

# Supporting Information

## Chiral Wide Bite Angle Diphosphine Ligands: Synthesis, Coordination Chemistry and Application in Pd-catalyzed Allylic Alkylation

Christine F. Czauderna,<sup>a,†</sup> Amanda G. Jarvis,<sup>a</sup> Frank J. L. Heutz,<sup>a</sup> David B. Cordes,<sup>a</sup> Alexandra M. Z. Slawin,<sup>a</sup> Jarl Ivar van der Vlugt,<sup>b</sup> Paul C. J. Kamer<sup>a\*</sup>

[a] EaSTCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, United Kingdom E-mail: [pcjk@st-andrews.ac.uk](mailto:pcjk@st-andrews.ac.uk)

[b] van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands

1- Compound 11F

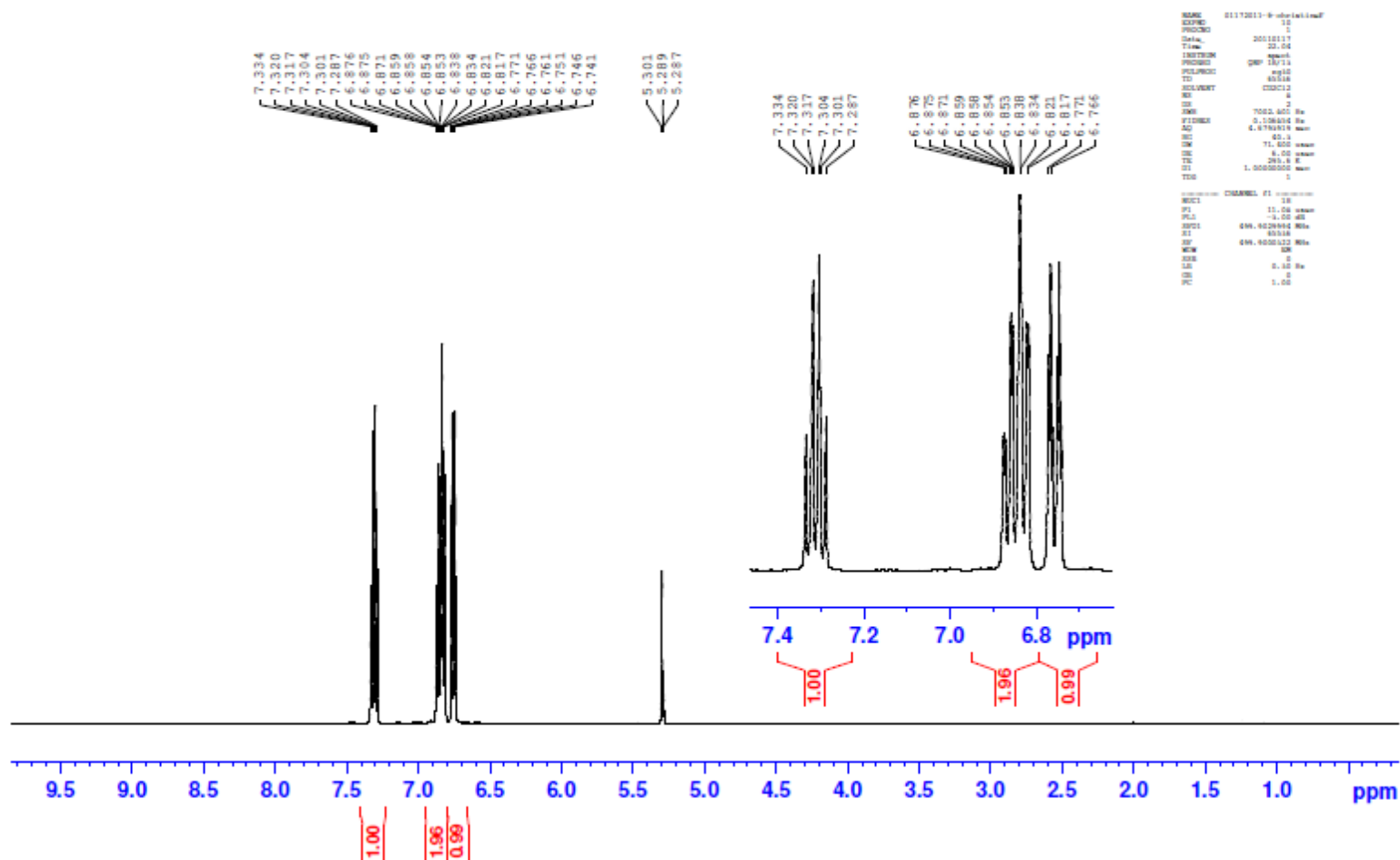
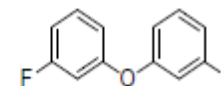
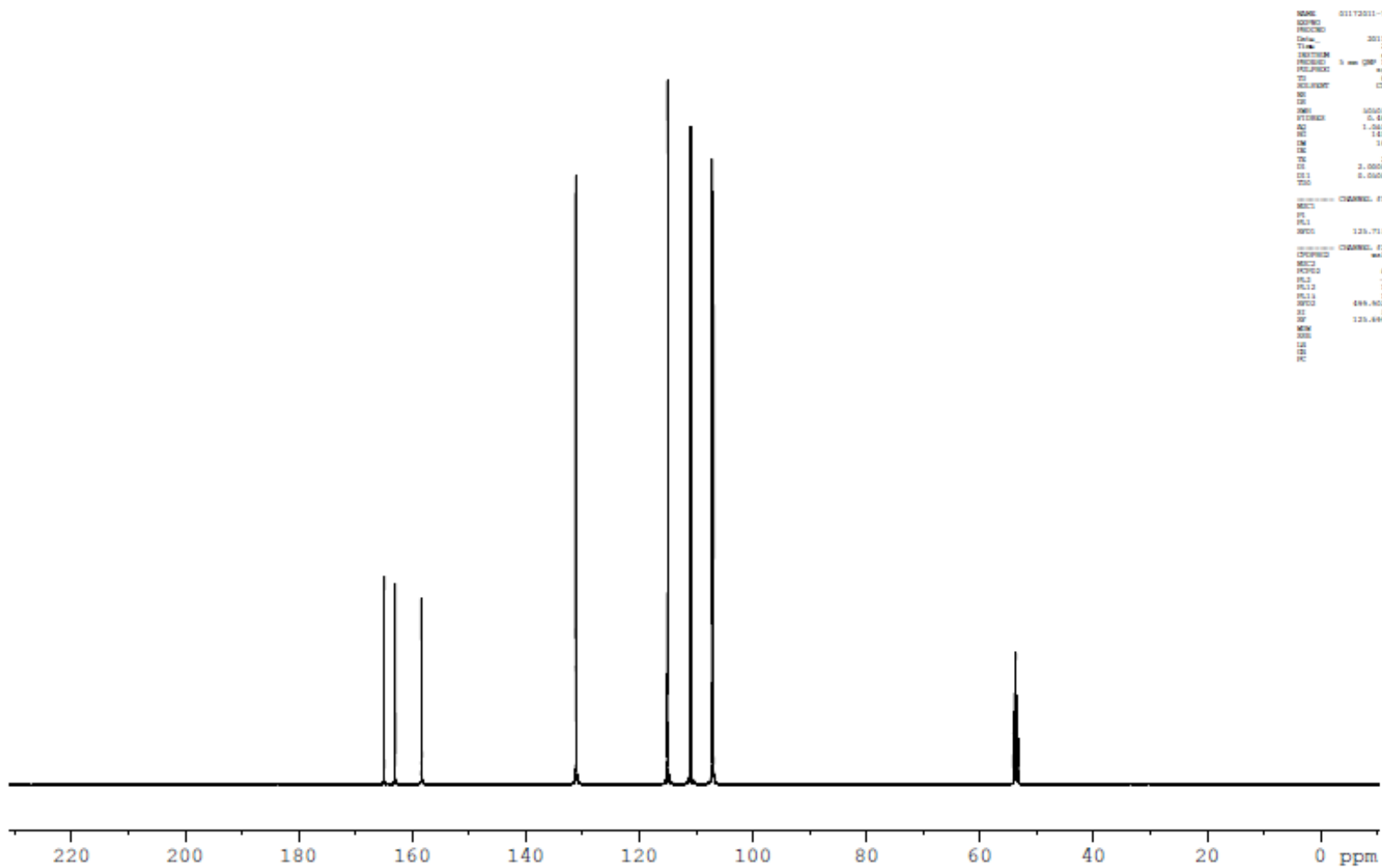
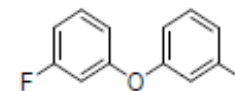


Figure S1 <sup>1</sup>H NMR spectrum of compound 11F (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)



```

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EXPNO 12
PROCNO 1
Date_ 20110117
Time 21.51
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 600
DS 4
SWH 5050.013 Hz
F2FREQ 5.42364 Hz
AQ 1.2608320 sec
RG 14368.0
DM 16.000 usec
DE 6.000 usec
TE 296.2 K
C2 2.00000000 sec
C3 0.00000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 13C
P1 6.10 usec
PL1 0.00 dB
SFO1 125.7617420 MHz
===== CHANNEL f2 =====
INSTRUM spect
NUC2 1H
PCPD2 60.00 usec
PL2 -2.00 dB
PL12 18.84 dB
SFO2 499.8023494 MHz
SI 32768
SF 125.4984647 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.60
  
