

Supporting Information

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

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1- Compound 11F

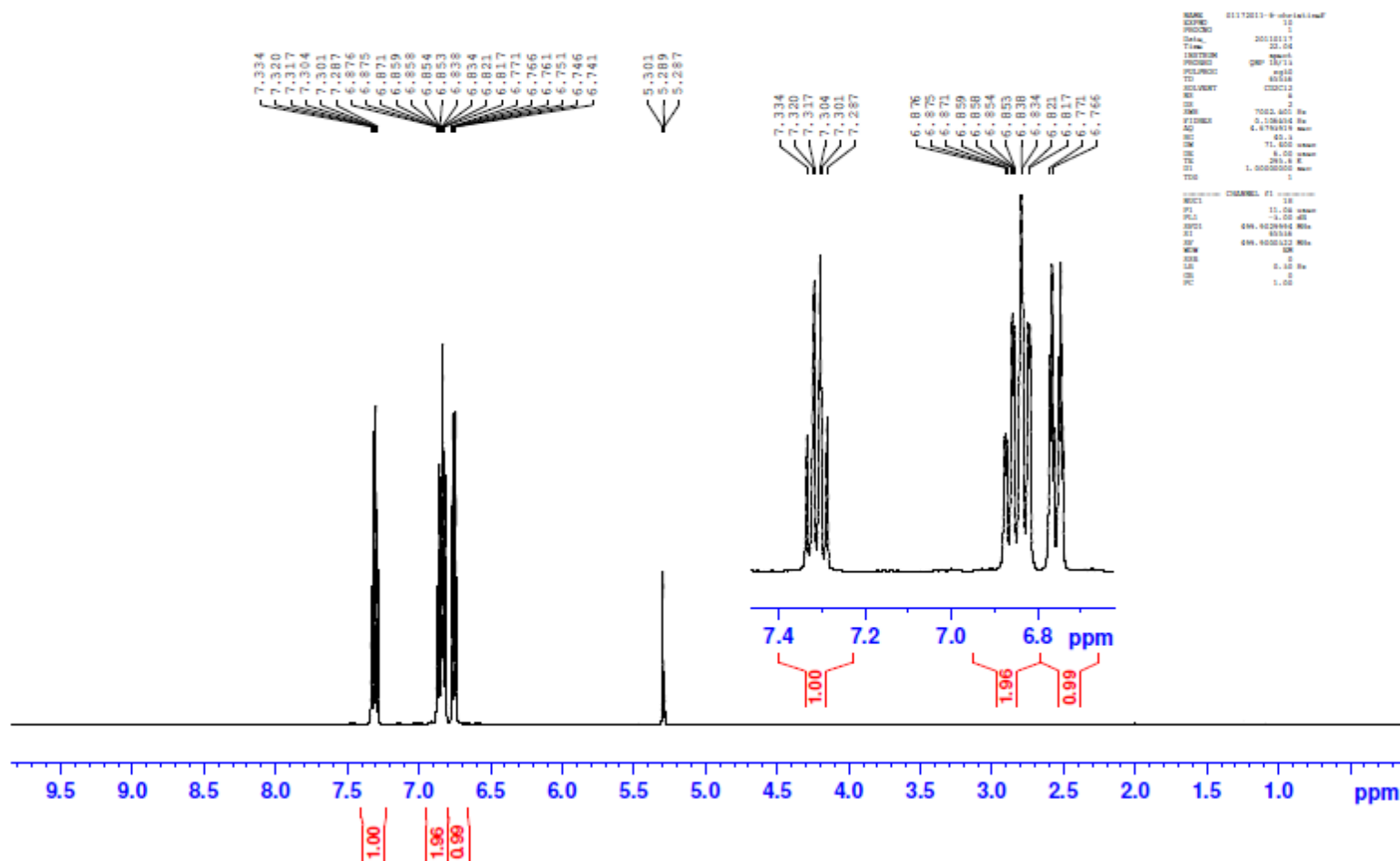
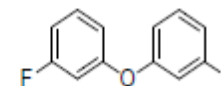


Figure S1 ¹H NMR spectrum of compound 11F (500 MHz, CD₂Cl₂, 296 K)

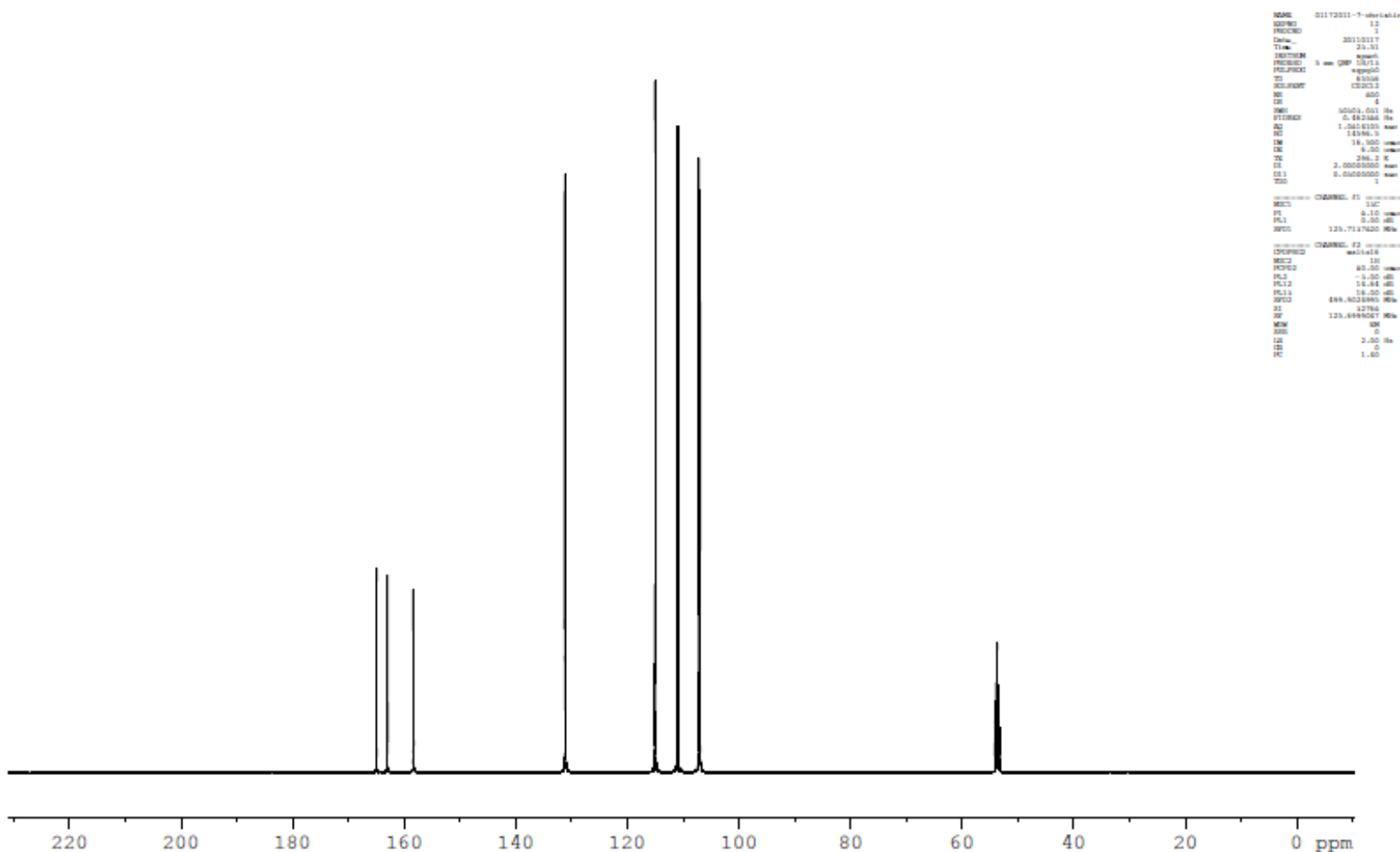
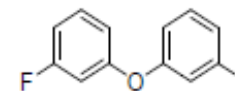


Figure S2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 11F (126 MHz, CD_2Cl_2 , 295 K)



CC5077

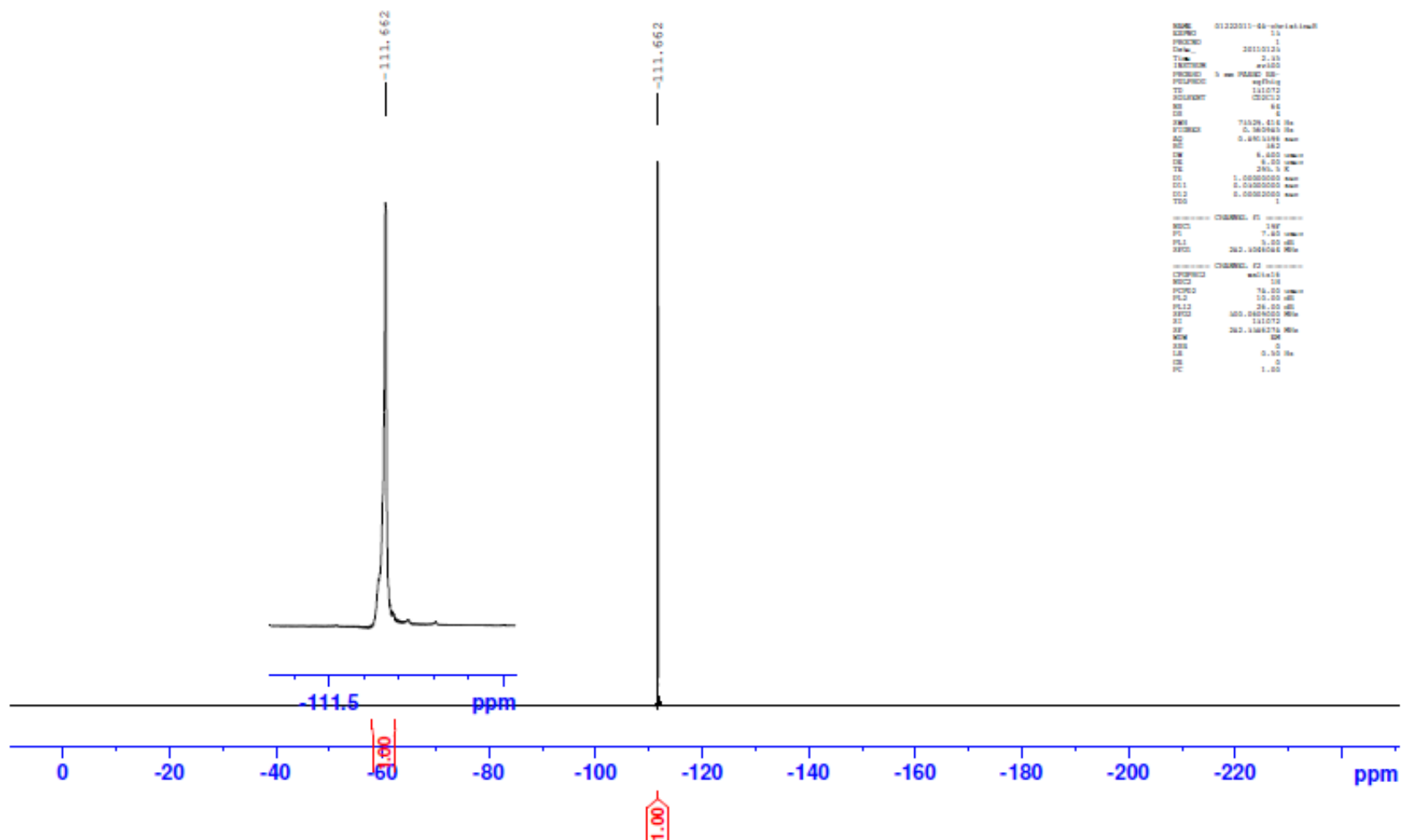
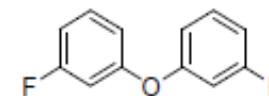


Figure S3 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of compound 11F (282 MHz, CD_2Cl_2 , 295 K)

2- Compound 11OMe



CC1073

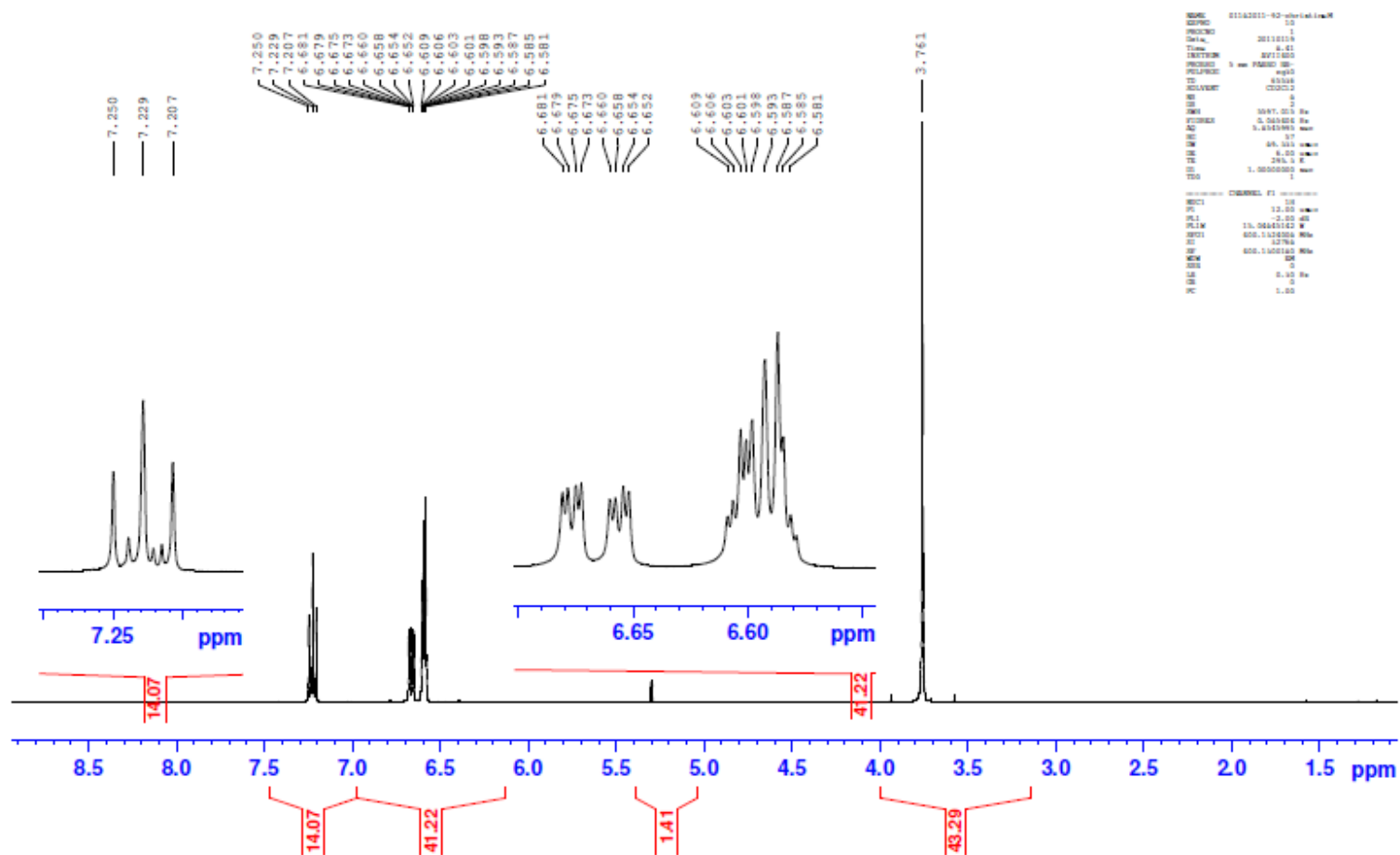
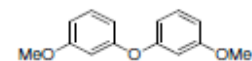


Figure S4 ^1H NMR spectrum of compound 11OMe (400 MHz, CD_2Cl_2 , 295 K)



CC1073

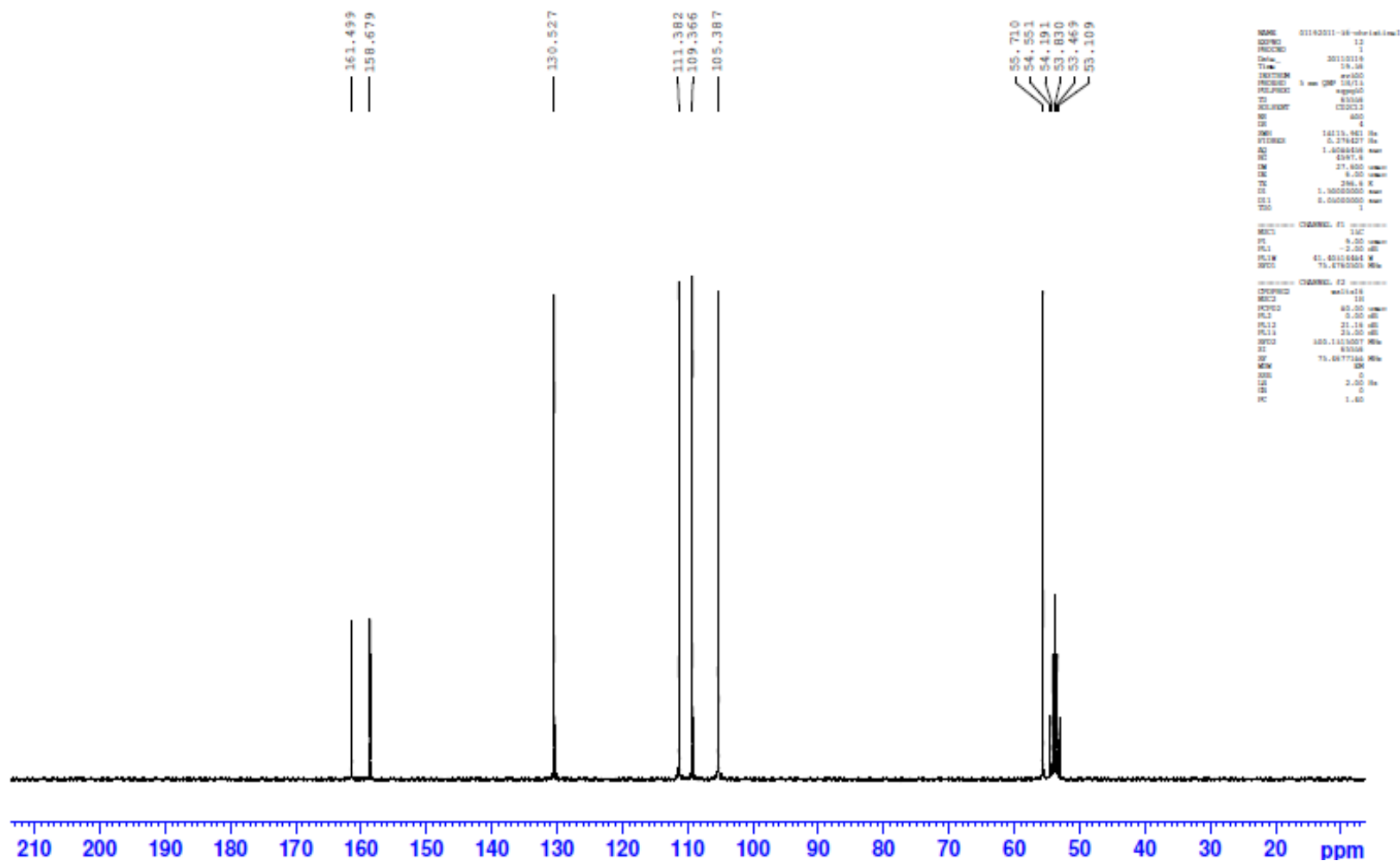
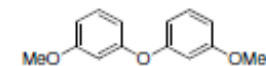


Figure S5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 11OMe (75 MHz, CD_2Cl_2 , 295 K)



CC1073

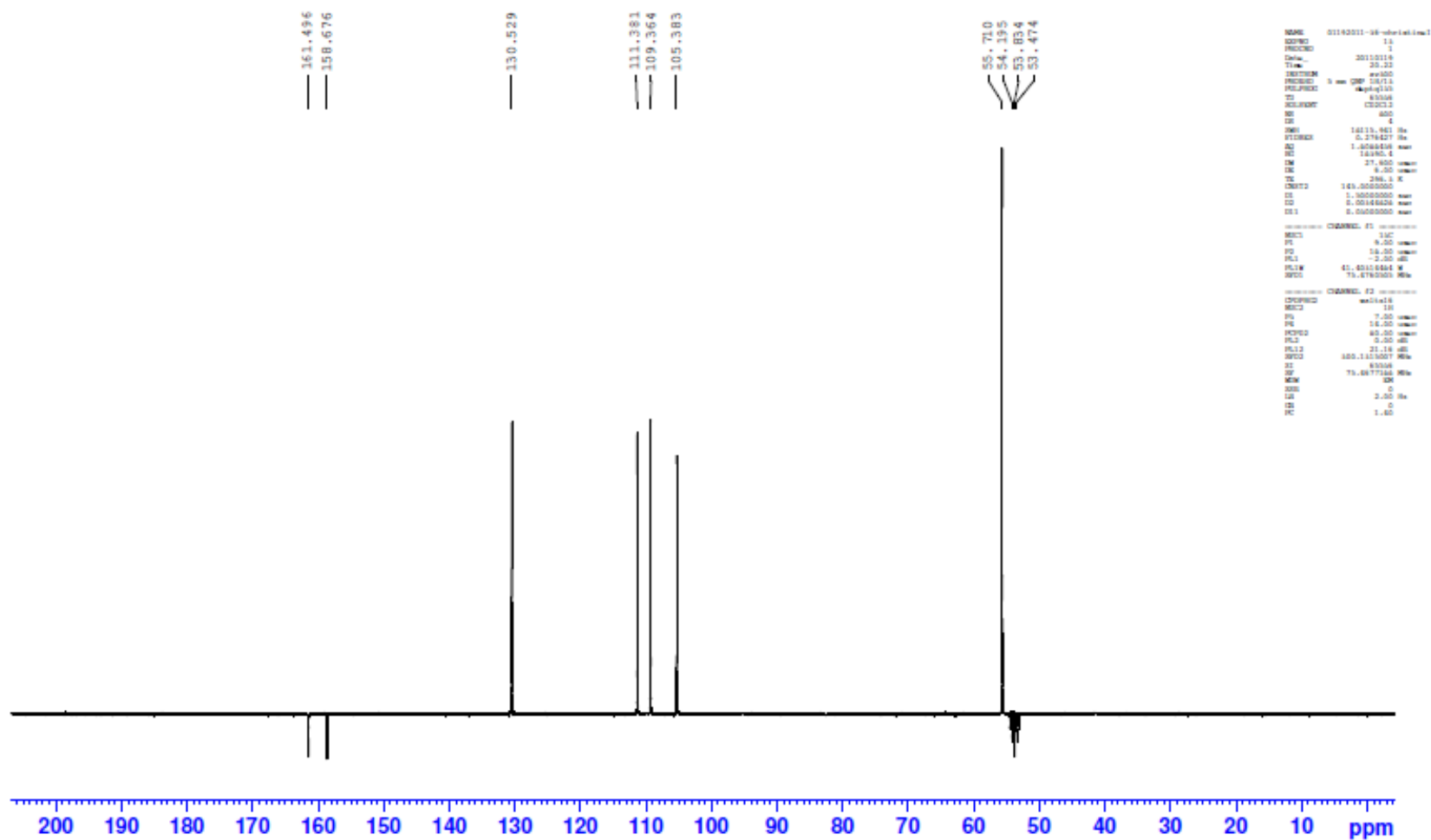
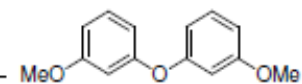


Figure S6 ^{13}C APT NMR spectrum of compound 11OMe (75 MHz, CD_2Cl_2 , 295 K)

