Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Iron cyclopentadienone complexes derived from C2-symmetric bis-propargylic alcohols; preparation and applications to catalysis.

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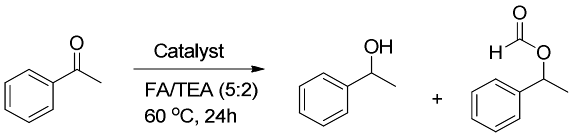
Additional results Tables and hydride formation experiments.

Table S1. Additional results for ATH of acetophenone reduction using iron catalysts **13, 18-21**.[a]



Entry	Catal-yst	Load-ing /mol%	Activa-tor	Time	T / °C	Alcohol /%	Formate / %	alcohol ee / %	Formate ee/ %
3	**18**	5	TMAO	24 h	40	13	0	2 (*S*)	-
4	**18**	1	TMAO	24 h	40	0	0	-	-
5	**19**	5	TMAO	24 h	40	16	0	29 (*R*)	-
6	**19**	1	TMAO	24 h	40	0	0	-	-
7	**20**	5	TMAO	24 h	40	9	1	21 (*R*)	[b]
8	**20**	1	TMAO	24 h	40	0.5	0.5	[b]	[b]
9	**21**	5	TMAO	24 h	40	14	0	37 (*R*)	-
10	**21**	1	TMAO	24 h	40	0	0	-	-

a. reaction conditions; [S] = *ca*. 1 M, TMAO (1 eq. relative to complexes) unless otherwise indicated, % conversions are given and the balance is unreduced ketone. b. not determined.

Table S2. Effect of water on reaction in anhydrous THF using catalyst **13**.[a]

Entry	Loading /mol%	Solvent	H_2O (%)[c]	Conv	ee
1	1	THF[b]	0	69.5	11.4 (*S*)
2	1	THF	0	31	12.6 (*S*)
3	1	THF[d]	0	25.7	12.0 (*S*)
4	1	THF	10	46.7	10.0 (*S*)
5	1	THF	50	83.4	12.6 (*S*)
6	1	THF	100	98.7	11.4 (*S*)
7	1	THF/H_2O (5/2)		99.8	13.6 (*S*)

a. Reaction conditions; 1 mol% catalyst, [S] = ca. 1.9 M, 30 bar H2, THF (0.7 mL) used as solvent b. “aged” THF, likely to contain water. c. relative to substrate. d. Test tube dried in oven overnight and cooled under flow of N_2.

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Observation of hydride formation on treatment of complex **13** in THF/H_20 **(**ADG231).

In a J. Young's NMR tube fitted with a d_6-DMSO capillary, under nitrogen atmosphere, complex **13** (20 mg, 4.1x10^{-2} mmol) was dissolved in THF (0.5 mL) and H_2O (74 µl, 4.1 mmol) was added. Then the mixture was degassed by three freeze-pump-thaw cycles, and heated to 80 ºC. ^{1}H NMR spectra were recorded before heating and after 3 and 19 hours at 80 80 ºC. On heating, insoluble materials were formed and a peak at -12.10 ppm consistent with a Fe-H species appeared. Furthermore, all the peaks broadened suggesting the formation of paramagnetic iron species.

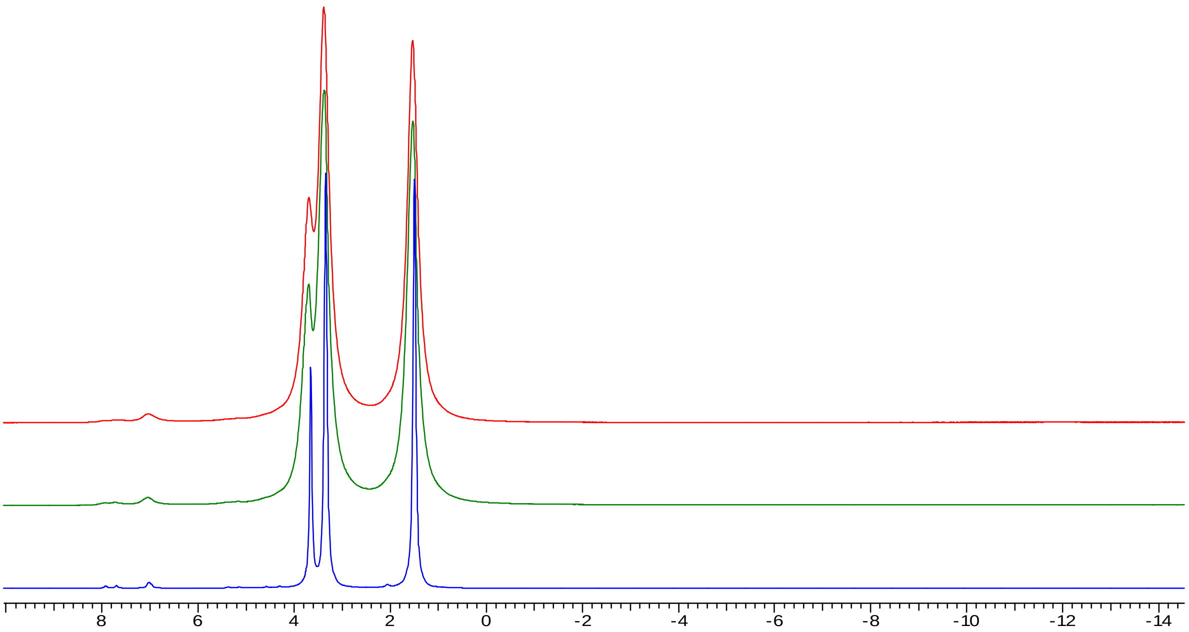


Figure 1. ^{1}H NMR series of the mixture of complex **13** with H_2O in THF (d6-DMSO capillary used to lock the signal) at room temperature (lower spectrum), 3 hours at 80 ºC (middle spectrum) and 19 hours at 80 ºC (upper spectrum).

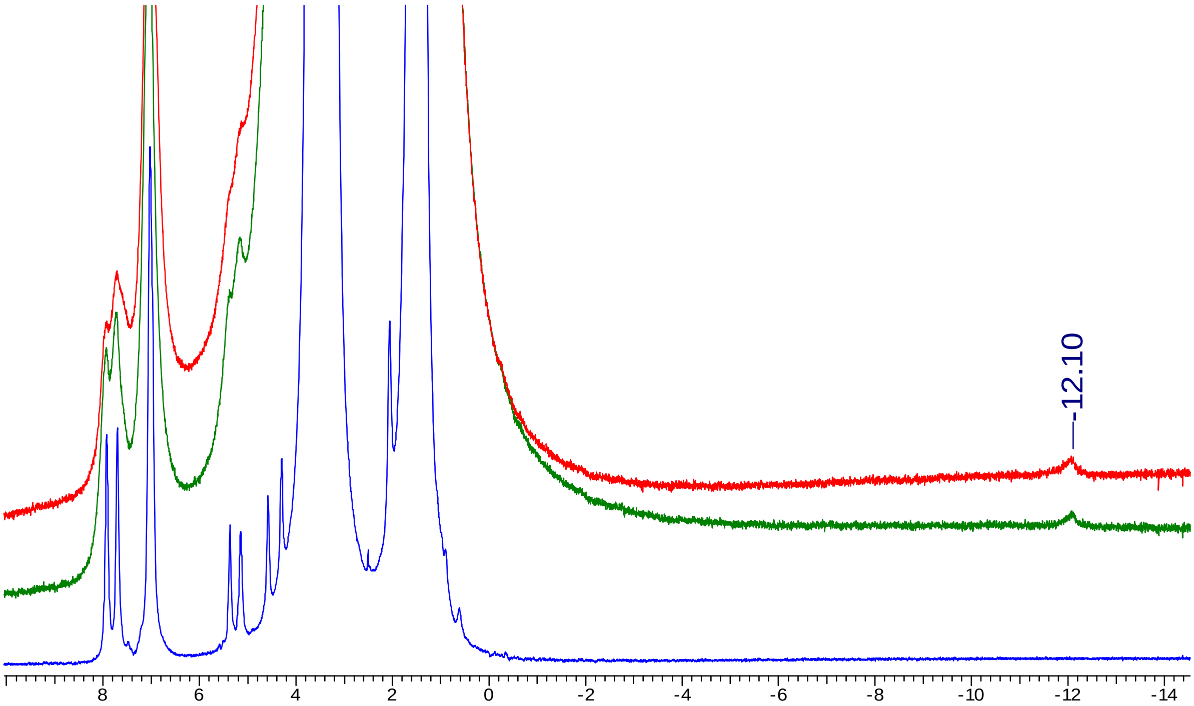


Figure 2. Expanded ^{1}H NMR series of the mixture of complex **13** with H_2O in THF (d6-DMSO capillary used to lock the signal) at room temperature (lower spectrum), 3 hours at 80

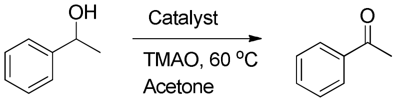
°C (middle spectrum) and 19 hours at 80 °C (upper spectrum). The signals due to the complex are visible in this expanded spectrum.

Table S3. Effect of water on acetophenone reduction in dry toluene using catalyst **13**.[a]

Entry	Loading/mol%	Additive	H_2O added/%[b]	Conv/%	Ee /%
1	1	none	0	18.8	6.8 (*S*)
2	1	none	0	25.2	6.8 (*S*)
3	1	TMAO (1%)	0	99.7	4 (*S*)
4	1	None	10	3.8	6.4 (*S*)
5	1	None	50	10.9	6.4 (*S*)
6	1	none	100	20.6	6.8 (*S*)

a. Reaction conditions; 1 mol% catalyst, [S] = ca. 1.9 M, 30 bar H_2, Toluene (0.7 mL) used as solvent, 80 °C, 18h. b. relative to substrate.

Table S4. Additional results for oxidation of 1-phenylethanol using iron catalysts **13, 18-21**.[a]



Entry	Catalyst	Loading / mol%	Time / h	Alcohol / %	Ketone / %	Alcohol ee / %
6	**18**	1	5	85	15	2 (*R*)
7	**18**	1	24	23	77	0 (*R*)
12	**19**	1	5	62	38	3 (*S*)
13	**19**	1	24	36	64	6 (*S*)
16	**20**	1	24	83	17	1 (*S*)
21	**21**	1	5	96	4	0 (*R*)
22	**21**	1	24	65	35	1 (*R*)

a. Reaction conditions; 60 °C, [S] = 0.19M, acetone solvent, TMAO (1 eq. relative to complexes).

Table S5. Reduction of acetylcyclohexane using iron catalysts **13**, **18-21**.[a]

Entry	APH/ATH	Catalyst	Loading / mol%	T / °C	Time / h	Alcohol[b] / %	Ketone / %
1	ATH	**18**	10	60	48	97	3
2	APH	**18**	1	60	72	Trace	>99
3	ATH	**19**	10	60	48	81	12
4	APH	**19**	1	60	72	Trace	>99
5	ATH	**20**	10	40	24	66	31
6	ATH	**21**	10	60	48	61	32
7	APH	**21**	1	60	72	Trace	>99

a. Reaction conditions; ATH: 100 mg of cyclohexylmethyl ketone, 10 mol% Fe Catalyst, 10 mol% TMAO, FA/TEA 5:2, [S] = 1.5M; APH: 30 bar H_2, 100 mg of cyclohexylmethyl ketone, 1 mol% Fe Catalyst, 5 mol% K_2CO_3, 0.5 ml iPrOH/0.2 ml H_2O b. products were racemic.

Table S6. ATH of 3,3-dimethyl-2-butanone using iron catalysts **13**, **18-21**.[a]

Entry	Conditions	Catalyst	Alcohol /%	ee / %
1	FA/TEA (5:2)	**18**	100	9 (*S*)
2	FA/TEA (5:2)	**19**	100	10 (*R*)
3	FA/TEA (5:2)	**20**	100	24 (*R*)
4	FA/TEA (5:2)	**21**	100	26 (*R*)
5	^{i}PrOH	**20**	10.9	1 (*R*)
6	^{i}PrOH	**21**	39.8	11 (*R*)
7	$HCO_2Na/H_2O/DMF$	**20**	0	-
8	$HCO_2Na/H_2O/DMF$	**21**	0	-

a. Conditions; 10 mol% catalyst used, 24 h, 60 °C, [S] = *ca*.1.5M for FA/TEA, ca. 0.2M for IPA and H_2O 1.5M; DMF ca. 1M.

Table S7. Pressure hydrogenation of 3,3-dimethyl-2-butanone using catalysts **18-21**.[a]

Reaction number	Catalyst	Alcohol			Ketone / %	Alcohol ee / %
		Total /%	R /%	S /%		
RCH1141	**18**	26	8.9	17.1	74	31 (*S*)
		10	3.5	6.6	90	31 (*S*)
RCH1050	**19**	0.4	0.2	0.2	99.6	-
		0.2	0.1	0.1	99.8	-
RCH1232	**19**	5.4	2.7	2.7	94.6	0
		6.2	2.9	3.3	93.8	-
RCH1051	**21**	5.2	4.2	1		62[b] (*R*)
		3.9	2.6	1.3		33[b] (*R*)
RCH1233	**20**	5.2	3.5	1.7	94.8	34[b] (*R*)
		5.4	3.7	1.7	94.6	38[b] (*R*)

a. 1 mol% catalyst, 72h, 60 °C, 30 bar H_2. b. Due to the low conversions, these values cannot be regarded as accurate.

Table S8. Transfer Hydrogenation using complexes **22-25**.[a]

Reac-tion	Ketone	Catalyst	Activa-tion	Time /h	T /°C	Alcohol			Formate			Ketone /%
						%	R%	S%	%	R%	S%	
RCH 1212	Acetophenone	**25**	TMAO	24 (dark)	60	0			0			100
RCH 1212	Acetophenone	**25**	TMAO	24 (Light)	60	1.1	0.6	0.5	1.9	1.2	0.7	97
RCH 1213	Acetophenone	**24**	TMAO	24 (dark)	60	0			0			100
RCH 1213	Acetophenone	**24**	TMAO	24 (Light)	60	12.2	7.2	5	8.9	5	3.9	78.9
RCH 1220	Acetophenone	**24**	Blue Light	24	25	0			0			100
RCH 1221	acetophenone	**25**	Blue Light	24	25	0			0			100
RCH	acetophe	**24**	UV (λ =	24	25	0			0			100

1224	none		365 nm)									
RCH 1225	acetophenone	**25**	UV (λ = 365 nm)	24	25	0			0			100
RCH 1217	acetophenone	**23**	TMAO	24	60	6	2.6	3.4	1	0.4	0.6	93
RCH 1216	acetophenone	**22**	TMAO	24	60	4.9	2.5	2.4	1.1	0.5	0.6	94
RCH 1222	acetophenone	**22**	Blue Light	24	25	0						100
RCH 1223	acetophenone	**23**	Blue Light	24	25	0						100
RCH 1226	acetophenone	**22**	UV (λ = 365 nm)	24	25	0						100
RCH 1227	acetophenone	**23**	UV (λ = 365 nm)	24	25	0						100
RCH 1214	Pinacolone	**25**	TMAO	24 (dark)	60	0						100
RCH 1214	Pinacolone	**25**	TMAO	24 (Light)	60	7	2.9	4.1				93
RCH 1215	Pinacolone	**24**	TMAO	24 (dark)	60	0						100
RCH 1215	Pinacolone	**24**	TMAO	24 (Light)	60	0.5	0.3	0.2				99.5
RCH 1217	Pinacolone	**23**	TMAO	24	60	0						100
RCH 1218	Pinacolone	**22**	TMAO	24	60	0						100

a. reaction conditions; [S] = *ca*. 1 M, TMAO (1 eq. relative to complexes) unless otherwise indicated.

Table S9. Pressure hydrogenation using Monophos complexes.[a]

Reaction	Ketone	Catalyst	Alcohol			Ketone /%
			Total /%	R /%	S /%	
RCH1206	Acetophenone	**24**	0.8	0.5	0.3	98.9
			0.6	0.4	0.2	99.1
RCH1207	Acetophenone	**25**	2	1.2	0.8	97.7
			2.1	1.2	0.9	97.7
RCH1229	Acetophenone	**22**	0.2	0.1	0.1	99.8
			0.2	0.1	0.1	99.8
RCH1228	Acetophenone	**23**	0.4	0.1	0.3	99.6
			0.2	0	0.2	99.8
RCH1208	pinacolone	**24**	1	0.5	0.5	98.9
			2	1	1	98.1
RCH1209	pinacolone	**25**	4.5	2.2	2.3	95.5
			3.1	1.5	1.6	96.9
RCH1231	Pinacolone	**22**	0.2	0.1	0.1	99.8
			0.2	0.1	0.1	99.8
RCH1230	Pinacolone	**23**	0.2	0.1	0.1	99.8
			0.4	0.2	0.2	99.6

a. Reaction conditions; 1 mol% catalyst, [[S] = 0.83 (100 mg), 30 bar H_2, iPrOH/H_2O (0.5 ml/0.2ml) used as solvent.

Table S10. Effect of added phosphine on APH of acetophenone using catalyst **13**.[a]

Entry	Activator (mol%)	Additive (%)	Conv	ee
1	TMAO (1%)	PPh_3 (1%)	93.5	10.6 (*S*)
2	TMAO (2%)	PPh_3 (1%)	60.4	7.8 (*S*)
3	TMAO (3%)	PPh_3 (1%)	11.2	8.8 (*S*)
4	TMAO (2%)	PPh_3 (2%)	0	
5	TMAO (3%)	PPh_3 (2%)	0	

a. Reaction conditions; 1 mol% catalyst, [S] = 1.9 M (206 mg, 200 μl), 30 bar H_2, iPrOH/H_2O (0.5 ml/ 0.2mL) used as solvent, 80 °C, 18h.

Table S11. Effect of added MONOPHOS on APH of acetophenone using catalyst **13**.[a]

Entry	Activator (mol%)	Additive (1 mol%)	Conv./%	Ee[b] /%
1	TMAO (1%)	(*R*)-MONOPHOS	99.8	10 (*S*)
2	TMAO (2%)	(*R*)-MONOPHOS	66.4	9 (*S*)
3	TMAO (1%)	(*S*)-MONOPHOS	99.7	12 (*S*)
4	TMAO (2%)	(*S*)-MONOPHOS	54.2	9 (*S*)

a Reaction conditions; 1 mol% catalyst, [S] = 1.9 M (206 mg, 200 μl), 30 bar H_2, iPrOH/H_2O (0.5 ml/ 0.2mL) used as solvent, 80 °C, 18h.

^{1}H-NMR of ATH reduction using catalyst **24**.

In a J. Young's borosilicate NMR tube, under nitrogen atmosphere, complex **24** (10 mg, 9.8×10^{-3} mmol) was dissolved in C_6D_6 (0.6 mL) and ^{1}H NMR spectrum was recorded (Figure 3). Acetophenone (5.7 µL, 4.9×10^{-2} mmol) was added. Then the mixture was degassed by three freeze-pump-thaw cycles, back-filled with hydrogen at -196 ºC and the NMR tube was sealed. The mixture was warmed to room temperature and irradiated under 365 nm UV light (Spectroline ERT-260C/F, 6 Watt, 8 cm from source)**.** The reaction progress was monitored by ^{1}H NMR. Figure 4 shows the ^{1}H NMR after 1 hour (lower spectrum), 3 hours (middle spectrum) and 4 hours (upper spectrum) irradiation. Figure 5 shows the zoom of the hydride region. Upon irradiation the peaks of complex **24** decreased and Fe-H species appeared. The main doublet at -12.11 ppm (*J* = 88.6 Hz) and the doublet at -12.18 ppm (*J* = 80.1 Hz) can be tentatively assigned to two hydride diastereoisomers or rotamers deriving from complex. The doublet at -11.40 ppm (*J* = 88.6 Hz) can be tentatively assigned to the hydride species derived from complex **25** present as impurity in **24**, on the basis of its similar integral value. After 4 h of UV irradiation, the mixture was heated at 80 ºC for 3 days and a NMR was recorded. The ^{1}H NMR indicated that after heating the complex **24** was re-formed (Figure 6) and the doublet at -12.18 ppm became the main hydride species (Figure 7). The mixture was filtered through a short plug of silica gel, washed through with EtOAc/petroleum ether 3/7 (until no further alcohol was eluted) and analysed by GC using the previously cited GC conditions. The conversion of acetophenone to alcohol by ^{1}H NMR (Figure 6) could not be established due to the low sensitivity of the NMR. Therefore the isolated product from the reaction was analysed by GC (Figure 8). This indicated a conversion of ca 5.9 % and a product ee of 18.% (*R*).

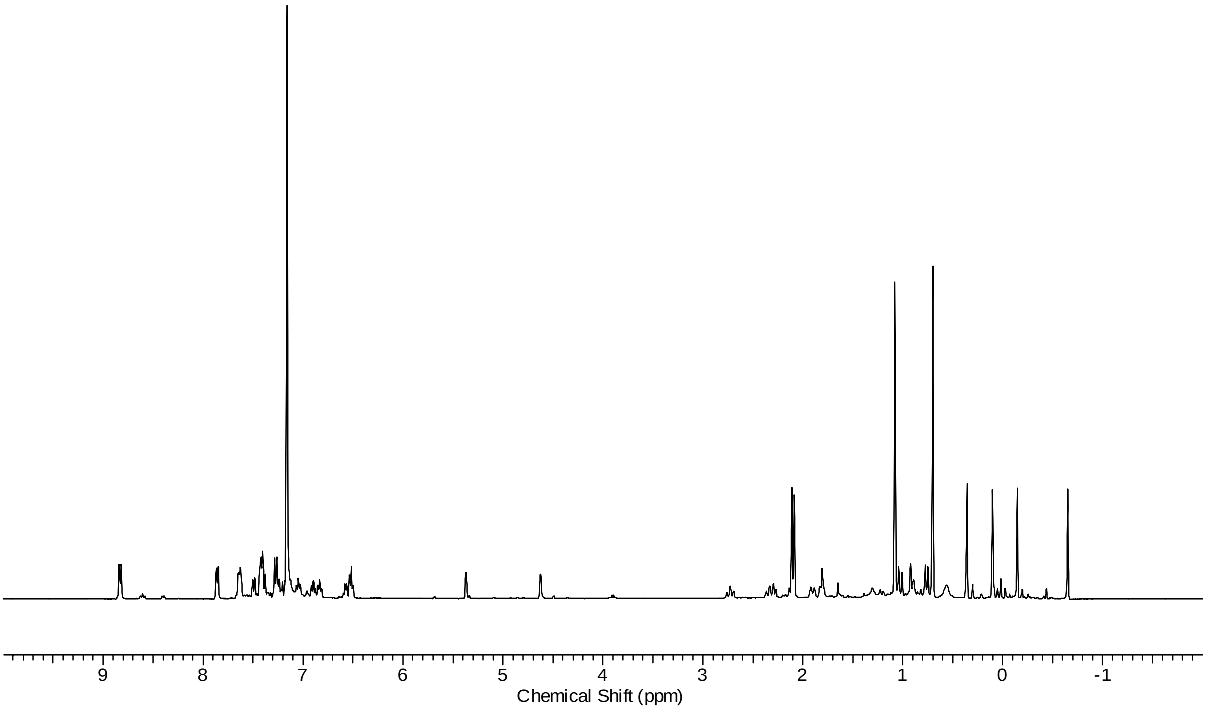


Figure 3. ^{1}H NMR of complex **24** in C_6D_6

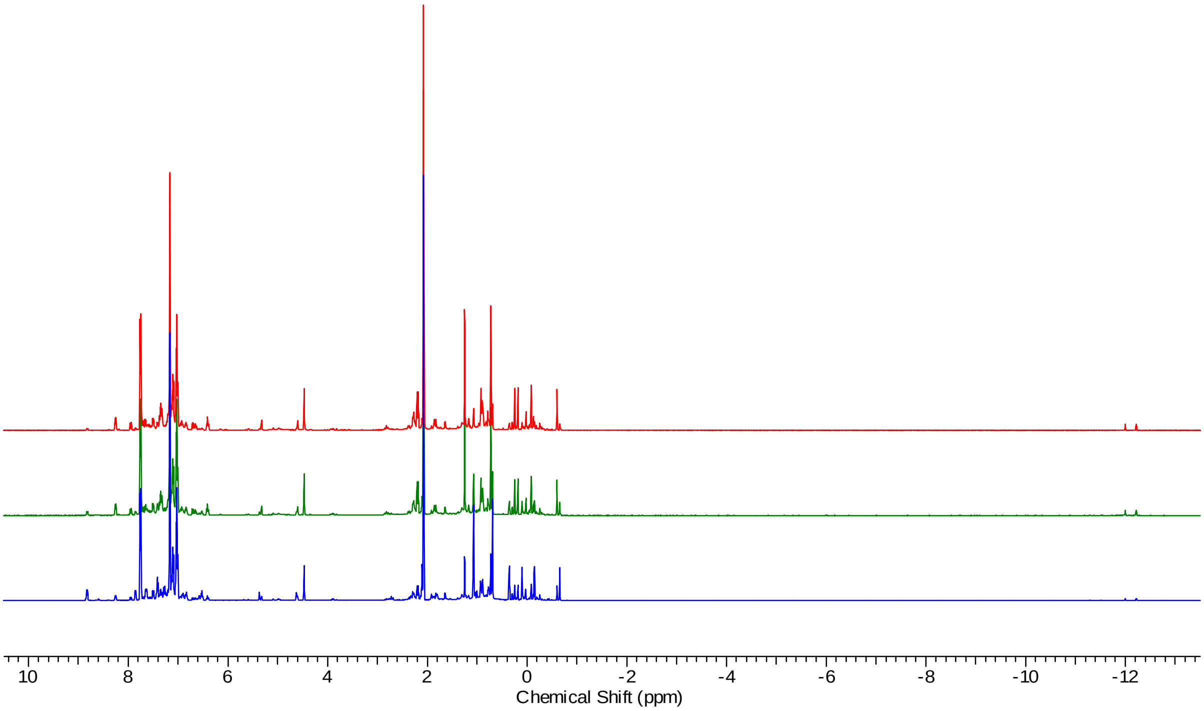


Figure 4. ^{1}H NMR series of the mixture of complex **24** and acetophenone under hydrogen pressure after 1 hour (lower spectrum), 3 hours (middle spectrum) and 4 hours (upper spectrum) irradiation at 365 nm.

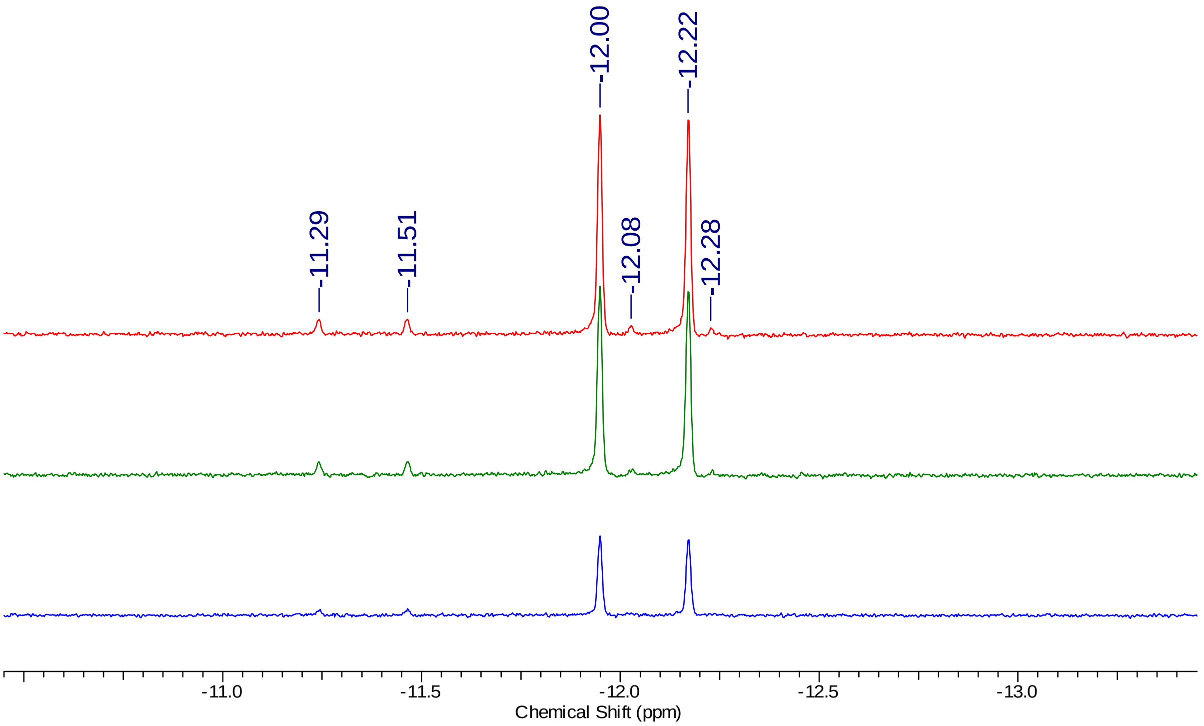


Figure 5. Zoom of the region of the ^{1}H NMR series of the mixture of complex **24** and acetophenone under hydrogen pressure after 1 hour (lower spectrum), 3 hours (middle spectrum) and 4 hours (upper spectrum) irradiation at 365 nm.

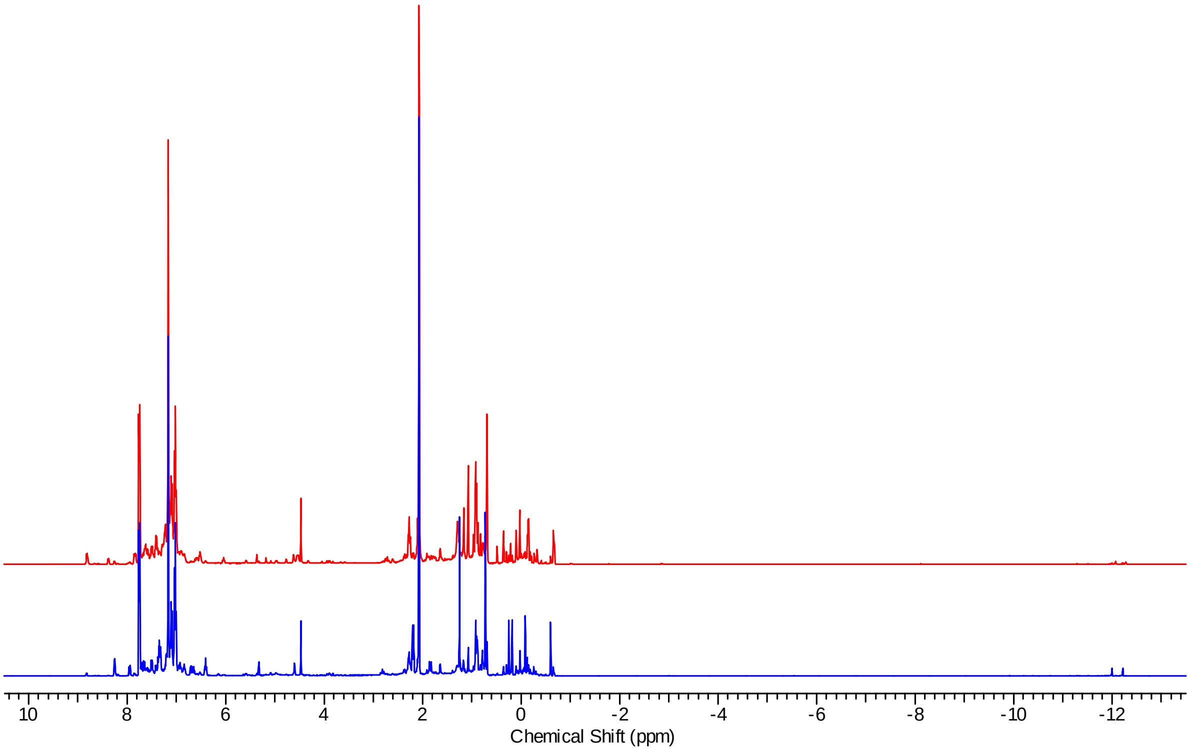


Figure 6. ^{1}H NMR series of the mixture of complex **24** and acetophenone under hydrogen pressure after 4 hours irradiation at 365 nm(lower spectrum) and after heating the mixture at 80 ºC for 3 days (upper spectrum).

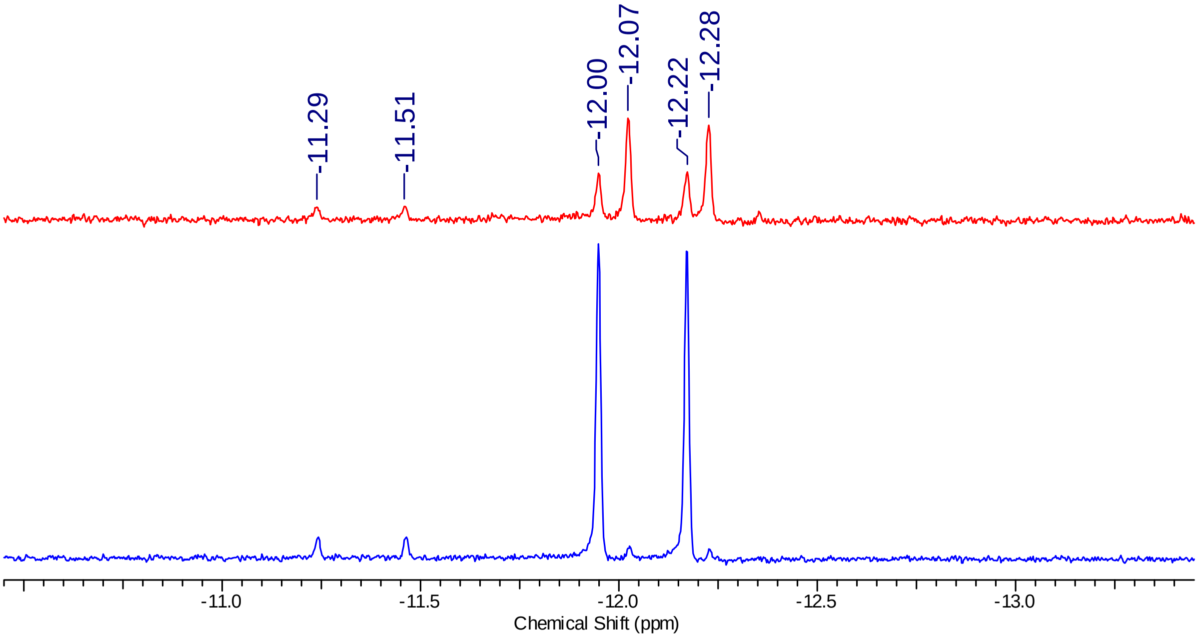
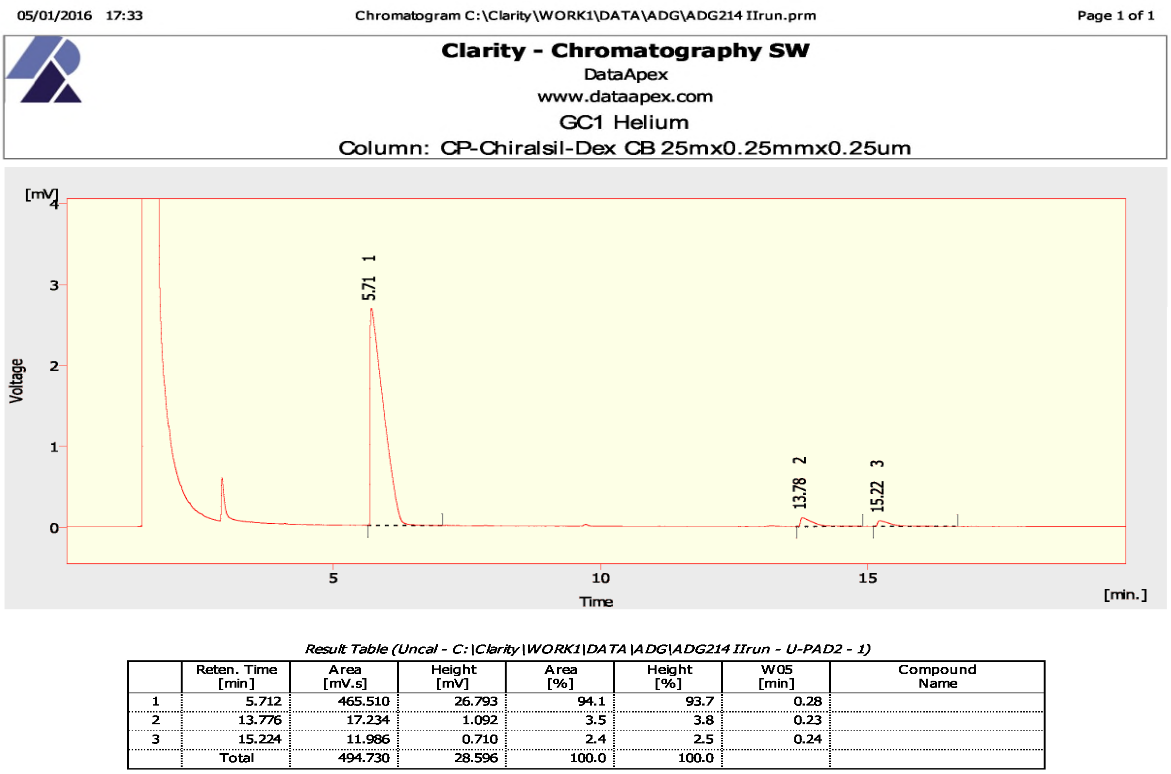


Figure 7. Zoom of the region of the ^{1}H NMR series (offset at -0.15 ppm) of the mixture of complex **24** and acetophenone under hydrogen pressure after 4 hours irradiation at 365 nm(lower spectrum) and after heating the mixture at 80 ºC for 3 days (upper spectrum).



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Clarity - Chromatography SW
DataApex
www.dataapex.com
GC1 Helium
Column: CP-Chiralsil-Dex CB 25mx0.25mmx0.25um

Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG214 IIrun - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.712	465.510	26.793	94.1	93.7	0.28	
2	13.776	17.234	1.092	3.5	3.8	0.23	
3	15.224	11.986	0.710	2.4	2.5	0.24	
	Total	494.730	28.596	100.0	100.0		

Figure 8. GC spectrum of isolated product mixture (He gas, 110 ^{o}C). 5.9% conv. ee 18.0% (*R*); ketone; 5.7 min, (*R*) isomer; 13.8 min, (*S*) isomer; 15.2 min.

Hydride species formed from complex **25**.

This experiment was carried out in order to establish the identity of the minor peaks in the above experiment. In a J. Young's borosilicate NMR tube, complex **25** (10 mg, $9.8x10^{-3}$ mmol) was dissolved in C_6D_6 (0.6 mL) and ^{1}H NMR spectrum was recorded (Figure 9). Then the mixture was degassed by three freeze-pump-thaw cycles, back-filled with hydrogen at -196 ºC and the NMR tube was sealed. The mixture was warmed at room temperature and irradiated under 365 nm UV light (Spectroline ERT-260C/F, 6 Watt, 8 cm from source)**.** The reaction progress was monitored by ^{1}H NMR. Figure 10 shows the ^{1}H NMR after 4 hours (lower spectrum), 8 hours (middle spectrum) and 10 hours (upper spectrum) irradiation. Figure 11 shows the zoom of the hydride region. Upon irradiation the peaks of complex **25** decreased and Fe-H species appeared. The ^{1}H NMR spectrum showed four visible doublets. The main doublet at -11.42 ppm (*J* = 88.8 Hz) and the doublet at -12.51 ppm (*J* = 81.5 Hz) can be tentatively assigned to two hydride diastereoisomers or rotamers derived from complex **25**, while the doublets at -12.11 ppm (*J* = 89.1 Hz) and at 12.19 ppm (*J* = 80.0 Hz) can be tentatively assigned to the hydride species deriving from complex **24** present as impurity. The $^1H\{^{31}P\}$ NMR spectrum showed two more hydride peaks at -9.81 and -12.41 ppm not visible in the ^1H NMR spectrum (Figure 12).

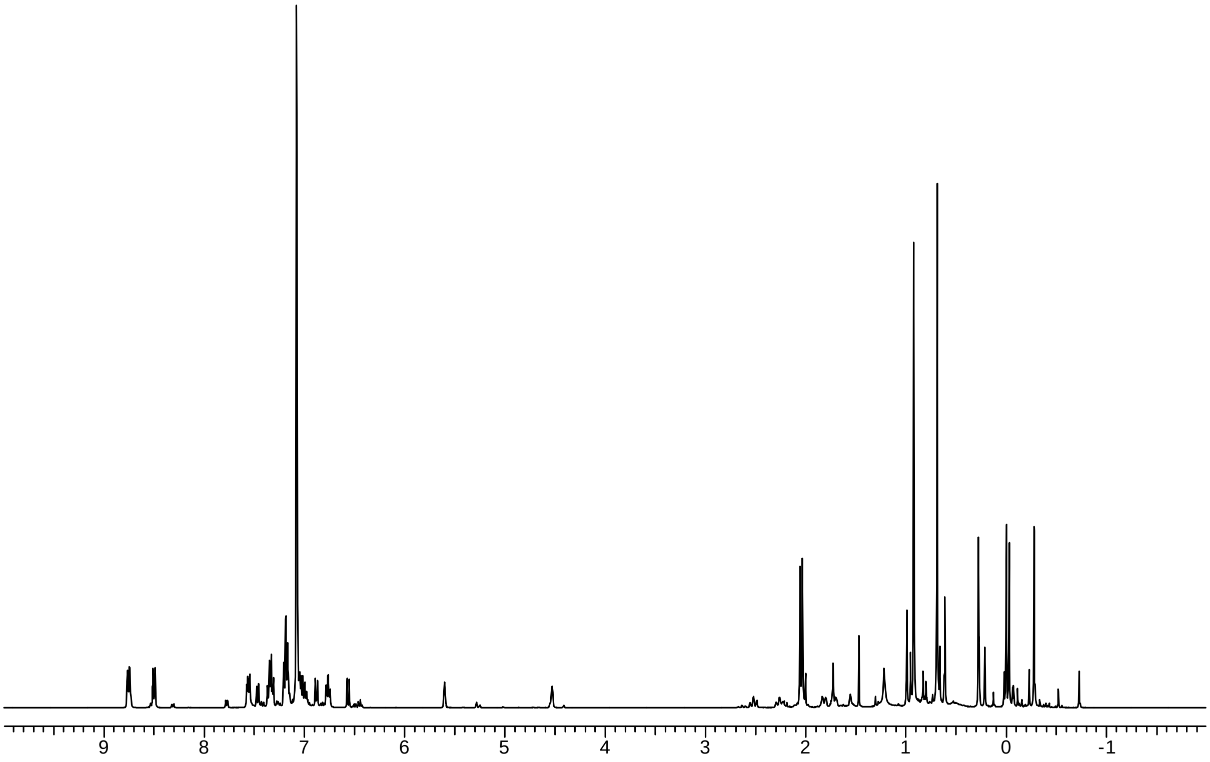


Figure 9. ^1H NMR of complex **25** in C_6D_6

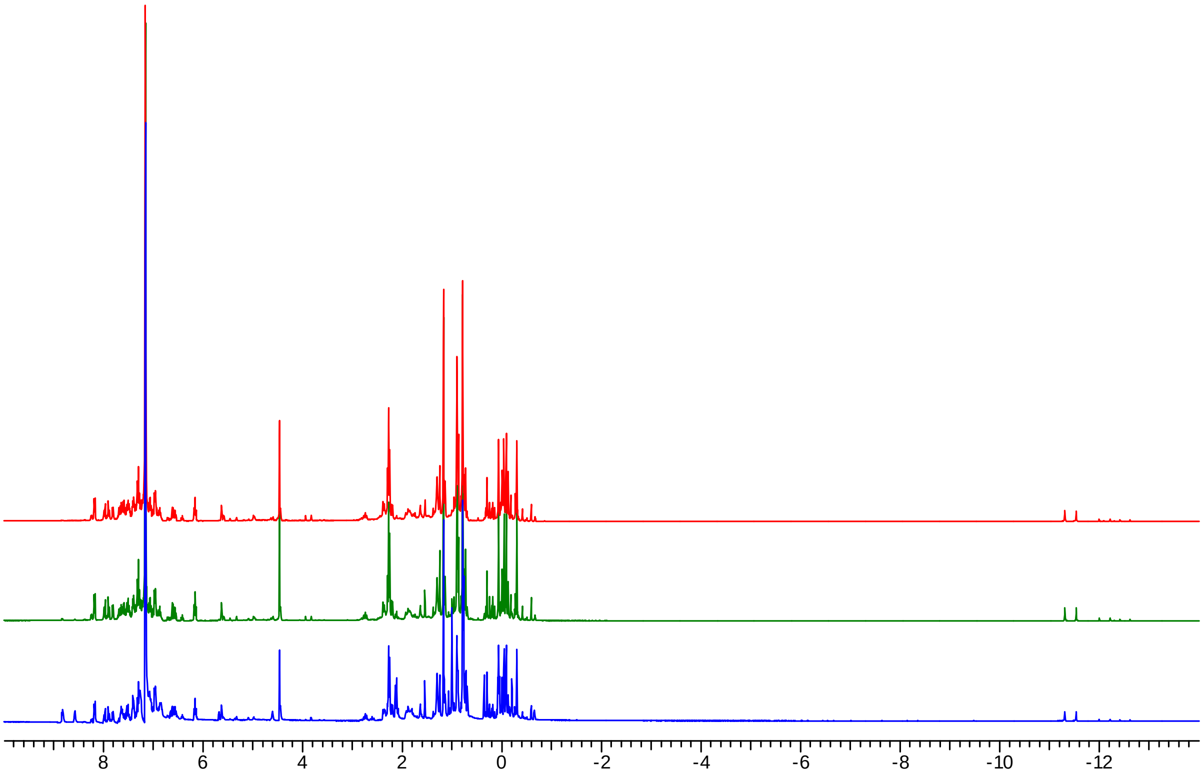


Figure 10. ^{1}H NMR series of the complex **25** under hydrogen pressure after 4 hours (lower spectrum), 8 hours (middle spectrum) and 10 hours (upper spectrum) irradiation at 365 nm.