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Figure S2  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 11F (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)

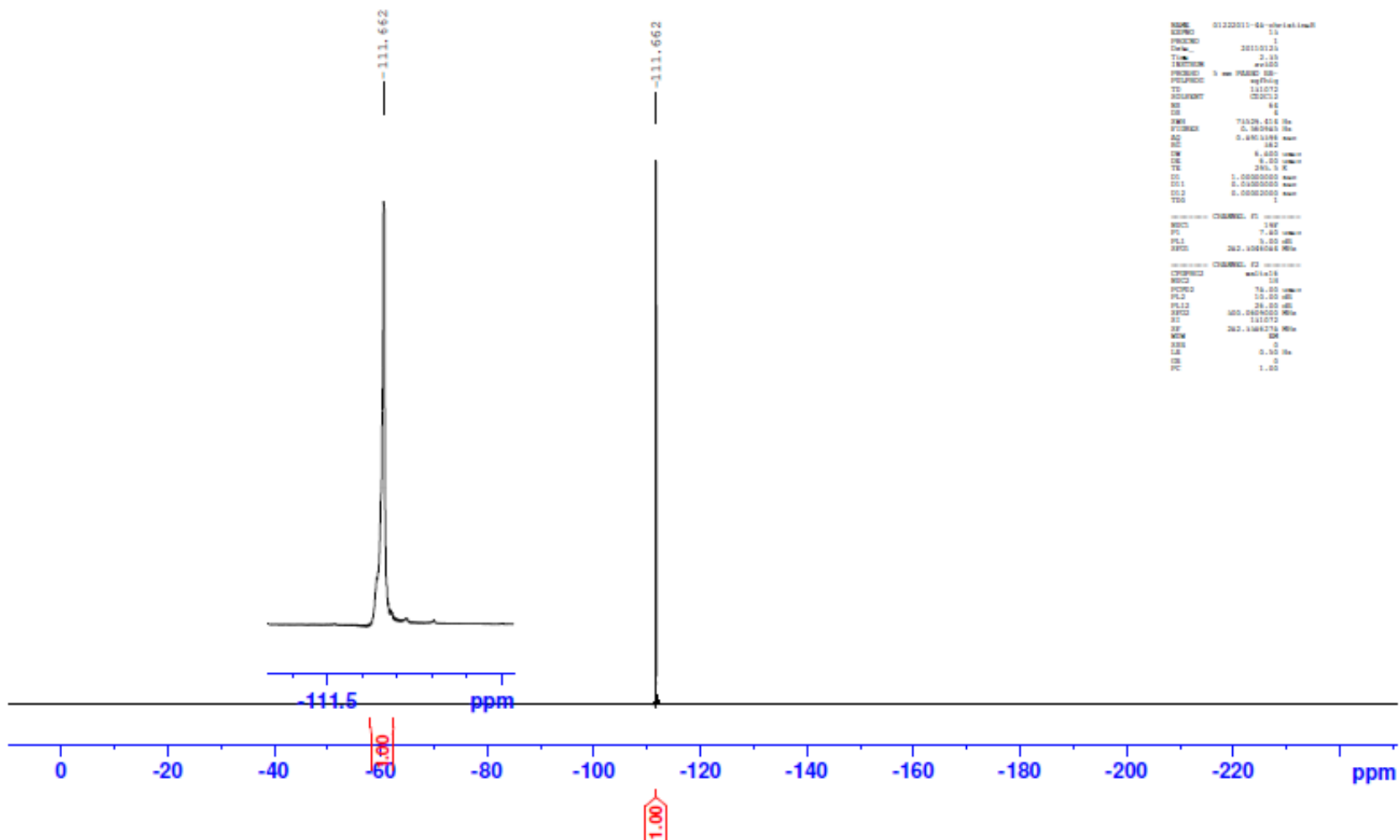
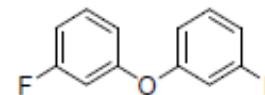


Figure S3  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of compound 11F (282 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)

2- Compound 11OMe



CC1073

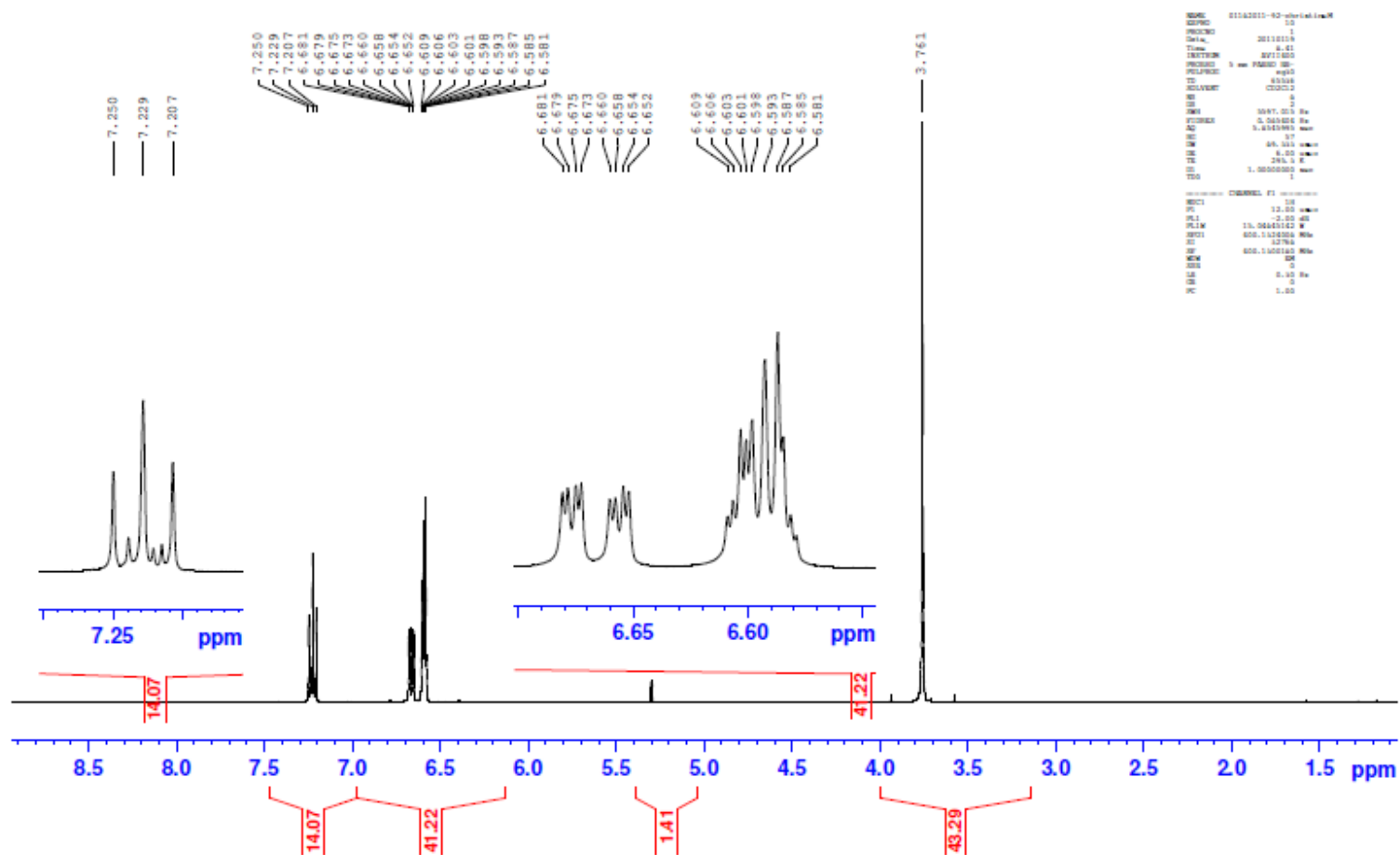
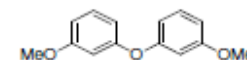


Figure S4 <sup>1</sup>H NMR spectrum of compound 11OMe (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)



CC1073

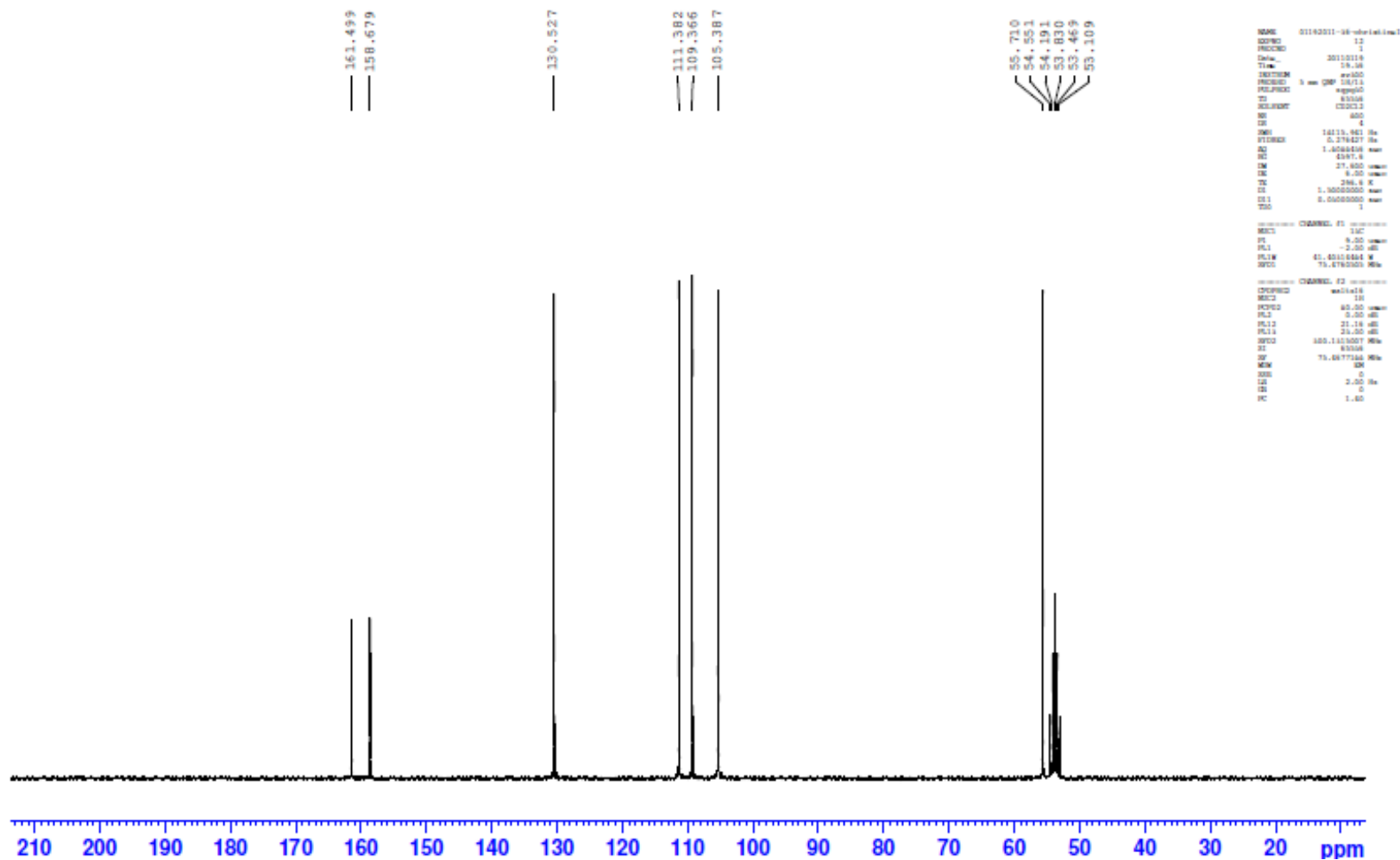
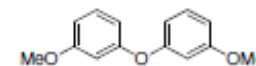


Figure S5  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 11OMe (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)



CC1073

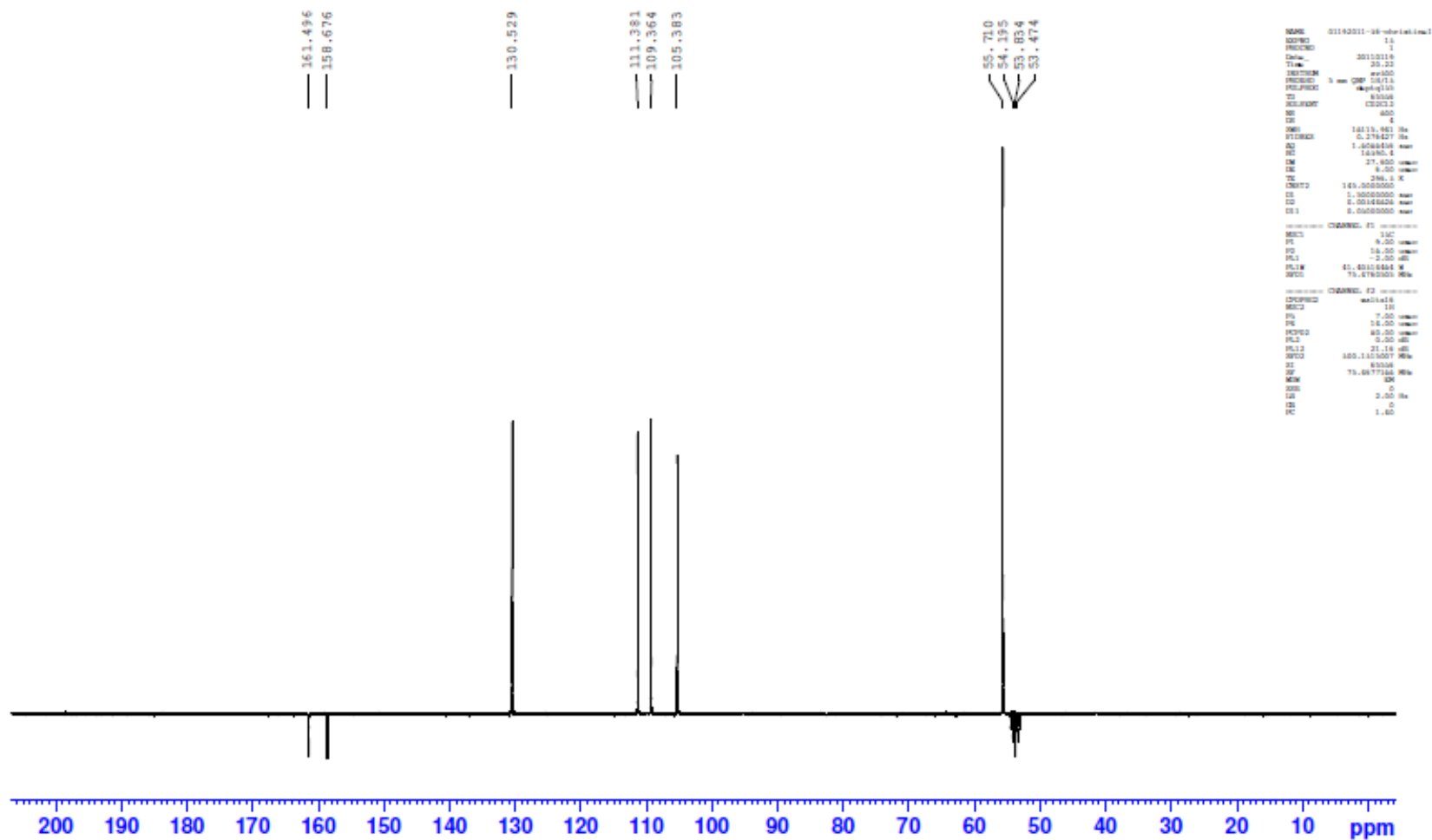
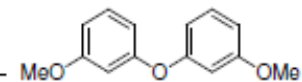


Figure S6  $^{13}\text{C}$  APT NMR spectrum of compound 11OMe (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)

3- Compound 12



CC2082

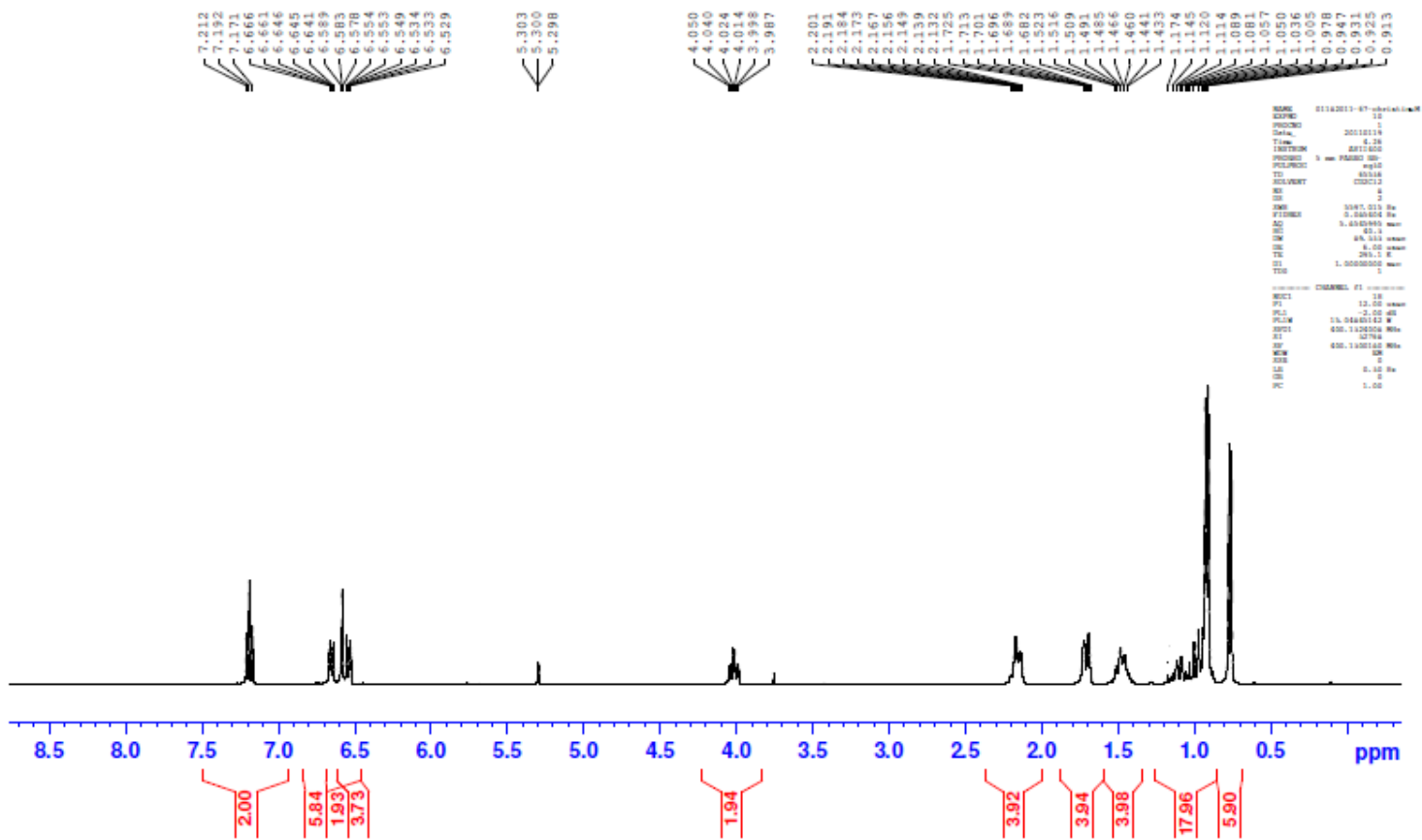
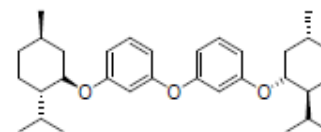


Figure S7 <sup>1</sup>H NMR spectrum of compound 12 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)





CC5082 after gCMS check

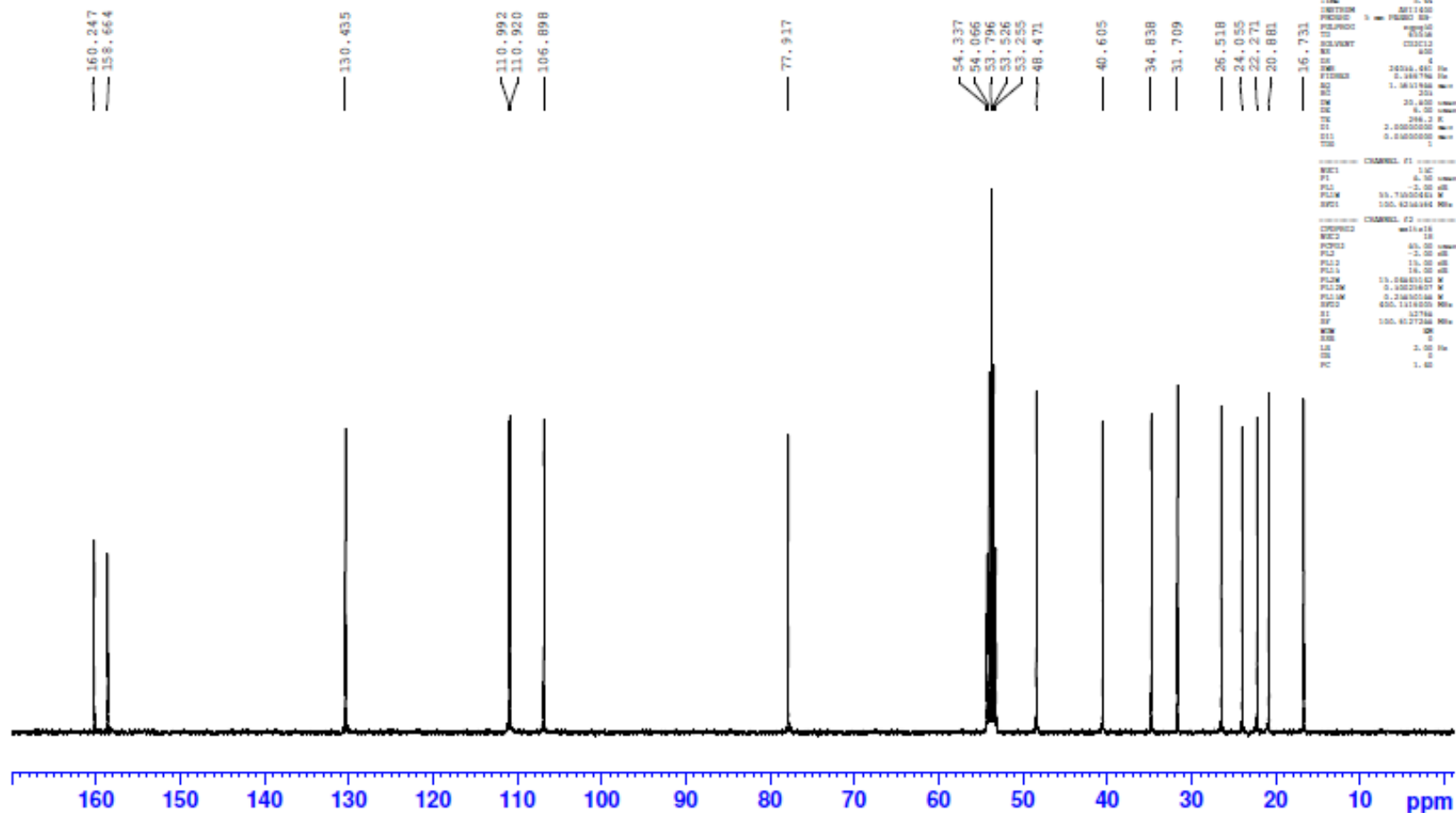
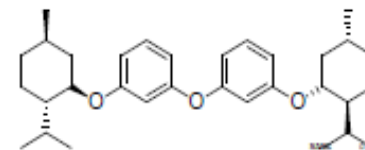


Figure S8  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 12 (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)

4- Compound 13

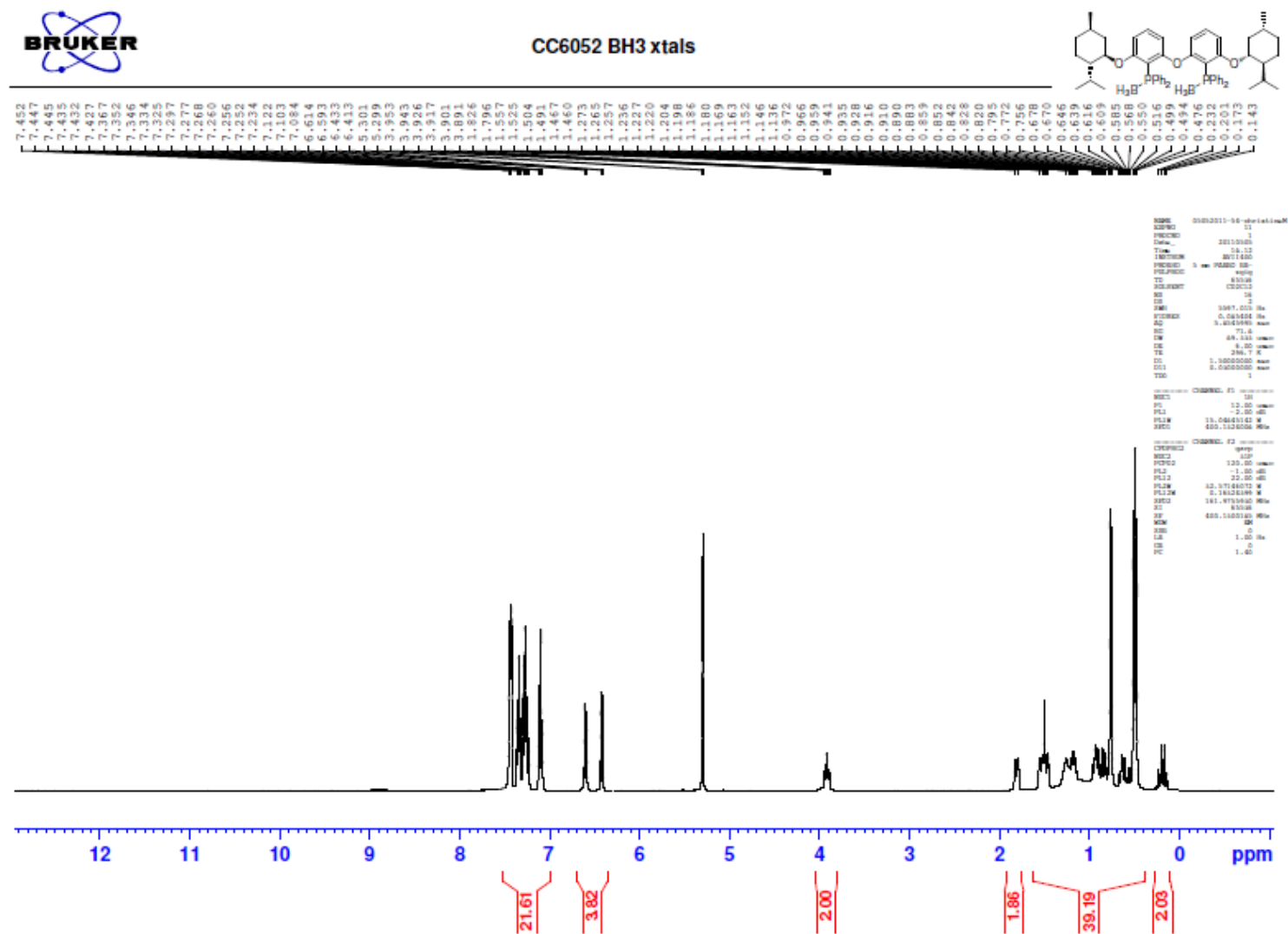


