Supporting Information

Synthesis of New Chiral Bidentate Isonitrile-Acyclic Diaminocarbene Palladium(II) Compounds and Their Catalytic Activity

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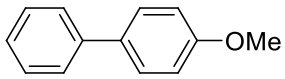
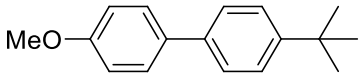
A Procedures for Catalytic Processes and Compound Characterization

General procedure for the Suzuki-Miyaura cross coupling: To a stirred solution of bromo benzene (1.0 mmol, 1.0 equiv.), boronic acid (1.2 mmol, 1.2 equiv.) and catalyst (1 mol%) in 2 ml of EtOH, KO^{t}Bu (1.0 mmol, 1.2 equiv.) was added at room temperature. The reaction mixture was stirred for 20 hours, extracted with DCM (3x 10 ml) and dried over $MgSO_4$. The biphenyls were obtained by column chromatography as white solids.



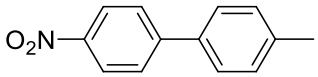
4-Methoxybiphenyl (table 2, entry 4)

According to the general procedure, bromo benzene (105 µl, 1.0 mmol, 1.0 equiv.), 4-methoxy phenylboronic acid (182 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5a** (1 mol%) afforded 4-methoxybiphenyl (138 mg, 0.75 mmol, 75 %) as white solid. NMR- data are in agreement with those reported in literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 4H), 7.47 – 7.40 (m, 2H), 7.36 – 7.29 (m, 1H), 7.04 – 6.97 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 139.8, 132.7, 127.7, 127.1, 125.7, 125.6, 113.1, 54.3.



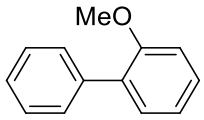
4-*tert*-Butyl-4'-methoxybiphenyl (table 2, entry 5)

According to the general procedure, 4-methoxybromo benzene (120 µl, 1.0 mmol, 1.0 equiv.), 4-*tert*-butyl phenylboronic acid (214 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5a** (1 mol%) afforded 4- *tert*-butyl-4'-methoxybiphenyl (200 mg, 0.83 mmol, 83 %) as white solid. NMR- data are in agreement with those reported in literature.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.38 (m, 5H), 7.02 – 6.91 (m, 2H), 3.85 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 149.6, 137.9, 133.6, 128.0, 126.4, 125.7, 114.1, 55.4.



4-Methyl-4'-nitrobiphenyl (table 2, entry 6)

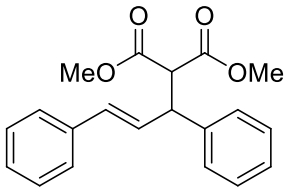
According to the general procedure, 4-nitrobromo benzene (202 mg, 1.0 mmol, 1.0 equiv.), 4-methyl phenylboronic acid (163 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5b** (1 mol%) afforded 4-methyl-4'-nitrobiphenyl (164 mg, 0.77 mmol, 77 %) as off-white solid. NMR- data are in agreement with those reported in literature.[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 – 8.25 (m, 2H), 7.76 – 7.69 (m, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 146.8, 139.1, 135.9, 129.9, 127.5, 127.3, 124.1, 21.3.



2-Methoxybiphenyl (table 2, entry 7)

According to the general procedure, bromo benzene (105 µl, 1.0 mmol, 1.0 equiv.), 2-methoxy phenylboronic acid (182 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5b** (1 mol%) afforded 2-methoxy biphenyl (150 mg, 0.81 mmol, 81 %) as off-white solid. NMR- data are in agreement with those reported in literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.49 – 7.40 (m, 2H), 7.40 – 7.31 (m, 2H), 7.23 – 7.10 (m, 2H), 6.96 – 6.87 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 142.8, 141.1, 129.8, 128.8, 127.4, 127.2, 119.7, 112.9, 112.7, 55.3.

Intermolecular Asymmetric Allylic Alkylation:



(*E*)-Dimethyl 2-(1,3-diphenylallyl)malonate (**12**) (table 3)

To a stirred solution of *rac*-(*E*)-1,3-diphenyl allylacetate (126 mg, 0.5 mmol, 1.0 equiv.), dimethyl malonate (172 µl, 1.5 mmol, 3.0 equiv.) and catalyst (10 mol%) in 3 ml THF, BSA (370 µL, 1.5 mmol, 3.0 equiv.) and KOAc (10 mg, 0.1 mmol, 20 mol%) was added. The reaction mixture was heated to 60 °C and stirred for the indicated time. After dilution with Et_2O (5 ml), the reaction was quenched with NH_4Cl (sat.) (25 ml), extracted with Et_2O (3x 25 ml), dried over $MgSO_4$. (*E*)-Dimethyl 2-(1,3-diphenylallyl)malonate (**11**) was obtaind by column chromatography as colorless oil. NMR- data are in agreement with those reported in literature.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 10H), 6.50 (d, J = 15.8 Hz, 1H), 6.34 (dd, J = 15.7, 8.5 Hz, 1H), 4.28 (dd, J = 10.9, 8.5 Hz, 1H), 3.97 (d, J = 10.9 Hz, 1H), 3.71 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 167.9, 140.3, 136.9, 131.9, 129.2, 128.9, 128.6, 128.0, 127.7, 127.3, 126.5, 57.8, 52.8, 52.6, 49.3. ESI-MS, m/z: [MH^+-$C_5H_8O_4$] 193.10, [MNH_4^+] 342.17, [2M+Na^+] 671.26.

B Optimization for the AAA

Table S1. Optimization of the reaction conditions for the AAA between *rac*-(*E*)-1,3-diphenyl allylacetate (10) and dimethyl malonate (11) using 4 as catalyst.

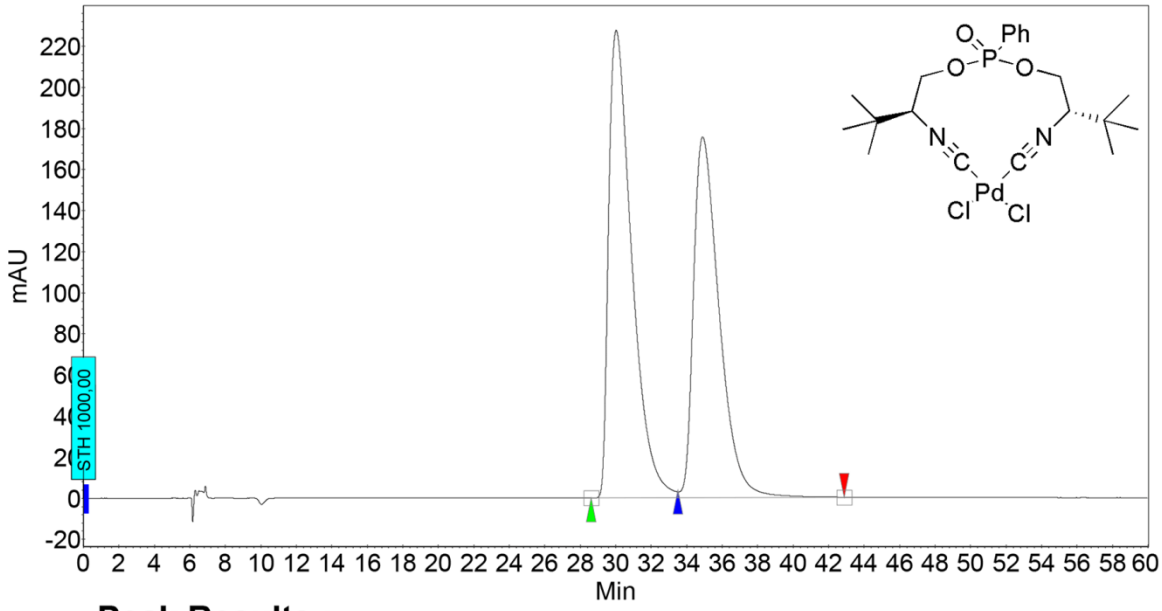
Entry	mol% of catalyst	Time [min]	Temperature [°C]	Yield [%]
1	1			9
2	5	60	60	42
3	10			100
4		30	60	51
5	10	60	40	27
6[a]		60	60	83

Conditions: *rac*-(*E*)-1,3-diphenyl allylacetate (1.0 equiv., 0.5 mmol, 126 mg), dimethyl malonate (3.0 equiv., 1.5 mmol, 172 µL), BSA (3.0 equiv., 1.5 mmol, 370 µL), KOAc (20 mol%, 0.1 mmol, 10 mg), catalyst **4**, 3 mL THF.

[a] 1.0 equiv. dimethyl malonate.

C Chiral HPLC Data

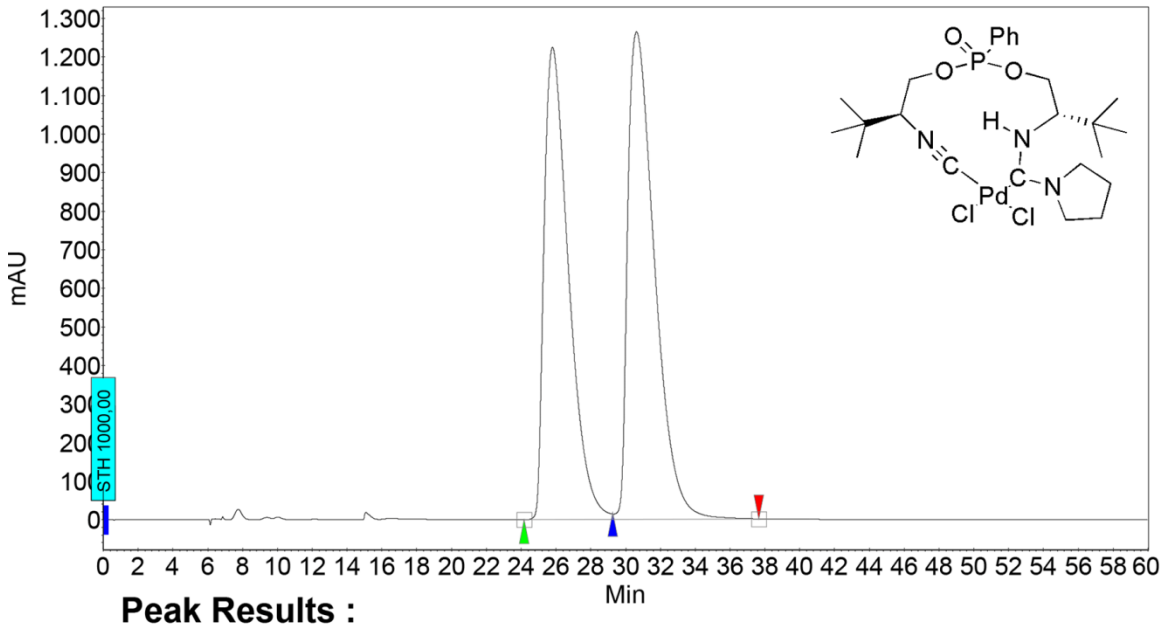
Enantiomeric excess was determined by chiral HPLC (Chiralcel OJ-H, n-Heptan/iPrOH 90/10, 0.5 ml/min, 254 nm)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	30,03	53,85	227,6	344,2	53,850
2	UNKNOWN	34,90	46,15	175,6	295,0	46,150
Total			100,00	403,2	639,2	100,000