3- Compound 12



CC2082

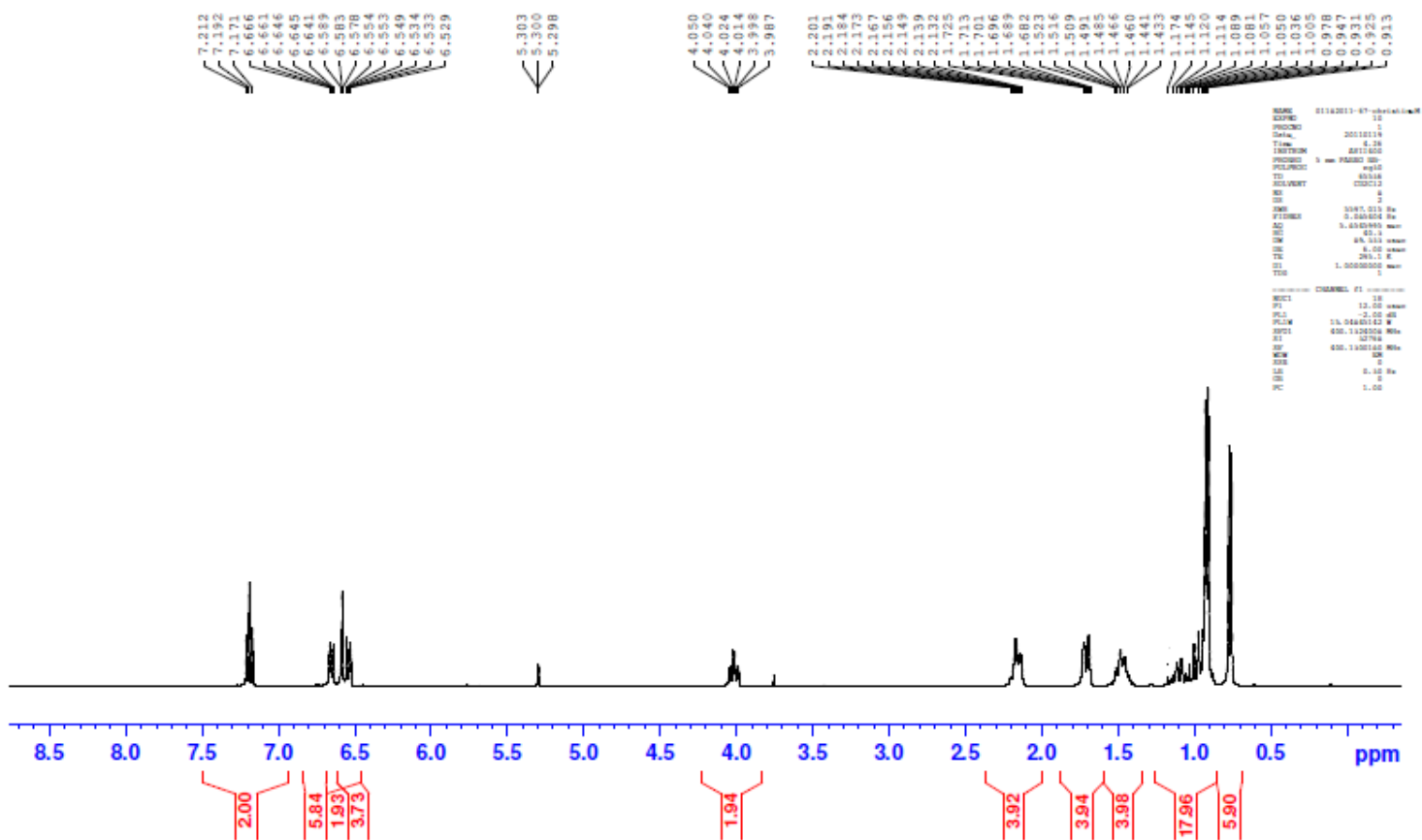
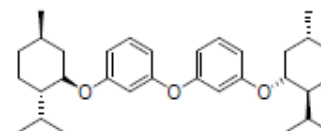
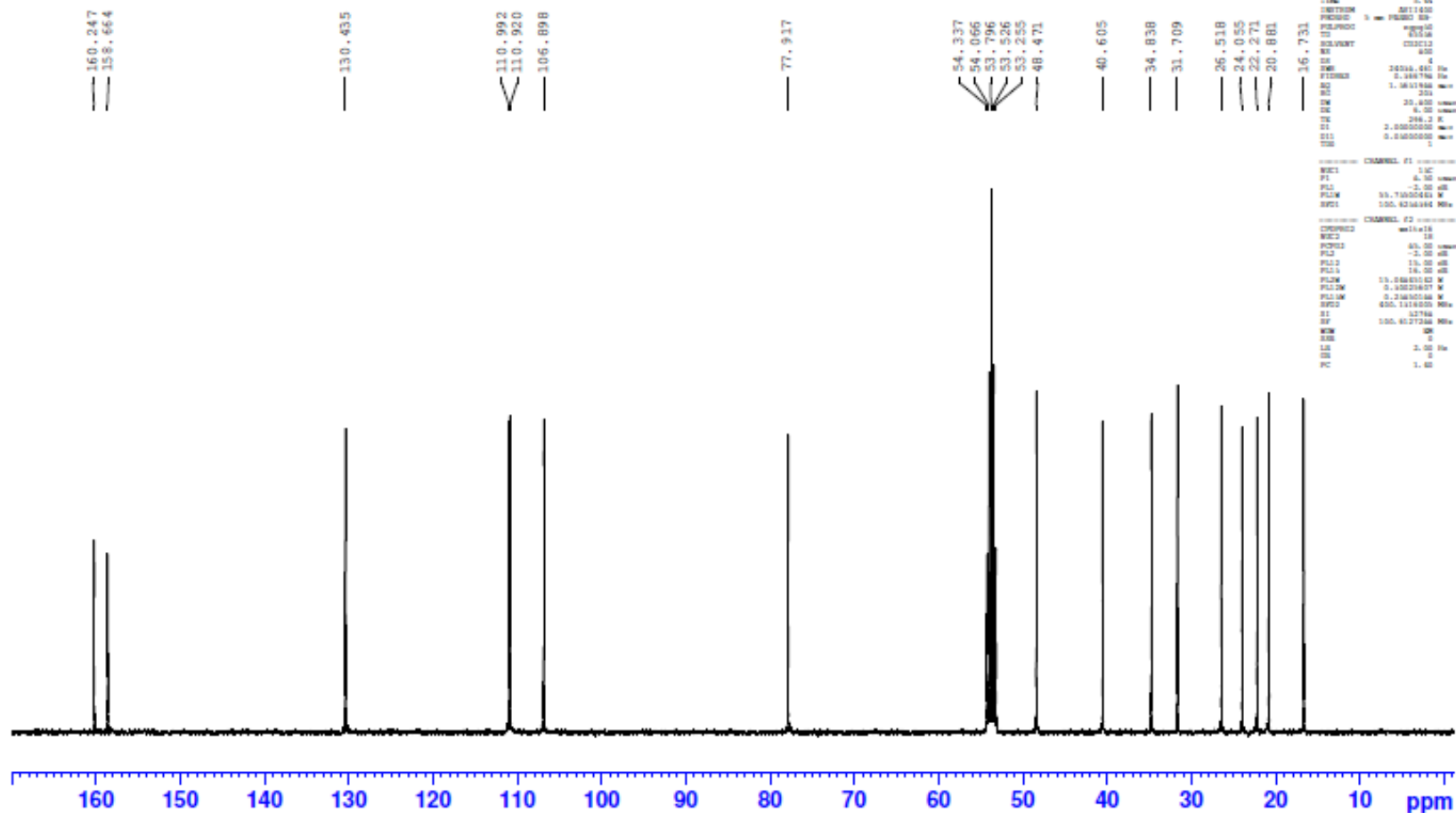
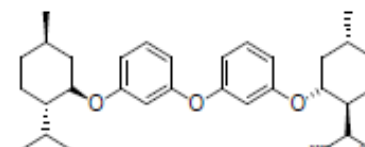


Figure S7 ^1H NMR spectrum of compound 12 (400 MHz, CD_2Cl_2 , 295 K)



CC5082 after gCMS check



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FIDRES: 0.244766 Hz
AQ: 0.1801866 sec
RG: 201
DE: 0.0010000000000000000
TE: 298.2 K
D1: 2.00000000 sec
d11: 0.00000000 sec
TD0: 5

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P1: 4.00 usec
PL1: -2.00 dB
PL12: 19.70000000 W
SFO1: 100.6261800 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: 1H
P2: 12.00 usec
PL2: -2.00 dB
PL13: 19.00000000 W
PL14: 19.00000000 W
PL15: 19.00000000 W
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PL17: 19.00000000 W
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PL99: 19.00000000 W
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Figure S8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 12 (101 MHz, CD_2Cl_2 , 295 K)

4- Compound 13

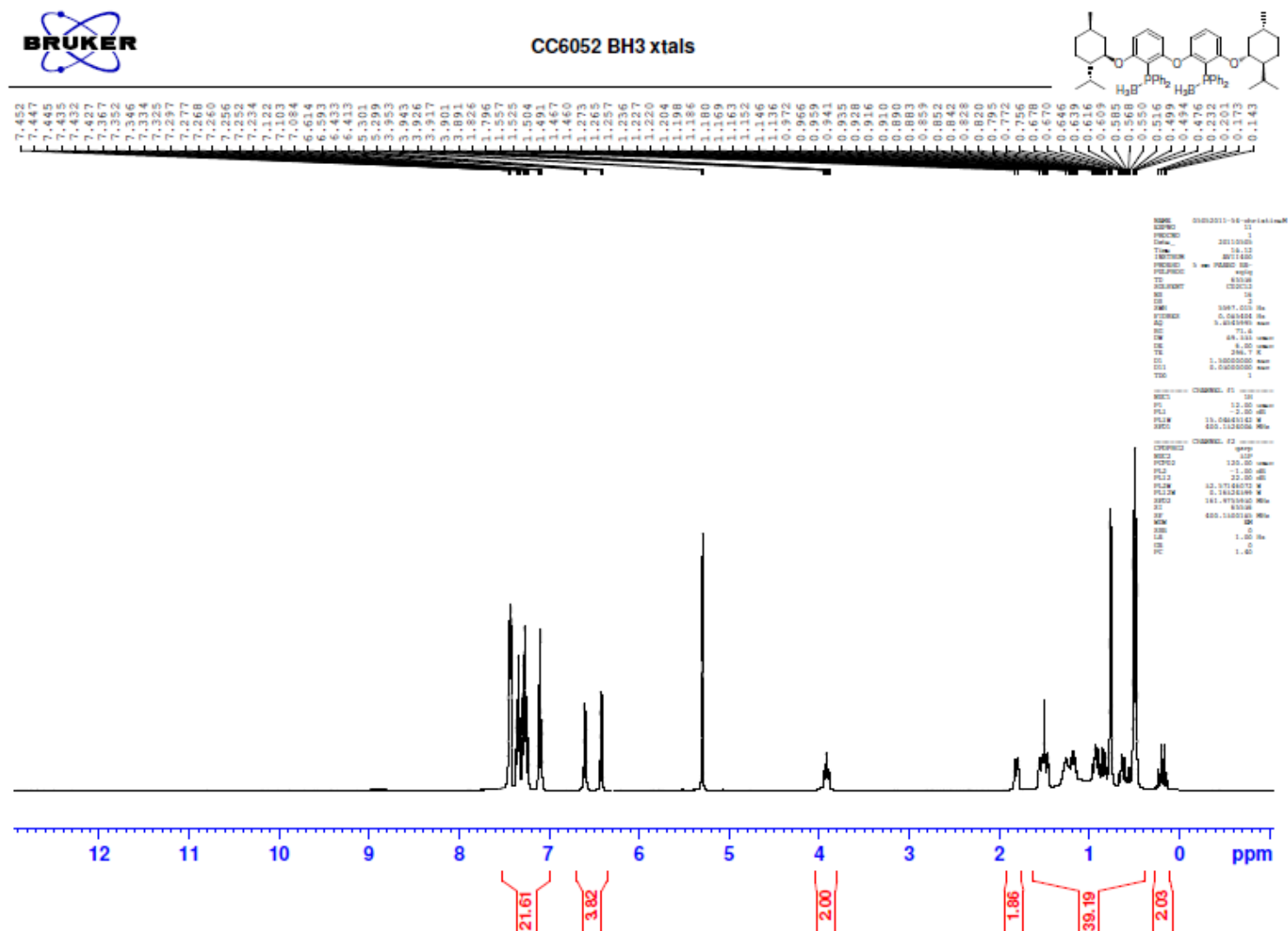


Figure S9 ¹H NMR spectrum of compound 13 (400 MHz, CD₂Cl₂, 296 K)



CC6052 BH3 xtals

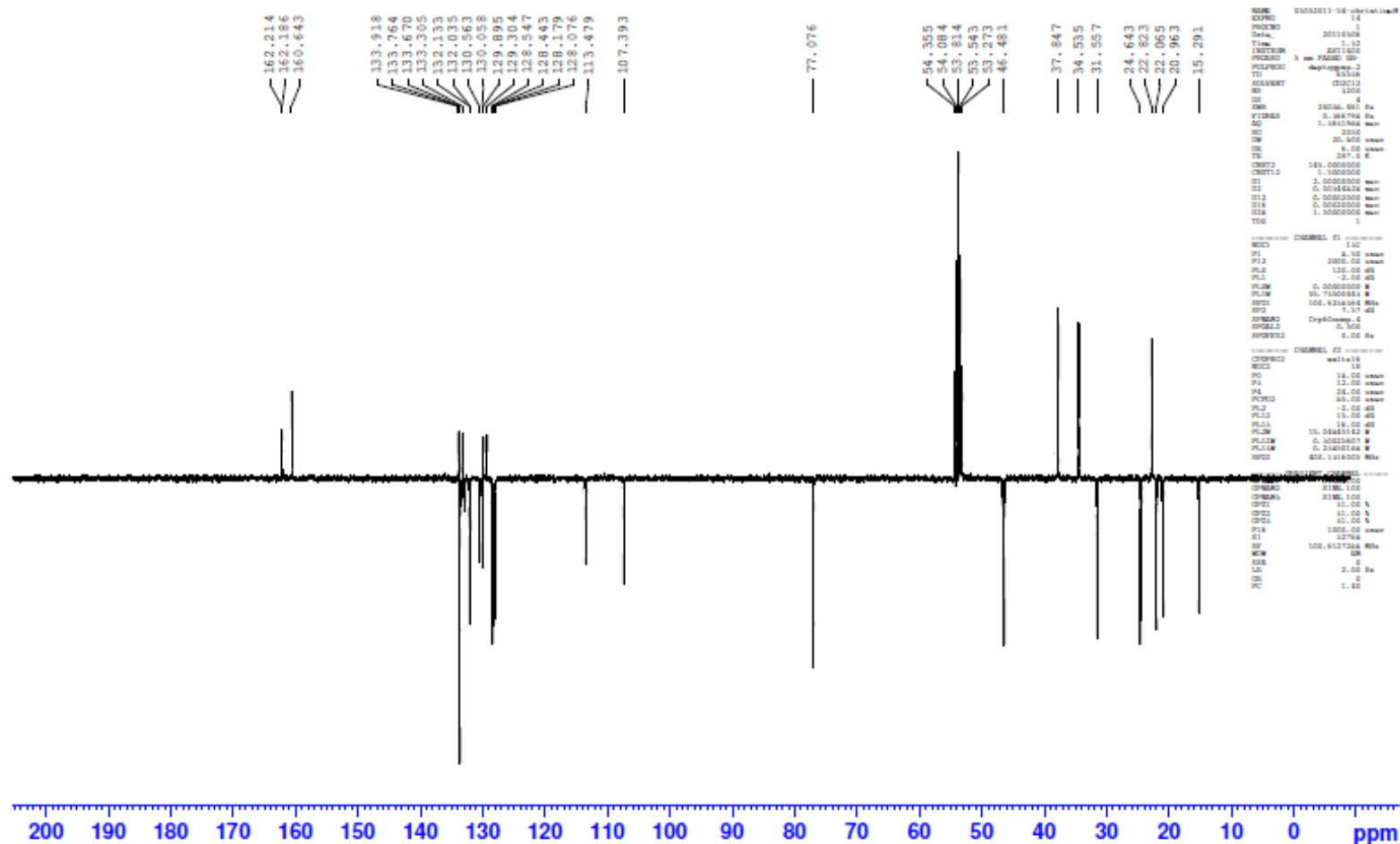
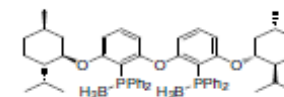


Figure S10 ¹³C APT NMR spectrum of compound 13 (101 MHz, CD₂Cl₂, 296 K)



CC6052 BH3 xtals

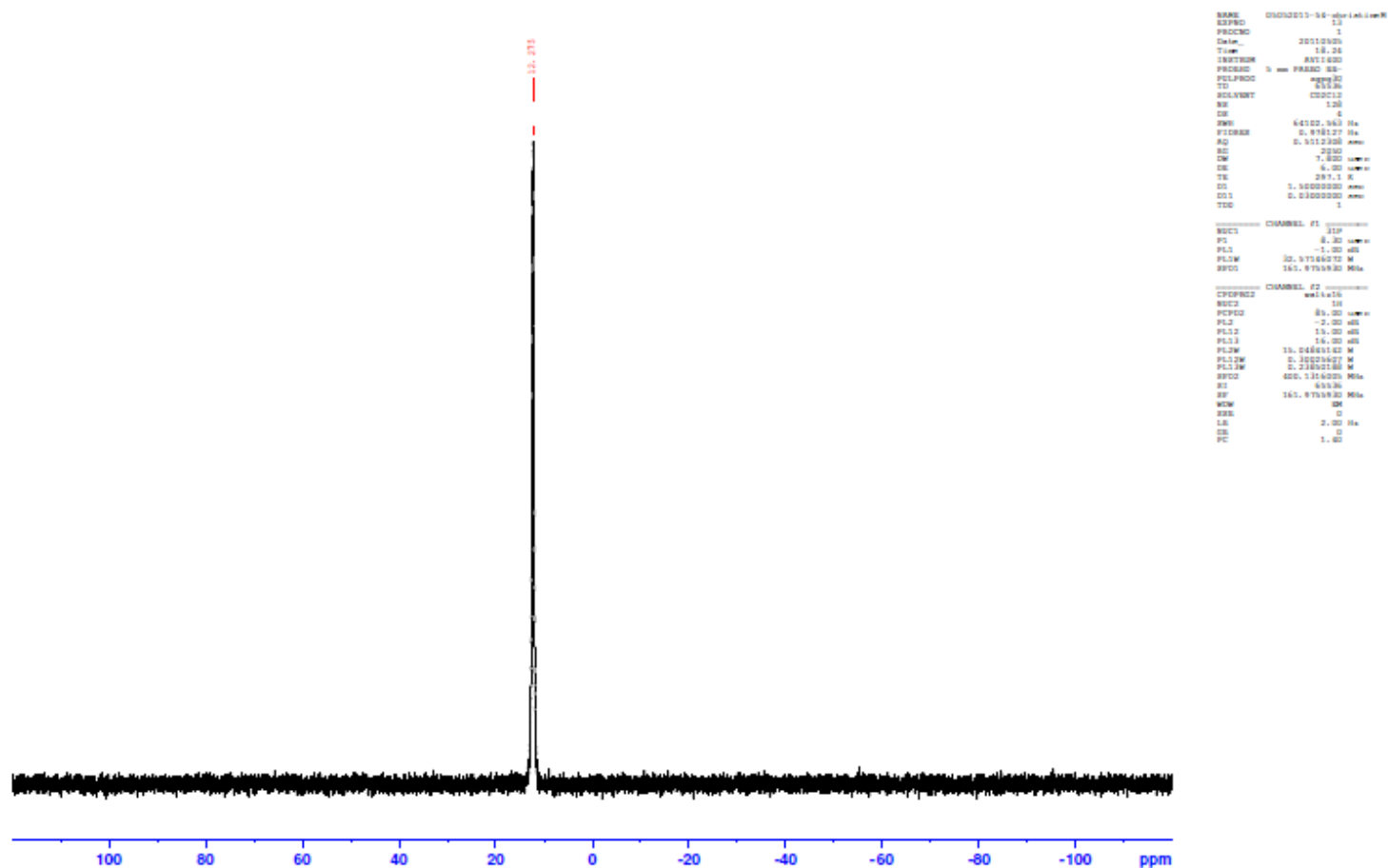
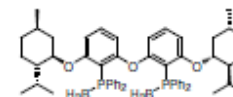


Figure S11 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 13 (161 MHz, CD_2Cl_2 , 296 K)

5- Compound 14

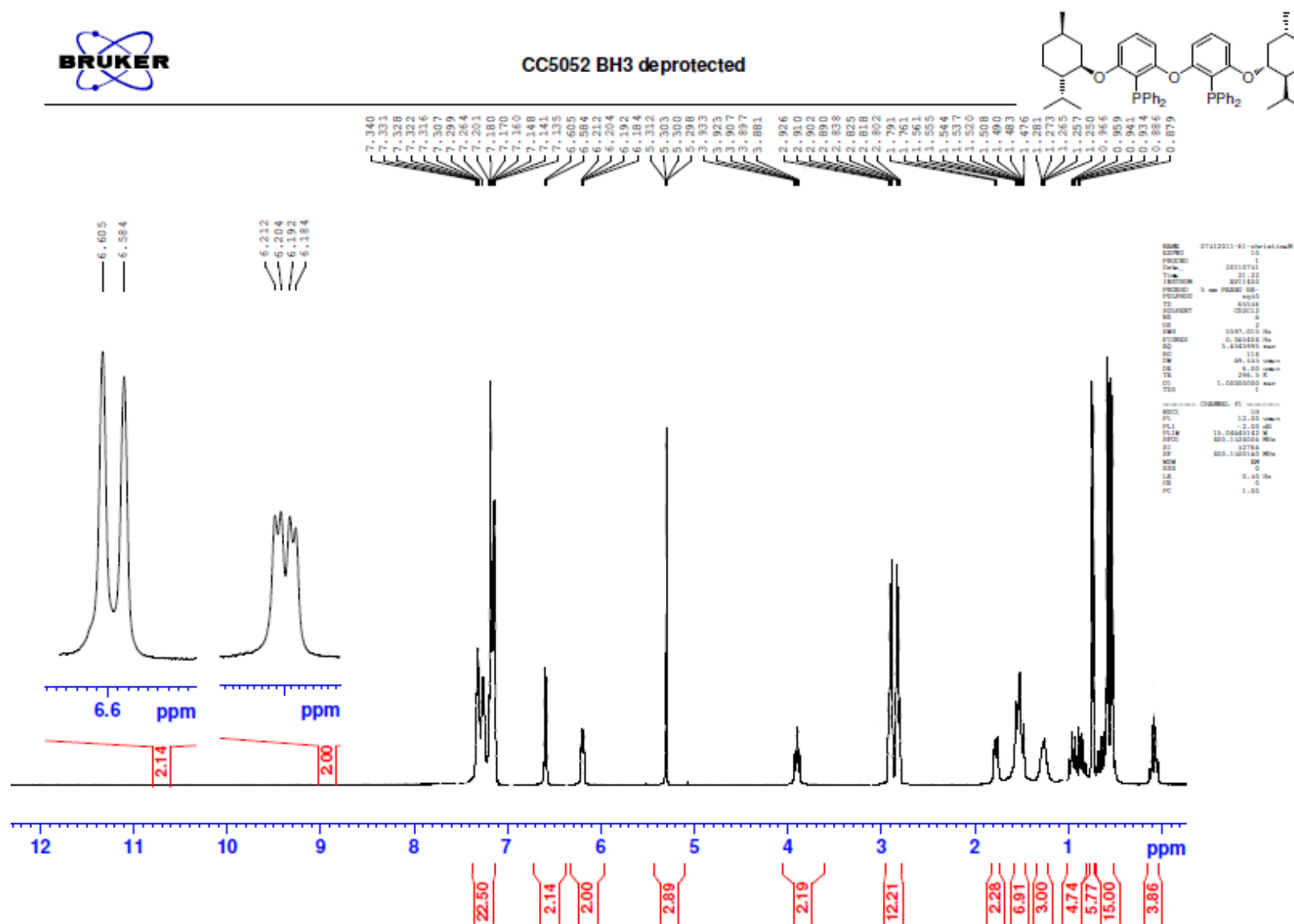


Figure S12 ¹H NMR spectrum of compound 14 (400 MHz, CD₂Cl₂, 296 K)



