Supplementary Information for:

Phosphine-free ruthenium NCN-ligand complexes and their use in catalytic CO_2 hydrogenation †

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DFT Calculated Energies and Cartesian Coordinates

Gaussian 09.[1] Basis Set: Ru SDD effective core potential and 6-31G** for all other atoms, solvation models are for tetrahydrofuran (THF), Enthalpies (H°, Hartrees), Free Energies (G°, Hartrees), and Cartesian Coordinates (Å) of Optimized Structures (1 atm, 298K). Three-dimensional visualization of optimized geometries were constructed using ChemCraft.

RuH(κ^2-NCN)(^{tBu}bpy)OtBu (**2**)

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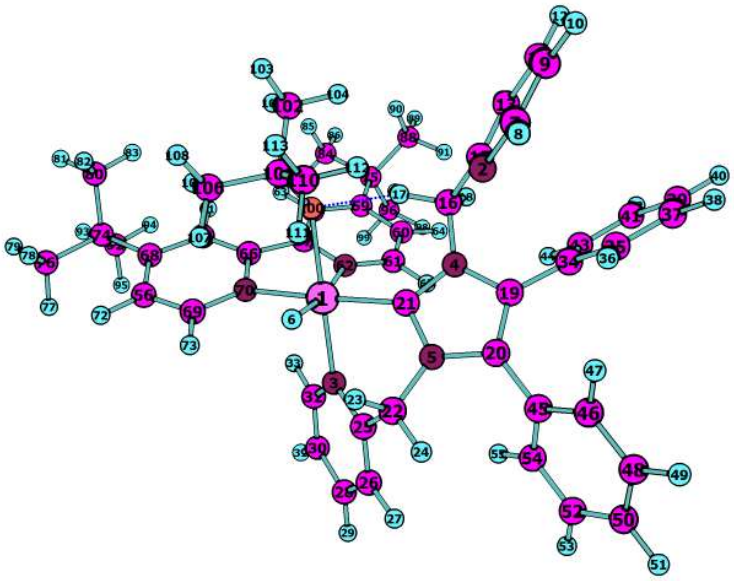
H° = -2398.337297
G° = -2398.479186



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N	10.7020060000	11.1633230000	11.0477910000
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C	11.5044050000	5.7651040000	10.9579020000
H	12.1558000000	5.7150390000	11.8400710000
C	10.9701230000	4.6054400000	10.4267290000
H	11.1857890000	3.6364430000	10.8818320000
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H	9.7018580000	3.8351880000	8.8575460000
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H	9.2569130000	6.1164920000	7.9344590000
C	10.4964330000	7.0785770000	9.4141290000

C	10.2456530000	8.4543980000	8.8756910000
H	11.0584520000	8.7622250000	8.1816060000
H	9.2997310000	8.4458850000	8.3035100000
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C	9.8030850000	10.4490780000	11.8094780000
C	10.9739540000	10.5726790000	9.8620050000
C	11.4082660000	12.3484480000	11.4269550000
H	12.4915830000	12.1326910000	11.3848680000
H	11.1495830000	12.6113230000	12.4608780000
C	11.0933490000	13.4791950000	10.5105960000
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C	10.3302590000	15.7191040000	10.1339240000
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Transition State: CO_2 + RuH(κ^2-NCN)(^{tBu}bpy)OtBu to Ru(HCO_2)(κ^2-NCN)(^{tBu}bpy)OtBu

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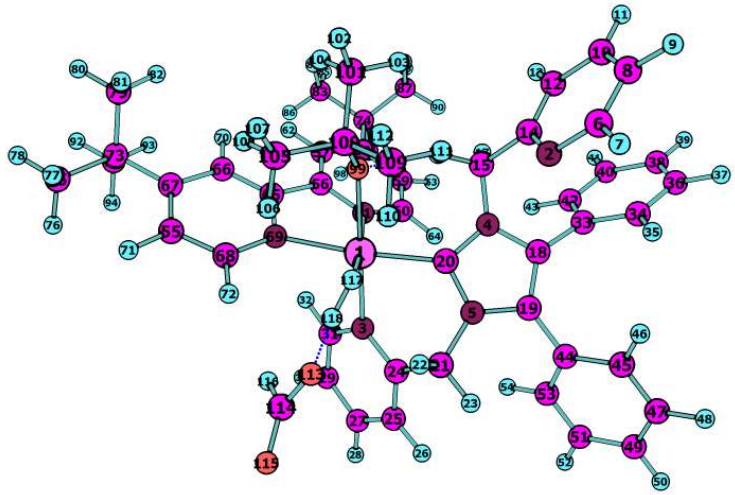
G° = -2586.982116



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C	9.7066900000	10.4309170000	11.6866230000
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H	10.8884800000	12.6373450000	12.4491080000
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C	10.4998310000	14.7024970000	10.9644920000
H	10.2872510000	14.8107250000	12.0314440000
C	10.2646050000	15.7350440000	10.0782170000
H	9.8681250000	16.6930930000	10.4231320000
C	10.5340740000	15.5089920000	8.7415620000
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C	11.0429370000	14.2864520000	8.3610230000
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C	8.6733650000	7.2449250000	12.0401890000
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H	7.1866370000	13.5376810000	14.0033910000
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H	15.9089050000	11.8188240000	1.5283590000
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H	13.6883760000	8.2664690000	5.7239080000
C	15.1802130000	10.0471950000	7.1661500000
H	15.3293880000	10.9261300000	7.8153800000
H	16.1278330000	9.4798410000	7.1626160000

H	14.9999690000	10.4100450000	6.1386330000
C	14.2990990000	8.7535000000	9.0791340000
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H	13.5076240000	8.0855970000	9.4535540000
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Ru(HCOO)(κ^2-NCN)(^{tBu}bpy)OtBu – H-Bound formate

THF

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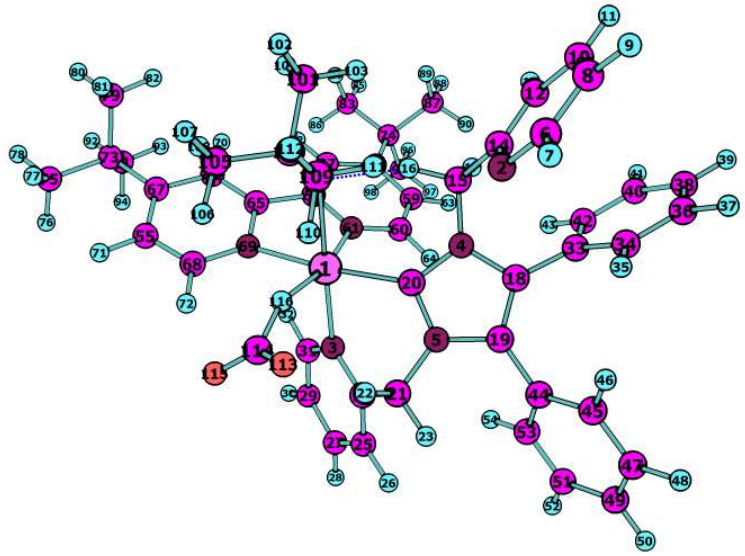
G° = -2586.987679



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H	10.8884800000	12.6373450000	12.4491080000
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C	10.4998310000	14.7024970000	10.9644920000
H	10.2872510000	14.8107250000	12.0314440000
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H	9.8681250000	16.6930930000	10.4231320000
C	10.5340740000	15.5089920000	8.7415620000
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C	11.0429370000	14.2864520000	8.3610230000
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C	8.5444960000	8.2200600000	11.0553650000
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H	9.5052740000	7.3064190000	12.7476650000
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Ru(OCHO)(κ^2-NCN)(^{tBu}bpy)OtBu – O-bound formate

THF

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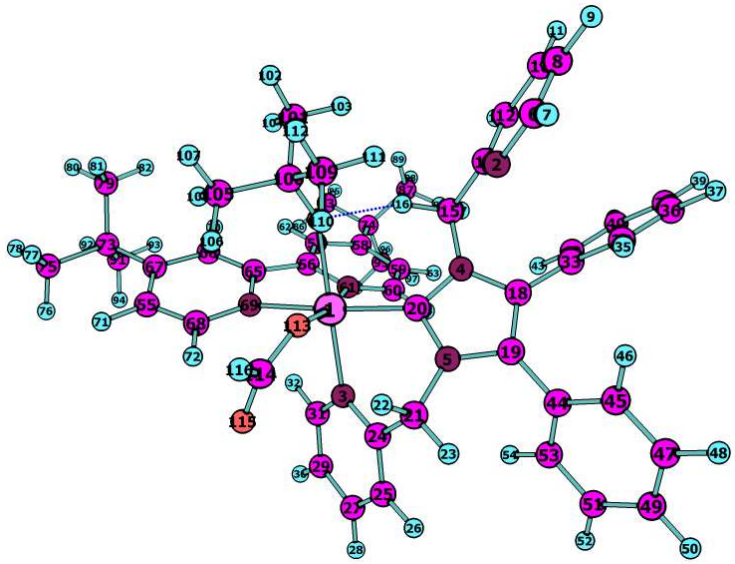
G° = -2587.011612



