Supplementary Information for:

Diastereoselective Synthesis of Half-Sandwich Chiral-at-Metal Cobaltacycles by Oxidative Cyclisation

Jahangir Amin and Christopher J. Richards

School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, U.K.

Fax: +44(0) 1603 592003; Tel: +44(0) 1603 593890

Contents

General Experimental Methods:

All reactions were performed under an inert nitrogen atmosphere using anhydrous solvents. Anhydrous THF was obtained by distillation from Na/benzophenone. Reagents and chemicals were obtained from commercial suppliers and used as received. Petroleum ether refers to the 40–60 °C boiling range for petroleum ether. Flash chromatography was carried out using silica gel Kieselgel Merck Type 9385 230–400 mesh (40–63 μm) and eluents as indicated. TLC was carried out on Kieselgel Merck 60 F_{254}, aluminium–backed silica gel sheets and visualised with a UV lamp (Minerlight Lamp UVGL-58 UV 254/365 nm), staining with $KMnO_4$ or visible spots enhanced with iodine in silica. ^{13}C spectra are proton–decoupled. NMR spectra were recorded at room temperature unless specified in deuterated solvents ($CDCl_3$, CD_2Cl_2) on a Varian 400 Lambda spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR, or a Joel JNM–EX operating at 270 MHz for ^1H and 67 MHz for ^{13}C and 109 MHz for ^{31}P NMR, or a Bruker ultrashield 400 MHz for ^1H and 100 MHz for ^{13}C and 376 MHz for ^{19}F NMR. Solvent peaks are used as internal reference relative to Me_4Si for ^1H NMR and ^{13}C NMR chemical shift (ppm). Coupling constants are given in Hz. Infrared spectra were recorded using a Shimadzu FTIR–8300 spectrophotometer (450–4000 cm^{-1}). Optical rotations were measured on a Jasco P–1010 instrument or a Perkin–Elmer model 241. Melting points were carried out using Griffin MFB-700–010U melting point apparatus. High performance liquid chromatography (analytical HPLC) was performed on a ChiralCel OD column containing cellulose tris(3,5–dimethylphenylcarbamate) coated on 10 μm silica–gel. Solvents used were HPLC grade. Compounds **3a**,[1] **3b**,[1] **3c**,[2] **4a**,[1] **4b**,[1] **5**,[3] **7a**,[1] **7c**,[1] are known compounds or are commercially available.

General procedure for the synthesis of 4c, *rac*–6 and (*S*)–6.

2–Iodobenzoic acid or 2-(phenylethynyl)benzoic acid **5** (1.1 eq.), *N,N'*–dicyclohexylcarbodiimide (DCC) (1.1 eq.) and 4–dimethylaminopyridine (0.2 eq.) were dissolved in dichloromethane (1 mL/ mmol) and cooled to 0 °C for 30 mins. A white precipitate was observed suggesting the formation of the corresponding active ester. Propargylic alcohol **3c** or but-3-yn-2-ol (1 eq.) was then added and the reaction mixture allowed to warm to room temperature, and then left to stir for 48 hours and monitored by TLC. The reaction mixture was filtered using a sinter removing *N,N'*–dicyclohexylurea (DCU). The crude mixture was then treated with 1 M hydrochloric acid (HCl) (2x10 mL/ mmol) and extracted with dichloromethane (2x10 mL/ mmol). The organic layer dried ($MgSO_4$), filtered and the solvent removed *in vacuo*, and the residue purified using silica gel column chromatography.

Synthesis of 4c

Using the general procedure, **3c** (1.00 g, 4.67 mmol) gave **4c** (1.90 g, 92%) as a colourless oil after silica gel column chromatography using 1:9 CH_2Cl_2/hexane:

IR (thin film) ν_{max} 1732 cm^{-1}; ^1H NMR (δ, 400 MHz, $CDCl_3$) 1.67 (3H, d, *J* 6.7 Hz, C*H*$_3$), 5.86 (1H, q, *J* 6.7 Hz, C*H*), 7.09 (1H, td, *J* 7.8, 1.7 Hz, ArC*H*), 7.34 (1H, td, *J* 7.6, 1.2 Hz, ArC*H*), 7.47-7.51 (4H, m, ArC*H*), 7.78 (1H, dd, *J* 7.8, 1.7 Hz, ArC*H*), 7.93 (1H, dd, *J* 7.6, 1.2 Hz, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$); 21.3 (*C*H$_3$), 62.1 (*C*H), 83.8 (C*C*), 89.6 (C*C*), 94.2 (Ar*C*I), 122.5 (Ar*C*H), 125.2 (Ar*C*H), 126.1 (Ar*C*H), 128.0 (Ar*C*H), 130.2 (q, *J* 33.0 Hz, Ar*C*F$_3$), 131.1 (ArC*H*), 132.1 (2xArC*H*), 132.8 (Ar*C*H), 134.8 (Ar*C*H), 141.4 (2xAr*C*H), 165.4 (*C*O); ^{19}F NMR (δ, 376 MHz, $CDCl_3$) –64.1; HRMS (*m*/*z*, ESI), $C_{18}H_{16}F_3INO_2$ $[M+NH_4]^+$ requires 462.0172, found 462.0169.

Synthesis of *rac*-6

Using the general procedure, **5** (2.00 g, 9.00 mmol) and but–3–yn–2–ol (0.86 mL, 11.0 mmol) gave **6** (2.32 g, 94%) as a colourless oil that crystallised upon standing after silica gel column chromatography using 1:9 EtOAc/petroleum ether 40–60 °C:

m.p. 40–42°C; IR (thin film) ν_{max} 1732 cm^{-1}; Anal. Calc. for $C_{19}H_{14}O_2$; C, 83.19; H, 5.14; Found; C, 83.17; H, 5.14; ^1H NMR (δ, 400 MHz, $CDCl_3$) 1.61 (3H, d, *J* 8.0 Hz, C*H*$_3$), 2.44 (1H, m, C*H*), 5.91 (1H, m, C*H*), 7.30–7.36 (4H, m, ArC*H*), 7.39–7.45 (1H, td, *J* 7.4, 1.2 Hz, ArC*H*), 7.50–7.59 (3H, m, ArC*H*), 7.93–7.96 (1H, dd, *J* 7.9, 1.0 Hz, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 21.6 (*C*H$_3$), 61.1 (*C*H), 73.8 (*C*C), 82.5 (*C*C), 88.5 (*C*C), 94.9 (*C*C), 123.5 (*C*Ar), 124.1 (*C*Ar), 128.2 (Ar*C*H), 128.6 (2xAr*C*H), 128.9 (Ar*C*H), 130.9 (Ar*C*H), 131.5 (*C*Ar), 132.0 (2xAr*C*H), 132.3 (Ar*C*H), 134.4 (Ar*C*H), 165.2 (*C*O); HRMS (*m*/*z*, ESI), $C_{19}H_{15}O_2$ $[M+H]^+$ requires 275.1065, found 275.1067.

Synthesis of (*S*)-6

Using the same procedure for *rac*-**6**, **5** (3.16 g, 14.26 mmol) and (*S*)–(–)–3–butyn–2–ol (1.18 mL, 15.0 mmol) gave (*S*)-**6** (3.74 g, 96%):

m.p. 42–44 °C; $[\alpha]_D$ = –47.5 (*c* 1.10, 25.0 °C , $CHCl_3$); ^1H NMR (δ, 400 MHz, $CDCl_3$) 1.61 (3H, d, *J* 6.8 Hz, C*H*$_3$), 2.48 (1H, s, C*H*), 5.71 (1H, q, *J* 6.8 Hz, C*H*), 7.26–7.36 (3H, m, ArC*H*), 7.42–7.48 (1H, td, *J* 7.4, 1.2 Hz, ArC*H*), 7.52–7.64 (4H, m, ArC*H*), 7.94–7.99 (1H, d, *J* 7.9 Hz, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 21.6 (*C*H$_3$), 61.1 (*C*H), 73.6 (*C*C), 82.4 (*C*C), 88.4 (*C*C), 94.9 (*C*C), 123.5 (*C*Ar), 124.1 (*C*Ar), 128.2 (Ar*C*H), 128.6 (2xAr*C*H), 128.8 (Ar*C*H), 130.9 (Ar*C*H), 131.5 (*C*Ar), 132.0 (2xAr*C*H), 132.2 (Ar*C*H), 134.4 (Ar*C*H), 165.2 (*C*O); HRMS (*m*/*z*, ESI), $C_{19}H_{18}NO_2$ $[M+NH_4]^+$ requires 292.1332, found 292.1329; HPLC (CHIRALCEL OD) 96.5:3.5 hexane/isopropyl alcohol, 1 mL/min Rt = 8 min 48 secs (*S*–enantiomer), Rt = 7 min 18 secs (*R*–enantiomer).

General Procedure for Sonogashira Cross-Coupling

In a Schlenk tube (100 mL) covered with aluminium foil the terminal alkyne (1 eq.) was stirred in anhydrous triethylamine (10 mL/mmol) and to this solution was added CuI (10 mol%), $PdCl_2(PPh_3)_2$ (3 mol%) and the solution warmed to 60°C before the addition of ArI (1 eq., unless specified). The reaction mixture was stirred overnight under nitrogen before being quenched with aqueous NH_4Cl (3x10 mL/mmol) and extracted with CH_2Cl_2 (10 mL/mmol). The organic layer and washed with sat. brine (10 mL/mmol) dried ($MgSO_4$), filtered and solvent removed *in vacuo.* The products were purified using silica gel column chromatography.

Synthesis of (*S*)-7a

Using the general procedure for Sonogashira cross-coupling, (*S*)-**6** (1.56 g, 5.69 mmol) and iodobenzene (0.68 mL, 6.1 mmol) gave (*S*)-**7a** (1.99 g, quantitative). Spectroscopic data corresponded to that previously reported for *rac*-**7a**.[1]

$[\alpha]_D$ = –90.7 (*c* 1.20, 25.0 °C, $CHCl_3$); HPLC (CHIRALCEL OD) 96.5:3.5 hexane/isopropyl alcohol, 1 mL/min Rt = 9 min 6 secs (*S*–enantiomer), Rt= 7 min 24 secs (*R*–enantiomer).

Synthesis of 7c

Using the general procedure for Sonogashira cross-coupling, **4c** (0.50 g, 1.13 mmol) and phenyl acetylene (0.13 mL, 1.2 mmol) gave **7c** (0.45 g, 96%) as a colourless oil that crystallised upon standing after silica gel column chromatography with 1:9 EtOAc/petroleum ether 40–60 °C:

m.p. 38–40 °C; Anal. Calc. for $C_{26}H_{17}F_3O_2$; C, 74.63; H, 4.10; Found; C, 74.71; H, 4.13; IR (thin film) ν_{max} 1724 cm^{-1}; ^{1}H NMR (δ, 400 MHz, $CDCl_3$) 1.67 (3H, d, *J* 8.1 Hz, C*H*$_3$), 5.91 (1H, q, *J* 8.1 Hz, C*H*), 7.20–7.25 (3H, m, ArC*H*), 7.32 (1H, td, *J* 5.2, 0.8 Hz, ArC*H*), 7.38–7.47 (5H, m, ArC*H*), 7.49–7.53 (2H, m, ArC*H*), 7.59 (1H, dd, *J* 5.2 , 0.6 Hz, ArC*H*), 7.95 (1H, dd, *J* 5.2, 0.6 Hz, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 21.5 (*C*H$_3$), 61.5 (*C*H), 83.5 (*C*C), 88.1 (C*C*), 90.0 (C*C*), 94.6 (*C*C), 123.3 (*C*Ar), 123.9 (*C*Ar), 125.2 (q, *J* 4.0 Hz, Ar*C*F$_3$), 126.2 (*C*Ar), 128.0 (Ar*C*H), 128.3 (2xAr*C*H), 128.5 (Ar*C*H), 129.8 (*C*Ar), 130.1 (Ar*C*H), 130.7 (Ar*C*H), 131.6 (Ar*C*H), 131.7 (2xAr*C*H), 131.9 (Ar*C*H), 132.1 (2xAr*C*H), 134.1 (Ar*C*H), 165.3 (*C*O); ^{19}F NMR (δ, 376 MHz, $CDCl_3$) –64.0; HRMS (*m*/*z*, EI), $C_{26}H_{17}F_3O_2$ $[M]^+$ requires 418.1175, found 418.1173.

Synthesis of 7d

Using the general procedure for Sonogashira cross-coupling, **4a** (0.25 g, 0.66 mmol) and 1–ethynyl–4–(trifluoromethyl)benzene (0.10 mL, 0.7 mmol) gave **7d** (0.26 g, 93%) as a colourless oil after silica gel column chromatography with 1:9 EtOAc/petroleum ether 40–60 °C:

IR (thin film) ν_{max} 1732 cm^{-1}; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 1.72 (3H, d, *J* 6.7 Hz, CH_3), 5.60 (1H, q, *J* 6.7 Hz, C*H*), 7.23–7–7.32 (4H, m, ArC*H*), 7.36–7.56 (6H, m, ArC*H*), 7.65–7.70 (2H, m, ArC*H*), 8.05 (1H, dd, *J* 7.6, 1.2 Hz, ArC*H*); ^{13}C NMR (δ, 67 MHz, $CDCl_3$) 21.8 (*C*H_3), 62.0 (*C*H), 85.1 (*C*C), 87.5 (*C*C), 90.5 (*C*C), 93.0 (*C*C), 122.3 (*C*Ar), 123.2 (*C*Ar), 125.3 (q, *J* 4.0 Hz, Ar*C*F3), 126.0 (*C*Ar), 127.2 (*C*Ar), 128.3 (2xAr*C*H), 128.6 (Ar*C*H), 128.8 (Ar*C*H), 128.9 (*C*Ar), 130.9 (Ar*C*H), 131.9 (2xAr*C*H), 132.0 (4xAr*C*H), 134.2 (Ar*C*H), 141.4 (Ar*C*H), 165.2 (*C*O); ^{19}F NMR (δ, 376 MHz, $CDCl_3$) –63.8; HRMS (*m*/*z*, ESI), $C_{26}H_{21}F_3O_2N$ $[M+NH_4]^+$ requires 436.1518, found 436.1519.

Synthesis of 7e

Using the general procedure for Sonogashira cross-coupling, **4a** (1.83 g, 4.86 mmol) and 3–iodopyridine (0.57 mL, 5.7 mmol) gave **7e** (1.67 g, 98%) as a pale yellow oil after silica gel column chromatography with 1:9 EtOAc/petroleum ether 40–60 °C:

IR (thin film) ν_{max} 1727 cm^{-1}; ^{1}H NMR (δ, 400 MHz, $CDCl_3$) 1.60 (3H, d, *J* 6.8 Hz, CH_3), 5.87 (1H, q, *J* 6.8 Hz, C*H*), 7.04 (1H, dd, *J* 5.2 Hz, ArC*H*), 7.11–7.19 (3H, m, ArC*H*), 7.25–7.30 (3H, m, ArC*H*), 7.38 (1H, t, *J* 7.6 Hz, ArC*H*), 7.53 (1H, d, *J* 7.6 Hz, ArC*H*), 7.74 (1H, d, *J* 8.0 Hz, ArC*H*), 7.92 (1H, d, *J* 7.6 Hz, ArC*H*), 8.38 (1H, d, *J* 4.4 Hz, ArC*H*), 8.73 (1H, s, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 21.9 (*C*H_3), 62.0 (*C*H), 85.2 (*C*C), 87.6 (*C*C), 91.1 (*C*C), 91.6 (*C*C), 120.7 (*C*Ar), 122.3 (*C*Ar), 123.2 (Ar*C*H), 123.3 (*C*Ar), 128.5 (2xAr*C*H), 128.8 (Ar*C*H), 128.8 (Ar*C*H), 131.0 (Ar*C*H), 131.8 (*C*Ar), 132.0 (2xAr*C*H), 132.2 (Ar*C*H), 134.3 (Ar*C*H), 138.8 (Ar*C*H), 148.9 (Ar*C*H), 152.4 (Ar*C*H), 165.1 (*C*O); HRMS (*m*/*z*, ESI), $C_{24}H_{18}NO_2$ $[M+H]^+$ requires 352.1332, found 352.1330.

Synthesis of 7f

Using the general procedure for Sonogashira cross-coupling **6**, (0.50 g, 1.82 mmol) and 1-bromo–2–iodobenzene (0.25 mL, 1.9 mmol) gave **7f** (0.75 g, 96%) as a pale yellow oil after silica gel column chromatography using 3:7 EtOAc/petroleum ether 40–60 °C:

IR (thin film) ν_{max} 1732 cm^{-1}; ^{1}H NMR (δ, 400 MHz, $CDCl_3$) 1.68 (3H, d, *J* 6.8 Hz, CH_3), 5.94 (1H, q, *J* 6.8 Hz, C*H*), 7.08 (1H, td, *J* 7.6, 1.6 Hz, ArC*H*), 7.14 (1H, td, *J* 7.6, 1.2 Hz, ArC*H*), 7.19–7.25 (3H, m, ArC*H*), 7.31– 7.35 (2H, m, ArC*H*), 7.44 (1H, td, *J* 7.6, 1.2 Hz, ArC*H*), 7.49 (1H, dd, *J* 8.0, 1.2 Hz, ArC*H*), 7.52–7.54 (2H, m, ArC*H*), 7.59 (1H, dd, *J* 7.6, 1.2 Hz, ArC*H*), 7.96 (1H, dd, *J* 8.0, 1.2 Hz, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 21.8 (*C*H_3), 61.9 (*C*H), 83.7 (*C*C), 88.4 (*C*C), 92.4 (*C*C), 94.9 (*C*C), 123.5 (*C*Ar), 124.1 (*C*Ar), 124.6 (*C*Ar), 126.0 (*C*Ar), 127.2 (Ar*C*H), 128.2 (Ar*C*H), 128.6 (2xAr*C*H), 128.7 (Ar*C*H), 130.0 (Ar*C*H), 131.0 (Ar*C*H), 131.8 (*C*Ar), 132.0 (2xAr*C*H), 132.1 (Ar*C*H), 132.6 (Ar*C*H), 133.8 (Ar*C*H), 134.3 (Ar*C*H), 165.5 (*C*O); HRMS (*m*/*z*, EI), $C_{25}H_{17}{}^{79}BrO_2$ $[M]^+$ requires 428.0406, found 428.0404.

Synthesis of 7g

Using the general procedure for Sonogashira cross-coupling **6**, (0.63 g, 2.30 mmol) and 4–chloro–3–iodopyridine (0.30 mL, 2.5 mmol) gave **7g** (0.86 g, 97%) as a pale yellow oil after silica gel column chromatography using 1:9 EtOAc/petroleum ether 40–60 °C:

IR (thin film) ν_{max} 1731 cm^{-1}; ^{1}H NMR (δ, 400 MHz, $CDCl_3$) 1.73 (3H, d, *J* 6.8 Hz, C*H*$_3$), 6.00 (1H, q, *J* 6.8 Hz, C*H*), 7.23–7.29 (4H, m, ArC*H*), 7.36–7.39 (1H, t, *J* 8.0 Hz, ArC*H*), 7.47–7.50 (1H, t, *J* 7.6 Hz, ArC*H*), 7.49–7.53 (1H, m, ArC*H*), 7.56–7.64 (1H, d, *J* 7.6 Hz, ArC*H*), 7.99–8.01 (2H, m, ArC*H*), 8.37 (1H, d, *J* 5.6 Hz, ArC*H*), 8.54 (1H, s, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 21.5 (*C*H$_3$), 61.5 (*C*H), 78.7 (*C*C), 88.4 (*C*C), 94.8 (*C*C), 96.2 (*C*C), 119.9 (*C*Ar), 123.4 (*C*Ar), 124.0 (*C*Ar), 124.1 (Ar*C*H), 128.1 (Ar*C*H), 128.5 (2xAr*C*H), 128.7 (Ar*C*H), 130.8 (Ar*C*H), 131.5 (*C*Ar), 131.8 (2xAr*C*H), 132.2 (Ar*C*H), 134.2 (Ar*C*H), 145.5 (*C*Ar), 149.6 (Ar*C*H), 153.7 (Ar*C*H), 165.2 (*C*O); HRMS (*m*/*z*, ESI) $C_{24}H_{17}{}^{35}ClNO_2$ $[M+H]^+$ requires 386.0942, found 386.0944.

General Procedures for the Synthesis of Metallocyclopentadiene Complexes 8a-g, (*S*)-8a and 11a, c and d

Procedure A: An oven dried Schlenk tube was fitted with a stirrer bar, rubber septa and nitrogen inlet. The flask was flushed with nitrogen and charged with diyne **7** (1 eq.) and chlorotris(triphenylphosphine)cobalt(I)[4] (1.4 eq.), THF (1 mL/mmol), and either **(i)**; sodium η^5–cyclopentadienide or **(ii)**; sodium η^5-carbomethoxycyclopentadienide (1.4 eq.). The reaction mixture was then heated to 66 °C for exactly 30 minutes before the solvent was removed *in vacuo.* The reaction mixture was then given an aqueous work up using ethyl acetate (10mL/mmol) and filtered through a Büchner funnel containing silica under reduced pressure with 20 mL/mmol of ethyl acetate. The organic material was concentrated and silica gel column chromatography was performed. [Note: sodium η^5-carbomethoxycyclopentadienide was synthesised *in situ* by adding to sodium cyclopentadienide (2.0 M in anhydrous THF, 1.14 eq.) dimethyl carbonate (3.45 eq.) and the resulting mixture heated at reflux for 4 hours before being added to chlorotris(triphenylphosphine)cobalt(I) (1 equiv)].[4]

Procedure B: An oven dried Schlenk tube was fitted with a stirrer bar, rubber septa and nitrogen inlet. The flask was flushed with nitrogen and charged with diyne **7** (1 eq.), (η^5–cyclopentadienyl)bis(triphenylphosphine)cobalt(I)[6] (1 eq.) and anhydrous THF (1 mL/mmol). The reaction mixture was then heated to 66 °C for exactly 30 minutes before the solvent was removed *in vacuo* and the crude reaction mixture worked up as described for Procedure A.

