Electronic Supplementary Material (ESI) for Dalton Transactions.

Coupling of CO_2 and Epoxides Catalysed by Novel *N*-Fused Mesoionic Carbene Complexes of Nickel(II)

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[d] *University of Innsbruck, Faculty of Chemistry and Pharmacy, Institute of General, Inorganic and Theoretical Chemistry, Innrain 80-82, 6020 Innsbruck*
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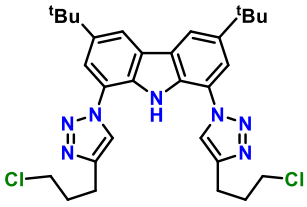
1. NMR spectra



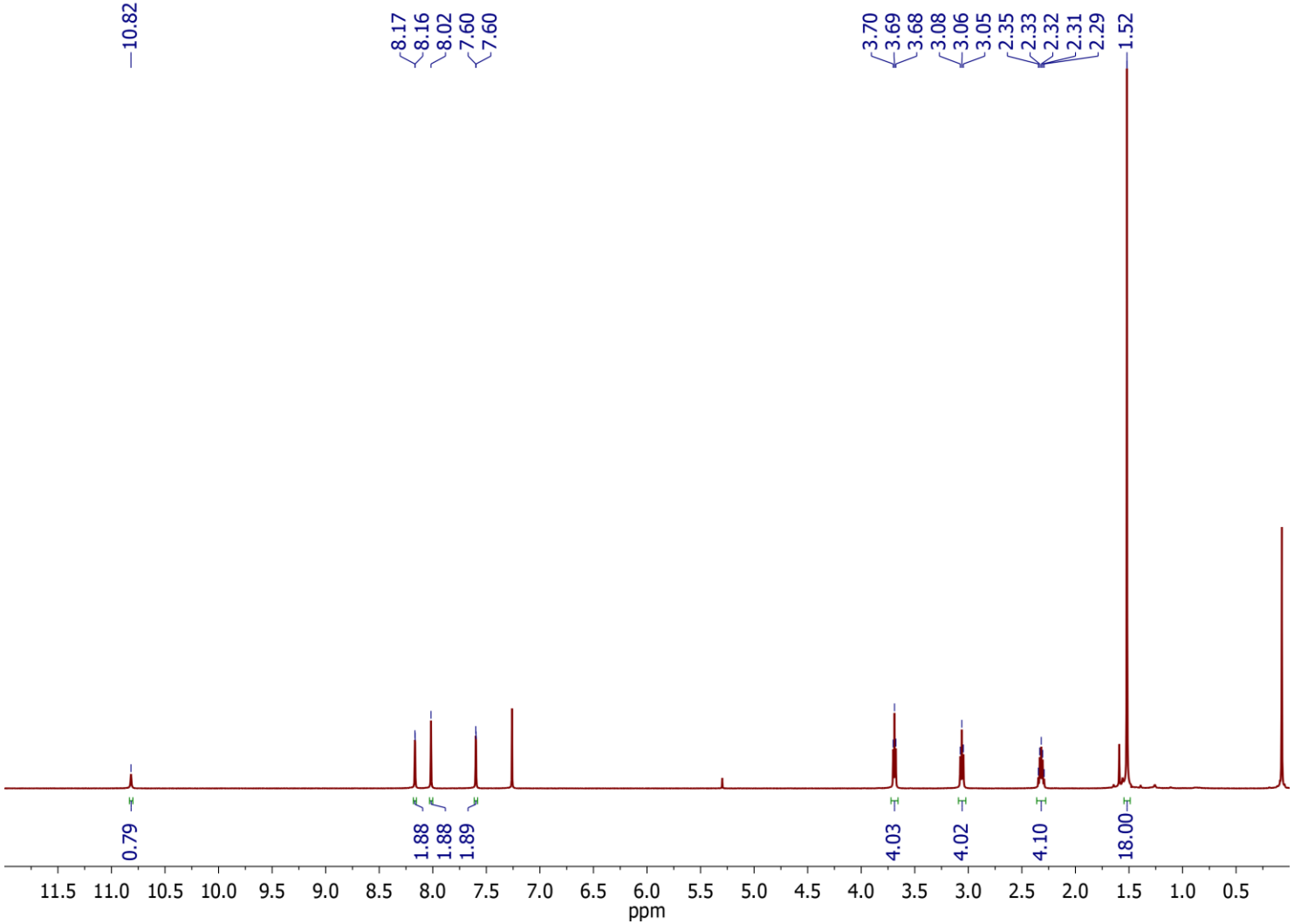
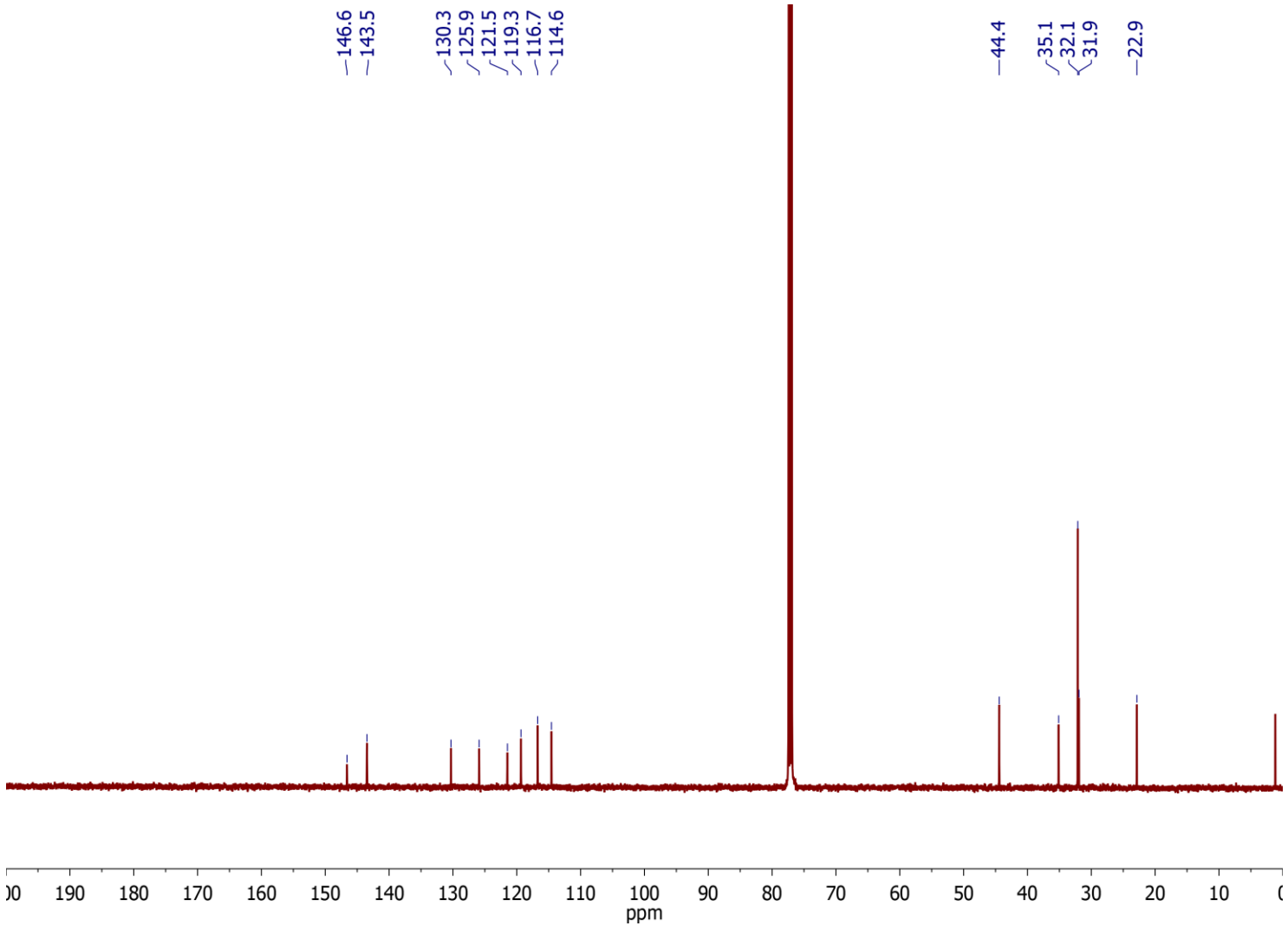


Figure S 1: *^{1}H NMR of **2a** in. $CDCl_3$ at 298 K. Small impurities of DCM and grease are present.*



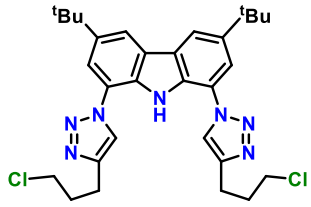
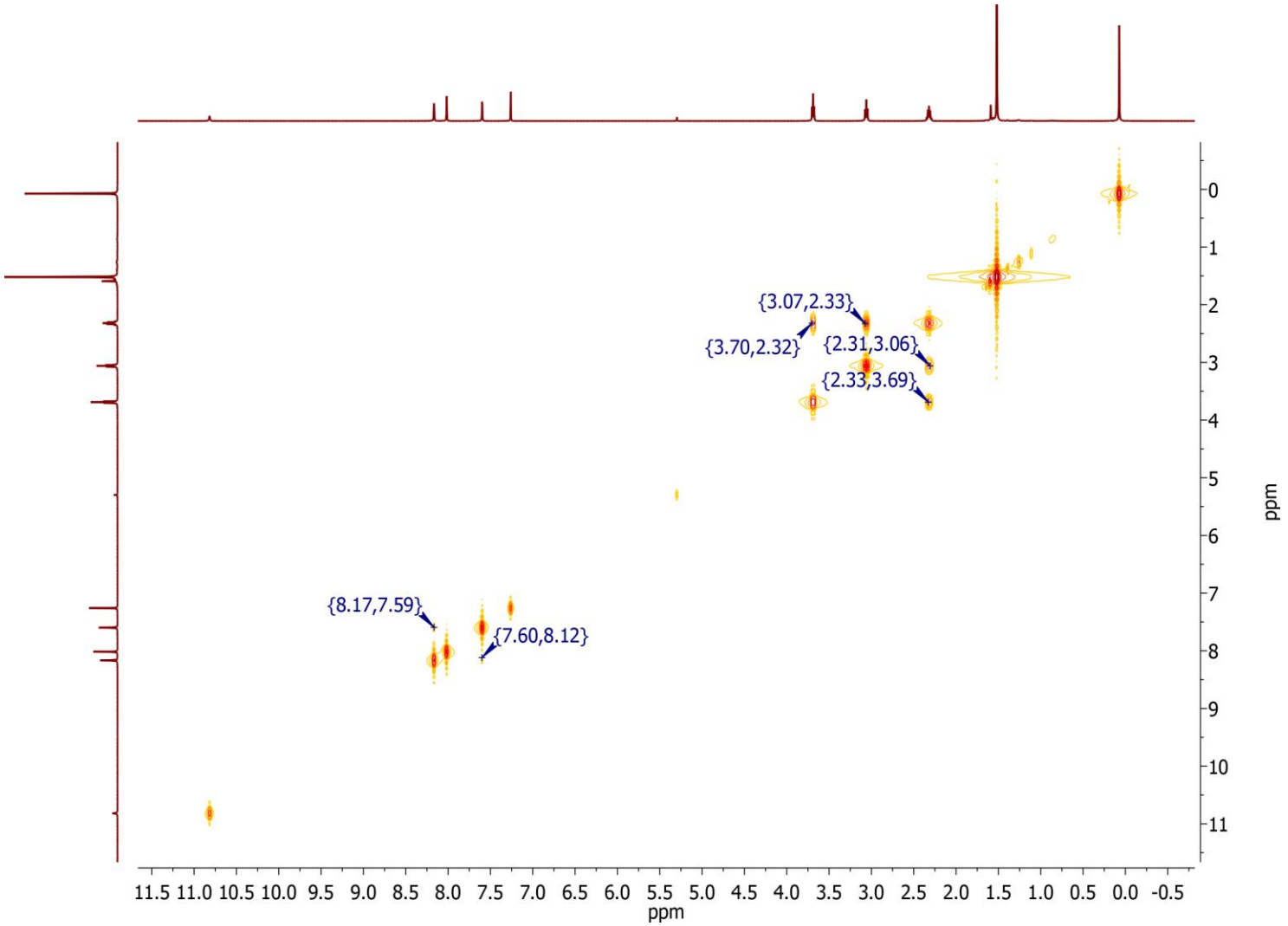


Figure S 2: *^{13}C NMR of **2a** in $CDCl_3$ at 298 K. Signal at 1.2 ppm belongs to grease.*



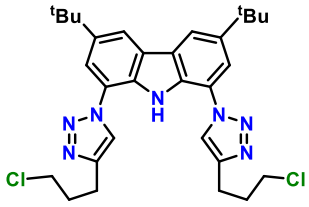
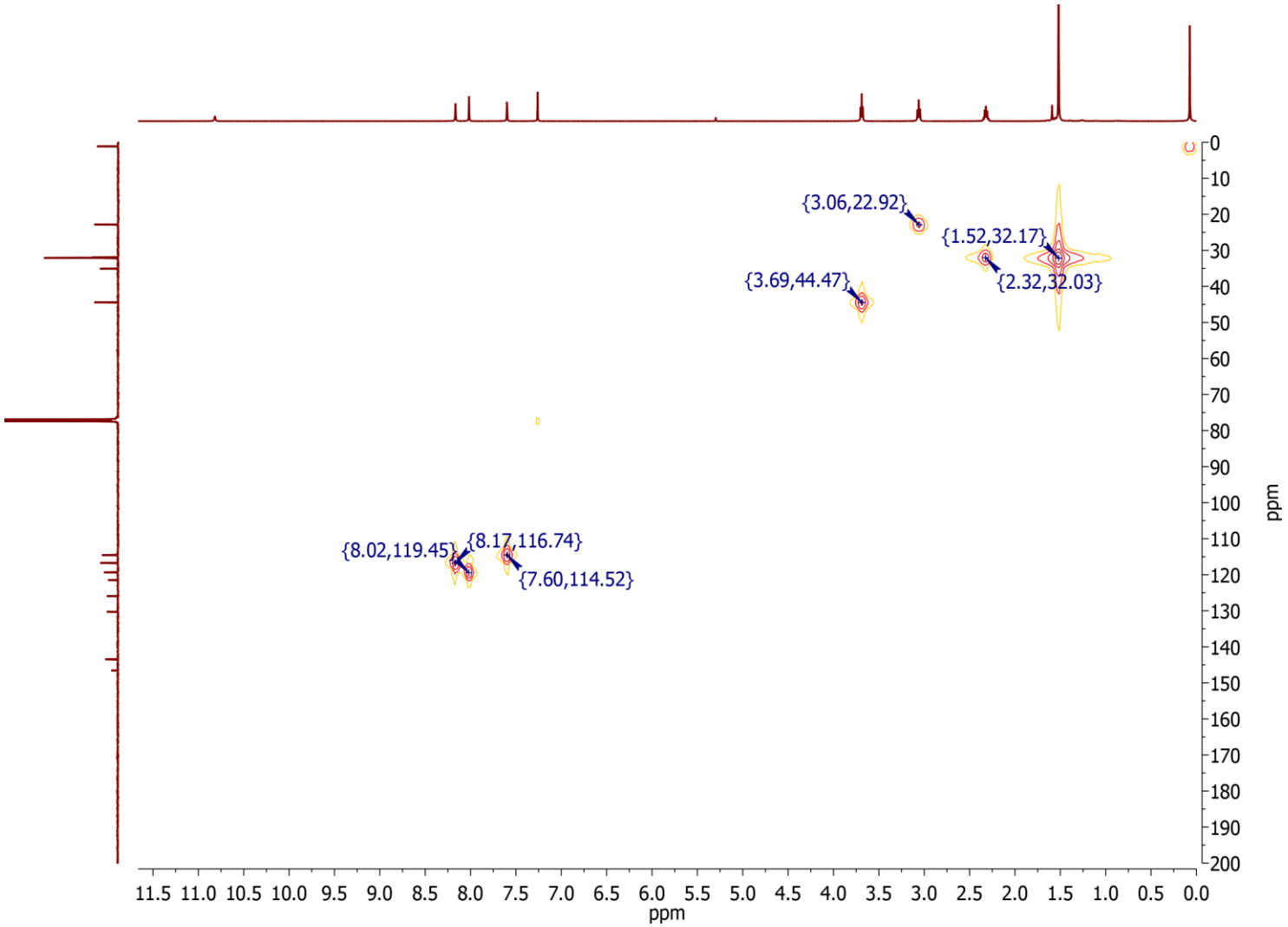


Figure S 3: *$^{1}H - ^{1}H$ COSY of **2a** in CDCl3 at 298 K.*



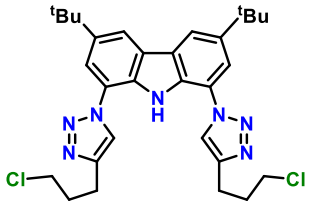
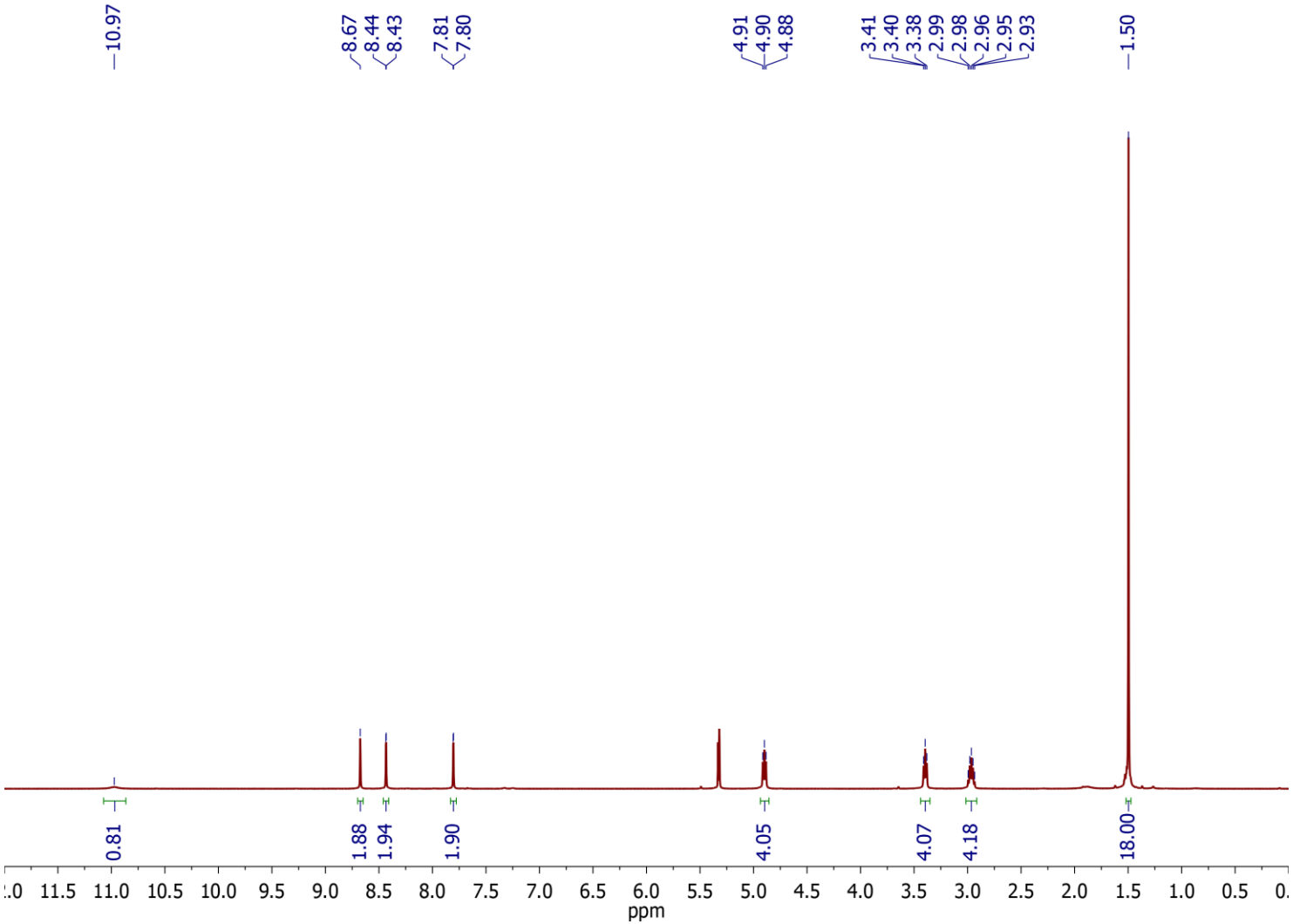


Figure S 4: *$^{1}H - ^{13}C$ HSQC of **2a** in $CDCl_3$ at 298 K.*



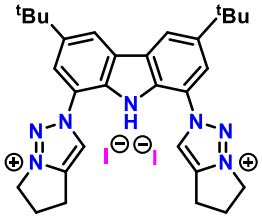
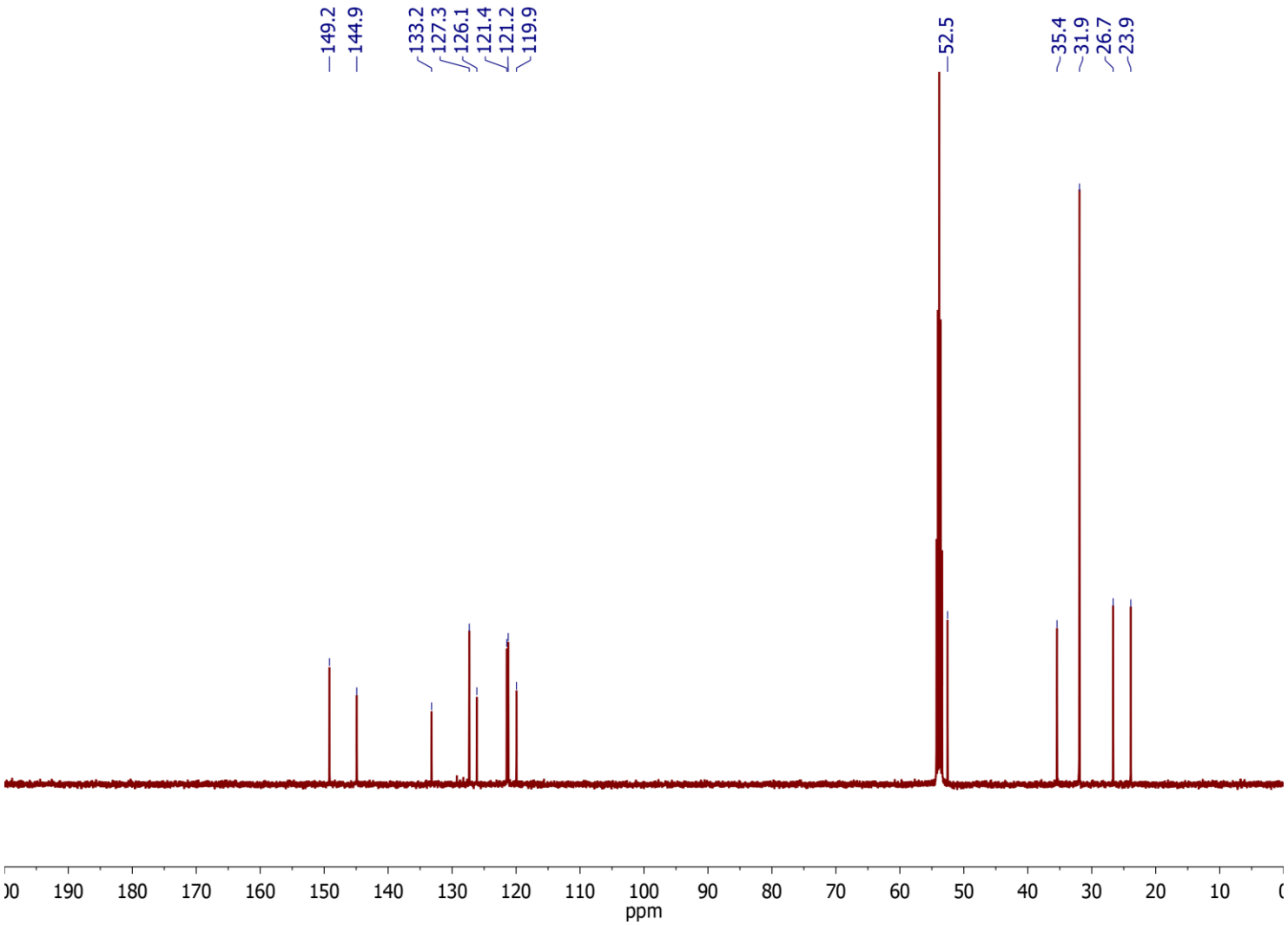


Figure S 5: *^{1}H NMR of **3a** in CD_2Cl_2 at 298 K*



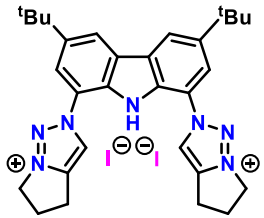
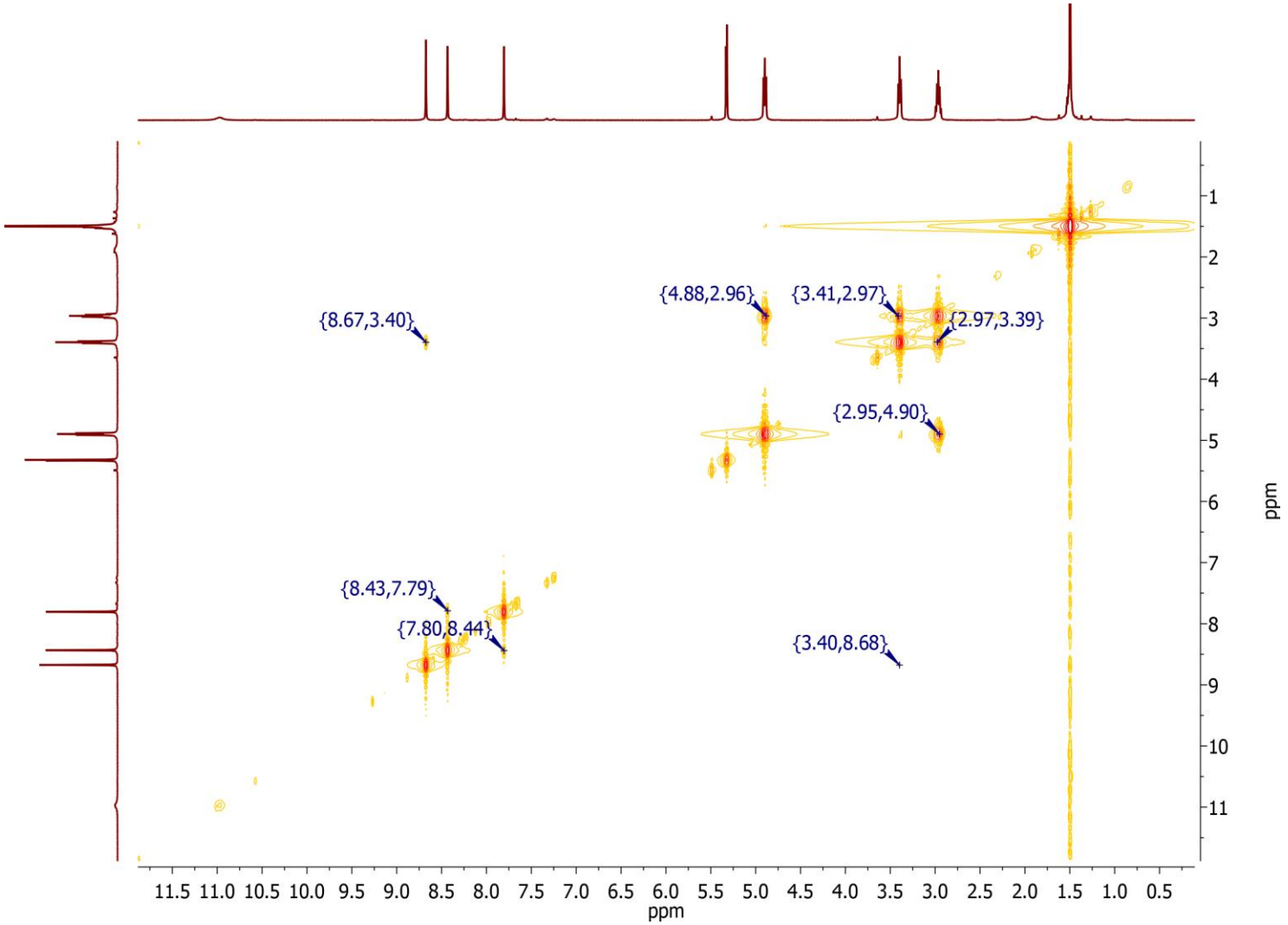


