Supporting Information for:

Iridium Complexes of Perimidine-based *N*-Heterocyclic Carbene Pincer Ligands via Aminal C–H Activation

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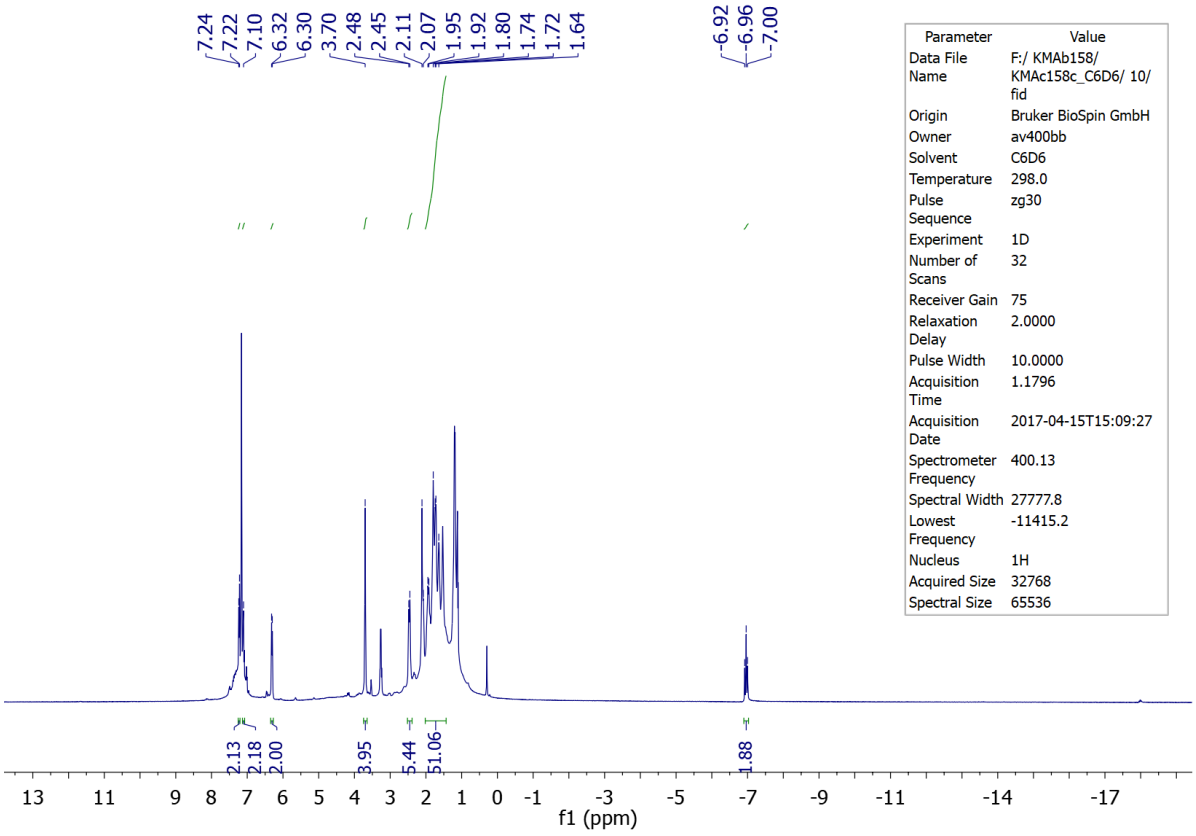
Table of Contents

trans-[$IrH_2Cl\{C(NCH_2PCy_2)_2C_{10}H_6\}$] (*trans*-5b)

^{1}H NMR Spectrum of Compound *trans*-5b



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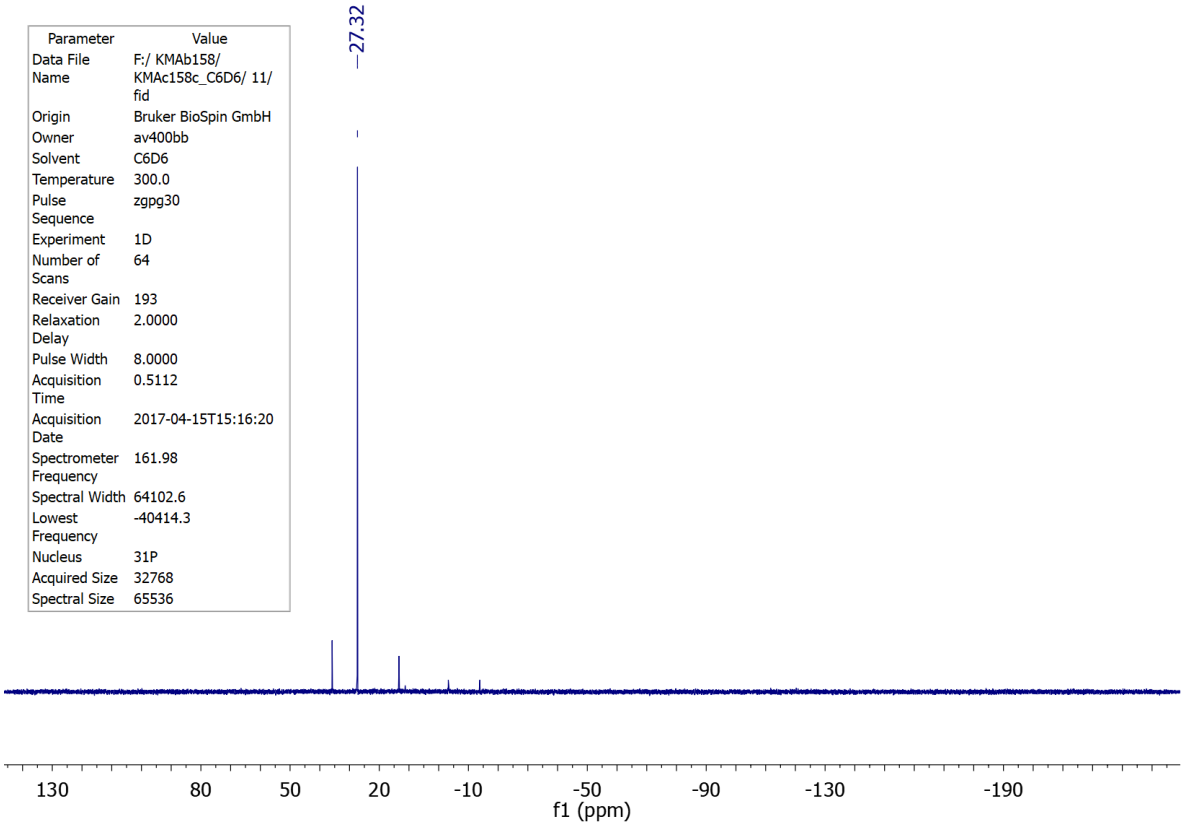
Acquired Size	32768
Spectral Size	65536

^{31}P{^{1}H} Spectrum of Compound *trans*-5b



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Spectral Width	64102.6
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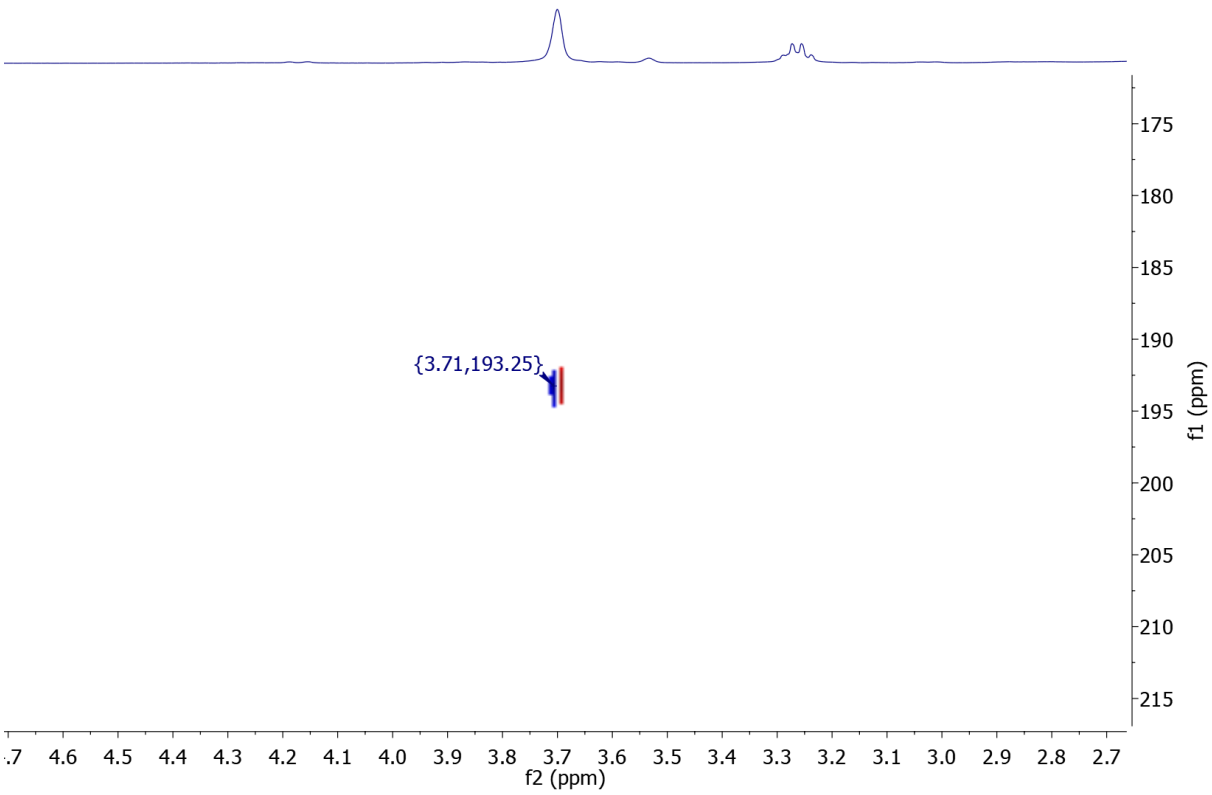
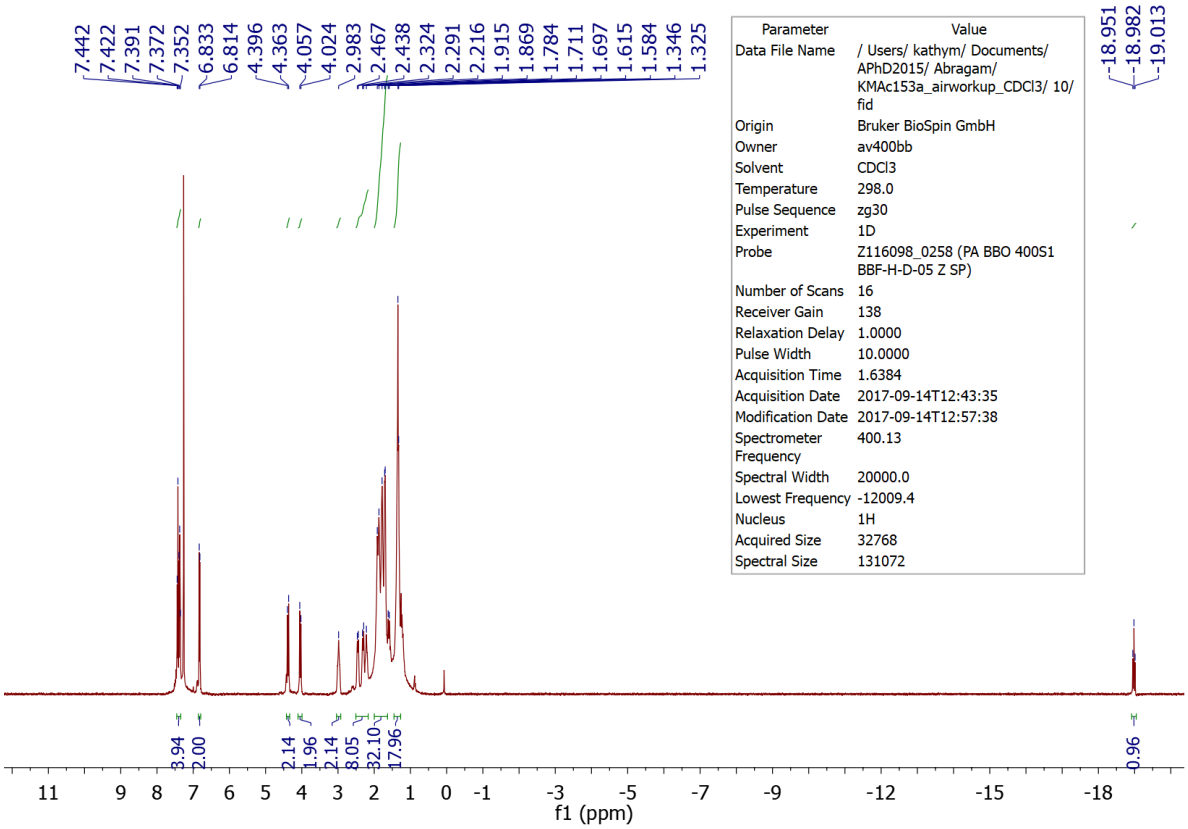
Nucleus	31P
Acquired Size	32768
Spectral Size	65536

$^{1}H^{13}C$ HMBC (carbene resonance) of Compound *trans*-5b



$[IrHCl_2\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (6b)

