Supporting Information

Palladium catalyzed hydrodefluorination of fluoro-(hetero)arenes.

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Table of Contents

Methods and Materials

All reagents and solvents were purchased from commercial sources and used without further purification unless noted otherwise. Reactions were monitored by LCMS on a Waters Acquity UPLC with water/acetonitrile as the mobile phase (0.1% trifluoroacetic acid modifier) and ESCI mass detection (100–2000m/z scan, 0.4 s scan time.) Mass detection was essential for reaction monitoring because most starting material/product pairs were poorly resolved by UPLC. Flash column chromatography was performed with a Teledyne ISCO CombiFlash Rf system using either silica (RediSep Gold Silica cartridges) or C18 modified silica (RediSep C18 Gold cartridges). ^{1}H NMR spectra were recorded on a Bruker Advance-400 spectrometer at 400 MHz or a Bruker Advance-300 spectrometer at 300 MHz. Automated mass-directed purification was performed on a Waters Autopurification system equipped with a Sunfire C18 column (5 micron, 150 x 30 mm) using water/acetonitrile (0.1% TFA modifier) as the mobile phase. High resolution mass spectroscopy (HRMS) was performed using an ExactiveTM Plus benchtop OribtrapTM mass spectrometer connected to an UltiMate 3000 UPLC system (Thermo Scientific). The mass spectrometer was operated in positive ionization mode for all substrates (except Flurbiprofen (**28**), which was acquired in negative ionization mode). Acquisition was a full scan from m/z 100 to 1000 with a resolution of 70,000.

General Procedures

General Procedure One: Hydrodefluorination

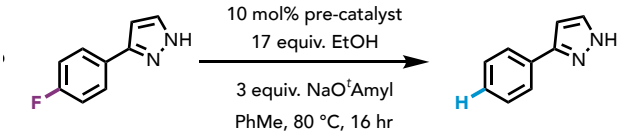
To a one dram vial with stirbar was added fluorinated substrate (0.4 mmol). The vial was sealed with a septum lined cap and purged under nitrogen for 2 minutes. Under nitrogen pressure, the sealed vial was charged with a stock solution in toluene containing RuPhos palladacycle generation 4 (0.02 mmol, 5 mol%, 1.6 mL, 0.0125M) and alcohol (typically *iso*-butanol, 1.2 mmol, 3 equiv., 1.6 mL, 0.75M). The mixture was stirred at room temperature for five minutes before adding a commercial solution in toluene of *sodium* tert-pentoxide (1.33 mmol, 3.33 equiv., 0.4 mL, 3.33M). The vial was transferred to a heating block stirring at 900 rpm. The reaction was monitored by LCMS until completion at which time the reaction mixture was transferred to a 20-mL scintillation vial with methanol (3x2mL) and the volatiles were removed under reduced pressure. Unless stated otherwise, reactions were worked up for chromatographic purification by neutralizing with saturated sodium bicarbonate (4 mL) and extraction with dichloromethane (3x3mL). The combined organic fractions were loaded onto Celite (5g) and volatiles were removed under reduced pressure. The crude material was then purified by flash chromatography as described for each sample.

General Procedure Two: Preparation of 1-(fluorophenyl)-pyrrolidines (8a-c)

The following general procedure is based on a previously reported method.[1] To a 20-mL vial with stirbar was added potassium carbonate (2.48g, 18 mmol, 1.1 equiv.). The vial was sealed with a septum line cap and purged under nitrogen for 10 minutes. Under nitrogen pressure, the sealed vial was charged with DMF (3 mL), fluoroaniline (1.78g, 16 mmol, 1 equiv.), and 1,4-dibromobutane (3.87g, 18 mmol, 1.1 equiv.). The vial was transferred to a heating block set to 60 °C and stirred at 900 rpm. The reaction was monitored by LCMS until completion at which time the reaction mixture was diluted with ethylacetate and filtered to remove most of the inorganic byproducts. The crude organic mixture was washed with aqueous sodium hydroxide (1M), loaded onto Celite (20g), and concentrated under reduced pressure. The crude material was then purified by flash chromatography as described for each sample.

Reaction Optimization

Varying pre-catalyst in HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a)



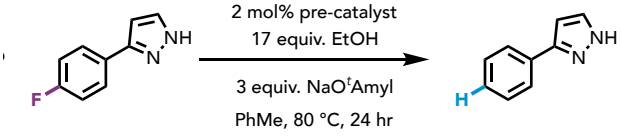
SI Figure 1: Reaction conditions used in determination of optimal pre-catalysts.

General procedure one was modified to evaluate various pre-catalysts for HDF of **4a**. Ten reactions were conducted in parallel using the pre-catalysts listed in SI Table 1 (PEPPSI refers to [1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride). The reactions were set up according to general procedure one, with the exception that the pre-catalysts were weighed out as solids and substrate was added in the alcohol/toluene stock solution. The reactions were monitored by LCMS and reaction progress was approximated by using UV-Vis traces at 280 nm to determine LCMS conversion (LCMS conversion=100*$A_{product}$/($A_{product}$ + $A_{reactant}$), where A is area under UV-Vis curve).

SI Table 1: Varying pre-catalysts in HDF of 4a.

pre-catalyst	conversion 1 hr.	conversion 16 hr.
Pd black	32%	80%
$Pd(OAc)_2$	43%	59%
PEPPSI	2%	50%
SPhos Pd G1	46%	66%
BrettPhos Pd G1	55%	97%
BrettPhos Pd G3	55%	97%
RuPhos Pd G3	48%	95%
RuPhos Pd G4	54%	97%
XPhos Pd G1	65%	97%
tBuXPhos Pd G1	42%	52%

Best pre-catalysts at low Pd loading (2 mol%) in HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a)



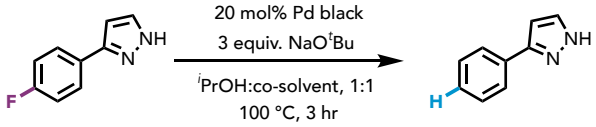
SI Figure 2: Reaction conditions used in determination of optimal pre-catalyst at low loading.

General procedure one was modified to evaluate various pre-catalysts for HDF of **4a**. Five reactions were conducted in parallel using the pre-catalysts listed in SI Table 2. The reactions were set up according to general procedure one, with the exception that the pre-catalysts were weighed out as solids and substrate was added in the alcohol/toluene stock solution.

SI Table 2: Varying pre-catalysts with low loading (2 mol%) in HDF of 4a.

pre-catalyst	conversion 24 hr.
Pd black	49%
XPhos Pd G1	46%
BrettPhos Pd G1	56%
BrettPhos Pd G3	59%
RuPhos Pd G4	80%

Varying solvent in HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a)



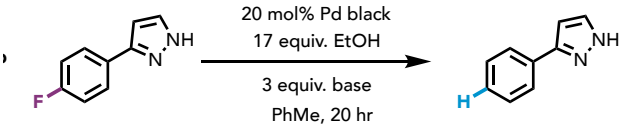
SI Figure 3: Reaction conditions used to evaluate compatible solvents in HDF of 4a.

General procedure one was modified to evaluate various pre-catalysts for HDF of **4a**. Nine reactions were conducted in parallel using the cosolvents listed in SI Table 3. The reactions were set up according to general procedure one with the following exceptions: all solid components were weighed out individually and the sealed vial was then charged with *iso*-propanol (1mL) and cosolvent (1mL). The results in SI Table 3 illustrate that HDF of **4a** is a robust reaction compatible with a variety solvents frequently employed in palladium catalysis.

SI Table 3: Varying solvents in HDF of 4a.

solvent	conversion 30 min.	conversion 60 min.	conversion 180 min.
iso-propanol	85%	96%	97%
tert-pentanol	86%	97%	97%
PhMe	87%	96%	97%
CPME	90%	97%	97%
Me-THF	96%	97%	97%
THF	79%	81%	83%
dioxane	60%	68%	86%
NMP	69%	76%	83%
HFIP	0%	0%	0%

Varying base in HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a)



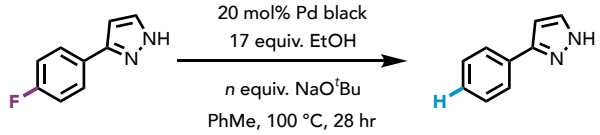
SI Figure 4: Reaction conditions used to evaluate compatible bases in HDF of 4a.

General procedure one was modified to evaluate various bases for HDF of **4a**. Two sets of reactions were conducted in parallel (80 and 100 °C, SI Table 4). The reactions were set up according to general procedure one, with the exception that the bases were weighed out as solids and substrate was added in the alcohol/toluene stock solution.

SI Table 4: Varying bases in HDF of 4a.

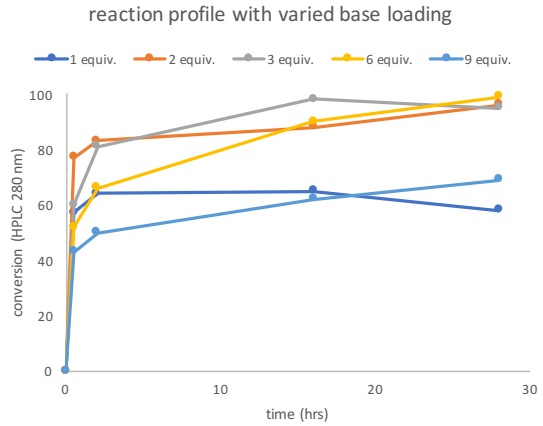
base	temperature	conversion 0.5 hr.	conversion 2 hr.	conversion 20 hr.
NaHMDS	80 °C	0%	0%	0%
Cs_2CO_3	80 °C	0%	0%	0%
^{t}BuOLi	80 °C	45%	46%	44%
^{t}BuOK	80 °C	4%	16%	32%
^{t}BuONa	80 °C	46%	51%	86%
^{t}BuONa	100 °C	66%	84%	97%
^{t}AmylONa	100 °C	57%	78%	97%
NaH	100 °C	50%	58%	97%

Varying base loading in HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a)



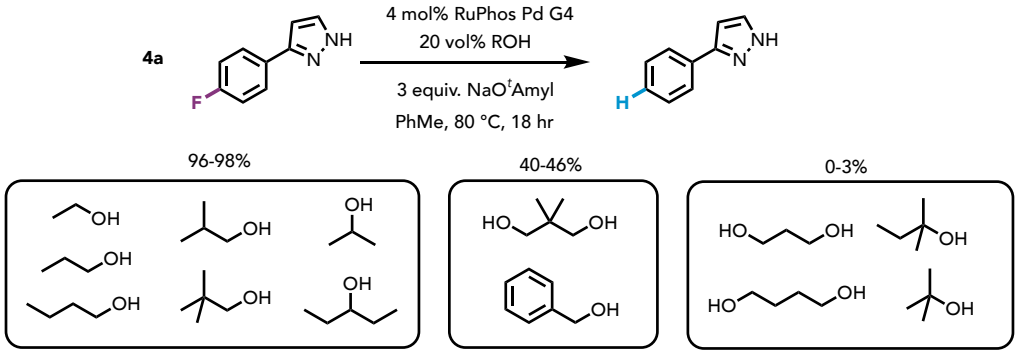
SI Figure 5: Reaction conditions used to determine optimal base loading in HDF of 4a.

General procedure one was modified to evaluate the effect of base loading on reaction efficiency. Five reactions were conducted in parallel with 1-9 equivalents of ^{t}BuONa. The reactions were set up according to general procedure one with the exception that the base (^{t}BuONa instead of ^{t}AmylONa) was weighed out as a solid rather than added as a toluene stock solution. The reaction profiles in SI Figure 6 indicate that the reaction proceeds efficiently with 2-6 equivalents of base and decreases in efficiency outside this range.



SI Figure 6: Reaction profiles showing LCMS conversion versus time for reactions with varying base loading.

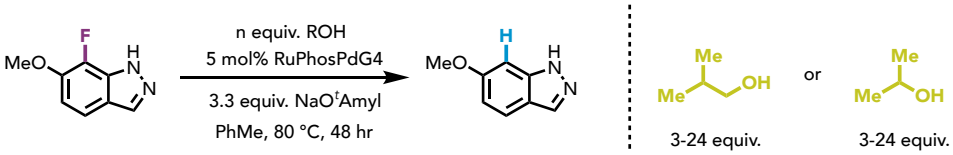
Varying alcohol/reductant in HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a)



SI Figure 7: Reaction conditions and LCMS conversions for various alcohols in HDF of 4a.

General procedure one was modified to evaluate the effect of different alcohols on reaction efficiency. Thirteen reactions were conducted in parallel using 20 volume percent of the alcohols shown in SI Figure 7. The reactions were set up according to general procedure one, with the exception that alcohol was omitted from the palladium stock solution and replaced with substrate (**4a**). The reaction vials were charged with alcohol after addition of catalyst and substrate. The data in SI Figure 7 indicate that primary and secondary alcohols are generally compatible terminal reductants whereas tertiary alcohols and diols generally result in lower yields.

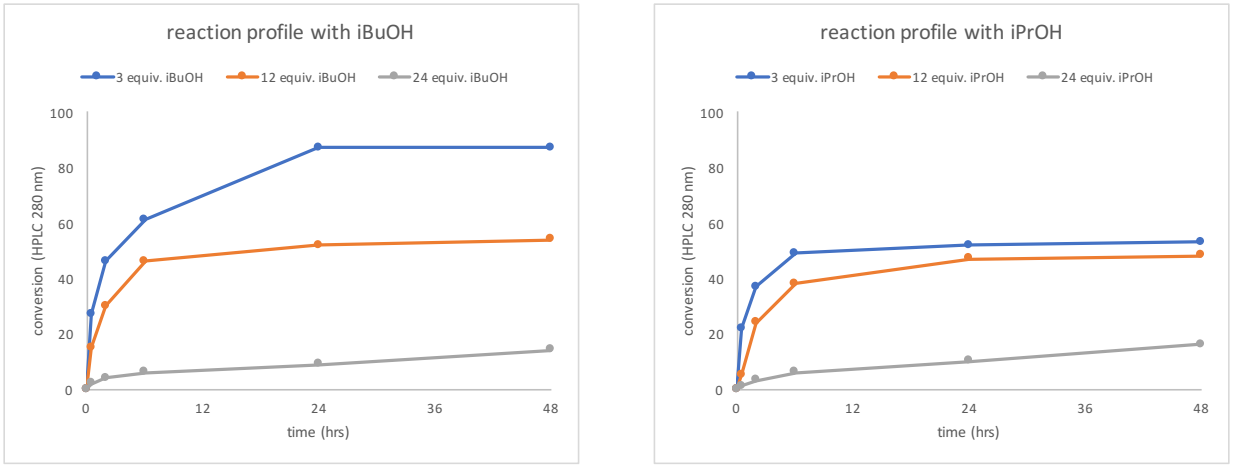
Varying alcohol identity and loading in HDF of 7-fluoro-6-methoxy-1H-indazole (5)



SI Figure 8: Reaction conditions for HDF of 7-fluoro-6-methoxy-1H-indazole (5) with varying equivalents of *iso*-butanol and *iso*-propanol.

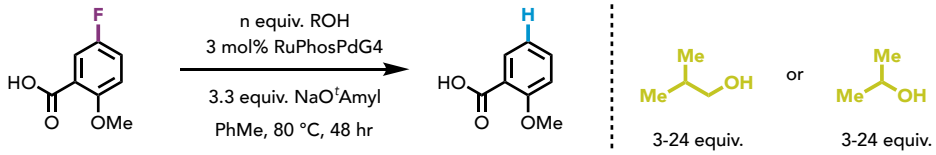
General procedure one was modified to evaluate the effect of different alcohol loadings (using *iso*-propanol and *iso*-butanol) on reaction efficiency. Six reactions were conducted in parallel using 3, 12, or 24 equivalents of alcohol. The reactions were set up according to general procedure one, with the exception that alcohol was omitted from the palladium stock solution and replaced with substrate (**5**). The reaction vials were charged with alcohol by gas tight syringe after addition of catalyst and substrate. The reactions were monitored by LCMS and reaction progress was approximated by using UV-Vis traces at 280 nm to determine LCMS conversion (LCMS conversion=100*$A_{product}$/($A_{product}$ + $A_{reactant}$), where A is area under UV-Vis curve).

Two important observations are evident in SI Figure 9. First, HDF of **5** is suppressed by higher alcohol loadings for reactions conducted with either *iso*-butanol or *iso*-propanol (blue > orange > grey). Second, regardless of alcohol loading, HDF of **5** is more efficient with *iso*-butanol than with *iso*-propanol (left plot > right plot for blue, orange, and grey curves).



SI Figure 9: Reaction profiles in HDF of 7-fluoro-6-methoxy-1H-indazole (7) with varying equivalents of *iso*-butanol (left) and *iso*-propanol (right).

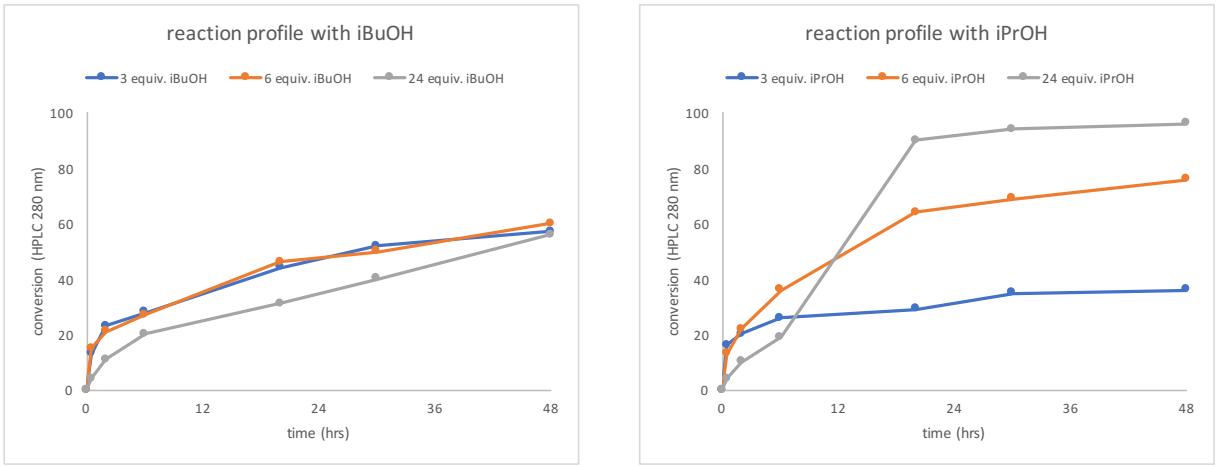
Varying alcohol identity and loading in HDF of 5-fluoro-2-methoxy-benzoic acid (6)



SI Figure 10: Reaction profiles in HDF of 5-fluoro-2-methoxy-benzoic acid (6) with varying equivalents of *iso*-butanol (left) and *iso*-propanol (right).

General procedure one was modified to evaluate the effect of different alcohol loadings (using *iso*-propanol and *iso*-butanol) on reaction efficiency. Six reactions were conducted in parallel using 3, 12, or 24 equivalents of alcohol. The reactions were set up according to general procedure one, with the exception that alcohol was omitted from the palladium stock solution and replaced with substrate (**6**). The reaction vials were charged with alcohol by gas tight syringe after addition of catalyst and substrate. The reactions were monitored by LCMS and reaction progress was approximated by using UV-Vis traces at 280 nm to determine LCMS conversion (LCMS conversion=100*$A_{product}$/($A_{product}$ + $A_{reactant}$), where A is area under UV-Vis curve).

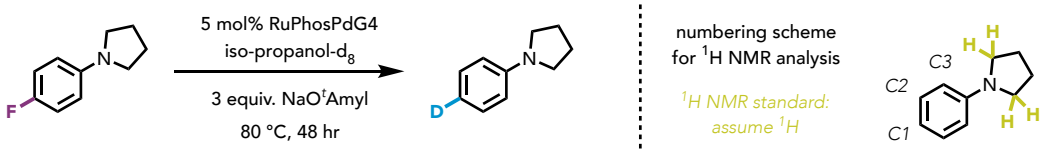
Two important observations are evident in SI Figure 11. First, in contrast to substrate **5**, the rate of HDF of **6** is not substantially perturbed from 3-24 equivalents of *iso*-butanol (SI Figure 11 left). Second, in contrast to reactions conducted with *iso*-butanol (and also in contrast to substrate **7**), HDF of **6** proceeds with greater efficiency in the presence of larger excesses of *iso*-propanol (SI Figure 11 right).



SI Figure 11: HDF of 5-fluoro-2-methoxy-benzoic acid with varying equivalents of *iso*-butanol (left) and *iso*-propanol (right).

Deuterodefluorination Reactions

Deuterodefluorination of 1-(4-fluorophenyl)pyrrolidine (8c)

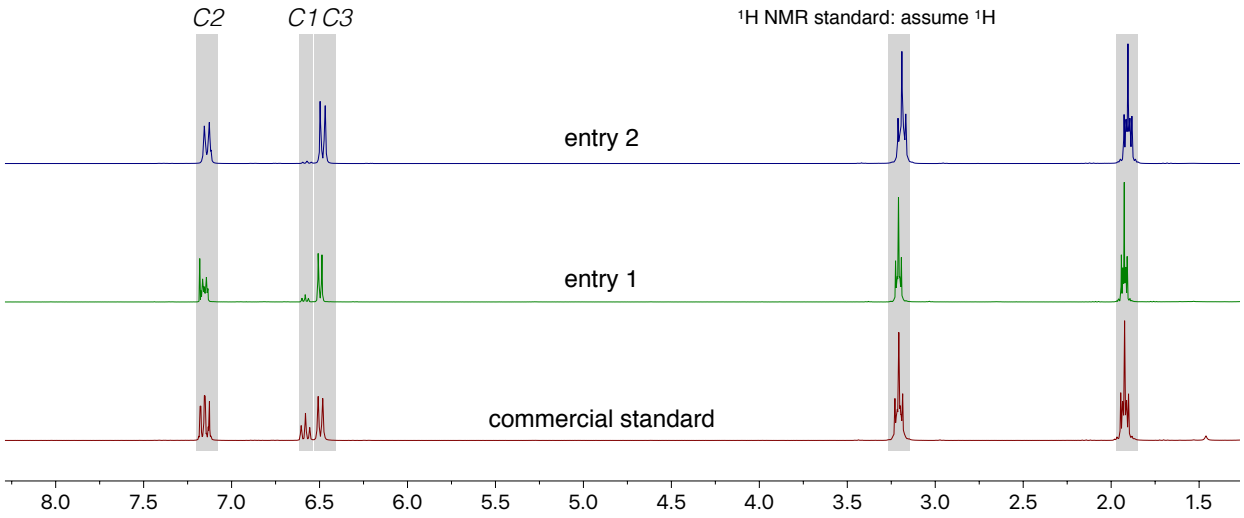


SI Figure 12: DDF of 1-(4-fluorophenyl)-pyrrolidine (8c).

Two reactions were conducted in parallel according to general procedure one with the exception that one was conducted with *iso*-propanol-d_8 (3 equiv.) and the second was conducted in neat *iso*-propanol-d_8. The reactions were purified by automated mass-directed purification on a Waters Autopurification system equipped with a Sunfire C18 column (5 micron, 150 x 30 mm) using water/acetonitrile (0.1% TFA modifier) as the mobile phase. The product containing fractions were concentrated under reduced pressure, neutralized with saturated aqueous sodium bicarbonate, and extracted with dichloromethane (3x3mL). The isolated products were then characterized by ^{1}H NMR spectroscopy and HRMS. The results of this analysis are summarized in SI Table 5 and SI Figure 13.

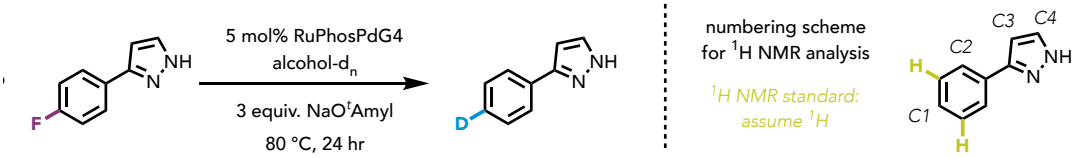
SI Table 5: DDF of 5c with 3 equiv. vs neat *iso*-propanol-d_8

entry	**1**	**2**
equivalents alcohol	3	67
solvent	PhMe	$(CD_3)_2CDOD$
^{1}H NMR		
% ^{2}H @ C1	70%	91%
% ^{2}H @ C2	8%	7%
% ^{2}H @ C3	<5%	<5%
HRMS		
% 0-^{2}H	20%	2%
% 1-^{2}H	80%	98%



SI Figure 13: Stacked ^{1}H NMR spectra from DDF of 1-(4-fluorophenyl)-pyrrolidine (5c).

Deuterodefluorination of 3-(4-fluorophenyl)-1H-pyrazole (4a)

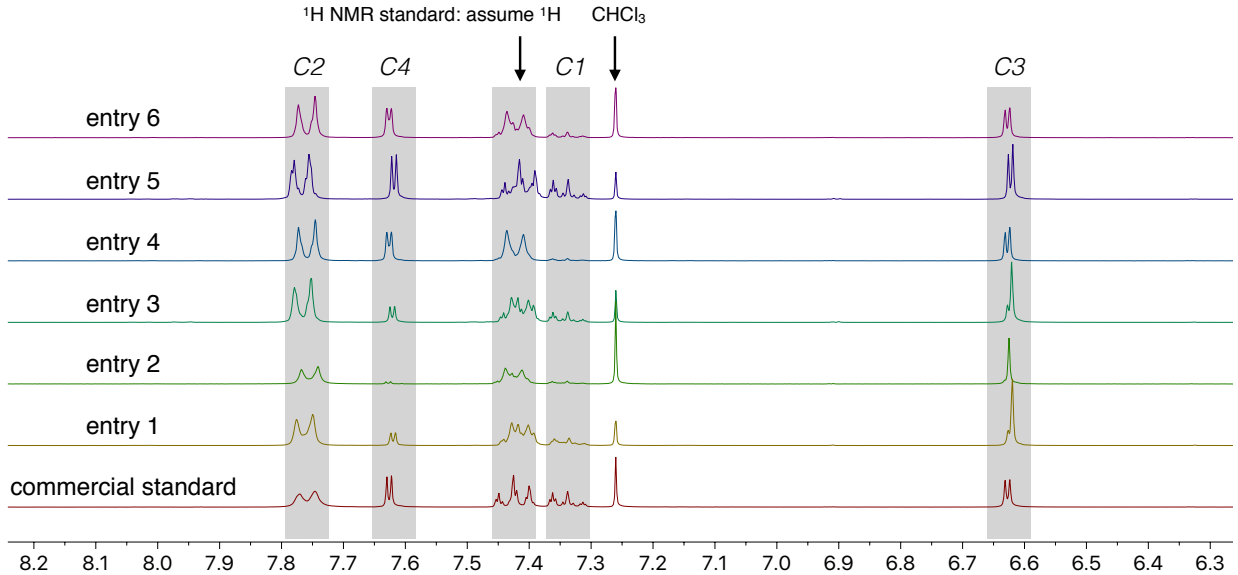


SI Figure 14: DDF of 3-(4-fluorophenyl)-1H-pyrazole (4a).

Six reactions were conducted in parallel according to general procedure one with various deuterated alcohols (3 equiv. or neat, see SI Table 6). The reactions were purified by automated mass-directed purification on a Waters Autopurification system equipped with a Sunfire C18 column (5 micron, 150 x 30 mm) using water/acetonitrile (0.1% TFA modifier) as the mobile phase. The product containing fractions were concentrated under reduced pressure, neutralized with saturated aqueous sodium bicarbonate, and extracted with dichloromethane (3x3mL). The isolated products were then characterized by ^{1}H NMR spectroscopy and HRMS. The results of this analysis are summarized in SI Table 6 and SI Figure 13.

SI Table 6: DDF of 4a with various deuterated alcohols.

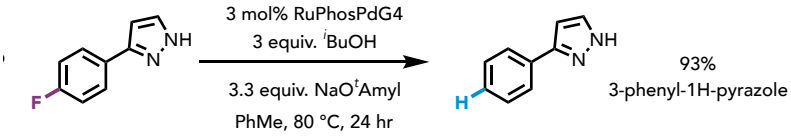
entry	**1**	**2**	**3**	**4**	**5**	**6**
alcohol	$(CD_3)_2CDOD$	$(CD_3)_2CDOD$	CD_3CD_2OD	CD_3CD_2OD	CH_3CH_2OD	CH_3CH_2OD
equivalents alcohol	3	67	3	70	3	70
solvent	PhMe	$(CD_3)_2CDOD$	PhMe	CD_3CD_2OD	PhMe	CH_3CH_2OD
^{1}H NMR						
% ^{2}H @ C1	51%	72%	51%	86%	11%	70%
% ^{2}H @ C2	<5%	5%	<5%	<5%	<5%	<5%
% ^{2}H @ C3	<5%	<5%	<5%	12%	<5%	14%
% ^{2}H @ C4	64%	92%	60%	8%	11%	<5%
HRMS						
% 0-^{2}H	7%	1%	10%	8%	61%	20%
% 1-^{2}H	31%	15%	41%	71%	35%	62%
% 2-^{2}H	40%	54%	42%	19%	5%	16%
% 3-^{2}H	17%	22%	6%	2%	0%	2%
%>3-^{2}H	5%	8%	1%	0%	0%	0%



SI Figure 15: Stacked ^{1}H NMR spectra from DDF of 3-(4-fluorophenyl)-1H-pyrazole (4a).

Experimental Section

HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a)



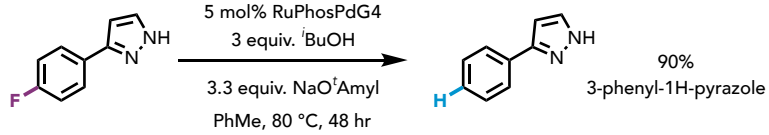
SI Figure 16: HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a).

General procedure one was modified by using 3 mol% RuPhos palladacycle generation 4 (0.012 mmol, 1.6 mL, 0.0075M) instead of 5 mol% Pd. Using the modified procedure, 3-phenyl-1H-pyrazole was prepared from 3-(4-fluorophenyl)-1H-pyrazole (**4a**, 64.9 mg, 0.400 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-60% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 3-phenyl-1H-pyrazole (53.8 mg) as a colorless solid in 93% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J*=7.1 Hz, 2H), 7.55 (d, *J*=2.2 Hz, 1H), 7.40-7.31 (m, 2H), 7.31-7.23 (m, 1H), 6.56 (d, *J*=2.2 Hz, 1H).

HRMS m/z calculated for C9H8N2: 145.0760, found: 145.0763, ppm error: 1.79

HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a) one mmol scale



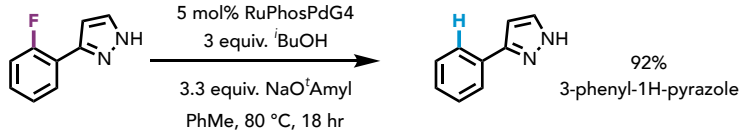
SI Figure 17: HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a) one mmol scale.

General procedure one was modified to 1 mmol scale. To a 20-mL vial with stirbar was added RuPhos palladacycle generation 4 (44.2 mg, 0.052 mmol) and (3-(4-fluorophenyl)-1H-pyrazole (**4a**, 162.6 mg, 1.003 mmol). The vial was sealed with a septum lined cap and purged under nitrogen for 2 minutes. Under nitrogen pressure, the sealed vial was charged with toluene (4 mL) and *iso*-butanol (3 mmol, 0.277 mL). The mixture was stirred for two minutes at room temperature, which afforded a pale yellow solution. The vial was then charged with a commercial solution in toluene of *sodium* tert-pentoxide (4 mmol, 3.33 equiv., 1.0 mL, 3.33M). Upon addition of base, the mixture turned pale green and then back to a yellow solution. The vial was placed in a pre-heated reaction block set to 80 °C with stirring at 600 rpm. The reaction mixture gradually turned from pale yellow to deep orange over the course of two hours. The reaction continued to darken until the mixture was no longer transparent (~8hrs). The reaction was monitored by LCMS until completion at which time the reaction mixture was concentrated under reduced pressure. The crude material was neutralized with saturated sodium bicarbonate (5 mL) and extracted with dichloromethane (4x3mL). The combined organic fractions were loaded onto Celite (10g) and volatiles were removed under reduced pressure. The crude material was purified by flash chromatography (RediSep 12g Gold Silica) using 0-40% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 3-phenyl-1H-pyrazole (129.6 mg) as a colorless solid in 90% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.56 (m, 2H), 7.48 (d, J=2.3 Hz, 1H), 7.33-7.23 (m, 2H), 7.24-7.14 (m, 1H), 6.48 (d, J=2.3 Hz, 1H).

HRMS m/z calculated for C9H8N2: 145.0760, found: 145.0763, ppm error: 1.79

HDF of 3-(2-fluorophenyl)-1H-pyrazole (4b)



SI Figure 18: HDF of 3-(2-fluorophenyl)-1H-pyrazole (4b).

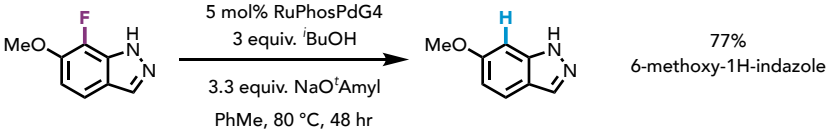
According to general procedure one, 3-phenyl-1H-pyrazole was prepared from 3-(2-fluorophenyl)-1H-pyrazole (**4b**, 64.5 mg, 0.398 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-70% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 3-phenyl-1H-pyrazole (52.7 mg) as a colorless solid in 92% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 11.26 (s, 1H), 7.80-7.66 (m, 2H), 7.57 (d, *J*=2.3 Hz, 1H), 7.40-7.29 (m, 2H), 7.29-7.19 (m, 1H), 6.58 (d, *J*=2.3 Hz, 1H).

^{13}C NMR (101 MHz, CD_3CN) δ 149.93, 133.66, 129.52, 128.48, 126.21, 118.15, 102.79.

HRMS m/z calculated for C9H8N2: 145.0760, found: 145.0763, ppm error: 2.07

HDF of 7-fluoro-6-methoxy-1H-indazole (5)



SI Figure 19: HDF of 7-fluoro-6-methoxy-1H-indazole (5).

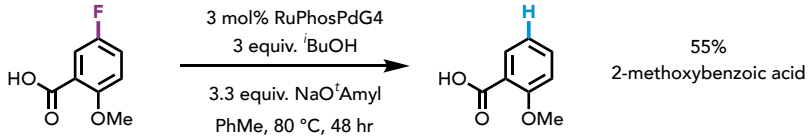
According to general procedure one, 6-methoxy-1H-indazole was prepared from 7-fluoro-6-methoxy-1H-indazole (**5**, 66.1 mg, 0.399 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-60% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 6-methoxy-1H-indazole (45.5 mg) as a beige solid in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.22 (s, 1H), 7.94 (s, 1H), 7.52 (d, J=9.3 Hz, 1H), 6.78-6.70 (m, 2H), 3.74 (d, J=1.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.73, 141.51, 134.51, 121.60, 117.95, 113.32, 90.78, 55.47.

HRMS m/z calculated for C9H8N2O: 149.0709, found: 149.0713, ppm error: 2.55

HDF of 5-fluoro-2-methoxybenzoic acid (6)



SI Figure 20: HDF of 5-fluoro-2-methoxybenzoic acid (6).

General procedure one was modified by using 3 mol% RuPhos palladacycle generation 4 (0.012 mmol, 1.6 mL, 0.0075M) instead of 5 mol% Pd. General procedure one was further modified in that the reaction was worked up by acidifying with hydrochloric acid (1M, 4mL), rather than neutralizing with sodium bicarbonate. Using the modified procedure, 2-methoxybenzoic acid was prepared from 5-fluoro-2-methoxybenzoic acid (**6**, 68.1 mg, 0.400 mmol) and purified by reverse phase chromatography (RediSep 50g C18 Gold column) using 0-40% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure, acidified with hydrochloric acid (1M, 4 mL), and extracted with dichloromethane (3x3mL) to afford 2-methoxybenzoic acid (33.3 mg) as a colorless solid in 55% yield. Starting material, 5-fluoro-2-methoxybenzoic acid, was also recovered from the chromatographic separation as a colorless solid (10.8 mg, 17% recovered starting material).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.09 (d, *J*=7.7 Hz, 1H), 7.51 (t, *J*=7.8 Hz, 1H), 7.06 (t, *J*=7.5 Hz, 1H), 7.00 (d, *J*=8.3 Hz, 1H), 4.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.70, 158.13, 135.15, 133.75, 122.16, 117.57, 111.70, 56.69.

HRMS m/z calculated for C8H8O3: 153.0546, found: 153.0548, ppm error: 1.76

HDF of *N*-(2-fluorophenyl)acetamide (7a)

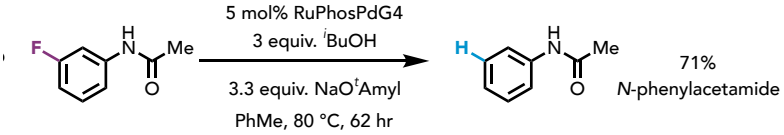
SI Figure 21: HDF of *N*-(2-fluorophenyl)acetamide (7a).

According to general procedure one, *N*-phenylacetamide was prepared from *N*-(2-fluorophenyl)acetamide(**7a**, 59.4 mg, 0.3878 mmol) and purified by normal phase chromatography (RediSep Gold Silica 4g) using 0-40% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford *N*-phenylacetamide (49.3mg) as a colorless solid in 94% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.43 (d, J=7.7 Hz, 2H), 7.22 (t, J=7.9 Hz, 2H), 7.01 (t, J=7.4 Hz, 1H), 2.07 (s, 3H).

HRMS m/z calculated for C8H9NO: 136.0757, found: 136.0760, ppm error: 2.28

HDF of *N*-(3-fluorophenyl)acetamide (7b)



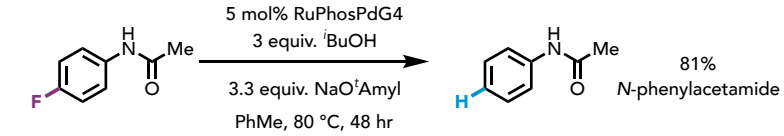
SI Figure 22: HDF of *N*-(3-fluorophenyl)acetamide (7b).

According to general procedure one, *N*-phenylacetamide was prepared from *N*-(3-fluorophenyl)acetamide(**7b**, 58.4 mg, 0.381 mmol) and purified by normal phase chromatography (RediSep Gold Silica 12g) using 0-60% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford *N*-phenylacetamide (36.4 mg) as a colorless solid in 71% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.43 (d, J=7.7 Hz, 2H), 7.22 (t, J=7.9 Hz, 2H), 7.00 (t, J=7.4 Hz, 1H), 2.08 (s, 3H).

HRMS m/z calculated for C8H9NO: 136.0757, found: 136.0760, ppm error: 2.43

HDF of *N*-(4-fluorophenyl)acetamide (7c)



SI Figure 23: HDF of *N*-(4-fluorophenyl)acetamide (4c).

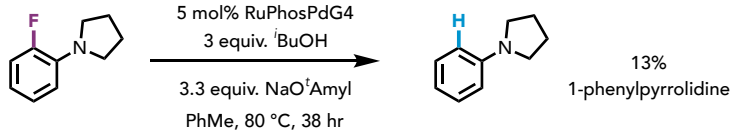
According to general procedure one, *N*-phenylacetamide was prepared from *N*-(4-fluorophenyl)acetamide(**7c**, 60.5 mg, 0.395 mmol) and purified by normal phase chromatography (RediSep Gold Silica 12g) using 0-80% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford *N*-phenylacetamide (43.4 mg) as a colorless solid in 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.43 (d, J=7.7 Hz, 2H), 7.21 (t, J=7.8 Hz, 2H), 7.01 (t, J=7.4 Hz, 1H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 168.96, 138.05, 128.93, 124.31, 120.15, 24.46.

HRMS m/z calculated for C8H9NO: 136.0757, found: 136.0760, ppm error: 2.06

HDF of 1-(2-fluorophenyl)pyrrolidine (8a)



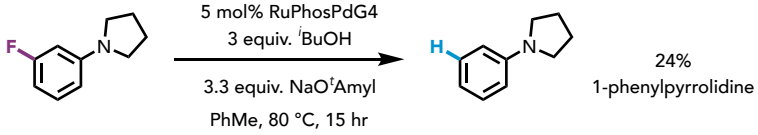
SI Figure 24: HDF of 1-(2-fluorophenyl)pyrrolidine (8a).

According to general procedure one, 1-phenylpyrrolidine was prepared from 1-(2-fluorophenyl)pyrrolidine (**8a**, 64.6mg, 0.391 mmol). The reaction was quenched with methanol after 38 hours (despite incomplete conversion) because the reaction mixture had solidified. The crude material was purified by reverse phase chromatography (RediSep 15.5g C18 Gold column) using 10-20% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure, basified with sodium hydroxide, and extracted with dichloromethane (3x3mL) to afford 1-phenylpyrrolidine (7.7 mg) as a yellow oil in 13% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.11 (m, 2H), 6.58 (t, J=7.3 Hz, 1H), 6.53-6.46 (m, 2H), 3.25-3.17 (m, 4H), 1.96-1.89 (m, 4H)

HRMS m/z calculated for C10H13N: 148.1121, found: 148.1123, ppm error: 1.42

HDF of 1-(3-fluorophenyl)pyrrolidine (8b)



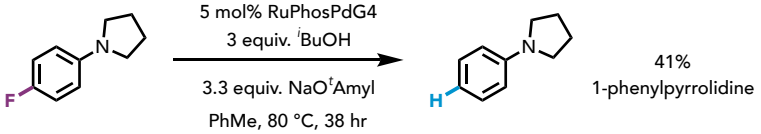
SI Figure 25: HDF of 1-(3-fluorophenyl)pyrrolidine (8b).

According to general procedure one, 1-phenylpyrrolidine was prepared from 1-(3-fluorophenyl)pyrrolidine (**8b**, 65.4mg, 0.396 mmol) and purified by reverse phase chromatography (RediSep 15.5g C18 Gold column) using 10-20% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure, basified with sodium hydroxide, and extracted with dichloromethane (3x3mL) to afford 1-phenylpyrrolidine (14.1 mg) as a yellow oil in 24% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.09 (m, 2H), 6.58 (tt, J=7.3, 1.1 Hz, 1H), 6.54-6.44 (m, 2H), 3.26-3.16 (m, 4H), 1.98-1.87 (m, 4H).

HRMS m/z calculated for C10H13N: 148.1121, found: 148.1123, ppm error: 1.28

HDF of 1-(4-fluorophenyl)pyrrolidine (8c)



SI Figure 26: HDF of 1-(4-fluorophenyl)pyrrolidine (8c).

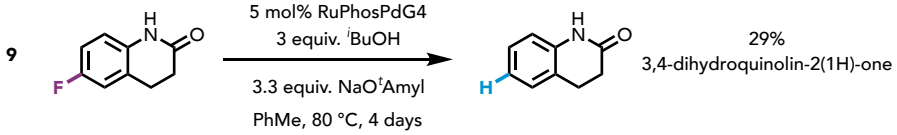
According to general procedure one, 1-phenylpyrrolidine was prepared from 1-(4-fluorophenyl)pyrrolidine (**8c**, 66.0 mg, 0.403 mmol) and purified by reverse phase chromatography (RediSep 15.5g C18 Gold column) using 10-20% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure, basified with sodium hydroxide, and extracted with dichloromethane (3x3mL) to afford 1-phenylpyrrolidine (24.2 mg) as a yellow oil in 41% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.04 (m, 2H), 6.58 (t, J=7.3 Hz, 1H), 6.49 (d, J=8.0 Hz, 2H), 3.44-2.78 (m, 4H), 2.25-1.59 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.00, 129.17, 115.38, 111.66, 47.60, 25.51.

HRMS m/z calculated for C10H13N: 148.1121, found: 148.1123, ppm error: 1.62

HDF of 6-fluoro-3,4-dihydroquinolin-2(1H)-one (9)



SI Figure 27: HDF of 6-fluoro-3,4-dihydroquinolin-2(1H)-one (9).

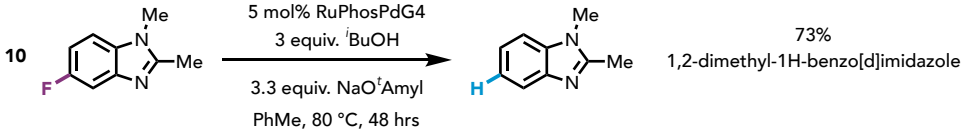
According to general procedure one, 3,4-dihydroquinolin-2(1H)-one was prepared from 6-fluoro-3,4-dihydroquinolin-2(1H)-one (**9**, 61.8 mg, 0.3742 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-100%% ethyl acetate in *n*-heptane. The product containing fractions were contaminated with starting material and were further purified by automated mass-directed purification was performed on a Waters Autopurification system equipped with a Sunfire C18 column (5 micron, 150 x 30 mm) using water/acetonitrile (0.1% TFA modifier) as the mobile phase. The product containing fractions were concentrated under reduced pressure, neutralized with saturated aqueous sodium bicarbonate, and extracted with dichloromethane (3x3mL) to afford 3,4-dihydroquinolin-2(1H)-one (16.0 mg) as a colorless solid in 29% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.10 (m, 2H), 6.91 (td, J=7.6, 1.2 Hz, 1H), 6.77 (d, J=8.1 Hz, 1H), 2.90 (dd, J=8.6, 6.5 Hz, 2H), 2.63-2.52 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.24, 137.32, 127.92, 127.54, 123.62, 123.07, 115.56, 30.74, 25.34.

HRMS m/z calculated for C9H9NO: 148.0757, found: 148.076, ppm error: 2.30

HDF of 5-fluoro-1,2-dimethyl-1H-benzo[d]imidazole (10)



SI Figure 28: HDF of 5-fluoro-1,2-dimethyl-1H-benzo[d]imidazole (10).

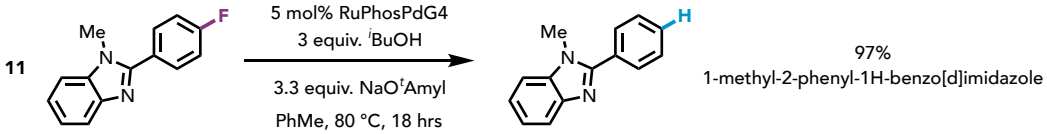
According to general procedure one, 1,2-dimethyl-1H-benzo[d]imidazole was prepared from 5-fluoro-1,2-dimethyl-1H-benzo[d]imidazole (**10**, 59.9 mg, 0.365 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 50-100% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 1,2-dimethyl-1H-benzo[d]imidazole (40.3 mg) as a colorless solid in 73% yield.

^{1}H NMR (300 MHz, CD_3CN) δ 7.60-7.51 (m, 1H), 7.44-7.35 (m, 1H), 7.29-7.12 (m, 2H), 3.72 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (75 MHz, CD_3CN) δ 153.26, 143.67, 137.01, 122.26, 121.96, 119.11, 110.10, 30.27, 13.78.

HRMS m/z calculated for C9H10N2: 147.0917, found: 147.0921, ppm error: 2.72

HDF of 2-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazole (11)



SI Figure 29: HDF of 2-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazole (11).

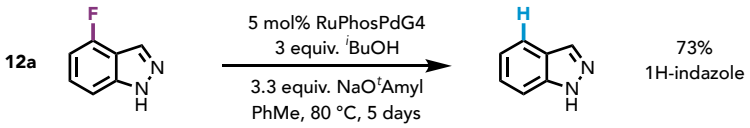
According to general procedure one, 1-methyl-2-phenyl-1H-benzo[d]imidazole was prepared from 2-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazole (**11**, 91.0 mg, 0.402 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 0-100% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 1-methyl-2-phenyl-1H-benzo[d]imidazole (81.4 mg) as a colorless solid in 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.69 (m, 1H), 7.66-7.59 (m, 2H), 7.38 (m, 3H), 7.27-7.15 (m, 3H), 3.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.77, 142.98, 136.60, 130.22, 129.74, 129.44, 128.70, 122.78, 122.44, 119.81, 109.70, 31.68.

HRMS m/z calculated for C14H12N2: 209.1073, found: 209.1079, ppm error: 2.58

HDF of 4-fluoro-1H-indazole (12a)



SI Figure 30: HDF of 4-fluoro-1H-indazole (12a).

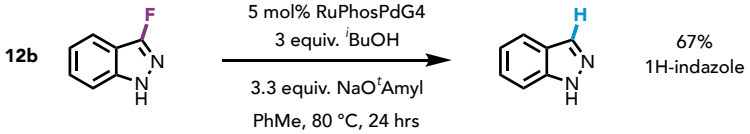
According to general procedure one, 1H-indazole was prepared from 4-fluoro-1H-indazole (**12a**, 53.5 mg, 0.393 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-30% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 1H-indazole (34.1 mg) as a colorless solid in 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.05 (s, 1H), 7.70 (d, J=8.1 Hz, 1H), 7.44 (d, J=8.4 Hz, 1H), 7.32 (t, J=7.6 Hz, 1H), 7.10 (t, J=7.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.10, 134.84, 126.88, 123.22, 121.03, 120.93, 109.80

HRMS m/z calculated for C6H7N2: 119.0604, found: 119.0608, ppm error: 3.78

HDF of 3-fluoro-1H-indazole (12b)



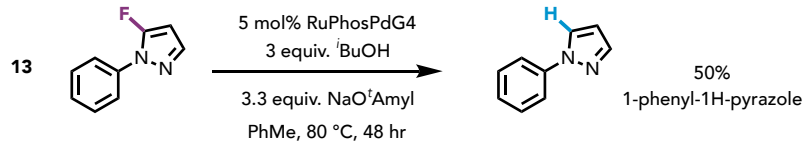
SI Figure 31: HDF of 3-fluoro-1H-indazole (12b).

According to general procedure one, 1H-indazole was prepared from 3-fluoro-1H-indazole (**12b**, 54.4 mg, 0.400 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-25% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 1H-indazole (32.1 mg) as a colorless solid in 67% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.03 (d, J=1.1 Hz, 1H), 7.71 (dt, J=8.1, 1.0 Hz, 1H), 7.44 (dq, J=8.4, 1.0 Hz, 1H), 7.33 (ddd, J=8.4, 6.8, 1.1 Hz, 1H), 7.11 (ddd, J=8.0, 6.8, 1.0 Hz, 1H)

HRMS m/z calculated for C6H7N2: 119.0604, found: 119.0609, ppm error: 4.79

HDF of 5-fluoro-1-phenyl-1H-pyrazole (13)



SI Figure 32: HDF of 5-fluoro-1-phenyl-1H-pyrazole (13).

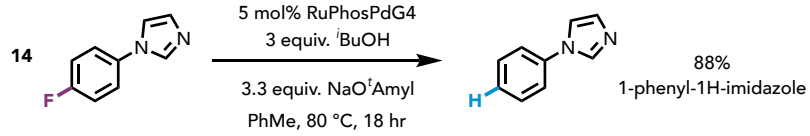
According to general procedure one, 1-phenyl-1H-pyrazole was prepared from 5-fluoro-1-phenyl-1H-pyrazole (**12**, 60.0 mg, 0.370 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-30% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure, to afford 1-phenyl-1H-pyrazole (26.7 mg) as a pale-yellow oil in 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, J=2.0 Hz, 1H), 7.67-7.58 (m, 3H), 7.41-7.32 (m, 2H), 7.24-7.16 (m, 1H), 6.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.10, 140.22, 129.46, 126.78, 126.47, 119.23, 107.62

HRMS m/z calculated for C9H8N2: 145.0760, found: 145.0762, ppm error: 1.24

HDF of 1-(4-fluorophenyl)-1H-imidazole (14)



SI Figure 33: HDF of 1-(4-fluorophenyl)-1H-imidazole (14).

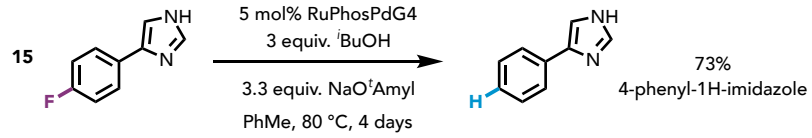
According to general procedure one, 1-phenyl-1H-imidazole was prepared from 1-(4-fluorophenyl)-1H-imidazole (**14**, 63.0 mg, 0.389 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 20-100% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 1-phenyl-1H-imidazole (49.1 mg) as a pale-yellow oil in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, J=1.2 Hz, 1H), 7.39 (m, 2H), 7.29 (m, 3H), 7.19 (t, J=1.4 Hz, 1H), 7.12 (t, J=1.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.35, 135.58, 130.40, 129.90, 127.50, 121.47, 118.25

HRMS m/z calculated for C9H8N2: 145.0760, found: 145.0763, ppm error: 2.00

HDF of 4-(4-fluorophenyl)-1H-imidazole (15)



SI Figure 34: HDF of 4-(4-fluorophenyl)-1H-imidazole (15).

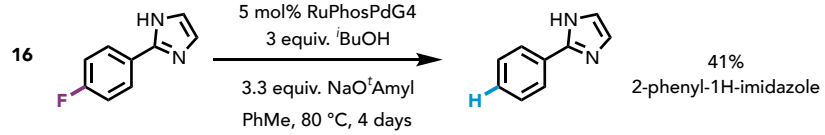
According to general procedure one, 4-phenyl-1H-imidazole was prepared from 4-(4-fluorophenyl)-1H-imidazole (**15**, 62.5 mg, 0.385 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 70-100% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 4-phenyl-1H-imidazole (44.7 mg) as a white solid in 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.68-7.60 (m, 3H), 7.34-7.26 (m, 3H), 7.22-7.13 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.74, 135.68, 132.94, 128.81, 127.05, 124.97, 115.42.

HRMS m/z calculated for C9H8N2: 145.0760, found: 145.0765, ppm error: 2.96

HDF of 2-(4-fluorophenyl)-1H-imidazole (16)



SI Figure 35: HDF of 2-(4-fluorophenyl)-1H-imidazole (16).

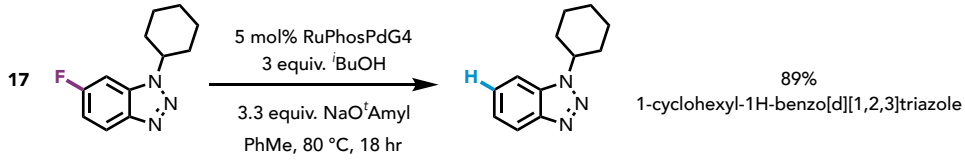
According to general procedure one, 2-phenyl-1H-imidazole was prepared from 2-(4-fluorophenyl)-1H-imidazole (**16**, 60.8 mg, 0.375 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 50-100% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 2-phenyl-1H-imidazole (21.9 mg) as a colorless solid in 41% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.30 (s, 1H), 7.87-7.74 (m, 2H), 7.29-7.15 (m, 3H), 7.04 (s, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.06, 129.67, 128.90, 125.74, 122.82

HRMS m/z calculated for C9H8N2: 145.0760, found: 145.0765, ppm error: 3.24

HDF of 1-cyclohexyl-6-fluoro-1H-benzo[d][1,2,3]triazole (17)



SI Figure 36: HDF of 1-cyclohexyl-6-fluoro-1H-benzo[d][1,2,3]triazole (17).

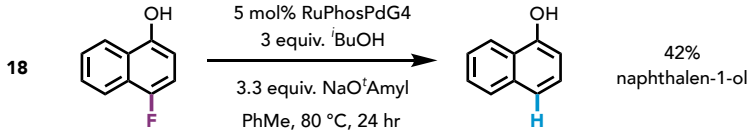
According to general procedure one, 1-cyclohexyl-1H-benzo[d][1,2,3]triazole was prepared from 1-cyclohexyl-6-fluoro-1H-benzo[d][1,2,3]triazole (**17**, 86.5 mg, 0.395 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-25% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 1-cyclohexyl-1H-benzo[d][1,2,3]triazole (70.6 mg) as a colorless solid in 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J=8.3 Hz, 1H), 7.50 (d, J=8.3 Hz, 1H), 7.37 (t, J=7.6 Hz, 1H), 7.26 (t, J=7.6 Hz, 1H), 4.58 (tt, J=10.3, 5.4 Hz, 1H), 2.16-1.99 (m, 4H), 1.98-1.86 (m, 2H), 1.78-1.69 (m, 1H), 1.52-1.37 (m, 2H), 1.41-1.23 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.12, 132.21, 126.76, 123.70, 120.03, 109.80, 59.02, 32.57, 25.60, 25.28.

HRMS m/z calculated for C12H15N3: 202.1339, found: 202.1343, ppm error: 2.33

HDF of 4-fluoronaphthalen-1-ol (18)



SI Figure 37: HDF of 4-fluoronaphthalen-1-ol (18).

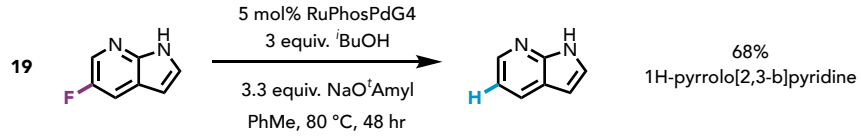
According to general procedure one, naphthalen-1-ol was prepared from 4-fluoronaphthalen-1-ol (**18**, 63.8 mg, 0.393 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-20% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford naphthalen-1-ol (24.1 mg) as a colorless solid in 42% yield.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.15-8.03 (m, 1H), 7.78-7.64 (m, 1H), 7.46-7.31 (m, 3H), 7.21 (dd, *J*=8.2, 7.4 Hz, 1H), 6.71 (dd, *J*=7.4, 1.0 Hz, 1H), 5.21 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.34, 134.79, 127.72, 126.49, 125.86, 125.32, 124.36, 121.54, 120.76, 108.67.

HRMS m/z calculated for C10H8O: 145.0648, found: 145.0649, ppm error: 0.83

HDF of 5-fluoro-1H-pyrrolo[2,3-b]pyridine (19)



SI Figure 38: HDF of 5-fluoro-1H-pyrrolo[2,3-b]pyridine (19).

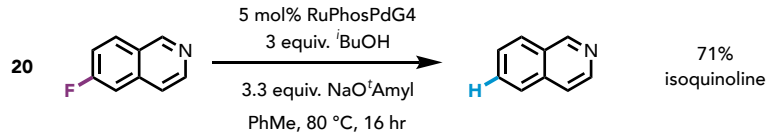
According to general procedure one, 1H-pyrrolo[2,3-b]pyridine was prepared from 5-fluoro-1H-pyrrolo[2,3-b]pyridine (**19**, 52.8 mg, 0.388 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-40% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 1H-pyrrolo[2,3-b]pyridine (31.2 mg) as a colorless solid in 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 8.27 (dd, J=4.8, 1.6 Hz, 1H), 7.89 (dd, J=7.8, 1.6 Hz, 1H), 7.32 (d, J=3.5 Hz, 1H), 7.01 (dd, J=7.8, 4.8 Hz, 1H), 6.43 (d, J=3.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.92, 142.26, 129.10, 125.43, 120.63, 115.73, 100.54.

HRMS m/z calculated for C7H6N2: 119.0604, found: 119.0610, ppm error: 5.04

HDF of 6-fluoroisoquinoline (20)



SI Figure 39: HDF of 6-fluoroisoquinoline (20).

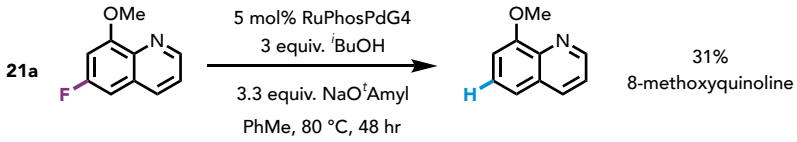
According to general procedure one, isoquinoline was prepared from 6-fluoroisoquinoline (**20**, 59.4 mg, 0.404 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 0-100% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford isoquinoline (37.8 mg) as a yellow oil in 71% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.53 (d, *J*=5.8 Hz, 1H), 7.95 (d, *J*=8.1 Hz, 1H), 7.80 (d, *J*=8.2 Hz, 1H), 7.74-7.51 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.55, 143.04, 135.75, 130.31, 128.67, 127.60, 127.22, 126.46, 120.44

HRMS m/z calculated for C9H7N: 130.0651, found: 130.0654, ppm error: 2.77

HDF of 6-fluoro-8-methoxyquinoline (21a)



SI Figure 40: HDF of 6-fluoro-8-methoxyquinoline (21a).

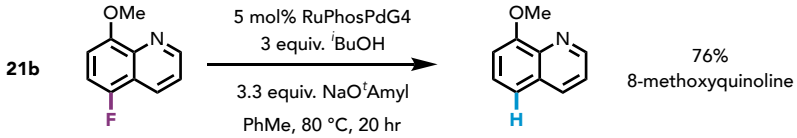
According to general procedure one, 8-methoxyquinoline was prepared from 6-fluoro-8-methoxyquinoline (**21a**, 71.3 mg, 0.402 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 0-60% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 8-methoxyquinoline (19.8 mg) as a yellow oil in 31% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, J=4.1, 1.9 Hz, 1H), 8.05 (dd, J=8.3, 2.1 Hz, 1H), 7.43-7.31 (m, 2H), 7.31 (d, J=8.2 Hz, 1H), 6.98 (d, J=7.6 Hz, 1H), 4.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.40, 149.28, 140.21, 135.90, 129.36, 126.73, 121.71, 119.56, 107.53, 55.98.

HRMS m/z calculated for C10H9NO: 160.0757, found: 160.0762, ppm error: 3.12

HDF of 5-fluoro-8-methoxyquinoline (21b)



SI Figure 41: HDF of 5-fluoro-8-methoxyquinoline (21b).

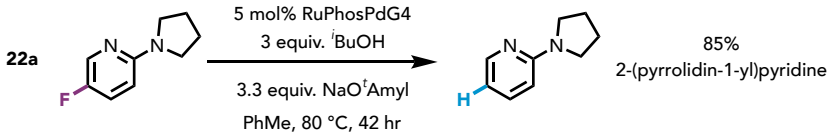
According to general procedure one, 8-methoxyquinoline was prepared from 5-fluoro-8-methoxyquinoline (**21b**, 78.1 mg, 0.441 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 0-70% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 8-methoxyquinoline (53.3 mg) as a yellow oil in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, J=4.2, 1.7 Hz, 1H), 7.95 (dd, J=8.3, 1.7 Hz, 1H), 7.29 (dd, J=8.3, 7.7 Hz, 1H), 7.29-7.18 (m, 2H), 6.88 (dd, J=7.6, 1.3 Hz, 1H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.37, 149.25, 140.18, 135.87, 129.33, 126.70, 121.68, 119.54, 107.50, 55.95.

HRMS m/z calculated for C10H9NO: 160.0757, found: 160.0760, ppm error: 2.12

HDF of 5-fluoro-2-(pyrrolidin-1-yl)pyridine (22a)



SI Figure 42: HDF of 5-fluoro-2-(pyrrolidin-1-yl)pyridine (22a).

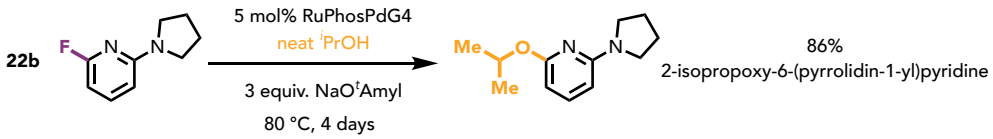
According to general procedure one, 2-(pyrrolidin-1-yl)pyridine was prepared from 5-fluoro-2-(pyrrolidin-1-yl)pyridine (**22a**, 67.4 mg, 0.406 mmol) and purified by normal phase chromatography (RediSep 4g Gold Silica) using 0-40% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 2-(pyrrolidin-1-yl)pyridine (51.1mg) as a pale-yellow oil in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (ddd, J=5.0, 2.0, 0.9 Hz, 1H), 7.33 (ddd, J=8.8, 7.1, 2.0 Hz, 1H), 6.42 (ddd, J=7.1, 5.0, 0.9 Hz, 1H), 6.26 (dt, J=8.5, 1.0 Hz, 1H), 3.43-3.29 (m, 4H), 1.98-1.85 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.32, 148.19, 136.87, 111.01, 106.47, 77.42, 77.11, 76.79, 46.61, 25.55.