Figure S 6: *^{13}C NMR of **3a** in CD_2Cl_2 at 298 K.*



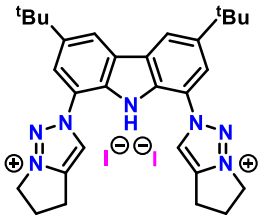
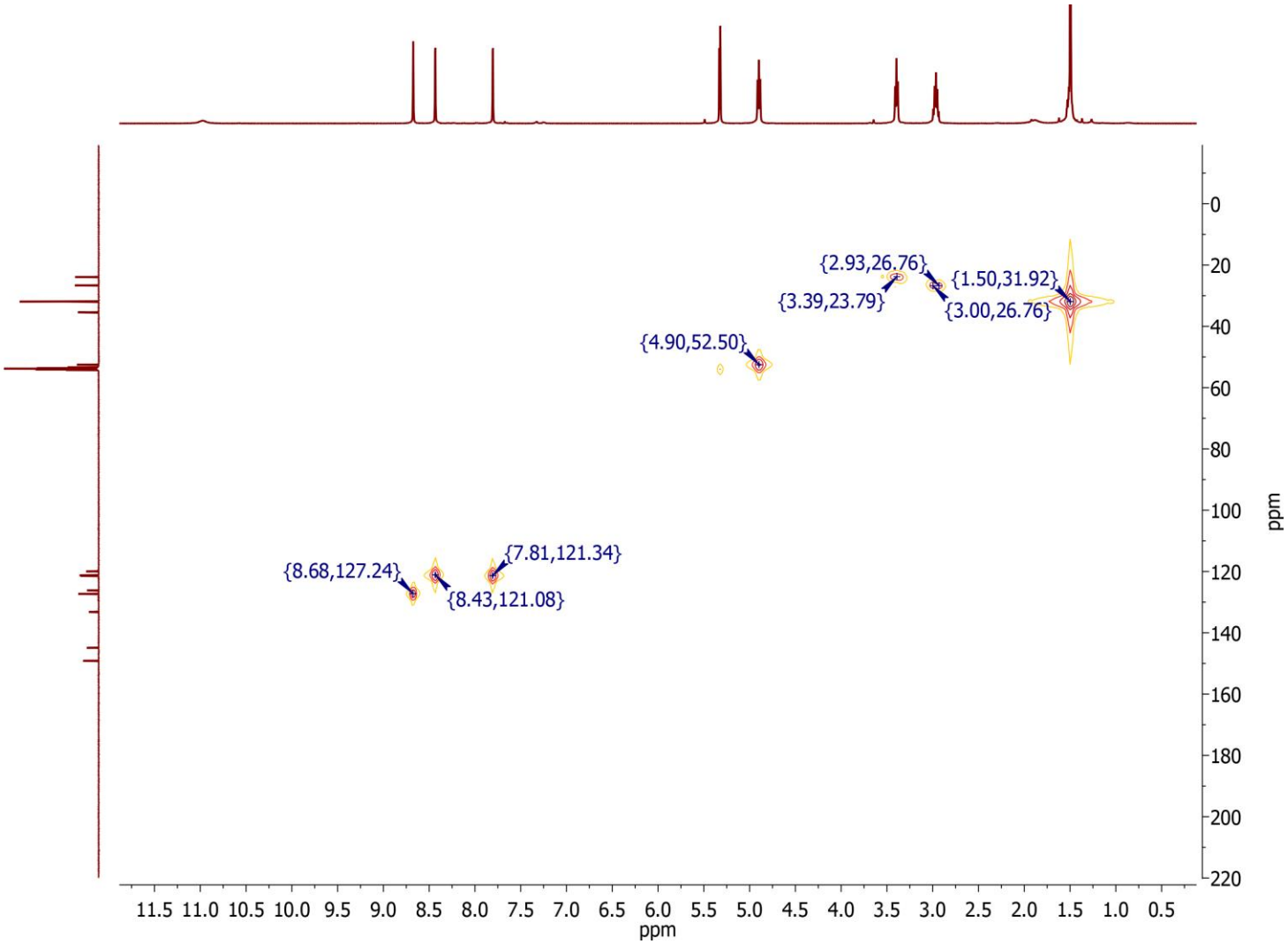


Figure S 7: *$^{1}H - ^{1}H$ COSY of **3a** in CD_2Cl_2 at 298 K.*



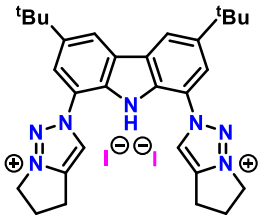
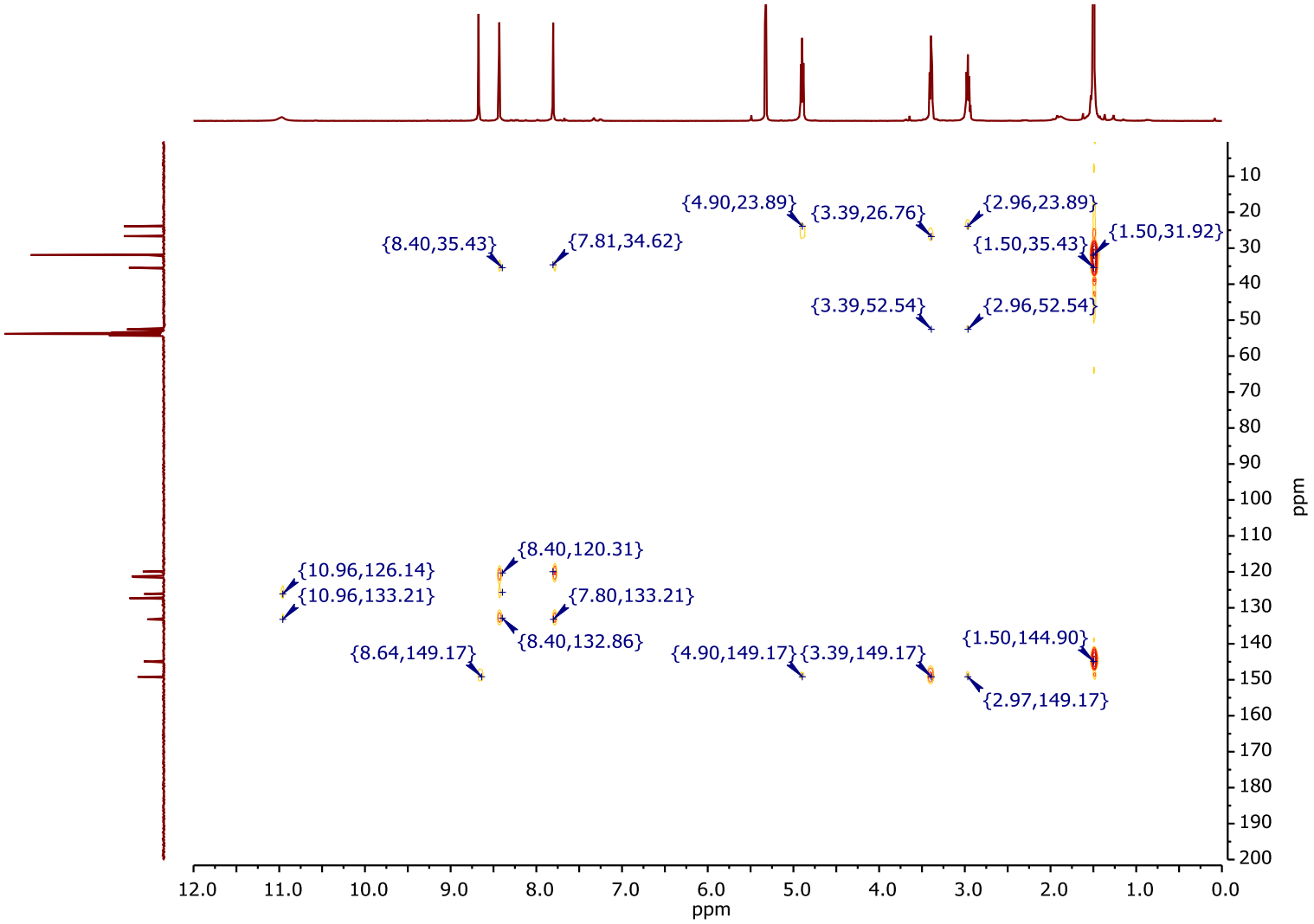


Figure S 8: *$^{1}H - ^{13}C$ HSQC of **3a** in CD_2Cl_2 at 298 K.*



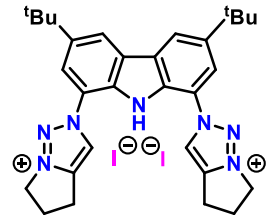
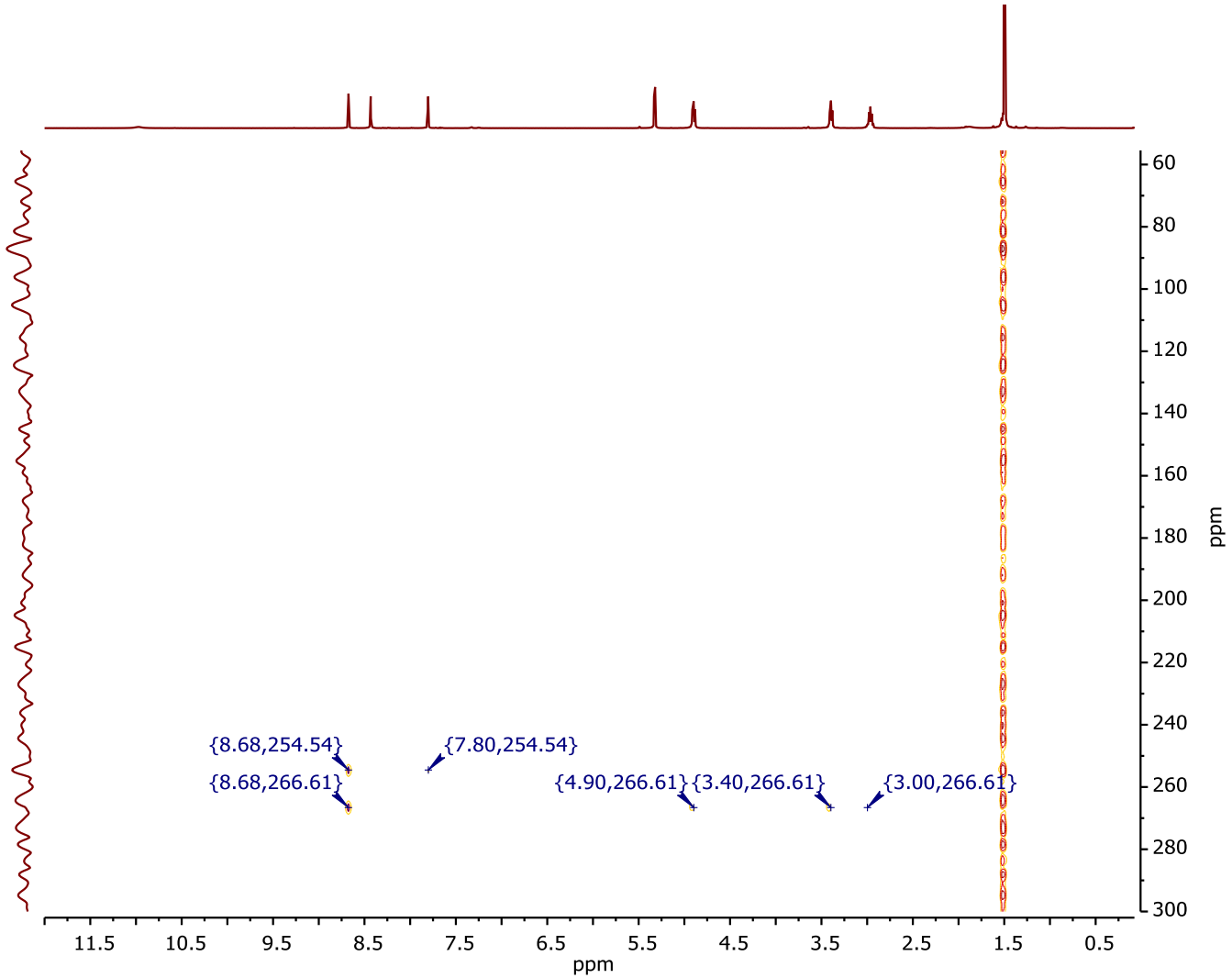


Figure S 9: *$^{1}H - ^{13}C$ HMBC of **3a** in CD_2Cl_2 at 298 K.*



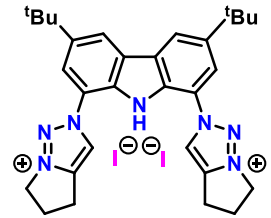
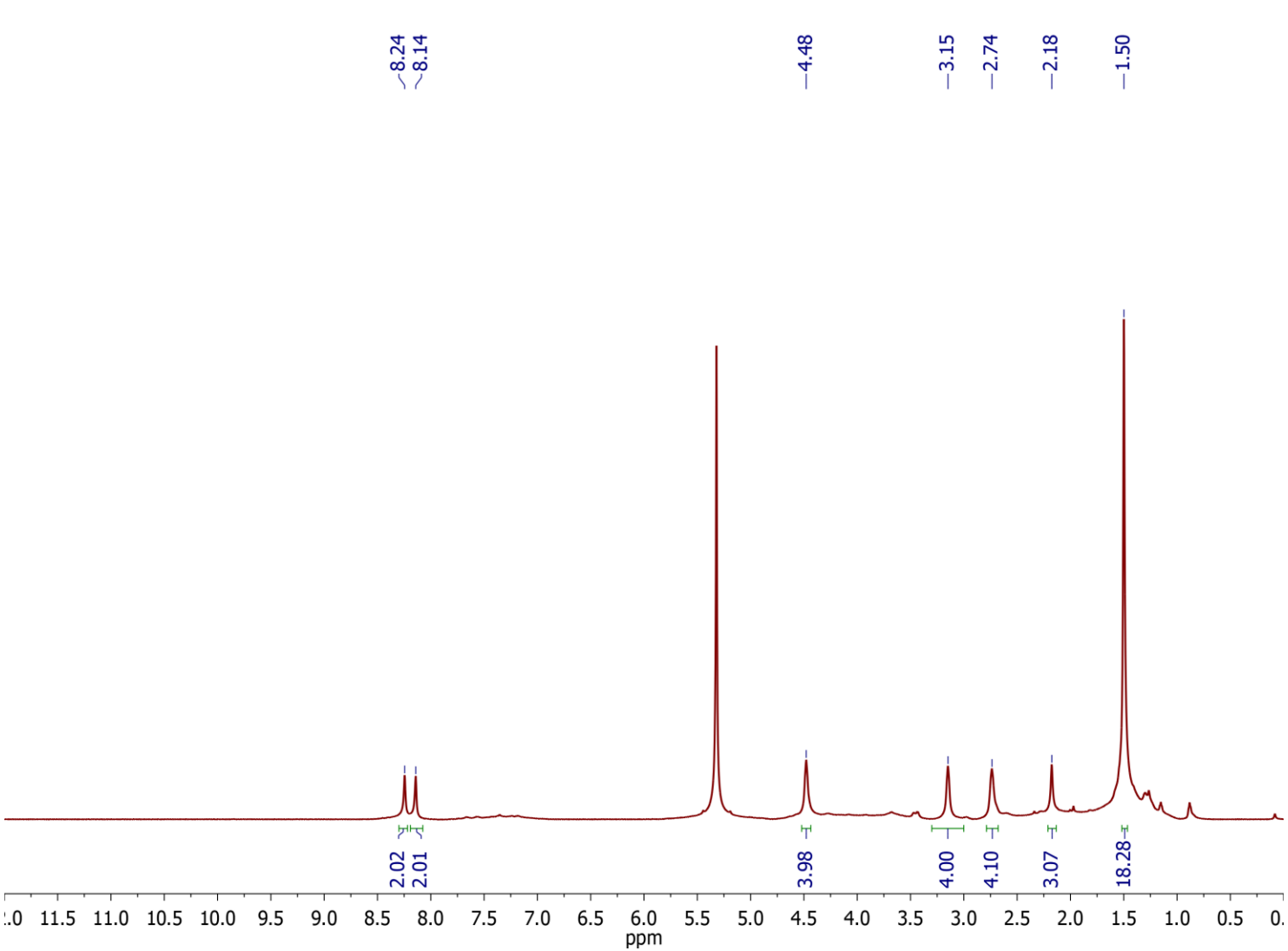


Figure S 10: *$^{1}H - ^{15}N$ HMBC of **3a** in CD_2Cl_2 at 298 K.*



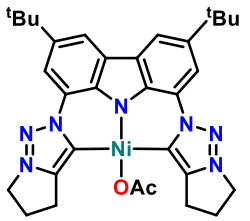
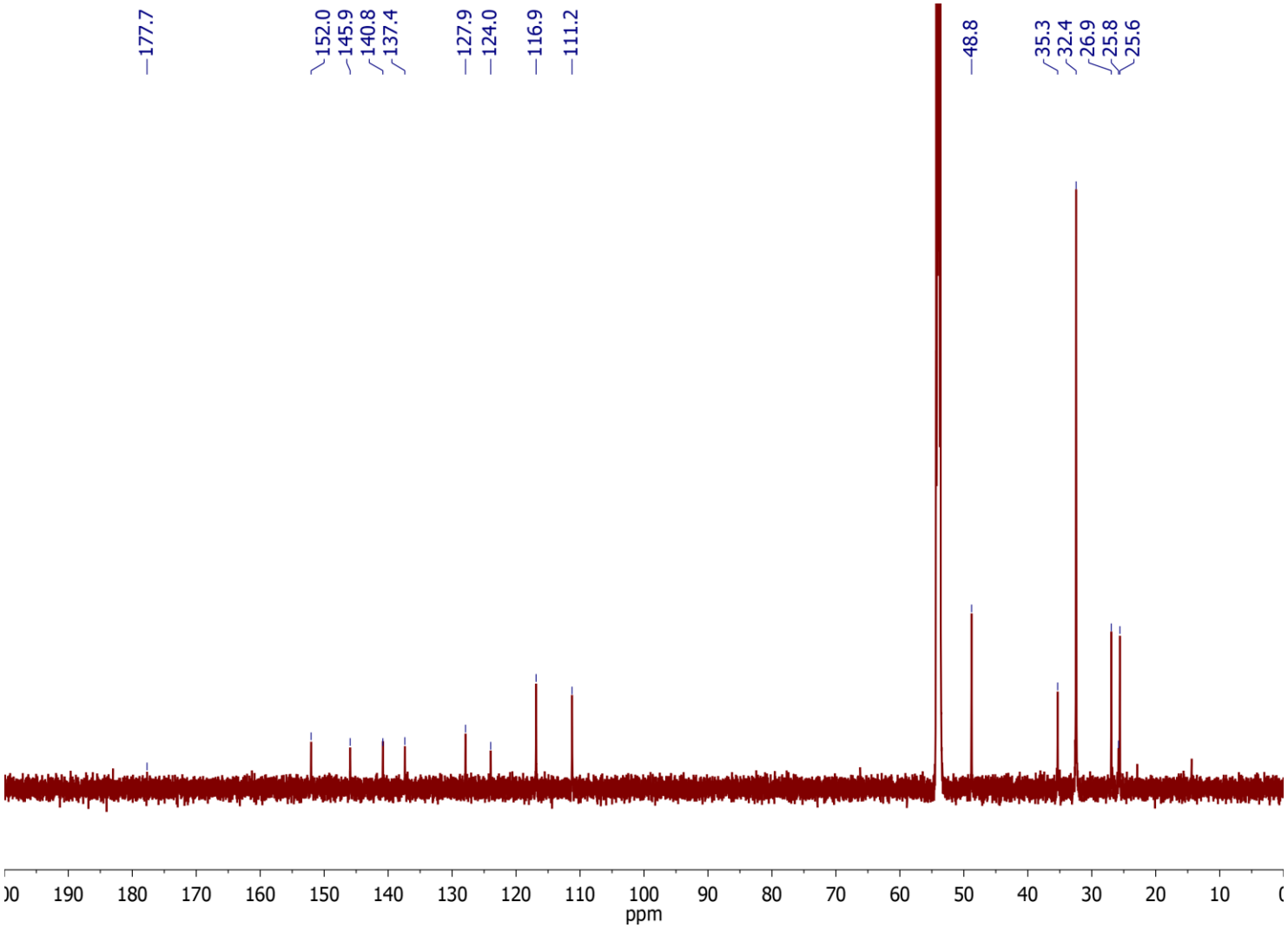


Figure S 11: ^{1}H NMR of ***4a*** in CD_2Cl_2 at 298 K



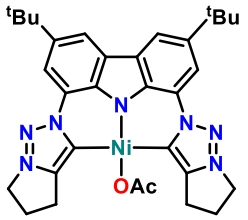
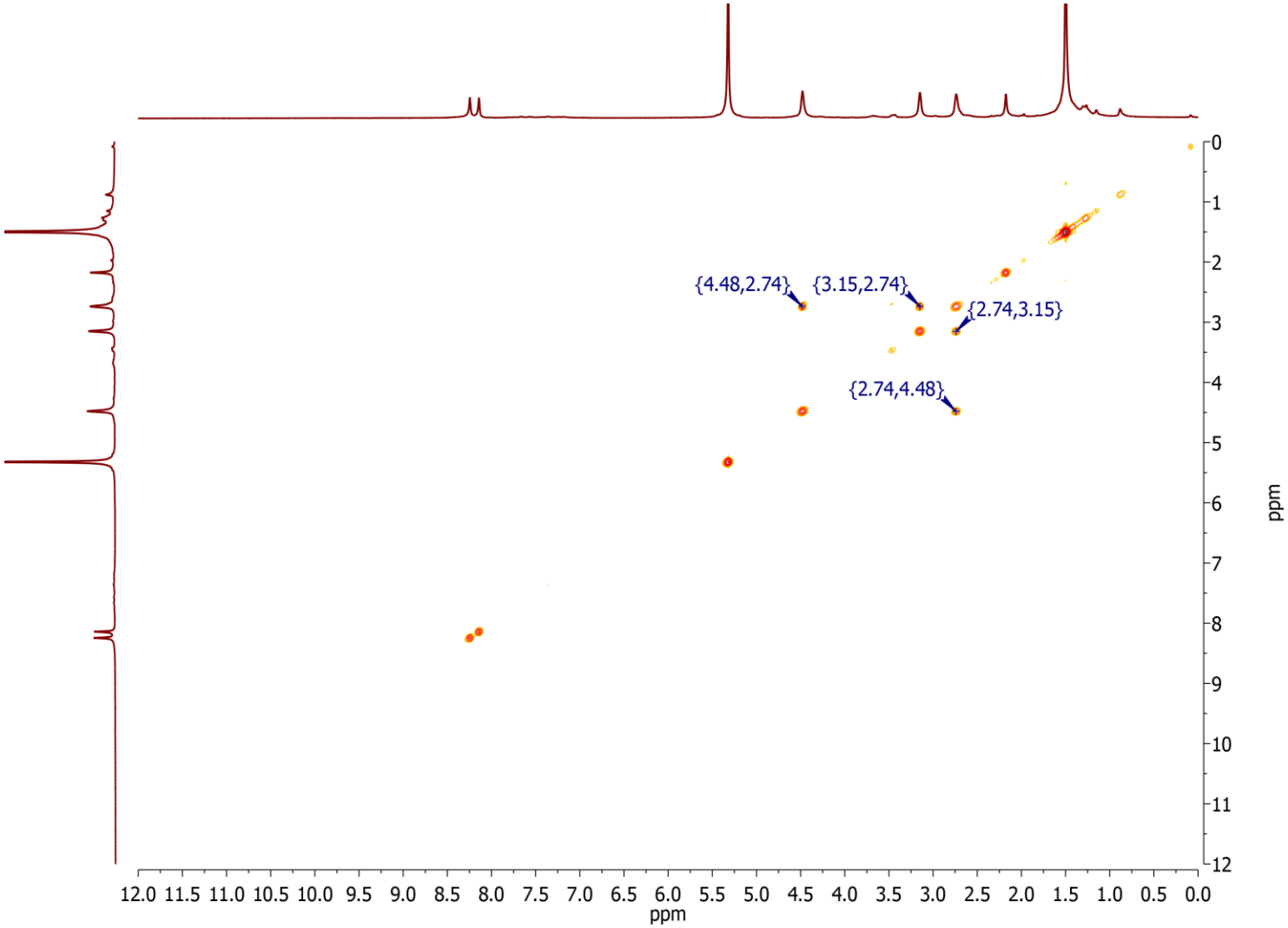


Figure S 12: *^{13}C NMR of **4a** in CD_2Cl_2 at 298 K.*



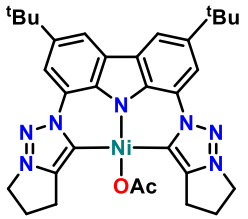
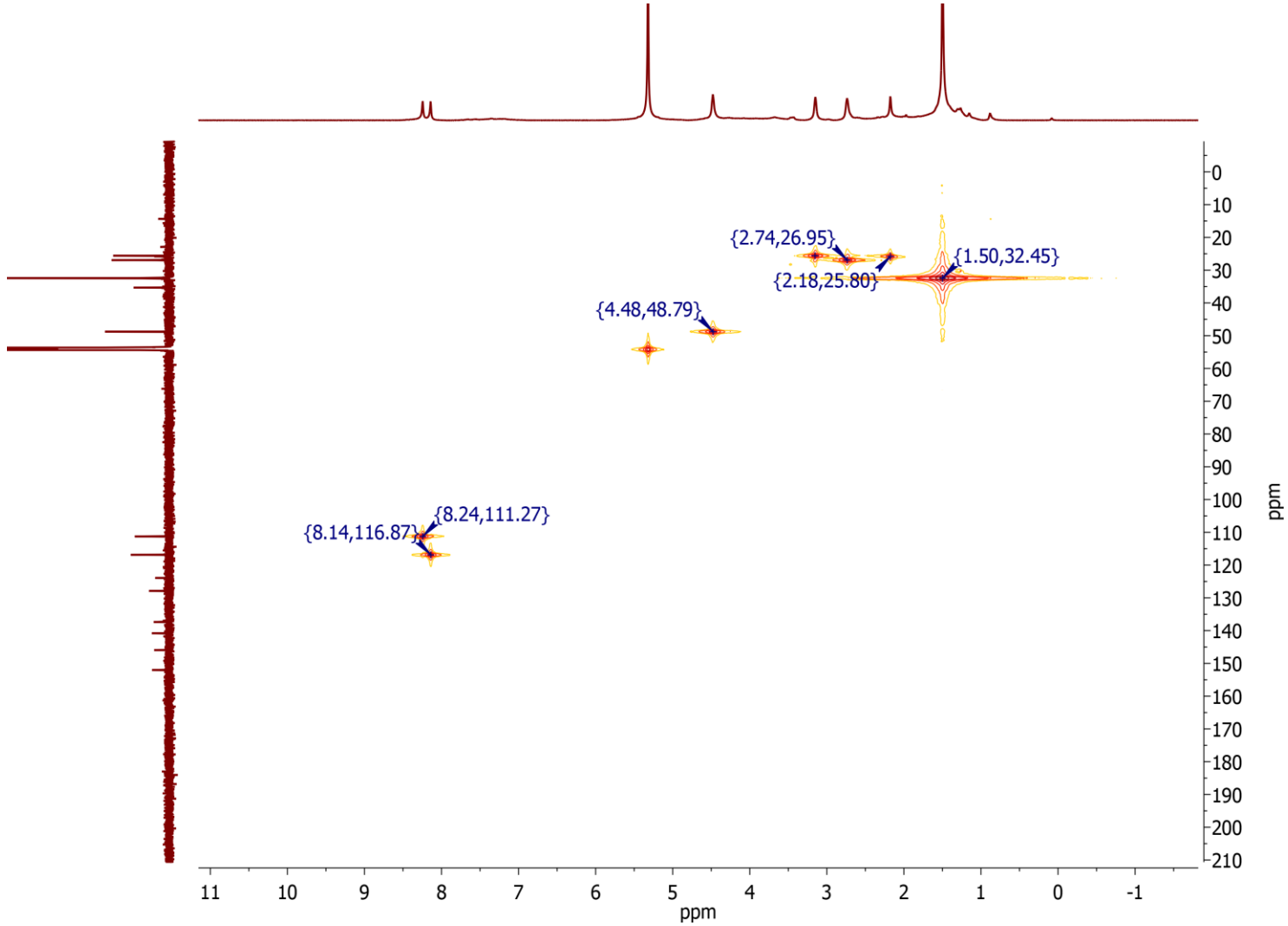


Figure S 13: *$^{1}H - ^{1}H$ COSY of **4a** in CD_2Cl_2 at 298 K.*



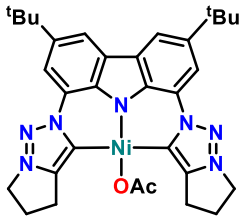
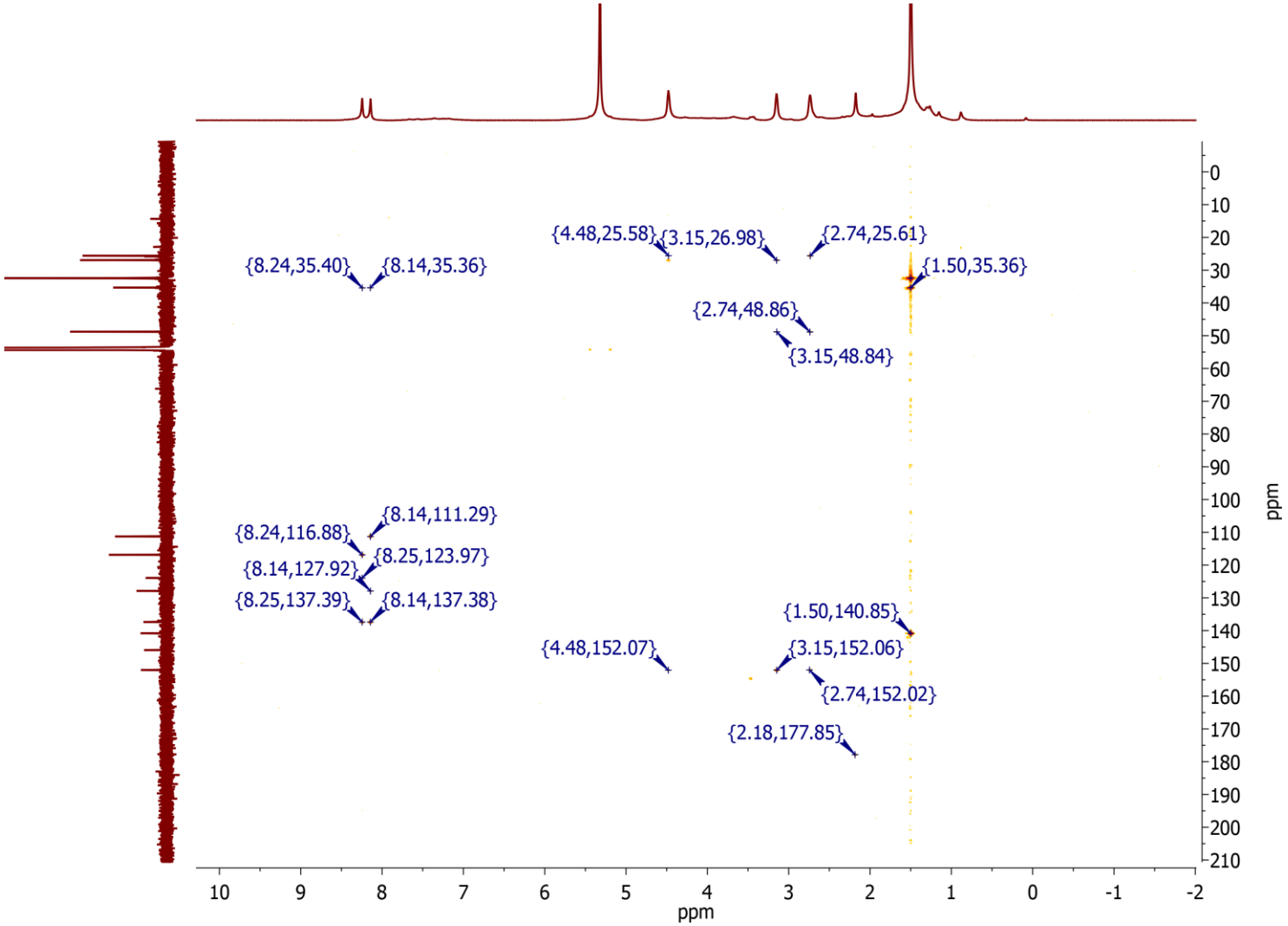