^{1}H NMR Spectrum of Compound 6b



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Temperature	298.0
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Experiment	1D
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Receiver Gain	138
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Nucleus	1H
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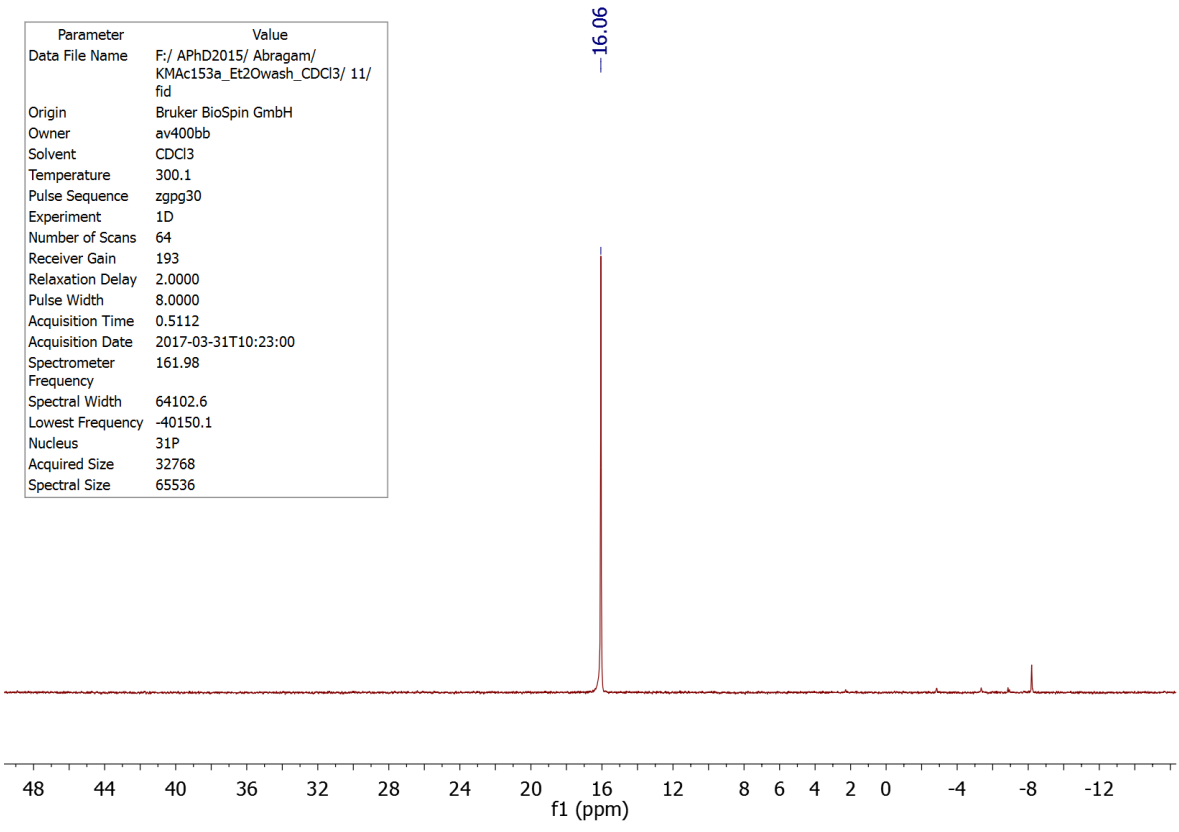
^{31}P{^{1}H} Spectrum of Compound 6b



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Owner	av400bb
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Temperature	300.1
Pulse Sequence	zgpg30
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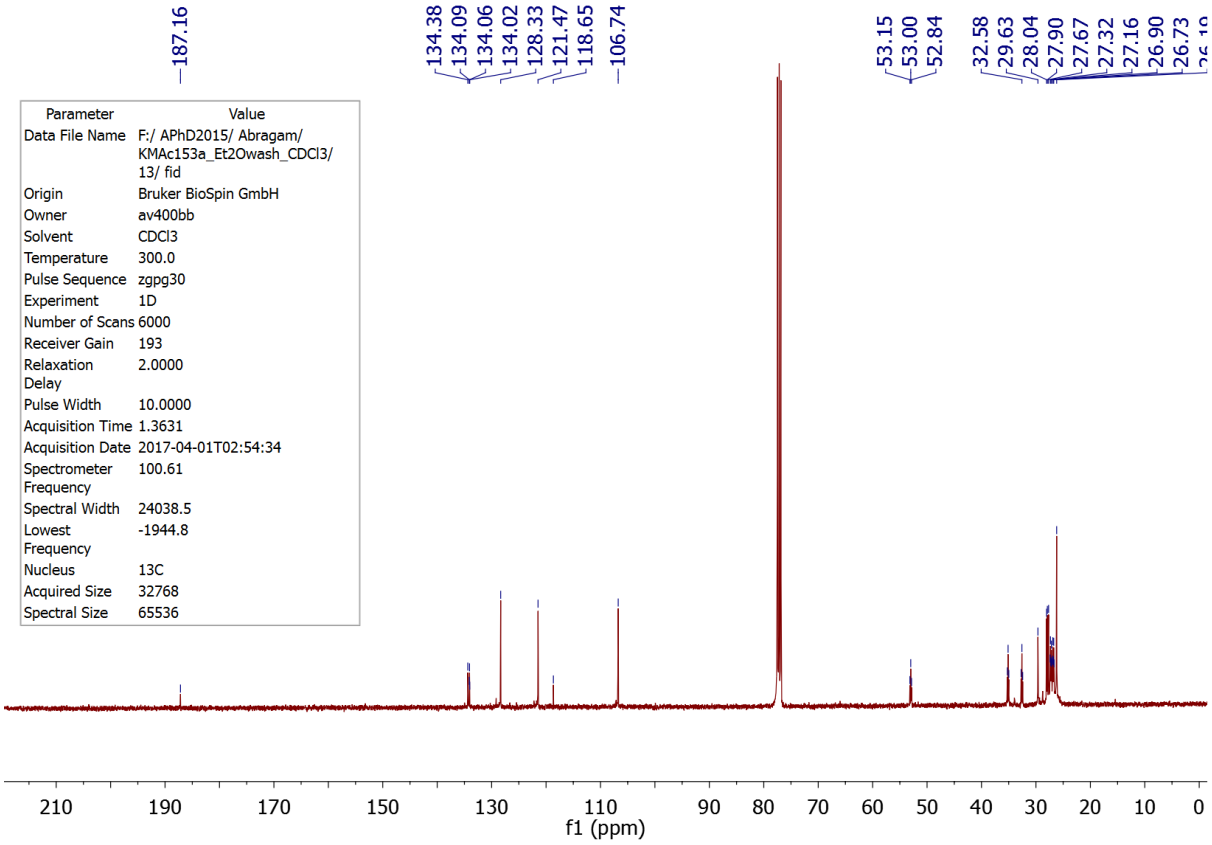
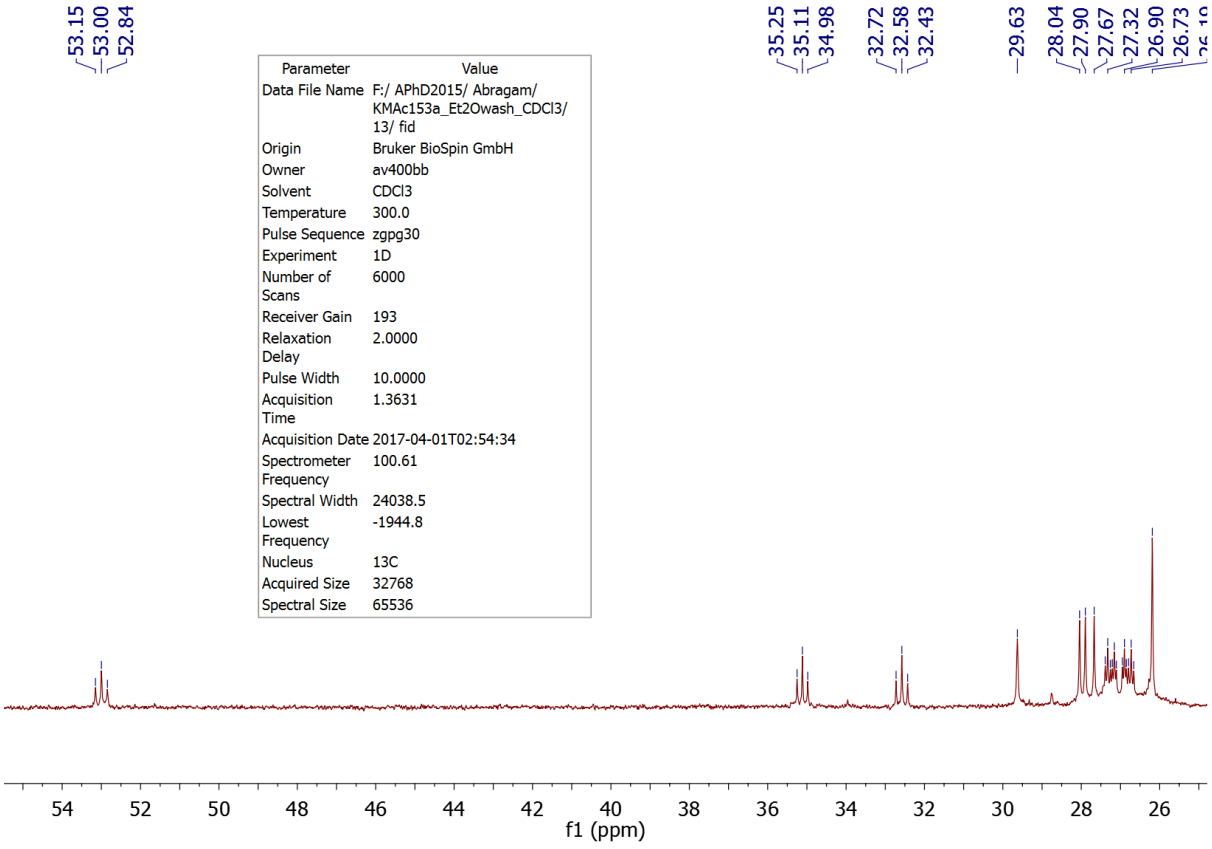
Lowest Frequency	-40150.1
Nucleus	31P
Acquired Size	32768
Spectral Size	65536

$^{13}C\{^{1}H\}$ Spectrum of Compound 6b





[IrCl{$CH_2(NCH_2PPh_2)_2C_{10}H_6$}(COD)] (8a)

^{1}H NMR Spectrum of Compound 8a

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Origin	Bruker BioSpin GmbH
Owner	av400bb
Solvent	CD2Cl2
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
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Relaxation Delay	1.0000
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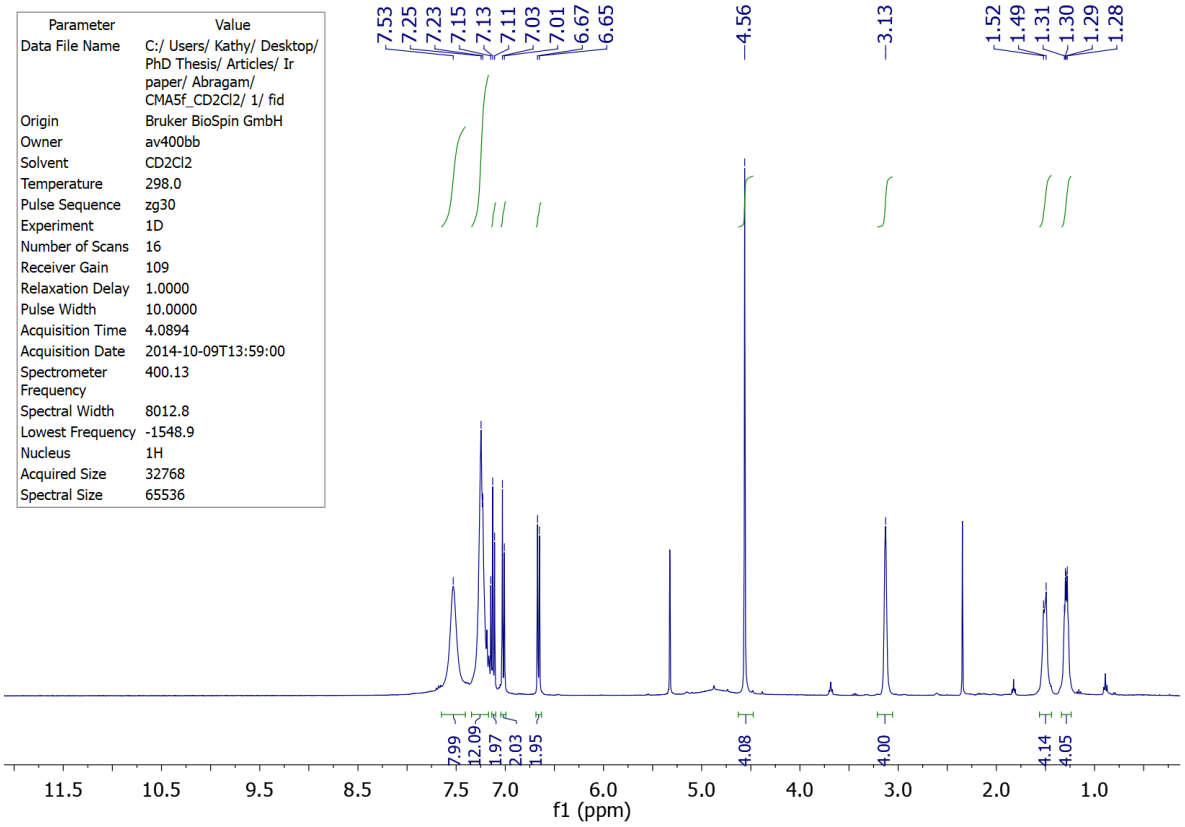
Lowest Frequency	-1548.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



^{31}P{^{1}H} Spectrum of Compound 8a

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Owner	av400bb
Solvent	CD2Cl2
Temperature	300.0
Pulse Sequence	zgpg30
Experiment	1D
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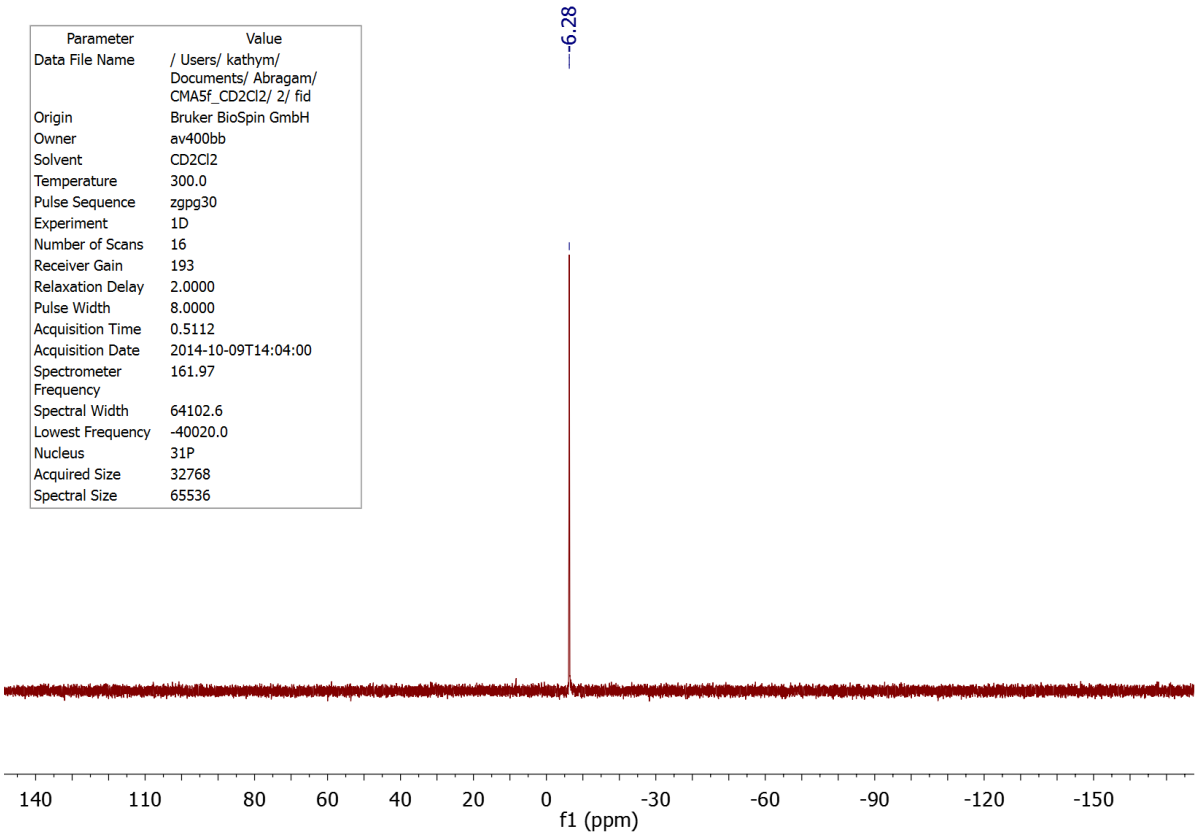
Acquired Size	32768
Spectral Size	65536