Figure S9  $^1\text{H}$  NMR spectrum of compound 13 (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



CC6052 BH3 xtals

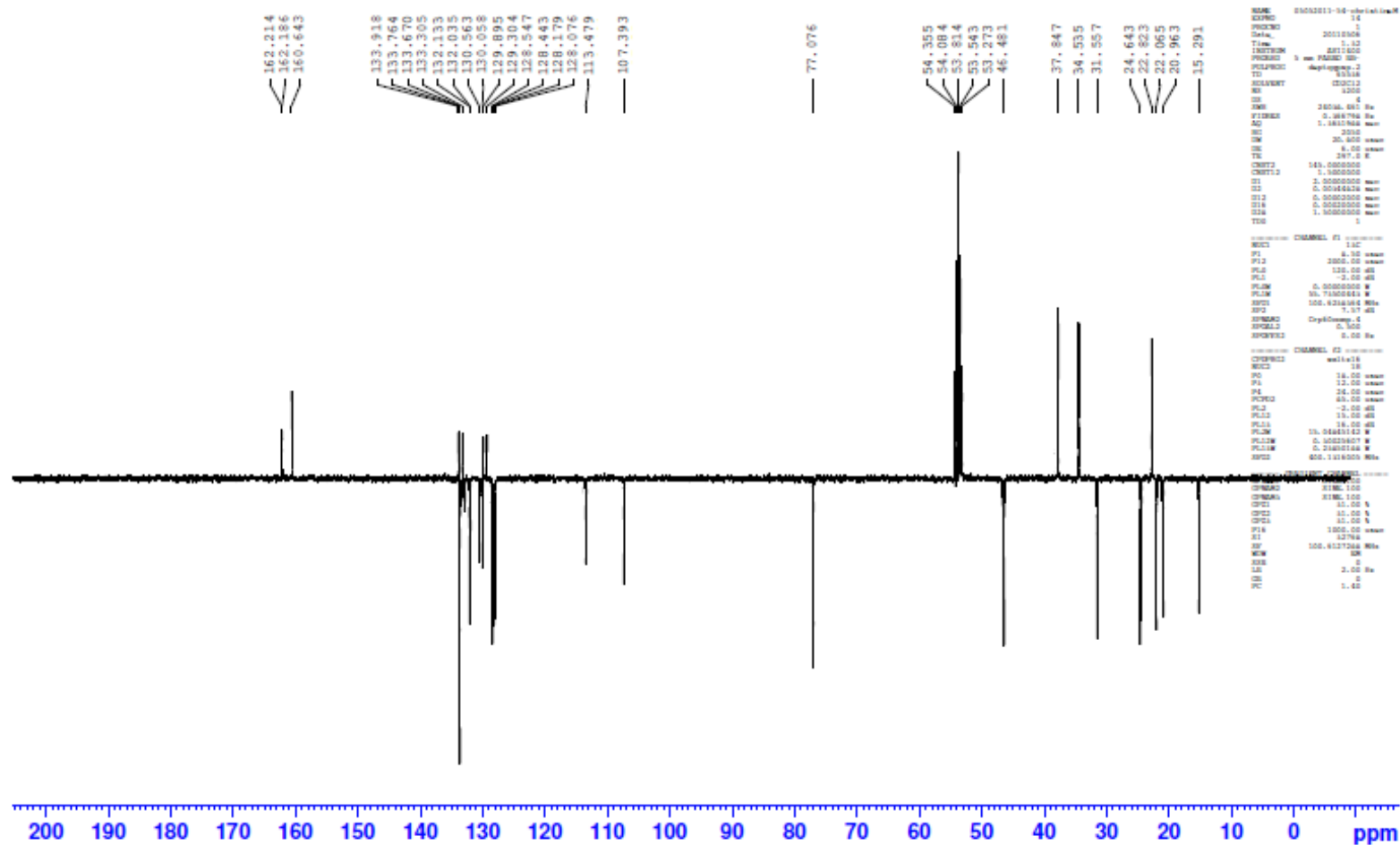
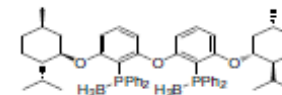


Figure S10 <sup>13</sup>C APT NMR spectrum of compound 13 (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)

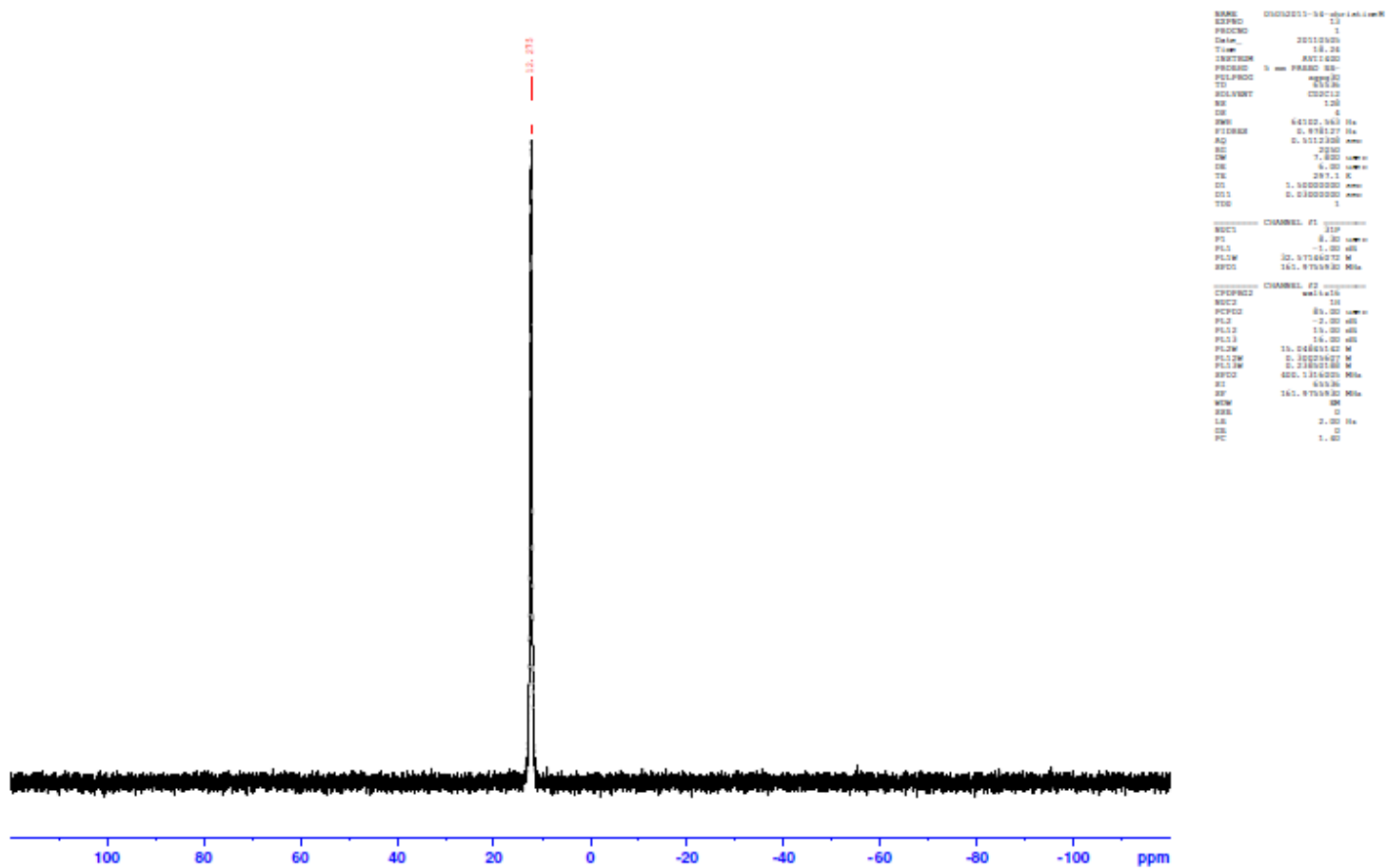
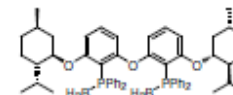


Figure S11  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 13 (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)

5- Compound 14

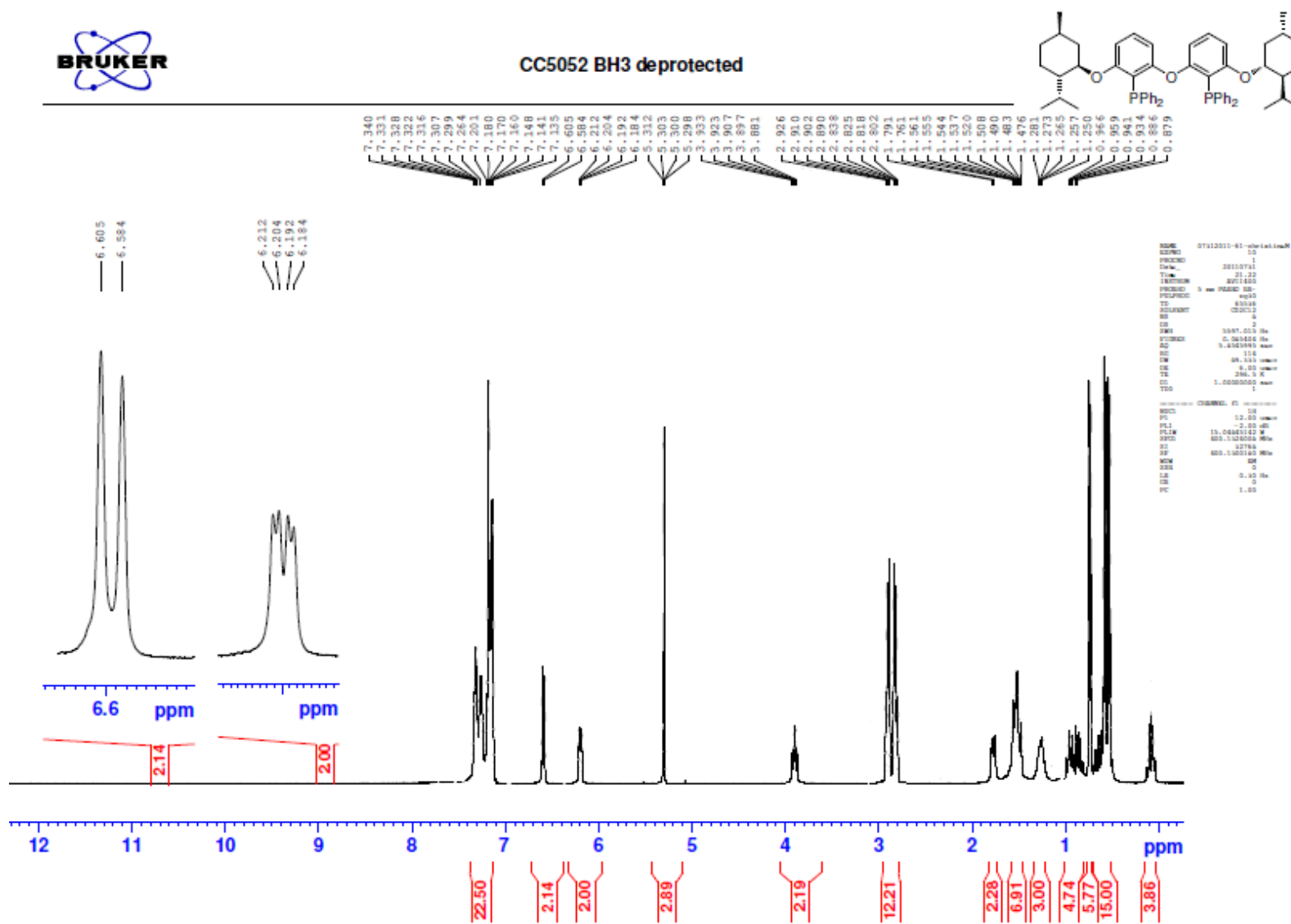


Figure S12 <sup>1</sup>H NMR spectrum of compound 14 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)



CC5052 BH3 deprotected

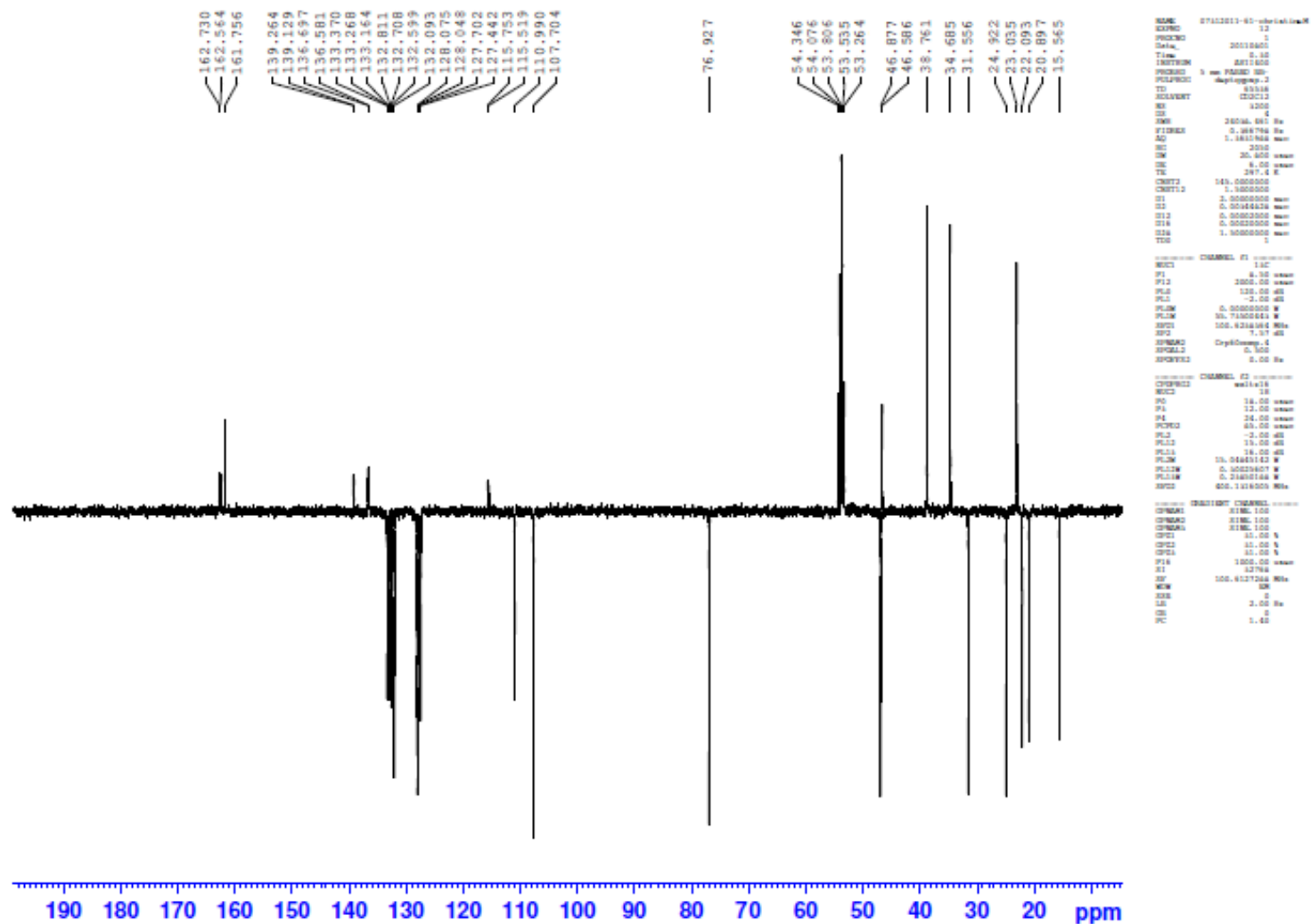
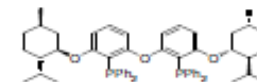


Figure S13 <sup>13</sup>C APT NMR spectrum of compound 14 (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)



CC5052 BH3 deprotected

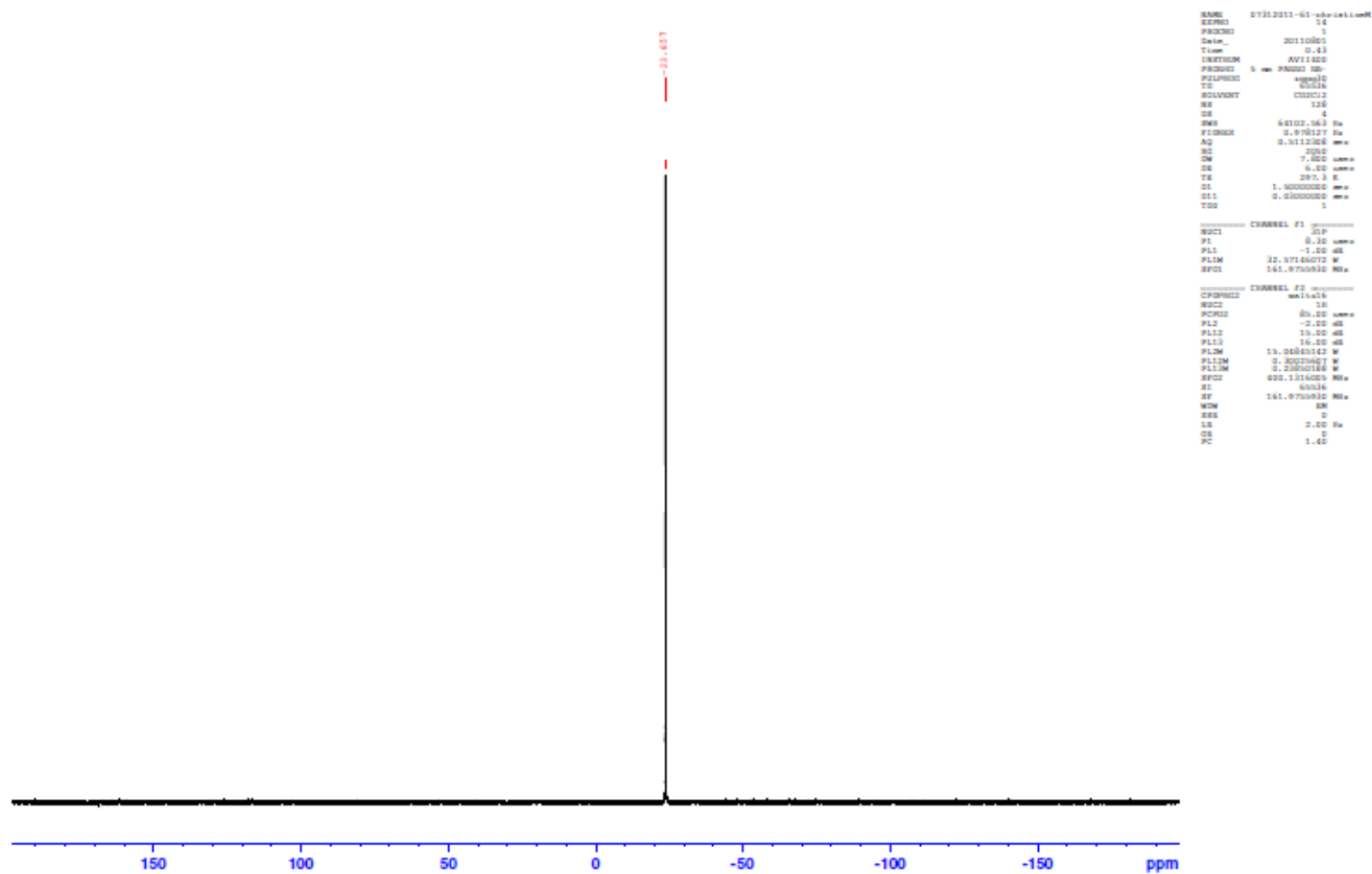
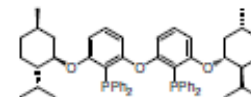


Figure S14  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 14 (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)

6- Compound 15

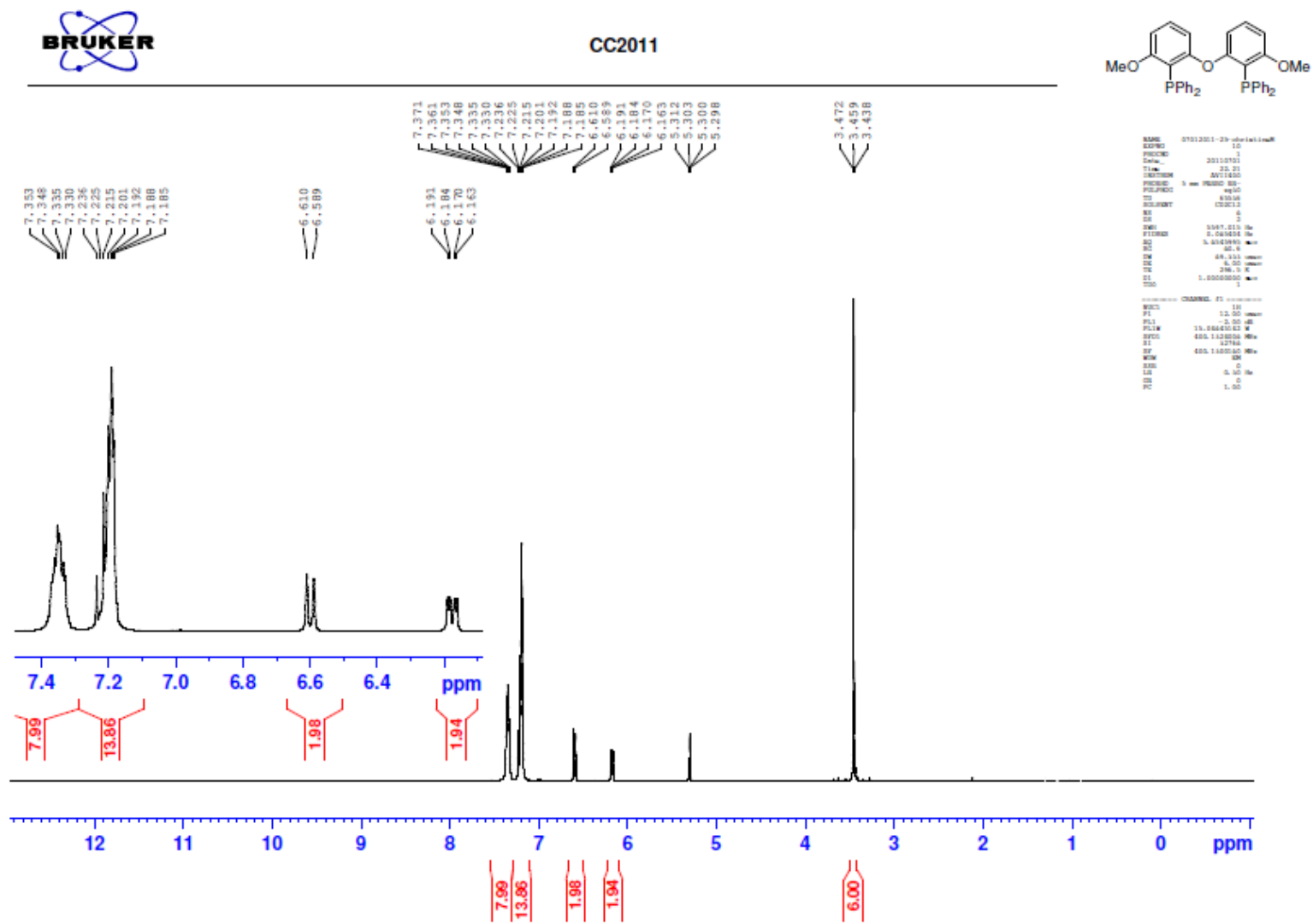


Figure S15 <sup>1</sup>H NMR spectrum of compound 15 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)





CC2011

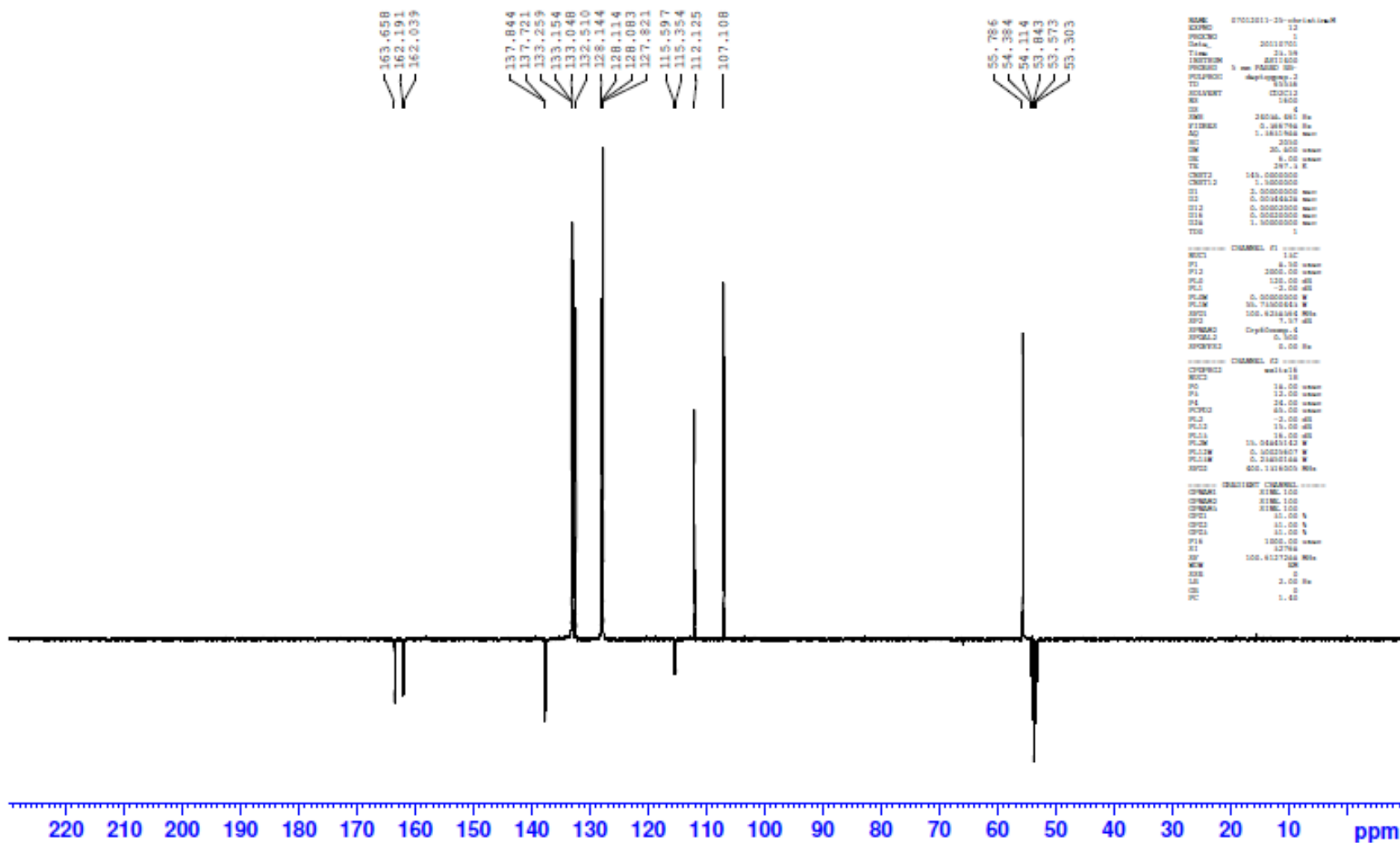
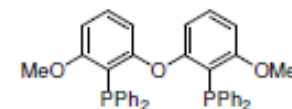


Figure S16 <sup>13</sup>C APT NMR spectrum of compound 15 (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)

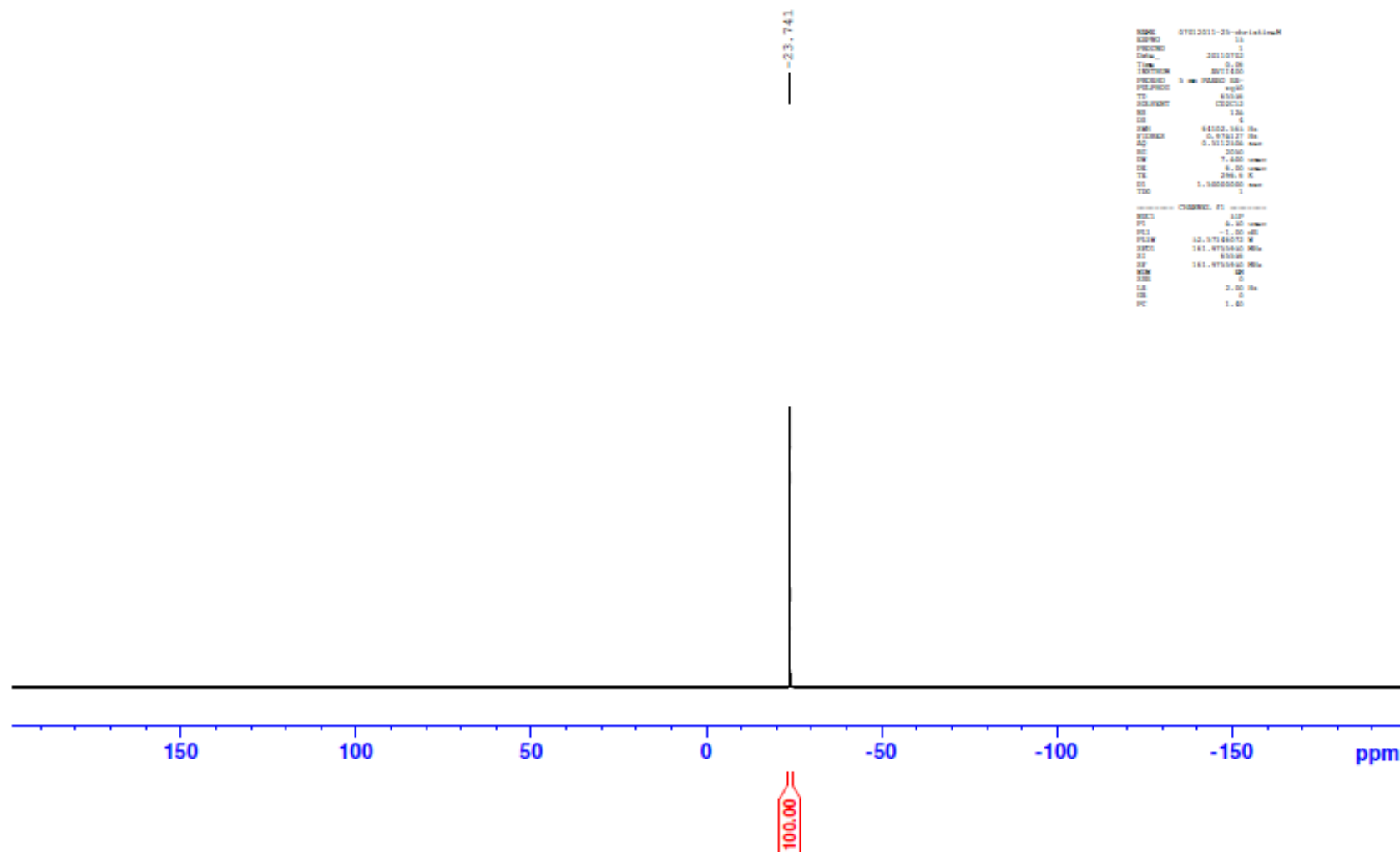