Figure S 14: *$^{1}H - ^{13}C$ HSQC of **4a** in CD_2Cl_2 at 298 K.*



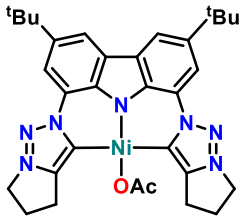


Figure S 15: $^{1}H - ^{13}C$ HMBC of ***4a*** in CD_2Cl_2 at 298 K

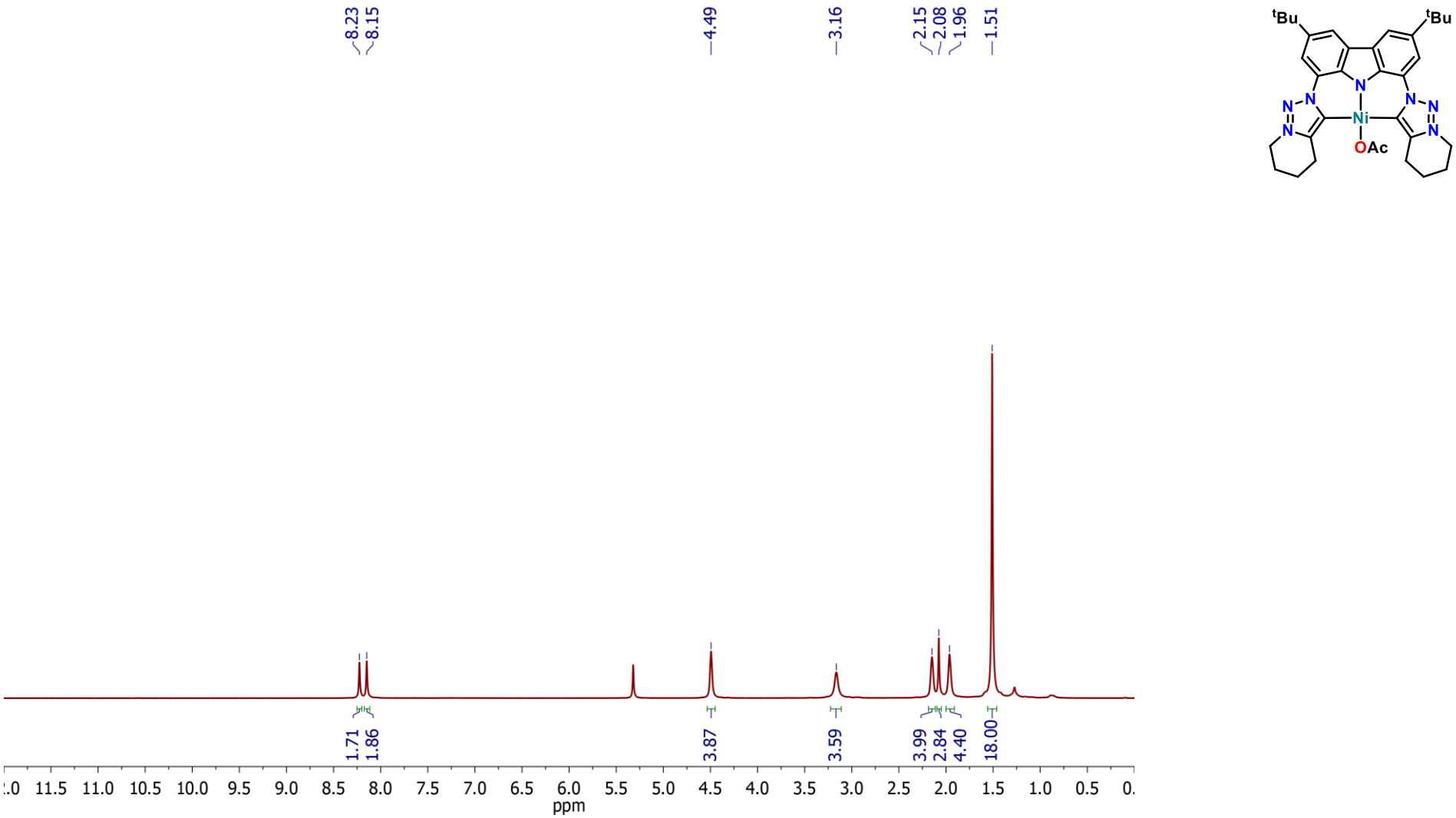
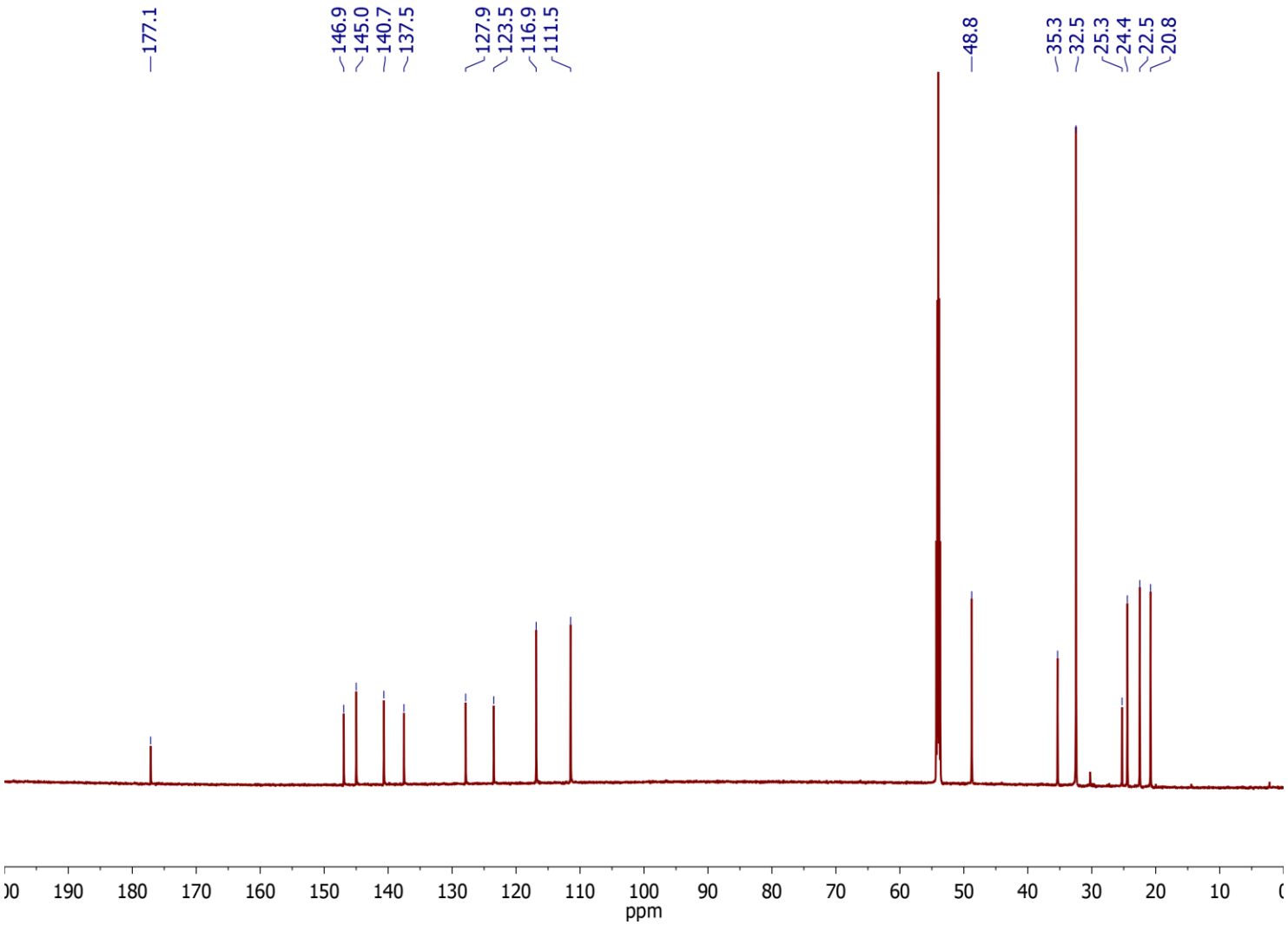


Figure S 16: ^{1}H *NMR of* ***4b*** *in* CD_2Cl_2 *at 298 K.*



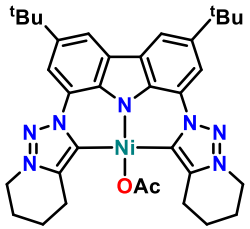
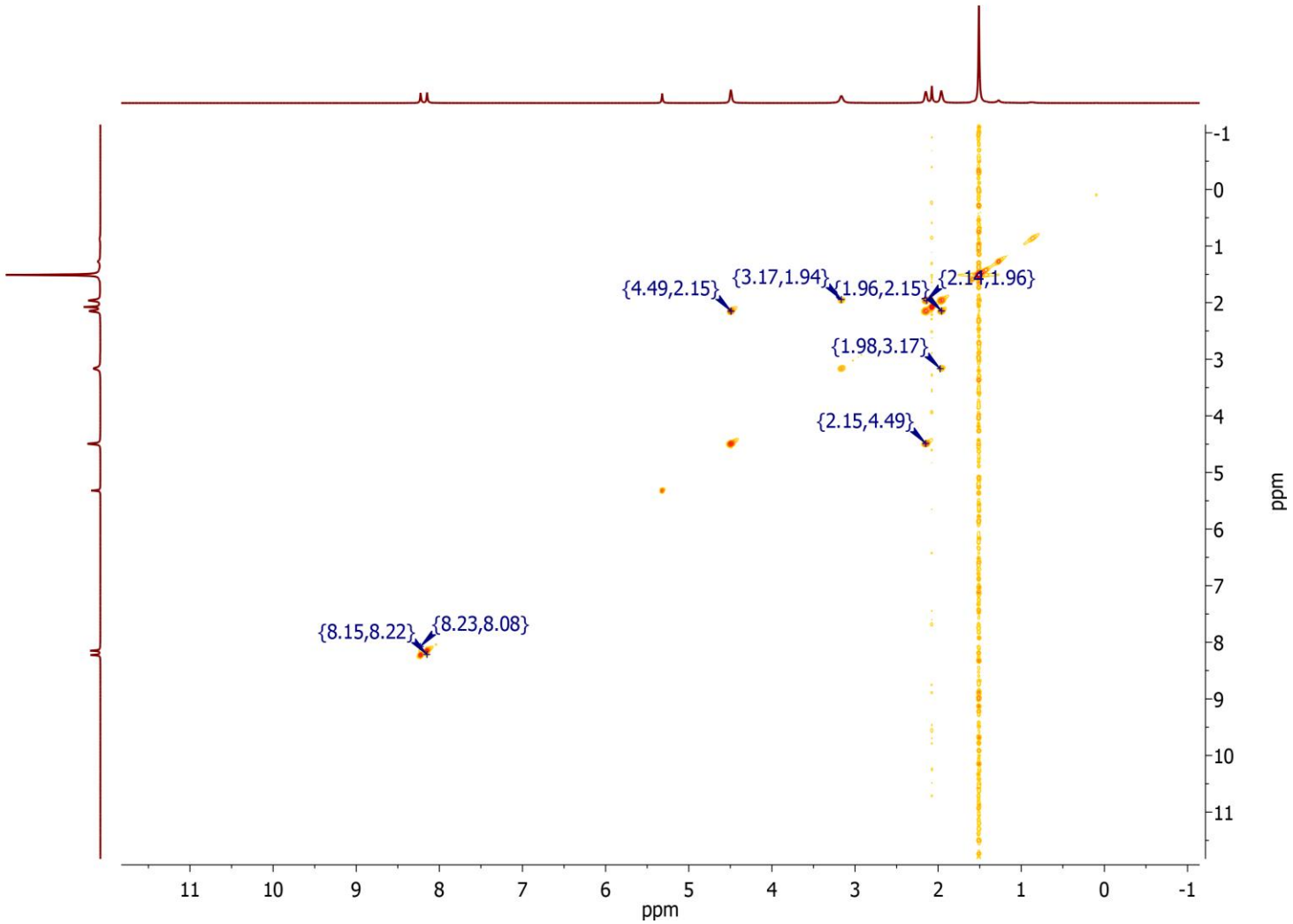


Figure S 17: *^{13}C NMR of **4b** in CD_2Cl_2 at 298 K.*



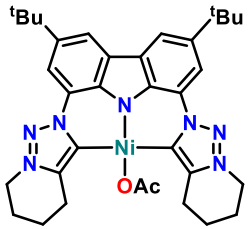
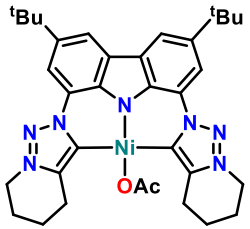


Figure S 18: *$^{1}H - {}^{1}H$ COSY of **4b** in CD_2Cl_2 at 298 K.*



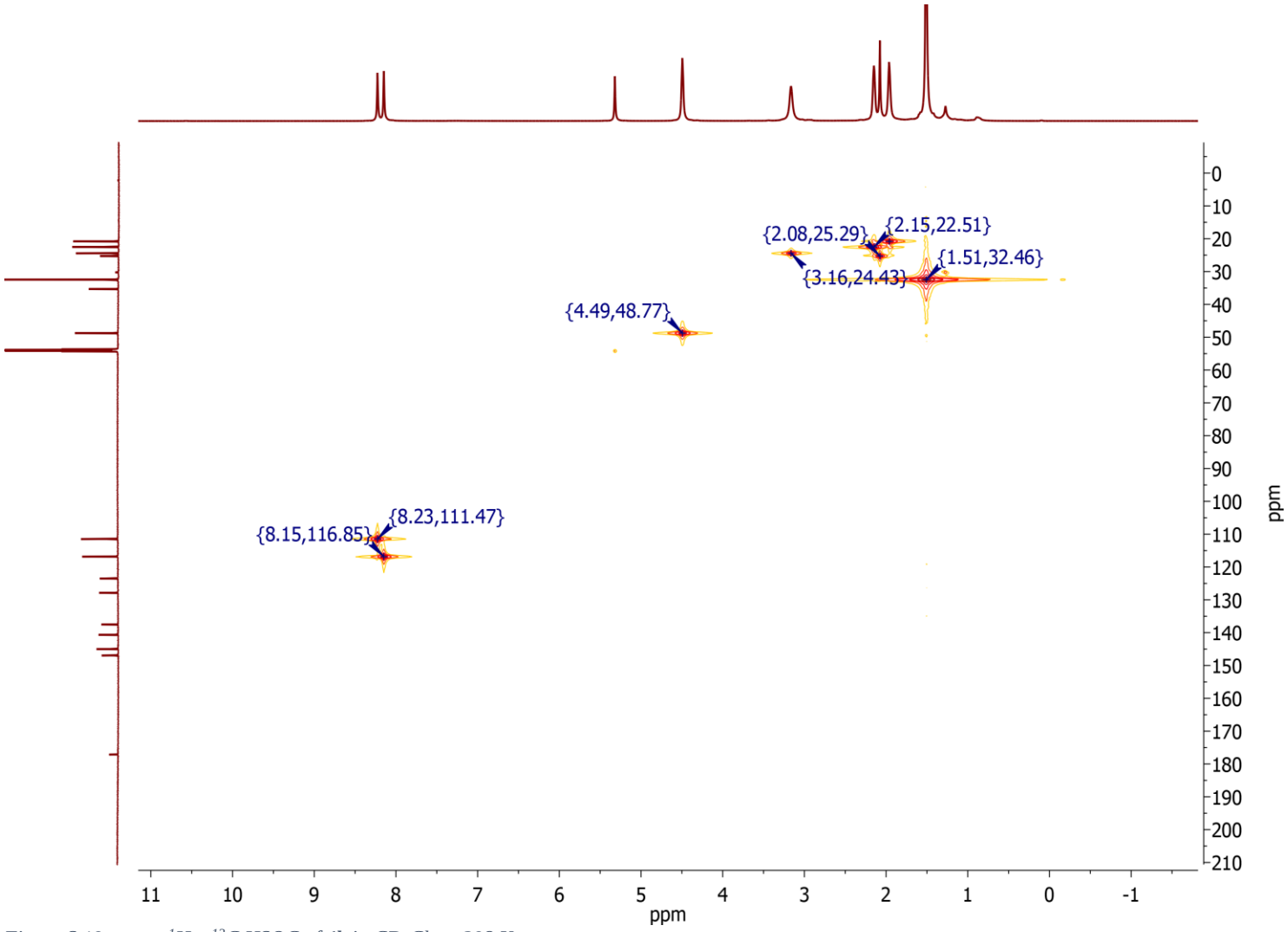
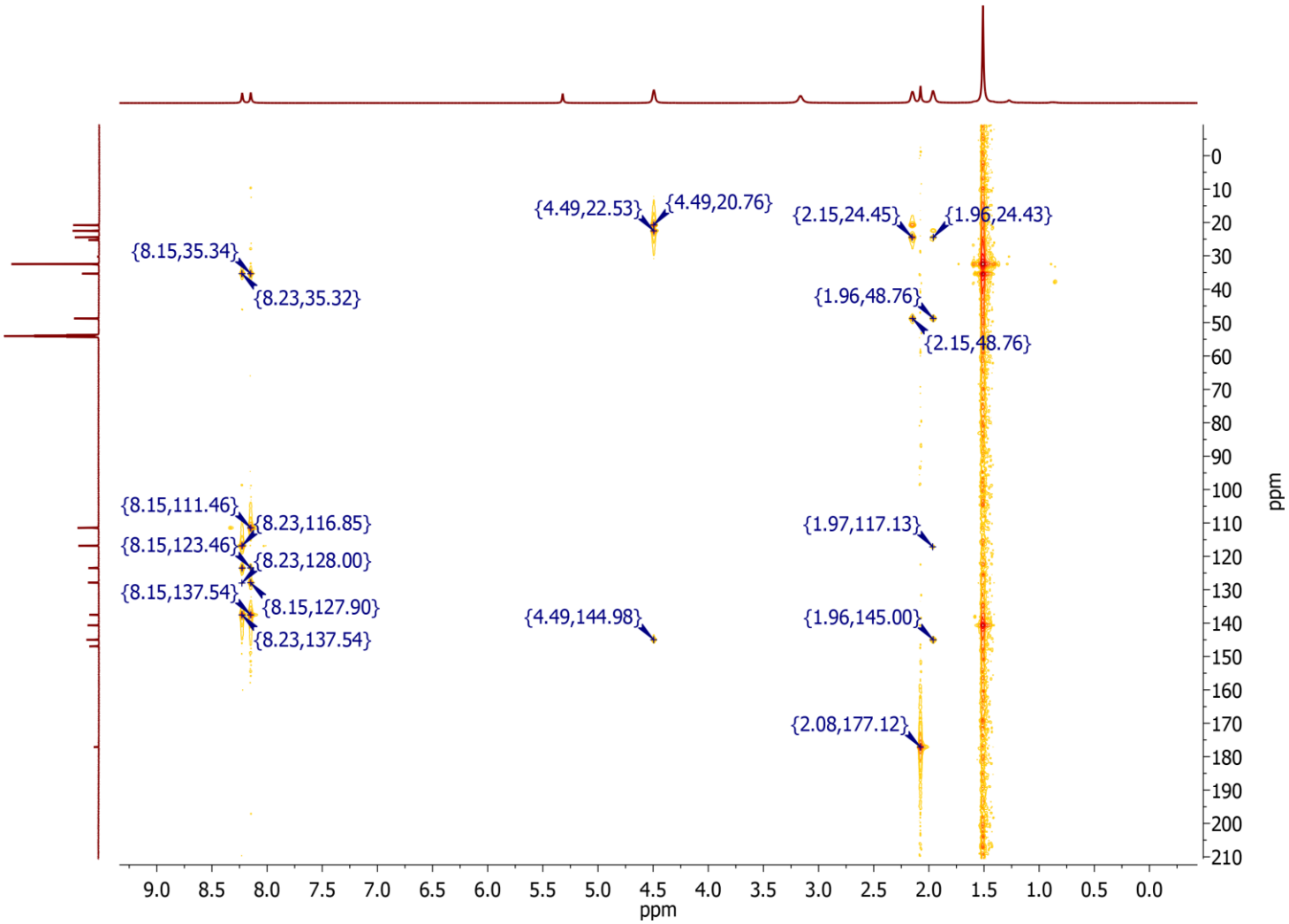


Figure S 19: *$^{1}H - ^{13}C$ HSQC of **4b** in CD_2Cl_2 at 298 K.*



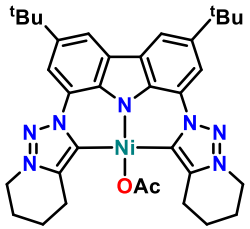


Figure S 20: $^{1}H - ^{13}C$ HMBC of ***4b*** in CD_2Cl_2 at 298 K

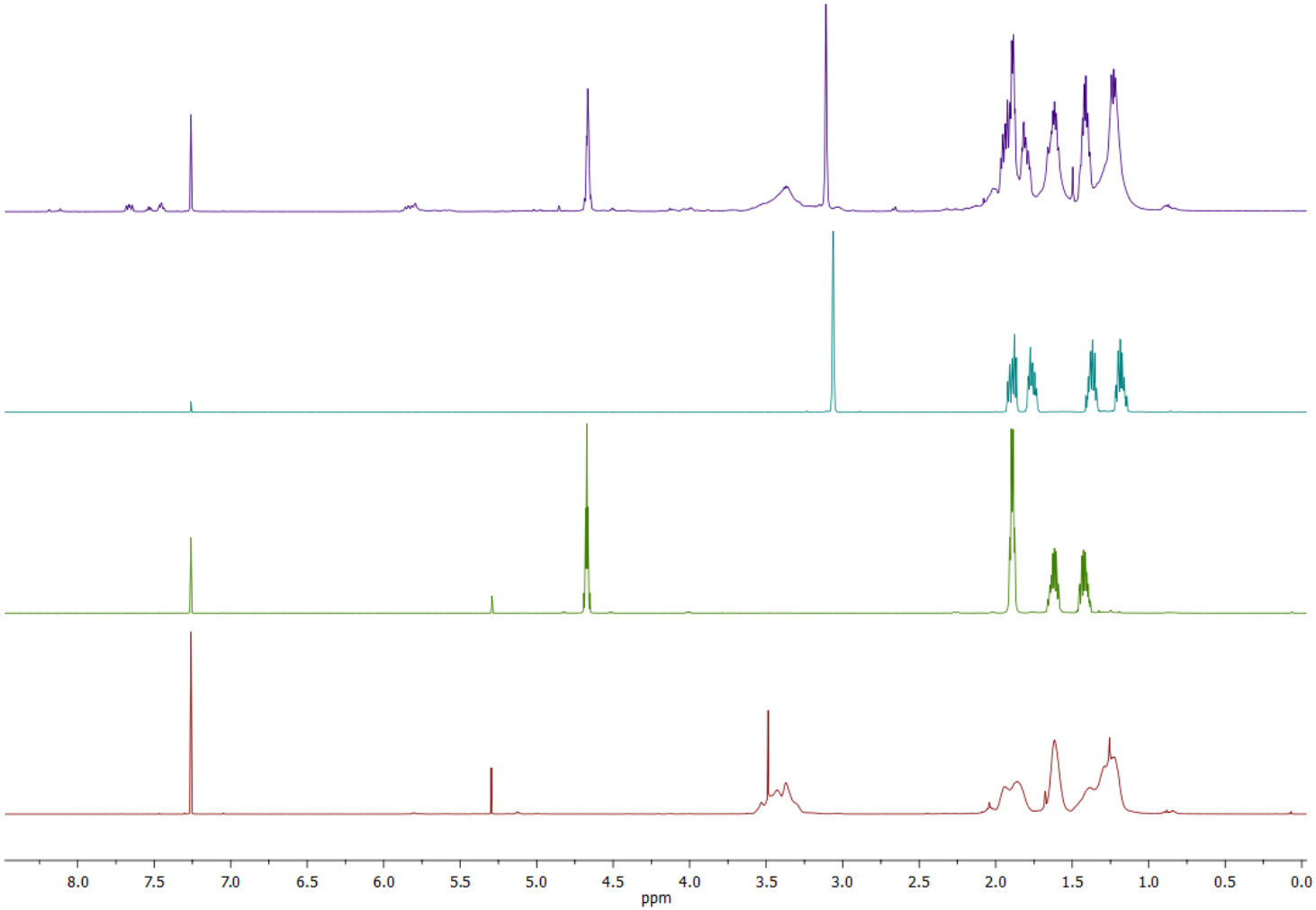
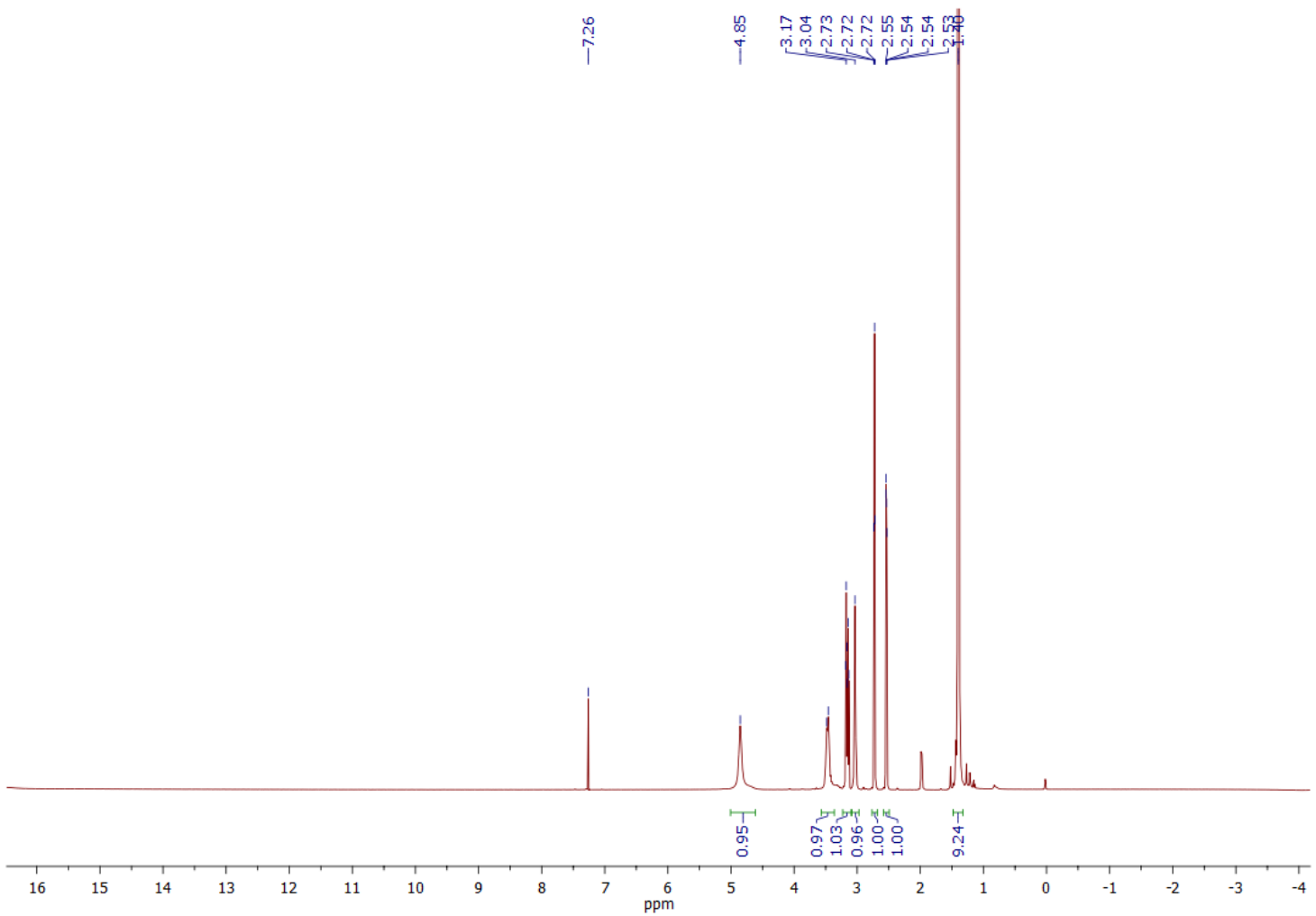


Figure S 21: Stacked ^{1}H –NMR spectra of crude sample from table 1 entry 8 (violet, top), CHO (blue, 2nd from top), cyclic carbonate from CHO (green, 3rd from top) and isolated polyether from CHO (red, bottom) in $CDCl_3$ at 298 K.