Synthesis of 8a

Using general procedure **A**, **7a** (0.57 g, 1.63 mmol) gave **8a** (0.53 g, 44%) as a red solid after silica gel column chromatography using 3:7 EtOAc/hexane. Using general procedure **B**, **7a** (0.30 g, 0.86 mmol) similarly gave **8a** (0.47 g, 75%). Ratio of isomers in solution ($CDCl_3$) 11 (a) : 1.5 (b) : 1 (c) : 1 (c):

^{1}H NMR (δ, 270 MHz, $CDCl_3$) 0.47 (3H, d, *J* 6.9 Hz, (b)–C*H*$_3$), 0.62 (3H, d, *J* 7.4 Hz, (c)–C*H*$_3$), 0.90 (3H, d, *J* 7.4 Hz, (c)–C*H*$_3$), 1.12 (3H, d, *J* 7.2 Hz, (a)–C*H*$_3$), 4.51 (5H, s, (b)–C$_5$*H*$_5$), 4.63 (5H, s, (c)–C$_5$*H*$_5$), 4.80 (5H, s, (a)–C$_5$*H*$_5$), 4.83 (5H, s, (c)– C$_5$*H*$_5$), 5.00 (1H, q, *J* 7.2 Hz, (a)–C*H*), 6.01 (1H, d, *J* 7.7 Hz, ArC*H*), 6.26 (2H, t, *J* 8.4 Hz, ArC*H*), 6.55 (1H, t, *J* 6.7 Hz, ArC*H*), 6.85–7.02 (10H, m, ArC*H*), 7.11–7.62 (15H, m, ArC*H*); ^{13}C NMR (δ, 67 MHz, $CDCl_3$) 20.3 ((a)–*C*H$_3$), 24.6, 58.6, 75.3, 81.3, 89.6 ((a)–*C*$_5$H$_5$), 90.0, 90.2, 90.5, 124.3 (Ar), 125.0 (Ar), 126.2 (Ar), 127.5 (Ar), 127.6 (Ar), 127.8 (Ar), 128.3 (Ar), 128.5 (Ar), 128.7 (Ar), 129.4 (Ar), 130.0 (Ar), 130.4 (Ar), 130.8 (Ar), 131.1 (Ar), 131.7 (Ar), 132.1 (Ar), 132.3 (Ar), 132.5 (Ar), 133.1 (Ar), 133.4 (Ar), 133.9 (Ar), 138.0 (Ar), 151.2, 152.6, 154.7, 172.4; ^{31}P NMR (δ, 109 MHz, $CDCl_3$) 49.3 (a)–(*P*Ph$_3$).

Synthesis of (*S*)-8a

Using the general procedure **A**, (*S*)-**7a** (0.50 g, 1.43 mmol) gave (*S*)-**8a** (0.78 g, 74%) as a red solid after silica gel column chromatography using 3:7 EtOAc/hexane. Using the general procedure **B**, (*S*)-**7a** (0.10 g, 0.29 mmol) gave (*S*)-**8a** (0.17 g, 81%). Ratio of isomers in solution ($CDCl_3$) 11 (a) : 1.5 (b) : 1 (c) : 1 (c):

m.p. 180–182 °C; $[\alpha]_D$ = –746.0 (*c* 0.002, 22.8 °C, $CHCl_3$); Anal. Calc. for $C_{48}H_{38}CoO_2P$: C, 78.25; H, 5.20; Found; C, 78.18; H, 5.29; IR (thin film) ν_{max} 1733 cm^{-1}; ^{1}H NMR (δ, 400 MHz, $CDCl_3$) 0.47 (3H, d, *J* 6.9 Hz, (b)–C*H*$_3$), 0.62 (3H, d, *J* 7.4 Hz, (c)–C*H*$_3$), 0.90 (3H, d, *J* 7.4 Hz, (c)–C*H*$_3$), 1.12 (3H, d, *J* 7.2 Hz, (a)–C*H*$_3$), 4.51 (5H, s, (b)–C$_5$*H*$_5$), 4.63 (5H, s, (c)–C$_5$*H*$_5$), 4.80 (5H, s, (a)–C$_5$*H*$_5$), 4.83 (5H, s, (c)–C$_5$*H*$_5$), 5.00 (1H, q, *J* 7.2 Hz, (a)–C*H*), 6.01 (1H, d, *J* 7.7 Hz, ArC*H*), 6.26 (2H, t, *J* 8.4 Hz, ArC*H*), 6.55 (1H, t, *J* 6.7 Hz, ArC*H*), 6.85–7.02 (10H, m, ArC*H*), 7.11–7.62 (15H, m, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 20.4 ((a)–*C*H$_3$), 75.4 (*C*H), 88.7 ((a)–*C*$_5$H$_5$), 90.1, 90.3, 90.7, 124.4 (Ar), 124.5 (Ar), 125.1 (Ar), 126.3 (Ar), 126.8 (Ar), 127.6 (Ar), 127.7 (Ar), 128.0 (Ar), 128.1 (Ar), 128.5 (Ar), 128.6 (Ar), 128.7 (Ar), 129.5 (Ar), 130.2 (Ar), 130.6 (Ar), 130.9 (Ar), 131.2 (Ar), 131.9 (Ar), 132.5 (Ar), 132.6 (Ar), 133.3 (Ar), 133.6 (Ar), 133.9 (Ar), 134.0 (Ar), 134.1 (Ar), 137.3 (Ar), 137.7 (Ar), 138.0 (Ar), 150.1, 151.3, 152.7, 154.8, 169.9, 170.2, 172.5, 180.4, 180.7; ^{31}P NMR (δ, 122 MHz, $CDCl_3$) 48.6 (a)–(*P*Ph$_3$); HRMS (*m*/*z*, FAB [NOBA]), $C_{48}H_{38}CoO_2P$ $[M]^+$ requires 736.1942, found 736.1942; HPLC (CHIRALCEL OD) 96.5:3.5 hexane/isopropyl alcohol, 1 mL/min Rt = 30 min 30 secs (*S*–enantiomer) [Rt = 34 min 48 sec (*R*–enantiomer)].

Synthesis of 8b

Using the general procedure **A**, **7b** (1.00 g, 2.64 mmol) gave **8b** as a dark red crystalline solid (1.11 g, 55%) after silica gel column chromatography using 3:7 EtOAc/hexane. Using the general procedure **B**, **7b** (0.25 g, 0.66 mmol) gave **8b** (0.40 g, 79%):

m.p. 208–21°C; Anal. Calc. for $C_{50}H_{42}CoO_2P$ C, 78.52; H, 5.54; Found; C, 78.42; H, 5.54; IR (thin film) ν_{max} 1734 cm^{-1}; ^1H NMR (δ, 400 MHz, $CDCl_3$) 0.60 (3H, d, *J* 6.4 Hz, C*H*$_3$), 0.65 (3H, d, *J* 6.4 Hz, C*H*$_3$), 1.06–1.26 (1H, m, C*H*), 4.28 (1H, d, *J* 11.2 Hz, CH), 4.81 (5H, s, C_5H_5), 5.96 (1H, d, *J* 7.6 Hz, ArC*H*), 6.18 (2H, t, *J* 10.4 Hz, ArC*H*), 6.41 (1H, t, *J* 7.6 Hz, ArC*H*), 6.66 (2H, t, *J* 10.8 Hz, ArC*H*), 6.83–6.90 (10H, m, ArC*H*), 6.96 (1H, t, *J* 6.8 Hz, ArC*H*), 7.11 (3H, t, *J* 8.8 Hz, ArC*H*), 7.17–7.28 (7H, m, ArC*H*), 7.38 (1H, t, *J* 7.2 Hz, ArC*H*), 7.56 (1H, d, *J* 8.0 Hz, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 19.6 (*C*H$_3$), 20.5 (*C*H$_3$), 29.9 (C*H*), 85.4, 85.5, 89.7 (*C*$_5$H$_5$), 124.2 (Ar), 124.4 (Ar), 125.2 (Ar), 126.7 (Ar), 127.3 (Ar), 127.7 (Ar), 128.0 (Ar), 128.2 (Ar), 128.3 (Ar), 128.6 (Ar), 128.7 (Ar), 129.4 (Ar), 129.9 (Ar), 130.4 (Ar), 130.6 (Ar), 130.7 (Ar), 130.9 (Ar), 131.1 (Ar), 131.2 (Ar), 132.4 (Ar), 132.5 (Ar), 132.9 (Ar), 133.0 (Ar), 133.8 (Ar), 133.9 (Ar), 134.0 (Ar), 134.1 (Ar), 137.1 (Ar), 137.5 (Ar), 138.3 (Ar), 138.3 (Ar), 150.0 (Ar), 150.8 (Ar), 152.7, 152.8, 152.9, 171.5, 171.8, 172.7, 180.5, 180.8; ^{31}P NMR (δ, 162 MHz, $CDCl_3$) 49.6 (*P*Ph$_3$); HRMS (*m*/*z*, FAB [NOBA]) $C_{50}H_{42}O_2PCo$ $[M]^+$ requires 764.2249, found 764.2238.

Synthesis of 8c

Using the general procedure **A**, **7c** (0.14 g, 0.34 mmol) gave **8c** (0.21 g, 78%) as a bright red solid after silica gel column chromatography using 3:7 EtOAc/hexane as the eluant solvent mixture. Ratio of isomers in solution ($CDCl_3$) 11 (a) : 1 (b) : 1 (b) : 1 (b):

IR (thin film) ν_{max} 1732 cm^{-1}; ^1H NMR (δ, 400 MHz, $CDCl_3$) 0.51 (3H, d, *J* 4.0 Hz, (b)–C*H*$_3$), 0.70 (3H, d, *J* 4.0 Hz, (b)–C*H*$_3$), 0.91 (3H, d, *J* 4.0 Hz, (b)–C*H*$_3$), 1.13 (3H, d, *J* 8.0 Hz, (a)–C*H*$_3$), 4.53 (5H, s, (b)–C_5H_5), 4.65 (5H, s, (b)–C_5H_5), 4.83 (5H, s, (a)–C_5H_5), 4.85 (5H, s, (b)–C_5H_5), 4.93 (1H, q, *J* 8.0 Hz, (a)–C*H*), 6.12 (1H, d, *J* 8.0 Hz, ArC*H*), 6.26 (2H, t, *J* 4.0 Hz, ArC*H*), 6.79–7.63 (25H, m, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 20.1, 21.0, 22.7, 29.4, 29.7, 31.9, 75.0, 89.6 ((a) *C*$_5$H$_5$), 89.9 ((b)–*C*$_5$H$_5$), 90.1 ((b)–*C*$_5$H$_5$), 90.4 ((b)–*C*$_5$H$_5$), 123.3 (Ar), 124.3 (Ar), 124.5 (Ar), 125.1 (Ar), 125.4 (Ar), 125.9 (Ar), 126.0 (Ar), 126.2 (Ar), 127.7 (Ar), 127.9 (Ar), 128.0 (Ar), 128.1 (Ar), 128.2 (Ar), 128.3 (Ar), 128.4 (Ar), 128.6 (Ar), 128.7 (Ar), 129.5 (Ar), 129.8 (Ar), 130.2 (Ar), 130.5 (Ar), 130.8 (Ar), 131.0 (Ar), 131.1 (Ar), 131.5 (Ar), 132.2 (Ar), 132.3 (Ar), 132.5 (Ar), 133.0 (Ar), 133.5 (Ar), 133.6 (Ar), 133.7 (Ar), 133.8 (Ar), 137.0 (Ar), 137.4 (Ar), 137.7 (Ar), 150.0, 152.4, 154.9, 166.5, 166.8; ^{19}F NMR (δ, 376 MHz, $CDCl_3$) –63.0 (b), 63.9 (b), –63.5

(a); ^{31}P NMR (δ, 109 MHz, $CDCl_3$) 48.6 (a)–(*P*Ph_3), 49.4 (b)–(*P*Ph_3), 49.5 (b)–(*P*Ph_3); HRMS (*m*/*z*, FAB [NOBA]), $C_{49}H_{37}CoF_3O_2P$ $[M]^+$ requires 804.1810, found 804.1809.

Synthesis of 8d

Using the general procedure **A**, **7d** (0.08 g, 0.19 mmol) gave complex **8d** (0.11 g, 72%) as a bright red crystalline solid after silica gel column chromatography using 3:7 EtOAc/hexane as the eluant solvent mixture. Using the general procedure **B**, **7d** (0.09 g, 0.22 mmol) similarly gave **8d** (0.14 g, 81%). Ratio of isomers in solution ($CDCl_3$) 11 (a) : 1 (b) : 1 (b) : 1 (b):

m.p. 178–180 °C; IR (thin film) ν_{max} 1733 cm^{-1}; ^{1}H NMR (δ, 270 MHz, $CDCl_3$) 0.42 (3H, d, *J* 6.7 Hz, (b)–C*H*$_3$), 0.58 (3H, d, *J* 7.4 Hz, (b)–C*H*$_3$), 1.12 (3H, d, *J* 7.2 Hz, (a)–C*H*$_3$), 1.53 (3H, d, *J* 6.4 Hz, (b)–C*H*$_3$), 4.50 (5H, s, (b)–C_5H_5), 4.62 (5H, s, (b)–C_5H_5), 4.80 (5H, s, (a)–C_5H_5), 4.83 (5H, s, (b) C_5H_5), 4.99 (1H, q, *J* 7.2 Hz, (a)–C*H*), 5.95 (1H, d, *J* 8.0 Hz, ArC*H*), 6.25 (2H, t, *J* 9.6 Hz, ArC*H*), 6.60 (1H, *J* 8.0 Hz, ArC*H*), 6.80–7.69 (24H, m, ArC*H*); ^{13}C NMR (δ, 67 MHz, $CDCl_3$) 20.2 (*C*H_3), 75.3 (*C*H), 82.1, 89.7 ((a)–*C*$_5H_5$), 90.1 ((b)–*C*$_5H_5$), 90.5 ((b)–*C*$_5H_5$), 124.4 (Ar), 124.6 (Ar), 125.5 (Ar), 126.1 (Ar), 127.7 (Ar), 127.9 (Ar), 128.0 (Ar), 128.5 (Ar), 128.7 (Ar), 129.7 (Ar), 130.2 (Ar), 130.5 (Ar), 130.8 (Ar), 131.0 (Ar), 131.2 (Ar), 132.1 (Ar), 132.3 (Ar), 133.0 (Ar), 133.5 (Ar), 133.7 (Ar), 133.8 (Ar), 134.0 (Ar), 135.7 (Ar), 136.4 (Ar), 137.3 (Ar), 151.0, 151.2, 154.6, 156.5, 171.7, 172.0, 172.1, 176.2, 176.6; ^{19}F NMR (δ, 376 MHz, $CDCl_3$) –63.2 (b), –63.1 (b), –63.3 (a); ^{31}P NMR (δ, 109 MHz, $CDCl_3$) 48.5 (a)–(*P*Ph_3), 51.9 (b)–(*P*Ph_3), 55.0 (b)–(*P*Ph_3); HRMS (*m*/*z*, FAB [NOBA]), $C_{49}H_{37}CoF_3O_2P$ $[M]^+$ requires 804.1810, found 804.1805.

Synthesis of 8e

Using the general procedure **B**, **7e** (0.30 g, 0.85 mmol) gave **8e** (0.56 g, 89%) as a bright red crystalline solid after silica gel column chromatography using 3:7 EtOAc/hexane as the eluant. Ratio of isomers in solution ($CDCl_3$) 10 (a) : 2 (b) : 1 (c) : 1 (c):

m.p. 206–208 °C; Anal. Calc. for $C_{47}H_{37}CoNO_2P$; C, 76.52; H, 5.06; N, 1.89; Found; C, 76.32; H, 5.09; N, 1.87; IR (thin film) ν_{max} 1733 cm^{-1}; ^{1}H NMR (δ, 400 MHz, $CDCl_3$) 1.04 (3H, d, *J* 7.3 Hz, C*H*$_3$), 4.47 (5H, s, (b)–C_5H_5), 4.59 (5H, s, (b)–C_5H_5), 4.76 (5H, s, (b)–C_5H_5), 4.80–04.90 (5H, brs, (a)–C_5H_5), 4.92 (1H, q, *J* 7.3 Hz, (a)–C*H*), 5.90 (1H, d, *J* 9.0 Hz, ArC*H*), 6.26 (2H, brs, ArC*H*), 6.55 (1H, t, *J* 9.0 Hz, ArC*H*), 6.76–7.58 (24H, m, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 20.3 (C*H*$_3$), 22.9, 29.9, 32.1, 75.4, 82.1, 89.9 ((a)–*C*$_5H_5$), 124.7 (Ar), 125.7 (Ar), 127.7 (Ar), 127.8 (Ar), 128.1 (Ar), 128.4 (Ar), 128.5 (Ar), 128.6 (Ar), 128.8 (Ar), 129.8 (Ar), 130.3 (Ar), 130.8 (Ar), 131.1 (Ar), 131.3 (Ar), 131.6 (Ar), 132.3 (Ar), 133.3 (Ar), 133.6 (Ar), 137.0, 151.0, 154.9, 172.0 (*CO*); ^{31}P NMR (δ, 162 MHz, $CDCl_3$) 49.4 (a)–(*P*Ph_3), 51.3 (b)–(*P*Ph_3); HRMS (*m*/*z*, FAB [NOBA]), $C_{47}H_{37}CoNO_2P$ $[M]^+$ requires 738.1957, found 738.1967.

Synthesis of 8f

Using the general procedure **A**, **7f** (0.31 g, 0.72 mmol) gave **8f** (0.43 g, 73%) as a bright red crystalline solid after silica gel column chromatography using 3:7 EtOAc/hexane. Using the general procedure **B**, **7f** (0.50 g, 1.17 mmol) gave **8f** (0.82 g, 86%). Ratio of isomers in solution ($CDCl_3$) 18 (a) : 2 (b) : 2 (b) : 1 (c):

m.p. 148–150°C; Anal. Calc. for $C_{48}H_{37}BrCoO_2P$; C, 70.68; H, 4.57; Found; C, 70.74; H,4.49; IR (thin film) ν_{max} 1734 cm^{-1}; ^1H NMR (δ, 400 MHz, $CDCl_3$) 0.23 (3H, d, *J* 7.2 Hz, (c)–C*H*$_3$), 0.36 (3H, d, *J* 6.8 Hz, (b)–C*H*$_3$), 1.04 (3H, d, *J* 6.8 Hz, (b)–C*H*$_3$), 1.29 (3H, d, *J* 7.2 Hz, (a)–C*H*$_3$), 4.64 (5H, s, (b)–C_5H_5), 4.72 (5H, s, (c)–C_5H_5), 4.86 (1H, q, *J* 7.2 Hz, (a)–C*H*), 4.95 (5H, s, (b)–C_5H_5), 4.97 (5H, s, (a)–C_5H_5), 5.98 (2H, t, *J* 8.8 Hz, ArC*H*), 6.20 (1H, d, *J* 4.0 Hz, Ar), 6.86–6.90 (4H, m, ArC*H*), 7.00 (1H, t, *J* 9.6 Hz, ArC*H*), 7.08–7.57 (20H, m, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 19.4 (*C*H$_3$), 76.0 (*C*H), 76.0, 88.8 ((a)–*C*$_5H_5$), 89.1 ((b)–*C*$_5H_5$), 90.0 ((c)–*C*$_5H_5$), 121.0 (Ar), 124.6 (Ar), 125.3 (Ar), 125.9 (Ar), 126.2 (Ar), 127.9 (Ar), 128.0 (Ar), 128.6 (Ar), 128.7 (Ar), 128.8 (Ar), 128.9 (Ar), 129.4 (Ar), 130.4 (Ar), 130.6 (Ar), 130.7 (Ar), 130.8 (Ar), 131.1 (Ar), 131.3 (Ar), 131.4 (Ar), 132.2 (Ar), 132.3 (Ar), 132.5 (Ar), 132.9 (Ar), 133.1 (Ar), 133.3 (Ar), 133.5 (Ar), 134.1 (Ar), 134.2 (Ar), 134.5 (Ar), 134.6 (Ar), 138.3, 138.7, 150.2, 150.5, 152.4, 155.5, 172.4 (*C*O); ^{31}P NMR (δ, 162 MHz, $CDCl_3$) 47.1 (*P*Ph$_3$); HRMS (*m*/*z*, FAB [NOBA]), $C_{48}H_{37}{}^{79}BrCoO_2P$; $[M]^+$ requires 814.1041, found 814.1040.

Synthesis of 8g

Using the general procedure **A**, **7g** (0.67 g, 1.74 mmol) gave **8g** (0.69 g, 51%) as a bright red crystalline solid after silica gel column chromatography using 3:7 EtOAc/hexane. Using the general procedure **B**, **7g** (0.09 g, 0.23 mmol) similarly gave **8g** (0.14 g, 78%). Ratio of isomers in solution ($CDCl_3$) 5 (a) : 2 (b) : 2 (b) : 1 (c):

m.p. 198–200 °C; Anal. Calc. for $C_{47}H_{36}O_2NClCoP$; C, 73.12; H, 4.70; N, 1.81; Found C, 73.21; H, 4.79; N, 1.84; IR (thin film) ν_{max} 1734 cm^{-1}; ^1H NMR (δ, 400 MHz, CD_2Cl_2) 0.27 (3H, brs, (c)–C*H*$_3$), 0.36 (3H, d, *J* 6.4 Hz, (b)–C*H*$_3$), 0.97 (3H, d, *J* 6.0 Hz, (b)–C*H*$_3$), 1.20 (3H, d, *J* 7.2 Hz, (a)–C*H*$_3$), 4.67 (5H, s, (b)–C_5H_5), 4.72 (5H, s, (c)–C_5H_5), 4.79 (1H, q, *J* 7.2 Hz, (a)–C*H*), 4.96 (5H, s, (a)–C_5H_5), 6.04 (2H, t, *J* 9.2 Hz, ArC*H*), 6.20–8.17 (25H, m, ArC*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 19.3, 29.9, 75.7, 88.1 ((a)–*C*$_5H_5$), 89.1 ((b)–*C*$_5H_5$), 89.8 ((b)–*C*$_5H_5$), 89.9 ((c)–*C*$_5H_5$), 124.8 (Ar), 125.4 (Ar), 125.8 (Ar), 127.9 (Ar), 128.0 (Ar), 128.1 (Ar), 128.7 (Ar), 128.8 (Ar), 128.9 (Ar), 129.0 (Ar), 129.5 (Ar), 130.2 (Ar), 130.4 (Ar), 130.7 (Ar), 130.8 (Ar), 131.1 (Ar), 131.3 (Ar), 131.4 (Ar), 132.2 (Ar), 132.3 (Ar), 137.5 (Ar), 138.0 (Ar), 138.3 (Ar), 139.5 (Ar), 146.1 (Ar), 150.3 (Ar), 152.1, 157.8, 172.0 (*C*O); ^{31}P NMR (δ, 162 MHz, $CDCl_3$) 47.3 (a)–

(*P*Ph_3), 51.9 (b)–(*P*Ph_3), 54.2 (b)–(*P*Ph_3); HRMS (*m*/*z*, ESI), $C_{47}H_{37}ClCoNO_2P$ $[M+H]^+$ requires 772.1577, found 772.1572.

