Electronic Supplementary Information for

Catalytic intramolecular hydroamination of aminoallenes using titanium and tantalum complexes of sterically encumbered chiral sulfonamides

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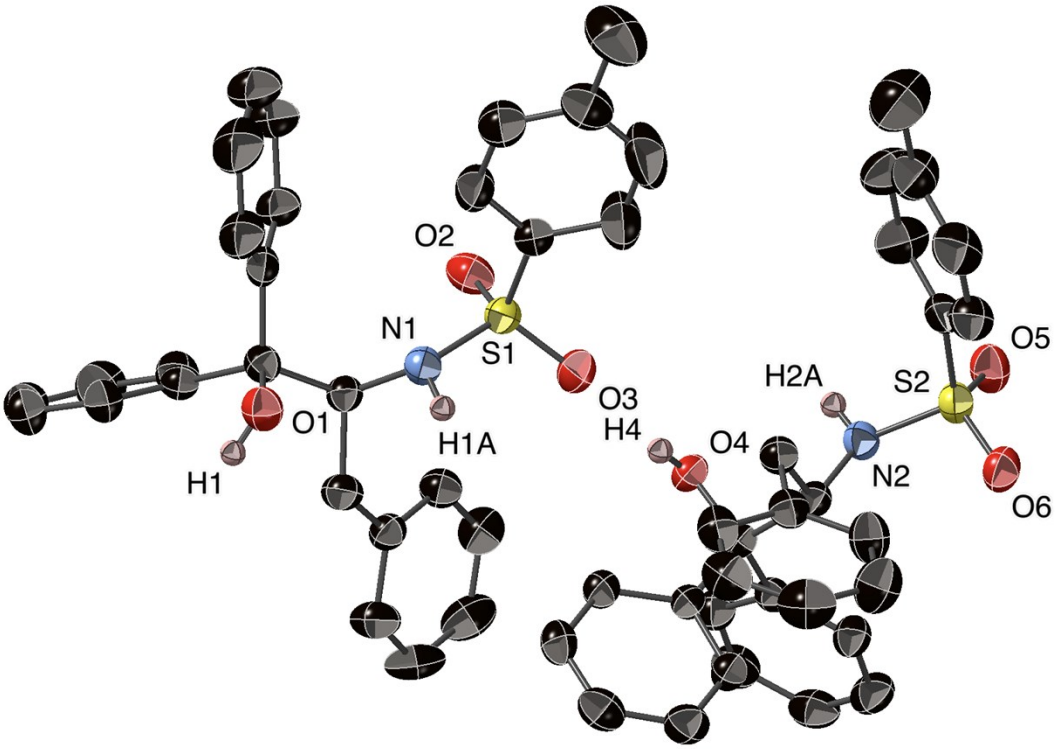


Figure S1 Thermal ellipsoid drawing of L-H_2**Ph1** (hydrogen atoms except H(1), H(1A), H(2A) and H(4) are omitted for clarity; ellipsoids shown at 50% probability).

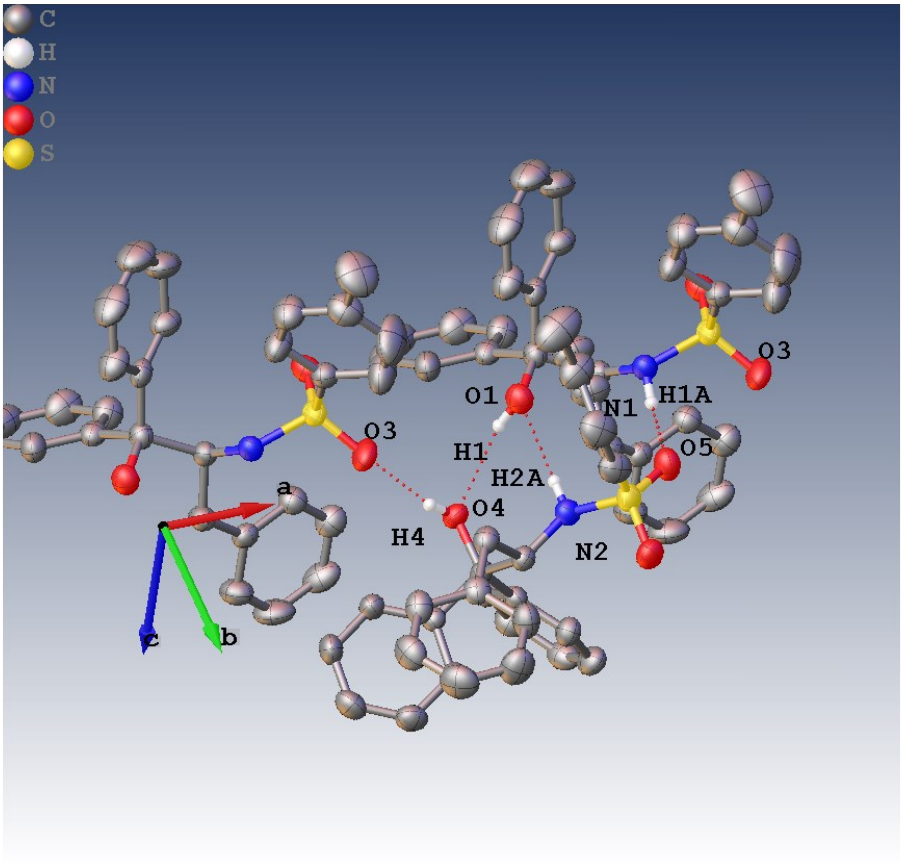


Figure S2 Thermal ellipsoid drawing of L-H_2**Ph1** (hydrogen atoms except H(1), H(1A), H(2A) and H(4) are omitted for clarity; ellipsoids shown at 50% probability).

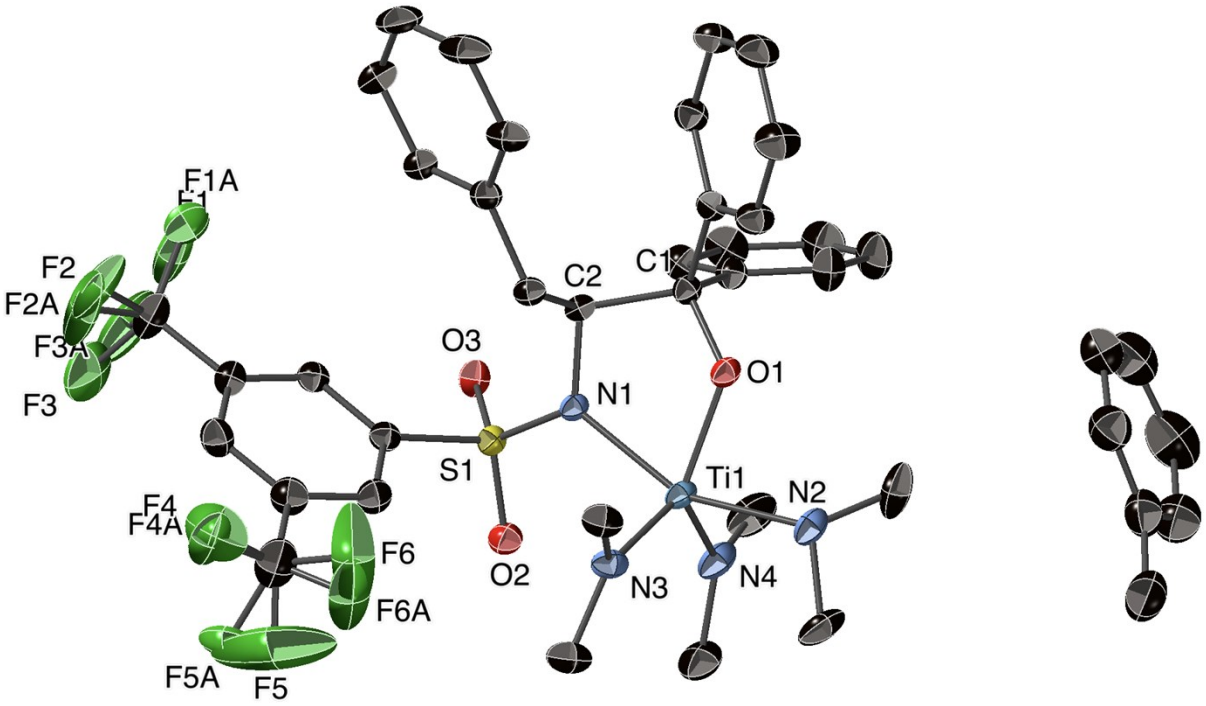


Figure S3 Thermal ellipsoid drawing of complex **TiPh3** showing one solvent molecule of toluene (hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability). F(1), F(2) and F(3) are modeled at 0.56 occupancy; F(1A), F(2A) and F(3A) are modeled at 0.44 occupancy; F(4), F(5) and F(6) are modeled at 0.52 occupancy; F(4A), F(5A) and F(6A) are modeled at 0.48 occupancy.

Table S1. Crystal data and structure refinement for L-H_2**Ph1**, **TiPh3**, **TaPh1**, **TaPh2** and **TaPh3**.

Compound	L-H_2**Ph1**	**TiPh3**	**TaPh1**	**TaPh2**	**TaPh3**
CCDC code	1970364	1970810	1970808	1970809	1970811
Formula	$C_{28}H_{27}NO_3S$	$C_{42}H_{48}F_6N_4O_3STi$	$C_{34}H_{43}N_4O_3STa$	$C_{34}H_{40}F_3N_4O_3STa$	$C_{35}H_{39}F_6N_4O_3STa$
Formula weight	457.56	850.8	768.73	822.71	890.71
Temperature, K	293(2)	100(2)	100(2)	100(2)	100(2)
Wavelength, Å	0.71073	1.54178	0.71073	0.71073	1.54178
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a, Å	9.1955(3)	8.1293(8)	13.3873(10)	10.0894(10)	8.8756(13)
b, Å	15.8730(5)	21.067(2)	15.0633(13)	11.9917(13)	11.4888(11)
c, Å	16.3458(5)	24.630(2)	16.5240(13)	28.308(3)	34.989(5)
α, °	90	90	90	90	90
β, °	92.775(3)	90	90	90	90
γ, °	90	90	90	90	90
Volume, $Å^3$	2383.03(14)	4218.1(7)	3332.2(5)	3424.9(6)	3567.8(8)
Z	4	4	4	4	4
Density (calcd) Mg/m^3	1.275	1.340	1.532	1.596	1.658
μ, mm^{-1}	0.166	2.776	3.400	3.326	6.865
θ range for data collection, °	1.8710 to 24.1390°.	2.760 to 74.427°.	1.829 to 36.392°.	1.439 to 36.399°.	2.526 to 74.559°.
Reflections measured	72070	52021	72114	73514	41686
Independent observed reflns. [I>2σ]	14398	8503	15757	16612	7123
Data / restraints / parameters	14398 / 1 / 603	8503 / 272 / 580	15757 / 267 / 450	16612 / 66 / 449	7123 / 0 / 457
Rint	0.0548	0.0479	0.0400	0.0496	0.0459
Final R indices [I>2σ(I)]	R1 = 0.0562, wR2 = 0.0993	R1 = 0.0326, wR2 = 0.0828	R1 = 0.0180, wR2 = 0.0375	R1 = 0.0236, wR2 = 0.0419	R1 = 0.0205, wR2 = 0.0506
R indices (all data)	R1 = 0.0947, wR2 = 0.1117	R1 = 0.0349, wR2 = 0.0847	R1 = 0.0201, wR2 = 0.0380	R1 = 0.0290, wR2 = 0.0430	R1 = 0.0205, wR2 = 0.0506
Goodness-of-fit on F2	1.016	1.037	0.993	1.016	1.082
Flack parameter	-0.01(3)	0.056(3)	0.007(2)	0.012(2)	0.084(4)
Largest diff. peak and hole, e Å-3	0.30 and -0.28	0.487 and -0.219	0.533 and -1.202	0.928 and -1.624	0.494 and -1.376

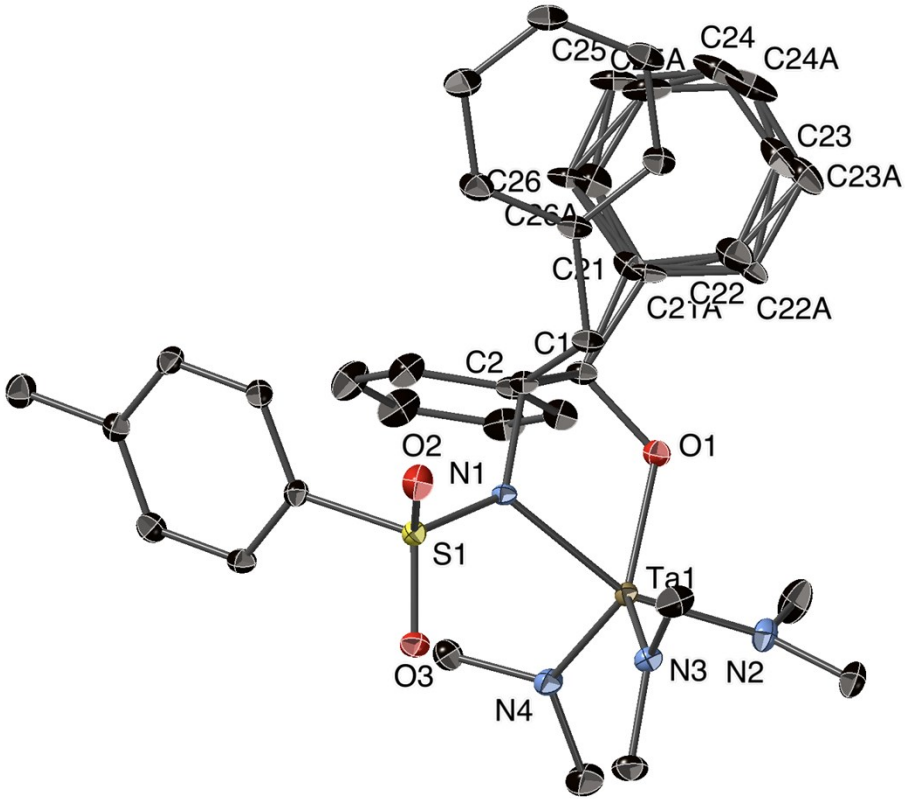


Figure S4 Thermal ellipsoid drawing of complex **TaPh1** (hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability). C(21)-C(26) are modeled at 0.58 occupancy; C(21A)-C(26A) are modeled at 0.42 occupancy. Selected bond distances (Å) and angles (°): Ta(1)-N(3) 1.9452(18), Ta(1)-N(4) 1.9558(17), Ta(1)-O(1) 1.9649(15), Ta(1)-N(2) 1.9859(17), Ta(1)-N(1) 2.1952(15), N(3)-Ta(1)-N(4)112.57(8), N(3)-Ta(1)-O(1) 130.78(7), N(4)-Ta(1)-O(1) 116.32(7), N(3)-Ta(1)-N(2) 93.03(8), N(4)-Ta(1)-N(2) 95.72(7), O(1)-Ta(1)-N(2) 87.69(7), N(3)-Ta(1)-N(1) 91.92(6), N(4)-Ta(1)-N(1) 101.48(6), O(1)-Ta(1)-N(1) 73.47(6), N(2)-Ta(1)-N(1) 158.68(7).

The geometry around the tantalum center in **TaPh1** is best described as a distorted trigonal bipyramid with $R_c(x)$ parameter of 9.39 for trigonal bipyramidal and 18.71 for square pyramidal.[1] The τ parameter is 0.47.[2] The TBP axis is between the ligand nitrogen N(1) and the NMe_2 nitrogen N(2) (Figure 3). One of the phenyl groups was disordered over two positions. Comparing to ligand structure in (Figure 1), the O-C-C-N dihedral angle reorients upon coordination to rotate the CPh_2 group by approximately 120° bringing the oxygen into a five-membered ring along with Ta(1), N(1), C(2), and C(1). The $ArSO_2$ substituent on the sulfonamide also rotates away to prevent steric interactions between the tolyl group and the $Ta(NMe_2)_3$ portion of the molecule.

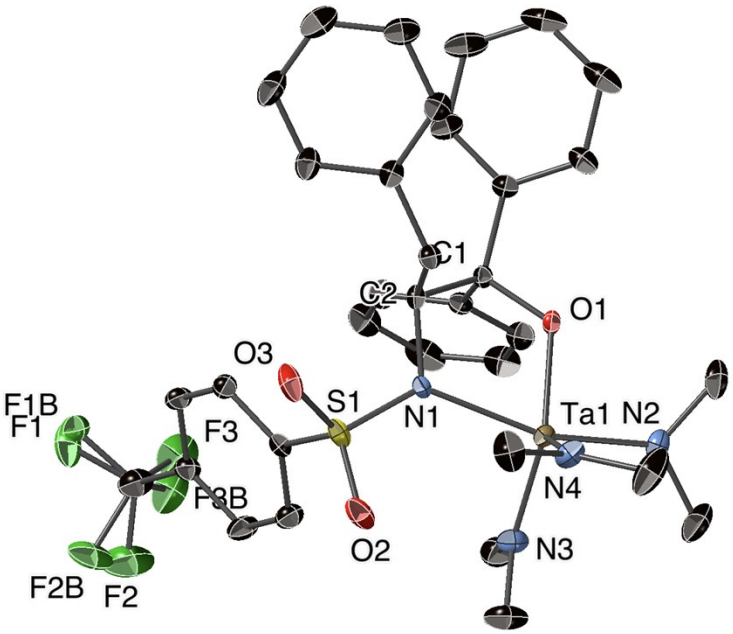


Figure S5 Thermal ellipsoid drawing of complex **TaPh2** (hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at 50% probability). F(1), F(2) and F(3) are modeled at 0.54 occupancy; F(1B), F(2B) and F(3B) are modeled at 0.46 occupancy. Selected bond distances (Å) and angles (°): Ta(1)-N(3) 1.948(2), Ta(1)-N(4) 1.960(2), Ta(1)-O(1) 1.9705(17), Ta(1)-N(2) 1.993(2), Ta(1)-N(1) 2.1720(19), N(3)-Ta(1)-N(4) 106.34(10), N(3)-Ta(1)-O(1) 137.55(8), N(4)-Ta(1)-O(1) 116.03(8), N(3)-Ta(1)-N(2) 93.35(10), N(4)-Ta(1)-N(2) 96.56(9), O(1)-Ta(1)-N(2) 84.67(8), N(3)-Ta(1)-N(1) 95.53(9), N(4)-Ta(1)-N(1) 102.11(9), O(1)-Ta(1)-N(1) 73.85(7), N(2)-Ta(1)-N(1) 156.12(8).

The geometry around the tantalum center in **TaPh2** is best described as a distorted trigonal bipyramid with $R_c(x)$ parameter of 11.35 for trigonal bipyramidal and 17.21 for square pyramidal.[1] The τ parameter is 0.31.[2] The TBP axis is between the ligand nitrogen N(1) and the NMe_2 nitrogen N(2). The CF_3 group was disordered over two positions.

Derivation of DOSY equations

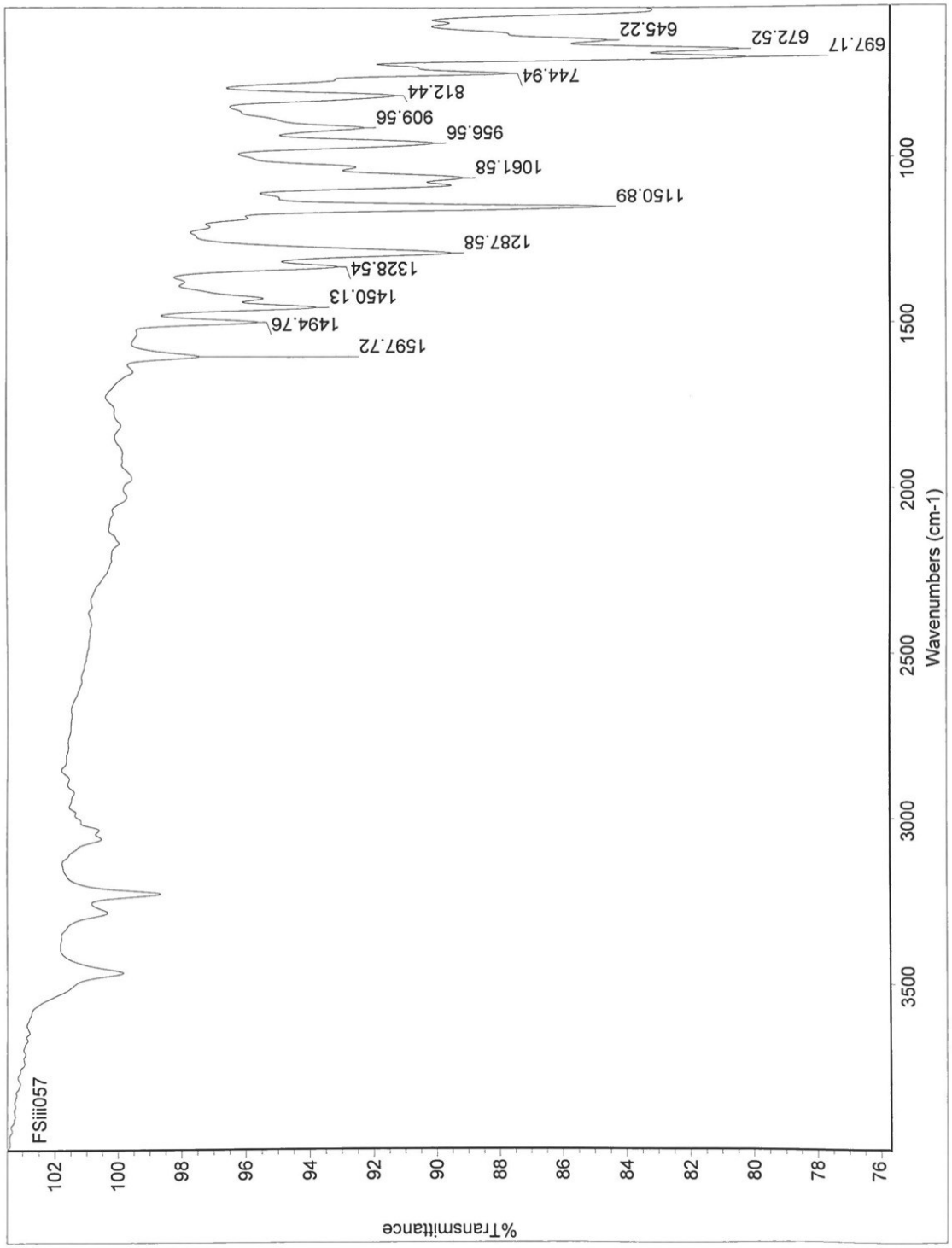
Solutions of all eight Ti and Ta complexes were prepared in C_6D_6 and their diffusion constants were determined as an average value calculated from fits to the signal intensity for two regions of the spectra: an aryl signal and an NMe_2 signal. Intensity was found to decay as a function of delay time according to the Stejskal-Tanner equation (eq. 1),[3-4] where g is the gyromagnetic ratio, g is gradient strength, d and Δ are delays and D is the diffusion constant. The resulting diffusion constants are reported units of m^2 sec^{-1} using the Bruker TopSpin 3.0 software package.

$$I = I_o e^{-(\gamma g \delta)^2 D(\Delta - \frac{\delta}{3})} \qquad \text{Eq 1.}$$

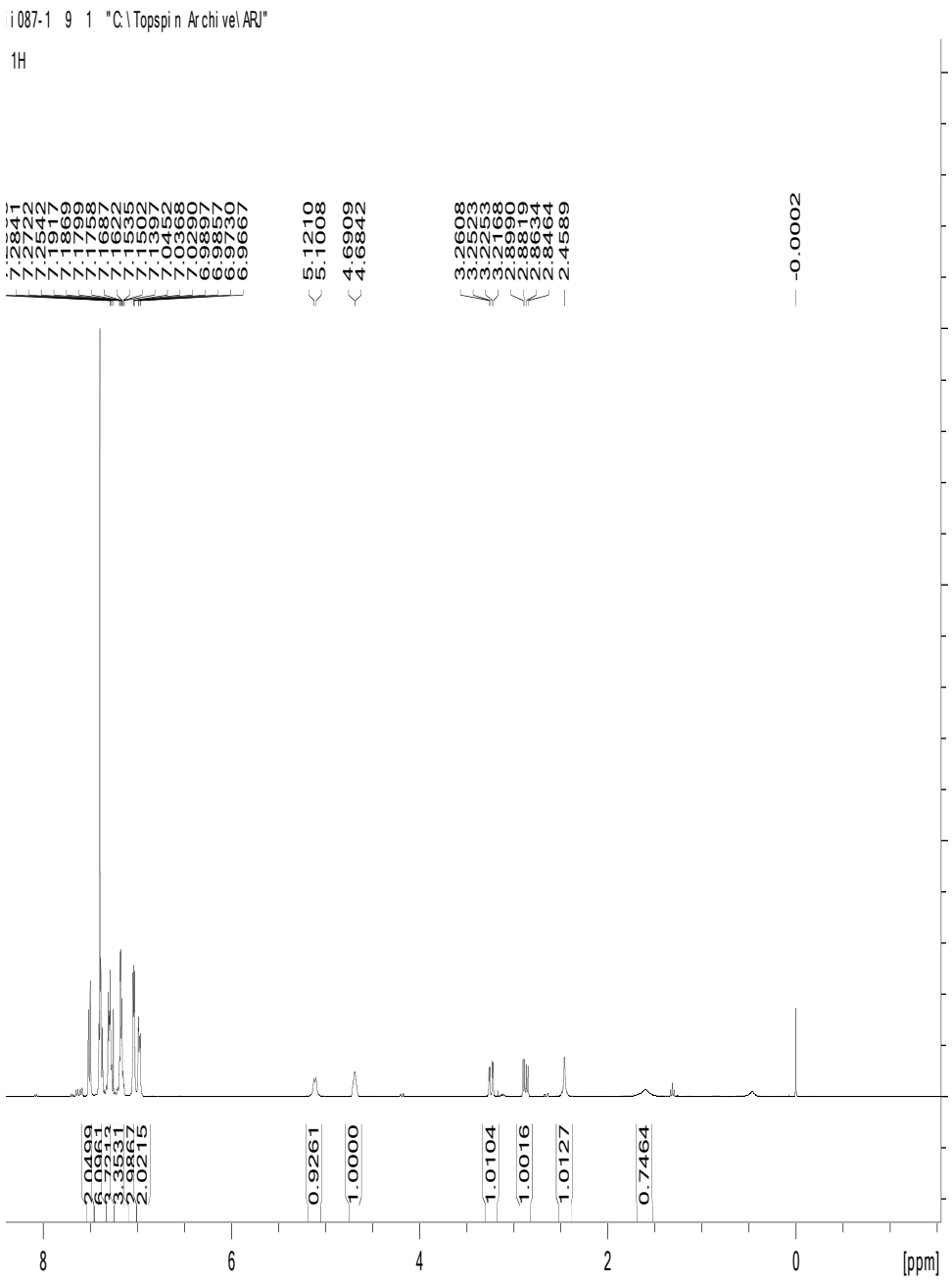
Hydrodynamic radii (r_h) were calculated from the diffusion constants using the Stokes-Einstein equation (equation 2), where k_B is Boltzmann's constant, and h is the solvent viscosity. These r_h values are reported in Table 2. This derivation assumes spherical particles that are larger than the solvent molecules. Systematic errors in the calculated radii can be reasonably assumed to be similar for this set of 8 complexes given their similar solid-state structures and chemical constitution.

