ELECTRONIC SUPPLEMENTARY INFORMATION

Manuscript ID: OB-ART-04-2016-000884

TITLE: The kinetics and mechanism of the organo-iridium catalysed racemisation of amines

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1. Rate data for racemisation
2. Synthesis of catalyst

Figure1. Change in enantiomeric excess % ee during the racemisation of deuterated and non -deuterated (*R*) and (*S*)- 6,7-dimethoxy-1-methyl-1,2,3,4 tetrahydro*iso*quinoline using 0.5 mol% [IrCp*I2]2 at 40°C in dichloromethane (DCM)

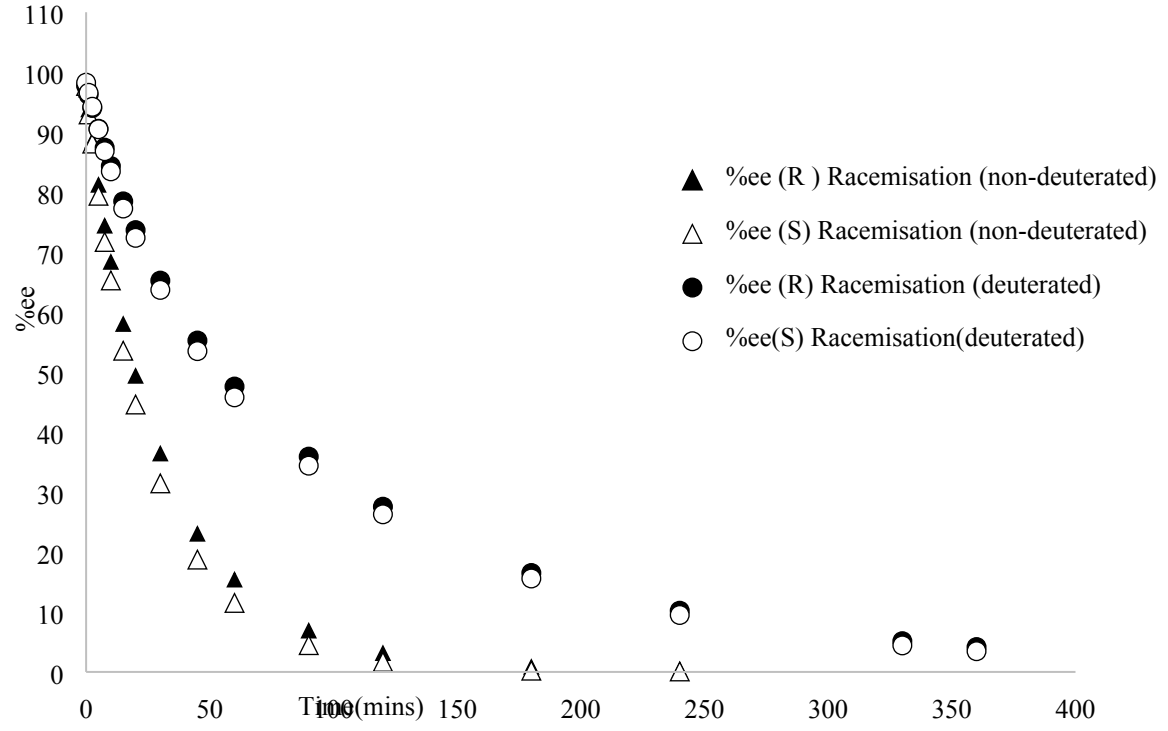


Figure 2. Changes in the concentration of *(S)*-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydro*iso*quinoline during its racemisation using 0.5 mol% [IrCp*I2]2 to give the corresponding *(R)* enantiomer at 40°C in DCM

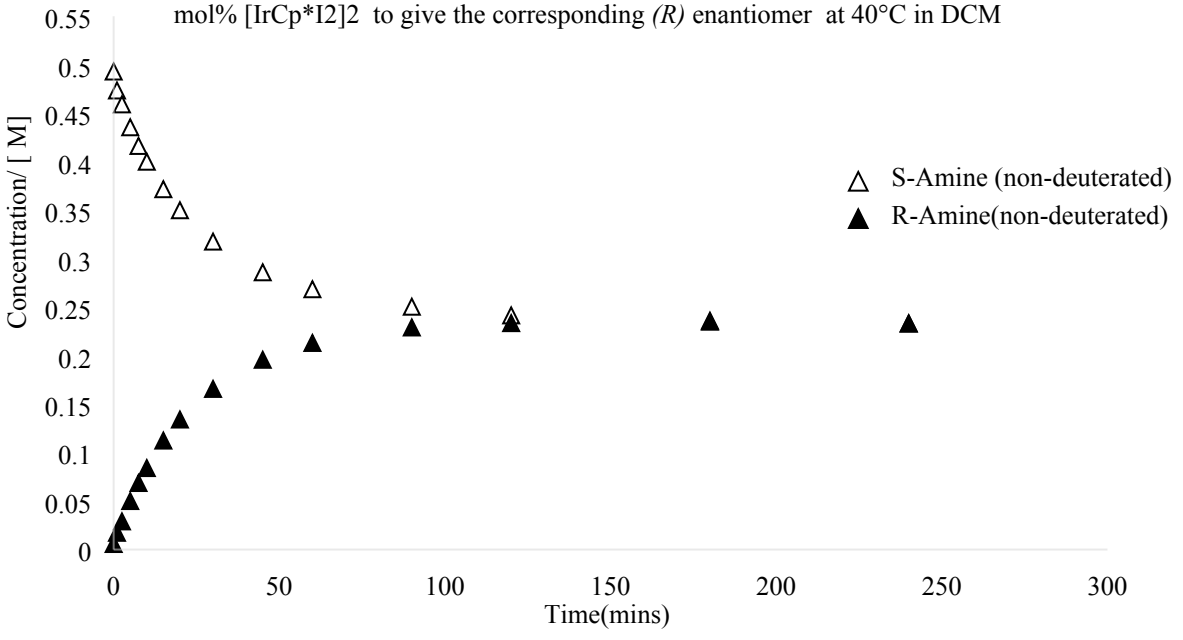


Figure 3 Changes in the concentration of *(R)*- 6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydro*iso*quinoline during its racemisation using 0.5 mol% [IrCp*I2]2 to give the corresponding *(S)* enantiomer at 40°C in DCM.