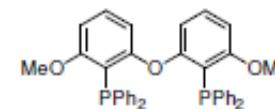


Figure S17  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 15 (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)

7- Compound 17a

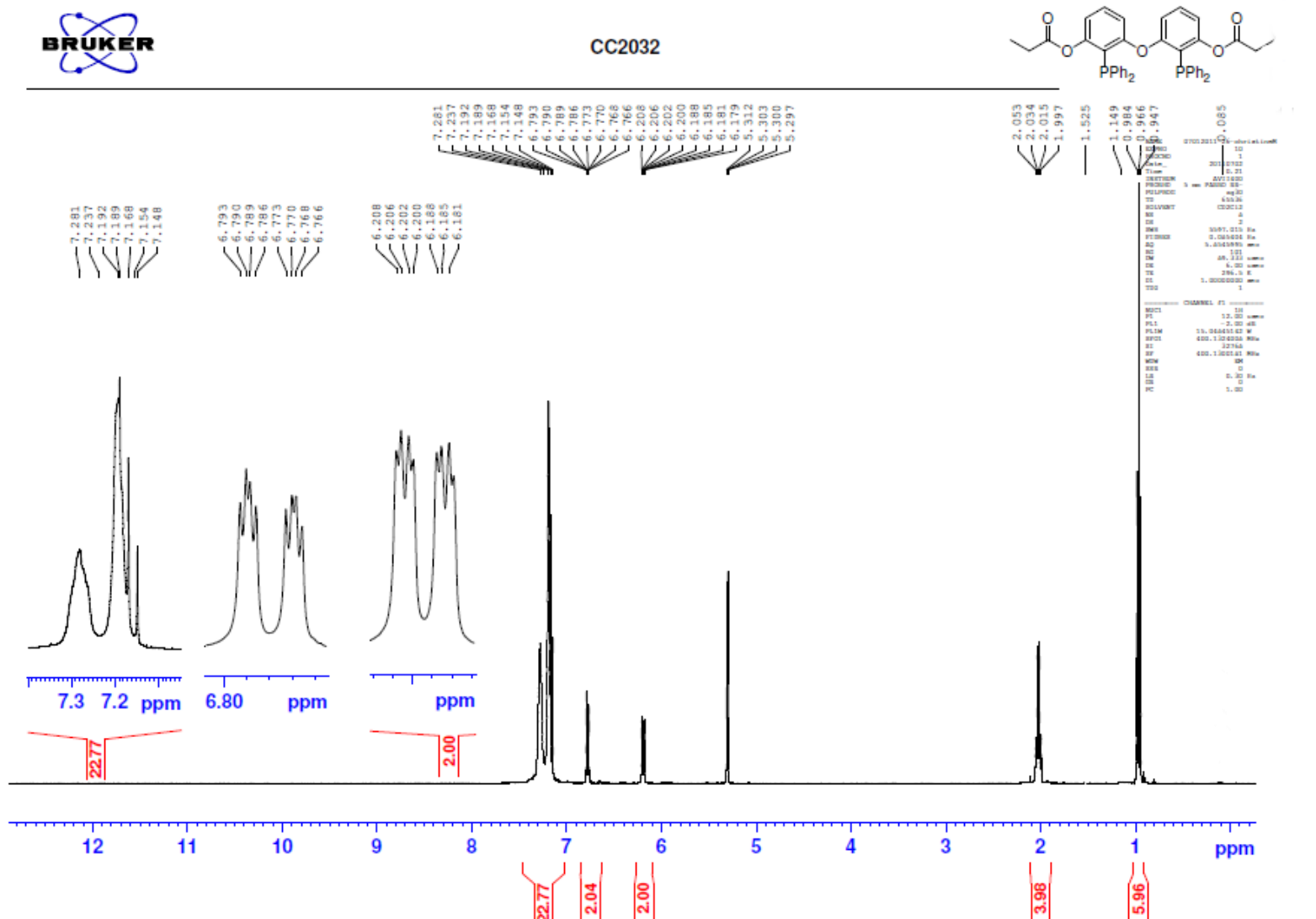


Figure S18 <sup>1</sup>H NMR spectrum of compound 17a (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

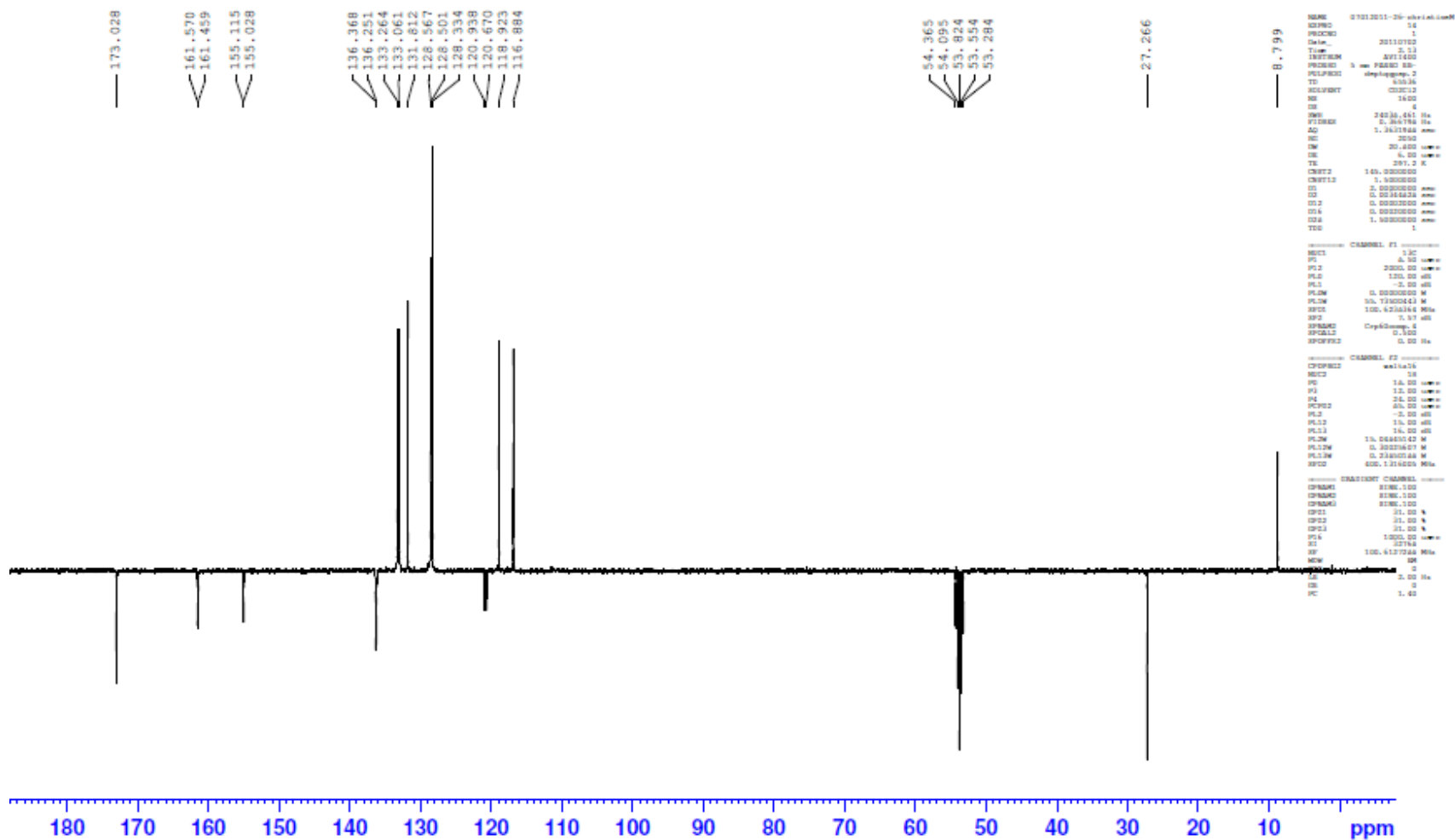
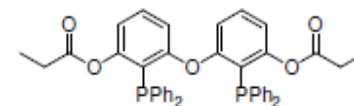


Figure S19 <sup>13</sup>C APT NMR spectrum of compound 17a (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



CC2032

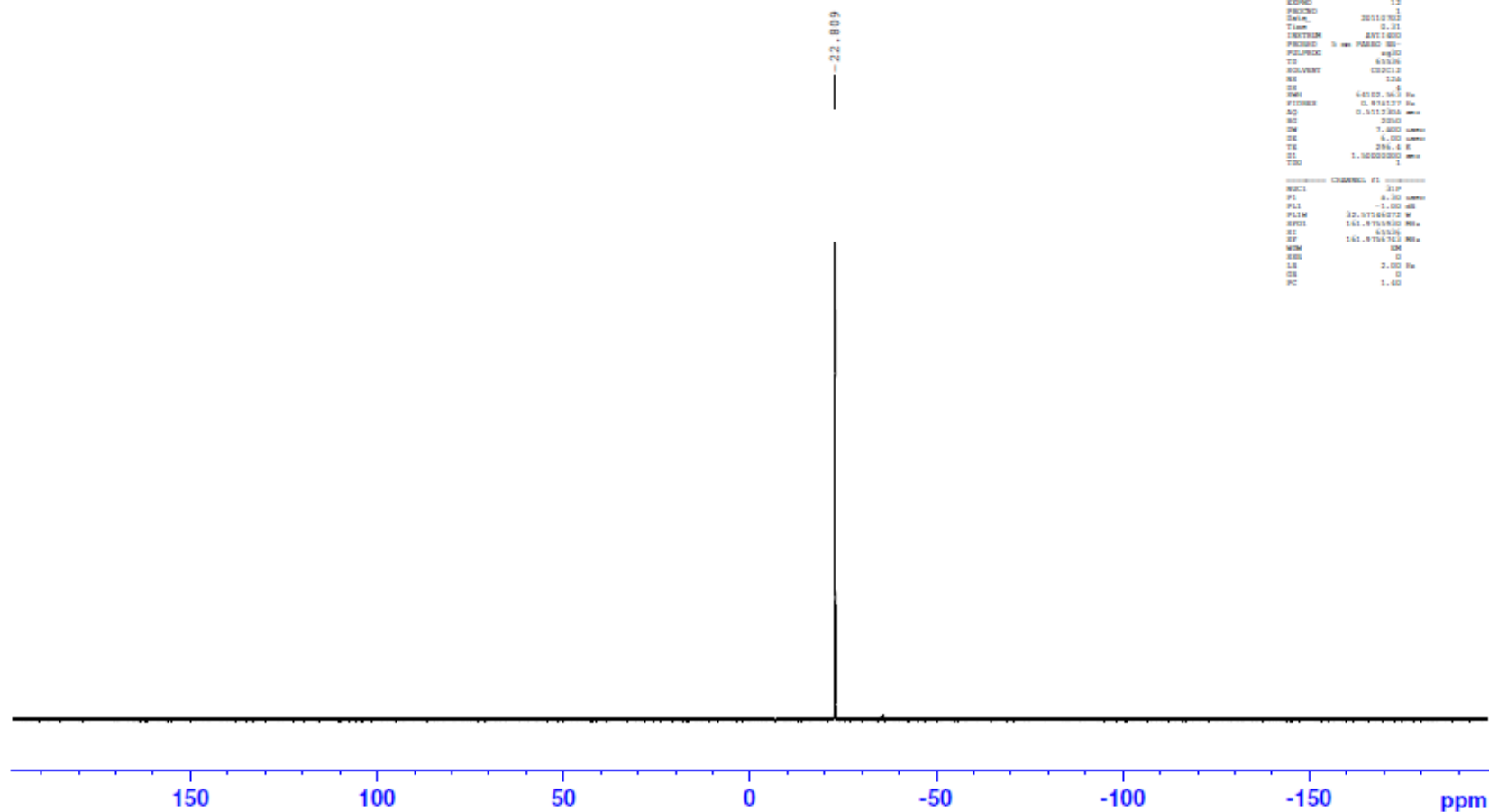
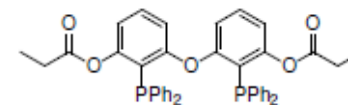


Figure S20  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 17a (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

8- Compound 17a

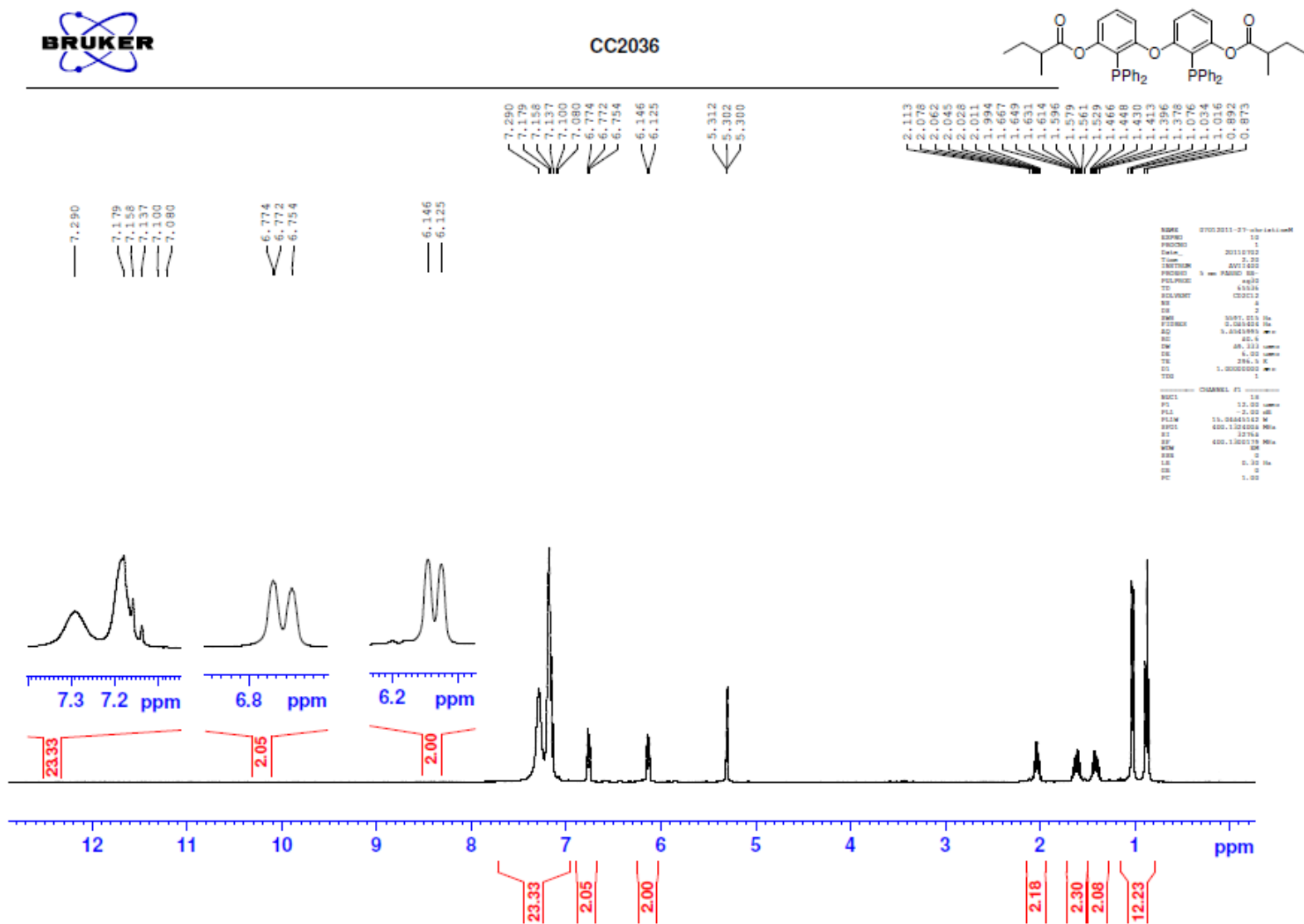


Figure S21 <sup>1</sup>H NMR spectrum of compound 17b (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

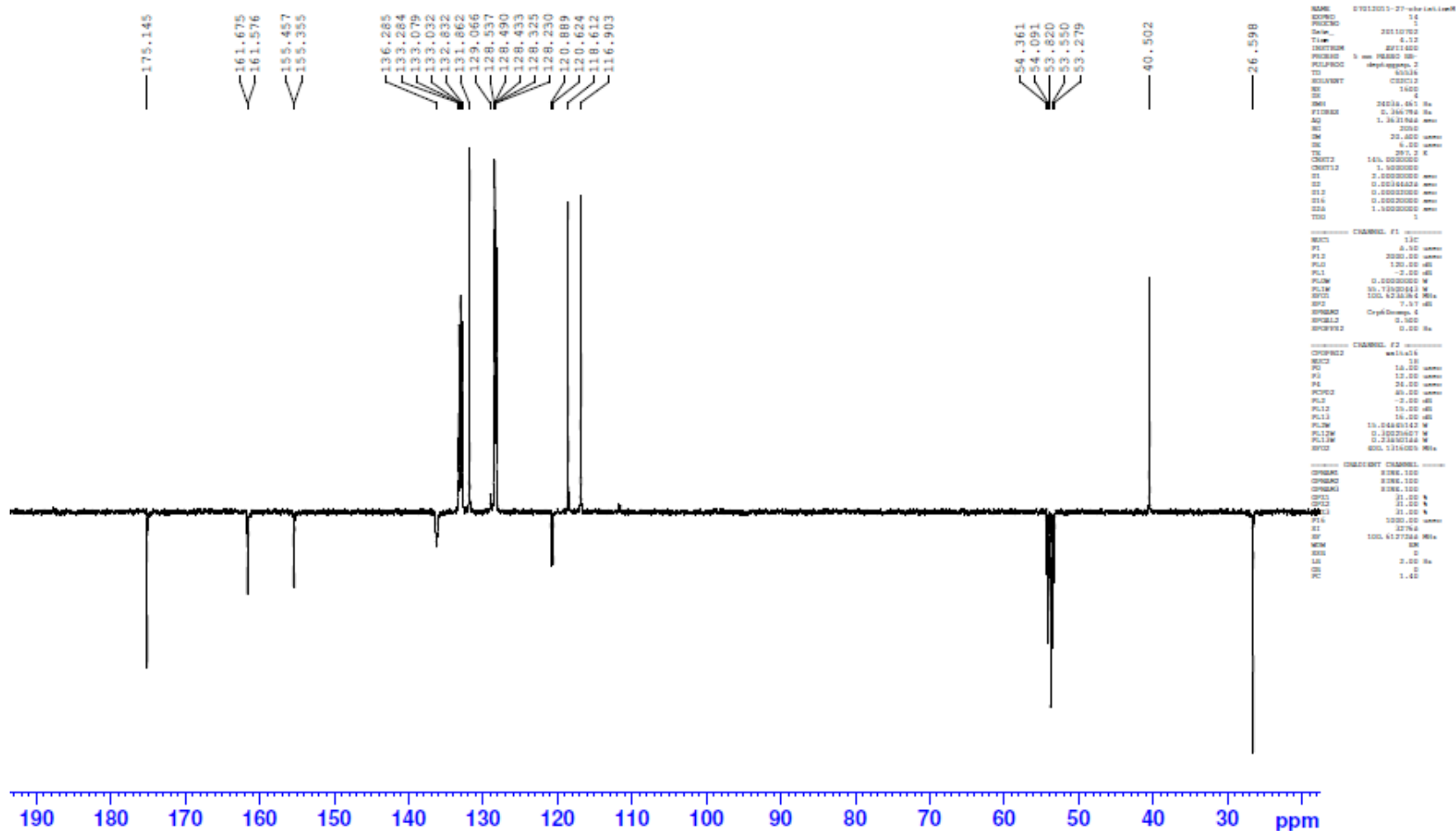
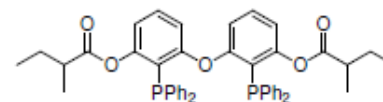


Figure S22 <sup>13</sup>C APT NMR spectrum of compound 17b (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



CC2036

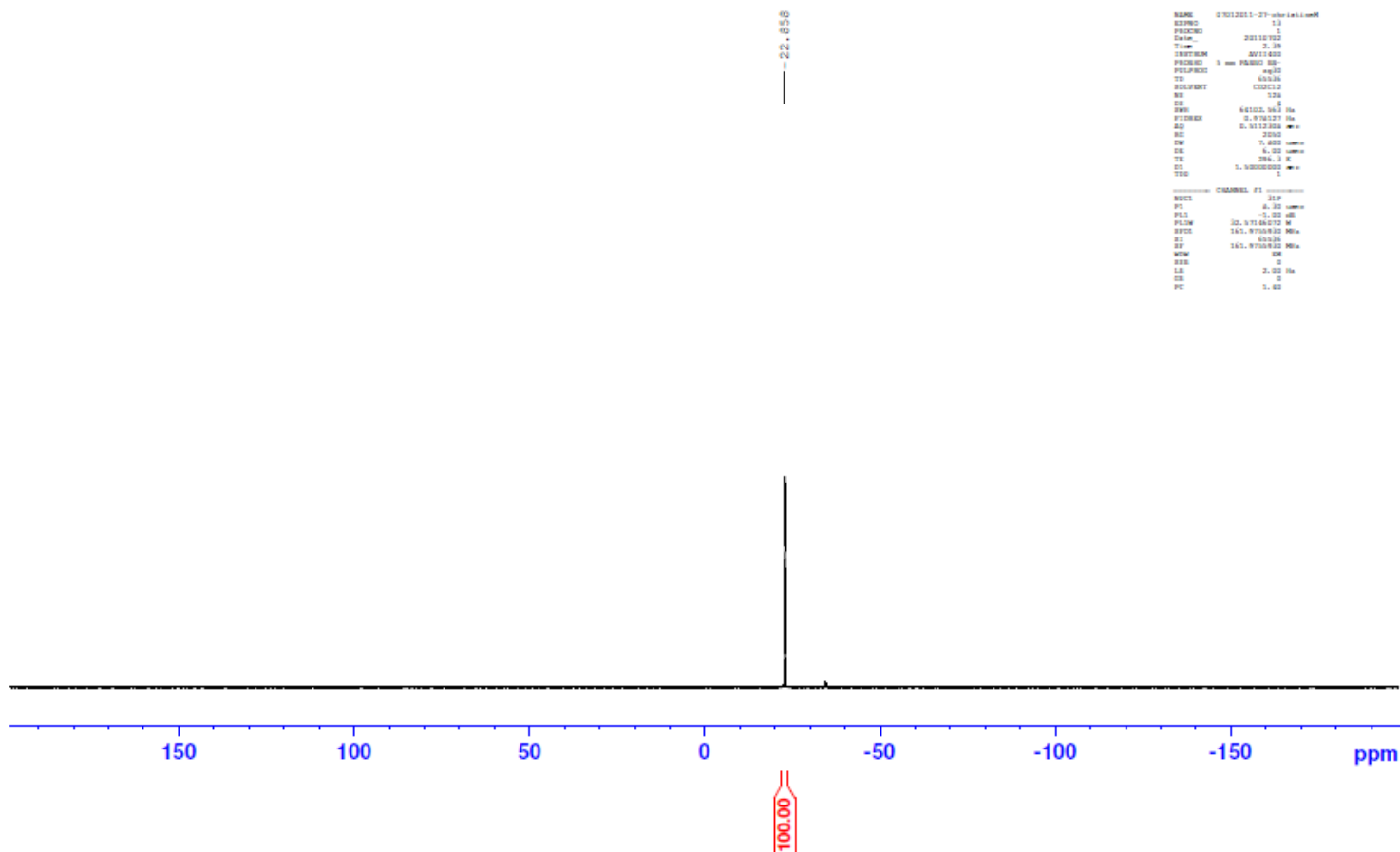
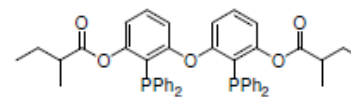


Figure S23  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 17b (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



9- Compound 17c



CC2039

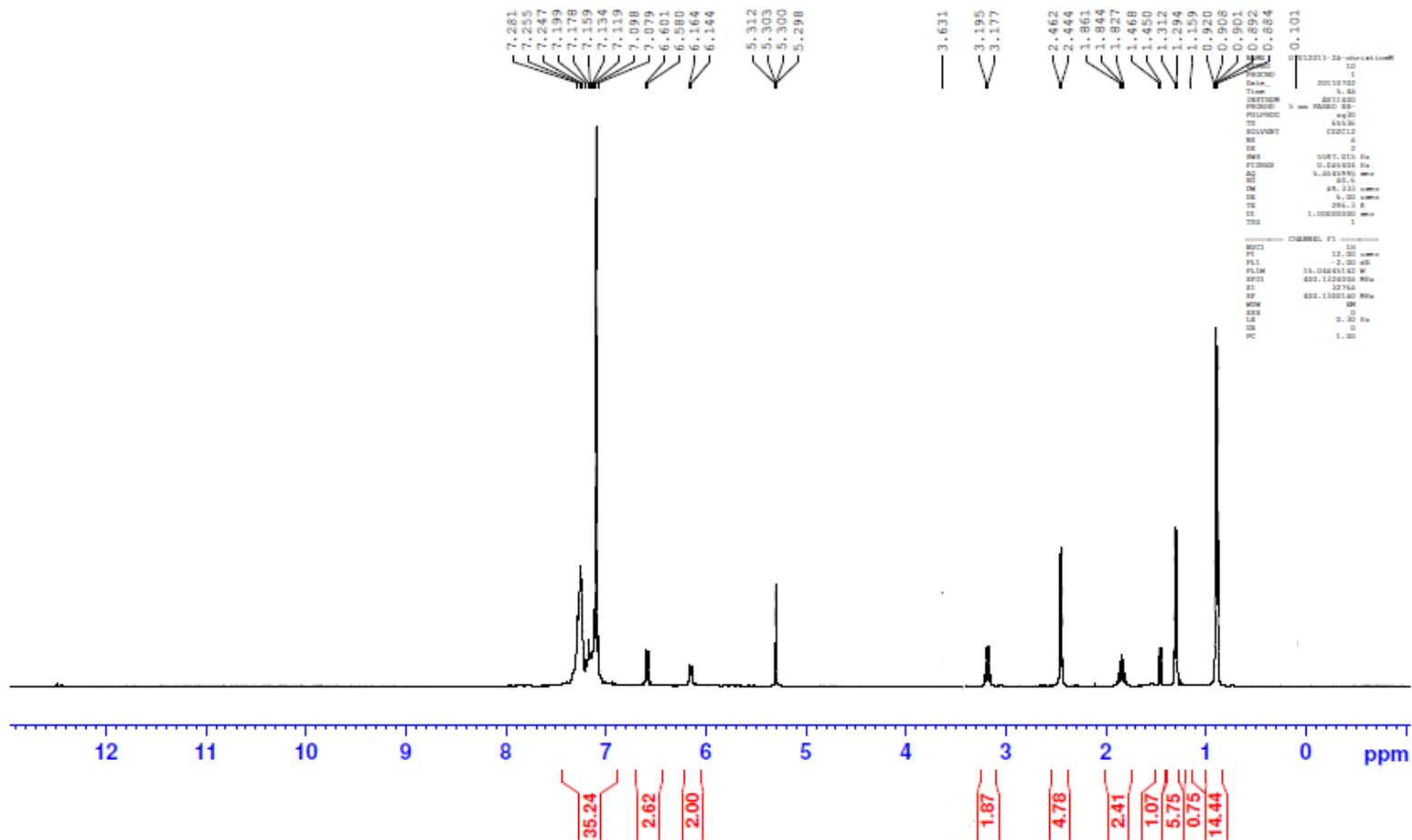
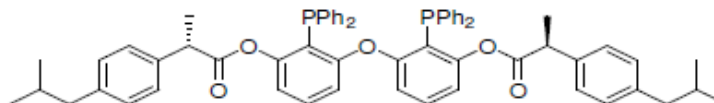


Figure S24 <sup>1</sup>H NMR spectrum of compound 17c (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