$$r_h = \frac{k_B T}{6\pi\eta D} \qquad \text{Eq 2.}$$

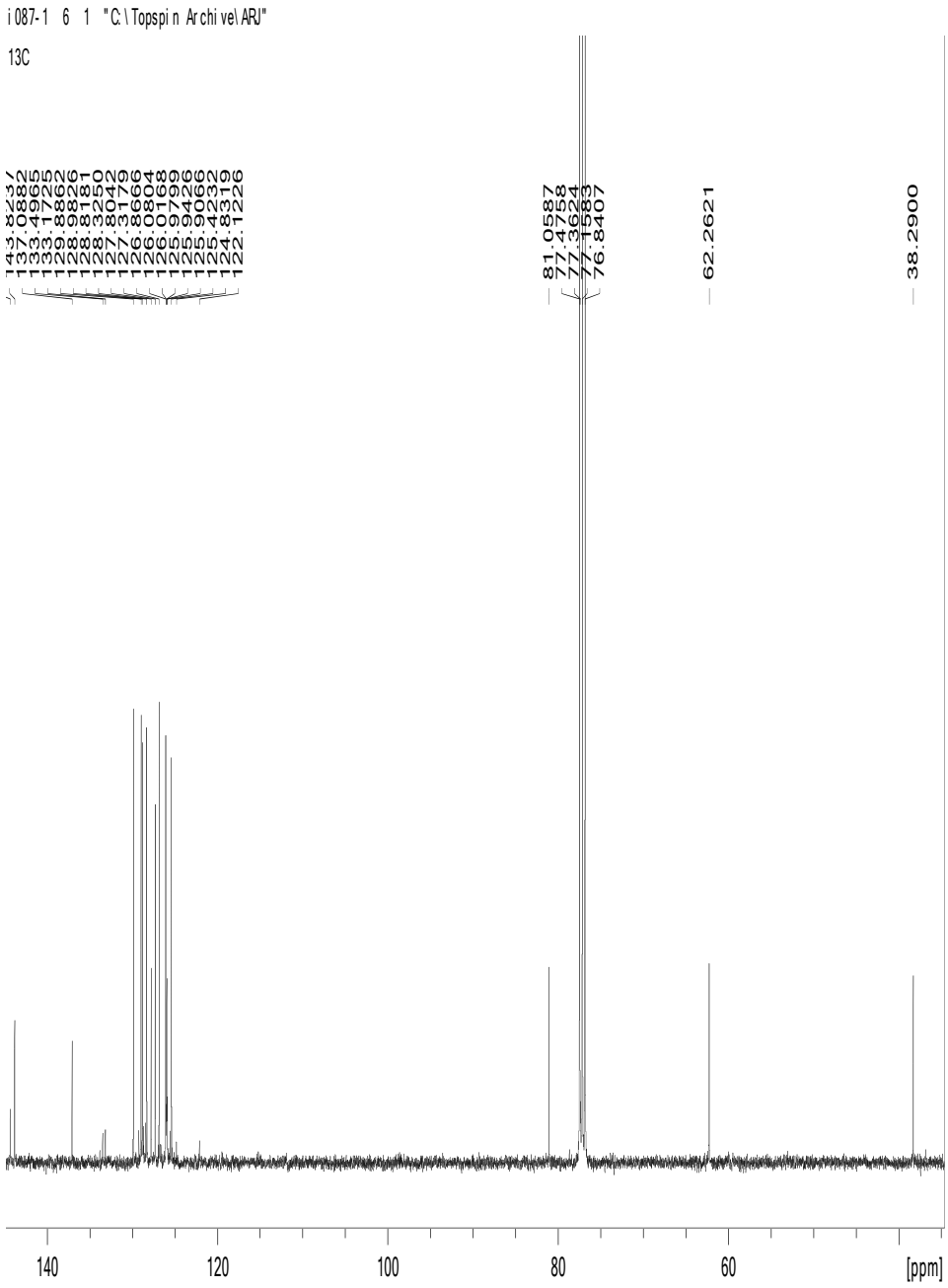
IR (diamond ATR) of L-H_2**Ph1**



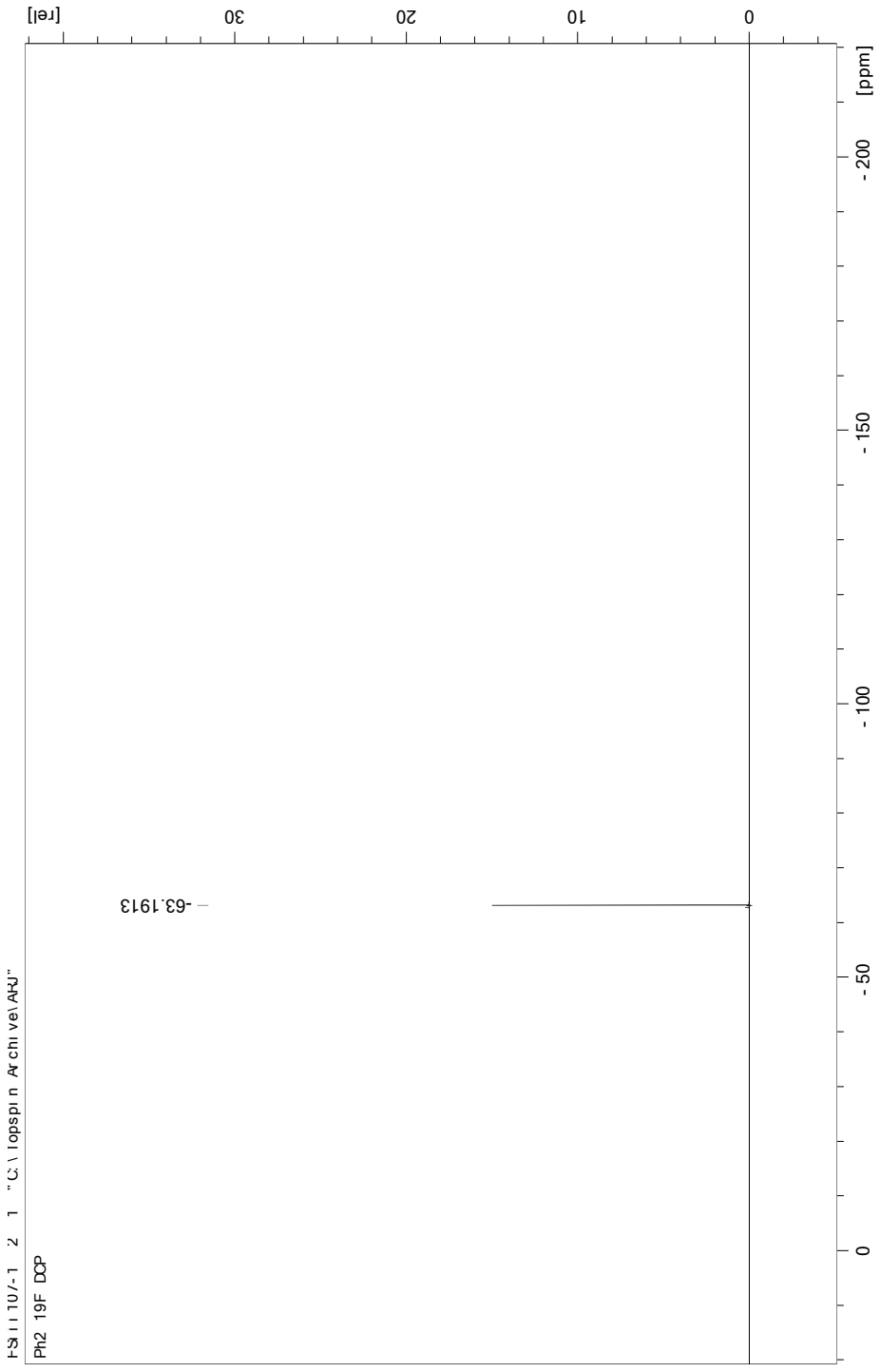
^{1}H NMR (400 MHz, $CDCl_3$) of L-H_2**Ph2**



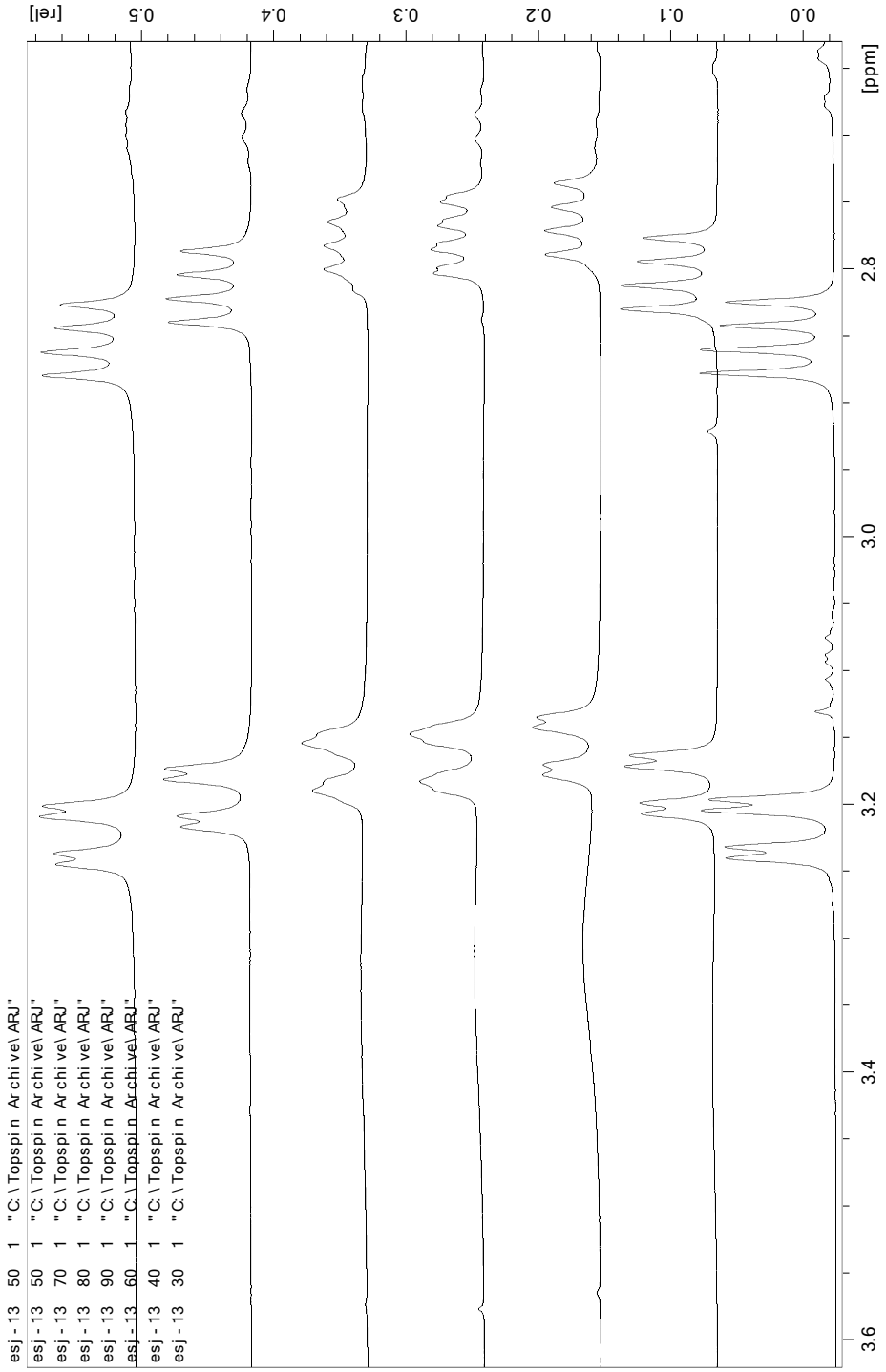
^{13}C NMR (100 MHz, $CDCl_3$) of L-H_2**Ph2**



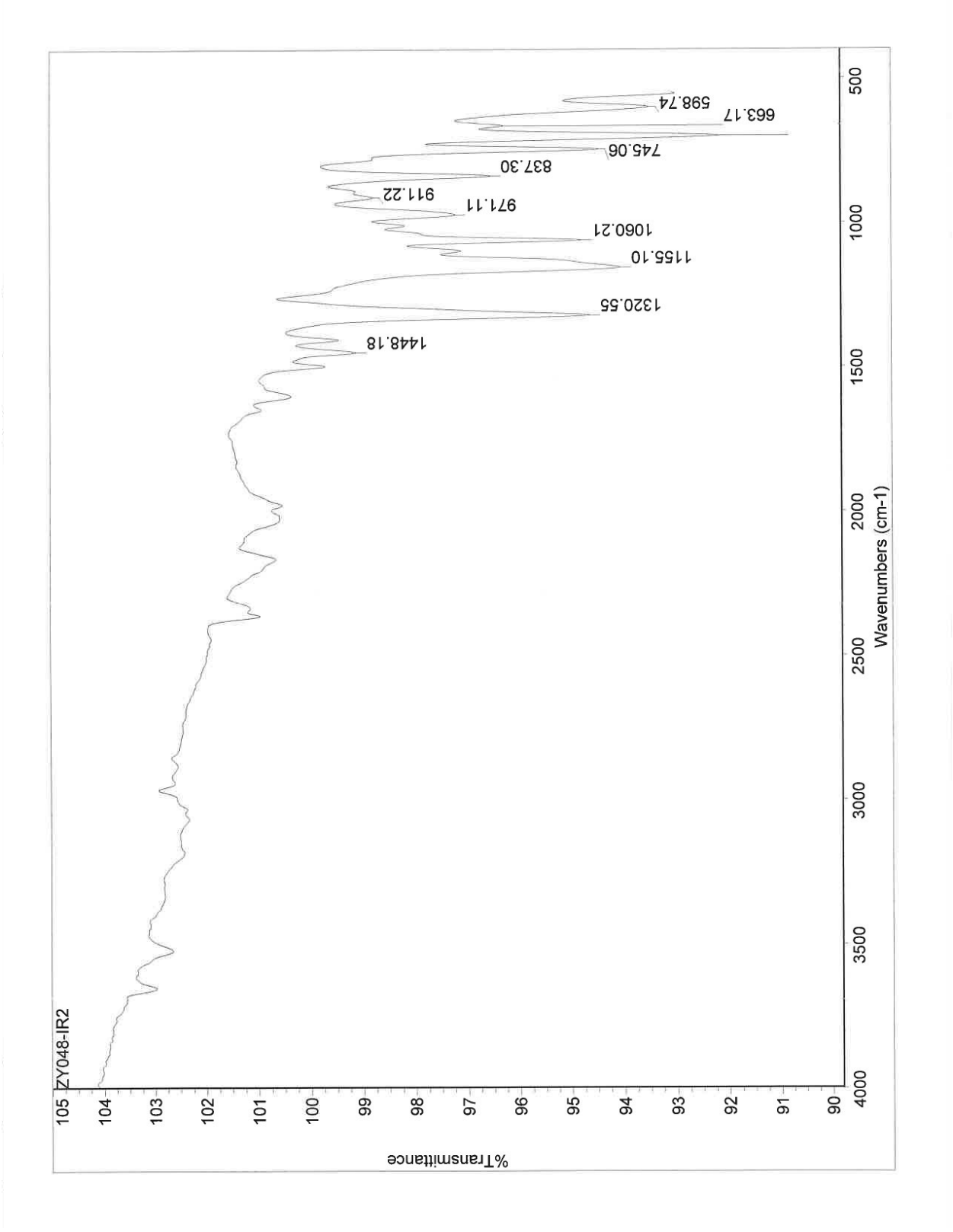
^{19}F NMR (376 MHz, $CDCl_3$) of L-H_2**Ph2**



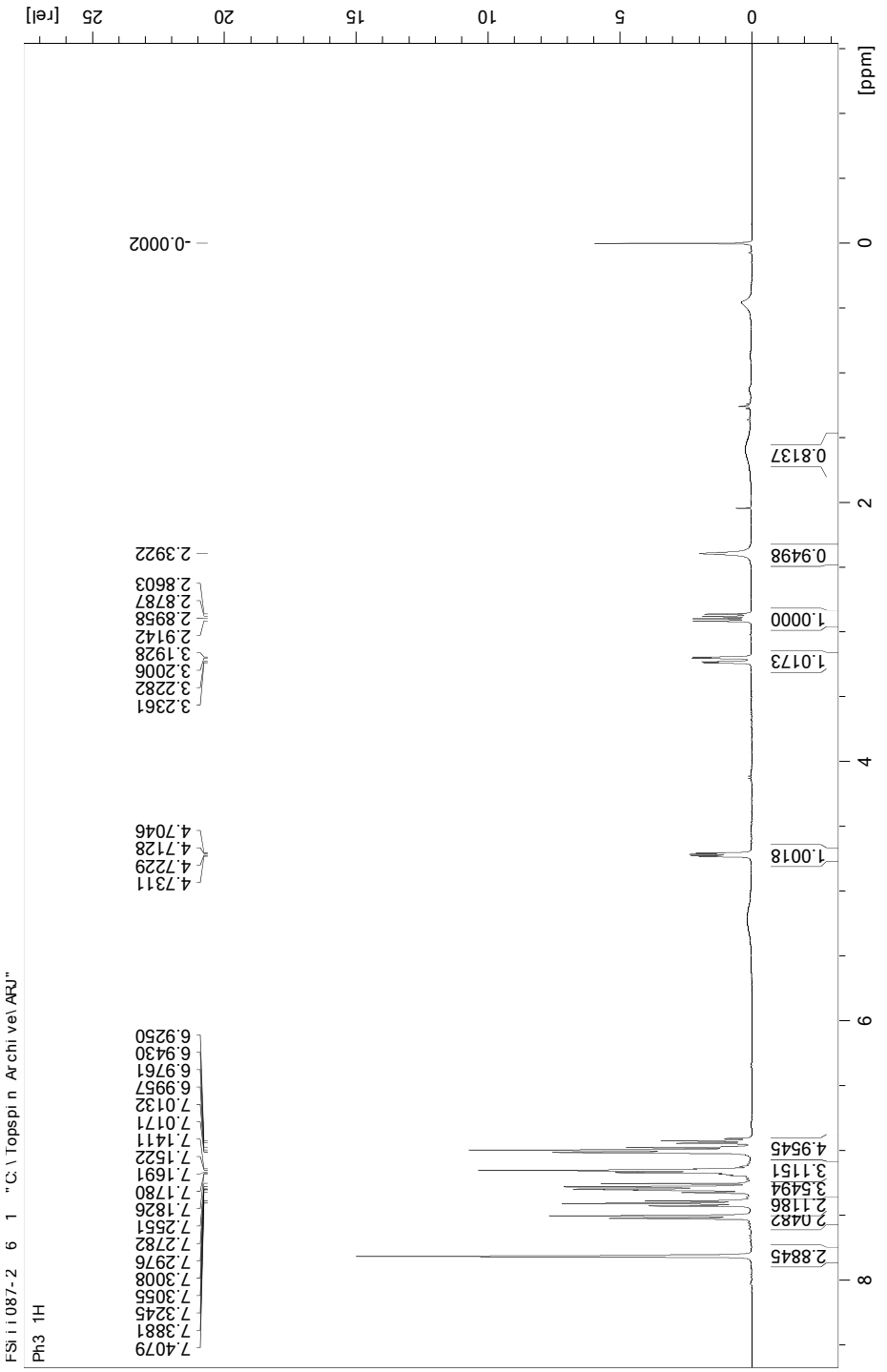
Chiral contact shift ^{1}H NMR experiment (400 MHz, $CDCl_3$) for D- and L-H_2**Ph2**



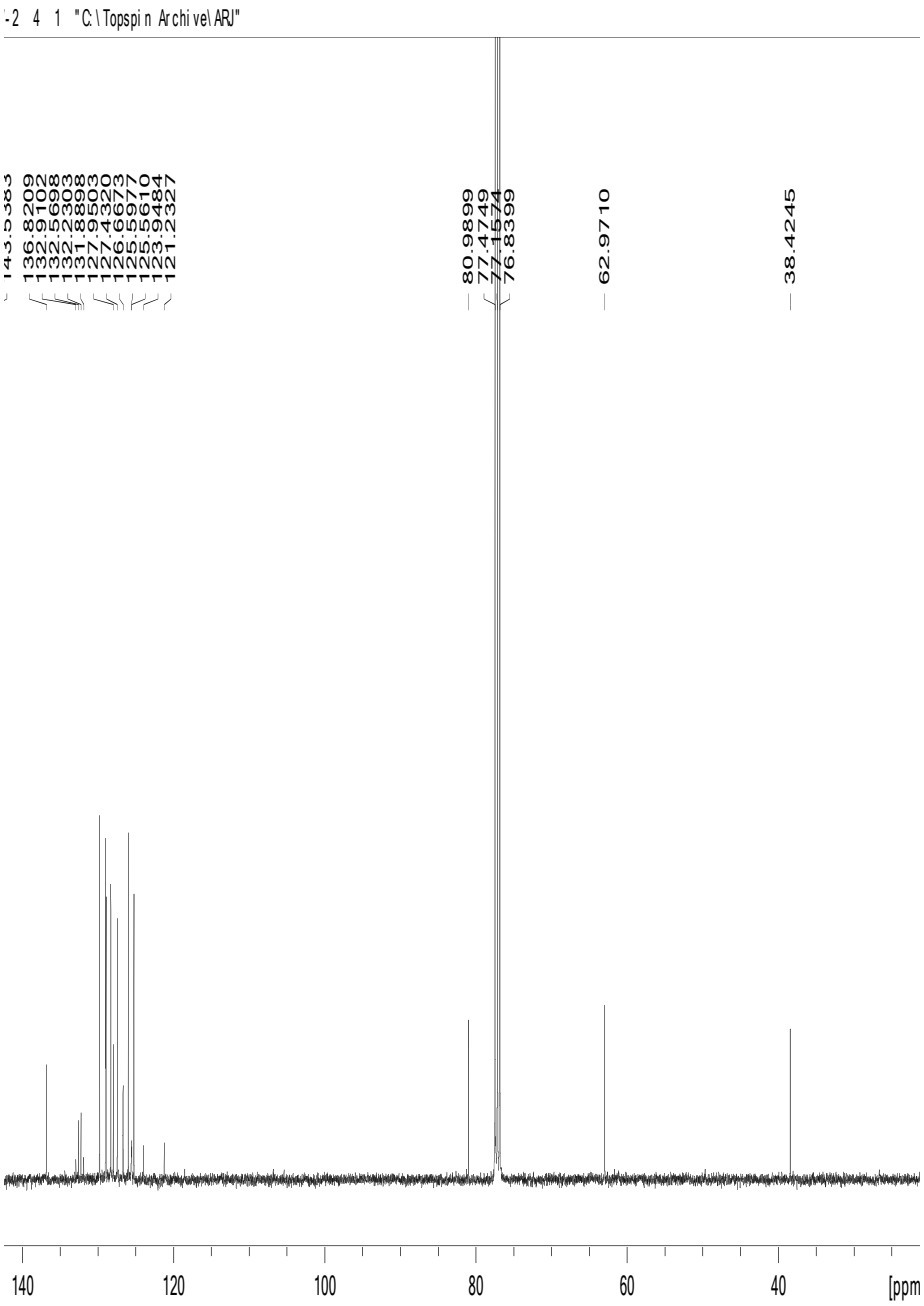
IR (diamond ATR) of L-H_2**Ph2**



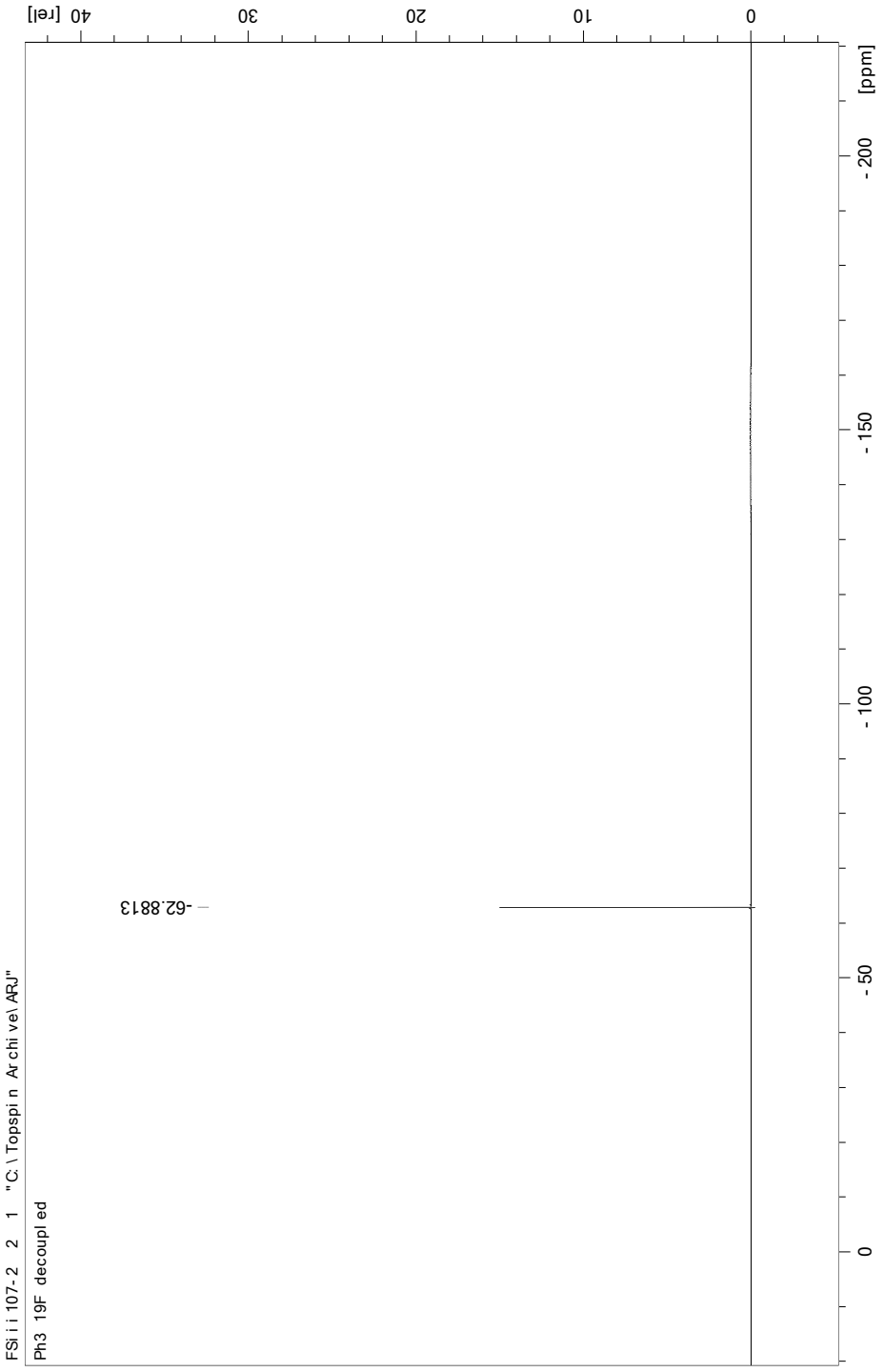
^{1}H NMR (400 MHz, $CDCl_3$) of L-H_2**Ph3**



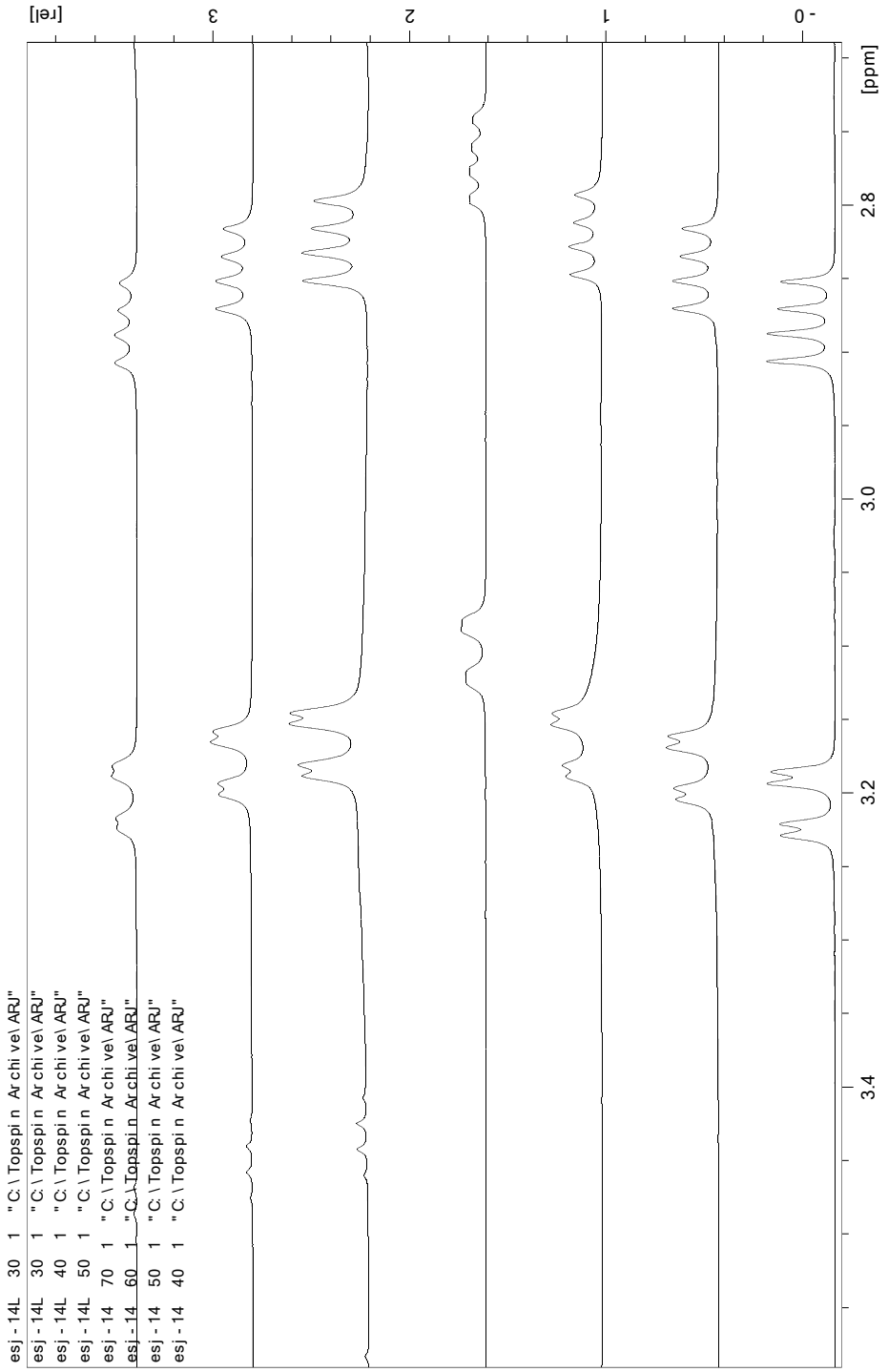
^{13}C NMR (100 MHz, $CDCl_3$) of L-H_2**Ph3**



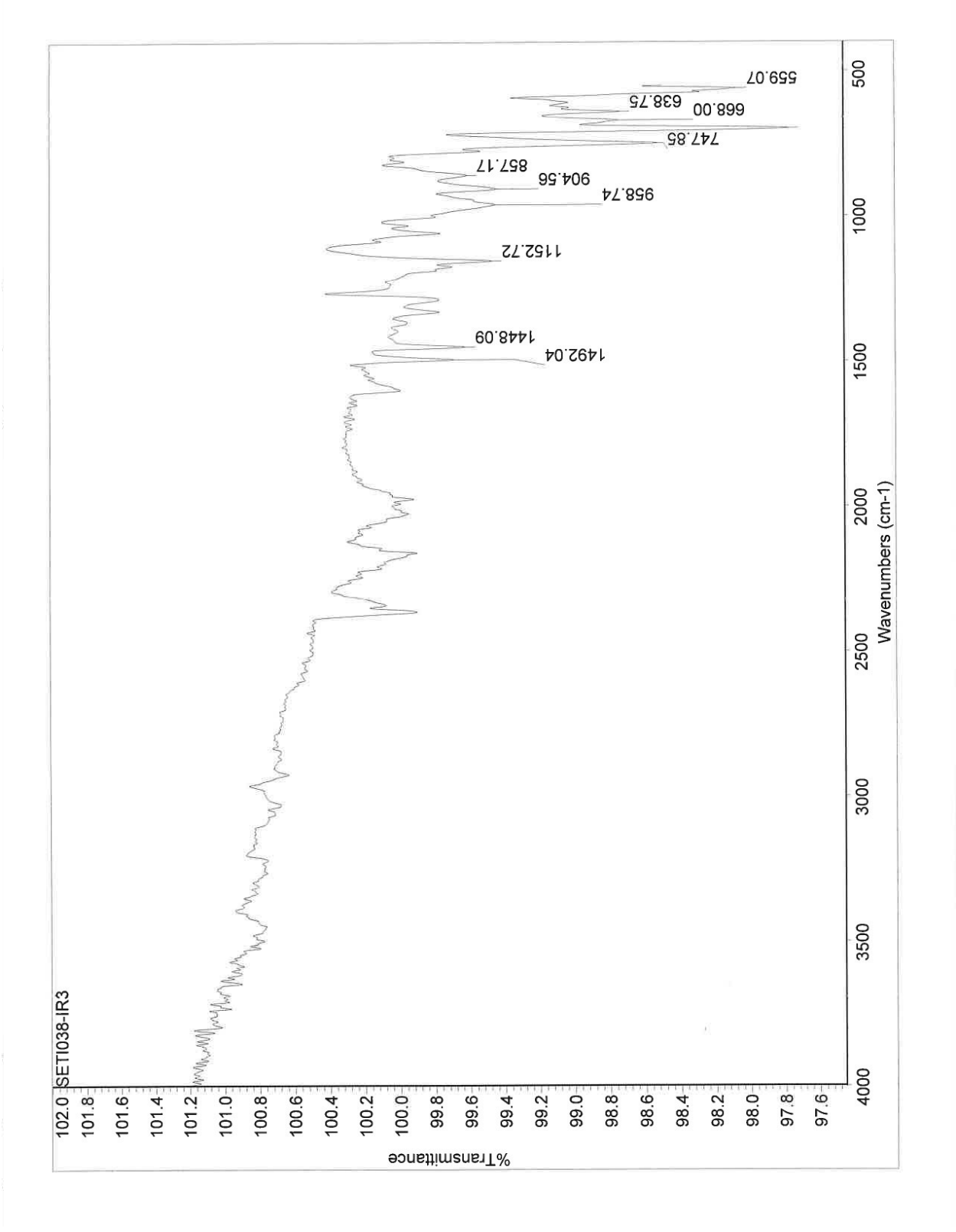
^{19}F NMR (376 MHz, $CDCl_3$) of L-H_2**Ph3**