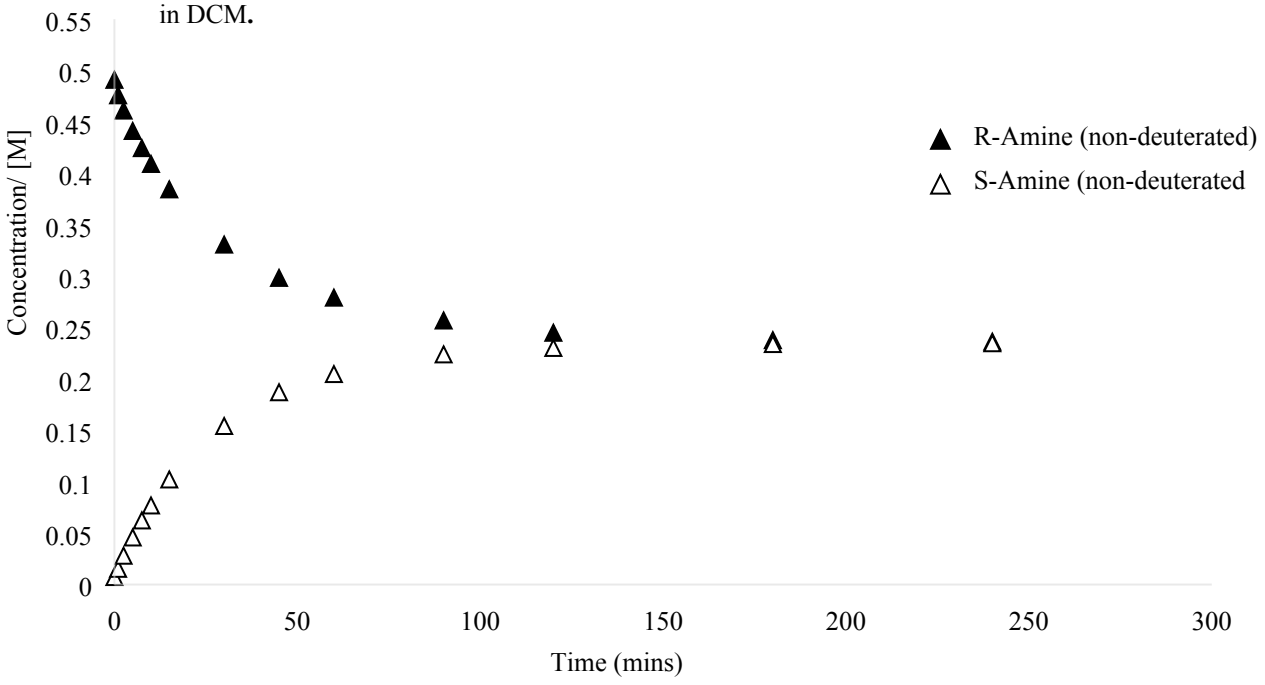


Figure 4 Changes in the concentrations of **deuterated** *(S)*- 6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydro*iso*quinoline during its racemisation using 0.5 mol% [IrCp*I2]2 to give the corresponding *(R)* enantiomer at 40°C in DCM