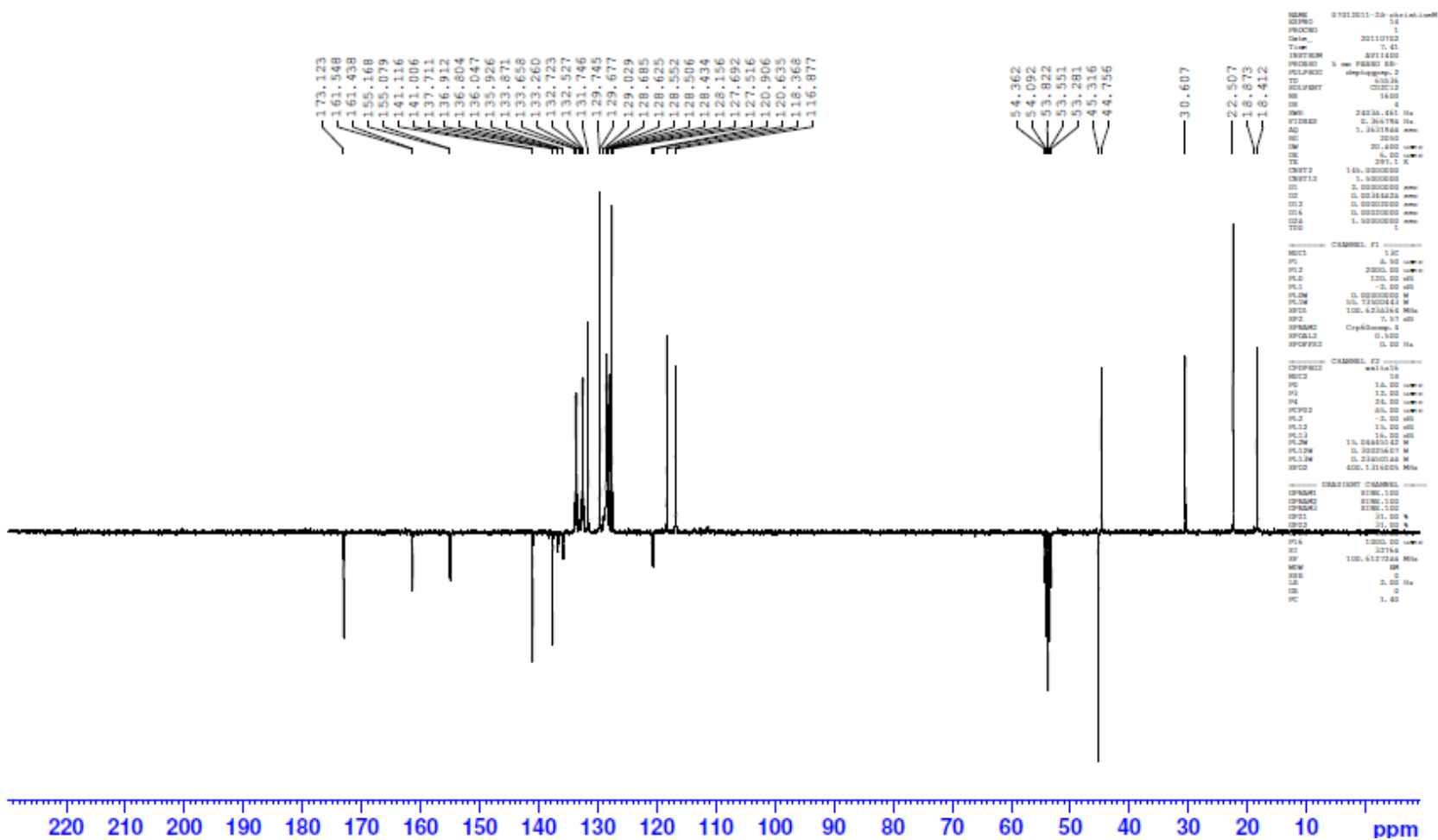
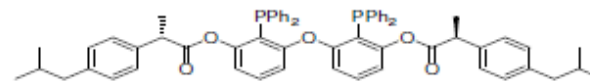
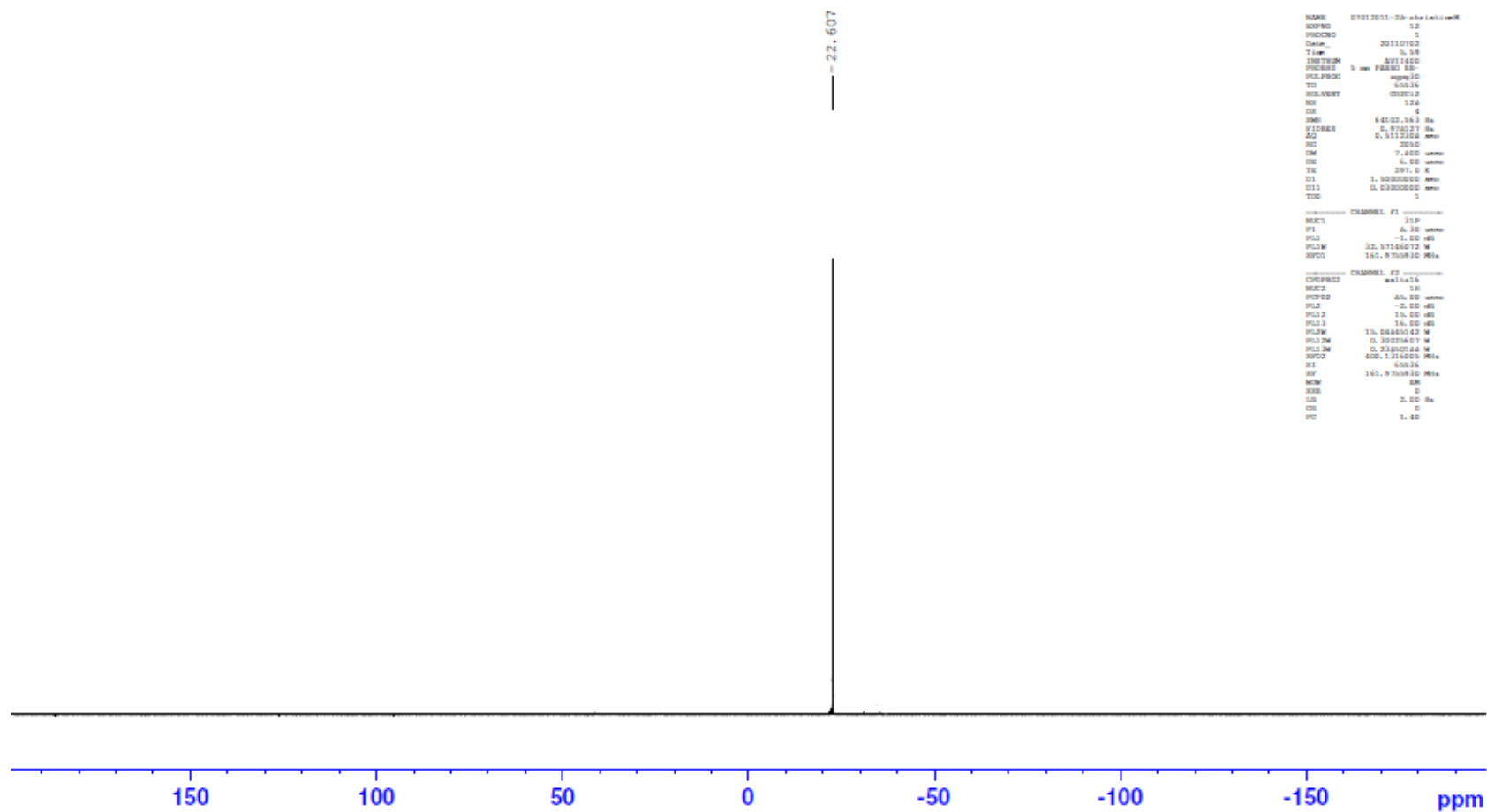
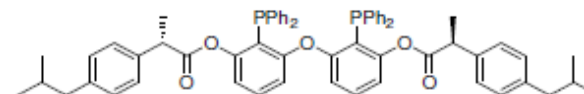


Figure S25 <sup>13</sup>C APT NMR spectrum of compound 17c (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



CC2039

Figure S26  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 17c (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

10- Compound 17d



CC2046

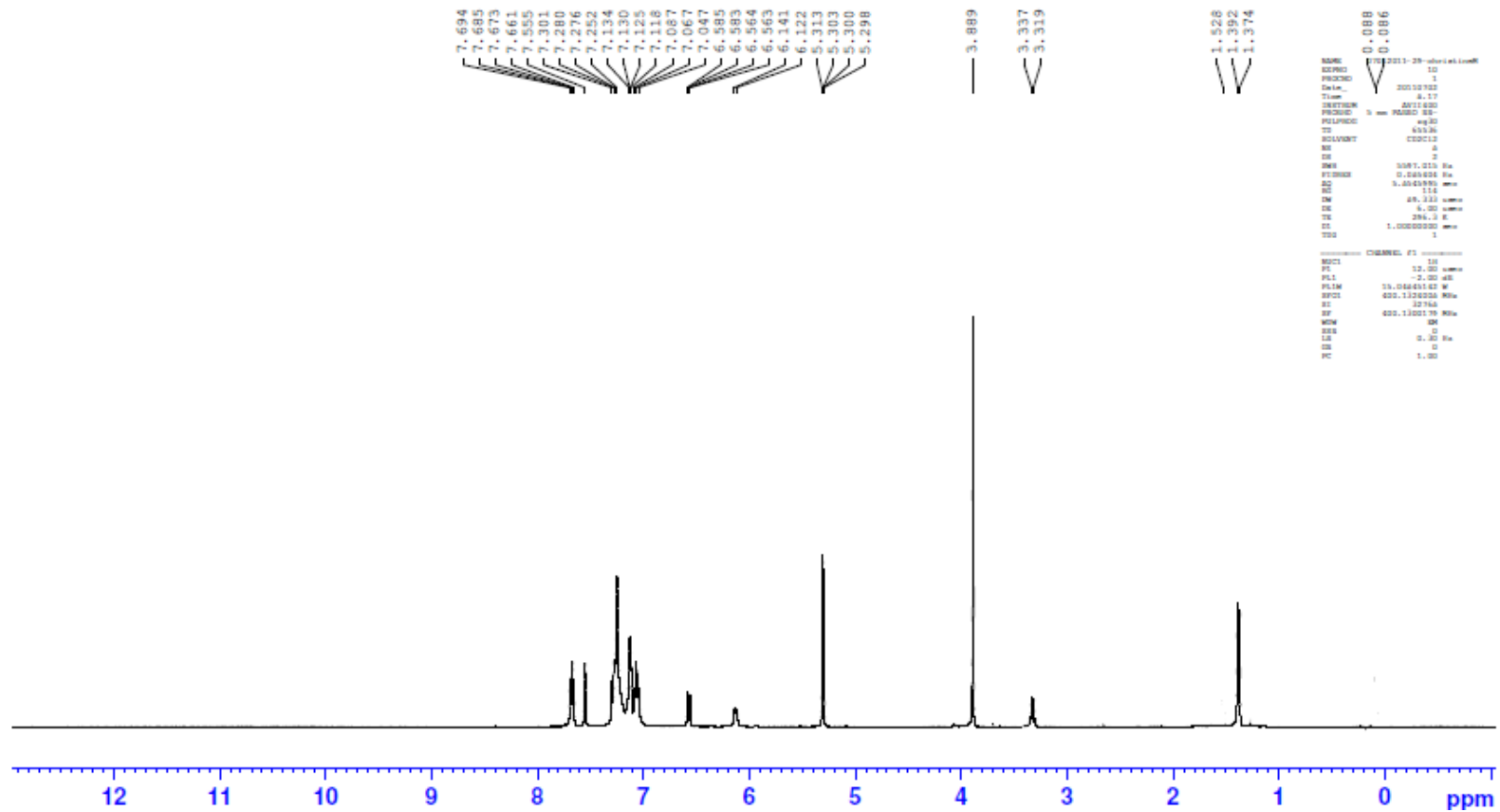
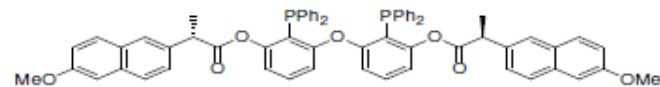


Figure S27 <sup>1</sup>H NMR spectrum of compound 17c (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

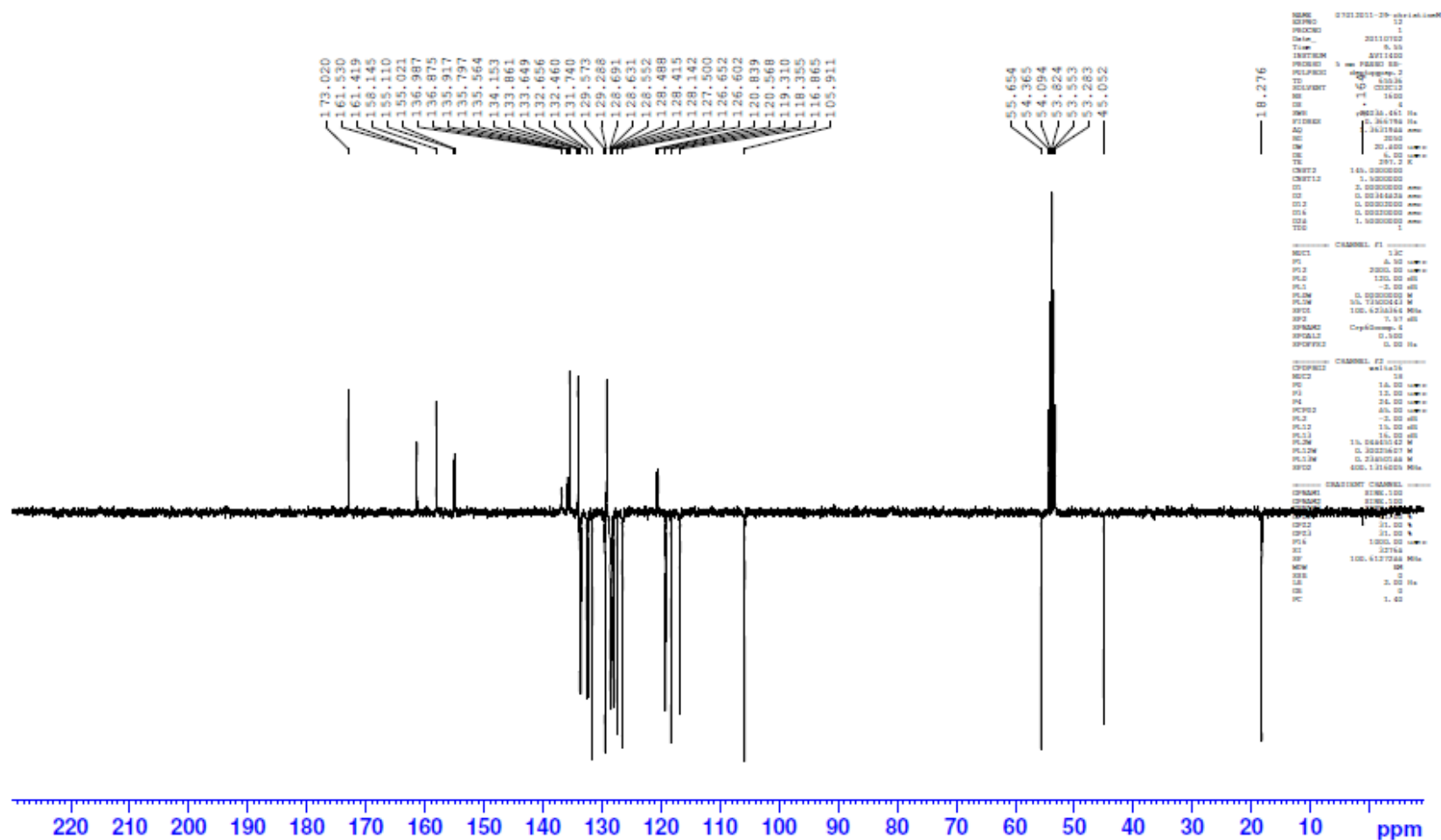
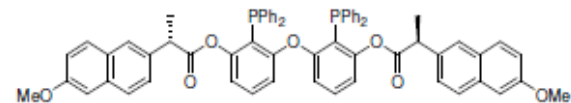


Figure S28 <sup>13</sup>C APT NMR spectrum of compound 17c (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



CC2046

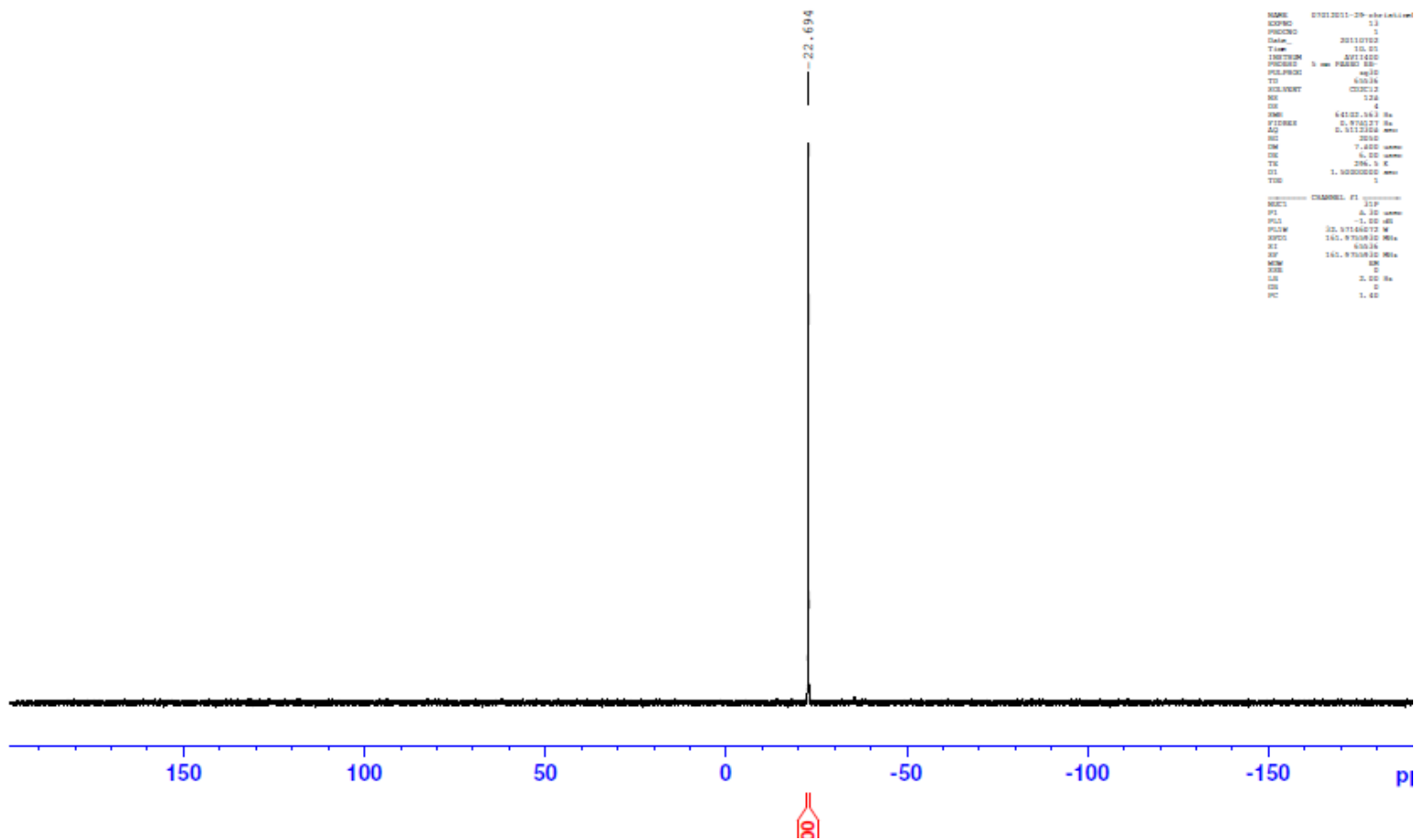
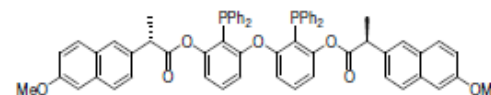


Figure S29  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 17c (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

## 11- Platinum Complexes

[PtCl<sub>2</sub>(**15**)]

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aj1.119

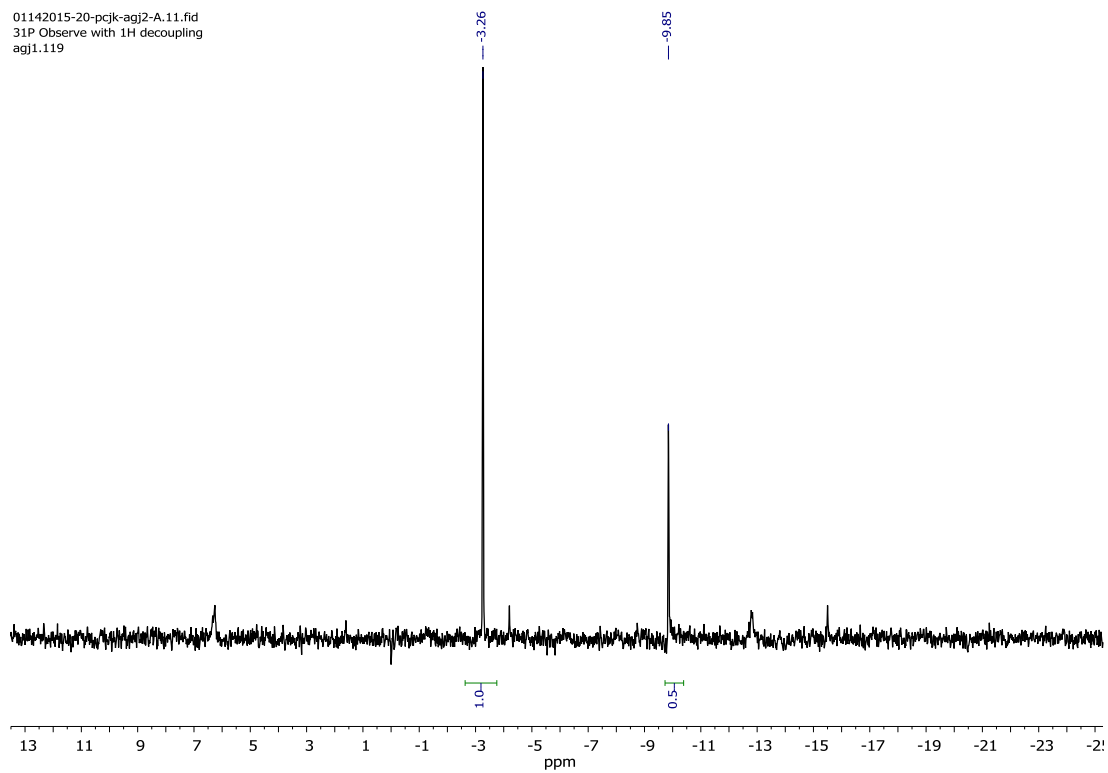


Figure S30: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(**15**) (202 MHz, CDCl<sub>3</sub>)

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1H Observe  
agj1.119

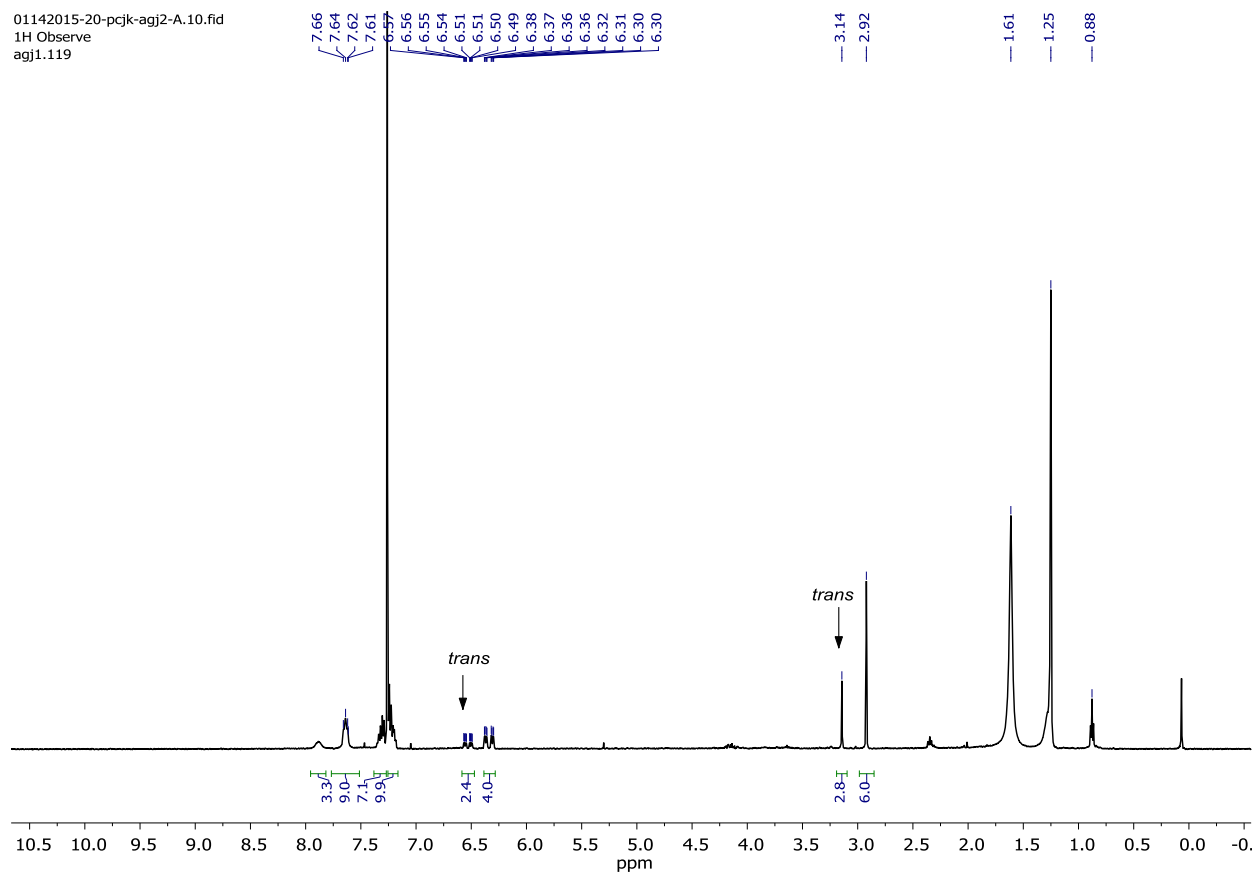


