Supplementary/Supporting Information:

Stereoselective Preparation of Conjugated (*Z*)-1,3-Enynes by Dehydration Reactions of Allenic Bromohydrins and the Use of the Enynes in Base-Mediated Tandem Allylation Ene-Carbocyclization Reactions with β-Ketoesters

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Table of Contents:

I. Experimental Section:

General Information and Materials: All commercially available chemicals were used without further purification. TLC analyses were run on a TLC glass plate (Silica gel 60 F254) and were visualized using UV and a solution of phosphomolybdic acid in ethanol (5 wt%) or *p*-anisaldehyde stain. Flash chromatography was performed using silica gel (70-230 mesh). ^{1}H spectra were recorded on a 300 MHz spectrometer. ^{13}C NMR spectra were recorded on a 75 MHz with complete proton decoupling spectrometer. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.24, δ_C (central line) 77.0]. Mass spectra were recorded under electron impact ionization (EI) conditions, and high-resolution mass spectra were recorded by electron impact ionization with magnetic sector.

General procedure for the synthesis of enynes 1: To a solution of allenol **5** (0.4 mmol) in $ClCH_2CH_2Cl$ (DCE, 2.5 mL) was added $Sc(OTf)_3$ (0.5 mmol%, 1 mg) at ambient temperature. The resulting mixture was heated to reflux under an nitrogen atmosphere. Reaction was monitored by TLC until no starting material was observed and normally the reaction was stirred at reflux for 1 h. The reaction was then cooled room temperature and concentrated in a rotary evaporator. The residue was purified by silica gel chromatography using hexanes as eluent to give the title product.

(*Z*)-(1-Bromopent-2-en-4-yn-2-yl)benzene (1a). Following the general procedure, the title compound was obtained (74 mg, 84%). A yellow oil, TLC (Et_2O/hexanes (1:9)) R_f = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (d, *J* = 2.4 Hz, 1 H), 4.61 (s, 2 H), 6.00 (d, *J* = 2.4 Hz, 1 H), 7.34-7.41 (m, 3 H), 7.49 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.4 (CH_2), 80.2 (C), 86.3 (CH), 109.6 (CH), 125.8 (CH x 2), 128.7 (CH x 2), 129.0 (CH), 136.9 (C), 149.2 (C); IR (neat) 3280, 1014, 1443 cm^{-1}; EI-MS *m/z* (rel intensity) 222 ($[M+2]^+$, 13), 220 ($[M]^+$, 13), 141 (100), 115 (36); HRMS $[M]^+$ calcd for $C_{11}H_9Br$: 219.9888, found 219.9896.

(*Z*)-1-bromo-4-(1-bromopent-2-en-4-yn-2-yl)benzene (1b). Following the general procedure, the title compound was obtained (72 mg, 60%, two-step overall yield). A yellow solid, mp 50-51 ^{o}C;

TLC (Et_2O/hexanes (1:9)) R_f = 0.60; ^1H NMR (300 MHz, $CDCl_3$) δ 3.52 (d, *J* = 2.4 Hz, 1 H), 4.56 (s, 2 H), 5.98 (d, *J* = 2.4 Hz, 1 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.0 (CH_2), 79.9 (C), 86.9 (CH), 110.0 (CH), 123.2 (C), 127.3 (CH x 2), 131.8 (CH x 2), 135.7 (C), 148.0 (C); IR (neat) 3280, 1488, 1012 cm^{-1}; EI-MS *m/z* (rel intensity) 300 ($[M+2]^+$, 35), 298 ($[M]^+$, 18), 219 (69), 140 (100); HRMS $[M]^+$ calcd for $C_{11}H_8Br_2$: 297.8993, found 297.8990.

(*Z*)-1-(1-Bromopent-2-en-4-yn-2-yl)-4-chlorobenzene (1c). Following the general procedure, the title compound was obtained (52 mg, 51%, two-step overall yield). A yellow solid, mp 39-40 ^oC; TLC (Et_2O/hexanes (1:9)) R_f = 0.60; ^1H NMR (300 MHz, $CDCl_3$) δ 3.52 (d, *J* = 2.7 Hz, 1 H), 4.56 (s, 2 H), 5.97 (d, *J* = 2.7 Hz, 1 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 7.41 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.1 (CH_2), 79.9 (C), 86.8 (CH), 110.0 (CH), 127.1 (CH x 2), 128.9 (CH x 2), 135.0 (C), 135.3 (C), 148.0 (C); IR (neat) 3284, 1594, 1494 cm^{-1}; EI-MS *m/z* (rel intensity) 256 ($[M+2]^+$, 40), 254 ($[M]^+$, 30), 175 (100), 139 (63); HRMS $[M]^+$ calcd for $C_{11}H_8BrCl$: 253.9498, found 253.9494.

(*Z*)-1-(1-Bromopent-2-en-4-yn-2-yl)-4-methylbenzene (1d). Following the general procedure, the title compound was obtained (47 mg, 50%, two-step overall yield). A yellow solid, mp 35-36 ^oC; TLC (Et_2O/hexanes (1:9)) R_f = 0.70; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3 H), 3.49 (d, *J* = 2.4 Hz, 1 H), 4.60 (s, 2 H), 5.98 (d, *J* = 2.4 Hz, 1 H), 7.18 (d, *J* = 8.1 Hz, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2 (CH_3), 29.4 (CH_2), 80.4 (C), 86.0 (CH), 108.6 (CH), 125.6 (CH x 2), 129.4 (CH x 2), 133.9 (C), 139.2 (C), 149.1 (C); IR (neat) 3286, 1520, 1431 cm^{-1}; EI-MS *m/z* (rel intensity) 236 ($[M+2]^+$, 20), 234 ($[M]^+$, 21), 155 (100), 115 (44); HRMS $[M]^+$ calcd for $C_{12}H_{11}Br$: 234.0044, found 234.0039.

(*Z*)-1-(1-Bromopent-2-en-4-yn-2-yl)-4-methoxybenzene (1e). Following the general procedure, the title compound was obtained (48 mg, 48%). A yellow solid, mp 44-45 ^{o}C; TLC (Et_2O/hexanes (1:9)) R_f = 0.43; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.47 (d, *J* = 2.4 Hz, 1 H), 3.81 (s, 3 H), 4.59 (s, 2 H), 5.92 (d, *J* = 2.4 Hz, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H), 7.43 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.5 (CH_2), 55.2 (CH_3), 80.5 (C), 85.7 (CH), 107.6 (CH), 114.0 (CH x 2), 127.1 (CH x 2), 129.2 (C), 148.5 (C), 160.2 (C); IR (neat) 3280, 1602, 1501 cm^{-1}; EI-MS *m/z* (rel intensity) 252 ($[M+2]^+$, 100), 250 ($[M]^+$, 99), 171 (95), 128 (61); HRMS $[M]^+$ calcd for $C_{12}H_{11}BrO$: 249.9993, found 249.9986.

(*Z*)-1-(1-Bromopent-2-en-4-yn-2-yl)-3-methoxybenzene (1f). Following the general procedure, the title compound was obtained (42 mg, 42%, two-step overall yield). A yellow solid, mp 39-40 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (d, *J* = 2.4 Hz, 1 H), 3.81 (s, 3 H), 4.58 (s, 2 H), 5.99 (d, *J* = 2.4 Hz, 1 H), 6.87-6.91 (m, 1 H), 7.00-7.08 (m, 2 H), 7.29 (t, *J* = 8.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.4 (CH_2), 55.2 (CH_3), 80.1 (C), 86.4 (CH), 109.9 (CH), 111.7 (CH), 114.3 (CH), 118.2 (CH), 129.7 (CH), 138.4 (C), 149.1 (C), 159.7 (C); IR (neat) 3280, 1602, 1501 cm^{-1}; EI-MS *m/z* (rel intensity) 252 ($[M+2]^+$, 14), 250 ($[M]^+$, 14), 171 (100), 128 (39); HRMS $[M]^+$ calcd for $C_{12}H_{11}BrO$: 249.9993, found 249.9996.

(*Z*)-1-(1-Bromopent-2-en-4-yn-2-yl)-2-methoxybenzene (1g). Following the general procedure, the title compound was obtained (88 mg, 88%). A yellow solid, mp 51-52 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.63; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.43 (d, *J* = 2.4 Hz, 1 H), 3.82 (s, 3 H), 4.72 (s, 2 H), 5.75 (d, *J* = 2.4 Hz, 1 H), 6.88-6.99 (m, 2 H), 7.22 (t, *J* = 7.8 Hz, 1 H), 7.30-7.36 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.3 (CH_2), 55.3 (CH_3), 79.8 (C), 85.1 (CH), 110.7 (CH), 111.9 (CH), 120.6 (CH), 127.2 (C), 130.0 (CH), 130.4 (CH), 150.0 (C), 156.4 (C); IR (neat) 3305,

1590, 1500 cm^{-1}; EI-MS *m/z* (rel intensity) 252 ($[M+2]^+$, 63), 250 ($[M]^+$, 61), 171 (98), 128 (100); HRMS $[M]^+$ calcd for $C_{12}H_{11}BrO$: 249.9993, found 249.9991.

(*Z*)-2-(1-Bromopent-2-en-4-yn-2-yl)naphthalene (1h). Following the general procedure, the title compound was obtained (44 mg, 41%, two-step overall yield). A yellow solid, mp 62-63 ^oC; TLC (Et_2O/hexanes (1:9)) R_f = 0.55; ^1H NMR (300 MHz, $CDCl_3$) δ 3.56 (d, *J* = 2.4 Hz, 1 H), 4.72 (s, 2 H), 6.15 (d, *J* = 2.4 Hz, 1 H), 7.47-7.59 (m, 3 H), 7.80-7.87 (m, 3 H), 7.96 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.3 (CH_2), 80.3 (C), 86.7 (CH), 109.9 (CH), 123.2 (CH), 125.4 (CH), 126.6 (CH), 126.7 (CH), 127.6 (CH), 128.4 (CH), 128.5 (CH), 133.1 (C), 133.4 (C), 134.0 (C), 149.1 (C); IR (neat) 3266, 2911, 1380 cm^{-1}; EI-MS *m/z* (rel intensity) 272 ($[M+2]^+$, 20), 270 ($[M]^+$, 20), 191 (100), 152 (19); HRMS $[M]^+$ calcd for $C_{15}H_{11}Br$: 270.0044, found 270.0047.

General procedure for the synthesis of methylenecyclopentenes 6 (or 7) from reaction of β-ketoester (or active methylene compound) with enynes 1. To a solution of enyne **1** (0.63 mmol) in DMF (0.6 mL) was added K_2CO_3 (240 mg, 1.74 mmol), Ag_2CO_3 (33 mg, 0.12 mmol), and ketoester or active methylene compound (0.6 mmol) at ambient temperature. The resulting mixture was stirred at ambient temperature under N_2. Reaction was monitored by TLC until no starting material was observed and normally the reaction was stirred at ambient temperature for 0.5 h. EtOAc (10 mL) and H_2O (10 mL) were added and the mixture was transferred to a separatory funnel. The aqueous layer was back extracted with EtOAc (10 mL x 2). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in a rotary evaporator. The residue was purified by silica gel chromatography using EtOAc/hexanes (1/50) as eluent to give the title product.

Ethyl 1-acetyl-2-methylene-4-phenylcyclopent-3-ene-1-carboxylate (6a). Following the general procedure, the title compound was obtained (148 mg, 87%). A yellow oil; TLC (EtOAc/hexanes (1:9)) R_f = 0.33; ^1H NMR (300 MHz, acetone-d_6) δ 1.28 (t, *J* = 7.2 Hz, 3 H), 2.23 (s, 3 H), 3.30 (d, *J* = 17.7 Hz, 1 H), 3.65 (d, *J* = 17.7 Hz, 1 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 5.27 (s, 1

H), 5.37 (s, 1 H), 6.57 (s, 1 H), 7.25-7.37 (m, 3 H), 7.45-7.49 (m, 2 H); ^{13}C NMR (75 MHz, acetone-d_6) δ 14.3 (CH_3), 25.9 (CH_3), 40.9 (CH_2), 62.2 (CH_2), 69.7 (C), 110.7 (CH_2), 126.8 (CH x 2), 128.1 (CH), 129.4 (CH), 129.5 (CH), 129.6 (CH), 135.5 (C), 146.6 (C), 152.0 (C), 171.0 (C), 202.0 (C); IR (neat) 2991, 1726, 1256 cm^{-1}; EI-MS *m/z* (rel intensity) 270 ($[M]^+$, 20), 228 (100), 181 (39), 155 (76); HRMS $[M]^+$ calcd for $C_{17}H_{18}O_3$: 270.1256, found 270.1257.

Ethyl 1-acetyl-4-(4-bromophenyl)-2-methylenecyclopent-3-ene-1-carboxylate (6b). Following the general procedure, the title compound was obtained (198 mg, 90%). A yellow oil; TLC (EtOAc/hexanes (1:9)) R_f = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 2.22 (s, 3 H), 3.25 (d, *J* = 17.4 Hz, 1 H), 3.57 (d, *J* = 17.4 Hz, 1 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 5.29 (s, 1 H), 5.37 (s, 1 H), 6.54 (s, 1 H), 7.31 (d, *J* = 8.7 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 25.6 (CH_3), 40.1 (CH_2), 61.8 (CH_2), 68.7 (C), 110.9 (CH_2), 122.4 (C), 127.2 (CH x 2), 127.6 (CH), 131.6 (CH x 2), 133.2 (C), 144.3 (C), 150.2 (C), 170.2 (C), 201.4 (C); IR (neat) 2984, 1712, 1236 cm^{-1}; EI-MS *m/z* (rel intensity) 350 ($[M+2]^+$, 8), 348 ($[M]^+$, 11), 306 (54), 183 (100); HRMS $[M]^+$ calcd for $C_{17}H_{17}BrO_3$: 348.0361, found 348.0367.

Ethyl 1-acetyl-4-(4-chlorophenyl)-2-methylenecyclopent-3-ene-1-carboxylate (6c). Following the general procedure, the title compound was obtained (159 mg, 83%). A yellow oil; TLC (EtOAc/hexanes (1:9)) R_f = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 2.22 (s, 3 H), 3.25 (d, *J* = 17.4 Hz, 1 H), 3.57 (d, *J* = 17.4 Hz, 1 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 5.28 (s, 1 H), 5.37 (s, 1 H), 6.52 (s, 1 H), 7.28 (d, *J* = 8.7 Hz, 2 H), 7.37 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 25.6 (CH_3), 40.1 (CH_2), 61.8 (CH_2), 68.7 (C), 110.8 (CH_2), 127.0 (CH x 2), 127.5 (CH), 128.6 (CH x 2), 132.8 (C), 134.1 (C), 144.2 (C), 150.2 (C), 170.2 (C), 201.9 (C); IR (neat) 2977, 1712, 1624 cm^{-1}; EI-MS *m/z* (rel intensity) 306 ($[M+2]^+$, 7), 304 ($[M]^+$, 20), 262 (100), 189 (50); HRMS $[M]^+$ calcd for $C_{17}H_{17}ClO_3$: 304.0866, found 304.0863.

Ethyl 1-acetyl-2-methylene-4-(*p*-tolyl)cyclopent-3-enecarboxylate (6d). Following the general procedure, the title compound was obtained (159 mg, 89%). A white solid, mp 40-41 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3 H), 2.23 (s, 3 H), 2.33 (s, 3 H), 3.28 (d, *J* = 17.7 Hz, 1 H), 3.64 (d, *J* = 17.7 Hz, 1 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 5.25 (s, 1 H), 5.34 (s, 1 H), 6.53 (s, 1 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 7.37 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 21.1 (CH_3), 25.4 (CH_3), 40.2 (CH_2), 61.6 (CH_2), 68.7 (C), 109.6 (CH_2), 125.8 (CH x 2), 126.1 (CH), 129.1 (CH x 2), 131.5 (C), 138.4 (C), 145.5 (C), 150.5 (C), 170.3 (C), 202.2 (C); IR (neat) 2984, 1729, 1621 cm^{-1}; EI-MS *m/z* (rel intensity) 284 ($[M]^+$, 20), 242 (100), 195 (53), 169 (64); HRMS $[M]^+$ calcd for $C_{18}H_{20}O_3$: 284.1412, found 284.1415.

Ethyl 1-acetyl-4-(4-methoxyphenyl)-2-methylenecyclopent-3-enecarboxylate (6e). Following the general procedure, the title compound was obtained (155 mg, 82%). A white solid, mp 87-88 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 2.22 (s, 3 H), 3.25 (d, *J* = 17.4 Hz, 1 H), 3.60 (d, *J* = 17.4 Hz, 1 H), 3.77 (s, 3 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 5.19 (s, 1 H), 5.29 (s, 1 H), 6.44 (s, 1 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 7.40 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 25.5 (CH_3), 40.3 (CH_2), 55.1 (CH), 61.6 (CH_2), 68.8 (C), 109.0 (CH_2), 113.8 (CH x 2), 125.1 (CH), 127.0 (C), 127.1 (CH x 2), 145.2 (C), 150.6 (C), 159.8 (C), 170.3 (C), 202.4 (C); IR (neat) 2984, 1729, 1506 cm^{-1}; EI-MS *m/z* (rel intensity) 300 ($[M]^+$, 38), 258 (100), 229 (42), 185 (56); HRMS $[M]^+$ calcd for $C_{18}H_{20}O_4$: 300.1362, found 300.1356.

Ethyl 1-acetyl-4-(3-methoxyphenyl)-2-methylenecyclopent-3-enecarboxylate (6f). Following the general procedure, the title compound was obtained (157 mg, 83%). A yellow oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 2.21 (s, 3 H), 3.26 (d, *J* = 17.7 Hz, 1 H), 3.62 (d, *J* = 17.7 Hz, 1 H), 3.77 (s, 3 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 5.26 (s, 1 H), 5.35 (s, 1 H), 6.55 (s, 1 H), 6.83 (d, *J* = 8.1 Hz, 1 H), 6.93 (t, *J* = 2.1 Hz, 1 H),

7.07 (d, J = 8.1 Hz, 1 H), 7.25 (d, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 25.4 (CH_3), 40.2 (CH_2), 55.0 (CH_3), 61.8 (CH_2), 68.6 (C), 110.3 (CH_2), 111.2 (CH), 113.8 (CH), 118.3 (CH), 127.3 (CH), 129.3 (CH), , 135.6 (C), 145.3 (C), 150.3 (C), 159.5 (C), 170.2 (C), 202.1 (C); IR (neat) 2979, 1714, 1575 cm^{-1}; EI-MS *m/z* (rel intensity) 300 ([M]$^+$, 20), 258 (100), 211 (54), 185 (59); HRMS [M]$^+$ calcd for $C_{18}H_{20}O_4$: 300.1362, found 300.1368.

Ethyl 1-acetyl-2-methylene-4-phenylcyclopent-3-ene-1-carboxylate (6h). Following the general procedure, the title compound was obtained (172 mg, 85%). A yellow solid, mp 70-72 ^{o}C; TLC (EtOAc/hexanes (1:10)) R_f = 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, J = 7.2 Hz, 3 H), 2.27 (s, 3 H), 3.43 (d, J = 17.4 Hz, 1 H), 3.77 (d, J = 17.4 Hz, 1 H), 4.27 (q, J = 7.2 Hz, 2 H), 5.31 (s, 1 H), 5.41 (s, 1 H), 6.70 (s, 1 H), 7.45-7.48 (m, 2 H), 7.66 (dd, J = 8.7, 1.5 Hz, 1 H), 7.77-7.82 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 25.6 (CH_3), 40.3 (CH_2), 61.8 (CH_2), 68.9 (C), 110.5 (CH_2), 123.6 (CH), 125.2 (CH), 126.4 (CH), 126.5 (CH), 127.6 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 131.8 (C), 133.2 (C), 133.3 (C), 145.5 (C), 150.5 (C), 170.4 (C), 202.3 (C); IR (neat) 2979, 1737, 1704 cm^{-1}; EI-MS *m/z* (rel intensity) 320 ([M]$^+$, 35), 278 (100), 231 (55), 205 (67); HRMS [M]$^+$ calcd for $C_{21}H_{20}O_3$: 320.1412, found 320.1419.

Ethyl 1-benzoyl-4-(4-bromophenyl)-2-methylenecyclopent-3-ene-1-carboxylate (7a). Following the general procedure, the title compound was obtained (215 mg, 83%). A yellow oil; TLC (EtOAc/hexanes (1:9)) R_f = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, J = 7.2 Hz, 3 H), 3.21 (d, J = 17.4 Hz, 1 H), 4.10 (d, J = 17.4 Hz, 1 H), 4.12-4.22 (m, 2 H), 5.24 (s, 1 H), 5.49 (s, 1 H), 6.64 (s, 1 H), 7.30 (d, J = 8.7 Hz, 2 H), 7.40-7.45 (m, 4 H), 7.50-7.55 (m, 1 H), 7.85 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6 (CH_3), 42.0 (CH_2), 62.0 (CH_2), 66.1 (C), 111.6 (CH_2), 122.3 (C), 127.2 (CH x 2), 127.9 (CH), 128.5 (CH x 2), 128.7 (CH x 2), 131.5 (CH x 2), 132.9 (CH), 133.3 (C), 134.6 (C), 143.4 (C), 150.5 (C), 170.9 (C), 193.8 (C); IR (neat) 2984, 1739, 1680 cm^{-1};

EI-MS *m/z* (rel intensity) 412 ($[M+2]^+$, 5), 410 ($[M]^+$, 5), 105 (100), 77 (15); HRMS $[M]^+$ calcd for $C_{22}H_{19}BrO_3$: 410.0518, found 410.0526.

Ethyl 4-(4-bromophenyl)-1-cyano-2-methylenecyclopent-3-ene-1-carboxylate (7b). Following the general procedure, the title compound was obtained (182 mg, 80%). A yellow solid, mp 106-107 ^oC; TLC (EtOAc/hexanes (1:9)) R_f = 0.25; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.2 Hz, 3 H), 3.40 (d, *J* = 17.1 Hz, 1 H), 3.71 (d, *J* = 17.1 Hz, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 5.34 (s, 1 H), 5.42 (s, 1 H), 6.56 (s, 1 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 42.7 (CH_2), 48.7 (C), 63.4 (CH_2), 109.7 (CH_2), 119.2 (C), 123.1 (C), 125.5 (CH), 127.4 (CH x 2), 131.8 (CH x 2), 132.4 (C), 145.1 (C), 150.2 (C), 166.8 (C); IR (neat) 2991, 2257, 1739 cm^{-1}; EI-MS *m/z* (rel intensity) 333 ($[M+2]^+$, 49), 331 ($[M]^+$, 48), 259 (92), 179 (100); HRMS $[M]^+$ calcd for $C_{16}H_{14}BrNO_2$: 331.0208, found 331.0200.

Allyl 1-acetyl-4-(4-bromophenyl)-2-methylenecyclopent-3-ene-1-carboxylate (7c). Following the general procedure, the title compound was obtained (185 mg, 81%). A yellow oil; TLC (EtOAc/hexanes (1:9)) R_f = 0.30; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 3 H), 3.27 (d, *J* = 17.7 Hz, 1 H), 3.60 (d, *J* = 17.7 Hz, 1 H), 4.66-4.69 (m, 2 H), 5.22-5.39 (m, 4 H), 5.84-5.97 (m, 1 H), 6.55 (s, 1 H), 7.32 (d, *J* = 8.7 Hz, 2 H), 7.45 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6 (CH_3), 40.1 (CH_2), 66.4 (CH_2), 68.8 (C), 111.1 (CH_2), 118.9 (CH_2), 122.5 (C), 127.3 (CH x 2), 127.6 (CH), 131.3 (CH), 131.6 (CH x 2), 133.2 (C), 144.4 (C), 150.1 (C), 169.9 (C), 201.8 (C); IR (neat) 3093, 2945, 1712 cm^{-1}; EI-MS *m/z* (rel intensity) 362 ($[M+2]^+$, 8), 360 ($[M]^+$, 9), 318 (33), 152 (100); HRMS $[M]^+$ calcd for $C_{18}H_{17}BrO_3$: 360.0361, found 360.0368.

Dimethyl 4-(4-bromophenyl)-2-methylenecyclopent-3-ene-1,1-dicarboxylate (7d). Following the general procedure, the title compound was obtained (170 mg, 81%). A yellow solid, mp 89-90 ^oC; TLC (EtOAc/hexanes (1:9)) R_f = 0.28; ^1H NMR (300 MHz, $CDCl_3$) δ 3.50 (s, 2 H),

3.75 (s, 6 H), 5.32 (s, 1 H), 5.36 (s, 1 H), 6.53 (s, 1 H), 7.29 (d, J = 8.7 Hz, 2 H), 7.43 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6 (CH_3), 42.0 (CH_2), 62.0 (CH_2), 66.1 (C), 111.6 (CH_2), 122.3 (C), 127.2 (CH x 2), 127.9 (CH), 128.5 (CH x 2), 128.7 (CH x 2), 131.5 (CH x 2), 132.9 (CH), 133.3 (C), 134.6 (C), 143.4 (C), 150.5 (C), 170.9 (C), 193.8 (C); IR (neat) 2951, 1726, 1270 cm^{-1}; EI-MS *m/z* (rel intensity) 352 ([M+2]$^+$, 66), 350 ([M]$^+$, 67), 290 (79), 152 (100); HRMS [M]$^+$ calcd for $C_{16}H_{15}BrO_4$: 350.0154, found 350.0145.

3-(4-Bromophenyl)-8,8-dimethyl-1-methylene-7,9-dioxaspiro[4.5]dec-2-ene-6,10-dione (7e). Following the general procedure, the title compound was obtained (164 mg, 74%). A yellow solid, mp 215-216 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (s, 3 H), 1.83 (s, 3 H), 3.51 (s, 2 H), 5.06 (s, 1 H), 5.25 (s, 1 H), 6.59 (s, 1 H), 7.32 (d, J = 8.7 Hz, 2 H), 7.47 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5 (CH_3), 30.6 (CH_3), 41.6 (CH_2), 56.6 (C) 105.2 (C), 107.5 (CH_2), 123.1 (C), 125.6 (CH), 127.6 (CH x 2), 131.7 (CH x 2), 132.6 (C), 146.8 (C), 155.1 (C), 168.8 (C x 2); IR (neat) 2917, 1739, 1291 cm^{-1}; EI-MS *m/z* (rel intensity) 364 ([M+2]$^+$, 22), 362 ([M]$^+$, 22), 276 (55), 152 (100); HRMS [M]$^+$ calcd for $C_{17}H_{15}BrO_4$: 362.0154, found 362.0160.

Ethyl 4-(4-bromophenyl)-2-methylcyclopenta-1,3-dienecarboxylate (8b). To a solution of **6b** (349 mg, 1.0 mmol) in EtOH (10 mL) was added NaOEt (75 mg, 1.1 mmol) at rt and the resulting mixture was stirred at rt for 15 min. Reaction was monitored by TLC until no starting material was observed and the reaction was concentrated. CH_2Cl_2 (15 mL), brine (15 mL) and H_2O (15 mL) were added and the mixture was transferred to a separatory funnel. The aqueous layer (upper layer) was back extracted with CH_2Cl_2 (15 mL x 2). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in a rotary evaporator. The residue was purified by silica gel chromatography using EtOAc/hexanes (1/200) as eluent to give the title product **8b** (231 mg, 75%). A white solid, mp 122-123 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.45; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 1.32 (t, *J* = 7.2 Hz, 3 H), 2.37 (m, 3 H), 3.66 (m, 2 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 6.74 (s, 1 H), 7.39 (d, *J* = 9.0 Hz, 2 H), 7.45 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4 (CH_3), 15.5 (CH_3), 42.0 (CH_2), 59.6 (CH_2), 121.9 (C), 127.0 (CH x 2), 128.2 (C), 131.8 (CH x 2), 132.4 (CH), 133.7 (C), 149.0 (C), 155.5 (C), 164.9 (C); IR (neat) 2993, 1675, 1478 cm^{-1}; EI-MS *m/z* (rel intensity) 308 ($[M+2]^+$, 99), 306 ($[M]^+$, 100), 235 (49), 154 (73); HRMS $[M]^+$ calcd for $C_{15}H_{15}BrO_2$: 306.0255, found 306.0264.

General procedure for the synthesis of cyclopentadienes 9 from acid promoted rearrangement reactions of methylenecyclopentenes 6. To a solution of **6** (0.3 mmol) in CH_2Cl_2 (0.6 mL) was added 12M HCl (30 μL) at rt and the resulting mixture was stirred at rt for 10 min. Reaction was monitored by TLC until no starting material was observed and H_2O (5 mL) was added. pH of the mixture was adjusted to 7 by 2N NaOH followed by addition of CH_2Cl_2 (5 mL). The mixture was transferred to a separatory funnel. The aqueous layer (upper layer) was back extracted with CH_2Cl_2 (5 mL x 2). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in a rotary evaporator. The residue was purified by silica gel chromatography using EtOAc/hexanes (1/50) as eluent to give the title product

(Z)-Ethyl 5-(1-hydroxyethylidene)-2-methyl-4-phenylcyclopenta-1,3-dienecarboxylate (9a). Following the general procedure, the title compound was obtained (74 mg, 91%). A light yellow solid, mp 69-70 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.2 Hz, 3 H), 1.91 (s, 3 H), 2.42 (s, 3 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 7.23-7.37 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3 (CH_3), 17.8 (CH_3), 23.8 (CH_3), 61.6 (CH_2), 113.8 (C), 118.3 (C), 127.0 (CH), 128.1 (CH), 129.0 (CH x 2), 129.1 (CH x 2), 139.8 (C), 146.9 (C), 148.2 (C), 170.9 (C), 176.4(C); IR (neat) 2974, 1714, 1595 cm^{-1}; EI-MS *m/z* (rel intensity) 270 ($[M]^+$, 16), 228 (100), 209 (37), 152 (33); HRMS $[M]^+$ calcd for $C_{17}H_{18}O_3$: 270.1256, found 270.1254.

Ethyl 5-acetyl-4-(4-bromophenyl)-2-methylcyclopenta-1,3-dienecarboxylate (9b). Following the general procedure, the title compound was obtained (97 mg, 93%). A white solid, mp 123-124 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3 H), 1.67 (s, 3 H), 2.46 (d, *J* = 2.1 Hz, 3 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 4.68 (d, *J* = 2.1 Hz, 1 H), 6.87 (s, 1 H), 7.39 (d, *J* = 9.0 Hz, 2 H), 7.44 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 15.4 (CH_3), 23.6 (CH_3), 60.1 (CH_2), 68.2 (CH), 123.0 (C), 128.0 (CH x 2), 128.1 (C), 131.7 (C), 132.0 (CH x 2), 135.1 (CH), 147.4 (C), 158.9 (C), 163.8 (C), 202.8 (C); IR (neat) 3082, 1714, 1667 cm^{-1}; EI-MS *m/z* (rel intensity) 350 ($[M+2]^+$, 15), 348 ($[M]^+$, 15), 306 (100), 152 (44); HRMS $[M]^+$ calcd for $C_{17}H_{17}BrO_3$: 348.0361, found 348.0370.

Ethyl 5-acetyl-4-(4-chlorophenyl)-2-methylcyclopenta-1,3-dienecarboxylate (9c). Following the general procedure, the title compound was obtained (85 mg, 93%). A white solid, mp 115-116 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3 H), 1.68 (s, 3 H), 2.46 (d, *J* = 2.1 Hz, 3 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 4.69 (s, 1 H), 6.86 (s, 1 H), 7.29 (d, *J* = 8.7 Hz, 2 H), 7.48 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 15.5 (CH_3), 23.6 (CH_3), 60.1 (CH_2), 68.3 (CH), 127.8 (CH x 2), 128.1 (C), 129.1 (CH x 2), 131.3 (C), 134.8 (C), 135.0 (CH), 147.5 (C), 159.0 (C), 163.5 (C), 202.9 (C); IR (neat) 2979, 1737, 1704 cm^{-1}; EI-MS *m/z* (rel intensity) 306 ($[M+2]^+$, 5), 304 ($[M]^+$, 15), 262 (100), 152 (43); HRMS $[M]^+$ calcd for $C_{17}H_{17}ClO_3$: 304.0866, found 304.0869.

Ethyl 5-acetyl-4-(4-methoxyphenyl)-2-methylcyclopenta-1,3-dienecarboxylate (9e). Following the general procedure, the title compound was obtained (81 mg, 90%). A light yellow solid, mp 90-91 ^{o}C; TLC (EtOAc/hexanes (1:9)) R_f = 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 1.66 (s, 3 H), 2.44 (d, *J* = 2.1 Hz, 3 H), 3.76 (s, 3 H), 4.10-4.27 (m, 2 H), 4.67 (d, *J* = 2.1 Hz, 1 H), 6.73 (s, 1 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 7.46 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 14.2 (CH_3), 15.5 (CH_3), 23.3 (CH_3), 55.2 (CH_3), 59.8 (CH_2), 68.2 (CH), 114.1 (CH x 2), 125.7 (C), 126.5 (C), 127.9 (CH x 2), 132.6 (CH), 148.8 (C), 159.6 (C), 160.1 (C), 164.0 (C), 203.3(C); IR (neat) 2985, 1708, 1672 cm^{-1}; EI-MS *m/z* (rel intensity) 300 ($[M]^+$, 23), 258 (100), 229 (39), 185 (23); HRMS $[M]^+$ calcd for $C_{18}H_{20}O_4$: 300.1362, found 300.1371.

