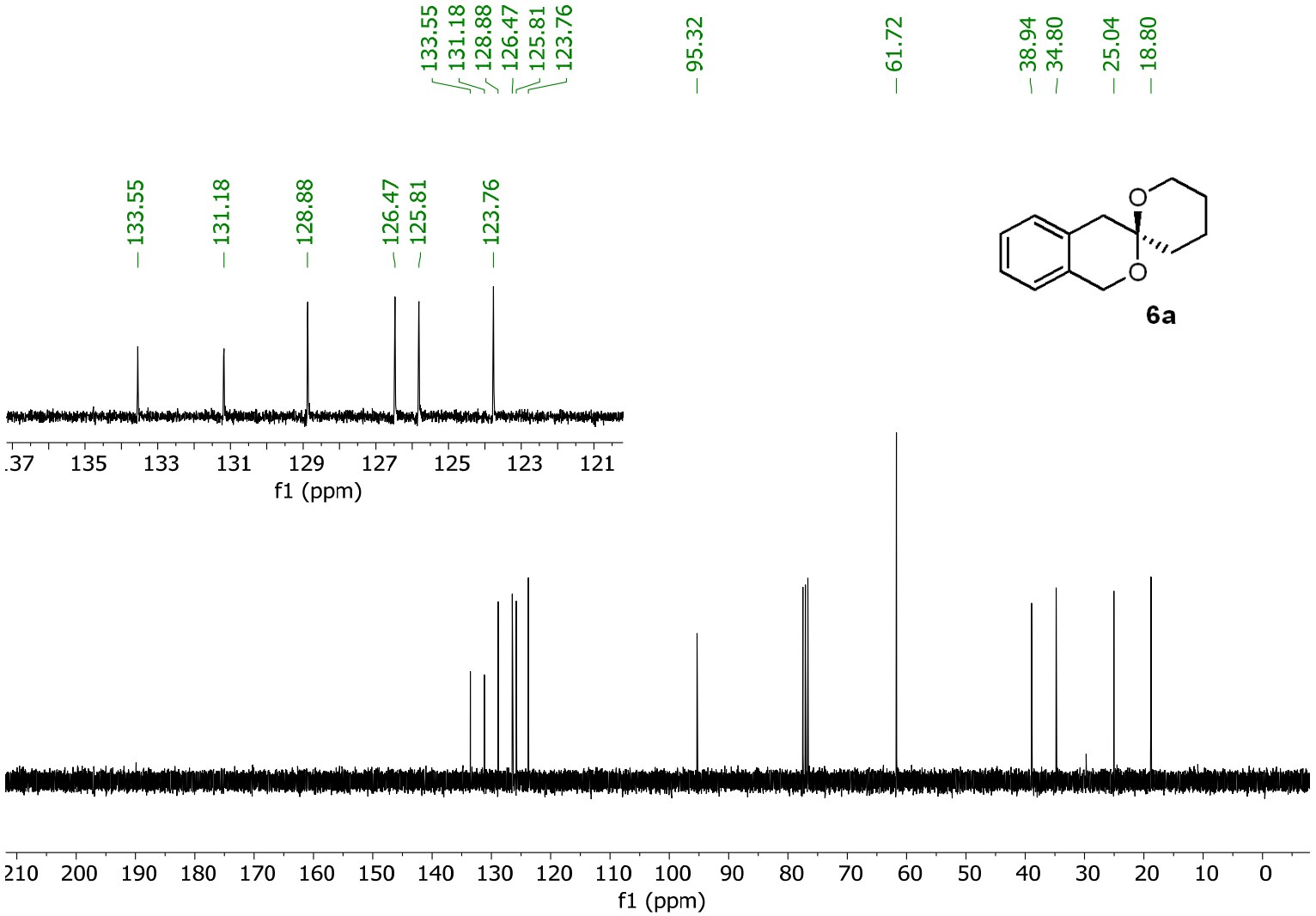
75 MHz ^{13}C-NMR Spectrum of compound **4c** ($CDCl_3$, 300 K)



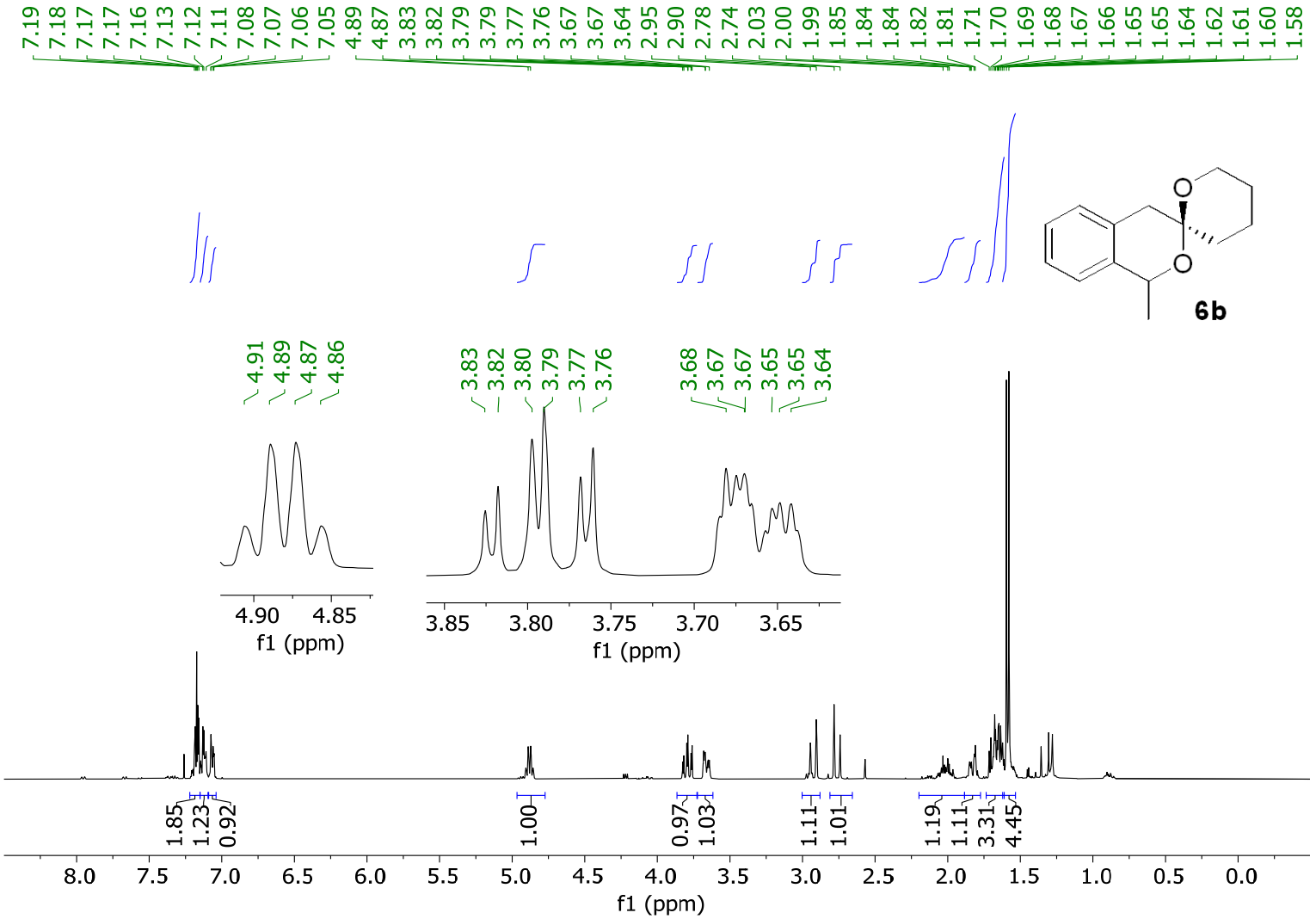
300 MHz ^{1}H-NMR Spectrum compound **6a** ($CDCl_3$, 300 K)



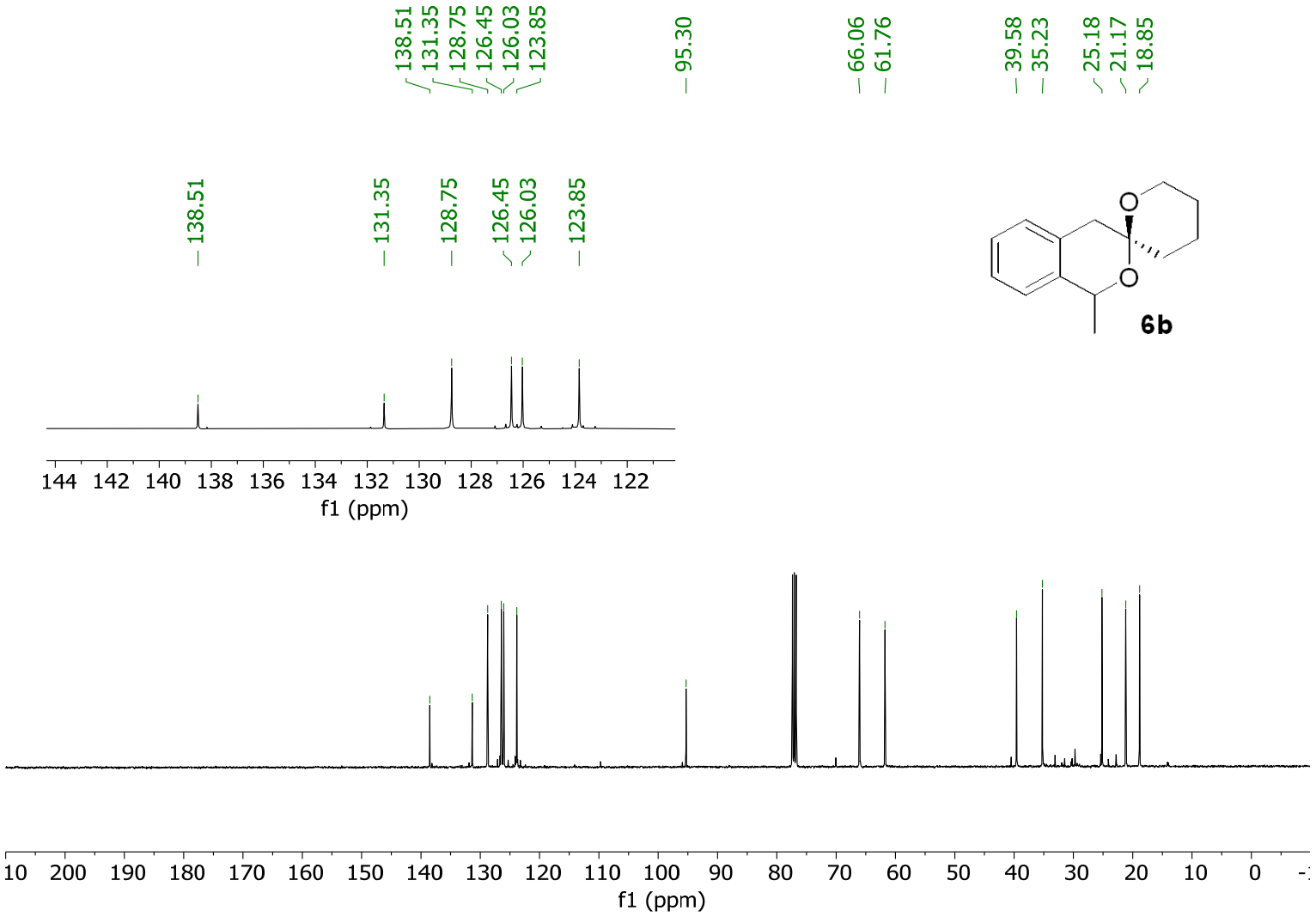
75 MHz ^{13}C-NMR Spectrum of compound **6a** ($CDCl_3$, 300 K)



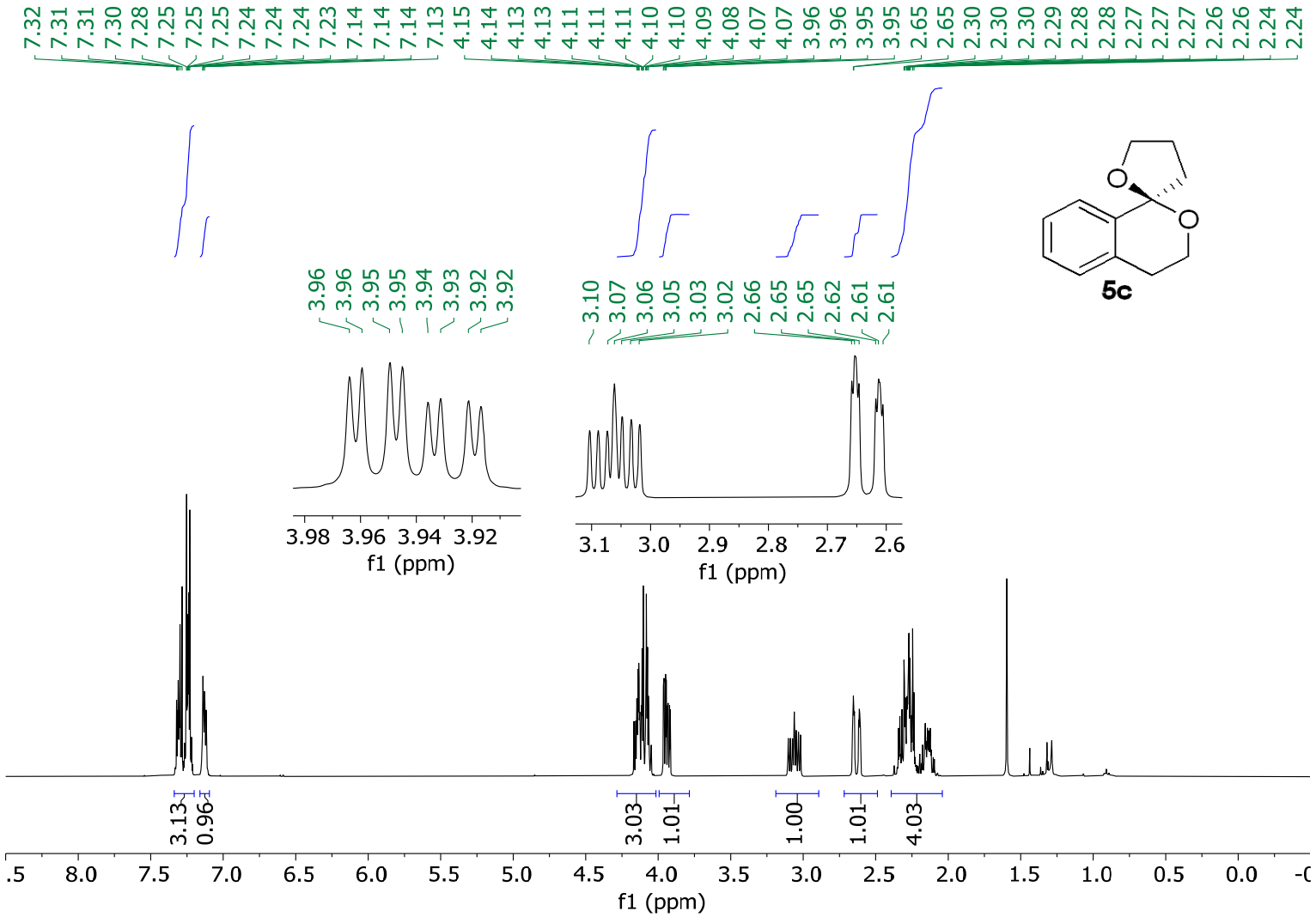
300 MHz ^{1}H-NMR Spectrum compound **6b** ($CDCl_3$, 300 K)



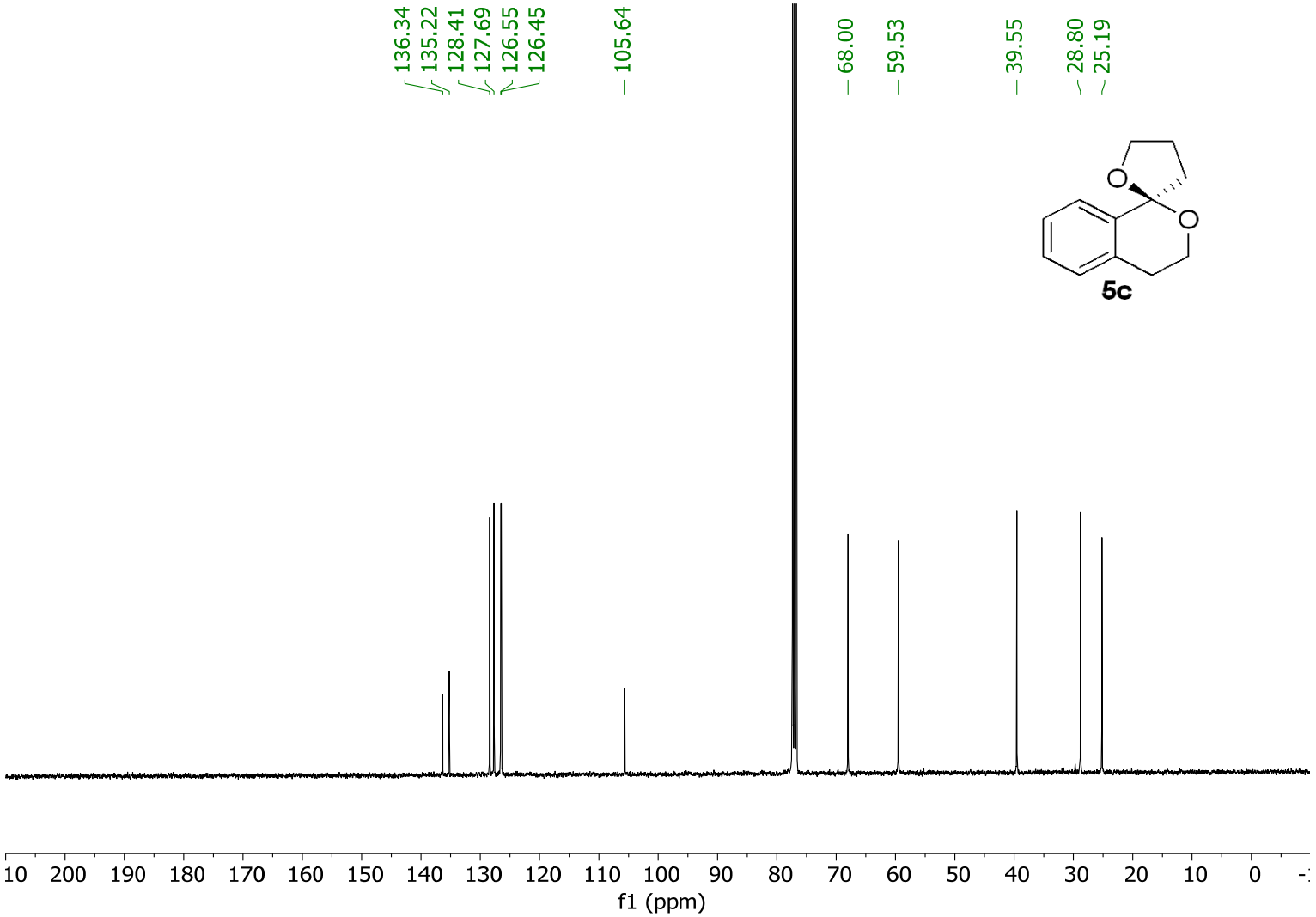
75 MHz ^{13}C-NMR Spectrum of compound **6b** ($CDCl_3$, 300 K)



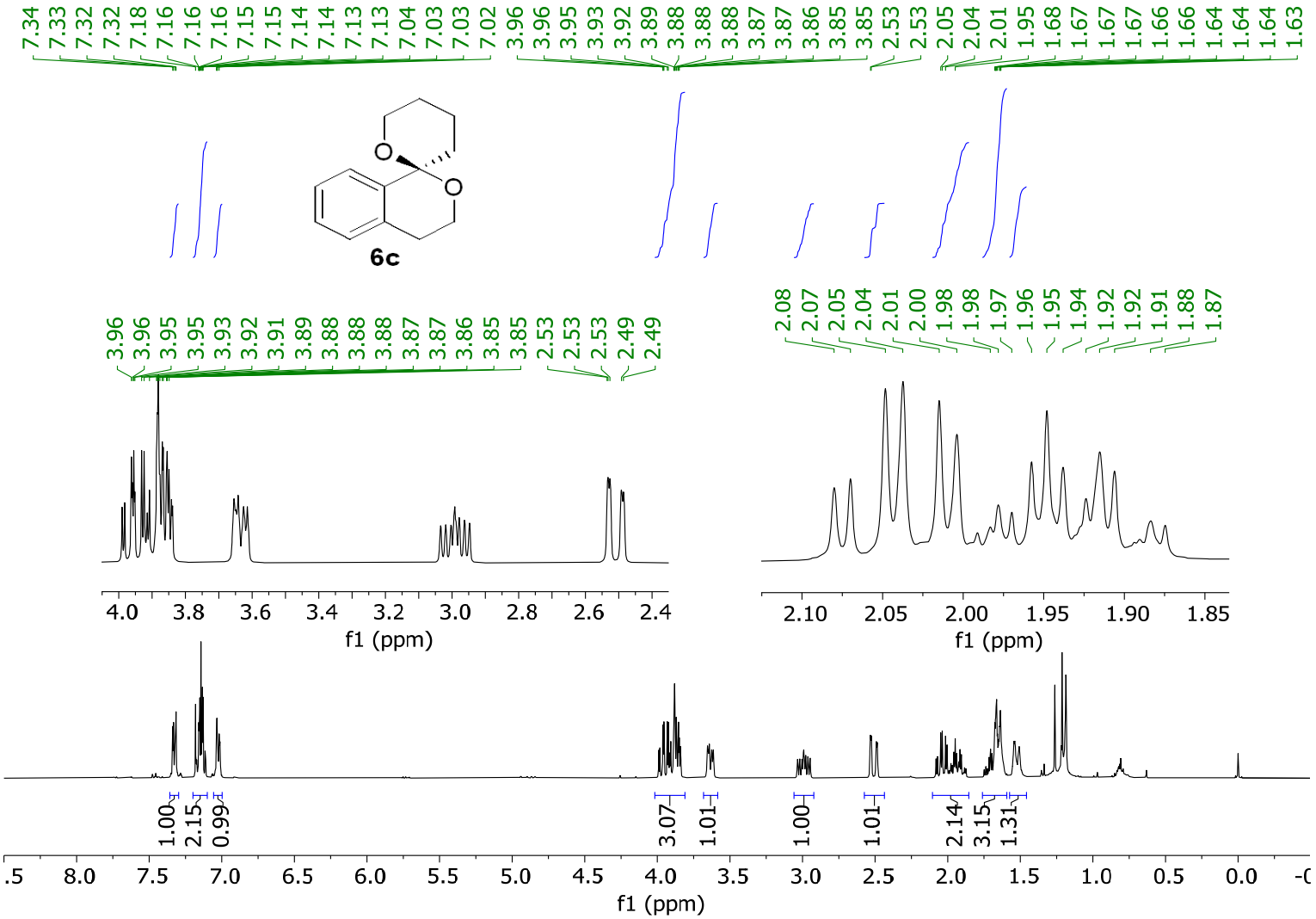
300 MHz ^{1}H-NMR Spectrum compound **5c** ($CDCl_3$, 300 K)