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Transition State TS-2: Formate + [Ru(H_2)(κ^2-NCN)(^{tBu}bpy)OtBu]$^+$ to Formic Acid + RuH(κ^2-NCN)(^{tBu}bpy)(OtBu)

THF

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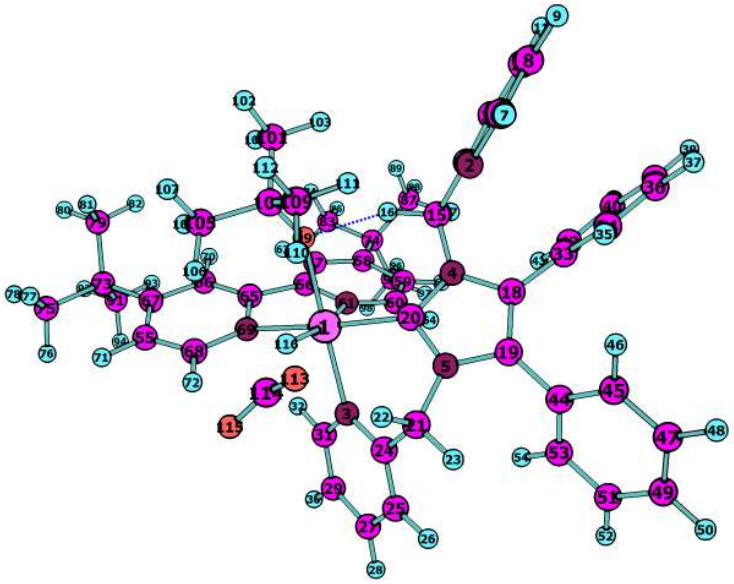
G° = -2586.982116



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O	12.8117370000	9.8511070000	7.5381790000
C	14.0094490000	9.2000380000	7.6524990000
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H	13.0731610000	7.3227370000	7.1022150000
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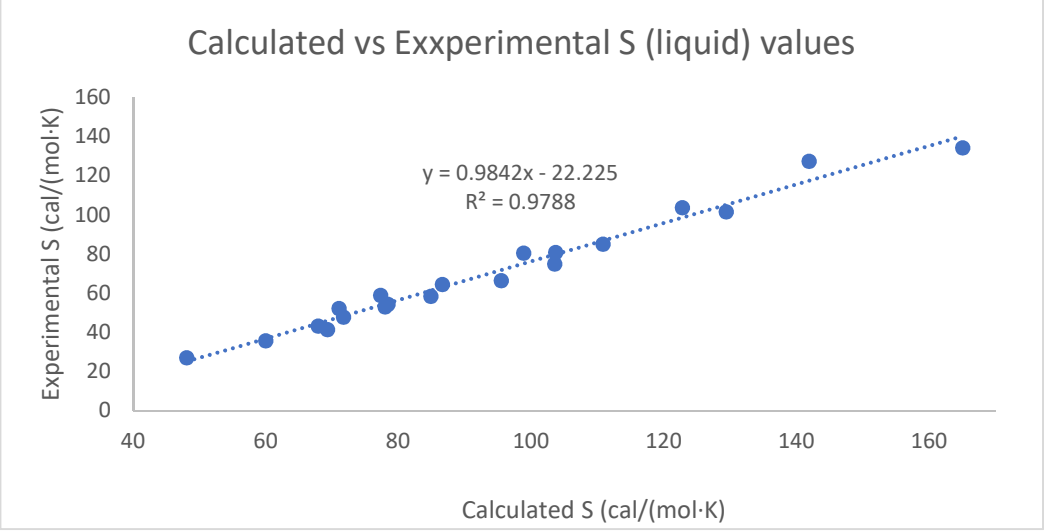
Corrections to energies as calculated by DFT[2]

Compound	S Liquid	S Gas	S DFT* (Truhlar corrected)
			cal/mol/K
Hydrogen cyanide	27	48.2	48.09183515
Acetonitrile	35.8	58.2	59.99587977
Benzene	41.4	64.3	69.30275483
Thiophene	43.3	66.6	67.913669
Acetone	47.8	70.6	71.72523633
Isopropylamine	52.2	74.6	71.0664729
Chromil chloride	53	78.8	78.00769269
trichloroethane	54.3	77.2	78.41599974
VOCl3	58.4	82.3	84.89419092
Butanal	58.9	82.1	77.33630121
Diethyl Sulfide	64.4	88	86.63686224
Tetrabromosilane	66.4	90.3	95.53332557
NiCO5	74.9	98.1	103.5479299
Triethylborane	80.5	104.6	98.87555026
FeCO5	80.8	NA	103.7141992
C6F5CF3	85	109.6	110.8616772
Diethylphthalate	101.6	NA	129.4038684
Hexamethyldisiloxane	103.7	127.9	122.8057107
Ethyl silicate	127.4	NA	141.8993268
Perfluoroheptane	134.3	NA	165.0633854
Entropy Correction	**-22.22512215**		



Species calculated using M11L/6-31G**/SDD/THF at 298K, 323K and their energies

Table S1: Definition of the species calculated using M11L/6-31G**/SDD/THF and their energies

Formula	**imaginary freq**	**ΔH (DFT)**	**S (DFT)**	**Truhlar correction**	**Gusev correction**	**G (DFT)**	**ΔG (DFT) Corrected**	
		Hartrees	cal/mol/K	cal/mol/K	cal/mol/K	cal/mol/K	298 K	323 K
H2		-1.165	31.172	-0.019	13.9	-1.179	-736	-736
CO2		-188.507	52.457	-0.032	22.22	-188.532	-118299	-118300
DBU		-461.755	96.276	-0.069	22.22	-461.801	-289777	-289779
RuH **(2)**		-2398.337	298.630	-8.814	22.22	-2398.479	-1505058	-1505065
Ru-H-CO2 **(TS-1)**	-808	-2586.831	318.852	-	22.22	-2586.982	-1623355	-1623355
RuHCO2		-2586.838	315.941	-9.296	22.22	-2586.988	-1623349	-1623356
RuOCHO		-2586.862	315.901	-9.959	22.22	-2587.012	-1623363	-1623371
RuH2-OCHO **(3)**		-2588.005	323.480	-10.347	22.22	-2588.159	-1624083	-1624090
RuH-H-OCHO **(TS-2)**	-603	-2588.000	322.661	-	22.22	-2588.153	-1624089	-1624090
RuH-HOCHO		-2588.009	322.805	-9.006	22.22	-2588.163	-1624086	-1624093
DBUH-OCHO		-651.436	122.515	-1.358	22.22	-651.494	-408811	-408814

Spectra of complexes 1, 2, 3 and the *tamyl* analogue of **2**.