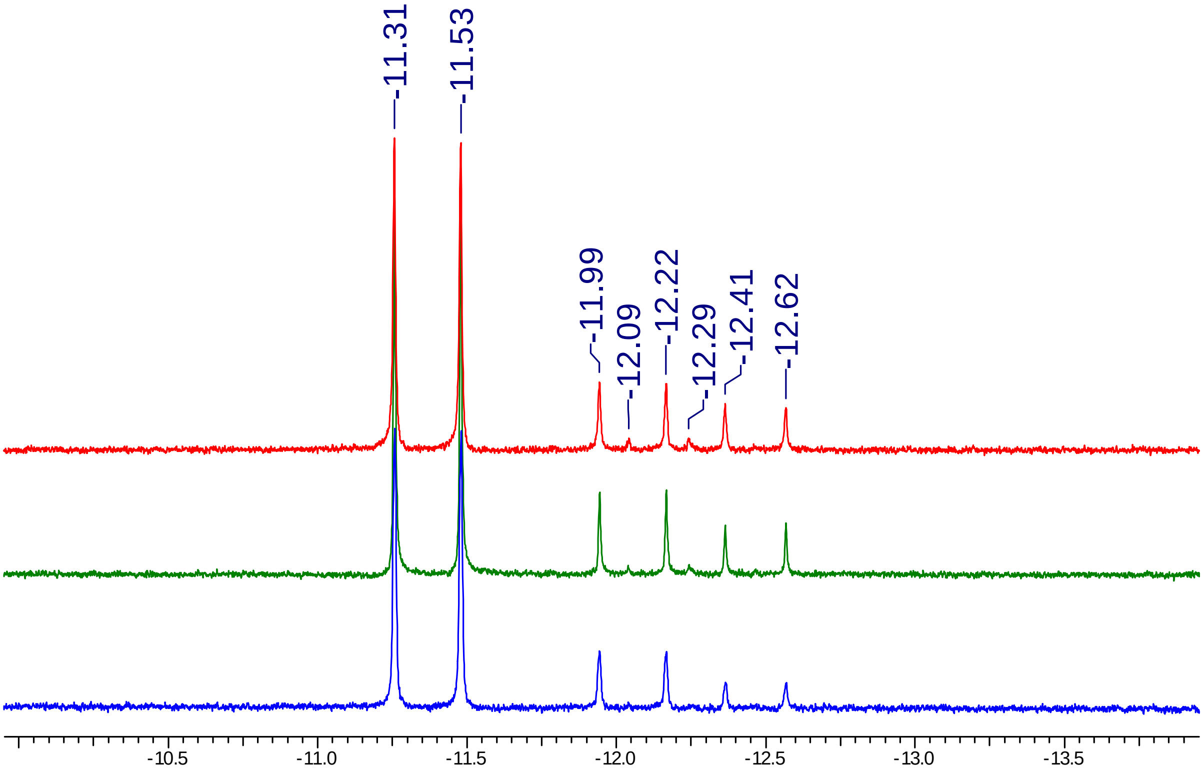


Figure 11. Zoom of the region of the ^{1}H NMR series of the complex **25** under hydrogen pressure after 4 hours (lower spectrum), 8 hours (middle spectrum) and 10 hours (upper spectrum) irradiation at 365 nm.

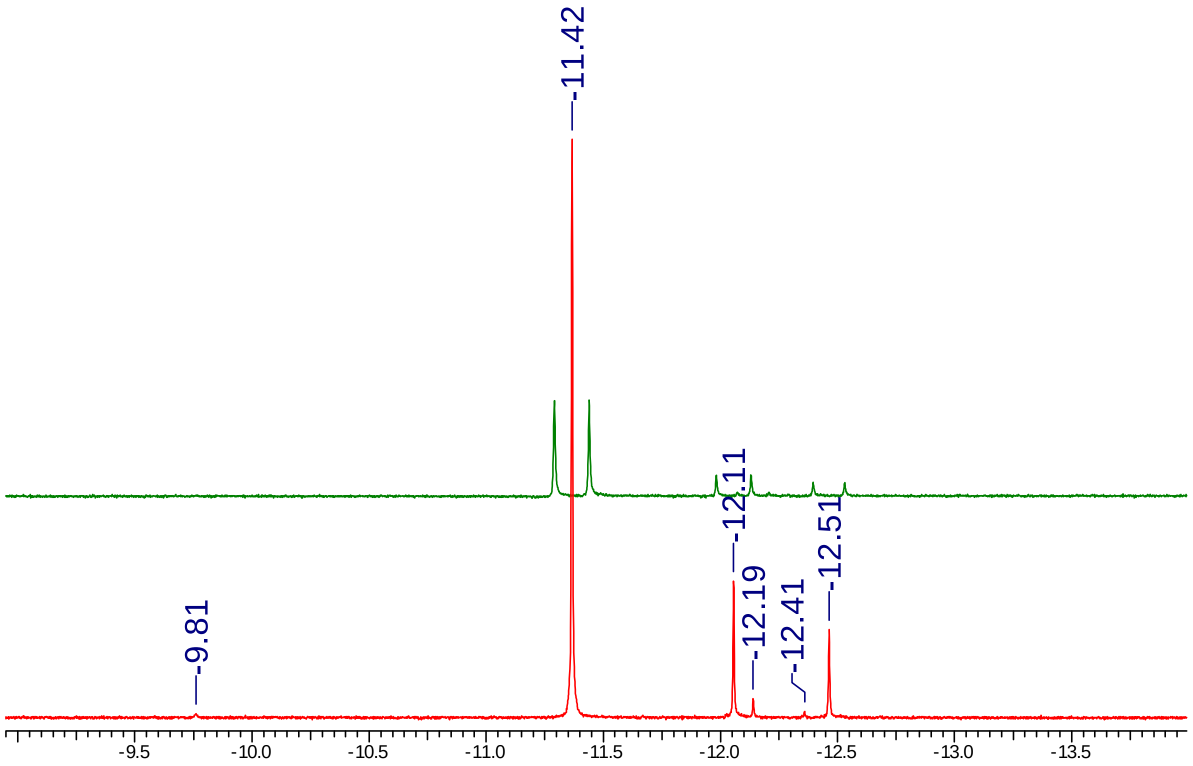
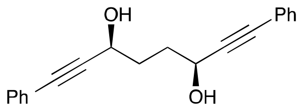
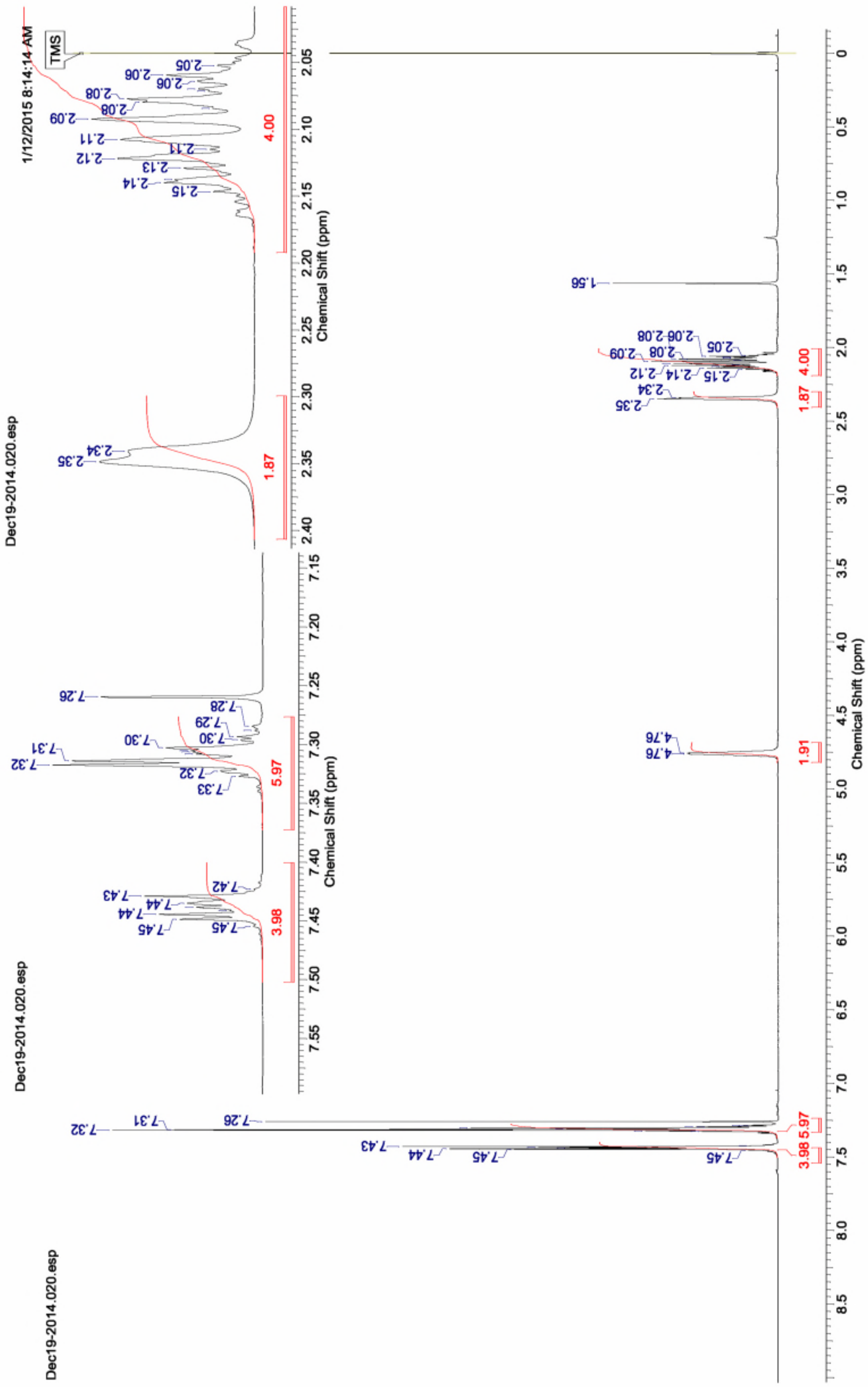


Figure 12. ^{1}H NMR (upper spectrum) and ^{1}H{^{31}P} NMR of the mixture of complex **25** under hydrogen pressure after 10 hours irradiation at 365 nm

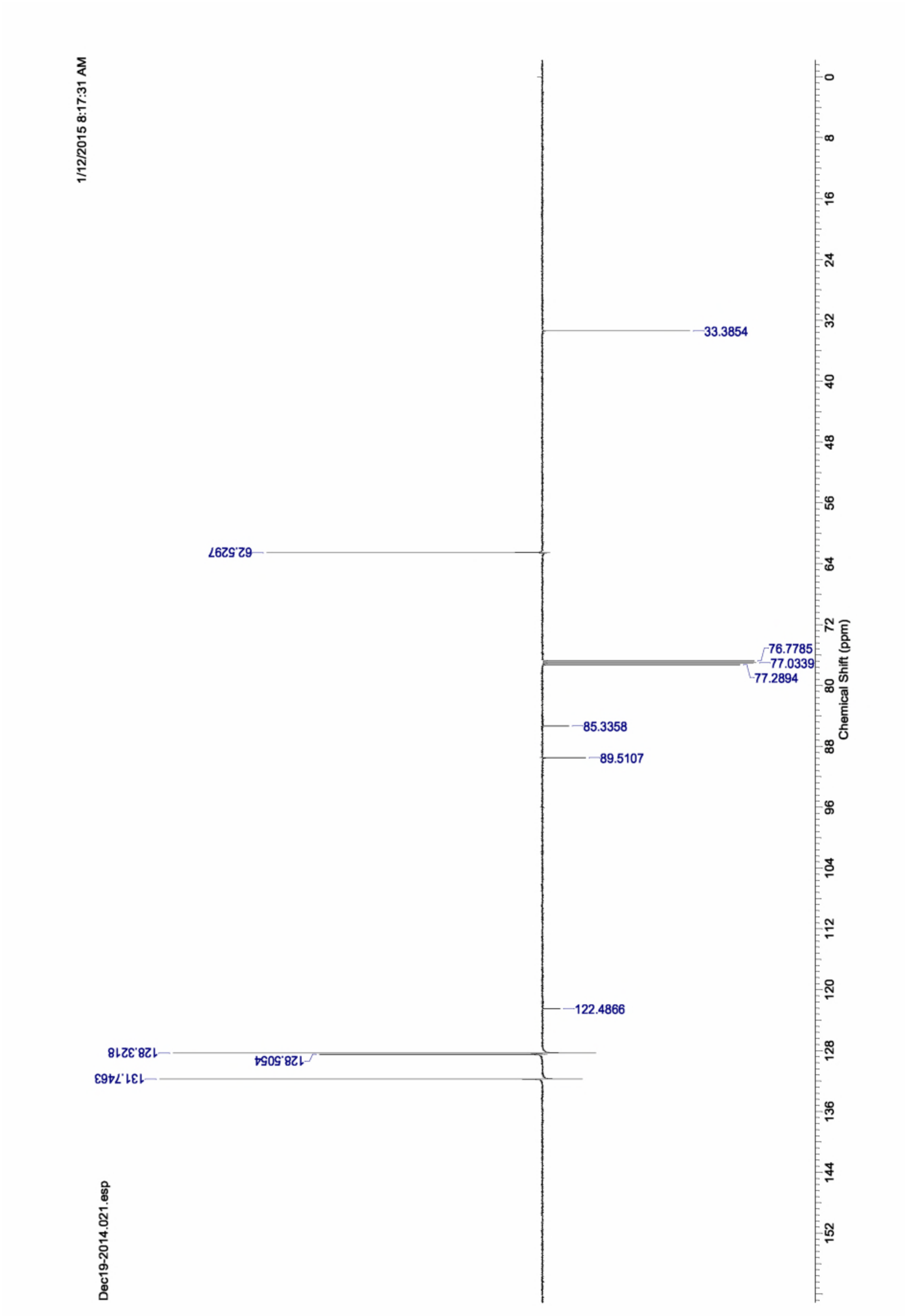
NMR spectra of complexes and intermediates



(*3S*,*6S*)-1,8-Diphenylocta-1,7-diyne-3,6-diol **12**.
δ_H (500 MHz, $CDCl_3$)

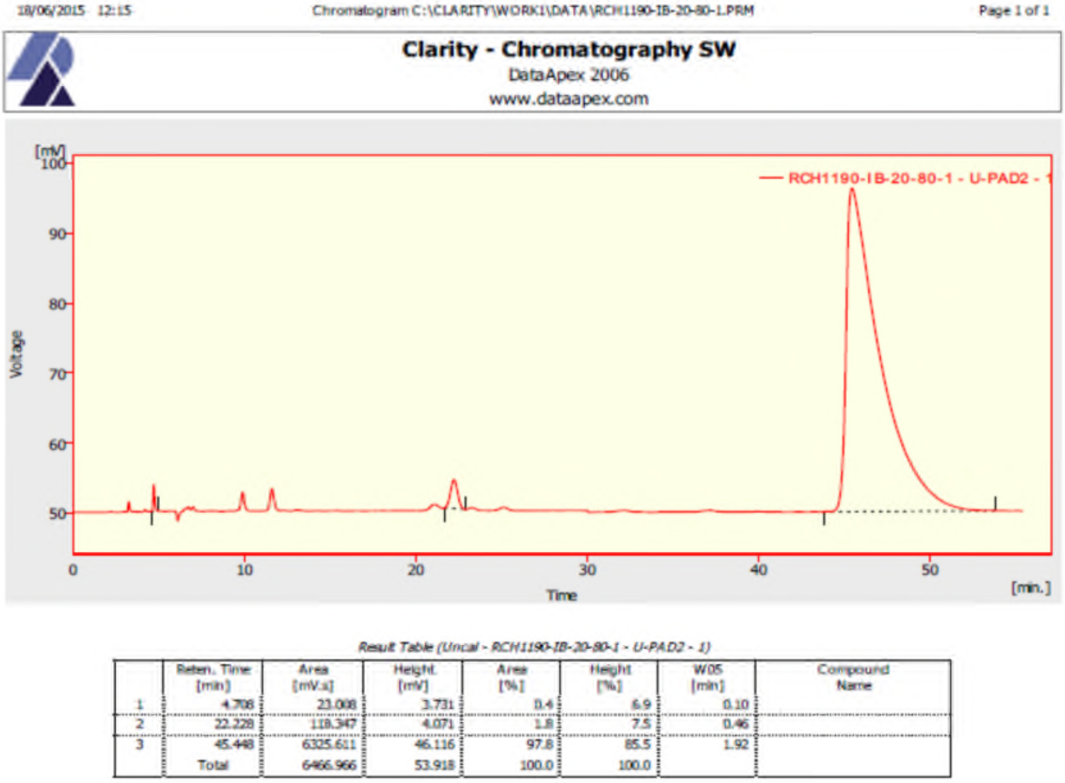


δ_C (125 MHz, $CDCl_3$)



HPLC Trace for diol 12.

Conditions: IB column, 30^{o}C, 80% Hexane: 20% *iso*-propanol, 1 ml/min. 99% ee and 96% de



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Clarity - Chromatography SW
DataApex 2006
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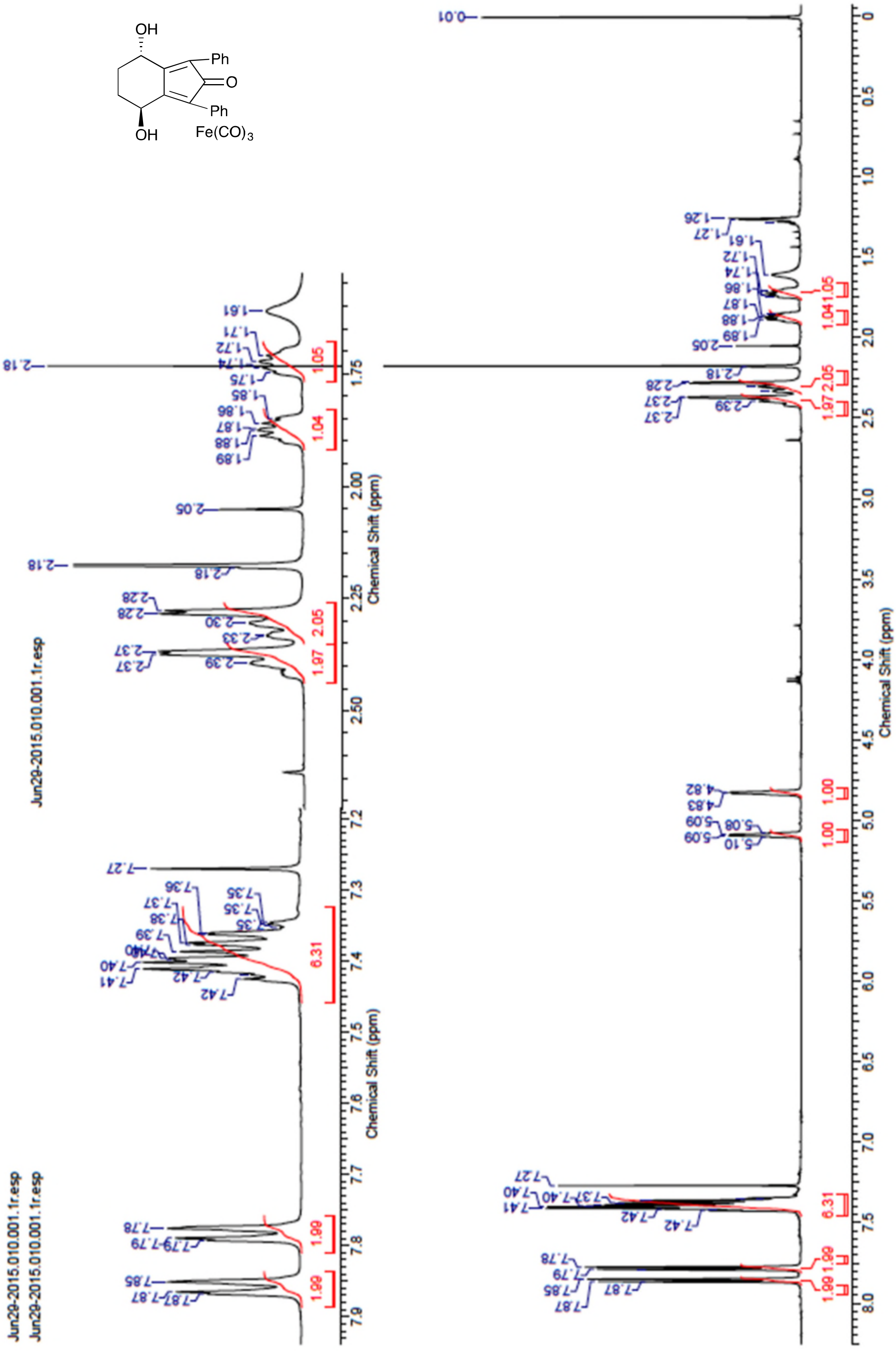
Result Table (Uncal - RCH1190-IB-20-80-1 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.708	23.008	3.731	0.4	6.9	0.10	
2	22.228	118.347	4.071	1.8	7.5	0.46	
3	45.448	6325.611	46.116	97.8	85.5	1.92	
	Total	6466.966	53.918	100.0	100.0		

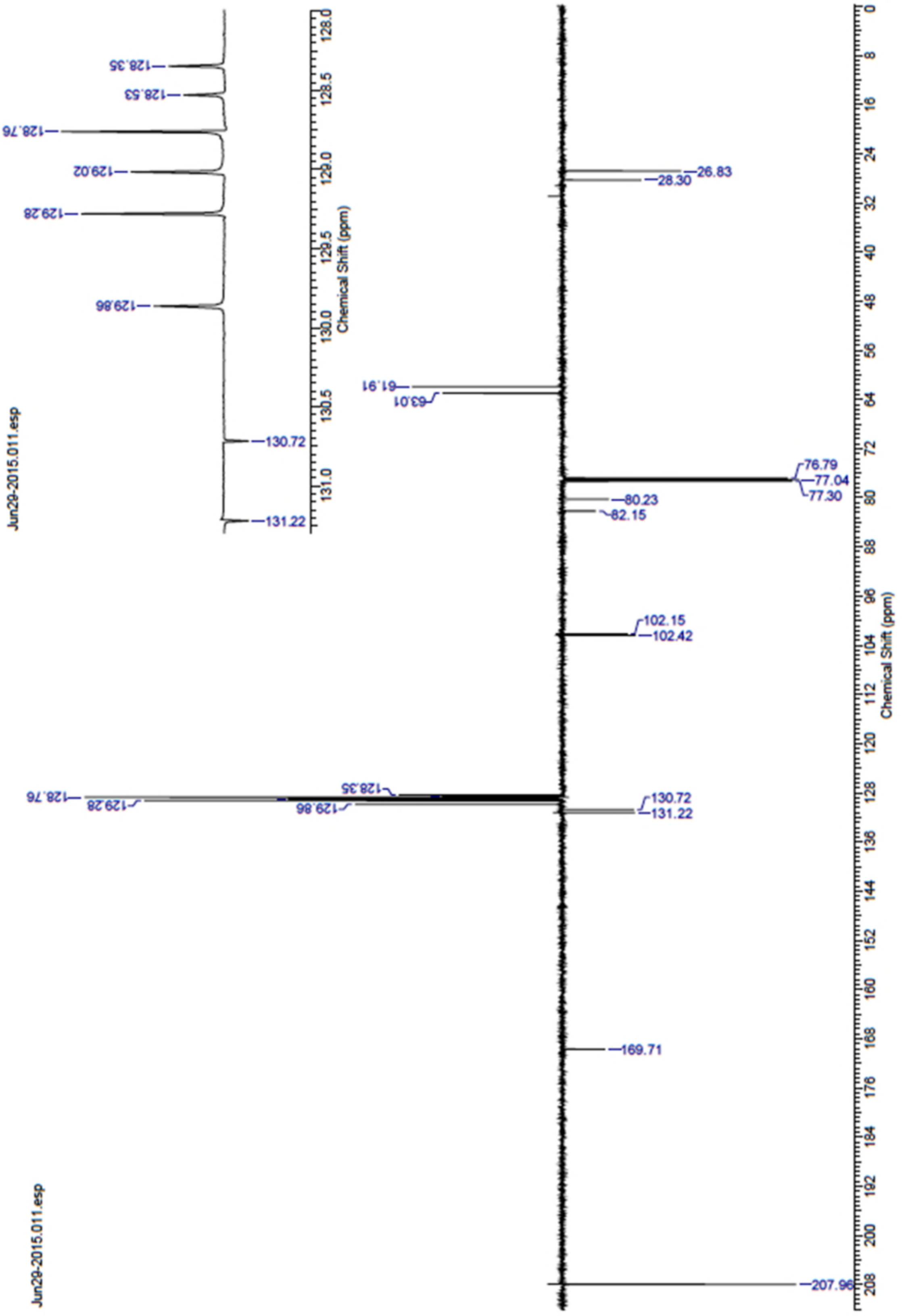
Reference to diol synthesis and ee determination: Fang, Z.; Wills, M. *J. Org. Chem.* **2013**, *78*, 8594–8605.

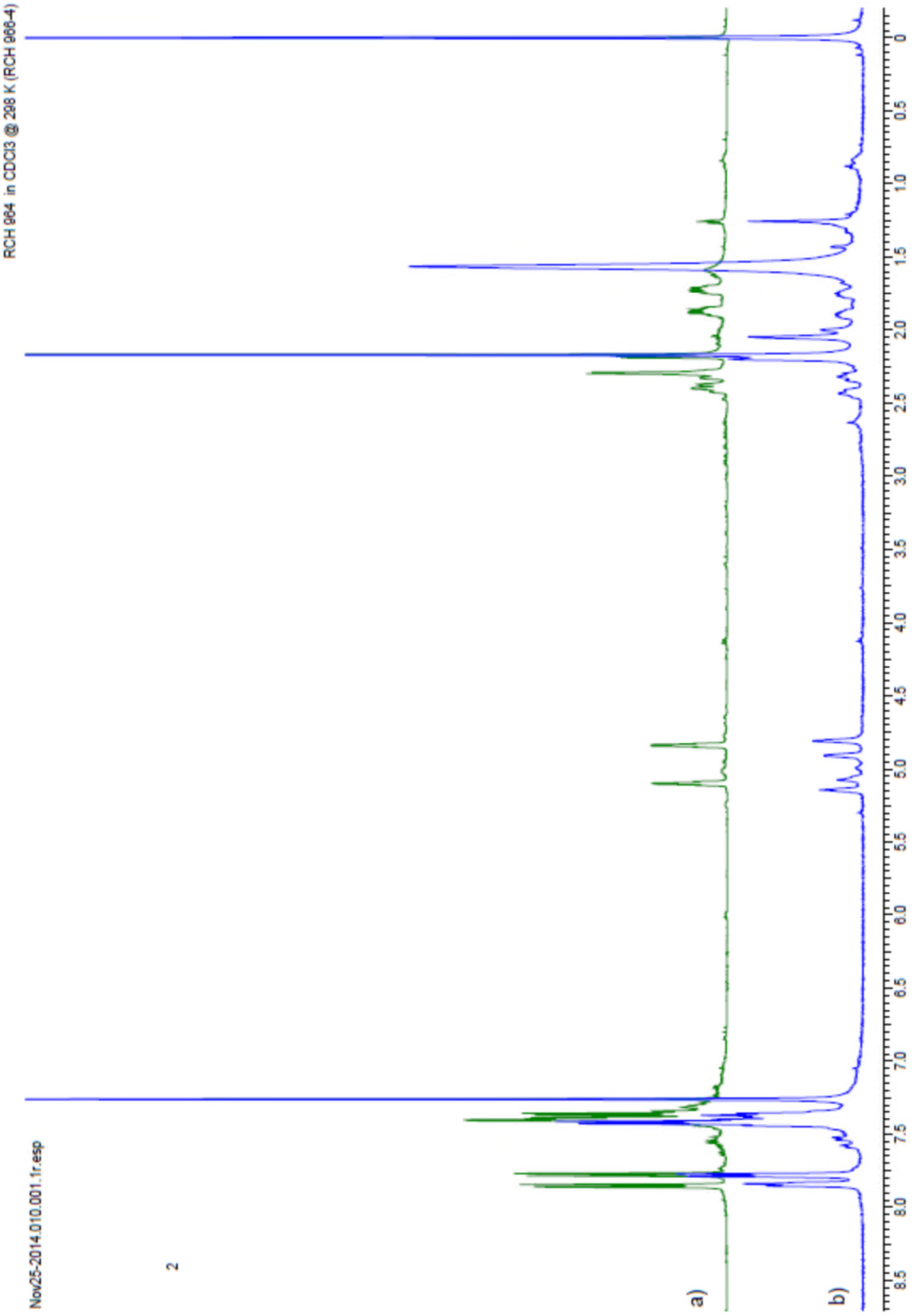
Tricarbonyl ((*4S,7S*)-4,7-dihydroxy-1,3-diphenyl-4,5,6,7-tetrahydro-2H-inden-2-one) iron **13**.

δ_H (500 MHz, $CDCl_3$)



δ_C (125 MHz, $CDCl_3$).

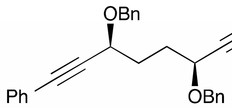


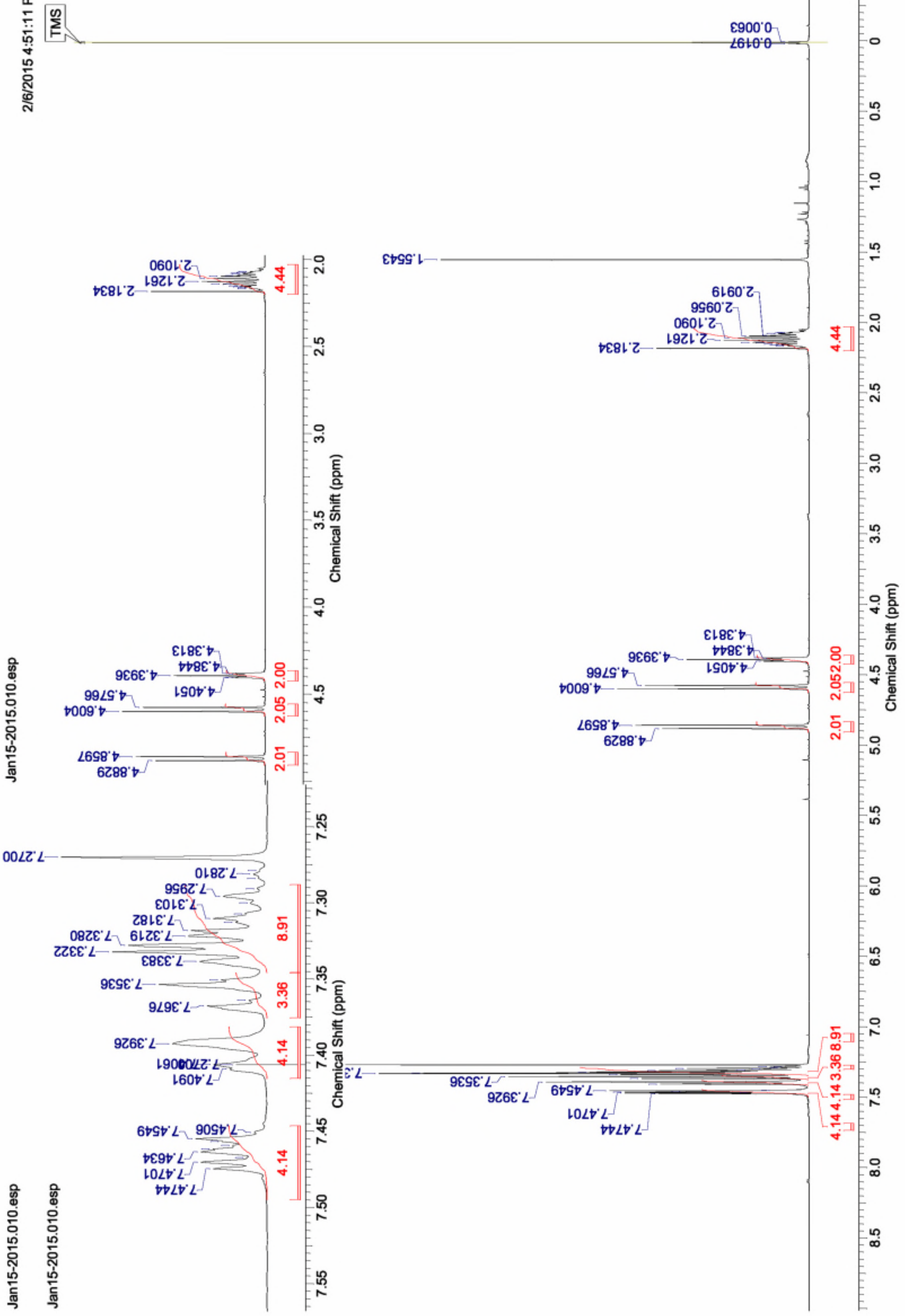


a) Enantiomerically-pure (*S*,*S*)-OH catalyst **13**; b) racemic/meso OH catalyst **13** from racemic diol.

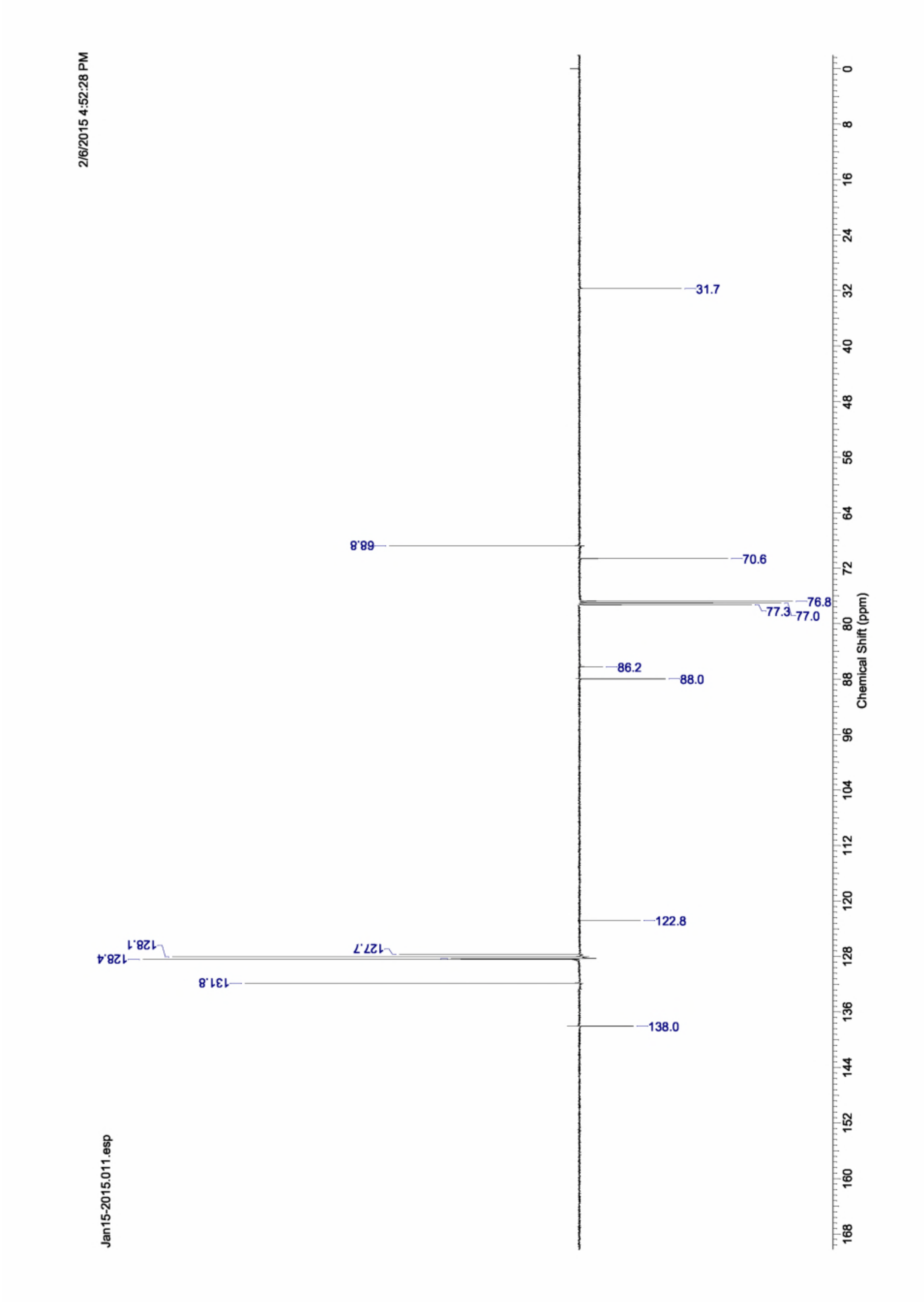
((*3S*,*6S*)-3,6-Bis(benzyloxy)octa-1,7-diyne-1,8-diyl)dibenzene **14**.

δ_H (500 MHz, $CDCl_3$)



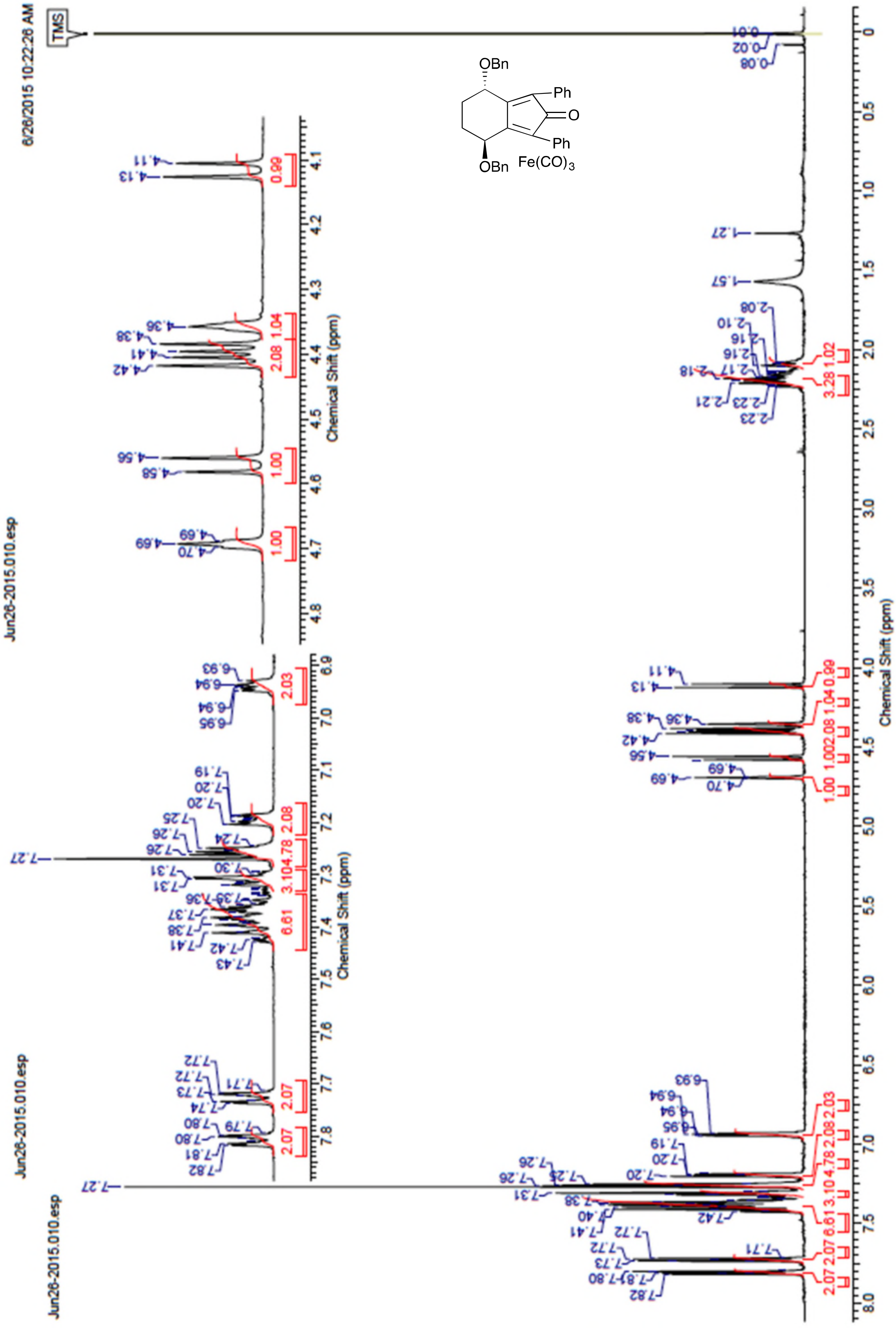


δ_C (125 MHz, $CDCl_3$)

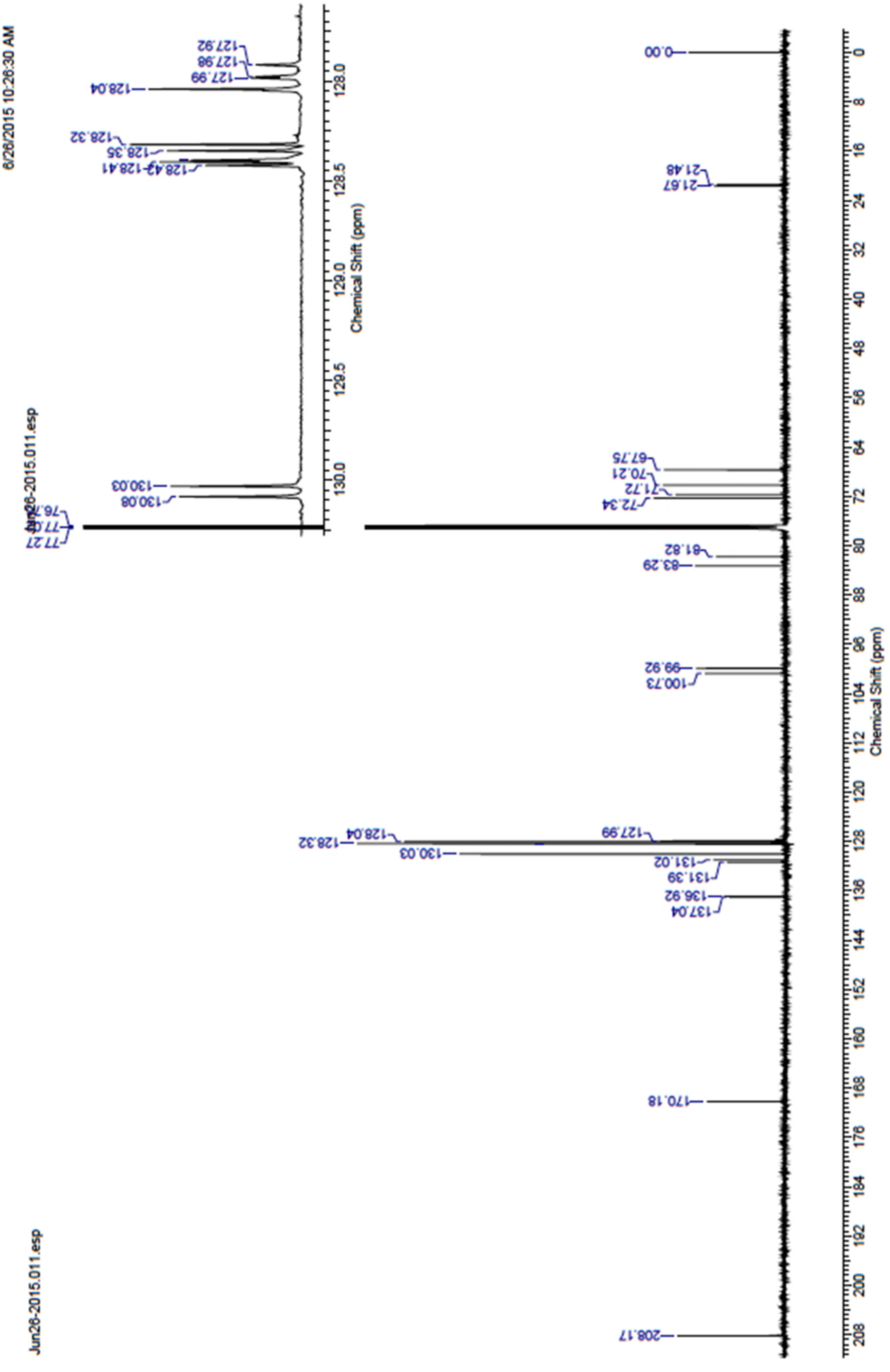


Tricarbonyl (*4S,7S*)-4,7-bis(benzyloxy)-1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one iron **18**.