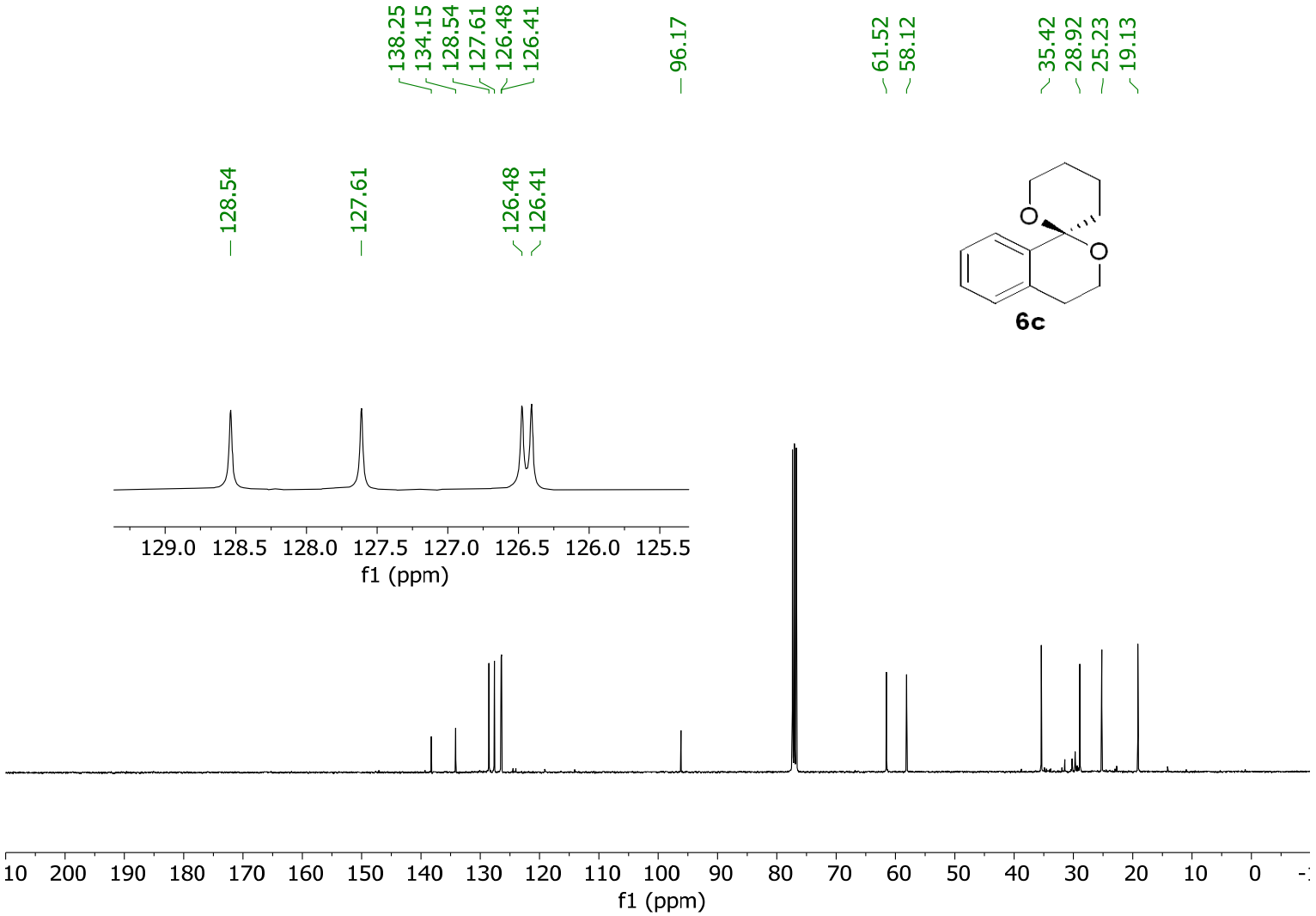
75 MHz ^{13}C-NMR Spectrum of compound **5c** ($CDCl_3$, 300 K)



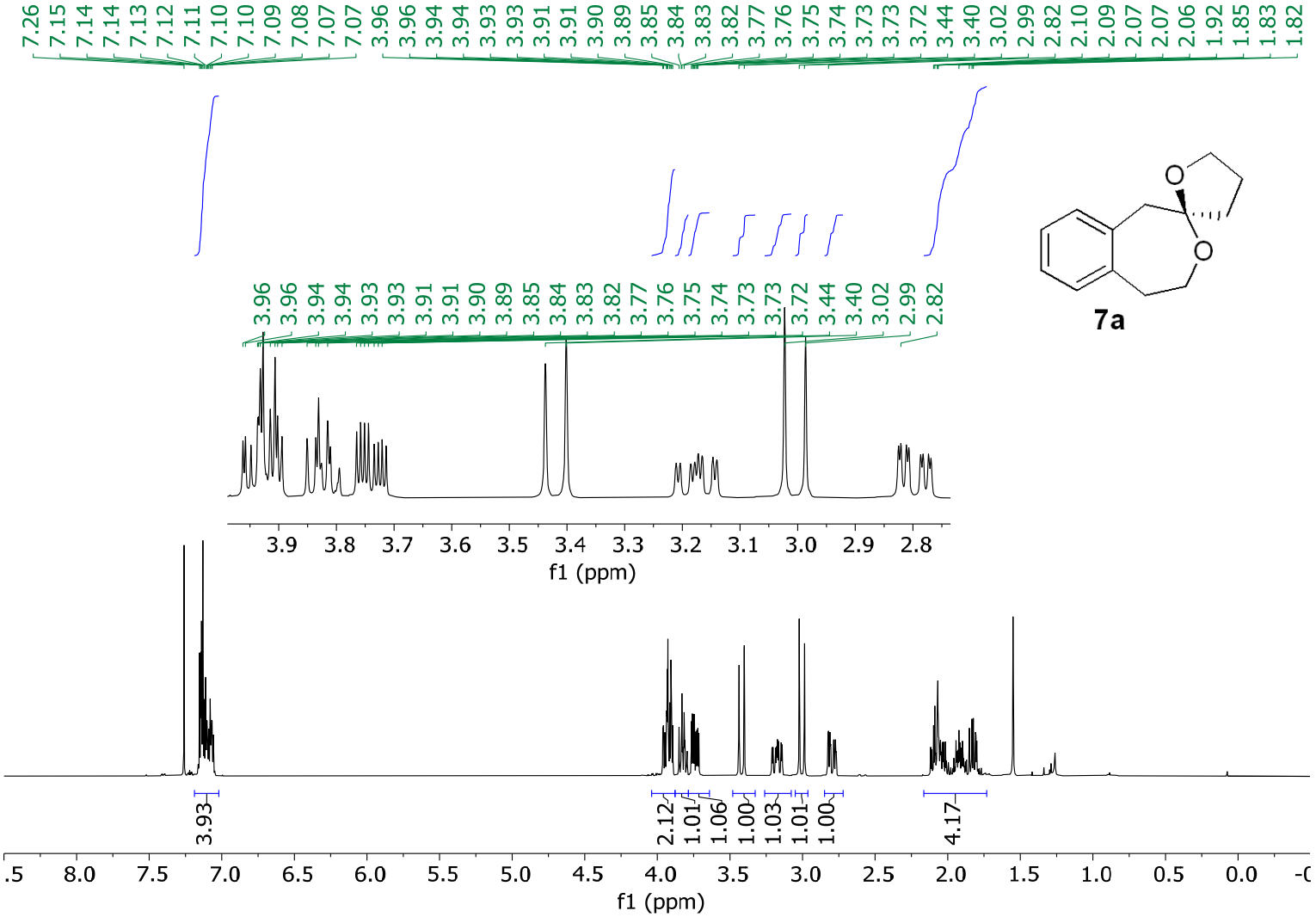
300 MHz ^{1}H-NMR Spectrum compound **6c** ($CDCl_3$, 300 K)



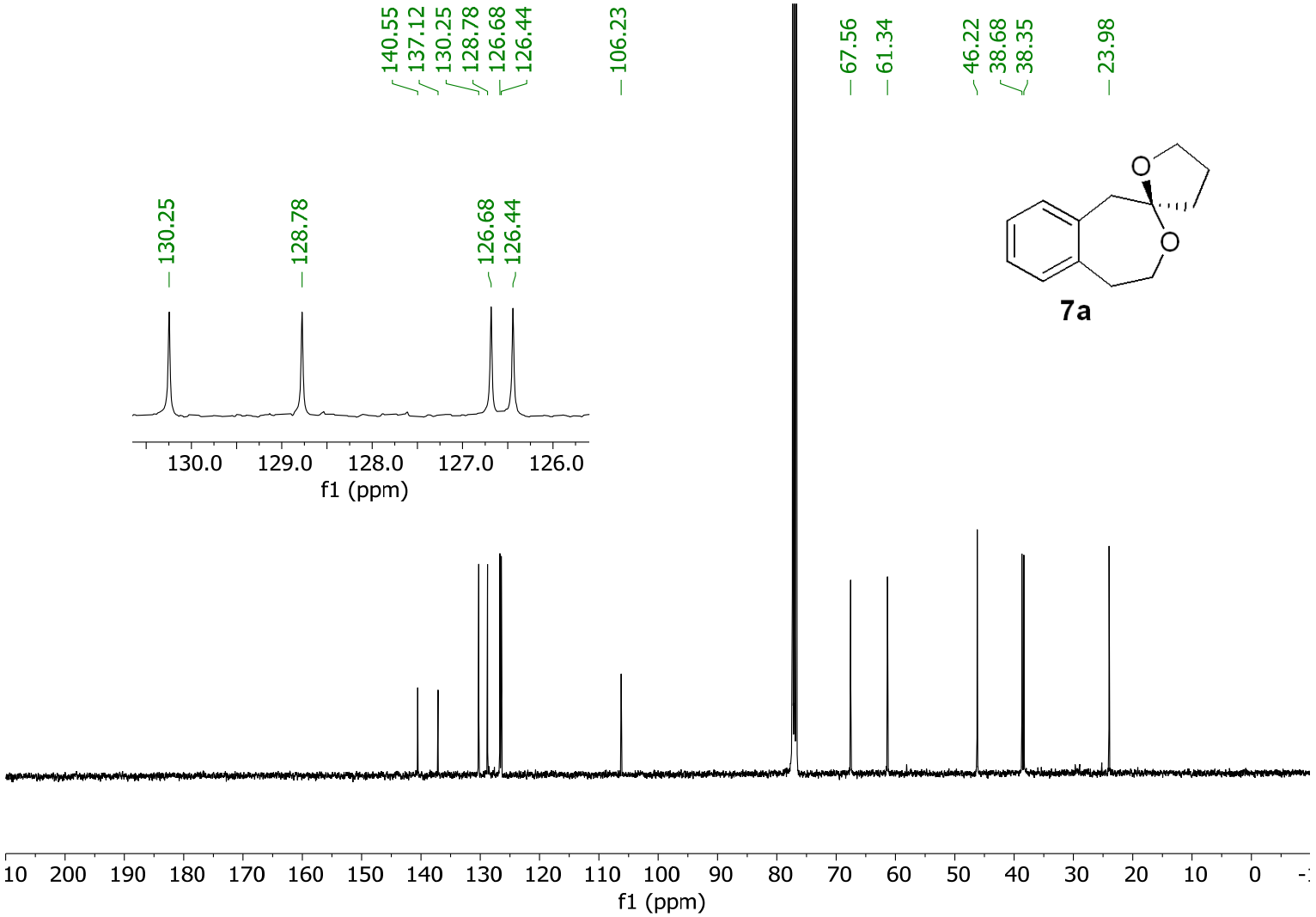
75 MHz ^{13}C-NMR Spectrum of compound **6c** ($CDCl_3$, 300 K)



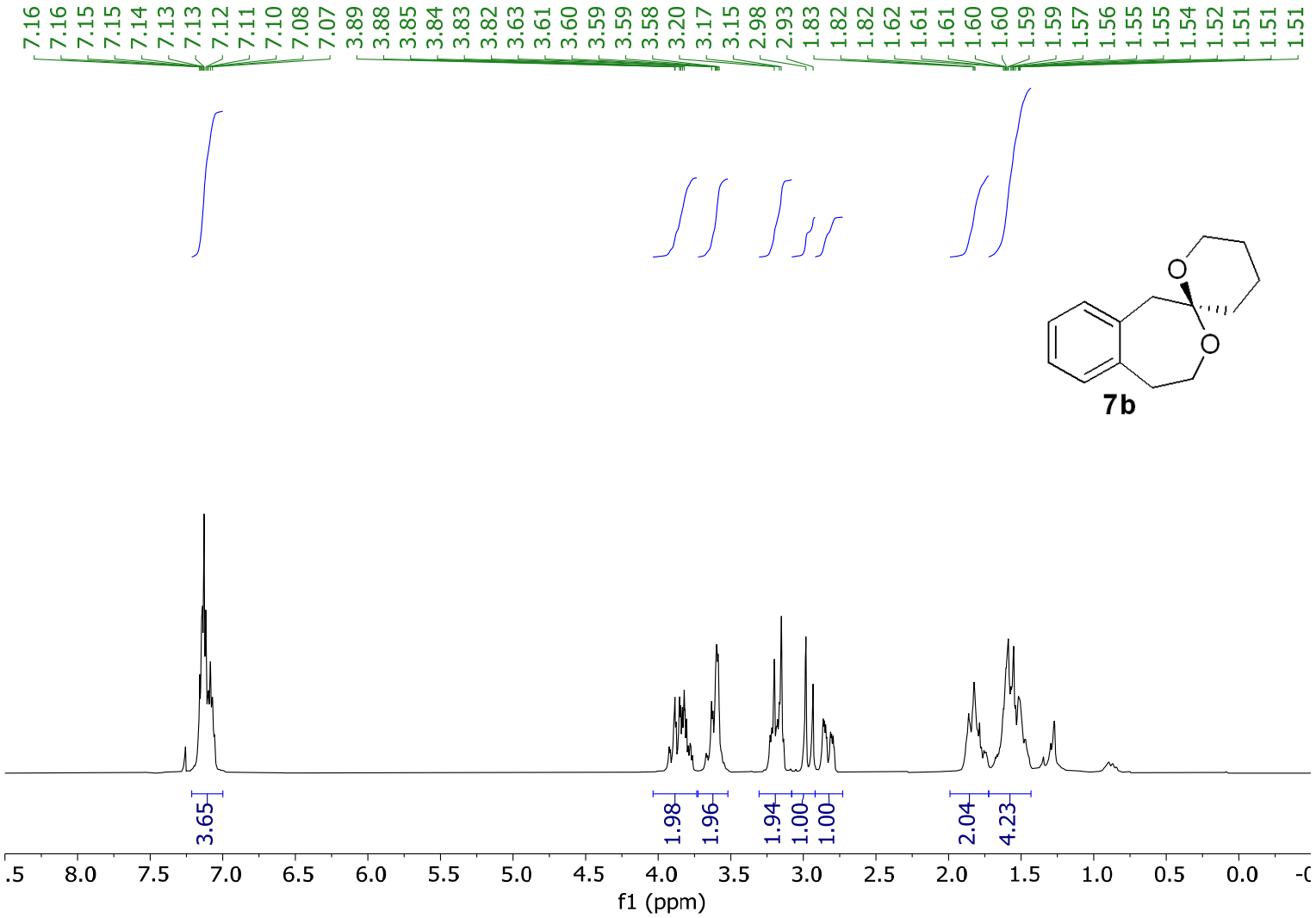
300 MHz ^{1}H-NMR Spectrum compound **7a** ($CDCl_3$, 300 K)



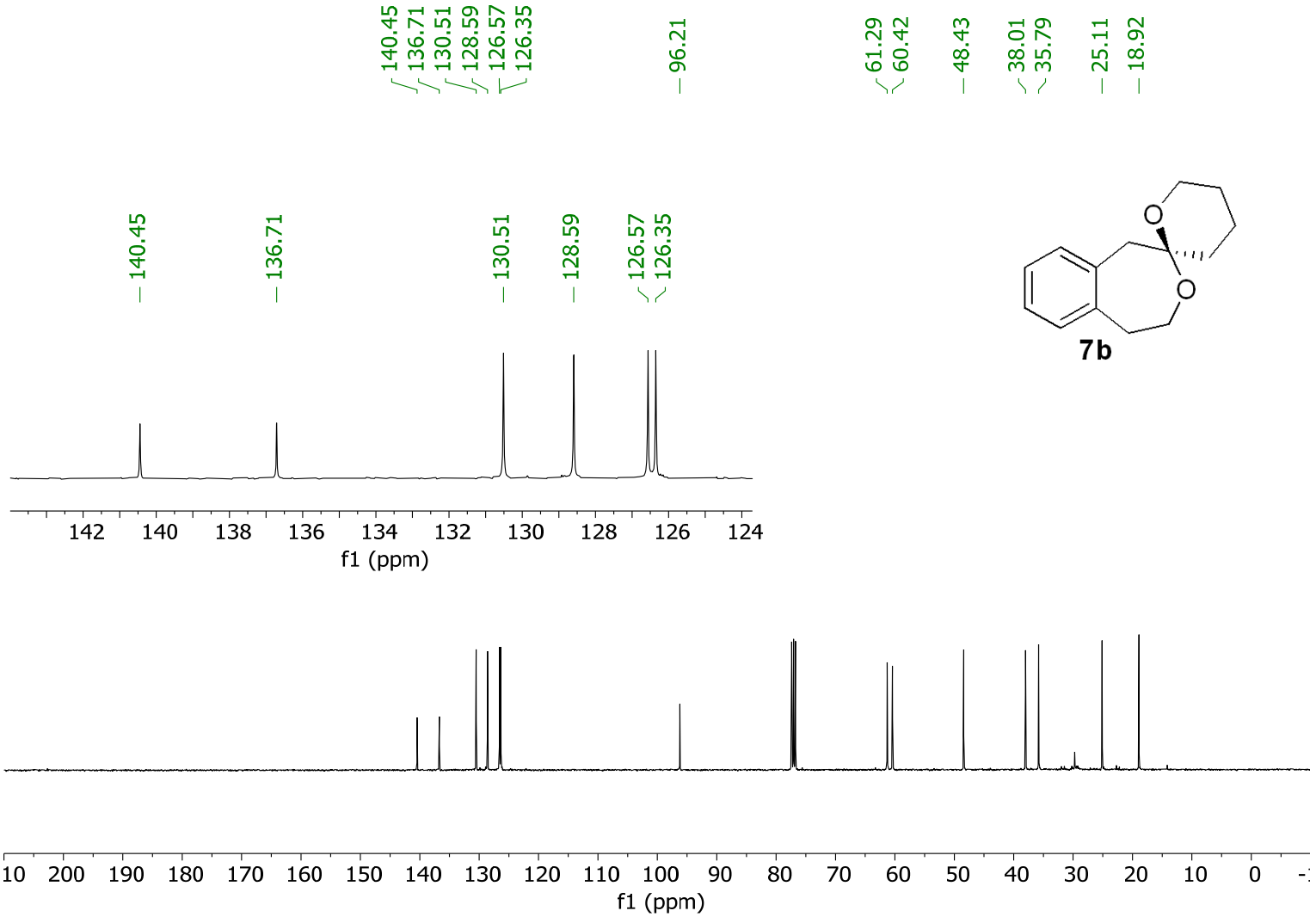
75 MHz ^{13}C-NMR Spectrum of compound **7a** ($CDCl_3$, 300 K)



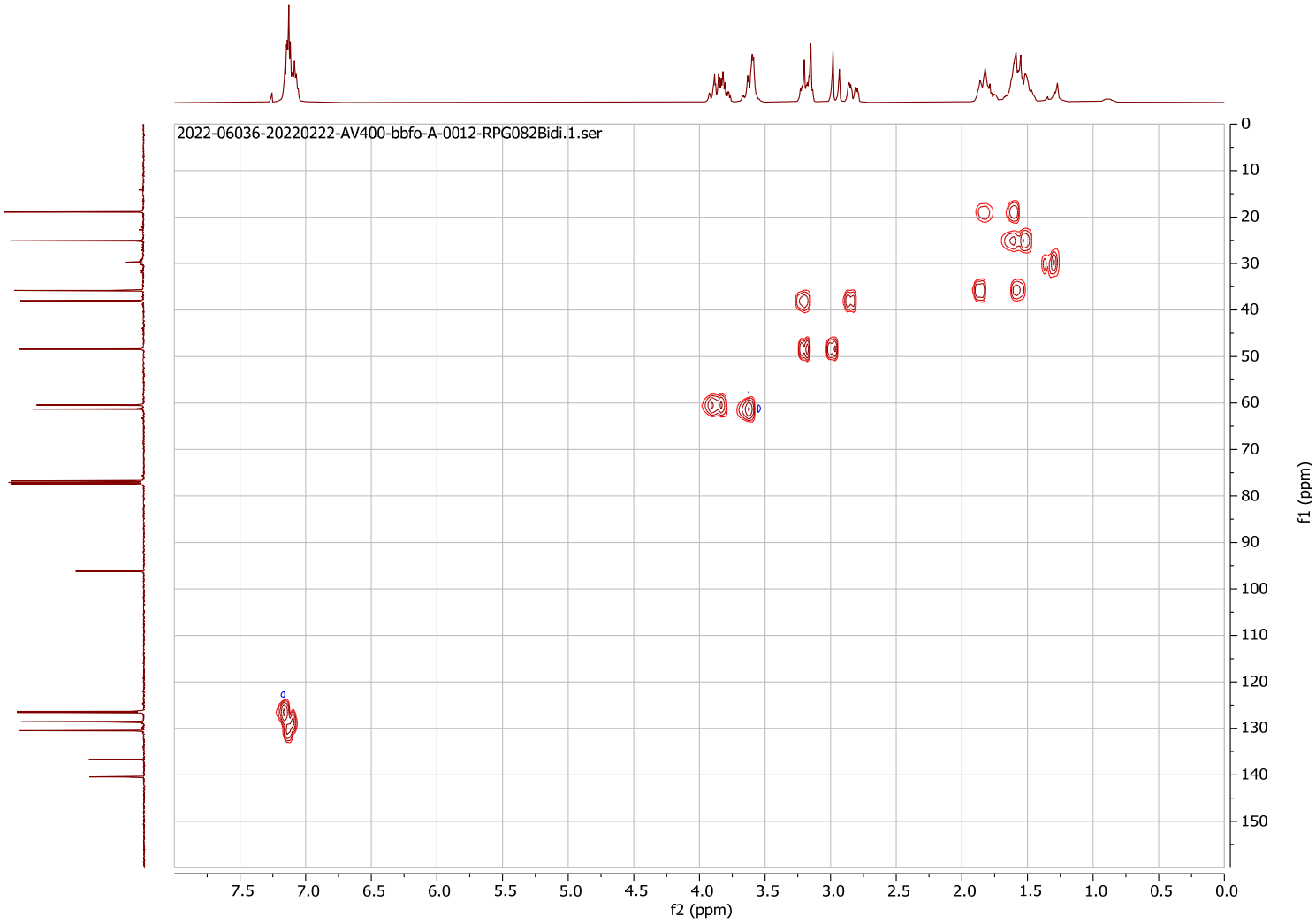
300 MHz ^{1}H-NMR Spectrum compound **7b** ($CDCl_3$, 300 K)