CC5052 BH3 deprotected

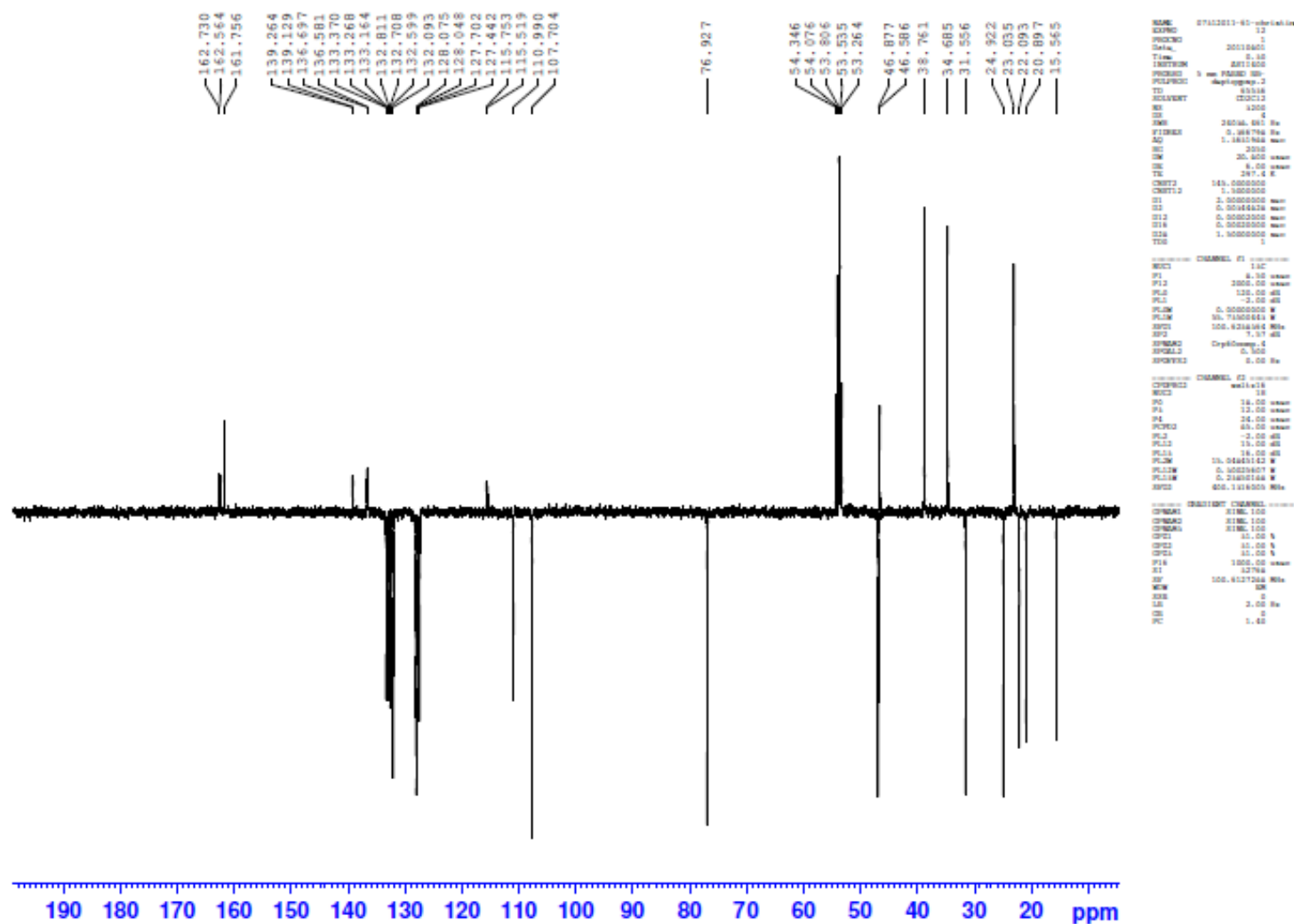
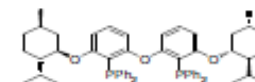
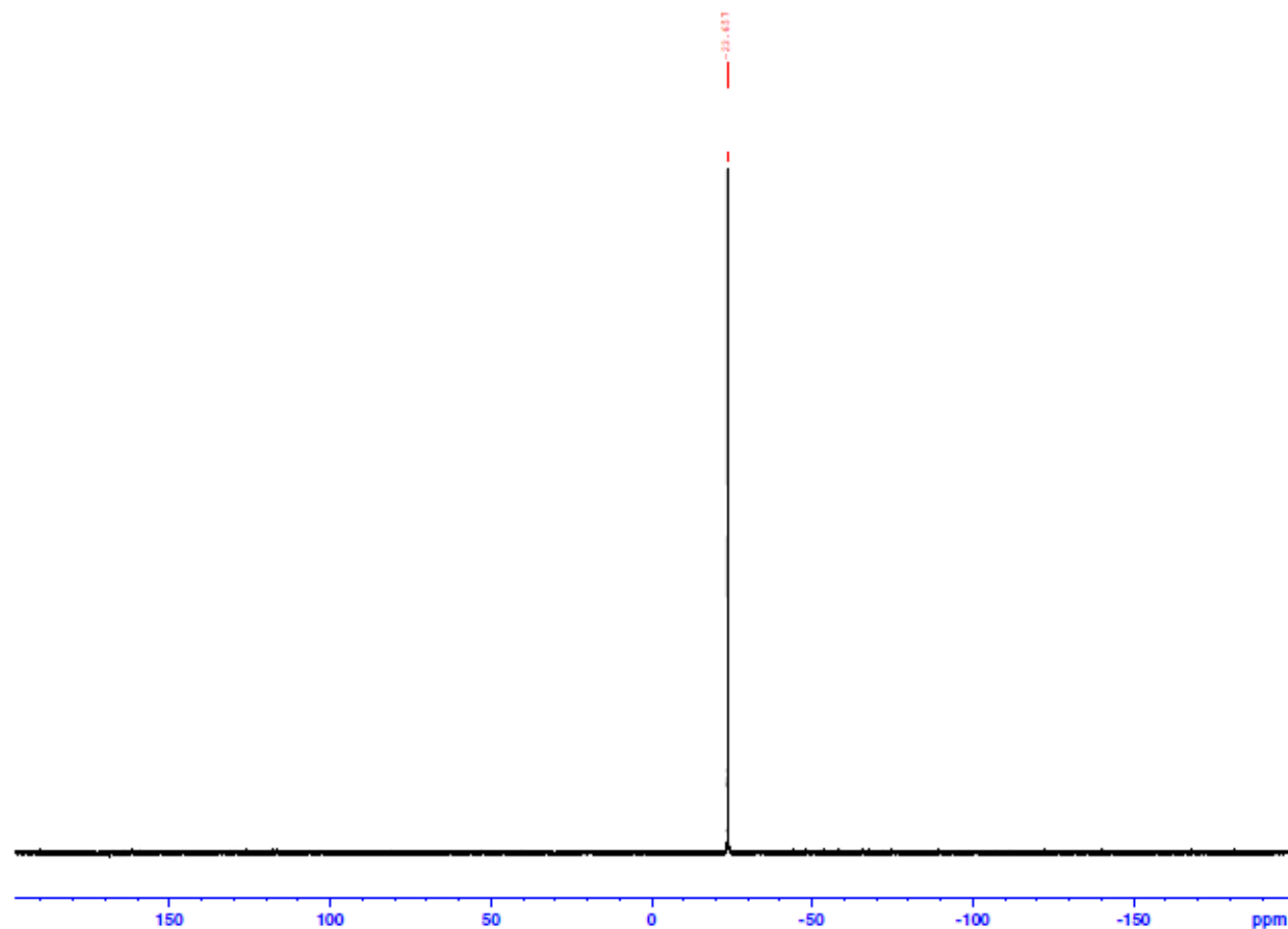
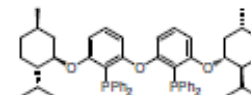


Figure S13 ¹³C APT NMR spectrum of compound 14 (101 MHz, CD₂Cl₂, 296 K)



CC5052 BH3 deprotected



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TD         65536
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DS         4
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DE          6.000 sec
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Sf1         0.00000000 sec
TDO         1

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P1         0.120 sec
PL1        -1.00 dB
PL1M       22.57144012 W
RFQ1       161.0750910 MHz

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NUC2       1H
PCPD2      00.00 sec
PL2        -2.00 dB
PL12       15.00 dB
PL13       16.00 dB
PL2M       15.0488142 W
PL12M      0.30275607 W
PL13M      0.20850186 W
RFQ2       400.1314000 MHz
SI         65536
SF         161.0750910 MHz
WDW        EM
SSB        0
LB         7.00 Hz
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Figure S14 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 14 (161 MHz, CD_2Cl_2 , 296 K)

6- Compound 15

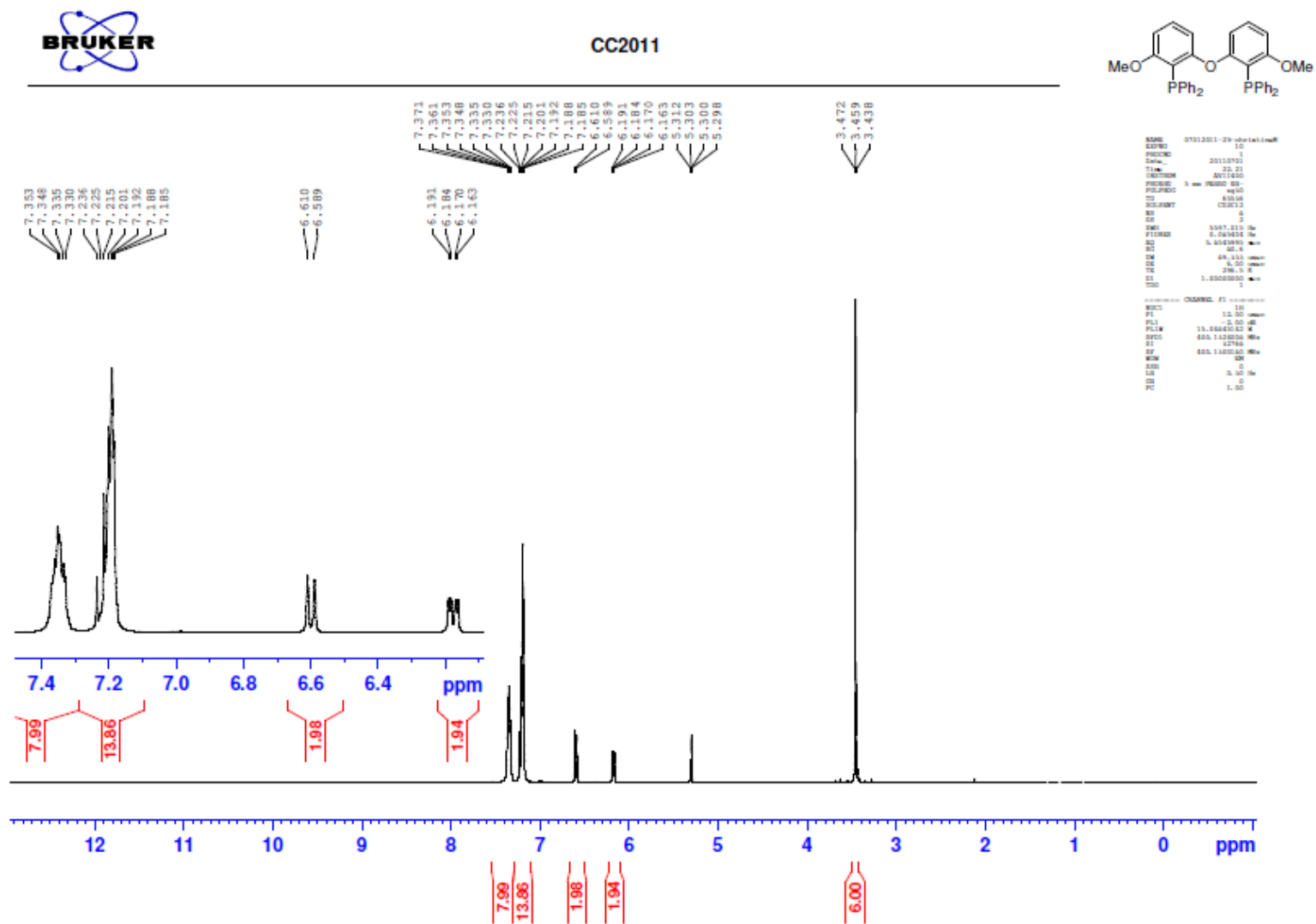


Figure S15 ^1H NMR spectrum of compound 15 (400 MHz, CD_2Cl_2 , 296 K)



CC2011

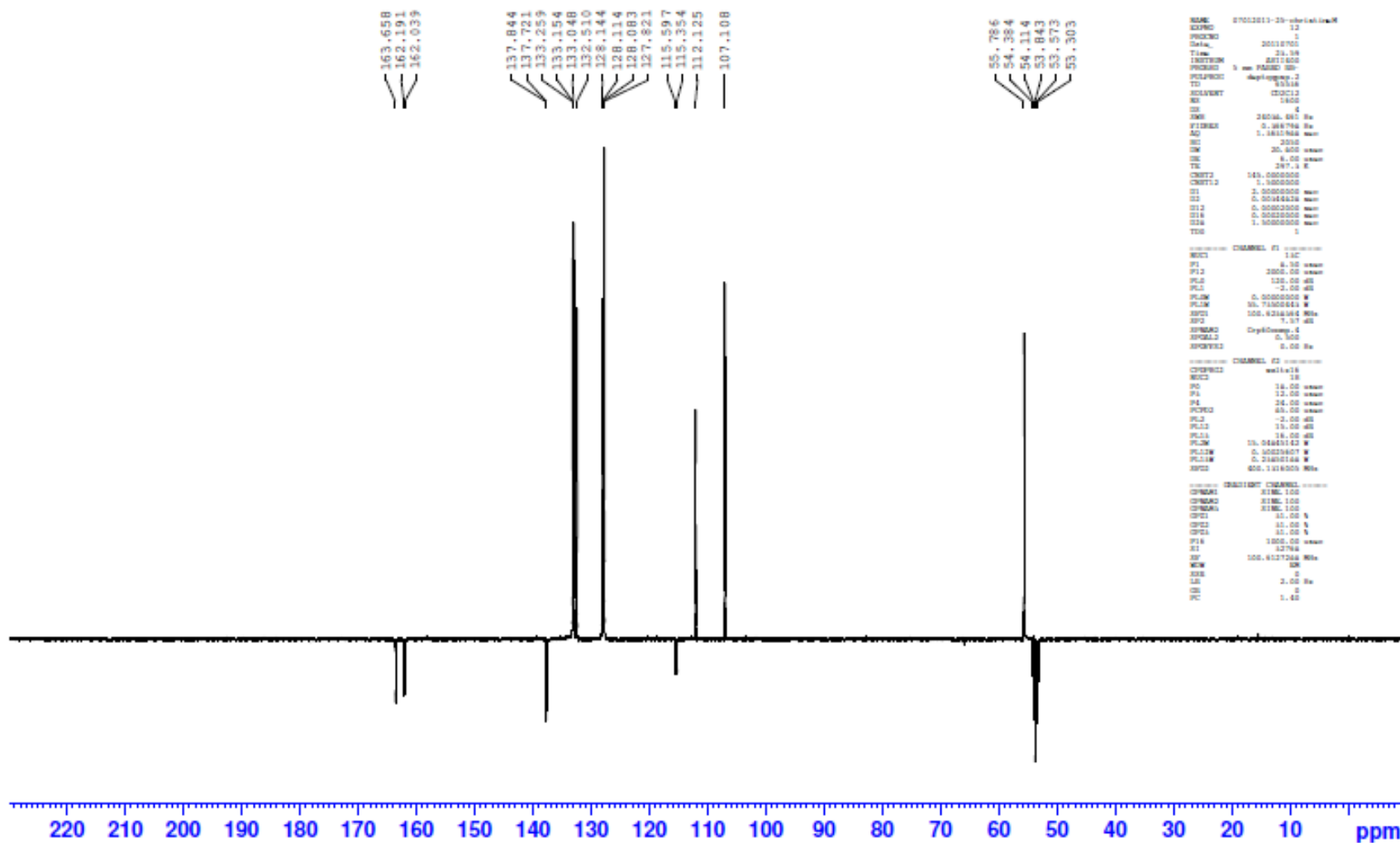
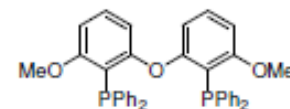


Figure S16 ¹³C APT NMR spectrum of compound 15 (101 MHz, CD₂Cl₂, 296 K)

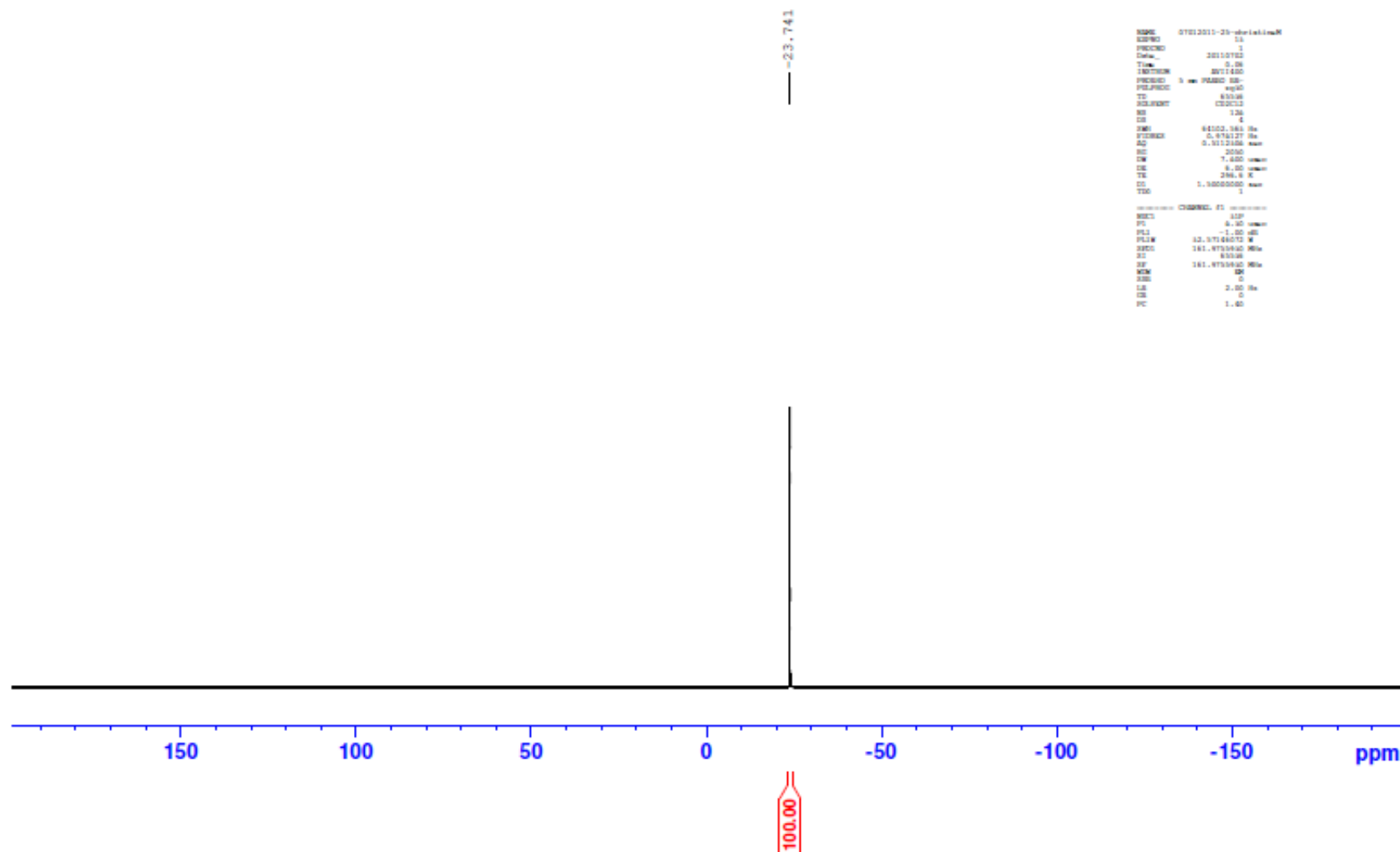
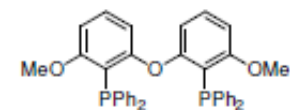


Figure S17 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 15 (161 MHz, CD_2Cl_2 , 296 K)

7- Compound 17a

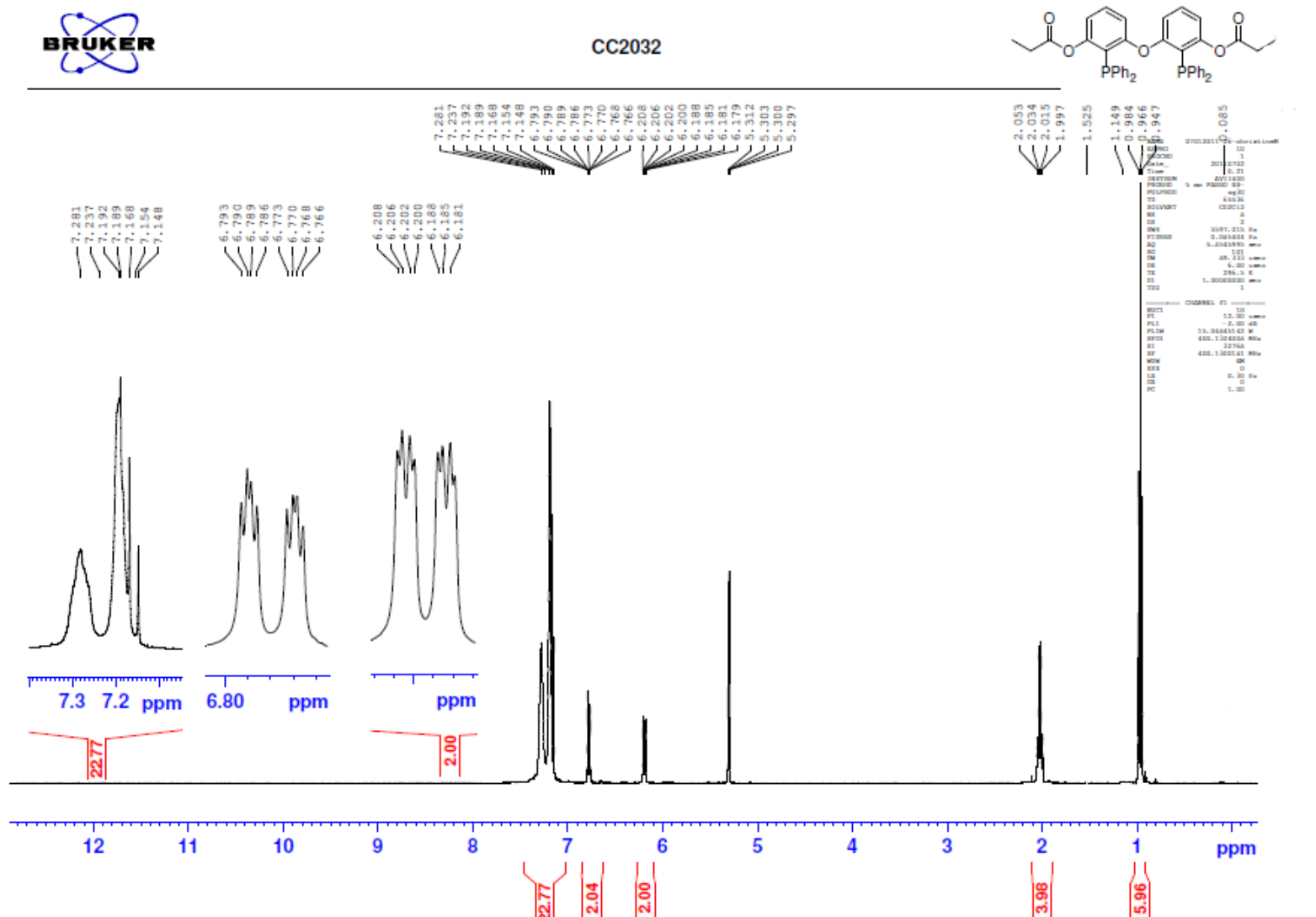


Figure S18 ^1H NMR spectrum of compound 17a (400 MHz, CD_2Cl_2 , 297 K)



CC2032

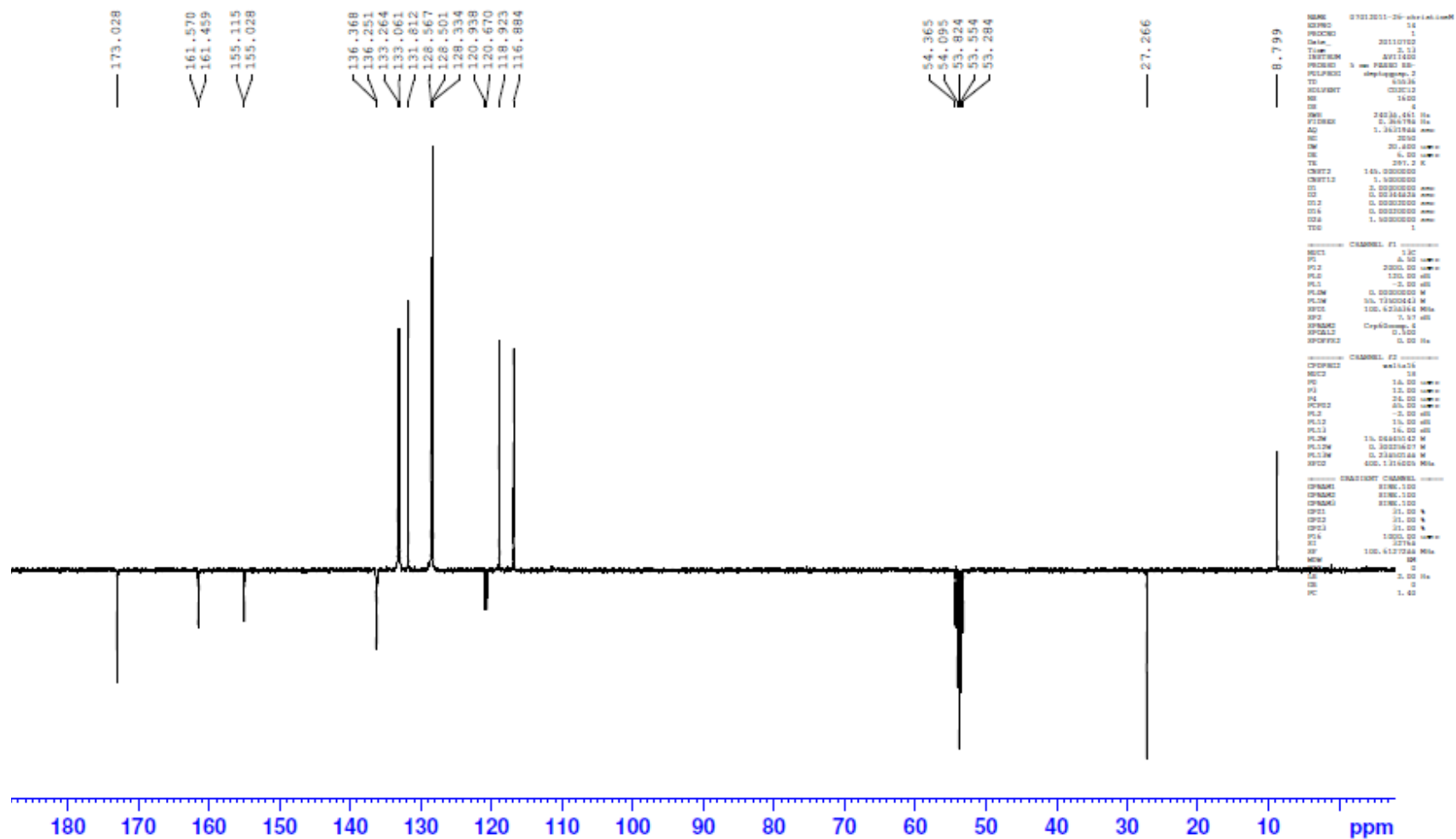
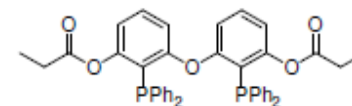


Figure S19 ¹³C APT NMR spectrum of compound 17a (101 MHz, CD₂Cl₂, 297 K)