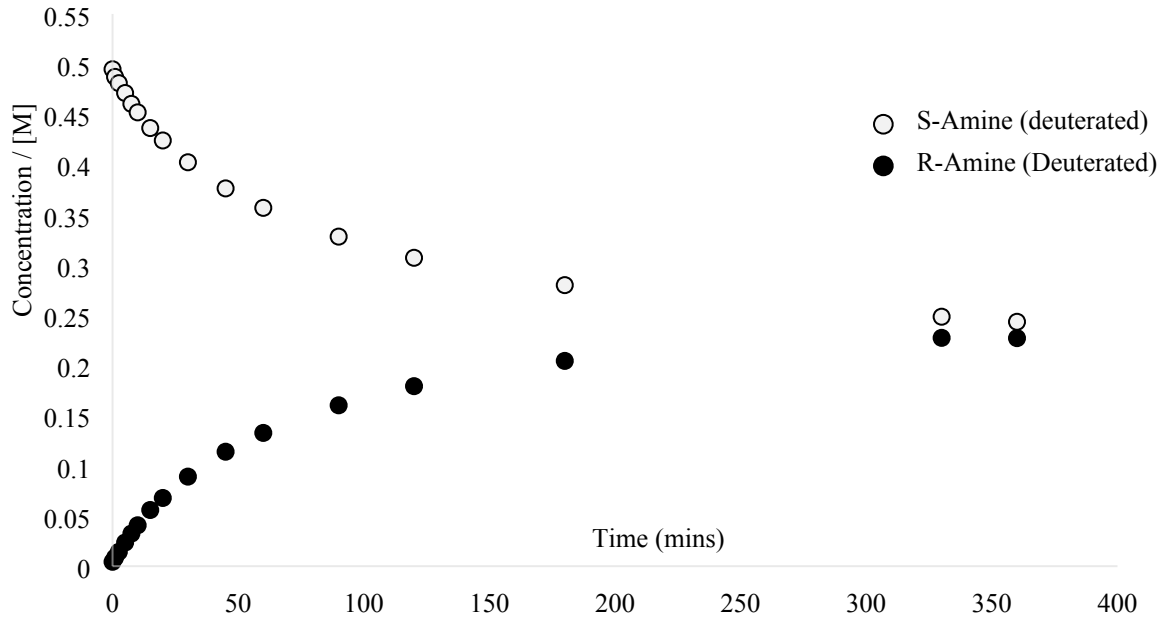
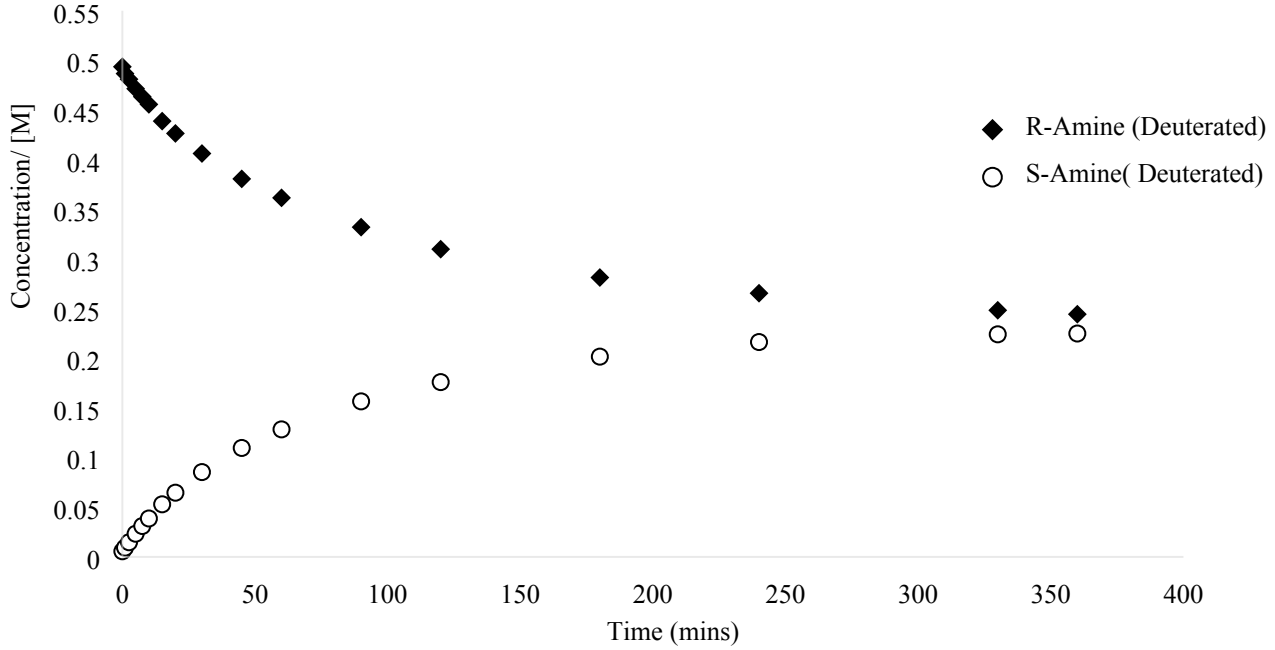
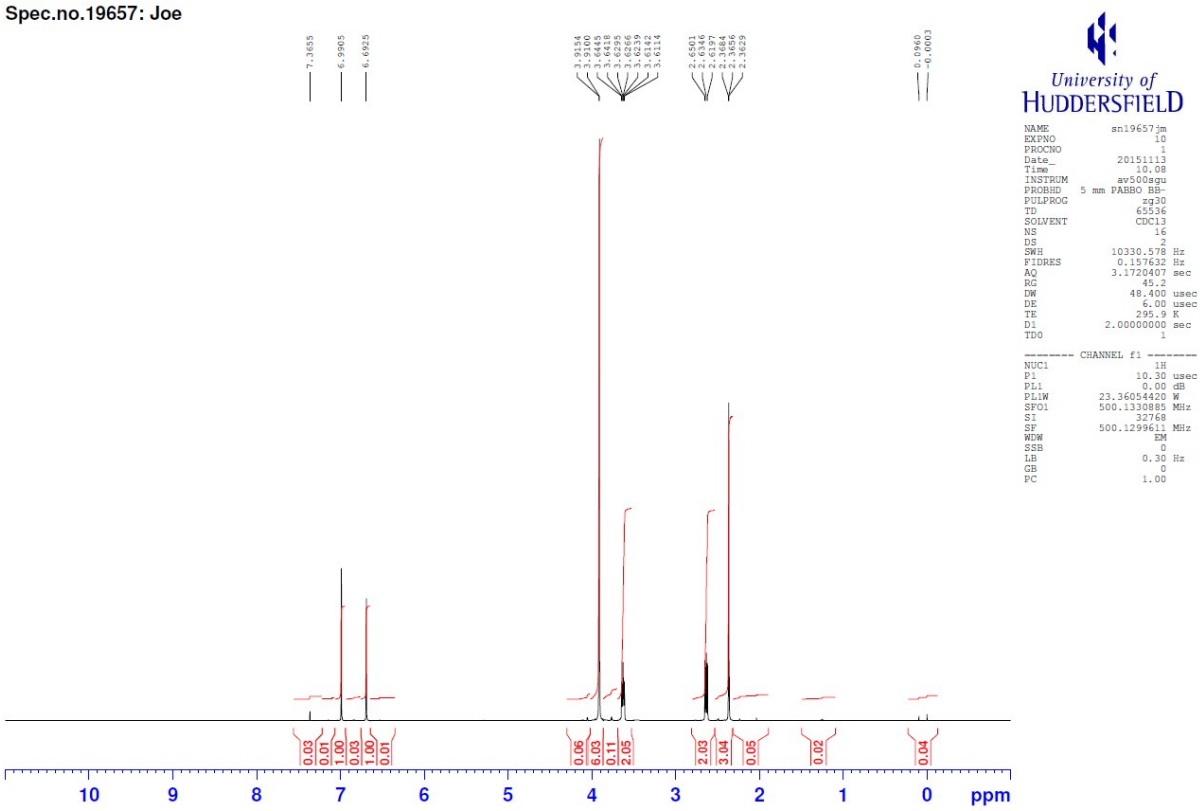


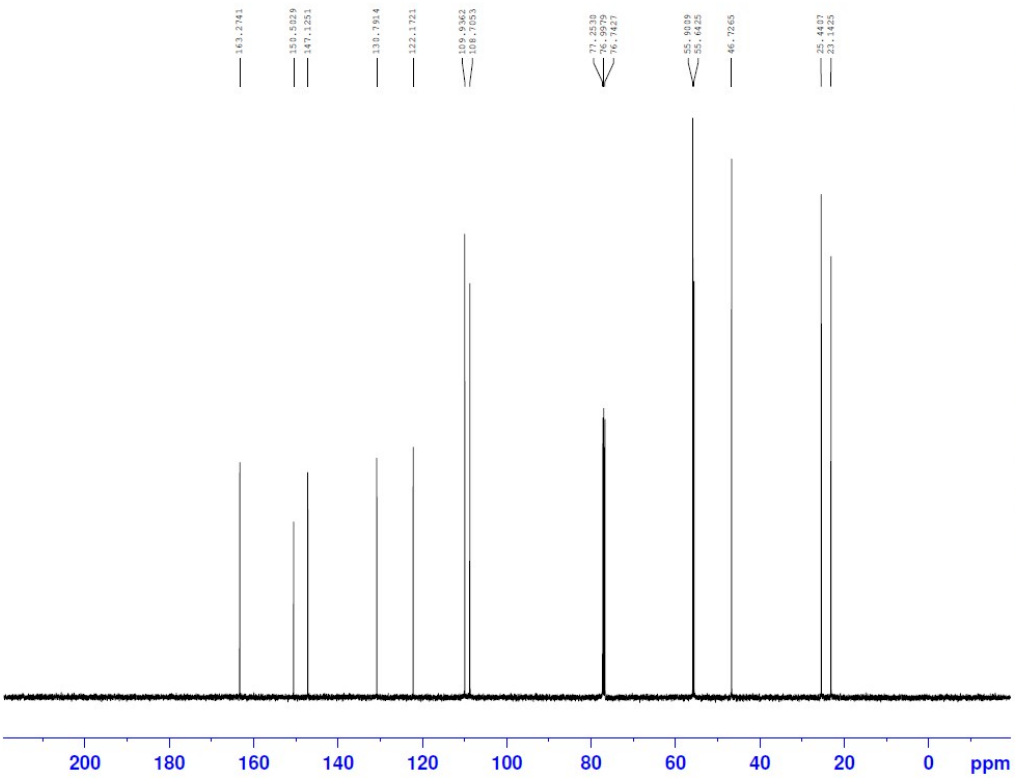
Figure 5 Changes in the concentration of **deuterated** *(R)*-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydro*iso*quinoline during its racemisation using 0.5 mol% [IrCp*I2]2 to give the corresponding *(S)* enantiomer at 40°C in DCM.