Ethyl 5-acetyl-2-methyl-4-(naphthalen-2-yl)cyclopenta-1,3-dienecarboxylate (9h). Following the general procedure, the title compound was obtained (87 mg, 91%). A light yellow solid, mp 121-122 ^oC; TLC (EtOAc/hexanes (1:9)) R_f = 0.20; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3 H), 1.71 (s, 3 H), 2.50 (d, *J* = 2.1 Hz, 3 H), 4.16-4.32 (m, 2 H), 4.87 (d, *J* = 2.1 Hz, 1 H), 7.00 (s, 1 H), 7.42-7.48 (m, 2 H), 7.66 (dd, *J* = 8.4, 2.1 Hz, 1 H), 7.74-7.84 (m, 3 H), 8.00 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 15.5 (CH_3), 23.5 (CH_3), 60.0 (CH_2), 68.3 (CH), 123.8 (CH), 126.2 (CH), 126.6 (CH), 126.7 (CH), 127.5 (CH), 127.7 (C), 128.5 (CH), 128.6 (CH), 130.2 (C), 133.2 (C), 133.3 (C), 135.1 (CH), 148.9 (C), 159.3 (C), 164.0 (C), 203.2 (C); IR (neat) 2974, 1708, 1672 cm^{-1}; EI-MS *m/z* (rel intensity) 320 ($[M]^+$, 19), 278 (100), 232 (29), 202 (41); HRMS $[M]^+$ calcd for $C_{21}H_{20}O_3$: 320.1412, found 320.1420.

II. X-Ray Crystallographic Analyses

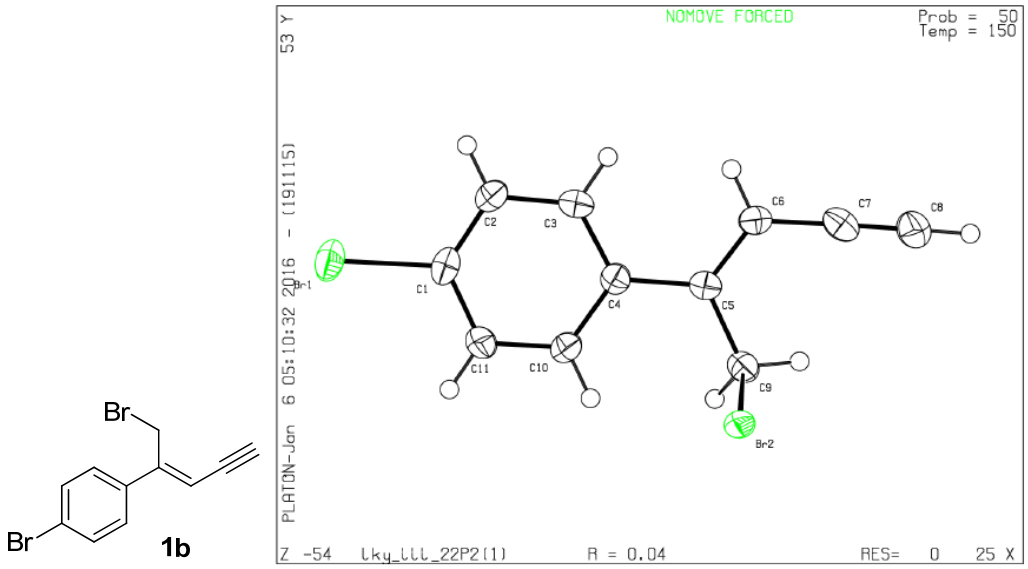


Table 1. Crystal data and structure refinement for **1b**.

Identification code	lky_iii_22801	
Empirical formula	C11 H8 Br2	
Formula weight	299.99	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 4.3644(3) Å	α= 90°.
	b = 15.4436(10) Å	β= 99.674(5)°.
	c = 7.8210(6) Å	γ = 90°.
Volume	519.66(6) $Å^3$	
Z	2	
Density (calculated)	1.917 Mg/m^3	
Absorption coefficient	7.748 mm^{-1}	
F(000)	288	
Crystal size	0.18 x 0.14 x 0.12 mm^3	
Theta range for data collection	2.64 to 28.27°.	
Index ranges	-5<=h<=5, -20<=k<=20, -10<=l<=10	
Reflections collected	7121	
Independent reflections	2531 [R(int) = 0.0333]	
Completeness to theta = 28.27°	100.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4566 and 0.3361
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2531 / 1 / 118
Goodness-of-fit on F^2	0.671
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1405
R indices (all data)	R1 = 0.0451, wR2 = 0.1476
Absolute structure parameter	0.98(3)
Largest diff. peak and hole	0.599 and -0.503 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for LKY_III_22801. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-10(2)	7007(1)	10588(1)	40(1)
Br(2)	3817(1)	3029(1)	6128(1)	28(1)
C(1)	739(14)	6308(4)	8696(9)	31(1)
C(2)	2312(17)	6645(5)	7457(10)	36(1)
C(3)	2799(16)	6103(4)	6100(9)	34(1)
C(4)	1778(14)	5247(4)	5952(7)	25(1)
C(5)	2376(13)	4681(4)	4518(8)	24(1)
C(6)	3972(14)	4946(4)	3275(8)	30(1)
C(7)	4657(16)	4420(5)	1923(8)	33(1)
C(8)	5227(17)	3959(5)	786(9)	40(2)
C(9)	1210(13)	3780(4)	4434(8)	28(1)
C(10)	187(16)	4945(4)	7232(9)	33(1)
C(11)	-323(16)	5459(5)	8624(9)	36(1)

Table 3. Bond lengths [Å] and angles [°] for LKY_III_22801.

Br(1)-C(1)	1.904(6)
Br(2)-C(9)	1.972(6)
C(1)-C(2)	1.380(10)
C(1)-C(11)	1.388(9)
C(2)-C(3)	1.396(10)
C(2)-H(2)	0.9300
C(3)-C(4)	1.394(9)
C(3)-H(3)	0.9300
C(4)-C(10)	1.391(9)
C(4)-C(5)	1.479(8)
C(5)-C(6)	1.351(9)
C(5)-C(9)	1.480(8)
C(6)-C(7)	1.405(10)
C(6)-H(6)	0.9300
C(7)-C(8)	1.198(11)
C(8)-H(8)	0.9300
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.395(9)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300

C(2)-C(1)-C(11)	122.0(6)
C(2)-C(1)-Br(1)	120.1(5)
C(11)-C(1)-Br(1)	117.9(5)
C(1)-C(2)-C(3)	117.7(6)
C(1)-C(2)-H(2)	121.2
C(3)-C(2)-H(2)	121.2
C(4)-C(3)-C(2)	123.0(6)
C(4)-C(3)-H(3)	118.5
C(2)-C(3)-H(3)	118.5
C(3)-C(4)-C(10)	116.7(6)
C(3)-C(4)-C(5)	121.9(5)
C(10)-C(4)-C(5)	121.4(5)
C(6)-C(5)-C(9)	117.9(6)

C(6)-C(5)-C(4)	123.0(5)
C(9)-C(5)-C(4)	119.1(5)
C(5)-C(6)-C(7)	124.6(6)
C(5)-C(6)-H(6)	117.7
C(7)-C(6)-H(6)	117.7
C(8)-C(7)-C(6)	178.8(7)
C(7)-C(8)-H(8)	180.0
C(5)-C(9)-Br(2)	111.6(4)
C(5)-C(9)-H(9A)	109.3
Br(2)-C(9)-H(9A)	109.3
C(5)-C(9)-H(9B)	109.3
Br(2)-C(9)-H(9B)	109.3
H(9A)-C(9)-H(9B)	108.0
C(11)-C(10)-C(4)	122.4(6)
C(11)-C(10)-H(10)	118.8
C(4)-C(10)-H(10)	118.8
C(1)-C(11)-C(10)	118.2(6)
C(1)-C(11)-H(11)	120.9
C(10)-C(11)-H(11)	120.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for LKY_III_22801. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	43(1)	36(1)	42(1)	-15(1)	10(1)	3(1)
Br(2)	34(1)	20(1)	31(1)	3(1)	11(1)	2(1)
C(1)	30(3)	29(3)	32(3)	-9(2)	2(2)	4(2)
C(2)	42(3)	25(3)	43(4)	-7(3)	14(3)	-6(2)
C(3)	41(3)	29(3)	34(3)	5(2)	13(2)	-5(3)
C(4)	28(3)	25(3)	20(2)	2(2)	0(2)	3(2)
C(5)	21(2)	26(3)	24(3)	4(2)	1(2)	0(2)
C(6)	34(3)	25(3)	31(3)	2(2)	7(2)	-4(2)
C(7)	32(3)	41(3)	28(3)	8(3)	7(2)	1(2)
C(8)	48(4)	43(4)	29(3)	-1(3)	9(3)	-4(3)
C(9)	27(3)	33(3)	24(3)	0(2)	5(2)	-4(2)
C(10)	37(3)	25(3)	40(3)	-6(3)	14(3)	-6(2)
C(11)	42(4)	31(3)	41(4)	-1(3)	23(3)	0(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for LKY_III_22801.

	x	y	z	U(eq)
H(2)	3023	7214	7525	43
H(3)	3853	6323	5256	41
H(6)	4668	5516	3318	36
H(8)	5670	3600	-96	48
H(9A)	1185	3553	3275	33
H(9B)	-906	3774	4664	33
H(10)	-565	4381	7157	40
H(11)	-1347	5239	9481	43

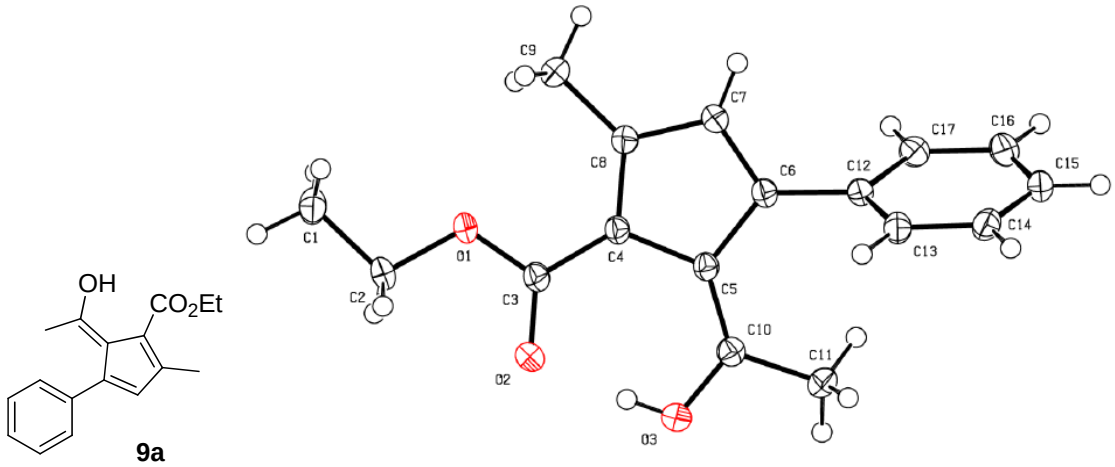


Table 1. Crystal data and structure refinement for **9a**.

Identification code	csh_3_14205	
Empirical formula	C17 H18 O3	
Formula weight	270.31	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 7.6236(2) Å	α= 90°.
	b = 6.9169(2) Å	β= 95.6170(10)°.
	c = 26.9337(7) Å	γ = 90°.
Volume	1413.44(7) $Å^3$	
Z	4	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	576	
Crystal size	0.18 x 0.14 x 0.12 mm^3	
Theta range for data collection	1.52 to 28.78°.	
Index ranges	-10<=h<=10, -9<=k<=9, -36<=l<=36	
Reflections collected	19971	
Independent reflections	3670 [R(int) = 0.0185]	
Completeness to theta = 28.78°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9897 and 0.9847	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3670 / 0 / 185	

Goodness-of-fit on F^2	1.137
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1393
R indices (all data)	R1 = 0.0442, wR2 = 0.1449
Largest diff. peak and hole	0.412 and -0.198 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for CSH_3_14205. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8369(1)	11445(1)	5414(1)	23(1)
O(3)	6614(1)	6045(1)	6063(1)	27(1)
C(4)	9537(1)	8956(1)	5933(1)	18(1)
C(8)	11242(1)	9714(1)	5974(1)	20(1)
C(6)	11339(1)	7048(1)	6486(1)	19(1)
C(12)	12036(1)	5731(1)	6892(1)	20(1)
C(10)	8233(1)	5844(1)	6278(1)	20(1)
C(3)	8025(1)	9836(1)	5657(1)	20(1)
C(7)	12315(1)	8532(2)	6314(1)	23(1)
C(9)	11944(1)	11460(2)	5732(1)	26(1)
C(5)	9555(1)	7194(1)	6244(1)	18(1)
C(13)	11337(1)	5791(1)	7352(1)	23(1)
C(17)	13447(1)	4500(2)	6834(1)	25(1)
C(15)	13400(2)	3372(2)	7680(1)	30(1)
C(1)	7554(2)	14145(2)	4894(1)	29(1)
C(14)	12021(2)	4627(2)	7744(1)	26(1)
C(16)	14112(2)	3313(2)	7227(1)	32(1)
C(11)	8423(1)	3963(1)	6554(1)	25(1)
O(2)	6486(1)	9233(1)	5644(1)	32(1)
C(2)	6862(1)	12409(2)	5146(1)	27(1)

Table 3. Bond lengths [Å] and angles [°] for CSH_3_14205.

O(1)-C(3)	1.3312(12)
O(1)-C(2)	1.4571(11)
O(3)-C(10)	1.3183(12)
C(4)-C(8)	1.3959(13)
C(4)-C(3)	1.4429(13)
C(4)-C(5)	1.4779(12)
C(8)-C(7)	1.4232(13)
C(8)-C(9)	1.4972(13)
C(6)-C(7)	1.3751(14)
C(6)-C(5)	1.4532(13)
C(6)-C(12)	1.4808(12)
C(12)-C(17)	1.3922(14)
C(12)-C(13)	1.3979(14)
C(10)-C(5)	1.3838(13)
C(10)-C(11)	1.4986(13)
C(3)-O(2)	1.2423(13)
C(13)-C(14)	1.3873(13)
C(17)-C(16)	1.3944(15)
C(15)-C(16)	1.3852(18)
C(15)-C(14)	1.3862(16)
C(1)-C(2)	1.5011(15)

C(3)-O(1)-C(2)	116.28(8)
C(8)-C(4)-C(3)	124.98(9)
C(8)-C(4)-C(5)	107.91(8)
C(3)-C(4)-C(5)	127.00(9)
C(4)-C(8)-C(7)	107.91(9)
C(4)-C(8)-C(9)	129.67(9)
C(7)-C(8)-C(9)	122.40(9)
C(7)-C(6)-C(5)	108.05(8)
C(7)-C(6)-C(12)	122.78(9)
C(5)-C(6)-C(12)	128.81(9)
C(17)-C(12)-C(13)	118.89(9)
C(17)-C(12)-C(6)	121.28(9)
C(13)-C(12)-C(6)	119.73(9)

O(3)-C(10)-C(5)	123.80(9)
O(3)-C(10)-C(11)	110.50(8)
C(5)-C(10)-C(11)	125.70(9)
O(2)-C(3)-O(1)	119.80(8)
O(2)-C(3)-C(4)	125.33(9)
O(1)-C(3)-C(4)	114.85(8)
C(6)-C(7)-C(8)	110.48(9)
C(10)-C(5)-C(6)	125.37(8)
C(10)-C(5)-C(4)	128.90(9)
C(6)-C(5)-C(4)	105.55(8)
C(14)-C(13)-C(12)	120.64(9)
C(16)-C(17)-C(12)	120.17(10)
C(16)-C(15)-C(14)	119.64(9)
C(13)-C(14)-C(15)	120.18(10)
C(15)-C(16)-C(17)	120.46(10)
O(1)-C(2)-C(1)	107.14(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for CSH_3_14205. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(1)	23(1)	25(1)	7(1)	-4(1)	2(1)
O(3)	21(1)	28(1)	31(1)	7(1)	-2(1)	-4(1)
C(4)	19(1)	19(1)	16(1)	2(1)	0(1)	1(1)
C(8)	20(1)	21(1)	20(1)	3(1)	1(1)	0(1)
C(6)	19(1)	21(1)	18(1)	2(1)	1(1)	2(1)
C(12)	19(1)	18(1)	22(1)	2(1)	-2(1)	0(1)
C(10)	21(1)	21(1)	18(1)	0(1)	2(1)	0(1)
C(3)	21(1)	22(1)	18(1)	2(1)	-1(1)	0(1)
C(7)	18(1)	26(1)	24(1)	6(1)	-1(1)	0(1)
C(9)	24(1)	26(1)	29(1)	8(1)	2(1)	-3(1)
C(5)	19(1)	19(1)	15(1)	1(1)	1(1)	2(1)
C(13)	25(1)	21(1)	22(1)	2(1)	0(1)	1(1)
C(17)	21(1)	24(1)	31(1)	4(1)	4(1)	2(1)
C(15)	26(1)	25(1)	35(1)	12(1)	-8(1)	-3(1)
C(1)	31(1)	27(1)	30(1)	9(1)	1(1)	5(1)
C(14)	31(1)	23(1)	22(1)	4(1)	-2(1)	-6(1)
C(16)	22(1)	27(1)	47(1)	10(1)	0(1)	6(1)
C(11)	26(1)	20(1)	27(1)	4(1)	2(1)	-3(1)
O(2)	20(1)	34(1)	40(1)	15(1)	-5(1)	-2(1)
C(2)	22(1)	28(1)	31(1)	10(1)	-5(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for CSH_3_14205.

	x	y	z	U(eq)
H(3)	6532	7072	5911	40
H(7)	13508	8735	6406	28
H(9A)	11671	11375	5377	39
H(9B)	13199	11523	5809	39
H(9C)	11413	12602	5854	39
H(13)	10405	6620	7397	27
H(17)	13947	4470	6533	30
H(15)	13844	2575	7941	36
H(1A)	8089	15018	5141	44
H(1B)	6601	14785	4700	44
H(1C)	8417	13741	4678	44
H(14)	11554	4688	8050	31
H(16)	15039	2476	7184	39
H(11A)	8101	4137	6887	37
H(11B)	9624	3533	6568	37
H(11C)	7665	3014	6385	37
H(2A)	6027	12802	5376	33
H(2B)	6269	11543	4901	33

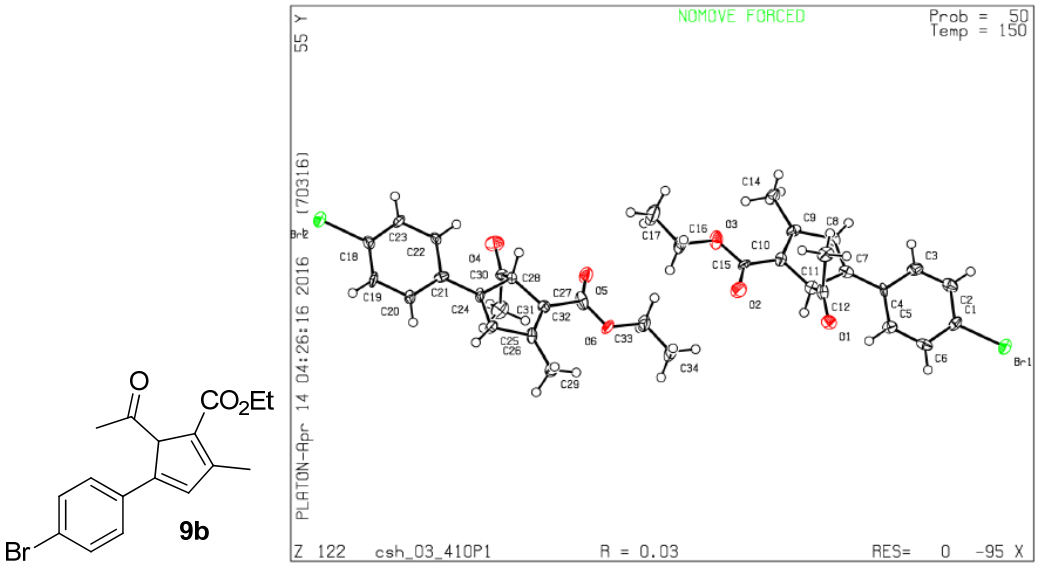


Table 1. Crystal data and structure refinement for **9b**.

Identification code	csh_03_4106	
Empirical formula	C34 H34 Br2 O6	
Formula weight	698.43	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.5076(6) Å	α= 94.761(4)°.
	b = 7.9269(6) Å	β= 94.576(4)°.
	c = 13.2339(10) Å	γ = 98.120(4)°.
Volume	773.64(10) $Å^3$	
Z	1	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	2.664 mm^{-1}	
F(000)	356	
Crystal size	0.16 x 0.14 x 0.12 mm^3	
Theta range for data collection	2.61 to 28.28°.	
Index ranges	-9<=h<=9, -10<=k<=10, -17<=l<=17	
Reflections collected	9113	
Independent reflections	5920 [R(int) = 0.0336]	
Completeness to theta = 28.28°	99.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7405 and 0.6752
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5920 / 3 / 385
Goodness-of-fit on F^2	0.763
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0951
R indices (all data)	R1 = 0.0336, wR2 = 0.0989
Absolute structure parameter	0.279(19)
Largest diff. peak and hole	0.415 and -0.569 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for CSH_03_4106. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-1944(1)	5589(1)	-4370(1)	30(1)
Br(2)	8505(1)	3012(1)	13173(1)	30(1)
C(1)	-1361(6)	5906(7)	-2930(4)	23(1)
C(2)	-2392(5)	6872(6)	-2322(4)	25(1)
C(4)	-549(5)	6374(5)	-847(3)	15(1)
C(5)	427(6)	5441(6)	-1464(4)	21(1)
C(6)	53(6)	5181(6)	-2489(4)	23(1)
C(3)	-1992(6)	7088(7)	-1310(4)	25(1)
C(11)	1574(5)	6229(6)	833(4)	18(1)
C(8)	-1170(5)	7219(6)	974(4)	21(1)
C(7)	-143(5)	6638(6)	245(4)	17(1)
C(10)	1322(6)	6672(6)	1912(3)	18(1)
C(9)	-296(6)	7247(6)	1989(4)	20(1)
O(1)	4221(4)	6647(5)	-77(3)	24(1)
C(12)	3282(6)	7300(7)	461(4)	21(1)
C(14)	-1136(6)	7816(8)	2919(4)	28(1)
C(15)	2767(6)	6538(6)	2673(3)	18(1)
C(17)	3187(9)	7045(12)	5437(5)	46(2)
C(16)	3913(6)	6763(9)	4410(4)	33(1)
C(13)	3614(7)	9215(6)	818(5)	27(1)
O(2)	4240(5)	6181(6)	2464(3)	36(1)
O(3)	2435(4)	6836(5)	3644(3)	29(1)
C(18)	7952(6)	2693(6)	11743(4)	20(1)
C(19)	8973(6)	1763(7)	11167(3)	26(1)
C(21)	7137(5)	2217(6)	9628(4)	20(1)
C(22)	6134(6)	3200(6)	10250(4)	19(1)
C(23)	6545(6)	3425(6)	11318(4)	21(1)
C(20)	8562(6)	1513(7)	10102(3)	22(1)
C(24)	6708(6)	1971(6)	8514(3)	19(1)
C(28)	4955(6)	2357(6)	8007(3)	17(1)
C(25)	7732(6)	1406(7)	7828(3)	20(1)
C(27)	5230(6)	1927(6)	6888(4)	19(1)

C(26)	6855(5)	1359(6)	6793(4)	20(1)
C(29)	7739(6)	792(7)	5891(4)	25(1)
O(4)	2317(4)	1930(5)	8910(3)	33(1)
C(30)	3310(6)	1300(6)	8337(4)	18(1)
C(32)	3748(6)	2098(7)	6101(4)	27(1)
C(34)	3349(9)	1466(10)	3389(5)	39(1)
C(33)	2645(7)	1747(8)	4385(4)	30(1)
C(31)	2929(8)	-519(8)	7984(5)	34(1)
O(5)	2321(5)	2454(6)	6348(3)	34(1)
O(6)	4141(4)	1720(5)	5161(3)	25(1)

Table 3. Bond lengths [Å] and angles [°] for CSH_03_4106.

Br(1)-C(1)	1.909(5)
Br(2)-C(18)	1.894(5)
C(1)-C(2)	1.413(7)
C(1)-C(6)	1.389(7)
C(2)-C(3)	1.341(8)
C(4)-C(3)	1.412(7)
C(4)-C(5)	1.378(7)
C(4)-C(7)	1.444(6)
C(5)-C(6)	1.356(8)
C(11)-C(10)	1.475(7)
C(11)-C(7)	1.540(6)
C(11)-C(12)	1.572(6)
C(8)-C(7)	1.372(7)
C(8)-C(9)	1.445(7)
C(10)-C(9)	1.364(6)
C(10)-C(15)	1.442(6)
C(9)-C(14)	1.492(7)
O(1)-C(12)	1.180(6)
C(12)-C(13)	1.531(7)
C(15)-O(2)	1.226(6)
C(15)-O(3)	1.338(6)
C(17)-C(16)	1.515(9)
C(16)-O(3)	1.453(6)
C(18)-C(23)	1.378(7)
C(18)-C(19)	1.368(7)
C(19)-C(20)	1.410(6)
C(21)-C(22)	1.418(7)
C(21)-C(20)	1.403(7)
C(21)-C(24)	1.474(6)
C(22)-C(23)	1.413(7)
C(24)-C(25)	1.326(7)
C(24)-C(28)	1.511(5)
C(28)-C(27)	1.529(7)
C(28)-C(30)	1.507(6)
C(25)-C(26)	1.466(6)

C(27)-C(26)	1.370(6)
C(27)-C(32)	1.491(6)
C(26)-C(29)	1.480(7)
O(4)-C(30)	1.230(6)
C(30)-C(31)	1.459(8)
C(32)-O(5)	1.209(6)
C(32)-O(6)	1.321(7)
C(34)-C(33)	1.470(9)
C(33)-O(6)	1.464(6)

C(2)-C(1)-C(6)	120.7(5)
C(2)-C(1)-Br(1)	119.3(4)
C(6)-C(1)-Br(1)	120.1(4)
C(1)-C(2)-C(3)	119.4(4)
C(3)-C(4)-C(5)	118.2(4)
C(3)-C(4)-C(7)	119.6(4)
C(5)-C(4)-C(7)	122.2(4)
C(6)-C(5)-C(4)	122.7(4)
C(5)-C(6)-C(1)	118.2(5)
C(2)-C(3)-C(4)	120.8(5)
C(10)-C(11)-C(7)	104.3(4)
C(10)-C(11)-C(12)	113.6(4)
C(7)-C(11)-C(12)	109.3(4)
C(7)-C(8)-C(9)	111.9(4)
C(8)-C(7)-C(4)	129.2(4)
C(8)-C(7)-C(11)	105.5(4)
C(4)-C(7)-C(11)	125.3(4)
C(9)-C(10)-C(11)	110.1(4)
C(9)-C(10)-C(15)	131.3(5)
C(11)-C(10)-C(15)	118.4(4)
C(10)-C(9)-C(14)	129.3(5)
C(10)-C(9)-C(8)	108.1(4)
C(14)-C(9)-C(8)	122.6(4)
O(1)-C(12)-C(13)	122.9(5)
O(1)-C(12)-C(11)	121.0(5)
C(13)-C(12)-C(11)	116.2(4)
O(2)-C(15)-O(3)	120.4(4)

O(2)-C(15)-C(10)	123.2(4)
O(3)-C(15)-C(10)	116.5(4)
C(17)-C(16)-O(3)	106.7(4)
C(15)-O(3)-C(16)	116.5(4)
C(23)-C(18)-C(19)	122.4(5)
C(23)-C(18)-Br(2)	118.7(4)
C(19)-C(18)-Br(2)	118.9(3)
C(20)-C(19)-C(18)	119.2(4)
C(22)-C(21)-C(20)	118.1(5)
C(22)-C(21)-C(24)	120.7(4)
C(20)-C(21)-C(24)	121.2(5)
C(21)-C(22)-C(23)	120.4(4)
C(18)-C(23)-C(22)	118.9(5)
C(19)-C(20)-C(21)	121.0(5)
C(25)-C(24)-C(21)	127.0(4)
C(25)-C(24)-C(28)	110.8(4)
C(21)-C(24)-C(28)	122.2(4)
C(27)-C(28)-C(24)	100.5(3)
C(27)-C(28)-C(30)	112.8(4)
C(24)-C(28)-C(30)	113.2(4)
C(24)-C(25)-C(26)	111.1(4)
C(26)-C(27)-C(32)	130.6(5)
C(26)-C(27)-C(28)	111.0(4)
C(32)-C(27)-C(28)	118.4(4)
C(27)-C(26)-C(25)	106.6(4)
C(27)-C(26)-C(29)	131.9(4)
C(25)-C(26)-C(29)	121.4(4)
O(4)-C(30)-C(31)	119.8(5)
O(4)-C(30)-C(28)	121.4(5)
C(31)-C(30)-C(28)	118.7(4)
O(5)-C(32)-O(6)	126.2(4)
O(5)-C(32)-C(27)	120.5(5)
O(6)-C(32)-C(27)	113.2(4)
O(6)-C(33)-C(34)	107.0(4)
C(32)-O(6)-C(33)	113.8(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for CSH_03_4106. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

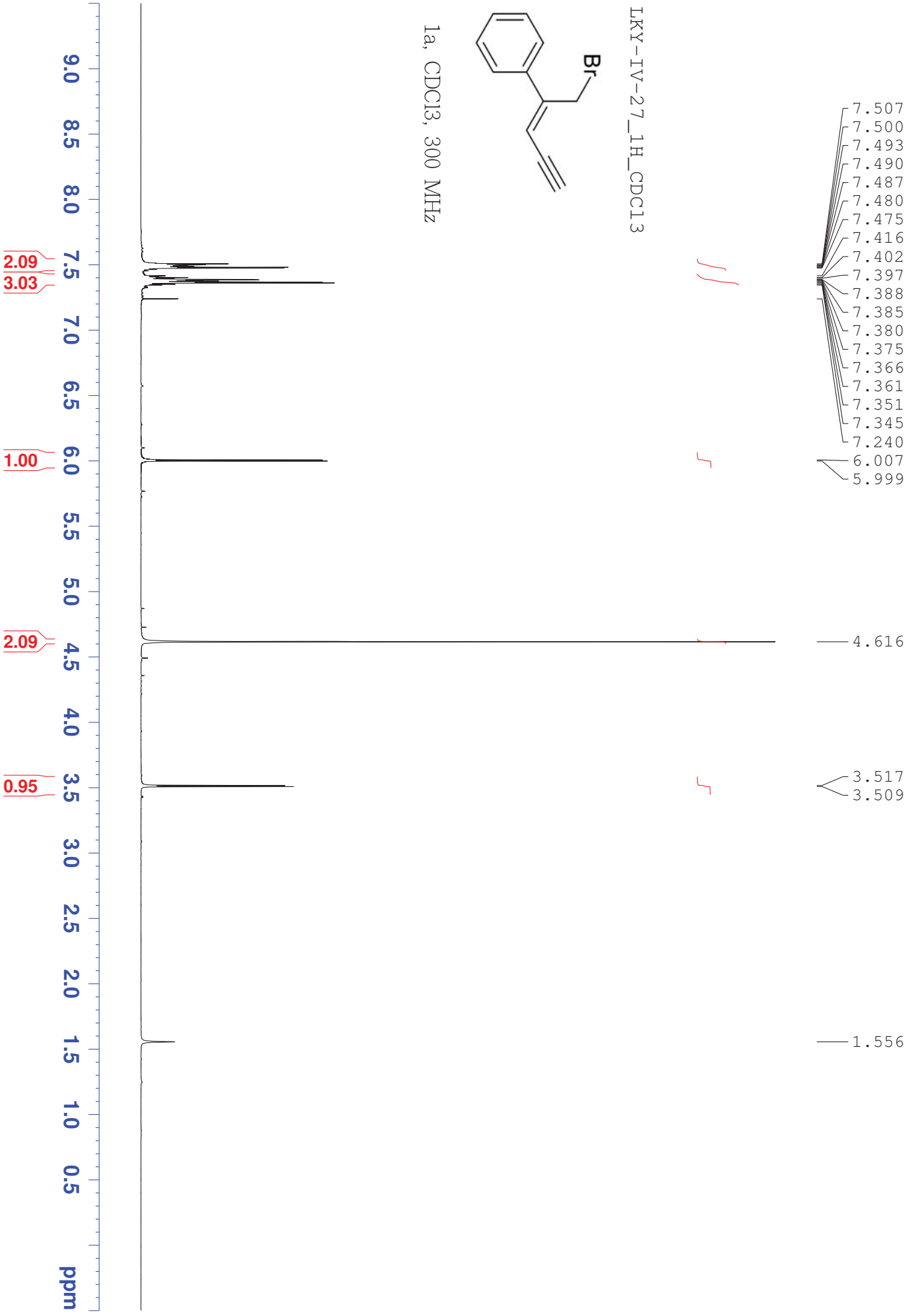
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	36(1)	38(1)	18(1)	0(1)	-2(1)	10(1)
Br(2)	37(1)	38(1)	16(1)	0(1)	-3(1)	11(1)
C(1)	22(2)	28(2)	15(2)	-5(2)	0(2)	-1(2)
C(2)	14(2)	26(2)	36(3)	1(2)	-3(2)	6(2)
C(4)	16(2)	12(2)	15(2)	8(2)	-4(1)	-2(2)
C(5)	15(2)	23(2)	24(2)	-3(2)	1(2)	2(2)
C(6)	18(2)	18(2)	35(3)	0(2)	2(2)	6(2)
C(3)	20(2)	31(3)	26(3)	-2(2)	9(2)	8(2)
C(11)	12(2)	19(2)	21(2)	2(2)	2(2)	-2(2)
C(8)	11(2)	22(2)	29(3)	8(2)	0(2)	-1(2)
C(7)	10(2)	16(2)	26(2)	3(2)	6(1)	0(1)
C(10)	19(2)	17(2)	16(2)	4(2)	1(2)	-4(2)
C(9)	23(2)	17(2)	19(2)	0(2)	10(2)	-1(2)
O(1)	18(2)	28(2)	28(2)	5(2)	8(1)	7(1)
C(12)	14(2)	27(2)	22(2)	9(2)	-2(2)	-1(2)
C(14)	19(2)	45(3)	20(3)	-2(2)	3(2)	4(2)
C(15)	27(2)	15(2)	12(2)	-2(2)	8(1)	5(2)
C(17)	40(3)	81(5)	21(3)	2(3)	-2(2)	20(3)
C(16)	24(2)	55(4)	18(2)	2(2)	-7(2)	7(2)
C(13)	37(2)	10(2)	30(3)	0(2)	6(2)	-9(2)
O(2)	28(2)	53(3)	28(2)	-5(2)	-2(2)	19(2)
O(3)	16(2)	47(2)	23(2)	8(2)	-3(1)	3(2)
C(18)	25(2)	17(2)	20(2)	6(2)	0(2)	4(2)
C(19)	29(2)	40(3)	8(2)	2(2)	-4(2)	11(2)
C(21)	14(2)	22(2)	22(2)	-6(2)	6(2)	1(2)
C(22)	27(2)	12(2)	18(2)	4(2)	-3(2)	4(2)
C(23)	29(2)	21(2)	11(2)	-3(2)	3(2)	3(2)
C(20)	20(2)	30(3)	16(2)	2(2)	-6(2)	8(2)
C(24)	22(2)	18(2)	13(2)	1(2)	-9(2)	0(2)
C(28)	21(2)	17(2)	13(2)	2(2)	-1(2)	5(2)
C(25)	19(2)	28(2)	14(2)	-1(2)	2(2)	4(2)
C(27)	17(2)	22(2)	18(2)	2(2)	1(2)	5(2)

C(26)	14(2)	27(2)	17(2)	6(2)	-3(2)	-1(2)
C(29)	24(2)	32(3)	19(2)	2(2)	3(2)	8(2)
O(4)	25(2)	37(2)	38(2)	0(2)	10(2)	5(2)
C(30)	17(2)	20(2)	17(2)	-2(2)	1(2)	6(2)
C(32)	14(2)	32(3)	31(3)	8(2)	-12(2)	-1(2)
C(34)	39(3)	57(4)	17(3)	-3(2)	-6(2)	8(3)
C(33)	28(2)	40(3)	20(2)	1(2)	-5(2)	9(2)
C(31)	29(2)	40(3)	31(3)	3(2)	8(2)	-2(2)
O(5)	29(2)	54(3)	20(2)	1(2)	-1(2)	18(2)
O(6)	26(2)	39(2)	11(2)	-5(1)	-1(1)	10(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for CSH_03_4106.