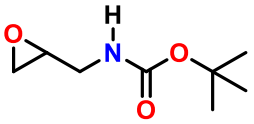
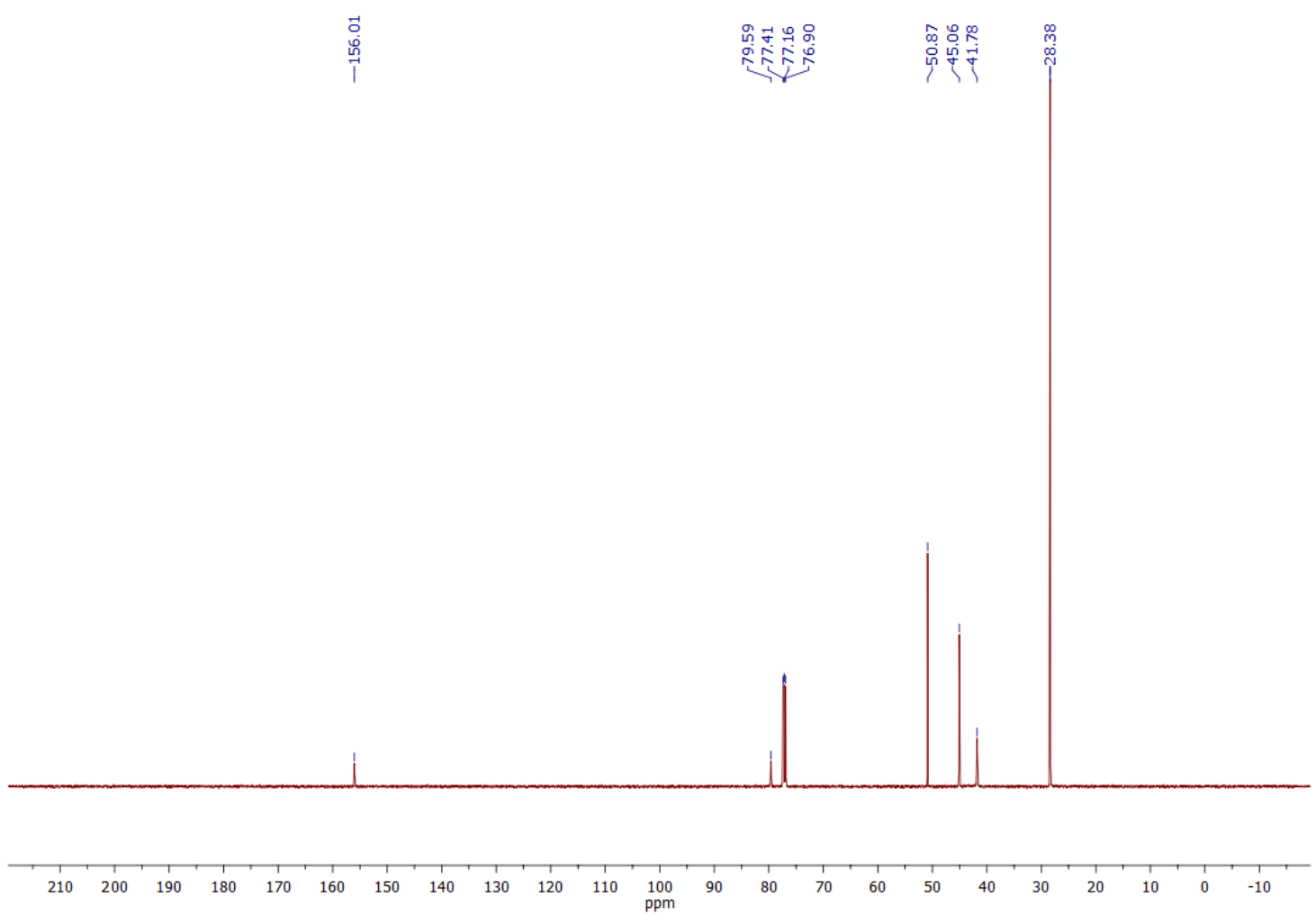


Figure S 22: *^{1}H-NMR of **tBOMC** in $CDCl_3$ at 303 K. Impurities of ethyl acetate and a small amount unknown byproduct are present.*



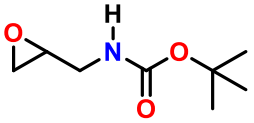


Figure S 23: *^{13}C-NMR of **tBOMC** in $CDCl_3$ at 303 K.*

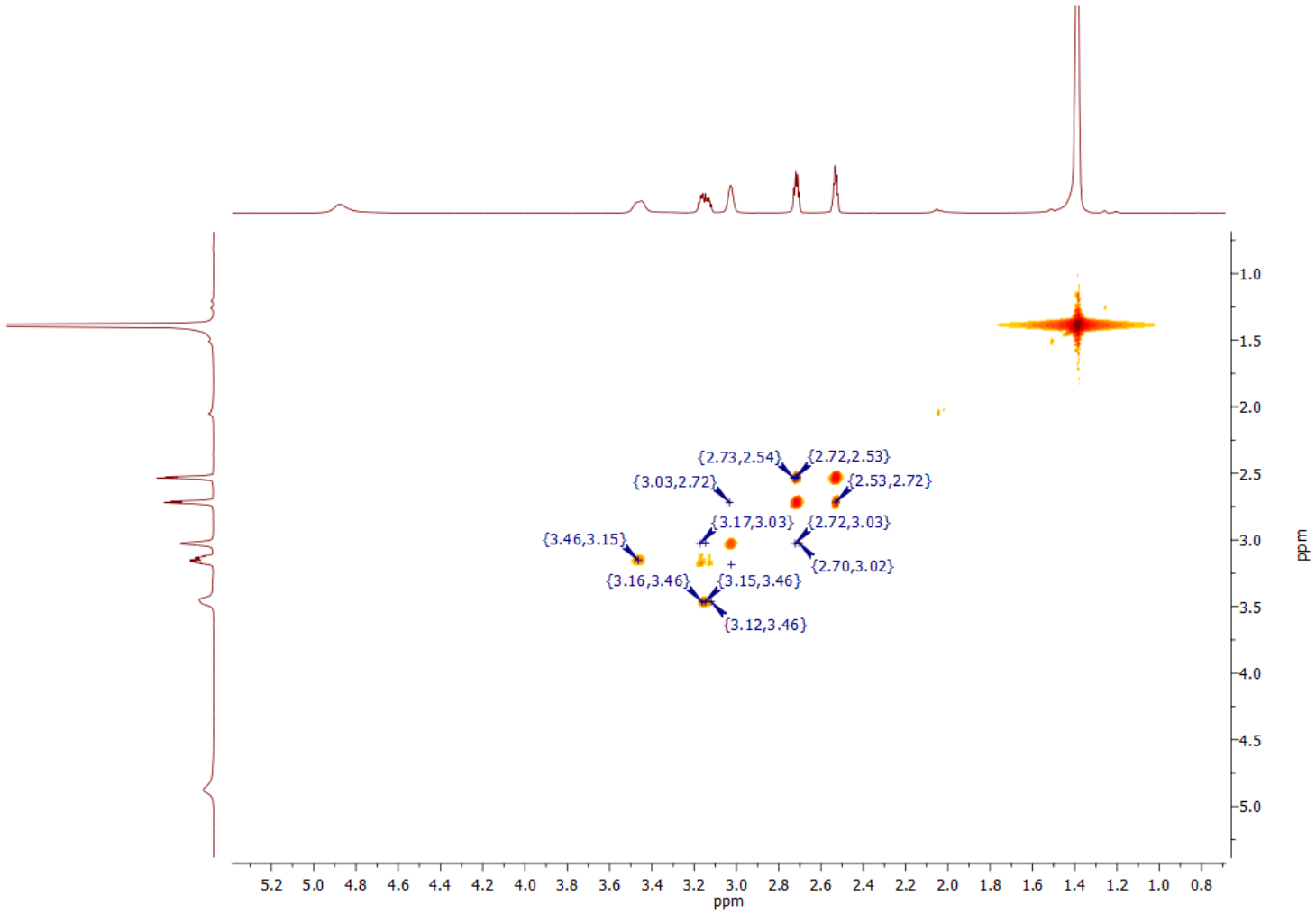
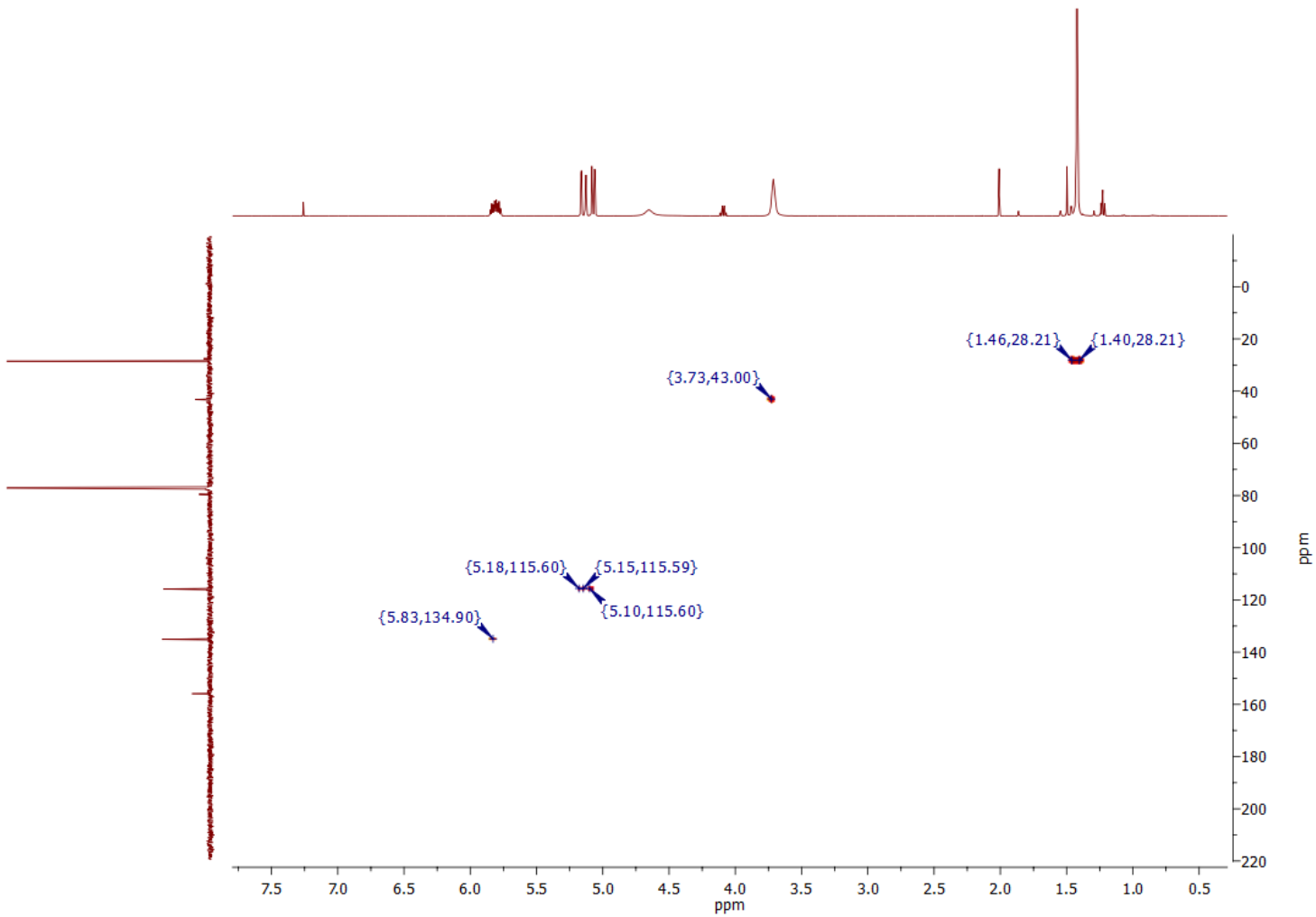


Figure S 24: ^{1}H-^{1}H-COSY of ***tBOMC*** *in* $CDCl_3$ *at 303 K*



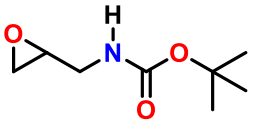
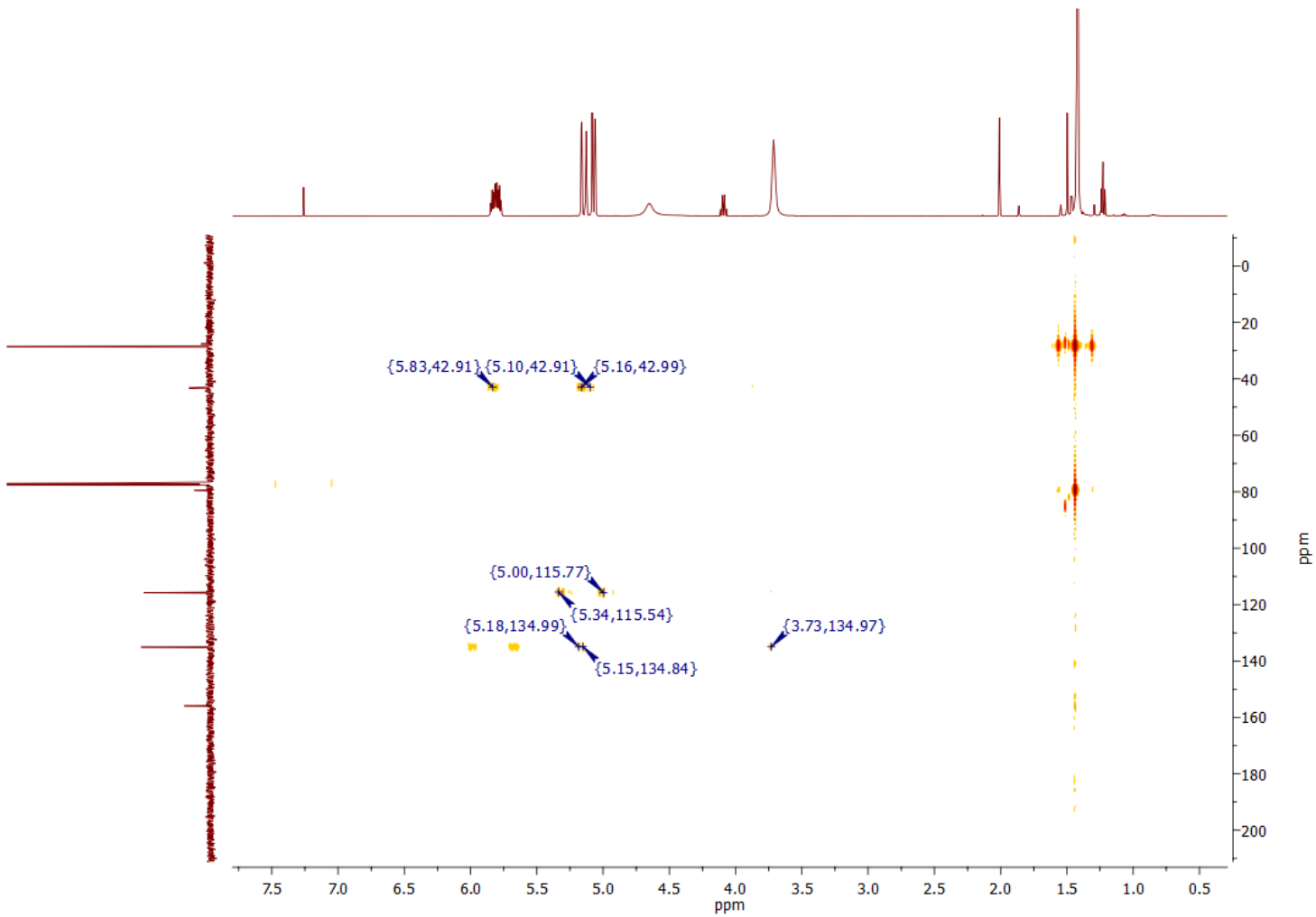


Figure S 25: ^{1}H-^{13}C-HSQC of ***tBOMC*** *in* $CDCl_3$ *at 303 K*



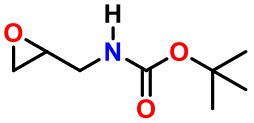
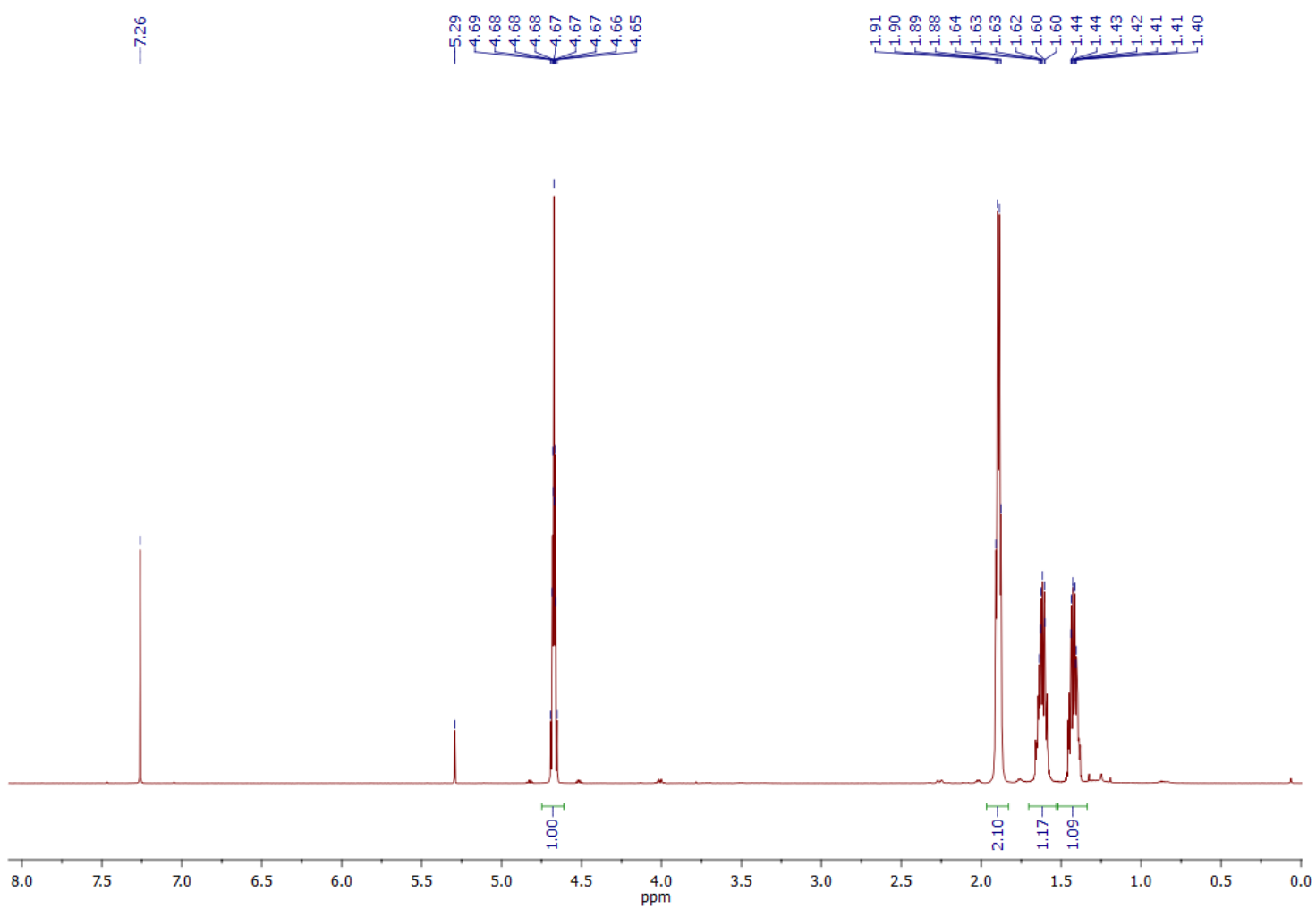


Figure S 26: *^{1}H-^{13}C-HMBC of **tBOMC** in $CDCl_3$ at 303 K*



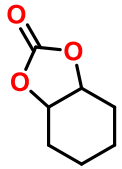
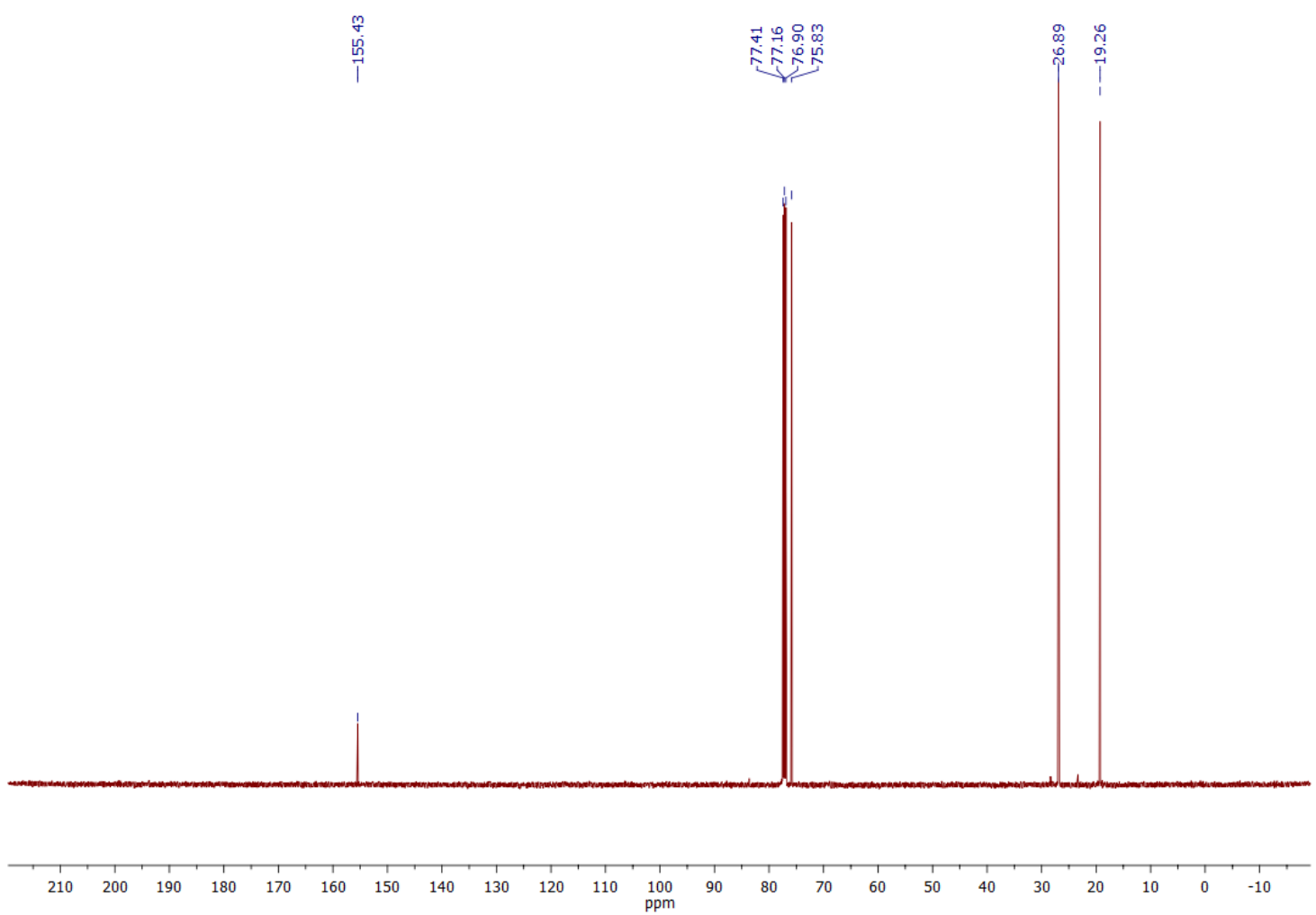


Figure S 27: *^{1}H-NMR of **5a** in $CDCl_3$ at 303K.*



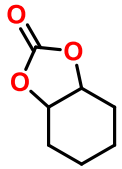
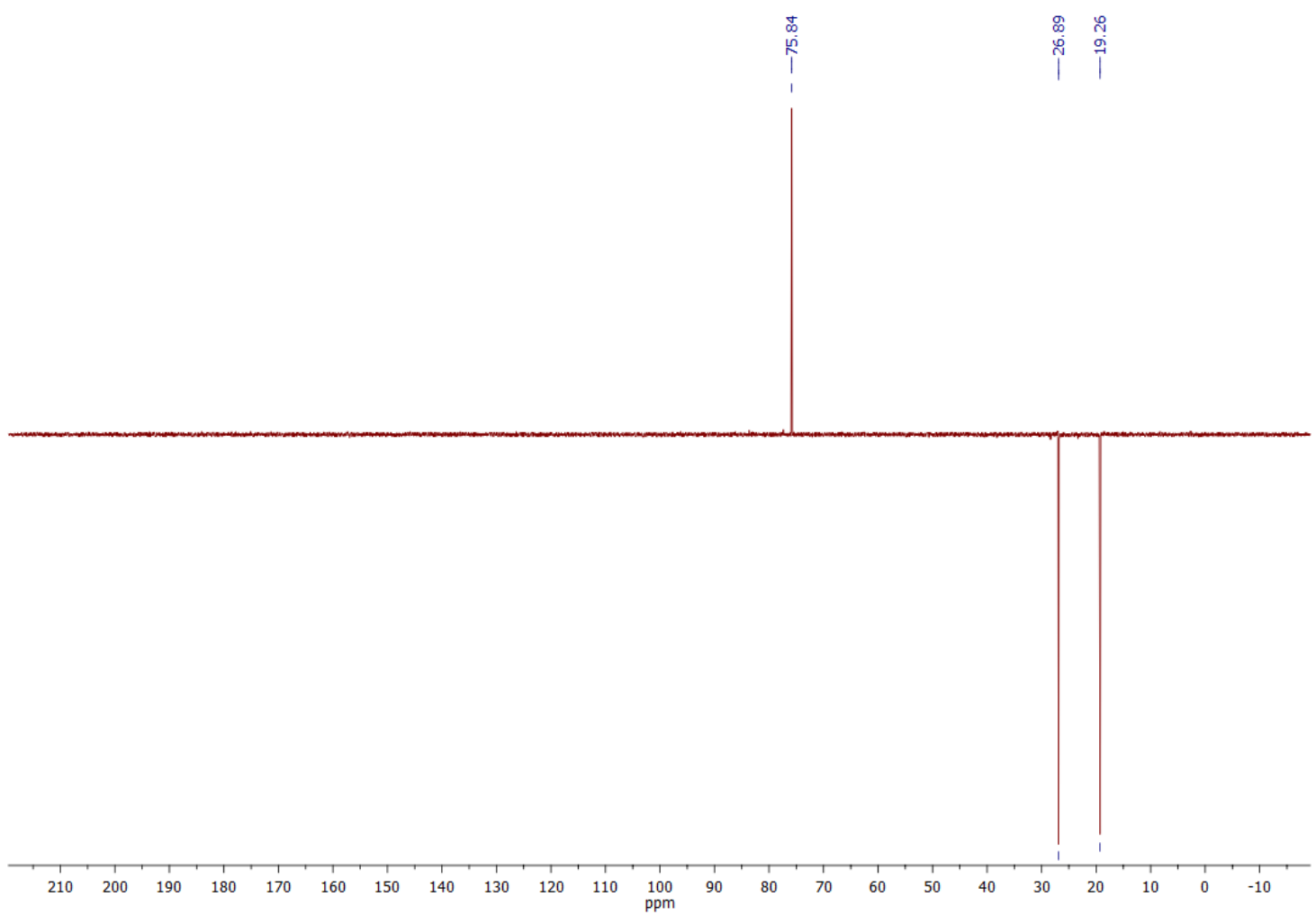