^{1}HNMR of 6,7-Dimethoxy-1-methyl-3,4 dihydroisoquinoline



13C H–decoupled



University of HUDDERSFIELD

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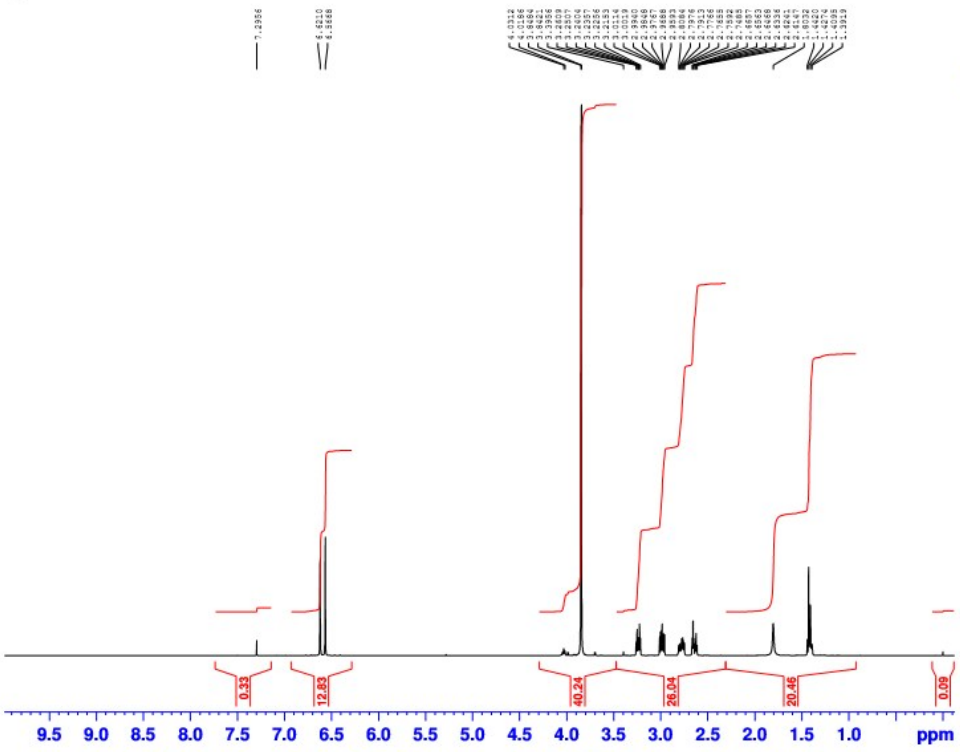
(S) 6, 7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (deuterated)