$^{13}C\{^{1}H\}$ Spectrum of Compound 8a

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Solvent	CD2Cl2
Temperature	300.0
Pulse Sequence	zgpg30
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Pulse Width	10.0000
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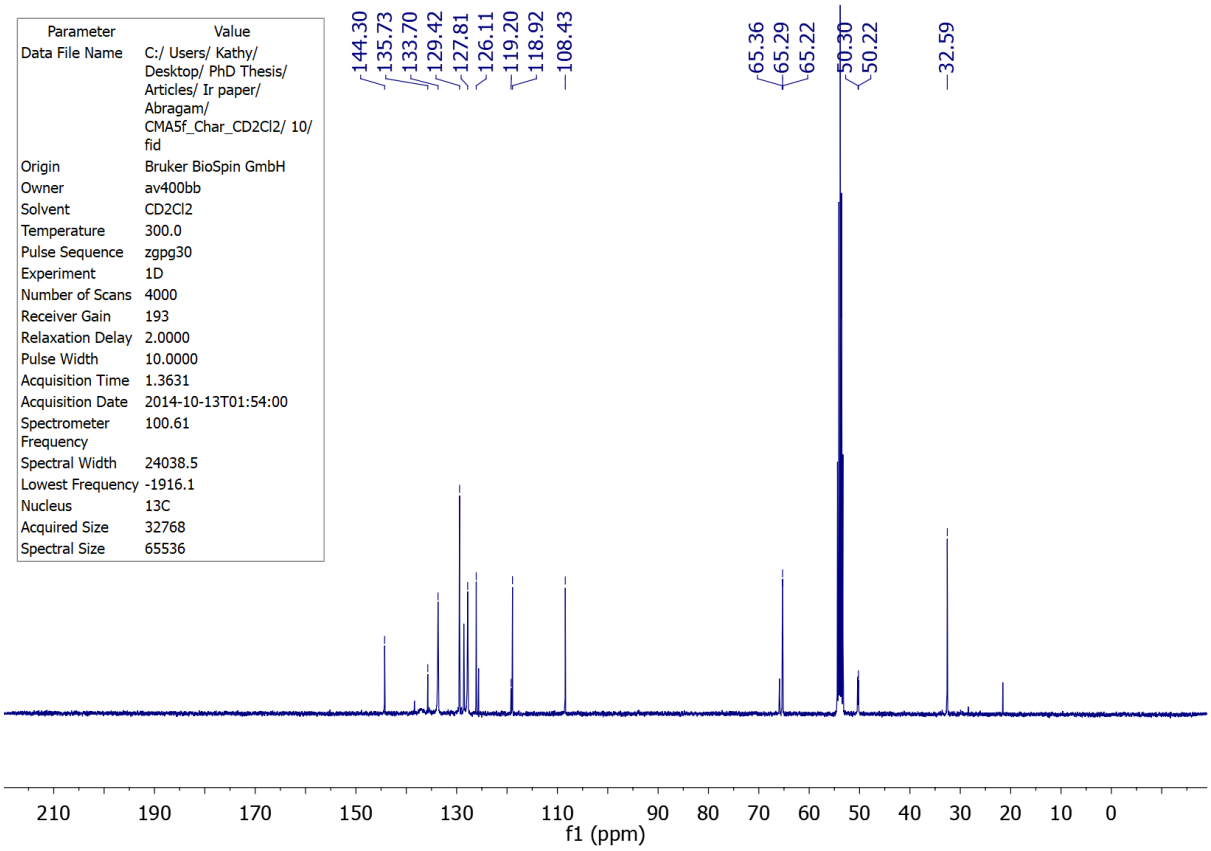
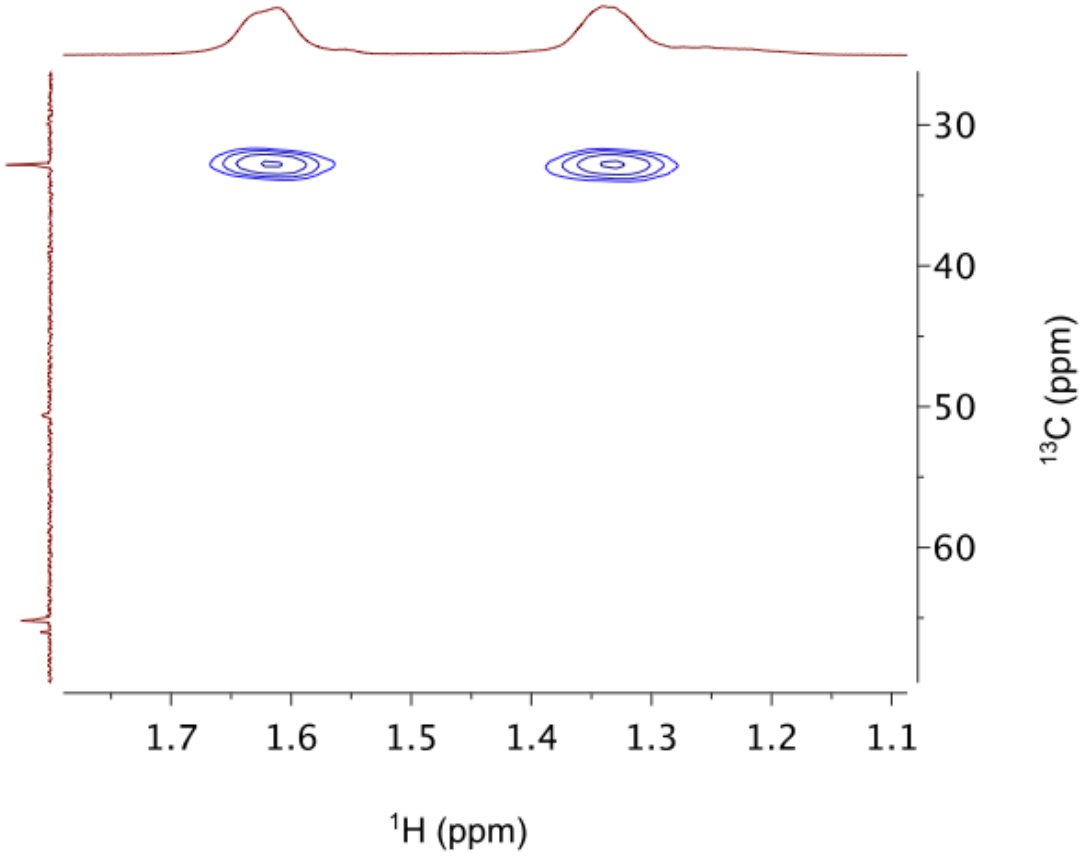
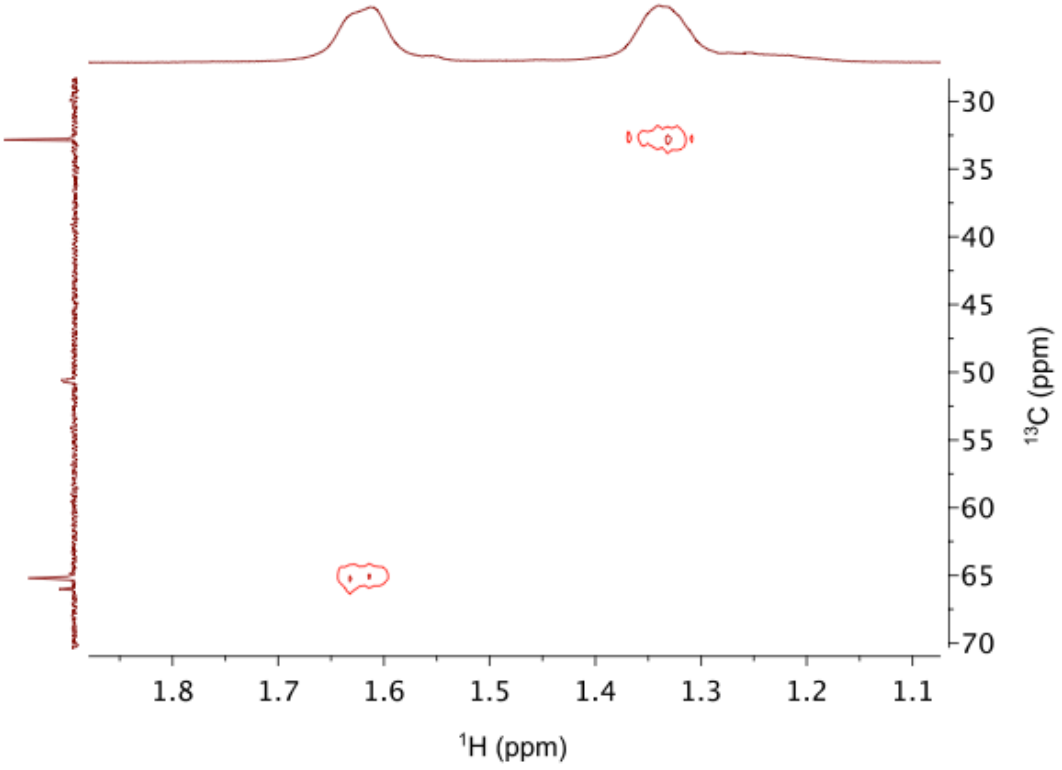
Spectral Size	65536



^{1}H(400 MHz)-^{13}C{100 MHz) HSQC and HMBC spectra of (8a) in the COD methylene region.





$[IrH\{CH(NCH_2PPh_2)_2C_{10}H_6\}(\eta^4\text{-}C_8H_{12})][BAr_F]$ [9a][BAr_F]

^{1}H NMR Spectrum of Compound [9a][BAr_F]

Parameter	Value
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Owner	av400bb
Solvent	CD2Cl2
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	31
Relaxation Delay	1.0000
Pulse Width	10.0000
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Spectrometer Frequency	400.13
Spectral Width	81521.7
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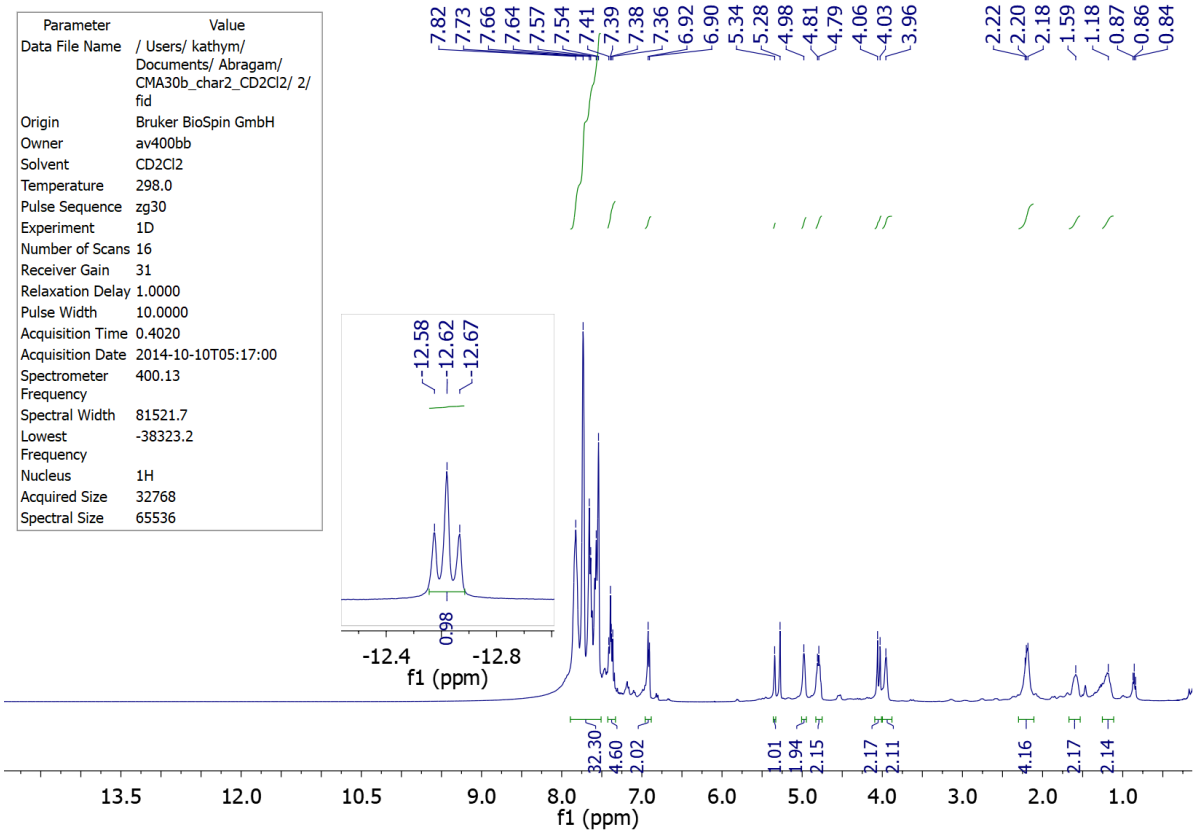
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



^{31}P{^{1}H} Spectrum of Compound [9a][BAr_F]