HRMS m/z calculated for C9H12N2: 149.1073, found: 149.1078, ppm error: 3.02

S_NAr of 2-fluoro-6-(pyrrolidin-1-yl)pyridine (22b) with *iso*-propanol



SI Figure 43: S_NAr of of 2-fluoro-6-(pyrrolidin-1-yl)pyridine (22b) with *iso*-propanol.

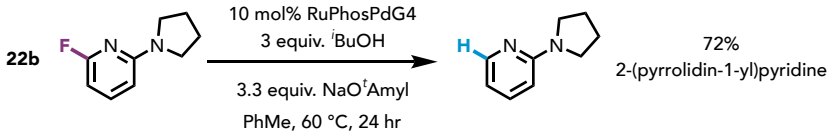
General procedure one was modified by conducting the reaction in neat *iso*-propanol (without *iso*-butanol) rather than in toluene. All components were weighed out as solids into a one dram vial with stirbar, which was purged under nitrogen and charged *iso*-propanol (2mL). Using the modified procedure, 2-isopropoxy-6-(pyrrolidin-1-yl)pyridine was prepared from 2-fluoro-6-(pyrrolidin-1-yl)pyridine (**22b**, 73.2 mg, 0.440 mmol) and purified by normal phase chromatography RediSep 12g Gold Silica) using 0-10% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 2-isopropoxy-6-(pyrrolidin-1-yl)pyridine (78.7.8 mg) as a colorless oil in 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J=7.9 Hz, 1H), 5.83 (d, J=7.8 Hz, 1H), 5.75 (d, J=8.0 Hz, 1H), 5.14 (h, J=6.2 Hz, 1H), 3.38-3.28 (m, 4H), 1.93-1.82 (m, 4H), 1.26 (d, J=6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.60, 156.35, 139.48, 97.19, 96.22, 67.25, 46.58, 25.49, 22.28.

HRMS m/z calculated for C12H18N2O: 207.1414, found: 207.1495, ppm error: 2.68

HDF of 2-fluoro-6-(pyrrolidin-1-yl)pyridine (22b)



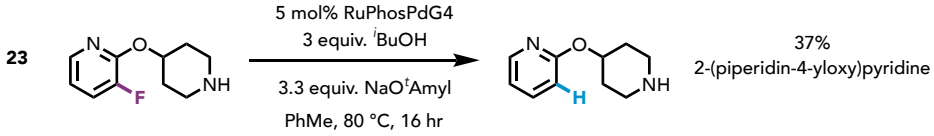
SI Figure 44: HDF of 2-fluoro-6-(pyrrolidin-1-yl)pyridine (22b).

General procedure one was modified by using 10 mol% RuPhos palladacycle generation 4 (0.04 mmol, 1.6 mL, 0.025M) instead of 5 mol% Pd and conducting the reaction at 60°C rather than 80°C. Using the modified procedure, 2-(pyrrolidin-1-yl)pyridine was prepared from 2-fluoro-6-(pyrrolidin-1-yl)pyridine (**22b**, 66.5 mg, 0.400 mmol) and purified by reverse phase chromatography (RediSep 15.5g C18 Gold column) using 0-10% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure, basified with sodium hydroxide, and extracted with dichloromethane (3x3mL) to afford 2-(pyrrolidin-1-yl)pyridine (42.8 mg) as a colorless oil in 72% yield. The material obtained in this manner afforded spectroscopic data consistent with those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (ddd, J=5.0, 2.0, 0.9 Hz, 1H), 7.33 (ddd, J=8.8, 7.1, 2.0 Hz, 1H), 6.42 (ddd, J=7.1, 5.0, 1.0 Hz, 1H), 6.26 (dt, J=8.5, 1.0 Hz, 1H), 3.45-3.30 (m, 4H), 2.00-1.83 (m, 4H).

HRMS m/z calculated for C9H12N2: 149.1073, found: 149.1078, ppm error: 3.15

HDF of 3-fluoro-2-(piperidin-4-yloxy)pyridine (23)



SI Figure 45: HDF of 3-fluoro-2-(piperidin-4-yloxy)pyridine (23).

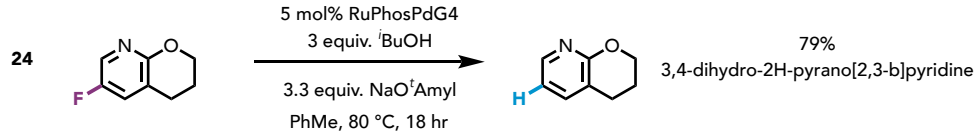
According to general procedure one, 2-(piperidin-4-yloxy)pyridine was prepared from 3-fluoro-2-(piperidin-4-yloxy)pyridine (**23**, 79.0 mg, 0.403 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 5-10% methanol in dichloromethane. The product containing fractions were concentrated under reduced pressure to afford 2-(piperidin-4-yloxy)pyridine (27.2 mg) as a colorless solid in 37% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J*=5.2, 2.0 Hz, 1H), 7.48 (ddd, *J*=8.7, 7.1, 2.1 Hz, 1H), 6.76 (dd, *J*=7.1, 5.0 Hz, 1H), 6.63 (d, *J*=8.3 Hz, 1H), 5.08 (tt, *J*=8.6, 4.0 Hz, 1H), 3.07 (dt, *J*=12.7, 4.6 Hz, 2H), 2.73 (ddd, *J*=12.7, 9.6, 3.1 Hz, 2H), 2.36-2.28 (m, 1H), 2.05-1.94 (m, 2H), 1.67-1.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.11, 146.80, 138.63, 116.48, 111.70, 70.80, 44.14, 32.37.

HRMS m/z calculated for C10H14N2O: 179.1179, found: 179.1183, ppm error: 2.40

HDF of 6-fluoro-3,4-dihydro-2H-pyrano[2,3-b]pyridine (24)



SI Figure 46: HDF of 6-fluoro-3,4-dihydro-2H-pyrano[2,3-b]pyridine (24).

According to general procedure one, 3,4-dihydro-2H-pyrano[2,3-b]pyridine was prepared from 6-fluoro-3,4-dihydro-2H-pyrano[2,3-b]pyridine (**24**, 60.5 mg, 0.395 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-100% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 3,4-dihydro-2H-pyrano[2,3-b]pyridine (42.1 mg) as a colorless oil in 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J=4.8 Hz, 1H), 7.29 (d, J=7.3 Hz, 1H), 6.78-6.71 (m, 1H), 4.29-4.22 (m, 2H), 2.72 (t, J=6.5 Hz, 2H), 1.93 (p, J=6.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.33, 146.36, 138.67, 117.27, 117.09, 67.15, 24.85, 21.76.

HRMS m/z calculated for C8H9NO: 136.0757, found: 136.0759, ppm error: 1.84

HDF of 4-(3-fluoropyridin-2-yl)morpholine (25)

SI Figure 47: HDF of 4-(3-fluoropyridin-2-yl)morpholine (25).

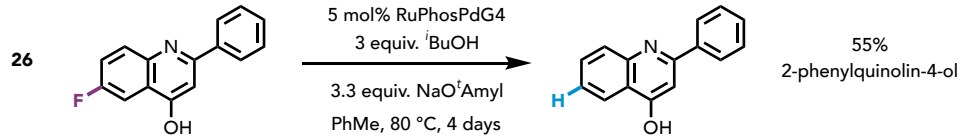
According to general procedure one, 4-(pyridin-2-yl)morpholine was prepared from 4-(3-fluoropyridin-2-yl)morpholine (**25**, 74.7 mg, 0.410 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-40% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 4-(pyridin-2-yl)morpholine (47.2 mg) as a straw-colored oil in 70% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (ddd, J=4.9, 2.0, 0.9 Hz, 1H), 7.36 (ddd, J=8.5, 7.2, 2.0 Hz, 1H), 6.58-6.45 (m, 2H), 3.74-3.64 (m, 4H), 3.41-3.31 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.62, 147.98, 137.54, 113.84, 106.95, 66.78, 45.61.

HRMS m/z calculated for C9H12N2O: 165.1022, found: 136.0759, ppm error: 2.36

HDF of 6-fluoro-2-phenylquinolin-4-ol (26)



SI Figure 48: HDF of 6-fluoro-2-phenylquinolin-4-ol (26).

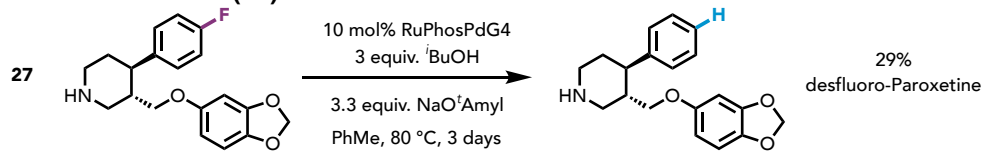
According to general procedure one, 2-phenylquinolin-4-ol was prepared from 6-fluoro-2-phenylquinolin-4-ol (**26**, 94.4 mg, 0.395 mmol) and purified by reverse phase chromatography (RediSep 15.5g C18 Gold column) using 0-50% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure to afford the trifluoroacetic acid salt of 2-phenylquinolin-4-ol (74.9 mg) as a colorless solid in 55% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 8.38 (d, J=8.3 Hz, 1H), 8.03 (d, J=8.5 Hz, 1H), 7.94 (t, J=7.7 Hz, 1H), 7.88 (d, J=7.3 Hz, 2H), 7.70-7.58 (m, 4H), 7.39 (s, 1H).

^{13}C NMR (101 MHz, CD_3CN) δ 174.70, 154.58, 140.70, 134.68, 132.94, 132.56, 129.99, 128.56, 127.05, 124.86, 122.08, 119.76, 105.94.

HRMS m/z calculated for C15H11NO: 222.0913, found: 222.0919, ppm error: 2.48

HDF of Paroxetine (27)



SI Figure 49: HDF of Paroxetine (27).

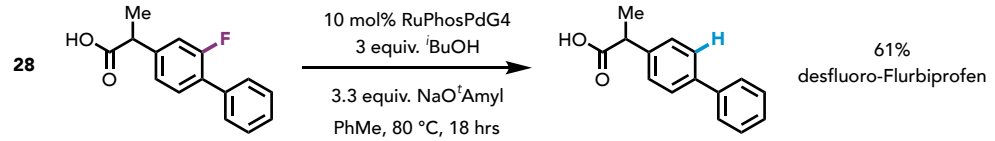
According to general procedure one, desfluoro-Paroxetine was prepared from Paroxetine (**27**, 128.1 mg, 0.389 mmol) and purified by automated mass-directed purification on a Waters Autopurification system equipped with a Sunfire C18 column (5 micron, 150 x 30 mm) using water/acetonitrile (0.1% TFA modifier) as the mobile phase. The pure product fraction was concentrated under reduced pressure, neutralized with saturated aqueous sodium bicarbonate, and extracted with dichloromethane (4x3mL) to afford desfluoro-Paroxetine (34.6 mg) as a colorless oil in 29% yield. A second fraction containing a mixture of starting material and product (76% starting material and 24% product by ^{1}H NMR) was isolated in the same manner to afford an additional 40.4 mg of mixed material accounting for approximately 32% of the mass balance.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.16 (m, 2H), 7.16-7.07 (m, 2H), 6.53 (d, J=8.4 Hz, 1H), 6.25 (s, 1H), 6.04 (d, J=8.4 Hz, 1H), 5.78 (s, 2H), 3.50 (d, J=9.1 Hz, 1H), 3.44-3.30 (m, 2H), 3.14 (d, J=12.0 Hz, 1H), 2.91 (s, 1H), 2.75-2.64 (m, 1H), 2.62 (t, J=11.6 Hz, 1H), 2.51 (td, J=11.4, 4.2 Hz, 1H), 2.09 (dtt, J=11.4, 7.8, 3.2 Hz, 1H), 1.82-1.64 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.41, 148.12, 144.05, 141.50, 128.69, 127.45, 126.62, 107.83, 105.58, 97.97, 69.55, 50.16, 46.90, 45.21, 42.46, 34.93.

HRMS m/z calculated for C19H21NO3: 312.1594, found: 312.1601, ppm error: 2.37

HDF of Flurbiprofen (28)



SI Figure 50: HDF of Flurbiprofen (28).

According to general procedure one, desfluoro-Flurbiprofen was prepared from Flurbiprofen (**28**, 97.0 mg, 0.397 mmol) and purified by normal phase chromatography (RediSep 12g Gold Silica) using 0-4% methanol in dichloromethane. The product containing fractions were concentrated under reduced pressure to afford a mixture of desfluoro-Flurbiprofen and **28** (90.4 mg) accounting for approximately 93% of the mass balance. The starting material and product were isolated by preparative supercritical fluid chromatography on a Chiracel OJ-H column and eluting with 30% methanol (5 mM ammonia modifier). The pure fractions were concentrated under reduced pressure, acidified with aqueous 1M hydrochloric acid, and extracted with dichloromethane (3x3 mL) to afford desfluoro-Flurbiprofen (54.9 mg) as a colorless solid in 61% yield.

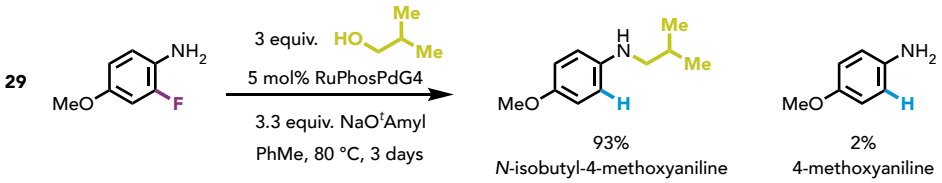
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (s, 1H), 7.51-7.42 (m, 4H), 7.37-7.27 (m, 4H), 7.30-7.19 (m, 1H), 3.69 (q, J=7.1 Hz, 1H), 1.45 (d, J=7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.09, 140.76, 140.46, 138.84, 128.83, 128.12, 127.50, 127.38, 127.16, 45.17, 18.17.

The starting material (**28**) underwent decarboxylation under HRMS negative ionization:
HRMS m/z calculated for C14H12F: 199.0923, found: 199.0928, ppm error: 0.24.

The desired product, desfluoro-Flurbiprofen was also decarboxylated under HRMS negative ionization:
HRMS m/z calculated for C14H13: 181.1017, found: 181.1016, ppm error: 3.51.

HDF and alkylation of 2-fluoro-4-methoxyaniline (29)



SI Figure 51: HDF and alkylation of 2-fluoro-4-methoxyaniline (29).

According to general procedure one, *N*-isobutyl-4-methoxyaniline was prepared from 2-fluoro-4-methoxyaniline (**29**, 56.5 mg, 0.400 mmol) and purified by reverse phase chromatography (RediSep 15.5g C18 Gold column) using 0-50% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure, neutralized with saturated aqueous sodium bicarbonate, and extracted with dichloromethane (3x3mL) to afford *N*-isobutyl-4-methoxyaniline (66.5 mg) as a colorless solid in 93% yield. A separate fraction containing the intended HDF product was treated in the same manner to afford 4-methoxy-aniline (1.0 mg) as a colorless solid in 2% yield that matched the ^{1}H NMR spectrum of commercial material and hit for HRMS—m/z calculated for C7H9NO: 124.07569, found: 124.0762, ppm error: 4.11

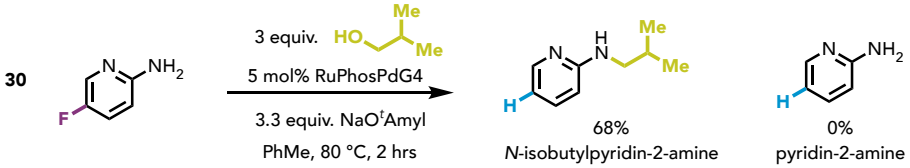
.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (bs, 1H), 7.10 (d, *J*=8.3 Hz, 2H), 6.73 (d, *J*=8.3 Hz, 2H), 3.69 (s, 3H), 2.91 (d, *J*=7.0 Hz, 2H), 1.93 (hept, *J*=6.8 Hz, 1H), 0.89 (d, *J*=6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.00, 132.13, 121.84, 114.96, 59.10, 55.54, 26.15, 20.13.

HRMS m/z calculated for C11H17NO: 180.1383, found: 180.1387, ppm error: 2.11

HDF and alkylation of 5-fluoropyridin-2-amine (30)



SI Figure 52: HDF and alkylation of 5-fluoropyridin-2-amine (30).

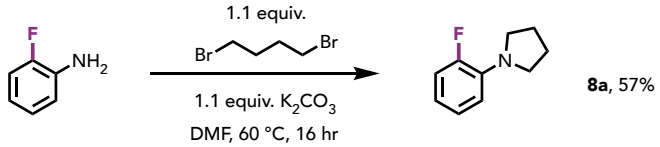
According to general procedure one, *N*-isobutylpyridin-2-amine was prepared from 5-fluoropyridin-2-amine (**30**, 46.4 mg, 0.414 mmol) and purified by reverse phase chromatography (RediSep 15.5g C18 Gold column) using 0-50% acetonitrile in water (0.1% TFA modifier). The product containing fractions were concentrated under reduced pressure, basified with saturated aqueous sodium carbonate, and extracted with dichloromethane (3x3mL) to afford *N*-isobutylpyridin-2-amine (42.5 mg) as a yellow oil in 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*=5.1 Hz, 1H), 7.37 (td, *J*=7.8, 6.8, 1.8 Hz, 1H), 6.48 (t, *J*=6.2 Hz, 1H), 6.33 (d, *J*=8.5 Hz, 1H), 5.12 (s, 1H), 3.04-2.96 (m, 2H), 1.94-1.68 (m, 1H), 0.91 (d, *J*=6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.56, 146.95, 138.07, 112.37, 106.59, 50.01, 28.24, 20.37.

HRMS m/z calculated for C9H14N2: 151.1230, found: 151.1234, ppm error: 2.91

Preparation of 1-(2-fluorophenyl)pyrrolidine (8a)



SI Figure 53: Preparation of 1-(2-fluorophenyl)pyrrolidine (8a).

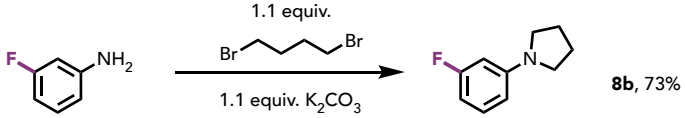
According to general procedure two, 1-(2-fluorophenyl)pyrrolidine (**8a**) was prepared from 2-fluoroaniline (1.5 mL, 1.727 g, 15.54 mmol) and purified by normal phase chromatography (RediSep 80g Gold Silica) using 0-20% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 1-(2-fluorophenyl)pyrrolidine (**8a**, 1.47g) as a colorless oil in 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.83 (m, 2H), 6.66-6.51 (m, 2H), 3.38-3.22 (m, 4H), 1.96-1.79 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.14-146.32 (m), 139.85-131.85 (m), 124.36 (d, J=3.0 Hz), 117.15 (d, J=7.2 Hz), 116.04 (d, J=21.0 Hz), 115.29 (d, J=5.0 Hz), 49.77 (d, J=4.9 Hz), 25.19 (d, J=1.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -126.97 (dddd, J=14.9, 9.7, 5.2, 2.6 Hz).

Preparation of 1-(3-fluorophenyl)pyrrolidine (8b)



SI Figure 54: Preparation of 1-(3-fluorophenyl)pyrrolidine (8b).

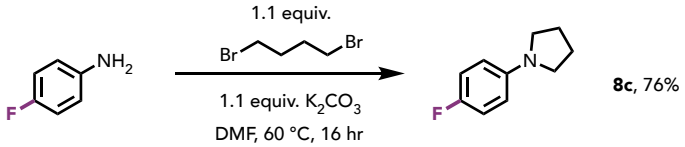
According to general procedure two, 1-(3-fluorophenyl)pyrrolidine (**8b**) was prepared from 3-fluoroaniline (1.5 mL, 1.734 g, 15.61 mmol) and purified by normal phase chromatography (RediSep 80g Gold Silica) using 0-20% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 1-(3-fluorophenyl)pyrrolidine (**8b**, 1.88g) as a colorless oil that solidified upon cooling to 4 °C in 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (td, J=8.2, 6.9 Hz, 1H), 6.32-6.08 (m, 3H), 3.25-3.09 (m, 4H), 2.01-1.84 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.14 (d, J=241.5 Hz), 149.49 (d, J=11.0 Hz), 130.07 (d, J=10.6 Hz), 107.33 (d, J=2.1 Hz), 101.73 (d, J=21.7 Hz), 98.43 (d, J=25.6 Hz), 47.68, 25.46.

^{19}F NMR (282 MHz, $CDCl_3$) δ -113.05 -113.18 (m).

Preparation of 1-(4-fluorophenyl)pyrrolidine (8c)



SI Figure 55: Preparation of 1-(4-fluorophenyl)pyrrolidine (8c).

According to general procedure two, 1-(4-fluorophenyl)pyrrolidine (**8c**) was prepared from 4-fluoroaniline (0.96 mL, 1.112 g, 10 mmol) and purified by normal phase chromatography (RediSep 80g Gold Silica) using 0-20% ethyl acetate in *n*-heptane. The product containing fractions were concentrated under reduced pressure to afford 1-(5-fluorophenyl)pyrrolidine (**8c**, 1.25g) as a colorless solid in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93-6.79 (m, 2H), 6.46-6.33 (m, 2H), 3.23-3.07 (m, 4H), 2.01-1.84 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.80 (d, J=233.0 Hz), 144.82, 115.46 (d, J=22.0 Hz), 112.04 (d, J=7.2 Hz), 48.09, 25.49.

^{19}F NMR (282 MHz, $CDCl_3$) δ -130.96 (tt, J=8.6, 4.4 Hz).

Feb08-2019.6.1.1r
E34457_0119_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 34

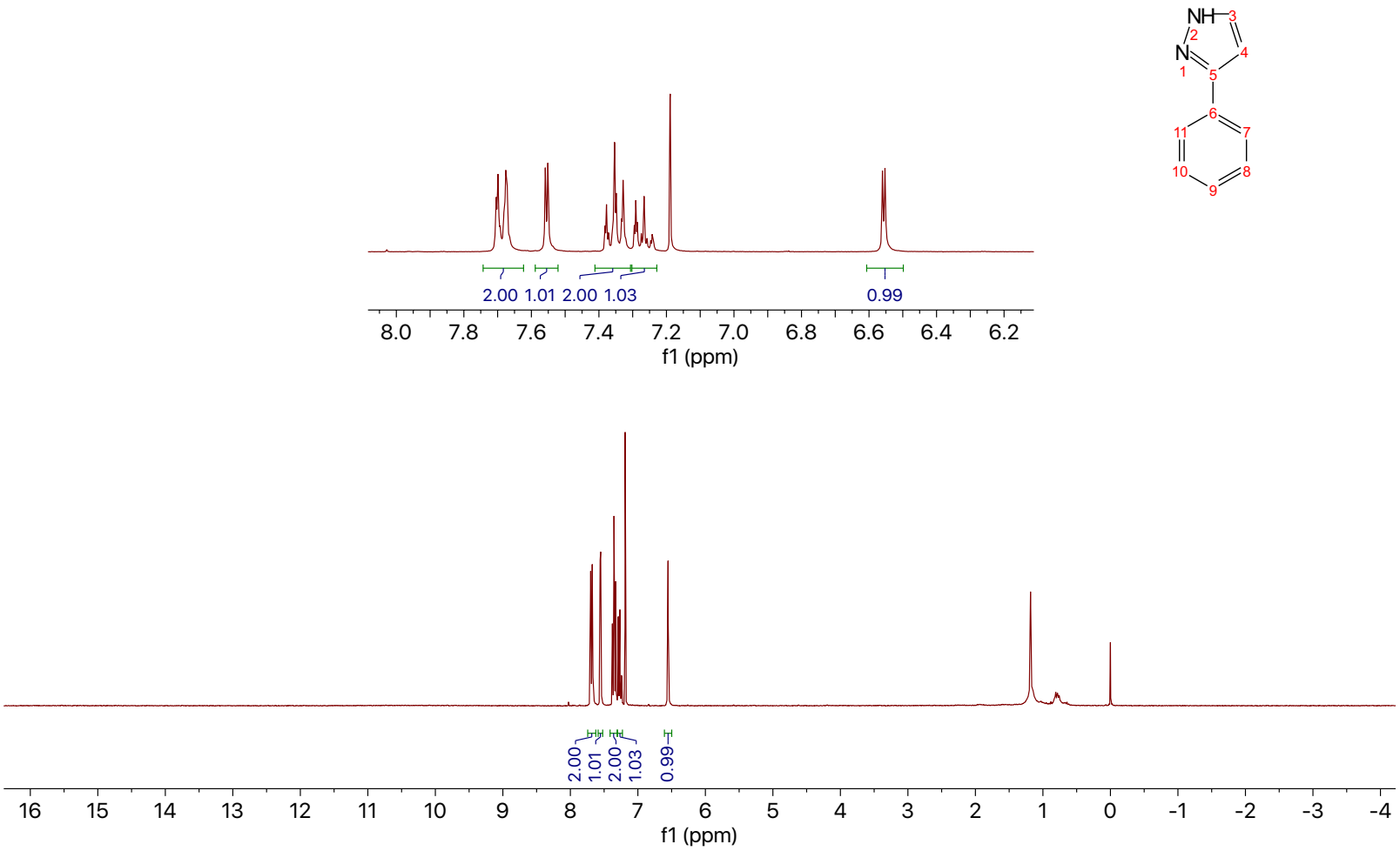
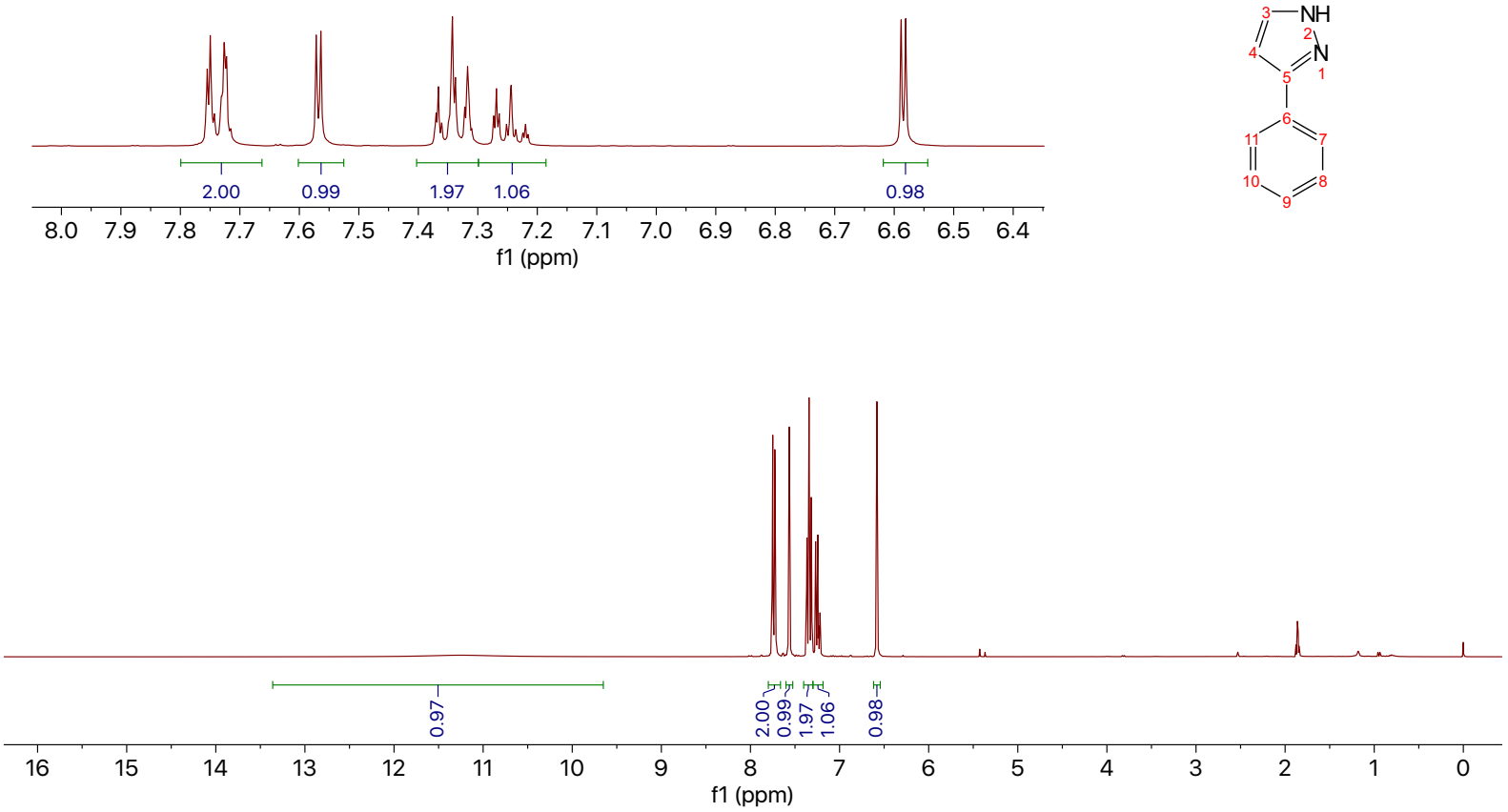
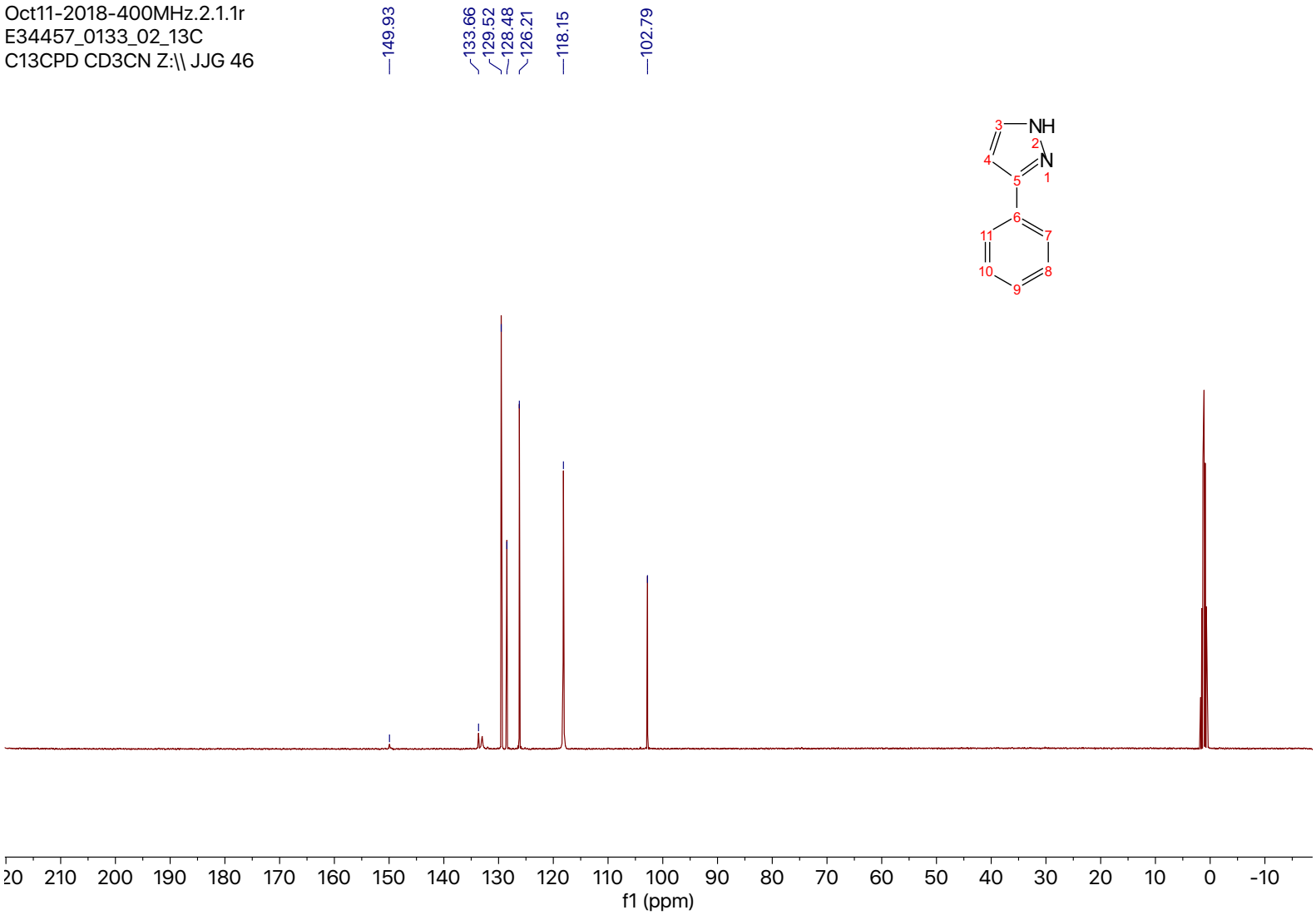


Figure 56: ^{1}H NMR spectrum of 3-phenyl-1H-pyrazole in $CDCl_3$ from HDF of 3-(4-fluorophenyl)-1H-pyrazole (4a).

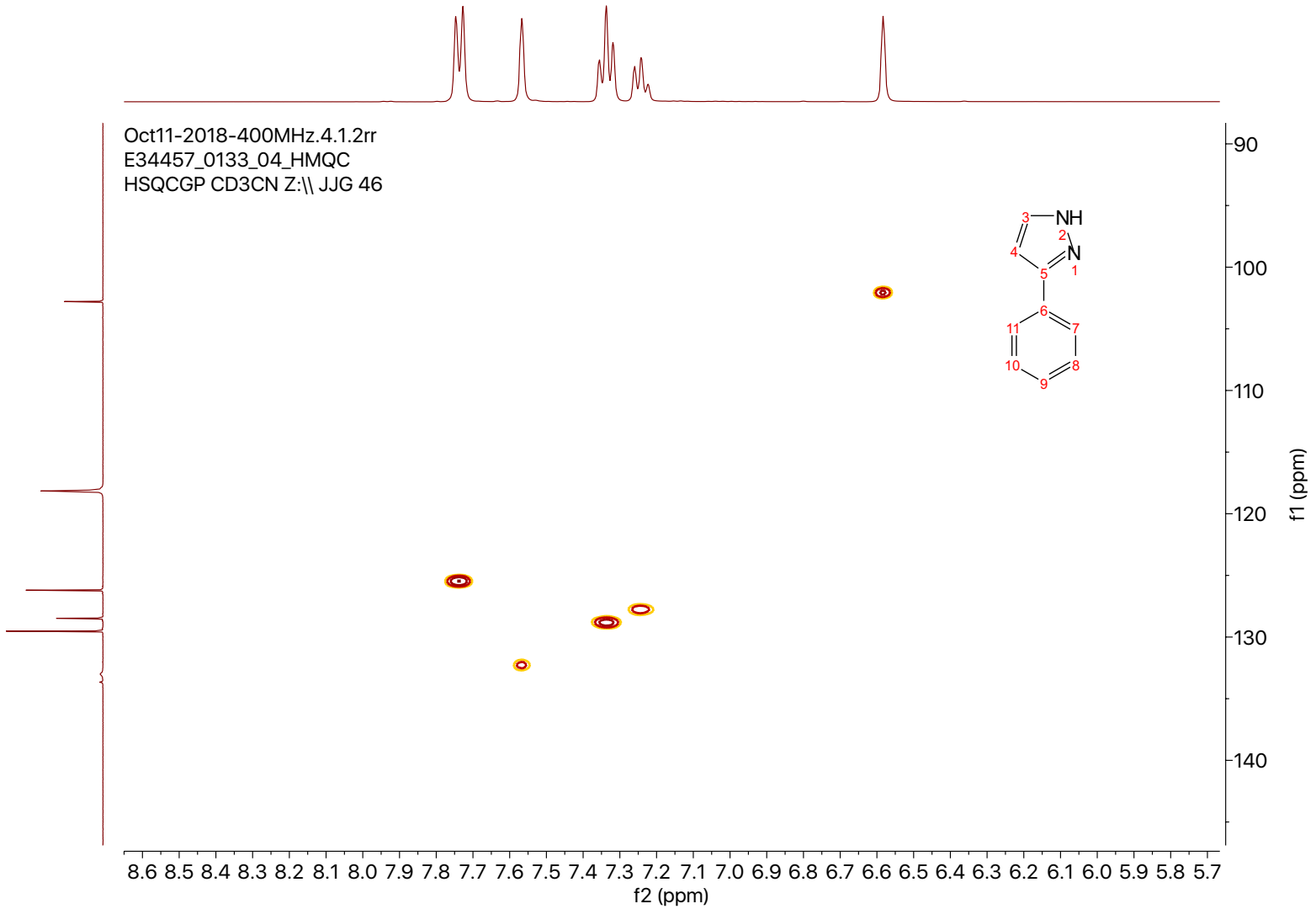
Oct10-2018.7.fid
E34457_0133_02_1H
A_PROTON CD3CN {Z:\Topspin} JJG 18



SI Figure 57: ^{1}H NMR spectrum of 3-phenyl-1H-pyrazole in CD_3CN from HDF of 3-(2-fluorophenyl)-1H-pyrazole (4b).



SI Figure 58: ^{13}C NMR spectrum of 3-phenyl-1H-pyrazole in CD_3CN from HDF of 3-(2-fluorophenyl)-1H-pyrazole (4b).



SI Figure 59: HSQC spectrum of 3-phenyl-1H-pyrazole in CD_3CN from HDF of 3-(2-fluorophenyl)-1H-pyrazole (**4b**).

Jan28-2019-400MHz.6.fid
E34457_0127_HSQC_1H
PROTON CDCl3 Z:\\ JJG 23

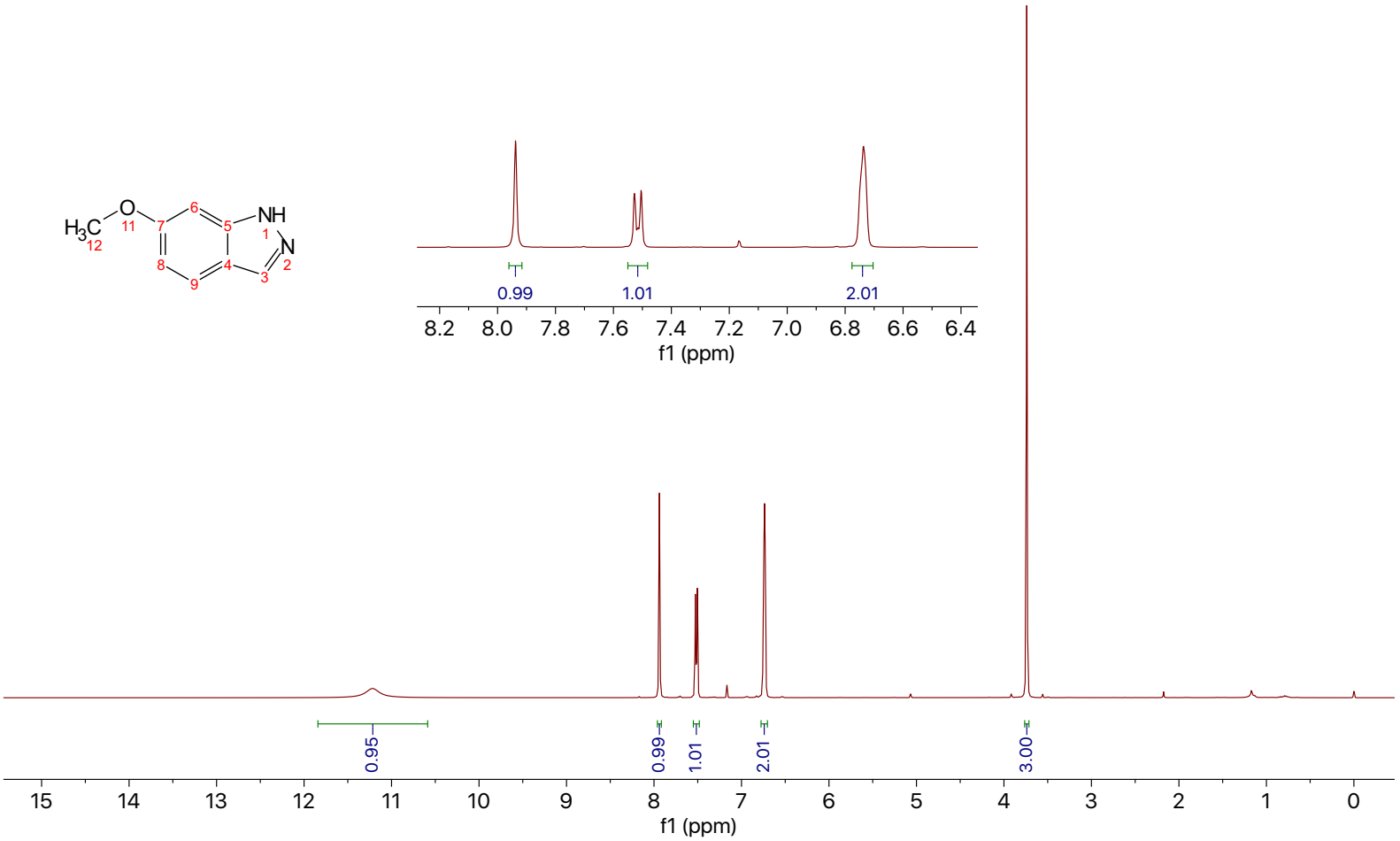
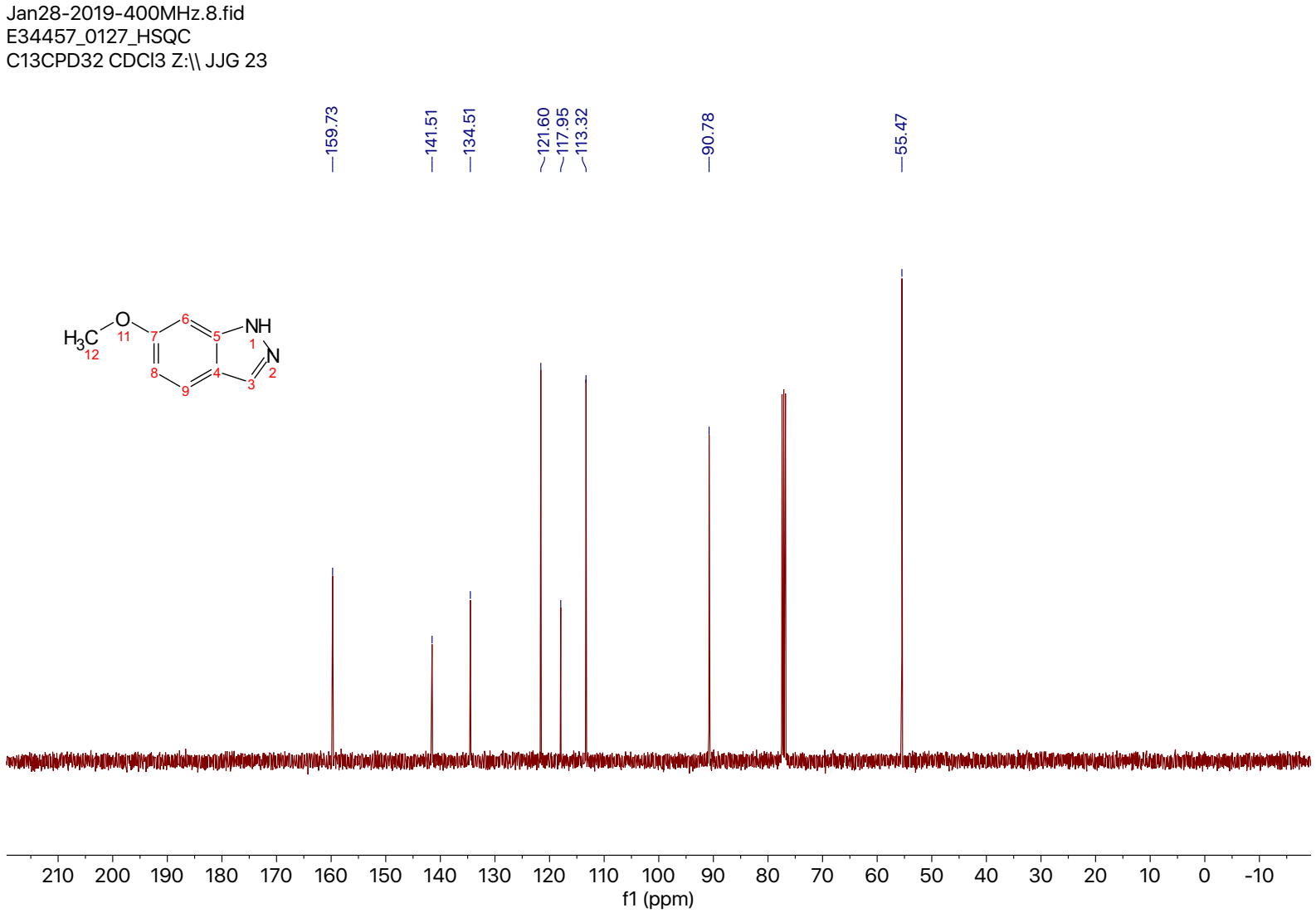
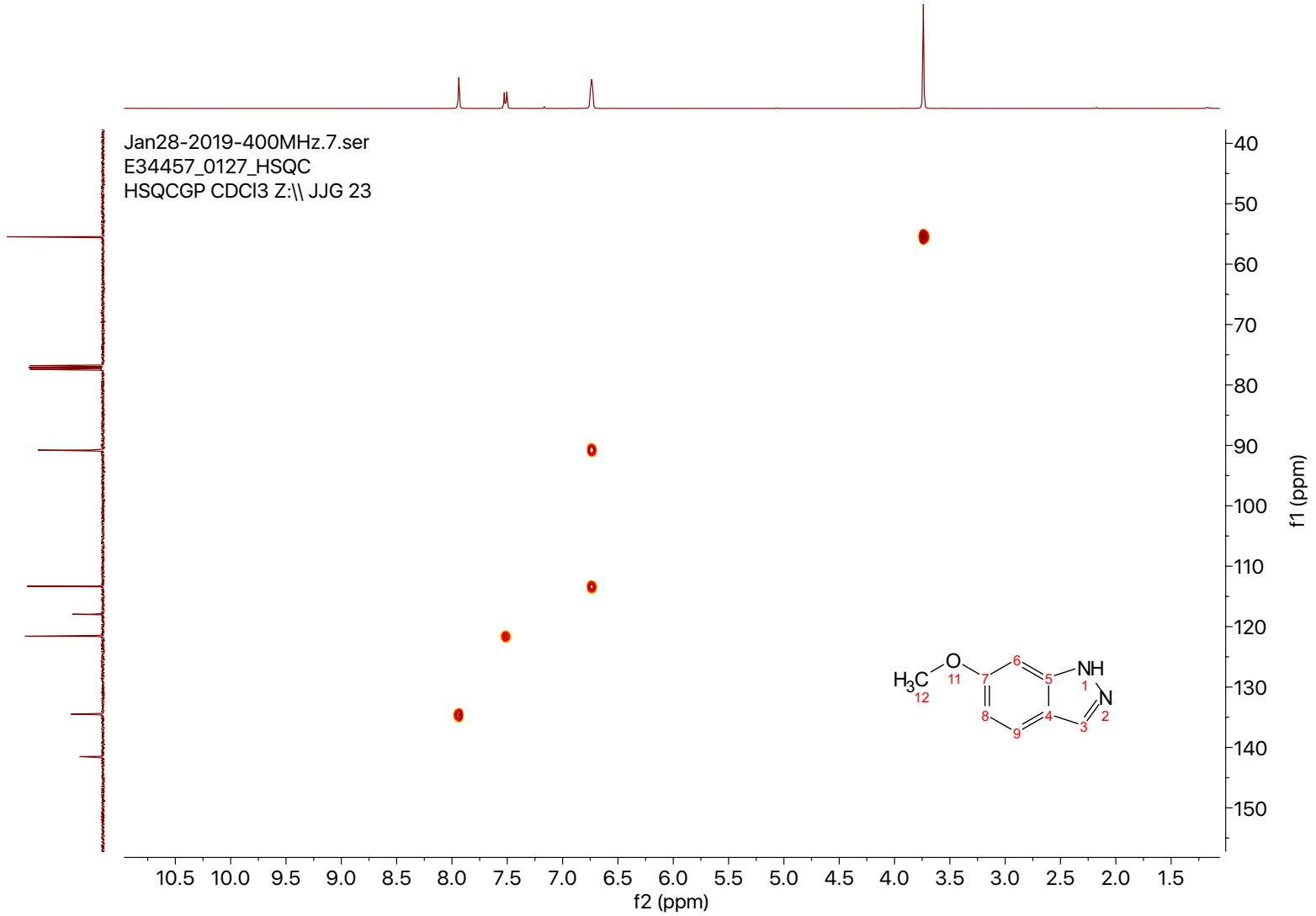


Figure 60: ^{1}H NMR spectrum of 6-methoxy-1H-indazole in $CDCl_3$ from HDF of 7-fluoro-6-methoxy-1H-indazole (5).

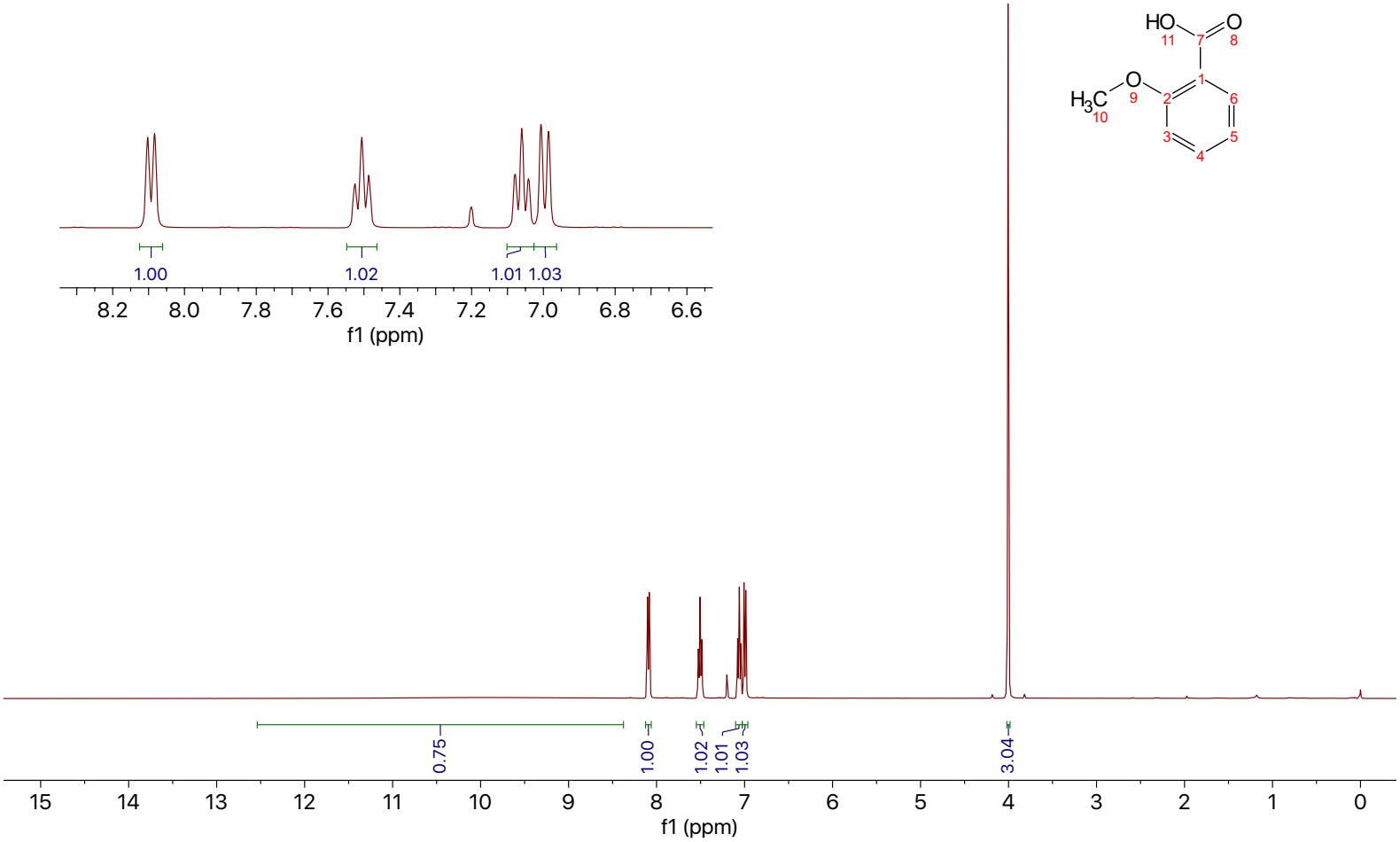


SI Figure 61: ^{13}C NMR spectrum of 6-methoxy-1H-indazole in $CDCl_3$ from HDF of 7-fluoro-6-methoxy-1H-indazole (5).

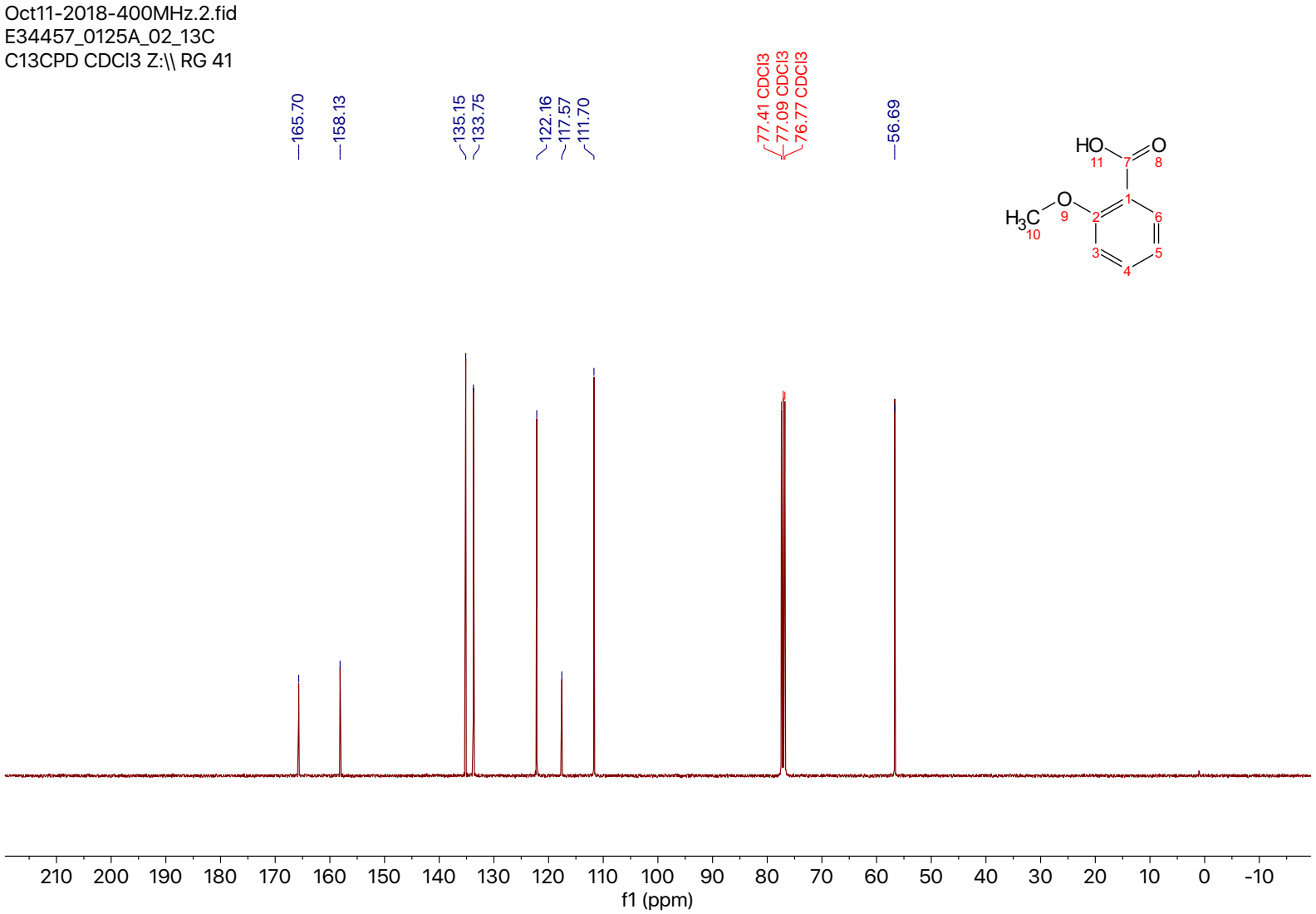


SI Figure 62: HSQC NMR spectrum of 6-methoxy-1H-indazole in $CDCl_3$ from HDF of 7-fluoro-6-methoxy-1H-indazole (5).

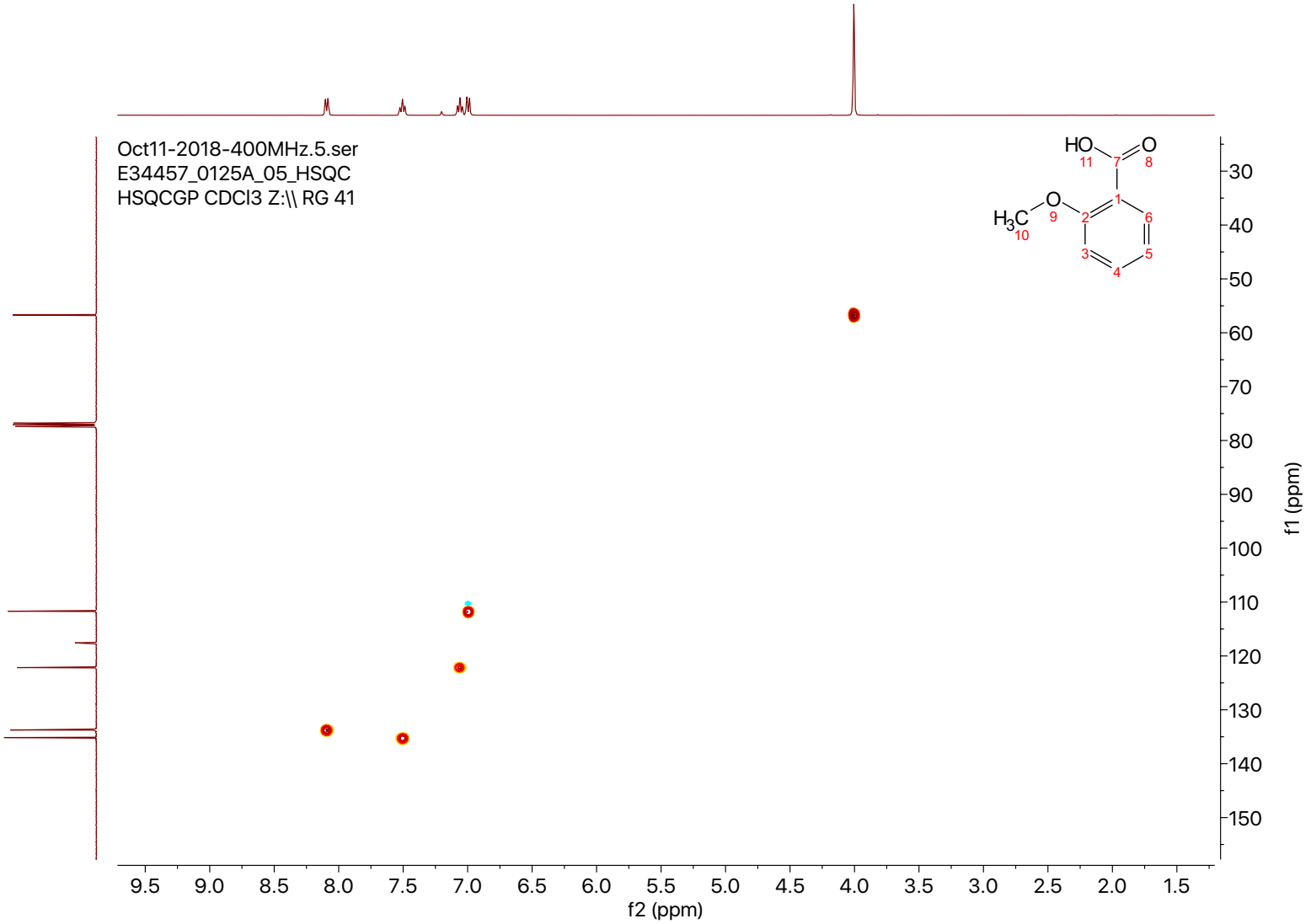
Oct11-2018-400MHz.4.fid
E34457_0125A_04_1H
PROTON CDCl3 Z:\\ RG 41



SI Figure 63: ^{1}H NMR spectrum of 2-methoxy-benzoic acid in $CDCl_3$ from HDF of 5-fluoro-2-methoxybenzoic acid (6).

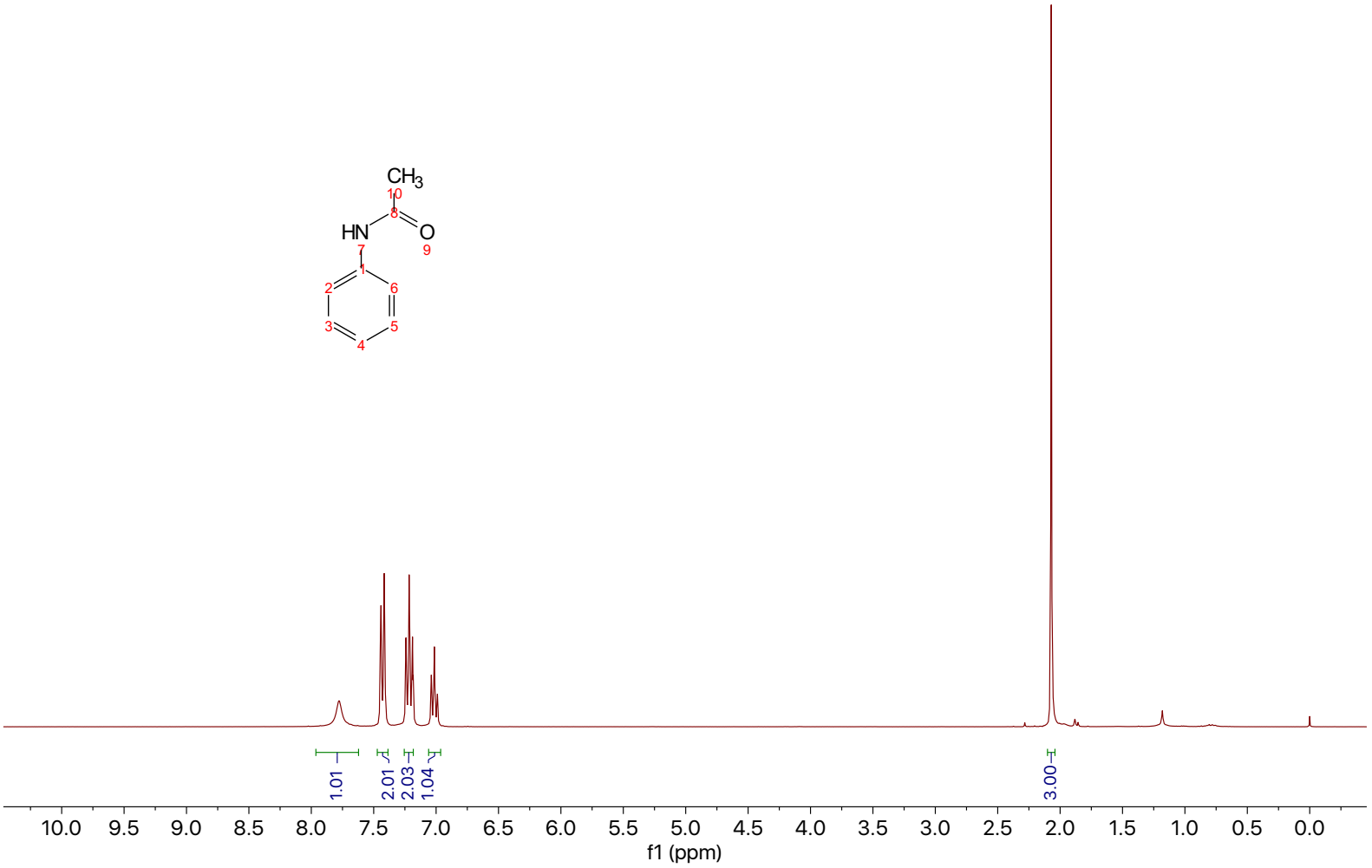


SI Figure 64: ^{13}C NMR spectrum of 2-methoxy-benzoic acid in $CDCl_3$ from HDF of 5-fluoro-2-methoxybenzoic acid (6).



