Electronic Supplementary Information (ESI)

Reactivities of zero-valent group 10 complexes toward organic isocyanates: synthesis of metallacycles containing dimeric isocyanate units, isocyanate cyclotrimerization, and computational chemistry

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4-methylbenzyl), **4** in $CDCl_3$. ^1H-(600 MH), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 5S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of $[Pd(PMe_3)\{-C(O)N(R)C(O)N(R)-\}]_4$ (R = 4-phenoxybenzyl), **5** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 6S. ^1H and $^{13}C\ \{^1H\}$ -NMR spectra of $(R\text{-}NCO)_3$ (R = 3-methylbenzyl), **6** in $CDCl_3$. ^1H-(600 MHz) and ^{13}C-NMR (150 MHz).

Figure 7S. ^1H and $^{13}C\{^1H\}$ -NMR spectra of $(R\text{-}NCO)_3$ (R = 4-methylbenzyl), **7** in $CDCl_3$. ^1H-(300 MHz) and ^{13}C-NMR (150 MHz).

Figure 8S. ^1H and $^{13}C\{^1H\}$ -NMR spectra of $(R\text{-}NCO)_3$ (R = 4-phenoxybenzyl), **8** in $CDCl_3$. ^1H-(600 MHz) and ^{13}C-NMR (150 MHz).

Figure 9S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{N(R)C(O)N(R)C(O)\}(PMe_3)_2]$ (R = 3-methylbenzyl), **9** in $CDCl_3$. ^1H-(300 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 10S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{N(R)C(O)N(R)C(O)\}(PMe_3)_2]$ (R = 4-methylbenzyl), **10** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz)

Figure 11S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{-N(R)C(O)N(R)C(O)\}(PMe_3)_2]$ (R = 4-fluorobenzyl), **11** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz)

Figure 12S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{-(R)C(O)N(R)C(O)-\}(PMe_3)_2]$ (R = 4-methoxybenzyl), **12** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 13S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{-N(R)C(O)N(R)C(O)-\}(PMe_3)_2]$ {R =(S)-(+)-1-(1-naphthyl)ethyl}, **13** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 14S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{N(R)C(O)N(R)C(O)-\}(PMe_3)_2]$ {R =(R)-(−)-1-(1-naphthyl)ethyl }, **14** in $CDCl_3$. ^1H-400 MHz, ^{13}C-NMR (100 MHz), and ^{31}P (162 MHz).

Figure 15S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{-N(R)C(O)N(R)C(O)-\}(PMe_3)_2]$ (R = 4-phenoxyphenyl, **15** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 16S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of *cis*-$[Pt\{-N(R)C(O)N(R)C(O)-\}(PMe_3)_2]$ (R = 2,6-difluorophenyl, **16** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 17S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of $Pt(DEPE)\{-N(R)C(O)N(R)C(O)-\}$ {R = (S)-(+)-1-(1-naphthyl)ethyl}, **17** in $CDCl_3$. ^1H-(400 MHz), ^{13}C-NMR (100 MHz), and ^{31}P (160 MHz).

Figure 18S. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of $Pt(DEPE)\{-N(R)C(O)N(R)C(O)-\}$ {R = (R)-(−)-1-(1-naphthyl)ethyl }, **18** in $CDCl_3$. ^1H-(600 MHz), ^{13}C-NMR (150 MHz), and ^{31}P (242 MHz).

Figure 19S. ^{1}H and $^{13}C\{^{1}H\}$ -NMR spectra of [SIPr•Benzyl-NCO], **19** in $CDCl_3$. ^{1}H-(300 MHz) and ^{13}C-NMR (75 MHz).

Figure 20S. ^{1}H and $^{13}C\{^{1}H\}$ -NMR spectra of [IPr•Phenyl-NCO], **20** in $CDCl_3$. ^{1}H-(300 MHz) and ^{13}C-NMR (75 MHz).

Table SM1. Details of crystal data, intensity collection, and refinement details.

complex	**10.**Et_2O	**16**	**17**	**18**	**19**
formula	$C_{28}H_{46}N_2O_3P_2Pt$	$C_{20}H_{24}F_4N_2O_2P_2Pt$	$C_{36}H_{46}N_2O_2P_2Pt$	$C_{36}H_{46}N_2O_2P_2Pt$	$C_{35}H_{45}N_3O$
fw	715.70	657.44	795.78	795.78	523.74
temperature, K	223(2)	223(2)	223(2)	223(2)	223(2)
crystal size (mm)	0.19 × 0.12 × 0.10	0.26 × 0.18 × 0.10	0.16× 0.09 × 0.04	0.19×0.11× 0.08	0.22 × 0.15× 0.09
crystal system	triclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	*P*−1	$Pca2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a, Å	9.7165(3)	20.3247(6)	8.6581(9)	8.6475(3)	11.892(1)
b, Å	11.7105(4)	10.1709(3)	17.404(2)	17.3751(7)	22.114(3)
c, Å	14.6358(5)	23.0532(6)	22.735(3)	22.7043(10)	13.276(2)
α, deg	87.102(1)	90	90	90	90
β, deg	77.839(1)	90	90	90	115.138(5)
γ, deg	73.501(1)	90	90	90	90
V, Å^3	1560.86(9)	4765.6(2)	3425.8(7)	3411.3(2)	3160.7(6)
Z	2	8	4	4	4
d_{cal}, g cm^{-3}	1.523	1.833	1.543	1.549	1.101
μ, mm^{-1}	4.627	6.073	4.223	4.241	0.066
F(000)	720	2544	1600	1600	1136
T_{min}	0.6046	0.7457	0.5833	0.5786	0.9856
T_{max}	0.7457	0.5008	0.7457	0.7457	0.9941
θ range (º)	2.233–28.563	2.407–32.191	2.140–28.284	2.143–28.374	1.89–28.35
No. of reflns Measured	55244	192681	115527	115054	138629
No. of reflns Unique	7839	11870	8492	8505	7882
No. of reflns with $I > 2\sigma(I)$	7251	10803	7028	7108	4564
No. of params Refined	327	559	430	338	360
Max., in Δρ (e Å^{-3})	0.726	1.270	0.881	0.859	0.172
Min., in Δρ (e Å^{-3})	−0.572	−0.969	−0.503	−0.496	−0.196
Absolute structure parameter		0.004(2)	−0.004(4)	−0007(3)	
GOF on F^2	1.100	1.081	1.043	1.066	1.023
*R*1[a]	0.0180	0.0223	0.0334	0.0317	0.0549
wR2[b]	0.0386	0.0491	0.0527	0.0470	0.1135

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|]$, [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table-SM2. Total energies of each compound and relative reaction energies (ΔE) calculated by the wB97XD-DFT method with Lanl2DZ basis sets. The alkyl group of R-NCO here is C_6H_5–CH_2–. (Hartree = 627.51 kacl/mol)

(Molecule No.) Metal		wB97XD	
		(Hartree)	(kcal/mol)
(A)		-438.6782	
(B)	M = Pd	-688.3420	
	M = Pt	-680.7630	
(C)		-309.3591	
(D)	M = Pd	-817.6489	
	ΔE_{Step-1} (Pd)	0.0121	7.6
	M = Pt	-810.0692	
	ΔE_{Step-1} (Pt)	0.0128	8.0
(E)	M = Pd	-1256.4077	
	ΔE_{Step-2} (Pd)	-0.0684	-42.9
	M = Pt	-1248.8497	
	ΔE_{Step-2} (Pt)	-0.0895	-56.1
(F)	M = Pd	-1695.1246	
	ΔE_{Step-3} (Pd)	-0.1072	-67.3
	M = Pt	-1687.5671	
	ΔE_{Step-3} (Pt)	-0.1287	-80.8
(G)		-1316.1717	
	ΔE_{Step-4}	-0.1372	-86.1
(H)		-126.0754	
(I)	M = Pd	-4521.4473	
	ΔE_{Tetra}(Pd)	-0.0979	-61.5
	M = Pt	-4491.2433	
	ΔE_{Tetra}(Pt)	-0.1460	-91.6

Table-SM3. The Cartesian coordinates of the optimized structure of (B), (D), and (F) for M = Pd and Pt complexes by the wB97XD/Lanl2DZ methodology.

B = $[(CH_3)_3P]_2M\cdots C_6H_5CHCH_2$, with M = Pd in Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.108482	-2.247872	-1.209947
2	1	0	-0.132687	-2.974627	-0.399918
3	6	0	-1.156185	-1.300457	-1.378262
4	1	0	-1.316057	-0.901835	-2.380141
5	1	0	0.459332	-2.562099	-2.082440
6	15	0	2.840639	-0.536398	0.334704
7	15	0	-0.185094	1.950811	-0.057889
8	6	0	3.043043	-0.345502	2.195033
9	1	0	2.444735	-1.106709	2.702307
10	1	0	4.091215	-0.447438	2.497092
11	1	0	2.673621	0.638336	2.497582
12	6	0	3.755622	-2.152553	0.046152
13	1	0	4.756965	-2.135948	0.490668
14	1	0	3.176514	-2.971125	0.481390
15	1	0	3.837812	-2.328232	-1.029648
16	6	0	4.113935	0.703239	-0.281942
17	1	0	3.775587	1.714248	-0.038866
18	1	0	5.095419	0.529799	0.172955
19	1	0	4.199767	0.621191	-1.368607
20	6	0	0.996991	3.350569	0.377614
21	1	0	1.679546	3.522965	-0.459537
22	1	0	0.456232	4.277690	0.597288
23	1	0	1.586376	3.065082	1.254310
24	6	0	-1.230009	2.772684	-1.385148
25	1	0	-1.606113	3.746601	-1.053076
26	1	0	-0.635587	2.901818	-2.293287
27	1	0	-2.075595	2.117739	-1.610616
28	6	0	-1.365195	2.008669	1.401887
29	1	0	-1.742421	3.023700	1.569087
30	1	0	-2.204221	1.335410	1.205684
31	1	0	-0.850240	1.658449	2.300356
32	6	0	-2.314363	-1.130096	-0.463635
33	6	0	-3.434562	-0.385219	-0.894154
34	6	0	-2.340303	-1.654199	0.849630
35	6	0	-4.529475	-0.157969	-0.048787
36	1	0	-3.446580	0.010585	-1.907080
37	6	0	-3.434204	-1.431873	1.693827
38	1	0	-1.489494	-2.220282	1.215115
39	6	0	-4.536225	-0.677474	1.254739
40	1	0	-5.376857	0.417976	-0.408327
41	1	0	-3.427734	-1.842267	2.699163
42	1	0	-5.381701	-0.504596	1.912369
43	46	0	0.583814	-0.324224	-0.514307

B = $[(CH_3)_3P]_2M\cdots C_6H_5CHCH_2$, with M = Pt in Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.215871	-2.184306	-1.062087
2	1	0	-0.325614	-2.928214	-0.272995
3	6	0	-1.249714	-1.173833	-1.258831
4	1	0	-1.416816	-0.842315	-2.284761
5	1	0	0.287189	-2.569265	-1.947913
6	15	0	2.711530	-0.499747	0.439113
7	15	0	-0.148696	1.977247	-0.005038
8	6	0	2.914234	-0.245798	2.287921
9	1	0	2.281852	-0.962903	2.817001
10	1	0	3.956460	-0.380148	2.596329
11	1	0	2.584173	0.762953	2.550481
12	6	0	3.543542	-2.162959	0.198987
13	1	0	4.549040	-2.177588	0.633080
14	1	0	2.927514	-2.934404	0.667388
15	1	0	3.601211	-2.376535	-0.871166
16	6	0	4.013549	0.667715	-0.243185
17	1	0	3.721930	1.697642	-0.021528
18	1	0	4.997100	0.465207	0.193827
19	1	0	4.065409	0.548548	-1.328250
20	6	0	1.088266	3.331178	0.408024
21	1	0	1.782595	3.451618	-0.428245
22	1	0	0.584038	4.284456	0.598616
23	1	0	1.656027	3.041680	1.297260
24	6	0	-1.128500	2.777958	-1.387801
25	1	0	-1.463261	3.782916	-1.109686
26	1	0	-0.512009	2.831194	-2.288354
27	1	0	-1.997817	2.148836	-1.595065
28	6	0	-1.352025	2.104549	1.426234
29	1	0	-1.700662	3.134032	1.561099
30	1	0	-2.204784	1.450159	1.224914
31	1	0	-0.864906	1.758317	2.341284
32	6	0	-2.449946	-1.014177	-0.390882
33	6	0	-3.554227	-0.271986	-0.863776
34	6	0	-2.520884	-1.529177	0.923841
35	6	0	-4.676437	-0.036043	-0.056773
36	1	0	-3.531037	0.117321	-1.879108
37	6	0	-3.642244	-1.299624	1.729791
38	1	0	-1.682006	-2.091847	1.320812
39	6	0	-4.727382	-0.546196	1.249327
40	1	0	-5.510451	0.538715	-0.448395
41	1	0	-3.670260	-1.703719	2.737404
42	1	0	-5.593969	-0.367206	1.877371
43	78	0	0.497210	-0.299305	-0.413042

D = $[(CH_3)_3P]_2M\cdots C_6H_5CH_2NCO$ with M = Pd in Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	3.106560	-0.046129	0.212332
2	15	0	-0.298025	2.026964	-0.281695
3	6	0	4.017610	1.588671	0.352939
4	1	0	3.608446	2.162071	1.189511
5	1	0	5.088905	1.430529	0.515625
6	1	0	3.874816	2.162250	-0.567061
7	6	0	3.651923	-0.954939	1.755878
8	1	0	4.743761	-0.975291	1.840001

9	1	0	3.226132	-0.474618	2.640249
10	1	0	3.267904	-1.976380	1.689693
11	6	0	4.083739	-0.946877	-1.106596
12	1	0	3.934717	-0.462212	-2.074550
13	1	0	5.152179	-0.965273	-0.866373
14	1	0	3.699814	-1.969013	-1.161138
15	6	0	0.688080	3.461049	-0.993001
16	1	0	0.995741	3.217121	-2.013413
17	1	0	0.097699	4.383682	-1.005602
18	1	0	1.586170	3.616462	-0.388564
19	6	0	-1.876688	2.126862	-1.292292
20	1	0	-2.291741	3.140673	-1.284114
21	1	0	-1.666485	1.828079	-2.322534
22	1	0	-2.609193	1.430137	-0.875873
23	6	0	-0.869741	2.759531	1.350385
24	1	0	-1.335210	3.740159	1.203442
25	1	0	-1.597147	2.081261	1.802906
26	1	0	-0.016744	2.859762	2.026611
27	7	0	-0.518127	-1.870825	-0.349420
28	6	0	0.674568	-2.282325	-0.169550
29	8	0	1.470606	-3.231264	-0.043966
30	6	0	-1.845295	-2.390151	-0.588135
31	1	0	-1.987514	-2.572667	-1.661216
32	1	0	-1.954609	-3.358396	-0.076327
33	6	0	-2.913061	-1.428760	-0.095410
34	6	0	-4.074192	-1.198737	-0.850189
35	6	0	-2.759139	-0.767471	1.136544
36	6	0	-5.070010	-0.324205	-0.384978
37	1	0	-4.199742	-1.695475	-1.808561
38	6	0	-3.752417	0.102295	1.606185
39	1	0	-1.852052	-0.929617	1.710392
40	6	0	-4.912229	0.328903	0.846100
41	1	0	-5.960491	-0.153027	-0.981090
42	1	0	-3.627865	0.597907	2.564295
43	1	0	-5.680425	1.003820	1.209022
44	46	0	0.760392	-0.202862	-0.149446

D = $[(CH_3)_3P]_2M\cdots C_6H_5CH_2NCO$ with M = Pt in Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	78	0	0.652688	-0.321793	-0.162138
2	15	0	2.908538	0.049684	0.330285
3	15	0	-0.221399	1.957373	-0.348207
4	6	0	3.368766	1.421996	1.519056
5	1	0	2.824351	1.277016	2.455376
6	1	0	4.444456	1.419577	1.721277
7	1	0	3.085258	2.389248	1.095107
8	6	0	3.695308	-1.455610	1.106944
9	1	0	4.784771	-1.359494	1.152311
10	1	0	3.293743	-1.581829	2.115551
11	1	0	3.406522	-2.336366	0.527579
12	6	0	4.005191	0.399304	-1.143778
13	1	0	3.665616	1.310871	-1.641776
14	1	0	5.049886	0.514396	-0.837725
15	1	0	3.919886	-0.432208	-1.846872

16	6	0	0.842923	3.241313	-1.210184
17	1	0	1.065129	2.896939	-2.223520
18	1	0	0.332824	4.208902	-1.260358
19	1	0	1.786001	3.361798	-0.669656
20	6	0	-1.838820	2.124058	-1.276657
21	1	0	-2.143999	3.172956	-1.353137
22	1	0	-1.723877	1.700607	-2.277321
23	1	0	-2.610481	1.556381	-0.750857
24	6	0	-0.621679	2.806518	1.273498
25	1	0	-1.010898	3.816345	1.106900
26	1	0	-1.372833	2.211508	1.798809
27	1	0	0.278700	2.857904	1.891067
28	7	0	-0.733024	-1.813424	-0.445504
29	6	0	0.423266	-2.362757	-0.177043
30	8	0	0.995991	-3.457875	-0.015896
31	6	0	-2.102160	-2.219873	-0.656320
32	1	0	-2.301742	-2.338453	-1.729386
33	1	0	-2.252243	-3.204117	-0.187752
34	6	0	-3.081462	-1.214985	-0.072556
35	6	0	-4.240733	-0.849898	-0.775483
36	6	0	-2.839694	-0.636280	1.187250
37	6	0	-5.145587	0.078586	-0.234710
38	1	0	-4.434214	-1.283130	-1.753106
39	6	0	-3.739914	0.289756	1.730676
40	1	0	-1.936523	-0.906390	1.725508
41	6	0	-4.896828	0.653257	1.020412
42	1	0	-6.035639	0.353216	-0.791596
43	1	0	-3.545744	0.722050	2.707692
44	1	0	-5.593906	1.370925	1.440566

F = $[(CH_3)_3P]_2M\cdots[C_6H_5CH_2NCO]_3$ with M = Pd in Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.086388	2.091776	1.878743
2	8	0	-2.319710	-0.306381	1.183421
3	8	0	-1.016162	1.024681	-2.914502
4	7	0	0.446831	-0.521268	-2.049427
5	7	0	-1.693698	-0.093541	-1.009120
6	6	0	1.244490	3.240243	2.517132
7	1	0	1.734174	2.790384	3.384180
8	1	0	0.809546	4.199787	2.812903
9	1	0	1.992625	3.407021	1.738651
10	6	0	-1.246410	1.912010	3.328584
11	1	0	-0.716554	1.461724	4.171794
12	1	0	-2.054760	1.243702	3.022180
13	1	0	-1.651176	2.884188	3.625710
14	6	0	-1.046120	3.174812	0.698244
15	1	0	-1.990835	2.685544	0.450261
16	1	0	-0.486841	3.319471	-0.228794
17	1	0	-1.259542	4.146953	1.152788
18	6	0	-1.396015	-0.158967	0.353678
19	6	0	-3.131336	-0.007269	-1.395992
20	1	0	-3.638897	-0.823633	-0.877025
21	6	0	-0.742499	0.180197	-2.027072
22	6	0	1.415327	-0.168782	-3.103870

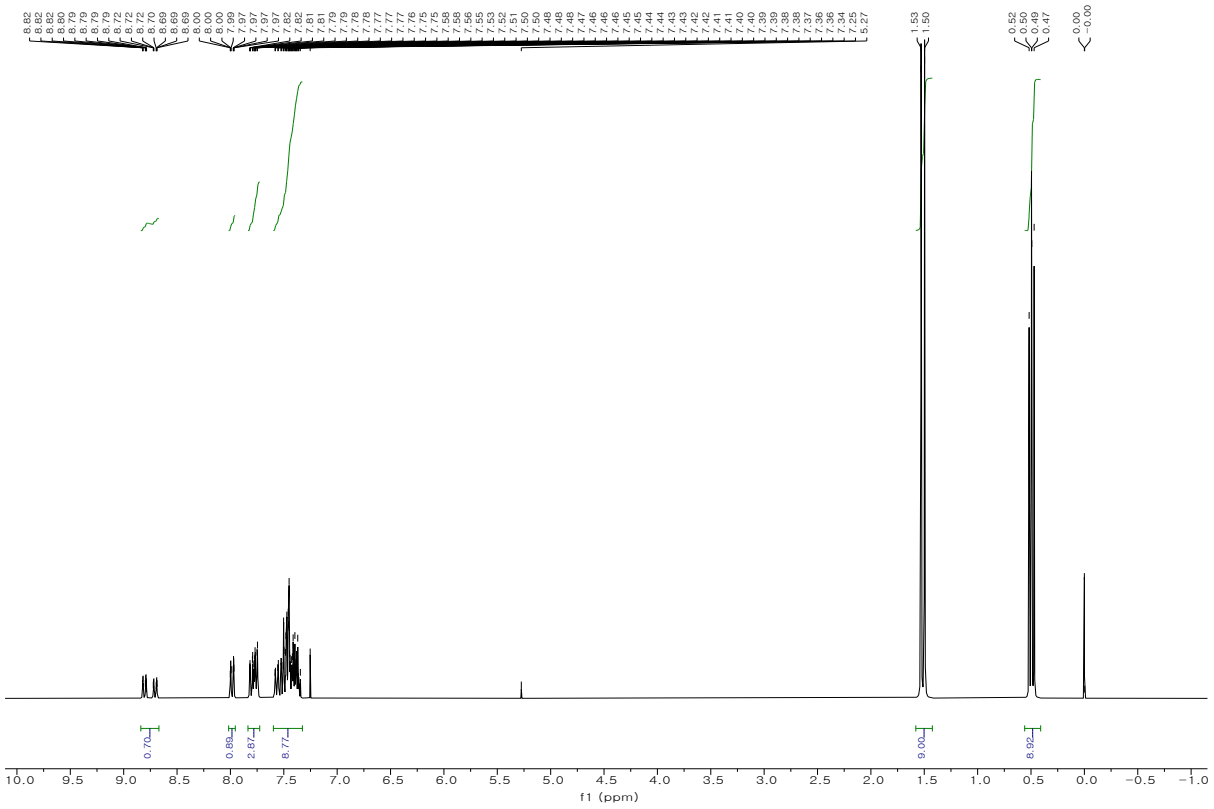
23	1	0	0.881568	0.394425	-3.872774
24	1	0	1.772593	-1.102396	-3.542899
25	46	0	0.510466	-0.025713	0.948807
26	15	0	2.868807	-0.329875	1.673322
27	6	0	3.857885	-1.230493	0.369687
28	1	0	4.813606	-1.575648	0.777058
29	1	0	3.281042	-2.080047	-0.000769
30	1	0	4.044585	-0.555877	-0.469050
31	6	0	4.038135	1.058423	2.141866
32	1	0	4.077105	1.786086	1.328579
33	1	0	3.694910	1.553320	3.053388
34	1	0	5.044029	0.660869	2.310880
35	6	0	3.031941	-1.463690	3.159776
36	1	0	2.582502	-2.432188	2.929143
37	1	0	4.085154	-1.614439	3.417824
38	1	0	2.507514	-1.033168	4.016464
39	1	0	-3.179395	-0.185043	-2.471369
40	6	0	0.690352	-1.812834	-1.400956
41	8	0	1.013347	-2.787397	-2.133674
42	7	0	0.599848	-1.811009	-0.065571
43	6	0	0.575410	-3.126910	0.601917
44	1	0	0.771337	-2.955915	1.664900
45	1	0	1.373326	-3.761294	0.193080
46	6	0	-0.768138	-3.820111	0.437714
47	6	0	-1.843804	-3.484580	1.278633
48	6	0	-0.965157	-4.766049	-0.583701
49	6	0	-3.097875	-4.084907	1.104614
50	1	0	-1.708994	-2.733431	2.051071
51	6	0	-2.218953	-5.371424	-0.757124
52	1	0	-0.143766	-5.000129	-1.252575
53	6	0	-3.288251	-5.033552	0.086949
54	1	0	-3.921479	-3.809584	1.755436
55	1	0	-2.361699	-6.097771	-1.550929
56	1	0	-4.258886	-5.500476	-0.048915
57	6	0	2.569901	0.660975	-2.570396
58	6	0	3.885469	0.400173	-2.985538
59	6	0	2.335845	1.732032	-1.688174
60	6	0	4.952233	1.192015	-2.529642
61	1	0	4.078303	-0.428803	-3.660276
62	6	0	3.395666	2.526640	-1.234597
63	1	0	1.319954	1.945064	-1.370052
64	6	0	4.710919	2.258621	-1.651391
65	1	0	5.963624	0.976746	-2.858394
66	1	0	3.198212	3.366181	-0.573835
67	1	0	5.532302	2.877088	-1.304224
68	6	0	-3.776158	1.326656	-1.048905
69	6	0	-4.573016	1.452343	0.103505
70	6	0	-3.580931	2.451955	-1.871869
71	6	0	-5.156259	2.684641	0.436521
72	1	0	-4.711374	0.589865	0.746168
73	6	0	-4.163832	3.683455	-1.540545
74	1	0	-2.948904	2.355443	-2.747712
75	6	0	-4.951356	3.804953	-0.383896
76	1	0	-5.767487	2.768373	1.329543
77	1	0	-4.006033	4.543863	-2.183064
78	1	0	-5.404536	4.758058	-0.129475

