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Supporting Information

Divergent Stereochemical Outcomes in the Insertion of Donor/Donor Carbenes into the C–H Bonds of Stereogenic Centers

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Materials and Instrumentation

General Comments. Chemicals were purchased and used without further purification unless otherwise specified. All reactions using anhydrous solvents were carried out under an atmosphere of industrial argon in flame-dried glassware with magnetic stirring. Anhydrous solvent was dispensed from a solvent purification system that passes solvent through two columns of dry neutral alumina. Reactions were monitored by thin layer chromatography (TLC, Merck), and detected by examination under UV light (254 nm and 365 nm). Flash column chromatography was performed using silica gel [230−400 mesh (40−63 μm)]. Extracts were concentrated in vacuo using both a rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate. ^{1}H and proton-decoupled ^{13}C spectra were measured in CDCl3 at 400, or 600 MHz, and 101 or 151 MHz respectively unless otherwise noted. All spectra in $CDCl_3$ were referenced at TMS = 0 ppm. High-resolution mass spectrometry was performed on positive mode and ESI/Orbitrap™, ESI/TOF, and CI/TOF techniques were generally used. For substrates 24 and 25 high-resolution mass spectrometry using the aforementioned techniques was not achieved; low-resolution mass spectrometry using an Advion© ASAP-APCI-MS was achieved and the corresponding data is reported for those. Melting points were taken on an EZ-melting apparatus and were uncorrected. Infrared spectra were taken on a Bruker Tensor 27 spectrometer.

General Procedure A (Mitsunobu reaction). To a flame-dried 100 mL round bottom flask under argon atmosphere was added phenol (1.0 equiv), alcohol (1.1 equiv), and THF (0.1 M). The reaction was cooled to 0 ^{o}C, then triphenylphosphine (1.3 equiv) and diisopropyl azodicarboxylate (1.3 equiv) were added sequentially. After stirring overnight and allowing the reaction to warm to room temperature, the reaction was concentrated *in vacuo* and purified by flash column chromatography to yield the desired ether.

General Procedure B (Benzophenone formation). To a flame-dried 100 mL round bottom flask under argon atmosphere was added aryl bromide (1.0 equiv) and THF (0.25 M). The reaction was cooled to -78 ^{o}C, then n-BuLi (1.2 equiv) was added and the reaction was stirred at -78 ^{o}C for two hours. A solution of weinreb (1.0 equiv) in THF (0.8 M) was added to the reaction mixture, then the reaction was stirred overnight while allowing it to warm to room temperature. The reaction was cooled back down to -78 ^{o}C and quenched with saturated NH_4Cl aqueous solution. The mixture was extracted three times with EtOAc, then the combined organic layers were dried over Na_2SO_4, concentrated *in vacuo*, and purified by flash column chromatography to yield the desired ketone.

General Procedure C (Hydrazone formation). Following a literature precedent[1], to an oven-dried 10-20 mL microwave vial under argon atmosphere was added the desired alkylated benzophenone (1.0 equiv) in anhydrous EtOH (0.1 M). Glacial acetic acid (2.0 equiv) and anhydrous hydrazine (8.0 equiv) were added dropwise to the solution. The reaction was heated to 80 ^{o}C for 3-12 hours until the starting material fully converted by TLC. After the reaction was cooled, it was diluted in diethyl ether (25 mL) then washed with water (2 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over Na_2SO_4, concentrated *in vacuo*, and purified by flash column chromatography to yield the desired hydrazone.

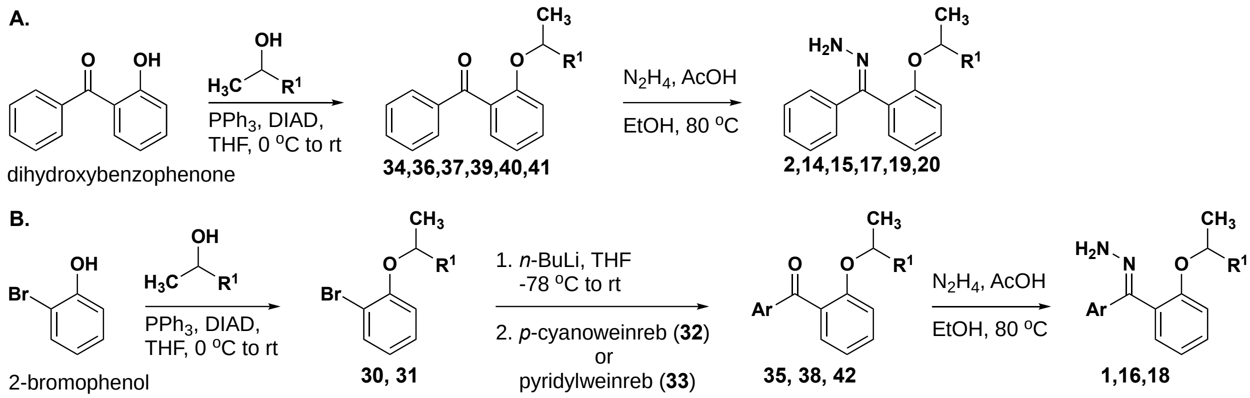
Note: Hydrazones were isolated as a mixture of E/Z isomers or used without further purification. As such ^{1}H peaks have been reported only for selected examples.

General Procedure D (One-pot sequential C-H insertion). To a flame-dried 20 mL scintillation vial under argon atmosphere was added a solution of hydrazone (1.0 equiv) in anhydrous CH_2Cl_2 (0.01 M). To the solution was added MnO_2 (8.0 equiv), and the suspension was stirred until full conversion of the starting material to diazo was observed by TLC. A color change of the solution from clear to magenta was observed from the formation of the diazo. The reaction was cooled to 0 ^oC then the desired dirhodium catalyst was added (1 mol %), and the reaction was stirred while allowing it to warm to room temperature until full conversion of diazo to the desired product was observed. The crude reaction mixture was filtered over Celite to remove MnO_2, concentrated *in vacuo*, and purified by flash column chromatography to yield the desired insertion product.

Note: it is necessary that the MnO2 used for the oxidation of hydrazones be ~85% pure with an average particle size of 2 microns, appearing as a fine black powder (e.g. Oakwood Chemical, CAS #: 1313-13-9, cat. #: 094454, lot #: 094454K03K).

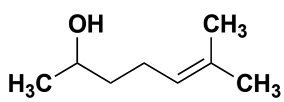
General Procedure E (synthesis of Weinreb amide). To a flame-dried round bottom flask was added the substituted benzoic acid (1.0 equiv) in DCM (0.3 M) and oxayl chloride (2.0 equiv). DMF (1.3 equiv) was added dropwise, and the solution was stirred for 1 h. The solution was then concentrated *in vacuo* and re-diluted in DCM (30 mL). To a separate flame-dried round bottom flask were added *N,O*-dimethylhydroxylamine hydrochloride (1.5 equiv), Et_3N (3.0 equiv), and DCM (0.3 M) and the solution was stirred for 10 min. The weinreb salt solution was cooled down to 0 ^oC, then the acyl chloride solution was added dropwise and stirred at rt overnight. Upon completion, the reaction was quenched with sat. aq. $NaHCO_3$ (50 mL) and the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with H_2O (2 x 30 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography to yield the desired Weinreb amide.

Starting Material Synthesis

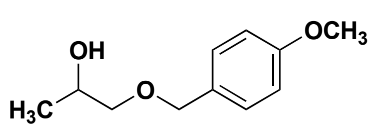


SI Figure 1. A. Synthesis of hydrazone intermediate from 2-hydroxybenzophenone. B. Synthesis of hydrazone intermediate from 2-bromophenol.

Alcohol Substrates



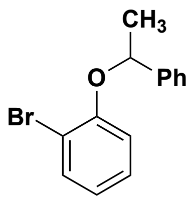
(28) 6-methylhept-5-en-2-ol was synthesized according to reported literature procedure[2] using 6-methylhept-5-en-2-one (5.0 g, 39.6 mmol), sodium borohydride (0.749 g, 19.8 mmol) with EtOH (132 mL, 0.3M) and H_2O (40 mL, 0.5 M with $NaBH_4$). After workup no further purification was needed to yield **28** as a clear oil (4.13g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (t, J = 8.0 Hz, 1H), 3.81 (q, J = 6.4 Hz, 1H), 2.08 (hept, J = 7.3 Hz, 2H), 1.69 (s, 3H), 1.63 (s, 3H), 1.53 – 1.44 (m, 3H), 1.19 (d, J = 6.1 Hz, 3H). ^{1}H NMR data was consistent with literature values.[2]



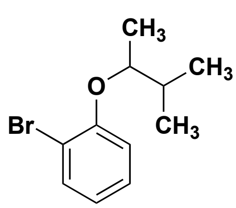
(29) 1-((4-methoxybenzyl)oxy)propan-2-ol was synthesized according to reported literature procedure[3] using propene oxide (1.00 g, 17.2 mmol), NaH (0.798 g, 19.8 mmol, 57% dispersion in mineral oil) with anhydrous DMF (27 mL, 0.7 M) and 4-methoxybenzyl alcohol (4.76 g, 34.4 mmol) with anhydrous DMF (17.2 mL, 2.0 M). The crude product was purified by flash column chromatogreaphy (40:60 EtOAc:Hexanes) affording alcohol **29** as a clear oil (2.56 g, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 2H), 6.97 –

6.82 (m, 2H), 4.62 (s, 1H), 4.49 (s, 1H), 3.81 (s, 4H), 3.45 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.25 (t, *J* = 8.8 Hz, 1H), 2.37 (br, 1H), 1.14 (d, *J* = 6.4 Hz, 2H). ^{1}H NMR data was consistent with literature values.[3]

Bromo-ether Substrates

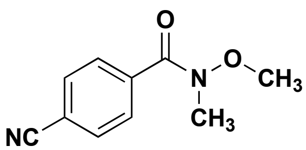


(30) 1-bromo-2-(1-phenylethoxy)benzene was synthesized according to general procedure A, 2-bromophenol (1.14 mL, 9.83 mmol), 1-phenylethan-1-ol (1.00 mL, 8.19 mmol), triphenylphosphine (2.79 g, 10.65 mmol), and DIAD (2.09 mL, 10.65 mmol) with anhydrous THF (82 mL) were used. The crude product was purified by flash column chromatography (10:90 EtOAc:hexanes) affording ether **30** as a light yellow oil (2.16 g, 95%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.32 (t, 2H), 7.24 (t, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.76 – 6.70 (m, 2H), 5.34 (q, *J* = 6.4 Hz, 1H), 1.67 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.43, 142.68, 133.45, 128.76(2), 128.26, 127.74, 125.71(2), 122.01, 115.60, 113.18, 77.41, 24.49; IR (thin film) 3063, 1584, 1494 cm^{-1}; TLC (20:80, EtOAc:hexanes) R_F = 0.85. Low-resolution MS (Advion ASAP-APCI) *m/z* calcd for C14H13BrO^{+}[M+H]$^{+}$ 277.0173, found 277.0. $[\alpha]_D^{23}$ = +32.0 (c = 0.30, $CHCl_3$).

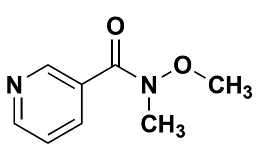


(31) 1-bromo-2-((3-methylbutan-2-yl)oxy)benzene was synthesized according to general procedure A, 2-bromophenol (3.35 mL, 28.9 mmol), 3-methyl-2-butanol (3.43 mL, 31.8 mmol), triphenylphosphine (9.10 g, 34.7 mmol), diisopropyl azodicarboxylate (6.81 mL, 34.7 mmol), and anhydrous THF (150 mL) were used. The crude product was purified by flash column chromatography (90:10, hexanes:EtOAc) affording ether **31** as a clear oil (3.97 g, 56%): ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J*

= 7.8 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 4.20 (p, *J* = 6.0 Hz, 1H), 1.97 (hd, *J* = 6.8, 5.1 Hz, 1H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.92, 133.59, 128.35, 121.51, 114.90, 113.58, 80.03, 77.37, 77.16, 76.95, 33.26, 18.29, 18.04, 16.10.; IR (thin film) 3184, 1773, 1704 cm^{-1}; Low-resolution MS (Advion ASAP-APCI) *m/z* calcd for $C_{11}H_{15}BrO^+$[M+H]$^+$ 243.0379.1307 found 243.0.

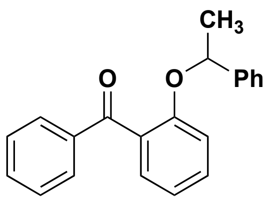


(32) 4-cyano-*N*-methoxy-*N*-methylbenzamide was synthesized according to general procedure E using 4-cyanobenzoic acid (8.00 g, 54.5 mmol) in CH_2Cl_2 (181 mL), oxalyl chloride (9.3 mL, 108.7 mmol), DMF (5.46 mL, 70.75 mmol), Et_3N (22.8 mL, 163.2 mmol), and *N,O*-dimethylhydroxylamine hydrochloride (7.96 g, 81.6 mmol) in CH_2Cl_2 (181 mL). The crude product was extracted from $NaHCO_3$ (150 mL) with CH_2Cl_2 (3 x 100 mL) and the combined organic layers were washed with $NaHCO_3$ (2 x 50 mL) and brine (1 x 50 mL). The crude product was purified by flash column chromatography (90:10, hexanes:EtOAc) affording **32** as a clear oil (7.86 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 3.53 (s, 3H), 3.38 (s, 3H). ^{1}H NMR data was consistent with literature values.[4]

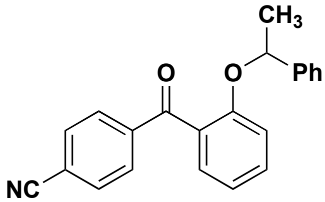


(33) *N*-methoxy-*N*-methylnicotinamide was synthesized by preparing a suspension of N-methoxy-N-methylamine•HCl (1.317 g, 13.50 mmol, 1.2 equiv.) in CH_2Cl_2 (45.0 mL), following a modified literature procedure.[4] This suspension was cooled to 0 ^{o}C and triethylamine (6.25 mL, 44.8 mmol, 3.9 equiv) was added slowly over 20 minutes, the resulting solution was cooled to 0 ^{o}C. To the solution was added nicotinoyl chloride•HCl (2.032 g, 11.41 mmol, 1.0 equiv) and the mixture was allowed to warm to rt and stirred for 23 h, The reaction mixture was quenched with sat. aq. $NaHCO_3$ (10 mL), and the organic layer was separated. The aqueous layer was then neutralized with 1 M HCl and extracted with CH_2Cl_2 (3 X 50 mL); the combined organic layers were washed with brine (2 X 100 mL) and dried over Na_2SO_4. The resulting solution was concentrated in vacuo and the crude product was purified using flash column chromatography (95:5, CH_2Cl_2:CH_3OH), affording **33** as a yellow oil (1.568 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 1.2 Hz, 1H), 8.69 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.03 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.37 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1H), 3.56 (s, 3H), 3.40 (s, 3H). ^{1}H NMR data was consistent with literature values.[4]

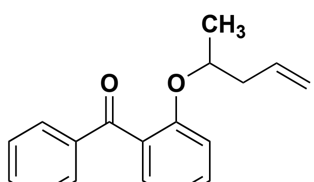
Ketone Substrates



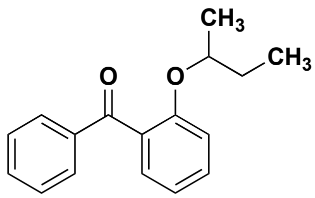
(34) Phenyl(2-(1-phenylethoxy)phenyl)methanone was synthesized according to general procedure A, 2-hydroxyphenyl)(phenyl)methanone (1.00 g, 5.04 mmol), 1-phenylethan-1-ol (0.607 mL, 5.04 mmol), triphenylphosphine (1.59 g, 6.05 mmol), and DIAD (1.19 mL, 6.05 mmol) with anhydrous THF (50 mL) were used. The crude product was purified by flash column chromatography (10:90 EtOAc:hexanes) affording ketone **34** as a clear oil (1.26 g, 83%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 6.7 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.28 – 7.22 (m, 4H), 7.06 – 7.00 (m, 3H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.20 (q, *J* = 7.0, 6.4 Hz, 1H), 1.25 (d, *J* = 6.5 Hz, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.81, 156.20, 142.33, 142.16, 133.17, 132.12(2), 130.41, 129.76(2), 128.76(2), 128.31, 127.93(2), 125.41, 121.12, 118.39, 115.67, 114.08, 77.37, 77.20, 77.16, 76.95, 23.77.; IR (thin film) 3018, 2361, 2339, 1664 cm^{-1}; TLC (10:90, EtOAc:hexanes) R_F = 0.2. AMM (ESI) *m/z* calcd for C21H18O2$^+$[M+H]$^+$ 327.1259; $[\alpha]_D^{23}$ = +124.4 (c = 1.4, $CHCl_3$).



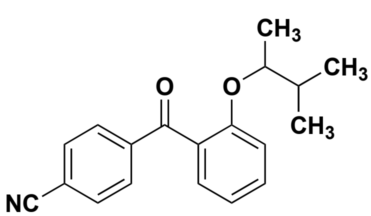
(35) 4-(2-(1-phenylethoxy)benzoyl)benzonitrile was synthesized according to general procedure B, 1-bromo-2-(1-phenylethoxy)benzene (5.00 g, 18.04 mmol) with anhydrous THF (60 mL), *n*-BuLi (2.28 M, 21.64 mmol, 9.50 mL), para-cyano Weinreb (4.12 g, 21.65 mmol) with anhydrous THF (27 mL) were used. The crude product was purified by flash column chromatography (30:70, EtOAc:hexanes) affording ketone **35** as a light yellow oil (2.66 g, 45%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.37 (t, 1H), 7.28 – 7.22 (m, 4H), 7.07 – 7.00 (m, 3H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.20 (q, *J* = 6.6 Hz, 1H), 1.25 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.81, 156.20, 142.33, 142.16, 133.16, 132.12(2), 130.41, 129.76,(2) 128.75(2), 128.31, 127.93, 125.41(2), 121.12, 118.39, 115.67, 114.08, 77.20, 23.77; IR (thin film) 2977, 2229, 1662, 1448, 1236 cm^{-1}; TLC (40:60, EtOAc:hexanes) R_F = 0.45. AMM (ESI) *m/z* calcd for C22H17NO2^{+}[M+H]$^{+}$ 328.1332, found 328.1333; $[\alpha]_D^{23}$ = +85.4 (c = 0.62, $CHCl_3$)



(36) (2-(pent-4-en-2-yloxy)phenyl)(phenyl)methanone was synthesized according to general procedure A, (2-hydroxyphenyl)(phenyl)methanone (5.51 g, 27.80 mmol), pent-4-en-2-ol (2.39 mL, 23.20 mmol), triphenylphosphine (7.92 g, 30.20 mmol), diisopropyl azodicarboxylate (5.93 mL, 30.20 mmol), and anhydrous THF (57 mL) were used. The crude product was purified by flash column chromatography (40:60, CH_2Cl_2:hexanes) affording ketone **36** as a light yellow oil (5.00 g, 81%): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.25 (h, *J* = 6.0 Hz, 1H), 1.47 – 1.31 (m, 2H), 1.07 (d, *J* = 6.1 Hz, 3H), 0.67 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.47, 149.25, 137.96, 133.82, 132.74, 131.93, 130.21, 130.01, 129.72(2), 128.18(2), 122.15, 118.40, 113.74, 74.24, 41.07, 18.01; IR (thin film) 3063, 2978, 1692, 1584, 1493 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{18}H_{18}O_2^+[M+H]^+$ 266.1307 found 267.1378; $[\alpha]_D^{23}$ = +95.5 (c = 0.35, $CHCl_3$)

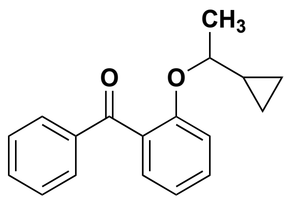


(37) (2-(sec-butoxy)phenyl)(phenyl)methanone was synthesized according to general procedure A, (2-hydroxyphenyl)(phenyl)methanone (0.50 g, 2.52 mmol), 2-butanol (0.26 mL, 2.77 mmol), triphenylphosphine (0.86 g, 3.28 mmol), diisopropyl azodicarboxylate (0.64 mL, 3.28 mmol), and anhydrous THF (25 mL) were used. The crude product was purified by flash column chromatography (40:60, CH_2Cl_2:hexanes) affording ether **37** as a light yellow oil (0.574 g, 90%): ^1H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (m, 4H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.25 (h, *J* = 6.0 Hz, 1H), 1.47 – 1.38 (m, 1H), 1.39 – 1.30 (m, 1H), 1.07 (d, *J* = 6.1 Hz, 3H), 0.67 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.41, 155.99, 138.53, 132.70, 131.89, 130.14, 129.93, 129.70(2), 128.15(2), 120.37, 113.59, 77.37, 77.16, 76.95, 75.38, 28.91, 18.63, 9.31. IR (thin film) 3020, 2975, 2361, 1776, 1664 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{17}H_{18}O_2^+[M+H]^+$ 255.1380 found 255.1379; $[\alpha]_D^{23}$ = -43.6 (c = 1.29, $CHCl_3$)

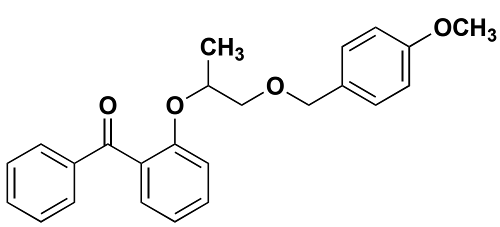


(38) 4-(2-((3-methylbutan-2-yl)oxy)benzoyl)benzonitrile was synthesized according to general procedure B, 1-bromo-2-((3-methylbutan-2-yl)oxy)benzene (1.96 g, 8.06 mmol) with anhydrous THF (56 mL), n-BuLi (1.7 M, 10.48 mmol, 6.16 mL), para-cyano Weinreb (1.89 g, 9.67 mmol) with anhydrous THF (23 mL) were used. The crude product was purified by flash column chromatography (30:70, EtOAc:hexanes) affording ketone **38** as a light yellow oil (1.37 g, 58%): ^1H NMR (400 MHz, Chloroform-*d*) δ 7.85

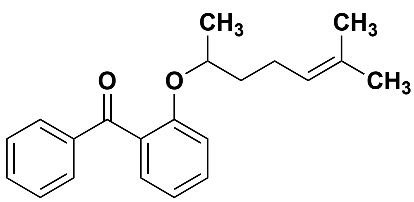
(d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.54 – 7.43 (m, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H), 4.17 (dt, 1H), 1.61 – 1.51 (m, 1H), 1.02 (d, J = 6.2 Hz, 3H), 0.65 – 0.55 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.00, 156.31, 142.32, 133.17, 132.11(2), 130.58, 129.81(2), 128.59, 120.65, 118.41, 115.59, 113.19, 79.05, 33.36, 17.59, 17.51, 15.26.; IR (thin film) 3046, 2971 1774 cm^{-1}; AMM (ESI) *m/z* calcd for $C19H19NO2^{+}[M-H]^{-}$ 293.1416, found 293.1809.



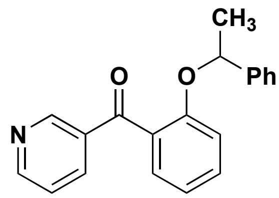
(39) (2-(1-cyclopropylethoxy)phenyl)(phenyl)methanone was synthesized according to general procedure A, (2-hydroxyphenyl)(phenyl)methanone (0.500 g, 2.52 mmol), 1-cyclopropylethan-1-ol (0.271 mL, 2.77 mmol), triphenylphosphine (0.860 g, 3.28 mmol), diisopropyl azodicarboxylate (0.644 mL, 3.28 mmol), and anhydrous THF (25 mL) were used. The crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording ketone **39** as a pale yellow oil (0.495 g, 74%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (dd, J = 8.3, 1.4 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.41 (m, 4H), 7.06 (td, J = 7.5, 1.0 Hz, 1H), 6.98 (d, J = 9.0 Hz, 1H), 3.89 (p, J = 6.2 Hz, 1H), 1.16 (d, J = 6.1 Hz, 3H), 0.79 (tdt, J = 8.2, 6.7, 5.1 Hz, 1H), 0.34 (tdd, J = 8.6, 5.5, 4.2 Hz, 1H), 0.27 (dddd, J = 9.2, 7.9, 5.4, 4.3 Hz, 1H), 0.08 (dtd, J = 9.4, 5.2, 4.3 Hz, 1H), 0.05 – - 0.00 (m, 1H);^{13}C NMR (150 MHz, $CDCl_3$) δ 197.28, 155.96, 138.38, 132.70, 131.84, 130.48, 129.92, 129.73(2), 128.17, 120.79, 114.84, 78.00, 22.04, 19.28, 16.40, 3.11, 1.60; IR (thin film) 2978, 1659, 1596 cm^{-1} AMM (ESI) *m/z* calcd for $C18H18O2^{+}[M+H]^{+}$ 267.1380, found 267.1378.



(40) (2-((1-((4-methoxybenzyl)oxy)propan-2-yl)oxy)phenyl)(phenyl)methanone was synthesized according to general procedure A, 2-hydroxyphenyl)(phenyl)methanone (1.00 g, 5.04 mmol), 1-((4-methoxybenzyl)oxy)propan-2-ol (1.09 g, 5.55 mmol), triphenylphosphine (1.72 g, 6.55 mmol), diisopropyl azodicarboxylate (1.29 mL, 6.55 mmol), and anhydrous THF (51 mL) were used. The crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording ketone **40** as a pale yellow oil (1.73 g, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.9 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (tt, *J* = 9.8, 6.8 Hz, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.07 – 6.97 (m, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.49 (h, *J* = 6.1 Hz, 1H), 4.27 (d, *J* = 2.0 Hz, 2H), 3.78 (s, 3H), 3.32 (dd, *J* = 10.2, 5.7 Hz, 1H), 3.23 (dd, *J* = 10.2, 4.9 Hz, 1H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.05, 159.20, 155.79, 138.33, 132.75, 131.88, 130.28, 130.10, 129.79, 129.73(2), 129.23(2), 128.17(2), 120.81, 114.05, 113.77(2), 77.48, 77.16, 76.84, 74.04, 73.04, 72.87, 55.33, 16.78; IR (thin film) 2923, 1663, 1597 cm^{-1}. AMM (ESI) *m/z* calcd for C24H24O4^{+}[M+H]$^{+}$ 377.1748, found 377.1731.

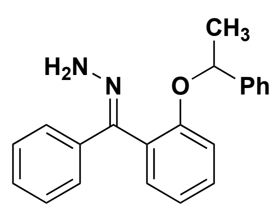


(41) (2-((6-methylhept-5-en-2-yl)oxy)phenyl)(phenyl)methanone was synthesized according to general procedure A, (2-hydroxyphenyl)(phenyl)methanone (1.00 g, 5.04 mmol), 6-methylhept-5-en-2-ol (0.712 g, 5.55 mmol), triphenylphosphine (1.72 g, 6.55 mmol), diisopropyl azodicarboxylate (1.29 mL, 6.55 mmol), and anhydrous THF (51 mL) were used. The crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording ketone **41** as a pale yellow oil (1.13 g, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.56 – 7.49 (m, 1H), 7.44 – 7.37 (m, 4H), 7.01 (td, *J* = 7.5, 0.9 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.95 (t, *J* = 7.2 Hz, 1H), 4.31 (h, *J* = 6.0 Hz, 1H), 1.79 (dt, *J* = 7.7, 7.7 Hz, 2H), 1.64 (s, 3H), 1.46 (s, 3H), 1.45 – 1.39 (m, 1H), 1.39 – 1.29 (m, 1H), 1.09 (d, *J* = 6.0 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 197.38, 155.95, 138.54, 132.73, 132.17, 131.88, 130.15, 129.92, 129.71(2), 128.18(2), 123.75, 120.36, 113.48, 77.48, 77.16, 76.84, 73.56, 36.25, 25.80, 23.71, 19.16, 17.73; IR (thin film) 2970, 1661, 1595 cm^{-1} AMM (ESI) *m/z* calcd for C21H24O2^{+}[M+H]$^{+}$ 309.1849, found 309.1858.



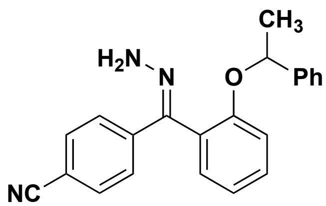
(42) (2-(1-phenylethoxy)phenyl)(pyridin-3-yl)methanone was synthesized according to general procedure B. 1-bromo-2-((3-methylbutan-2-yl)oxy)benzene (0.500 g, 1.80 mmol) with anhydrous THF (6.7 mL), n-BuLi (2.28 M, 2.34 mmol, 1.03 mL), *N*-methoxy-*N*-methylnicotinamide (0.359 g, 2.16 mmol) with anhydrous THF (2.7 mL) were used. The crude product was purified by flash column chromatography (50:50, EtOAc:hexanes) affording ketone **42** as a yellow oil (0.221 g, 41%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 1.6 Hz, 1H), 8.76 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.13 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.49 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.45 – 7.31 (m, 2H), 7.30 – 7.19 (m, 4H), 7.13 – 7.07 (m, 2H), 7.02 (td, *J* = 7.5, 0.9 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 5.22 (q, *J* = 6.4 Hz, 1H), 1.25 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.54, 156.04, 152.79, 151.07, 142.28, 136.33, 134.15, 132.87, 130.19, 128.67(2), 128.42, 127.68, 125.29(2), 123.20, 120.97, 114.07, 77.03, 23.84; IR (thin film) 3032, 2978, 1663, 1596, 1301 cm^{-1}; AMM (ESI) *m/z* calcd for C20H19N3O$^+$[M+H]$^+$ 304.1332, found 304.1331.

Hydrazone Substrates

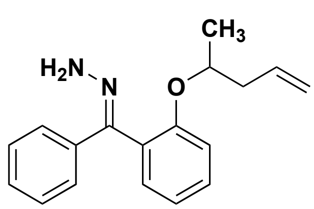


(15) Phenyl(2-(1-phenylethoxy)phenyl)methylene)hydrazine was synthesized according to general procedure C, phenyl(2-(1-phenylethoxy)phenyl)methanone (0.600 g, 1.98 mmol), hydrazine (0.623 mL, 19.84 mmol), glacial acetic acid (0.230 mL, 3.97 mmol) with anhydrous EtOH (6.6 mL) were used. After workup, the mixture was purified by flash column chromatography (30:70, EtOAc:hexanes) affording hydrazone **15** as a yellow oil (0.478 g, 76%): Note: due to restricted rotation and the mix of isomers many of the ^{1}H peaks are broadened, see attached spectra ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 –

7.41 (m, 2H), 7.37 – 7.17 (m, 8H), 7.17 – 7.06 (m, 2H), 7.06 – 6.95 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 5.45 – 5.14 (m, 2H), 1.37 (s, 3H); IR (thin film) 3015, 2997, 2361, 2339 cm^{-1}; AMM (ESI) *m/z* calcd for C21H20N2O$^+$[M+H]$^+$ 317.1649, found 317.1651; $[\alpha]_D^{22}$ = +48.0 (c = 1.9, $CHCl_3$)

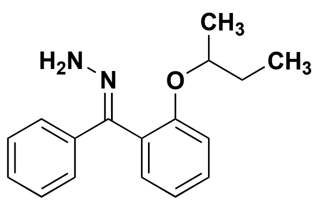


(1) 4-(hydrazineylidene(2-(1-phenylethoxy)phenyl)methyl)benzonitrile was synthesized according to general procedure C, 4-(2-(1-phenylethoxy)benzoyl)benzonitrile (0.423 g, 1.29 mmol), hydrazine (0.324 mL, 10.32 mmol), glacial acetic acid (0.148 mL, 2.58 mmol) with anhydrous EtOH (4.3 mL) were used. After workup hydrazone **1** was afforded as a mix of two isomers and a light yellow oil (0.348 g, 87%): Note: due to restricted rotation and the mix of isomers many of the ^{1}H peaks are broadened, see attached spectra. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.47 (m, 3H), 7.37 – 7.17 (m, 5H), 7.17 – 6.97 (m, 3H), 6.97 – 6.81 (m, 1H), 5.80 – 5.53 (m, 2H), 5.36 – 5.16 (m, 1H), 3.70 (qd, *J* = 7.0, 0.9 Hz, 1H), 1.60 – 1.40 (m, 2H), 1.40 – 1.28 (m, 1H), 1.24 (h, *J* = 7.2 Hz, 2H); IR (thin film) 3417, 2977, 2223 cm^{-1}; TLC (40:60, EtOAc:hexanes) R_F = 0.85. AMM (ESI) *m/z* calcd for C22H19NO3$^+$[M+H]$^+$ 342.1601, found 342.1603; $[\alpha]_D^{22}$ = +65.7 (c = 1.2, $CHCl_3$)

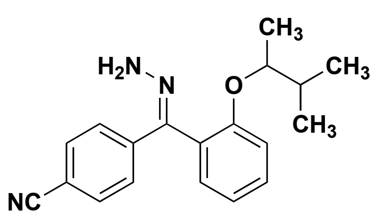


(2) ((2-(pent-4-en-2-yloxy)phenyl)(phenyl)methylene)hydrazine was synthesized according to general procedure C, (2-(pent-4-en-2-yloxy)phenyl)(phenyl)methanone (0.689 g, 2.59 mmol), hydrazine (0.651 mL, 20.72 mmol), glacial acetic acid (0.296 mL, 5.18 mmol), and anhydrous EtOH (8.6 mL) were used. After workup, hydrazone **2** was afforded as a light yellow oil (0.629, 87%) and was carried through to the insertion.

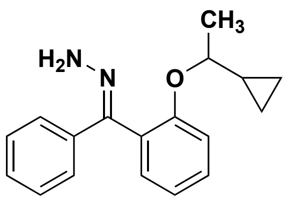
Note: due to restricted rotation and the mix of isomers many of the ^{1}H peaks are broadened, see attached spectra: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H), 7.35 – 7.23 (m, 3H), 7.19 – 7.11 (m, 1H), 7.11 – 7.03 (m, 2H), 5.44 (s, 2H), 5.13 – 4.82 (m, 2H), 4.40 (s, 1H), 2.47 – 2.07 (m, 2H), 1.38 – 1.00 (m, 3H); IR (thin film) 3404, 3060, 2975, 1641, 1596 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{18}H_{20}N_2O^+[M+H]^+$ 281.1649, found 281.1649.



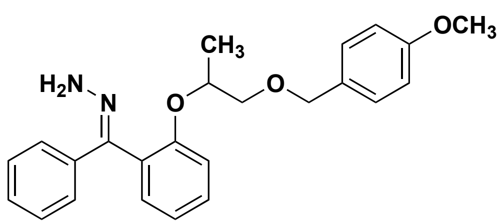
(14) ((2-(*sec*-butoxy)phenyl)(phenyl)methylene)hydrazine was synthesized according to general procedure C, (2-(sec-butoxy)phenyl)(phenyl)methanone (0.143 g, 0.563 mmol), hydrazine (0.179 mL, 5.63 mmol), glacial acetic acid (0.064 g, 1.13 mmol), and anhydrous EtOH (1.88 mL) were used. After workup, the mixture was purified by flash column chromatography (20:80, EtOAc:hexanes) affording hydrazone **14** as a yellow oil (0.116 g, 77%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 1H), 7.29 – 7.20 (m, 3H), 7.13 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.08 – 6.99 (m, 2H), 5.45 (s, 2H), 4.28 (h, *J* = 6.1 Hz, 1H), 1.72 – 1.35 (m, 2H), 1.35 – 0.97 (m, 4H), 0.97 – 0.55 (m, 3H); IR (thin film) 3023, 2997, 2363, 2337 cm^{-1} AMM (ESI) *m/z* calcd for $C_{19}H_{21}N_3O^+[M+H]^+$ 308.1758, found 308.1760. $[\alpha]_D^{23}$ = -10.2 (c = 0.53, $CHCl_3$)



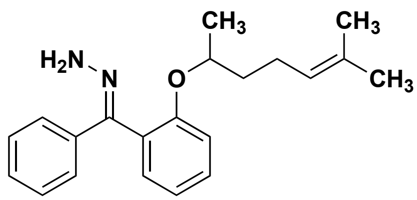
(18) 4-(hydrazineylidene(2-((3-methylbutan-2-yl-oxy)phenyl)methyl)benzonitrile was synthesized according to general procedure C, 4-(2-((3-methylbutan-2-yl)oxy)benzoyl)benzonitrile (1.37 g, 4.65 mmol), hydrazine (1.17 mL, 37.20 mmol), glacial acetic acid (0.532 g, 9.30 mmol), and anhydrous EtOH (15.5 mL) were used. After workup, the mixture was purified by flash column chromatography (50:50, EtOAc:hexanes) affording hydrazone **18** as an orange oil (0.455 g, 32%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 3H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.09 – 6.99 (m, 1H), 5.67 (s, 1H), 4.14 (dt, *J* = 14.7, 6.6 Hz, 1H), 1.25 (td, *J* = 6.4, 3.4 Hz, 1H), 1.21 – 1.09 (m, 1H), 1.00 (td, *J* = 7.3, 3.7 Hz, 2H), 0.89 – 0.58 (m, 4H); IR (thin film) 3021, 2998, 2325 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{19}H_{21}N_3O^+[M+H]^+$ 308.1758, found 308.1760.



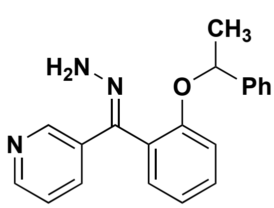
(17) ((2-(1-cyclopropylethoxy)phenyl)(phenyl)methylene)hydrazine was synthesized according to general procedure C, (2-(1-cyclopropylethoxy)phenyl)(phenyl)methanone (0.363g, 1.36 mmol), hydrazine (0.342 mL, 10.88 mmol), glacial acetic acid (0.156 mL, 2.72 mmol), and anhydrous EtOH (4.5 mL) were used. After workup, the mixture was purified by flash column chromatography (40:60 EtOAc:Hexanes) affording hydrazone **17** as a yellow oil (0.236g, 62%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 1H), 7.09 – 7.02 (m, 1H), 3.72 (qd, *J* = 7.0, 1.5 Hz, 1H), 1.43 (s, 1H), 1.29 – 1.20 (m, 3H), 0.51 – 0.07 (m, 1H); IR (thin film) 3400, 2978, 1724, 1484 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{18}H_{20}N_2O^+[M+H]^+$ 281.1649, found 281.1649.



(19) (2-((1-((4-methoxybenzyl)oxy)propan-2-yl)oxy)phenyl)(phenyl)methylene)hydrazine was synthesized according to general procedure C, (2-((1-((4-methoxybenzyl)oxy)propan-2-yl)oxy)phenyl)(phenyl)methanone (0.181 g, 0.481 mmol), hydrazine (0.121 mL, 3.85 mmol), glacial acetic acid (0.055 mL, 0.962 mmol), and anhydrous EtOH (1.6 mL) were used. After workup, the mixture was purified by flash column chromatography (80:20 EtOAc:Hexanes) affording hydrazone **19** as a clear oil (0.179 g, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.43 – 7.35 (m, 1H), 7.31 – 7.22 (m, 3H), 7.21 – 7.04 (m, 5H), 6.91 – 6.76 (m, 2H), 5.43 (s, 2H), 4.56 (q, *J* = 5.8 Hz, 1H), 4.48 – 4.21 (m, 2H), 3.79 (s, 3H), 3.43 (s, 2H), 1.30 – 1.06 (m, 4H); IR (thin film) 3406, 3000, 1511; AMM (ESI) *m/z* calcd for $C_{24}H_{26}N_2O3^+$[M+H]$^+$ 391.2016, found 391.2005.

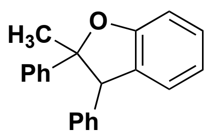


(20) ((2-((6-methylhept-5-en-2-yl)oxy)phenyl)(phenyl)methylene)hydrazine was synthesized according to general procedure C, (2-((6-methylhept-5-en-2-yl)oxy)phenyl)(phenyl)methanone (0.500 g, 1.62 mmol), hydrazine (0.407 mL, 13.0 mmol), glacial acetic acid (0.185 mL, 3.24 mmol), and anhydrous EtOH (5.4 mL) were used. After workup, the mixture was purified by flash column chromatography (70:30 EtOAc:Hexanes) affording hydrazone **20** as a clear oil (0.173 g, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.43 – 7.36 (m, 1H), 7.30 – 7.22 (m, 3H), 7.14 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.08 – 6.99 (m, 2H), 5.43 (s, 2H), 4.97 (s, 1H), 4.35 (h, *J* = 6.1 Hz, 1H), 1.97 (s, 1H), 1.65 (s, 4H), 1.56 (s, 2H), 1.49 – 1.36 (m, 3H), 1.24 – 1.03 (m, 3H); IR (thin film) 3404, 2968, 1595, 1482; AMM (ESI) *m/z* calcd for $C_{21}H_{26}N_2O^+$[M+H]$^+$ 323.2118, found 323.2113.



(16) 3-(hydrazineylidene(2-(1-phenylethoxy)phenyl)methyl)pyridine was synthesized according to general procedure C, **(**2-(1-phenylethoxy)phenyl)(pyridin-3-yl)methanone (0.200 g, 0.659 mmol), hydrazine (0.180 mL, 5.27 mmol), glacial acetic acid (0.075 mL, 1.32 mmol), and anhydrous EtOH (2.2 mL) were used. After workup, the mixture was purified by flash column chromatography (70:30 EtOAc:Hexanes) affording hydrazone **16** as a clear oil (0.173 g, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.50 (d, *J* = 4.8 Hz, 1H), 7.82 (s, 1H), 7.47 – 7.08 (m, 8H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.60 (s, 2H), 5.27 (s, 1H), 1.70 – 1.21 (m, 3H); IR (thin film) 3397, 2977, 1663, 1597; AMM (ESI) *m/z* calcd for $C_{20}H_{19}N_3O^+[M+H]^+$ 318.1601, found 318.1606.

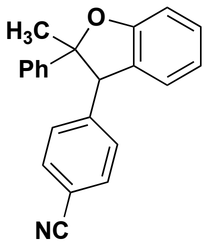
Insertion Substrates



(22) 2-methyl-2,3,-diphenyl-2,3-dihydrobenzofuran was synthesized according to general procedure D, phenyl(2-(1-phenylethoxy)phenyl)methylene)hydrazine (0.035 g, 0.111), manganese(IV) dioxide (0.076 g, 0.885 mmol), $Rh_2(mes)_4$ (0.00095 g, 0.001 mmol) with anhydrous DCM (7.37 mL). After filtration, the crude product was purified by flash column chromatography (10:90, EtOAc:hexanes) affording dihydrobenzofuran **22** as a light yellow oil (0.027 g, 86%):

All catalysts screened (Rh_2(R-PTAD)$_4$, Rh_2(S-PTAD)$_4$, $Rh_2(mes)_4$) with both racemic and enantiopure starting material yielded >95:5 dr of the same, single diastereomer. The racemic standard was never able to be separated on a chiral HPLC to obtain enantiomeric ratios.

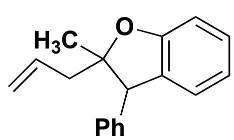
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.7 Hz, 1H), 7.06 – 6.92 (m, 10H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.75 – 6.66 (m, 2H), 4.64 (s, 1H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.37, 142.17, 139.85, 130.97, 129.34(2), 128.88, 128.54, 127.87(2), 127.42(2), 126.74, 126.54, 126.05(2), 121.07, 109.79, 93.50, 77.48, 77.16, 76.84, 61.11, 29.40; IR (thin film) 3028, 2967, 1216 cm^{-1}; AMM (ESI) *m/z* calcd for C21H18O$^+[M+H]^+$ 287.1473, found 287.1471. $[\alpha]_D^{23}$ = -3.47 (c = 1.4, $CHCl_3$).



(5) 4-(2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-yl)benzonitrile was synthesized according to general procedure D, 4-(hydrazineylidene(2-(1-phenylethoxy)phenyl)methyl)benzonitrile (0.450 g, 1.32 mmol), manganese(IV) dioxide (0.908 g, 10.56 mol), Rh_2(R-PTAD)$_4$ (0.021 g, 0.0132 mmol) with anhydrous DCM (88 mL). After filtration, the crude product was purified by flash column chromatography (20:80, EtOAc:hexanes) affording dihydrobenzofuran **5** as a light yellow oil (0.336 g, 82%):

All catalysts screened (Rh_2(R-PTAD)$_4$, Rh_2(S-PTAD)$_4$, Rh_2(mes)$_4$) with both racemic and enantiopure starting material yielded >95:5 dr of the same, single diastereomer. The corresponding enantiomeric ratios can be found in the main text, Table 1.

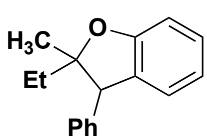
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 3H), 7.08 – 7.00 (m, 6H), 6.94 (d, J = 7.3 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 7.8 Hz, 2H), 4.64 (s, 1H), 1.93 (s, 3H);^{13}C NMR (150 MHz, $CDCl_3$) δ 159.13, 145.99, 141.48, 131.67(2), 129.88(2), 129.84, 129.50, 127.81(2), 127.03, 125.92, 125.79(2), 121.41, 118.93, 110.44, 110.30, 93.38, 60.81, 29.40; IR (thin film) 2974, 2226, 1596, 1497 cm^{-1}; TLC (10:90, EtOAc:hexanes) R_F = 0.9. AMM (ESI) *m/z* calcd for C22H17NO$^+$[M+H]$^+$ 312.1383, found 312.1376. $[\alpha]_D^{23}$ = -5.62 (c = 0.69, $CHCl_3$).



(6) 2-allyl-2-methyl-3-phenyl-2,3-dihydrobenzofuran was synthesized according to general procedure D, ((2-(pent-4-en-2-yloxy)phenyl)(phenyl)methylene)hydrazine (0.550 g, 1.96 mmol), manganese(IV) dioxide (1.35 g, 15.68 mmol), Rh_2(R-PTAD)$_4$ (0.031 g, 0.0196 mmol), and anhydrous CH_2Cl_2 (130.7 mL) were used. After filtration, the mixture was purified by flash column chromatography (10:90, EtOAC:hexanes) affording dihydrobenzofuran **6** as a light yellow oil (0.338 g, 77%):

NMR reported is with Rh_2(*R*-PTAD)$_4$ and racemic SM yielding a 47:53 dr (trans:cis). The peaks reported are the major diastereomer of the mixture of two diastereomers, that couldn't be separate by flash column chromatography or prep-TLC. The singlets at 4.49 and 4.41 are the double benzylic protons at the former carbene center, and used to determine the dr.

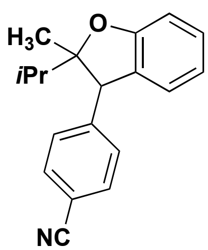
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 7H), 7.18 (dt, *J* = 7.9, 4.0 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.09 – 6.97 (m, 4H), 6.91 – 6.81 (m, 4H), 6.01 – 5.90 (m, 1H, minor diastereomer), 5.80 – 5.70 (m, 1H, major diastereomer), 5.25 – 5.18 (m, 2H, minor diastereomer), 5.01 (d, *J* = 10.2 Hz, 1H, major diastereomer), 4.89 (dd, *J* = 17.0, 2.0 Hz, 1H, major diastereomer), 4.49 (s, 1H, minor diastereomer), 4.41 (s, 1H, major diastereomer), 2.63 – 2.53 (m, 2H, minor diastereomer), 2.23 (dd, *J* = 14.4, 6.2 Hz, 1H, major diastereomer), 1.67 (dd, *J* = 14.3, 8.2 Hz, 1H, major diastereomer), 1.54 (s, 4H, major diastereomer), 0.96 (s, 3H, minor diastereomer); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.05, 139.16, 133.85, 130.60, 129.43, 128.76, 128.53, 127.39, 126.02, 120.65, 118.23, 110.14, 109.86, 91.00, 77.48, 77.16, 76.84, 59.12, 41.41, 25.94, 0.15; IR (thin film) 3028, 2976, 1640, 1596 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{18}H_{18}O_2^+$[M+H]$^+$ 251.1431 found 251.1429.



(21) 2-ethyl-2-methyl-3-phenyl-2,3-dihydrobenzofuran was synthesized according to general procedure D, ((2-(*sec*-butoxy)phenyl)(phenyl)methylene)hydrazine (0.025 g, 0.093 mmol), manganese(IV) dioxide (0.064 g, 0.744 mmol), Rh_2(S-PTAD)$_4$ (0.0015 g, 0.00097 mmol), and anhydrous CH_2Cl_2 (6.2 mL) were used. The filtered mixtures was purified by flash column chromatography (05:95, EtOAc:hexanes) affording insertion **21** as a clear oil (0.020 g, 91%):

NMR reported is with a catalyst yielding a 46:54 dr. The peaks reported are a mixture of two diastereomers, that couldn't be separate by flash column chromatography or prep-TLC. The singlets at 4.42 and 4.37 are the double benzylic protons at the former carbene center, and used to determine the dr.

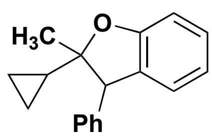
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (ddt, *J* = 14.1, 12.5, 4.6 Hz, 7H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.08 (ddd, *J* = 7.7, 6.1, 1.6 Hz, 4H), 7.02 (dd, *J* = 7.4, 6.0 Hz, 3H), 6.89 – 6.80 (m, 4H), 4.42 (s, 1H), 4.37 (s, 1H), 1.95 – 1.79 (m, 2H), 1.53 (s, 4H), 1.46 (dt, *J* = 14.6, 7.3 Hz, 1H), 1.06 (t, *J* = 7.4 Hz, 3H), 1.03 – 0.97 (m, 1H), 0.93 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.38, 159.15, 140.29, 139.59, 130.99, 130.61, 129.40, 129.36, 128.67, 128.65, 128.42, 128.37, 127.17, 127.11, 126.13, 126.05, 120.47, 120.42, 110.02, 109.78, 92.43, 91.99, 77.48, 77.36, 77.16, 76.84, 59.21, 56.32, 34.47, 29.85, 29.44, 25.08, 22.13, 8.47, 8.33; IR (thin film) 2973, 1597, 1478 cm^{-1};AMM (ESI) *m/z* calcd for $C_{17}H_{18}O_2^+$[M+H]$^+$ 239.1431 found 239.1426.



(25) 4-(2-isopropyl-2-methyl-2,3-dihydrobenzofuran-3-yl)benzonitrile was synthesized according to general procedure D, 4-(hydrazineylidene(2-((3-methylbutan-2-yl-oxy)phenyl)methyl)benzonitrile (0.030 g, 0.098 mmol), manganese(IV) dioxide (0.067 g, 0.781 mmol), Rh_2(mes)$_4$ (0.00084 g, 0.00098 mmol), and anhydrous CH_2Cl_2 (6.5 mL) were used. After filtration, the mixtures was purified by preparative TLC (10:90 EtOAC:Hexanes, SiliaPlate™ Preparative, 1,000 μm, 20 x 20 cm, with F254 indicator) affording dihydrobenzofuran **25** as a light yellow oil (0.019 g, 70%):

NMR reported is with the Rh_2(mes)$_4$ catalyst yielding a 81:19 dr. The peaks reported are a mixture of two diastereomers that couldn't be separate by flash column chromatography or prep-TLC; with the major diastereomer peaks reported. The singlets at 4.54 and 4.13 are the double benzylic protons at the former carbene center, for each the major and minor diastereomer respectively.

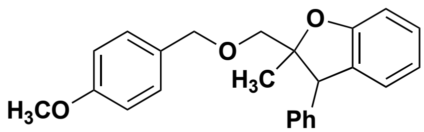
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.54 – 7.52 (m, 1H), 7.23 – 7.18 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.90 (m, 1H), 6.85 (ddd, *J* = 9.1, 7.6, 1.4 Hz, 2H), 4.54 (s, 1H), 2.08 (p, *J* = 6.8 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 4H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.44, 146.48, 132.43, 132.06(2), 130.24(2), 129.32, 129.16, 125.82, 121.03, 110.72, 109.76, 94.61, 77.48, 77.36, 77.16, 76.84, 31.73, 19.99, 18.31, 17.61; IR (thin film) 2965, 2228, 1597, 1480 cm^{-1} ;AMM (ESI) *m/z* calcd for C19H19NO^{+}[M+H]$^{+}$ 278.1540 found 278.1539.



(24) 2-cyclopropyl-2-methyl-3-phenyl-2,3-dihydrobenzofuran was synthesized according to general procedure D, ((2-(1-cyclopropylethoxy)phenyl)(phenyl)methylene) hydrazine (0.025 g, 0.089 mmol), manganese(IV) dioxide (0.061 g, 0.712 mmol), $Rh_2(mes)_4$ (0.00080 g, 0.00089 mmol), and anhydrous CH_2Cl_2 (5.9 mL) were used. After filtration, the mixtures was purified by flash column chromatography (05:95 EtOAC:Hexanes) affording dihydrobenzofuran **24** as a clear oil (0.099 g, 44%):

NMR reported is with the Rh_2(*R*-PTAD)$_4$ catalyst yielding a 15:85 dr. The peaks reported are a mixture of two diastereomers, that couldn't be separate by flash column chromatography or prep-TLC. The singlets at 4.64 and 4.52 are the double benzylic protons at the former carbene center, for each the minor and major diastereomer respectively with the peaks for the major diastereomer reported below.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 8H), 7.23 – 7.12 (m, 8H), 7.07 – 7.00 (m, 2H), 6.89 – 6.83 (m, 3H), 6.83 – 6.73 (m, 3H), 4.64 (s, 0.32H), 4.52 (s, 1H), 1.53 (s, 3H), 1.34 – 1.22 (m, 1H), 0.91 – 0.86 (m, 4H), 0.59 – 0.47 (m, 4H), 0.39 – 0.27 (m, 5H), 0.19 – 0.06 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.80, 139.70, 130.76, 129.71, 129.43, 128.68, 128.43, 128.18, 127.09, 125.94, 120.45, 109.43, 90.66, 59.49, 26.70, 17.55, 2.35, 0.94; IR (thin film) 3458, 3009, 1477 cm^{-1}; AMM (ESI) *m/z* calcd for C18H18O^+[M-H]$^-$ 248.9616 found 248.9616.

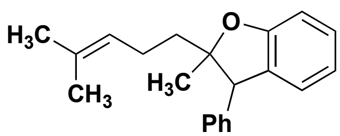


(26) 2-(((4-methoxybenzyl)oxy)methyl)-2-methyl-3-phenyl-2,3-dihydrobenzofuran was synthesized according to general procedure D, (2-((1-((4-methoxybenzyl)oxy)propan-2-yl)oxy)phenyl)(phenyl)methylene)hydrazine (0.025 g, 0.064 mmol), manganese(IV) dioxide (0.044 g, 0.512 mmol), Rh_2(*R*-PTAD)$_4$ (0.001 g, 0.00064 mmol), and anhydrous CH_2Cl_2 (4.3 mL) were used. After filtration, the mixtures was purified by flash column chromatography (20:80 EtOAC:Hexanes) affording dihydrobenzofuran **26** as a clear oil (0.019 g, 84%, 44:56 dr):

NMR reported is with the Rh_2(*R*-PTAD)$_4$ catalyst yielding a 44:56 dr. The peaks reported are a mixture of two diastereomers, that couldn't be separate by flash column chromatography or prep-TLC. The singlets at 4.67 and 4.39 are the double benzylic protons at the former carbene center, for each the minor and major diastereomer respectively with the peaks for the major and minor diastereomers reported below (the aryl protons are overlapping and therefore can't be assigned clearly to the major or minor diastereomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 8H), 7.22 – 7.16 (m, 2H), 7.10 – 7.00 (m, 7H), 6.92 – 6.84 (m, 5H), 6.82 – 6.77 (m, 2H), 4.67 (s, 1H, minor diastereomer), 4.64 – 4.54 (m, 2H, minor diastereomer), 4.39 (s, 1H, major diastereomer), 4.22 (d, *J* = 11.6 Hz, 1H, major diastereomer), 4.05 (d, *J* = 11.6 Hz, 1H, major diastereomer), 3.81 (s, 2H, minor diastereomer), 3.78 (s, 3H, major diastereomer), 3.59 (s, 2H, minor diastereomer), 3.26 (d, *J* = 10.0 Hz, 1H, major diastereomer), 3.00 (d, *J* = 10.0 Hz, 1H, major diastereomer), 1.62 (s, 3H, major diastereomer), 0.96 (s, 2H, minor diastereomer).

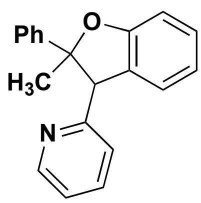
^{13}C NMR (100 MHz, $CDCl_3$) δ 59.36, 159.28, 159.13, 159.08, 139.84, 138.96, 130.48, 130.45, 130.37, 130.17, 129.49, 129.48, 129.36, 129.13, 128.78, 128.63, 128.40, 128.30, 127.28, 127.14, 126.21, 125.88, 120.80, 120.75, 113.92, 113.68, 110.15, 109.94, 91.35, 90.49, 77.48, 77.16, 76.84, 75.04, 73.37, 73.23, 72.98, 57.72, 55.43, 55.38, 53.38, 24.67, 20.58, 0.14.; IR (thin film) 3003, 1476, 1459 cm^{-1}; AMM (ESI) *m/z* calcd for C24H24O3Na $[M+Na]^+$ 383.1623 found 383.1619.