Spec.no.20077: Joe



University of HUDDERSFIELD

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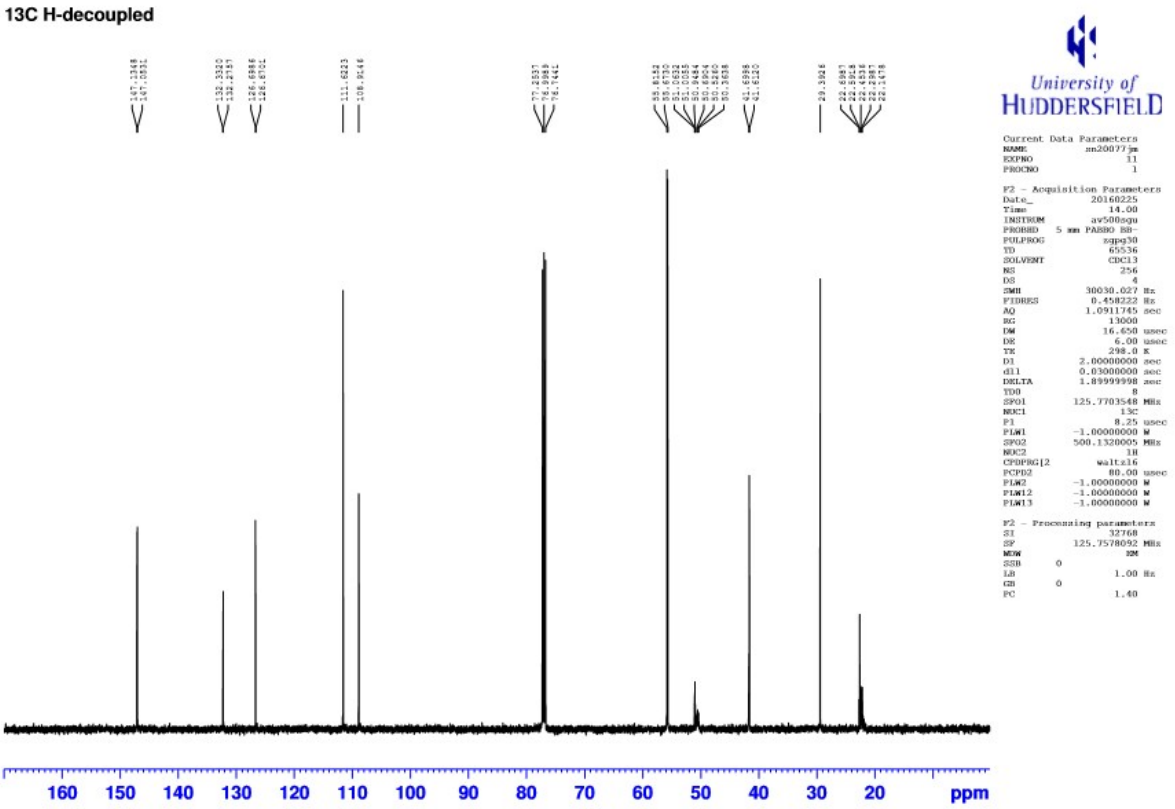
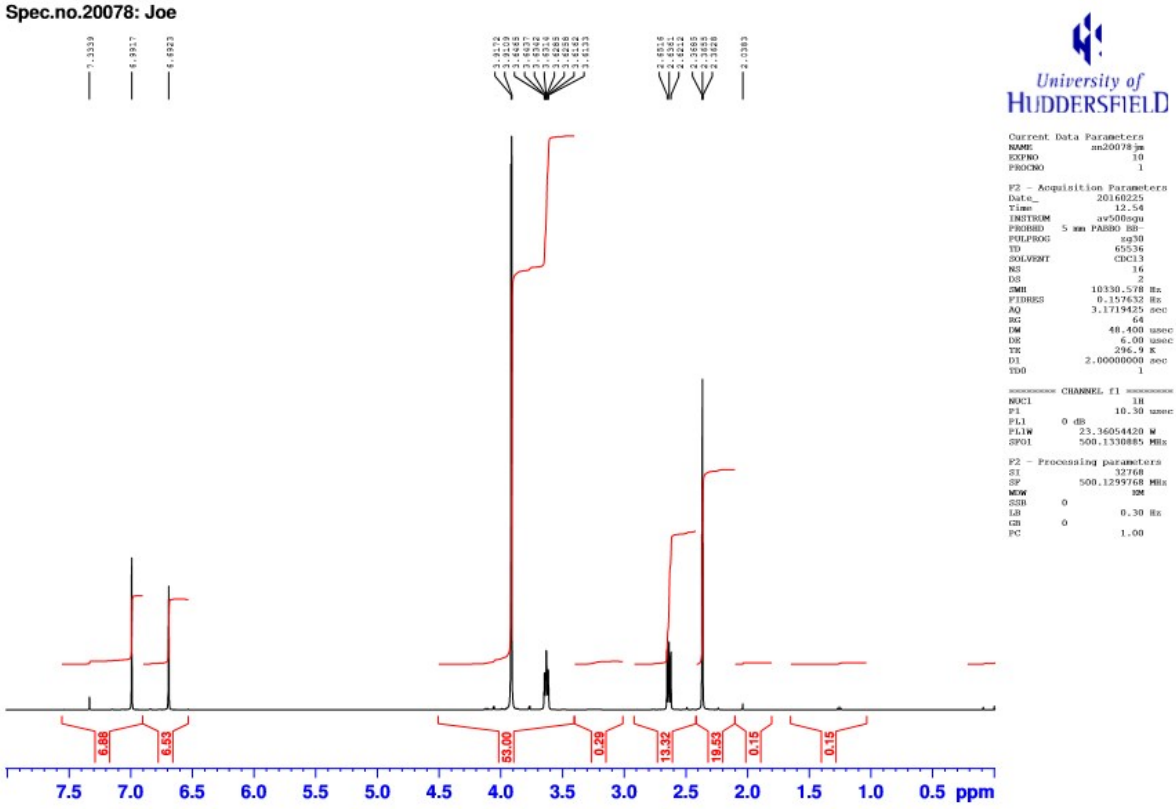


(R)-6, 7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (deuterated)



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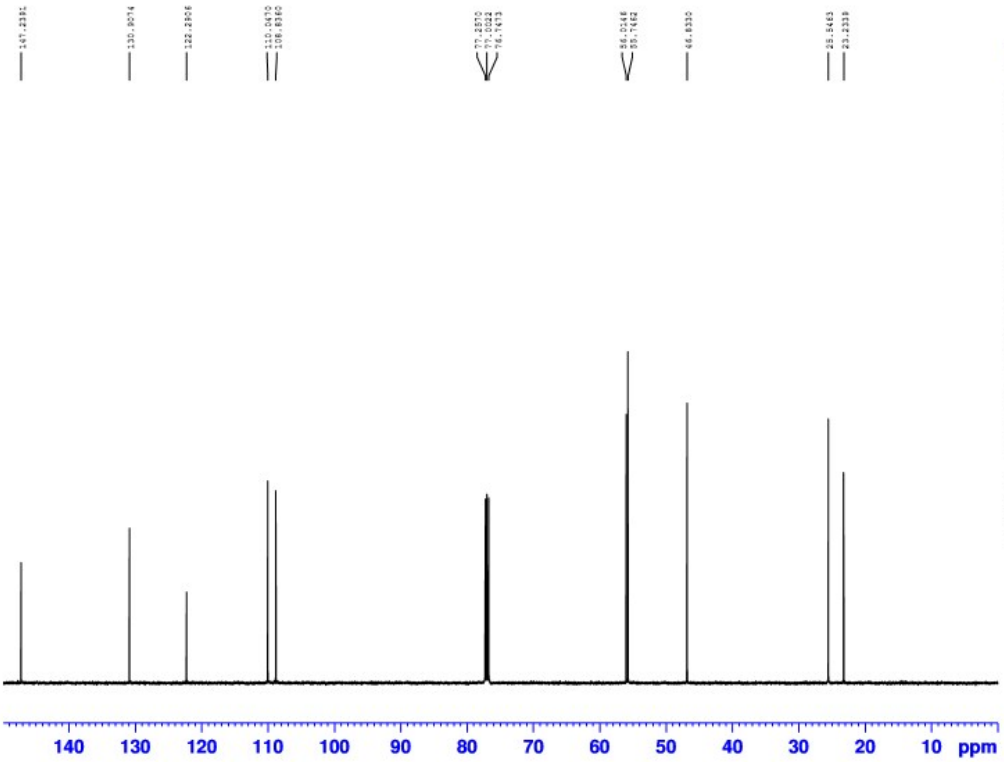