Synthesis of 11a

Using the general procedure **A**, **7a** (0.18 g, 0.51 mmol) gave **11a** as a red solid (0.26 g, 64%) after silica gel column chromatography using 3:7 EtOAc/hexane. Ratio of isomers in solution ($CDCl_3$) 13 (a) : 1 (b) : 1 (b).

m.p. 178–180 °C; IR (thin film) ν_{max} 1694 cm^{-1}; ^1H NMR (δ, 270 MHz, $CDCl_3$) 0.39 (3H, d, *J* 6.9 Hz, (b)–CH_3), 0.51 (3H, d, *J* 7.2 Hz, (b)–CH_3), 1.05 (3H, d, *J* 7.2 Hz, (a)–CH_3), 3.53 (3H, s, (b)–OCH_3), 3.57 (3H, s, (a)–OCH_3), 3.60 (3H, s, (b)–OCH_3), 3.66 (3H, s, (b)–OCH_3), 4.29 (1H, brs, C*H*), 4.52 (1H, brs, C*H*), 4.96 (1H, q, *J* 7.2 Hz, (a)–C*H*), 5.62 (1H, brs, C*H*), 6.09 (1H, brs, C*H*), 6.30 (2H, t, *J* 9.2 Hz, ArC*H*), 6.63–7.64 (27H, m, ArC*H*); ^{13}C NMR (δ, 67 MHz, $CDCl_3$) 20.0 ((a)–*C*H_3), 29.8, 52.1, 75.3, 75.4, 77.4, 85.6, 85.6, 89.6, 91.1, 95.1, 98.6, 124.7 (Ar), 125.0 (Ar), 125.5 (Ar), 127.5 (Ar), 127.7 (Ar), 127.9 (Ar), 128.1 (Ar), 128.2 (Ar), 128.5 (Ar), 128.7 (Ar), 129.3 (Ar), 129.6 (Ar), 130.0 (Ar), 130.4 (Ar), 130.9 (Ar), 131.2 (Ar), 131.3 (Ar), 131.9 (Ar), 132.0 (Ar), 132.1 (Ar), 132.3 (Ar), 132.7 (Ar), 132.8 (Ph), 133.0 (Ar), 133.6 (Ar), 133.8 (Ar), 134.1 (Ar), 134.2 (Ar), 138.2, 138.3, 167.0, 169.6, 170.0, 172.1; ^{31}P NMR (δ, 109 MHz, $CDCl_3$) 52.6 (b)–(*P*Ph_3), 50.0 (a)–(*P*Ph_3), 49.2 (b)–(*P*Ph_3); HRMS (*m*/*z*, FAB [NOBA]), $C_{50}H_{40}CoO_4P$ $[M]^+$ requires 794.1991, found 794.1995.

Synthesis of 11c

Using the general procedure **A**, **7c** (0.07g, 0.17 mmol) gave **11c** (0.07g, 49%) as a bright red crystalline solid after silica gel column chromatography using 3:7 EtOAc/hexane. Ratio of isomers in solution ($CDCl_3$) 10 (a) : 2 (b) : 1 (c):

IR (thin film) ν_{max} 1701 cm^{-1}; ^1H NMR (δ, 270 MHz, $CDCl_3$) 0.54 (3H, d, *J* 6.9 Hz, (c)-CH_3), 0.65 (3H, d, *J* 7.4 Hz, (b)–CH_3), 1.10 (3H, d, *J* 7.2 Hz, (a)–CH_3), 3.62 (3H, s, (a)–OCH_3), 3.76 (b)–OCH_3), 4.14 (1H, brs, C*H*), 4.82 (1H, brs, C*H*), 4.95 (1H, q, *J* 7.2 Hz, (a)–C*H*), 5.55 (1H, brs, C*H*), 6.11–8.13 (29H, m, ArC*H,* C*H*); ^{13}C NMR (δ, 100 MHz, $CDCl_3$) 19.9 (*C*H_3), 21.0, 52.0 (*C*H), 75.2, 84.9, 85.6, 88.6, 89.6, 92.0, 96.5, 96.6, 124.9 (Ar), 125.6 (Ar), 127.5 (Ar), 127.9 (Ar), 128.0 (Ar), 128.1 (Ar), 128.2 (Ar), 128.6 (Ar), 128.7 (Ar), 129.2 (Ar), 129.4 (Ar), 129.7 (Ar), 129.9 (Ar), 130.3 (Ar), 130.6 (Ar), 130.8 (Ar), 130.9 (Ar), 131.2 (Ar), 131.4 (Ar), 131.7 (Ar), 131.9 (Ar), 132.3 (Ar), 132.4 (Ar), 132.9 (Ar), 133.1 (Ar), 133.6 (Ar), 133.7 (Ar), 134.0 (Ar), 134.3 (Ar), 135.6 (Ar), 136.0 (Ar), 150.5, 150.9, 151.0, 153.9, 155.6, 155.6, 165.6, 165.9, 166.7; ^{19}F NMR (δ, 376 MHz, $CDCl_3$) –63.0 (b), –63.5 (a); ^{31}P NMR (δ, 109 MHz, $CDCl_3$) 49.8 (a)–(*P*Ph_3), 52.4 (b)–(*P*Ph_3); HRMS (*m*/*z*, FAB [NOBA]), $C_{51}H_{39}CoF_3O_4P$ $[M]^+$ requires 862.1865, found 862.1870.

Synthesis of 11d

Using the general procedure **A**, **7d** (0.09 g, 0.21 mmol) gave **11d** (0.12 g, 65%) as a bright red crystalline solid after silica gel column chromatography using 3:7 EtOAc/hexane as the eluant solvent mixture. Ratio of isomers in solution ($CDCl_3$) 24 (a) : 3 (b) : 3 (b) : 2 (c):

m.p.170–172°C; IR (thin film) ν_{max} 1695 cm^{-1}; ^1H NMR (δ, 400 MHz, $CDCl_3$) 0.30 (3H, d, *J* 8.0 Hz, (c)–CH_3), 0.48 (3H, d, *J* 8.0 Hz, (b)–CH_3), 0.83 (3H, d, *J* 8.0 Hz, (b)–CH_3), 1.07 (3H, d, *J* 8.0 Hz, (a)–CH_3), 3.20 (3H, s, (c)–OCH_3), 3.45 (3H, s, (b)–OCH_3), 3.57 (3H, s, (b)–OCH_3), 3.59 (3H, s, (a)–OCH_3), 4.21 (1H, s, C*H*), 4.59 (1H, s, C*H*), 4.95 (1H, q, *J* 8.0 Hz, (a)–C*H*), 5.76 (1H, s, C*H*), 5.86 (1H, s, C*H*), 6.39 (1H, t, *J* 12.0 Hz, ArC*H*), 6.66 (1H, t, *J* 12.0 Hz, ArC*H*), 6.76–7.65 (26H, m, ArC*H*); ^{13}C NMR (δ, 67 MHz, $CDCl_3$) 19.9 (*C*H_3), 52.2 (*C*H), 75.2, 85.6, 85.7, 87.1, 93.5, 94.0, 100.2, 124.1 (Ar), 124.2 (Ar), 125.4 (Ar), 125.7 (Ar), 126.0 (Ar), 126.2 (Ar), 126.7 (Ar), 127.9 (Ar), 128.2 (Ar), 128.7 (Ar), 129.5 (Ar), 130.0 (Ar), 130.1 (Ar), 130.5 (Ar), 131.2 (Ar), 131.3 (Ar), 131.6 (Ar), 132.1 (Ar), 132.7 (Ar), 133.0 (Ar), 133.1 (Ar), 133.2 (Ar), 134.0 (Ar), 134.1 (Ar), 135.2 (Ar), 137.4 (Ar), 137.5 (Ar), 150.4, 152.8, 152.9, 154.6, 167.0, 171.7, 172.6, 172.9, 173.1, 173.3, 173.5; ^{19}F NMR (δ, 376 MHz, $CDCl_3$) –63.9 (a), –63.8 (b), –63.2 (b), –63.1 (c); ^{31}P NMR (δ, 109 MHz, $CDCl_3$) 48.8 (b)–(*P*Ph_3), 49.2 (a)–(*P*Ph_3), 50.1 (c)–(*P*Ph_3), 51.3 (b)–(*P*Ph_3); HRMS (*m*/*z*, FAB [NOBA]), $C_{51}H_{39}CoF_3O_4P$ $[M]^+$ requires 862.1865, found 862.1862.

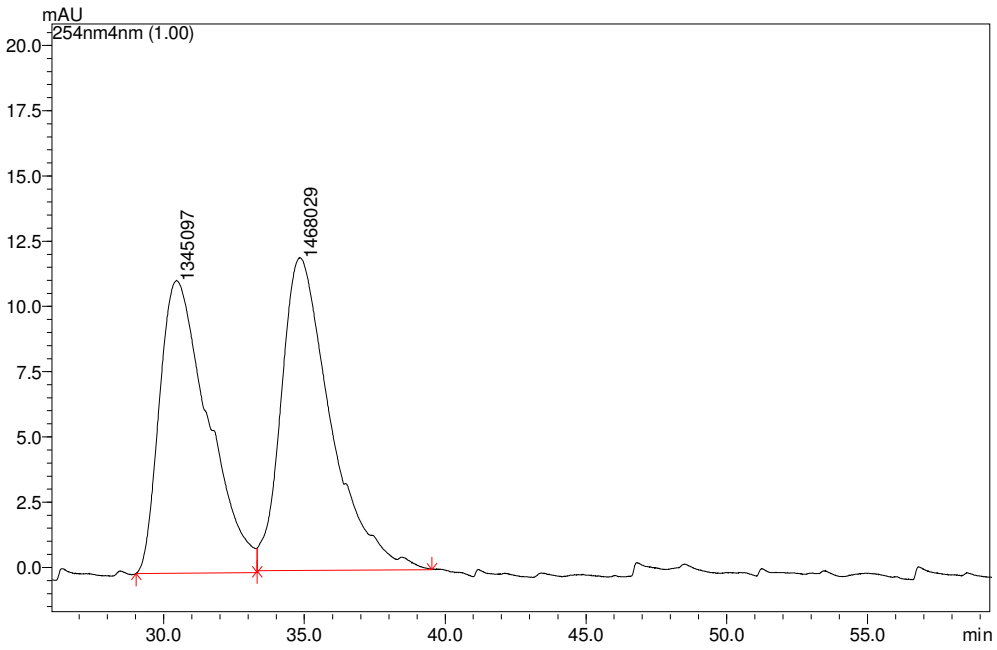
References

1. C. J. Taylor, M. Motevalli and C. J. Richards, *Organometallics*, 2006, **25**, 2899.
2. B. Tao, J. C. Ruble, D. A. Hoic and G. C. Fu, *J. Am. Chem. Soc*., 1999, **121**, 5091.
3. D. L. J. Clive, Y. Tao, A. Khodabocus, Y.-J. Wu, A. G. Angoh, S. M. Bennett, C. N. Boddy, L. Bordeleau and D. Kellner, *J. Am. Chem. Soc*., 1994, **116**, 11275.
4. Y. Wakatsuki and H. Yamazaki, *Inorg. Synth.,* 1989, **26**, 189.

HPLC Trace

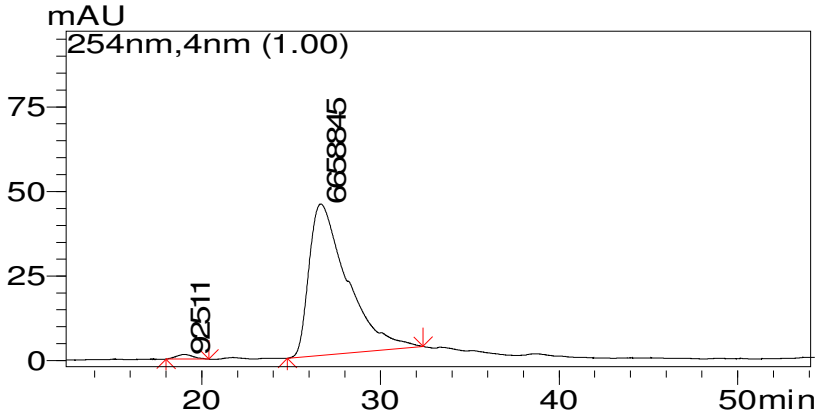
1. *Rac*-**8**

(CHIRALCEL OD) 96.5:3.5 hexane/isopropyl alcohol, 1 mL/min.



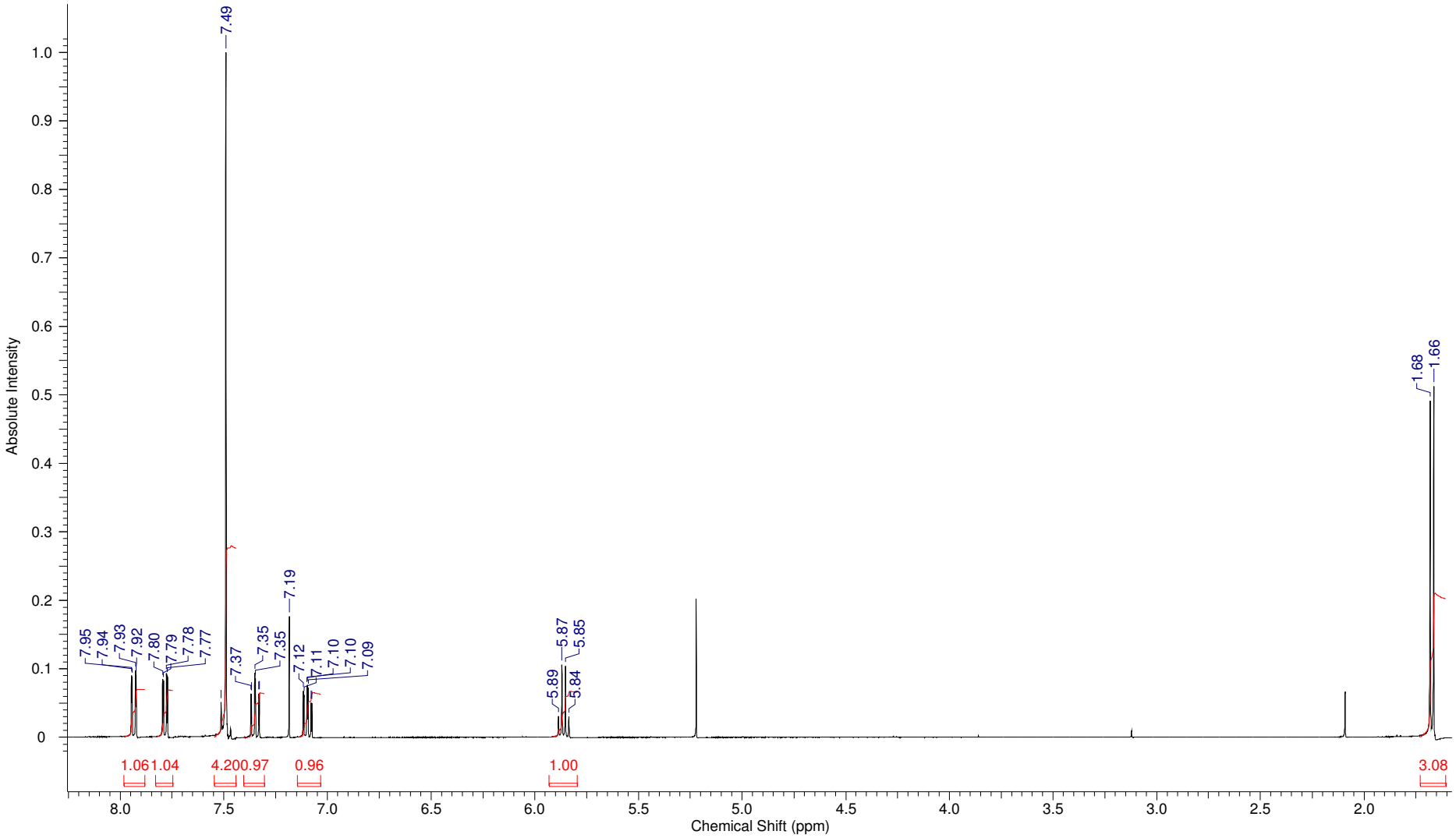
Peak	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	30.452	1345097	11213	29.024	33.323	46.2394
2	34.843	1468029	11991	33.323	39.531	50.4653

2. (*S*)-**8**

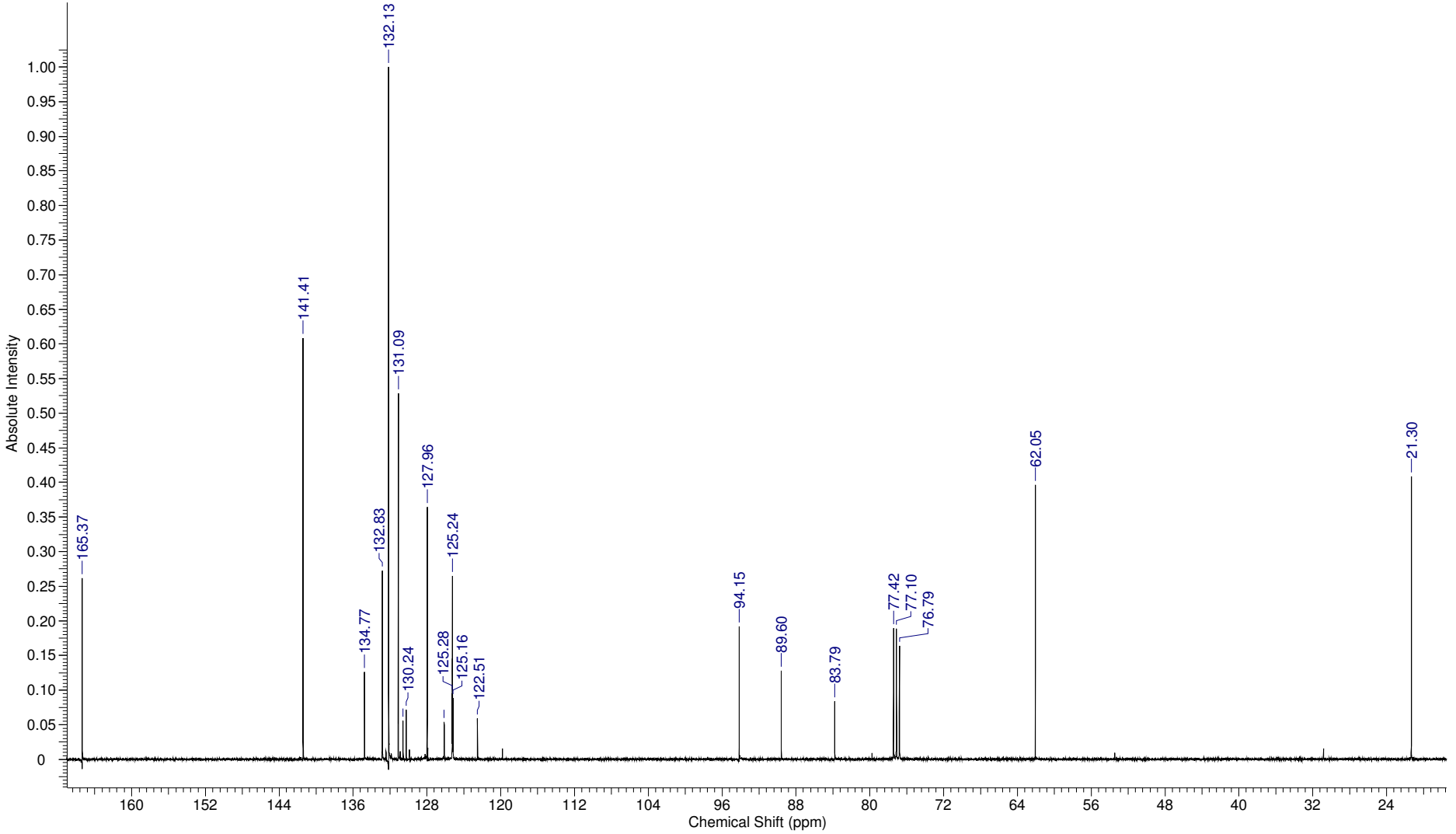


Peak	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	26.650	6658845	44789	24.789	32.373	94.4426

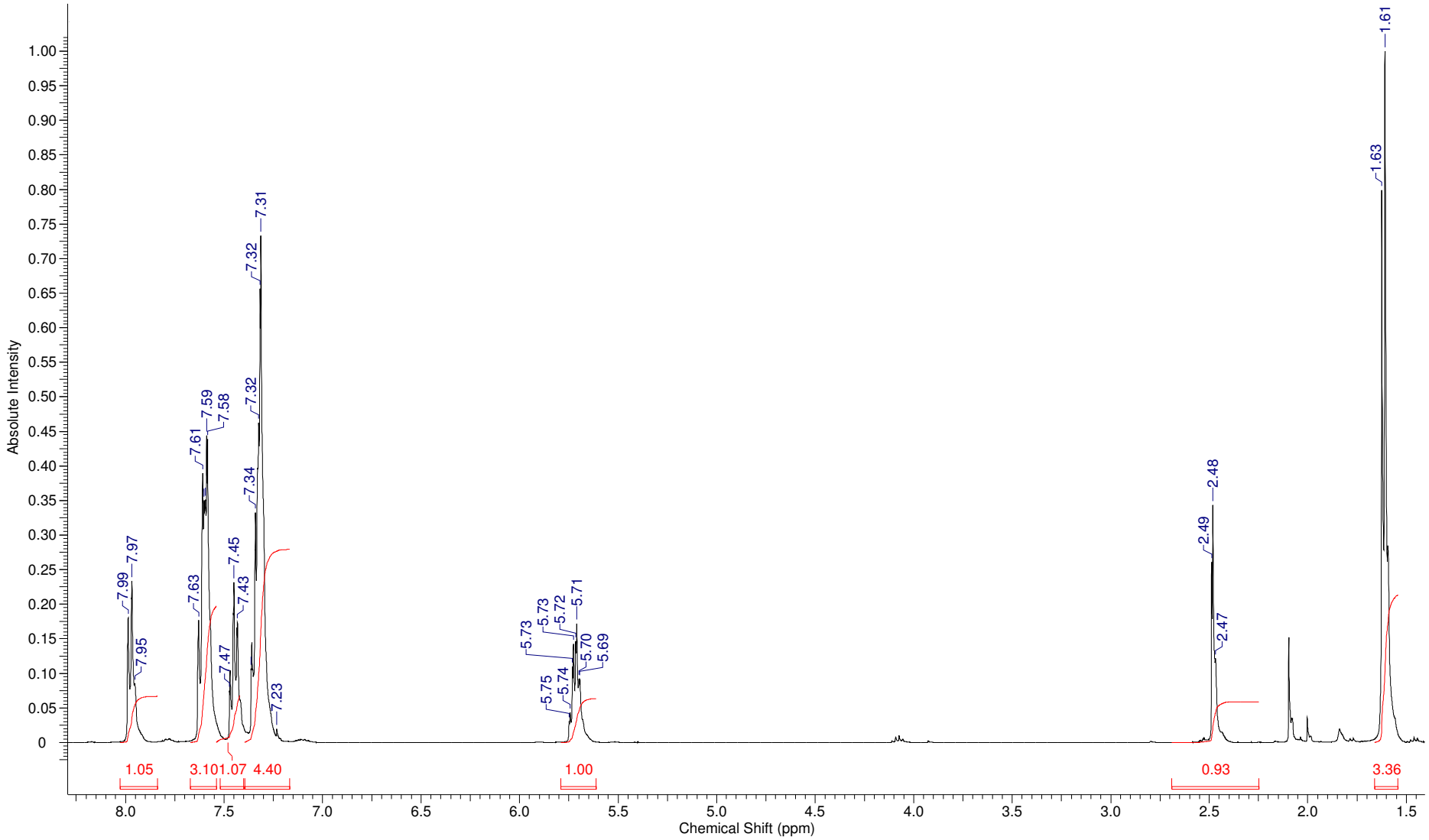
4c ^{1}H NMR (400 MHz, $CDCl_3$)



