Supporting Information

A Dinuclear Palladium Catalyst for α-Hydroxylation of Carbonyls with O_2

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Materials and Methods

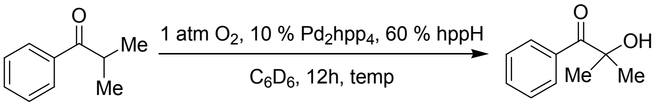
Reactions were carried out under ambient atmosphere unless otherwise specified. Anhydrous solvents were obtained either by filtration through drying columns[1] (ether, CH_2Cl_2) on an mBraun system or by distillation over sodium (ether, pentane). Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds. NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^1H and ^{13}C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. The following solvent chemical shifts were used as reference values (ppm): $CDCl_3$ = 7.26 (^1H), 77.0(^{13}C); CD_2Cl_2 = 5.32 (^1H), 53.8 (^{13}C). Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. UV-VIS spectra were obtained on a Perkin Elmer Lambda 750 UV-visible spectrophotometer. High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers at the Harvard University Mass Spectrometry Facilities. $Pd(OAc)_2$ was purchased from Strem. $^{18}O_2$ was purchased from Cambridge Isotope. Compounds **2**, **4**, **5**, **8** – **11**, and **16** were purchased from Aldrich. Compound **12** was purchased from Alfa Aesar. Compounds **18** – **20** were purchased from TCI. All chemicals were used without purification.

Experimental Data

Effect of temperature on reaction

General procedure: To a solution of Pd_2hpp_4 (**1**) (8 mg, 0.01 mmol, 0.1 equiv) and hppH (**2**) (9 mg, 0.06 mmol, 0.06 equiv) in C_6D_6 (1 mL) at chosen temperature was added 2-methyl-1-phenylpropan-1-one (15 mg, 0.10 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at chosen temperature under 1 atm of oxygen. The conversion of isopropyl phenyl ketone to the corresponding hydroxylated product was measured by ratio of product/SM in ^1H NMR in C_6D_6. Conversion of SM to product is shown as a function of temperature in Table S1.

Table S1. Evaluation of reaction temperature



Temperature	Conversion (vs SM)

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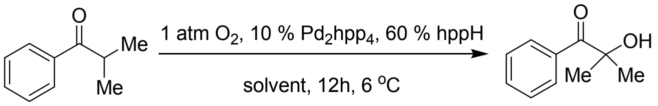
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518

50 °C	0 %
23 °C	60 %
6 °C	80 %
-78 °C	0 %

Effect of solvent on the reaction

General procedure: To a solution of **1** (8 mg, 0.01 mmol, 0.1 equiv) and **2** (9 mg, 0.06 mmol, 0.6 equiv) in chosen solvent (1 mL) at 6 °C was added 2-methyl-1-phenylpropan-1-one (15 mg, 0.10 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo*. The conversion of the reaction was measured by ratio of product/SM in ^{1}H NMR of the crude mixture and is shown as a function of solvent in Table S2.

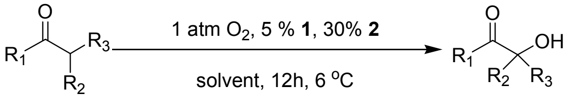
Table S2. Evaluation of solvent in the reaction

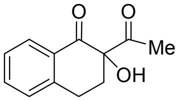
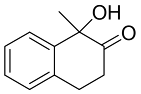
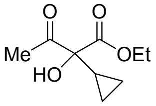
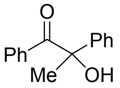
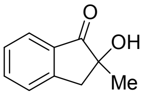
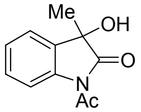
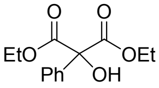
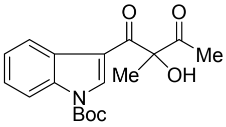
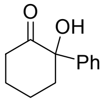


Solvent	Conversion (vs SM)
THF	82 %
toluene	82 %
benzene	60 %
ether	72 %
nitromethane	0 %
acetone	< 5 %
ethyl acetate	68 %
dioxane	53 %
acetonitrile	52 %

THF has been chosen as solvent, but similar results can be obtained with toluene or benzene. Table S3 shows the reaction yields of hydroxylated products for a selection of nine substrates.

Table S3. Hydroxylation in THF, benzene, and toluene



Product	THF	benzene	Product	THF	benzene	toluene
	96%[a,b]	99%[b]		77%[b]	50%[b]	n.d.
	94%[b]	85%[b]		99%	99%	99%
	88%	84%		70%	n.d.	70%
	97%	73%		70%	n.d.	60%
	70%	70%				

[a] 2.5 mol% of 1 was used. [b] no 2 was added

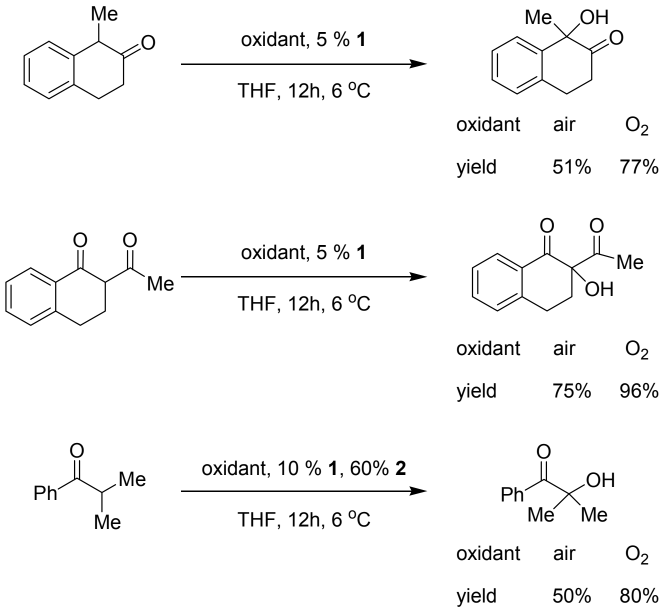
Oxidant O_2 versus air in the reaction

General procedure: Example of Pd_2hpp_4-catalyzed α-hydroxylation of **3** to **4** in air.

To a solution of **1** (38 mg, 0.050 mmol, 0.050 equiv) in THF (10 mL) at 6 °C was added 3,4-dihydro-1-methylnaphthalen-2(1*H*)-one (160 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 20 h at 6 °C under air. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 90 mg of compound **4** as a yellowish oil (51 % yield).

Scheme S1 shows the results of using air and O_2 at 1 atm in the Pd_2hpp_4-catalyzed alpha-hydroxylation reaction. Yields with air as oxidant are 20–30% lower.

Scheme S1. Result of using O_2 versus air in the reaction



Determination of peroxide content in THF

We determined the content of peroxide content in THF after vigorous stirring of THF under 1 atm of O_2 at 6 °C for 12 h by standard iodometric titration using KI and $Na_2S_2O_3$[2]:

Distilled THF (without BHT): 0.003M of peroxide.

THF with BHT: 0.001M of peroxide.

THF with BHT was used in all examples of Pd_2hpp_4-catalyzed hydroxylation reaction. Using pre-aerated (as described previously) THF (without BHT) in the Pd_2hpp_4-catalyzed hydroxylation reaction of 1-methyl-2-tetralone resulted in only trace amounts of product. This result together with the fact that the reaction could be carried out in benzene/toluene, exclude the possibility of THF peroxide being responsible for the oxidation of substrates in the title reaction. It also shows that THF peroxide is not accumulated as a dangerous byproduct during the reaction to significant levels. For large scale applications, we recommend toluene as a suitable substitute solvent.

Comparison of Pd/C to Pd_2hpp_4-catalyzed α-hydroxylation

In reference 9e (Monguchi, Y. *et al. Synlett* **2008**, *15*, 2291), the author reported α-hydroxylation of beta-ketoesters using Pd/C and O_2 with stoichiometric Et_3N as base and reducing reagent. The author proposed that the reaction proceeded through a radical mechanism based on a result shown in Scheme S2. Homocoupling product instead of hydroxylation product was obtained. However,

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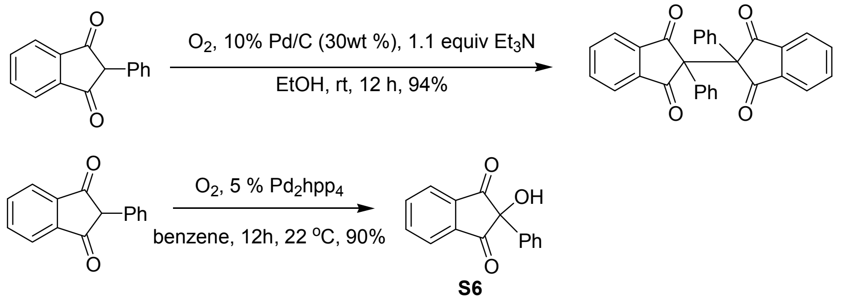
[2] www.basf.com/diols/pdfs/thf_brochure.pdf

with the same substrate using Pd_2hpp_4 as catalyst under our presented reaction conditions, 90% of the hydroxylated product was obtained (Scheme S2).

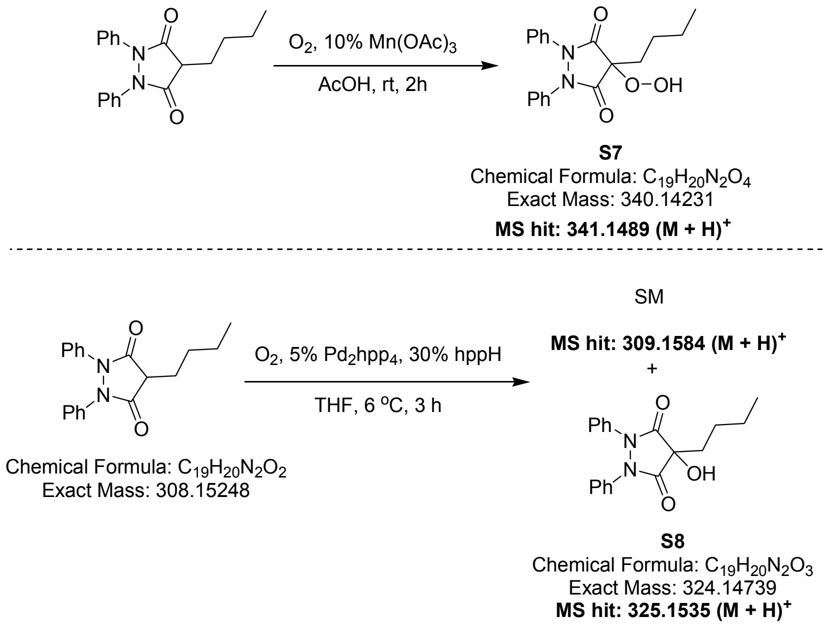
Scheme S2. α-Homo-coupling and α-hydroxylation of 2-phenyl-1,3-indandione



Detection of hydroperoxide in Pd_2hpp_4-catalyzed α-hydroxylation

In the isolation of all products presented in the Pd_2hpp_4-catalyzed α-hydroxylation, no hydroperoxides were detected by mass spectrometry of the products. As shown in the following scheme, we independently prepared a known α-hydroperoxide and compared the massspec of Pd_2hpp_4-catalyzed α-hydroxylation of the same starting compound.[3] No hydroperoxide, or its fragmentation was found in the Pd_2hpp_4-catalyzed reaction mixture.

Scheme S3. Hydroperoxylation and hydroxylation of phenylbutazone



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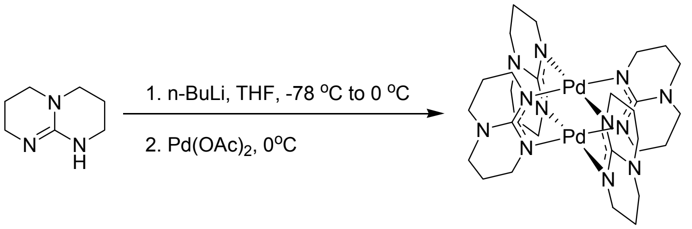
[3] Rahman, M. T.; Nishino, H. *Org. Lett.* **2003**, *5*, 2887.

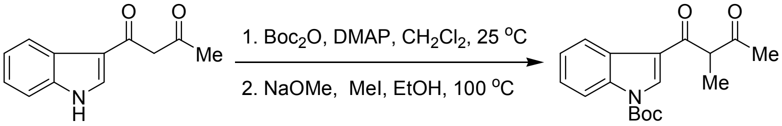
Experimental Procedures and Compound Characterization

Pd_2hpp_4 (1)



To a solution of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (2.78 g, 20.0 mmol, 1.00 equiv) in dry and degassed THF (200 ml) was added 2.5 M n-BuLi (8.8 mL, 22 mmol, 1.1 equiv) at -78 °C. The resulting mixture was warmed to 0 °C and was stirred for 3 h at 0 °C. $Pd(OAc)_2$ (2.25 g, 10.0 mmol, 0.50 equiv) was added to the reaction. The reaction mixture was heated to boiling and filtered. Solvent was removed *in vacuo* and the residue was dissolved in benzene (100mL). Red crystals (2.50 g, 3.26 mmol, 65 %) of **1** were obtained by vapor diffusion of hexanes into the benzene solution. NMR Spectroscopy: ^{1}H NMR (500 MHz, C_6D_6 25 ºC, δ): 3.73 (t, *J* = 7.5 Hz, 16 H), 2.70 (t, *J* = 7.5 Hz, 16 H), 1.74 (pentet, *J* = 7.5 Hz, 16 H).[4]

tert-Butyl 3-(2-methyl-3-oxobutanoyl)-1*H*-indole-1-carboxylate (S1)



To a solution of 1-(1H-indol-3-yl)butane-1,3-dione (2.00 g, 9.93 mmol, 1.00 equiv) and DMAP (40 mg, 0.33 mmol, 0.33 equiv) in dry CH_2Cl_2 (25 ml) was added di-tert-butyl dicarbonate (2.17 g, 9.93 mmol, 1.00 equiv). The resulting mixture was stirred at 0 °C for 1 h and warmed to 25 °C for 12 h. Solvent was removed *in vacuo* and the residue was triturated with ether (2 x 25 ml) to afford 2.50 g of the NBoc- protected indole product as a yellow solid (84 % yield). The latter was used in the next step without further purification.

To a solution of the NBoc- protected indole product (500 mg, 1.74 mmol, 1.00 equiv) obtained from previous step in dry EtOH (8 ml) at 0 °C was added NaOMe (142 mg, 2.62 mmol, 1.50 equiv). The orange colored reaction mixture was stirred for 20 min at 0 °C and MeI (247 mg, 1.74 mmol, 1.00 equiv) was added. The reaction was heated to reflux (100 °C) for 18 h, and then additional MeI (296 mg, 2.09 mmol, 1.20 equiv) was added. The reaction was heated at 100 °C for 10 h, cooled to 25 °C, and quenched with 10 mL of sat. NH_4Cl(aq). The aqueous layer was

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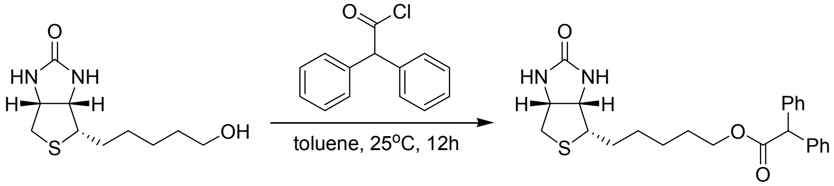
[4] Cotton, F. A.; Gu, J.; Murillo, C. A.; Timmons, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 13280.

extracted with EtOAc (3 x 10 ml) and the combined organic phases were dried with Na_2SO_4. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (10:1) to afford 300 mg of **S1** as a light yellow solid (55 % yield).

R_f = 0.30 (hexanes : EtOAc = 10 : 1). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.38 (d, *J* = 7.5 Hz, 1 H), 8.33 (s, 1H), 8.13 (d, *J* = 7.5 Hz, 1 H), 7.41–7.35 (m, 2 H), 4.28 (q, *J* = 7 Hz, 1 H), 2.19 (s, 3 H), 1.72 (s, 9 H), 1.49 (d, *J* = 7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 205.14(C), 192.60(C), 148.87(C), 135.57(C), 133.08(CH), 127.37(C), 125.83(CH), 124.62(CH), 122.67(CH), 119.37(C), 115.00(C), 85.74(C), 58.95(CH), 28.06(C), 27.43(CH_3), 13.69(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{18}H_{21}NO_4$ + H], 316.1543. Found, 316.1547.

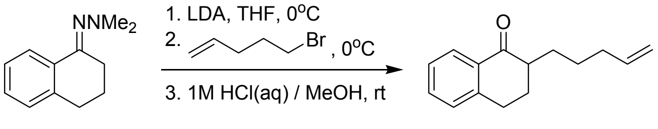
5-((3a*R*,6*S*,6a*S*)-Hexahydro-2-oxo-1*H*-thieno[3,4-d]imidazol-6-yl)pentyl 2,2-diphenylacetate (S2)



To diphenylacetic acid (507 mg, 2.39 mmol, 1.10 equiv) in a 25 mL flame-dried round bottom flask was added $SOCl_2$ (10 mL) at 0 °C. The reaction mixture was heated at reflux for 2 h. $SOCl_2$ was removed by distillation at 60 mbar. The resulting acyl chloride was dissolved in dry toluene (10 mL) and added via syringe to a vigorously stirring suspension of (3aR,6S,6aS)-tetrahydro-6-(5-hydroxypentyl)-1*H*-thieno[3,4-d]imidazol-2(3*H*)-one (500 mg, 2.17 mmol, 1.00 equiv) in toluene (20 mL) at 23 °C and stirred for 12 h. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (10:1) to afford 650 mg of compound **S2** as a light yellow solid (71 % yield).

R_f = 0.30 (CH_2Cl_2 : MeOH = 10 : 1). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.25–7.22 (m, 10 H), 5.36 (s, 1H), 5.06 (s, 1 H), 5.02 (s, 1 H), 4.47 (dd, *J* = 7.5 Hz, 5.0 Hz, 1 H), 4.24 (dd, *J* = 7.5 Hz, 5.0 Hz, 1 H), 4.15 (t, *J* = 6.5 Hz, 2 H), 3.09 (dd, *J* = 1.0 Hz, *J* = 0.5 Hz, 1 H), 2.89 (dd, *J* = 1.5 Hz, *J* = 0.5 Hz, 1 H), 2.70 (d, *J* = 1.0 Hz, 1 H), 1.67–1.54 (m, 4 H), 1.42–1.25 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 172.55(C), 163.87(C), 138.66(C), 128.54(CH), 128.48(CH), 127.15(CH), 65.11(CH_2), 61.86(CH), 60.04(CH), 57.09(CH), 55.49(CH), 40.46(CH_2), 28.39(CH_2), 28.35(CH_2), 28.15(CH_2), 25.63(CH_2). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{24}H_{28}N_2O_3S$ + Na], 447.1713. Found, 447.1713.

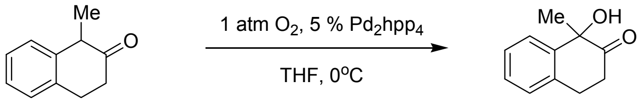
3,4-dihydro-2-(pent-4-enyl)naphthalen-1(2*H*)-one (S10)



To a solution of diisopropylamine (7.9 mL, 11 mmol, 1.1 equiv) in dry THF (25 ml) at -78°C was added 1.6 M n-Butyl lithium (6.9 mL, 11 mmol, 1.1 equiv). The mixture was warmed to at 0 °C and stirred at 0 °C for 1 h. 1-(2,3-dihydronaphthalen-4(1*H*)-ylidene)-2,2-dimethylhydrazine (1.8 g, 10 mmol, 1.0 equiv) was added to the reaction and the mixture was stirred at 0 °C for 1 h. 5-bromo-1-pentene was added to the reaction and the mixture was stirred at 0 °C for 12 h. The reaction mixture was quenched with 30 mL of sat. NH_4Cl(aq). The aqueous layer was extracted with EtOAc (3 × 30 ml) and the combined organic phases were dried with Na_2SO_4. Solvent was removed *in vacuo.* The residue was dissolved in 40 mL MeOH. 30 mL of 1 M HCl (aq) was added and the mixture was stirred at 23 °C for 12 h. MeOH was removed *in vacuo.* The residue aqueous mixture was extracted with EtOAc (3 × 30 ml) and the combined organic phases were dried with Na_2SO_4. The residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (12:1) to afford 1850 mg of **S1** as a light yellow oil (86 % yield).

R_f = 0.50 (hexanes : EtOAc = 12 : 1). ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.03 (d, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.29 (t, *J* = 7.5 Hz, 1 H), 7.22 (d, *J* = 7.5 Hz, 1 H), 5.83 (ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 6.5 Hz, 1 H), 5.02 (dd, *J* = 17 Hz, *J* = 1.5 Hz, 1 H), 4.95 (d, *J* = 10 Hz, 1 H), 3.03–2.97 (m, 2 H), 2.50–2.45 (m, 1 H), 2.62–2.21 (m, 1 H), 2.13–2.08 (m, 2 H), 1.99–1.86 (m, 2 H), 1.57–1.46 (m, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 199.23(C), 143.39(C), 138.08(CH), 132.54(CH), 132.06(C), 128.21(CH), 126.85(CH), 126.00(CH), 114.15(CH_2), 46.88(CH), 33.47(CH_2), 28.58 (CH_2), 27.96(CH_2), 27.88(CH_2), 25.87(CH_2). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{15}H_{18}O$ + H], 215.1430. Found, 215.1436.

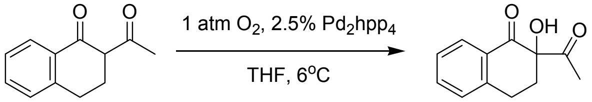
3,4-Dihydro-1-hydroxy-1-methylnaphthalen-2(1*H*)-one (4)



To a solution of Pd_2hpp_4 (38 mg, 0.050 mmol, 0.050 equiv) in THF (10 mL) at 0 °C was added 3,4-dihydro-1-methylnaphthalen-2(1*H*)-one (160 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 20 h at 0 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 135 mg of compound **4** as a yellowish oil (77 % yield).

R_f = 0.35 (EtOAc : hexanes = 1 : 4). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.66 (dd, *J* = 7.5 Hz, *J* = 1 Hz, 1 H), 7.34–7.31 (m, 1 H), 7.27–7.24 (m, 1 H), 7.17 (d, *J* = 8.5 Hz, 1 H), 3.93 (s, 1 H), 3,31 (ddd, *J* = 9 Hz, *J* = 9 Hz, *J* = 9 Hz, 1H), 3.09 (ddd, *J* = 16.5 Hz, *J* = 9 Hz, *J* = 4 Hz, 1H), 2.96 (ddd, *J* = 16.5 Hz, *J* = 9 Hz, *J* = 4 Hz, 1H), 2.65 (ddd, *J* = 9 Hz, *J* = 9 Hz, *J* = 8 Hz, 1H), 1.56 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 212.95(C), 140.75(C), 133.70(C), 127.66(CH), 127.60(CH), 127.49(CH), 125.27(CH), 76.04(C), 33.43(CH_2), 27.79(CH_2), 27.68(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{11}H_{12}O_2$ + Na], 199.0730. Found, 199.0724.