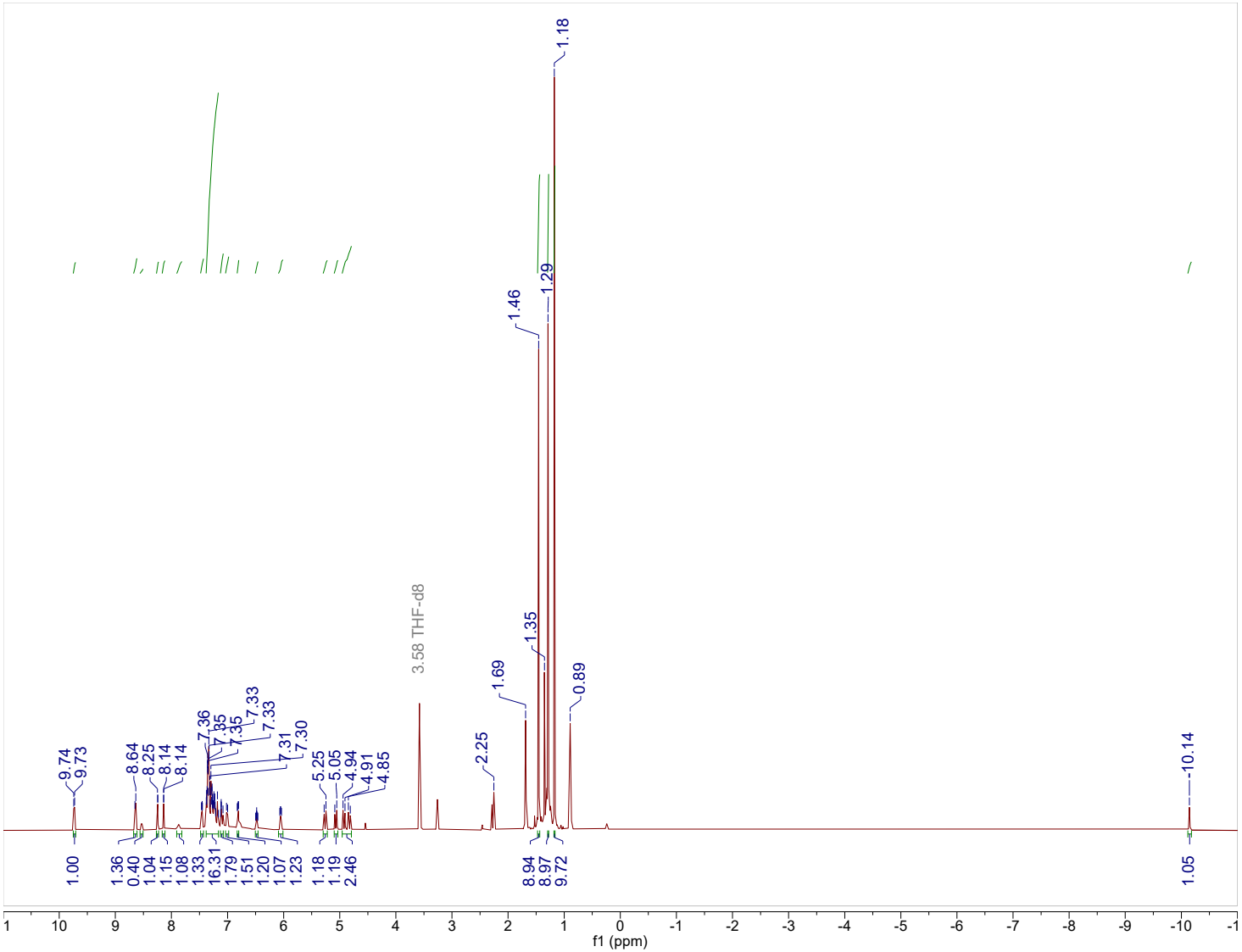


*Figure S1: [1]H NMR spectrum (400 MHz, THF-d8) of **2***

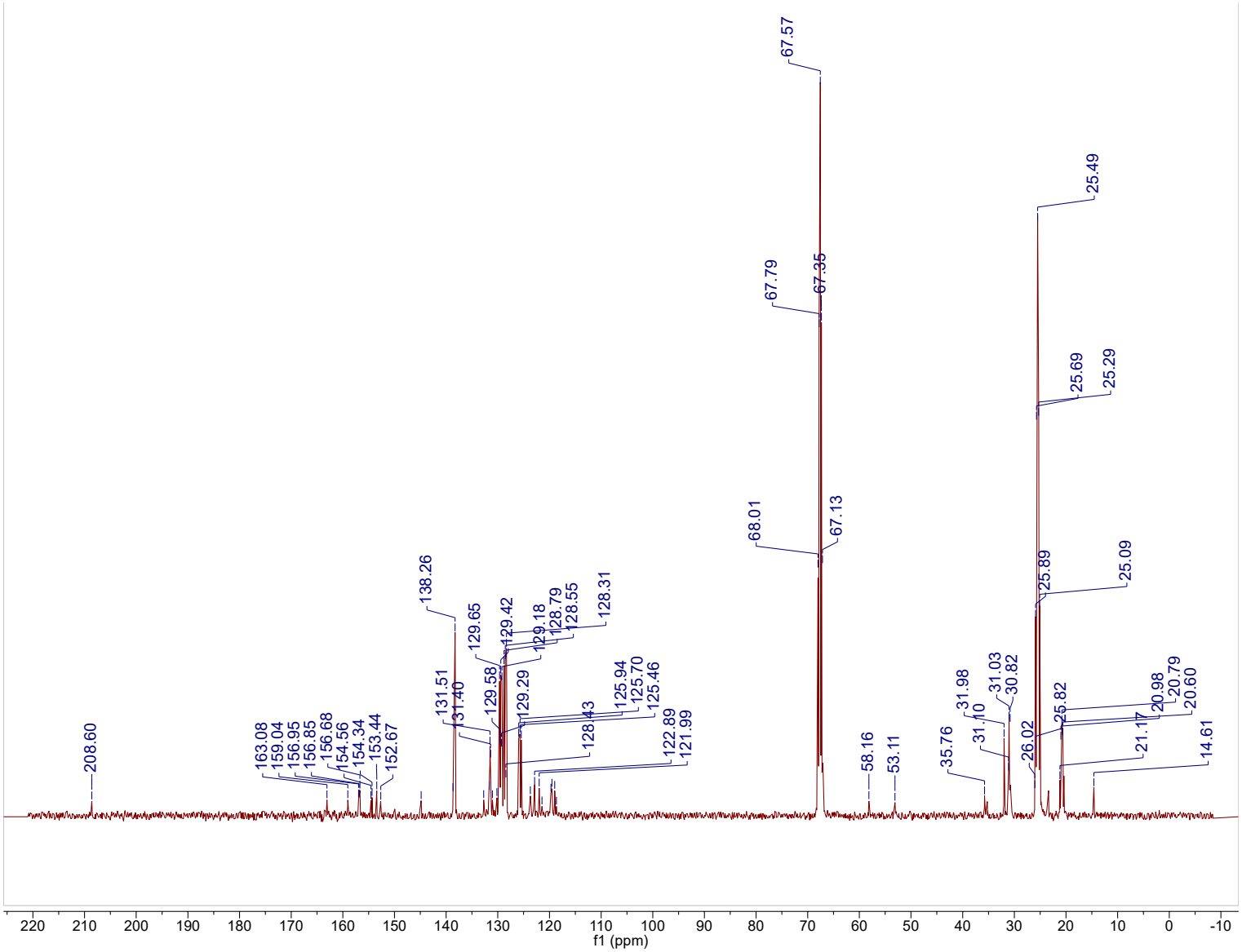


*Figure S2: ^{13}C NMR spectrum (101 MHz, THF) of **2***