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Owner	av400bb
Solvent	CD2Cl2
Temperature	300.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	16
Receiver Gain	193
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	0.5112
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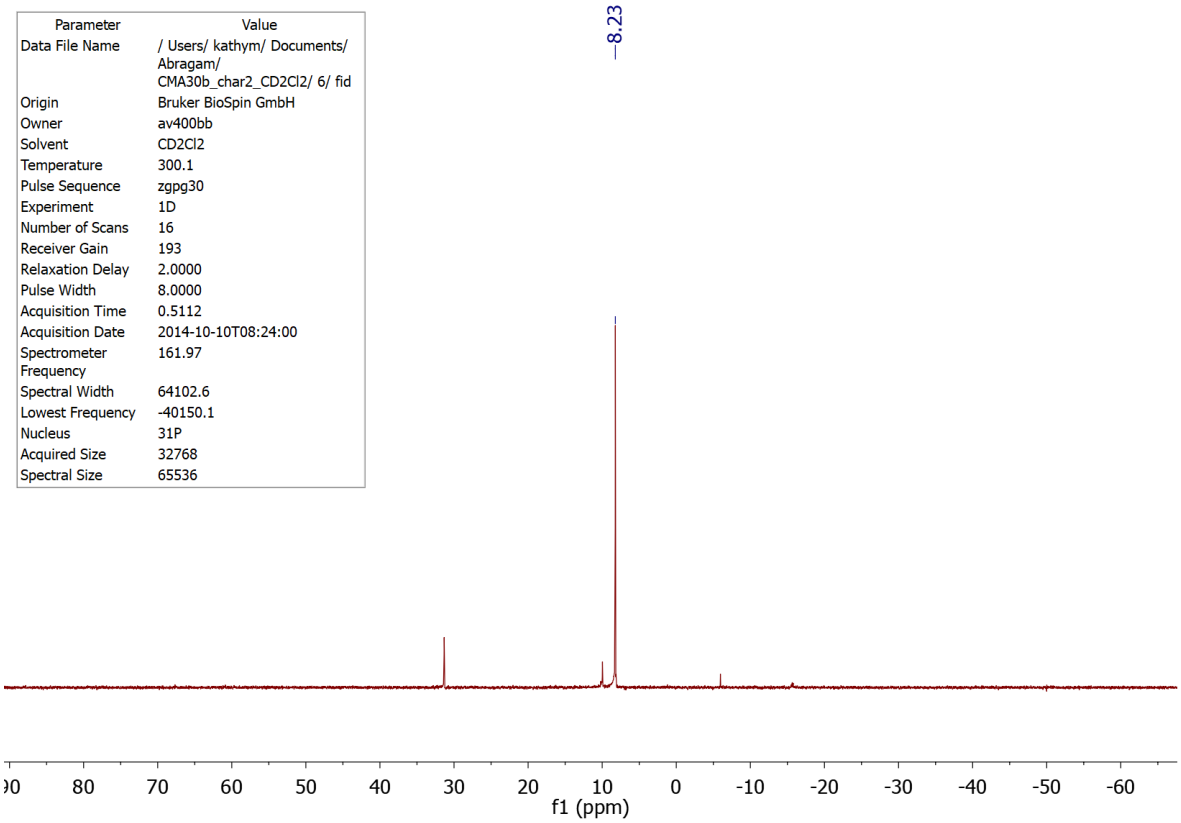
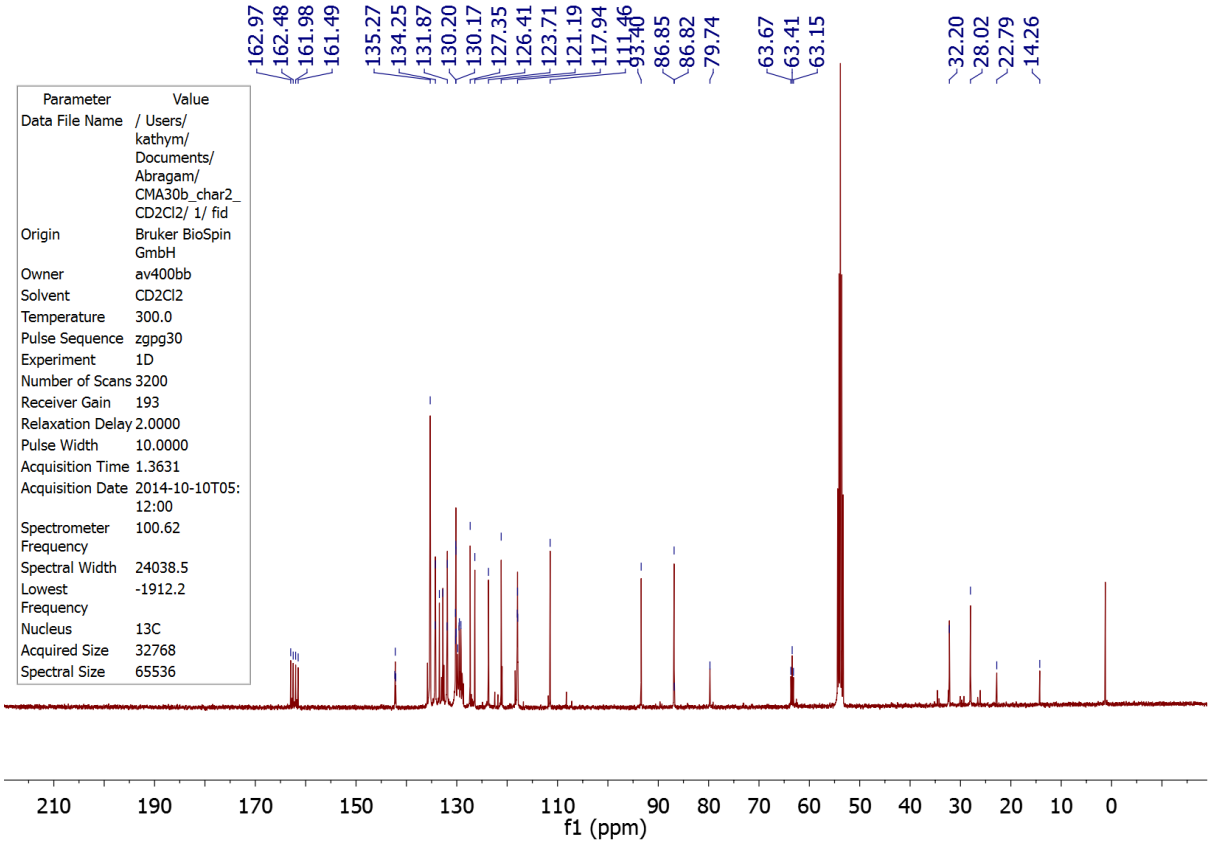
Spectrometer Frequency	161.97
Spectral Width	64102.6
Lowest Frequency	-40150.1
Nucleus	31P
Acquired Size	32768
Spectral Size	65536

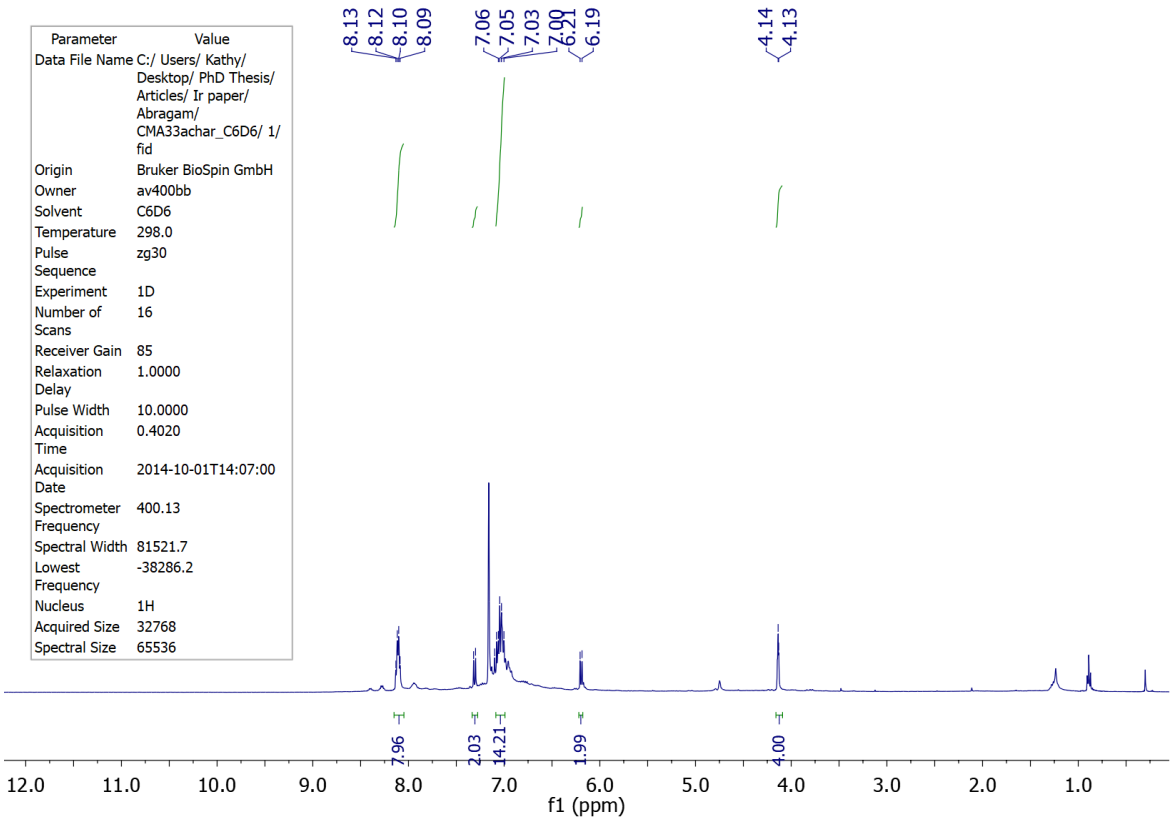


$^{13}C\{^{1}H\}$ Spectrum of Compound [9a][BAr_F]



$[IrCl\{C(NCH_2PPh_2)_2C_{10}H_6\}]$ (10a)

^1H NMR Spectrum of Compound 10a



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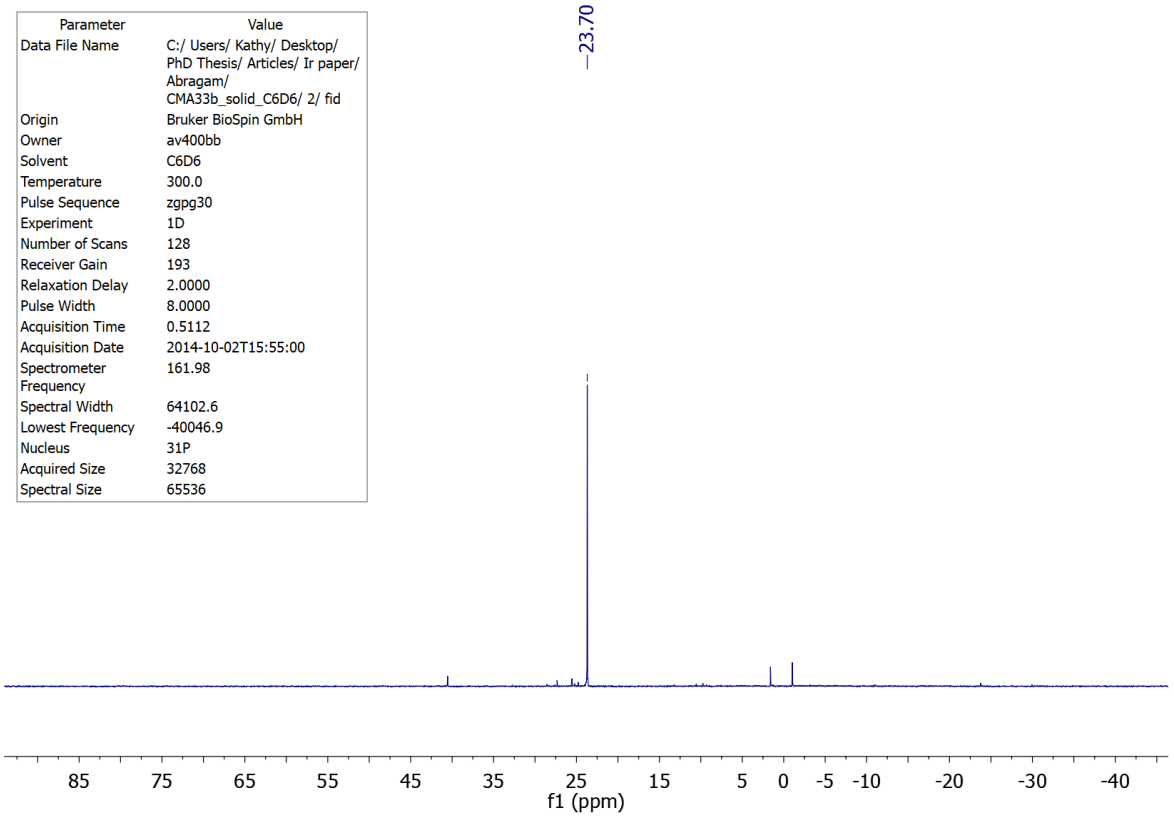
Solvent	C6D6
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	85
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	0.4020
Acquisition Date	2014-10-01T14:07:00
Spectrometer Frequency	400.13
Spectral Width	81521.7
Lowest Frequency	-38286.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