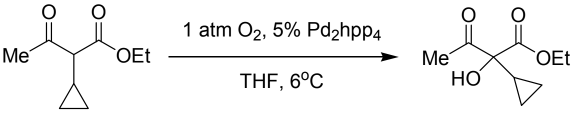
2-Acetyl-3,4-dihydro-2-hydroxynaphthalen-1(2*H*)-one (5)



To a solution of Pd$_2$hpp$_4$ (10 mg, 0.013 mmol, 0.025 equiv) in THF (5 mL) at 6 °C was added 2-acetyl-3,4-dihydronaphthalen-1(2*H*)-one (94 mg, 0.50 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (2:1) to afford 98 mg of compound **5** as a white solid (96 % yield).

R$_f$ = 0.30 (EtOAc : hexanes = 1 : 2). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$ 25 ºC, δ): 8.02 (d, *J* = 7 Hz, 1 H), 7.53 (t, *J* = 7 Hz, 1 H), 7.33 (t, *J* = 7 Hz, 1 H), 4.64 (s, 1 H), 3.12 (m, 2 H), 2.60 (td, *J* = 5 Hz, *J* = 14 Hz, 1 H), 2.28 (s, 3 H), 2.22–2.16 (m, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC, δ): 206.85(C), 196.55(C), 144.15(C), 134.46(CH), 130.39(C), 128.92(CH), 127.76(CH), 126.87(CH), 81.73(C), 32.28(CH$_2$), 25.47(CH$_2$), 24.99(CH$_3$). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [C$_{12}$H$_{12}$O$_3$ + Na], 227.0679. Found, 227.0673.

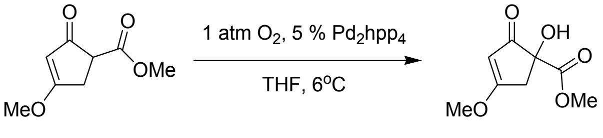
Ethyl 2-cyclopropyl-2-hydroxy-3-oxobutanoate (6)



To a solution of Pd$_2$hpp$_4$ (19 mg, 0.025 mmol, 0.05 equiv) in THF (4 mL) at 6 °C was added ethyl 2-cyclopropyl-3-oxobutanoate (85 mg, 0.50 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (6:1) to afford 87 mg of compound **6** as a colorless oil (94 % yield).

R$_f$ = 0.25 (EtOAc : hexanes = 1 : 6) NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$ 25 ºC, δ): 4.28 (qd, *J* = 7 Hz, *J* = 1 Hz, 2 H), 3.88 (s, 1 H), 1.65–1.59 (m, 1 H), 1.31 (t, *J* = 7 Hz, 3 H), 0.64–0.60 (m, 1 H), 0.50–0.39 (m, 2 H), 0.37–0.32 (m, 1 H),. ^{13}C NMR (125 MHz, CDCl$_3$, 25 ºC, δ): 204.72(C), 171.07(C), 81.11(C), 62.41(CH$_2$), 24.51(CH$_3$), 14.45(CH), 13.97(CH$_2$), 0.17(CH$_2$), -0.35(CH$_2$). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [C$_9$H$_{14}$O$_4$ + Na], 209.0784. Found, 209.0786.

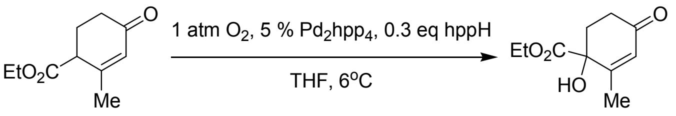
Methyl 1-hydroxy-4-methoxy-2-oxocyclopent-3-enecarboxylate (7)



To a solution of Pd$_2$hpp$_4$ (19 mg, 0.010 mmol, 0.050 equiv) in THF (2 mL) at 6 °C was added methyl 4-methoxy-2-oxocyclopent-3-enecarboxylate (35 mg, 0.20 mmol, 1.0 equiv) and the reaction was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (1:1) to afford 36 mg of compound **7** as a white solid (97 % yield).

R$_f$ = 0.20 (EtOAc : hexanes = 1 : 1) NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$ 25 °C, δ): 5.34 (s, 1H), 3.94 (s, 3 H), 3.80 (s, 3 H), 3.18 (d, J = 17.5 Hz, 1 H), 2.75 (d, J = 17.5 Hz, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, δ): 199.40(C), 189.94(C), 171.47(C), 101.01(CH), 79.01(C), 59.15(CH$_3$), 53.40(CH$_3$), 40.52(CH$_2$). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_8H_{10}O_5$ + H], 187.0601. Found, 187.0603.

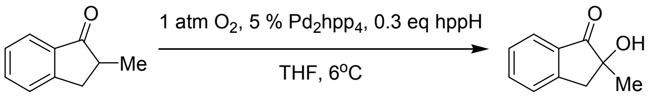
Ethyl 1-hydroxy-2-methyl-4-oxocyclohex-2-enecarboxylate (8)



To a solution of Pd$_2$hpp$_4$ (16 mg, 0.020 mmol, 0.050 equiv) in THF (4 mL) at 6 °C was added ethyl 2-methyl-4-oxocyclohex-2-enecarboxylate (73 mg, 0.40 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (1:1) to afford 72 mg of compound **8** as a pale yellow oil (90 % yield).

R$_f$ = 0.20 (EtOAc : hexanes = 1 : 1). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$ 25 °C, δ): 4.37–4.32 (m, 2 H), 3.77 (s, 1 H), 2.65–2.61 (m, 2 H), 2.41–2.36 (m, 1 H), 2.25–2.20 (m, 1 H), 1.91 (s, 3 H), 1.33 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, δ): 197.90(C), 174.18(C), 157.35(C), 129.17(CH), 73.92(C), 63.02(CH$_2$), 33.81(CH$_2$), 33.61(CH$_2$), 18.57(CH$_3$), 13.97(CH$_3$). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{10}H_{14}O_4$ – OCH_2CH_3], 153.0552. Found, 153.0545.

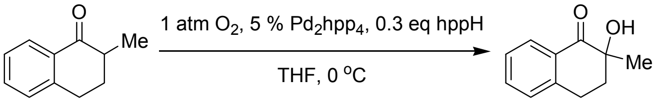
2,3-Dihydro-2-hydroxy-2-methylinden-1-one (9)



To a solution of Pd$_2$hpp$_4$ (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in THF (2 mL) at 6 °C was added 2,3-dihydro-2-methylinden-1-one (73 mg, 0.50 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (3:1) to afford 71 mg of compound **9** as a colorless oil (88 % yield).

R$_f$ = 0.25 (EtOAc : hexanes = 1 : 3). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$ 25 °C, δ): 7.79 (d, J = 8 Hz, 1 H), 7.64 (t, J = 8 Hz, 1 H), 7.45–7.29 (m, 2 H), 3.25 (ABq, $\Delta\nu_{AB}$ = 19 Hz, J_{AB} = 17 Hz, 2 H), 2.57 (s, 1 H), 1.45 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, δ): 208.05(C), 151.15(C), 135.78(CH), 133.49(C), 127.81(CH), 126.70(CH), 124.86(CH), 77.36(C), 42.19(CH_2), 25.56(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{10}H_{10}O_2$ + Na], 185.0573. Found, 185.0540.

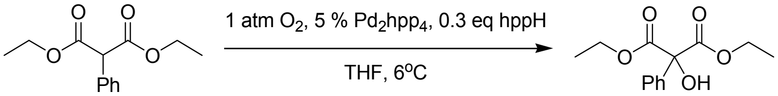
3,4-Dihydro-2-hydroxy-2-methylnaphthalen-1(2*H*)-one (10)



To a solution of Pd_2hpp_4 (38 mg, 0.050 mmol, 0.050 equiv) and hppH (42 mg, 0.30 mmol, 0.30 equiv) in THF (10 mL) at 0 °C was added 3,4-dihydro-2-methylnaphthalen-1(2*H*)-one (160 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 12 h at 0 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 160 mg of compound **10** as a white solid (91 % yield).

R_f = 0.30 (EtOAc : hexanes = 1 : 4). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.03 (d, *J* = 7.5 Hz, 1 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 1 H), 7.26 (d, *J* = 7.5 Hz, 1 H), 3.85 (s, 1 H), 3.14–3.00 (m, 2 H), 2.86–2.16 (m, 2 H), 1.39 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 201.52(C), 143.24(C), 133.86(CH), 129.79(C), 128.83(CH), 127.82(CH), 126.68(CH), 73.41(C), 35.73(CH_2), 26.62(CH_2), 23.70(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{11}H_{12}O_2$ + Na], 199.0730. Found, 199.0727.

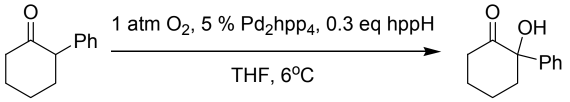
Diethyl 2-hydroxy-2-phenylmalonate (11)



To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in THF (1.5 mL) at 6 °C was added diethyl 2-phenylmalonate (47 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (5:1) to afford 49 mg of compound **11** as a white solid (97 % yield).

R_f = 0.25 (EtOAc : hexanes = 1 : 5). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.66–7.64 (m, 2 H), 7.39–7.34 (m, 3 H), 4.36–4.25 (m, 5 H), 1.29 (t, *J* = 8.5 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 169.85(C), 135.90(C), 128.55(CH), 127.93(CH), 126.60(CH), 79.94(C), 62.94(CH_2), 13.89(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_{16}O_5$ + Na], 275.0890. Found, 275.0893.

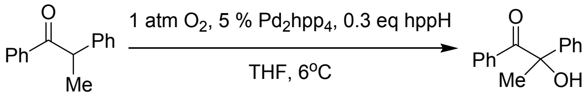
2-Hydroxy-2-phenylcyclohexanone (12)



To a solution of Pd_2hpp_4 (38 mg, 0.050 mmol, 0.050 equiv) and hppH (42 mg, 0.30 mmol, 0.30 equiv) in THF (10 mL) at 6 °C was added 2-phenylcyclohexanone (174 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 133 mg of compound **12** as a white solid (70 % yield).

R_f = 0.30 (EtOAc : hexanes = 1 : 4). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.41–7.37 (m, 2 H), 7.33–7.30 (m, 3 H), 4.49 (s, 1 H), 3.02–2.98 (m, 1 H), 2.55–2.52 (m, 1 H), 2.46–2.39 (m, 1 H), 2.08–2.03 (m, 1 H), 1.88–1.71 (m, 4 H), . ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 212.67(C), 139.92(C), 129.11(CH), 128.29(CH), 126.35(CH), 80.02(C), 38.87(CH_2), 38.82(CH_2), 28.31(CH_2), 23.03(CH_2). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{12}H_{14}O_2$ + K], 229.0625. Found, 225.0635.

2-Hydroxy-1,2-diphenylpropan-1-one (13)

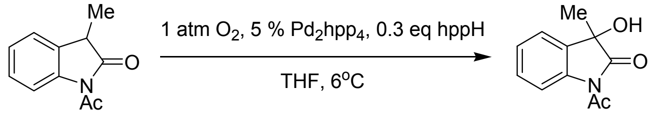


In THF: To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in THF (2 mL) at 6 °C was added 1,2-diphenylpropan-1-one (42 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (8:1) to afford 45 mg of compound **13** as a white solid (99 % yield).

In toluene: To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in toluene (2 mL) at 6 °C was added 1,2-diphenylpropan-1-one (42 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (8:1) to afford 45 mg of compound **13** as a white solid (99 % yield).

R_f = 0.30 (EtOAc : hexanes = 1 : 8). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.67–7.64 (m, 2 H), 7.45–7.41 (m, 3 H), 7.38–7.35 (m, 2 H), 7.32–7.25 (m, 3 H), 4.74 (s, 1 H), 1.88 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 201.96(C), 142.41(C), 133.40(C), 132.96(CH), 130.17(CH), 128.94(CH), 128.25(CH), 128.17(CH), 125.91(CH), 79.03(C), 26.00(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{15}H_{14}O_2$ + Na], 249.0886. Found, 249.0878.

1-Acetyl-3-hydroxy-3-methylindolin-2-one (14)

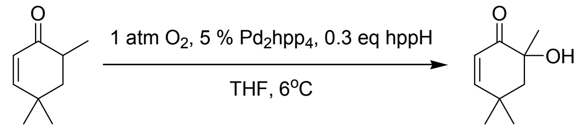


In THF: To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in THF (2 mL) at 6 ^oC was added 1-acetyl-3-methylindolin-2-one (38 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 ^oC under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (10:1) to afford 29 mg of compound **14** as a white solid (70 % yield).

In toluene: To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in toluene (2 mL) at 6 ^oC was added 1-acetyl-3-methylindolin-2-one (38 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 ^oC under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (10:1) to afford 29 mg of compound **14** as a white solid (70 % yield).

R_f = 0.15 (CH_2Cl_2 : MeOH = 10 : 1). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.21 (d, J = 8 Hz, 1 H), 7.43 (d, J = 8 Hz, 1 H), 7.36 (t, J = 8 Hz, 1 H), 7.24 (t, J = 8 Hz, 1 H), 2.65 (s, 3 H), 1.63 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 179.01(C), 170.70(C), 139.13(C), 130.28(C), 130.17(CH), 125.81(CH), 123.23(CH), 116.92(CH), 73.56(C), 26.49(CH_3), 25.68(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{11}H_{11}NO_3$ + Na], 228.0631. Found, 228.0630.

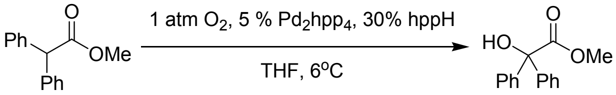
6-Hydroxy-4,4,6-trimethylcyclohex-2-enone (15)



To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in THF (5 mL) at 6 ^oC was added 4,4,6-trimethylcyclohex-2-enone (69 mg, 0.50 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 ^oC under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 55 mg of compound **15** as a pale yellow oil (71 % yield).

R_f = 0.30 (EtOAc : hexanes = 1 : 4). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 6.62 (d, J = 10 Hz, 1 H), 5.91 (d, J = 10 Hz, 1 H), 3.36 (s, 1H), 2.03 (ABq, $\Delta\nu_{AB}$ = 20 Hz, J_{AB} = 13.5 Hz, 2 H), 1.41 (s, 3 H), 1.26 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 202.31(C), 159.51(CH), 122.94(CH), 72.17(C), 48.01(CH_2), 34.17(C), 32.32(CH_3), 28.07(CH_3), 27.45(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_9H_{14}O_2$ + Na], 117.0886. Found, 117.0867.

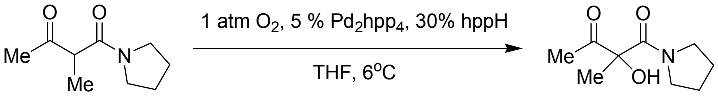
Methyl 2-hydroxy-2,2-diphenylacetate (16)



To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in THF (2 mL) at 6 °C was added methyl 2,2-diphenylacetate (113 mg, 0.500 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (10:1) to afford 93 mg of compound **16** as a white solid (77 % yield).

R_f = 0.30 (EtOAc : hexanes = 1 : 10). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.43–7.32 (m, 10 H), 4.18 (s, 1H), 3.86 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 174.93(C), 141.87(C), 128.8(CH), 128.04(CH), 127.33(CH), 81.06(C), 53.52(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{15}H_{14}O_3$ + H], 243.1016. Found, 243.1016.

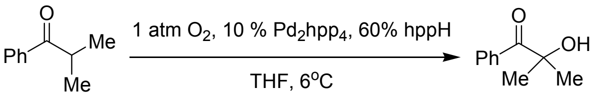
2-Hydroxy-2-methyl-1-(pyrrolidin-1-yl)butane-1,3-dione (17)



To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in THF (2 mL) at 6 °C was added 2-methyl-1-(pyrrolidin-1-yl)butane-1,3-dione (34 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (10:1) to afford 30 mg of compound **17** as a white solid (80 % yield).

R_f = 0.20 (CH_2Cl_2 : MeOH = 10 : 1). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 4.98 (s, 1 H), 3.54 (td, J = 7 Hz, J = 2 Hz, 2H), 3.47 (dt, J = 11 Hz, J = 7 Hz, 1H), 3.29 (dt, J = 11 Hz, J = 7 Hz, 1H), 2.22 (s, 3 H), 1.91–1.79 (m, 4 H), 1.55 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 206.67(C), 168.44(C), 80.91(C), 48.04(CH_2), 47.00(CH_2), 26.66(CH_2), 24.35(CH_3), 23.26(CH_2), 21.61(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_9H_{15}NO_3$ + H], 186.1125. Found, 186.1127.

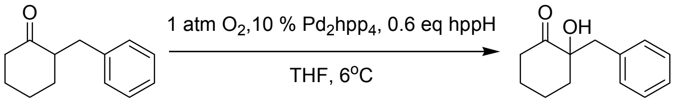
2-Hydroxy-2-methyl-1-phenylpropan-1-one (18)



To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in THF (2 mL) at 6 °C was added 2-methyl-1-phenylpropan-1-one (148 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Then Pd_2hpp_4 (19 mg, 0.025 mmol, 0.05 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) were added to the reaction mixture and stirred for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 131 mg of compound **18** as a colorless oil (80 % yield).

R_f = 0.25 (EtOAc : hexanes = 1 : 4). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.00 (d, *J* = 7.5 Hz, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 4.07 (s, 1 H), 1.64 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 204.76(C), 133.74(C), 132.96(CH), 129.61(CH), 128.45(CH), 76.24(C), 28.42(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{10}H_{12}O_2$ + Na], 187.0729. Found, 187.0712.

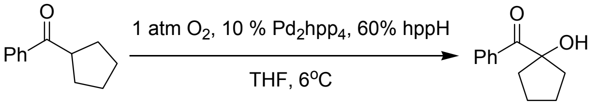
2-Benzyl-2-hydroxycyclohexanone (19)



To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in THF (2 mL) at 6 °C was added 2-benzylcyclohexanone (188 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Then Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) were added to the reaction mixture and stirred for 12 h at 6°C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (6:1) to afford 138 mg of compound **19** as a white solid (68 % yield).

R_f = 0.20 (EtOAc : Hexanes = 1 : 6). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.28–7.19 (m, 5 H), 3.85 (s, 1 H), 3.14 (d, *J* = 14 Hz, 1 H), 2.98 (d, *J* = 14 Hz, 1 H), 2.73–2.66 (td, *J* = 14 Hz, *J* = 6 Hz, 1 H), 2.56–2.53 (m, 1 H), 2.23–2.16 (m, 2 H), 1.92–1.84 (m, 2 H), 1.75–1.63 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 213.13(C), 135.26(C), 130.00(CH), 128.15(CH), 126.88(CH), 79.20(C), 43.21(CH_2), 40.32(CH_2), 38.51(CH_2), 27.91(CH_2), 22.71(CH_2). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_{16}O_2$ + Na], 227.1043. Found, 227.1039

(1-Hydroxycyclopentyl)(phenyl)methanone (20)

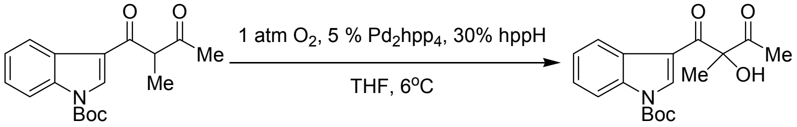


To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in THF (5 mL) at 6 °C was added cyclopentyl(phenyl)methanone (87 mg, 0.50 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6°C under 1 atm of oxygen.

Then Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) were added to the reaction mixture and stirred for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 57 mg of compound **20** as a colorless oil (60 % yield).

R_f = 0.50 (EtOAc : Hexanes = 1 : 4). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 °C, δ): 7.99–7.97 (m, 2 H), 7.57–7.47 (m, 3 H), 3.78 (s, 1 H), 2.41–2.35 (m, 2 H), 2.05–2.02 (m, 2 H), 1.94–1.90 (m, 4 H), . ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, δ): 203.77(C), 133.86(C), 132.80(CH), 129.55(CH), 128.29(CH), 87.09(C), 40.87(CH_2), 25.51(CH_2). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{12}H_{14}O_2$ + Na], 213.0886. Found, 213.0875.

tert-Butyl 3-(2-hydroxy-2-methyl-3-oxobutanoyl)-1*H*-indole-1-carboxylate (21)

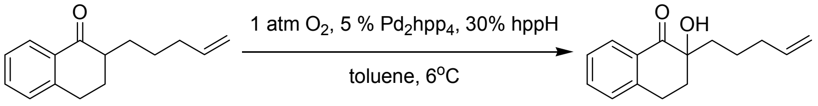


In THF: To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in THF (2 mL) at 6 °C was added **S1** (63 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (10:1) to afford 46 mg of compound **21** as a white solid (70 % yield).

In toluene: To a solution of Pd_2hpp_4 (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in toluene (2 mL) at 6 °C was added **S1** (63 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (10:1) to afford 40 mg of compound **21** as a white solid (60 % yield).

R_f = 0.30 (CH_2Cl_2 : MeOH = 10 : 1). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 °C, δ): 8.58 (d, J = 2 Hz, 1H), 8.41–8.38 (m, 1 H), 8.15–8.13 (m, 1 H), 7.41–7.35 (m, 2 H), 5.18 (s, 1 H), 2.26 (s, 1 H), 1.75 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, δ): 207.93(C), 193.29(C), 148.71(C), 135.37(CH), 134.83(C), 128.16(C), 125.75(CH), 124.72(CH), 122.59(CH), 114.96(CH), 114.94(C), 85.58(C), 85.75(C), 28.02(CH_3), 24.74(CH_3), 24.59(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{18}H_{21}NO_5$ + H], 332.1493. Found, 332.1496.

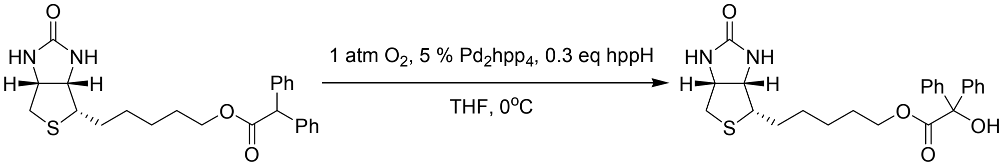
3,4-dihydro-2-hydroxy-2-(pent-4-enyl)naphthalen-1(2*H*)-one (22)



To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in toluene (5 mL) at 6 °C was added 2-allyl-1-tetralone (107 mg, 0.50 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (12:1) to afford 82 mg of compound **22** as a colorless oil (71 % yield).