75 MHz ^{13}C-NMR Spectrum of compound **7b** ($CDCl_3$, 300 K)

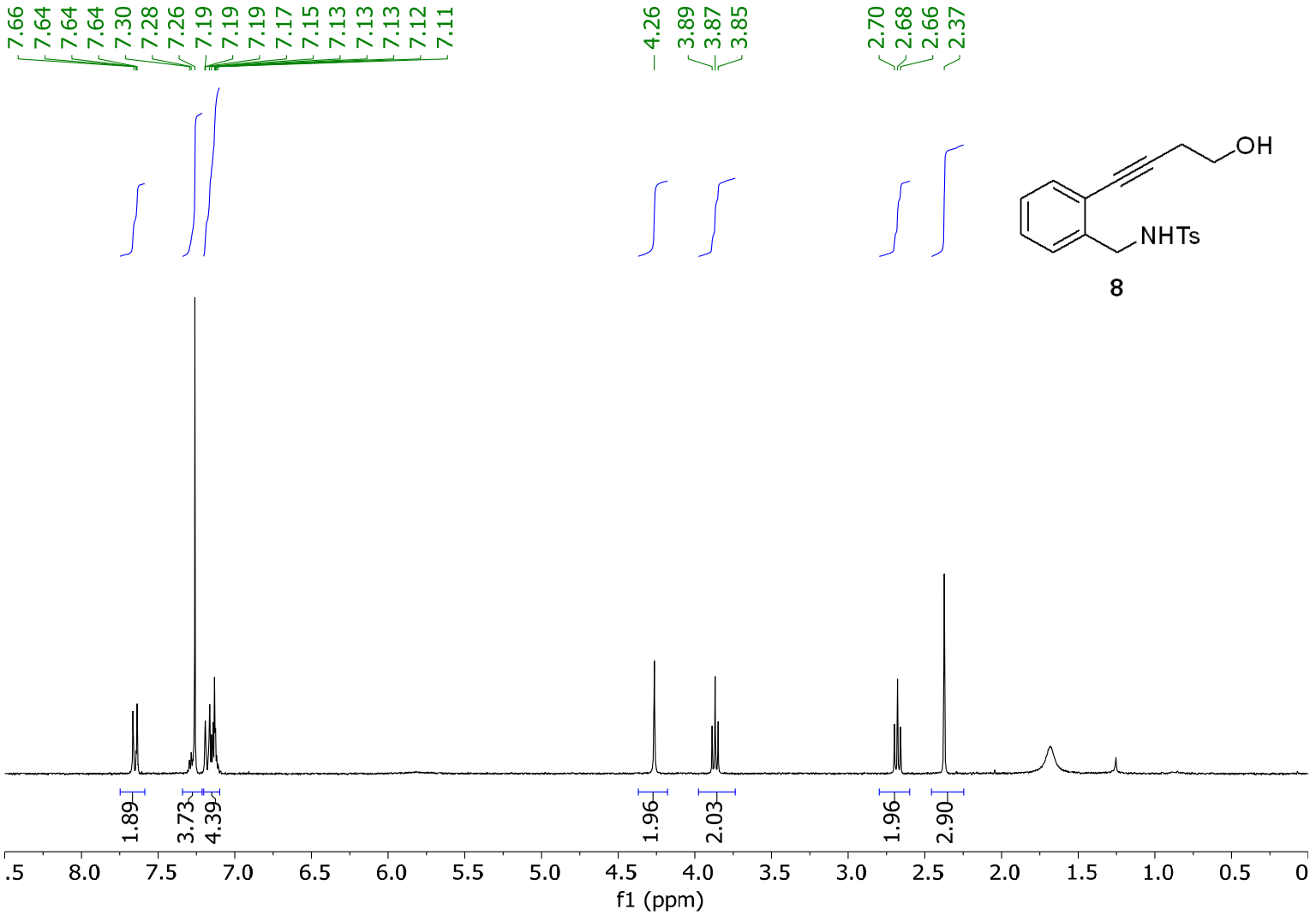


HSQC Spectrum of compound **7b** ($CDCl_3$, 300 K)

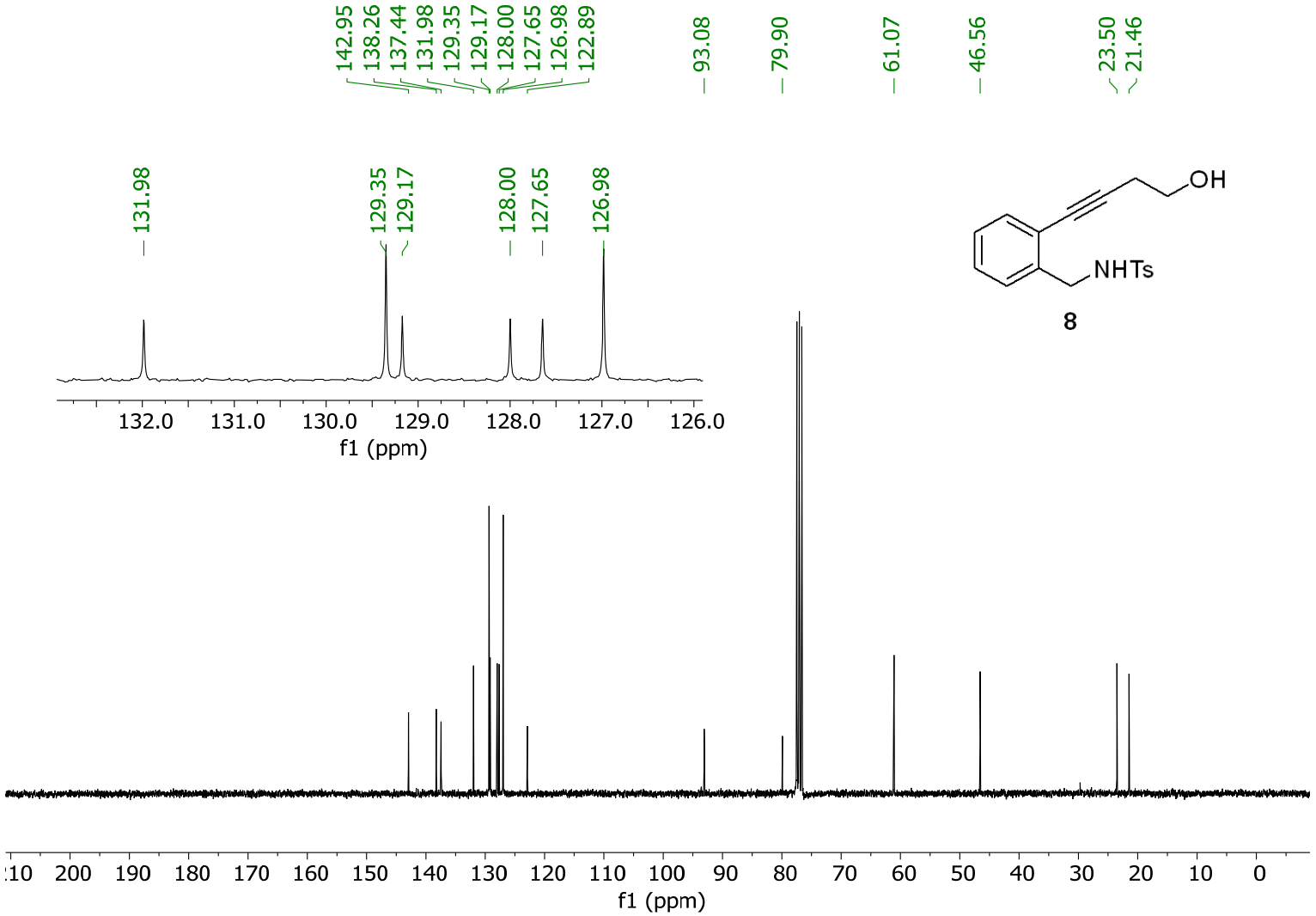


HMBC Spectrum of compound **7b** ($CDCl_3$, 300 K)

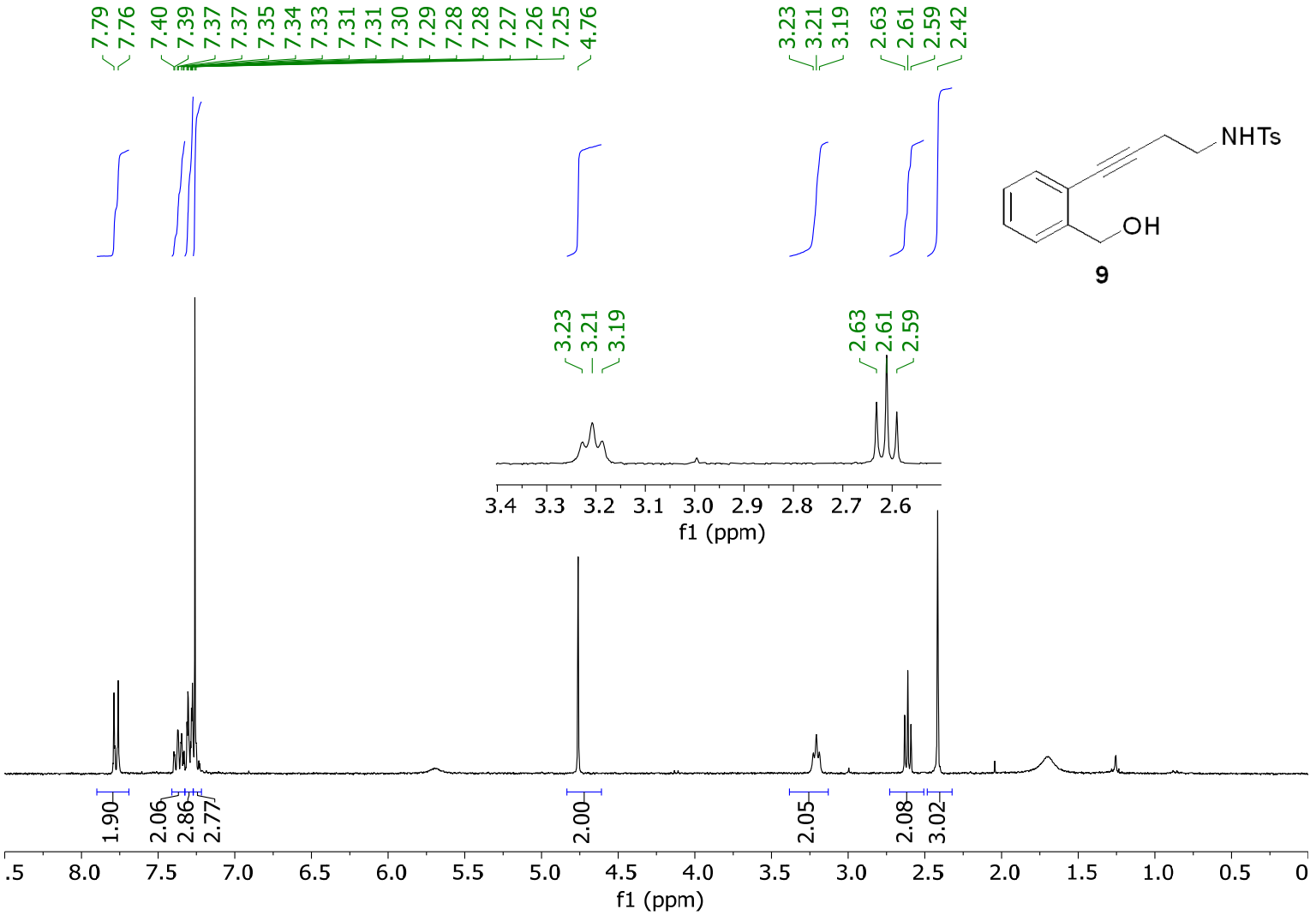
300 MHz ^{1}H-NMR Spectrum compound **8** ($CDCl_3$, 300 K)



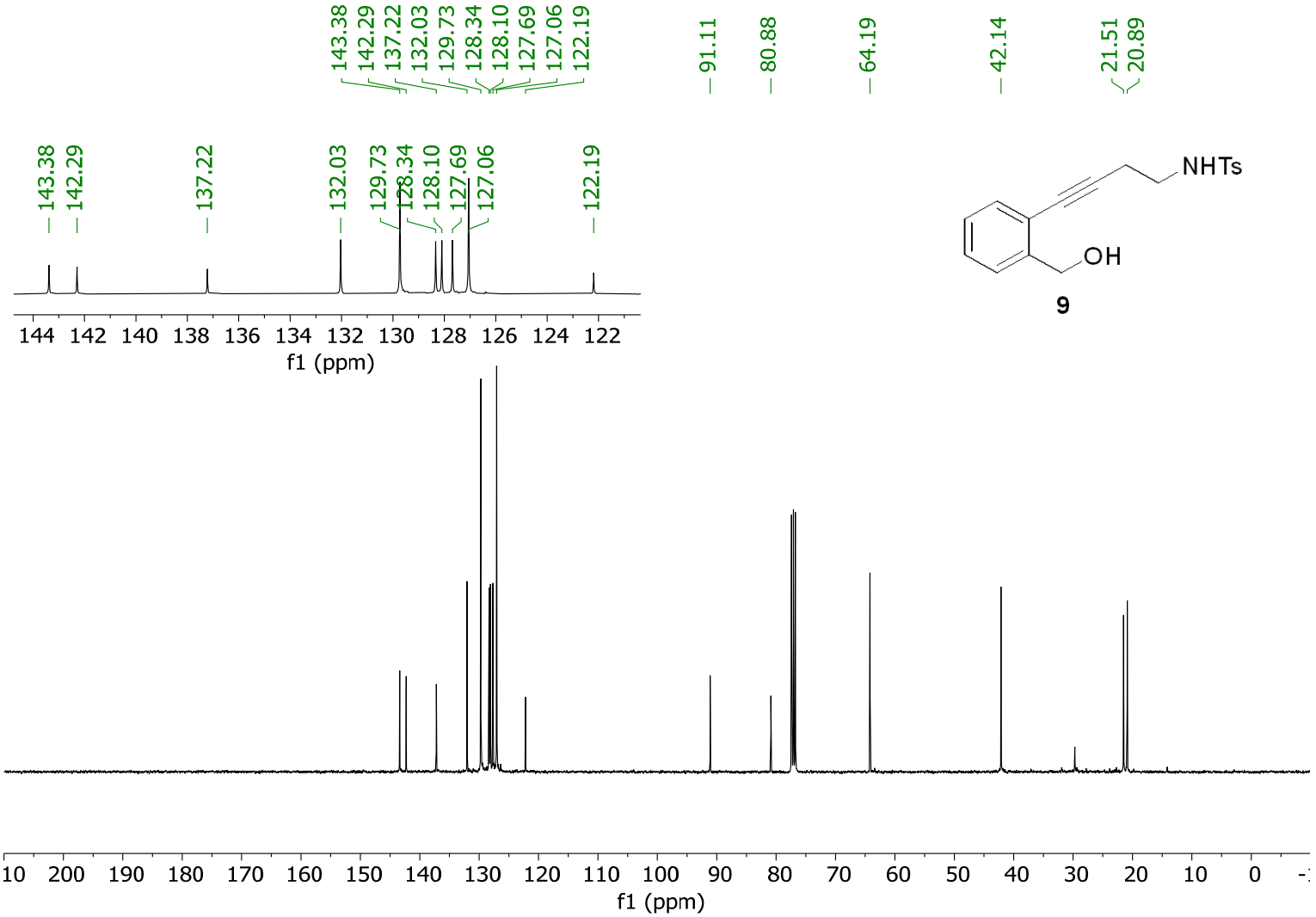
75 MHz ^{13}C-NMR Spectrum of compound **8** ($CDCl_3$, 300 K)



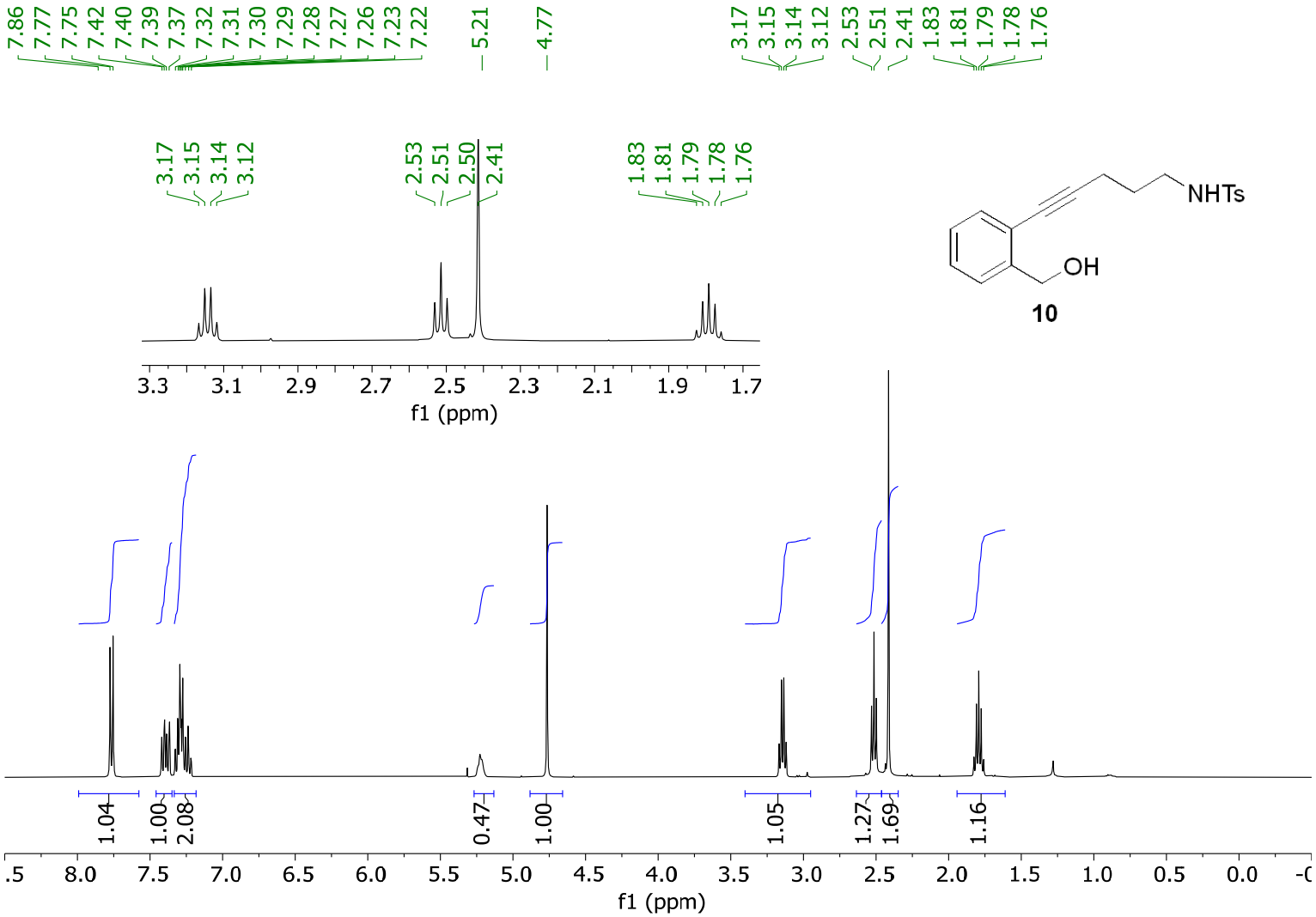
300 MHz ^{1}H-NMR Spectrum compound **9** ($CDCl_3$, 300 K)



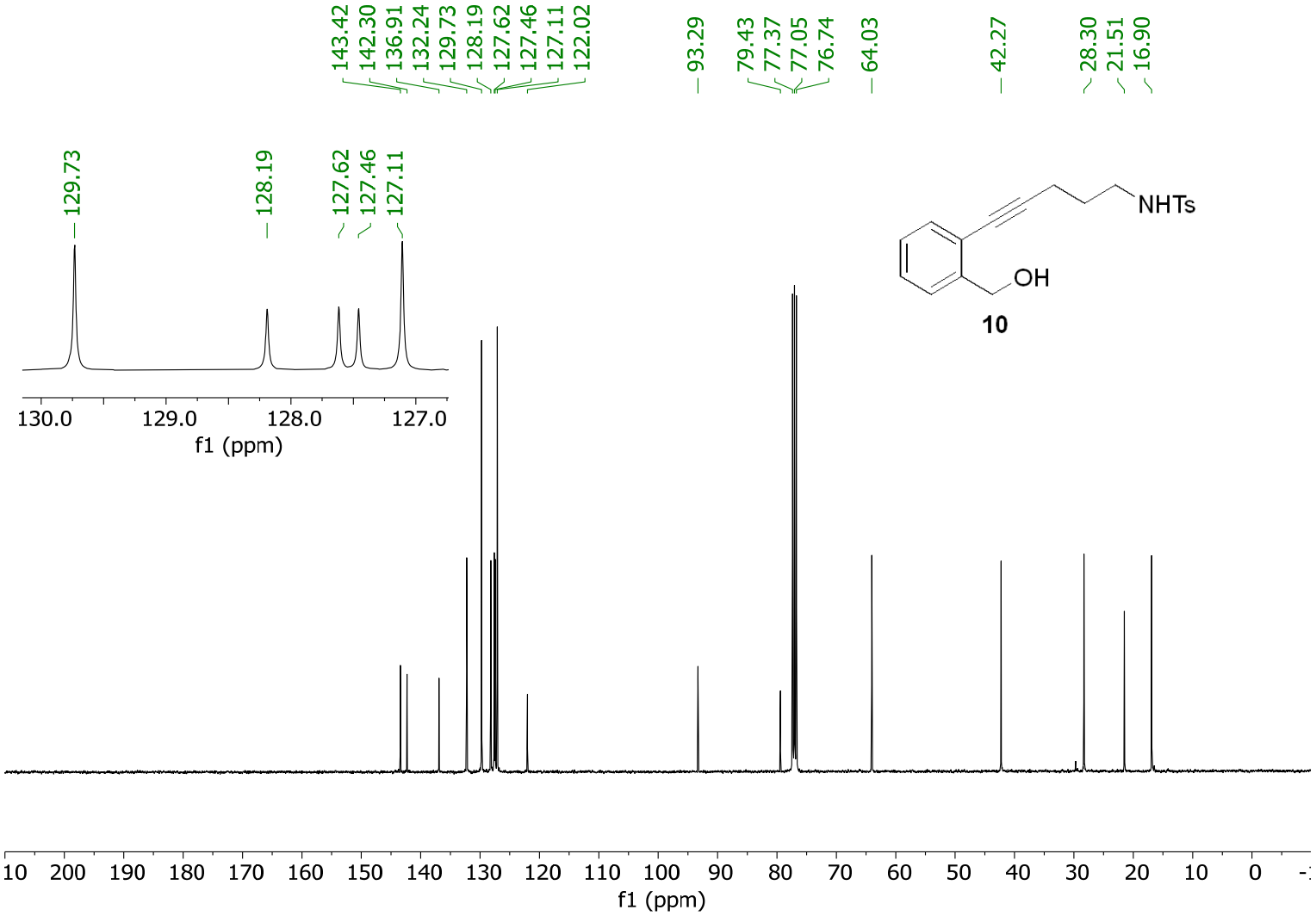
75 MHz ^{13}C-NMR Spectrum of compound **9** ($CDCl_3$, 300 K)