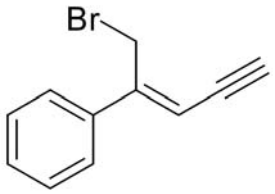
	x	y	z	U(eq)
H(2)	-3339	7353	-2622	30
H(5)	1382	4971	-1164	25
H(6)	726	4534	-2886	28
H(3)	-2673	7717	-907	30
H(11)	1644	5004	716	21
H(8)	-2294	7554	832	25
H(14A)	-619	7339	3497	42
H(14B)	-2415	7433	2828	42
H(14C)	-914	9043	3030	42
H(17A)	2410	6031	5566	70
H(17B)	2514	7989	5436	70
H(17C)	4175	7294	5959	70
H(16A)	4324	5657	4336	39
H(16B)	4920	7646	4342	39
H(13A)	4061	9847	279	40
H(13B)	4488	9424	1401	40
H(13C)	2502	9574	996	40
H(19)	9927	1301	11475	31
H(22)	5200	3701	9953	23
H(23)	5877	4056	11728	25
H(20)	9246	873	9708	26
H(28)	4876	3578	8137	20
H(25)	8858	1081	7982	24
H(29A)	6902	695	5294	37
H(29B)	8112	-300	5979	37
H(29C)	8777	1614	5815	37
H(34A)	3684	340	3312	58
H(34B)	4389	2304	3346	58
H(34C)	2433	1569	2857	58
H(33A)	2207	2841	4449	35
H(33B)	1655	851	4460	35

H(31A)	2606	-655	7262	51
H(31B)	1947	-1055	8323	51
H(31C)	3983	-1044	8135	51

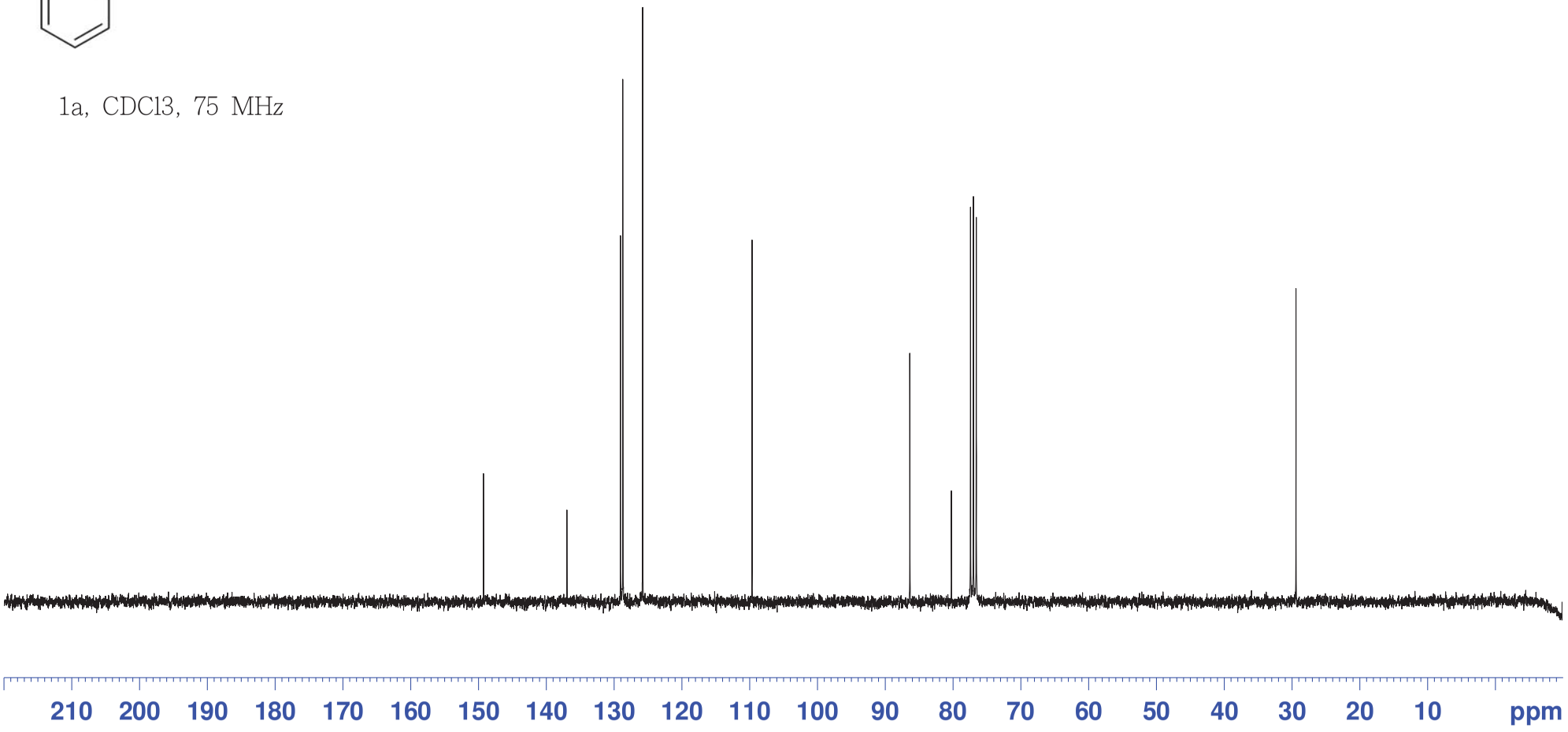

LKY-IV-27_1H_CDC13
1a, CDC13, 300 MHz
Br
7.507
7.500
7.493
7.490
7.487
7.480
7.475
7.416
7.402
7.397
7.388
7.385
7.380
7.375
7.366
7.361
7.351
7.345
7.240
6.007
5.999
4.616
3.517
3.509
1.556
2.09
3.03
1.00
2.09
0.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

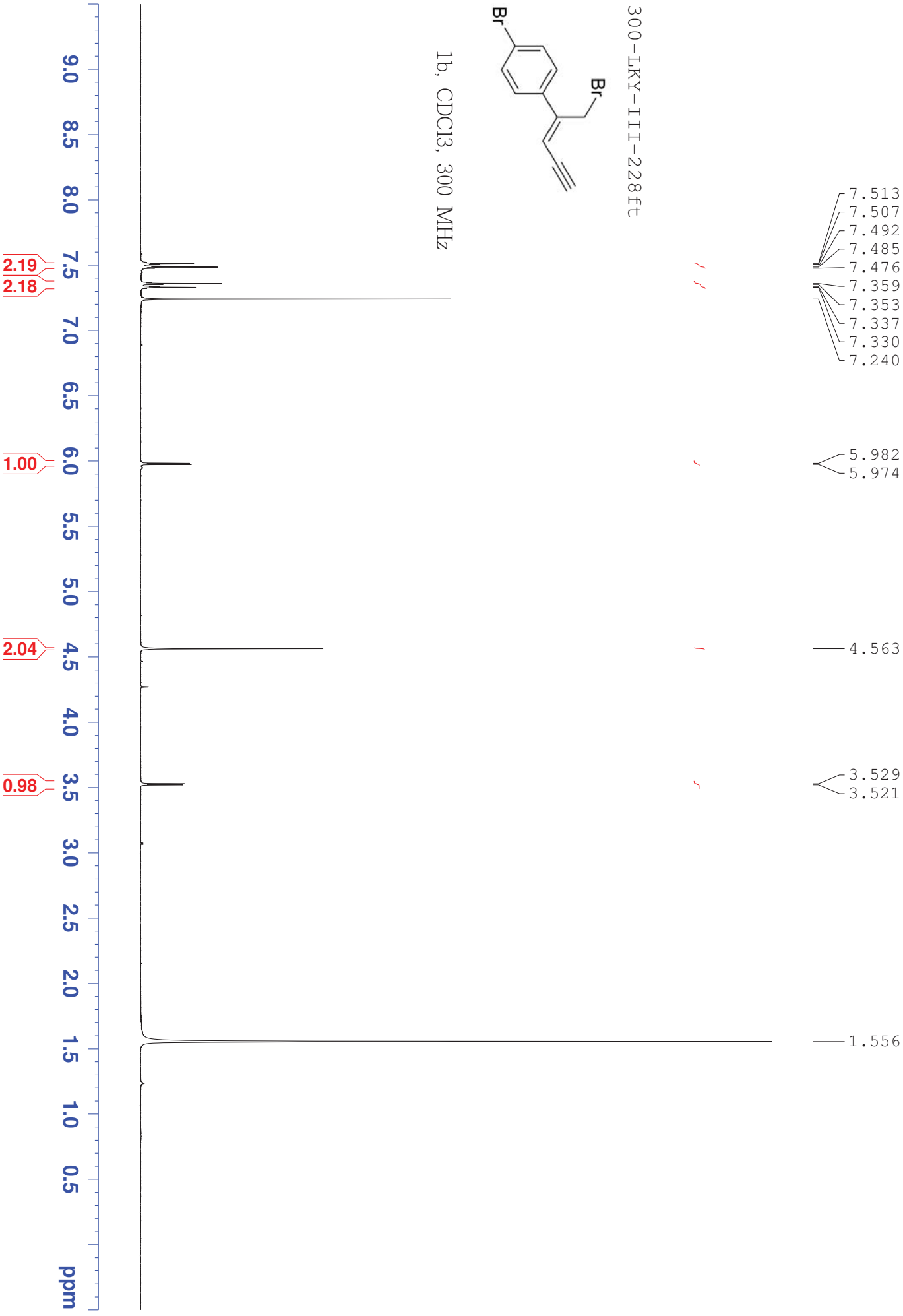
149.25
136.95
129.07
128.72
125.80
109.65
86.38
80.24
77.43
77.00
76.58
29.41

LKY-IV-27_13C_CDCl3



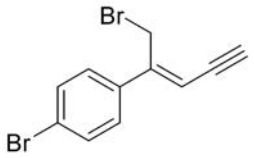
1a, CDCl3, 75 MHz



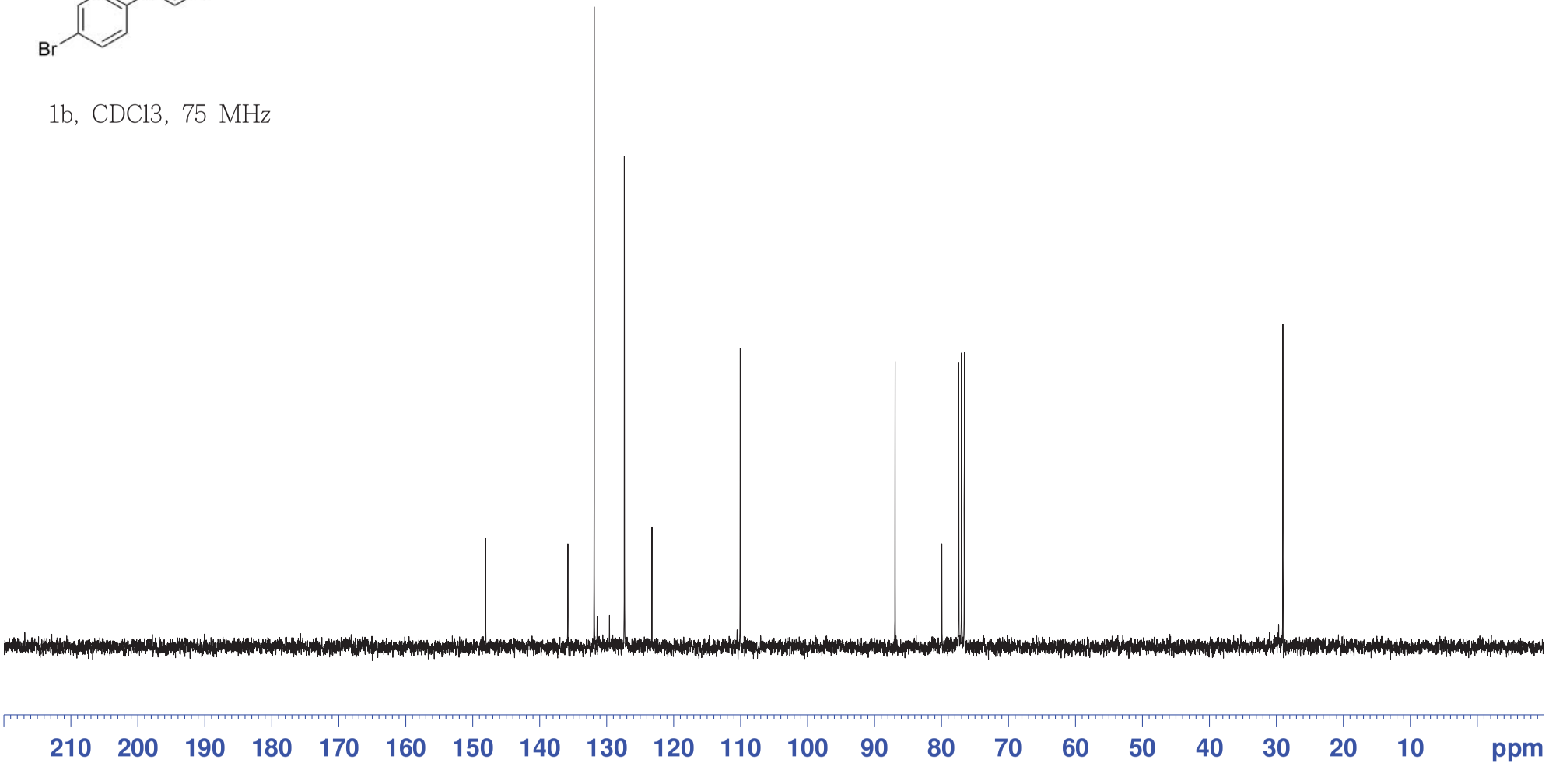

300-LKY-III-228ft
1b, CDCl3, 300 MHz
Br
Br
7.513
7.507
7.492
7.485
7.476
7.359
7.353
7.337
7.330
7.240
5.982
5.974
4.563
3.529
3.521
1.556
2.19
2.18
1.00
2.04
0.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

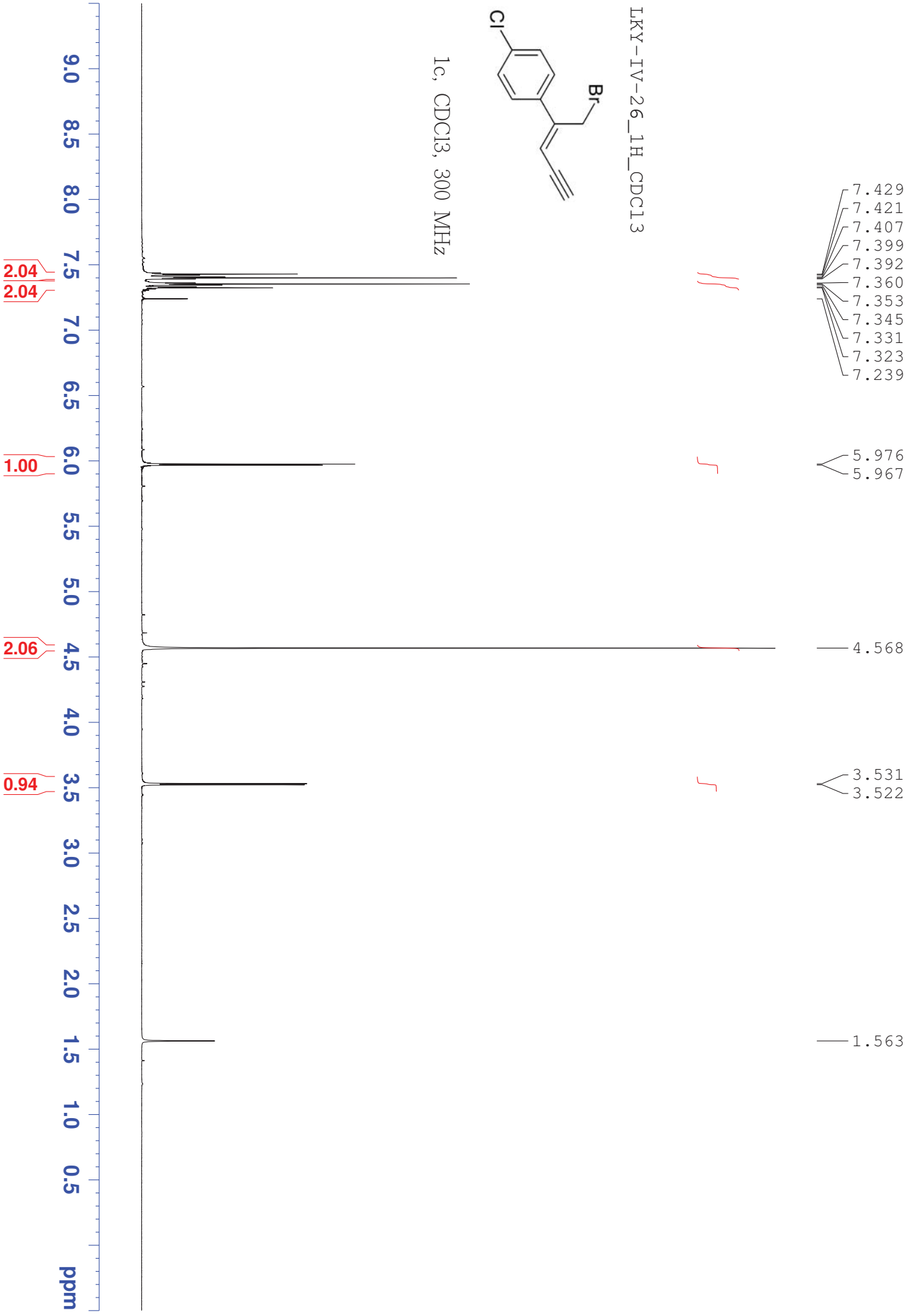
148.07
135.79
131.86
127.35
123.26
110.07
86.93
79.95
77.42
77.00
76.58
29.02

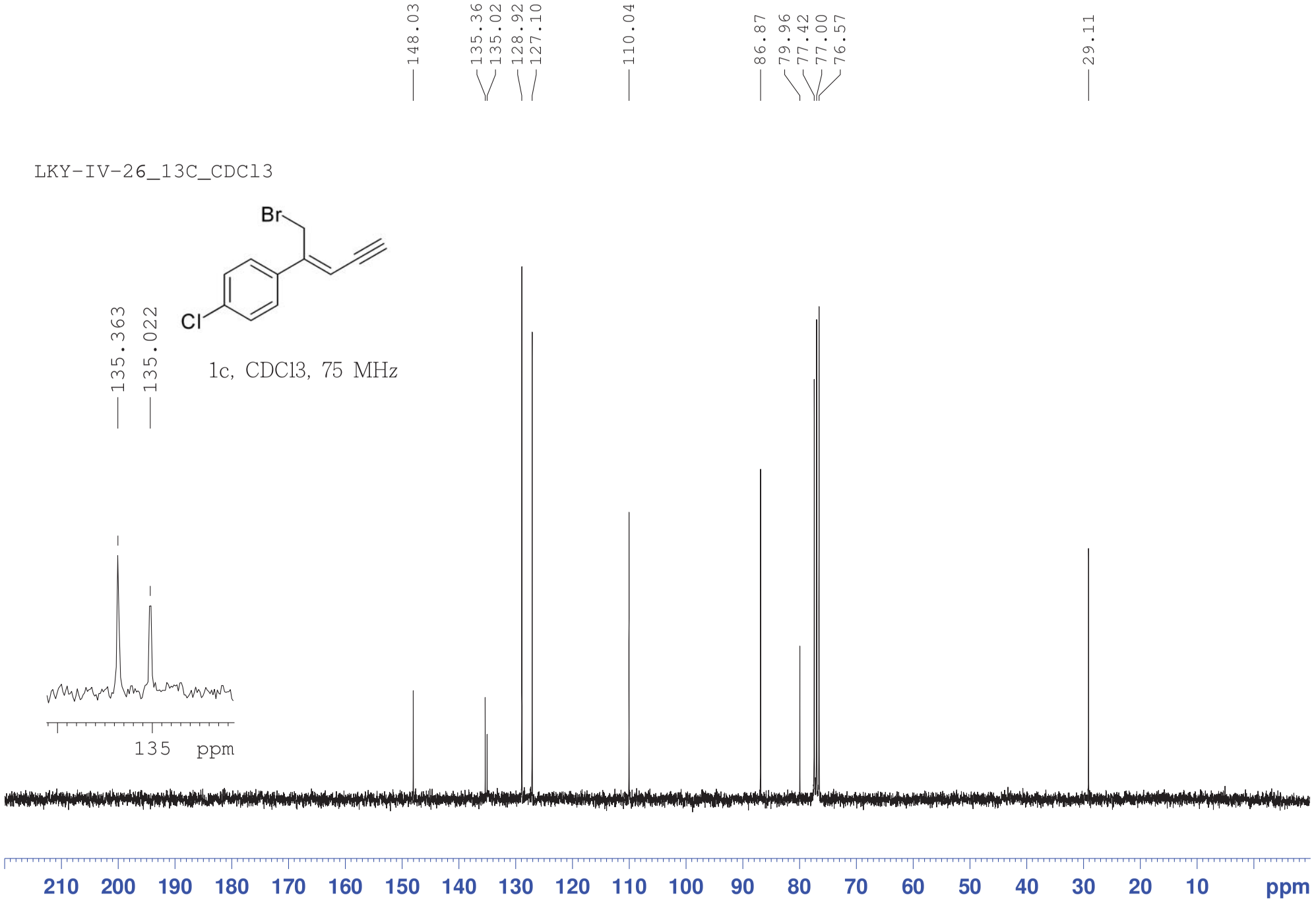
LKY-III-228_13C

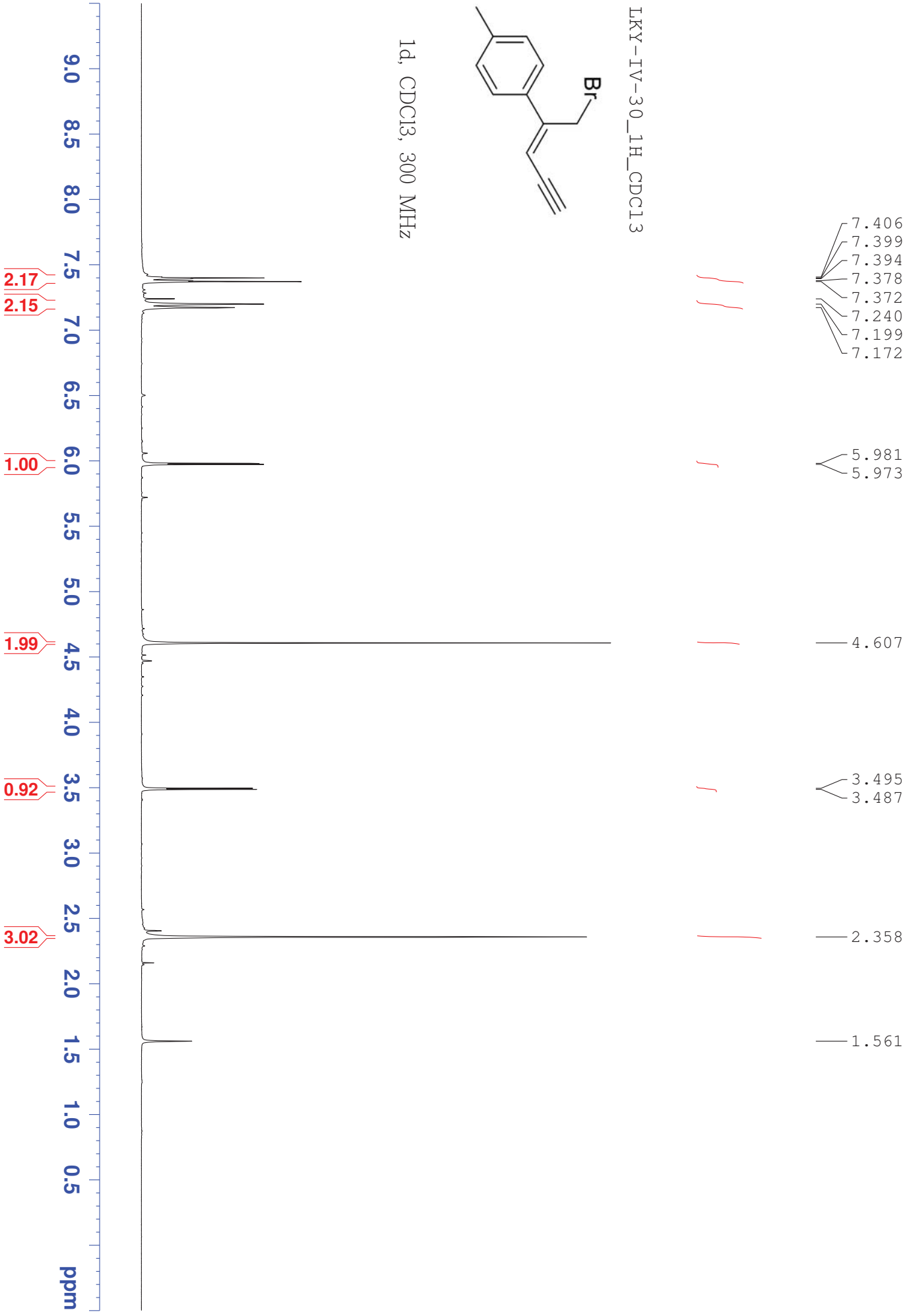


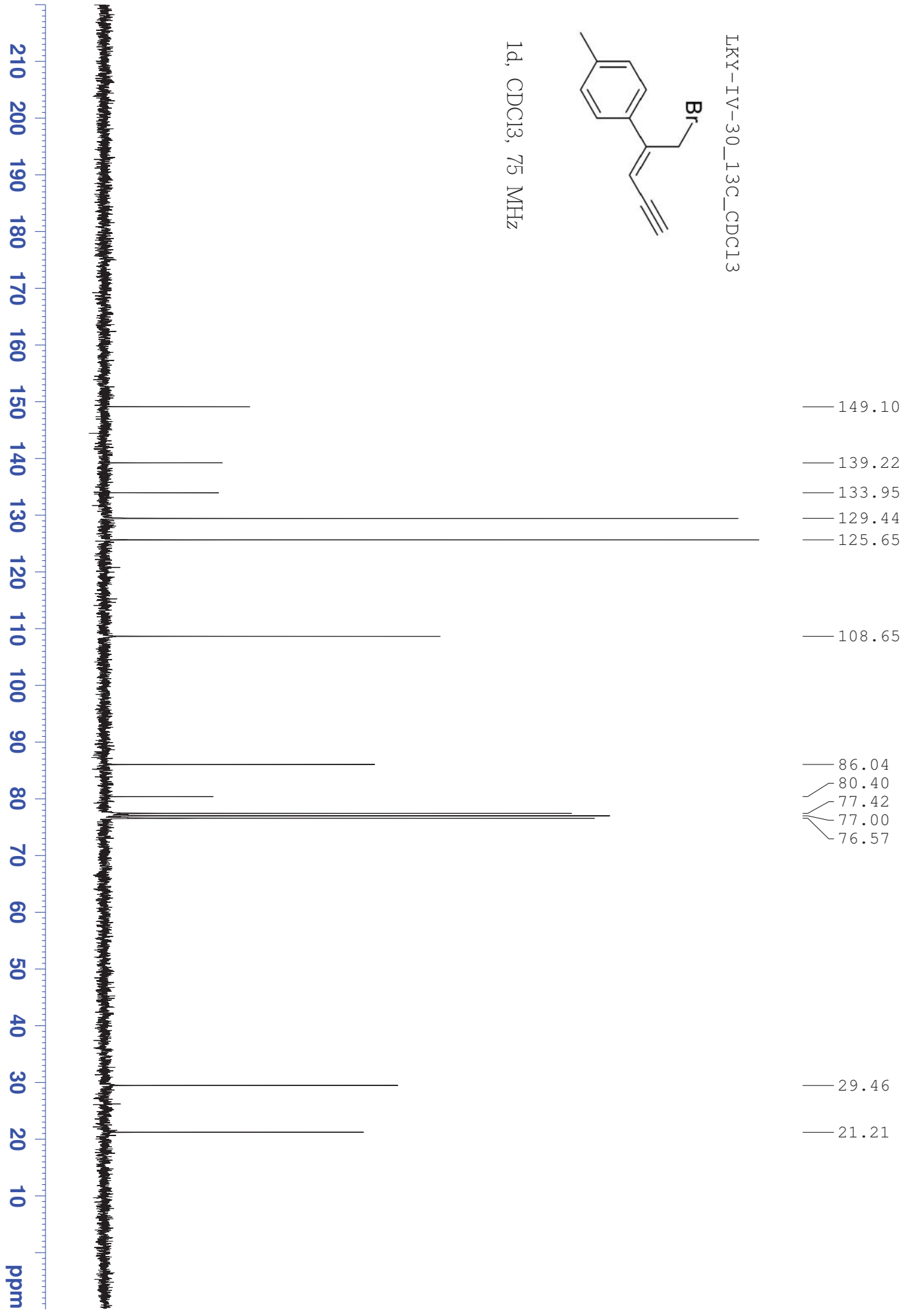
1b, CDCl3, 75 MHz

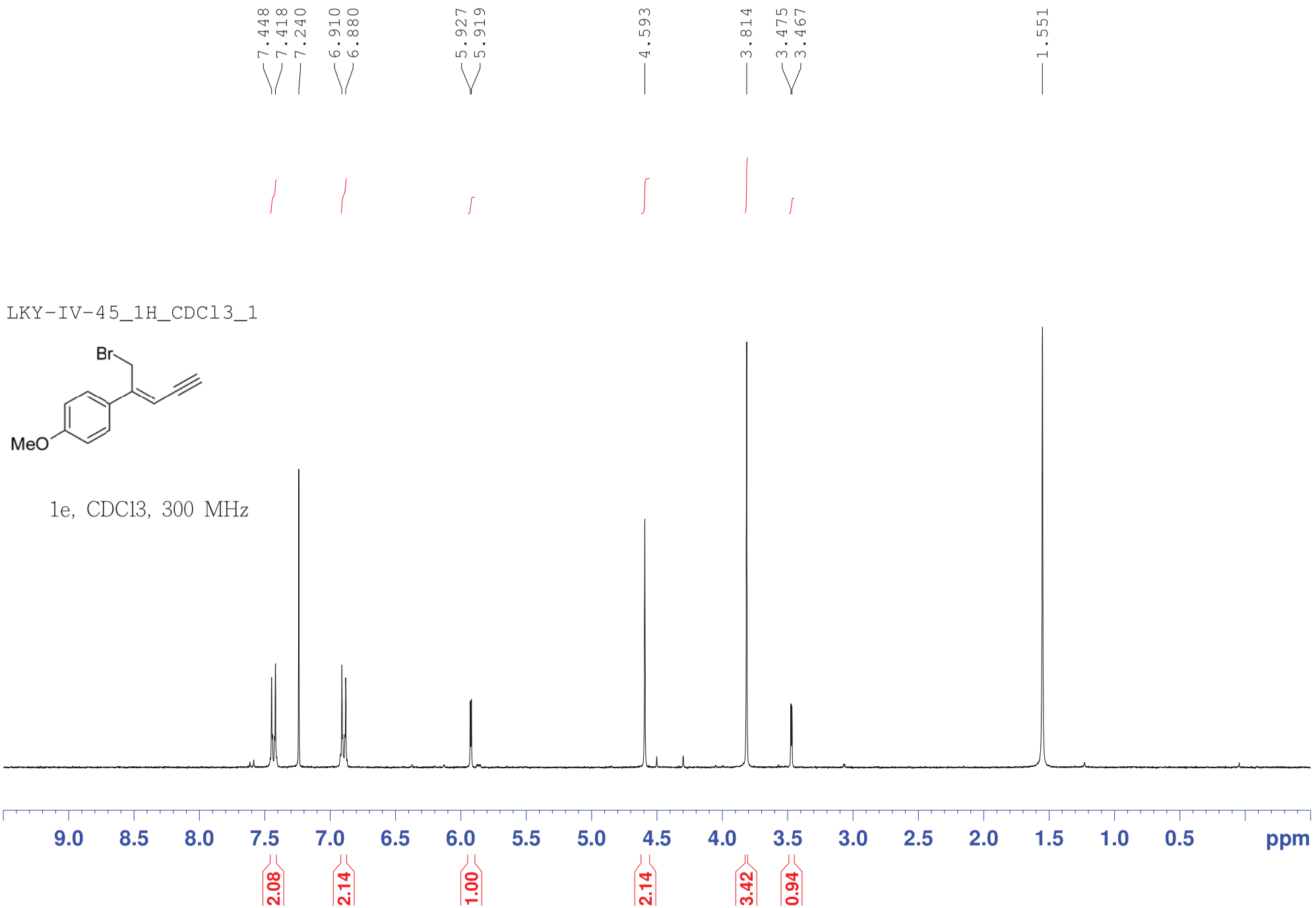



LKY-IV-26_1H_CDC13
1c, CDC13, 300 MHz
Cl
Br
7.429
7.421
7.407
7.399
7.392
7.360
7.353
7.345
7.331
7.323
7.239
5.976
5.967
4.568
3.531
3.522
1.563
2.04
2.04
1.00
2.06
0.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