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TE                    298.0 K
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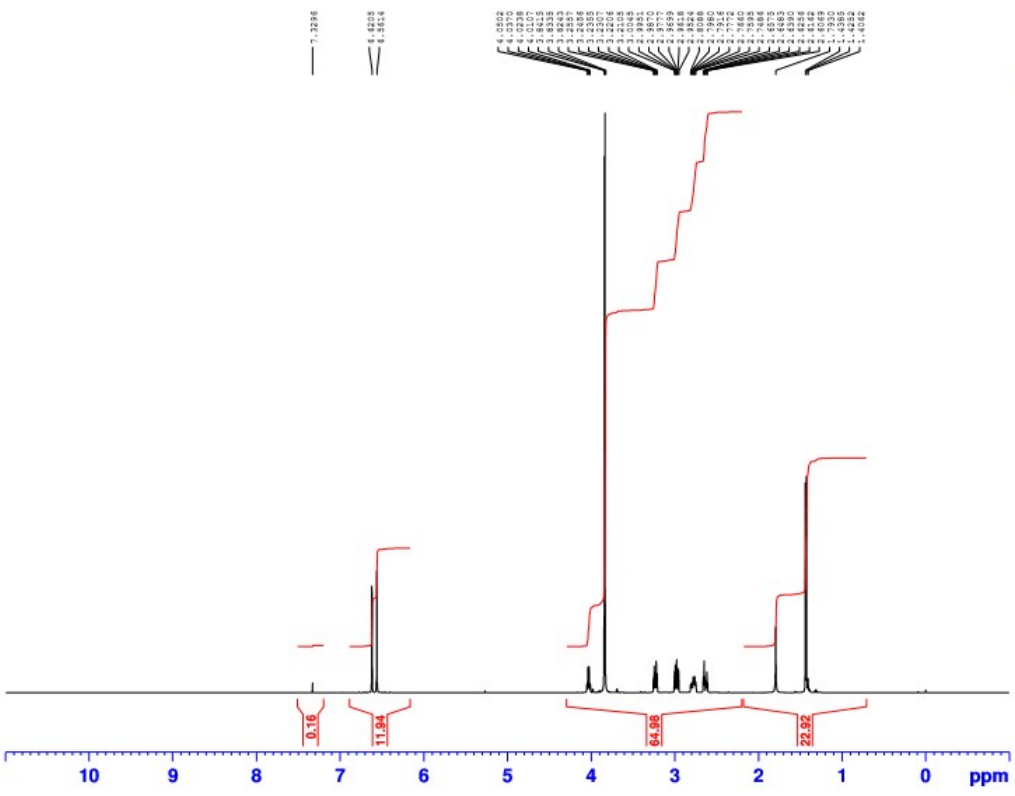
(R)-6, 7-Dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (non-deuterated)

Spec.no.20075: Joe



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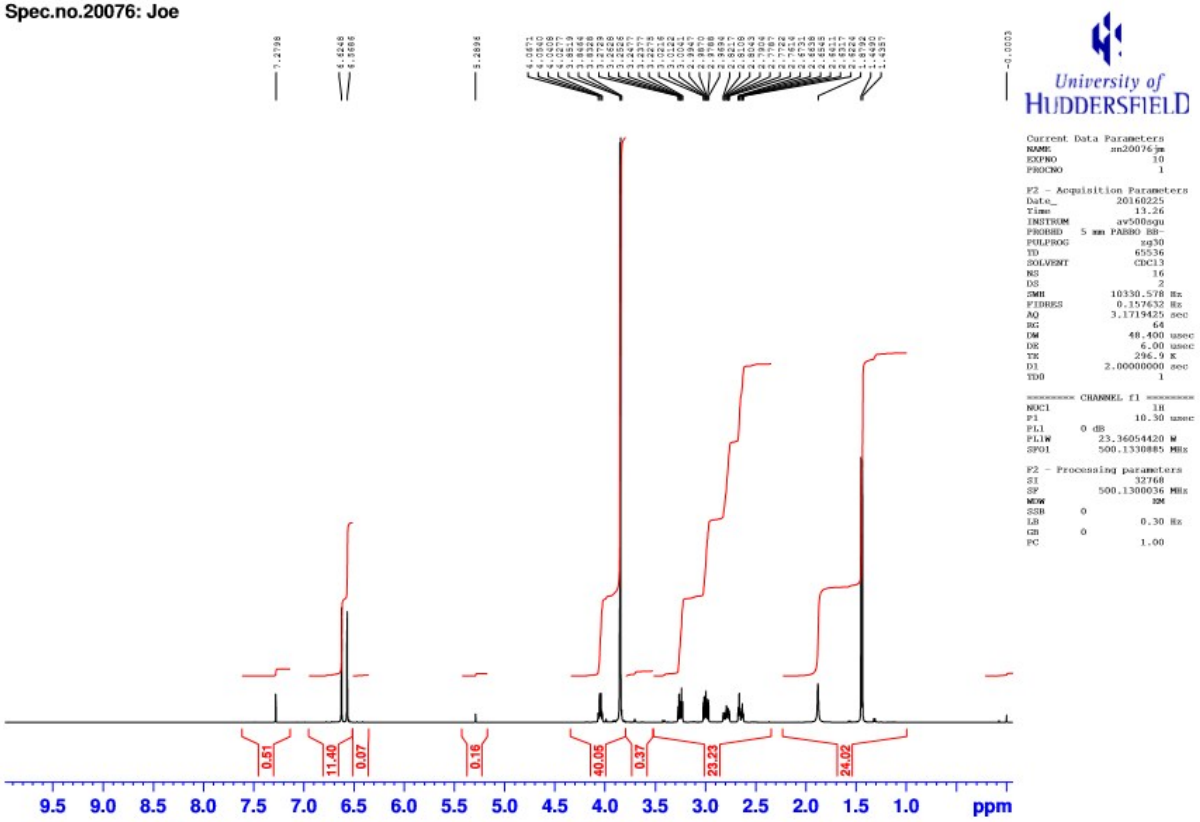
(S)-6, 7-Dimethoxy-1-methyl-1, 2, 3, 4-tetrahydroisoquinoline (non-deuterated)