(27) 2-methyl-2-(4-methylpent-3-en-1-yl)-3-phenyl-2,3-dihydrobenzofuran was synthesized according to general procedure D, ((2-((6-methylhept-5-en-2-yl)oxy)phenyl)(phenyl)methylene)hydrazine (0.025 g, 0.078 mmol), manganese(IV) dioxide (0.053 g, 0.620 mmol), Rh_2(*S*-PTAD)$_4$ (0.0001 g, 0.0078 mmol), and anhydrous CH_2Cl_2 (5.2 mL) were used. After filtration, the mixtures was purified by flash column chromatography (10:90 EtOAC:Hexanes) affording dihydrobenzofuran **27** as a clear oil (0.016 g, 68%):

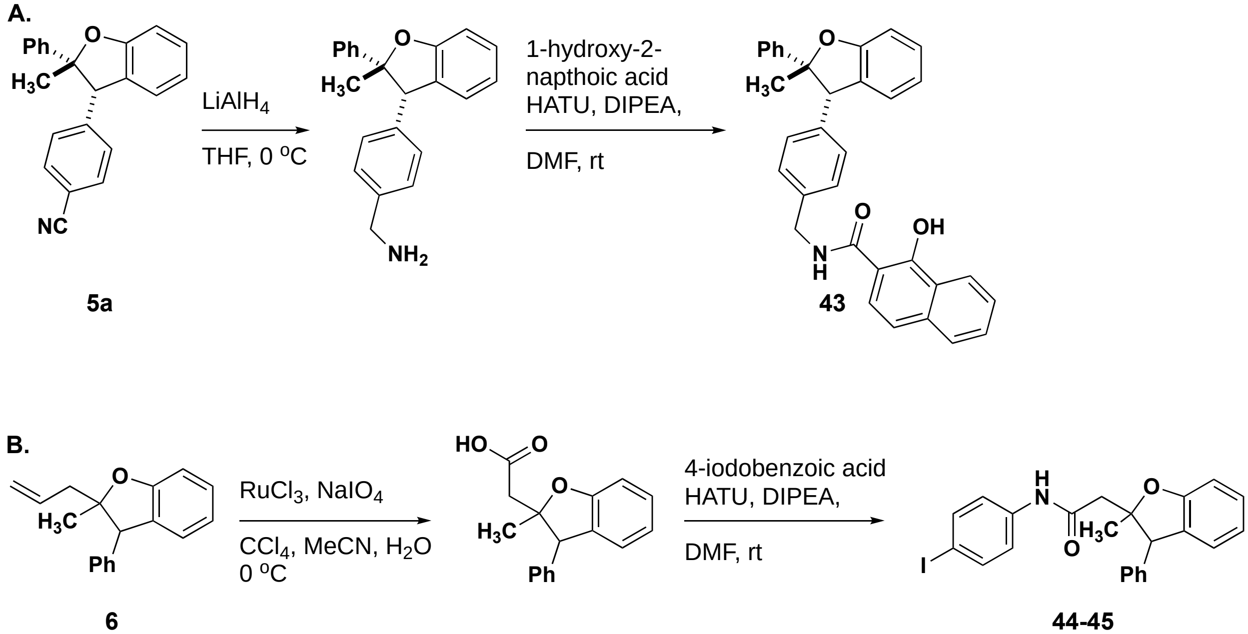
NMR reported is with the Rh_2(*S*-PTAD)$_4$ catalyst yielding a 39:61 dr. The peaks reported are a mixture of two diastereomers, that couldn't be separate by flash column chromatography or prep-TLC. The singlets at 4.45 and 4.37 are the double benzylic protons at the former carbene center, for each the minor and major diastereomer respectively with the peaks for the major diastereomer reported below.

^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.34 – 7.22 (m, 6H), 7.21 – 7.15 (m, 2H), 7.09 (ddt, *J* = 9.5, 7.8, 1.6 Hz, 4H), 7.03 (ddd, *J* = 7.6, 2.9, 1.5 Hz, 2H), 6.85 (tt, *J* = 8.0, 2.5 Hz, 4H), 5.15 (t, *J* = 7.1 Hz, 1H, minor diastereomer), 4.85 (t, *J* = 7.1 Hz, 1H, major diastereomer), 4.45 (s, 1H, minor diastereomer), 4.37 (s, 1H, major diastereomer), 2.29 – 2.15 (m, 2H, minor diastereomer), 2.12 – 1.99 (m, 1H), 1.96 – 1.78 (m, 3H), 1.69 (d, *J* = 1.5 Hz, 2H), 1.62 (d, *J* = 1.3 Hz, 1H), 1.57 (s, 6H, major diastereomer), 1.55 (s, 1H), 1.47 (s, 4H), 1.09 – 0.98 (m, 1H), 0.95 (s, 2H, minor diastereomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.36, 159.11, 140.10, 139.39, 132.10, 131.53, 131.00, 130.73, 130.50, 129.41(2), 129.36(2), 128.69, 128.64, 128.45(2), 128.40(2), 127.21, 127.16, 126.13, 126.01, 124.35, 124.04, 120.48, 120.45, 110.04, 109.84, 92.00, 91.70, 77.48, 77.16, 76.84, 59.35, 56.89, 41.88, 36.57, 25.84, 25.75, 22.81, 22.73, 17.83, 17.67, 0.15; IR (thin film) 3028, 2970, 1597, 1478 cm^{-1}; AMM (ESI) *m/z* calcd for $C21H24O^+[M+H]^+$ 293.1900 found 293.1903.

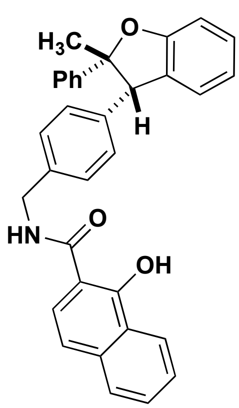


(23) 2-(2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-yl)pyridine was synthesized according to general procedure D, 3-(hydrazineylidene(2-(1-phenylethoxy)phenyl)methyl)pyridine (0.015 g, 0.047 mmol), manganese(IV) dioxide (0.033 g, 0.328 mol), Rh_2(R-PTAD)$_4$ (0.00073 g, 0.00047 mmol) with anhydrous DCM (3.1 mL). After filtration, the crude product was purified by flash column chromatography (40:60, EtOAc:hexanes) affording dihydrobenzofuran **23** as a light yellow oil (0.013 g, 96%): All catalysts screened (Rh_2(R-PTAD)$_4$, Rh_2(S-PTAD)$_4$, Rh_2(mes)$_4$) yielded >95:5 dr of the same, single diastereomer. ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.21 (m, 1H), 8.18 (s, 1H), 7.33 – 7.24 (m, 2H), 7.12 – 6.99 (m, 6H), 6.92 (dtd, *J* = 15.6, 7.4, 1.3 Hz, 2H), 6.88 – 6.77 (m, 2H), 4.64 (s, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.26, 150.16, 148.24, 141.65, 136.43, 136.00, 129.96, 129.36, 127.89(2), 126.96, 125.93(2), 125.86, 122.96, 121.37, 110.15, 93.33, 58.27, 29.25; IR (thin film) 2985, 1738, 1372 cm^{-1}; AMM (ESI) *m/z* calcd for $C20H17NO^+[M+H]^+$ 287.1310 found 288.1380.

Crystal Structure Substrates

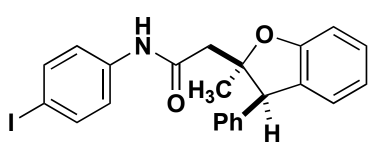


SI Figure 2. A. Synthesis of **33** from insertion product **5a** B. Synthesis of **34** and **35** from insertion product **6**.



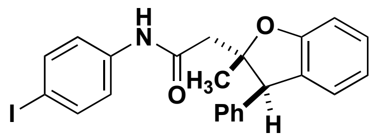
(43) 1-hydroxy-*N*-(4-((2R,3S)-2-methyl-2-phenyl-2,3-dihydrobenzofurna-3-yl)benzyl)-2-napthamide was synthesized over two steps. First, following a modified literature procedure[5], lithium aluminum hydride (0.228g, 6.00 mmol, 6.0 equiv) was added to a flame dried round bottom under Ar charged with THF (6.0 mL, 0.1M). The solution was cooled to 0 ^{o}C, then a solution of enantiopure **5a** (0.313g, 1.00 mmol, 1.0 equiv) in THF (10.0 mL, 0.1M) was added dropwise. The reaction was stirred for 12 hours while being allowed to warm to room temperature. The solution was cooled back down to 0 ^{o}C and 0.228 mL of H_2O then 0.228 mL of 15% NaOH(aq) then 0.684 mL of H_2O were added sequentially. The mixture was stirred at room temperature for 15 minutes, then dried over Mg_2SO_4, filtered, and concentrated to afford the primary amine **36** as a light yellow oil and a single diastereomer (0.267g, 85%, >95:5 dr). The compound wasn't purified forward and carried straight through to the next reaction.

Second, 1-hydroxy-2-napthoic acid (0.107g, 0.571 mmol, 1.2 equiv), HATU (0.221g, 0.571 mmol, 1.2 equiv), DIPEA (0.176 mL, 1.05 mmol, 2.2 equiv), and DMF (4.76 mL, 0.1M) were added to a flame dried round bottom under Ar and stirred for 10 minutes. Amine intermediate (0.150g, 0.476 mmol, 1.0 equiv) was added and the reaction was stirred overnight. The reaction was diluted in CH_2Cl_2 (10 mL), washed with brine (10 mL x 3), dried over Na_2SO_4, and concentrated. The mixture was purified by flash column chromatography (30:70 CH_2Cl_2:Hexanes) to yield a single diastereomer and single enantiomer of **43** as a white solid (0.113g, 49%). **43** was recrystallized from a mixture of CH_2Cl_2 and Hexanes to afford the crystal structure reported. mp 84-85 ^oC; 1H NMR (600 MHz, $CDCl_3$) δ 13.74 (s, 1H), 8.42 (d, *J* = 7.3 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.57 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.27 – 7.19 (m, 3H), 7.06 – 6.97 (m, 8H), 6.97 – 6.92 (m, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 2H), 6.38 (t, *J* = 5.7 Hz, 1H), 4.63 (s, 1H), 4.49 (d, *J* = 5.5 Hz, 2H), 1.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.32, 160.75, 159.09, 142.00, 139.75, 136.28, 135.77, 130.74, 129.65(2), 128.94, 128.86, 127.38, 127.34(2), 127.30(2), 127.28, 126.46, 125.90(2), 125.83, 125.67, 123.87, 120.98, 120.64, 118.14, 109.80, 106.43, 93.30, 60.54, 43.33, 29.31; IR (thin film) 3432, 3056, 2975, 1620, 1595 cm^{-1}; AMM (ESI) *m/z* calcd for $C33H27NO3^+[M+H]^+$ 485.1991, found 486.2060. $[\alpha]_D^{23}$ = +7.88 (c = 0.38, $CHCl_3$).



(44) Cis-N-(4-iodophenyl)-2-2-methyl-3-phenyl-2,3-dihydrobenzofuran-2-yl)acetamide was synthesized over two steps following the prep below. mp 130-132 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 6H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.00 – 6.92 (m, 2H), 4.48 (s, 1H), 2.52

(d, J = 14.9 Hz, 1H), 1.95 (d, J = 15.0 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.64, 157.71, 138.16, 138.01(2), 137.81, 129.76, 129.23(2), 129.21, 128.92(2), 128.00, 126.44, 121.95, 121.89(2), 110.27, 89.97, 87.33, 77.48, 77.16, 76.84, 59.39, 45.86, 25.84; IR (thin film) 3314, 2975, 1667, 1585 cm^{-1}; AMM (ESI) *m/z* calcd for $C_{23}H_{20}INO_2^+$[M+H]$^+$ 470.0612, found 470.0608. $[\alpha]_D^{23}$ = +13.7 (c = 0.18, $CHCl_3$).



(45) Trans-N-(4-iodophenyl)-2-2-methyl-3-phenyl-2,3-dihydrobenzofuran-2-yl)acetamide was synthesized over two steps following the prep below. mp 144-145 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.60 (d, J = 8.2 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.28 – 7.22 (m, 3H), 7.15 (d, J = 7.4 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 6.98 – 6.90 (m, 2H), 4.60 (s, 1H), 2.96 (d, J = 14.8 Hz, 1H), 2.85 (d, J = 14.9 Hz, 1H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.12, 157.76, 138.15, 138.04(2), 137.64, 129.77, 129.34(2), 129.14, 128.74(2), 127.76, 126.54, 121.95(2), 121.92, 110.12, 90.49, 87.57, 56.78, 49.10, 22.48; IR (thin film) 3269, 2926, 1704, 1597 cm^{-1};AMM (ESI) *m/z* calcd for $C_{23}H_{20}INO_2^+$[M+H]$^+$ 470.0612, found 470.0608. $[\alpha]_D^{23}$ = +23.1 (c = 0.17, $CHCl_3$).

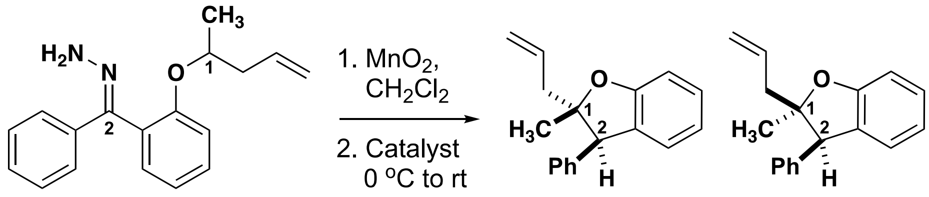
First following a literature procedure[6], (**6)** 2-allyl-2-methyl-3-phenyl-2,3-dihydrobenzofuran (0.250g, 0.998 mmol, 1.0 equiv) **(**derived from enantiopure starting material, and insertion catalyzed by Rh_2(*R*-PTAD)$_4$) was added to a solution of carbon tetrachloride (10 mL, 0.1M) in a round bottom. Then acetonitrile (10 mL, 0.1M) and H_2O (15 mL, 0.07M) were added sequentially. The mixture was cooled down to 0 ^oC then $NaIO_4$ (1.06g, 4.99 mmol, 5.0 equiv) was added. $RuCl_3$ (0.0207g, 0.0998 mmol, 0.1 equiv) was added portionwise, then the reaction was stirred overnight while allowing it to warm to room temperature. The reaction was quenched with 2M NaOH(aq) (5 mL) and extracted with CH_2Cl_2 (10 mL x 1). The aqueous layer was acidified with 1M HCl until a pH <1 was reached, then extracted with CH_2Cl_2 (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The mixture was purified by flash column chromatography (90:9.8:0.2 EtOAc:Hex:AcOH) affording carboxylic acid as a clear oil and mixture of diastereomers (0.119g, 44%, 85:15 dr trans:cis).

Second, carboxylic acid was added to a solution of HATU (0.170g, 0.448 mmol, 1.2 equiv), DIPEA (0.137 mL, 0.821 mmol, 2.2 equiv) in CH_2Cl_2 (0.1M). The reaction was stirred for 15 minutes, then 4-iodobenzoic acid (0.105g, 0.448 mmol, 1.2 equiv) was added. The reaction was stirred overnight, then diluted in CH_2Cl_2 and washed with brine (5 mL x 3). The organic layer was dried over Na_2SO_4 and concentrated to yield a mixture of diastereomers of amides **44** & **45** (yield = 29%). The mixture was purified and diastereomers separated by flash column chromatography (90:10 EtOAc:Hex) affording minor cis diastereomer **44** as a white solid (0.0085g, 5%) and major trans diastereomer **45** as a white solid (0.043, 25%). These enantiomerically pure diastereomers were then recrystallized in a mixture of CH_2Cl_2:Hexanes to afford the crystal structures reported.

References

1) C. Soldi, K. N. Lamb, R. A. Squitieri, M. González-López, M. J. Di Maso, J. T. Shaw, *J. Am. Chem. Soc.* **2014**, 136, 15142-15145
2) Curini, M.; Epifano, F.; Marcotullio, M.C.; Montanari, F. *Synlett*, **2004**, 2, 368-370.
3) Pilli, R.A.; Victor, M.M.; De Meijere, A. *J. Org. Chem.* **2000**, 65(19), 5915-5916
4) Niu, T.; Wang, K.-H.; Huang, D.; Xu, C.; Su, Y.; Hu, Y.; Fu, Y. *Synthesis* **2013**, *46*, 320-330.
5) Bernardes, G.J.L; Casi, G.; Trussel, S.; Hartmann, I.; Schwager, K.; Scheuermann, J.; Neri, D. *Angew. Chem. Int.* **2012**, 51, 941-944.
6) Murakata, M.; Ikeda, T. *Org. Biomol. Chem.* **2017**, 15, 6632-6639.

SI Table 1: Catalyst Screen

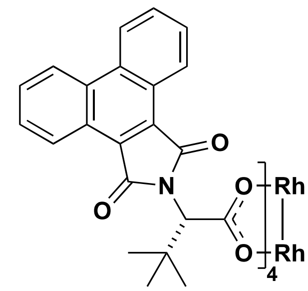


2 6a 6b

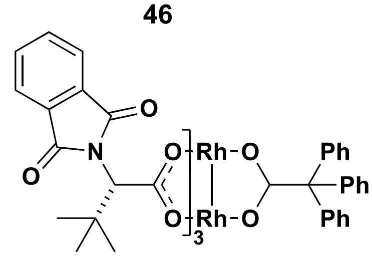
Catalyst	yield	dr[a]	er[b]	
Rh_2(R-PTAD)$_4$	70%	47:53	91:09	86:14
Rh_2(R-TCPTTL)$_4$	31%	57:43	76:24	85:15
Rh_2(R-DOSP)$_4$	15%	60:40	39:61	37:63
S-**46**	70%	49:51	49:51	48:52
Rh_2(4S-MPPIM)$_4$	NR	NR	NR	NR
Rh_2(esp)$_4$	77%	43:57	02:98	13:87
S-**47**	78%	52:48	48:52	47:53

[a] dr determined by 1H NMR analysis of unpurified reaction mixtures. [b] er determined by chiral HPLC

Catalyst structures

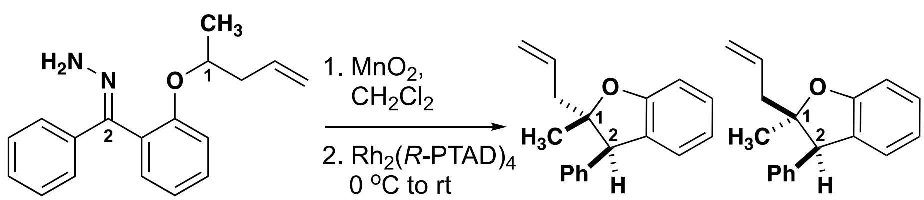


46



47

SI Table 2: Solvent Screen

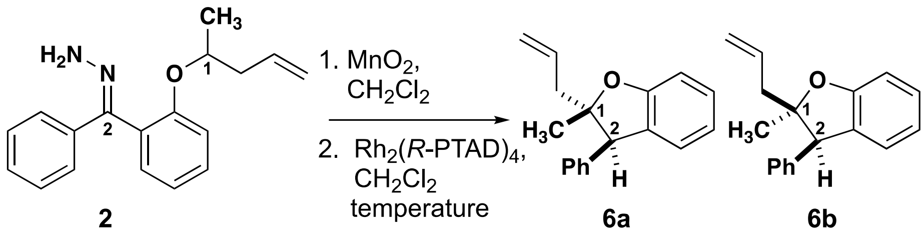


2 6a 6b

Solvent	yield	dr[a]	er[b]	
Pentane	29%	50:50	86:14	83:17
Cyclohexane	9%	51:49	83:17	89:11
Benzene	42%	42:58	92:08	88:12
DCM	70%	47:53	91:09	86:14
DCE	21%	52:48	91:09	90:10
MeCN	23%	54:46	82:18	85:15
DMF	24%	51:49	84:16	83:17
IPA	32%	48:52	91:09	87:13

[a] dr determined by 1H NMR analysis of unpurified reaction mixtures. [b] er determined by chiral HPLC

SI Table 3: Temperature Screen



Temperature (°C)	yield	dr[a]	er[b]	
-27 °C	45%	46:54	91:09	84:16
-10 °C	38%	46:54	92:08	87:13
0 °C to 23 °C	70%	47:53	91:09	86:14
23 °C	42%	46:54	90:10	83:!7
60 °C	16%	57:43	80:20	81:19

[a] dr determined by 1H NMR analysis of unpurified reaction mixtures. [b] er determined by chiral HPLC

HPLC Sample Preparation: Approximately 4-5 mgs of the compound to be analyzed was weighed into a vial. The sample was dissolved in a mixture of 10% isopropanol/hexanes solution such that the concentration was 1 mg/mL. About 1 mL of the solution was taken up in a syringe and passed through a 0.2 micron syringe filter into a 1.5 mL HPLC vial.

HPLC Methods and Materials: Enantiomer ratios were determined by chiral HPLC with one of the following columns (denoted as AD, AS, or OD on individual HPLC traces): AD = Phenomenex Lux®, 5 µm Amylose-1 LC Column, 250x4.6mm, part #: 00G-4732-E0; AS = Daicel Chiralpak®, AS-H 5 µm, 250x4.6mm, column #: ASH0CE-LF002; OD = Phenomenex Lux®, 5 µm Cellulose-1 LC Column, 250x4.6mm, part #: 00G-4459-E0. Isocratic solvent mixture (hexanes: isopropanol), flow rate, injection volume, and analysis-wavelength are denoted on individual HPLC traces.
Note: unless otherwise specified, 1mL/min is the default HPLC method flow-rate.

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==== HPLC Analysis Report ====

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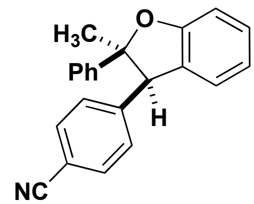

5a

Enantiopure SM

Enantiopure Pdt

$Rh_2(mes)_4$

<Chromatogram>

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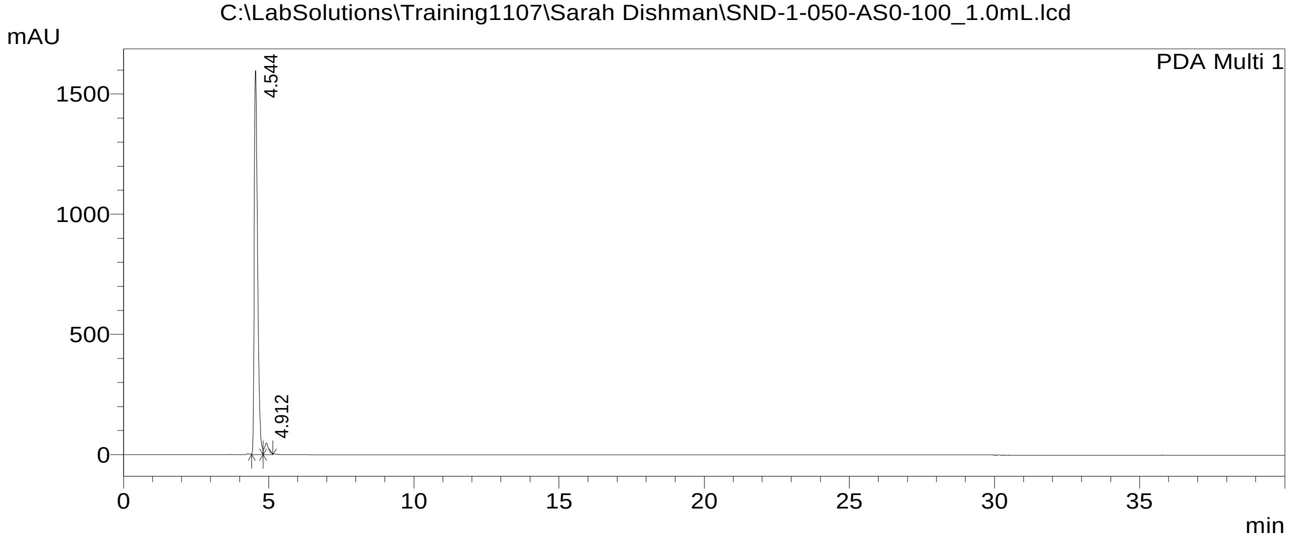

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PDA Ch1 235nm 4nm

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2	4.912	479254	47732	3.649	2.901
Total		13133532	1645108	100.000	100.000

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==== HPLC Analysis Report ====

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Report File Name : UCD Default.lcr
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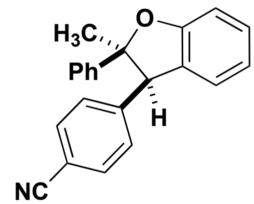
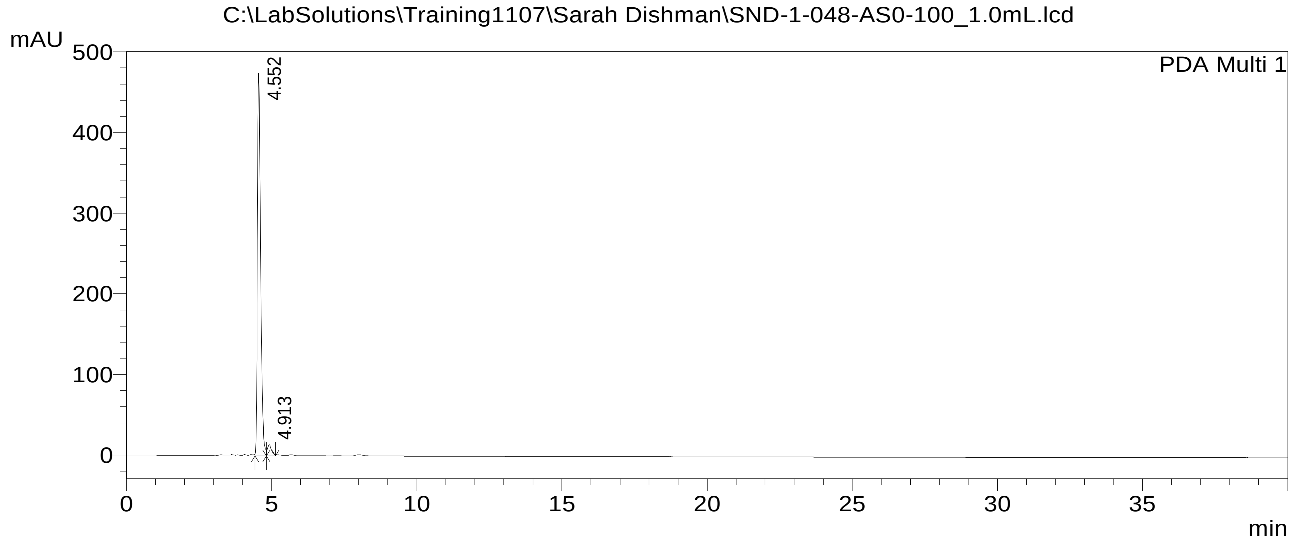


5a
Enantiopure SM
Enantiopure Pdt
Rh_2(*R*-PTAD)$_4$

<Chromatogram>



1 PDA Multi 1/235nm 4nm

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PDA Ch1 235nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.552	3649923	474903	96.198	97.135
2	4.913	144239	14010	3.802	2.865
Total		3794162	488913	100.000	100.000

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==== HPLC Analysis Report ====

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Sample ID	: 1
Tray#	: 1
Vail #	: 86
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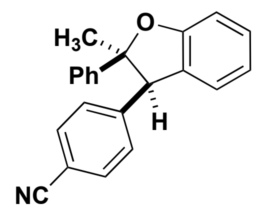

5a
Enantiopure SM
Enantiopure Pdt
Rh_2(*S*-PTAD)$_4$

<Chromatogram>

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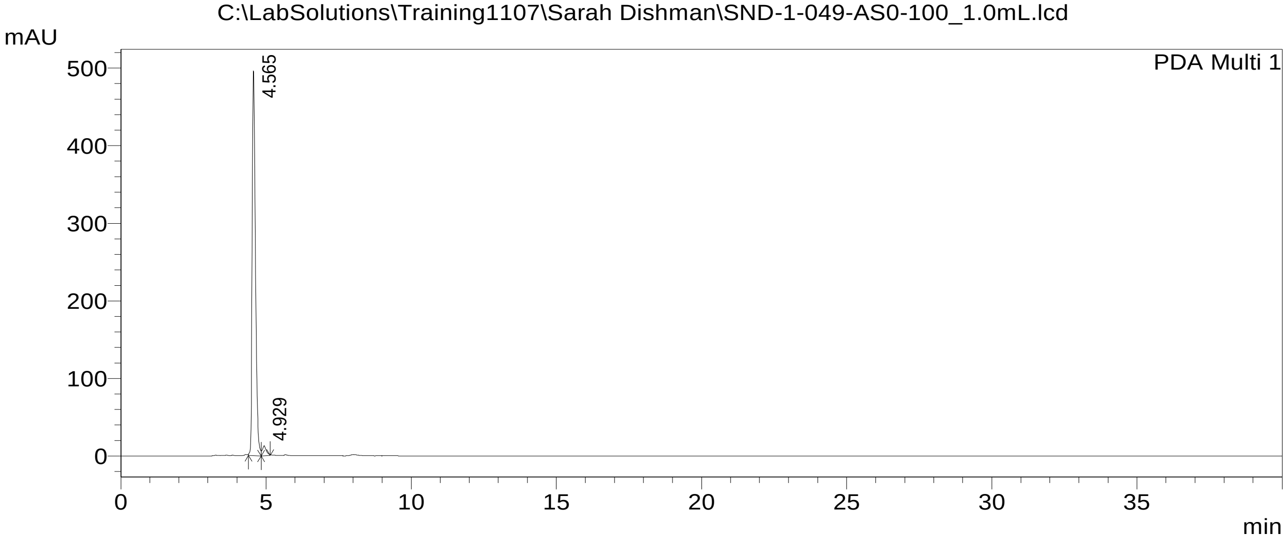

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1	4.565	3837807	496241	96.857	97.526
2	4.929	124551	12587	3.143	2.474
Total		3962359	508827	100.000	100.000

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==== HPLC Analysis Report ====

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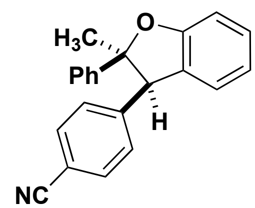

5a

Racemic SM

Racemic Pdt

Rh_2(*R*-PTAD)$_4$

<Chromatogram>

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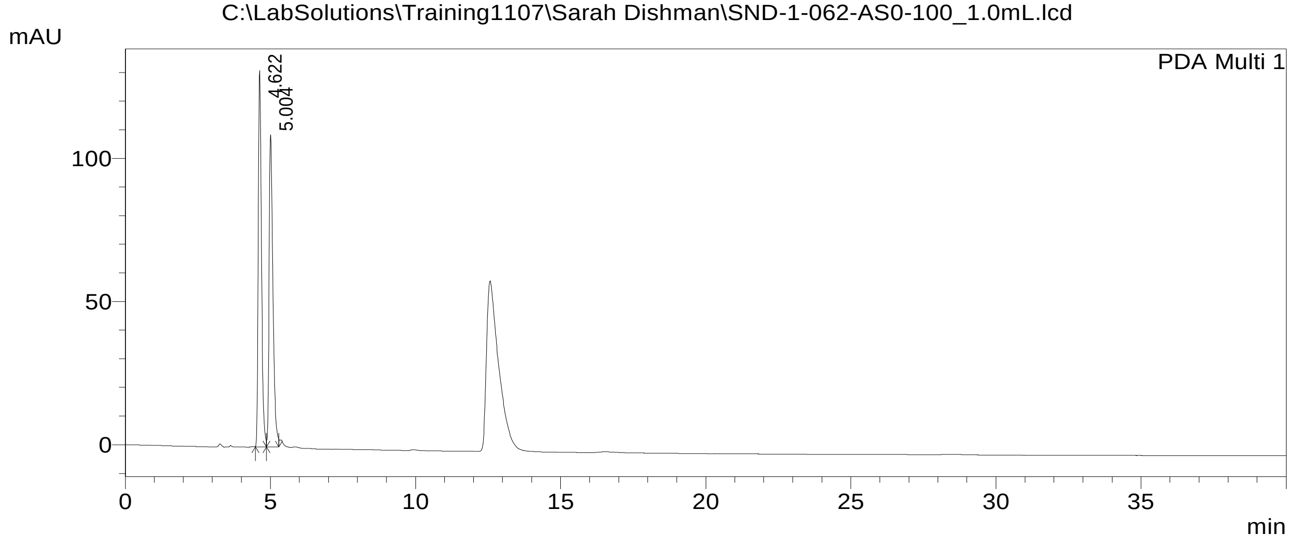

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Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.622	1008674	131489	50.352	54.654
2	5.004	994572	109096	49.648	45.346
Total		2003246	240585	100.000	100.000

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==== HPLC Analysis Report ====

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Vail #	: 71
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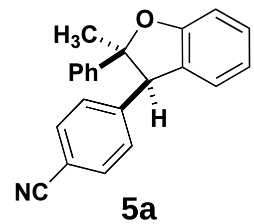


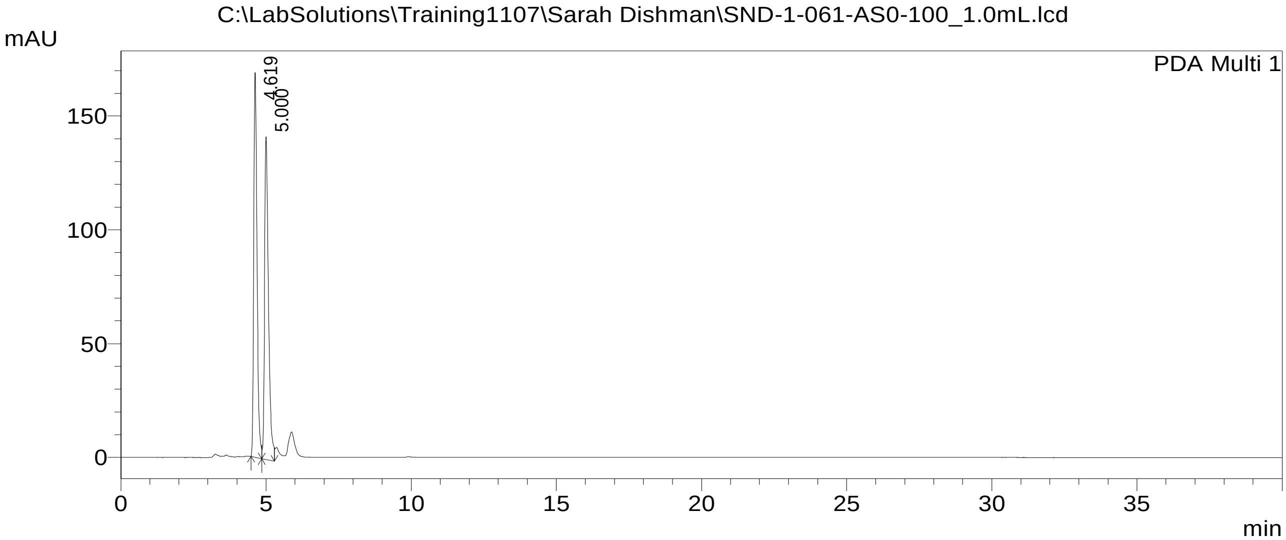
5a

Racemic SM

Racemic Pdt

Rh_2(*S*-PTAD)$_4$

<Chromatogram>



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PDA Ch1 235nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.619	1312223	168965	49.798	54.372
2	5.000	1322894	141792	50.202	45.628
Total		2635117	310758	100.000	100.000

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==== HPLC Analysis Report ====

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Sample ID	: 1
Tray#	: 1
Vail #	: 38
Injection Volume	: 2 uL
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Method File Name	: AS-0_100_40min.lcm
Batch File Name	: 04-24-19_SND-066,069.lcb
Report File Name	: UCD Default.lcr
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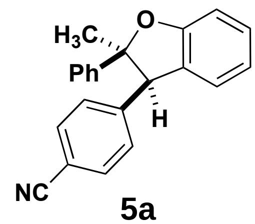
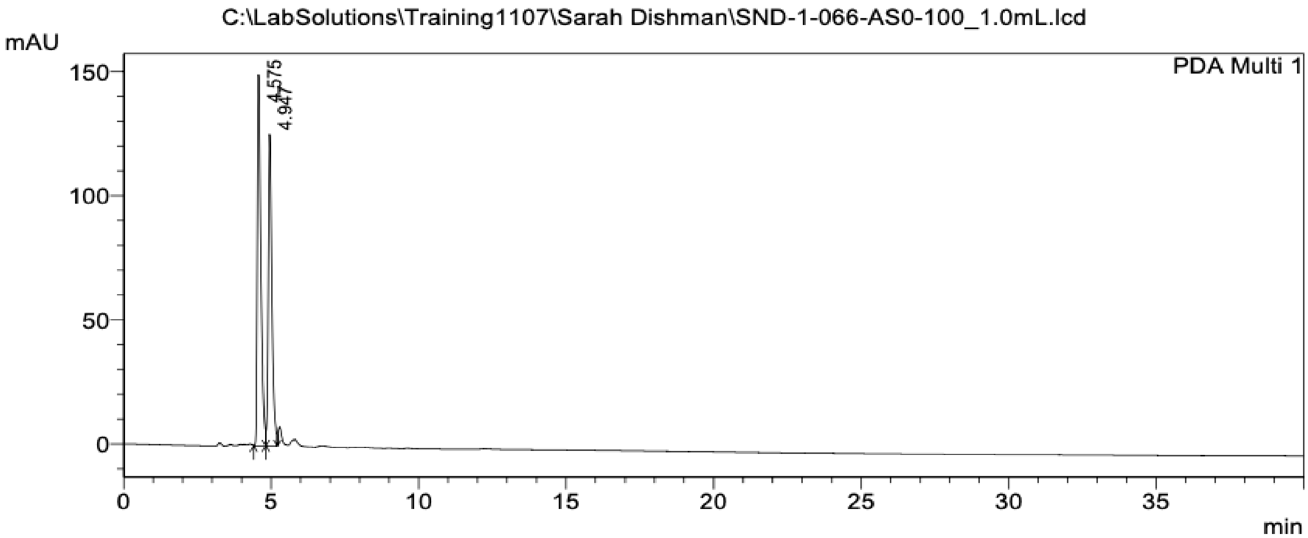


5a

Racemic SM
Racemic Pdt
$Rh_2(OAc)_4$

<Chromatogram>



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Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.575	1253623	149346	52.781	54.334
2	4.947	1121527	125519	47.219	45.666
Total		2375150	274865	100.000	100.000

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==== HPLC Analysis Report ====

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Acquired by	: Admin
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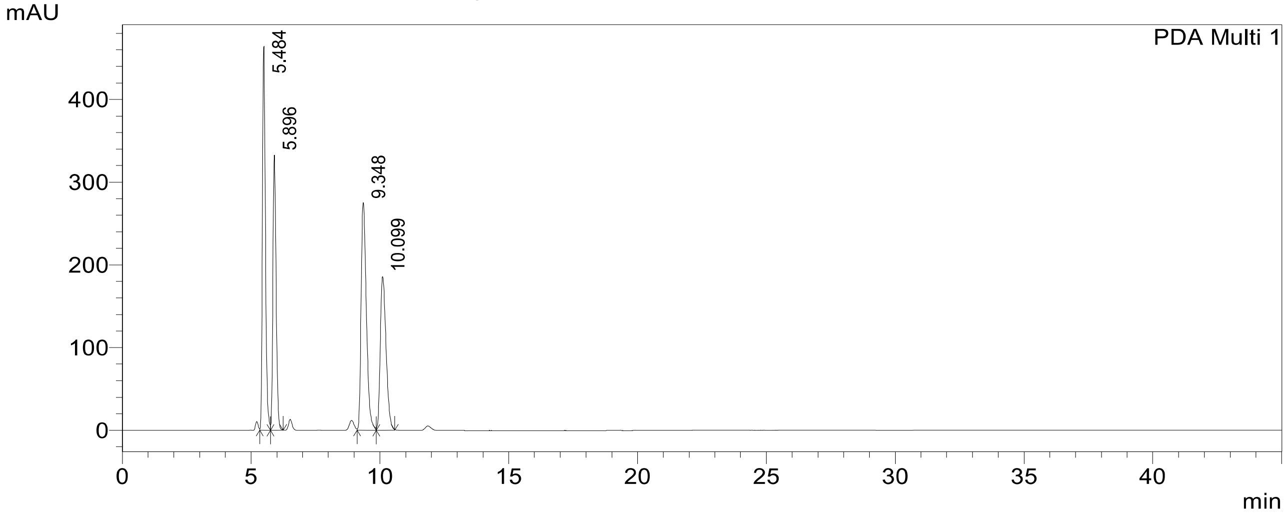
Sample ID	: 1
Tray#	: 1
Vail #	: 37
Injection Volume	: 2 uL
Data File Name	: SND-1-097-OD100-0_1.0mL.lcd
Method File Name	: OD-100_0_Hexane_IPA_60min.lcm
Batch File Name	: 06-03-19_3.lcb
Report File Name	: UCD Default.lcr
Data Acquired	: 6/3/2019 11:50:58 PM
Data Processed	: 6/4/2019 12:50:58 AM

6a/b
Racemic SM
Racemic Pdt
$Rh_2(mes)_4$
57:43 dr
Racemic

<Chromatogram>



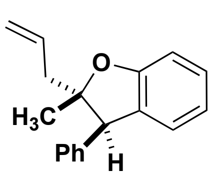
1 PDA Multi 1/283nm 4nm

< Peak Table >

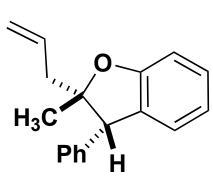
PeakTable C:\LabSolutions\Training1107\Sarah Dishman\SND-1-097-OD100-0_1.0mL.lcd

PDA Ch1 283nm 4nm

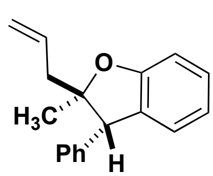
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.484	3771977	464212	27.990	36.896
2	5.896	2884662	332550	21.406	26.431
3	9.348	3912561	275452	29.033	21.893
4	10.099	2906882	185956	21.571	14.780
Total		13476082	1258169	100.000	100.000



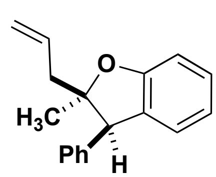
Peak 1
Trans-(S,R)



Peak 2
Cis-(S,S)



Peak 3
Trans-(R,S)



Peak 4
Cis-(R,R)

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==== HPLC Analysis Report ====

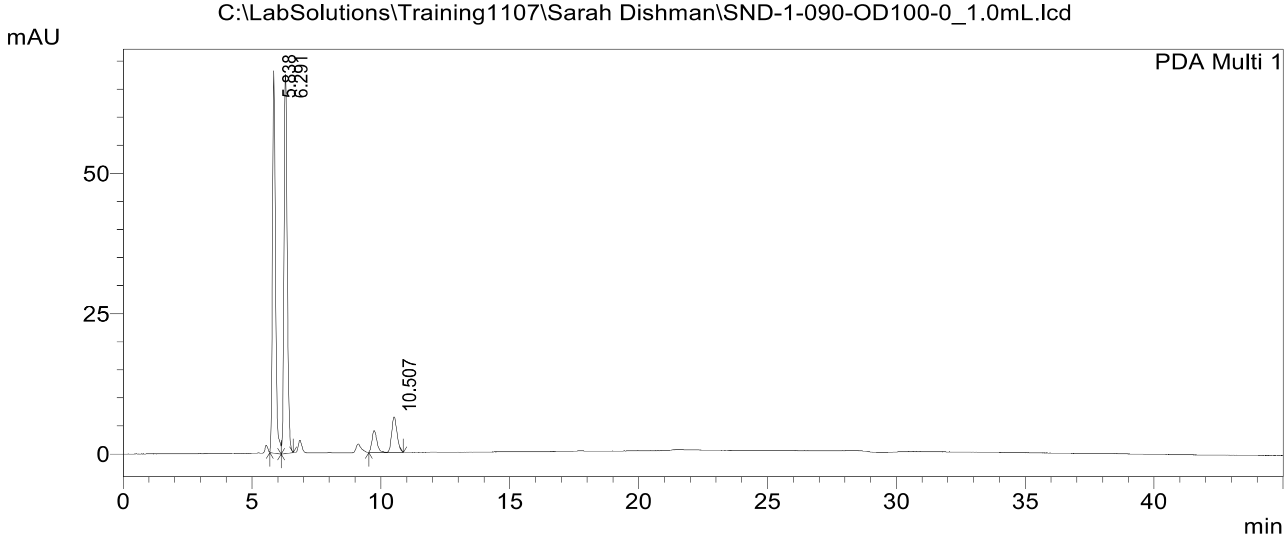
C:\LabSolutions\Training1107\Sarah Dishman\SND-1-090-OD100-0_1.0mL.lcd

Acquired by	: Admin
Sample Name	: 1
Sample ID	: 1
Tray#	: 1
Vail #	: 38
Injection Volume	: 2 uL
Data File Name	: SND-1-090-OD100-0_1.0mL.lcd
Method File Name	: OD-100_0_Hexane_IPA_60min.lcm
Batch File Name	: 06-03-19_3.lcb
Report File Name	: UCD Default.lcr
Data Acquired	: 6/4/2019 1:01:33 AM
Data Processed	: 6/4/2019 2:01:35 AM

47:53 dr 6a/b
Racemic SM
Mixed dr Pdt
Rh_2(*R*-PTAD)$_4$

<Chromatogram>

C:\LabSolutions\Training1107\Sarah Dishman\SND-1-090-OD100-0_1.0mL.lcd

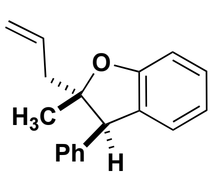


1 PDA Multi 1/283nm 4nm

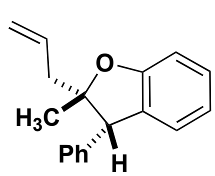
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Sarah Dishman\SND-1-090-OD100-0_1.0mL.lcd
PDA Ch1 283nm 4nm

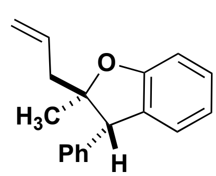
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.838	562623	68131	43.085	47.935
2	6.291	593778	67598	45.470	47.560
3	10.507	149455	6402	11.445	4.505
Total		1305857	142132	100.000	100.000



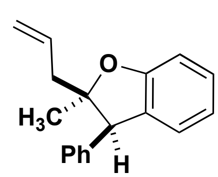
Peak 1
Trans-(S,R)



Peak 2
Cis-(S,S)



Peak 3
Trans-(R,S)



Peak 4
Cis-(R,R)

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UCDAVIS UNIVERSITY OF CALIFORNIA Department of Chemistry

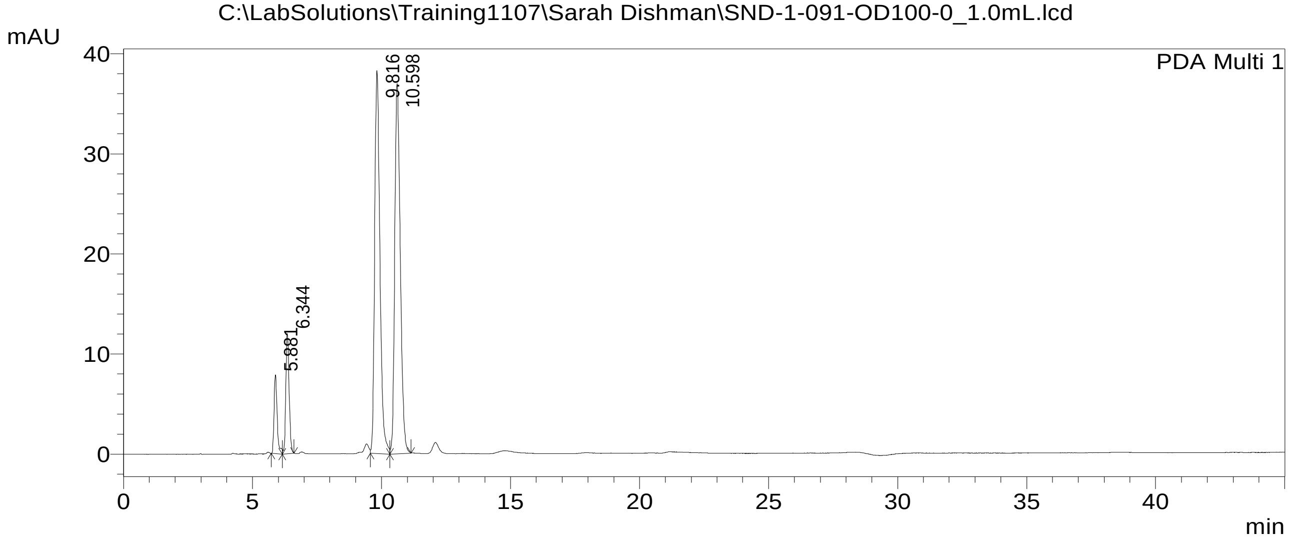
==== HPLC Analysis Report ====

C:\LabSolutions\Training1107\Sarah Dishman\SND-1-091-OD100-0_1.0mL.lcd

Acquired by	: Admin
Sample Name	: 1
Sample ID	: 1
Tray#	: 1
Vail #	: 39
Injection Volume	: 2 uL
Data File Name	: SND-1-091-OD100-0_1.0mL.lcd
Method File Name	: OD-100_0_Hexane_IPA_60min.lcm
Batch File Name	: 06-03-19_3.lcb
Report File Name	: UCD Default.lcr
Data Acquired	: 6/4/2019 2:12:08 AM
Data Processed	: 6/4/2019 3:12:11 AM

6a/b
Racemic SM
Mix dr Pdt
Rh_2(*S*-PTAD)$_4$

<Chromatogram>

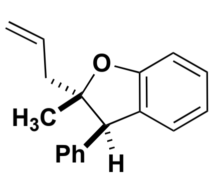


1 PDA Multi 1/283nm 4nm

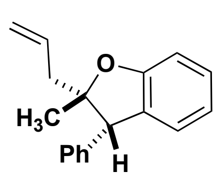
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Sarah Dishman\SND-1-091-OD100-0_1.0mL.lcd
PDA Ch1 283nm 4nm

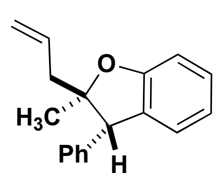
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.881	67042	7876	5.283	8.278
2	6.344	106549	11996	8.396	12.609
3	9.816	540813	38273	42.617	40.229
4	10.598	554589	36993	43.703	38.884
Total		1268992	95137	100.000	100.000



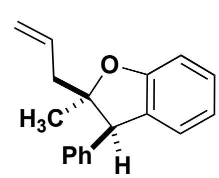
Peak 1
Trans-(S,R)



Peak 2
Cis-(S,S)



Peak 3
Trans-(R,S)



Peak 4
Cis-(R,R)

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UCDAVIS Department of Chemistry

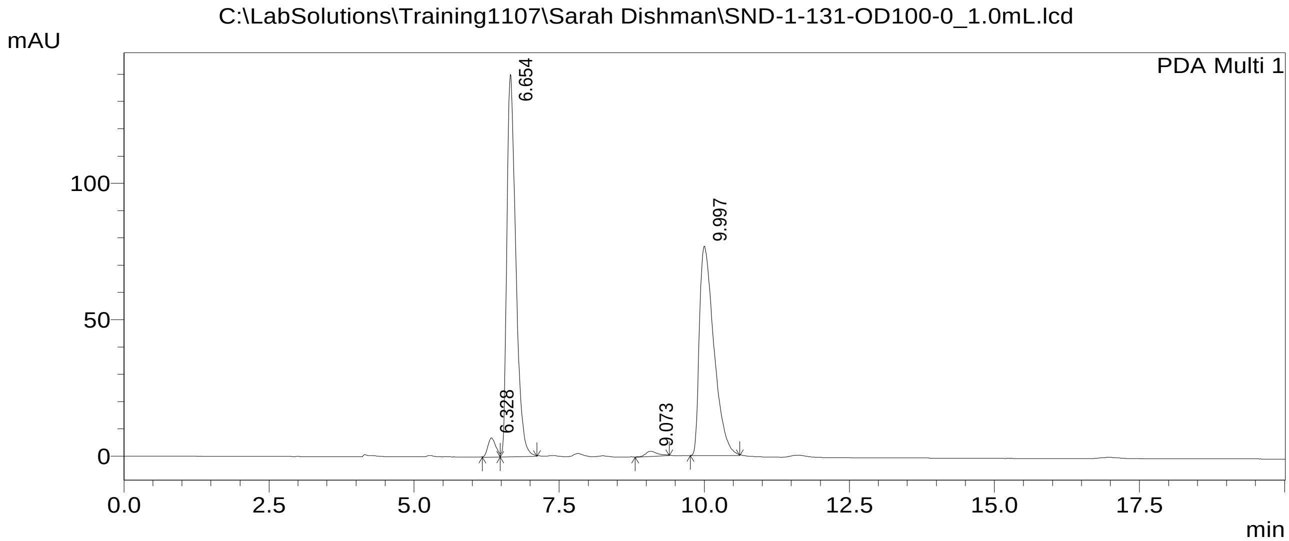
==== HPLC Analysis Report ====

C:\LabSolutions\Training1107\Sarah Dishman\SND-1-131-OD100-0_1.0mL.lcd

Acquired by	: Admin
Sample Name	: 1
Sample ID	: 1
Tray#	: 1
Vail #	: 39
Injection Volume	: 5 uL
Data File Name	: SND-1-131-OD100-0_1.0mL.lcd
Method File Name	: OD-100_0_Hexane_IPA_20min.lcm
Batch File Name	: 06-19-19_SND-129-131.lcb
Report File Name	: UCD Default.lcr
Data Acquired	: 6/19/2019 9:21:29 PM
Data Processed	: 6/19/2019 9:41:31 PM

6a/b
Enantiopure SM
Enantiopure, mixed dr Pdt
$Rh_2(mes)_4$

<Chromatogram>



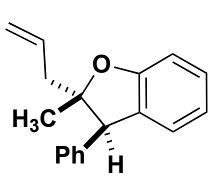
1 PDA Multi 1/283nm 4nm

< Peak Table >

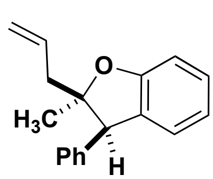
PeakTable C:\LabSolutions\Training1107\Sarah Dishman\SND-1-131-OD100-0_1.0mL.lcd

PDA Ch1 283nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.328	67653	7083	2.297	3.135
2	6.654	1509797	140236	51.270	62.067
3	9.073	28302	1915	0.961	0.847
4	9.997	1339047	76711	45.472	33.951
Total		2944798	225945	100.000	100.000



Peak 2
Trans-(S,R)



Peak 4
Cis-(R,R)

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==== HPLC Analysis Report ====

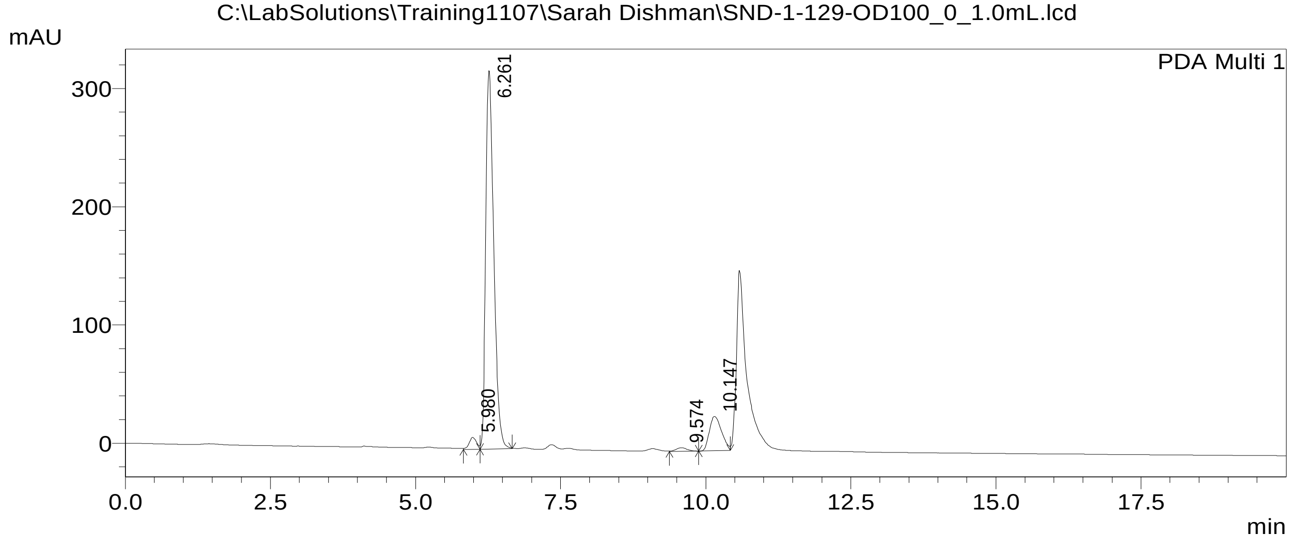
C:\LabSolutions\Training1107\Sarah Dishman\SND-1-129-OD100_0_1.0mL.lcd

Acquired by : Admin
Sample Name : 1
Sample ID : 1
Tray# : 1
Vail # : 37
Injection Volume : 5 uL
Data File Name : SND-1-129-OD100_0_1.0mL.lcd
Method File Name : OD-100_0_Hexane_IPA_20min.lcm
Batch File Name : 06-19-19_SND-129-131.lcb
Report File Name : UCD Default.lcr
Data Acquired : 6/19/2019 8:30:18 PM
Data Processed : 6/19/2019 8:50:19 PM

6a/b
Enantiopure SM
Enantiopure Pdt
Rh_2(*R*-PTAD)$_4$

<Chromatogram>

C:\LabSolutions\Training1107\Sarah Dishman\SND-1-129-OD100_0_1.0mL.lcd

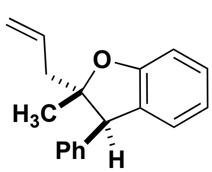


1 PDA Multi 1/283nm 4nm

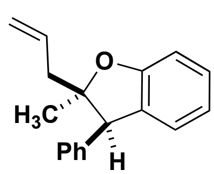
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Sarah Dishman\SND-1-129-OD100_0_1.0mL.lcd
PDA Ch1 283nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.980	91770	10083	2.511	2.784
2	6.261	3097857	319888	84.757	88.321
3	9.574	39610	3106	1.084	0.858
4	10.147	425745	29109	11.648	8.037
Total		3654981	362186	100.000	100.000



Peak 2
Trans-(S,R)



Peak 4
Cis-(R,R)

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==== HPLC Analysis Report ====

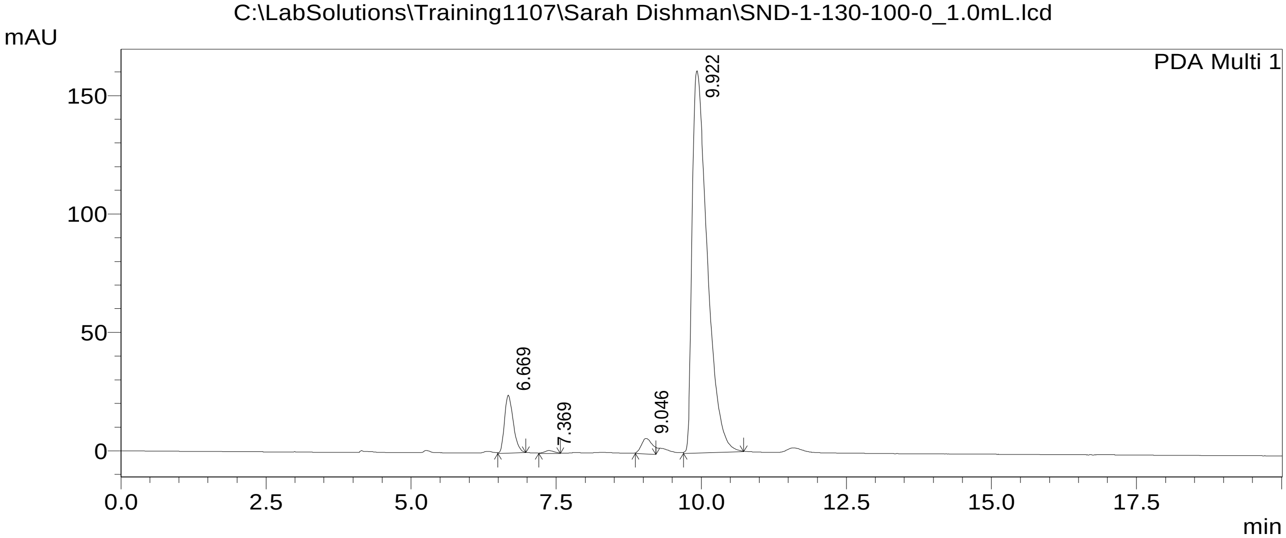
C:\LabSolutions\Training1107\Sarah Dishman\SND-1-130-100-0_1.0mL.lcd

Acquired by	: Admin
Sample Name	: 1
Sample ID	: 1
Tray#	: 1
Vail #	: 38
Injection Volume	: 5 uL
Data File Name	: SND-1-130-100-0_1.0mL.lcd
Method File Name	: OD-100_0_Hexane_IPA_20min.lcm
Batch File Name	: 06-19-19_SND-129-131.lcb
Report File Name	: UCD Default.lcr
Data Acquired	: 6/19/2019 8:55:54 PM
Data Processed	: 6/19/2019 9:15:56 PM

6/b
Enantiopure SM
Enantiopure Pdt
Rh_2(*S*-PTAD)$_4$

<Chromatogram>

C:\LabSolutions\Training1107\Sarah Dishman\SND-1-130-100-0_1.0mL.lcd



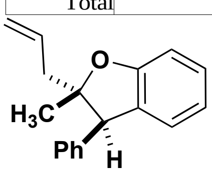
1 PDA Multi 1/283nm 4nm

< Peak Table >

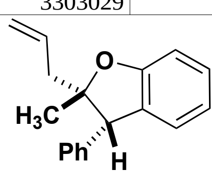
PeakTable C:\LabSolutions\Training1107\Sarah Dishman\SND-1-130-100-0_1.0mL.lcd

PDA Ch1 283nm 4nm

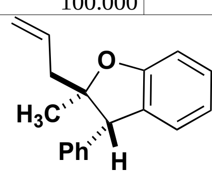
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.669	258443	24561	7.824	12.672
2	7.369	15528	1247	0.470	0.644
3	9.046	86561	6559	2.621	3.384
4	9.922	2942497	161461	89.085	83.301
Total		3303029	193829	100.000	100.000



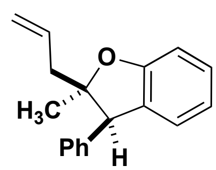
Peak 1
Trans-(S,R)



Peak 2
Cis-(S,S)



Peak 3
Trans-(R,S)



Peak 4
Cis-(R,R)

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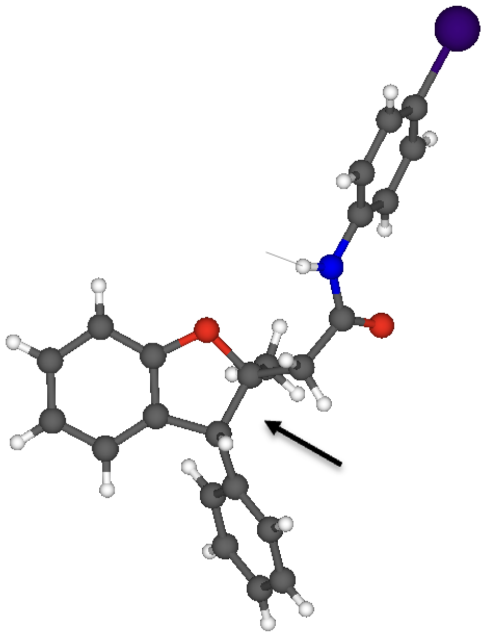
X-Ray Crystallography Data



Arrows point to newly formed C–C bond from insertion reaction.