148.03
135.36
135.02
128.92
127.10
110.04
86.87
79.96
77.42
77.00
76.57
29.11
LKY-IV-26_13C_CDCl3
Br
Cl
135.363
135.022
1c, CDCl3, 75 MHz
135 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

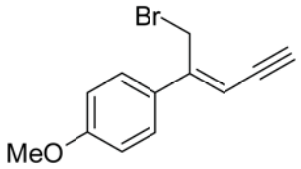

LKY-IV-30_1H_CDC13
1d, CDC13, 300 MHz
Br
7.406
7.399
7.394
7.378
7.372
7.240
7.199
7.172
5.981
5.973
4.607
3.495
3.487
2.358
1.561
2.17
2.15
1.00
1.99
0.92
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


LKY-IV-30_13C_CDC13
1d, CDCl3, 75 MHz
Br
149.10
139.22
133.95
129.44
125.65
108.65
86.04
80.40
77.42
77.00
76.57
29.46
21.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

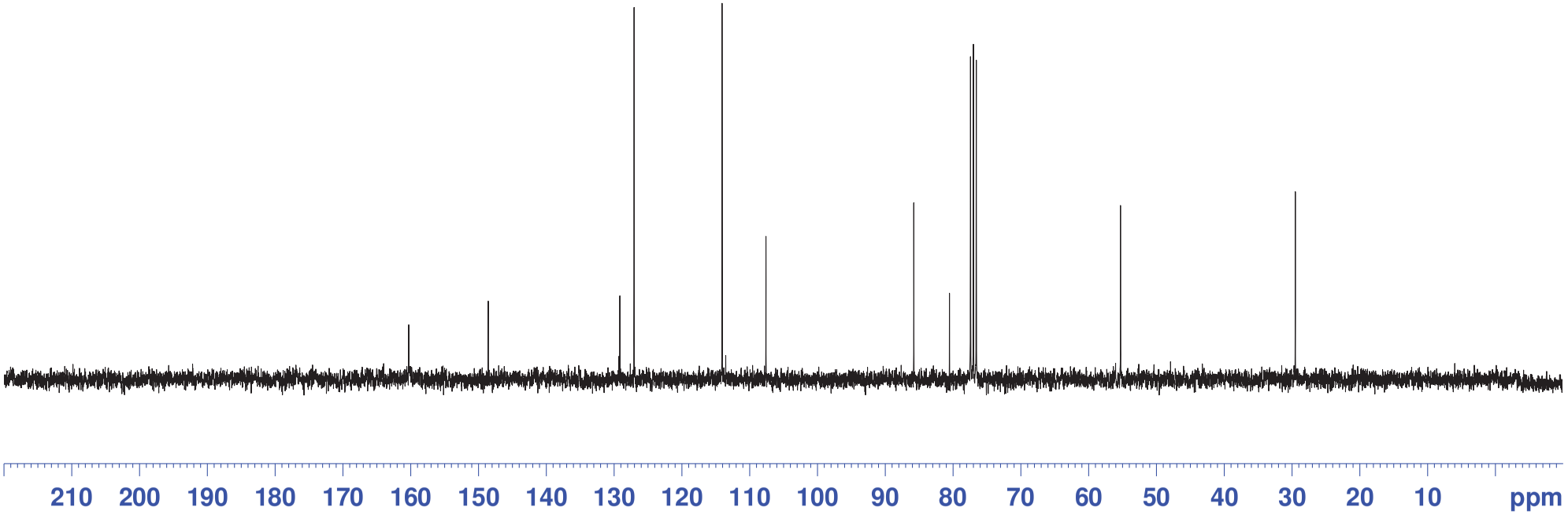

7.448
7.418
7.240
6.910
6.880
5.927
5.919
4.593
3.814
3.475
3.467
1.551
LKY-IV-45_1H_CDCl3_1
Br
MeO
1e, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.08
2.14
1.00
2.14
3.42
0.94

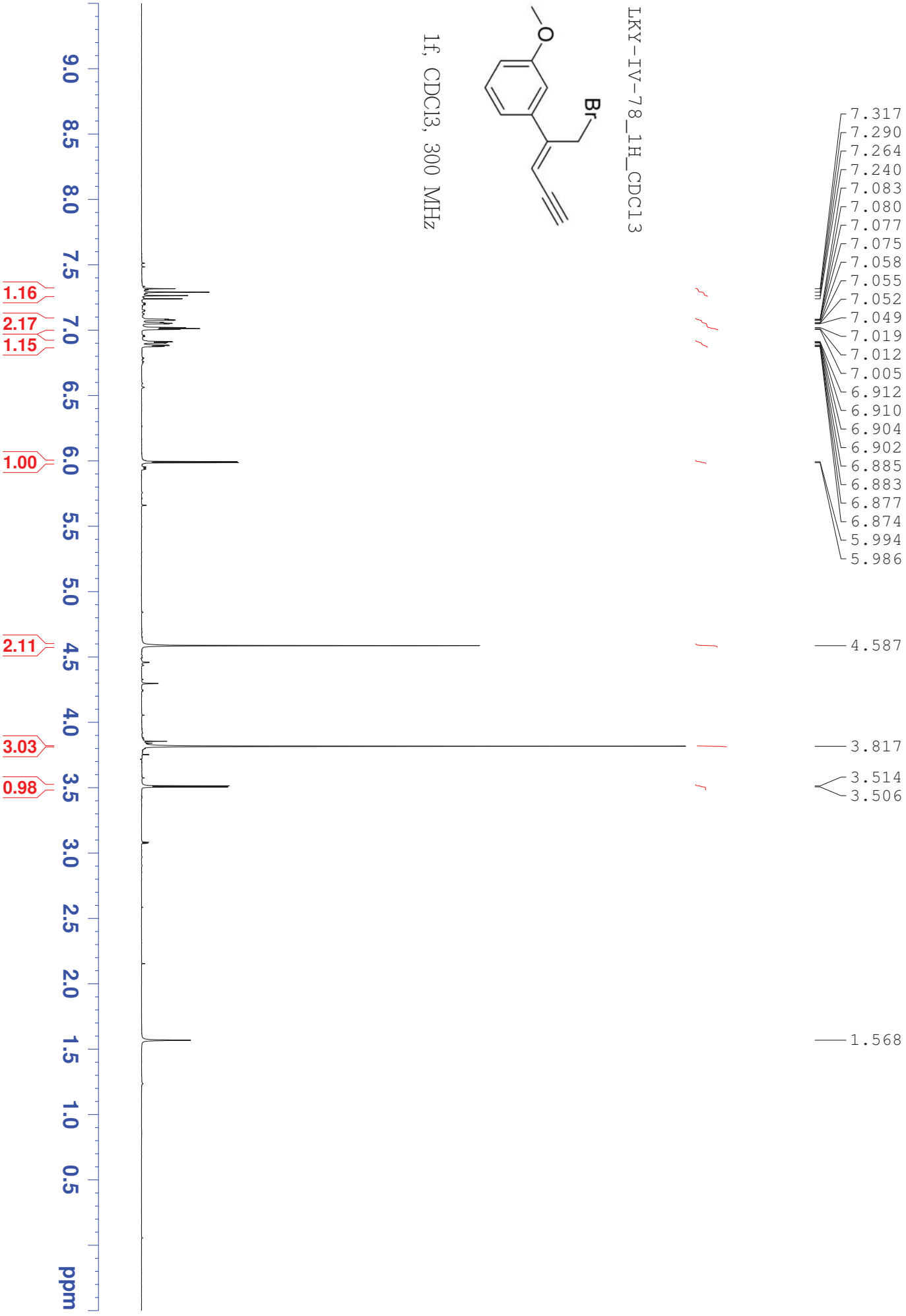
160.29
148.56
129.16
127.06
114.07
107.61
85.79
80.53
77.43
77.00
76.58
55.29
29.51

LKY-IV-45_13C_CDCl3



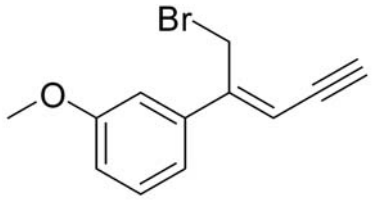
1e, CDCl3, 75 MHz



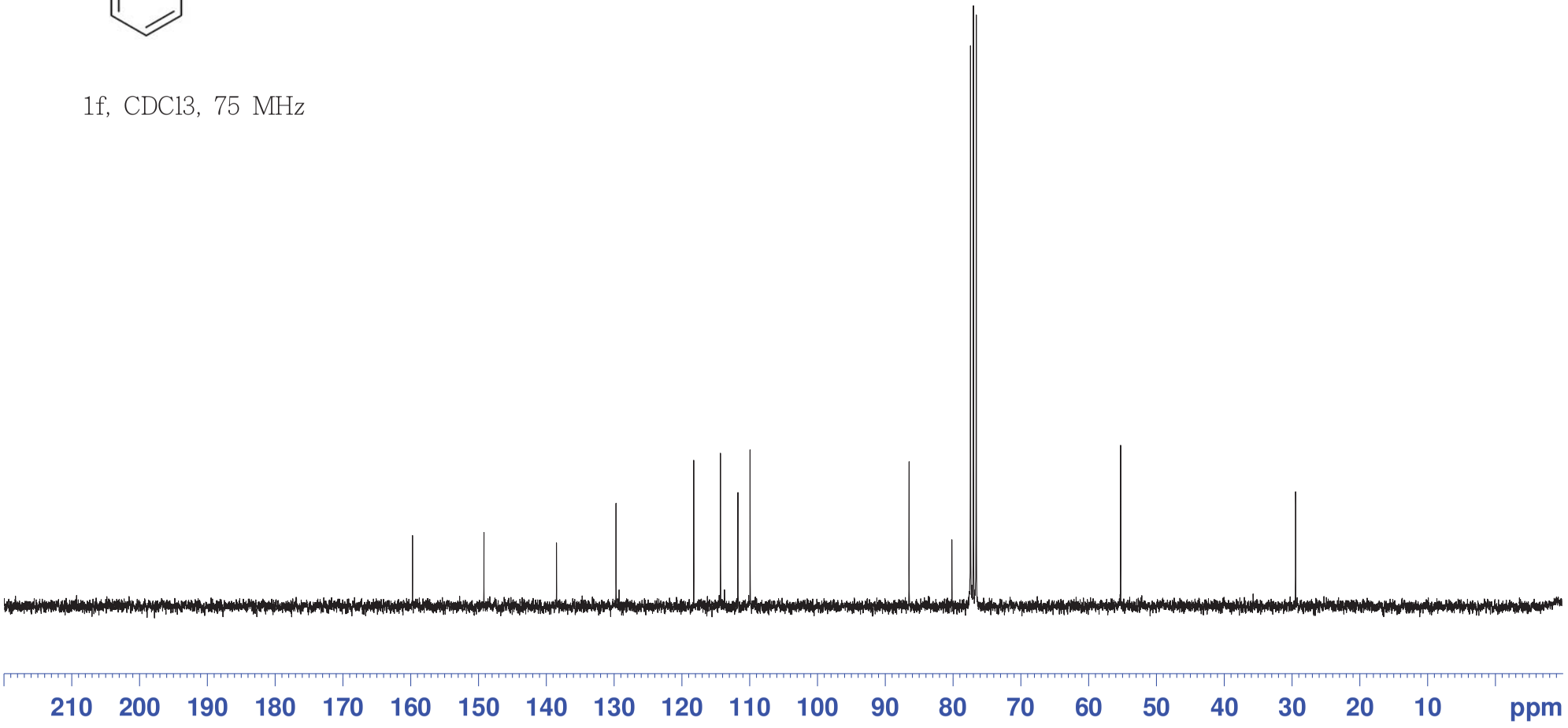

LKY-IV-78_1H_CDC13
1f, CDC13, 300 MHz
Br
O
7.317
7.290
7.264
7.240
7.083
7.080
7.077
7.075
7.058
7.055
7.052
7.049
7.019
7.012
7.005
6.912
6.910
6.904
6.902
6.885
6.883
6.877
6.874
5.994
5.986
4.587
3.817
3.514
3.506
1.568
1.16
2.17
1.15
1.00
2.11
3.03
0.98
ppm

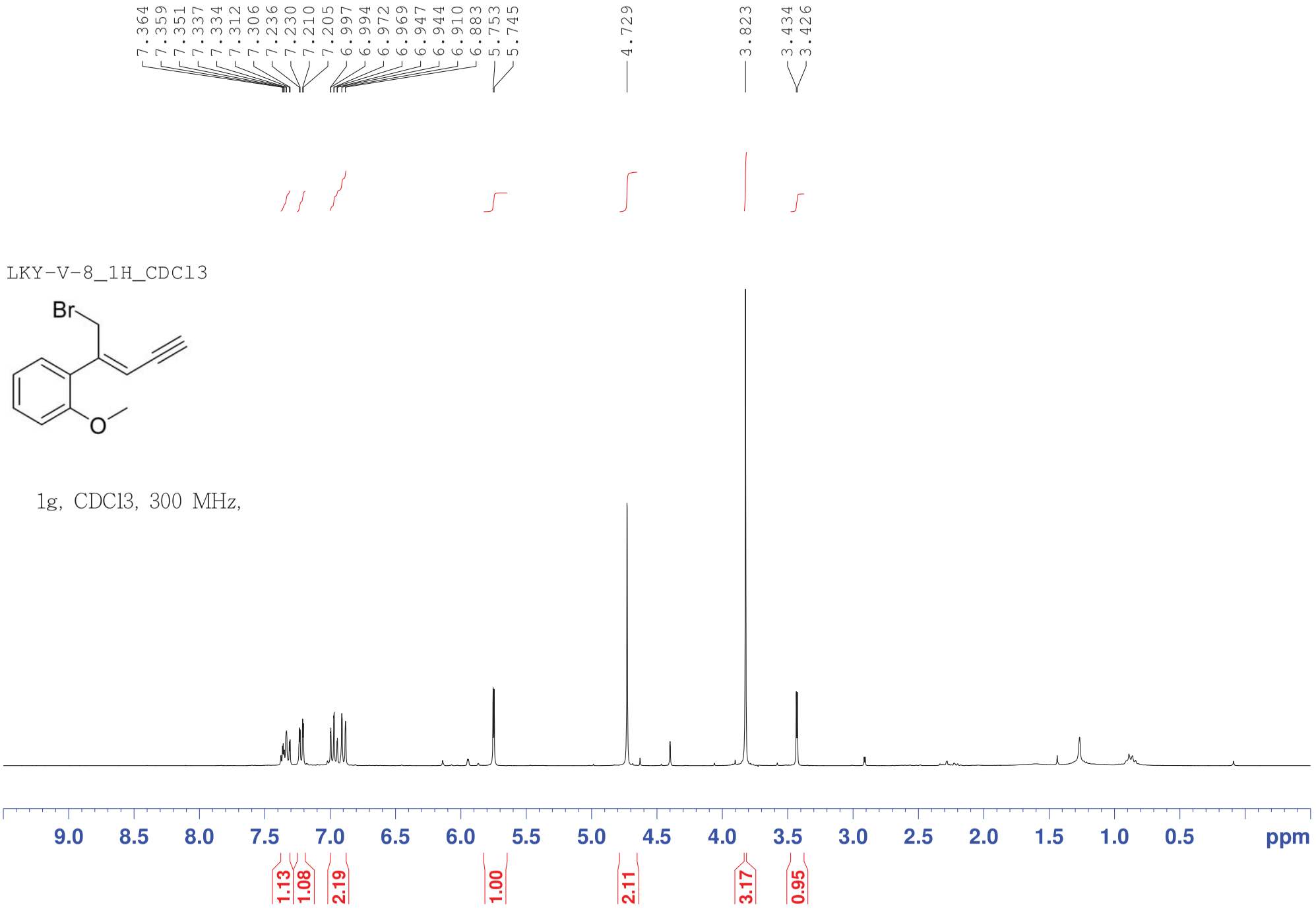
159.73
149.19
138.49
129.72
118.26
114.32
111.75
109.94
86.49
80.17
77.42
77.00
76.57
55.28
29.46

LKY-IV-78_13C_CDCl3



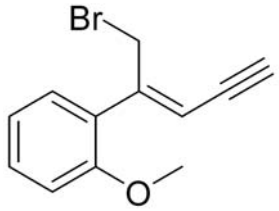
1f, CDCl3, 75 MHz



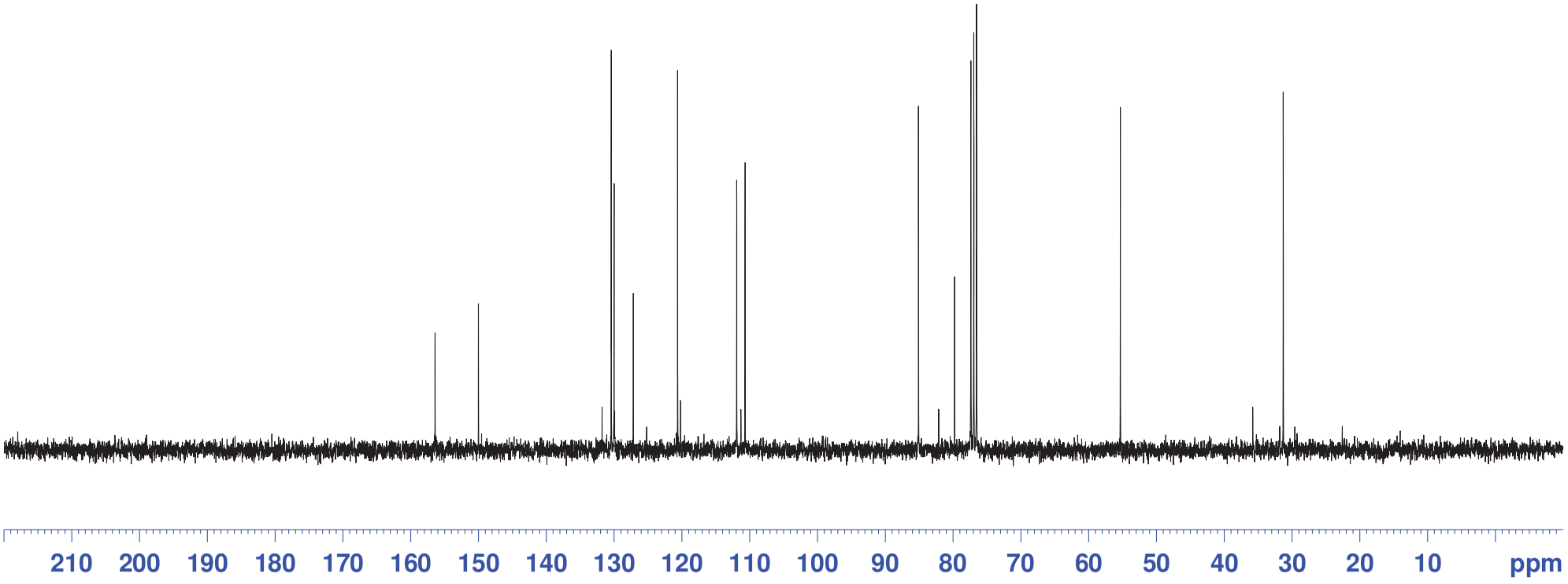

7.364
7.359
7.351
7.337
7.334
7.312
7.306
7.236
7.230
7.210
7.205
6.997
6.994
6.972
6.969
6.947
6.944
6.910
6.883
5.753
5.745
4.729
3.823
3.434
3.426
LKY-V-8_1H_CDCl3
Br
O
1g, CDCl3, 300 MHz,
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.13
1.08
2.19
1.00
2.11
3.17
0.95

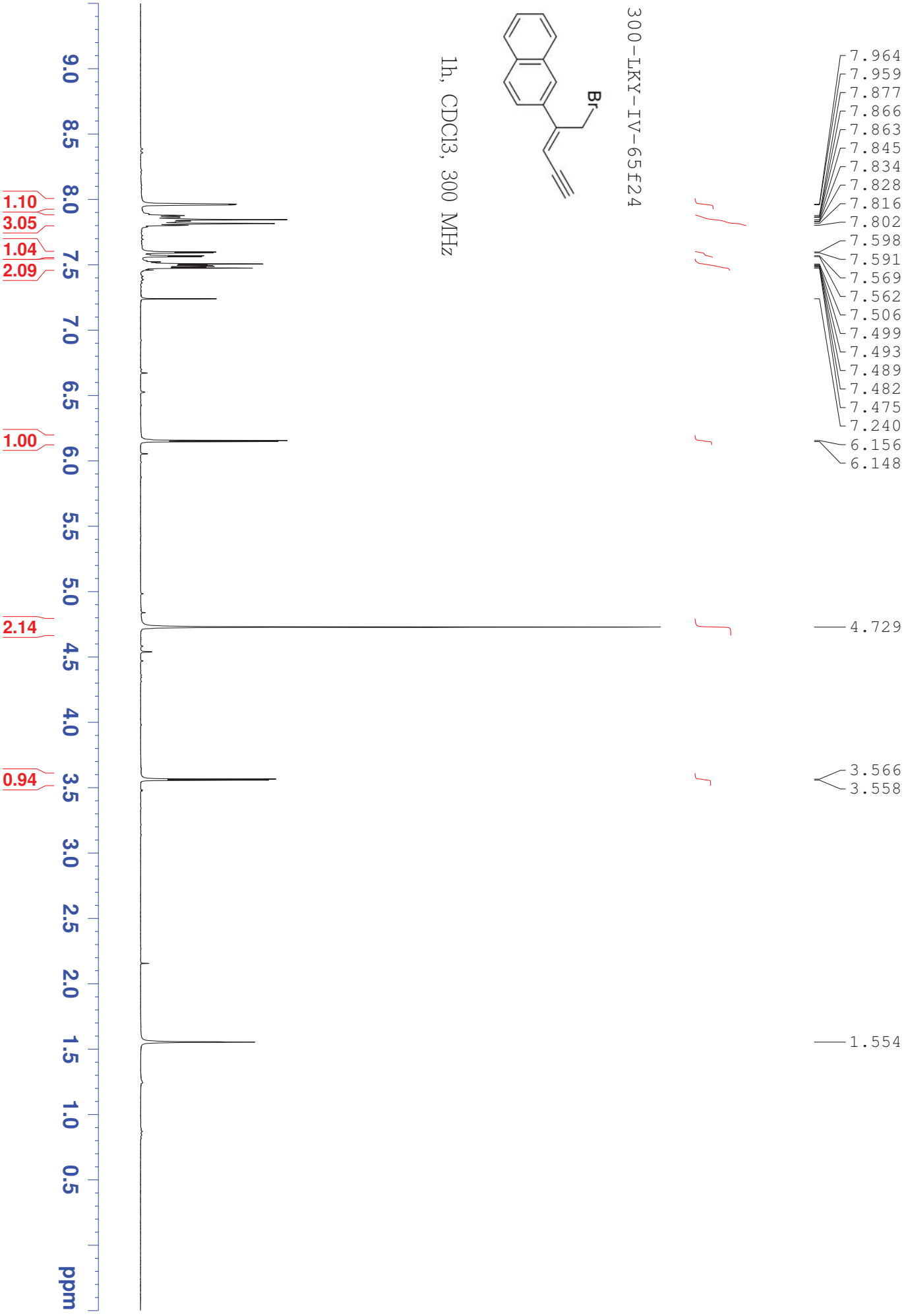
156.46
150.05
130.46
130.05
127.21
120.67
111.96
110.72
85.15
79.82
77.42
77.00
76.58
55.37
31.34