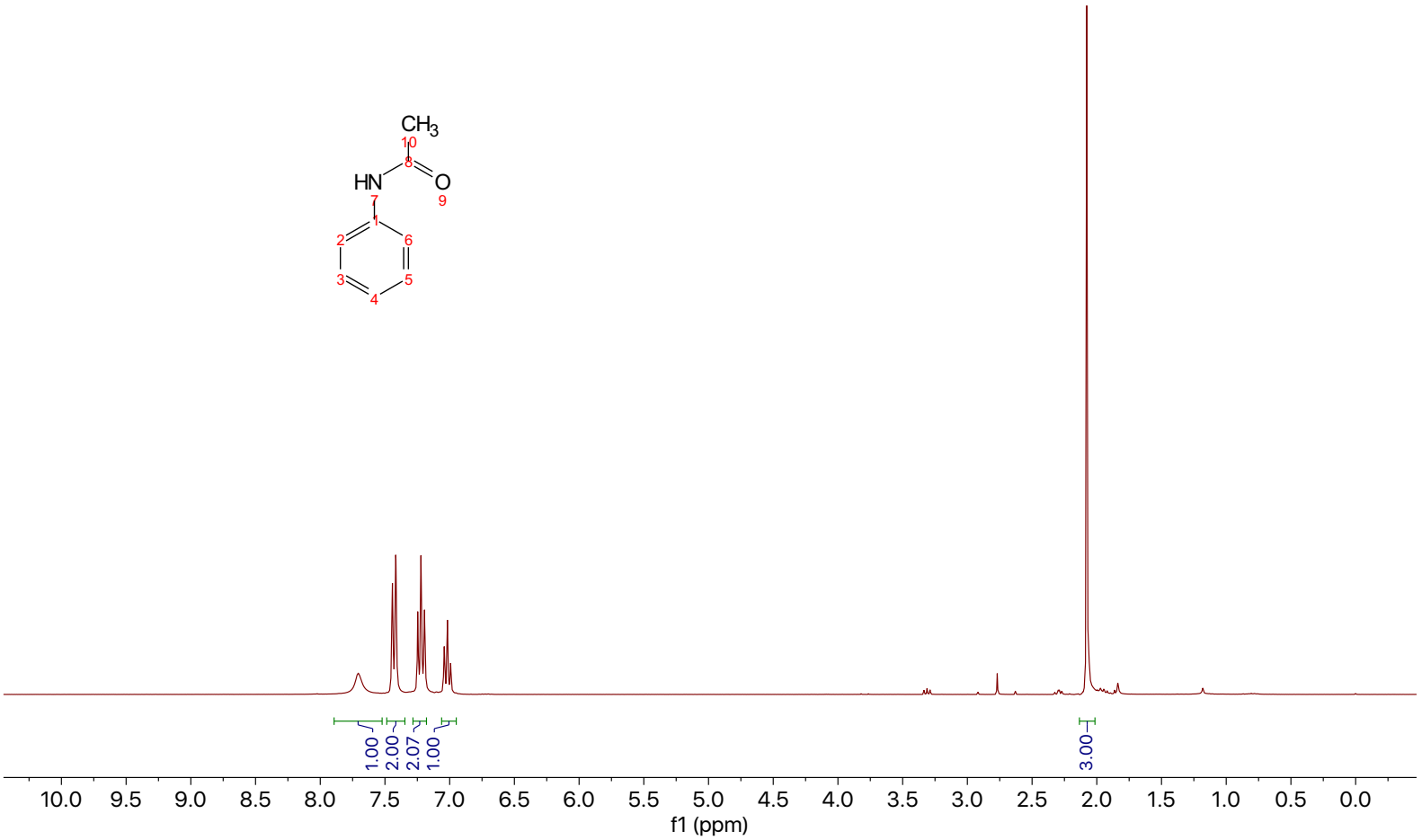
SI Figure 65: HSQC spectrum of 2-methoxy-benzoic acid in $CDCl_3$ from HDF of 5-fluoro-2-methoxybenzoic acid (6).

Jan17-2019.1.fid
E34456_0258_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 59

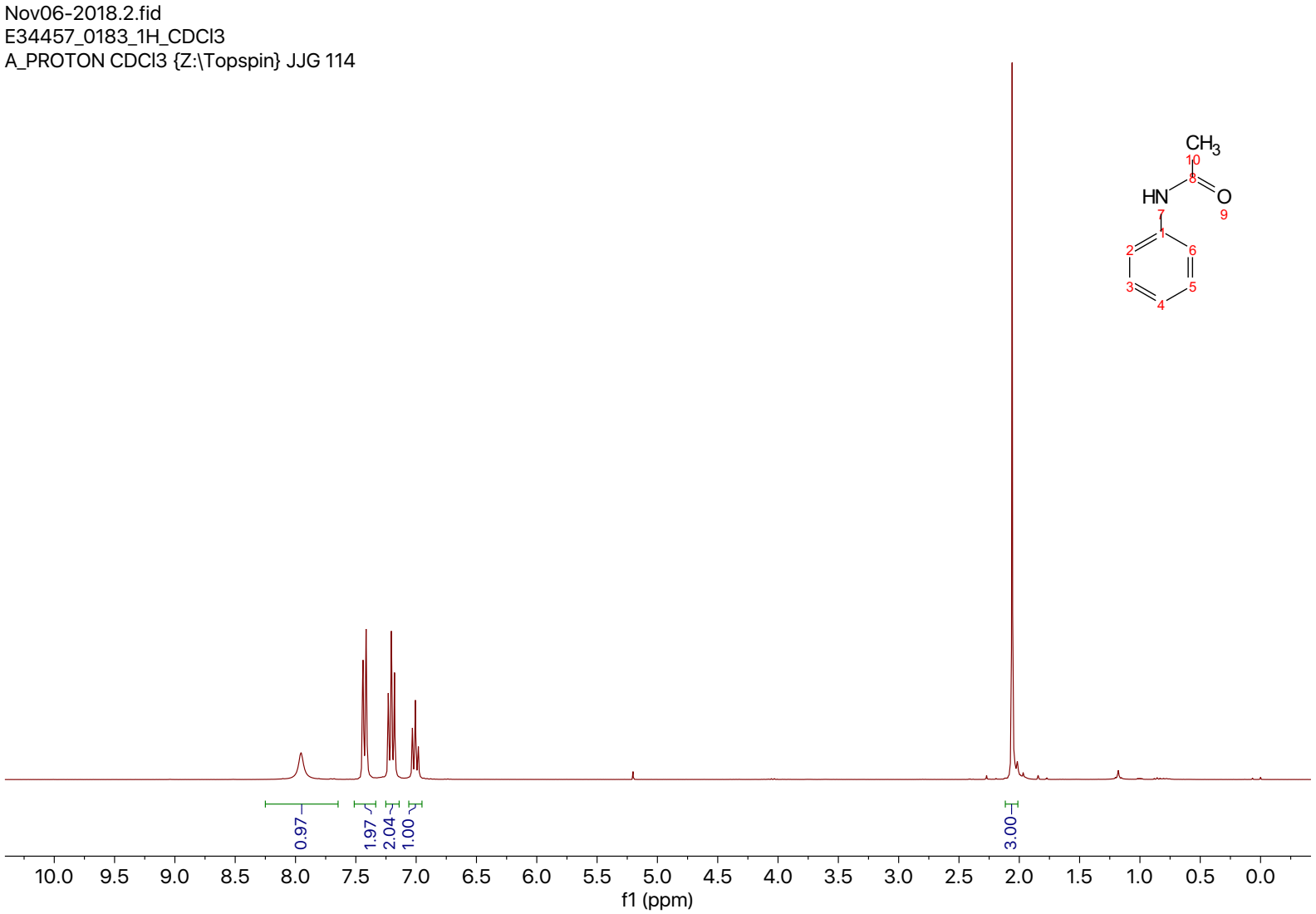


SI Figure 66: ^{1}H NMR spectrum of *N*-phenylacetamide in $CDCl_3$ from HDF *N*-(2-fluorophenyl)acetamide (7a).

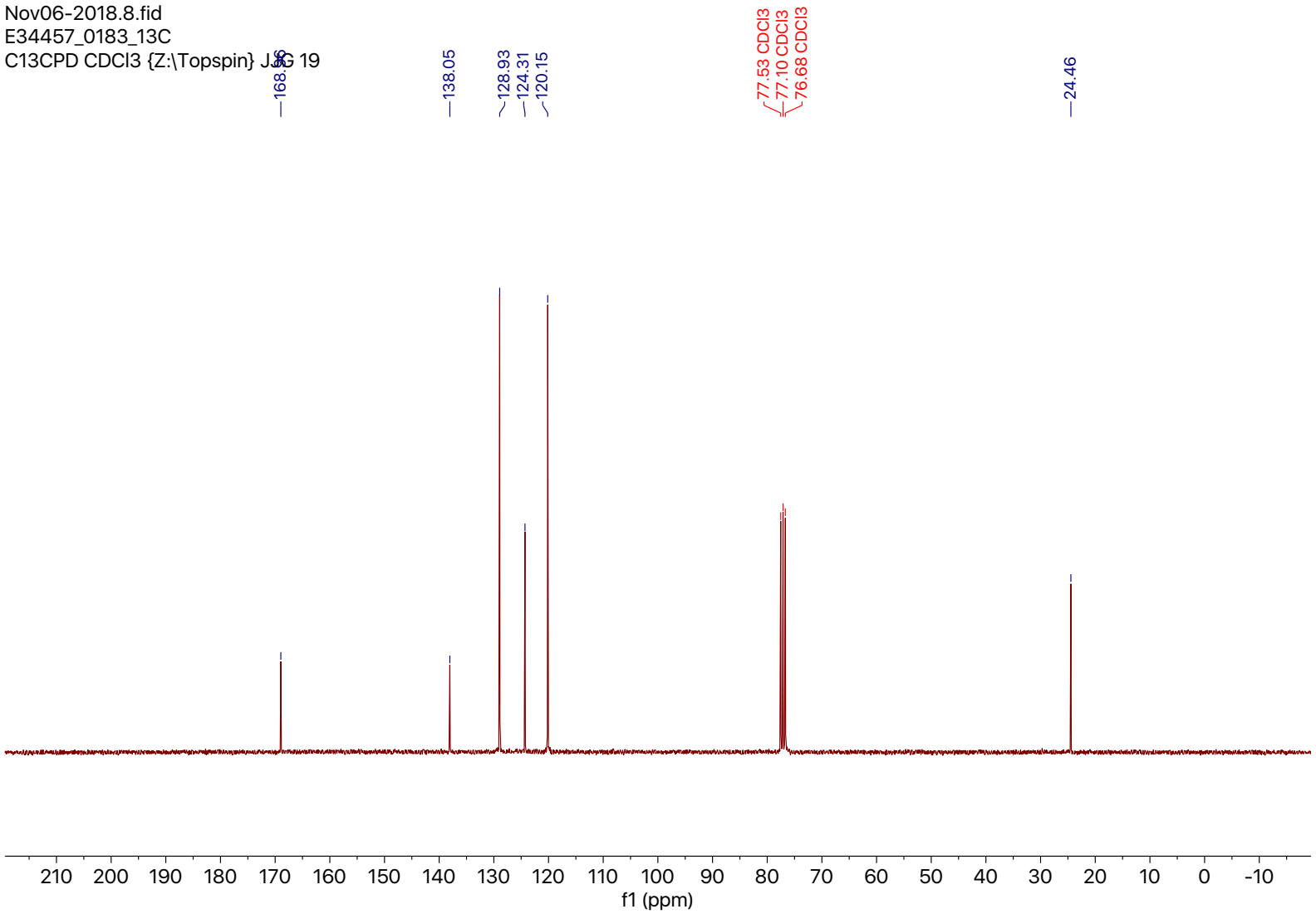
Jan18-2019.1.fid
E34457_0257_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 7



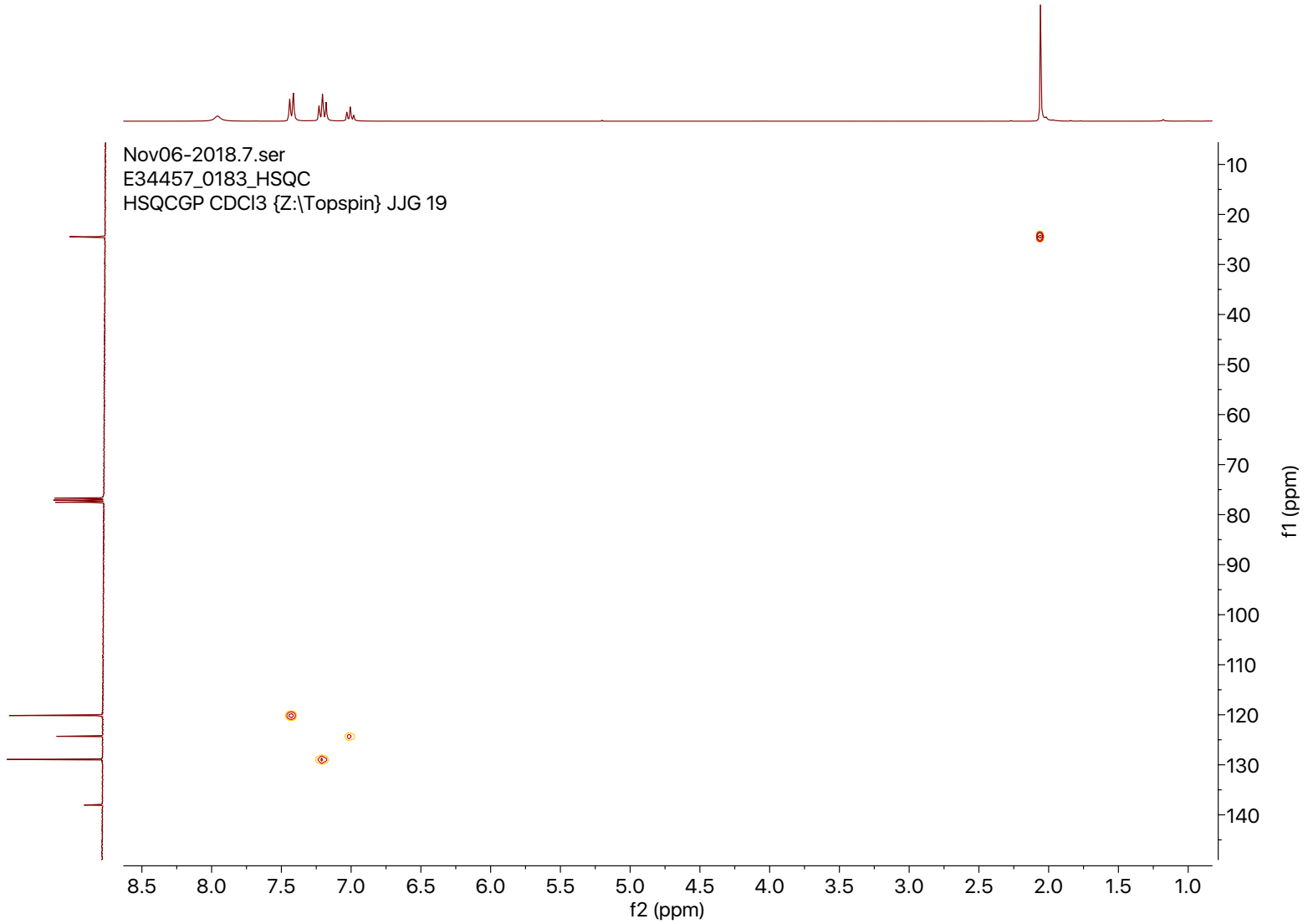
SI Figure 67: ^{1}H NMR spectrum of *N*-phenylacetamide in $CDCl_3$ from HDF *N*-(3-fluorophenyl)acetamide (7b).



SI Figure 68: ^{1}H NMR spectrum of *N*-phenylacetamide in $CDCl_3$ from HDF *N*-(4-fluorophenyl)acetamide (7c).

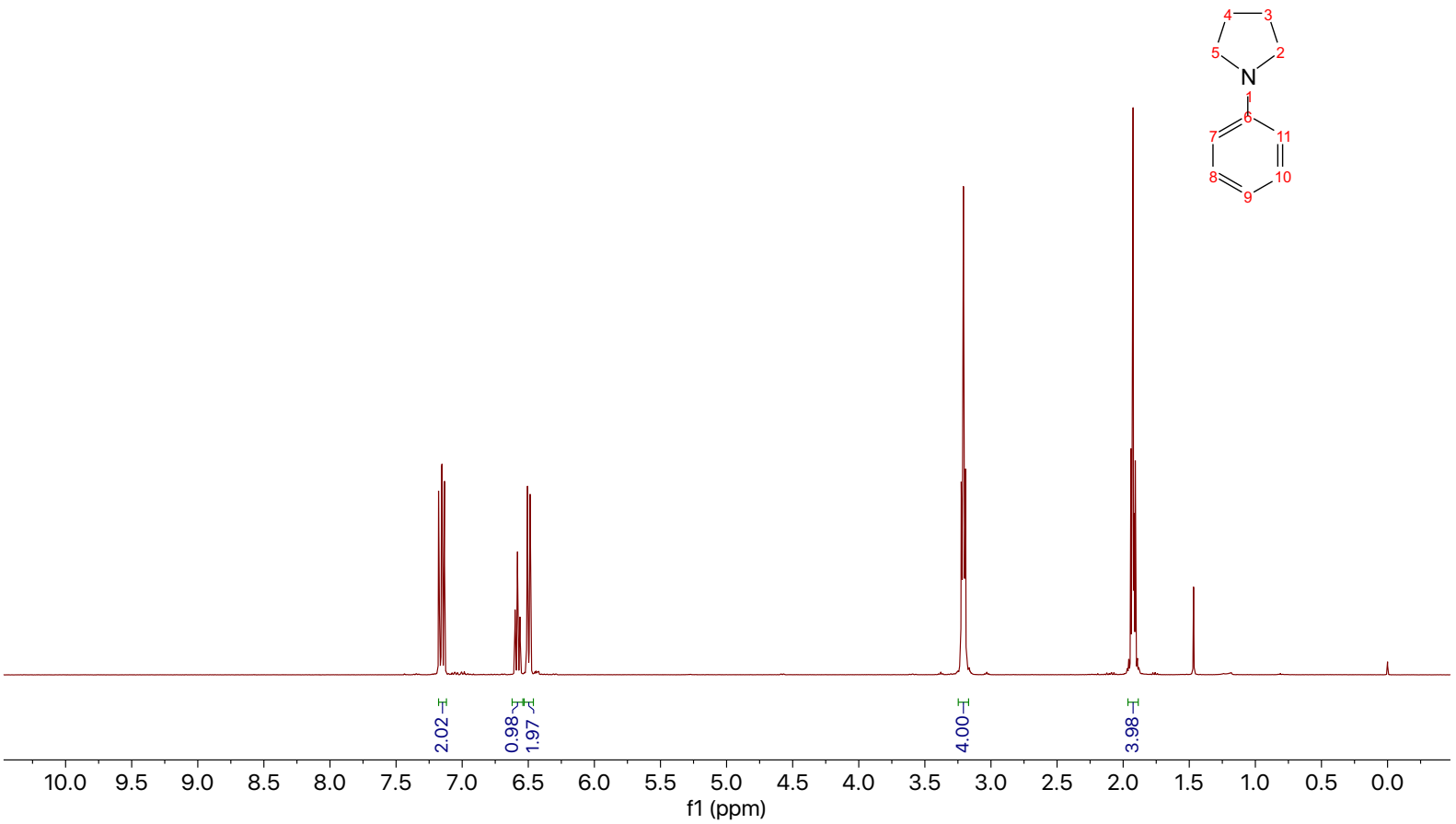


SI Figure 69: ^{13}C NMR spectrum of *N*-phenylacetamide in $CDCl_3$ from HDF *N*-(4-fluorophenyl)acetamide (7c).



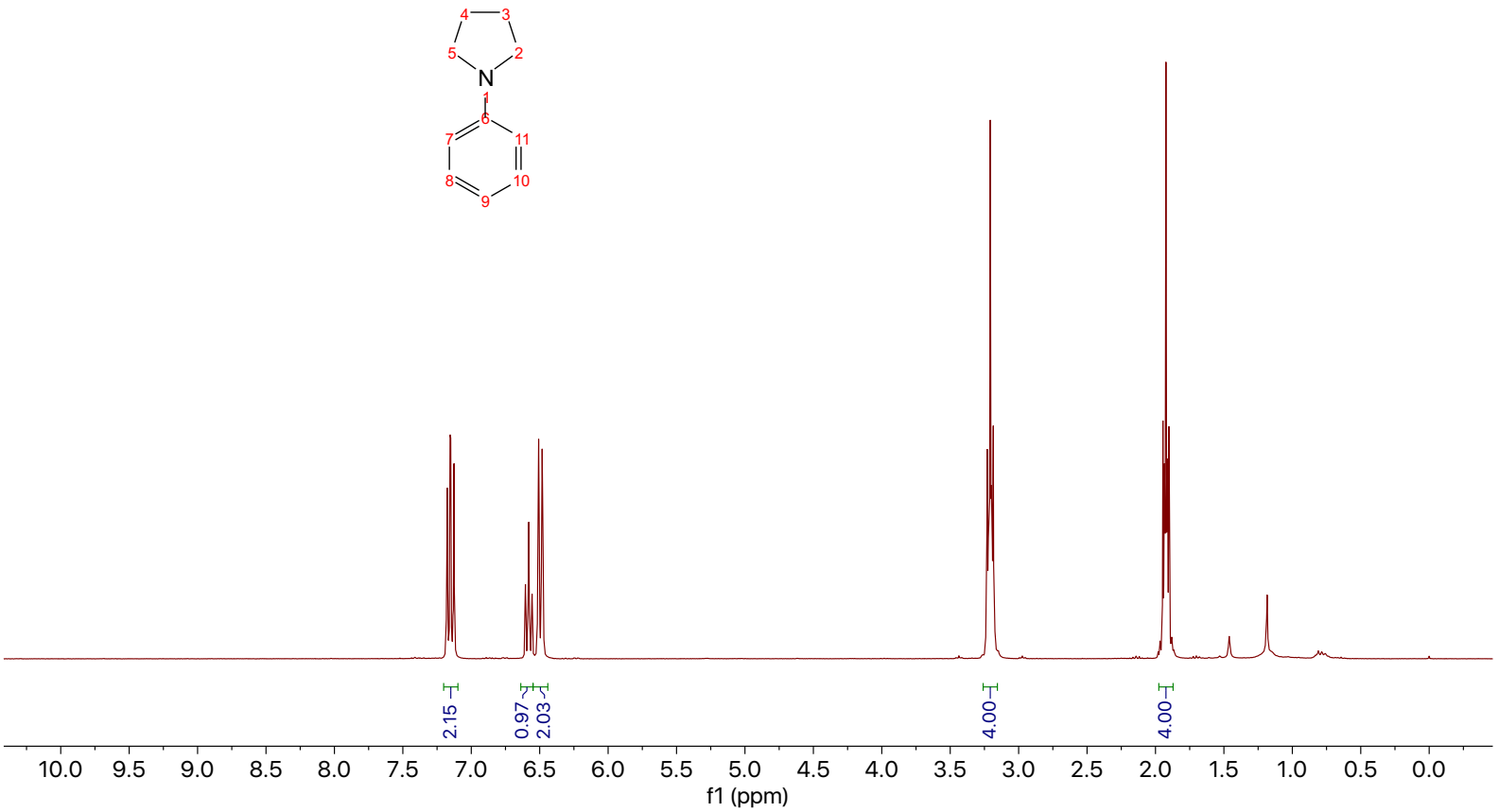
SI Figure 70: HSQC spectrum of *N*-phenylacetamide in $CDCl_3$ from HDF *N*-(4-fluorophenyl)acetamide (7c).

Jan25-2019-400MHz.1.fid
E34457_0256_1H
A_PROTON CDCl3 Z:\\ JJG 1



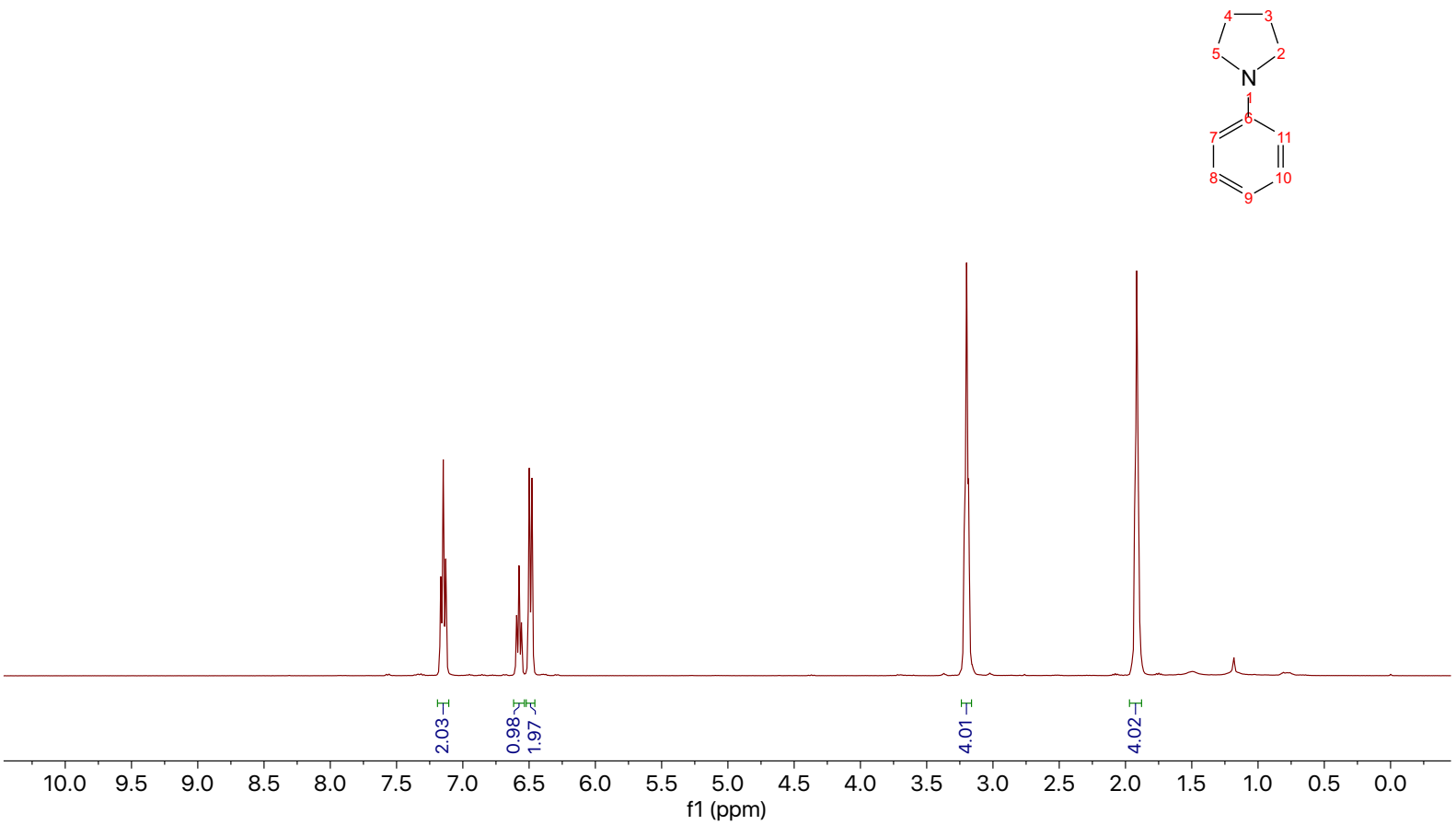
SI Figure 71: ^{1}H NMR spectrum of 1-phenylpyrrolidine in $CDCl_3$ from HDF of 1-(2-fluorophenyl)pyrrolidine (8a).

Jan17-2019.2.fid
E34456_0255_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 60

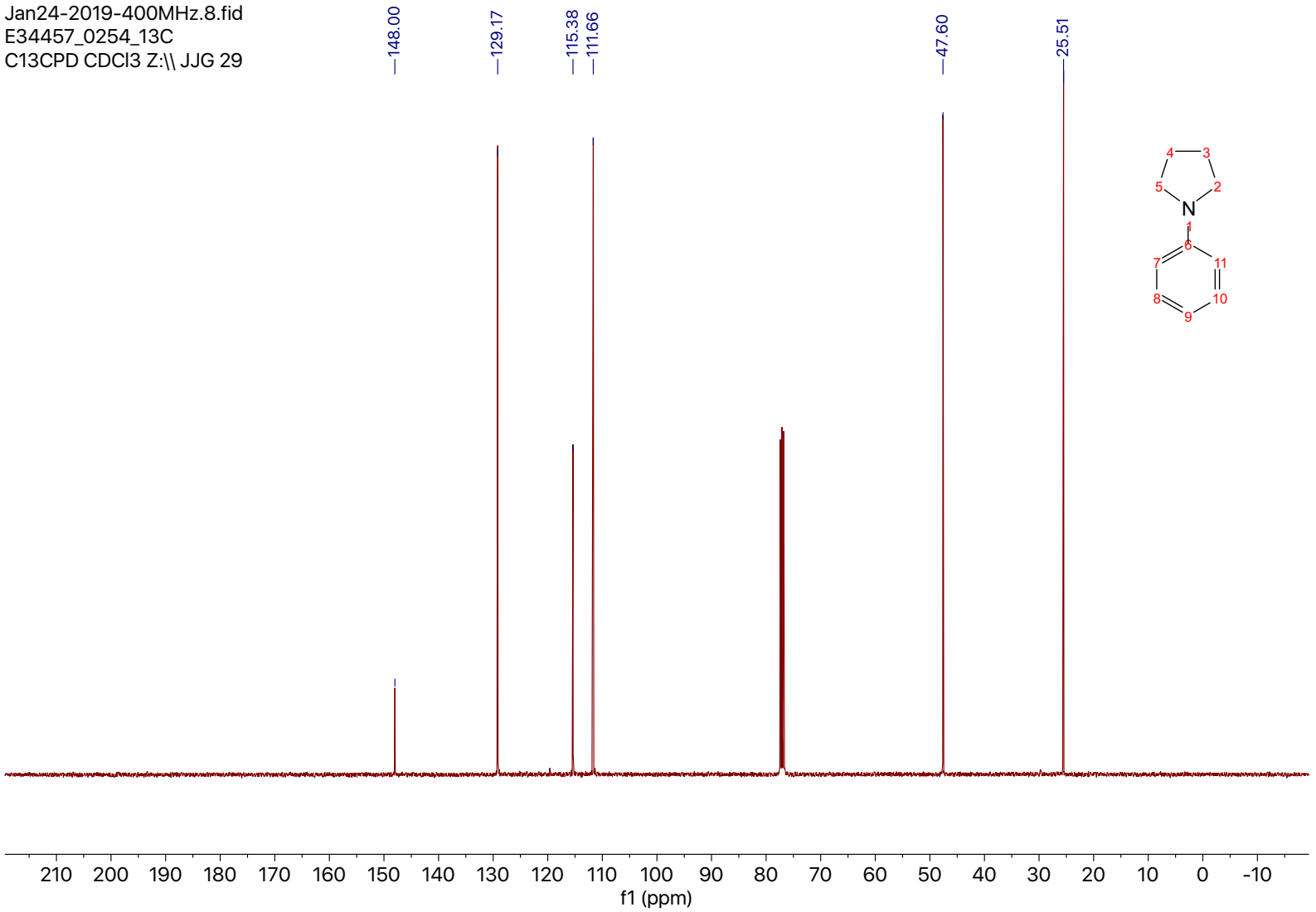


SI Figure 72: ^{1}H NMR spectrum of 1-phenylpyrrolidine in $CDCl_3$ from HDF of 1-(3-fluorophenyl)pyrrolidine (8b).

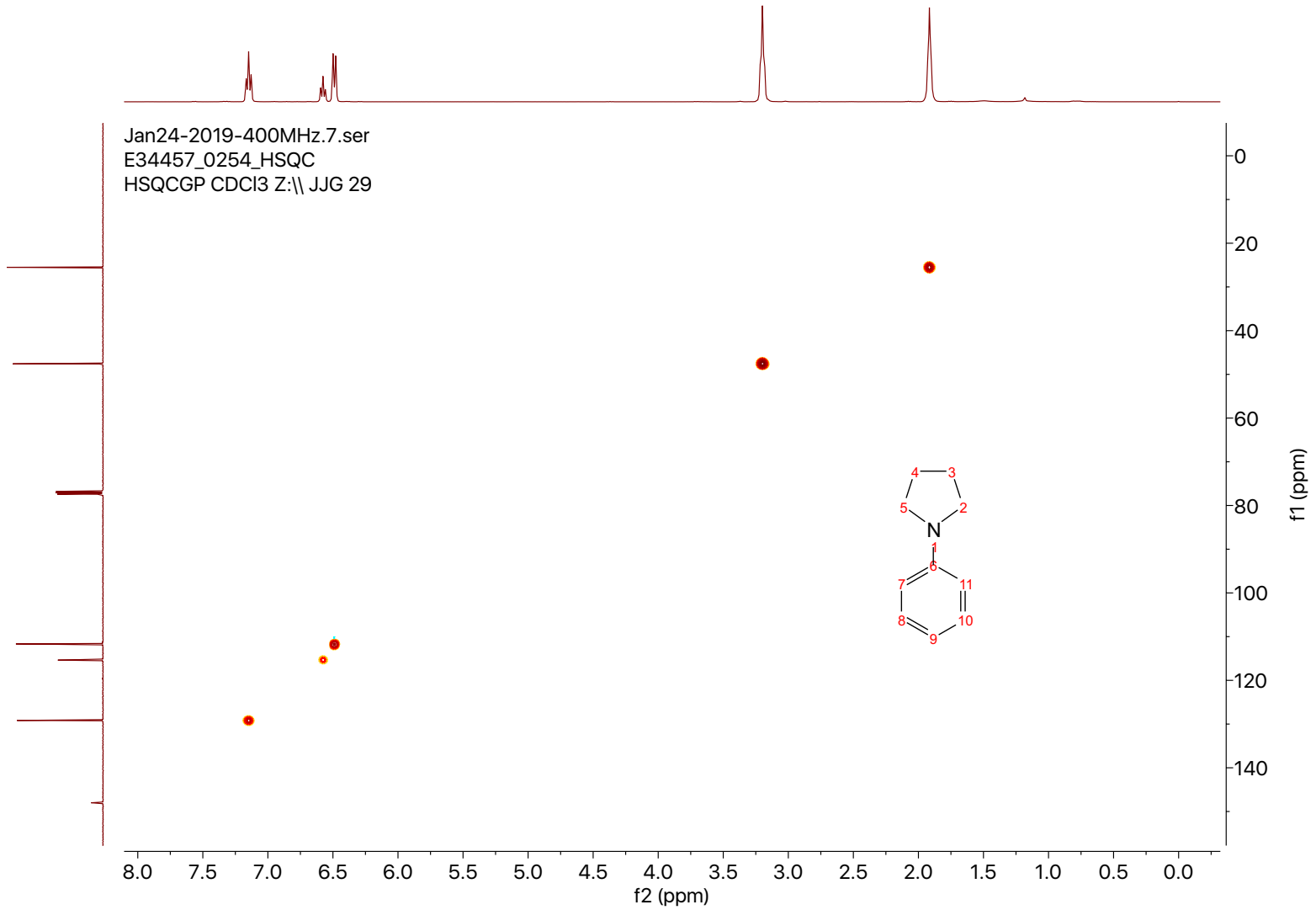
Jan24-2019-400MHz.6.fid
E34457_0254_HSQC_1H
PROTON CDCl3 Z:\\ JJG 29



SI Figure 73: ^{1}H NMR spectrum of 1-phenylpyrrolidine in $CDCl_3$ from HDF of 1-(4-fluorophenyl)pyrrolidine (8c).

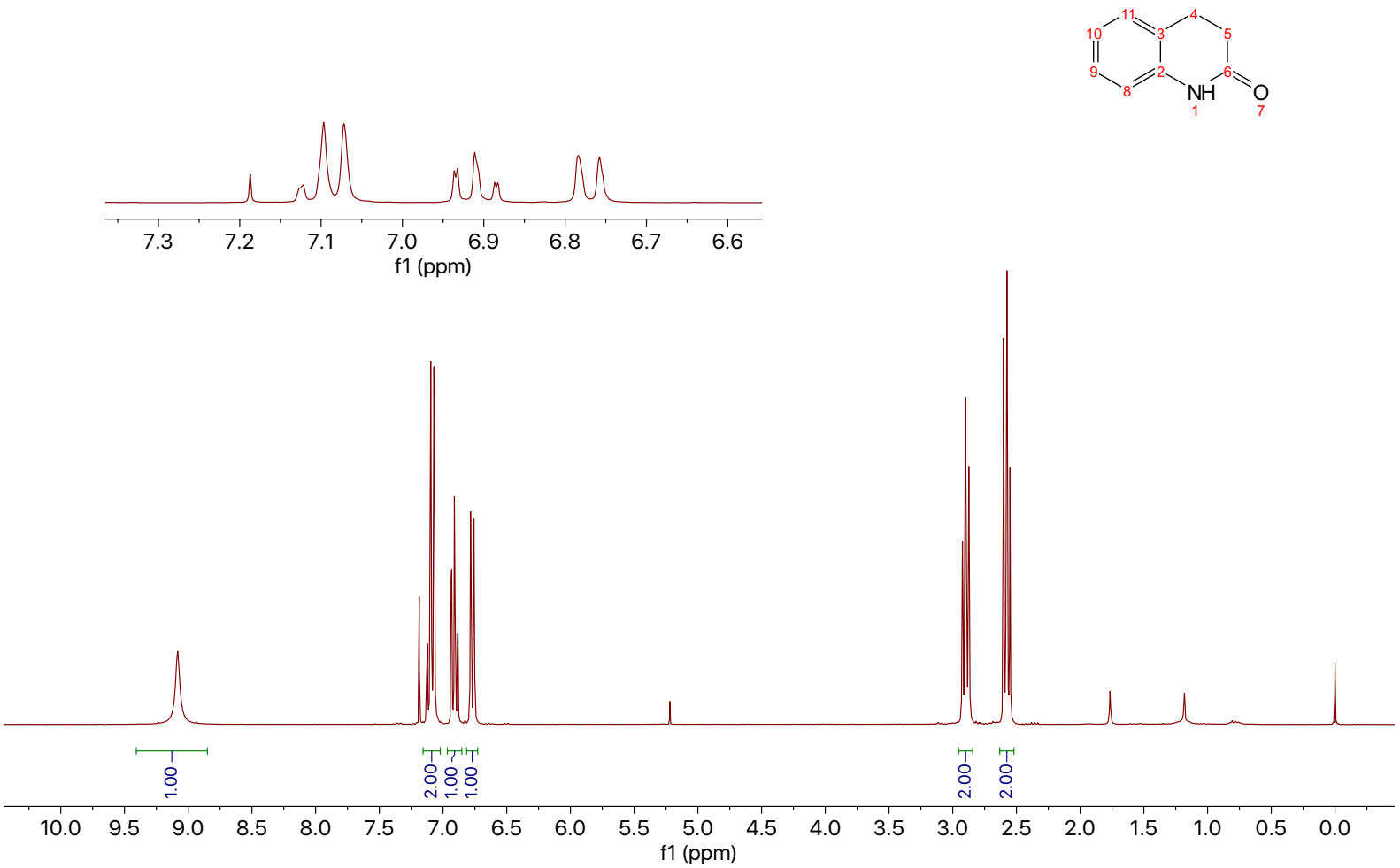


SI Figure 74: ^{13}C NMR spectrum of 1-phenylpyrrolidine in $CDCl_3$ from HDF of 1-(4-fluorophenyl)pyrrolidine (8c).

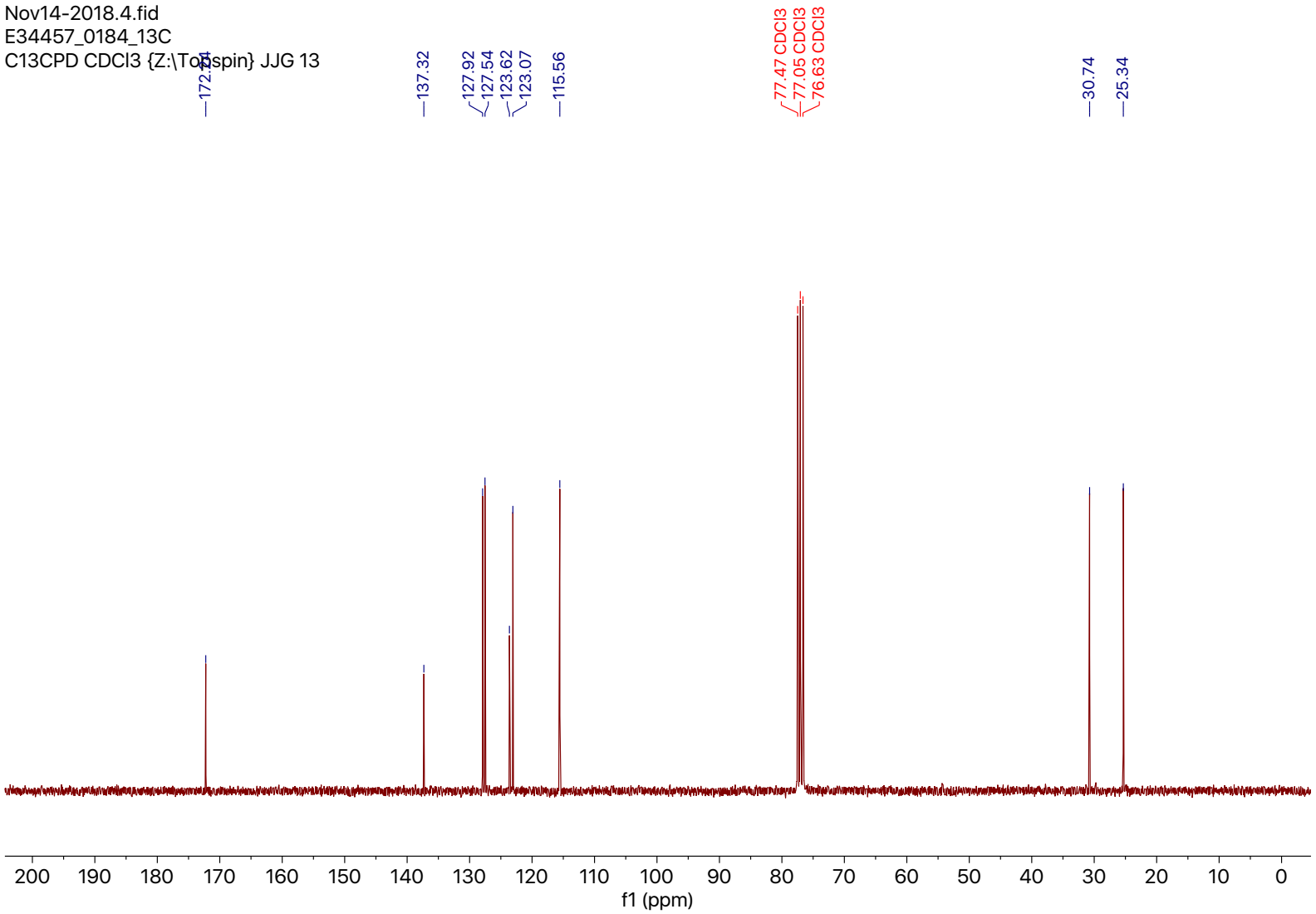


SI Figure 75: HSQC spectrum of 1-phenylpyrrolidine in $CDCl_3$ from HDF of 1-(4-fluorophenyl)pyrrolidine (8c).

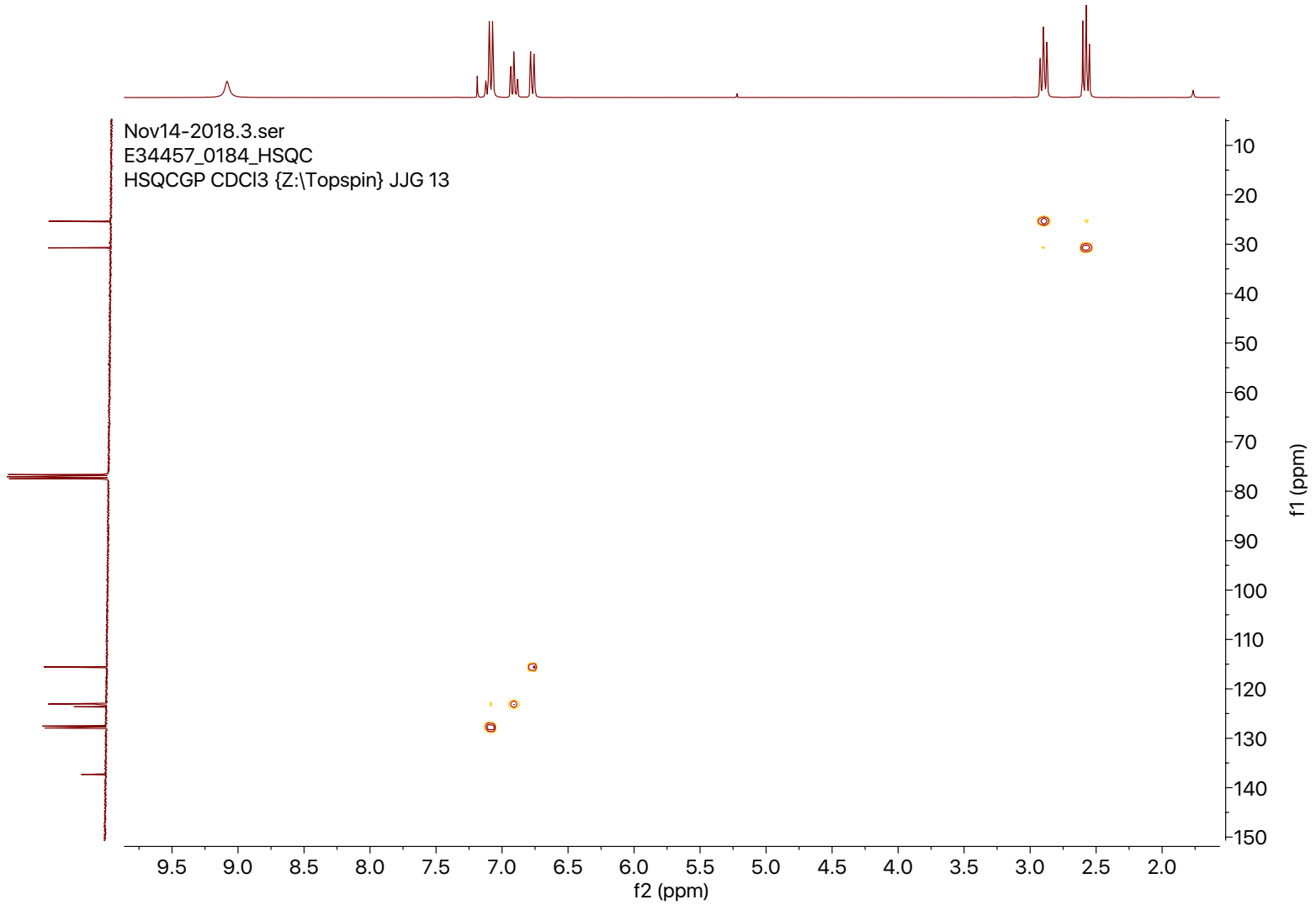
Nov14-2018.1.fid
E34457_0184_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 13



SI Figure 76: ^{1}H NMR spectrum of 3,4-dihydroquinolin-2(1H)-one in $CDCl_3$ from HDF of 6-fluoro-3,4-dihydroquinolin-2(1H)-one (9).

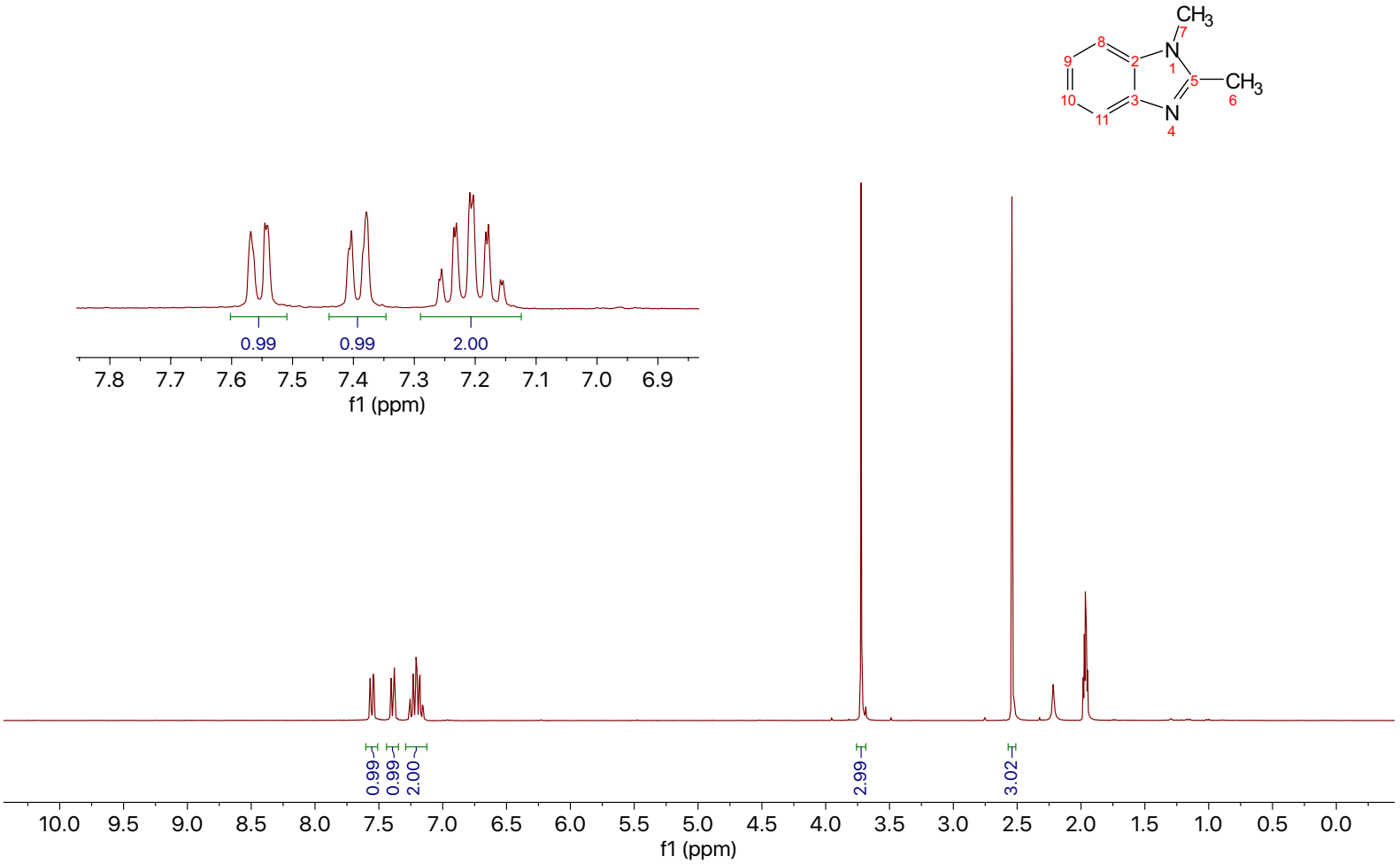


SI Figure 77: ^{13}C NMR spectrum of 3,4-dihydroquinolin-2(1H)-one in $CDCl_3$ from HDF of 6-fluoro-3,4-dihydroquinolin-2(1H)-one (9).

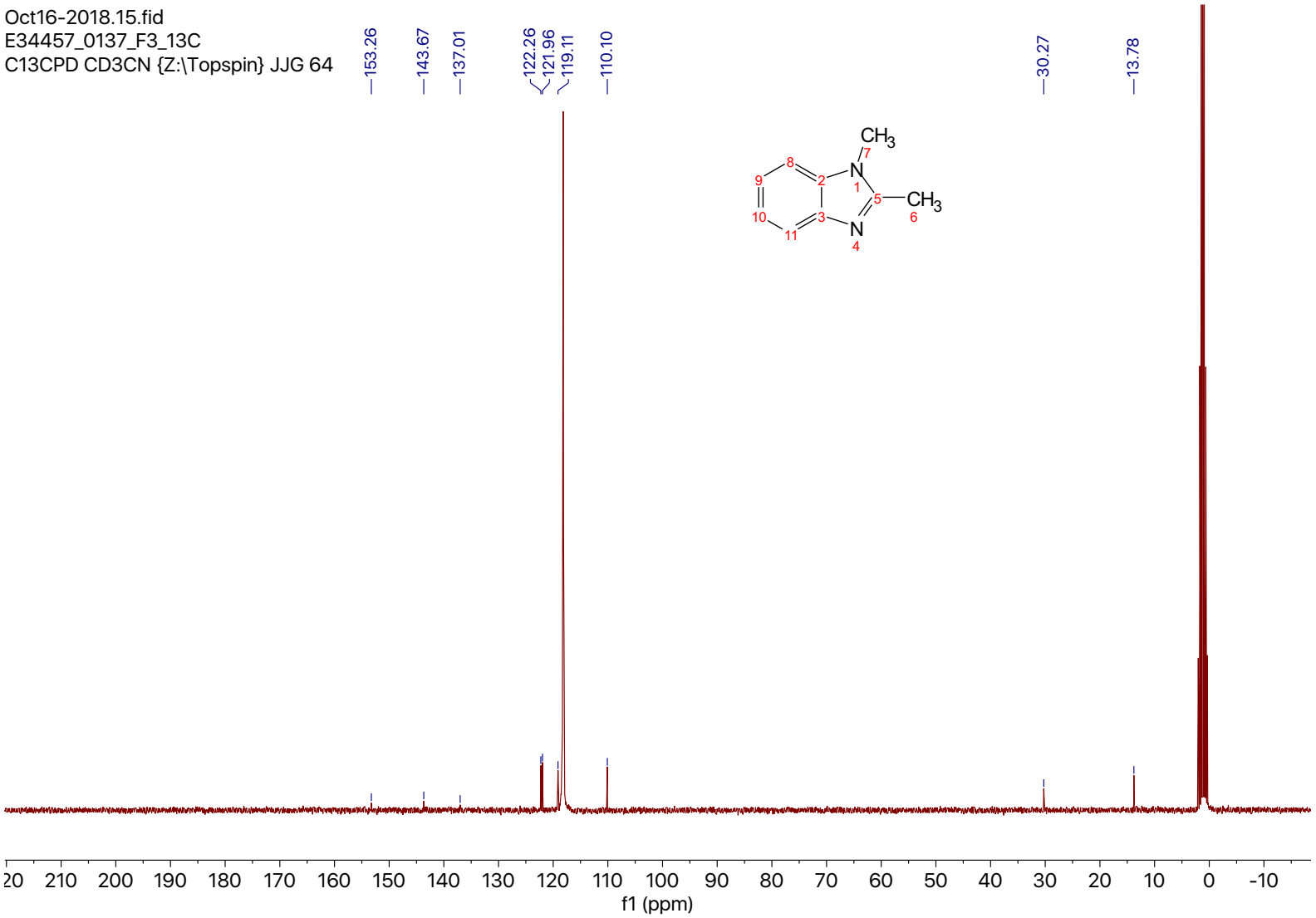


SI Figure 78: HSQC spectrum of 3,4-dihydroquinolin-2(1H)-one in $CDCl_3$ from HDF of 6-fluoro-3,4-dihydroquinolin-2(1H)-one (9).

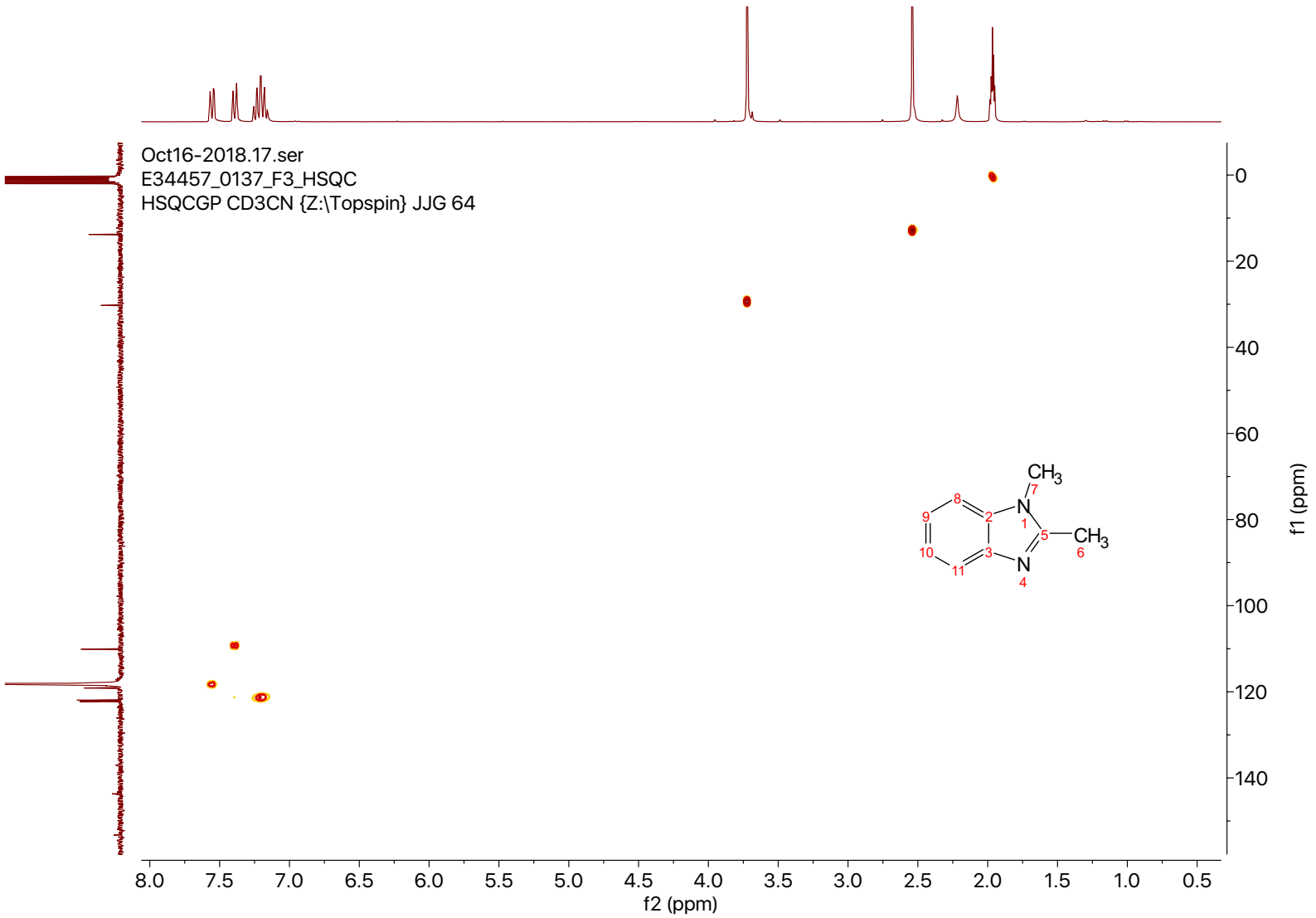
Oct16-2018.16.fid
E34457_0137_F3_HSQC_1H
PROTON CD3CN {Z:\Topspin} JJG 64



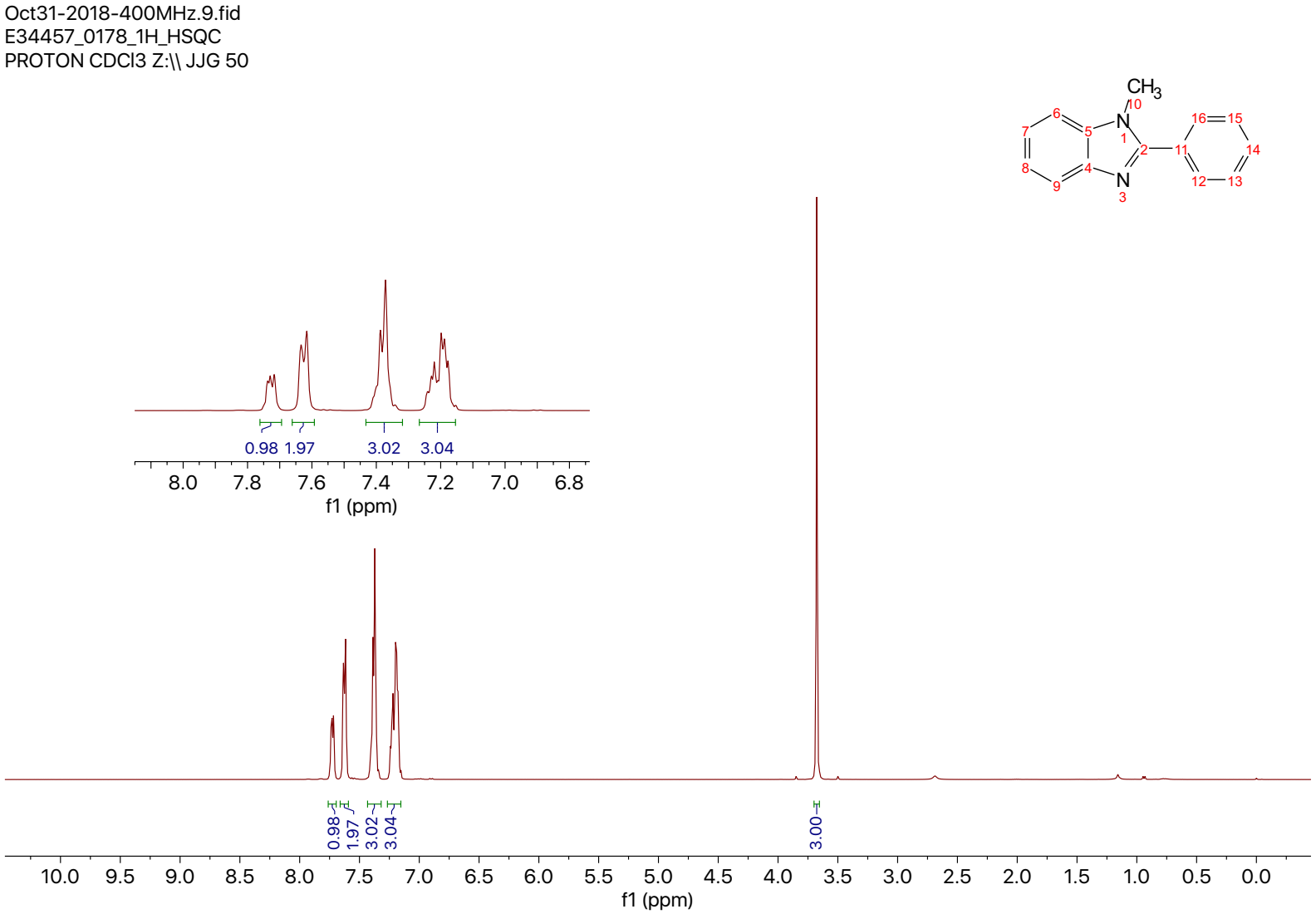
SI Figure 79: ^{1}H NMR spectrum of 1,2-dimethyl-1H-benzo[d]imidazole in $CDCl_3$ from HDF of 5-fluoro-1,2-dimethyl-1H-benzo[d]imidazole (10).