δ_H (500 MHz, $CDCl_3$)

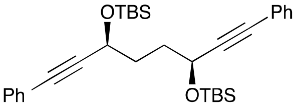


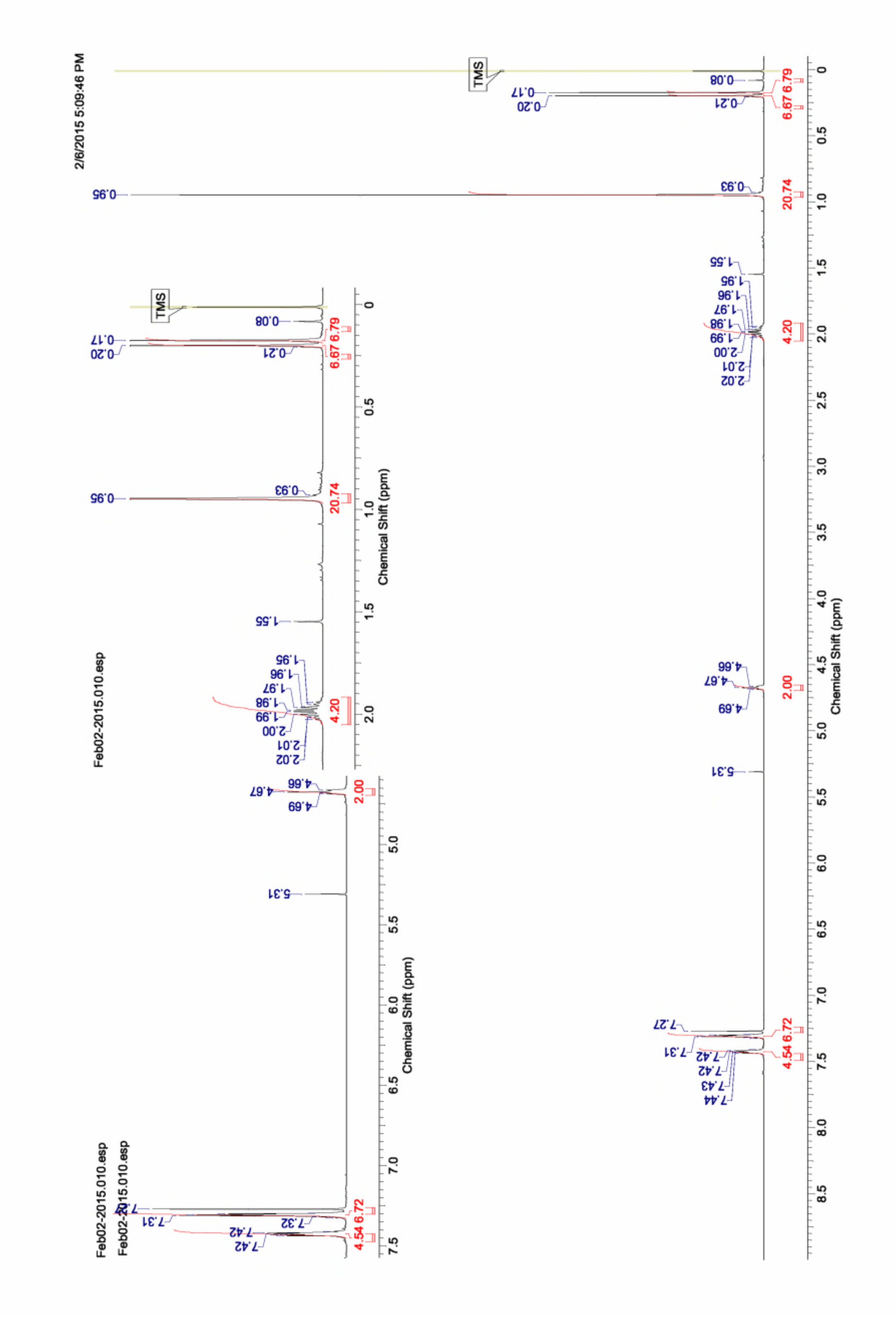
δ_C (125 MHz, $CDCl_3$)



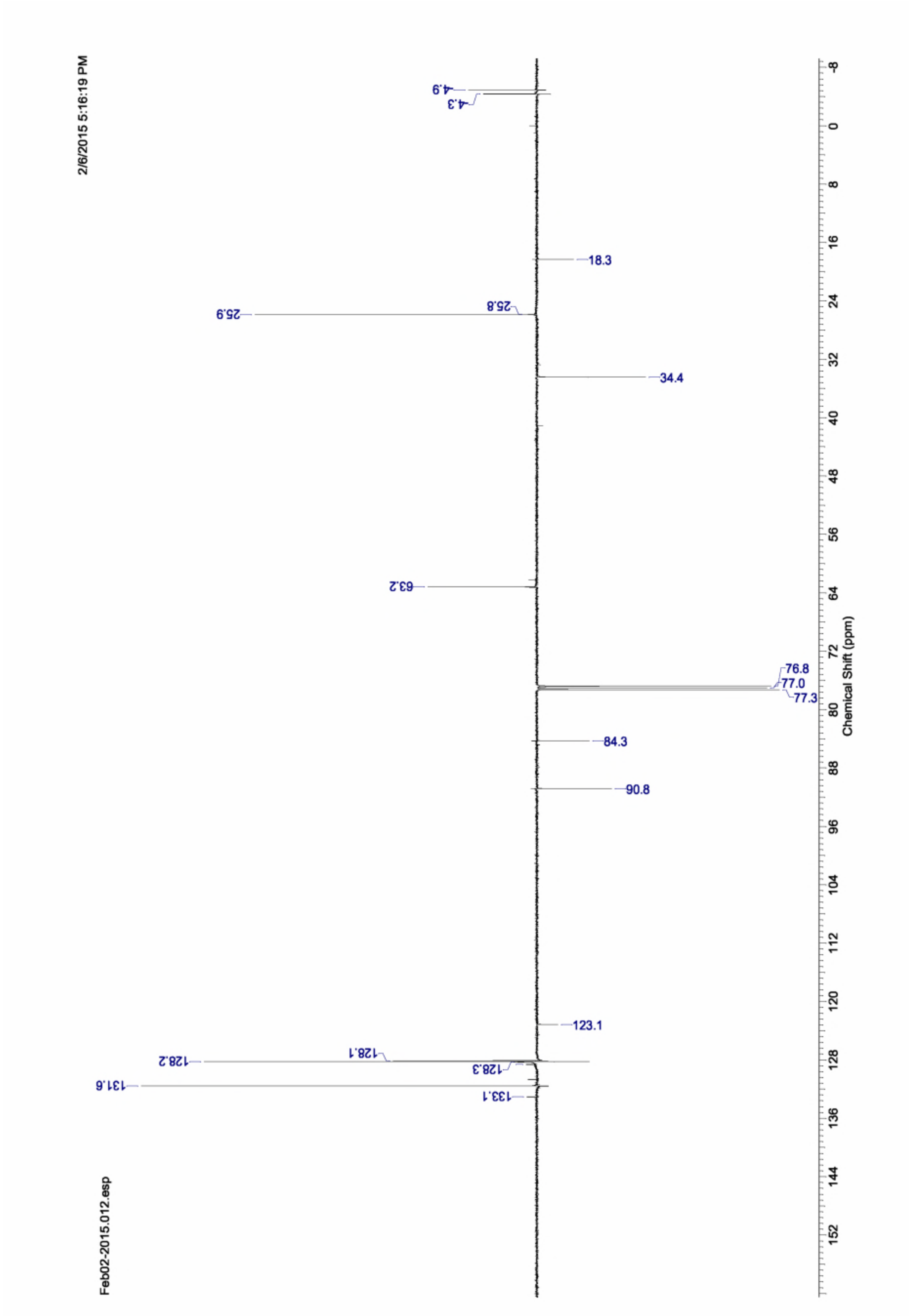
(*3S*,*6S*)-3,6-Bis(tert-butyldimethylsilyloxy)octa-1,7-diyne-1,8-diyl)dibenzene **15**.

δ_H (500 MHz, $CDCl_3$)

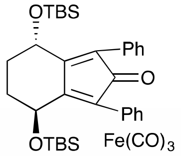




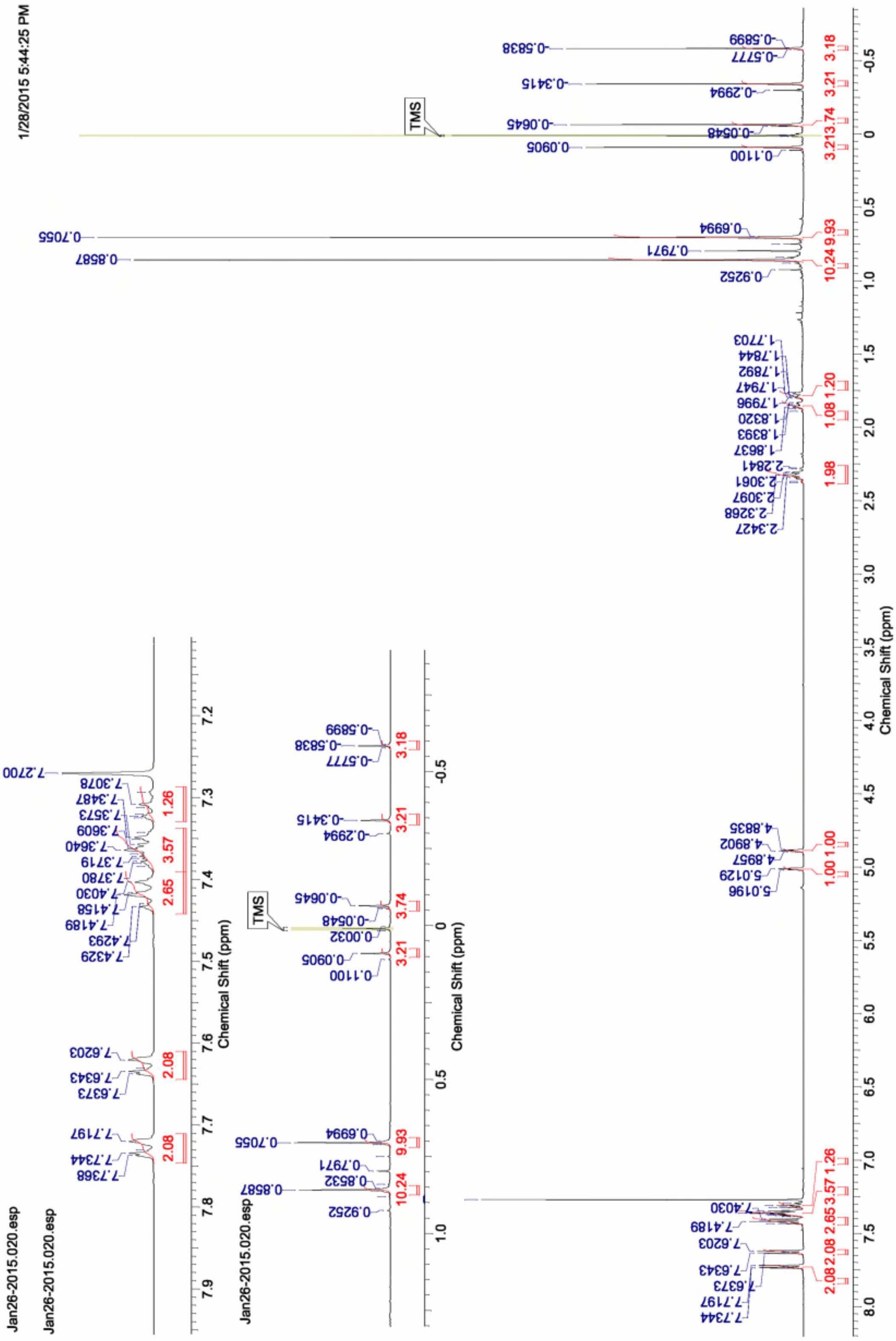
δ_C (125 MHz, $CDCl_3$)



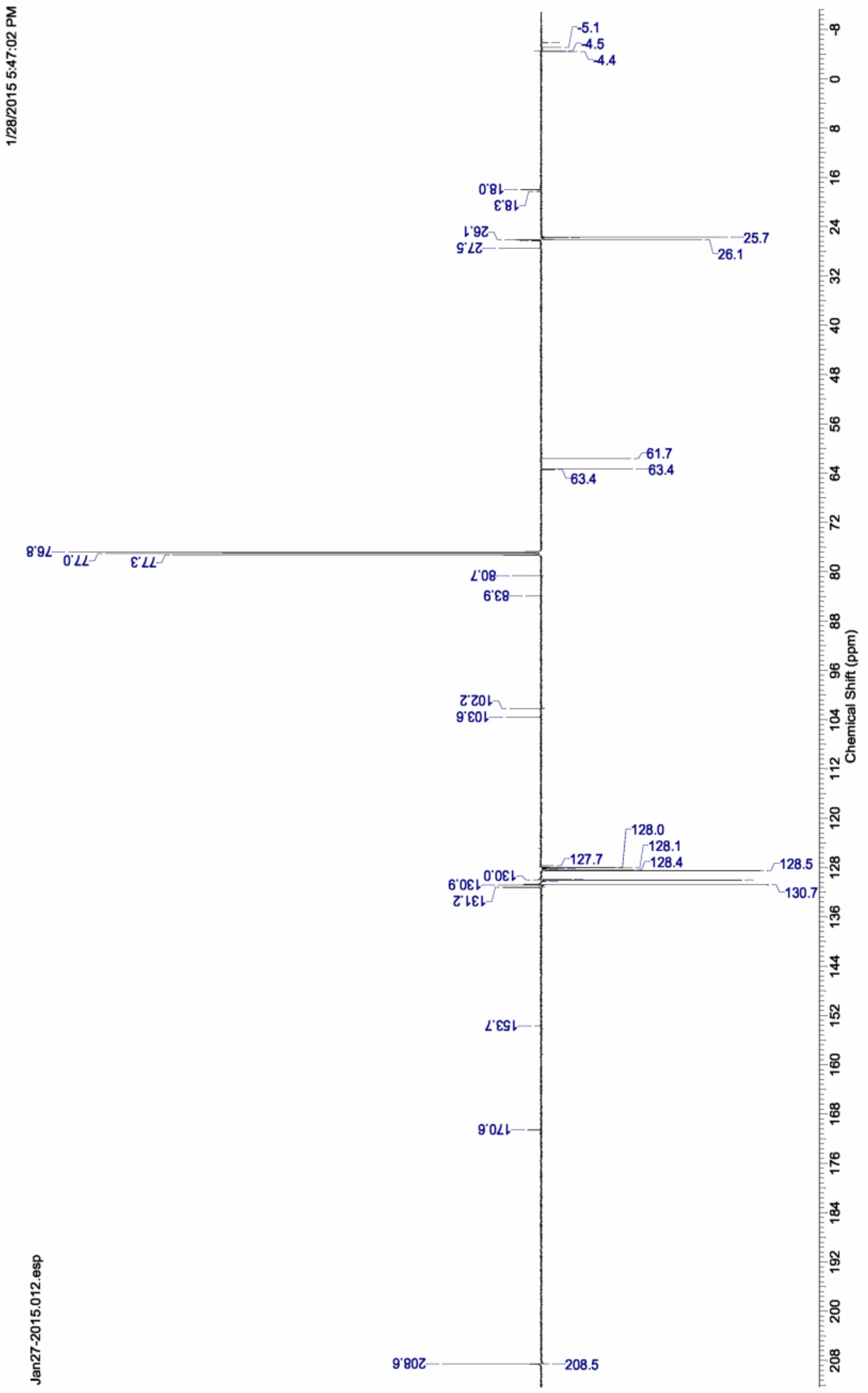
Tricarbonyl ((4*S*,7*S*)-4,7-bis((*tert*-butyldimethylsilyl)oxy)-1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron **19**.



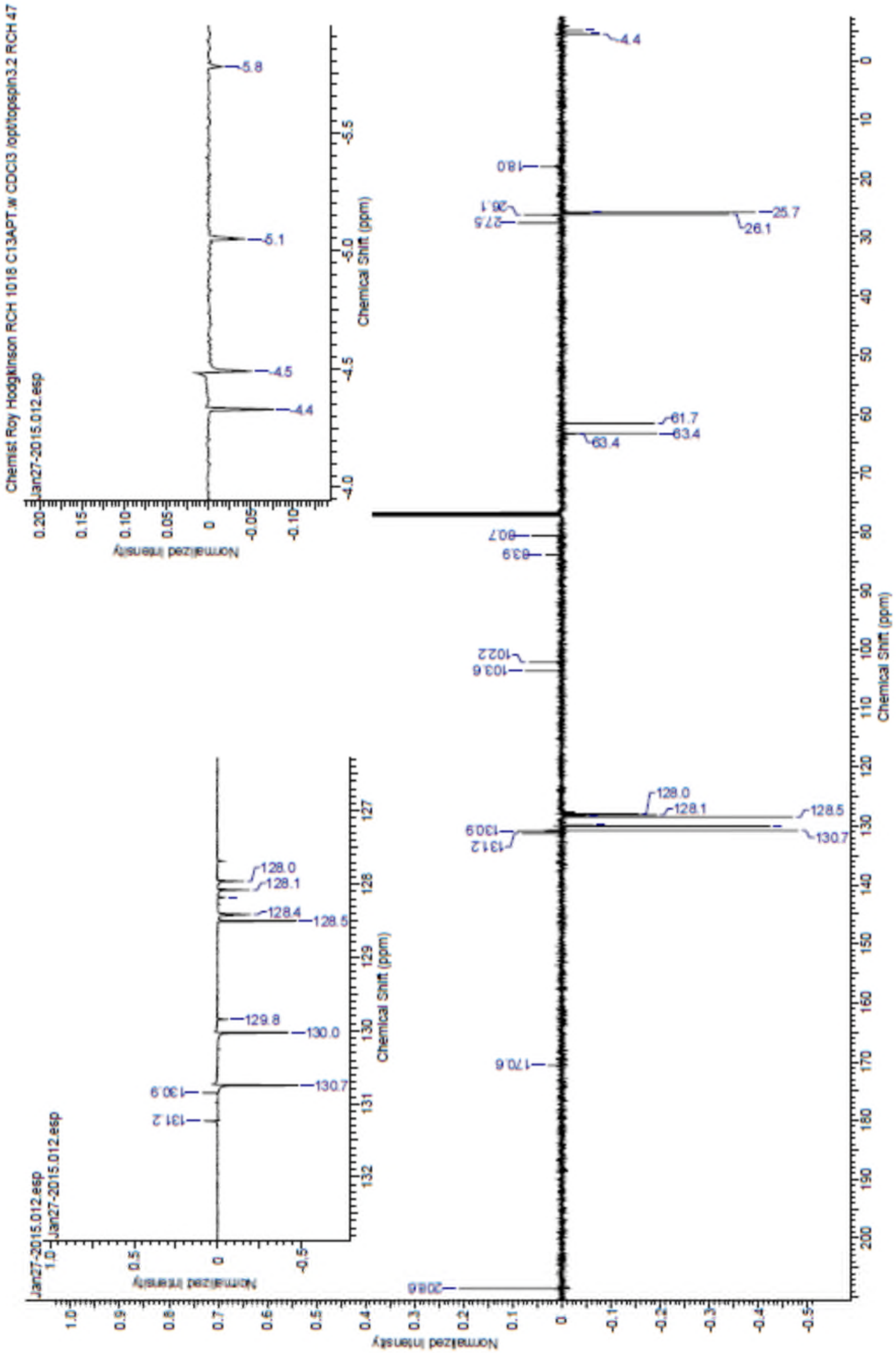
δ_H (500 MHz, CDCl$_3$)



δ_C (125 MHz, $CDCl_3$)

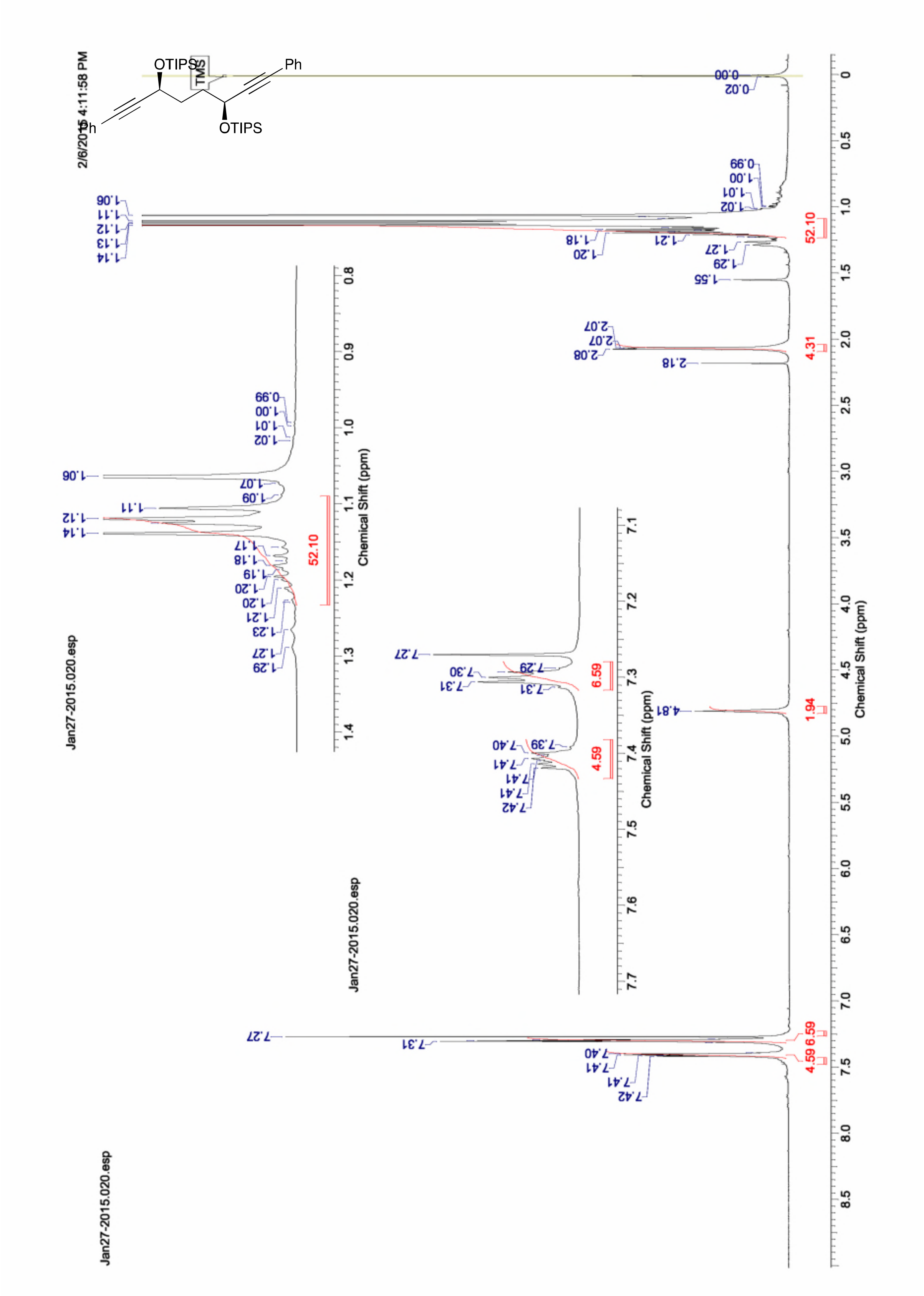


Parts of the 13C NMR have been expanded below.

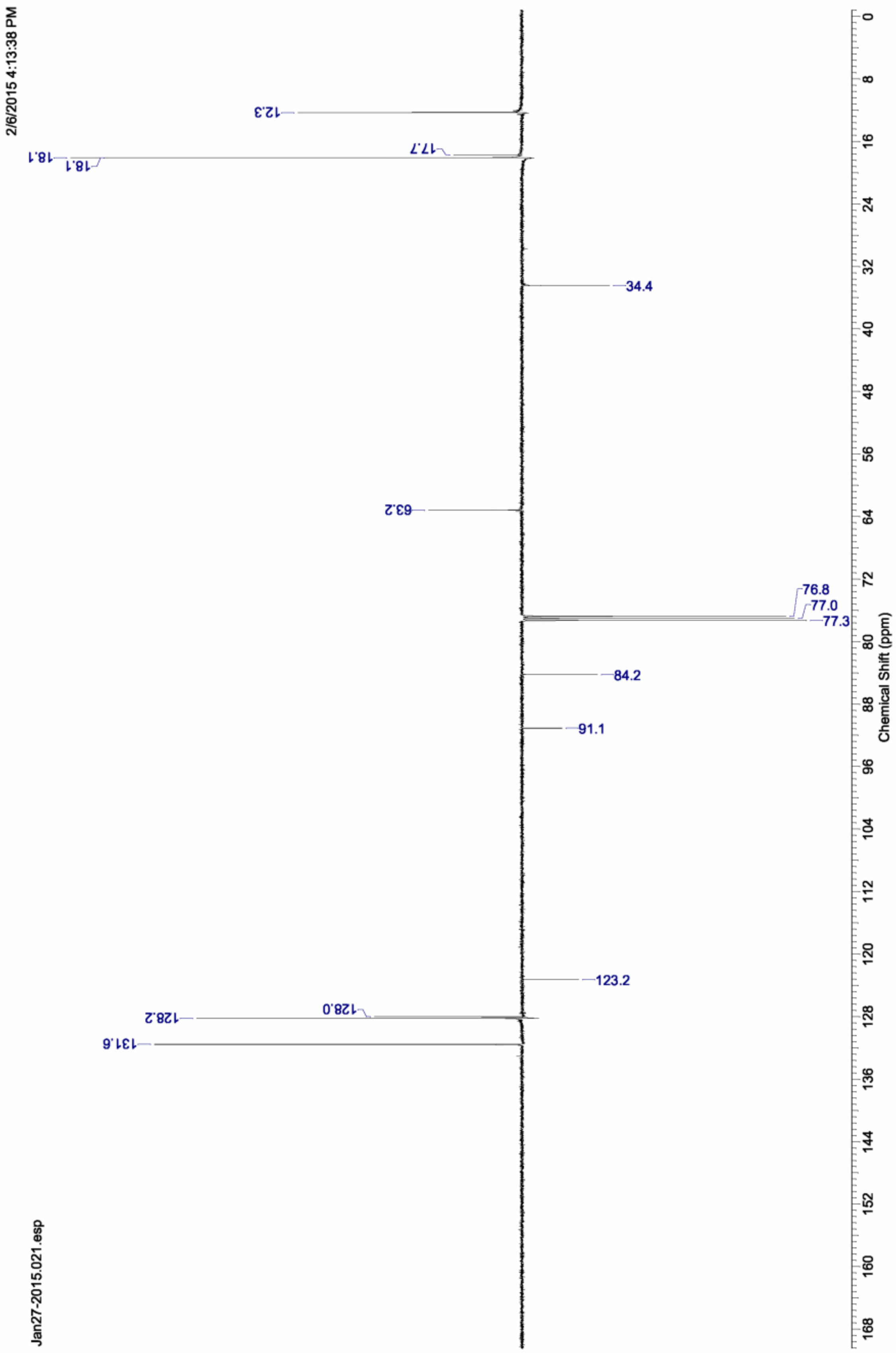


((*3S*,*6S*)-3,6-Bis(triisopropylsilyloxy)octa-1,7-diyne-1,8-diyl)dibenzene **16**.

δ_H (500 MHz, $CDCl_3$)

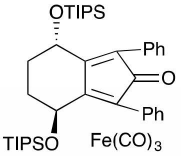


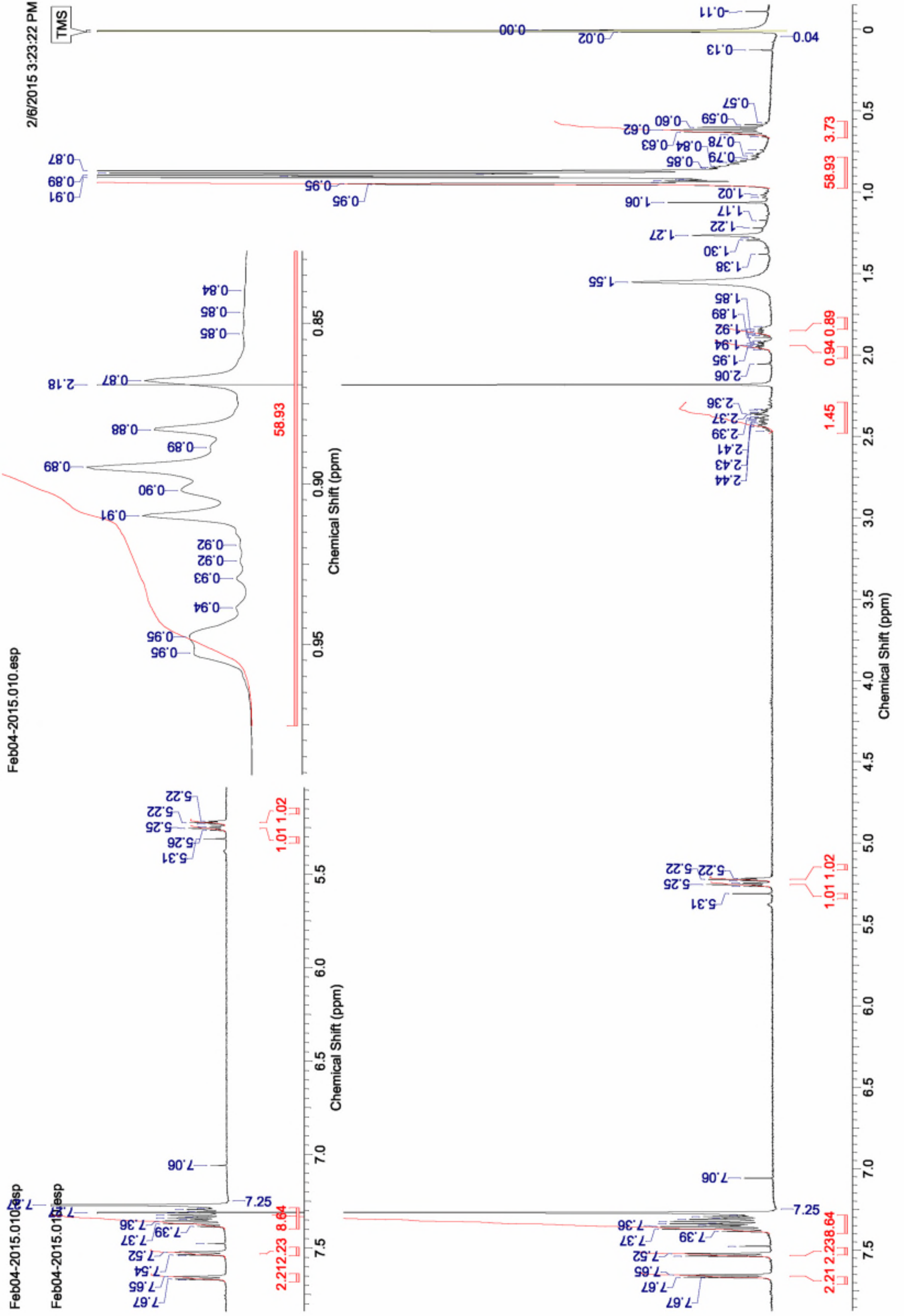
δ_C (125 MHz, $CDCl_3$)



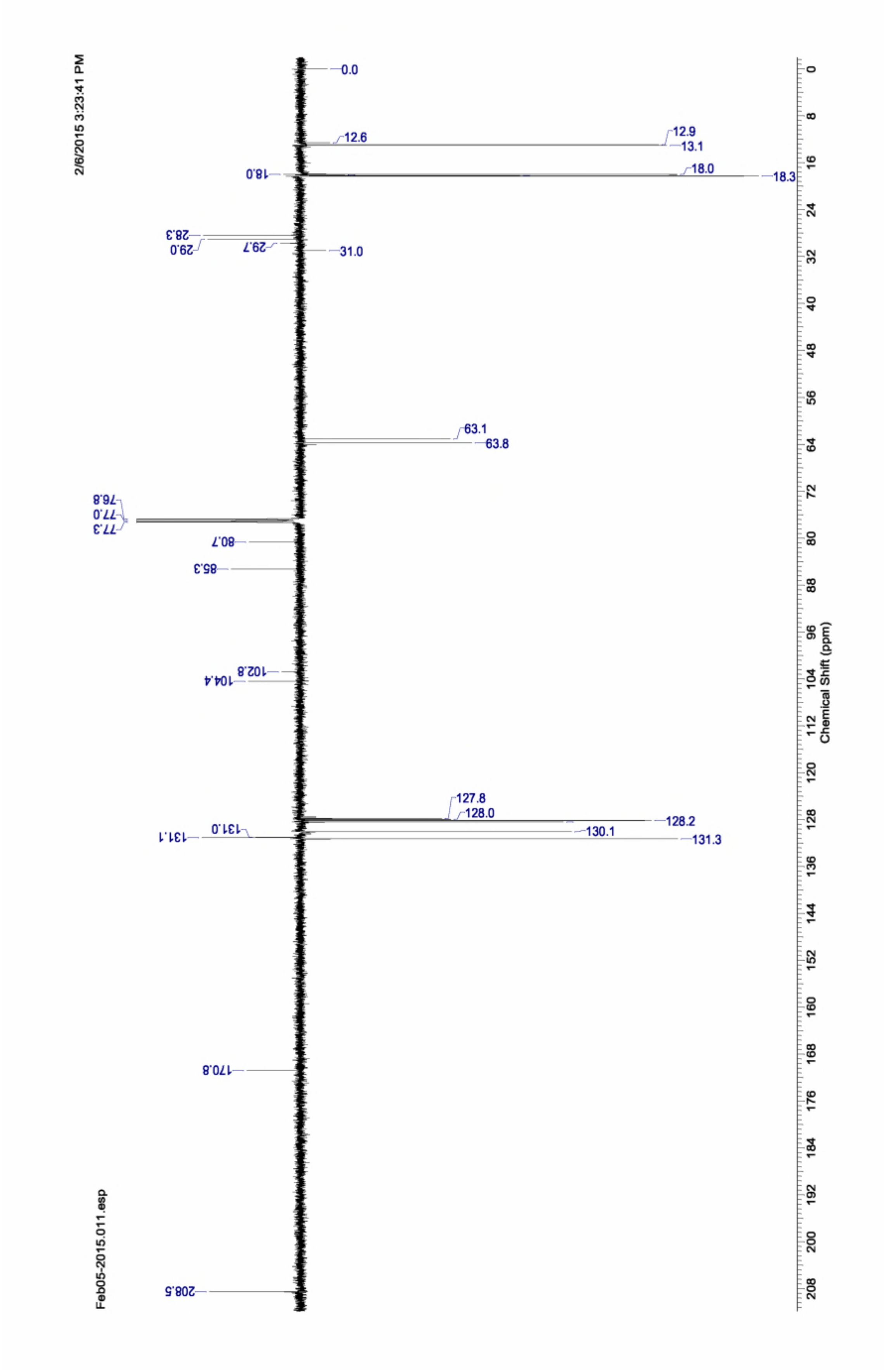
Tricarbonyl ((*4S,7S*)-1,3-diphenyl-4,7-bis((triisopropylsilyl)oxy)-4,5,6,7-tetrahydro-2H-inden-2-one) iron **20**.

δ_H (500 MHz, $CDCl_3$)



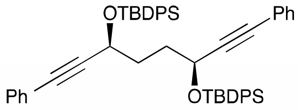


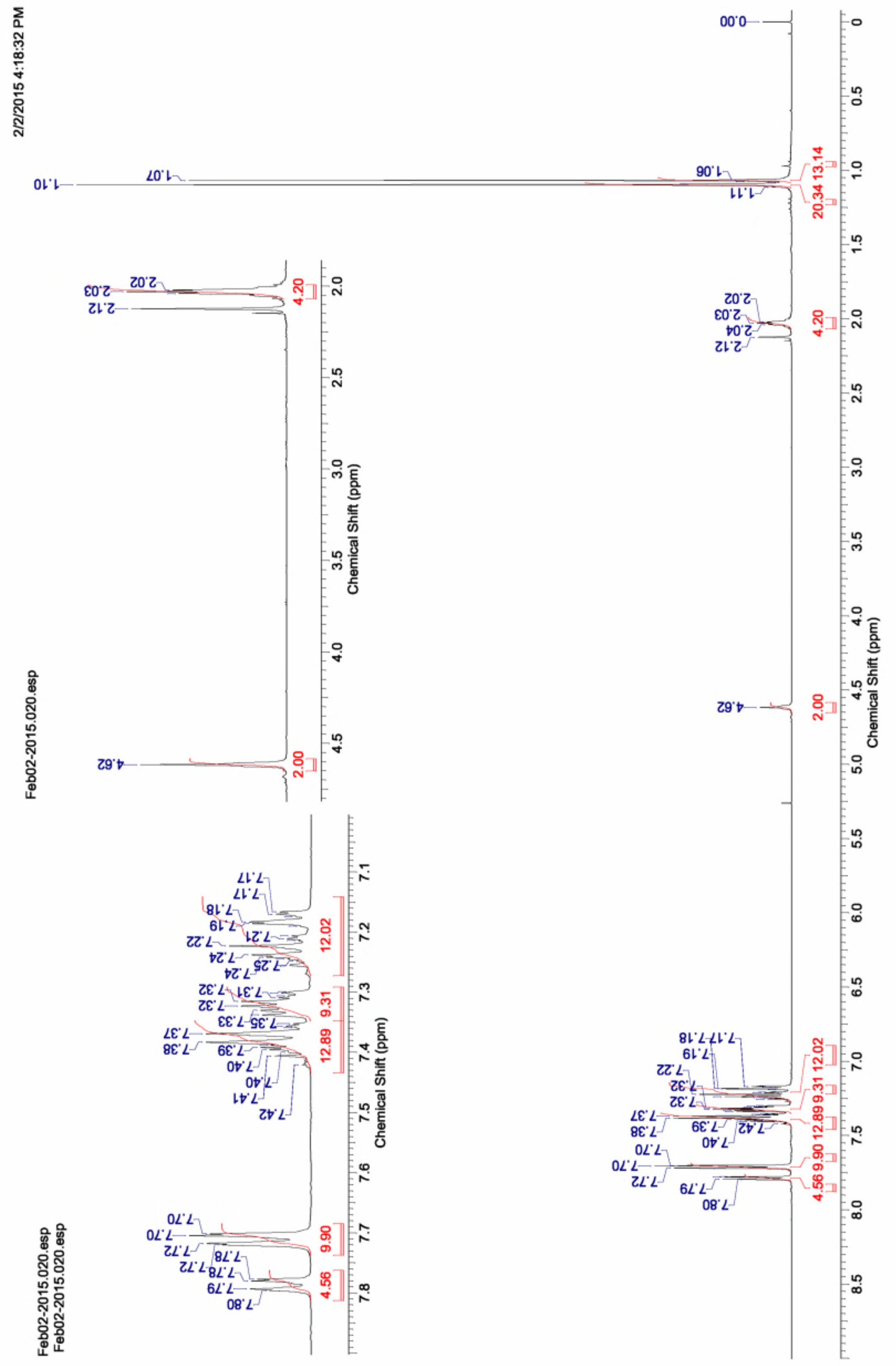
δ_C (125 MHz, $CDCl_3$)



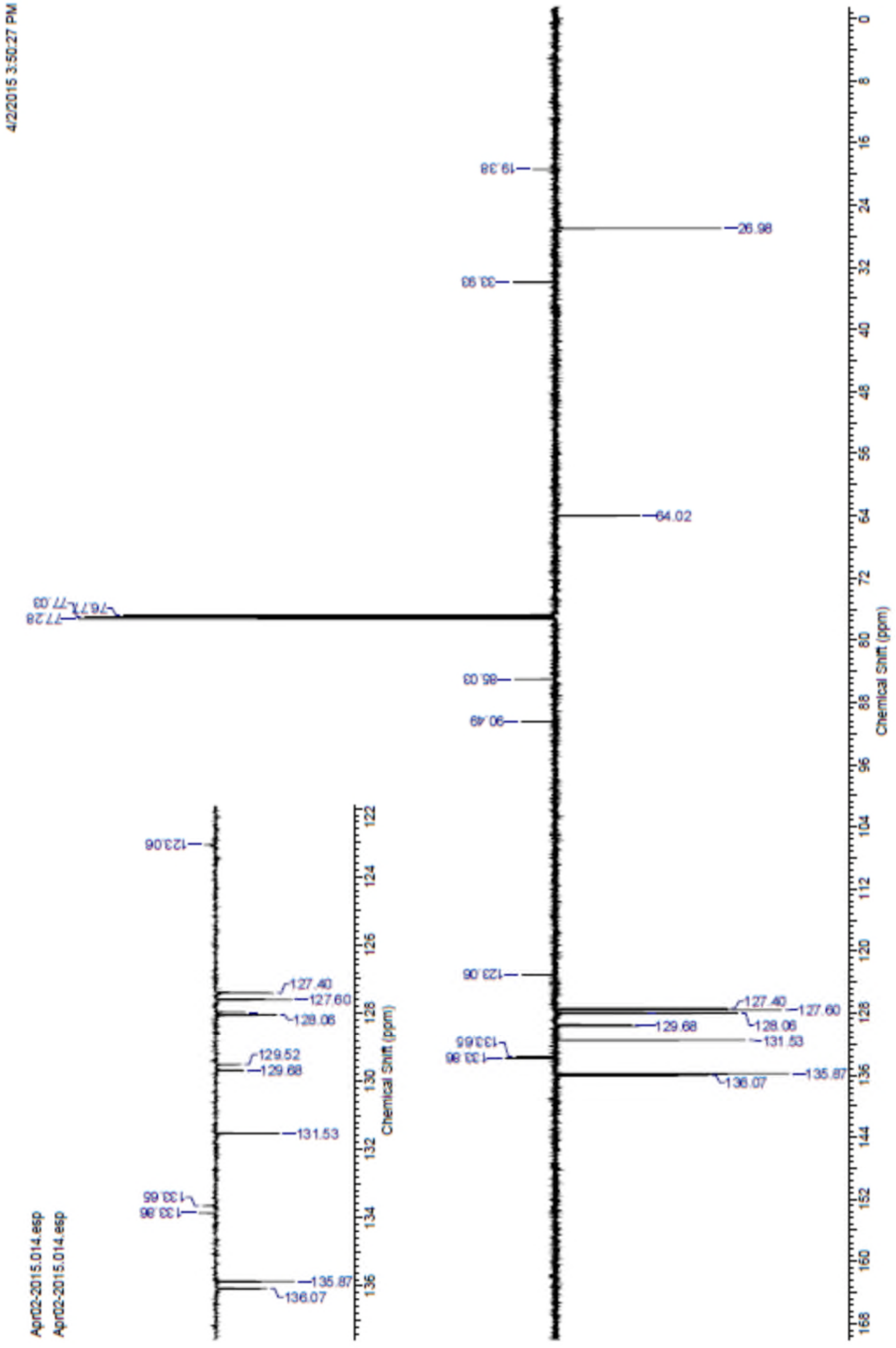
((3*S*,6*S*)-3,6-Bis(dimethylphenylsilyloxy)octa-1,7-diyne-1,8-diyl)dibenzene **17**.