CC2032

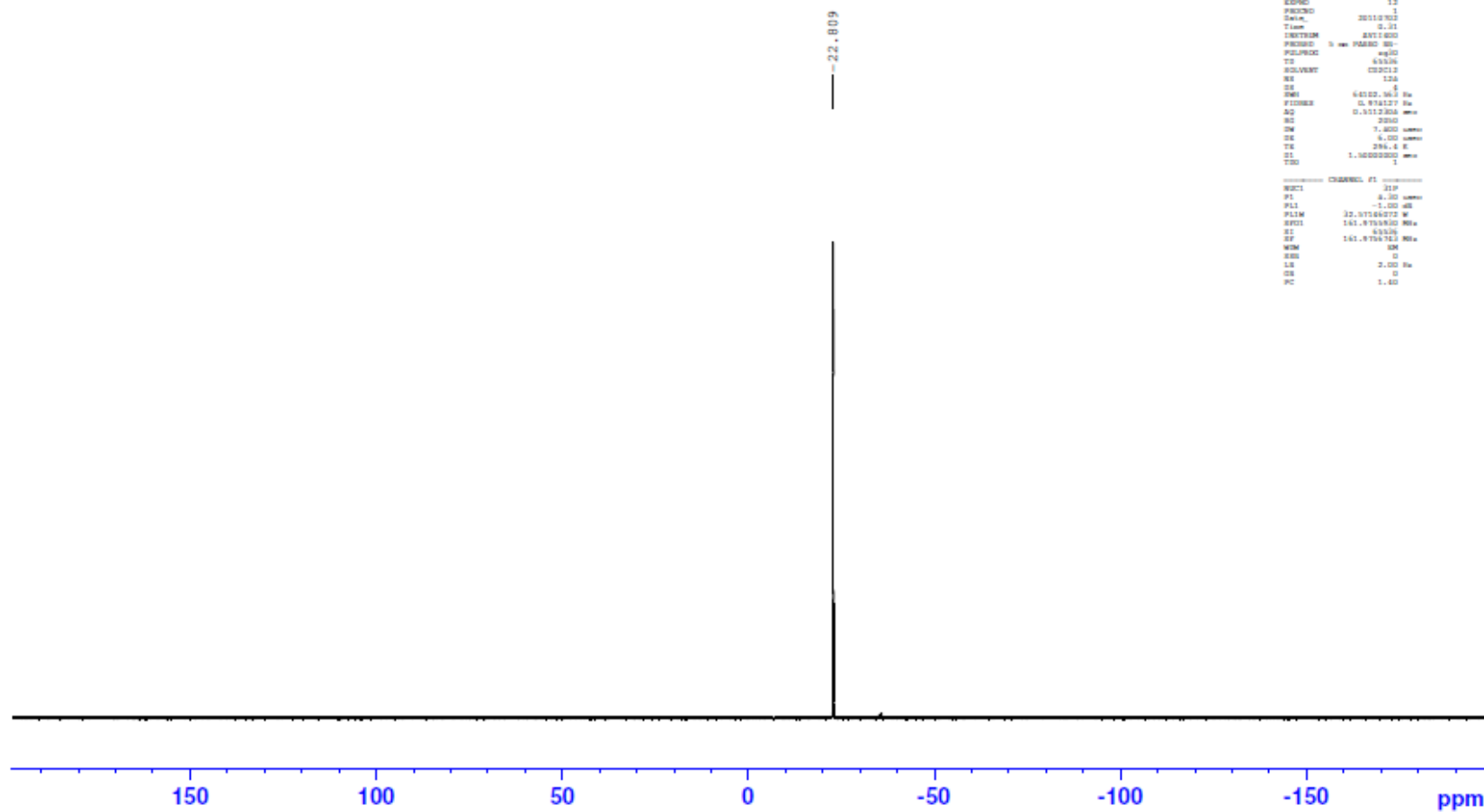
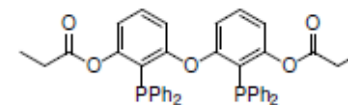


Figure S20 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 17a (161 MHz, CD₂Cl₂, 297 K)

8- Compound 17a

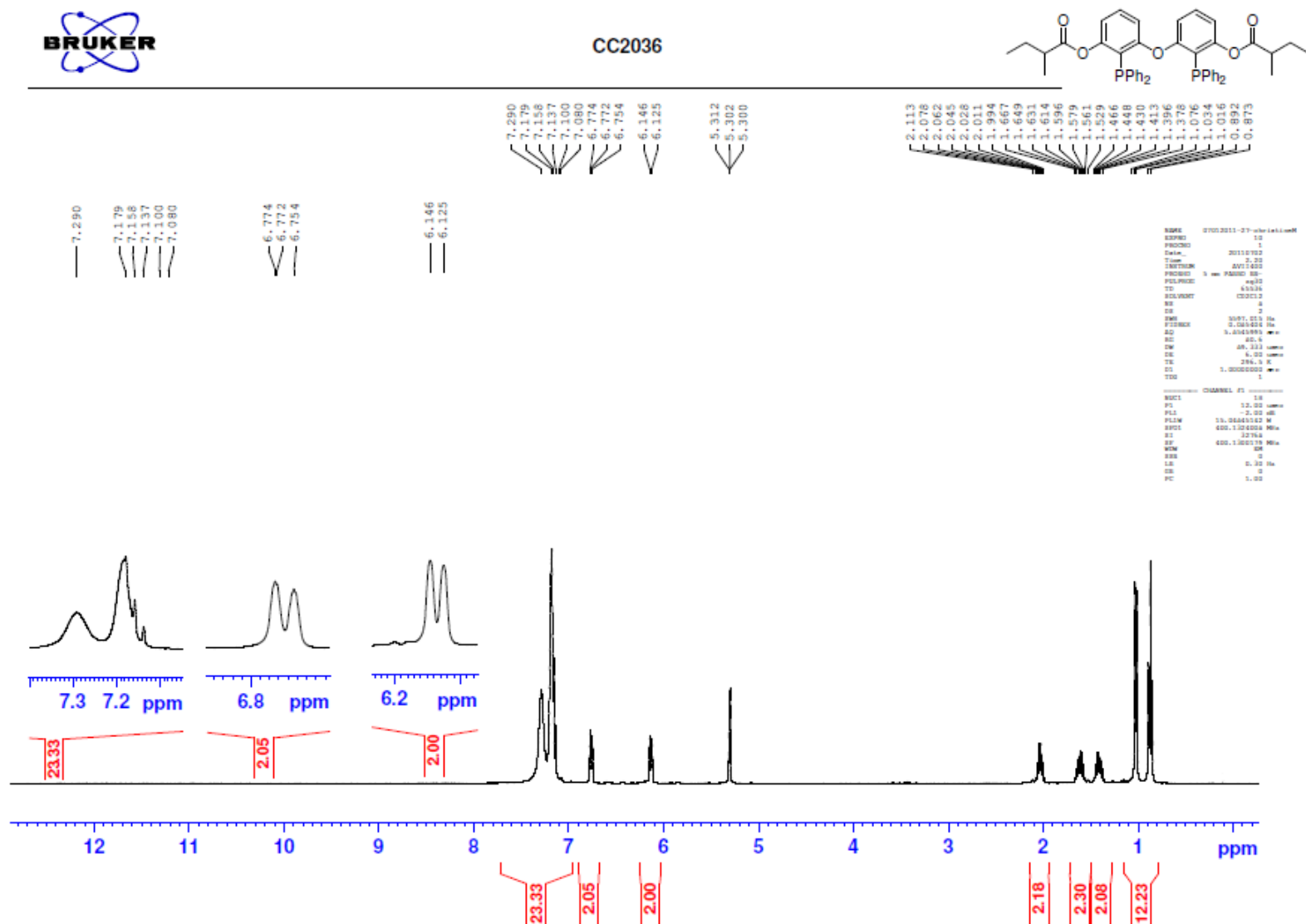


Figure S21 ¹H NMR spectrum of compound 17b (400 MHz, CD₂Cl₂, 297 K)

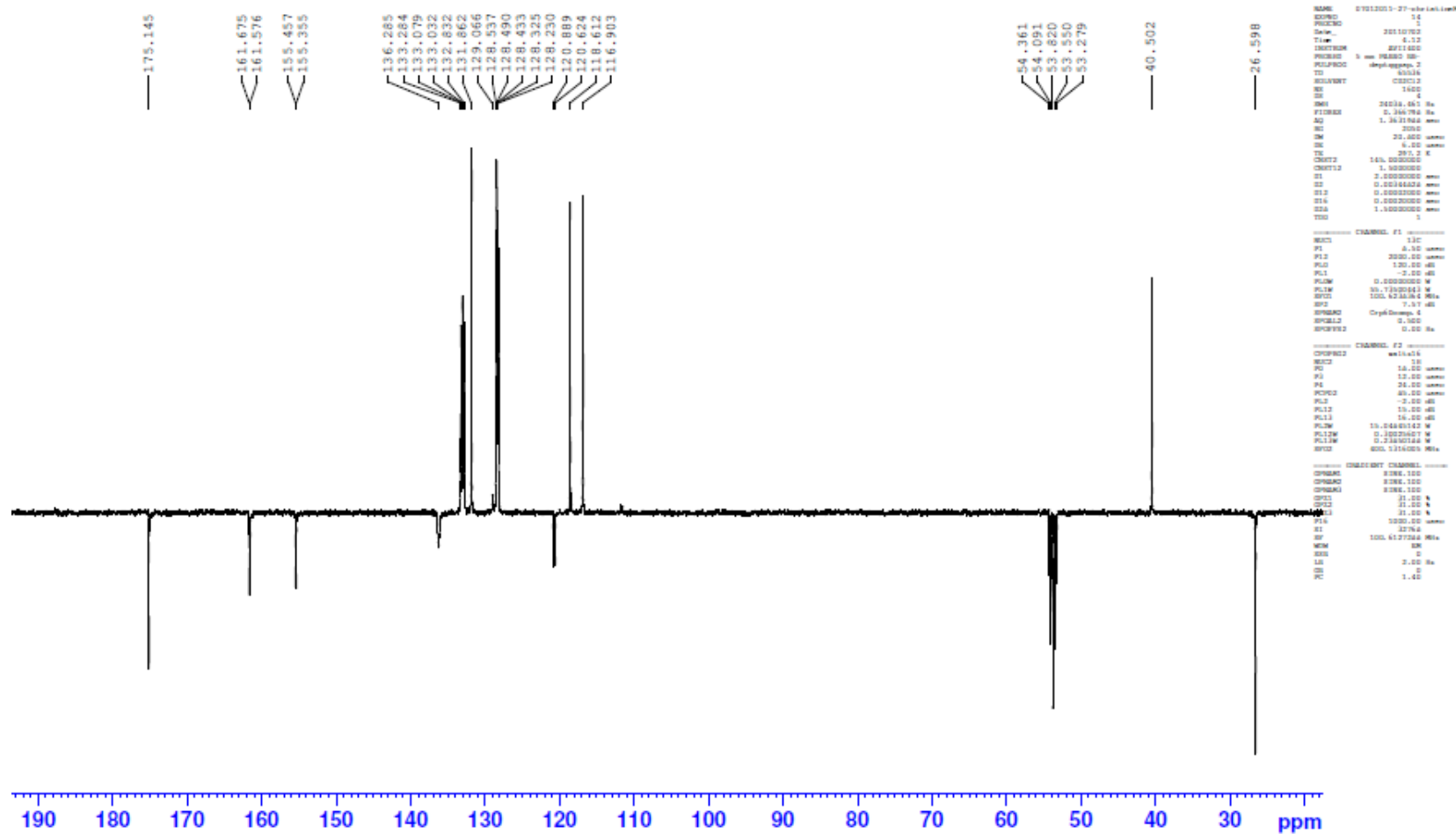
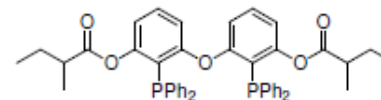
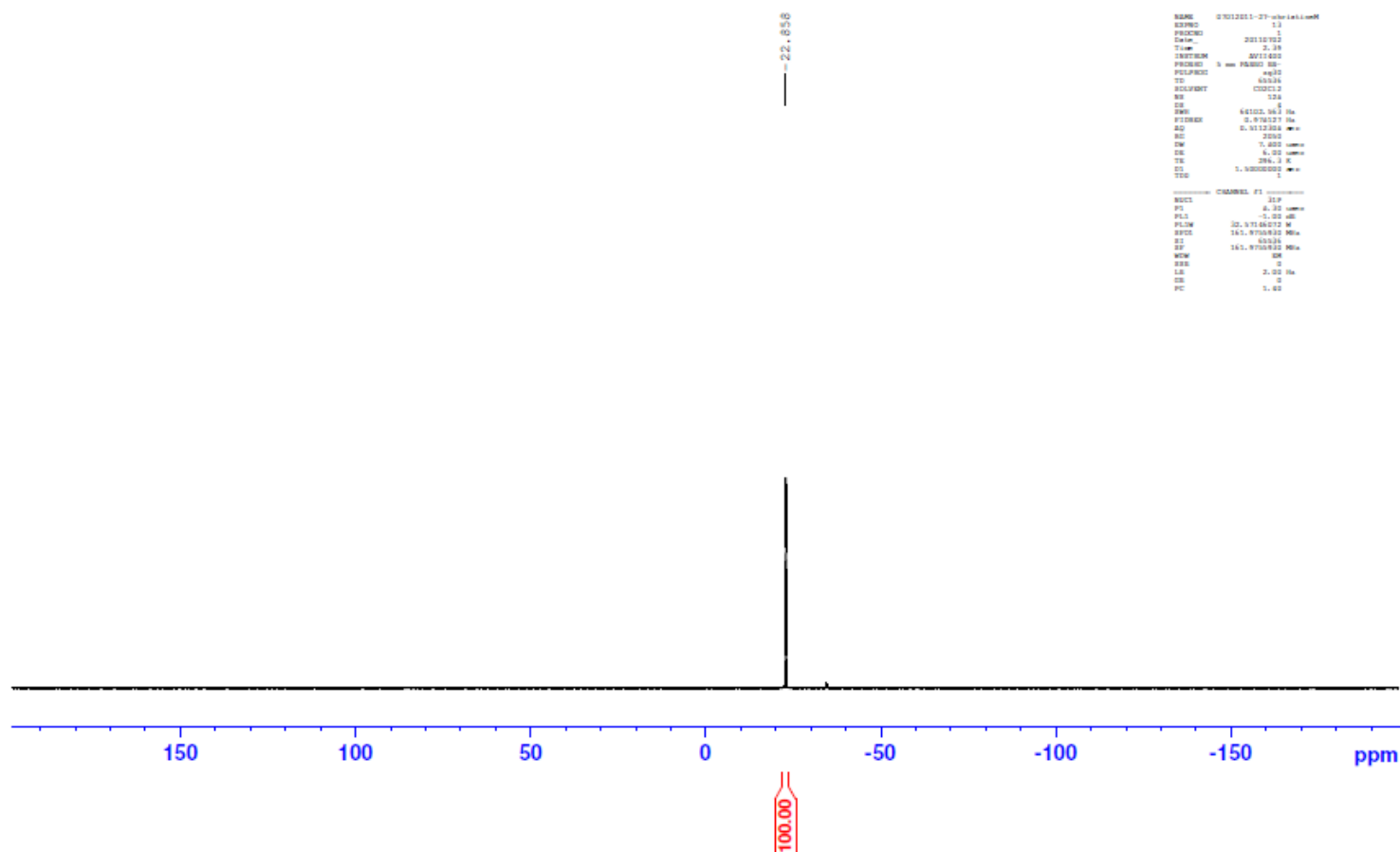
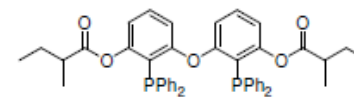


Figure S22 ^{13}C APT NMR spectrum of compound **17b** (101 MHz, CD_2Cl_2 , 297 K)



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SWH 64000.000 MHz
FIDRES 0.0000000 Hz
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DL 6.00 s
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DQ 1.0000000 s
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NUC2 1H
P2 145.0000000 MHz
PL2 0.00 dB
PC2 0.0000000 s
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DS 4
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FIDRES 0.0000000 Hz
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DL 6.00 s
TE 298.2 K
DQ 1.0000000 s
TD 1

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Figure S23 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **17b** (161 MHz, CD_2Cl_2 , 297 K)

9- Compound 17c

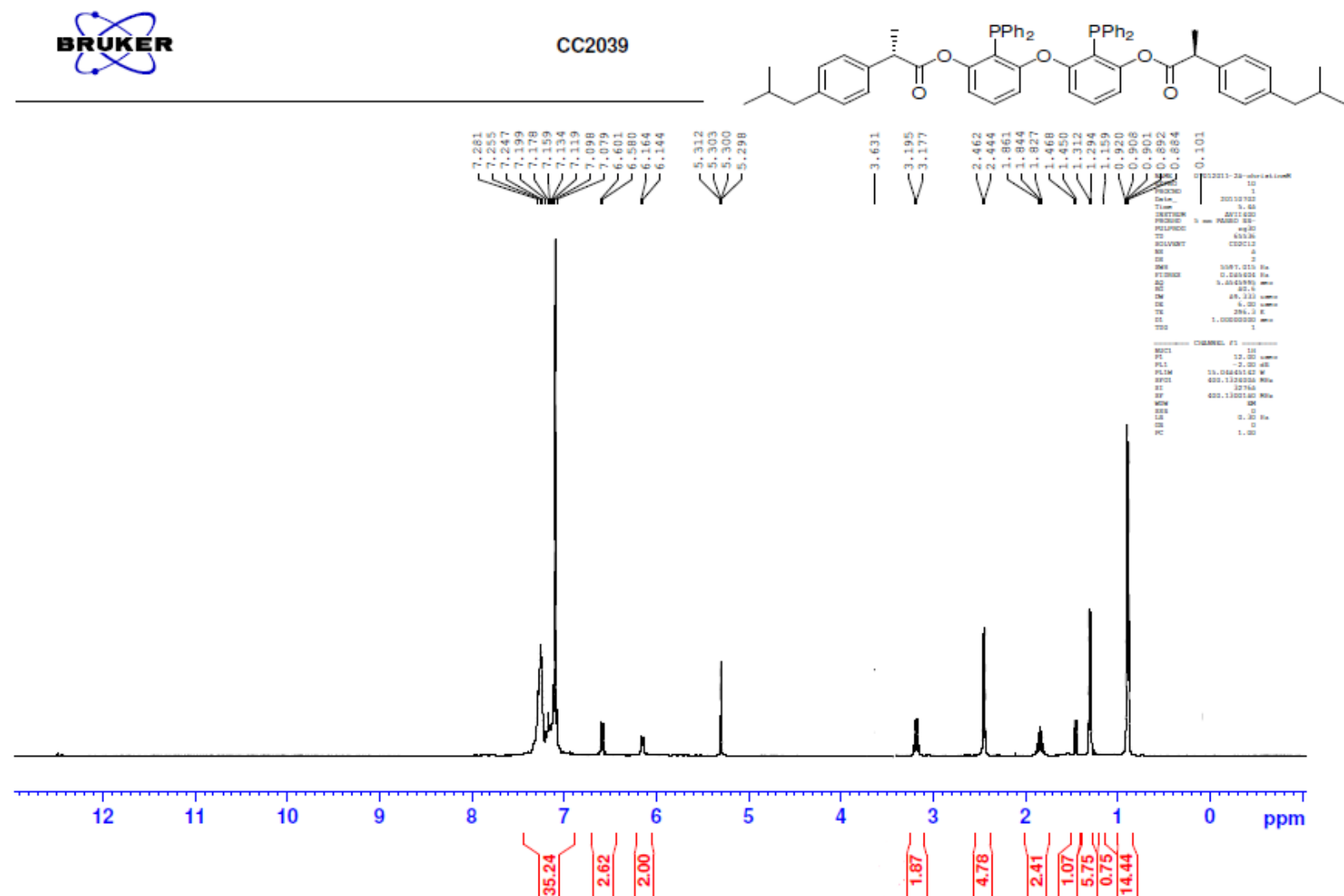


Figure S24 ¹H NMR spectrum of compound 17c (400 MHz, CD₂Cl₂, 297 K)

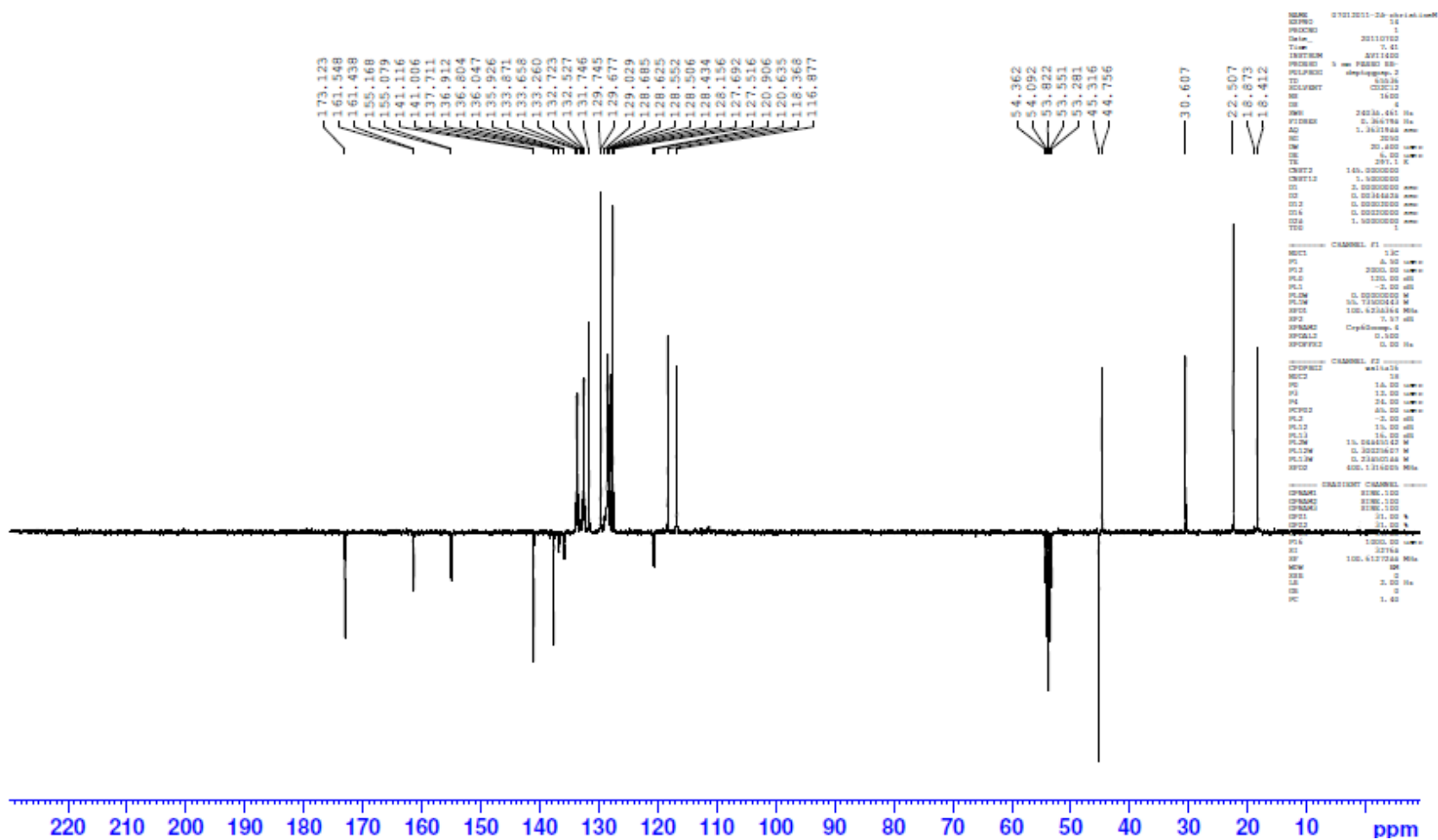
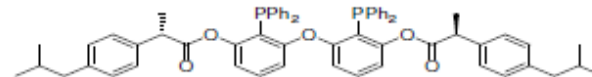


Figure S25 ^{13}C APT NMR spectrum of compound **17c** (101 MHz, CD_2Cl_2 , 297 K)