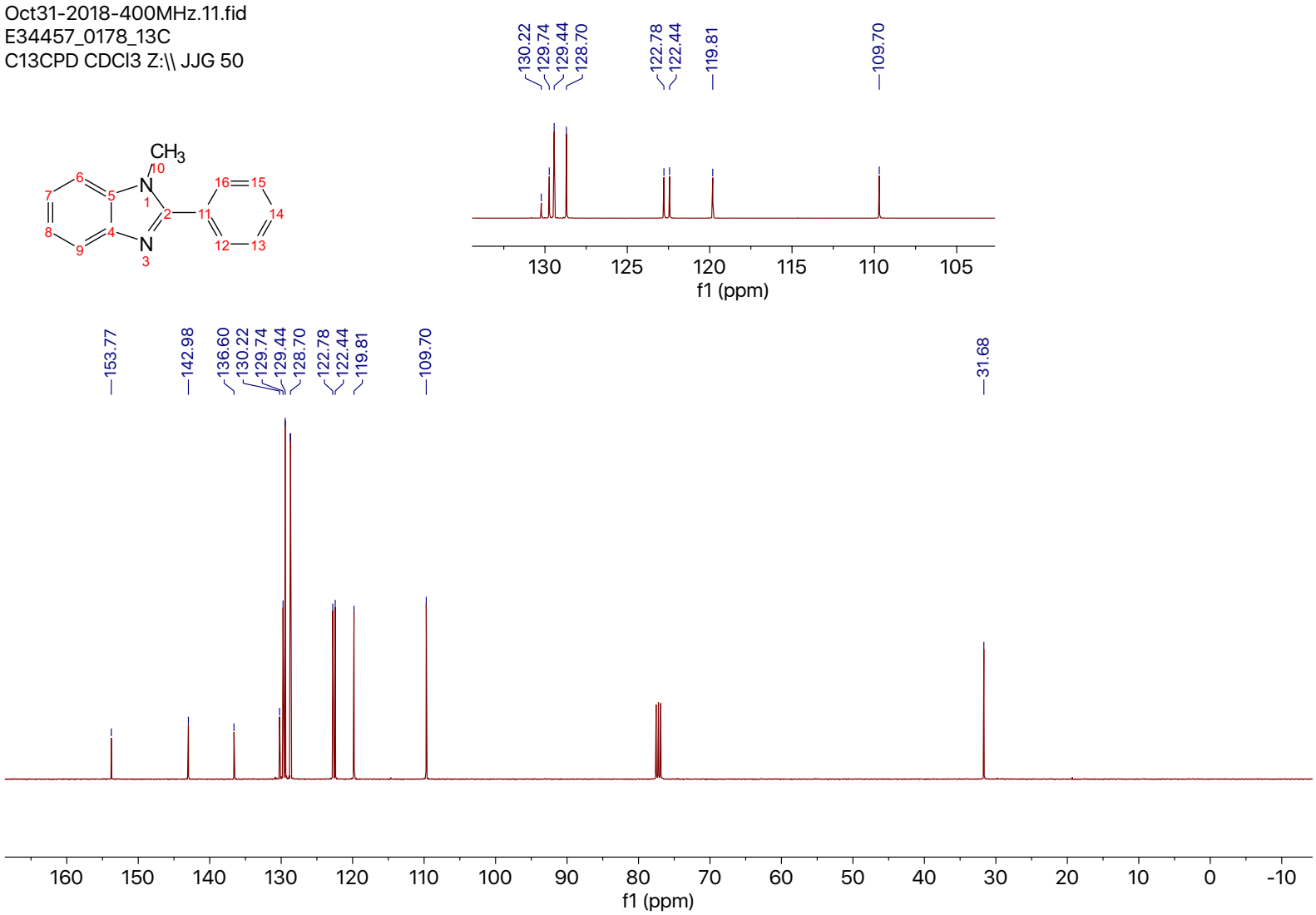
SI Figure 80: ^{13}C NMR spectrum of 1,2-dimethyl-1H-benzo[d]imidazole in $CDCl_3$ from HDF of 5-fluoro-1,2-dimethyl-1H-benzo[d]imidazole (10).



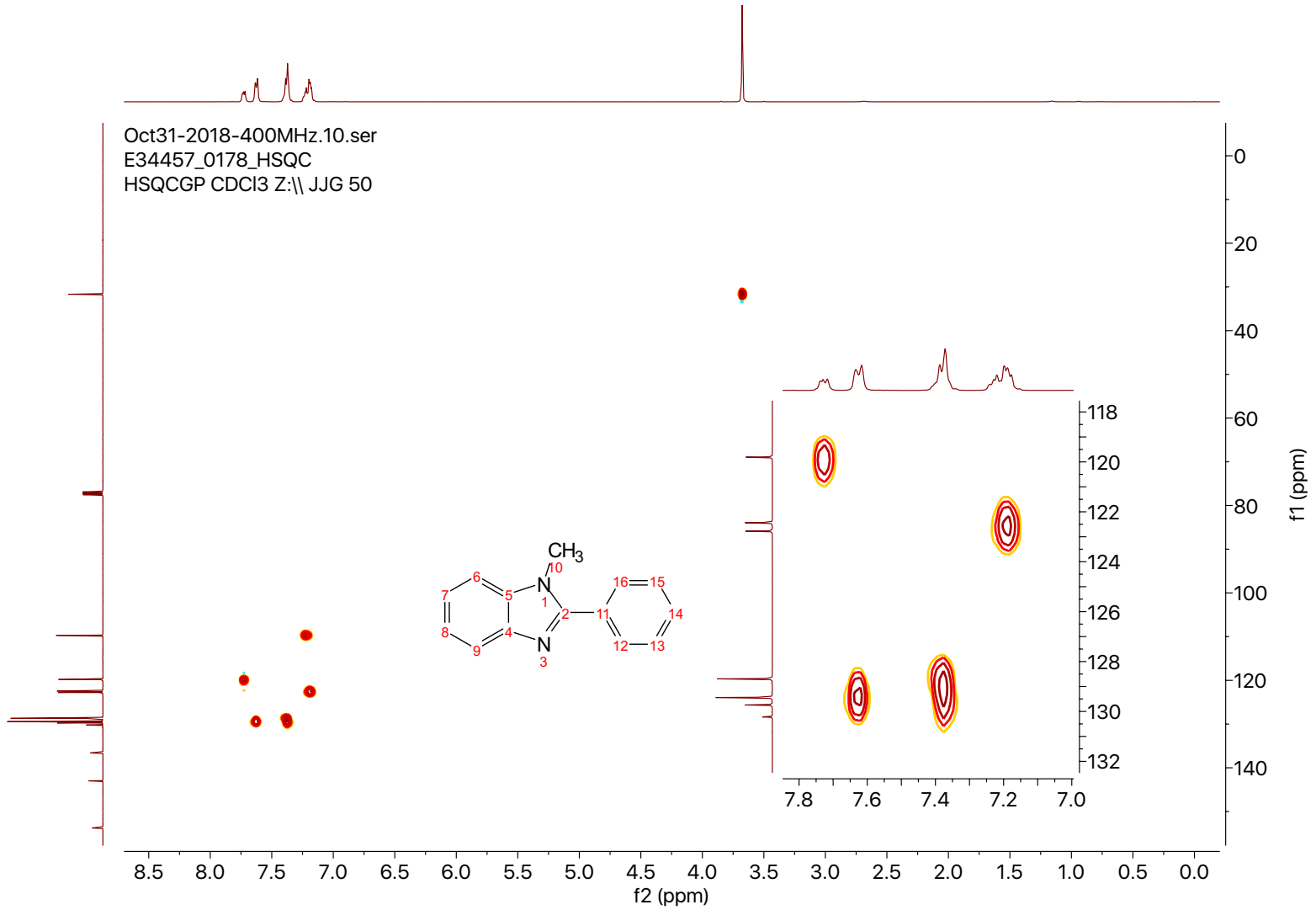
SI Figure 81: HSQC spectrum of 1,2-dimethyl-1H-benzo[d]imidazole in $CDCl_3$ from HDF of 5-fluoro-1,2-dimethyl-1H-benzo[d]imidazole (10).



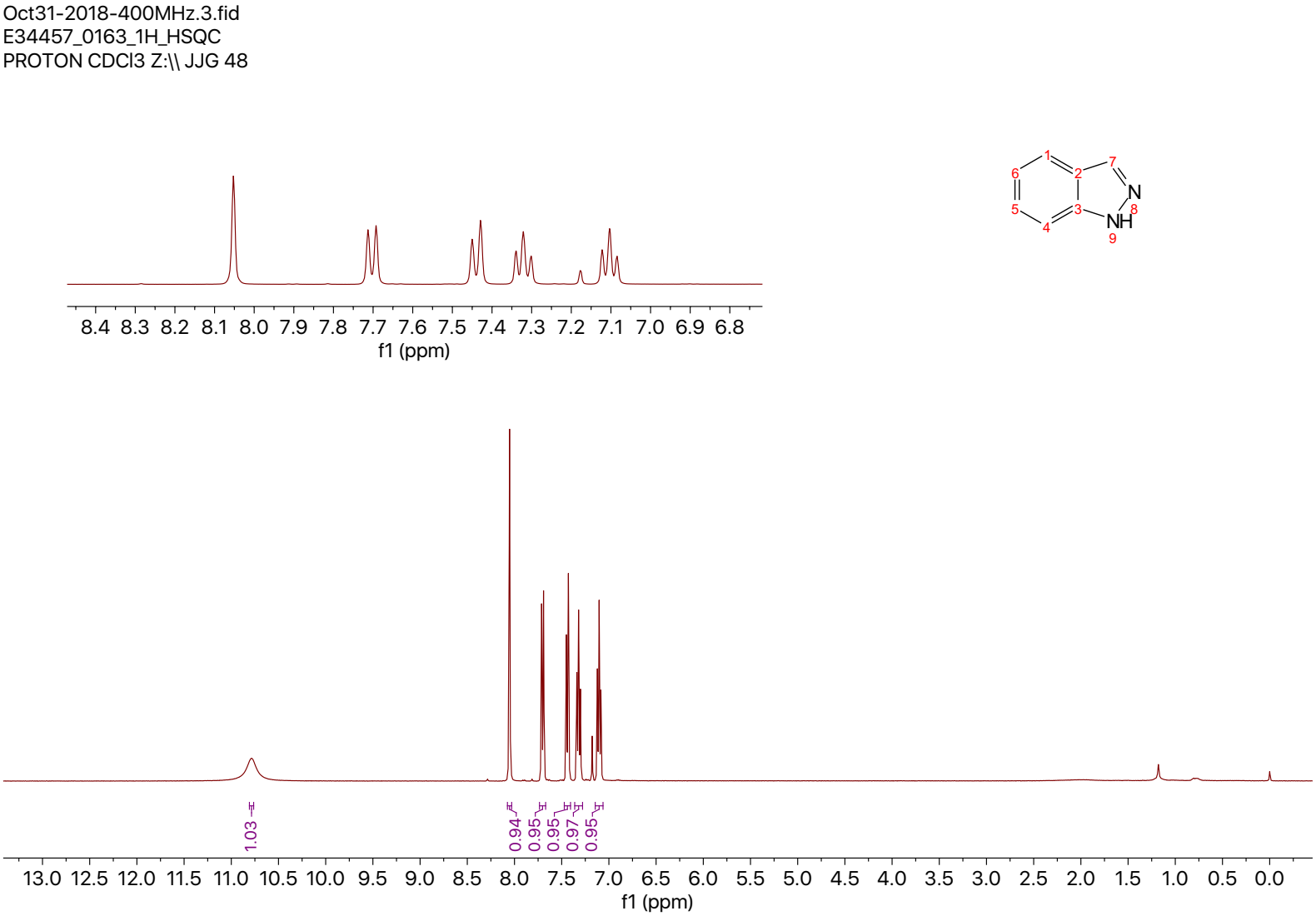
SI Figure 82: ^{1}H NMR spectrum 1-methyl-2-phenyl-1H-benzo[d]imidazole in $CDCl_3$ from HDF of 2-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazole (11)



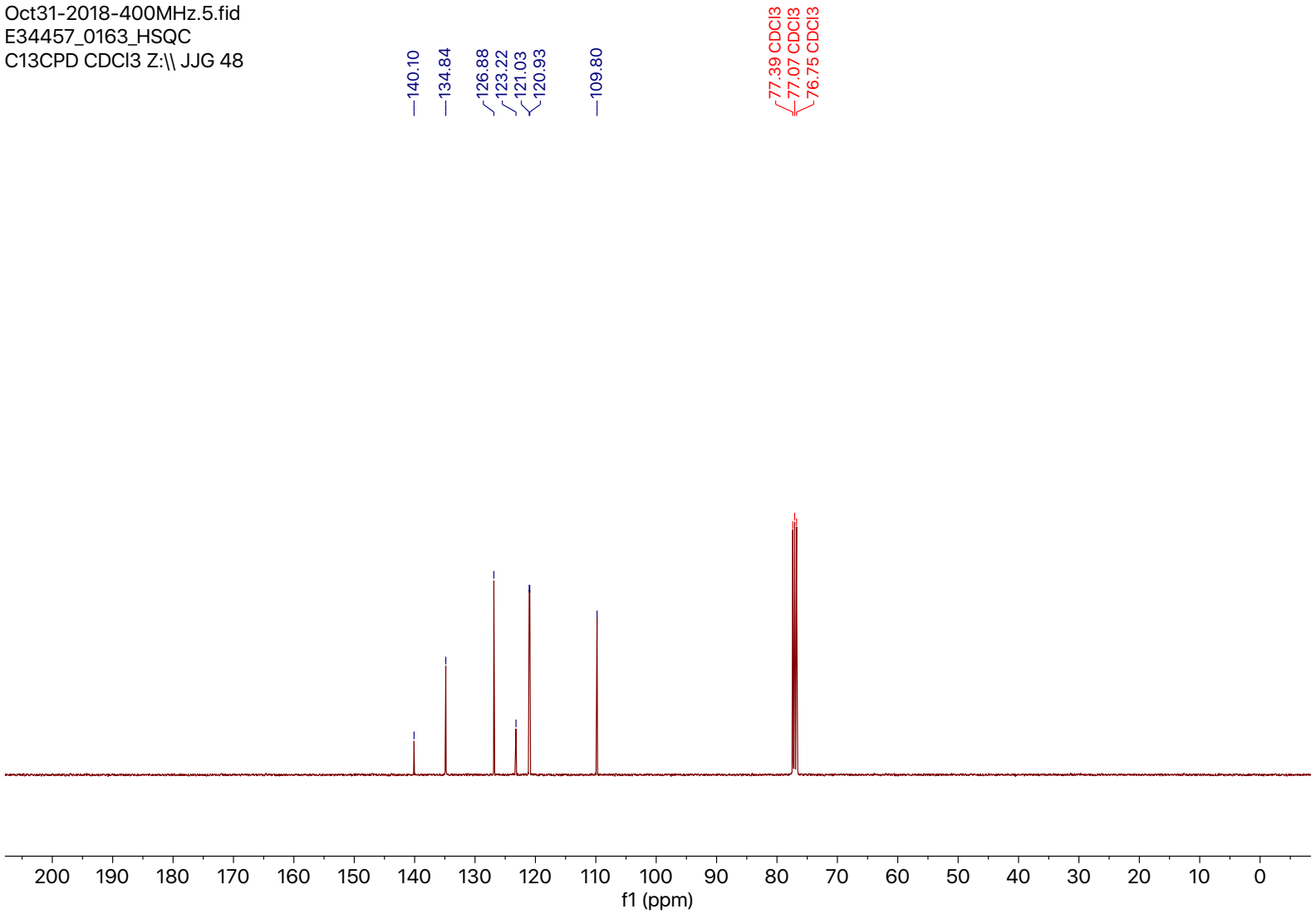
SI Figure 83: ^{13}C NMR spectrum 1-methyl-2-phenyl-1H-benzo[d]imidazole in $CDCl_3$ from HDF of 2-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazole (11)



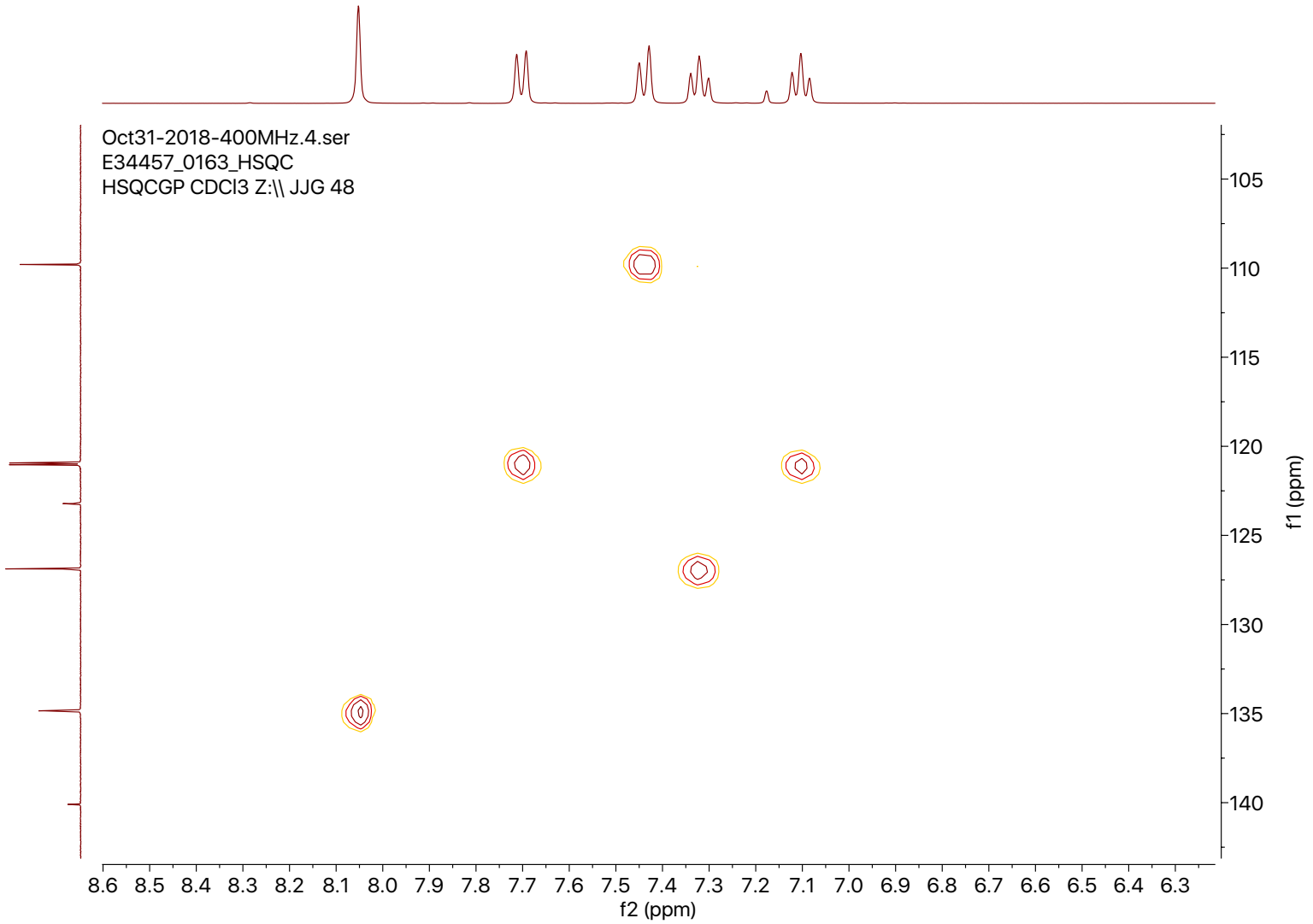
SI Figure 84: HSQC spectrum 1-methyl-2-phenyl-1H-benzo[d]imidazole in $CDCl_3$ from HDF of 2-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazole (11)



SI Figure 85: ^{1}H NMR spectrum 1H-indazole in $CDCl_3$ from HDF of 4-fluoro-1H-indazole (12a)

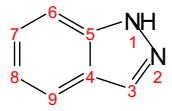


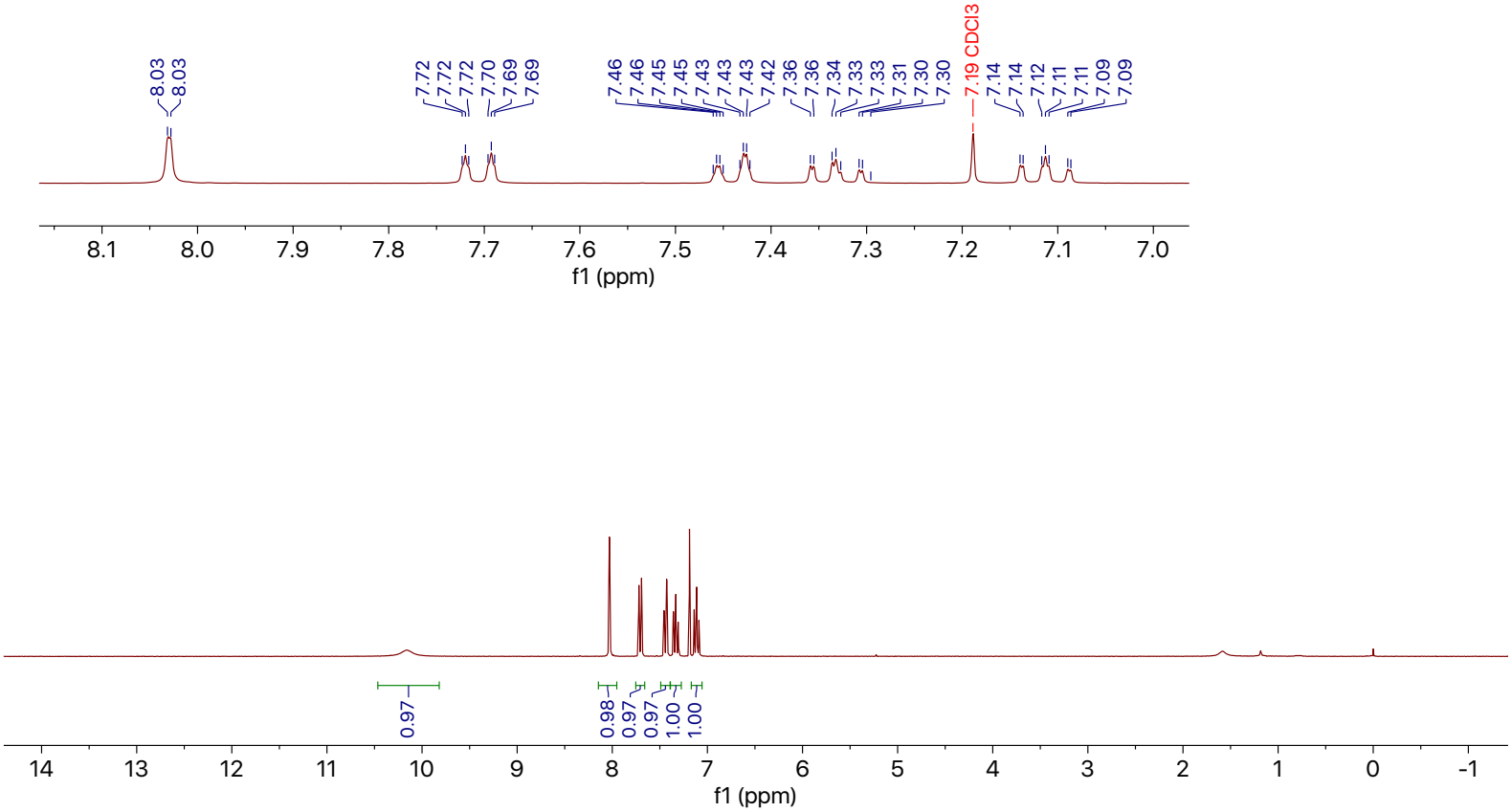
SI Figure 86: ^{13}C NMR spectrum 1H-indazole in $CDCl_3$ from HDF of 4-fluoro-1H-indazole (12a)



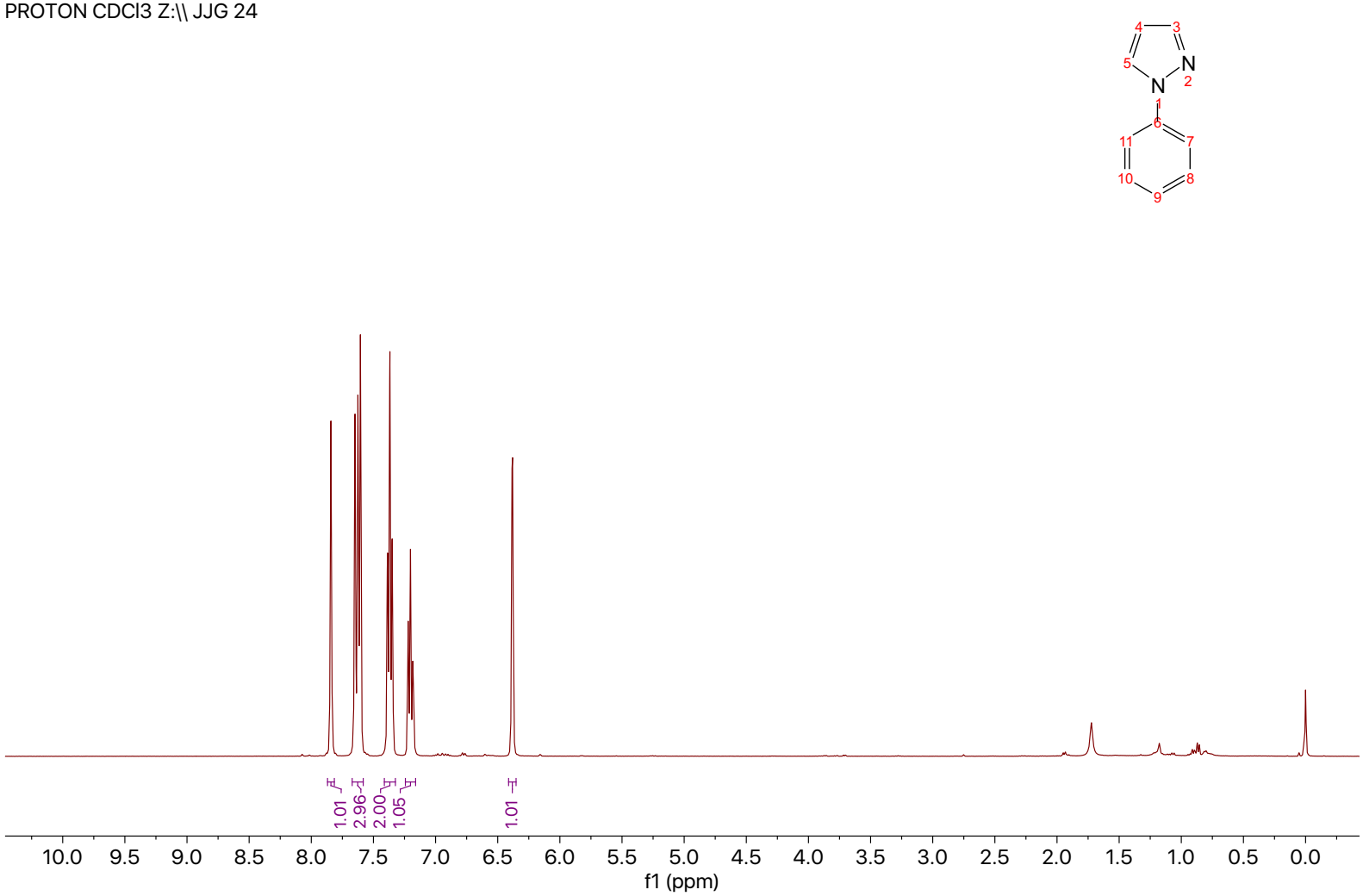
SI Figure 87: HSQC spectrum 1H-indazole in $CDCl_3$ from HDF of 4-fluoro-1H-indazole (12a)

Dec05-2018.1.fid
E34457_0211_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 12

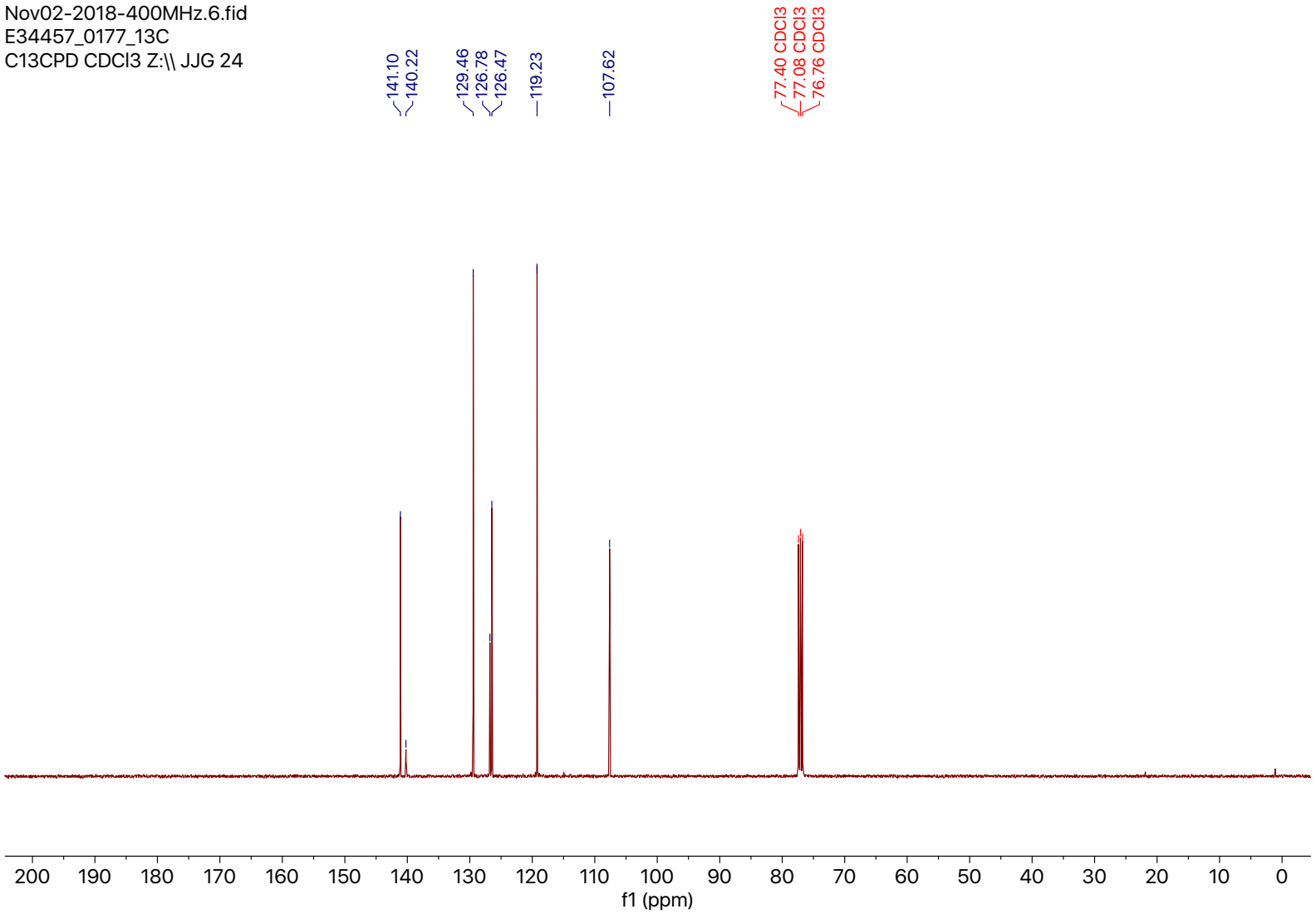




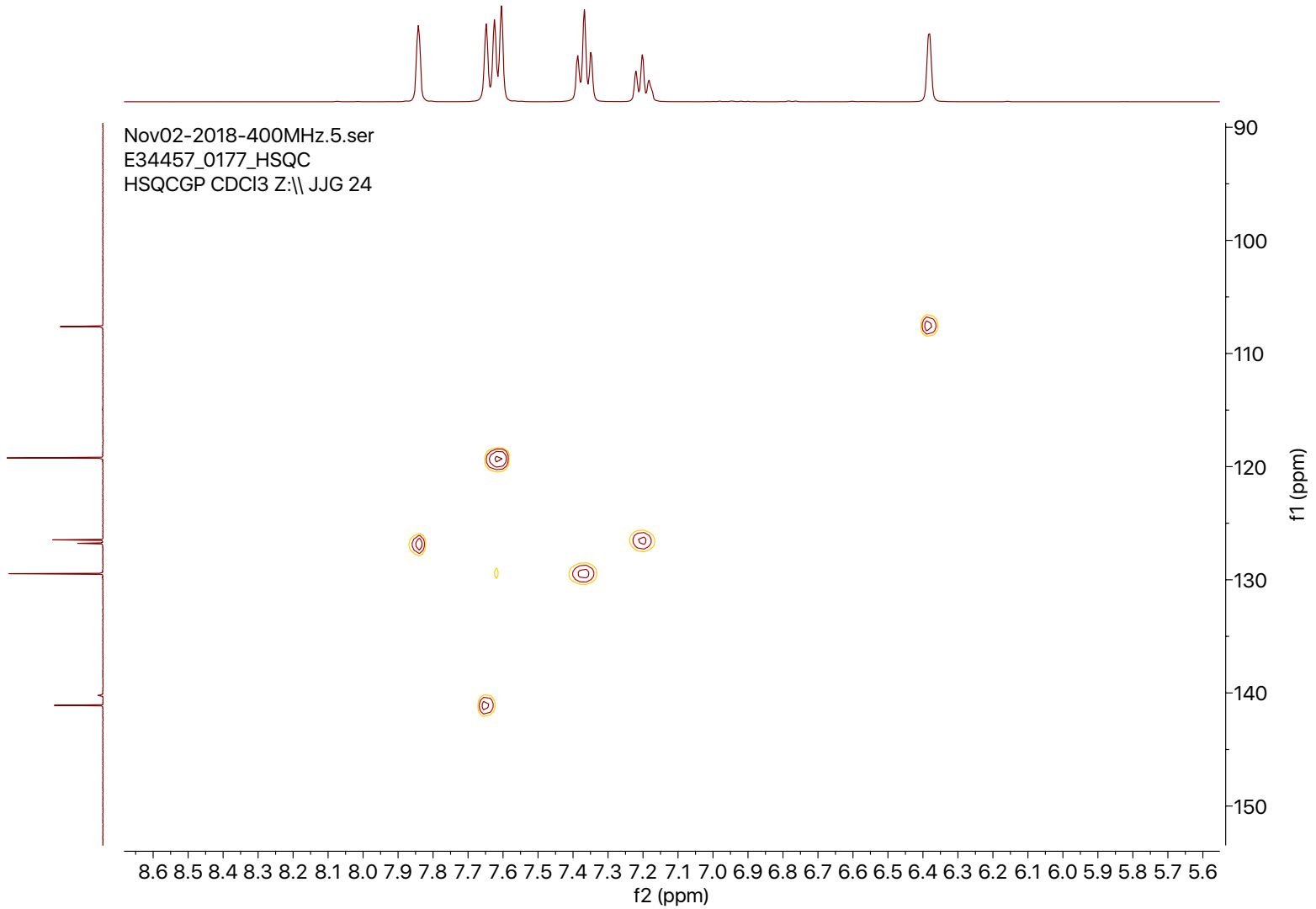
SI Figure 88: ^{1}H NMR spectrum 1H-indazole in $CDCl_3$ from HDF of 3-fluoro-1H-indazole (12b)



SI Figure 89: ^{1}H NMR spectrum 1-phenyl-1H-pyrazole in $CDCl_3$ from HDF of 5-fluoro-1-phenyl-1H-pyrazole (13)

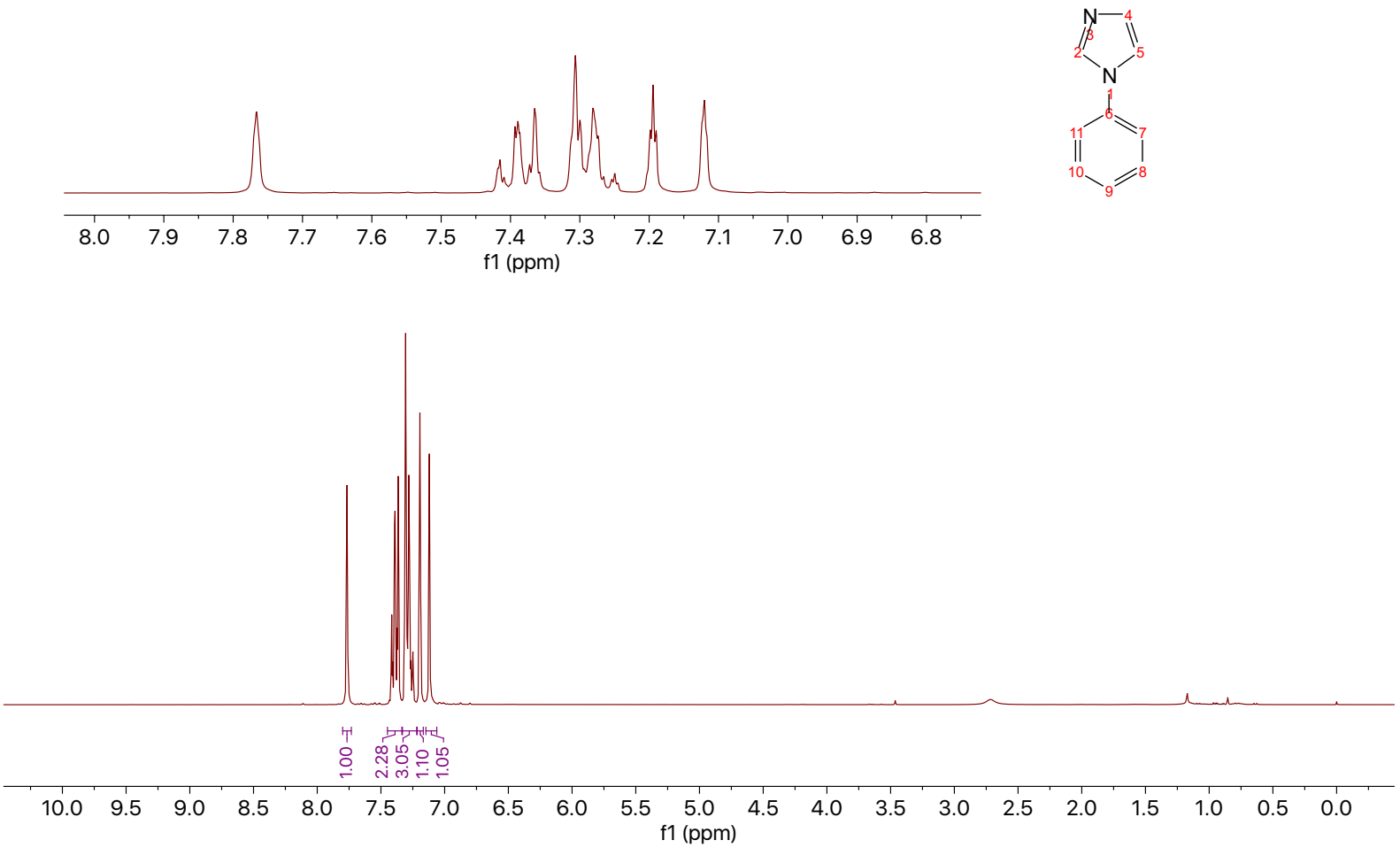


SI Figure 90: ^{13}C NMR spectrum 1-phenyl-1H-pyrazole in $CDCl_3$ from HDF of 5-fluoro-1-phenyl-1H-pyrazole (13)

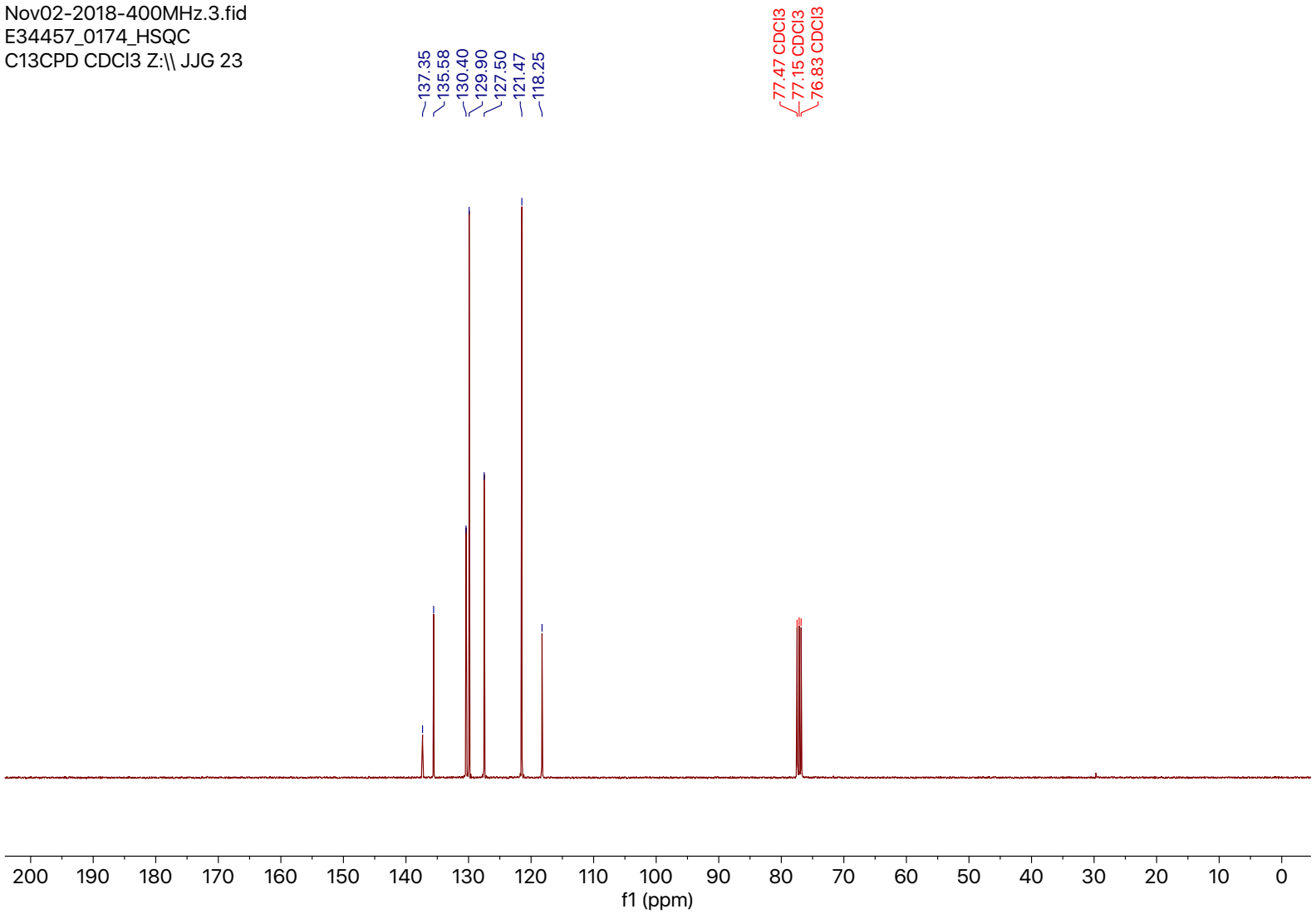


SI Figure 91: HSQC spectrum 1-phenyl-1H-pyrazole in $CDCl_3$ from HDF of 5-fluoro-1-phenyl-1H-pyrazole (13)

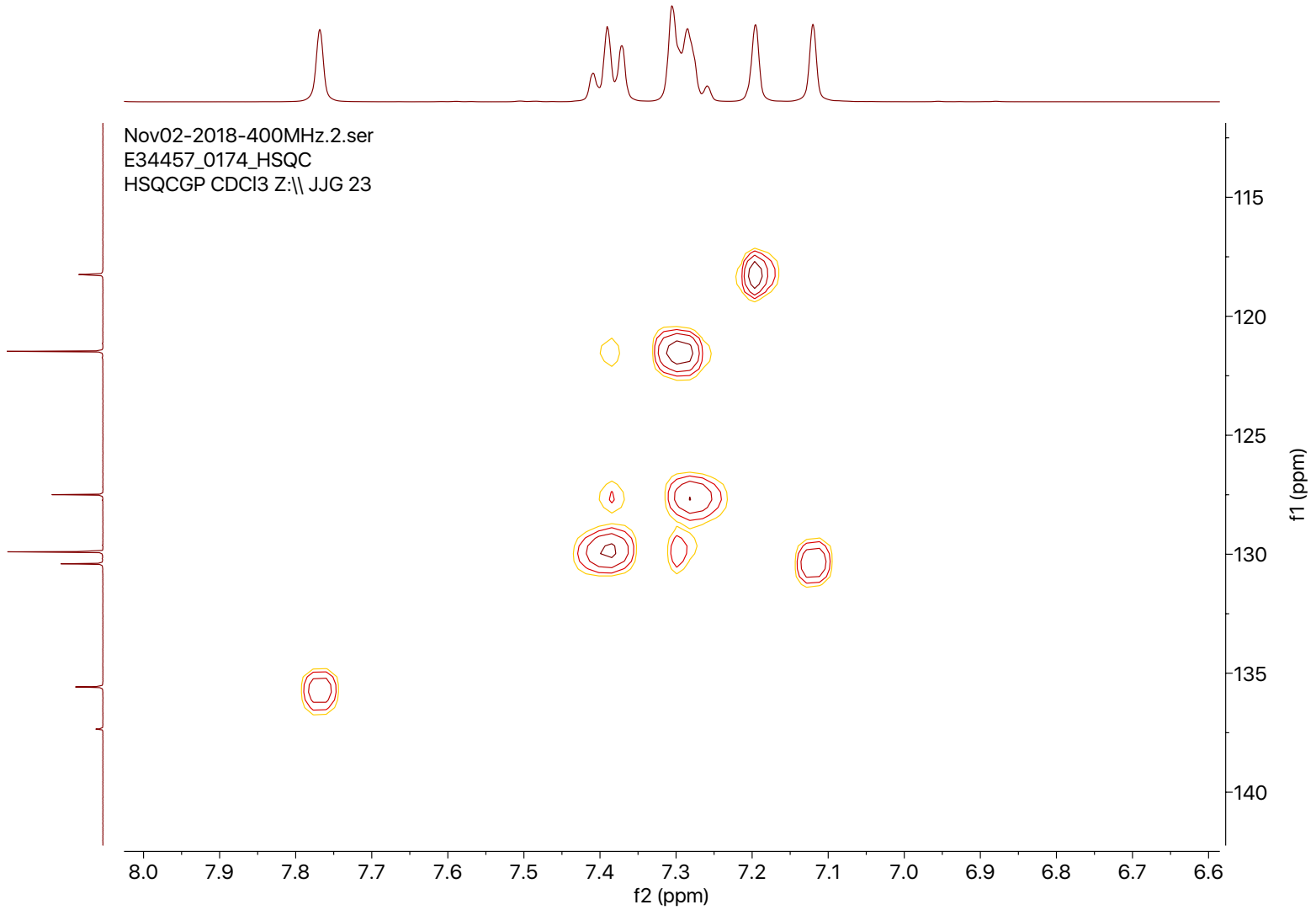
Oct31-2018.8.fid
E34457_0174_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 9



SI Figure 92: ^{1}H NMR spectrum 1-phenyl-1H-imidazole in $CDCl_3$ from HDF of 1-(4-fluorophenyl)-1H-imidazole (14)

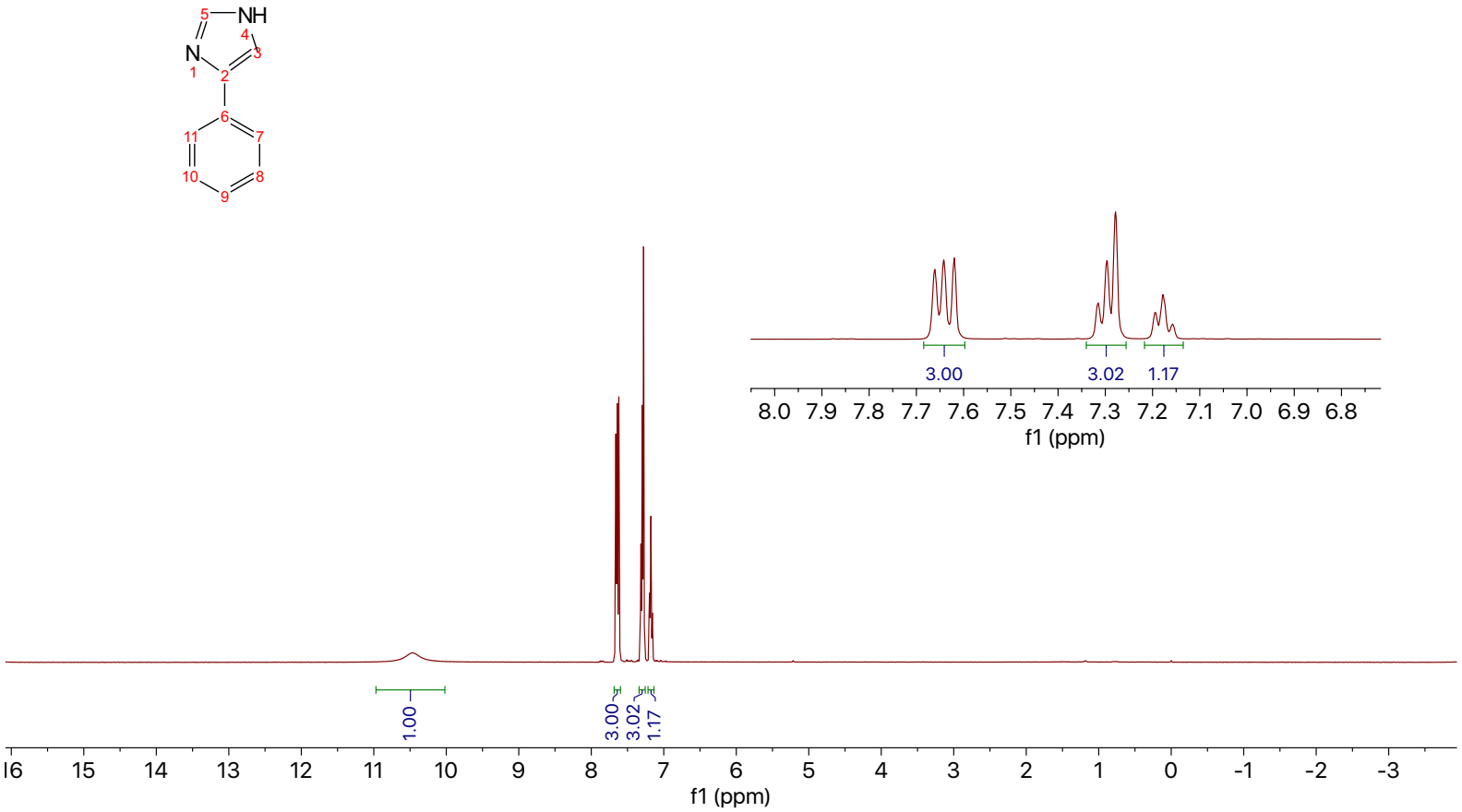


SI Figure 93: ^{13}C NMR spectrum 1-phenyl-1H-imidazole in $CDCl_3$ from HDF of 1-(4-fluorophenyl)-1H-imidazole (14)



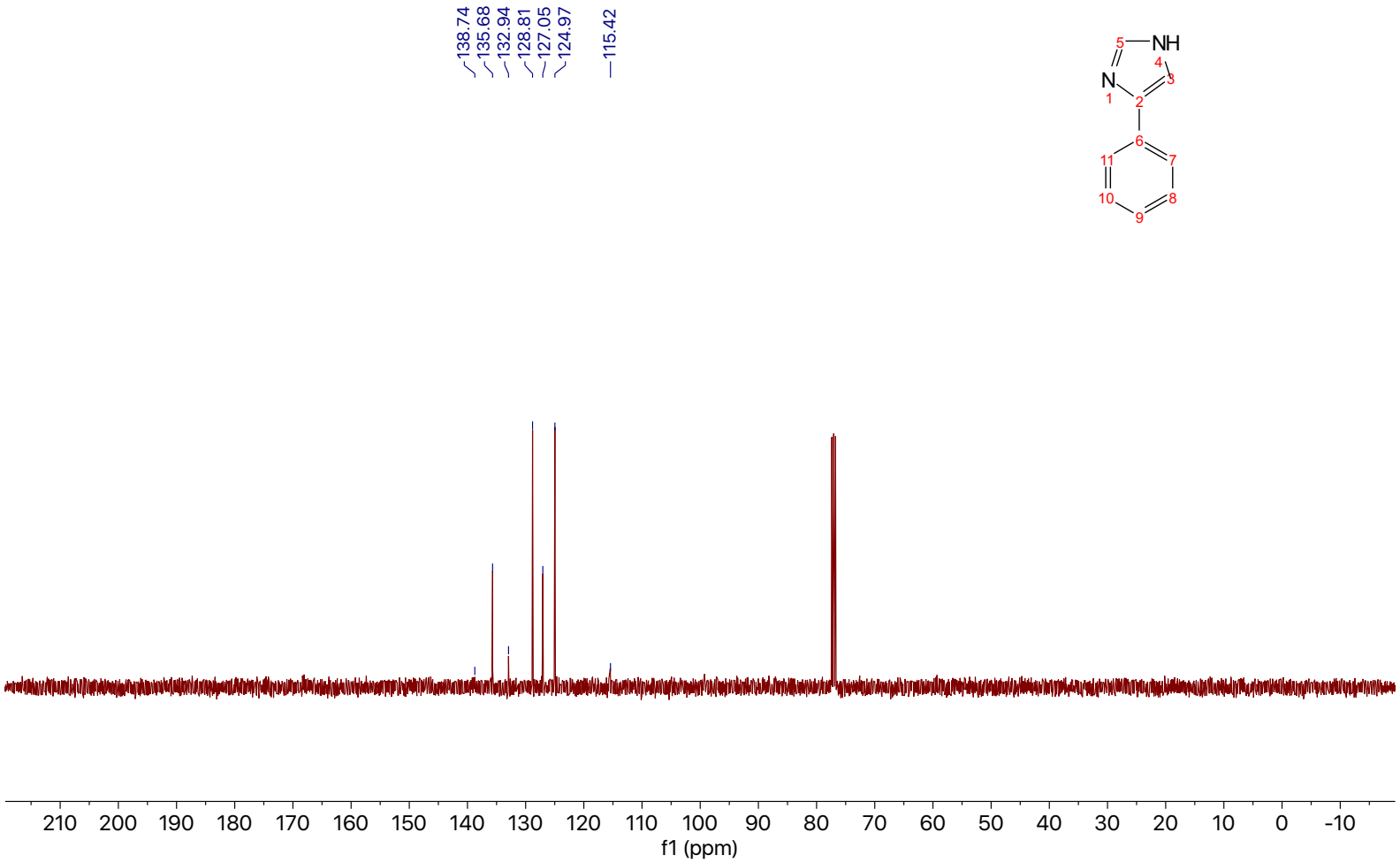
SI Figure 94: HSQC spectrum 1-phenyl-1H-imidazole in $CDCl_3$ from HDF of 1-(4-fluorophenyl)-1H-imidazole (14)

Jan24-2019-400MHz.24.fid
E34457_0170_HSQC_1H
PROTON CDCl3 Z:\\ JJG 47

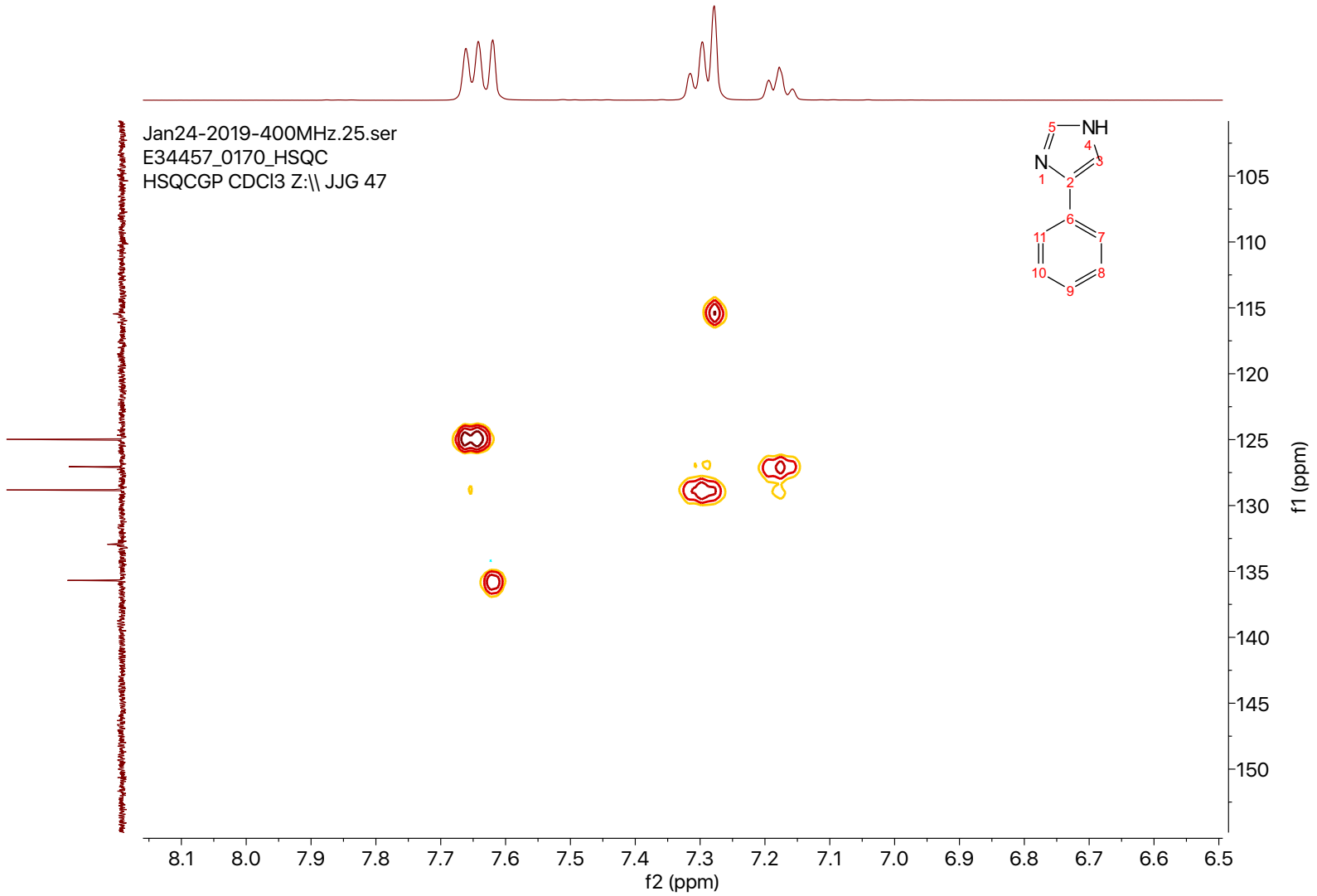


SI Figure 95: ^{1}H NMR spectrum of 4-phenyl-1H-imidazole in $CDCl_3$ from HDF of 4-(4-fluorophenyl)-1H-imidazole (15)

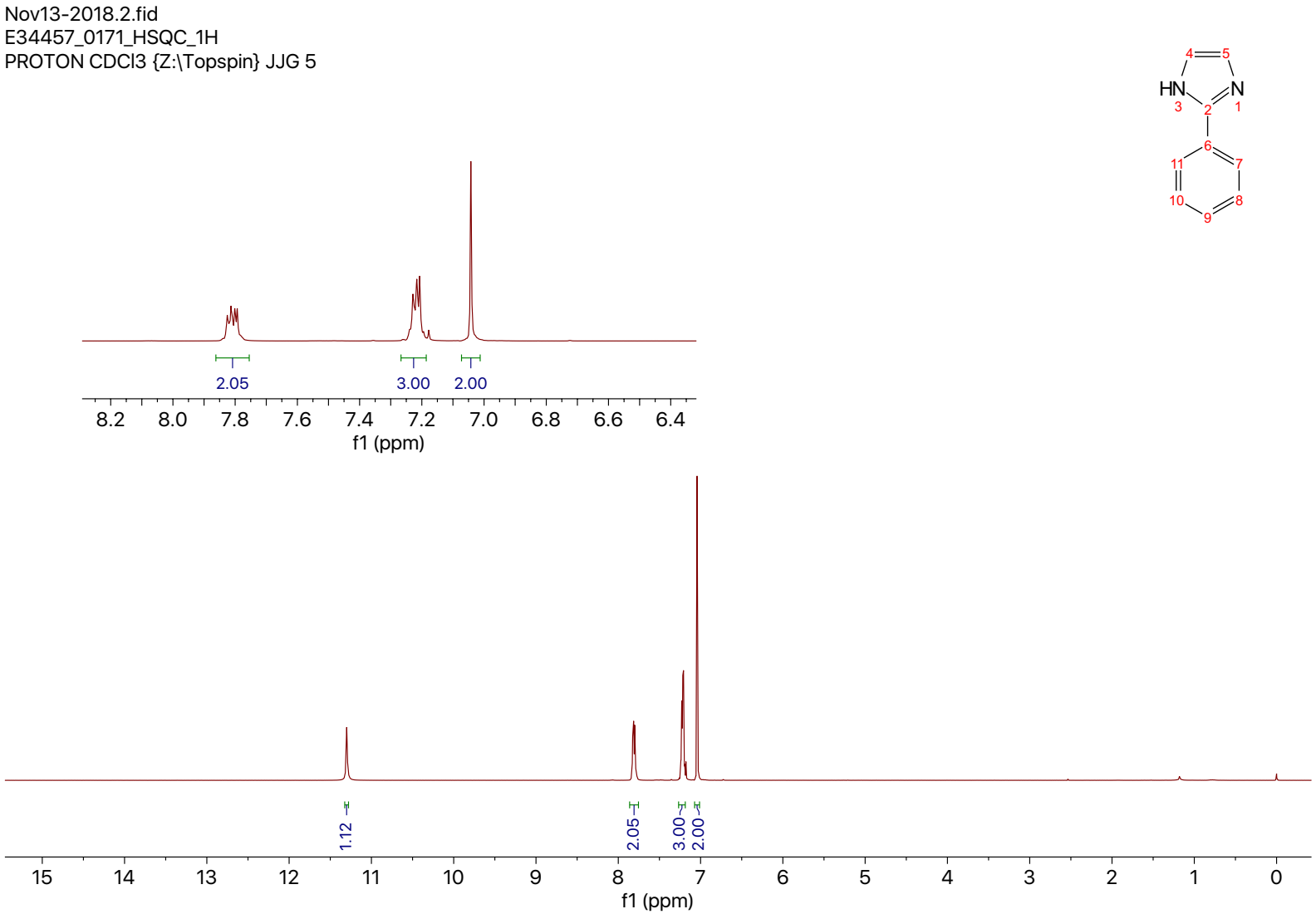
Jan24-2019-400MHz.26.fid
E34457_0170_13C
C13CPD32 CDCl3 Z:\\ JJG 47



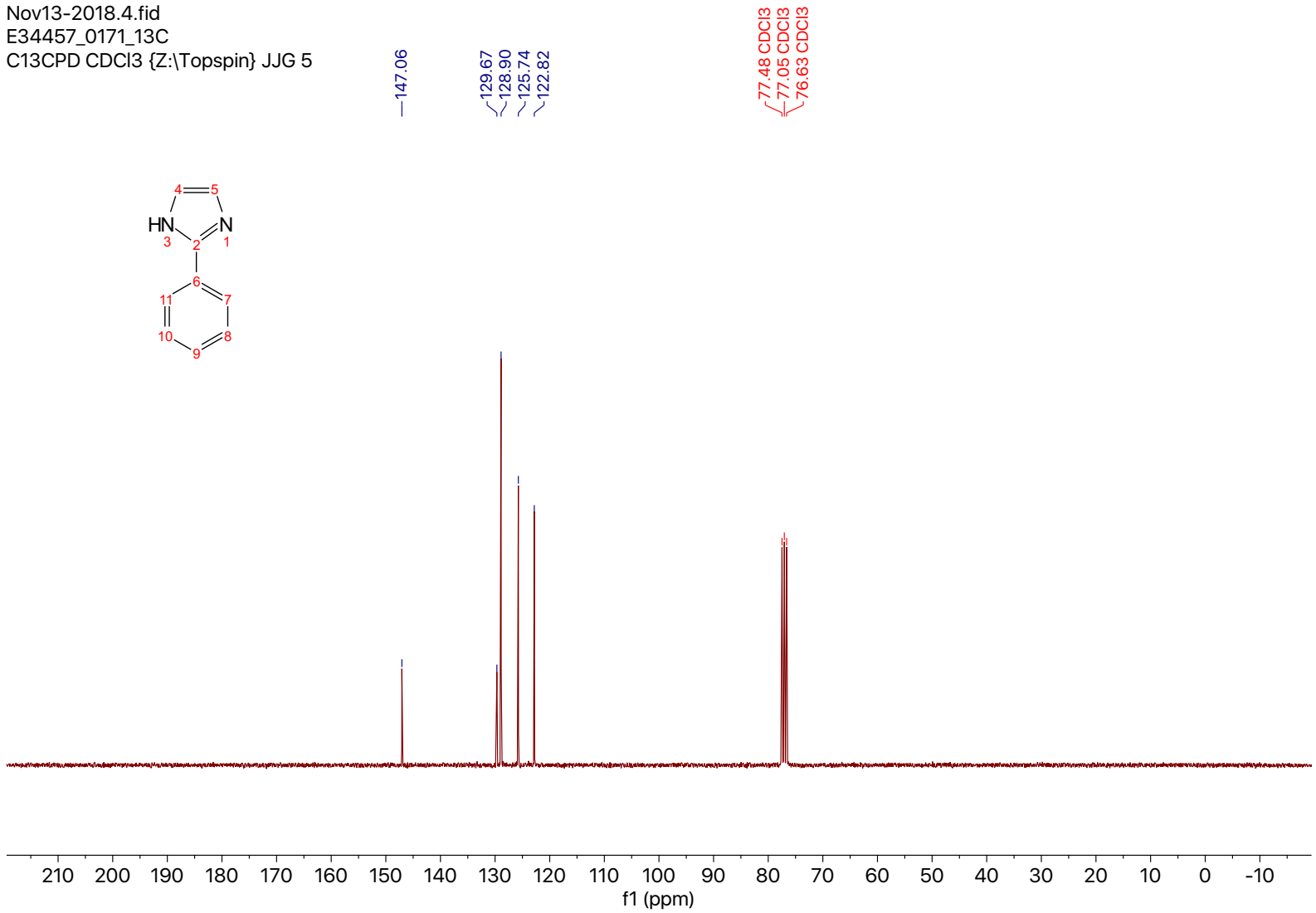
SI Figure 96: ^{13}C NMR spectrum of 4-phenyl-1H-imidazole in $CDCl_3$ from HDF of 4-(4-fluorophenyl)-1H-imidazole (15)