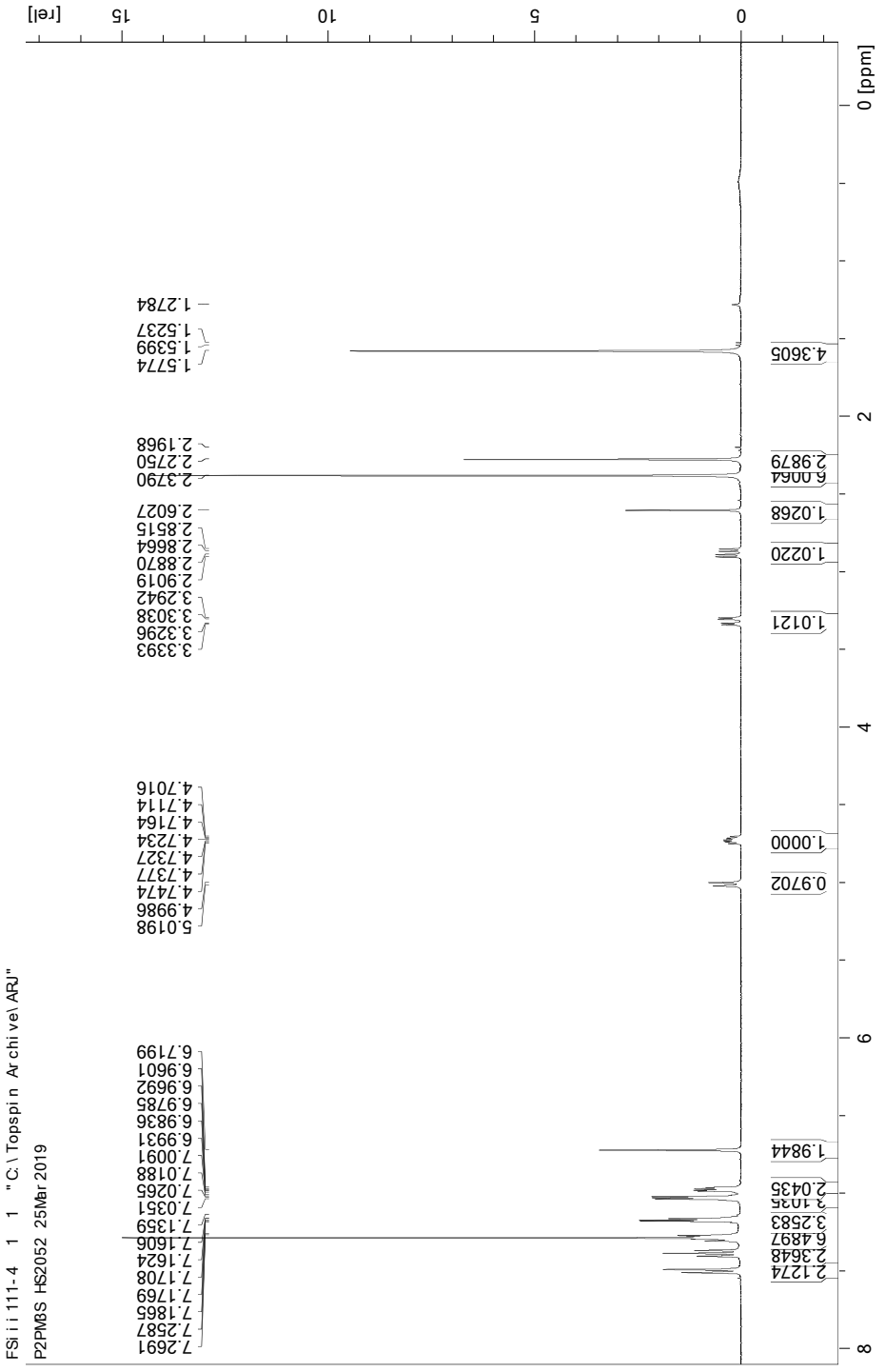
Chiral contact shift ^{1}H NMR experiment (400 MHz, $CDCl_3$) for D- and L-H_2**Ph3**



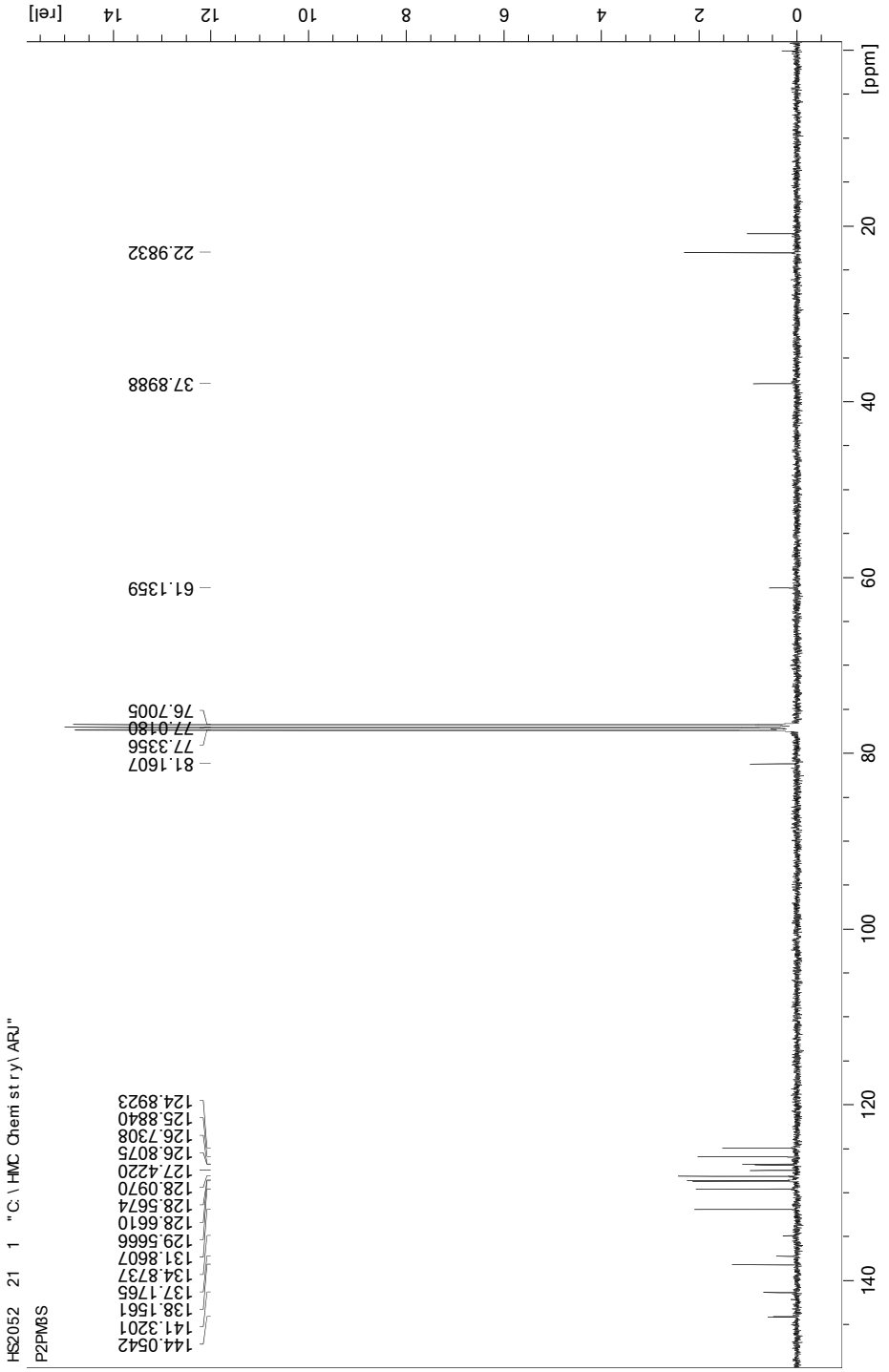
IR (diamond ATR) of L-H_2**Ph3**



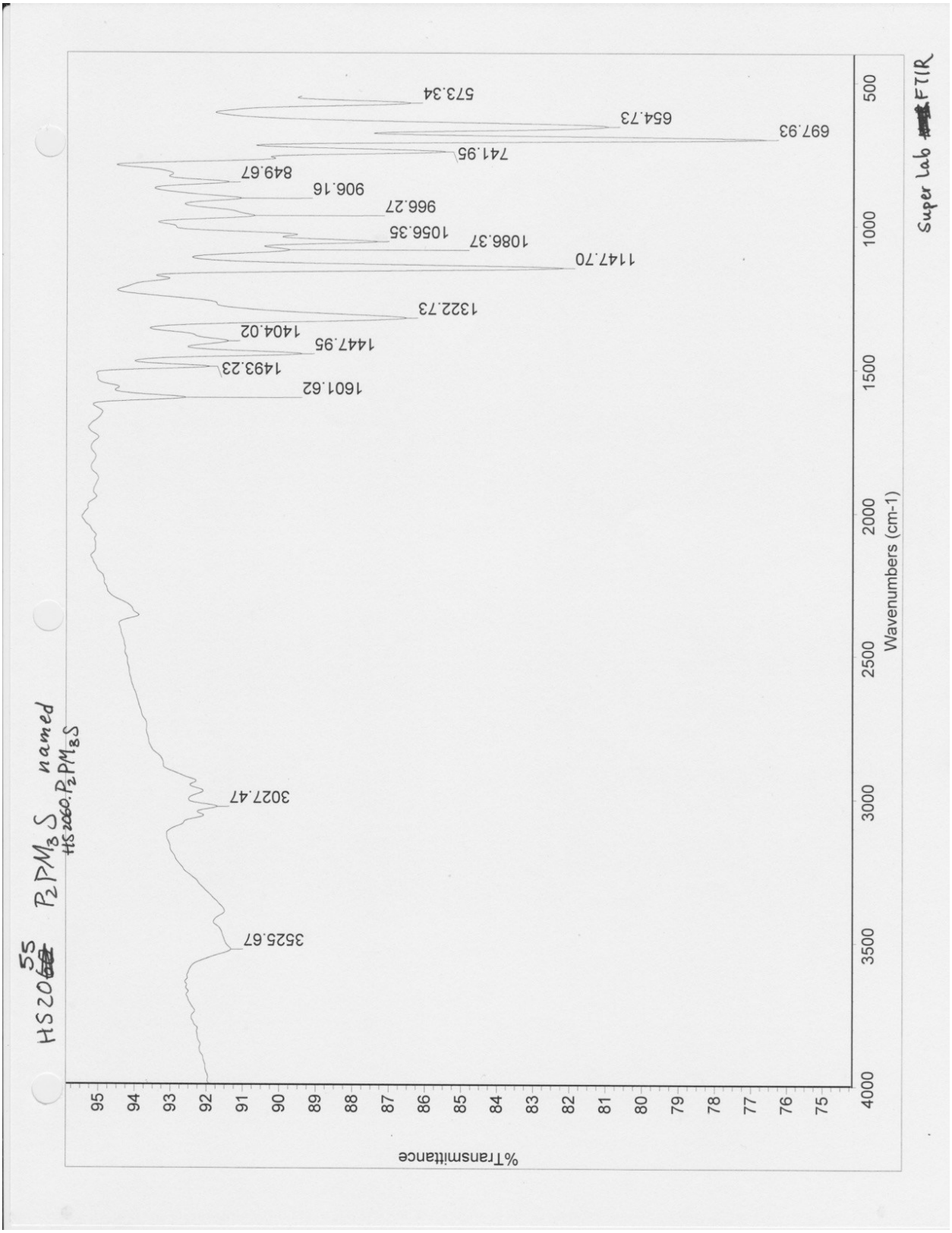
^{1}H NMR (400 MHz, $CDCl_3$) of L-H_2**Ph4**



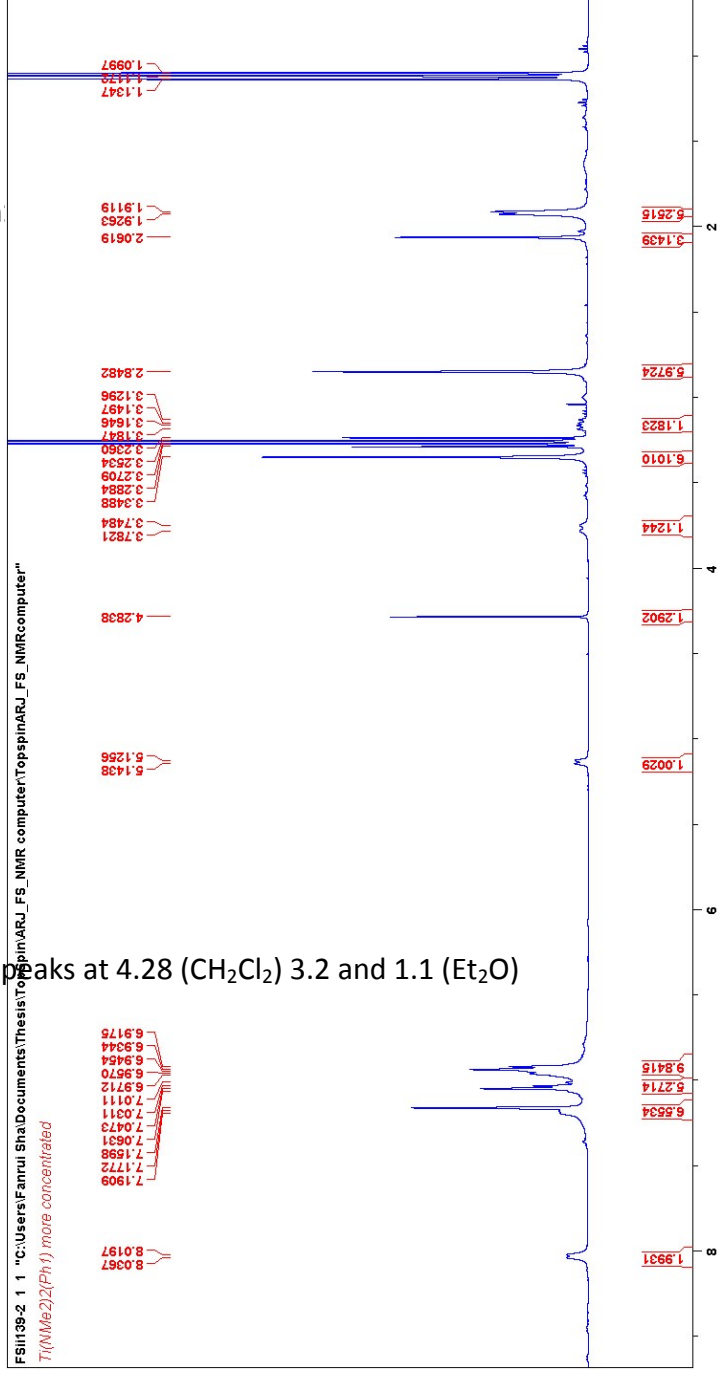
^{13}C NMR (100 MHz, $CDCl_3$) of L-H_2**Ph4**



IR (diamond ATR) of L-H_2**Ph4**

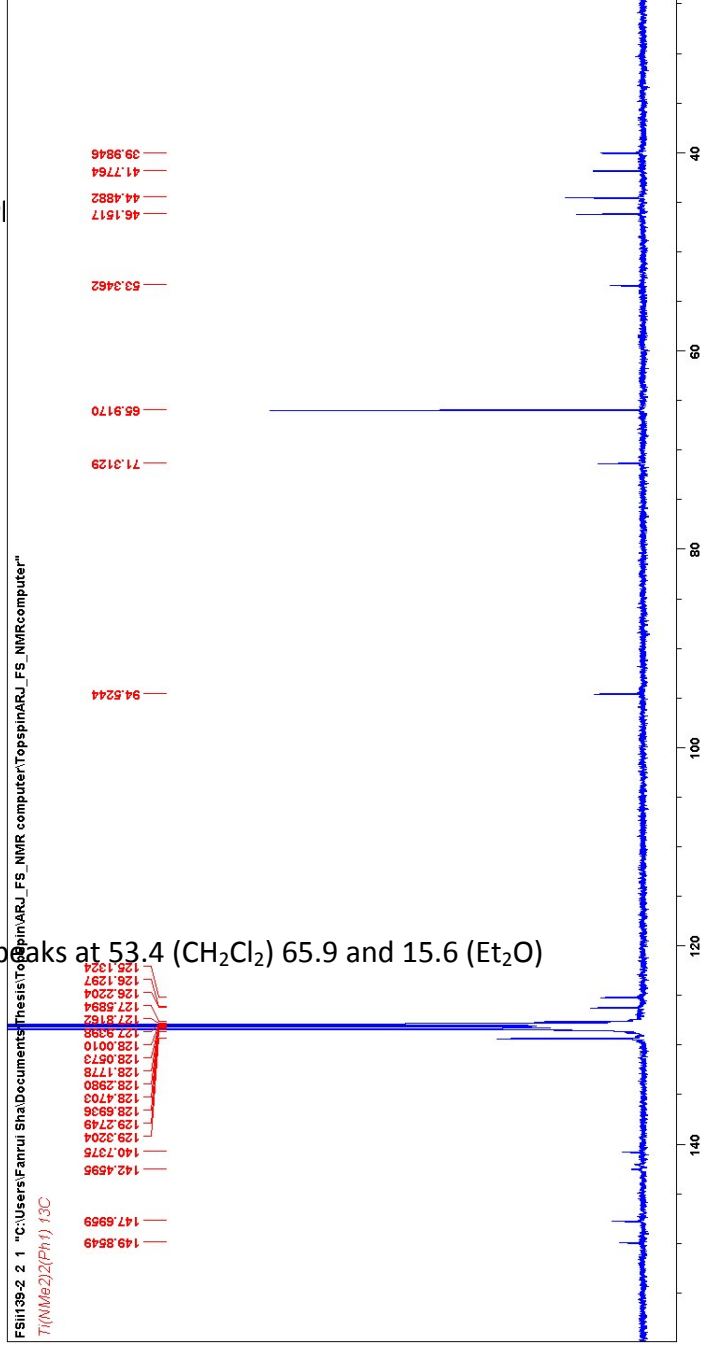


^{1}H NMR (400 MHz, C_6D_6) of **TiPh**



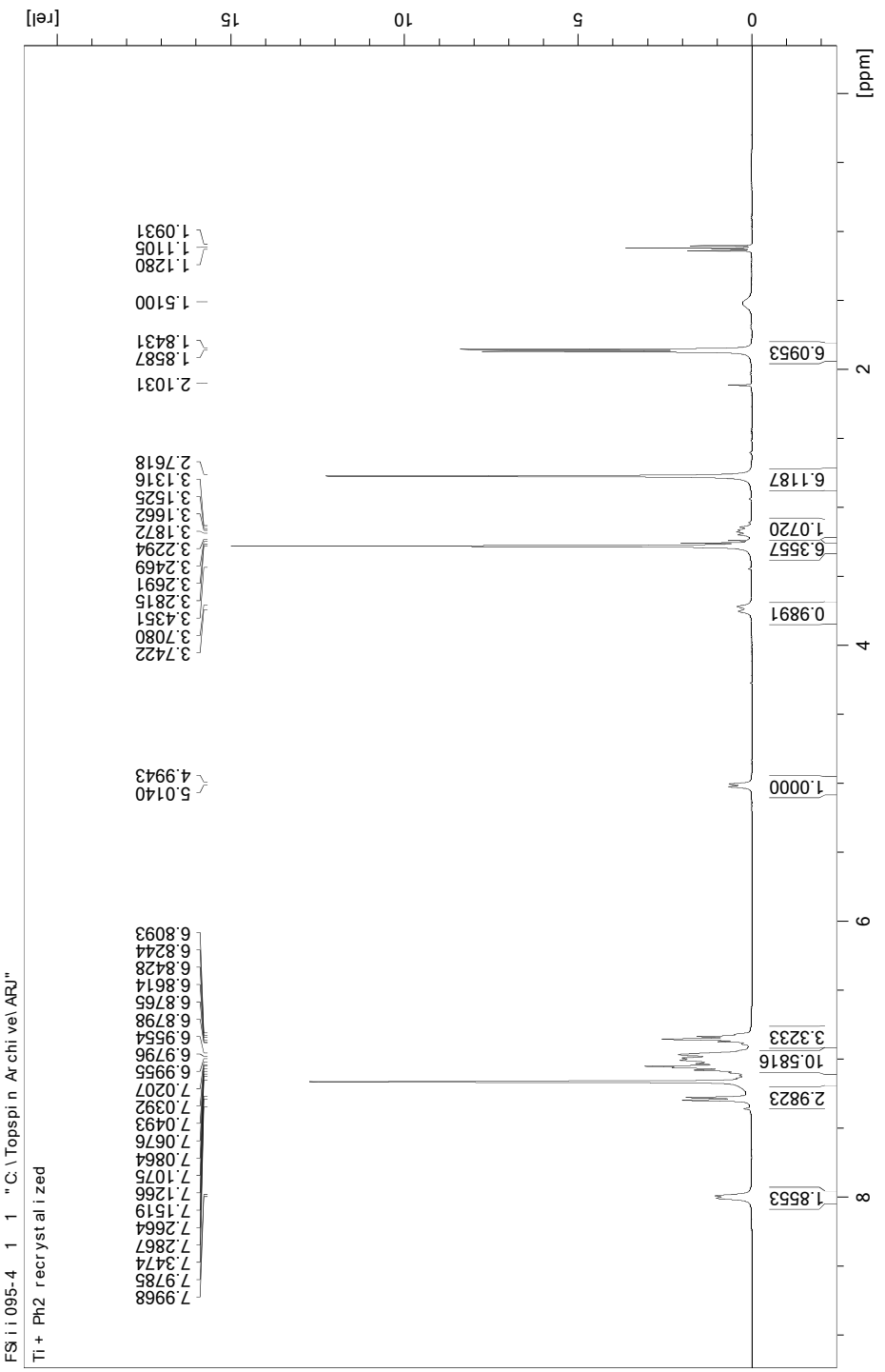
Solvent peaks at 4.28 (CH_2Cl_2) 3.2 and 1.1 (Et_2O)

^{13}C NMR (100 MHz, C_6D_6) of **TiPI**

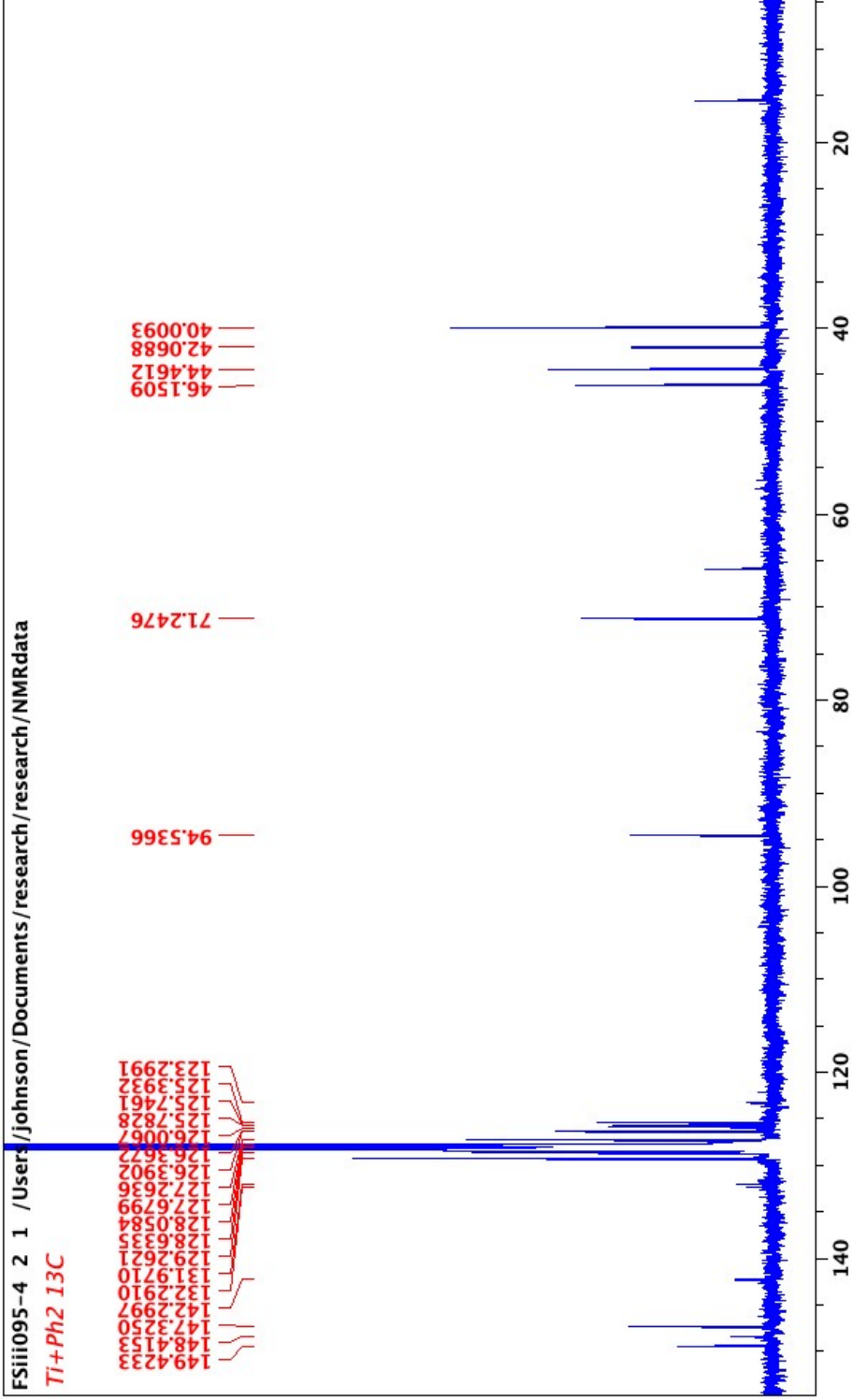


Solvent peaks at 53.4 (CH_2Cl_2) 65.9 and 15.6 (Et_2O)

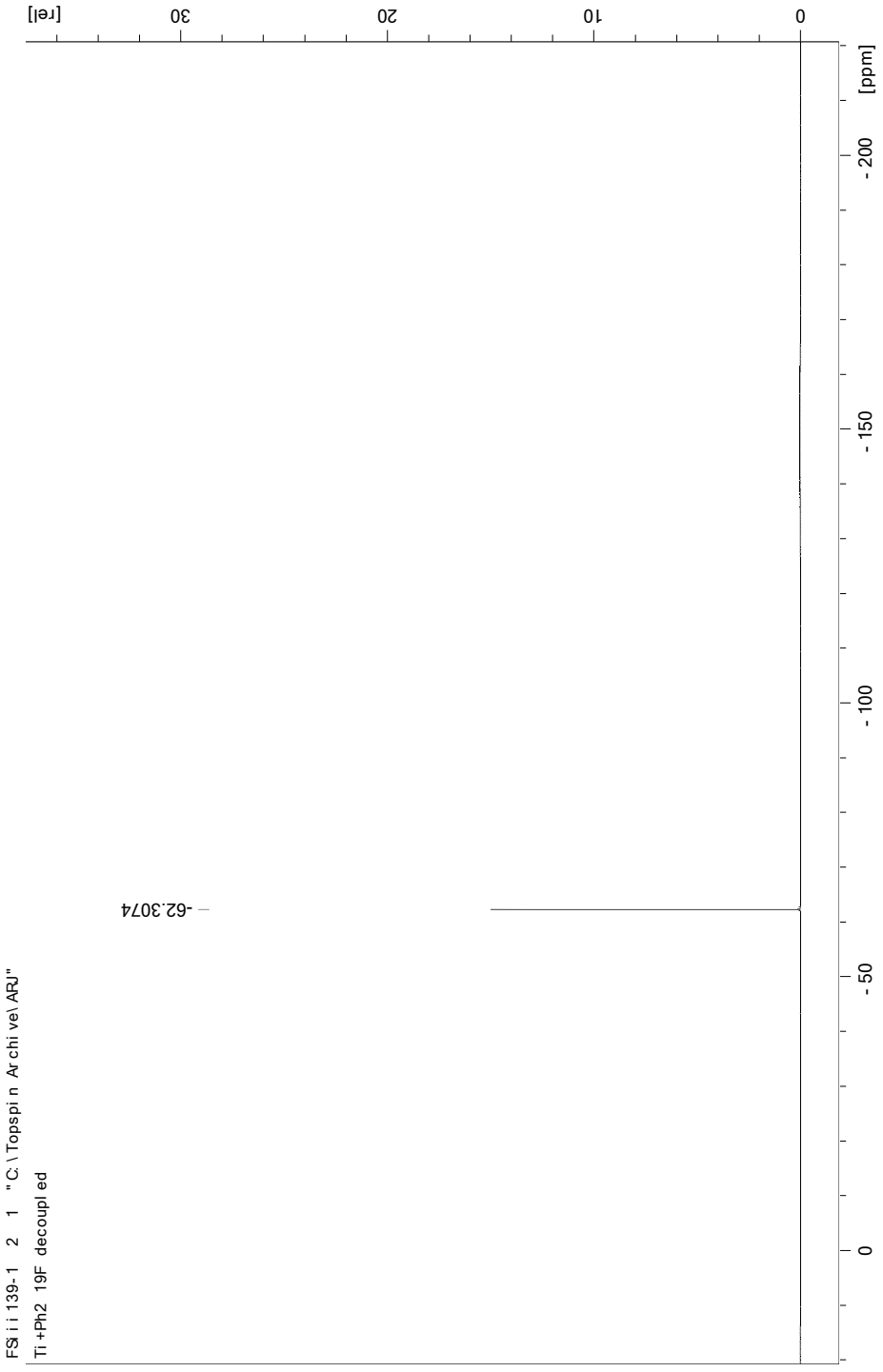
^{1}H NMR (400 MHz, C_6D_6) of **TiPh2** {Ti(Ph2)$(NMe_2)_2$}