δ_H (500 MHz, $CDCl_3$)



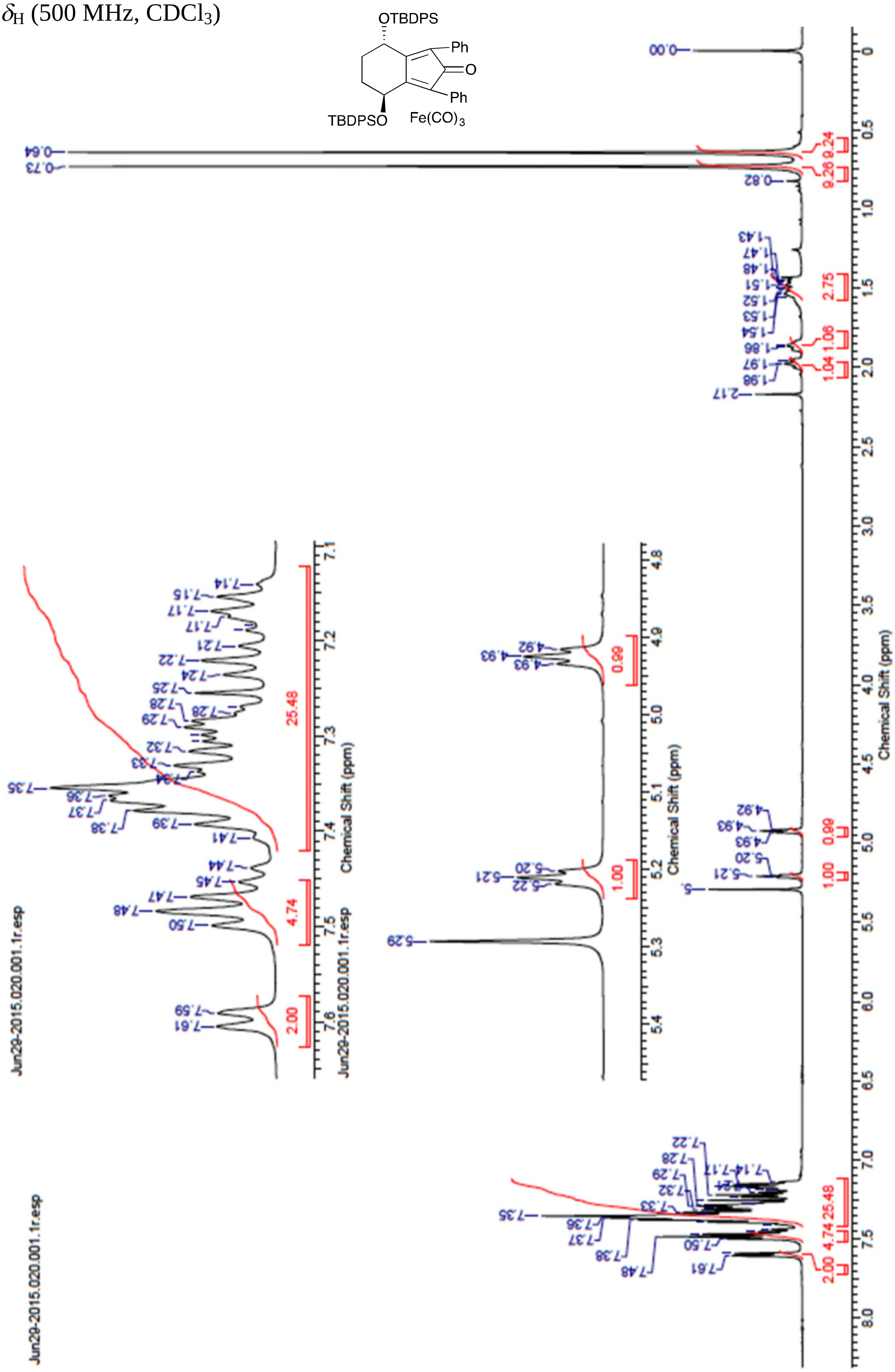


δ_C (125 MHz, CDCl$_3$).

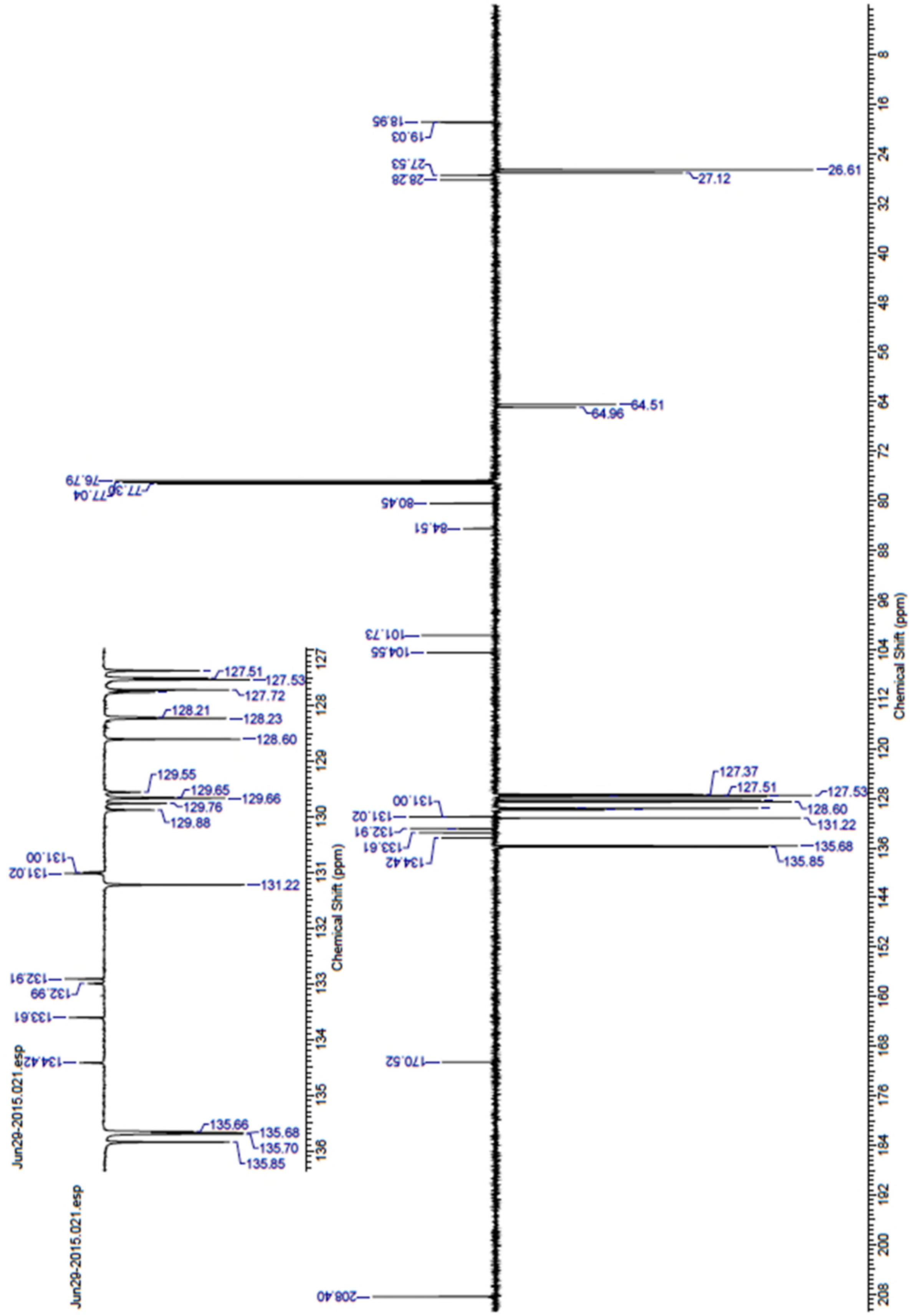


Tricarbonyl ((*4S,7S*)-4,7-bis((tert-butyldiphenylsilyl)oxy)-1,3-diphenyl-4,5,6,7-tetrahydro-2H-inden-2-one) iron **21**.

δ_H (500 MHz, $CDCl_3$)

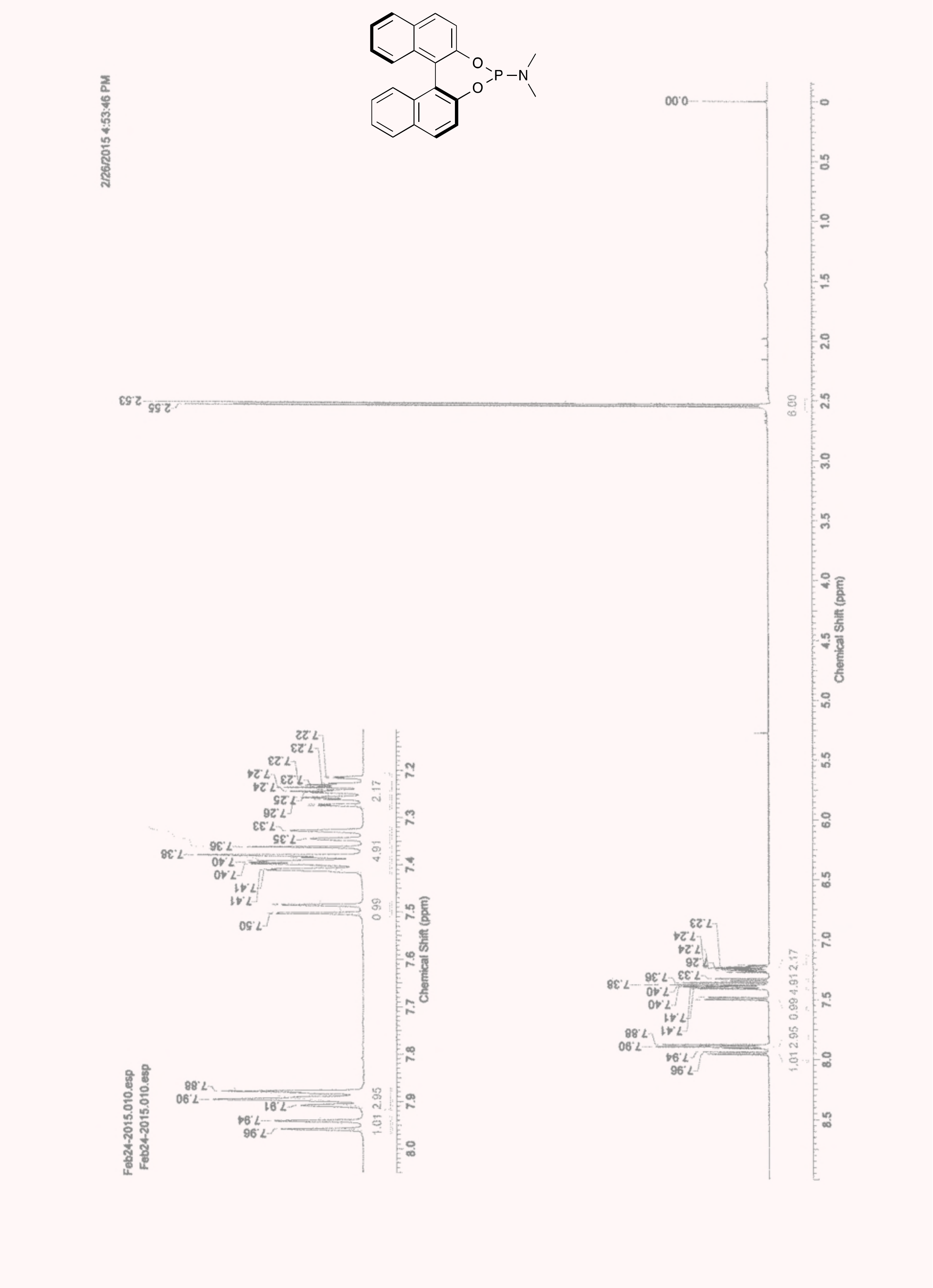


δ_C (125 MHz, $CDCl_3$)

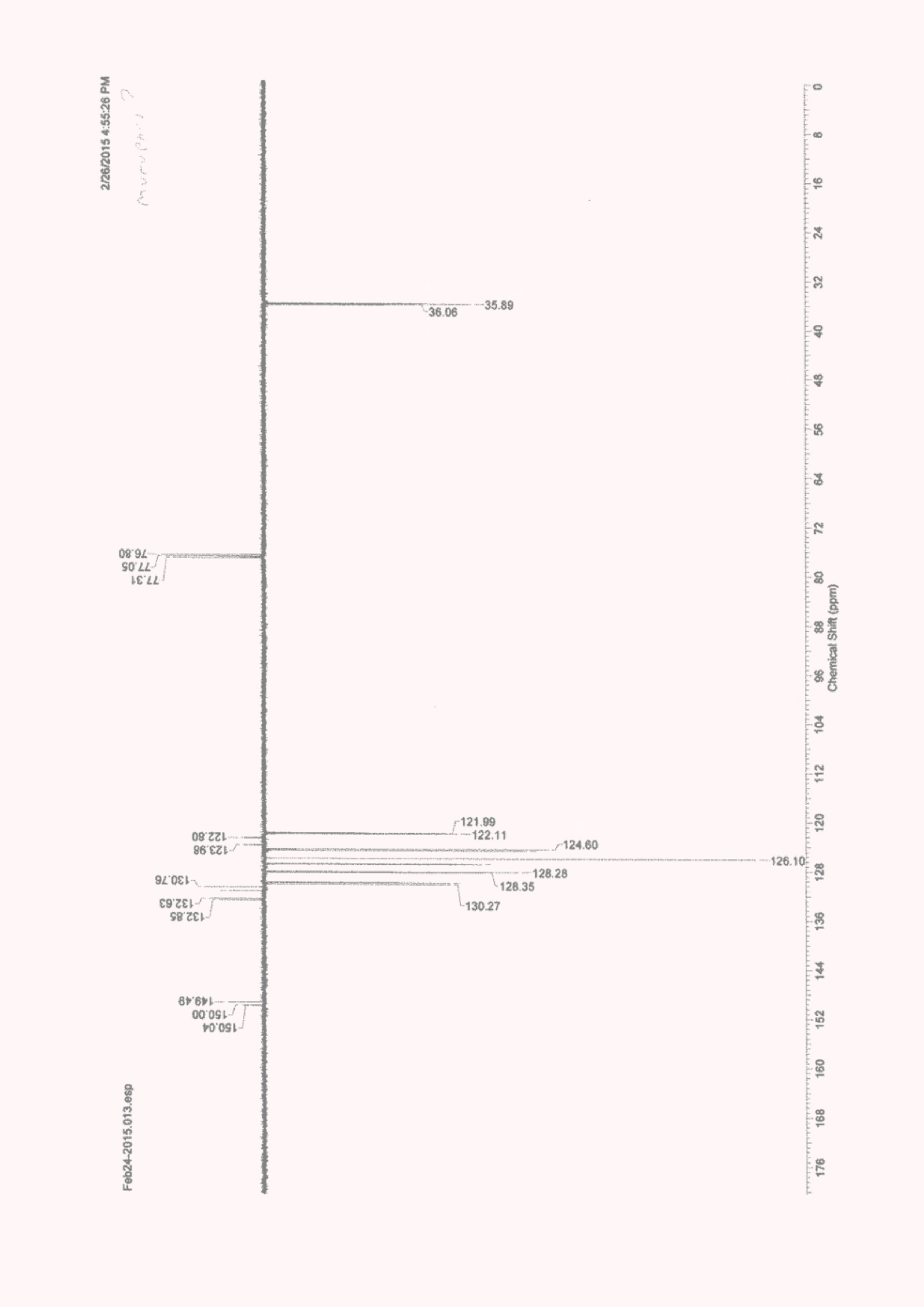


(*S*)-*N*,*N*-Dimethyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine ((S)-MONOPHOS).

δ_H (500 MHz, $CDCl_3$)



δ_C (125 MHz, $CDCl_3$)



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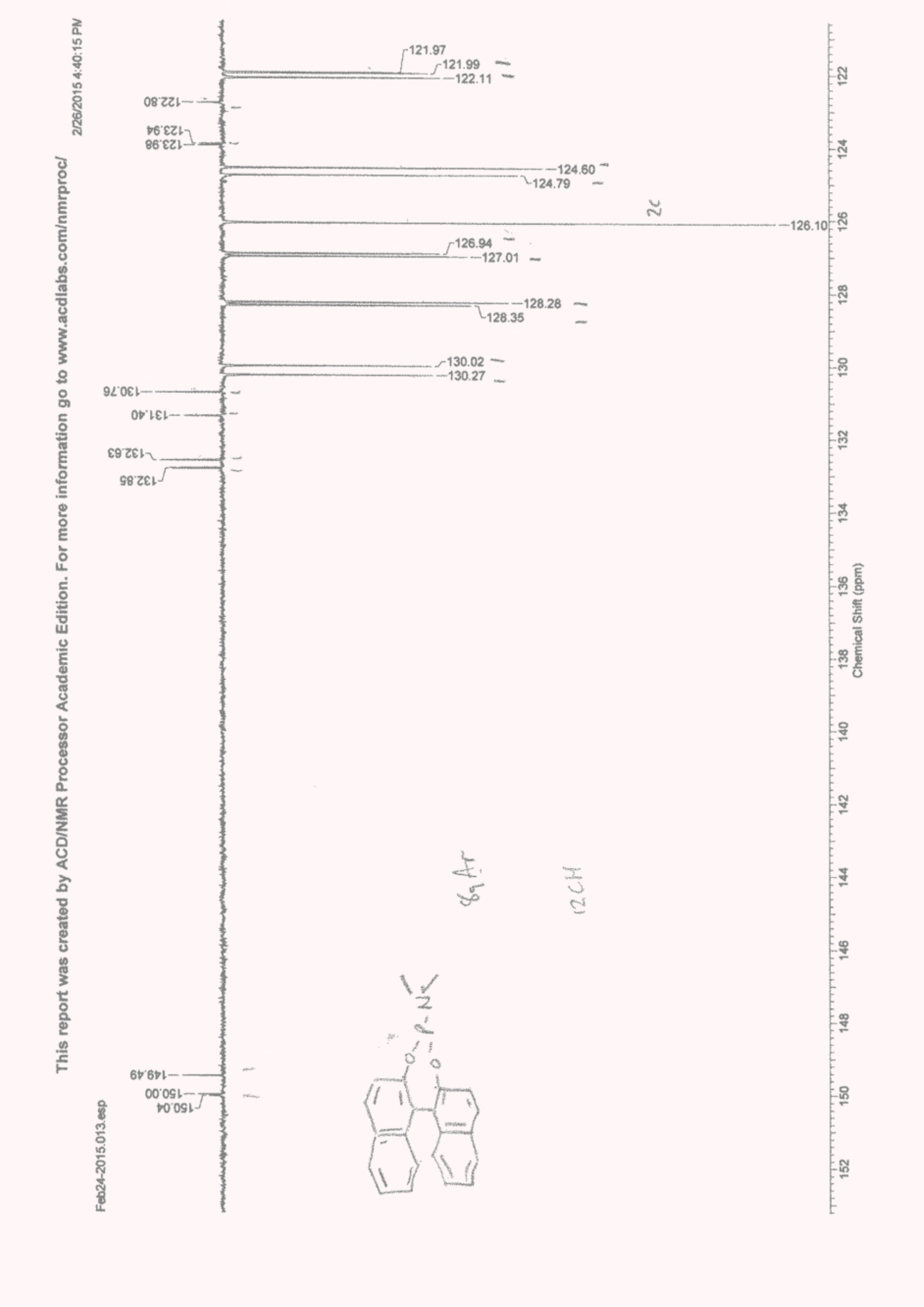
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130.27
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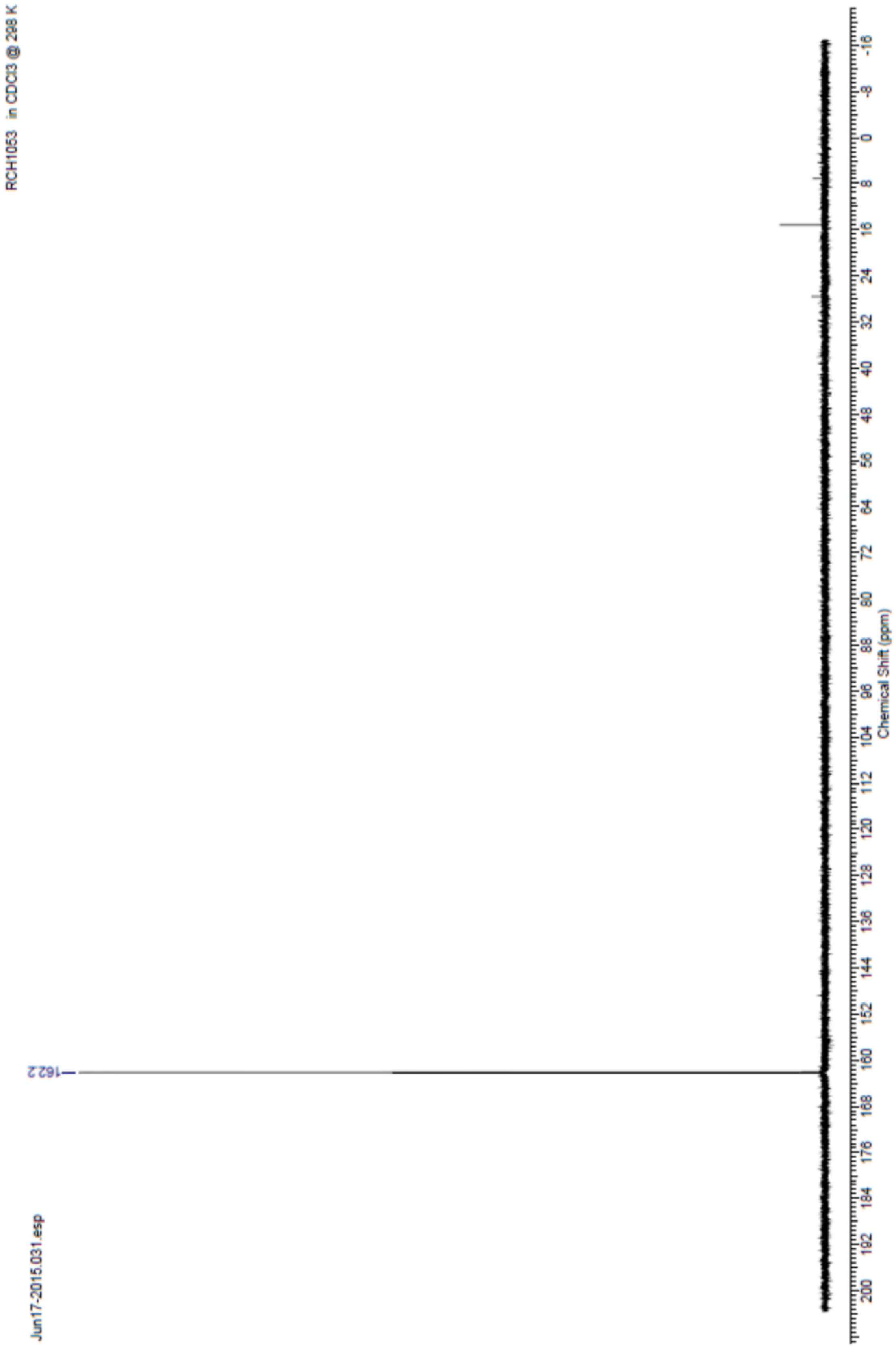
131.40
132.63
132.85
149.49
150.00
150.04
2C
8q Ar
12CH
O
O
P
N
122
124
126
128
130
132
134
136
138
140
142
144
146
148
150
152
Chemical Shift (ppm)

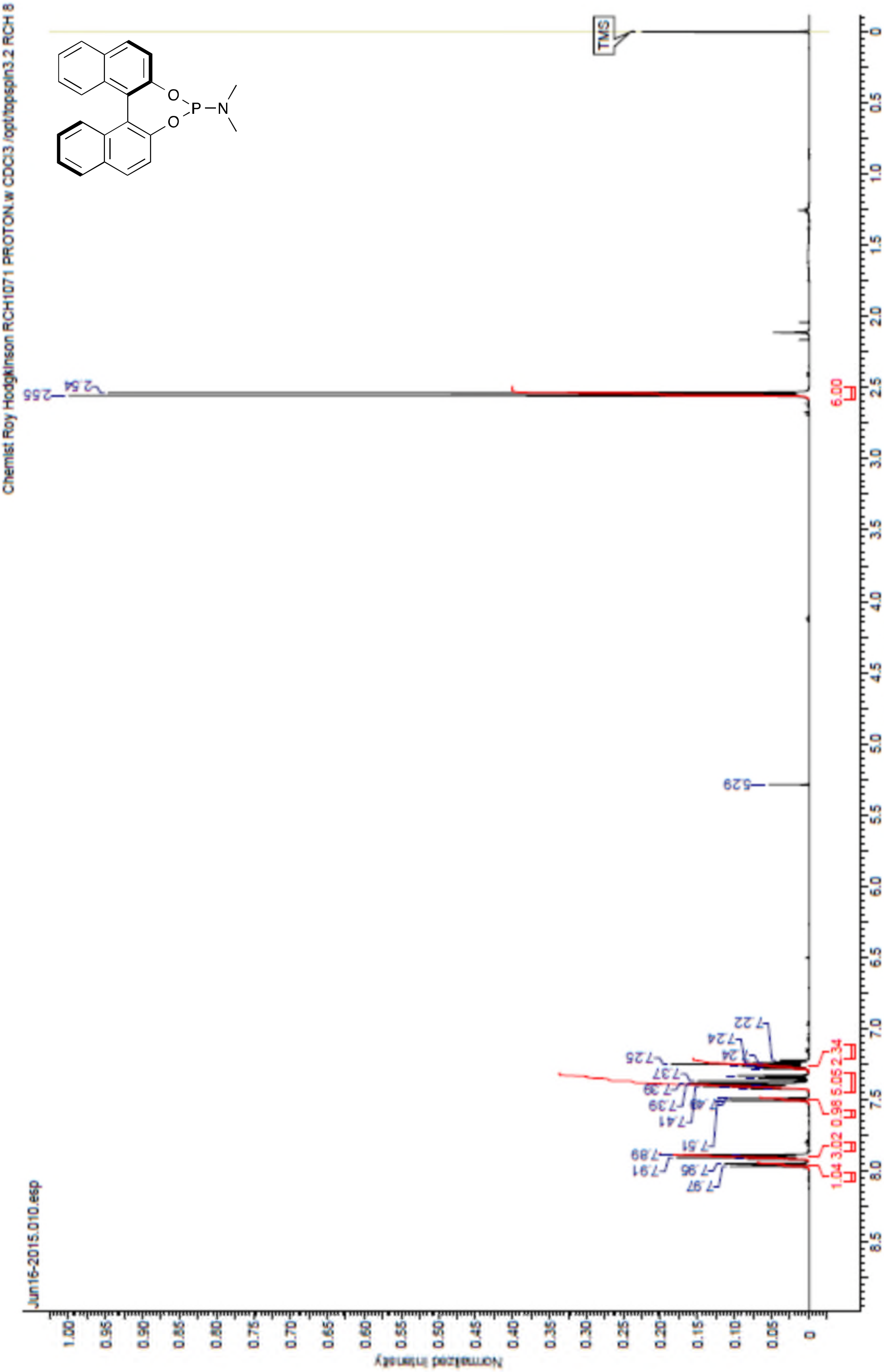
P-NMR

δP (202 MHz, $CDCl_3$)

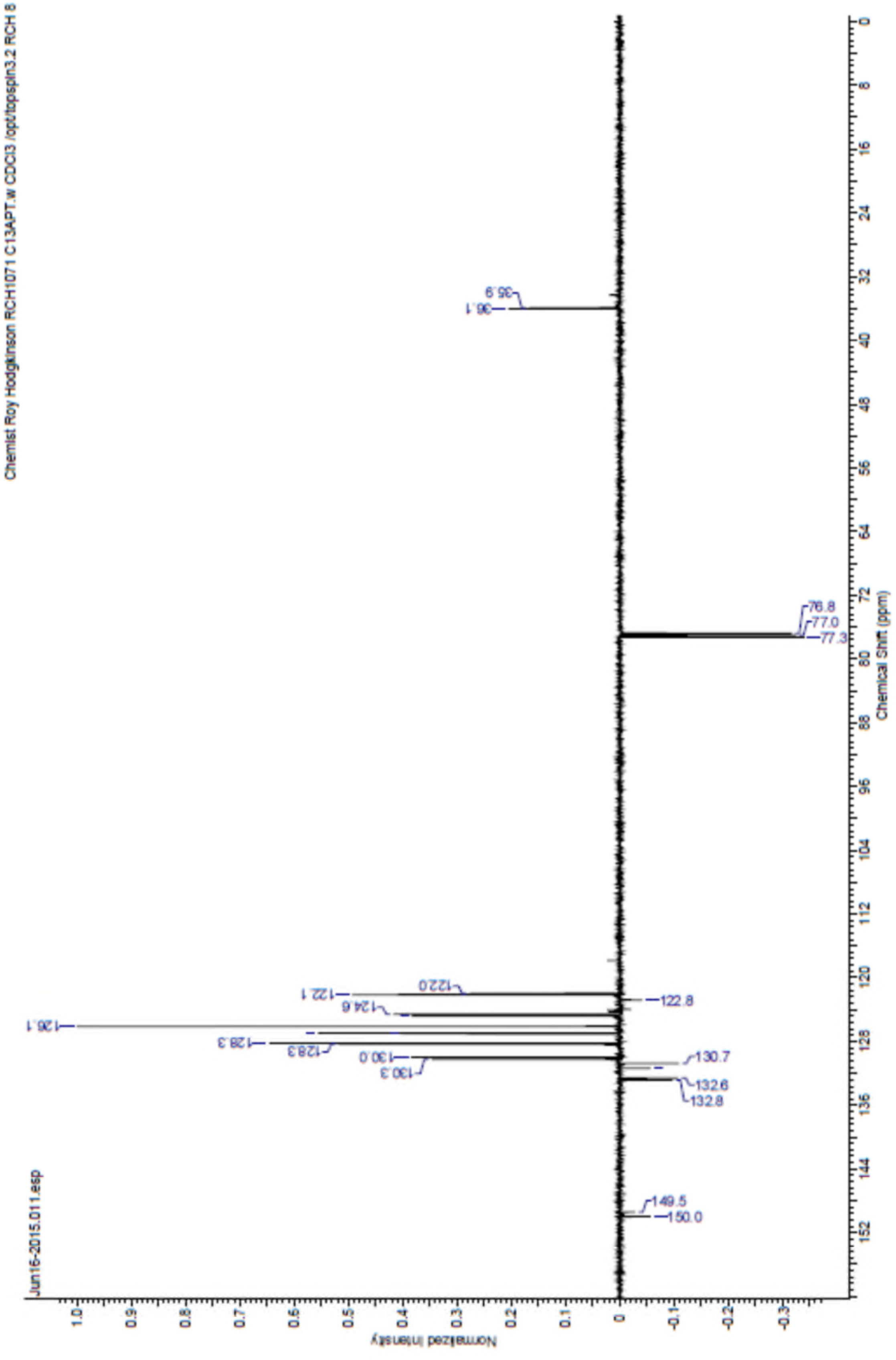


(*R*)-*N*,*N*-Dimethyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine ((R)-MONOPHOS).

δ_H (500 MHz, $CDCl_3$)

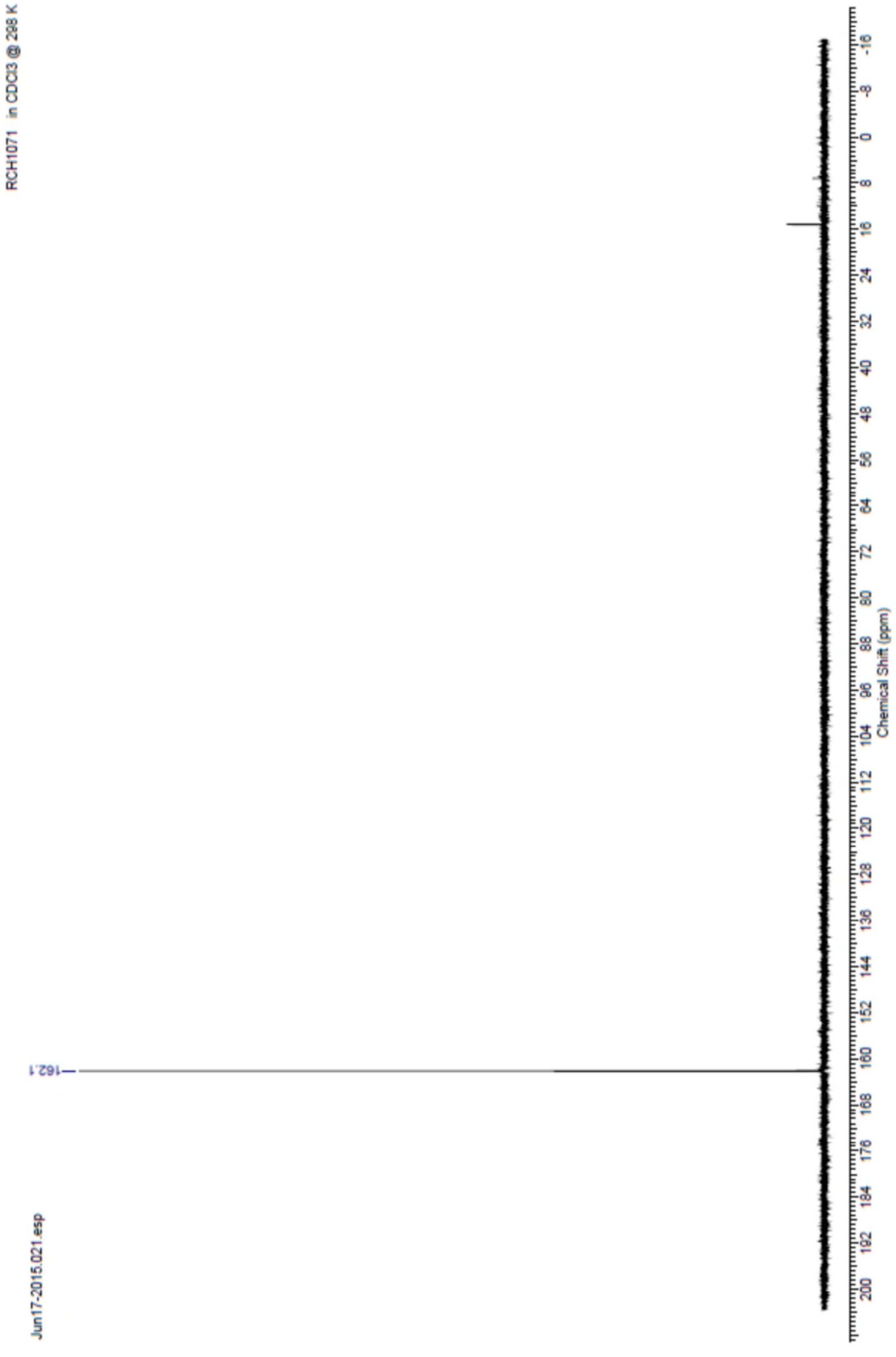


δ_C (125 MHz, $CDCl_3$)



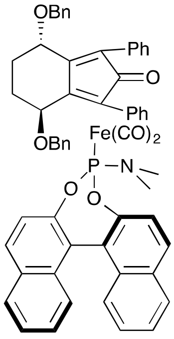
P-NMR

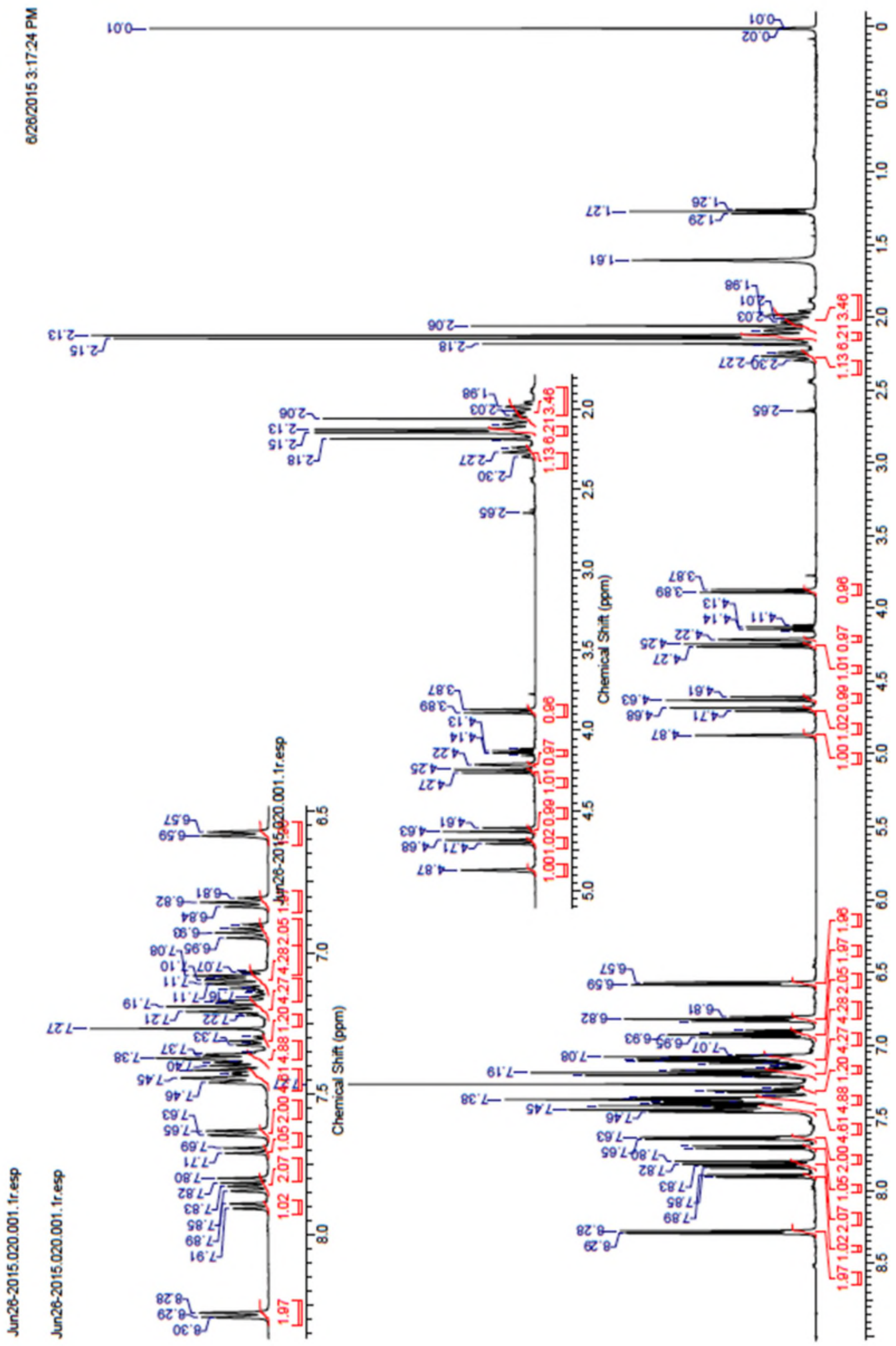
δ_P (202 MHz, $CDCl_3$)



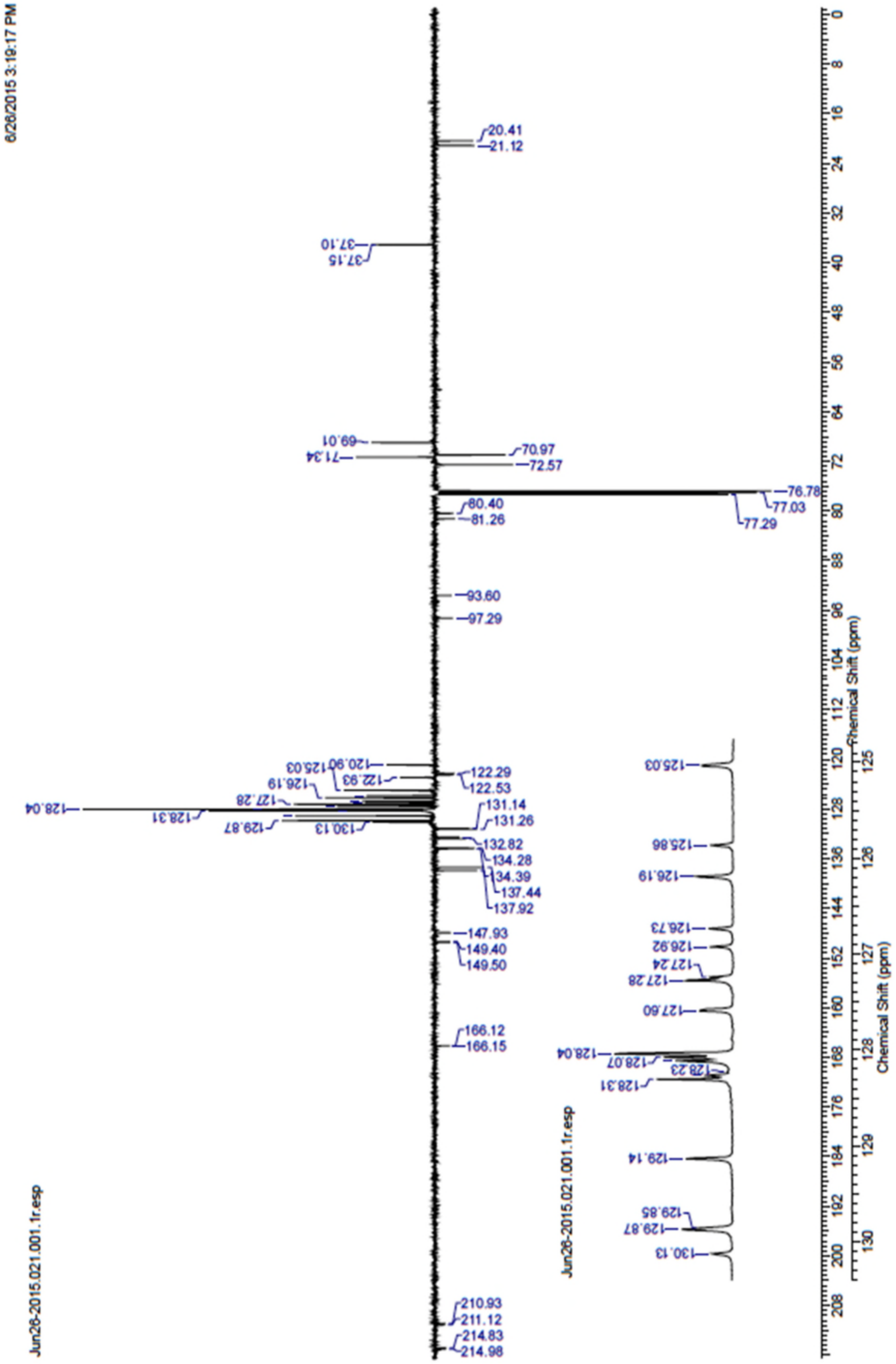
Dicarbonyl-((*4S*,*7S*)-4,7-bis(benzyloxy)-1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one-(*S*)-*N*,*N*- dimethyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine) iron **22**.