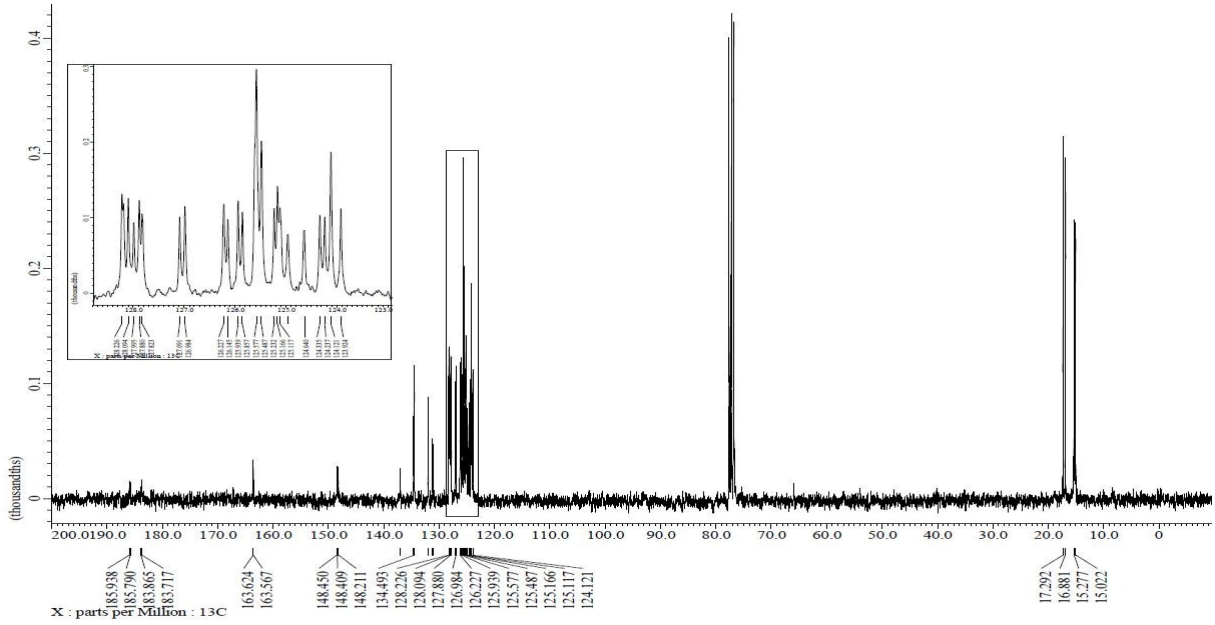
F = $[(CH_3)_3P]_2M\cdots[C_6H_5CH_2NCO]_3$ with M = Pt in Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.457495	-0.643662	-2.477948
2	8	0	-2.442347	0.753671	-0.297451
3	8	0	-0.804949	-2.419263	2.424166
4	7	0	0.646696	-0.646647	2.293894
5	7	0	-1.590235	-0.485639	1.417153
6	6	0	0.676778	-1.269361	-3.823391
7	1	0	1.175540	-0.425496	-4.306699
8	1	0	0.098362	-1.814893	-4.574841
9	1	0	1.430505	-1.933811	-3.395142
10	6	0	-1.649218	0.466326	-3.383059
11	1	0	-1.102554	1.296076	-3.838371
12	1	0	-2.344670	0.862646	-2.638893
13	1	0	-2.188400	-0.090161	-4.155492
14	6	0	-1.476854	-2.144942	-2.048544
15	1	0	-2.340369	-1.831489	-1.457888
16	1	0	-0.886311	-2.841503	-1.449607
17	1	0	-1.827139	-2.644213	-2.956610
18	6	0	-1.421043	0.253511	0.228724
19	6	0	-2.990000	-0.773176	1.834857
20	1	0	-3.507029	0.188472	1.870175
21	6	0	-0.573011	-1.242291	2.052840
22	6	0	1.698100	-1.468784	2.917515
23	1	0	1.213459	-2.323620	3.395699
24	1	0	2.169622	-0.863826	3.695187
25	15	0	2.697417	0.996669	-1.328806
26	6	0	3.865245	1.226639	0.108222
27	1	0	4.822598	1.630383	-0.235658
28	1	0	3.419111	1.894823	0.845988
29	1	0	4.027615	0.256654	0.584450
30	6	0	3.693985	-0.137451	-2.434088
31	1	0	3.693260	-1.142490	-2.008632
32	1	0	3.267928	-0.166088	-3.438518
33	1	0	4.725653	0.222696	-2.495894
34	6	0	2.815924	2.621817	-2.254991
35	1	0	2.428930	3.429484	-1.629729
36	1	0	3.853758	2.841884	-2.523883
37	1	0	2.209159	2.568478	-3.162703
38	1	0	-2.940020	-1.190985	2.841845
39	6	0	0.871053	0.795460	2.361950
40	8	0	1.135522	1.301227	3.485835
41	7	0	0.825182	1.435268	1.183503
42	6	0	0.815885	2.909145	1.218137
43	1	0	1.482323	3.285661	0.432669
44	1	0	1.208317	3.233598	2.187625
45	6	0	-0.590146	3.437523	0.999153
46	6	0	-0.979104	3.972285	-0.237227
47	6	0	-1.543604	3.313452	2.024995
48	6	0	-2.303680	4.379524	-0.453205
49	1	0	-0.249896	4.051152	-1.040638
50	6	0	-2.867255	3.716058	1.812238
51	1	0	-1.243137	2.889115	2.979166
52	6	0	-3.251120	4.250773	0.571419

53	1	0	-2.597089	4.783375	-1.417090
54	1	0	-3.598660	3.612098	2.607574
55	1	0	-4.279079	4.556464	0.404775
56	6	0	2.719856	-1.961739	1.907672
57	6	0	4.092878	-1.904860	2.193831
58	6	0	2.301377	-2.531072	0.690091
59	6	0	5.037407	-2.408530	1.283559
60	1	0	4.426709	-1.463812	3.128847
61	6	0	3.238823	-3.039856	-0.216320
62	1	0	1.241137	-2.585551	0.464684
63	6	0	4.612892	-2.979646	0.075424
64	1	0	6.095399	-2.358218	1.519496
65	1	0	2.900757	-3.498016	-1.141481
66	1	0	5.339351	-3.379837	-0.624620
67	6	0	-3.723091	-1.727843	0.902335
68	6	0	-4.695971	-1.241638	0.011023
69	6	0	-3.435940	-3.105852	0.916423
70	6	0	-5.367101	-2.114481	-0.858918
71	1	0	-4.901719	-0.177256	-0.016529
72	6	0	-4.104115	-3.978853	0.045681
73	1	0	-2.674774	-3.473009	1.596323
74	6	0	-5.070713	-3.486554	-0.846349
75	1	0	-6.114081	-1.725207	-1.543531
76	1	0	-3.874710	-5.039655	0.066556
77	1	0	-5.590092	-4.163509	-1.517658
78	78	0	0.420060	0.462500	-0.573229

Figure 1S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pd{–N(Ar)C(O)N(Ar)C(O)–}$(PR_3)_2$ (PR_3 = PMe_3, Ar = 1-naphthyl), **1** in $CDCl_3$.




(thousandths)
X : parts per Million : 13C
185.938
185.790
183.865
183.717
163.624
163.567
148.450
148.409
148.211
134.493
128.226
128.094
127.880
126.984
126.227
125.939
125.577
125.487
125.166
125.117
124.121
17.292
16.881
15.277
15.022

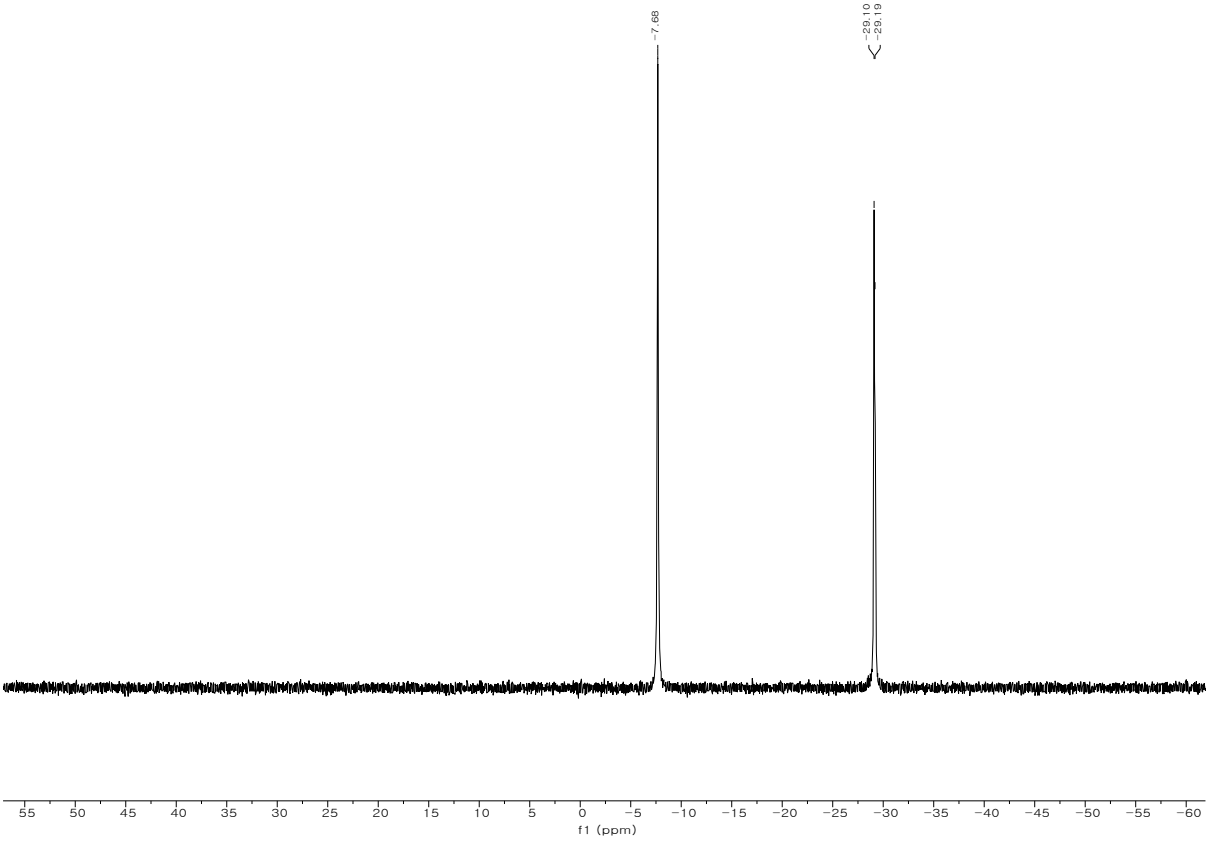
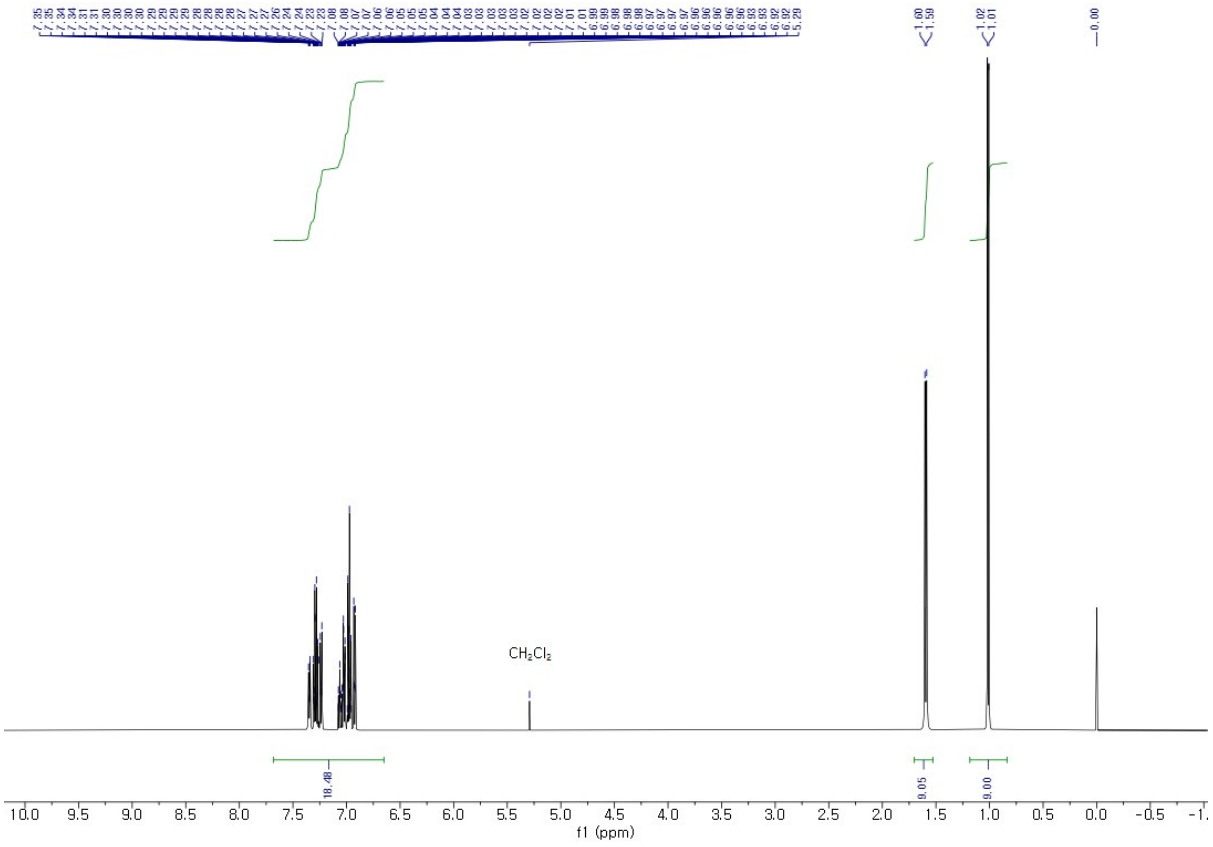
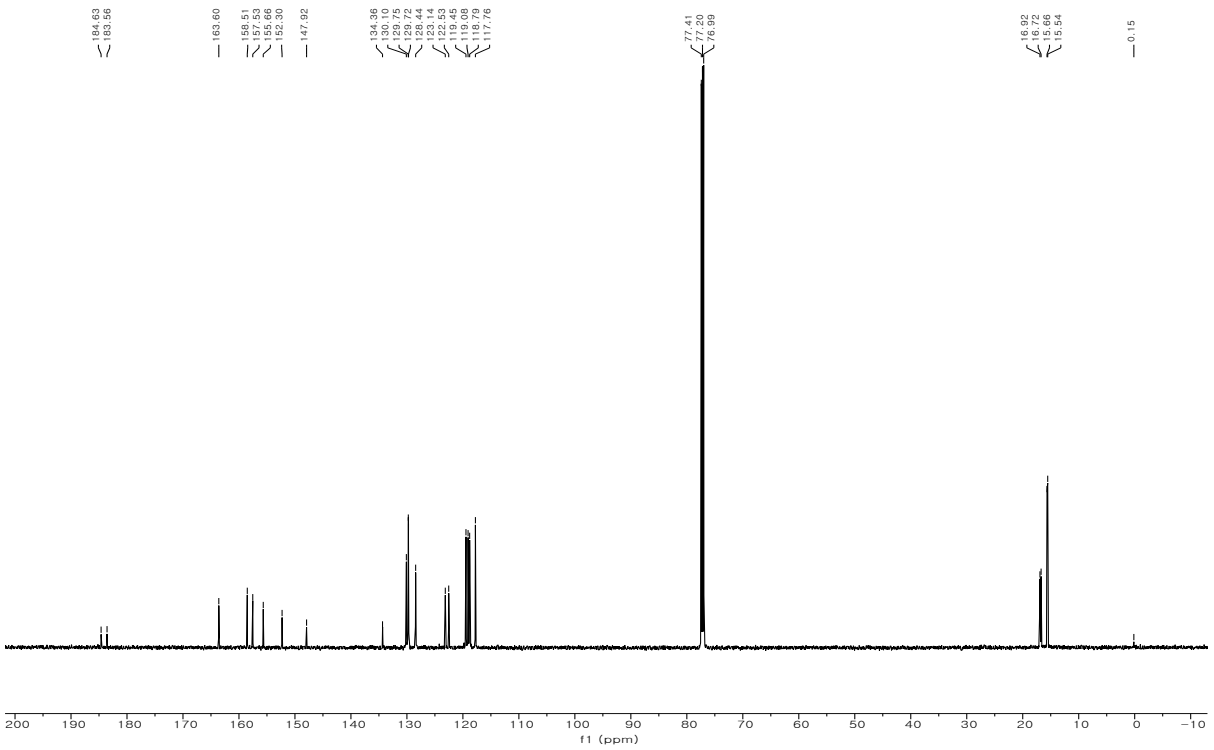

7.68
29.10
29.19
f1 (ppm)

Figure 2S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pd{–N(Ar)C(O)N(Ar)C(O)–}$(PR_3)_2$ (PR_3 = PMe_3, Ar = 4-phenoxyphenyl), **2** in $CDCl_3$.




184.63
183.56
163.60
158.51
157.53
155.66
152.30
147.92
134.98
130.10
129.75
129.72
128.44
123.14
122.53
119.45
119.08
118.79
117.76
77.41
77.20
76.99
16.92
16.72
15.66
15.54
0.15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