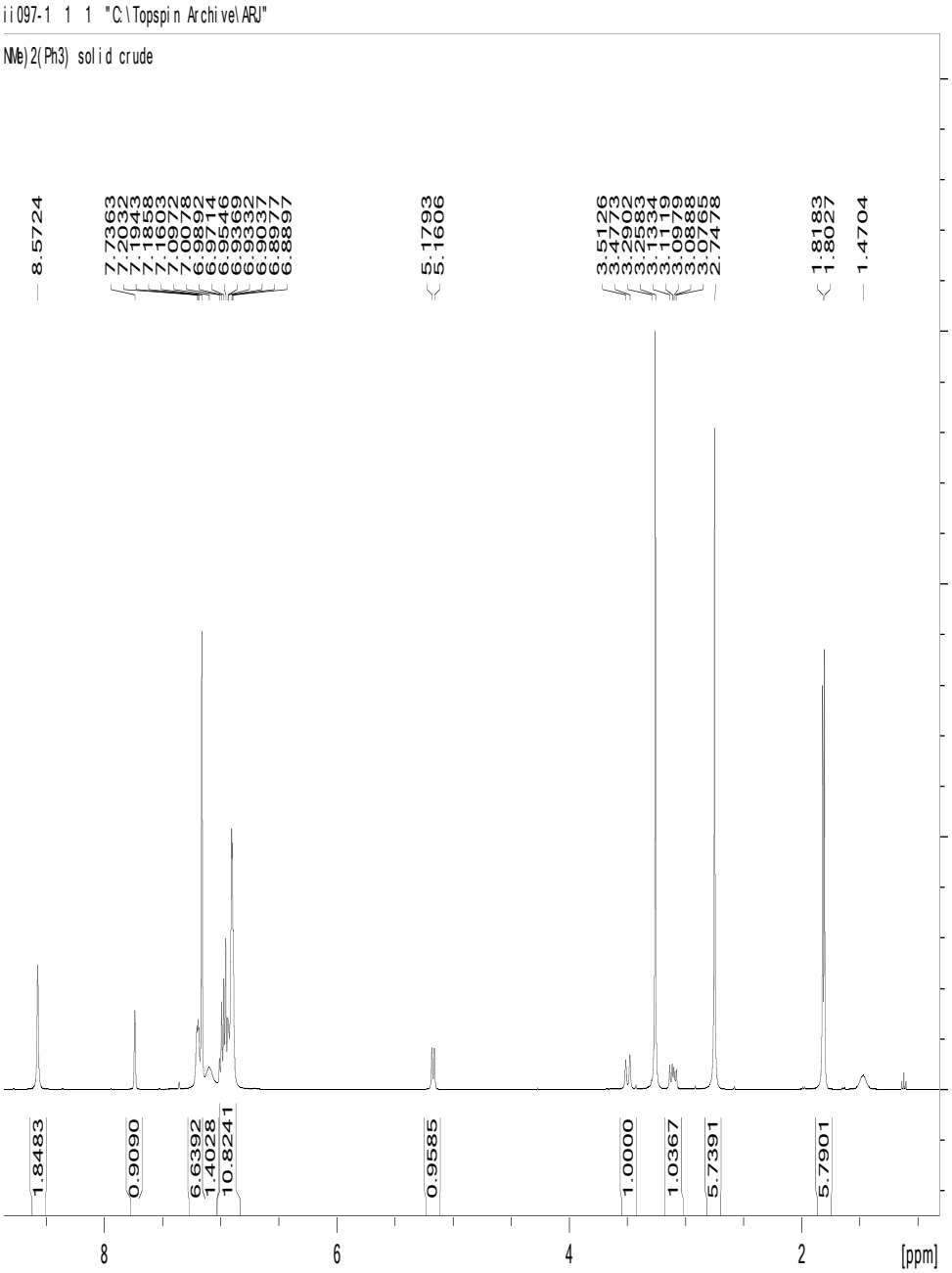
^{13}C NMR (100 MHz, C_6D_6) o



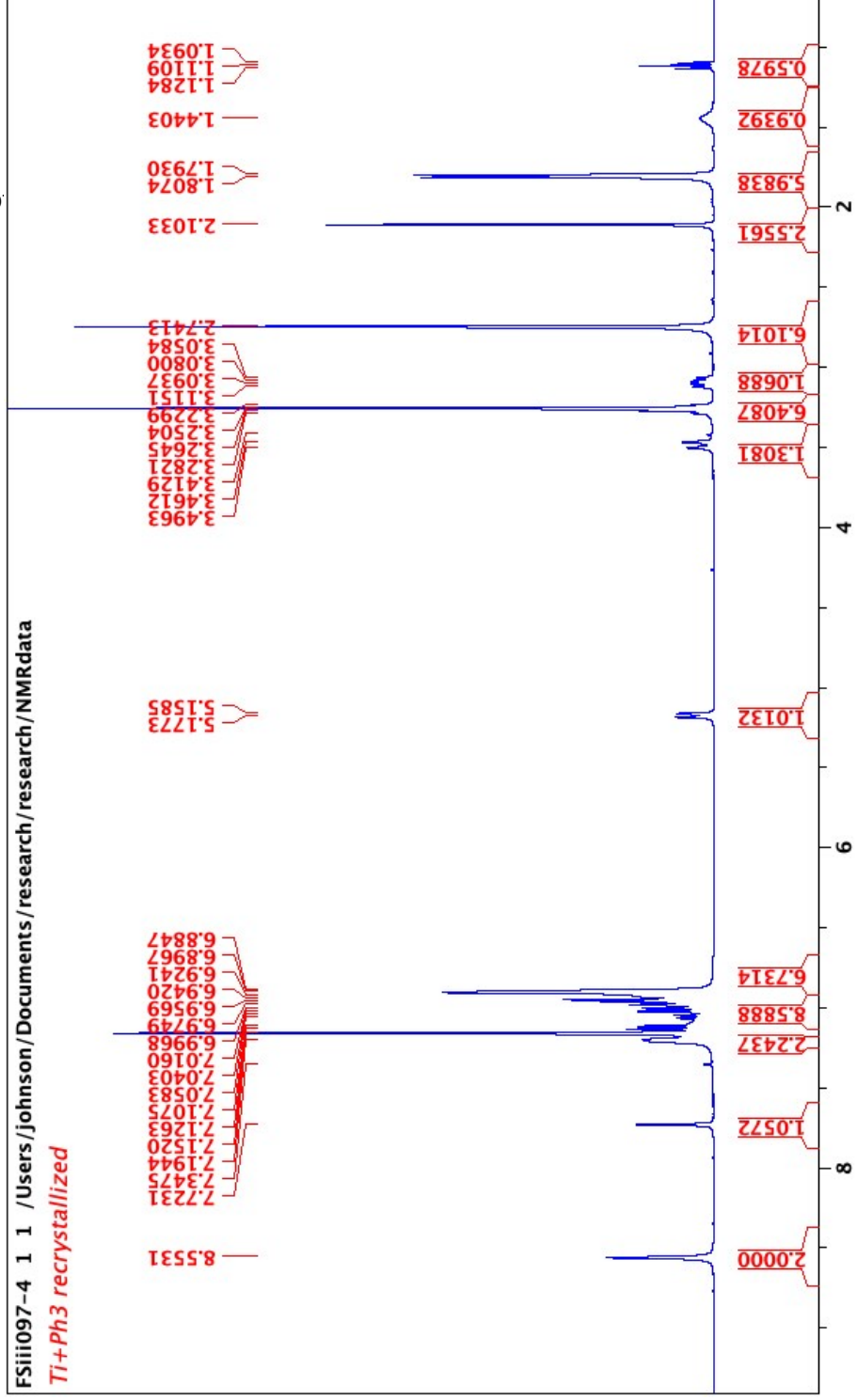
^{19}F NMR (376 MHz, C_6D_6) of **TiPh2** {Ti(Ph2)$(NMe_2)_2$}



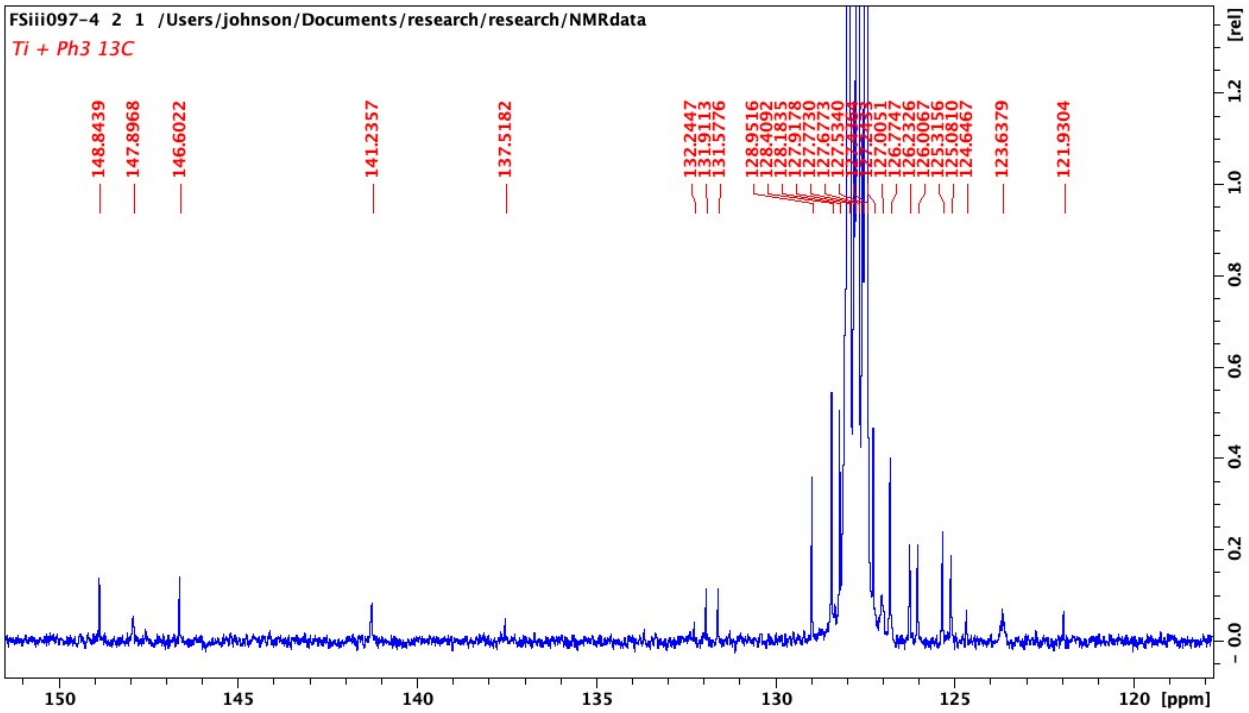
Crude ^{1}H NMR (400 MHz, C_6D_6) of **TiPh3** {Ti(Ph3)$(NMe_2)_2(HNMe_2)$}



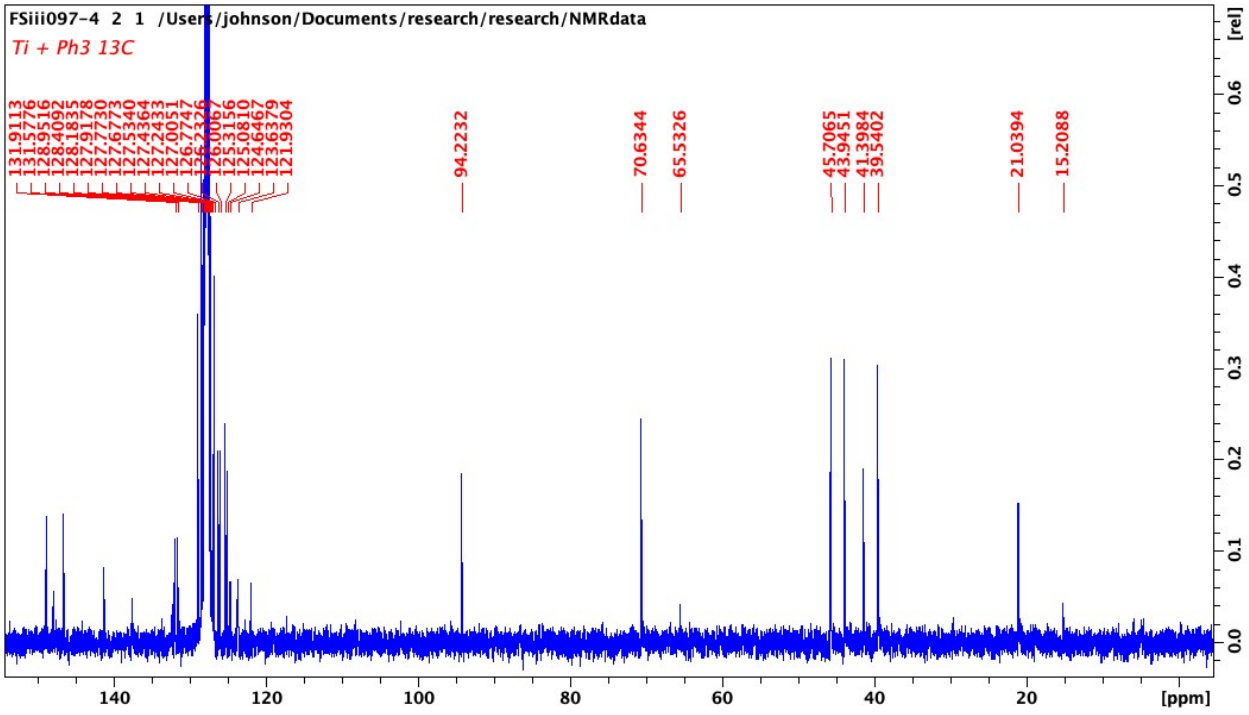
^{1}H NMR (400 MHz, C_6D_6) o



^{13}C NMR (100 MHz, C_6D_6) of **TiPh3·C_7H_8** {Ti(Ph3)$(NMe_2)_2(HNMe_2)\cdot C_7H_8$}



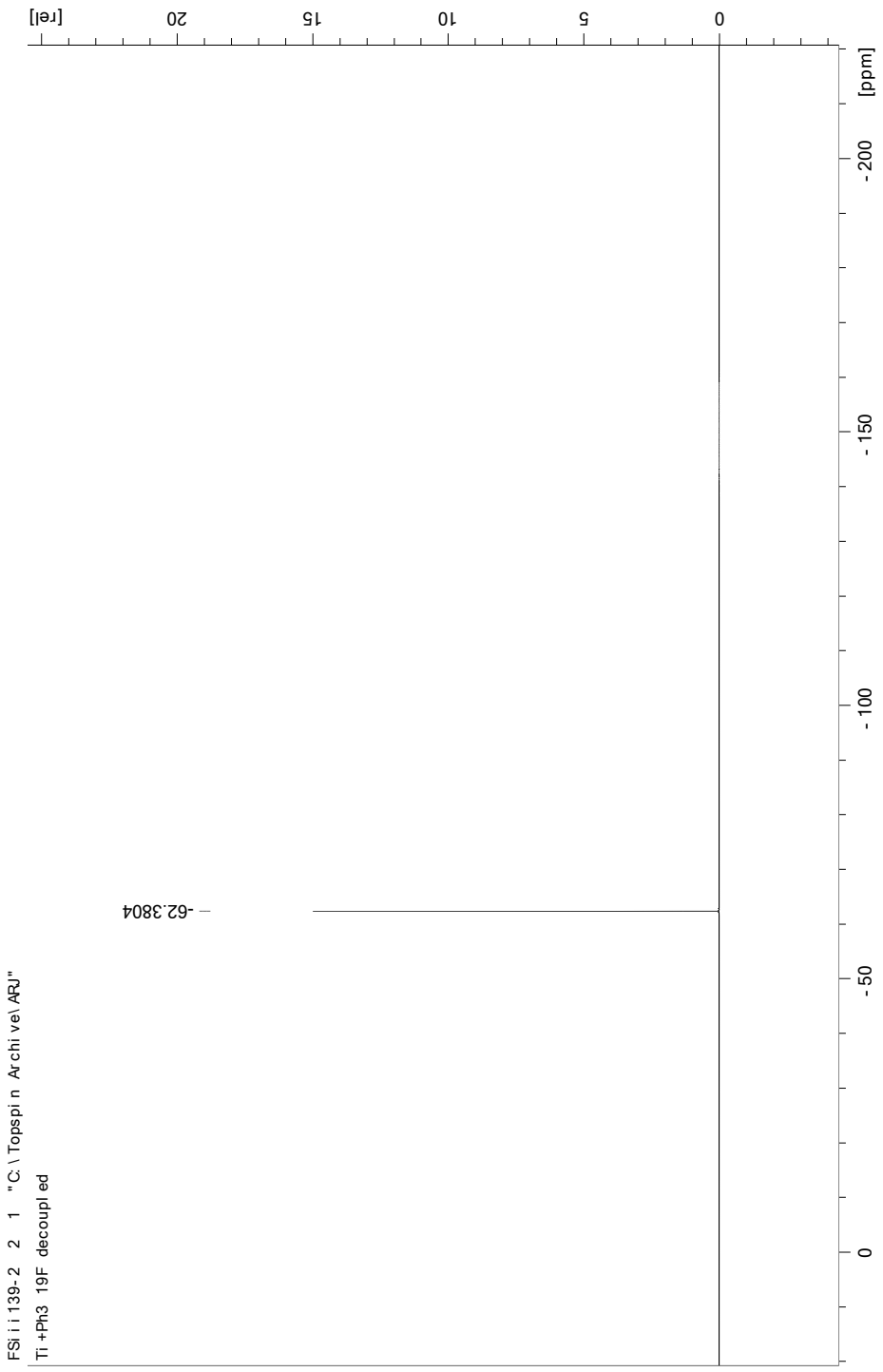
Aromatic region



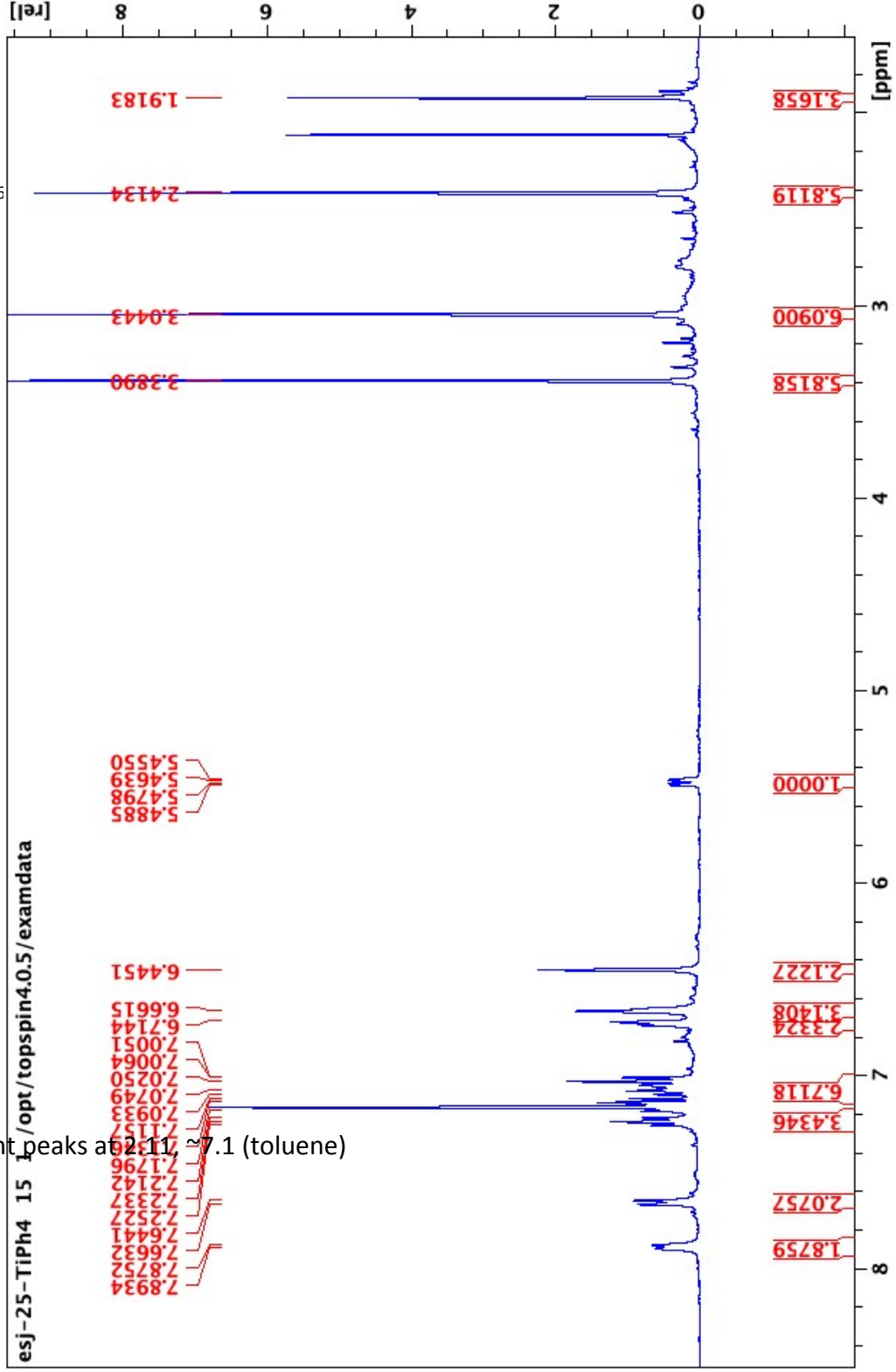
Full spectrum

Solvent peaks at 53.4 (CH_2Cl_2) 65.5 and 15.2 (Et_2O)

^{19}F NMR (376 MHz, C_6D_6) of **TiPh3·C_7H_8** {Ti(Ph3)$(NMe_2)_2(HNMe_2)\cdot C_7H_8$}

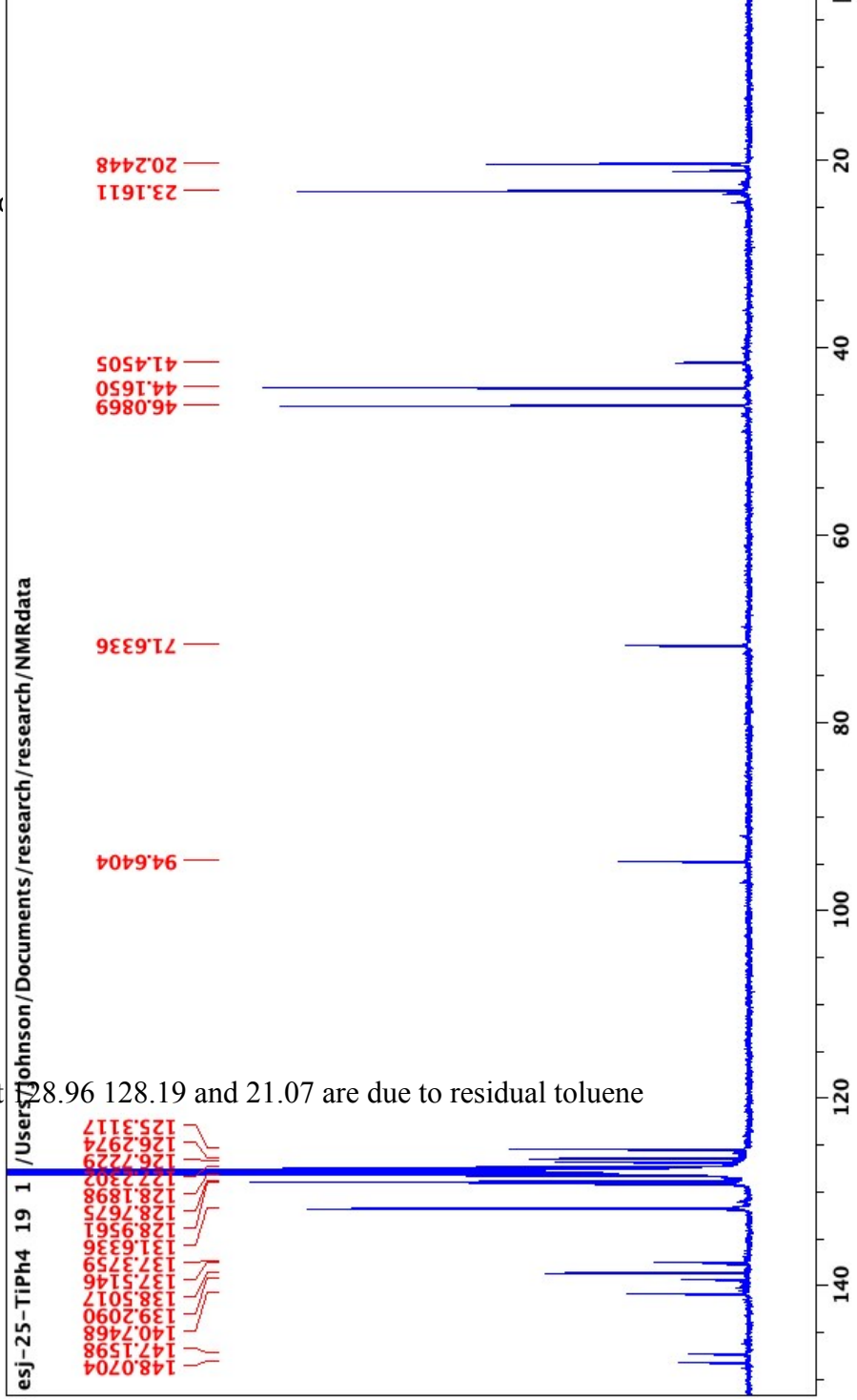


^{1}H NMR (400 MHz, C_6



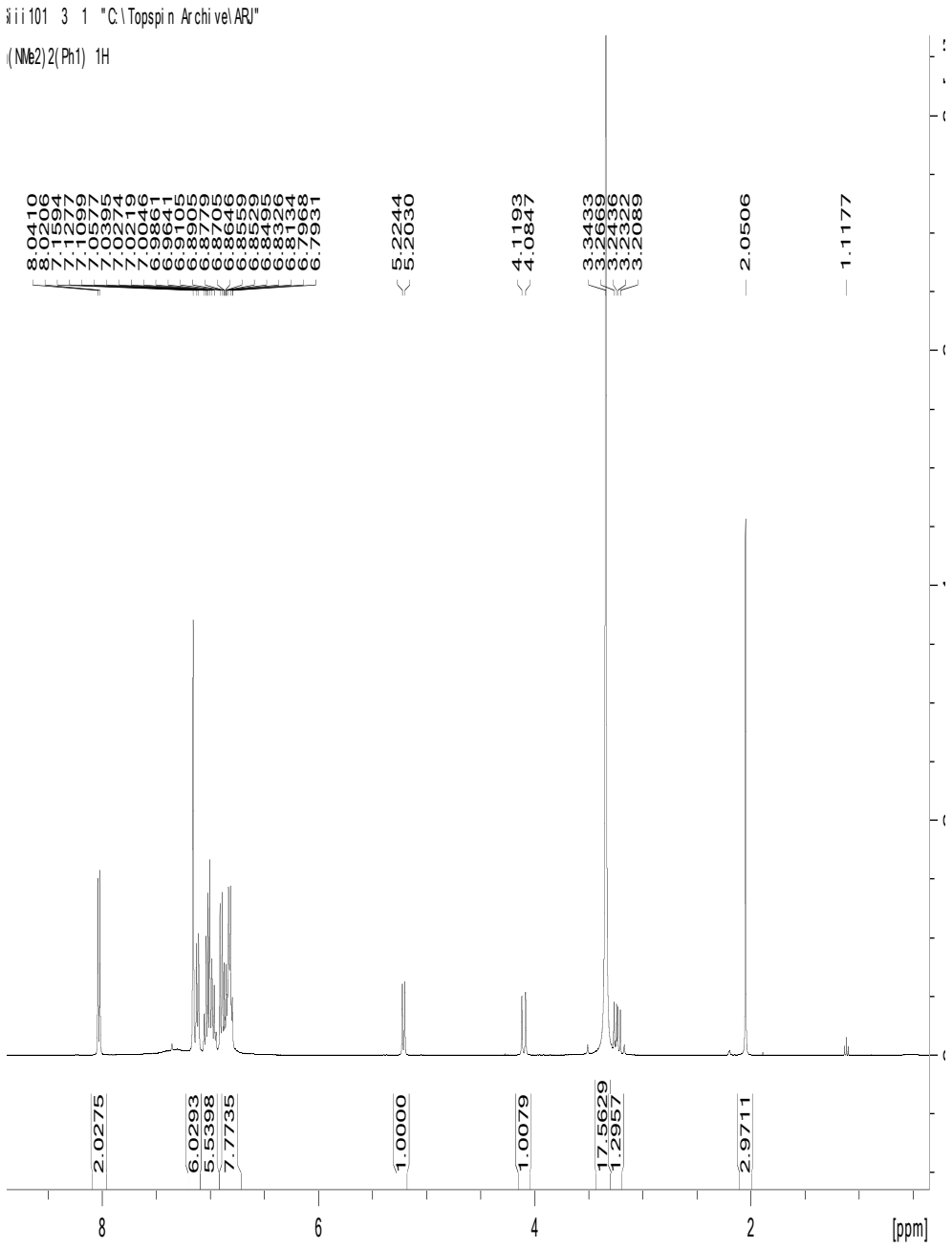
Solvent peaks at 2.11, ~7.1 (toluene)