Spec.no.20076: Joe



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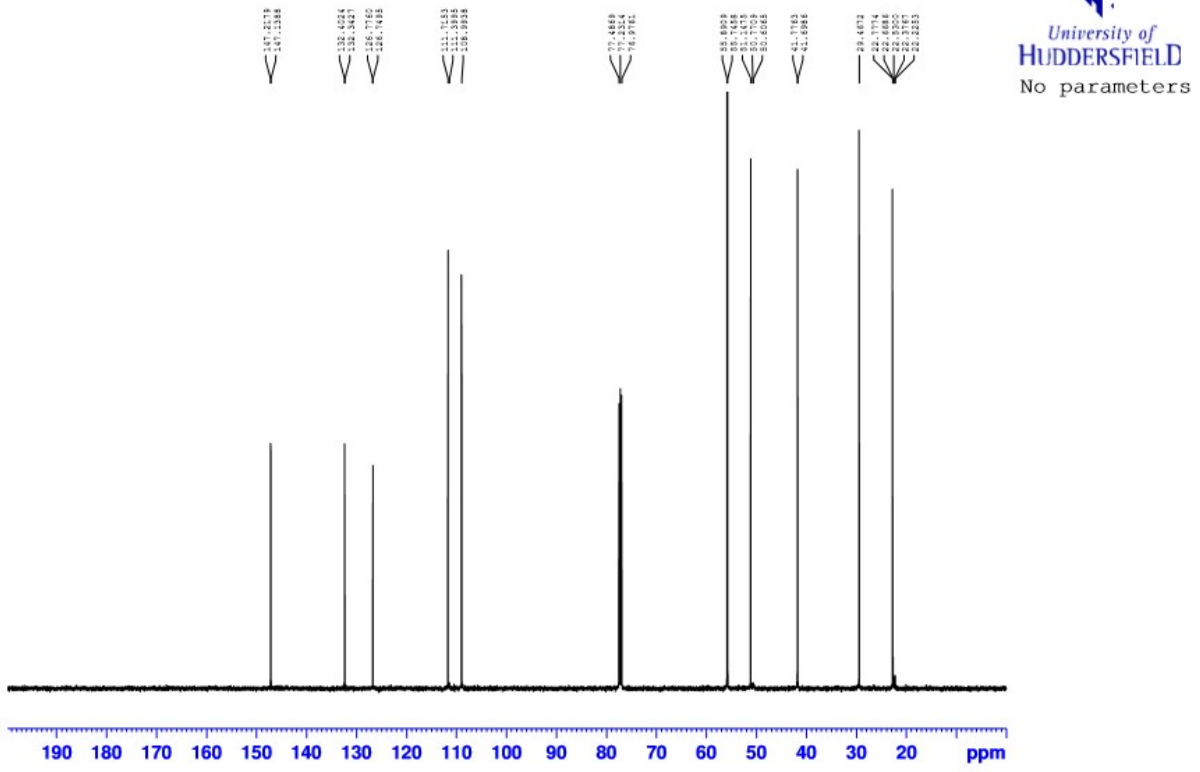
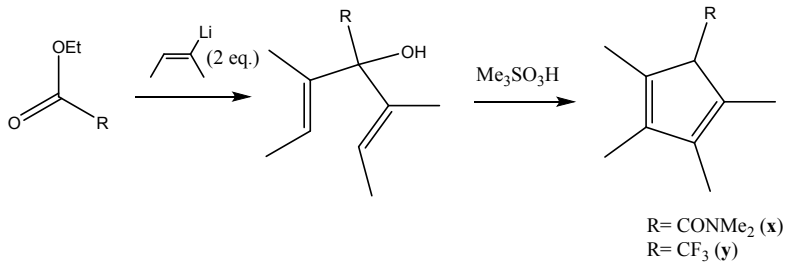
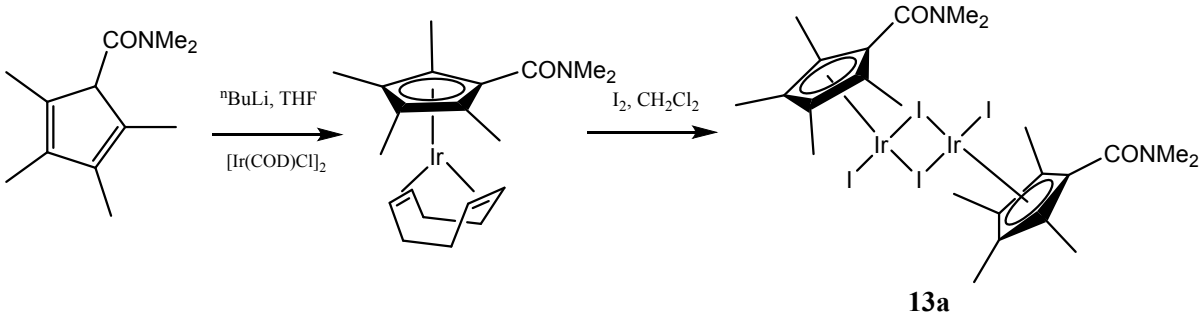


The substituted tetramethylcyclopentadienes were synthesised from known starting materials in two steps in good yield, **(Scheme 1)**.



Scheme 1 Synthesis of substituted tetramethylcyclopentadienes **x** and **y**

Reaction conditions: Preparation of iridium Cp* chloride dimers are often achieved by refluxing pentamethylcyclopentadiene with iridium trichloride (hydrate) in alcoholic solvent. However, all attempts to prepare the iridium complex of *N,N*-2,3,4,5-hexamethylcyclopenta-2-,4-diene carboxamide **(x)**, or 1-trifluoromethyl-2,3,4,5-tetramethylcyclopentadiene **(y)** by this route were unsuccessful. An alternative procedure for the preparation of iridium Cp' halide complexes was performed by way of the cyclooctadiene complexes. The cyclooctadienyl complex of **(x)** was prepared by the reaction of iridium cyclooctadiene chloride with the corresponding cyclopentadienyl anion, which was in turn prepared by the treatment of the substituted cyclopentadiene **(x)** with ^{n}butyl lithium in THF at -78^{0}C. The addition of iodine to a solution of the resultant cod complex in dichloromethane at room temperature, followed by heating to 45^{0}C for eight hours afforded the required iridium complex dimer (**13a**).