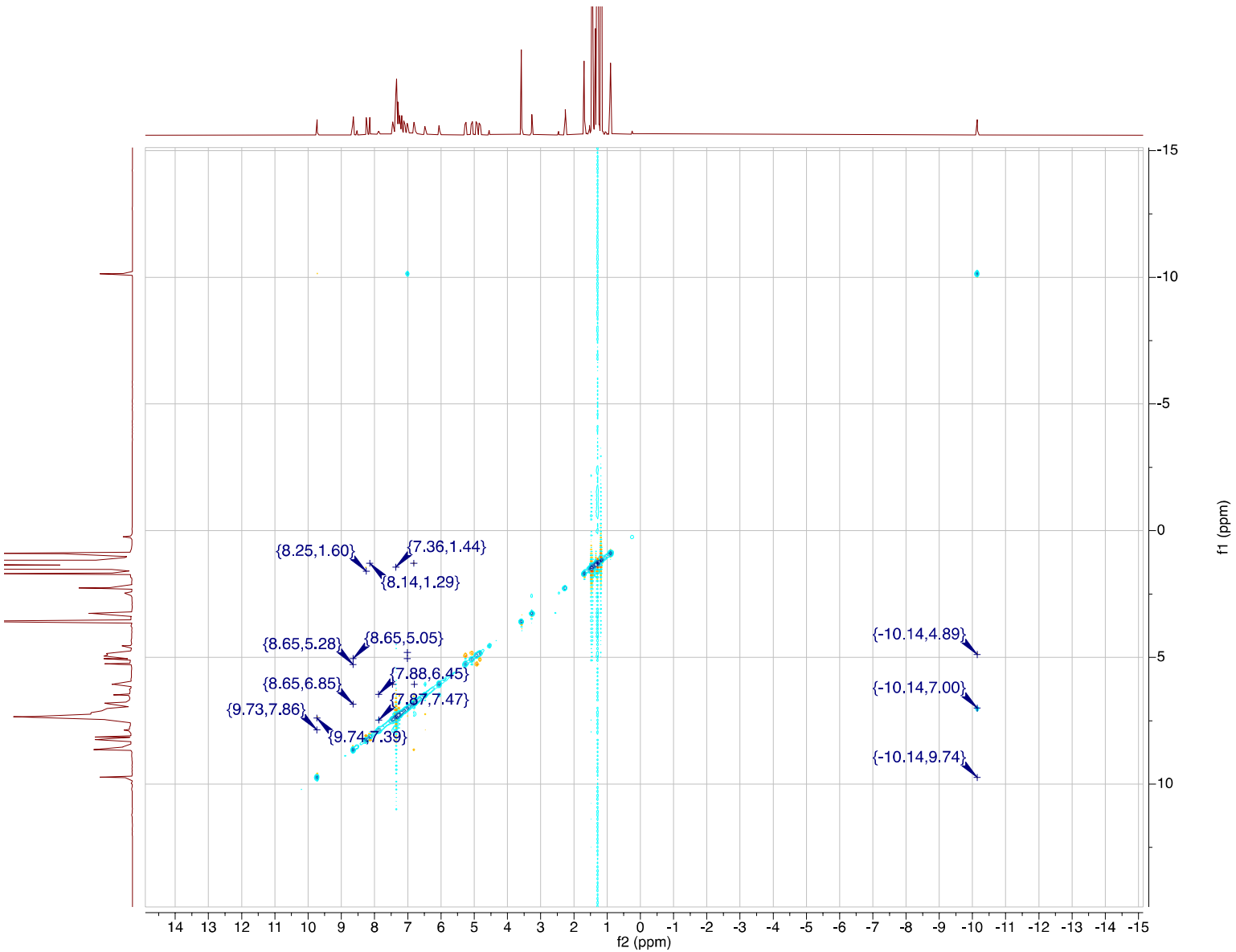


*Figure S3: ^{1}H-^{1}H NOESY spectrum (400 MHz, THF-d8) of **2***

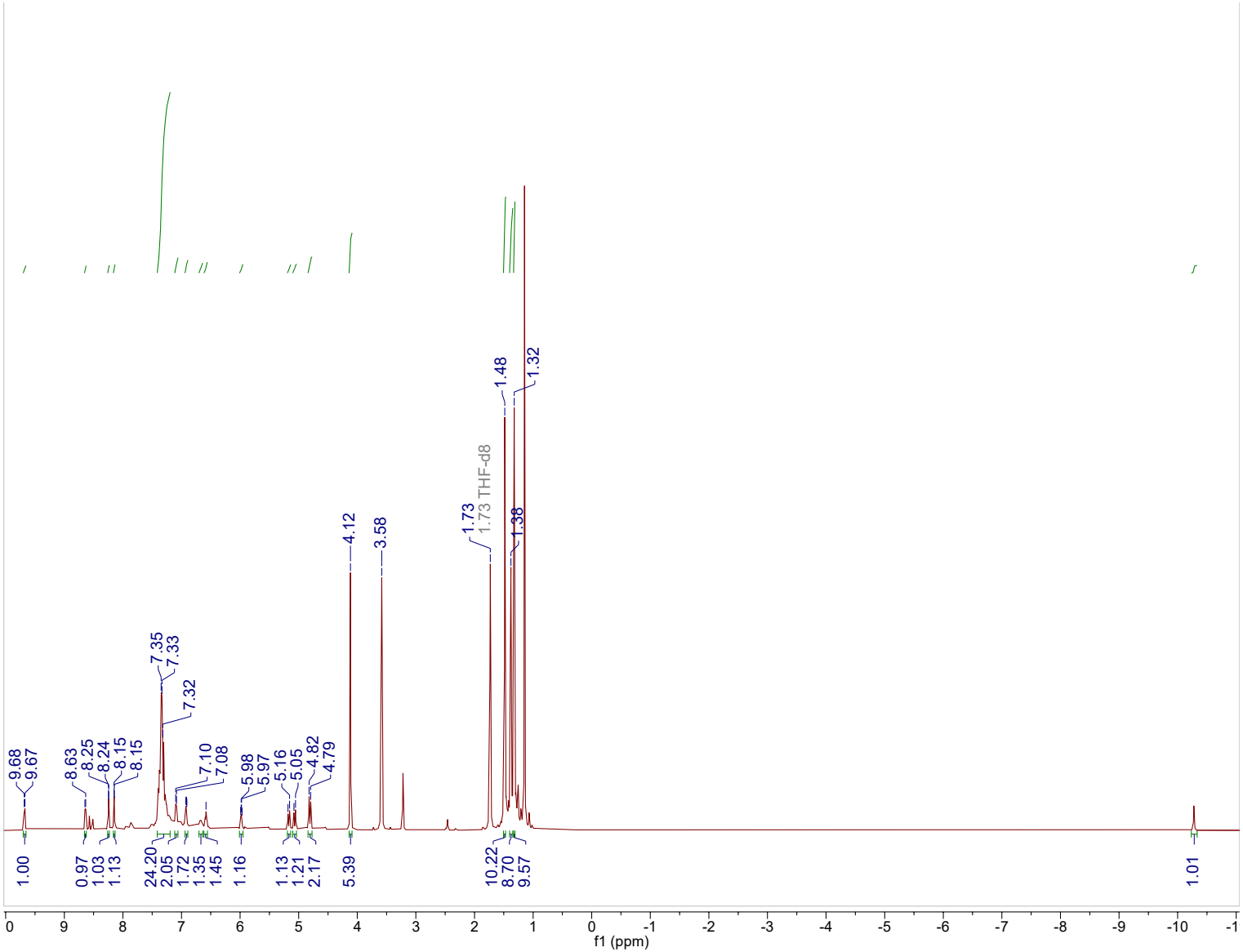


*Figure S4: [1]H NMR Spectrum (500 MHz, THF-d8) of **2** with Ferrocene internal standard*