R$_f$ = 0.30 (hexanes : EtOAc = 8 : 1). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$ 25 °C, δ): 8.01 (d, *J* = 7.5 Hz, 1 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 7.5 Hz, 1 H), 5.78–5.69 (m, 1 H), 4.95 (d, *J* = 18 Hz, *J* = 1 Hz, 1 H), 4.91 (d, *J* = 10 Hz, 1 H), 3.82 (s, 1 H), 3.08 (ddd, *J* = 17.5 Hz, *J* = 12.5 Hz, *J* = 5 Hz, 1 H), 3.01–2.97 (m, 1 H), 2.36–2.32 (m, 1 H), 2.15 (dt, *J* = 13 Hz, *J* = 5.5 Hz, 1 H), 2.02–2.00 (m, 2 H), 1.72–1.65 (m, 1 H), 1.61–1.54 (m, 2 H), 1.46–1.40 (m, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, δ): 201.82(C), 143.36(C), 138.16(CH), 133.92(CH), 130.17(C), 128.94(CH), 127.89(CH), 126.82(CH), 114.80(CH$_2$), 75.57(C), 34.85(CH$_2$), 33.81(CH$_2$), 33.66(CH$_2$), 26.47(CH$_2$), 22.13(CH$_2$),. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{15}H_{18}O_2$ + H], 231.1380. Found, 231.1382.

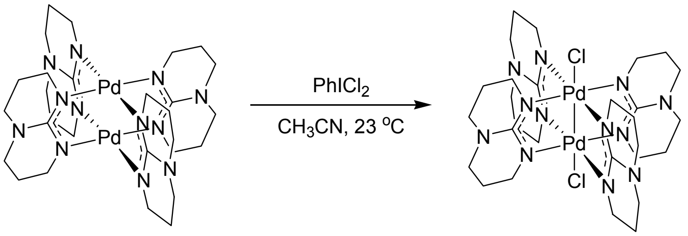
5-((3a*R*,6*S*,6a*S*)-Hexahydro-2-oxo-1*H*-thieno[3,4-d]imidazol-6-yl)pentyl 2-hydroxy-2,2-diphenylacetate (23)



To a solution of Pd$_2$hpp$_4$ (8 mg, 0.01 mmol, 0.05 equiv) and hppH (8.5 mg, 0.060 mmol, 0.30 equiv) in THF (2 mL) at 6°C was added **S2** (85 mg, 0.20 mmol, 1.0 equiv) and the reaction mixture was stirred vigorously for 12 h at 6°C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$ / MeOH (10:1) to afford 82 mg of compound **23** as a white solid (93 % yield).

R$_f$ = 0.25 (CH$_2$Cl$_2$: MeOH = 10 : 1). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$ 25 °C, δ): 7.43–7.41 (m, 2 H), 7.35–7.30 (m, 3 H), 5.89 (s, 1 H), 5.29 (s, 1 H), 4.54 (s, 1 H), 4.43 (t, *J* = 0.5 Hz, 1 H), 4.26–4.19 (m, 3 H), 3.04 (q, *J* = 0.5 Hz, 1H), 2.85 (dd, *J* = 1.5 Hz, *J* = 0.5 Hz, 1H), 2.65 (d, *J* = 1.5 Hz, 1H), 1.67–1.51 (m, 4 H), 1.36–1.19 (m, 4 H). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, δ): 174.45(C), 163.63(C), 142.10(C), 128.03(CH), 127.95(CH), 127.26(CH), 81.05(C), 66.61(CH$_2$), 61.87(CH), 60.05(CH), 55.46(CH), 40.49(CH$_2$), 28.37(CH$_2$), 28.34(CH$_2$), 28.04(CH$_2$), 25.57(CH$_2$). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{24}H_{28}N_2O_4S$ + Na], 463.1662. Found, 463.1662.

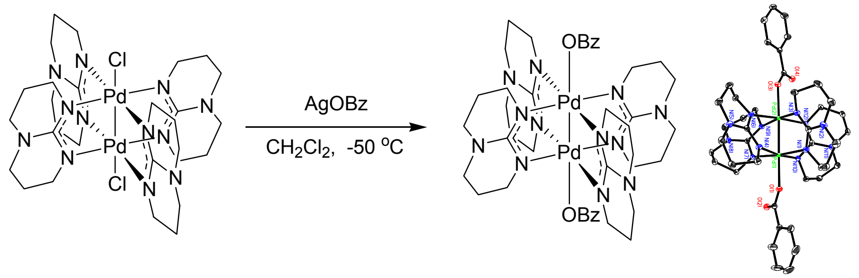
$Pd_2hpp_4Cl_2$ (S3)



To a suspension of Pd_2hpp_4 (535 mg, 0.700 mmol, 1.00 equiv) in acetonitrile (10 mL) at 23 °C was added $PhICl_2$ (192 mg, 0.700 mmol, 1.00 equiv) and the reaction was stirred for 1 h at 23 °C. Dark green precipitate from the reaction mixture was filtered over a glass fiber filter paper and the solid residue was triturated with benzene (5 mL). The suspension was filtered over a glass fiber filter paper, the dark green residue collected, and dissolved in CH_2Cl_2. Solvent was removed in vacuo to afford 230 mg of compound S3 as a dark green solid (27 % yield). A crystal of S3 was obtained by layering pentane onto a solution of S3 in CH_2Cl_2 at 0 °C and the unit cell parameter as determined by X-ray diffraction matched the reported data.[3]

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_2Cl_2 –50 ºC, δ): 3.90–3.84 (m, 8 H), 3.12–3.05 (m, 16 H), 2.93–2.88 (m, 8 H), 1.88–1.81 (m, 8 H), 1.72–1.65 (m, 8 H). ^{13}C NMR (1.25 MHz, CD_2Cl_2, 25 ºC, δ): 165.06, 48.83, 48.60, 25.98. UV-VIS Spectroscopy (CH_2Cl_2, 22 °C): 648 nm ($\varepsilon = 1.08 \times 10^2$ M^{-1} cm^{-1}); 324 nm ($\varepsilon = 3.30 \times 10^3$ M^{-1} cm^{-1}).

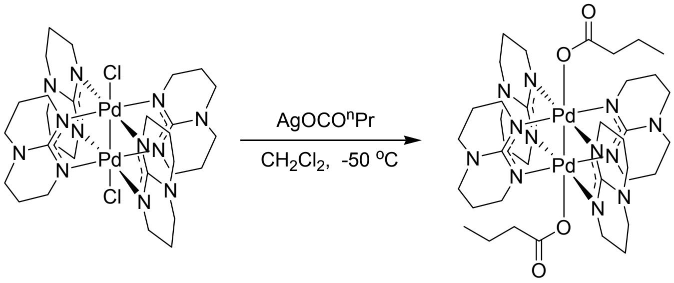
$Pd_2hpp_4(OBz)_2$ (24) (CCDC 784627)



The following experiment was carried out in a nitrogen filled drybox: To a suspension of AgOBz (205 mg, 0.900 mmol, 5.00 equiv) in CH_2Cl_2 (5 mL) at –50 °C was added **S3** (150 mg, 0.180 mmol, 1.00 equiv) and the reaction was stirred for 2 h at –50 °C. The reaction mixture was filtered through a glass fiber filter paper at –50 °C . The filtrate was concentrated in vacuo at –50 °C to afford 150 mg of compound **24** as a dark green solid (83 % yield). The compound was crystallized as dark green needles by diffusing pentane into a dichloromethane solution of **24** at –50 °C for 72 h. For X-ray crystallographic data of **24** see x-ray section.

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ –50 ºC, δ): 8.03–8.01 (m, 4 H), 7.37–7.33 (m, 6 H), 3.41 (br, 16 H), 3.02 (br, 16 H), 1.80 (br, 16H). ^{13}C NMR (125 MHz, $CDCl_3$, –50 ºC, δ): 168.66, 162.76, 138.32, 129.53, 129.23, 127.54, 48.40, 46.46, 24.61.

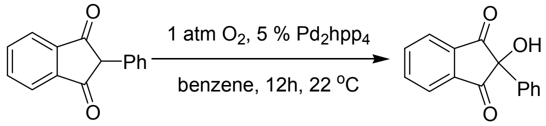
$Pd_2hpp_4(OCO^nPr)_2$ (S4)



The following experiment was carried out in a nitrogen filled drybox: To a suspension of $AgOCO^nPr$ (47 mg, 0.24 mmol, 5.0 equiv) in CH_2Cl_2 (6 mL) at –50 ºC was added **S3** (40 mg, 0.050 mmol, 1.0 equiv) and the reaction mixture was stirred for 2 h at –50 ºC. The reaction mixture was filtered through a glass fiber filter paper at –50 °C. The residue was concentrated in vacuo at –50 °C to afford 33 mg of compound **S4** as a dark green solid (70 % yield).

NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ –50 ºC, δ): 3.29 (br, 16 H), 3.00–2.97 (m, 16 H), 2.13 (t, J = 7 Hz, 4 H), 1.76–1.72 (m, 16 H), 1.58–1.51 (m, 4 H), 0.84 (t, *J* = 7 Hz, 6 H),^{13}C NMR (125 MHz, $CDCl_3$, –50 ºC, δ): 176.69, 162.68, 48.43, 46.01, 41.62, 24.43, 19.99, 14.09.

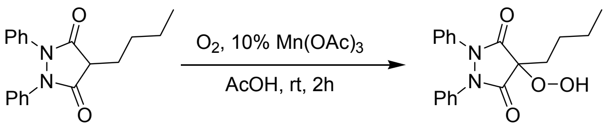
2-Hydroxy-2-phenyl-2H-indene-1,3-dione (S6)



To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) benzene (5 mL) at 22 °C was added 2-phenyl-2H-indene-1,3-dione (111 mg, 0.500 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 12 h at 22 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (20:1) to afford 106 mg of compound **23** as a yellow solid (90 % yield).

R_f = 0.30 (CH_2Cl_2 : MeOH = 20 : 1). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 8.08 (dd, *J* = 6 Hz, *J* = 3 Hz, 2 H), 7.96–7.92 (m, 2 H), 7.42–7.39 (m, 2 H), 7.35–7.31 (m, 3 H), 3.30 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 197.88(C), 141.04(C), 136.65(CH), 136.50(C), 128.88(CH), 128.78(CH), 126.17(CH), 124.24(CH), 79.45(C). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{15}H_{10}O_3$ + Na], 261.0522. Found, 261.0519.

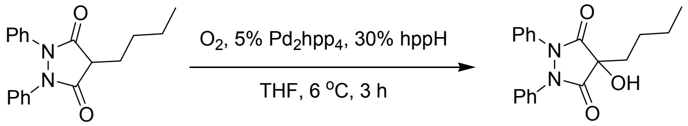
2-Hydroxy-2-phenyl-2H-indene-1,3-dione (S7)



A mixture of 4-butyl-1,2-diphenylpyrazolidine-3,5-dione (1 mmol) and manganese(III) acetate dihydrate (0.1 mmol) in glacial acetic acid (30 mL) was stirred at 23 °C for 2 h in air, and then the reaction was quenched by adding water (25 mL) to the mixture. The aqueous reaction mixture was extracted three times with dichloromethane (30 mL) and the combined extract was washed with water, a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was purified by recrystallization from diethyl ether-hexane to afford 300 mg of compound **S7** as a white solid (88 % yield).[2]

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.02 (br, 1 H), 7.36–7.31 (m, 6 H), 7.25–7.20 (m, 4 H), 2.01–1.98 (m, 2 H), 1.44–1.32 (m, 4 H), 0.88 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 168.72(C), 134.66(C), 128.90(CH), 127.37(CH), 123.23(CH), 85.02(C), 31.76(CH_2), 24.11(CH_2), 22.32(CH_2), 13.34(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{19}H_{20}N_2O_4$ + H], 341.1501. Found, 341.1489.

4-Butyl-4-hydroxy-1,2-diphenylpyrazolidine-3,5-dione (S8)



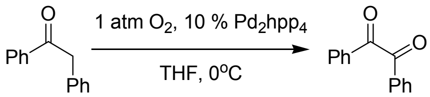
To a solution of Pd_2hpp_4 (19 mg, 0.025 mmol, 0.050 equiv) and hppH (21 mg, 0.15 mmol, 0.30 equiv) in THF (6 mL) at 22 °C was added 2-phenyl-2H-indene-1,3-dione (154 mg, 0.500 mmol, 1.00 equiv) and the reaction mixture was stirred vigorously for 12 h at 6 °C under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (2:1) to afford 75 mg of compound **S8** as a yellow solid (46 % yield).

R$_f$ = 0.30 (hexanes : EtOAc = 2 : 1). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.33–7.28 (m, 8 H), 7.21–7.17 (m, 2 H), 3.83 (br, 1H), 2.07–2.03 (m, 2 H), 1.41–1.25 (m, 4 H), 0.87 (t, *J* = 7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 170.36(C), 134.96(C), 129.03(CH), 127.16(CH), 122.67(CH), 74.07(C), 37.36(CH_2), 24.53(CH_2), 22.51(CH_2), 13.64(CH_3). Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{19}H_{20}N_2O_3$ + H], 325.1552. Found, 325.1535

C–H oxidation of acidic methylene groups

Oxidation of unsubstituted malonates and 1,3-diketones with **1** afforded mixtures of products and recovered starting materials. The only case in which we were able to isolate the α-oxidized product was the oxidation of benzyl phenylketone to benzil:

Benzil (S5)

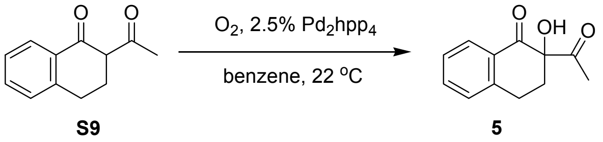


To a solution of Pd_2hpp_4 (77 mg, 0.10 mmol, 0.10 equiv) at 6 ^oC was added benzyl phenylketone (196 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred for 12 h at 6 ^oC under 1 atm of oxygen. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (4:1) to afford 140 mg of **S5** as a pale yellow solid (67 % yield).

R_f = 0.25 (hexanes : EtOAc = 4 : 1). NMR Spectroscopy: ^1H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 7.98 (d, J = 7.5 Hz, 8 H), 7.67 (t, J = 7.5 Hz, 4 H), 7.52 (t, J = 7.5 Hz, 8 H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 194.52, 134.83, 132.92, 129.82, 128.96.

Oxygen uptake experiment

The oxygen uptake experiments of Pd_2hpp_4 catalyzed α-hydroxylation of 2-acetyl-3,4-dihydronaphthalen-1(2*H*)-one (**S9**) were done on 1, 0.5, 0.3 and 0.15 mmol of the starting material. (Table S4) The following procedure describes experiment done on 0.5 mmol scale:



To a 100 mL Schlenk tube equipped with magnetic stirring bar at 22 ^oC was added a solution of **1** (9.6 mg, 0.013 mmol, 0.025 equiv) in benzene (5 mL). The solution was stirred under 1 atm of O_2 for 10 min after which a solution of **S9** (94 mg, 0.50 mmol, 1.0 equiv) in benzene (1 mL) was added. The Schlenk tube was closed immediately with a threaded Teflon stopcock and the reaction mixture was stirred for 12 hr at 22 ^oC. The sidearm of the Schlenk tube was connected to the apparatus shown in following figure and the oil levels at both ends were equilibrated.[5] The stopcock was marginally opened to allow a steady change in oil levels and the movable arm was adjusted to regulate atmospheric pressure inside the Schlenk tube. O_2 uptake readings were completed by comparing oil levels before and after the opening of the Schlenk tube.

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[5] Appleton, T. G. *J. Chem. Educ.* **1977**, *54*, 443.

Figure S1. Oxygen uptake measurement setup

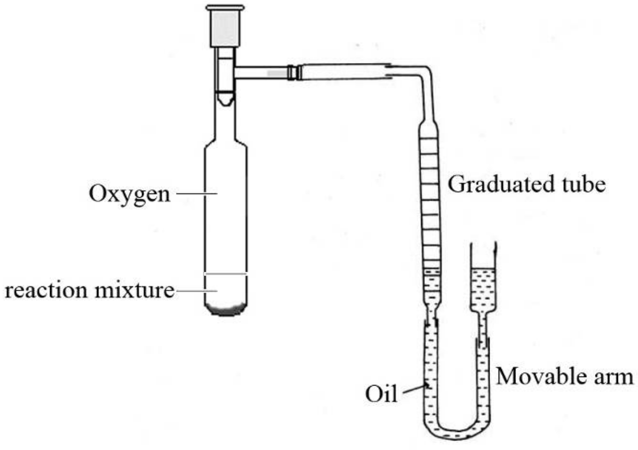
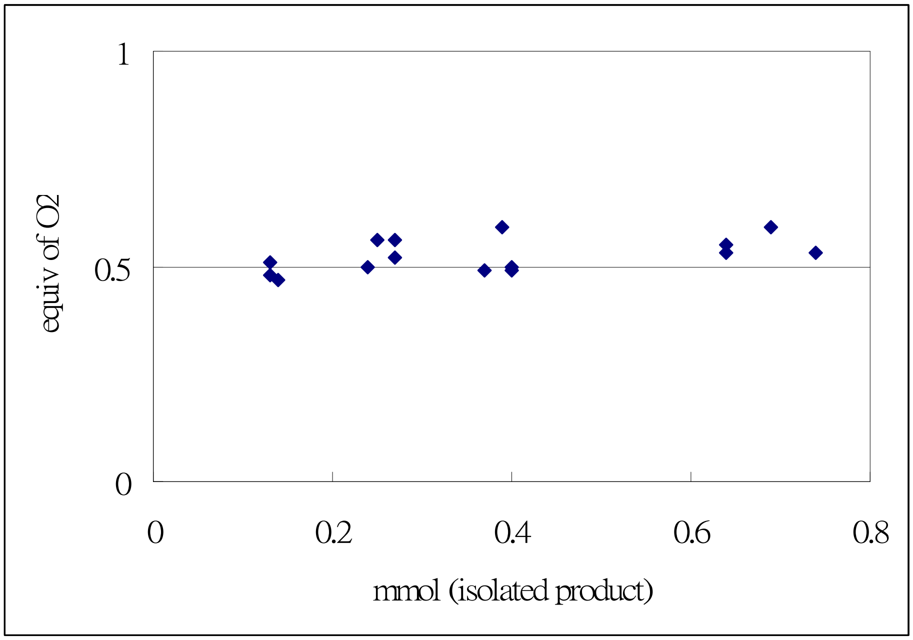


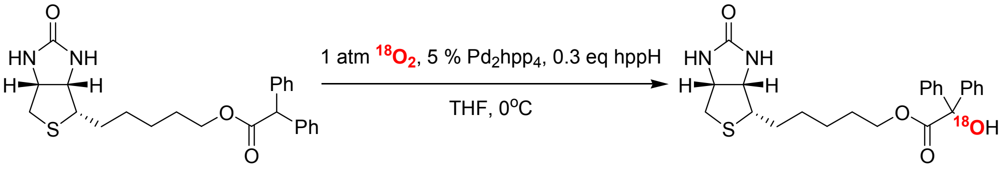
Table S4. Result of Oxygen uptake experiments

Entry	Reaction scale (mmol of SM)	Isolated product (mg)	Yield (%)	O_2 uptake (mL)	Equiv of O_2
1	1	140	69	10	0.59
2	1	150	74	9.6	0.54
3	1	130	64	8.2	0.53
4	1	130	64	8.5	0.54
5	0.5	82	80	4.8	0.50
6	0.5	82	80	4.7	0.48
7	0.5	80	78	5.6	0.59
8	0.5	75	74	4.4	0.49
9	0.3	56	90	3.6	0.56
10	0.3	51	83	3.5	0.56
11	0.3	48	80	3.0	0.50
12	0.3	56	90	3.4	0.52
13	0.15	27	87	1.6	0.51
14	0.15	29	93	1.6	0.47
15	0.15	27	87	1.5	0.48

The correlation of equivalent of O_2 consumed versus reaction scale (in mmol of isolated product) is shown in following plot.

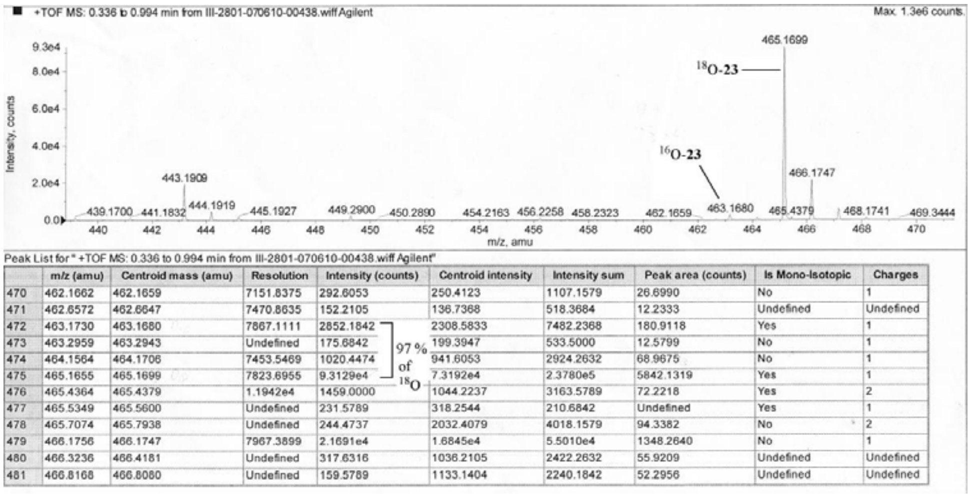


^{18}O isotope experiment



^{18}O was purchased from Cambridge Isotope with 98 % isotopic purity. The experiment was carried out according to the procedure reported for the oxidation of **S2** to **23** under 1 atm of $^{18}O_2$. The percentage of ^{18}O enrichment was examined by mass spectrometry as shown in following figure. The data calculated for 97 % ^{18}O enrichment of **23**.