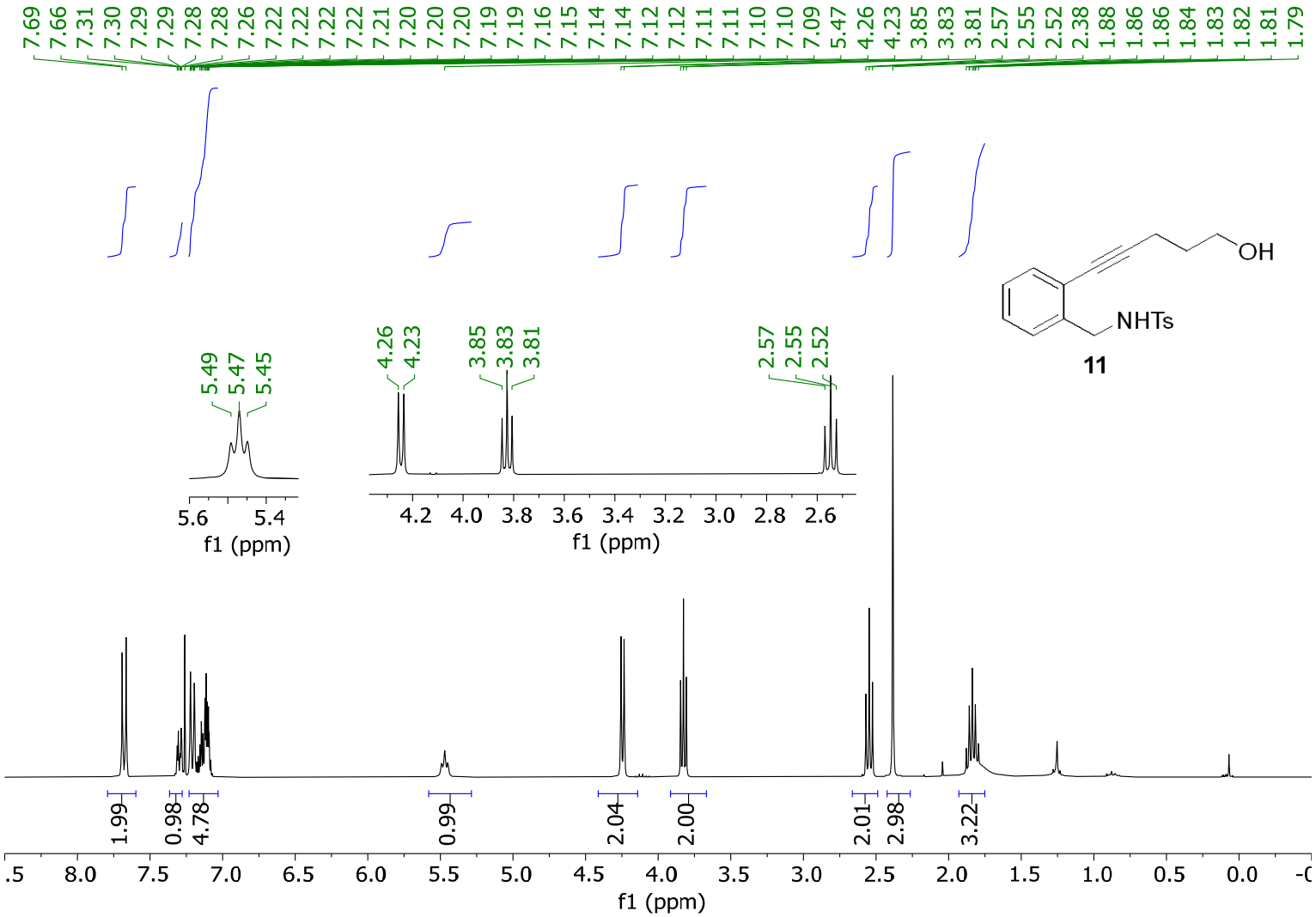
300 MHz ^{1}H-NMR Spectrum compound **10** ($CDCl_3$, 300 K)



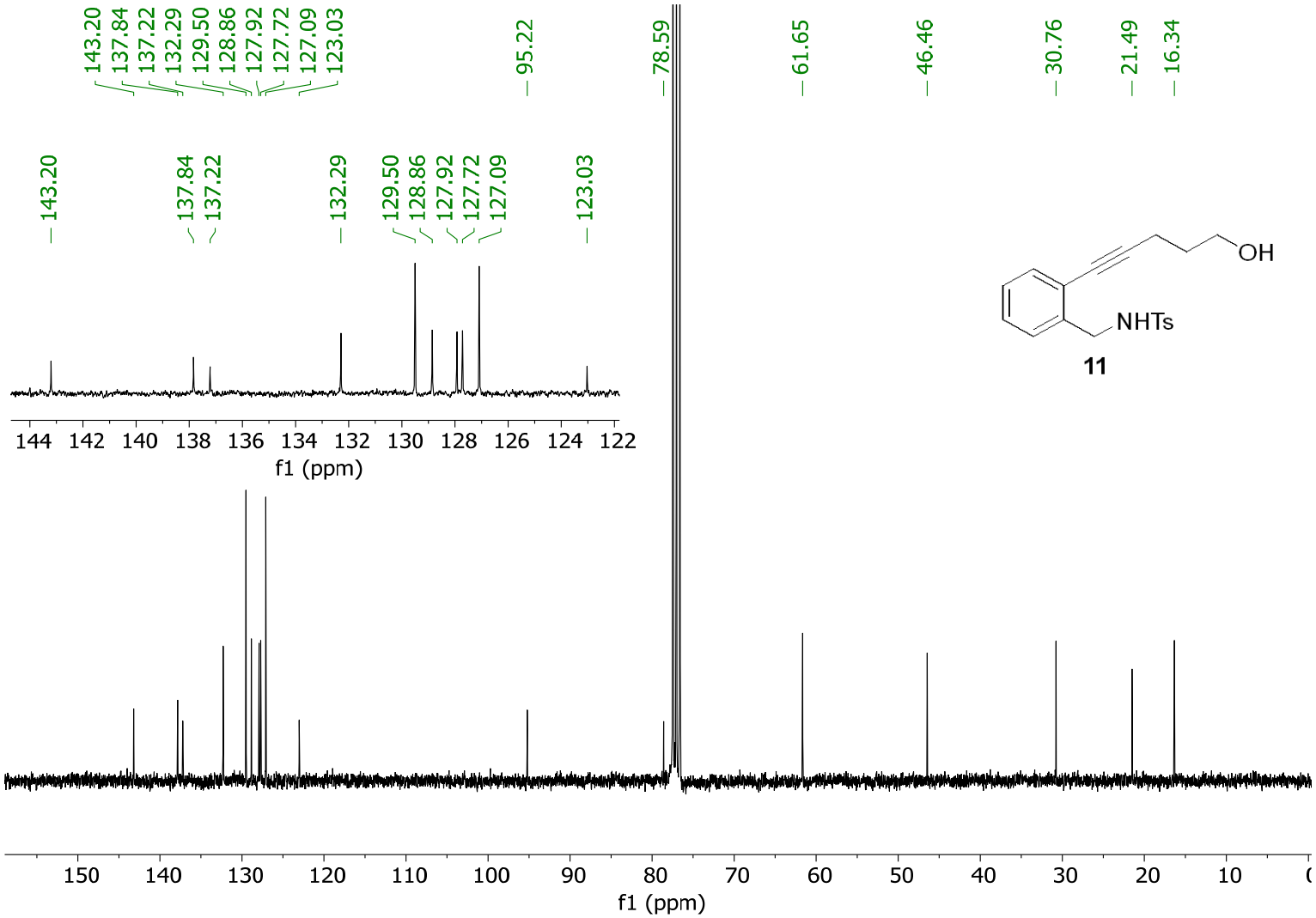
75 MHz ^{13}C-NMR Spectrum of compound **10**($CDCl_3$, 300 K)



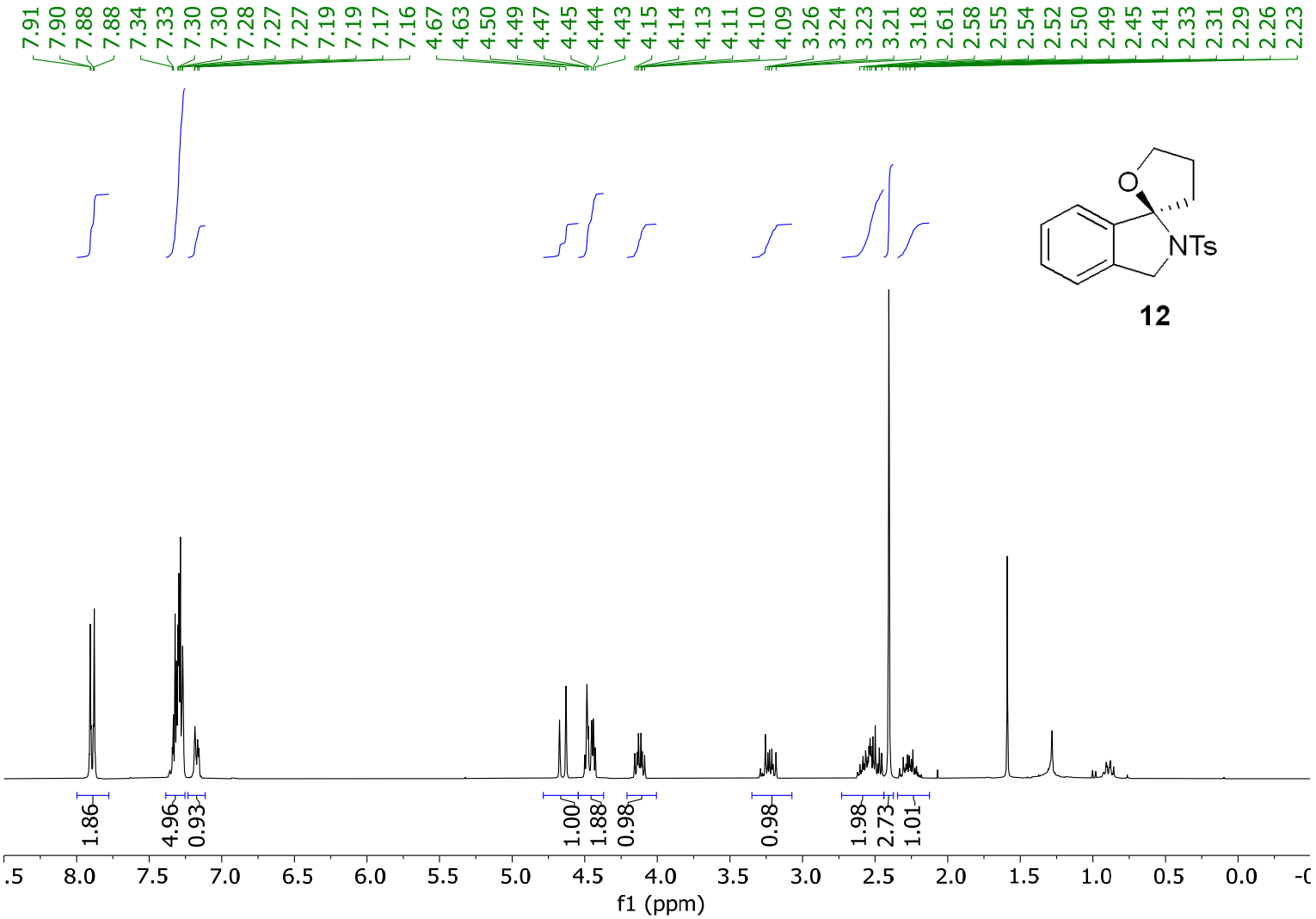
300 MHz ^{1}H-NMR Spectrum compound **11** ($CDCl_3$, 300 K)



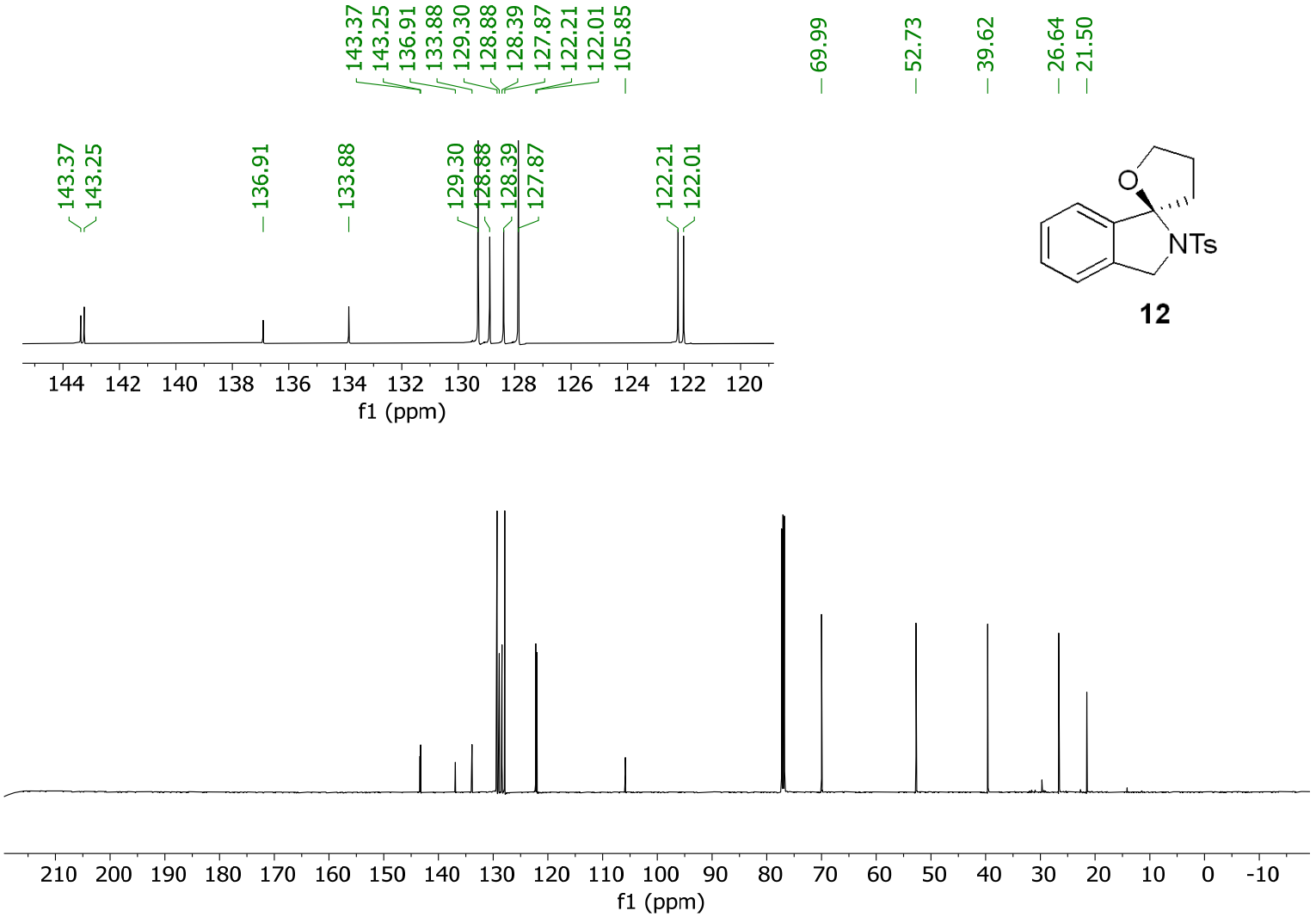
75 MHz ^{13}C-NMR Spectrum of compound **11** ($CDCl_3$, 300 K)



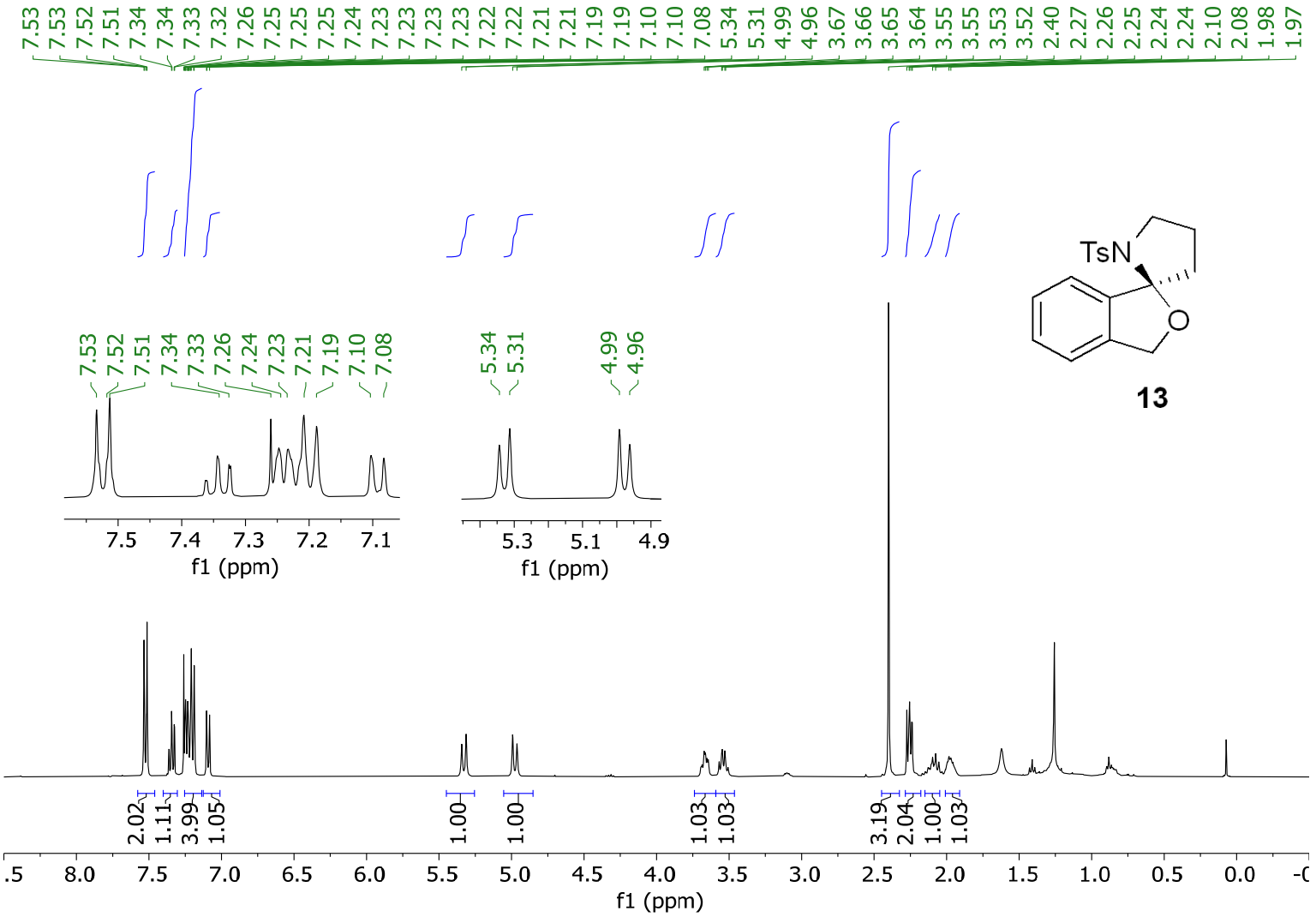
300 MHz ^{1}H-NMR Spectrum compound **12** ($CDCl_3$, 300 K)



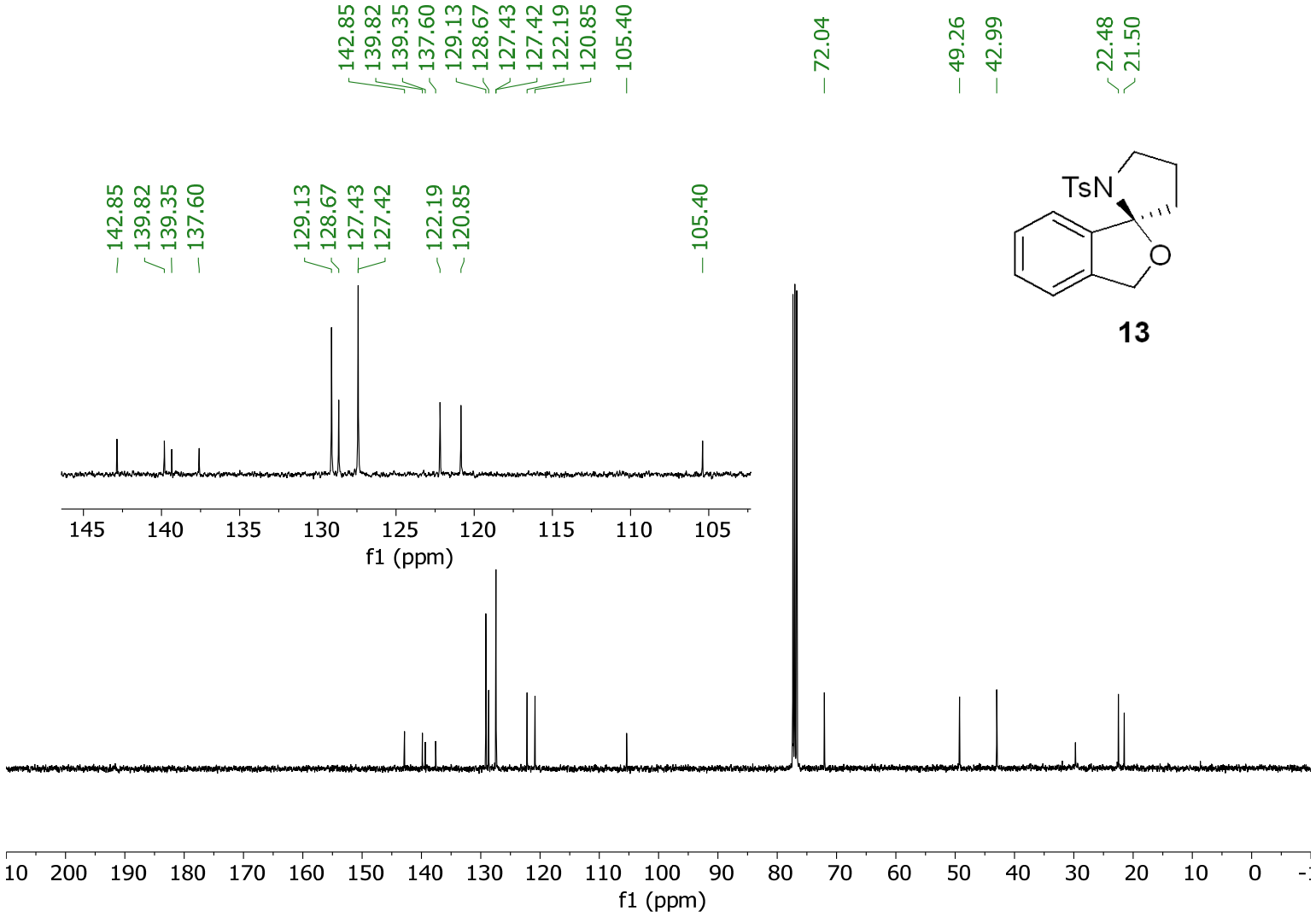
75 MHz ^{13}C-NMR Spectrum of compound **12** ($CDCl_3$, 300 K)