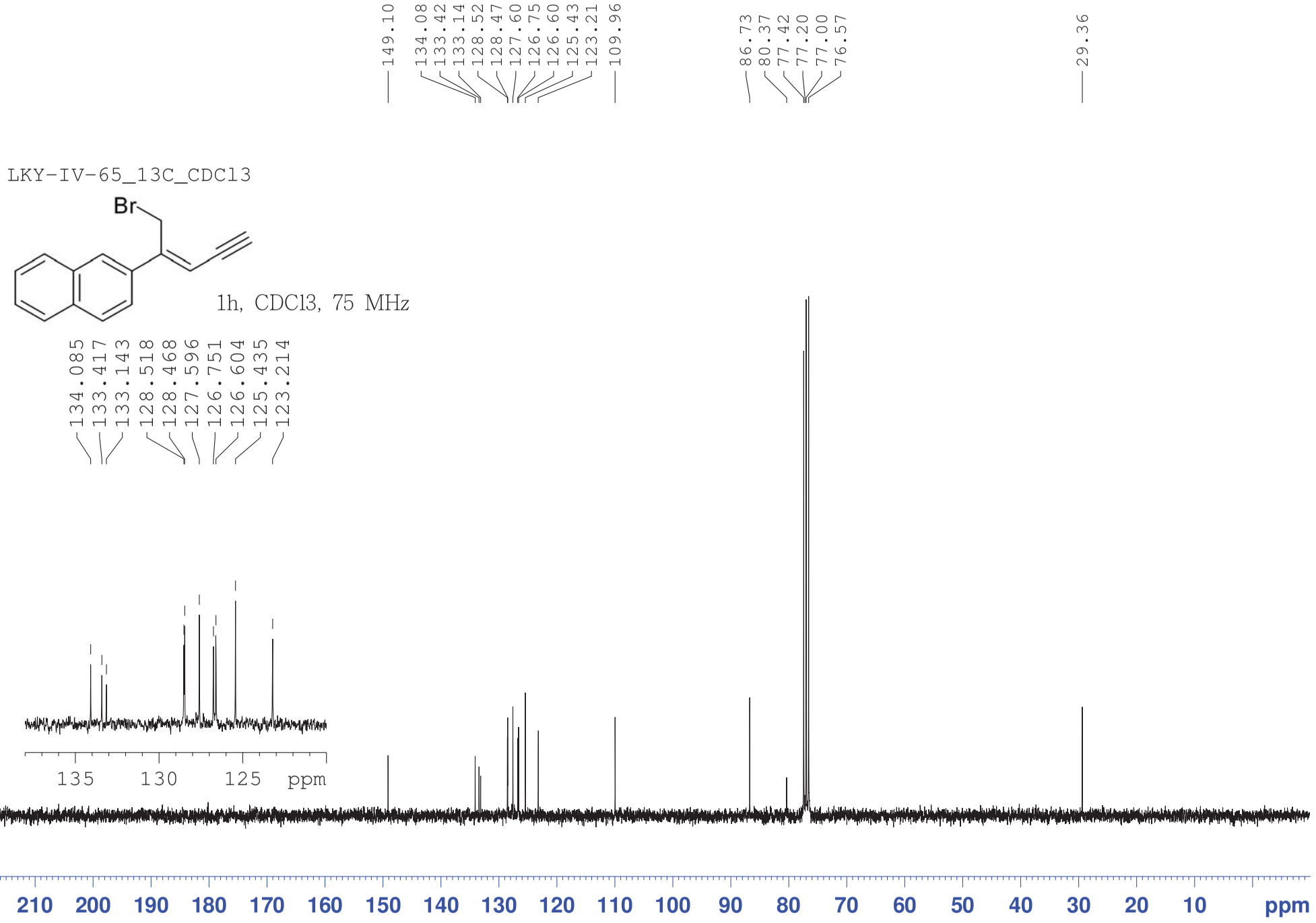
LKY-V-8_13C_CDCl3

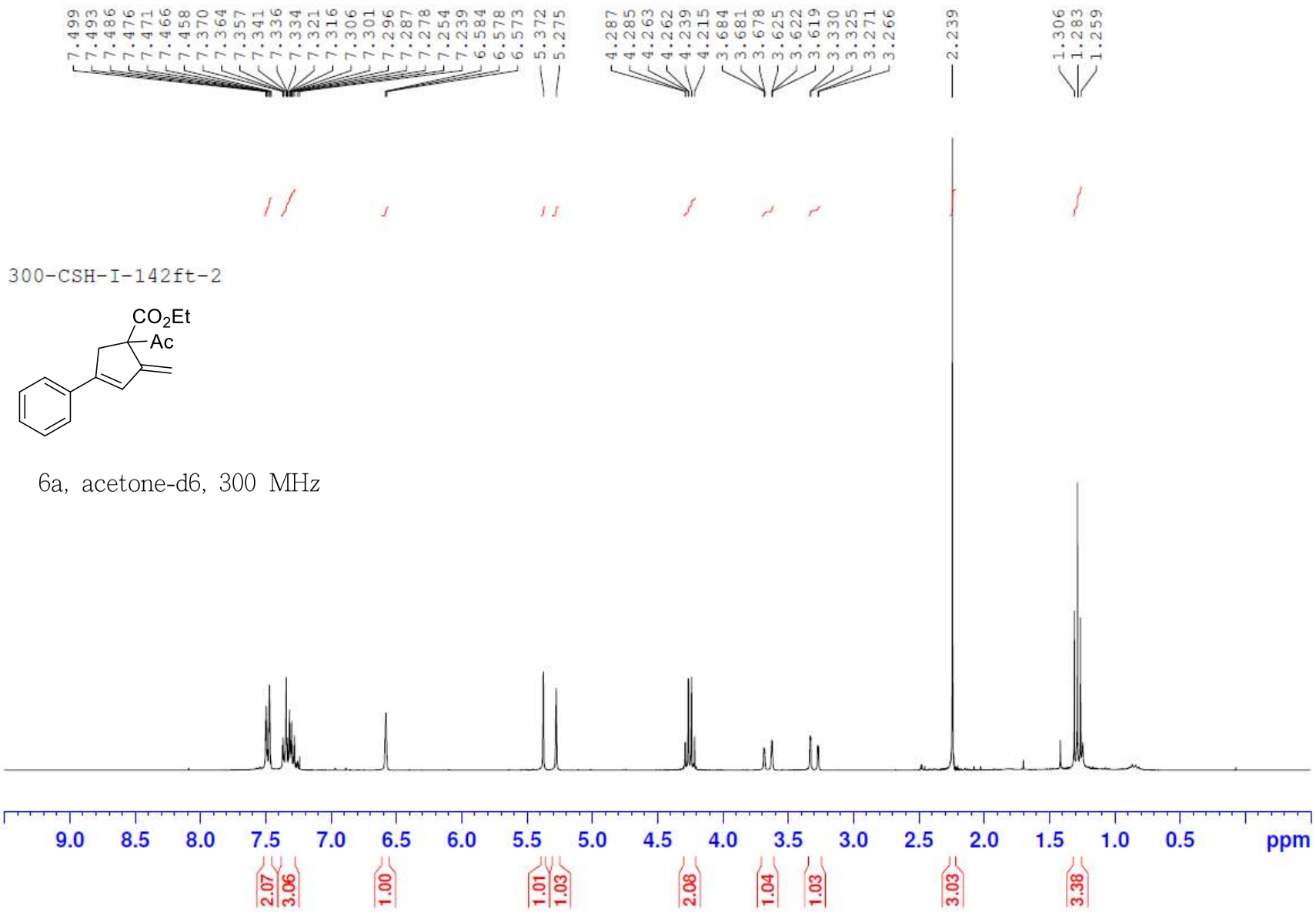


1g, CDCl3, 75 MHz,

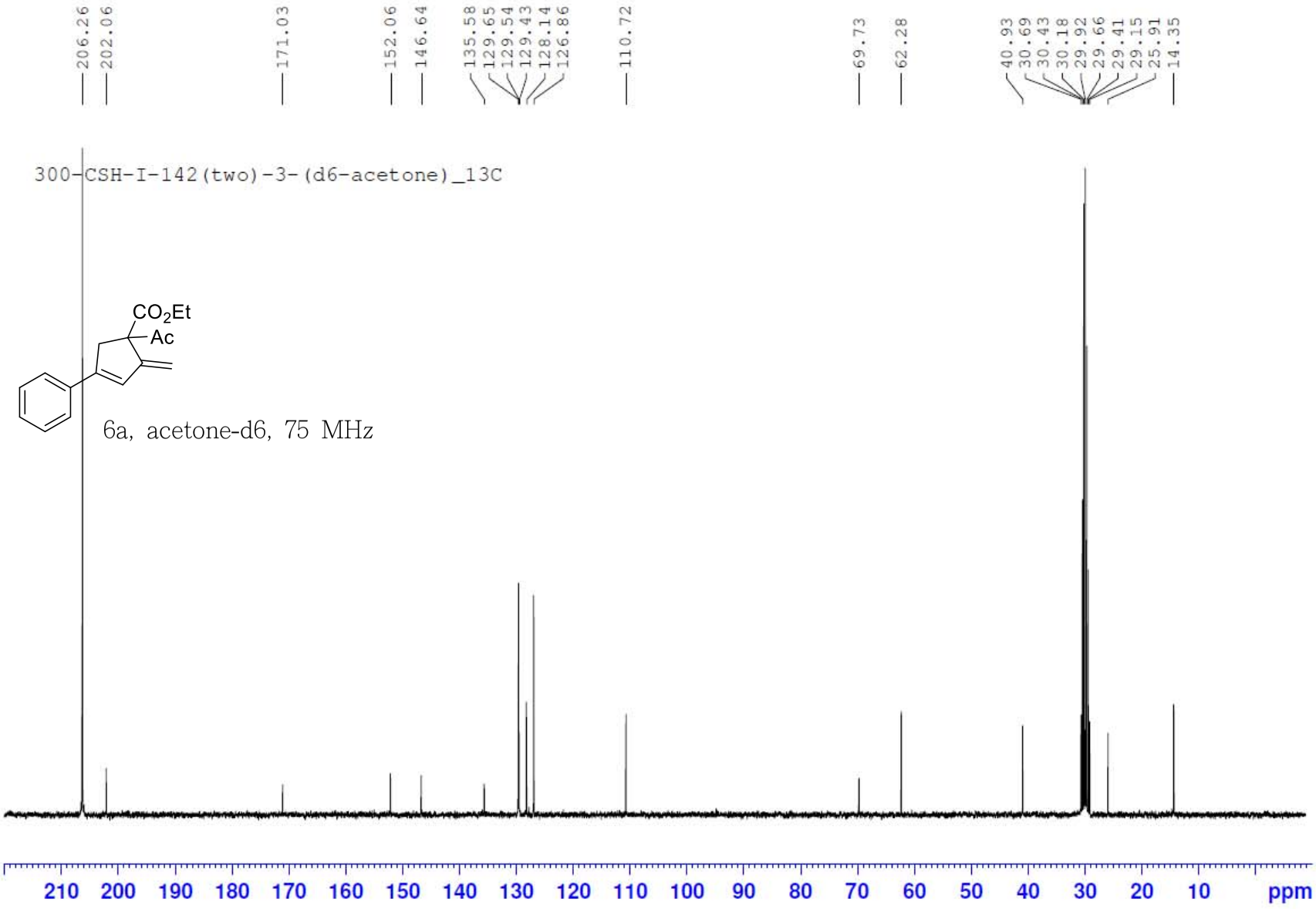


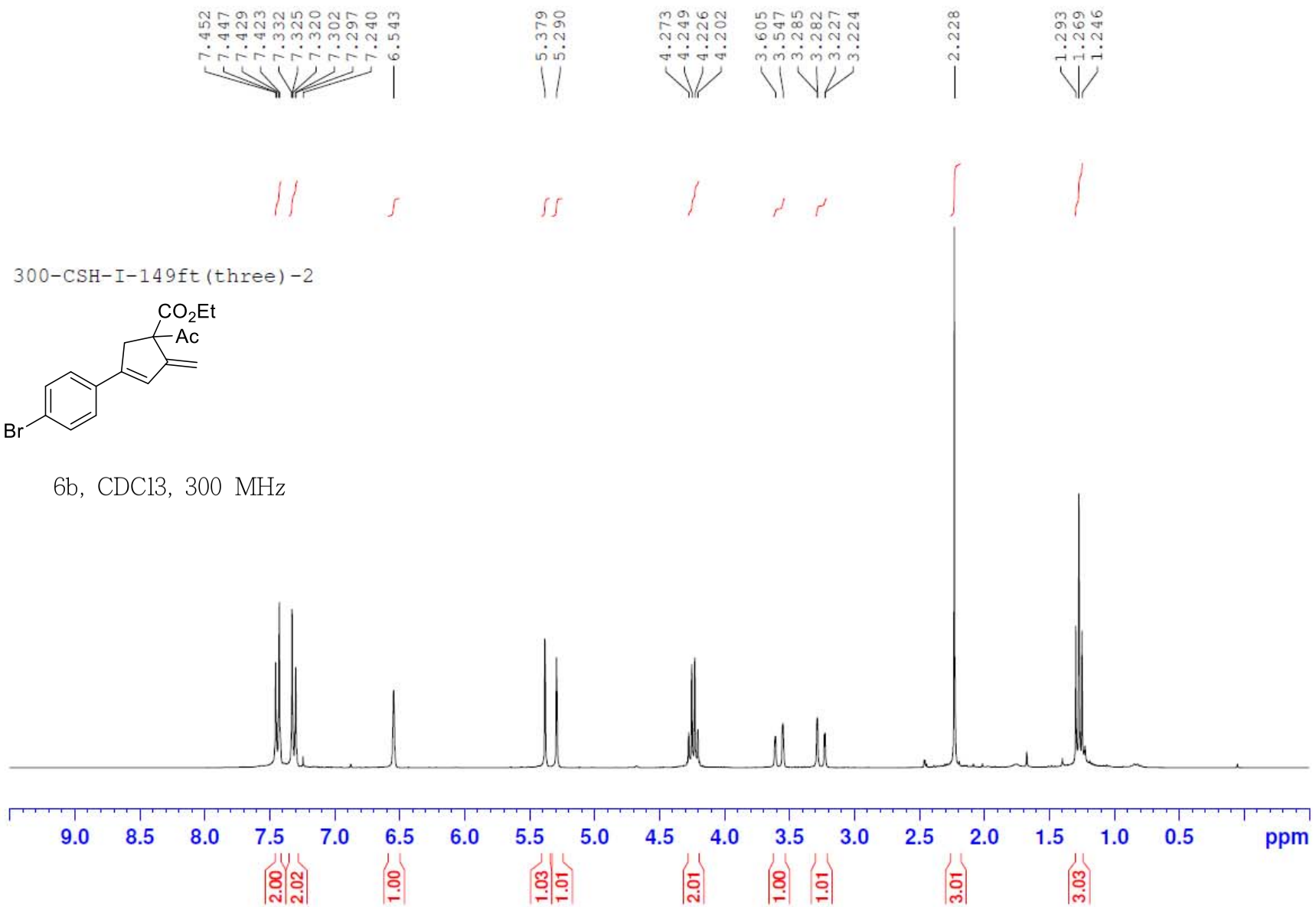

300-LKY-IV-65f24
1h, CDCl3, 300 MHz
Br
7.964
7.959
7.877
7.866
7.863
7.845
7.834
7.828
7.816
7.802
7.598
7.591
7.569
7.562
7.506
7.499
7.493
7.489
7.482
7.475
7.240
6.156
6.148
4.729
3.566
3.558
1.554
1.10
3.05
1.04
2.09
1.00
2.14
0.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


149.10
134.08
133.42
133.14
128.52
128.47
127.60
126.75
126.60
125.43
123.21
109.96
86.73
80.37
77.42
77.20
77.00
76.57
29.36
LKY-IV-65_13C_CDCl3
Br
1h, CDCl3, 75 MHz
134.085
133.417
133.143
128.518
128.468
127.596
126.751
126.604
125.435
123.214
135
130
125
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



6a, acetone-d6, 300 MHz

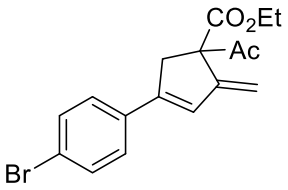

206.26
202.06
171.03
152.06
146.64
135.58
129.65
129.54
129.43
128.14
126.86
110.72
69.73
62.28
40.93
30.69
30.43
30.18
29.92
29.66
29.41
29.15
25.91
14.35
300-CSH-I-142(two)-3-(d6-acetone)_13C
CO2Et
Ac
6a, acetone-d6, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



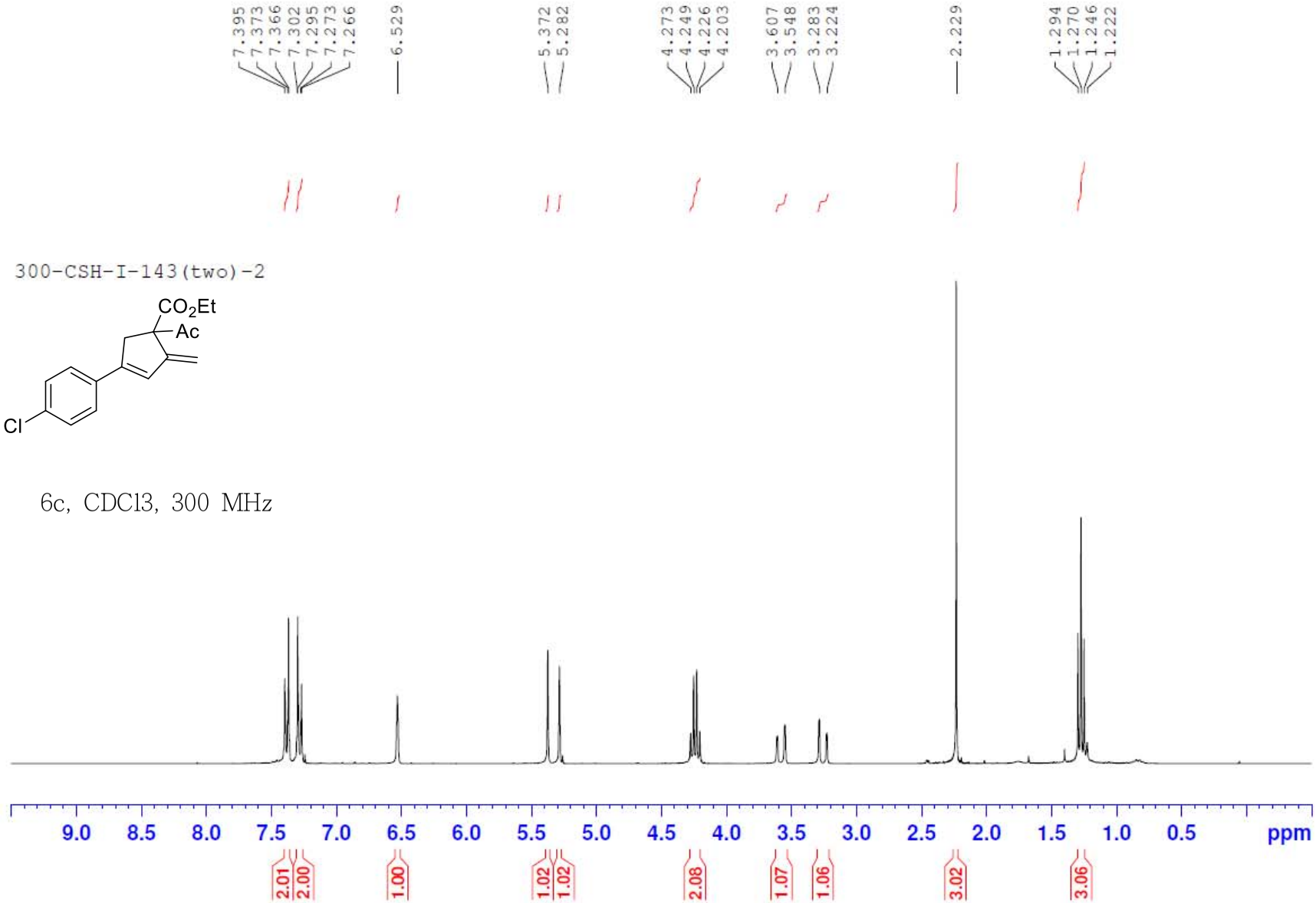
6b, CDCl3, 300 MHz

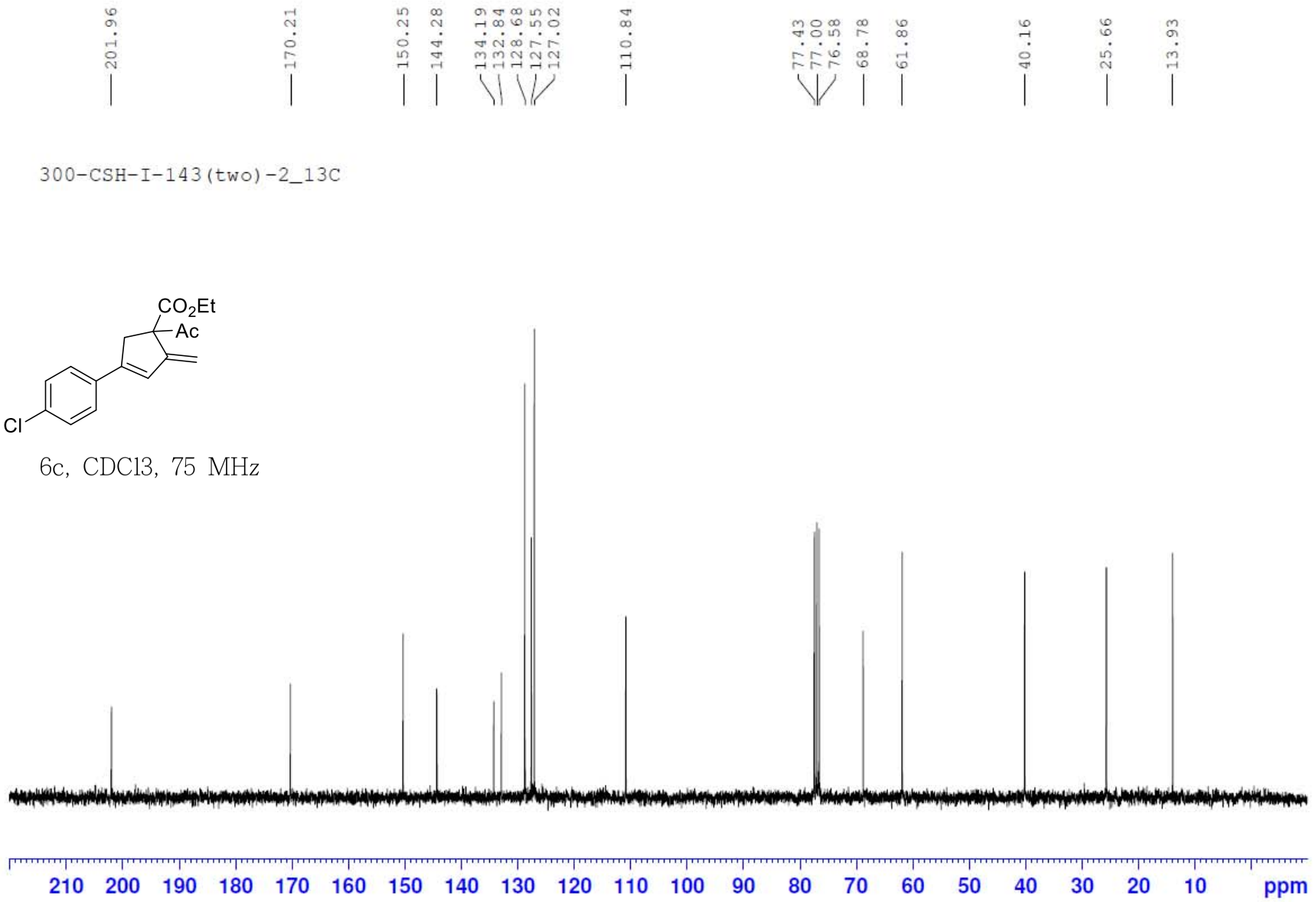
201.94
170.21
150.23
144.32
133.26
131.62
127.66
127.29
122.45
110.94
77.43
77.00
76.58
68.76
61.87
40.10
25.67
13.93

300-CSH-I-149ft(three)-2-13C

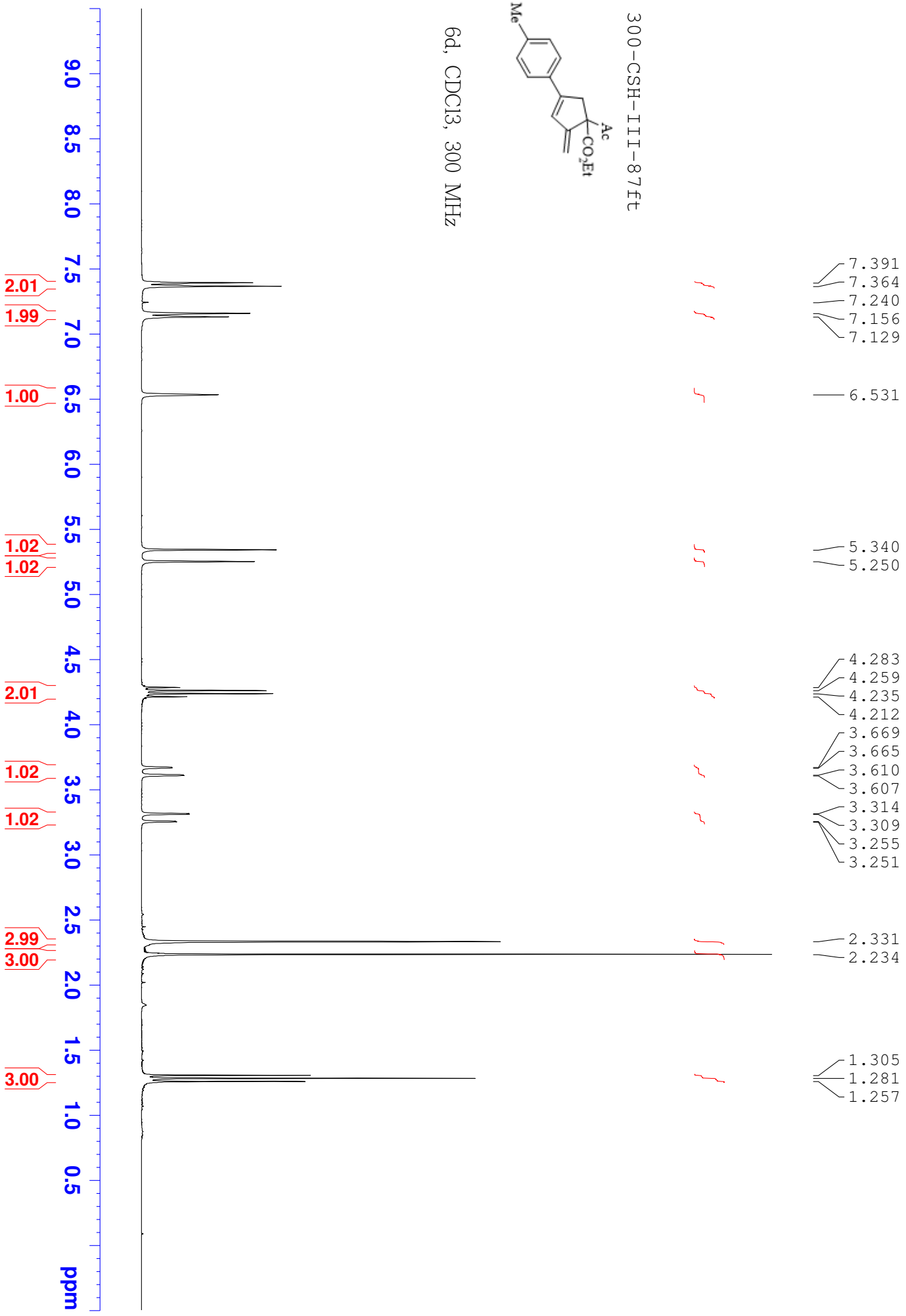


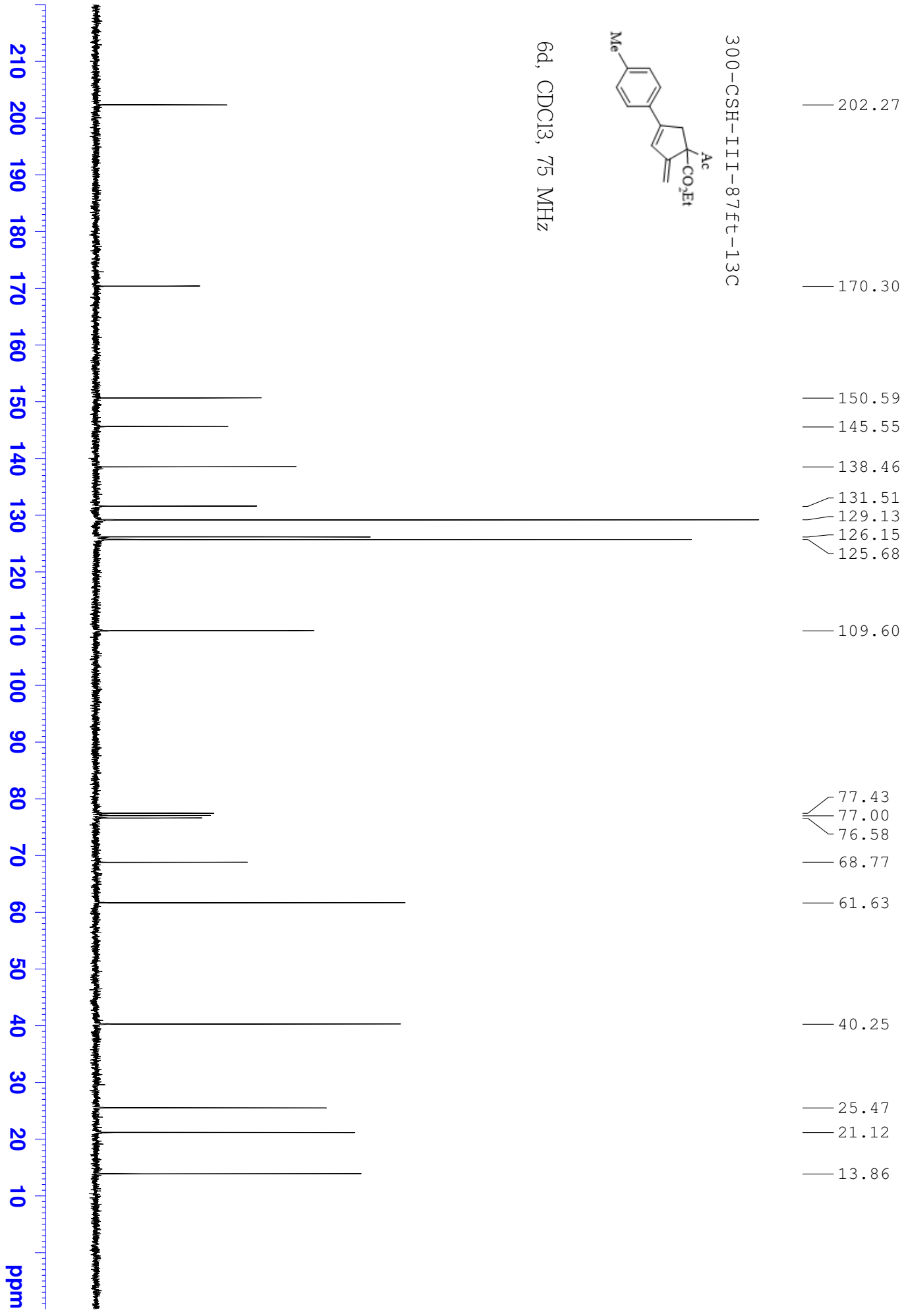
6b, CDCl3, 75 MHz

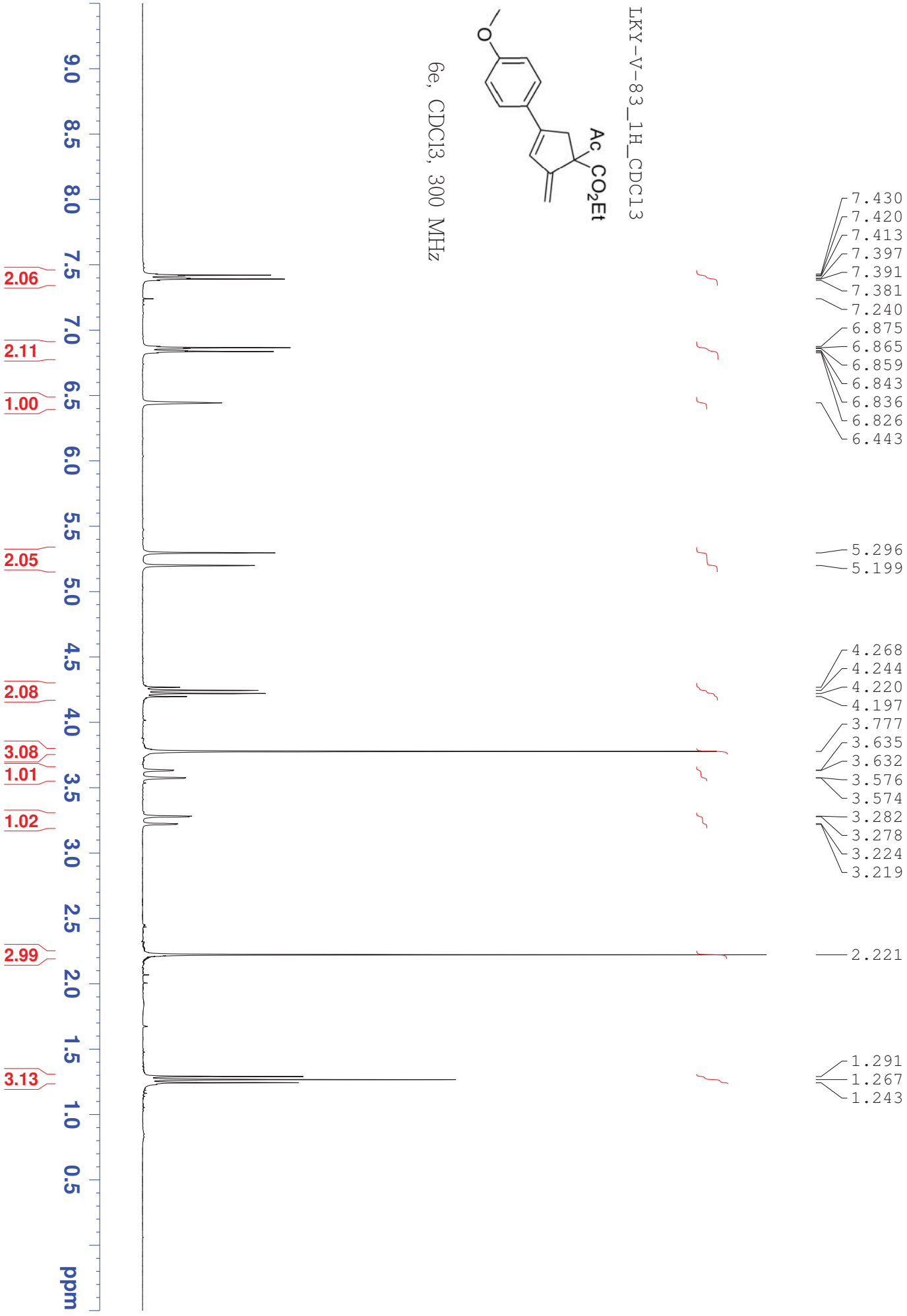

7.395
7.373
7.366
7.302
7.295
7.273
7.266
6.529
5.372
5.282
4.273
4.249
4.226
4.203
3.607
3.548
3.283
3.224
2.229
1.294
1.270
1.246
1.222
300-CSH-I-143(two)-2
CO2Et
Ac
Cl
6c, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
2.00
1.00
1.02
1.02
2.08
1.07
1.06
3.02
3.06

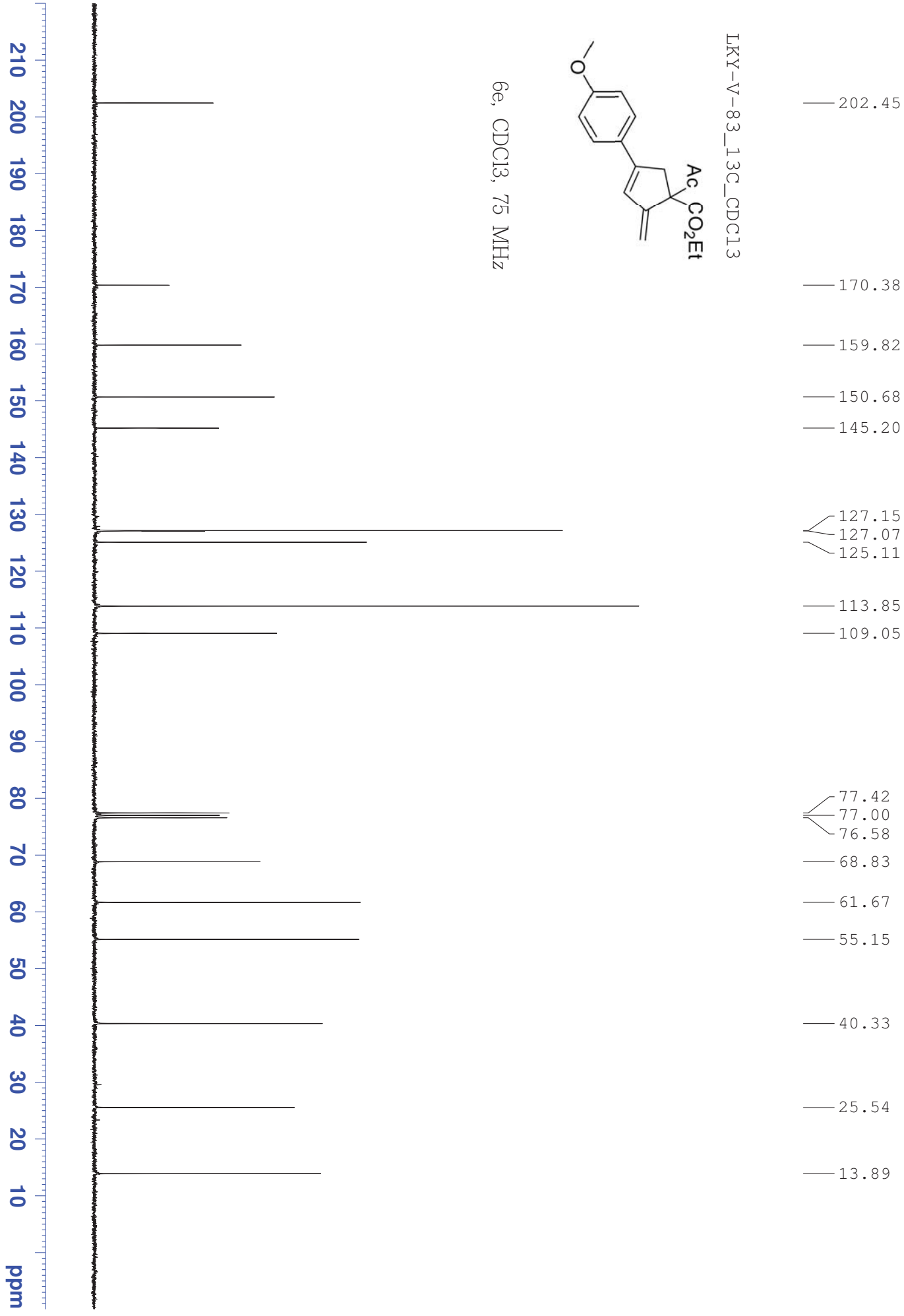


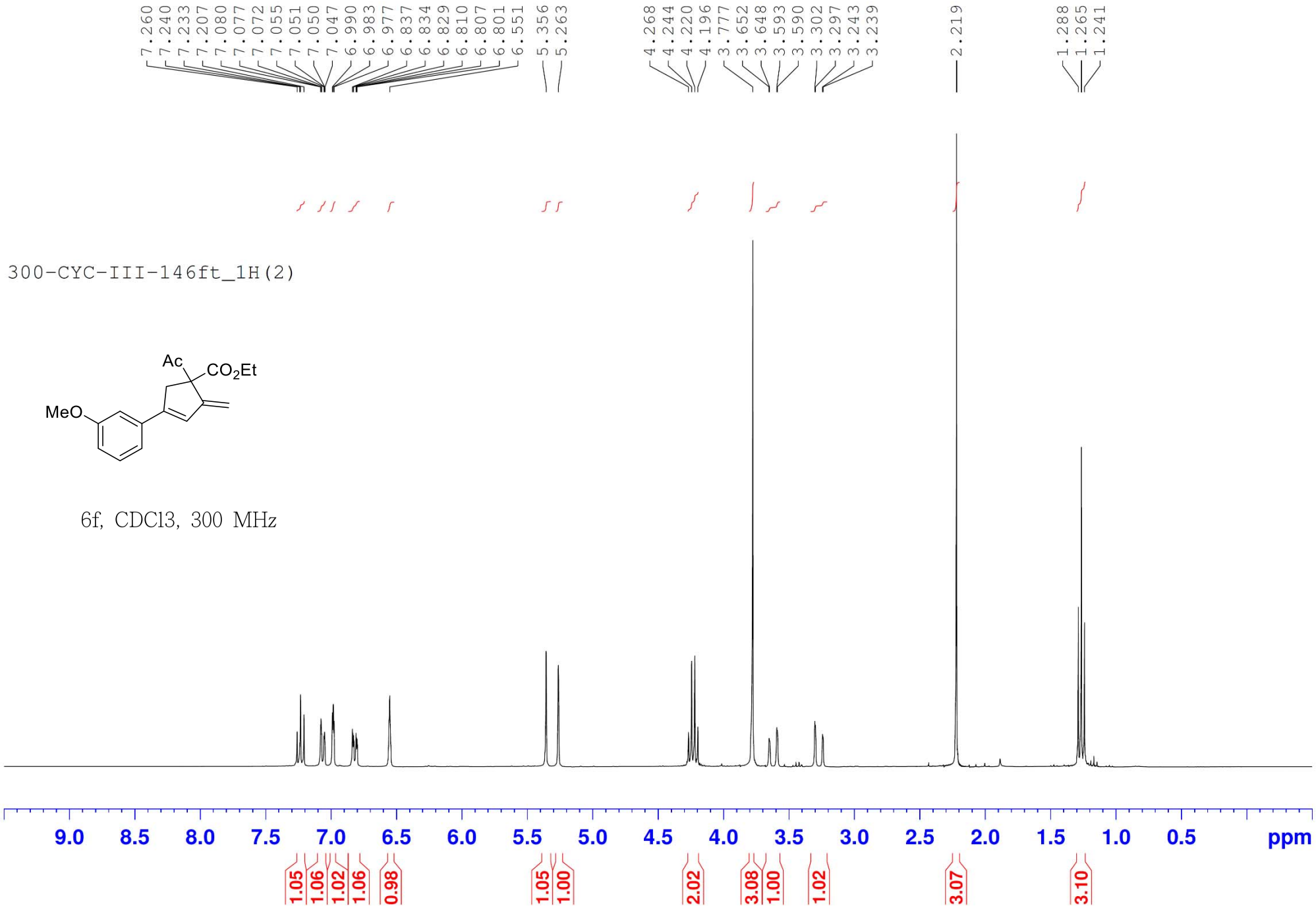
6c, CDCl3, 75 MHz


300-CSH-III-87ft
6d, CDCl3, 300 MHz
Me
Ac
CO2Et
7.391
7.364
7.240
7.156
7.129
6.531
5.340
5.250
4.283
4.259
4.235
4.212
3.669
3.665
3.610
3.607
3.314
3.309
3.255
3.251
2.331
2.234
1.305
1.281
1.257
2.01
1.99
1.00
1.02
1.02
2.01
1.02
1.02
2.99
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