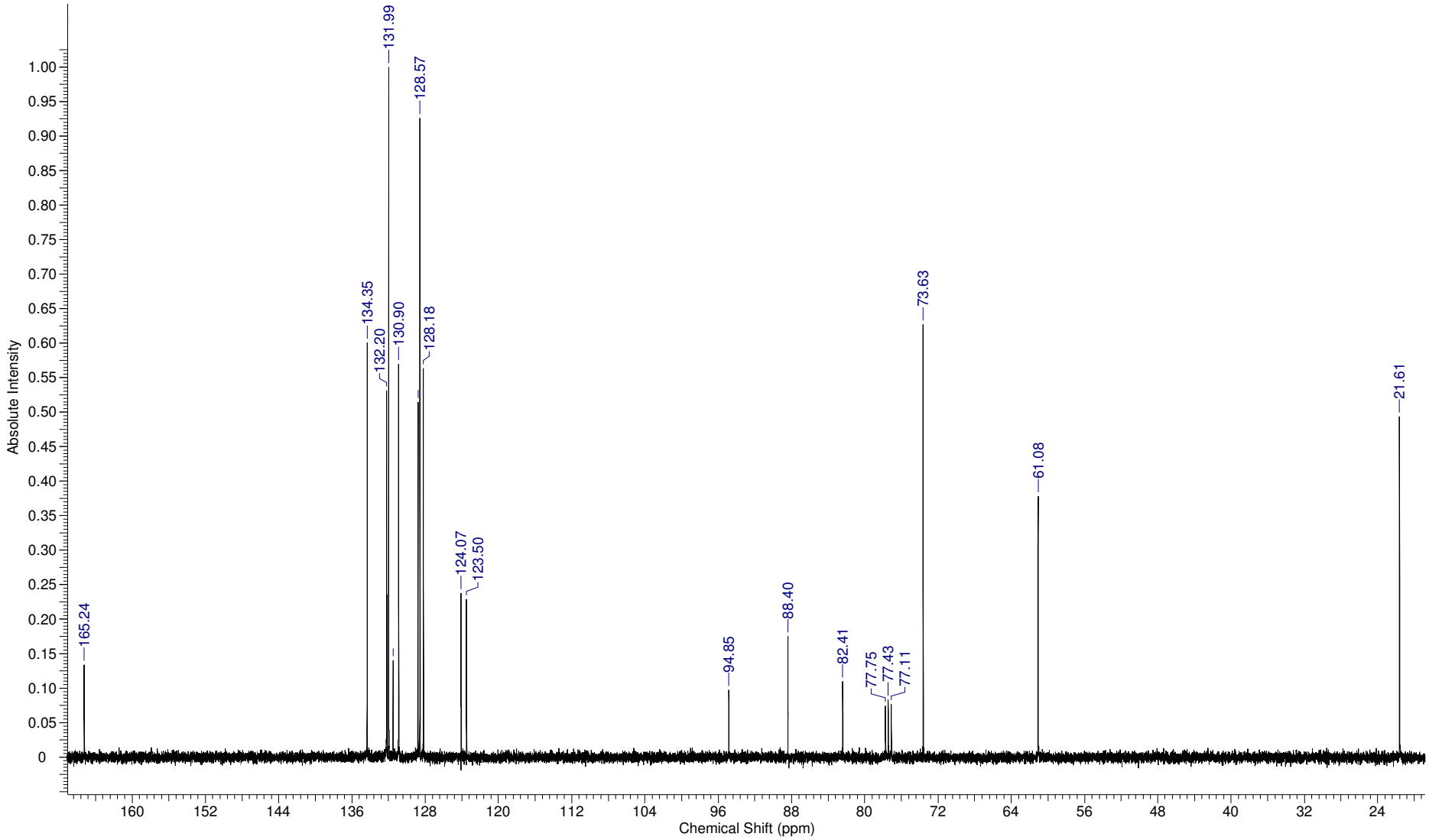
4c ^{13}C NMR (100 MHz, $CDCl_3$)



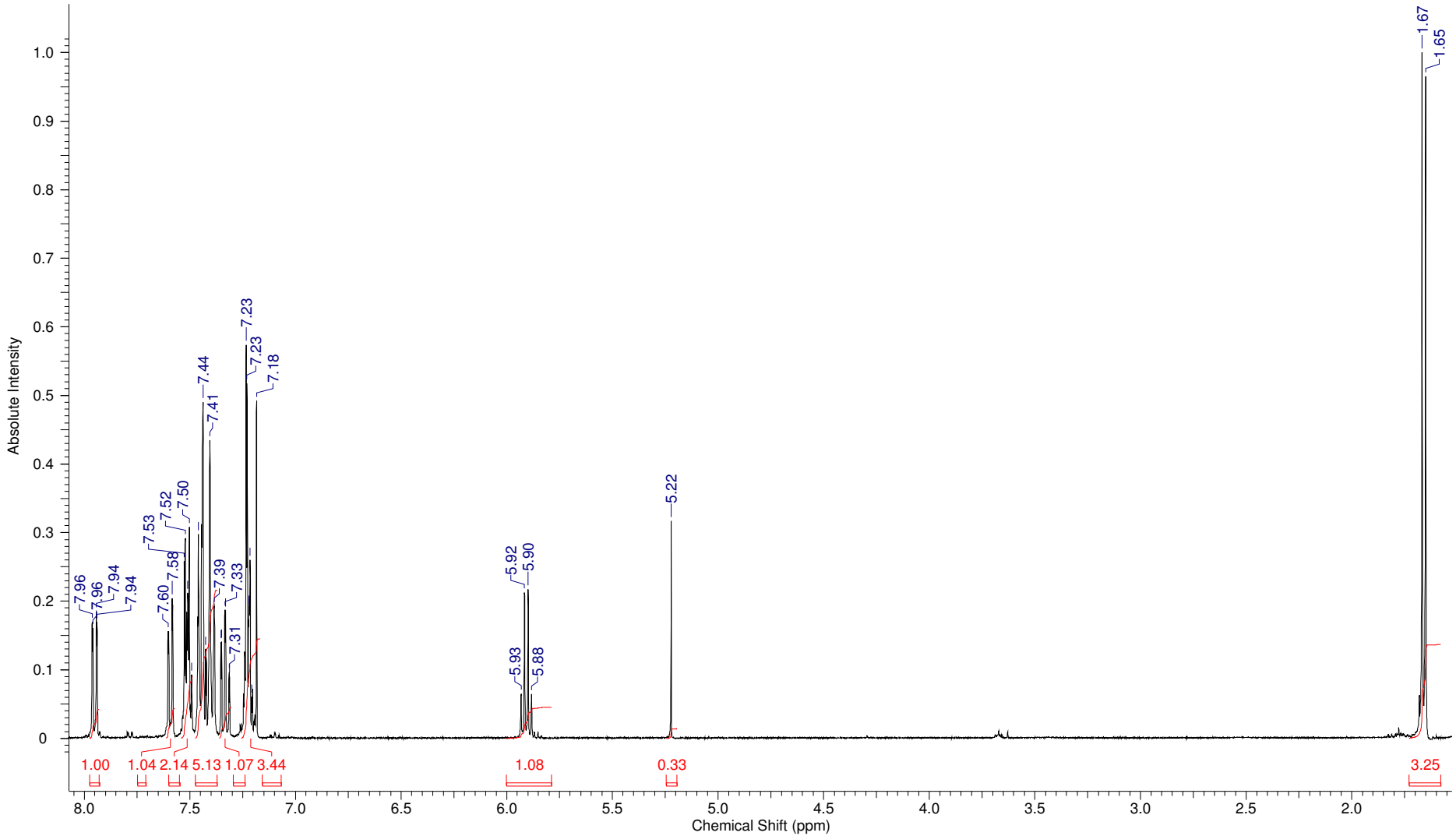
(*S*)-6 ^{1}H NMR (400 MHz, $CDCl_3$)



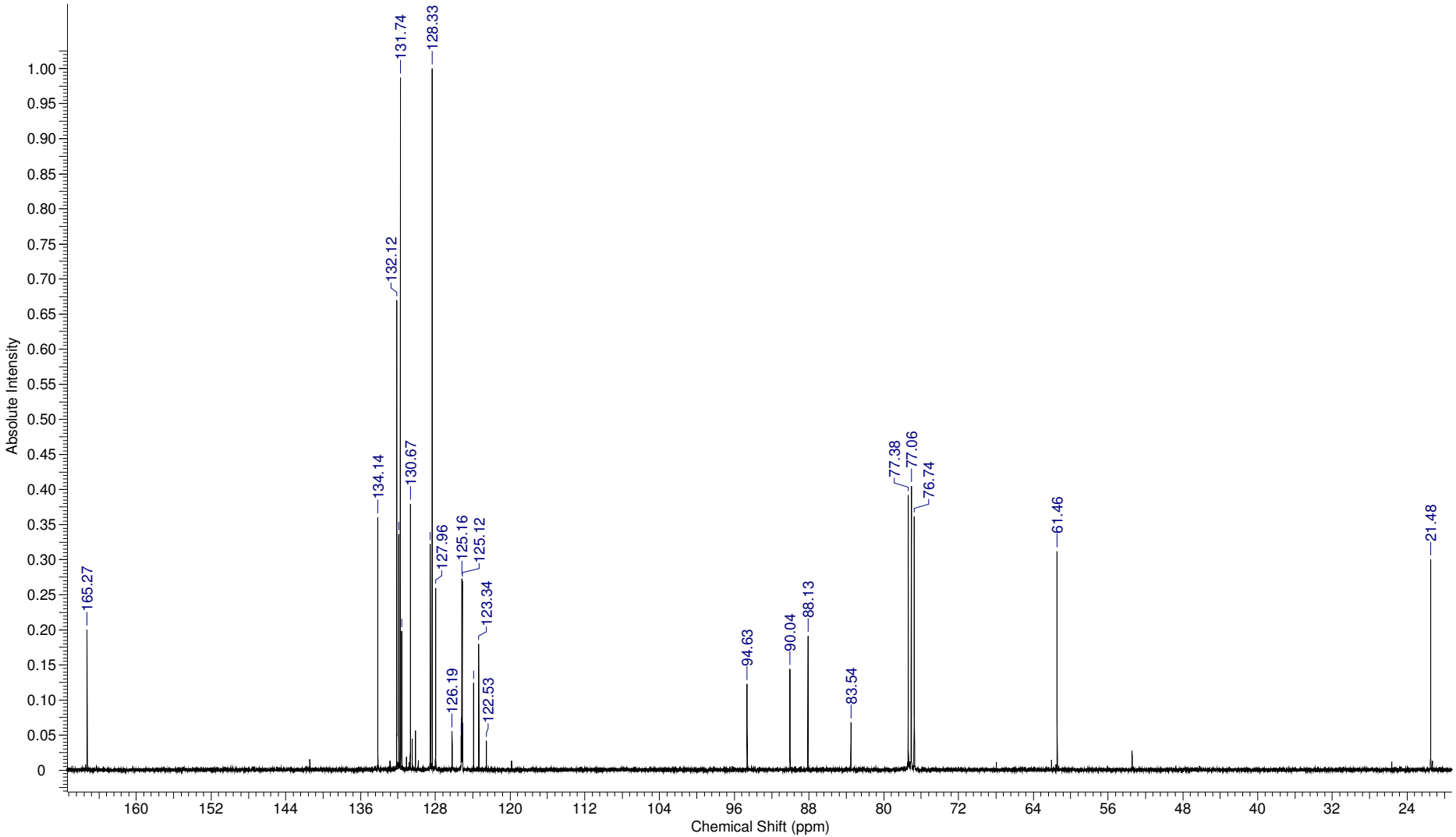
(*S*)-6 ^{13}C NMR (100 MHz, $CDCl_3$)



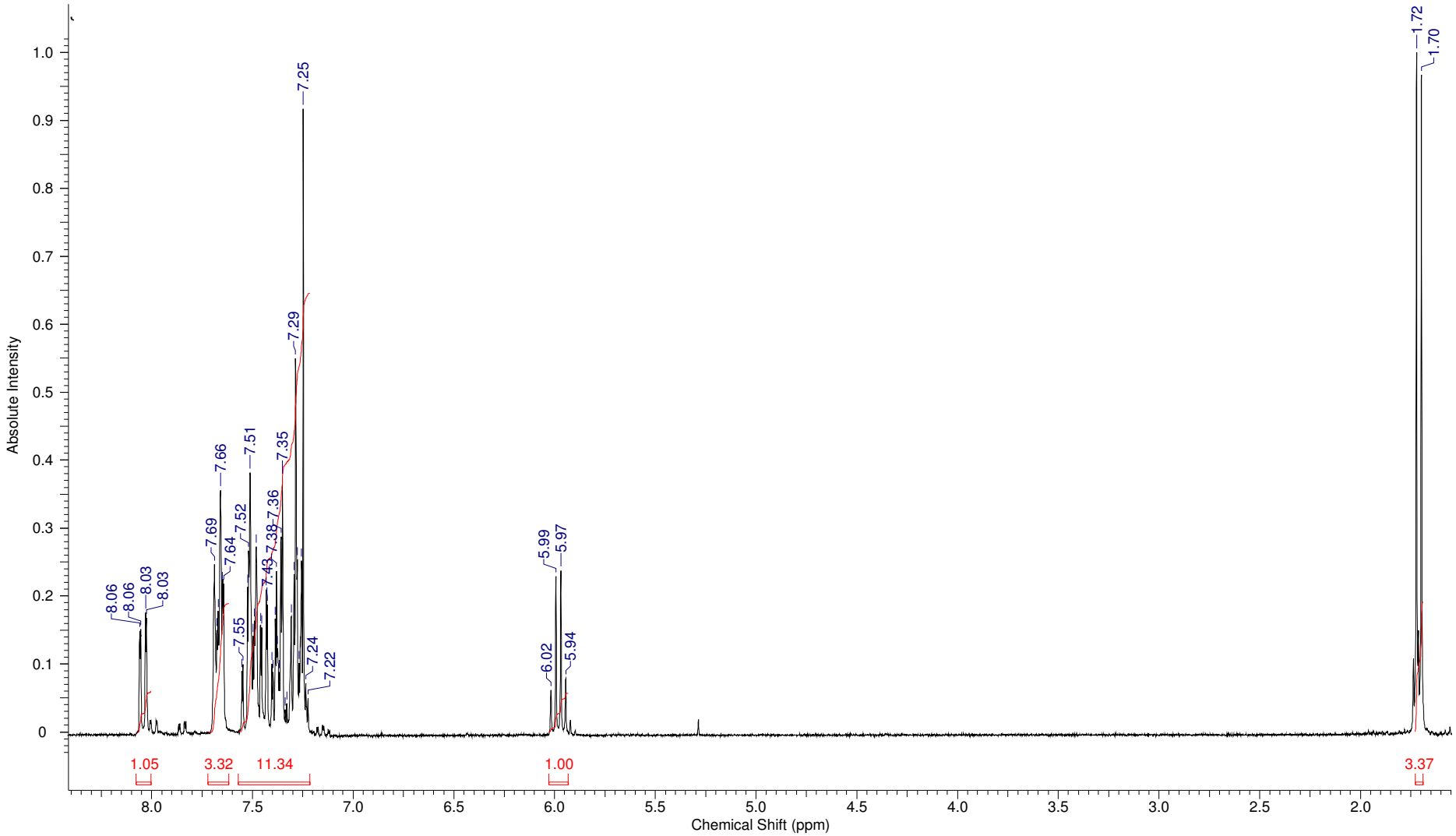
7c ^{1}H NMR (400 MHz, $CDCl_3$)



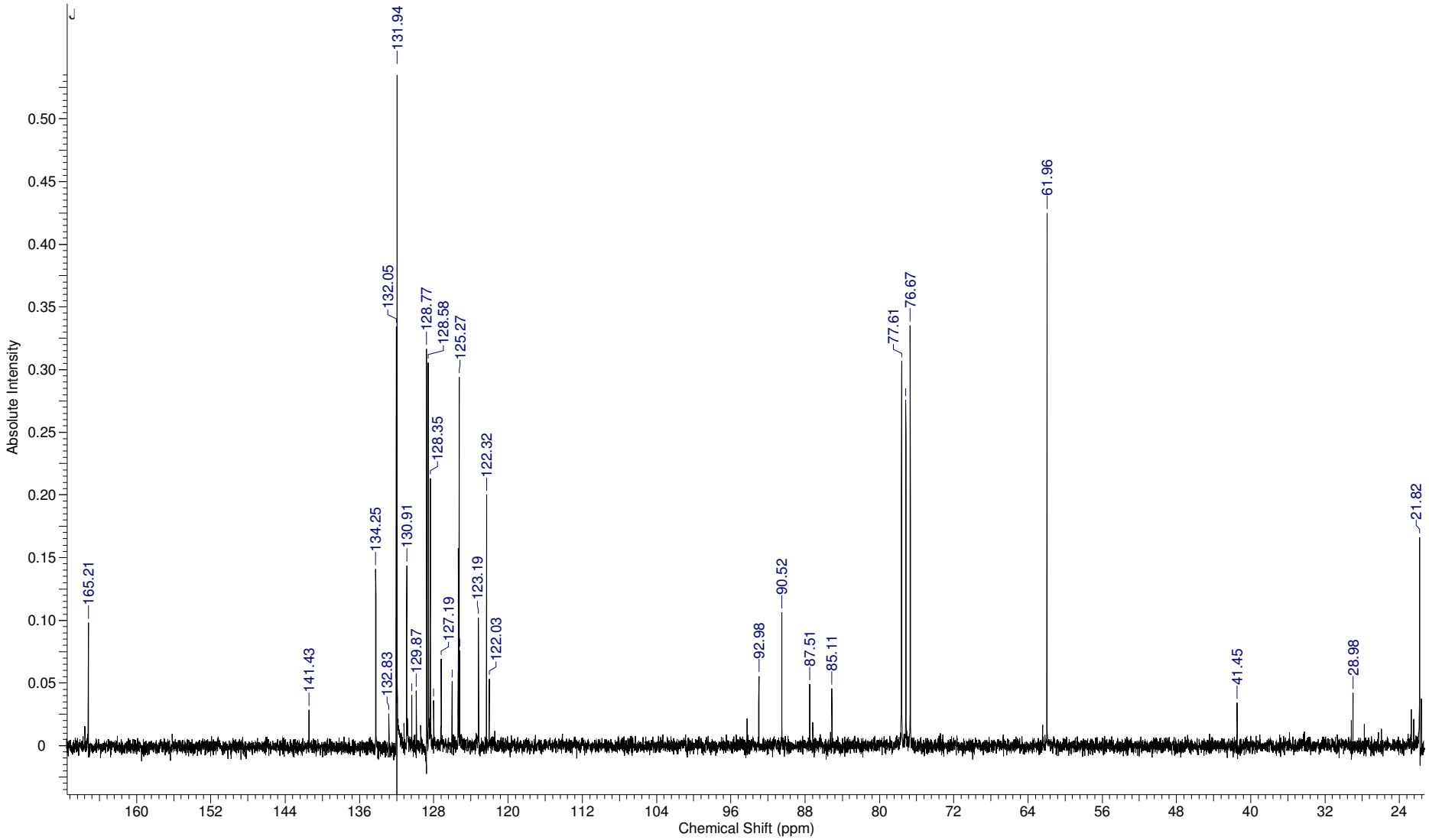
7c ^{13}C NMR (100 MHz, $CDCl_3$)



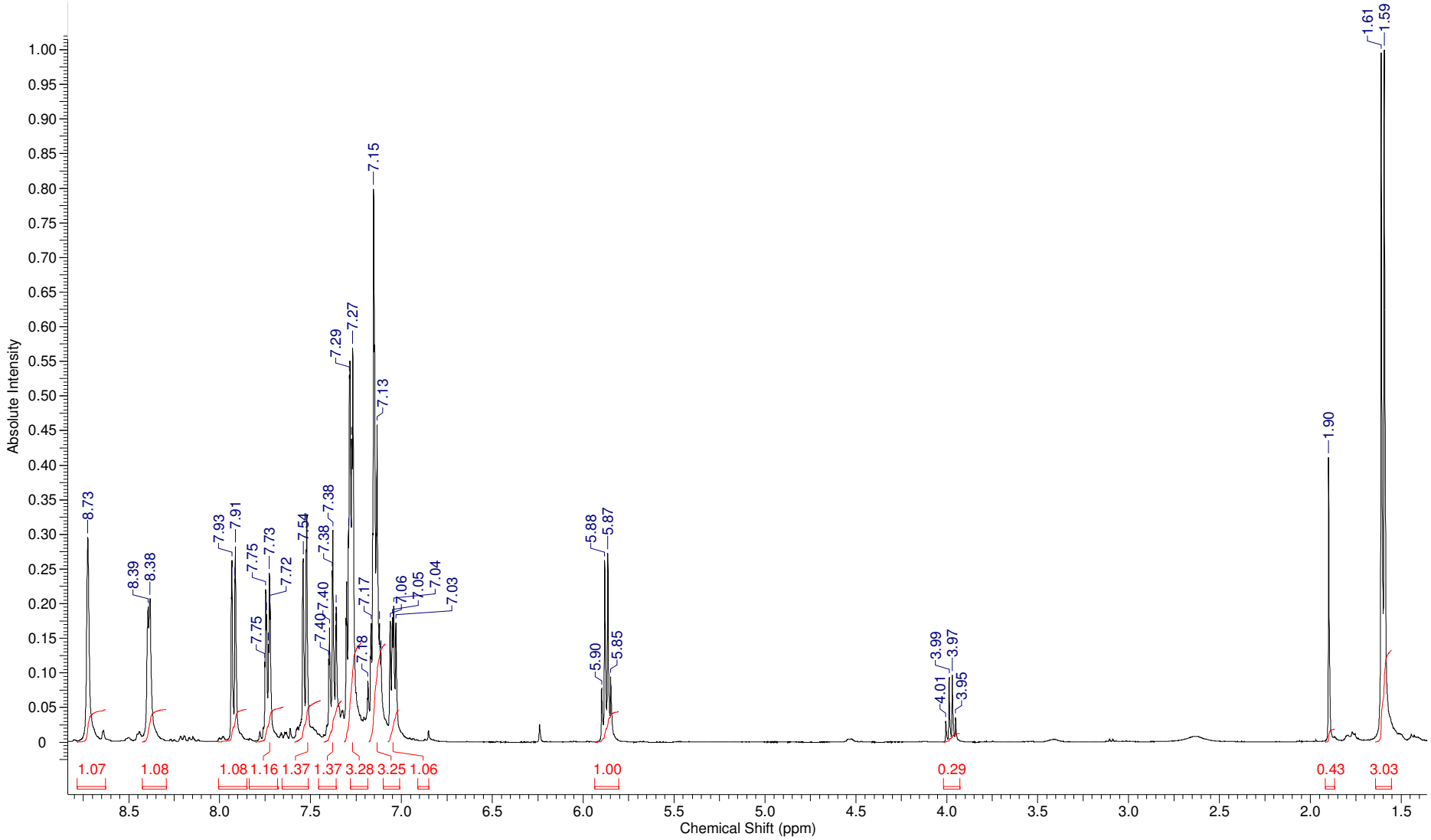
7d ^{1}H NMR (δ, 270 MHz, $CDCl_3$)