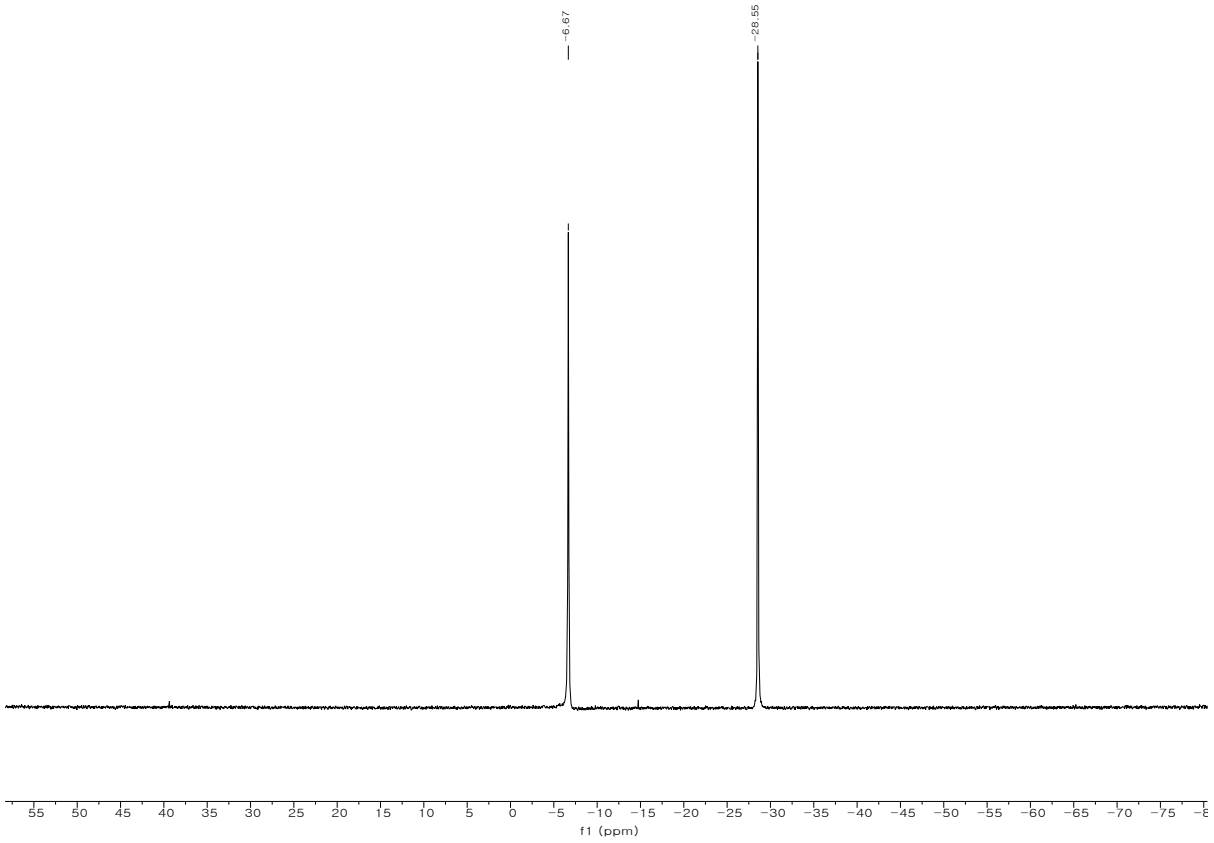
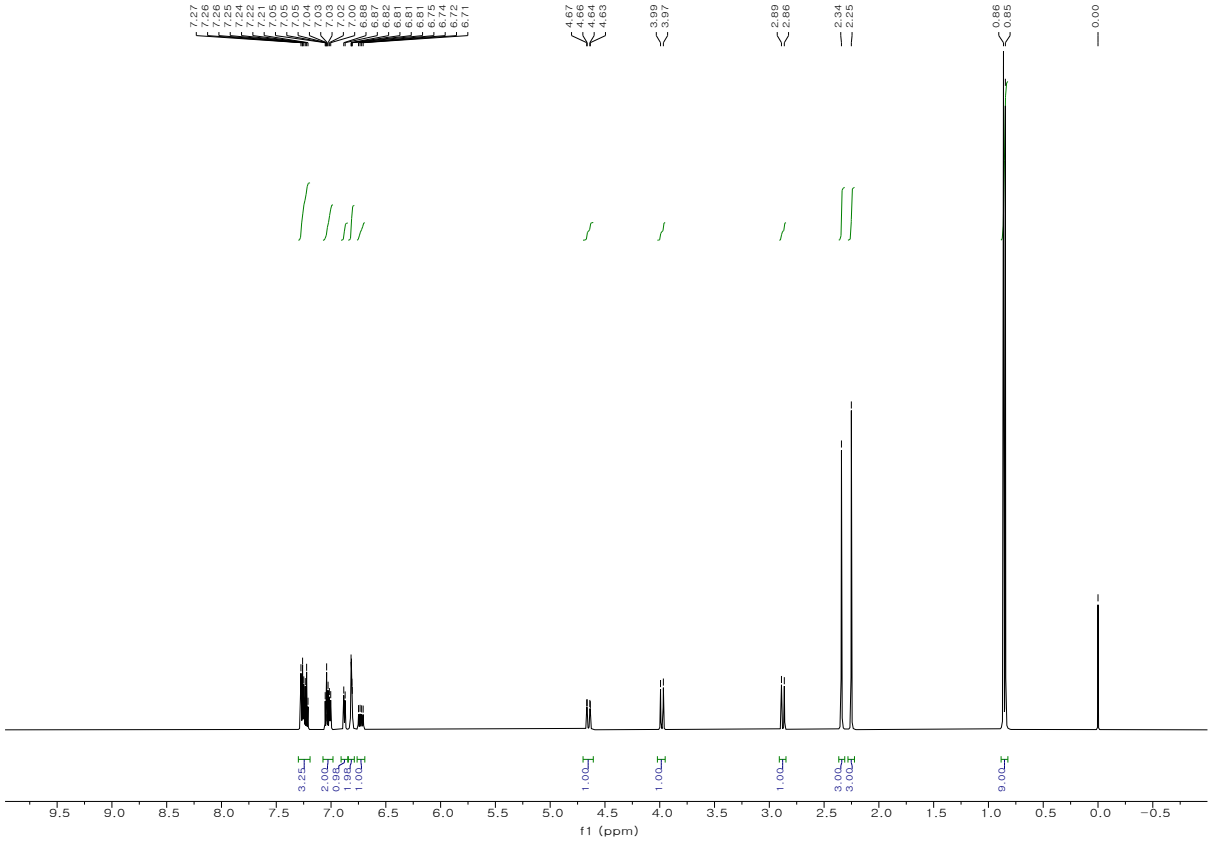
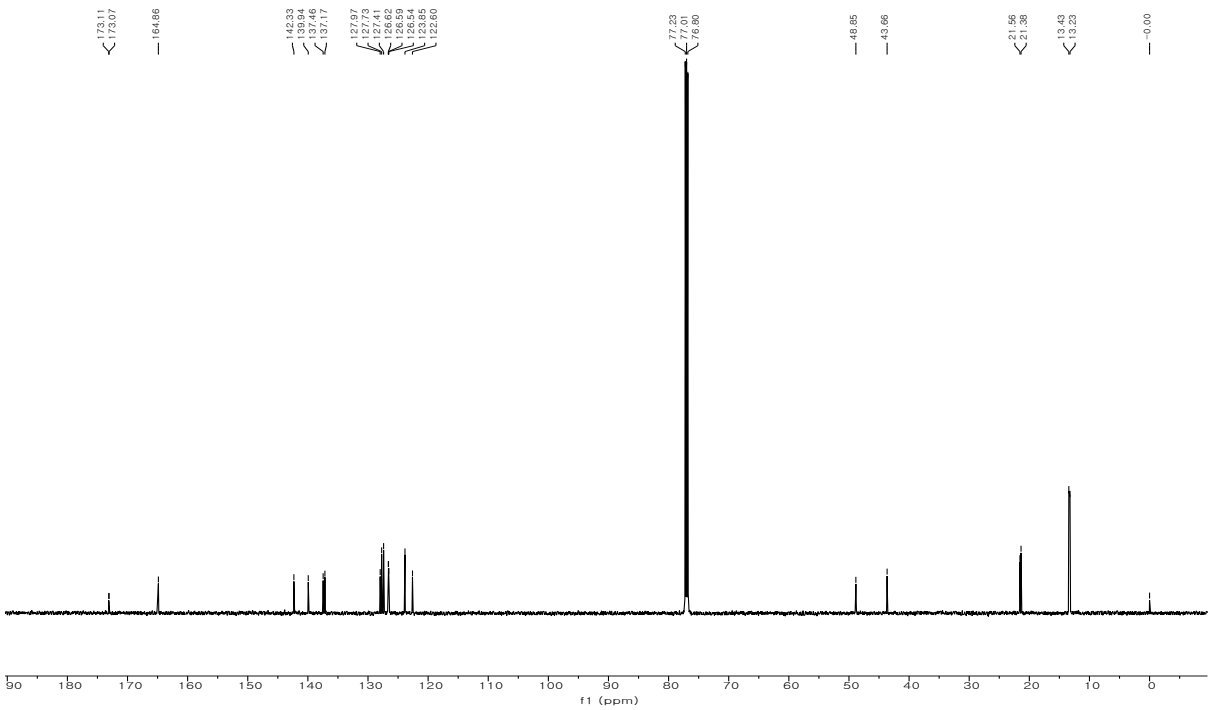

−6.67
−28.55
55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 −60 −65 −70 −75
f1 (ppm)

Figure 3S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of $[Pd(PMe_3)\{-C(O)N(R)C(O)N(R)-\}]_4$ (R = 3-methylbenzyl), **3** in $CDCl_3$.




173.11
173.07
164.86
142.33
139.94
137.46
137.17
127.97
127.73
127.41
126.62
126.59
126.54
123.85
122.60
77.23
77.01
76.80
48.85
43.66
21.56
21.38
13.43
13.23
0.00
f1 (ppm)

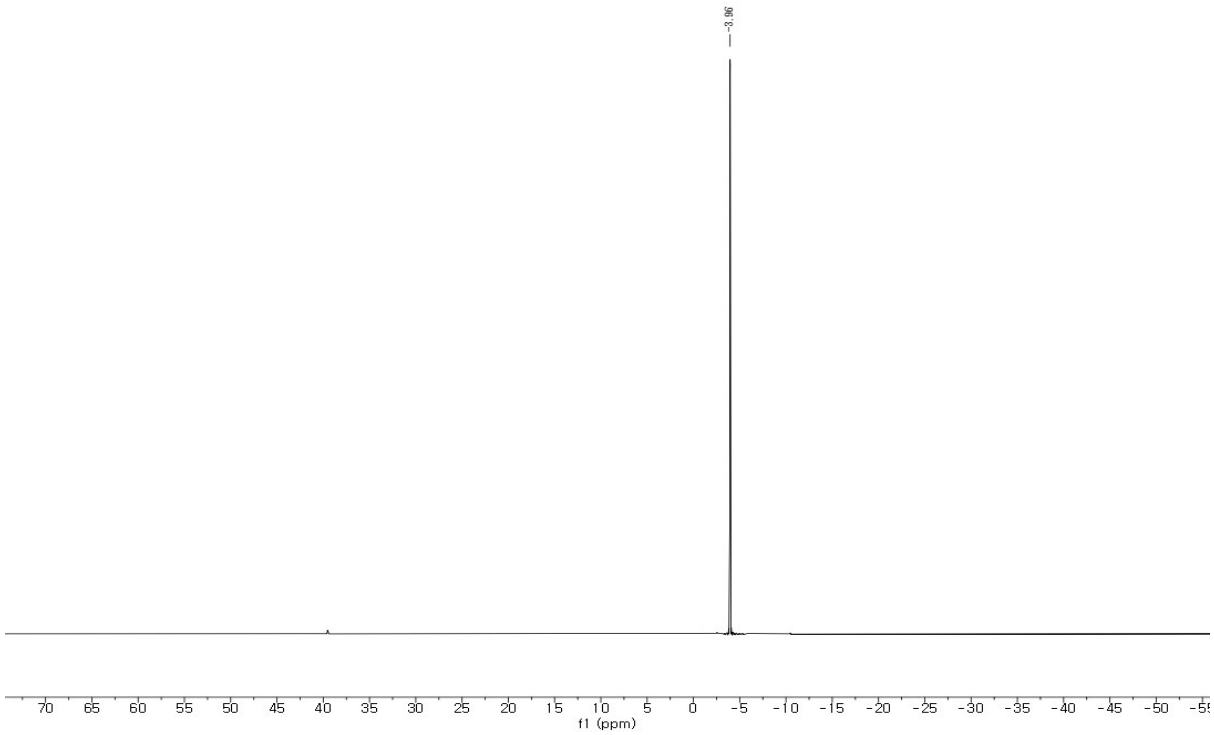
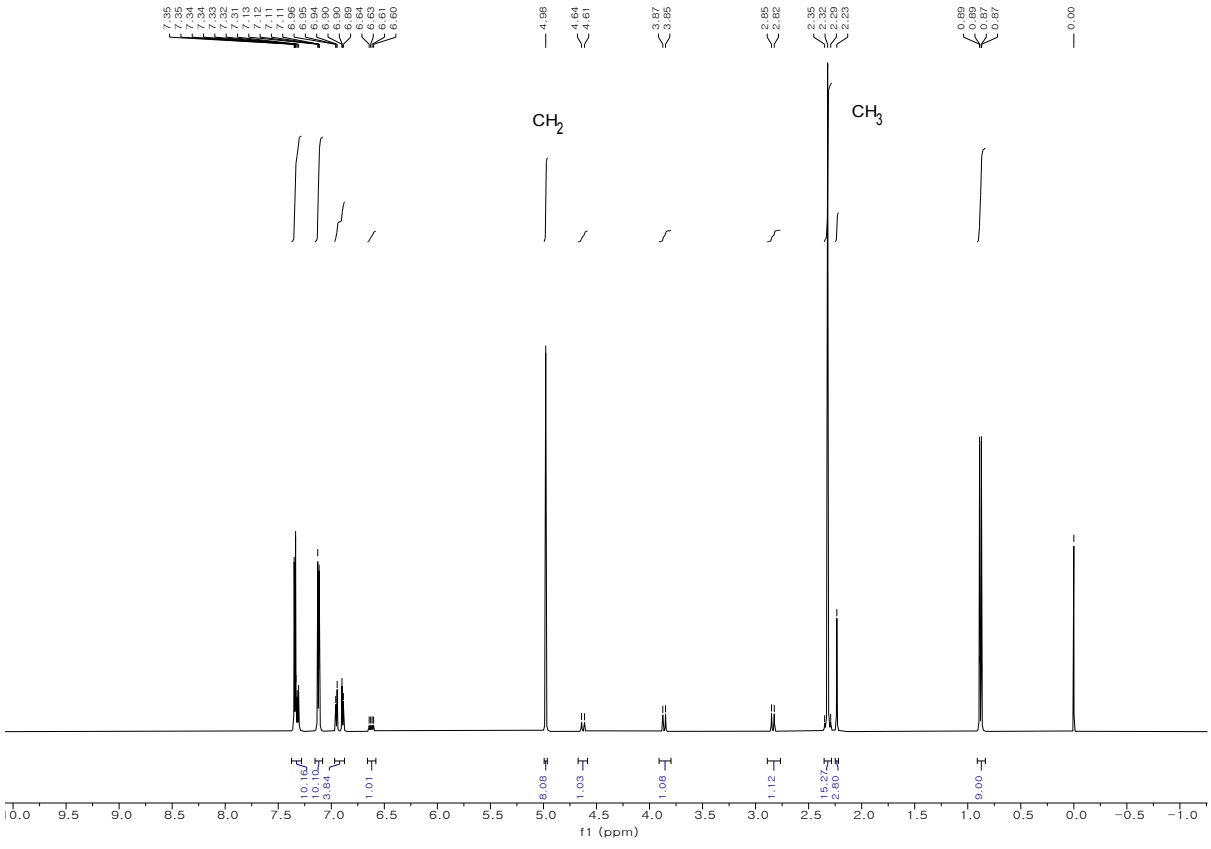
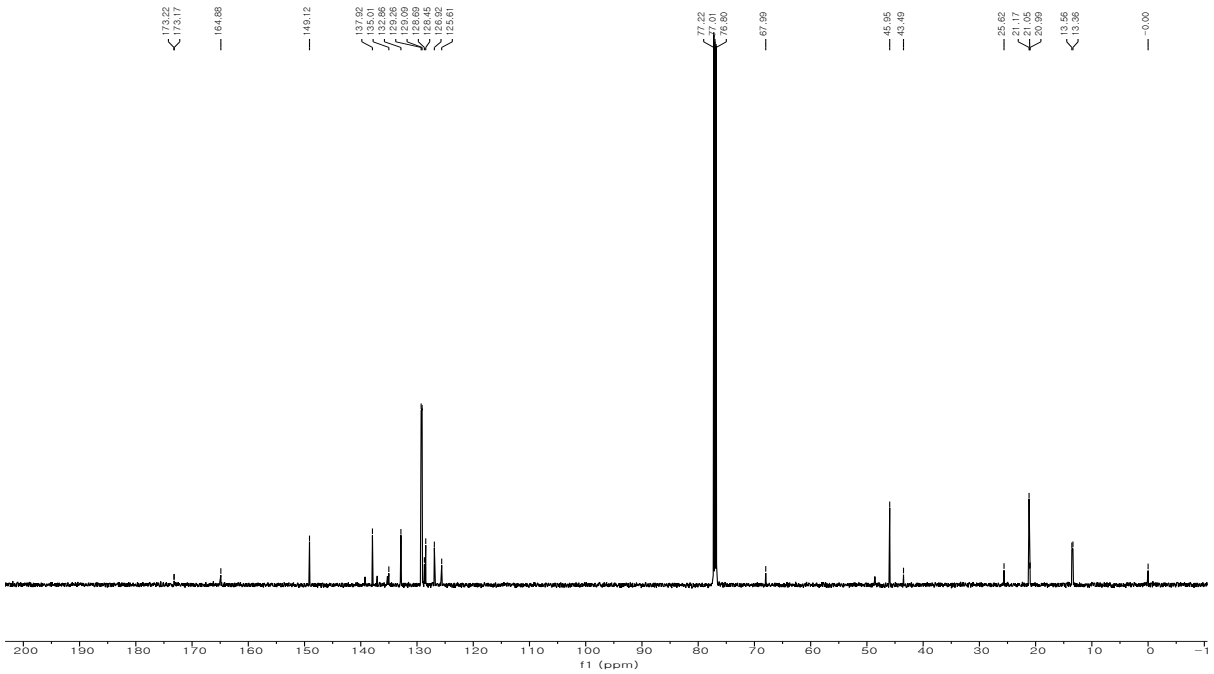

-8.96
f1 (ppm)

Figure 4S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of $[Pd(PMe_3)\{-C(O)N(R)C(O)N(R)-\}]_4$ (R = 4-methylbenzyl), **4** in $CDCl_3$.




173.22
173.17
164.88
149.12
137.92
135.01
132.86
129.26
129.09
128.89
128.45
126.92
125.61
77.22
77.01
76.80
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43.49
25.62
21.17
21.05
20.99
13.56
13.36
-0.00
f1 (ppm)

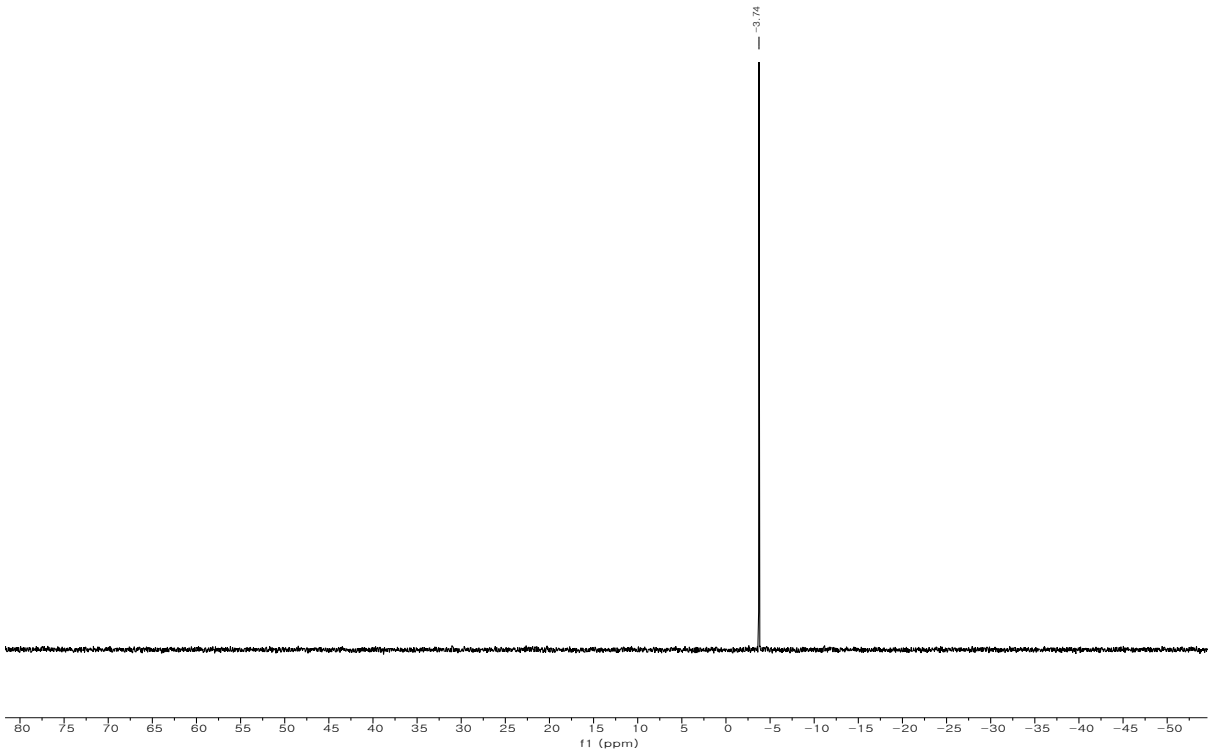
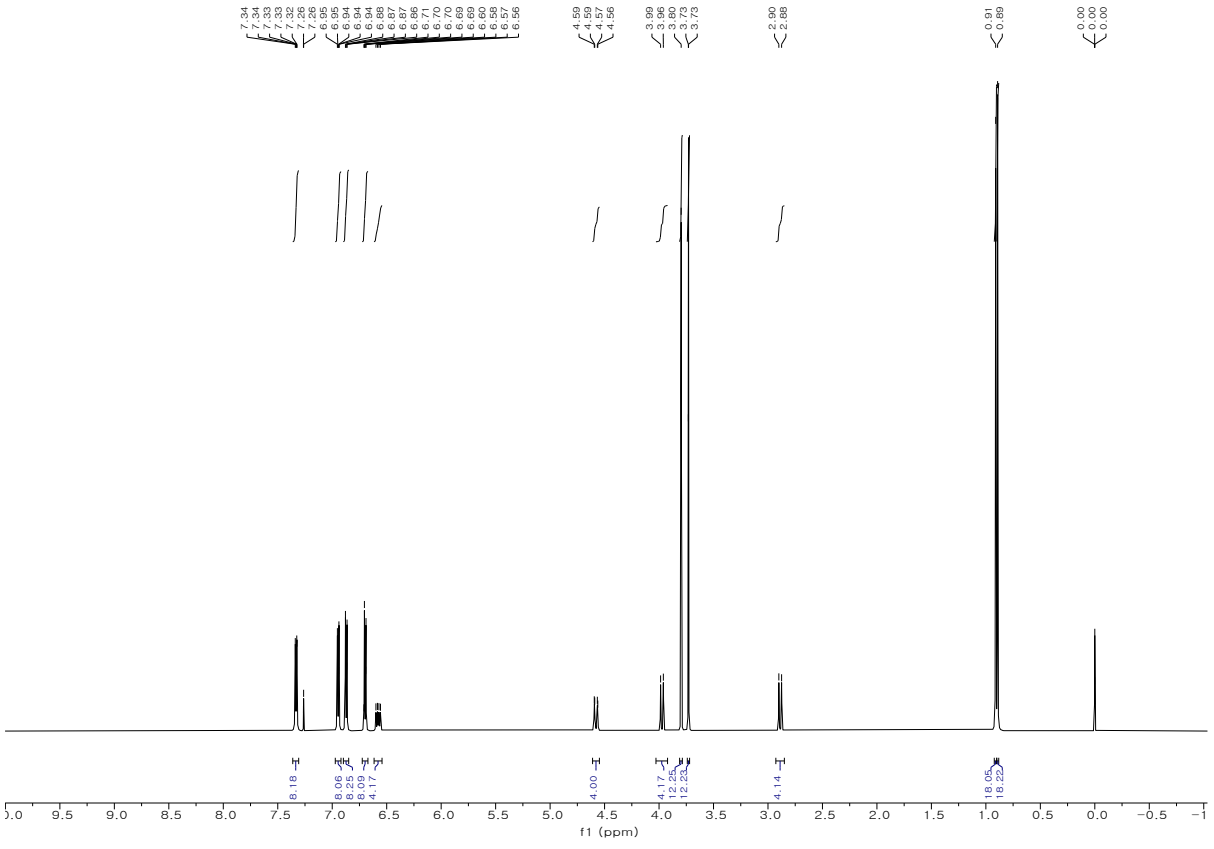
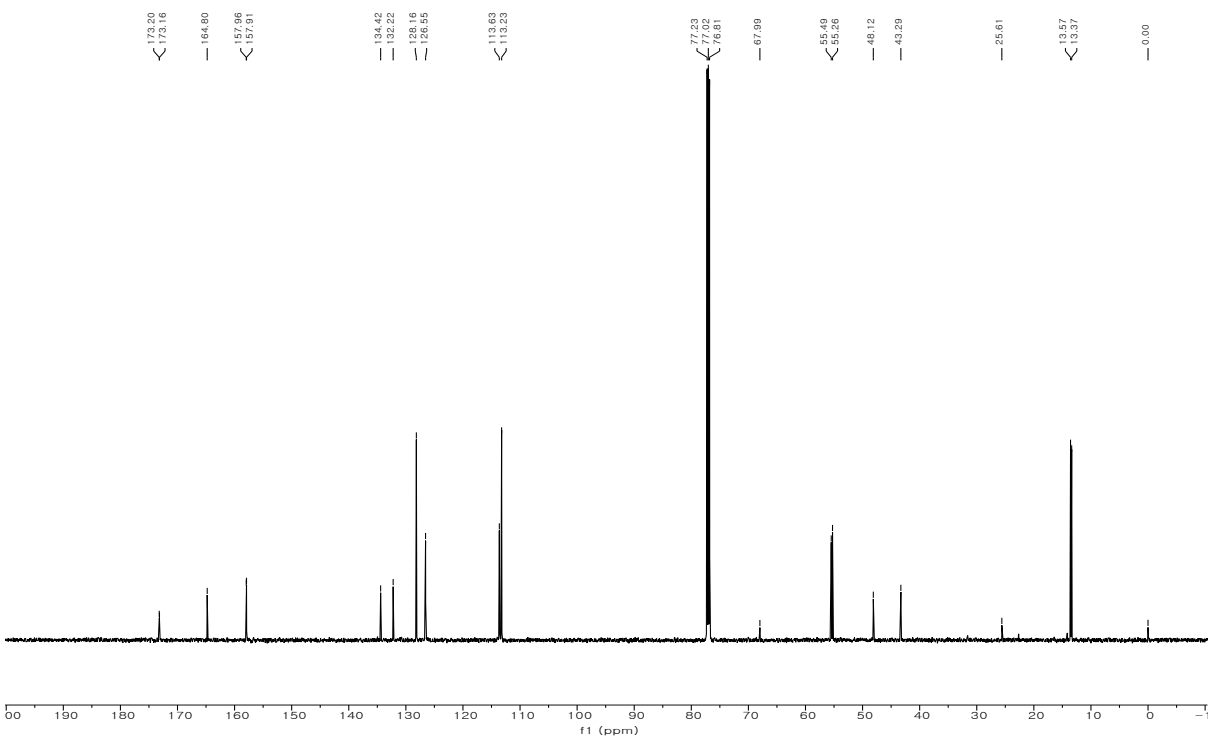

-3.74
f1 (ppm)

Figure 5S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of $[Pd(PMe_3)\{-C(O)N(R)C(O)N(R)-\}]_4$ (R = 4-phenoxybenzyl), **5** in $CDCl_3$.