$^{31}P\{^1H\}$ Spectrum of Compound 10a



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Owner	av400bb
Solvent	C6D6
Temperature	300.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	193
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	0.5112
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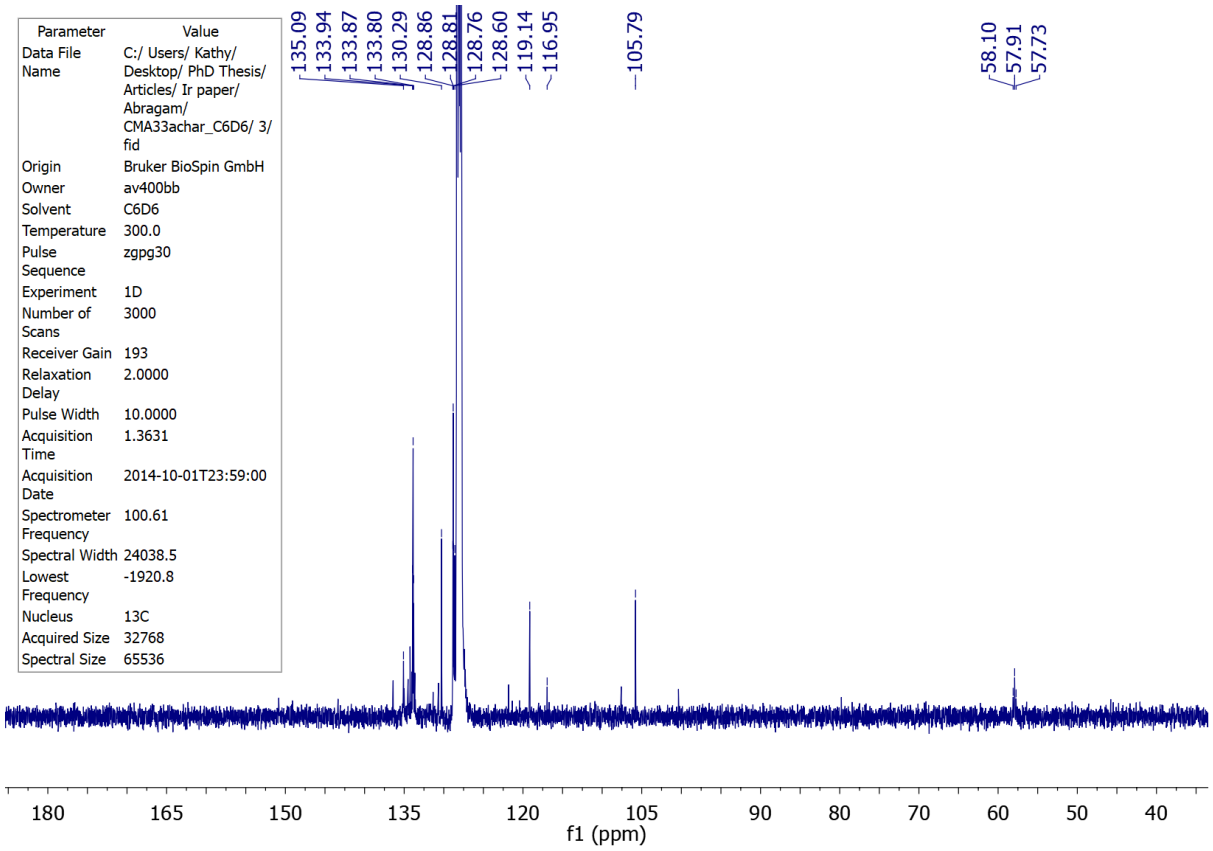
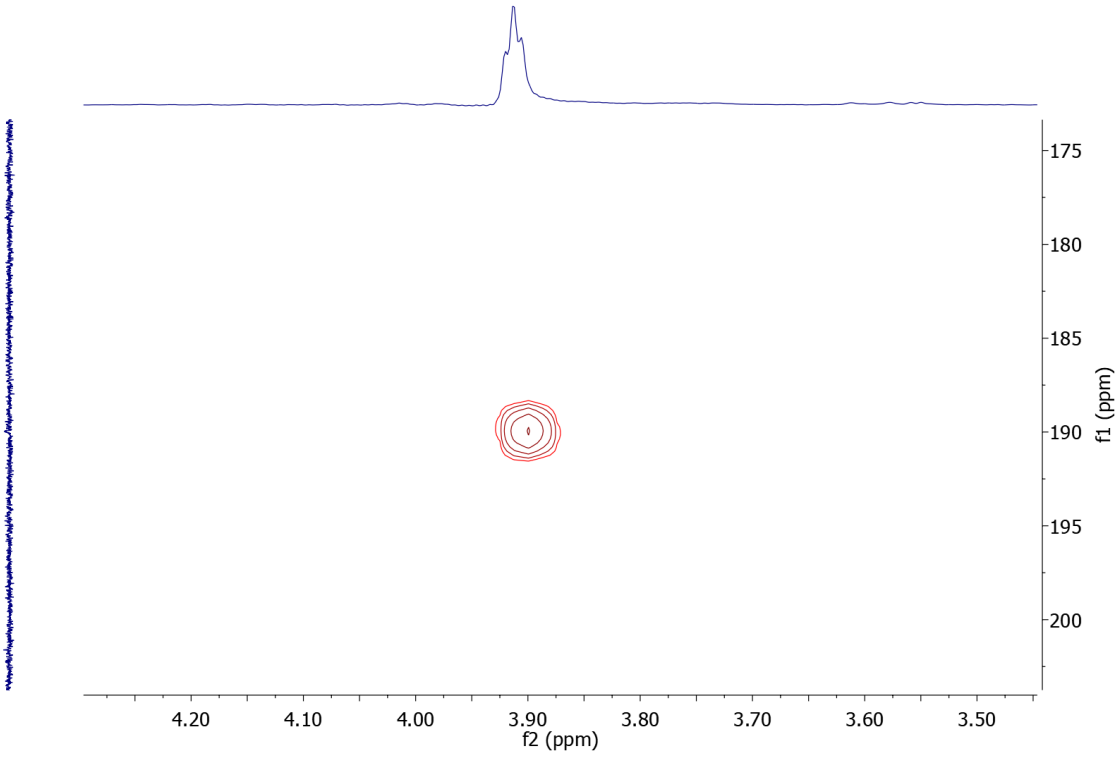
Spectrometer Frequency	161.98
Spectral Width	64102.6
Lowest Frequency	-40046.9
Nucleus	31P
Acquired Size	32768
Spectral Size	65536

$^{13}C\{^{1}H\}$ Spectrum of Compound 10a

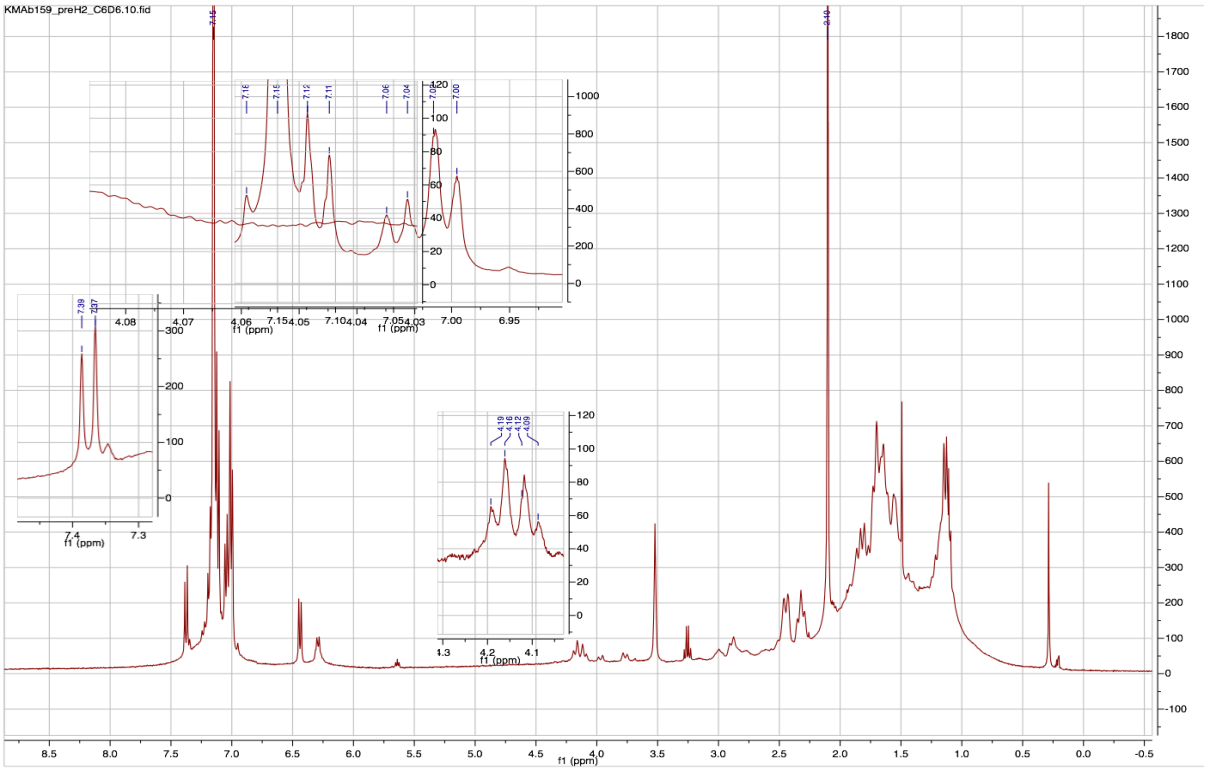


$^{1}H^{13}C$ HMBC (carbene resonance)



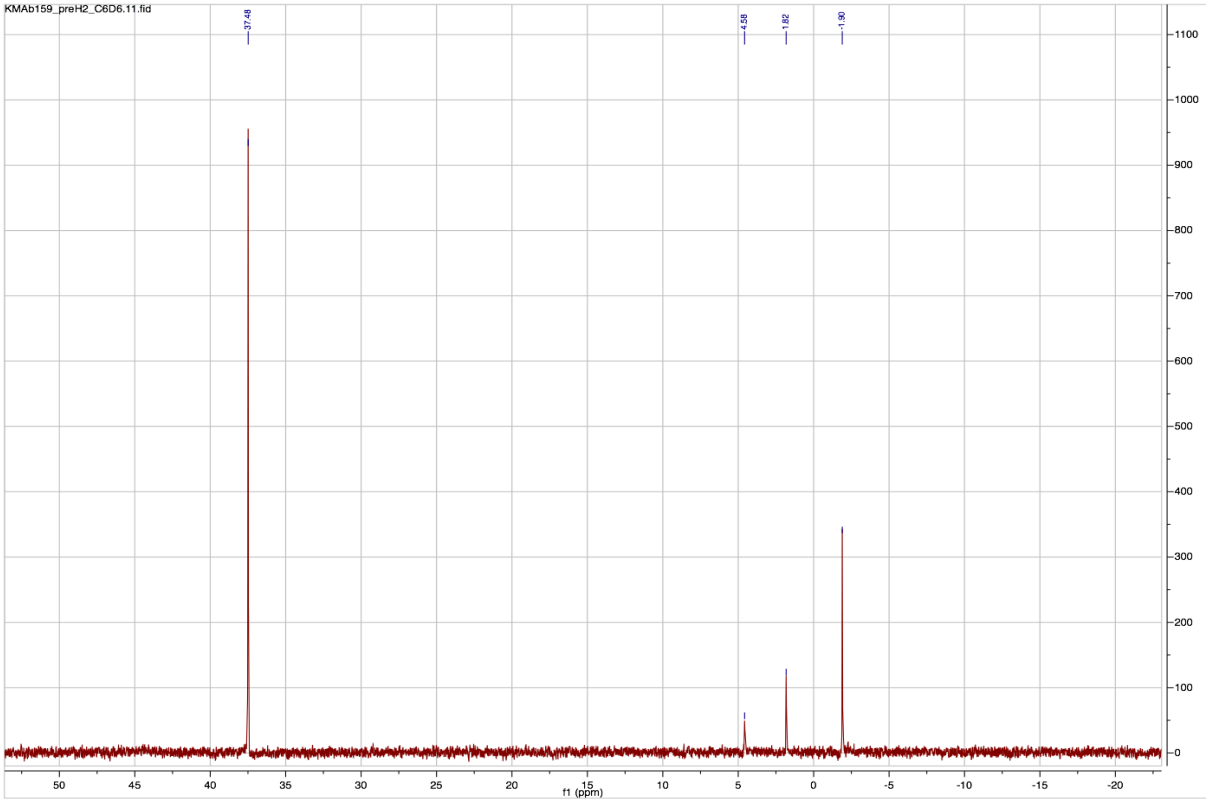
[IrCl{C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}] (10a)

^{1}H NMR Spectrum of Compound 10b



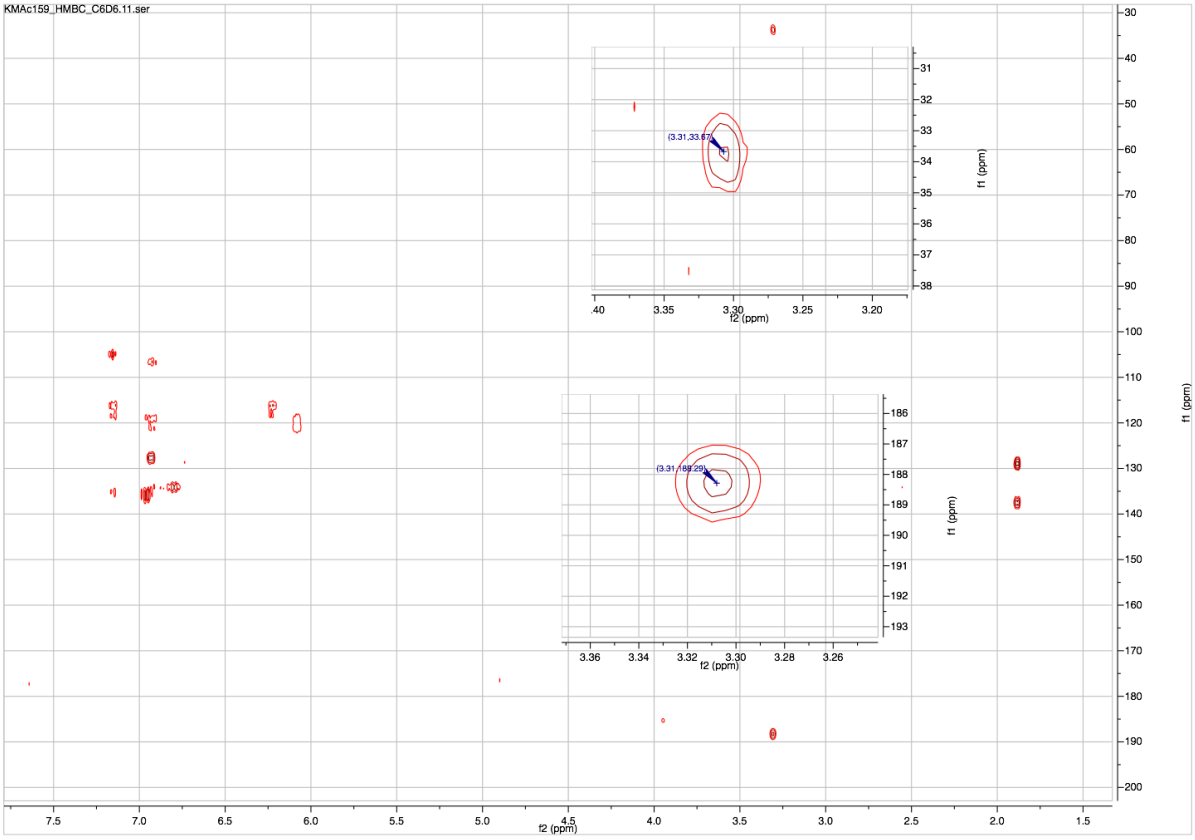
^{31}P{^{1}H} NMR Spectrum of Compound 10b

Peaks at δ_P = 4.58, 1.82 and –1.90 correspond to minor but inseparable impurities.