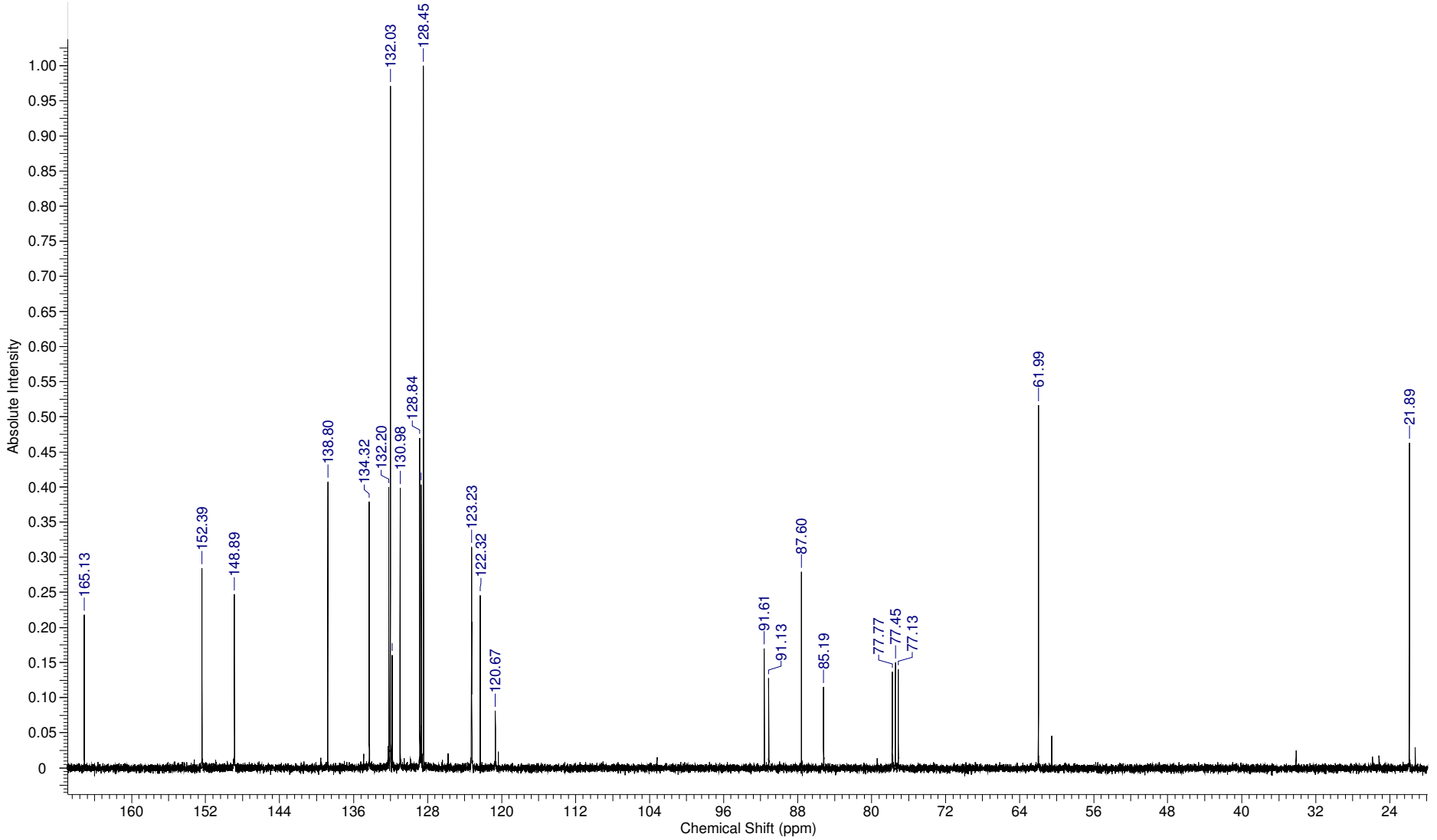
7d ^{13}C NMR (δ, 67 MHz, $CDCl_3$)



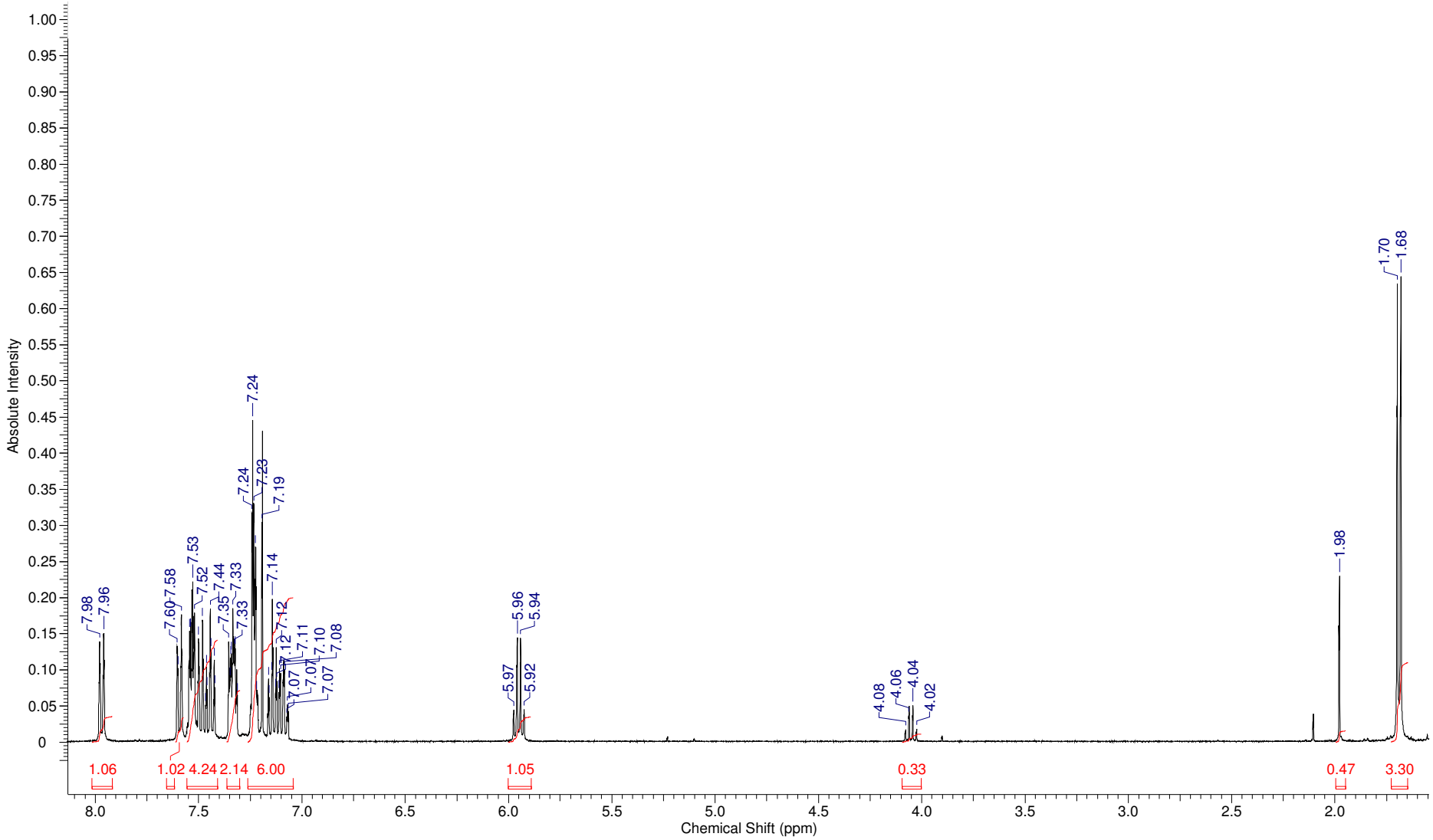
7e ^{1}H NMR (400 MHz, $CDCl_3$)



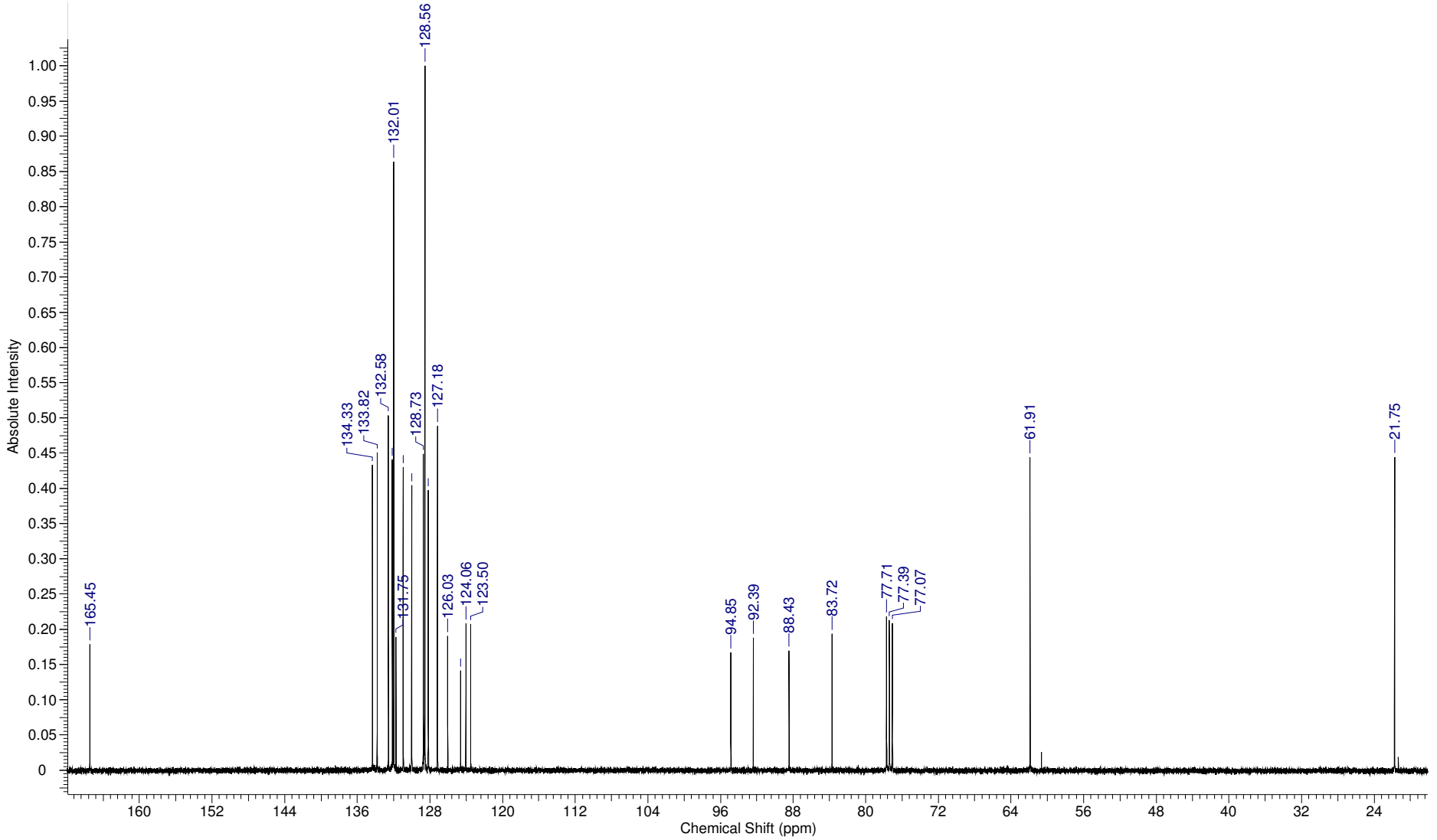
7e ^{13}C NMR (100 MHz, $CDCl_3$)



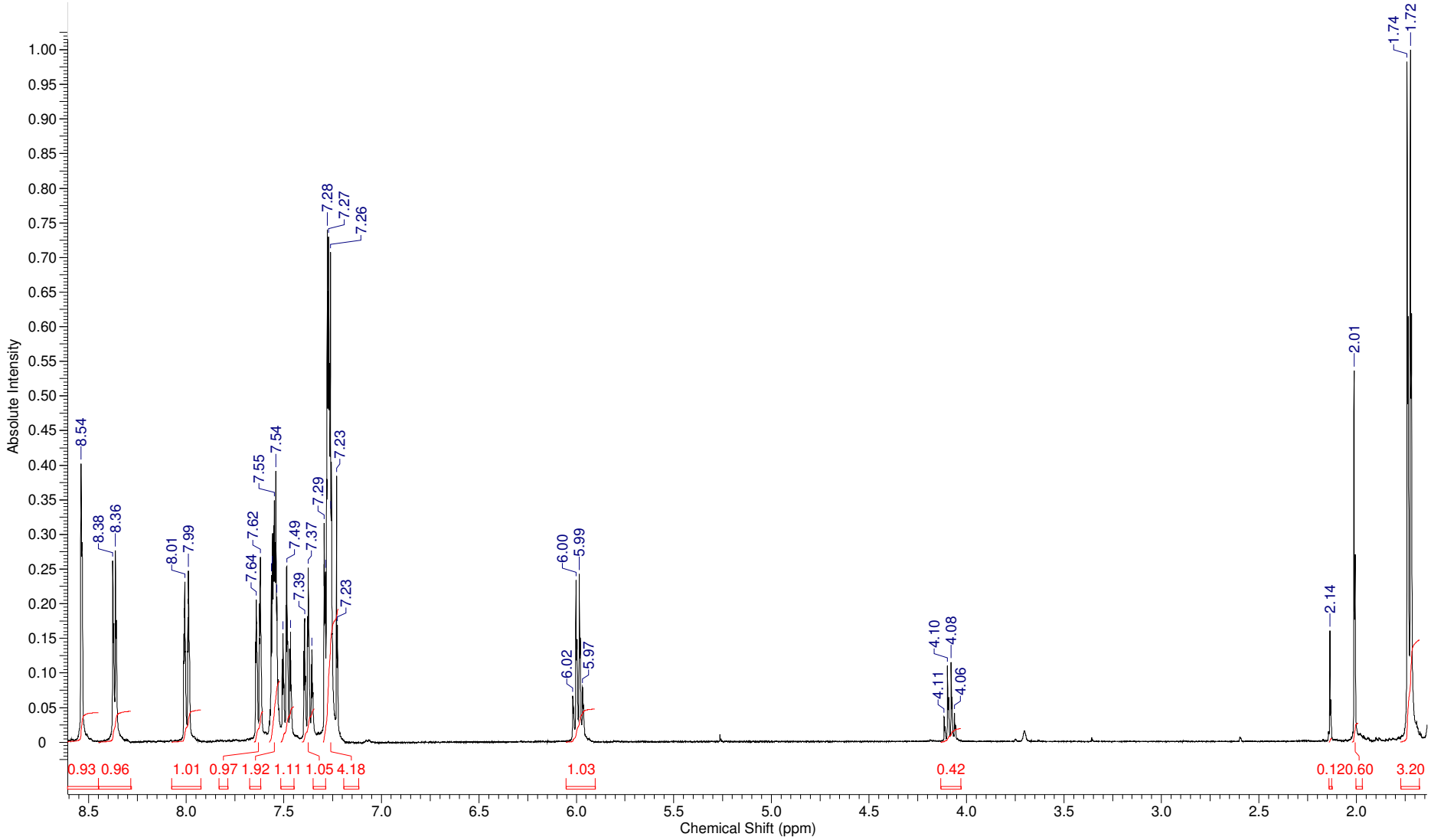
7f ^{1}H NMR (400 MHz, $CDCl_3$)



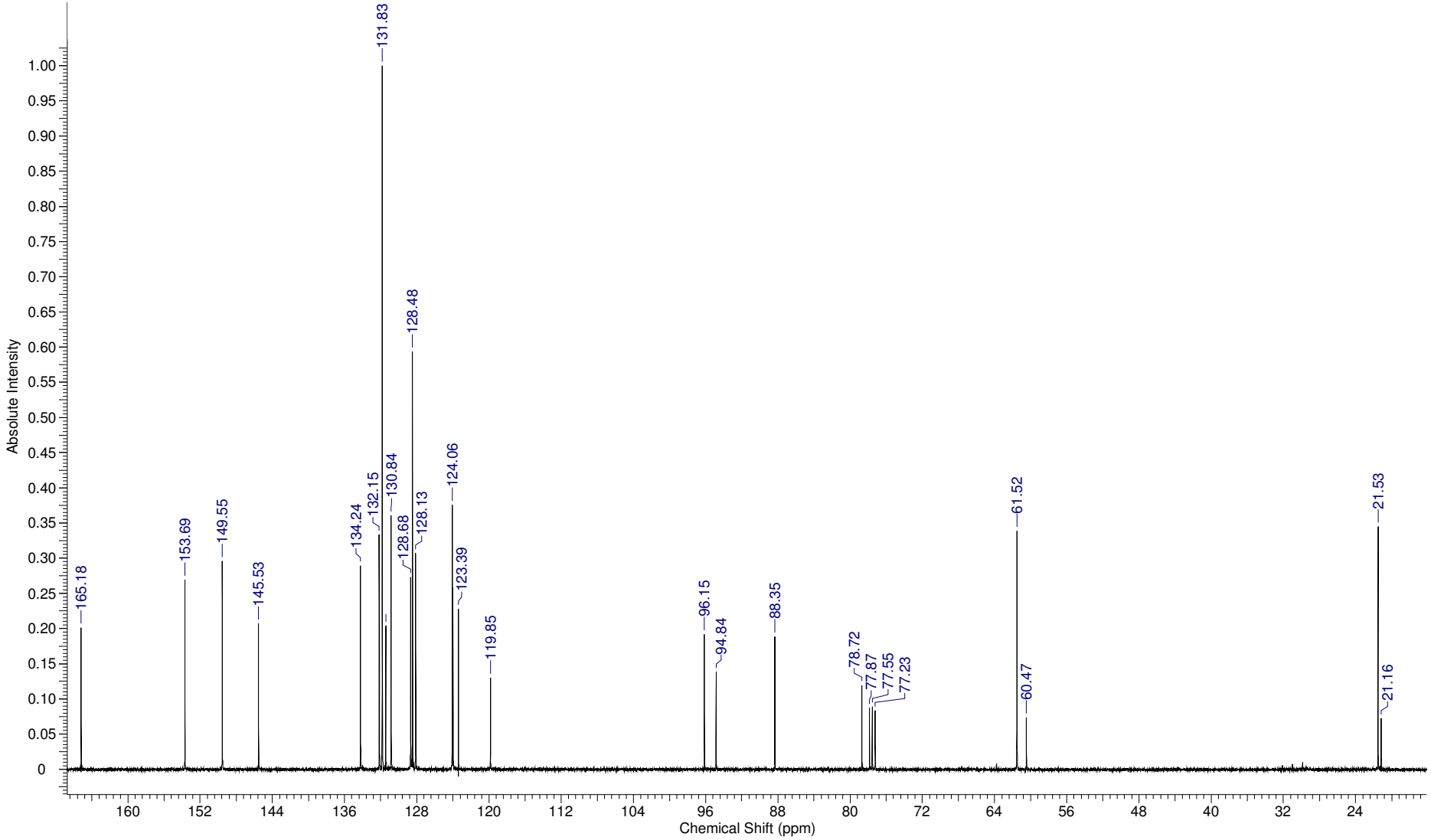
7f ^{13}C NMR (100 MHz, $CDCl_3$)