173.20
173.16
164.80
157.96
157.91
134.42
132.22
128.16
126.55
113.63
113.23
77.23
77.02
76.81
67.99
55.49
55.26
48.12
43.29
25.61
13.57
13.37
0.00
f1 (ppm)

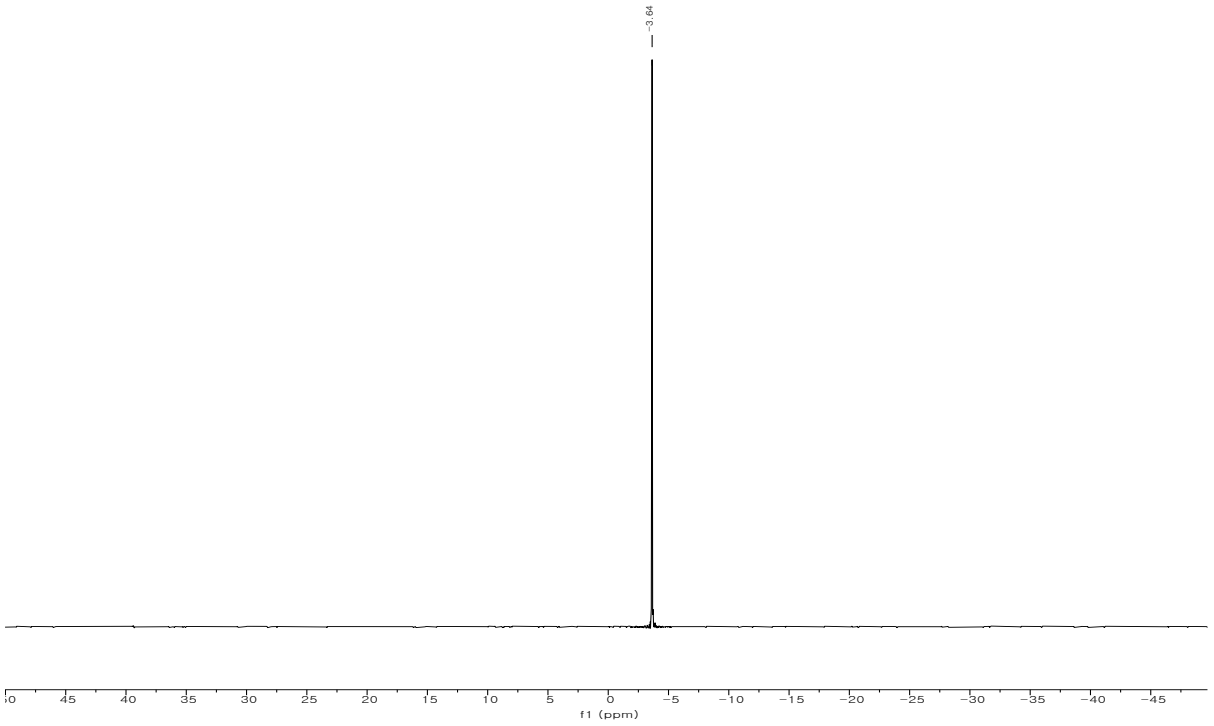
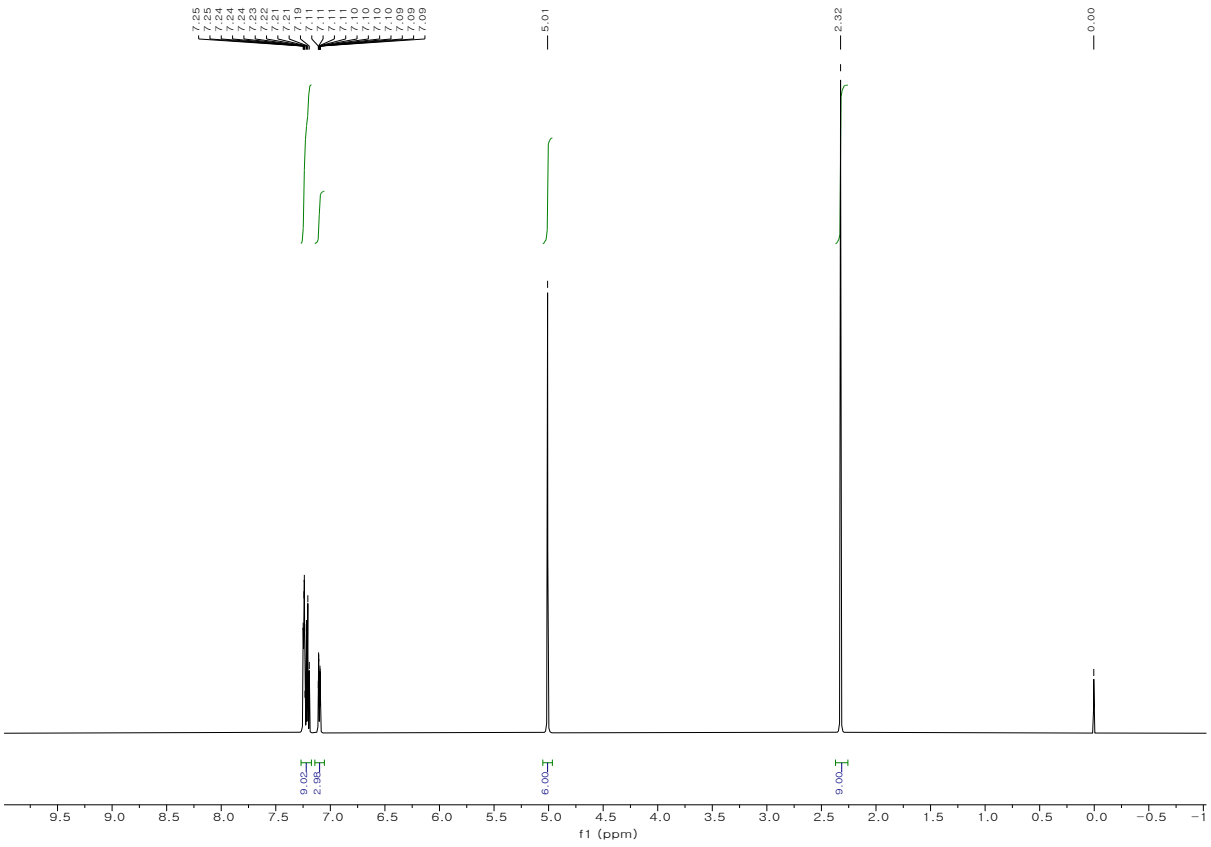

-3.64
f1 (ppm)

Figure 6S. ^{1}H and ^{13}C $\{^{1}H\}$ -NMR spectra of $(R\text{-}NCO)_3$ (R = 3-methylbenzyl), **6** in $CDCl_3$.



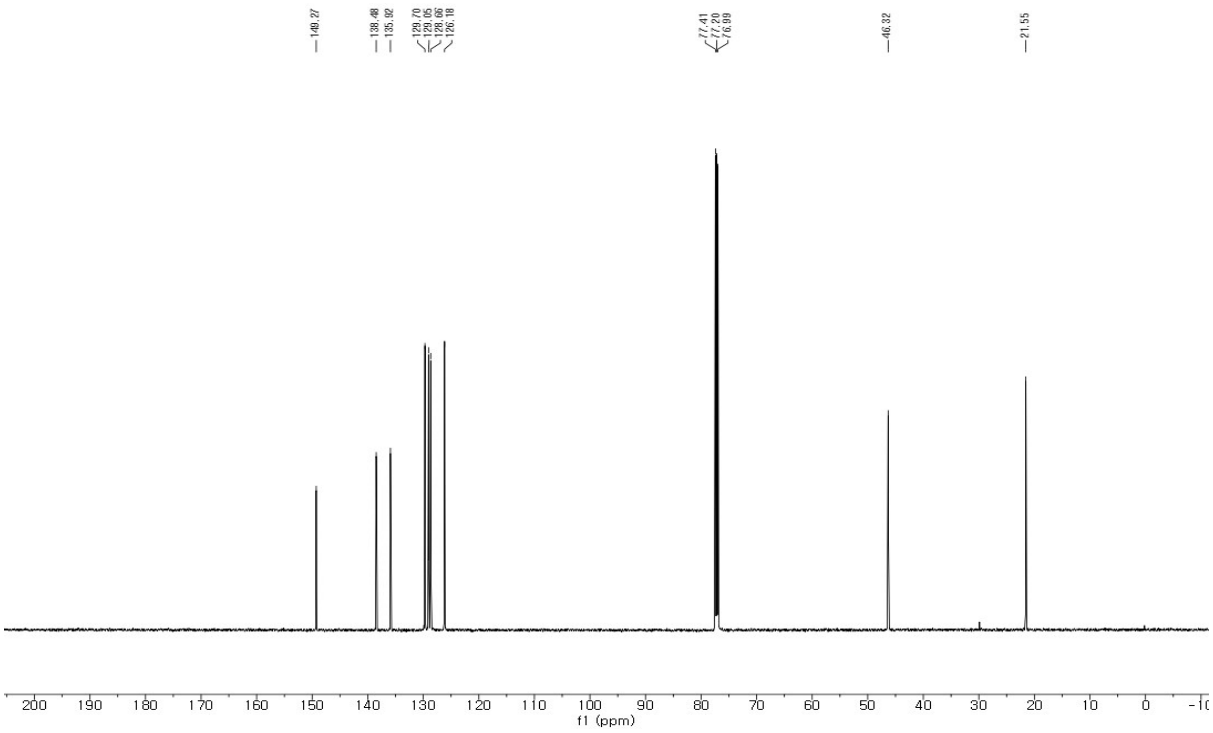
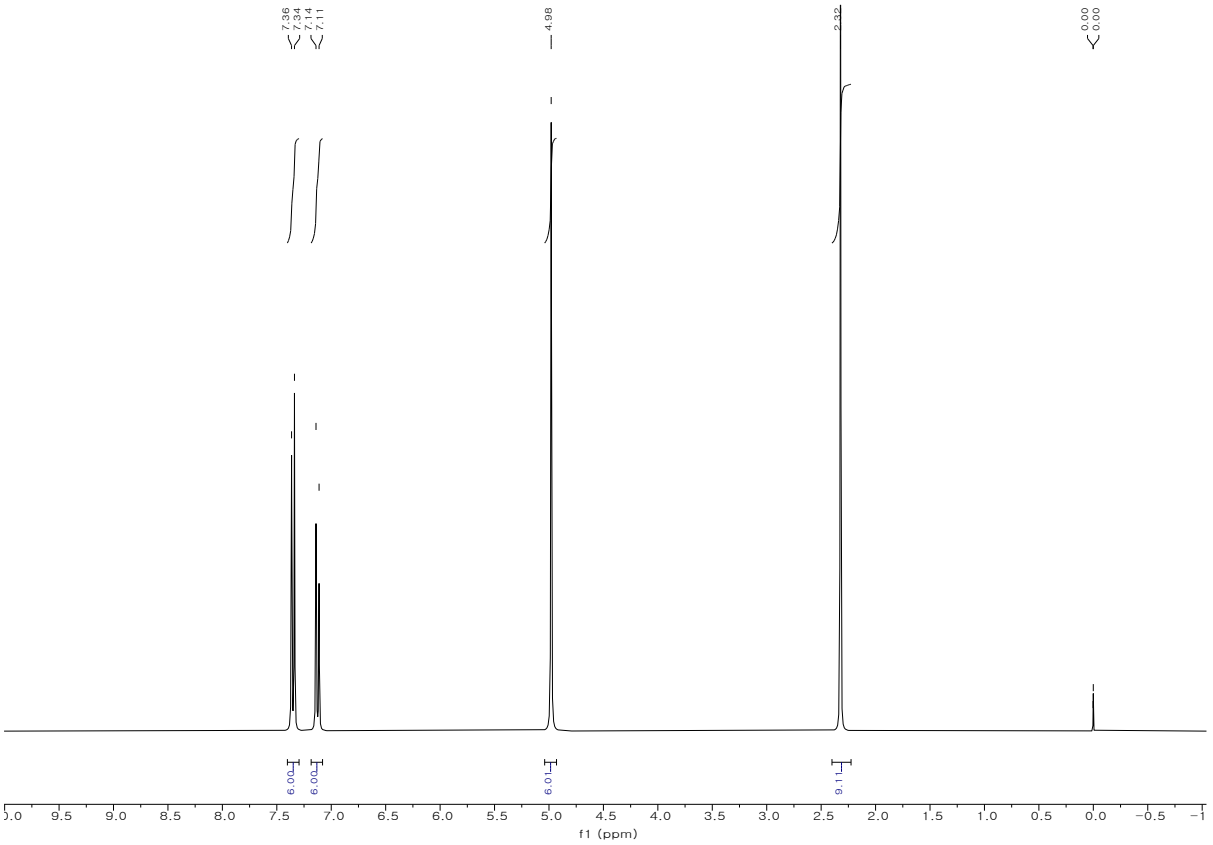


Figure 7S. ^{1}H and $^{13}C\{^{1}H\}$ -NMR spectra of $(R\text{-}NCO)_3$ (R = 4-methylbenzyl), **7** in $CDCl_3$.



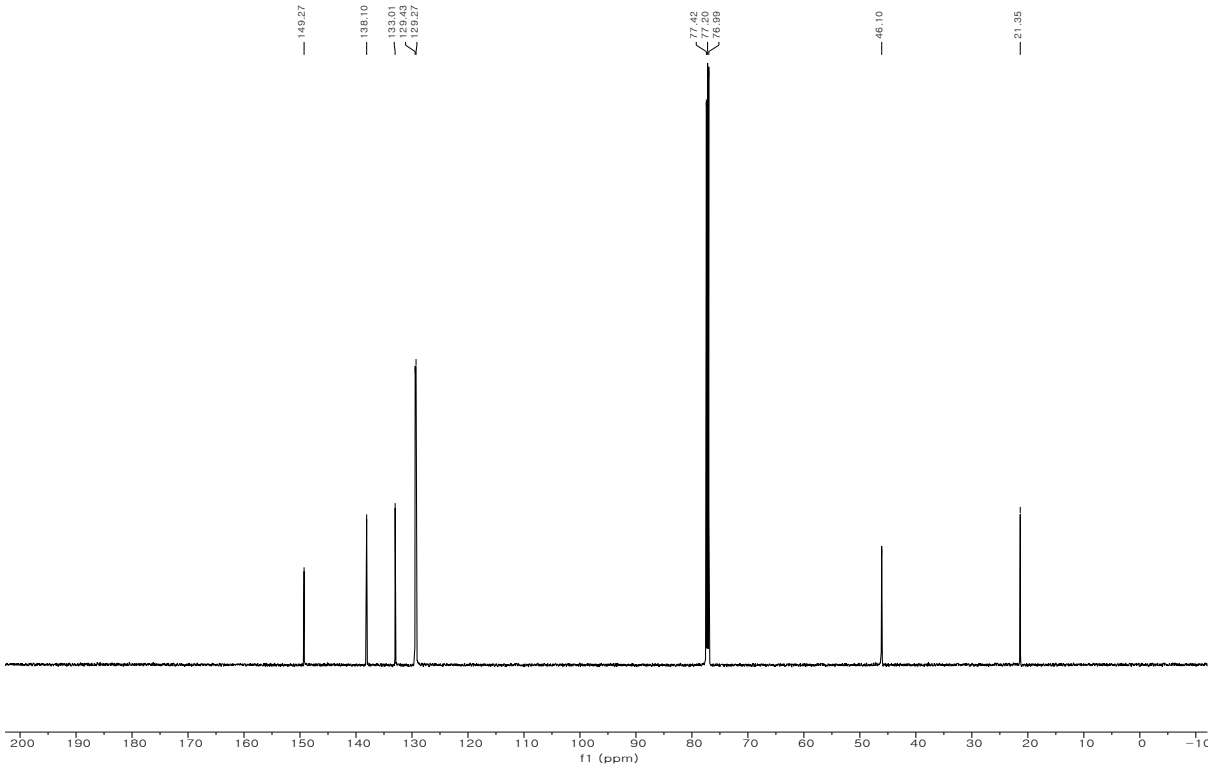
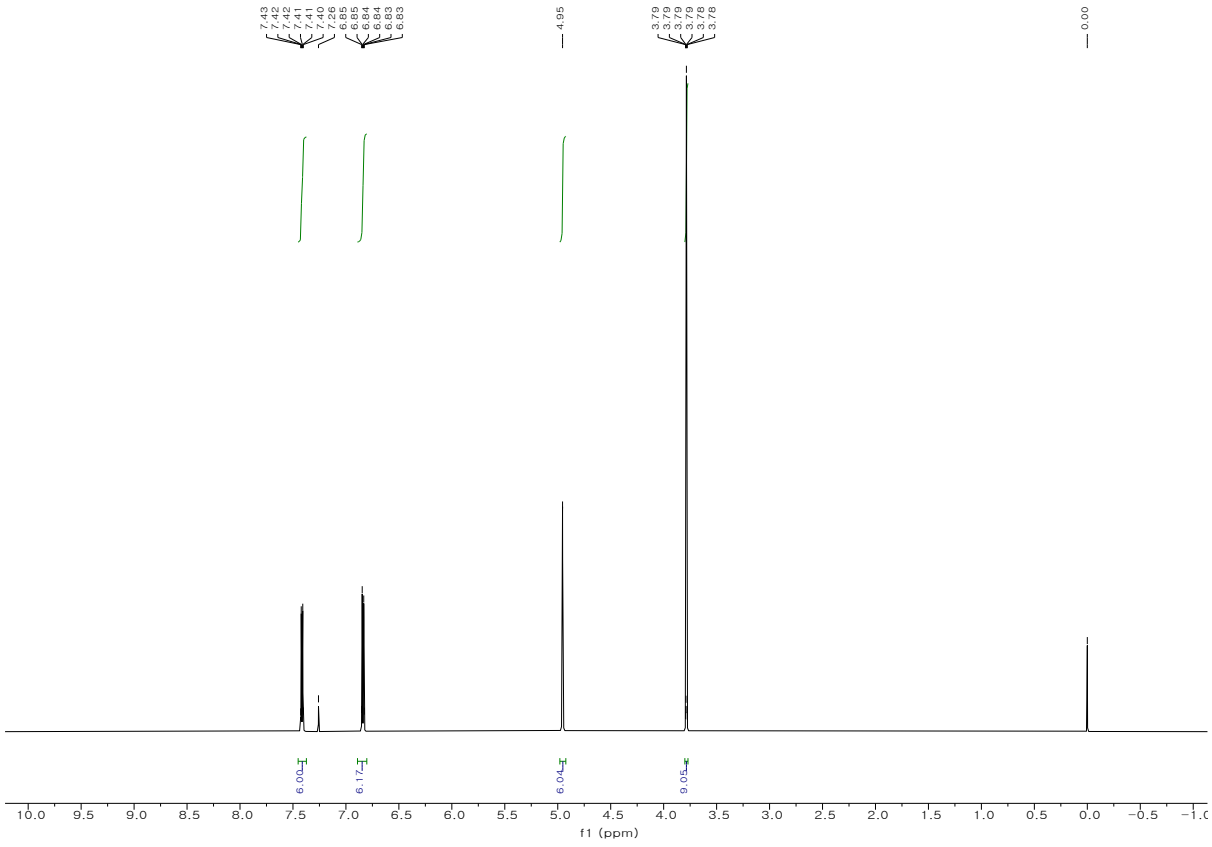


Figure 8S. ^{1}H and $^{13}C\{^{1}H\}$ -NMR spectra of $(R\text{-}NCO)_3$ (R = 4-phenoxybenzyl), **8** in $CDCl_3$.