^{13}C NMR (100 MHz, C_6D_6) δ

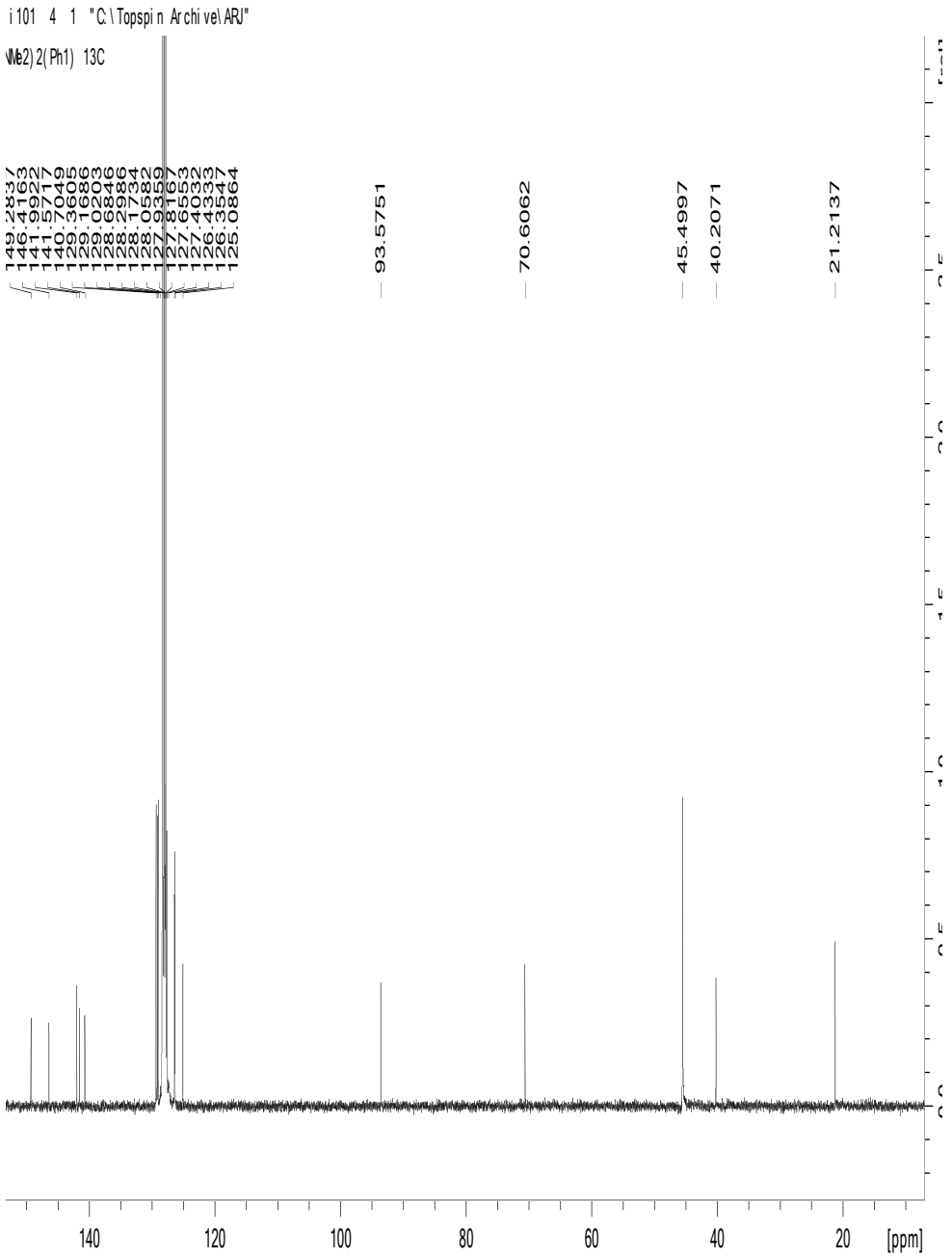


Peaks at 128.96 128.19 and 21.07 are due to residual toluene

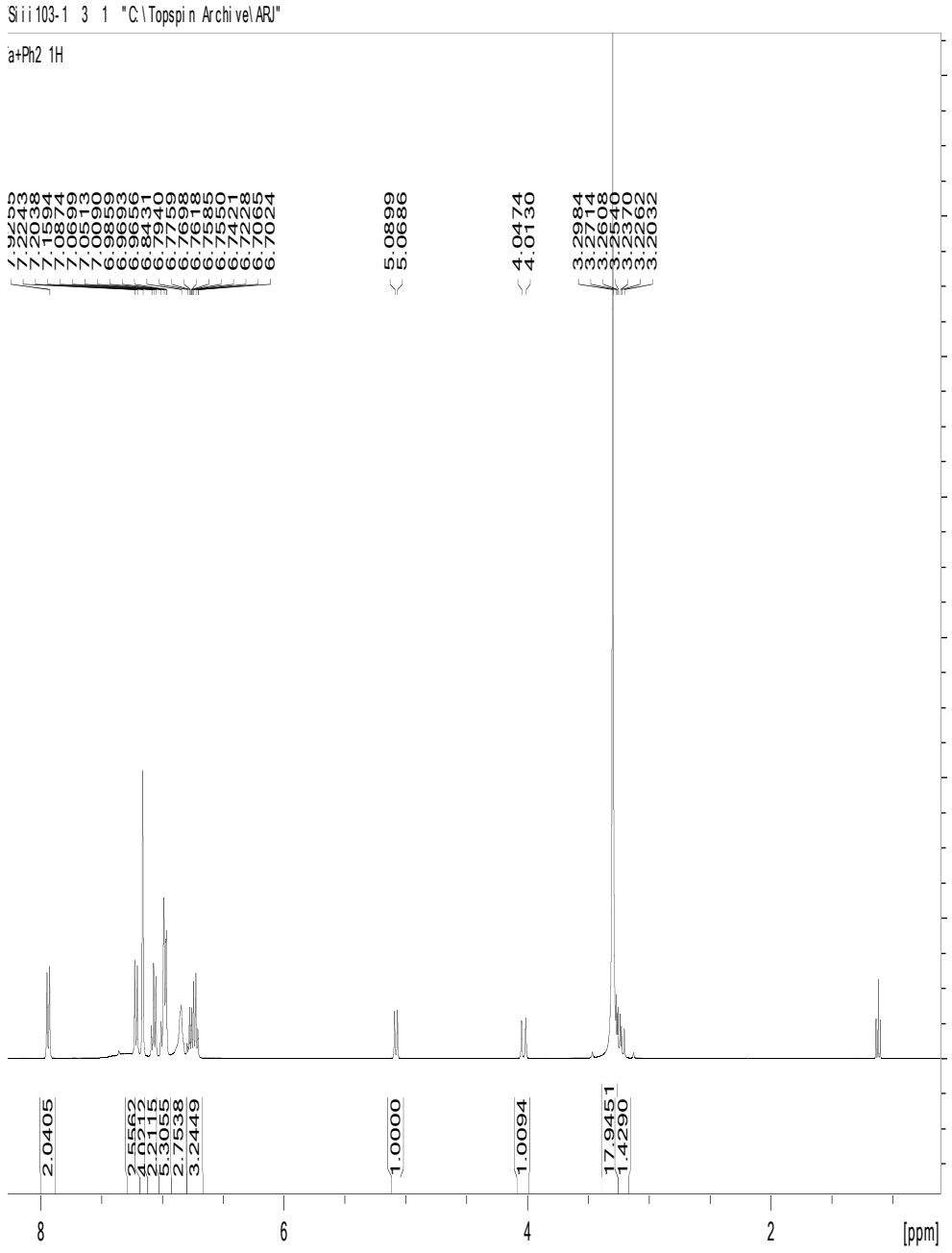
^{1}H NMR (400 MHz, C_6D_6) of **TaPh1** {Ta(Ph1)$(NMe_2)_3$}



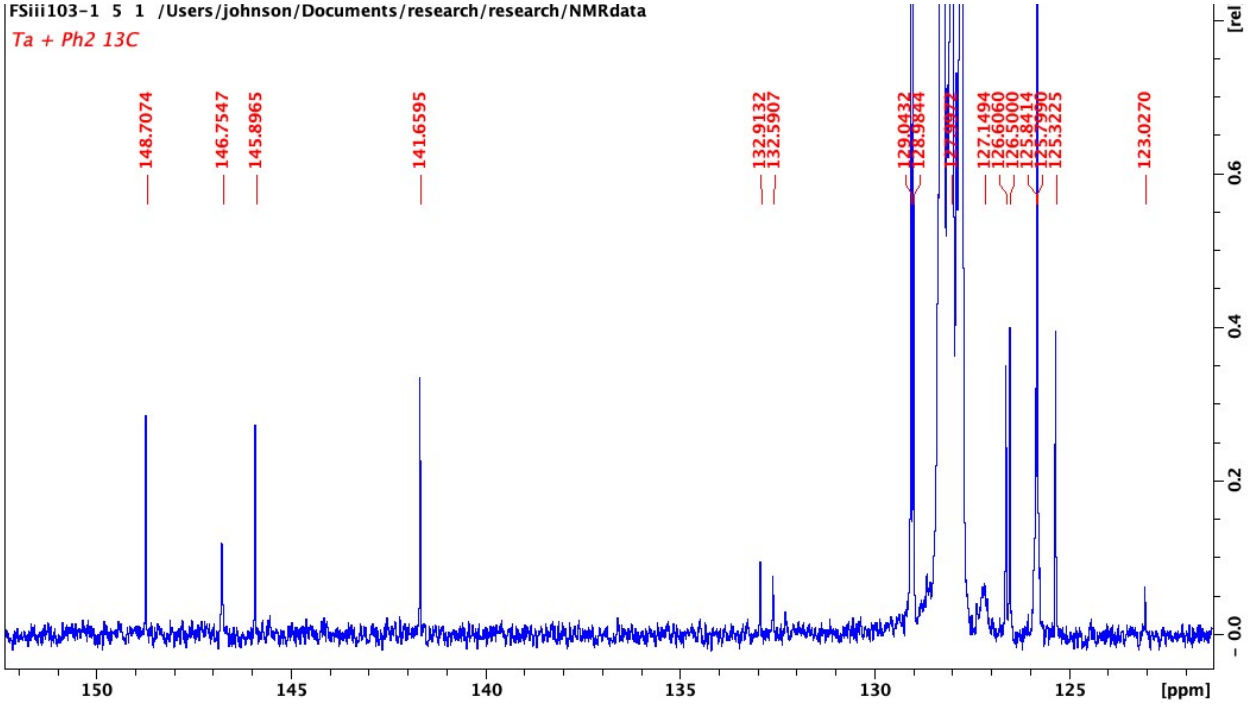
^{13}C NMR (100 MHz, C_6D_6) of **TaPh1** {Ta(Ph1)$(NMe_2)_3$}



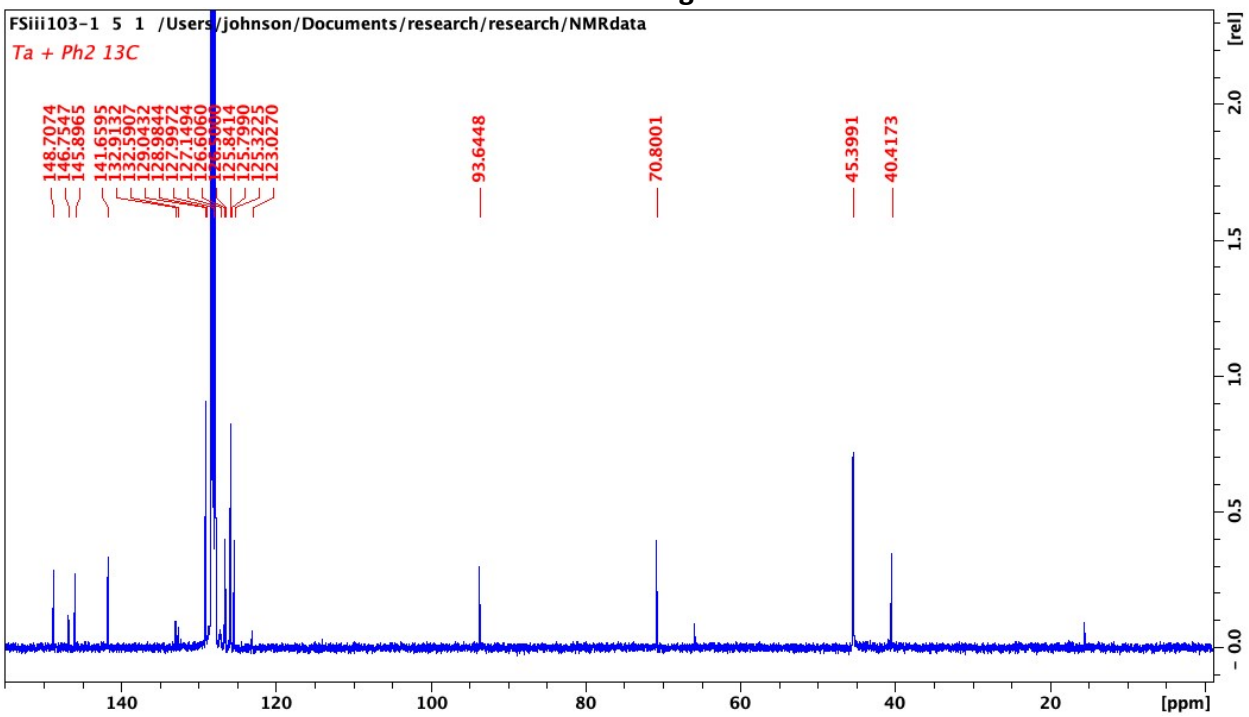
^{1}H NMR (400 MHz, C_6D_6) of **TaPh2** {Ta(Ph2)$(NMe_2)_3$}



^{13}C NMR (100 MHz, C_6D_6) of **TaPh2** {Ta(Ph2)$(NMe_2)_3$}

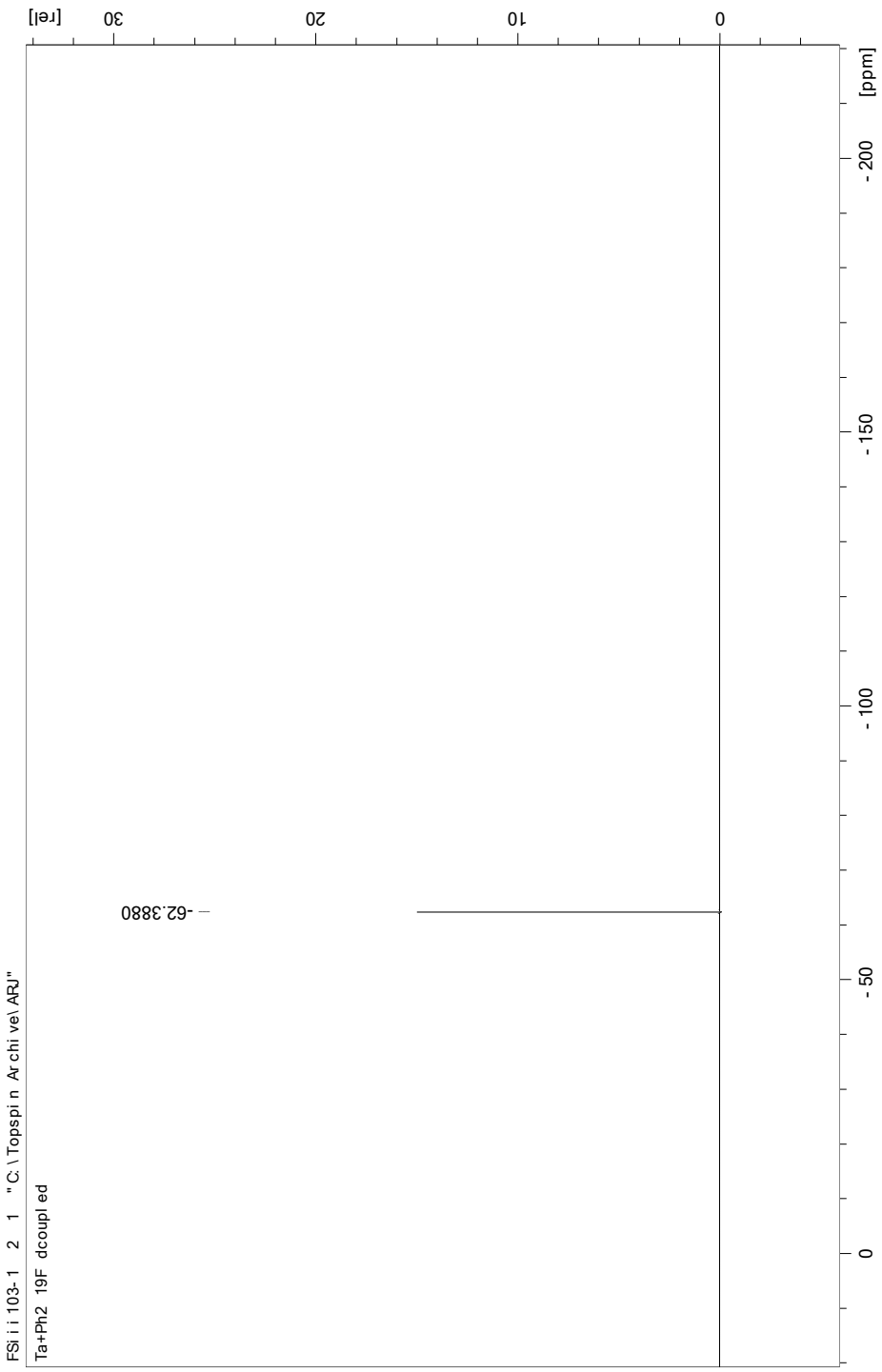


Aromatic Region

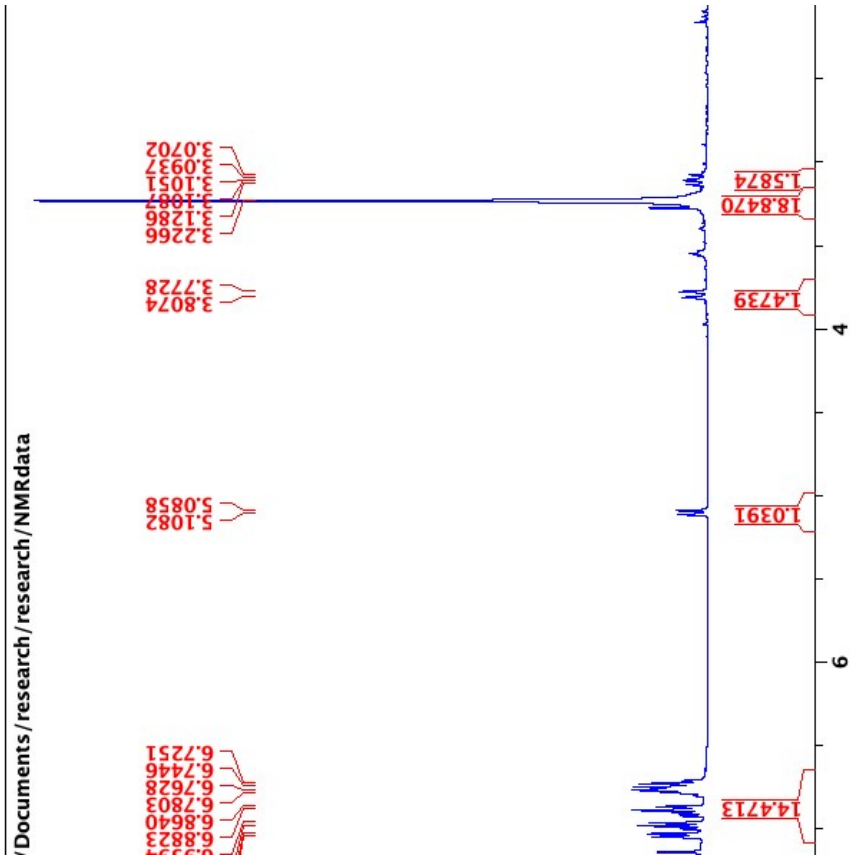


Full Spectrum

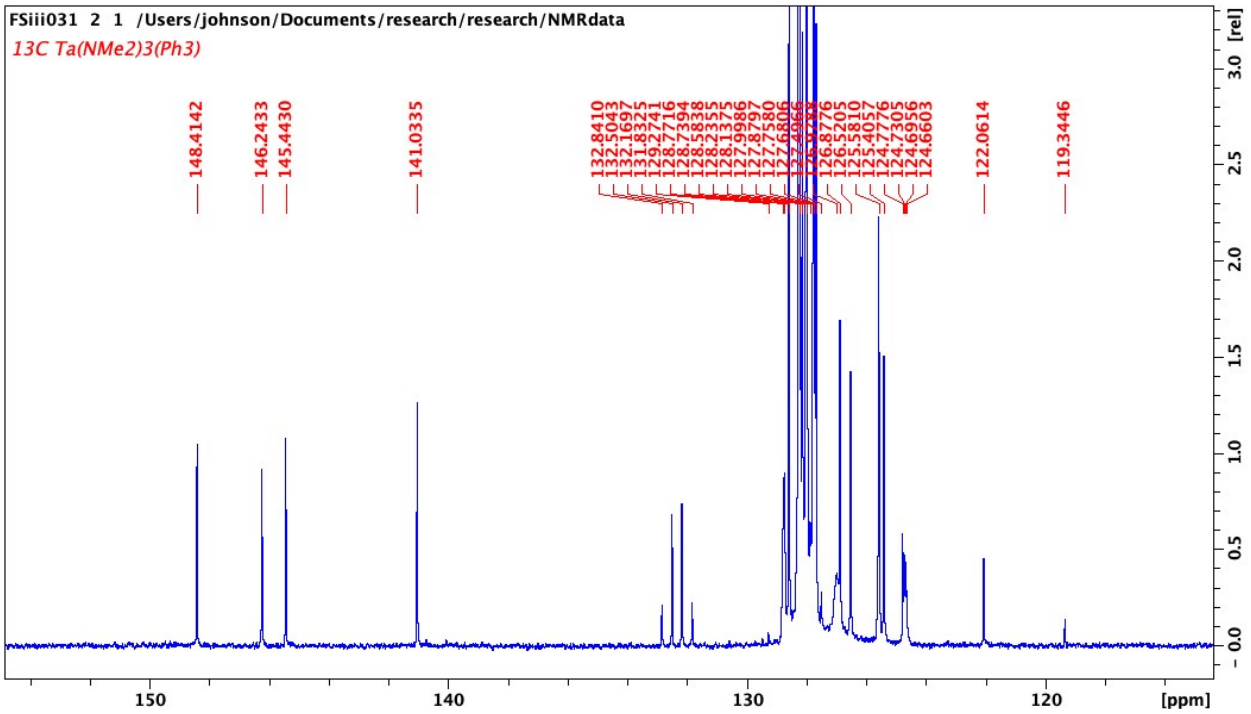
^{19}F NMR (376 MHz, C_6D_6) of **TaPh3** {Ta(Ph3)$(NMe_2)_3$}



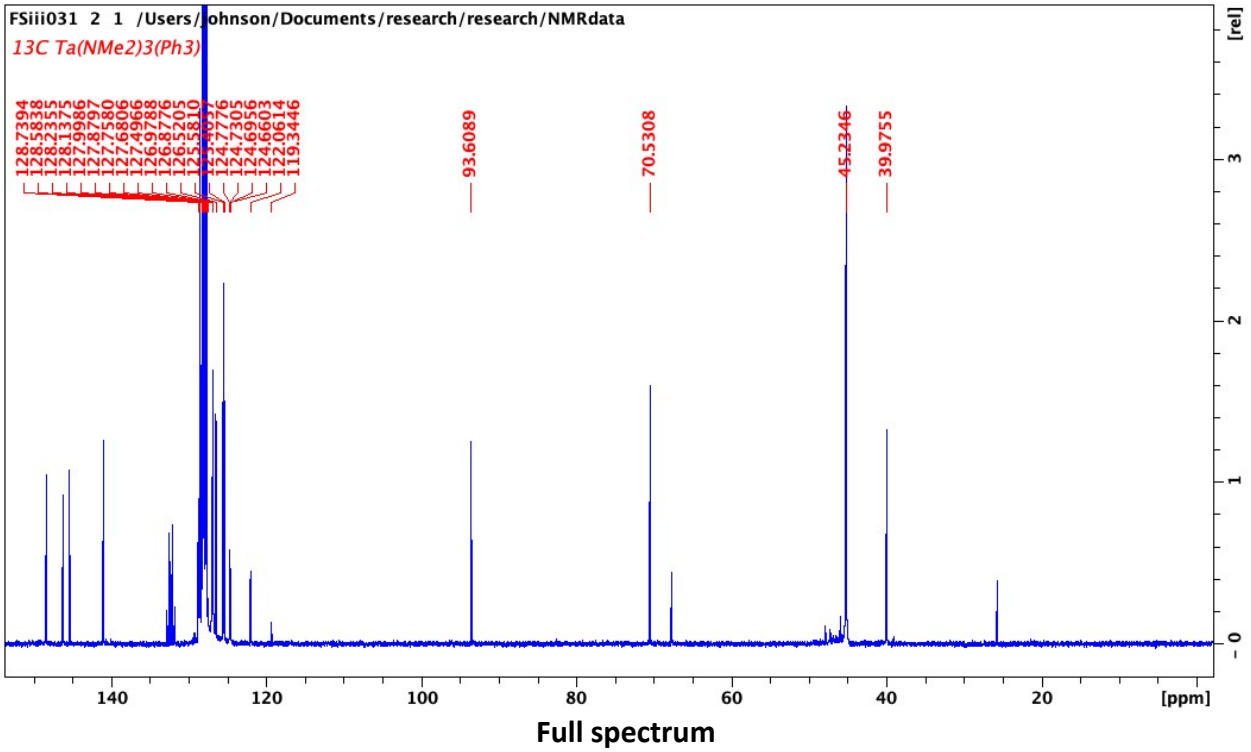
^{1}H NMR (400 MHz, C_6D_6) of **TaPh3** {Ta(Ph3)$(NMe_2)_3$}



^{13}C NMR (100 MHz, C_6D_6) of **TaPh3** {$Ta(Ph3)(NMe_2)_3$}

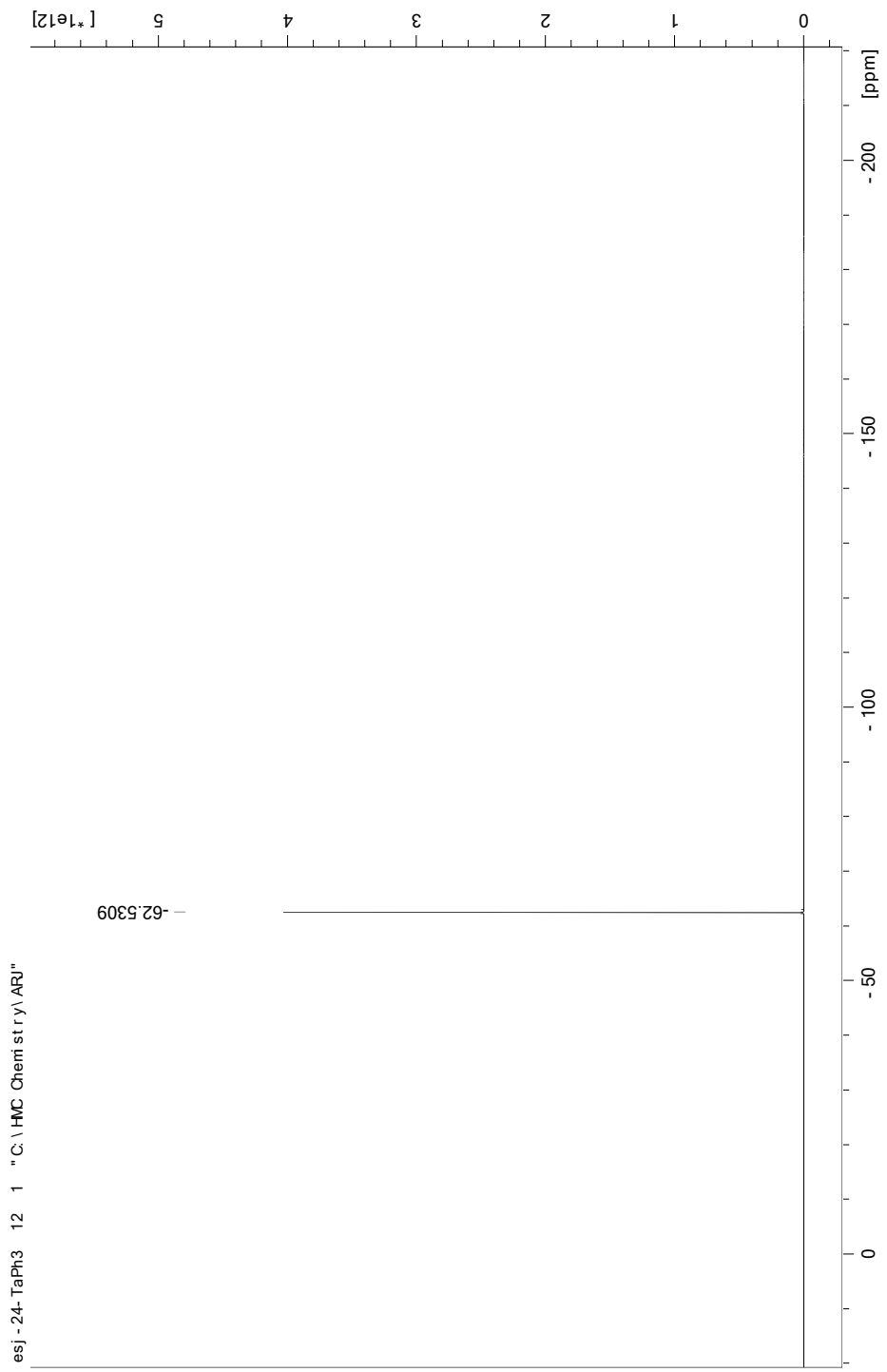


Aromatic Region

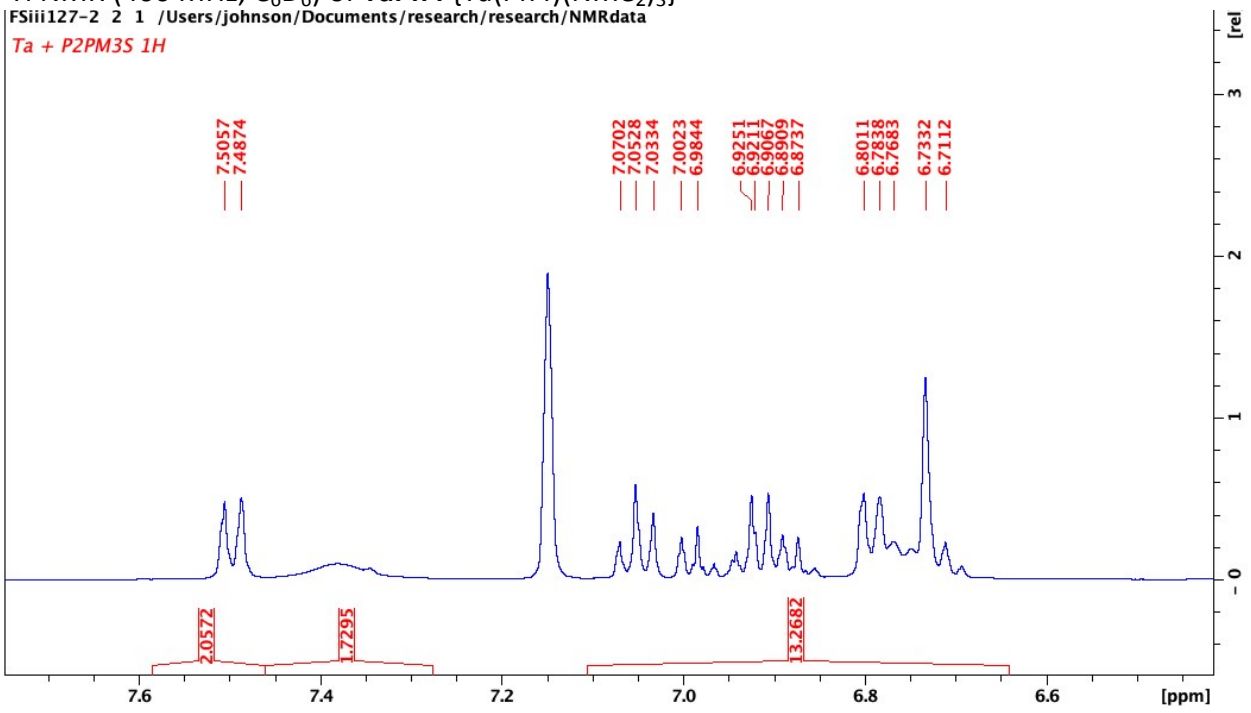


Full spectrum

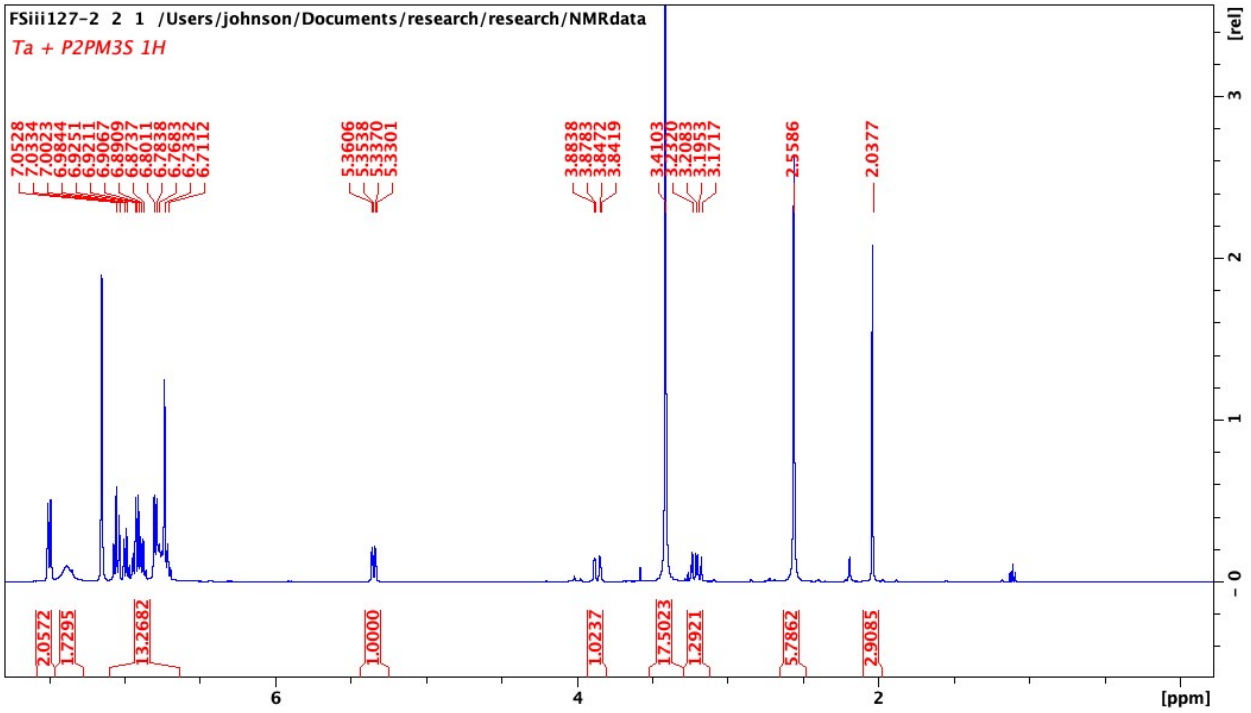
^{19}F NMR (376 MHz, C_6D_6) of **TaPh3** {$Ta(Ph3)(NMe_2)_3$}