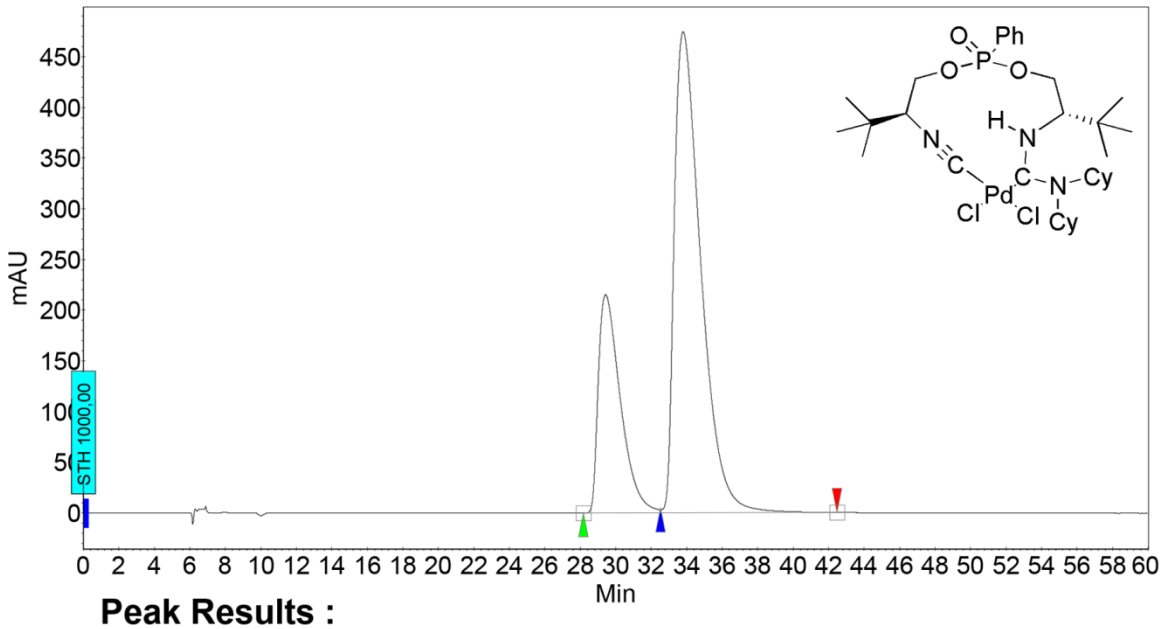
Figure S1. HPLC-Spetra for Table 3, Entry 1.



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25,80	46,84	1224,7	1994,7	46,842
2	UNKNOWN	30,63	53,16	1264,1	2263,6	53,158
Total			100,00	2488,8	4258,3	100,000

Figure S2. HPLC-Spetra for Table 3, Entry 2.

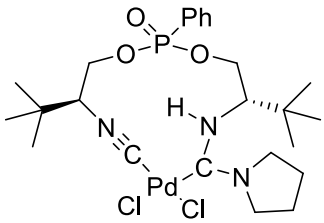


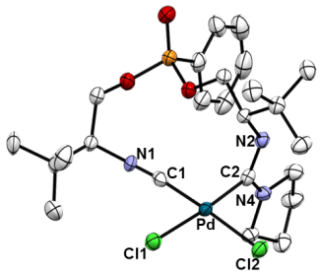
Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	29,43	27,45	215,5	311,8	27,454
2	UNKNOWN	33,80	72,55	474,5	823,9	72,546
Total			100,00	690,0	1135,7	100,000

Figure S3. HPLC-Spetra for Table 3, Entry 3

D Solid-State Structures





Compound	**5a**
Formula	$C_{24}H_{38}N_3O_3PCl_2Pd$
$D_{calc.}$/ g cm^{-3}	1.398
μ/mm^{-1}	7.436
Formula Weight	624.84
Colour	colourless
Shape	prism
Max Size/mm	0.30
Mid Size/mm	0.19
Min Size/mm	0.06
T/K	123
Crystal System	orthorhombic
Flack Parameter	-0.026(5)
Hooft Parameter	-0.014(3)
Space Group	$P2_12_12_1$
a/Å	12.91450(9)
b/Å	18.83710(10)
c/Å	24.40150(13)
α/°	90
β/°	90
γ/°	90
V/Å^3	5936.19(6)
Z	8
Z'	2
Θ_{min}/°	3.623
Θ_{max}/°	66.636
Measured Refl.	41098
Independent Refl.	10287
Reflections Used	10116
R_{int}	0.0645
Parameters	619
Restraints	0
Largest Peak	0.633
Deepest Hole	-1.093
GooF	1.029
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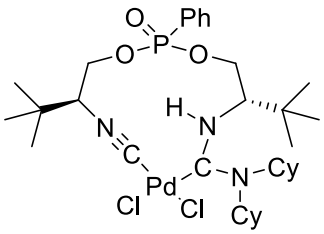
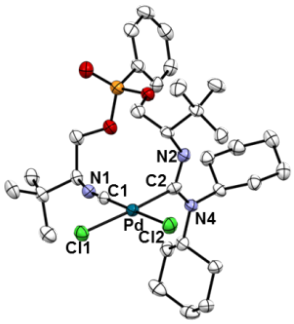
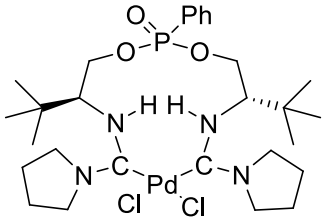
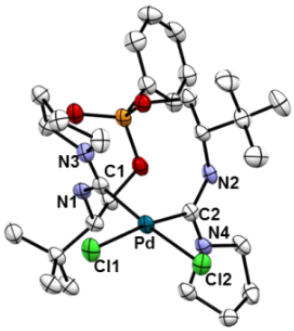
wR_2	0.0882
R_1 (all data)	0.0353
R_1	0.0349





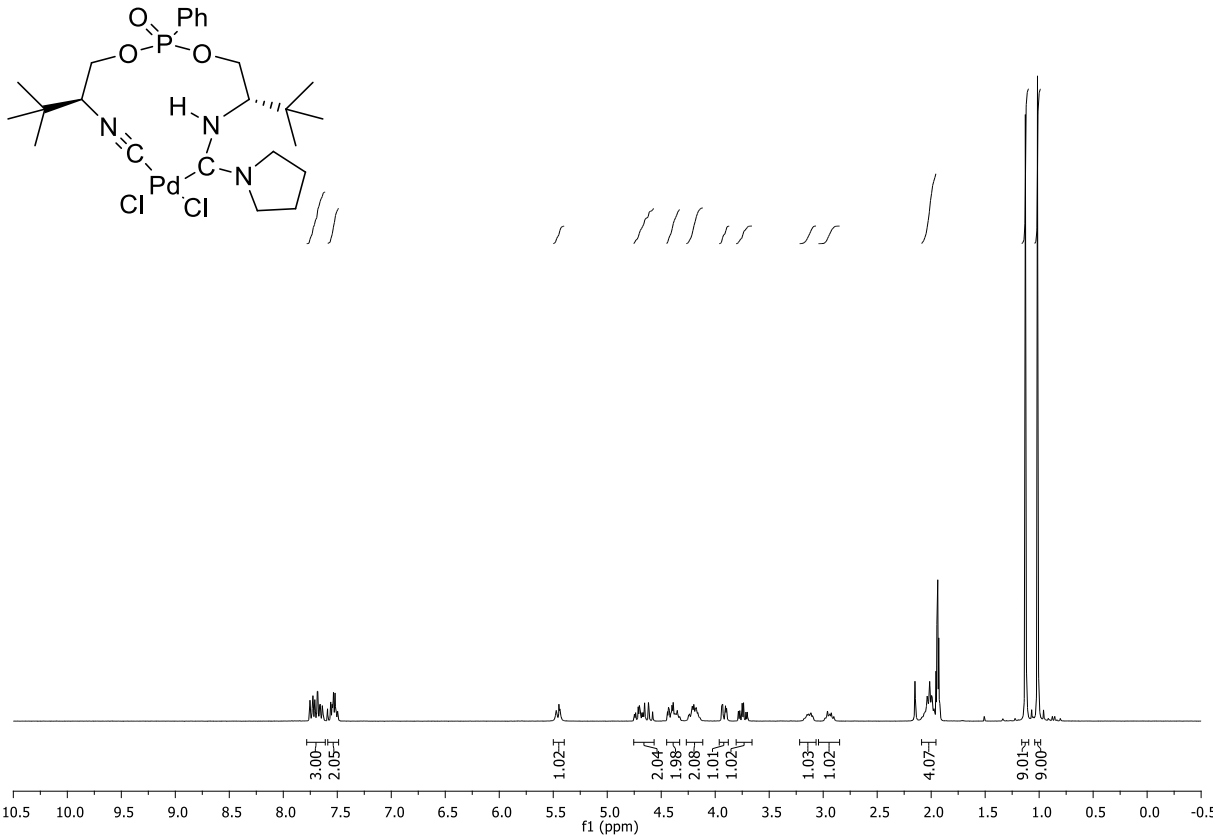
Compound	**5c**
Formula	$C_{32}H_{52}Cl_2N_3O_3PPd$
$D_{calc.}$/ g cm^{-3}	1.386
μ/mm^{-1}	6.350
Formula Weight	735.03
Colour	colourless
Shape	needle
Max Size/mm	0.18
Mid Size/mm	0.02
Min Size/mm	0.01
T/K	122.98(17)
Crystal System	monoclinic
Flack Parameter	0.005(9)
Hooft Parameter	0.013(9)
Space Group	$P2_1$
a/Å	9.56244(16)
b/Å	17.2200(3)
c/Å	10.7458(2)
α/°	90
β/°	95.6935(15)
γ/°	90
V/Å^3	1760.73(5)
Z	2
Z'	1
Θ_{min}/°	4.134
Θ_{max}/°	70.857
Measured Refl.	7961
Independent Refl.	4862
Reflections Used	4555
R_{int}	0.0458
Parameters	379
Restraints	1
Largest Peak	1.044
Deepest Hole	-1.041
GooF	1.012
wR_2 (all data)	0.1008
wR_2	0.0983
R_1 (all data)	0.0430
R_1	0.0396