Major diastereomer using Rh_2(R-PTAD)$_4$ is Trans-(S,R)

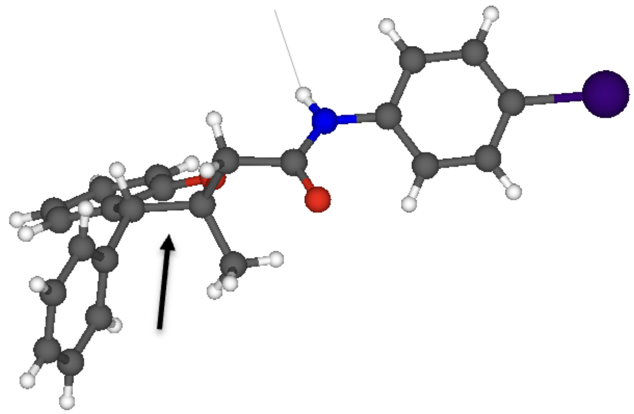


Table 1. Crystal data and structure refinement for [$C_{23}H_{20}NO_2I$].

Identification code	JF2873FF (SND-02-11)	
Empirical formula	C23 H20 I N O2	
Formula weight	469.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.7754(5) Å	□= 99.2233(18)°.
	b = 8.8984(6) Å	□= 96.0361(18)°.
	c = 12.8772(8) Å	□ = 91.1970(17)°.
Volume	986.31(11) $Å^3$	
Z, Z'	2, 2	
Density (calculated)	1.580 Mg/m^3	
Absorption coefficient	1.641 mm^{-1}	
F(000)	468	
Crystal size	0.308 x 0.096 x 0.038 mm^3	

Crystal color and habit	Colorless Plate
Diffractometer	Bruker Photon100 CMOS
Theta range for data collection	2.336 to 29.998°.
Index ranges	-12<=h<=12, -12<=k<=12, -18<=l<=18
Reflections collected	49290
Independent reflections	11503 [R(int) = 0.0213]
Observed reflections (I > 2sigma(I))	10996
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8365 and 0.7842
Solution method	SHELXT (Sheldrick, 2014)
Refinement method	SHELXL-2018/3 (Sheldrick, 2018) Full-matrix least-squares on F^2
Data / restraints / parameters	11503 / 9 / 530
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0194, wR2 = 0.0399
R indices (all data)	R1 = 0.0217, wR2 = 0.0408
Absolute structure parameter	-0.034(4)
Extinction coefficient	0.0076(4)
Largest diff. peak and hole	0.522 and -0.523 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for JF2873FF. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1510(3)	5924(3)	2669(2)	14(1)
O(1)	2967(2)	5114(2)	2707(2)	18(1)
C(2)	1912(3)	7429(3)	2248(2)	16(1)
C(3)	3287(3)	6975(3)	1687(2)	16(1)
C(4)	4065(4)	7686(5)	1004(3)	20(1)

C(5)	5394(3)	7075(3)	659(2)	23(1)
C(6)	5954(3)	5784(3)	1014(2)	23(1)
C(7)	5186(3)	5040(3)	1697(2)	22(1)
C(8)	3848(3)	5662(3)	2018(2)	17(1)
C(9)	340(3)	4871(3)	1932(2)	21(1)
C(10)	1088(3)	6307(3)	3807(2)	16(1)
C(11)	387(3)	4978(3)	4212(2)	14(1)
N(11)	1384(2)	4185(2)	4770(2)	16(1)
O(11)	-992(3)	4649(3)	4024(2)	18(1)
C(12)	1023(3)	2845(3)	5172(2)	15(1)
C(13)	1935(3)	2525(3)	6055(2)	16(1)
C(14)	1649(3)	1218(3)	6475(2)	18(1)
C(15)	453(3)	213(3)	5992(2)	17(1)
I(15)	-49(1)	-1778(1)	6592(1)	23(1)
C(16)	-441(4)	507(4)	5105(3)	20(1)
C(17)	-166(4)	1835(4)	4690(3)	19(1)
C(18)	660(3)	8126(3)	1606(2)	19(1)
C(19)	-53(4)	9413(3)	2065(3)	28(1)
C(20)	-1126(4)	10135(4)	1462(4)	41(1)
C(21)	-1497(4)	9578(5)	395(4)	43(1)
C(22)	-801(4)	8289(5)	-74(4)	34(1)
C(23)	276(3)	7579(4)	532(2)	26(1)
C(31)	7309(3)	4118(3)	7091(2)	16(1)
O(31)	8795(2)	4918(2)	7064(2)	19(1)
C(32)	7792(3)	2611(3)	7501(2)	15(1)
C(33)	9282(3)	3137(3)	8163(2)	18(1)
C(34)	10184(5)	2498(5)	8914(3)	24(1)
C(35)	11603(3)	3166(4)	9310(2)	26(1)
C(36)	12141(3)	4441(4)	8938(2)	26(1)
C(37)	11252(3)	5101(3)	8180(2)	24(1)
C(38)	9816(4)	4431(4)	7818(2)	18(1)
C(39)	6427(3)	5170(3)	7845(2)	20(1)
C(40)	6509(3)	3755(3)	5956(2)	16(1)
C(41)	5653(4)	5058(3)	5579(2)	15(1)
N(41)	6416(2)	5887(2)	4987(2)	16(1)
O(41)	4355(3)	5332(3)	5811(2)	19(1)

C(42)	5906(3)	7208(3)	4599(2)	15(1)
C(43)	4791(4)	8123(4)	5039(3)	18(1)
C(44)	4372(4)	9424(4)	4638(3)	21(1)
C(45)	5056(3)	9829(3)	3793(2)	18(1)
I(45)	4324(1)	11779(1)	3189(1)	25(1)
C(46)	6176(3)	8933(3)	3349(2)	18(1)
C(47)	6603(3)	7628(3)	3758(2)	16(1)
C(48)	6630(3)	1788(3)	8012(2)	18(1)
C(49)	6242(3)	2304(3)	9028(2)	23(1)
C(50)	5172(4)	1499(5)	9467(3)	28(1)
C(51)	4475(3)	166(4)	8906(3)	29(1)
C(52)	4880(4)	-386(4)	7913(3)	28(1)
C(53)	5946(3)	420(3)	7467(2)	22(1)

Table 3. Bond lengths [Å] and angles [°] for JF2873FF.

C(1)-O(1)	1.481(3)
C(1)-C(9)	1.517(4)
C(1)-C(10)	1.536(3)
C(1)-C(2)	1.570(3)
O(1)-C(8)	1.375(3)
C(2)-C(3)	1.500(4)
C(2)-C(18)	1.509(4)
C(2)-H(2)	1.0000
C(3)-C(8)	1.389(4)
C(3)-C(4)	1.389(5)
C(4)-C(5)	1.382(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.384(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.400(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.383(4)

C(7)-H(7)	0.9500
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.511(4)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-O(11)	1.229(4)
C(11)-N(11)	1.355(4)
N(11)-C(12)	1.416(3)
N(11)-H(11)	0.8800
C(12)-C(17)	1.389(4)
C(12)-C(13)	1.392(3)
C(13)-C(14)	1.388(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.390(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.379(5)
C(15)-I(15)	2.100(2)
C(16)-C(17)	1.399(5)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(23)	1.393(4)
C(18)-C(19)	1.395(4)
C(19)-C(20)	1.391(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.386(7)
C(20)-H(20)	0.9500
C(21)-C(22)	1.391(7)
C(21)-H(21)	0.9500
C(22)-C(23)	1.389(5)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(31)-O(31)	1.479(3)
C(31)-C(39)	1.522(4)
C(31)-C(40)	1.535(3)

C(31)-C(32)	1.568(3)
O(31)-C(38)	1.378(4)
C(32)-C(33)	1.506(4)
C(32)-C(48)	1.508(4)
C(32)-H(32)	1.0000
C(33)-C(34)	1.386(5)
C(33)-C(38)	1.388(4)
C(34)-C(35)	1.380(5)
C(34)-H(34)	0.9500
C(35)-C(36)	1.392(5)
C(35)-H(35)	0.9500
C(36)-C(37)	1.396(4)
C(36)-H(36)	0.9500
C(37)-C(38)	1.384(4)
C(37)-H(37)	0.9500
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-C(41)	1.511(4)
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-O(41)	1.227(4)
C(41)-N(41)	1.357(4)
N(41)-C(42)	1.412(3)
N(41)-H(41)	0.8800
C(42)-C(43)	1.393(4)
C(42)-C(47)	1.396(3)
C(43)-C(44)	1.383(5)
C(43)-H(43)	0.9500
C(44)-C(45)	1.389(5)
C(44)-H(44)	0.9500
C(45)-C(46)	1.390(4)
C(45)-I(45)	2.098(3)
C(46)-C(47)	1.392(4)
C(46)-H(46)	0.9500
C(47)-H(47)	0.9500

C(48)-C(53)	1.393(4)
C(48)-C(49)	1.396(4)
C(49)-C(50)	1.388(5)
C(49)-H(49)	0.9500
C(50)-C(51)	1.380(5)
C(50)-H(50)	0.9500
C(51)-C(52)	1.380(5)
C(51)-H(51)	0.9500
C(52)-C(53)	1.391(4)
C(52)-H(52)	0.9500
C(53)-H(53)	0.9500

O(1)-C(1)-C(9)	106.7(2)
O(1)-C(1)-C(10)	107.63(19)
C(9)-C(1)-C(10)	113.7(2)
O(1)-C(1)-C(2)	104.29(19)
C(9)-C(1)-C(2)	114.0(2)
C(10)-C(1)-C(2)	109.9(2)
C(8)-O(1)-C(1)	107.1(2)
C(3)-C(2)-C(18)	115.2(2)
C(3)-C(2)-C(1)	101.29(19)
C(18)-C(2)-C(1)	118.1(2)
C(3)-C(2)-H(2)	107.2
C(18)-C(2)-H(2)	107.2
C(1)-C(2)-H(2)	107.2
C(8)-C(3)-C(4)	119.9(3)
C(8)-C(3)-C(2)	108.7(2)
C(4)-C(3)-C(2)	131.3(3)
C(5)-C(4)-C(3)	119.4(3)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	119.9(3)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(5)-C(6)-C(7)	121.8(3)
C(5)-C(6)-H(6)	119.1

C(7)-C(6)-H(6)	119.1
C(8)-C(7)-C(6)	117.1(3)
C(8)-C(7)-H(7)	121.4
C(6)-C(7)-H(7)	121.4
O(1)-C(8)-C(7)	125.3(3)
O(1)-C(8)-C(3)	112.8(2)
C(7)-C(8)-C(3)	121.9(3)
C(1)-C(9)-H(9A)	109.5
C(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(1)	114.1(2)
C(11)-C(10)-H(10A)	108.7
C(1)-C(10)-H(10A)	108.7
C(11)-C(10)-H(10B)	108.7
C(1)-C(10)-H(10B)	108.7
H(10A)-C(10)-H(10B)	107.6
O(11)-C(11)-N(11)	123.5(3)
O(11)-C(11)-C(10)	121.1(3)
N(11)-C(11)-C(10)	115.4(2)
C(11)-N(11)-C(12)	125.9(2)
C(11)-N(11)-H(11)	117.0
C(12)-N(11)-H(11)	117.0
C(17)-C(12)-C(13)	119.9(3)
C(17)-C(12)-N(11)	122.0(3)
C(13)-C(12)-N(11)	118.1(2)
C(14)-C(13)-C(12)	120.6(2)
C(14)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	119.2(2)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4
C(16)-C(15)-C(14)	120.6(3)
C(16)-C(15)-I(15)	118.3(2)

C(14)-C(15)-I(15)	121.12(19)
C(15)-C(16)-C(17)	120.2(3)
C(15)-C(16)-H(16)	119.9
C(17)-C(16)-H(16)	119.9
C(12)-C(17)-C(16)	119.4(3)
C(12)-C(17)-H(17)	120.3
C(16)-C(17)-H(17)	120.3
C(23)-C(18)-C(19)	118.7(3)
C(23)-C(18)-C(2)	121.2(2)
C(19)-C(18)-C(2)	119.9(3)
C(20)-C(19)-C(18)	120.5(3)
C(20)-C(19)-H(19)	119.7
C(18)-C(19)-H(19)	119.7
C(21)-C(20)-C(19)	120.2(4)
C(21)-C(20)-H(20)	119.9
C(19)-C(20)-H(20)	119.9
C(20)-C(21)-C(22)	120.0(3)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0
C(23)-C(22)-C(21)	119.6(4)
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-H(22)	120.2
C(22)-C(23)-C(18)	121.1(3)
C(22)-C(23)-H(23)	119.5
C(18)-C(23)-H(23)	119.5
O(31)-C(31)-C(39)	106.3(2)
O(31)-C(31)-C(40)	108.4(2)
C(39)-C(31)-C(40)	114.0(2)
O(31)-C(31)-C(32)	103.13(19)
C(39)-C(31)-C(32)	114.0(2)
C(40)-C(31)-C(32)	110.3(2)
C(38)-O(31)-C(31)	106.6(2)
C(33)-C(32)-C(48)	117.1(2)
C(33)-C(32)-C(31)	100.8(2)
C(48)-C(32)-C(31)	117.9(2)
C(33)-C(32)-H(32)	106.7

C(48)-C(32)-H(32)	106.7
C(31)-C(32)-H(32)	106.7
C(34)-C(33)-C(38)	119.9(3)
C(34)-C(33)-C(32)	132.2(3)
C(38)-C(33)-C(32)	107.6(2)
C(35)-C(34)-C(33)	119.1(4)
C(35)-C(34)-H(34)	120.4
C(33)-C(34)-H(34)	120.4
C(34)-C(35)-C(36)	120.4(3)
C(34)-C(35)-H(35)	119.8
C(36)-C(35)-H(35)	119.8
C(35)-C(36)-C(37)	121.3(3)
C(35)-C(36)-H(36)	119.3
C(37)-C(36)-H(36)	119.3
C(38)-C(37)-C(36)	117.0(3)
C(38)-C(37)-H(37)	121.5
C(36)-C(37)-H(37)	121.5
O(31)-C(38)-C(37)	124.8(3)
O(31)-C(38)-C(33)	112.9(3)
C(37)-C(38)-C(33)	122.2(3)
C(31)-C(39)-H(39A)	109.5
C(31)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(31)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(41)-C(40)-C(31)	114.7(2)
C(41)-C(40)-H(40A)	108.6
C(31)-C(40)-H(40A)	108.6
C(41)-C(40)-H(40B)	108.6
C(31)-C(40)-H(40B)	108.6
H(40A)-C(40)-H(40B)	107.6
O(41)-C(41)-N(41)	123.3(3)
O(41)-C(41)-C(40)	120.9(3)
N(41)-C(41)-C(40)	115.8(2)
C(41)-N(41)-C(42)	126.5(2)

C(41)-N(41)-H(41)	116.7
C(42)-N(41)-H(41)	116.7
C(43)-C(42)-C(47)	119.2(3)
C(43)-C(42)-N(41)	123.2(3)
C(47)-C(42)-N(41)	117.5(2)
C(44)-C(43)-C(42)	120.3(3)
C(44)-C(43)-H(43)	119.9
C(42)-C(43)-H(43)	119.9
C(43)-C(44)-C(45)	120.3(3)
C(43)-C(44)-H(44)	119.9
C(45)-C(44)-H(44)	119.9
C(44)-C(45)-C(46)	120.2(3)
C(44)-C(45)-I(45)	118.5(2)
C(46)-C(45)-I(45)	121.30(19)
C(45)-C(46)-C(47)	119.5(2)
C(45)-C(46)-H(46)	120.3
C(47)-C(46)-H(46)	120.3
C(46)-C(47)-C(42)	120.6(2)
C(46)-C(47)-H(47)	119.7
C(42)-C(47)-H(47)	119.7
C(53)-C(48)-C(49)	118.0(3)
C(53)-C(48)-C(32)	119.0(2)
C(49)-C(48)-C(32)	123.0(2)
C(50)-C(49)-C(48)	120.8(3)
C(50)-C(49)-H(49)	119.6
C(48)-C(49)-H(49)	119.6
C(51)-C(50)-C(49)	120.5(3)
C(51)-C(50)-H(50)	119.7
C(49)-C(50)-H(50)	119.7
C(52)-C(51)-C(50)	119.4(3)
C(52)-C(51)-H(51)	120.3
C(50)-C(51)-H(51)	120.3
C(51)-C(52)-C(53)	120.3(3)
C(51)-C(52)-H(52)	119.9
C(53)-C(52)-H(52)	119.9
C(52)-C(53)-C(48)	121.0(3)

C(52)-C(53)-H(53)	119.5
C(48)-C(53)-H(53)	119.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for JF2873FF. The anisotropic displacement factor exponent takes the form: -2□^{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}
C(1)	14(1)	15(1)	15(1)	4(1)	3(1)	3(1)
O(1)	17(1)	19(1)	22(1)	8(1)	7(1)	4(1)
C(2)	18(1)	16(1)	14(1)	4(1)	2(1)	2(1)
C(3)	13(1)	19(1)	14(1)	2(1)	-1(1)	-2(1)
C(4)	19(2)	22(2)	19(2)	5(1)	0(1)	-4(1)
C(5)	19(1)	30(1)	20(1)	4(1)	4(1)	-7(1)
C(6)	14(1)	31(1)	22(1)	-2(1)	4(1)	-1(1)
C(7)	18(1)	23(1)	24(1)	2(1)	2(1)	1(1)
C(8)	17(1)	20(1)	14(1)	2(1)	3(1)	-1(1)
C(9)	23(1)	23(1)	17(1)	2(1)	1(1)	-4(1)
C(10)	17(1)	16(1)	16(1)	5(1)	3(1)	1(1)
C(11)	16(1)	14(1)	13(1)	2(1)	3(1)	3(1)
N(11)	13(1)	16(1)	19(1)	6(1)	1(1)	1(1)
O(11)	14(1)	22(1)	22(1)	9(1)	3(1)	3(1)
C(12)	15(1)	14(1)	16(1)	3(1)	5(1)	3(1)
C(13)	13(1)	18(1)	17(1)	3(1)	2(1)	1(1)
C(14)	19(1)	20(1)	15(1)	4(1)	3(1)	4(1)
C(15)	22(1)	13(1)	19(1)	4(1)	7(1)	2(1)
I(15)	30(1)	18(1)	25(1)	8(1)	7(1)	0(1)
C(16)	20(2)	15(1)	22(2)	2(1)	0(1)	-2(1)
C(17)	19(2)	20(2)	18(2)	3(1)	0(1)	2(1)
C(18)	17(1)	23(1)	22(1)	12(1)	6(1)	3(1)
C(19)	28(2)	24(1)	40(2)	15(1)	16(1)	6(1)

C(20)	27(2)	28(2)	78(3)	31(2)	20(2)	12(2)
C(21)	19(2)	52(2)	69(3)	47(2)	2(2)	2(2)
C(22)	20(2)	49(2)	39(2)	30(2)	-3(2)	-4(2)
C(23)	20(1)	36(2)	24(1)	14(1)	2(1)	3(1)
C(31)	15(1)	16(1)	16(1)	4(1)	2(1)	1(1)
O(31)	17(1)	20(1)	21(1)	6(1)	-2(1)	-2(1)
C(32)	15(1)	16(1)	16(1)	4(1)	3(1)	4(1)
C(33)	17(1)	21(1)	17(1)	1(1)	4(1)	6(1)
C(34)	23(2)	30(2)	20(2)	9(1)	4(1)	9(1)
C(35)	20(1)	36(2)	22(1)	4(1)	0(1)	12(1)
C(36)	17(1)	32(2)	26(1)	-3(1)	-2(1)	4(1)
C(37)	20(1)	23(1)	26(1)	0(1)	1(1)	1(1)
C(38)	18(2)	20(1)	16(1)	1(1)	1(1)	5(1)
C(39)	24(1)	19(1)	19(1)	2(1)	2(1)	6(1)
C(40)	16(1)	15(1)	16(1)	3(1)	1(1)	0(1)
C(41)	15(1)	14(1)	17(1)	2(1)	-1(1)	-2(1)
N(41)	13(1)	17(1)	17(1)	5(1)	3(1)	0(1)
O(41)	14(1)	23(1)	23(1)	9(1)	2(1)	0(1)
C(42)	13(1)	15(1)	15(1)	2(1)	-1(1)	-3(1)
C(43)	20(2)	16(1)	18(1)	2(1)	6(1)	-2(1)
C(44)	23(2)	18(2)	21(2)	-1(1)	5(1)	2(1)
C(45)	21(1)	14(1)	19(1)	4(1)	-1(1)	-1(1)
I(45)	32(1)	18(1)	26(1)	8(1)	1(1)	3(1)
C(46)	18(1)	20(1)	16(1)	3(1)	0(1)	-3(1)
C(47)	12(1)	18(1)	16(1)	2(1)	1(1)	-2(1)
C(48)	15(1)	19(1)	22(1)	9(1)	3(1)	6(1)
C(49)	24(1)	25(1)	24(1)	7(1)	6(1)	7(1)
C(50)	24(2)	41(2)	24(2)	15(2)	9(1)	12(1)
C(51)	20(1)	38(2)	35(2)	24(1)	5(1)	5(1)
C(52)	25(2)	30(2)	32(2)	15(1)	-1(1)	-2(1)
C(53)	22(1)	23(1)	23(1)	9(1)	2(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for JF2873FF.

	x	y	z	U(eq)
H(2)	2275	8211	2879	17(8)
H(4)	3688	8585	775	32(10)
H(5)	5922	7541	179	44(11)
H(6)	6885	5392	789	22(8)
H(7)	5567	4145	1930	23(8)
H(9A)	652	4714	1215	36(10)
H(9B)	-666	5330	1925	22(9)
H(9C)	278	3889	2181	26(9)
H(10A)	2025	6687	4281	24(9)
H(10B)	356	7140	3840	13(7)
H(11)	2343	4535	4894	30(10)
H(13)	2762	3207	6374	32(10)
H(14)	2263	1012	7085	20(8)
H(16)	-1246	-195	4776	30(9)
H(17)	-788	2044	4084	28(9)
H(19)	196	9800	2797	25(9)
H(20)	-1604	11013	1781	39(11)
H(21)	-2227	10075	-17	64(15)
H(22)	-1061	7898	-803	37(11)
H(23)	758	6706	210	32(10)
H(32)	8055	1887	6873	12(4)
H(34)	9829	1611	9153	41(11)
H(35)	12218	2754	9841	26(9)
H(36)	13132	4871	9206	42(11)
H(37)	11616	5969	7924	27(9)
H(39A)	6993	5336	8554	19(8)
H(39B)	5414	4703	7873	30(10)
H(39C)	6306	6149	7595	25(9)
H(40A)	7289	3440	5471	56(13)
H(40B)	5777	2879	5910	29(9)

H(41)	7320	5571	4829	26(9)
H(43)	4318	7852	5616	21(8)
H(44)	3612	10044	4942	32(10)
H(46)	6646	9209	2771	23(8)
H(47)	7375	7019	3462	18(8)
H(49)	6716	3218	9425	33(10)
H(50)	4917	1869	10158	37(13)
H(51)	3724	-368	9201	42(11)
H(52)	4429	-1319	7532	23(9)
H(53)	6211	32	6781	27(9)

Table 6. Torsion angles [°] for JF2873FF.

C(9)-C(1)-O(1)-C(8)	98.6(2)
C(10)-C(1)-O(1)-C(8)	-139.1(2)
C(2)-C(1)-O(1)-C(8)	-22.4(3)
O(1)-C(1)-C(2)-C(3)	23.0(2)
C(9)-C(1)-C(2)-C(3)	-93.0(2)
C(10)-C(1)-C(2)-C(3)	138.1(2)
O(1)-C(1)-C(2)-C(18)	149.7(2)
C(9)-C(1)-C(2)-C(18)	33.8(3)
C(10)-C(1)-C(2)-C(18)	-95.2(3)
C(18)-C(2)-C(3)-C(8)	-144.9(2)
C(1)-C(2)-C(3)-C(8)	-16.3(3)
C(18)-C(2)-C(3)-C(4)	40.0(4)
C(1)-C(2)-C(3)-C(4)	168.6(3)
C(8)-C(3)-C(4)-C(5)	0.0(5)
C(2)-C(3)-C(4)-C(5)	174.7(3)
C(3)-C(4)-C(5)-C(6)	-1.4(5)
C(4)-C(5)-C(6)-C(7)	1.9(4)
C(5)-C(6)-C(7)-C(8)	-0.9(4)
C(1)-O(1)-C(8)-C(7)	-169.3(3)
C(1)-O(1)-C(8)-C(3)	12.9(3)
C(6)-C(7)-C(8)-O(1)	-178.0(3)

C(6)-C(7)-C(8)-C(3)	-0.5(4)
C(4)-C(3)-C(8)-O(1)	178.8(3)
C(2)-C(3)-C(8)-O(1)	3.0(3)
C(4)-C(3)-C(8)-C(7)	0.9(4)
C(2)-C(3)-C(8)-C(7)	-174.8(3)
O(1)-C(1)-C(10)-C(11)	-78.3(3)
C(9)-C(1)-C(10)-C(11)	39.6(3)
C(2)-C(1)-C(10)-C(11)	168.7(2)
C(1)-C(10)-C(11)-O(11)	-84.5(3)
C(1)-C(10)-C(11)-N(11)	94.4(3)
O(11)-C(11)-N(11)-C(12)	3.2(4)
C(10)-C(11)-N(11)-C(12)	-175.7(2)
C(11)-N(11)-C(12)-C(17)	28.2(4)
C(11)-N(11)-C(12)-C(13)	-154.0(3)
C(17)-C(12)-C(13)-C(14)	-1.3(4)
N(11)-C(12)-C(13)-C(14)	-179.1(2)
C(12)-C(13)-C(14)-C(15)	1.1(4)
C(13)-C(14)-C(15)-C(16)	0.0(4)
C(13)-C(14)-C(15)-I(15)	-179.65(19)
C(14)-C(15)-C(16)-C(17)	-0.9(5)
I(15)-C(15)-C(16)-C(17)	178.8(3)
C(13)-C(12)-C(17)-C(16)	0.4(5)
N(11)-C(12)-C(17)-C(16)	178.2(3)
C(15)-C(16)-C(17)-C(12)	0.7(5)
C(3)-C(2)-C(18)-C(23)	38.7(4)
C(1)-C(2)-C(18)-C(23)	-81.0(3)
C(3)-C(2)-C(18)-C(19)	-136.4(3)
C(1)-C(2)-C(18)-C(19)	103.9(3)
C(23)-C(18)-C(19)-C(20)	-0.1(4)
C(2)-C(18)-C(19)-C(20)	175.1(3)
C(18)-C(19)-C(20)-C(21)	0.1(5)
C(19)-C(20)-C(21)-C(22)	0.2(5)
C(20)-C(21)-C(22)-C(23)	-0.6(5)
C(21)-C(22)-C(23)-C(18)	0.6(5)
C(19)-C(18)-C(23)-C(22)	-0.3(4)
C(2)-C(18)-C(23)-C(22)	-175.4(3)

C(39)-C(31)-O(31)-C(38)	93.0(2)
C(40)-C(31)-O(31)-C(38)	-144.1(2)
C(32)-C(31)-O(31)-C(38)	-27.2(2)
O(31)-C(31)-C(32)-C(33)	28.9(2)
C(39)-C(31)-C(32)-C(33)	-85.9(2)
C(40)-C(31)-C(32)-C(33)	144.4(2)
O(31)-C(31)-C(32)-C(48)	157.6(2)
C(39)-C(31)-C(32)-C(48)	42.8(3)
C(40)-C(31)-C(32)-C(48)	-86.9(3)
C(48)-C(32)-C(33)-C(34)	36.4(4)
C(31)-C(32)-C(33)-C(34)	165.7(3)
C(48)-C(32)-C(33)-C(38)	-150.5(2)
C(31)-C(32)-C(33)-C(38)	-21.3(3)
C(38)-C(33)-C(34)-C(35)	0.2(5)
C(32)-C(33)-C(34)-C(35)	172.5(3)
C(33)-C(34)-C(35)-C(36)	-1.8(5)
C(34)-C(35)-C(36)-C(37)	1.7(5)
C(35)-C(36)-C(37)-C(38)	0.1(4)
C(31)-O(31)-C(38)-C(37)	-167.8(3)
C(31)-O(31)-C(38)-C(33)	14.6(3)
C(36)-C(37)-C(38)-O(31)	-179.2(3)
C(36)-C(37)-C(38)-C(33)	-1.8(4)
C(34)-C(33)-C(38)-O(31)	179.4(3)
C(32)-C(33)-C(38)-O(31)	5.3(3)
C(34)-C(33)-C(38)-C(37)	1.7(5)
C(32)-C(33)-C(38)-C(37)	-172.4(3)
O(31)-C(31)-C(40)-C(41)	-82.2(3)
C(39)-C(31)-C(40)-C(41)	35.9(3)
C(32)-C(31)-C(40)-C(41)	165.6(2)
C(31)-C(40)-C(41)-O(41)	-81.9(3)
C(31)-C(40)-C(41)-N(41)	97.5(3)
O(41)-C(41)-N(41)-C(42)	3.6(5)
C(40)-C(41)-N(41)-C(42)	-175.8(2)
C(41)-N(41)-C(42)-C(43)	21.4(4)
C(41)-N(41)-C(42)-C(47)	-160.9(3)
C(47)-C(42)-C(43)-C(44)	0.6(5)

N(41)-C(42)-C(43)-C(44)	178.3(3)
C(42)-C(43)-C(44)-C(45)	0.1(5)
C(43)-C(44)-C(45)-C(46)	-0.5(5)
C(43)-C(44)-C(45)-I(45)	178.2(3)
C(44)-C(45)-C(46)-C(47)	0.1(4)
I(45)-C(45)-C(46)-C(47)	-178.50(19)
C(45)-C(46)-C(47)-C(42)	0.6(4)
C(43)-C(42)-C(47)-C(46)	-1.0(4)
N(41)-C(42)-C(47)-C(46)	-178.8(2)
C(33)-C(32)-C(48)-C(53)	-131.4(3)
C(31)-C(32)-C(48)-C(53)	108.0(3)
C(33)-C(32)-C(48)-C(49)	46.2(3)
C(31)-C(32)-C(48)-C(49)	-74.4(3)
C(53)-C(48)-C(49)-C(50)	-1.9(4)
C(32)-C(48)-C(49)-C(50)	-179.6(3)
C(48)-C(49)-C(50)-C(51)	0.3(5)
C(49)-C(50)-C(51)-C(52)	1.6(5)
C(50)-C(51)-C(52)-C(53)	-2.0(5)
C(51)-C(52)-C(53)-C(48)	0.3(5)
C(49)-C(48)-C(53)-C(52)	1.6(4)
C(32)-C(48)-C(53)-C(52)	179.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for JF2873FF [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(41)-H(41)...O(11)#1	0.88	2.01	2.860(3)	162
N(11)-H(11)...O(41)	0.88	2.06	2.890(3)	156
C(13)-H(13)...O(41)	0.95	2.57	3.320(3)	136
C(17)-H(17)...O(11)	0.95	2.34	2.858(5)	114
N(41)-H(41)...O(11)#1	0.88	2.01	2.860(3)	162
C(43)-H(43)...O(41)	0.95	2.30	2.852(4)	117

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Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

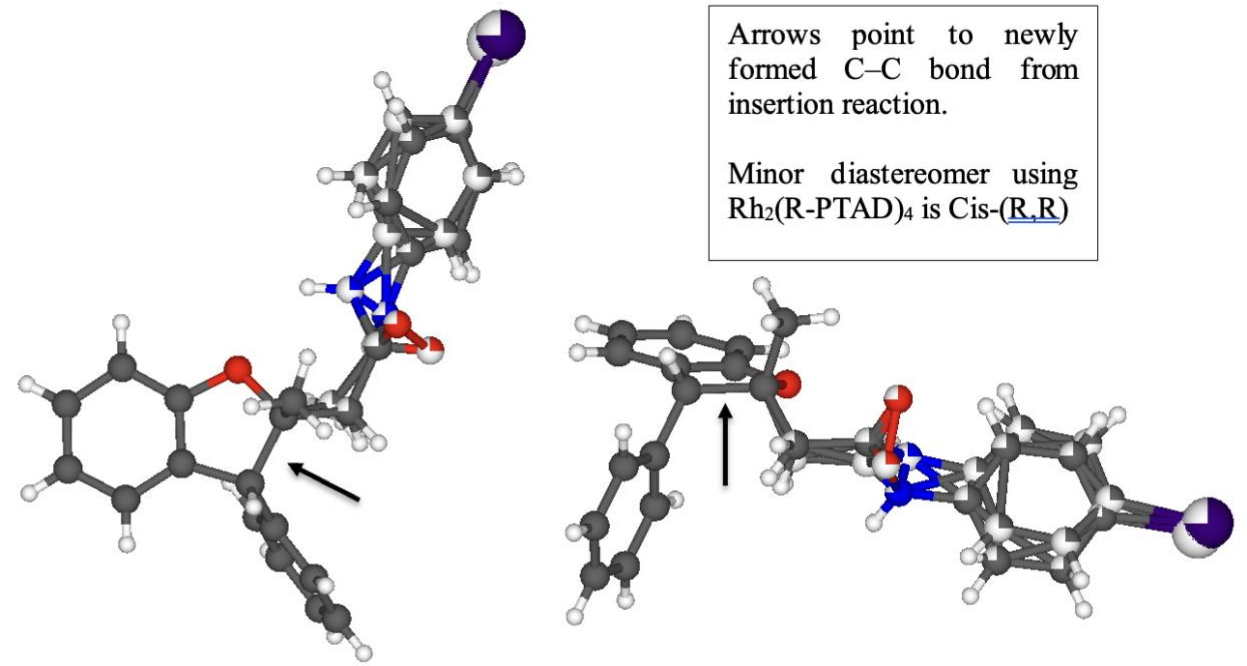


Table 1. Crystal data and structure refinement for [$C_{23}H_{20}INO_2$].

Identification code	JF2892FMI (SND-II-011-MINOR)	
Empirical formula	C23 H20 I N O2	
Formula weight	469.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 14.3788(8) Å	α= 90°.
	b = 7.5241(5) Å	β= 90°.
	c = 35.493(2) Å	γ = 90°.
Volume	3839.9(4) $Å^3$	
Z	8	
Density (calculated)	1.624 Mg/m^3	
Absorption coefficient	1.686 mm^{-1}	
F(000)	1872	
Crystal size	0.303 x 0.182 x 0.104 mm^3	
Crystal color and habit	Yellow Block	
Diffractometer	Bruker Photon100 CMOS	
Theta range for data collection	2.697 to 27.537°.	
Index ranges	-18<=h<=18, -9<=k<=9, -45<=l<=46	

Reflections collected	32003
Independent reflections	4415 [R(int) = 0.0203]
Observed reflections (I > 2sigma(I))	3980
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7785 and 0.6939
Solution method	SHELXT (Sheldrick, 2014)
Refinement method	SHELXL-2018/3 (Sheldrick, 2018) Full-matrix least-squares on F^2
Data / restraints / parameters	4415 / 22 / 334
Goodness-of-fit on F^2	1.155
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0715
R indices (all data)	R1 = 0.0403, wR2 = 0.0738
Extinction coefficient	0.00564(15)
Largest diff. peak and hole	0.758 and -0.738 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for JF2892FMI. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4736(2)	4616(4)	3501(1)	36(1)
O(1)	4978(1)	3739(3)	3857(1)	39(1)
C(2)	5137(2)	3371(4)	3182(1)	38(1)
C(3)	5812(2)	2259(4)	3404(1)	40(1)
C(4)	6474(2)	1035(4)	3287(1)	53(1)
C(5)	6983(2)	106(4)	3555(1)	59(1)
C(6)	6825(2)	390(4)	3931(1)	55(1)
C(7)	6163(2)	1615(4)	4054(1)	46(1)
C(8)	5668(2)	2518(4)	3782(1)	37(1)
C(9)	5250(2)	6377(4)	3492(1)	46(1)

C(10)	3680(3)	4938(6)	3474(1)	36(1)
C(11)	3312(3)	6057(6)	3792(1)	33(1)
N(11)	2694(2)	5241(4)	4017(1)	37(1)
O(11)	3527(2)	7630(4)	3827(1)	46(1)
C(12)	2265(2)	5991(4)	4340(1)	37(1)
C(13)	2799(2)	6861(4)	4610(1)	39(1)
C(14)	2379(2)	7560(5)	4930(1)	40(1)
C(15)	1424(2)	7390(5)	4980(1)	41(1)
C(16)	890(2)	6521(5)	4711(1)	43(1)
C(17)	1311(2)	5821(4)	4391(1)	43(1)
I(15)	789(1)	8762(2)	5447(1)	42(1)
C(10B)	3669(6)	4276(17)	3559(4)	32(2)
C(11B)	3138(10)	5541(16)	3818(3)	31(2)
N(11B)	3231(6)	5274(11)	4188(2)	30(2)
O(11B)	2721(5)	6826(10)	3689(2)	41(2)
C(12B)	2657(6)	6144(10)	4463(2)	25(2)
C(13B)	3079(4)	6803(11)	4786(2)	35(2)
C(14B)	2543(5)	7597(13)	5065(2)	29(3)
C(15B)	1585(5)	7733(13)	5021(2)	28(3)
C(16B)	1163(4)	7074(11)	4697(2)	25(2)
C(17B)	1699(6)	6280(10)	4418(2)	29(2)
I(15B)	779(3)	8308(5)	5436(1)	73(1)
C(18)	4443(2)	2259(4)	2964(1)	36(1)
C(19)	4057(2)	722(4)	3115(1)	36(1)
C(20)	3422(2)	-269(4)	2910(1)	39(1)
C(21)	3170(2)	262(4)	2552(1)	43(1)
C(22)	3548(2)	1783(4)	2398(1)	49(1)
C(23)	4182(2)	2775(4)	2602(1)	46(1)

Table 3. Bond lengths [Å] and angles [°] for JF2892FMI.

C(1)-O(1)	1.467(3)
C(1)-C(9)	1.518(4)
C(1)-C(10)	1.540(4)
C(1)-C(10B)	1.569(8)

C(1)-C(2)	1.578(4)
O(1)-C(8)	1.378(3)
C(2)-C(3)	1.503(4)
C(2)-C(18)	1.515(4)
C(2)-H(2)	1.0000
C(3)-C(8)	1.373(4)
C(3)-C(4)	1.388(4)
C(4)-C(5)	1.389(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.371(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.395(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.379(4)
C(7)-H(7)	0.9500
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.502(7)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-O(11)	1.229(5)
C(11)-N(11)	1.346(5)
N(11)-C(12)	1.418(4)
N(11)-H(11)	0.8800
C(12)-C(13)	1.3900
C(12)-C(17)	1.3900
C(13)-C(14)	1.3900
C(13)-H(13)	0.9500
C(14)-C(15)	1.3900
C(14)-H(14)	0.9500
C(15)-C(16)	1.3900
C(15)-I(15)	2.155(3)
C(16)-C(17)	1.3900
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500

C(10B)-C(11B)	1.529(18)
C(10B)-H(10C)	0.9900
C(10B)-H(10D)	0.9900
C(11B)-O(11B)	1.227(10)
C(11B)-N(11B)	1.335(9)
N(11B)-C(12B)	1.434(7)
N(11B)-H(11B)	0.8800
C(12B)-C(13B)	1.3900
C(12B)-C(17B)	1.3900
C(13B)-C(14B)	1.3900
C(13B)-H(13B)	0.9500
C(14B)-C(15B)	1.3900
C(14B)-H(14B)	0.9500
C(15B)-C(16B)	1.3900
C(15B)-I(15B)	1.925(6)
C(16B)-C(17B)	1.3900
C(16B)-H(16B)	0.9500
C(17B)-H(17B)	0.9500
C(18)-C(19)	1.391(4)
C(18)-C(23)	1.392(4)
C(19)-C(20)	1.387(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.380(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.379(5)
C(21)-H(21)	0.9500
C(22)-C(23)	1.382(4)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500

O(1)-C(1)-C(9)	107.2(2)
O(1)-C(1)-C(10)	110.9(3)
C(9)-C(1)-C(10)	110.0(3)
O(1)-C(1)-C(10B)	92.6(5)
C(9)-C(1)-C(10B)	128.4(5)
O(1)-C(1)-C(2)	105.3(2)

C(9)-C(1)-C(2)	109.0(2)
C(10)-C(1)-C(2)	114.2(3)
C(10B)-C(1)-C(2)	110.7(6)
C(8)-O(1)-C(1)	107.7(2)
C(3)-C(2)-C(18)	112.7(2)
C(3)-C(2)-C(1)	101.0(2)
C(18)-C(2)-C(1)	117.0(2)
C(3)-C(2)-H(2)	108.6
C(18)-C(2)-H(2)	108.6
C(1)-C(2)-H(2)	108.6
C(8)-C(3)-C(4)	119.3(3)
C(8)-C(3)-C(2)	109.6(2)
C(4)-C(3)-C(2)	131.0(3)
C(3)-C(4)-C(5)	119.5(3)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
C(6)-C(5)-C(4)	120.0(3)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	121.4(3)
C(5)-C(6)-H(6)	119.3
C(7)-C(6)-H(6)	119.3
C(8)-C(7)-C(6)	117.3(3)
C(8)-C(7)-H(7)	121.4
C(6)-C(7)-H(7)	121.4
C(3)-C(8)-O(1)	113.1(3)
C(3)-C(8)-C(7)	122.5(3)
O(1)-C(8)-C(7)	124.4(3)
C(1)-C(9)-H(9A)	109.5
C(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(1)	113.0(3)
C(11)-C(10)-H(10A)	109.0

C(1)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10B)	109.0
C(1)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
O(11)-C(11)-N(11)	123.1(4)
O(11)-C(11)-C(10)	121.8(4)
N(11)-C(11)-C(10)	115.0(4)
C(11)-N(11)-C(12)	125.9(3)
C(11)-N(11)-H(11)	117.1
C(12)-N(11)-H(11)	117.1
C(13)-C(12)-C(17)	120.0
C(13)-C(12)-N(11)	120.2(3)
C(17)-C(12)-N(11)	119.8(3)
C(14)-C(13)-C(12)	120.0
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	120.0
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.0
C(14)-C(15)-I(15)	118.27(18)
C(16)-C(15)-I(15)	121.34(19)
C(17)-C(16)-C(15)	120.0
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(12)	120.0
C(16)-C(17)-H(17)	120.0
C(12)-C(17)-H(17)	120.0
C(11B)-C(10B)-C(1)	117.8(10)
C(11B)-C(10B)-H(10C)	107.9
C(1)-C(10B)-H(10C)	107.9
C(11B)-C(10B)-H(10D)	107.9
C(1)-C(10B)-H(10D)	107.9
H(10C)-C(10B)-H(10D)	107.2
O(11B)-C(11B)-N(11B)	122.4(12)
O(11B)-C(11B)-C(10B)	120.5(10)

N(11B)-C(11B)-C(10B)	116.7(9)
C(11B)-N(11B)-C(12B)	122.8(9)
C(11B)-N(11B)-H(11B)	118.6
C(12B)-N(11B)-H(11B)	118.6
C(13B)-C(12B)-C(17B)	120.0
C(13B)-C(12B)-N(11B)	118.2(7)
C(17B)-C(12B)-N(11B)	121.8(7)
C(12B)-C(13B)-C(14B)	120.0
C(12B)-C(13B)-H(13B)	120.0
C(14B)-C(13B)-H(13B)	120.0
C(13B)-C(14B)-C(15B)	120.0
C(13B)-C(14B)-H(14B)	120.0
C(15B)-C(14B)-H(14B)	120.0
C(16B)-C(15B)-C(14B)	120.0
C(16B)-C(15B)-I(15B)	116.7(5)
C(14B)-C(15B)-I(15B)	121.8(5)
C(15B)-C(16B)-C(17B)	120.0
C(15B)-C(16B)-H(16B)	120.0
C(17B)-C(16B)-H(16B)	120.0
C(16B)-C(17B)-C(12B)	120.0
C(16B)-C(17B)-H(17B)	120.0
C(12B)-C(17B)-H(17B)	120.0
C(19)-C(18)-C(23)	118.8(3)
C(19)-C(18)-C(2)	121.5(2)
C(23)-C(18)-C(2)	119.7(3)
C(20)-C(19)-C(18)	120.4(3)
C(20)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(21)-C(20)-C(19)	120.1(3)
C(21)-C(20)-H(20)	119.9
C(19)-C(20)-H(20)	119.9
C(22)-C(21)-C(20)	120.0(3)
C(22)-C(21)-H(21)	120.0
C(20)-C(21)-H(21)	120.0
C(21)-C(22)-C(23)	120.1(3)
C(21)-C(22)-H(22)	120.0

C(23)-C(22)-H(22)	120.0
C(22)-C(23)-C(18)	120.7(3)
C(22)-C(23)-H(23)	119.7
C(18)-C(23)-H(23)	119.7

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for JF2892FMI. The anisotropic displacement factor exponent takes the form: -2□^{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}
C(1)	35(1)	36(1)	38(1)	-9(1)	-2(1)	-1(1)
O(1)	37(1)	38(1)	41(1)	2(1)	10(1)	5(1)
C(2)	40(1)	33(1)	43(2)	-9(1)	10(1)	-9(1)
C(3)	30(1)	33(1)	56(2)	-13(1)	5(1)	-7(1)
C(4)	36(2)	46(2)	77(2)	-31(2)	9(2)	-6(1)
C(5)	31(2)	41(2)	104(3)	-26(2)	2(2)	2(1)
C(6)	34(2)	35(2)	95(3)	0(2)	-1(2)	-1(1)
C(7)	38(2)	41(2)	60(2)	7(1)	5(1)	-1(1)
C(8)	27(1)	31(1)	54(2)	-3(1)	9(1)	-2(1)
C(9)	69(2)	30(1)	38(1)	-5(1)	-7(1)	-2(1)
C(10)	35(2)	34(3)	39(2)	0(2)	-8(2)	1(2)
C(11)	23(2)	34(3)	41(2)	6(2)	-3(1)	-1(2)
N(11)	39(2)	35(2)	38(2)	5(1)	-7(2)	-10(1)
O(11)	39(1)	28(1)	71(2)	3(1)	16(1)	2(1)
C(12)	29(2)	38(2)	44(2)	10(2)	-8(2)	-8(2)
C(13)	35(2)	39(3)	43(3)	16(2)	-7(2)	-2(2)
C(14)	43(2)	40(2)	37(3)	5(2)	-13(2)	-6(2)
C(15)	38(2)	46(3)	40(3)	6(2)	-5(2)	3(2)
C(16)	33(2)	51(3)	46(2)	4(2)	-11(2)	-1(2)
C(17)	39(3)	44(3)	47(2)	4(2)	-18(2)	-7(2)
I(15)	37(1)	59(1)	29(1)	-5(1)	-4(1)	9(1)
C(10B)	31(3)	31(4)	35(4)	-1(3)	-8(3)	9(3)

C(11B)	22(4)	32(4)	40(3)	2(3)	-2(3)	-3(3)
N(11B)	29(4)	31(4)	31(4)	0(3)	2(3)	10(3)
O(11B)	50(4)	34(3)	39(3)	-2(3)	9(3)	17(3)
C(12B)	20(5)	12(5)	43(7)	-3(4)	10(5)	1(4)
C(13B)	39(6)	28(5)	40(6)	15(5)	2(5)	14(5)
C(14B)	28(5)	37(6)	22(5)	-2(5)	-2(4)	2(4)
C(15B)	38(7)	16(5)	31(6)	2(4)	-2(5)	-5(5)
C(16B)	20(5)	29(6)	27(5)	-8(4)	-3(4)	-1(4)
C(17B)	39(7)	23(5)	24(4)	-6(4)	-10(5)	5(5)
I(15B)	82(2)	77(2)	61(1)	12(1)	-11(1)	18(1)
C(18)	46(2)	30(1)	31(1)	-5(1)	3(1)	-4(1)
C(19)	41(1)	35(1)	31(1)	0(1)	-2(1)	-3(1)
C(20)	39(1)	29(1)	49(2)	-1(1)	-4(1)	-1(1)
C(21)	48(2)	41(2)	41(2)	-13(1)	-12(1)	7(1)
C(22)	69(2)	49(2)	30(1)	-3(1)	-8(1)	13(2)
C(23)	67(2)	34(1)	36(1)	4(1)	4(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for JF2892FMI.

	x	y	z	U(eq)
H(2)	5495	4118	3000	40(8)
H(4)	6578	834	3026	52(10)
H(5)	7442	-727	3477	64(11)
H(6)	7173	-261	4111	61(11)
H(7)	6058	1819	4315	43(9)
H(9A)	5072	7091	3711	56(10)
H(9B)	5089	7019	3261	64(11)
H(9C)	5922	6159	3498	59(11)
H(10A)	3540	5532	3232	43

H(10B)	3356	3778	3476	43
H(11)	2541	4141	3959	45
H(13)	3452	6977	4575	47
H(14)	2744	8155	5114	48
H(16)	238	6404	4745	52
H(17)	946	5227	4207	52
H(10C)	3367	4310	3308	39
H(10D)	3592	3056	3658	39
H(11B)	3662	4534	4267	36
H(13B)	3734	6710	4817	43
H(14B)	2831	8047	5287	35
H(16B)	509	7167	4667	30
H(17B)	1411	5830	4197	35
H(19)	4230	349	3361	40(8)
H(20)	3160	-1315	3015	39(8)
H(21)	2736	-421	2411	53(10)
H(22)	3373	2149	2152	56(10)
H(23)	4441	3819	2494	59(10)

Table 6. Torsion angles [°] for JF2892FMI.

C(9)-C(1)-O(1)-C(8)	-98.7(3)
C(10)-C(1)-O(1)-C(8)	141.3(3)
C(10B)-C(1)-O(1)-C(8)	129.6(5)
C(2)-C(1)-O(1)-C(8)	17.3(3)
O(1)-C(1)-C(2)-C(3)	-17.3(3)
C(9)-C(1)-C(2)-C(3)	97.5(3)
C(10)-C(1)-C(2)-C(3)	-139.2(3)
C(10B)-C(1)-C(2)-C(3)	-116.2(5)
O(1)-C(1)-C(2)-C(18)	105.4(3)
C(9)-C(1)-C(2)-C(18)	-139.8(3)
C(10)-C(1)-C(2)-C(18)	-16.5(4)
C(10B)-C(1)-C(2)-C(18)	6.5(6)
C(18)-C(2)-C(3)-C(8)	-113.8(3)

C(1)-C(2)-C(3)-C(8)	11.9(3)
C(18)-C(2)-C(3)-C(4)	62.6(4)
C(1)-C(2)-C(3)-C(4)	-171.7(3)
C(8)-C(3)-C(4)-C(5)	-0.5(4)
C(2)-C(3)-C(4)-C(5)	-176.6(3)
C(3)-C(4)-C(5)-C(6)	0.6(5)
C(4)-C(5)-C(6)-C(7)	-0.6(5)
C(5)-C(6)-C(7)-C(8)	0.6(5)
C(4)-C(3)-C(8)-O(1)	-178.6(2)
C(2)-C(3)-C(8)-O(1)	-1.7(3)
C(4)-C(3)-C(8)-C(7)	0.5(4)
C(2)-C(3)-C(8)-C(7)	177.4(3)
C(1)-O(1)-C(8)-C(3)	-10.3(3)
C(1)-O(1)-C(8)-C(7)	170.5(3)
C(6)-C(7)-C(8)-C(3)	-0.5(4)
C(6)-C(7)-C(8)-O(1)	178.5(3)
O(1)-C(1)-C(10)-C(11)	58.6(4)
C(9)-C(1)-C(10)-C(11)	-59.8(4)
C(2)-C(1)-C(10)-C(11)	177.3(3)
C(1)-C(10)-C(11)-O(11)	66.8(5)
C(1)-C(10)-C(11)-N(11)	-116.9(4)
O(11)-C(11)-N(11)-C(12)	-5.6(7)
C(10)-C(11)-N(11)-C(12)	178.2(3)
C(11)-N(11)-C(12)-C(13)	-48.3(5)
C(11)-N(11)-C(12)-C(17)	133.1(4)
C(17)-C(12)-C(13)-C(14)	0.0
N(11)-C(12)-C(13)-C(14)	-178.6(3)
C(12)-C(13)-C(14)-C(15)	0.0
C(13)-C(14)-C(15)-C(16)	0.0
C(13)-C(14)-C(15)-I(15)	-172.9(3)
C(14)-C(15)-C(16)-C(17)	0.0
I(15)-C(15)-C(16)-C(17)	172.7(3)
C(15)-C(16)-C(17)-C(12)	0.0
C(13)-C(12)-C(17)-C(16)	0.0
N(11)-C(12)-C(17)-C(16)	178.6(3)
O(1)-C(1)-C(10B)-C(11B)	80.7(9)

C(9)-C(1)-C(10B)-C(11B)	-33.7(12)
C(2)-C(1)-C(10B)-C(11B)	-171.8(7)
C(1)-C(10B)-C(11B)-O(11B)	94.8(15)
C(1)-C(10B)-C(11B)-N(11B)	-78.7(14)
O(11B)-C(11B)-N(11B)-C(12B)	18(2)
C(10B)-C(11B)-N(11B)-C(12B)	-169.0(9)
C(11B)-N(11B)-C(12B)-C(13B)	-137.6(10)
C(11B)-N(11B)-C(12B)-C(17B)	44.8(13)
C(17B)-C(12B)-C(13B)-C(14B)	0.0
N(11B)-C(12B)-C(13B)-C(14B)	-177.6(8)
C(12B)-C(13B)-C(14B)-C(15B)	0.0
C(13B)-C(14B)-C(15B)-C(16B)	0.0
C(13B)-C(14B)-C(15B)-I(15B)	165.6(7)
C(14B)-C(15B)-C(16B)-C(17B)	0.0
I(15B)-C(15B)-C(16B)-C(17B)	-166.3(7)
C(15B)-C(16B)-C(17B)-C(12B)	0.0
C(13B)-C(12B)-C(17B)-C(16B)	0.0
N(11B)-C(12B)-C(17B)-C(16B)	177.6(8)
C(3)-C(2)-C(18)-C(19)	39.2(4)
C(1)-C(2)-C(18)-C(19)	-77.2(4)
C(3)-C(2)-C(18)-C(23)	-140.7(3)
C(1)-C(2)-C(18)-C(23)	102.8(3)
C(23)-C(18)-C(19)-C(20)	-0.2(4)
C(2)-C(18)-C(19)-C(20)	179.8(3)
C(18)-C(19)-C(20)-C(21)	0.2(4)
C(19)-C(20)-C(21)-C(22)	-0.2(4)
C(20)-C(21)-C(22)-C(23)	0.2(5)
C(21)-C(22)-C(23)-C(18)	-0.2(5)
C(19)-C(18)-C(23)-C(22)	0.3(5)
C(2)-C(18)-C(23)-C(22)	-179.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for JF2892FMI [Å and °].