^{1}H NMR (400 MHz, C_6D_6) of **TaPh4** {Ta(Ph4)(NMe_2)$_3$}

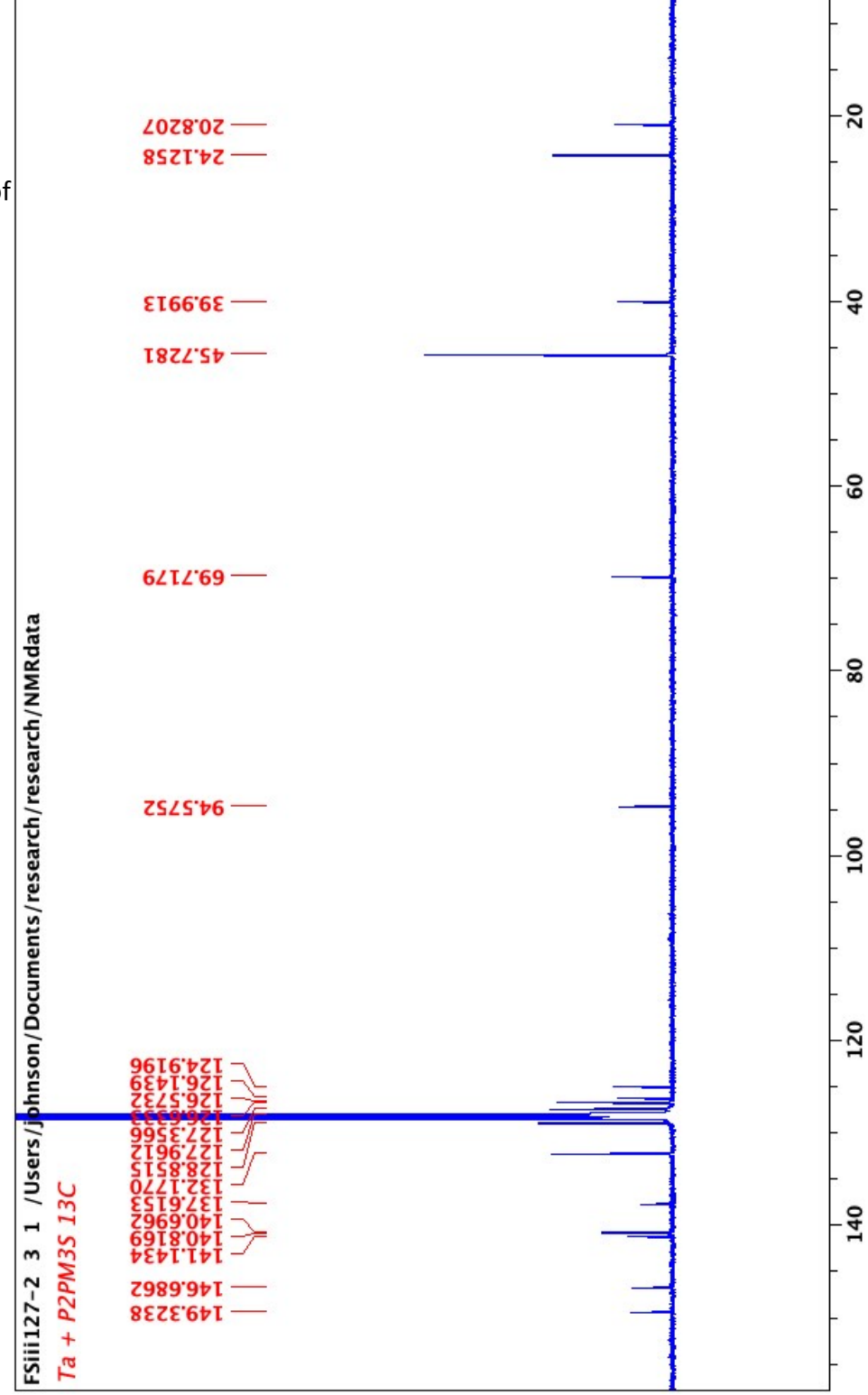


aromatic region

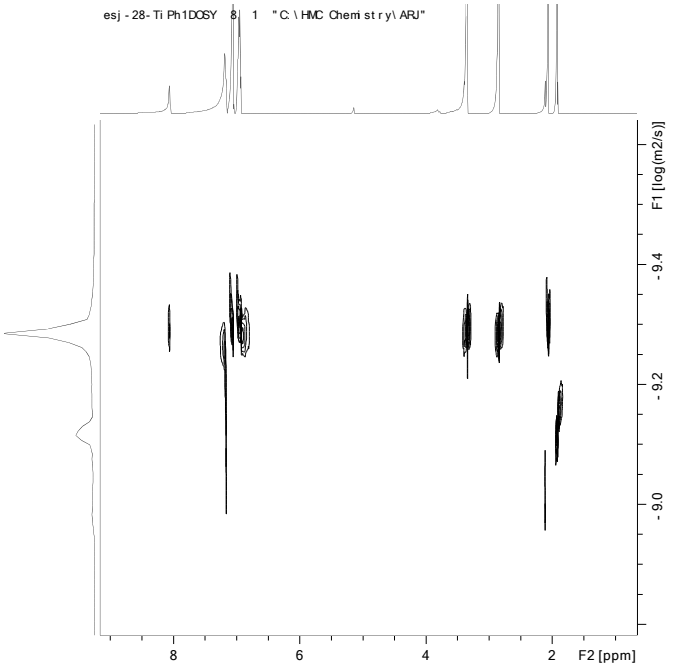


Full spectrum

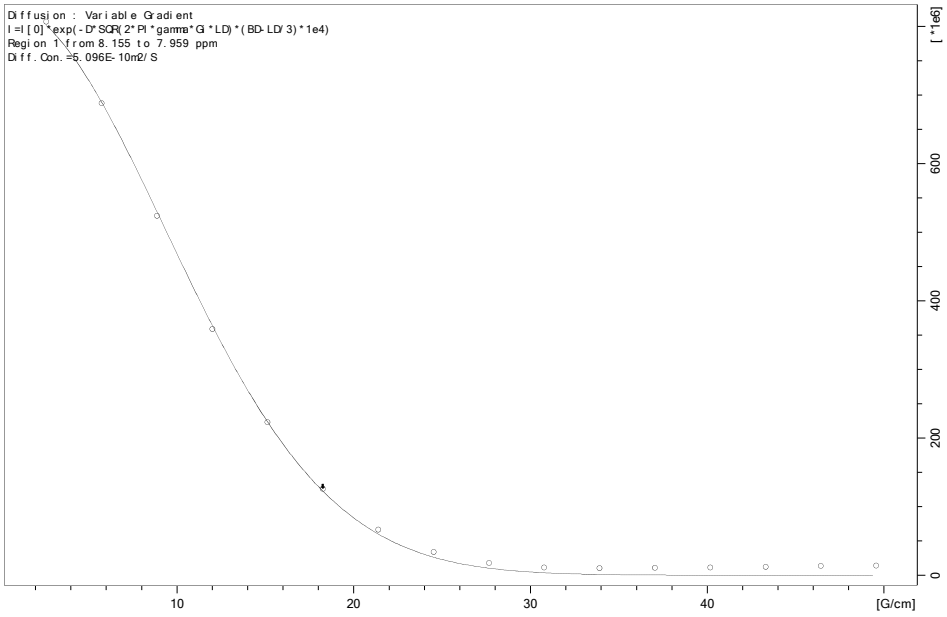
^{13}C NMR (100 MHz, C_6D_6) of



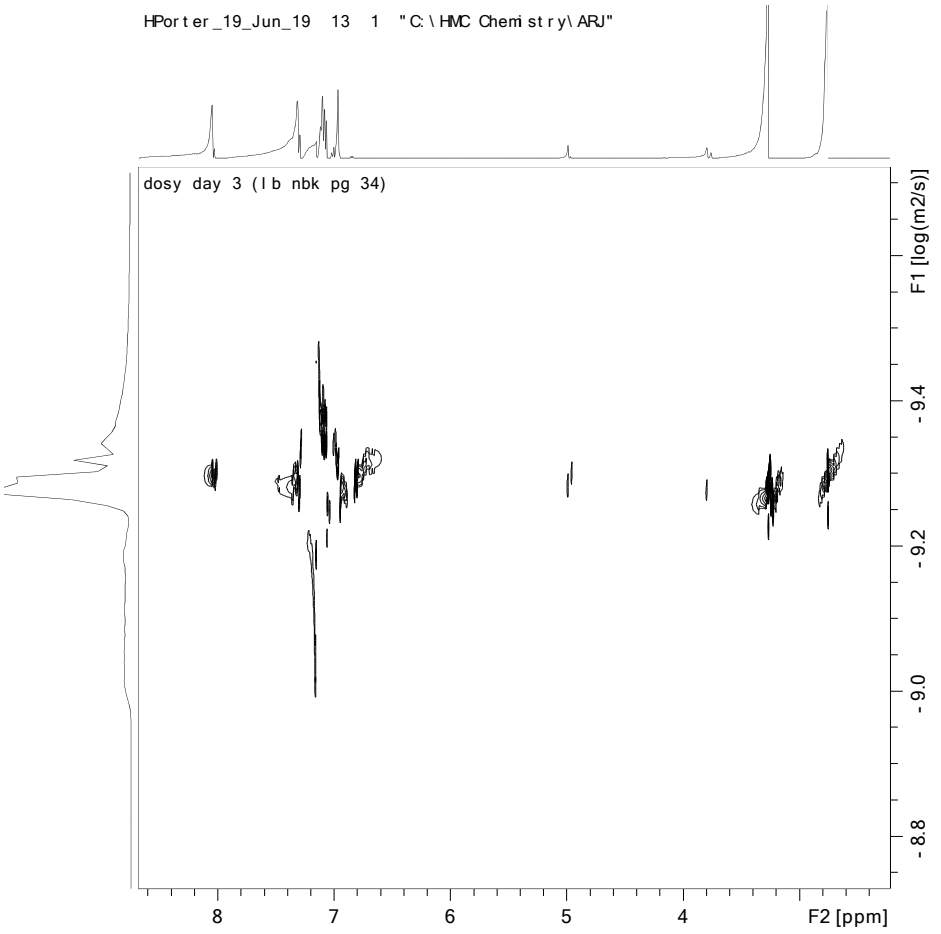
DOSY NMR (400 MHz, C_6D_6) of **TiPh1** {Ti(Ph1)$(NMe_2)_2(HNMe_2)$}



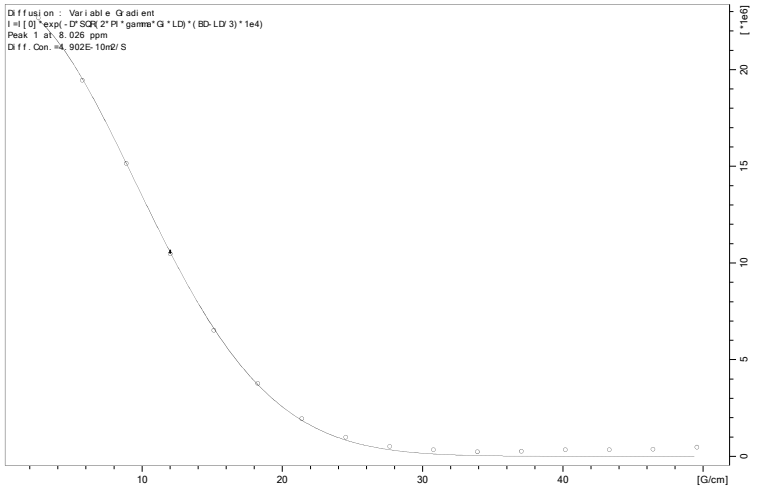
TiPh1 DOSY fit plot


Diffusion : Variable Gradient
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
Region 1\from 8.155 to 7.959 ppm
Diff. Con. =5.096E-10m2/S
[*1e6]
600
400
200
0
10
20
30
40
[G/cm]

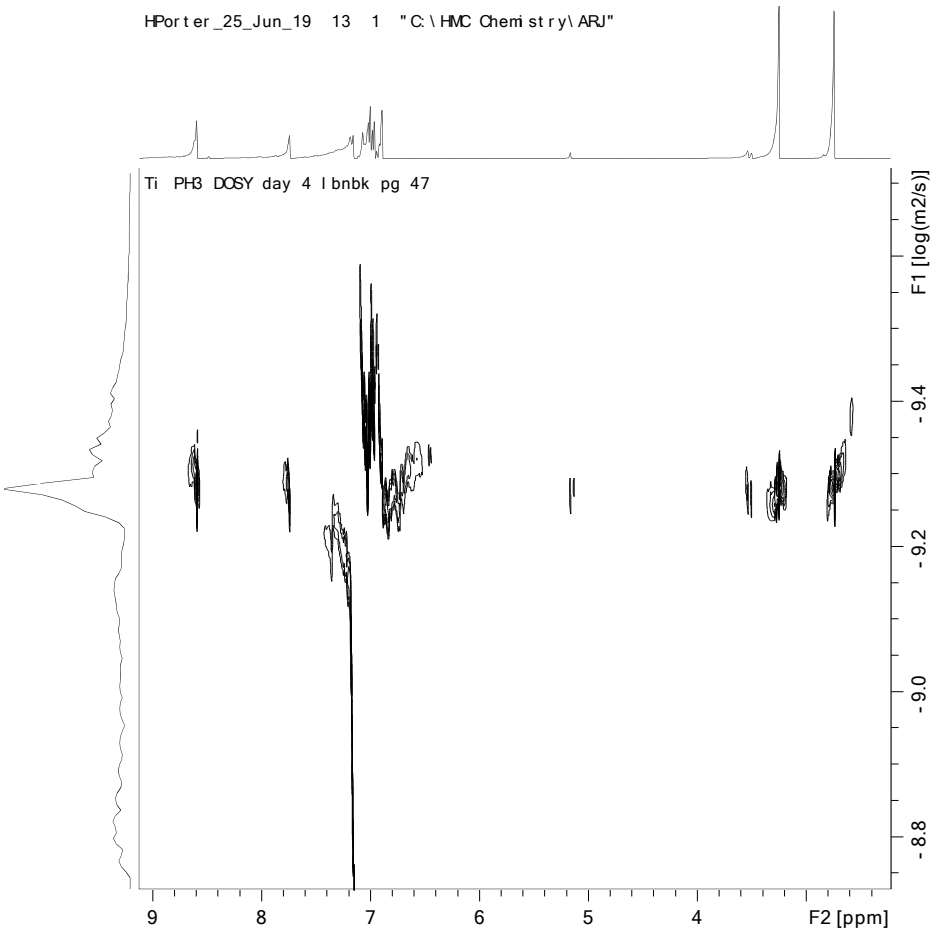
DOSY NMR (400 MHz, C_6D_6) of **TiPh2** {Ti(Ph2)$(NMe_2)_2(HNMe_2)$}



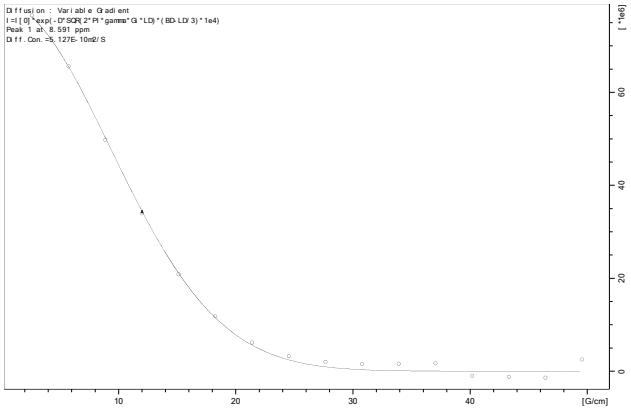
TiPh2 DOSY fit plot


Diffusion : Variable Gradient
I =I [0] *exp(- D* SQR(2* PI * gamma* Gi * LD) * (BD- LD/ 3) * 1e4)
Peak 1 at\ 8. 026 ppm
Diff. Con. =4. 902E- 10m2/ S
0
5
10
15
20
[*1e6]
10
20
30
40
[G/cm]

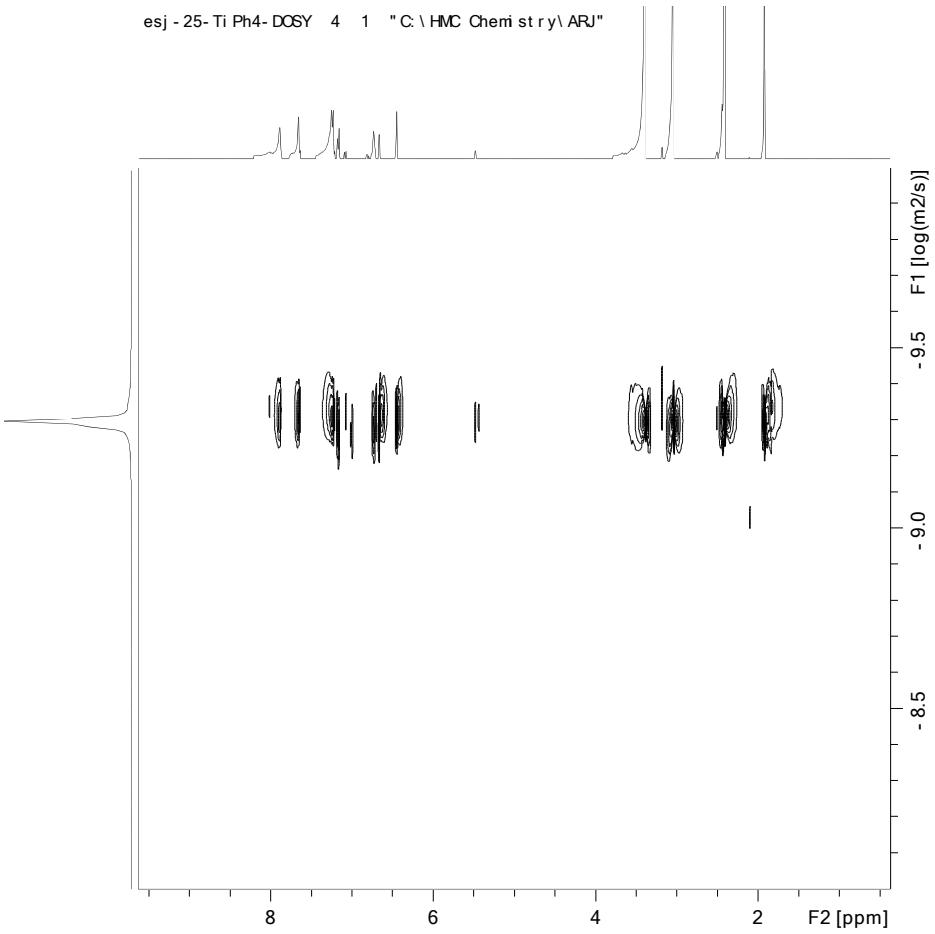
DOSY NMR (400 MHz, C_6D_6) of **TiPh3** {Ti(Ph3)$(NMe_2)_2(HNMe_2)$}



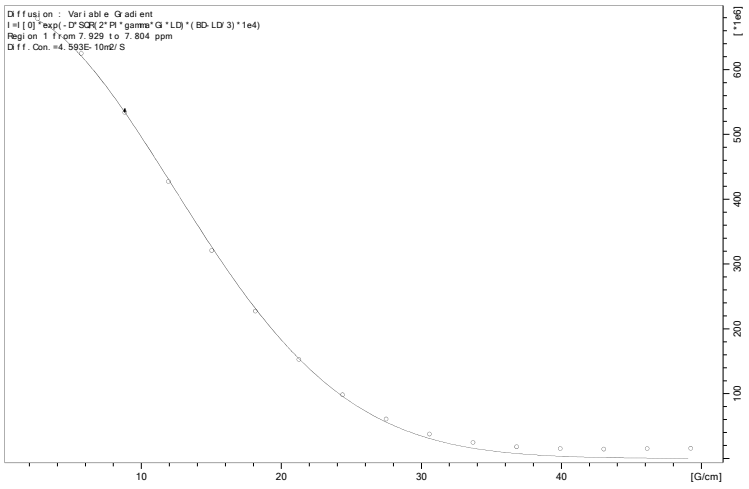
TiPh3 DOSY fit plot


Diffusion : Variable Gradient
I=I[0]*exp(-D*SQR(2*PI*gamma*G*LD)*(BD-LD/3)*1e4)
Peak 1 at 8.591 ppm
Diff. Con. =5.127E-10m2/S
[*1e6]
60
40
20
0
10
20
30
40
[G/cm]

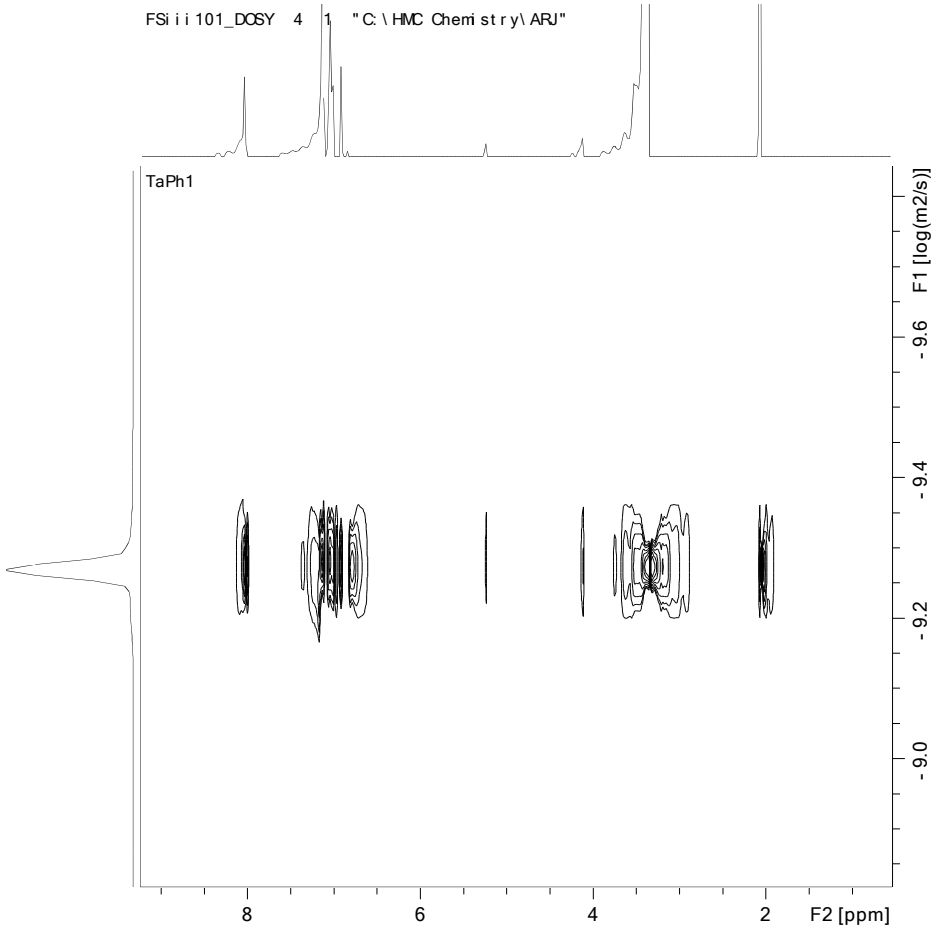
DOSY NMR (400 MHz, C_6D_6) of **TiPh4** {Ti(Ph4)$(NMe_2)_2$}



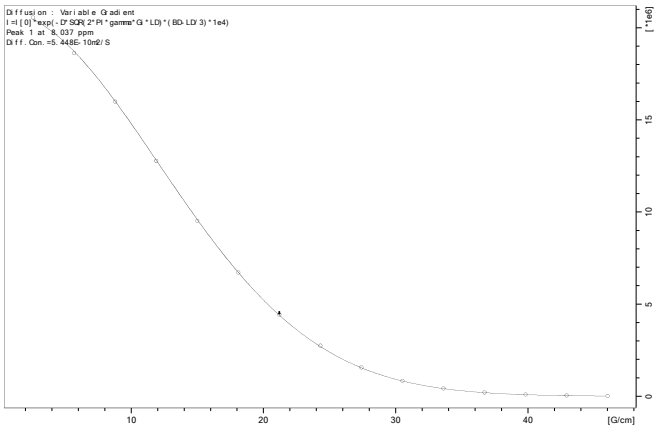
TiPh4 DOSY fit plot


Diffusion : Variable Gradient
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
Region 1 from 7.929 to 7.804 ppm
Diff. Con. =4.593E-10m2/S
[*1e6]
600
500
400
300
200
100
10
20
30
40
[G/cm]

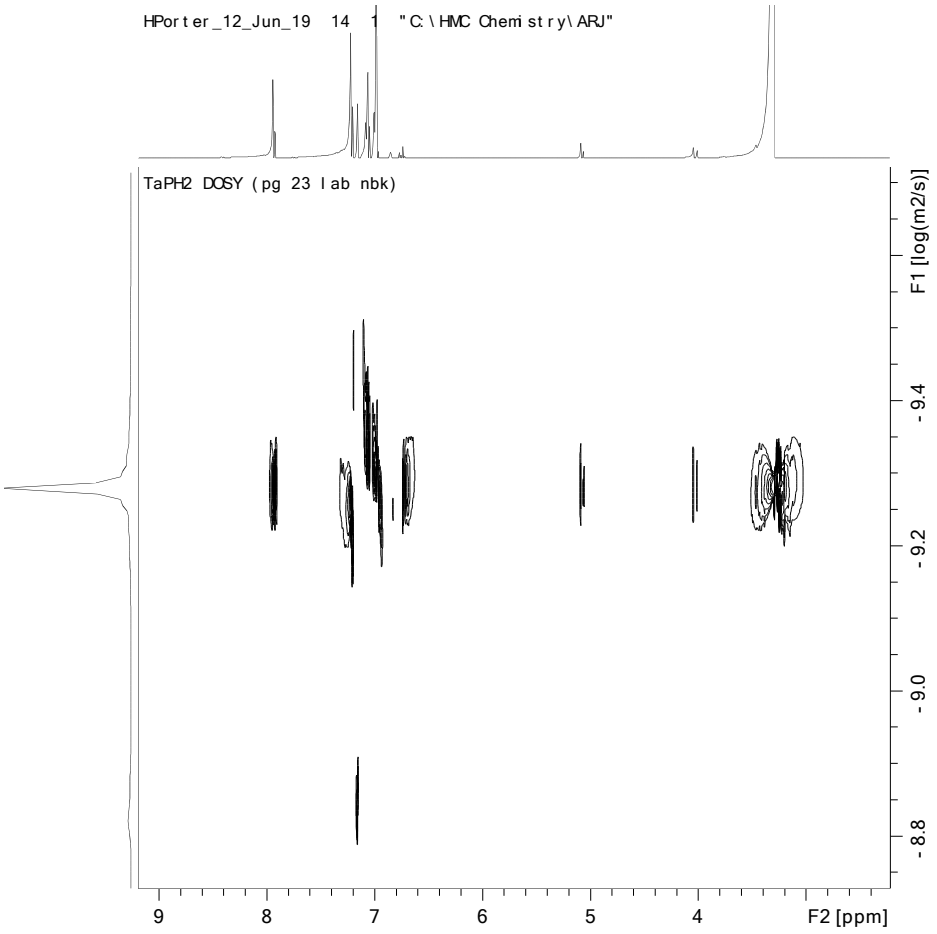
DOSY NMR (400 MHz, C_6D_6) of **TaPh1** {Ta(Ph1)$(NMe_2)_3$}



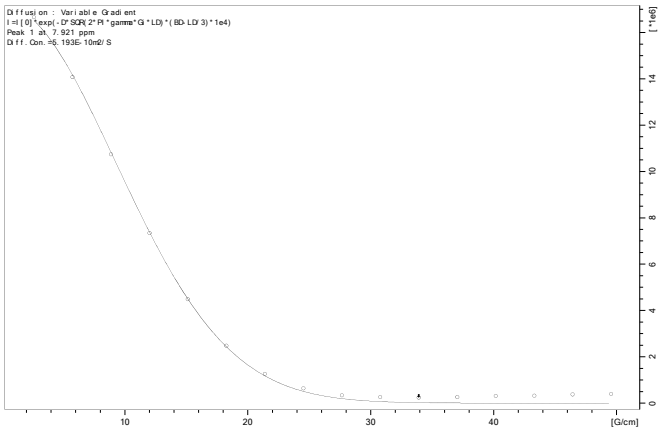
TaPh1 DOSY fit plot


Diffusion : Variable Gradient
I =I [0] * exp(- D* SQR(2* PI * gamma* G * LD) * (BD- LD/ 3) * 1e4)
Peak 1 at 8.037 ppm
Diff. Con. =5.448E-10m2/ S
[*1e6]
15
10
5
0
10
20
30
40
[G/cm]