Figure S 28: *^{13}C -NMR of **5a** in CDCl3 at 303K.*



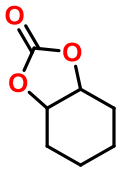


*Figure S 29: DEPT135-NMR of **5a** in $CDCl_3$ at 303K.*

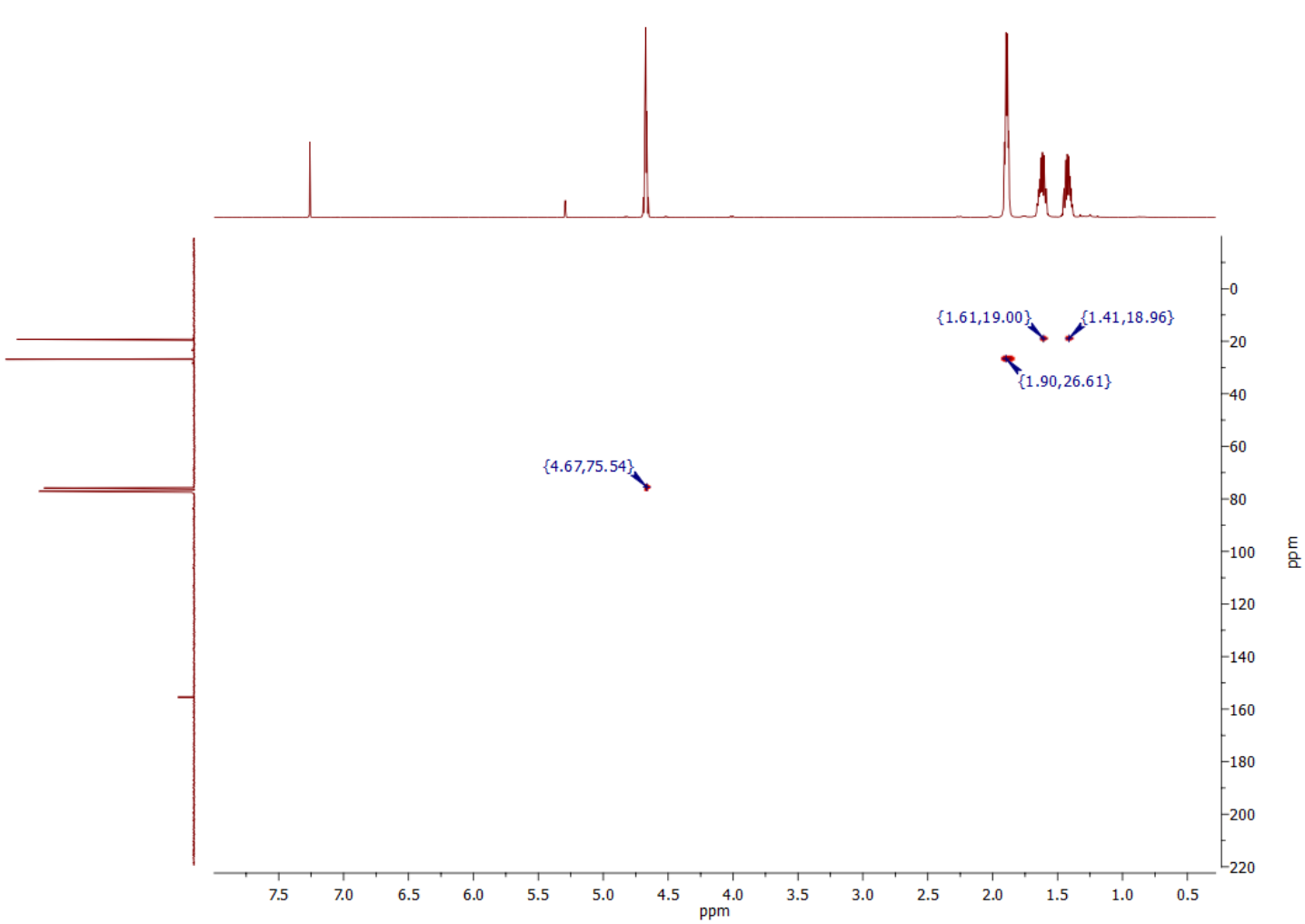


Figure S 30: ^{1}H-^{13}C-HSQC-NMR of ***5a*** *in* $CDCl_3$ *at 303K.*

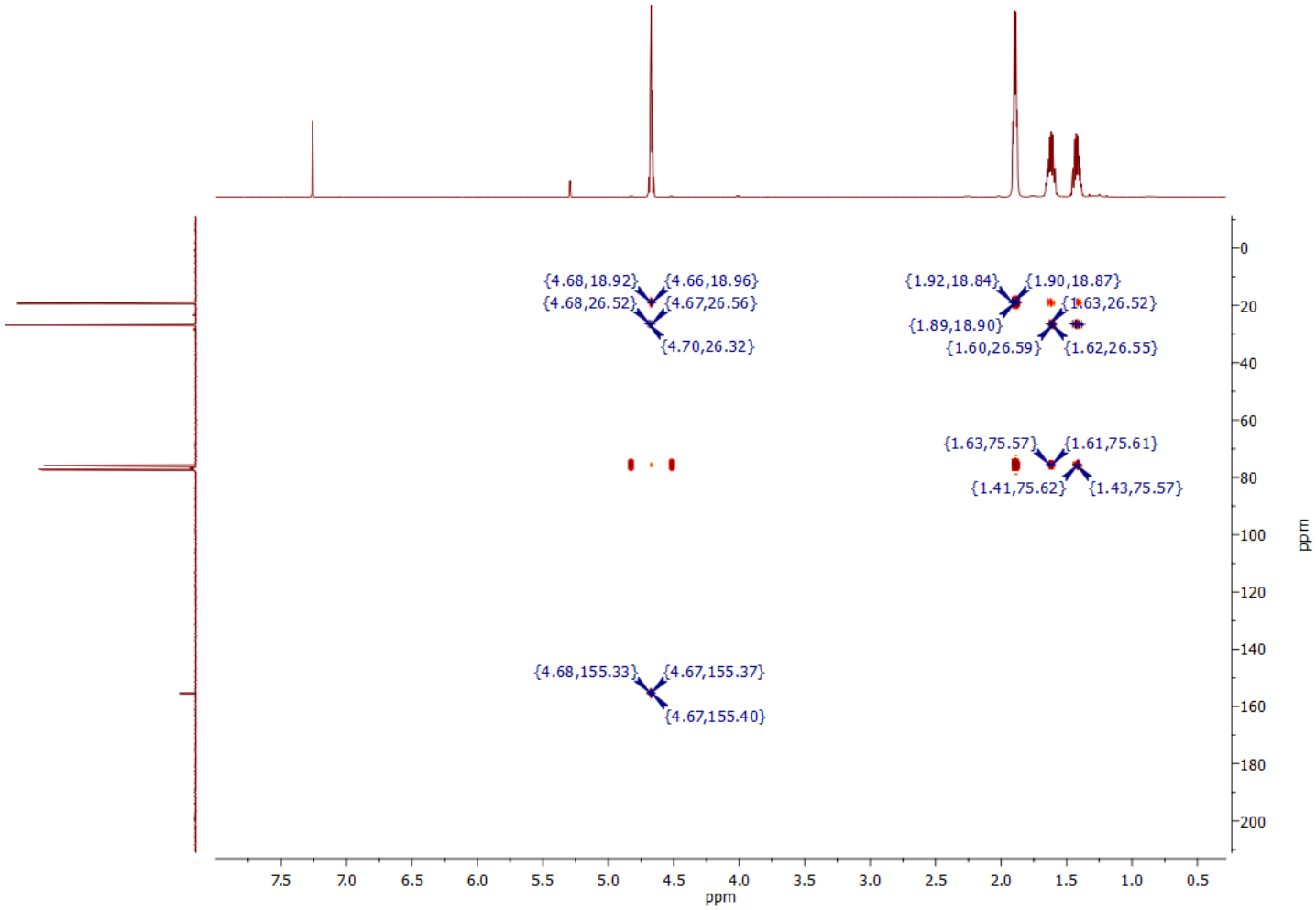
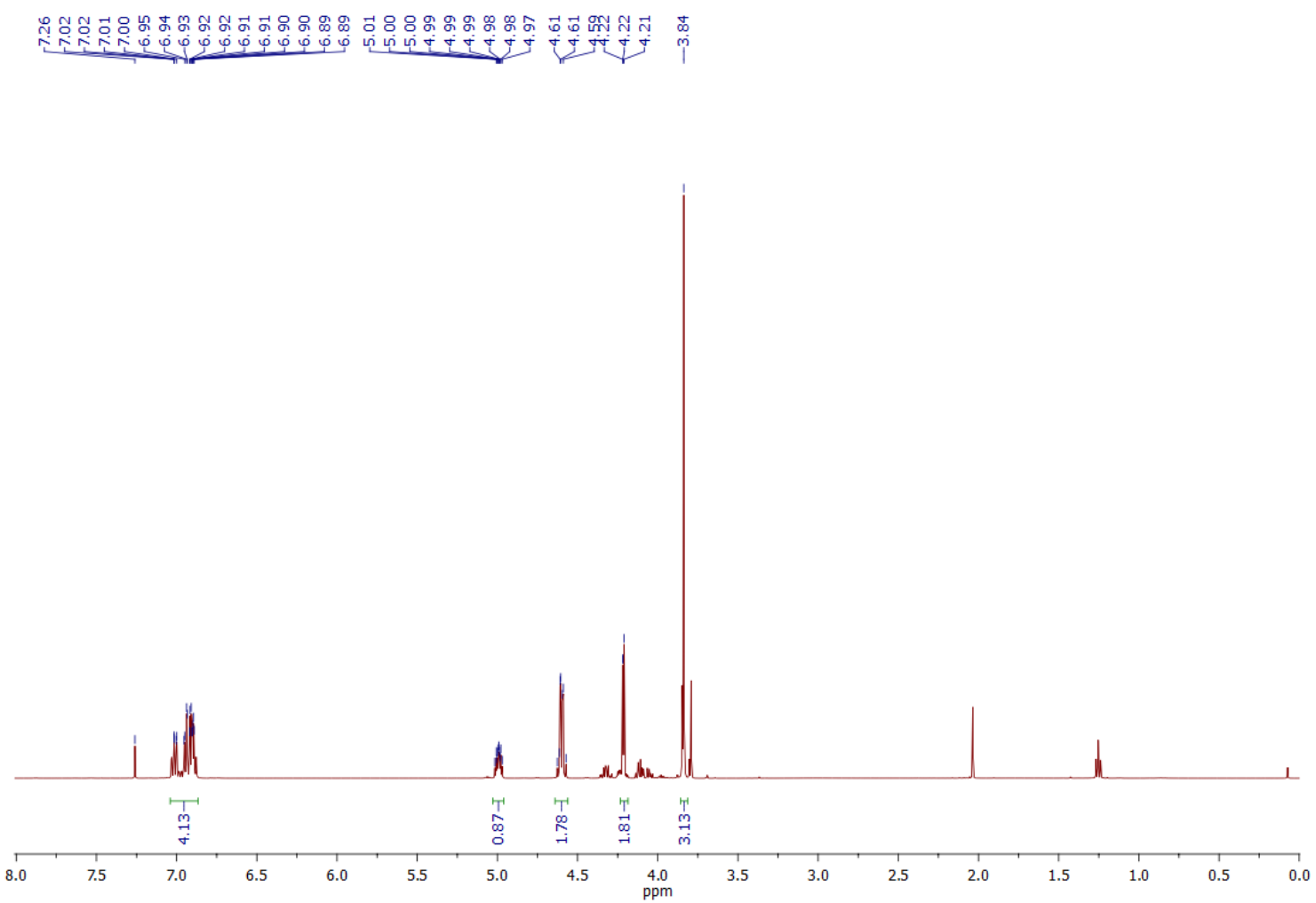


Figure S 31: ^{1}H-^{13}C-HMBC-NMR of ***5a*** *in* $CDCl_3$ *at 303K.*



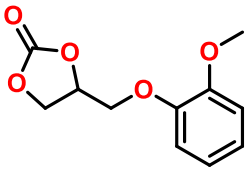


Figure S 32: *^{1}H-NMR of **5b** in $CDCl_3$ at 303 K. Impurities of ethyl acetate and a small amount unknown byproduct are present.*

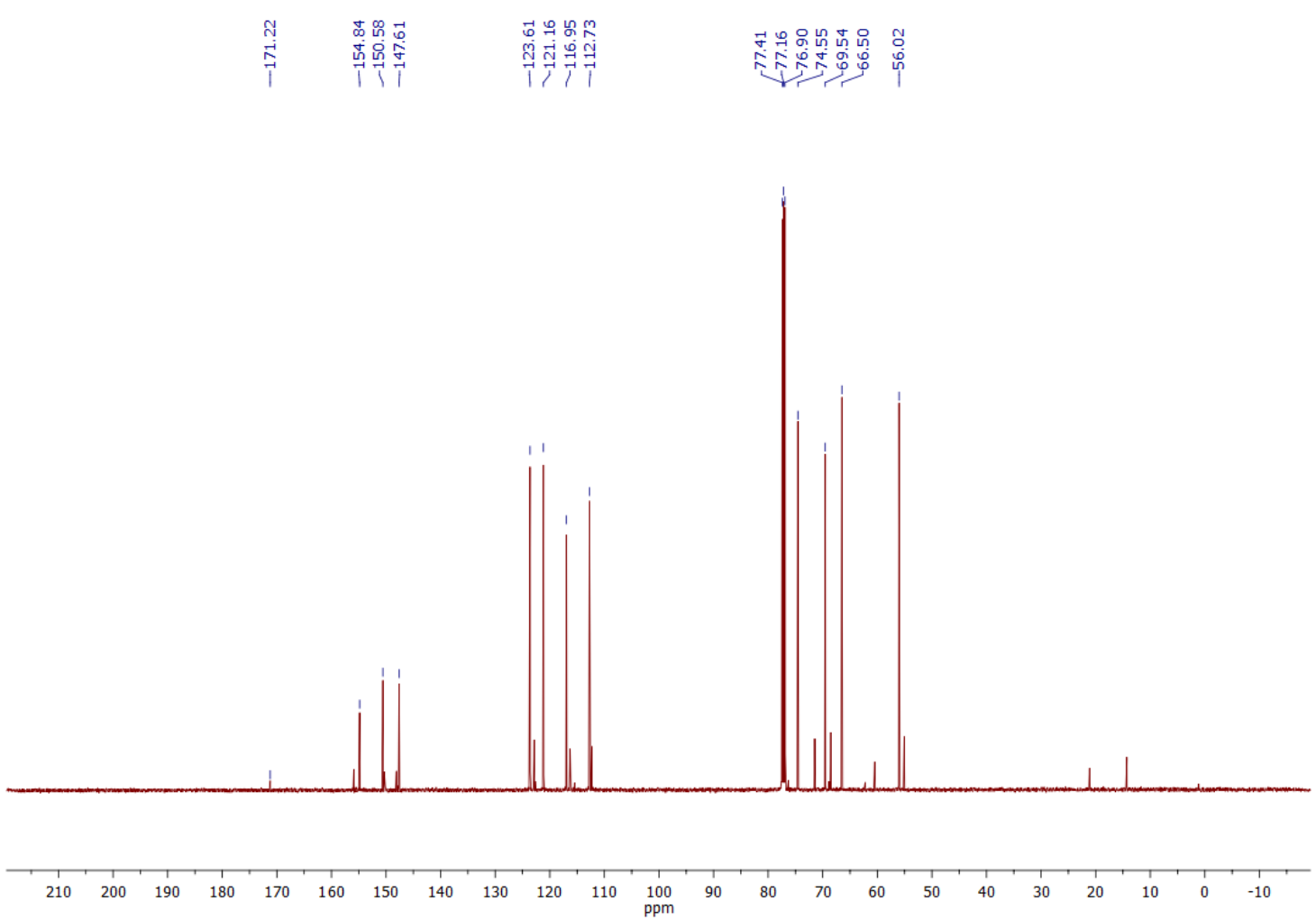
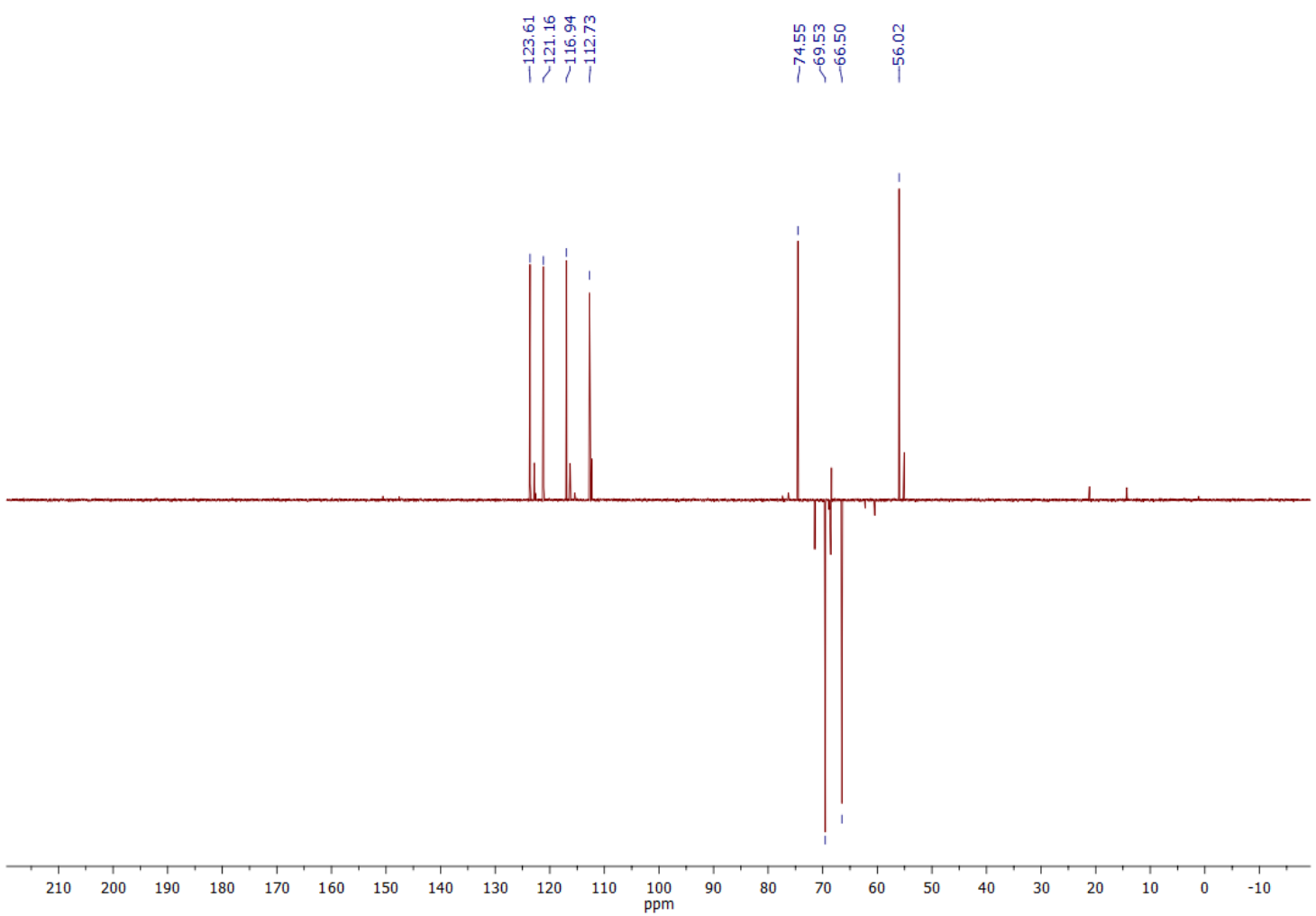


Figure S 33: ^{13}*C-NMR of* ***5b*** *in* $CDCl_3$ *at 303 K. Impurities of ethyl acetate and a small amount unknown byproduct are present.*



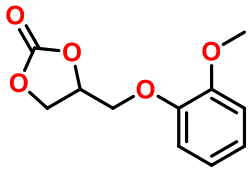
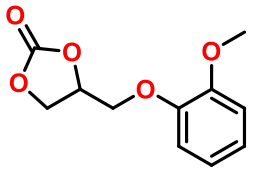


*Figure S 34: DEPT135-NMR of **5b** in $CDCl_3$ at 303 K. Impurities of ethyl acetate and a small amount unknown byproduct are present.*



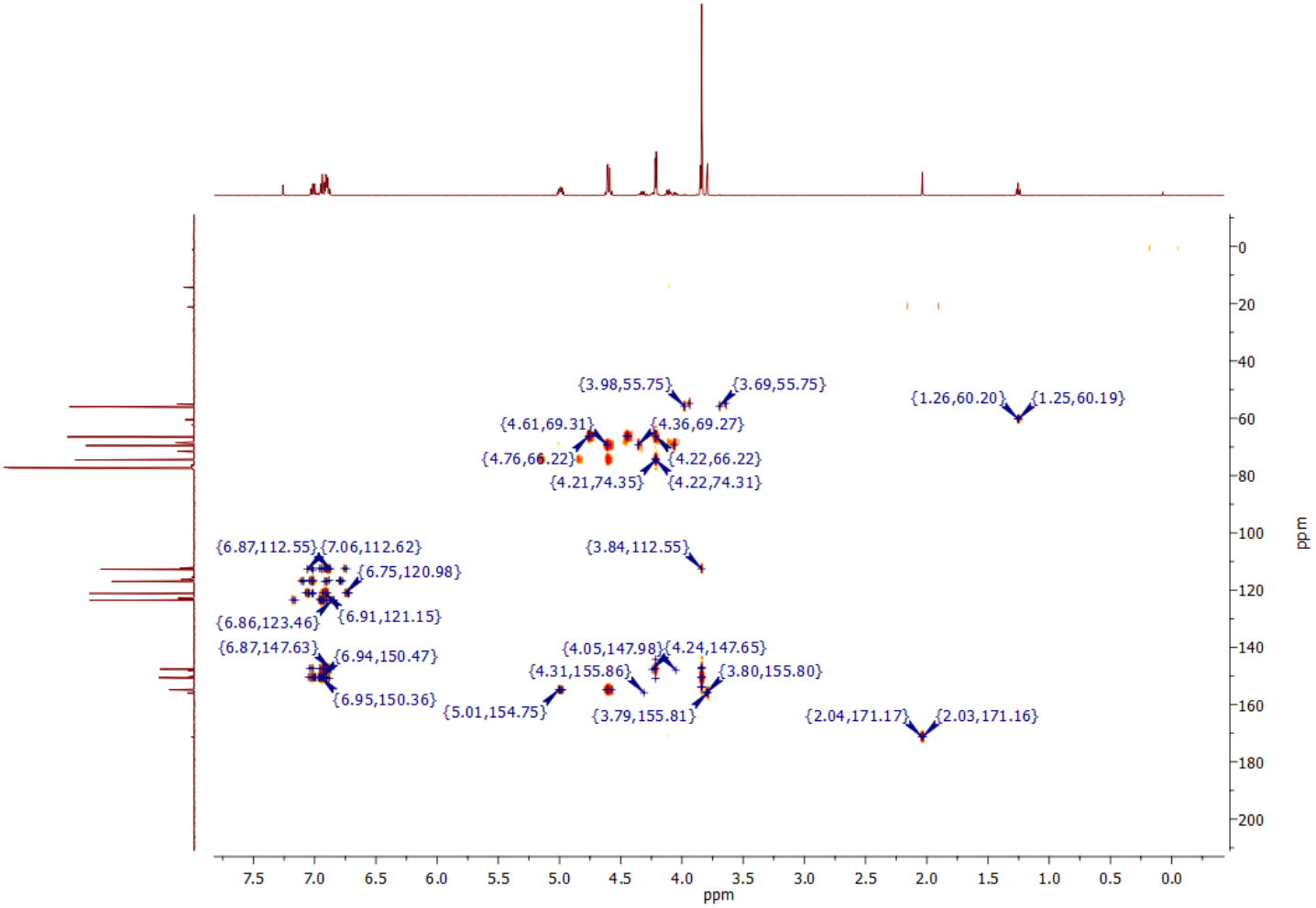
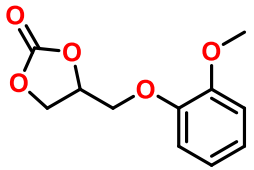


Figure S 35: *^{1}H-^{13}C-HMBC-NMR of **5b** in $CDCl_3$ at 303 K. Impurities of ethyl acetate and a small amount unknown byproduct are present.*



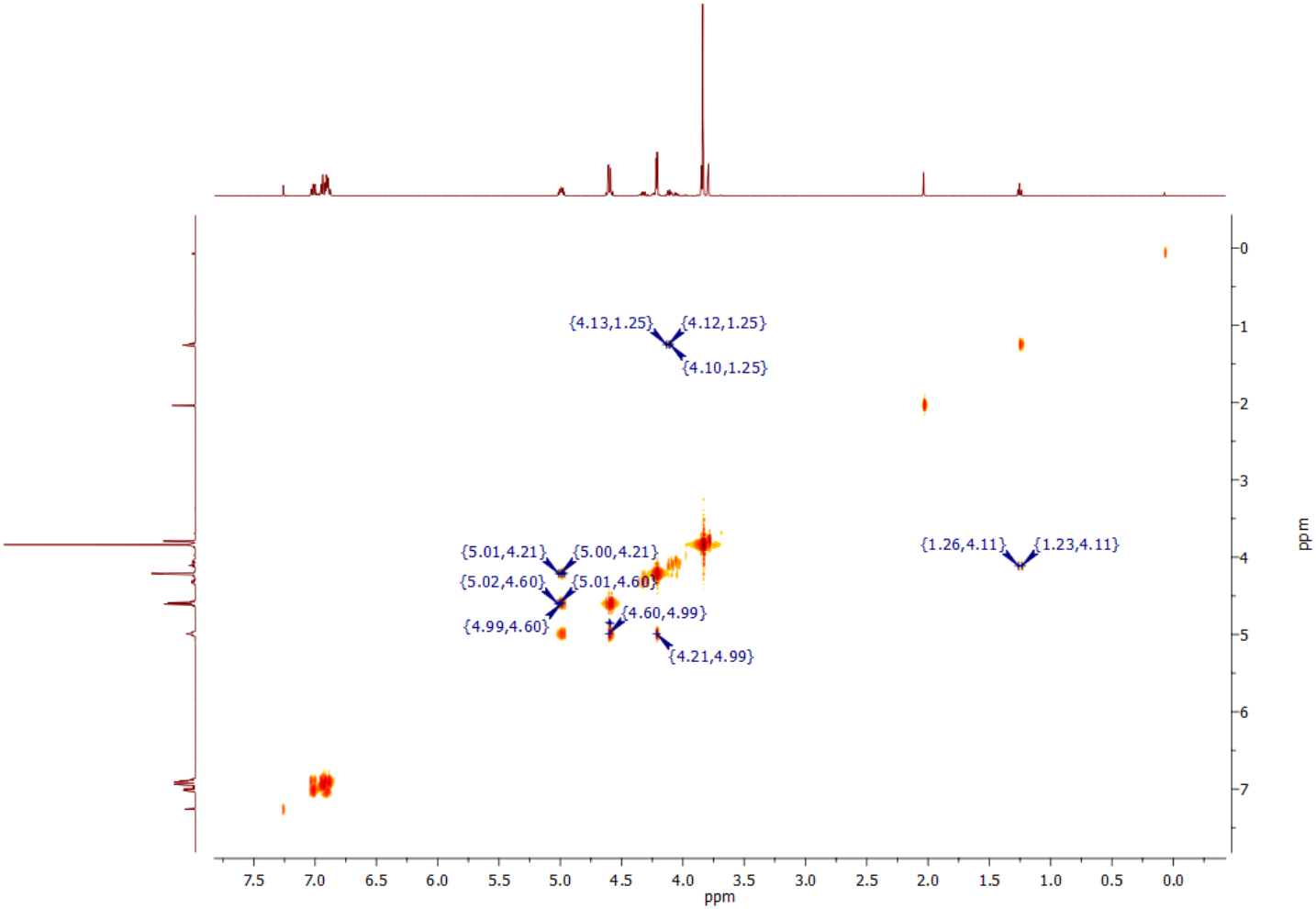
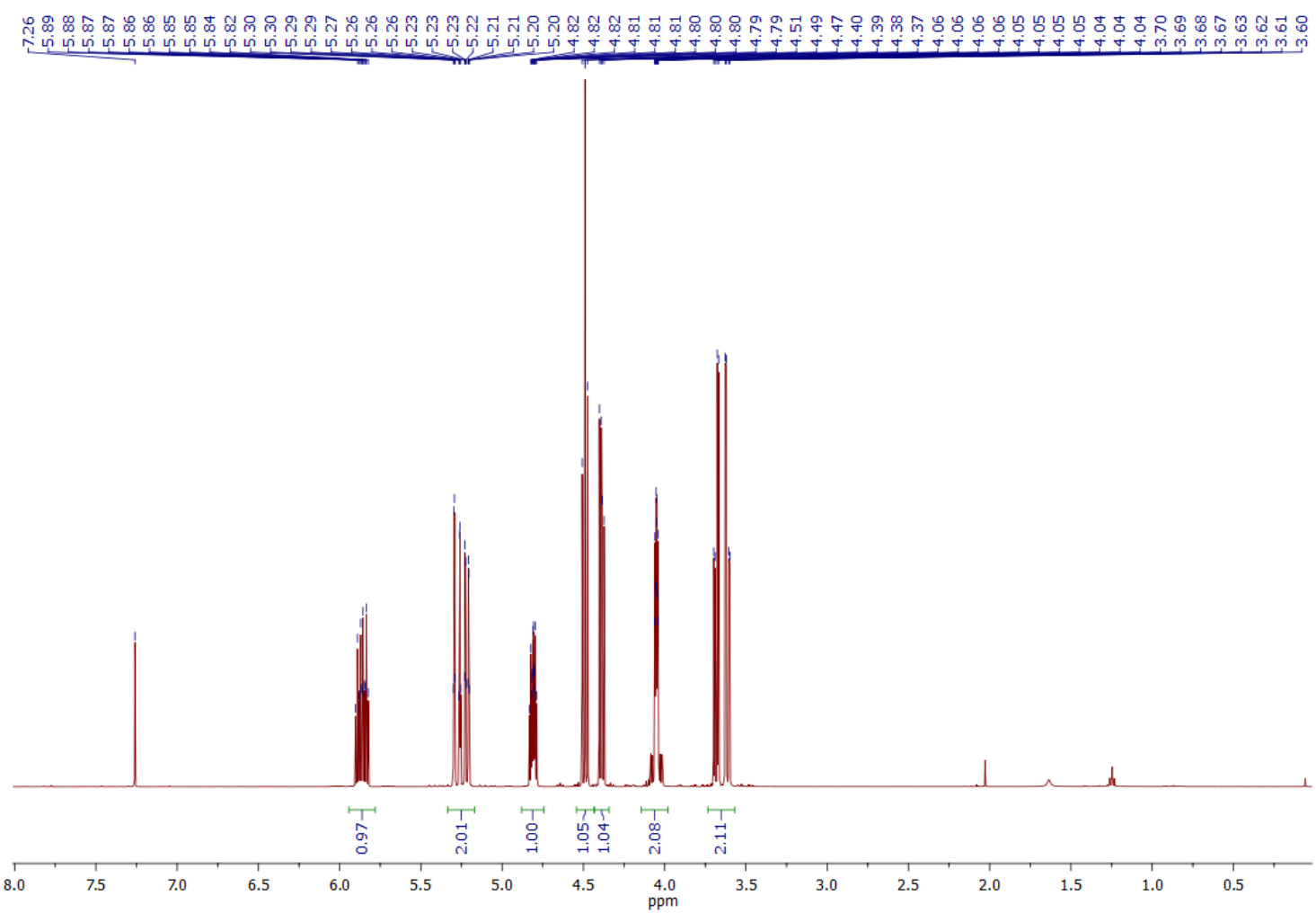


Figure S 36: *^{1}H-^{1}H-COSY-NMR of **5b** in $CDCl_3$ at 303 K. Impurities of ethyl acetate and a small amount unknown byproduct are present.*