Figure S31:  $^1\text{H}$  NMR of  $\text{PtCl}_2(15)$  (500 MHz,  $\text{CDCl}_3$ ) (major product *cis*-isomer, minor product *trans*-isomer)

[ $\text{PtCl}_2(17a)$ ]

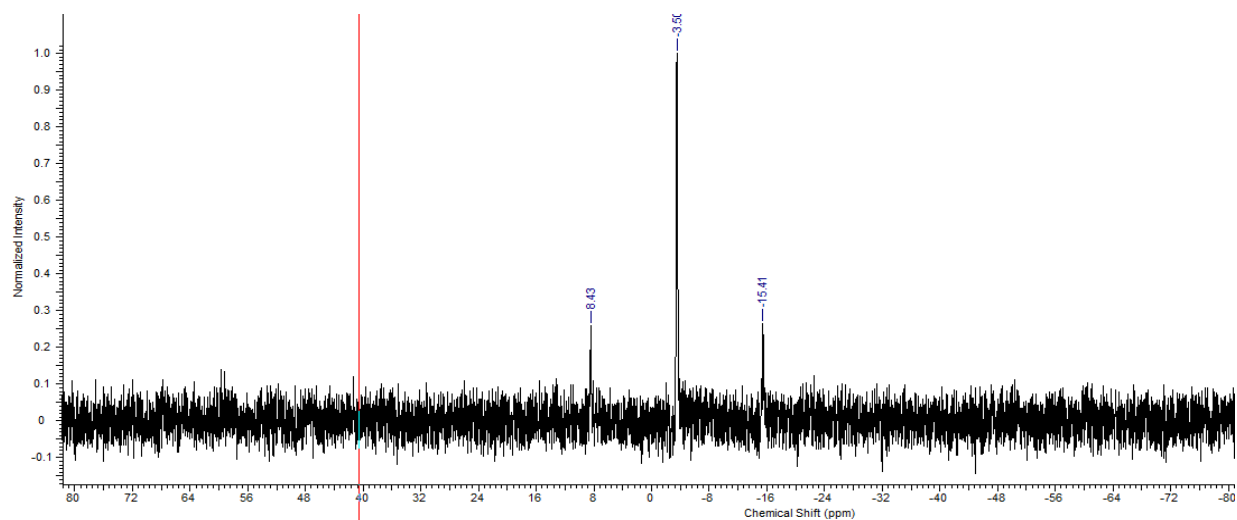


Figure S32:  $^{31}\text{P}\{^1\text{H}\}$  NMR of  $\text{PtCl}_2(17a)$  (162 MHz,  $\text{CDCl}_3$ )



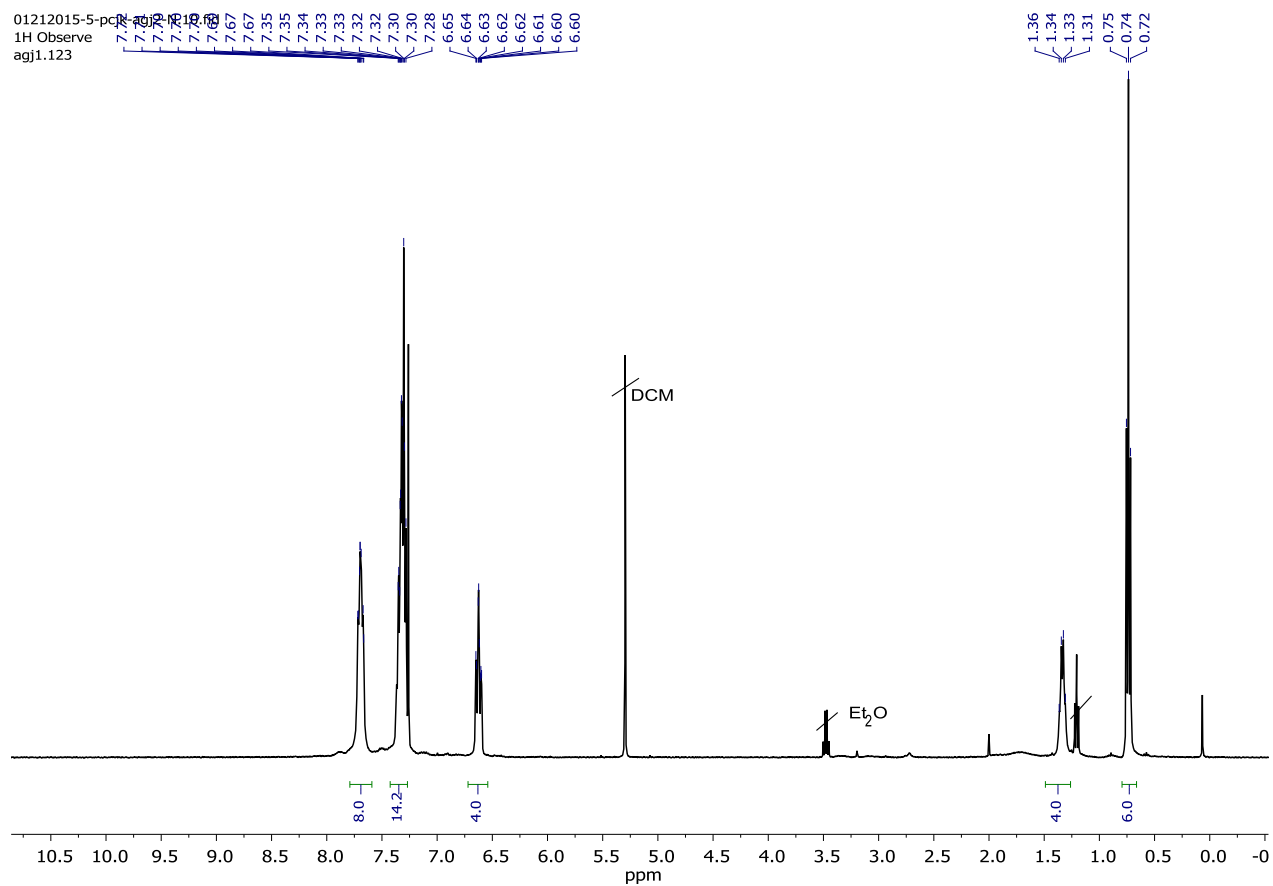


Figure S33: <sup>1</sup>H NMR of PtCl<sub>2</sub>(17a) (400 MHz, CDCl<sub>3</sub>)

[PtCl<sub>2</sub>(17b)]

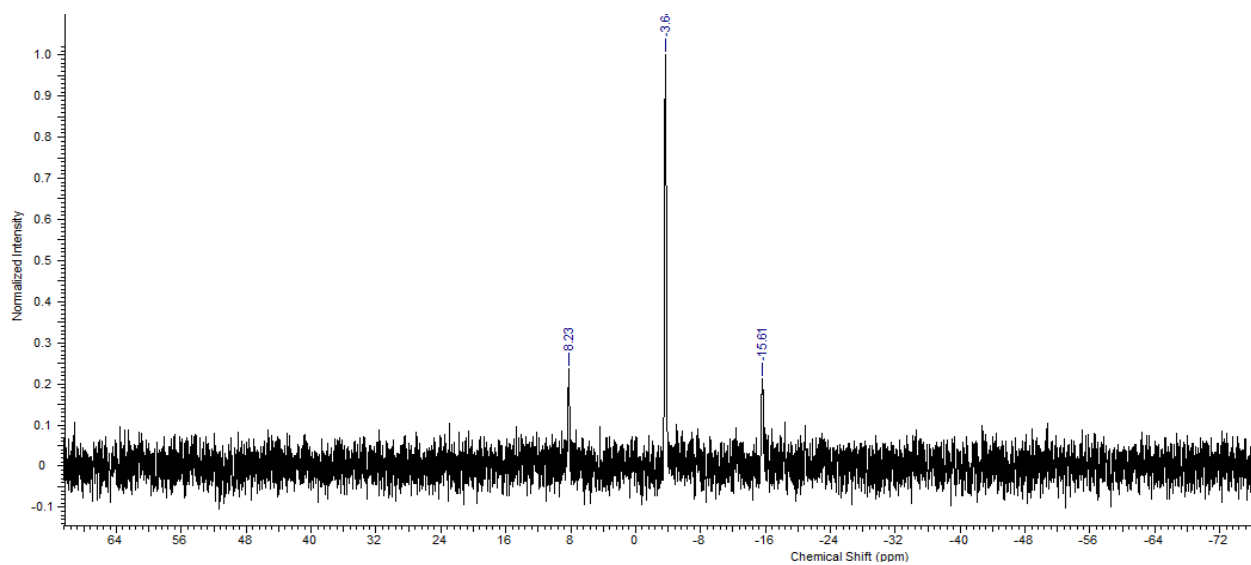


Figure S34: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(17b) (162 MHz, CDCl<sub>3</sub>)

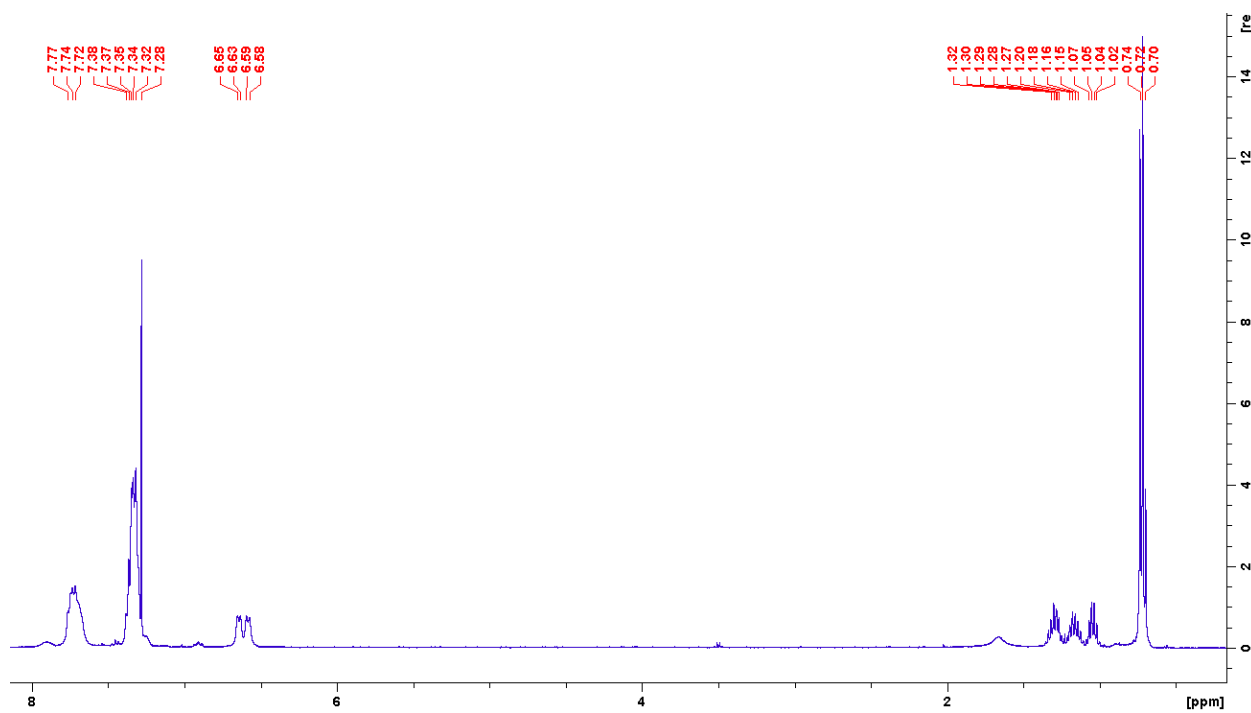


Figure S35: <sup>1</sup>H NMR of PtCl<sub>2</sub>(17b) (400 MHz, CDCl<sub>3</sub>)

[PtCl<sub>2</sub>(17c)]

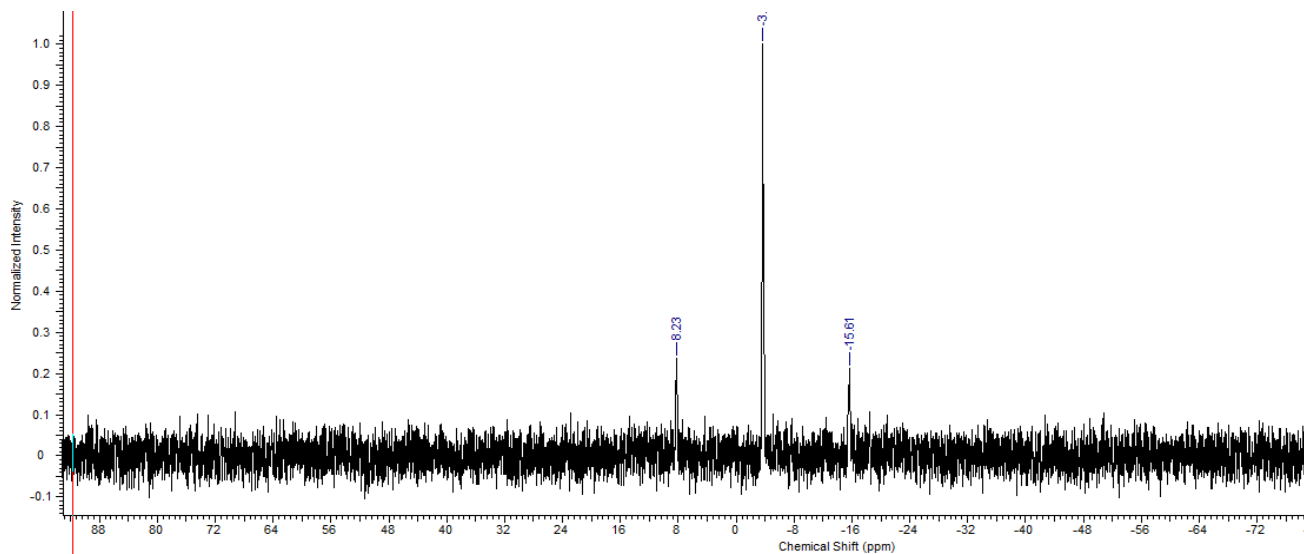


Figure S36: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(17c) (162 MHz, CDCl<sub>3</sub>)

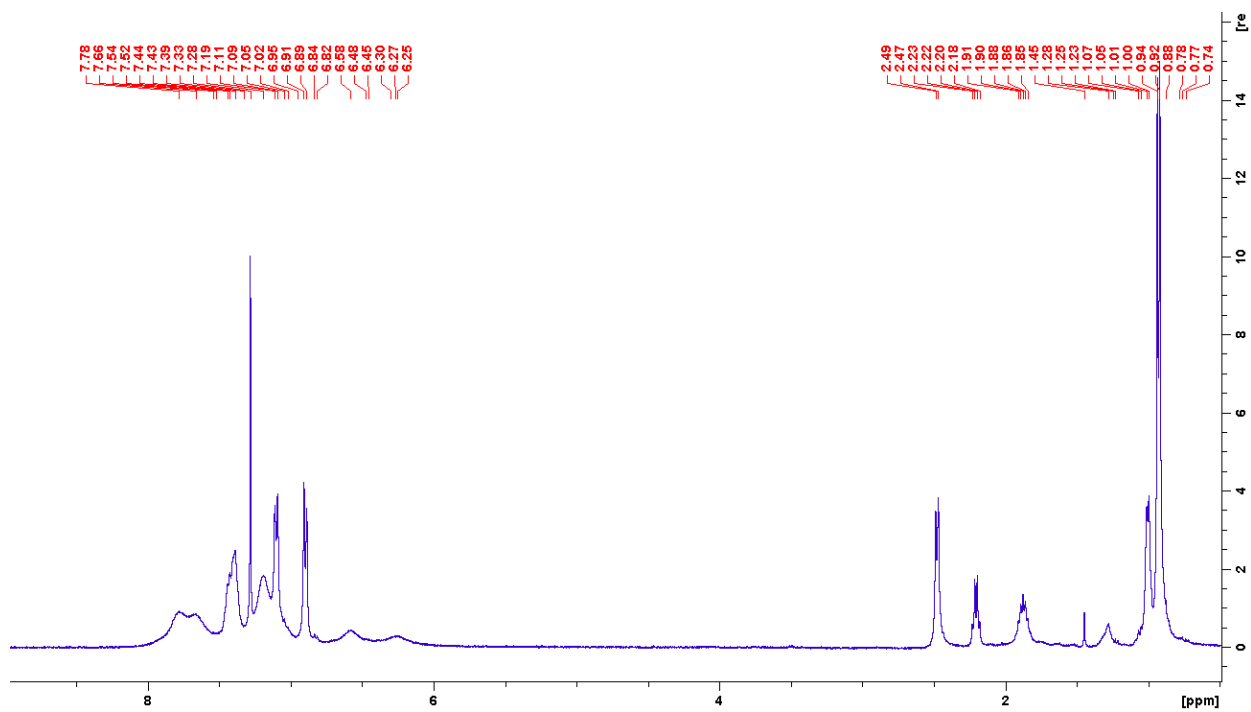


Figure S37: <sup>1</sup>H NMR of PtCl<sub>2</sub>(17c) (400 MHz, CDCl<sub>3</sub>)

## 12- Phosphine selenide compounds

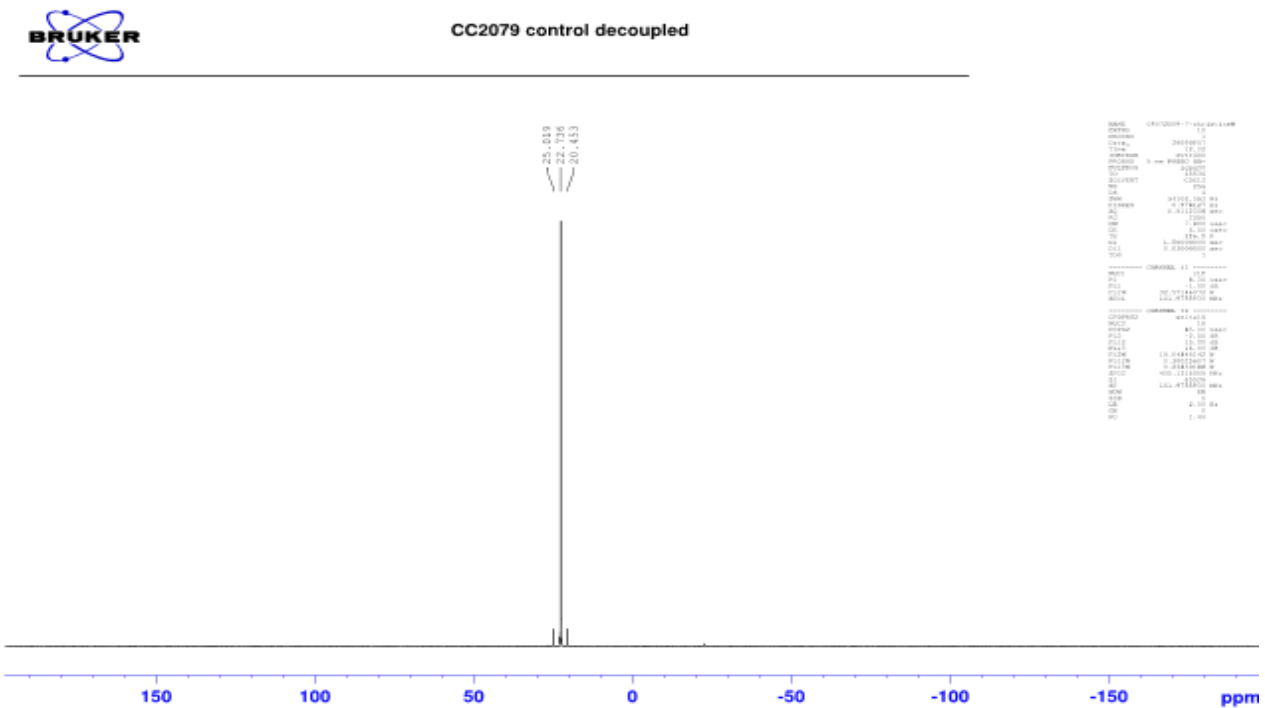


Figure S38  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of diselenide of **15** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

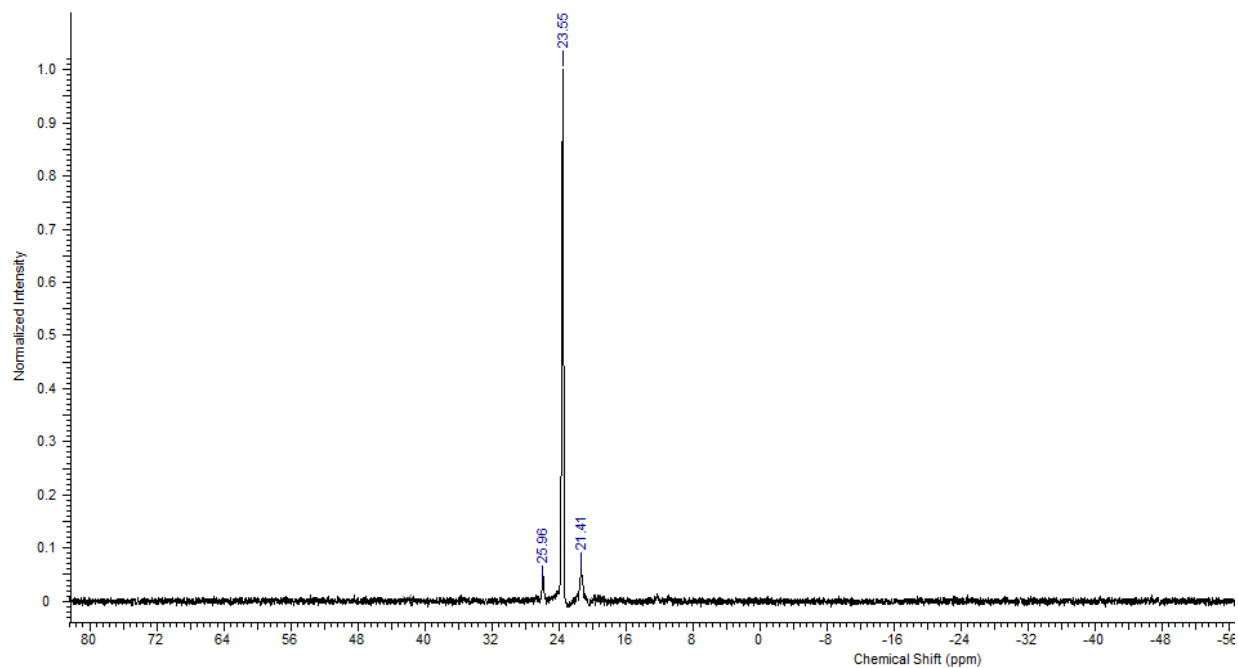


Figure S39  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of diselenide of **17a** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

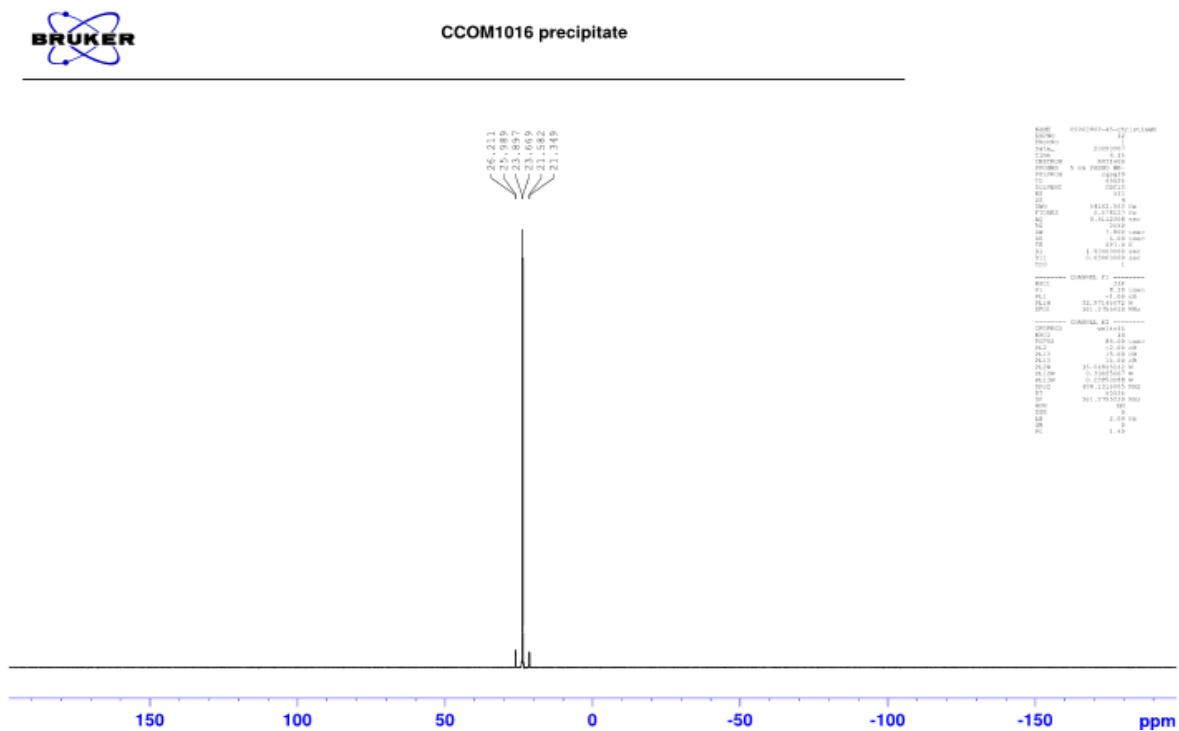


Figure S40  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of diselenide of **17b** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