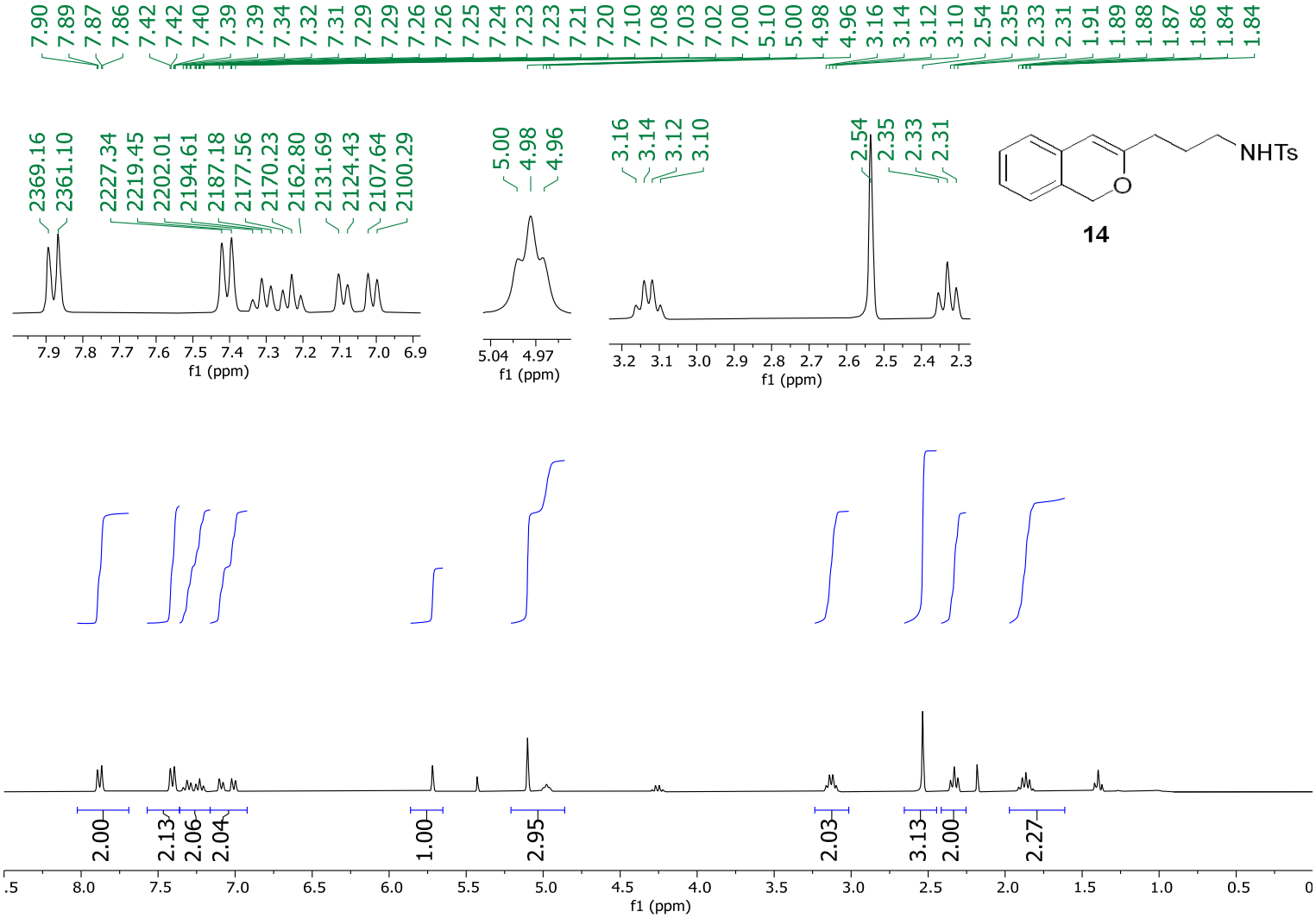
300 MHz ^{1}H-NMR Spectrum compound **13** ($CDCl_3$, 300 K)



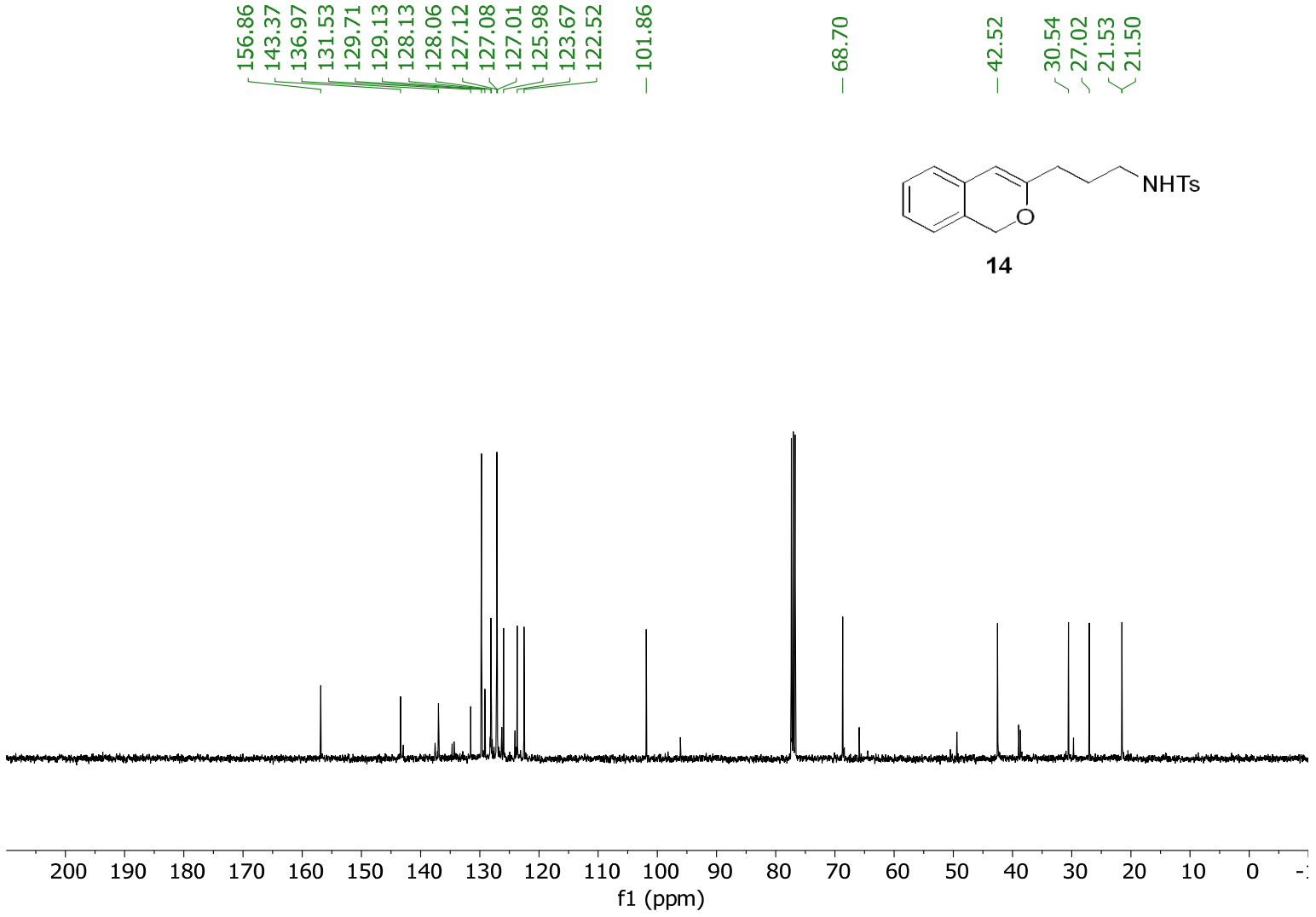
75 MHz ^{13}C-NMR Spectrum of compound **13** ($CDCl_3$, 300 K)



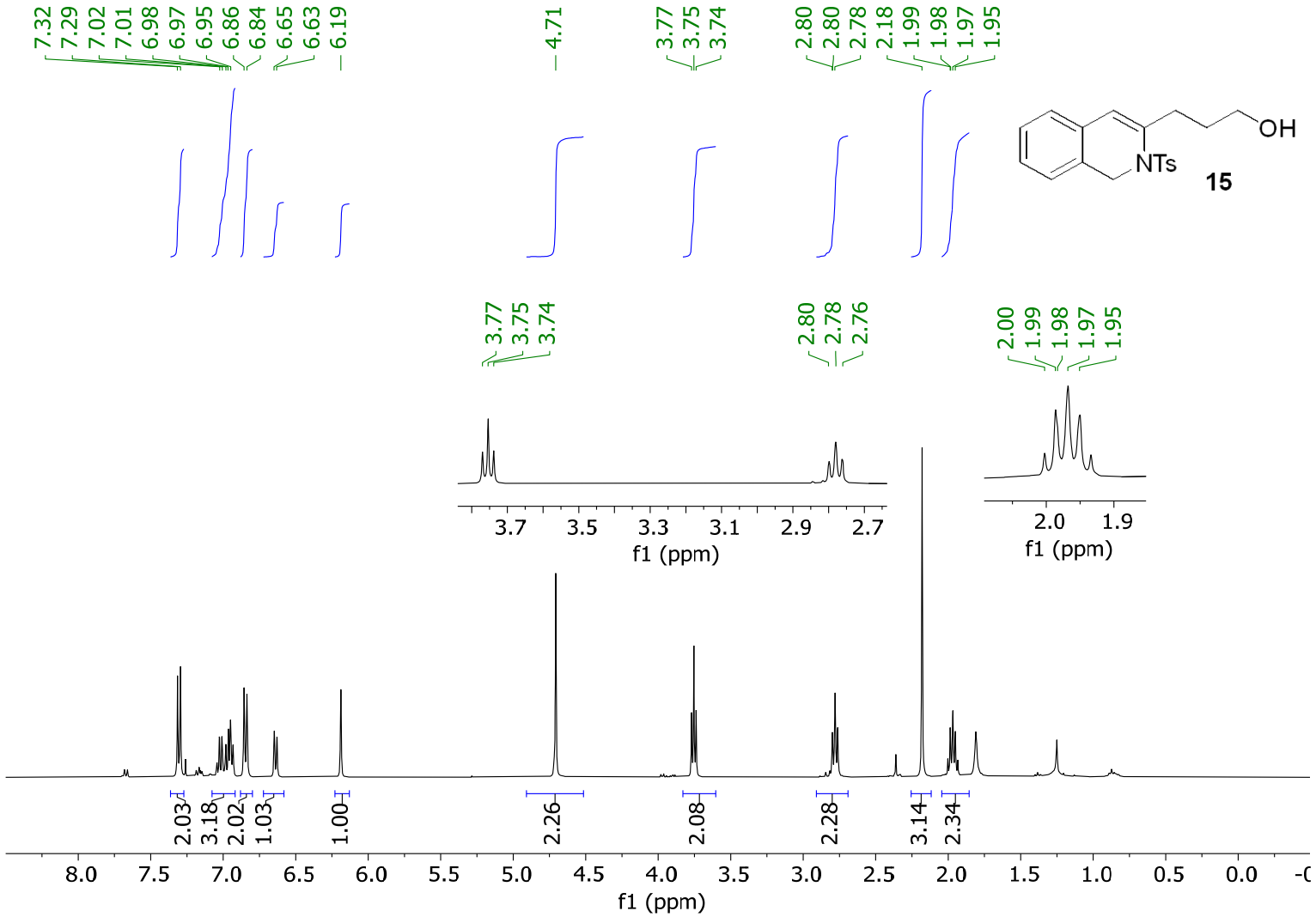
300 MHz ^{1}H-NMR Spectrum of compound **14** ($CDCl_3$, 300 K)



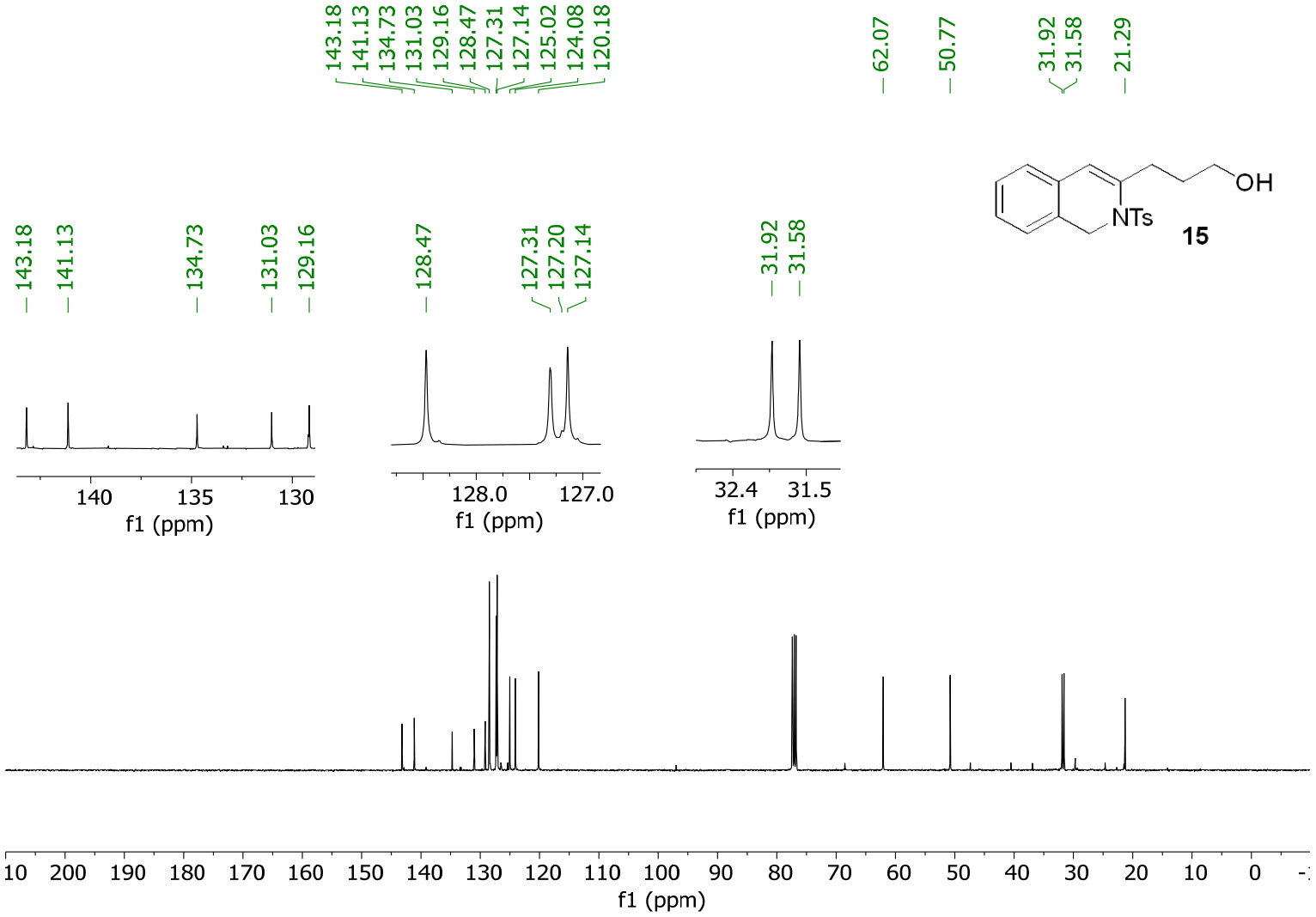
75 MHz ^{13}C-NMR Spectrum of compound **14** ($CDCl_3$, 300 K)



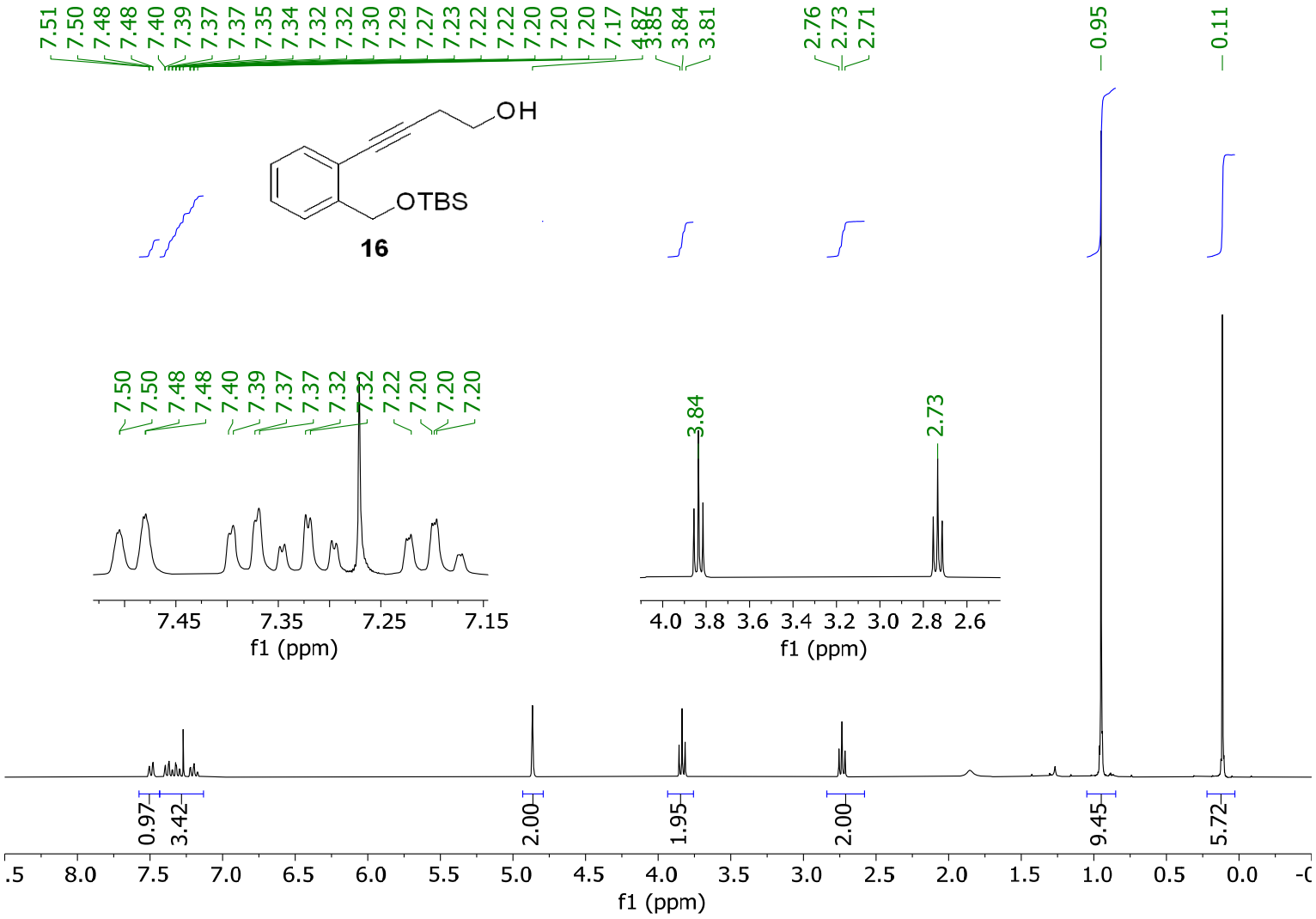
300 MHz ^{1}H-NMR Spectrum compound **15** ($CDCl_3$, 300 K)