Figure S2. Mass spectrometry measurement of ^{18}O enrichment 23

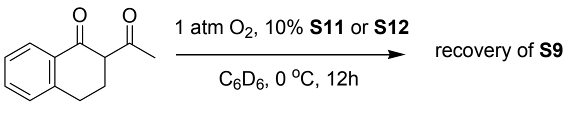


Peak List for " +TOF MS: 0.336 to 0.994 min from III-2801-070610-00438.wiff Agilent"

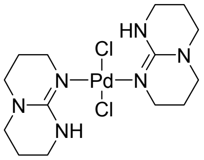
	m/z (amu)	Centroid mass (amu)	Resolution	Intensity (counts)	Centroid intensity	Intensity sum	Peak area (counts)	Is Mono-Isotopic	Charges
470	462.1662	462.1659	7151.8375	292.6053	250.4123	1107.1579	26.6990	No	1
471	462.6572	462.6647	7470.8635	152.2105	136.7368	518.3684	12.2333	Undefined	Undefined
472	463.1730	463.1680	7867.1111	2852.1842	2308.5833	7482.2368	180.9118	Yes	1
473	463.2959	463.2943	Undefined	175.6842	199.3947	533.5000	12.5799	No	1
474	464.1564	464.1706	7453.5469	1020.4474	941.6053	2924.2632	68.9675	No	1
475	465.1655	465.1699	7823.6955	9.3129e4	7.3192e4	2.3780e5	5842.1319	Yes	1
476	465.4364	465.4379	1.1942e4	1459.0000	1044.2237	3163.5789	72.2218	Yes	2
477	465.5349	465.5600	Undefined	231.5789	318.2544	210.6842	Undefined	Yes	1
478	465.7074	465.7938	Undefined	244.4737	2032.4079	4018.1579	94.3382	No	2
479	466.1756	466.1747	7967.3899	2.1691e4	1.6845e4	5.5010e4	1348.2640	No	1
480	466.3236	466.4181	Undefined	317.6316	1036.2105	2422.2632	55.9209	Undefined	Undefined
481	466.8168	466.8080	Undefined	159.5789	1133.1404	2240.1842	52.2956	Undefined	Undefined

Experiments with mononuclear Palladium complexes

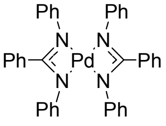
S11, $PdCl_2(hppH)_4$,[6] and **S12**, $Pd(TPA)_2$[7] were tested in following reaction for their reactivity in the α-hydroxylation reaction of **S9**. $PdCl_2(hppH)_2$ is a known Pd complex with two hppHs as L-type ligands. $Pd(TPA)_2$ is a mononuclear complex featuring two chelating amidates. Starting material was recovered in both reactions with no product formation.



S9



S11, $PdCl_2(hppH)_2$



S12, $Pd(TPA)_2$

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[6] Oakley, S. H.; Coles, M. P.; Hitchcock P. B. *Inorg. Chem.* **2004**, *43*, 7564.

[7] Berry, J. F.; Cotton, F. A.; Ibragimov, S. A.; Murillo, C. A.; Wang X. *Inorg. Chem.* **2005**, *44*, 6129.

UV-vis Data

Figure S3. UV-VIS Spectrum of $Pd_2hpp_4Cl_2$ (S3) in CH_2Cl_2 at 22 °C

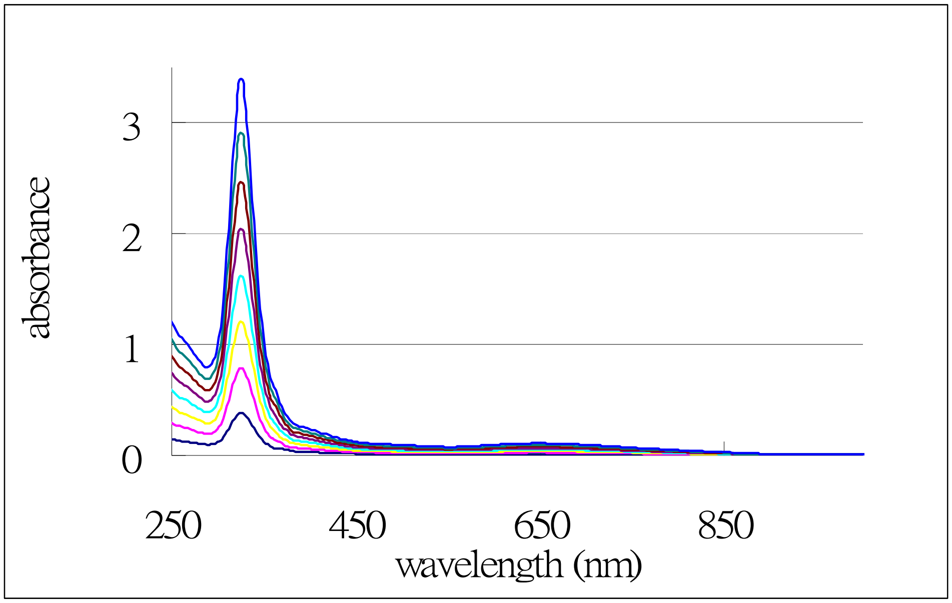


Figure S4. Molar Absorptivity Determination at 324nm

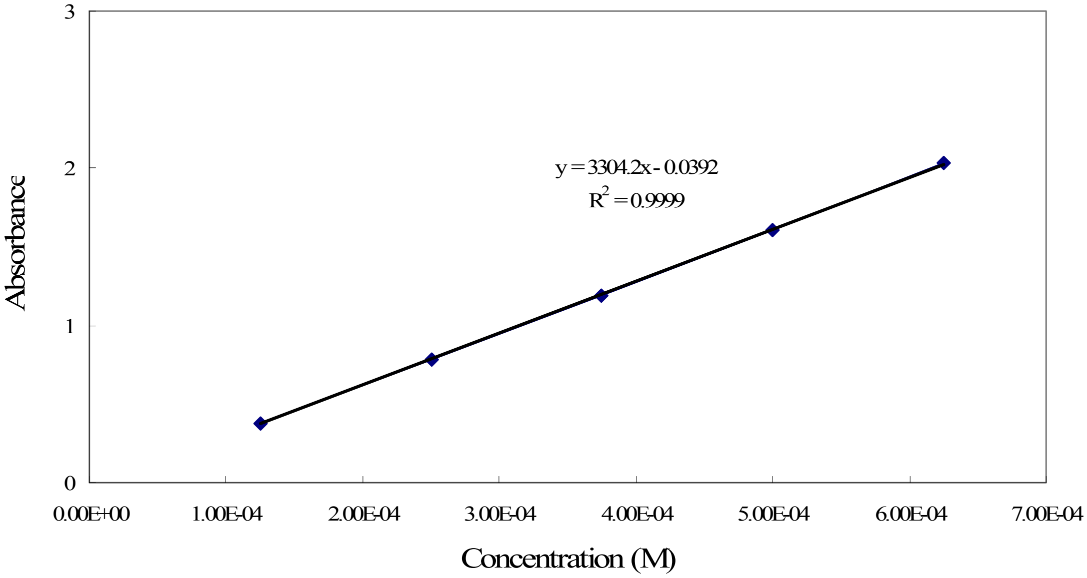


Figure S5. Molar Absorptivity Determination at 648nm

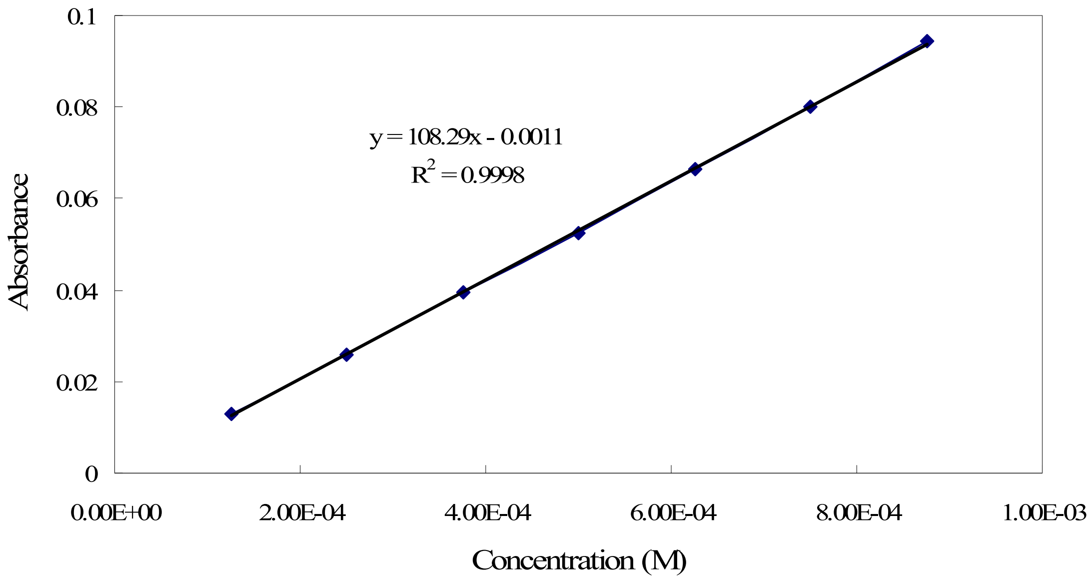
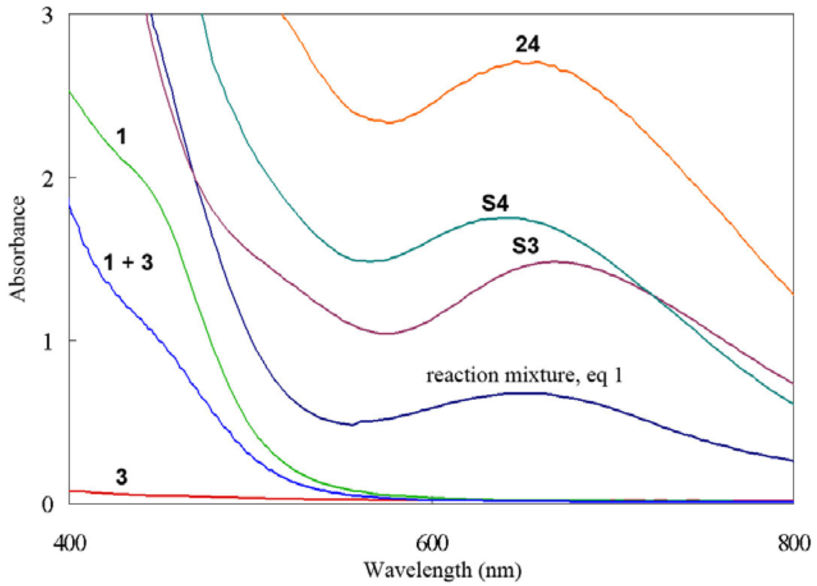


Figure S6. UV-VIS Spectrum comparison of 1-catalyzed α-hydroxylation of 3 (1) with dimeric Pd(III) complexes derived from 1

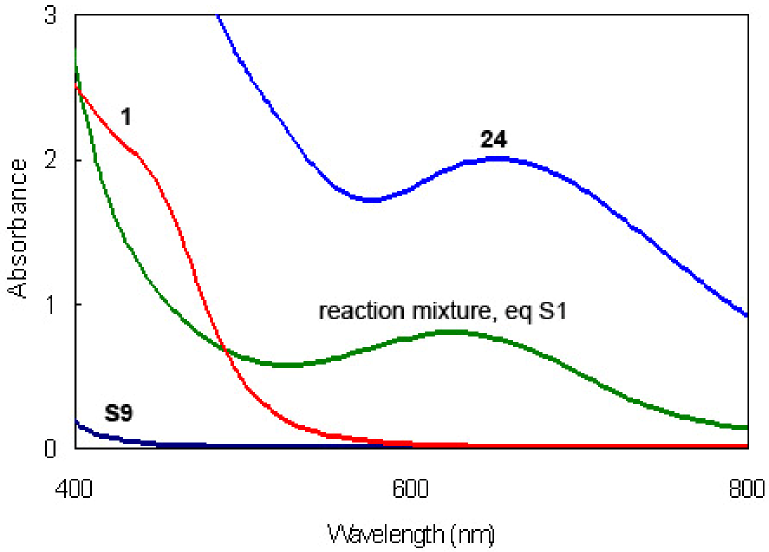


UV absorption spectrum of **1**, **3**, **24**, **S3**, **S4** and **1**+**3** in THF were measured in following concentration and temperature: **1**: 0.005M at 0 °C; **3**: 0.03M at 0 °C; **24**: 0.001M at –78 °C; S3: 0.001M at 0 °C; **S4**: 0.001M at –78 °C; **1** + **3** : 0.003M of **1** and 0.03M of **3** (degassed) at 0 °C.

UV absorption measurement of reaction mixture of eq 1:

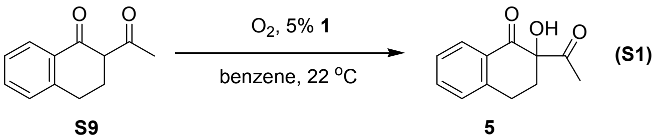
To a 0.03M solution of **3** (2mL) in THF at 0 °C in a cuvette was added 0.6 mL of 0.005M THF solution of **1** at 0 °C. The solution was bubbled with O_2 for 5 sec and the UV absorption was measured.

Figure S7. UV-VIS Spectrum comparison of 1-catalyzed α-hydroxylation of S9 (S1) with 24



UV absorption measurement of reaction mixture of eq S1:

To a 0.02M solution of **S9** (1.8 mL) in benzene at 22 °C in a cuvette was added 0.2 mL of 0.01M benzene solution of **1** at 22 °C. The solution was bubbled with O_2 for 5 sec and the UV-vis absorption was measured.



DFT Computations

Density functional theory (DFT) calculations were performed using Gaussian09[8] at the Odyssey

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[8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; , J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd; J. J. Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Normand; J. Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Cossi, J. M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adam, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.

cluster at Harvard University. **S3** was used as the compound in the DFT computation due to the simpler structure compared to **24** and **S4.** All three of complexes **24**, **S3**, and **S4** display similar UV-vis absorptions at around 650 nm. Geometry optimizations were carried out using the atomic coordinates of the crystal structure of **S3**[4] as a starting point with the B3PW91[9] hybrid functional. B3LYP[10] and and M06[11] hybrid functionals used the optimized structure of **S3** with B3PW91 as a starting point. The unrestricted wave function was used for the singlet ground state of **S3**. BS I includes SDD quasirelativistic pseudopotentials on Pd (28) and Cl (10) with basis sets (Pd: (8s7p6d)/[6s5p3d][12]; Cl: (4s5p)/[2s3p][13]) extended by polarization functions (Pd: f, 1.472[14]; Cl: d, 0.640[15]), and 6-31G(d,p)[16] on H, C, N. All geometry optimizations were performed using the above functionals with the BS I basis set, followed by frequency calculations on each optimized structure with corresponding functional/BS I. Time-dependent density functional theory[17] (TD-DFT) calculations were performed using the above functionals and BS I on the geometry optimized in vacuum by the above functionals with the BS I basis set. TD-DFT calculations were also carried out on B3P86[18] and mPW1PW91[19] functionals with the BS I basis set using the optimized structure of **S3** with B3PW91. Molecular orbitals of **S3** were generated using an isosurface value of 0.02 on the optimized structure of S3 with B3PW91/BS I. UV-vis spectrum was simulated by GaussView5.[20]

W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels; A. D. Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski; J. Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford CT, 2009.

[9] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244-13249.

[10] Kohn, W.; Becke, A. D.; Parr, R. G., *J. Phys. Chem*. **1996**, *100*, 12974-12980.

[11] Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res*. **2008**, *41*, 157–167.

[12] (a) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123-141. (b) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1991**, *78*, 247-266.

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[14] Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett*. **1993**, *208*, 111-114.

[15] Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett*. **1993**, *208*, 237-240.

[16] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

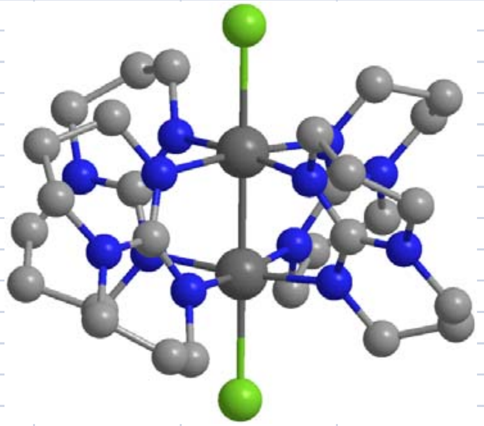
[17] Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys*. **1998**, *109*, 8218–8224.

[18] Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.

[19] Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664-675.

[20] Dennington, R., II; Keith, T. A.; Millam, J. M. *GaussView*, Version 5.0.8; Semichem, Inc.

Table S5. The optimized structure of S3 with B3PW91/BS I and cartesian coordinates (Å)



Pd	2.6255000017	2.6255000154	9.6663511669
Pd	2.6255000151	2.6255000020	12.0836575393
Cl	2.6254999973	2.6255000220	7.1600955479
Cl	2.6255000264	2.6254999970	14.5899127152
N	4.3114496793	1.4794765350	9.7824877724
N	5.4924697994	-0.2414701172	10.8750041879
C	5.2294536731	1.4585799197	8.6573850878
C	6.6010919421	0.9502893394	9.0692958364
C	6.4321410508	-0.3798804149	9.7757460180
C	4.5148689229	0.7361312804	10.8750044280
N	3.7715240996	0.9395507438	11.9675213426
C	3.7924201277	0.0215463458	13.0926237058
C	4.3007106240	-1.3500919069	12.6807127784
C	5.6308803542	-1.1811410917	11.9742626179
N	0.9395503340	3.7715235083	9.7824877714
N	-0.2414699390	5.4924699781	10.8750043154
C	0.0215462768	3.7924199809	8.6573851302
C	-1.3500919680	4.3007106593	9.0692958402
C	-1.1811409957	5.6308804124	9.7757460053
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C	1.4585797833	5.2294536042	13.0926237473
C	0.9502893559	6.6010918759	12.6807127980
C	-0.3798803761	6.4321411210	11.9742626255
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N	5.4924700540	5.4924698792	10.8750042491
C	3.7924200451	5.2294537074	8.6573851080
C	4.3007106478	6.6010919709	9.0692958485
C	5.6308803996	6.4321410600	9.7757460291
C	4.5148687148	4.5148689438	10.8750044462
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C	5.2294536368	3.7924201936	13.0926237252
C	6.6010919050	4.3007106320	12.6807127769
C	6.4321411373	5.6308803594	11.9742626000
N	1.4794765172	0.9395503410	9.7824877702
N	-0.2414700430	-0.2414698578	10.8750042480
C	1.4585799892	0.0215463132	8.6573851084
C	0.9502893287	-1.3500919368	9.0692958217
C	-0.3798804274	-1.1811409847	9.7757459866
C	0.7361312990	0.7361310735	10.8750044475
N	0.9395507494	1.4794759247	11.9675213445
C	0.0215463810	1.4585798449	13.0926237287
C	-1.3500918731	0.9502893449	12.6807128109
C	-1.1811410610	-0.3798803856	11.9742626485
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H	4.8293340593	0.8360290254	7.8449329340
H	7.2414933028	0.8355895557	8.1886104018
H	7.0835893906	1.6645474876	9.7473272374
H	6.0952528441	-1.1507486070	9.0630064587
H	7.3871465383	-0.7224179991	10.1934030127
H	2.7798134153	-0.0465380468	13.4984370805
H	4.4149707703	0.4216656792	13.9050761369
H	4.4154101817	-1.9904934041	13.5613981425
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H	6.4017485209	-0.8442525883	12.6870020430
H	5.9734180421	-2.1361466173	11.5566058227
H	-0.0465381295	2.7798133532	8.2515714768
H	0.4216658860	4.4149707401	7.8449328747
H	-1.9904932922	4.4154104669	8.1886103819
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H	2.4711864444	5.2975379650	13.4984372514
H	0.8360290293	4.8293342552	13.9050760891
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H	4.8293343020	4.4149709153	13.9050760972
H	7.2414934172	4.4154101842	13.5613981298
H	7.0835891539	3.5864524300	12.0026812728
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H	0.8360291906	0.4216659355	7.8449328881
H	0.8355895283	-1.9904932667	8.1886103667
H	1.6645474308	-1.8325894475	9.7473272268
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H	-0.7224181158	-2.1361464743	10.1934028870
H	-0.0465380138	2.4711865413	13.4984371413
H	0.4216657377	0.8360291780	13.9050761305
H	-1.9904933611	0.8355897802	13.5613981808
H	-1.8325891691	1.6645475141	12.0026813057
H	-0.8442525985	-1.1507485611	12.6870020811
H	-2.1361465819	-0.7224180503	11.5566058239

Table S6. Metric comparison between DFT optimized and X-ray determined structure of S3.

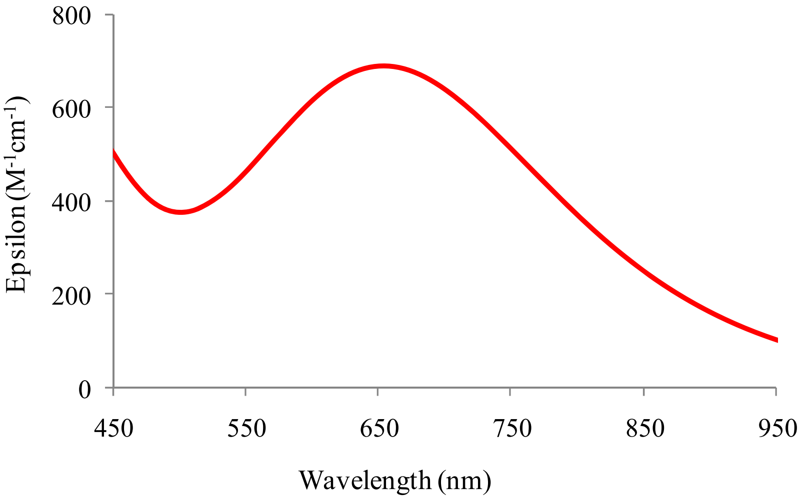
functional/BS I	Pd-Pd (Å)	Pd-N (Å)	Pd-Cl (Å)
X-ray data	**2.39**	**2.03**	**2.47**
B3PW91	**2.42**	**2.04**	**2.51**
M06	2.44	2.05	2.51
B3LYP	2.44	2.06	2.54

Table S7. Experimental and calculated absorption spectra (TD-DFT) of S3.

functional/BS I	wavelength (nm)	transition	oscillator strength
experimental	648		
B3PW91[a]	770	MO 174 → MO 176	0.009
mPW1PW91[a]	673	MO 174 → MO 176	0.015
B3P86[a]	702	MO 174 → MO 176	0.013
B3LYP[a]	763	MO 174 → MO 176	0.009
M06[b]	721	MO 174 → MO 176	0.012

a) TD-DFT was performed on the optimized structure of **S3** with B3PW91/BS I. b) TD-DFT was performed on the optimized structure of **S3** with M06/BS I.

Figure S8. Simulated UV-VIS Spectrum of S3 with TD-mPW1PW91/BS I using the optimized structure of S3 with B3PW91/BS I.