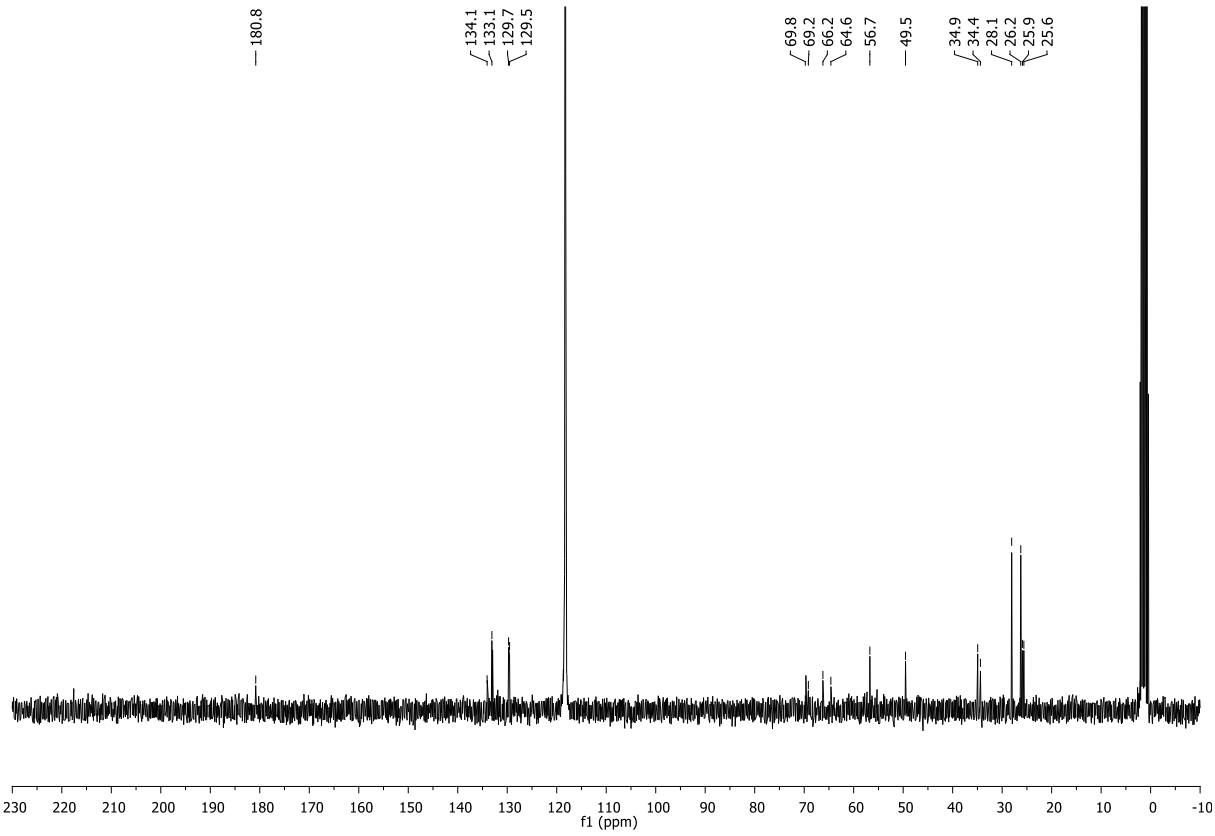


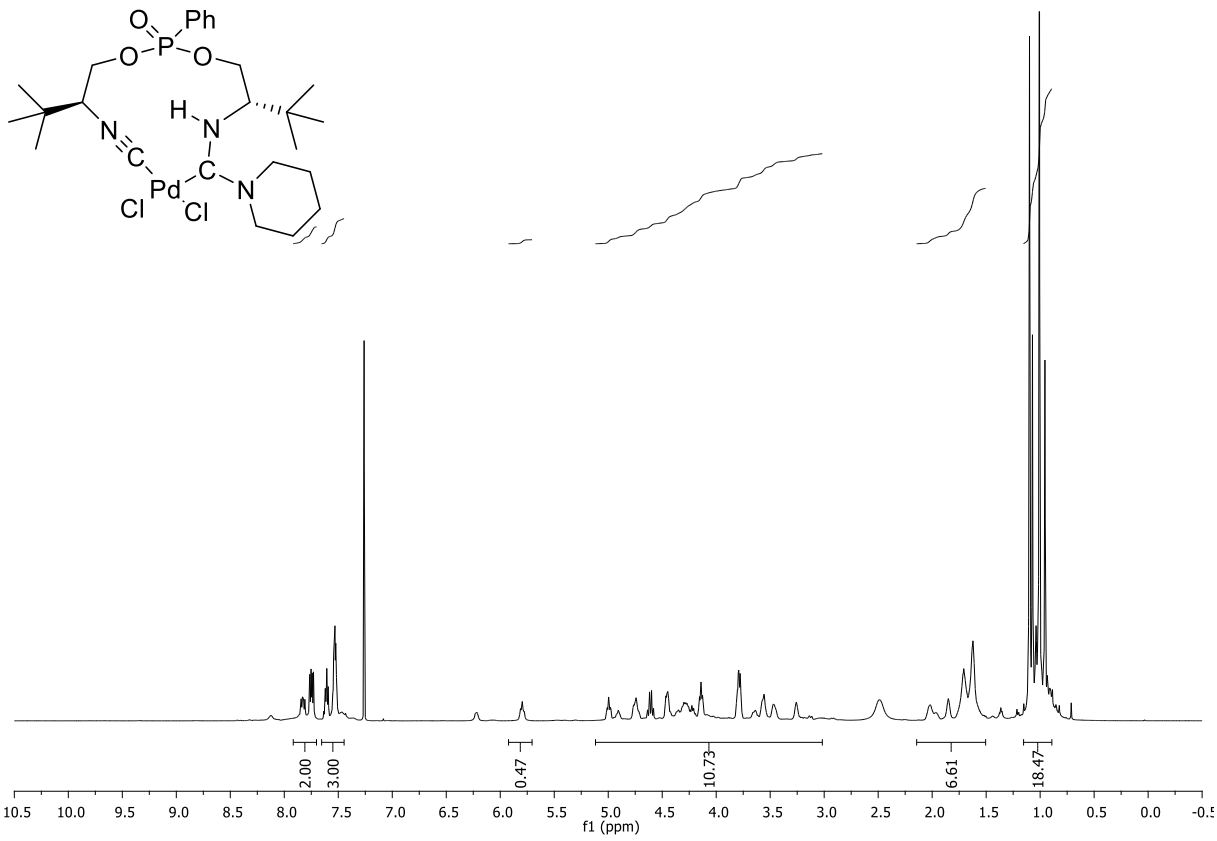


Compound	**6**
Formula	$C_{32}H_{57}N_4O_4PCl_2Pd$
$D_{calc.}$/ g cm^{-3}	1.372
μ/mm^{-1}	6.048
Formula Weight	770.08
Colour	colourless
Shape	needle
Max Size/mm	0.41
Mid Size/mm	0.07
Min Size/mm	0.05
T/K	123.00(10)
Crystal System	orthorhombic
Flack Parameter	-0.038(9)
Hooft Parameter	-0.018(7)
Space Group	$P2_12_12_1$
a/Å	13.9031(3)
b/Å	16.1632(4)
c/Å	16.5945(4)
α/°	90
β/°	90
γ/°	90
V/Å^3	3729.10(14)
Z	4
Z'	1
Θ_{min}/°	3.818
Θ_{max}/°	74.046
Measured Refl.	17492
Independent Refl.	6887
Reflections Used	6375
R_{int}	0.0694
Parameters	403
Restraints	0
Largest Peak	1.385
Deepest Hole	-1.018
GooF	1.034
wR_2 (all data)	0.1342
wR_2	0.1296
R_1 (all data)	0.0529
R_1	0.0487