^{13}C-^{1}H HMBC NMR Spectrum of Compound 10b

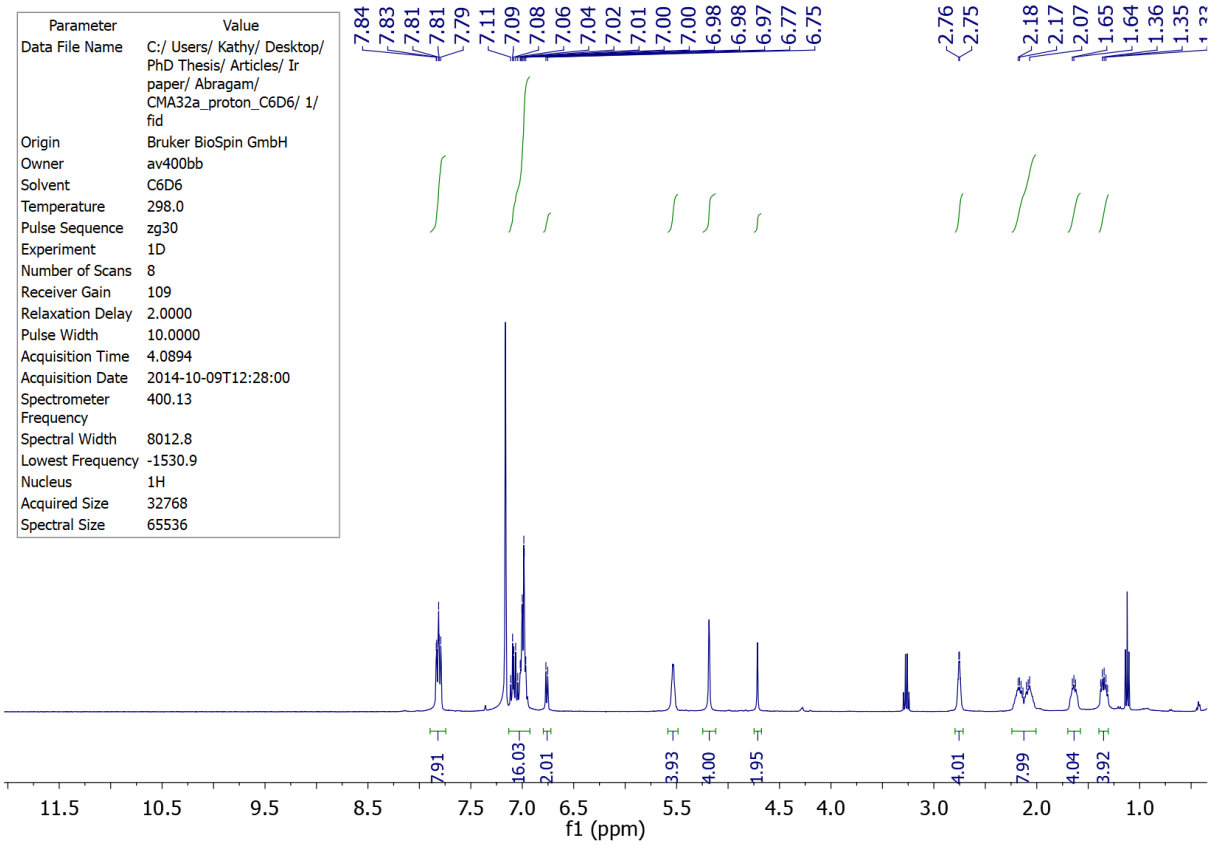
PCH_2N (δ_H = 3.31) Correlation to NHC Carbene (δ_C = 199.3)



$[Ir_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_2(\eta\text{-}C_8H_{12})_2]$ (11a)

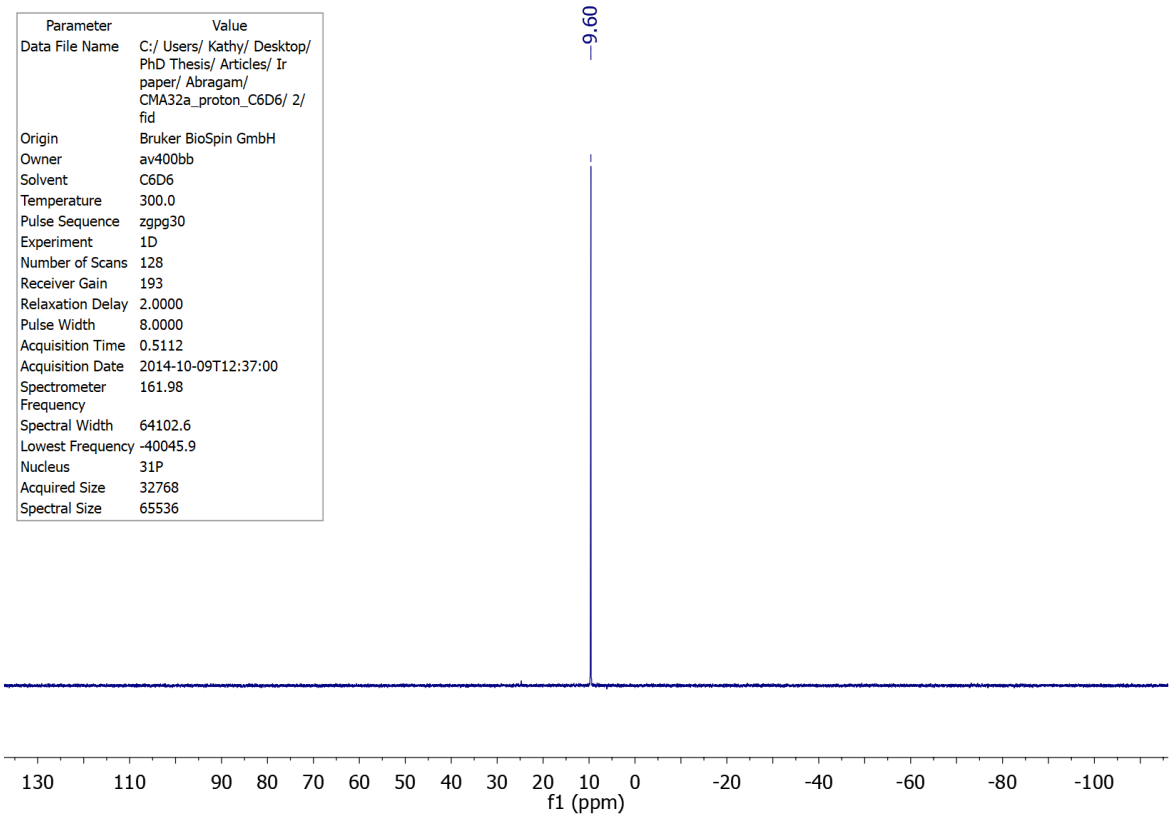
^{1}H NMR Spectrum of Compound 11a

Parameter	Value
Data File Name	C:/ Users/ Kathy/ Desktop/ PhD Thesis/ Articles/ Ir paper/ Abragam/ CMA32a_proton_C6D6/ 1/ fid
Origin	Bruker BioSpin GmbH
Owner	av400bb
Solvent	C6D6
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	8
Receiver Gain	109
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	4.0894
Acquisition Date	2014-10-09T12:28:00
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1530.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

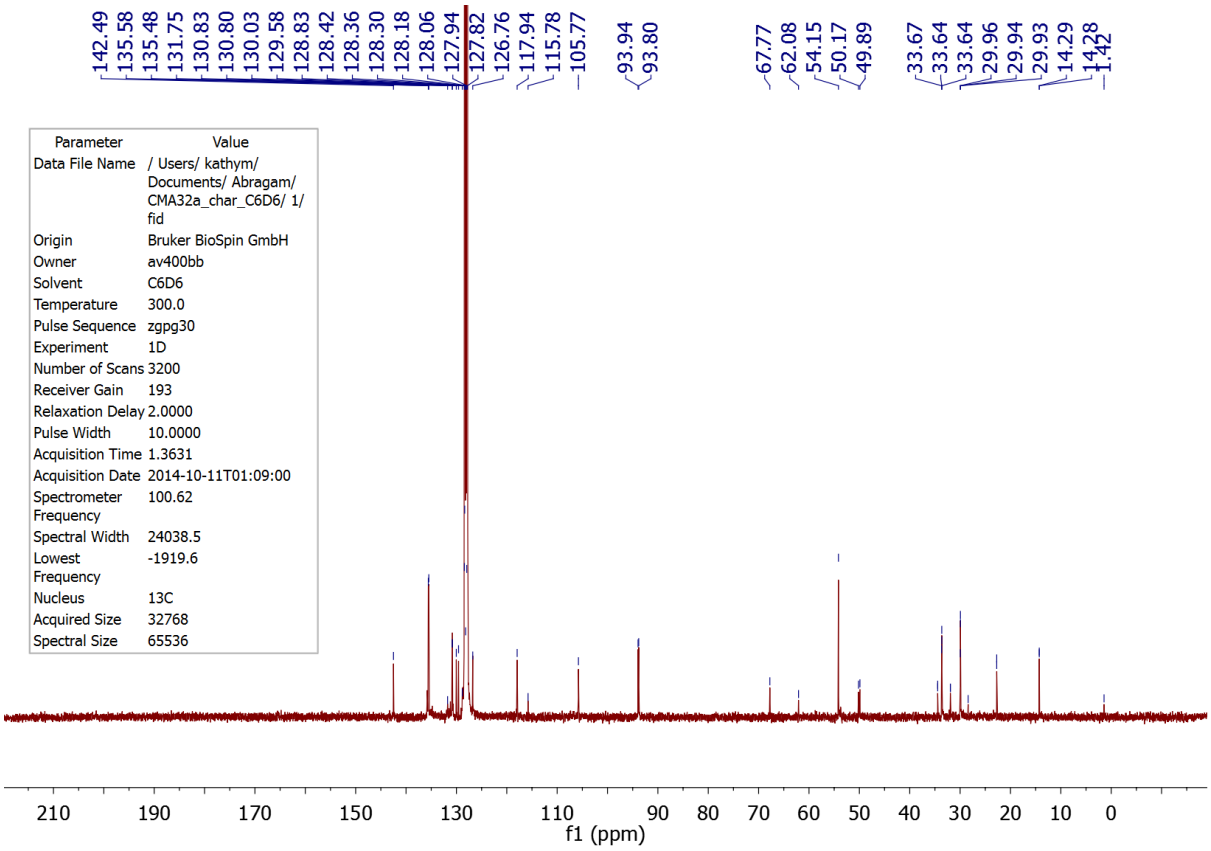


^{31}P{^{1}H} Spectrum of Compound 11a

Parameter	Value
Data File Name	C:/ Users/ Kathy/ Desktop/ PhD Thesis/ Articles/ Ir paper/ Abragam/ CMA32a_proton_C6D6/ 2/ fid
Origin	Bruker BioSpin GmbH
Owner	av400bb
Solvent	C6D6
Temperature	300.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	193
Relaxation Delay	2.0000
Pulse Width	8.0000
Acquisition Time	0.5112
Acquisition Date	2014-10-09T12:37:00
Spectrometer Frequency	161.98
Spectral Width	64102.6
Lowest Frequency	-40045.9
Nucleus	31P
Acquired Size	32768
Spectral Size	65536

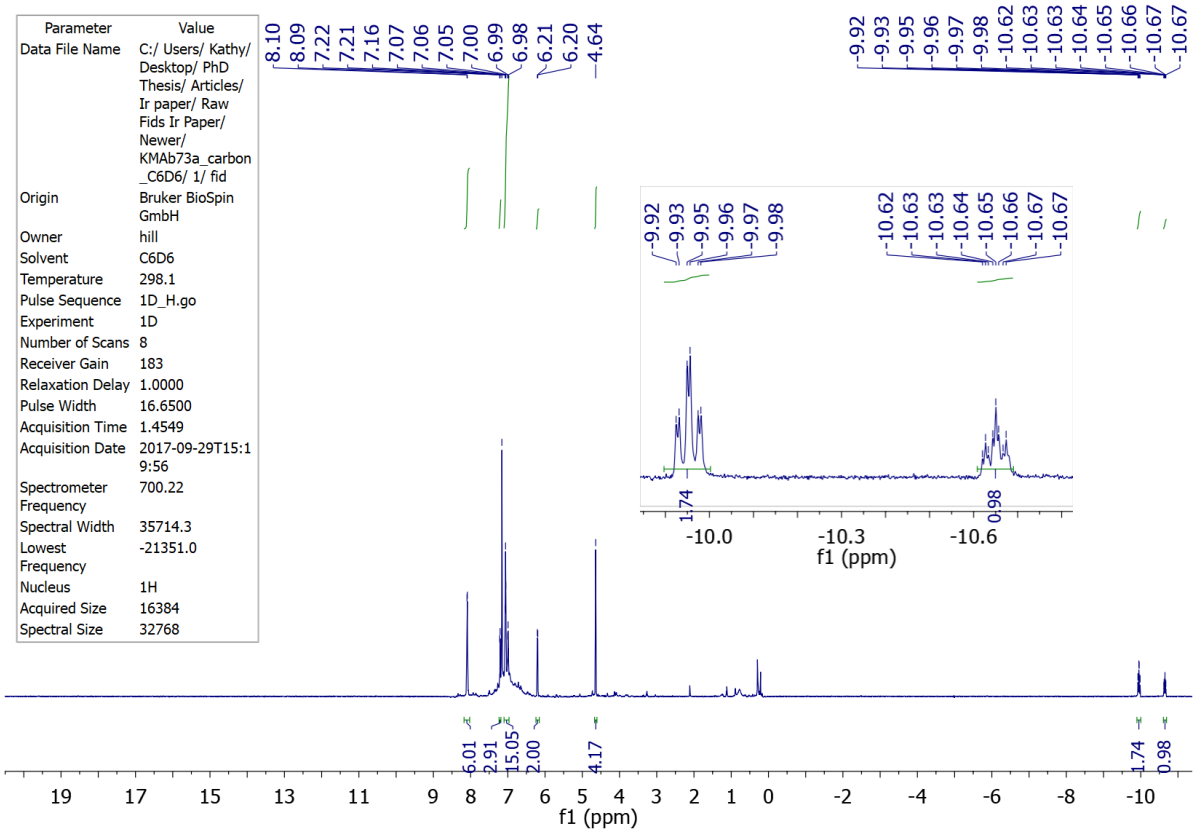


$^{13}C\{^{1}H\}$ Spectrum of Compound 11a

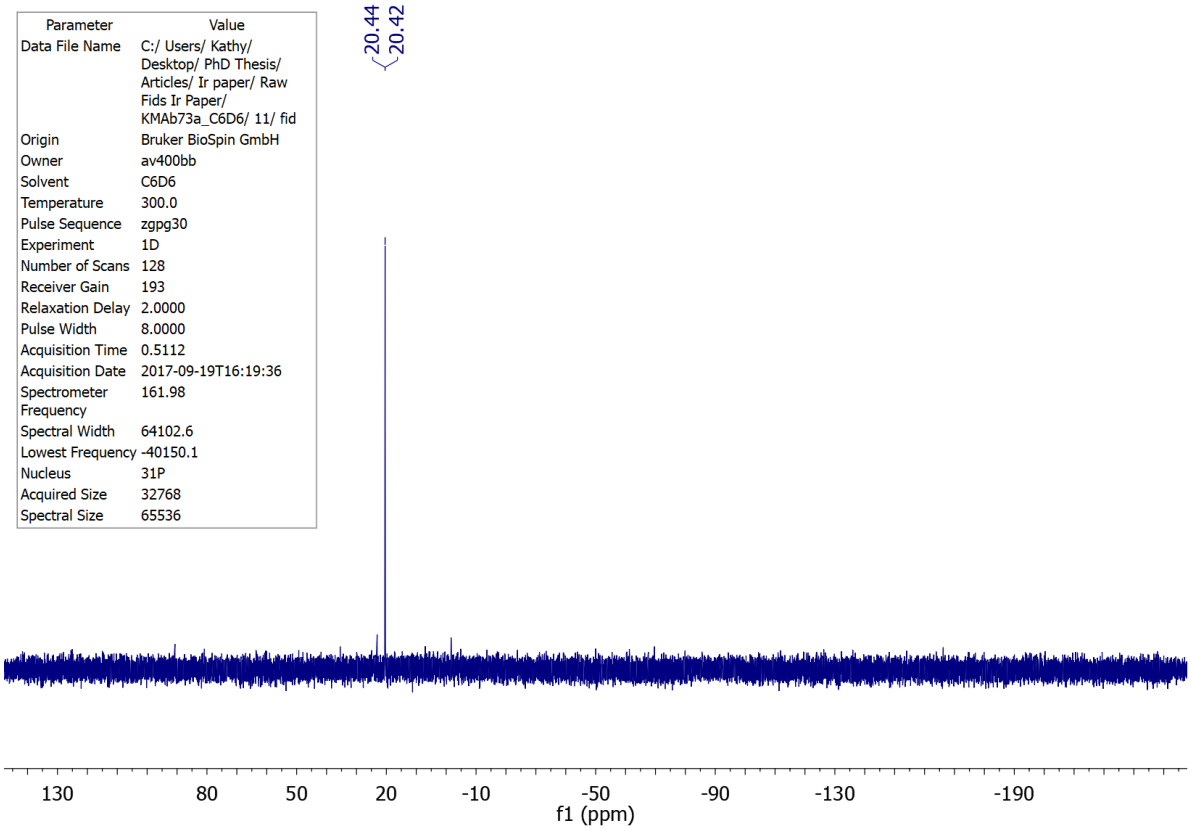


$[IrH_3\{C(NCH_2PPh_2)_2C_{10}H_6\}]$ (14a)