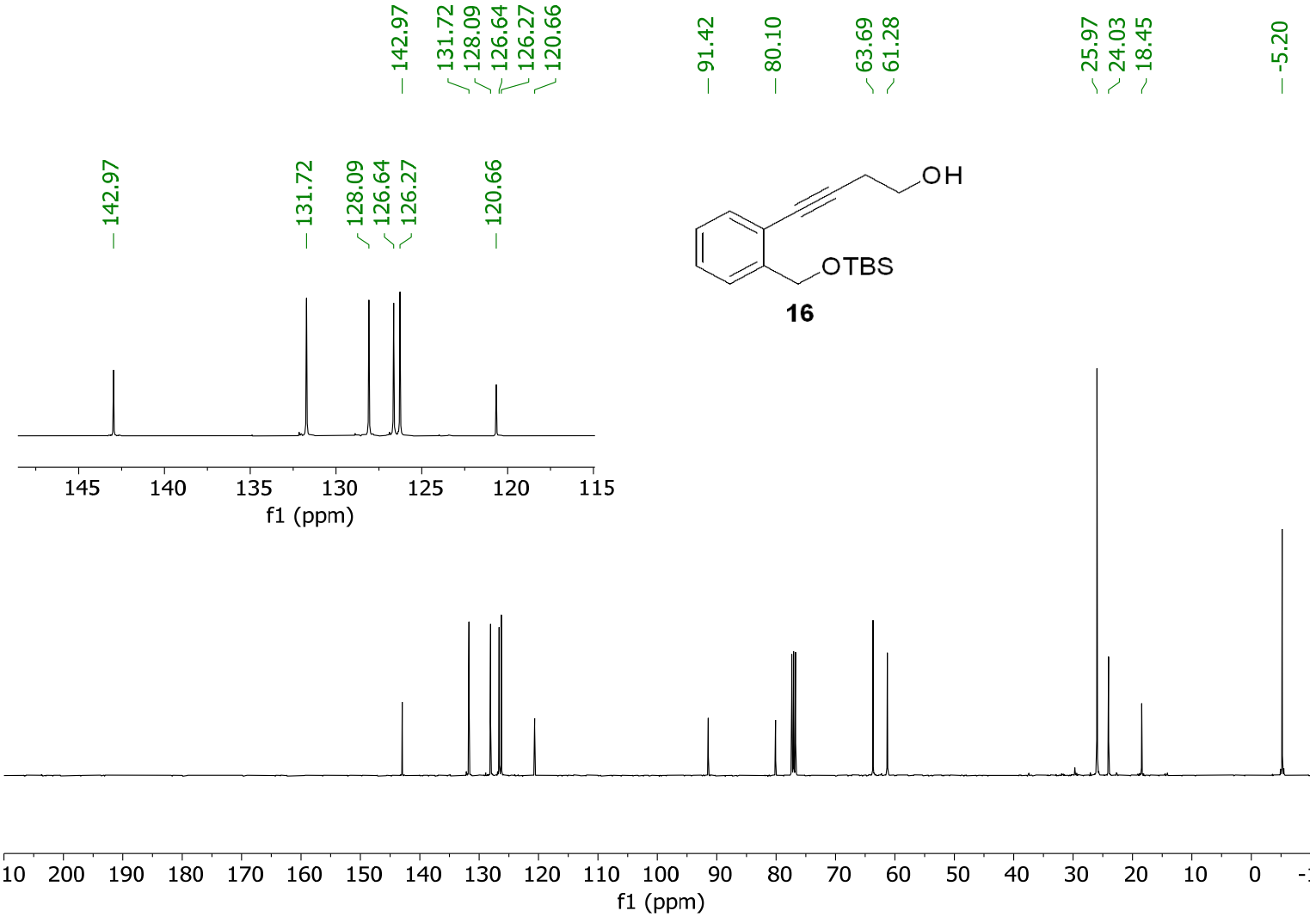
75 MHz ^{13}C-NMR Spectrum of compound **15** ($CDCl_3$, 300 K)



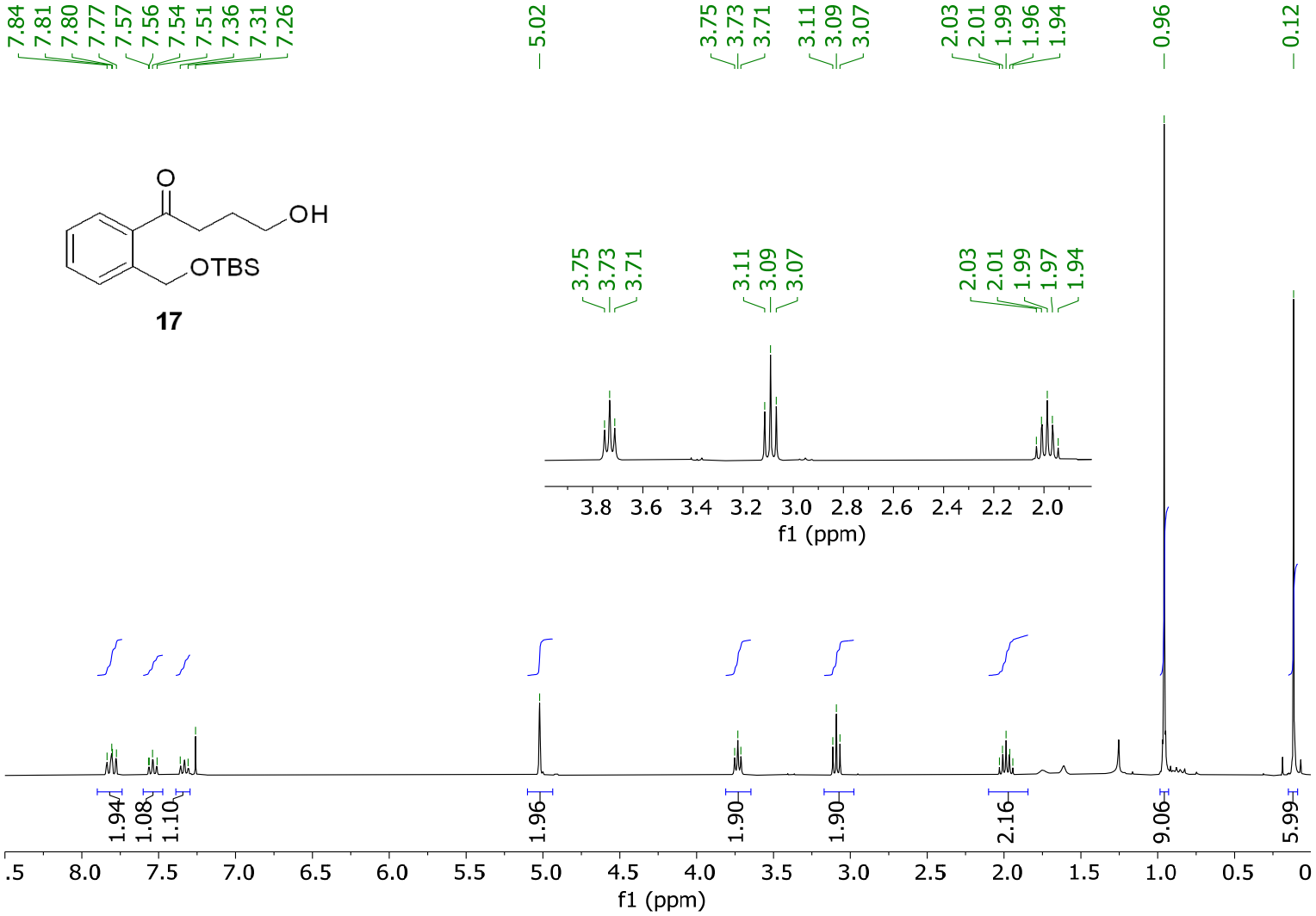
300 MHz ^{1}H-NMR Spectrum of compound **16** ($CDCl_3$, 300 K)



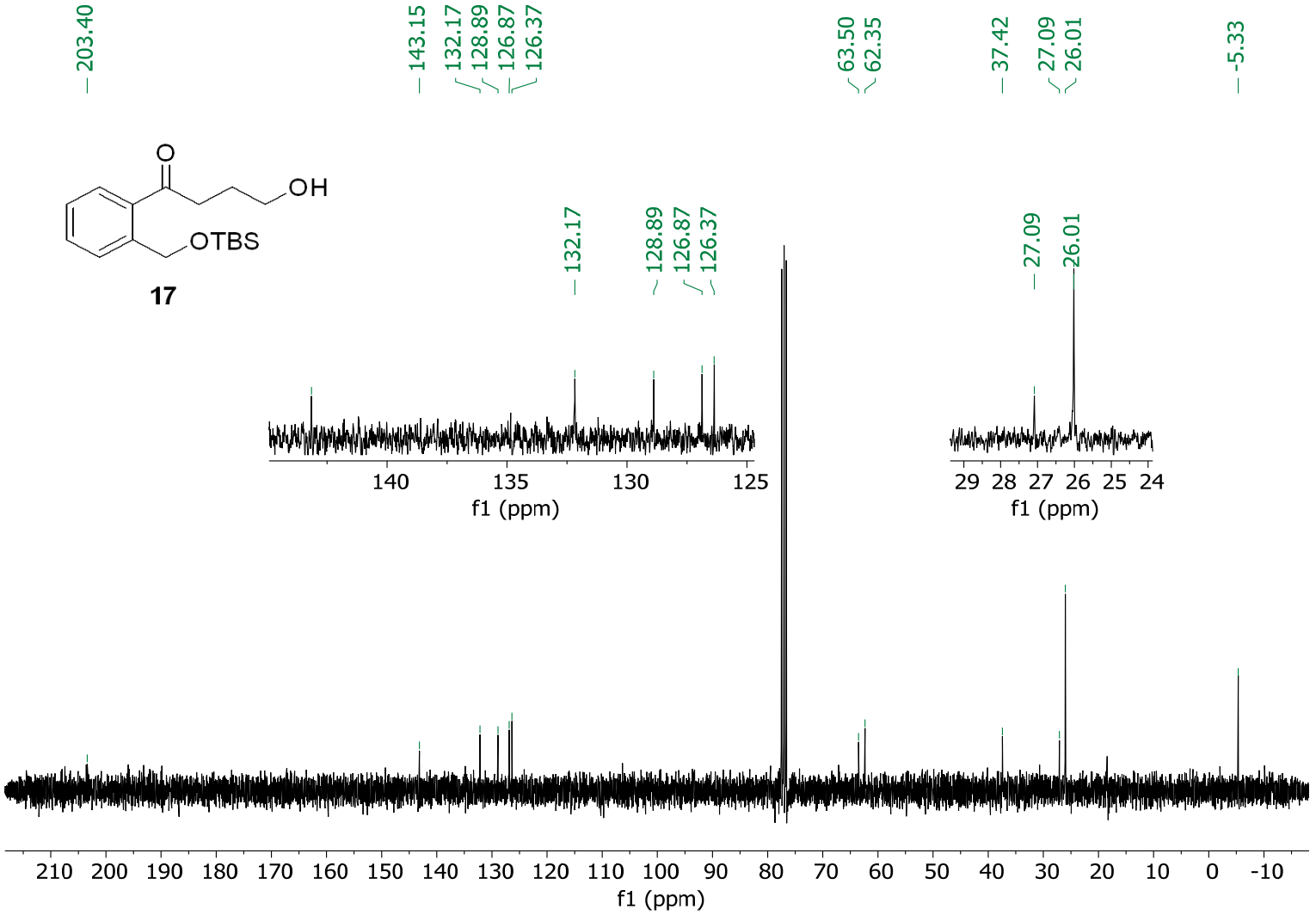
75 MHz ^{13}C-NMR Spectrum of compound **16** ($CDCl_3$, 300 K)



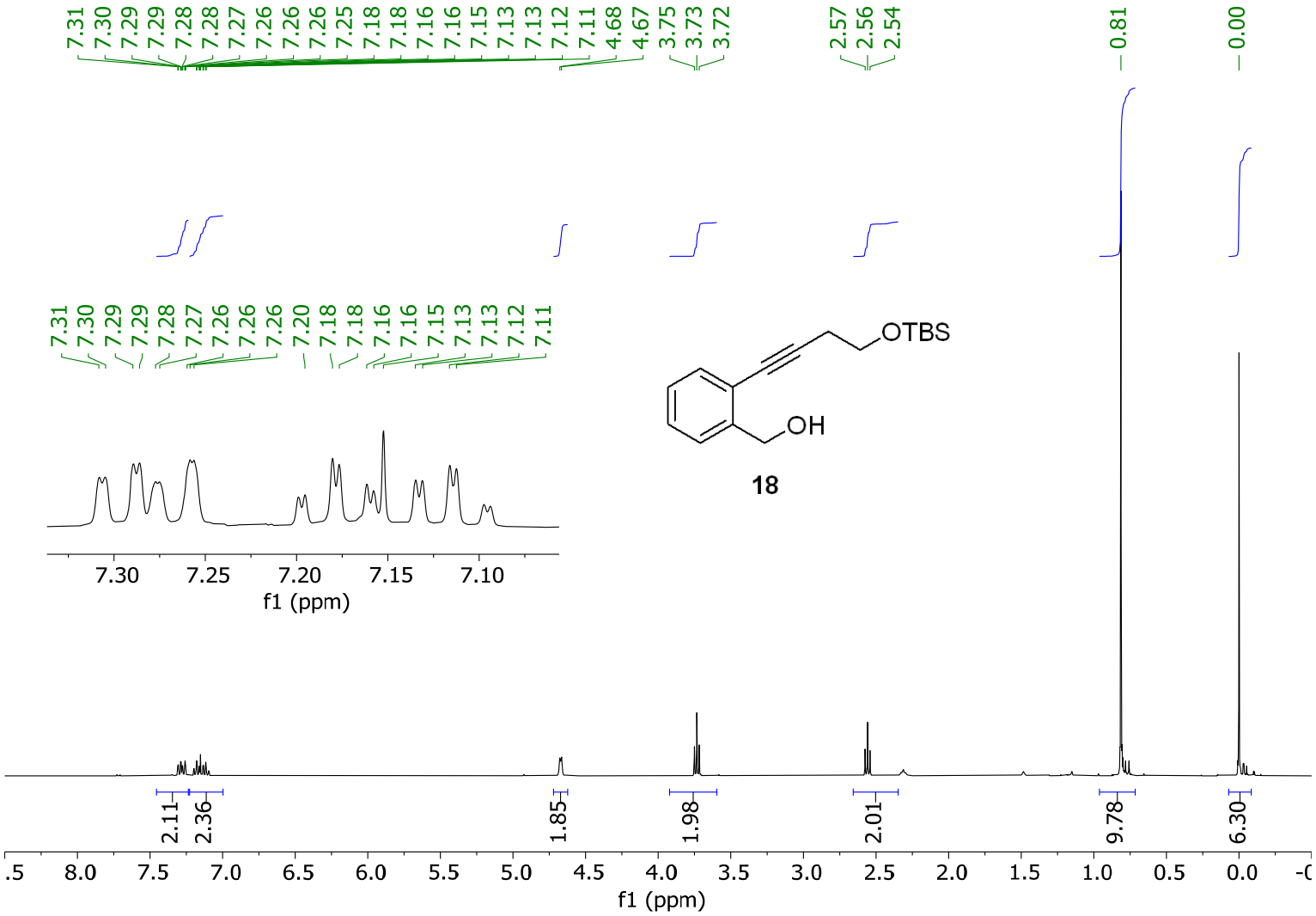
300 MHz ^{1}H-NMR Spectrum of compound **17** ($CDCl_3$, 300 K)



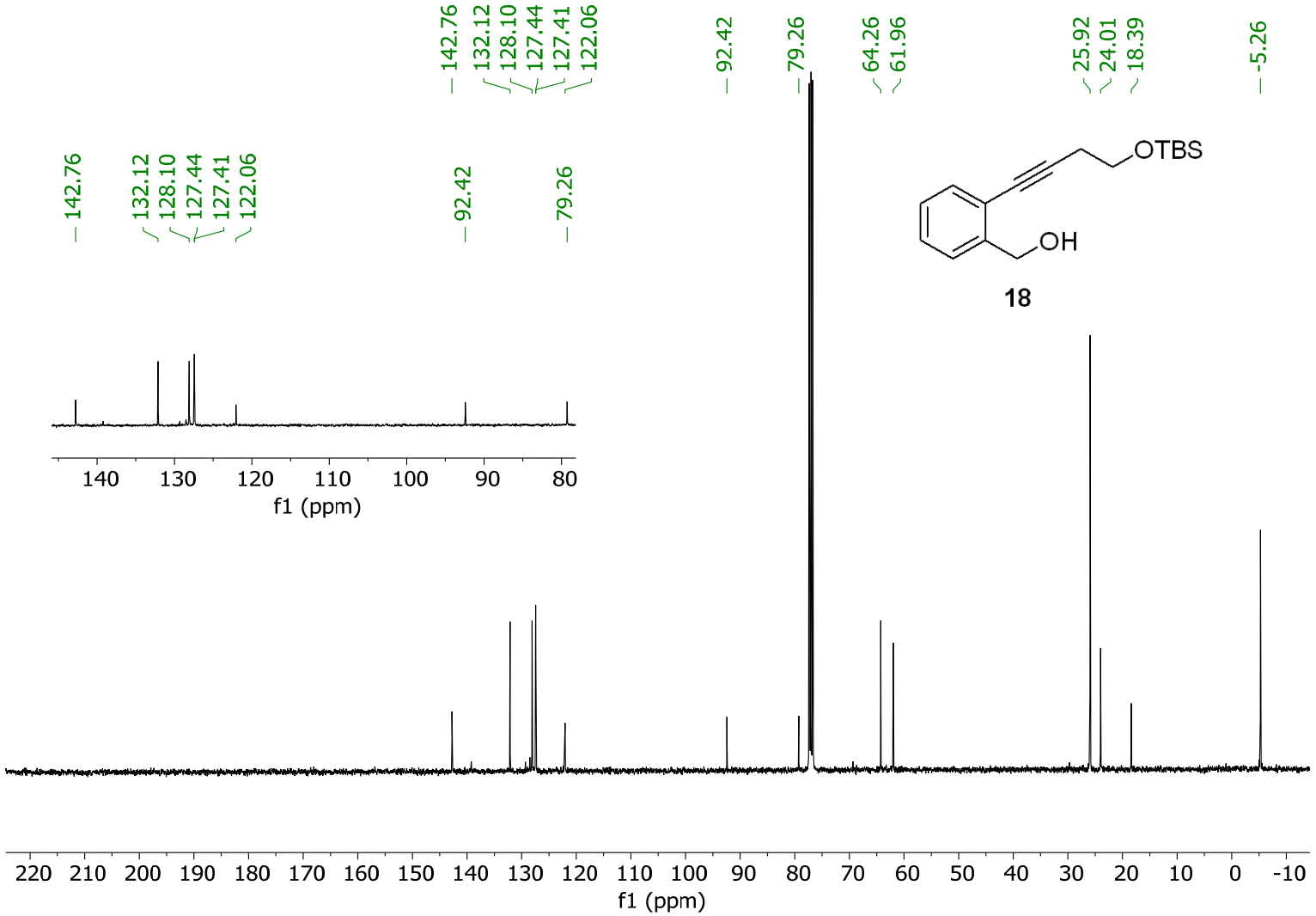
75 MHz ^{13}C-NMR Spectrum of compound **17** ($CDCl_3$, 300 K)



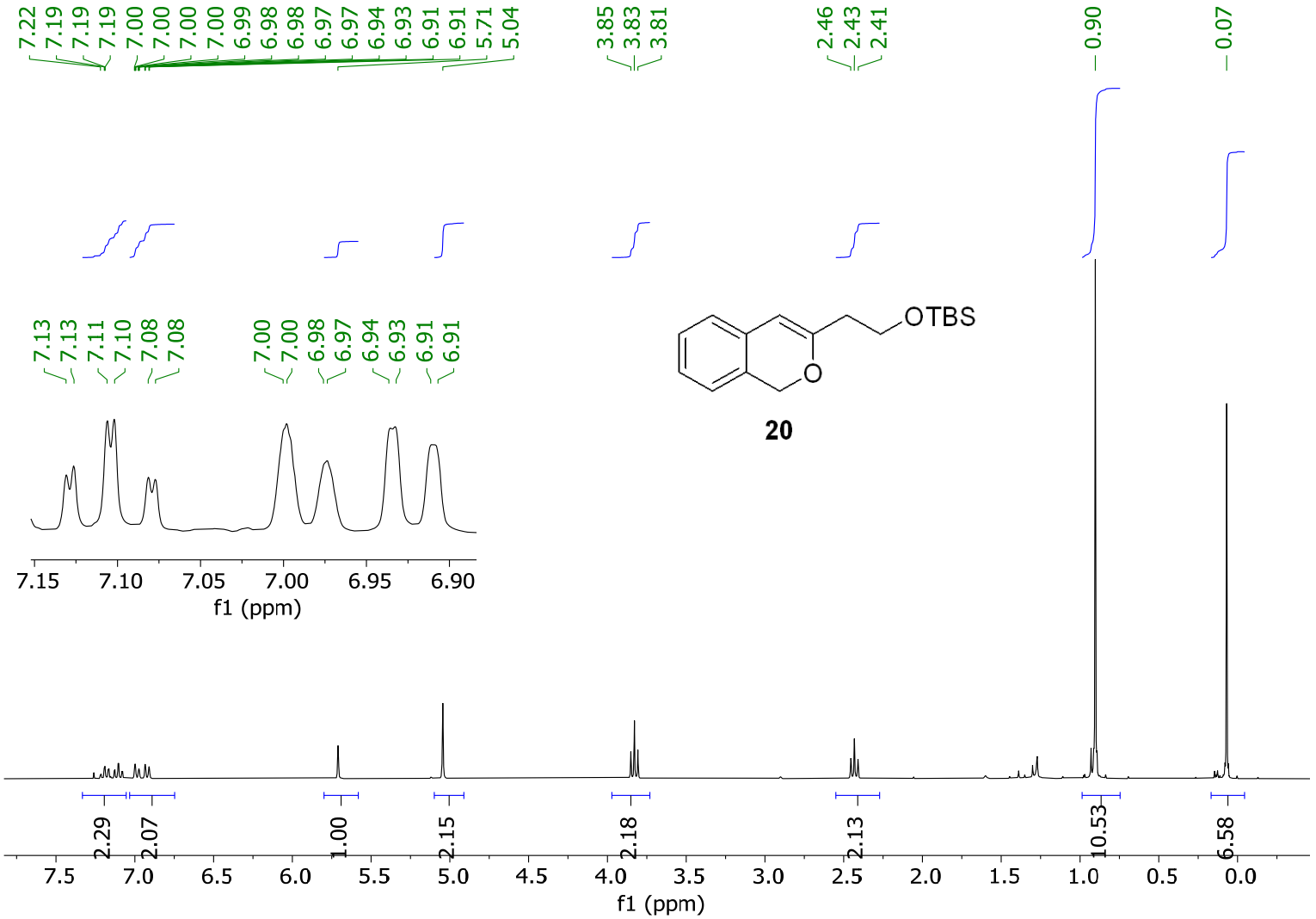
300 MHz ^{1}H-NMR Spectrum of compound **18** ($CDCl_3$, 300 K)