E NMR-Spectra



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C
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Cl
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6.61
18.47
10.5 10.0 9.5 9.0 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 0.0 -0.5
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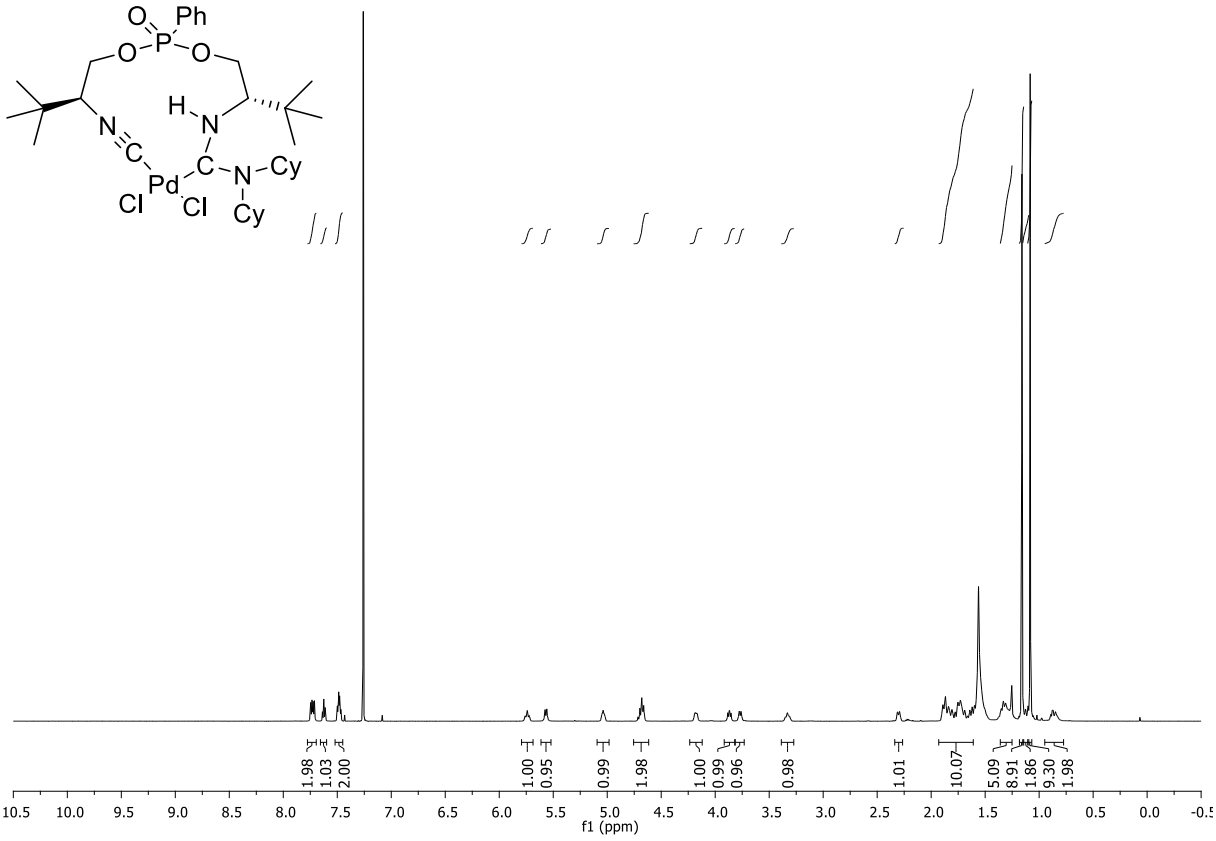