300-CSH-III-87ft-13C
6d, CDCl3, 75 MHz
Me
Ac
CO2Et
202.27
170.30
150.59
145.55
138.46
131.51
129.13
126.15
125.68
109.60
77.43
77.00
76.58
68.77
61.63
40.25
25.47
21.12
13.86
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

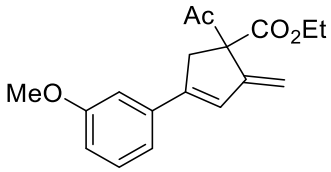

LKY-V-83_1H_CDCl3
6e, CDCl3, 300 MHz
Ac
CO2Et
7.430
7.420
7.413
7.397
7.391
7.381
7.240
6.875
6.865
6.859
6.843
6.836
6.826
6.443
5.296
5.199
4.268
4.244
4.220
4.197
3.777
3.635
3.632
3.576
3.574
3.282
3.278
3.224
3.219
2.221
1.291
1.267
1.243
2.06
2.11
1.00
2.05
2.08
3.08
1.01
1.02
2.99
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


LKY-V-83_13C_CDC13
6e, CDCl3, 75 MHz
Ac
CO2Et
202.45
170.38
159.82
150.68
145.20
127.15
127.07
125.11
113.85
109.05
77.42
77.00
76.58
68.83
61.67
55.15
40.33
25.54
13.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

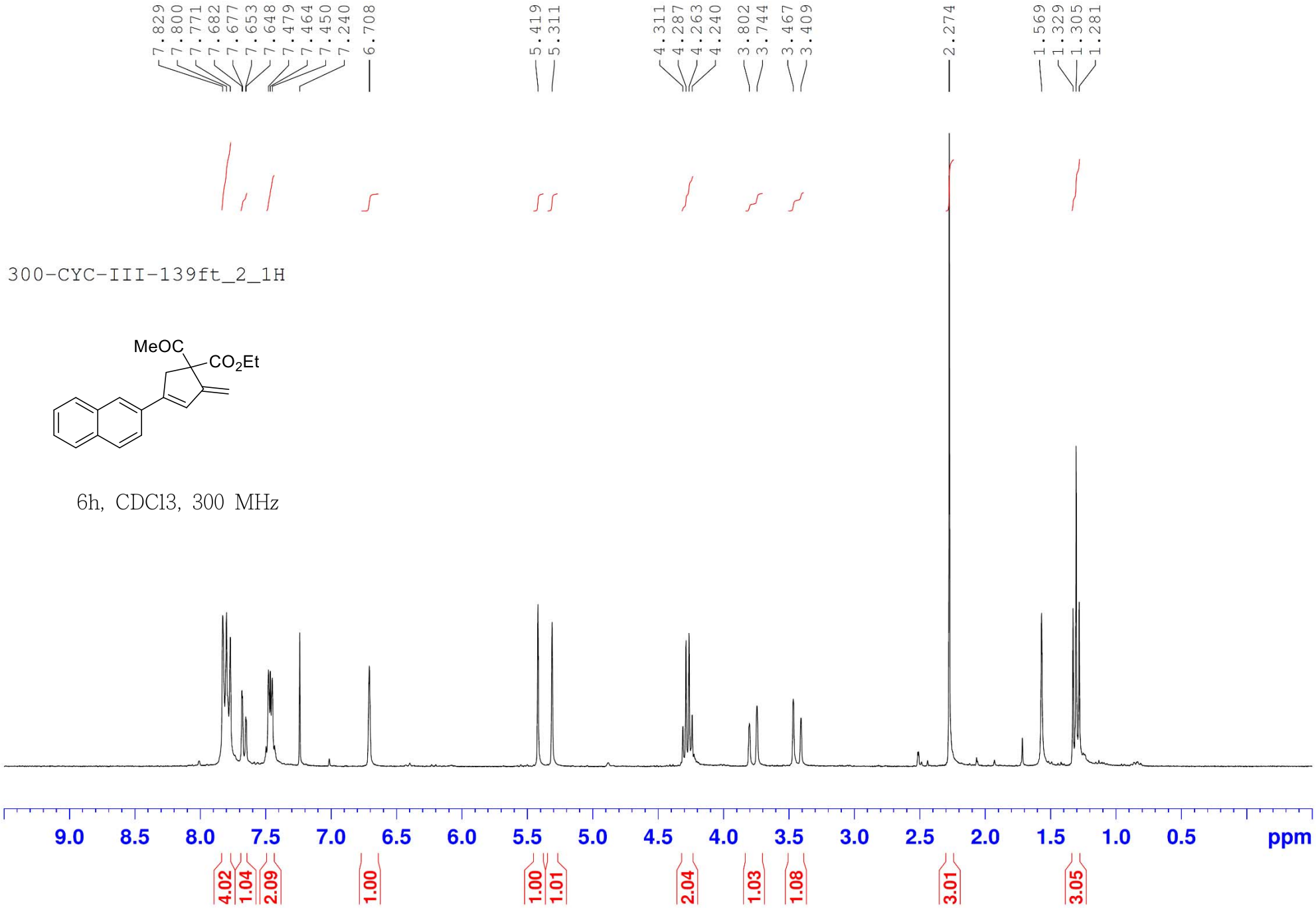

7.260
7.240
7.233
7.207
7.080
7.077
7.072
7.055
7.051
7.050
7.047
6.990
6.983
6.977
6.837
6.834
6.829
6.810
6.807
6.801
6.551
5.356
5.263
4.268
4.244
4.220
4.196
3.777
3.652
3.648
3.593
3.590
3.302
3.297
3.243
3.239
2.219
1.288
1.265
1.241
300-CYC-III-146ft_1H(2)
Ac
CO2Et
MeO
6f, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.05
1.06
1.02
1.06
0.98
1.05
1.00
2.02
3.08
1.00
1.02
3.07
3.10

202.10
170.20
159.51
150.34
145.39
135.64
129.39
127.37
118.31
113.89
111.26
110.34
77.42
77.00
76.58
68.69
61.68
55.05
40.24
25.48
13.84

300-CYC-III-146ft_13C

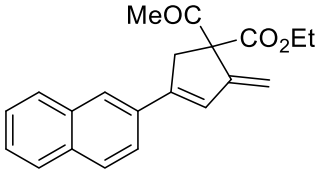


6f, CDCl3, 75 MHz

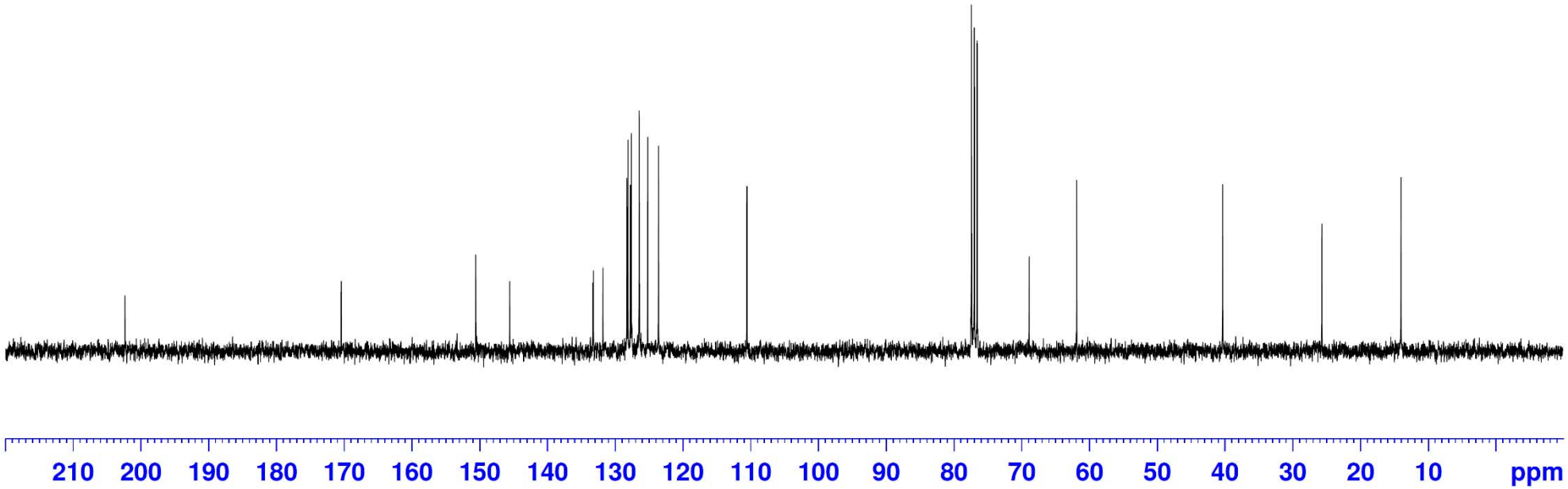

7.829
7.800
7.771
7.682
7.677
7.653
7.648
7.479
7.464
7.450
7.240
6.708
5.419
5.311
4.311
4.287
4.263
4.240
3.802
3.744
3.467
3.409
2.274
1.569
1.329
1.305
1.281
300-CYC-III-139ft_2_1H
MeOC
CO2Et
6h, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.02
1.04
2.09
1.00
1.00
1.01
2.04
1.03
1.08
3.01
3.05

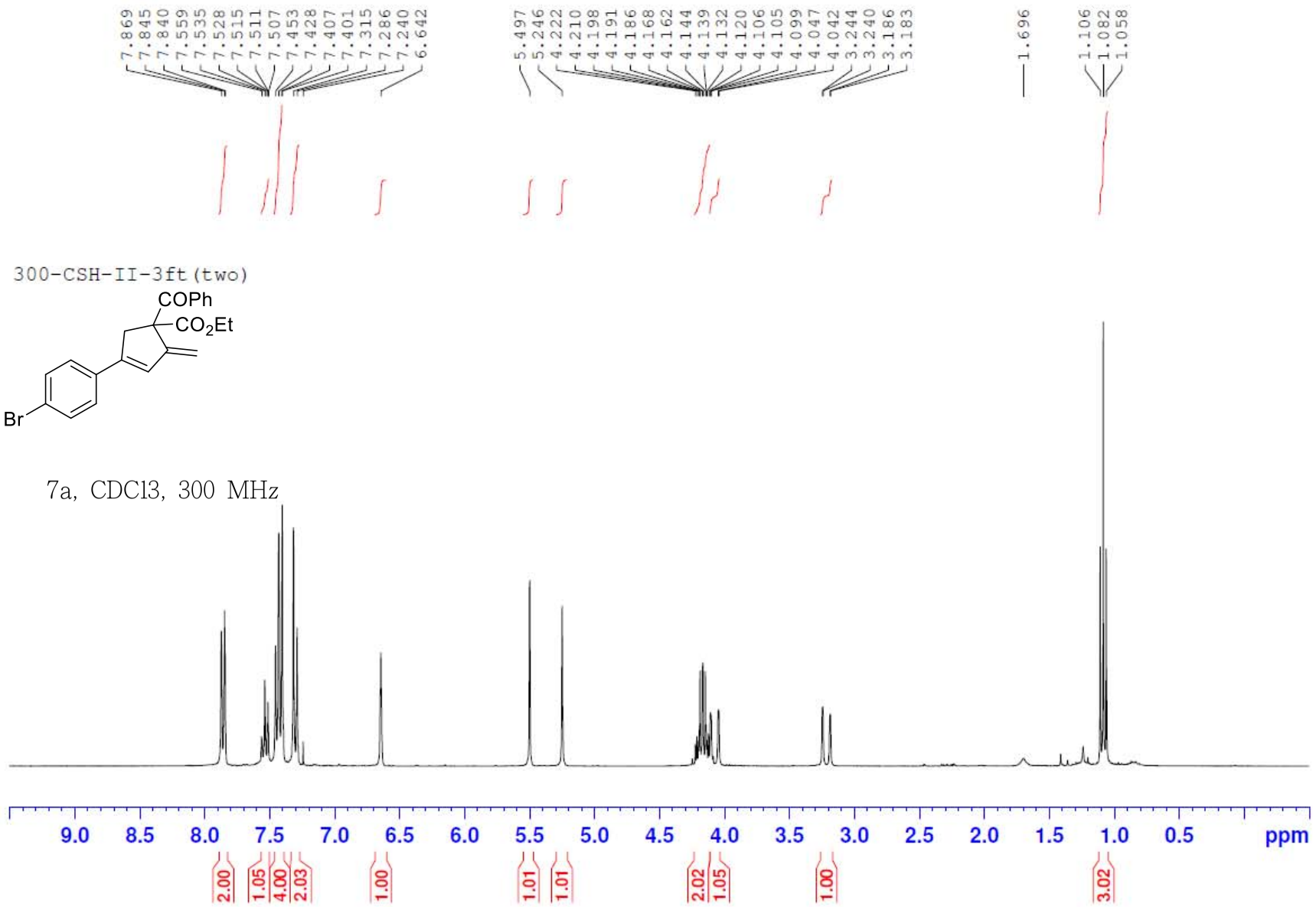
202.36
170.44
150.58
145.56
133.29
133.21
131.80
128.28
128.11
127.76
127.61
126.48
126.46
125.22
123.62
110.57
77.43
77.00
76.58
68.90
61.89
40.34
25.69
14.01

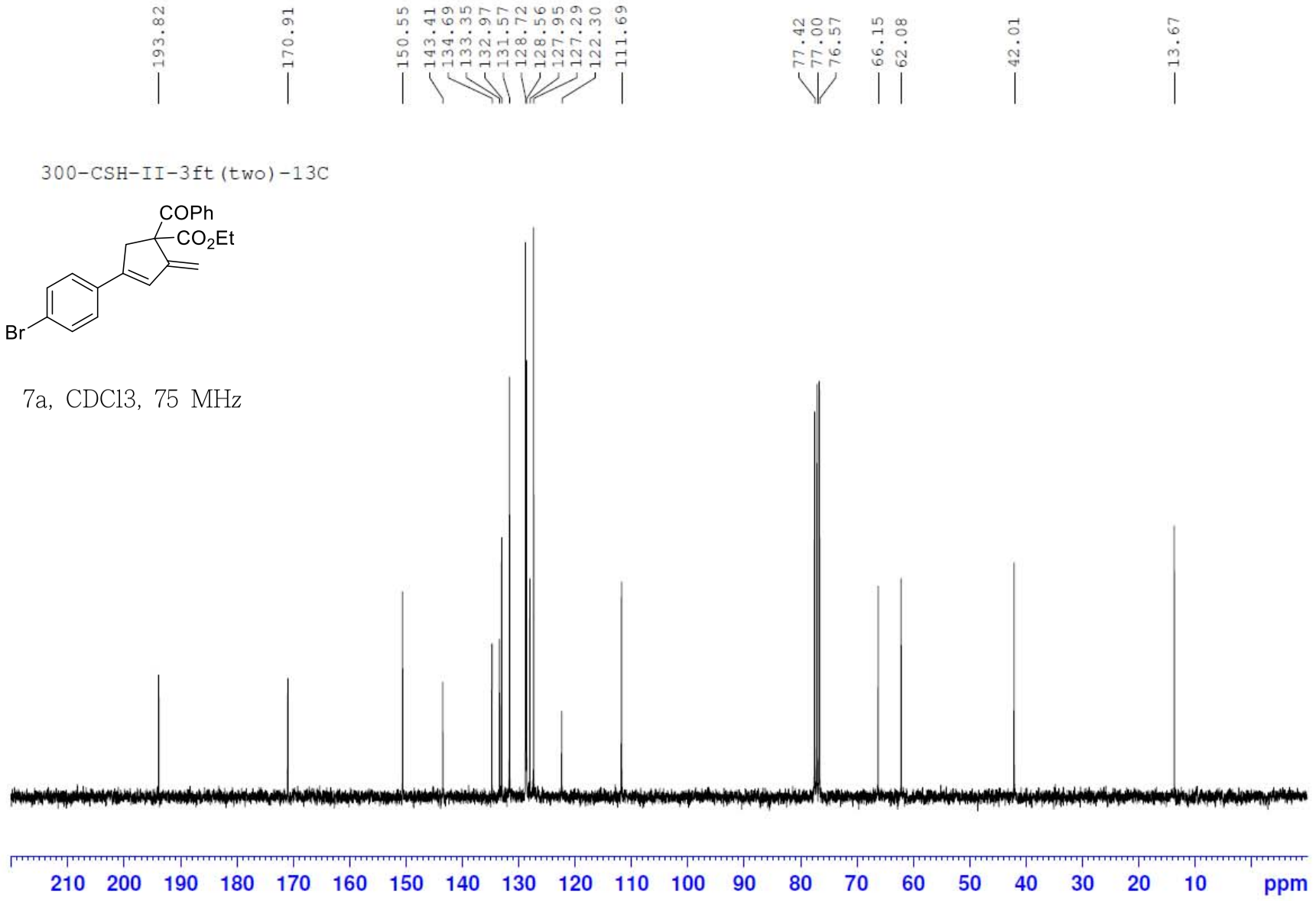
300-CYC-III-139ft_2_13C

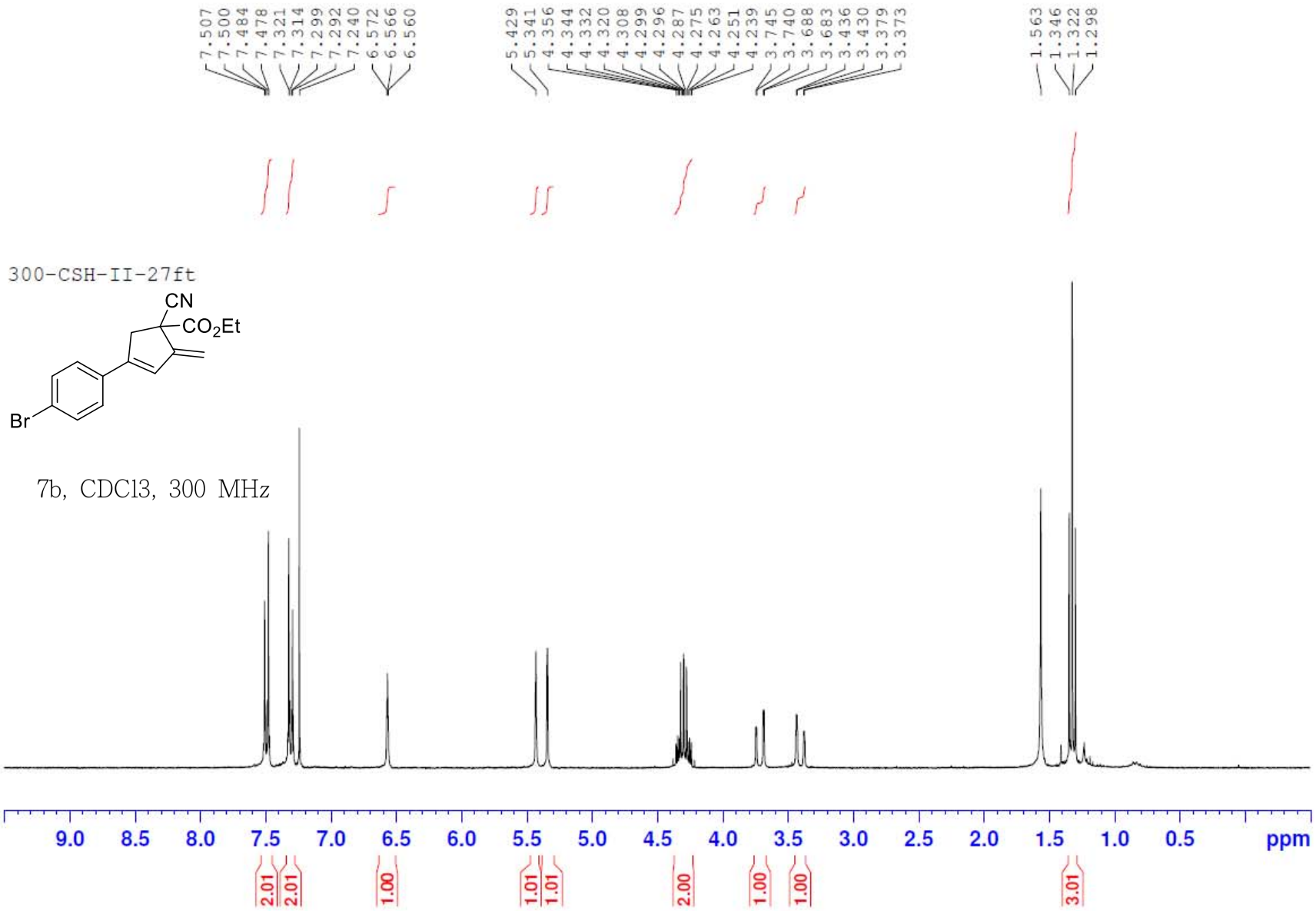


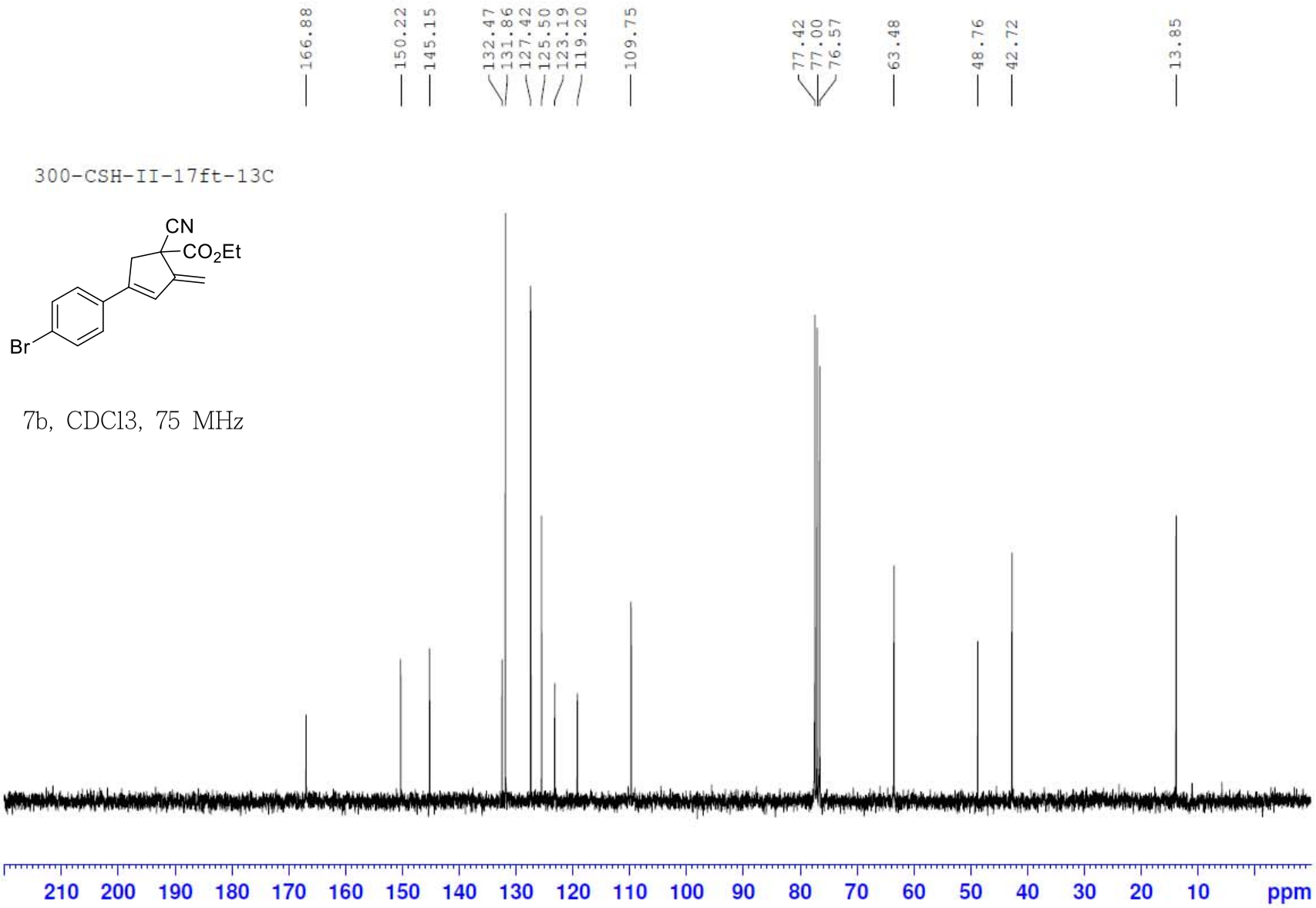
6h, CDCl3, 75 MHz

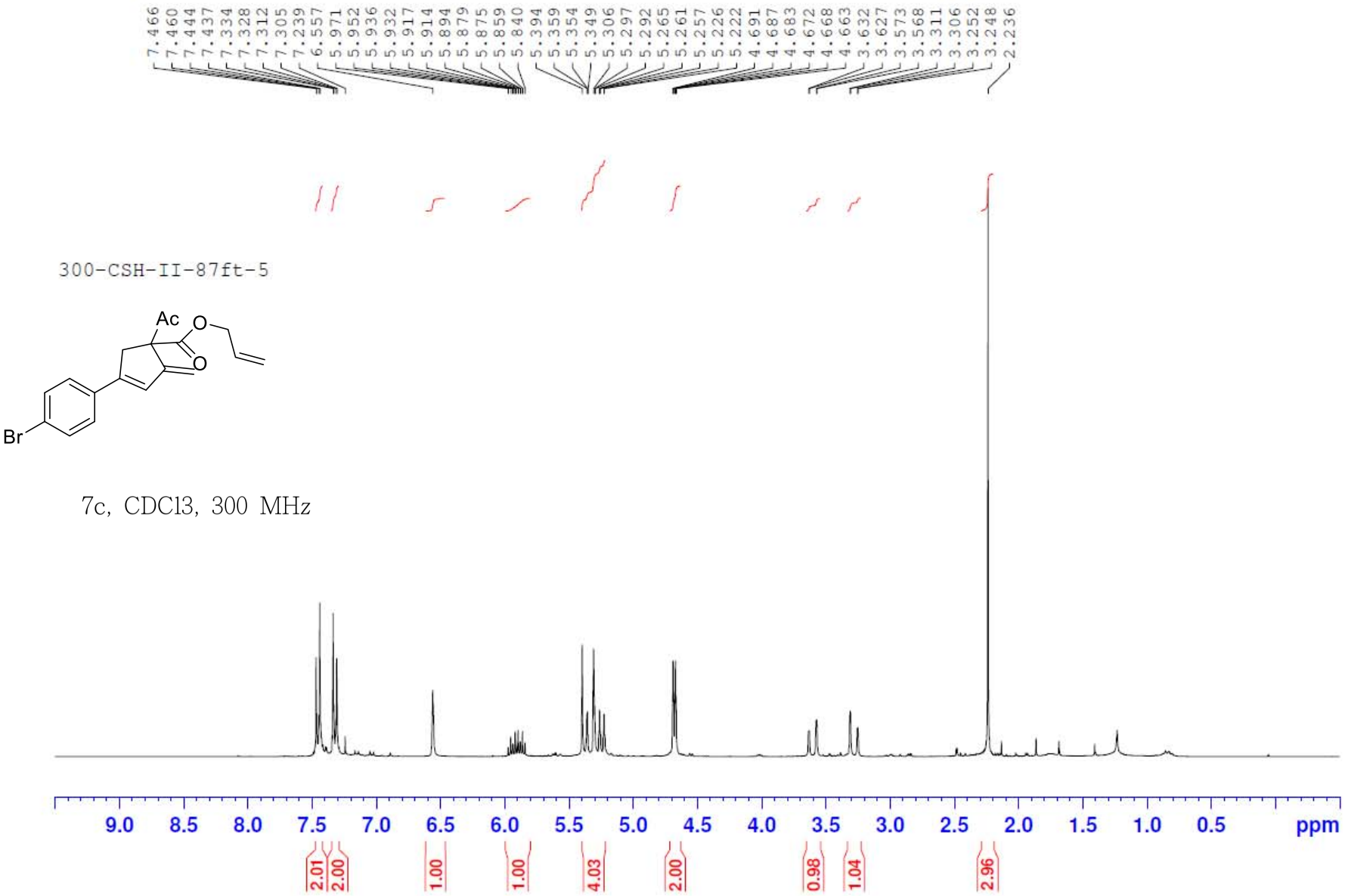



7.869
7.845
7.840
7.559
7.535
7.528
7.515
7.511
7.507
7.453
7.428
7.407
7.401
7.315
7.286
7.240
6.642
5.497
5.246
4.222
4.210
4.198
4.191
4.186
4.168
4.162
4.144
4.139
4.132
4.120
4.106
4.105
4.099
4.047
4.042
3.244
3.240
3.186
3.183
1.696
1.106
1.082
1.058
300-CSH-II-3ft(two)
COPh
CO2Et
Br
7a, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.05
4.00
2.03
1.00
1.01
1.01
2.02
1.05
1.00
3.02

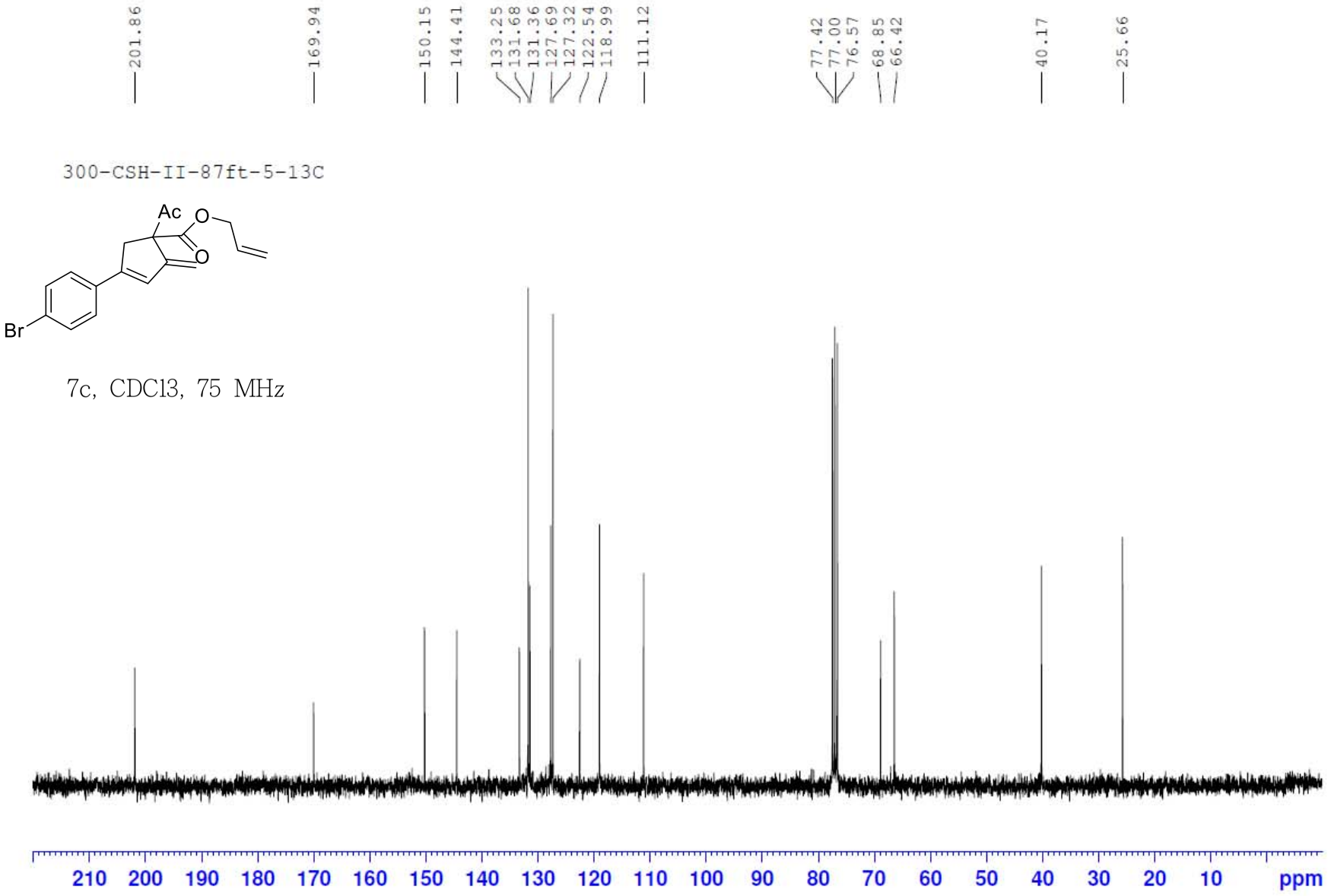

193.82
170.91
150.55
143.41
134.69
133.35
132.97
131.57
128.72
128.56
127.95
127.29
122.30
111.69
77.42
77.00
76.57
66.15
62.08
42.01
13.67
300-CSH-II-3ft(two)-13C
COPh
CO2Et
Br
7a, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