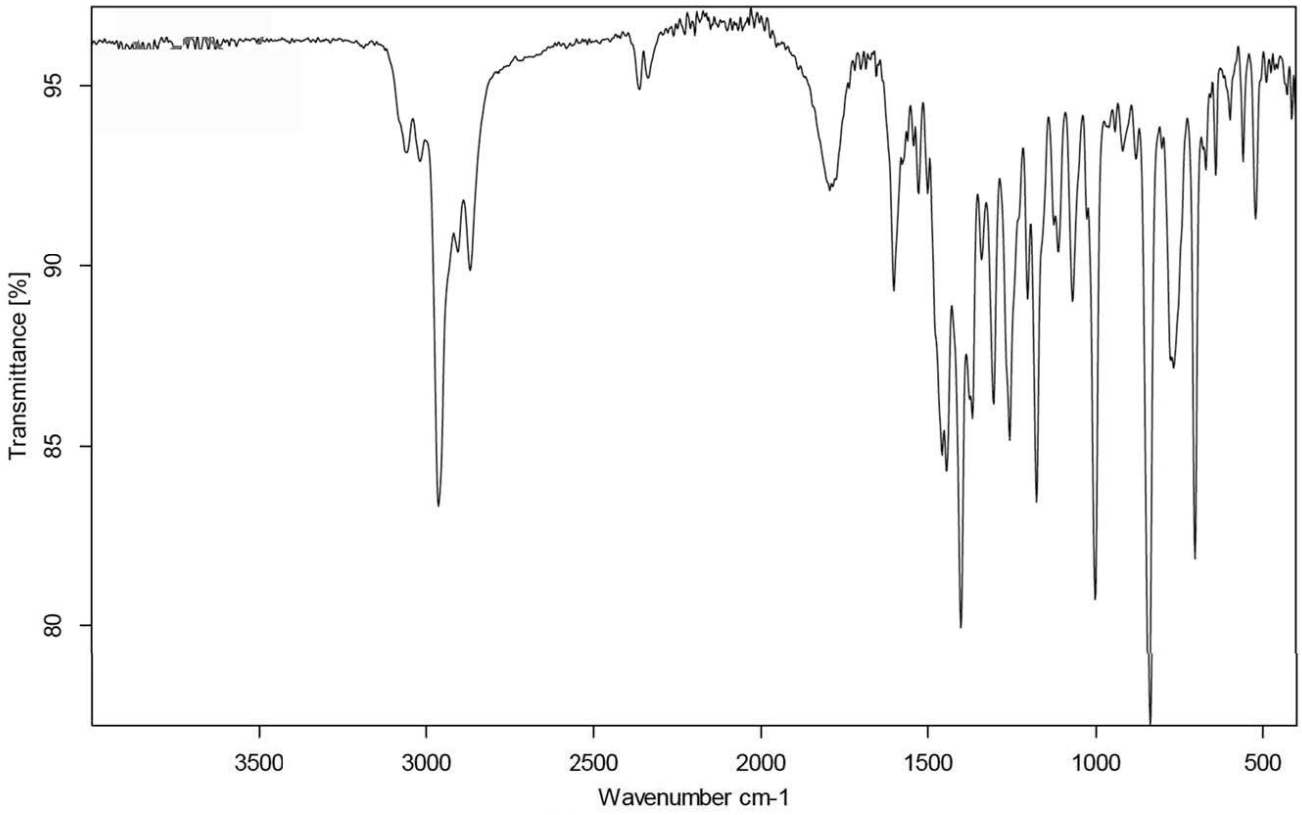


Figure S5: IR Spectrum of **2**

S25

*Figure S5: IR Spectrum of **2***

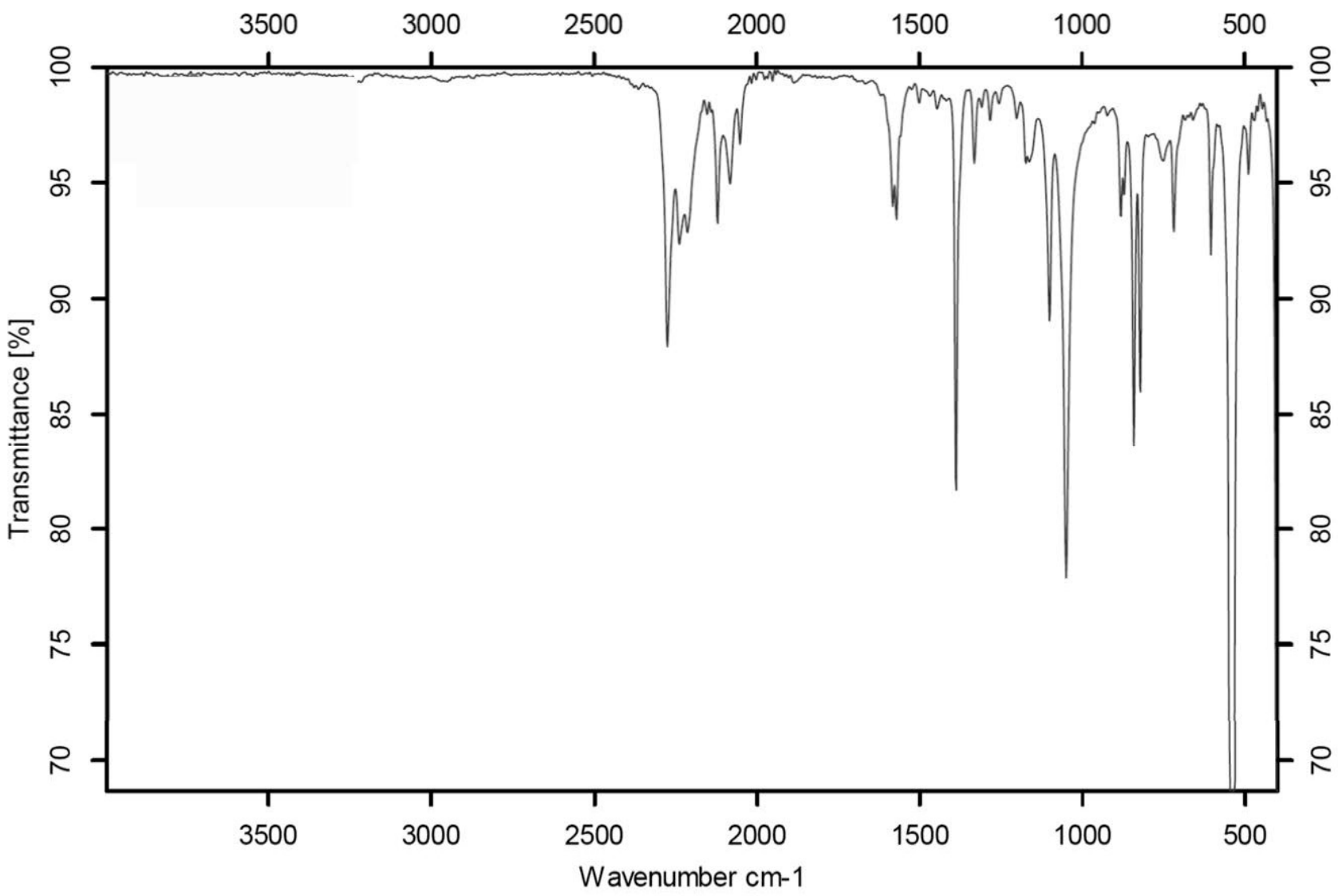


*Figure S6: IR Spectrum of isotopologue of **2** synthesized under D_2 gas*

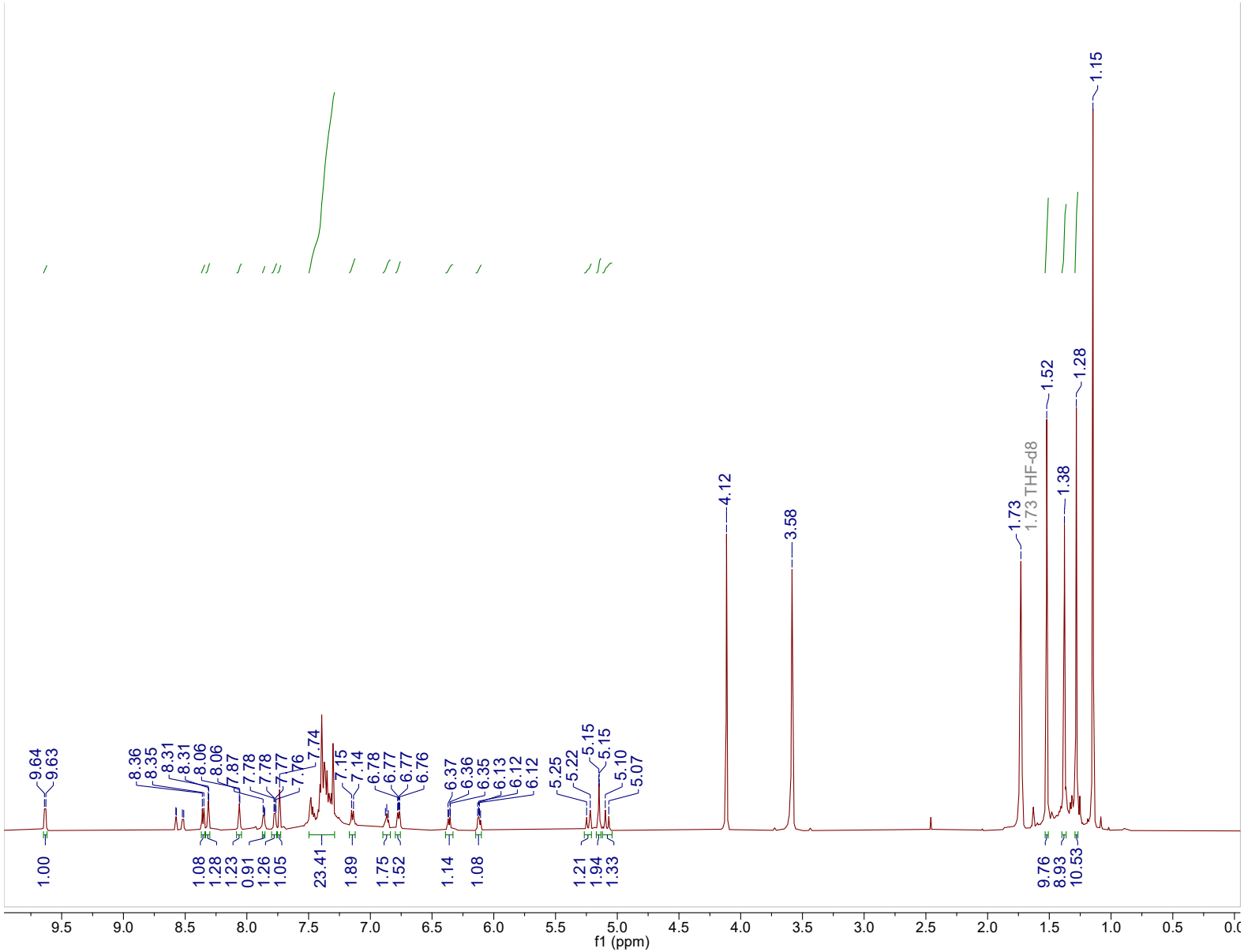


*Figure S7: [1]H NMR Spectrum (500 MHz, THF-d8) of **3** with Ferrocene internal standard*