Calculated absorption band of **S3** corresponds to HOMO-1→ LUMO transition.[21]

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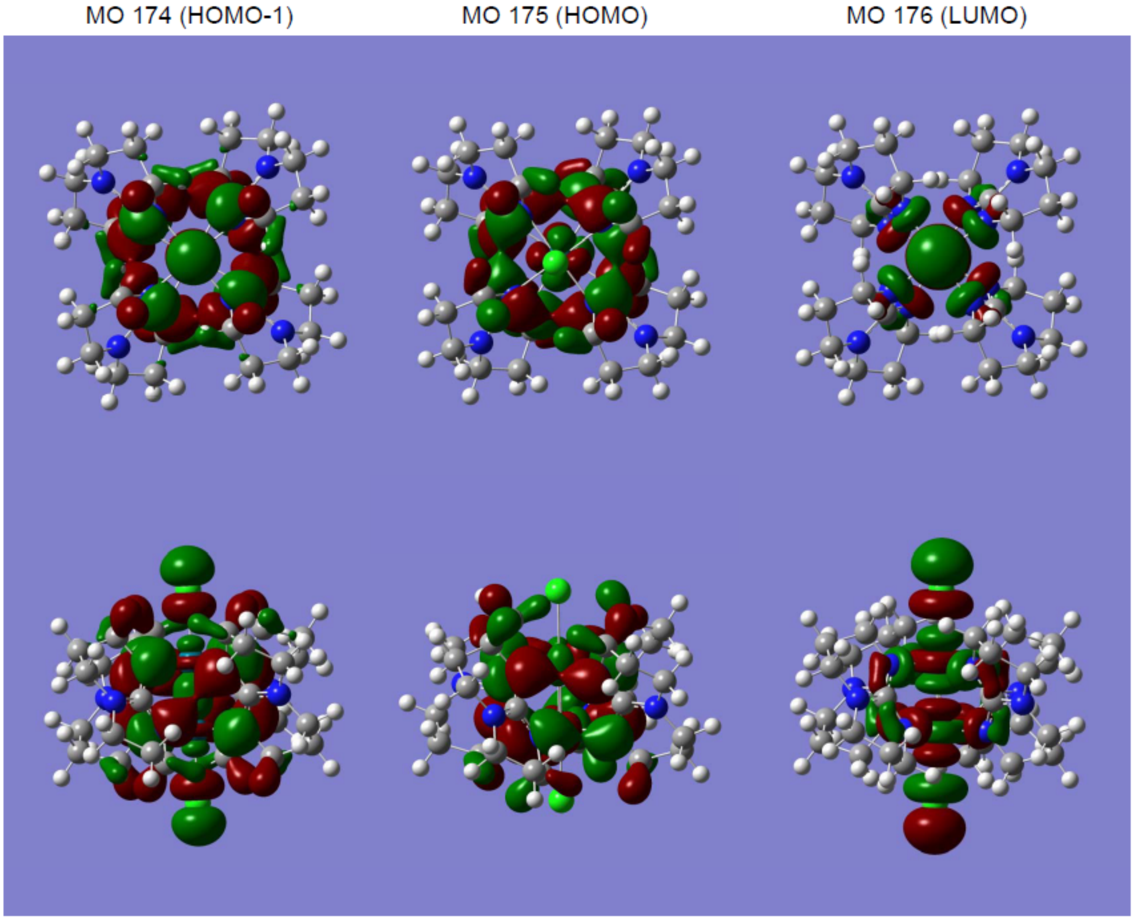
[21] Cotton, F. A.; Koshevoy, I. O.; Lahuerta, P.; Murillo, C. A.; Sanau´, M.; Ubeda, M. A.; Zhao, Q. L. *J. Am. Chem. Soc*. **2006**, *128*, 13674.

Figure S9. Molecular orbitals of S3



Molecular orbital plots of the HOMO-1, HOMO and the LUMO for the **S3** shown along the Pd-Pd axis. HOMO-1 and LUMO have antibonding characters on the Pd-Cl interaction.[21]

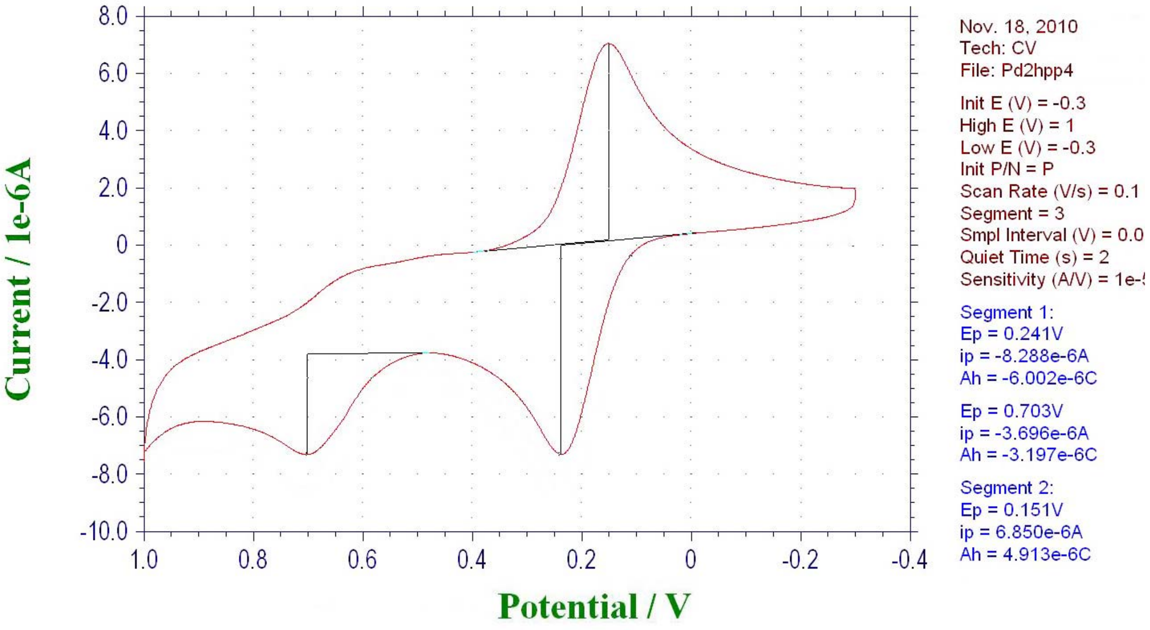
Discussion of the result of DFT calculation

We have computationally investigated the transition that corresponds to the observed UV-vis absorption of **S3** at 648 nm. During geometry optimizations, the B3PW91 functional was found to provide the best agreement between computed and experimentally determined Pd–Pd distance (2.42 Å (computed) versus 2.39 Å (experimental) as shown in Table S6). The UV-vis absorption band of **S3** was calculated based on the optimized structures of **S3** (as shown in Table S7). The computed absorption maxima were found to differ over a range of 673 to 770 nm depending on the functional employed. Despite these differences, all of the calculated absorptions were found to be composed of the excitation of MO 174 (HOMO -1) to MO 176 (LUMO). As shown in Figure S9, MO 174 has a Pd–Pd bonding character with participation of the ligand backbone. And the MO 176 is a Pd–Pd antibonding orbital. Thus the DFT calculation result has shown that the observed UV-vis feature of **S3** at 648 nm is likely a result of metal–metal bonding to metal–metal antibonding transition, which also has been observed from the UV-vis spectrum of dinuclear

Pd(III) complexes **24**, **S4** and the reaction mixture of eq 1 and eq S1. The result is also in accord with TD-DFT calculation of UV absorptions of dinuclear Pd(III) complex reported by Cotton.[21]

Electrochemical Data

Cyclic Voltammetry of 1



Nov. 18, 2010
Tech: CV
File: Pd2hpp4

Init E (V) = -0.3
High E (V) = 1
Low E (V) = -0.3
Init P/N = P
Scan Rate (V/s) = 0.1
Segment = 3
Smpl Interval (V) = 0.0
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-!

Segment 1:
Ep = 0.241V
ip = -8.288e-6A
Ah = -6.002e-6C

Ep = 0.703V
ip = -3.696e-6A
Ah = -3.197e-6C

Segment 2:
Ep = 0.151V
ip = 6.850e-6A
Ah = 4.913e-6C

The CV of **1** was obtained from a 0.01 mM solution of **1** in CH_2Cl_2 with a glassy carbon working electrode. $NBu_4 \cdot PF_6$ (0.1 M) was used as the electrolyte. The CV was obtained at a scan rate of 0.1 V/s against Ag/AgCl and was confirmed external standard of ferrocene.

The reversible oxidation wave at $E_{1/2}$ = -304 mV (vs Fc/Fc+) is assigned to the Pd(II)–Pd(II) to Pd(II)–Pd(III) redox couple. The irreversible oxidation wave at 203 mV (vs. Fc/Fc+) is assigned to the oxidation of Pd(II)–Pd(III) to Pd(III)–Pd(III). For comparison, most bimetallic palladium complexes were reported to have first oxidation wave at 250~500 mV (vs Fc/Fc+) and second wave at 500~1000 mV (vs Fc/Fc+).[7, 22]

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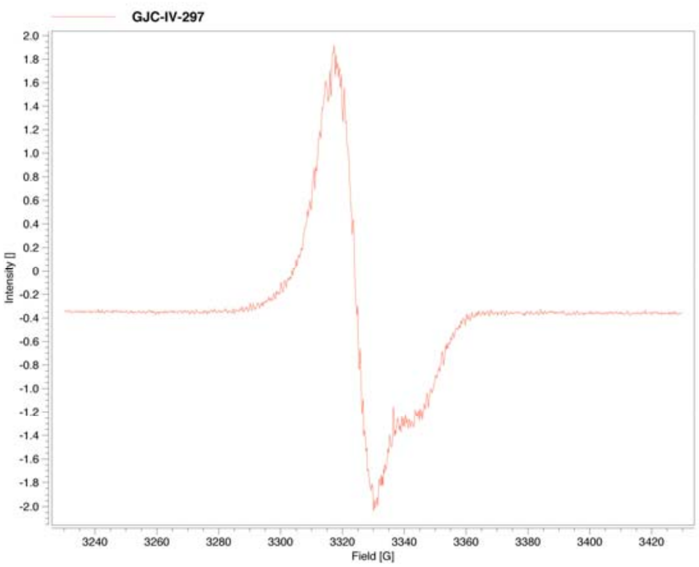
[22] Powers, D. C.; Geibel, M. A. L.; Klein, J. E. M. N.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 17050.

Electron Paramagnetic Resonance Spectrum of 1-catalyzed α-hydroxylation of S9



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FILE NAME           GJC-IV-297

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DATASET TYPE        Experimental 1D Real, Intensity(Field)

AXIS STRUCTURE      Field: indexed

AXIS DATA FORMAT    Intensity: double
                    Field: double

AXIS RANGE          Field [G]: 3230 to 3429.8, 1024 pts
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AVAILABLE PARAMETERS

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Time                           21:28:33
State of Aggregation           C
Averaged Scans                 10
Resonator                      shqe1019
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Field Mod. Frequency [Hz]      100000
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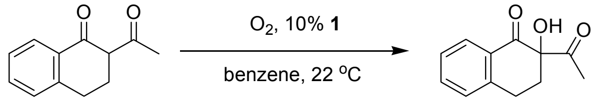

S9 **5** **(S2)**

To a solution of 1 (7 mg, 0.01 mmol, 0.1 equiv) in benzene (2 mL) at 22 ^{o}C was added S9 (19 mg, 0.10 mmol, 1.0 equiv). The solution was stirred under 1 atm of O_2 for 1 min at 23 ^{o}C and moved into a liquid nitrogen bath. A Freeze-Pump-Thaw procedure was applied to the reaction mixture. The solution was transferred to a 4 mm EPR tube and sealed under N_2 atmosphere. The EPR data was collected on a Bruker ESP300E operating at X-band frequency (9 GHz). q value of the sample at frozen 77 K was measured at 2.0088. EPR signals of known Pd_2^{5+} complexes in paddle construction with amidate ligands were reported at q = 2.010~2.014 in X-band.[23]

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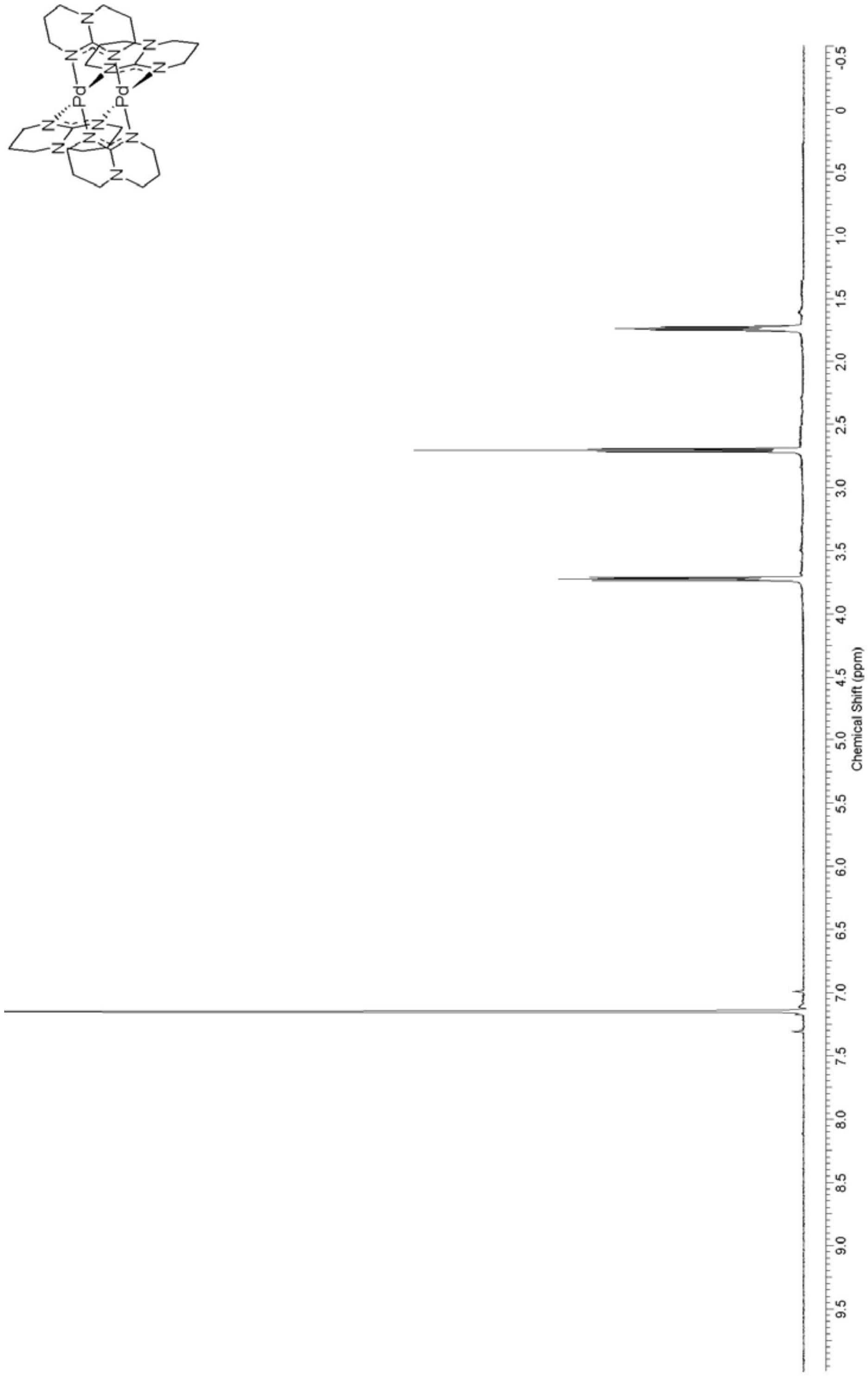
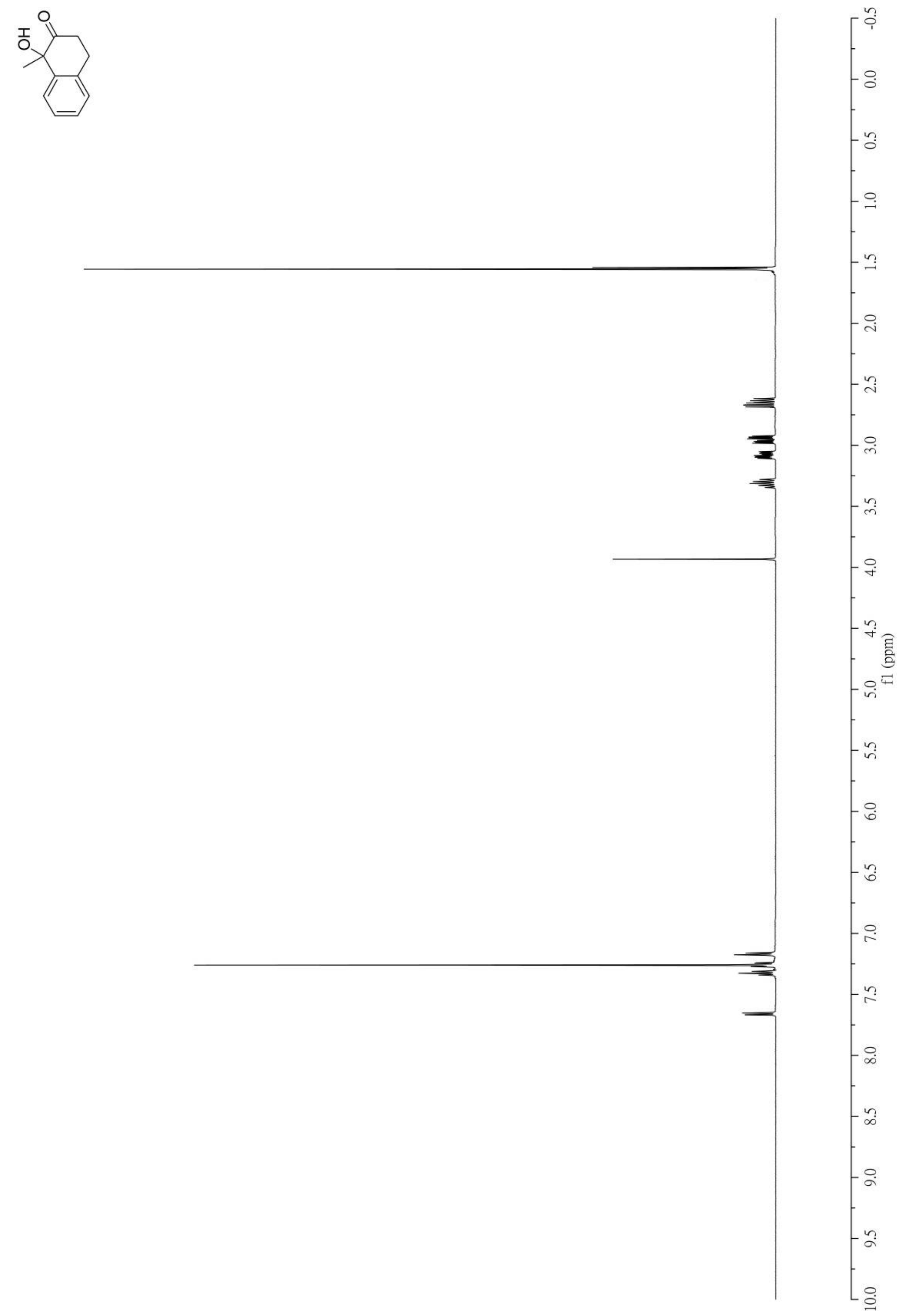
[23] (a) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144. (b) Berry, J. F.; Bill, E.; Bothe, E.; Cotton, F. A.; Dalal, N. S.; Ibragimov, S. A.; Kaur, N.; Liu, C. Y.; Murillo, C. A.; Nellutla, S.; North, J. M.; Villagra´ n, D. *J. Am. Chem. Soc.* **2007**, *129*, 1393.