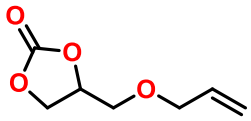
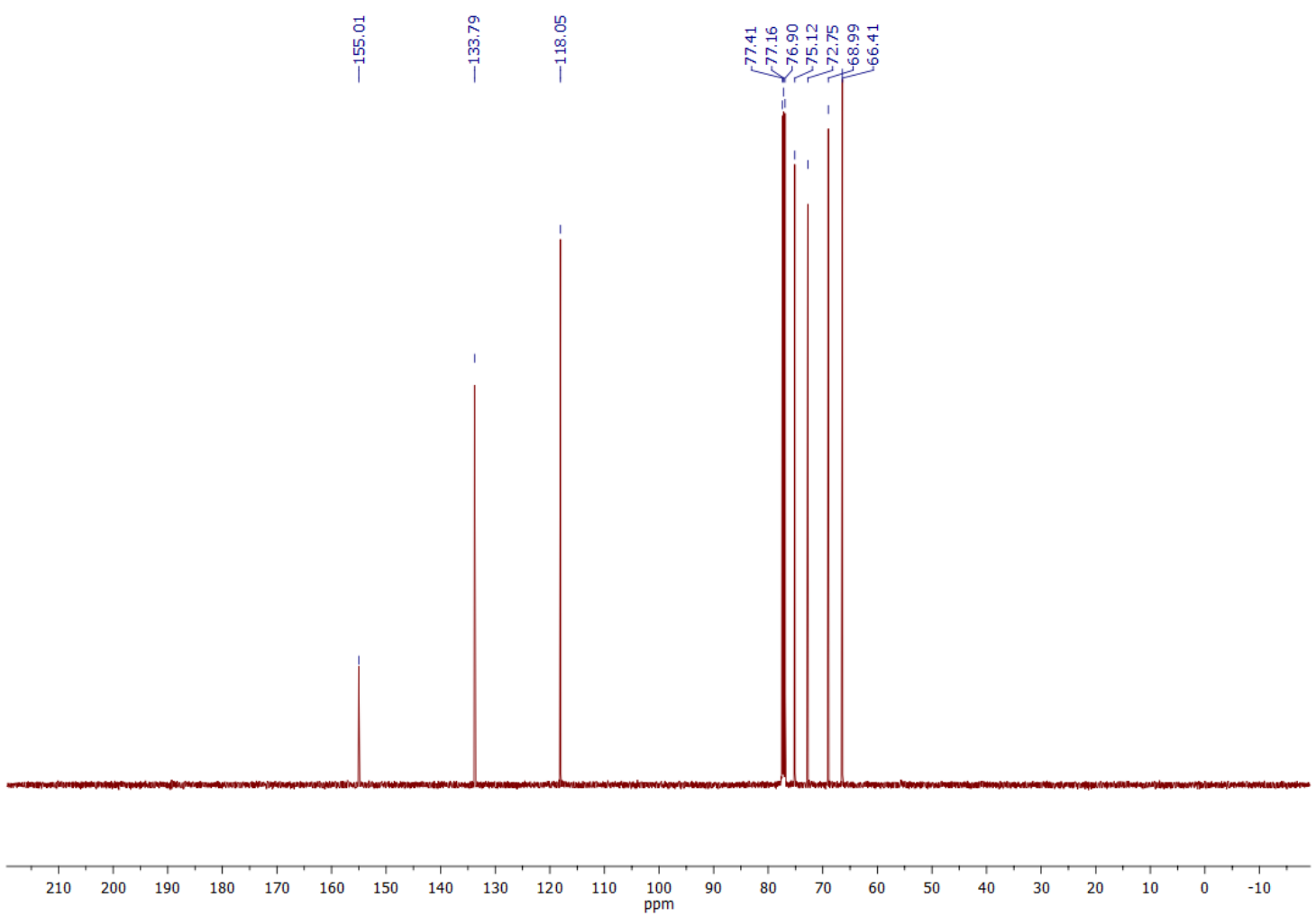


Figure S 37: *^{1}H-NMR of **5c** in $CDCl_3$ at 303 K. Impurities of cyclohexane and ethyl acetate are present.*



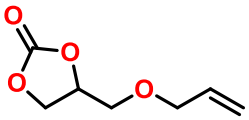
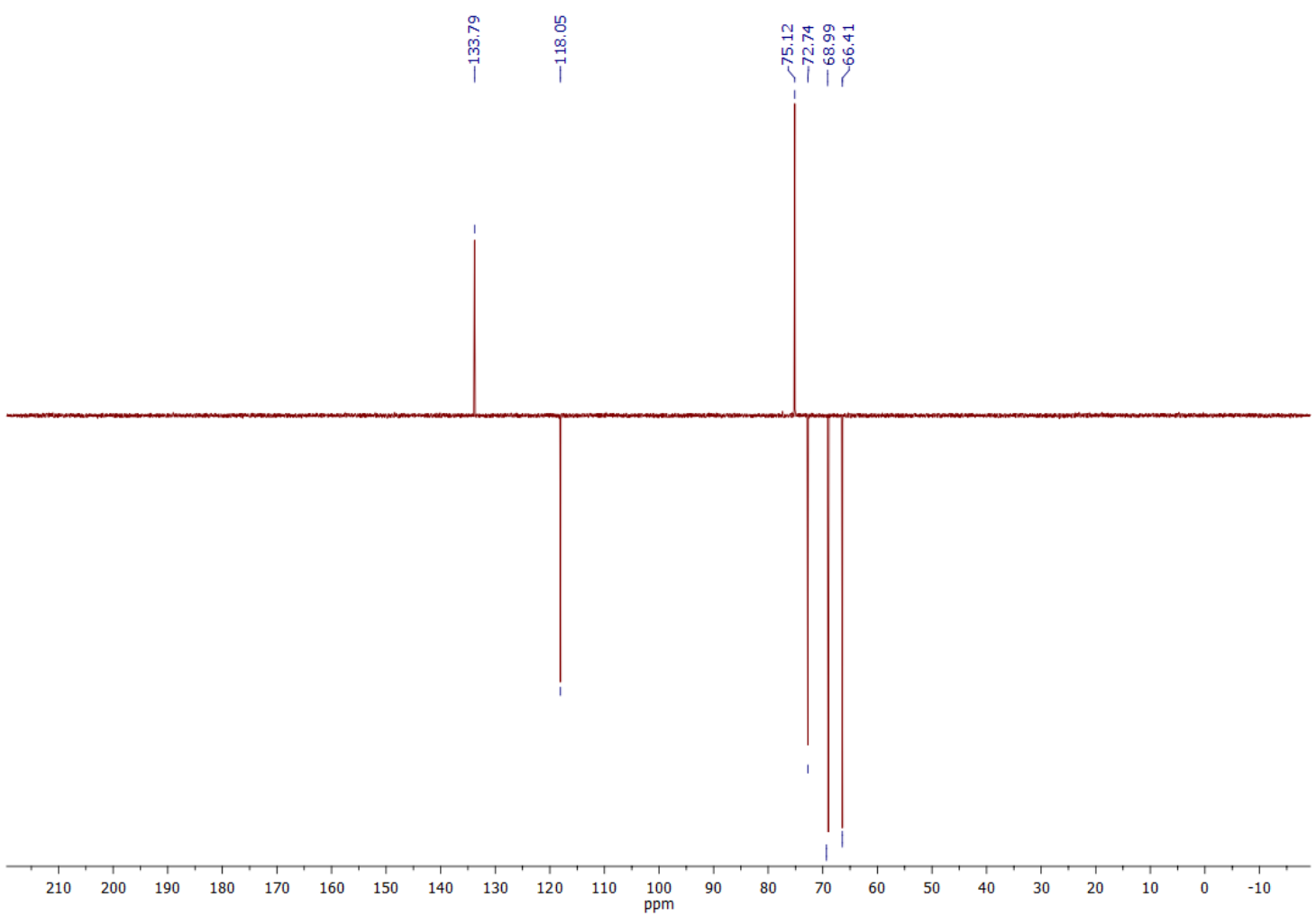


Figure S 38: *^{13}C-NMR of **5c** in $CDCl_3$ at 303 K.*



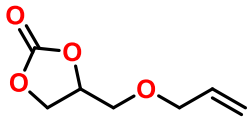
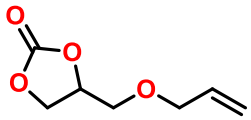


*Figure S 39: DEPT135-NMR of **5c** in $CDCl_3$ at 303 K.*



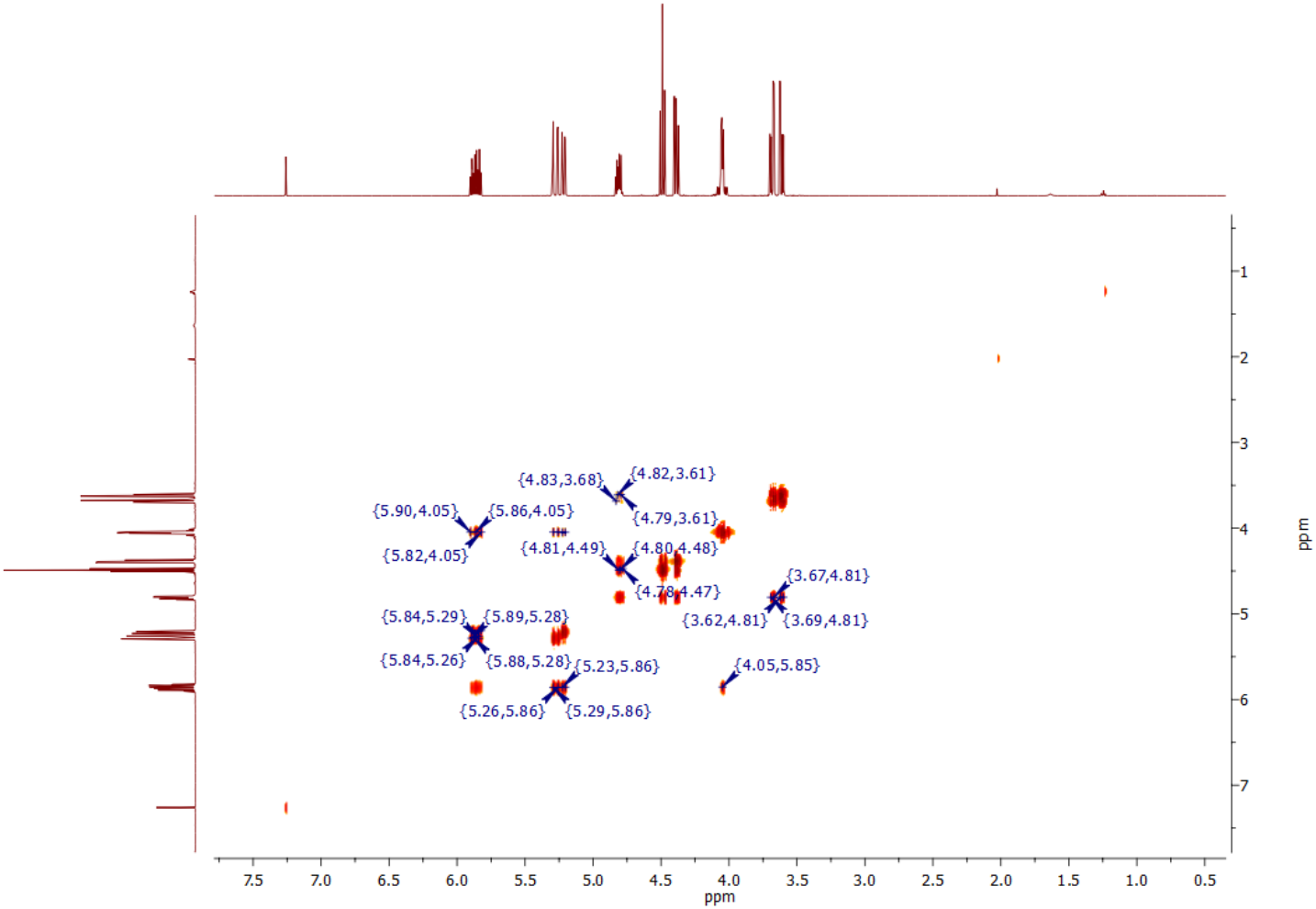
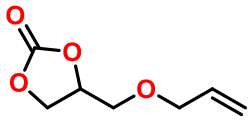


Figure S 40: *^{1}H-^{1}H-COSY-NMR of **5c** in $CDCl_3$ at 303 K.*



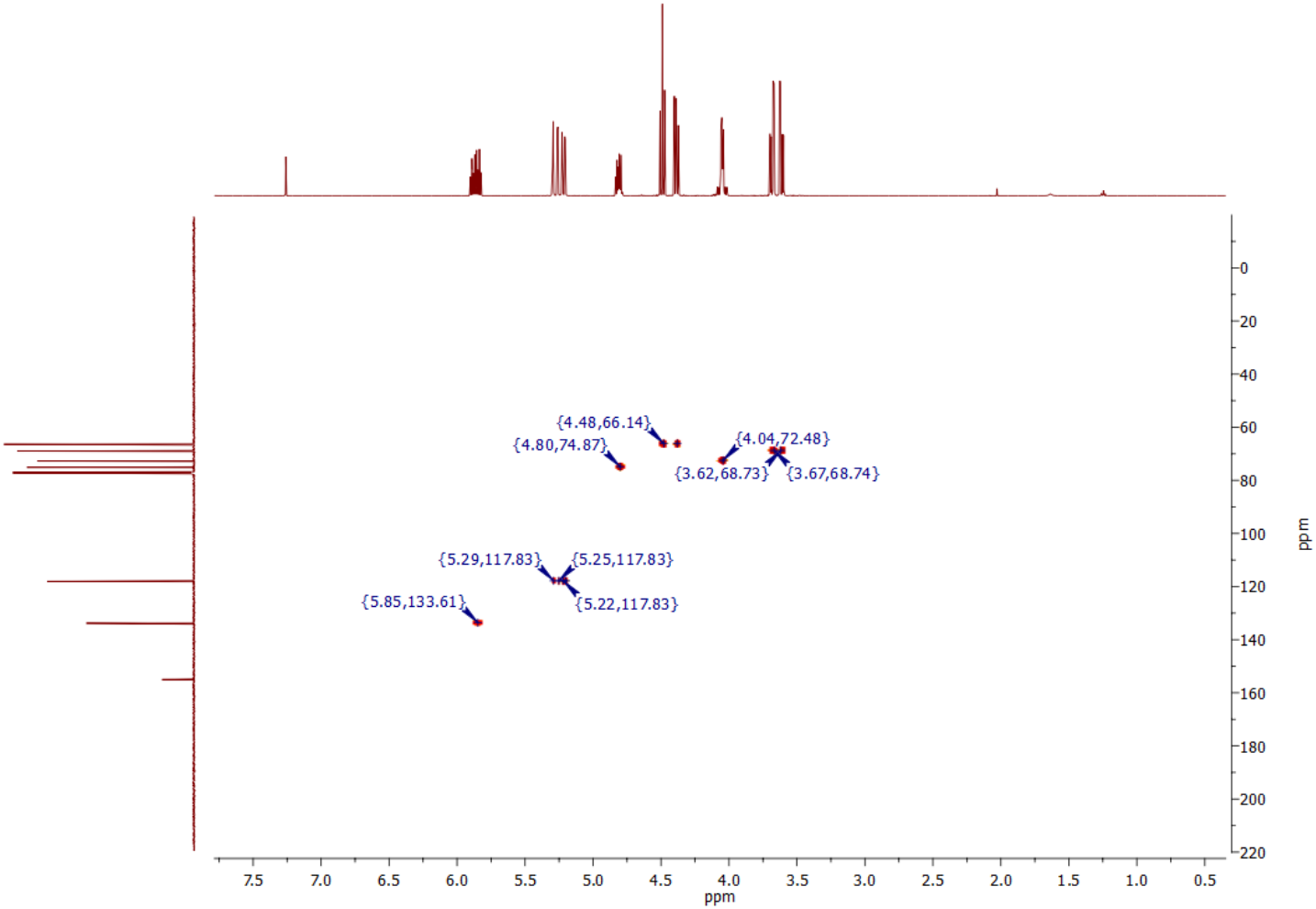
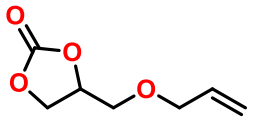


Figure S 41: ^{1}H-^{13}C-HSQC-NMR of ***5c*** *in* $CDCl_3$ *at 303 K.*



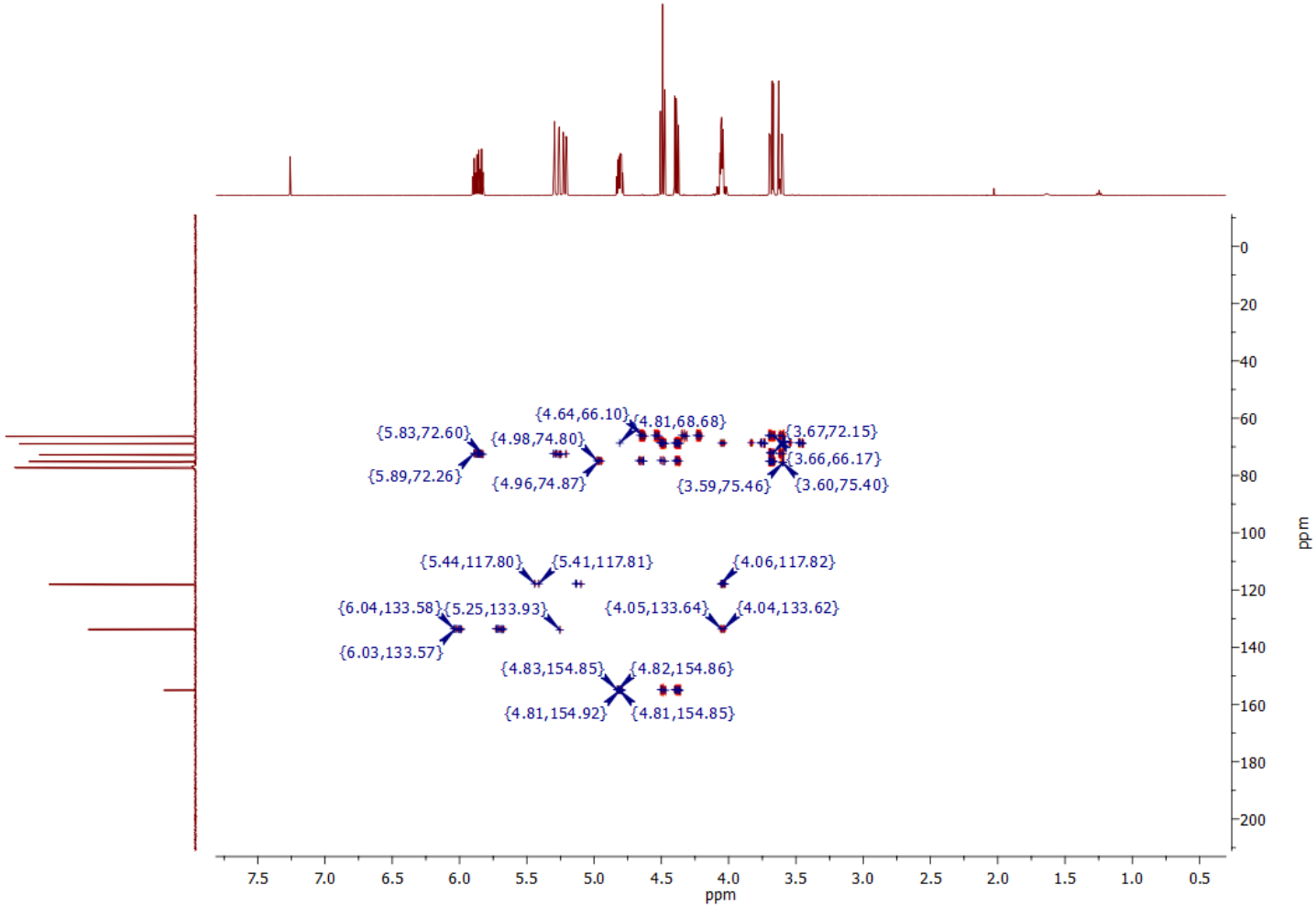
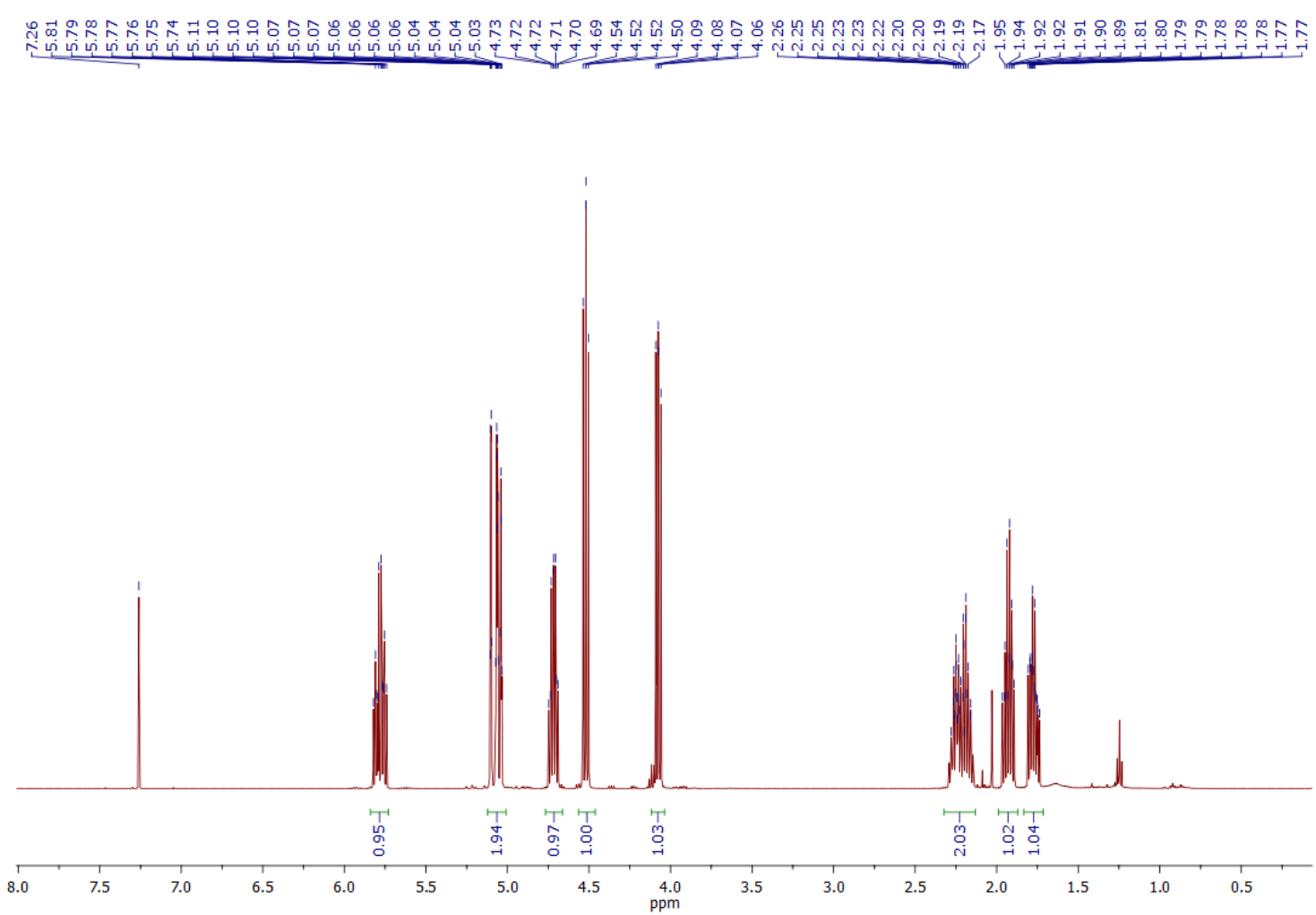


Figure S 42: *^{1}H-^{13}C-HMBC-NMR of **5c** in $CDCl_3$ at 303 K.*



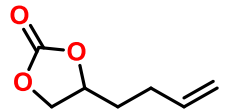
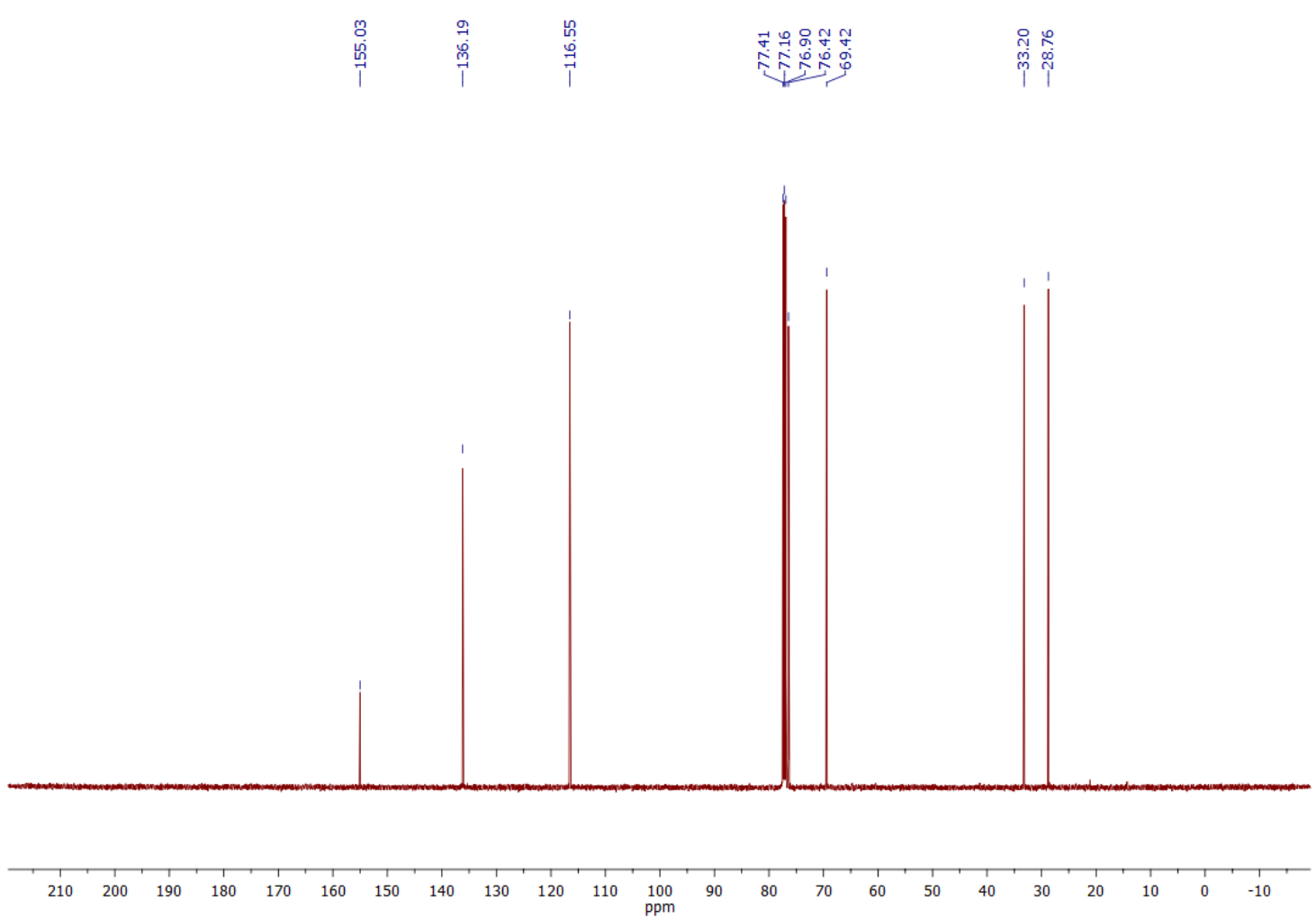


Figure S 43: *^{1}H-NMR of **5d** in $CDCl_3$ at 303 K. Impurities of cyclohexane and ethyl acetate are present.*



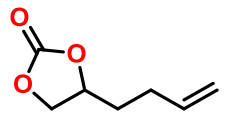
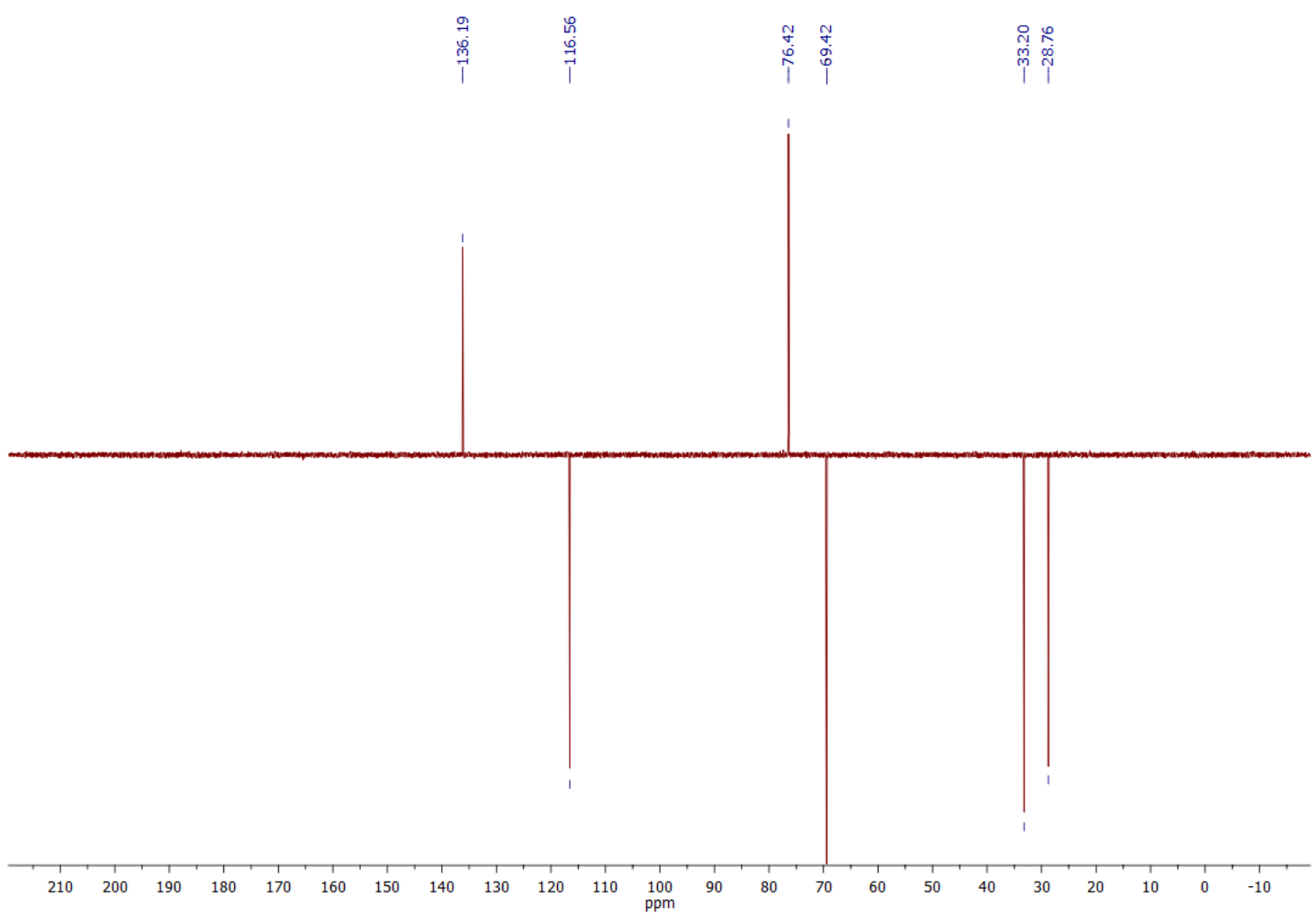


Figure S 44: *^{13}C-NMR of **5d** in $CDCl_3$ at 303 K.*



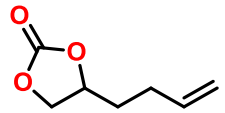


*Figure S 45: DEPT135-NMR of **5d** in $CDCl_3$ at 303 K.*

.