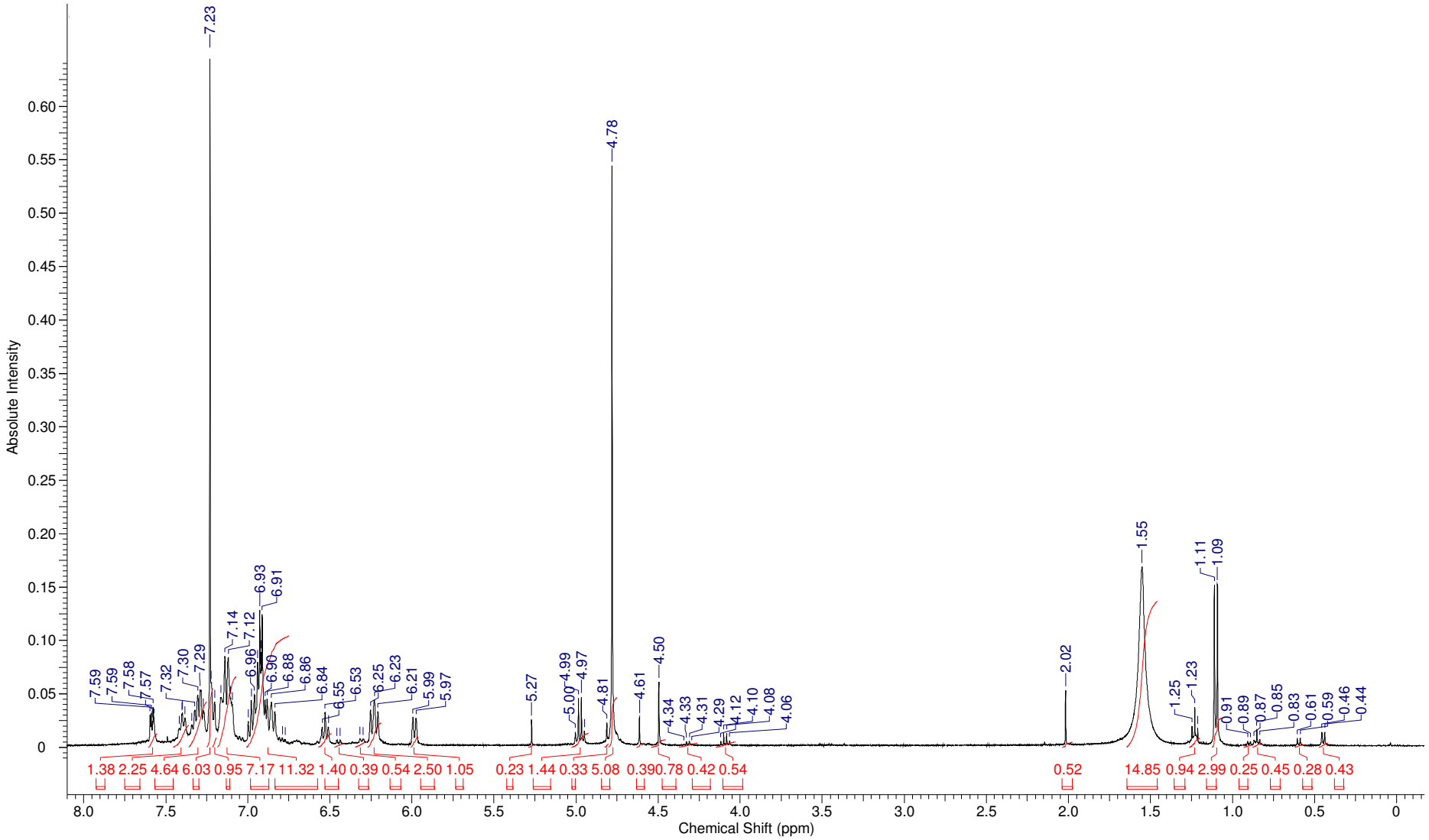
7g ^{1}H NMR (400 MHz, $CDCl_3$)



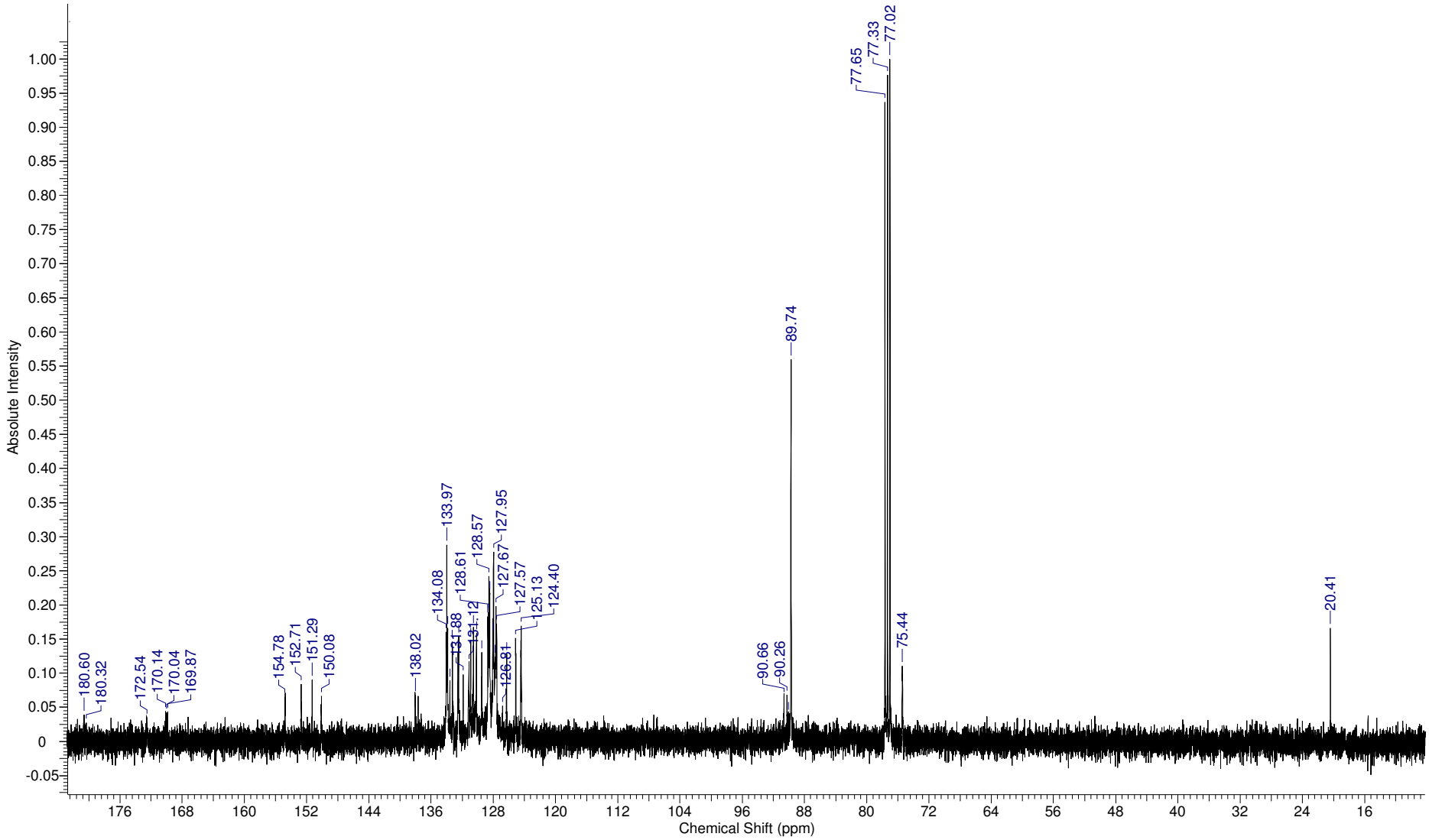
7g ^{13}C NMR (100 MHz, $CDCl_3$)



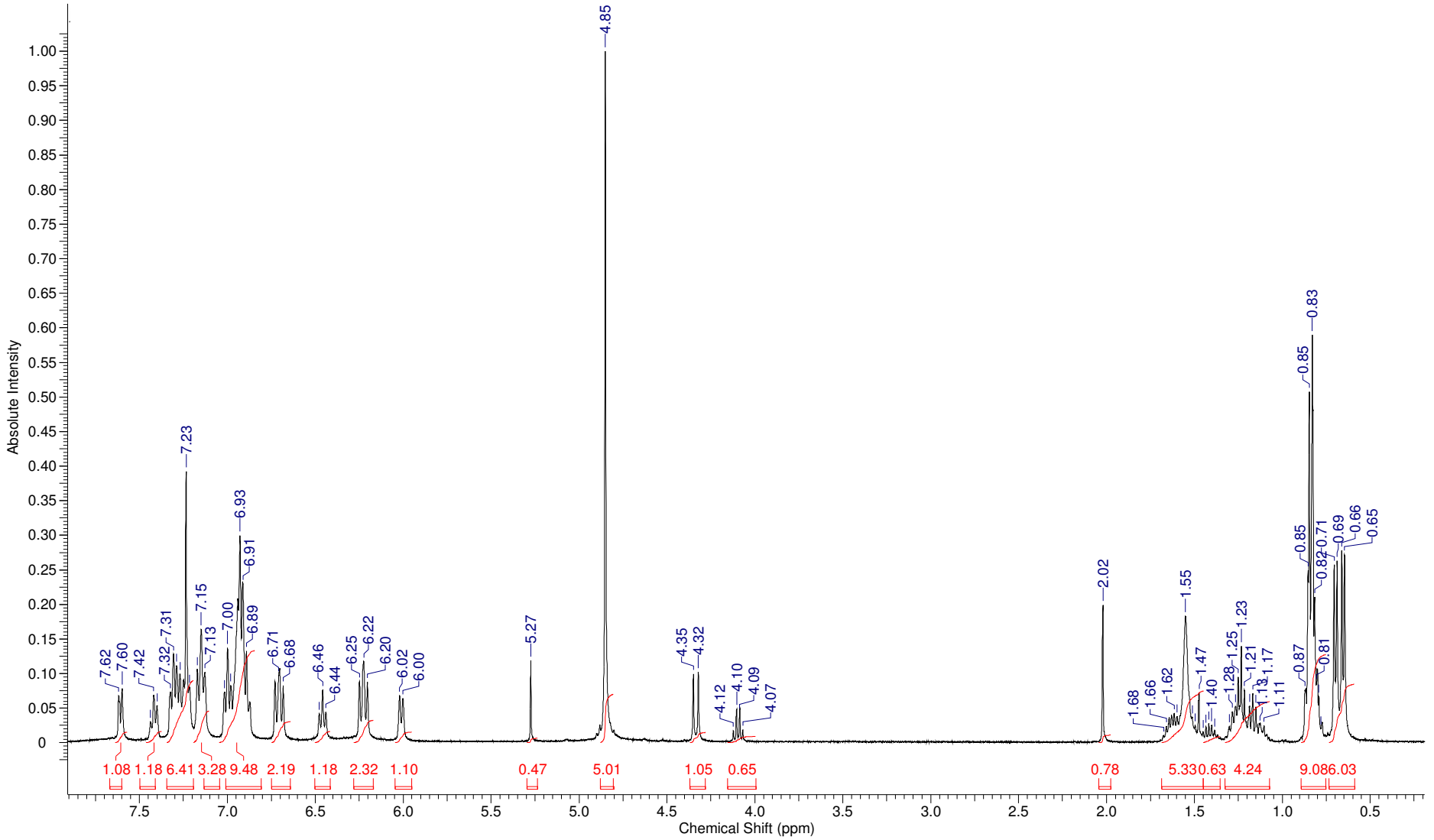
(*S*)-8a ^{1}H NMR (400 MHz, $CDCl_3$)



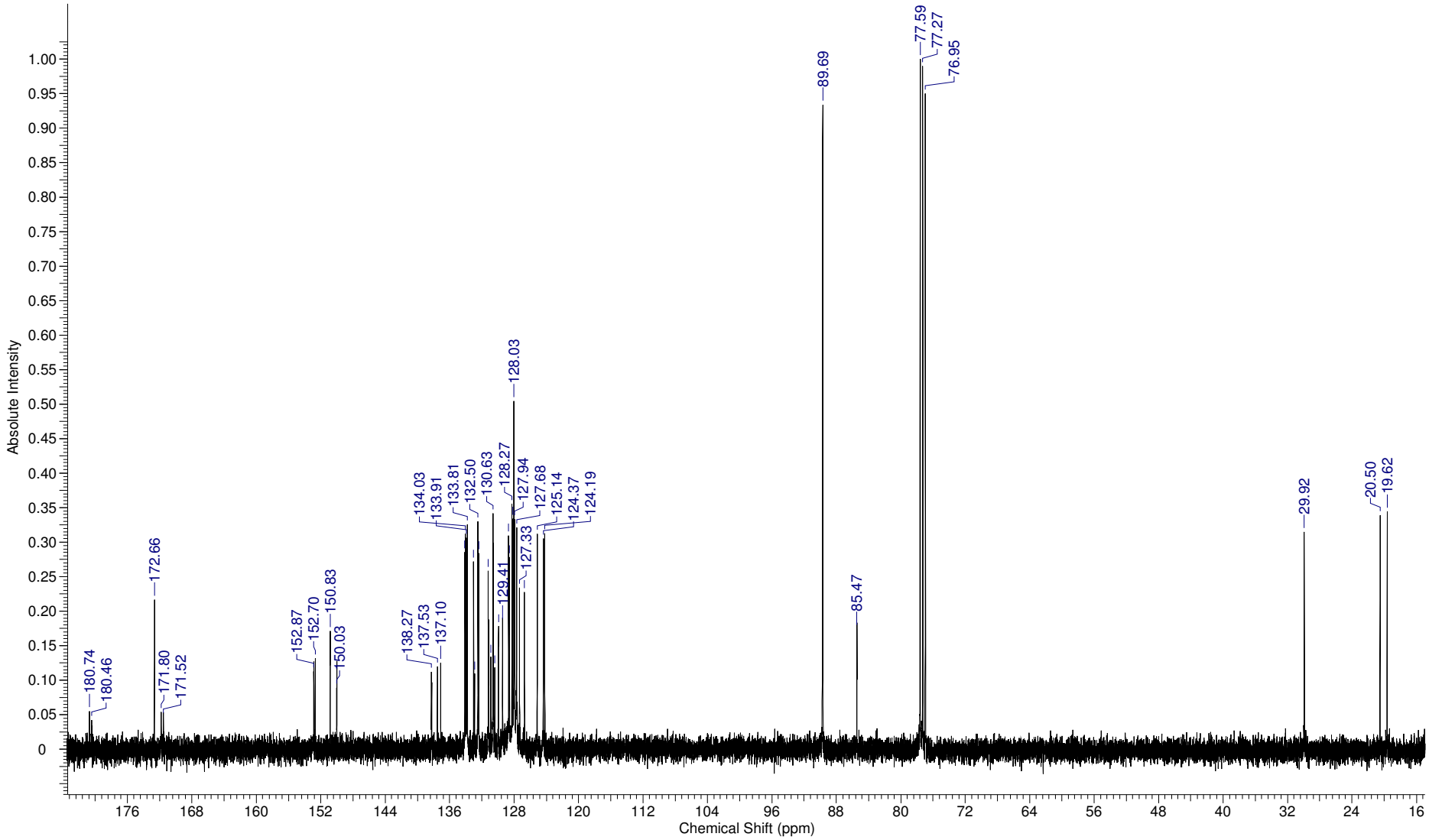
(*S*)-8a ^{13}C NMR (100 MHz, $CDCl_3$)



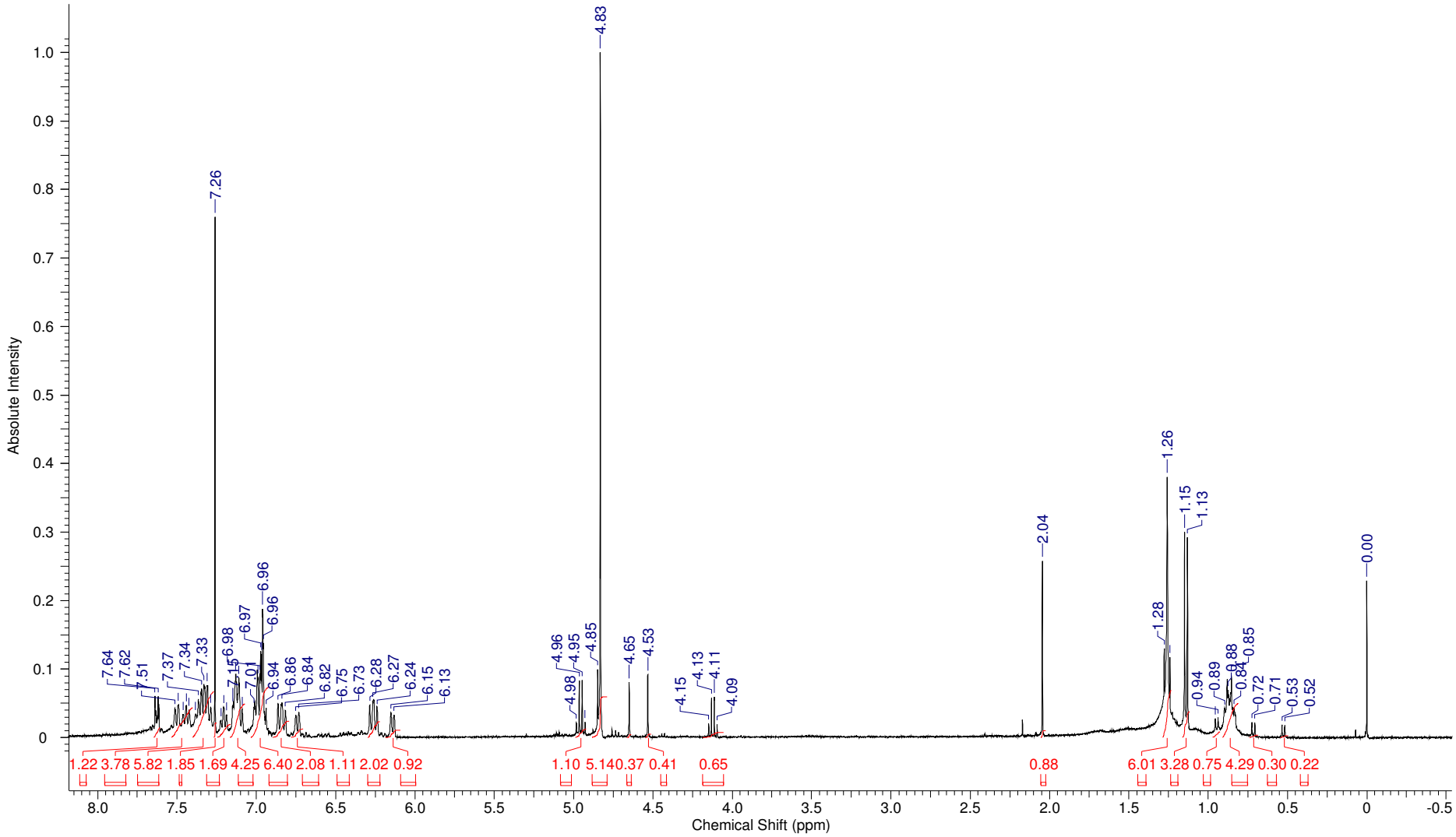
8b ^{1}H NMR (400 MHz, $CDCl_3$)



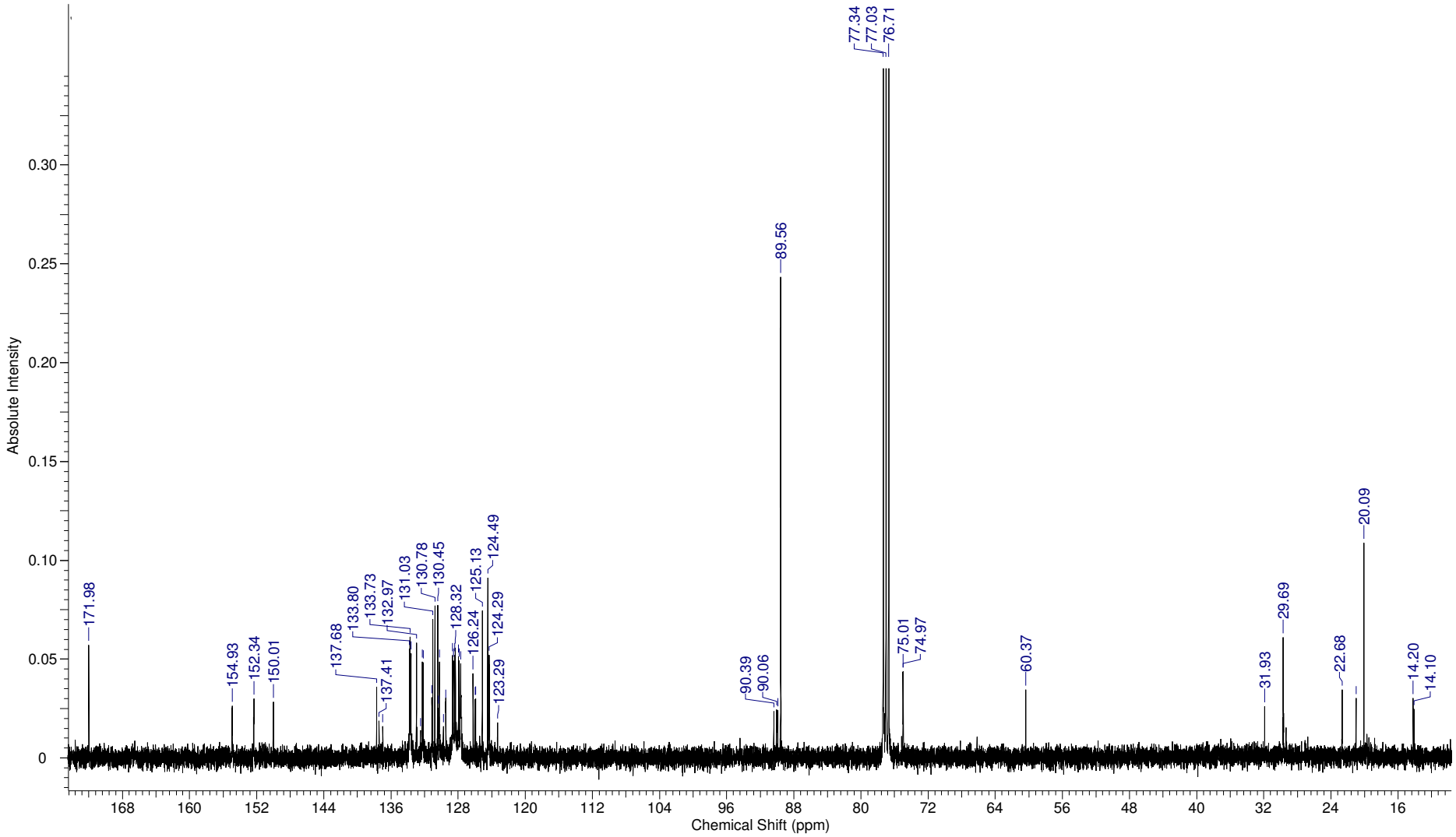
8b ^{13}C NMR (100 MHz, $CDCl_3$)