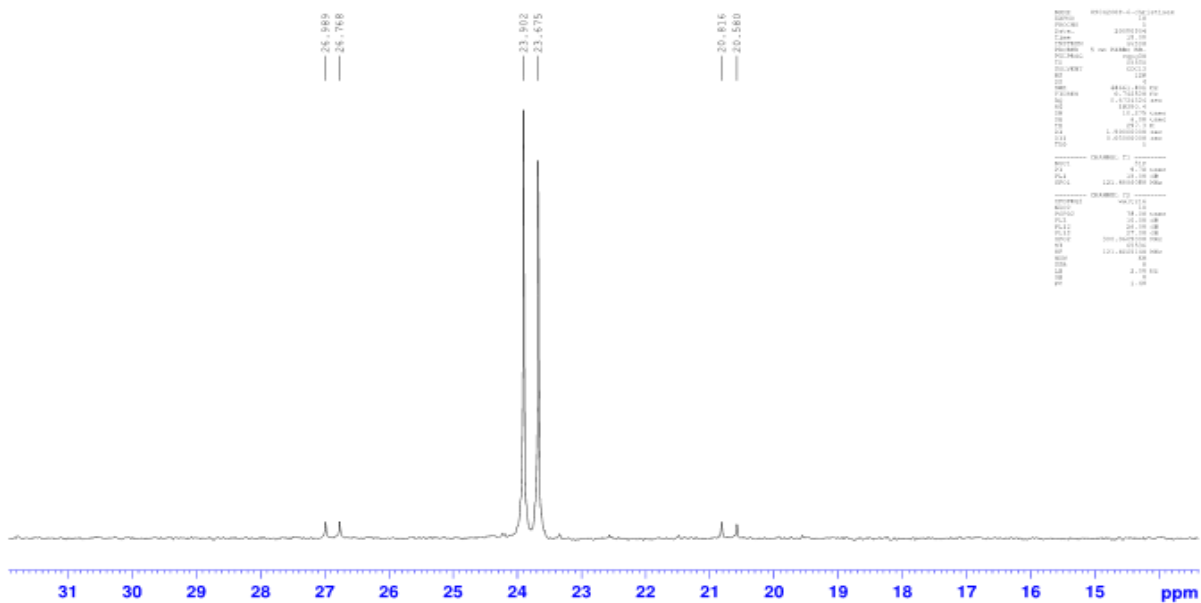


Figure S41  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of diselenide of 17c (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

13- Nickel complexes

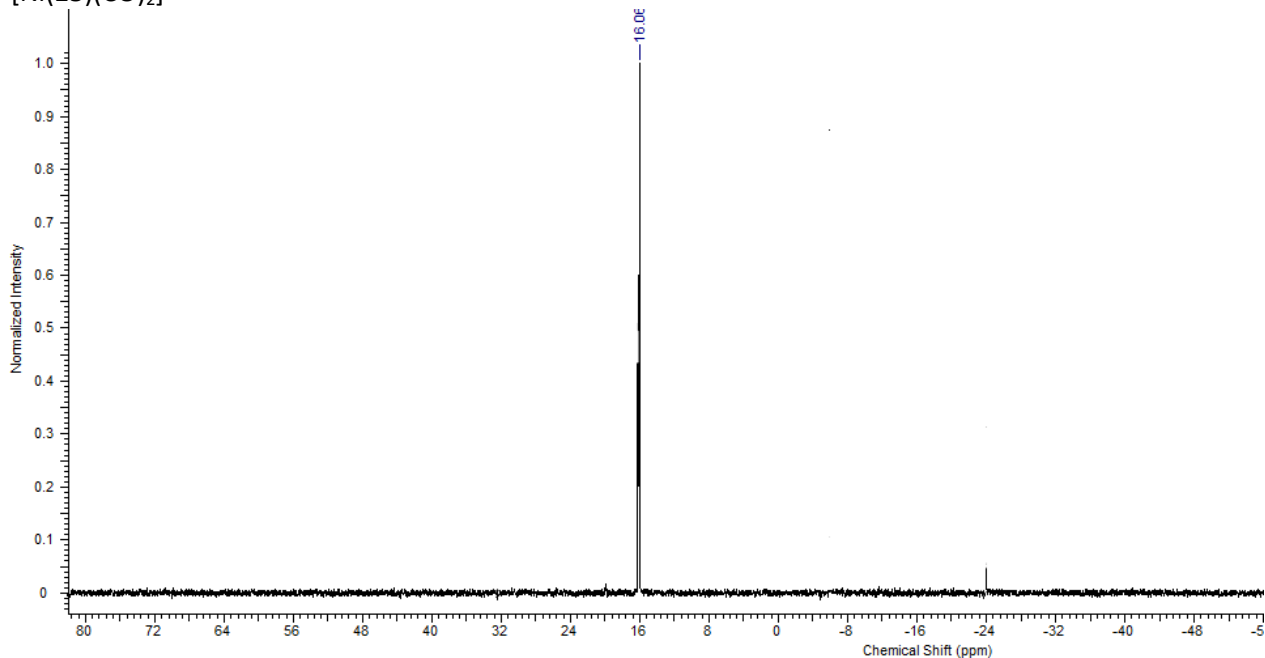
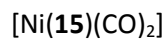


Figure S42  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(15)(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

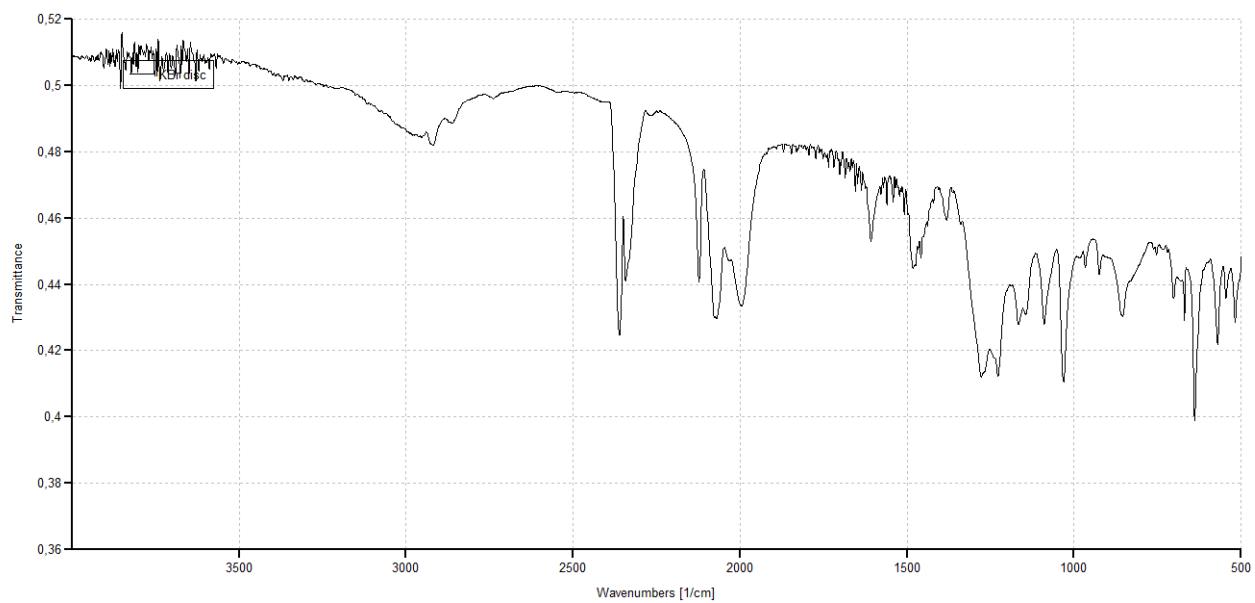


Figure S43 IR spectrum of  $[\text{Ni}(15)(\text{CO})_2]$  (KBr)

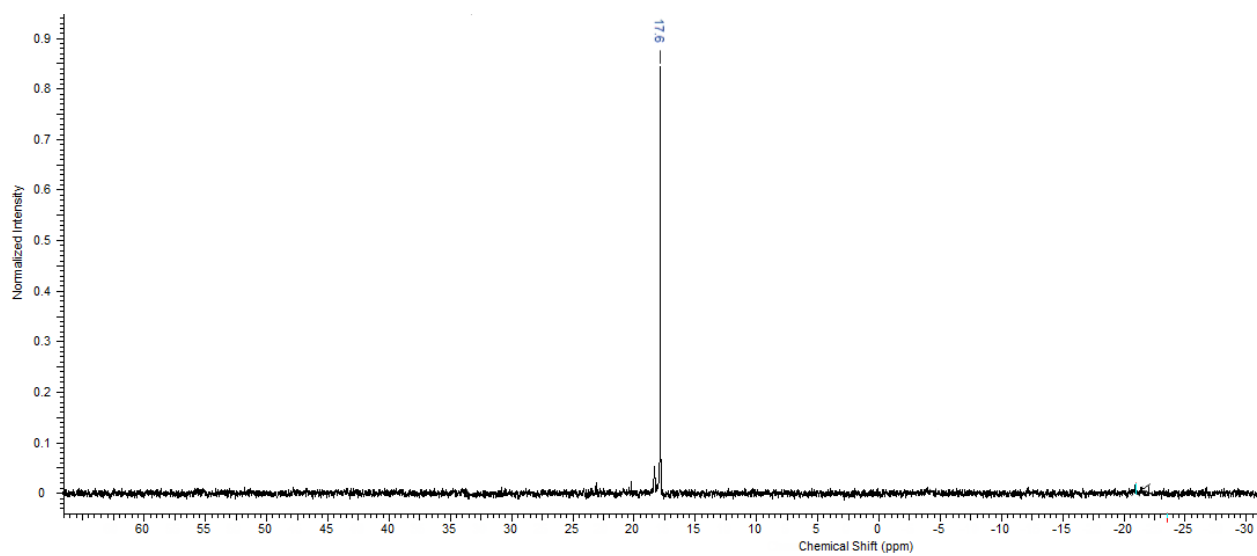


Figure S44  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{a})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

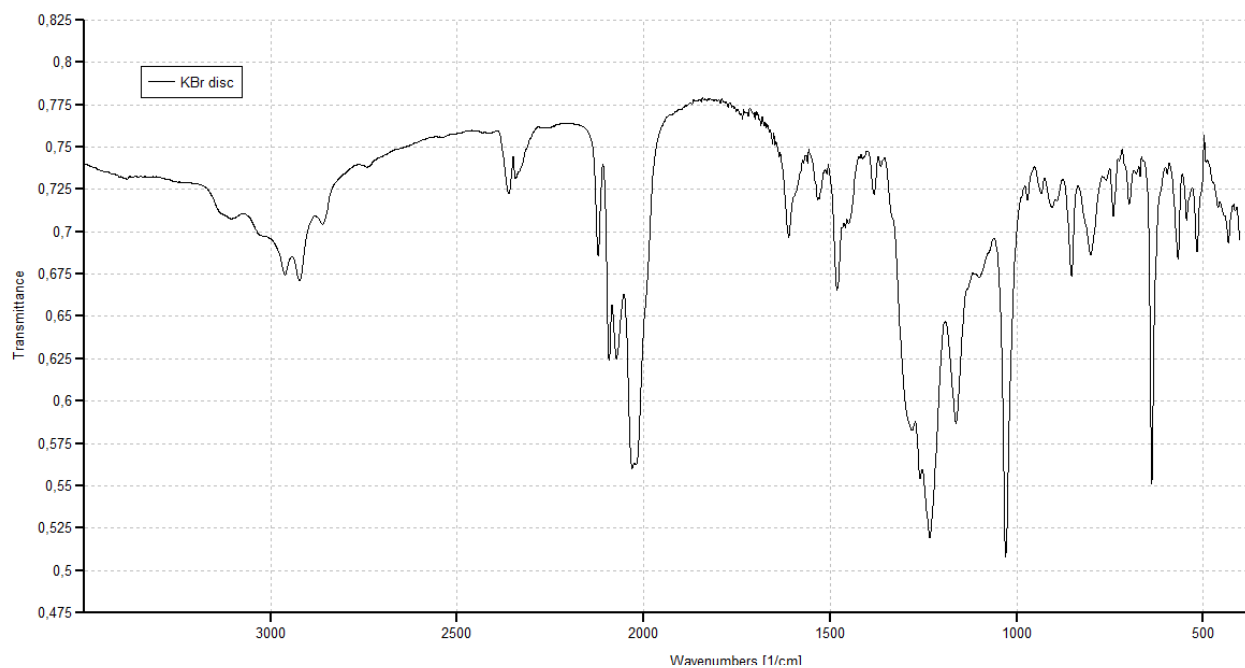


Figure S45 IR spectrum of  $[\text{Ni}(17\text{a})(\text{CO})_2]$  (KBr)

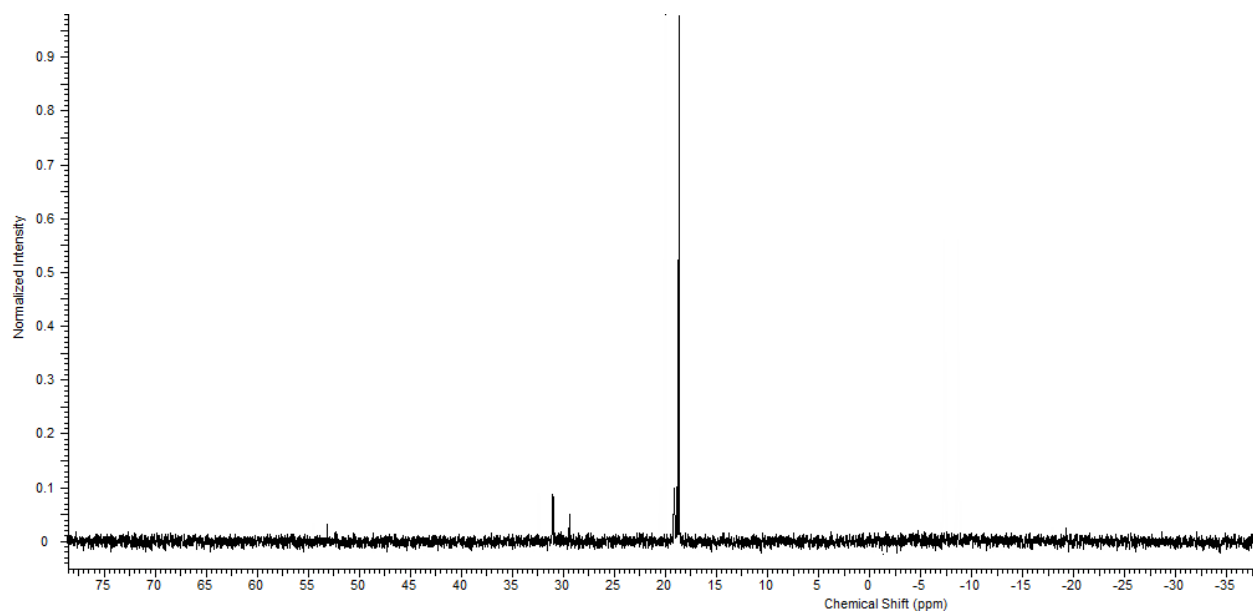


Figure S46  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{b})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



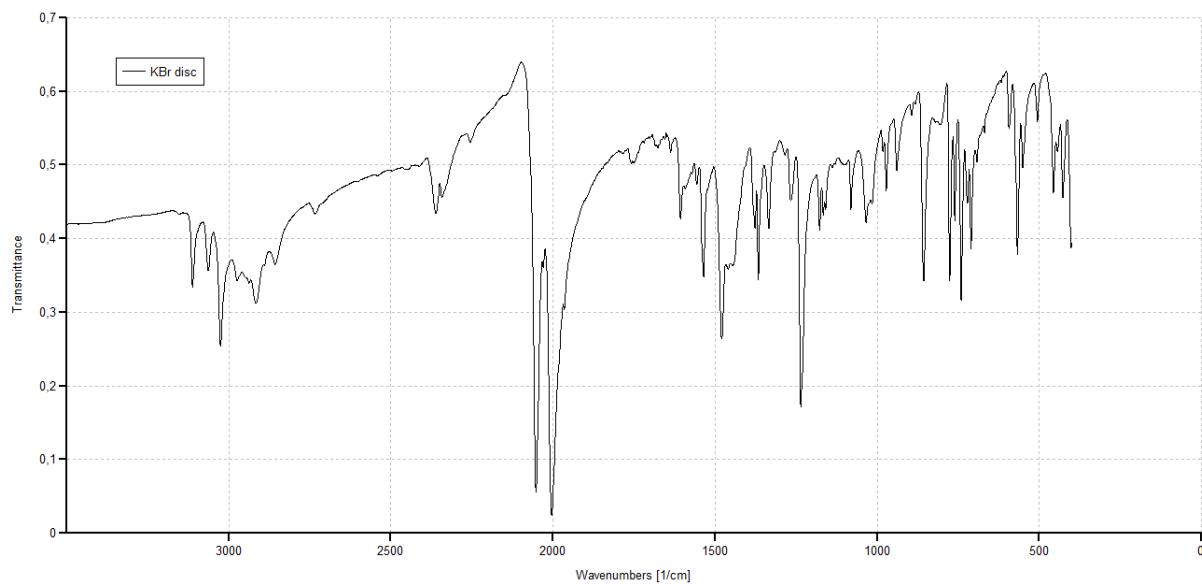


Figure S47 IR spectrum of  $[\text{Ni}(17\text{b})(\text{CO})_2]$  (KBr)

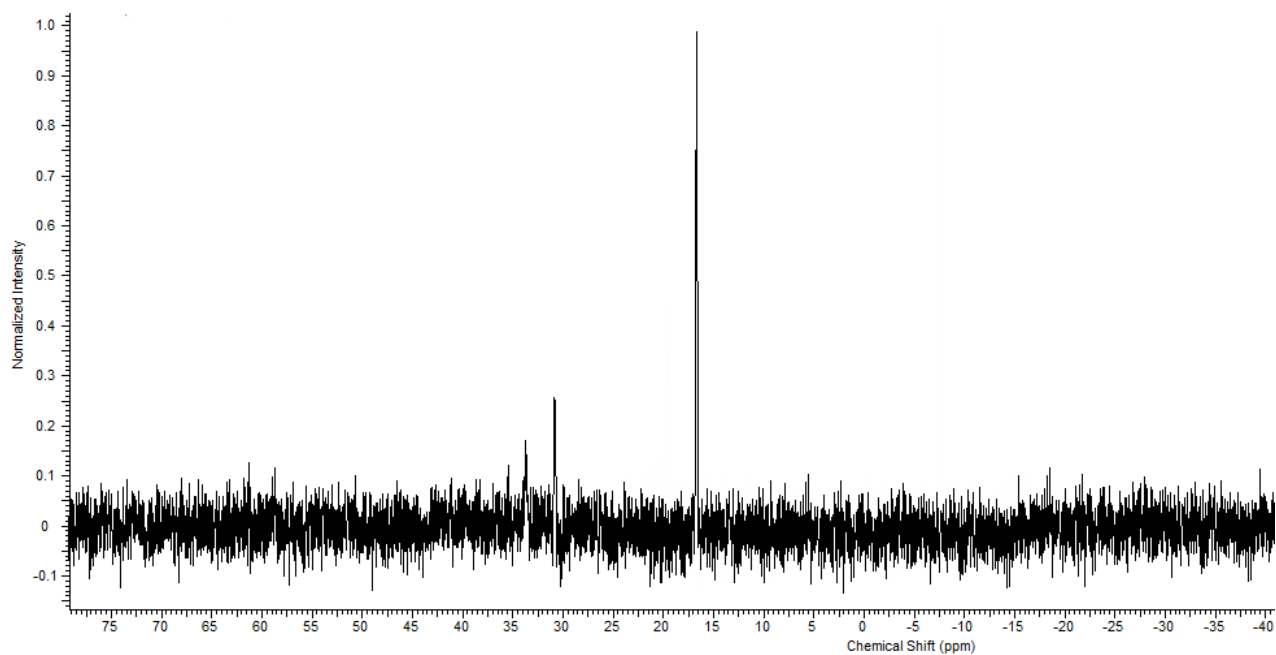


Figure S48  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{c})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

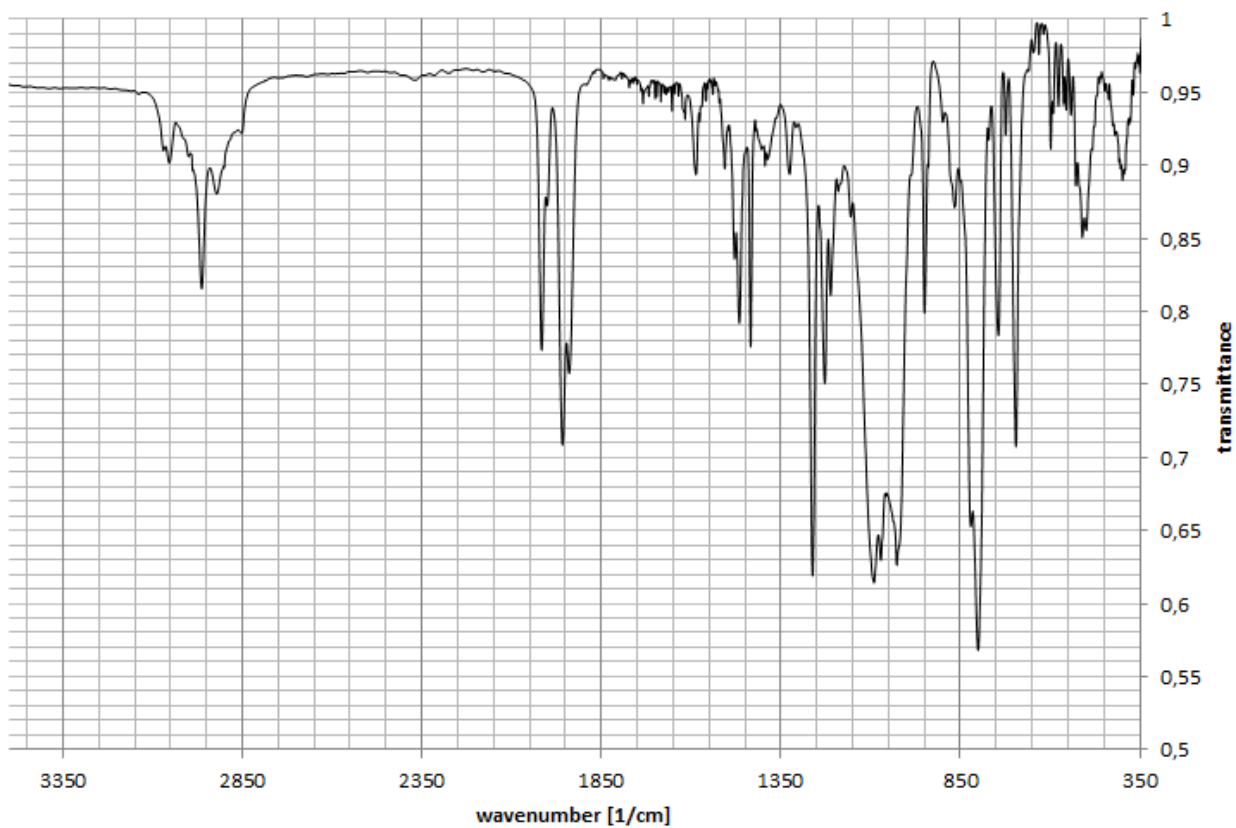


Figure S49 IR spectrum of  $[\text{Ni}(\mathbf{17c})(\text{CO})_2]$  (KBr)

#### 14- Palladium complexes

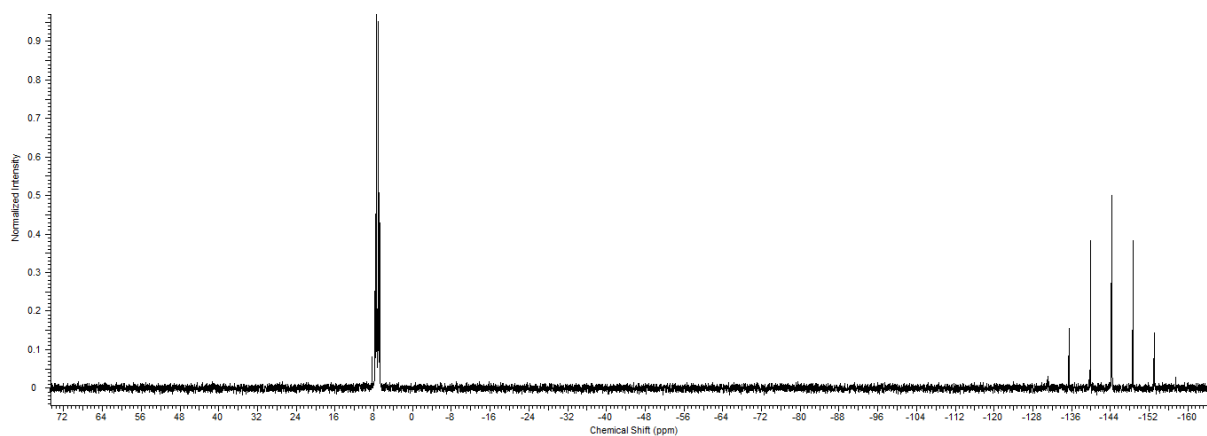


Figure S50  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(\mathbf{14})]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