δ_H (500 MHz, $CDCl_3$)



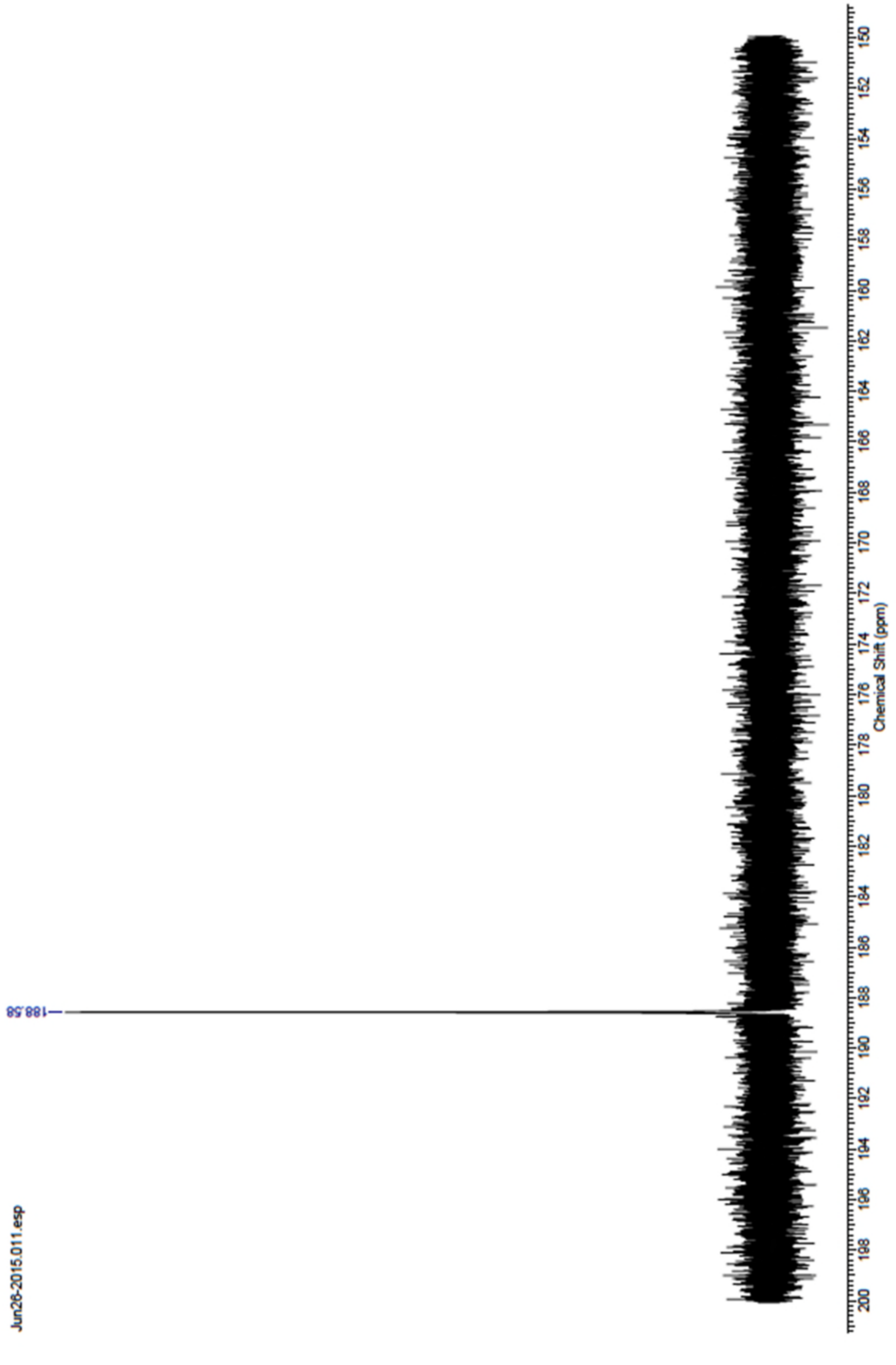


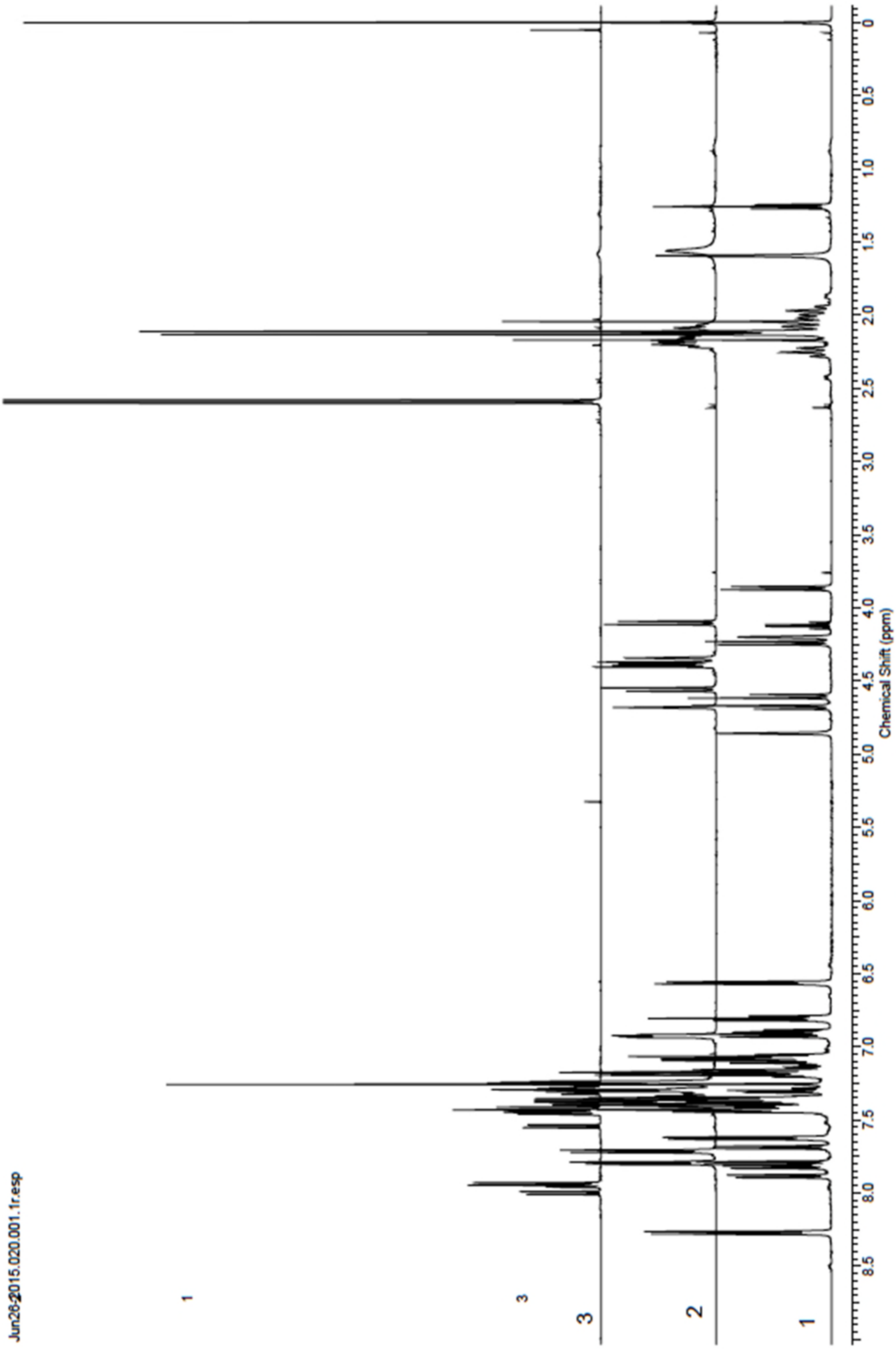
δ_C (125 MHz, $CDCl_3$)



P-NMR

δ_P (242 MHz, $CDCl_3$)

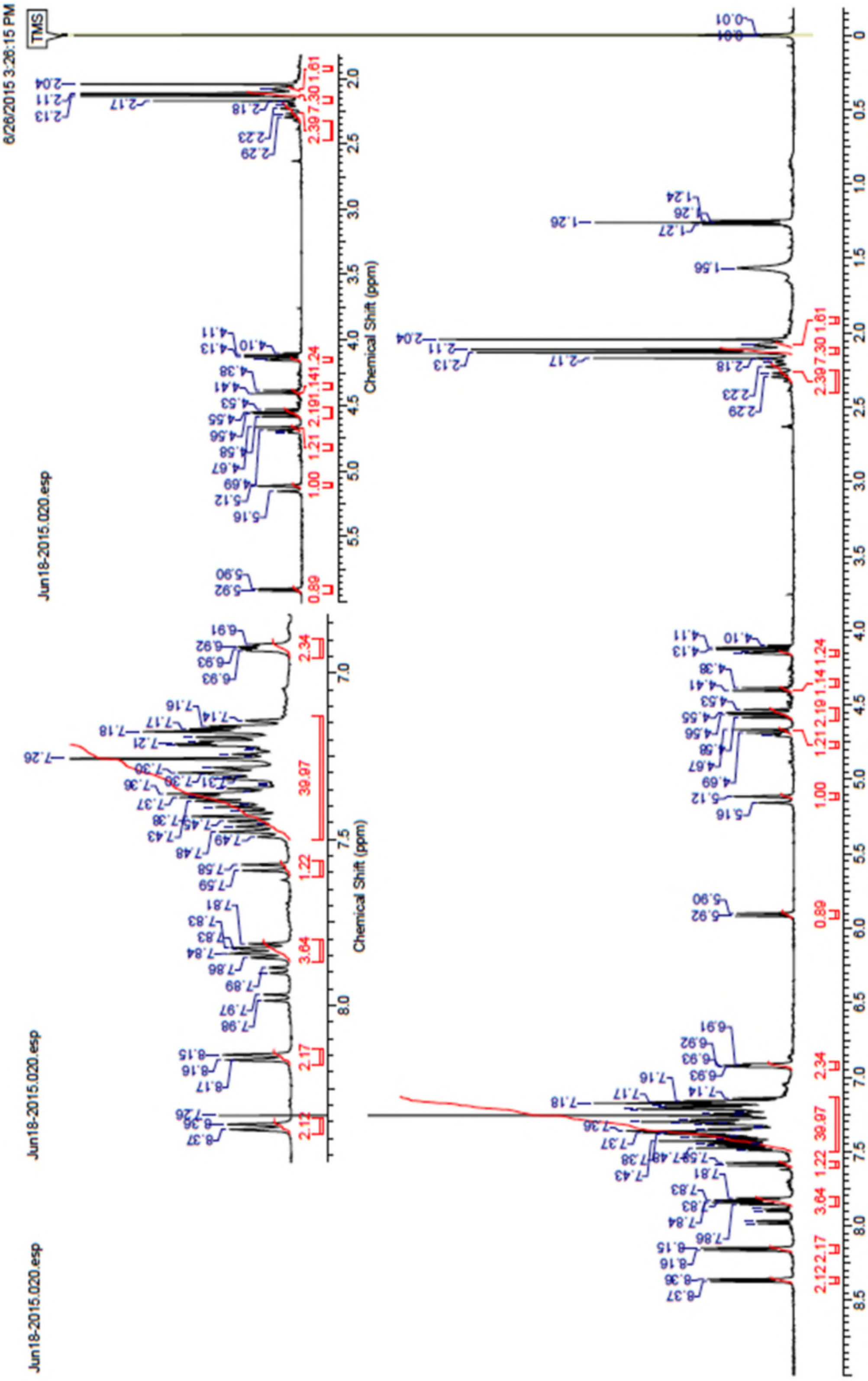


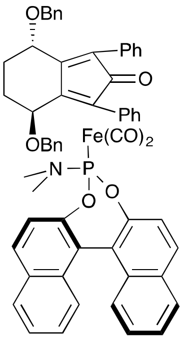


1) OBn catalyst with S-Monophos; 2) OBn Catalyst; 3) S-Monophos.

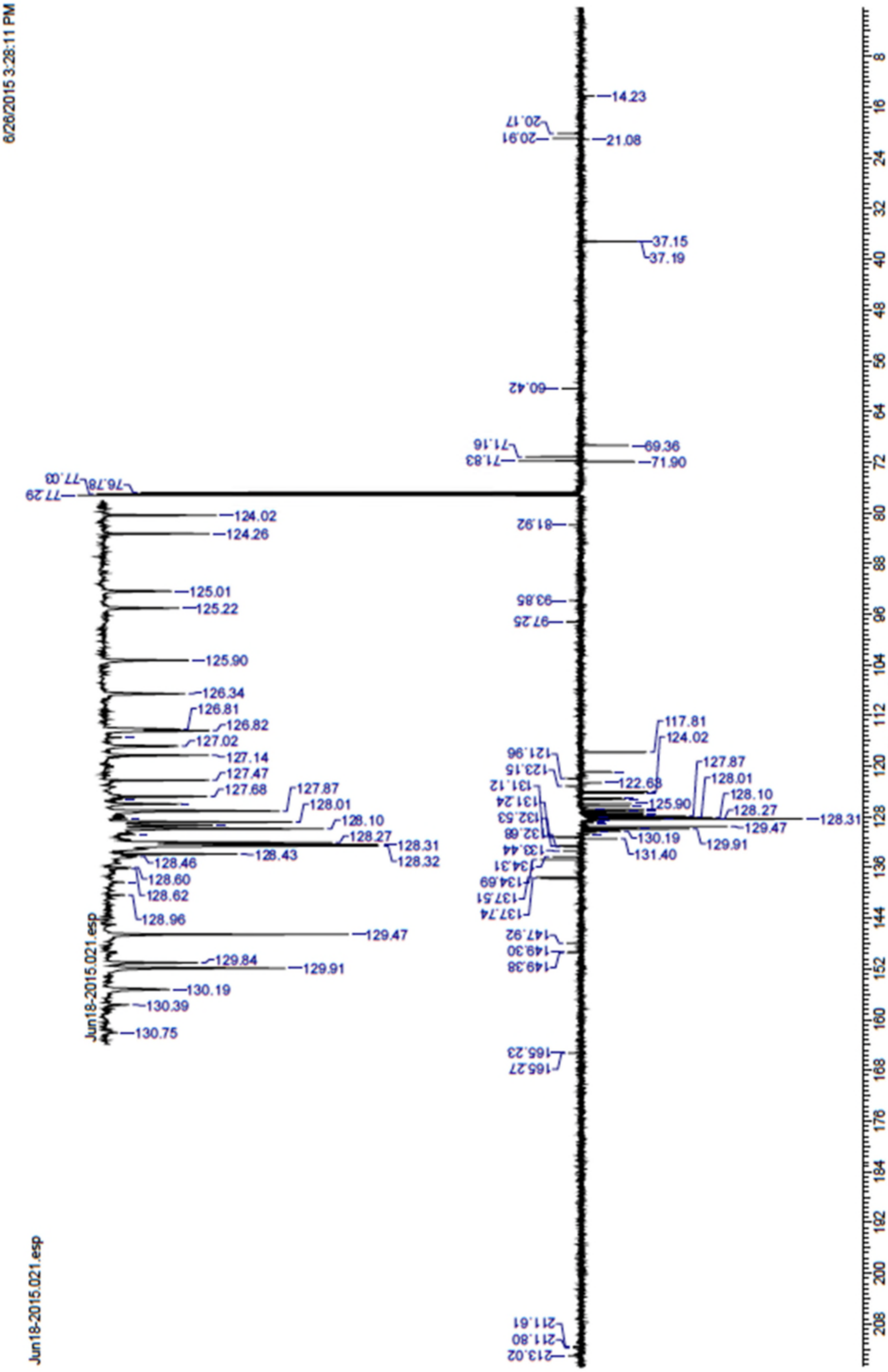
Dicarbonyl-((4*S*,7*S*)-4,7-bis(benzyloxy)-1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one-(*R*)-*N*,*N*-dimethyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine) iron **23**.

δ_H (500 MHz, $CDCl_3$)



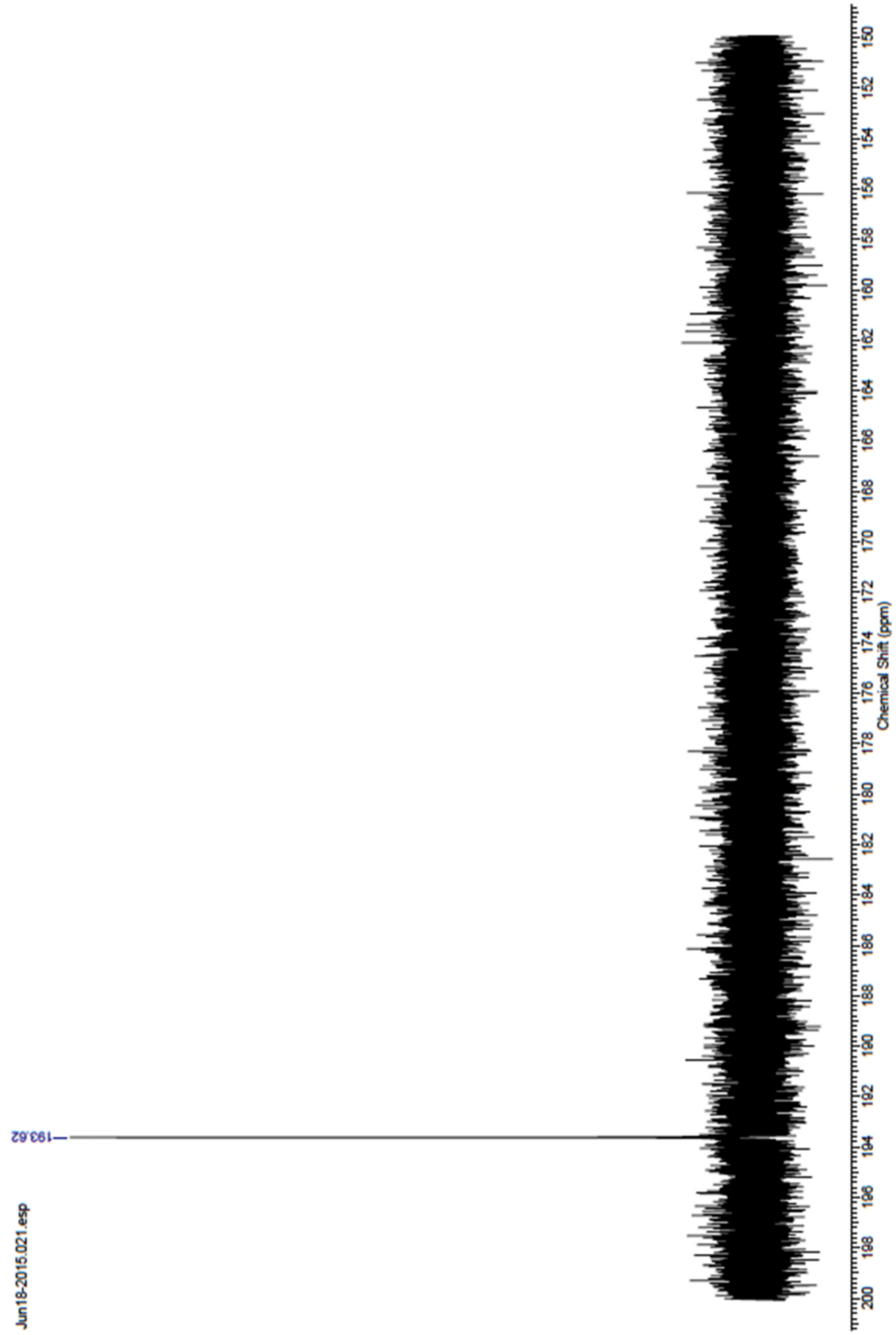


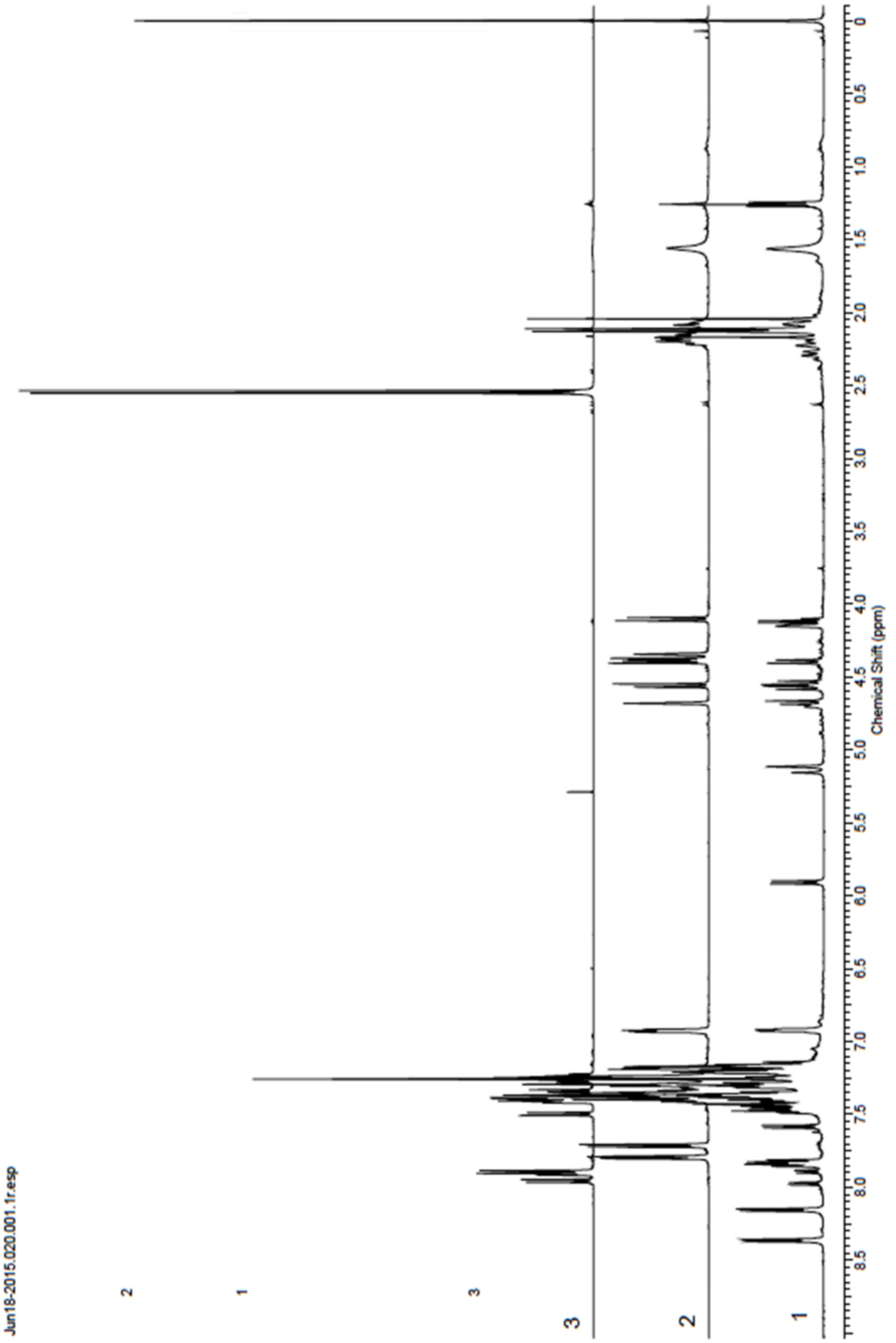
δ_C (125 MHz, $CDCl_3$)



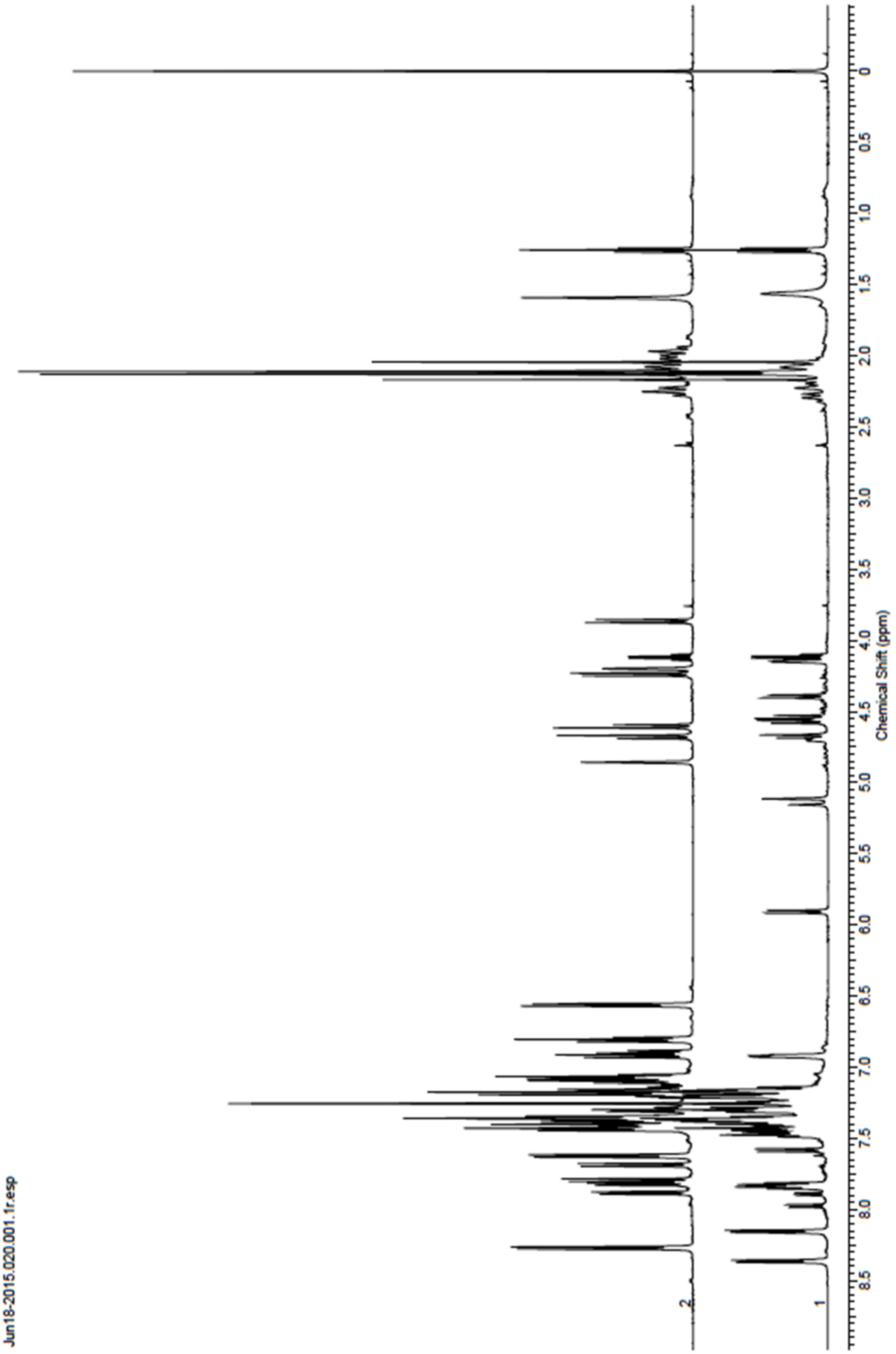
P-NMR

δ_P (242 MHz, $CDCl_3$)





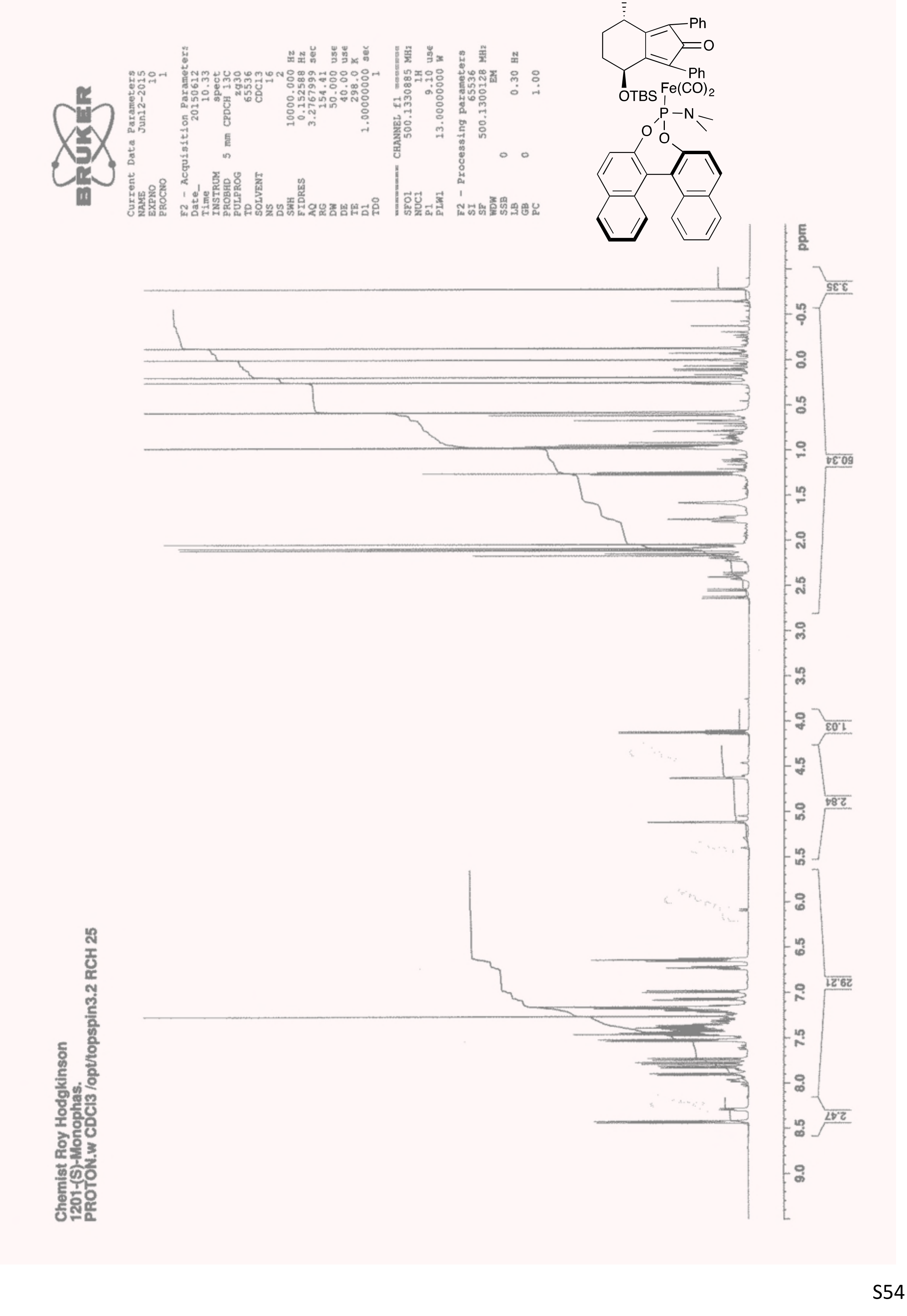
1) OBn catalyst with R-Monophos; 2) OBn Catalyst; 3) R-Monophos.



1) OBn Catalyst with R-Monophos; 2) OBn Catalyst with S-Monophos.

Dicarbonyl-((*4S*,*7S*)-4,7-bis((*tert*-butyldimethylsilyl)oxy)-1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one-(*S*)-*N*,*N*-dimethyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine) iron **24**.

δ_H (500 MHz, $CDCl_3$)



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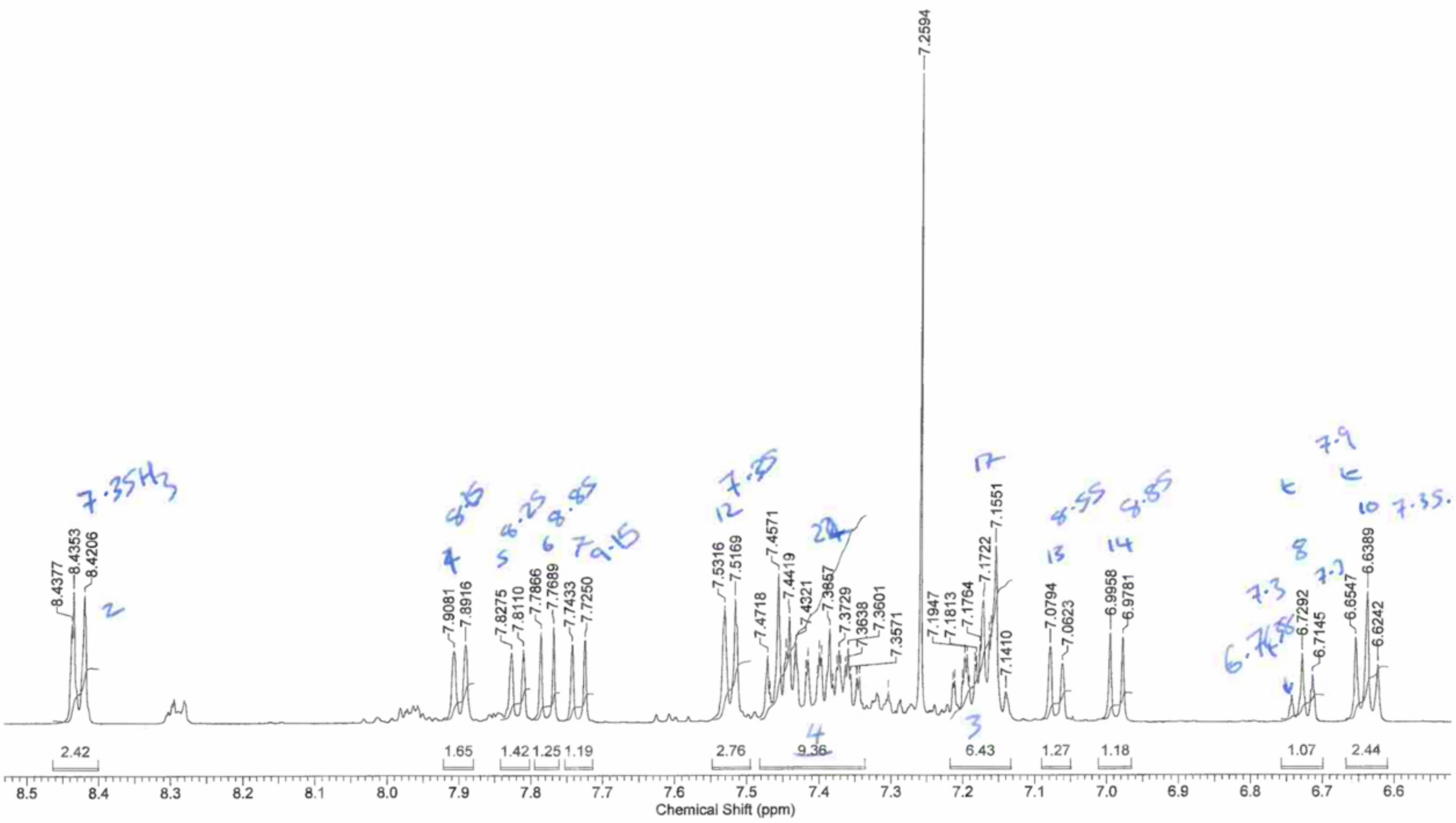

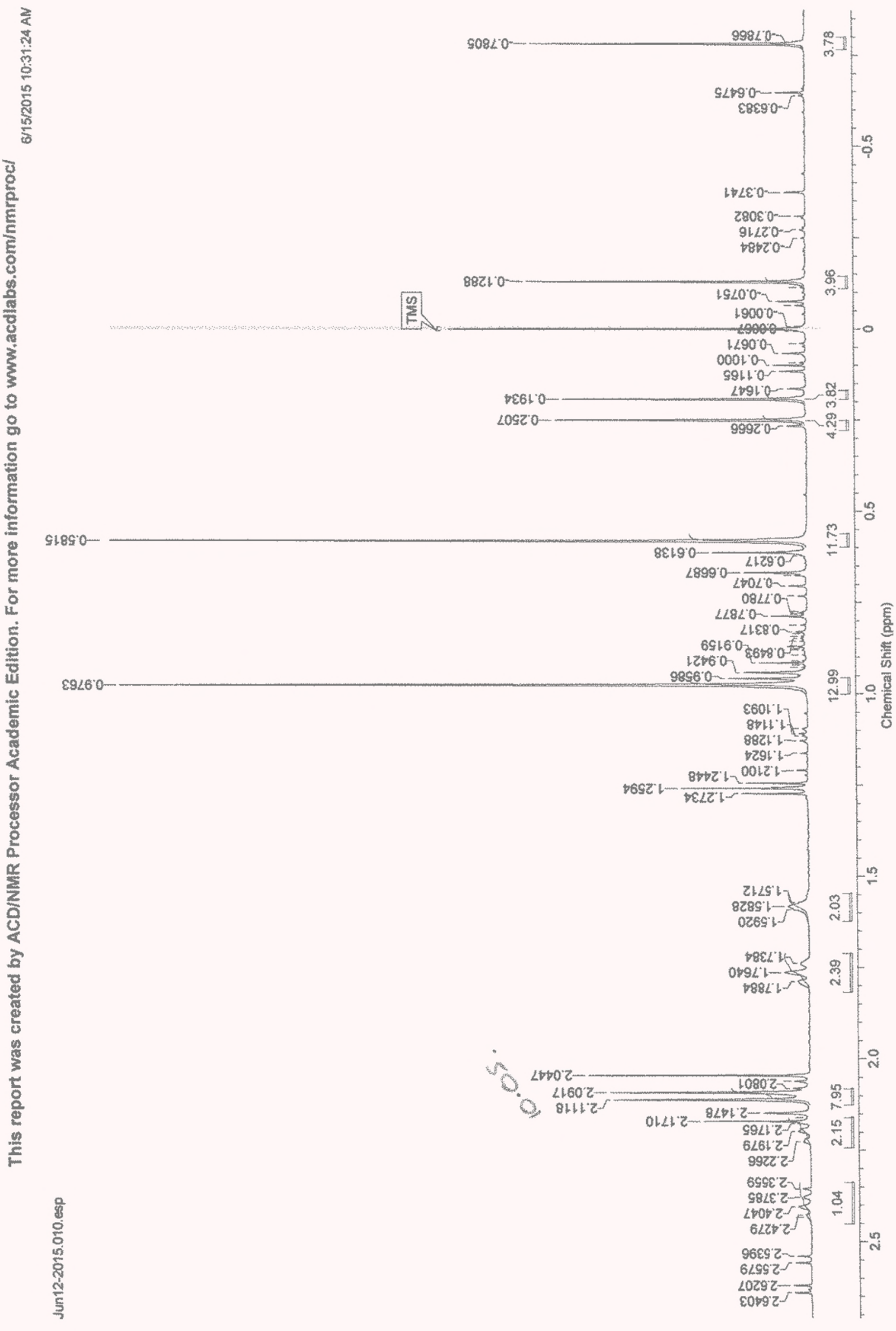
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1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

δ_C (125 MHz, $CDCl_3$)

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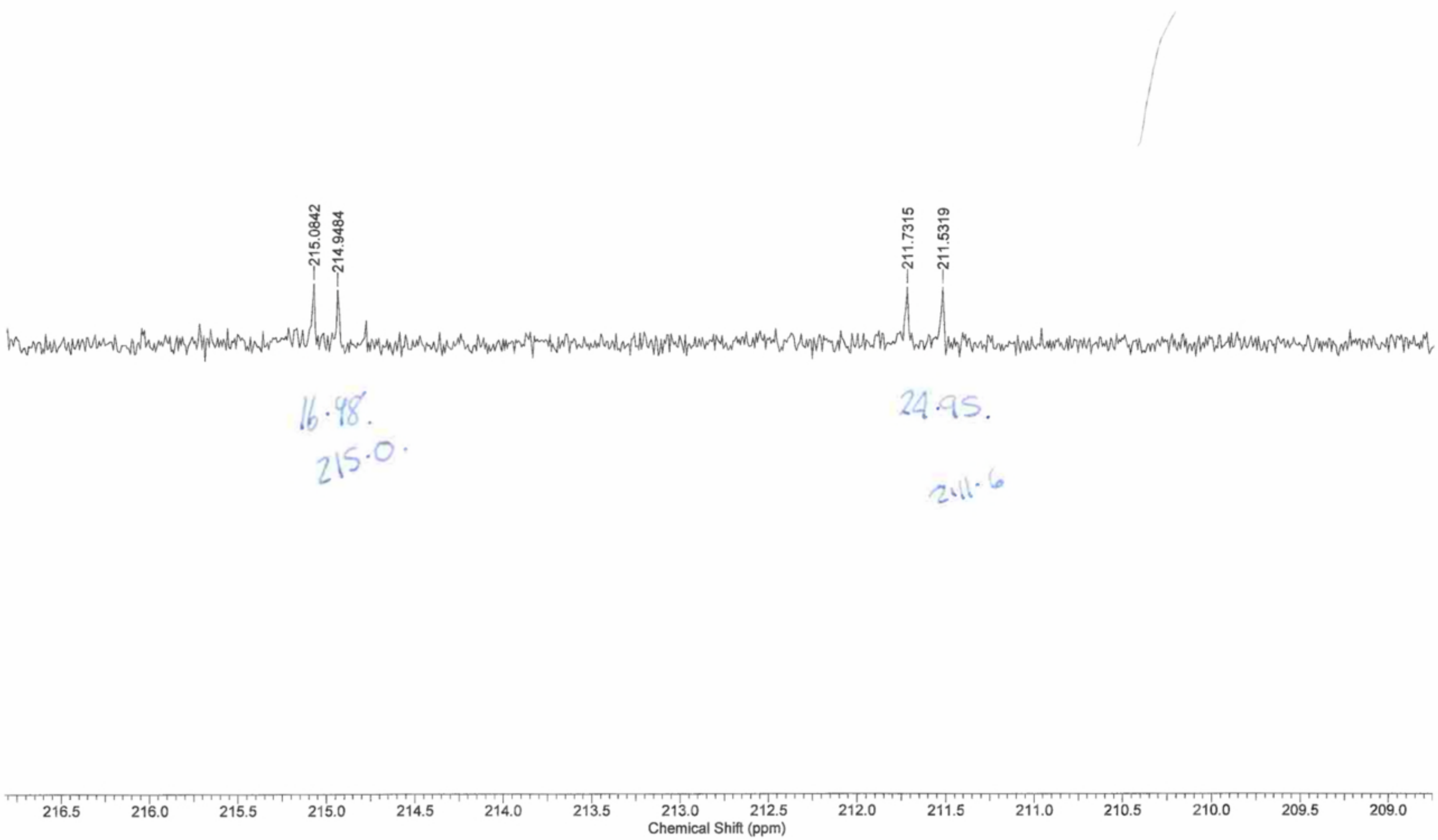