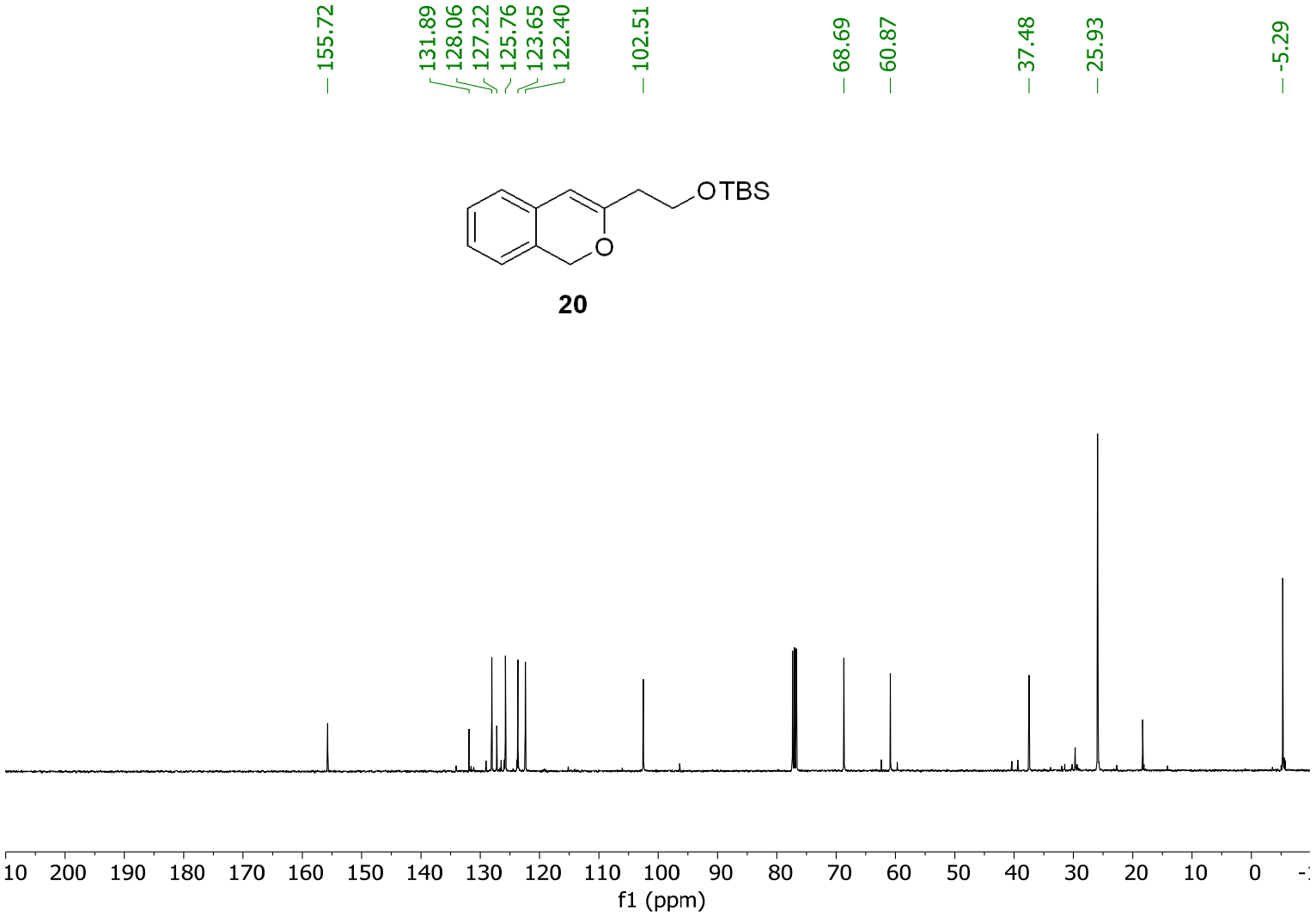
75 MHz ^{13}C-NMR Spectrum of compound **18** ($CDCl_3$, 300 K)



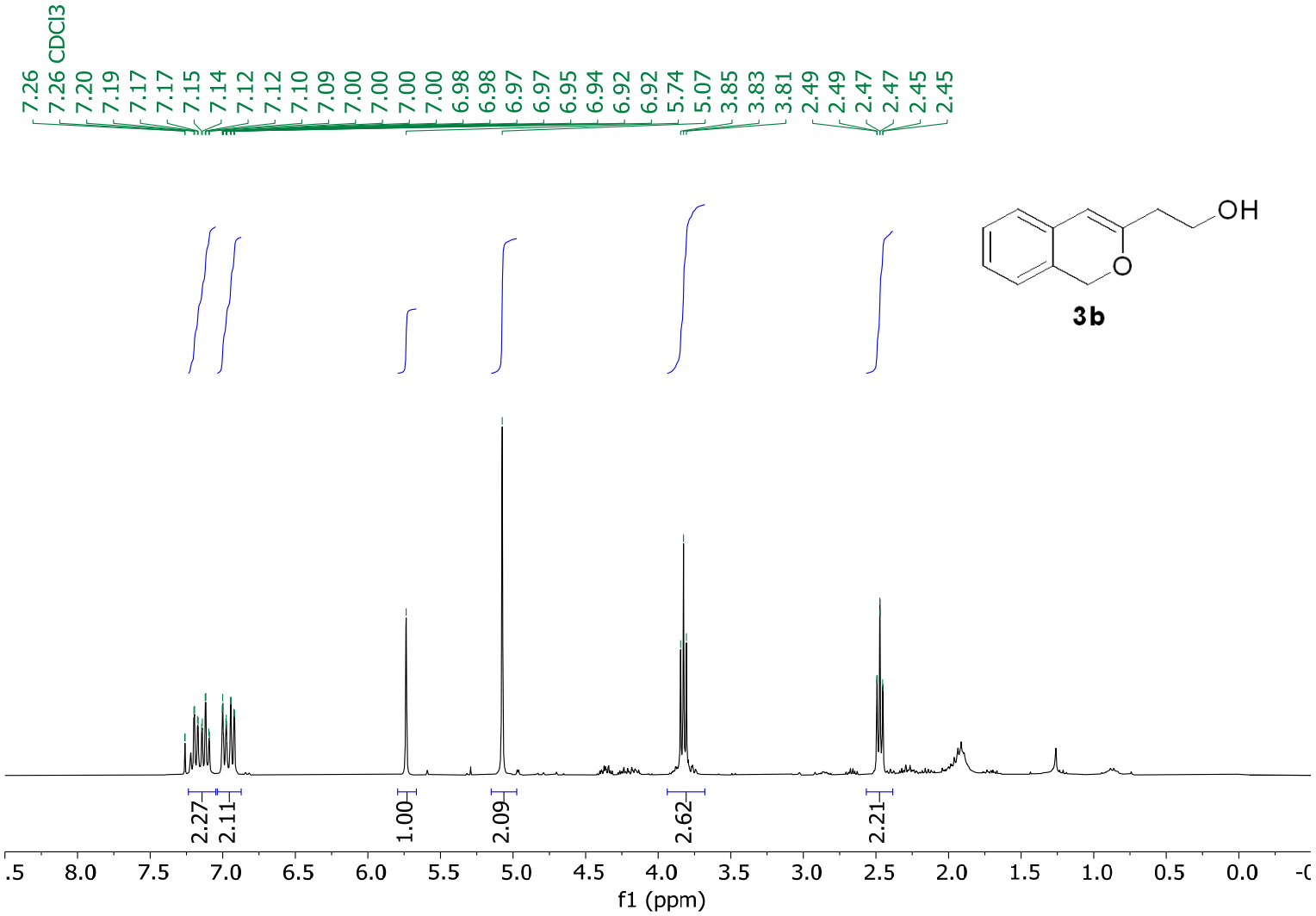
300 MHz ^{1}H-NMR Spectrum compound **20** ($CDCl_3$, 300 K)



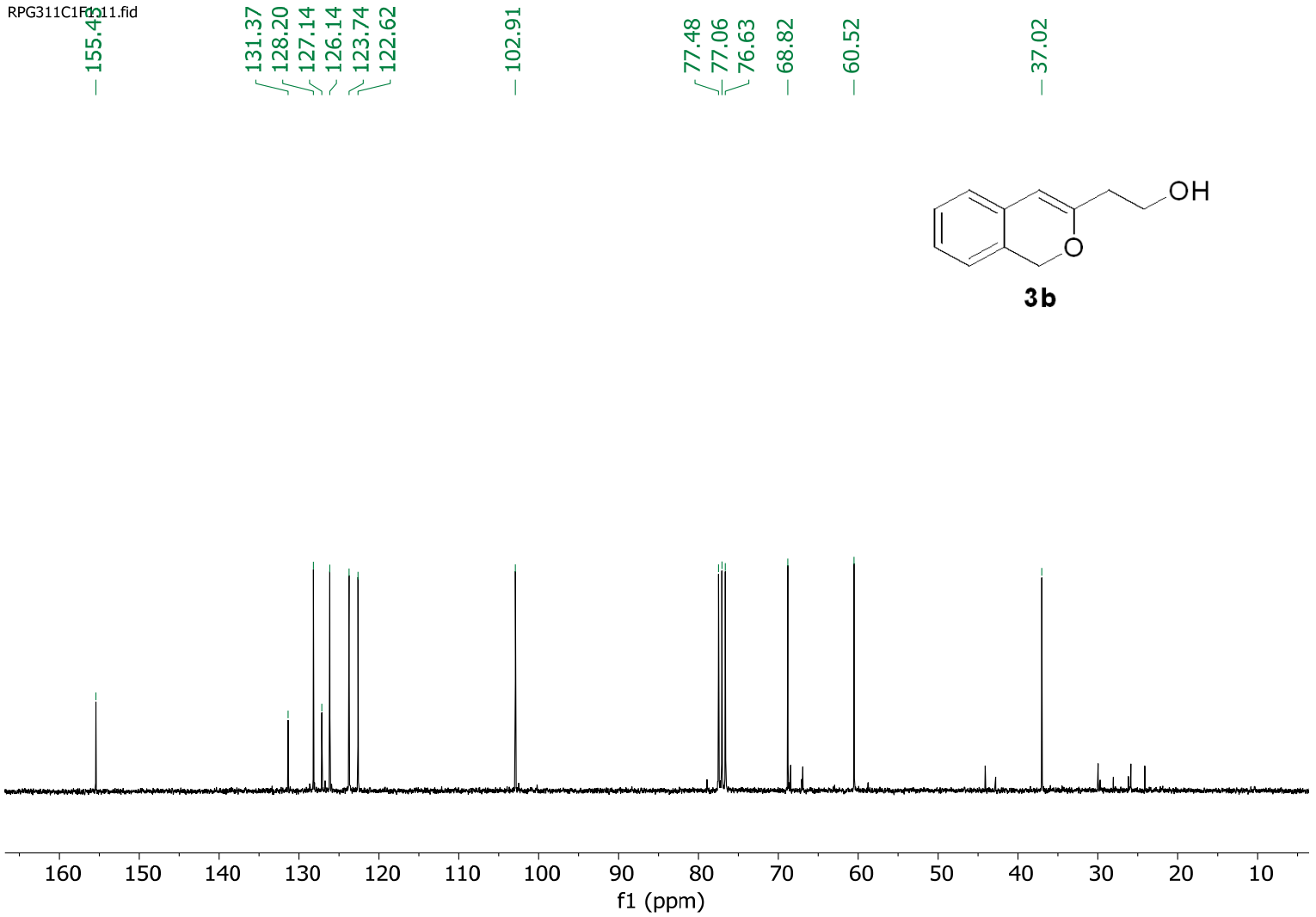
75 MHz ^{13}C-NMR Spectrum of compound **20** ($CDCl_3$, 300 K)



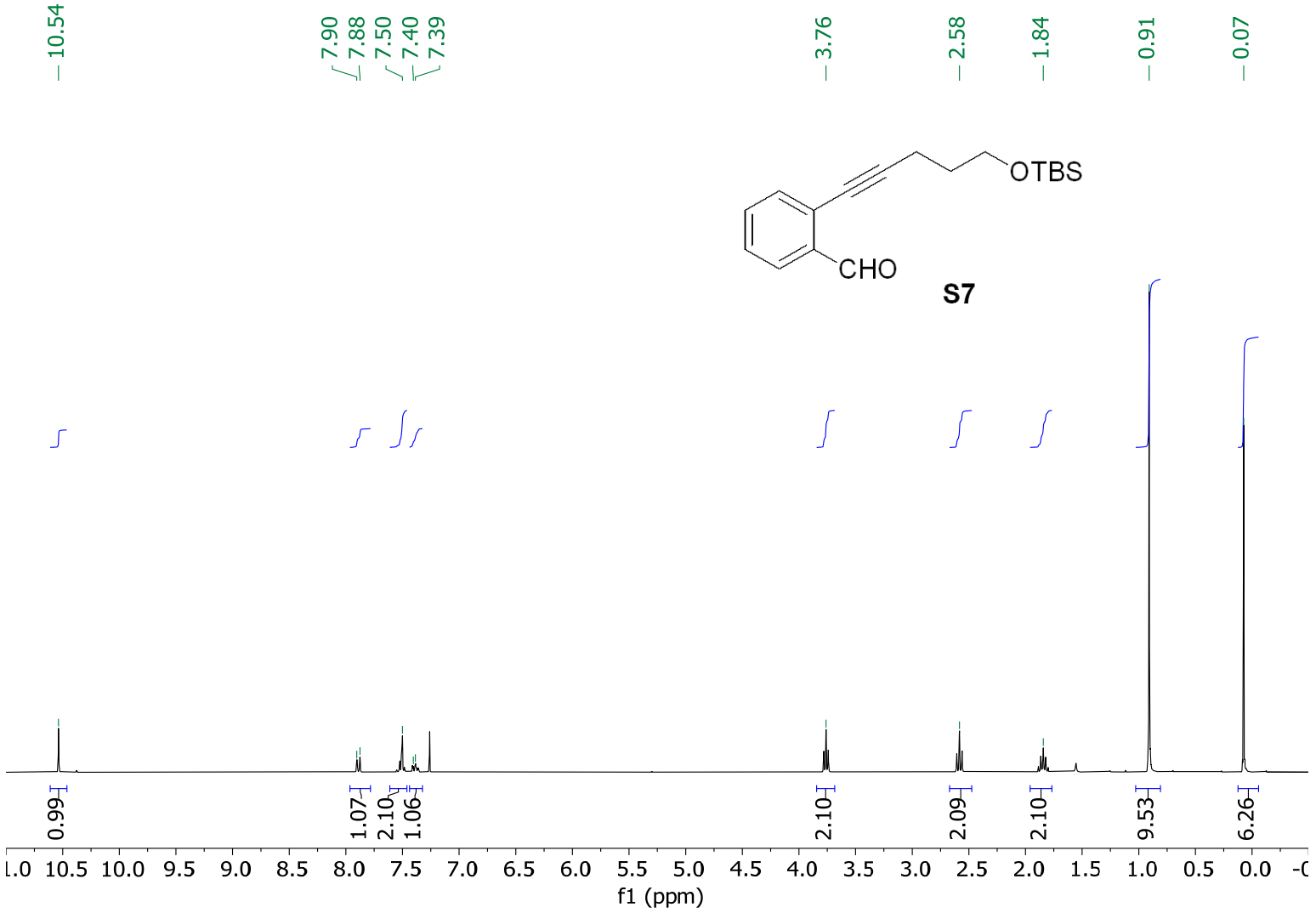
300 MHz ^{1}H-NMR Spectrum compound **3b** ($CDCl_3$, 300 K)



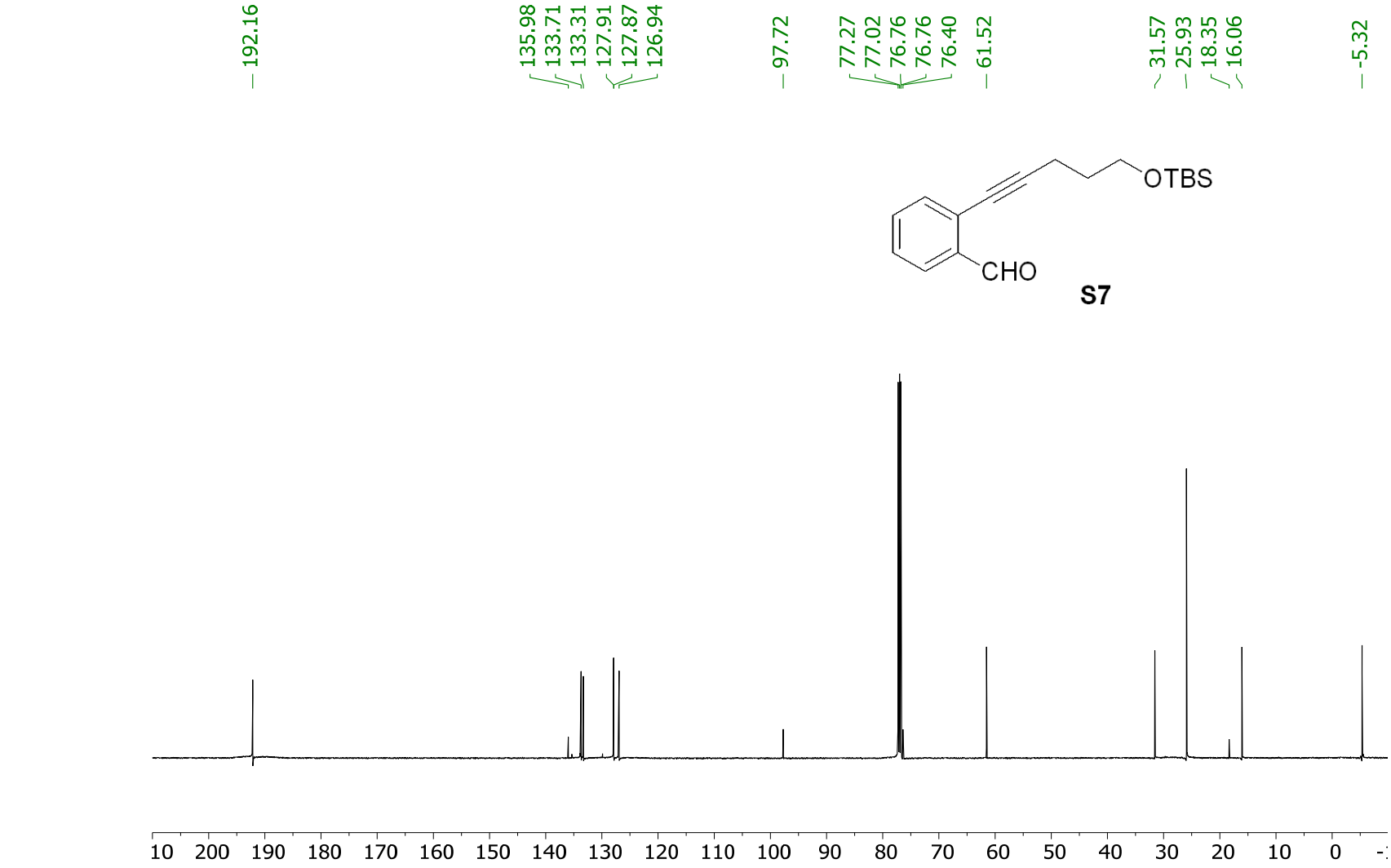
75 MHz ^{13}C-NMR Spectrum of compound **3b** ($CDCl_3$, 300 K)



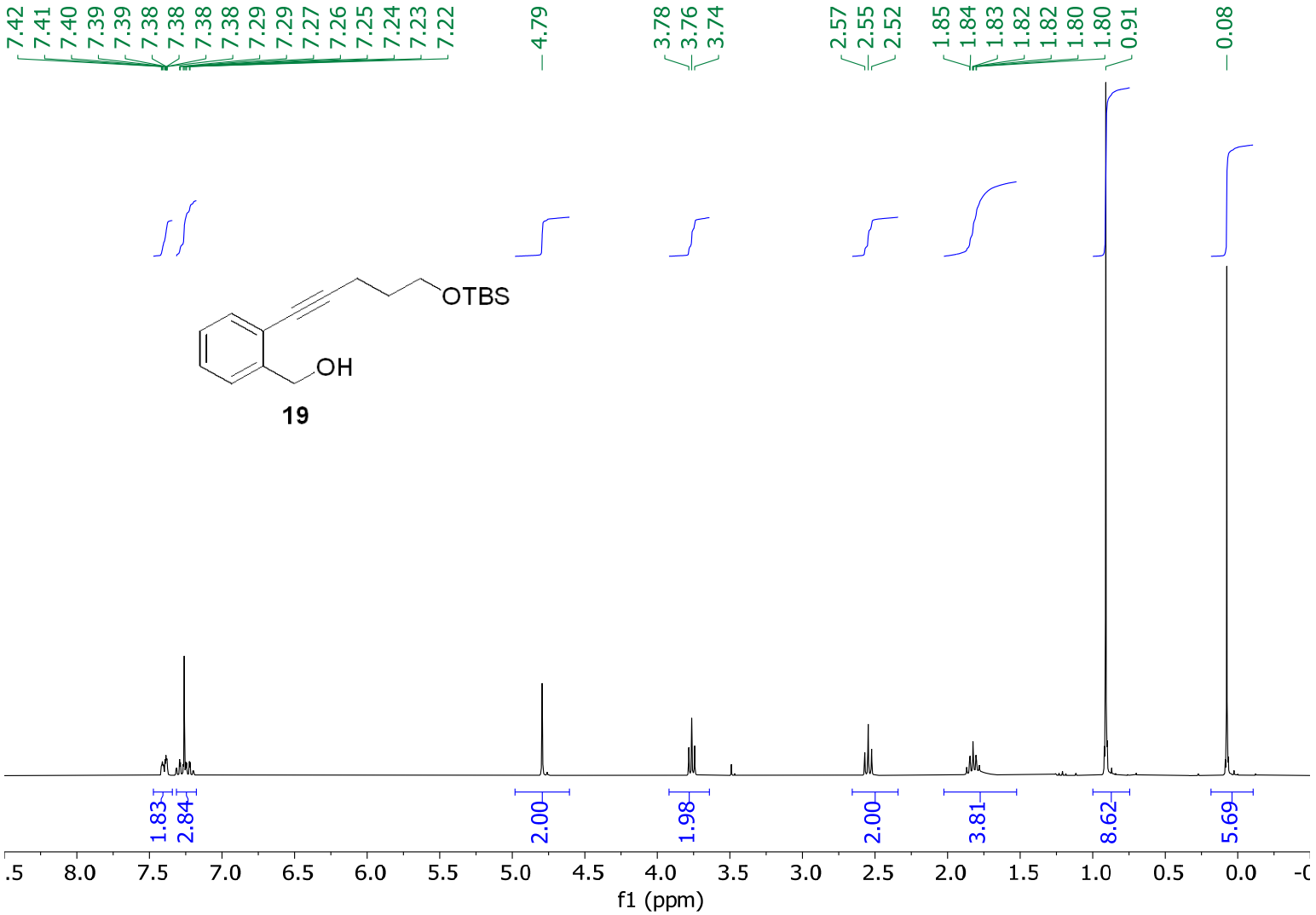
300 MHz ^{1}H-NMR Spectrum compound **S7** ($CDCl_3$, 300 K)