_

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9A)...O(11)	0.98	2.29	2.906(4)	120
C(9)-H(9A)...I(15)#1	0.98	3.23	3.847(3)	123
C(9)-H(9A)...I(15B)#1	0.98	3.21	3.887(5)	128
N(11)-H(11)...O(11)#2	0.88	1.97	2.719(4)	143
C(17)-H(17)...O(11)#2	0.95	2.49	3.135(4)	125
N(11B)-H(11B)...O(1)	0.88	2.46	3.005(7)	121
C(13B)-H(13B)...I(15B)#1	0.95	3.07	3.962(7)	156

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,-z+1   #2 -x+1/2,y-1/2,z

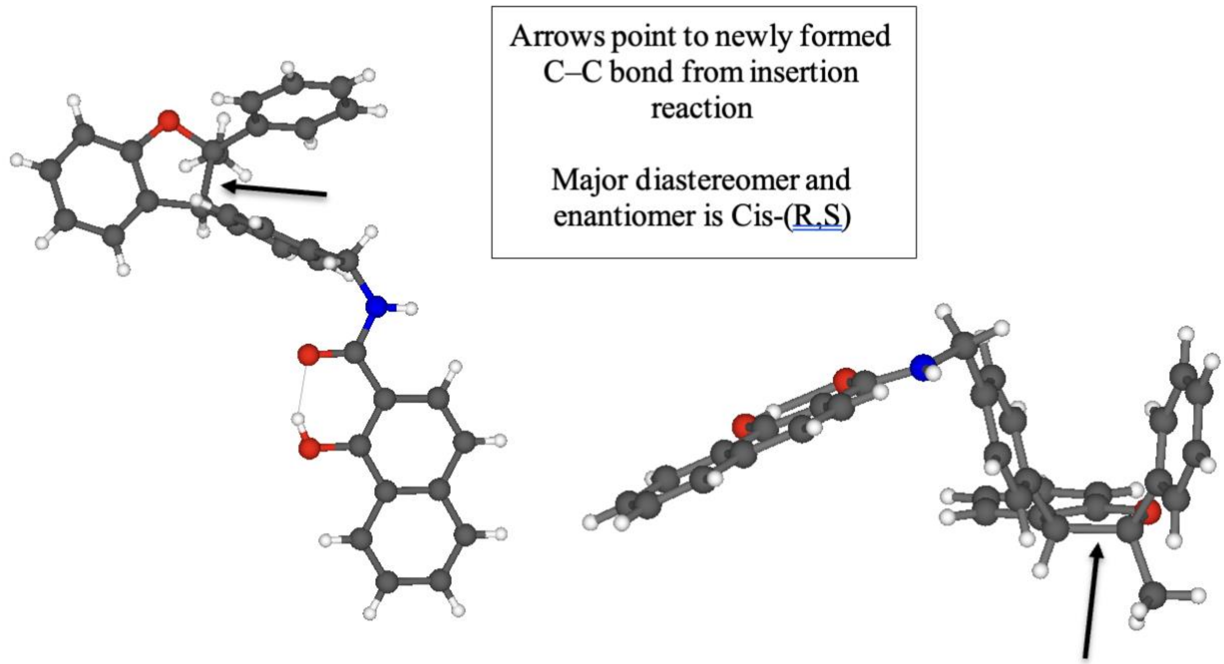


Table 1. Crystal data and structure refinement for [$C_{33}H_{27}NO_3$].

Identification code	JF2920F (SND-II-110B)	
Empirical formula	C33 H27 N O3	
Formula weight	485.55	
Temperature	90(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 6.3151(4) Å	α= 85.4422(16)°.
	b = 11.1980(7) Å	β= 85.4490(17)°.
	c = 17.7567(10) Å	γ = 86.8128(17)°.
Volume	1246.24(13) Å^3	
Z	2	
Density (calculated)	1.294 Mg/m^3	
Absorption coefficient	0.653 mm^{-1}	
F(000)	512	
Crystal size	0.491 x 0.283 x 0.110 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Bruker APEX-II CCD	
Theta range for data collection	2.503 to 69.434°.	

Index ranges	-7<=h<=6, -13<=k<=13, -21<=l<=21
Reflections collected	20993
Independent reflections	8303 [R(int) = 0.0229]
Observed reflections (I > 2sigma(I))	8280
Completeness to theta = 67.679°	95.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8692 and 0.7714
Solution method	SHELXT (Sheldrick, 2014)
Refinement method	SHELXL-2018/3 (Sheldrick, 2018) Full-matrix least-squares on F^2
Data / restraints / parameters	8303 / 3 / 883
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0289, wR2 = 0.0778
R indices (all data)	R1 = 0.0290, wR2 = 0.0778
Absolute structure parameter	0.05(8)
Largest diff. peak and hole	0.149 and -0.168 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for JF2920F. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9249(4)	2914(2)	9207(1)	28(1)
O(1)	11134(3)	2411(1)	9571(1)	35(1)
C(2)	8885(4)	2048(2)	8559(1)	26(1)
C(3)	10528(4)	1048(2)	8716(1)	27(1)
C(4)	11002(4)	-18(2)	8374(1)	33(1)
C(5)	12670(4)	-776(2)	8625(1)	37(1)
C(6)	13829(4)	-479(2)	9210(1)	35(1)
C(7)	13367(4)	584(2)	9557(1)	33(1)
C(8)	11721(4)	1328(2)	9294(1)	30(1)
C(9)	9747(4)	4175(2)	8900(1)	30(1)
C(10)	11788(5)	4427(2)	8604(1)	41(1)

C(11)	12211(7)	5542(3)	8245(2)	62(1)
C(12)	10633(7)	6421(3)	8175(2)	69(1)
C(13)	8599(7)	6204(3)	8486(2)	63(1)
C(14)	8143(5)	5082(2)	8847(1)	41(1)
C(15)	7408(4)	2861(2)	9813(1)	38(1)
C(16)	9057(3)	2636(2)	7759(1)	25(1)
C(17)	7281(4)	3251(2)	7468(1)	29(1)
C(18)	7417(4)	3882(2)	6761(1)	30(1)
C(19)	9333(3)	3910(2)	6321(1)	26(1)
C(20)	11099(3)	3271(2)	6602(1)	26(1)
C(21)	10960(3)	2649(2)	7307(1)	27(1)
C(22)	9589(4)	4634(2)	5566(1)	28(1)
N(22)	7764(3)	4643(2)	5110(1)	26(1)
C(23)	7299(3)	3652(2)	4797(1)	22(1)
O(23)	8430(2)	2704(1)	4908(1)	27(1)
C(24)	5454(3)	3668(2)	4335(1)	23(1)
C(25)	4915(3)	2589(2)	4074(1)	22(1)
O(25)	6097(2)	1564(1)	4209(1)	27(1)
C(26)	3082(3)	2541(2)	3660(1)	24(1)
C(27)	2426(3)	1448(2)	3422(1)	27(1)
C(28)	624(4)	1430(2)	3044(1)	30(1)
C(29)	-587(4)	2502(2)	2872(1)	30(1)
C(30)	37(4)	3571(2)	3085(1)	29(1)
C(31)	1863(3)	3620(2)	3490(1)	24(1)
C(32)	2494(4)	4717(2)	3734(1)	27(1)
C(33)	4210(3)	4734(2)	4147(1)	26(1)
C(41)	7684(3)	7482(2)	710(1)	25(1)
O(41)	6018(2)	7058(1)	277(1)	27(1)
C(42)	7997(3)	6468(2)	1380(1)	25(1)
C(43)	6206(3)	5671(2)	1302(1)	25(1)
C(44)	5464(4)	4681(2)	1749(1)	29(1)
C(45)	3831(4)	4054(2)	1504(1)	32(1)
C(46)	2978(4)	4401(2)	818(1)	32(1)
C(47)	3673(4)	5402(2)	373(1)	29(1)
C(48)	5253(3)	6033(2)	639(1)	25(1)
C(49)	6903(3)	8675(2)	1001(1)	25(1)

C(50)	4786(4)	8865(2)	1261(1)	30(1)
C(51)	4097(4)	9901(2)	1604(1)	36(1)
C(52)	5519(5)	10769(2)	1683(1)	40(1)
C(53)	7612(4)	10608(2)	1407(1)	38(1)
C(54)	8309(4)	9567(2)	1072(1)	32(1)
C(55)	9642(4)	7565(2)	161(1)	32(1)
C(56)	8128(3)	6931(2)	2156(1)	23(1)
C(57)	6341(3)	7065(2)	2657(1)	25(1)
C(58)	6468(3)	7541(2)	3349(1)	26(1)
C(59)	8392(3)	7897(2)	3564(1)	24(1)
C(60)	10192(3)	7763(2)	3063(1)	26(1)
C(61)	10061(3)	7275(2)	2374(1)	26(1)
C(62)	8598(4)	8366(2)	4332(1)	28(1)
N(62)	6601(3)	8842(2)	4689(1)	26(1)
C(63)	5270(3)	8152(2)	5133(1)	25(1)
O(63)	5682(3)	7040(1)	5236(1)	29(1)
C(64)	3315(3)	8724(2)	5486(1)	24(1)
C(65)	1884(3)	8018(2)	5933(1)	25(1)
O(65)	2253(3)	6827(1)	6082(1)	32(1)
C(66)	-59(4)	8530(2)	6261(1)	27(1)
C(67)	-1594(4)	7820(2)	6681(1)	33(1)
C(68)	-3440(4)	8348(2)	6983(1)	38(1)
C(69)	-3835(4)	9599(2)	6889(1)	37(1)
C(70)	-2393(4)	10305(2)	6480(1)	33(1)
C(71)	-475(4)	9794(2)	6146(1)	28(1)
C(72)	1021(4)	10503(2)	5702(1)	29(1)
C(73)	2827(4)	9984(2)	5380(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for JF2920F.

C(1)-O(1)	1.464(3)
C(1)-C(9)	1.513(3)
C(1)-C(15)	1.521(3)
C(1)-C(2)	1.600(3)
O(1)-C(8)	1.366(3)

C(2)-C(3)	1.508(3)
C(2)-C(16)	1.516(3)
C(2)-H(2)	1.00(3)
C(3)-C(8)	1.384(3)
C(3)-C(4)	1.390(3)
C(4)-C(5)	1.393(3)
C(4)-H(4)	1.02(3)
C(5)-C(6)	1.389(4)
C(5)-H(5)	0.97(4)
C(6)-C(7)	1.390(3)
C(6)-H(6)	1.00(3)
C(7)-C(8)	1.383(3)
C(7)-H(7)	0.99(3)
C(9)-C(10)	1.388(4)
C(9)-C(14)	1.397(3)
C(10)-C(11)	1.385(4)
C(10)-H(10)	1.00(4)
C(11)-C(12)	1.367(6)
C(11)-H(11)	1.04(5)
C(12)-C(13)	1.384(6)
C(12)-H(12)	0.98(4)
C(13)-C(14)	1.398(4)
C(13)-H(13)	1.01(4)
C(14)-H(14)	0.98(3)
C(15)-H(15A)	0.99(3)
C(15)-H(15B)	1.02(4)
C(15)-H(15C)	1.00(3)
C(16)-C(21)	1.391(3)
C(16)-C(17)	1.396(3)
C(17)-C(18)	1.389(3)
C(17)-H(17)	1.03(3)
C(18)-C(19)	1.389(3)
C(18)-H(18)	1.02(3)
C(19)-C(20)	1.395(3)
C(19)-C(22)	1.512(3)
C(20)-C(21)	1.383(3)

C(20)-H(20)	0.97(3)
C(21)-H(21)	0.95(3)
C(22)-N(22)	1.459(3)
C(22)-H(22A)	1.02(3)
C(22)-H(22B)	0.99(3)
N(22)-C(23)	1.338(3)
N(22)-H(22)	0.90(3)
C(23)-O(23)	1.257(2)
C(23)-C(24)	1.475(3)
C(24)-C(25)	1.396(3)
C(24)-C(33)	1.425(3)
C(25)-O(25)	1.351(2)
C(25)-C(26)	1.425(3)
O(25)-H(25A)	0.97(4)
C(26)-C(27)	1.419(3)
C(26)-C(31)	1.421(3)
C(27)-C(28)	1.367(3)
C(27)-H(27)	0.95(3)
C(28)-C(29)	1.412(3)
C(28)-H(28)	0.95(3)
C(29)-C(30)	1.371(3)
C(29)-H(29)	0.97(3)
C(30)-C(31)	1.413(3)
C(30)-H(30)	1.01(3)
C(31)-C(32)	1.422(3)
C(32)-C(33)	1.358(3)
C(32)-H(32)	0.97(3)
C(33)-H(33)	0.96(3)
C(41)-O(41)	1.471(2)
C(41)-C(49)	1.513(3)
C(41)-C(55)	1.515(3)
C(41)-C(42)	1.595(3)
O(41)-C(48)	1.363(3)
C(42)-C(43)	1.501(3)
C(42)-C(56)	1.519(3)
C(42)-H(42)	1.03(3)

C(43)-C(48)	1.386(3)
C(43)-C(44)	1.392(3)
C(44)-C(45)	1.394(3)
C(44)-H(44)	1.01(3)
C(45)-C(46)	1.390(3)
C(45)-H(45)	0.95(3)
C(46)-C(47)	1.390(3)
C(46)-H(46)	1.02(3)
C(47)-C(48)	1.388(3)
C(47)-H(47)	0.97(3)
C(49)-C(50)	1.390(3)
C(49)-C(54)	1.393(3)
C(50)-C(51)	1.386(3)
C(50)-H(50)	0.98(3)
C(51)-C(52)	1.382(4)
C(51)-H(51)	0.96(3)
C(52)-C(53)	1.381(4)
C(52)-H(52)	0.96(4)
C(53)-C(54)	1.384(3)
C(53)-H(53)	1.03(3)
C(54)-H(54)	1.02(3)
C(55)-H(55A)	0.96(3)
C(55)-H(55B)	1.03(3)
C(55)-H(55C)	0.99(3)
C(56)-C(57)	1.390(3)
C(56)-C(61)	1.393(3)
C(57)-C(58)	1.388(3)
C(57)-H(57)	0.98(3)
C(58)-C(59)	1.390(3)
C(58)-H(58)	0.97(3)
C(59)-C(60)	1.396(3)
C(59)-C(62)	1.517(3)
C(60)-C(61)	1.390(3)
C(60)-H(60)	0.99(3)
C(61)-H(61)	0.99(3)
C(62)-N(62)	1.459(3)

C(62)-H(62A)	0.91(3)
C(62)-H(62B)	1.00(3)
N(62)-C(63)	1.341(3)
N(62)-H(62)	0.88(3)
C(63)-O(63)	1.260(2)
C(63)-C(64)	1.476(3)
C(64)-C(65)	1.391(3)
C(64)-C(73)	1.428(3)
C(65)-O(65)	1.350(2)
C(65)-C(66)	1.427(3)
O(65)-H(65A)	0.93(3)
C(66)-C(67)	1.416(3)
C(66)-C(71)	1.426(3)
C(67)-C(68)	1.368(4)
C(67)-H(67)	0.99(3)
C(68)-C(69)	1.408(4)
C(68)-H(68)	0.95(3)
C(69)-C(70)	1.366(4)
C(69)-H(69)	1.00(3)
C(70)-C(71)	1.417(3)
C(70)-H(70)	0.99(3)
C(71)-C(72)	1.419(3)
C(72)-C(73)	1.356(3)
C(72)-H(72)	0.97(3)
C(73)-H(73)	0.98(3)

O(1)-C(1)-C(9)	106.48(17)
O(1)-C(1)-C(15)	106.49(18)
C(9)-C(1)-C(15)	113.79(19)
O(1)-C(1)-C(2)	106.00(16)
C(9)-C(1)-C(2)	113.26(16)
C(15)-C(1)-C(2)	110.21(18)
C(8)-O(1)-C(1)	108.90(16)
C(3)-C(2)-C(16)	114.95(17)
C(3)-C(2)-C(1)	101.12(16)
C(16)-C(2)-C(1)	114.90(16)

C(3)-C(2)-H(2)	110.9(15)
C(16)-C(2)-H(2)	108.5(15)
C(1)-C(2)-H(2)	106.1(15)
C(8)-C(3)-C(4)	119.3(2)
C(8)-C(3)-C(2)	109.76(18)
C(4)-C(3)-C(2)	131.0(2)
C(3)-C(4)-C(5)	118.8(2)
C(3)-C(4)-H(4)	120.2(16)
C(5)-C(4)-H(4)	120.9(16)
C(6)-C(5)-C(4)	120.8(2)
C(6)-C(5)-H(5)	118(2)
C(4)-C(5)-H(5)	121(2)
C(5)-C(6)-C(7)	120.9(2)
C(5)-C(6)-H(6)	119.1(17)
C(7)-C(6)-H(6)	119.9(17)
C(8)-C(7)-C(6)	117.3(2)
C(8)-C(7)-H(7)	121.7(18)
C(6)-C(7)-H(7)	120.9(18)
O(1)-C(8)-C(7)	123.4(2)
O(1)-C(8)-C(3)	113.66(19)
C(7)-C(8)-C(3)	122.9(2)
C(10)-C(9)-C(14)	118.5(2)
C(10)-C(9)-C(1)	120.2(2)
C(14)-C(9)-C(1)	121.1(2)
C(11)-C(10)-C(9)	120.7(3)
C(11)-C(10)-H(10)	123(2)
C(9)-C(10)-H(10)	116(2)
C(12)-C(11)-C(10)	120.9(3)
C(12)-C(11)-H(11)	121(3)
C(10)-C(11)-H(11)	118(3)
C(11)-C(12)-C(13)	119.4(3)
C(11)-C(12)-H(12)	122(2)
C(13)-C(12)-H(12)	118(2)
C(12)-C(13)-C(14)	120.4(3)
C(12)-C(13)-H(13)	124(2)
C(14)-C(13)-H(13)	116(2)

C(9)-C(14)-C(13)	120.0(3)
C(9)-C(14)-H(14)	117.5(17)
C(13)-C(14)-H(14)	122.4(17)
C(1)-C(15)-H(15A)	108.4(19)
C(1)-C(15)-H(15B)	108.7(19)
H(15A)-C(15)-H(15B)	110(3)
C(1)-C(15)-H(15C)	111.2(19)
H(15A)-C(15)-H(15C)	107(3)
H(15B)-C(15)-H(15C)	111(3)
C(21)-C(16)-C(17)	117.61(19)
C(21)-C(16)-C(2)	122.64(19)
C(17)-C(16)-C(2)	119.66(18)
C(18)-C(17)-C(16)	121.3(2)
C(18)-C(17)-H(17)	119.4(16)
C(16)-C(17)-H(17)	119.3(16)
C(17)-C(18)-C(19)	120.6(2)
C(17)-C(18)-H(18)	121.8(16)
C(19)-C(18)-H(18)	117.5(16)
C(18)-C(19)-C(20)	118.16(18)
C(18)-C(19)-C(22)	122.63(19)
C(20)-C(19)-C(22)	119.18(19)
C(21)-C(20)-C(19)	121.03(19)
C(21)-C(20)-H(20)	121.5(17)
C(19)-C(20)-H(20)	117.4(17)
C(20)-C(21)-C(16)	121.2(2)
C(20)-C(21)-H(21)	121.0(16)
C(16)-C(21)-H(21)	117.8(16)
N(22)-C(22)-C(19)	114.48(18)
N(22)-C(22)-H(22A)	107.4(16)
C(19)-C(22)-H(22A)	109.7(16)
N(22)-C(22)-H(22B)	109.6(15)
C(19)-C(22)-H(22B)	107.5(14)
H(22A)-C(22)-H(22B)	108(2)
C(23)-N(22)-C(22)	120.43(17)
C(23)-N(22)-H(22)	121.8(19)
C(22)-N(22)-H(22)	117.6(19)

O(23)-C(23)-N(22)	119.40(19)
O(23)-C(23)-C(24)	120.42(17)
N(22)-C(23)-C(24)	120.17(17)
C(25)-C(24)-C(33)	118.97(18)
C(25)-C(24)-C(23)	118.30(17)
C(33)-C(24)-C(23)	122.72(17)
O(25)-C(25)-C(24)	121.24(18)
O(25)-C(25)-C(26)	118.08(16)
C(24)-C(25)-C(26)	120.68(17)
C(25)-O(25)-H(25A)	103.4(19)
C(27)-C(26)-C(31)	119.2(2)
C(27)-C(26)-C(25)	122.07(18)
C(31)-C(26)-C(25)	118.76(17)
C(28)-C(27)-C(26)	120.5(2)
C(28)-C(27)-H(27)	122.9(19)
C(26)-C(27)-H(27)	116.6(19)
C(27)-C(28)-C(29)	120.5(2)
C(27)-C(28)-H(28)	119.6(18)
C(29)-C(28)-H(28)	119.9(18)
C(30)-C(29)-C(28)	120.1(2)
C(30)-C(29)-H(29)	118.6(14)
C(28)-C(29)-H(29)	121.3(14)
C(29)-C(30)-C(31)	120.9(2)
C(29)-C(30)-H(30)	117.9(15)
C(31)-C(30)-H(30)	121.2(15)
C(30)-C(31)-C(26)	118.82(18)
C(30)-C(31)-C(32)	121.56(19)
C(26)-C(31)-C(32)	119.62(19)
C(33)-C(32)-C(31)	120.46(19)
C(33)-C(32)-H(32)	119.3(17)
C(31)-C(32)-H(32)	120.2(17)
C(32)-C(33)-C(24)	121.40(18)
C(32)-C(33)-H(33)	120.9(17)
C(24)-C(33)-H(33)	117.7(17)
O(41)-C(41)-C(49)	108.11(16)
O(41)-C(41)-C(55)	105.57(16)

C(49)-C(41)-C(55)	113.42(18)
O(41)-C(41)-C(42)	105.04(15)
C(49)-C(41)-C(42)	112.19(15)
C(55)-C(41)-C(42)	111.86(17)
C(48)-O(41)-C(41)	109.26(15)
C(43)-C(42)-C(56)	116.36(16)
C(43)-C(42)-C(41)	102.16(16)
C(56)-C(42)-C(41)	114.95(15)
C(43)-C(42)-H(42)	109.7(14)
C(56)-C(42)-H(42)	108.4(14)
C(41)-C(42)-H(42)	104.6(14)
C(48)-C(43)-C(44)	119.2(2)
C(48)-C(43)-C(42)	109.03(18)
C(44)-C(43)-C(42)	131.78(19)
C(43)-C(44)-C(45)	119.1(2)
C(43)-C(44)-H(44)	119.7(15)
C(45)-C(44)-H(44)	121.2(15)
C(46)-C(45)-C(44)	120.5(2)
C(46)-C(45)-H(45)	120.7(17)
C(44)-C(45)-H(45)	118.7(17)
C(45)-C(46)-C(47)	121.0(2)
C(45)-C(46)-H(46)	120.2(17)
C(47)-C(46)-H(46)	118.8(17)
C(48)-C(47)-C(46)	117.4(2)
C(48)-C(47)-H(47)	121.2(17)
C(46)-C(47)-H(47)	121.4(17)
O(41)-C(48)-C(43)	113.76(18)
O(41)-C(48)-C(47)	123.56(18)
C(43)-C(48)-C(47)	122.7(2)
C(50)-C(49)-C(54)	118.43(19)
C(50)-C(49)-C(41)	120.34(18)
C(54)-C(49)-C(41)	121.03(19)
C(51)-C(50)-C(49)	121.0(2)
C(51)-C(50)-H(50)	118.9(15)
C(49)-C(50)-H(50)	120.1(15)
C(52)-C(51)-C(50)	120.0(2)

C(52)-C(51)-H(51)	122.6(17)
C(50)-C(51)-H(51)	117.4(17)
C(53)-C(52)-C(51)	119.6(2)
C(53)-C(52)-H(52)	119(2)
C(51)-C(52)-H(52)	122(2)
C(52)-C(53)-C(54)	120.5(2)
C(52)-C(53)-H(53)	120.8(18)
C(54)-C(53)-H(53)	118.6(19)
C(53)-C(54)-C(49)	120.5(2)
C(53)-C(54)-H(54)	120.6(16)
C(49)-C(54)-H(54)	118.8(16)
C(41)-C(55)-H(55A)	105.0(16)
C(41)-C(55)-H(55B)	110.0(18)
H(55A)-C(55)-H(55B)	107(2)
C(41)-C(55)-H(55C)	109.3(16)
H(55A)-C(55)-H(55C)	115(2)
H(55B)-C(55)-H(55C)	110(2)
C(57)-C(56)-C(61)	117.88(18)
C(57)-C(56)-C(42)	121.88(18)
C(61)-C(56)-C(42)	120.20(18)
C(58)-C(57)-C(56)	121.20(19)
C(58)-C(57)-H(57)	120.3(17)
C(56)-C(57)-H(57)	118.5(17)
C(57)-C(58)-C(59)	120.99(19)
C(57)-C(58)-H(58)	120.3(17)
C(59)-C(58)-H(58)	118.6(16)
C(58)-C(59)-C(60)	118.04(18)
C(58)-C(59)-C(62)	122.12(19)
C(60)-C(59)-C(62)	119.78(18)
C(61)-C(60)-C(59)	120.77(19)
C(61)-C(60)-H(60)	121.0(16)
C(59)-C(60)-H(60)	118.3(16)
C(60)-C(61)-C(56)	121.10(19)
C(60)-C(61)-H(61)	120.6(17)
C(56)-C(61)-H(61)	118.3(17)
N(62)-C(62)-C(59)	114.03(17)

N(62)-C(62)-H(62A)	106.5(15)
C(59)-C(62)-H(62A)	110.0(15)
N(62)-C(62)-H(62B)	107.2(15)
C(59)-C(62)-H(62B)	110.5(15)
H(62A)-C(62)-H(62B)	108(2)
C(63)-N(62)-C(62)	122.49(17)
C(63)-N(62)-H(62)	117.5(17)
C(62)-N(62)-H(62)	119.8(17)
O(63)-C(63)-N(62)	120.22(19)
O(63)-C(63)-C(64)	121.32(18)
N(62)-C(63)-C(64)	118.45(17)
C(65)-C(64)-C(73)	118.49(19)
C(65)-C(64)-C(63)	119.36(17)
C(73)-C(64)-C(63)	122.15(18)
O(65)-C(65)-C(64)	122.35(19)
O(65)-C(65)-C(66)	116.63(18)
C(64)-C(65)-C(66)	121.02(18)
C(65)-O(65)-H(65A)	101.8(19)
C(67)-C(66)-C(71)	119.3(2)
C(67)-C(66)-C(65)	122.0(2)
C(71)-C(66)-C(65)	118.65(19)
C(68)-C(67)-C(66)	120.1(2)
C(68)-C(67)-H(67)	121.5(17)
C(66)-C(67)-H(67)	118.4(17)
C(67)-C(68)-C(69)	120.8(2)
C(67)-C(68)-H(68)	119.3(19)
C(69)-C(68)-H(68)	119.8(19)
C(70)-C(69)-C(68)	120.4(2)
C(70)-C(69)-H(69)	124.5(18)
C(68)-C(69)-H(69)	115.0(18)
C(69)-C(70)-C(71)	120.7(2)
C(69)-C(70)-H(70)	120.4(16)
C(71)-C(70)-H(70)	118.9(16)
C(70)-C(71)-C(72)	121.8(2)
C(70)-C(71)-C(66)	118.7(2)
C(72)-C(71)-C(66)	119.5(2)

C(73)-C(72)-C(71)	120.39(19)
C(73)-C(72)-H(72)	124.1(18)
C(71)-C(72)-H(72)	115.6(18)
C(72)-C(73)-C(64)	121.9(2)
C(72)-C(73)-H(73)	120.2(15)
C(64)-C(73)-H(73)	117.9(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for JF2920F. 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}
C(1)	30(1)	31(1)	22(1)	-2(1)	-4(1)	-1(1)
O(1)	41(1)	30(1)	37(1)	-8(1)	-16(1)	4(1)
C(2)	27(1)	28(1)	25(1)	-3(1)	-1(1)	-6(1)
C(3)	30(1)	26(1)	24(1)	2(1)	1(1)	-6(1)
C(4)	42(1)	28(1)	29(1)	-1(1)	-2(1)	-6(1)
C(5)	50(2)	25(1)	34(1)	1(1)	4(1)	-1(1)
C(6)	35(1)	30(1)	38(1)	7(1)	2(1)	-1(1)
C(7)	34(1)	30(1)	35(1)	6(1)	-6(1)	-7(1)
C(8)	33(1)	27(1)	28(1)	0(1)	-2(1)	-5(1)
C(9)	43(1)	31(1)	18(1)	-7(1)	-5(1)	-4(1)
C(10)	48(2)	51(2)	28(1)	-5(1)	-5(1)	-21(1)
C(11)	87(3)	72(2)	33(1)	9(1)	-18(1)	-52(2)
C(12)	118(3)	50(2)	47(2)	17(1)	-44(2)	-46(2)
C(13)	113(3)	33(1)	49(2)	-6(1)	-39(2)	4(2)
C(14)	61(2)	34(1)	31(1)	-8(1)	-12(1)	4(1)
C(15)	43(2)	45(1)	26(1)	-4(1)	5(1)	-7(1)
C(16)	28(1)	26(1)	23(1)	-7(1)	-3(1)	-4(1)
C(17)	27(1)	36(1)	25(1)	-8(1)	-2(1)	-1(1)
C(18)	32(1)	31(1)	28(1)	-6(1)	-7(1)	3(1)

C(19)	33(1)	22(1)	23(1)	-6(1)	-6(1)	-3(1)
C(20)	25(1)	28(1)	25(1)	-4(1)	-1(1)	-3(1)
C(21)	25(1)	29(1)	26(1)	-4(1)	-4(1)	-2(1)
C(22)	32(1)	27(1)	26(1)	-3(1)	-7(1)	-5(1)
N(22)	32(1)	21(1)	24(1)	-1(1)	-8(1)	0(1)
C(23)	28(1)	20(1)	19(1)	0(1)	0(1)	-1(1)
O(23)	30(1)	22(1)	29(1)	-1(1)	-6(1)	2(1)
C(24)	27(1)	22(1)	20(1)	0(1)	0(1)	-2(1)
C(25)	25(1)	21(1)	20(1)	0(1)	2(1)	-1(1)
O(25)	29(1)	19(1)	32(1)	-2(1)	-5(1)	1(1)
C(26)	25(1)	25(1)	21(1)	-2(1)	3(1)	-2(1)
C(27)	26(1)	26(1)	29(1)	-4(1)	0(1)	-2(1)
C(28)	32(1)	31(1)	29(1)	-7(1)	-1(1)	-8(1)
C(29)	24(1)	39(1)	27(1)	-5(1)	-2(1)	-4(1)
C(30)	30(1)	31(1)	25(1)	0(1)	-1(1)	1(1)
C(31)	25(1)	27(1)	19(1)	-1(1)	2(1)	-2(1)
C(32)	32(1)	24(1)	26(1)	1(1)	-3(1)	4(1)
C(33)	32(1)	19(1)	25(1)	-1(1)	-3(1)	-1(1)
C(41)	25(1)	30(1)	21(1)	-2(1)	-4(1)	0(1)
O(41)	29(1)	29(1)	25(1)	-3(1)	-8(1)	0(1)
C(42)	24(1)	26(1)	24(1)	-2(1)	-2(1)	3(1)
C(43)	26(1)	24(1)	25(1)	-8(1)	-2(1)	3(1)
C(44)	33(1)	26(1)	28(1)	-5(1)	-2(1)	2(1)
C(45)	35(1)	26(1)	36(1)	-8(1)	2(1)	-1(1)
C(46)	27(1)	32(1)	39(1)	-16(1)	-1(1)	1(1)
C(47)	27(1)	30(1)	30(1)	-12(1)	-4(1)	5(1)
C(48)	24(1)	26(1)	26(1)	-8(1)	0(1)	5(1)
C(49)	29(1)	26(1)	20(1)	1(1)	-4(1)	1(1)
C(50)	30(1)	30(1)	29(1)	-2(1)	-3(1)	3(1)
C(51)	40(2)	36(1)	31(1)	-4(1)	-3(1)	11(1)
C(52)	57(2)	29(1)	36(1)	-7(1)	-12(1)	10(1)
C(53)	51(2)	29(1)	37(1)	-1(1)	-14(1)	-6(1)
C(54)	34(1)	31(1)	29(1)	2(1)	-7(1)	-2(1)
C(55)	30(1)	42(1)	25(1)	-1(1)	1(1)	2(1)
C(56)	24(1)	21(1)	24(1)	0(1)	-5(1)	2(1)
C(57)	23(1)	28(1)	25(1)	-2(1)	-5(1)	-2(1)

C(58)	24(1)	29(1)	27(1)	-3(1)	-4(1)	-1(1)
C(59)	27(1)	21(1)	26(1)	0(1)	-7(1)	0(1)
C(60)	24(1)	25(1)	30(1)	-1(1)	-7(1)	-3(1)
C(61)	24(1)	26(1)	26(1)	1(1)	-1(1)	-1(1)
C(62)	28(1)	27(1)	29(1)	-4(1)	-7(1)	0(1)
N(62)	30(1)	21(1)	28(1)	-4(1)	-5(1)	0(1)
C(63)	31(1)	21(1)	23(1)	-5(1)	-10(1)	0(1)
O(63)	37(1)	21(1)	30(1)	-3(1)	-6(1)	2(1)
C(64)	29(1)	22(1)	24(1)	-4(1)	-8(1)	-1(1)
C(65)	31(1)	23(1)	23(1)	-4(1)	-9(1)	-2(1)
O(65)	39(1)	21(1)	35(1)	-1(1)	-3(1)	-2(1)
C(66)	31(1)	31(1)	21(1)	-4(1)	-10(1)	-2(1)
C(67)	35(1)	36(1)	28(1)	-2(1)	-6(1)	-5(1)
C(68)	34(1)	48(1)	31(1)	-4(1)	-2(1)	-6(1)
C(69)	33(1)	49(1)	31(1)	-6(1)	-6(1)	5(1)
C(70)	36(1)	37(1)	28(1)	-9(1)	-10(1)	6(1)
C(71)	34(1)	30(1)	22(1)	-6(1)	-11(1)	2(1)
C(72)	37(1)	23(1)	29(1)	-2(1)	-10(1)	4(1)
C(73)	32(1)	22(1)	26(1)	-2(1)	-6(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for JF2920F.

	x	y	z	U(eq)
H(2)	7420(40)	1760(20)	8672(14)	25(6)
H(4)	10160(40)	-230(20)	7939(16)	31(6)
H(5)	13050(50)	-1520(30)	8390(20)	52(9)
H(6)	14970(50)	-1060(30)	9396(16)	36(7)
H(7)	14240(50)	820(30)	9955(18)	45(8)

H(10)	12890(60)	3770(30)	8670(20)	51(9)
H(11)	13750(80)	5690(50)	8020(30)	93(15)
H(12)	10890(70)	7220(40)	7920(20)	71(11)
H(13)	7350(70)	6800(40)	8450(20)	69(11)
H(14)	6710(50)	4890(30)	9062(17)	37(7)
H(15A)	7310(50)	2020(30)	10030(19)	45(8)
H(15B)	6040(60)	3140(30)	9570(20)	50(9)
H(15C)	7650(50)	3360(30)	10240(20)	47(8)
H(17)	5860(50)	3260(20)	7790(16)	34(7)
H(18)	6160(50)	4380(30)	6563(16)	35(7)
H(20)	12400(50)	3250(20)	6274(16)	34(7)
H(21)	12150(40)	2190(20)	7491(15)	27(6)
H(22A)	9840(50)	5500(30)	5650(16)	34(7)
H(22B)	10870(40)	4300(20)	5282(14)	23(6)
H(22)	7030(50)	5350(30)	5023(16)	35(7)
H(25A)	7230(60)	1810(30)	4493(19)	47(8)
H(27)	3300(50)	750(30)	3533(17)	40(7)
H(28)	210(50)	690(30)	2883(17)	36(7)
H(29)	-1880(40)	2500(20)	2611(15)	25(6)
H(30)	-880(40)	4320(20)	2956(15)	29(6)
H(32)	1690(50)	5460(20)	3610(16)	32(6)
H(33)	4610(50)	5470(30)	4329(16)	33(7)
H(42)	9420(40)	6030(20)	1230(14)	22(6)
H(44)	6060(40)	4460(20)	2253(15)	26(6)
H(45)	3330(50)	3380(30)	1813(16)	33(7)
H(46)	1810(50)	3930(30)	636(18)	46(8)
H(47)	3080(50)	5650(30)	-107(17)	36(7)
H(50)	3760(40)	8270(20)	1202(14)	24(6)
H(51)	2610(50)	9980(30)	1779(17)	39(7)
H(52)	5090(60)	11480(40)	1930(20)	66(11)
H(53)	8700(50)	11250(30)	1462(18)	46(8)
H(54)	9840(50)	9460(30)	851(17)	39(7)
H(55A)	9870(40)	6780(30)	-22(16)	31(6)
H(55B)	10940(50)	7720(30)	445(18)	47(8)
H(55C)	9400(40)	8220(20)	-234(16)	32(6)
H(57)	4990(50)	6800(20)	2517(16)	35(7)

H(58)	5190(50)	7670(20)	3685(16)	31(6)
H(60)	11560(50)	8030(20)	3210(15)	33(7)
H(61)	11350(50)	7140(30)	2033(17)	37(7)
H(62A)	9090(40)	7770(20)	4658(14)	17(5)
H(62B)	9630(40)	9020(20)	4287(14)	26(6)
H(62)	6180(40)	9590(30)	4581(15)	26(6)
H(65A)	3540(50)	6690(30)	5803(19)	42(8)
H(67)	-1270(50)	6940(30)	6763(16)	37(7)
H(68)	-4470(50)	7860(30)	7257(17)	39(7)
H(69)	-5250(50)	9900(30)	7104(18)	44(8)
H(70)	-2680(40)	11190(30)	6408(16)	32(6)
H(72)	650(50)	11360(30)	5649(17)	38(7)
H(73)	3860(40)	10480(20)	5077(15)	28(6)

Table 6. Torsion angles [°] for JF2920F.

C(9)-C(1)-O(1)-C(8)	-128.27(17)
C(15)-C(1)-O(1)-C(8)	110.0(2)
C(2)-C(1)-O(1)-C(8)	-7.4(2)
O(1)-C(1)-C(2)-C(3)	6.89(19)
C(9)-C(1)-C(2)-C(3)	123.28(19)
C(15)-C(1)-C(2)-C(3)	-108.0(2)
O(1)-C(1)-C(2)-C(16)	-117.53(19)
C(9)-C(1)-C(2)-C(16)	-1.1(3)
C(15)-C(1)-C(2)-C(16)	127.6(2)
C(16)-C(2)-C(3)-C(8)	120.11(19)
C(1)-C(2)-C(3)-C(8)	-4.3(2)
C(16)-C(2)-C(3)-C(4)	-58.2(3)
C(1)-C(2)-C(3)-C(4)	177.4(2)
C(8)-C(3)-C(4)-C(5)	0.0(3)
C(2)-C(3)-C(4)-C(5)	178.2(2)
C(3)-C(4)-C(5)-C(6)	0.6(3)
C(4)-C(5)-C(6)-C(7)	-0.5(3)
C(5)-C(6)-C(7)-C(8)	-0.2(3)

C(1)-O(1)-C(8)-C(7)	-175.8(2)
C(1)-O(1)-C(8)-C(3)	5.0(2)
C(6)-C(7)-C(8)-O(1)	-178.3(2)
C(6)-C(7)-C(8)-C(3)	0.8(3)
C(4)-C(3)-C(8)-O(1)	178.49(19)
C(2)-C(3)-C(8)-O(1)	-0.1(2)
C(4)-C(3)-C(8)-C(7)	-0.7(3)
C(2)-C(3)-C(8)-C(7)	-179.31(19)
O(1)-C(1)-C(9)-C(10)	36.3(2)
C(15)-C(1)-C(9)-C(10)	153.3(2)
C(2)-C(1)-C(9)-C(10)	-79.8(2)
O(1)-C(1)-C(9)-C(14)	-149.40(19)
C(15)-C(1)-C(9)-C(14)	-32.4(3)
C(2)-C(1)-C(9)-C(14)	94.5(2)
C(14)-C(9)-C(10)-C(11)	-1.7(3)
C(1)-C(9)-C(10)-C(11)	172.7(2)
C(9)-C(10)-C(11)-C(12)	0.0(4)
C(10)-C(11)-C(12)-C(13)	1.9(4)
C(11)-C(12)-C(13)-C(14)	-2.2(4)
C(10)-C(9)-C(14)-C(13)	1.5(3)
C(1)-C(9)-C(14)-C(13)	-173.0(2)
C(12)-C(13)-C(14)-C(9)	0.5(4)
C(3)-C(2)-C(16)-C(21)	-25.8(3)
C(1)-C(2)-C(16)-C(21)	91.0(2)
C(3)-C(2)-C(16)-C(17)	157.83(18)
C(1)-C(2)-C(16)-C(17)	-85.4(2)
C(21)-C(16)-C(17)-C(18)	-1.7(3)
C(2)-C(16)-C(17)-C(18)	174.80(18)
C(16)-C(17)-C(18)-C(19)	0.5(3)
C(17)-C(18)-C(19)-C(20)	1.1(3)
C(17)-C(18)-C(19)-C(22)	-176.86(19)
C(18)-C(19)-C(20)-C(21)	-1.4(3)
C(22)-C(19)-C(20)-C(21)	176.62(18)
C(19)-C(20)-C(21)-C(16)	0.1(3)
C(17)-C(16)-C(21)-C(20)	1.4(3)
C(2)-C(16)-C(21)-C(20)	-175.00(19)

C(18)-C(19)-C(22)-N(22)	-38.0(3)
C(20)-C(19)-C(22)-N(22)	144.08(18)
C(19)-C(22)-N(22)-C(23)	-70.0(2)
C(22)-N(22)-C(23)-O(23)	1.1(3)
C(22)-N(22)-C(23)-C(24)	-179.89(17)
O(23)-C(23)-C(24)-C(25)	4.5(3)
N(22)-C(23)-C(24)-C(25)	-174.53(17)
O(23)-C(23)-C(24)-C(33)	-175.43(17)
N(22)-C(23)-C(24)-C(33)	5.5(3)
C(33)-C(24)-C(25)-O(25)	177.12(17)
C(23)-C(24)-C(25)-O(25)	-2.8(3)
C(33)-C(24)-C(25)-C(26)	-3.4(3)
C(23)-C(24)-C(25)-C(26)	176.68(16)
O(25)-C(25)-C(26)-C(27)	3.0(3)
C(24)-C(25)-C(26)-C(27)	-176.50(18)
O(25)-C(25)-C(26)-C(31)	-177.87(16)
C(24)-C(25)-C(26)-C(31)	2.6(3)
C(31)-C(26)-C(27)-C(28)	-1.1(3)
C(25)-C(26)-C(27)-C(28)	178.08(18)
C(26)-C(27)-C(28)-C(29)	1.3(3)
C(27)-C(28)-C(29)-C(30)	-0.2(3)
C(28)-C(29)-C(30)-C(31)	-1.3(3)
C(29)-C(30)-C(31)-C(26)	1.5(3)
C(29)-C(30)-C(31)-C(32)	-178.1(2)
C(27)-C(26)-C(31)-C(30)	-0.4(3)
C(25)-C(26)-C(31)-C(30)	-179.53(17)
C(27)-C(26)-C(31)-C(32)	179.29(18)
C(25)-C(26)-C(31)-C(32)	0.1(3)
C(30)-C(31)-C(32)-C(33)	177.52(19)
C(26)-C(31)-C(32)-C(33)	-2.1(3)
C(31)-C(32)-C(33)-C(24)	1.4(3)
C(25)-C(24)-C(33)-C(32)	1.4(3)
C(23)-C(24)-C(33)-C(32)	-178.69(18)
C(49)-C(41)-O(41)-C(48)	-114.88(17)
C(55)-C(41)-O(41)-C(48)	123.44(17)
C(42)-C(41)-O(41)-C(48)	5.1(2)

O(41)-C(41)-C(42)-C(43)	-7.96(19)
C(49)-C(41)-C(42)-C(43)	109.24(18)
C(55)-C(41)-C(42)-C(43)	-122.00(18)
O(41)-C(41)-C(42)-C(56)	-134.91(17)
C(49)-C(41)-C(42)-C(56)	-17.7(2)
C(55)-C(41)-C(42)-C(56)	111.1(2)
C(56)-C(42)-C(43)-C(48)	134.39(18)
C(41)-C(42)-C(43)-C(48)	8.3(2)
C(56)-C(42)-C(43)-C(44)	-47.6(3)
C(41)-C(42)-C(43)-C(44)	-173.7(2)
C(48)-C(43)-C(44)-C(45)	2.2(3)
C(42)-C(43)-C(44)-C(45)	-175.6(2)
C(43)-C(44)-C(45)-C(46)	1.1(3)
C(44)-C(45)-C(46)-C(47)	-2.4(3)
C(45)-C(46)-C(47)-C(48)	0.4(3)
C(41)-O(41)-C(48)-C(43)	0.3(2)
C(41)-O(41)-C(48)-C(47)	-179.53(18)
C(44)-C(43)-C(48)-O(41)	175.79(16)
C(42)-C(43)-C(48)-O(41)	-5.9(2)
C(44)-C(43)-C(48)-C(47)	-4.4(3)
C(42)-C(43)-C(48)-C(47)	173.85(18)
C(46)-C(47)-C(48)-O(41)	-177.16(18)
C(46)-C(47)-C(48)-C(43)	3.1(3)
O(41)-C(41)-C(49)-C(50)	38.8(2)
C(55)-C(41)-C(49)-C(50)	155.53(18)
C(42)-C(41)-C(49)-C(50)	-76.5(2)
O(41)-C(41)-C(49)-C(54)	-146.45(17)
C(55)-C(41)-C(49)-C(54)	-29.7(3)
C(42)-C(41)-C(49)-C(54)	98.2(2)
C(54)-C(49)-C(50)-C(51)	-1.9(3)
C(41)-C(49)-C(50)-C(51)	172.93(19)
C(49)-C(50)-C(51)-C(52)	0.8(3)
C(50)-C(51)-C(52)-C(53)	1.1(3)
C(51)-C(52)-C(53)-C(54)	-1.9(3)
C(52)-C(53)-C(54)-C(49)	0.8(3)
C(50)-C(49)-C(54)-C(53)	1.1(3)

C(41)-C(49)-C(54)-C(53)	-173.69(19)
C(43)-C(42)-C(56)-C(57)	-26.4(3)
C(41)-C(42)-C(56)-C(57)	92.9(2)
C(43)-C(42)-C(56)-C(61)	155.81(18)
C(41)-C(42)-C(56)-C(61)	-84.9(2)
C(61)-C(56)-C(57)-C(58)	0.8(3)
C(42)-C(56)-C(57)-C(58)	-176.97(18)
C(56)-C(57)-C(58)-C(59)	-0.2(3)
C(57)-C(58)-C(59)-C(60)	0.0(3)
C(57)-C(58)-C(59)-C(62)	-177.09(18)
C(58)-C(59)-C(60)-C(61)	-0.6(3)
C(62)-C(59)-C(60)-C(61)	176.55(18)
C(59)-C(60)-C(61)-C(56)	1.4(3)
C(57)-C(56)-C(61)-C(60)	-1.4(3)
C(42)-C(56)-C(61)-C(60)	176.41(17)
C(58)-C(59)-C(62)-N(62)	-22.5(3)
C(60)-C(59)-C(62)-N(62)	160.41(17)
C(59)-C(62)-N(62)-C(63)	88.3(2)
C(62)-N(62)-C(63)-O(63)	-2.5(3)
C(62)-N(62)-C(63)-C(64)	178.36(16)
O(63)-C(63)-C(64)-C(65)	-0.8(3)
N(62)-C(63)-C(64)-C(65)	178.27(17)
O(63)-C(63)-C(64)-C(73)	179.54(18)
N(62)-C(63)-C(64)-C(73)	-1.4(3)
C(73)-C(64)-C(65)-O(65)	-177.78(18)
C(63)-C(64)-C(65)-O(65)	2.6(3)
C(73)-C(64)-C(65)-C(66)	1.9(3)
C(63)-C(64)-C(65)-C(66)	-177.75(16)
O(65)-C(65)-C(66)-C(67)	-4.0(3)
C(64)-C(65)-C(66)-C(67)	176.28(18)
O(65)-C(65)-C(66)-C(71)	177.29(17)
C(64)-C(65)-C(66)-C(71)	-2.4(3)
C(71)-C(66)-C(67)-C(68)	-1.1(3)
C(65)-C(66)-C(67)-C(68)	-179.78(19)
C(66)-C(67)-C(68)-C(69)	-0.5(3)
C(67)-C(68)-C(69)-C(70)	1.2(4)

C(68)-C(69)-C(70)-C(71)	-0.2(4)
C(69)-C(70)-C(71)-C(72)	178.3(2)
C(69)-C(70)-C(71)-C(66)	-1.4(3)
C(67)-C(66)-C(71)-C(70)	2.1(3)
C(65)-C(66)-C(71)-C(70)	-179.22(18)
C(67)-C(66)-C(71)-C(72)	-177.64(19)
C(65)-C(66)-C(71)-C(72)	1.1(3)
C(70)-C(71)-C(72)-C(73)	-178.97(19)
C(66)-C(71)-C(72)-C(73)	0.7(3)
C(71)-C(72)-C(73)-C(64)	-1.3(3)
C(65)-C(64)-C(73)-C(72)	-0.1(3)
C(63)-C(64)-C(73)-C(72)	179.59(18)

Symmetry transformations used to generate equivalent atoms:

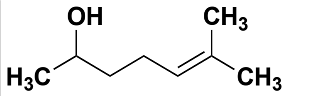
Table 7. Hydrogen bonds for JF2920F [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(22)-H(22A)...O(65)#1	1.02(3)	2.39(3)	3.281(3)	145(2)
N(22)-H(22)...O(63)	0.90(3)	2.08(3)	2.939(2)	158(3)
O(25)-H(25A)...O(23)	0.97(4)	1.55(3)	2.4680(19)	155(3)
N(62)-H(62)...O(25)#2	0.88(3)	2.25(3)	3.104(2)	164(2)
O(65)-H(65A)...O(63)	0.93(3)	1.67(3)	2.547(2)	157(3)

Symmetry transformations used to generate equivalent atoms:

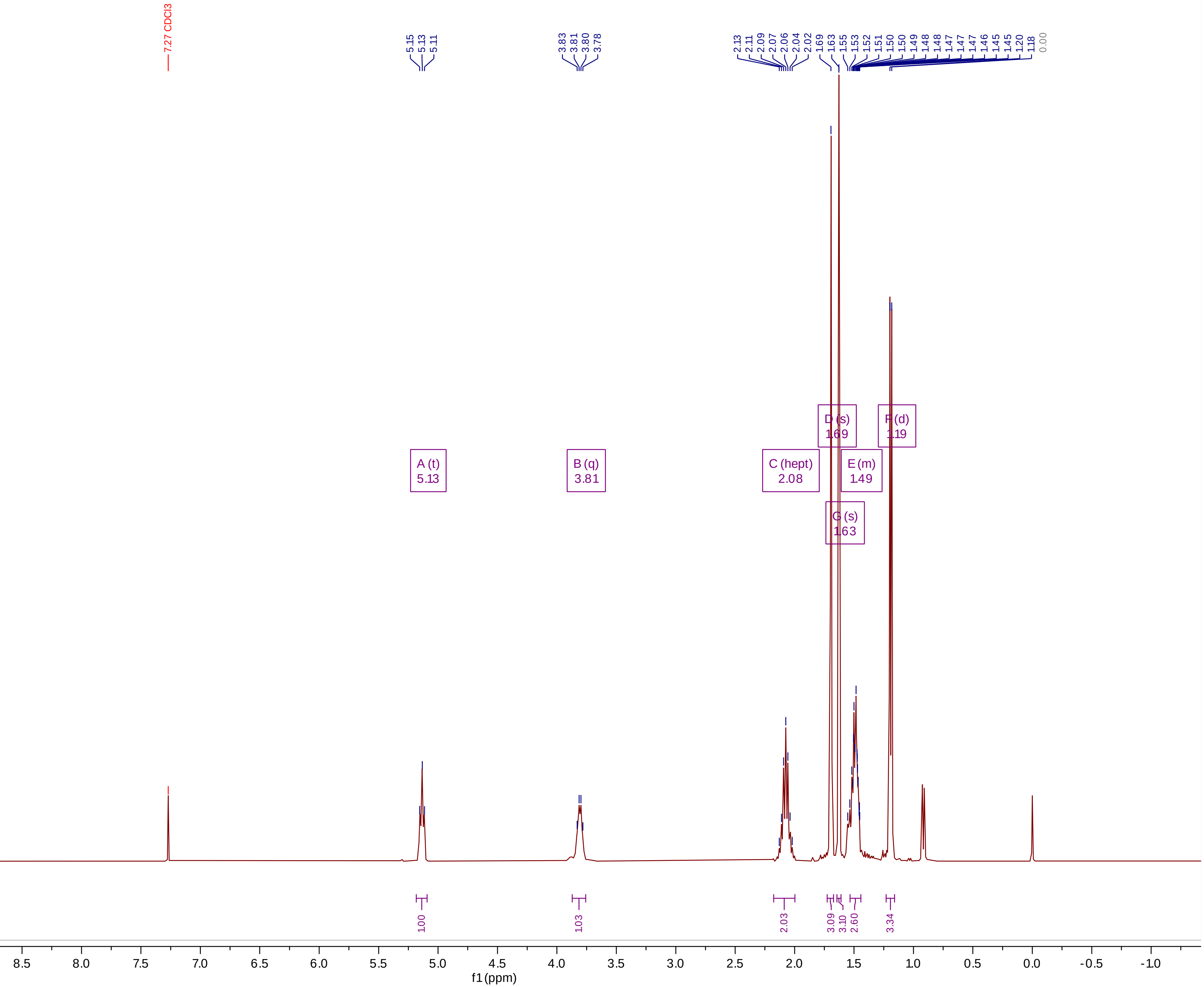
#1 x+1,y,z   #2 x,y+1,z

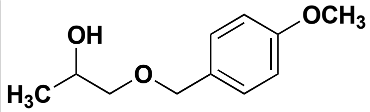
NMR Spectra



28

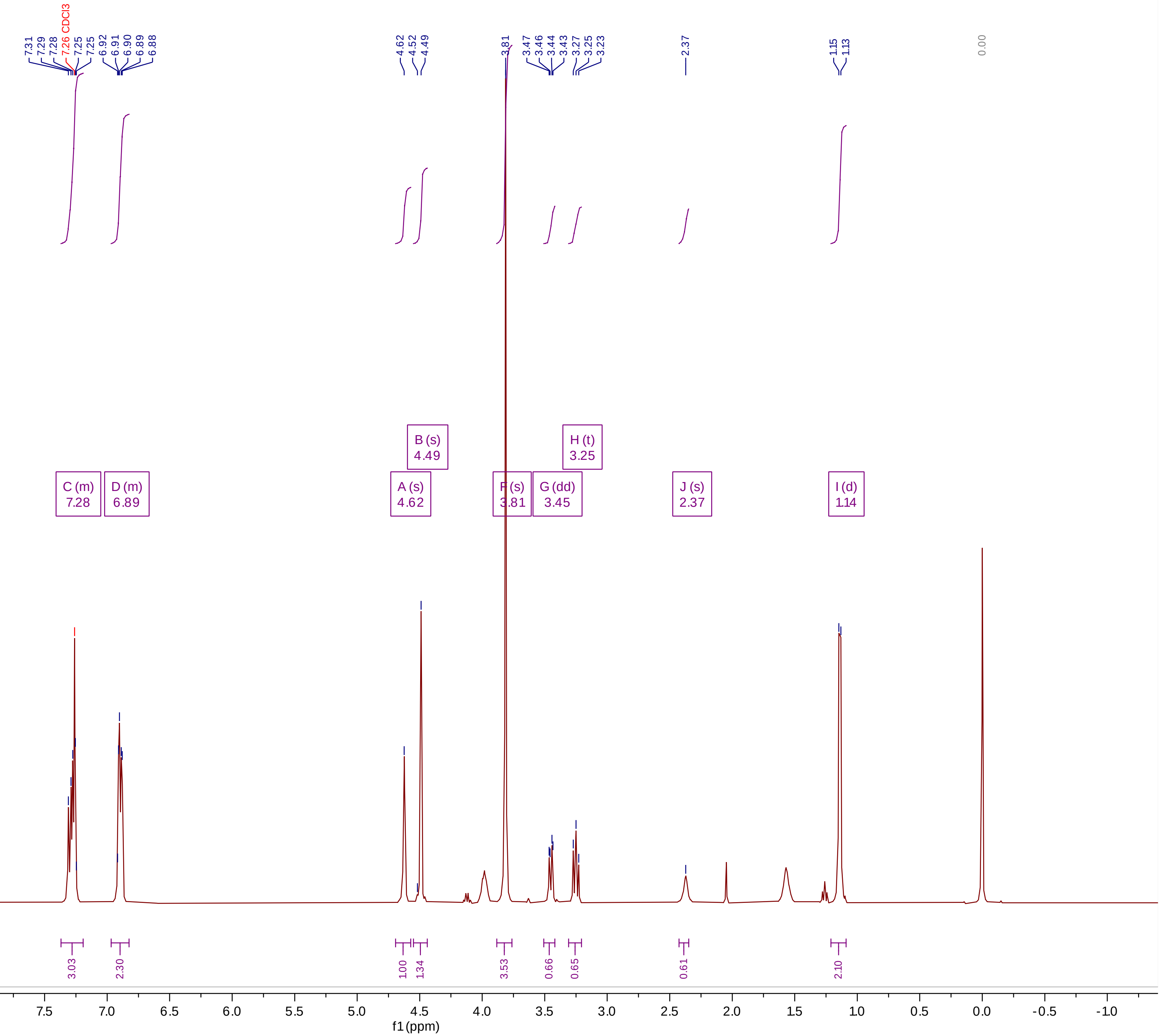
^{1}H, 400 MHz, CDCl$_3$

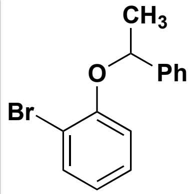




29

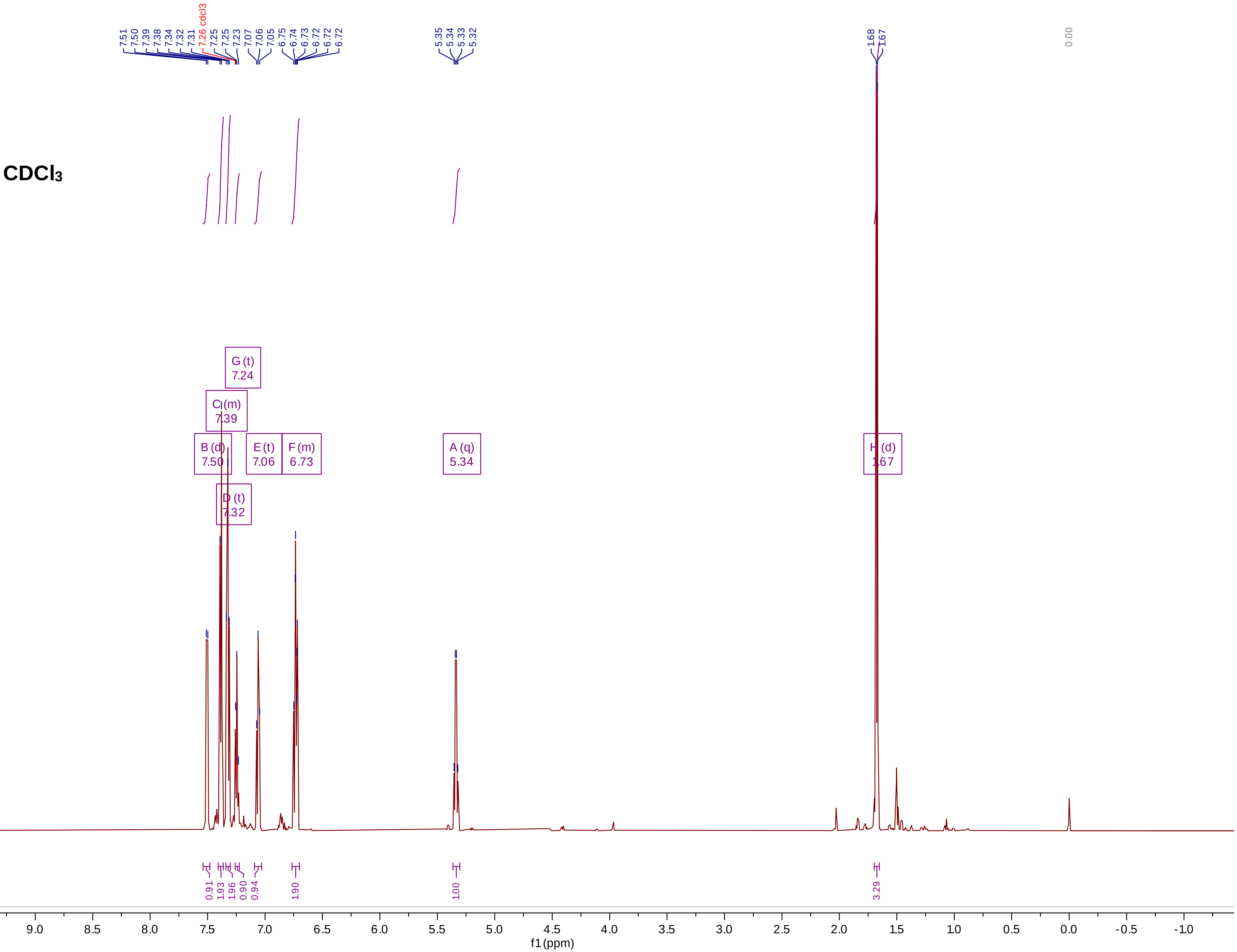
^{1}H, 400 MHz, $CDCl_3$

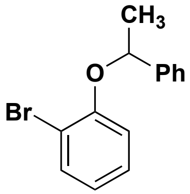




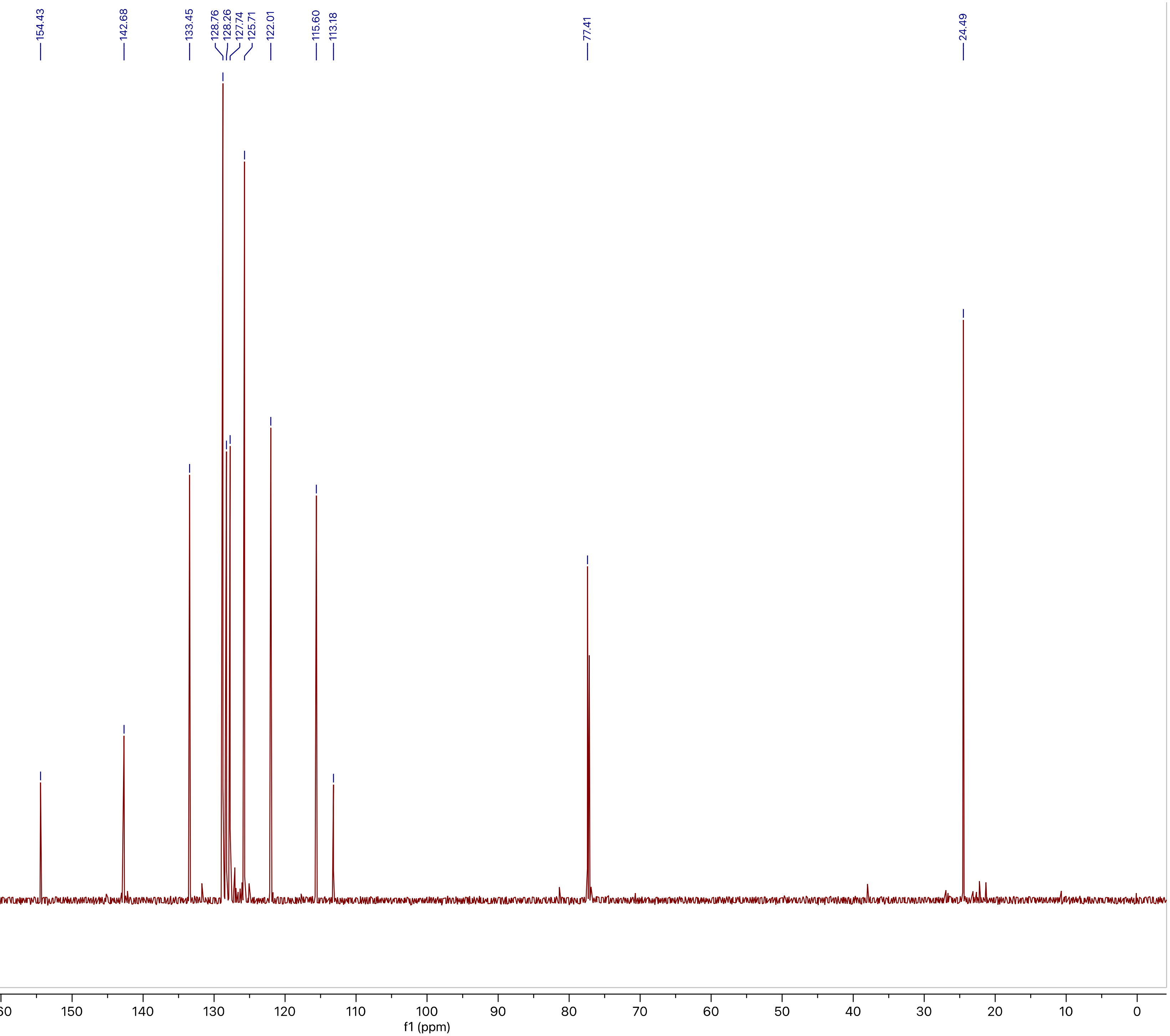
30

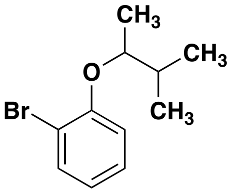
^{1}H, 600 MHz, $CDCl_3$





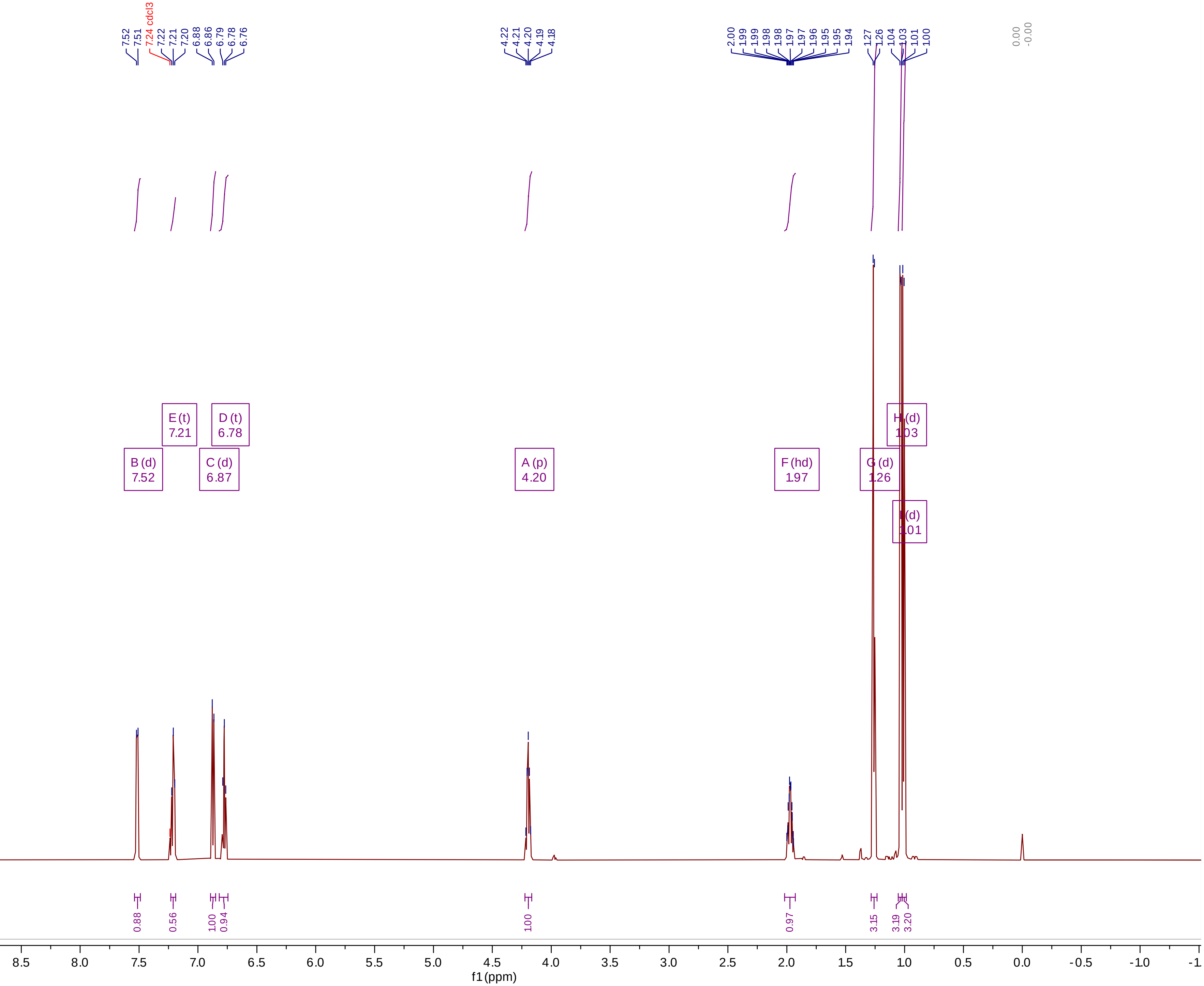
30
^{13}C, 150 MHz, $CDCl_3$

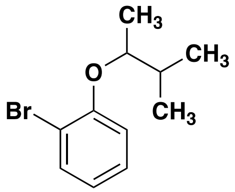




31

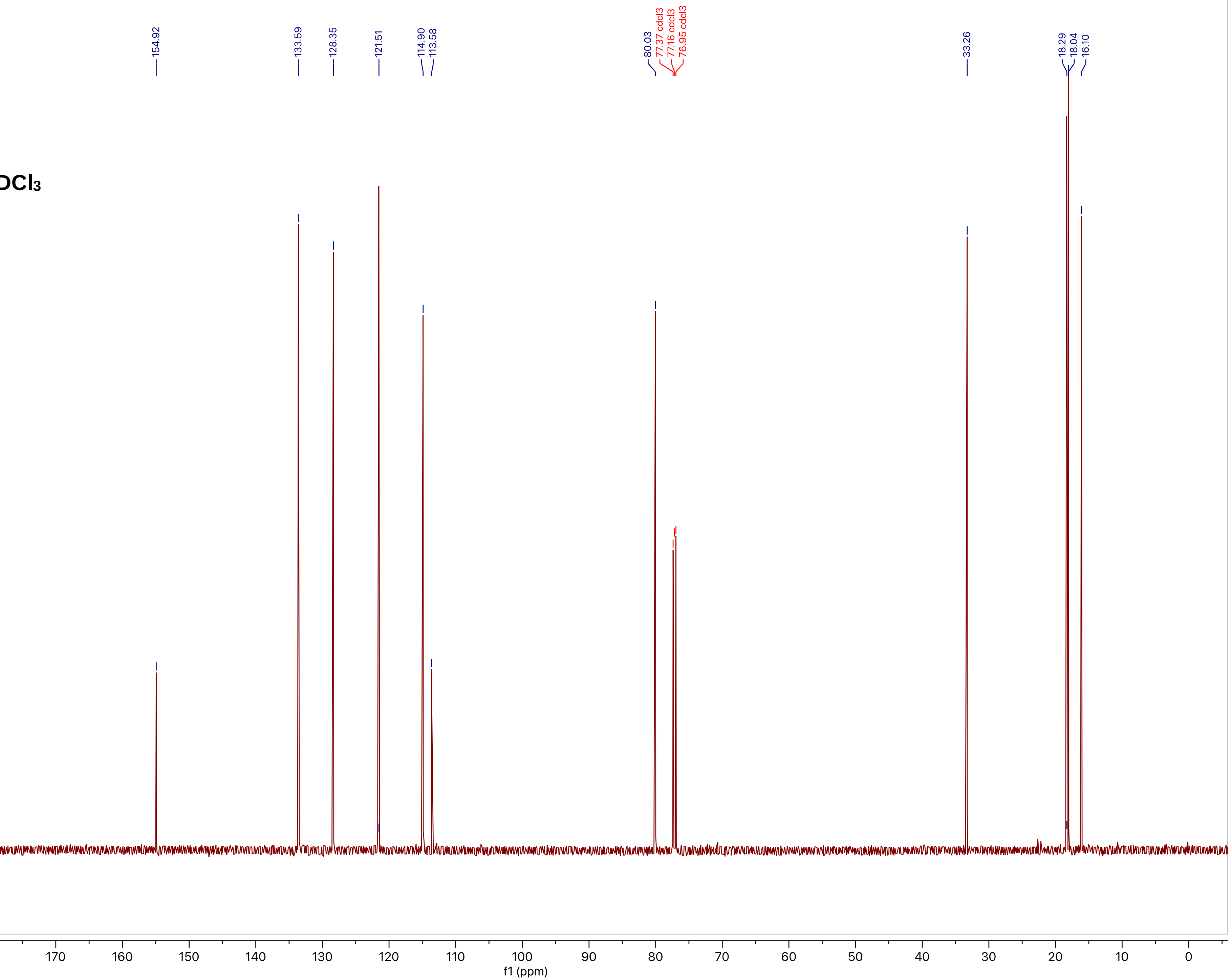
^{1}H, 600 MHz, $CDCl_3$

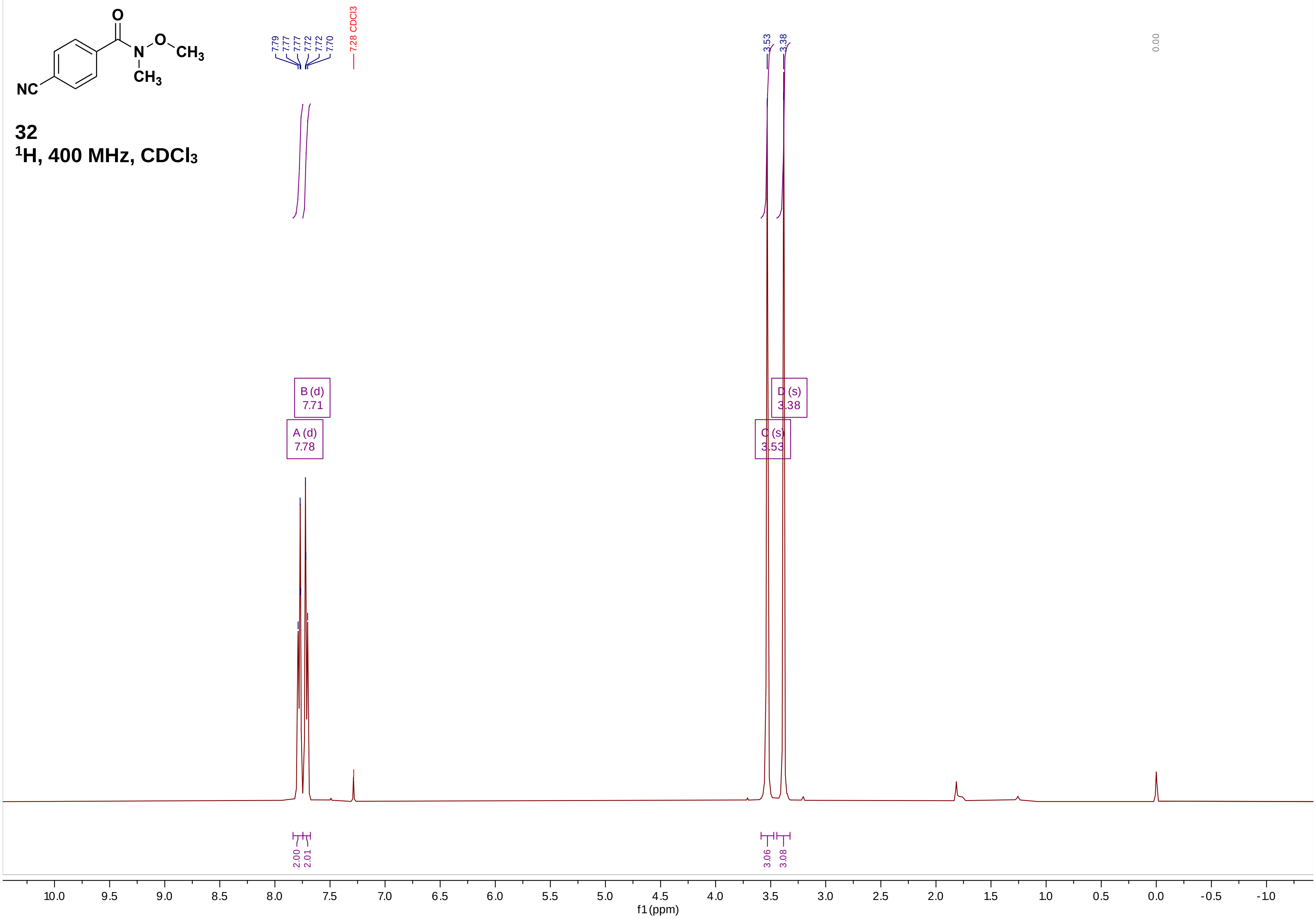




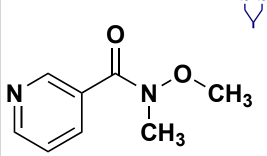
31

^{13}C, 150 MHz, $CDCl_3$



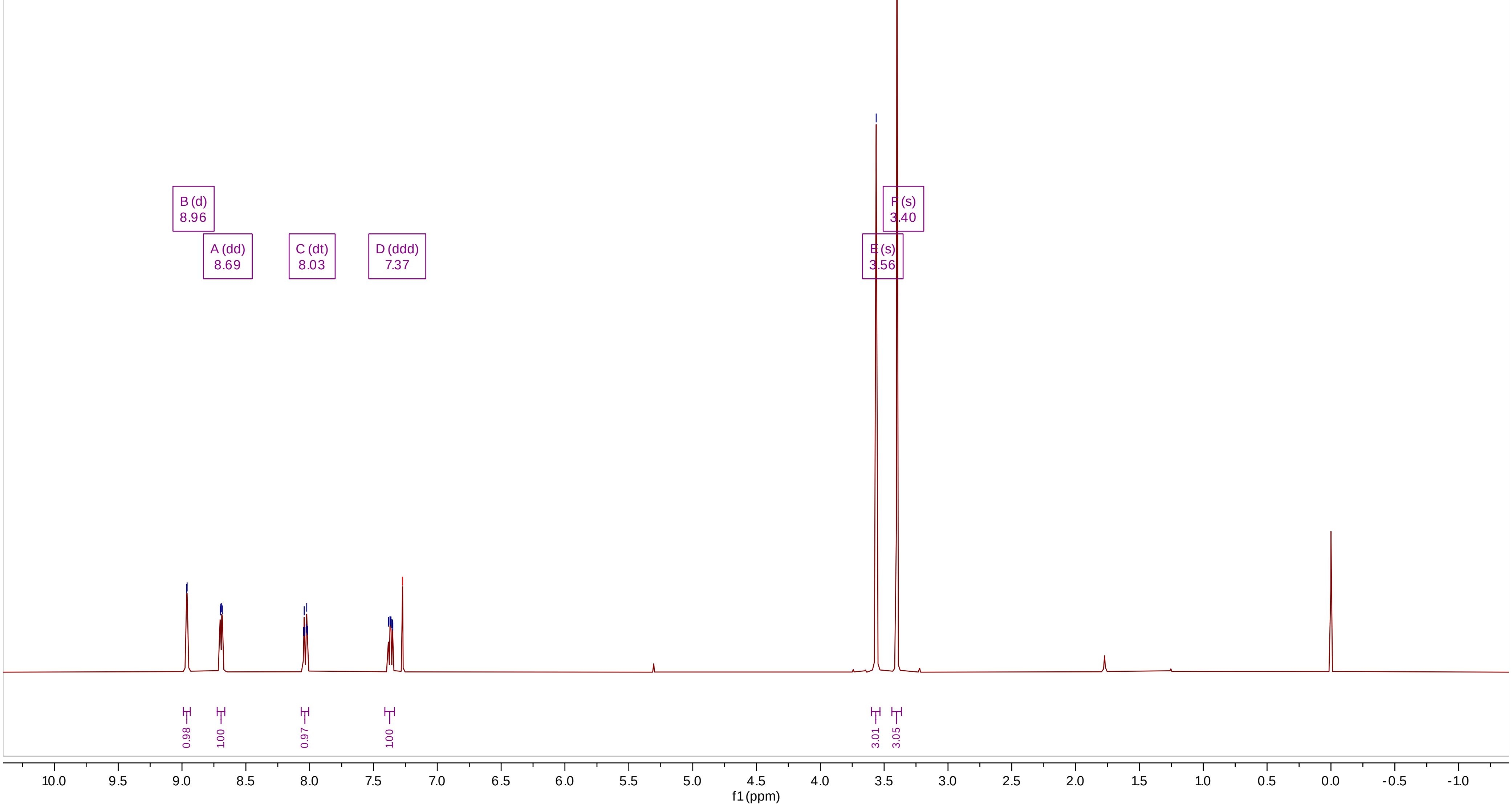


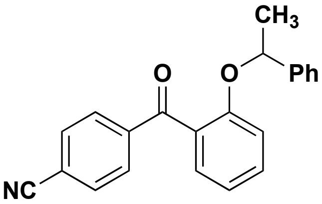
NC
O
N
O
CH3
CH3
32
1H, 400 MHz, CDCl3
7.79
7.77
7.77
7.72
7.72
7.70
7.28 CDCl3
3.53
3.38
0.00
B (d)
7.71
A (d)
7.78
D (s)
3.38
C (s)
3.53
2.00
2.01
3.06
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



33

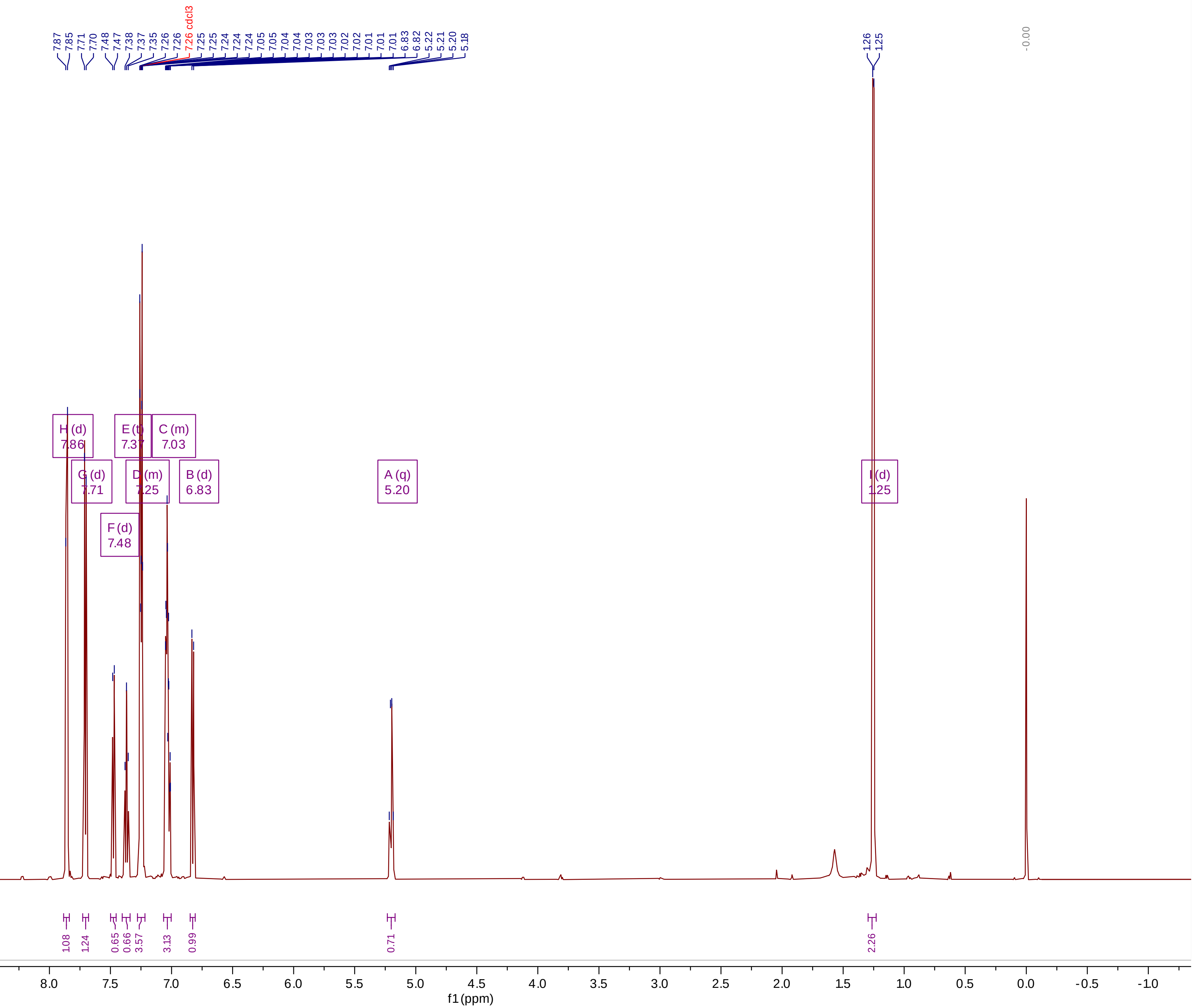
^{1}H, 400 MHz, $CDCl_3$

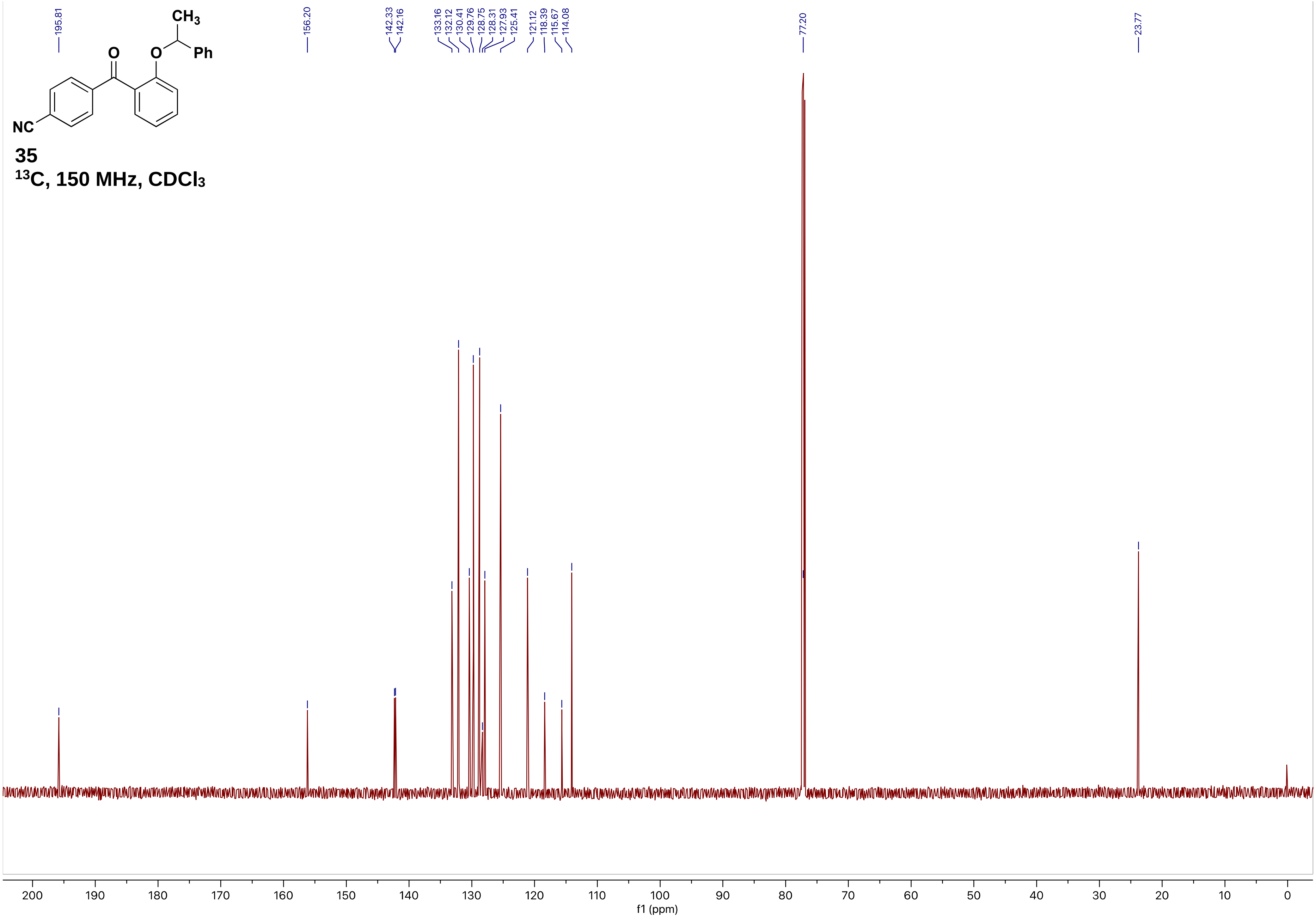


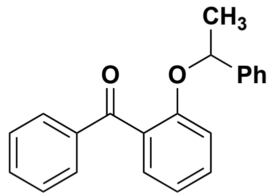


35

^{1}H, 600 MHz, $CDCl_3$

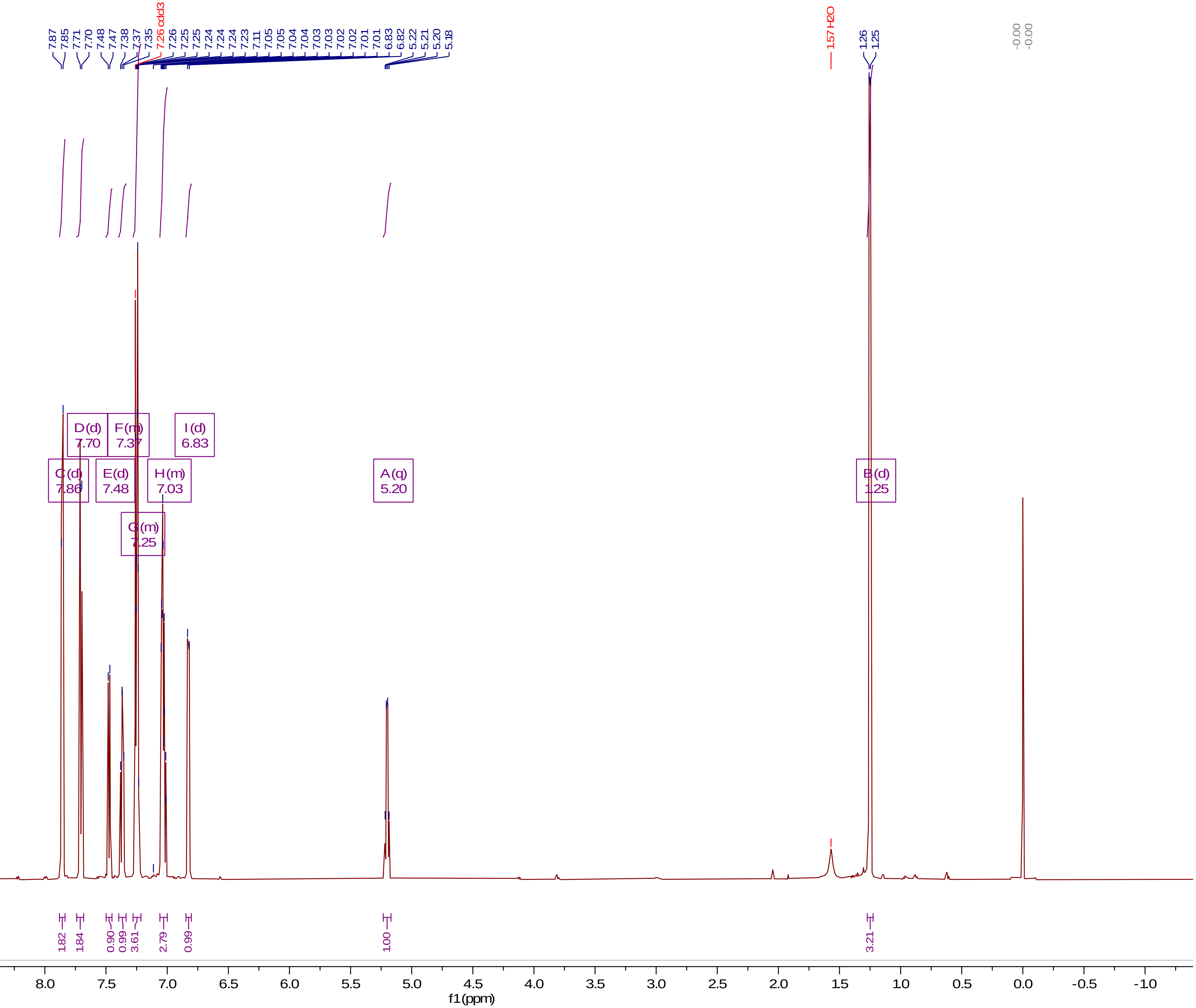


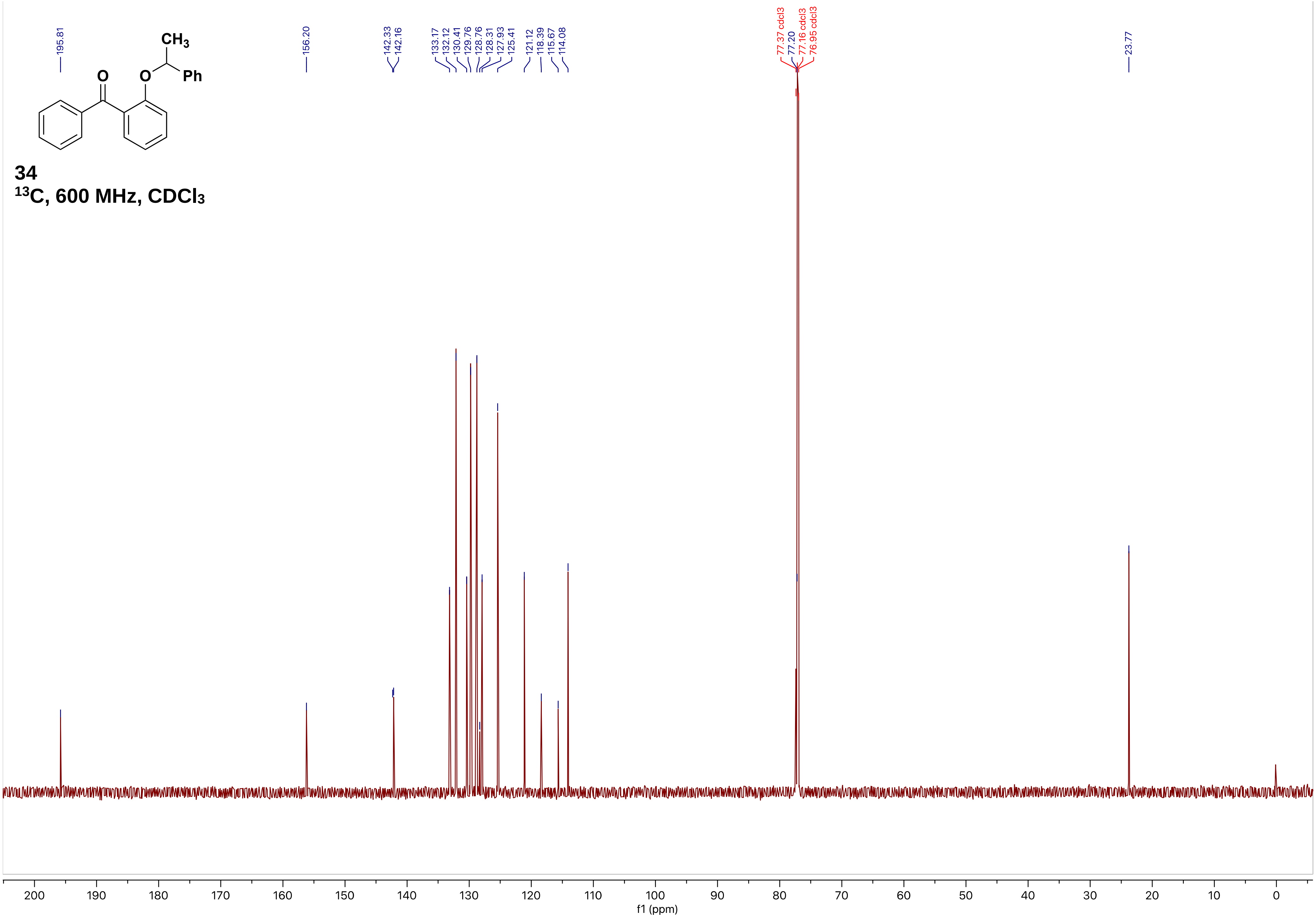

195.81
156.20
142.33
142.16
133.16
132.12
130.41
129.76
128.75
128.31
127.93
125.41
121.12
118.39
115.67
114.08
77.20
23.77
CH3
O
O
Ph
NC
35
13C, 150 MHz, CDCl3
f1 (ppm)