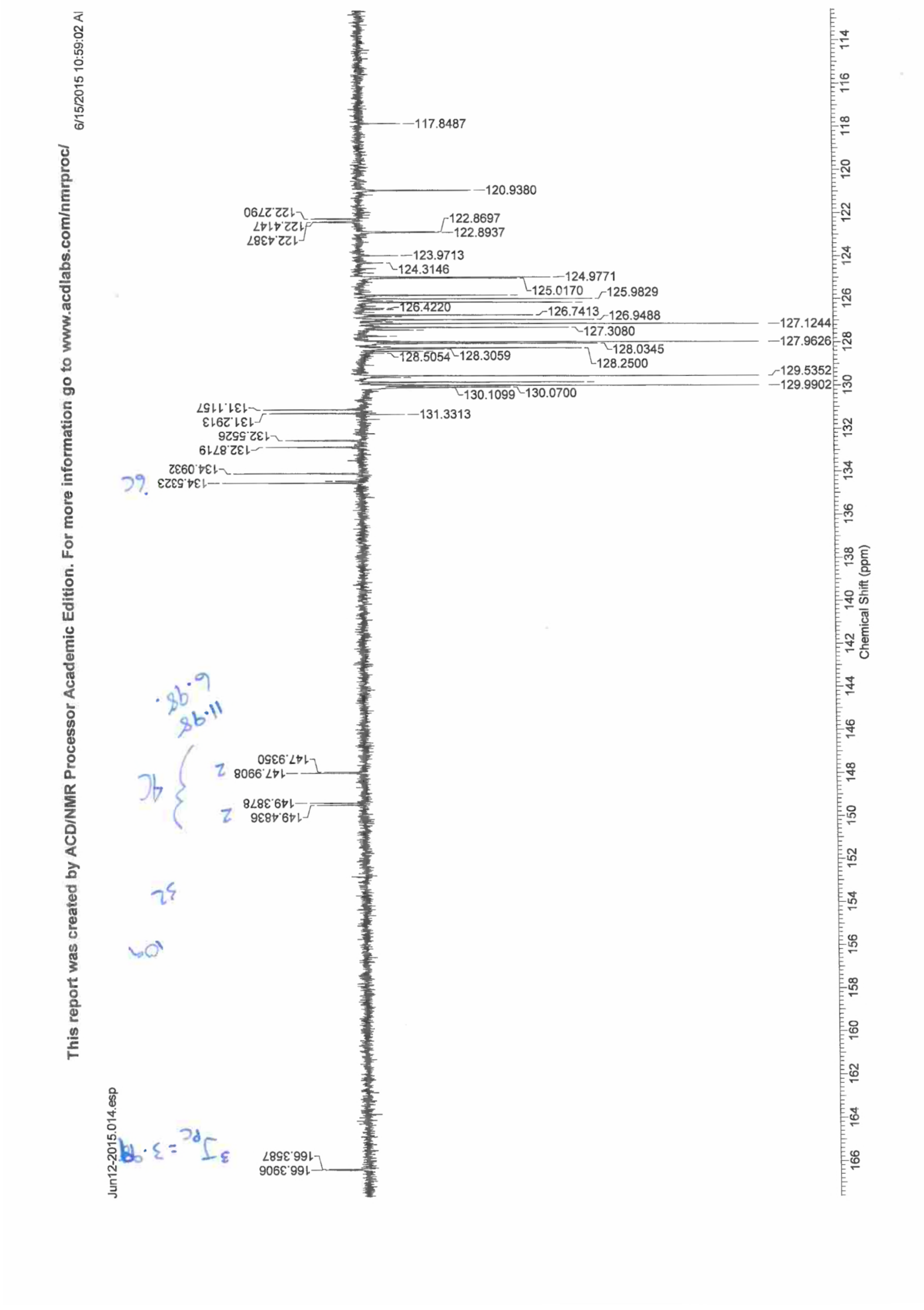
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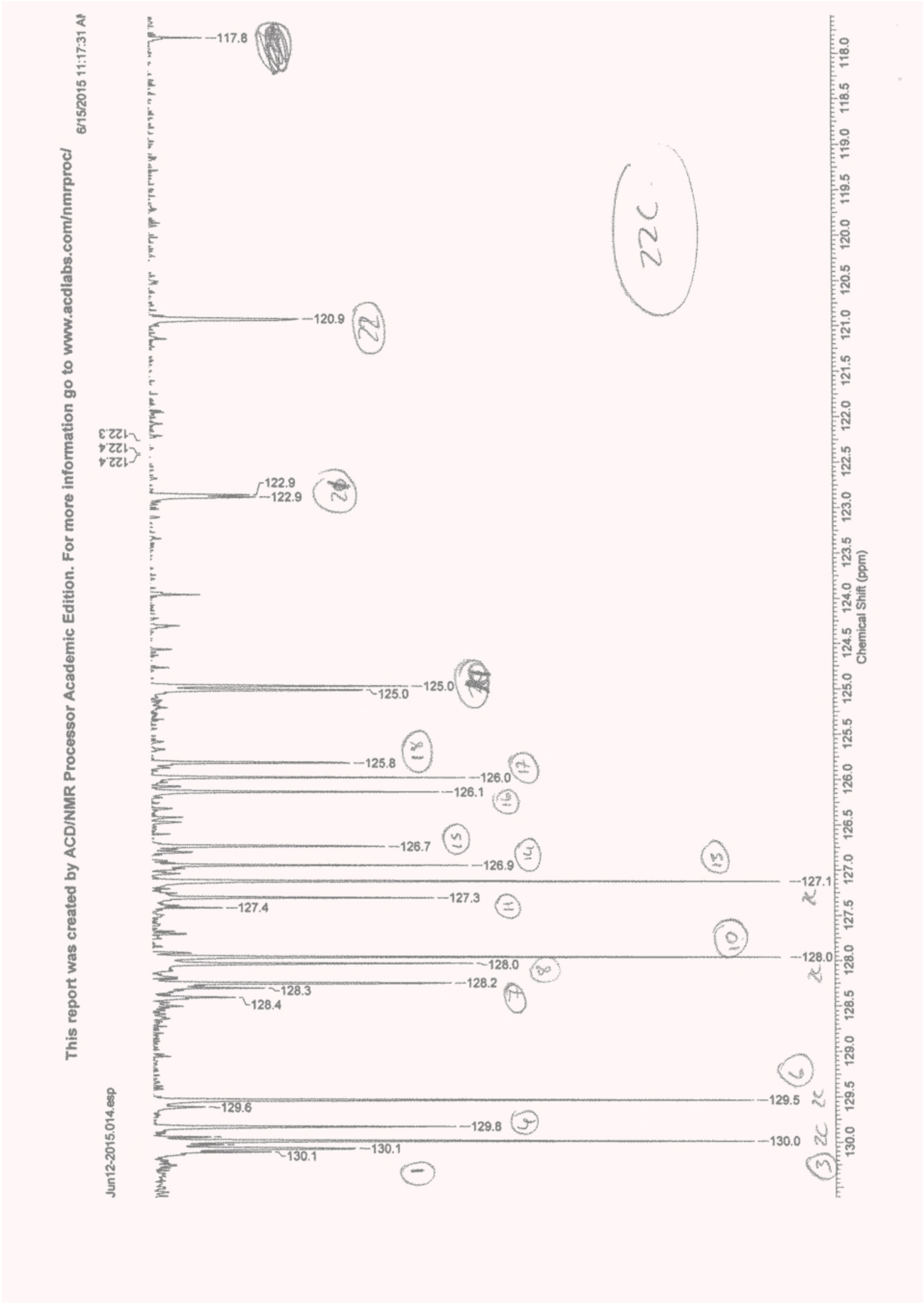
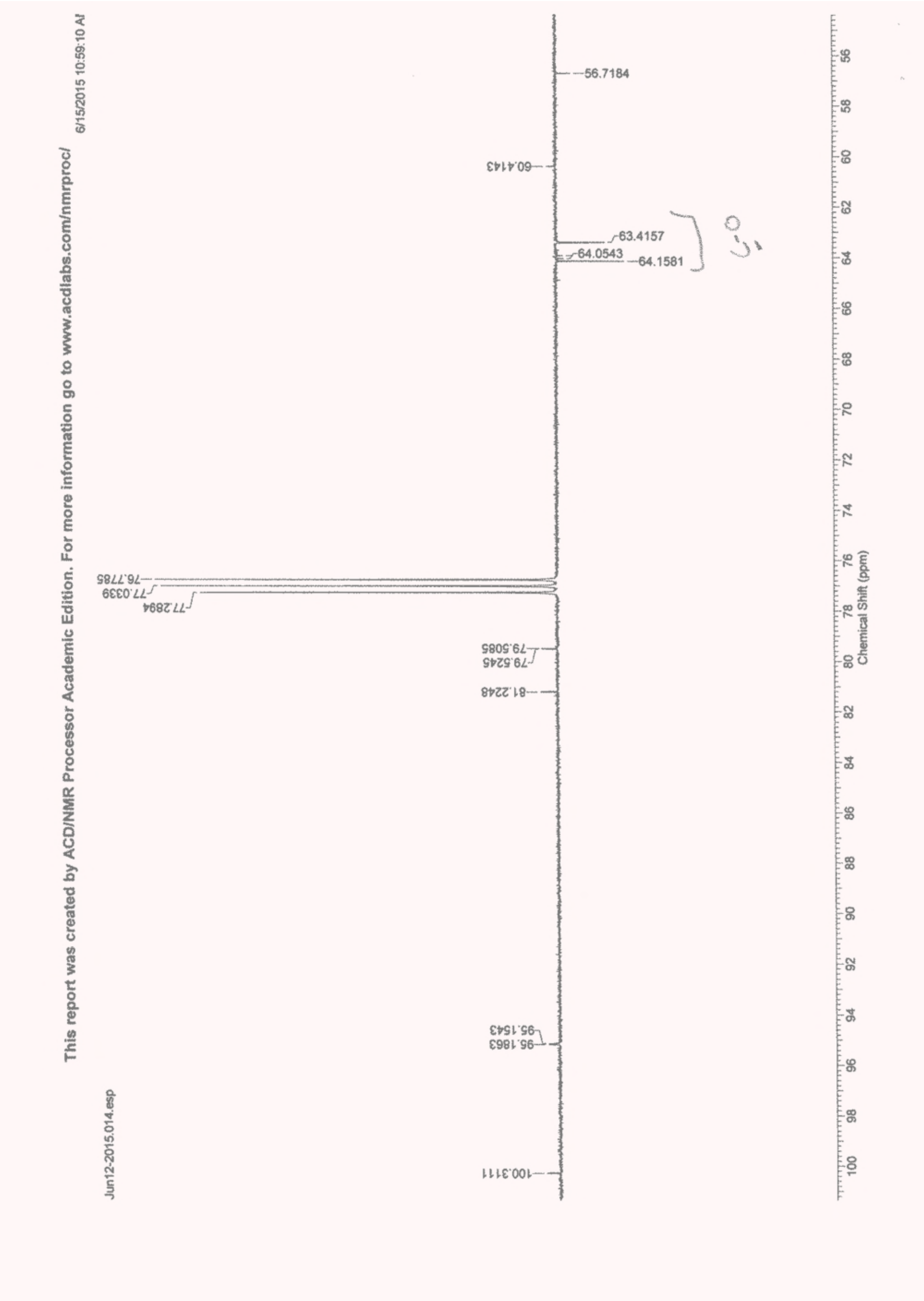
2
4C
52
60
$^3J_{PC} = 3.98$
114
116
118
120
122
124
126
128
130
132
134
136
138
140
142
144
146
148
150
152
154
156
158
160
162
164
166
Chemical Shift (ppm)

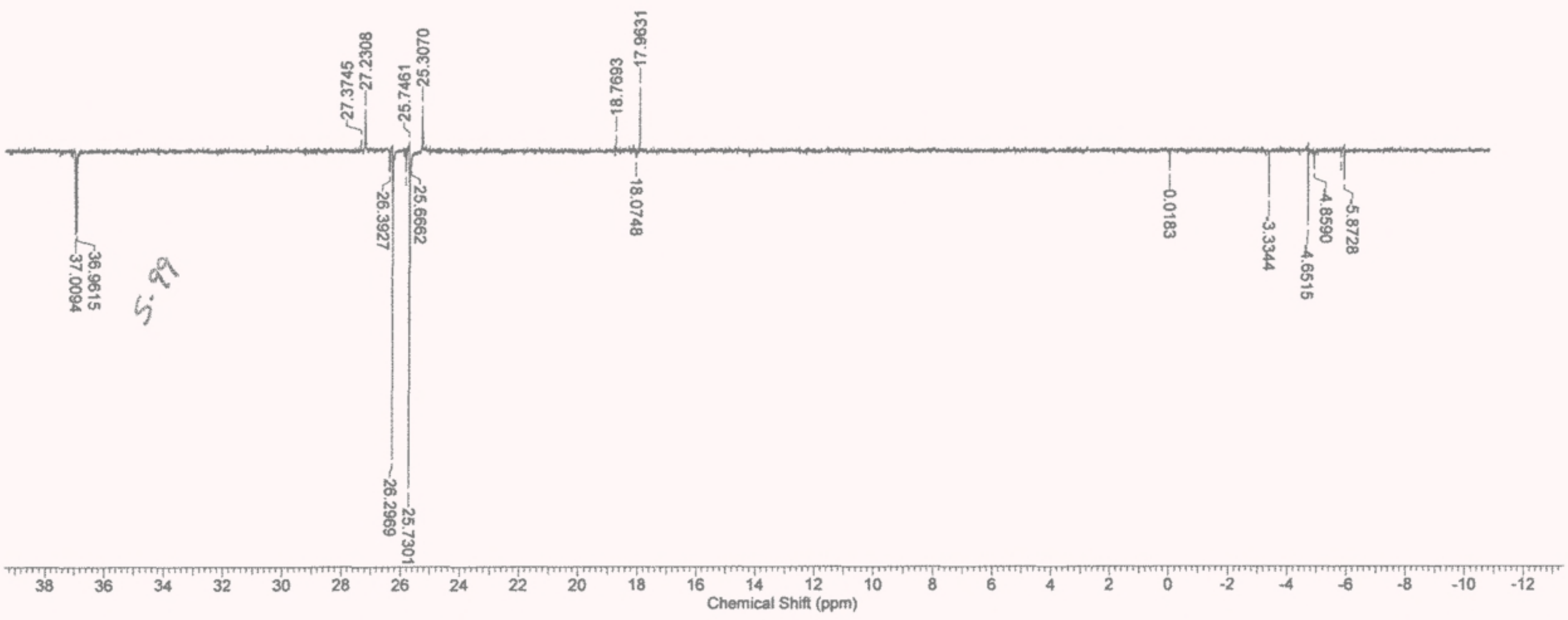

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
6/15/2015 11:17:31 AM
Jun12-2015.014.esp
117.8
120.9
122.3
122.4
122.4
122.9
122.9
125.0
125.0
125.8
126.0
126.1
126.7
126.9
127.1
127.3
127.4
128.0
128.0
128.2
128.3
128.4
129.5
129.6
129.8
130.0
130.1
130.1
22C
21
20
19
18
17
16
15
14
13
11
10
8
7
6
4
3
1
2c
2c
2c
2c
Chemical Shift (ppm)
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
123.5
123.0
122.5
122.0
121.5
121.0
120.5
120.0
119.5
119.0
118.5
118.0


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
6/15/2015 10:59:10 A
Jun12-2015.014.esp
56.7184
60.4143
63.4157
64.0543
64.1581
C-O
76.7785
77.0339
77.2894
79.5085
79.5245
81.2248
95.1543
95.1863
100.3111
56
58
60
62
64
66
68
70
72
74
76
78
80
82
84
86
88
90
92
94
96
98
100
Chemical Shift (ppm)

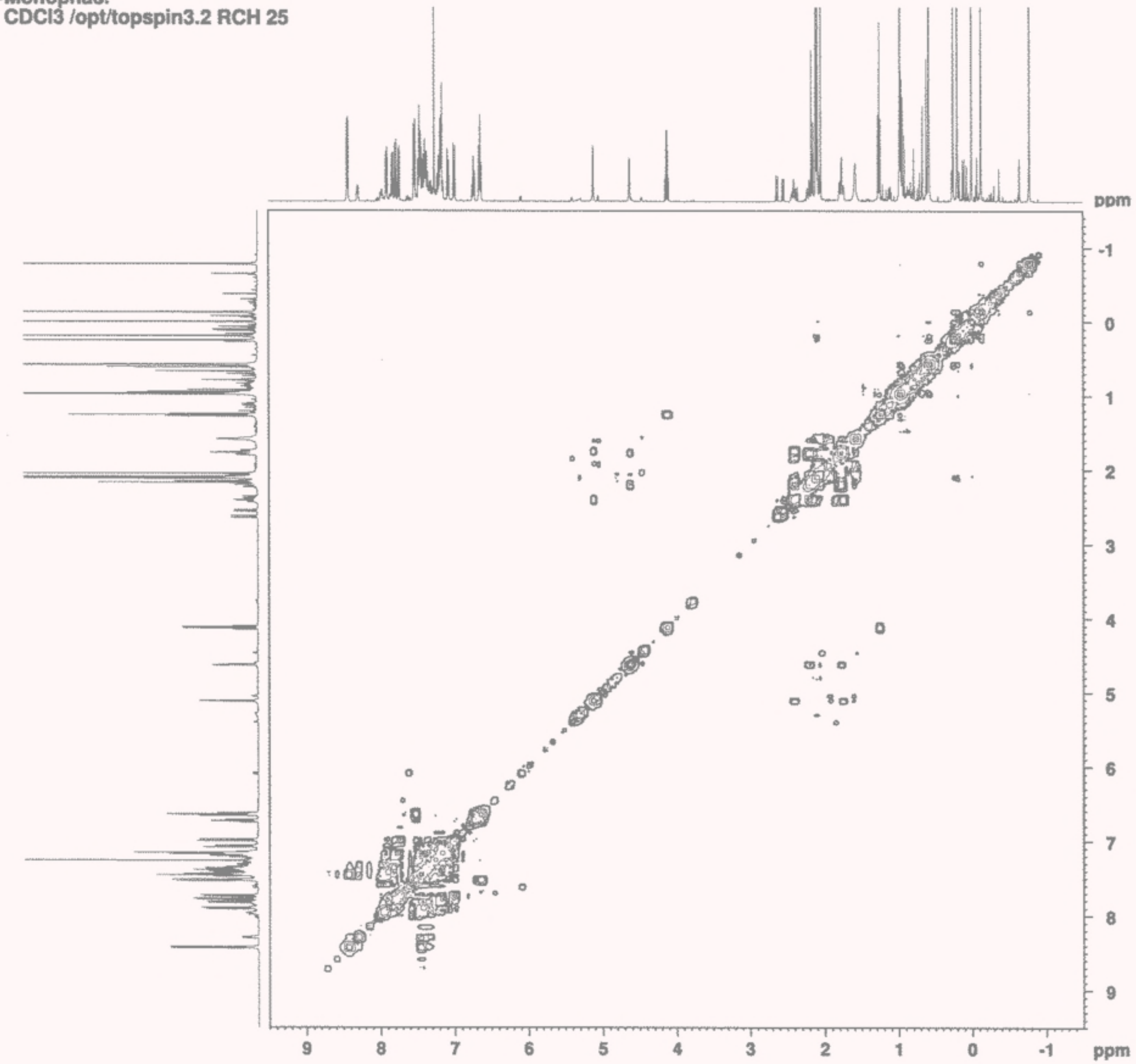
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

6/15/2015 10:59:18 AM

Jun12-2015.014.esp

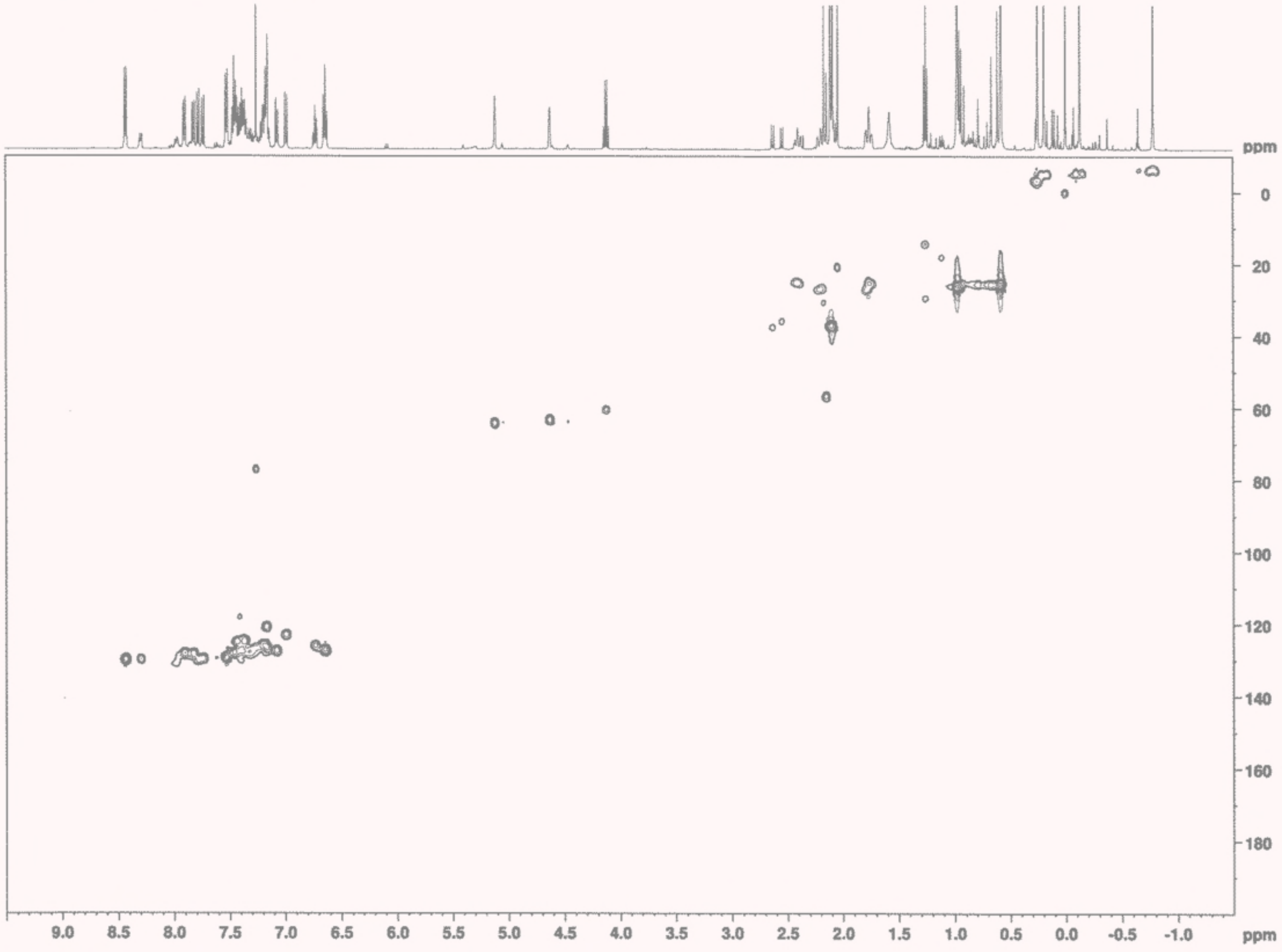


Chemist Roy Hodgkinson
1201-(S)-Monophas.
COSY.w CDCl3 /opt/topspin3.2 RCH 25

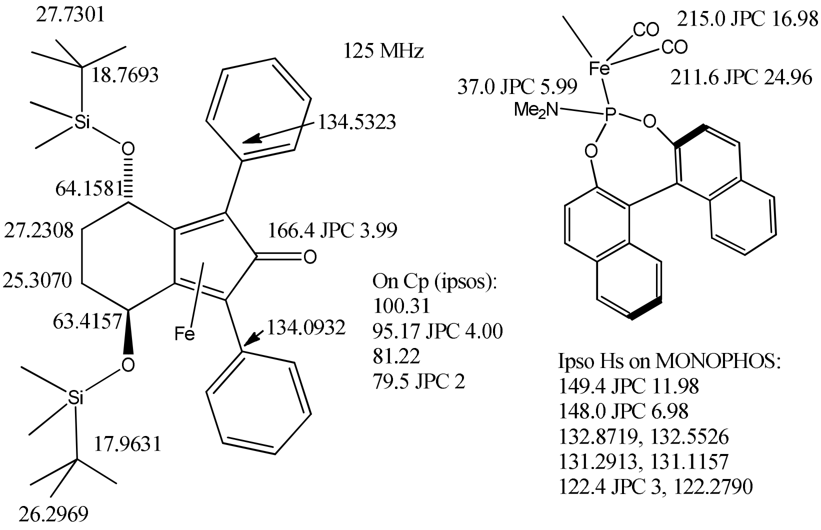


```
Current Data Parameters
NAME             Jun12-2015
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150612
Time                  10.34
INSTRUM               spect
PROBHD   5 mm CPDCH 13C
PULPROG         cosygpppqf
TD                     2048
SOLVENT               CDCl3
NS                        1
DS                        8
SWH                8064.516 Hz
FIDRES             3.937752 Hz
AQ                0.1269760 sec
RG                    60.07
DW                   62.000 usec
DE                    40.00 usec
TE                    298.0 K
D0               0.00000300 sec
D1               2.02047992 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00012400 sec

======== CHANNEL f1 ========
SFO1            500.1315878 MHz
NUC1                     1H
P0                     9.10 usec
P1                     9.10 usec
P17                 2500.00 usec
PLW1            13.00000000 W
PLW10            1.59249997 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPZ1                  10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                      128
SFO1               500.1316 MHz
FIDRES            63.004032 Hz
SW                   16.125 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     1024
SF              500.1300128 MHz
WDW                   QSINE
SSB       0
LB        0 Hz
GB        0
PC                     1.40

F1 - Processing parameters
SI                     1024
MC2                      QF
SF              500.1300128 MHz
WDW                   QSINE
SSB       0
LB        0 Hz
GB        0
```

Chemist Roy Hodgkinson
1201-(S)-Monophas.
HSQC.w CDCl3 /opt/topspin3.2 RCH 25



```
Current Data Parameters
NAME          Jun12-2015
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150612
Time               10.40
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG         hsqcetgp
TD                  1024
SOLVENT            CDCl3
NS                     4
DS                    16
SWH             7812.500 Hz
FIDRES          7.629395 Hz
AQ             0.0655360 sec
RG                185.92
DW                64.000 usec
DE                 40.00 usec
TE                 298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            1.51023996 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
IN0           0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1         500.1315878 MHz
NUC1                  1H
P1                  9.10 usec
P2                 18.20 usec
P28        0 usec
PLW1         13.00000000 W

======== CHANNEL f2 ========
SFO2         125.7697355 MHz
NUC2                 13C
CPDPRG[2            garp
P3                  9.50 usec
P4                 19.00 usec
PCPD2              63.70 usec
PLW2         24.00000000 W
PLW12         0.51266003 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            125.7697 MHz
FIDRES        206.679901 Hz
SW               210.345 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           500.1300128 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2         echo-antiecho
SF           125.7577885 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
```



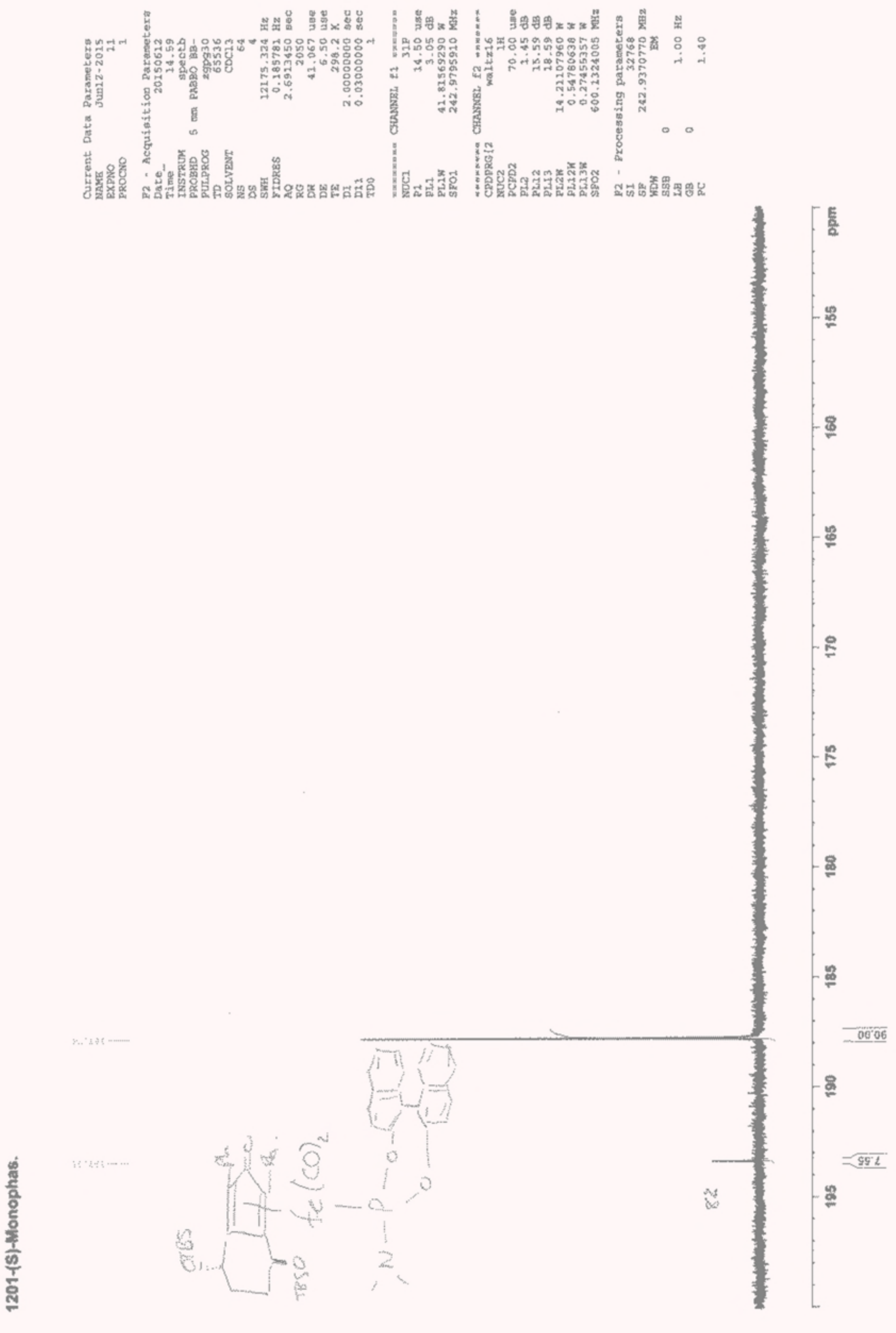
On Cp (ipsos):
100.31
95.17 JPC 4.00
81.22
79.5 JPC 2

Ipso Hs on MONOPHOS:
149.4 JPC 11.98
148.0 JPC 6.98
132.8719, 132.5526
131.2913, 131.1157
122.4 JPC 3, 122.2790

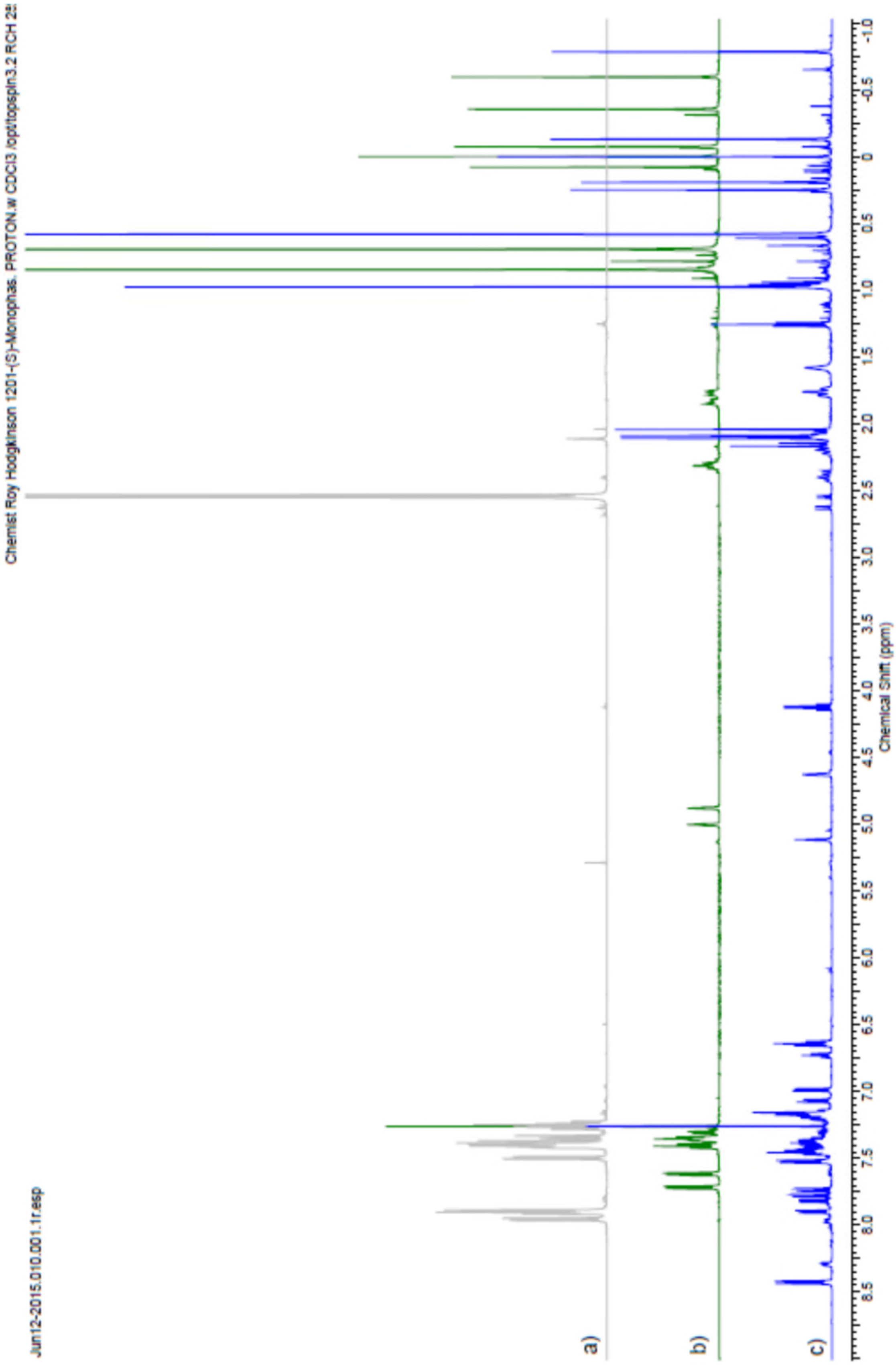
4 x SiMe: -3.3344, -4.6515, -4.8590, -5.8728.
Aromatic CH: 130.07, 129.99 (2C), 129.83, 129.54 (2C), 128.25, 128.03, 127.96 (2C), 127.31, 127.12 (2C), 126.95, 126.74, 126.14, 125.98, 125.82, 125.02, 124.98, 122.88 (JPC 2.5), 120.9. (22 ArH).

P-NMR

δ_P (242 MHz, $CDCl_3$)



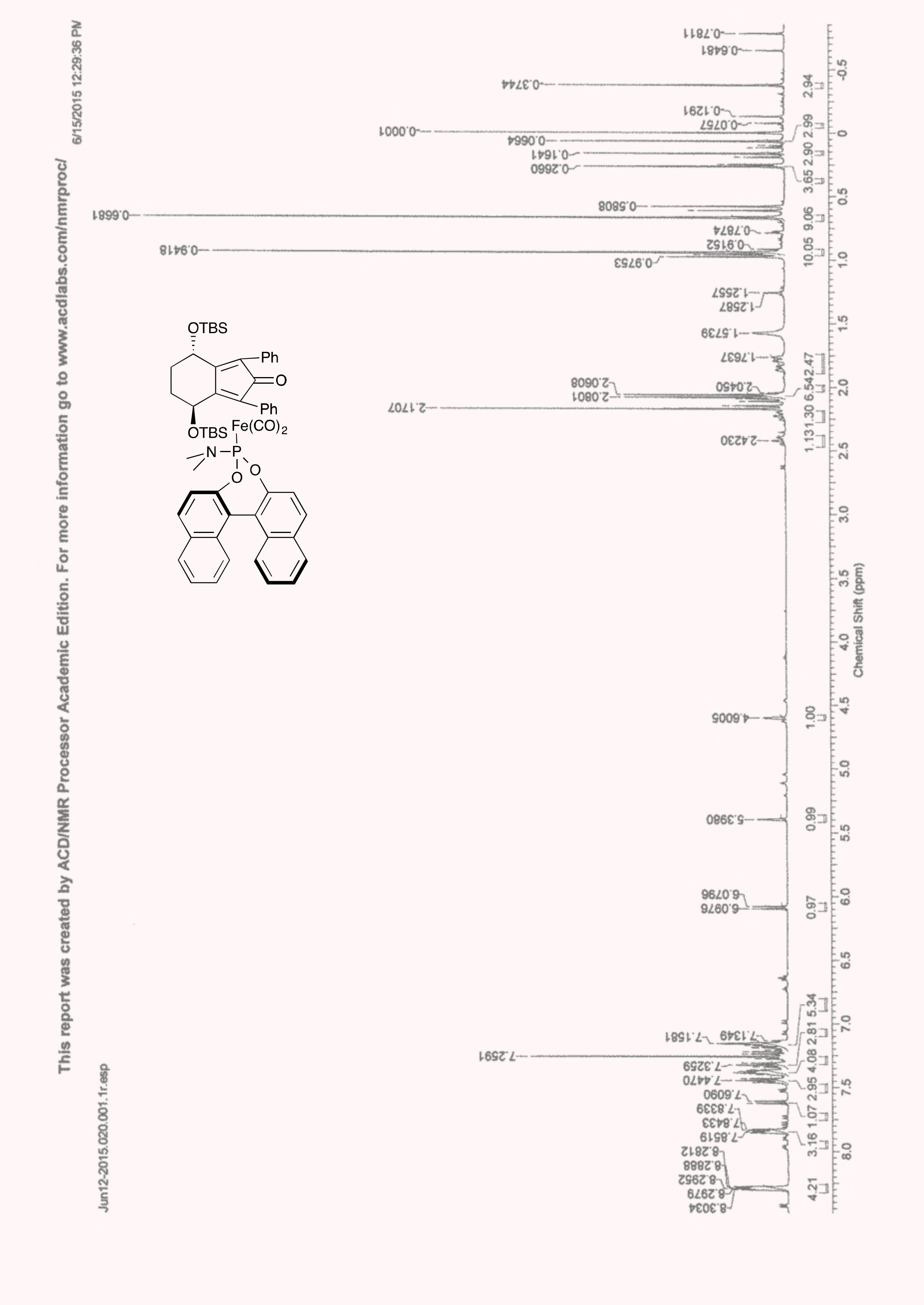
S66



a) S-Monophos; b) OTBS Catalyst; c) OTBS catalyst with S-Monophos

Dicarbonyl-((*4S*,*7S*)-4,7-bis((*tert*-butyldimethylsilyl)oxy)-1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one-(*R*)-*N*,*N*-dimethyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine) iron **25**.