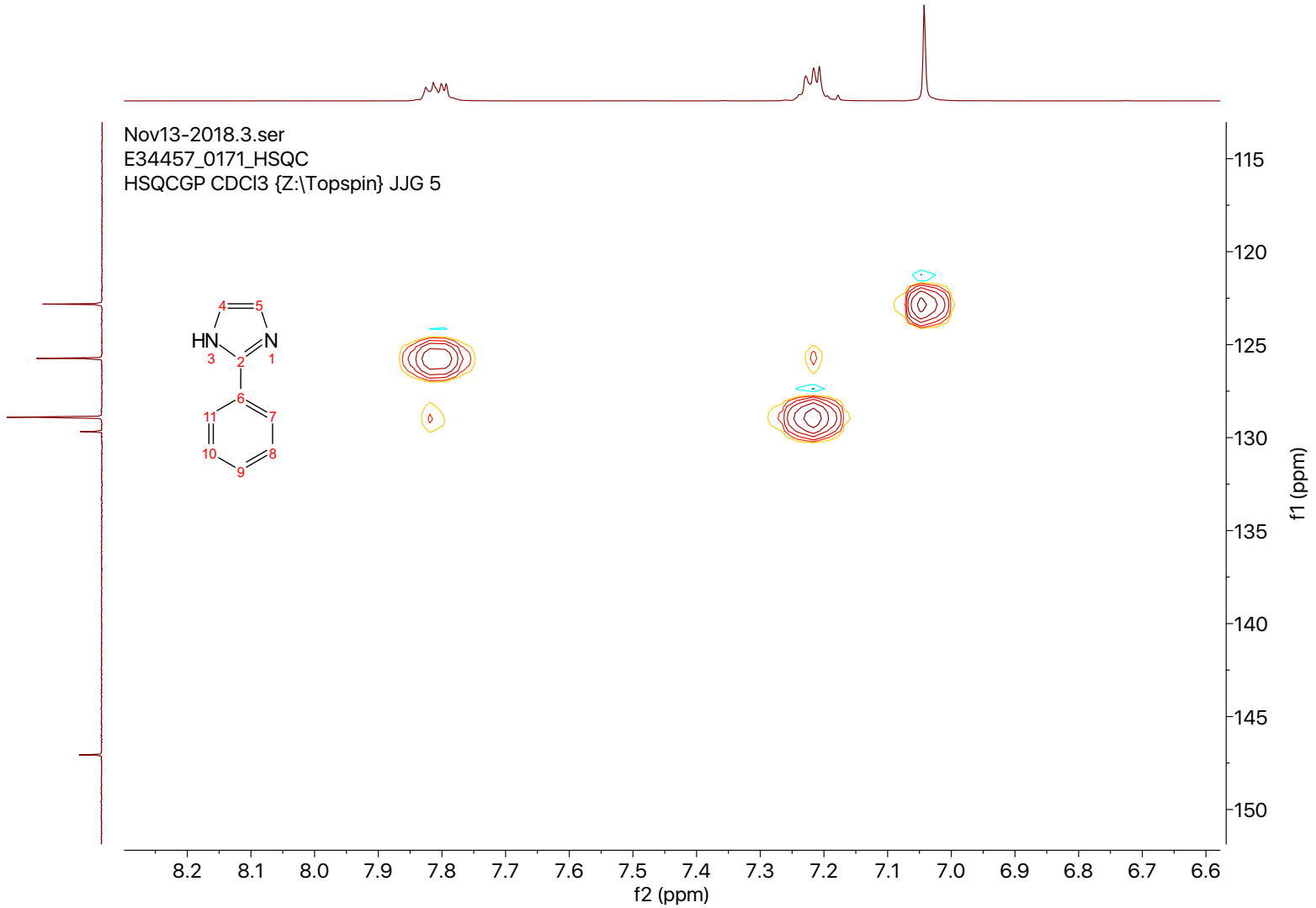
SI Figure 97: HSQC spectrum of 4-phenyl-1H-imidazole in $CDCl_3$ from HDF of 4-(4-fluorophenyl)-1H-imidazole (15)



SI Figure 98: ^{1}H NMR spectrum of 2-phenyl-1H-imidazole in $CDCl_3$ from HDF of 2-(4-fluorophenyl)-1H-imidazole (16)

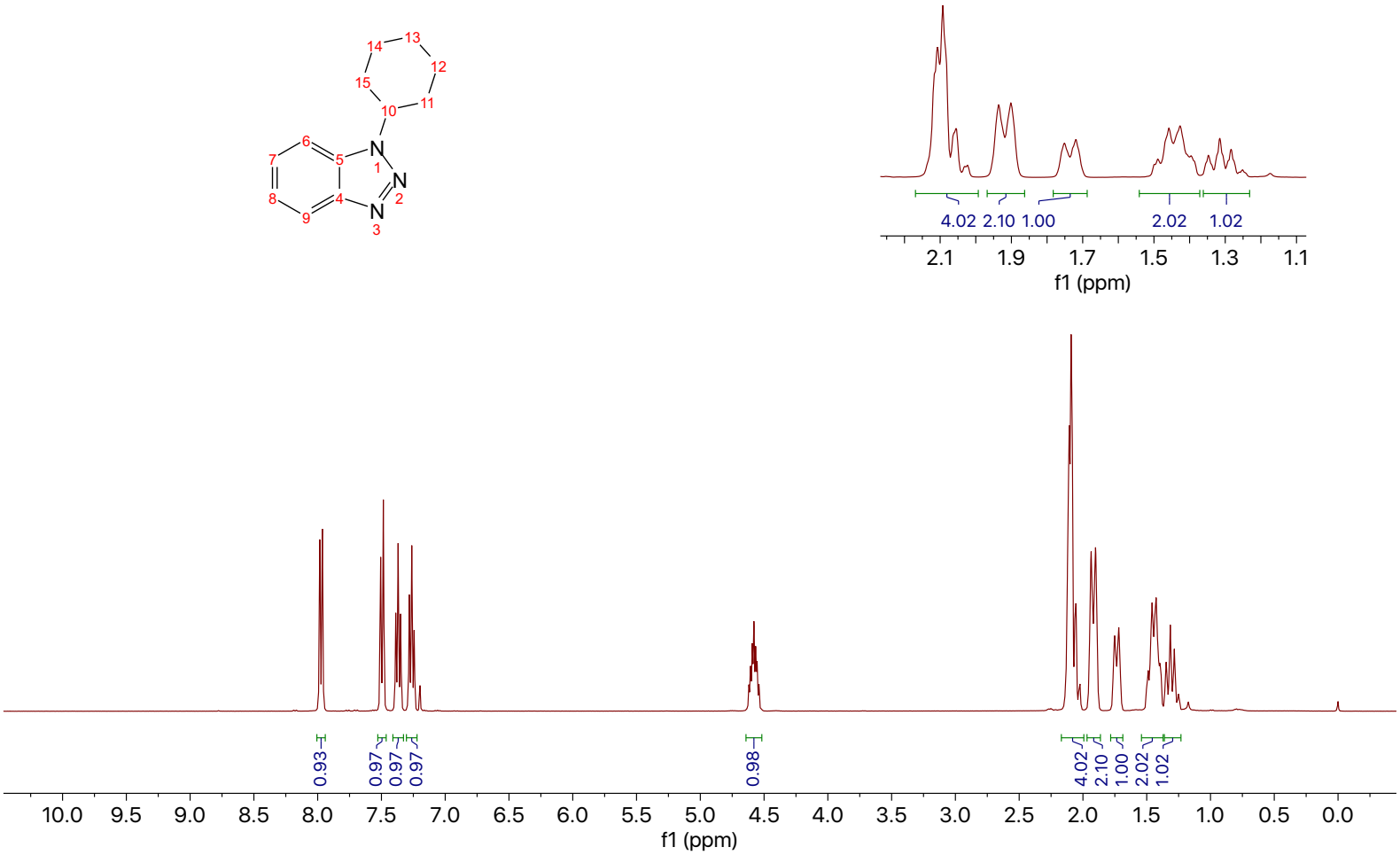


SI Figure 99: ^{13}C NMR spectrum of 2-phenyl-1H-imidazole in $CDCl_3$ from HDF of 2-(4-fluorophenyl)-1H-imidazole (16)

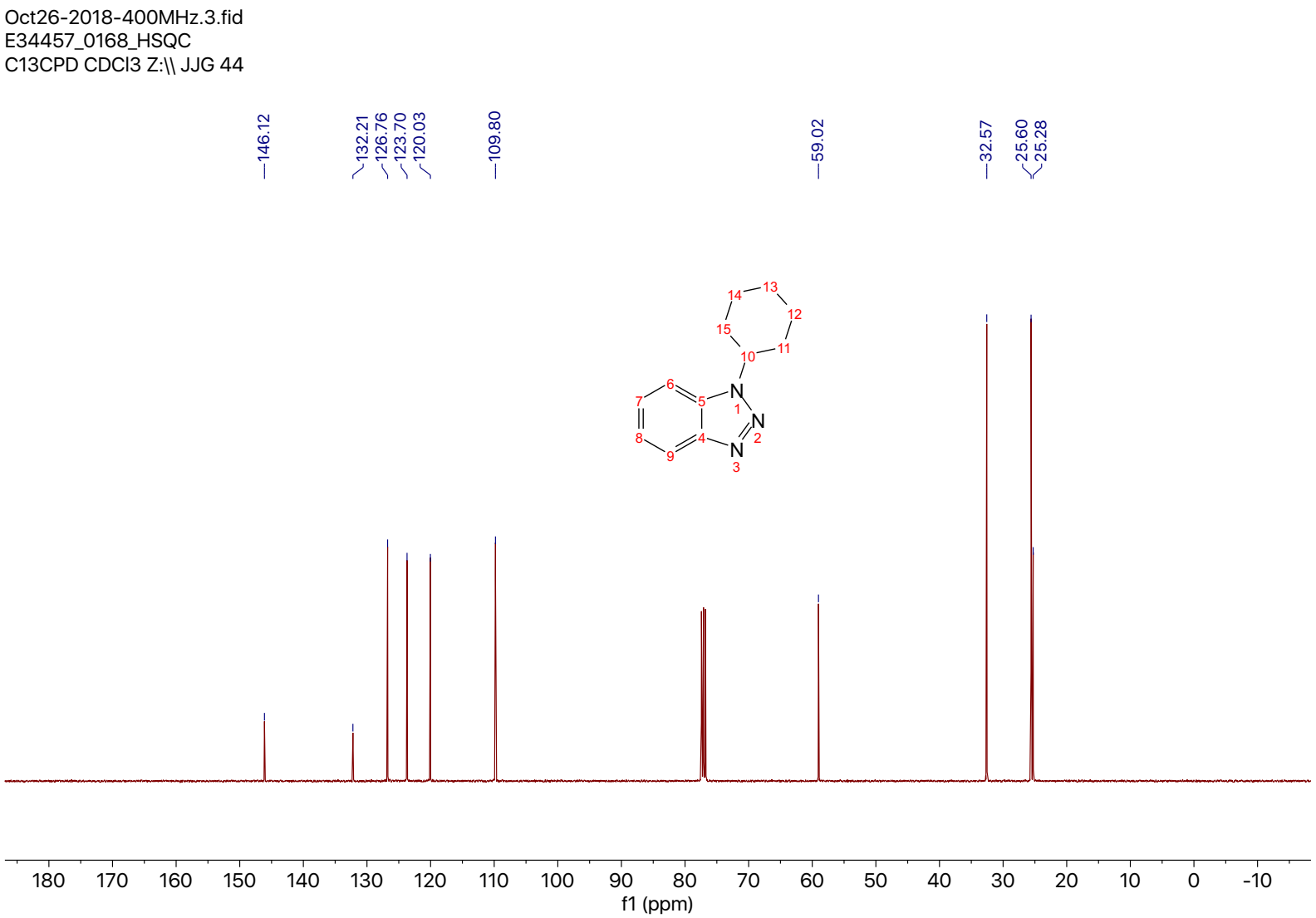


SI Figure 100: HSQC spectrum of 2-phenyl-1H-imidazole in $CDCl_3$ from HDF of 2-(4-fluorophenyl)-1H-imidazole (16).

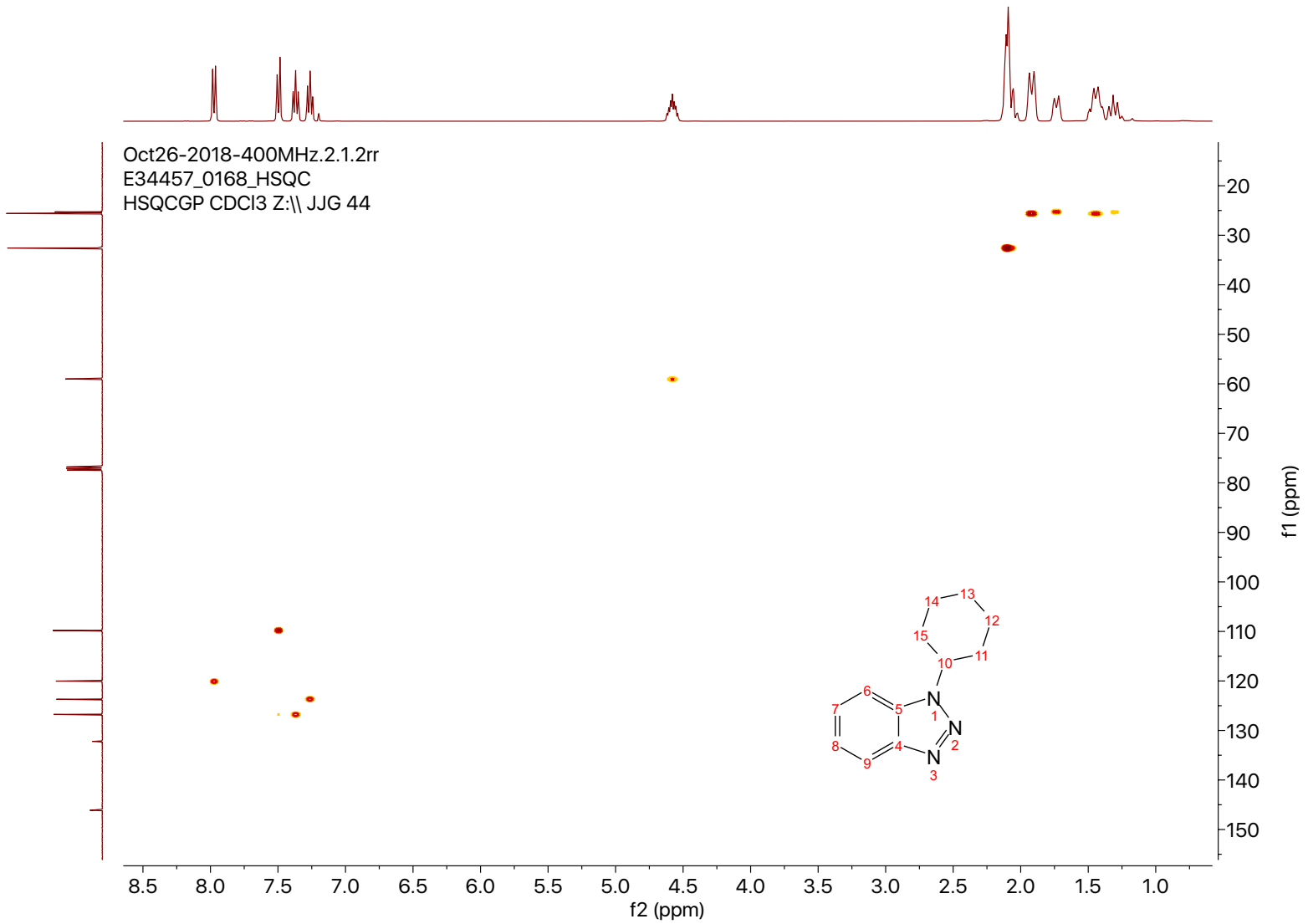
Oct26-2018-400MHz.1.fid
E34457_0168_1H_HSQC
PROTON CDCl3 Z:\\ JJG 44



SI Figure 101: ^{1}H NMR spectrum of 1-cyclohexyl-1H-benzo[d][1,2,3]triazole in $CDCl_3$ from HDF of 1-cyclohexyl-6-fluoro-1H-benzo[d][1,2,3]triazole (17).

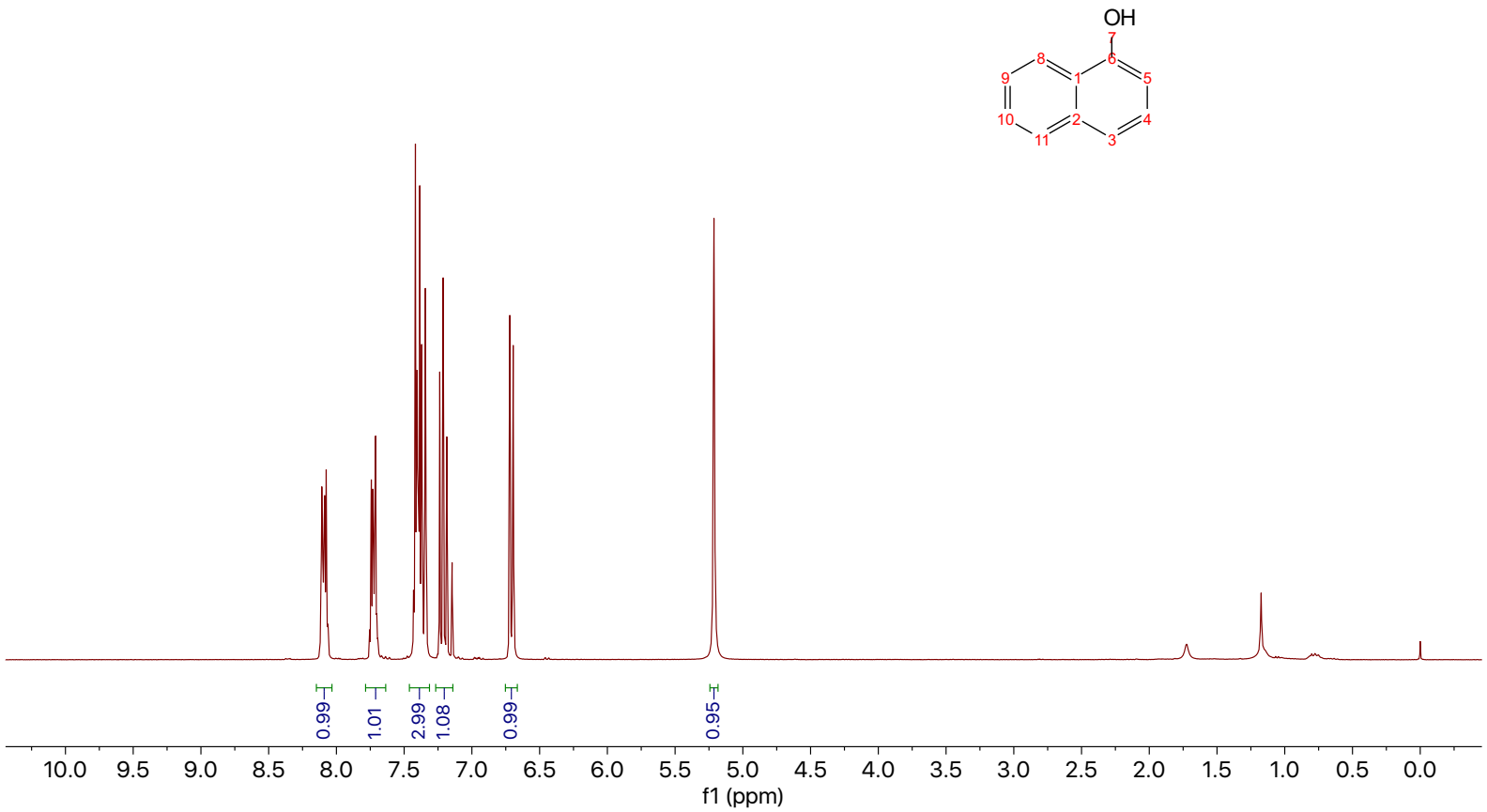


SI Figure 102: ^{13}C NMR spectrum of 1-cyclohexyl-1H-benzo[d][1,2,3]triazole in $CDCl_3$ from HDF of 1-cyclohexyl-6-fluoro-1H-benzo[d][1,2,3]triazole (17).

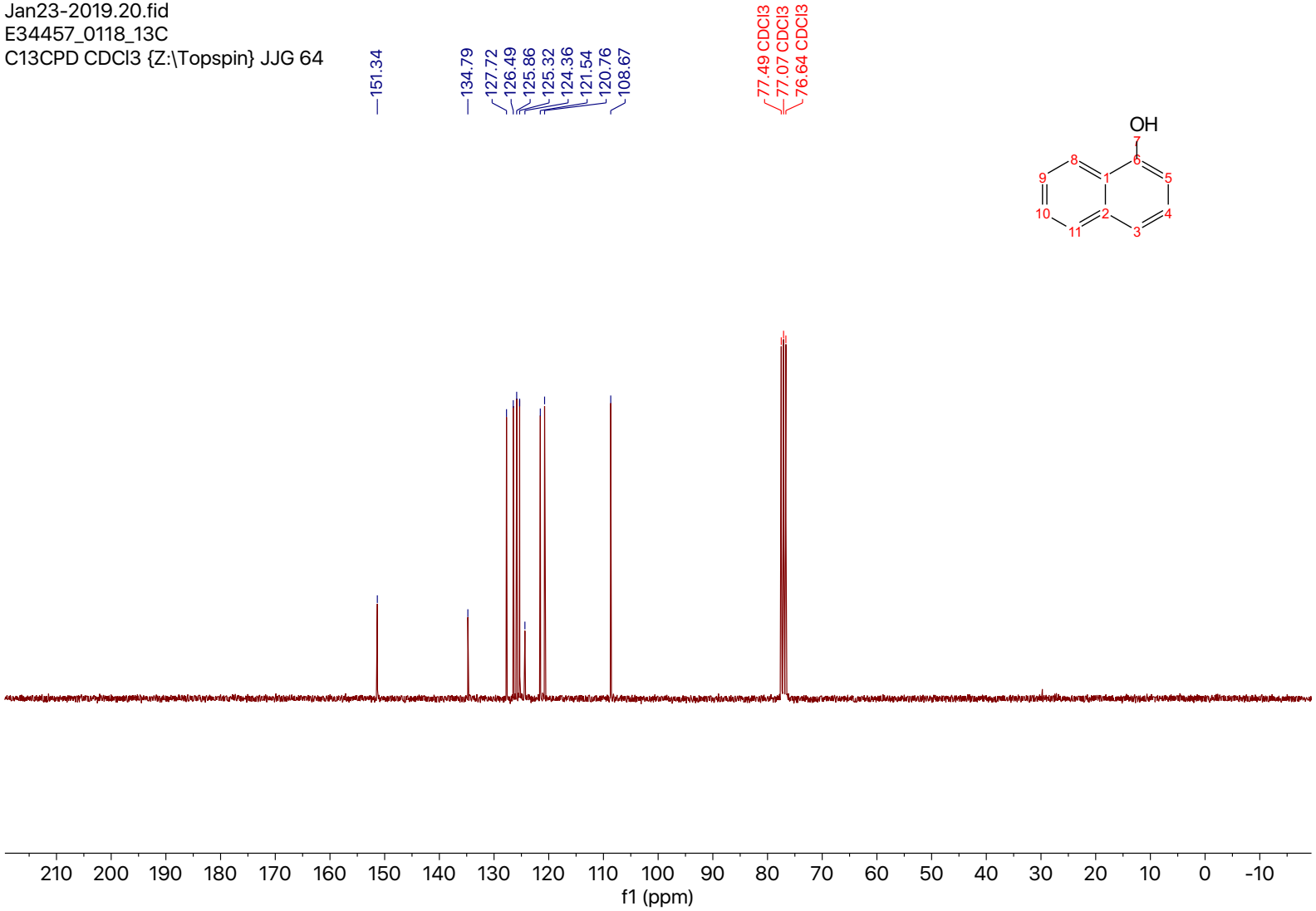


SI Figure 103: HSQC spectrum of 1-cyclohexyl-1H-benzo[d][1,2,3]triazole in $CDCl_3$ from HDF of 1-cyclohexyl-6-fluoro-1H-benzo[d][1,2,3]triazole (17).

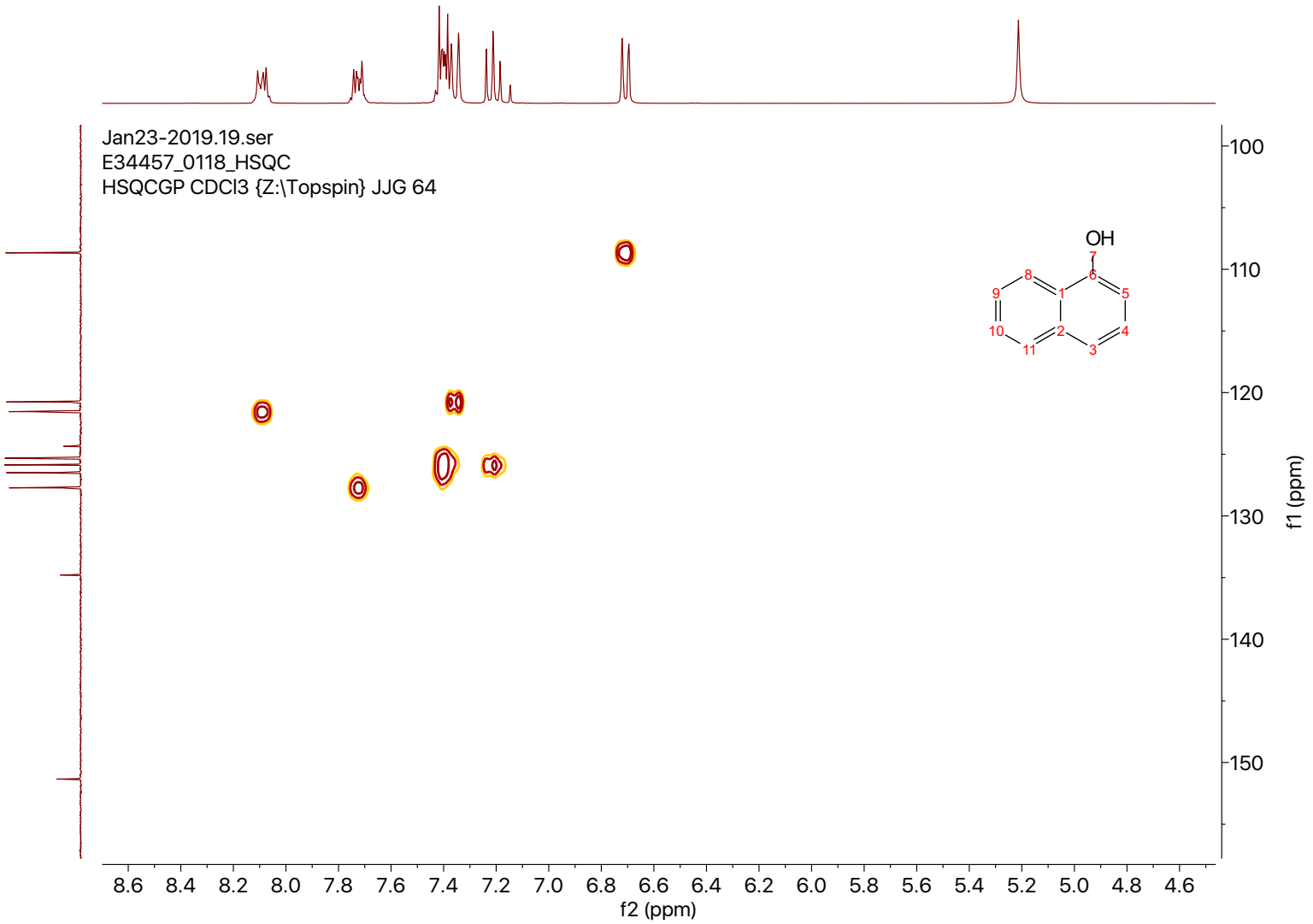
Jan23-2019.18.fid
E34457_0118_HSQC_1H
PROTON CDCl3 {Z:\Topspin} JJG 64



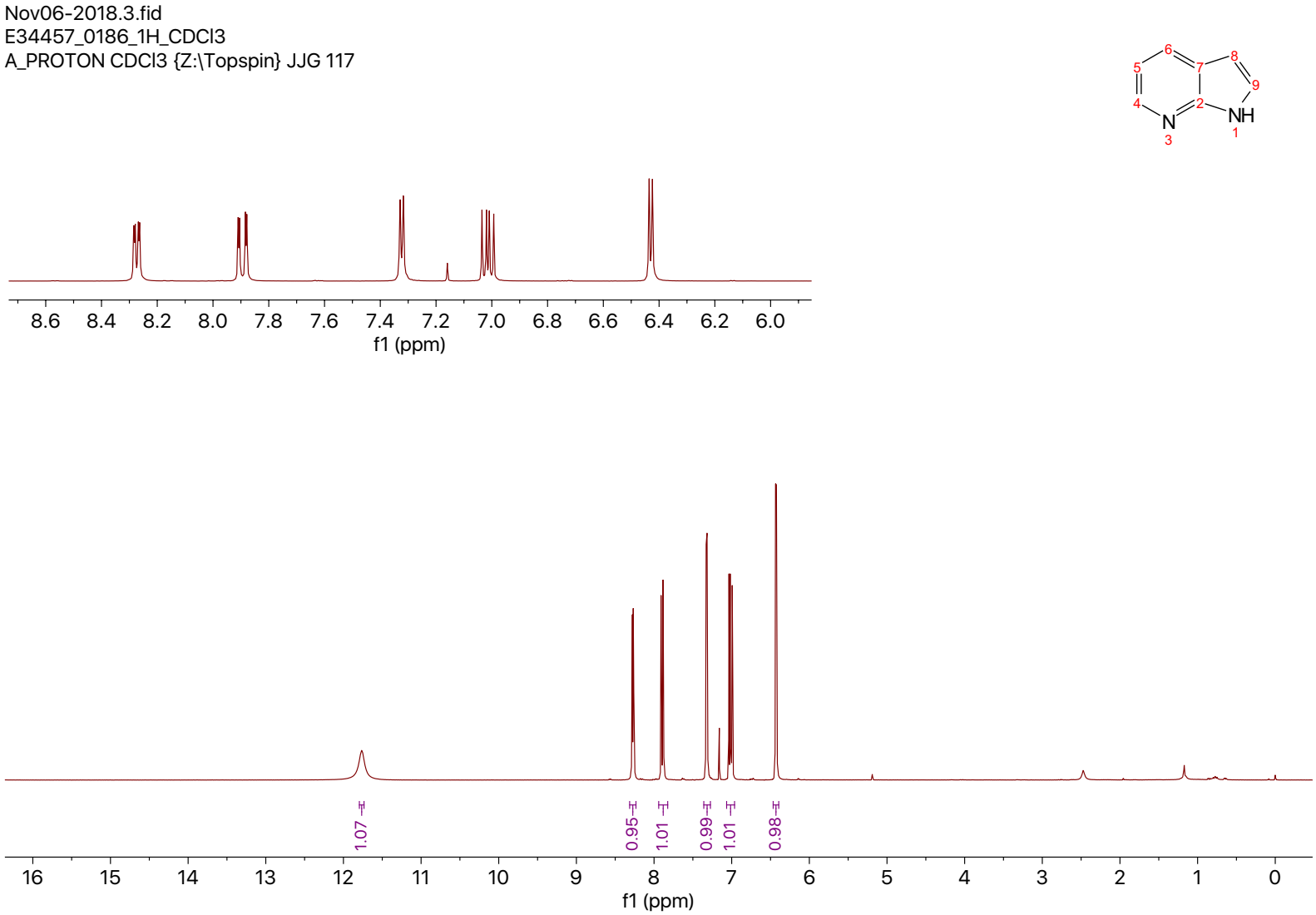
SI Figure 104: ^{1}H NMR spectrum of naphthalen-1-ol in $CDCl_3$ from HDF of 4-fluoronaphthalen-1-ol (18).



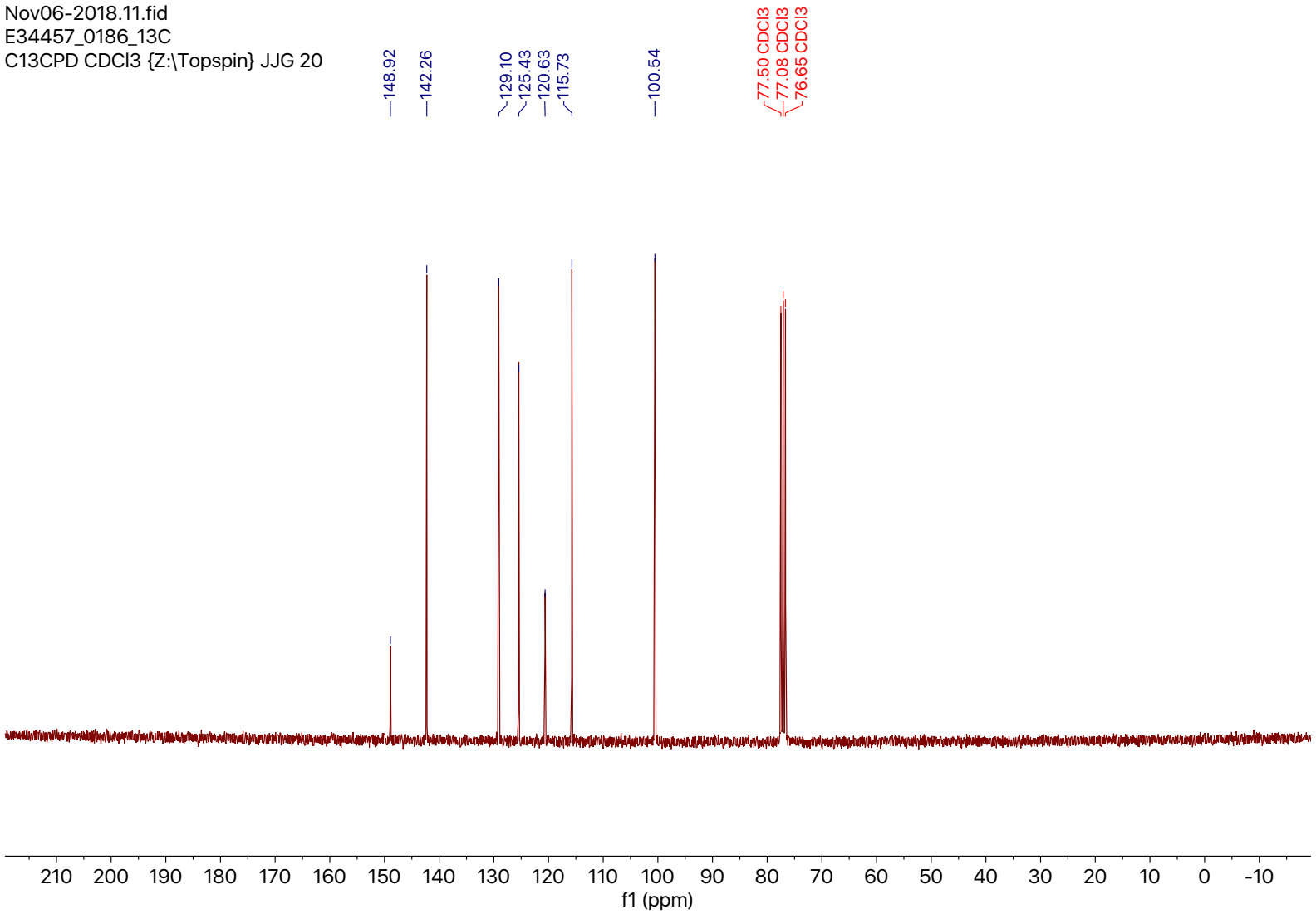
SI Figure 105: ^{13}C NMR spectrum of naphthalen-1-ol in $CDCl_3$ from HDF of 4-fluoronaphthalen-1-ol (18).



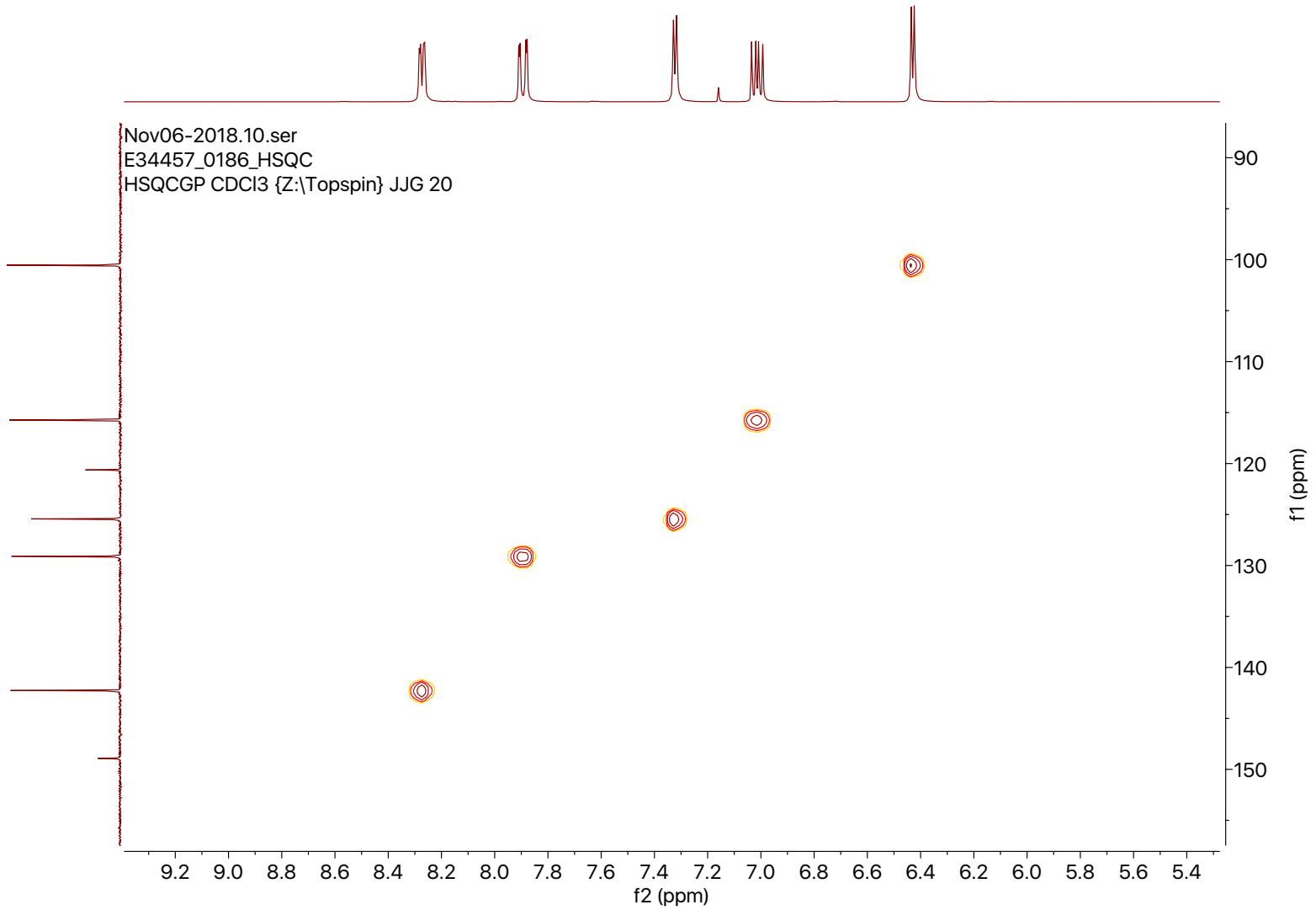
SI Figure 106: HSQC spectrum of naphthalen-1-ol in $CDCl_3$ from HDF of 4-fluoronaphthalen-1-ol (18).



SI Figure 107: ^{1}H NMR spectrum of 1H-pyrrolo[2,3-b]pyridine in $CDCl_3$ from HDF of 5-fluoro-1H-pyrrolo[2,3-b]pyridine (19).

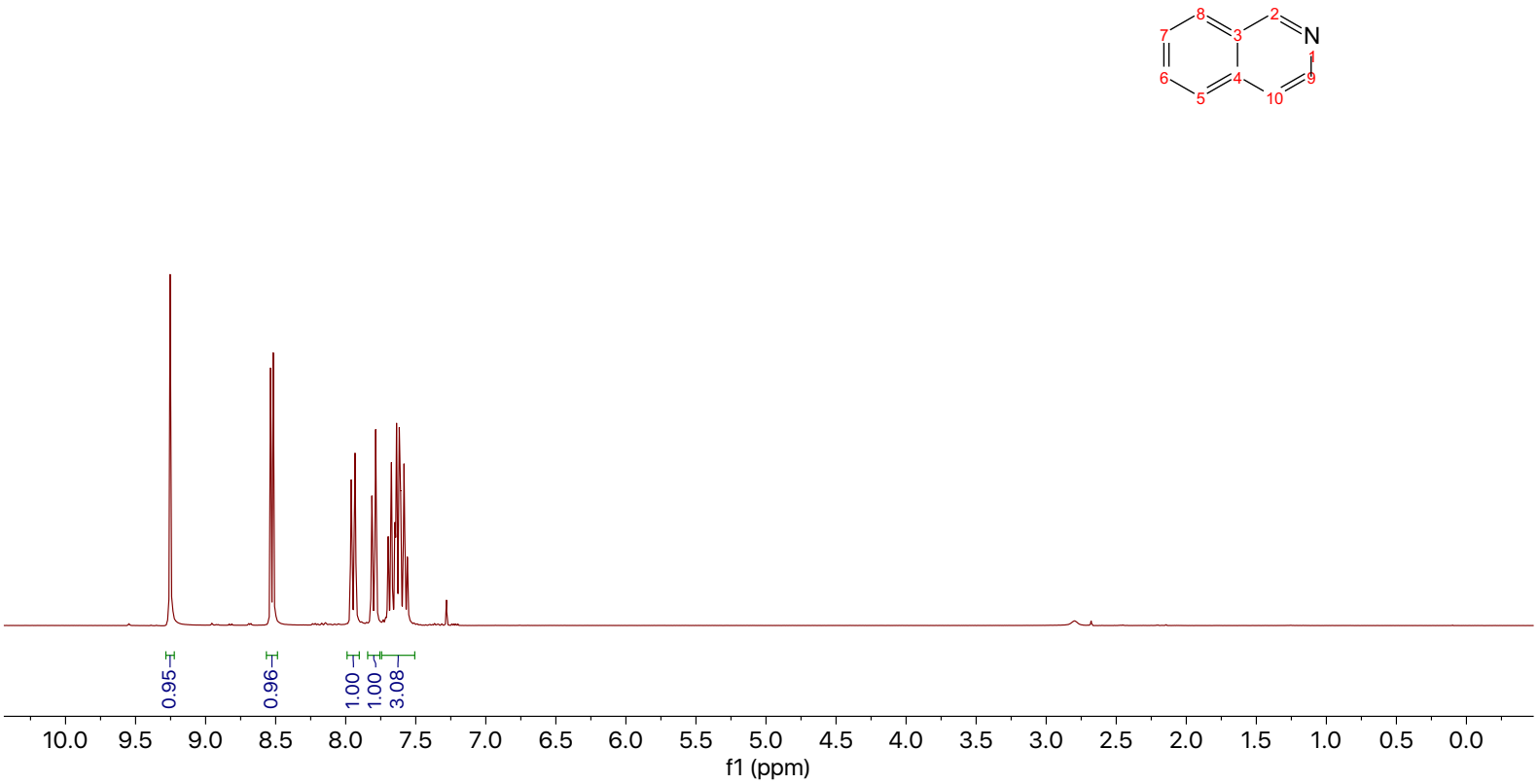


SI Figure 108: ^{13}C NMR spectrum of 1H-pyrrolo[2,3-b]pyridine in $CDCl_3$ from HDF of 5-fluoro-1H-pyrrolo[2,3-b]pyridine (19).

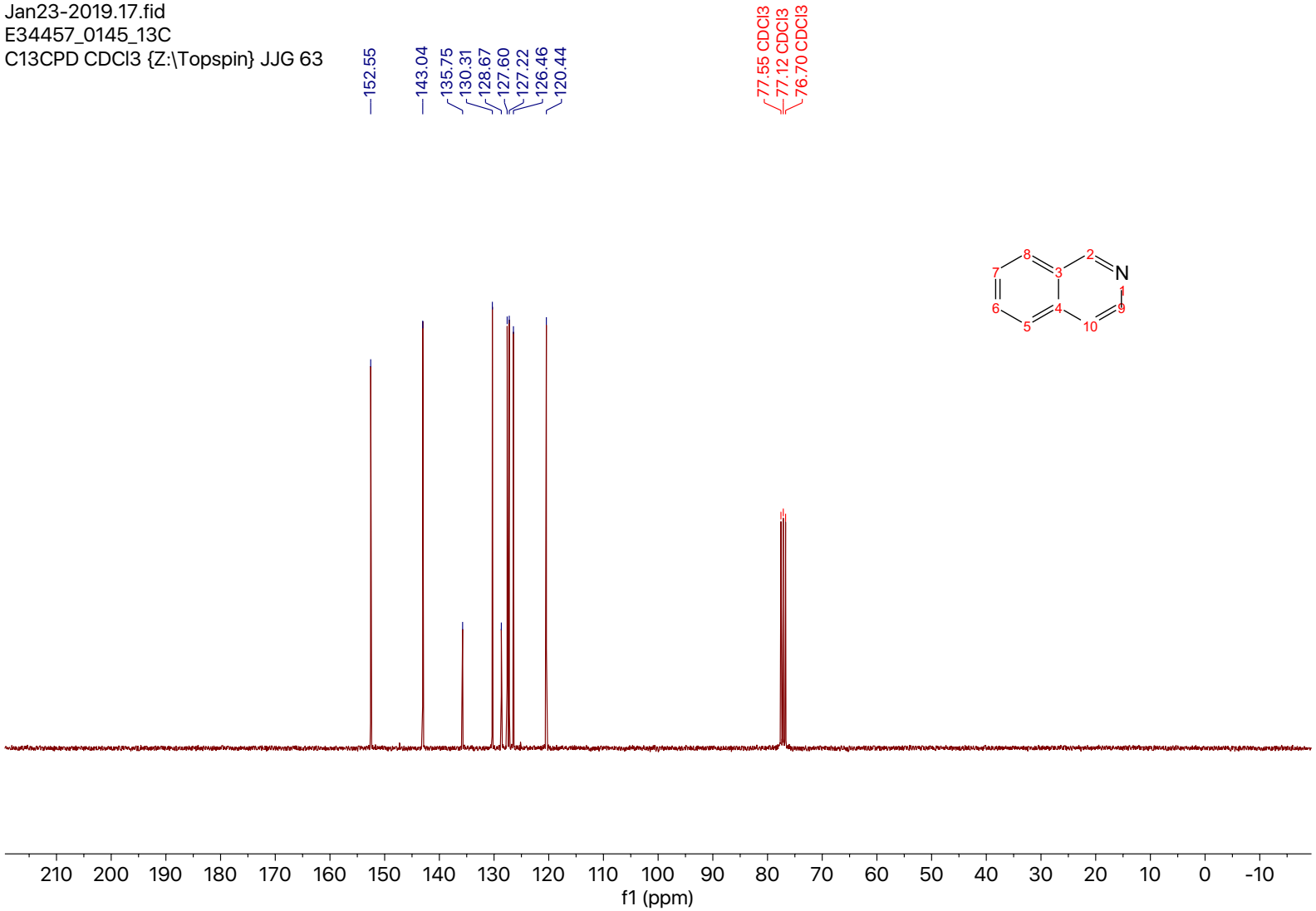


SI Figure 109: HSQC spectrum of 1H-pyrrolo[2,3-b]pyridine in $CDCl_3$ from HDF of 5-fluoro-1H-pyrrolo[2,3-b]pyridine (19).

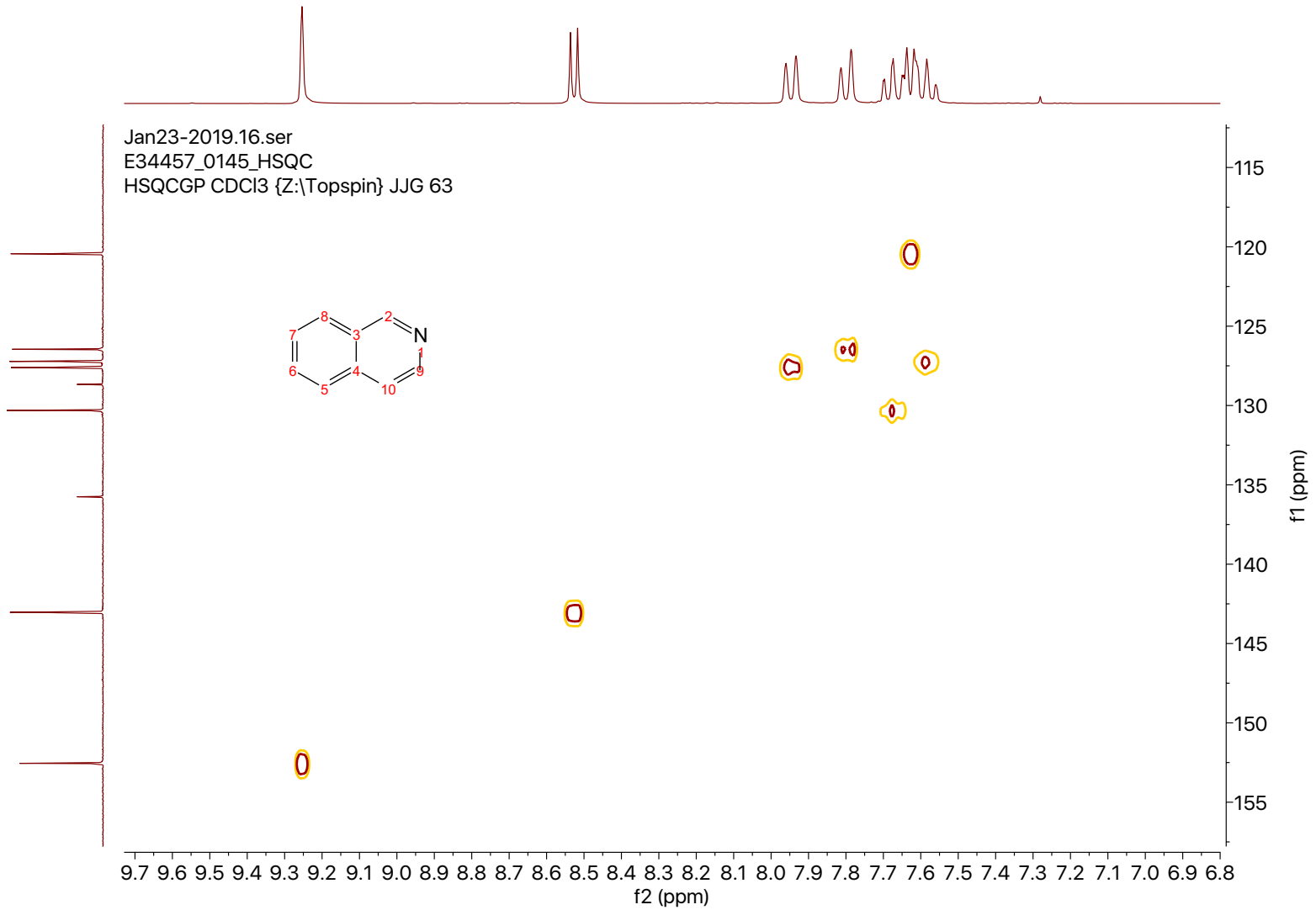
Jan23-2019.15.fid
E34457_0145_HSQC_1H
PROTON CDCl3 {Z:\Topspin} JJG 63



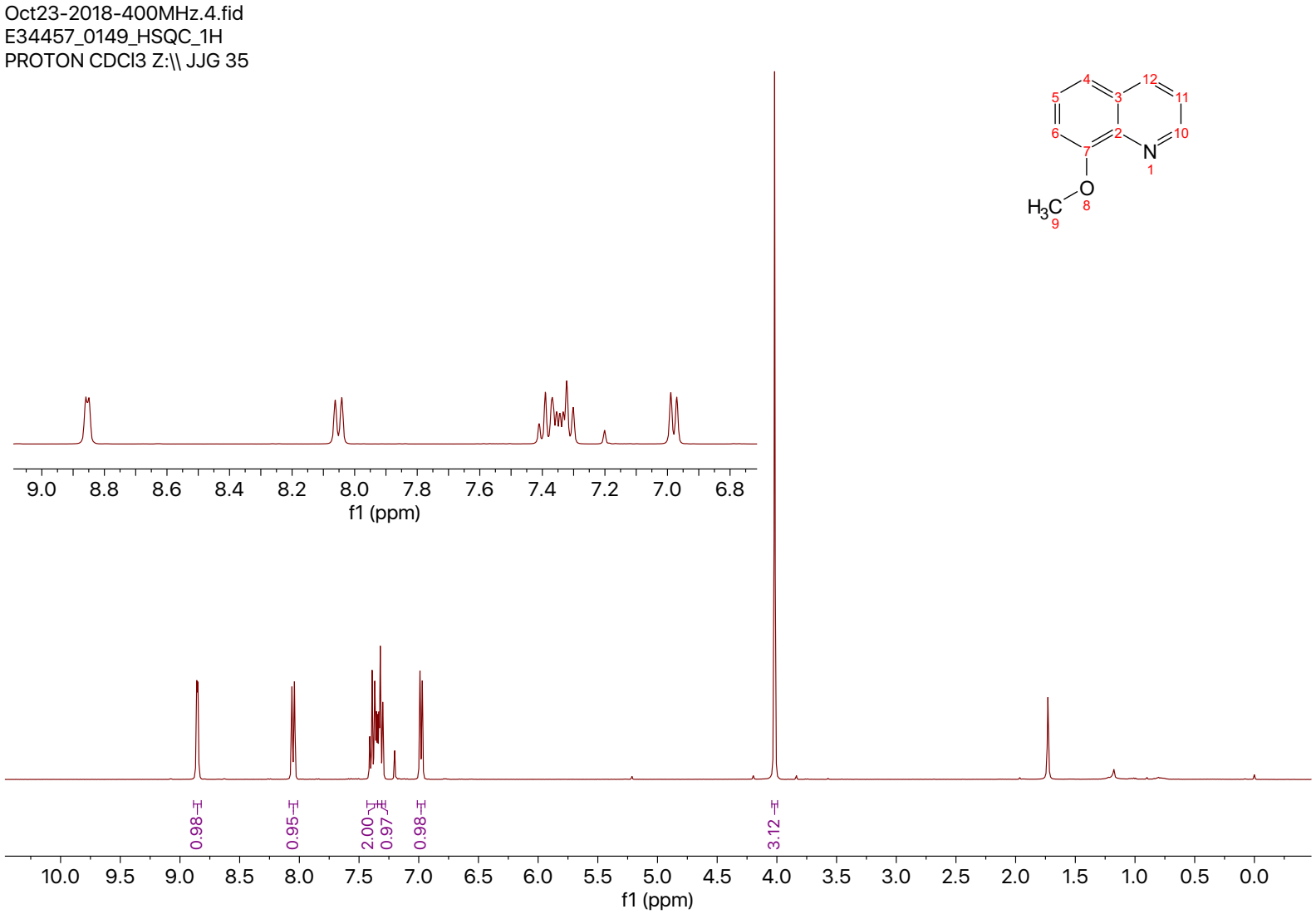
SI Figure 110: ^{1}H NMR spectrum of isoquinoline in $CDCl_3$ from HDF of 6-fluoroisoquinoline (20).



SI Figure 111: ^{13}C NMR spectrum of isoquinoline in $CDCl_3$ from HDF of 6-fluoroisoquinoline (20).

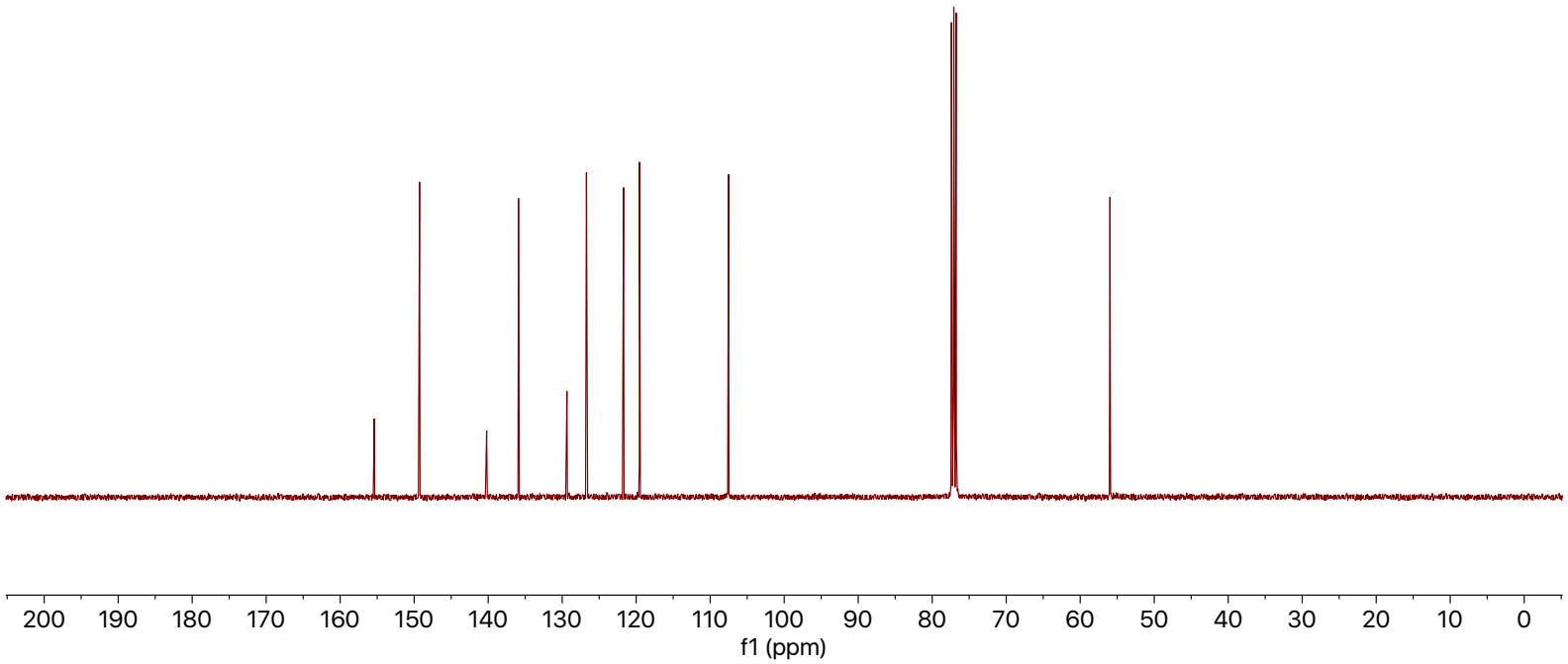


SI Figure 112: HSQC spectrum of isoquinoline in $CDCl_3$ from HDF of 6-fluoroisoquinoline (20).

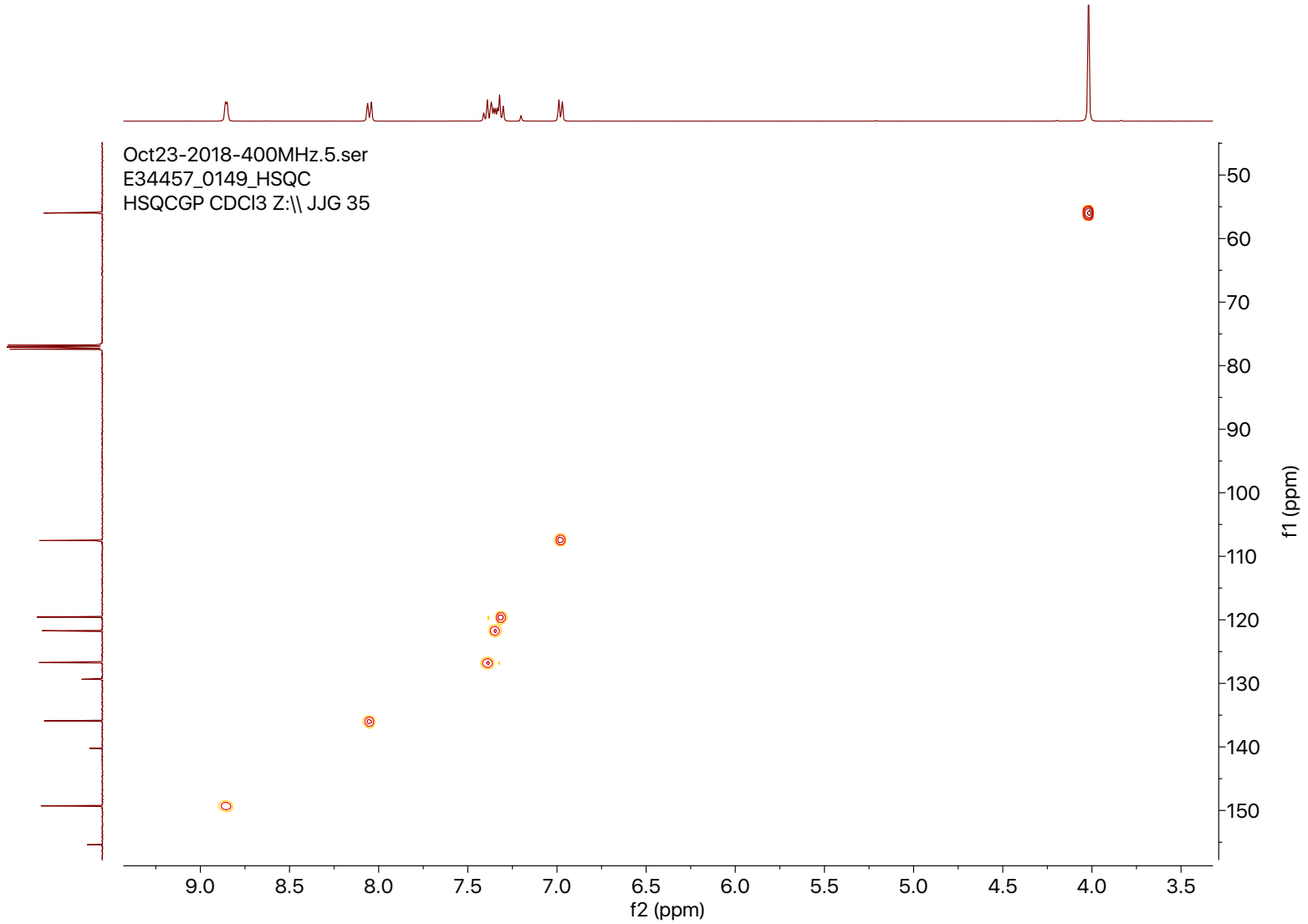


SI Figure 113: ^{1}H NMR spectrum of 8-methoxyquinoline in $CDCl_3$ from HDF of 6-fluoro-8-methoxyquinoline (21a).