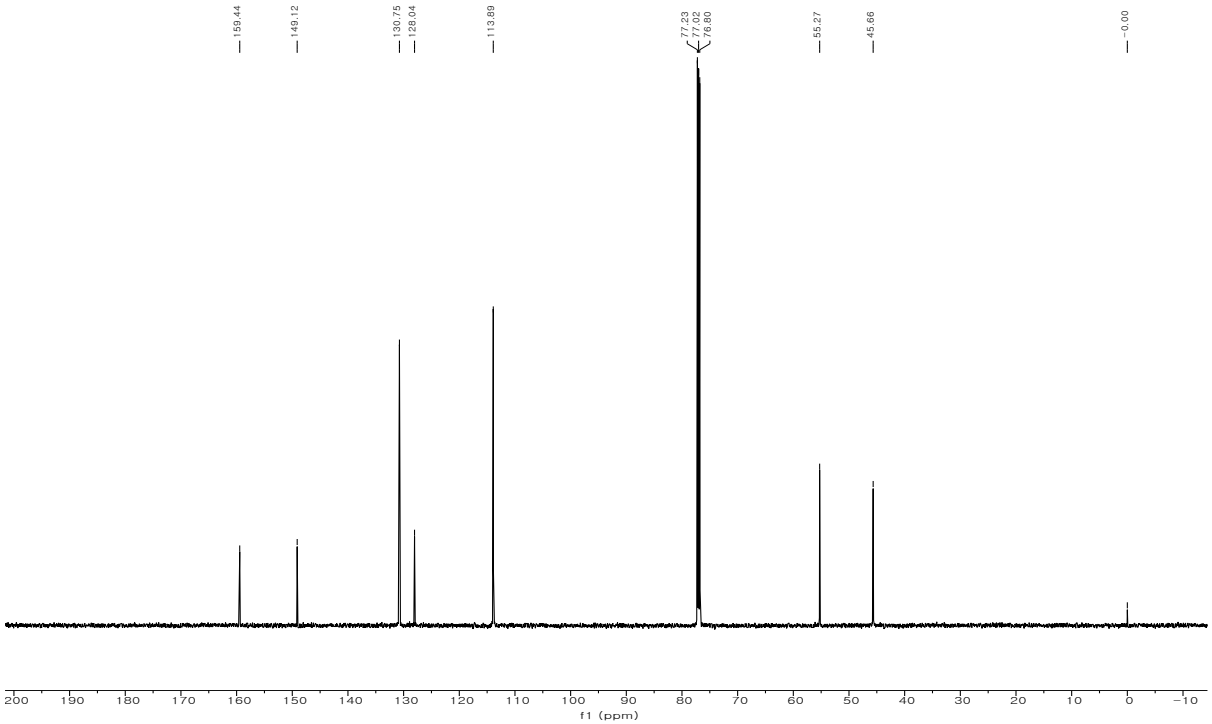
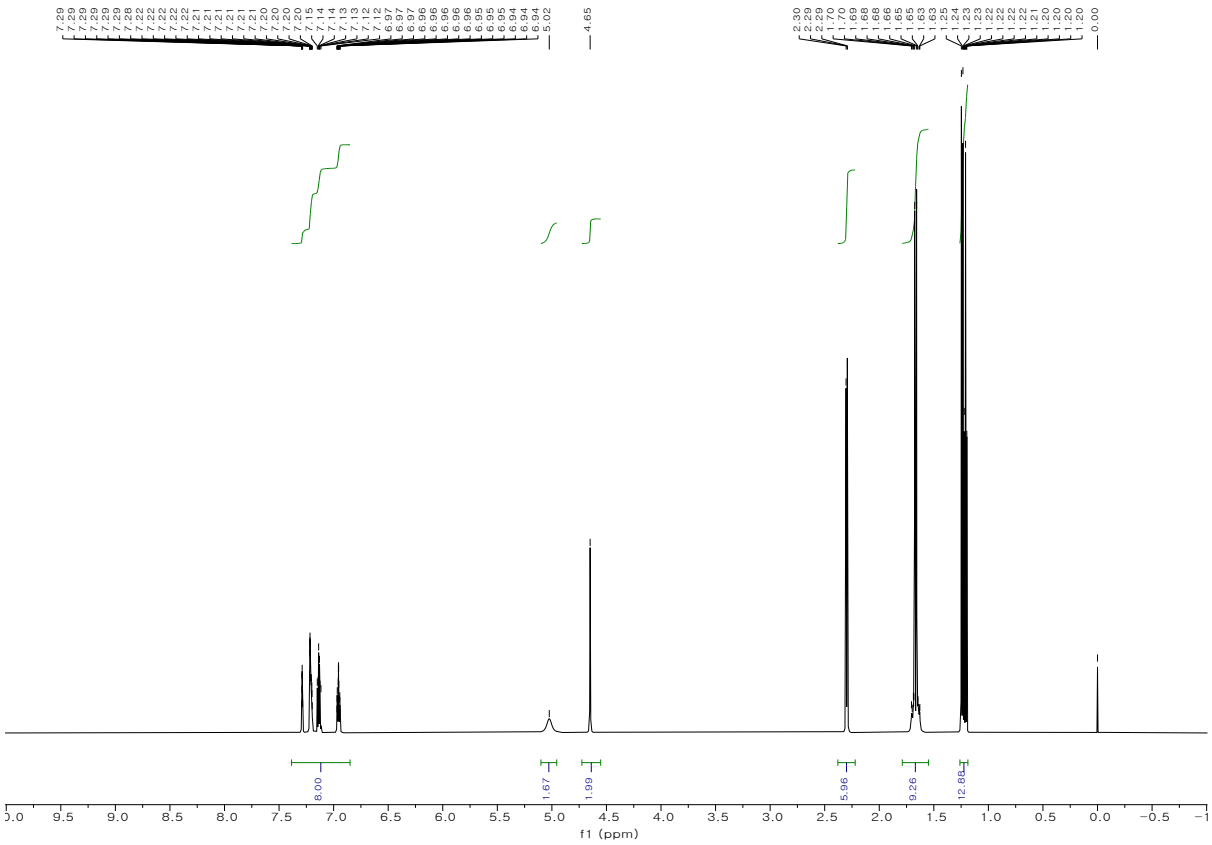
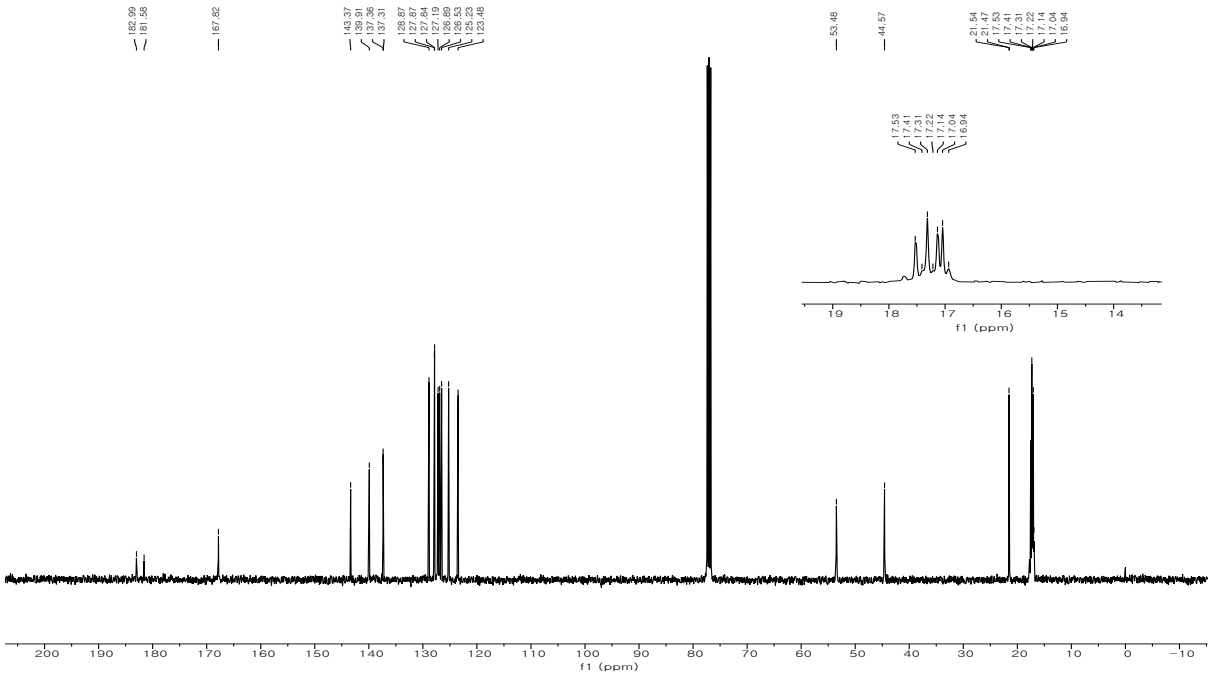


Figure 9S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{N(R)C(O)N(R)C(O)}$(PMe_3)_2$] (R = 3-methylbenzyl), **9** in $CDCl_3$.




182.99
181.58
167.82
143.37
139.01
137.36
137.31
128.87
127.87
127.84
127.19
126.89
125.53
125.22
123.48
53.48
44.57
21.54
21.47
17.53
17.41
17.31
17.22
17.14
17.04
16.94
f1 (ppm)

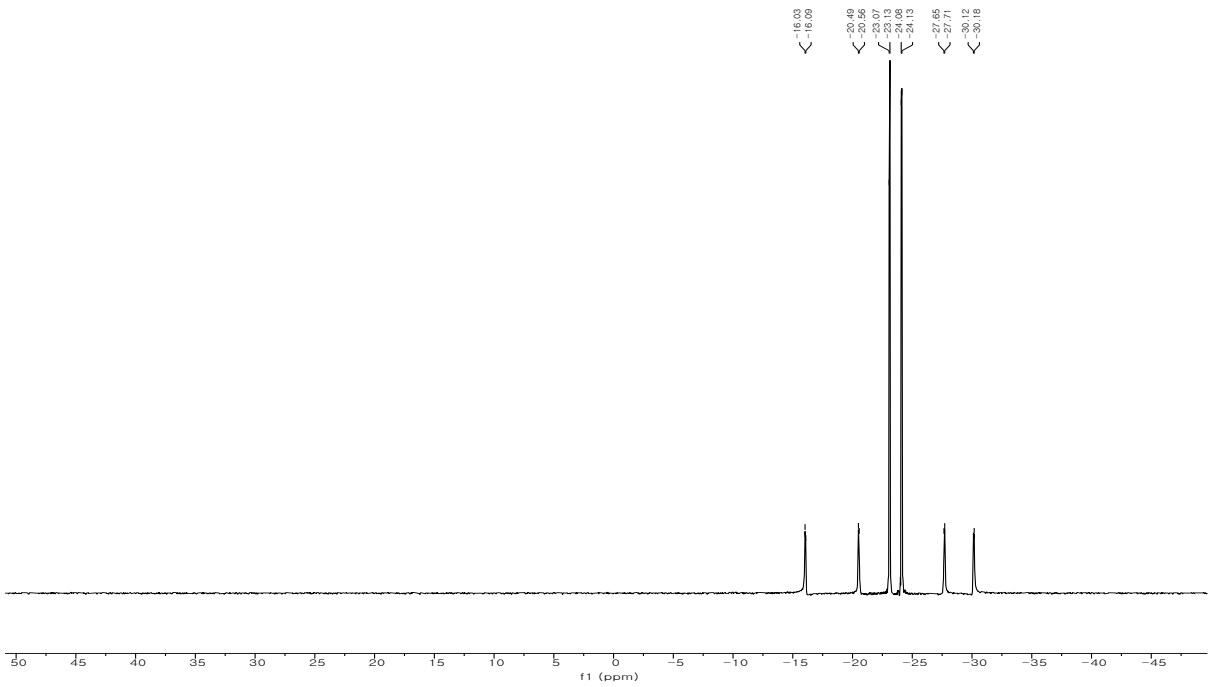
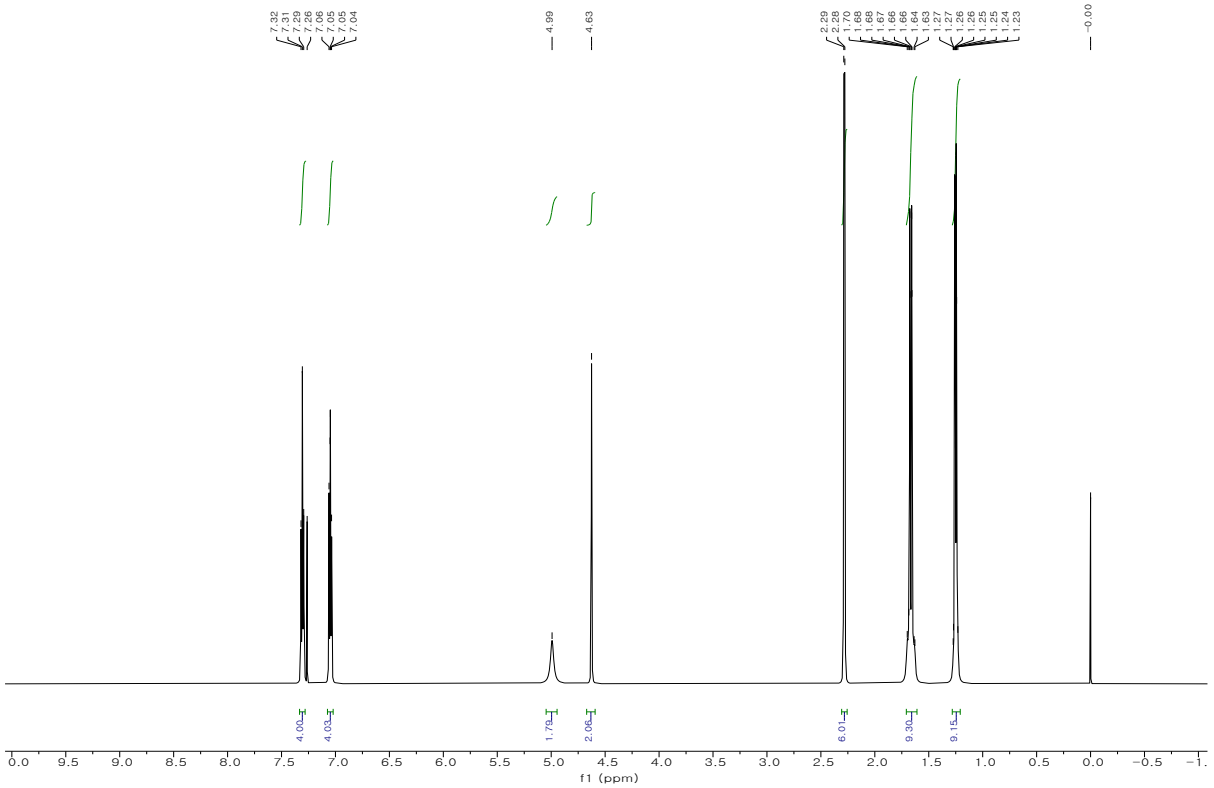
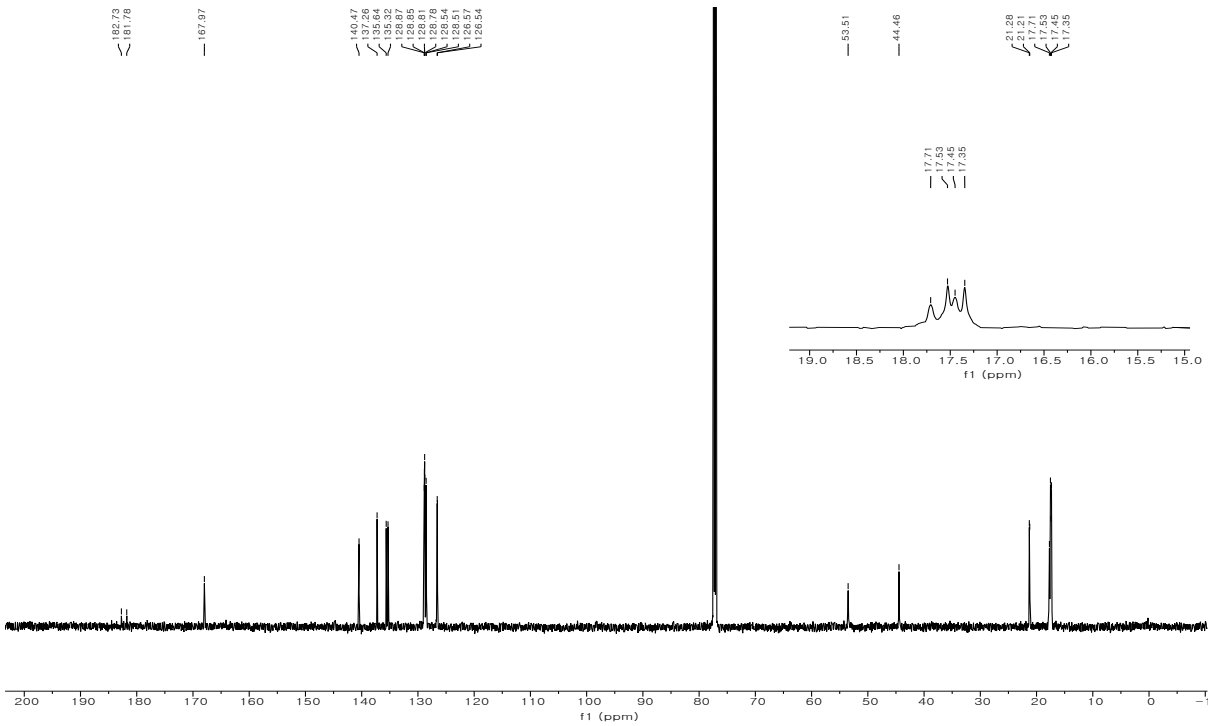

-16.03
-16.09
-20.49
-20.56
-23.07
-23.13
-24.08
-24.13
-27.65
-27.71
-30.12
-30.18
f1 (ppm)

Figure 10S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{N(R)C(O)N(R)C(O)}$(PMe_3)_2$] (R = 4-methylbenzyl), **10** in $CDCl_3$.




182.73
181.78
167.97
140.47
137.26
135.64
135.32
129.07
128.85
128.81
128.78
128.54
128.15
126.57
126.54
53.51
44.46
21.28
21.21
17.71
17.53
17.45
17.35
f1 (ppm)

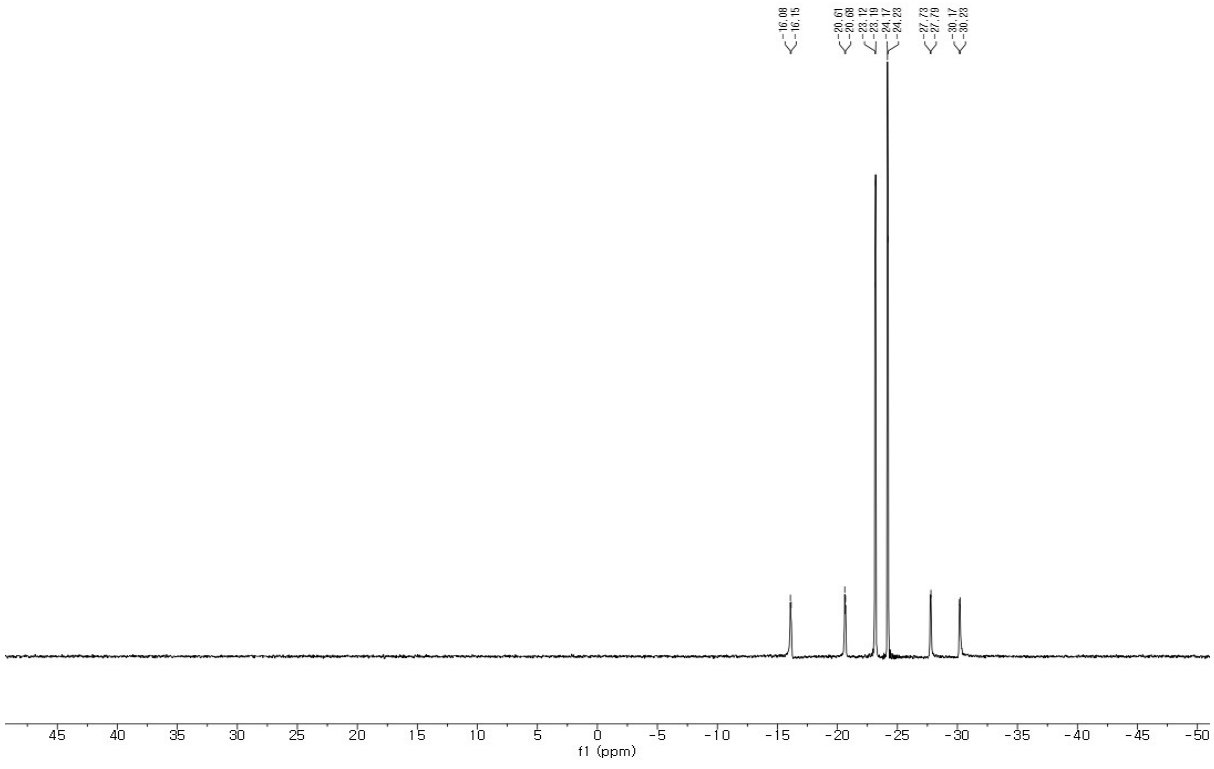
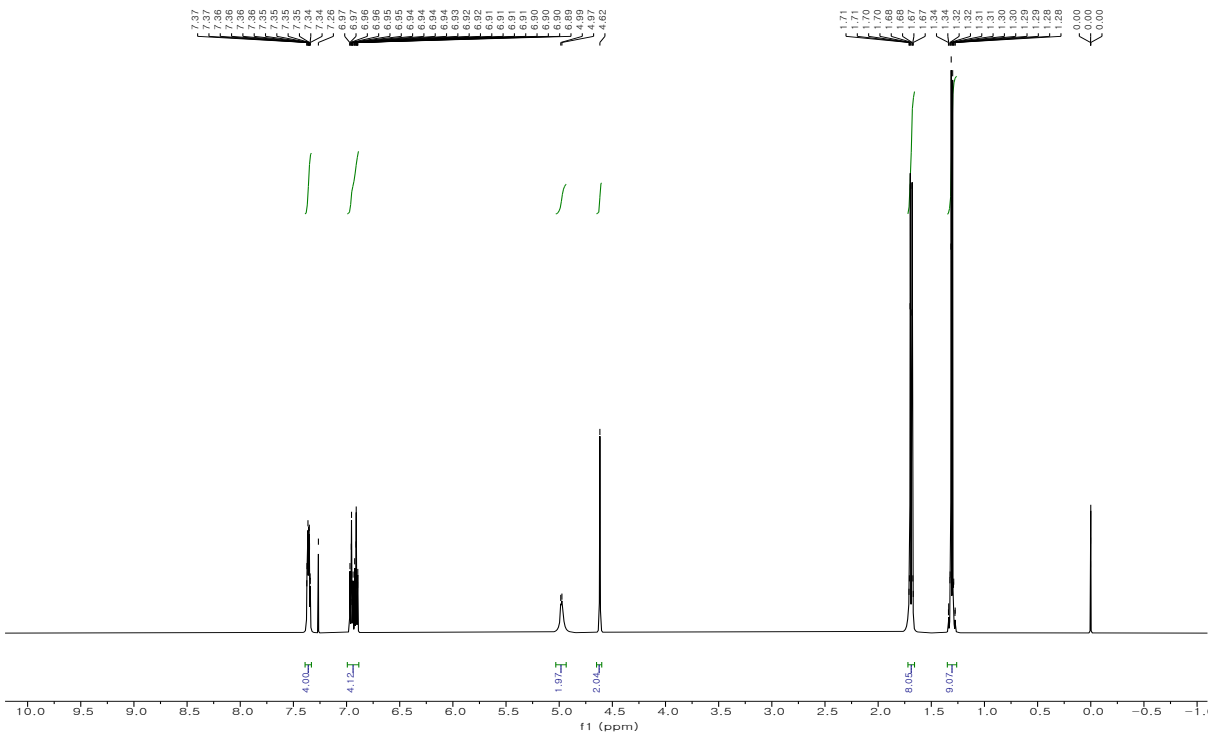
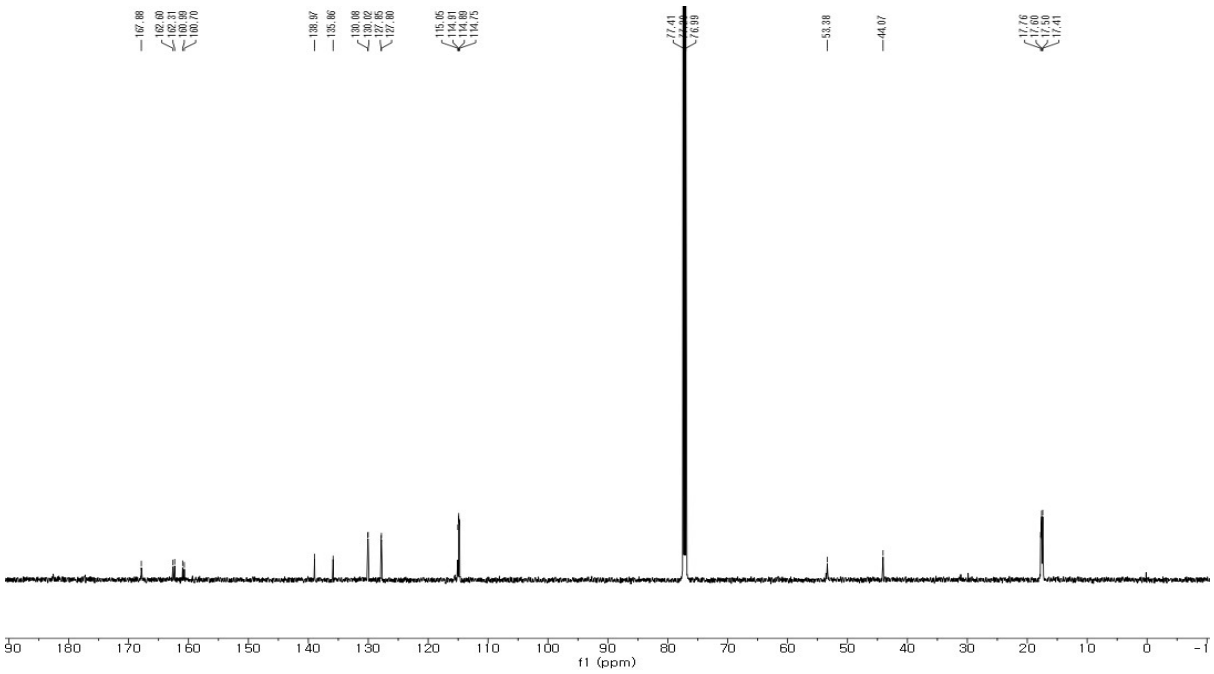

16.08
16.15
20.61
20.68
23.12
23.19
24.17
24.23
27.73
27.79
30.17
30.23
f1 (ppm)

Figure 11S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{–N(R)C(O)N(R)C(O)}$(PMe_3)_2$] (R = 4-fluorobenzyl), **11** in $CDCl_3$.