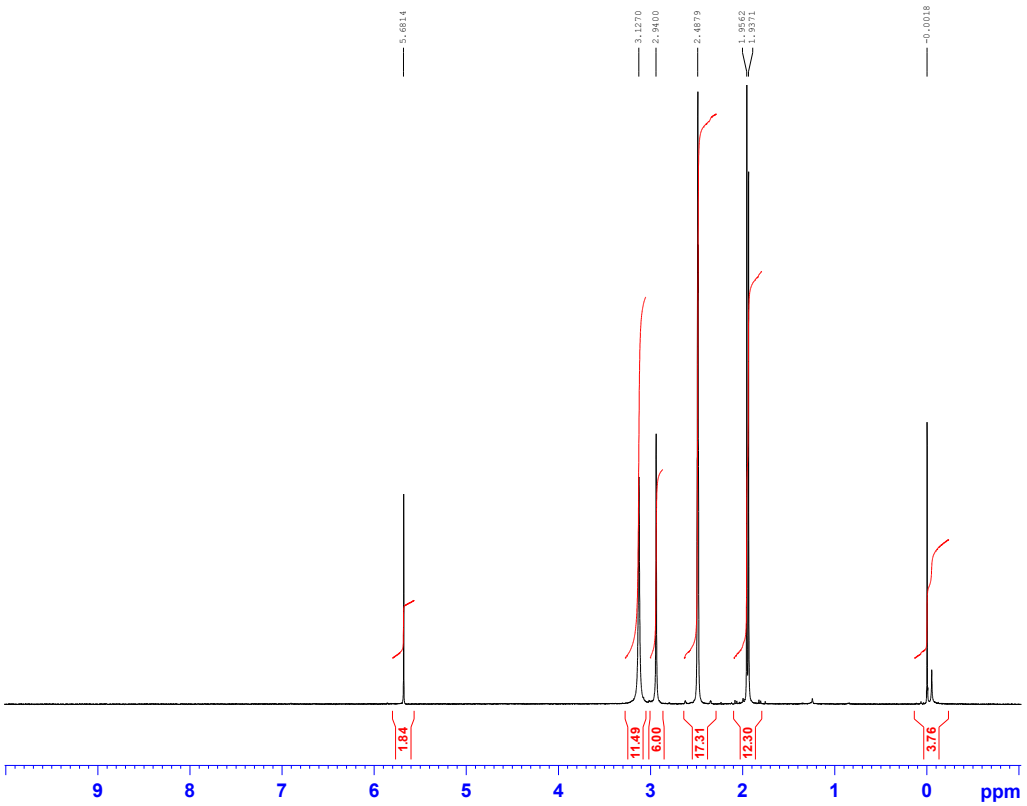
13a

<u>Preparation of di-μ-iodo-(η^{5}-*N,N,*-2,3,4,5-hexamethylcyclopenta-2,4-dienyl carboxamide)iridium(III) iodide dimer (13a)</u>

To a solution of (1,5-cyclooctadiene)(η^{5}-*N,N,*-2,3,4,5-hexamethylcyclopenta-2,4-dienyl carboxamide)iridium (2.00g, 4.05mmol) in CH_2Cl_2 (100mL), at room temperature under argon, was added solution of iodine (2.06g, 8.12mmol, 2.0eq.) in CH_2Cl_2 (30mL) in a drop-wise fashion. The colour of the reaction mixture changed from orange to deep red/purple during the addition. The reaction mixture was stirred at room temperature for one hour and then heated to 45^{0}C for 8 hours. After cooling overnight, the solvent was removed *in vacuo* to leave a deep red solid, which was triturated with diethyl ether and collected by filtration (2.31g, 89%). IR (solid) 1647, 1443, 1398, 1373 cm^{-1}; ^{1}H NMR (500MHz, 343K, DMSO) δppm 1.94 (6H, *s*, 2x CH_3), 1.96 (6H, *s*, 2x CH_3), 2.94 (6H, *s*, $N(CH_3)_2$); ^{13}C NMR (500MHz, DMSO) δppm 10.22 (2x CH_3), 10.83 (2x CH_3), 34.95 ($N(CH_3)_2$), 55.38 (Cp'-C), 93.35 (Cp'-C), 99.25 (Cp'-C), 161.66 (C=O); HRMS Calcd for $C_{24}H_{36}I_3Ir_2N_2O_2$ $(M-I)^{+}$ 1146.9123, found 1146.9097.

^{1}H and ^{13}C NMR of di-μ-iodo-(η^{5}-*N,N,*-2,3,4,5-hexamethylcyclopenta-2,4-dienyl carboxamide)iridium(III) iodide dimer (13a)

GMSII/11/4: 343K



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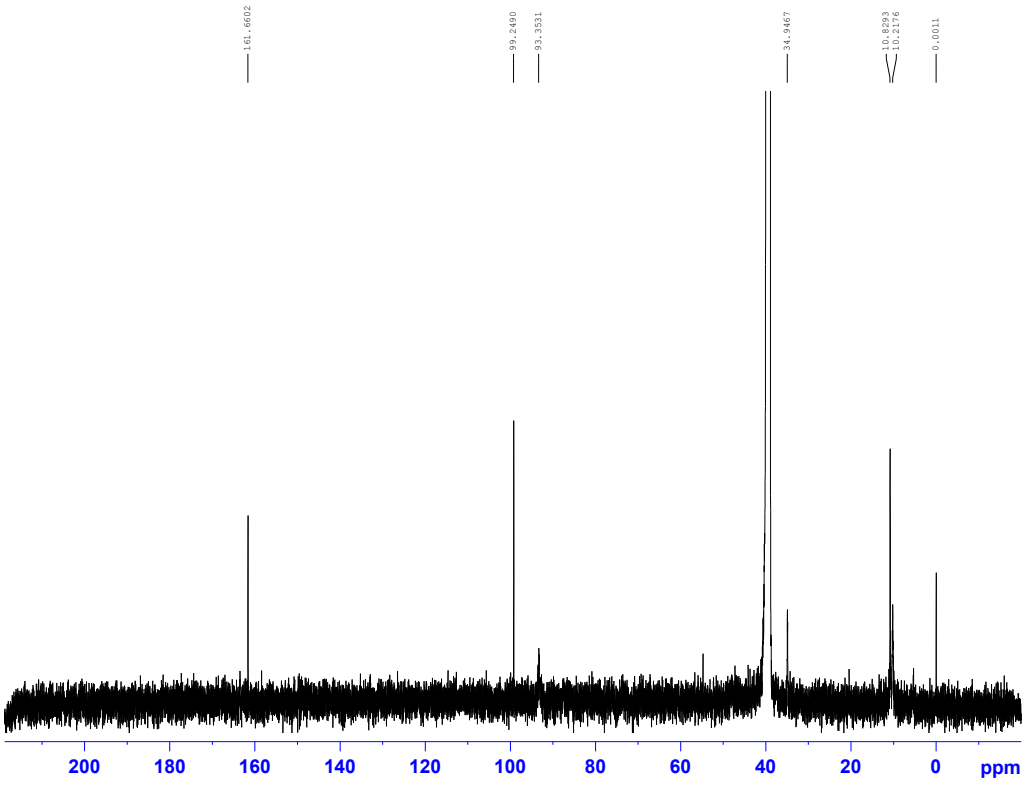
13C H-decoupled



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PLW1       -1.00000000 W
SFO2       500.1320005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
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PLW13      -1.00000000 W

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