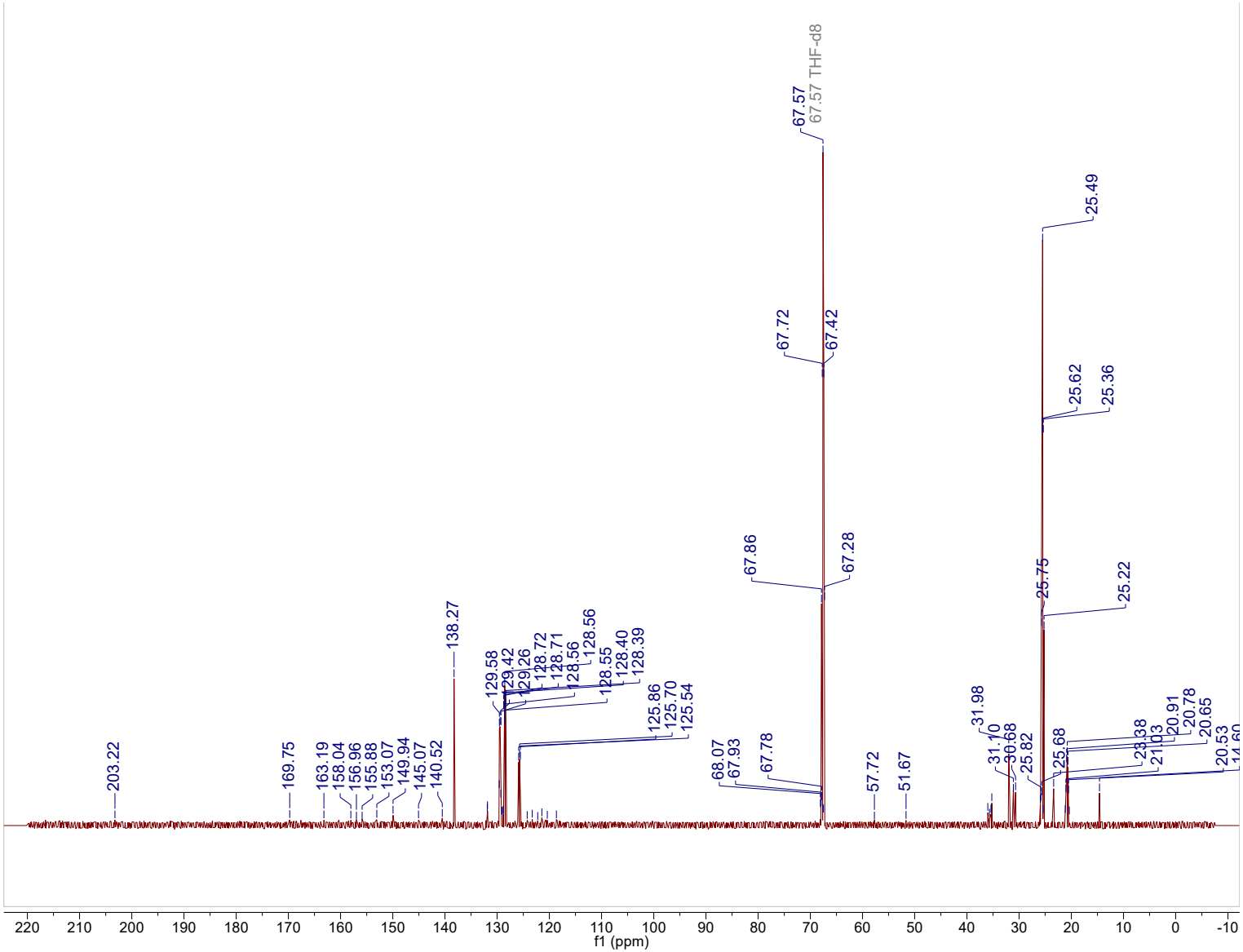


*Figure S8: ^{13}C NMR Spectrum (151 MHz, THF-d8) of **3***

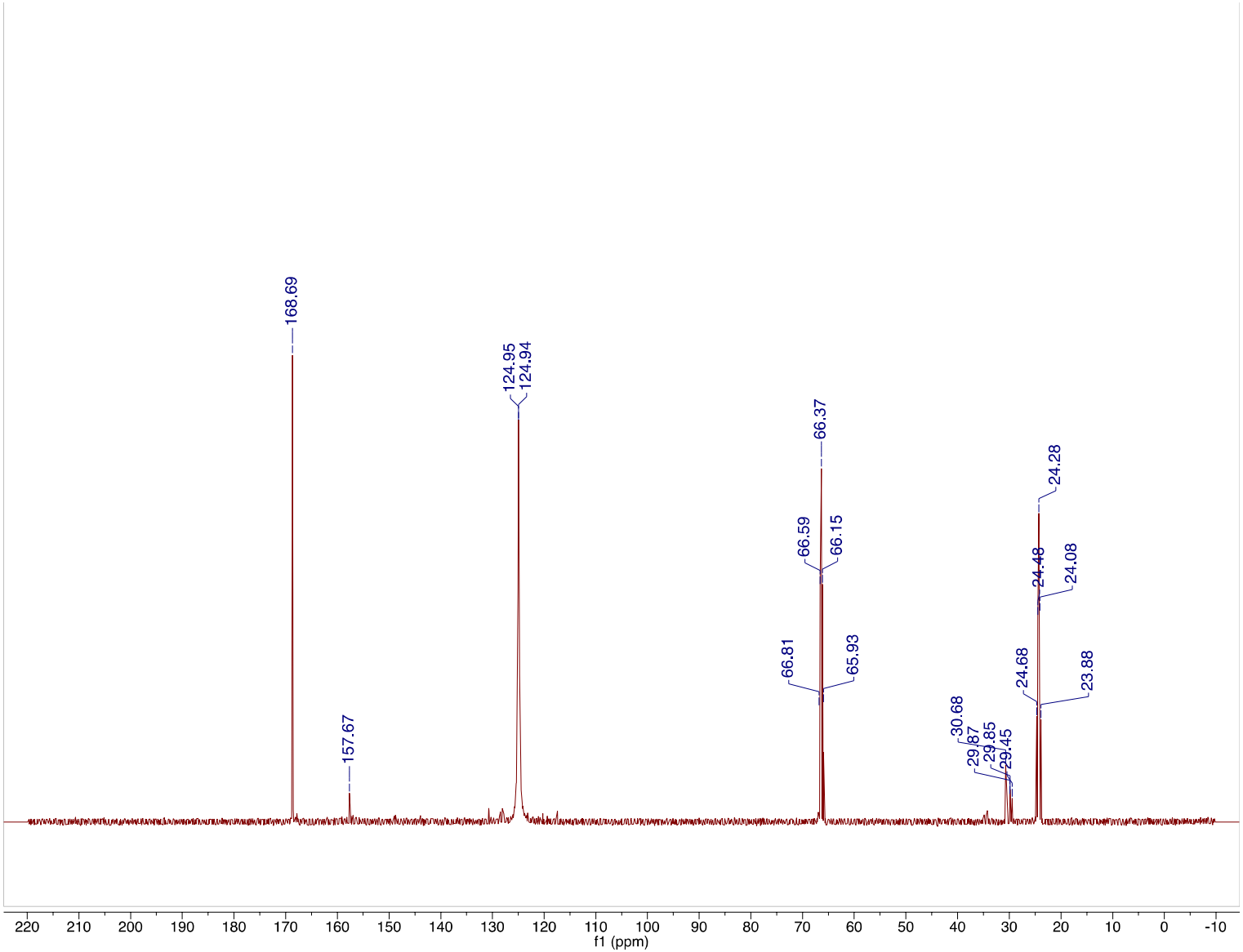


*Figure S9: ^{13}C NMR Spectrum of **3** (151 MHz, THF-d8) using ^{13}C labelled CO_2*