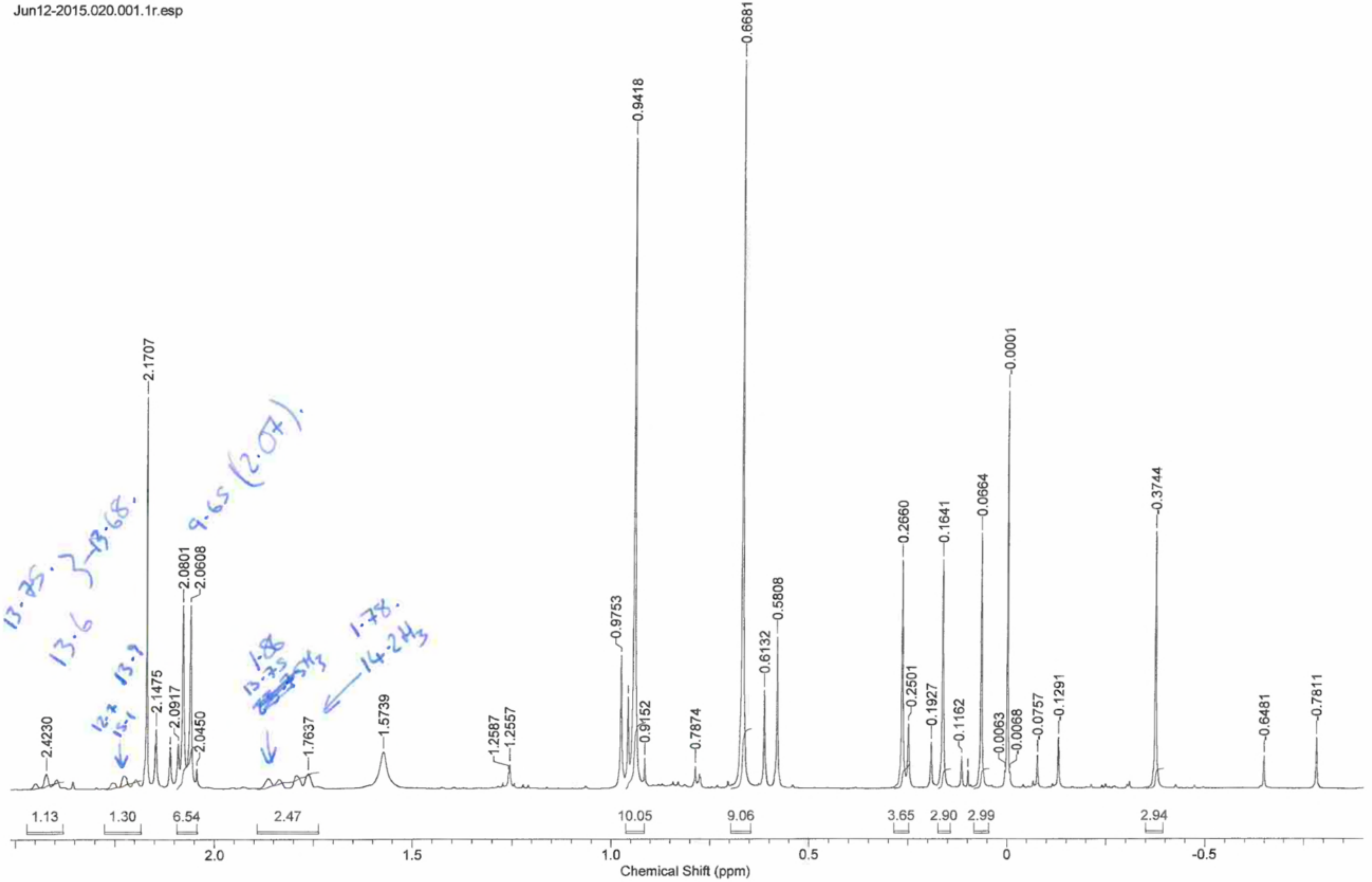
δ_H (500 MHz, $CDCl_3$)

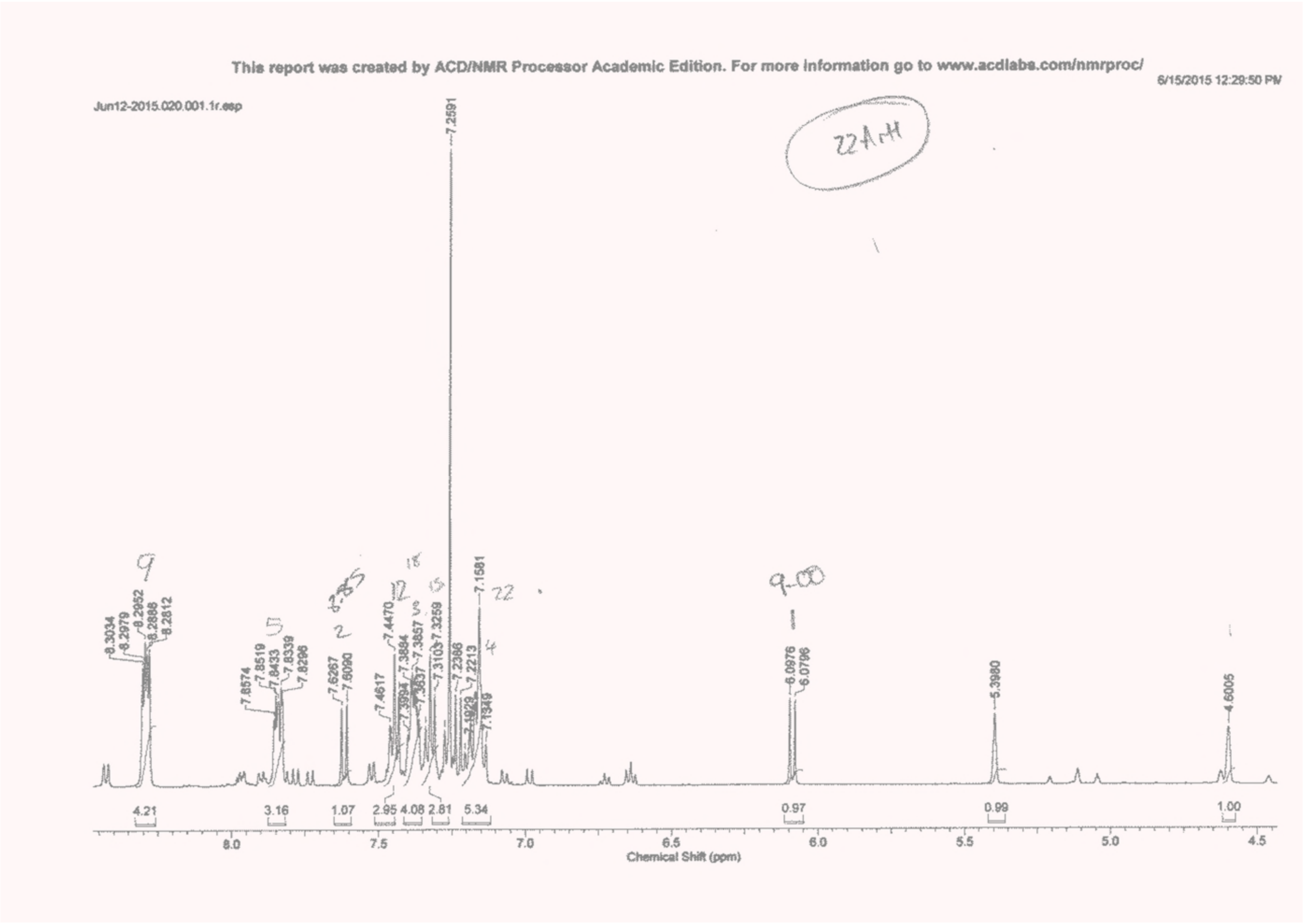


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

6/15/2015 12:29:57 PM

Jun12-2015.020.001.1r.esp



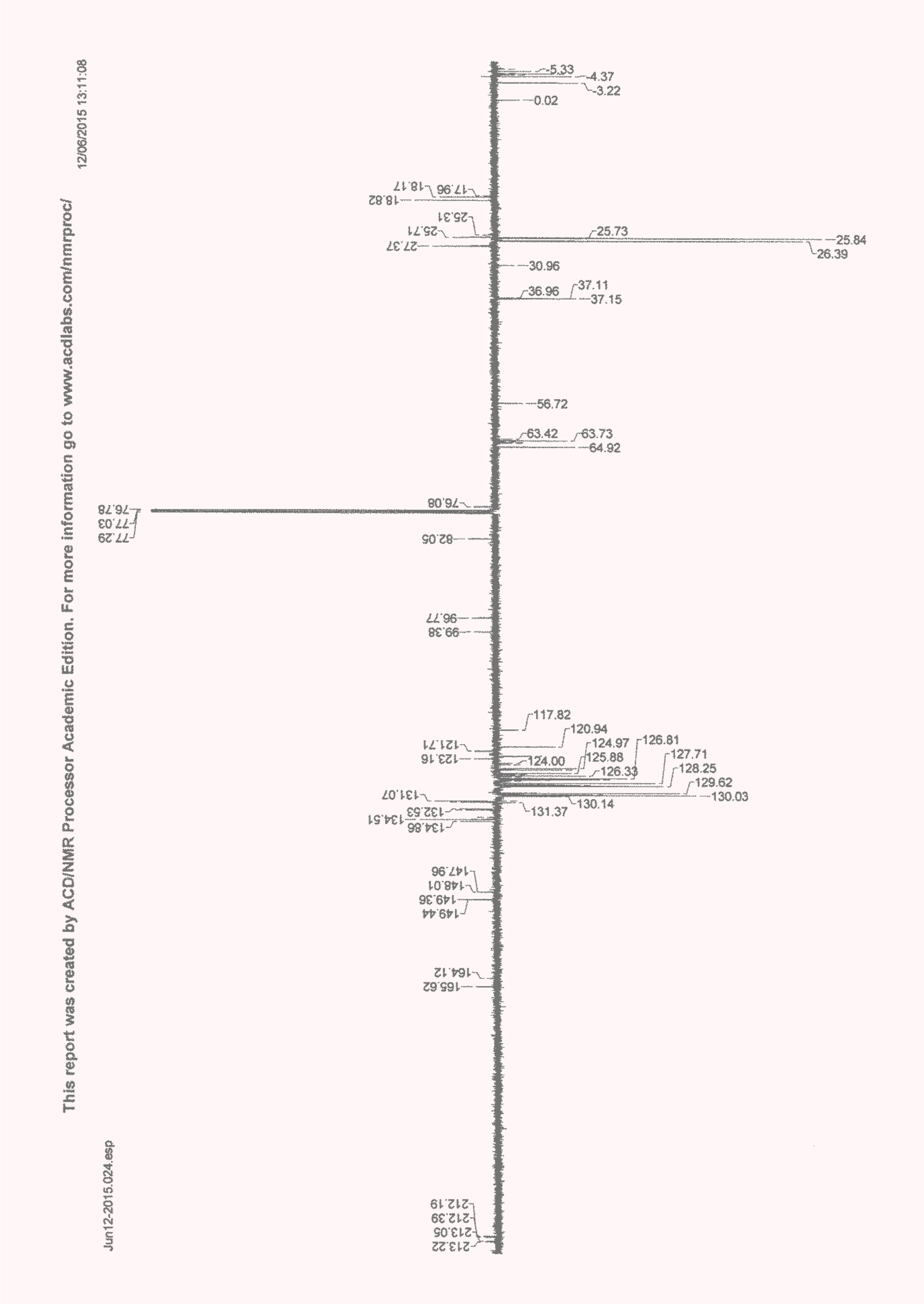


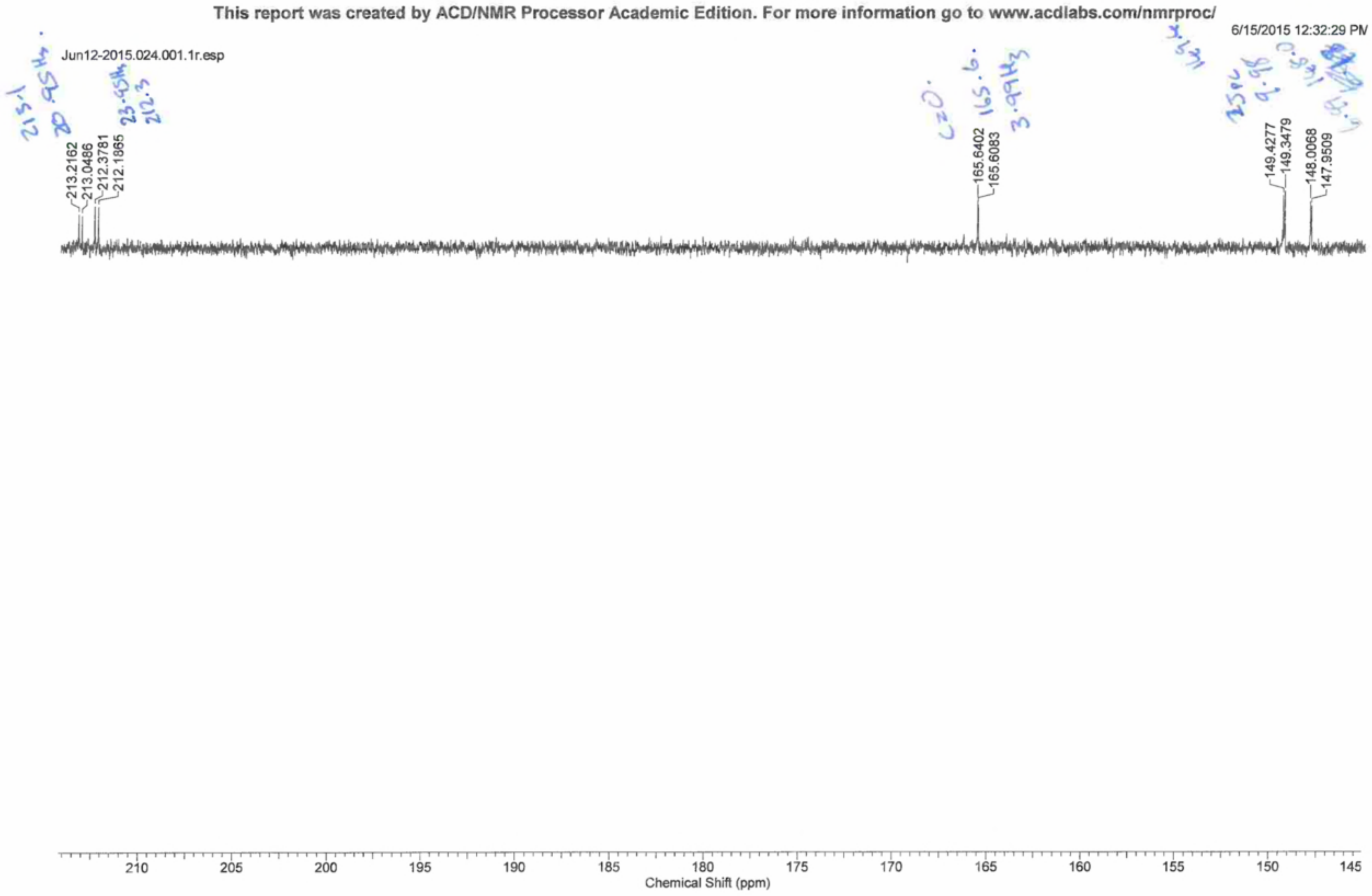
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

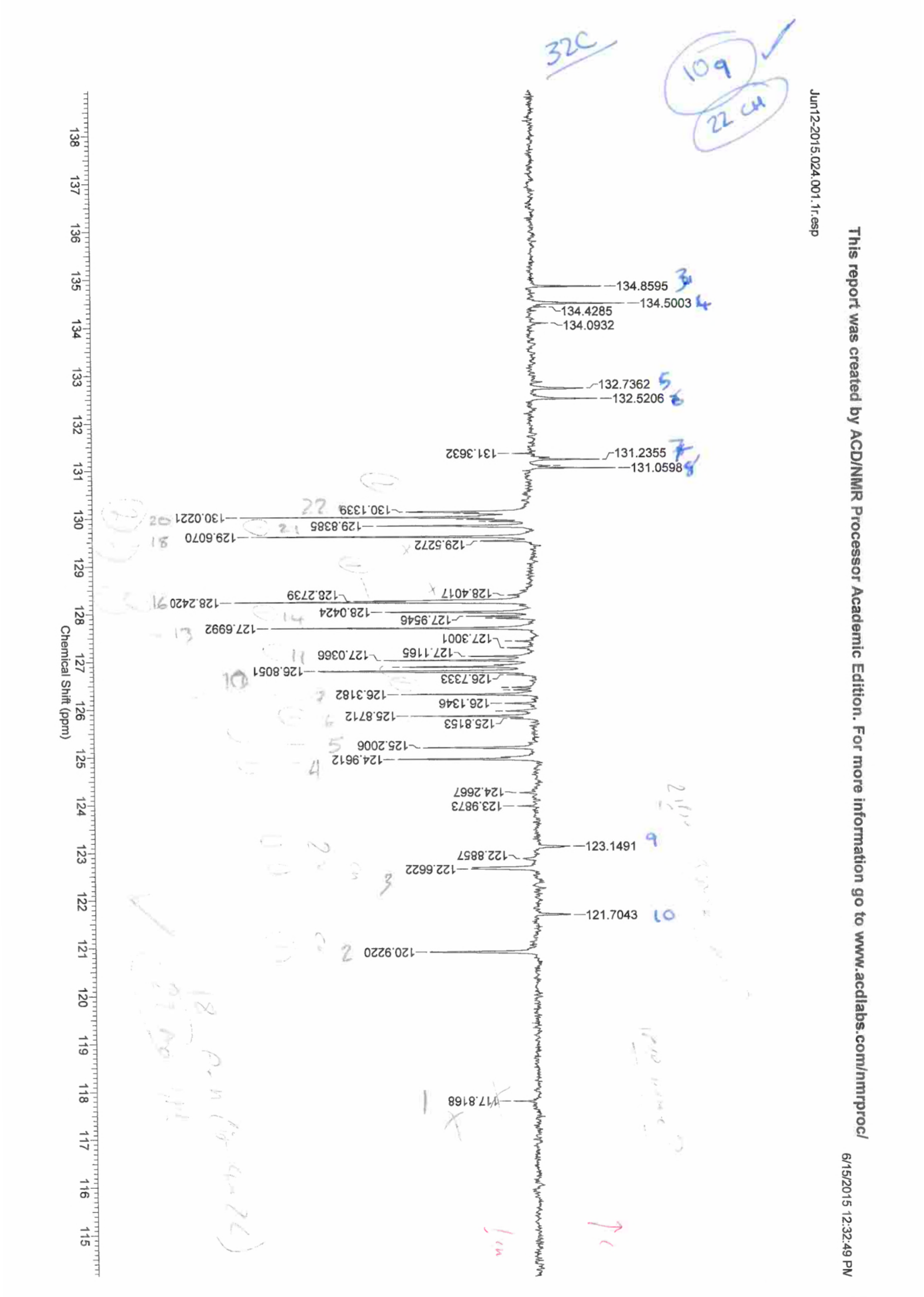
6/15/2015 12:29:50 PM

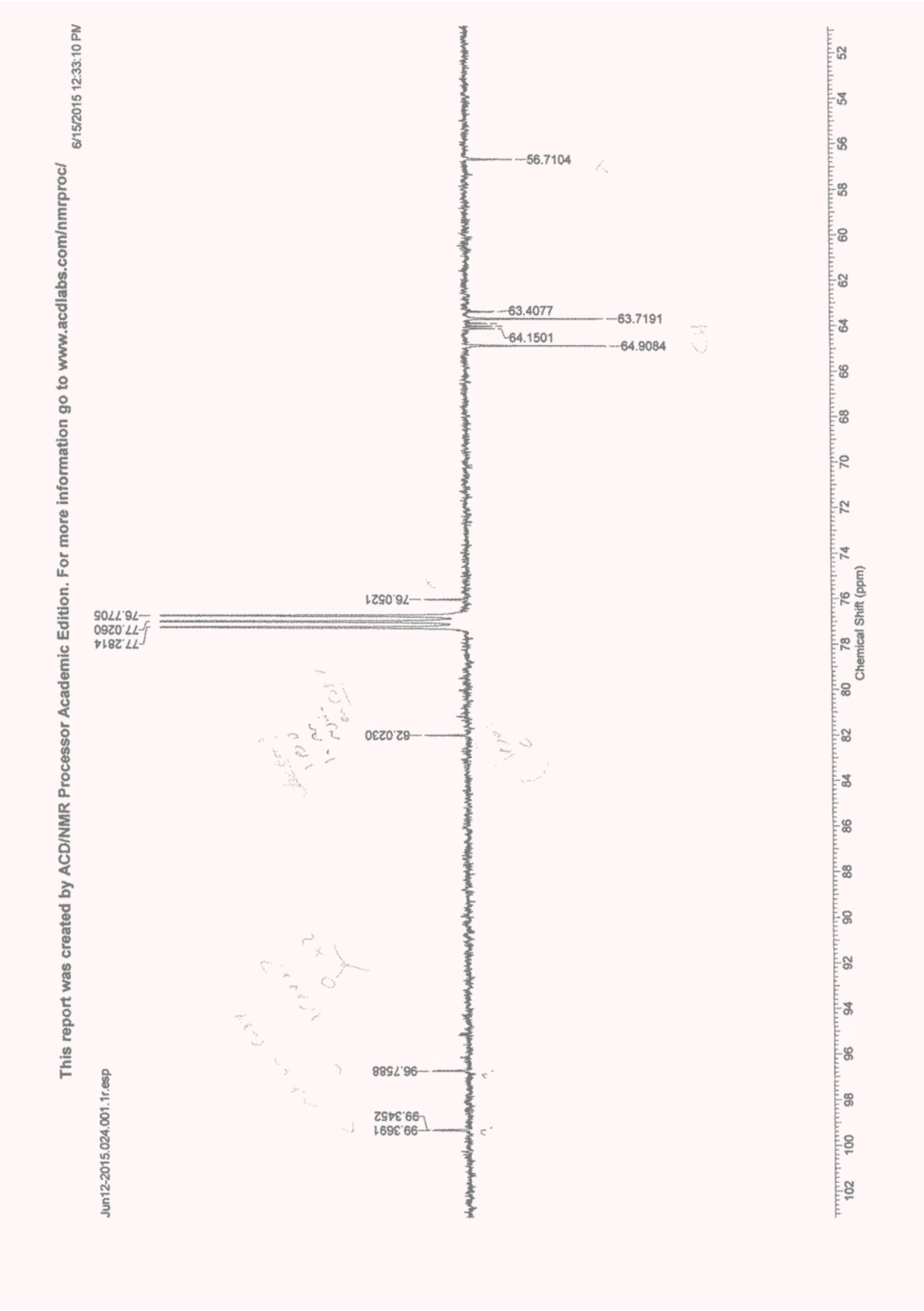
Jun12-2015.020.001.1r.esp

δ_C (125 MHz, $CDCl_3$)




This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
Jun12-2015.024.001.1r.esp
6/15/2015 12:32:29 PM
213.2162
213.0486
212.3781
212.1865
213.1
20.95Hz.
23.95Hz
212.3
165.6402
165.6083
C=O.
165.6.
3.99Hz
149.4277
149.3479
148.0068
147.9509
149.4
9.98
148.0
210
205
200
195
190
185
180
175
170
165
160
155
150
145
Chemical Shift (ppm)

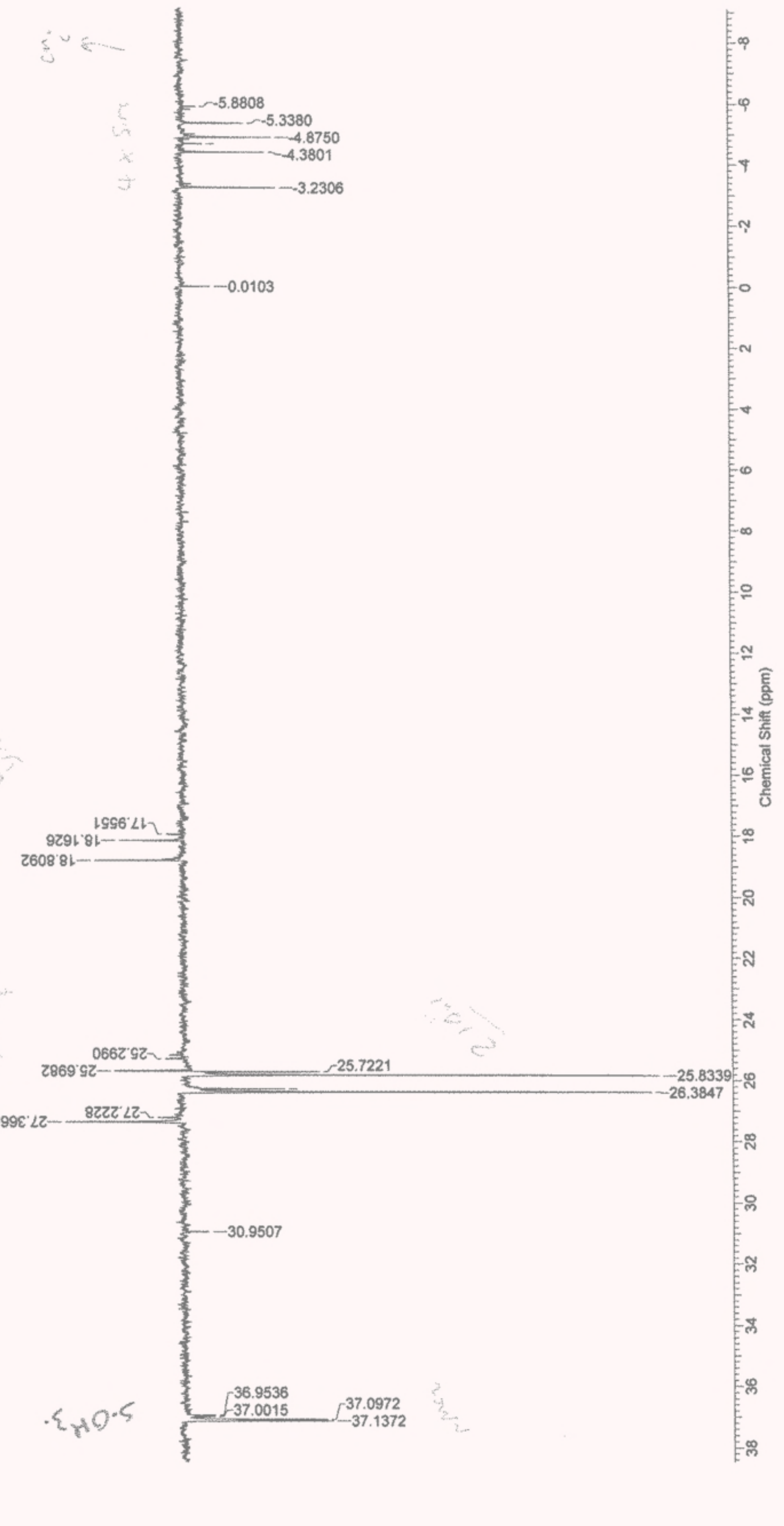

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
Jun12-2015.024.001.1r.esp
6/15/2015 12:32:49 PM
32C
109
22 CH
134.8595 3
134.5003 4
134.4285
134.0932
132.7362 5
132.5206 6
131.2355 7
131.0598 8
123.1491 9
121.7043 10
Chemical Shift (ppm)
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
116
115


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
6/15/2015 12:33:10 PM
Jun12-2015.024.001.1r.esp
56.7104
63.4077
63.7191
64.1501
64.9084
76.0521
76.7705
77.0260
77.2814
82.0230
96.7588
99.3452
99.3691
Chemical Shift (ppm)
52
54
56
58
60
62
64
66
68
70
72
74
76
78
80
82
84
86
88
90
92
94
96
98
100
102

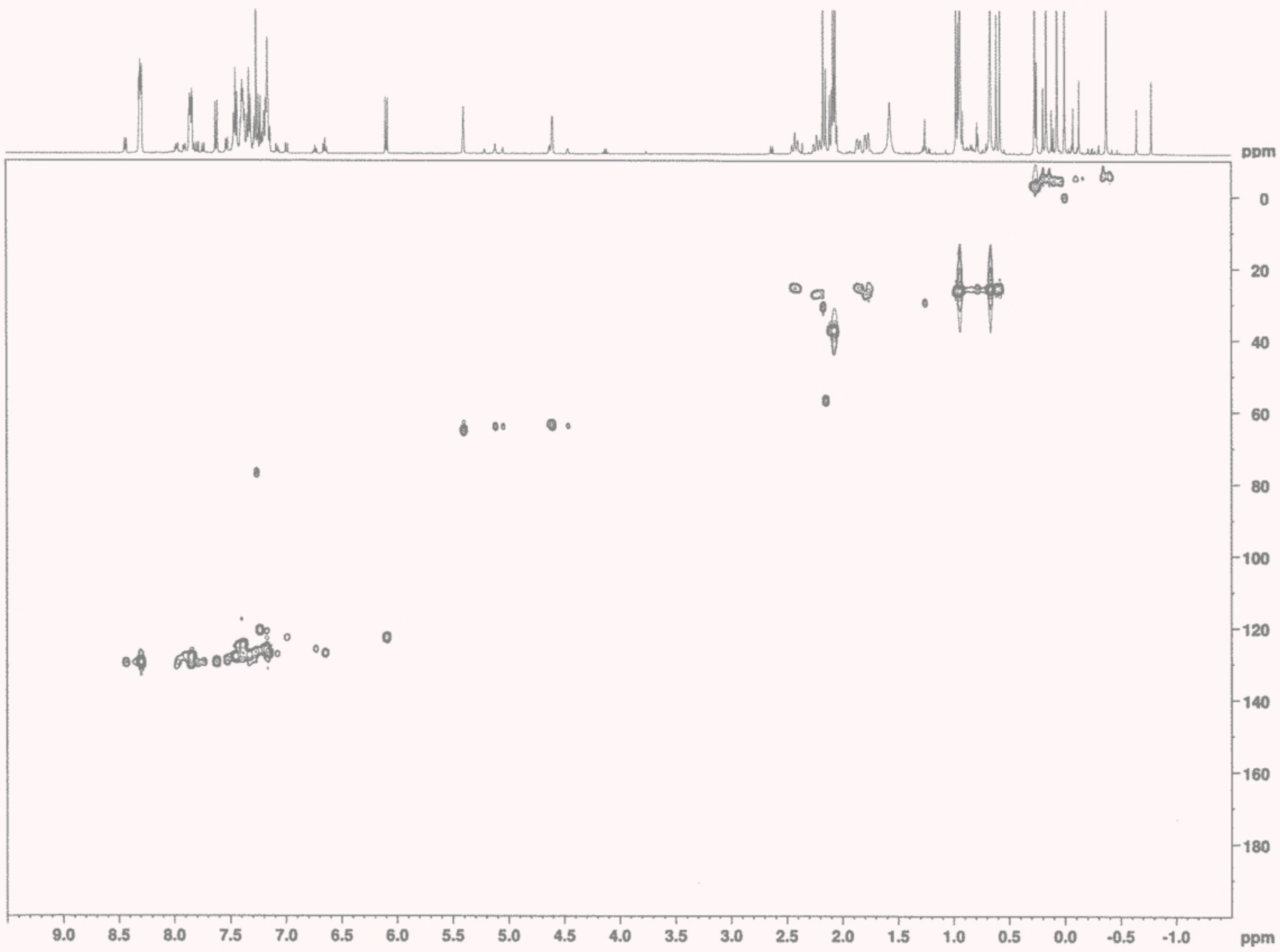
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

6/15/2015 12:33:24 PM

Jun12-2015.024.001.1r.esp

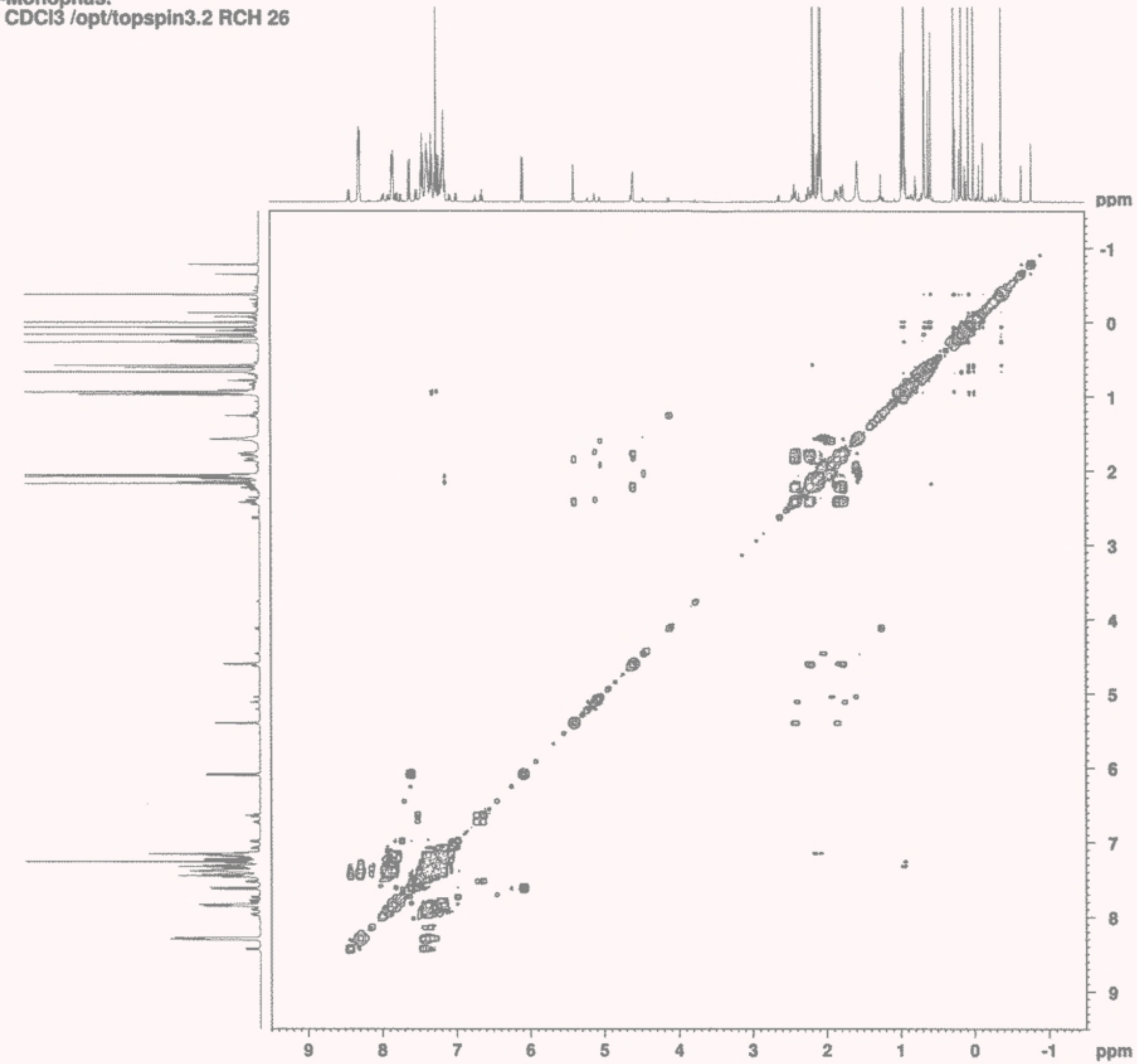


HSQC.w CDCl3 /opt/topspin3.2 RCH 26
phas.



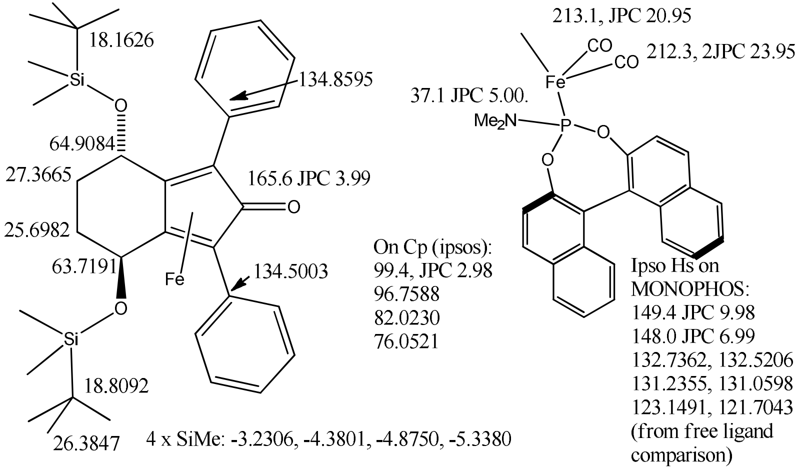
```
Current Data Parameters
NAME            Jun12-2015
EXPNO                   22
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150612
Time                 11.49
INSTRUM              spect
PROBHD   5 mm CPDCH 13C
PULPROG           hsqcetgp
TD                    1024
SOLVENT              CDCl3
NS                       4
DS                      16
SWH               5434.783 Hz
FIDRES            5.307405 Hz
AQ               0.0942080 sec
RG                  185.92
DW                  92.000 usec
DE                   40.00 usec
TE                   298.0 K
CNST2          145.0000000
D0              0.00000300 sec
D1              1.48156798 sec
D4              0.00172414 sec
D11             0.03000000 sec
D16             0.00020000 sec
IN0             0.00001890 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1          500.1319222 MHz
NUC1                    1H
P1                    9.10 usec
P2                   18.20 usec
P28       0 usec
PLW1           13.00000000 W

======== CHANNEL f2 ========
SFO2          125.7697355 MHz
NUC2                   13C
CPDPRG[2              garp
P3                    9.50 usec
P4                   19.00 usec
PCPD2                63.70 usec
PLW2           24.00000000 W
PLW12           0.51266003 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPNAM[2]        SMSQ10.100
GPZ1                 80.00 %
GPZ2                 20.10 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     128
SFO1              125.7697 MHz
FIDRES          206.679901 Hz
SW                 210.345 ppm
FnMODE       Echo-Antiecho

F2 - Processing parameters
SI                    1024
SF             500.1300126 MHz
WDW                  QSINE
SSB                      2
LB        0 Hz
GB        0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2         echo-antiecho
SF             125.7577885 MHz
WDW                  QSINE
SSB                      2
LB        0 Hz
GB        0
```

Chemist Roy Hodgkinson
1202-(R)-Monophas.
COSY.w CDCl3 /opt/topspin3.2 RCH 26



```
Current Data Parameters
NAME            Jun12-2015
EXPNO                   21
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150612
Time                 11.43
INSTRUM              spect
PROBHD   5 mm CPDCH 13C
PULPROG         cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                       8
SWH               5681.818 Hz
FIDRES            2.774325 Hz
AQ               0.1802240 sec
RG                   60.07
DW                  88.000 usec
DE                   40.00 usec
TE                   298.0 K
D0              0.00000300 sec
D1              1.96313596 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00017600 sec

======== CHANNEL f1 ========
SFO1           500.1319222 MHz
NUC1                    1H
P0                    9.10 usec
P1                    9.10 usec
P17                2500.00 usec
PLW1           13.00000000 W
PLW10           1.59249997 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     128
SFO1              500.1319 MHz
FIDRES           44.389206 Hz
SW                  11.361 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             500.1300126 MHz
WDW                  QSINE
SSB       0
LB        0 Hz
GB        0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.1300126 MHz
WDW                  QSINE
SSB       0
LB        0 Hz
GB        0
```

Couplings ARE calculated here. COSY used.



On Cp (ipsos):
99.4, JPC 2.98
96.7588
82.0230
76.0521

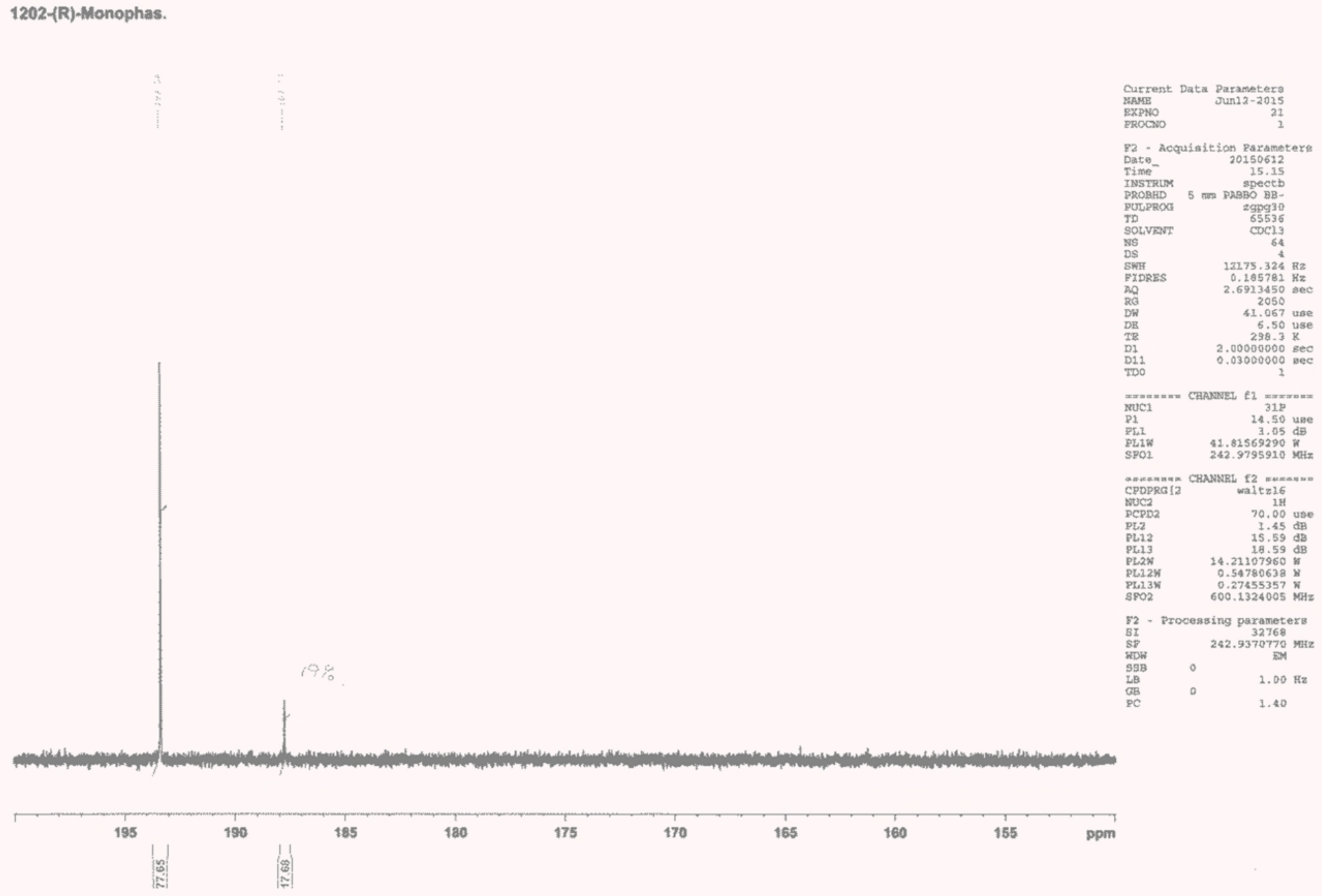
Ipso Hs on
MONOPHOS:
149.4 JPC 9.98
148.0 JPC 6.99
132.7362, 132.5206
131.2355, 131.0598
123.1491, 121.7043
(from free ligand
comparison)

4 x SiMe: -3.2306, -4.3801, -4.8750, -5.3380

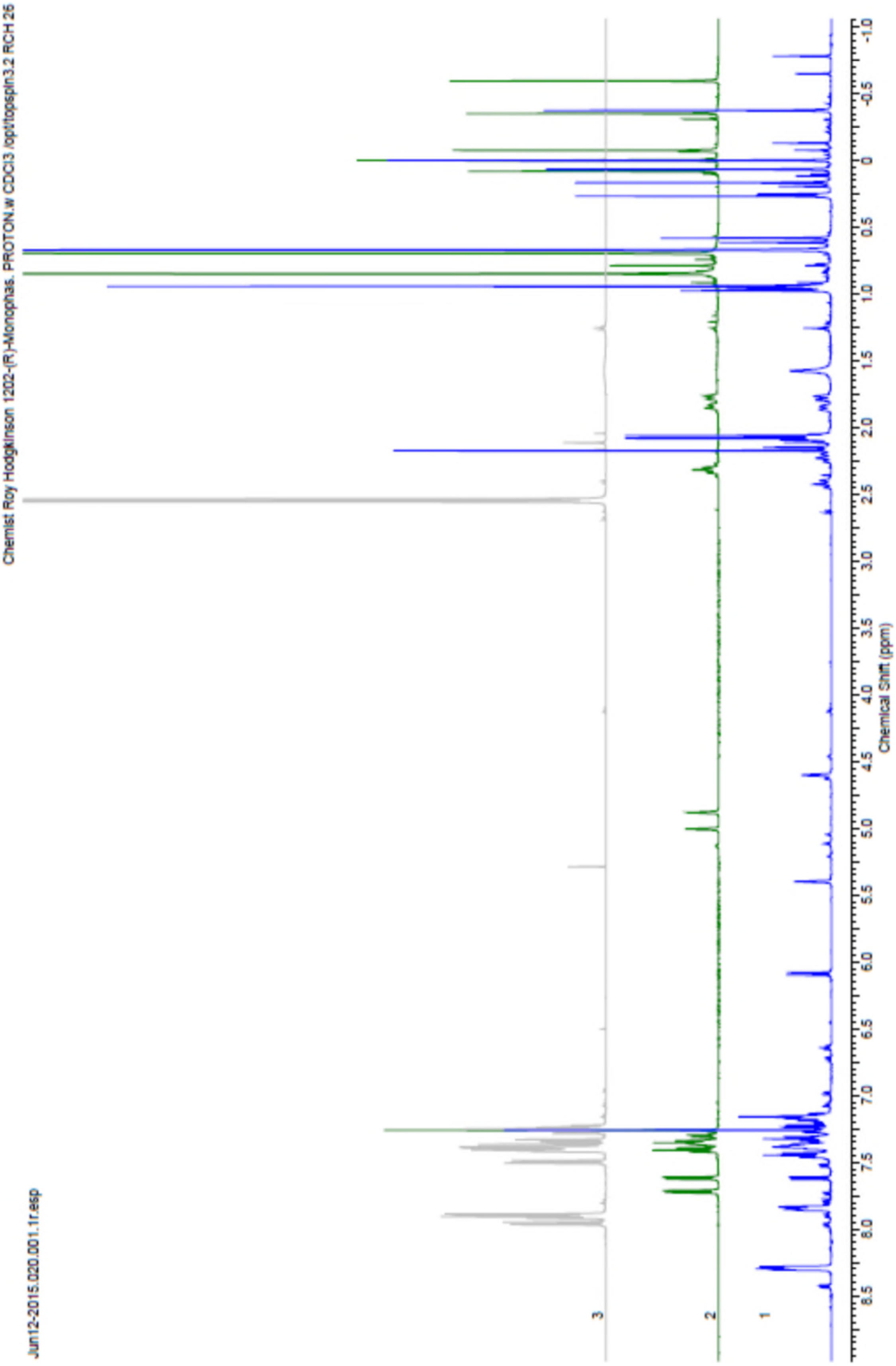
Aromatic CH: 130.1339, 130.0221 (2C), 129.8385, 129.6070 (2C), 128.2739, 128.2420, 128. 0424, 127.6992 (2C), 127.1165, 126.9 (not labelled but distinct), 126.8051 (2C), 126.3182, 125. 8712, 125.2006, 124.9612, 122.6622 (2C), 120.9220. (22 ArH).

P-NMR.