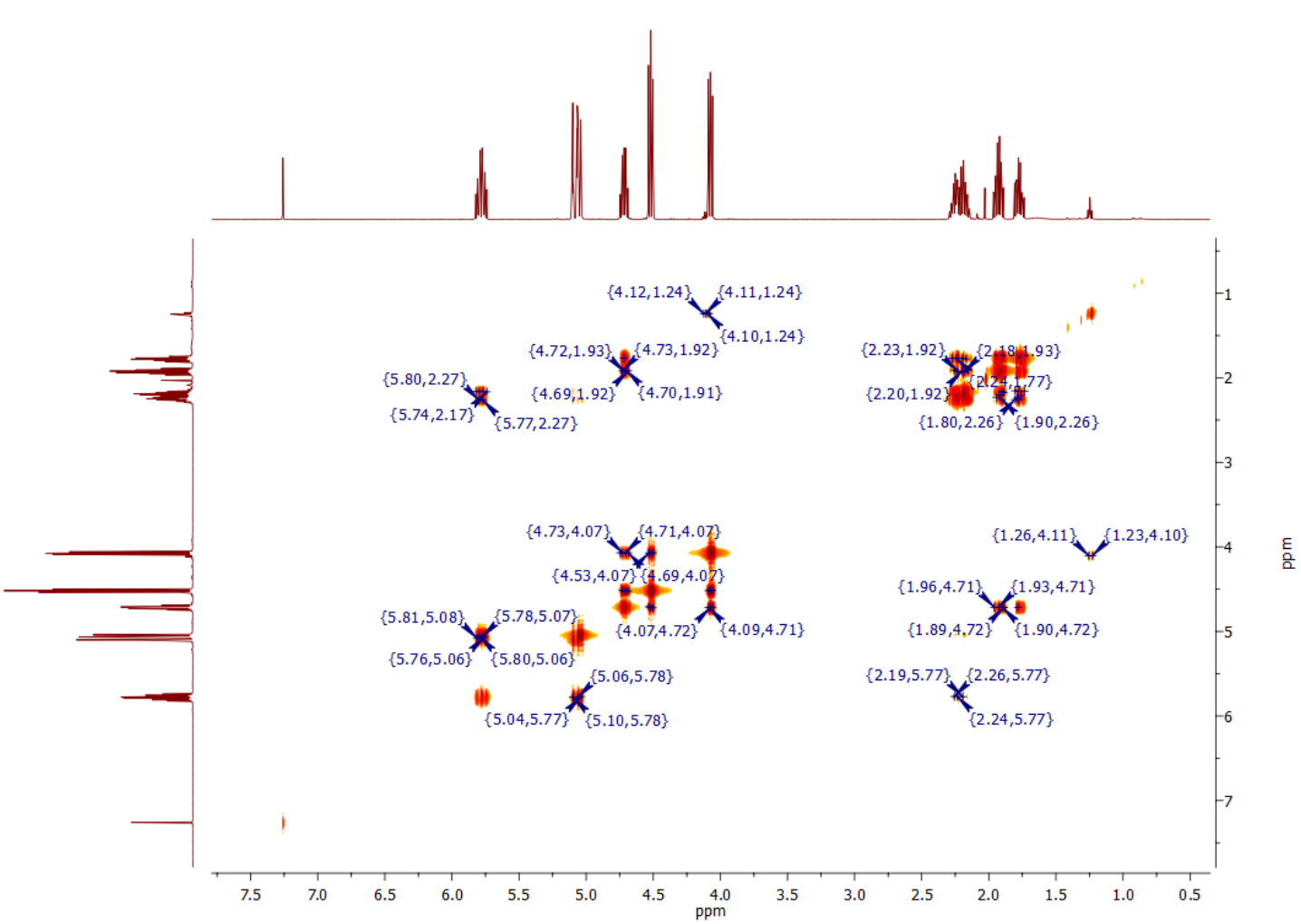


Figure S 46: ^{1}H-^{1}H-COSY-NMR of ***5d*** *in* $CDCl_3$ *at 303 K.*

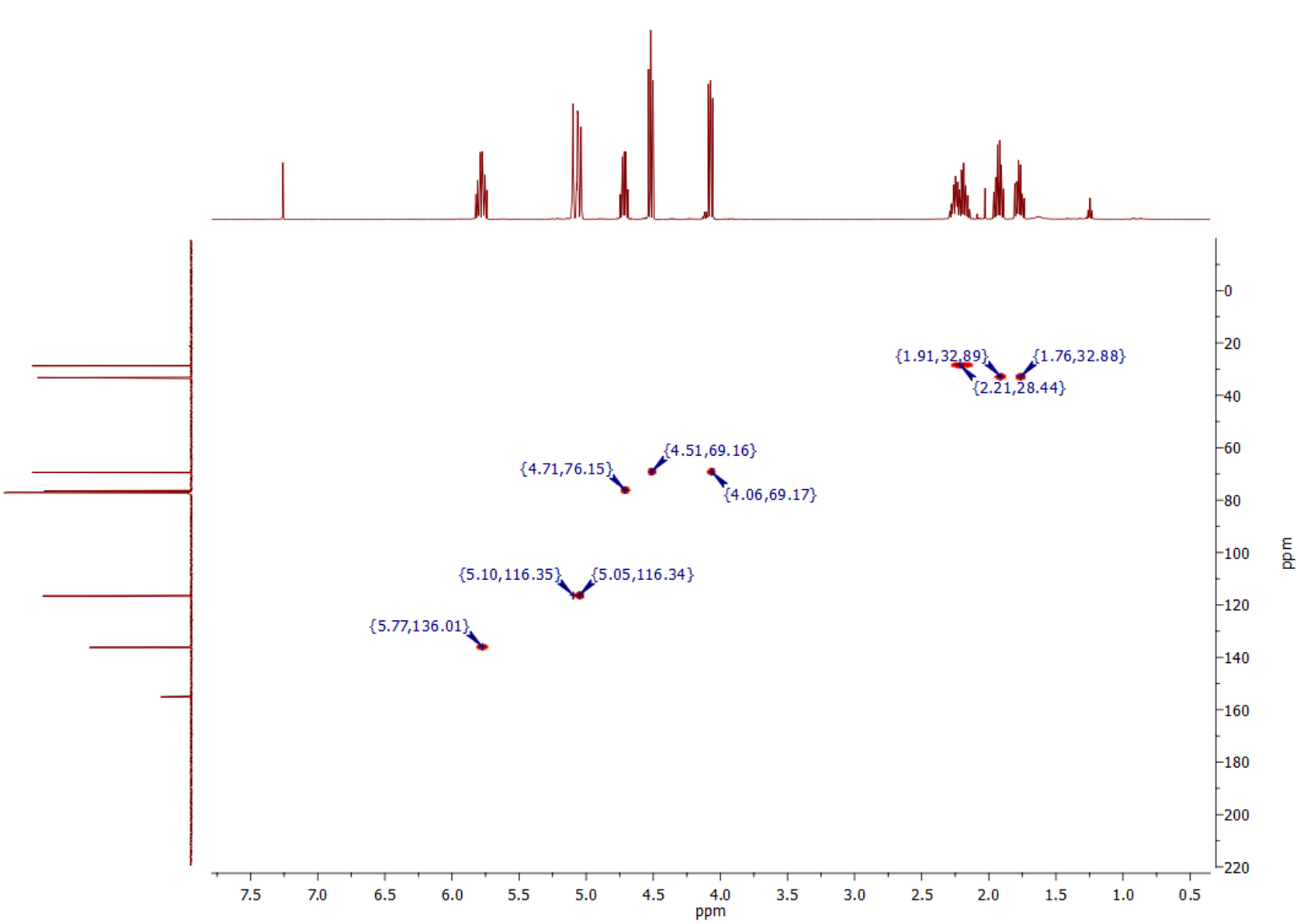
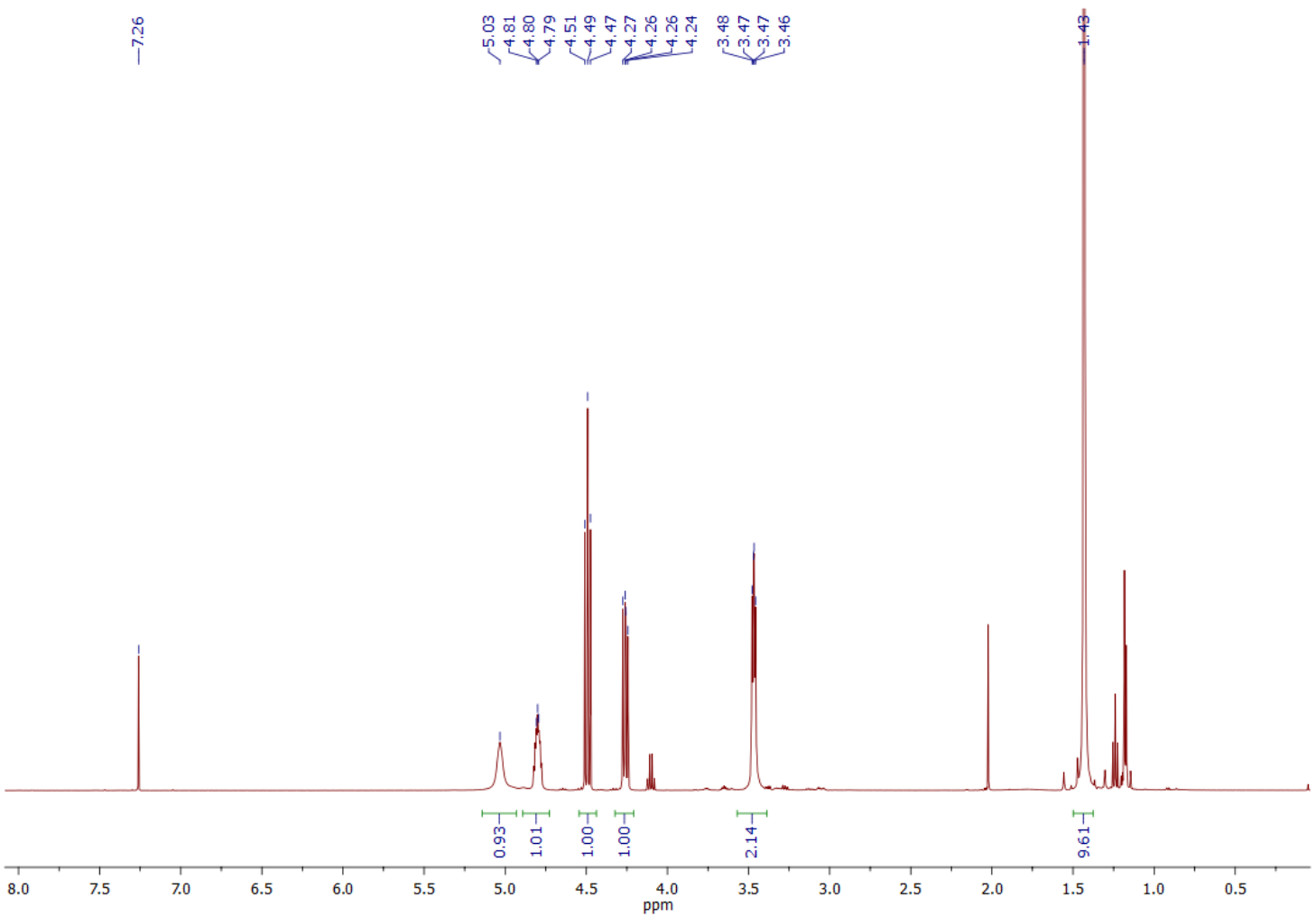


Figure S 47: *^{1}H-^{13}C-HSQC-NMR of **5d** in $CDCl_3$ at 303 K.*



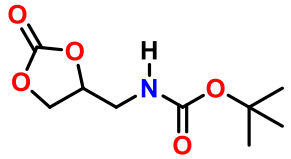
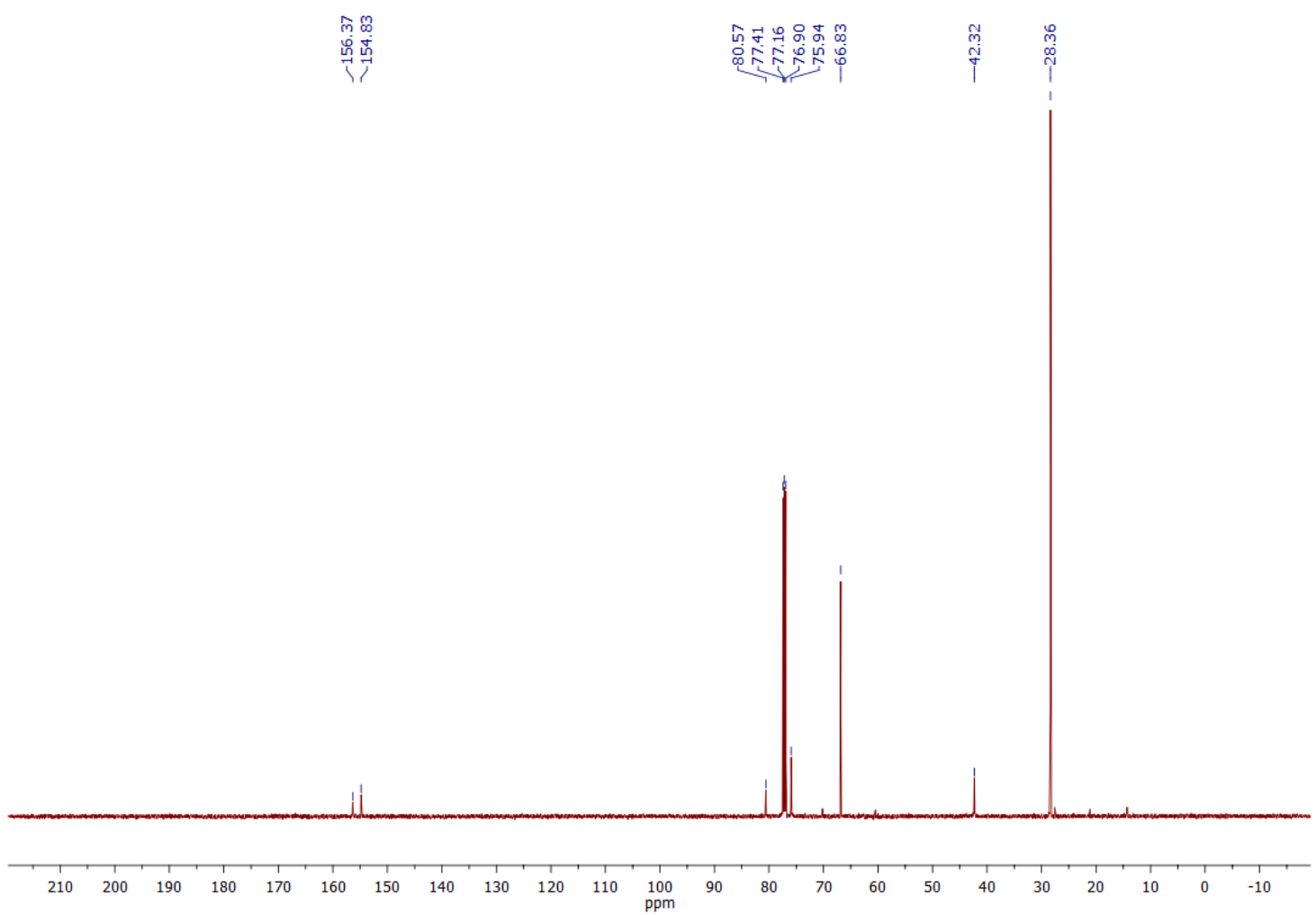


Figure S 48: *^{1}H-NMR of **5e** in $CDCl_3$ at 303 K. Impurities of cyclohexane and ethyl acetate are present.*



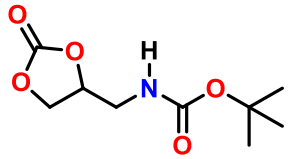
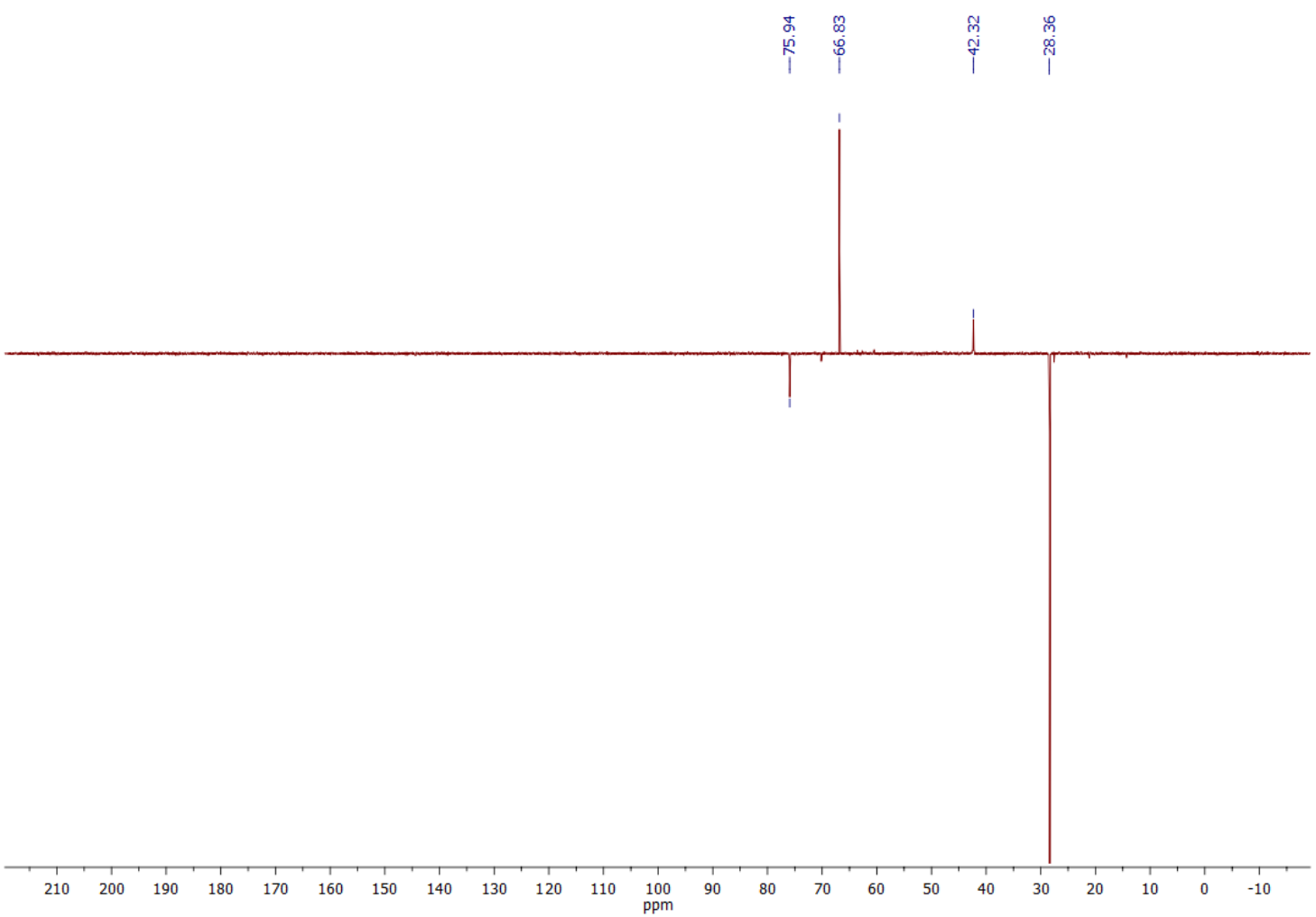


Figure S 49: ^{13}*C-NMR of* ***5e*** *in* $CDCl_3$ *at 303 K. Impurities of cyclohexane and ethyl acetate are present.*



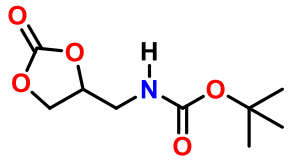
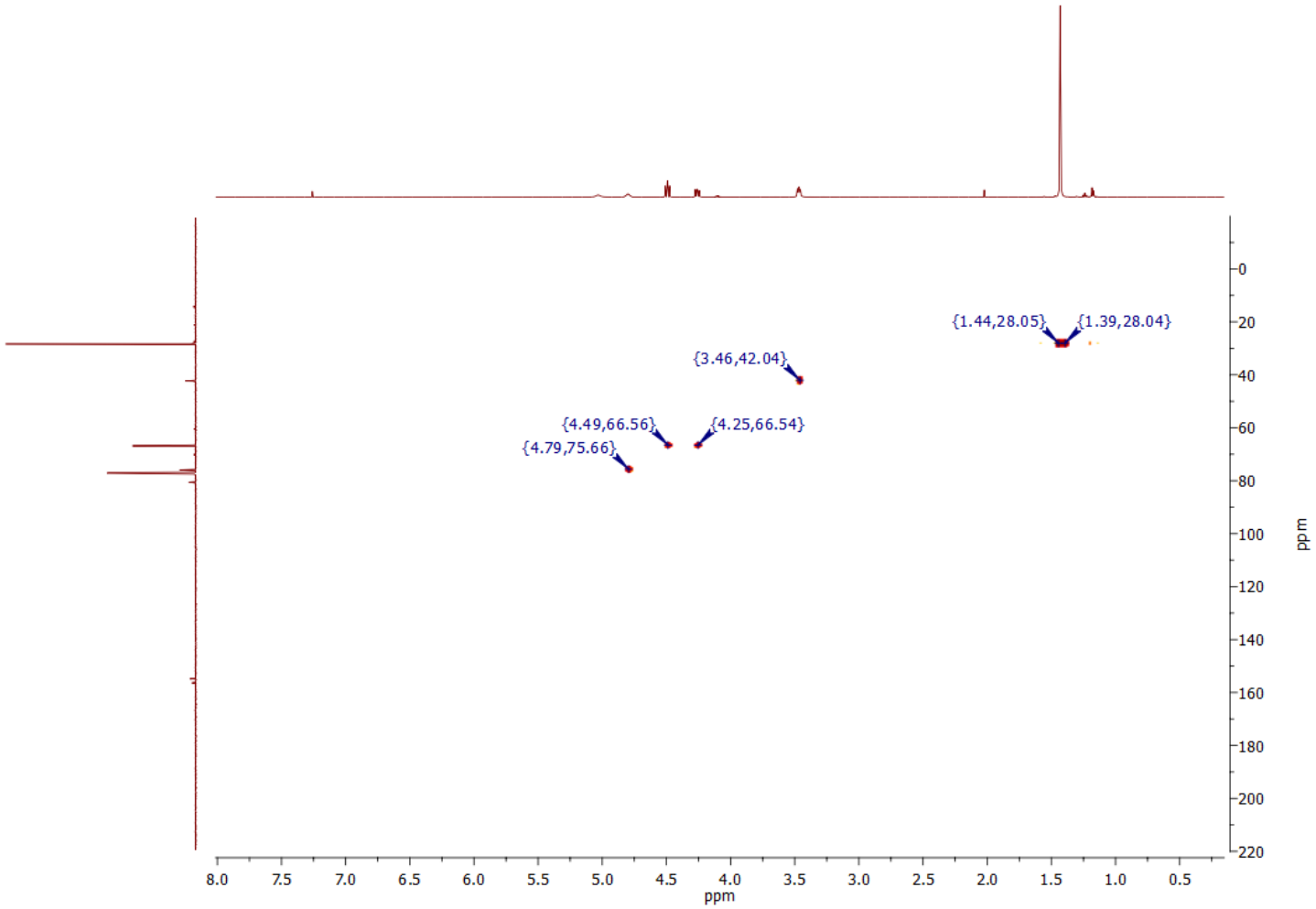


*Figure S 50: DEPT135-NMR of **5e** in $CDCl_3$ at 303 K. Impurities of cyclohexane and ethyl acetate are present.*



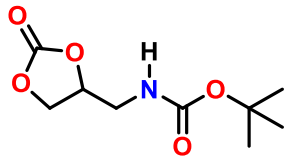
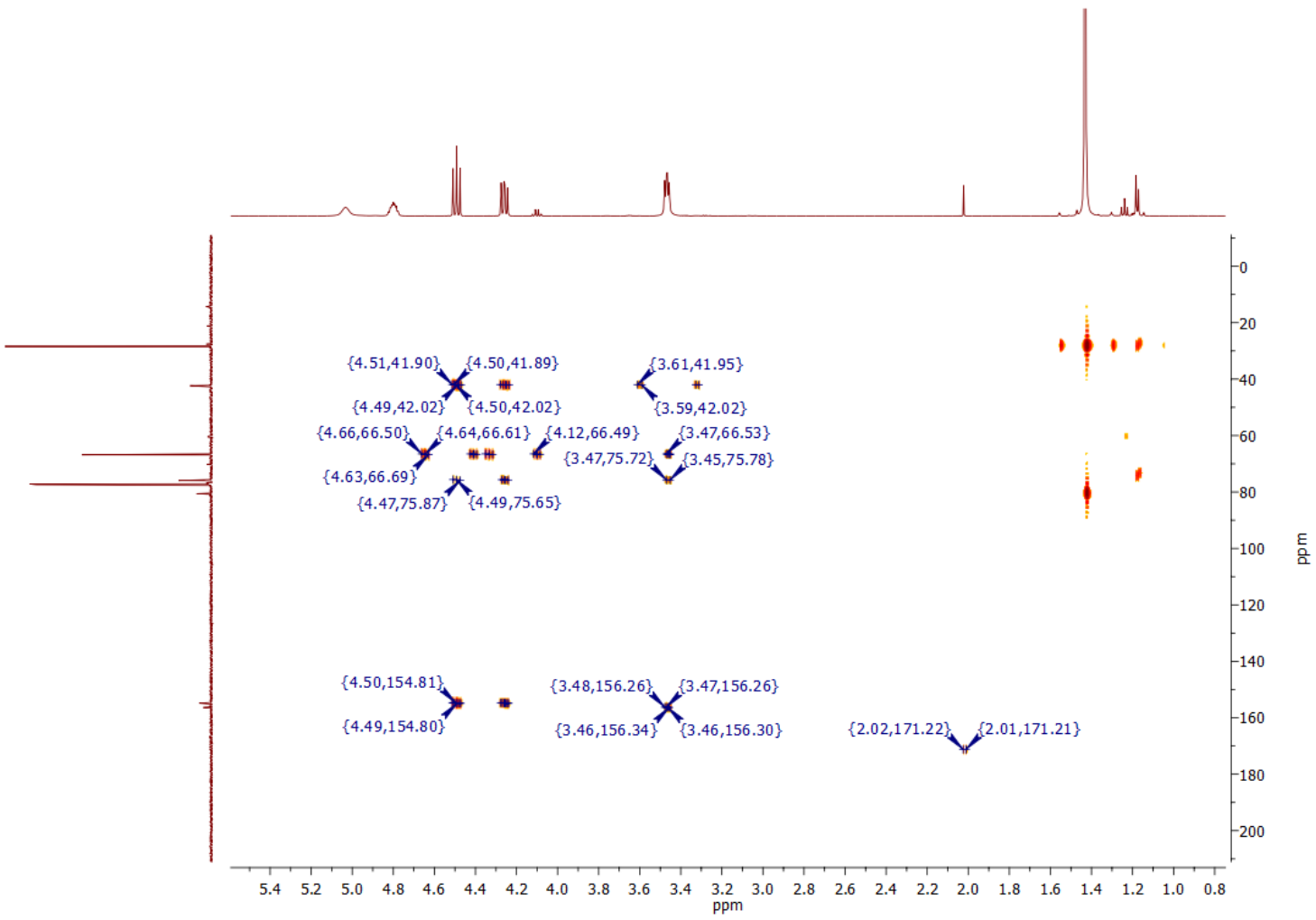