^{1}H NMR Spectrum of Compound 14a

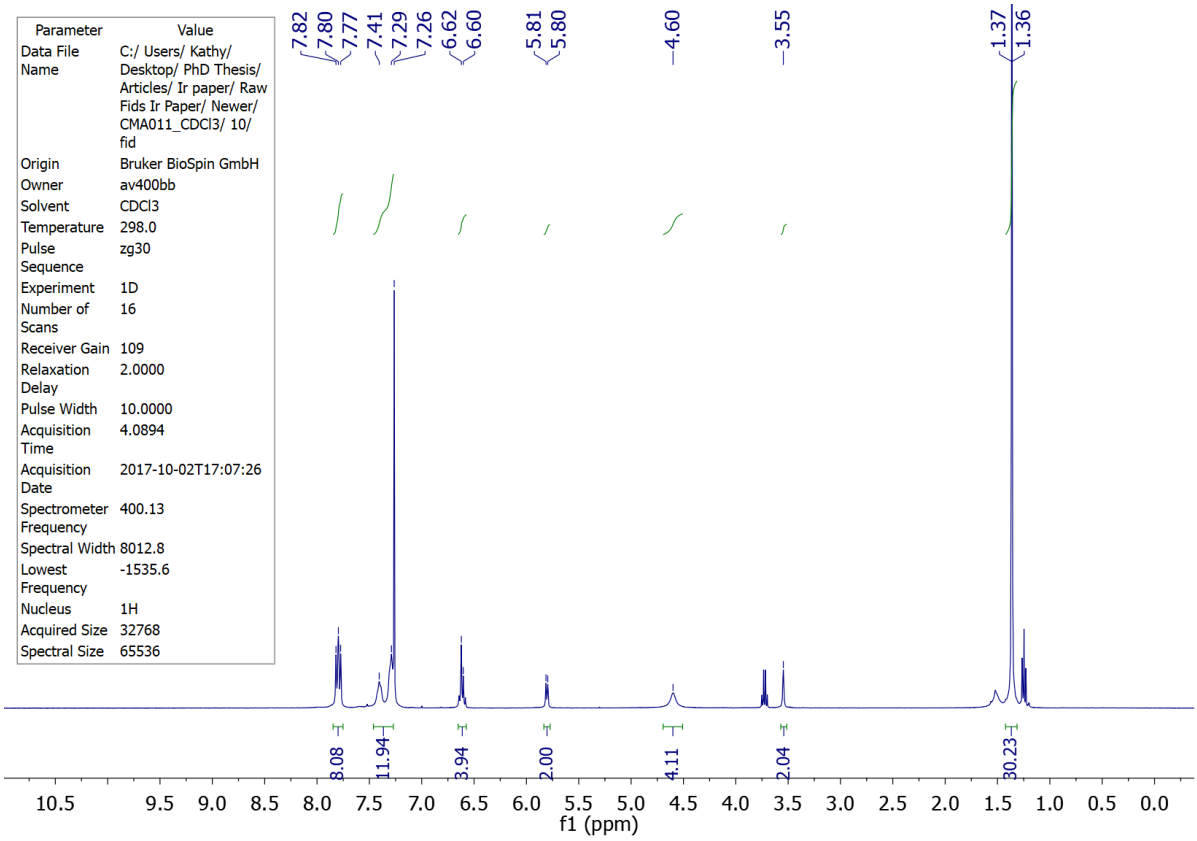


^{31}P{^{1}H} NMR Spectrum of Compound 14a

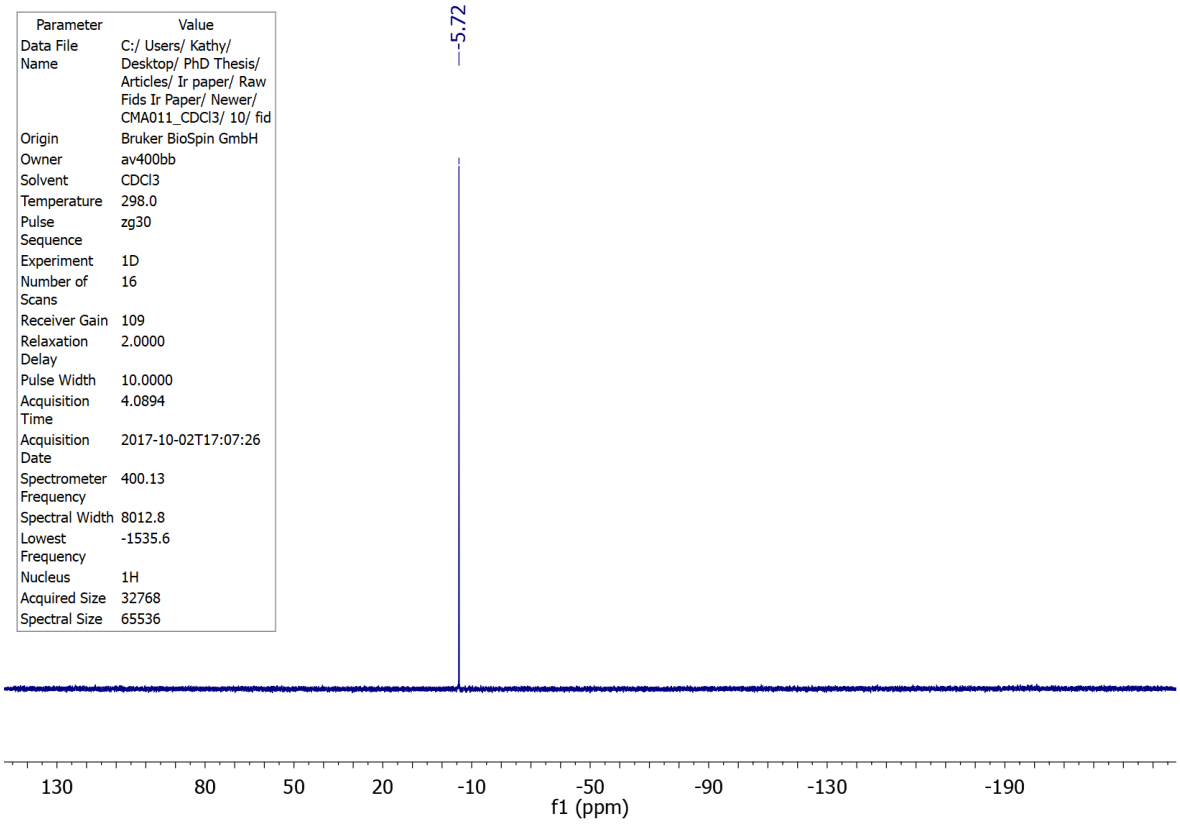


$[Ir_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_2(\eta\text{-}C_5Me_5)_2]$ (12a)