34

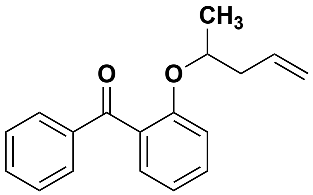
^{1}H, 600 MHz, $CDCl_3$



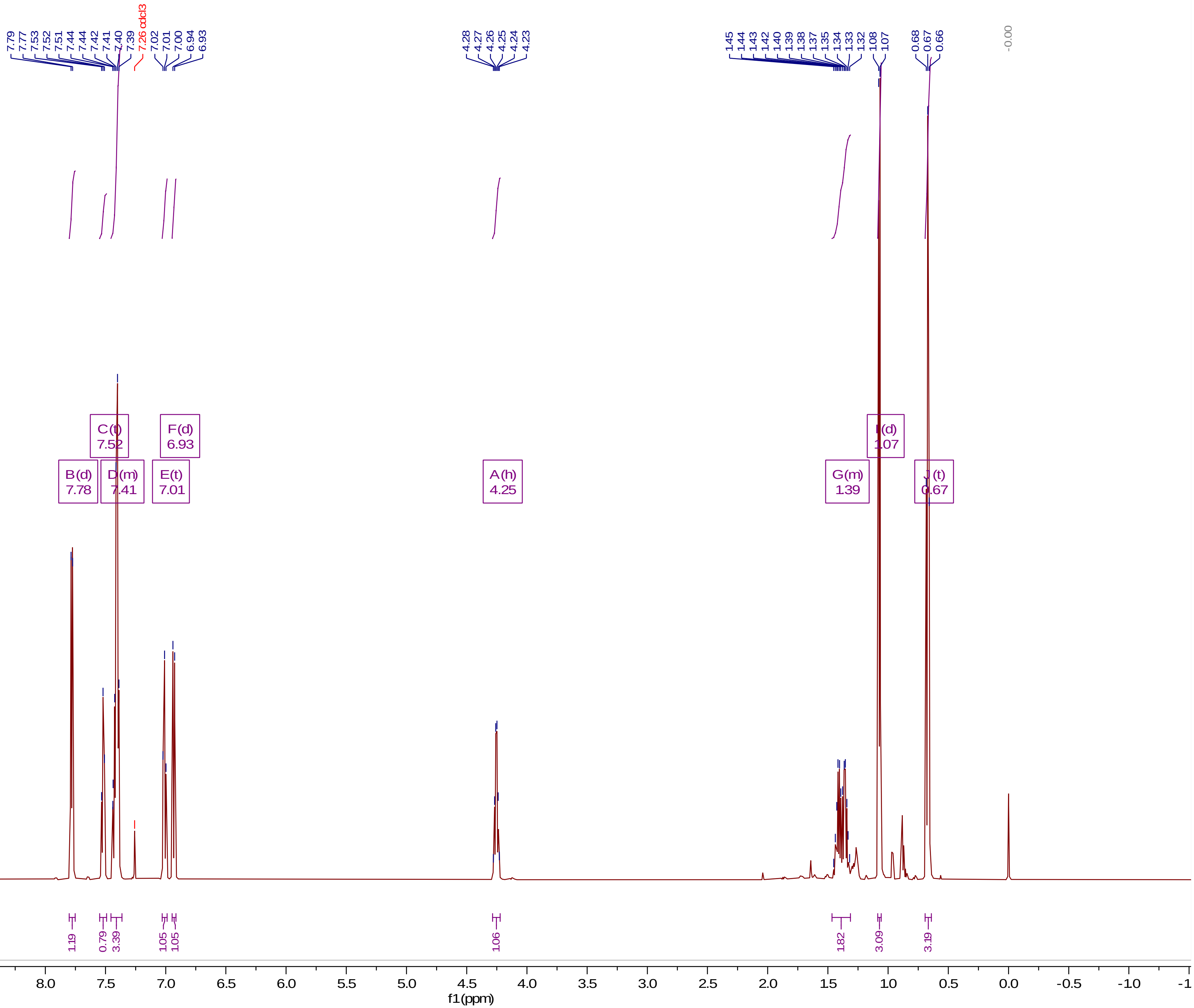


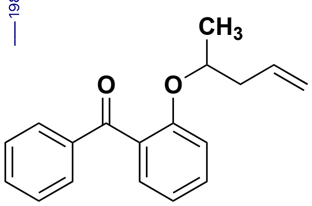
34

^{13}C, 600 MHz, $CDCl_3$



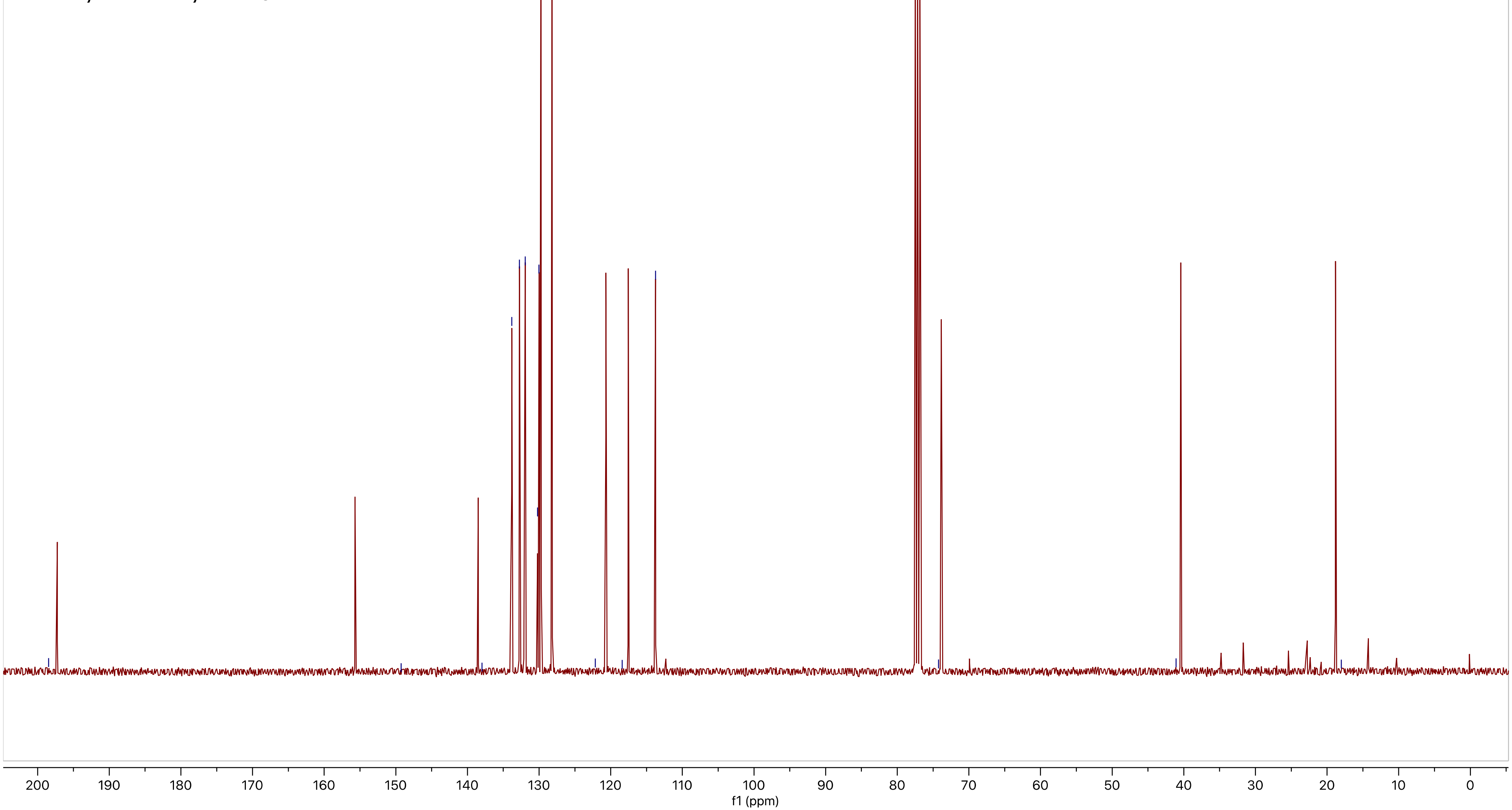
36
^{1}H, 600 MHz, CDCl$_3$

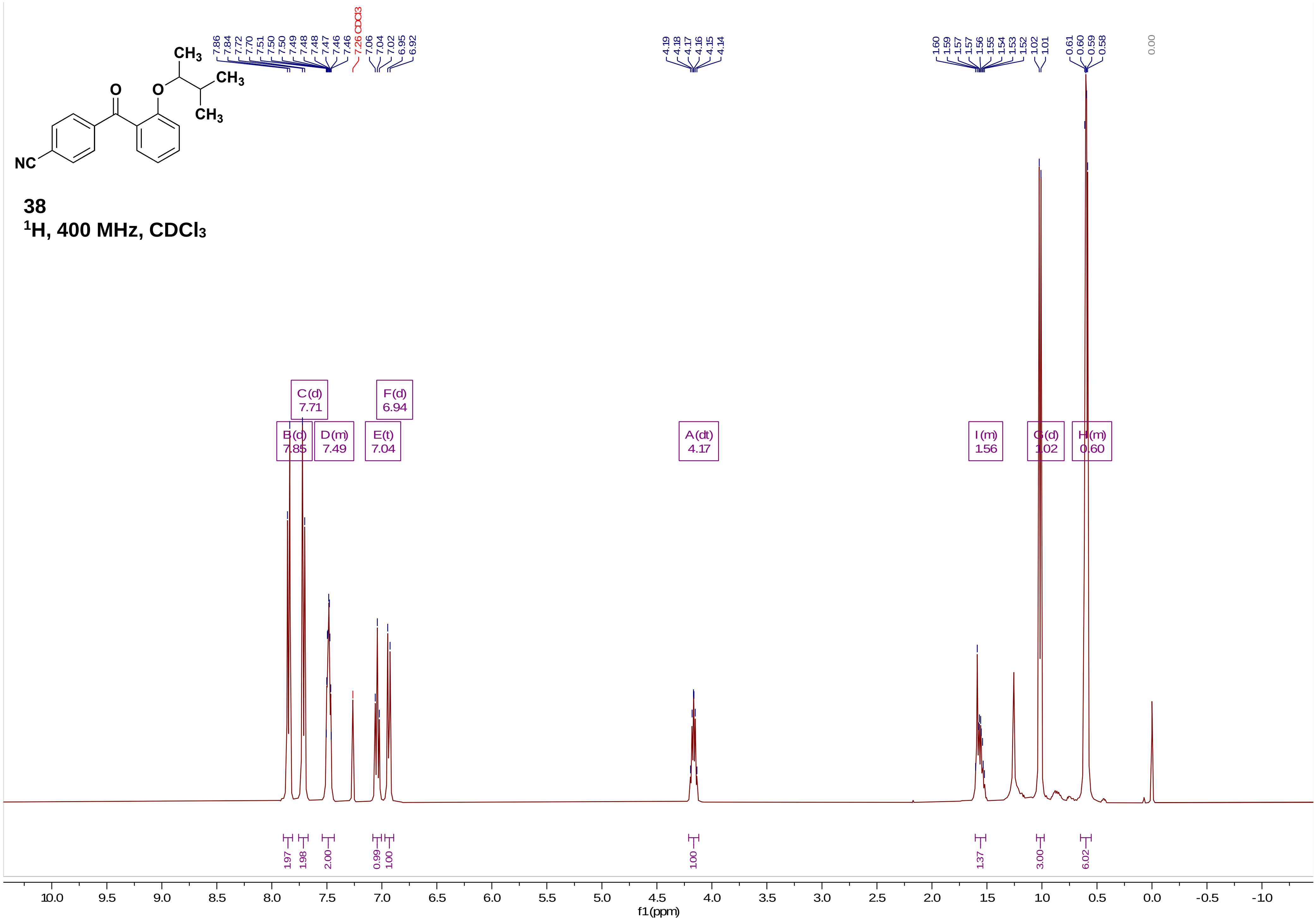




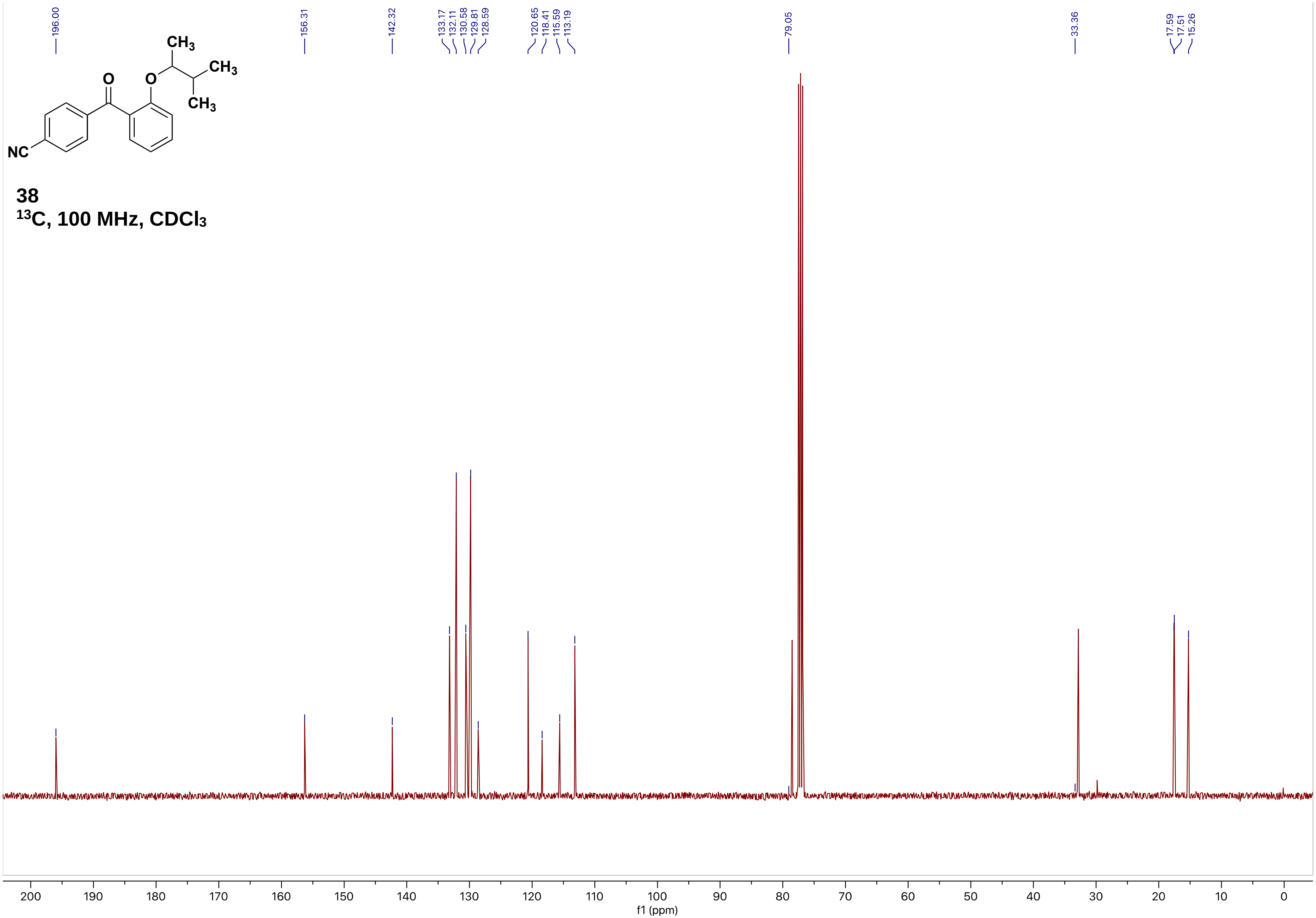
36

^{13}C, 100 MHz, $CDCl_3$

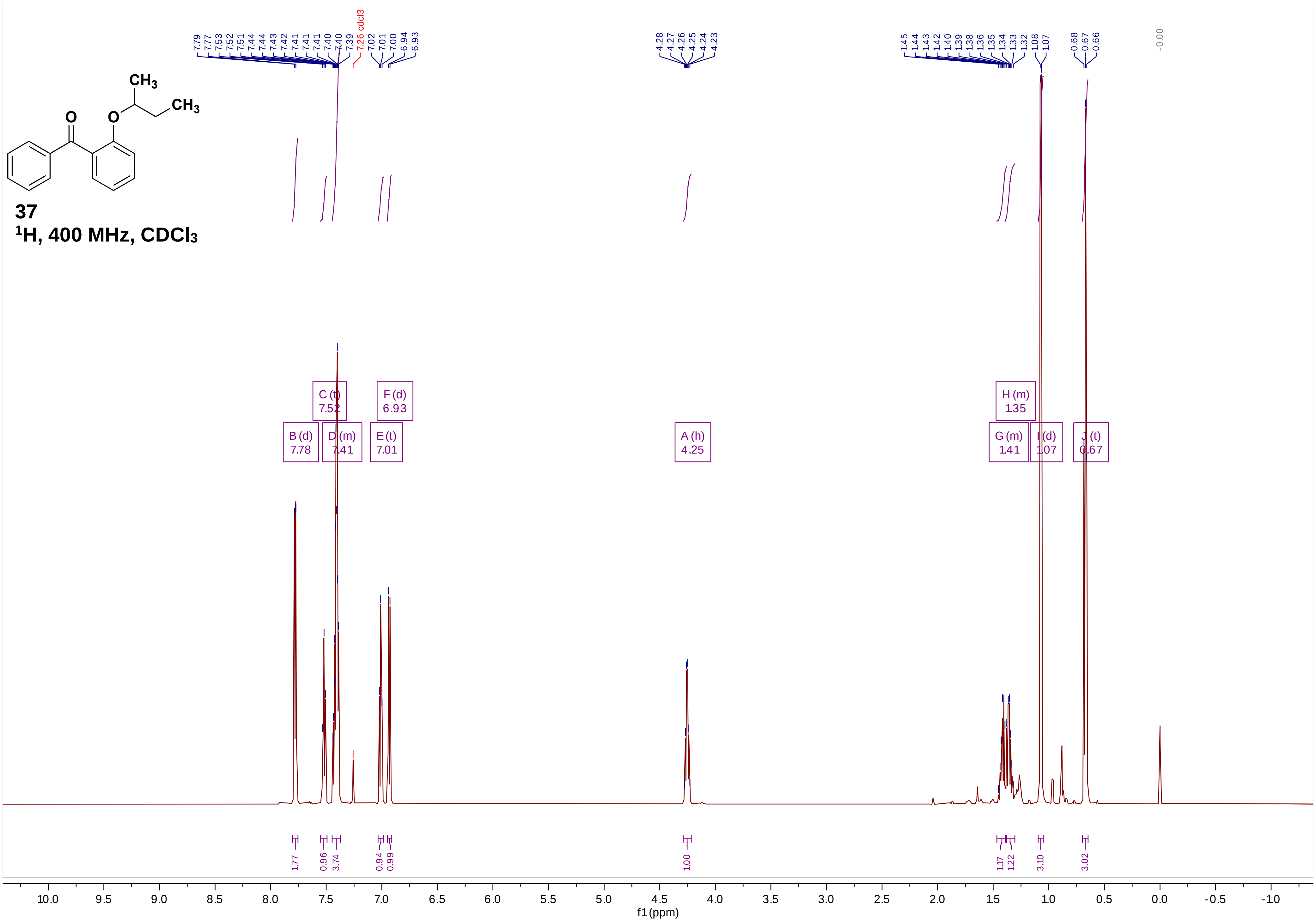


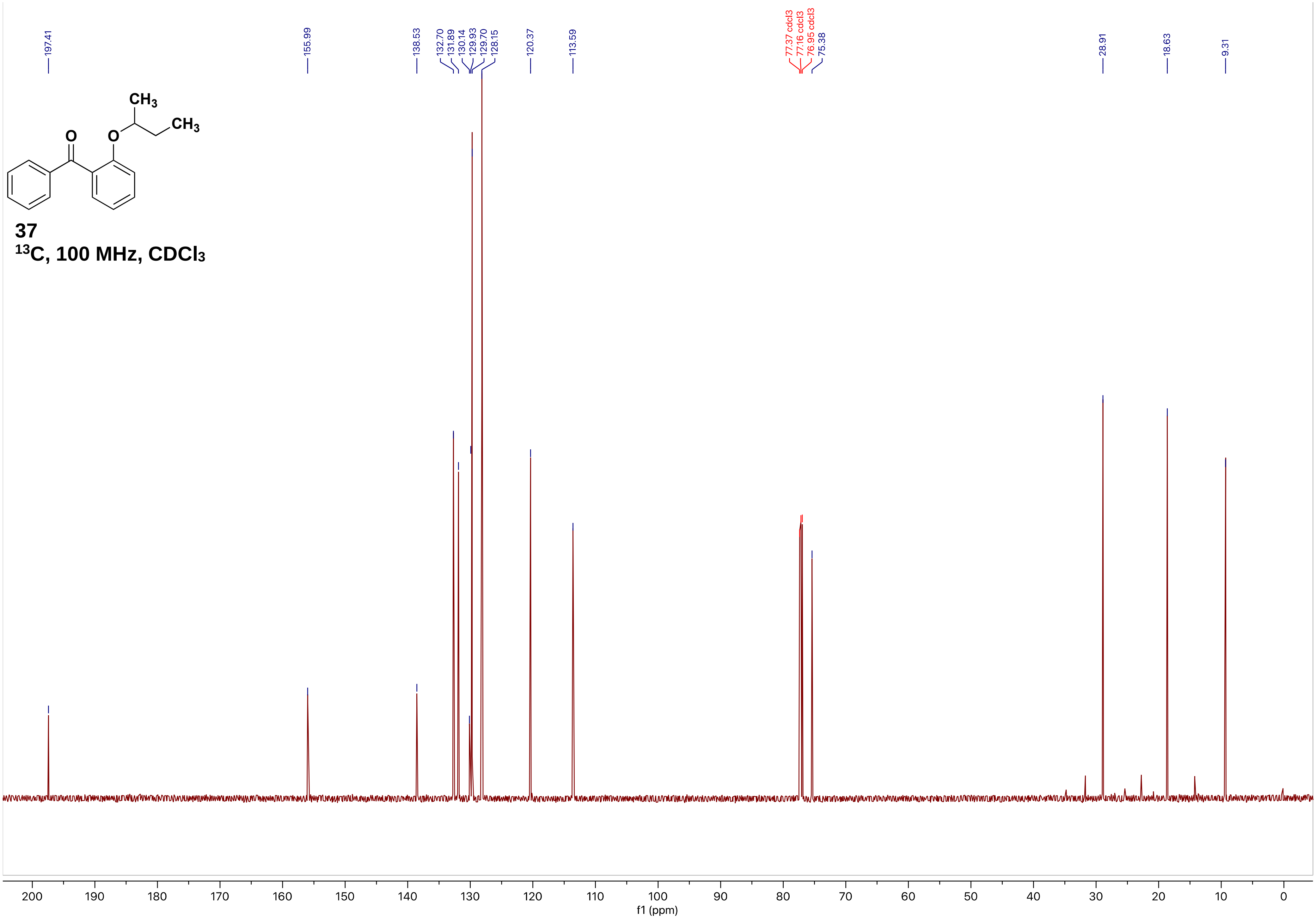


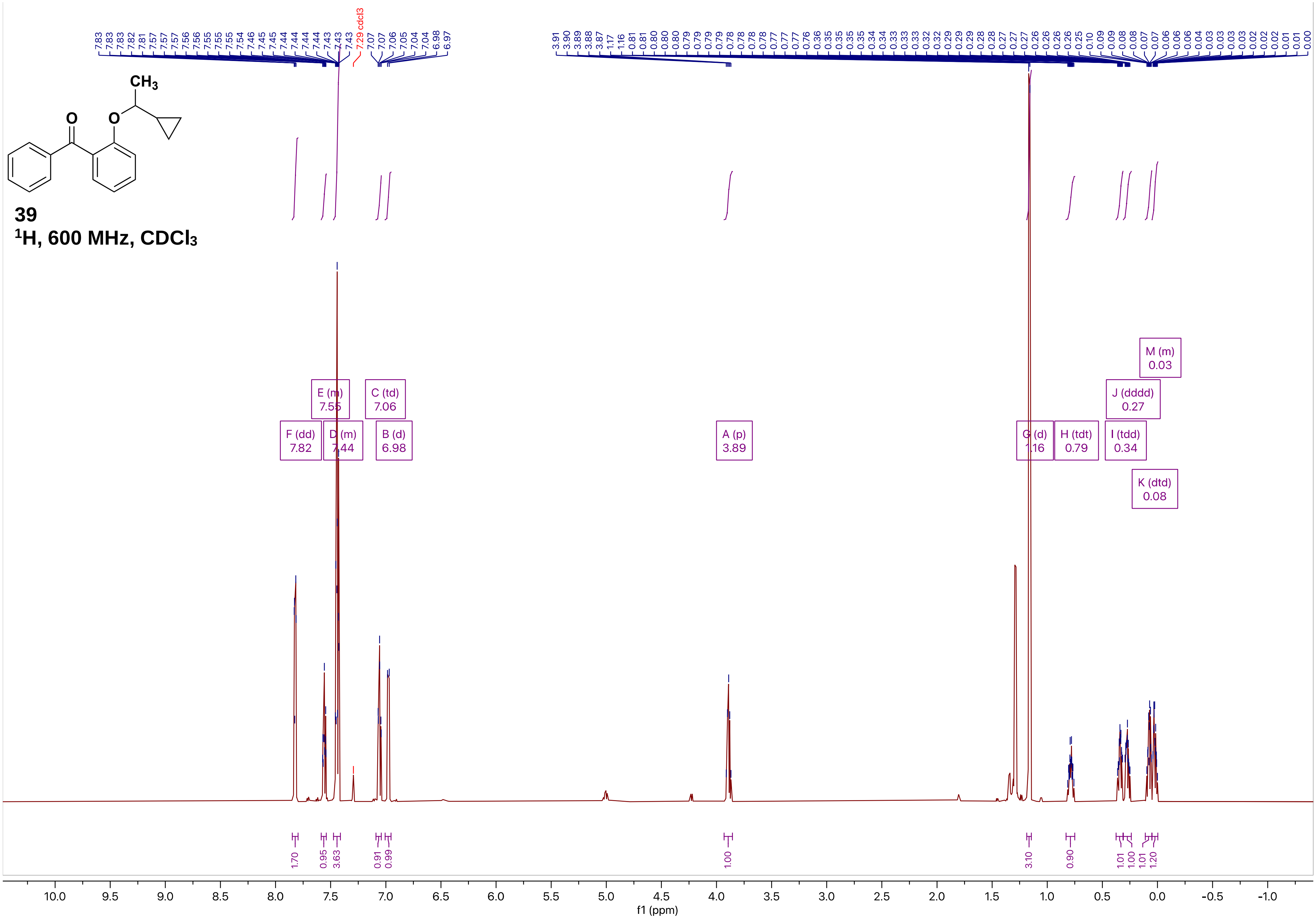
38
^{1}H, 400 MHz, CDCl$_3$
NC
O
O
CH$_3$
CH$_3$
CH$_3$
7.86 7.84 7.72 7.70 7.51 7.50 7.50 7.49 7.48 7.48 7.47 7.46 7.46
7.26 CDCl3
7.06 7.04 7.02 6.95 6.92
4.19 4.18 4.17 4.16 4.15 4.14
1.60 1.59 1.57 1.57 1.56 1.55 1.54 1.53 1.52 1.02 1.01
0.61 0.60 0.59 0.58
0.00
C(d) 7.71
F(d) 6.94
B(d) 7.85
D(m) 7.49
E(t) 7.04
A(dt) 4.17
I(m) 1.56
G(d) 1.02
H(m) 0.60
1.97 1.98 2.00 0.99 1.00 1.00 1.37 3.00 6.02
10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)

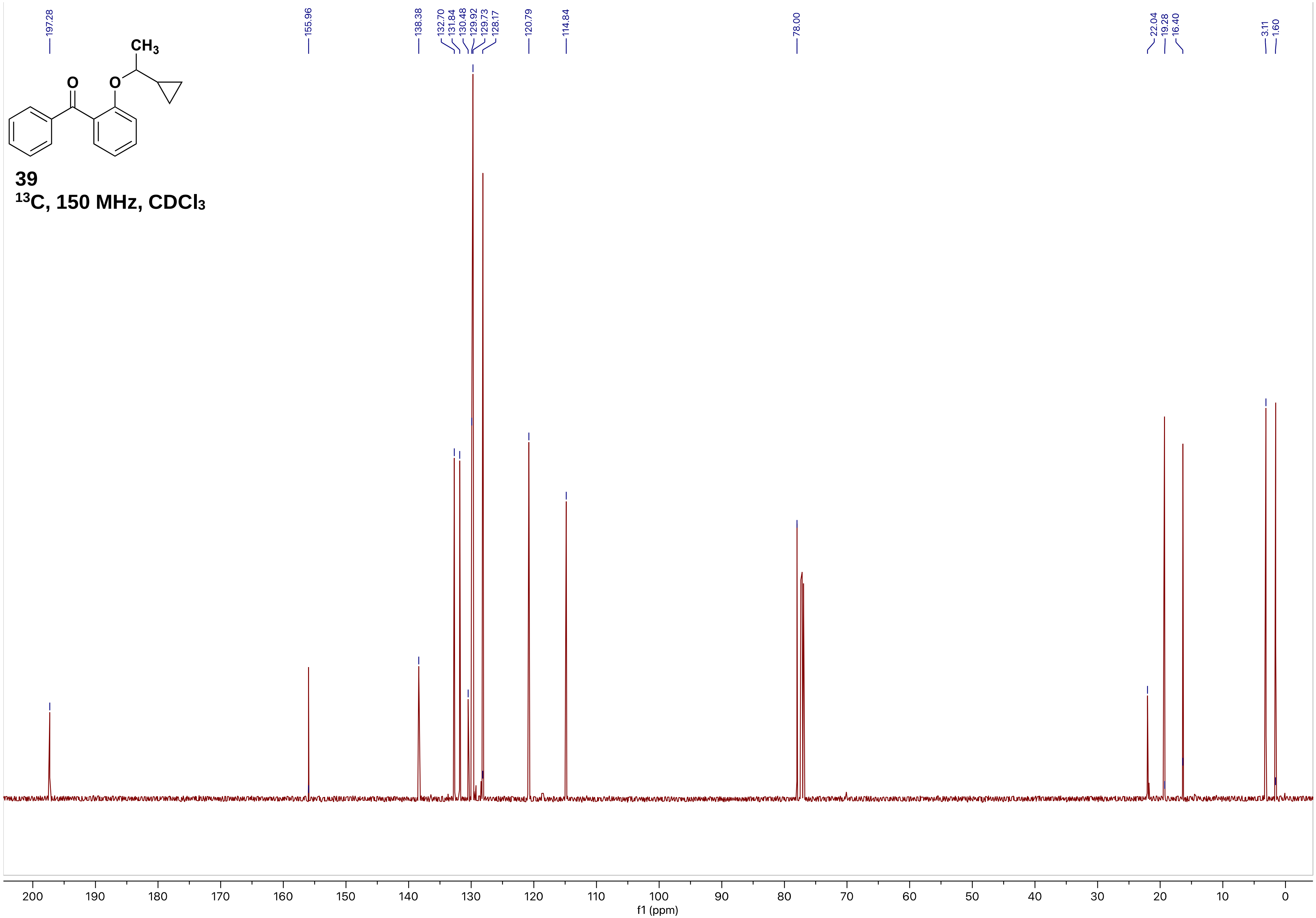


196.00
156.31
142.32
133.17
132.11
130.58
129.81
128.59
120.65
118.41
115.59
113.19
79.05
33.36
17.59
17.51
15.26
NC
O
O
CH3
CH3
CH3
38
13C, 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
CH3
O
O
37
1H, 400 MHz, CDCl3
7.79
7.77
7.53
7.52
7.51
7.44
7.44
7.43
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.26 cdcl3
7.02
7.01
7.00
6.94
6.93
4.28
4.27
4.26
4.25
4.24
4.23
1.45
1.44
1.43
1.42
1.40
1.39
1.38
1.36
1.35
1.34
1.33
1.32
1.08
1.07
0.68
0.67
0.66
-0.00
C (t) 7.52
F (d) 6.93
B (d) 7.78
D (m) 7.41
E (t) 7.01
A (h) 4.25
H (m) 1.35
G (m) 1.41
I (d) 1.07
J (t) 0.67
1.77
0.96
3.74
0.94
0.99
1.00
1.17
1.22
3.10
3.02
10.0
9.5
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
0.0
-0.5
-1.0
f1 (ppm)

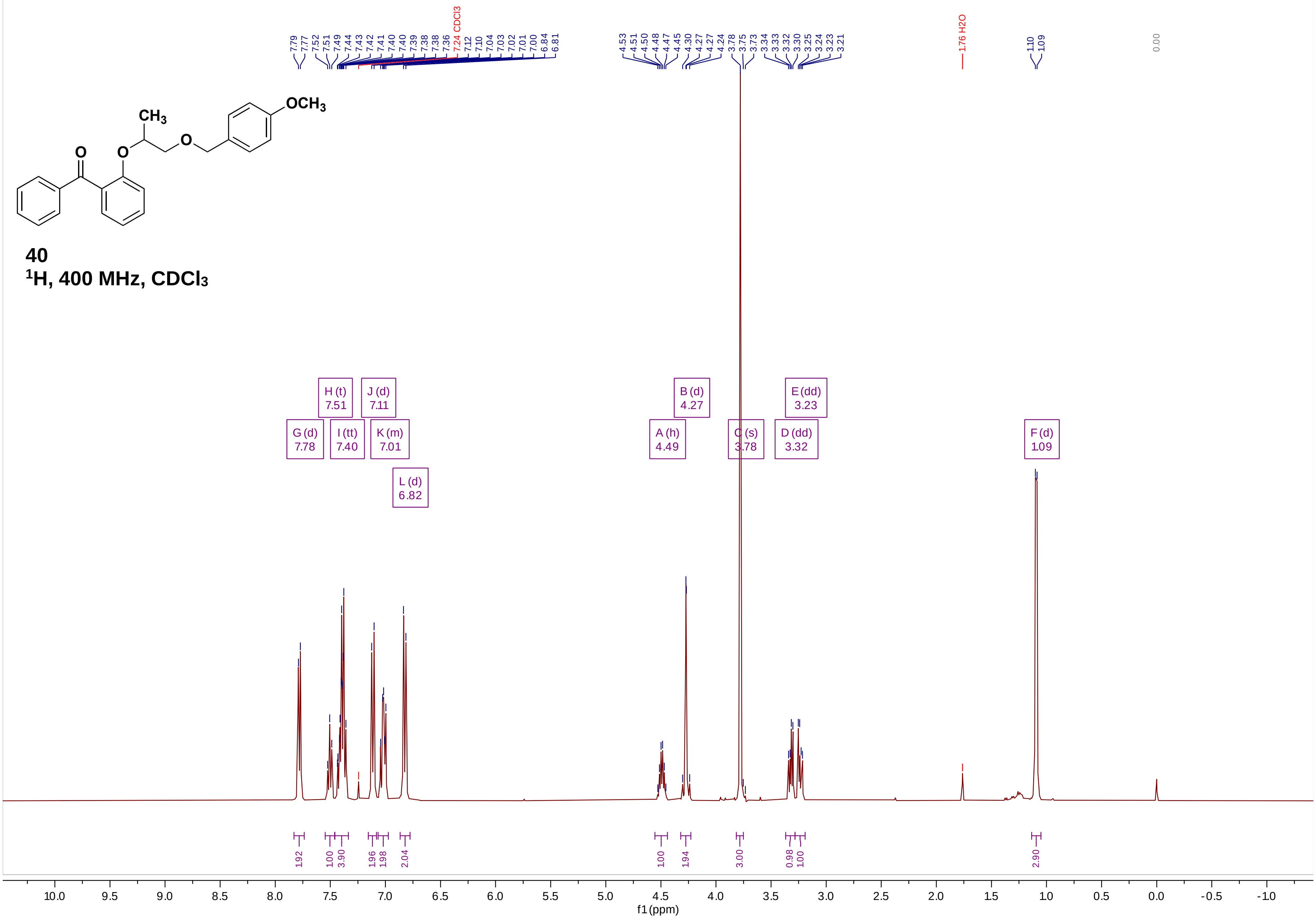

197.41
155.99
138.53
132.70
131.89
130.14
129.93
129.70
128.15
120.37
113.59
77.37 cdcl3
77.16 cdcl3
76.95 cdcl3
75.38
28.91
18.63
9.31
CH3
CH3
O
O
37
13C, 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

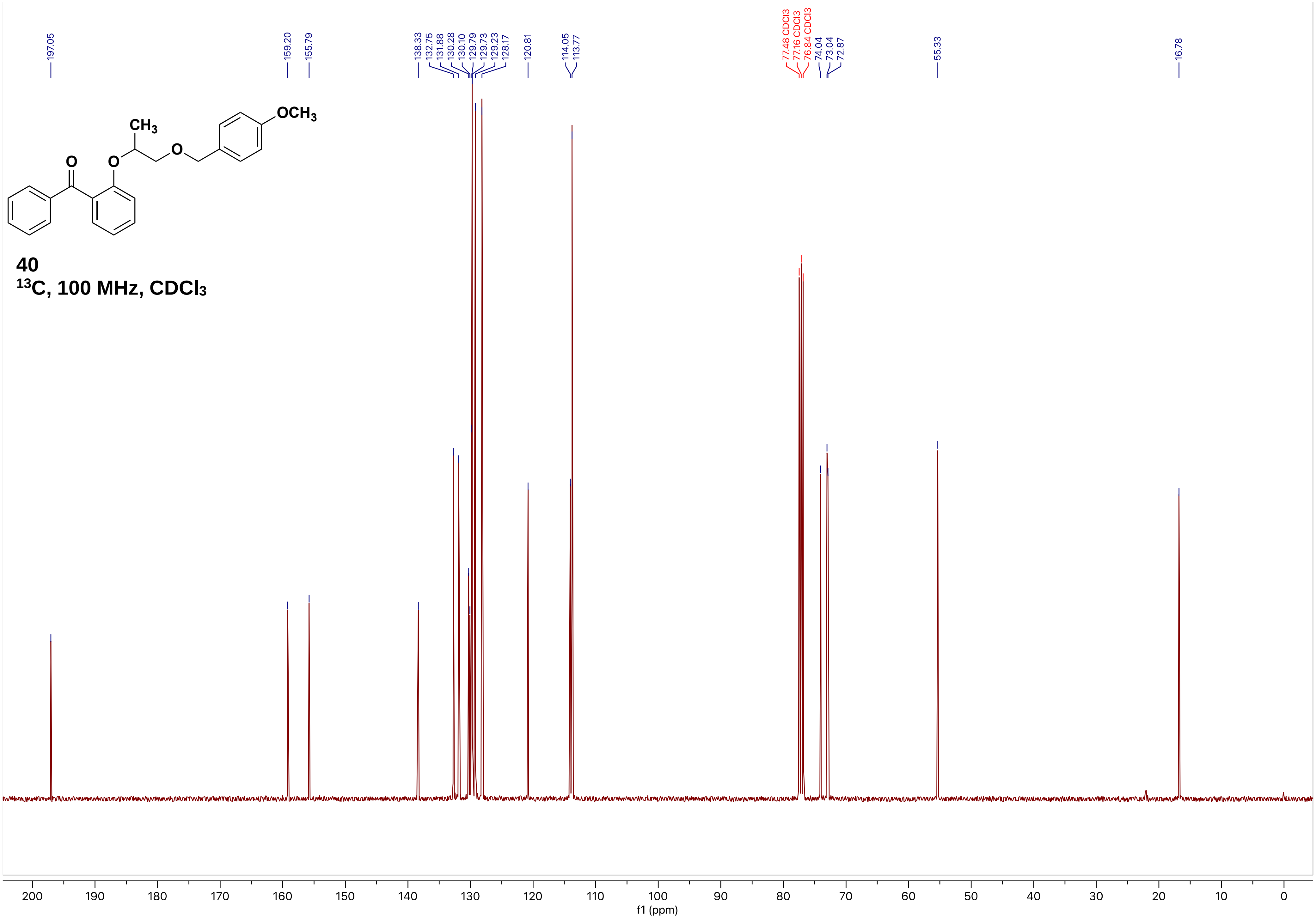

39
¹H, 600 MHz, CDCl₃
F (dd) 7.82
E (m) 7.55
D (m) 7.44
C (td) 7.06
B (d) 6.98
A (p) 3.89
G (d) 1.16
H (tdt) 0.79
I (tdd) 0.34
J (dddd) 0.27
K (dtd) 0.08
M (m) 0.03
f1 (ppm)

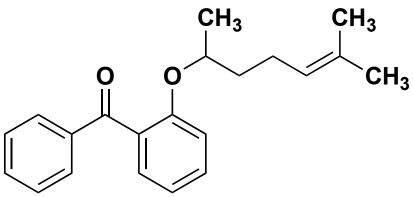


39

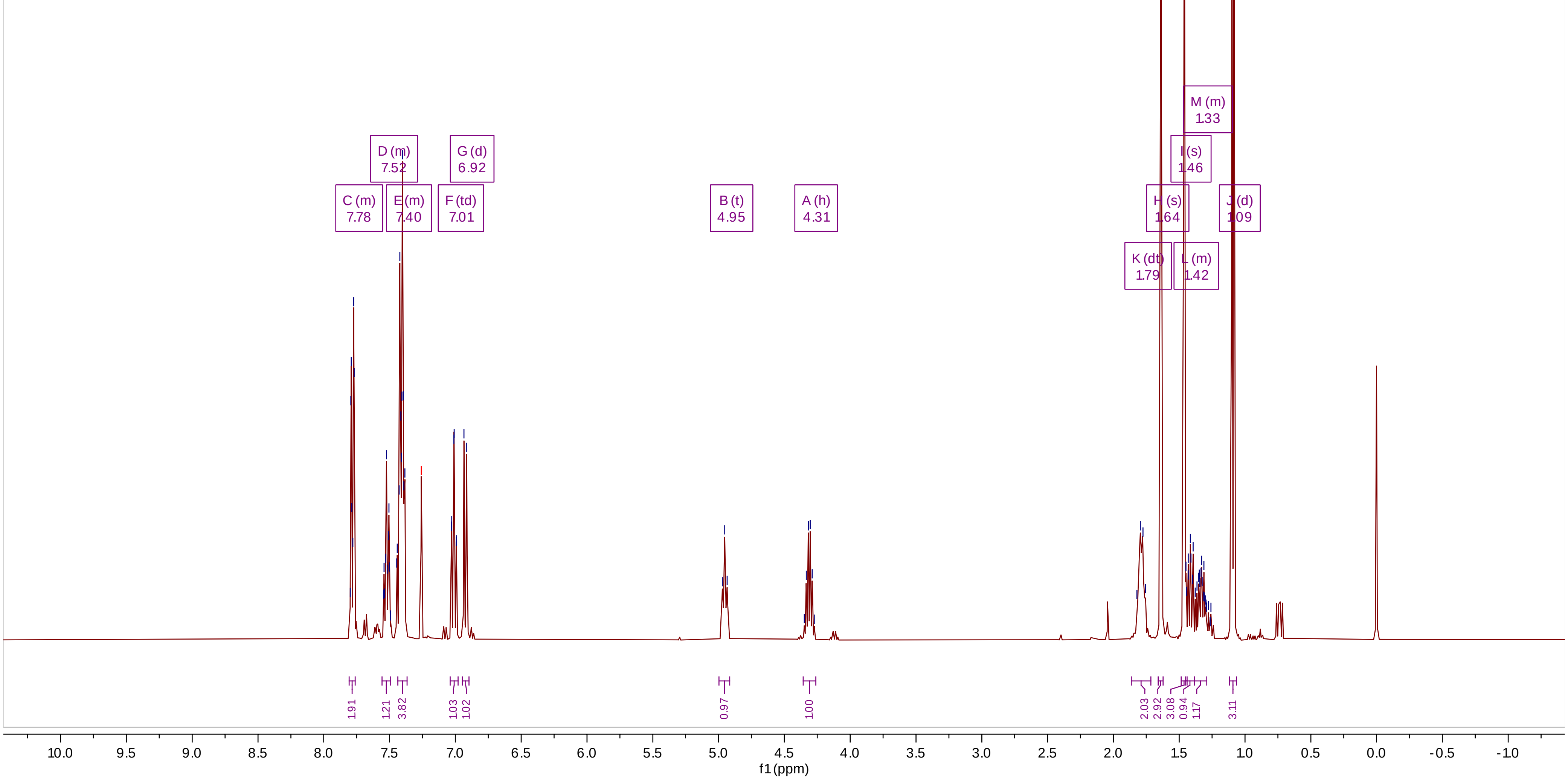
^{13}C, 150 MHz, $CDCl_3$

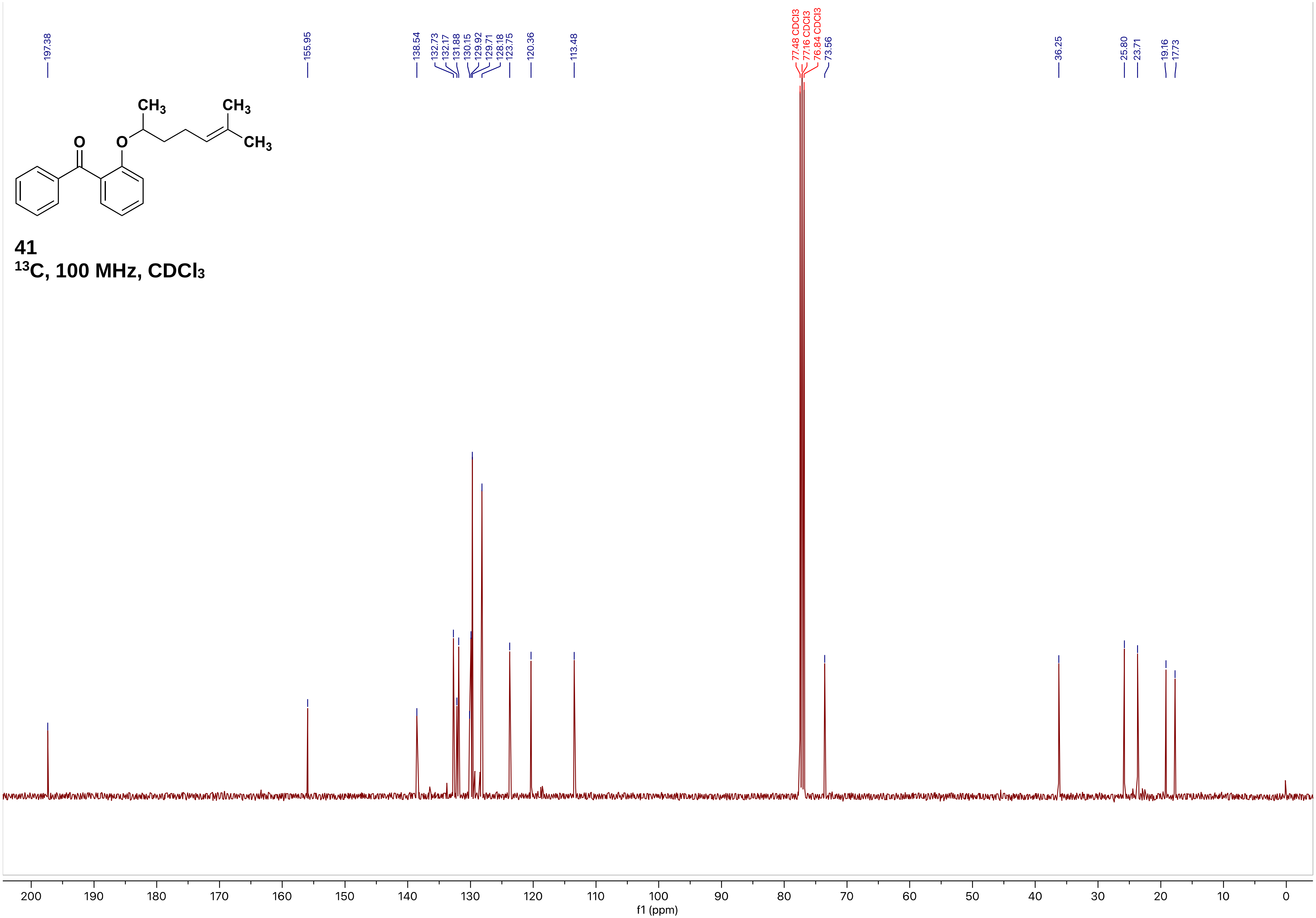

7.79 7.77 7.52 7.51 7.49 7.44 7.43 7.42 7.41 7.40 7.40 7.39 7.38 7.38 7.36 7.24 CDCl3 7.12 7.10 7.04 7.03 7.02 7.01 7.00 6.84 6.81
4.53 4.51 4.50 4.48 4.47 4.45 4.30 4.27 4.27 4.24 3.78 3.75 3.73 3.34 3.33 3.32 3.30 3.25 3.24 3.23 3.21
1.76 H2O
1.10 1.09
0.00
OCH3
CH3
O
O
O
40
1H, 400 MHz, CDCl3
H (t) 7.51
J (d) 7.11
G (d) 7.78
I (tt) 7.40
K (m) 7.01
L (d) 6.82
B (d) 4.27
A (h) 4.49
C (s) 3.78
E (dd) 3.23
D (dd) 3.32
F (d) 1.09
1.92 1.00 3.90 1.96 1.98 2.04 1.00 1.94 3.00 0.98 1.00 2.90
10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)

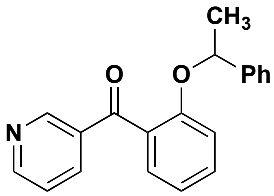

197.05
159.20
155.79
138.33
132.75
131.88
130.28
130.10
129.79
129.73
129.23
128.17
120.81
114.05
113.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.04
73.04
72.87
55.33
16.78
OCH3
CH3
O
O
O
40
13C, 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



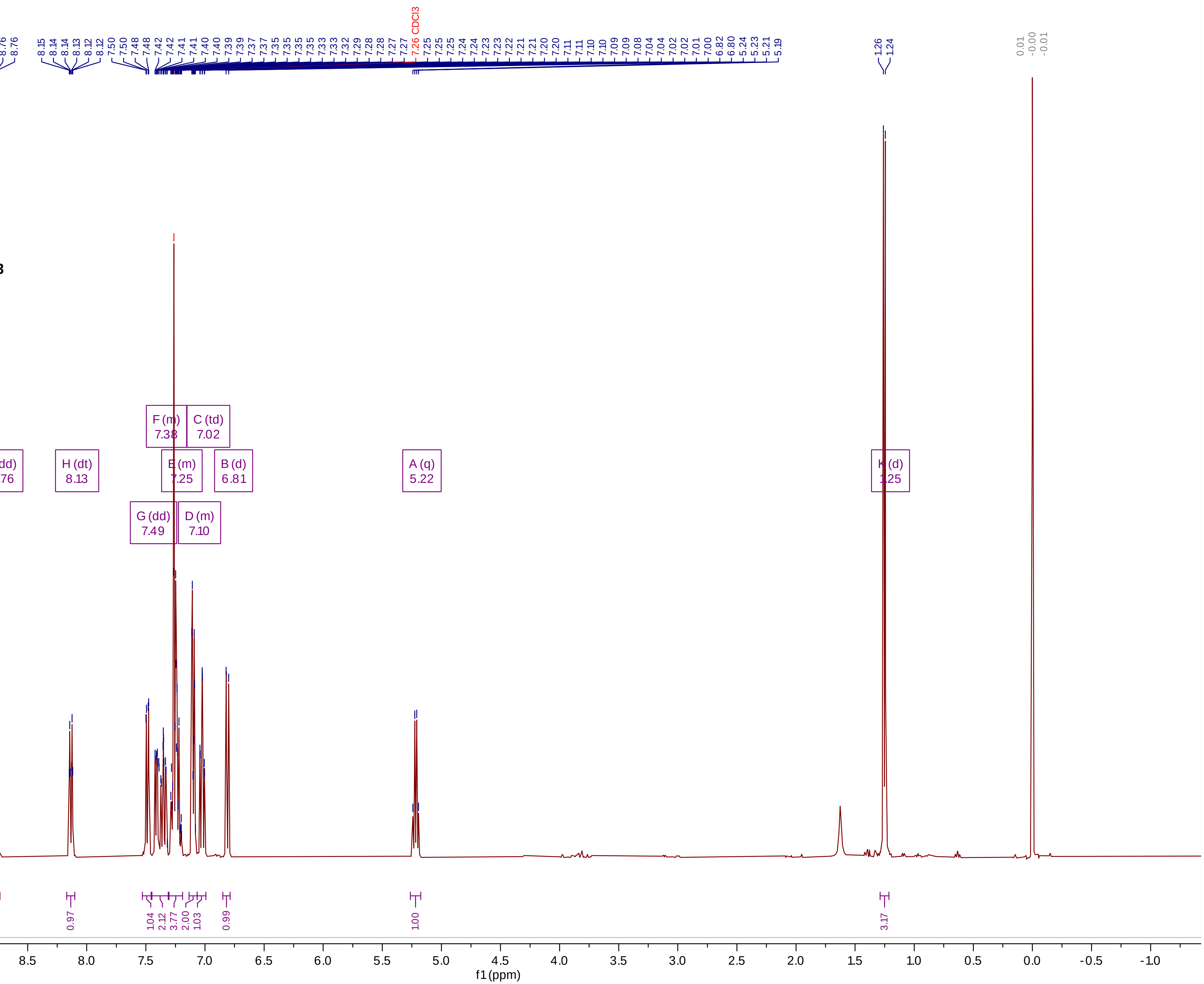
41
^{1}H, 400 MHz, $CDCl_3$

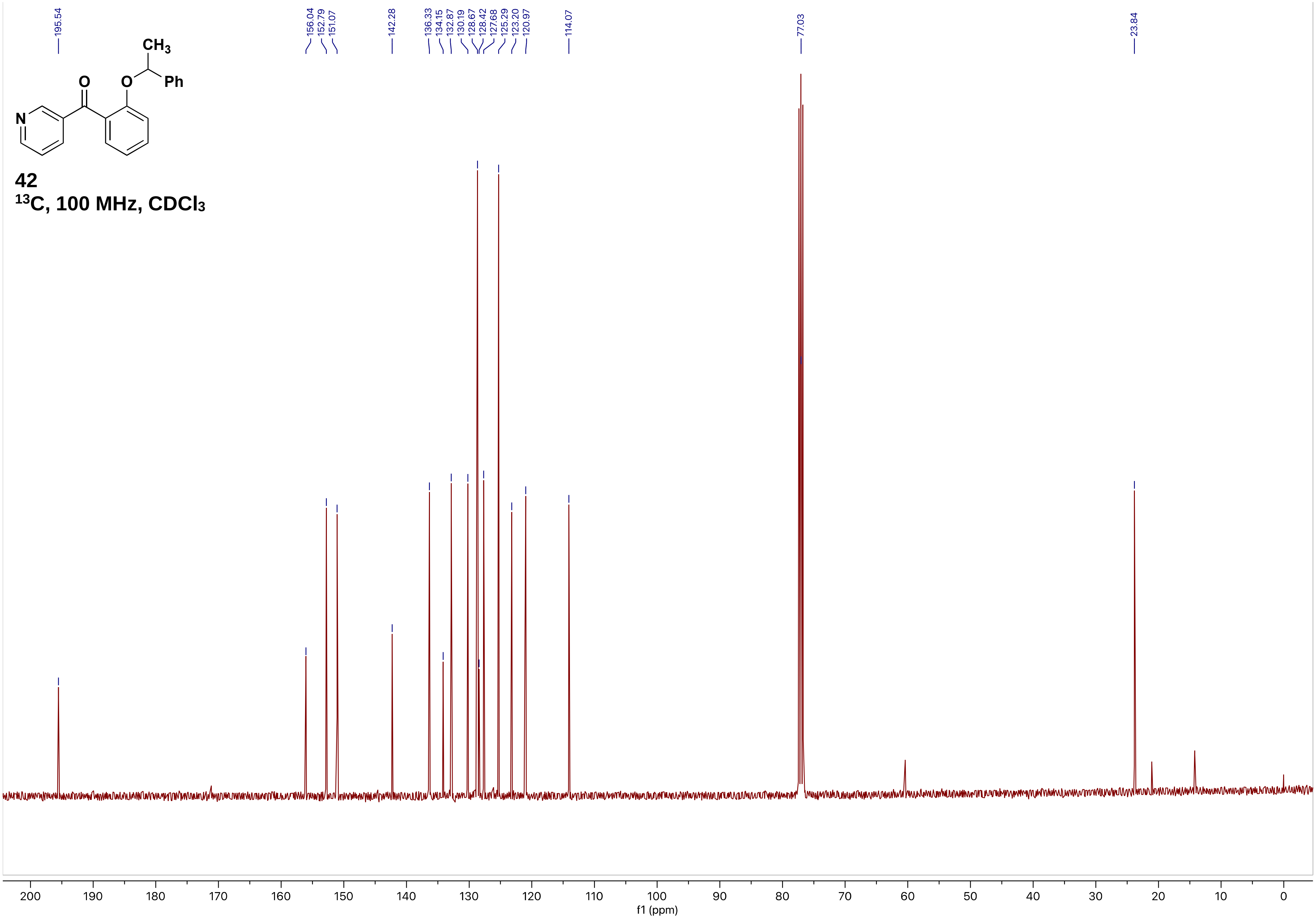


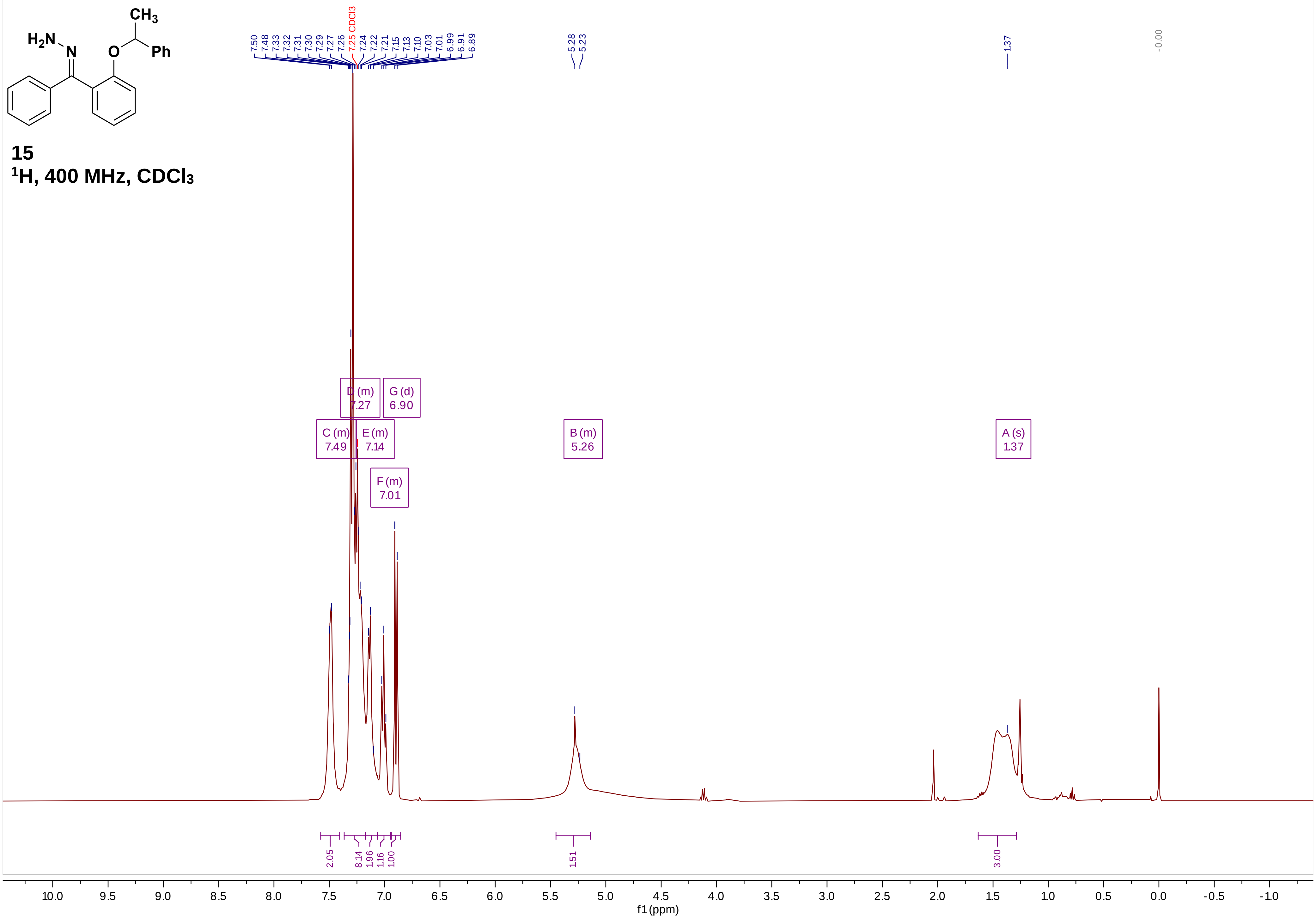

197.38
155.95
138.54
132.73
132.17
131.88
130.15
129.92
129.71
128.18
123.75
120.36
113.48
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.56
36.25
25.80
23.71
19.16
17.73
41
^{13}C, 100 MHz, $CDCl_3$
f1 (ppm)



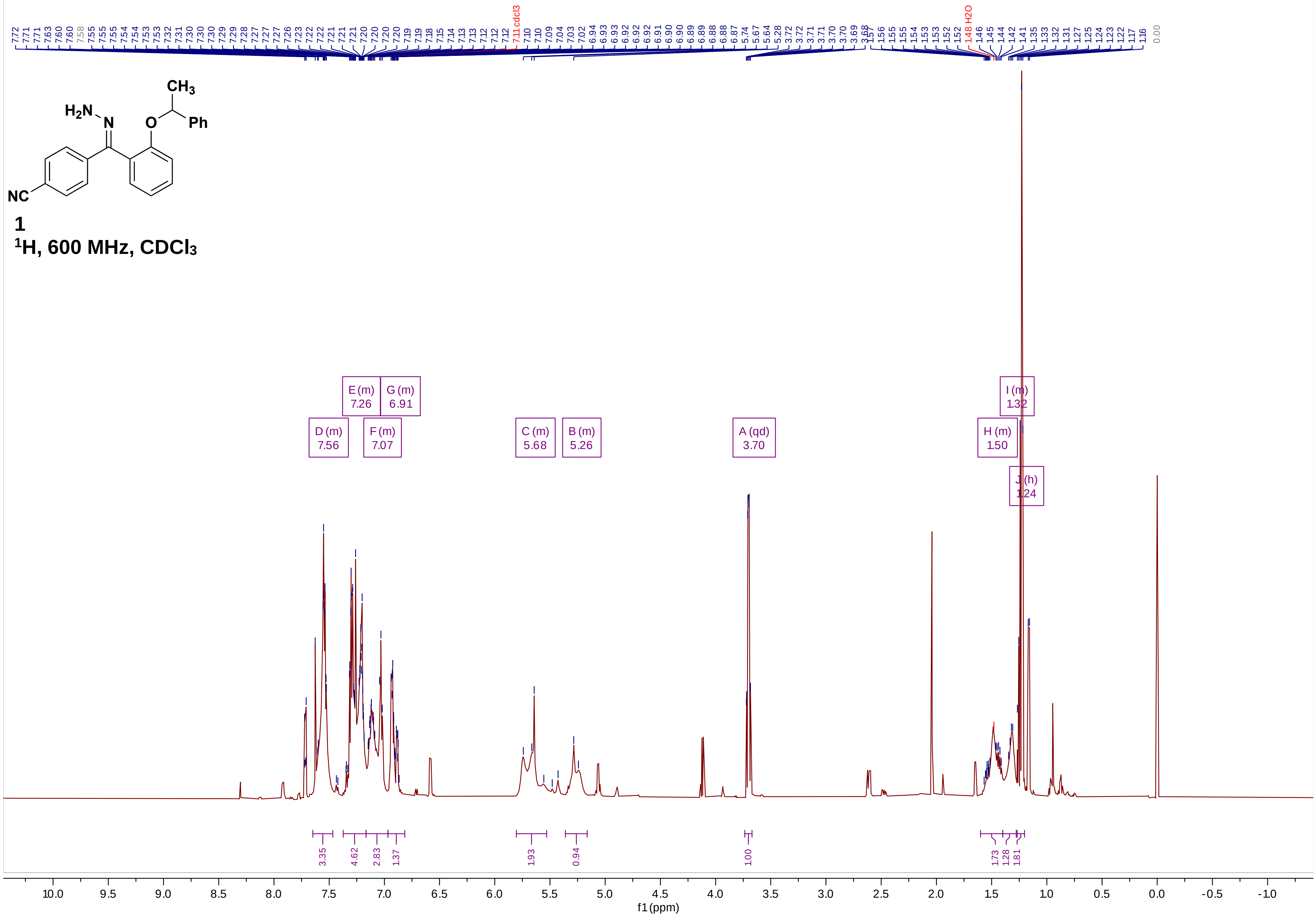
42
^{1}H, 400 MHz, $CDCl_3$



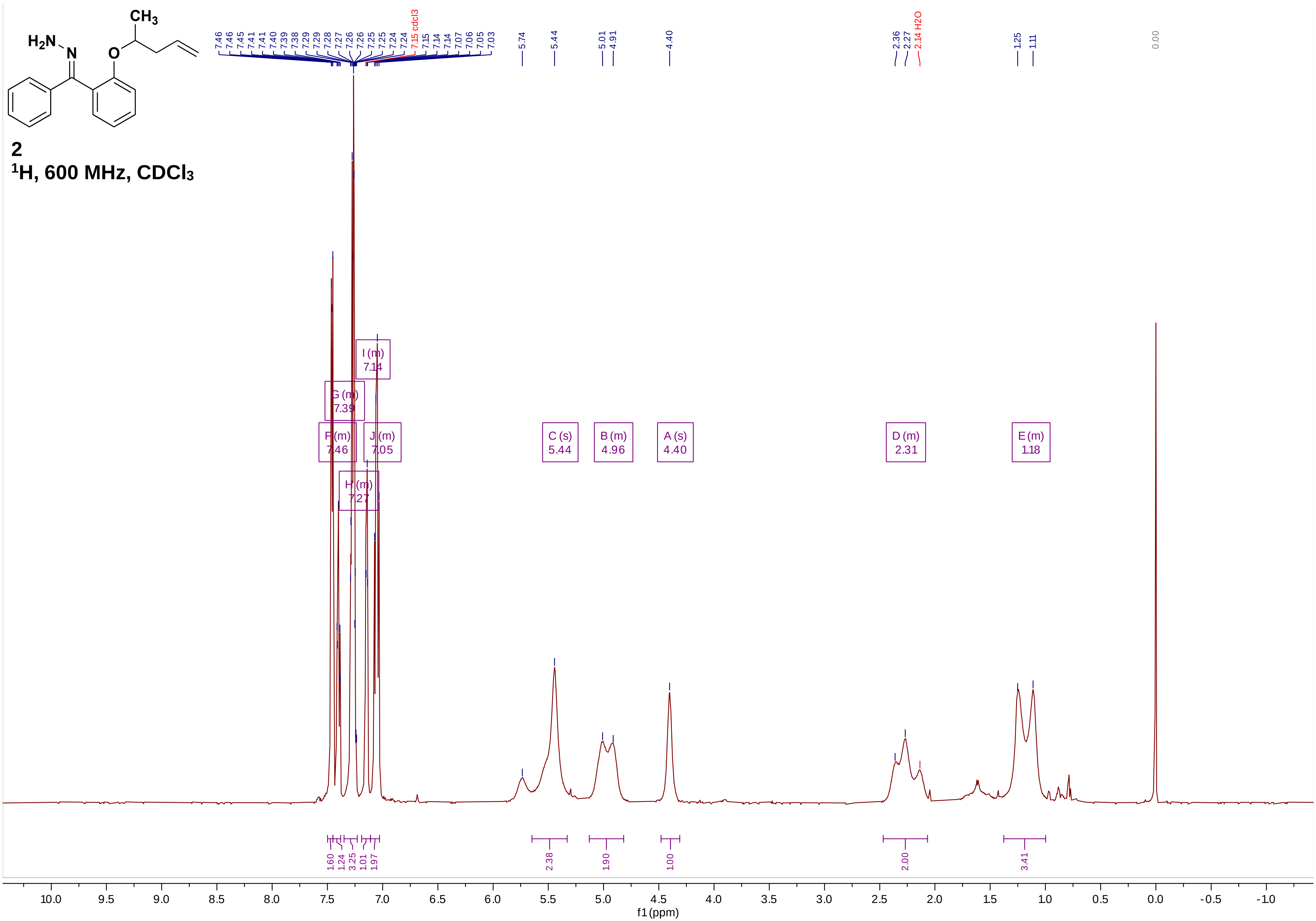

195.54
156.04
152.79
151.07
142.28
136.33
134.15
132.87
130.19
128.67
128.42
127.68
125.29
123.20
120.97
114.07
77.03
23.84
CH3
O
O
Ph
N
42
13C, 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

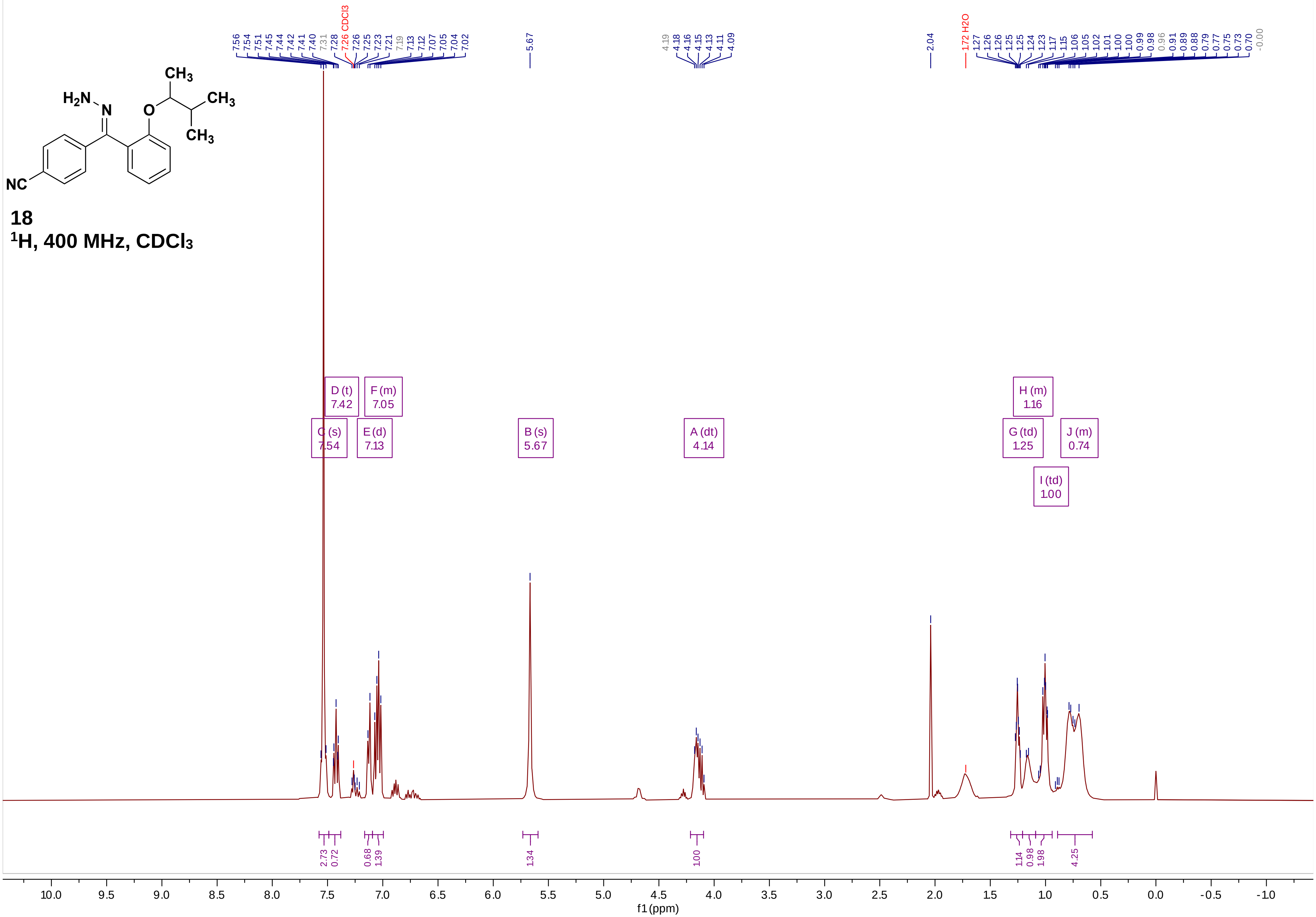


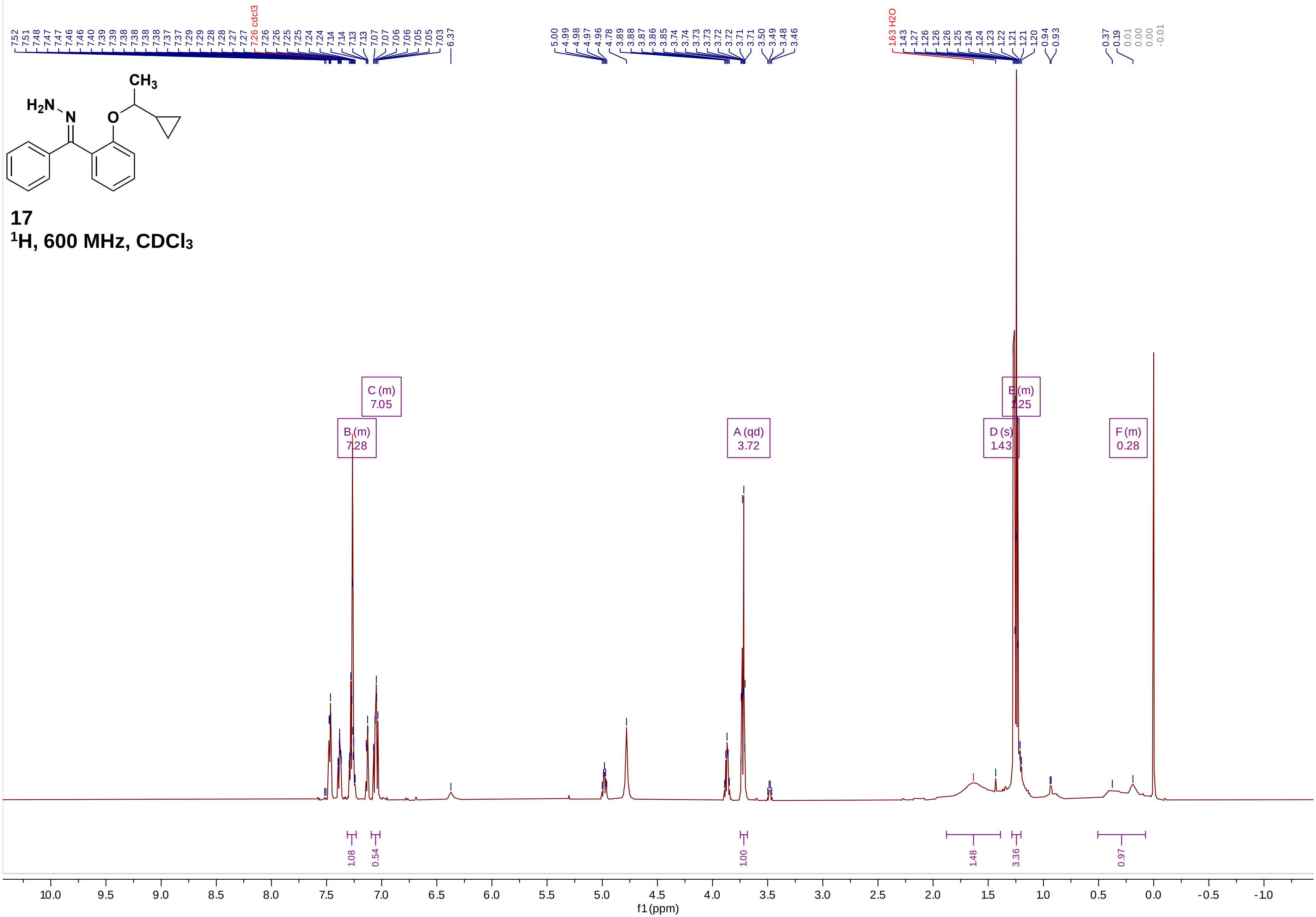
H2N
N
O
CH3
Ph
15
1H, 400 MHz, CDCl3
7.50
7.48
7.33
7.32
7.31
7.30
7.29
7.27
7.26
7.25 CDCl3
7.24
7.22
7.21
7.15
7.13
7.10
7.03
7.01
6.99
6.91
6.89
5.28
5.23
1.37
-0.00
D (m)
7.27
G (d)
6.90
C (m)
7.49
E (m)
7.14
F (m)
7.01
B (m)
5.26
A (s)
1.37
2.05
8.14
1.96
1.16
1.00
1.51
3.00
f1 (ppm)