CC2039

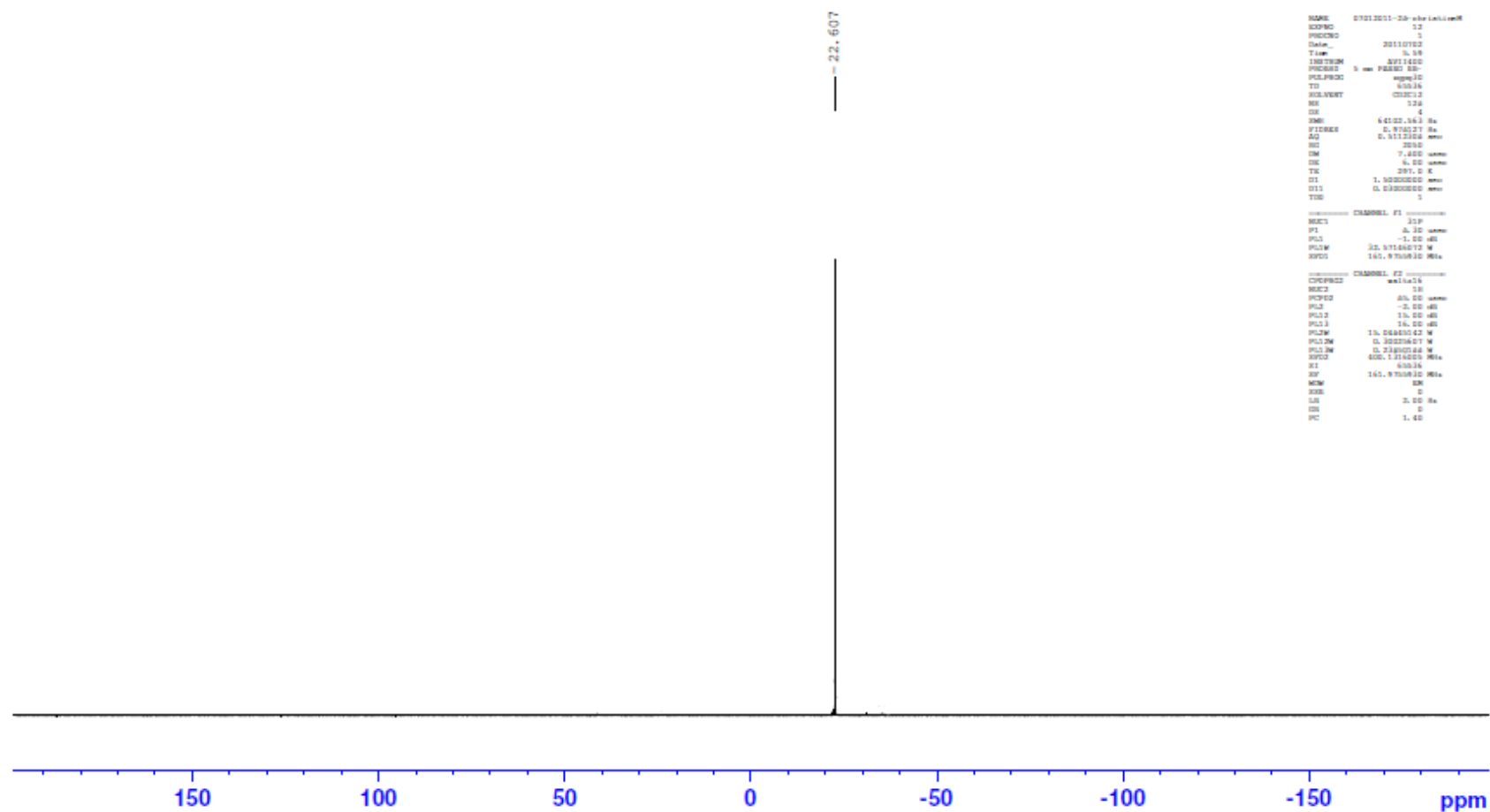
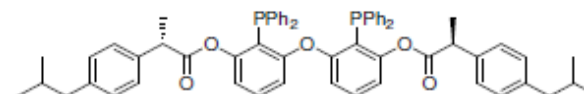


Figure S26 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 17c (161 MHz, CD_2Cl_2 , 297 K)

10- Compound 17d



CC2046

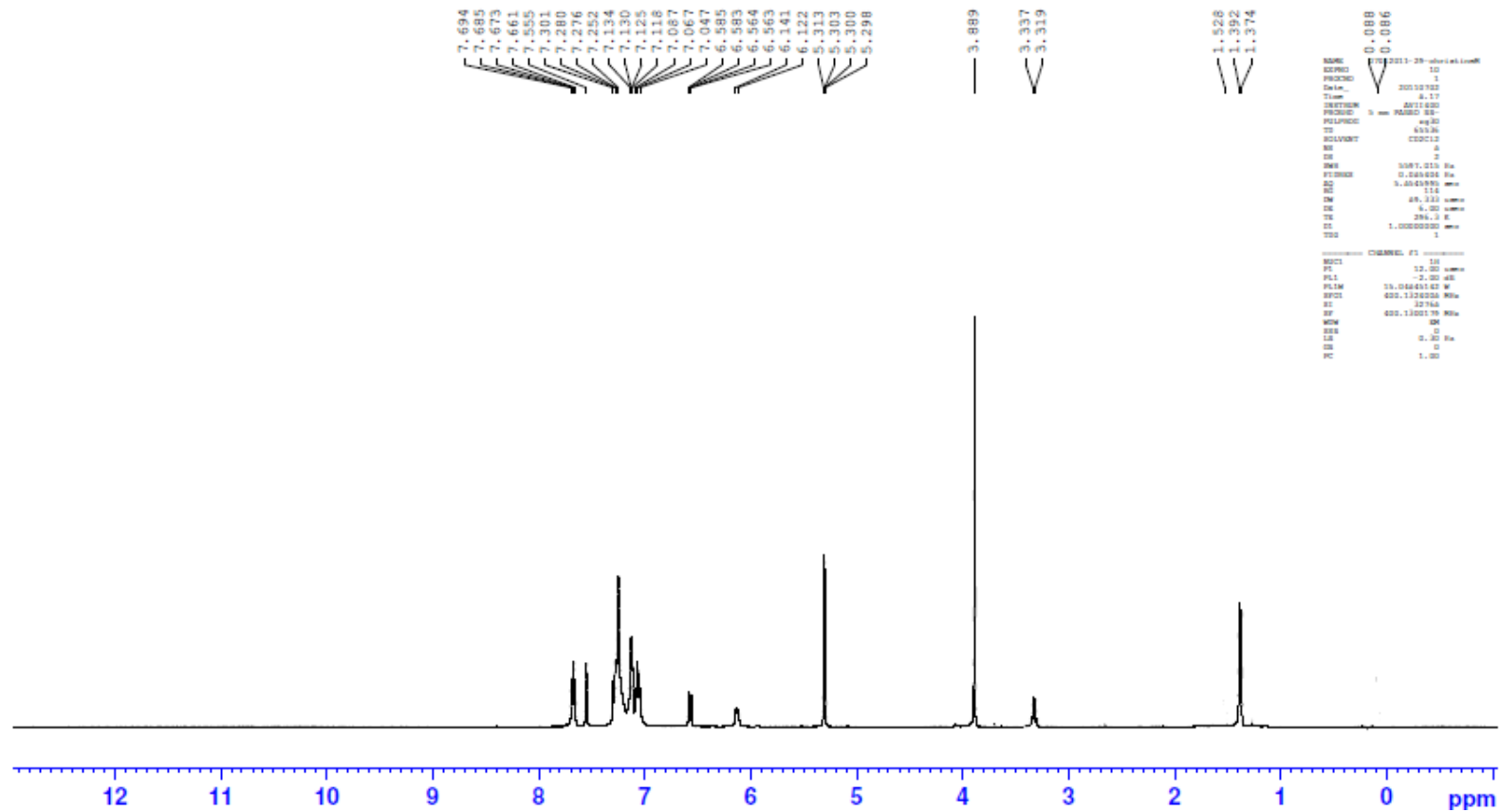
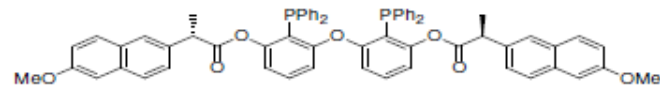


Figure S27 ¹H NMR spectrum of compound 17c (400 MHz, CD₂Cl₂, 297 K)

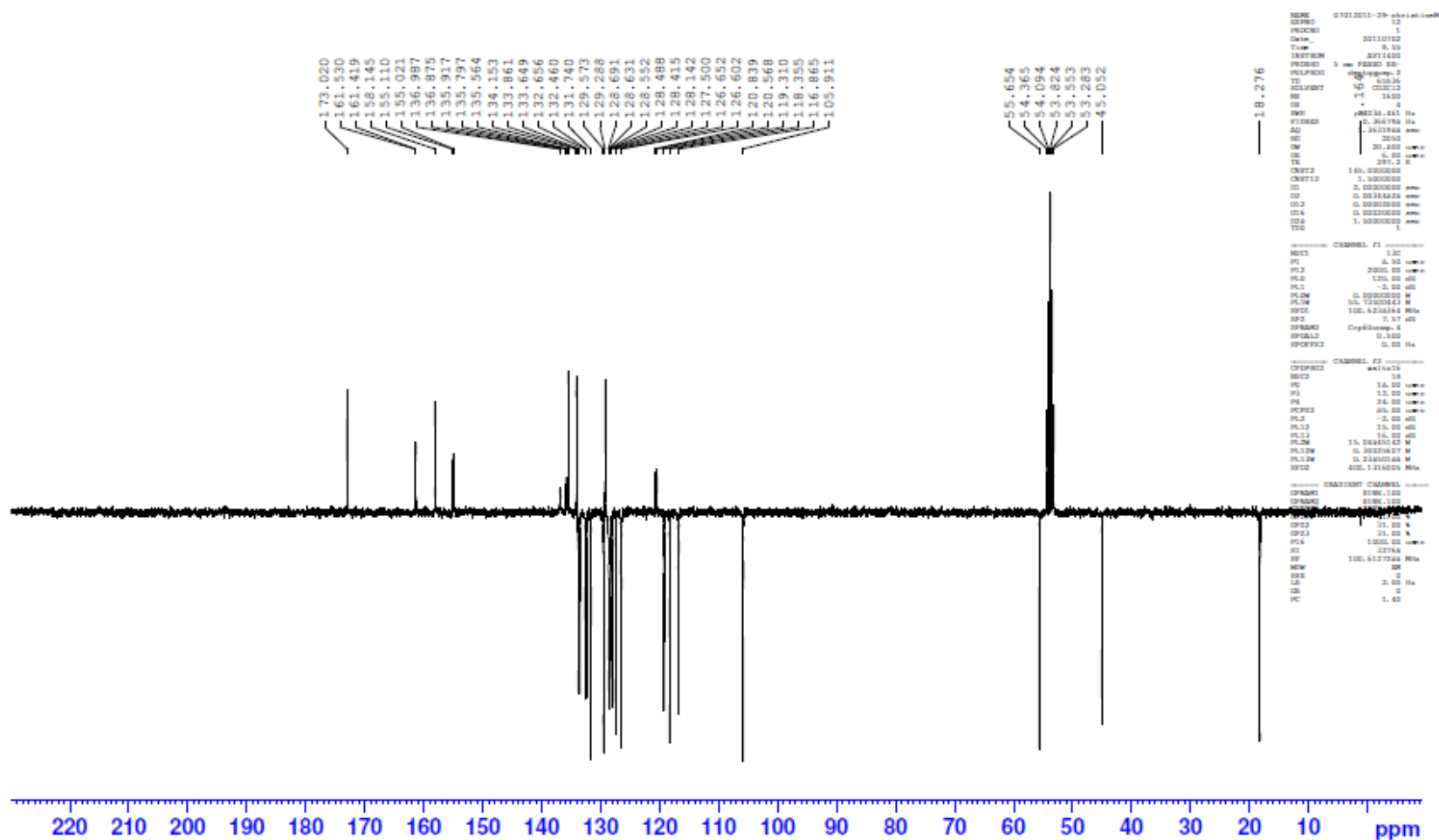
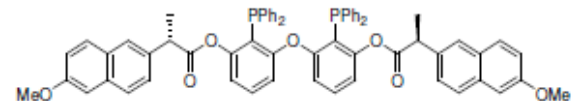


Figure S28 ^{13}C APT NMR spectrum of compound **17c** (101 MHz, CD_2Cl_2 , 297 K)

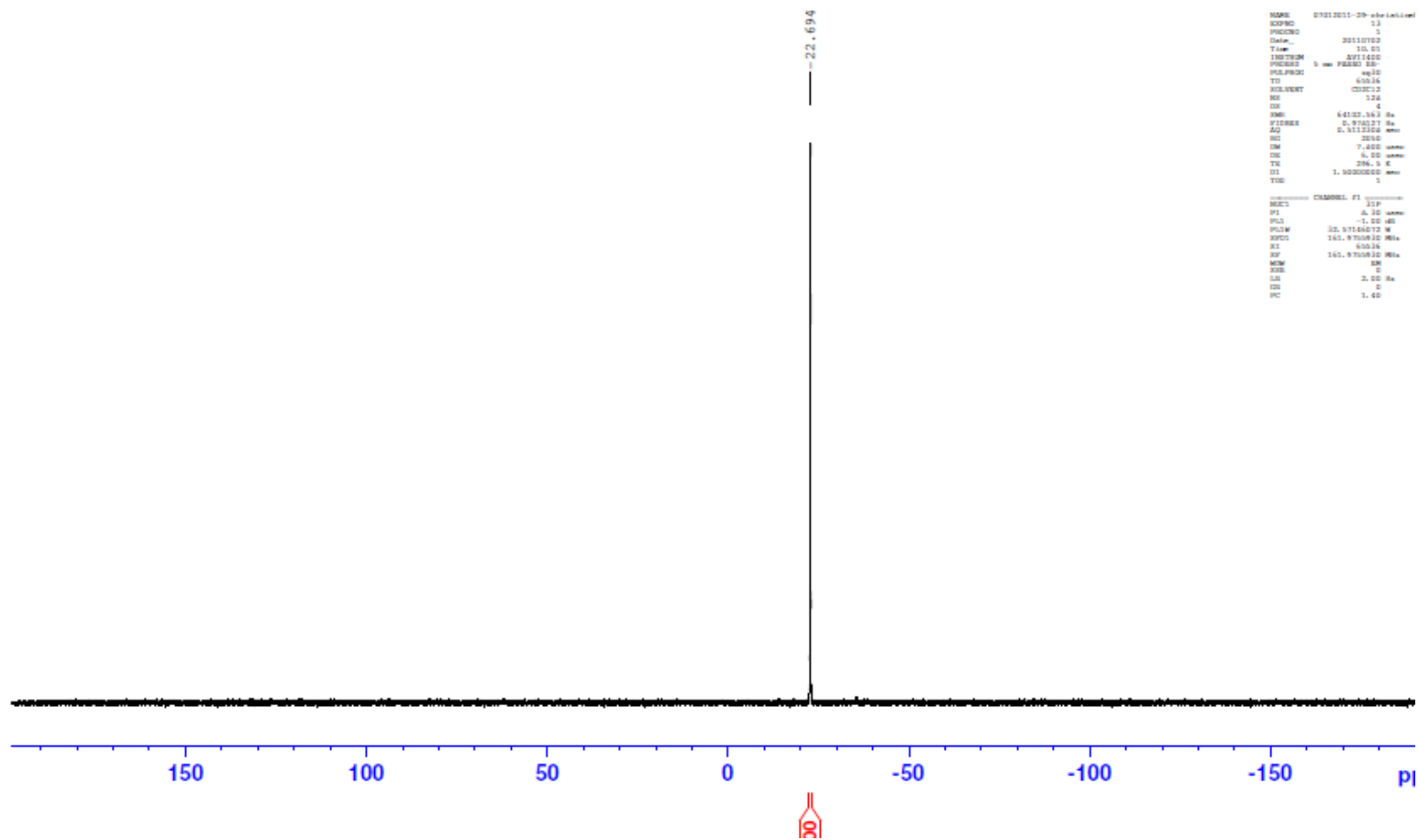
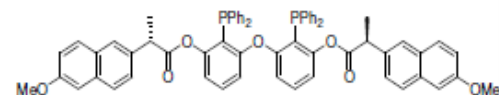


Figure S29 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **17c** (161 MHz, CD_2Cl_2 , 297 K)

11- Platinum Complexes

[PtCl₂(15)]

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agj1.119

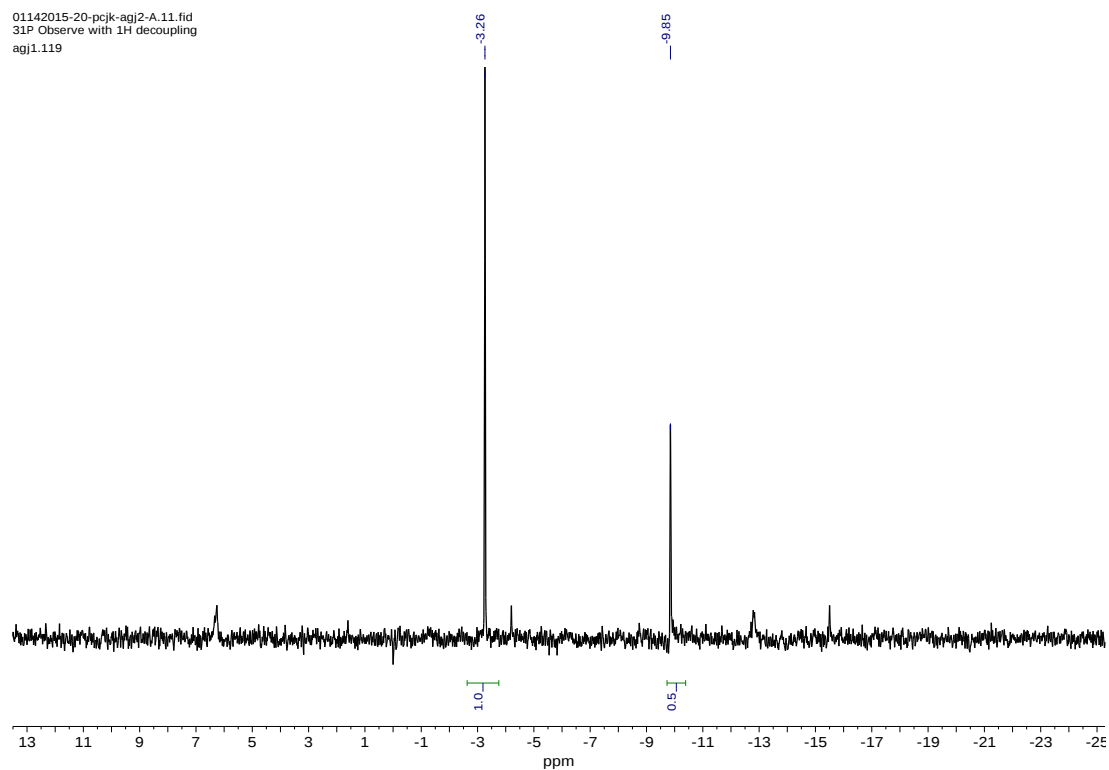


Figure S30: ³¹P{¹H} NMR of PtCl₂(15) (202 MHz, CDCl₃)

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1H Observe
agj1.119

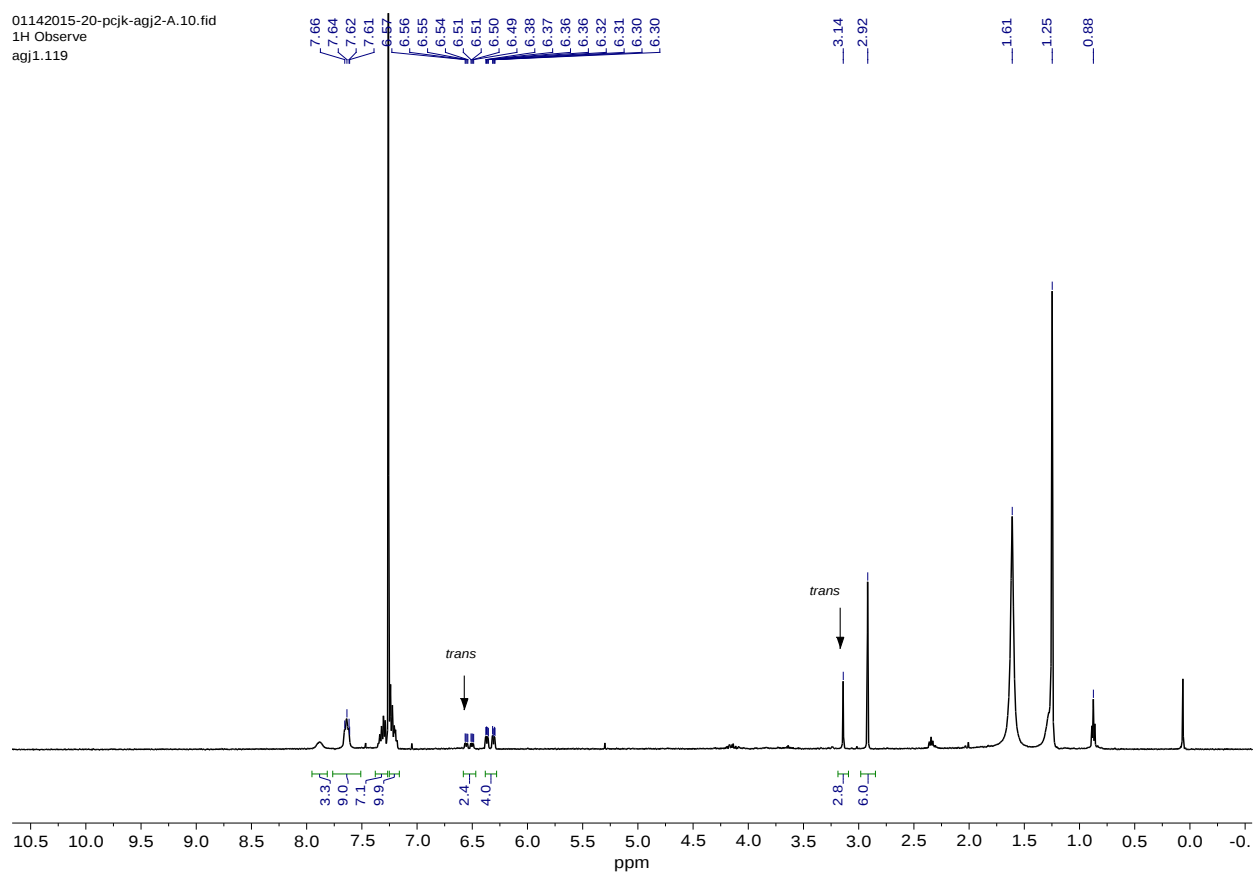


Figure S31: ^1H NMR of $\text{PtCl}_2(15)$ (500 MHz, CDCl_3) (major product *cis*-isomer, minor product *trans*-isomer)

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

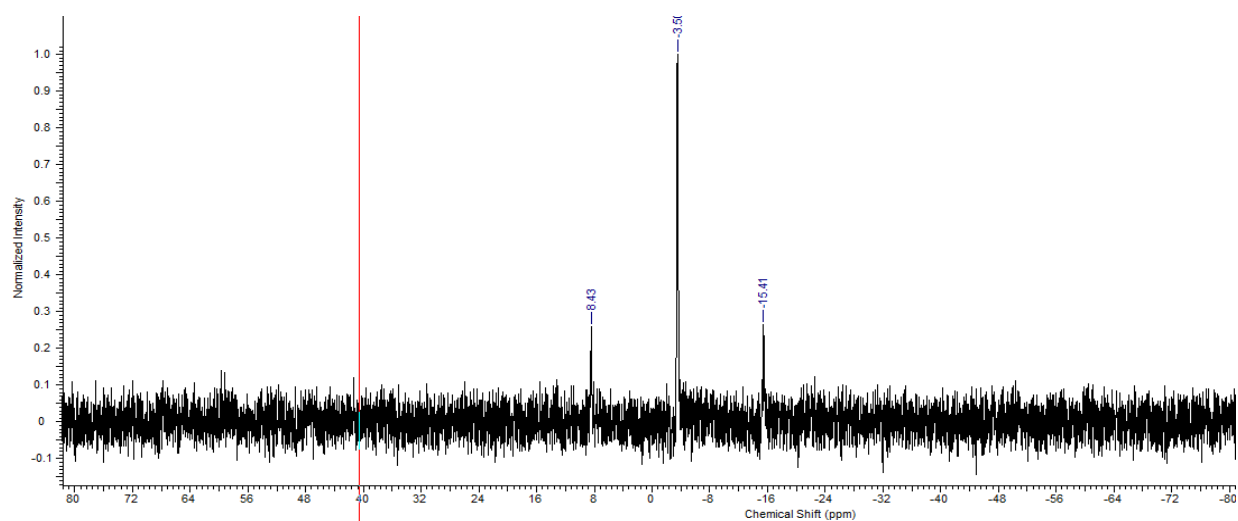


Figure S32: $^{31}\text{P}\{^1\text{H}\}$ NMR of $\text{PtCl}_2(17a)$ (162 MHz, CDCl_3)

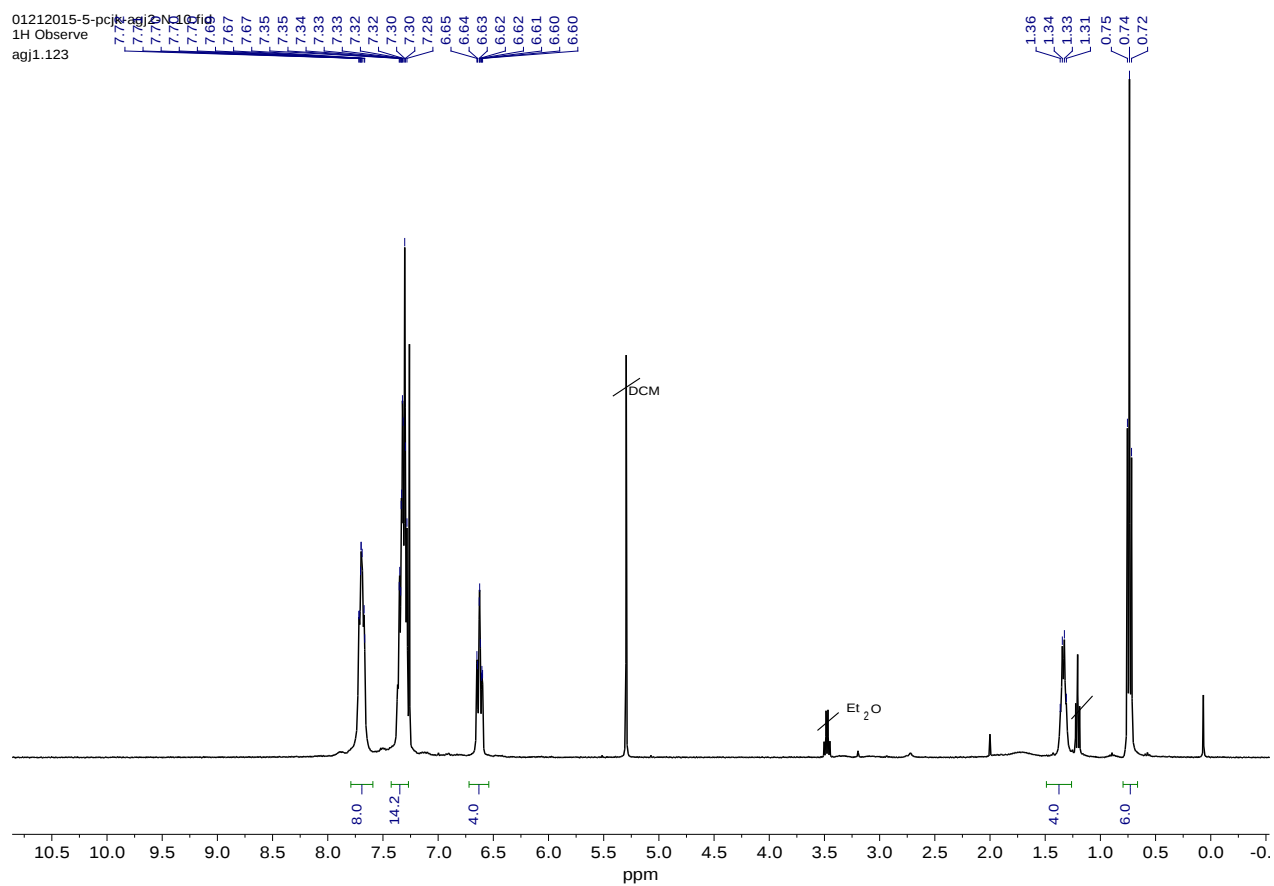


Figure S33: ¹H NMR of PtCl₂(17a) (400 MHz, CDCl₃)