167.88
162.60
162.31
160.99
160.70
138.97
135.86
130.08
130.02
127.85
127.80
115.05
114.91
114.89
114.75
17.41
16.98
53.38
44.07
17.76
17.60
17.50
17.41
f1 (ppm)

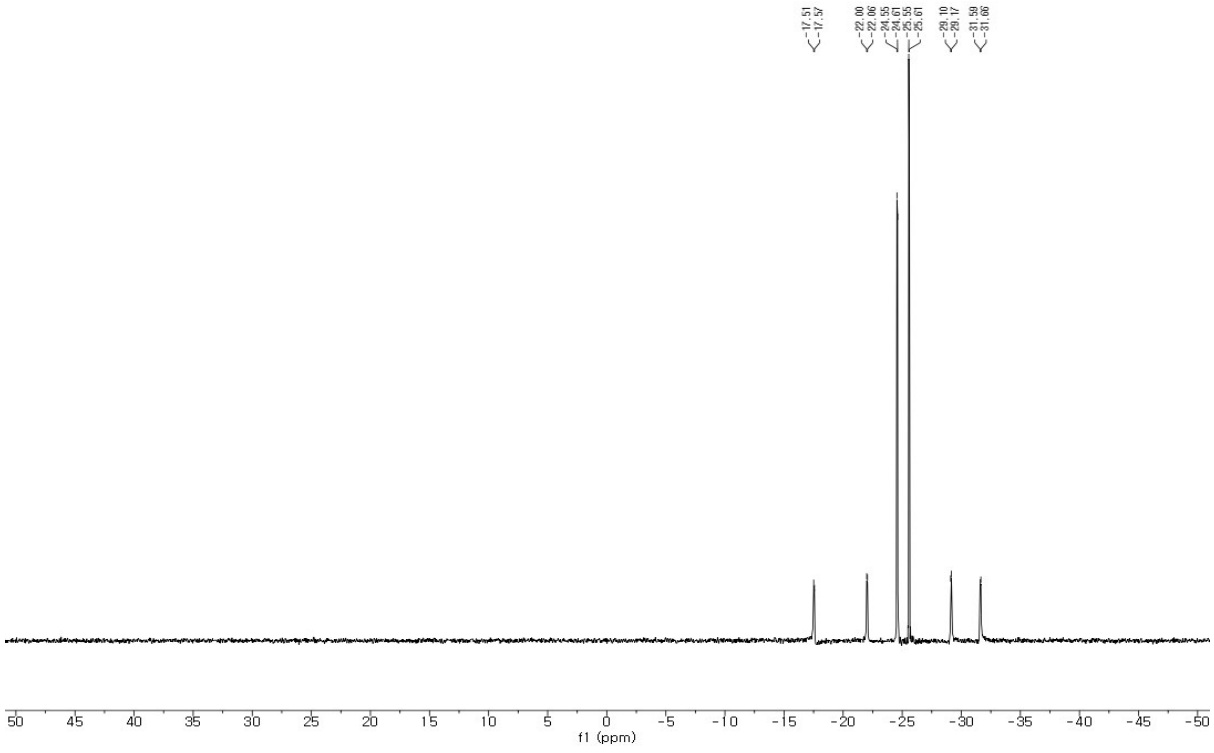
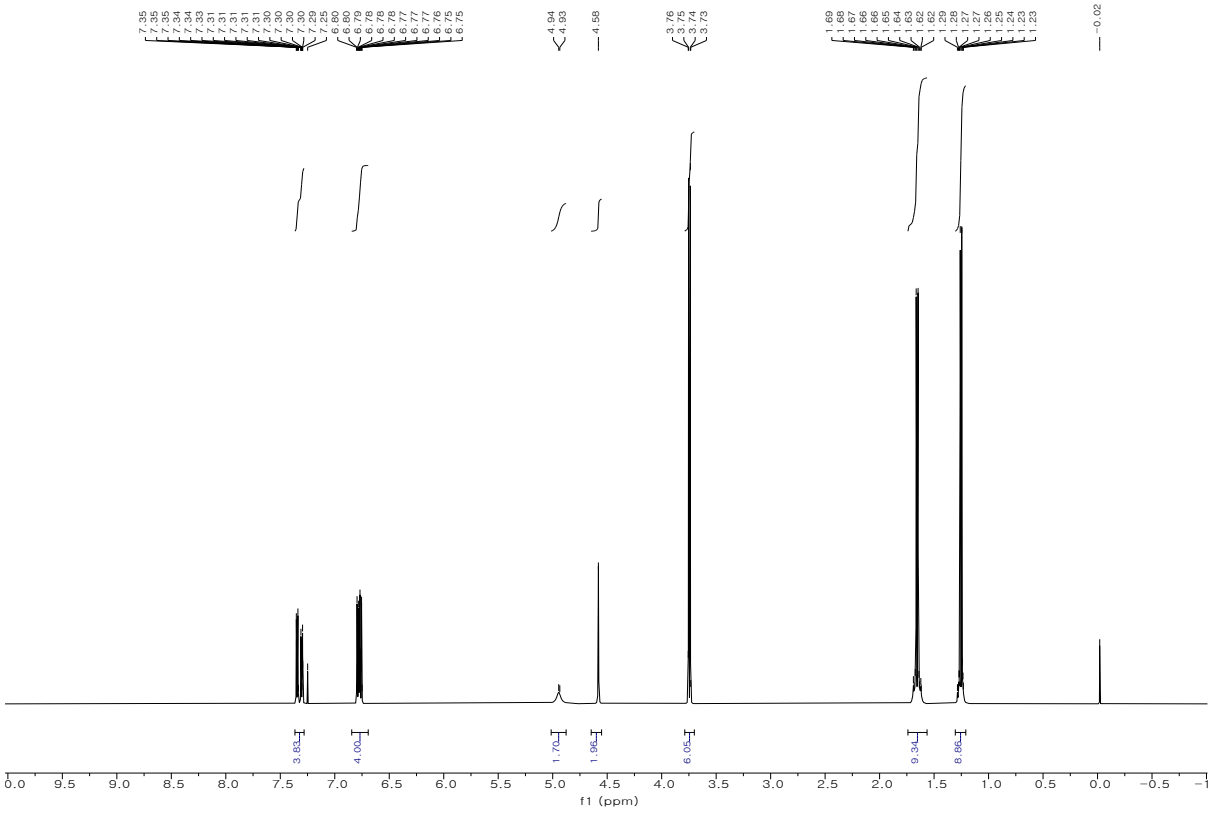
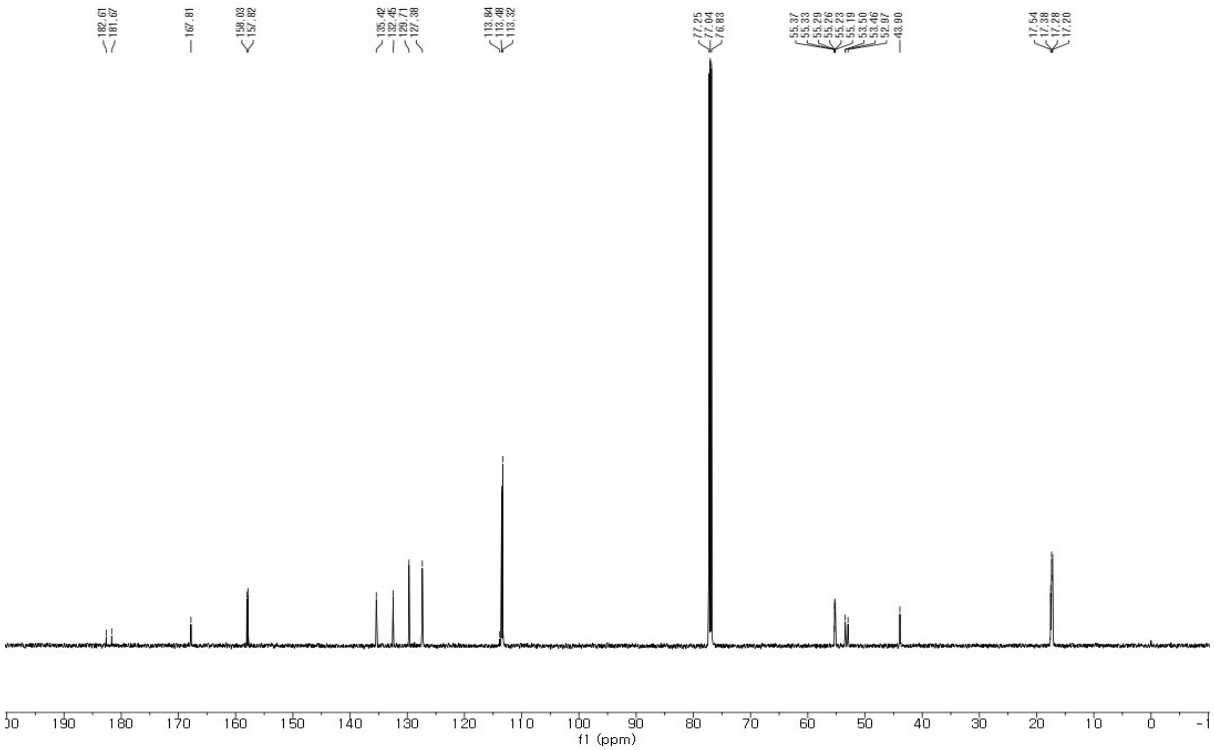

17.51
17.57
22.00
22.06
24.55
24.61
25.55
25.61
29.10
29.17
31.59
31.66
f1 (ppm)

Figure 12S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{– (R)C(O)N(R)C(O)–}$(PMe_3)_2$] (R = 4-methoxybenzyl), **12** in $CDCl_3$.




182.61
181.67
167.81
158.03
157.82
135.42
132.45
129.71
127.38
113.84
113.48
113.32
77.25
77.04
76.83
55.37
55.33
55.29
55.26
55.23
55.19
53.50
53.46
52.97
43.90
17.54
17.28
17.28
17.20
f1 (ppm)

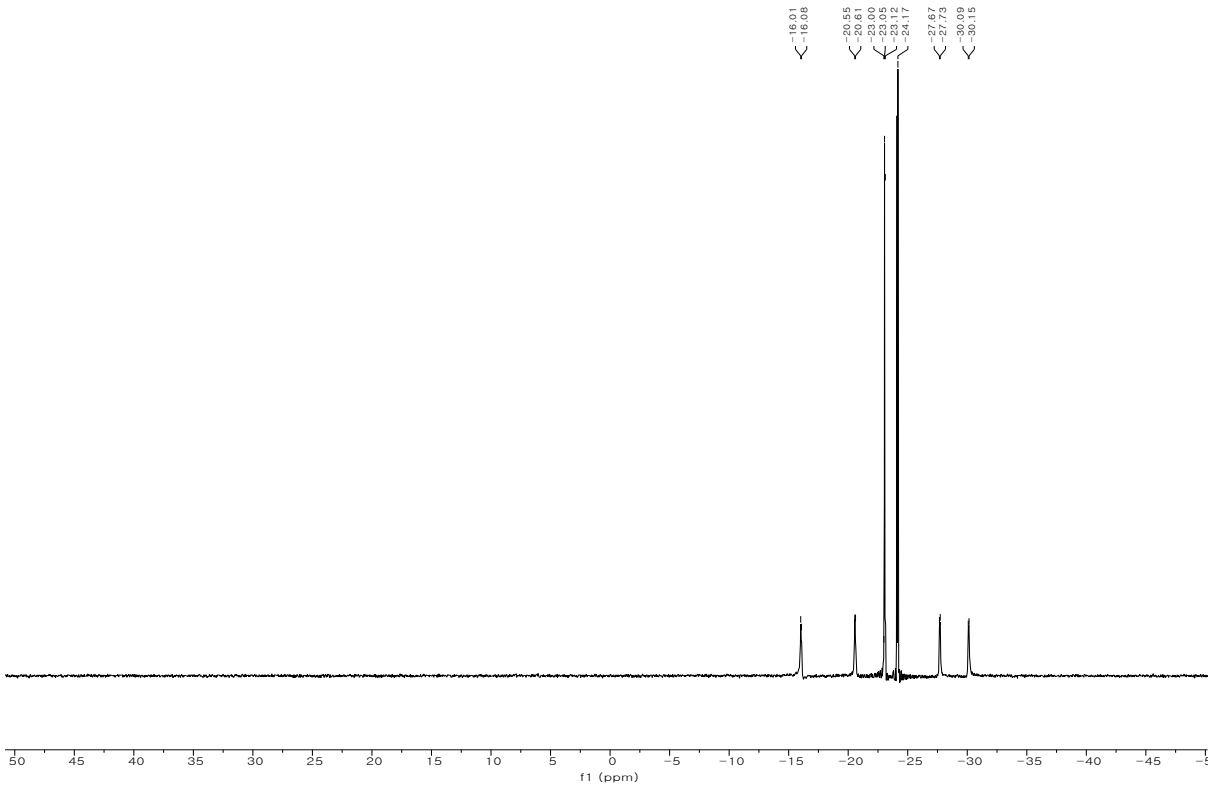
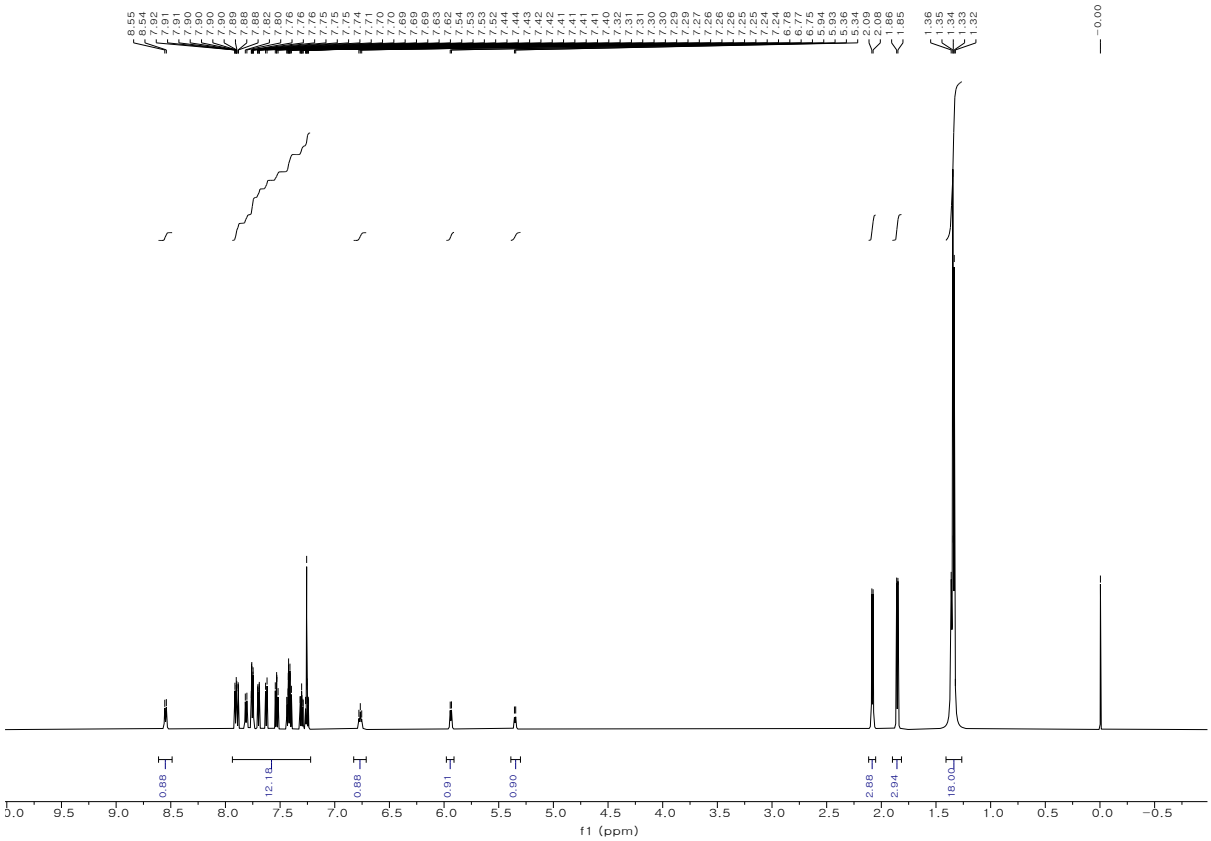
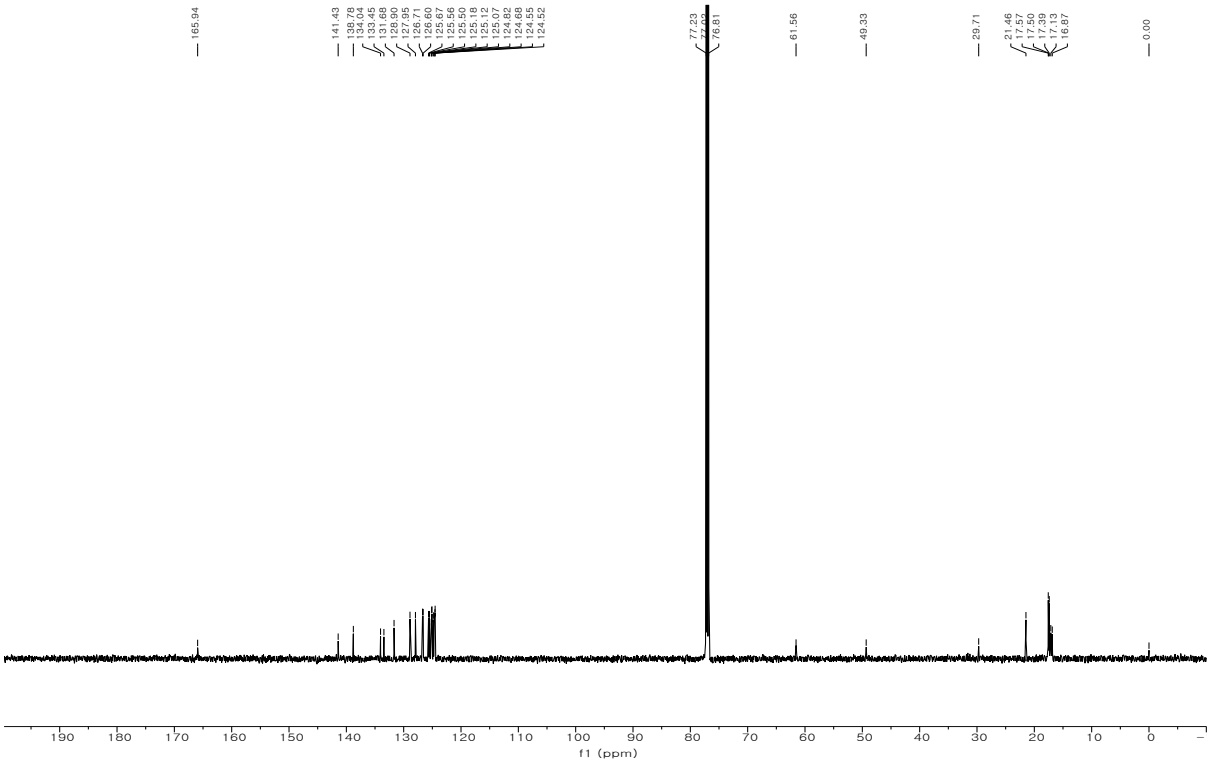

16.01
16.08
20.55
20.61
23.00
23.05
23.12
24.17
27.67
27.73
30.09
30.15
f1 (ppm)

Figure 13S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{–N(R)C(O)N(R)C(O)–}$(PMe_3)_2$] {R =(S)-(+)-1-(1-naphthyl)ethyl}, **13** in $CDCl_3$.