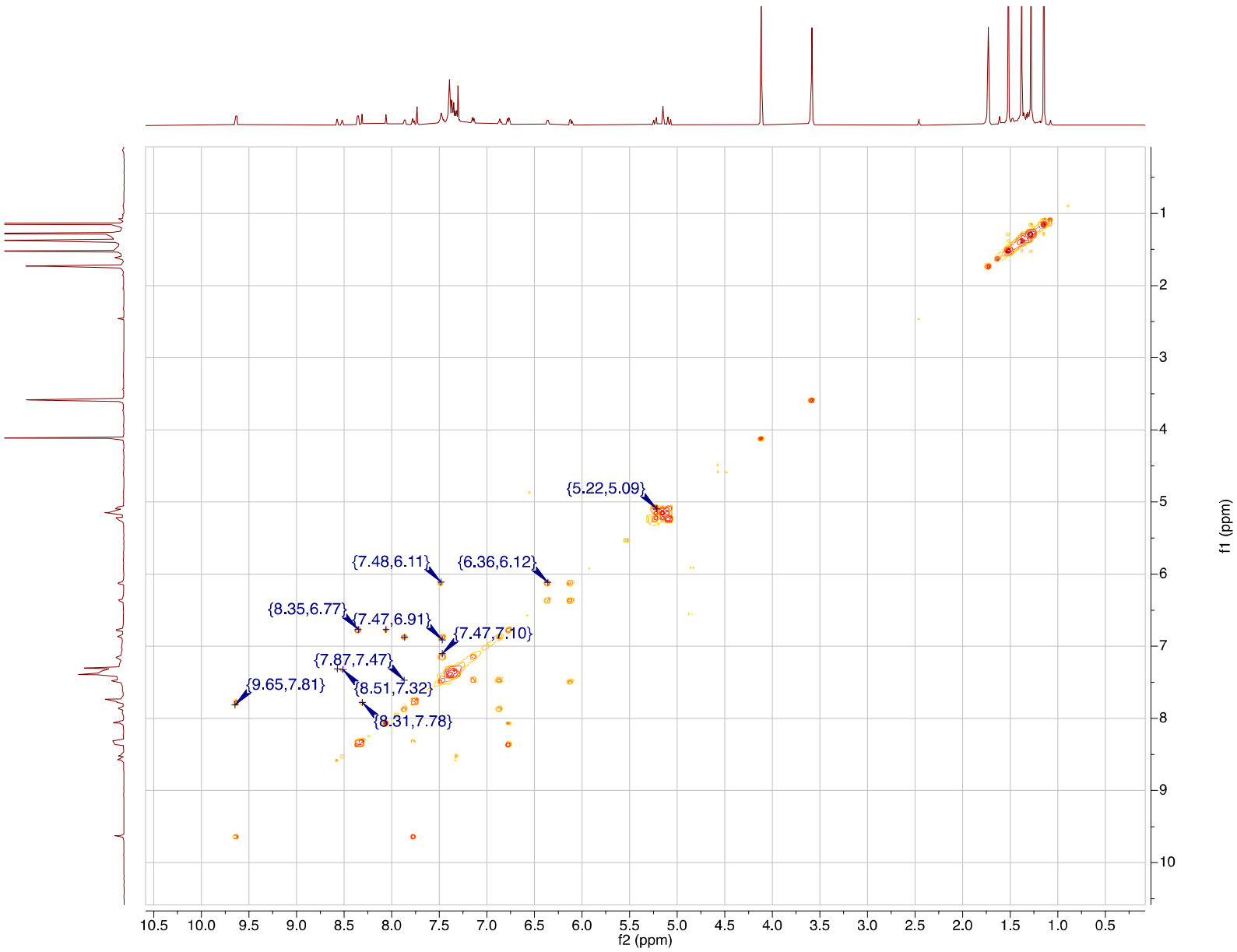


*Figure S10: ^{1}H-^{1}H COSY spectrum (500 MHz, THF-d8) of **3** with Ferrocene internal standard*

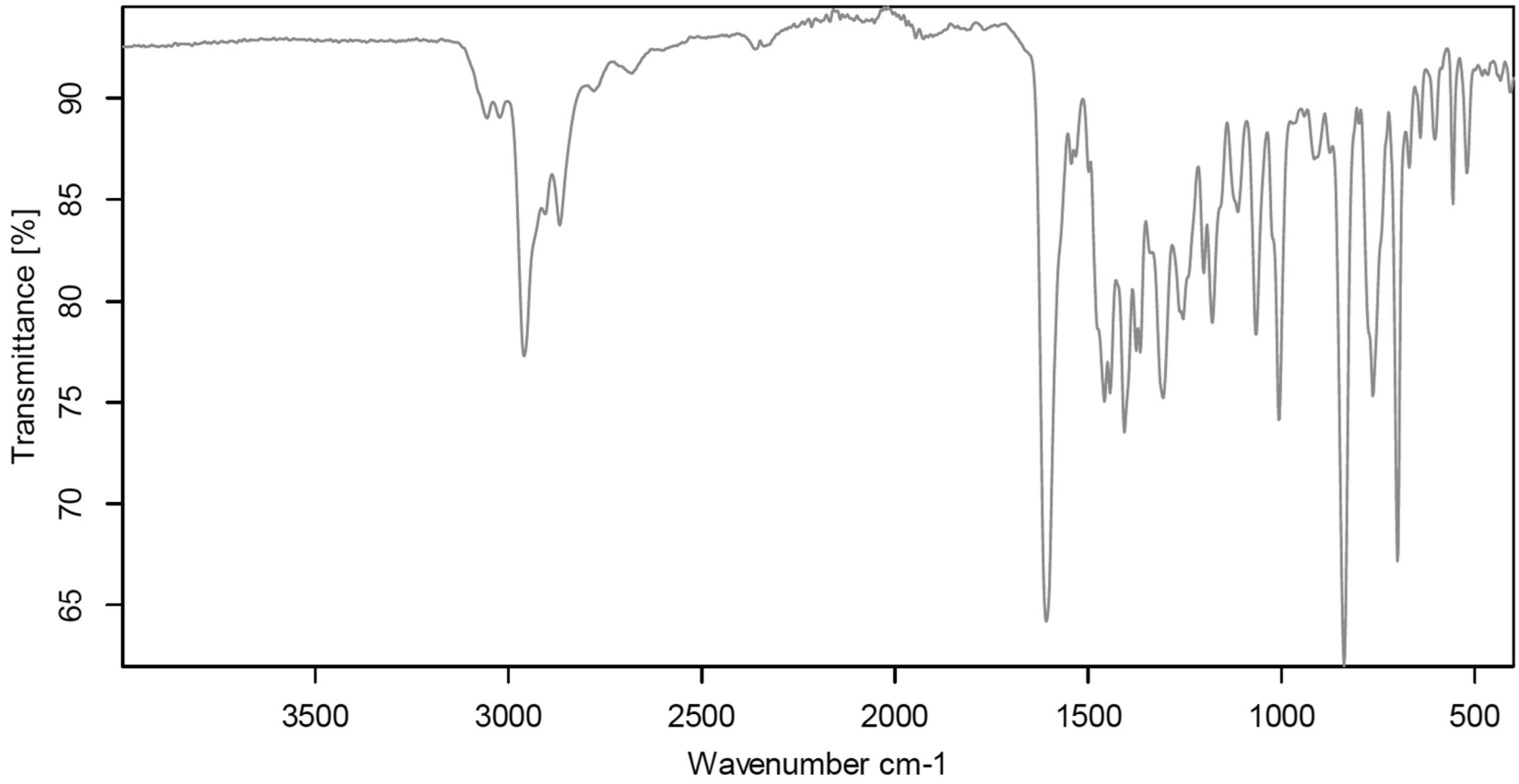
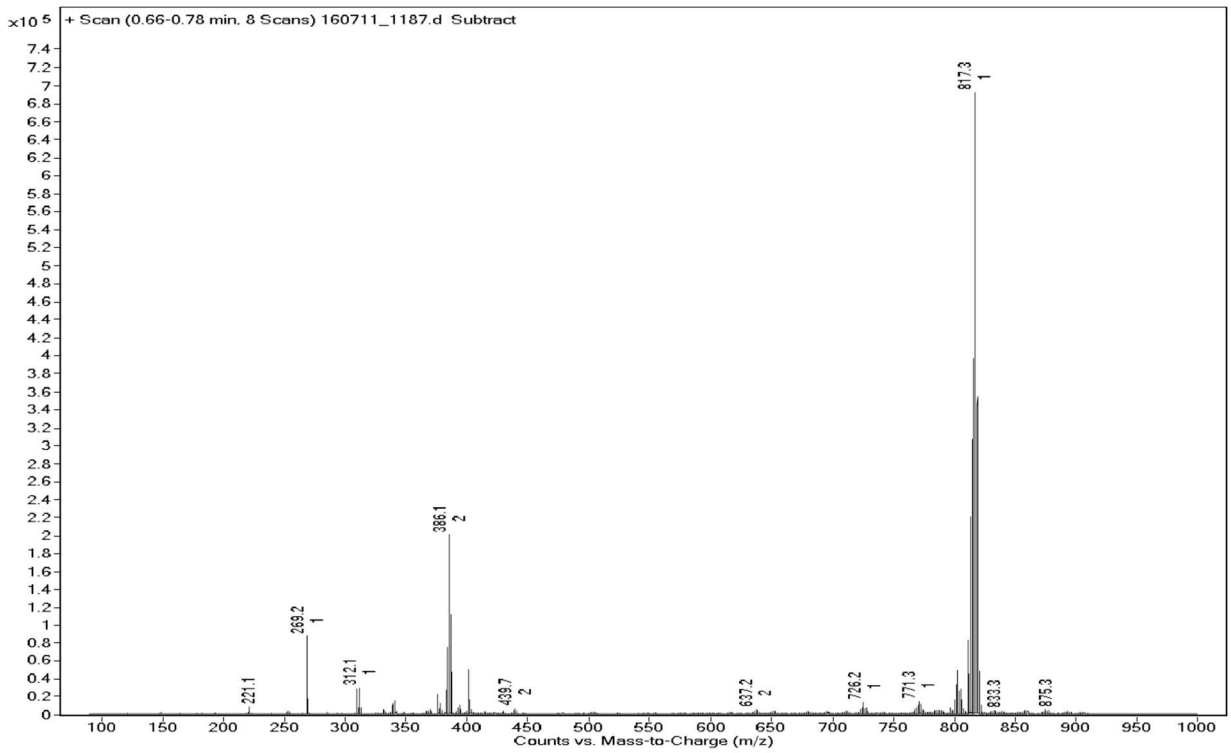
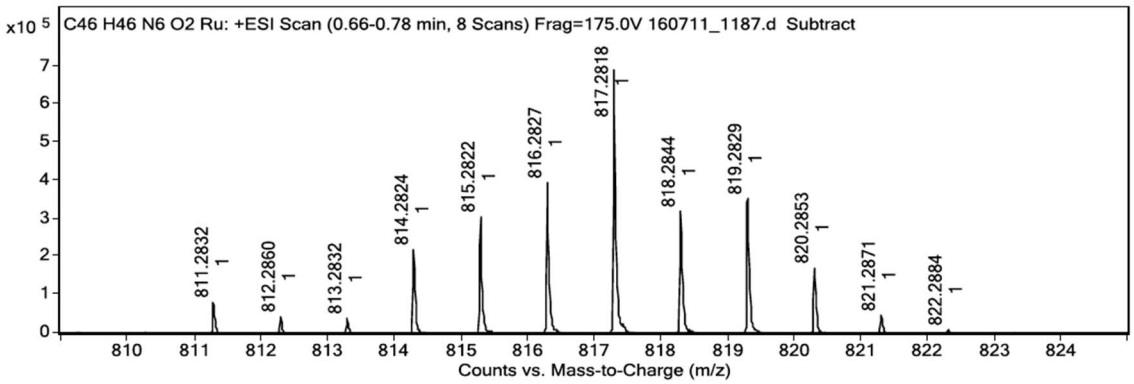