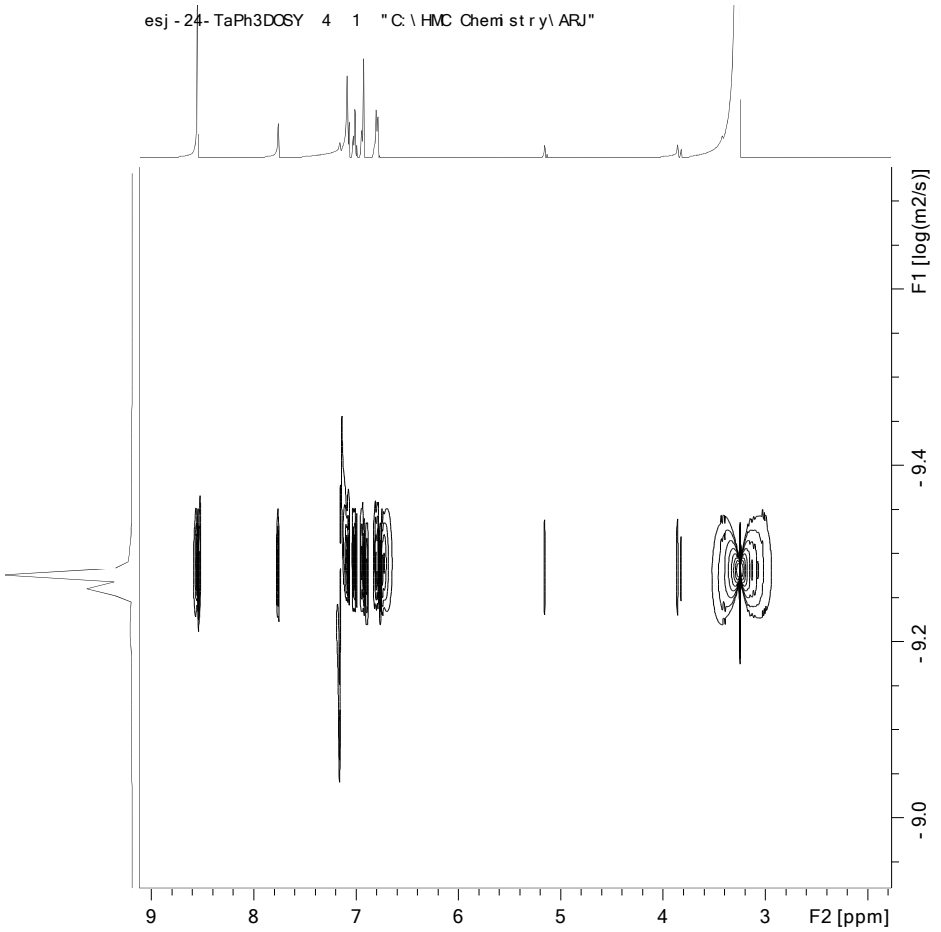
DOSY NMR (400 MHz, C_6D_6) of **TaPh2** {Ta(Ph2)$(NMe_2)_3$}



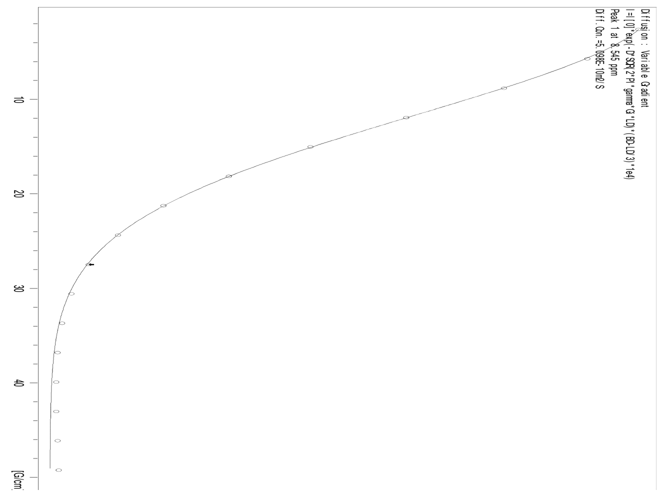
TaPh2 DOSY fit plot


Diffusion : Variable Gradient
I=I(0)*exp(-D*SQR(2*PI*gamma*G*LD)*(BD-LD/3)*1e4)
Peak 1 at: 7.921 ppm
Diff. Con.=5.193E-10m2/S
[*1e6]
0
2
4
6
8
10
12
14
10
20
30
40
[G/cm]

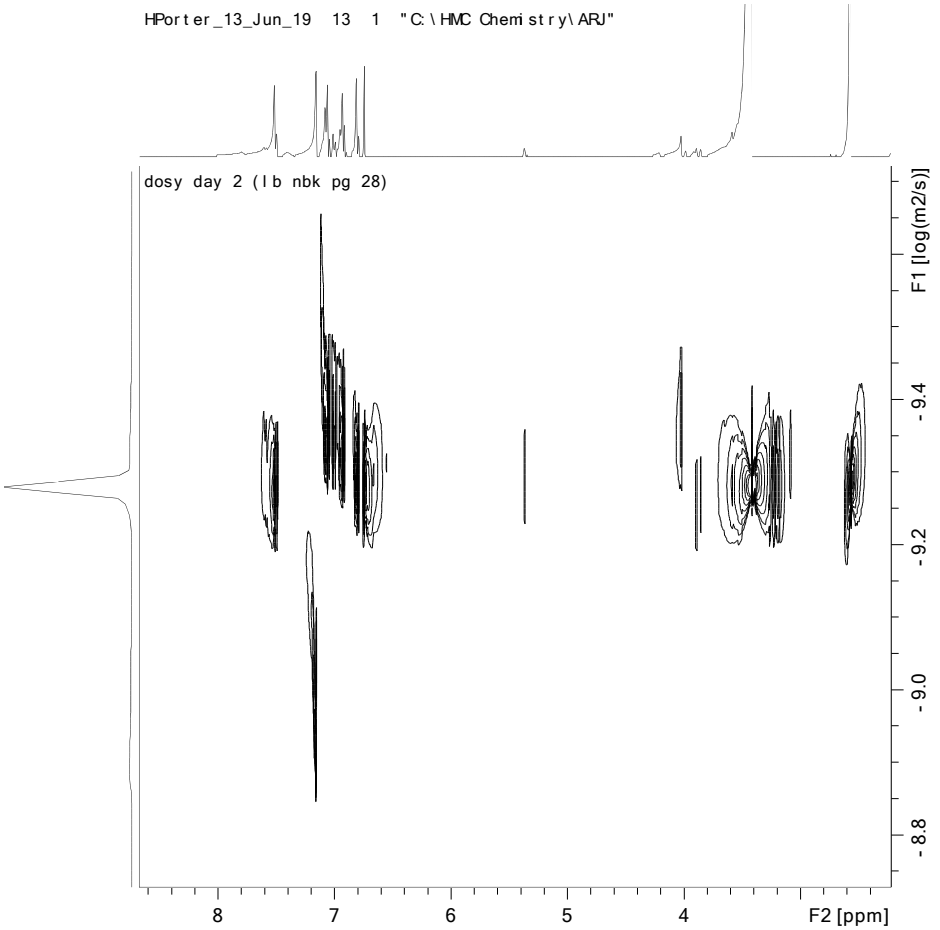
DOSY NMR (400 MHz, C_6D_6) of **TaPh3** {Ta(Ph3)$(NMe_2)_3$}



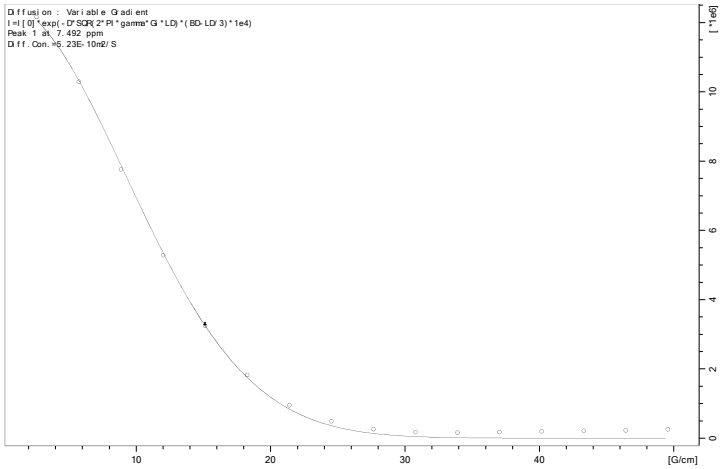
TaPh3 DOSY fit plot


Diffusion : Variable Gradient
I=I[0]*exp(-D*SQR(2*PI*gamma*G*LD)*(BD-LD/3)*1e4)
Peak 1 at 8.545 ppm
Diff. Con. =5.098E-10m2/s
10
20
30
40
[G/cm

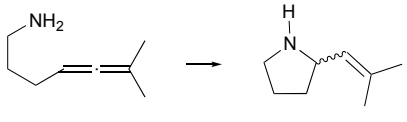
DOSY NMR (400 MHz, C_6D_6) of **TaPh4** {Ta(Ph4)$(NMe_2)_3$}



TaPh4 DOSY fit plot


Diffusion : Variable Gradient
I =I [0] *exp(- D*SQR(2* PI * gamma* G * LD) * (8D- LD/ 3) * 1e4)
Peak 1 at 7.492 ppm
Diff. Con. 45.23E-10m2/ S
[*1e6]
0
2
4
6
8
10
10
20
30
40
[G/cm]

GC traces for the hydroamination of 6-methyl-hepta-4,5-dienylamine 1b at 135 °C with *in situ* catalysts (5 mol% catalyst). Retention times are ± 0.3 min from run to run.

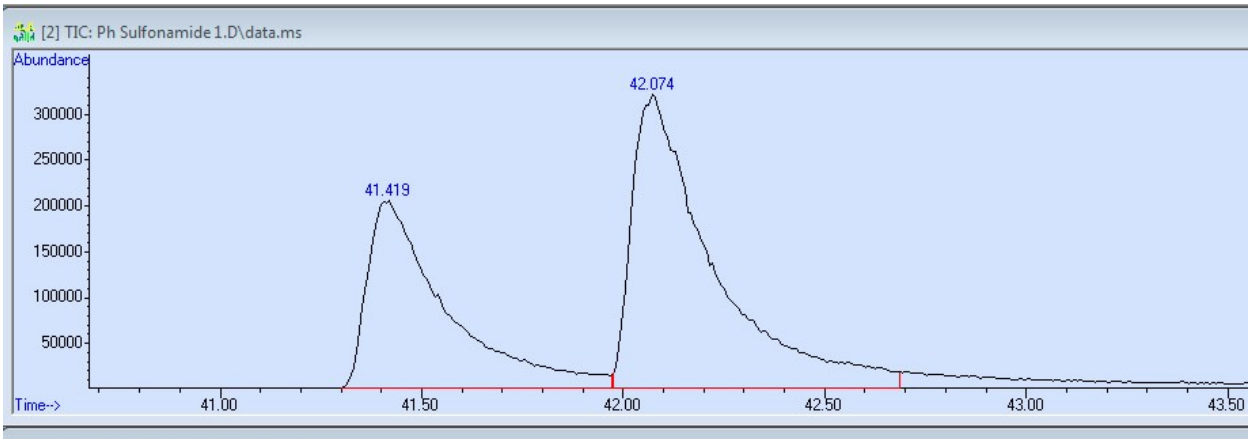


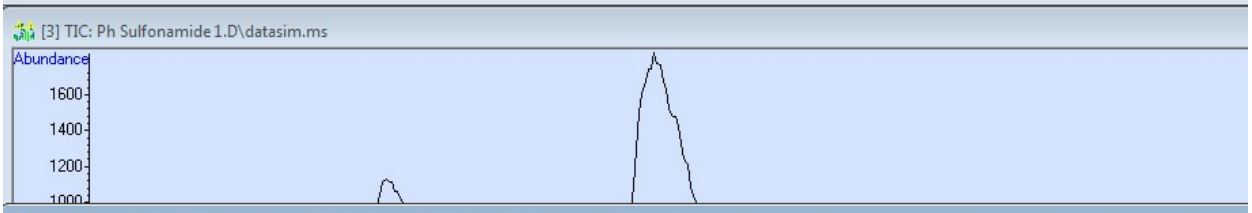
1b **3b**

41.5, 42.1 min

Representative GC traces are shown; each ee is an average of 2 injections for each of 2 runs.

TiPh1





D:\MassHunter\GCMS\1\data\Johnson Lab\Ph Sulfonamide 1.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : Ph Sulfonamide 1.D
Acq On : 12 Jul 2018 09:37
Operator : arj
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

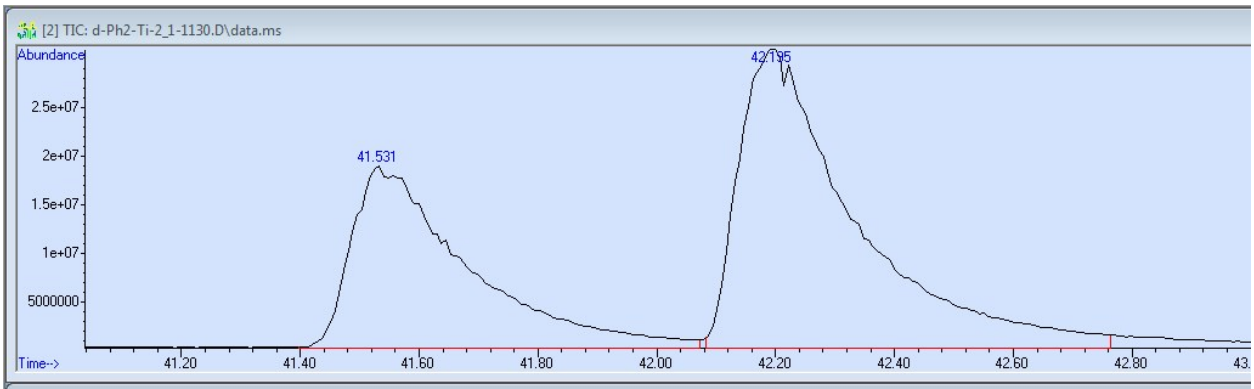
Integration Parameters: events.e
Integrator: ChemStation

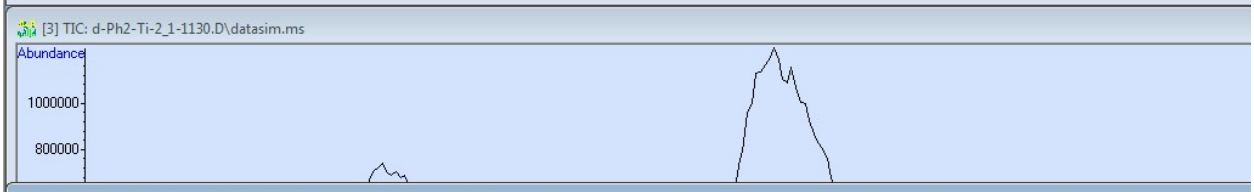
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: Ph Sulfonamide 1.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.419	4840	4856	4930	M	205798	27718937	61.97%	38.259%
2	42.074	4930	4943	5025	M2	321987	44731316	100.00%	61.741%

TiPh2





D:\MassHunter\GCMS\1\data\Johnson Lab\d-Ph2-Ti-2_1-1130.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : d-Ph2-Ti-2_1-1130.D
Acq On : 30 Nov 2018 09:46
Operator : fs
Sample : di-Ph2-Ti
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

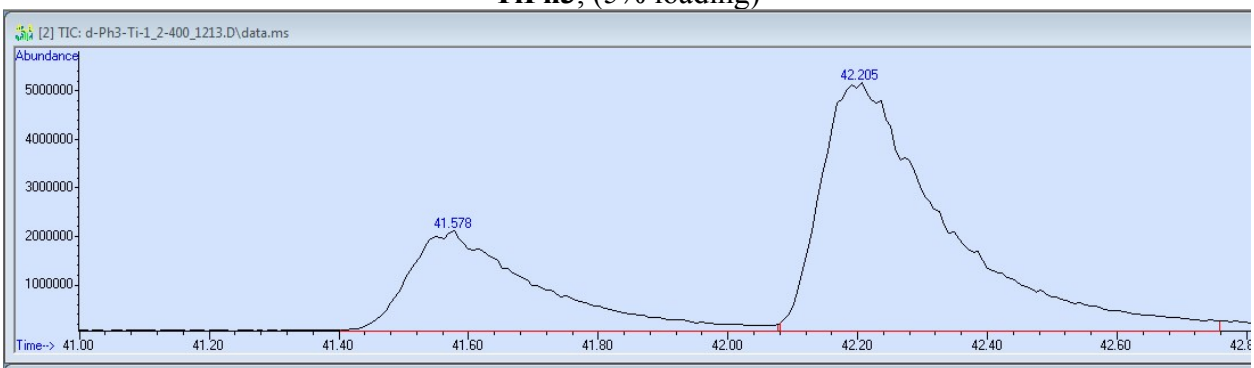
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

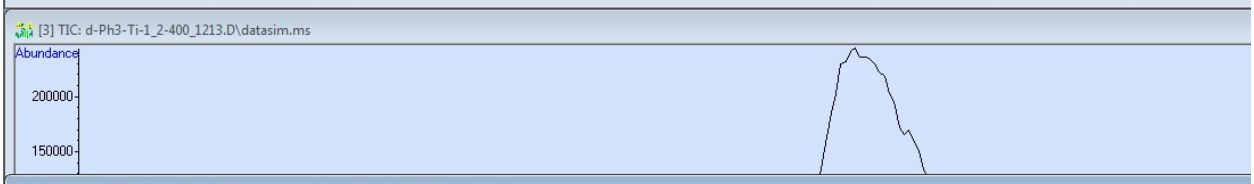
Signal : TIC: d-Ph2-Ti-2_1-1130.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.531	4853	4871	4943	M	18901659	2555789535	60.63%	37.745%
2	42.195	4944	4959	5035	M2	30912987	4215494111	100.00%	62.255%

Sum of corrected areas: 6771283646

TiPh3, (5% loading)





D:\MassHunter\GCMS\1\data\Johnson Lab\d-Ph3-Ti-1_2-400_1213.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : d-Ph3-Ti-1_2-400_1213.D
Acq On : 13 Dec 2018 11:53
Operator : fs
Sample : di-Ph3-Ti
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

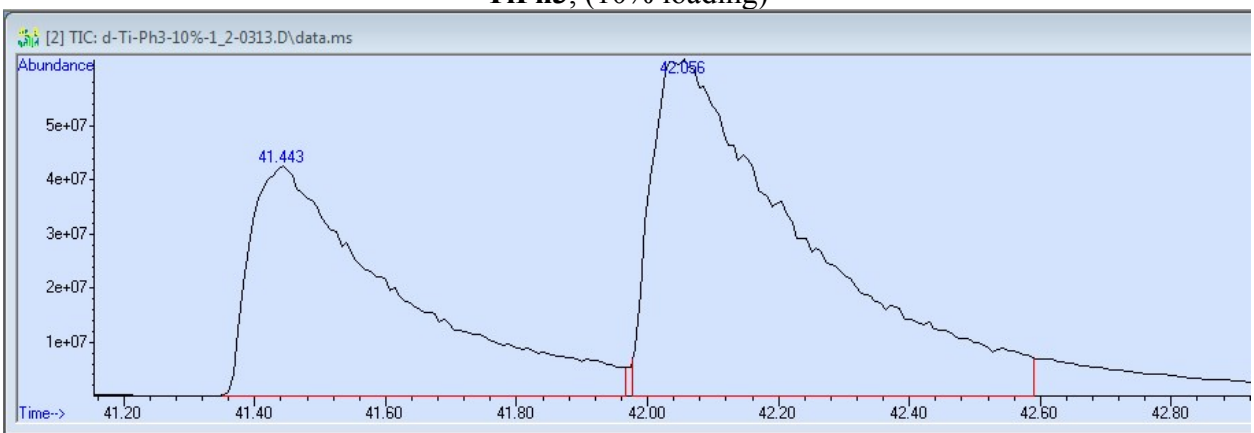
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: d-Ph3-Ti-1_2-400_1213.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.578	4854	4877	4944	M6	2057874	285417725	41.45%	29.302%
2	42.205	4944	4961	5035	M4	5125755	688622622	100.00%	70.698%

Sum of corrected areas: 974040347

TiPh3, (10% loading)



D:\MassHunter\GCMS\1\data\Johnson Lab\d-Ti-Ph3-10%-1_2-0313.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : d-Ti-Ph3-10%-1_2-0313.D
Acq On : 14 Mar 2019 02:24
Operator : fs
Sample : d-Ti-Ph3-10%-1_2
Misc :
ALS Vial : 5 Sample Multiplier: 1

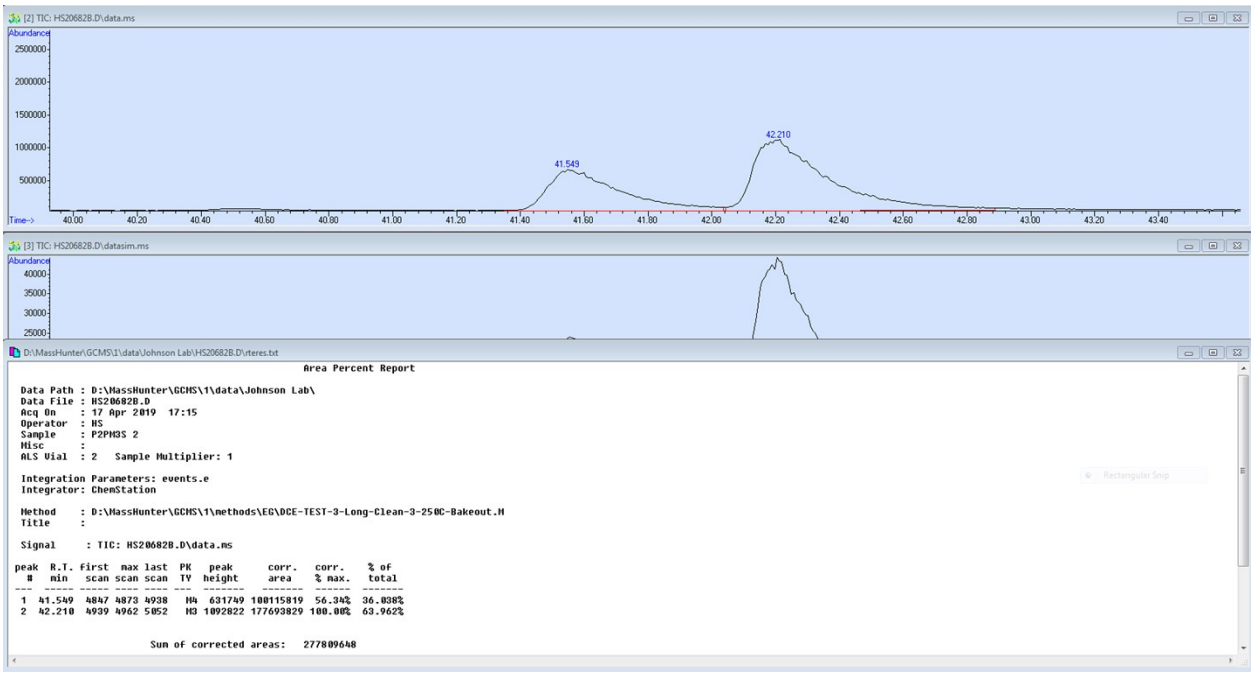
Integration Parameters: events.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: d-Ti-Ph3-10%-1_2-0313.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.443	4847	4859	4929	M	42571901	6694813677	65.64%	39.628%
2	42.056	4930	4941	5012	M3	62350679	10199310990	100.00%	60.372%

TiPh4



Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : HS20682B.D
Acq On : 17 Apr 2019 17:15
Operator : HS
Sample : P2PH3S 2
Misc :
ALS Vial : 2 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

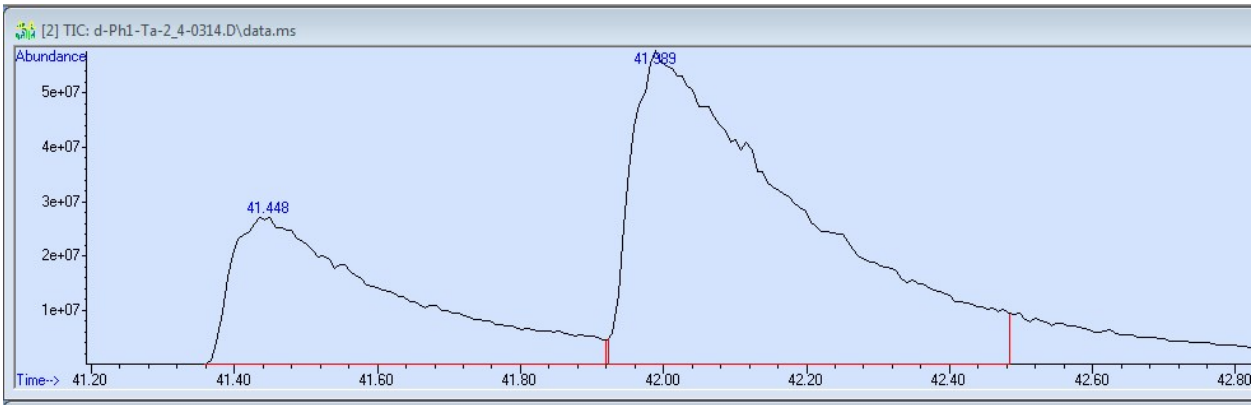
Method : D:\MassHunter\GCMS\1\methods\EG\DCE-TEST-3-Long-Clean-3-250C-Bakeout.M
Title :

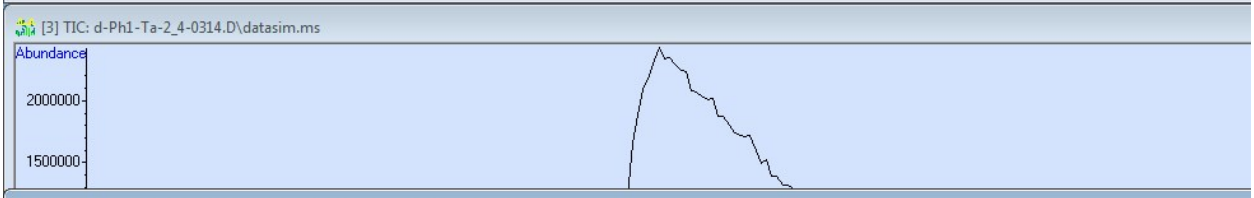
Signal : TIC: HS20682B.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.549	4847	4873	4938	M4	631749	100115819	56.34%	36.038%
2	42.210	4939	4962	5052	M3	1092822	177693829	100.00%	63.962%

Sum of corrected areas: 277809648

TaPh1





D:\MassHunter\GCMS\1\data\Johnson Lab\d-Ph1-Ta-2_4-0314.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : d-Ph1-Ta-2_4-0314.D
Acq On : 14 Mar 2019 19:55
Operator : fs
Sample : d-Ph1-Ta-2_4
Misc :
ALS Vial : 2 Sample Multiplier: 1

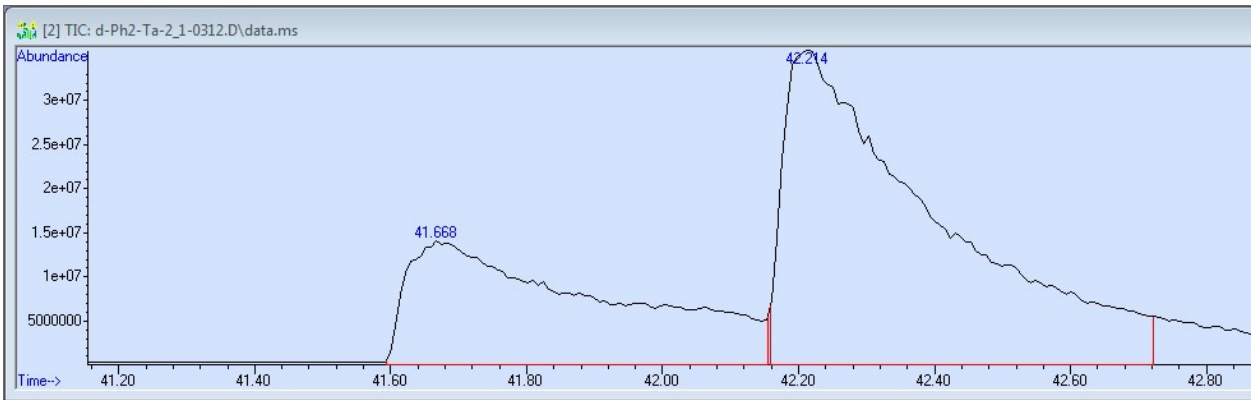
Integration Parameters: events.e
Integrator: ChemStation

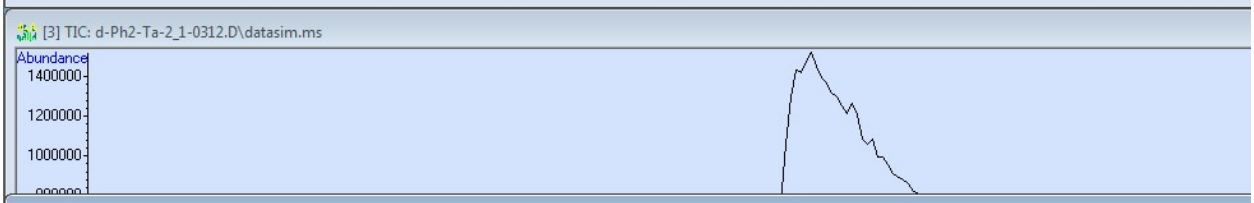
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: d-Ph1-Ta-2_4-0314.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.448	4848	4860	4923	M2	27152433	4332552889	45.39%	31.220%
2	41.989	4923	4932	4998	M2	57709509	9545005380	100.00%	68.780%

TaPh2





D:\MassHunter\GCMS\1\data\Johnson Lab\d-Ph2-Ta-2_1-0312.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : d-Ph2-Ta-2_1-0312.D
Acq On : 13 Mar 2019 10:23
Operator : fs
Sample : d-Ta-Ph2(2-1)
Misc :
ALS Vial : 8 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