[PtCl₂(**17b**)]

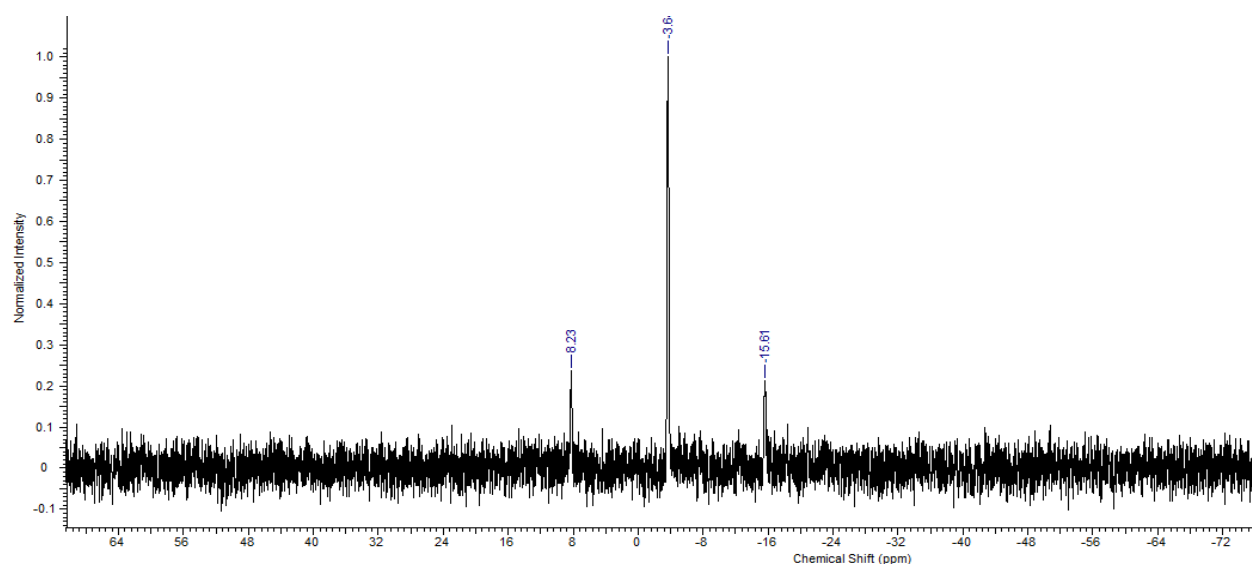


Figure S34: ³¹P{¹H} NMR of PtCl₂(**17b**) (162 MHz, CDCl₃)

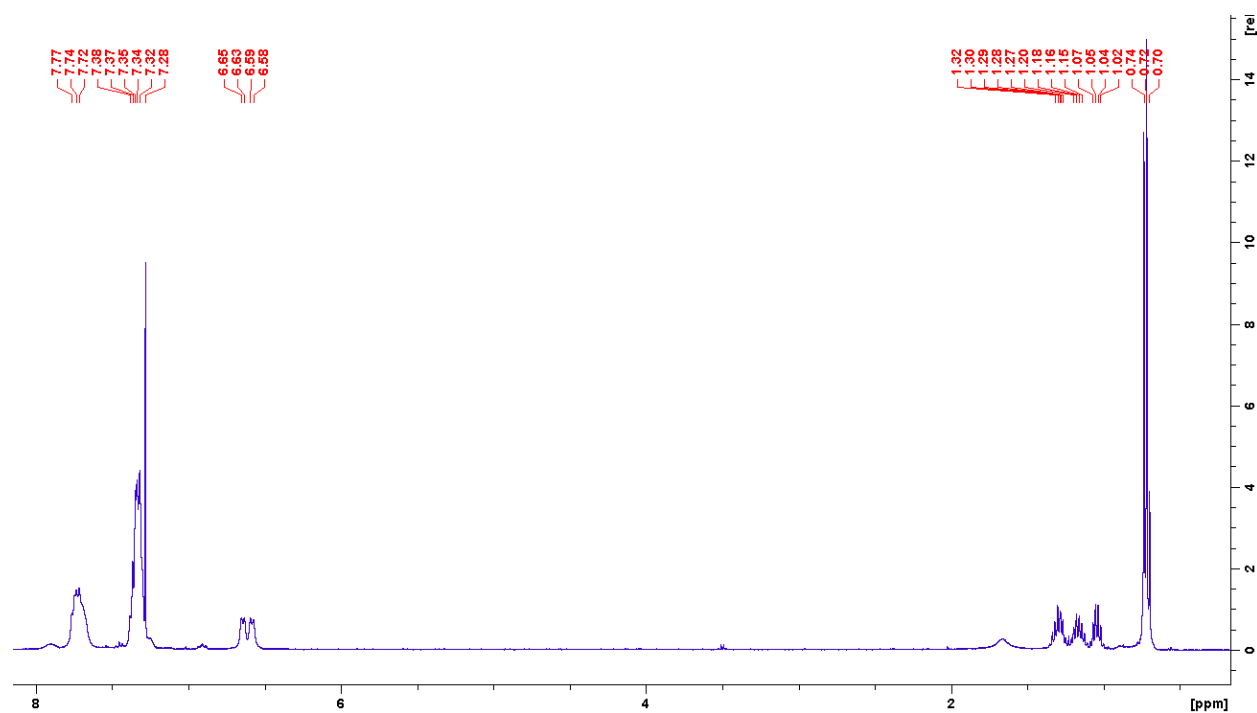


Figure S35: ¹H NMR of PtCl₂(**17b**) (400 MHz, CDCl₃)

[PtCl₂(**17c**)]

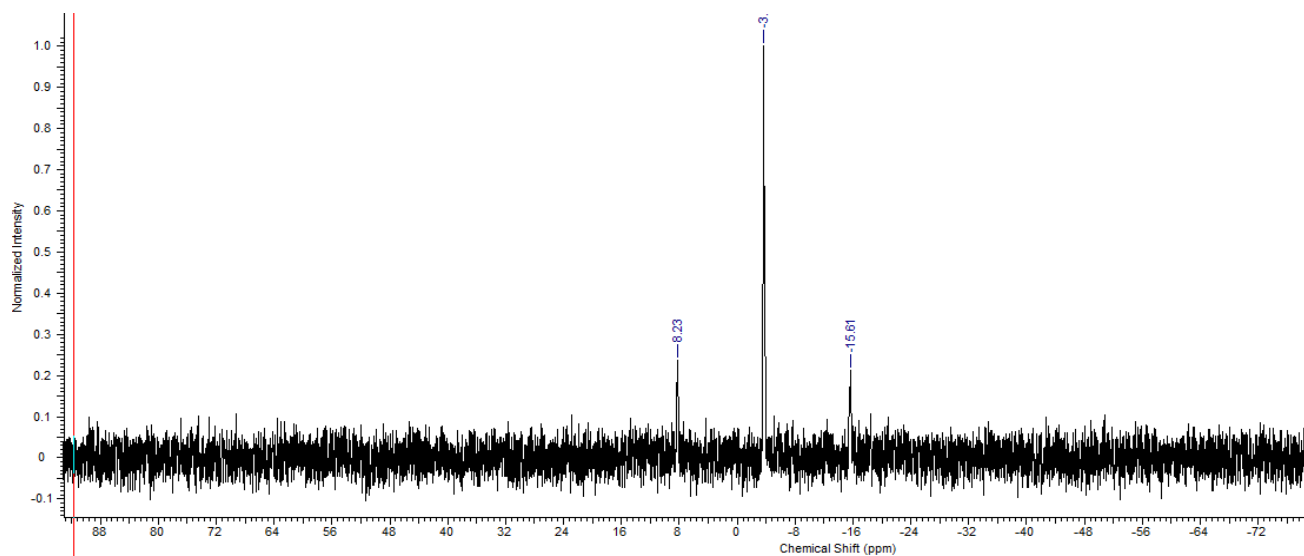


Figure S36: ³¹P{¹H} NMR of PtCl₂(**17c**) (162 MHz, CDCl₃)

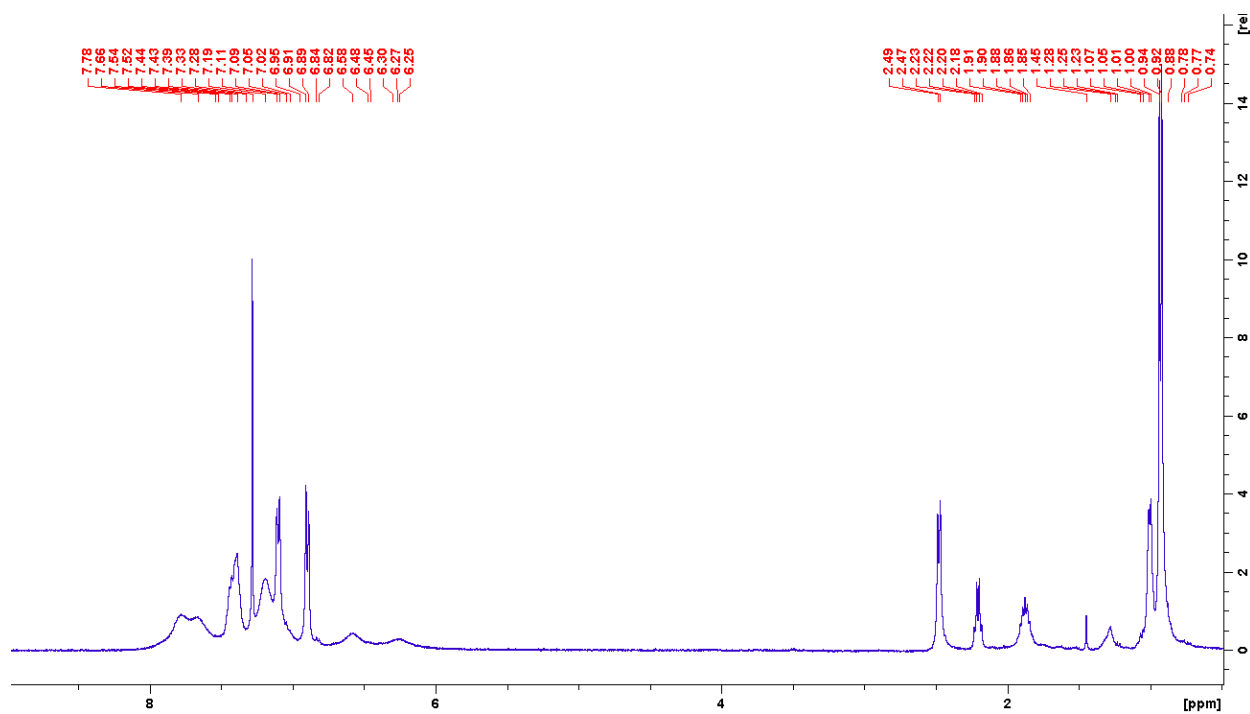


Figure S37: ¹H NMR of PtCl₂(**17c**) (400 MHz, CDCl₃)

13C NMR spectrum of 1,4-bis(2-oxo-2-phenylethyl)benzene. The spectrum shows a triplet for the carbonyl carbons at approximately 200 ppm, a multiplet for the aromatic carbons between 120 and 140 ppm, and a multiplet for the methylene carbons at approximately 40 ppm. The x-axis is labeled from 150 to -50 ppm.

Chemical structure: O=C(Cc1ccc(cc1)Cc2ccc(cc2)C(=O)C)C

Peak list (ppm):

Peak	Chemical Shift (ppm)
1	200.453
2	200.319
3	200.186
4	132.471
5	132.471
6	132.471
7	132.471
8	132.471
9	132.471
10	132.471
11	132.471
12	132.471
13	132.471
14	132.471
15	132.471
16	132.471
17	132.471
18	132.471
19	132.471
20	132.471
21	132.471
22	132.471
23	132.471
24	132.471
25	132.471
26	132.471
27	132.471
28	132.471
29	132.471
30	132.471
31	132.471
32	132.471
33	132.471
34	132.471
35	132.471
36	132.471
37	132.471
38	132.471
39	132.471
40	132.471
41	132.471
42	132.471
43	132.471
44	132.471
45	132.471
46	132.471
47	132.471
48	132.471
49	132.471
50	132.471
51	132.471
52	132.471
53	132.471
54	132.471
55	132.471
56	132.471
57	132.471
58	132.471
59	132.471
60	132.471
61	132.471
62	132.471
63	132.471
64	132.471
65	132.471
66	132.471
67	132.471
68	132.471
69	132.471
70	132.471
71	132.471
72	132.471
73	132.471
74	132.471
75	132.471
76	132.471
77	132.471
78	132.471
79	132.471
80	132.471
81	132.471
82	132.471
83	132.471
84	132.471
85	132.471
86	132.471
87	132.471
88	132.471
89	132.471
90	132.471
91	132.471
92	132.471
93	132.471
94	132.471
95	132.471
96	132.471
97	132.471
98	132.471
99	132.471
100	132.471
101	132.471
102	132.471
103	132.471
104	132.471
105	132.471
106	132.471
107	132.471
108	132.471
109	132.471
110	132.471
111	132.471
112	132.471
113	132.471
114	132.471
115	132.471
116	132.471
117	132.471
118	132.471
119	132.471
120	132.471
121	132.471
122	132.471
123	132.471
124	132.471
125	132.471
126	132.471
127	132.471
128	132.471
129	132.471
130	132.471
131	132.471
132	132.471
133	132.471
134	132.471
135	

S36

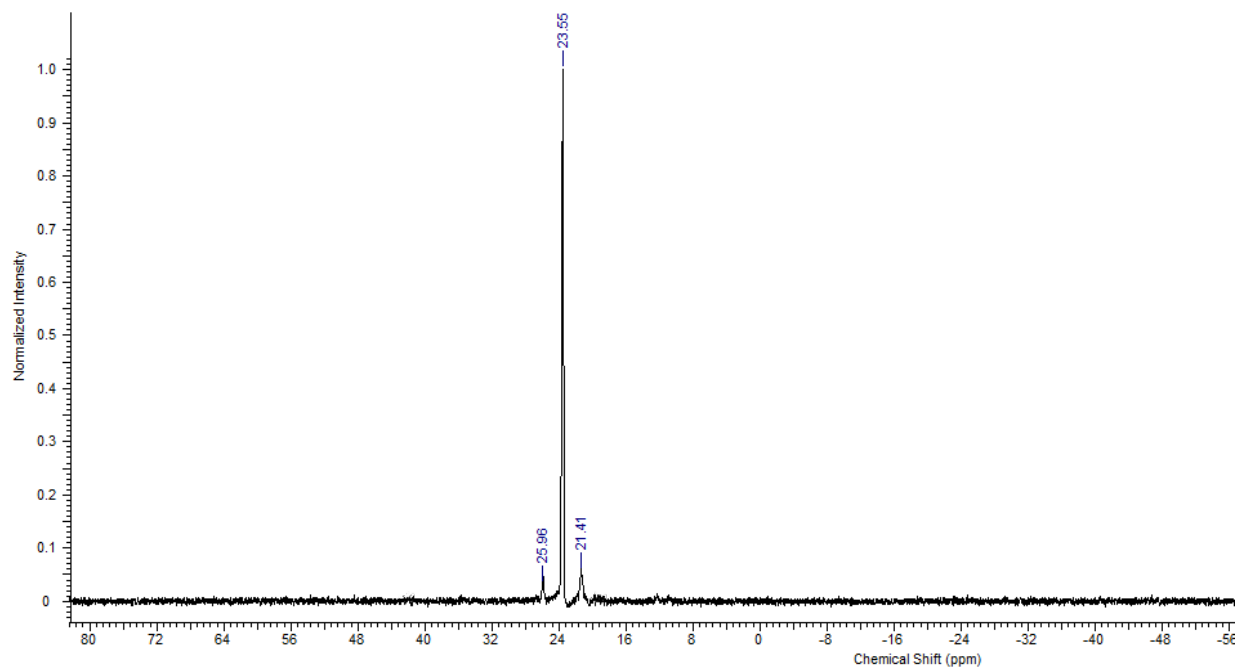


Figure S39 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of diselenide of **17a** (161 MHz, CD_2Cl_2 , 297 K)

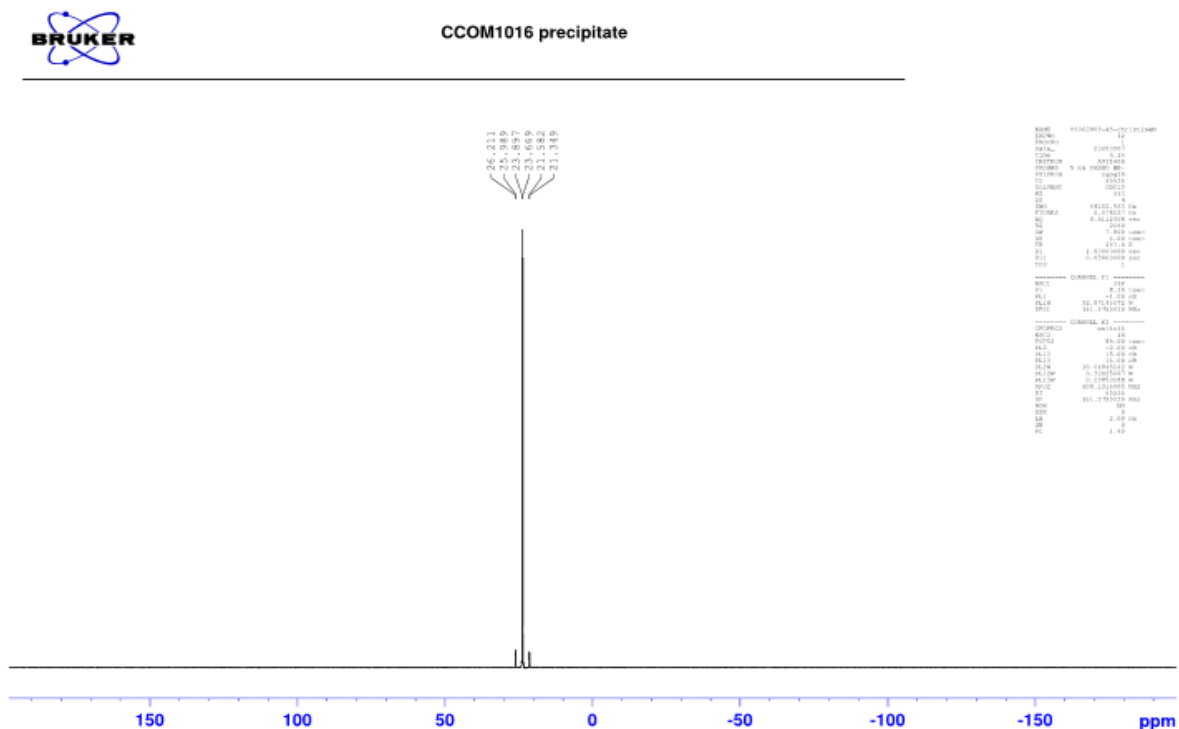
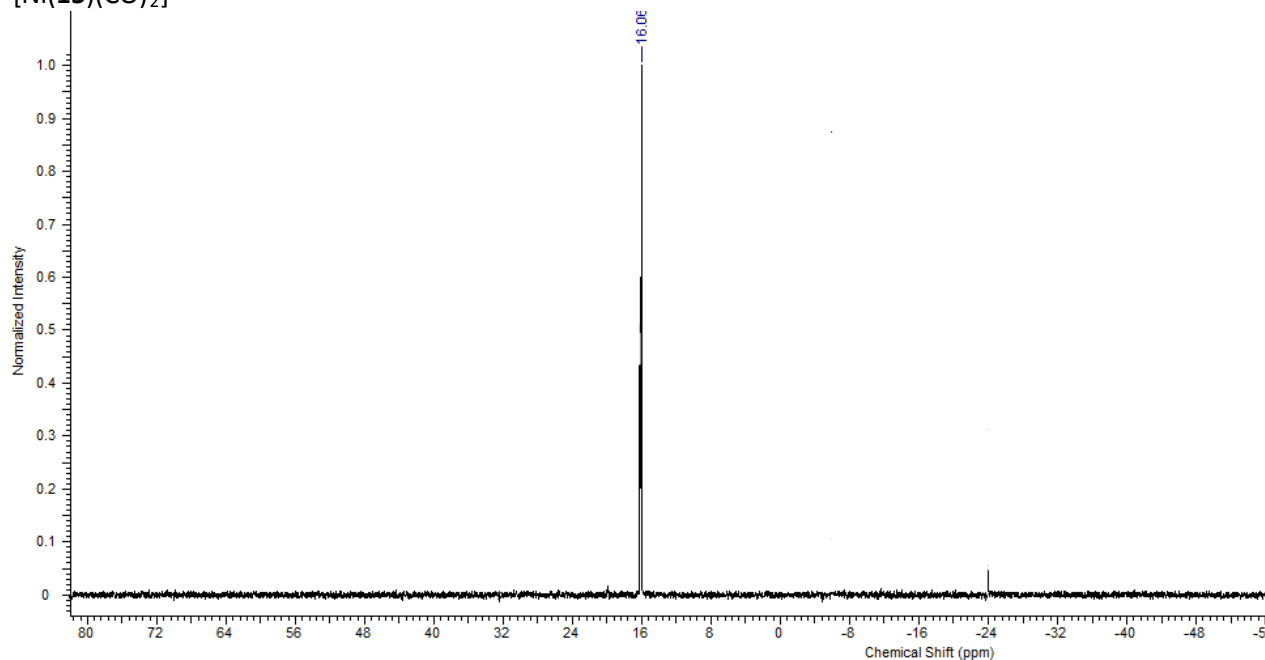


Figure S40 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of diselenide of **17b** (161 MHz, CD_2Cl_2 , 297 K)



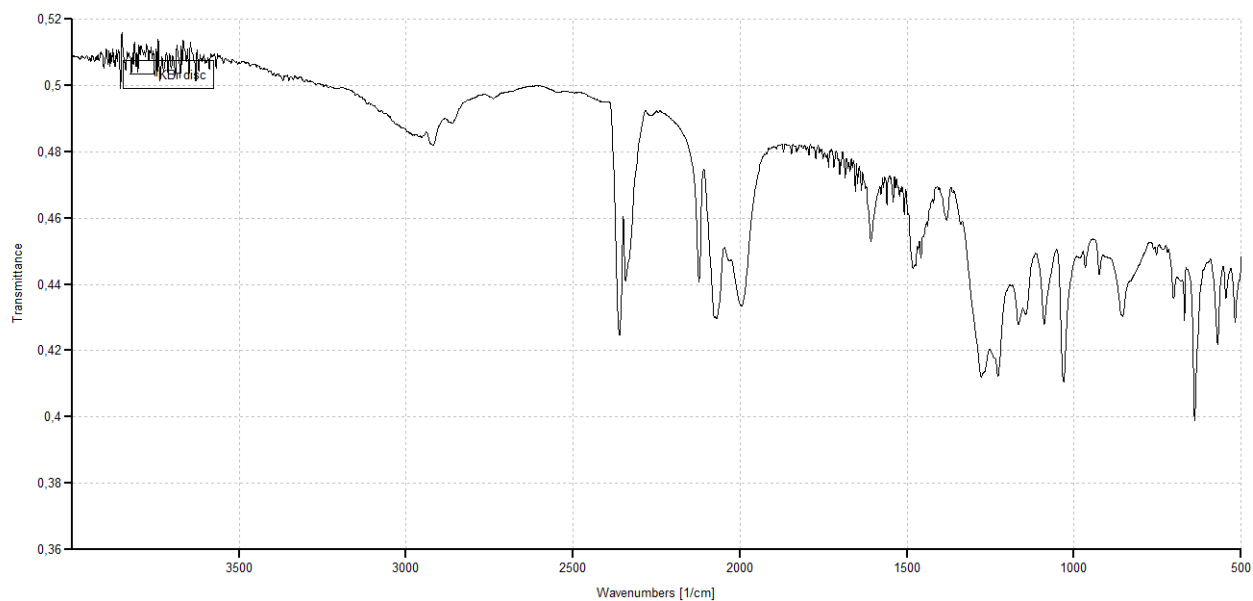


Figure S43 IR spectrum of $[\text{Ni}(\mathbf{15})(\text{CO})_2]$ (KBr)