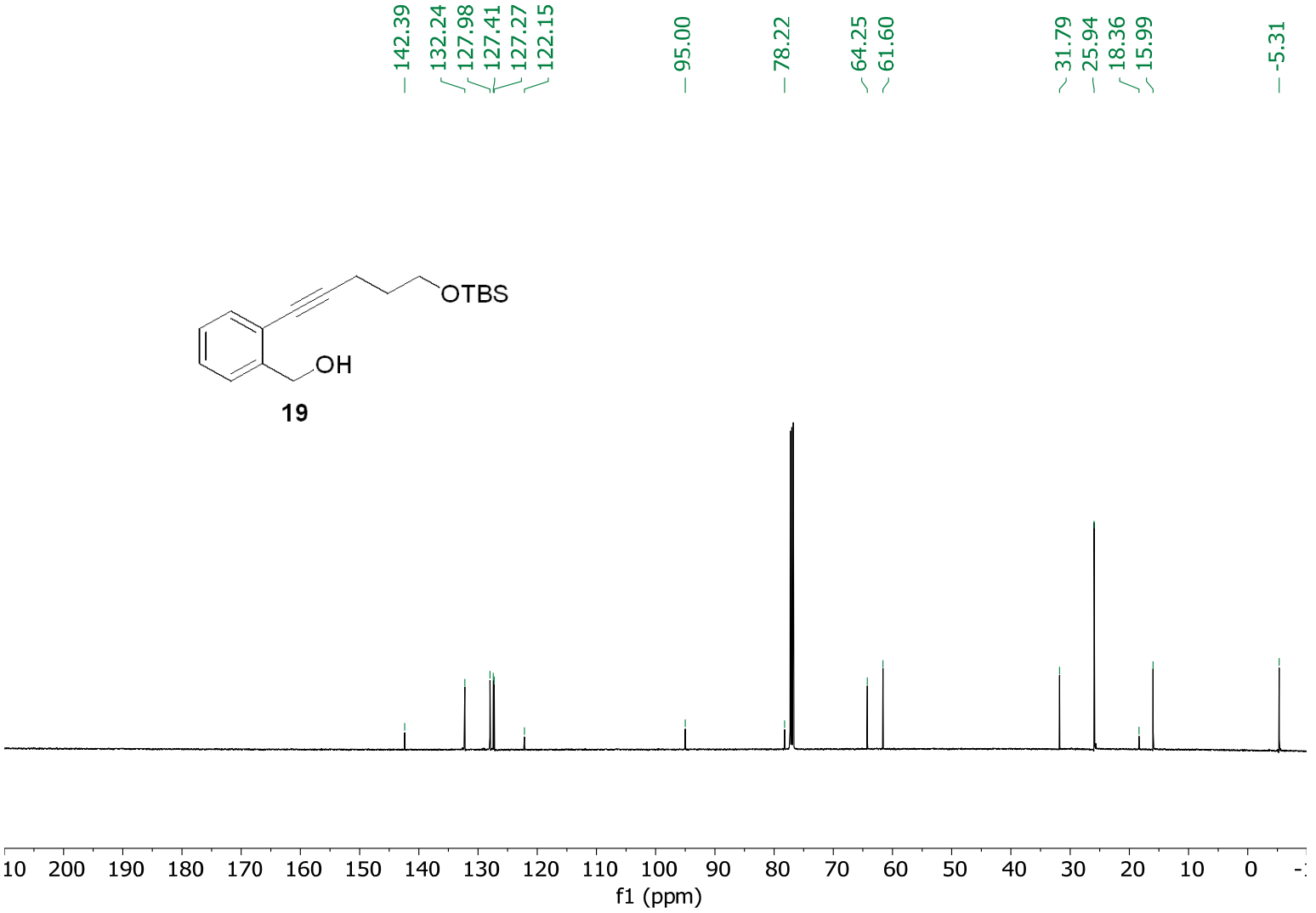
75 MHz ^{13}C-NMR Spectrum compound **S7** ($CDCl_3$, 300 K)



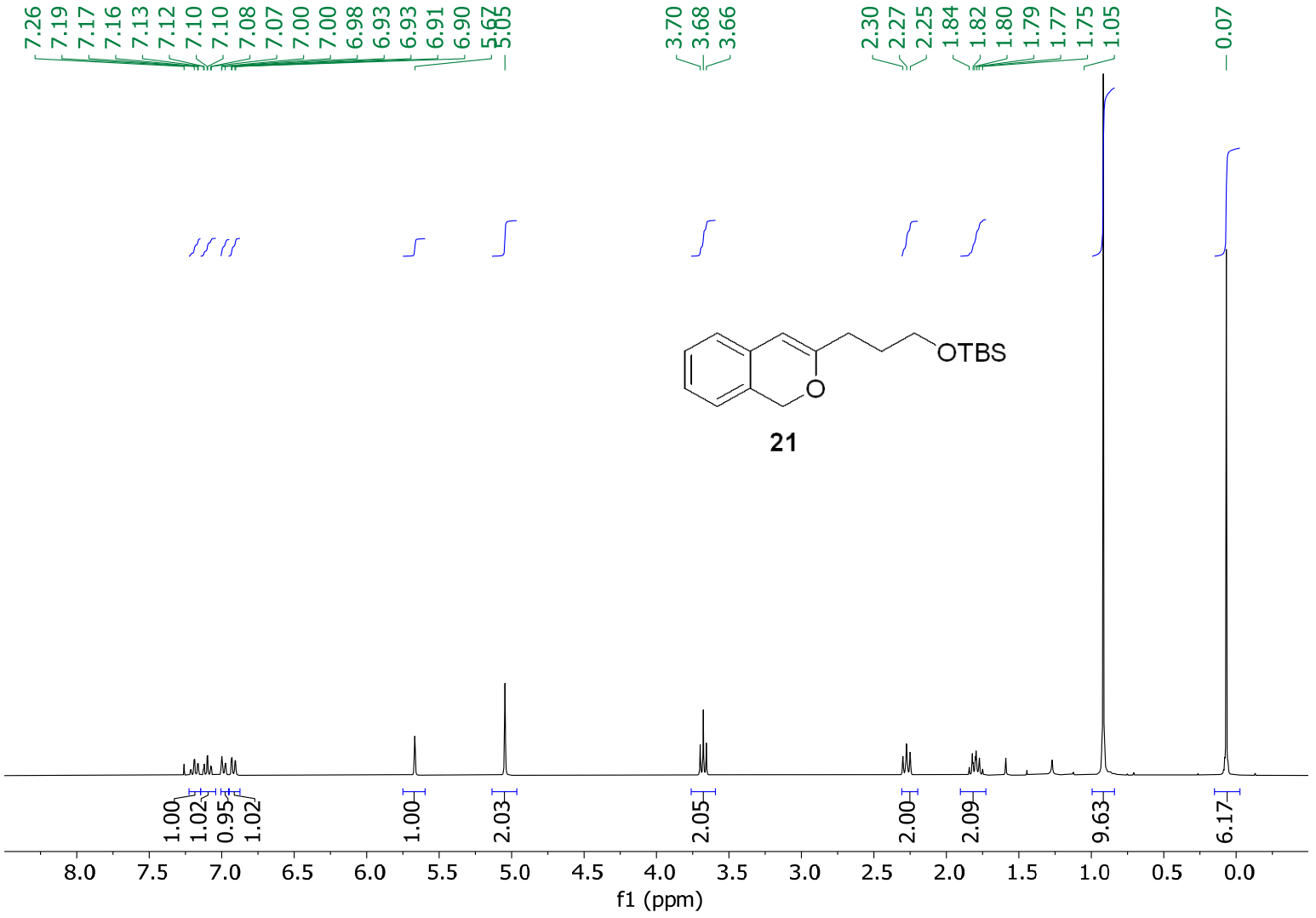
300 MHz ^{1}H-NMR Spectrum compound **19** ($CDCl_3$, 300 K)



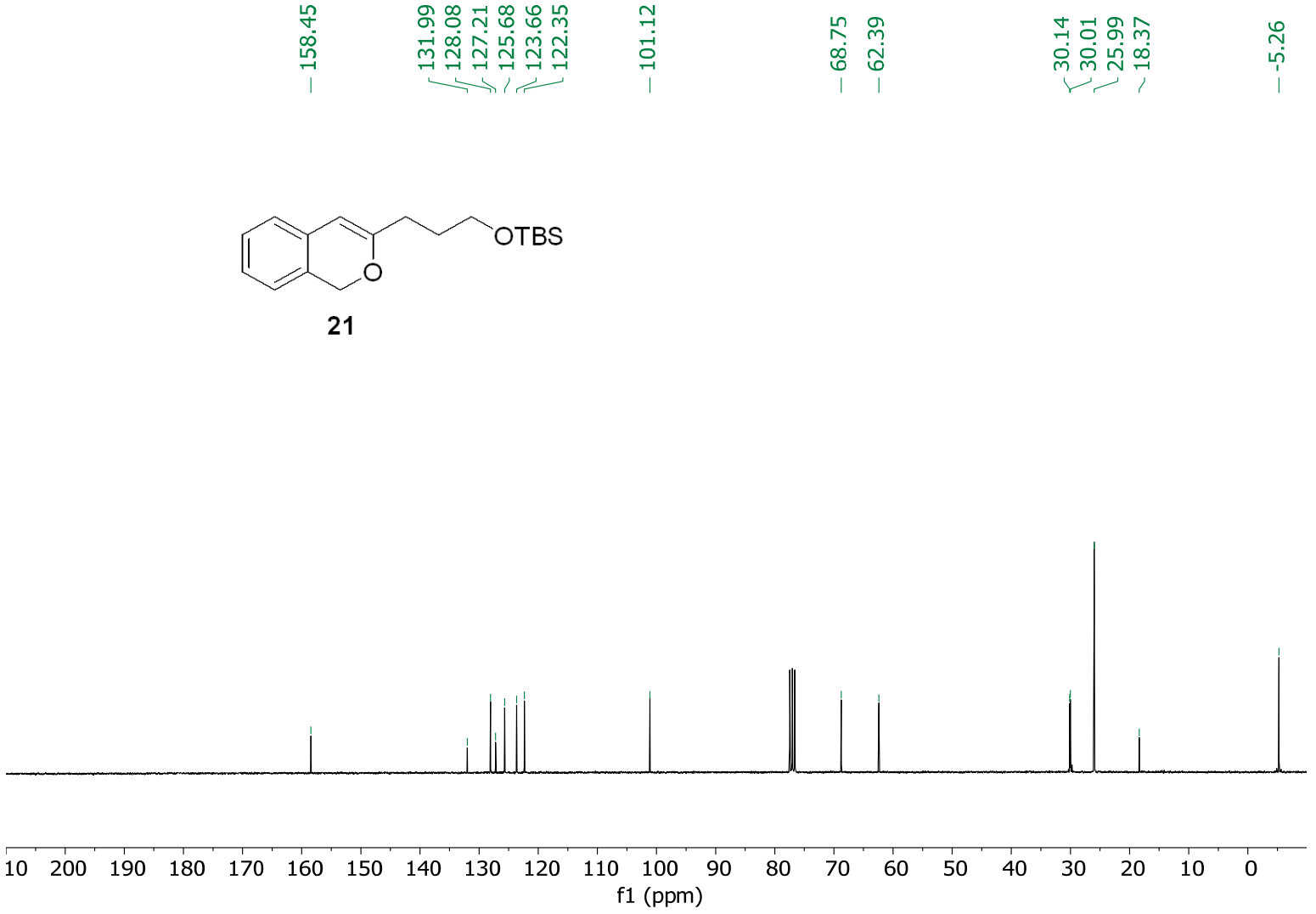
75 MHz ^{13}C-NMR Spectrum compound **19** ($CDCl_3$, 300 K)



300 MHz ^{1}H-NMR Spectrum compound **21** ($CDCl_3$, 300 K)

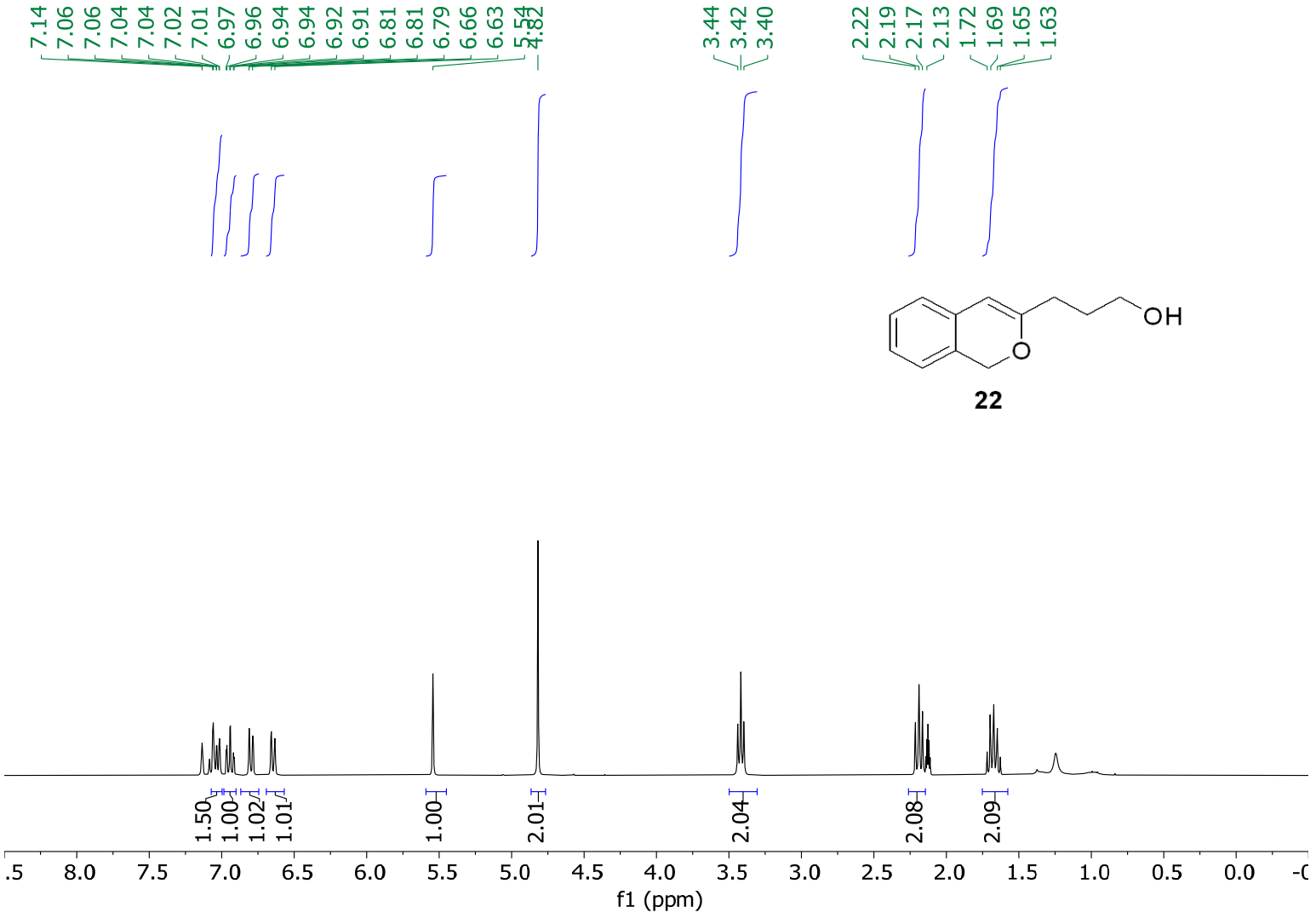


75 MHz ^{13}C-NMR Spectrum compound **21** ($CDCl_3$, 300 K)

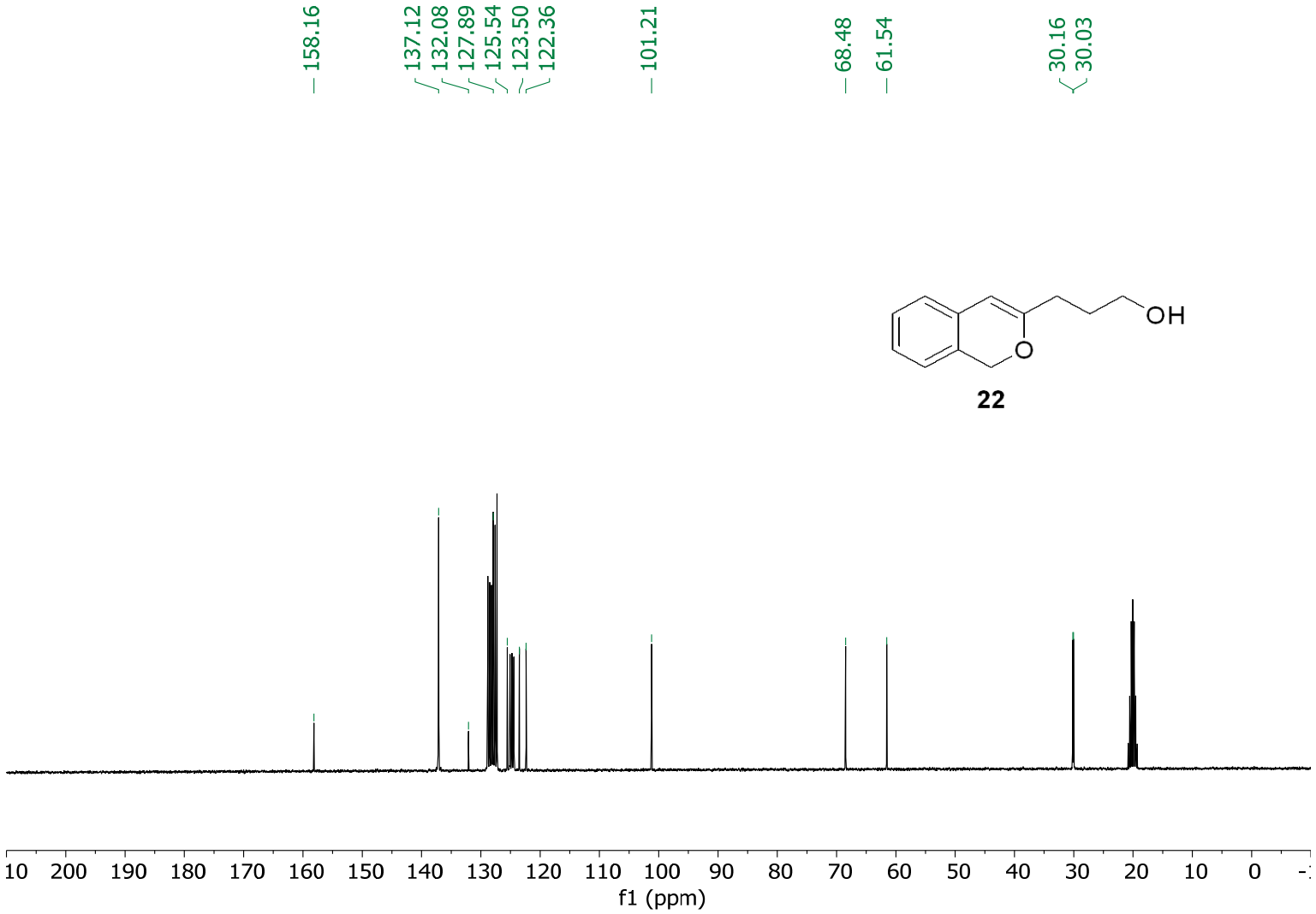


21

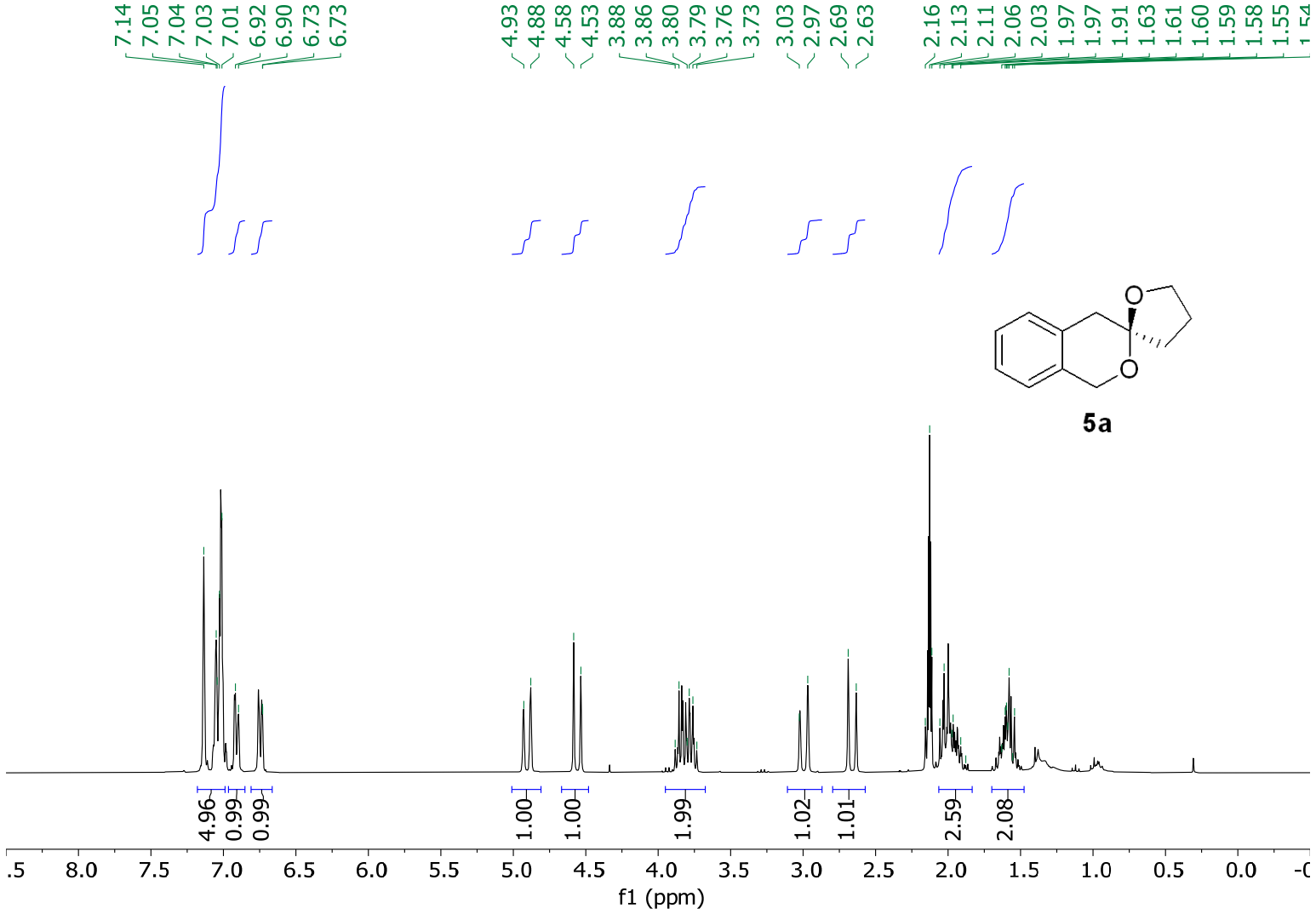
300 MHz ^{1}H-NMR Spectrum compound **22** (Toluene-d_8, 300 K)



75 MHz ^{13}C-NMR Spectrum compound **22** (Toluene-d_8, 300 K)



300 MHz ^{1}H-NMR Spectrum compound **5a** (Toluene-d_8, 300 K)



5a

75 MHz ^{13}C-NMR Spectrum compound **5a** (Toluene-d_8, 300 K)