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1.00
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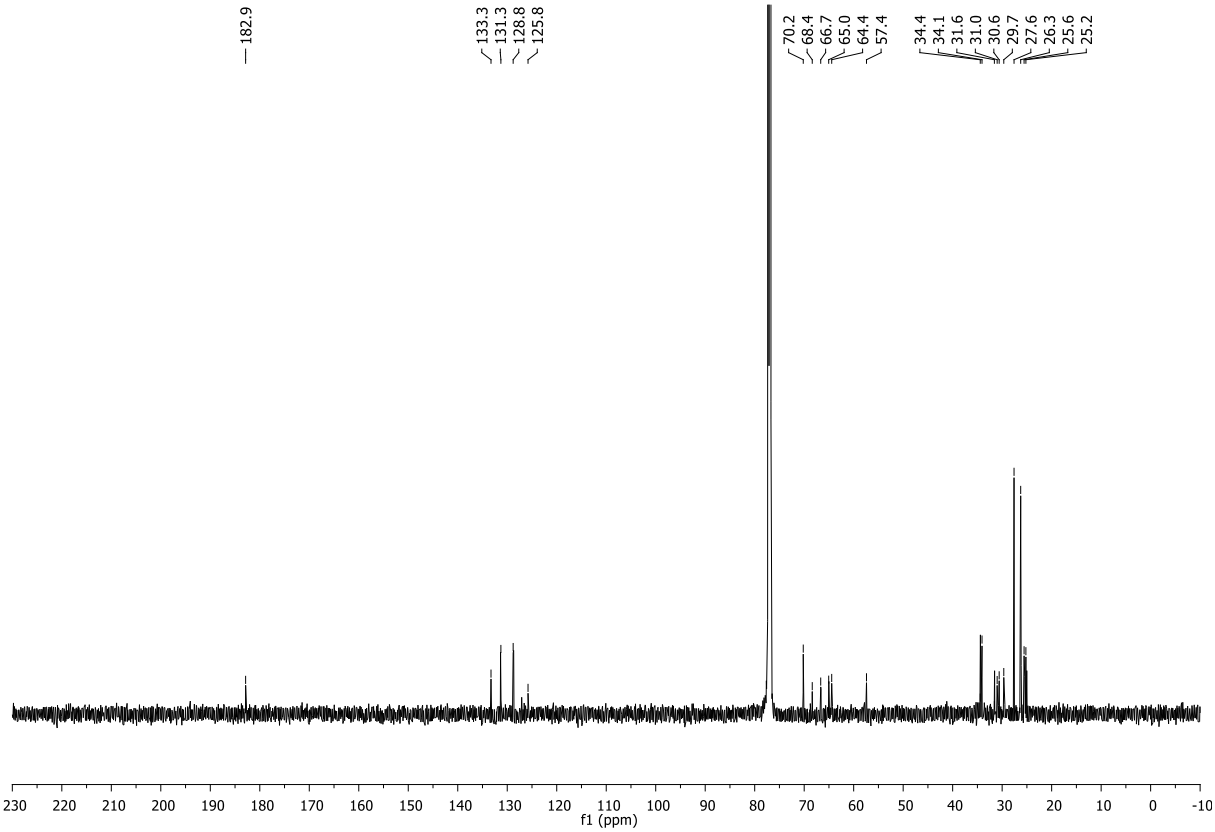
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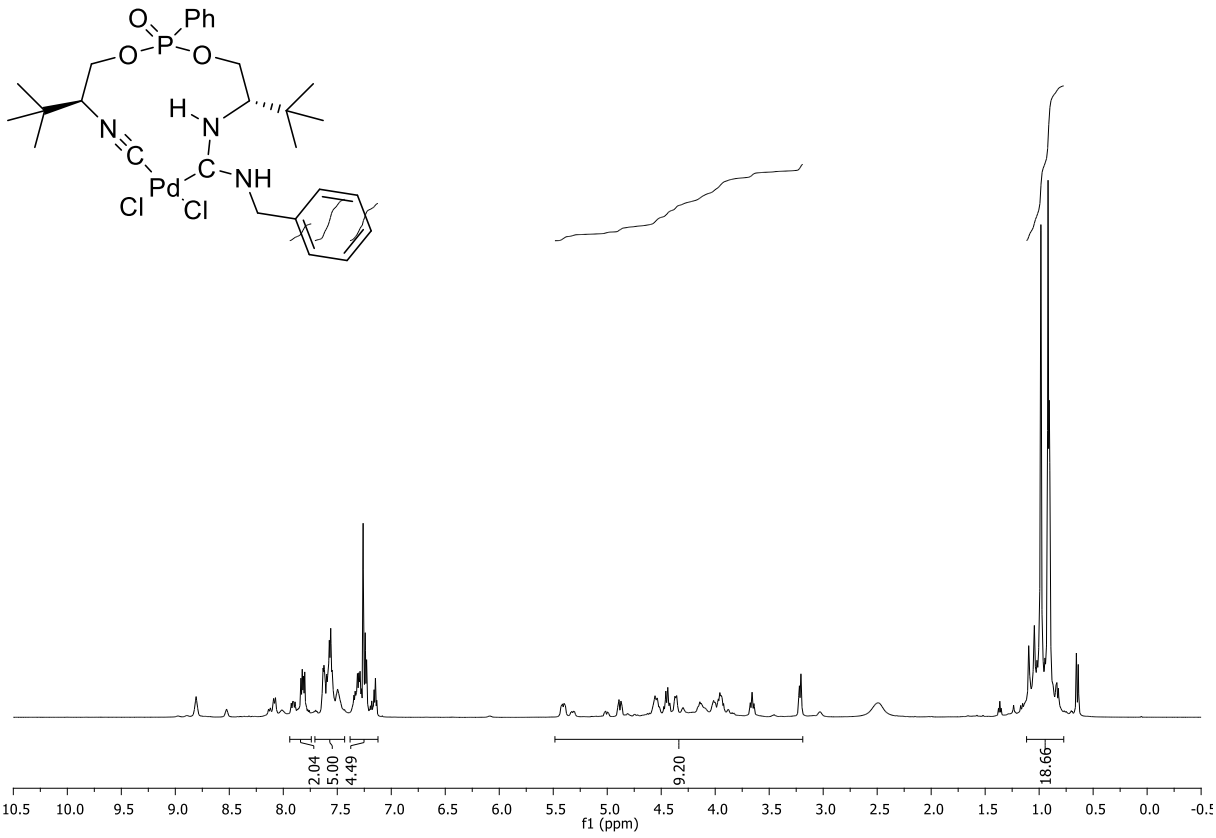
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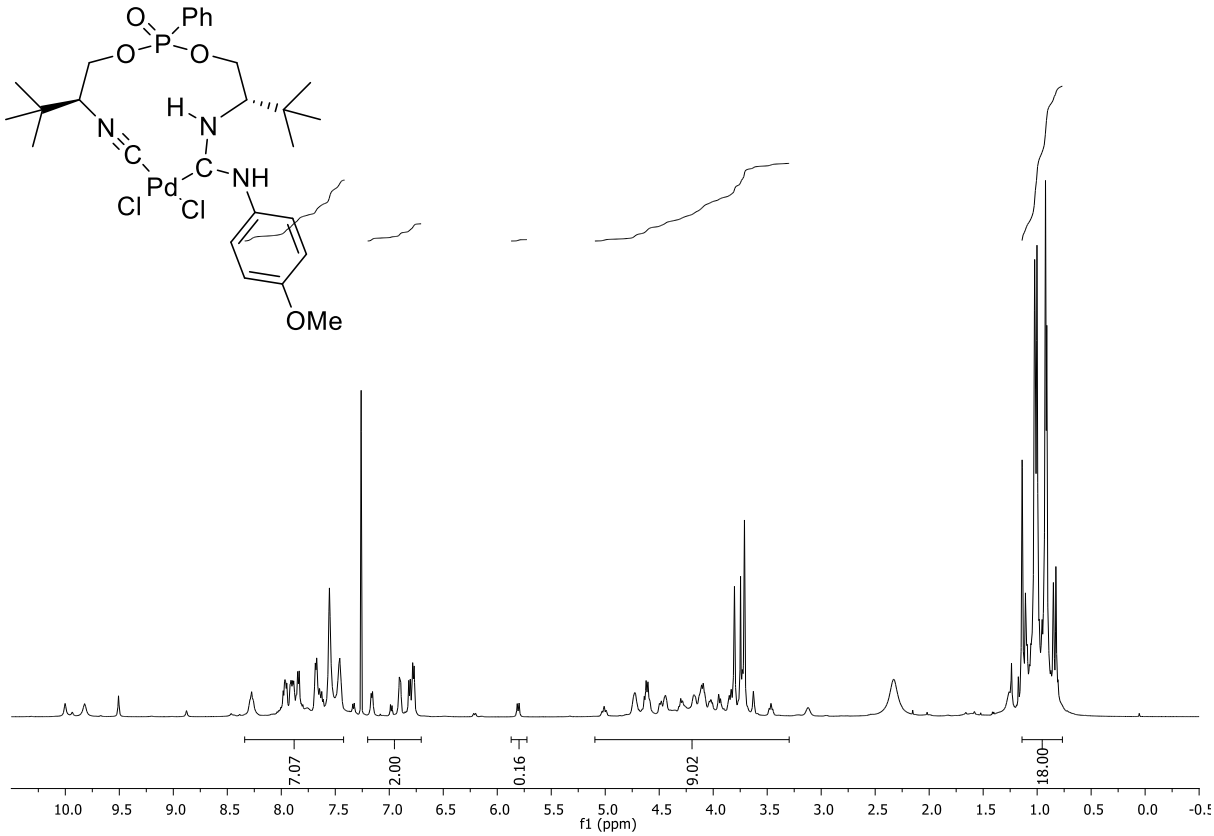