Figure S 51: *^{1}H-^{13}C-HSQC-NMR of **5e** in $CDCl_3$ at 303 K.*



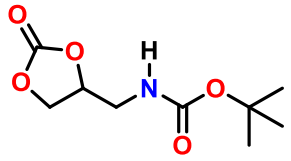
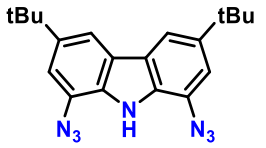


Figure S 52: *^{1}H-^{13}C-HMBC-NMR of **5e** in $CDCl_3$ at 303 K.*

2. IR Spectra



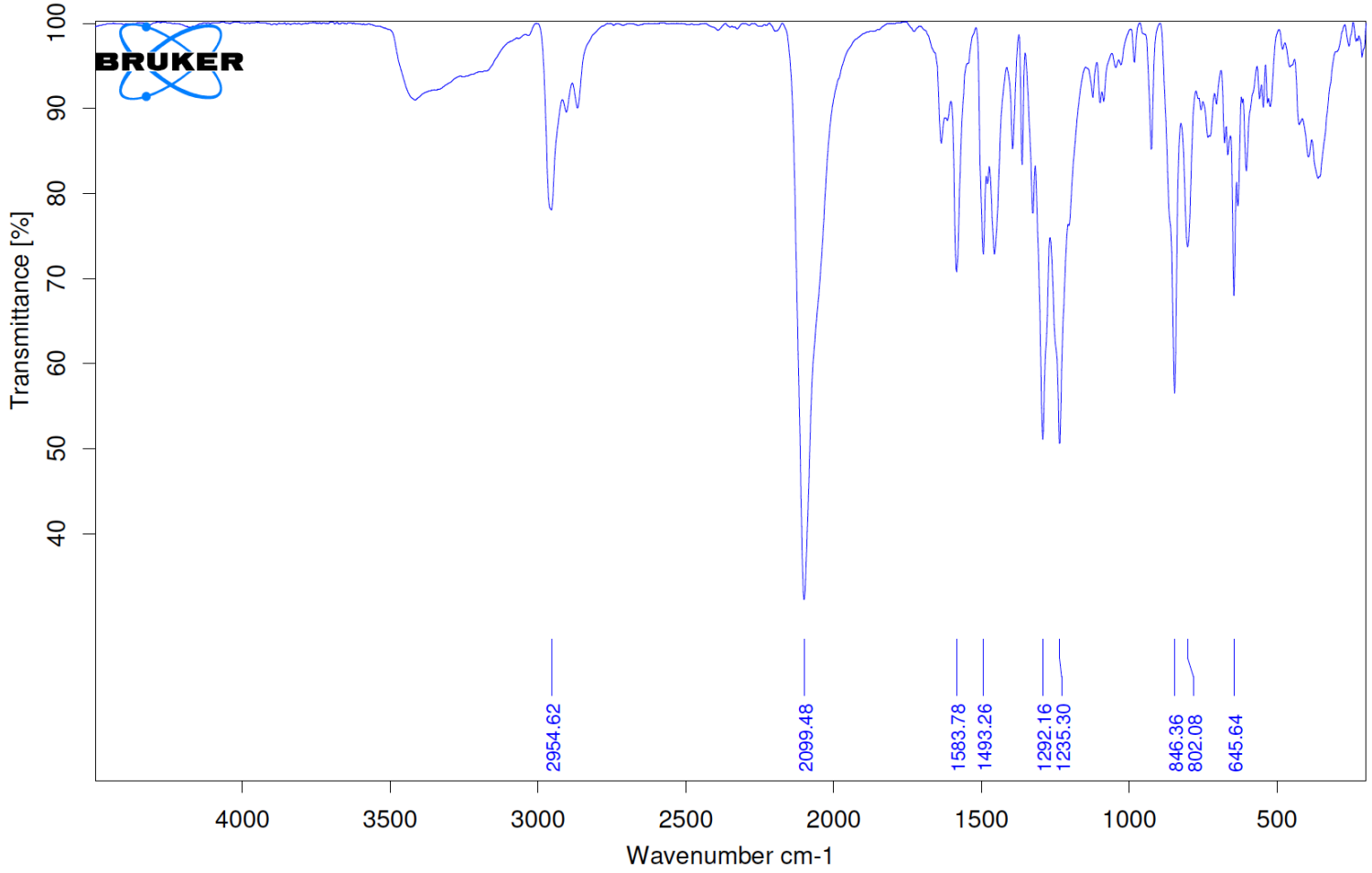
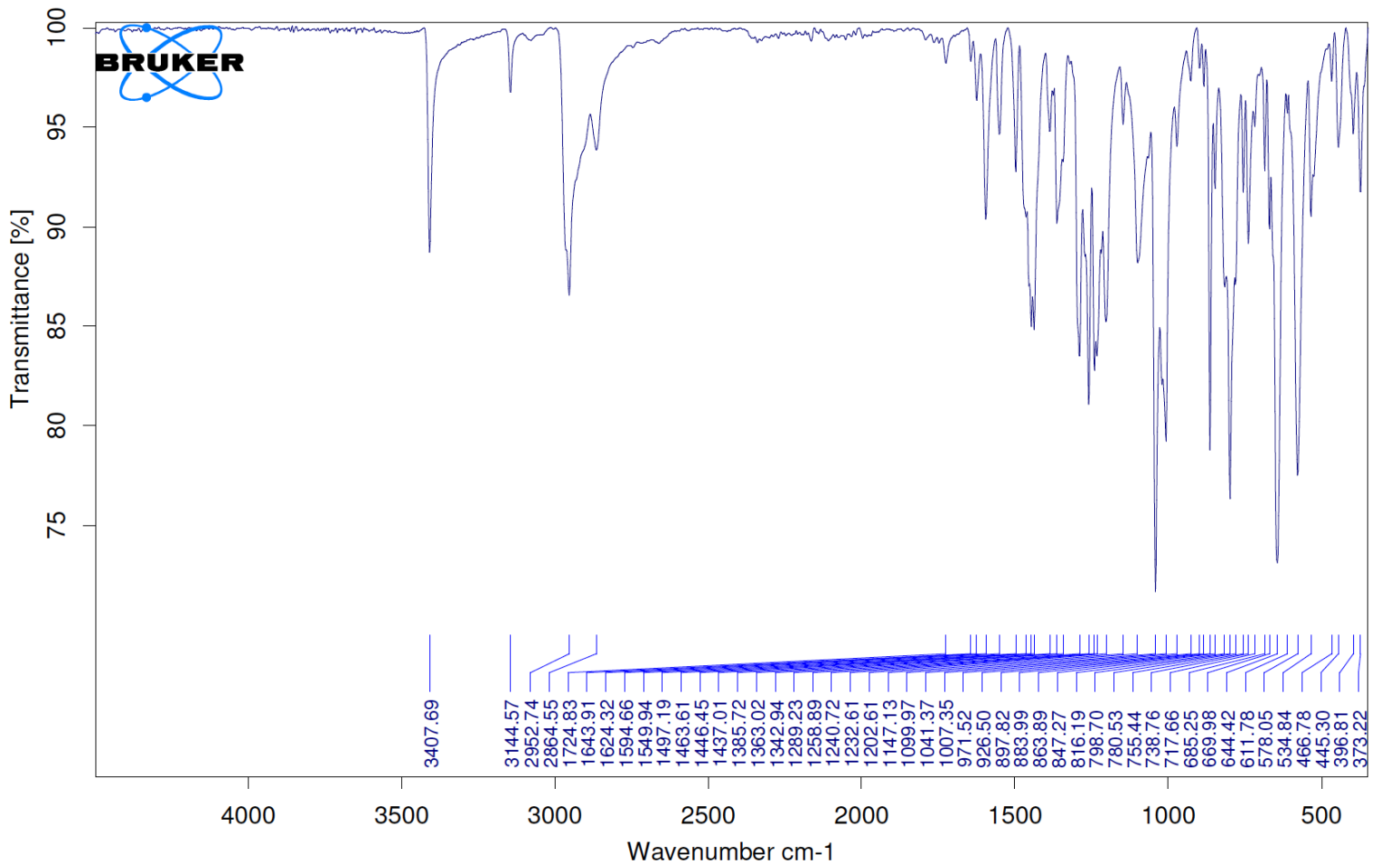


*Figure S 53: FT-IR (ATR) of solid **1** at 298 K.*



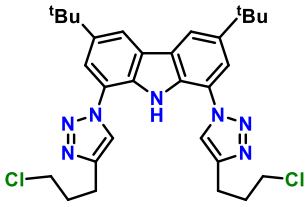
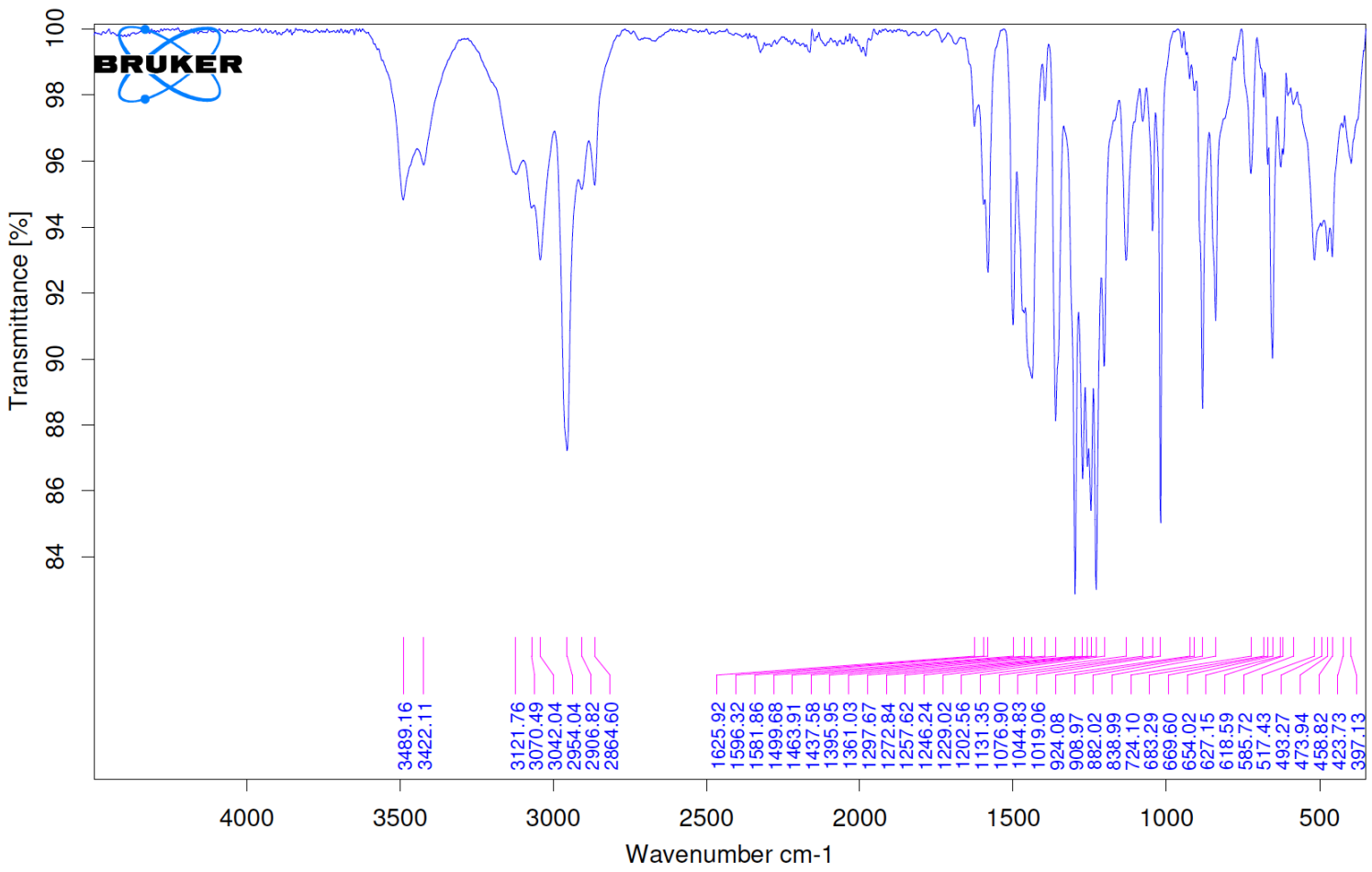


*Figure S 54: FT-IR (ATR) of solid **2a** at 298 K.*



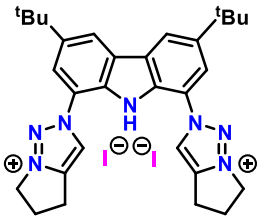
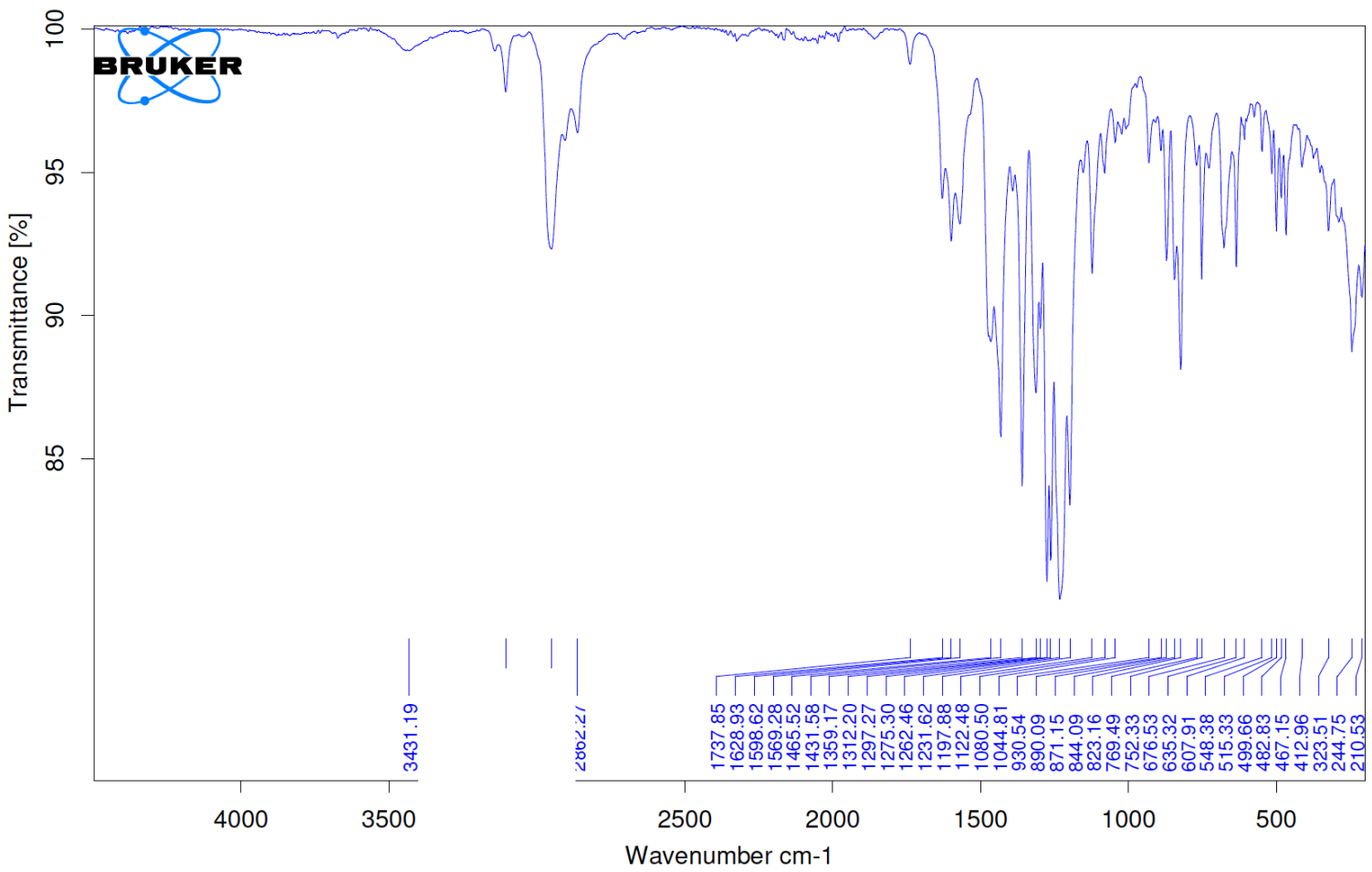


*Figure S 55: FT-IR (ATR) of solid **3a** at 298 K.*



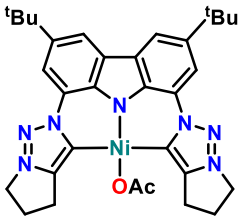
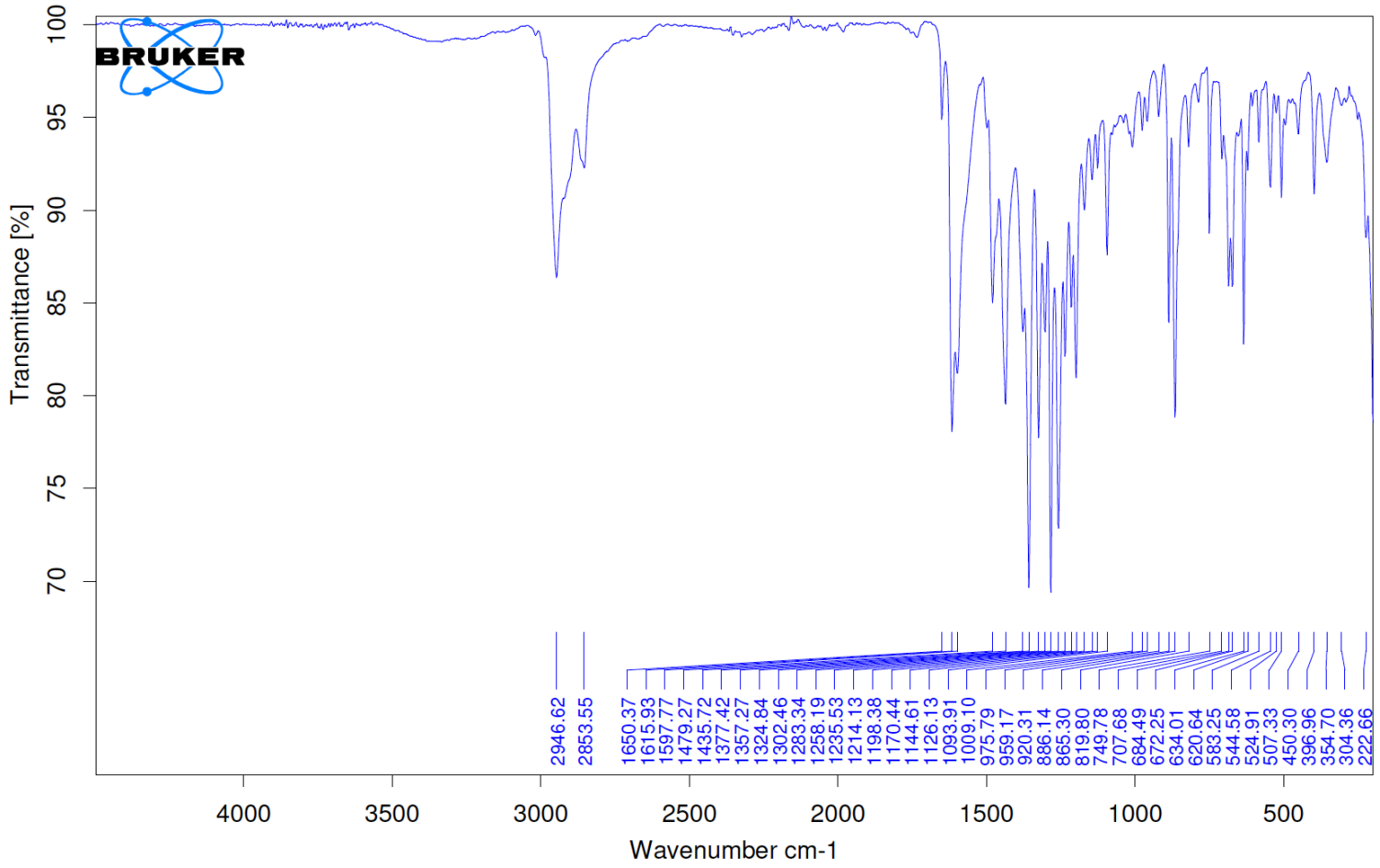


*Figure S 56: FT-IR (ATR) of solid **4a** at 298 K.*



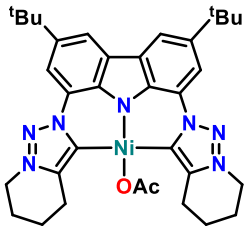


*Figure S 57: FT-IR (ATR) of solid **4b** at 298 K.*

3. Crystallographic details

Table S1: Crystallographic details

	3a (5 CH_2Cl_2)*	**4a (H_2O)**	**4b (CH_2Cl_2)**
Chemical formula	2 ($C_{30}H_{37}N_7I_2$) 5 CH_2Cl_2	$C_{32}H_{37}N_7O_2Ni_1$ H_2O	$C_{34}H_{41}N_7O_2Ni_1$ CH_2Cl_2
M_r	1923.56	628.41	723.37
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a (Å)	11.504(2)	7.126(2)	7.5365(4)
b (Å)	17.383(3)	14.133(3)	13.8963(7)
c (Å)	22.798(4)	15.931(3)	16.4272(9)
α (°)	69.113(3)	104.37(3)	86.456(2)
β (°)	85.019(3)	98.75(2)	83.953(2)
γ (°)	88.293(3)	92.59(2)	78.005(2)
V (Å^3)	4226.6(1)	1530.4(6)	1672.1(2)
Z	2	2	2
Densitiy (g cm^{-3})	1.511	1.364	1.437
F(000)	1908	664	760
Radiation Type	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$
μ (mm)	1.835	0.679	0.784
Crystal size	0.2x0.15x0.13	0.14x0.13x.0.09	0.20x0.19x0.09
Meas. Refl.	35126	25007	23936
Indep. Refl.	15512	6766	6784
Obsvd. [$I > 2\sigma(I)$]	11549	5338	6519
R_{int}	0.0407	0.0460	0.0351
R [all data]	0.0722	0.0405	0.0282
wR(F^2)	0.2154	0.1017	0.0722
S	1.029	1.040	1.031
$\Delta\rho_{max}$	3.022	0.761	0.353
$\Delta\rho_{min}$	-2.034	-0.351	-0.426
CCDC	1996487	1996486	1996485

*The DCM molecules were partly heavily disordered wherefore we applied the SQUEEZE algorithm. [1]

Table S2: Selected bond lengths and angles

	3a (5 CH_2Cl_2)	**4a (H_2O)**	**4b (CH_2Cl_2)**
Ni1-N10	-	1.854(2)	1.861(2)
Ni1-C1	-	1.947(2)	1.943(2)
Ni1-C2	-	1.945(2)	1.931(2)
Ni1-O1	-	1.880(2)	1.878(1)
N10-C11	1.38(1)	1.391(3)	-
N10-C13	-	-	1.376(2)
C11-C16	1.38(1)	1.394(3)	-
C13-C18	-	-	1.392(2)
C16-N1	1.45(1)	1.425(3)	-
C18-N1	-	-	1.424(2)
N1-N3	1.33(1)	1.348(2)	1.338(2)
N3-N5	1.30(1)	1.312(2)	1.318(2)
N5-C3	1.33(2)	1.351(3)	1.360(2)
C3-C1	1.36(1)	1.396(3)	1.409(3)
C1-N1	1.34(1)	1.391(3)	1.384(1)
N10-C17	1.37(1)	1.384(3)	-
N10-C19	-	-	1.379(2)
C17-C22	1.39(1)	1.396(2)	-
C19-C24	-	-	1.394(3)
C22-N2	1.43(1)	1.420(3)	-
C24-N2	-	-	1.425(2)
N2-N4	1.33(1)	1.354(2)	1.340(2)
N4-N6	1.32(1)	1.311(2)	1.325(2)
N6-C4	1.34(1)	1.344(3)	1.359(2)
C4-C2	1.36(1)	1.403(3)	1.394(3)
C2-N2	1.37(1)	1.391(3)	1.382(2)
C1-Ni1-C2	-	176.30(9)	173.39(7)
N10-Ni1-O1	-	175.44(7)	176.11(7)

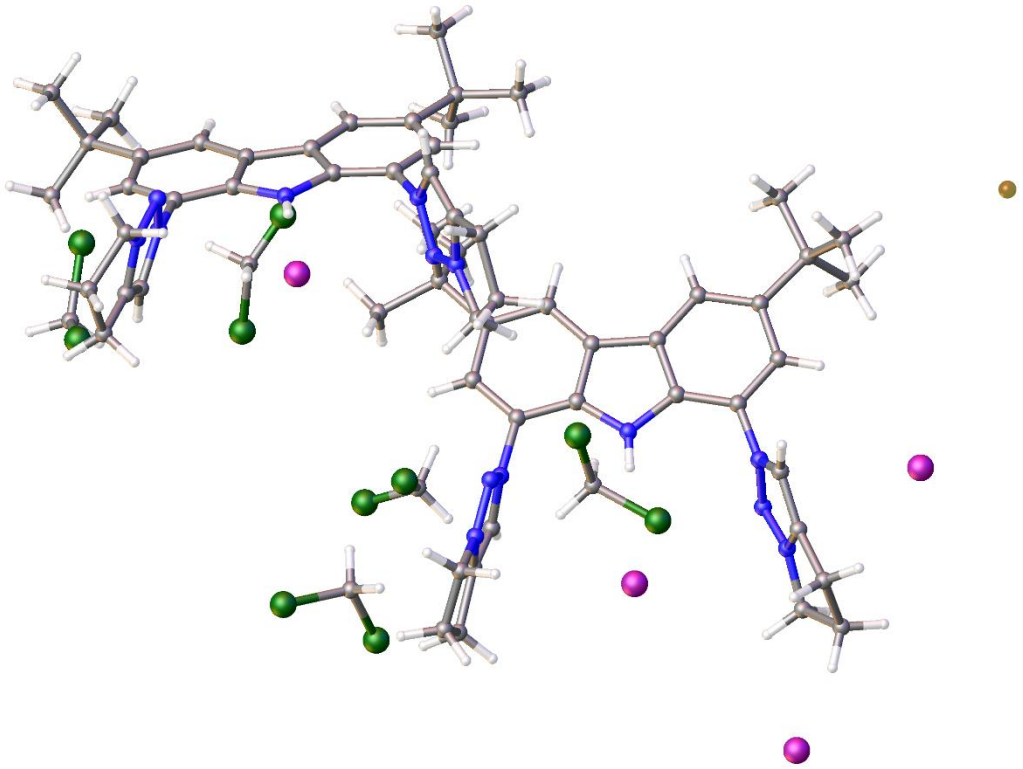


Figure S 58: *Solid state structure of **3a** including solvent molecules and counter ions before the SQUEEZE algorithm was applied.*

Due to slight unresolvable disorders, three atoms (in a DCM, a 5-membered ring and a ^{t}Bu group) has to be restrained using ISOR 0.001 instructions.

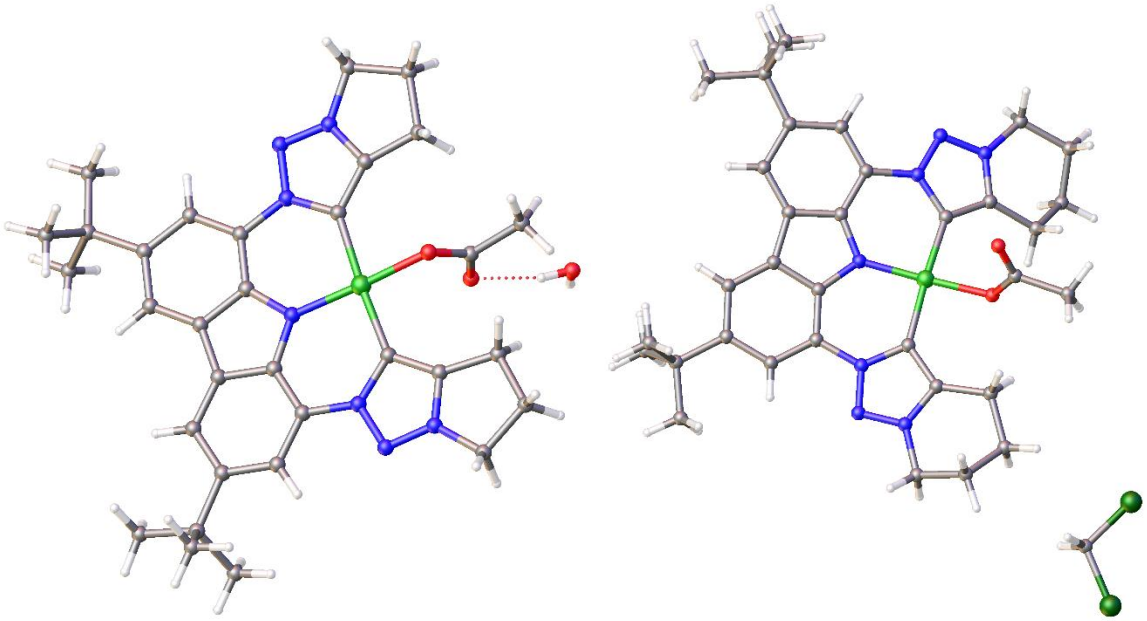


Figure S 59: *Solid state structure of **4a** (left) and **4b** (right) including solvent molecules, hydrogen atoms and counter ions. Hydrogen bonding is indicated by dotted red lines.*

4. Literature

1 A. L. Spek, *Acta crystallographica. Section C, Structural chemistry*, 2015, **71**, 9–18.

Author Contributions

The project was designed by SH. Ligand and metal complex synthesis was carried out by FAW, ND and SH. Catalytic experiments were carried out by BS. Xray structures were solved by RS, RHI, HO and SH. The manuscript was written by SH, JP and DK and proof-read by all authors.