CH3
H2N
N
O
Ph
NC
1
1H, 600 MHz, CDCl3
D (m) 7.56
E (m) 7.26
F (m) 7.07
G (m) 6.91
C (m) 5.68
B (m) 5.26
A (qd) 3.70
H (m) 1.50
I (m) 1.32
J (h) 1.24
3.35
4.62
2.83
1.37
1.93
0.94
1.00
1.73
1.28
1.81
f1 (ppm)

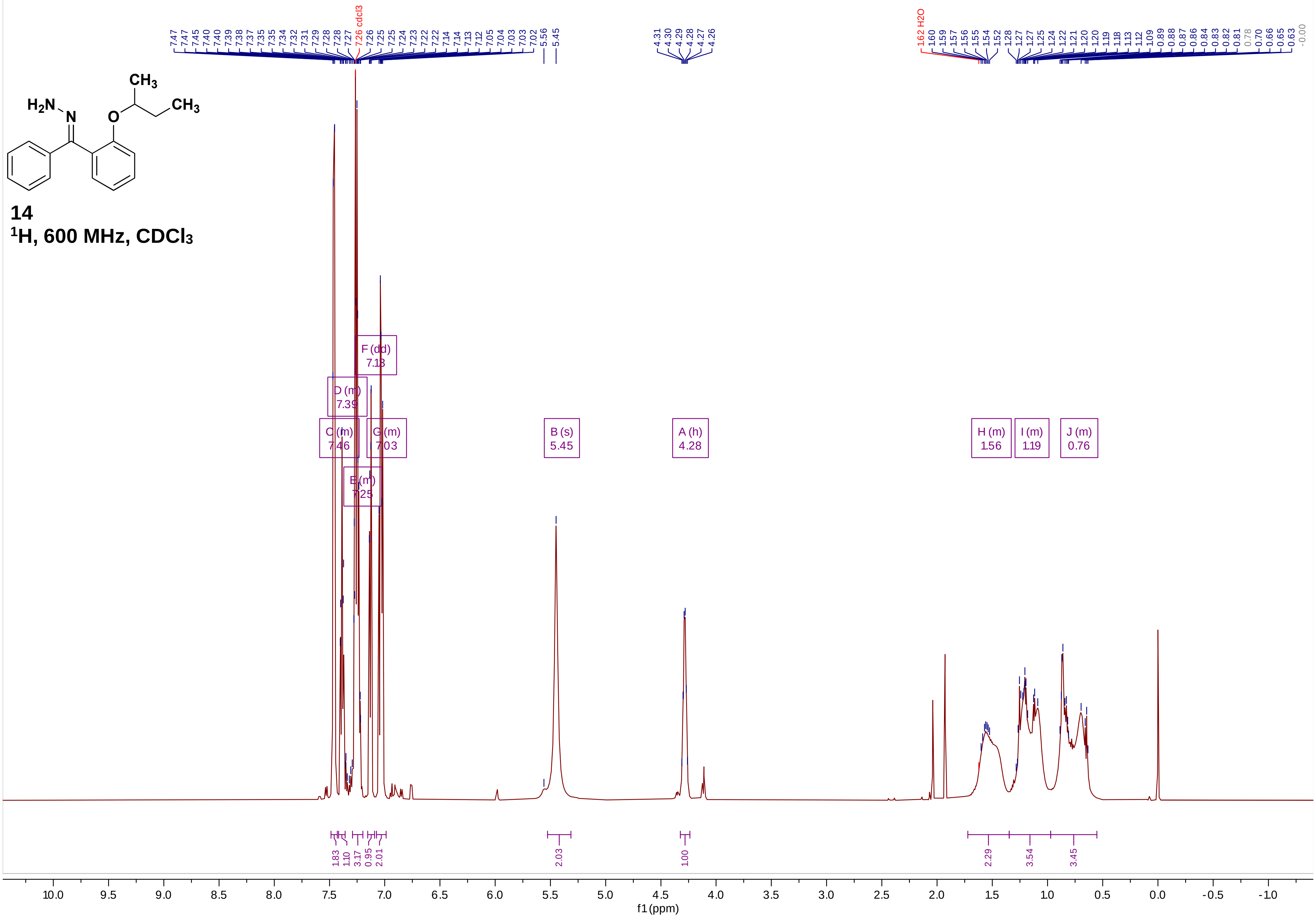

CH3
H2N
N
O
2
1H, 600 MHz, CDCl3
7.46 7.46 7.45 7.41 7.41 7.40 7.39 7.38 7.29 7.29 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.15 cdcl3 7.15 7.14 7.14 7.07 7.06 7.05 7.03
5.74
5.44
5.01
4.91
4.40
2.36
2.27
2.14 H2O
1.25
1.11
0.00
I (m) 7.14
G (m) 7.39
F (m) 7.46
J (m) 7.05
H (m) 7.27
C (s) 5.44
B (m) 4.96
A (s) 4.40
D (m) 2.31
E (m) 1.18
1.60 1.24 3.25 1.01 1.97
2.38
1.90
1.00
2.00
3.41
10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)

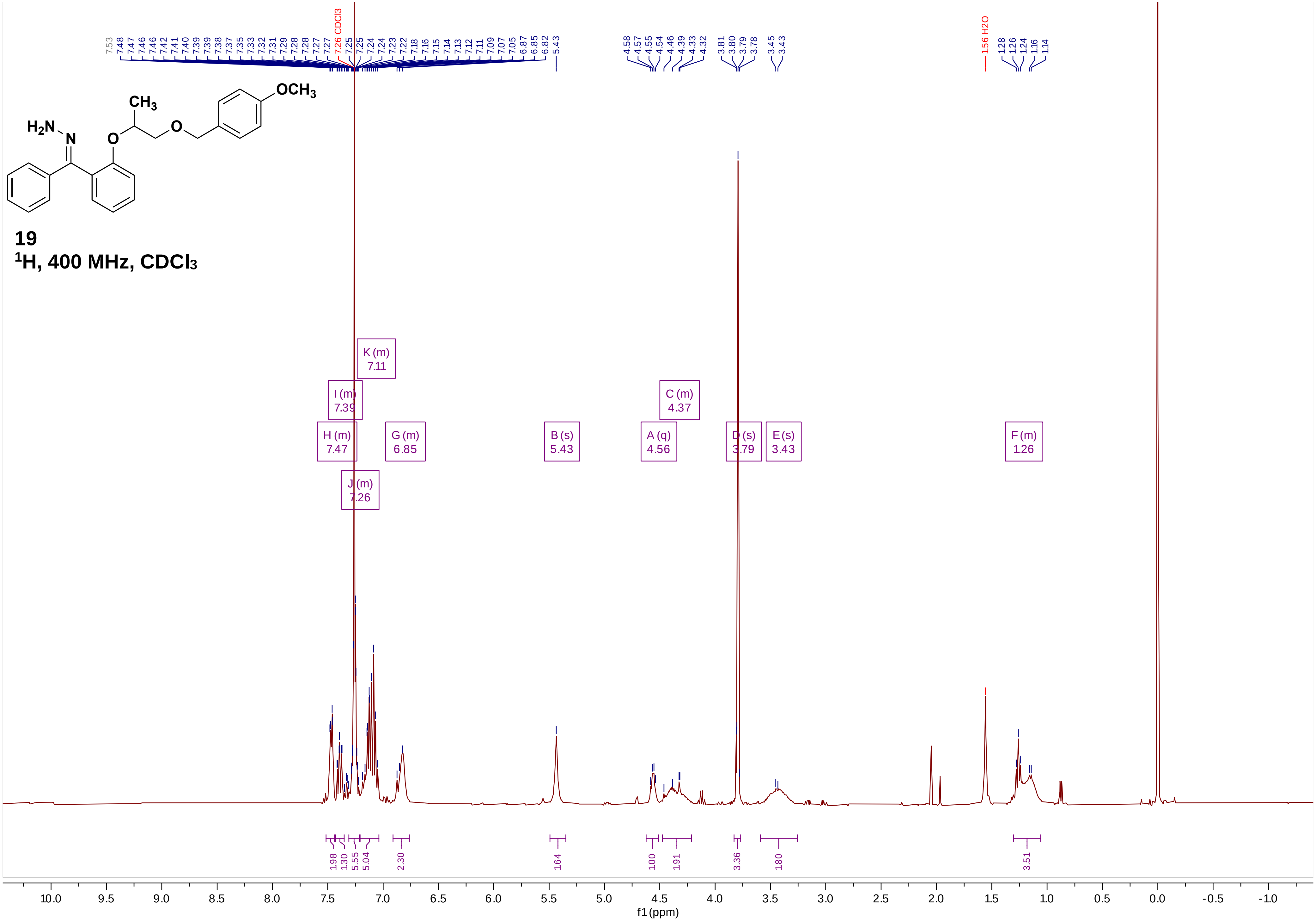

18
1H, 400 MHz, CDCl3
7.56 7.54 7.51 7.45 7.44 7.42 7.41 7.40 7.31 7.28 7.26 CDCl3 7.26 7.25 7.23 7.21 7.19 7.13 7.12 7.07 7.05 7.04 7.02
5.67
4.19 4.18 4.16 4.15 4.13 4.11 4.09
2.04
1.72 H2O 1.27 1.26 1.26 1.25 1.25 1.24 1.23 1.17 1.15 1.06 1.05 1.02 1.01 1.00 1.00 0.99 0.98 0.96 0.91 0.89 0.88 0.79 0.77 0.75 0.73 0.70 -0.00
D (t) 7.42
F (m) 7.05
C (s) 7.54
E (d) 7.13
B (s) 5.67
A (dt) 4.14
H (m) 1.16
G (td) 1.25
J (m) 0.74
I (td) 1.00
2.73 0.72 0.68 1.39 1.34 1.00 1.14 0.98 1.98 4.25
10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)

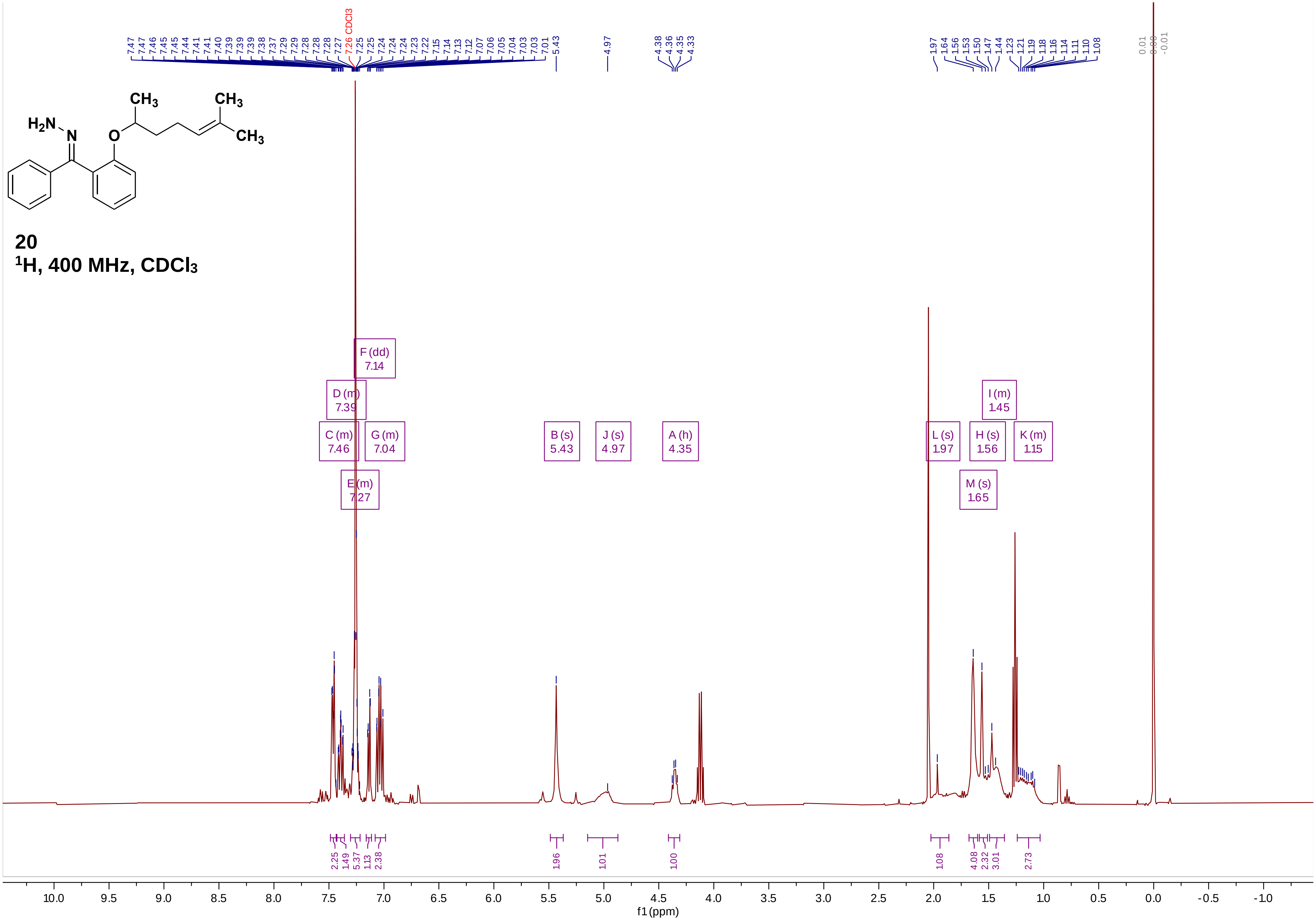


17

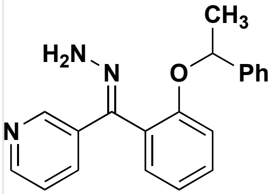
^{1}H, 600 MHz, CDCl$_3$


14
¹H, 600 MHz, CDCl3
f1 (ppm)


19
1H, 400 MHz, CDCl3
f1 (ppm)

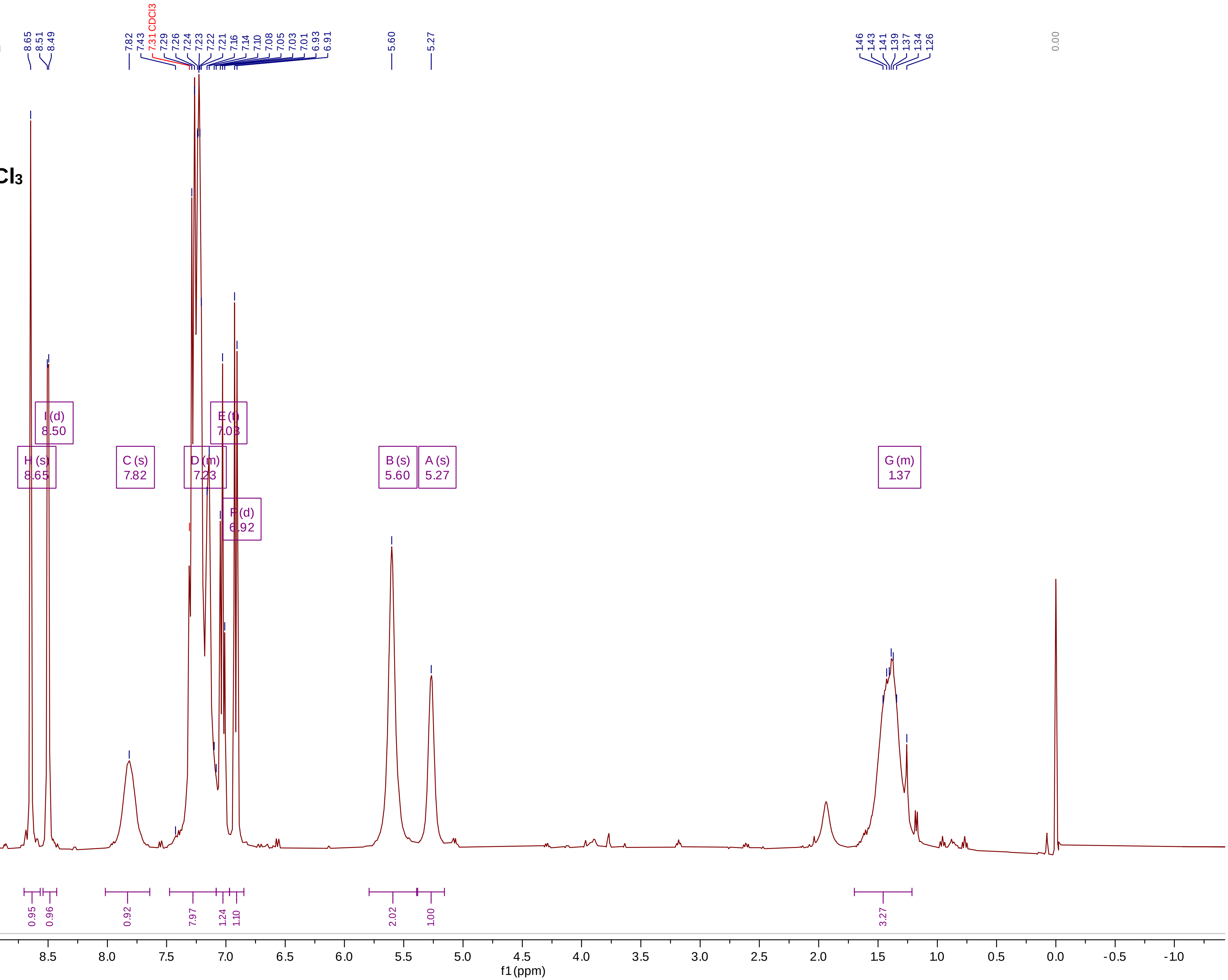


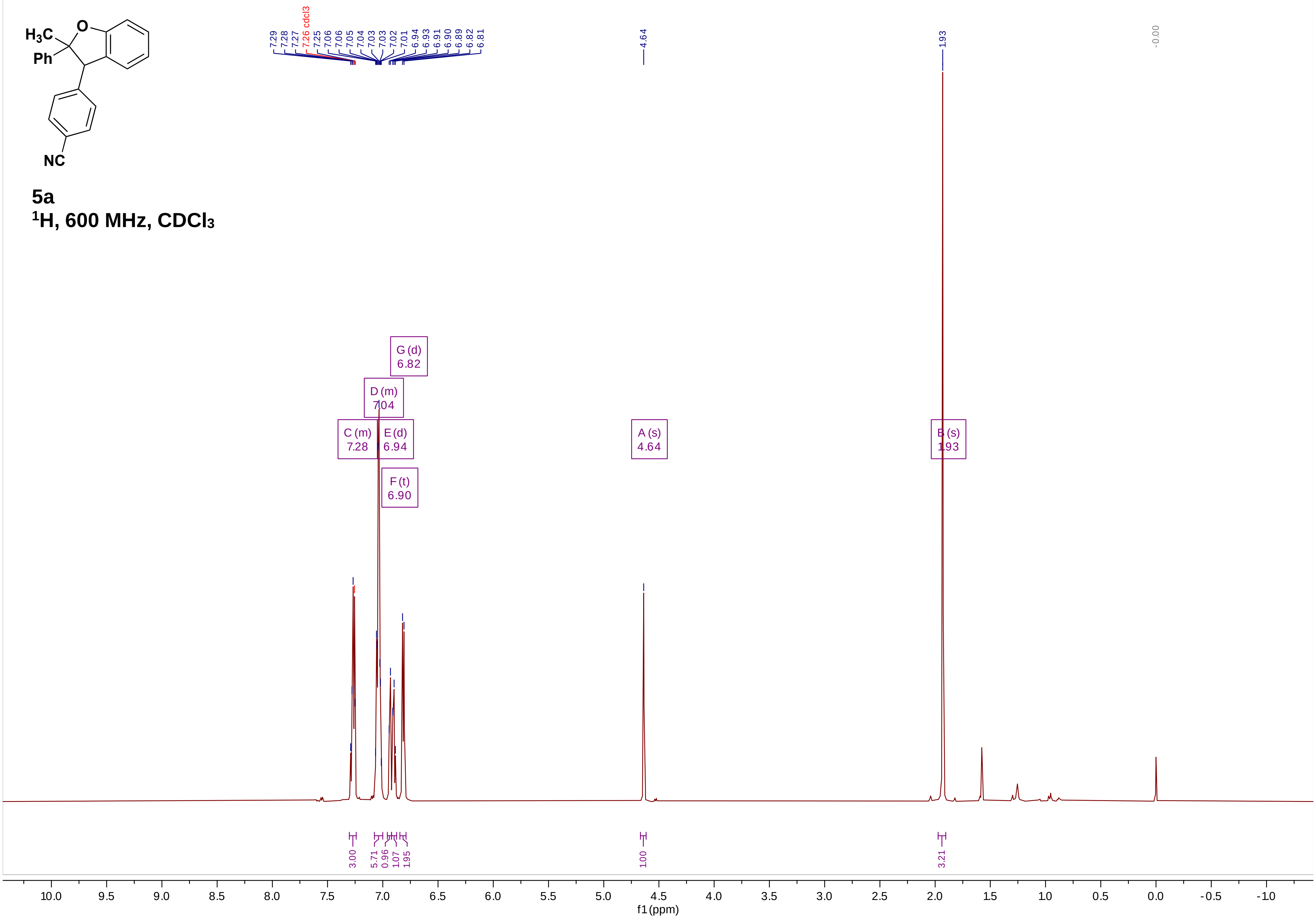
7.47 7.47 7.46 7.45 7.45 7.44 7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.37 7.29 7.29 7.28 7.28 7.28 7.27 7.26 CDCl3 7.25 7.25 7.24 7.24 7.24 7.23 7.22 7.15 7.14 7.13 7.12 7.07 7.06 7.05 7.04 7.03 7.03 7.01 5.43
4.97
4.38 4.36 4.35 4.33
1.97 1.64 1.56 1.53 1.50 1.47 1.44 1.23 1.21 1.19 1.18 1.16 1.14 1.11 1.10 1.08
0.01 0.00 -0.01
CH3
CH3
H2N
N
O
CH3
20
1H, 400 MHz, CDCl3
F (dd) 7.14
D (m) 7.39
C (m) 7.46
G (m) 7.04
E (m) 7.27
B (s) 5.43
J (s) 4.97
A (h) 4.35
I (m) 1.45
L (s) 1.97
H (s) 1.56
K (m) 1.15
M (s) 1.65
2.25 1.49 5.37 1.13 2.38
1.96
1.01
1.00
1.08
4.08 2.32 3.01
2.73
10.0 9.5 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 0.0 -0.5 -1.0
f1 (ppm)



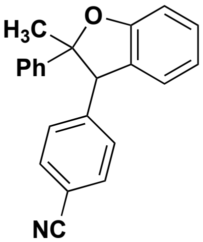
16

^{1}H, 400 MHz, $CDCl_3$



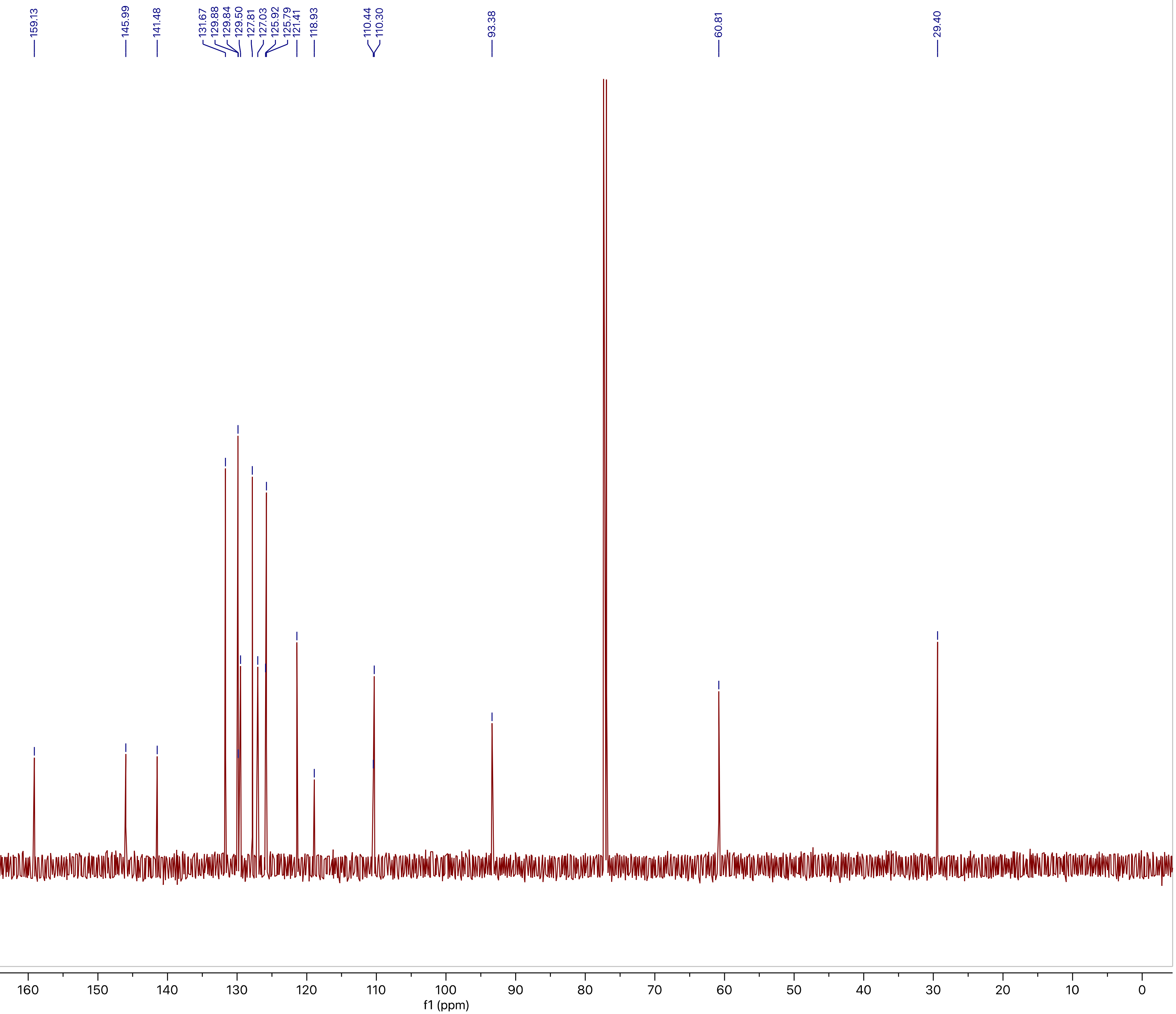


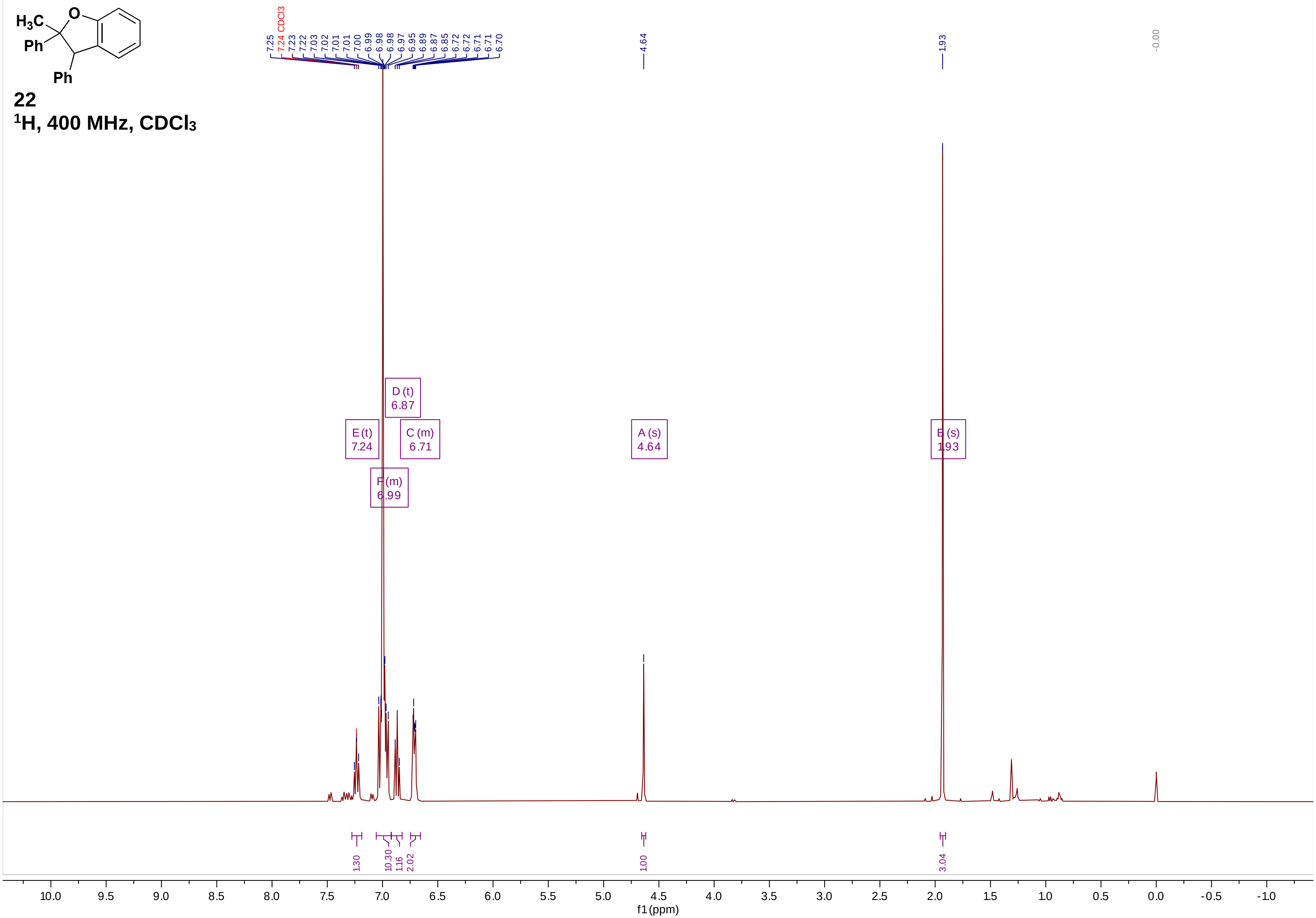
H3C
O
Ph
NC
5a
1H, 600 MHz, CDCl3
7.29 7.28 7.27 7.26 cdcl3 7.25 7.06 7.06 7.05 7.04 7.03 7.03 7.02 7.01 6.94 6.93 6.91 6.90 6.89 6.82 6.81
4.64
1.93
-0.00
G (d) 6.82
D (m) 7.04
C (m) 7.28
E (d) 6.94
F (t) 6.90
A (s) 4.64
B (s) 1.93
3.00
5.71
0.96
1.07
1.95
1.00
3.21
f1 (ppm)



5a

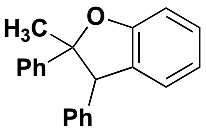
^{13}C, 150 MHz, $CDCl_3$





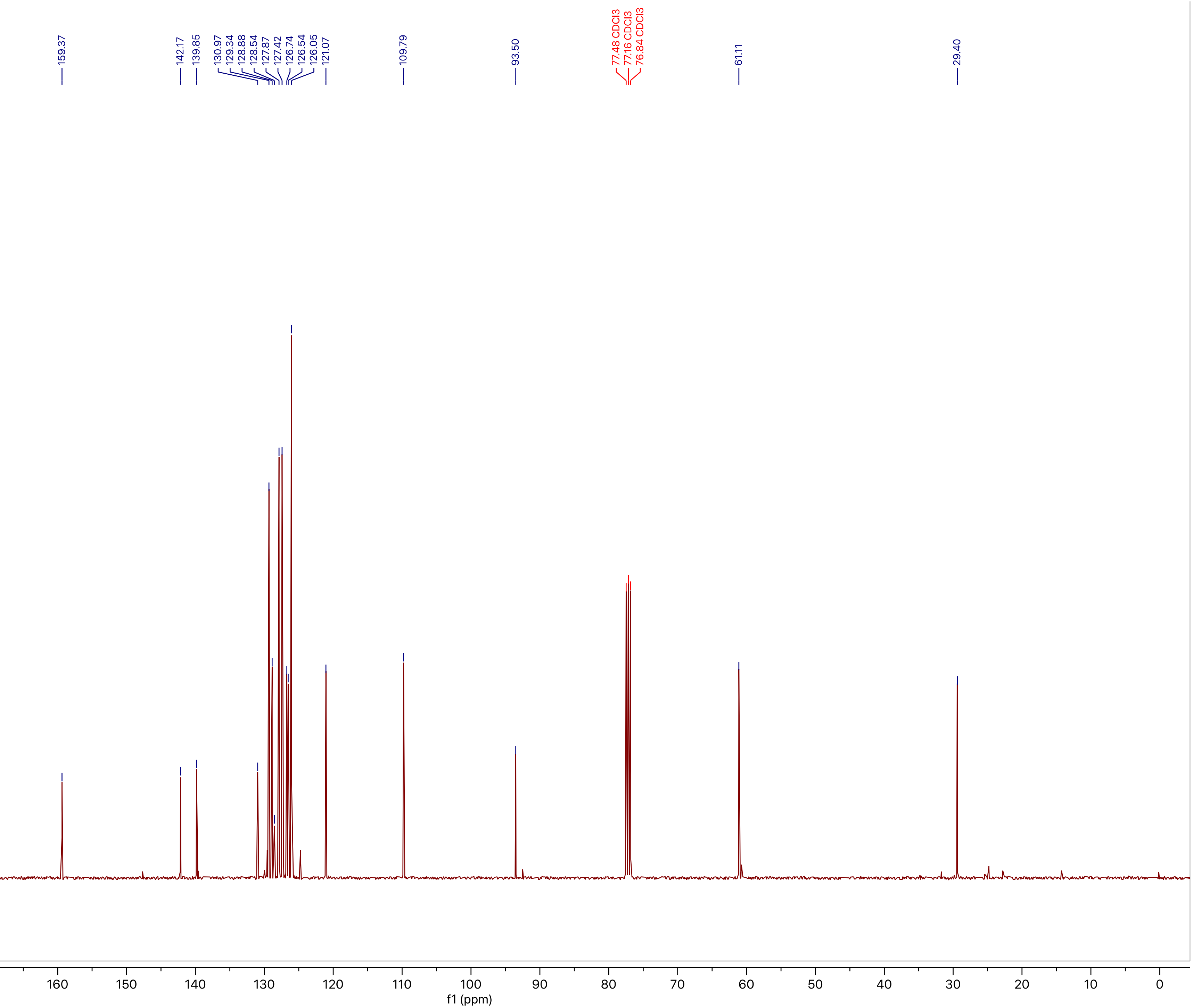
22

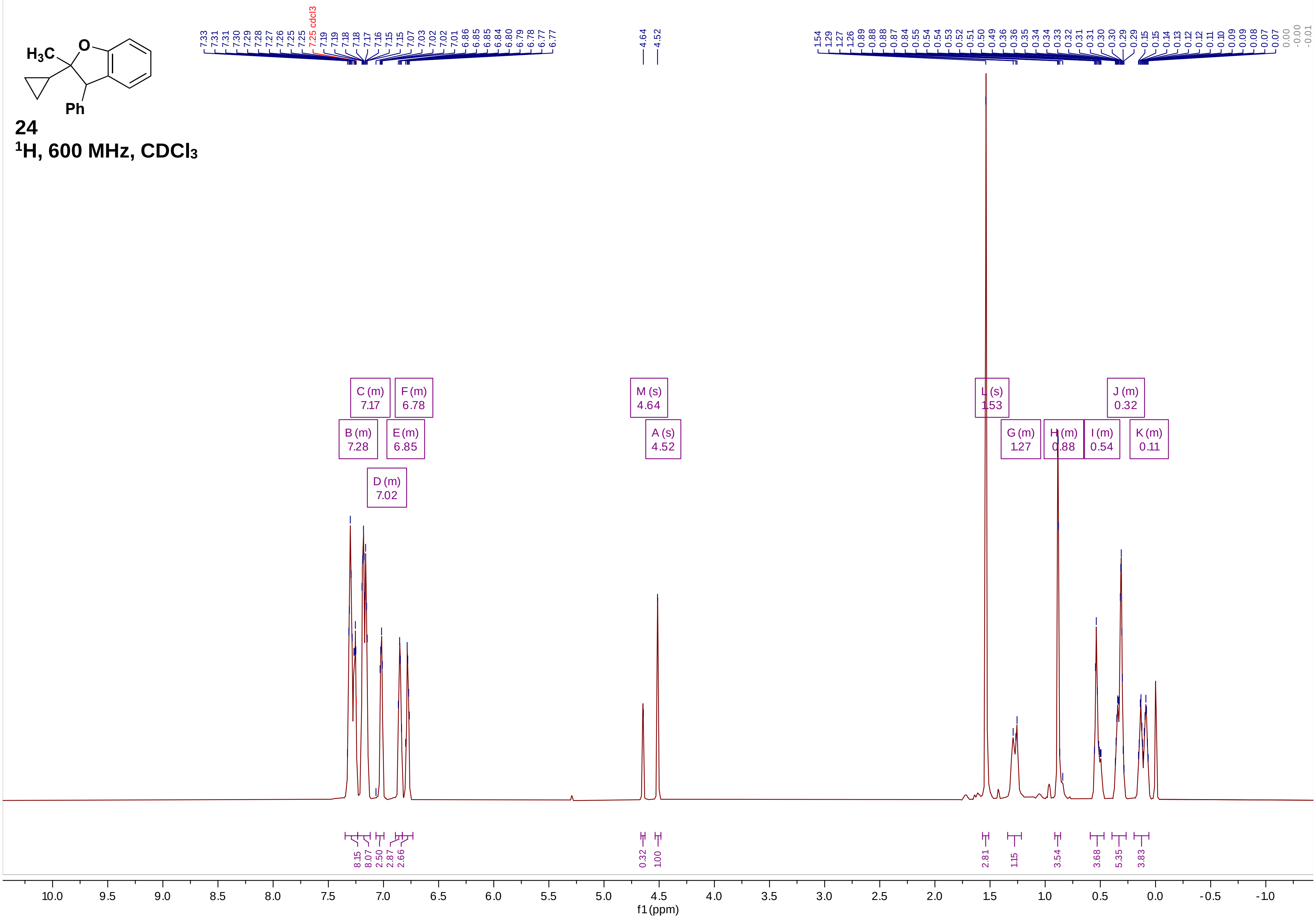
^{1}H, 400 MHz, CDCl$_3$



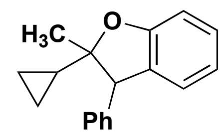
22

^{13}C, 100 MHz, $CDCl_3$



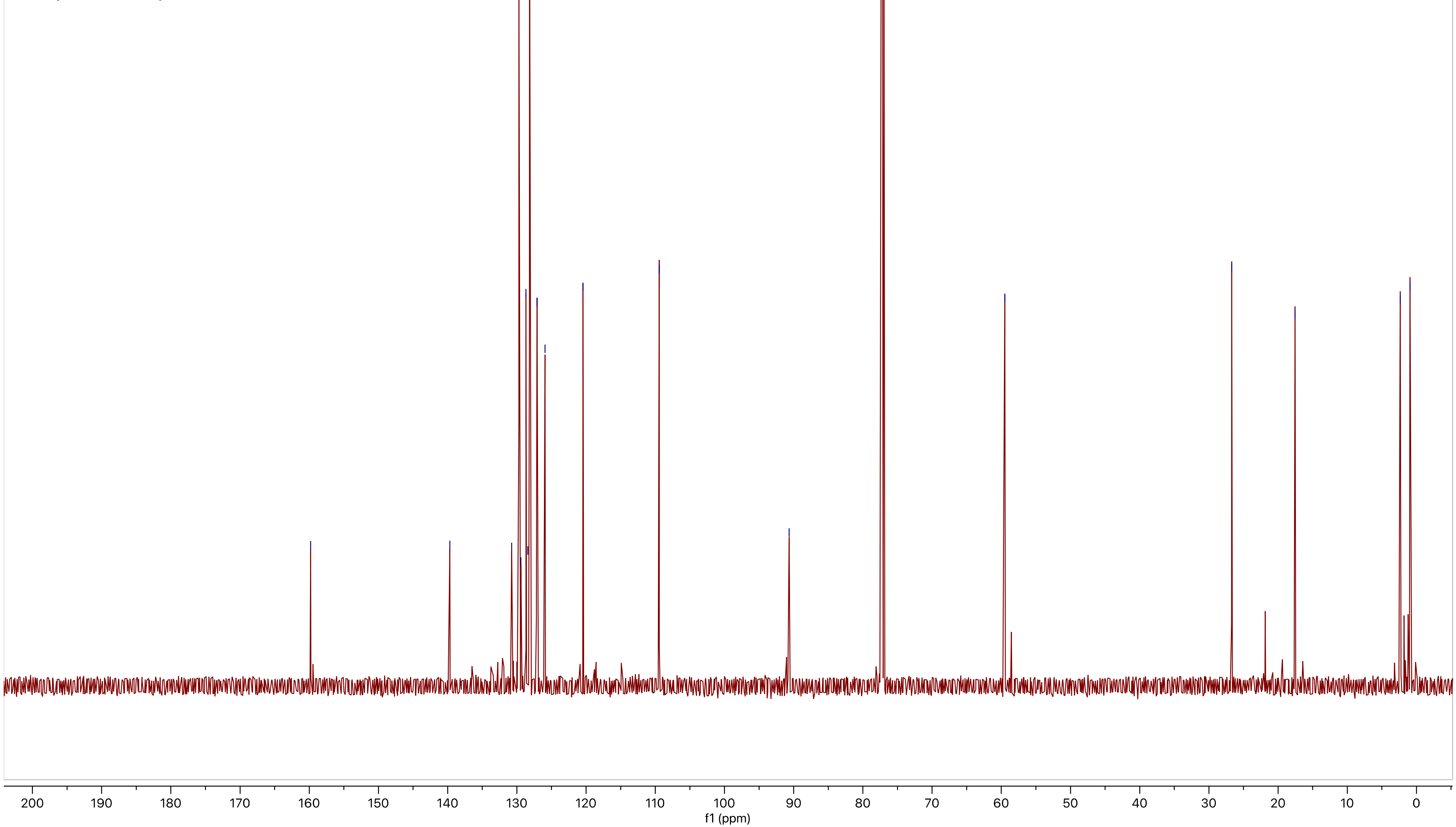


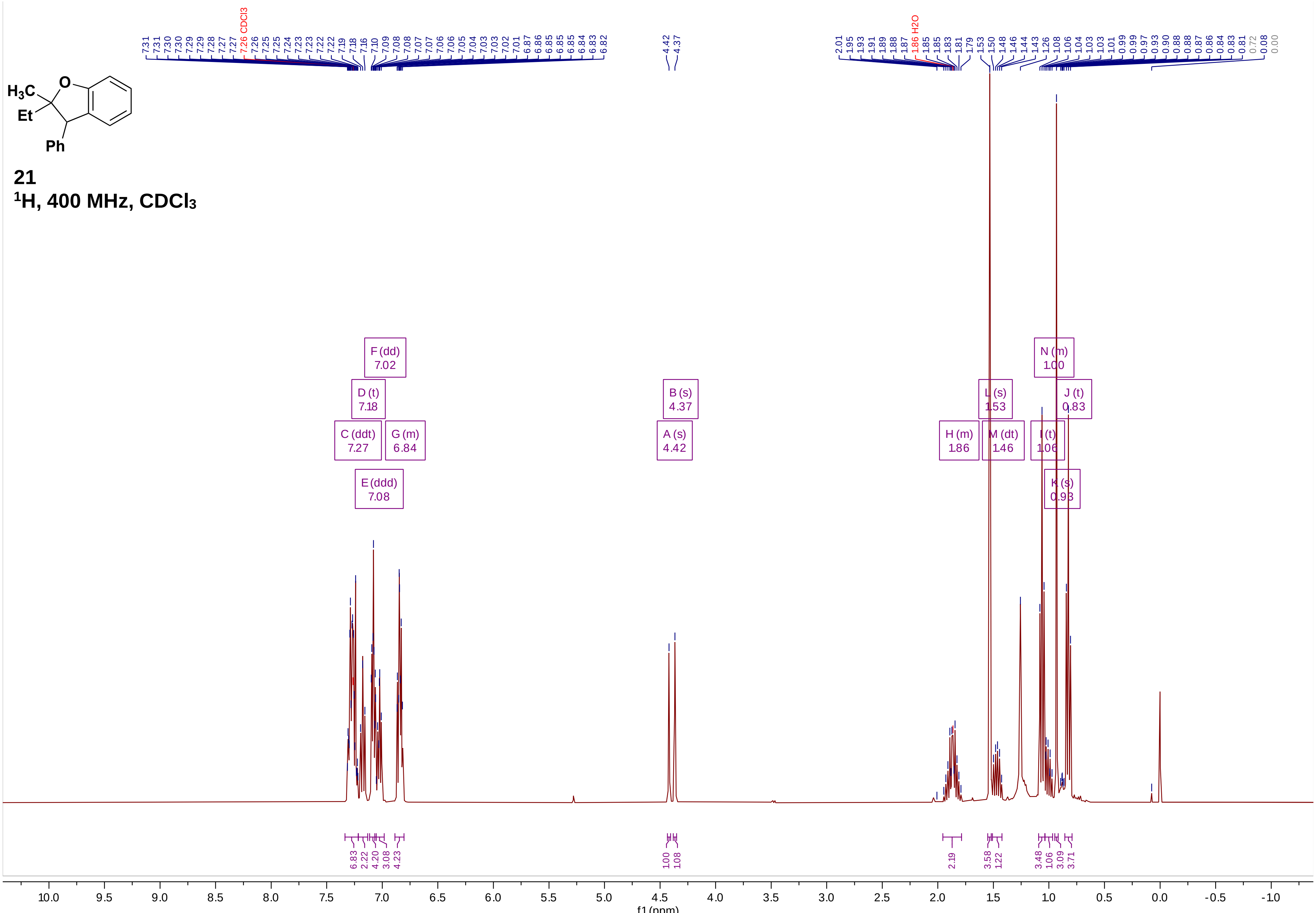
Note: Spectra is a mix of diastereomers, with the minor and major diastereomer peaks that can be assigned reported in the text above.



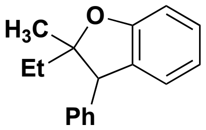
24

^{13}C, 150 MHz, CDCl$_3$



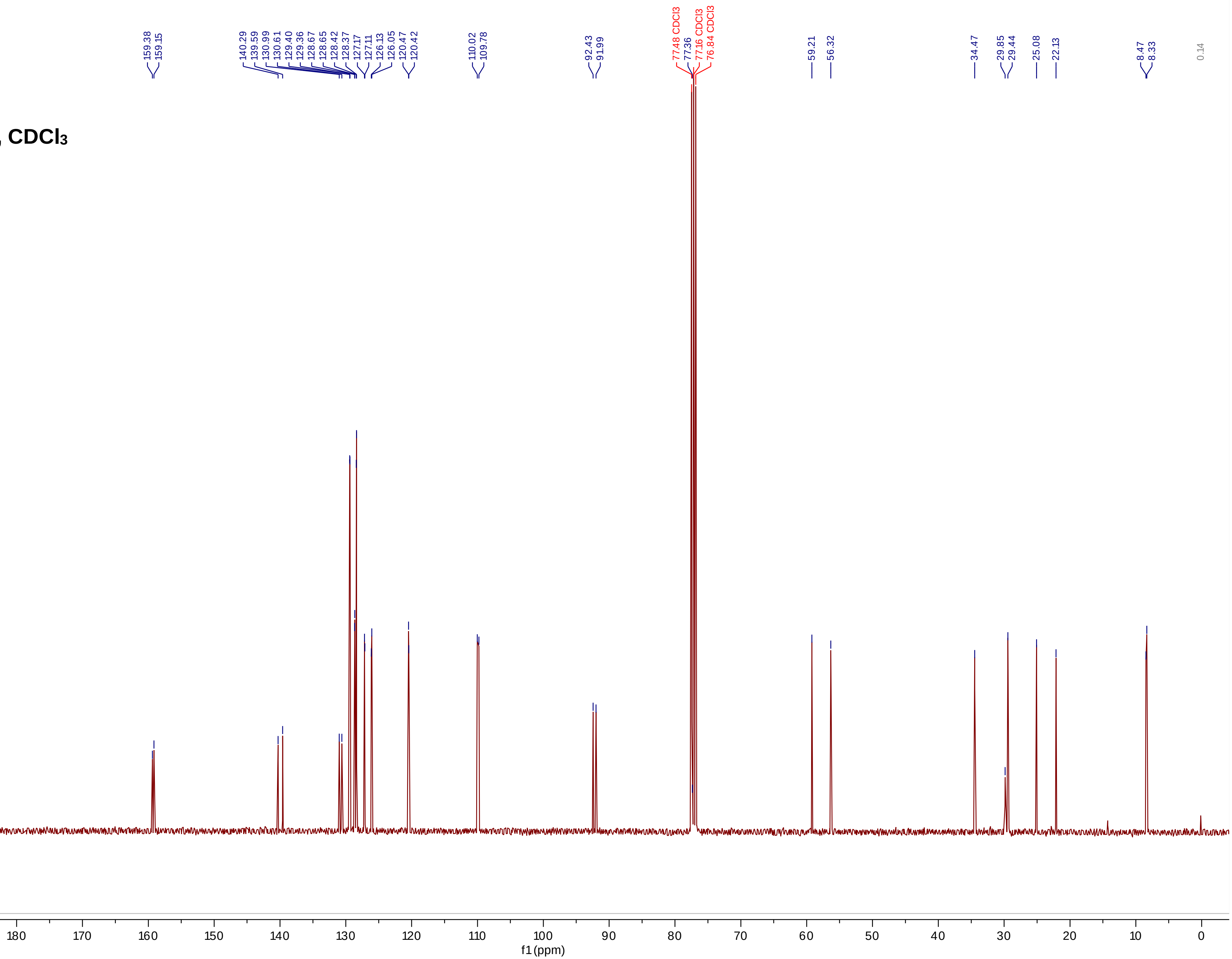


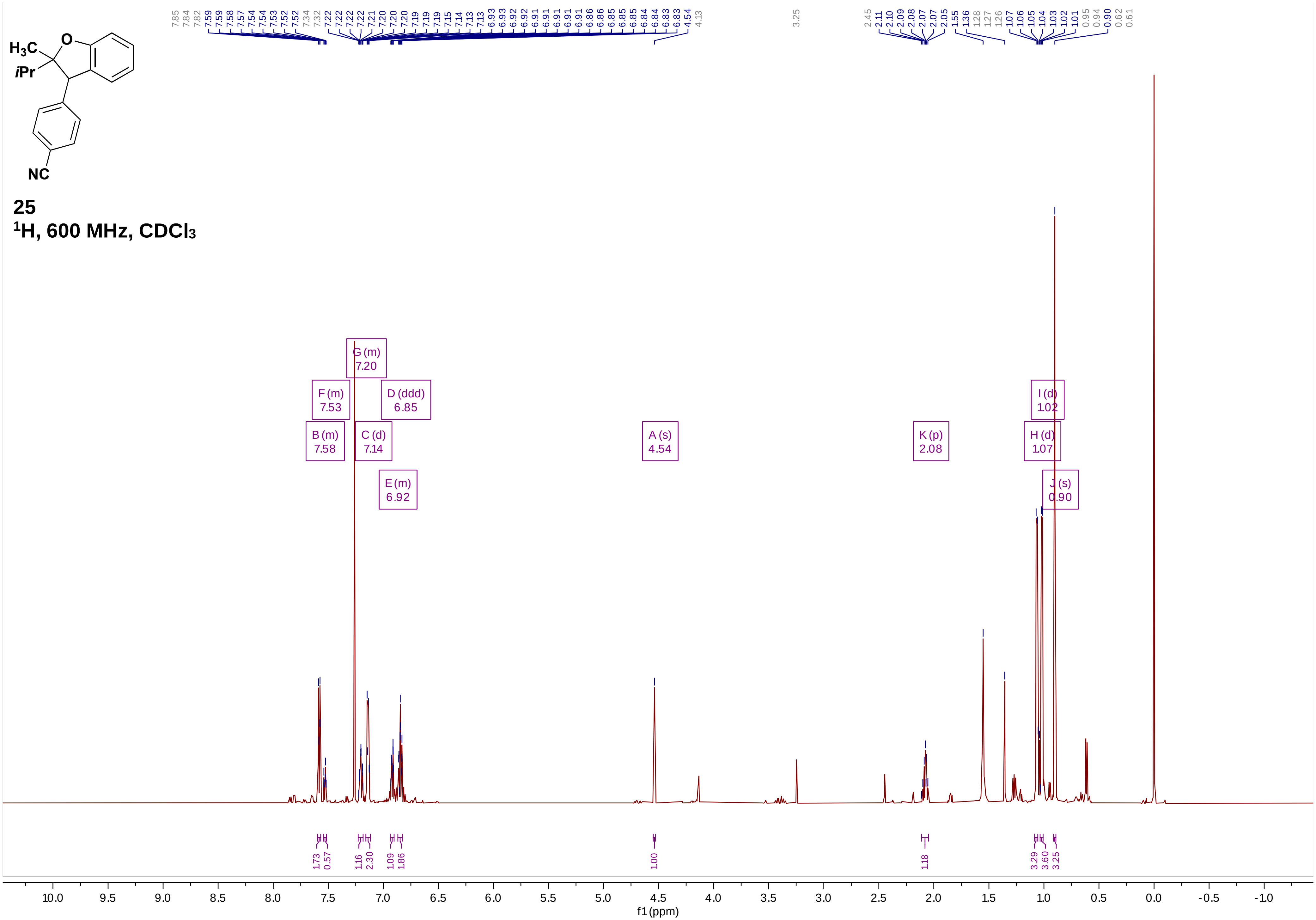
Note: Spectra is a mix of diastereomers, with the minor and major diastereomer peaks that can be assigned reported in the text above.