*Figure S4: IR Spectrum of complex **3***





Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	811.2832	811.2831	0.1	12.2	13.0	0.8
2	812.2860	812.2862	-0.2	6.3	6.8	0.5
3	813.2832	813.2833	-0.1	5.8	6.2	0.4
4	814.2824	814.2817	0.7	31.3	32.6	1.3
5	815.2822	815.2815	0.7	43.3	46.0	2.7
6	816.2827	816.2820	0.7	56.7	59.9	3.2
7	817.2818	817.2811	0.7	100.0	100.0	0.0
8	818.2844	818.2836	0.8	45.6	45.4	-0.2
9	819.2829	819.2821	0.8	51.5	55.2	3.7
10	820.2853	820.2845	0.8	25.1	25.0	-0.1
11	821.2871	821.2873	-0.2	6.7	6.4	-0.3

*Figure S5: ESI-MS spectra for **3** showing dissociation of –OtBu ligand*

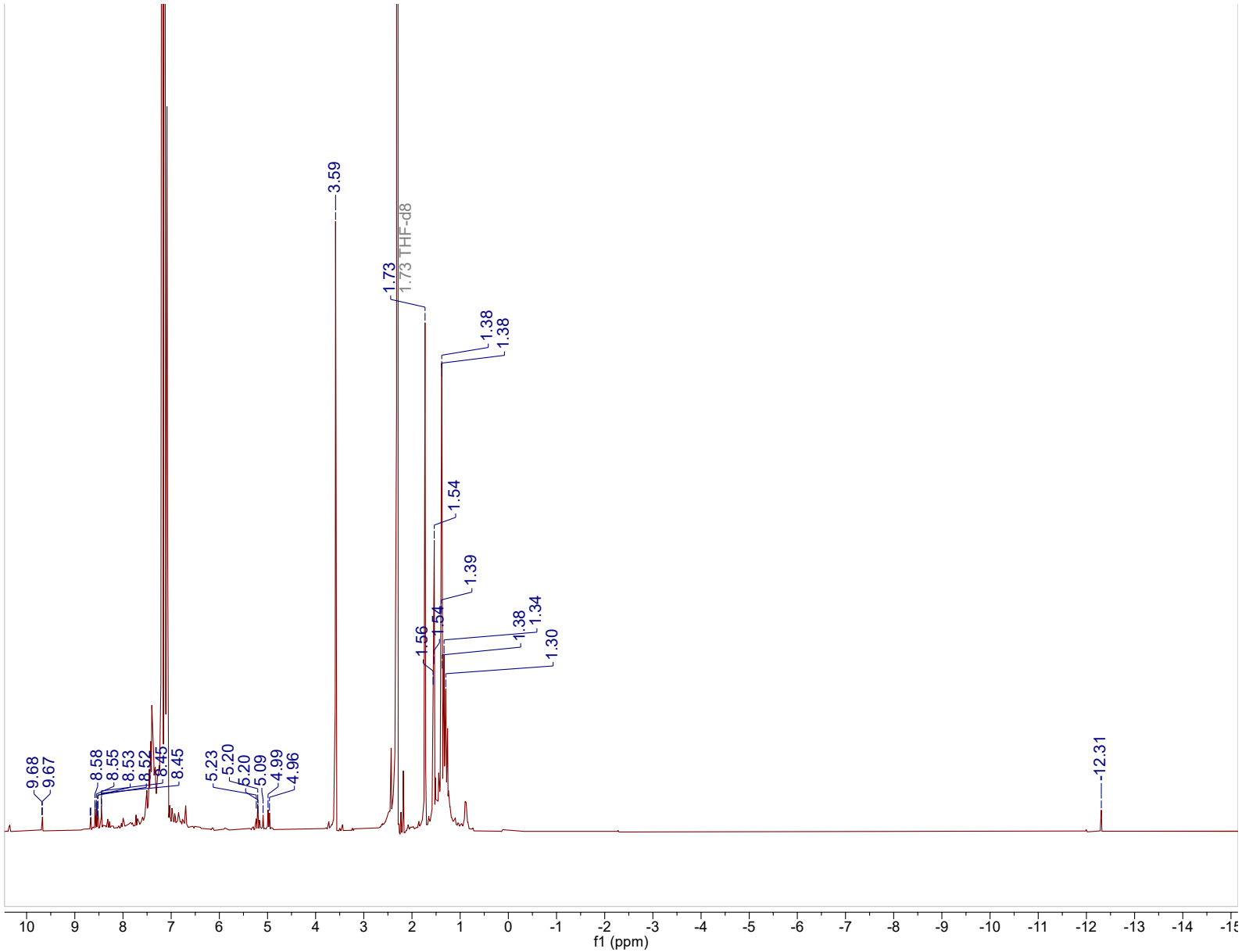


*Figure S6: [1]H NMR Spectrum (500 MHz, THF-d8) of OtAmyl analogue of **3***

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2. D. G. Gusev and D. M. Spasyuk, *ACS Catal.*, 2018, **8**, 6851-6861.