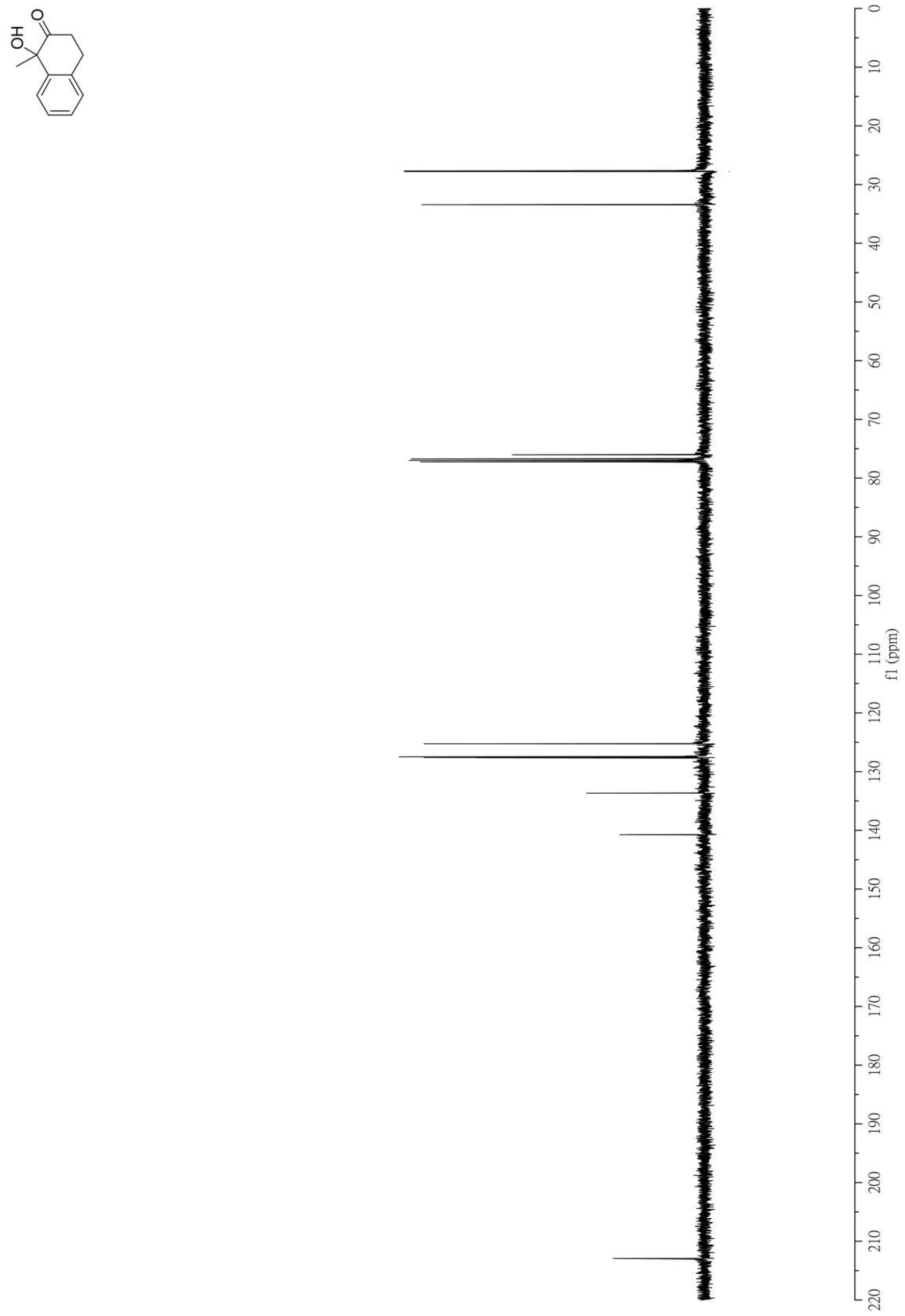
Spectroscopic Data



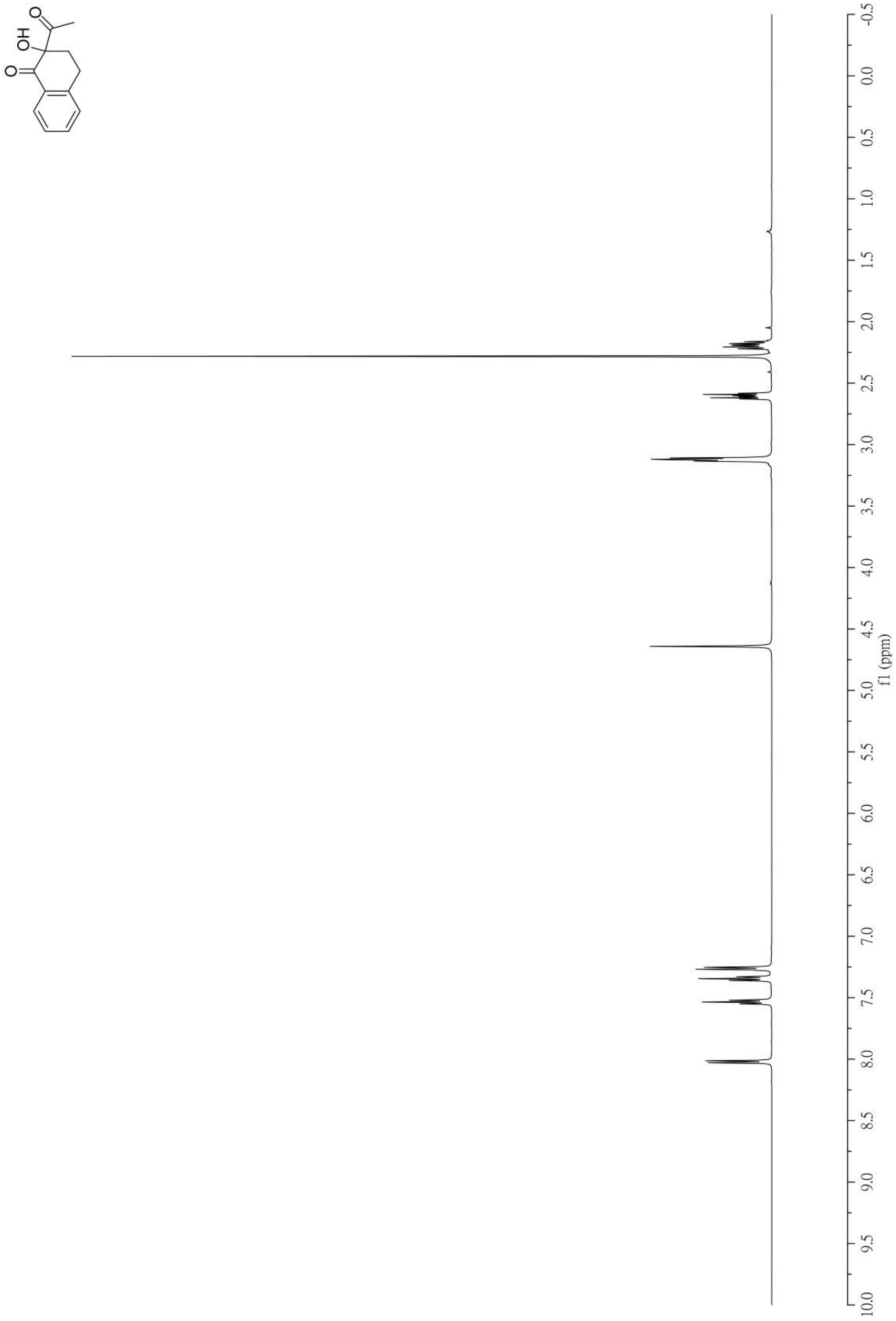
^{1}H NMR spectrum of **1** in $CDCl_3$ at 23 °C



^{1}H NMR spectrum of **4** in $CDCl_3$ at 23 °C



^{13}C NMR spectrum of **4** in $CDCl_3$ at 23 °C



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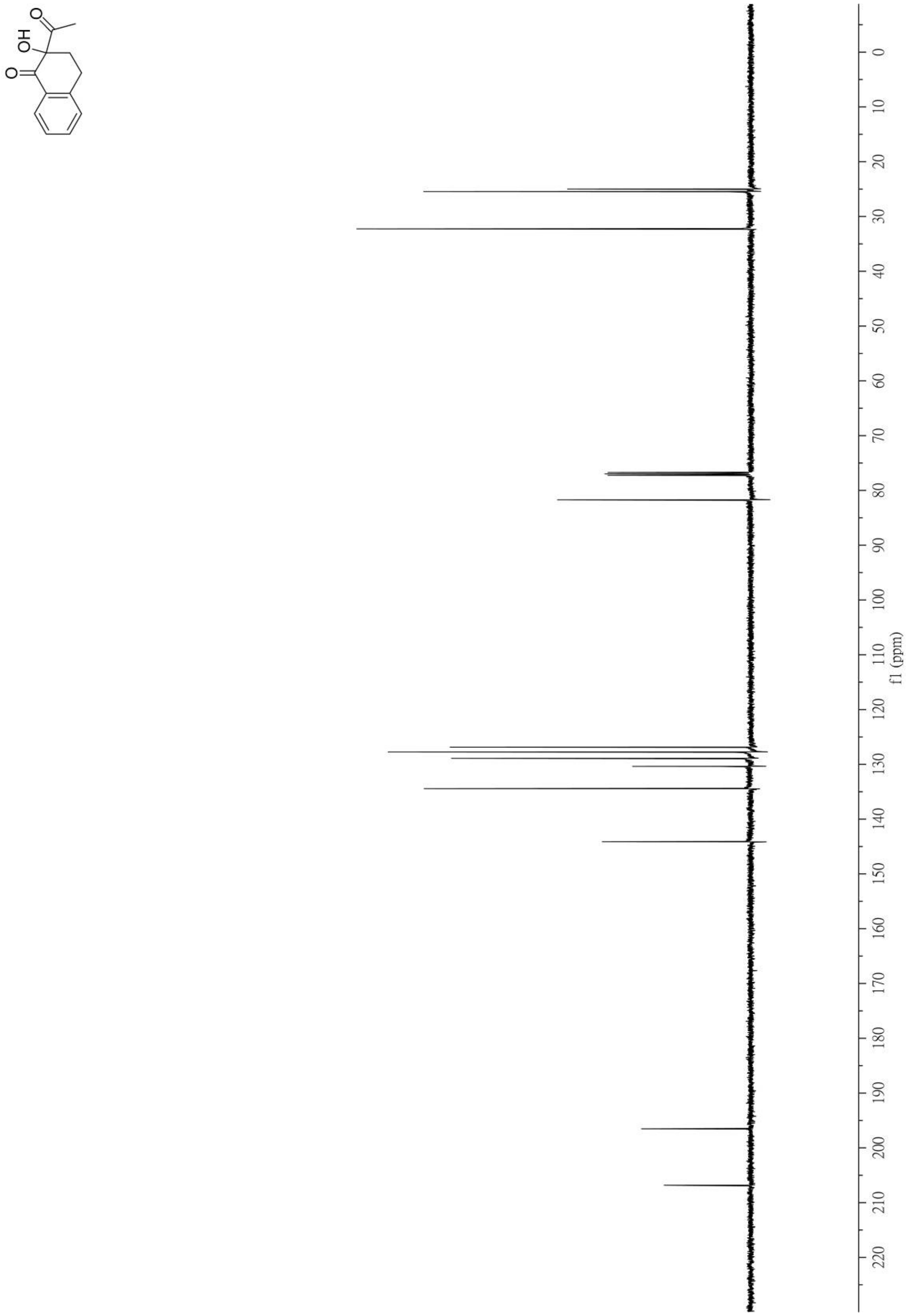
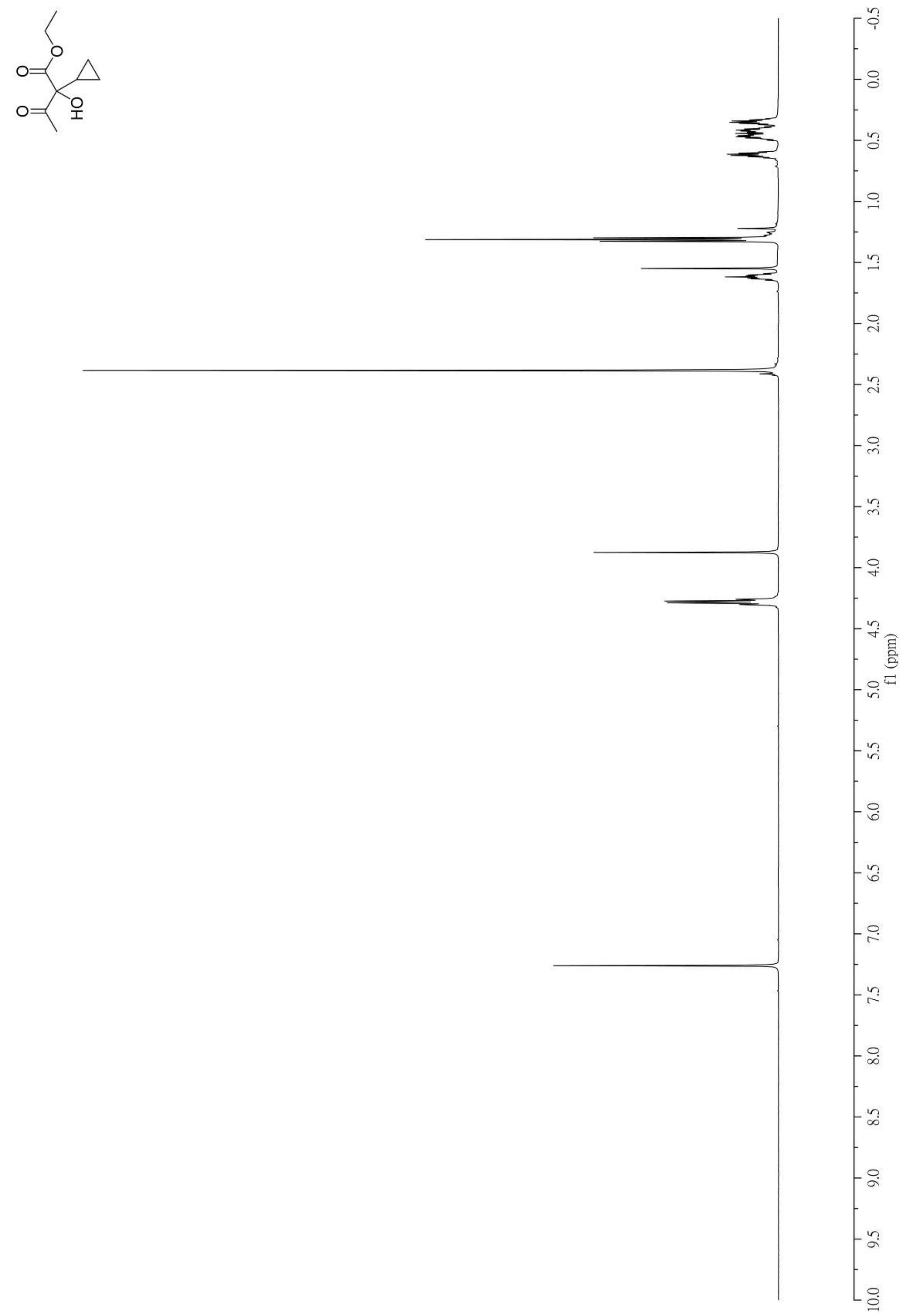
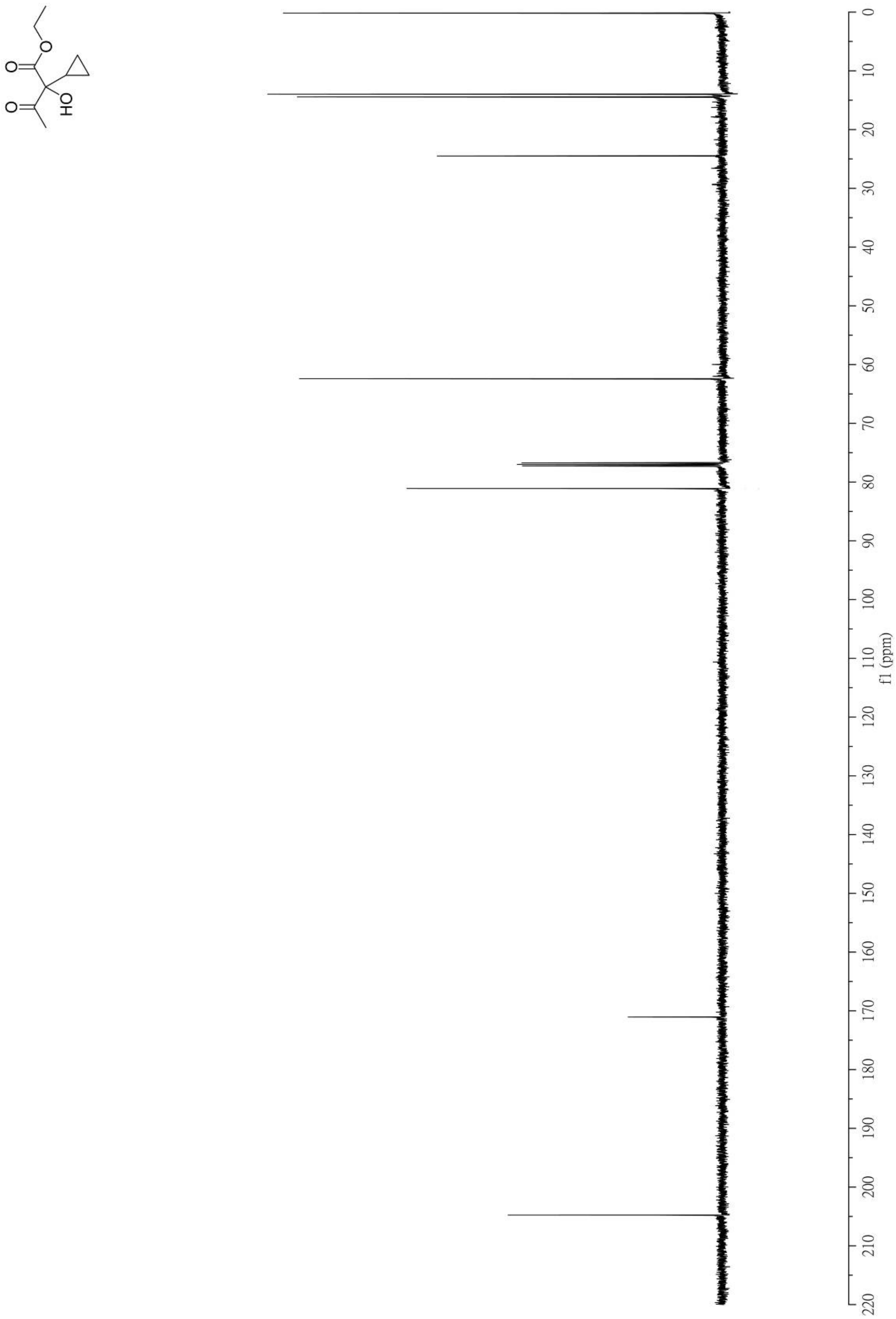


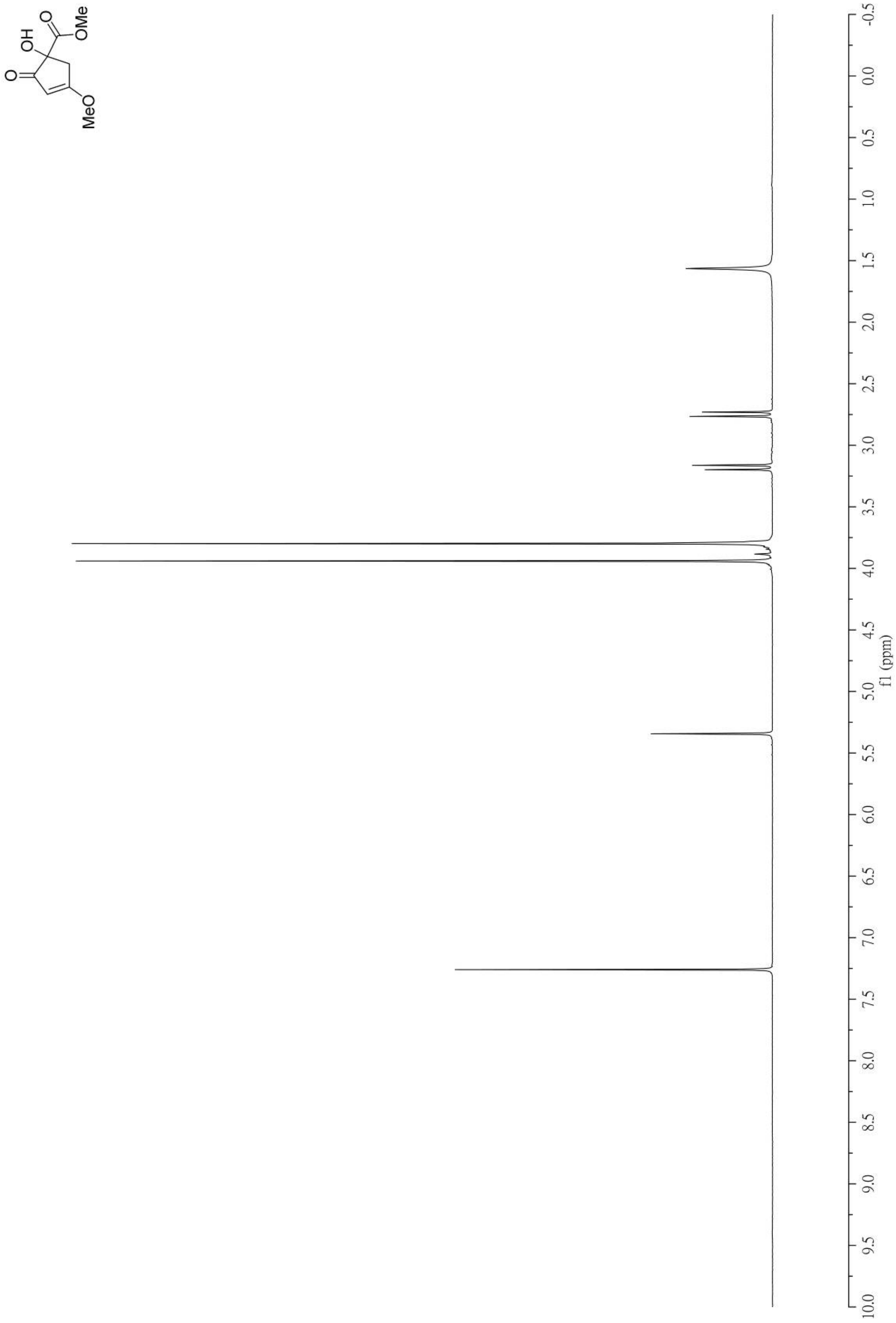
^{13}C NMR spectrum of **5** in $CDCl_3$ at 23 °C