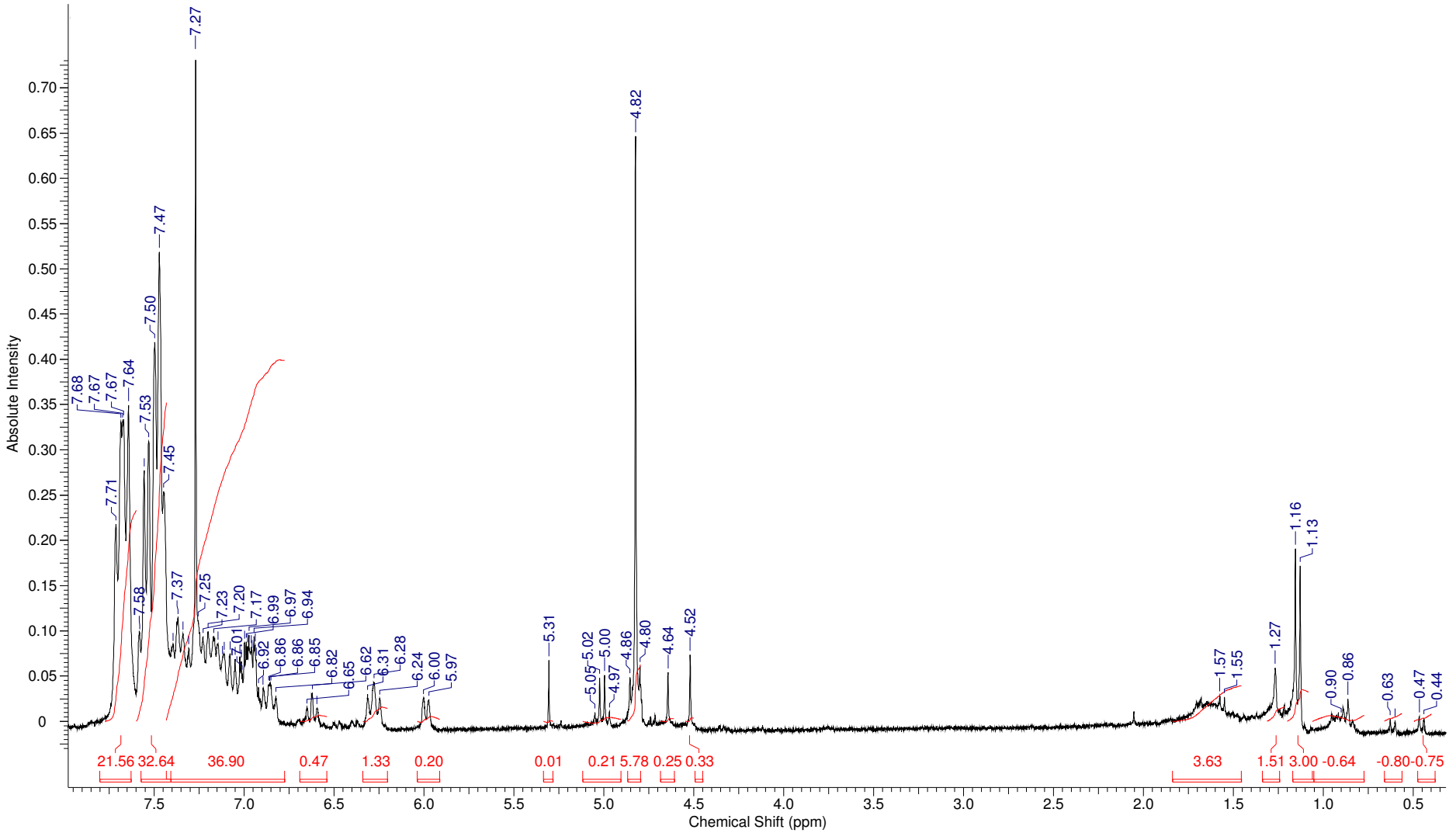
8c ^{1}H NMR (400 MHz, $CDCl_3$)



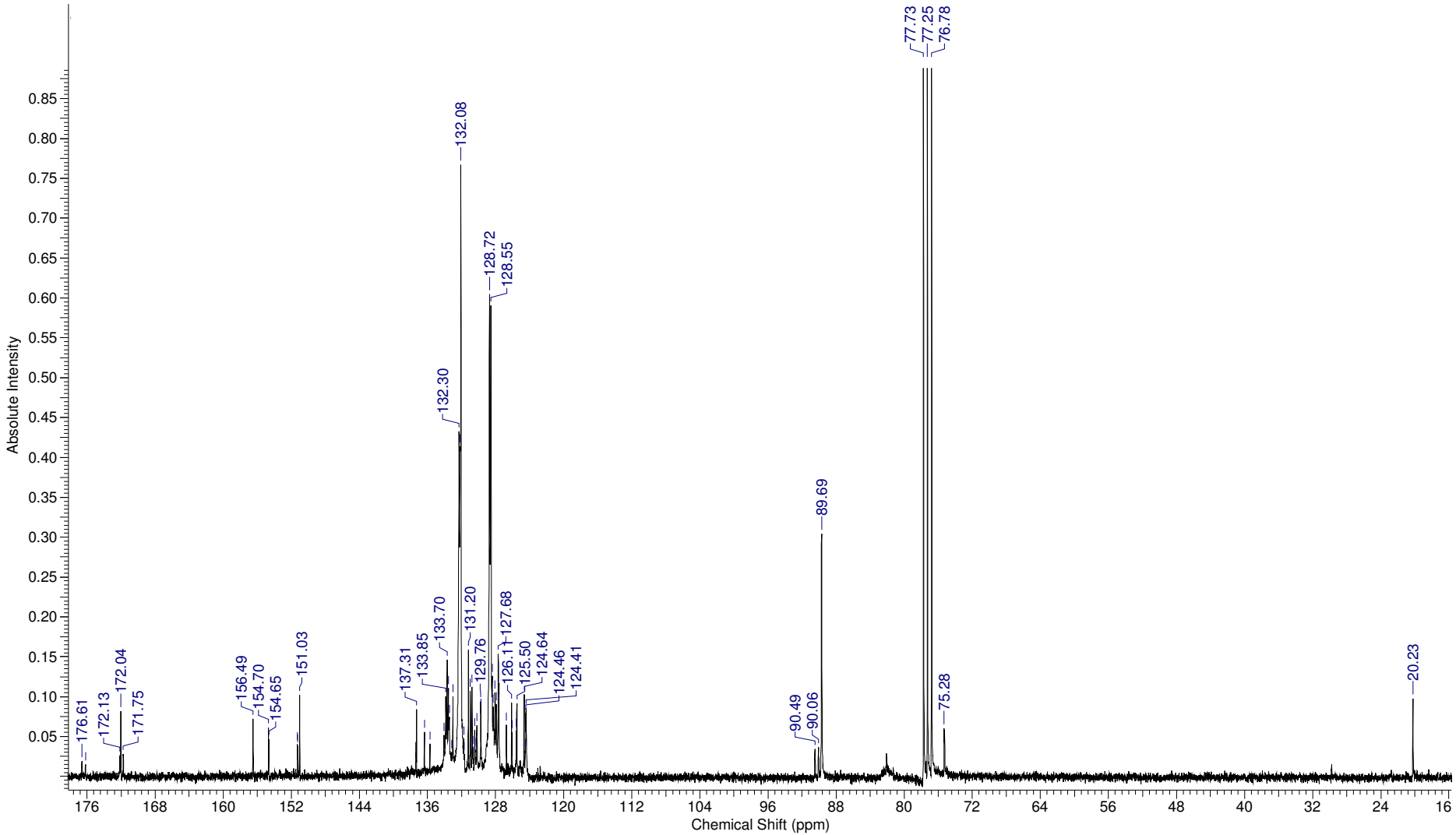
8c ^{13}C NMR (100 MHz, $CDCl_3$)



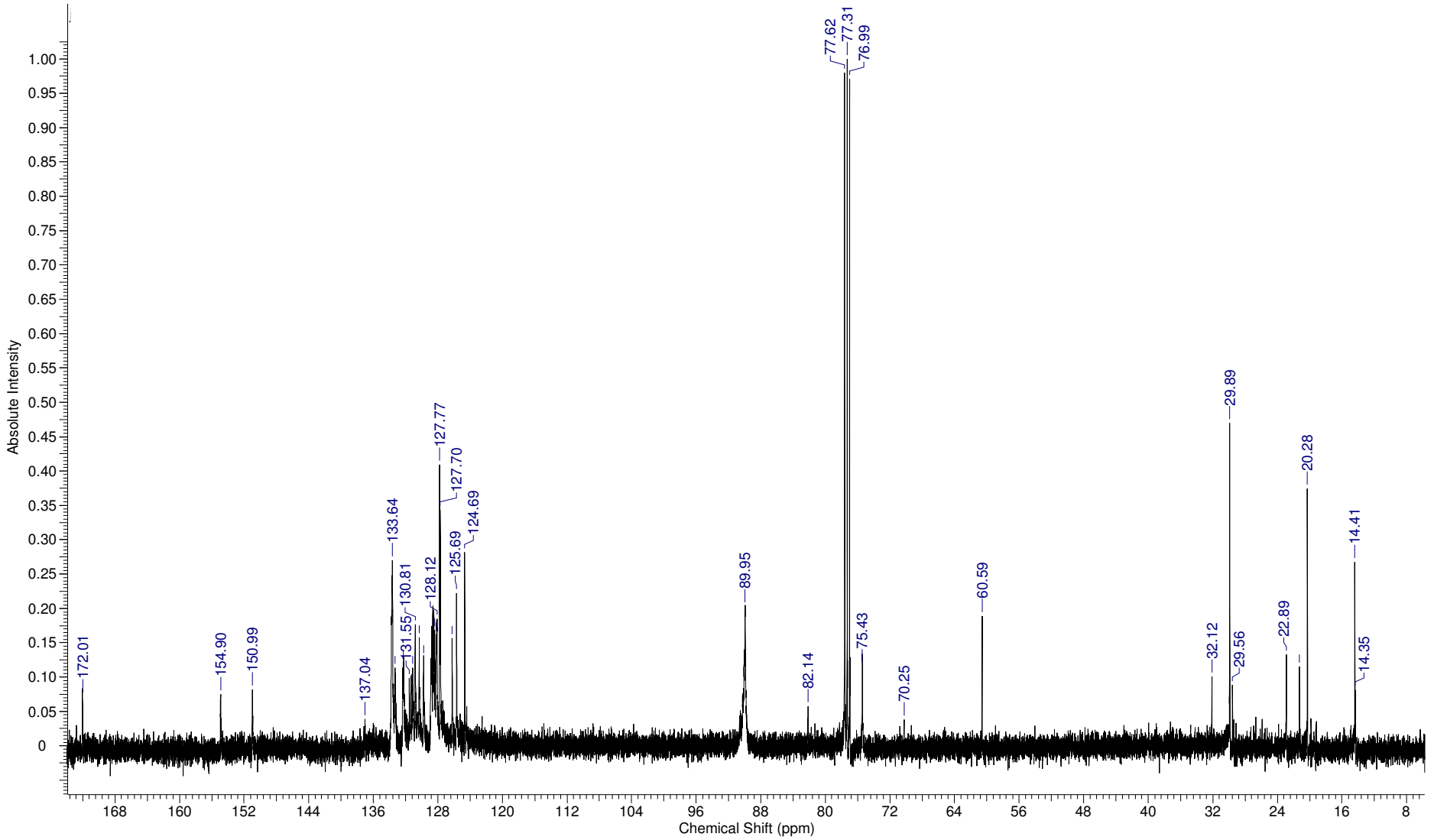
8d ^{1}H NMR (δ, 270 MHz, $CDCl_3$)



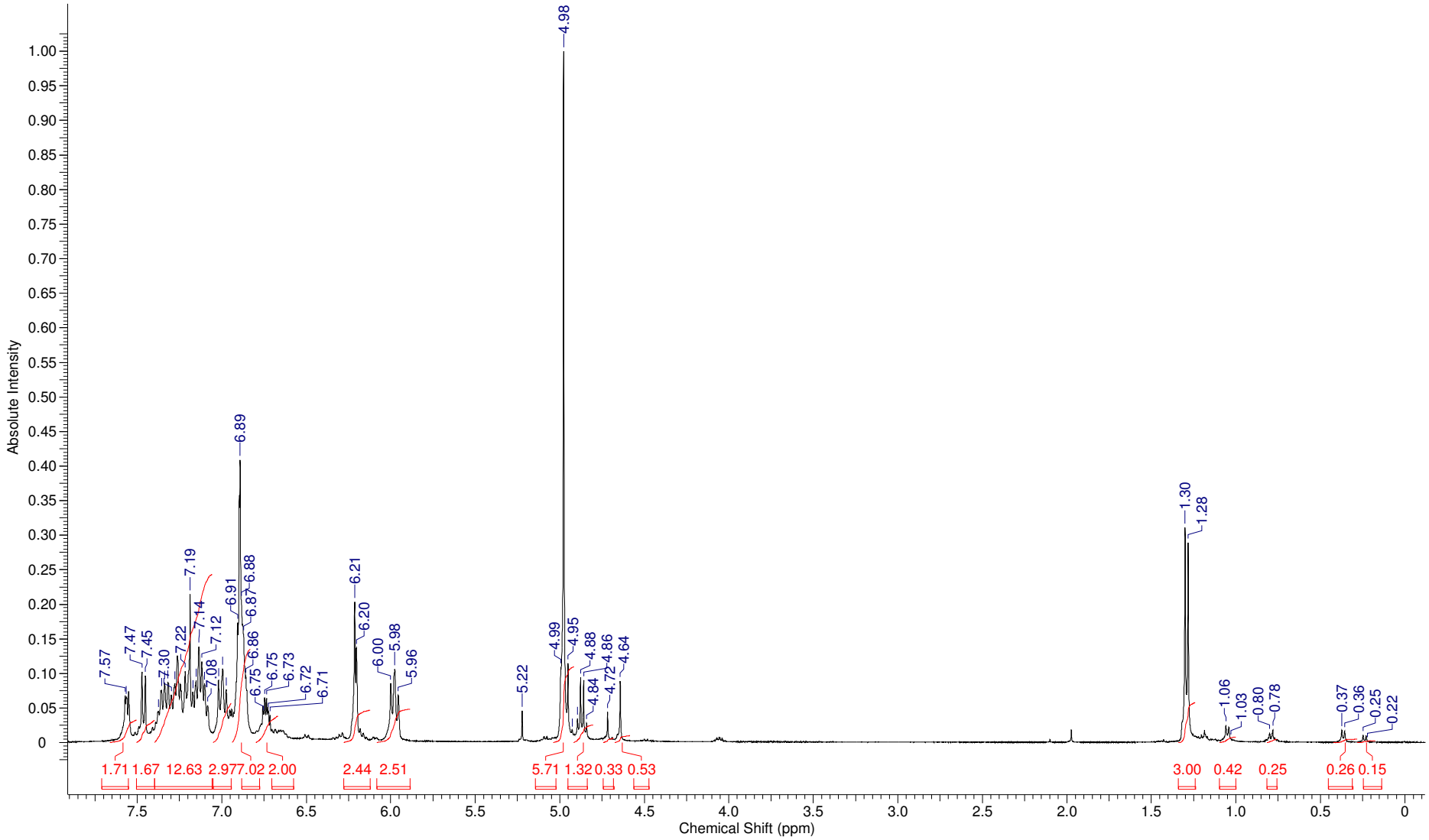
8d ^{13}C NMR (δ, 67 MHz, $CDCl_3$)



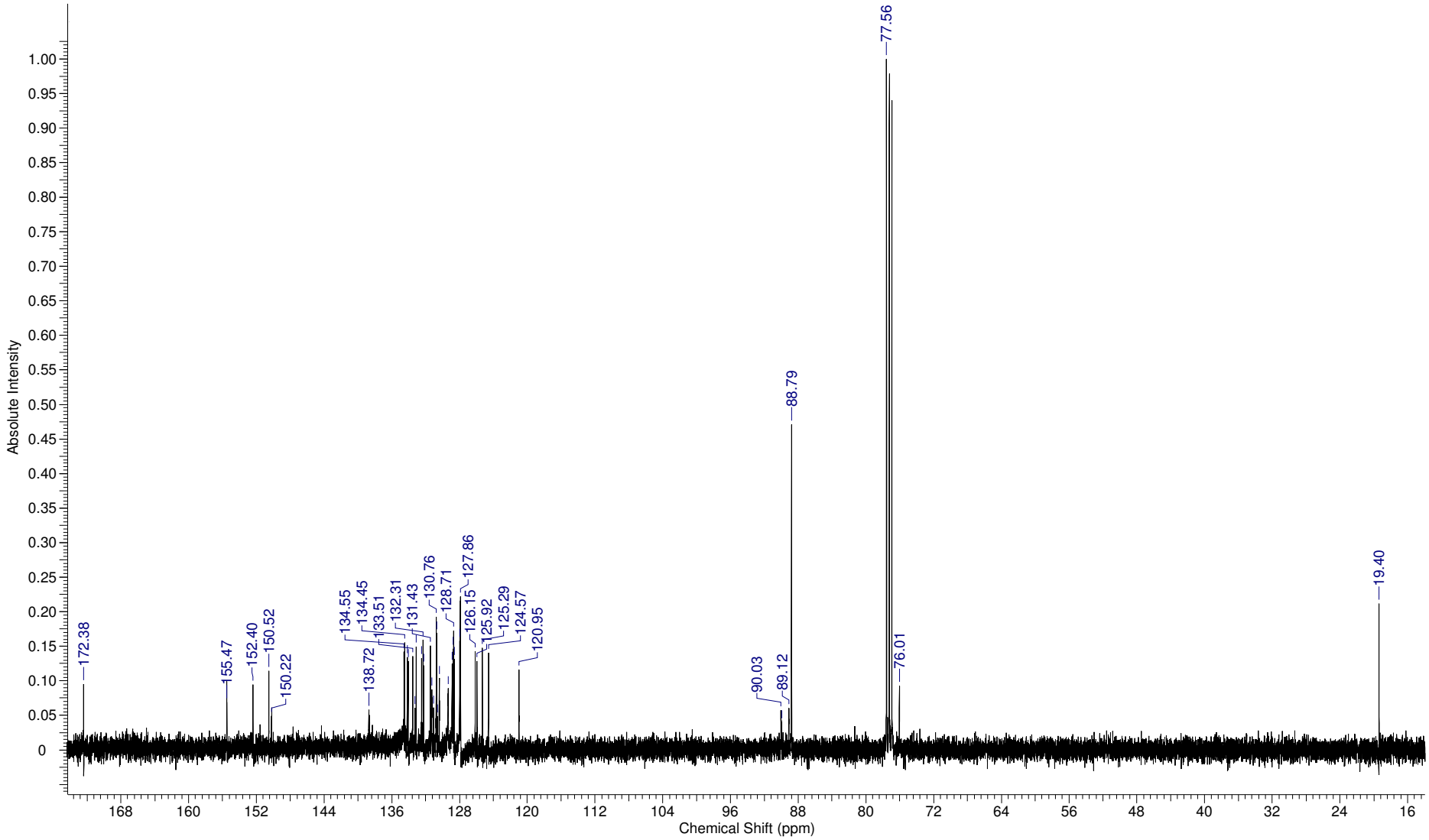
8e ^{13}C NMR (100 MHz, $CDCl_3$)



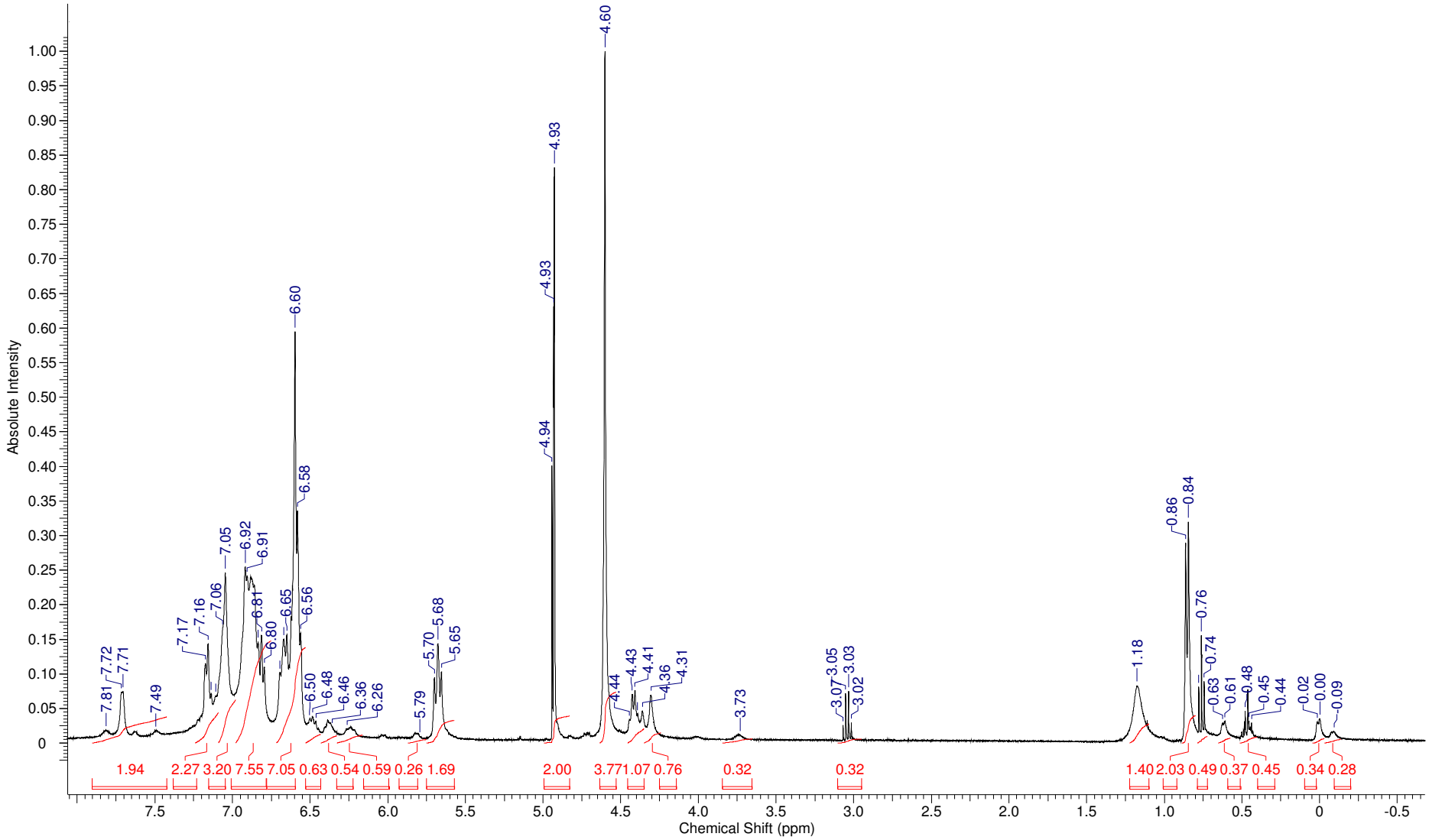
8f ^{1}H NMR (400 MHz, $CDCl_3$)