f1 (ppm)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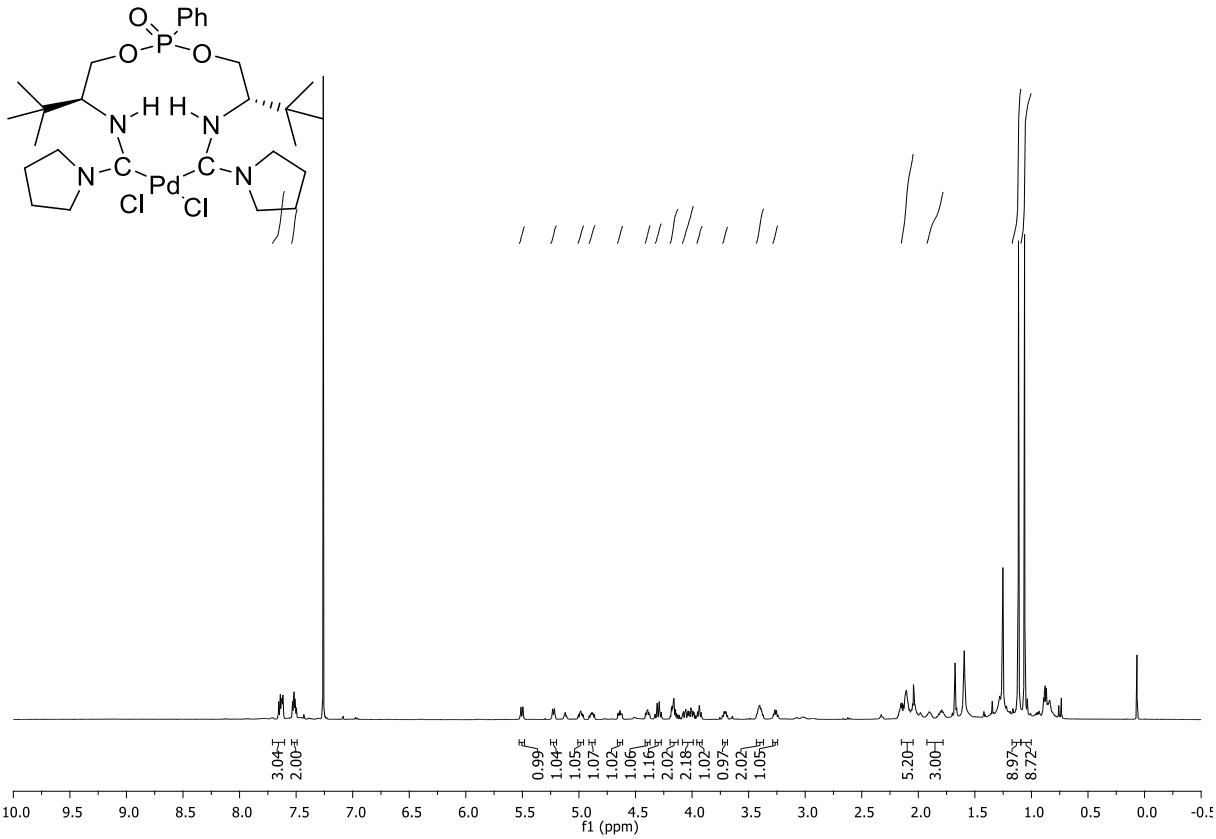
f1 (ppm)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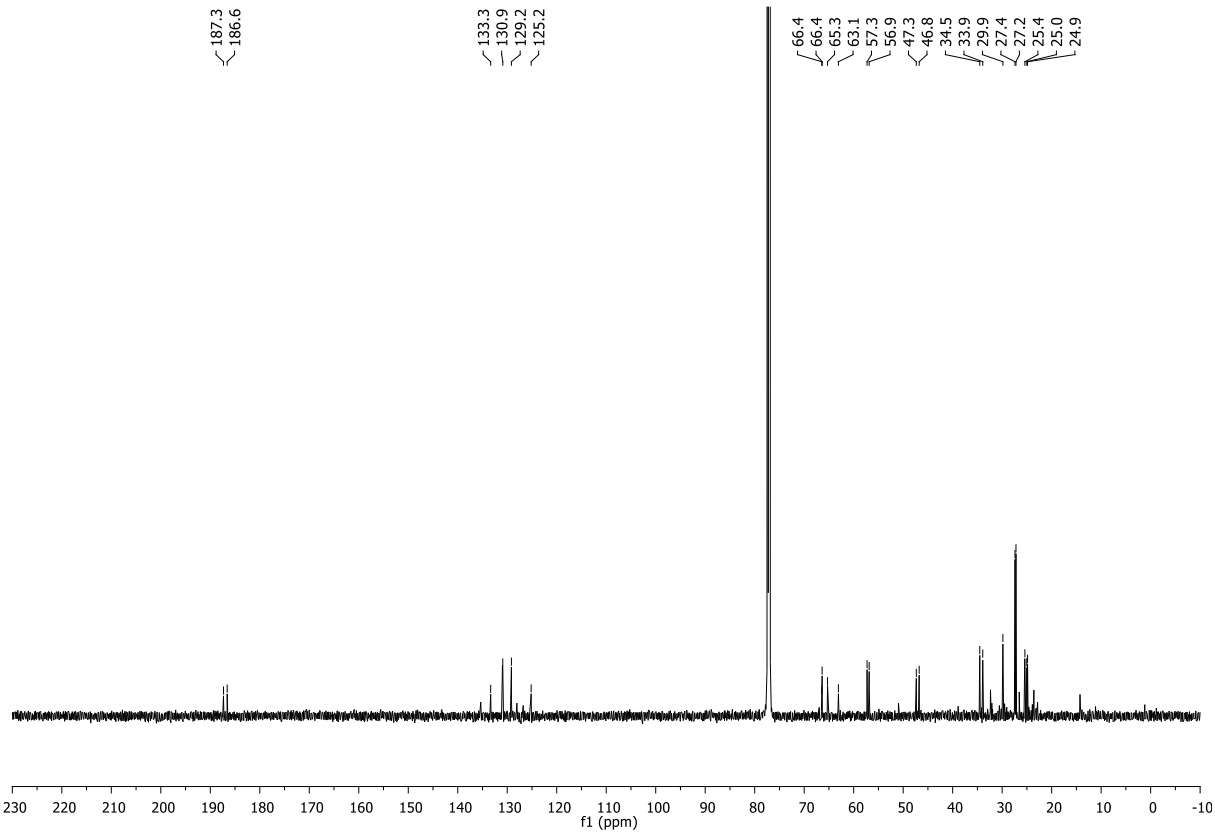
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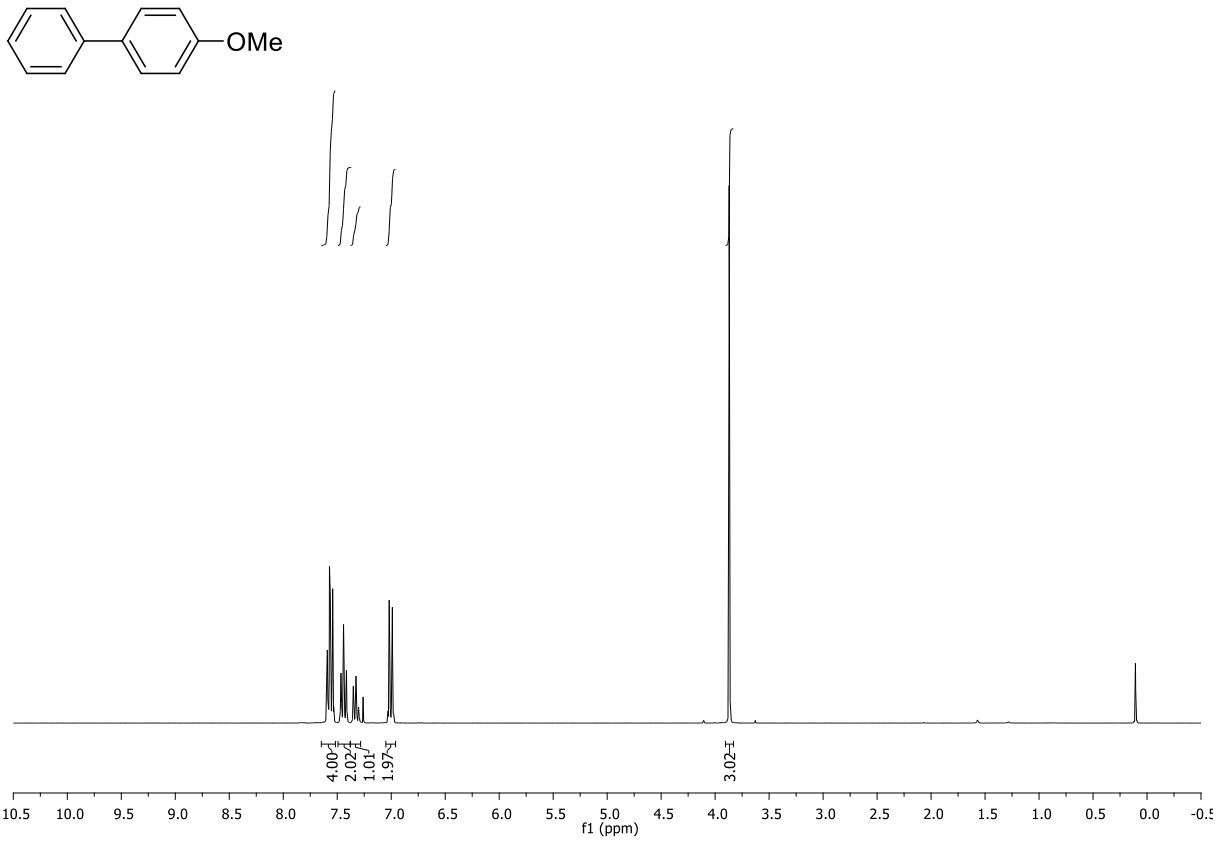
f1 (ppm)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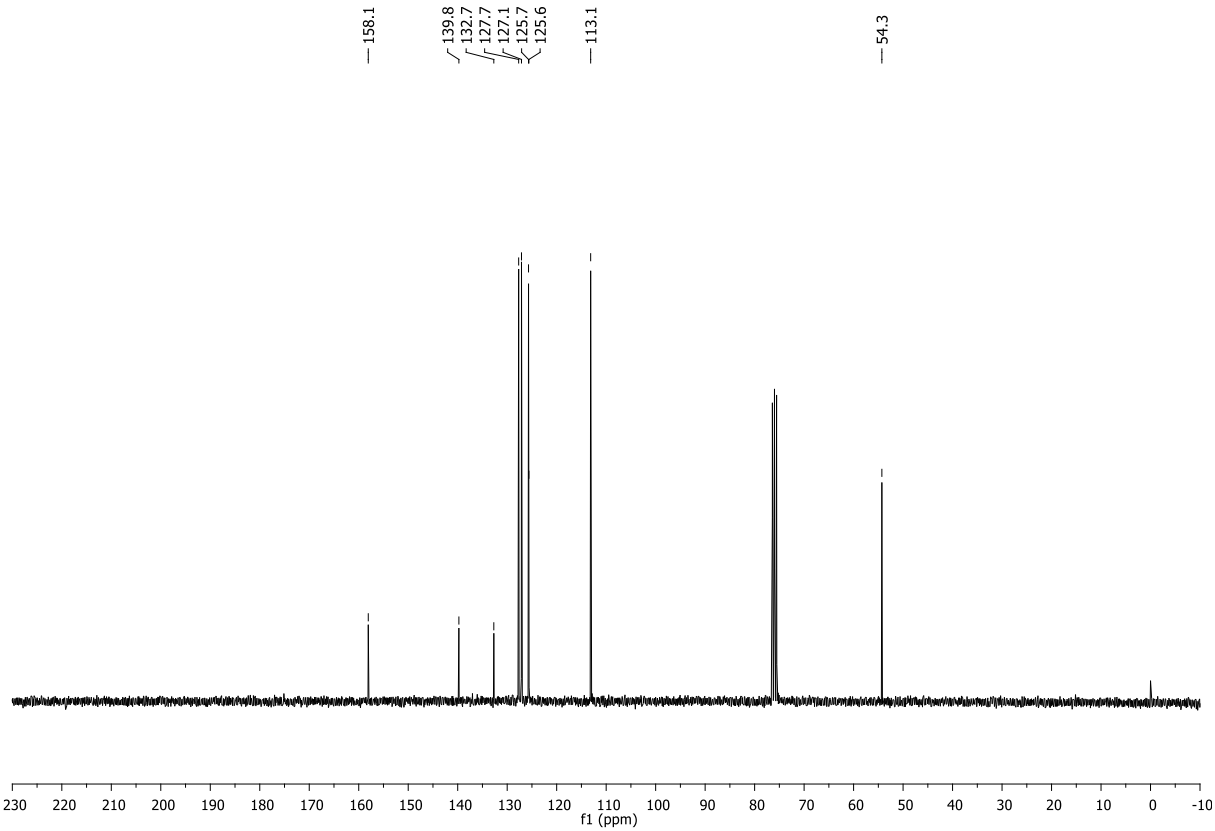