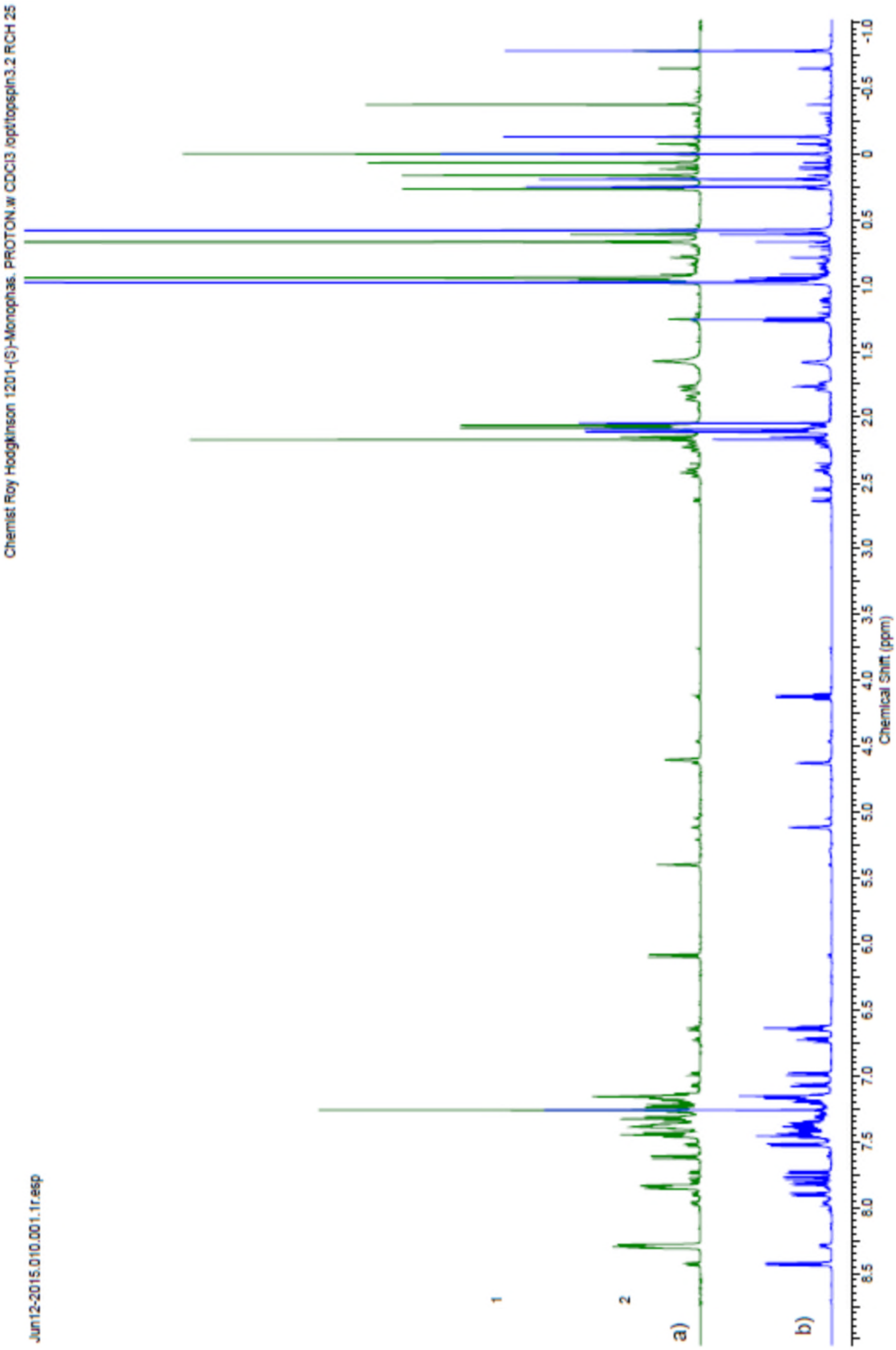
δ_P (242 MHz, $CDCl_3$)



```
Current Data Parameters
NAME          Jun12-2015
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150612
Time               15.15
INSTRUM           spectb
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            12175.324 Hz
FIDRES          0.185781 Hz
AQ             2.6913450 sec
RG                  2050
DW                41.067 use
DE                  6.50 use
TE                 298.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 31P
P1                 14.50 use
PL1                 3.05 dB
PL1W         41.81569290 W
SFO1         242.9795910 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              70.00 use
PL2                 1.45 dB
PL12               15.59 dB
PL13               18.59 dB
PL2W         14.21107960 W
PL12W         0.54780638 W
PL13W         0.27455357 W
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 32768
SF           242.9370770 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



1: OTBS catalyst with R-Monophos; 2: OTBS Catalyst; 3) R-Monophos.



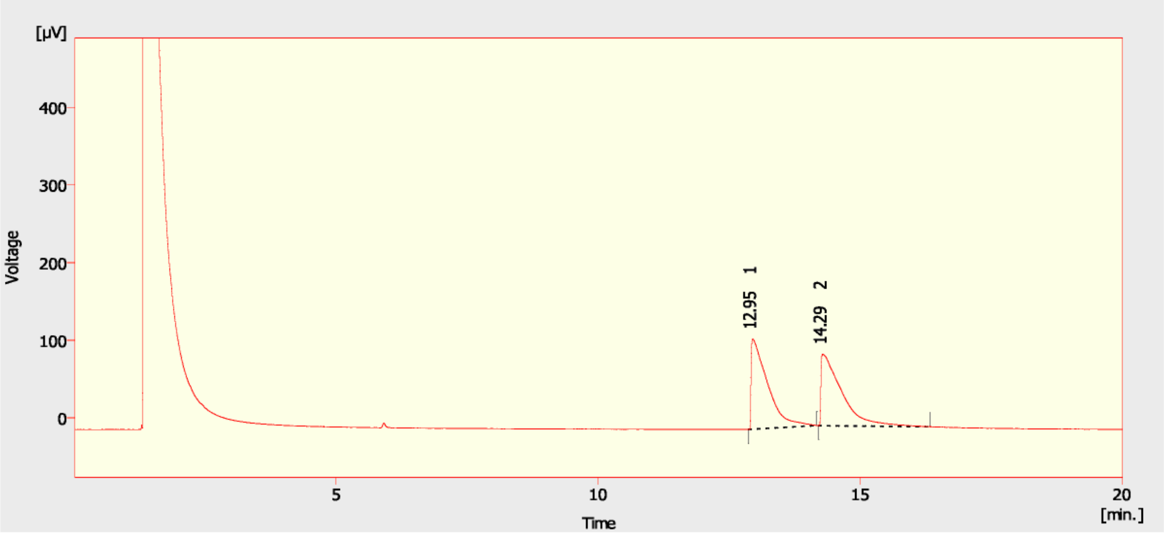
a) OTBS with R-Monophos **24**; b) OTBS with S-Monophos **25**. Each complex contains ca 10% of the other diastereosiomer, as discussed in the paper.

GC data for reduction products.

I-Phenylethanol. Racemic, 110 °C.

05/01/2016 17:32 Chromatogram C:\Clarity\WORK1\DATA\ADG\ADG racemic 1-phenylethanol He.prm Page 1 of 1

Clarity - Chromatography SW
DataApex
www.dataapex.com
GC1 Helium
Column: CP-Chiralsil-Dex CB 25mx0.25mmx0.25um

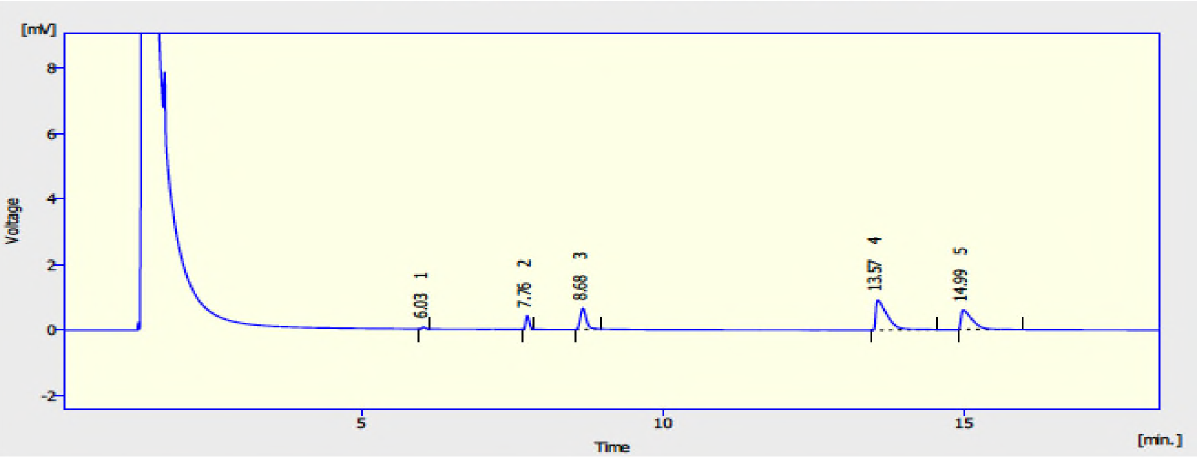


Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG racemic 1-phenylethanol He - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.952	25.289	1.160	50.0	55.7	0.33	
2	14.292	25.295	0.924	50.0	44.3	0.40	
	Total	50.584	2.085	100.0	100.0		

Chiral (RCH1047, Catalyst OTIPS, 99.2% conversion, 32% ee) 110 °C.

Clarity - Chromatography SW
DataApex
www.dataapex.com
GC1 Helium
Column: CP-Chiralsil-Dex CB 25mx0.25mmx0.25um

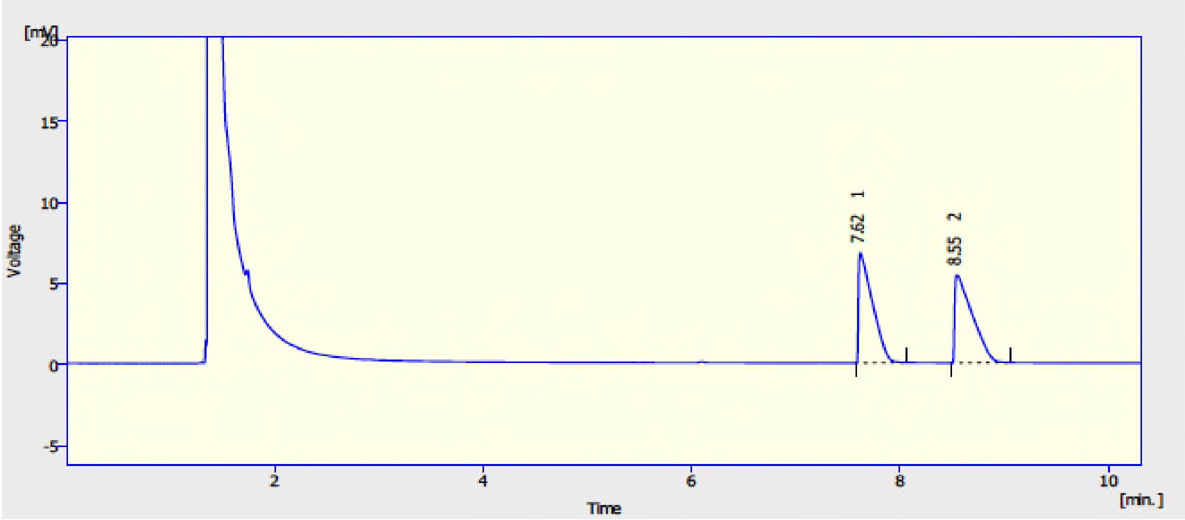


Result Table (Uncal - C:\CLARITY\WORK1\DATA\ROY\RCH1047-24-110 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.032	0.218	0.064	0.8	2.4	0.05	
2	7.756	1.698	0.420	6.6	15.9	0.07	
3	8.680	4.362	0.645	16.8	24.4	0.11	
4	13.568	11.946	0.917	46.1	34.7	0.20	
5	14.992	7.695	0.594	29.7	22.5	0.20	
	Total	25.920	2.639	100.0	100.0		

1-Phenylethyl formate (racemic) 110 °C.

Clarity - Chromatography SW
DataApex
www.dataapex.com
GC1 Helium
Column: CP-Chiralsil-Dex CB 25mx0.25mmx0.25um

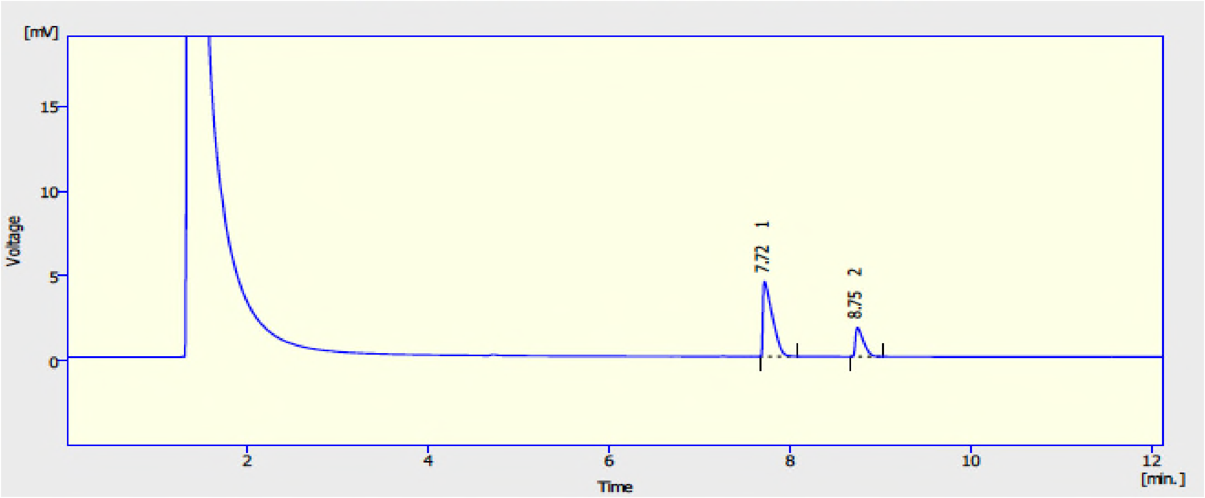


Result Table (Uncal - C:|CLARITY|WORK1|DATA|ROY|RCH1074-110 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.620	62.779	6.773	50.0	55.7	0.15	
2	8.548	62.876	5.394	50.0	44.3	0.19	
	Total	125.654	12.167	100.0	100.0		

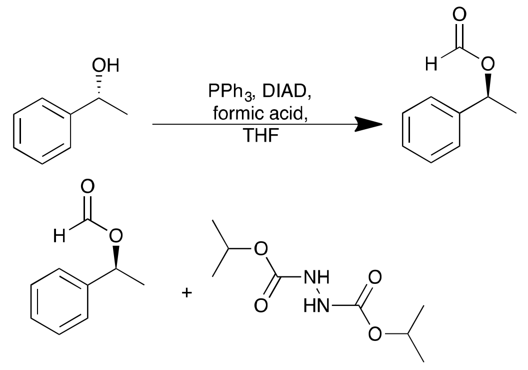
Enriched sample (51% ee (*S*) from (*R*) enantiomer of alcohol using Mitsunobu reaction described below) 110 °C.

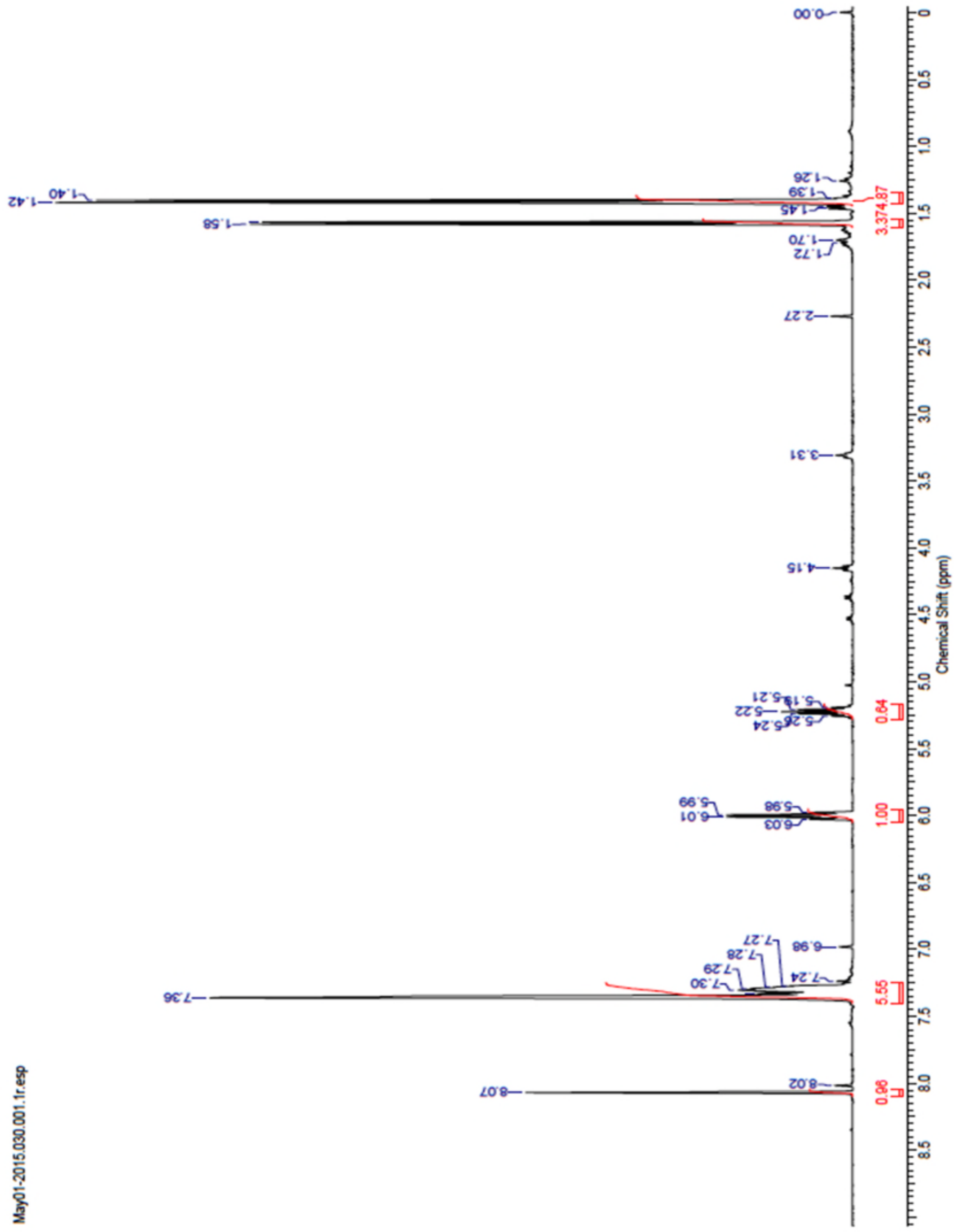
Clarity - Chromatography SW
DataApex
www.dataapex.com
GC1 Helium
Column: CP-Chiralsil-Dex CB 25mx0.25mmx0.25um



Result Table (Uncal - C:|Clarity|WORK1|DATA|Old data|RCH1136 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.724	31.907	4.426	75.4	72.2	0.12	
2	8.748	10.433	1.707	24.6	27.8	0.10	
	Total	42.341	6.133	100.0	100.0		

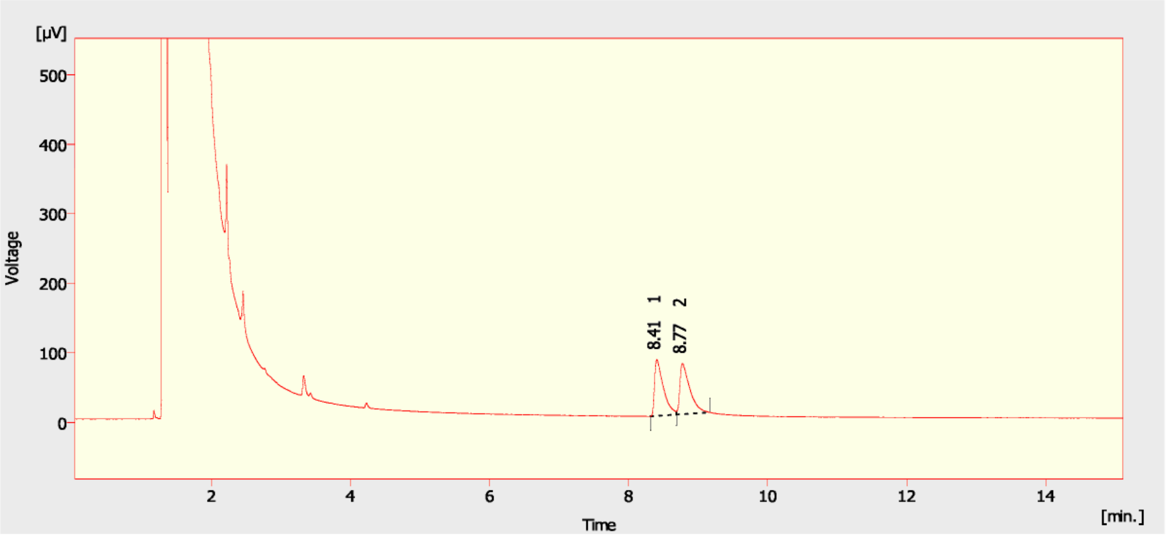

OH
PPh$_3$, DIAD,
formic acid,
THF
O
H
O
+
O
O
NH
HN
O
O


May01-2015.030.001.1r.esp
8.07
8.02
7.36
7.30
7.29
7.28
7.27
7.24
6.98
6.03
6.01
5.99
5.98
5.26
5.24
5.22
5.21
5.18
4.15
3.31
2.27
1.72
1.70
1.58
1.45
1.42
1.40
1.39
1.26
0.00
0.96
5.55
1.00
0.64
3,374.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

3,3-Dimethyl-2-butanol. 70 °C.
Racemic

05/01/2016 17:30 Chromatogram C:\Clarity\WORK1\DATA\ADG\ADG racemic 3,3-dimethyl-2-butanol He ok.prm Page 1 of 1

Clarity - Chromatography SW
DataApex
www.dataapex.com
GC1 Helium
Column: CP-Chiralsil-Dex CB 25mx0.25mmx0.25um

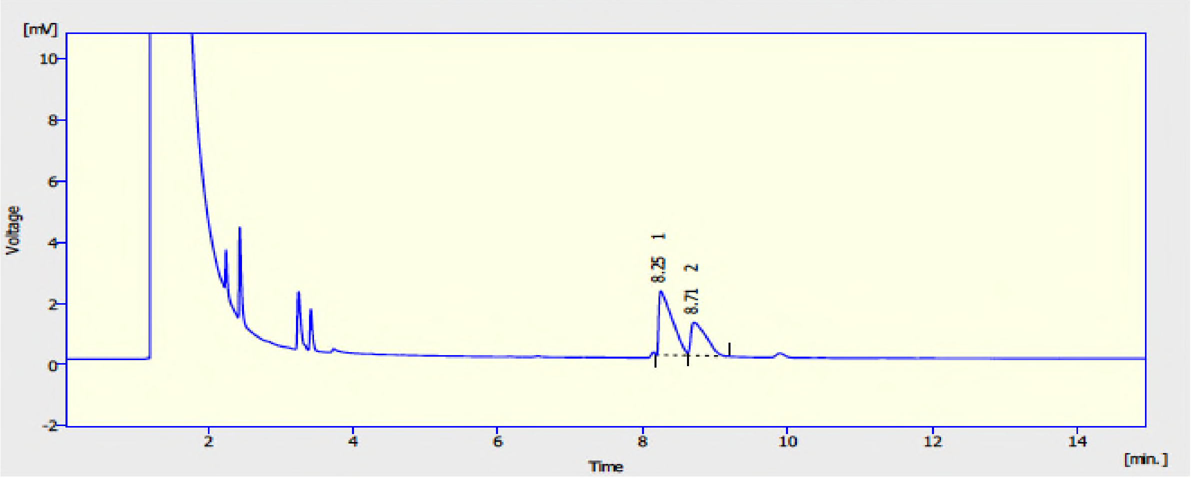


Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG racemic 3,3-dimethyl-2-butanol He ok - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.408	7.123	0.808	49.6	52.6	0.14	
2	8.772	7.241	0.729	50.4	47.4	0.15	
	Total	14.363	1.537	100.0	100.0		

Chiral (RCH1184-OTBDPS catalyst, 100% conv. With a 26% ee). 70 °C.

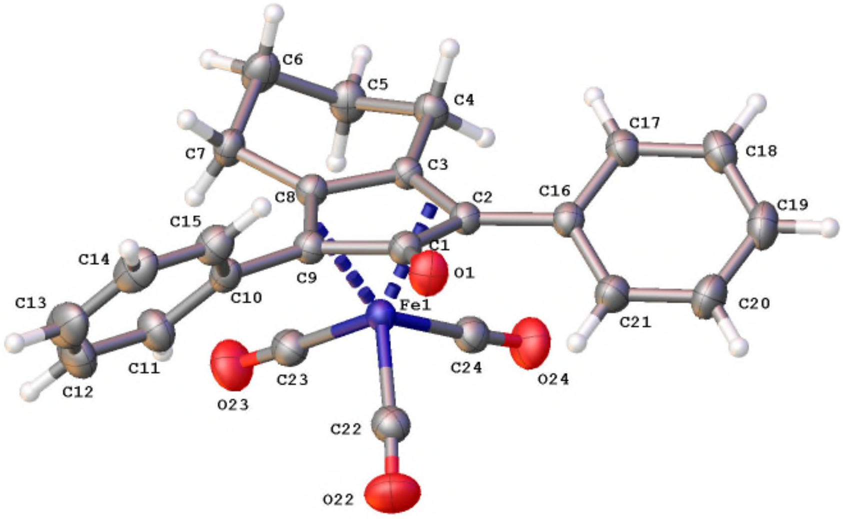
Clarity - Chromatography SW
DataApex
www.dataapex.com
GC1 Helium
Column: CP-Chiralsil-Dex CB 25mx0.25mmx0.25um



Result Table (Uncal - C:\CLARITY\WORK1\DATA\ROY\RCH1184-24-70 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.248	26.876	2.094	62.9	65.8	0.21	
2	8.708	15.820	1.088	37.1	34.2	0.24	
	Total	42.696	3.182	100.0	100.0		

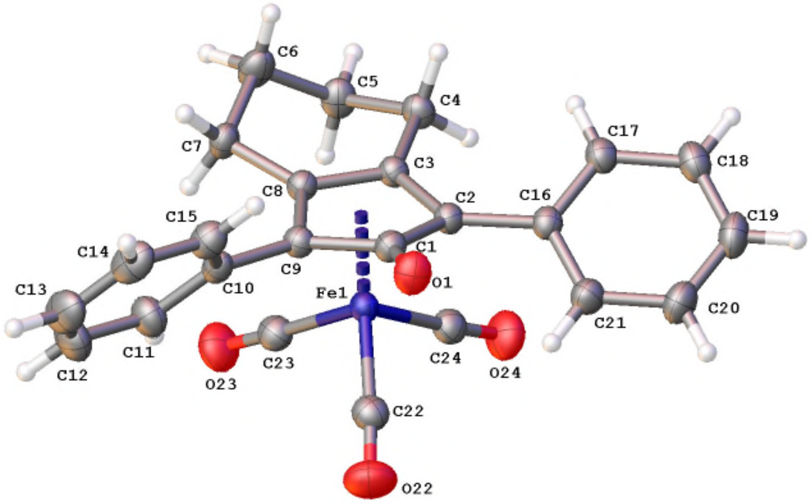
The X-ray crystallographic structure of **4b** (CCDC 1431241, local code ADG2).



solid state structure of adg2 with atom labels and thermal ellipsoids at 50% probability level

Eta4 coordination drawn to the butadiene part C2 C3 C8 C9 as bonds to the centre of the double bonds.

Below, different pictures with different bonding pictures



Picture with one bond to the centroid of the butadiene system

Crystal structure determination of [adg2]

The asymmetric unit contains the complex, there are two complexes in the unit cell. The CP ring is not flat but puckered. The iron appears to bind to just the butadiene fragment and the C=O bond is puckered above the ring plane, indicating expected Eta4 bonding.

Crystal structure determination of [adg2]

Experimental

Single crystals of $C_{24}H_{18}FeO_4$ **[adg2]** were grown from a solution of hot benzene upon cooling to rt. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{24}H_{18}FeO_4$ (M =426.23 g/mol): triclinic, space group P-1 (no. 2), a = 9.12907(18) Å, b = 9.72040(17) Å, c = 11.56823(16) Å, α = 80.5397(13)°, β = 70.1570(15)°, γ = 77.6372(16)°, V = 938.50(3) Å^3, Z = 2, T = 150(2) K, μ(MoKα) = 0.833 mm^{-1}, $Dcalc$ = 1.508 g/cm^3, 57661 reflections measured (4.814° ≤ 2Θ ≤ 64.582°), 6365 unique (R_{int} = 0.0336, R_{sigma} = 0.0198) which were used in all calculations. The final R_1 was 0.0317 (I > 2σ(I)) and wR_2 was 0.1148 (all data).

Table 1 Crystal data and structure refinement for adg2.

Identification code	adg2
Empirical formula	$C_{24}H_{18}FeO_4$
Formula weight	426.23
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.12907(18)
b/Å	9.72040(17)
c/Å	11.56823(16)
α/°	80.5397(13)

β/°	70.1570(15)
γ/°	77.6372(16)
Volume/Å^3	938.50(3)
Z	2
ρ_{calc}g/cm^3	1.508
μ/mm^{-1}	0.833
F(000)	440.0
Crystal size/mm^3	0.3 × 0.3 × 0.25 yellow block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.814 to 64.582
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 13$, $-17 \le l \le 17$
Reflections collected	57661
Independent reflections	6365 [R_{int} = 0.0336, R_{sigma} = 0.0198]
Data/restraints/parameters	6365/0/262
Goodness-of-fit on F^2	1.294
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0973
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.1148
Largest diff. peak/hole / e Å^{-3}	0.82/-0.86

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of: All C(H) groups, All C(H,H) groups

2.a Secondary CH2 refined with riding coordinates:

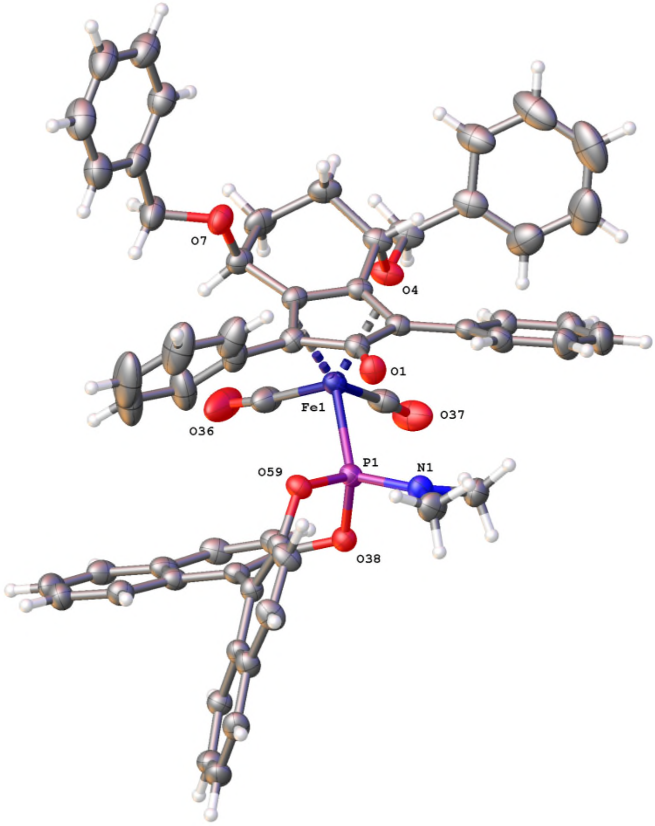
C4(H4A,H4B), C5(H5A,H5B), C6(H6A,H6B), C7(H7A,H7B)

2.b Aromatic/amide H refined with riding coordinates:

C11(H11), C12(H12), C13(H13), C14(H14), C15(H15), C17(H17), C18(H18), C19(H19), C20(H20), C21(H21)

This report has been created with Olex2, compiled on 2015.01.26 svn.r3151 for OlexSys.

The X-ray crystallographic structure of complex (*SS*,*S*)-**22** (CCDC 1431242, local code RH2).



Solid state structure of rh2 with key atoms labeled. Thermal ellipsoids are drawn at 50% probability level.

Crystal structure determination of [rh2]

The asymmetric unit contains the compound, there are 4 in the unit cell.

Some of the thermal parameters of the benzyl and phenyl groups are rather large indicating some thermal motion but were not modeled as disordered.

The Flack parameter -0.005(1) is small with a small error and the stereochemistry of the refined structure also matches the known stereochemistry of the BINOL starting material (*S*).

Hooft y: -0.0030(11) (Olex2)

Flack x: -0.005(1) (Shelxl2014)

Experimental

Single crystals of $C_{59}H_{48}FeNO_7P$ **[rh2]** were grown from a slowly evaporating solution of

EtOAc at rt. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the XL [3] refinement package using Least Squares minimisation.

1 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{59}H_{48}FeNO_7P$ (M =969.80 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.35102(7) Å, b = 19.11081(15) Å, c = 24.09710(17) Å, V = 4766.80(6) Å^3, Z = 4, T = 150(2) K, μ(CuKα) = 3.316 mm^{-1}, $Dcalc$ = 1.351 g/cm^3, 42062 reflections measured (7.338° ≤ 2Θ ≤ 156.204°), 10112 unique (R_{int} = 0.0375, R_{sigma} = 0.0300) which were used in all calculations. The final R_1 was 0.0361 (I > 2σ(I)) and wR_2 was 0.1006 (all data).

Table 1 Crystal data and structure refinement for rh2.

Identification code	rh2
Empirical formula	$C_{59}H_{48}FeNO_7P$
Formula weight	969.80
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.35102(7)
b/Å	19.11081(15)
c/Å	24.09710(17)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4766.80(6)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	3.316
F(000)	2024.0

Crystal size/mm^3	0.3 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.338 to 156.204
Index ranges	$-12 \le h \le 12$, $-21 \le k \le 24$, $-30 \le l \le 30$
Reflections collected	42062
Independent reflections	10112 [R_{int} = 0.0375, R_{sigma} = 0.0300]
Data/restraints/parameters	10112/84/624
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0361, wR_2 = 0.0977
Final R indexes [all data]	R_1 = 0.0390, wR_2 = 0.1006
Largest diff. peak/hole / e Å^{-3}	0.54/-0.36
Flack parameter	-0.0050(13)

Refinement model description

Number of restraints - 84, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of: All C(H) groups, All C(H,H) groups

At 1.5 times of: All C(H,H,H) groups

2. Uiso/Uaniso restraints and constraints

C10 ≈ C15 ≈ C14 ≈ C13 ≈ C12 ≈ C11: within 1.7A with sigma of 0.004 and sigma for terminal atoms of 0.008

O7 ≈ C29 ≈ C30 ≈ C35 ≈ C34 ≈ C33 ≈ C32 ≈ C31: within 1.7A with sigma of 0.002 and sigma for terminal atoms of 0.004

3.a Ternary CH refined with riding coordinates: C4(H4), C7(H7)

3.b Secondary CH2 refined with riding coordinates:

C5(H5A,H5B), C6(H6A,H6B), C22(H22A,H22B), C29(H29A,H29B)

3.c Aromatic/amide H refined with riding coordinates:

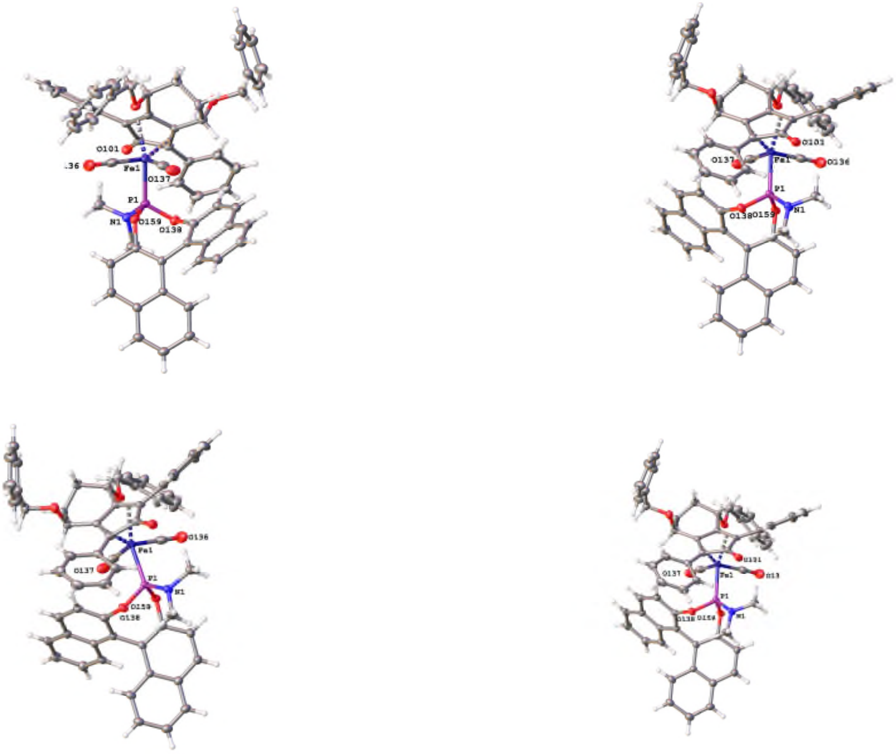
C11(H11), C12(H12), C13(H13), C14(H14), C15(H15), C17(H17), C18(H18), C19(H19), C20(H20), C21(H21), C24(H24), C25(H25), C26(H26), C27(H27), C28(H28), C31(H31), C32(H32), C33(H33), C34(H34), C35(H35), C40(H40), C41(H41), C43(H43), C44(H44), C45(H45), C46(H46), C51(H51), C52(H52), C53(H53), C54(H54), C56(H56), C57(H57)

3.d Idealised Me refined as rotating group: C60(H60A,H60B,H60C), C61(H61A,H61B,H61C)

This report has been created with Olex2, compiled on 2015.01.26 svn.r3150 for OlexSys.

The X-ray crystallographic structure of complex (*SS*,*R*)-**23** (CCDC14311243, local code RH3).

rh3



Just slightly different views of one of the crystallographically independent but chemically equivalent molecules in the asymmetric unit of rh3. Thermal ellipsoids are drawn at 50% probability level and only key atoms are labeled.

Crystal structure determination of [rh3]

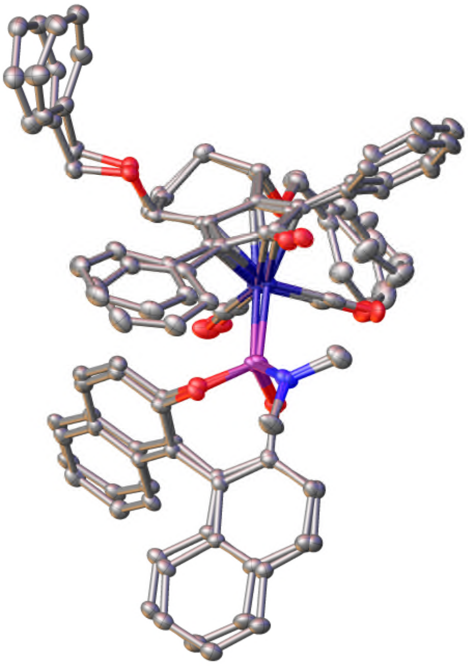
The asymmetric unit contains two crystallographically independent but chemically identical complexes (see later for an overlay). There are 4 molecules in the unit cell. The crystals were small and weakly diffracting and this registers a C alert in the cif checker.

The Flack parameter -0.017(4) is small with a small error and the stereochemistry of the refined structure also matches the known stereochemistry of the BINOL starting material (*R*).

Hooft y: -0.017(3) (Olex2)

Flack x: -0.017(4) (Shelx 2014)

Below is a picture of an overlay of the two molecules in the asymmetric unit using the ’match’ algorithm in Olex2 with the statistics for the fit below that.



Alignment statistics

Alignment RMSD {Fe2,C236,O236,...} to {Fe1,C136,O136,...} without inversion) is 0.468 A

Alignment RMSD {Fe2,C236,O236,...} to {Fe1,C136,O136,...} with inversion) is 3.758 A

The statistics show that the molecules are very similar (only a volume of 0.468A cubed difference between the two structures) the difference being mainly rotations of the aromatic rings and not different stereochemistry.

Attempts to match the second molecule by inverting it (so the enantiomer of the 2nd molecule) has a poor fit (3.758A cubed out).

The molecules are crystallographically independent but stereochemically identical.

Experimental

Single crystals of $C_{59}H_{48}FeNO_7P$ **[rh3]** were grown from a slowly evaporating solution of EtOAc at rt. A suitable crystal was selected and mounted on a Mitegen head with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the

XL [3] refinement package using Least Squares minimisation.

1 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{59}H_{48}FeNO_7P$ (M =969.80 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 8.9958(5) Å, b = 22.5355(9) Å, c = 23.3422(15) Å, β = 99.763(6)°, V = 4663.5(4) Å^3, Z = 4, T = 150(2) K, μ(CuKα) = 3.389 mm^{-1}, $Dcalc$ = 1.381 g/cm^3, 50097 reflections measured (7.686° ≤ 2Θ ≤ 157.392°), 18903 unique (R_{int} = 0.0914, R_{sigma} = 0.1131) which were used in all calculations. The final R_1 was 0.0634 (I > 2σ(I)) and wR_2 was 0.1964 (all data).

Table 1 Crystal data and structure refinement for rh3.

Identification code	rh3
Empirical formula	$C_{59}H_{48}FeNO_7P$
Formula weight	969.80
Temperature/K	150(2)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	8.9958(5)
b/Å	22.5355(9)
c/Å	23.3422(15)
α/°	90
β/°	99.763(6)
γ/°	90
Volume/Å^3	4663.5(4)
Z	4
ρ_{calc}g/cm^3	1.381
μ/mm^{-1}	3.389
F(000)	2024.0
Crystal size/mm^3	0.2 × 0.08 × 0.06 orange block
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.686 to 157.392
Index ranges	-11 ≤ h ≤ 11, -27 ≤ k ≤ 28, -29 ≤ l ≤ 29

Reflections collected	50097
Independent reflections	18903 [R_{int} = 0.0914, R_{sigma} = 0.1131]
Data/restraints/parameters	18903/1/1247
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1614
Final R indexes [all data]	R_1 = 0.0962, wR_2 = 0.1964
Largest diff. peak/hole / e Å^{-3}	0.43/-0.94
Flack parameter	-0.010(4)

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of: All C(H) groups, All C(H,H) groups

At 1.5 times of: All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates: C104(H104), C107(H107), C204(H204), C207(H207)

2.b Secondary CH2 refined with riding coordinates: C105(H10A,H10B), C106(H10C,H10D), C122(H12A,H12B), C129(H12C,H12D), C205(H20A, H20B), C206(H20C,H20D), C222(H22A,H22B), C229(H22C,H22D)

2.c Aromatic/amide H refined with riding coordinates: C111(H111), C112(H112), C113(H113), C114(H114), C115(H115), C117(H117), C118(H118), C119(H119), C120(H120), C121(H121), C124(H124), C125(H125), C126(H126), C127(H127), C128(H128), C131(H131), C132(H132), C133(H133), C134(H134), C135(H135), C140(H140), C141(H141), C143(H143), C144(H144), C145(H145), C146(H146), C151(H151), C152(H152), C153(H153), C154(H154), C156(H156), C157(H157), C211(H211), C212(H212), C213(H213), C214(H214), C215(H215), C217(H217), C218(H218), C219(H219), C220(H220), C221(H221), C224(H224), C225(H225), C226(H226), C227(H227), C228(H228), C231(H231), C232(H232), C233(H233), C234(H234), C235(H235), C240(H240), C241(H241), C243(H243), C244(H244), C245(H245), C246(H246), C251(H251), C252(H252), C253(H253), C254(H254), C256(H256), C257(H257)

2.d Idealised Me refined as rotating group;

C160(H16A,H16B,H16C),C161(H16D,H16E,H16F), C260(H26A,H26B,H26C), C261(H26D, H26E,H26F)

This report has been created with Olex2, compiled on 2015.01.26 svn.r3151 for OlexSys.