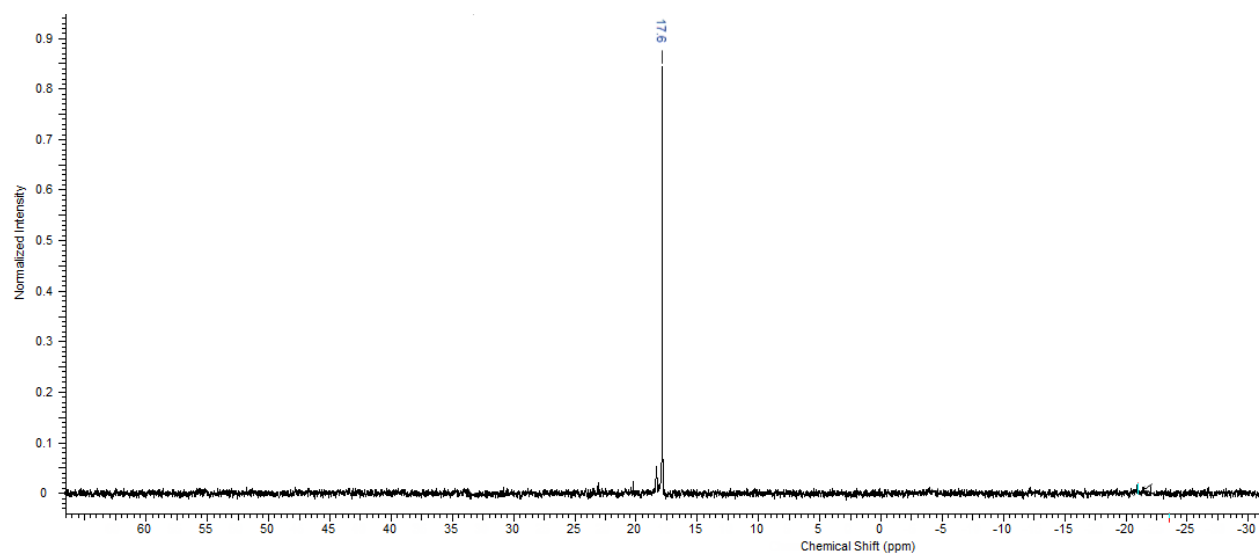


Figure S44 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ni}(\mathbf{17a})(\text{CO})_2]$ (161 MHz, CD_2Cl_2 , 297 K)

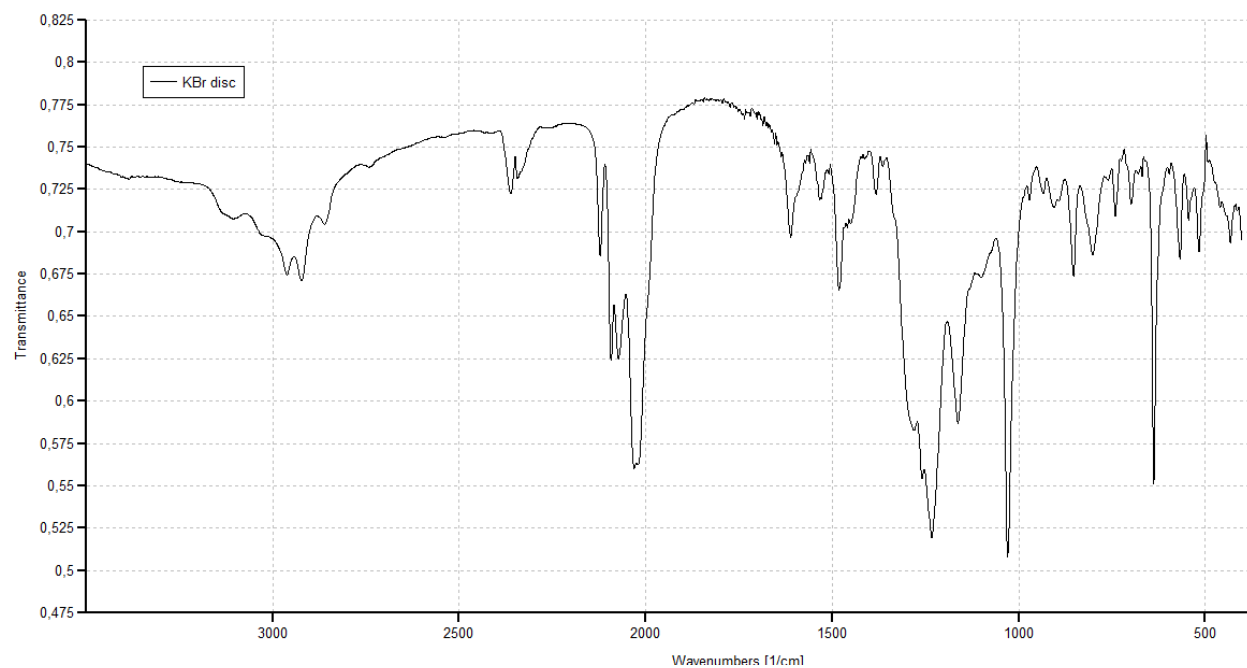


Figure S45 IR spectrum of $[\text{Ni}(\text{17a})(\text{CO})_2]$ (KBr)

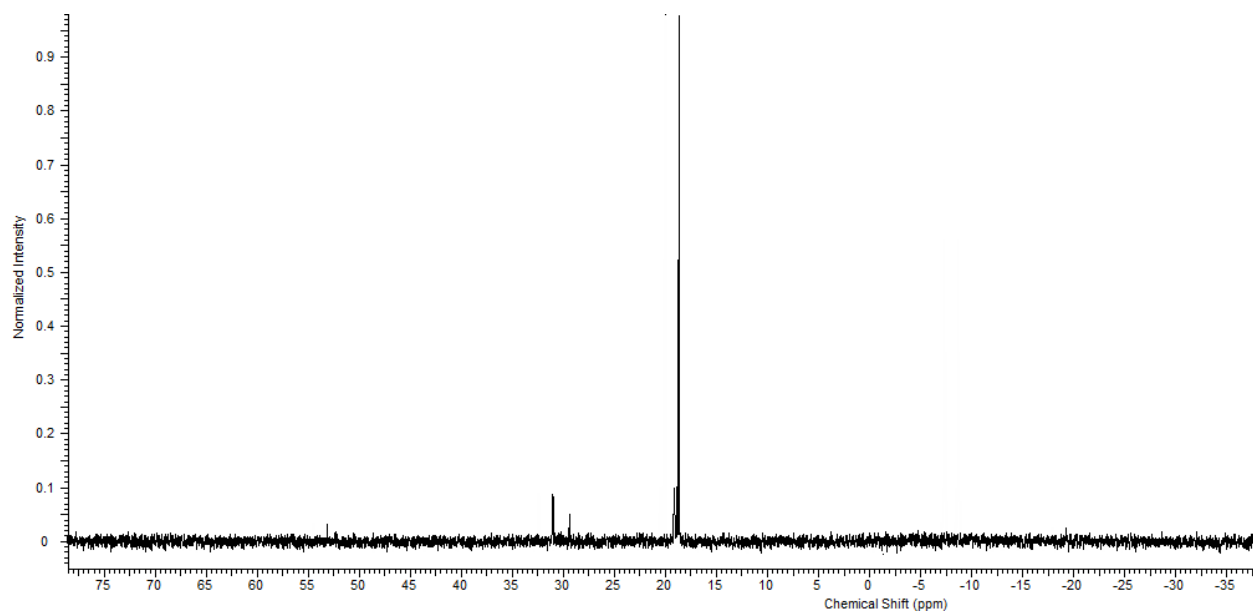


Figure S46 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ni}(\text{17b})(\text{CO})_2]$ (161 MHz, CD_2Cl_2 , 297 K)

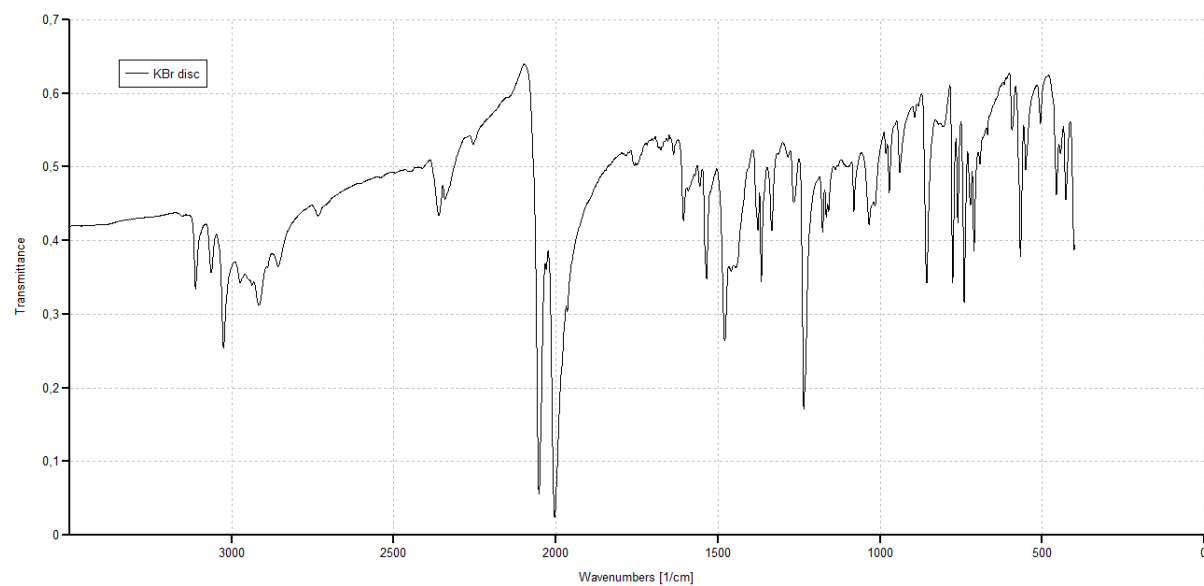


Figure S47 IR spectrum of $[\text{Ni}(\mathbf{17b})(\text{CO})_2]$ (KBr)

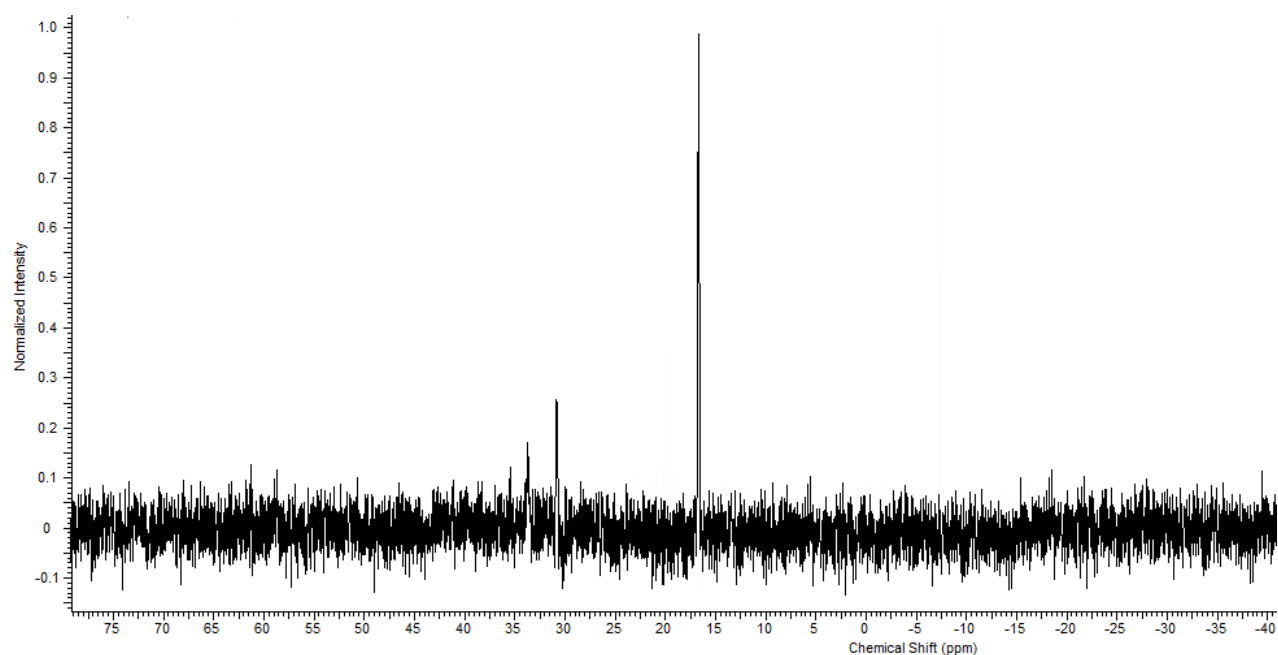


Figure S48 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ni}(\mathbf{17c})(\text{CO})_2]$ (161 MHz, CD_2Cl_2 , 297 K)

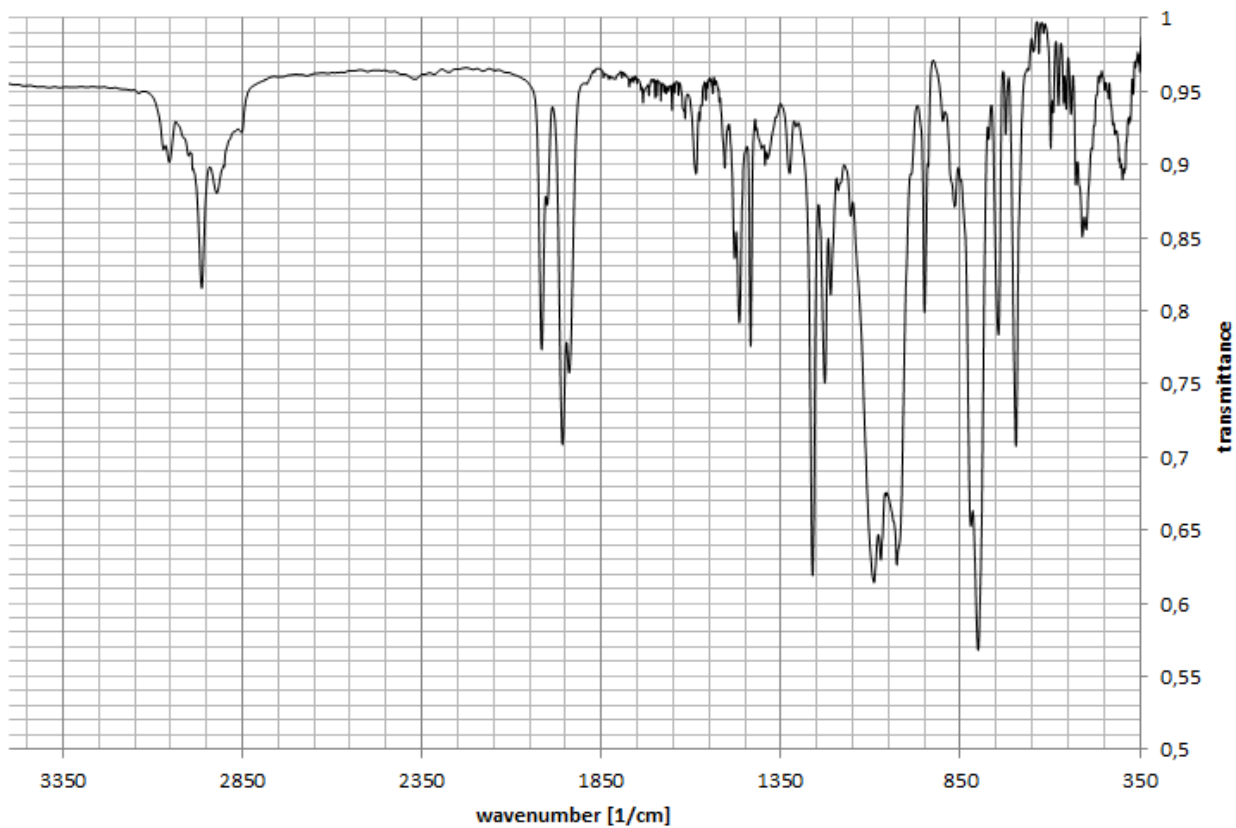


Figure S49 IR spectrum of $[\text{Ni}(\mathbf{17c})(\text{CO})_2]$ (KBr)

14- Palladium complexes

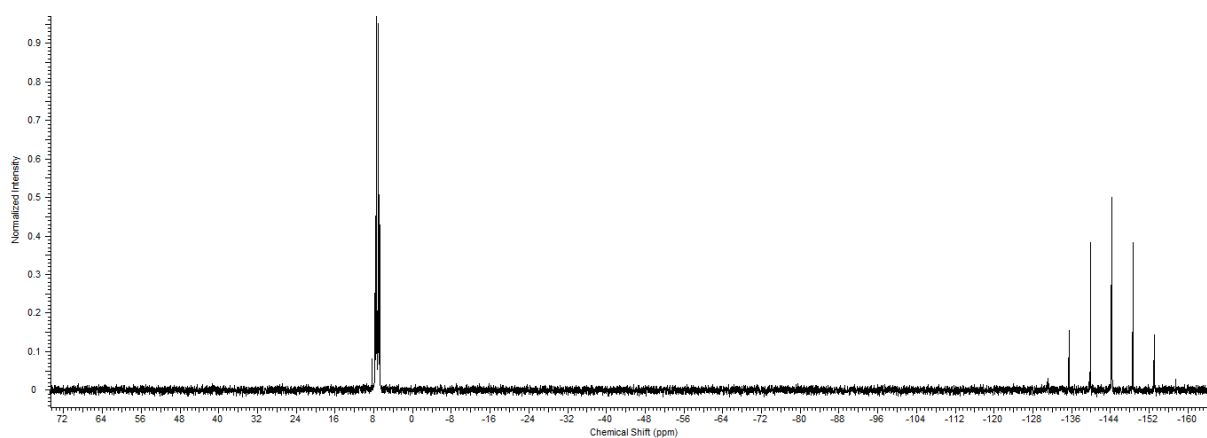


Figure S50 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(\mathbf{14})]^+$ (161 MHz, CD_2Cl_2 , 297 K)

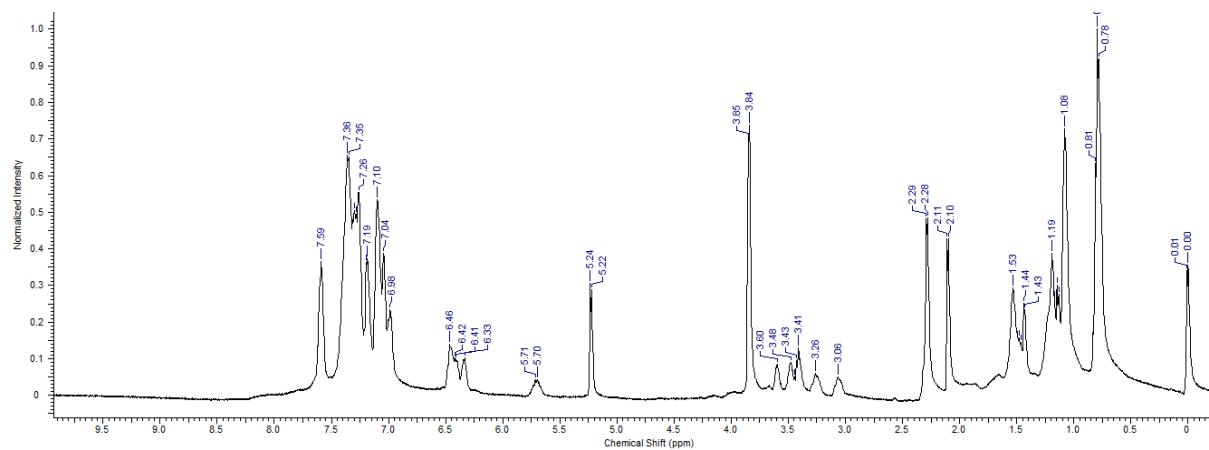


Figure S51 ^1H NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(14)]^+$ (400 MHz, CD_2Cl_2 , 297 K)

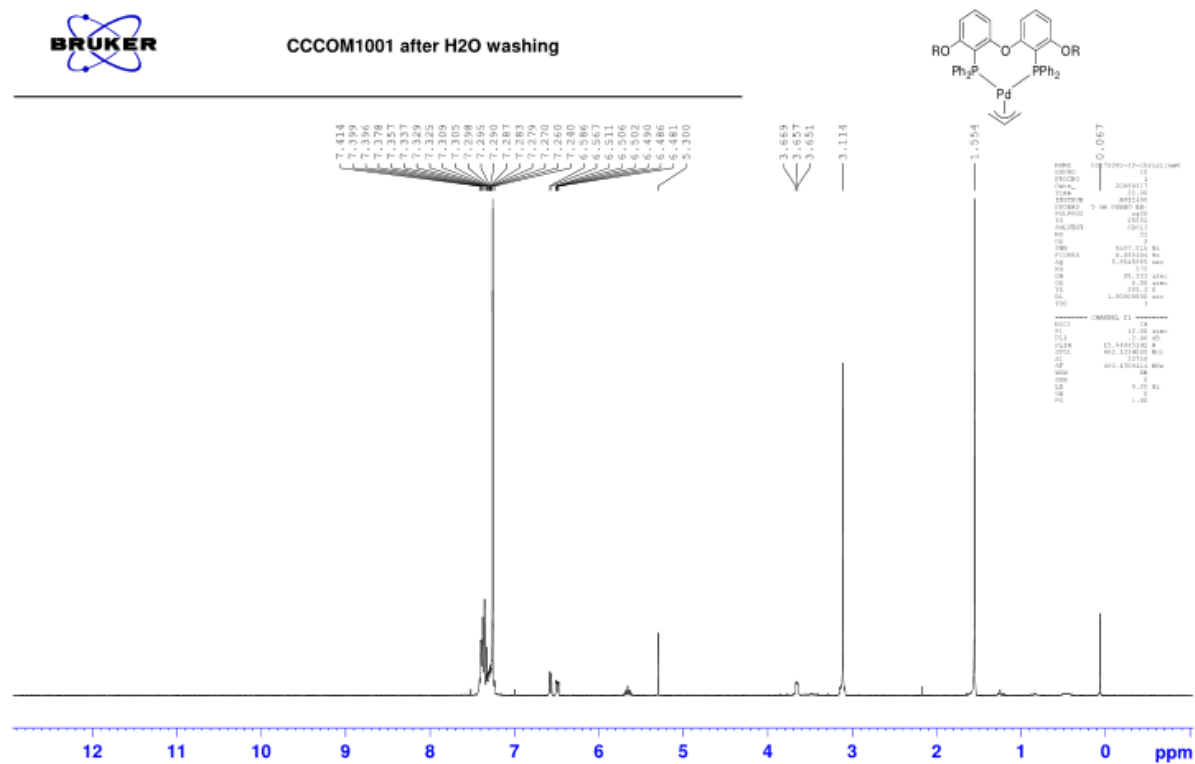


Figure S52 ^1H NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$ (500 MHz, CD_2Cl_2 , 297 K)



CCCOM1001 after H2O washing

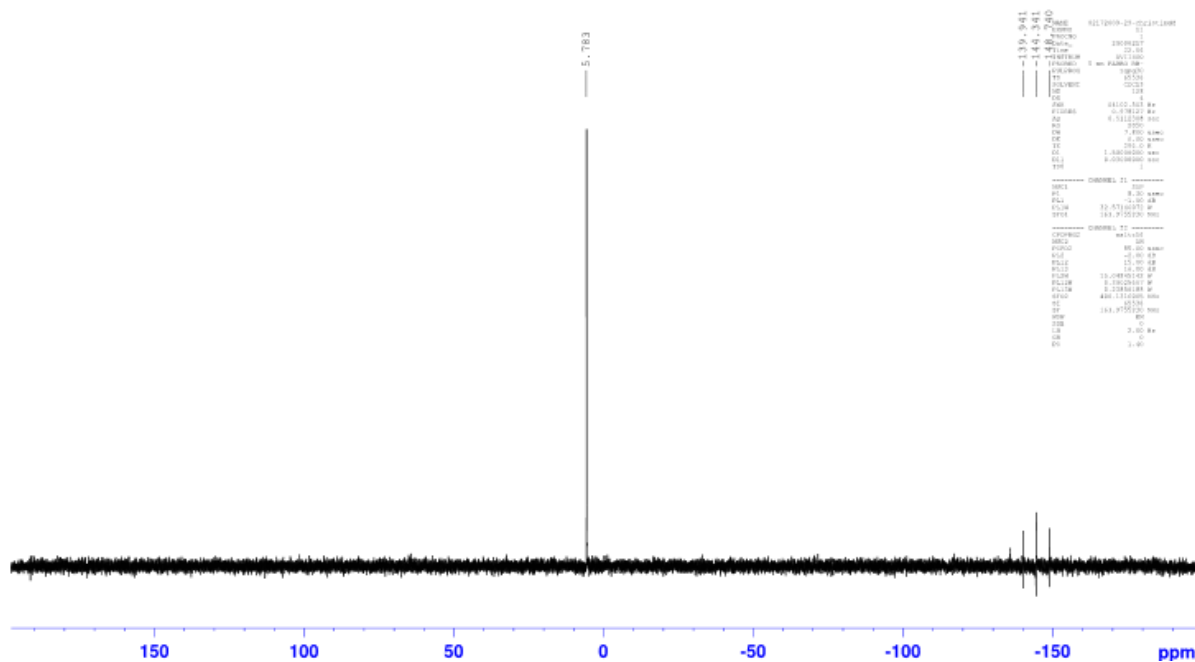
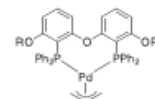