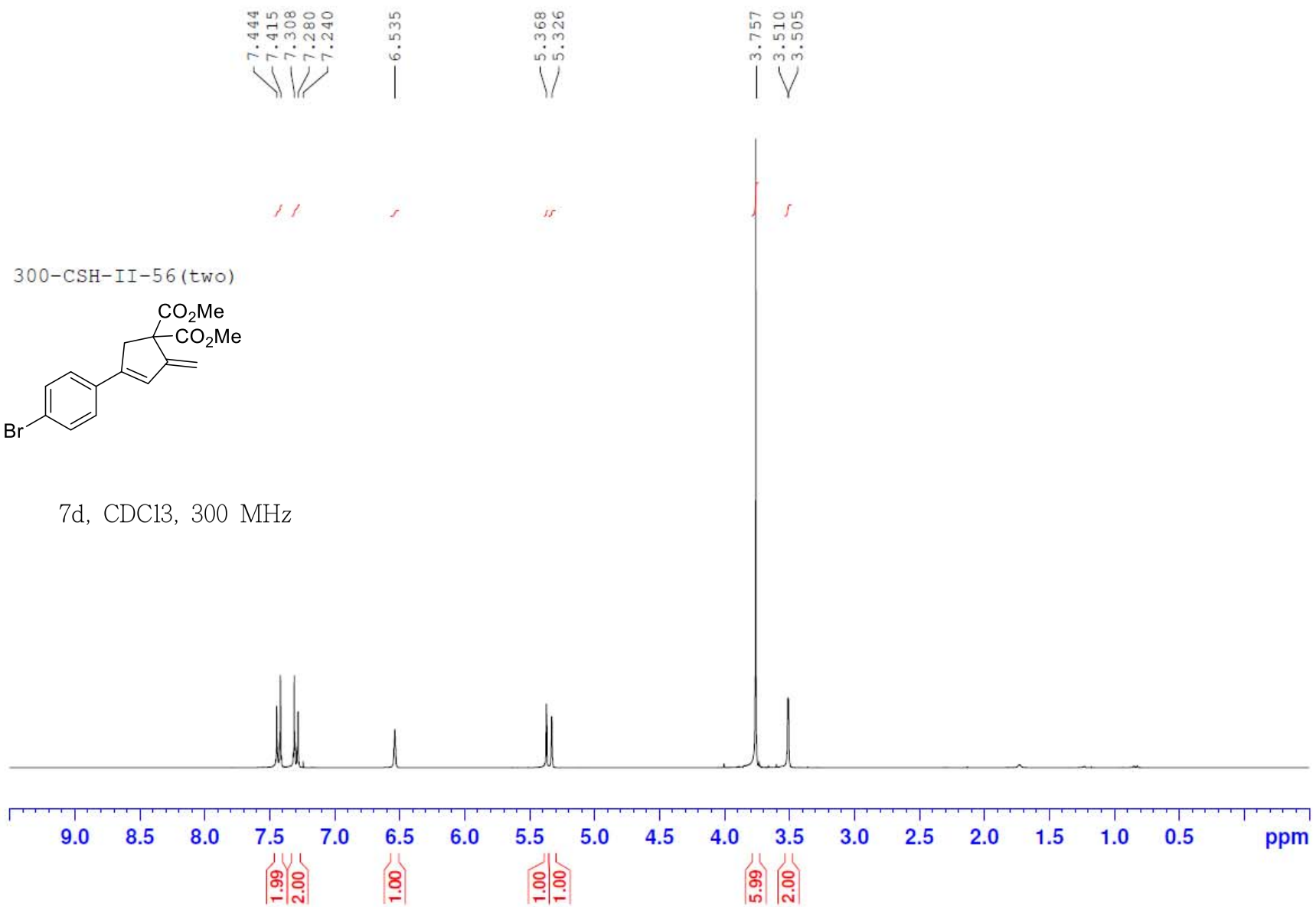

7.507
7.500
7.484
7.478
7.321
7.314
7.299
7.292
7.240
6.572
6.566
6.560
5.429
5.341
4.356
4.344
4.332
4.320
4.308
4.299
4.296
4.287
4.275
4.263
4.251
4.239
3.745
3.740
3.688
3.683
3.436
3.430
3.379
3.373
1.563
1.346
1.322
1.298
300-CSH-II-27ft
CN
CO2Et
Br
7b, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
2.01
1.00
1.01
1.01
2.00
1.00
1.00
3.01


166.88
150.22
145.15
132.47
131.86
127.42
125.50
123.19
119.20
109.75
77.42
77.00
76.57
63.48
48.76
42.72
13.85
300-CSH-II-17ft-13C
CN
CO2Et
Br
7b, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

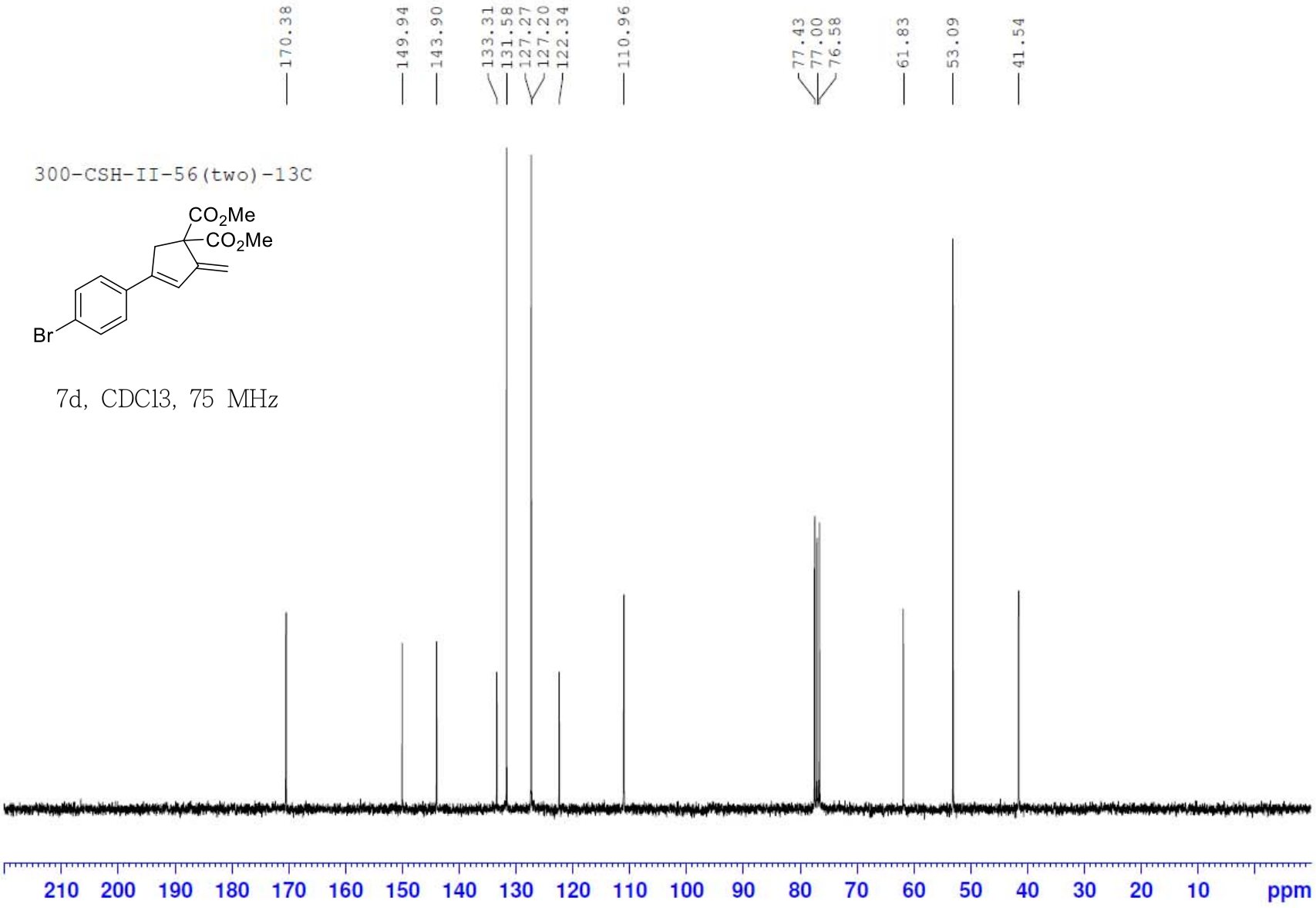


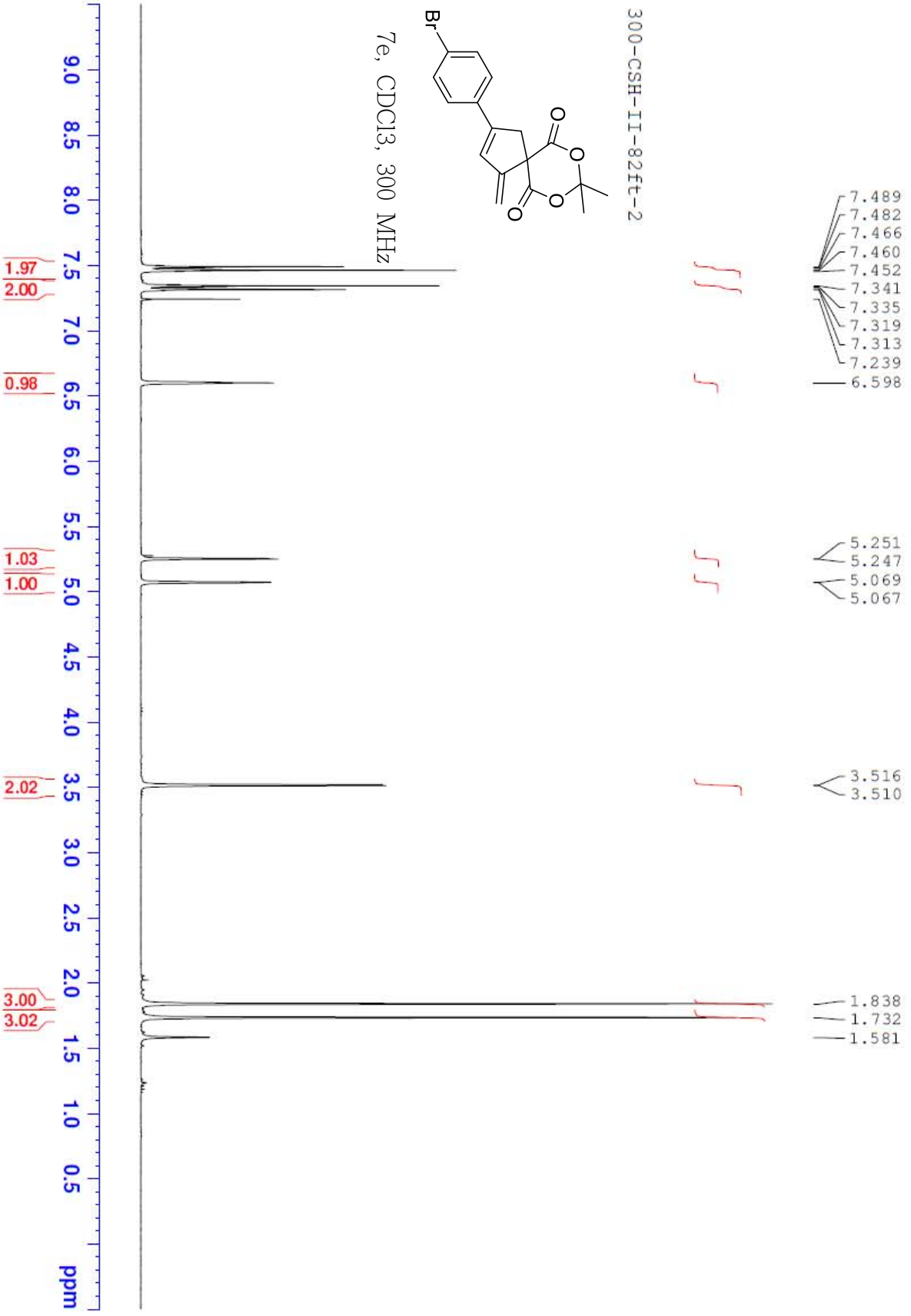
7c, CDCl3, 300 MHz

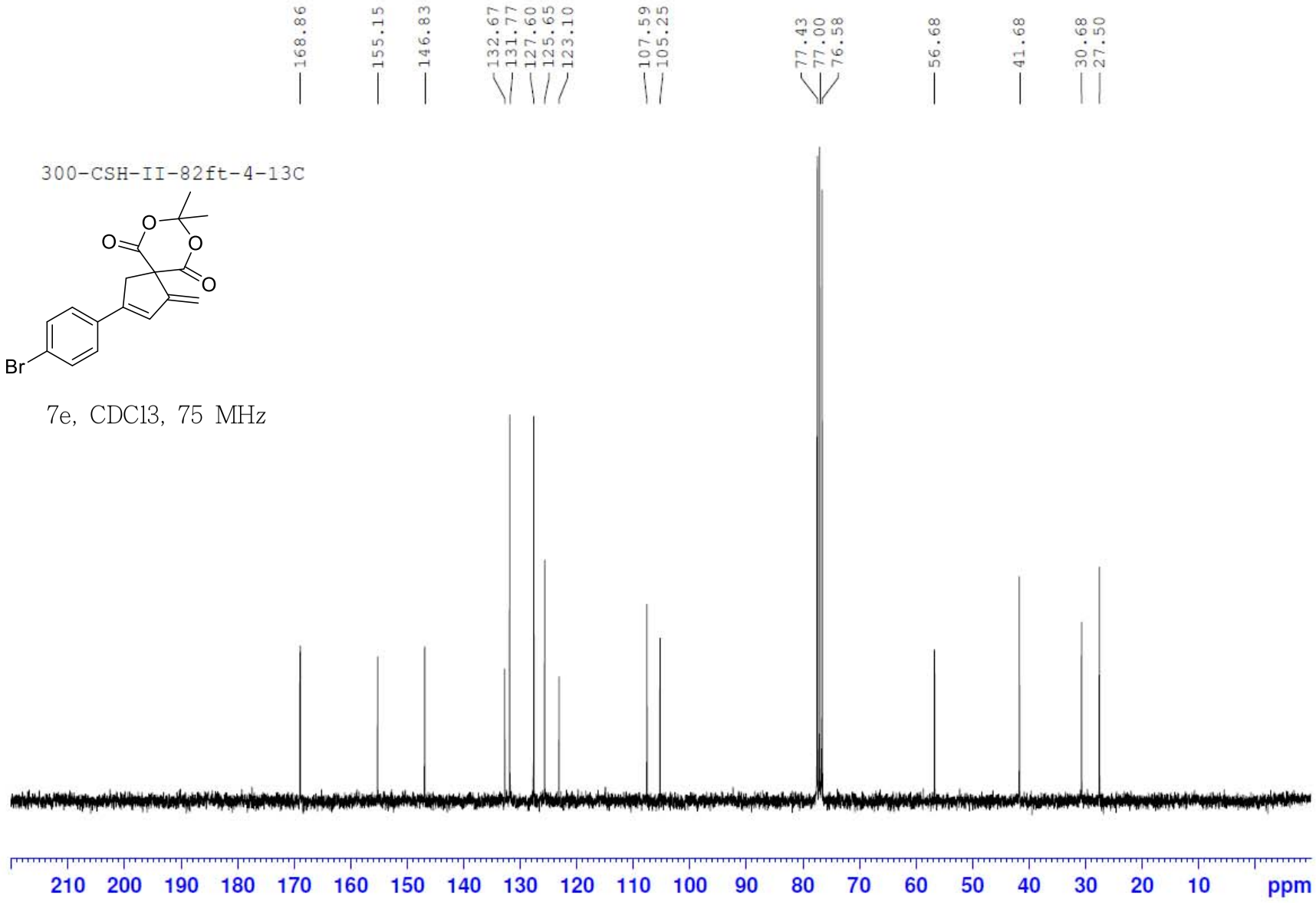

201.86
169.94
150.15
144.41
133.25
131.68
131.36
127.69
127.32
122.54
118.99
111.12
77.42
77.00
76.57
68.85
66.42
40.17
25.66
300-CSH-II-87ft-5-13C
Ac
O
O
Br
7c, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

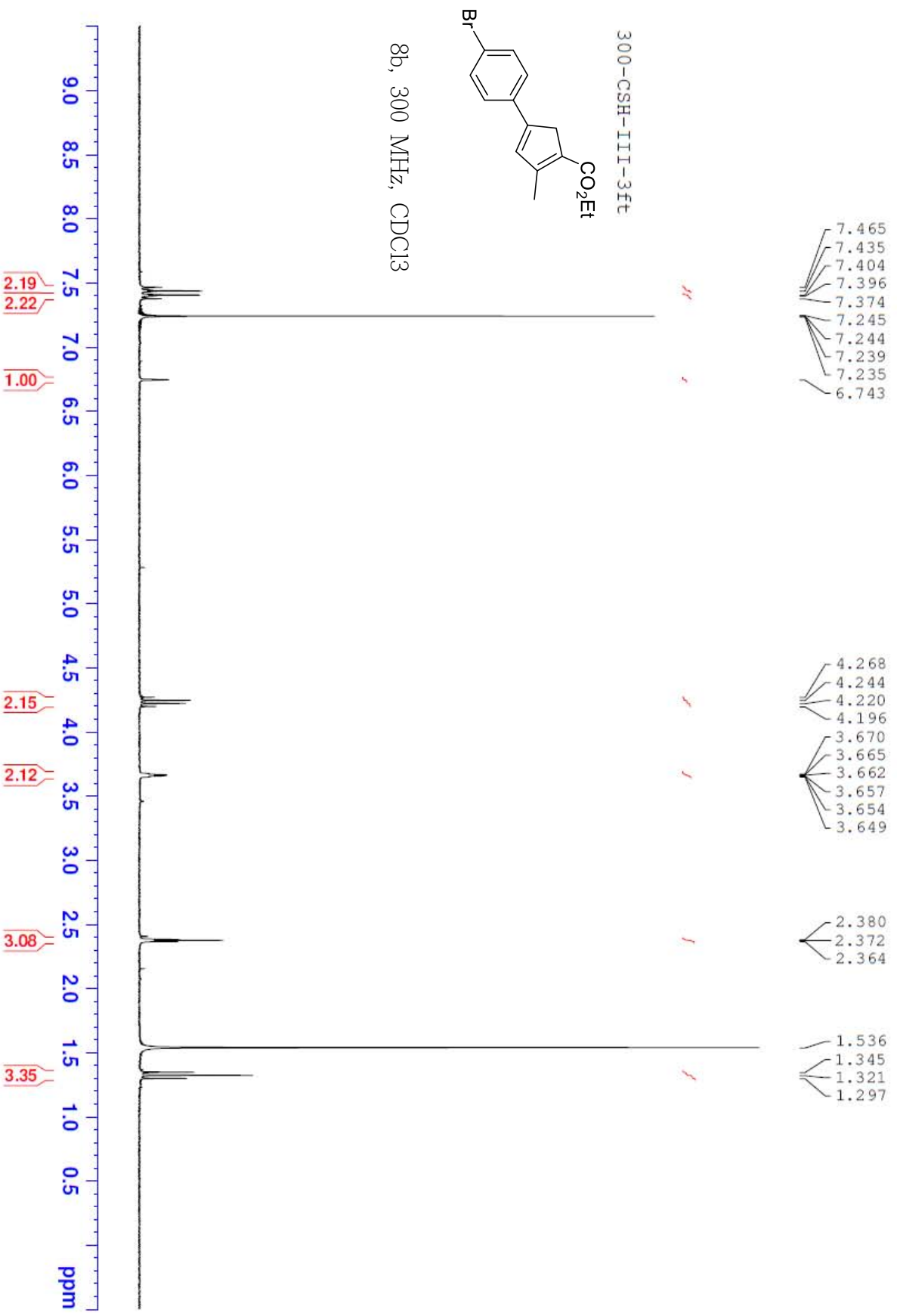


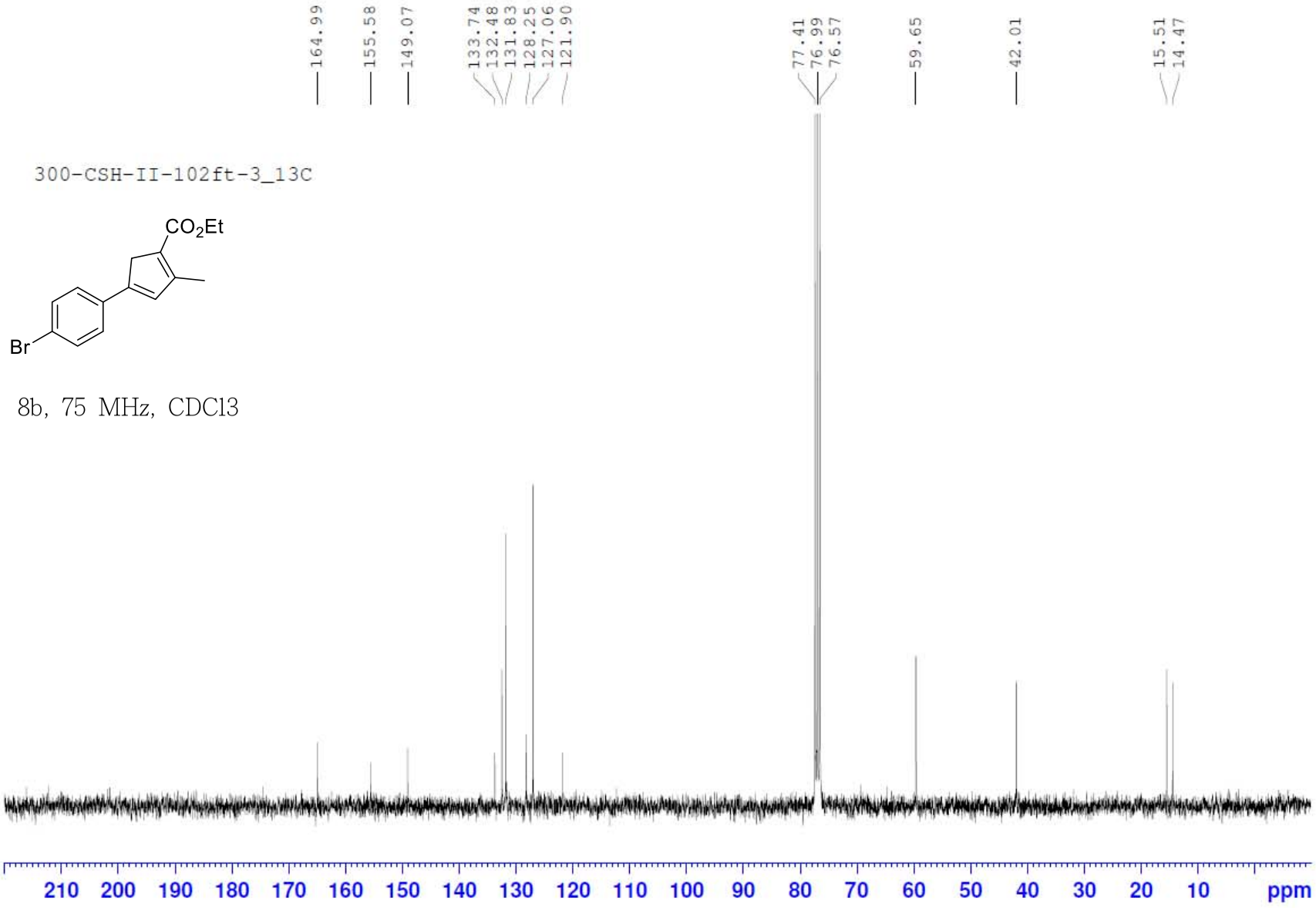
7d, CDCl3, 300 MHz


170.38
149.94
143.90
133.31
131.58
127.27
127.20
122.34
110.96
77.43
77.00
76.58
61.83
53.09
41.54
300-CSH-II-56(two)-13C
CO2Me
CO2Me
Br
7d, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

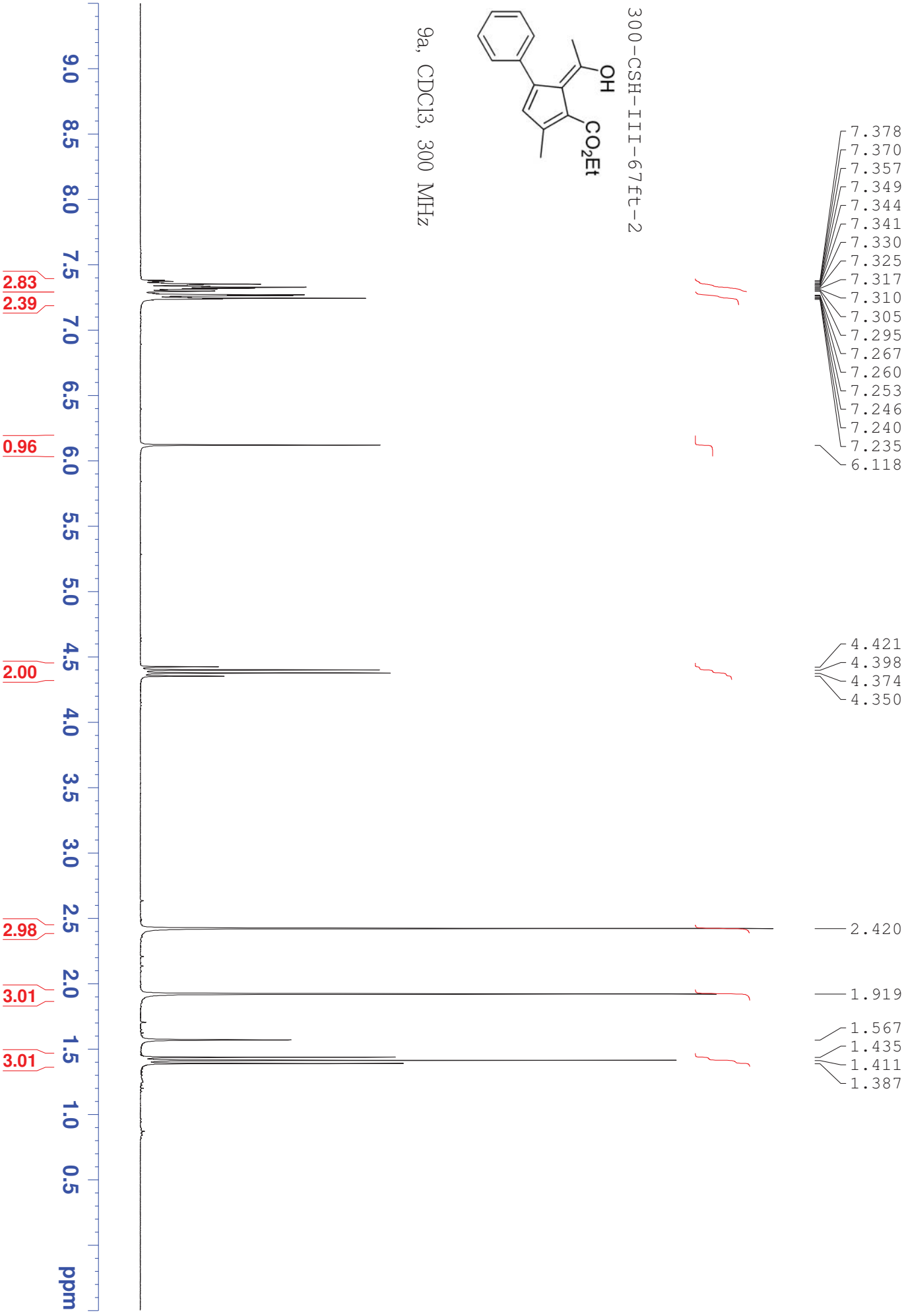

300-CSH-II-82ft-2
7e, CDCl3, 300 MHz
Br
O
O
O
O
7.489
7.482
7.466
7.460
7.452
7.341
7.335
7.319
7.313
7.239
6.598
5.251
5.247
5.069
5.067
3.516
3.510
1.838
1.732
1.581
1.97
2.00
0.98
1.03
1.00
2.02
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

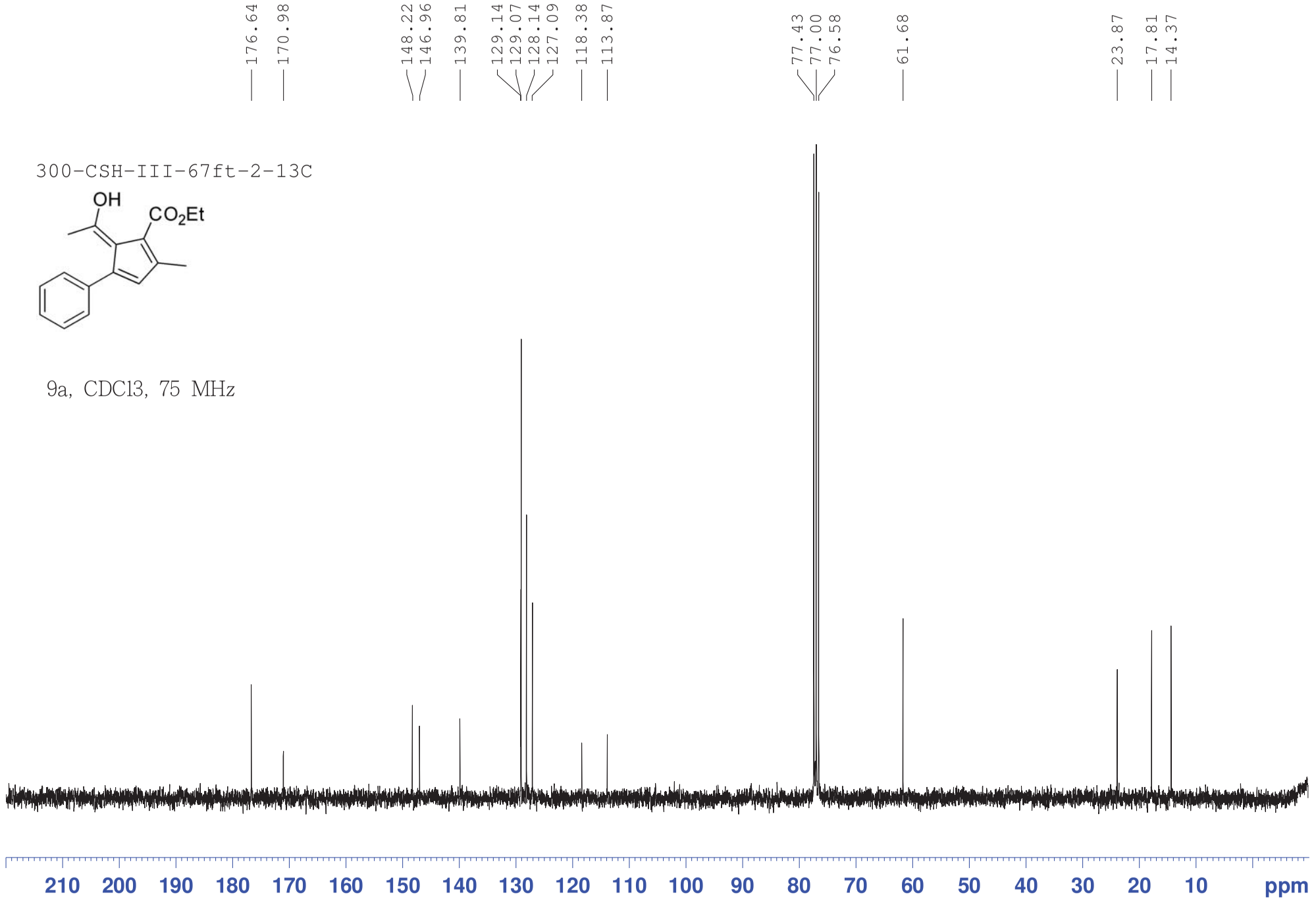

168.86
155.15
146.83
132.67
131.77
127.60
125.65
123.10
107.59
105.25
77.43
77.00
76.58
56.68
41.68
30.68
27.50
300-CSH-II-82ft-4-13C
O
O
O
O
Br
7e, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