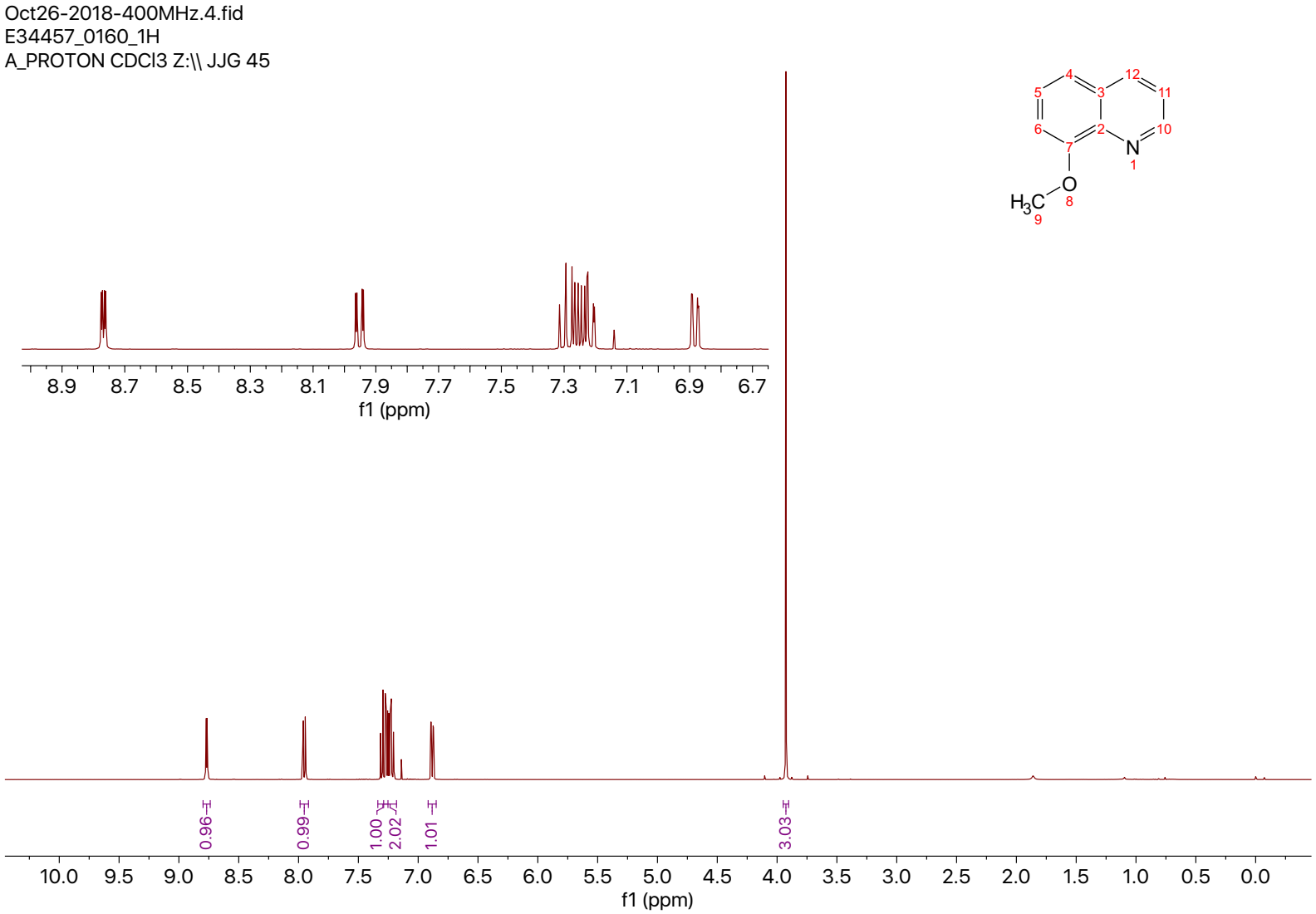
Oct23-2018-400MHz.6.fid
E34457_0149_13C
C13CPD CDCl3 Z:\\ JJG 35



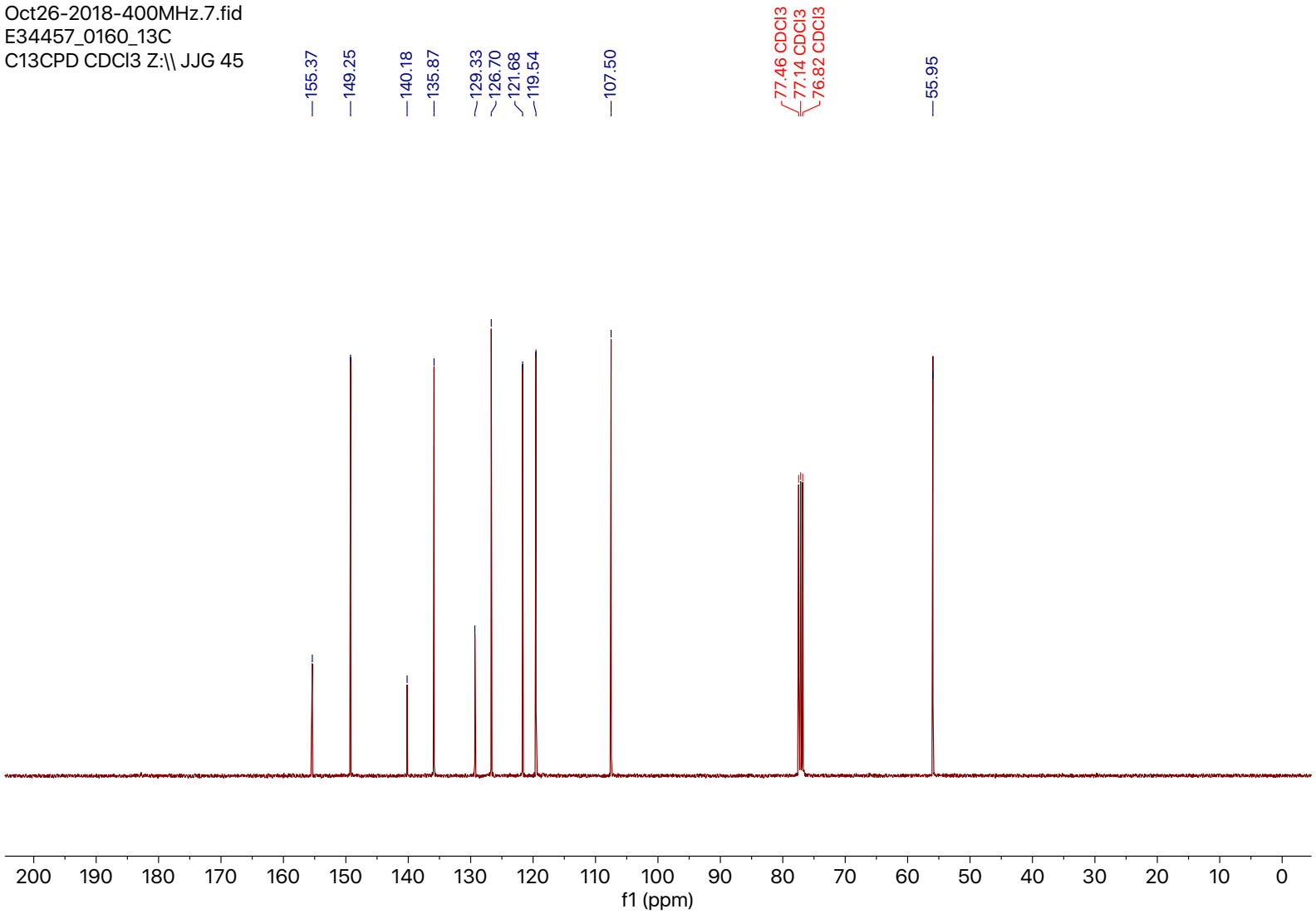
SI Figure 114: ^{13}C NMR spectrum of 8-methoxyquinoline in $CDCl_3$ from HDF of 6-fluoro-8-methoxyquinoline (21a).



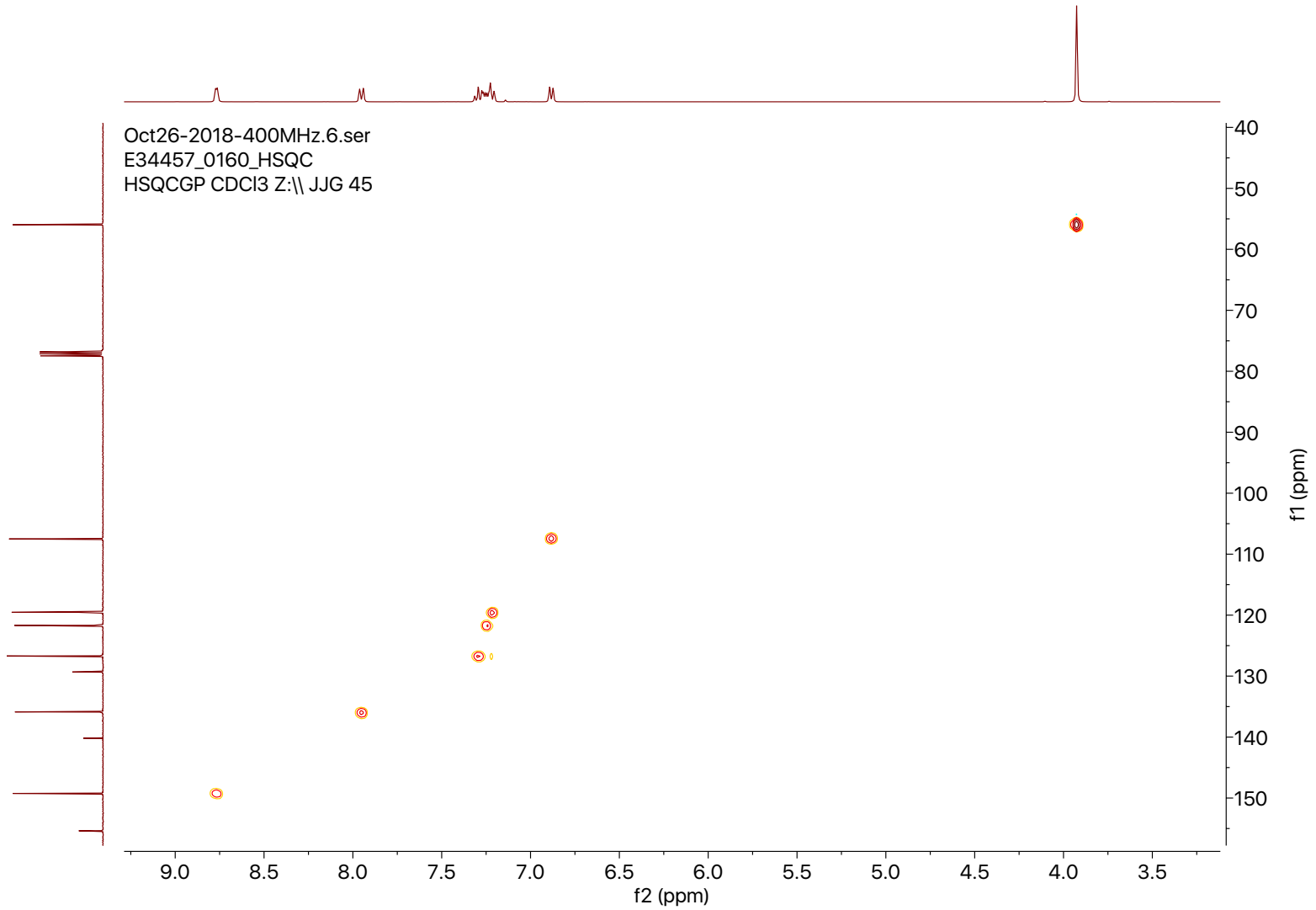
SI Figure 115: HSQC NMR spectrum of 8-methoxyquinoline in $CDCl_3$ from HDF of 6-fluoro-8-methoxyquinoline (21a).



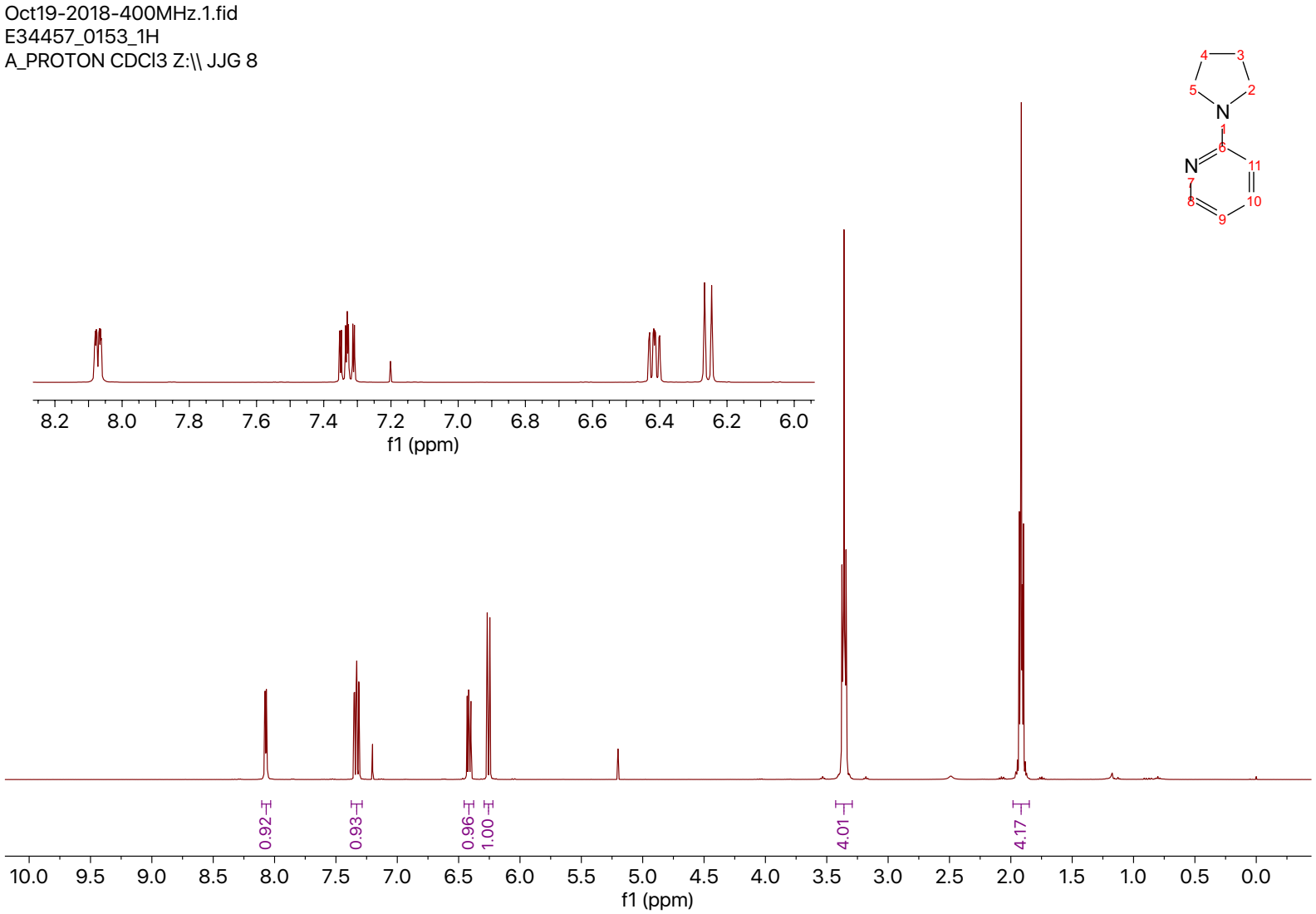
SI Figure 116: ^{1}H NMR spectrum of 8-methoxyquinoline in $CDCl_3$ from HDF of 5-fluoro-8-methoxyquinoline (21b).



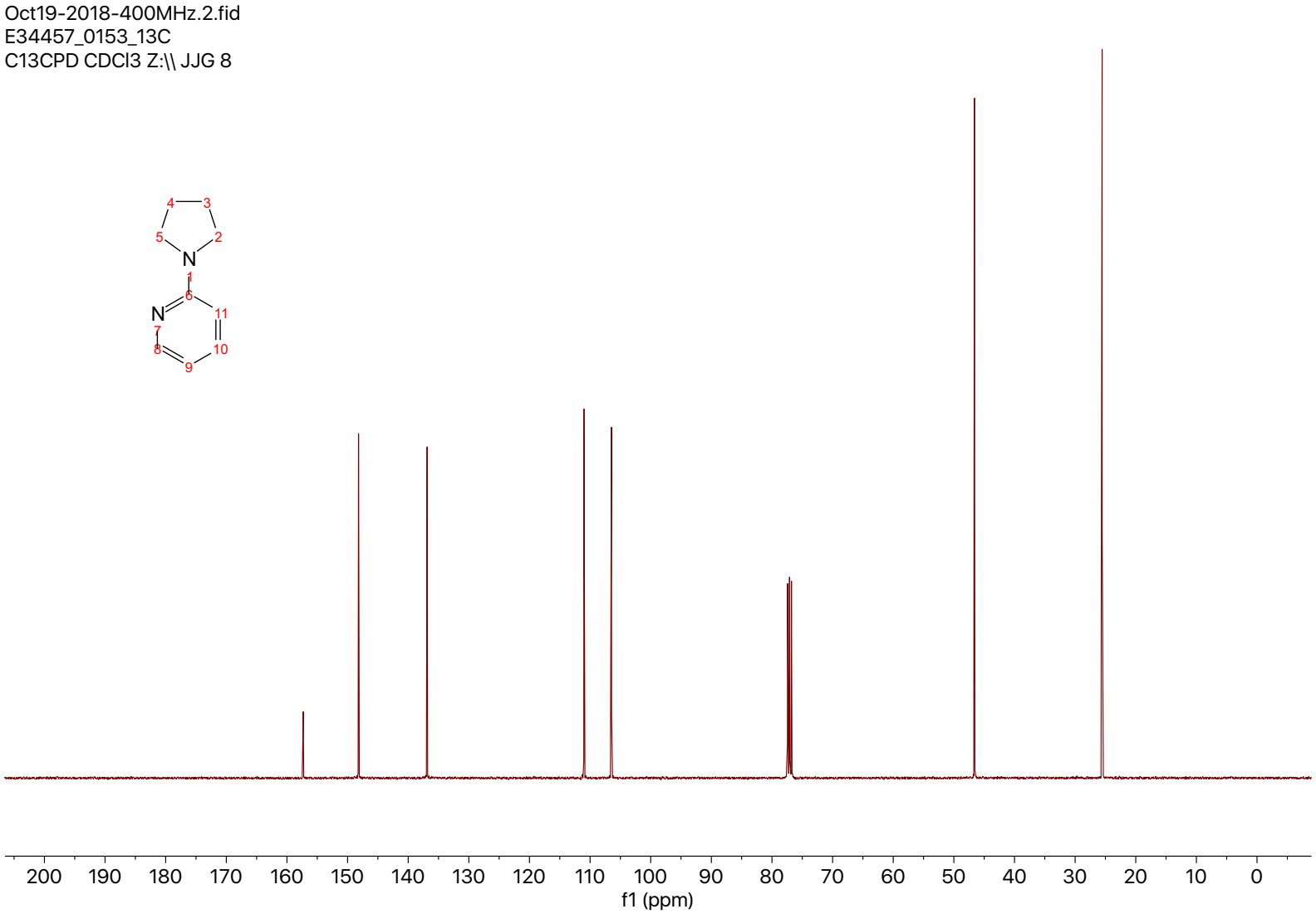
SI Figure 117: ^{13}C NMR spectrum of 8-methoxyquinoline in $CDCl_3$ from HDF of 5-fluoro-8-methoxyquinoline (21b).



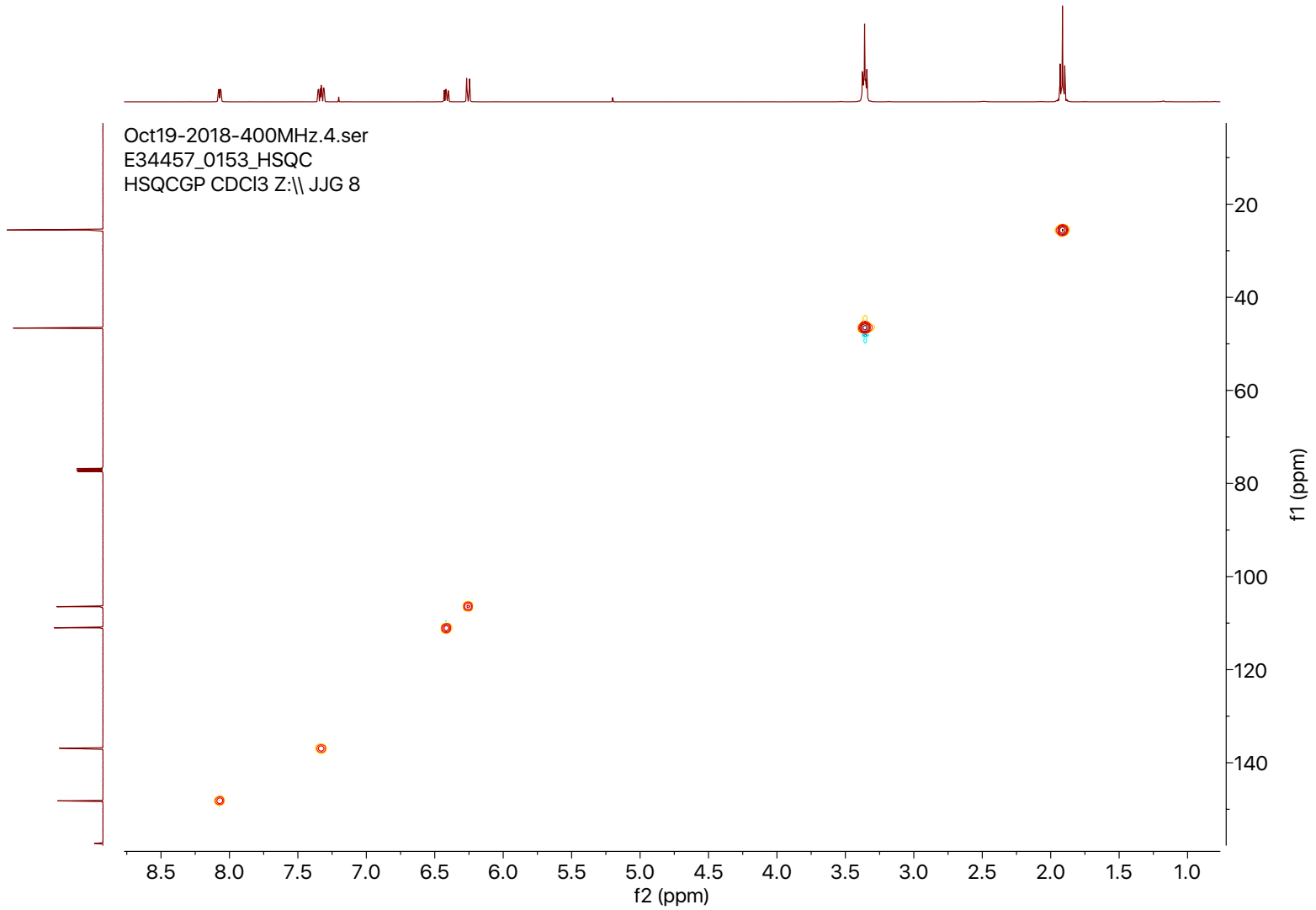
SI Figure 118: HSQC NMR spectrum of 8-methoxyquinoline in $CDCl_3$ from HDF of 5-fluoro-8-methoxyquinoline (21b).



SI Figure 119: ^{1}H NMR spectrum of 2-(pyrrolidin-1-yl)pyridine in $CDCl_3$ from HDF of 5-fluoro-2-(pyrrolidin-1-yl)pyridine (22a).

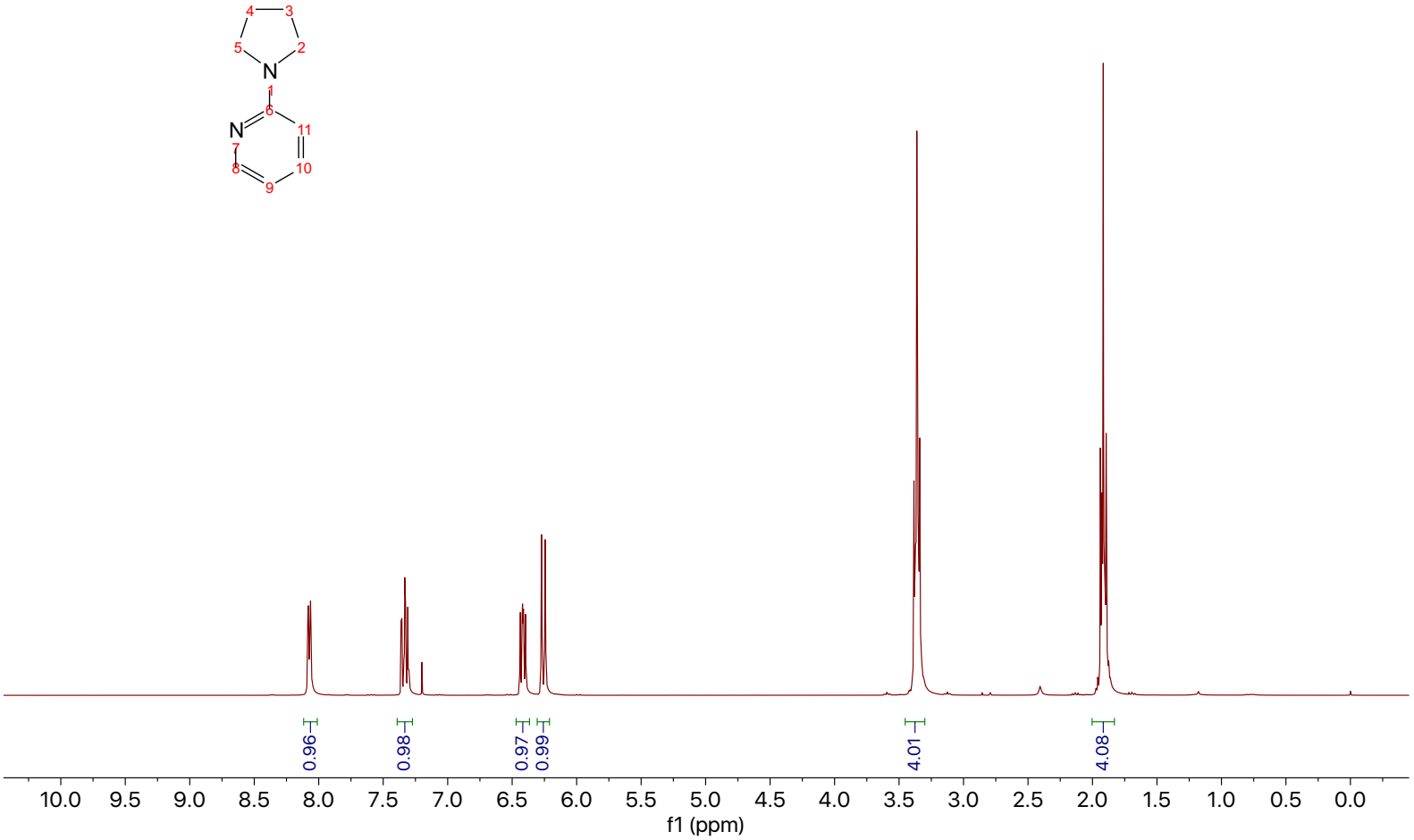


SI Figure 120: ^{13}C NMR spectrum of 2-(pyrrolidin-1-yl)pyridine in $CDCl_3$ from HDF of 5-fluoro-2-(pyrrolidin-1-yl)pyridine (22a).



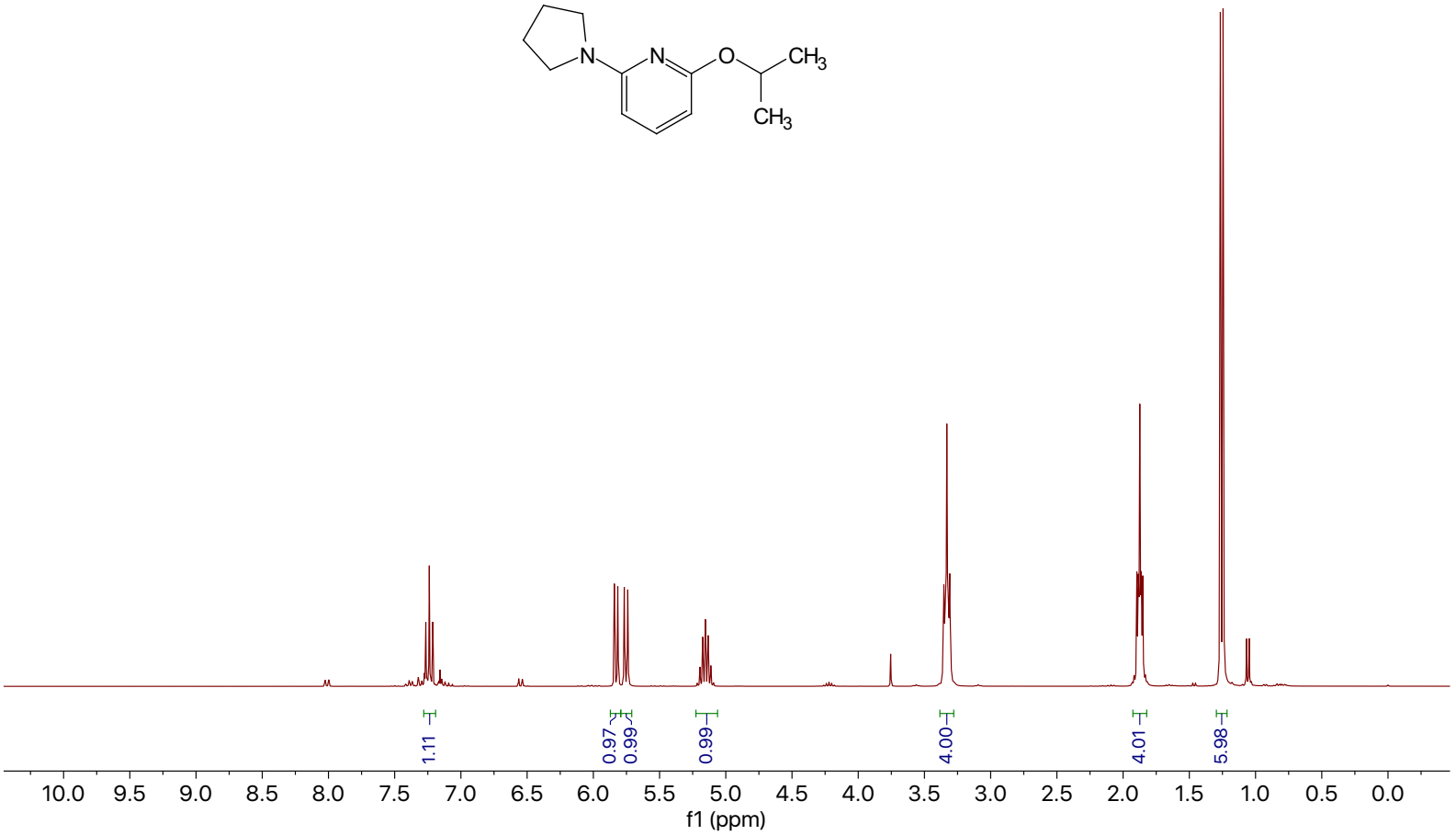
SI Figure 121: HSQC NMR spectrum of 2-(pyrrolidin-1-yl)pyridine in $CDCl_3$ from HDF of 5-fluoro-2-(pyrrolidin-1-yl)pyridine (22a).

Jan23-2019.11.fid
E34457_0249_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 34



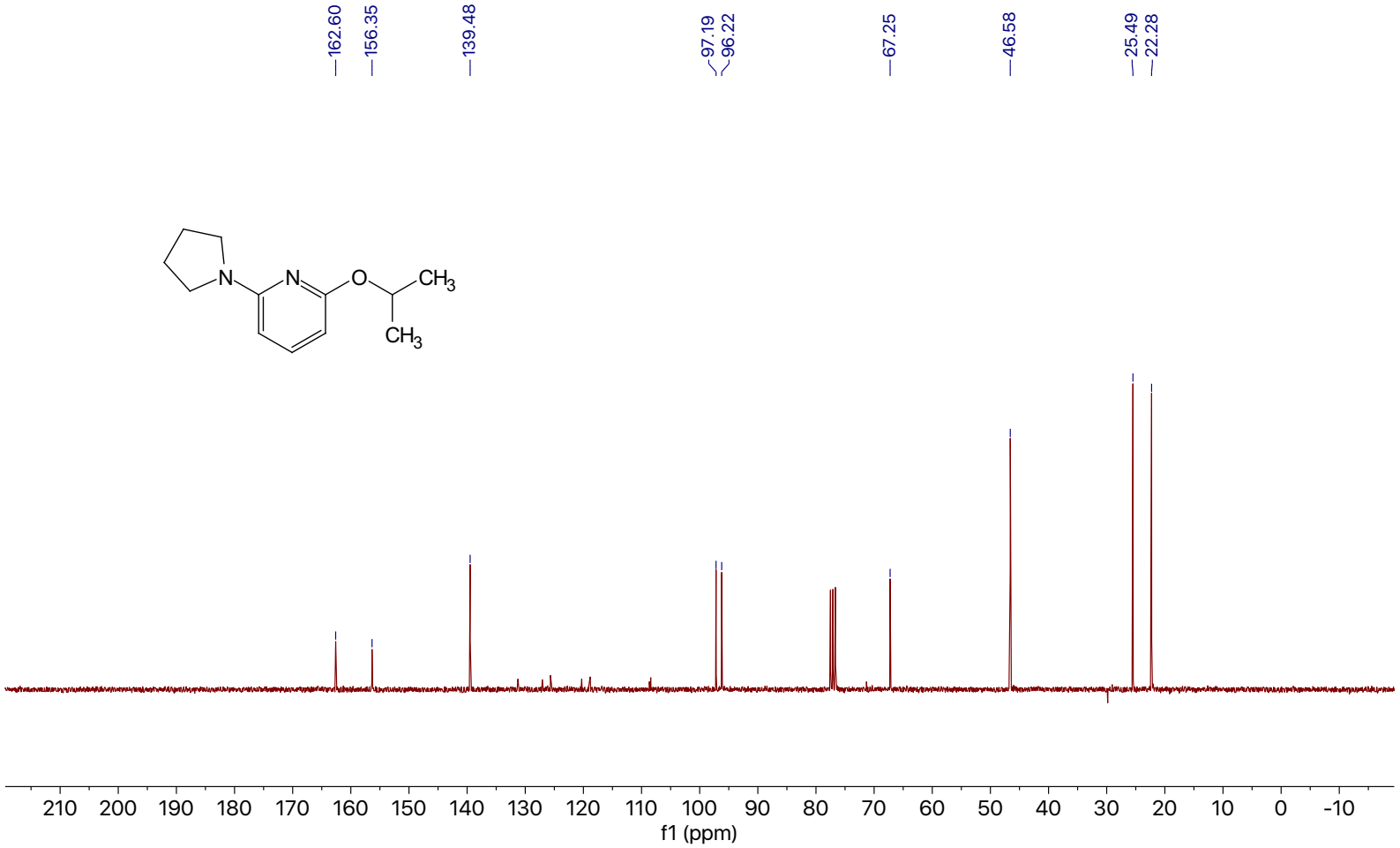
SI Figure 122: ^{1}H NMR spectrum of 2-(pyrrolidin-1-yl)pyridine in $CDCl_3$ from HDF of 2-fluoro-6-(pyrrolidin-1-yl)pyridine (22b).

Mar05-2019.1.fid
E34457_0290_HSQC_1H
PROTON CDCl3 Z:\\ JJG 108

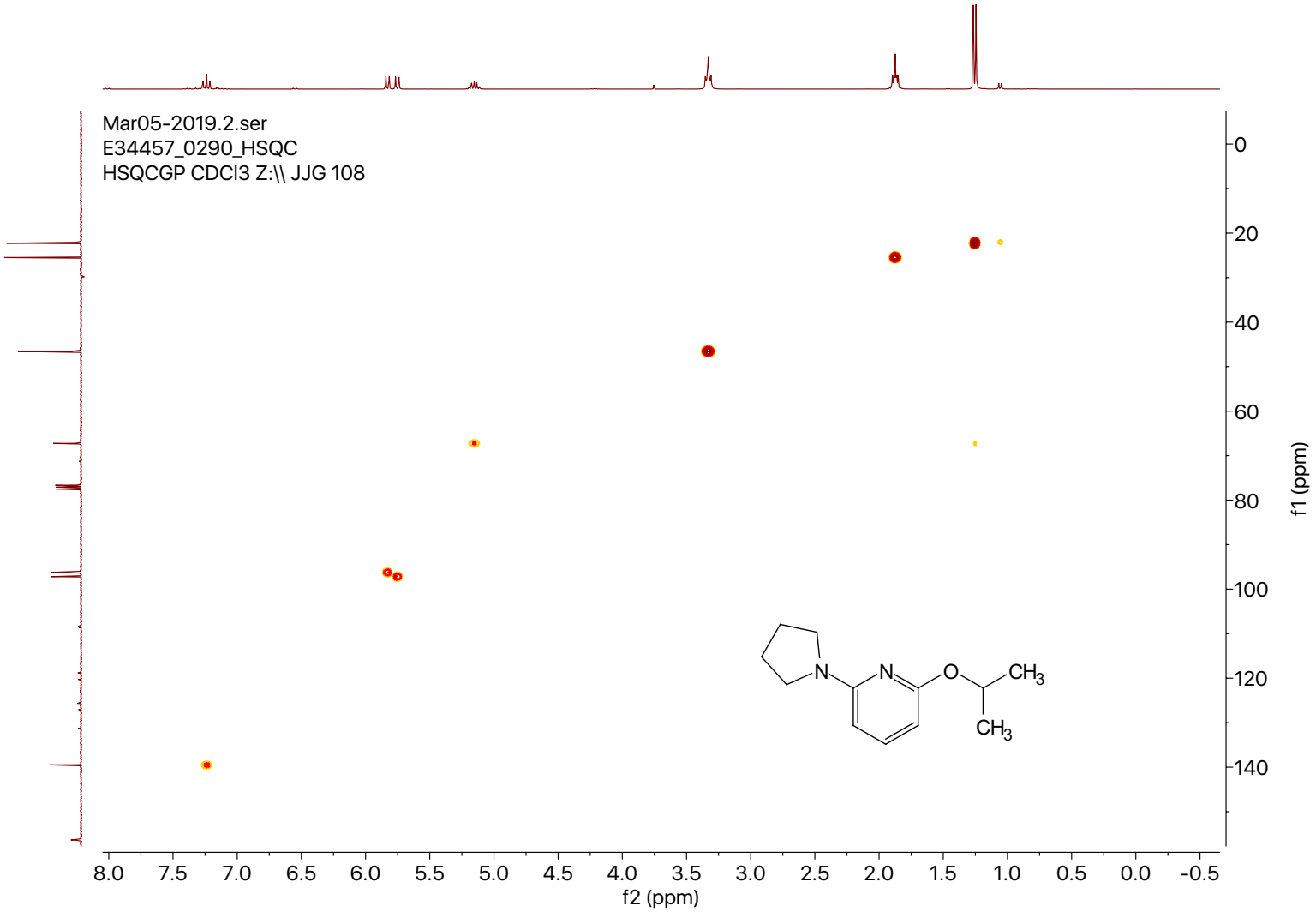


SI Figure 123: ^{1}H NMR spectrum of 2-isopropoxy-6-(pyrrolidin-1-yl)pyridine in $CDCl_3$ from SNAr of 22a with *iso*-propanol.

Mar05-2019.3.fid
E34457_0290_13C
C13CPD32 CDCl3 Z:\\ JJG 108

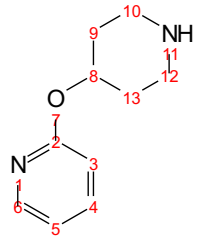


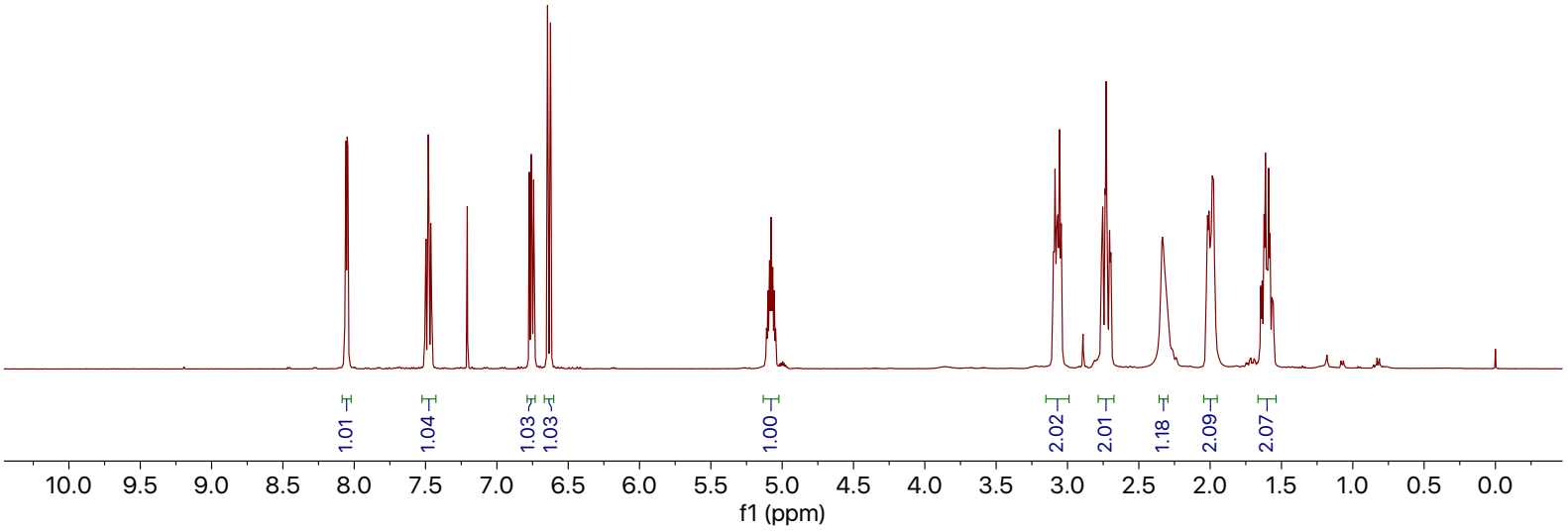
SI Figure 124: ^{13}C NMR spectrum of 2-isopropoxy-6-(pyrrolidin-1-yl)pyridine in $CDCl_3$ from SNAr of 22a with *iso*-propanol.



SI Figure 125: HSQC spectrum of 2-isopropoxy-6-(pyrrolidin-1-yl)pyridine in $CDCl_3$ from SNAr of 22a with *iso*-propanol.

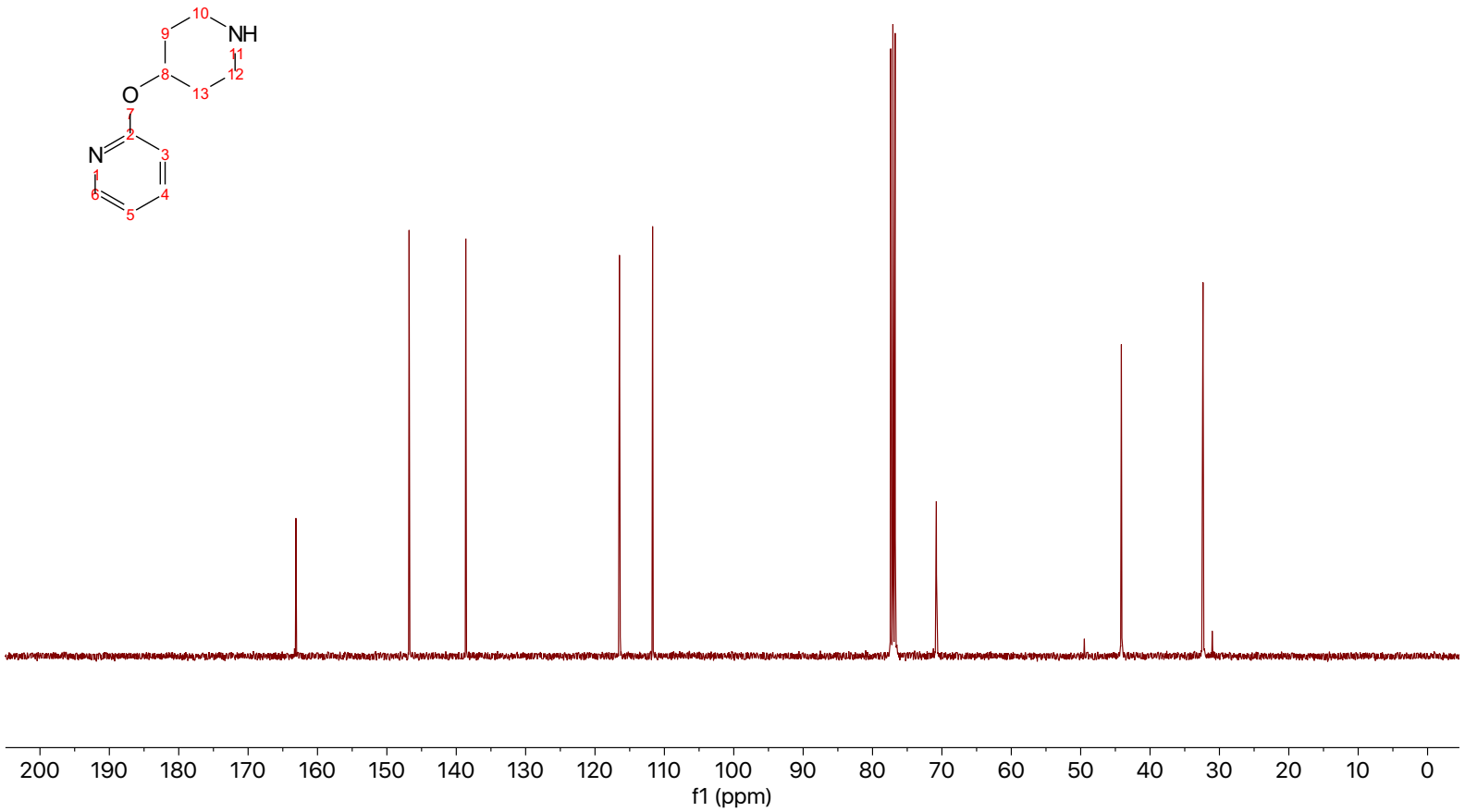
Oct19-2018-400MHz.9.fid
E34457_0155_1H
A_PROTON CDCl3 Z:\\ JJG 10



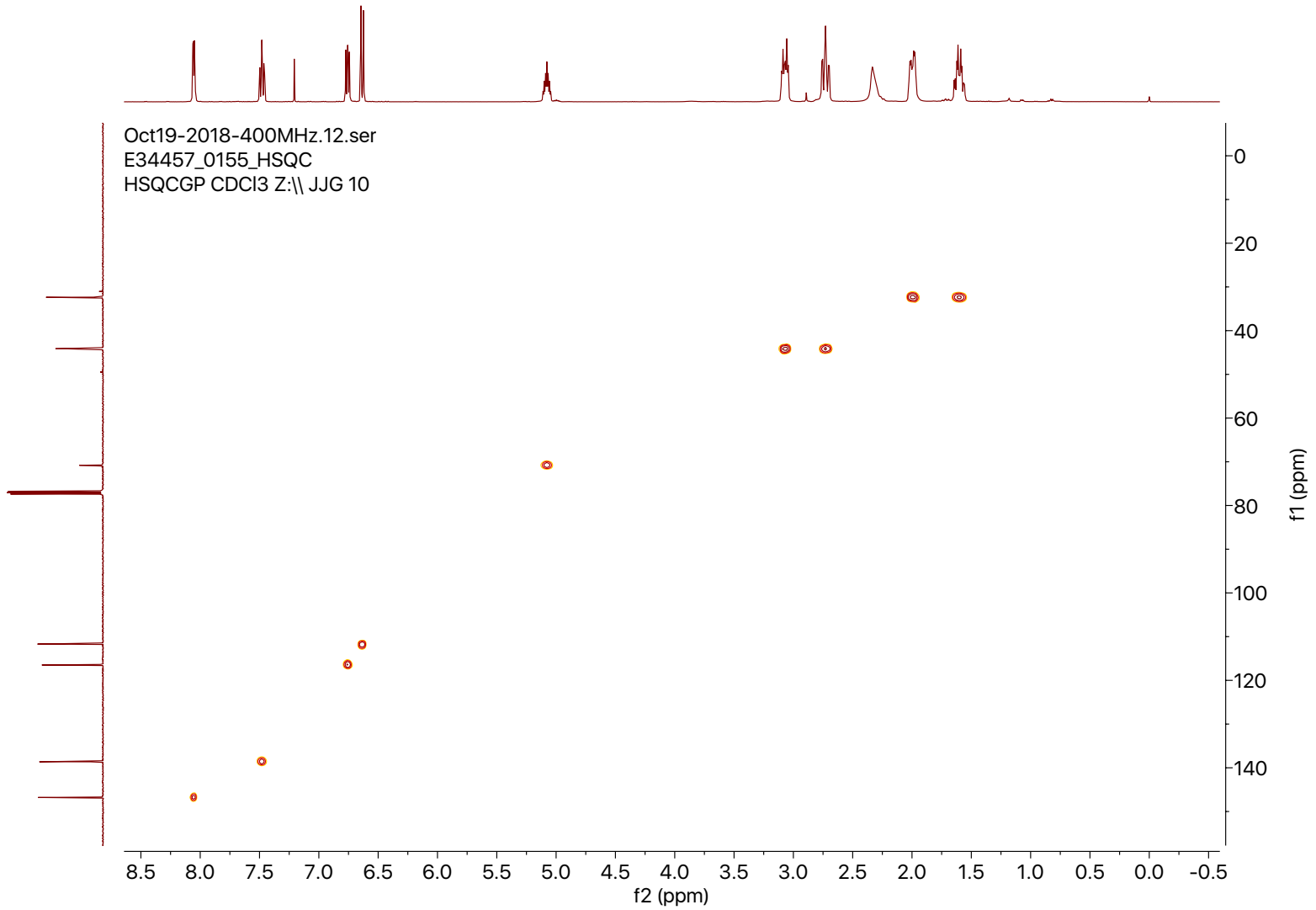


SI Figure 126: ^{1}H NMR spectrum of 2-(piperidin-4-yloxy)pyridine in $CDCl_3$ from HDF of 3-fluoro-2-(piperidin-4-yloxy)pyridine (23).

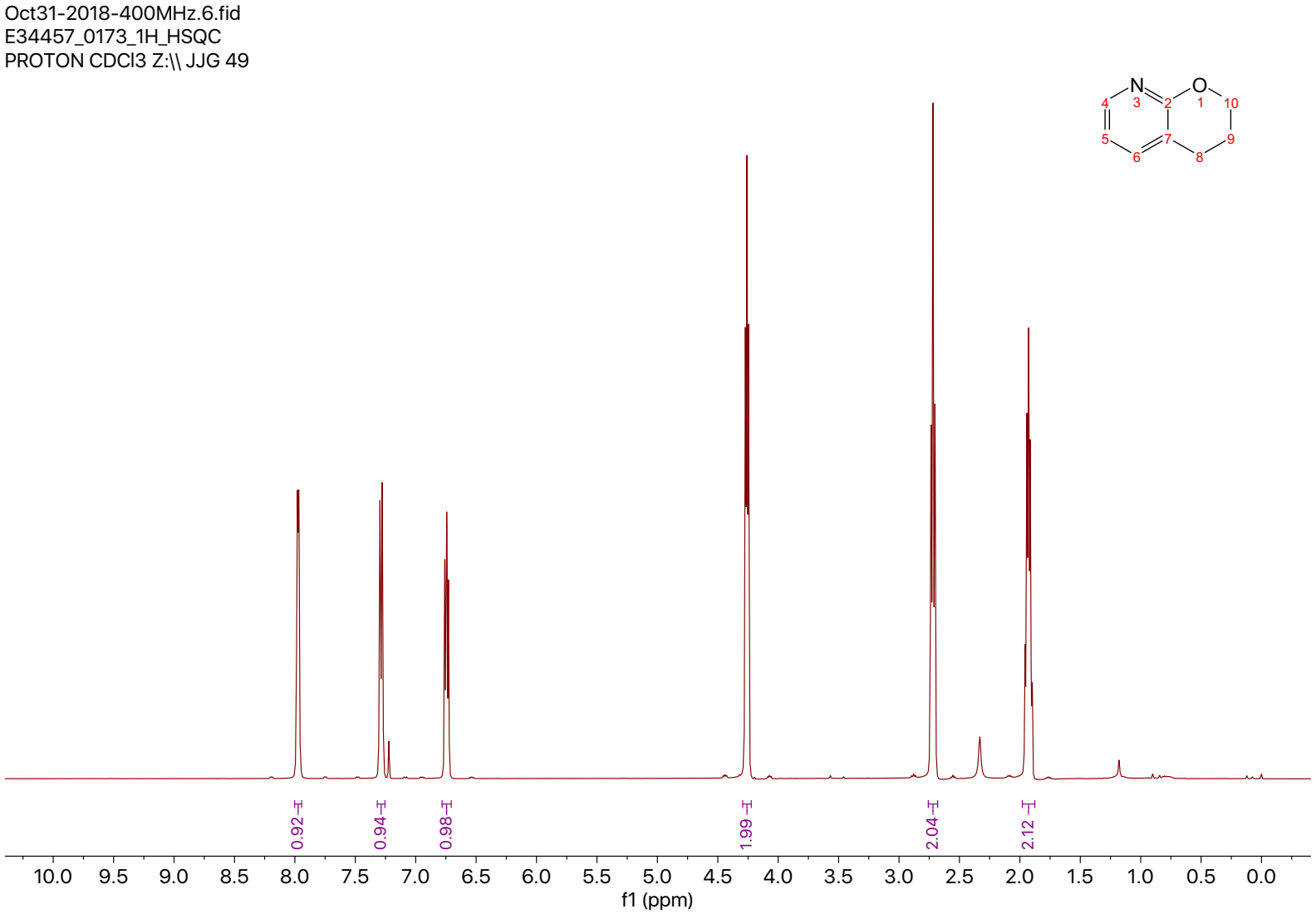
Oct19-2018-400MHz.10.fid
E34457_0155_13C
C13CPD CDCl3 Z:\\ JJG 10



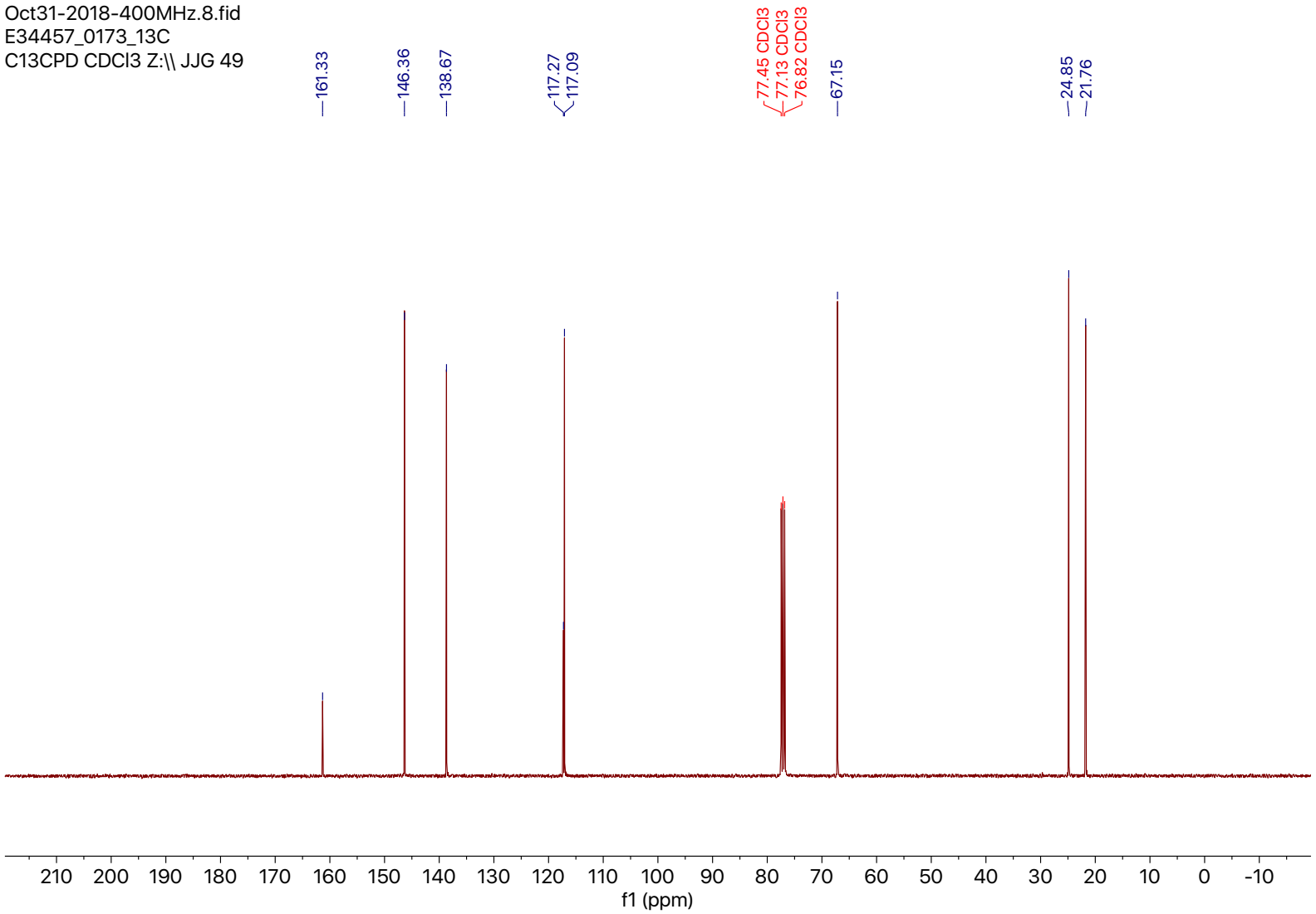
SI Figure 127: ^{13}C NMR spectrum of 2-(piperidin-4-yloxy)pyridine in $CDCl_3$ from HDF of 3-fluoro-2-(piperidin-4-yloxy)pyridine (23).



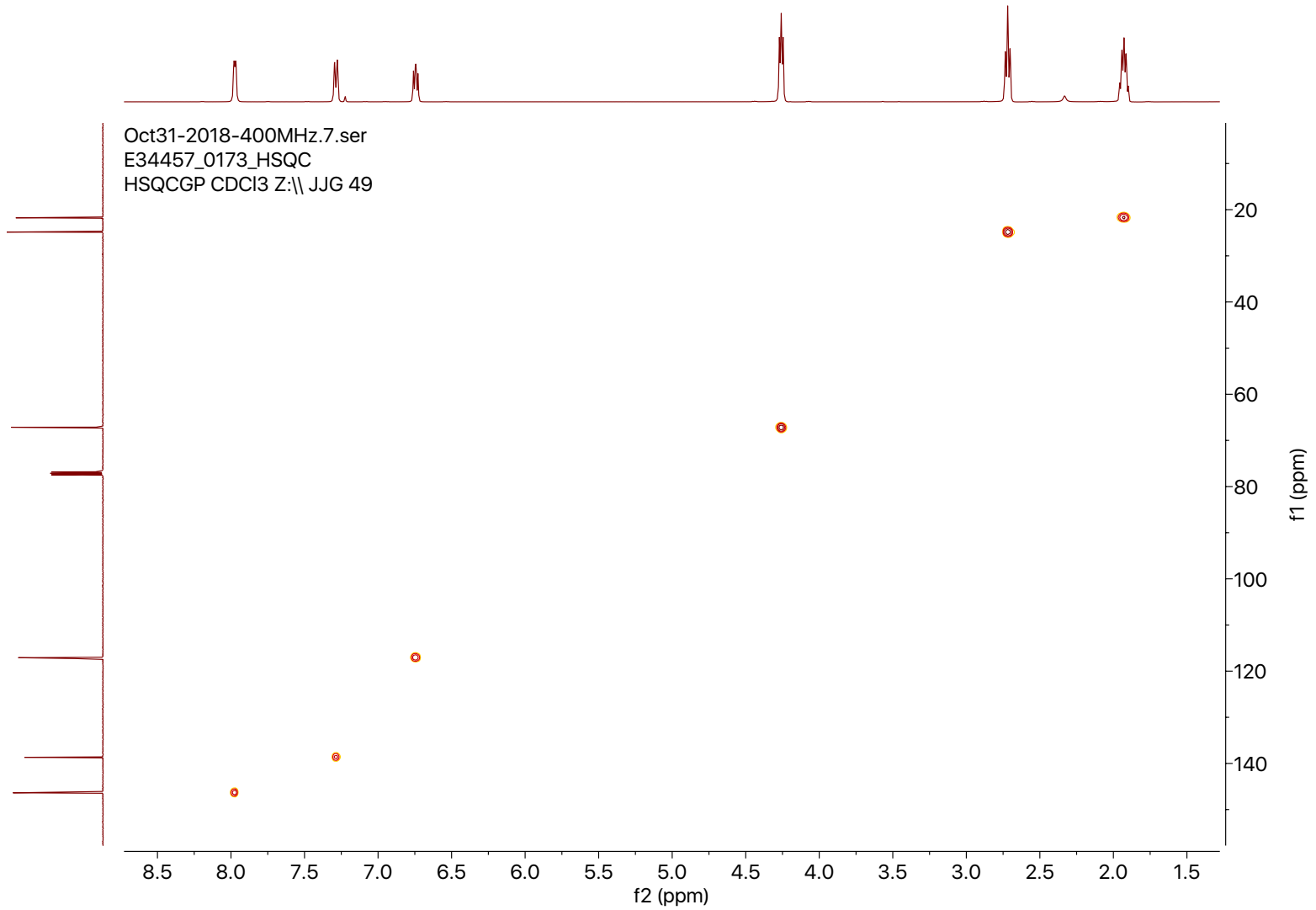
SI Figure 128: HSQC NMR spectrum of 2-(piperidin-4-yloxy)pyridine in $CDCl_3$ from HDF of 3-fluoro-2-(piperidin-4-yloxy)pyridine (23).