165.94
141.43
138.78
134.04
134.45
131.68
128.90
127.95
126.71
126.60
125.67
125.56
125.50
125.18
125.12
125.07
124.82
124.68
124.55
124.52
77.23
77.02
76.81
61.56
49.33
29.71
21.46
17.57
17.50
17.30
17.13
16.87
0.00
f1 (ppm)

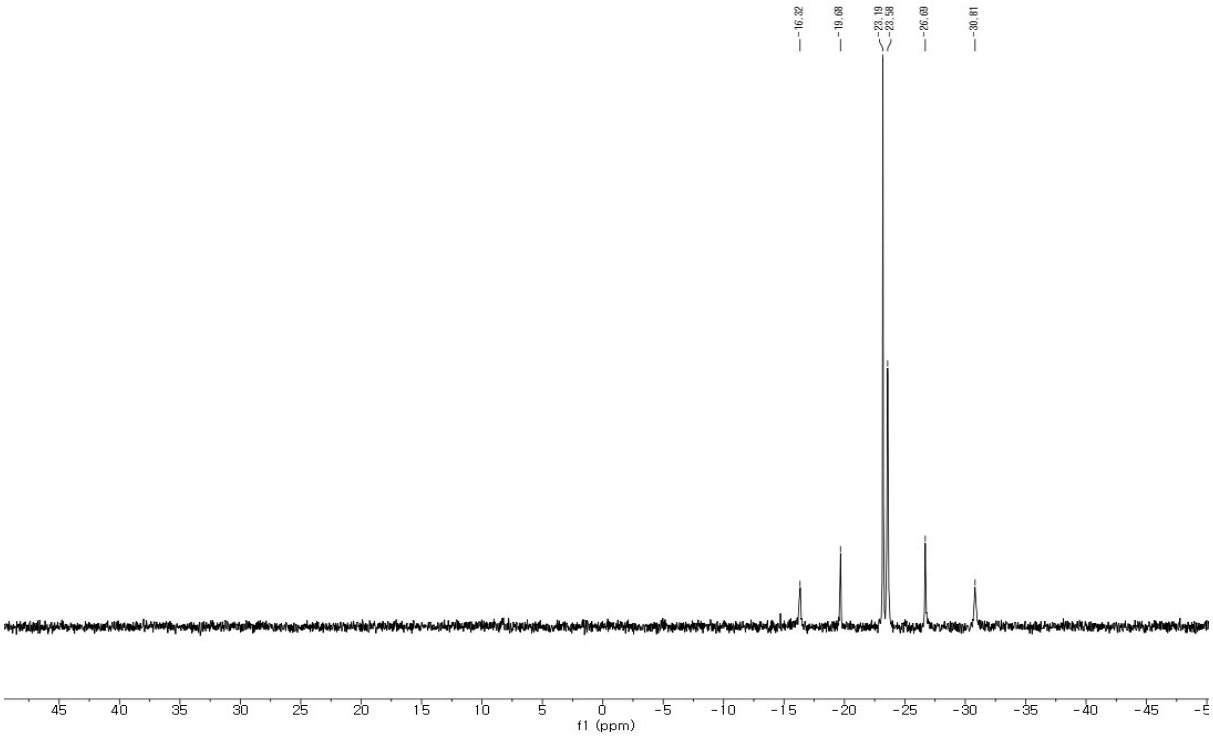
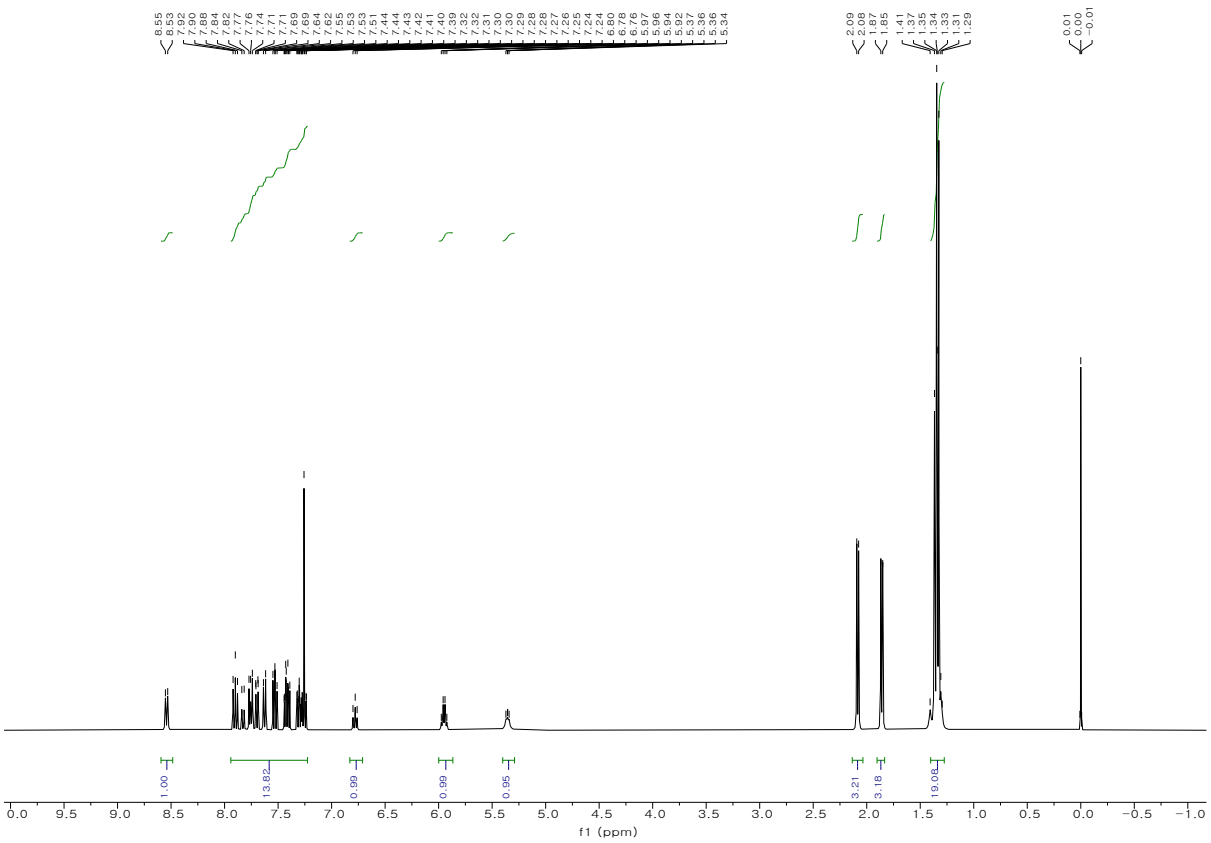
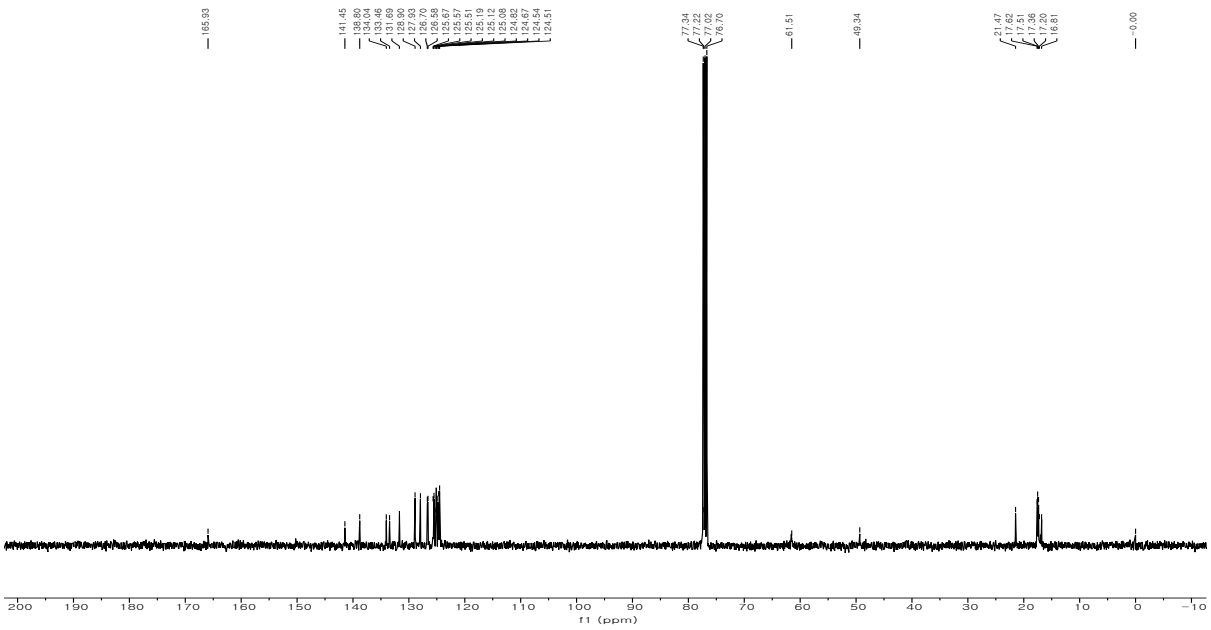

16.32
19.68
23.19
23.36
26.69
30.81
f1 (ppm)

Figure 14S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{N(R)C(O)N(R)C(O)–}$(PMe_3)_2$] {R =(R)-(−)-1-(1-naphthyl)ethyl }, **14** in $CDCl_3$.


f1 (ppm)


f1 (ppm)

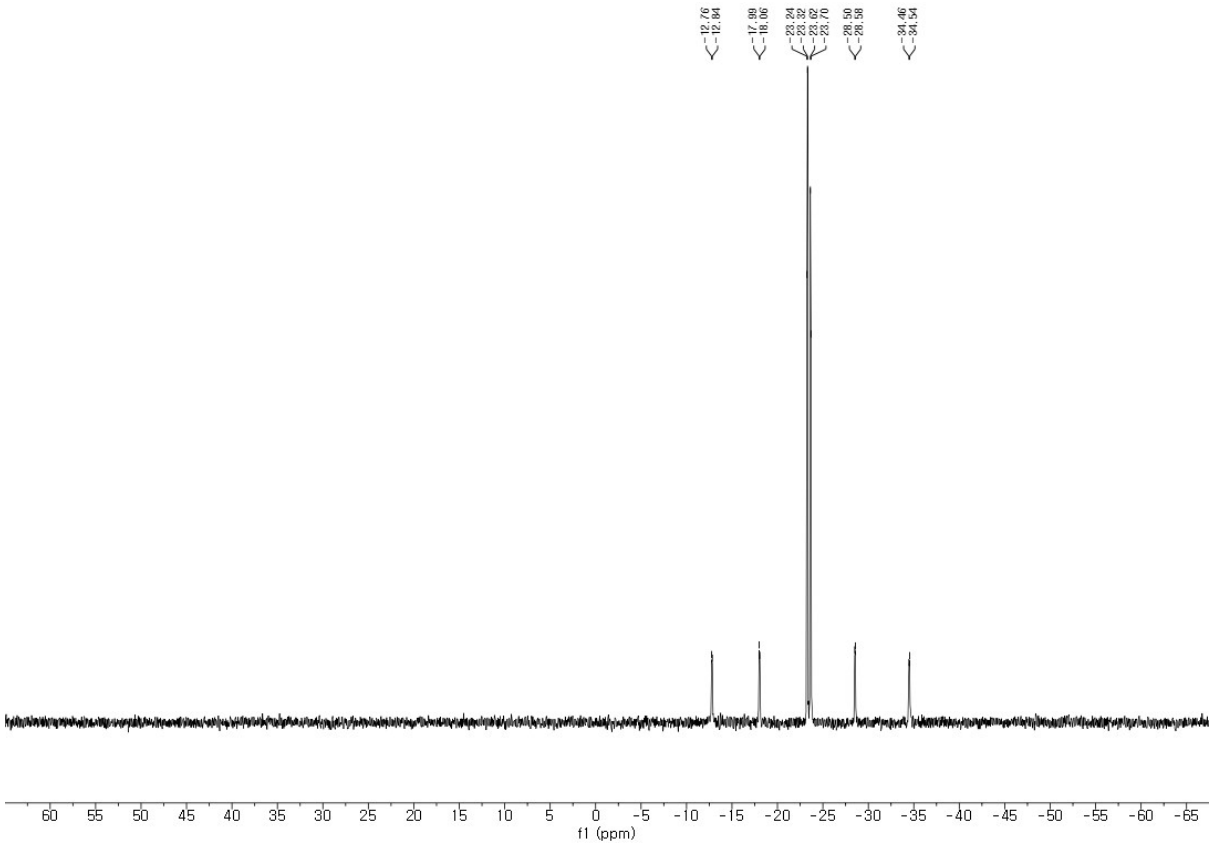
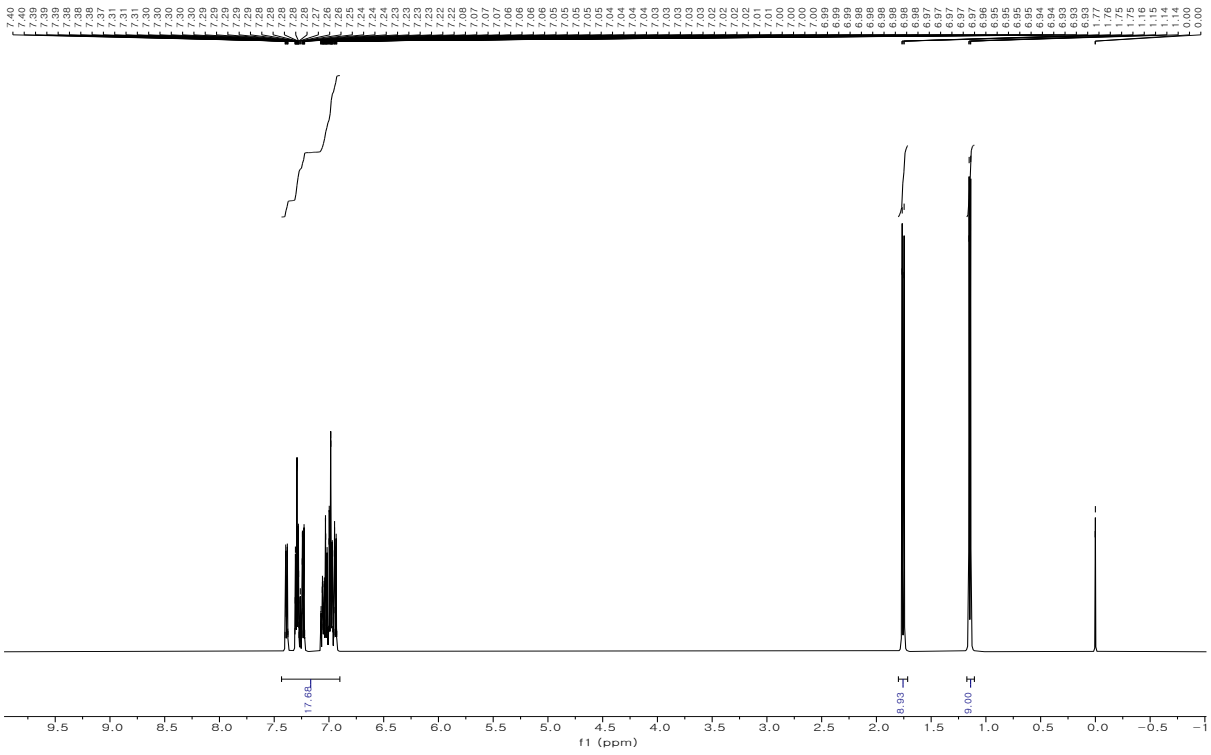
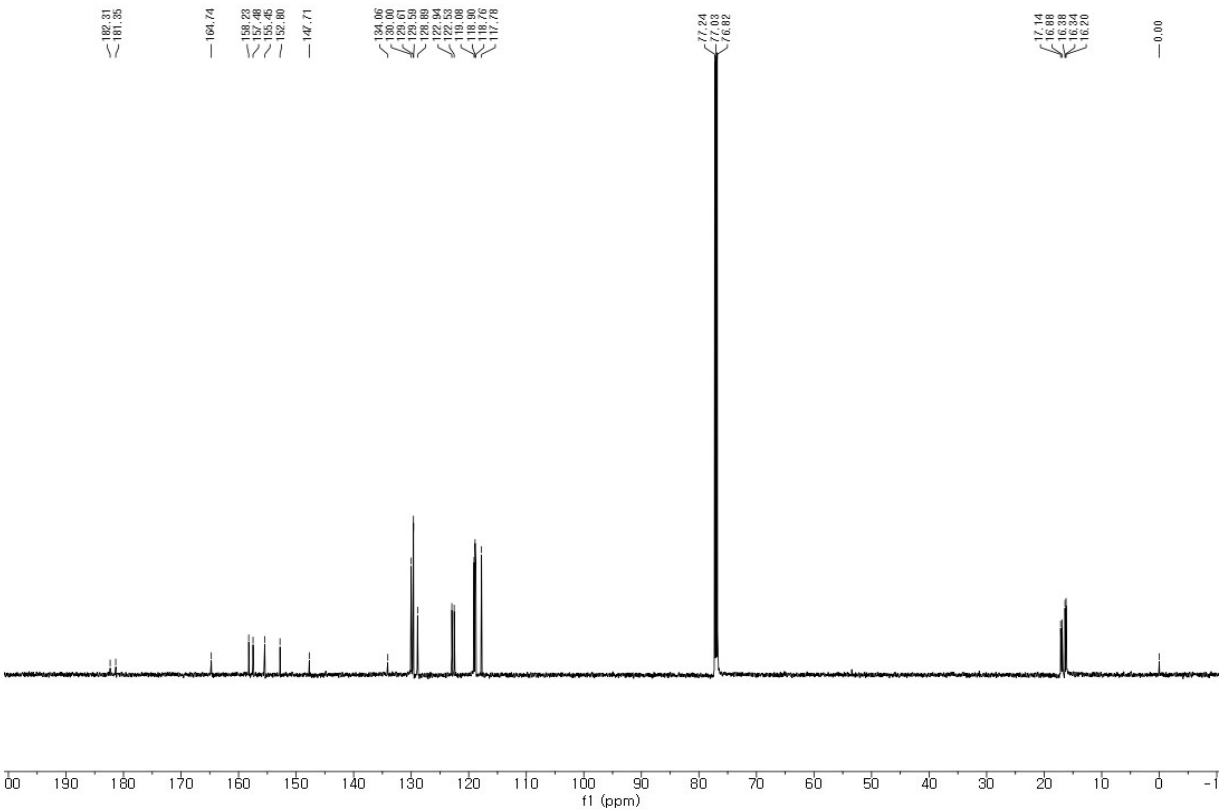

12.76
12.84
17.89
18.06
23.24
23.32
23.62
23.70
28.50
28.58
34.46
34.54
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65
f1 (ppm)

Figure 15S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{–N(R)C(O)N(R)C(O)–}$(PMe_3)_2$] (R = 4-phenoxyphenyl, **15** in $CDCl_3$.





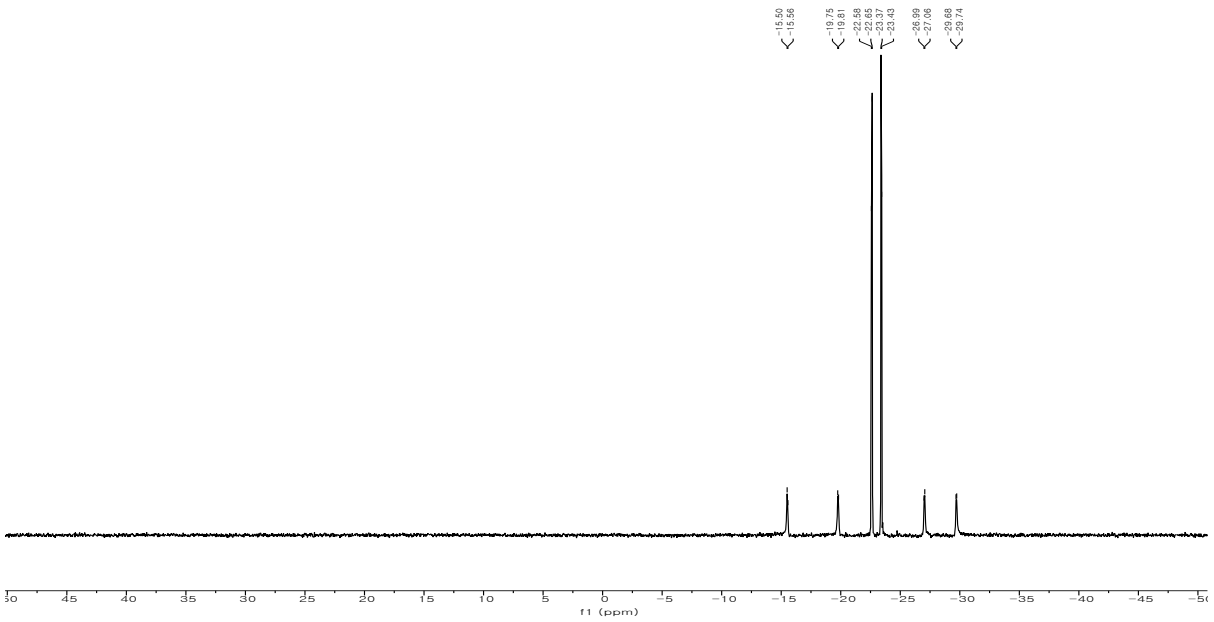
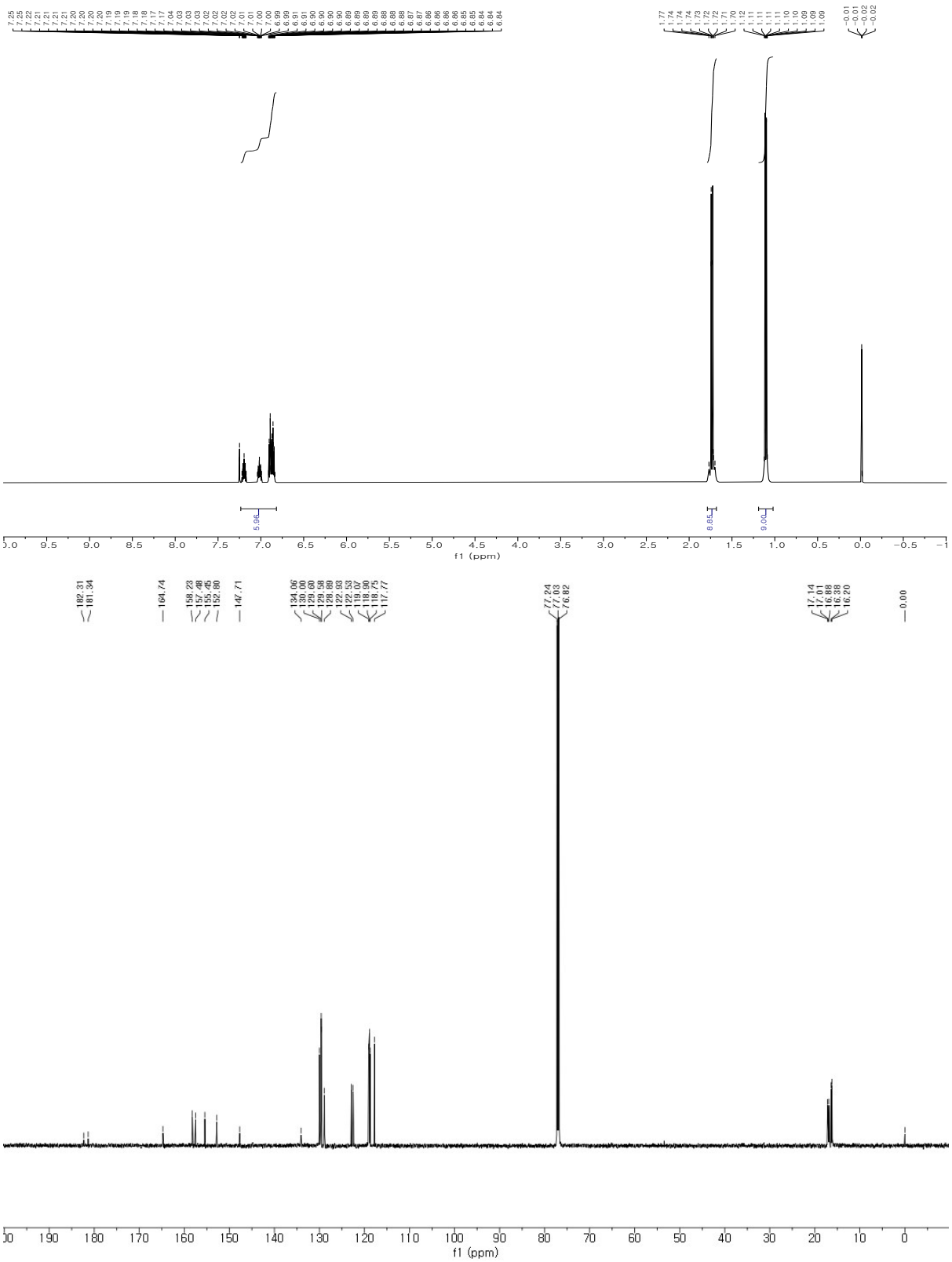

15.50
15.56
19.75
19.81
22.58
22.65
23.37
23.43
26.99
27.06
29.68
29.74
f1 (ppm)

Figure 16S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of *cis*-[Pt{–N(R)C(O)N(R)C(O)–}$(PMe_3)_2$] (R = 2,6-difluorophenyl, **16** in $CDCl_3$.