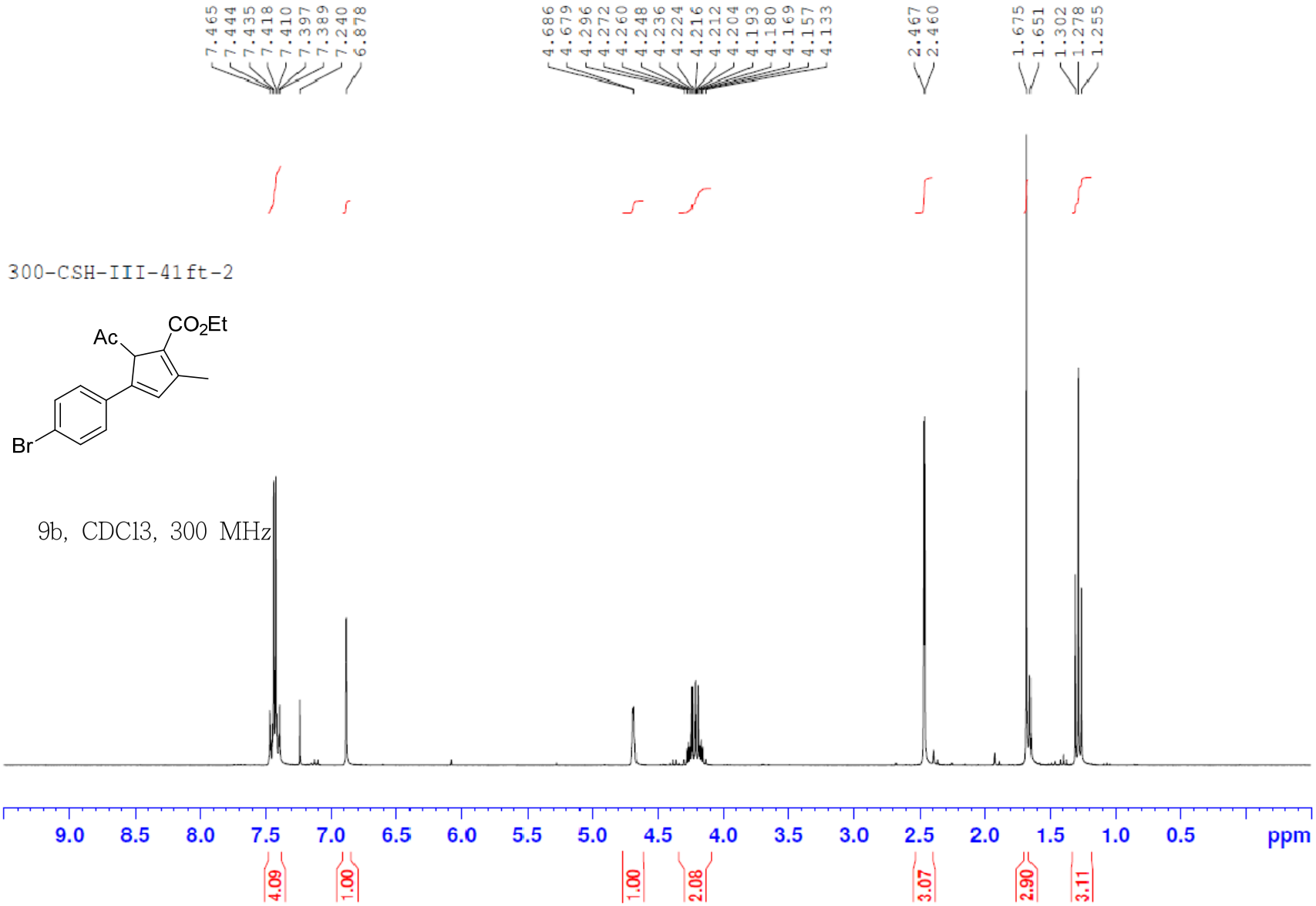

300-CSH-III-3ft
8b, 300 MHz, CDCl3
Br
CO2Et
7.465
7.435
7.404
7.396
7.374
7.245
7.244
7.239
7.235
6.743
4.268
4.244
4.220
4.196
3.670
3.665
3.662
3.657
3.654
3.649
2.380
2.372
2.364
1.536
1.345
1.321
1.297
2.19
2.22
1.00
2.15
2.12
3.08
3.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

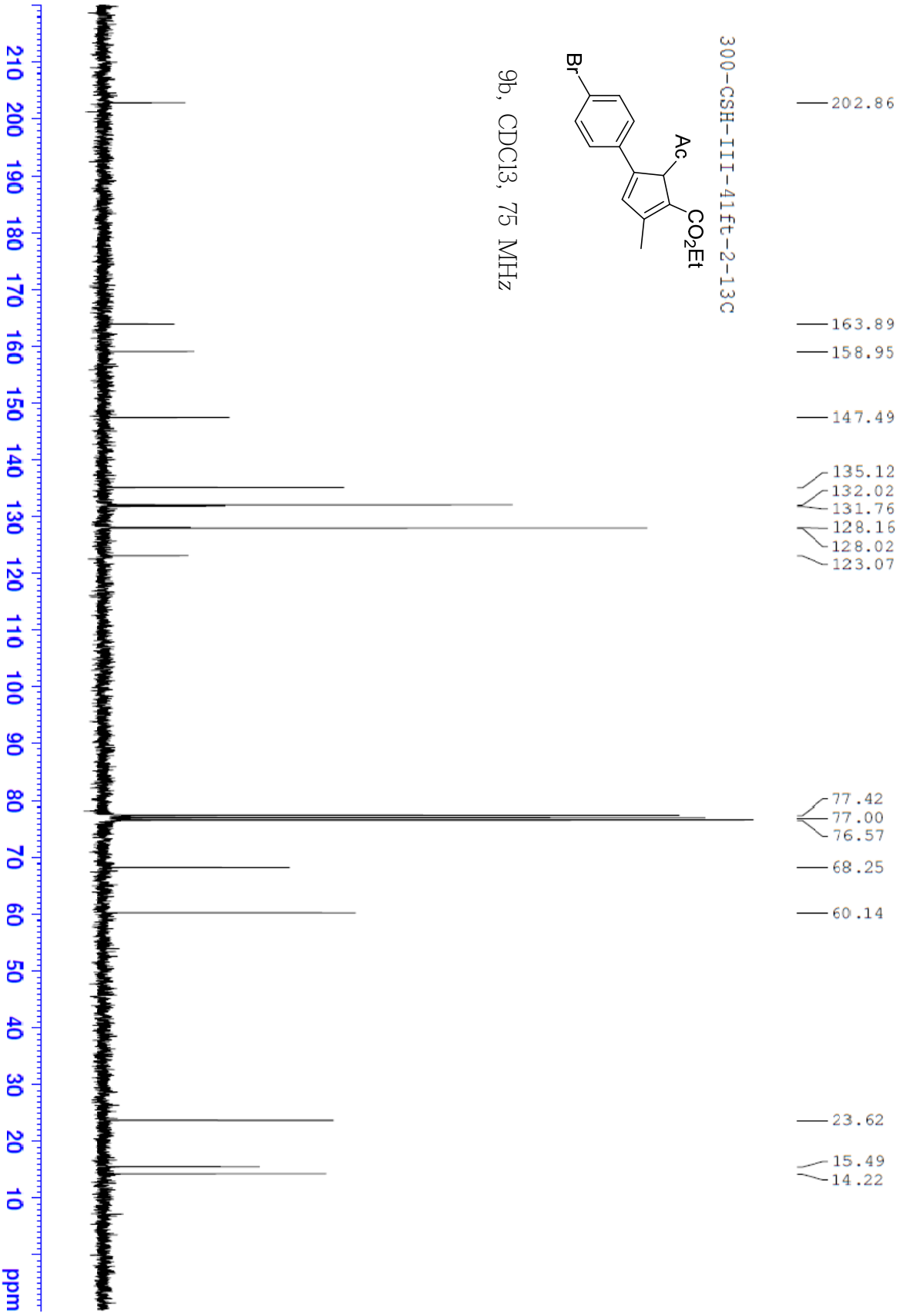


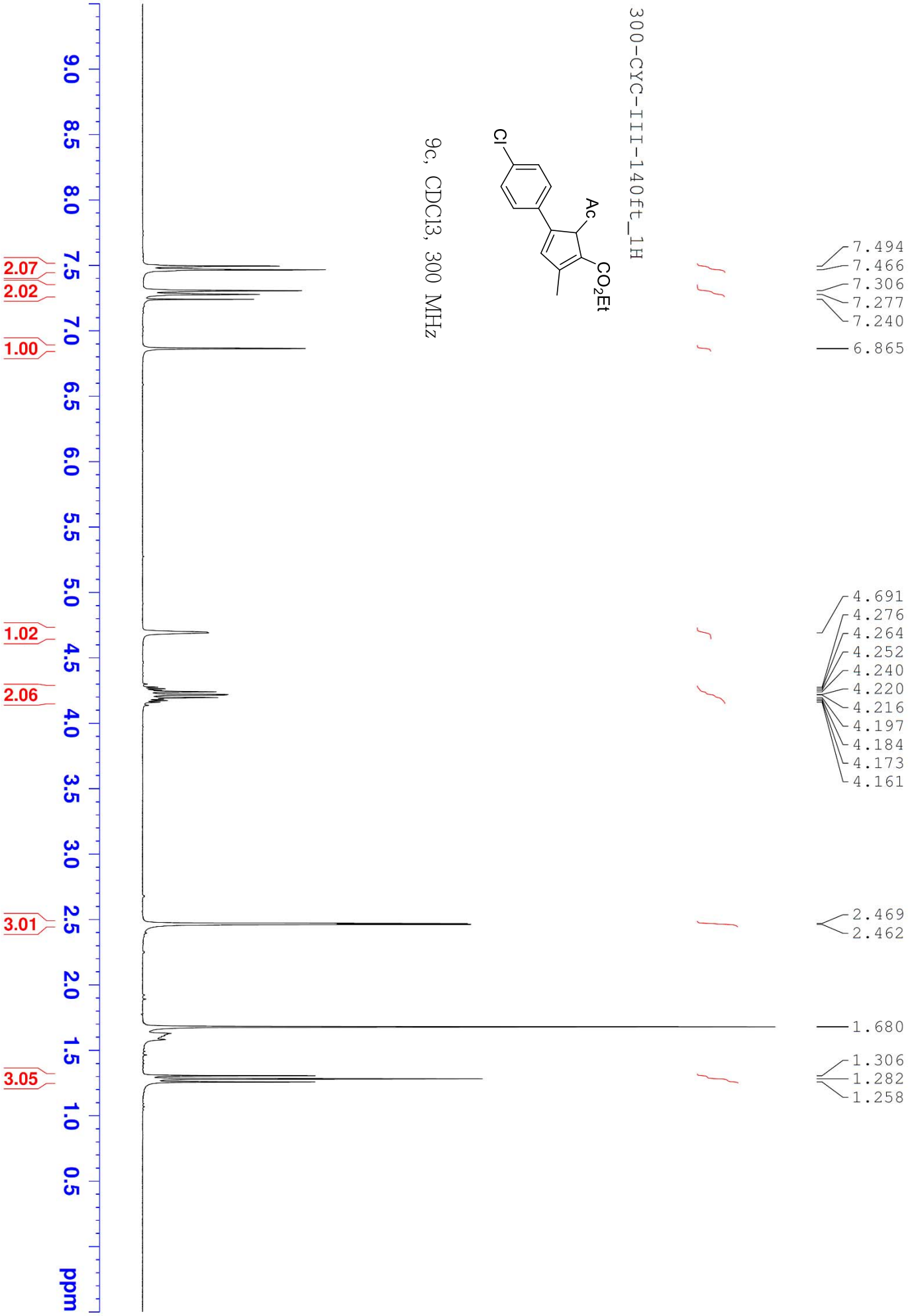
8b, 75 MHz, CDCl3

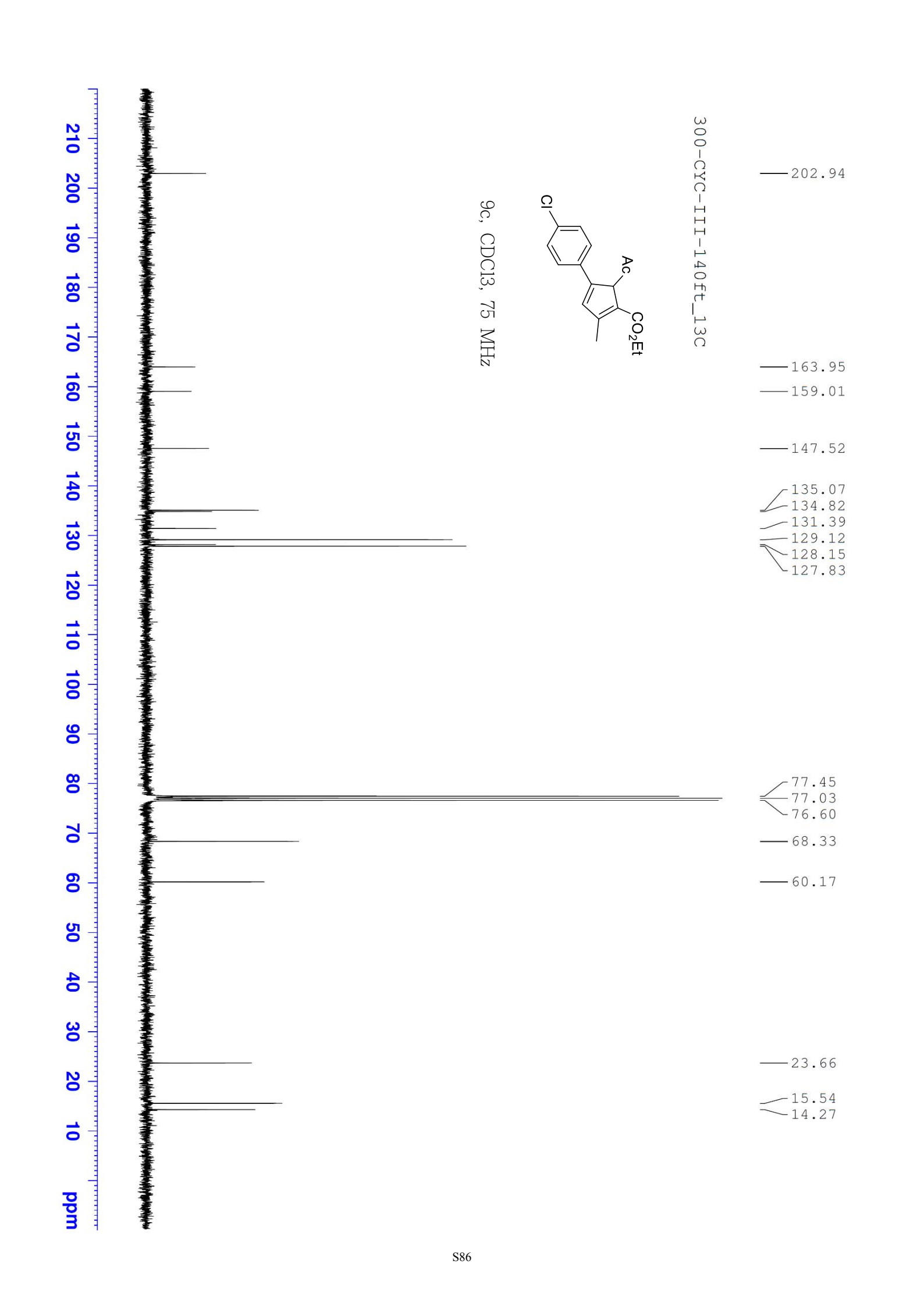

300-CSH-III-67ft-2
9a, CDCl3, 300 MHz
OH
CO2Et
7.378
7.370
7.357
7.349
7.344
7.341
7.330
7.325
7.317
7.310
7.305
7.295
7.267
7.260
7.253
7.246
7.240
7.235
6.118
4.421
4.398
4.374
4.350
2.420
1.919
1.567
1.435
1.411
1.387
2.83
2.39
0.96
2.00
2.98
3.01
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

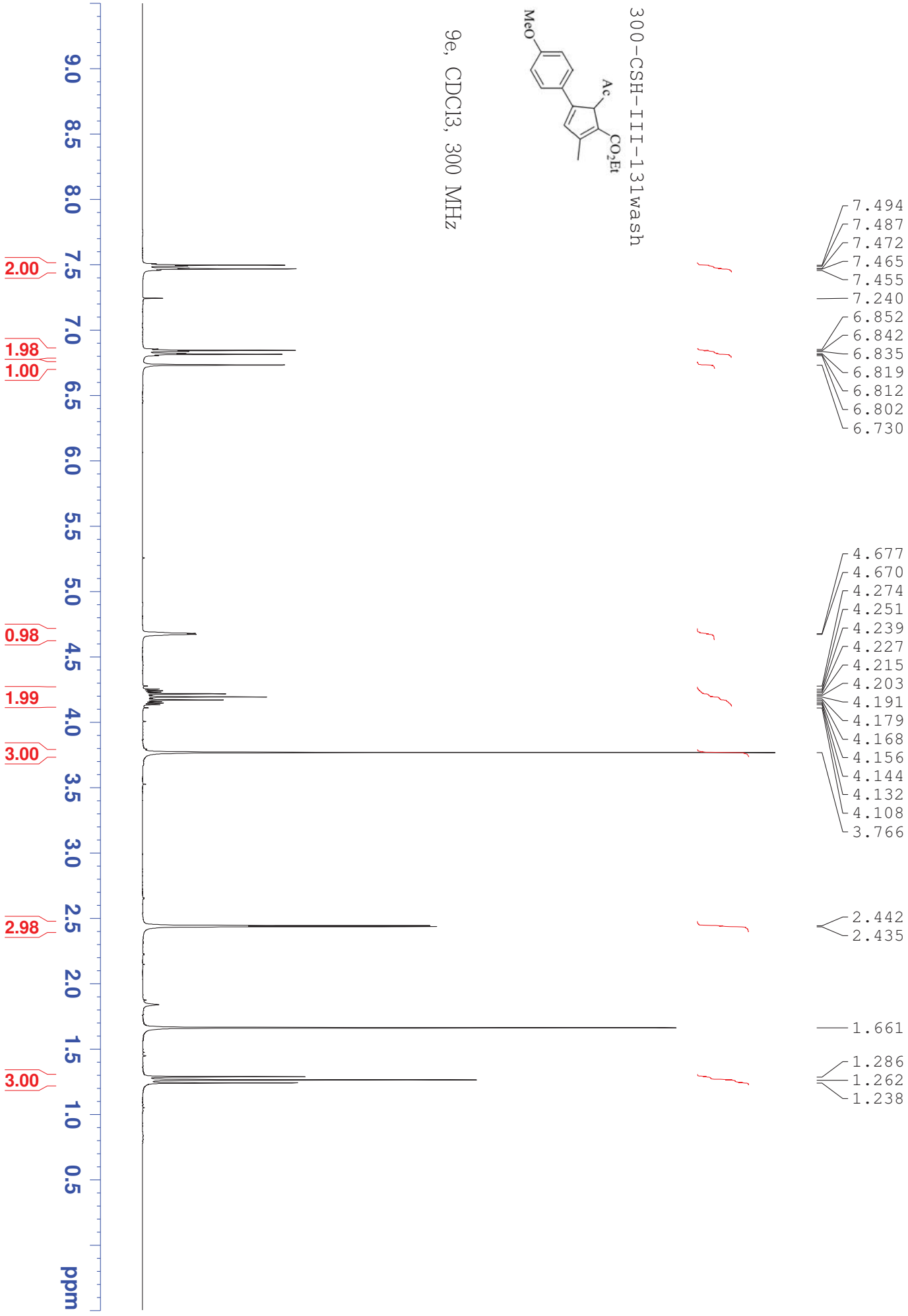

176.64
170.98
148.22
146.96
139.81
129.14
129.07
128.14
127.09
118.38
113.87
77.43
77.00
76.58
61.68
23.87
17.81
14.37
300-CSH-III-67ft-2-13C
OH
CO2Et
9a, CDCl3, 75 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

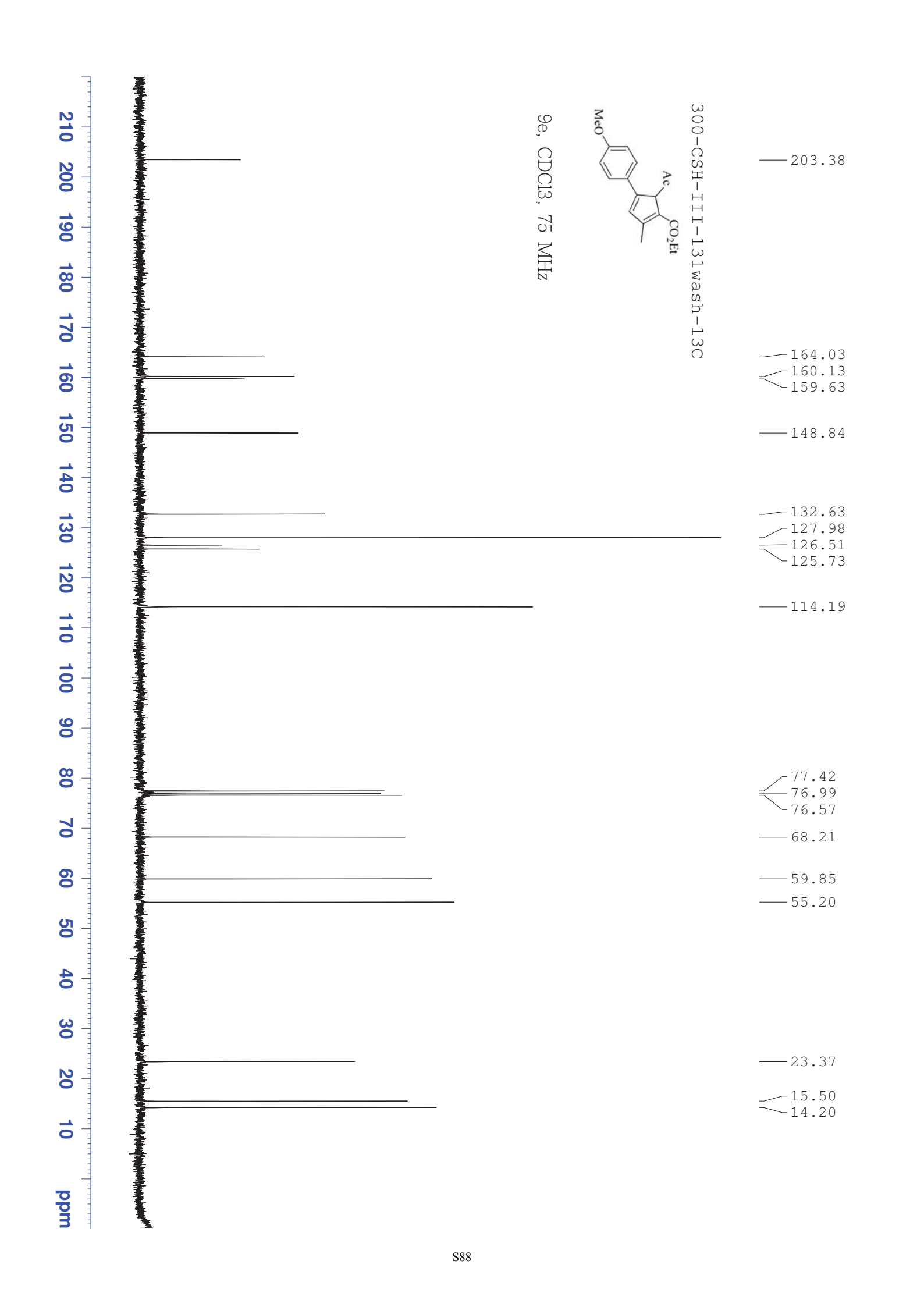

7.465
7.444
7.435
7.418
7.410
7.397
7.389
7.240
6.878
4.686
4.679
4.296
4.272
4.260
4.248
4.236
4.224
4.216
4.212
4.204
4.193
4.180
4.169
4.157
4.133
2.467
2.460
1.675
1.651
1.302
1.278
1.255
300-CSH-III-41ft-2
Ac
CO2Et
Br
9b, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.09
1.00
1.00
2.08
3.07
2.90
3.11

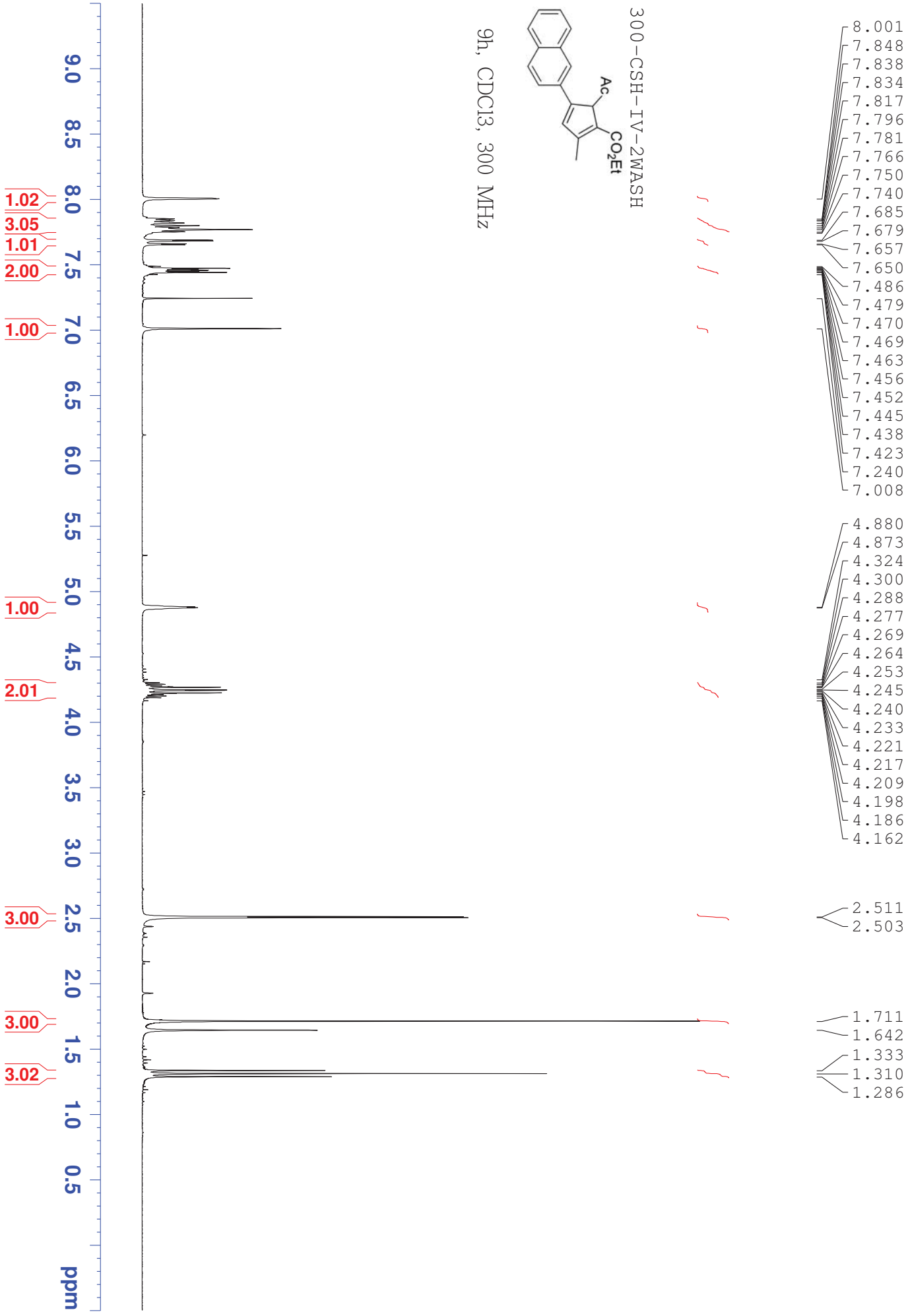

300-GSH-III-41ft-2-13C
9b, CDCl3, 75 MHz
Br
Ac
CO2Et
202.86
163.89
158.95
147.49
135.12
132.02
131.76
128.16
128.02
123.07
77.42
77.00
76.57
68.25
60.14
23.62
15.49
14.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

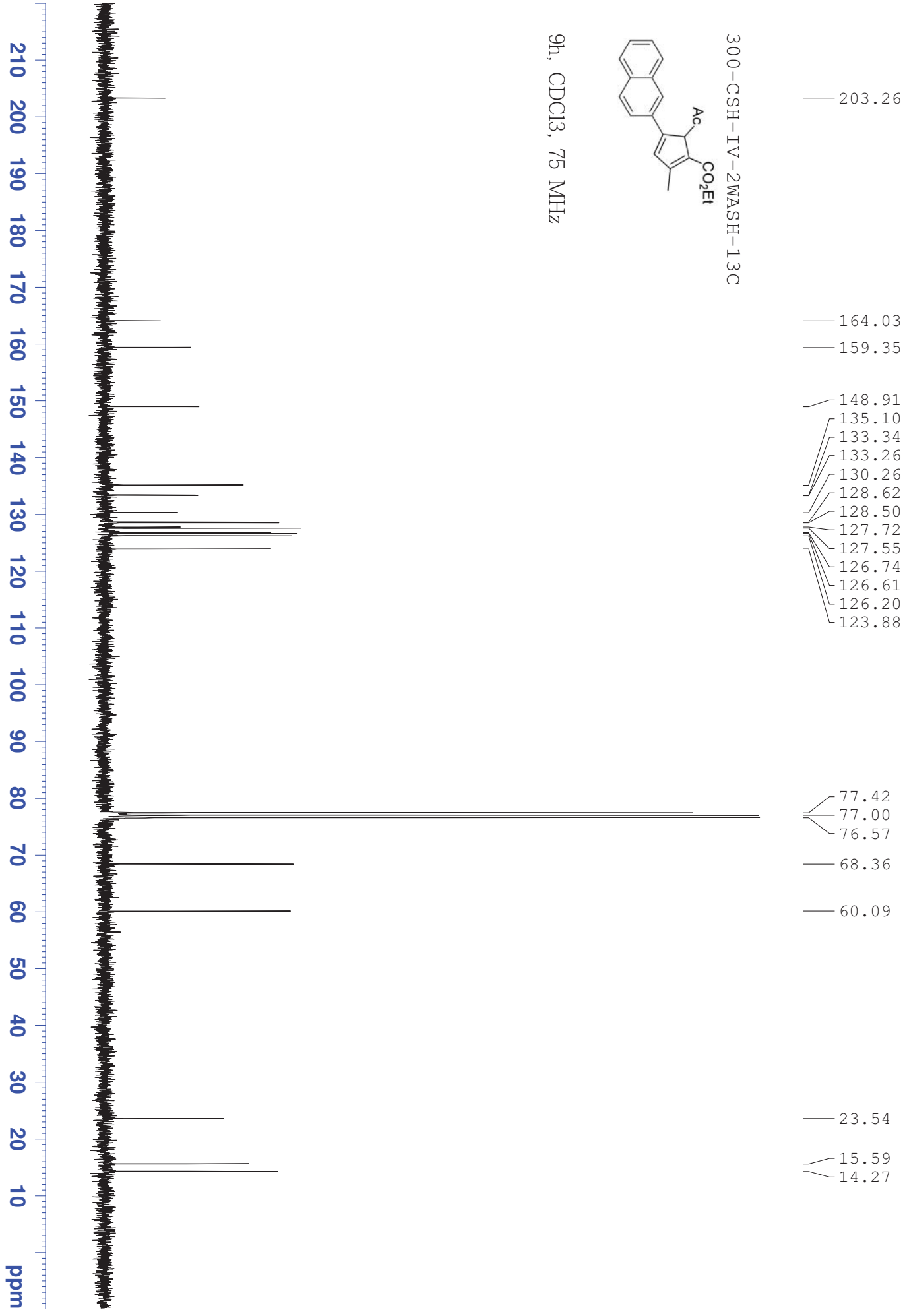

300-CYC-III-140ft_1H
9c, CDCl3, 300 MHz
Cl
Ac
CO2Et
7.494
7.466
7.306
7.277
7.240
6.865
4.691
4.276
4.264
4.252
4.240
4.220
4.216
4.197
4.184
4.173
4.161
2.469
2.462
1.680
1.306
1.282
1.258
2.07
2.02
1.00
1.02
2.06
3.01
3.05
ppm


300-CYC-III-140ft_13C
9c, CDCl3, 75 MHz
Cl
Ac
CO2Et
202.94
163.95
159.01
147.52
135.07
134.82
131.39
129.12
128.15
127.83
77.45
77.03
76.60
68.33
60.17
23.66
15.54
14.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


300-CSH-III-131wash
9e, CDCl3, 300 MHz
MeO
Ac
CO2Et
7.494
7.487
7.472
7.465
7.455
7.240
6.852
6.842
6.835
6.819
6.812
6.802
6.730
4.677
4.670
4.274
4.251
4.239
4.227
4.215
4.203
4.191
4.179
4.168
4.156
4.144
4.132
4.108
3.766
2.442
2.435
1.661
1.286
1.262
1.238
2.00
1.98
1.00
0.98
1.99
3.00
2.98
3.00
ppm


300-CSH-III-131wash-13C
9e, CDCl3, 75 MHz
MeO
Ac
CO2Et
203.38
164.03
160.13
159.63
148.84
132.63
127.98
126.51
125.73
114.19
77.42
76.99
76.57
68.21
59.85
55.20
23.37
15.50
14.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


300-CSH-IV-2WASH
9h, CDCl3, 300 MHz
Ac
CO2Et
8.001
7.848
7.838
7.834
7.817
7.796
7.781
7.766
7.750
7.740
7.685
7.679
7.657
7.650
7.486
7.479
7.470
7.469
7.463
7.456
7.452
7.445
7.438
7.423
7.240
7.008
4.880
4.873
4.324
4.300
4.288
4.277
4.269
4.264
4.253
4.245
4.240
4.233
4.221
4.217
4.209
4.198
4.186
4.162
2.511
2.503
1.711
1.642
1.333
1.310
1.286
1.02
3.05
1.01
2.00
1.00
1.00
2.01
3.00
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


300-CSH-IV-2WASH-13C
9h, CDCl3, 75 MHz
Ac
CO2Et
203.26
164.03
159.35
148.91
135.10
133.34
133.26
130.26
128.62
128.50
127.72
127.55
126.74
126.61
126.20
123.88
77.42
77.00
76.57
68.36
60.09
23.54
15.59
14.27
ppm