^{1}H NMR spectrum of **6** in $CDCl_3$ at 23 °C



^{13}C NMR spectrum of **6** in CDCl$_3$ at 23 °C



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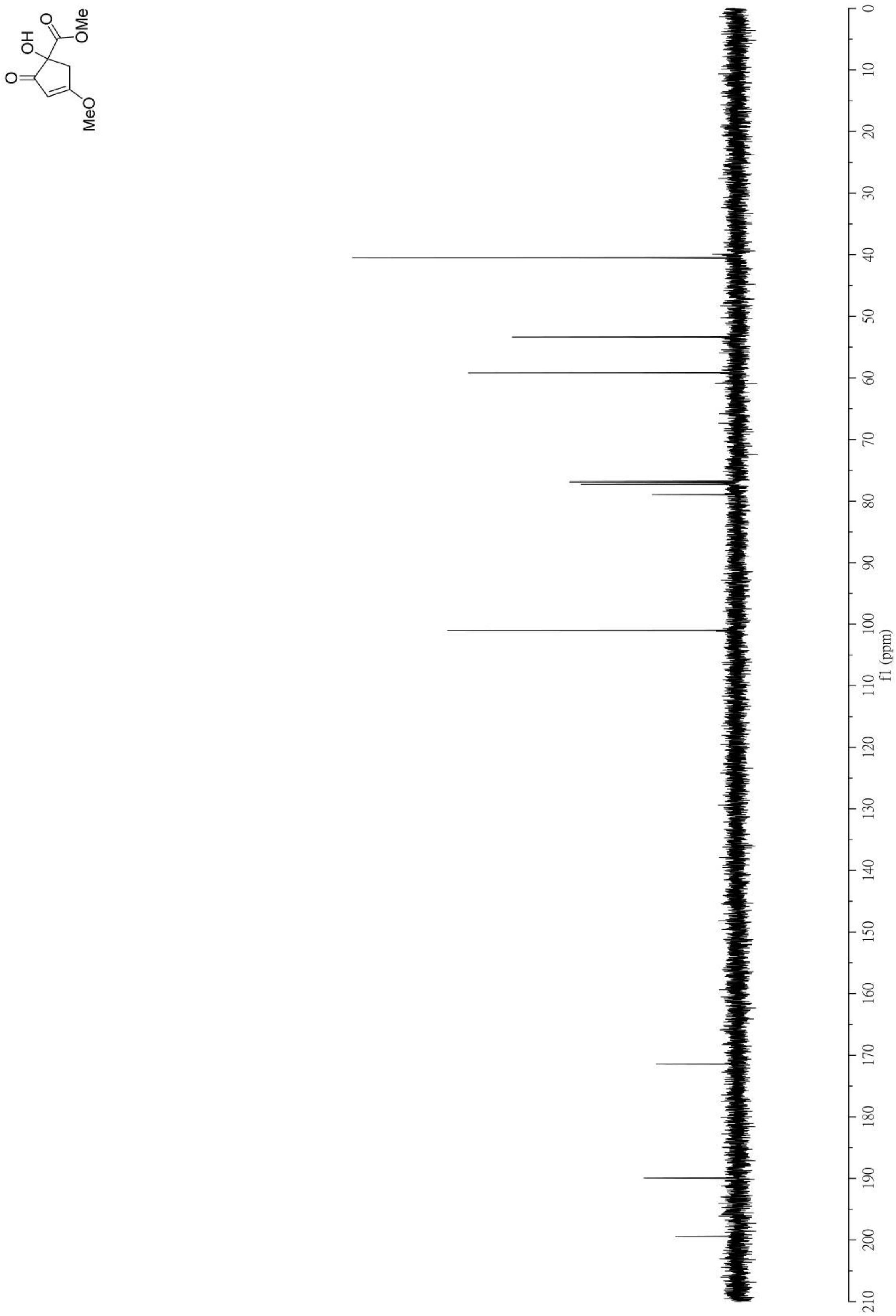
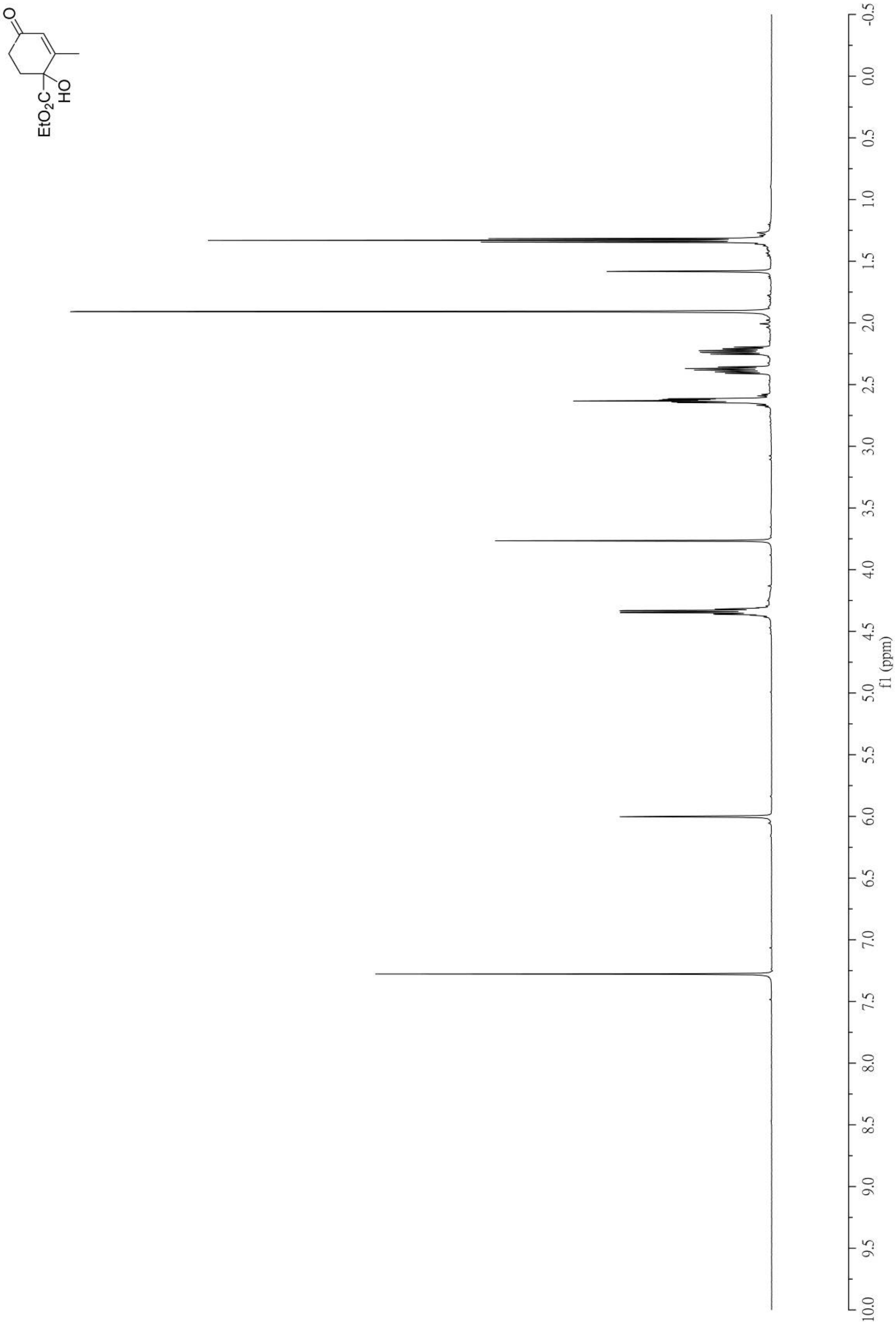
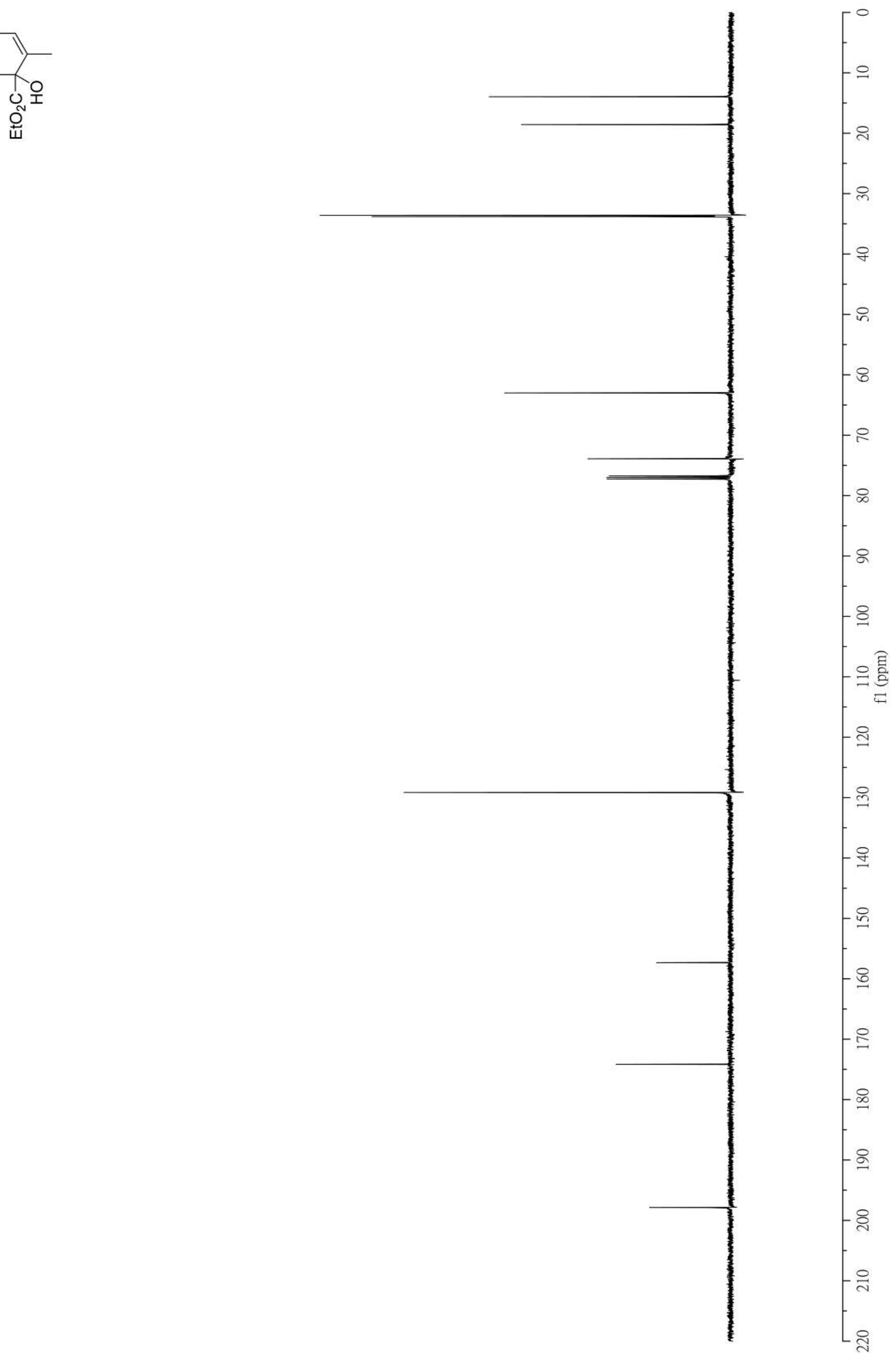


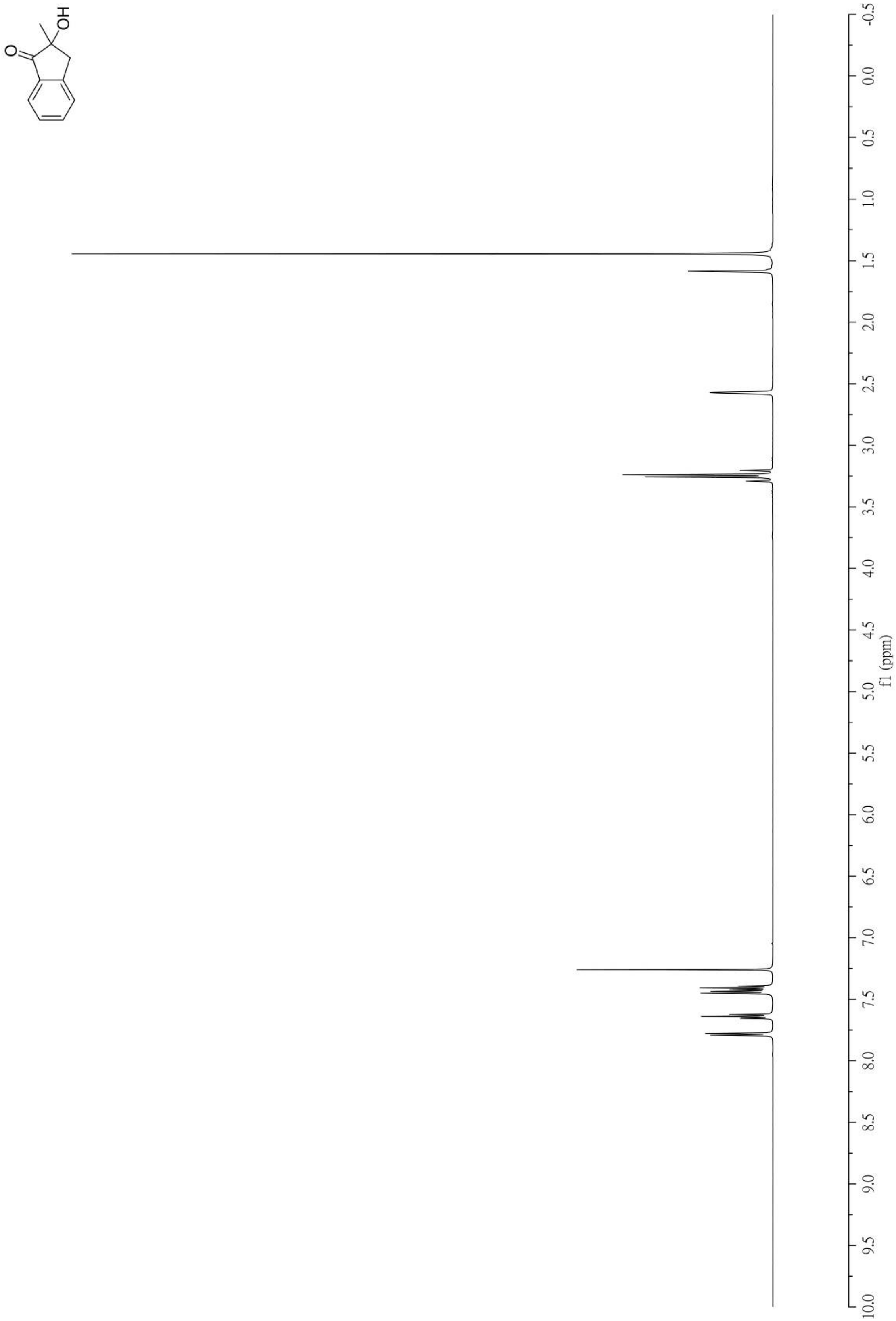
^{13}C NMR spectrum of **7** in CDCl$_3$ at 23 °C



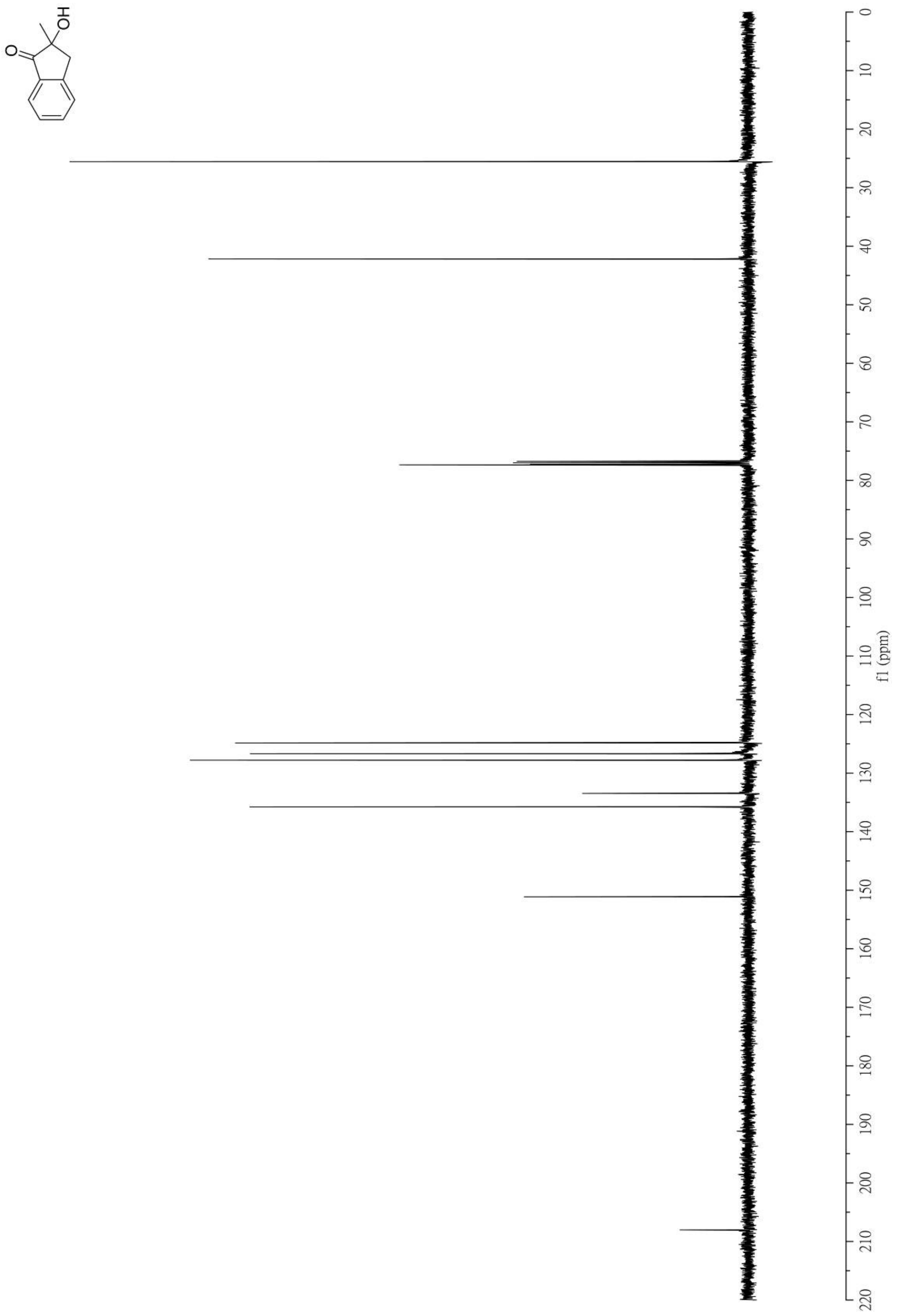
^{1}H NMR spectrum of **8** in CDCl$_3$ at 23 °C



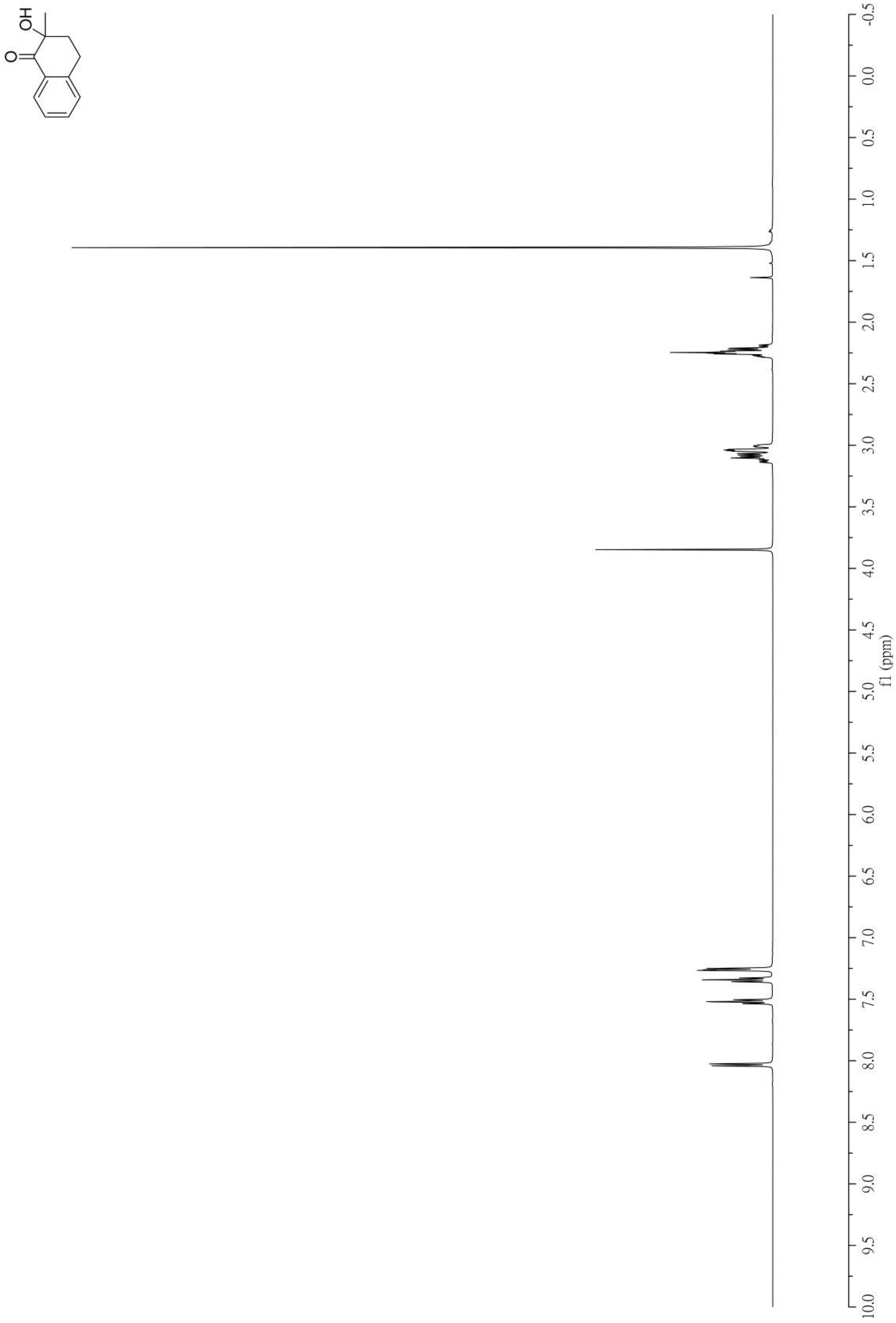
^{13}C NMR spectrum of **8** in $CDCl_3$ at 23 °C



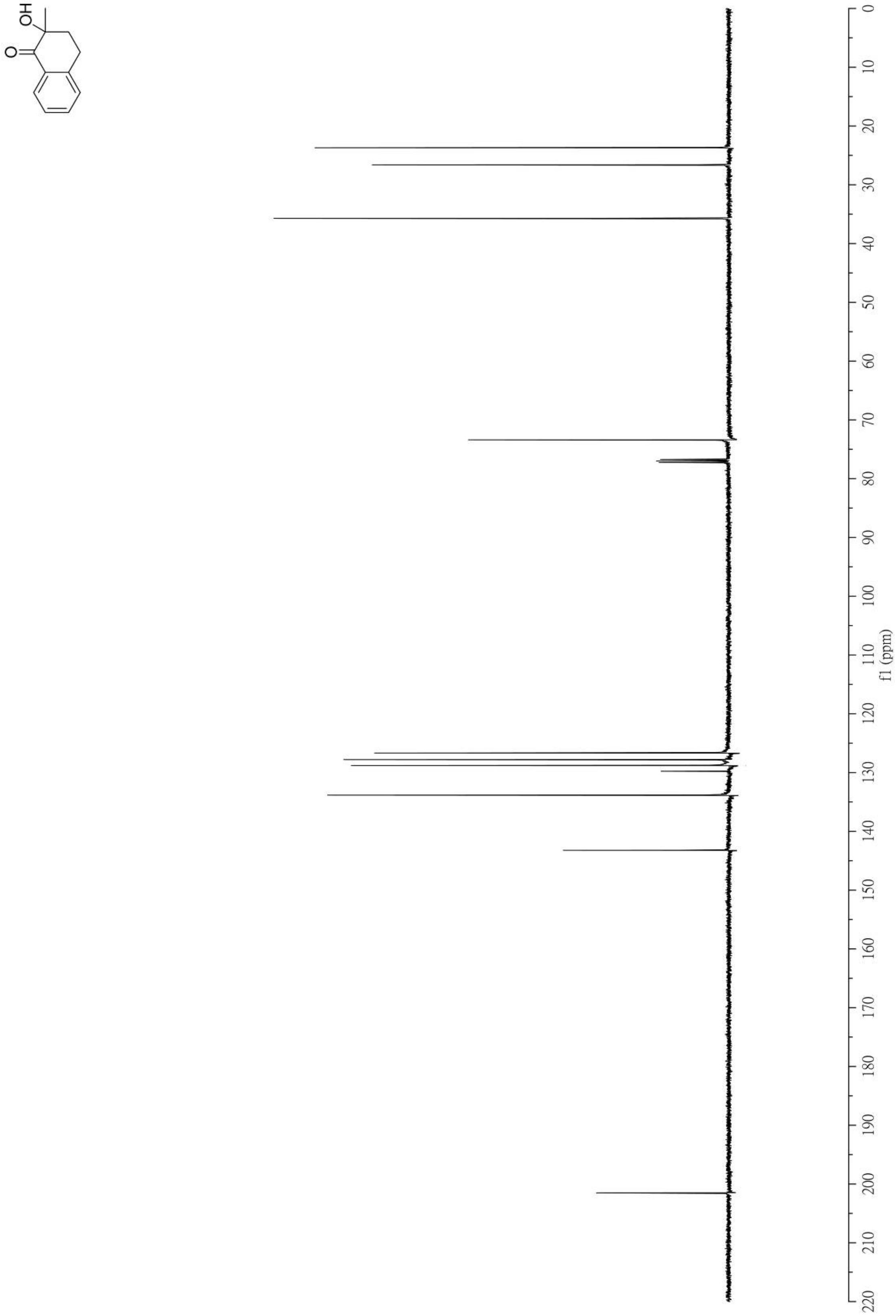
^{1}H NMR spectrum of **9** in $CDCl_3$ at 23 °C