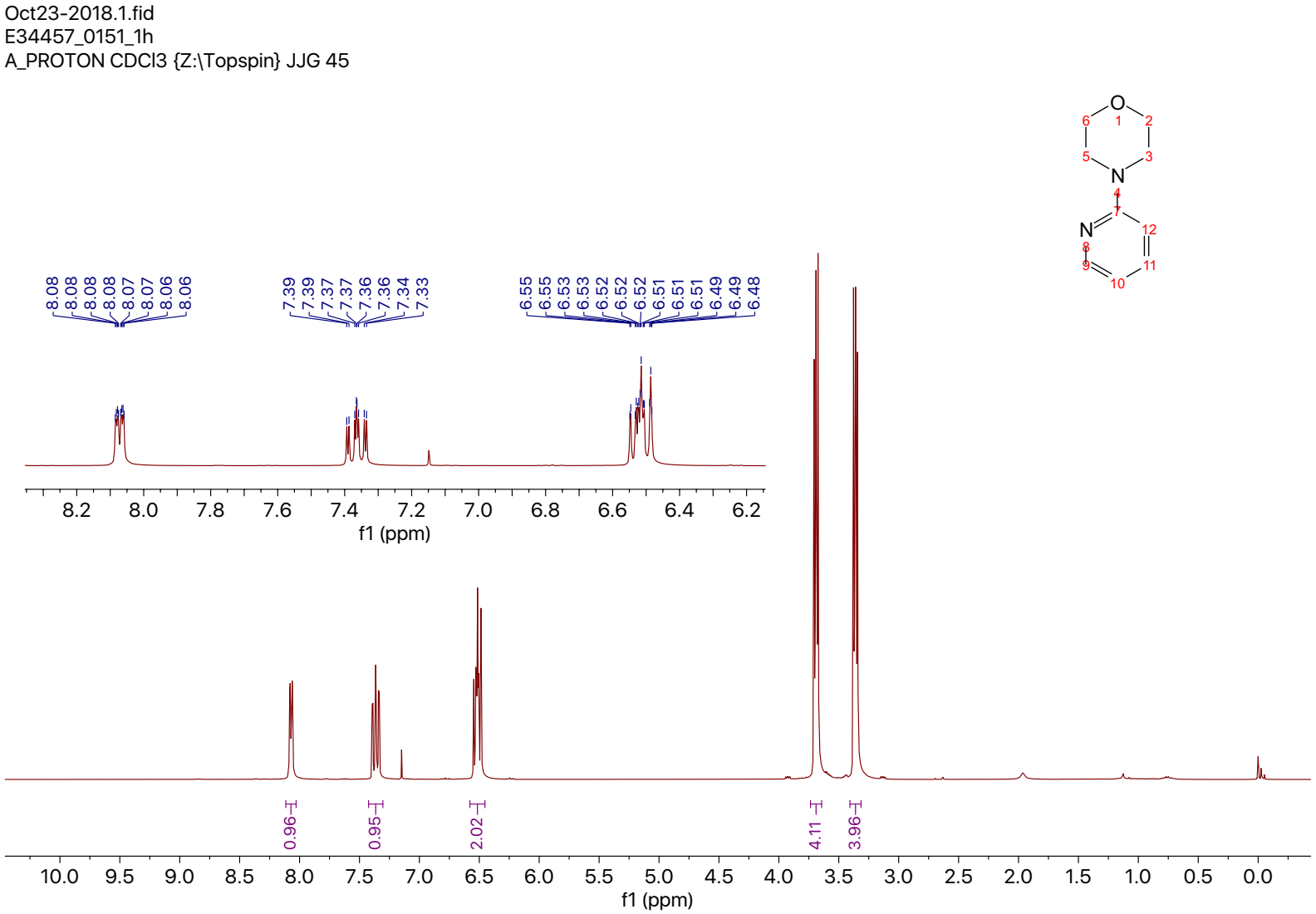
SI Figure 129: ^{1}H NMR spectrum of 3,4-dihydro-2H-pyrano[2,3-b]pyridine in $CDCl_3$ from HDF of 6-fluoro-3,4-dihydro-2H-pyrano[2,3-b]pyridine (24).



SI Figure 130: ^{13}C NMR spectrum of 3,4-dihydro-2H-pyrano[2,3-b]pyridine in $CDCl_3$ from HDF of 6-fluoro-3,4-dihydro-2H-pyrano[2,3-b]pyridine (24).

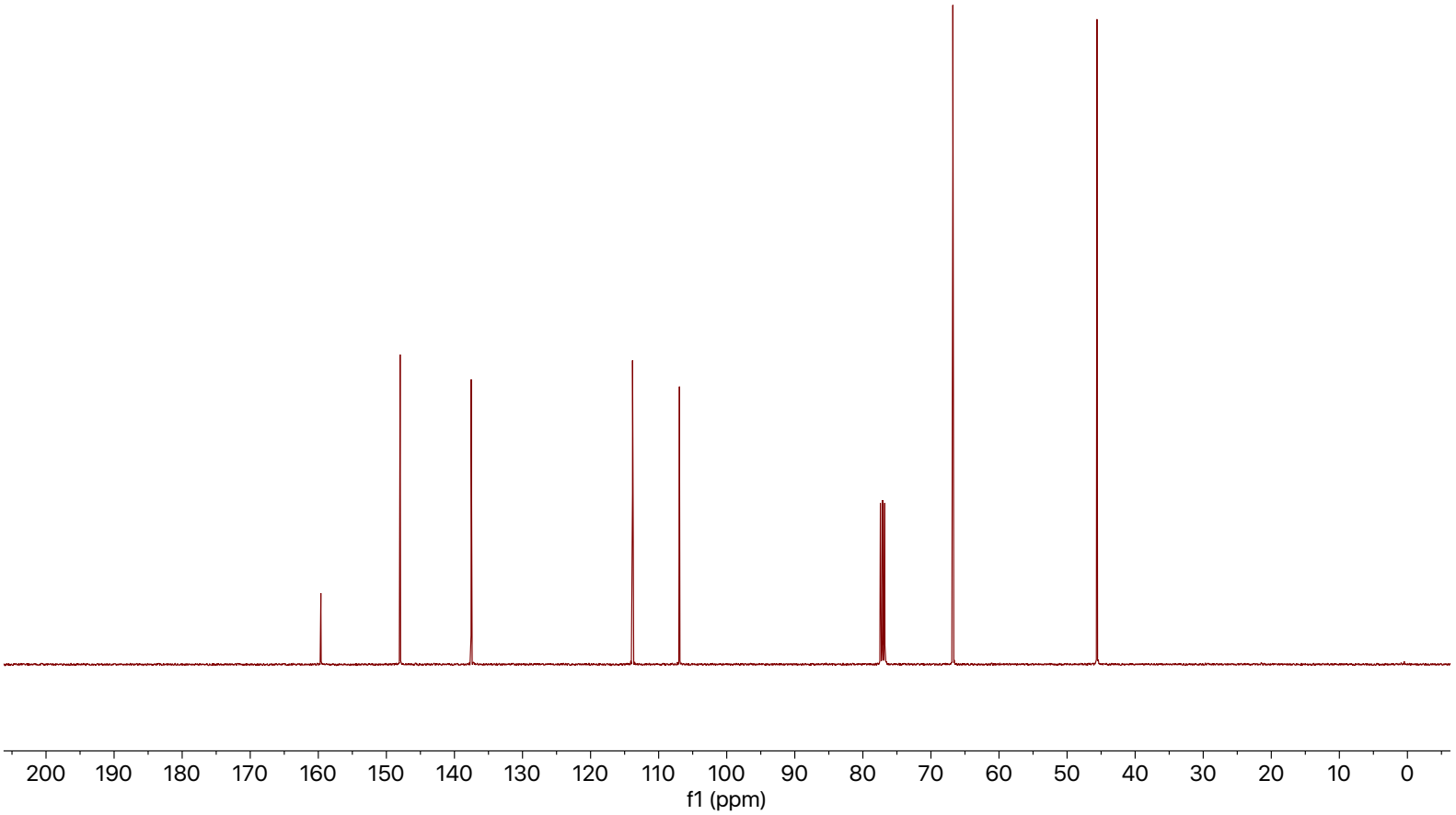


SI Figure 131: HSQC NMR spectrum of 3,4-dihydro-2H-pyrano[2,3-b]pyridine in $CDCl_3$ from HDF of 6-fluoro-3,4-dihydro-2H-pyrano[2,3-b]pyridine (24).

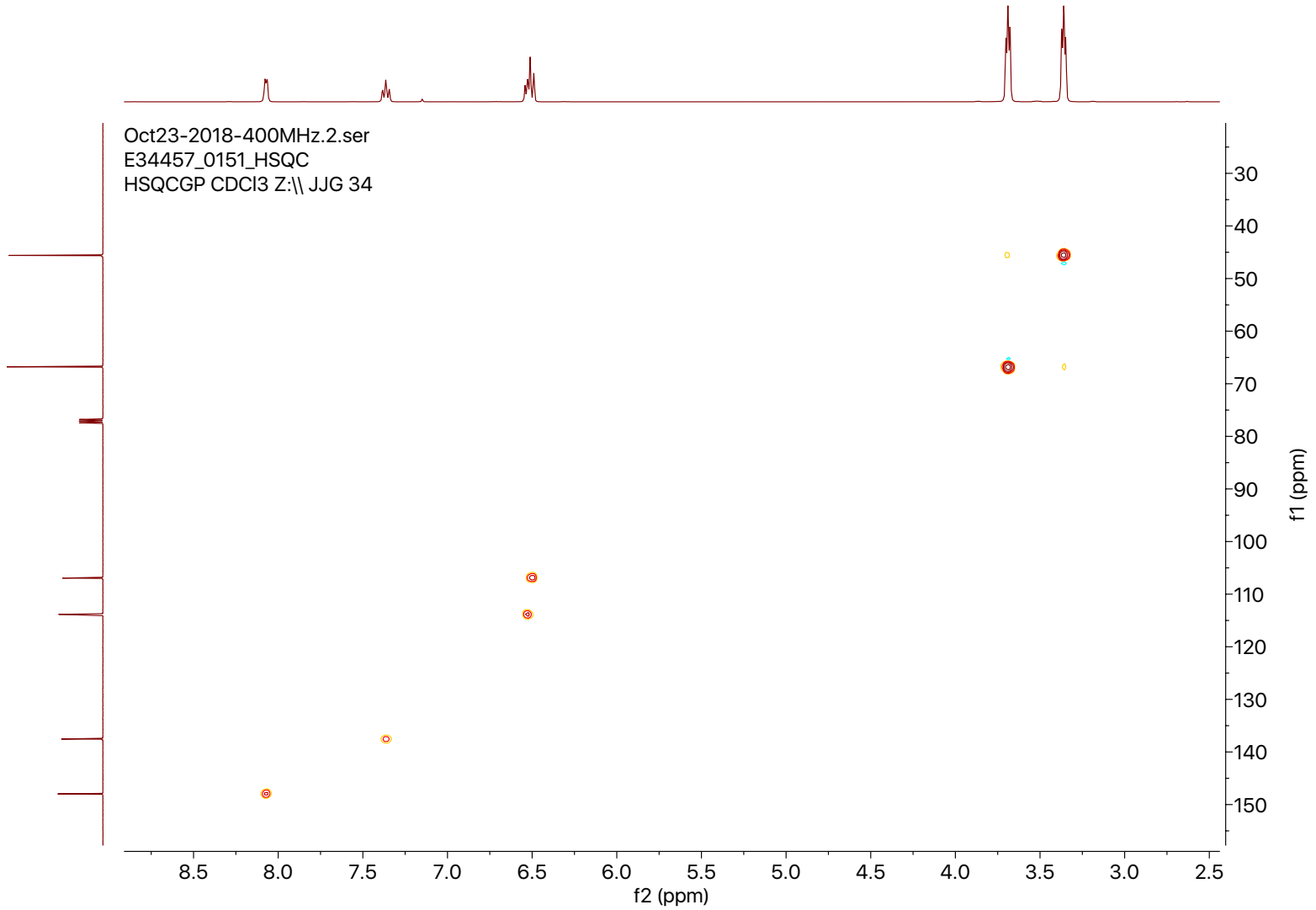


SI Figure 132: ^{1}H NMR spectrum of 4-(pyridin-2-yl)morpholine in $CDCl_3$ from HDF of 4-(3-fluoropyridin-2-yl)morpholine (25).

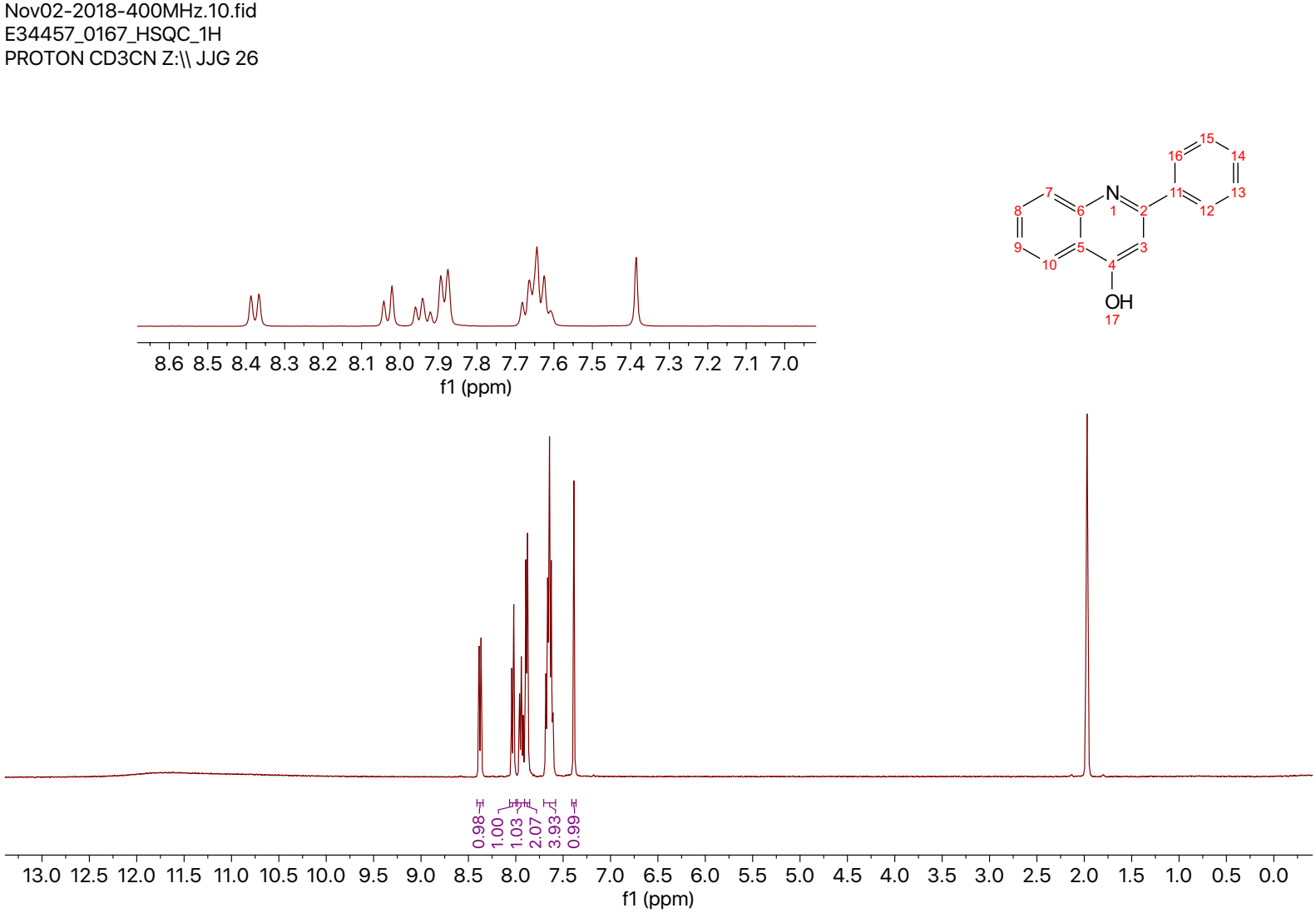
Oct23-2018-400MHz.3.fid
E34457_0151_13C
C13CPD CDCl3 Z:\\ JJG 34



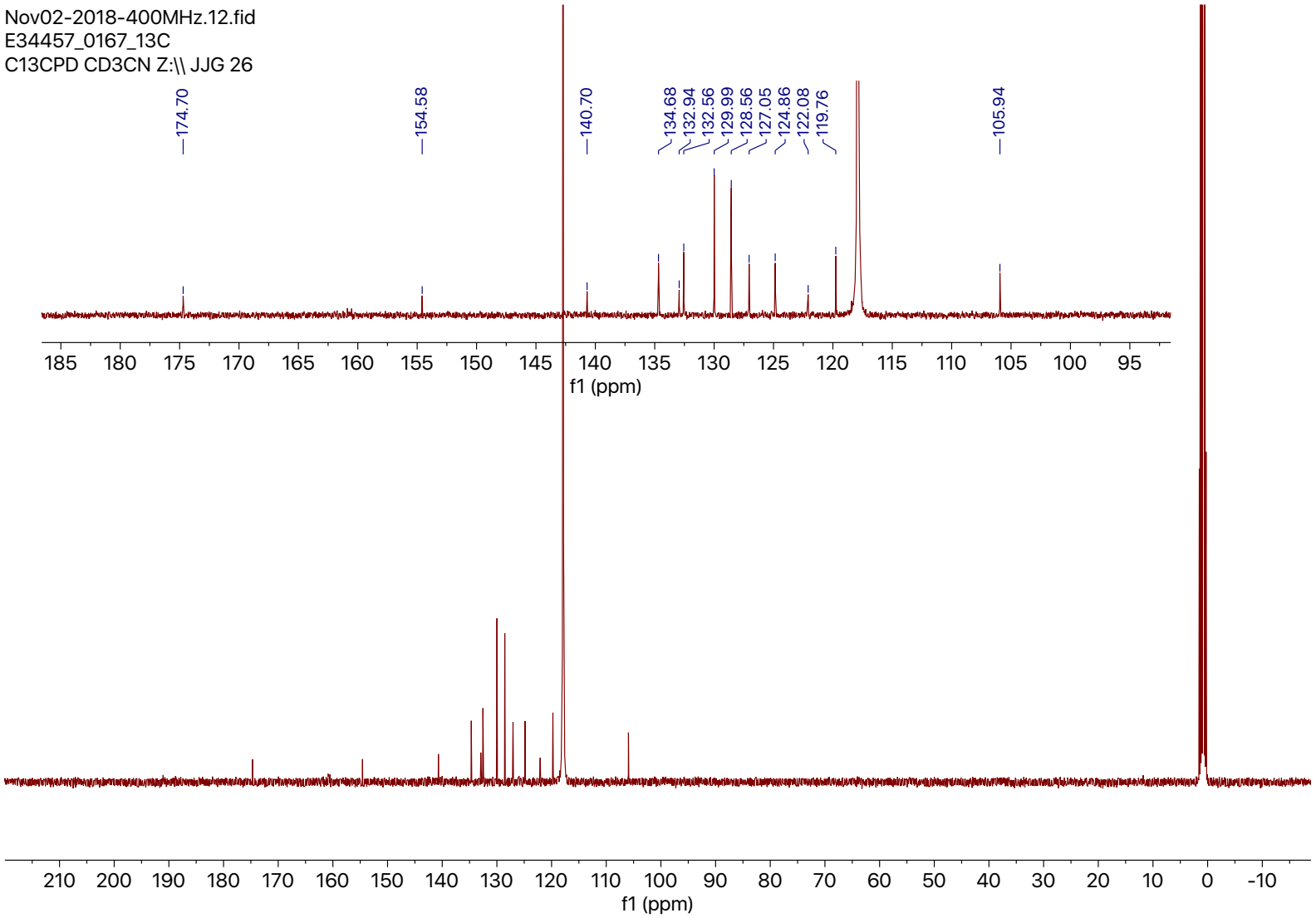
SI Figure 133: ^{13}C NMR spectrum of 4-(pyridin-2-yl)morpholine in $CDCl_3$ from HDF of 4-(3-fluoropyridin-2-yl)morpholine (25).



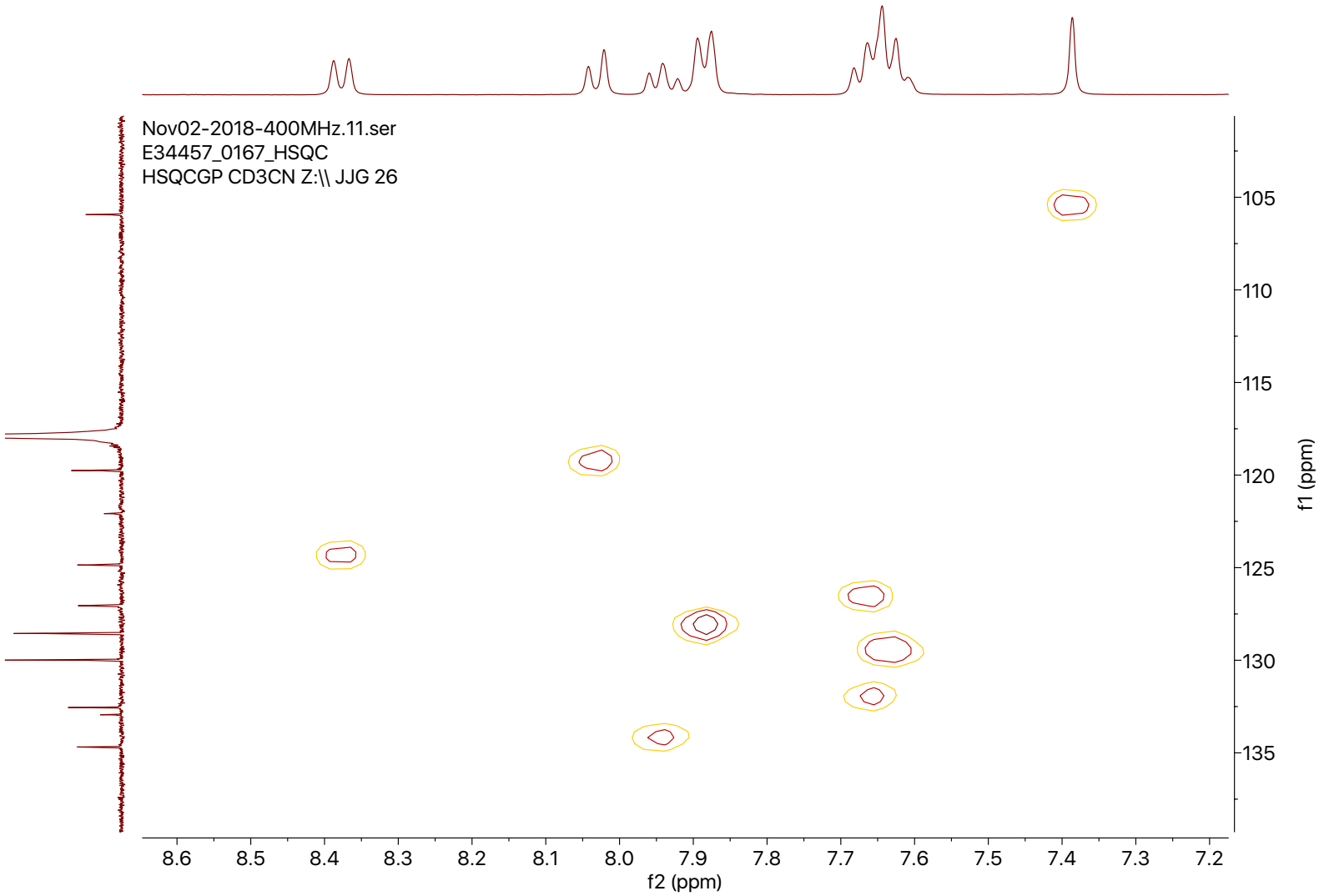
SI Figure 134: HSQC NMR spectrum of 4-(pyridin-2-yl)morpholine in $CDCl_3$ from HDF of 4-(3-fluoropyridin-2-yl)morpholine (25).



SI Figure 135: ^{1}H NMR spectrum of 2-phenylquinolin-4-ol (TFA salt) in CD_3CN from HDF of 6-fluoro-2-phenylquinolin-4-ol (26).

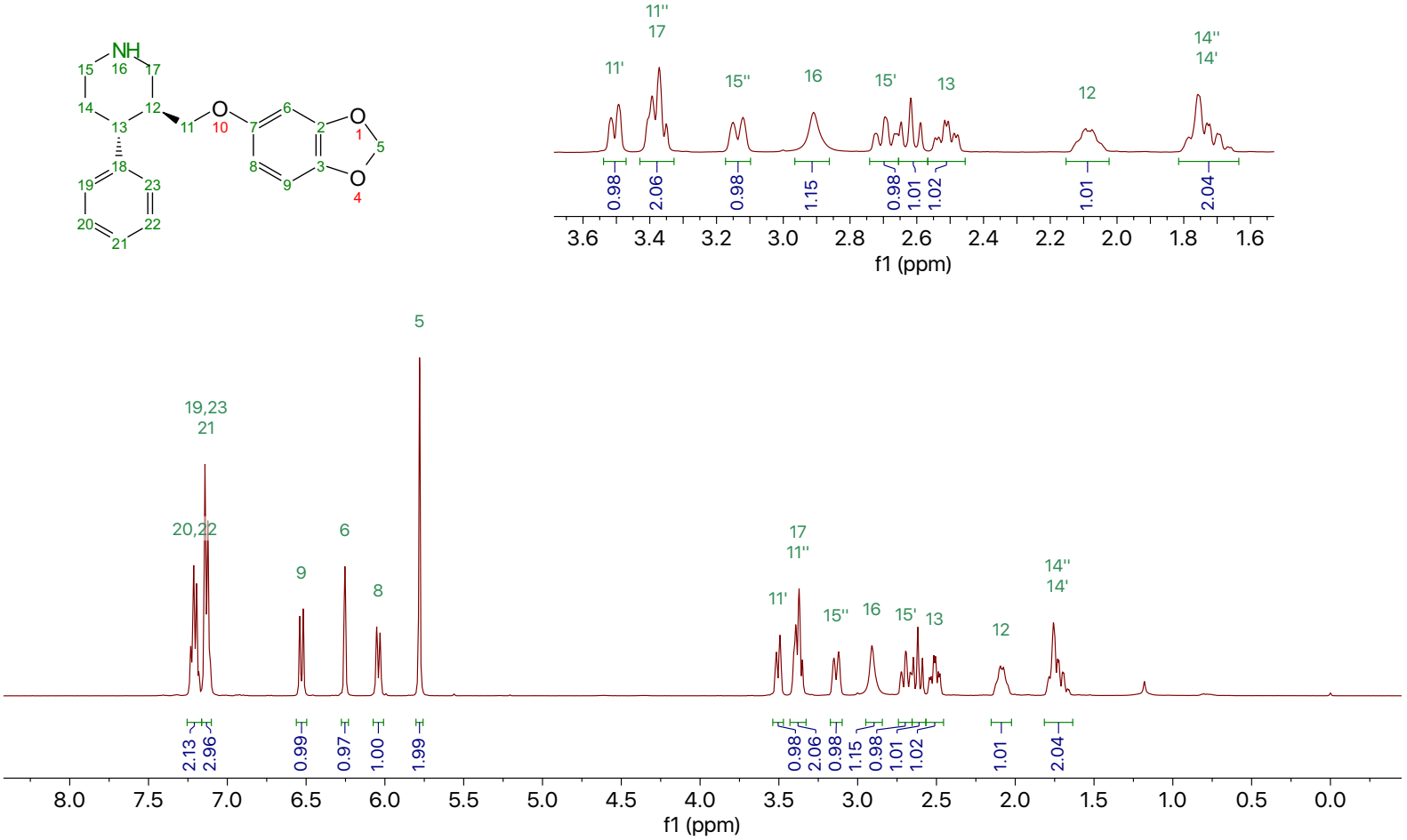


SI Figure 136: ^{13}C NMR spectrum of 2-phenylquinolin-4-ol (TFA salt) in CD_3CN from HDF of 6-fluoro-2-phenylquinolin-4-ol (26).

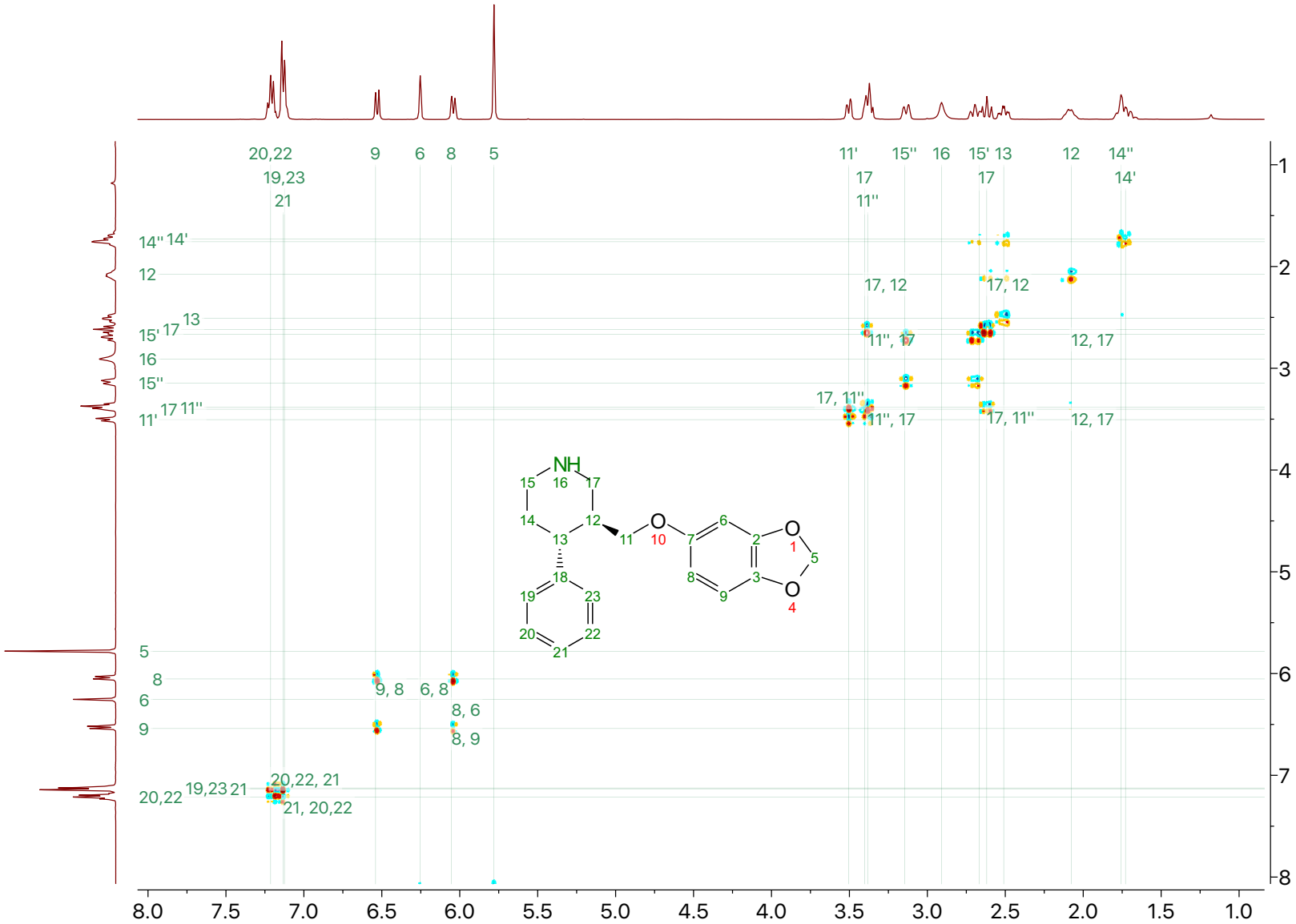


SI Figure 137: HSQC NMR spectrum of 2-phenylquinolin-4-ol (TFA salt) in CD_3CN from HDF of 6-fluoro-2-phenylquinolin-4-ol (26).

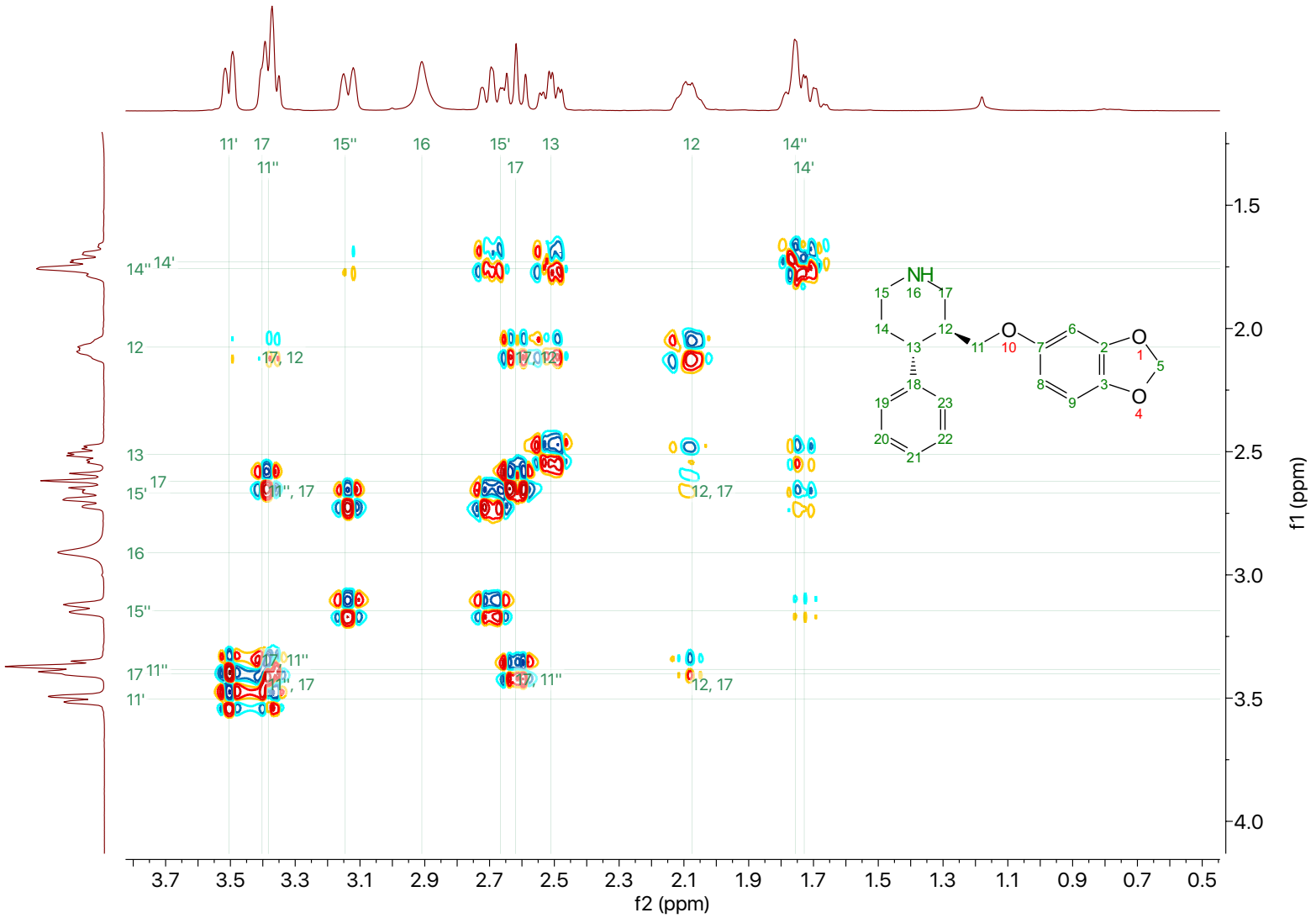
Dec06-2018-400MHz.1.fid
E34457_0198_HSQC_1H
PROTON CDCl3 Z:\\ JJG 45



SI Figure 138: ^{1}H NMR spectrum of desfluoro-Paroxetine in $CDCl_3$ from HDF of Paroxetine (27).

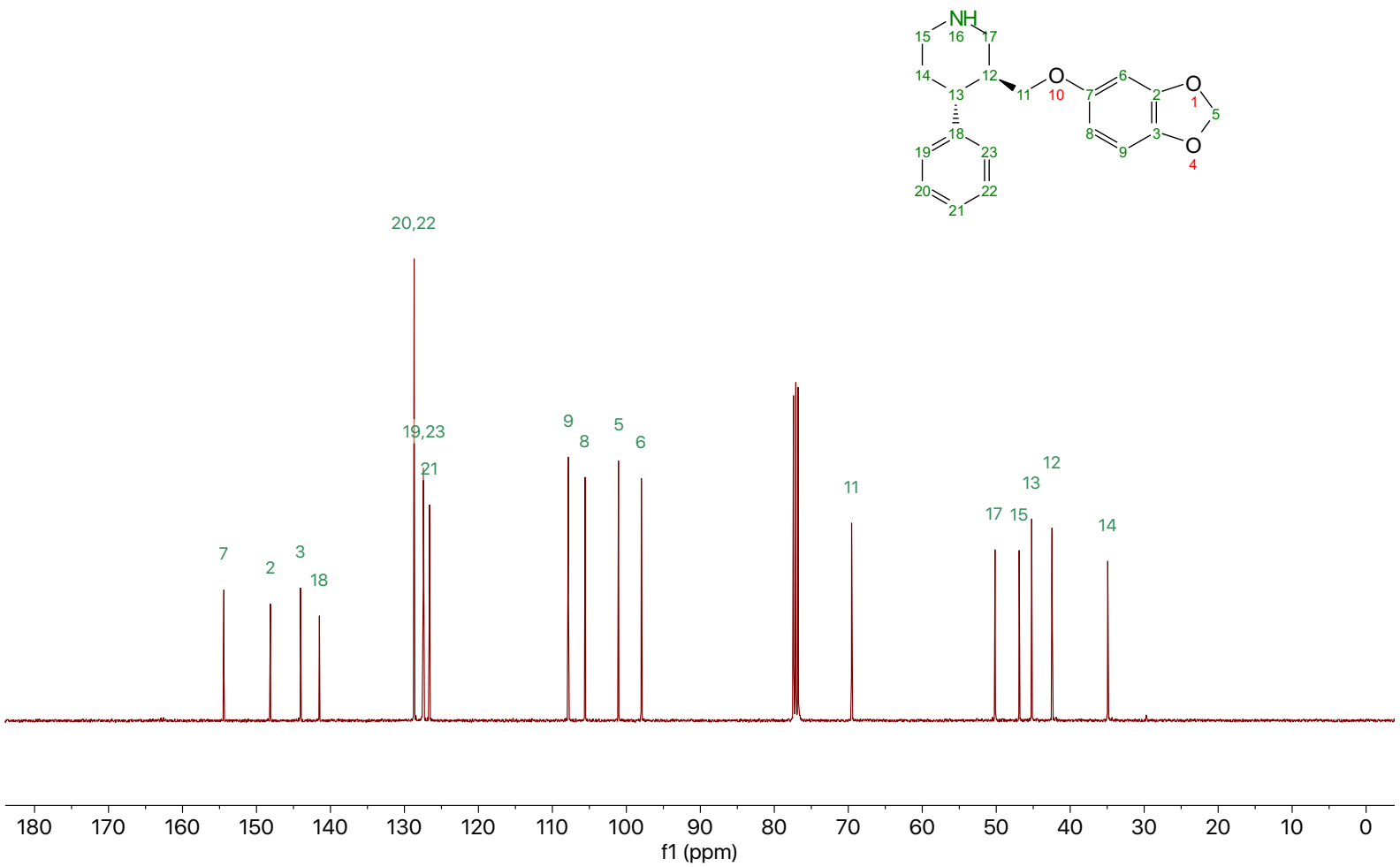


SI Figure 139: COSY NMR spectrum of desfluoro-Paroxetine in $CDCl_3$ from HDF of Paroxetine (27).

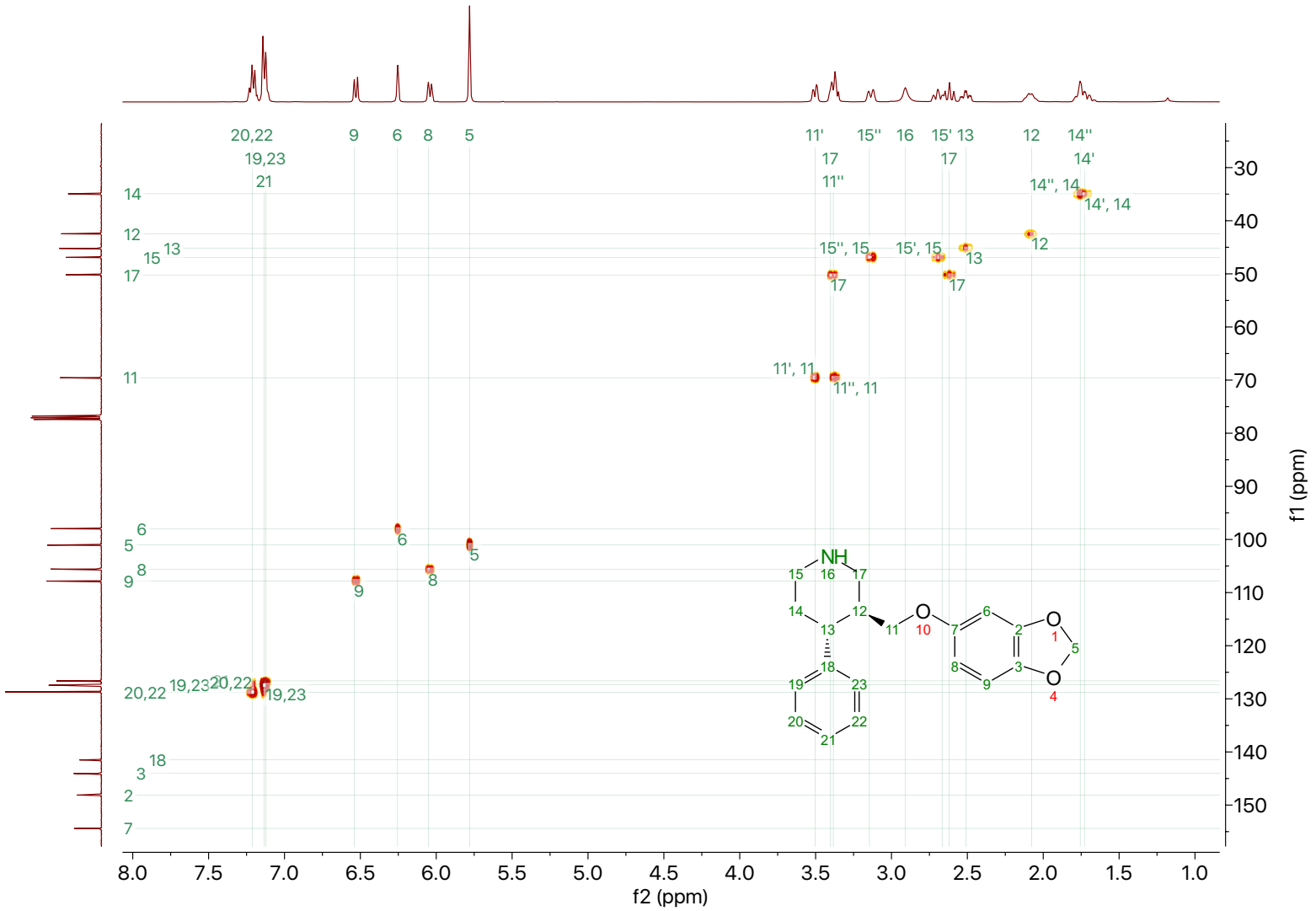


SI Figure 140: Expanded aliphatic region of COSY NMR spectrum of desfluoro-Paroxetine in $CDCl_3$ from HDF of Paroxetine (27).

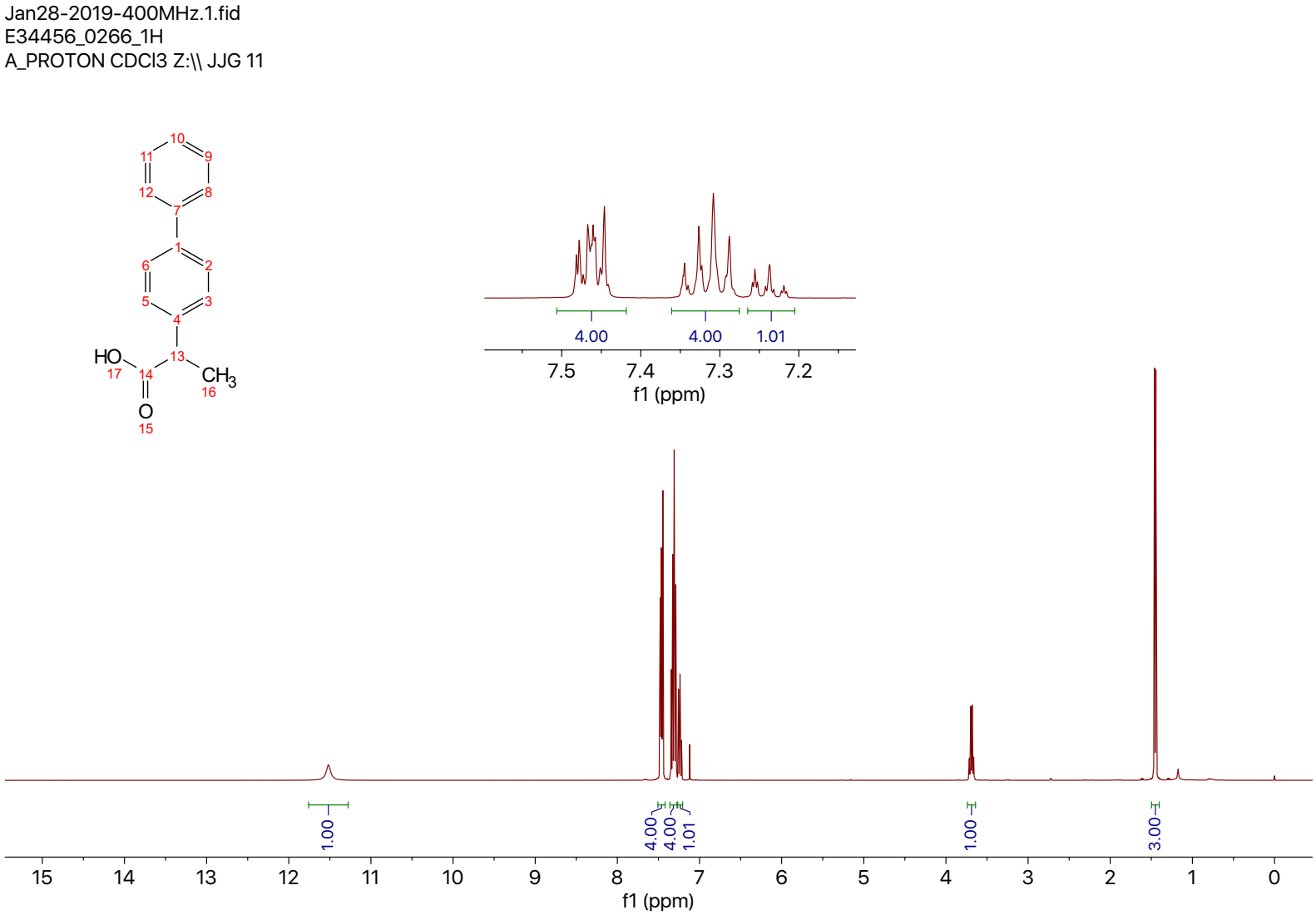
Dec06-2018-400MHz.3.fid
E34457_0198_13C
C13CPD CDCl3 Z:\\ JJG 45



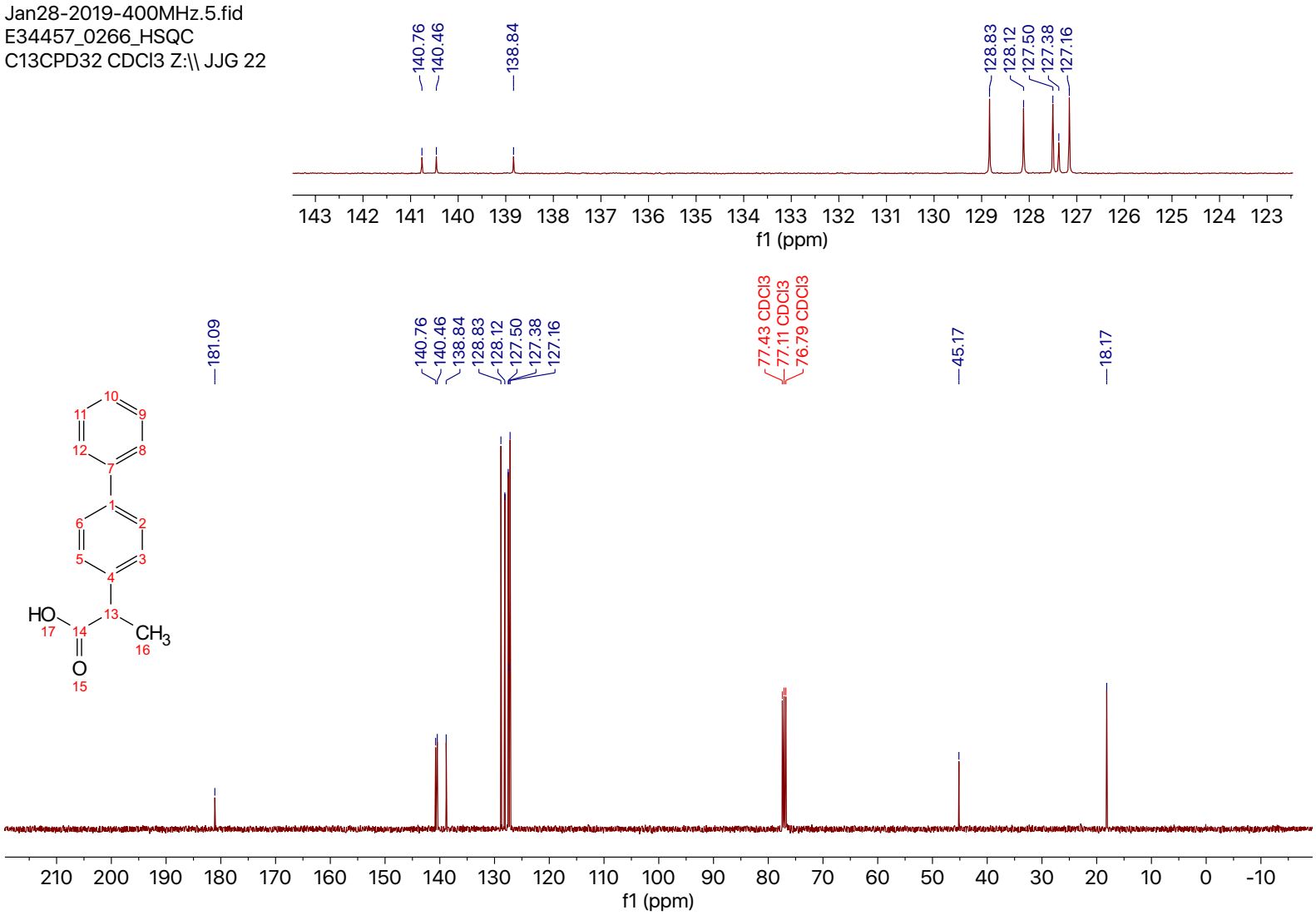
SI Figure 141: ^{13}C NMR spectrum of desfluoro-Paroxetine in $CDCl_3$ from HDF of Paroxetine (27).



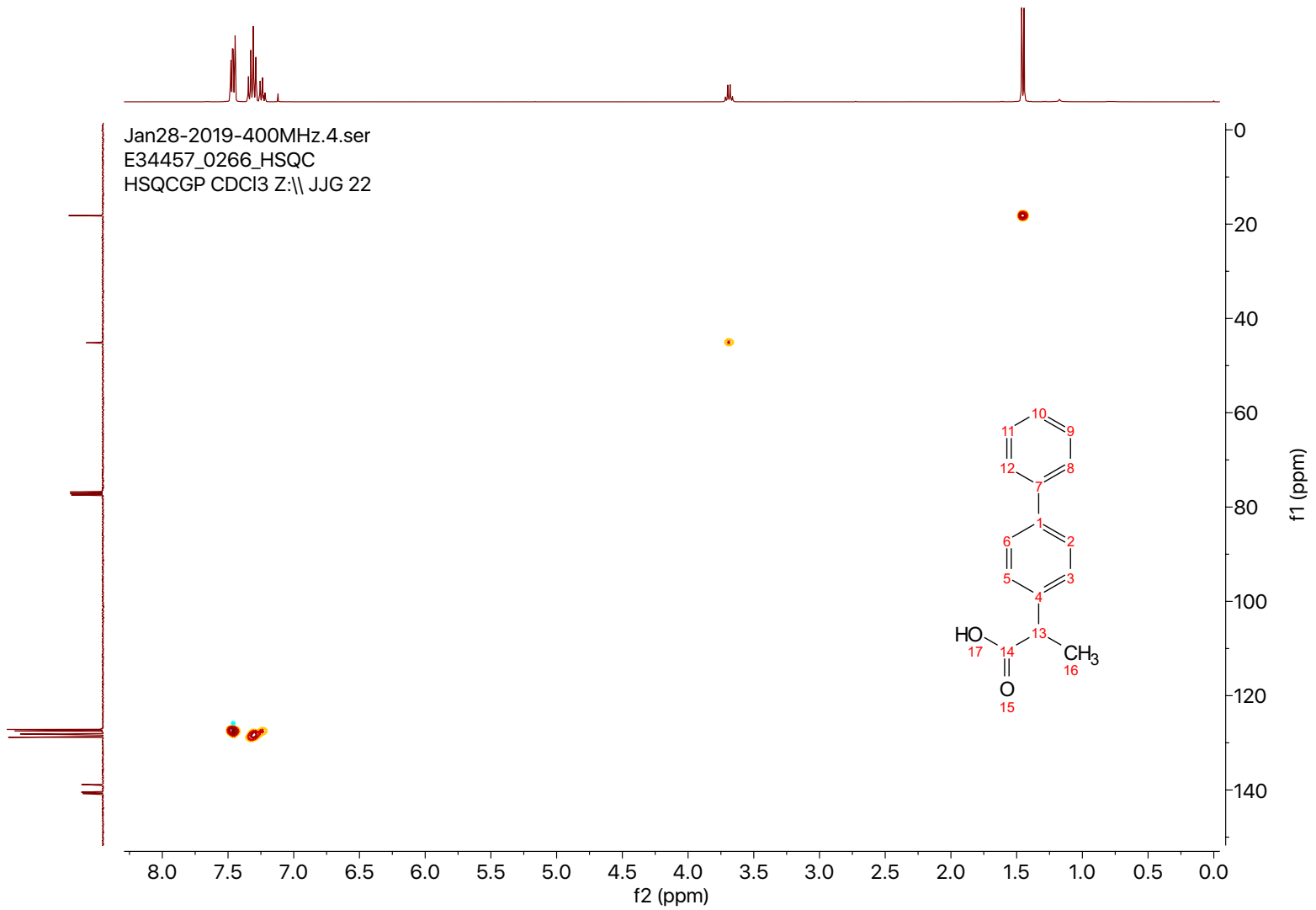
SI Figure 142: HSQC NMR spectrum of desfluoro-Paroxetine in $CDCl_3$ from HDF of Paroxetine (27).



SI Figure 143: ^{1}H NMR spectrum of desfluoro- Flurbiprofen in $CDCl_3$ from HDF of Flurbiprofen (28).

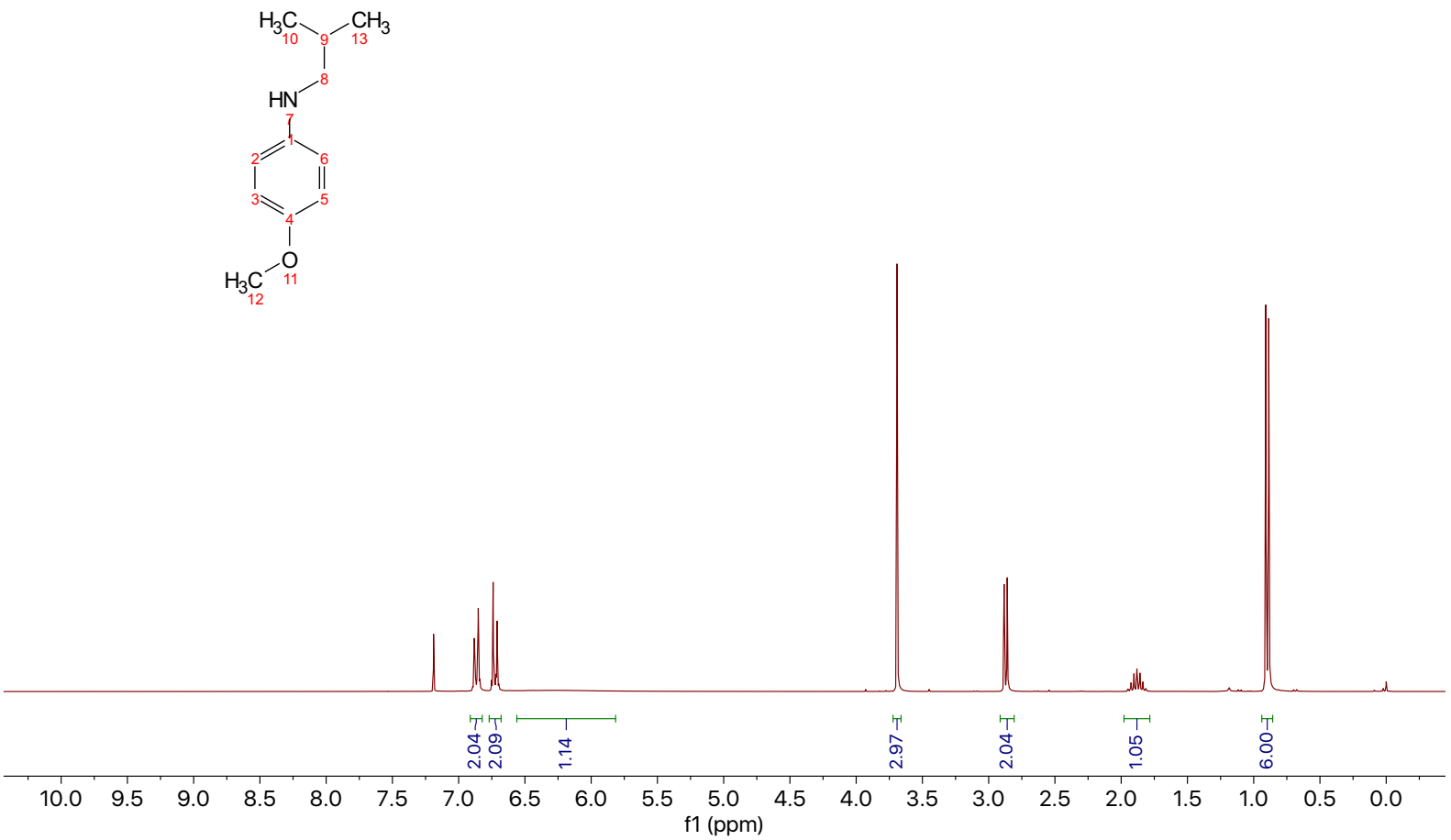


SI Figure 144: ^{13}C NMR spectrum of desfluoro- Flurbiprofen in $CDCl_3$ from HDF of Flurbiprofen (28).

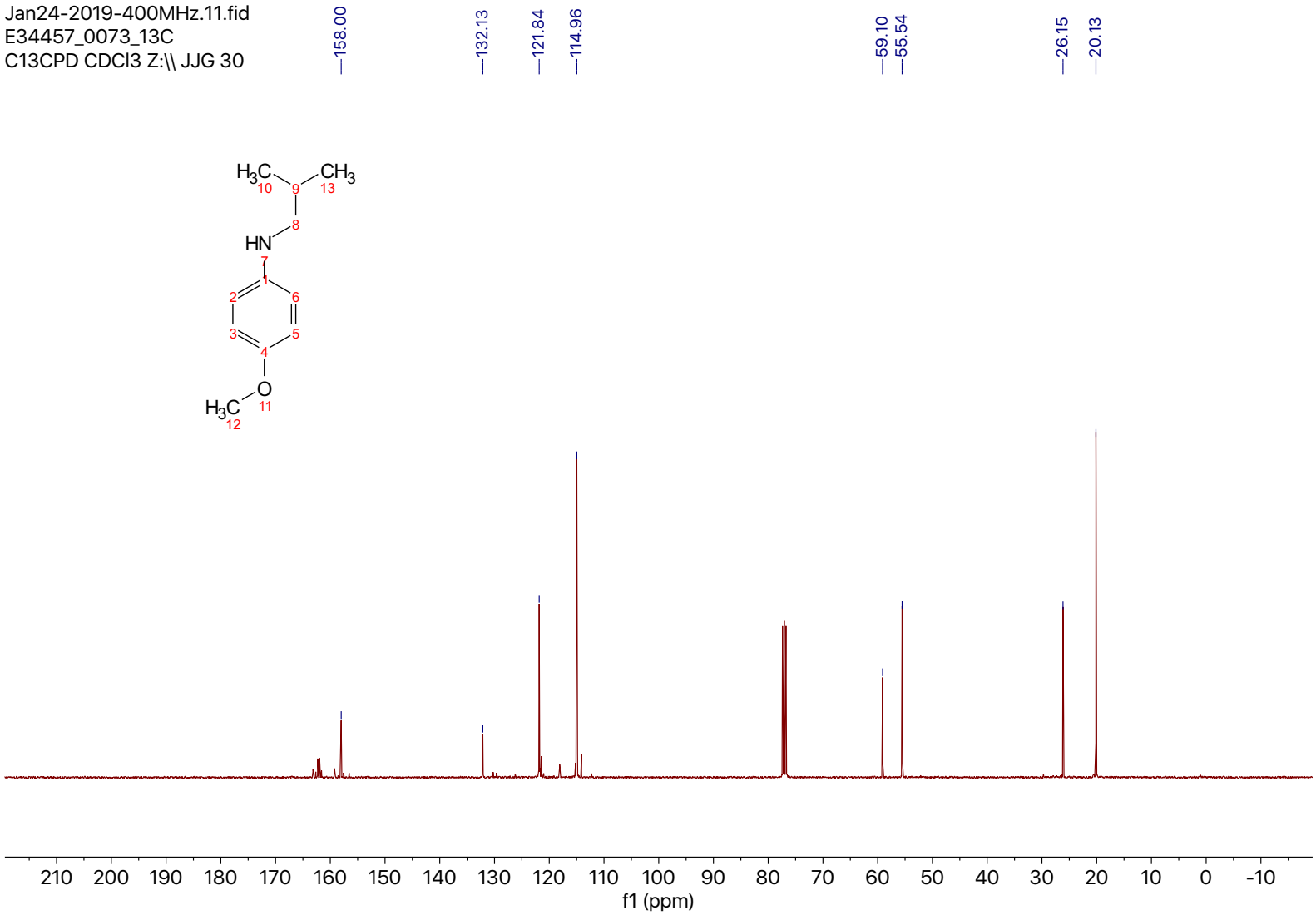


SI Figure 145: HSQC NMR spectrum of desfluoro- Flurbiprofen in $CDCl_3$ from HDF of Flurbiprofen (28).

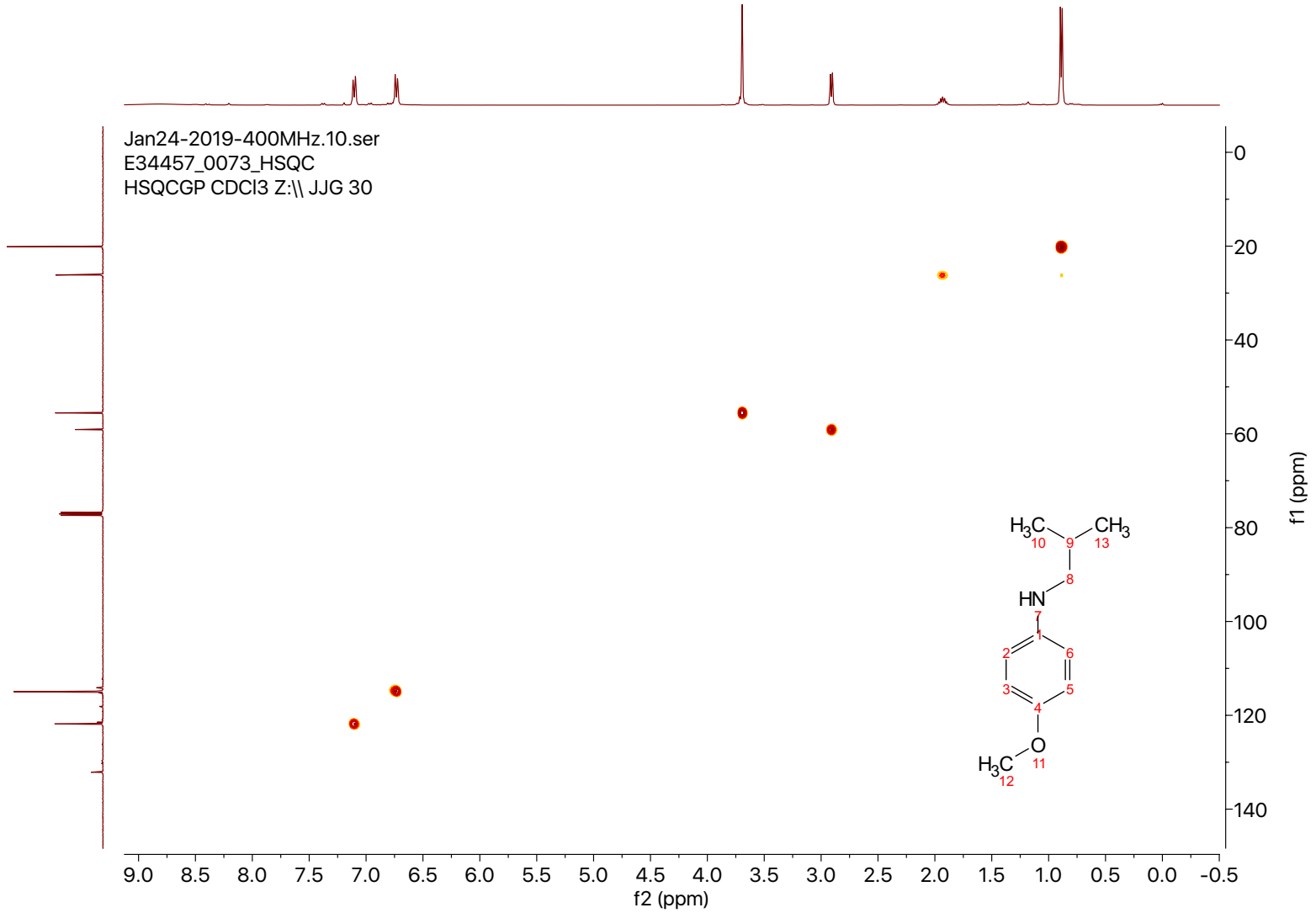
Aug29-2018.5.fid
E34457_0073_C_36-40
A_PROTON CDCl3 {Z:\Topspin} JJG 28



SI Figure 146: ^{1}H NMR spectrum of *N*-isobutyl-4-methoxyaniline in $CDCl_3$ from HDF and alkylation of 2-fluoro-4-methoxyaniline (29).