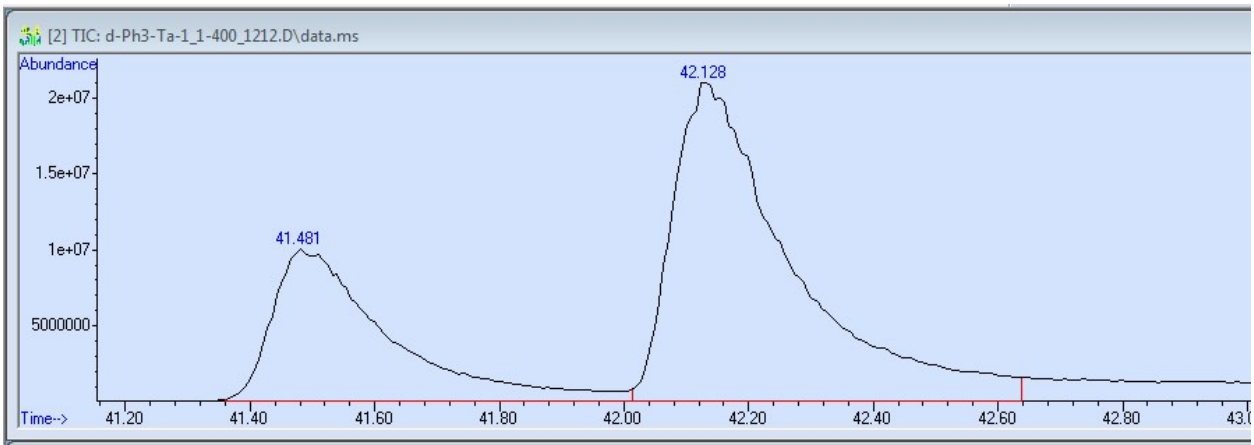
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: d-Ph2-Ta-2_1-0312.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.668	4879	4889	4954	M3	14021431	2842792639	51.11%	33.825%
2	42.214	4955	4962	5030	M2	35640343	5561592609	100.00%	66.175%

Sum of corrected areas: 8404385248

TaPh3



D:\MassHunter\GCMS\1\data\Johnson Lab\d-Ph3-Ta-1_1-400_1212.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : d-Ph3-Ta-1_1-400_1212.D
Acq On : 12 Dec 2018 15:52
Operator : fs
Sample : d-Ph3-Ta
Misc :
ALS Vial : 2 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

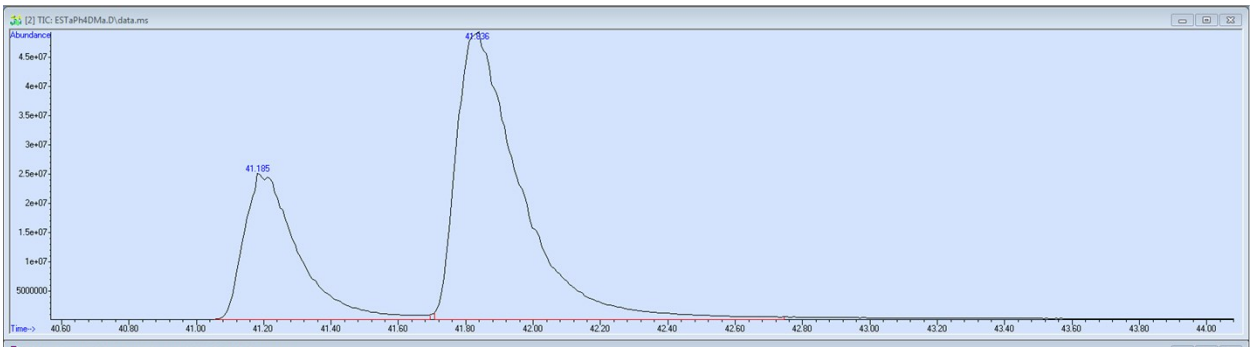
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: d-Ph3-Ta-1_1-400_1212.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.481	4848	4864	4935	M5	10041750	1302024696	46.59%	31.782%
2	42.128	4935	4951	5019	M2	21012239	2794650458	100.00%	68.218%

Sum of corrected areas: 4096675154

TaPh4



D:\MassHunter\GCMS\1\data\Johnson Lab\ESTaPh4DMa.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : ESTaPh4DMa.D
Acq On : 31 Jan 2020 14:06
Operator : ES
Sample : TaPh4DMesj-30a
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

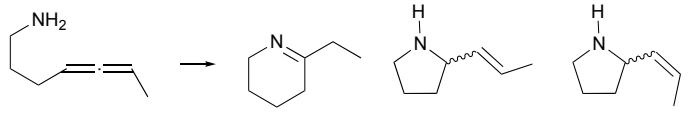
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\VLSI036.D\chiraldexbDM_400split_new.M
Title :

Signal : TIC: ESTaPh4DMa.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	41.185	4807	4824	4893	M	25326946	2808111707	42.98%	30.059%
2	41.836	4894	4912	5033	M3	49544113	6533739132	100.00%	69.941%

Sum of corrected areas: 9341850838

Hydroamination of hepta-4,5-dienylamine at 110 °C with *in situ* catalysts (5 mol% catalyst) to give tetrahydropyridine **2a**, *Z*- or *E*-α-vinylpyrrolidines *Z*- and *E*-**3a**. Retention times are ± 0.3 min from run to run.

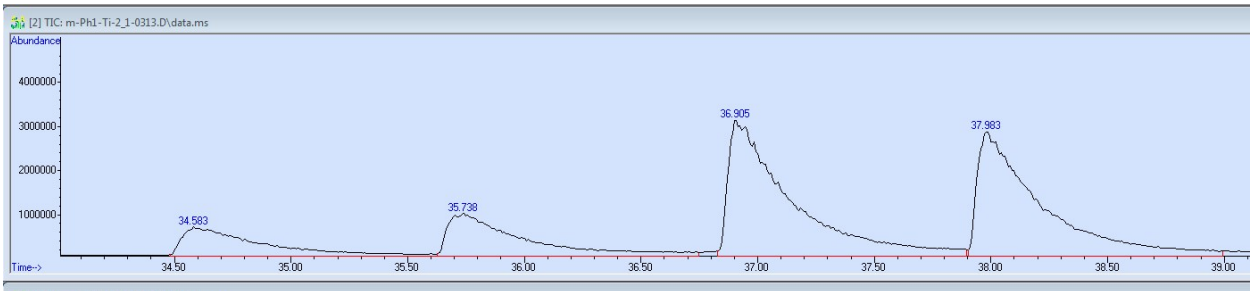


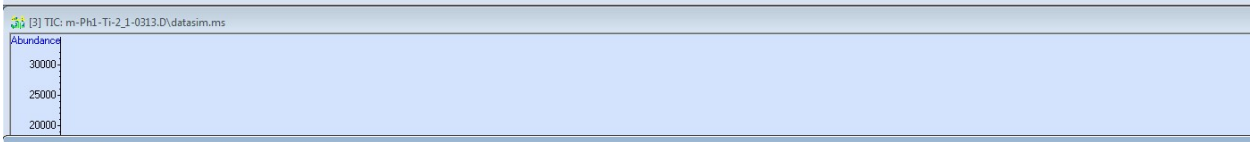
1a **2a** ***E*-3a** ***Z*-3a**

34.5, 35.7 min **36.9, 37.9 min**

Representative GC traces are shown; each ee is an average of 2 injections for each of 2 runs.

TiPh1





D:\MassHunter\GCMS\1\data\Johnson Lab\m-Ph1-Ti-2_1-0313.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : m-Ph1-Ti-2_1-0313.D
Acq On : 13 Mar 2019 22:52
Operator : fs
Sample : m-Ph1-Ti-2_1
Misc :
ALS Vial : 4 Sample Multiplier: 1

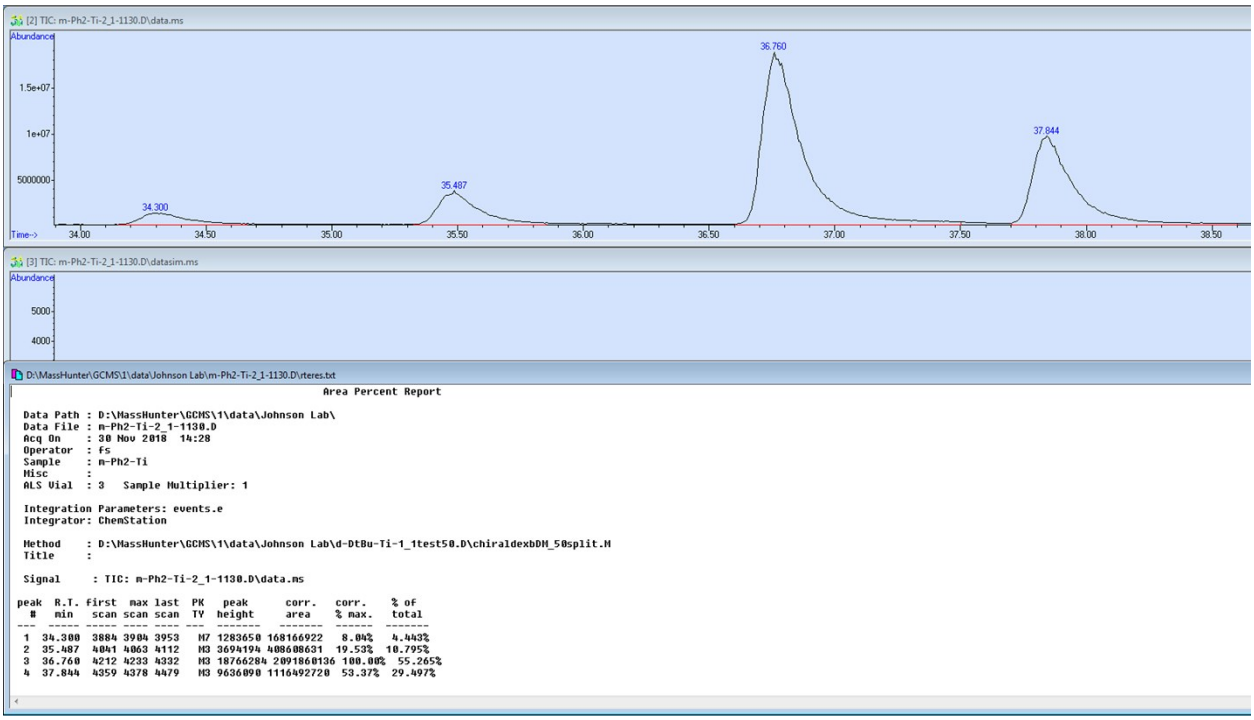
Integration Parameters: events.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: m-Ph1-Ti-2_1-0313.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	34.583	3929	3942	4082	M5	662570	153442943	26.86%	10.423%
2	35.738	4082	4097	4232	M3	971880	215271671	37.68%	14.623%
3	36.905	4242	4253	4385	M2	3097344	571347799	100.00%	38.810%
4	37.983	4386	4397	4532	M2	2831947	532091604	93.13%	36.144%

TiPh2



Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : m-Ph2-Ti-2_1-1130.D
Acq On : 30 Nov 2018 14:28
Operator : fs
Sample : m-Ph2-Ti
Misc :
ALS Vial : 3 Sample Multiplier: 1

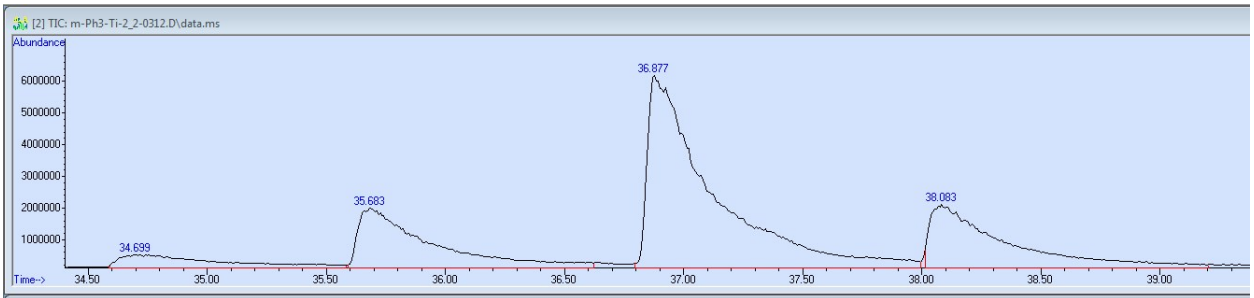
Integration Parameters: events.e
Integrator: ChemStation

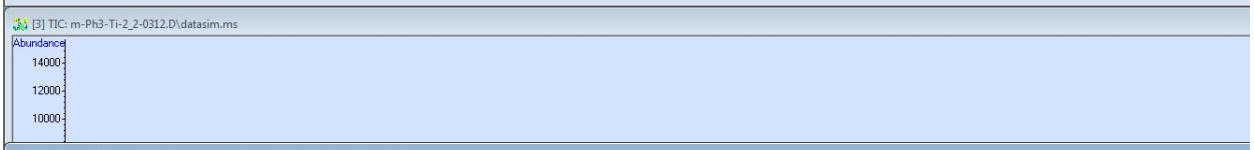
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDH_50split.M
Title :

Signal : TIC: m-Ph2-Ti-2_1-1130.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	34.300	3884	3904	3953	M7	1283650	168166922	8.04%	4.443%
2	35.487	4041	4063	4112	M3	3694194	408608631	19.53%	10.795%
3	36.760	4212	4233	4332	M3	18766284	2091860136	100.00%	55.265%
4	37.844	4359	4378	4479	M3	9636090	1116492720	53.37%	29.497%

TiPh3





D:\MassHunter\GCMS\1\data\Johnson Lab\m-Ph3-Ti-2_2-0312.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : m-Ph3-Ti-2_2-0312.D
Acq On : 13 Mar 2019 02:10
Operator : fs
Sample : m-Ti-Ph3(2-2)
Misc :
ALS Vial : 4 Sample Multiplier: 1

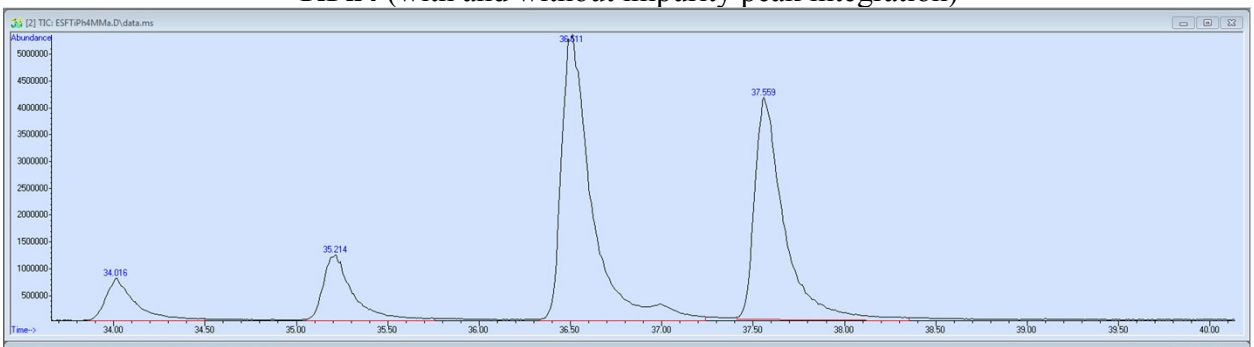
Integration Parameters: events.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: m-Ph3-Ti-2_2-0312.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	34.699	3943	3958	4076	M7	421937	122760228	10.68%	5.831%
2	35.683	4077	4089	4215	M4	1902082	395991699	34.47%	18.809%
3	36.877	4238	4249	4398	M2	6091600	1148943845	100.00%	54.573%
4	38.083	4401	4410	4560	M3	2012890	437628475	38.09%	20.787%

TiPh4 (with and without impurity peak integration)



D:\MassHunter\GCMS\1\data\Johnson Lab\ESFTiPh4MMa.D\rteres.txt

Area Percent Report

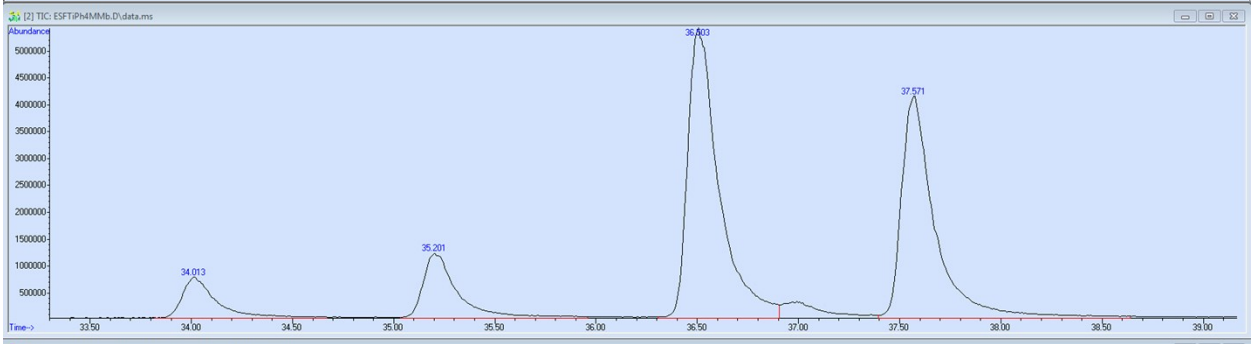
Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : ESFTiPh4MMa.D
Acq On : 01 Feb 2020 04:12
Operator : ES
Sample : FTiPh4MMa
Misc :
ALS Vial : 7 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\data\Johnson Lab\VLSI036.D\chiraldexbDH_400split_new.M
Title :

Signal : TIC: ESFTiPh4MMa.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	34.016	3846	3866	3931	M3	798836	88639838	14.36%	6.741%
2	35.214	4005	4027	4099	M4	1235964	140033784	22.69%	10.650%
3	36.511	4176	4200	4297	M2	5345883	617155642	100.00%	46.937%
4	37.559	4320	4340	4446	M3	4147628	469036775	76.00%	35.672%



D:\MassHunter\GCMS\1\data\Johnson Lab\ESFTiPh4MMb.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : ESFTiPh4MMb.D
Acq On : 01 Feb 2020 05:23
Operator : ES
Sample : FTiPh4MMb
Misc :
ALS Vial : 7 Sample Multiplier: 1

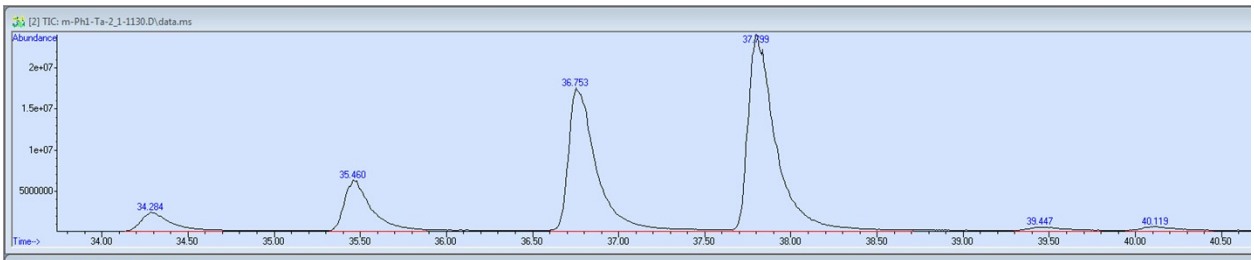
Integration Parameters: events.e
Integrator: ChemStation

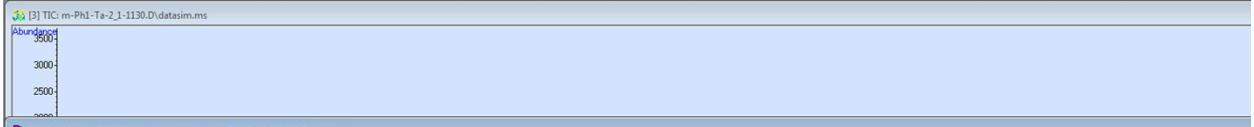
Method : D:\MassHunter\GCMS\1\data\Johnson Lab\VLSI036.D\chiraldexbDH_400split_new.M
Title :

Signal : TIC: ESFTiPh4MMb.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	34.013	3840	3866	3954	M3	762992	91403599	15.75%	7.055%
2	35.201	4002	4025	4126	M4	1211272	144357468	24.88%	11.143%
3	36.503	4173	4199	4252	M2	5411810	580186445	100.00%	44.784%
4	37.571	4318	4342	4484	M2	4150883	479588107	82.66%	37.019%

TaPh1

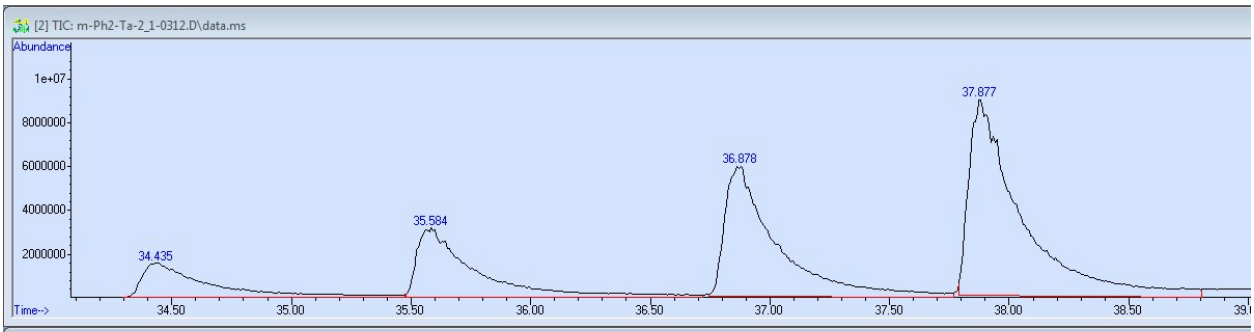




D:\MassHunter\GCMS\1\data\Johnson Lab\m-Ph1-Ta-2_1-1130.D\rteres.txt

```
Data File : m-Ph1-Ta-2_1-1130.D
Acq On    : 30 Nov 2018  16:49
Operator  : fs
Sample    : m-Ph1-Ta
Misc      :
ALS Vial  : 4   Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method    : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDH_50split.M
Title     :

Signal     : TIC: m-Ph1-Ta-2_1-1130.D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #   min   scan scan scan  TY  height     area    % max.   total
---  ----- ----- ---- ---- --- -------  -------  ------  -------
 1  34.284  3882 3902 3958   M5 2299519 279257306  10.30%   4.775%
 2  35.460  4041 4059 4116   M3 6278352 683082893  25.22%  11.683%
 3  36.753  4212 4232 4354   M3 17429660 1995671783  73.68%  34.125%
 4  37.799  4354 4372 4493   M2 23976893 2711379459 100.00%  46.364%
 5  39.447  4572 4592 4639   M5  492856  86058710   3.17%   1.472%

 6  40.119  4659 4682 4726   M2  560017  91874909   3.39%   1.571%
```

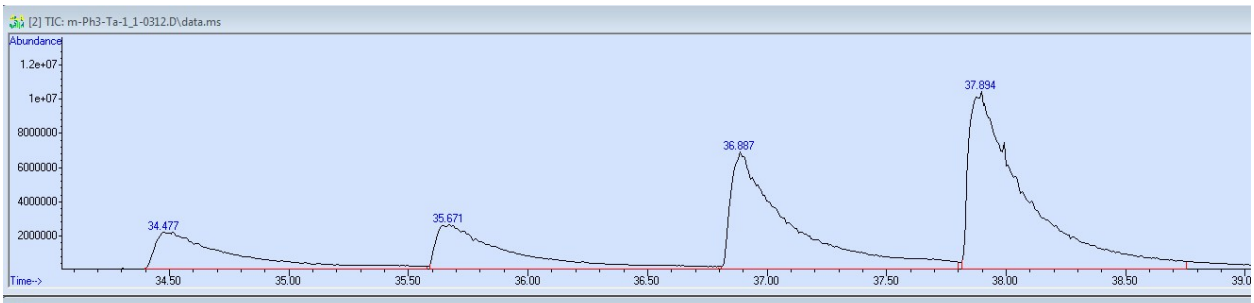
TaPh2

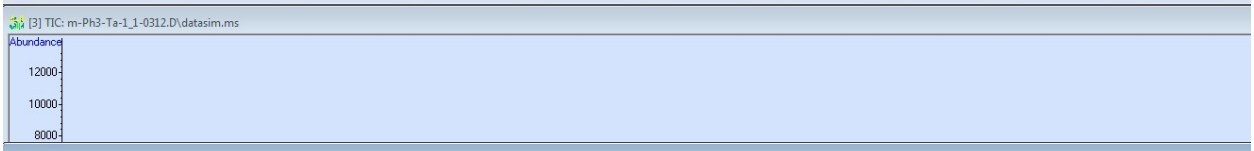


D:\MassHunter\GCMS\1\data\Johnson Lab\m-Ph2-Ta-2_1-0312.D\rteres.txt

```
  Data File : m-Ph2-Ta-2_1-0312.D
  Acq On    : 12 Mar 2019  20:17
  Operator  : fs
  Sample    : m-Ta-Ph2(2-1)
  Misc      :
  ALS Vial  : 2   Sample Multiplier: 1

  Integration Parameters: events.e
  Integrator: ChemStation

  Method    : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
  Title     :

  Signal     : TIC: m-Ph2-Ta-2_1-0312.D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #   min   scan scan scan  TY  height     area    % max.   total
---  ----- ----- ---- ---- ---  -------   -------  ------  -------
 1  34.435  3904 3922 4061   M6 1567343 299211948  21.99%   9.668%
 2  35.584  4062 4076 4228   M4 3164339 534517903  39.29%  17.271%
 3  36.878  4231 4249 4368   M3 5946125 900616908  66.20%  29.100%
 4  37.877  4371 4383 4506   M  8969594 1360508779 100.00%  43.960%


                     Sum of corrected areas:  3094855538
  Signal     : TIC: m-Ph2-Ta-2_1-0312.D\datasim.ms
```

TaPh3





D:\MassHunter\GCMS\1\data\Johnson Lab\m-Ph3-Ta-1_1-0312.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : m-Ph3-Ta-1_1-0312.D
Acq On : 13 Mar 2019 03:20
Operator : fs
Sample : m-Ta-Ph3(1-1)
Misc :
ALS Vial : 5 Sample Multiplier: 1

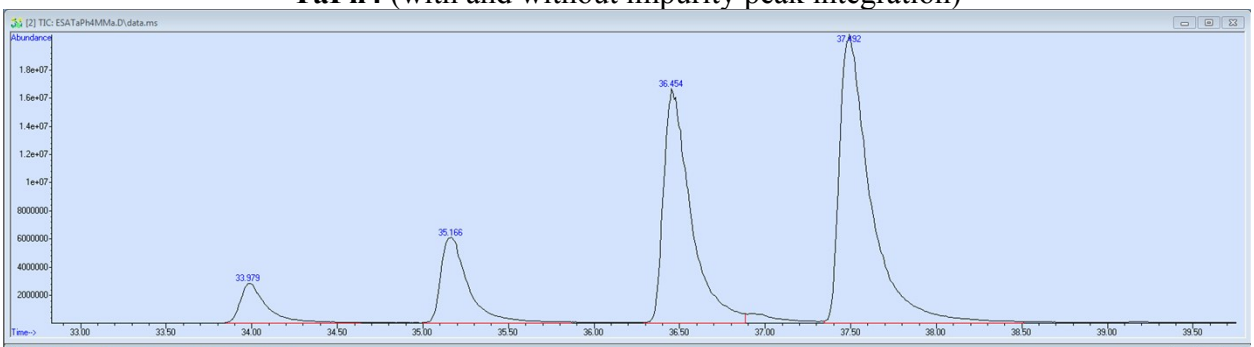
Integration Parameters: events.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\data\Johnson Lab\d-DtBu-Ti-1_1test50.D\chiraldexbDM_50split.M
Title :

Signal : TIC: m-Ph3-Ta-1_1-0312.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	34.477	3917	3928	4075	M5	2155021	483125001	28.14%	12.348%
2	35.671	4077	4088	4238	M5	2602902	548360403	31.94%	14.016%
3	36.887	4240	4250	4372	M3	683764 4	1164435631	67.83%	29.762%
4	37.894	4374	4385	4500	M2	10417592	1716604989	100.00%	43.875%

TaPh4 (with and without impurity peak integration)



D:\MassHunter\GCMS\1\data\Johnson Lab\ESATaPh4MMa.D\rteres.txt

Area Percent Report

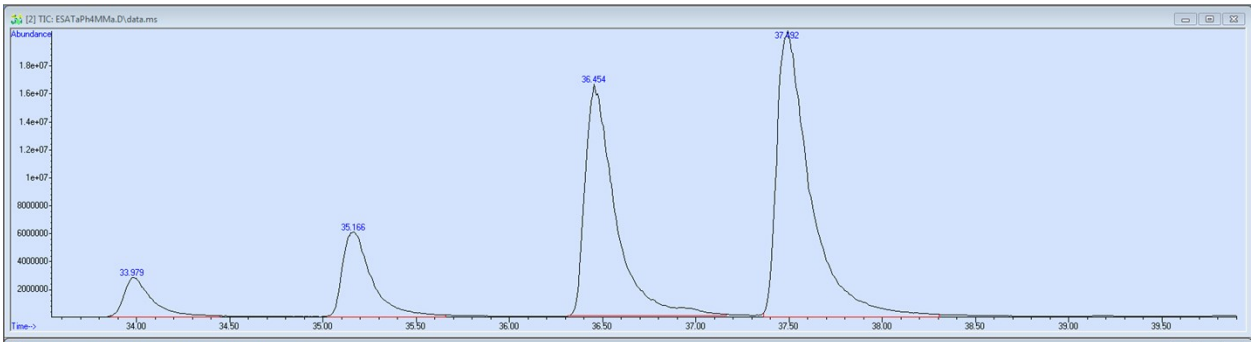
Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : ESATaPh4MMa.D
Acq On : 01 Feb 2020 01:51
Operator : ES
Sample : ATaPh4MMa
Misc :
ALS Vial : 6 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\data\Johnson Lab\VLSI036.D\chiraldexbDM_400split_new.M
Title :

Signal : TIC: ESATaPh4MMa.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	33.979	3844	3861	3949	MA	2835591	308972848	11.92%	5.689%
2	35.166	3998	4020	4114	M3	6078081	687659128	26.52%	12.661%
3	36.454	4171	4192	4250	M	16684618	1842146250	71.05%	33.916%
4	37.492	4311	4331	4467	M2	20495484	2592668357	100.00%	47.734%



D:\MassHunter\GCMS\1\data\Johnson Lab\ESATaPh4MMa.D\rteres.txt

Area Percent Report

Data Path : D:\MassHunter\GCMS\1\data\Johnson Lab\
Data File : ESATaPh4MMa.D
Acq On : 01 Feb 2020 01:51
Operator : ES
Sample : ATaPh4MMa
Misc :
ALS Vial : 6 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method : D:\MassHunter\GCMS\1\data\Johnson Lab\VLSI036.D\chiraldexbDM_400split_new.M
Title :

Signal : TIC: ESATaPh4MMa.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	33.979	3846	3861	3924	MA	2835591	308871337	11.69%	5.549%
2	35.166	4001	4020	4086	M3	6078081	672572160	26.14%	12.404%
3	36.454	4173	4192	4287	M	16680650	1875820036	72.90%	34.594%
4	37.492	4314	4331	4440	M2	20495484	2573081998	100.00%	47.453%

References

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