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127.1
125.7
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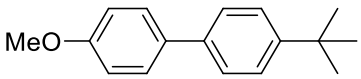
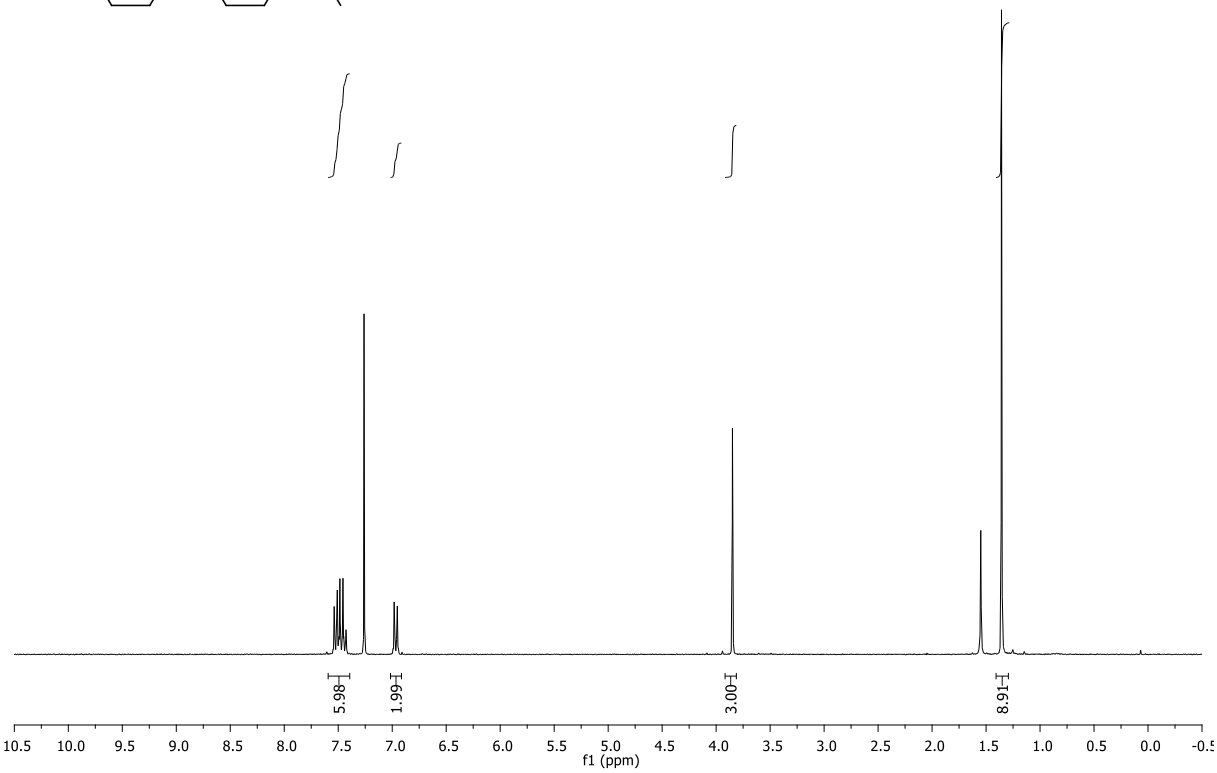
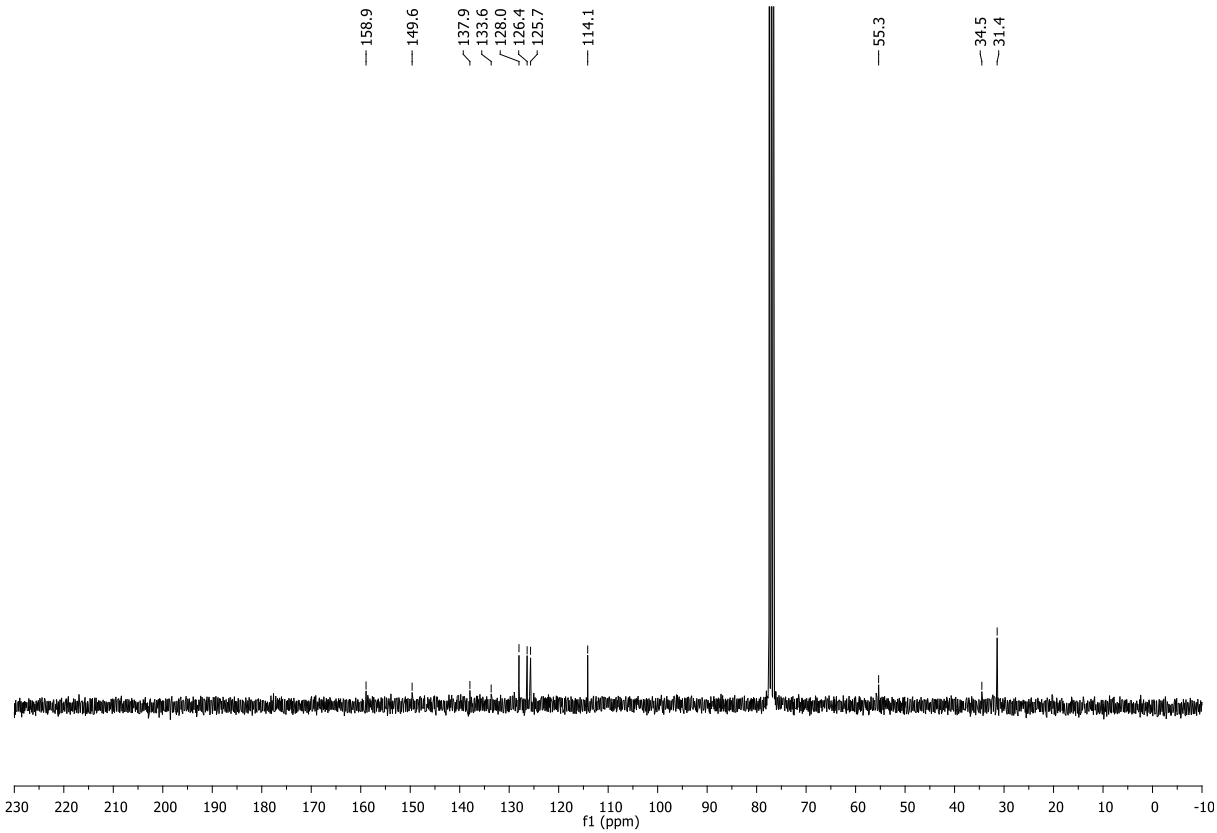
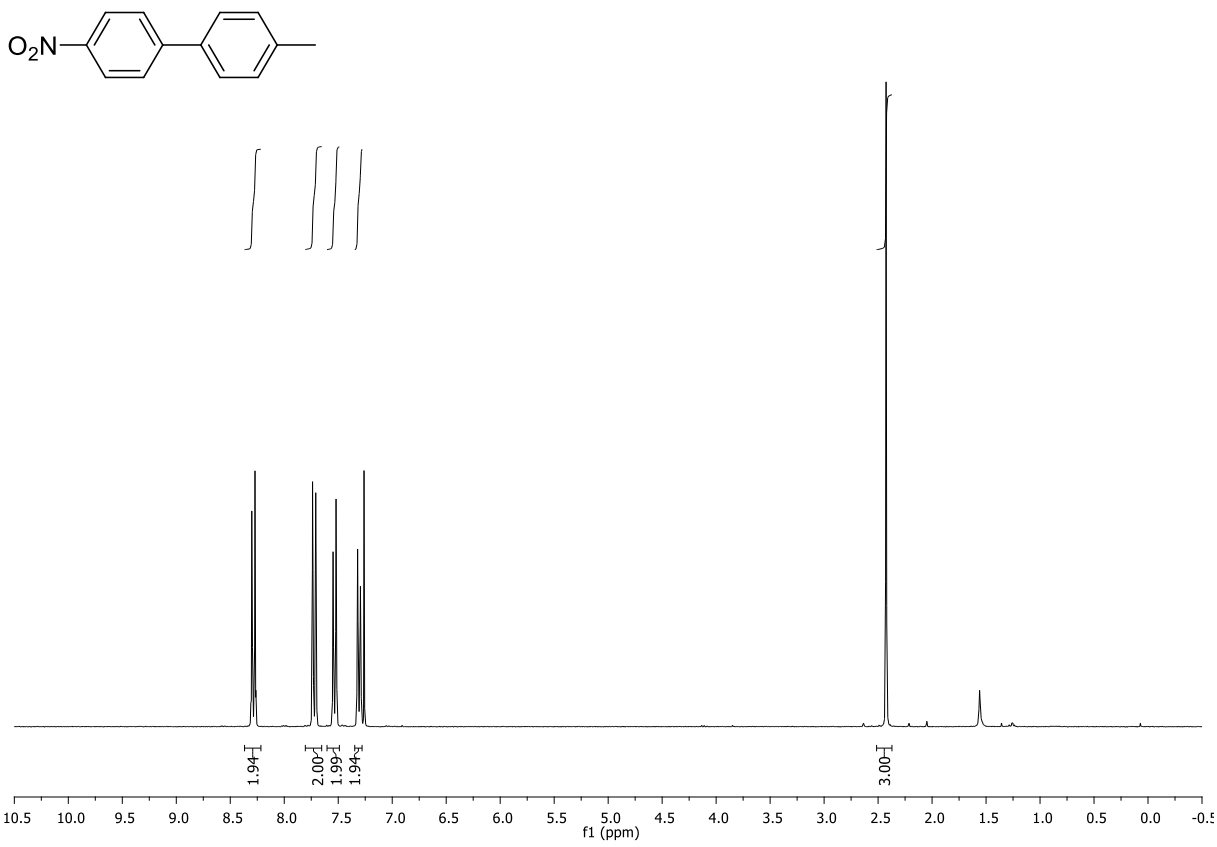
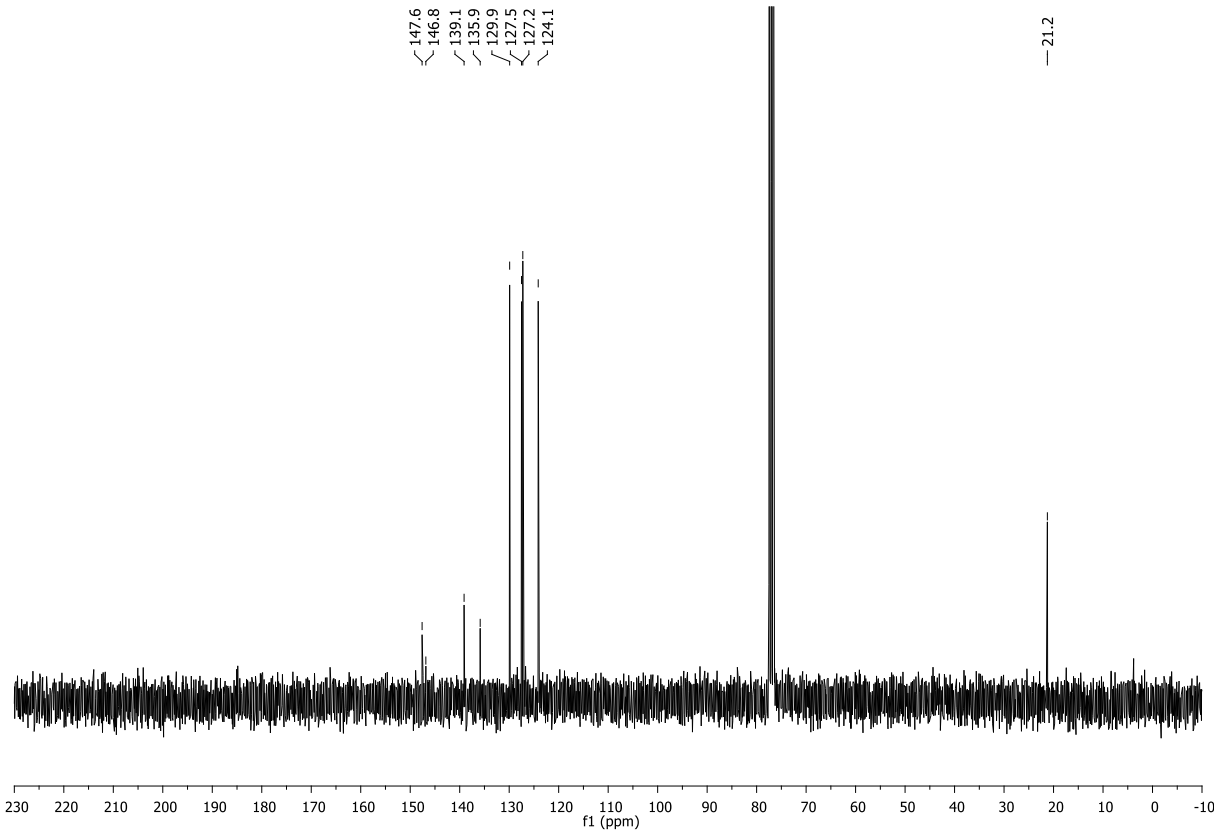
113.1
54.3
f1 (ppm)