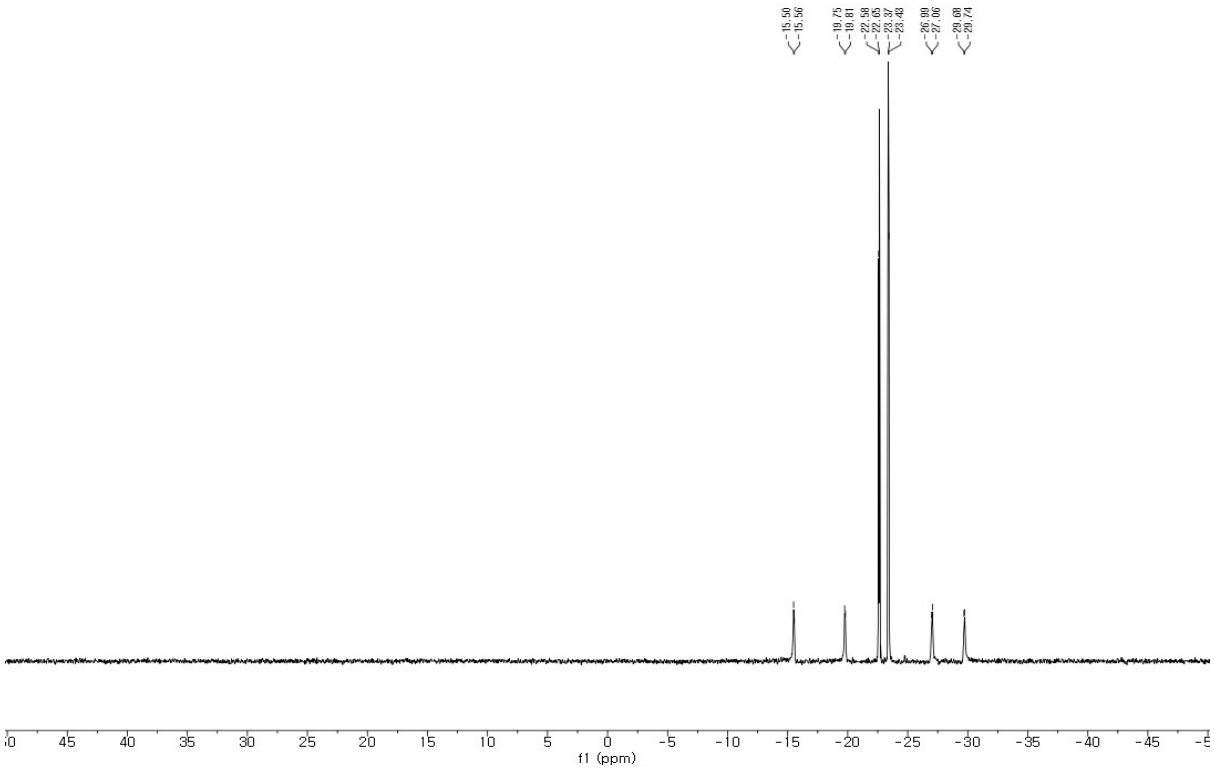
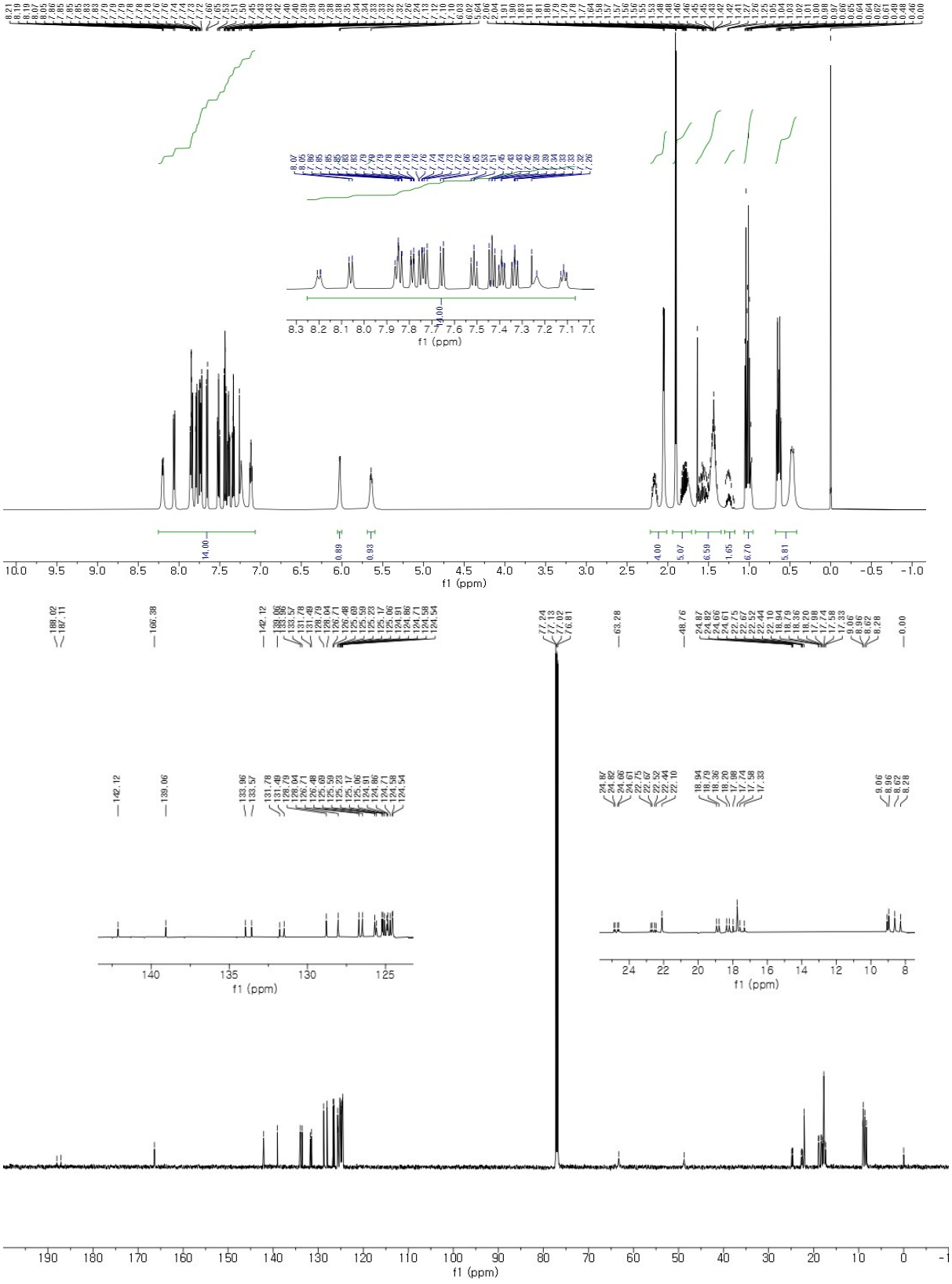

-15.50
-15.56
-19.75
-19.81
-22.38
-22.45
-23.37
-23.43
-26.99
-27.06
-29.68
-29.74
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

Figure 17S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of Pt(DEPE){–N(R)C(O)N(R)C(O)–} {R = (S)-(+)-1-(1-naphthyl)ethyl}, **17** in $CDCl_3$.



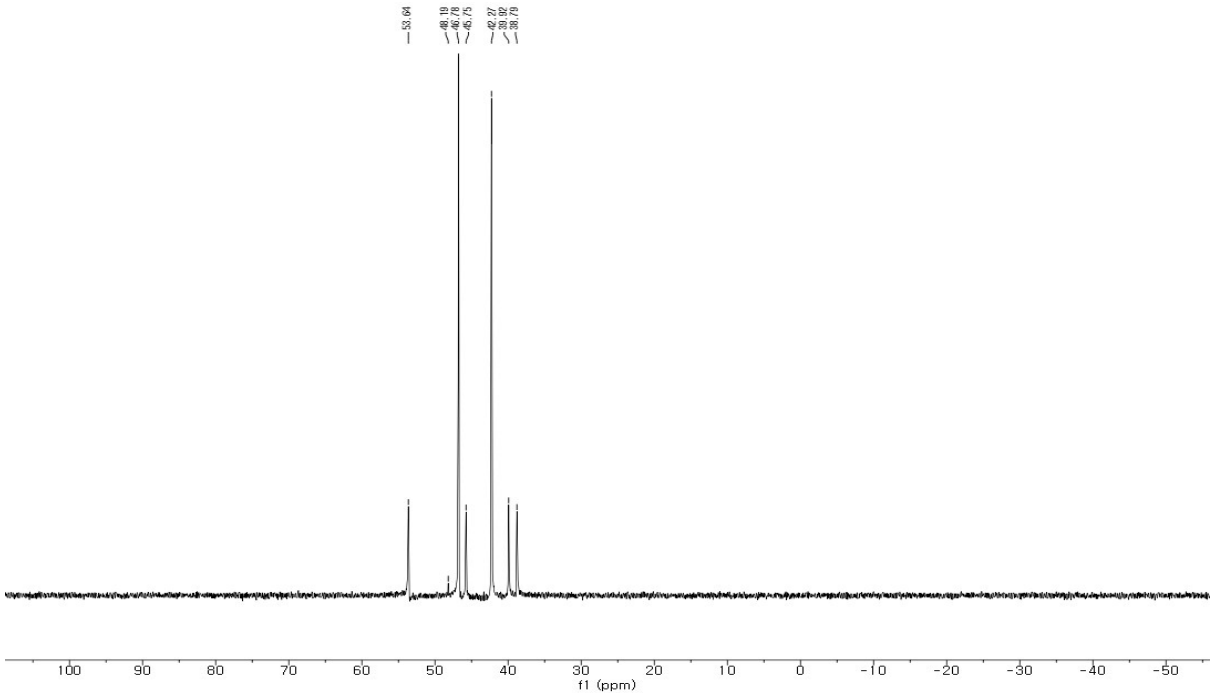
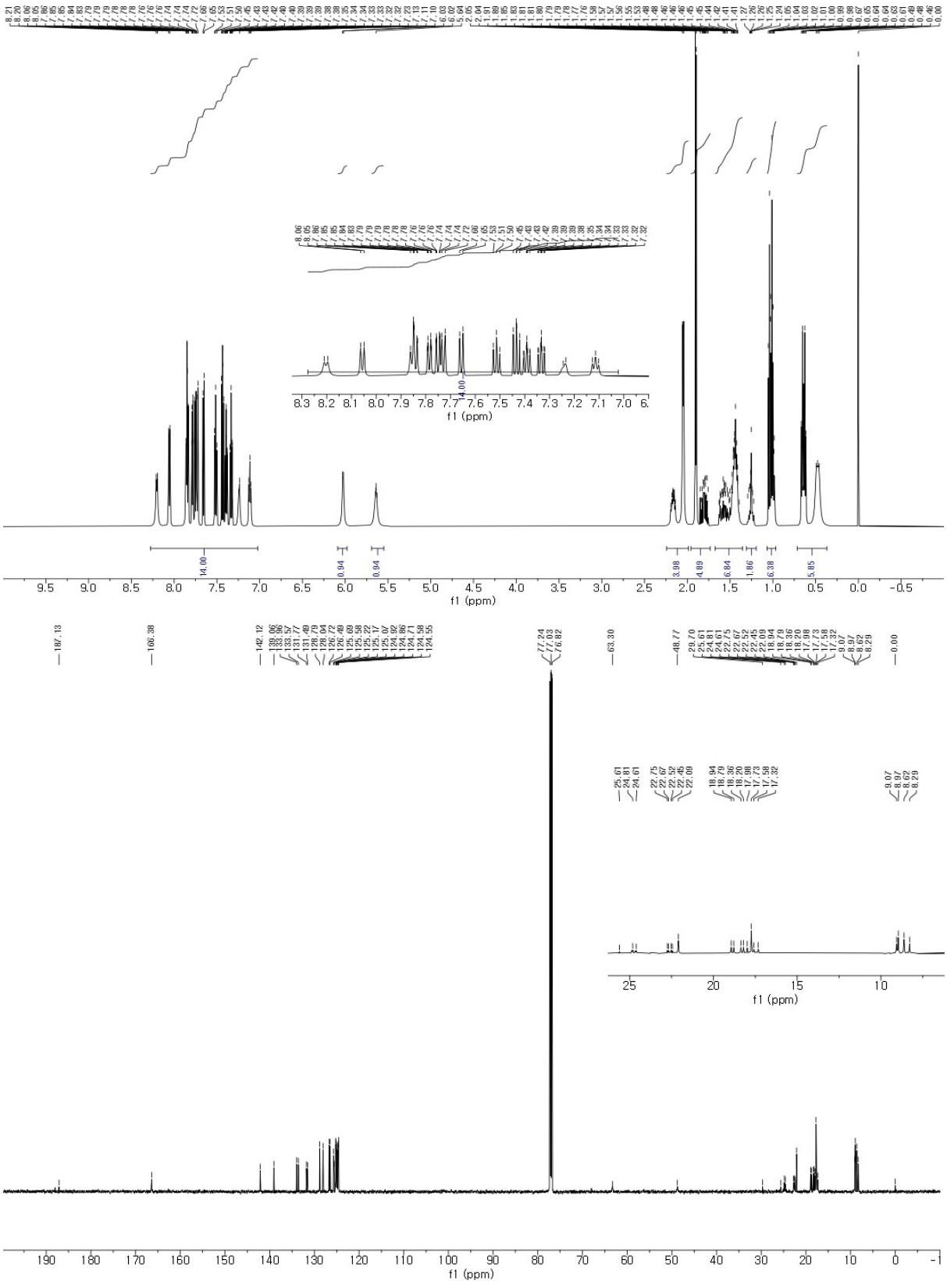

53.64
48.18
46.73
45.75
42.27
39.92
38.79
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

Figure 18S. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR spectra of Pt(DEPE){–N(R)C(O)N(R)C(O)–} {R = (R)-(−)-1-(1-naphthyl)ethyl }, **18** in $CDCl_3$.



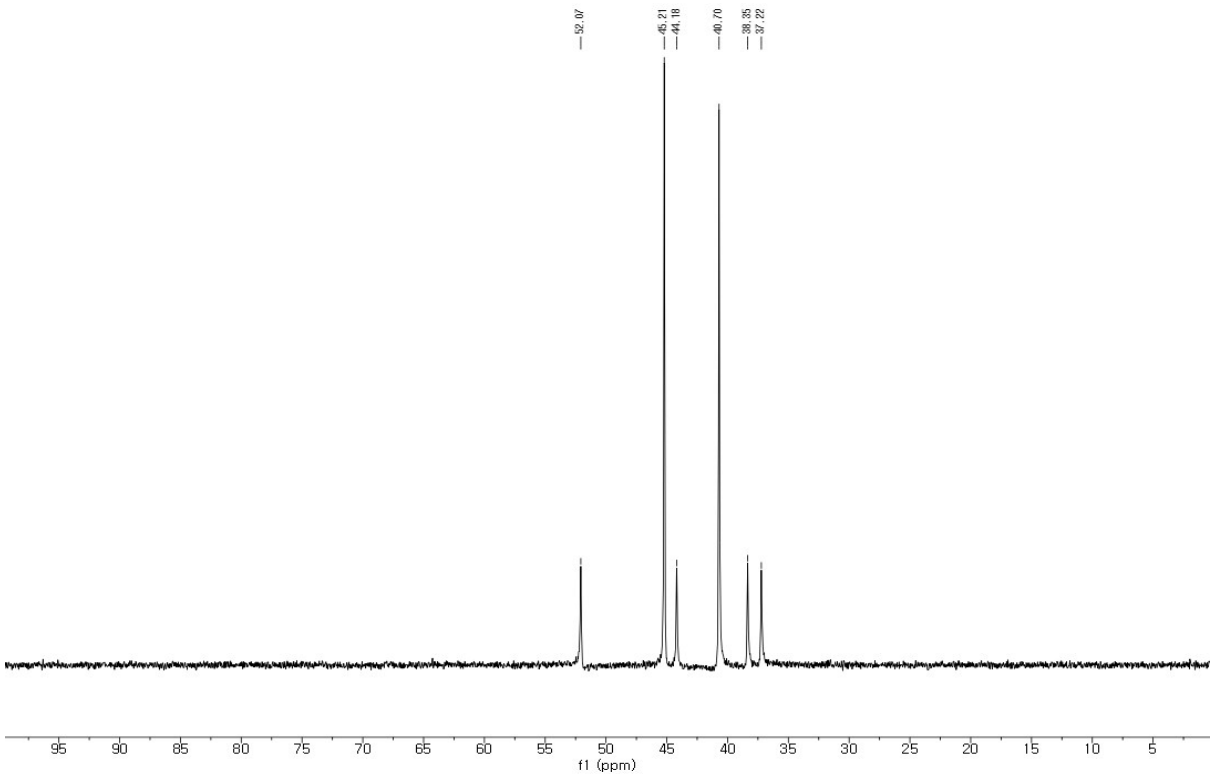

52.07
45.21
44.18
40.70
38.35
37.22
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

Figure 19S. ^{1}H and $^{13}C\{^{1}H\}$ -NMR spectra of [SIPr•Benzyl-NCO], **19** in $CDCl_3$.

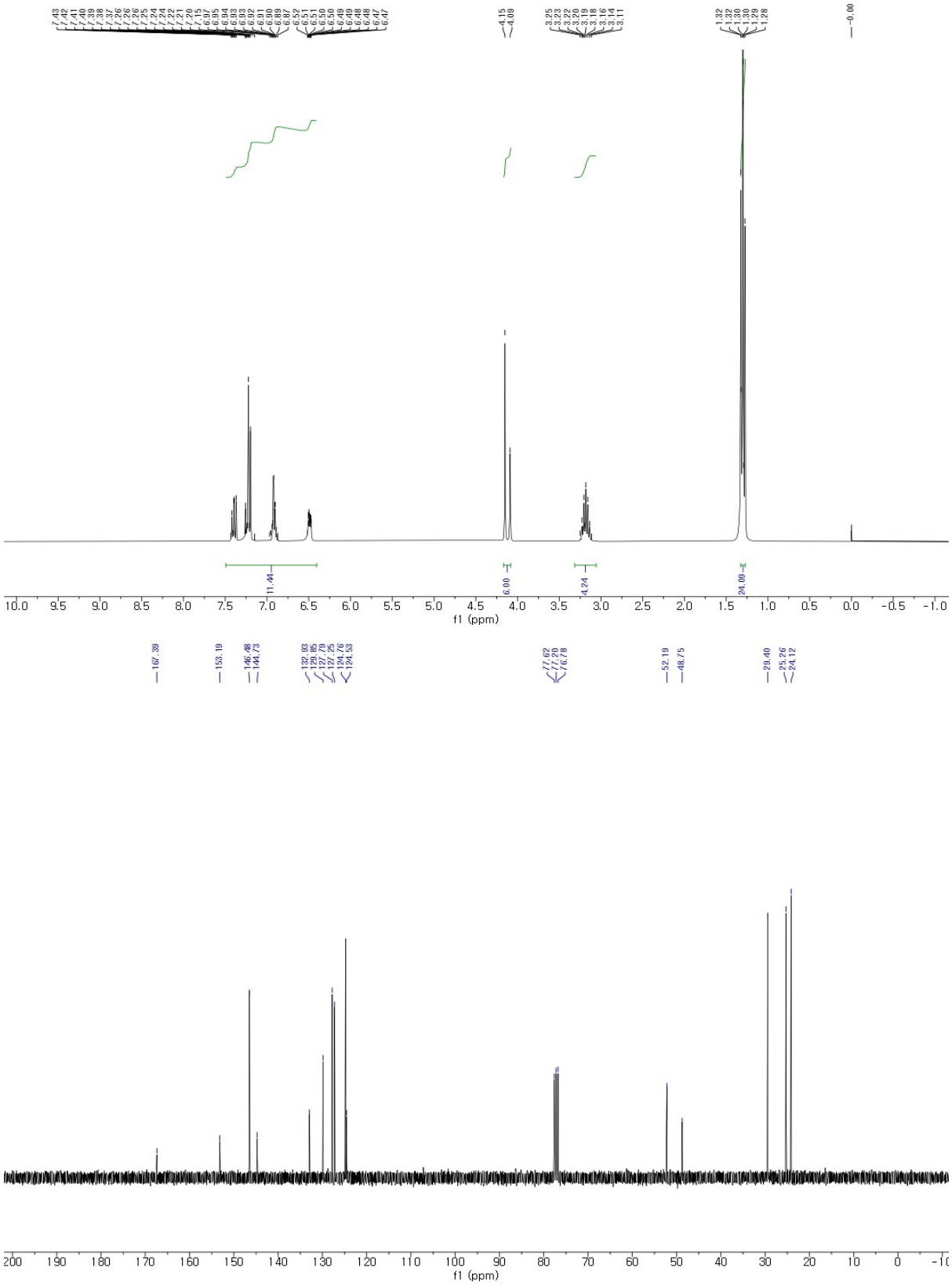


Figure 20S. ^{1}H and $^{13}C\{^{1}H\}$ -NMR spectra of [IPr•Phenyl-NCO], **20** in $CDCl_3$.