21

^{13}C, 100 MHz, $CDCl_3$

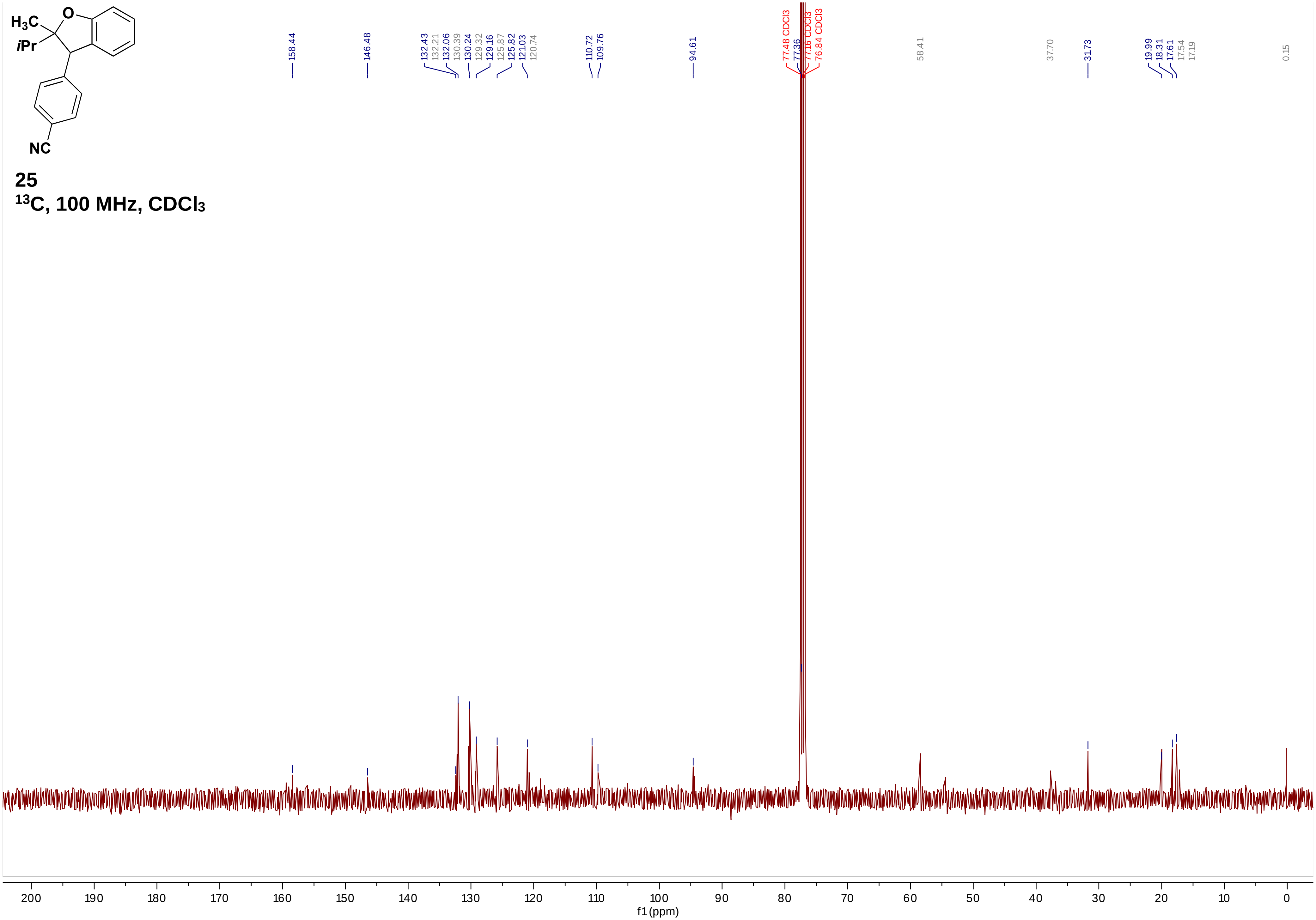


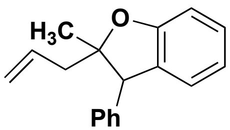


25

^{1}H, 600 MHz, CDCl$_3$

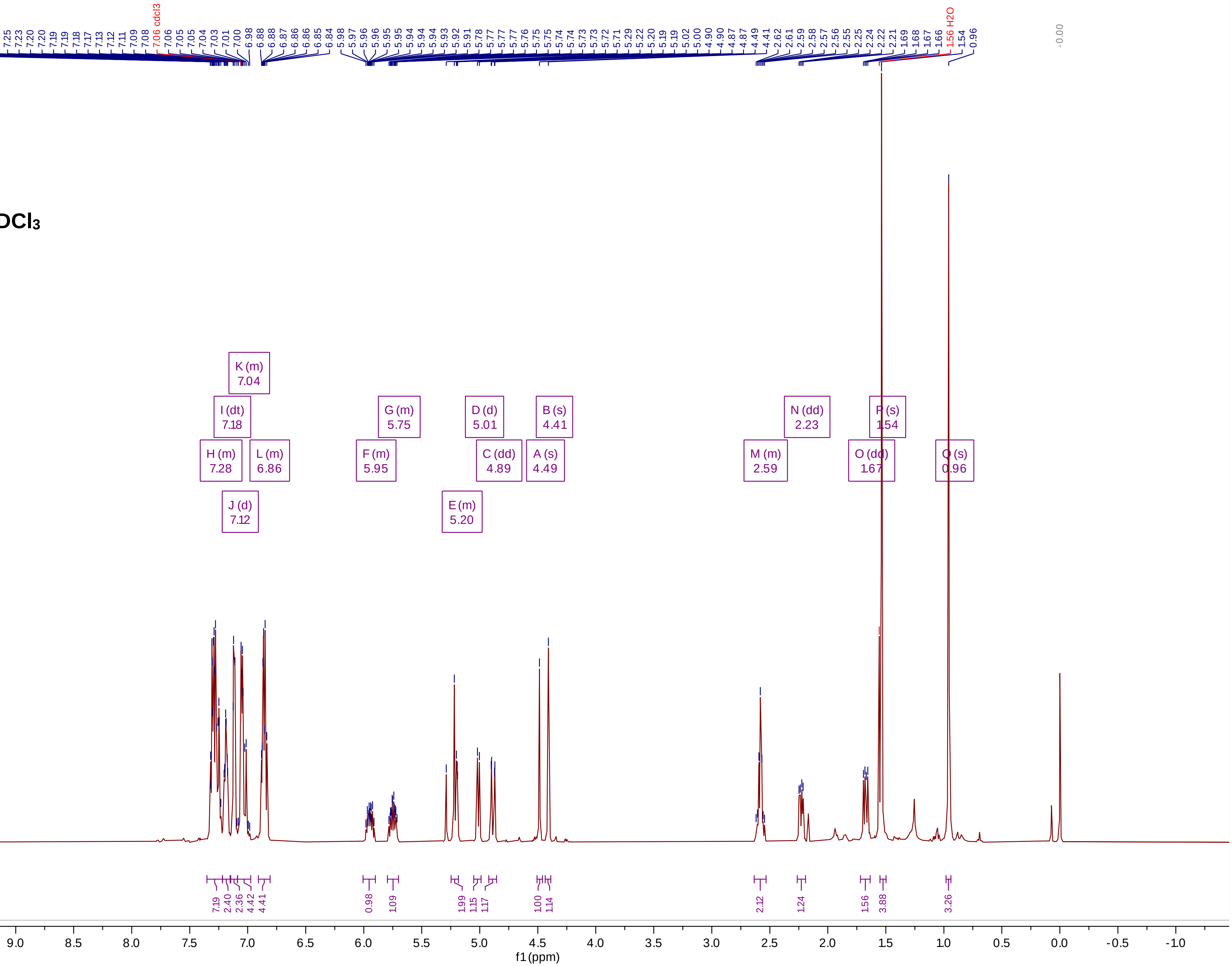
Note: Peaks in grey correspond to the minor diastereomer (81:19 dr in this spectra), with the diagnostic peaks reported in the main text with the compound.


H3C
O
iPr
NC
25
13C, 100 MHz, CDCl3
158.44
146.48
132.43
132.21
132.06
130.39
130.24
129.32
129.16
125.87
125.82
121.03
120.74
110.72
109.76
94.61
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
58.41
37.70
31.73
19.99
18.31
17.61
17.54
17.19
0.15
f1 (ppm)

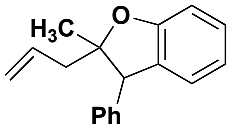


6

^{1}H, 600 MHz, $CDCl_3$

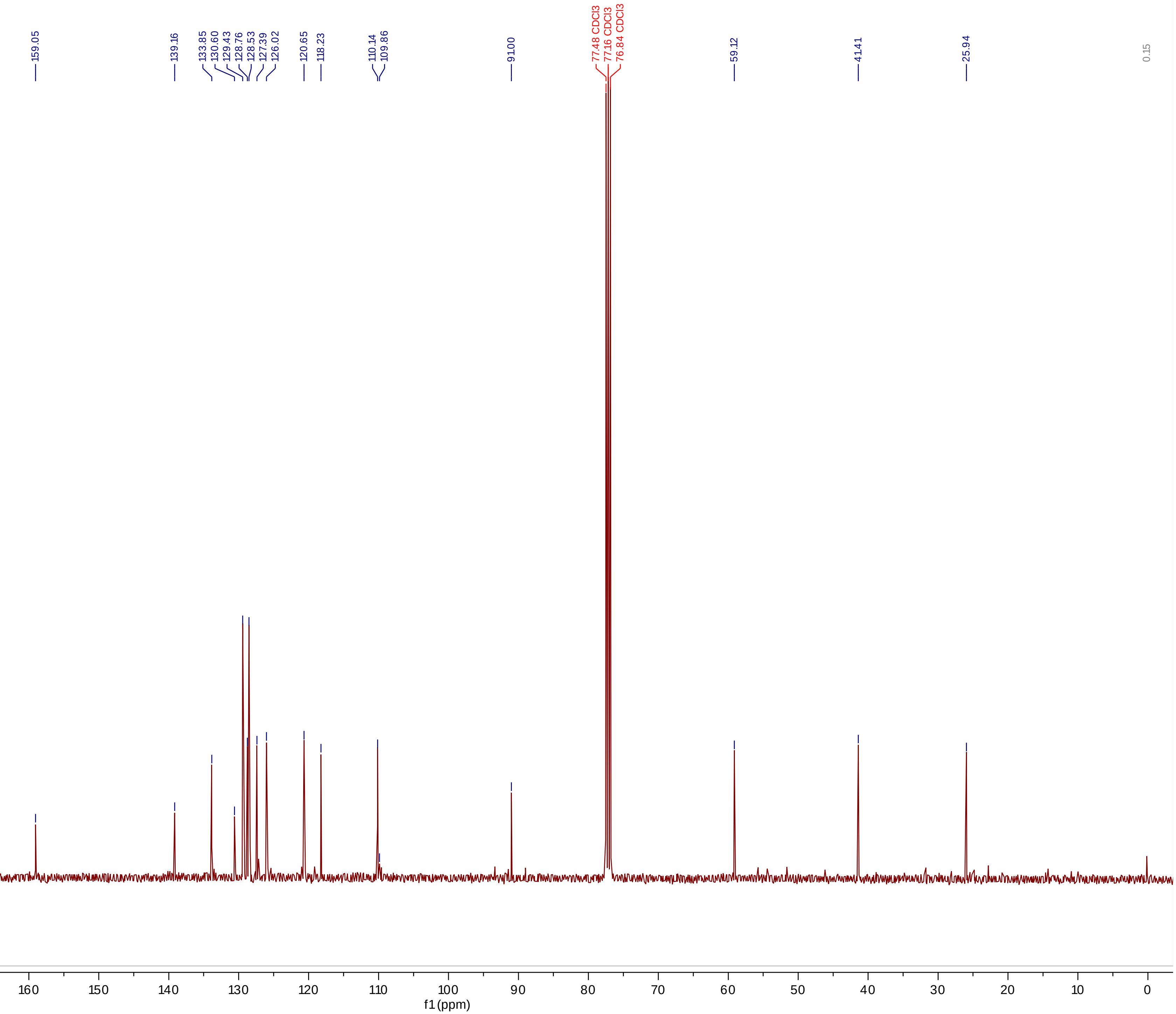


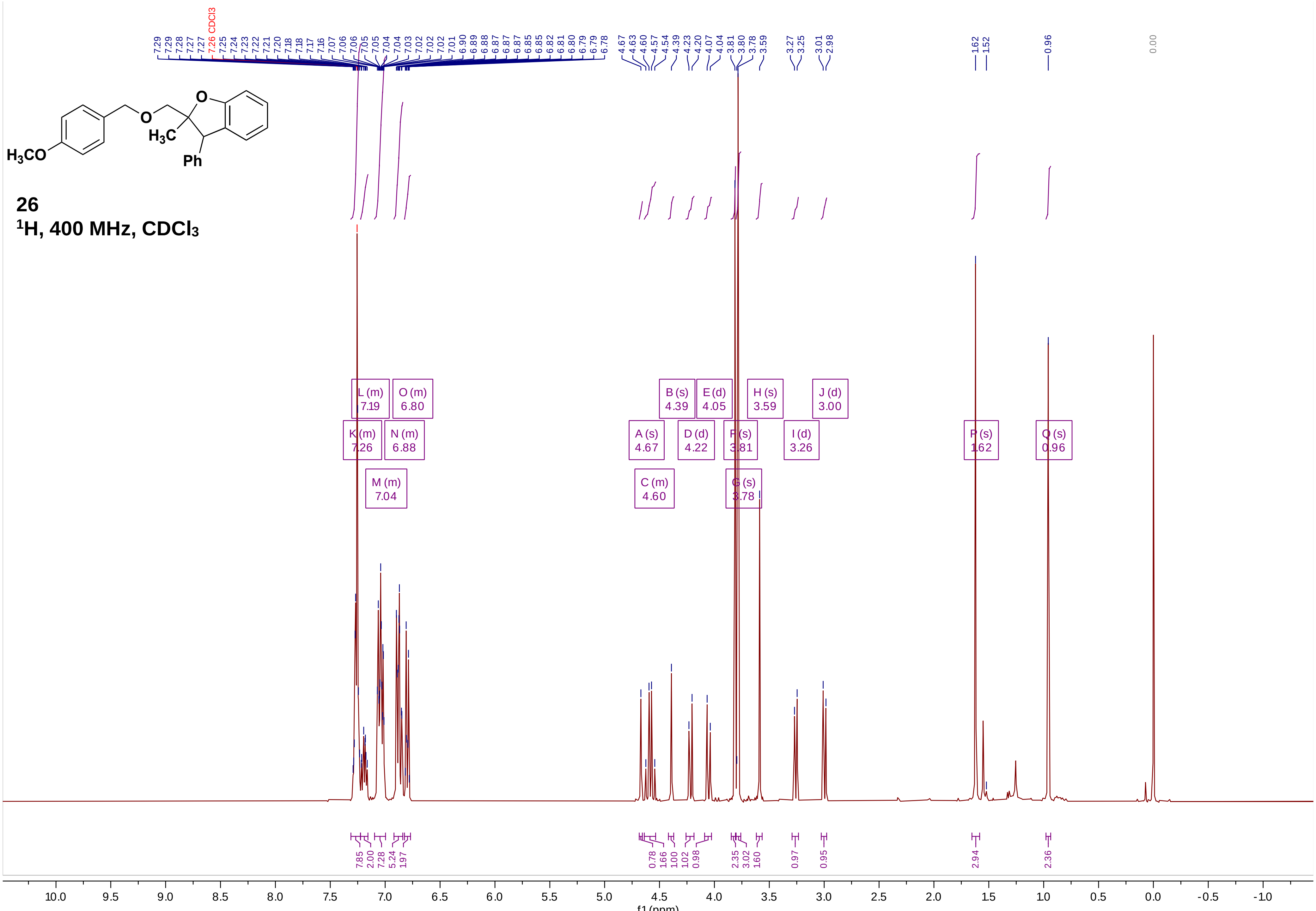
Note: Spectra is a mix of diastereomers, with the minor and major diastereomer peaks that can be assigned reported in the text above.



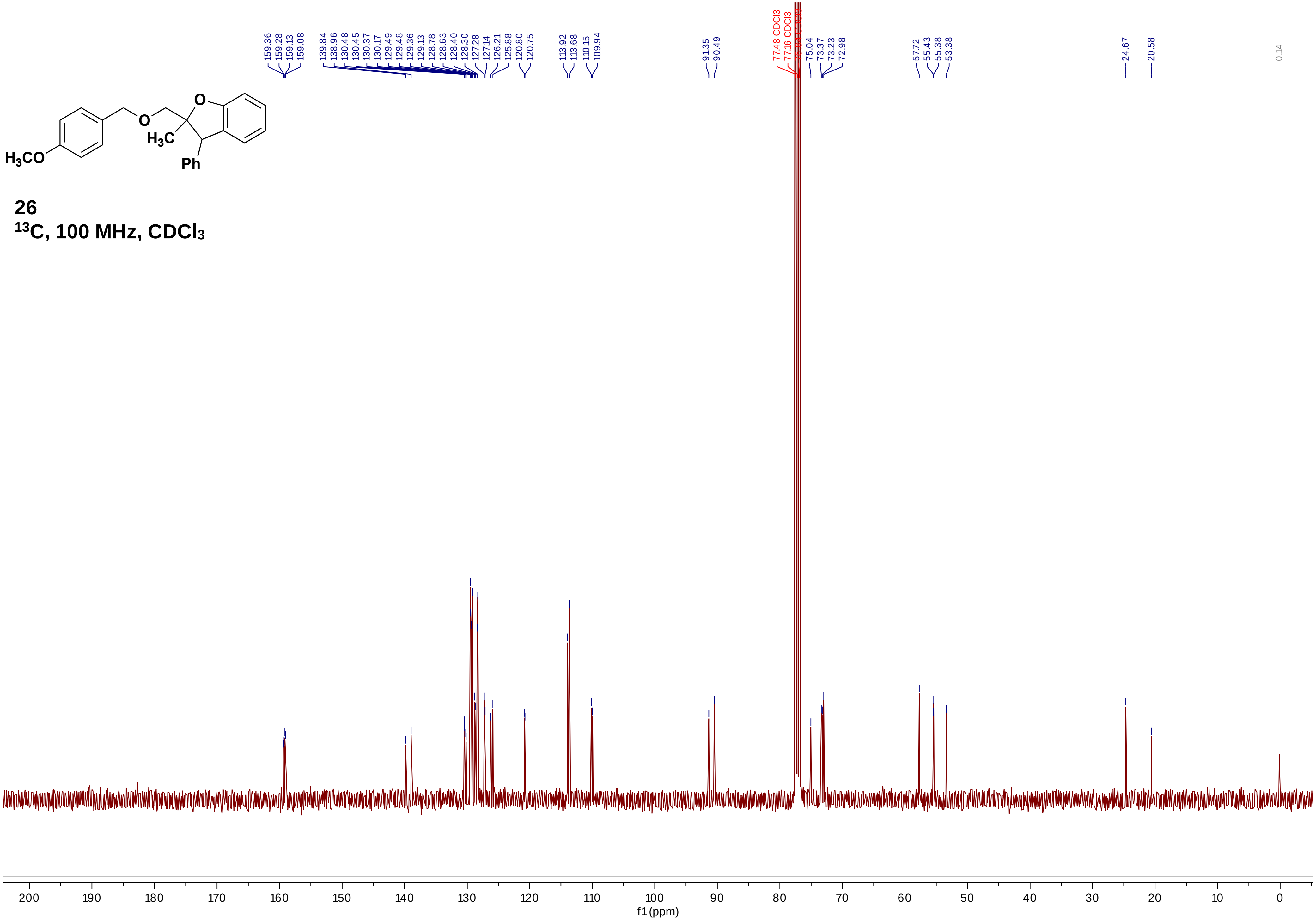
6

^{13}C, 150 MHz, CDCl$_3$



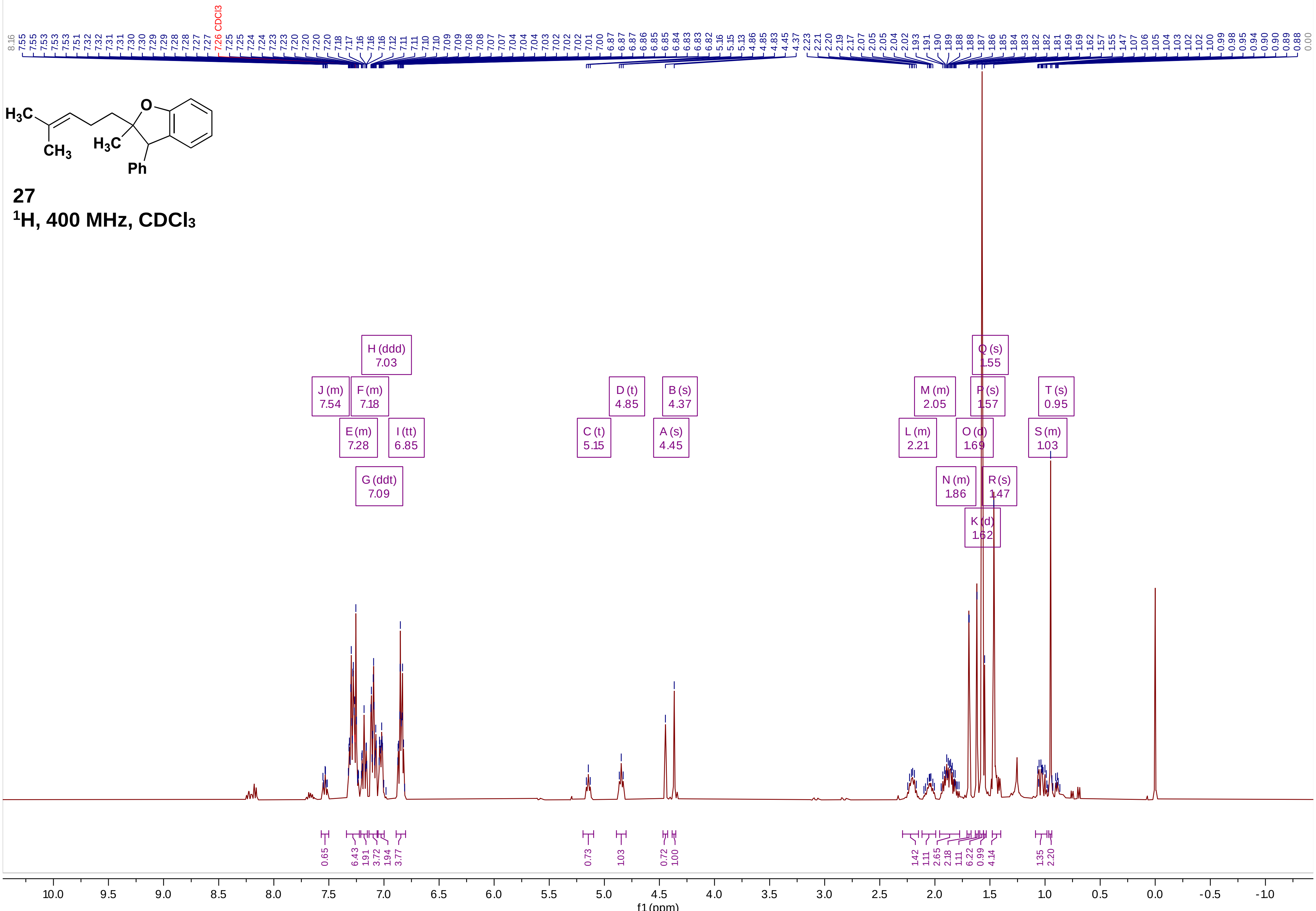


Note: Spectra is a mix of diastereomers, with the minor and major diastereomer peaks that can be assigned reported in the text above.

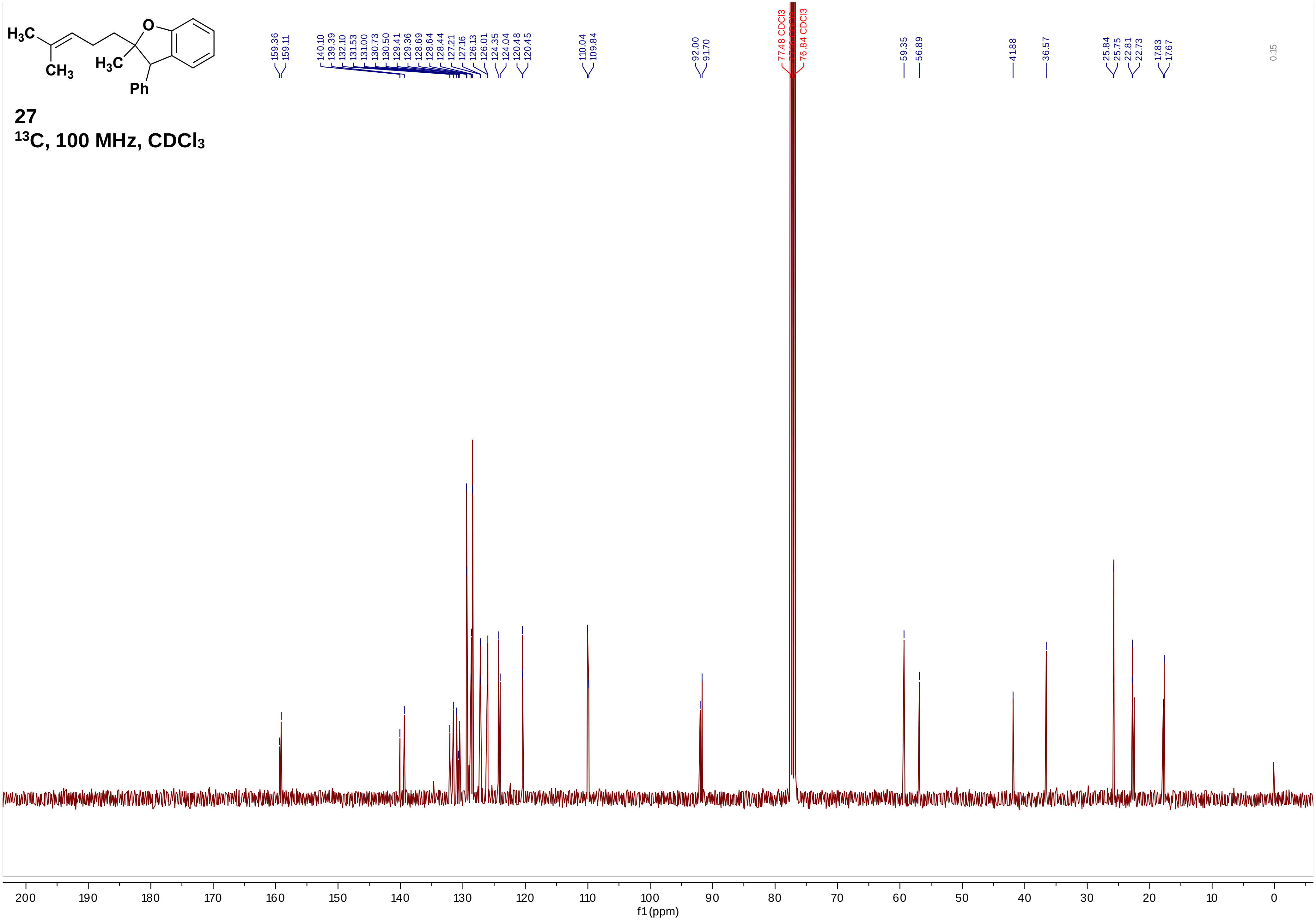


26

^{13}C, 100 MHz, CDCl$_3$

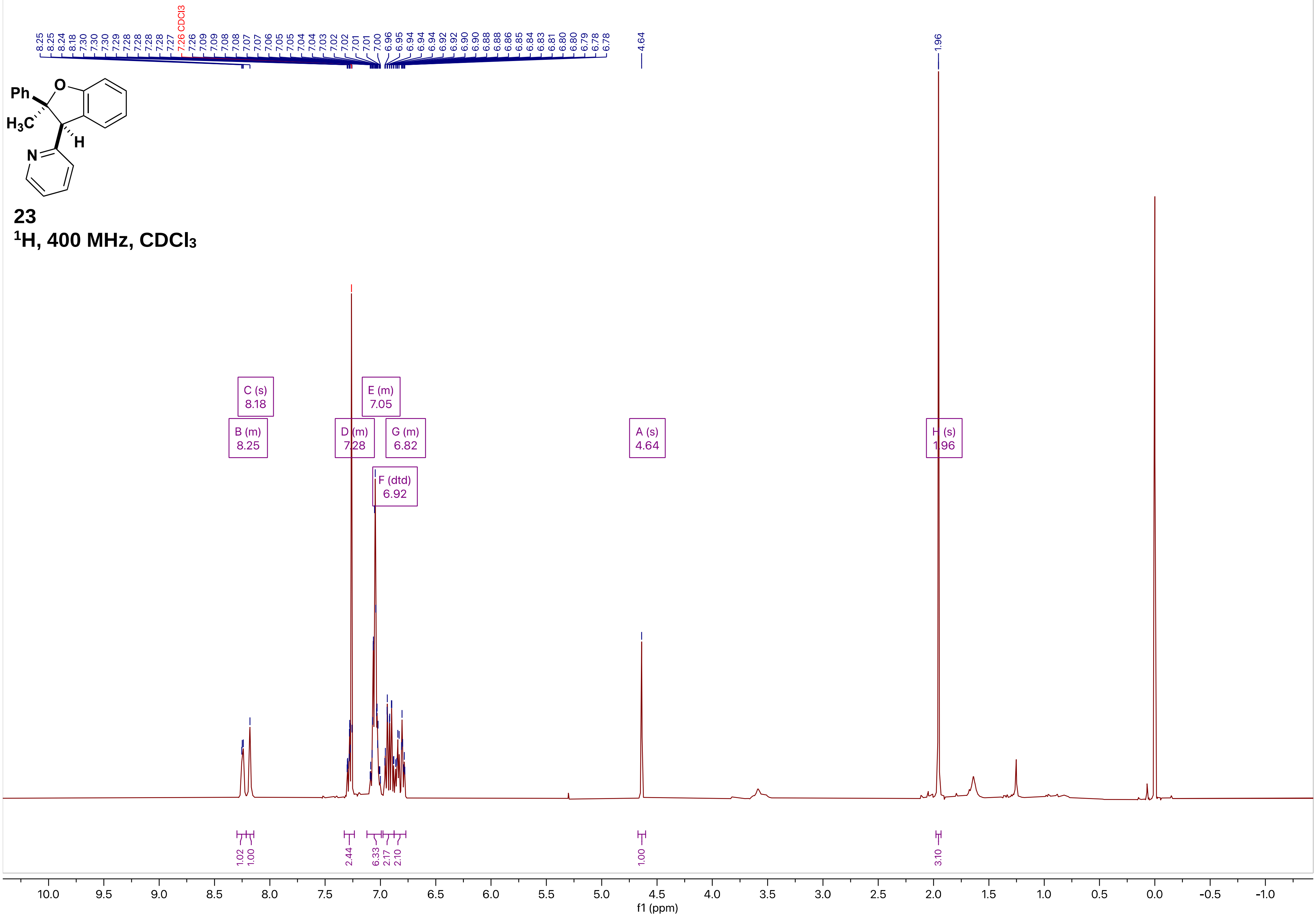


Note: Spectra is a mix of diastereomers, with the minor and major diastereomer peaks that can be assigned reported in the text above.



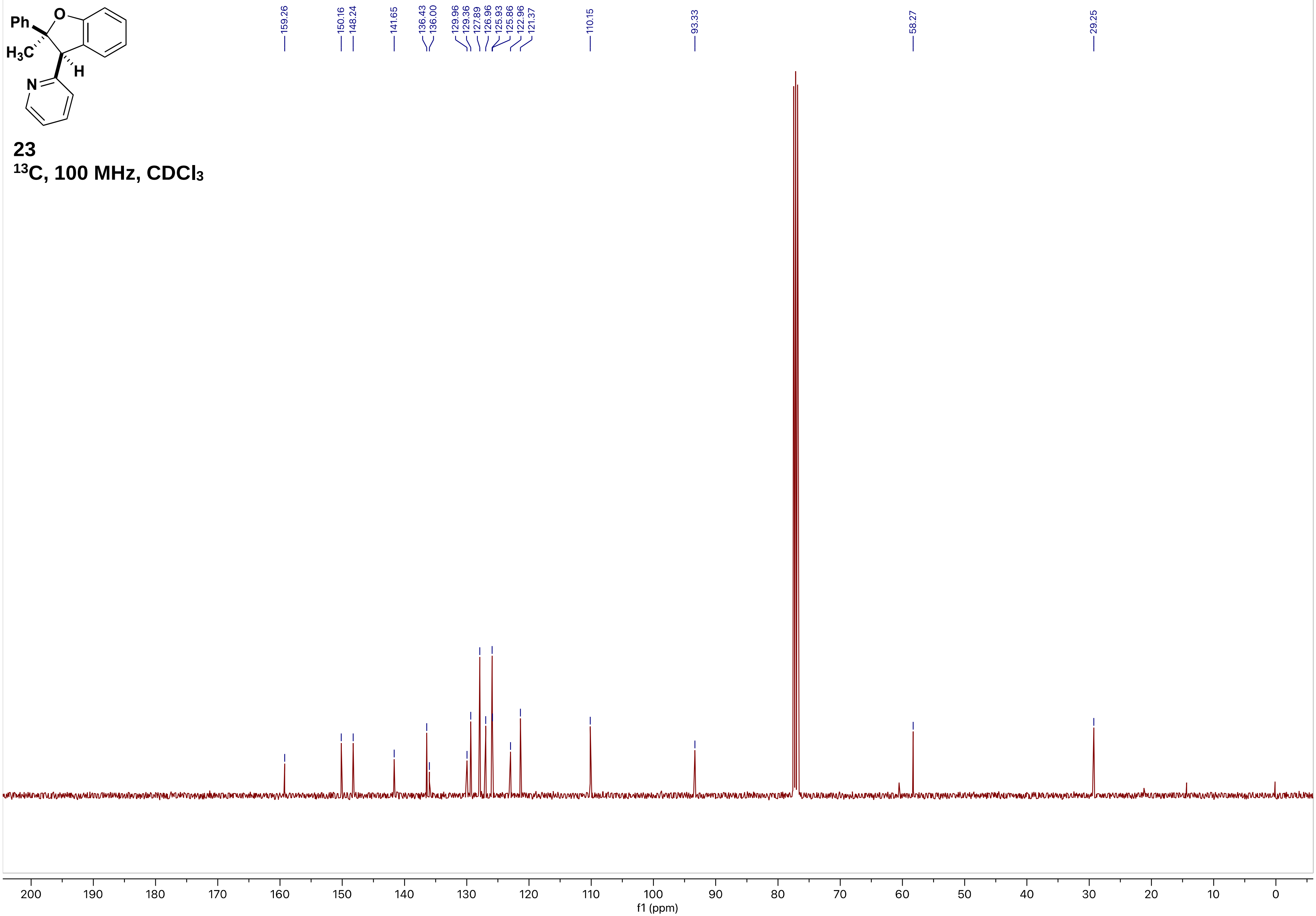
27

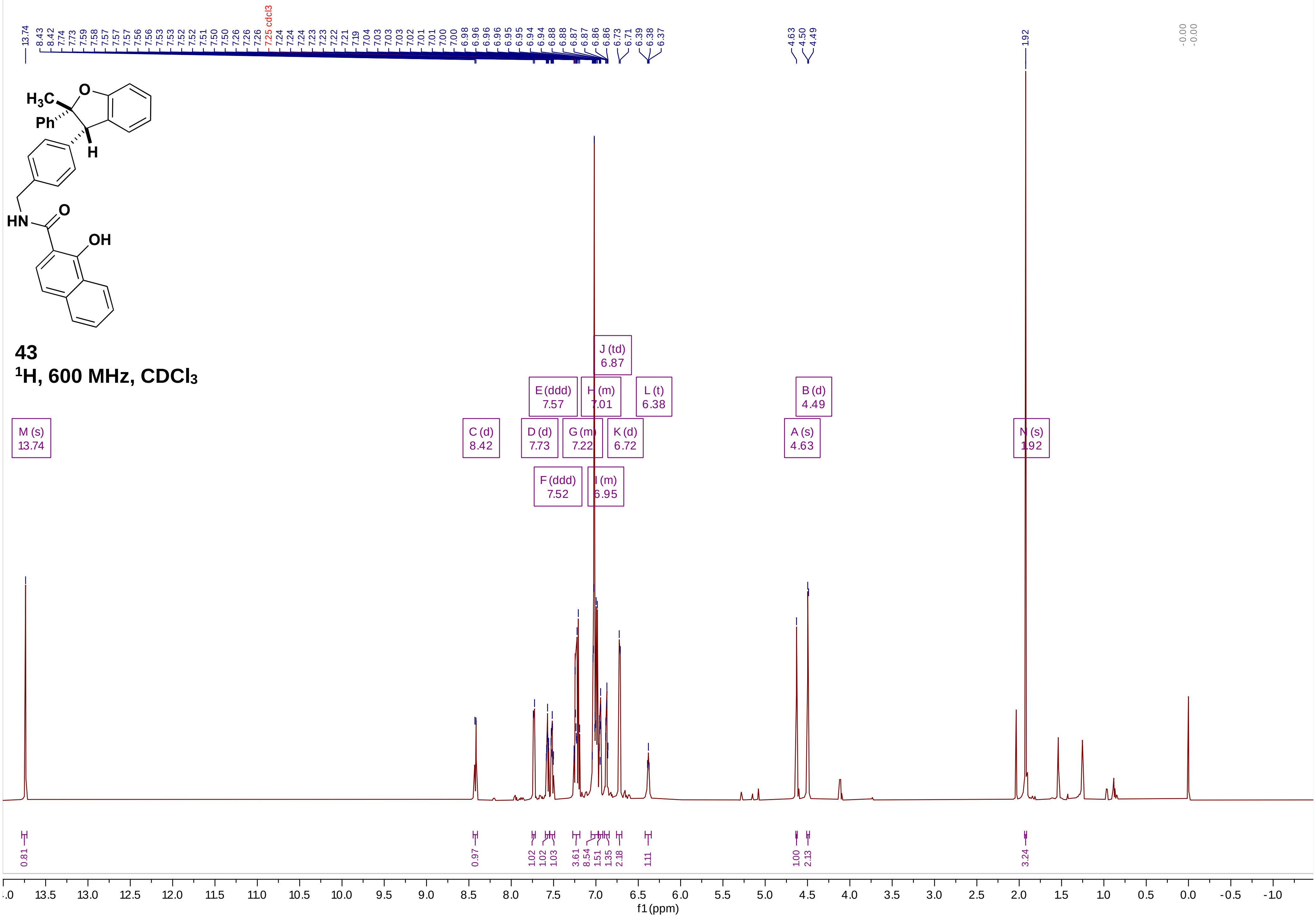
^{13}C, 100 MHz, CDCl$_3$

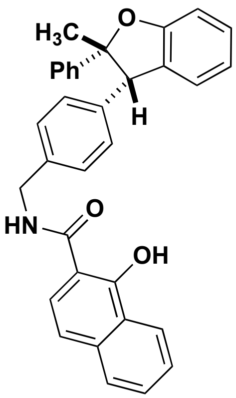


23

^{1}H, 400 MHz, CDCl$_3$

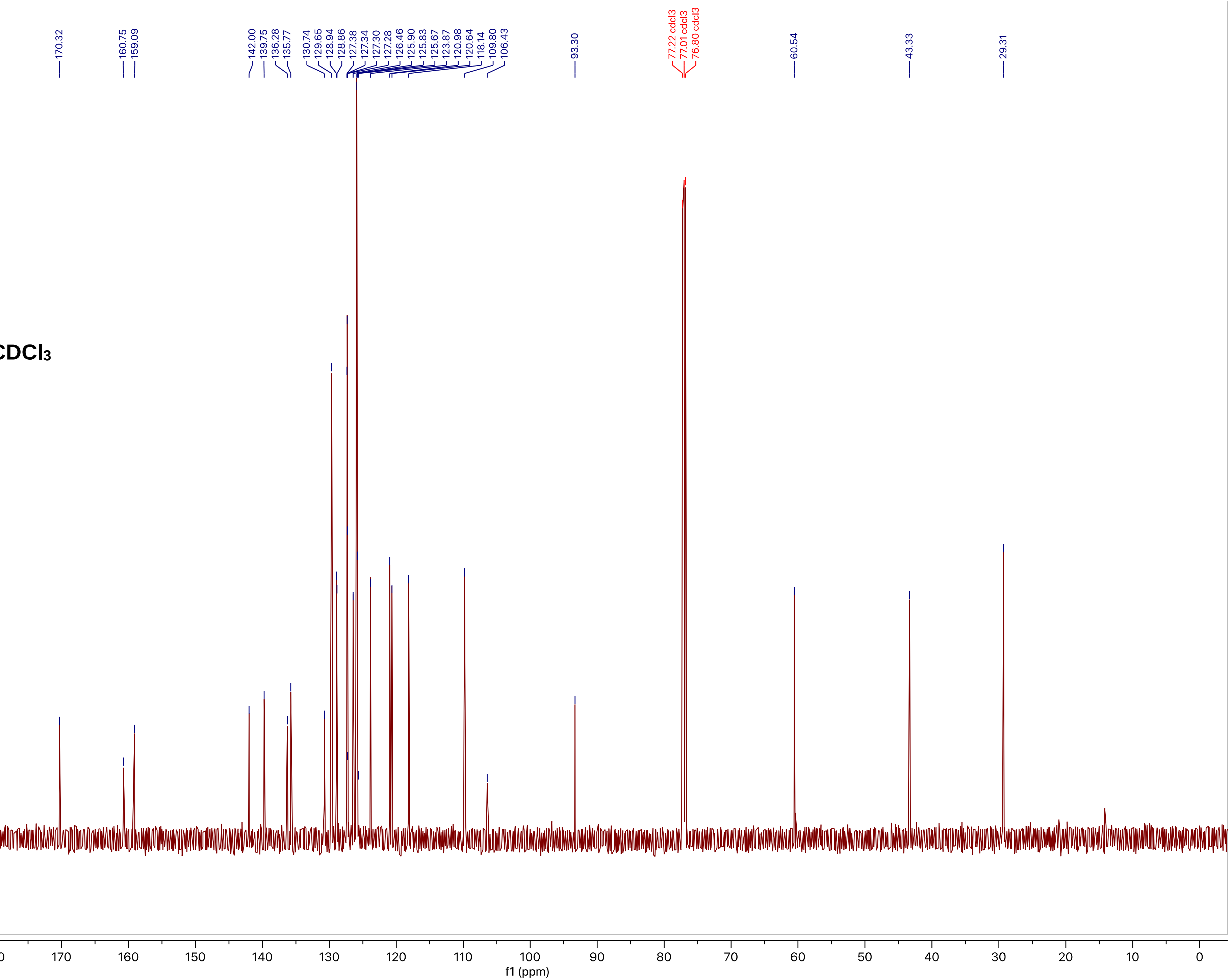

Ph
O
H3C
H
N
23
13C, 100 MHz, CDCl3
159.26
150.16
148.24
141.65
136.43
136.00
129.96
129.36
127.89
126.96
125.93
125.86
122.96
121.37
110.15
93.33
58.27
29.25
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

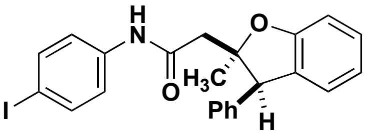

43
^{1}H, 600 MHz, CDCl$_3$
M (s) 13.74
C (d) 8.42
D (d) 7.73
E (ddd) 7.57
F (ddd) 7.52
G (m) 7.22
H (m) 7.01
I (m) 6.95
J (td) 6.87
K (d) 6.72
L (t) 6.38
A (s) 4.63
B (d) 4.49
N (s) 1.92
f1 (ppm)



43

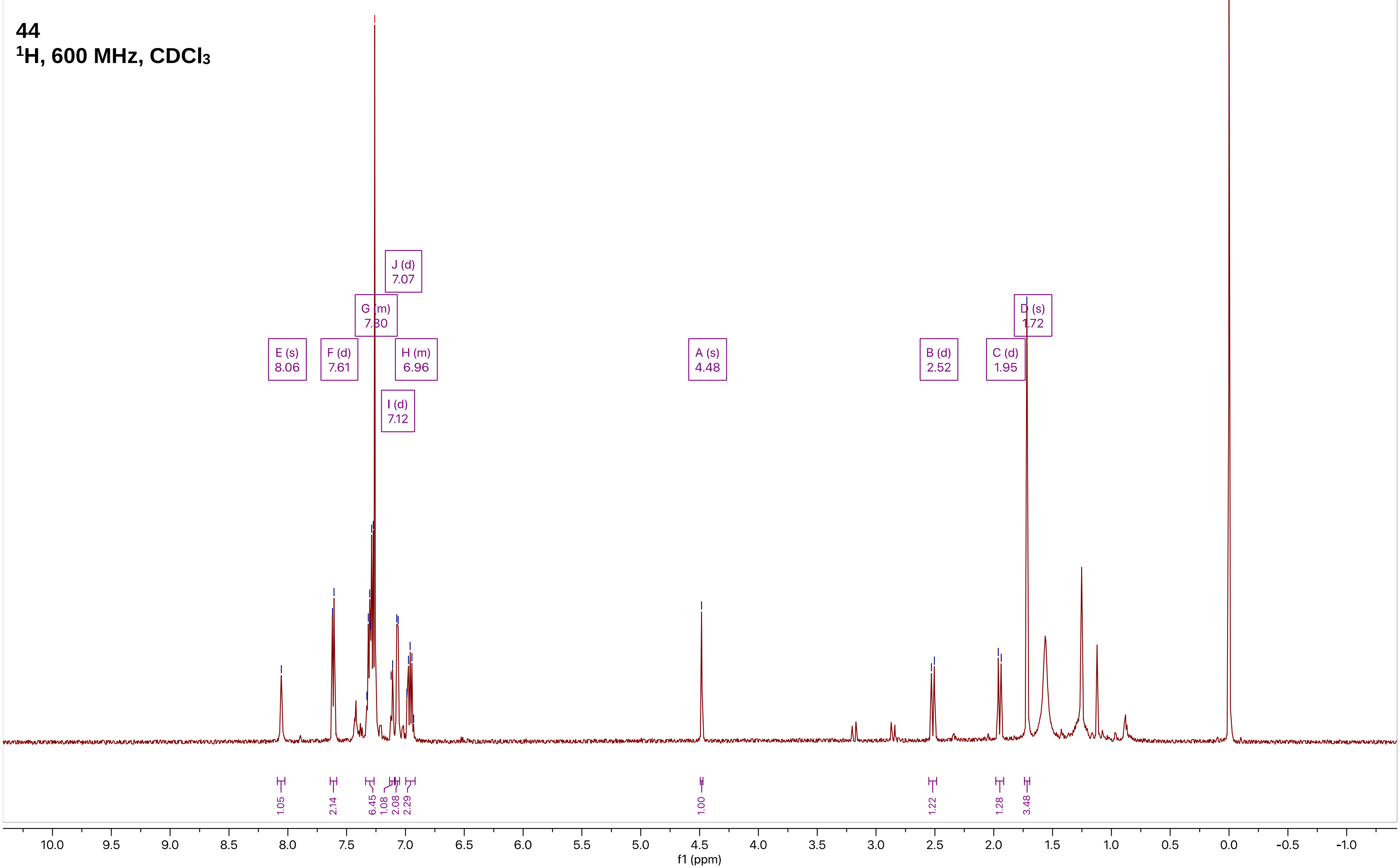
^{13}C, 150 MHz, $CDCl_3$

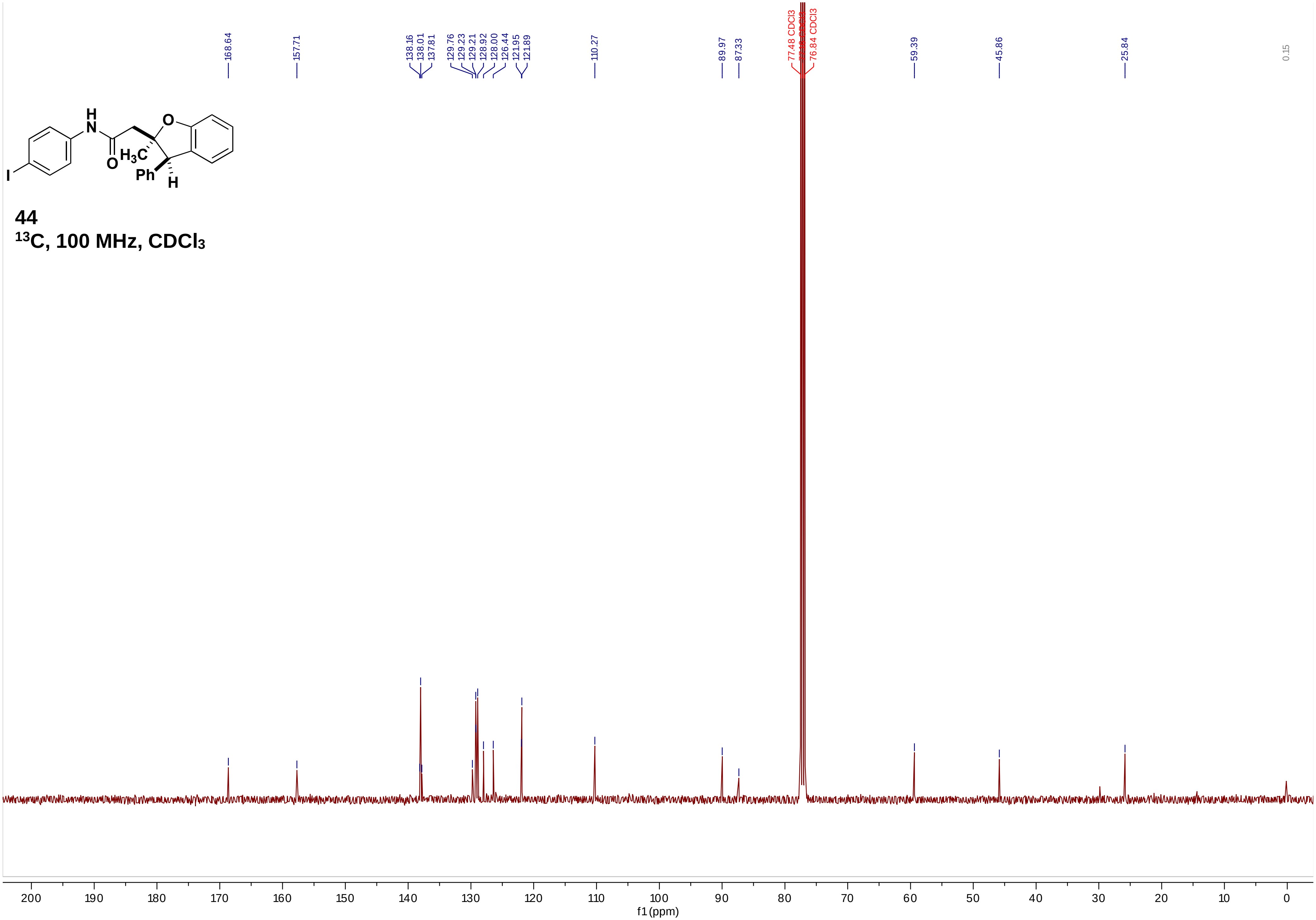


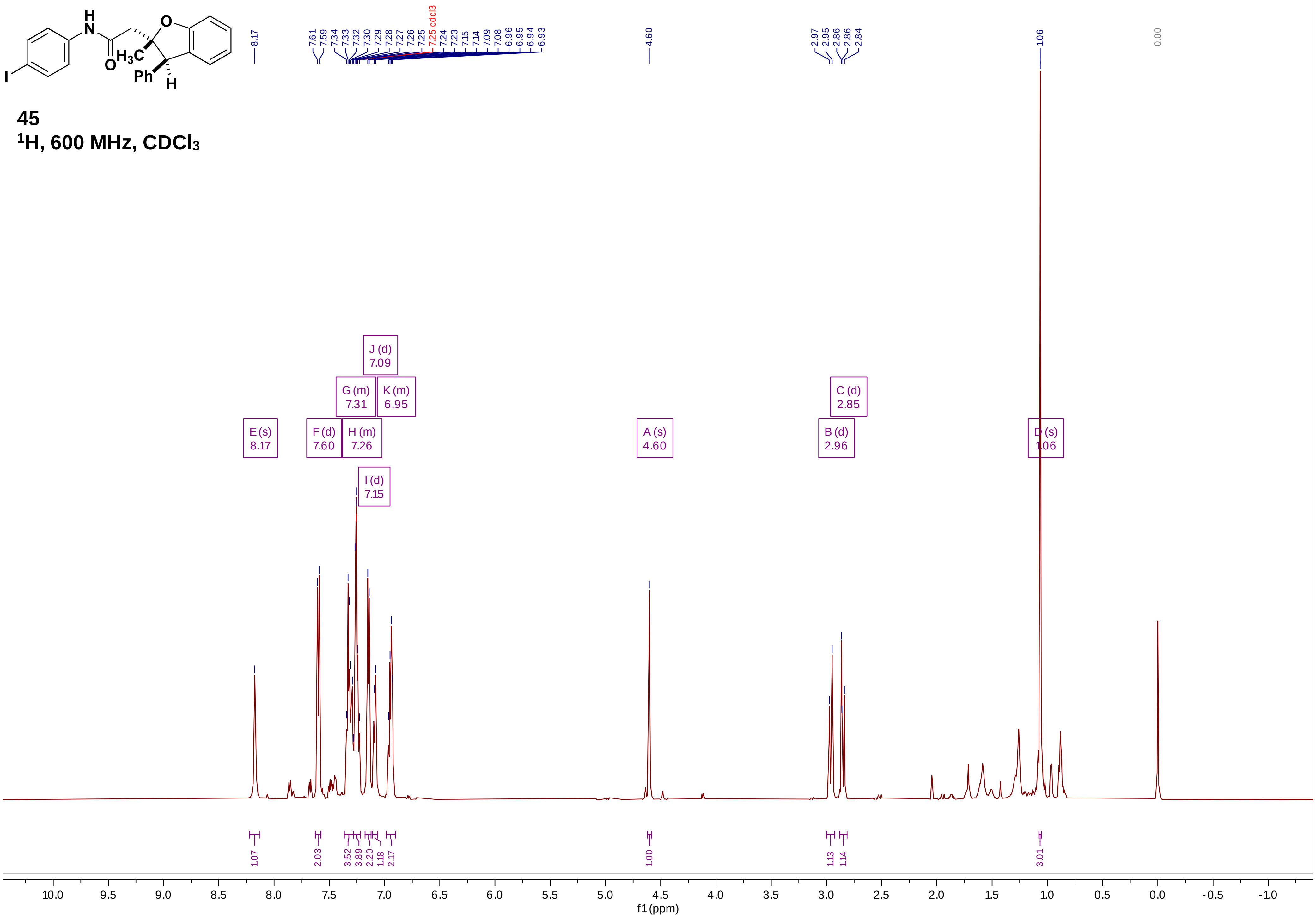


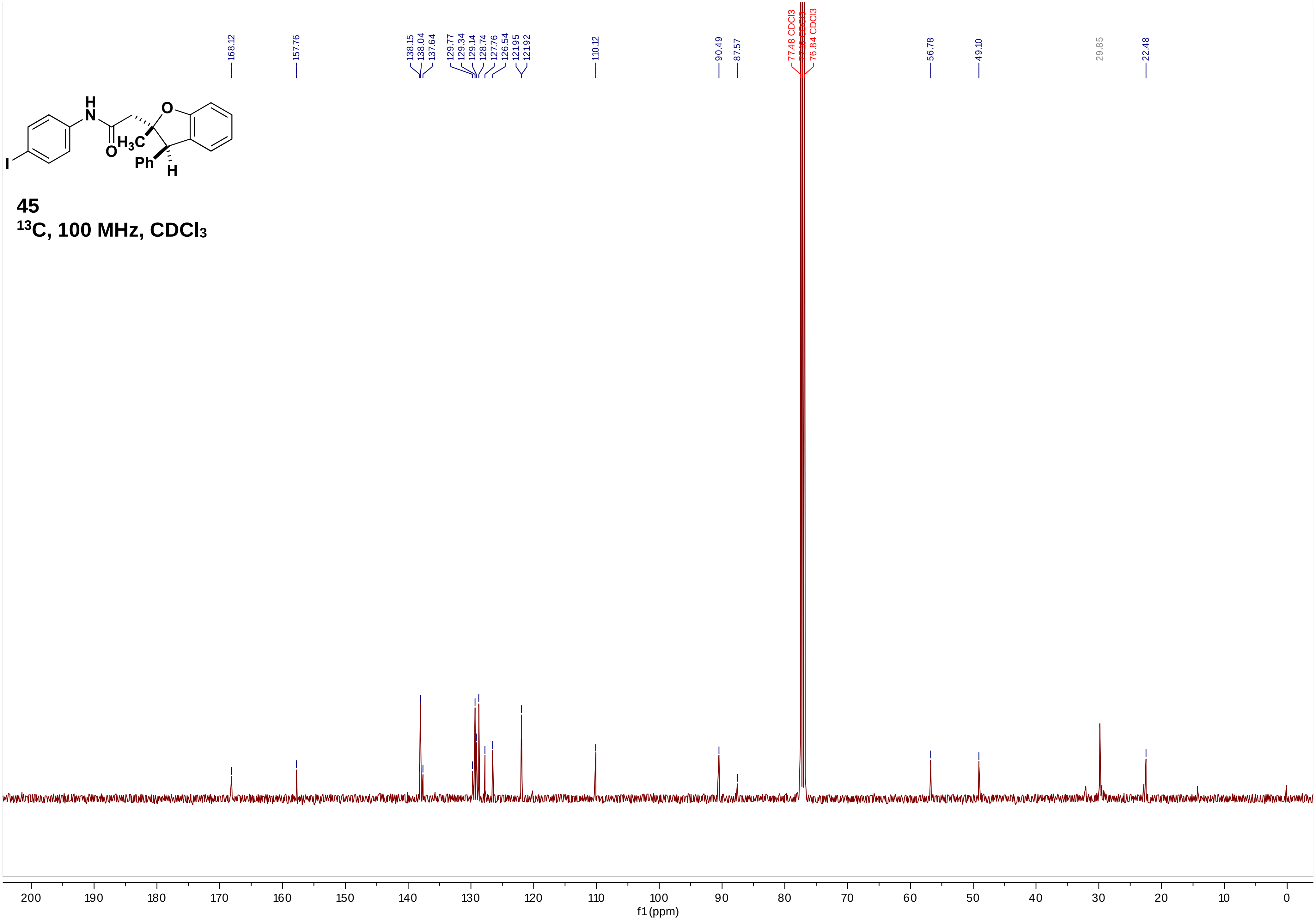
44

^{1}H, 600 MHz, CDCl$_3$




168.64
157.71
138.16
138.01
137.81
129.76
129.23
129.21
128.92
128.00
126.44
121.95
121.89
110.27
89.97
87.33
77.48 CDCl3
76.84 CDCl3
59.39
45.86
25.84
0.15
44
13C, 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


45
1H, 600 MHz, CDCl3
8.17
7.61
7.59
7.34
7.33
7.32
7.30
7.29
7.28
7.27
7.26
7.25
7.25 cdcl3
7.24
7.23
7.15
7.14
7.09
7.08
6.96
6.95
6.94
6.93
4.60
2.97
2.95
2.86
2.86
2.84
1.06
0.00
J (d) 7.09
G (m) 7.31
K (m) 6.95
C (d) 2.85
E (s) 8.17
F (d) 7.60
H (m) 7.26
A (s) 4.60
B (d) 2.96
D (s) 1.06
I (d) 7.15
1.07
2.03
3.52
3.89
2.20
1.18
2.17
1.00
1.13
1.14
3.01
f1 (ppm)



45

^{13}C, 100 MHz, $CDCl_3$