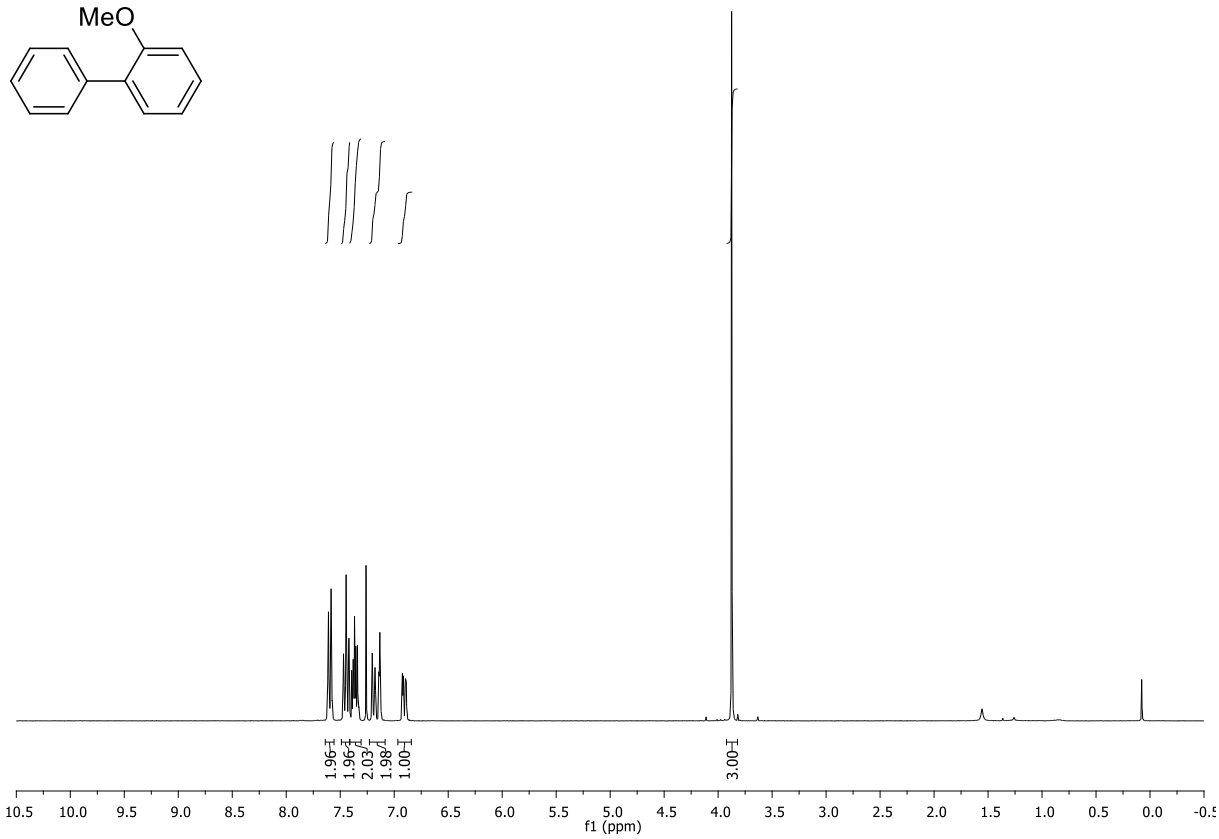

MeO

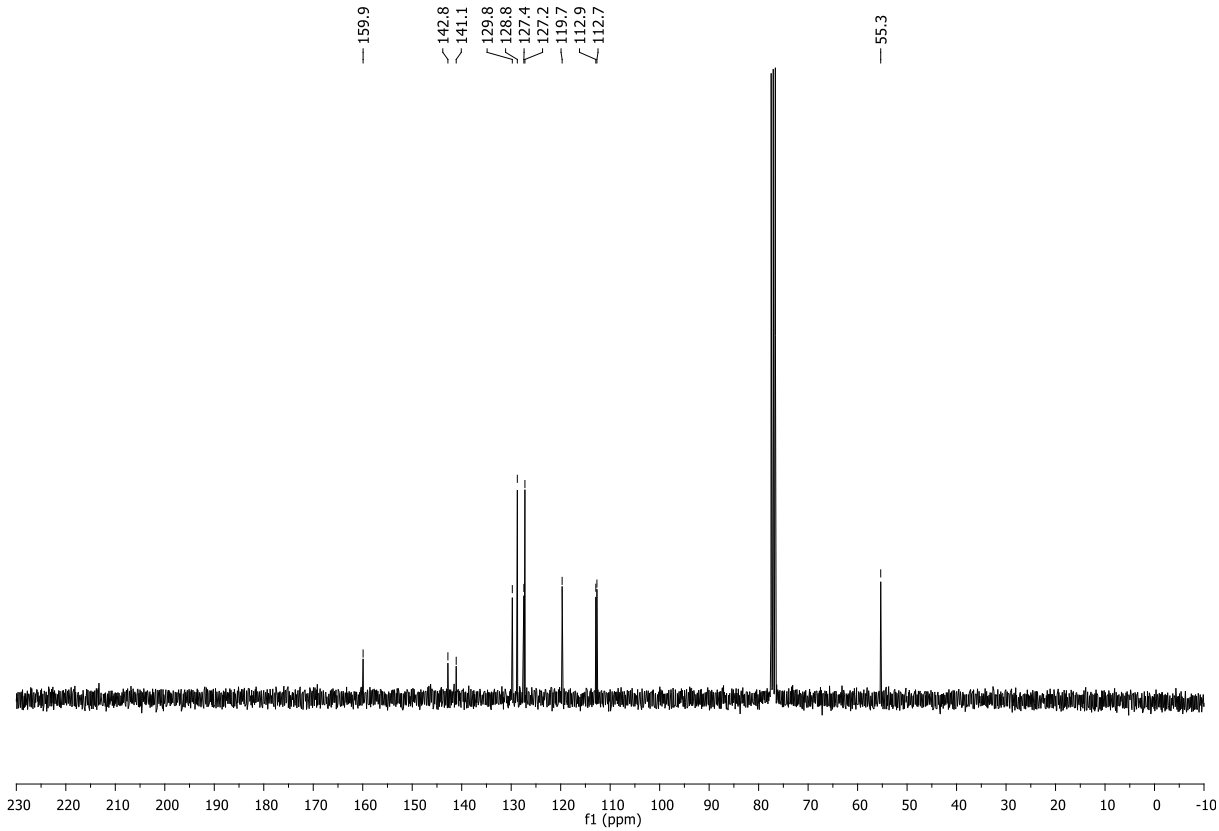

5.98
1.99
3.00
8.91
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

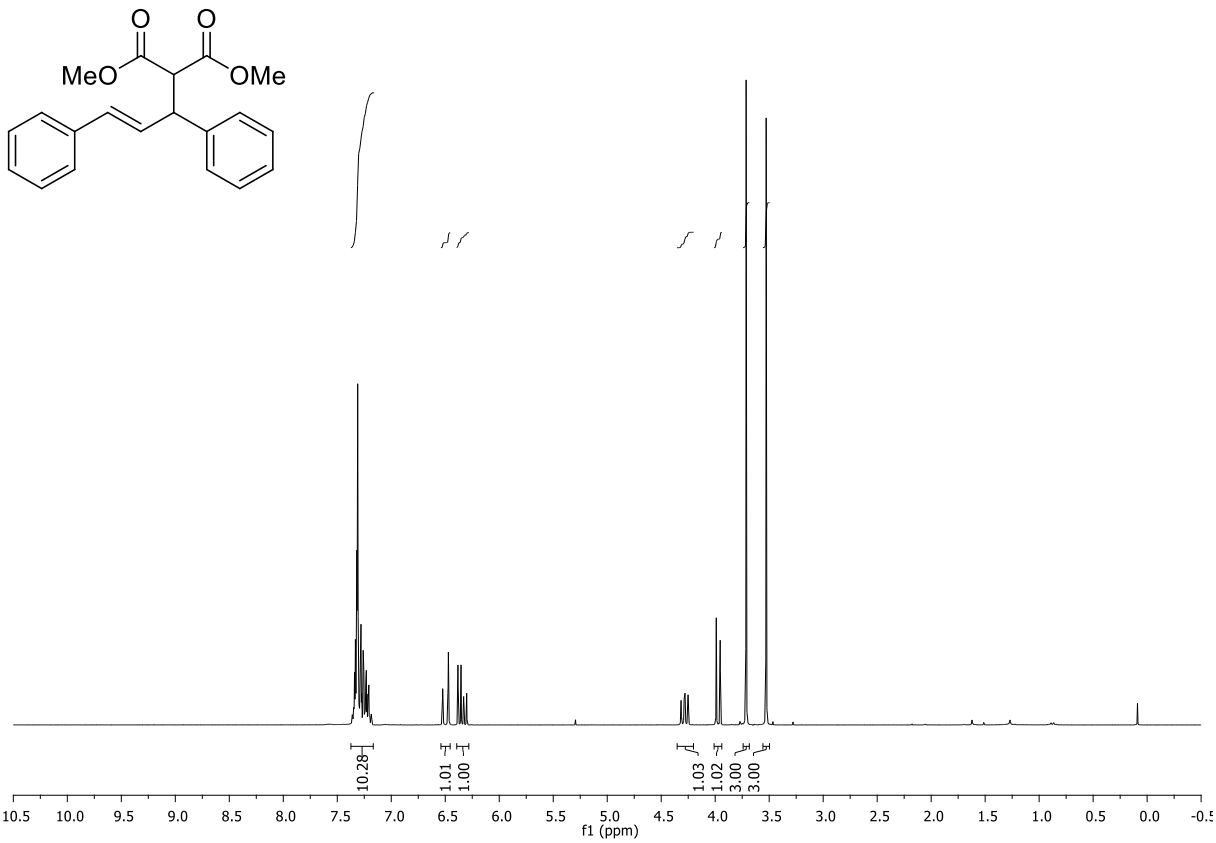

158.9
149.6
137.9
133.6
128.0
126.4
125.7
114.1
55.3
34.5
31.4
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

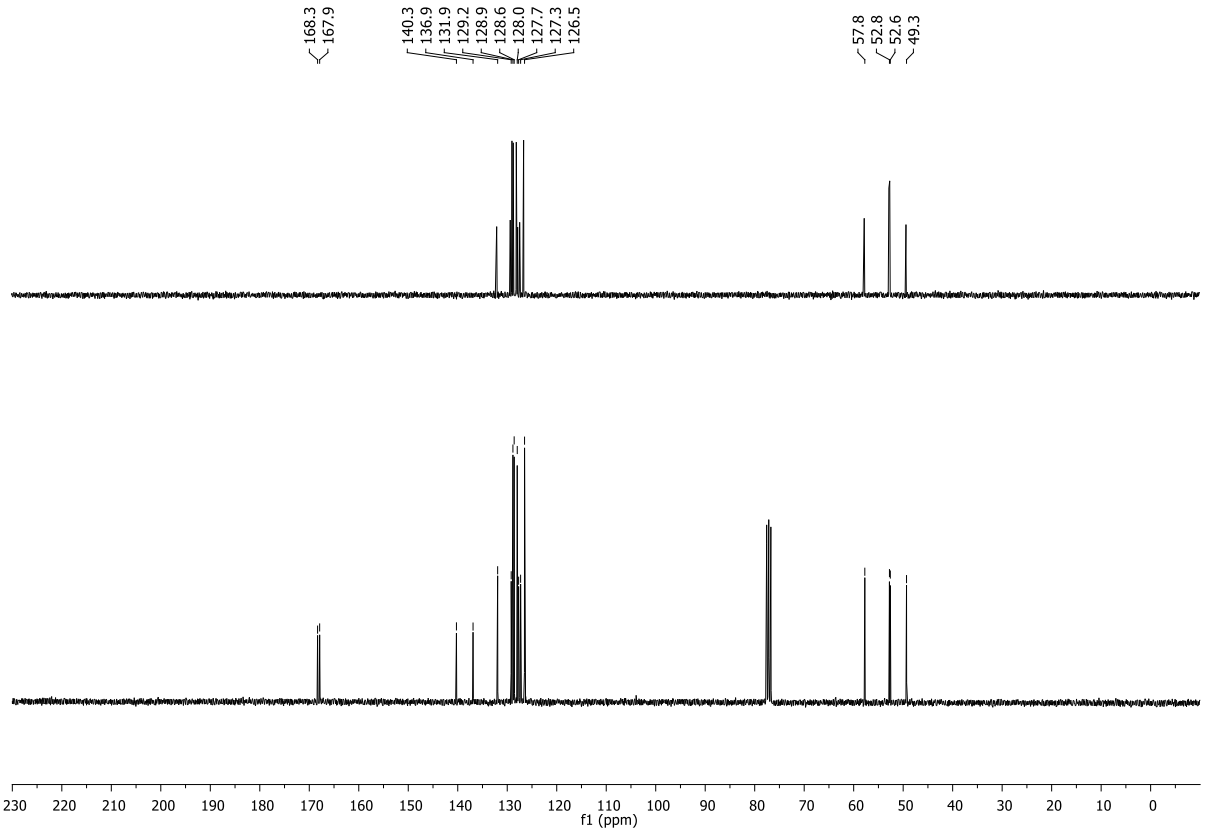

O2N
1.94
2.00
1.99
1.94
3.00
f1 (ppm)


147.6
146.8
139.1
135.9
129.9
127.5
127.2
124.1
21.2
f1 (ppm)


MeO
1.96
1.96
2.03
1.98
1.00
3.00
f1 (ppm)


159.9
142.8
141.1
129.8
128.8
127.4
127.2
119.7
112.9
112.7
55.3
f1 (ppm)


MeO
OMe
10.28
1.01
1.00
1.03
1.02
3.00
3.00
f1 (ppm)


168.3
167.9
140.3
136.9
131.9
129.2
128.9
128.6
128.0
127.7
127.3
126.5
57.8
52.8
52.6
49.3
f1 (ppm)

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