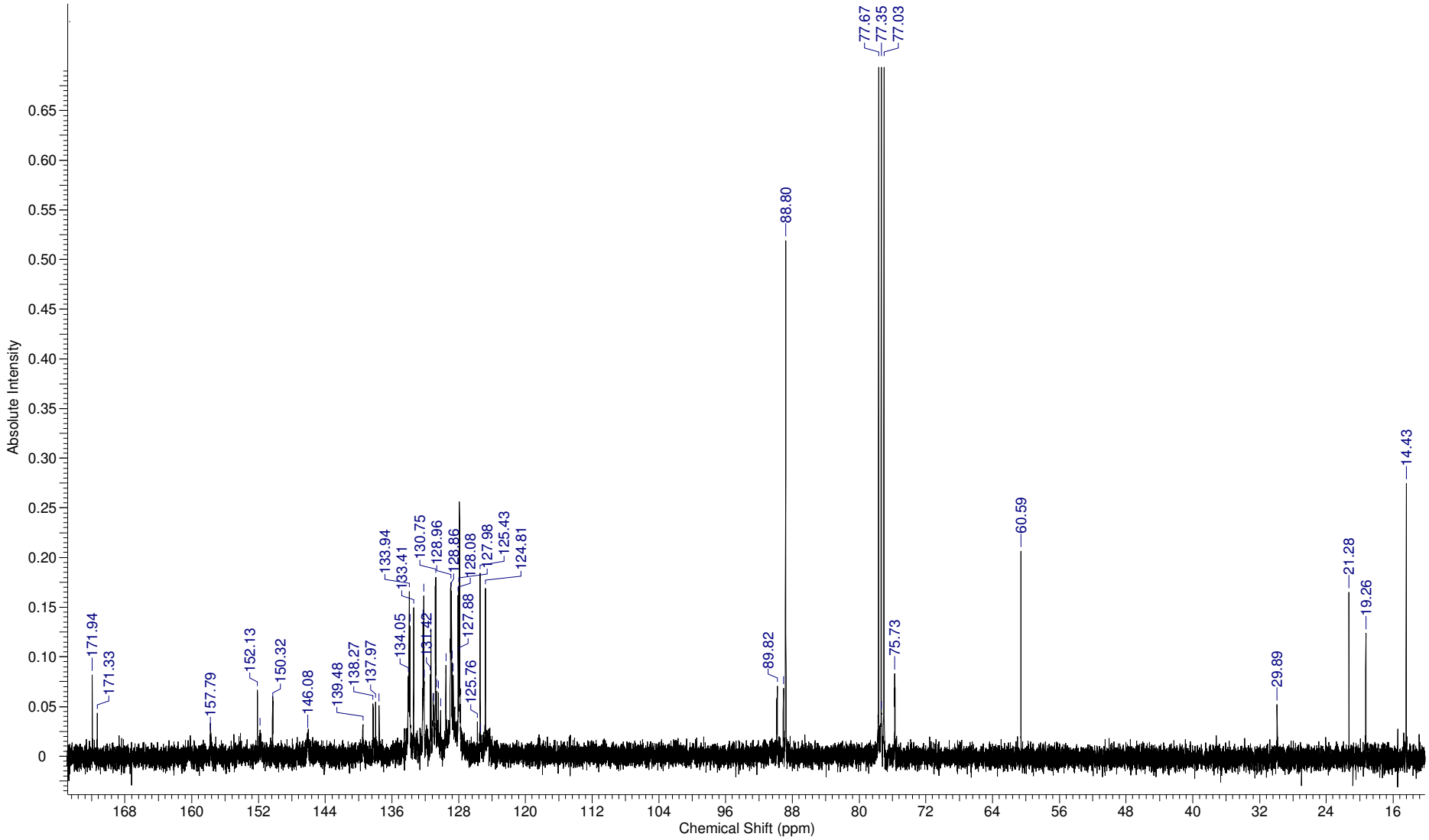
8f ^{13}C NMR (100 MHz, $CDCl_3$)



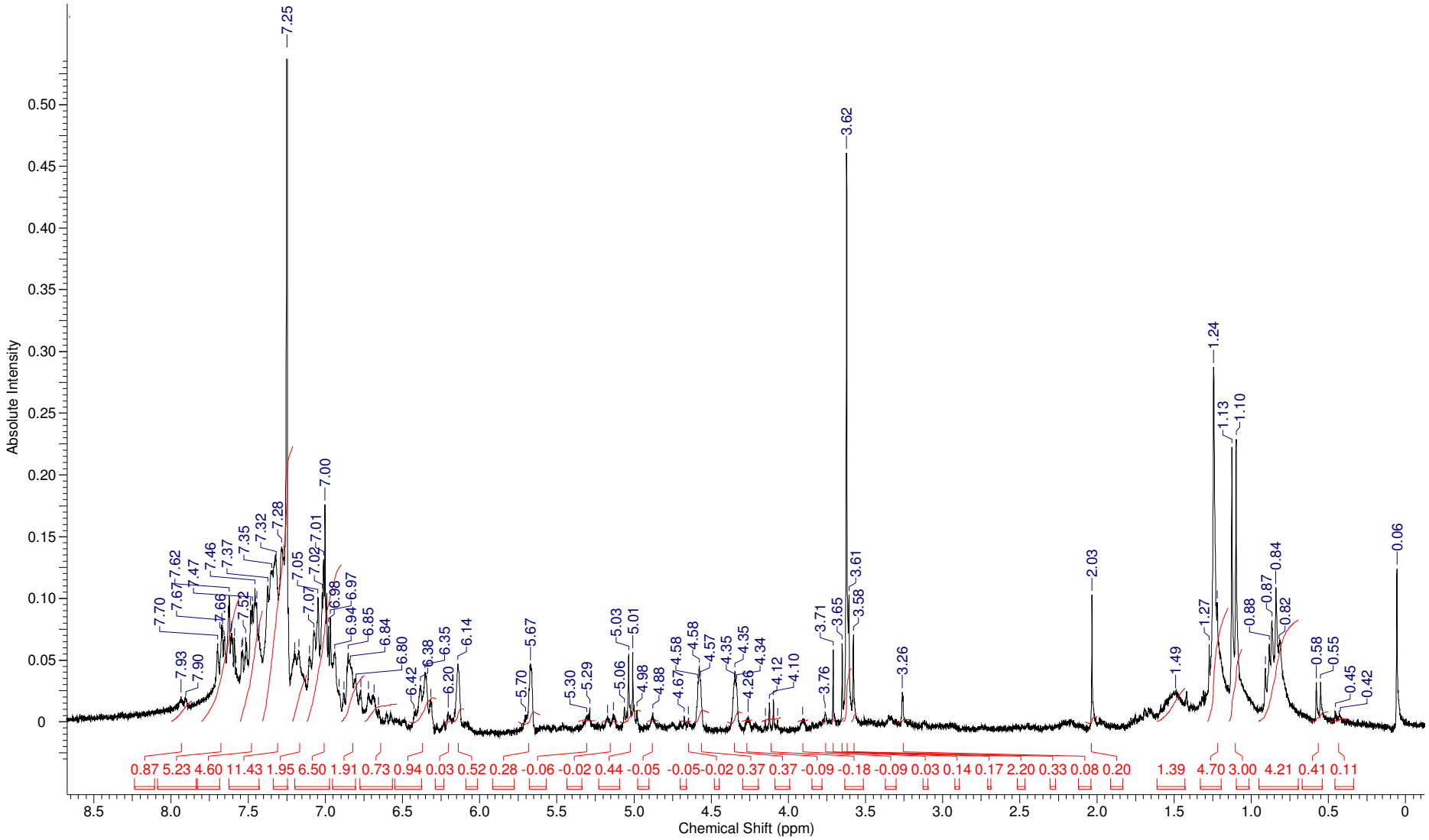
8g ^{1}H NMR (400 MHz, CD_2Cl_2)[Spectrum offset by -0.35 ppm]



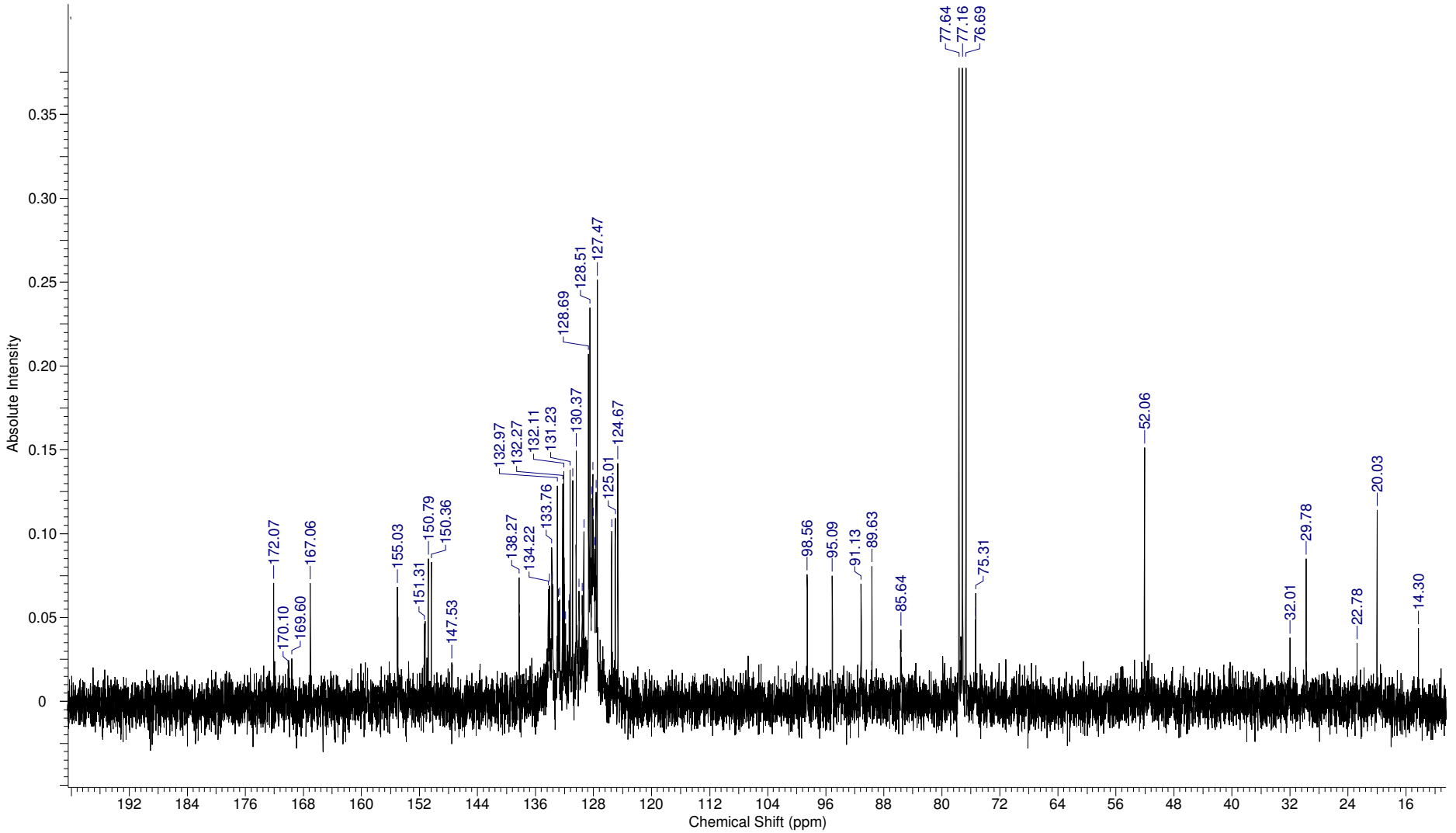
8g ^{13}C NMR (100 MHz, CD_2Cl_2)



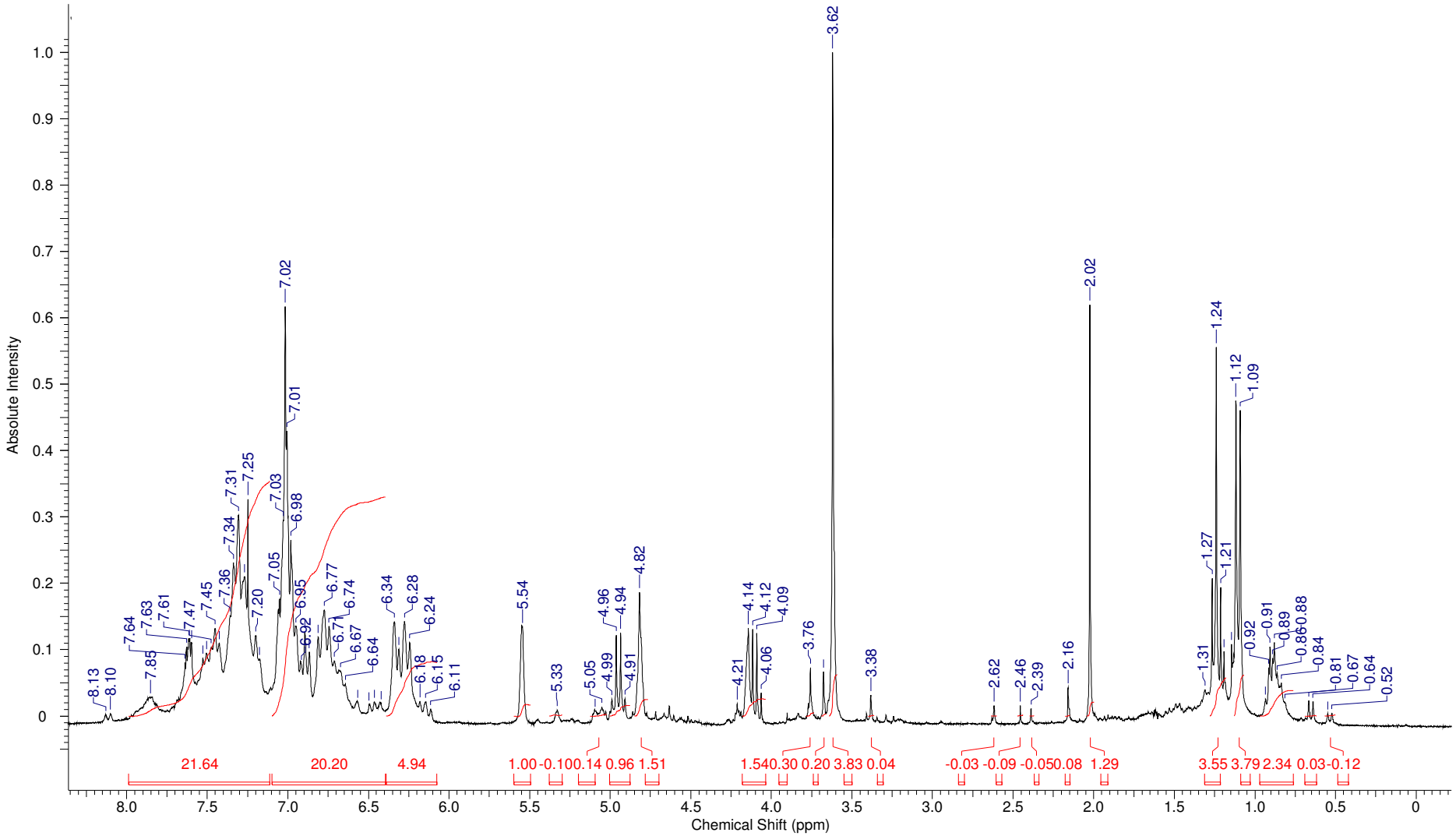
11a ^{1}H NMR (δ, 270 MHz, $CDCl_3$)



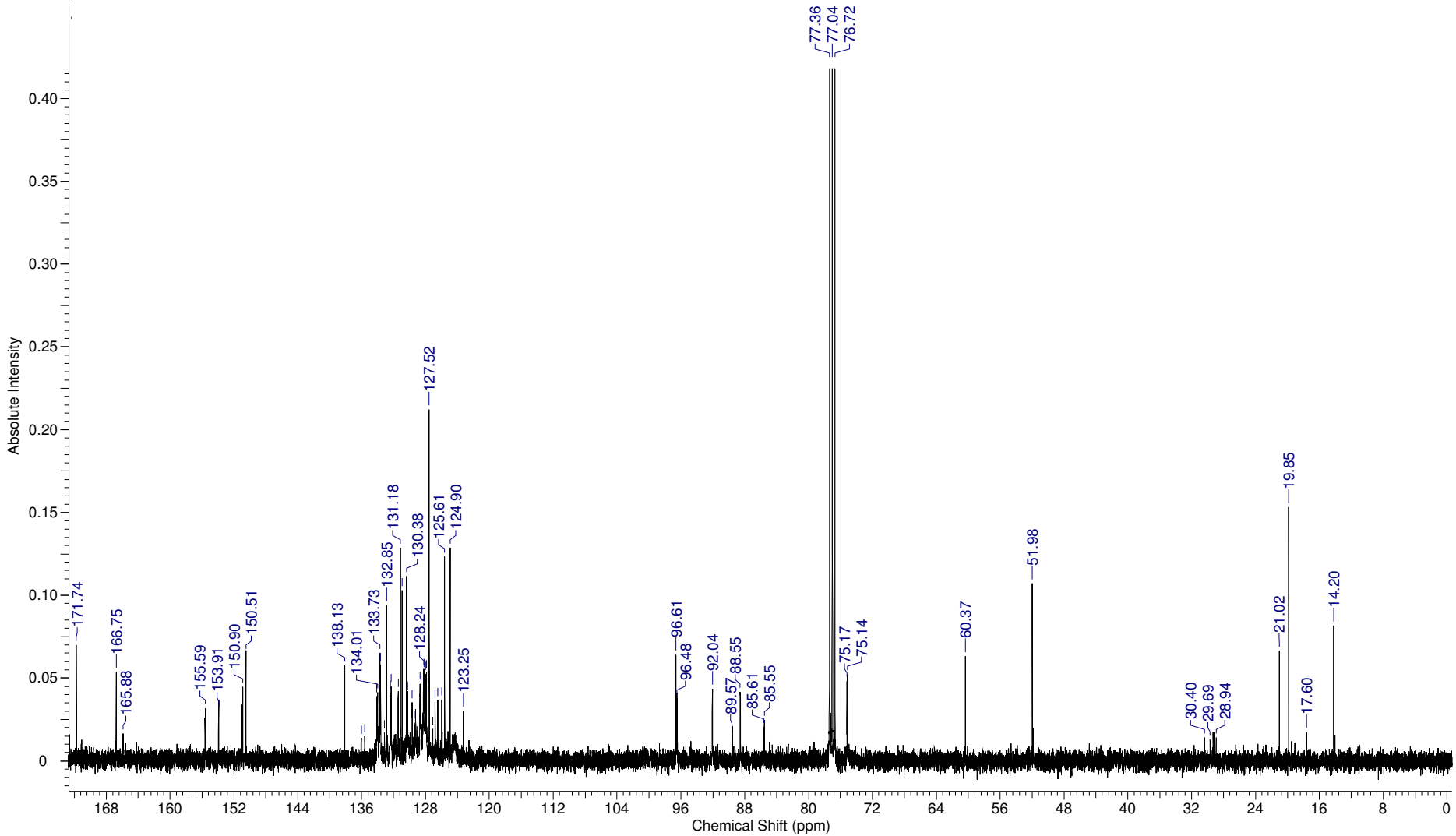
11a ^{13}C NMR (δ, 67 MHz, $CDCl_3$)



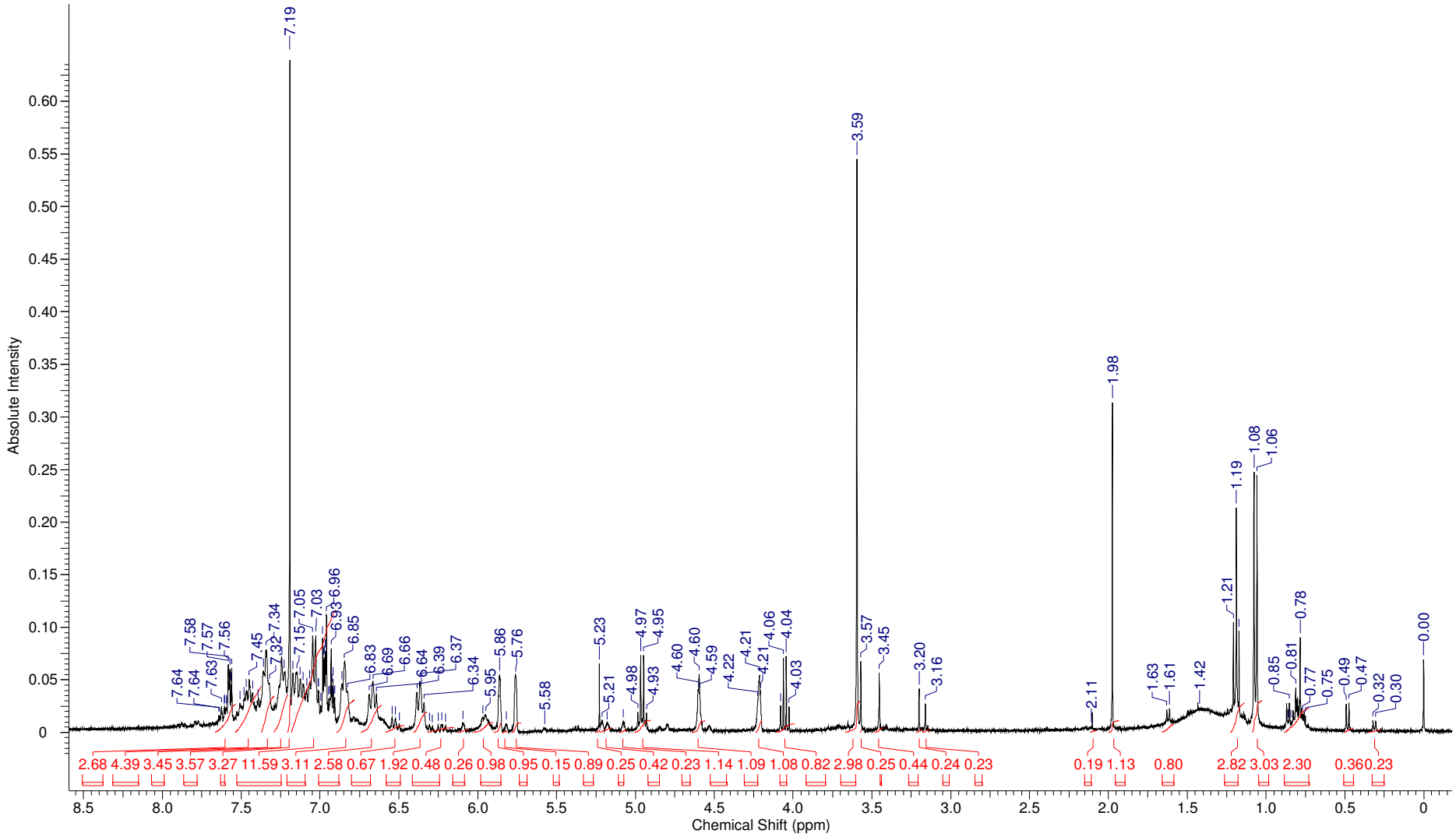
11c ^{1}H NMR (δ, 270 MHz, $CDCl_3$)



11c ^{13}C NMR (100 MHz, $CDCl_3$)



11d ^{1}H NMR (400 MHz, $CDCl_3$)



11d ^{13}C NMR (δ, 67 MHz, $CDCl_3$)