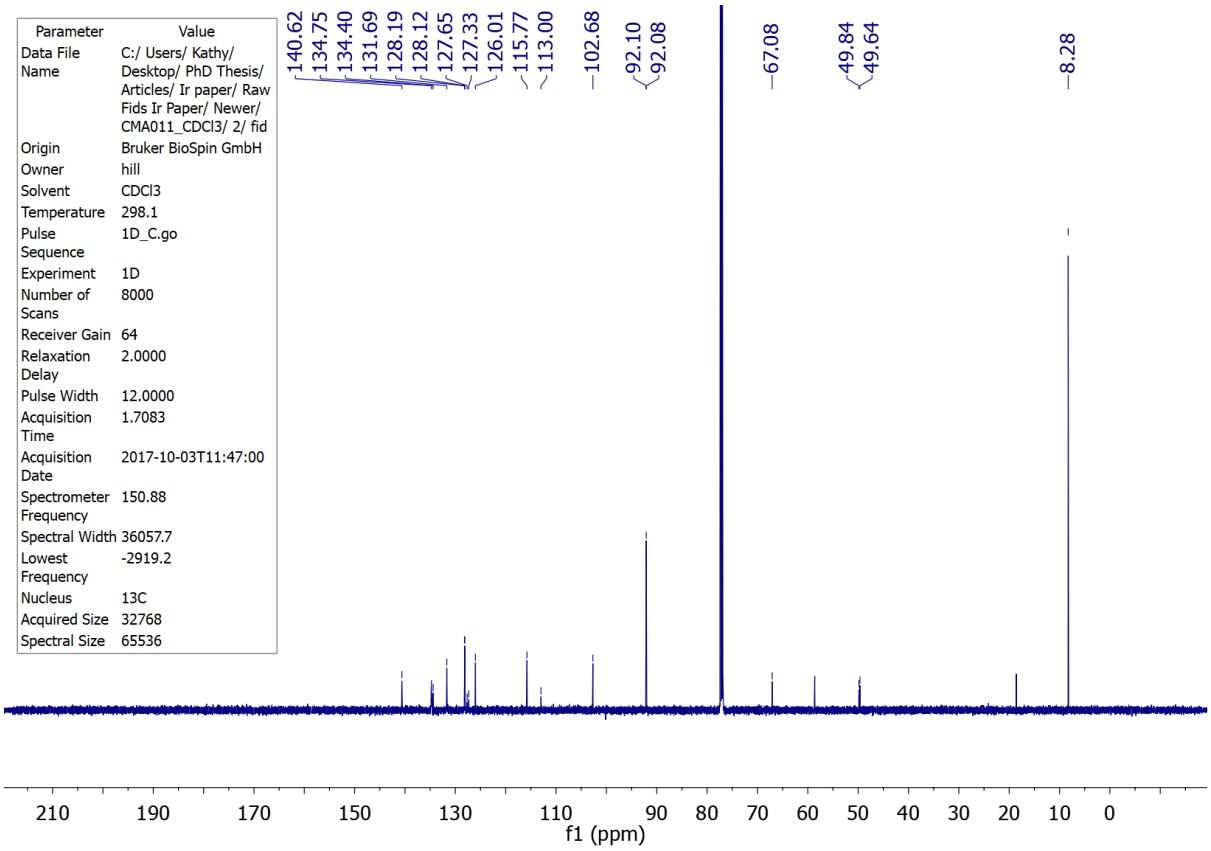
^1H NMR Spectrum of Compound 12a



$^{31}P\{^1H\}$ NMR Spectrum of Compound 12a

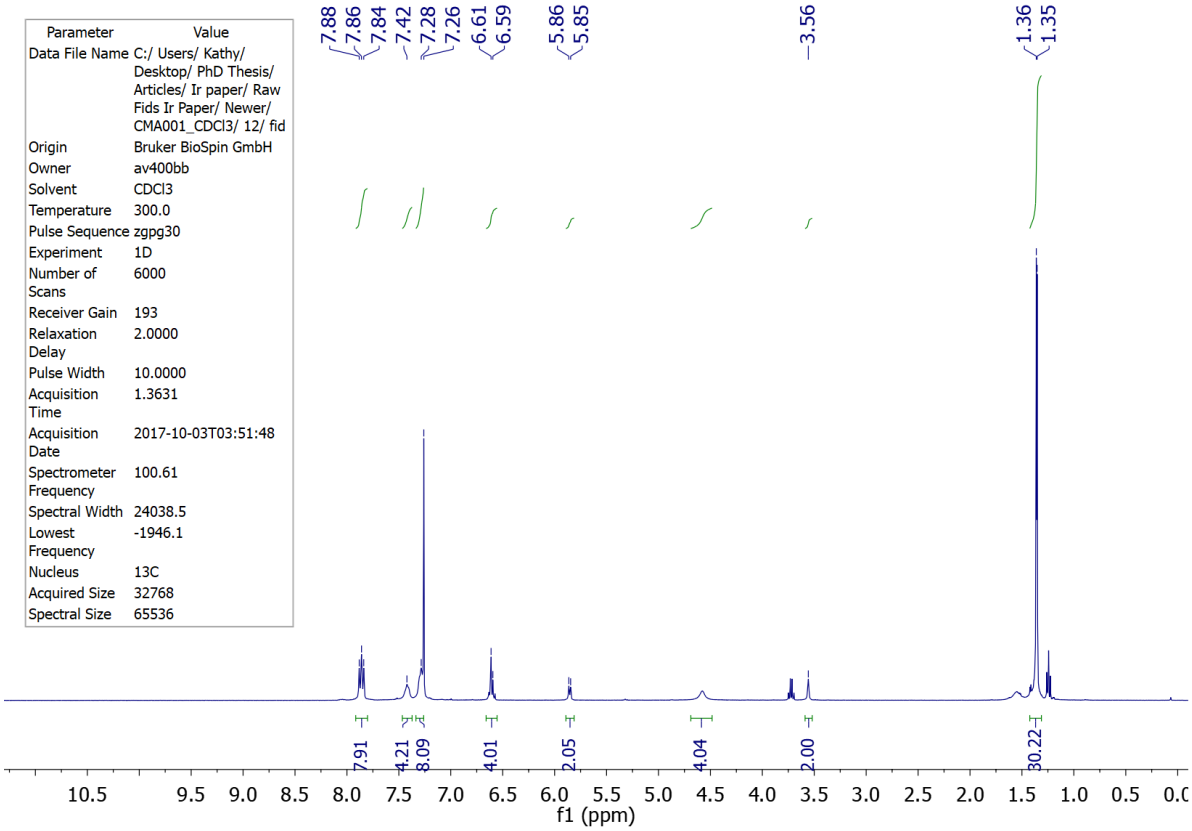


$^{13}C\{^{1}H\}$ NMR Spectrum of Compound 12a

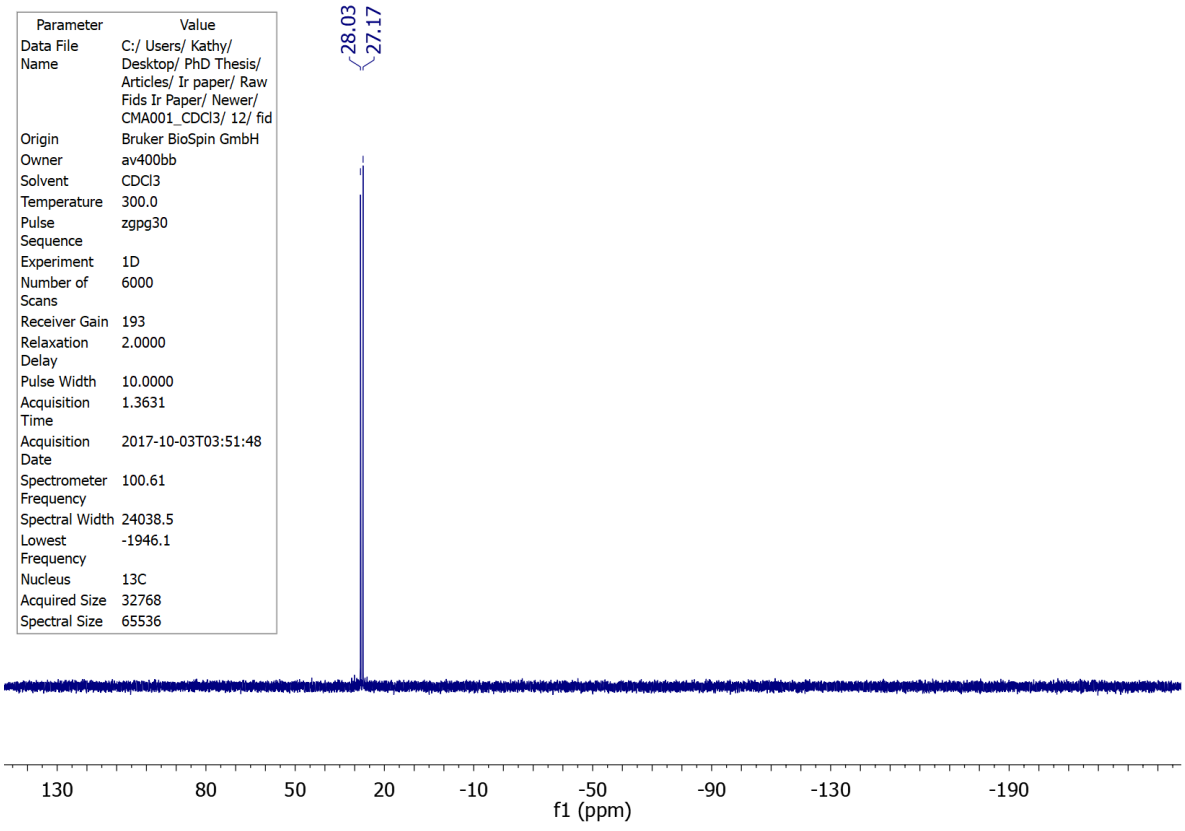


$[Rh_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_2(\eta\text{-}C_5Me_5)_2]$ (13a)

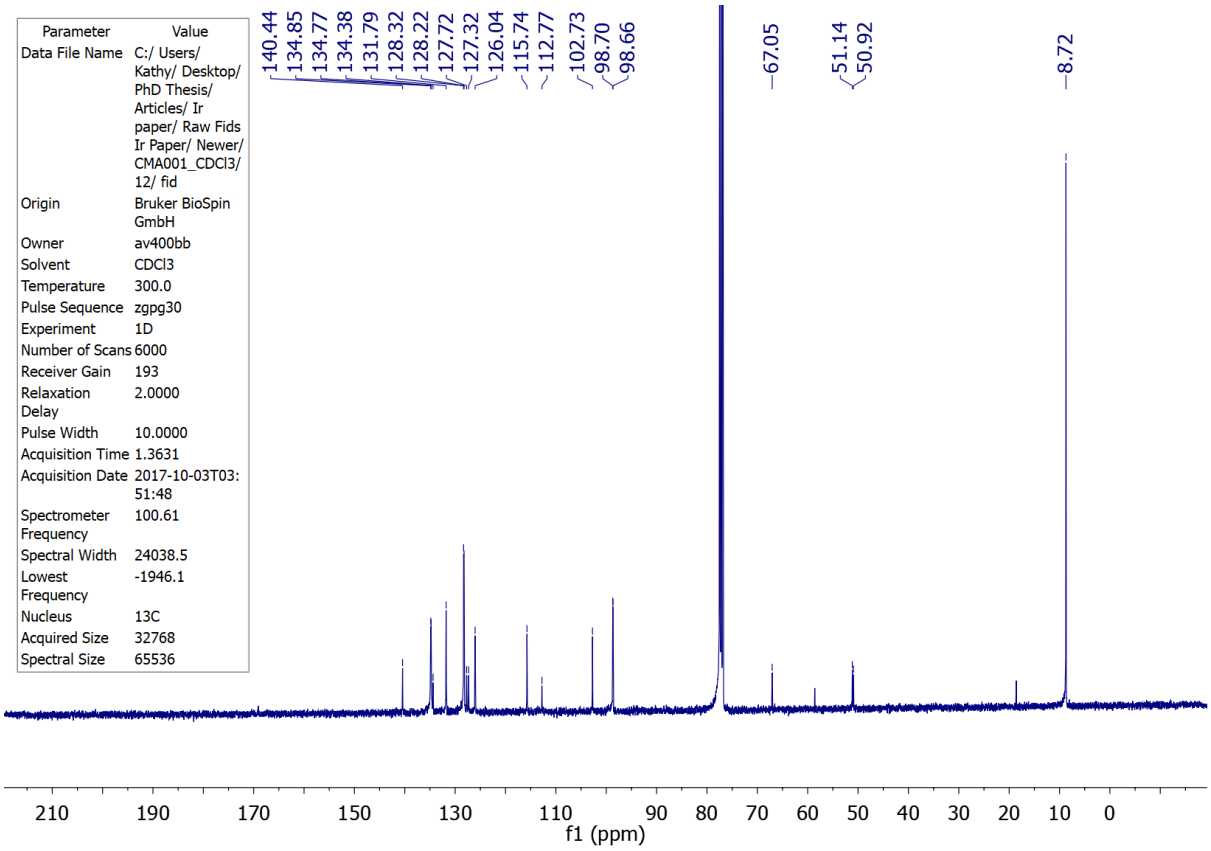
^{1}H NMR Spectrum of Compound 13a



^{31}P{^{1}H} NMR Spectrum of Compound 13a

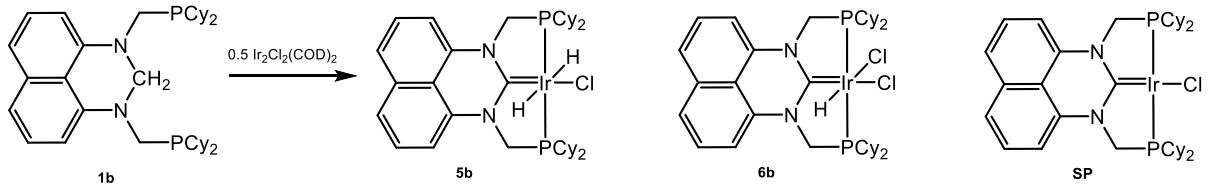


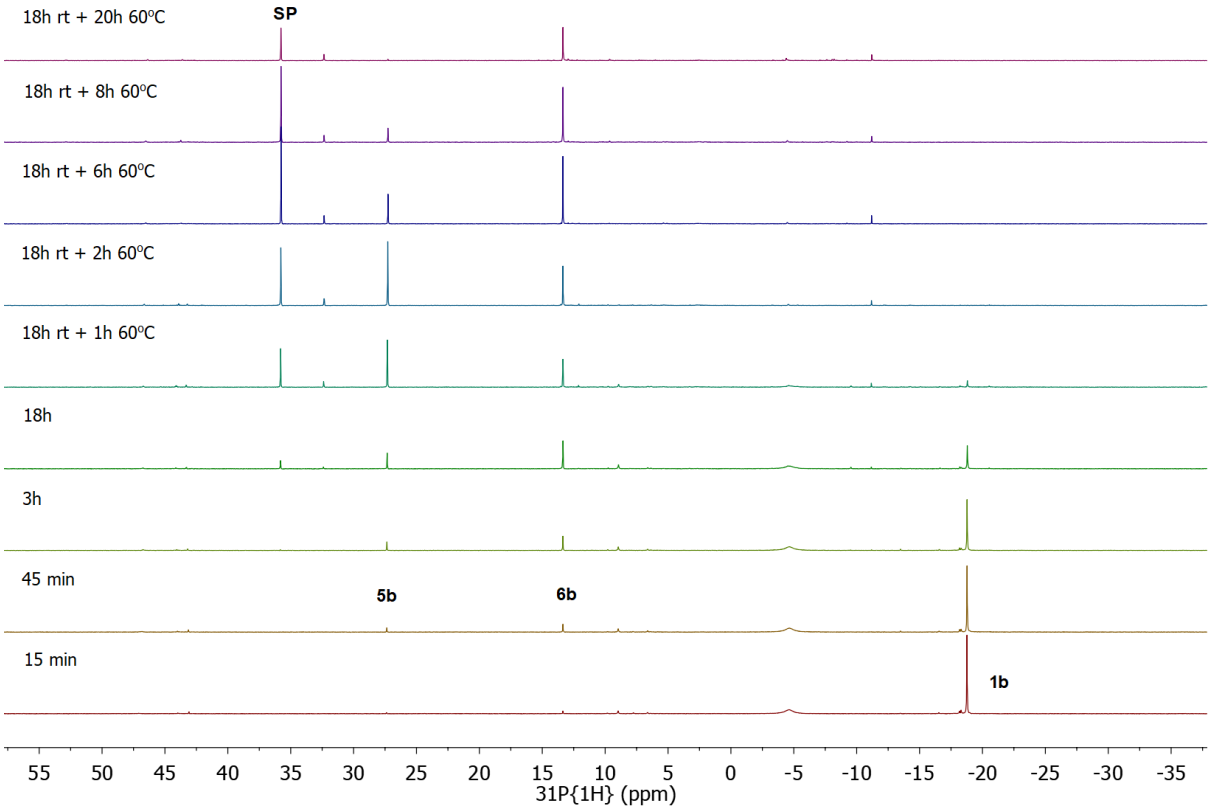
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound 13a



NMR scale reaction: Compound 1b with 0.5 $Ir_2Cl_2(COD)_2$

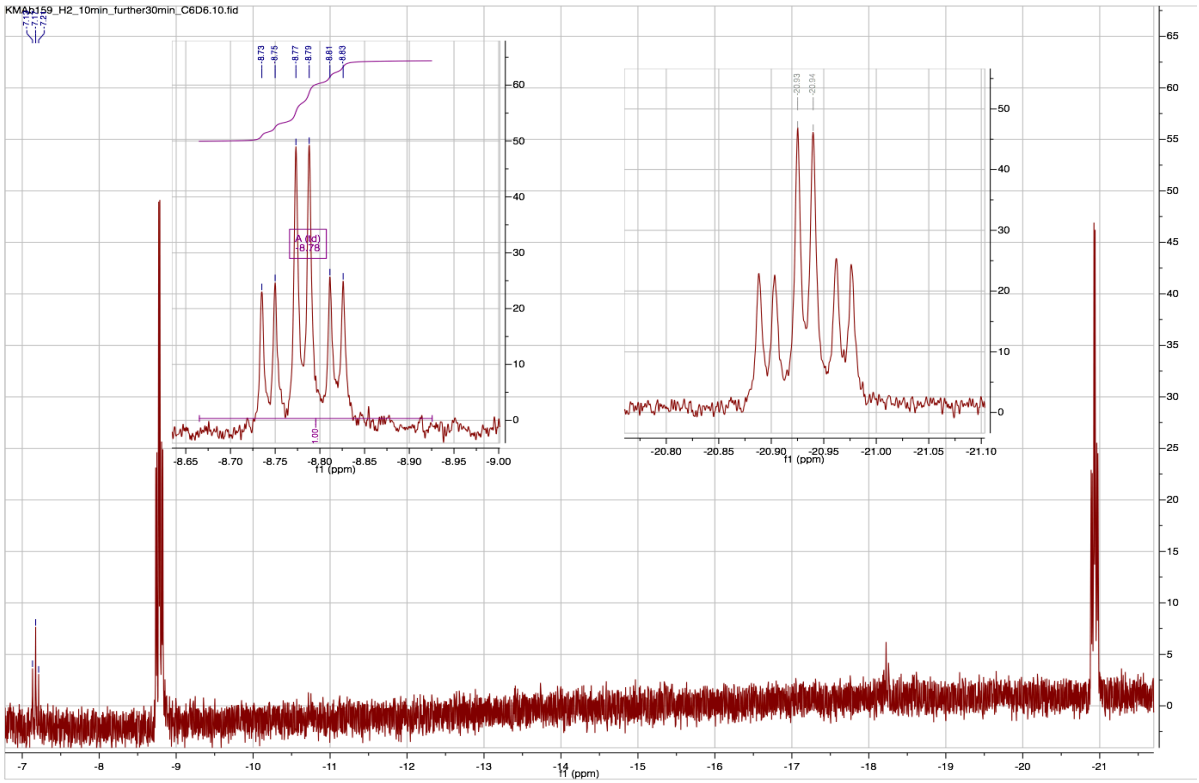
SP = 10b





NMR scale reaction: Hydrogenation of 10b to provide *cis*-5b

NB: Traces of *trans*-**5b** observed at $\delta_H = -7.17$.



Time Course ^{1}H and ^{31}P NMR Spectra for Hydrogenation of 10b to afford *cis*-5b

1 Atmosphere, $t_{0.5} \approx 8$ minutes.