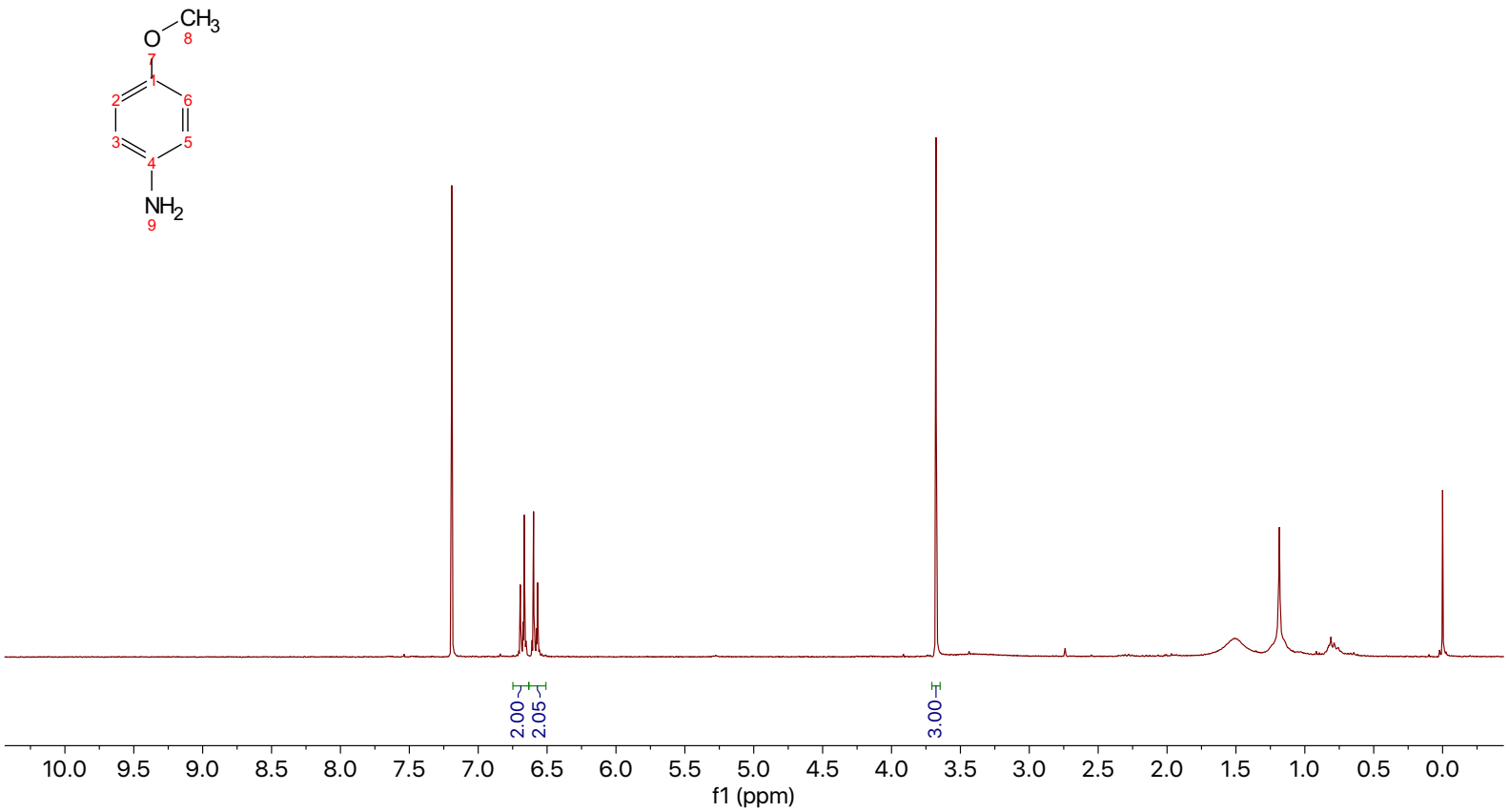


SI Figure 147: ^{13}C NMR spectrum of *N*-isobutyl-4-methoxyaniline in $CDCl_3$ from HDF and alkylation of 2-fluoro-4-methoxyaniline (29).



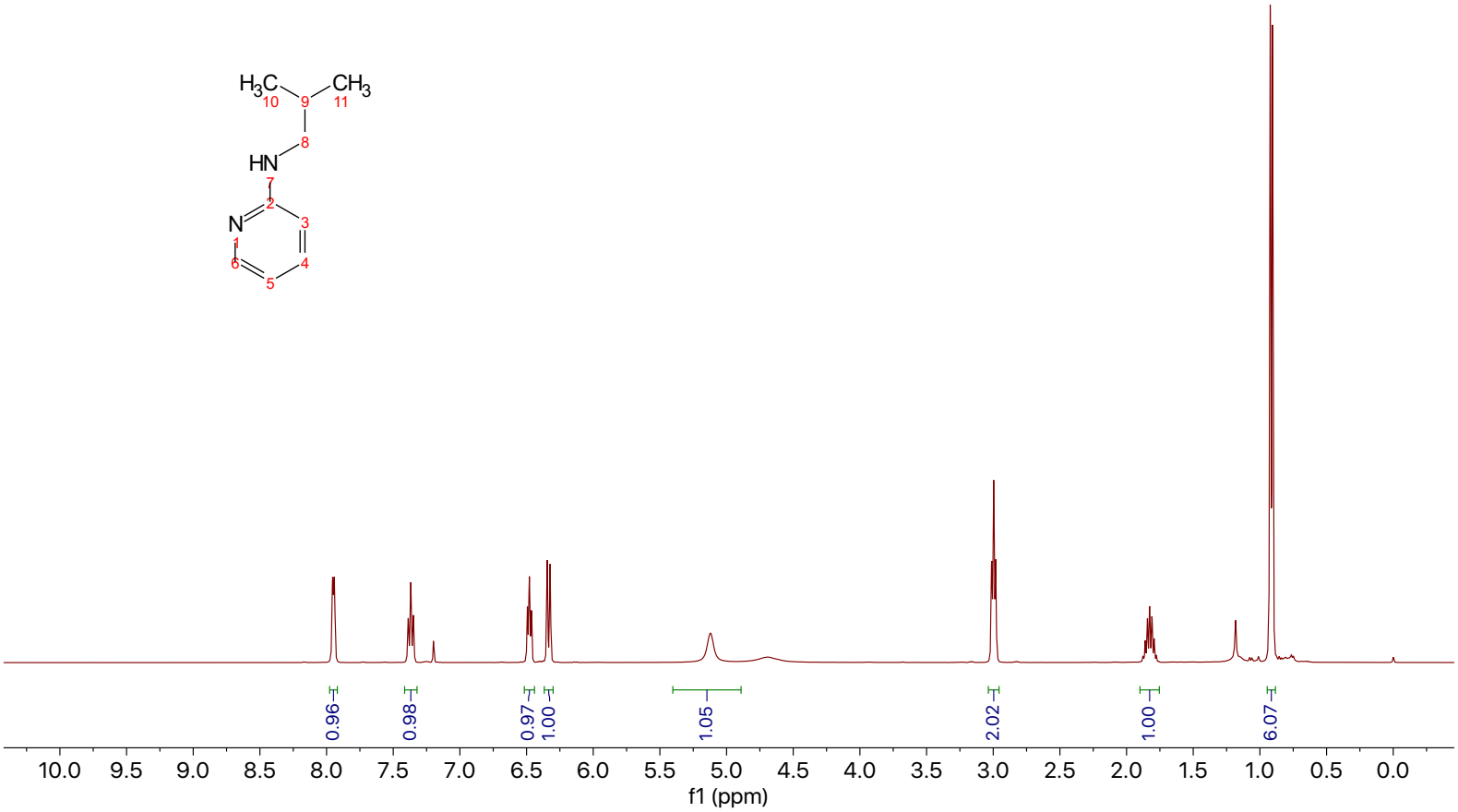
SI Figure 148: HSQC NMR spectrum of *N*-isobutyl-4-methoxyaniline in $CDCl_3$ from HDF and alkylation of 2-fluoro-4-methoxyaniline (29).

Aug29-2018.6.fid
E34457_0073_C_F32-33
A_PROTON CDCl3 {Z:\Topspin} JJG 29

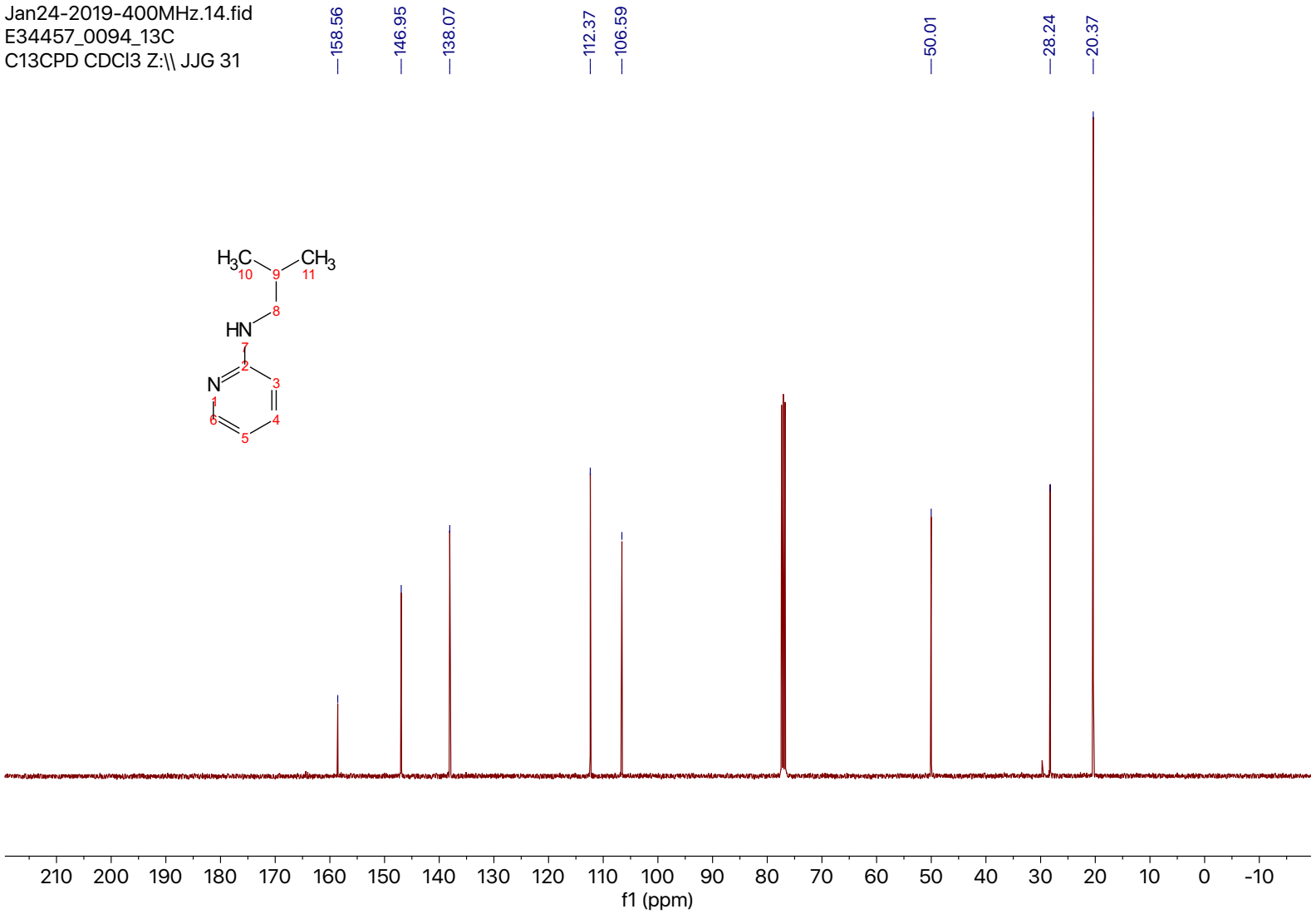


SI Figure 149: ^{1}H NMR spectrum of 4-methoxyaniline in $CDCl_3$ from HDF of 2-fluoro-4-methoxyaniline (29).

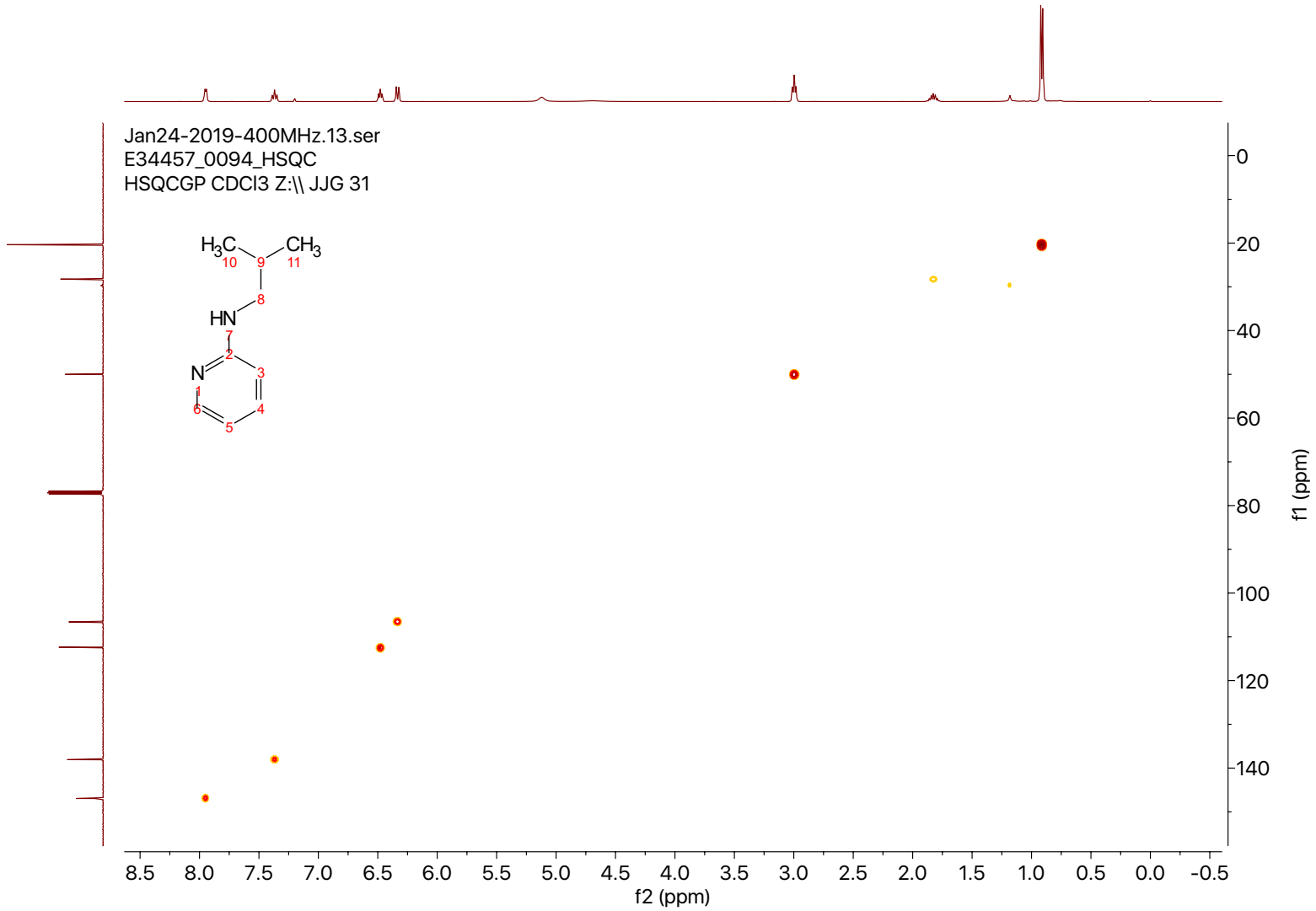
Jan24-2019-400MHz.12.fid
E34457_0094_HSQC_1H
PROTON CDCl3 Z:\\ JJG 31



SI Figure 150: ^{1}H NMR spectrum of *N*-isobutylpyridin-2-amine in $CDCl_3$ from HDF and alkylation of 5-fluoropyridin-2-amine (30).

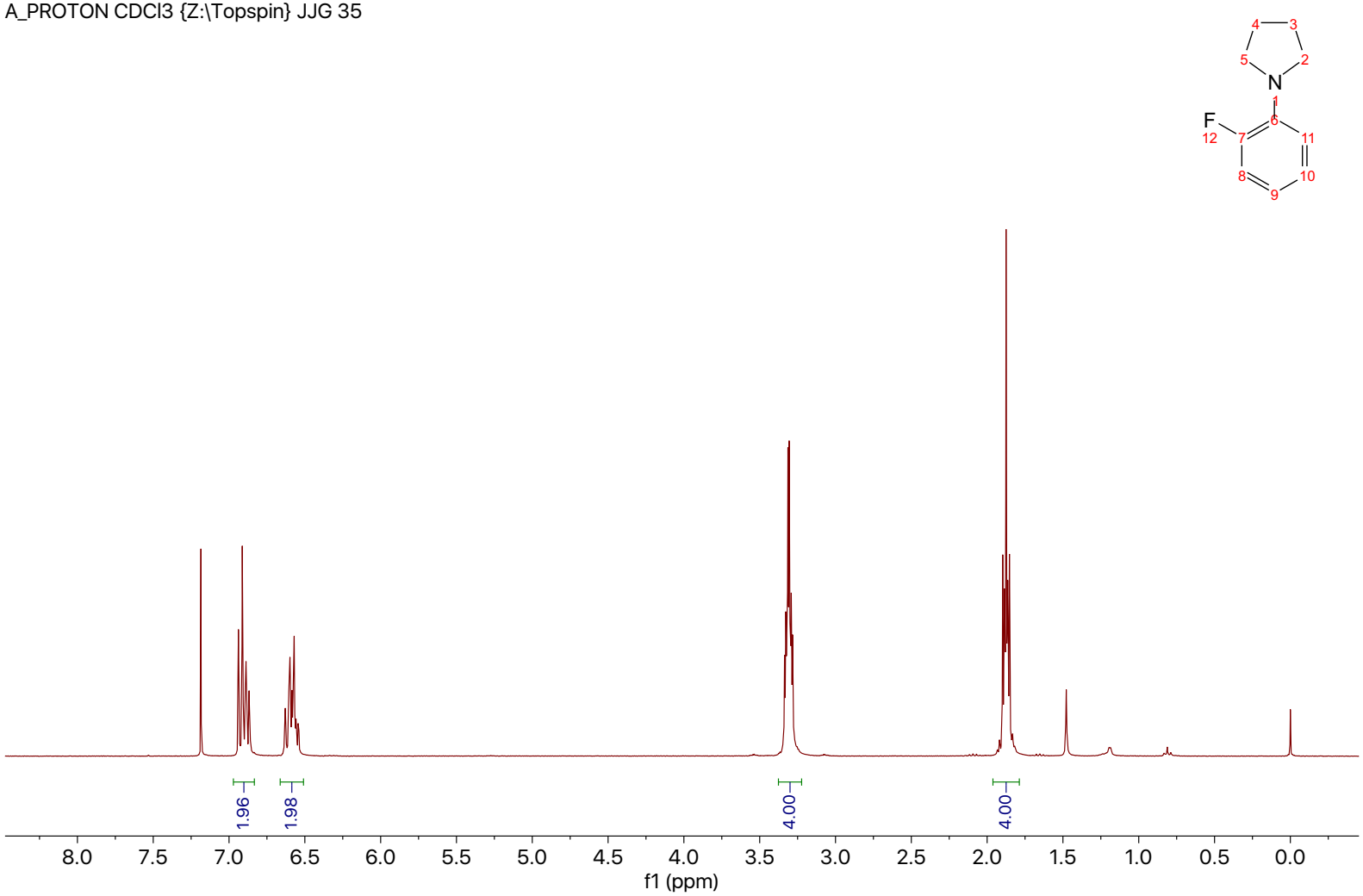


SI Figure 151: ^{13}C NMR spectrum of *N*-isobutylpyridin-2-amine in $CDCl_3$ from HDF and alkylation of 5-fluoropyridin-2-amine (30).



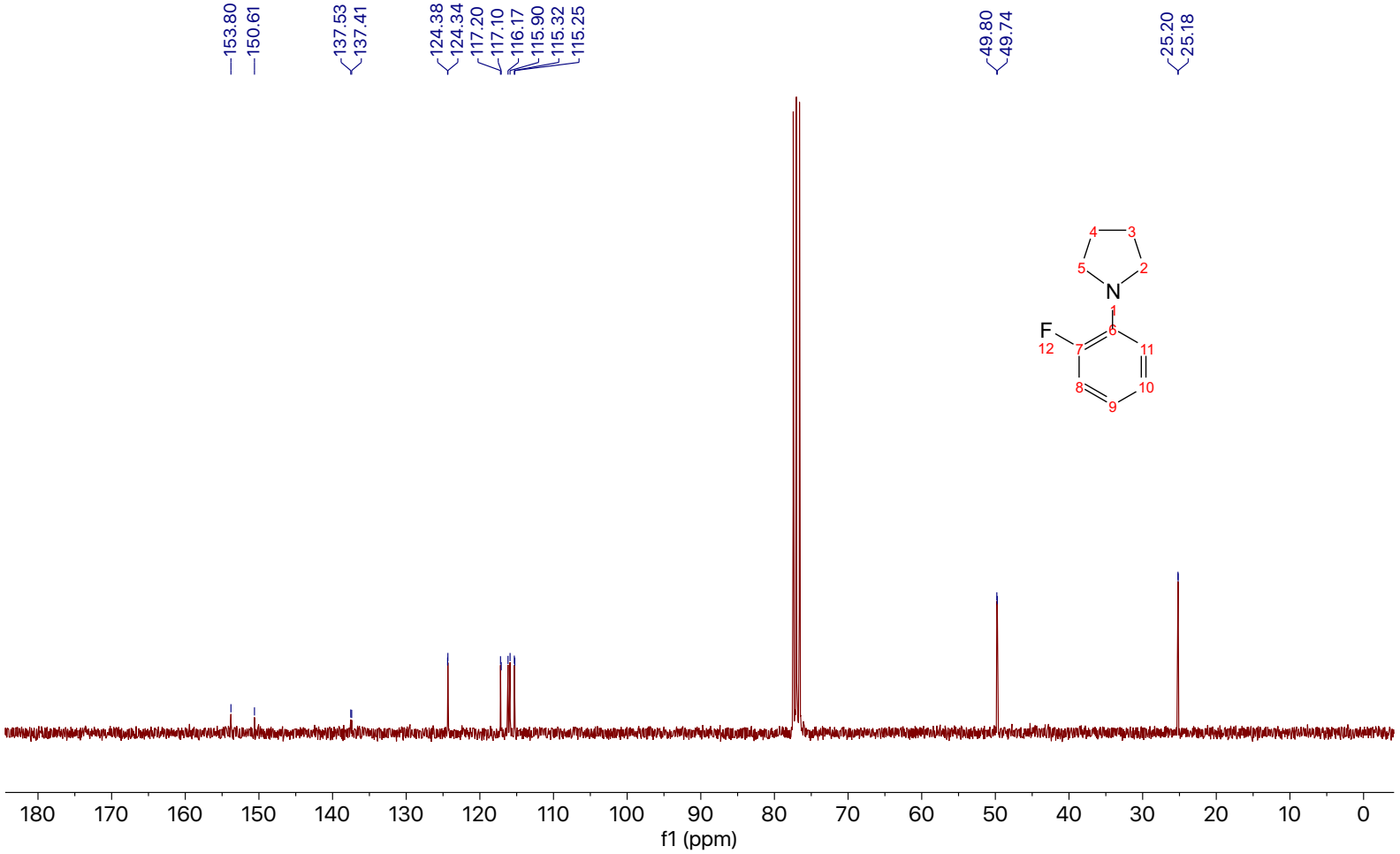
SI Figure 152: HSQC NMR spectrum of *N*-isobutylpyridin-2-amine in $CDCl_3$ from HDF and alkylation of 5-fluoropyridin-2-amine (30).

Dec19-2018.1.fid
E34457_0243_1H
A_PROTON CDCl3 {Z:\Topspin} JJG 35

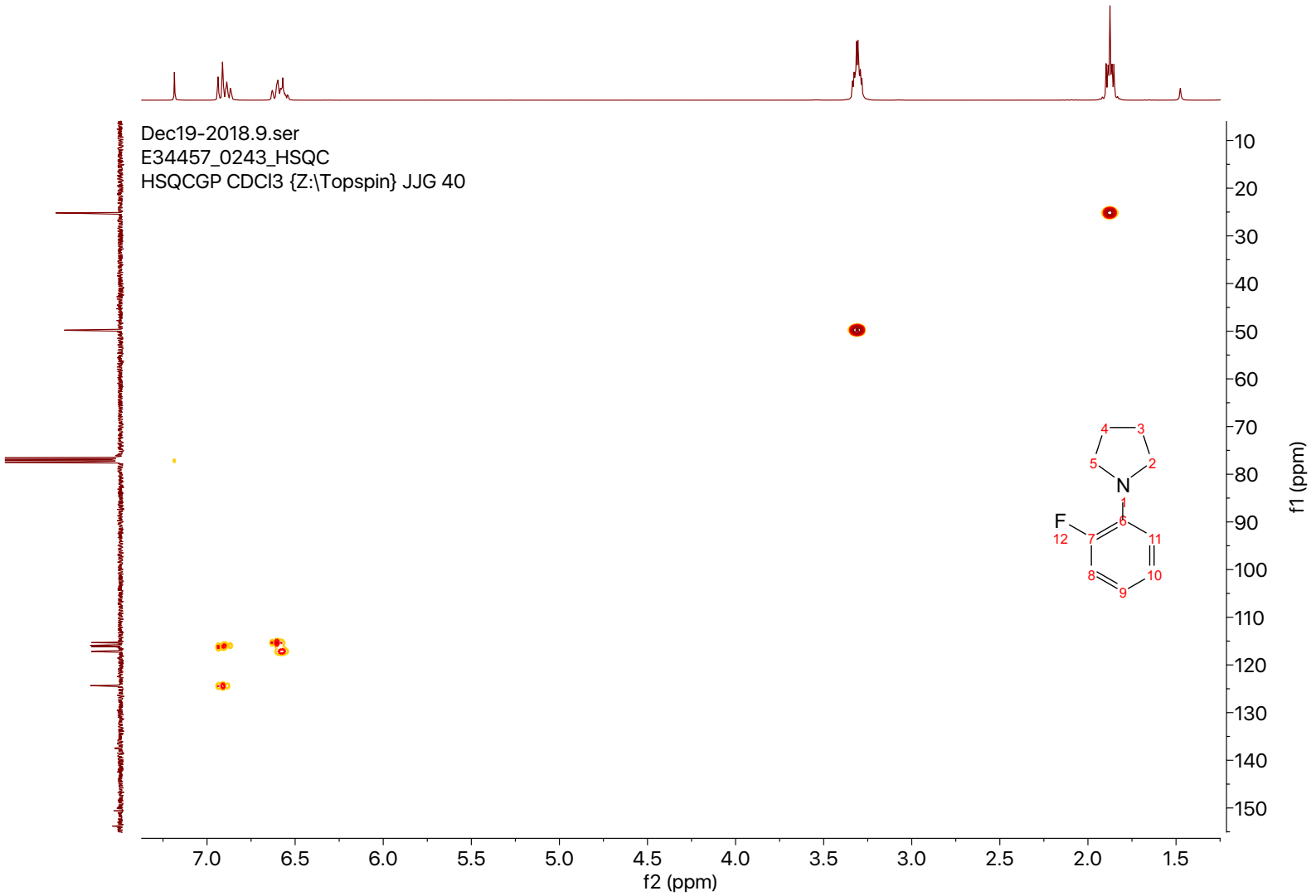


SI Figure 153: ^{1}H NMR spectrum of 1-(2-fluorophenyl)pyrrolidine (8a) in $CDCl_3$.

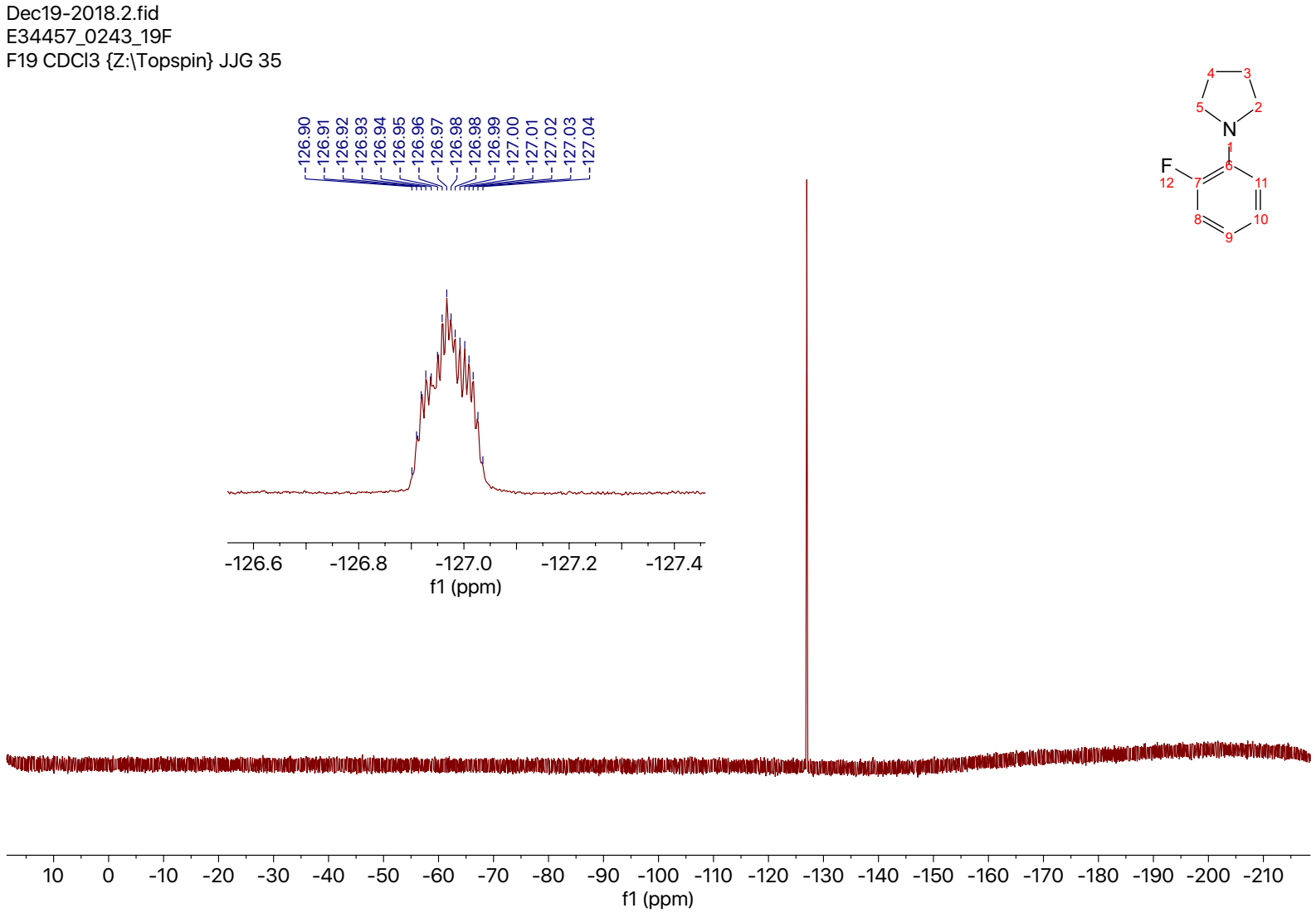
Dec19-2018.10.fid
E34457_0243_13C
C13CPD CDCl3 {Z:\Topspin} JJG 40



SI Figure 154: ^{13}C NMR spectrum of 1-(2-fluorophenyl)pyrrolidine (8a) in $CDCl_3$.

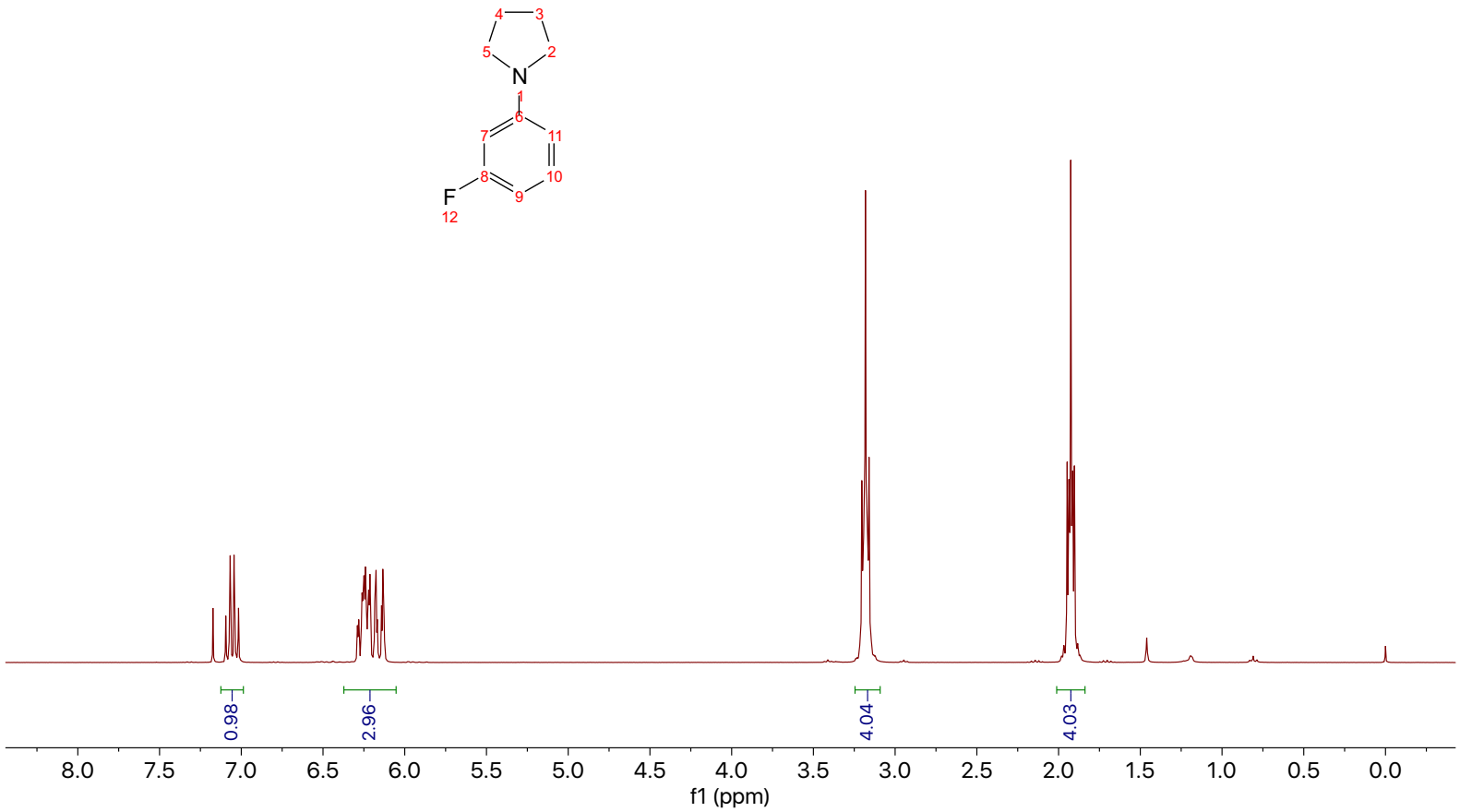


SI Figure 155: HSQC spectrum of 1-(2-fluorophenyl)pyrrolidine (8a) in $CDCl_3$.

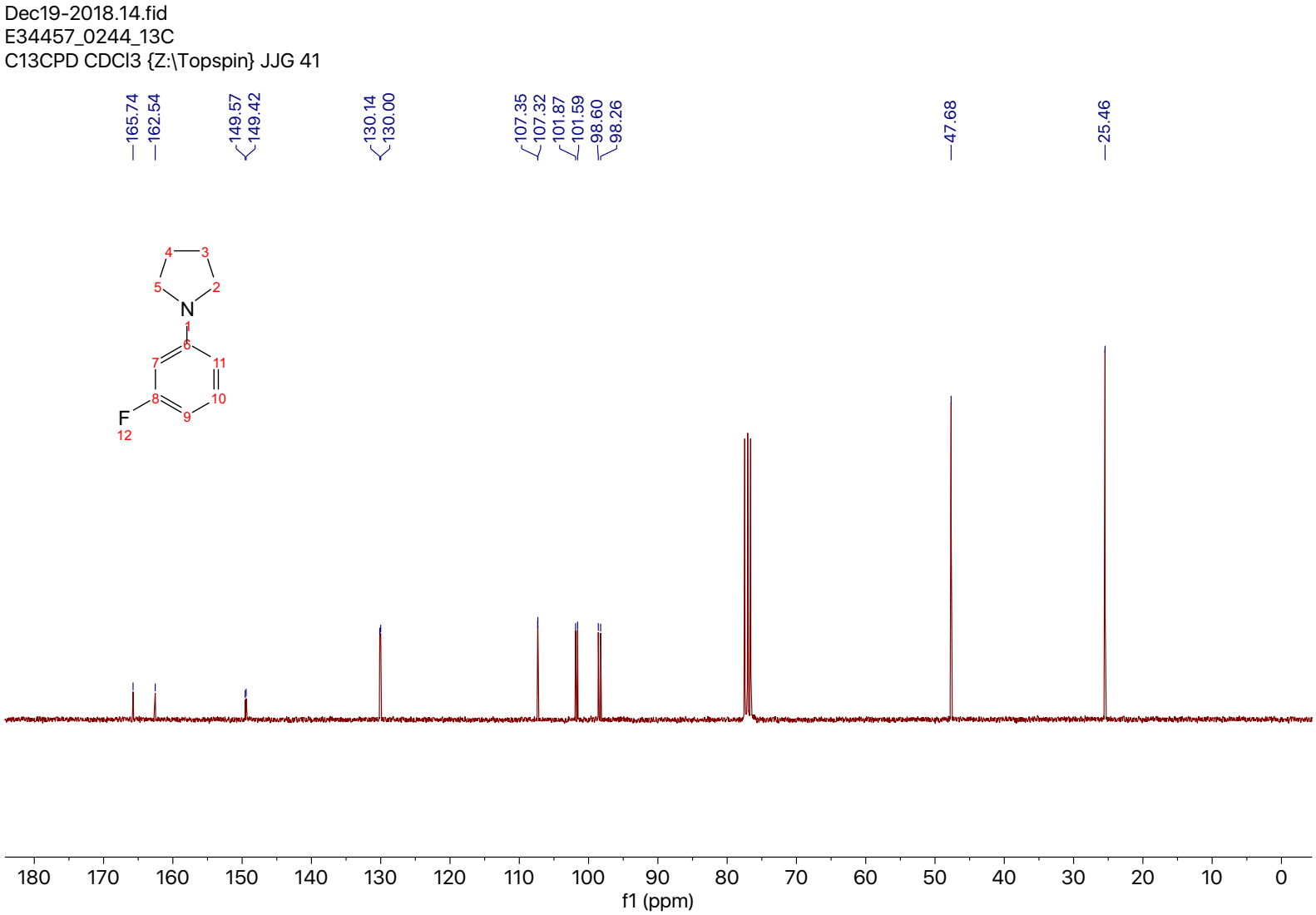


SI Figure 156: ^{19}F NMR spectrum of 1-(2-fluorophenyl)pyrrolidine (8a) in $CDCl_3$.

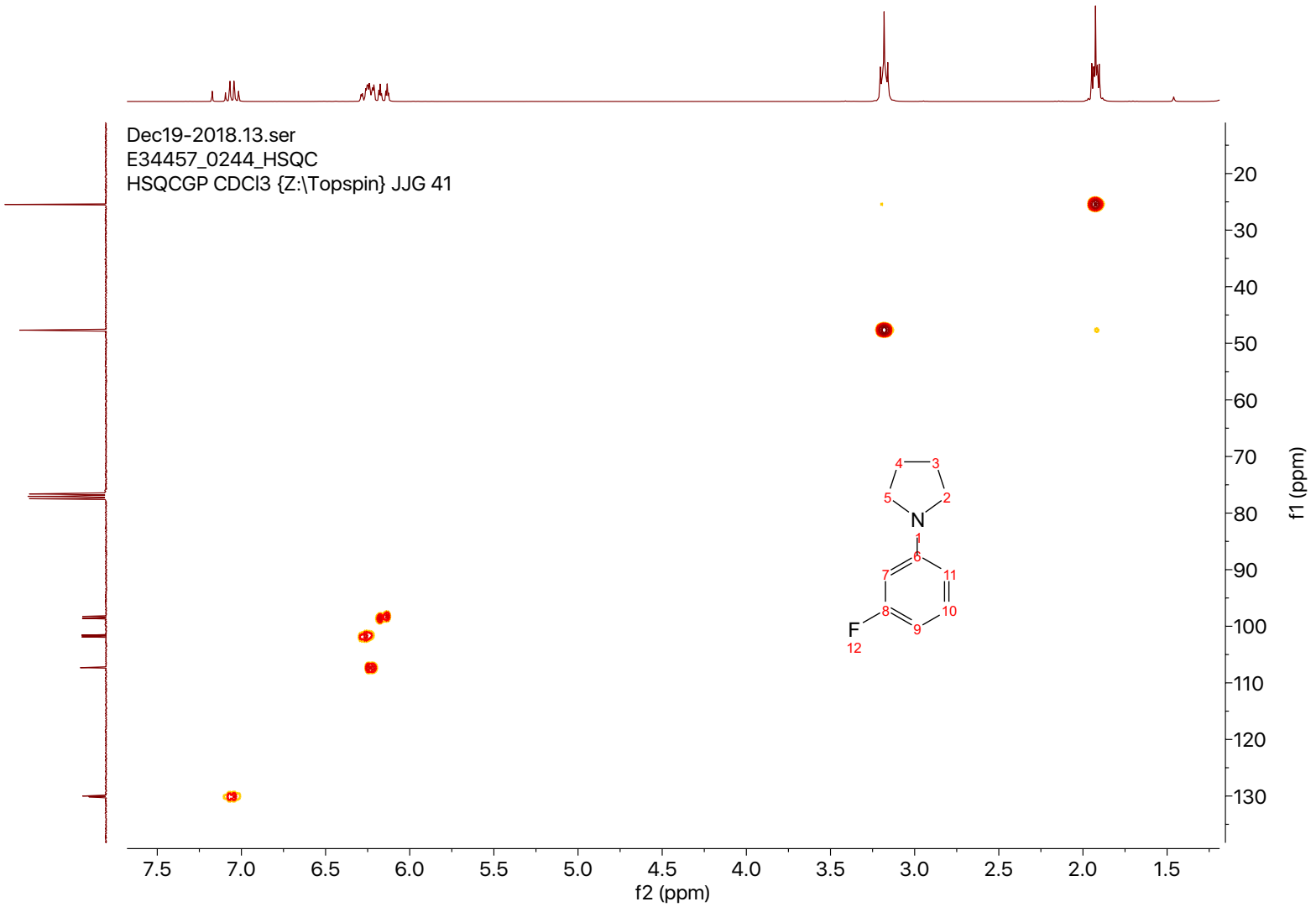
Dec19-2018.12.fid
E34457_0244_HSQC_1H
PROTON CDCl3 {Z:\Topspin} JJG 41



SI Figure 157: ^{1}H NMR spectrum of 1-(3-fluorophenyl)pyrrolidine (8b) in $CDCl_3$.

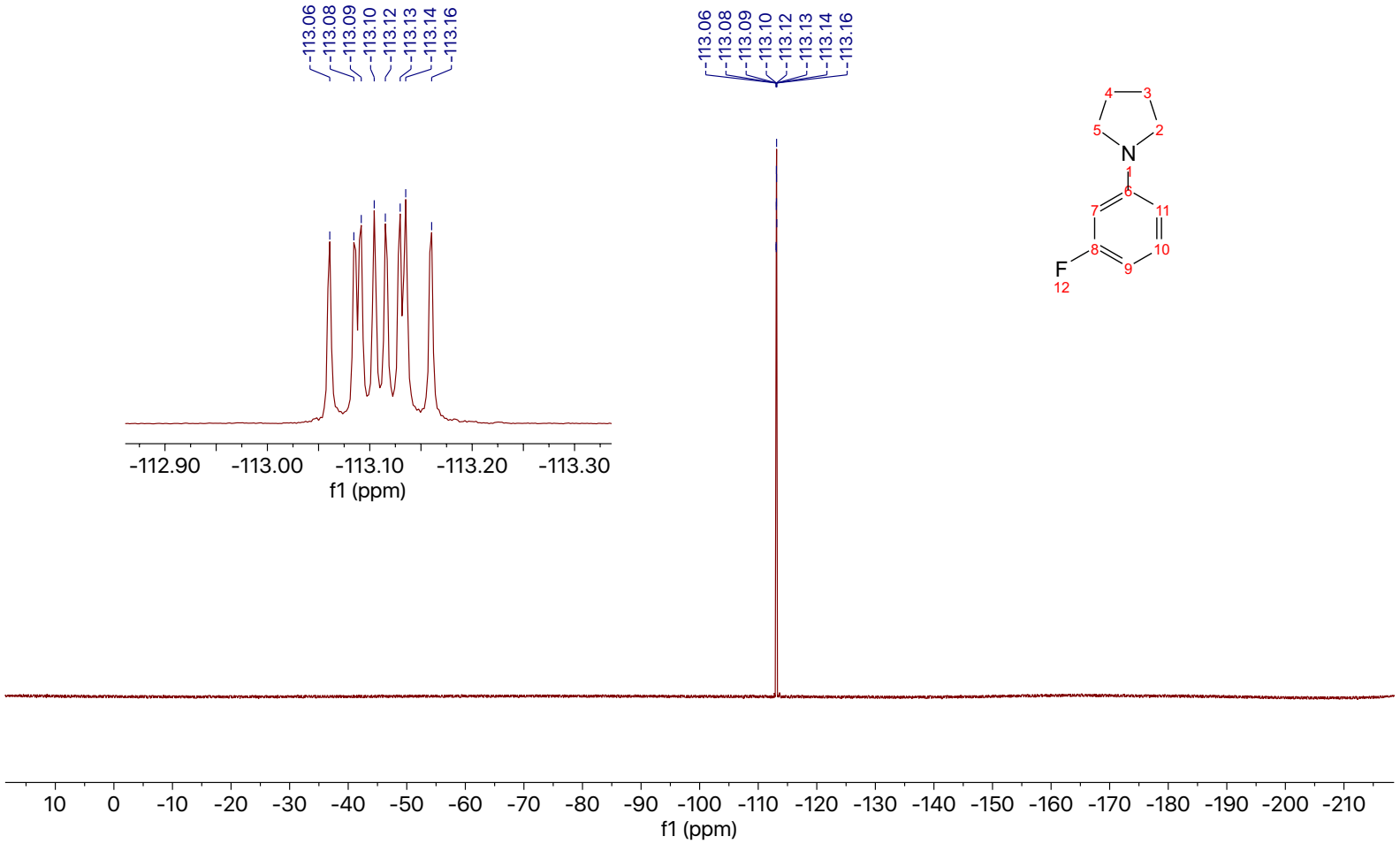


SI Figure 158: ^{13}C NMR spectrum of 1-(3-fluorophenyl)pyrrolidine (8b) in $CDCl_3$.



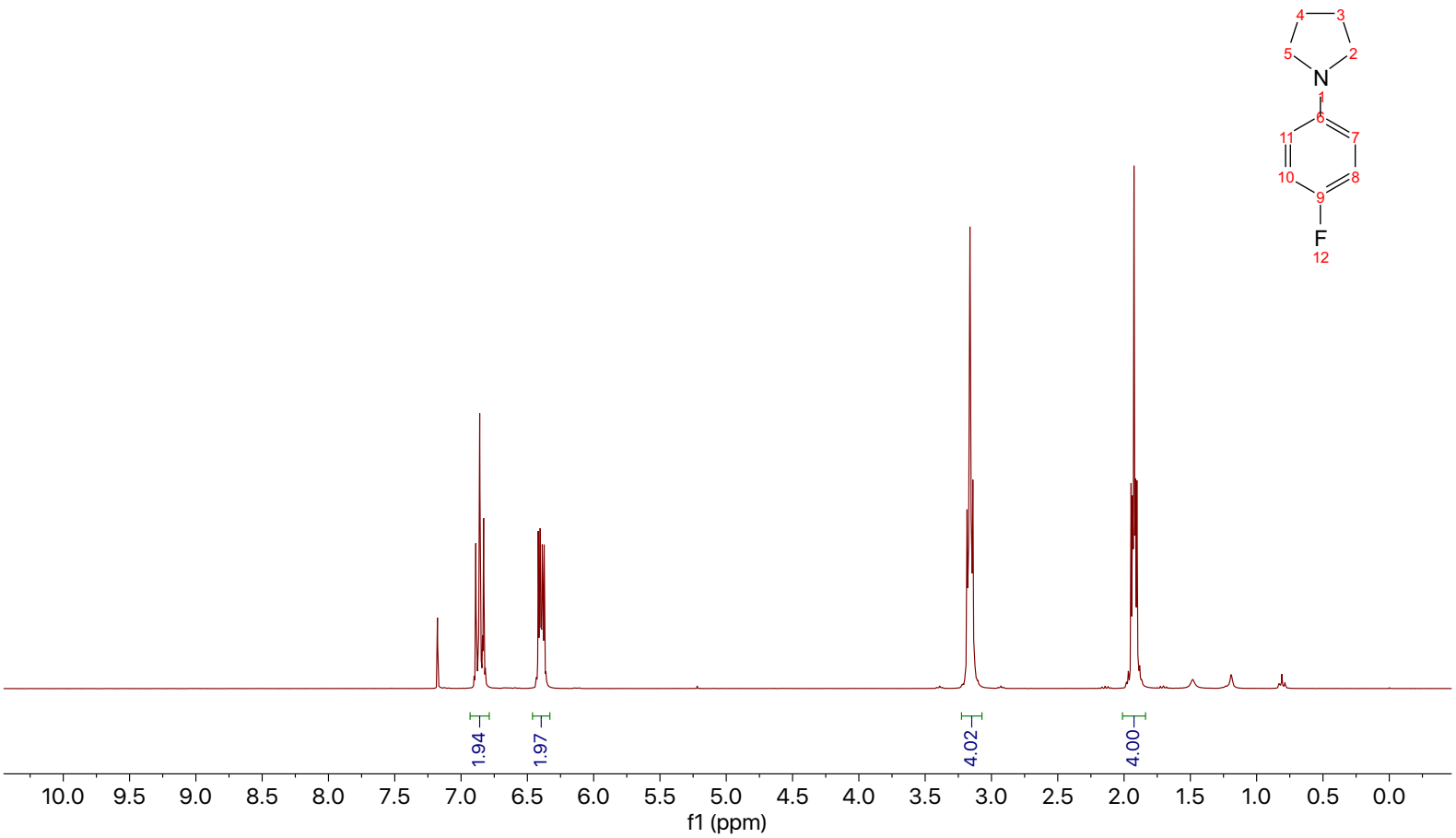
SI Figure 159: HSQC NMR spectrum of 1-(3-fluorophenyl)pyrrolidine (8b) in $CDCl_3$.

Dec19-2018.15.fid
E34457_0244_19F
F19 CDCl3 {Z:\Topspin} JJG 41

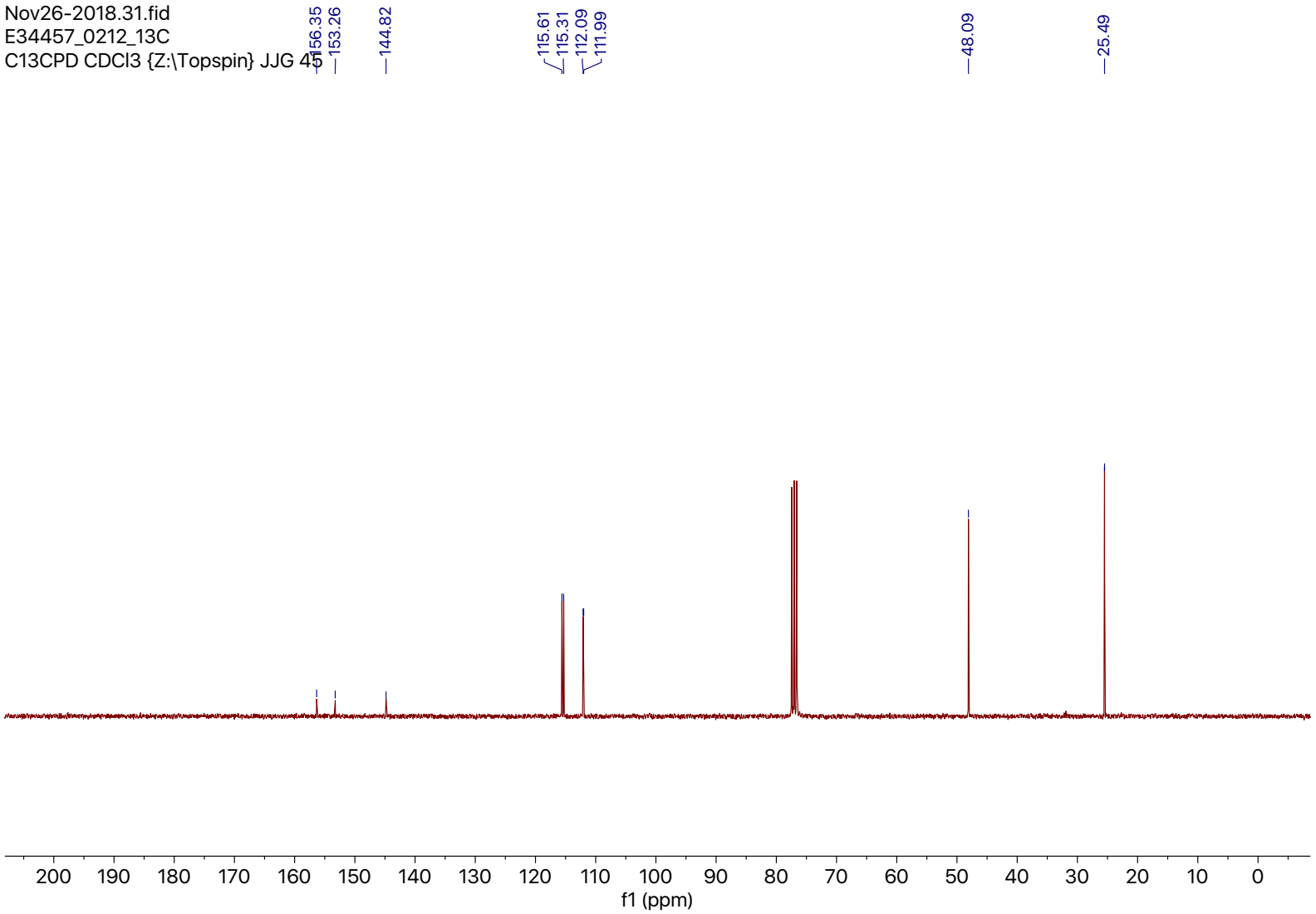


SI Figure 160: ^{19}F NMR spectrum of 1-(3-fluorophenyl)pyrrolidine (8b) in $CDCl_3$.

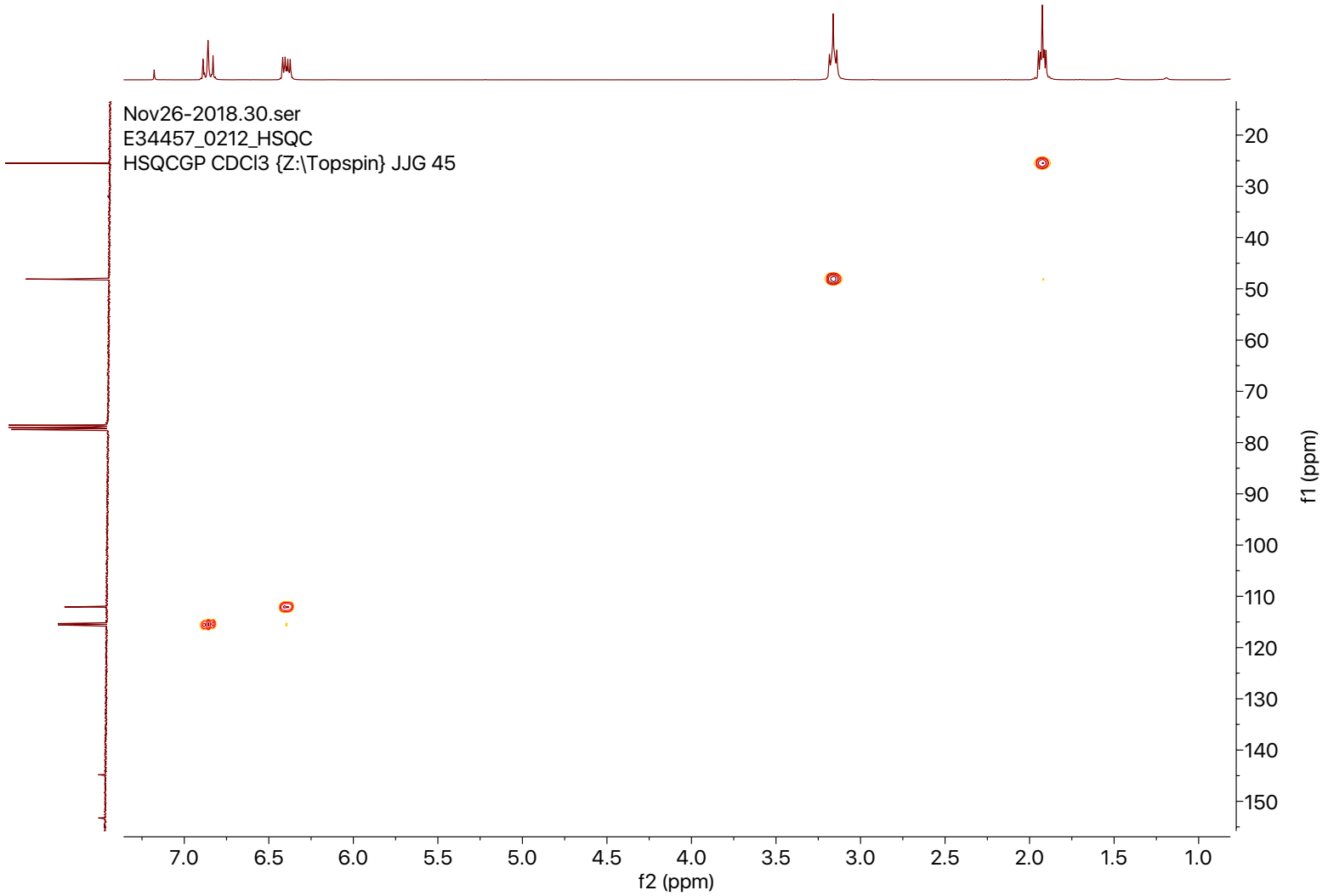
Nov26-2018.29.fid
E34457_0212_HSQC_1H
PROTON CDCl3 {Z:\Topspin} JJG 45



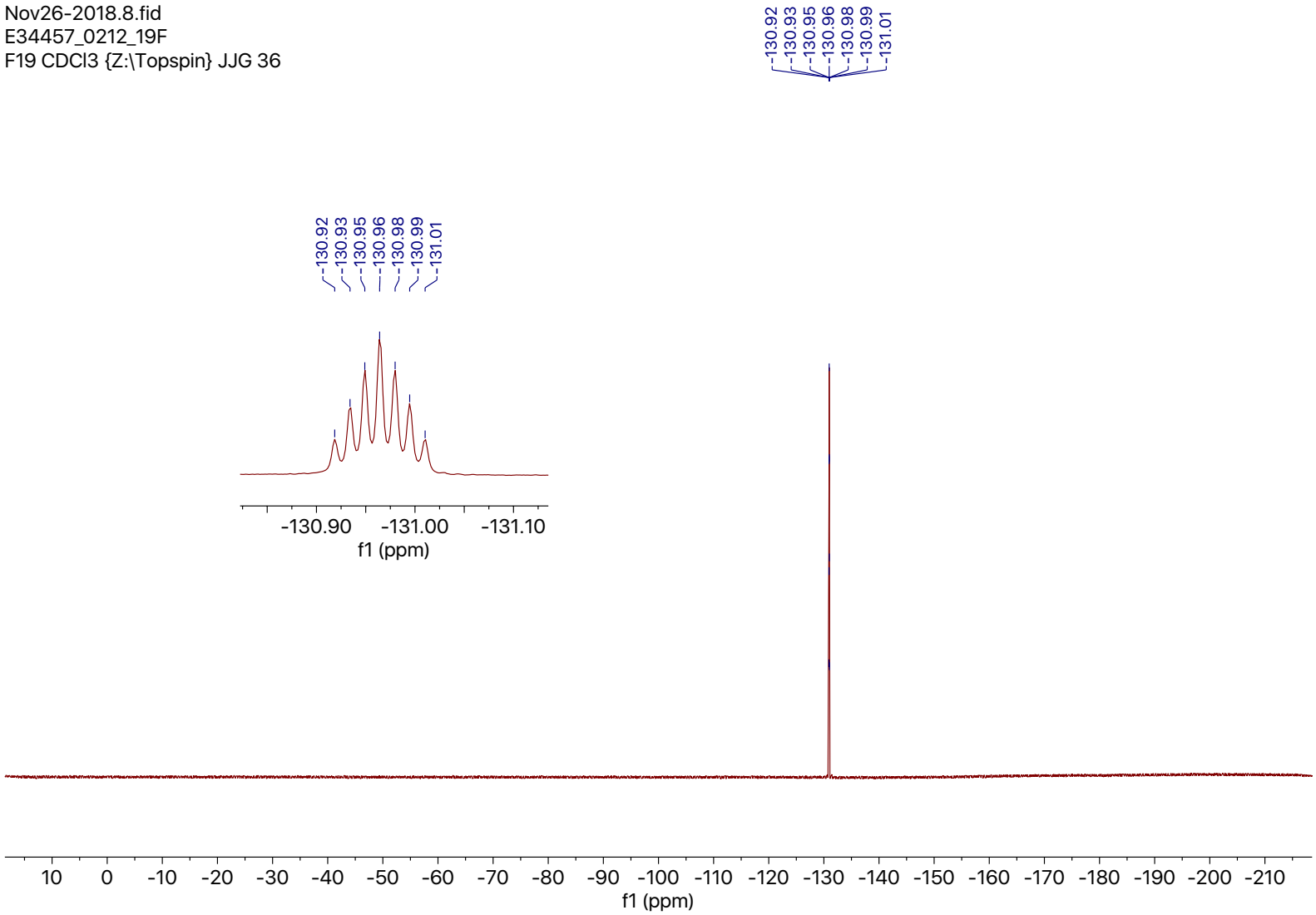
SI Figure 161: ^{1}H NMR spectrum of 1-(4-fluorophenyl)pyrrolidine (8c) in $CDCl_3$.



SI Figure 162: ^{13}C NMR spectrum of 1-(4-fluorophenyl)pyrrolidine (8c) in $CDCl_3$.



SI Figure 163: HSQ spectrum of 1-(4-fluorophenyl)pyrrolidine (8c) in $CDCl_3$.



SI Figure 164: ^{19}F NMR spectrum of 1-(4-fluorophenyl)pyrrolidine (8c) in $CDCl_3$.

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