Figure S53 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$ (202 MHz, CD_2Cl_2 , 297 K)



CCCOM1001

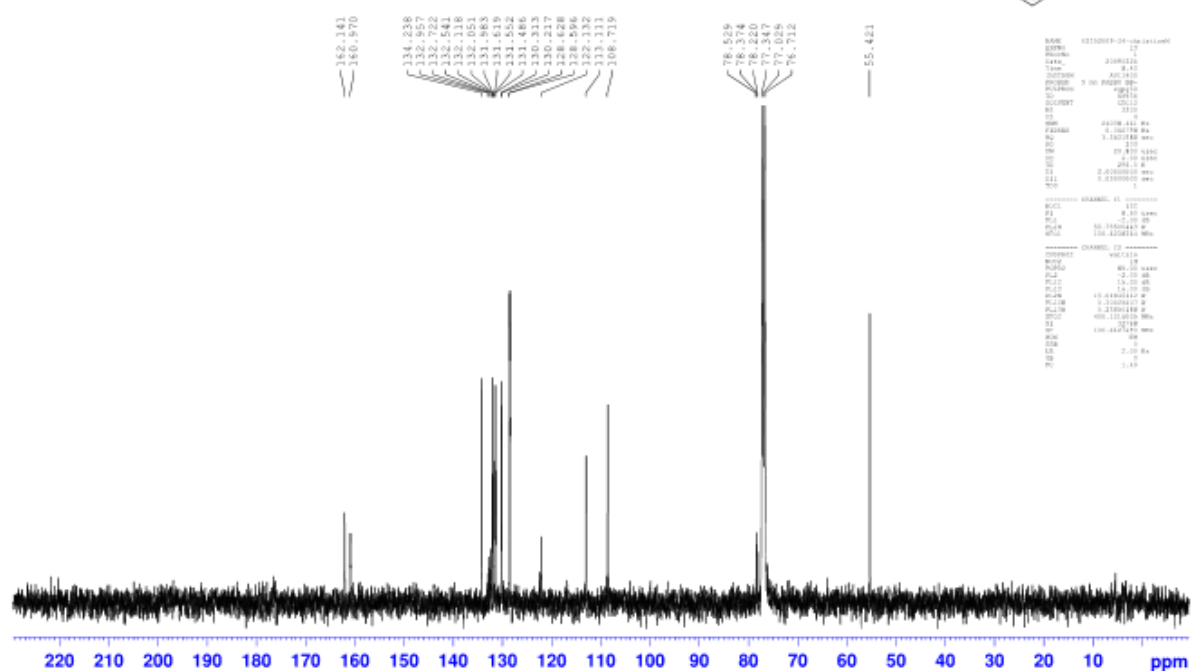
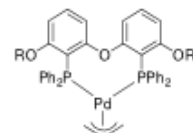


Figure S54 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$ (100 MHz, CD_2Cl_2 , 297 K)



CCCOM1004 after washing with H₂O

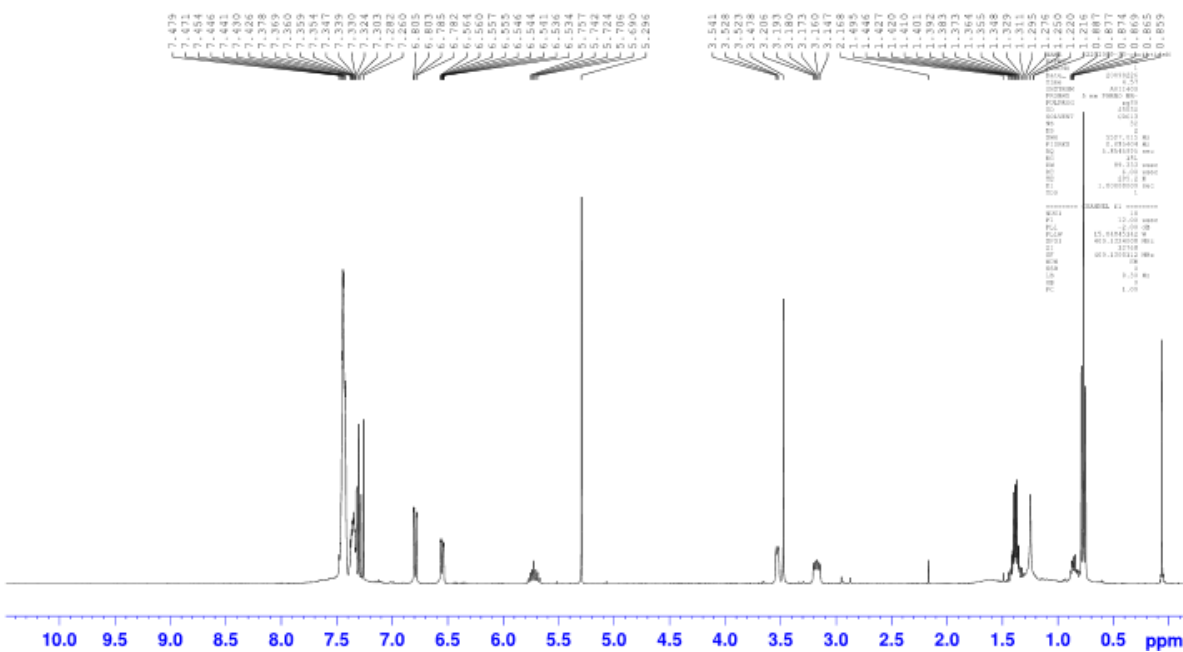
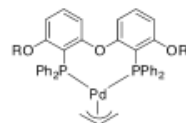
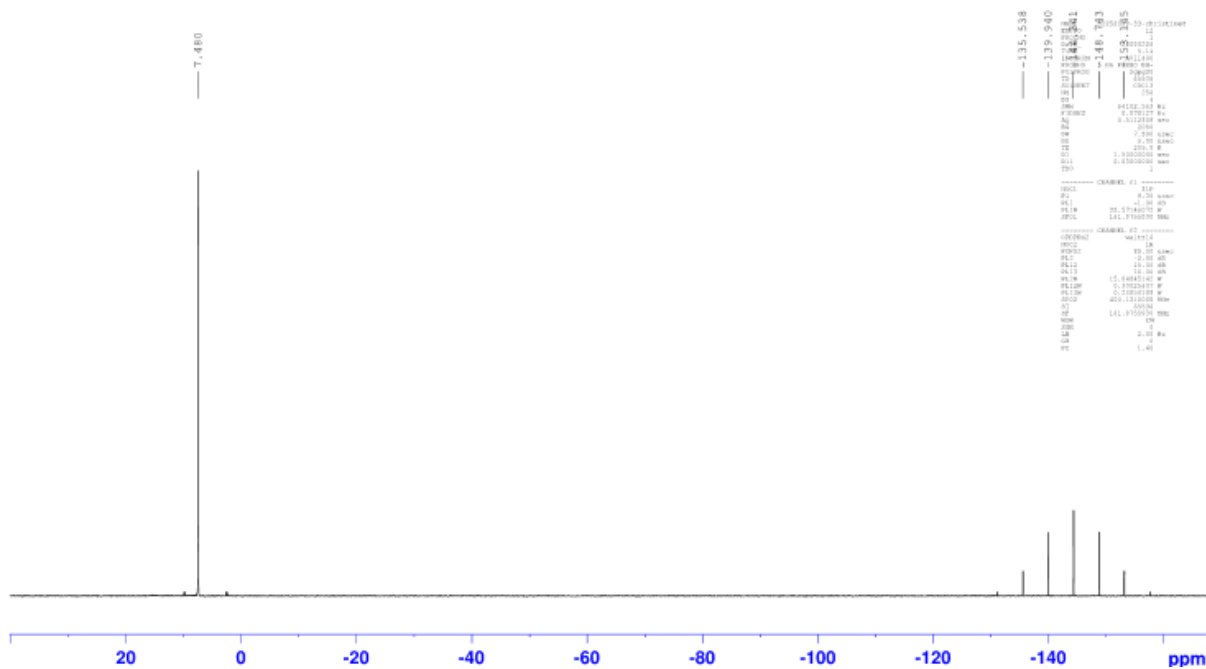
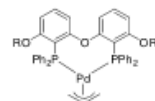
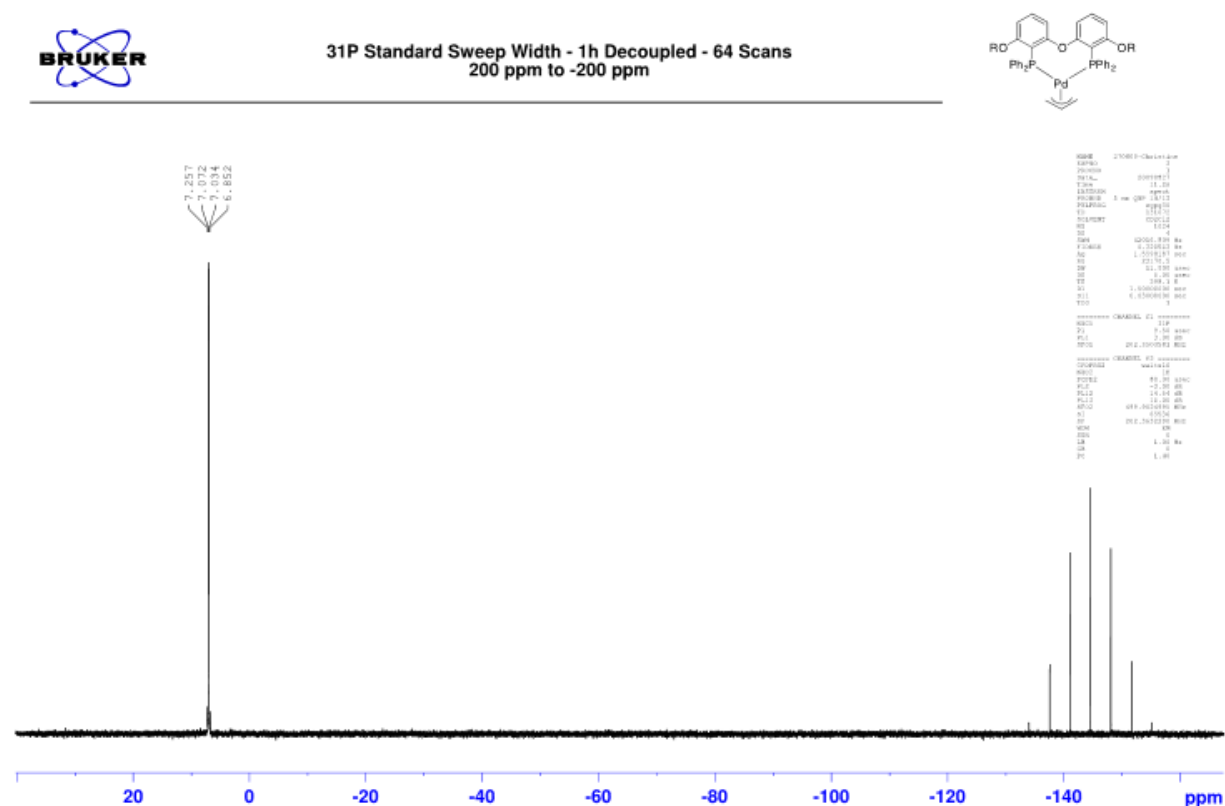
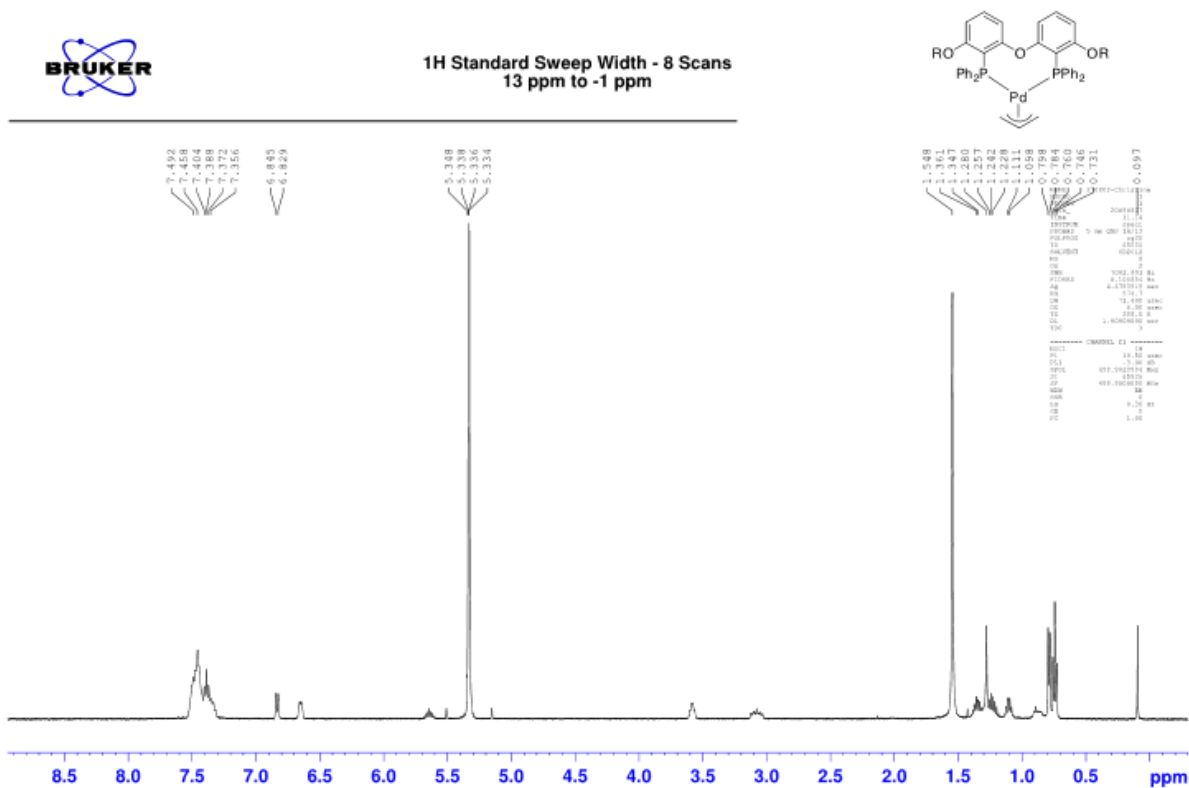


Figure S55 ^1H NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(17a)]^+$ (400 MHz, CD_2Cl_2 , 297 K)



CCCOM1004 after washing with H₂O





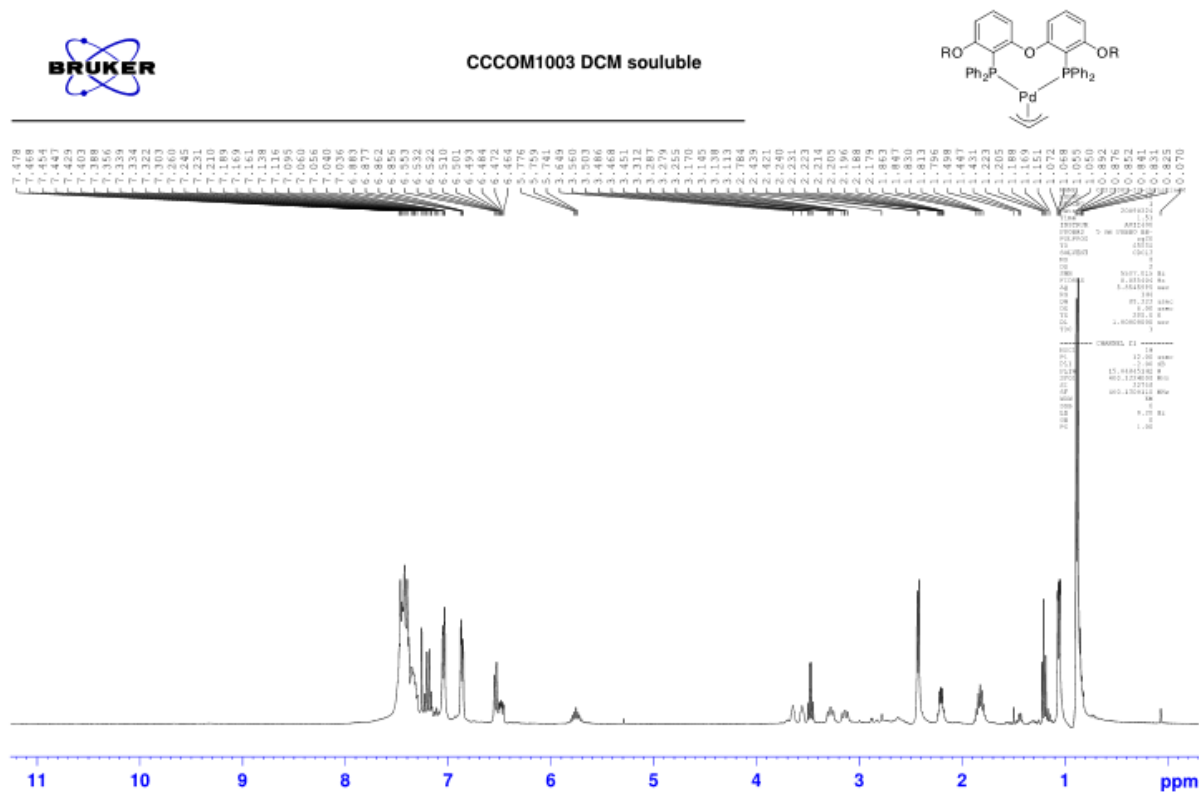


Figure S59 ^1H NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(17\text{c})]^+$ (400 MHz, CD_2Cl_2 , 297 K)

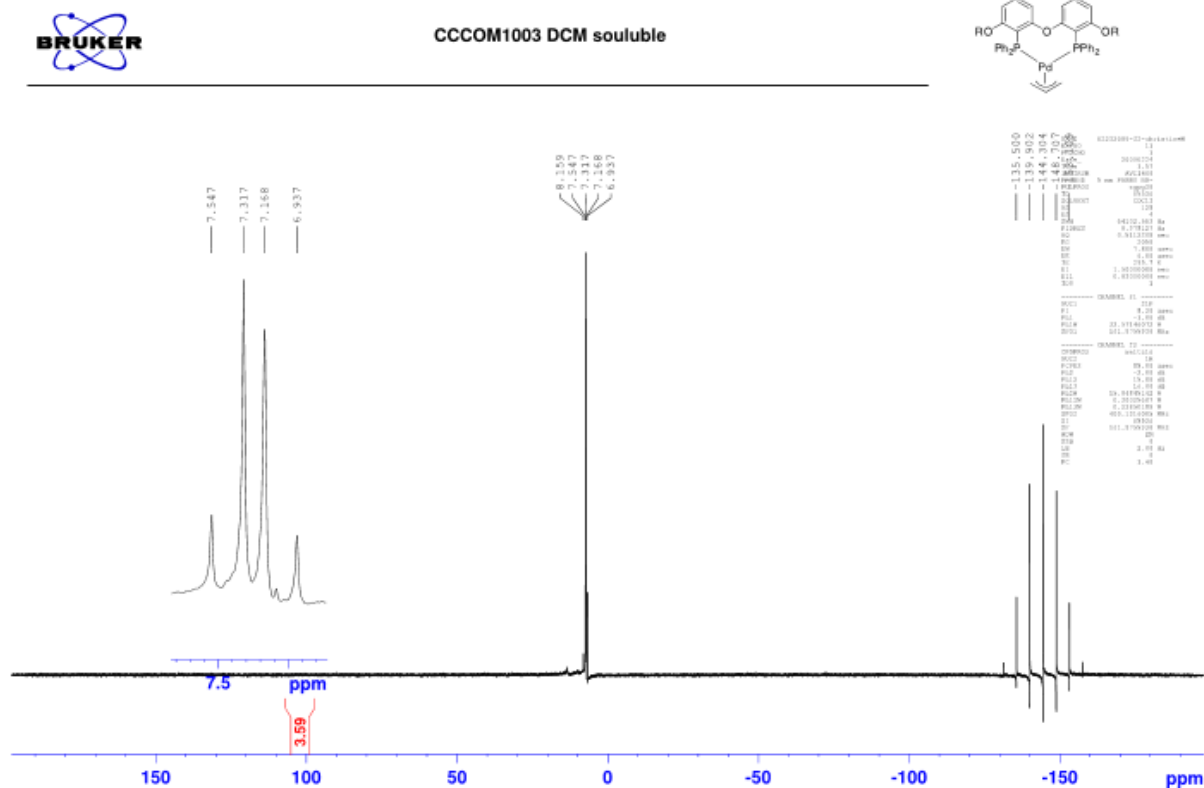


Figure S60 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(\mathbf{17c})]^+$ (161 MHz, CD_2Cl_2 , 297 K)

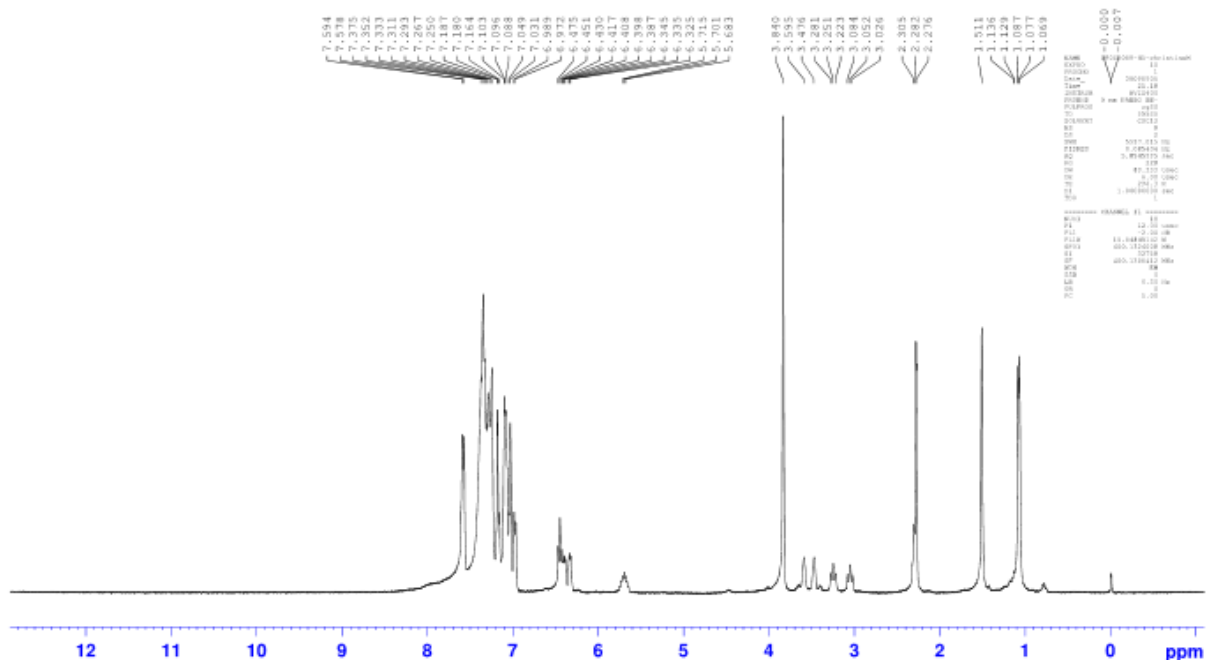
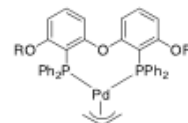


Figure S61 ^1H NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(17\text{d})]^+$ (400 MHz, CD_2Cl_2 , 297 K)

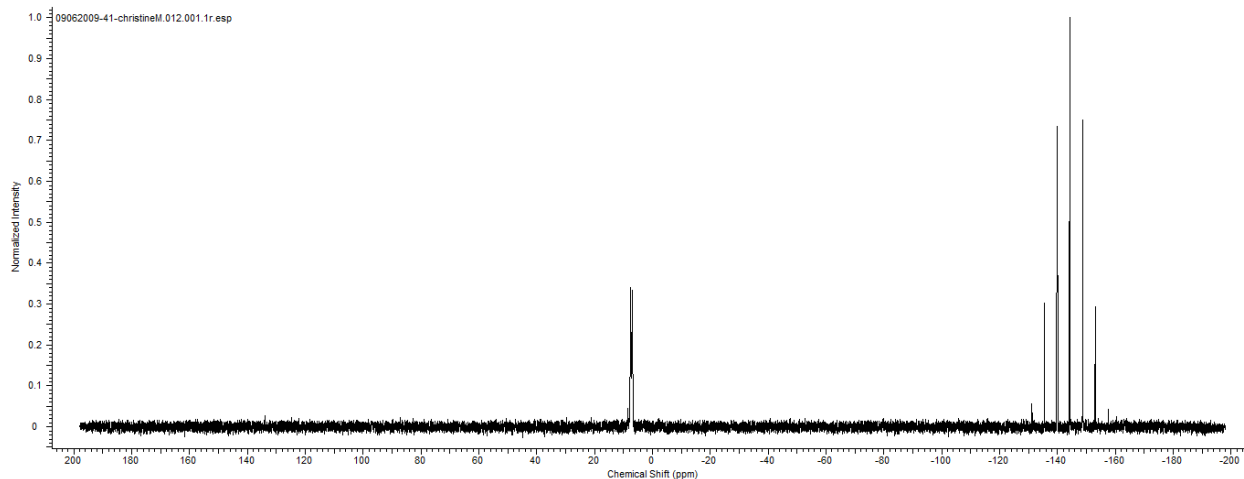


Figure S62 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pd}(\eta^3\text{-allyl})(17\text{d})]^+$ (161 MHz, CD_2Cl_2 , 297 K)