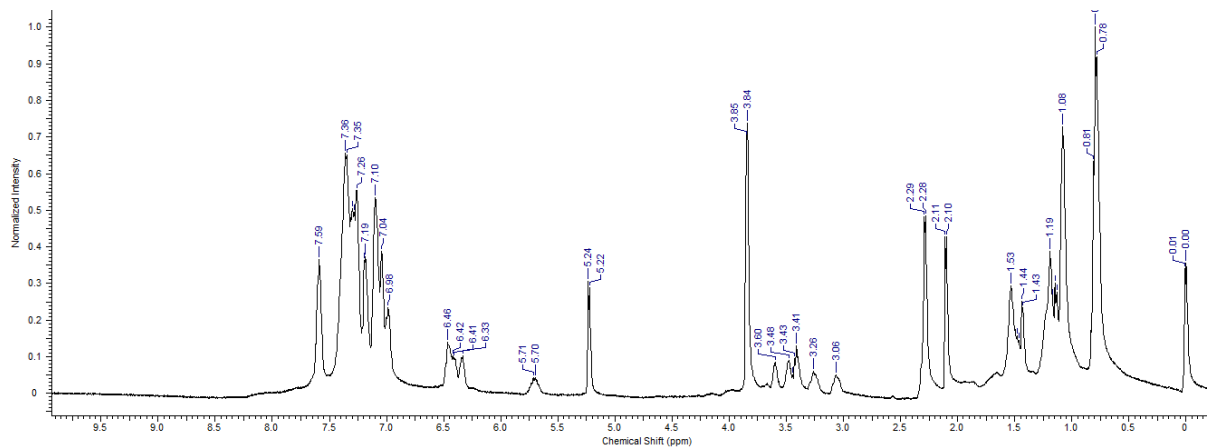


Figure S51  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(14)]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

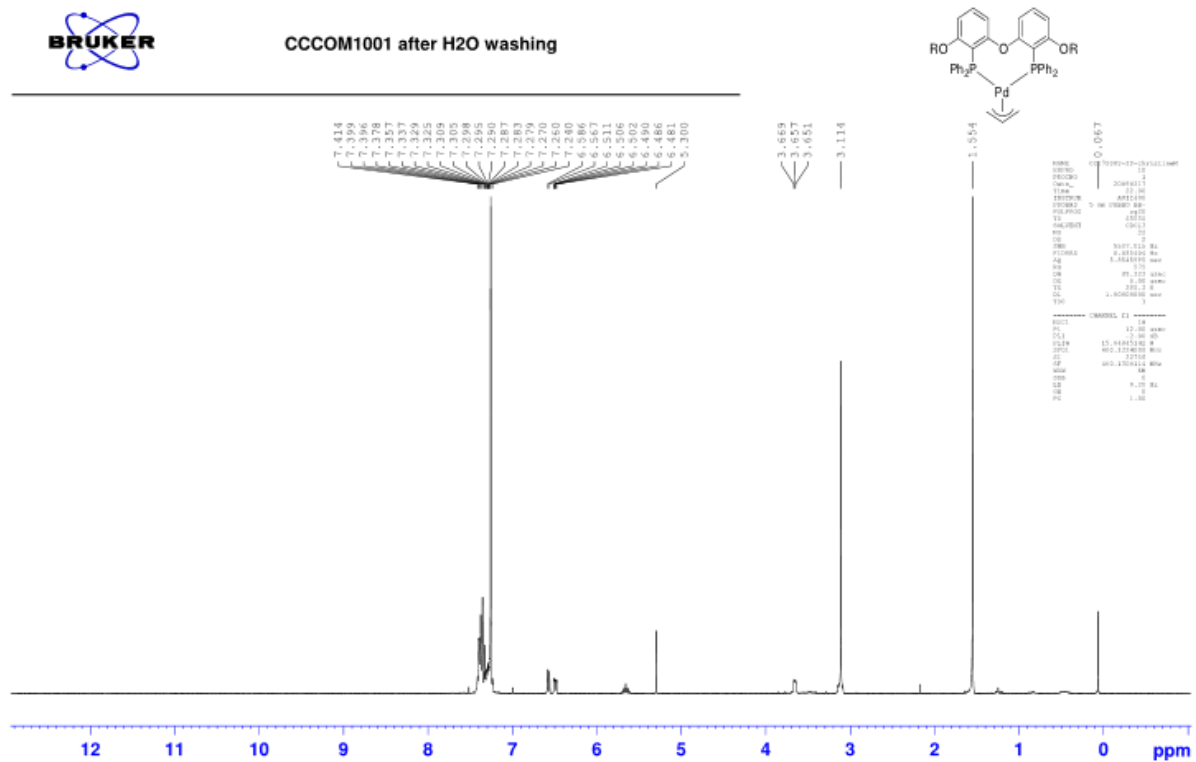


Figure S52  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CCCOM1001 after H2O washing

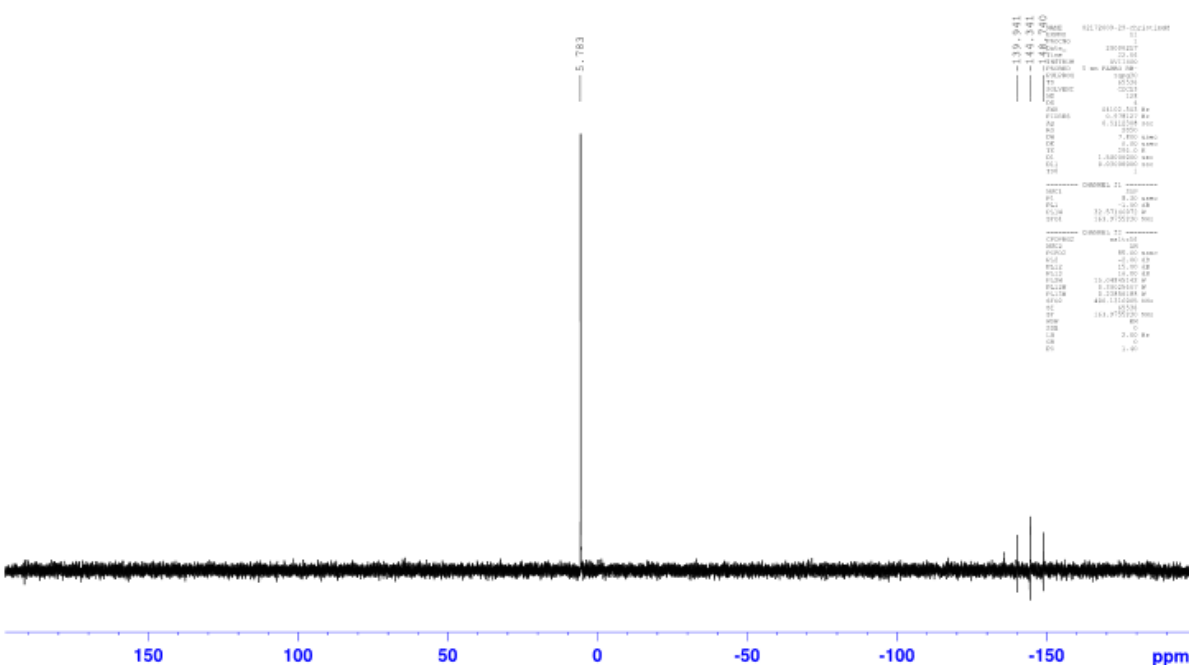
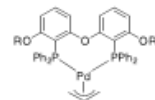


Figure S53  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$  (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CCCOM1001

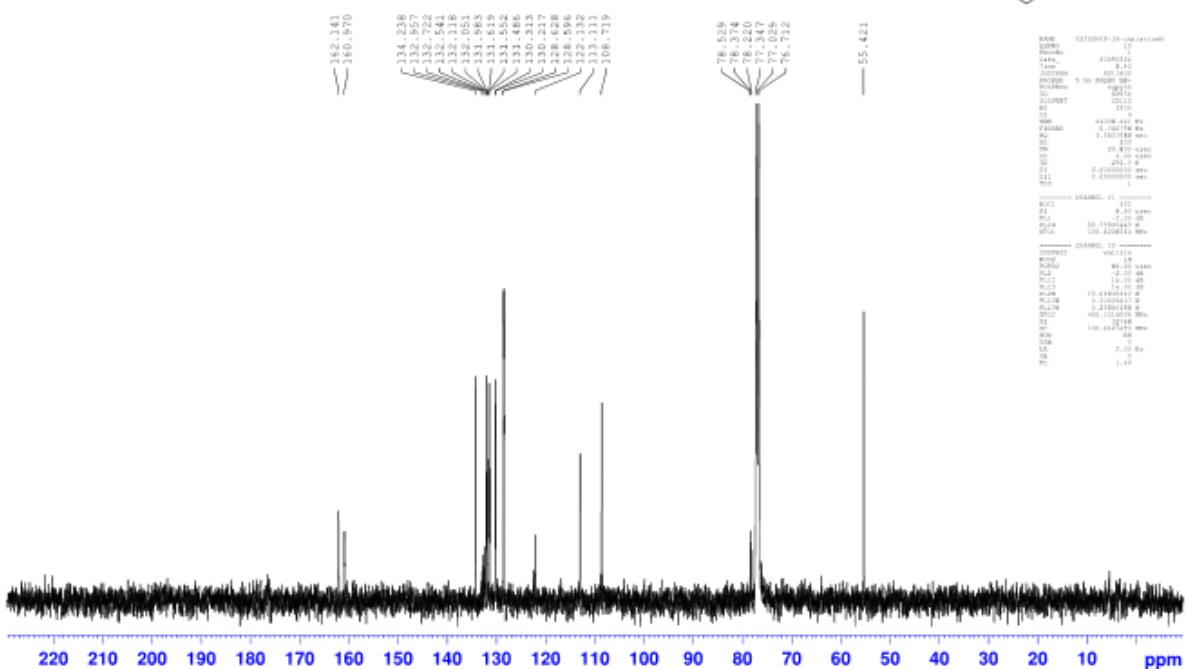
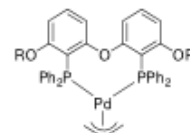
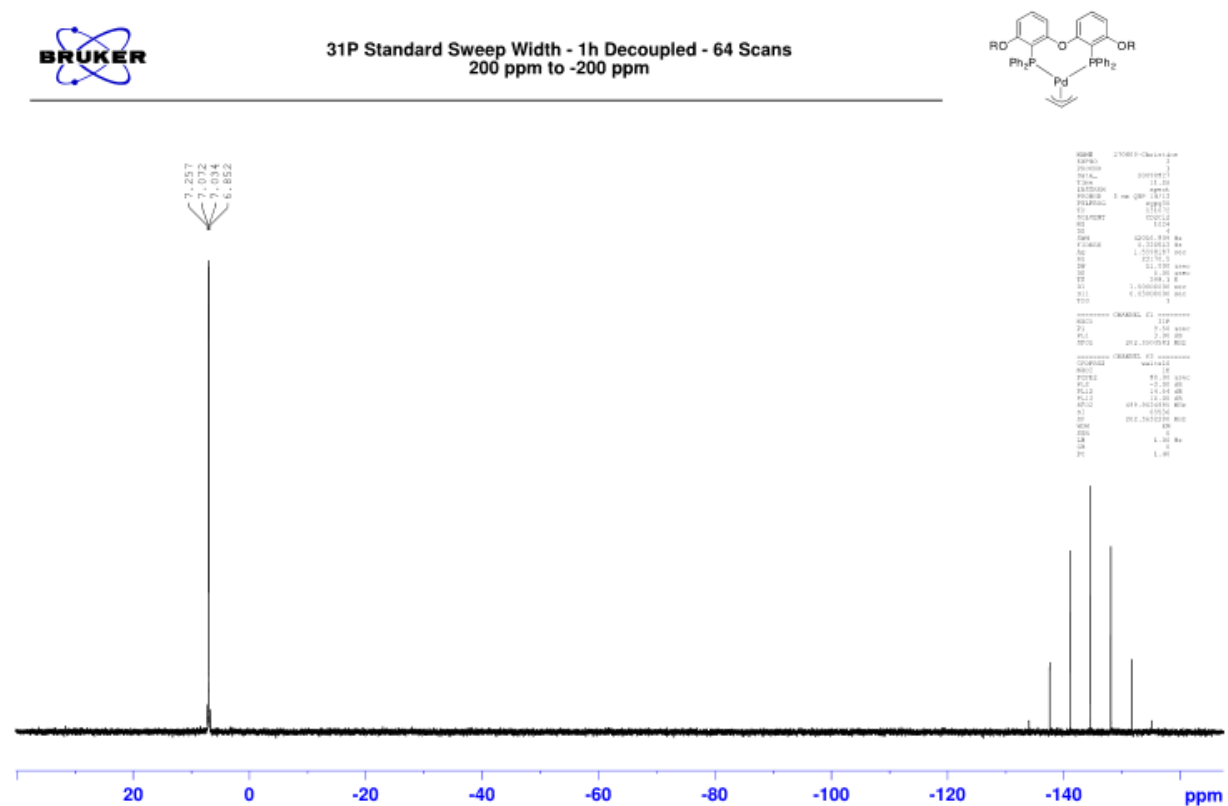
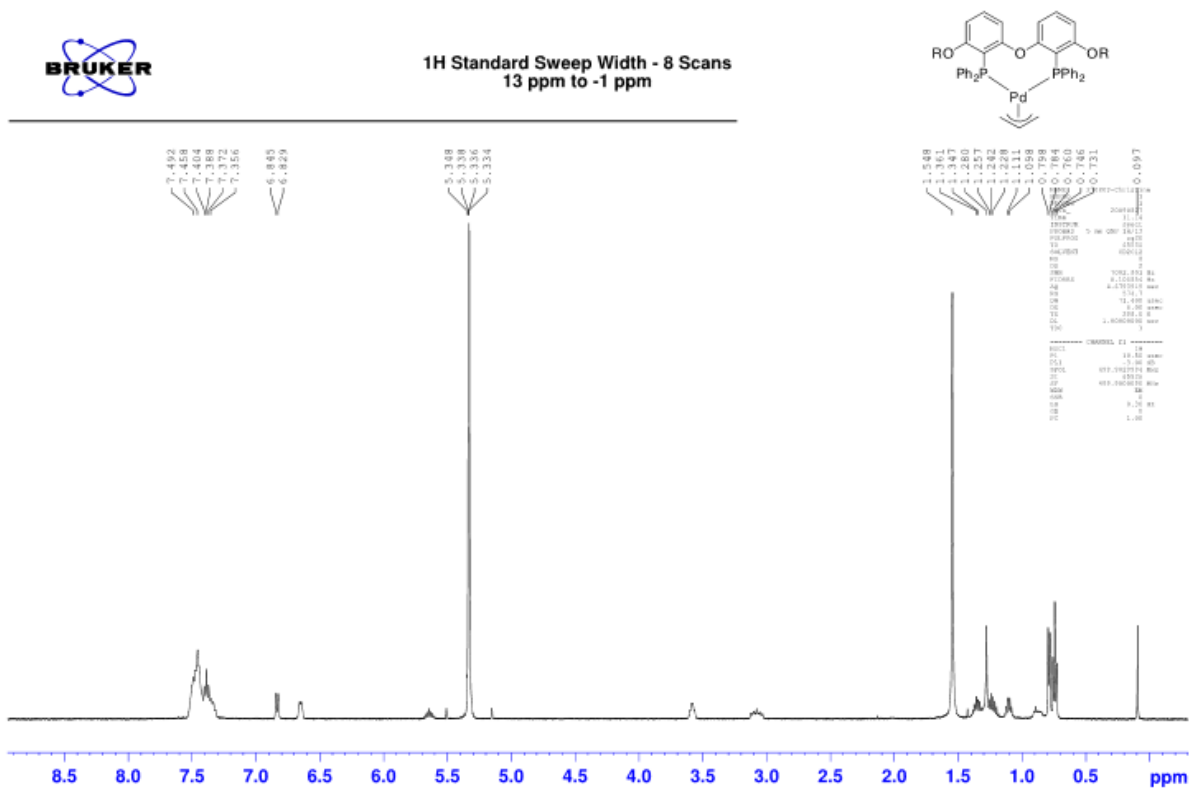


Figure S54  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)





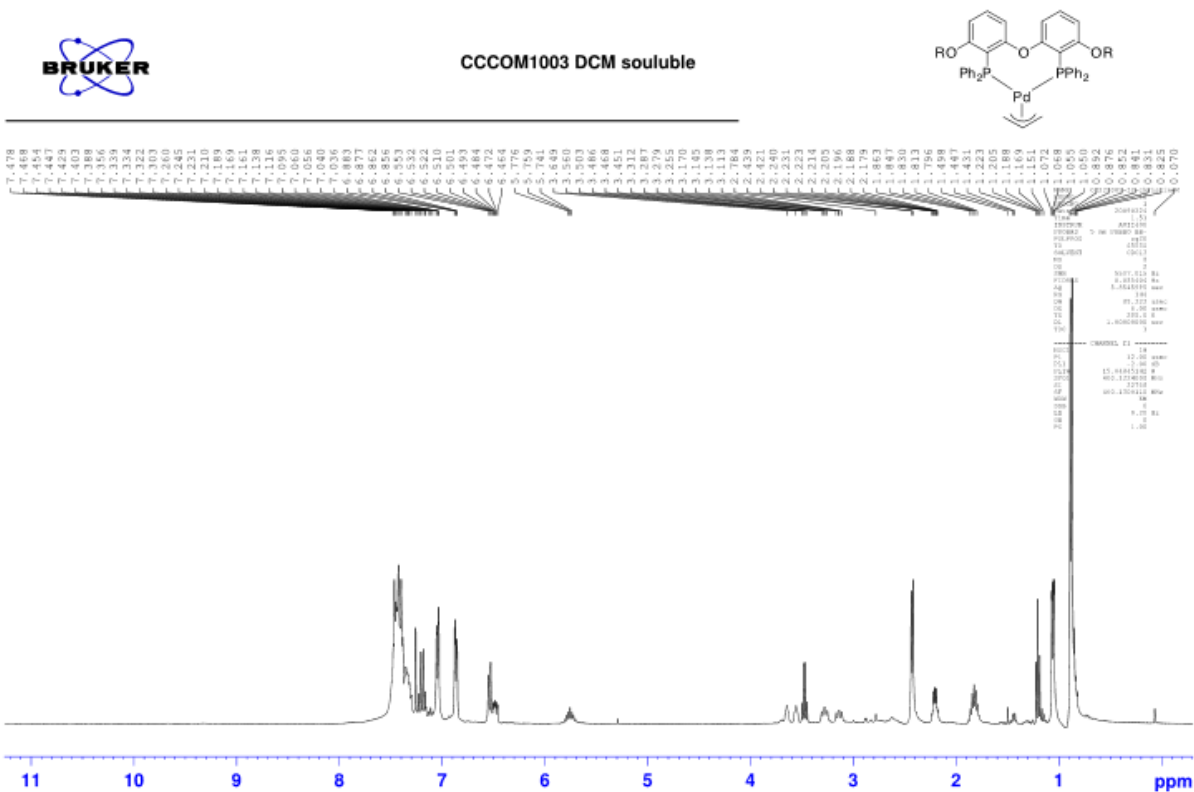


Figure S59  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{c})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

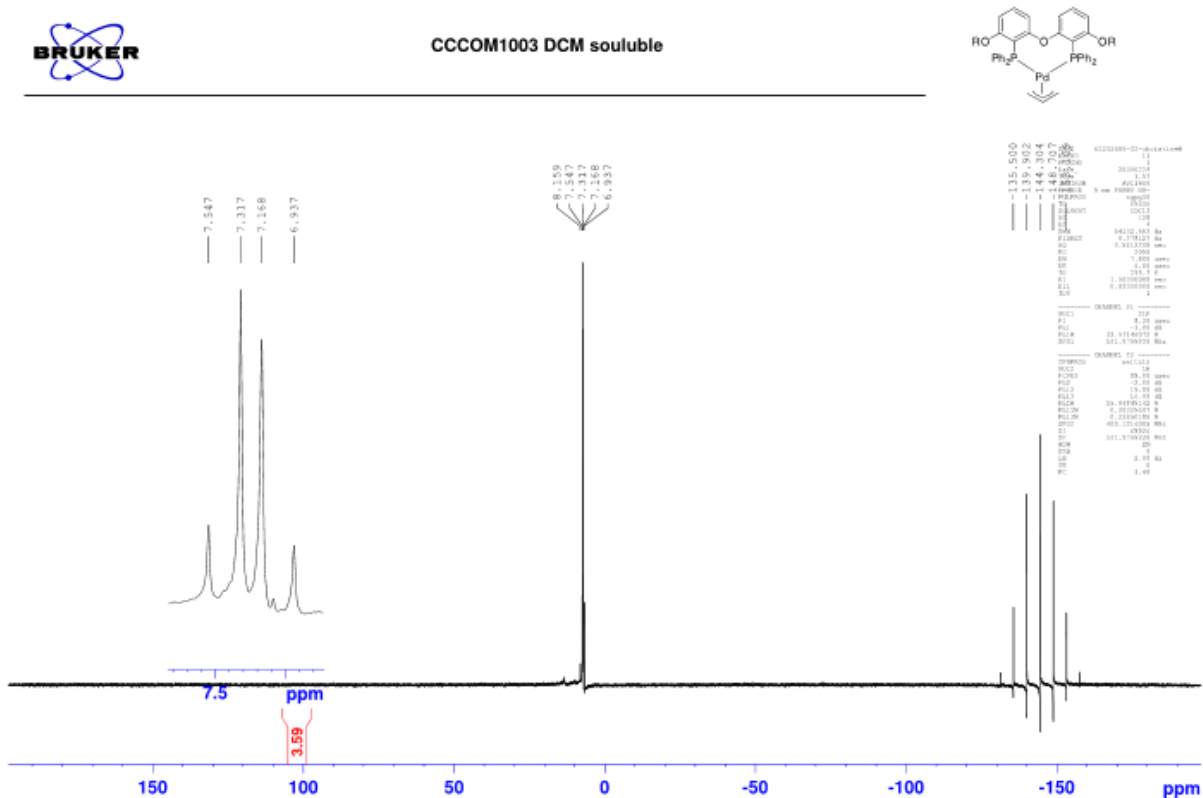


Figure S60  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{c})]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CCCOM1006 precip

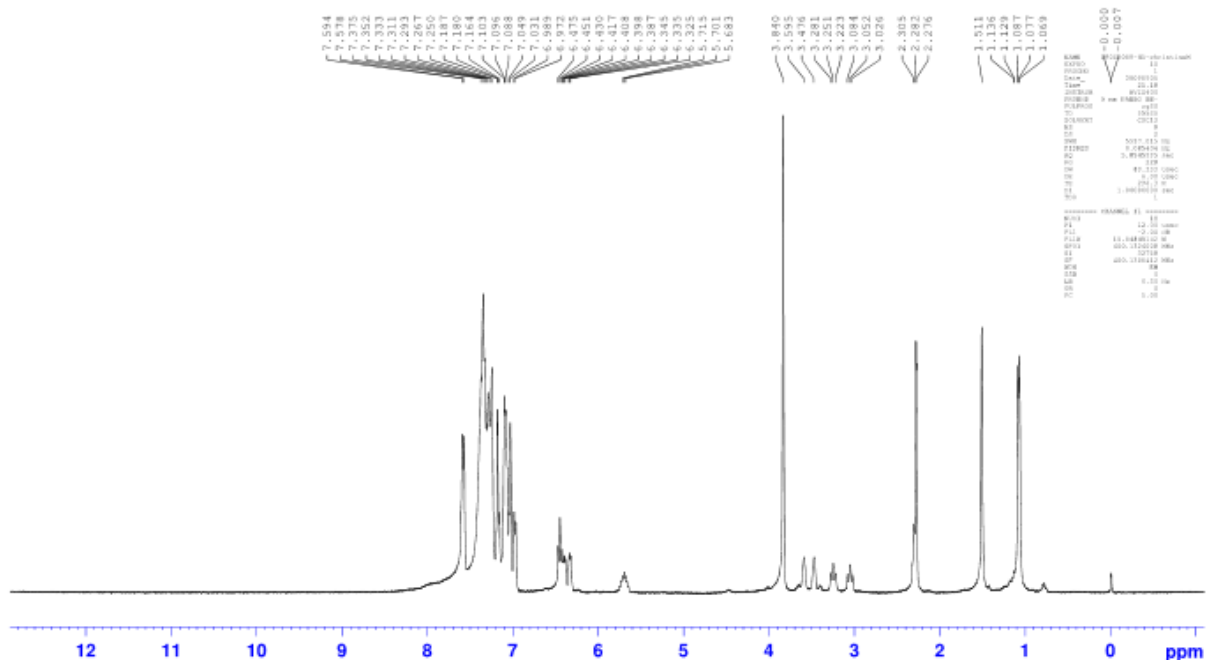
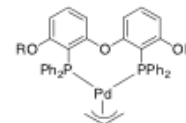


Figure S61  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{d})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

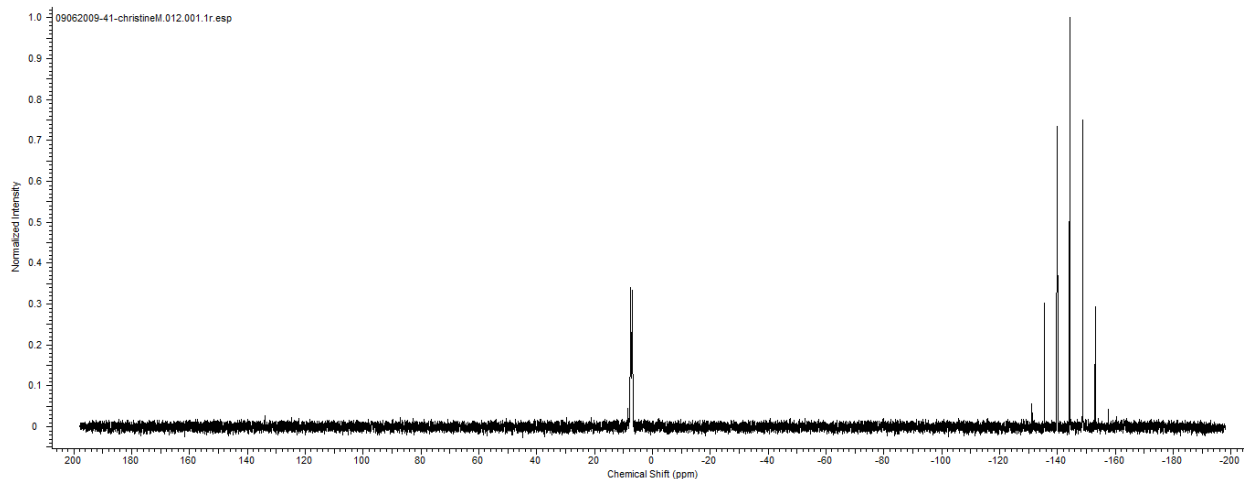


Figure S62  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{d})]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)