^{13}C NMR spectrum of **9** in $CDCl_3$ at 23 °C



^{1}H NMR spectrum of **10** in $CDCl_3$ at 23 °C



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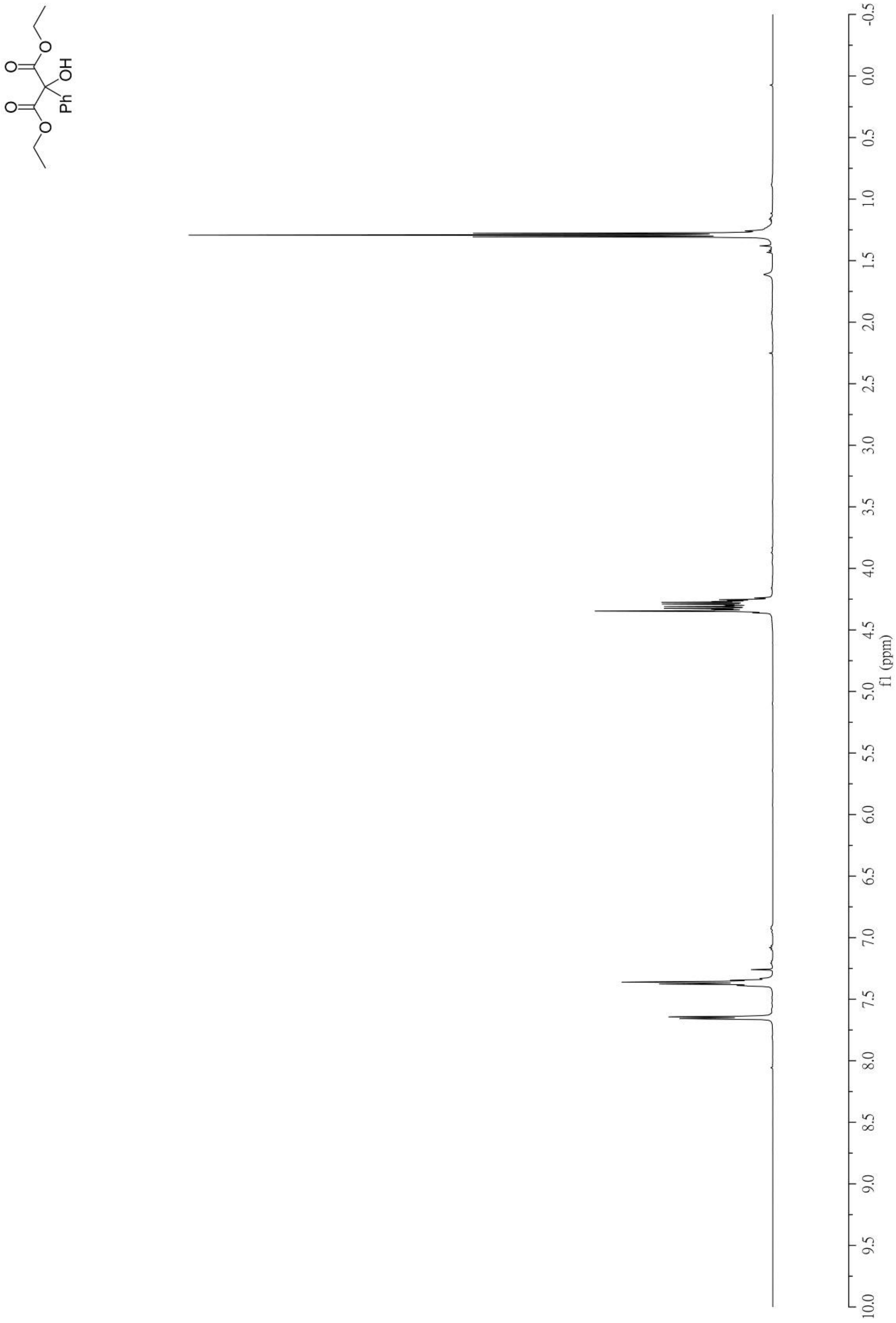
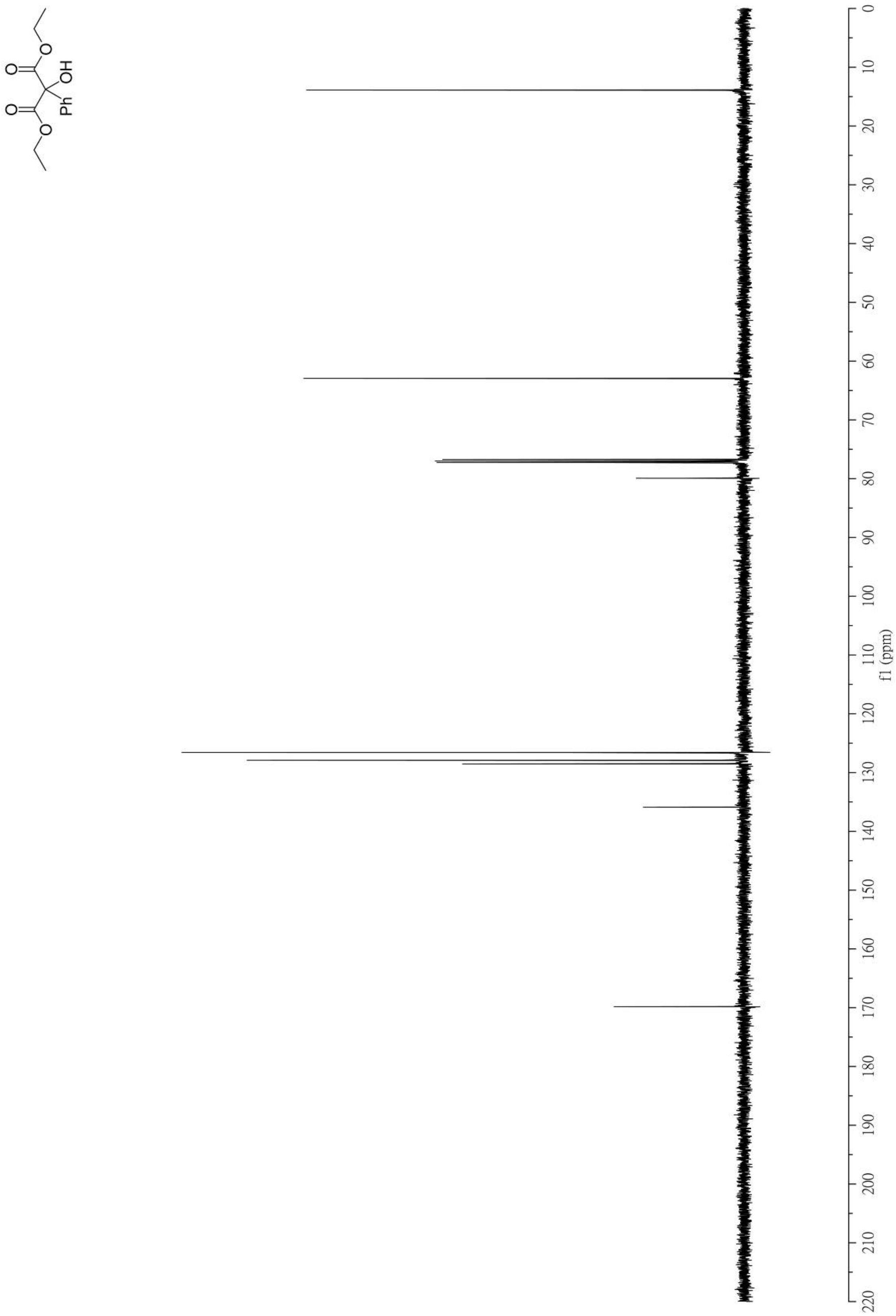


^{1}H NMR spectrum of **11** in $CDCl_3$ at 23 °C



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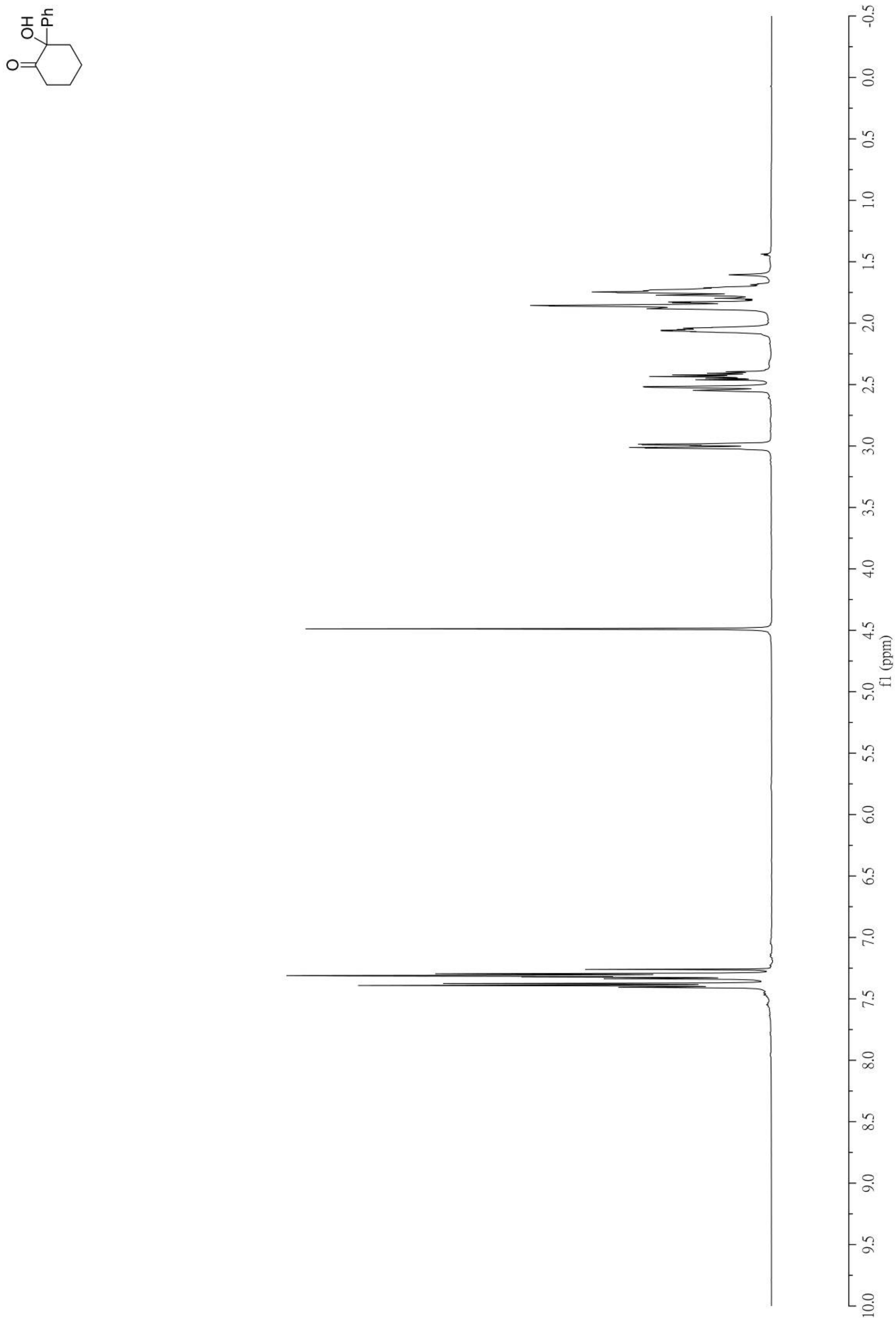
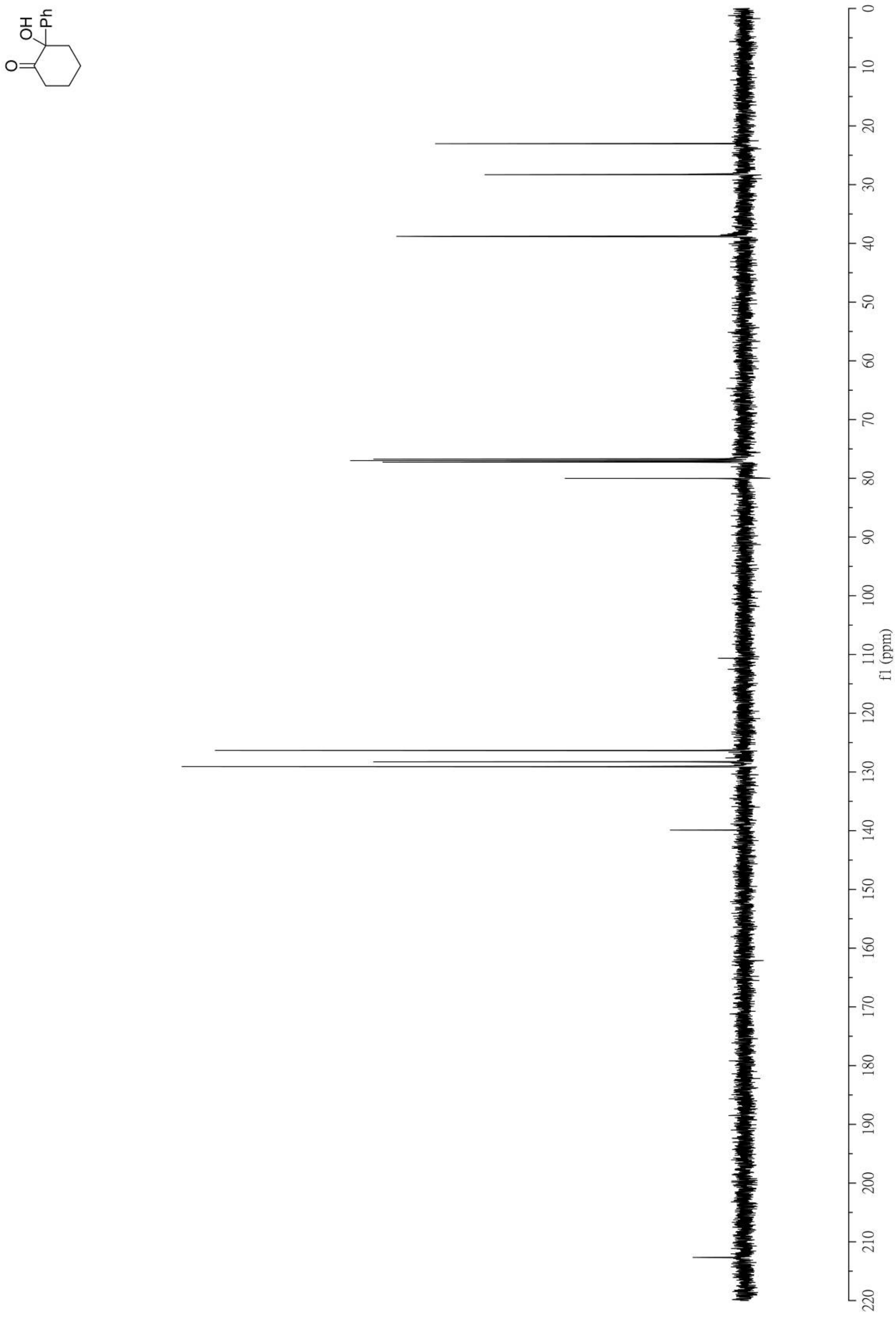
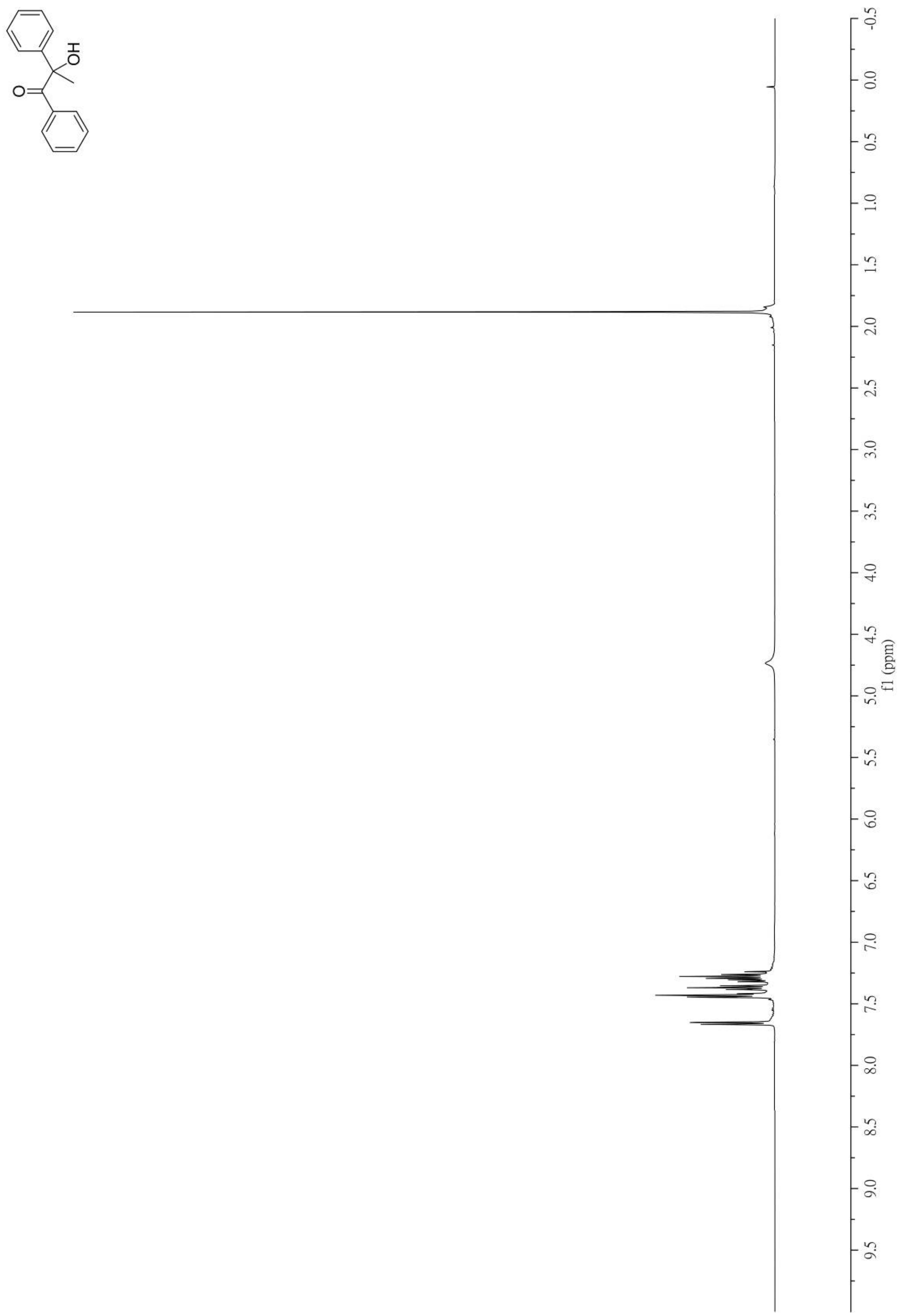


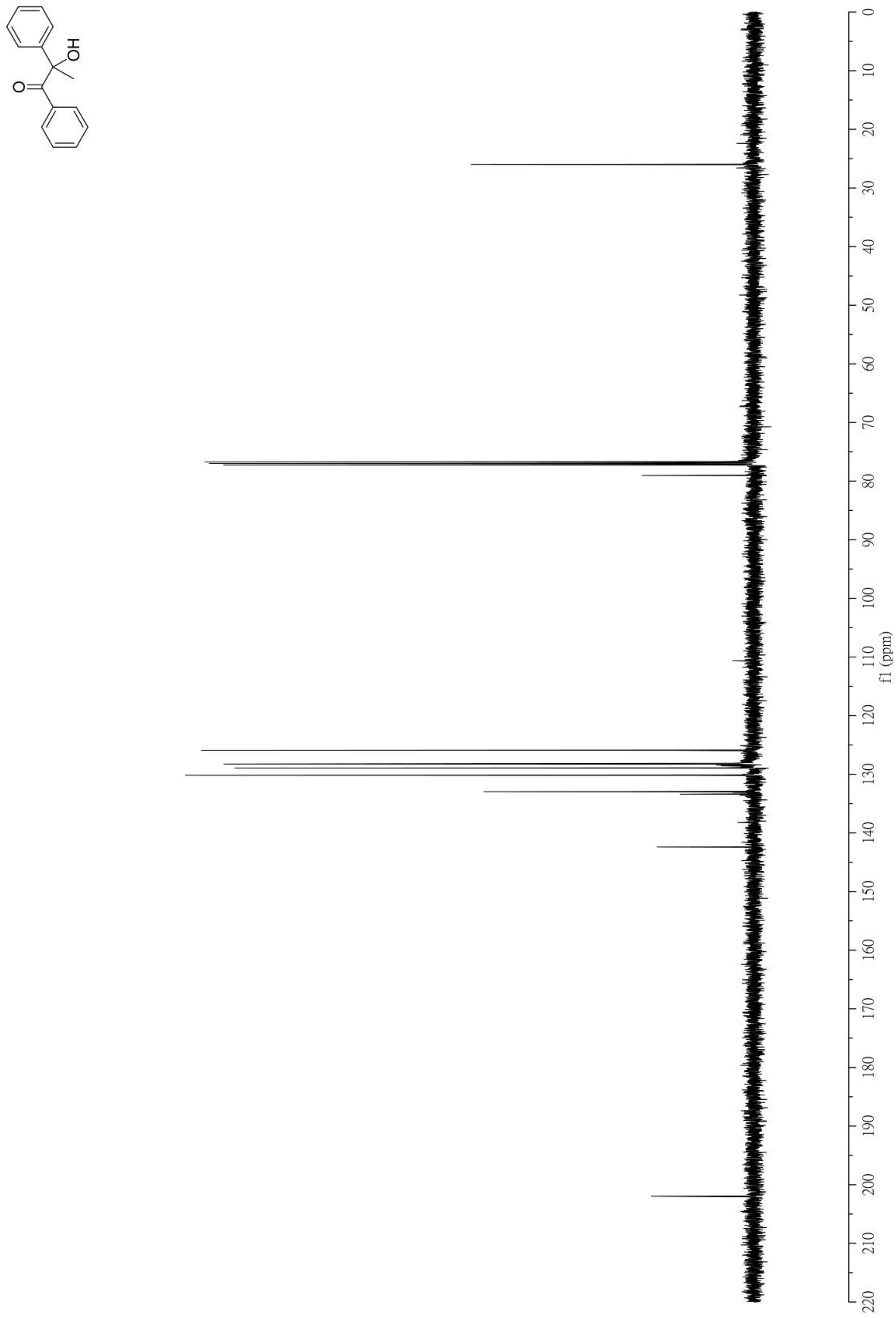
^{1}H NMR spectrum of **12** in $CDCl_3$ at 23 °C



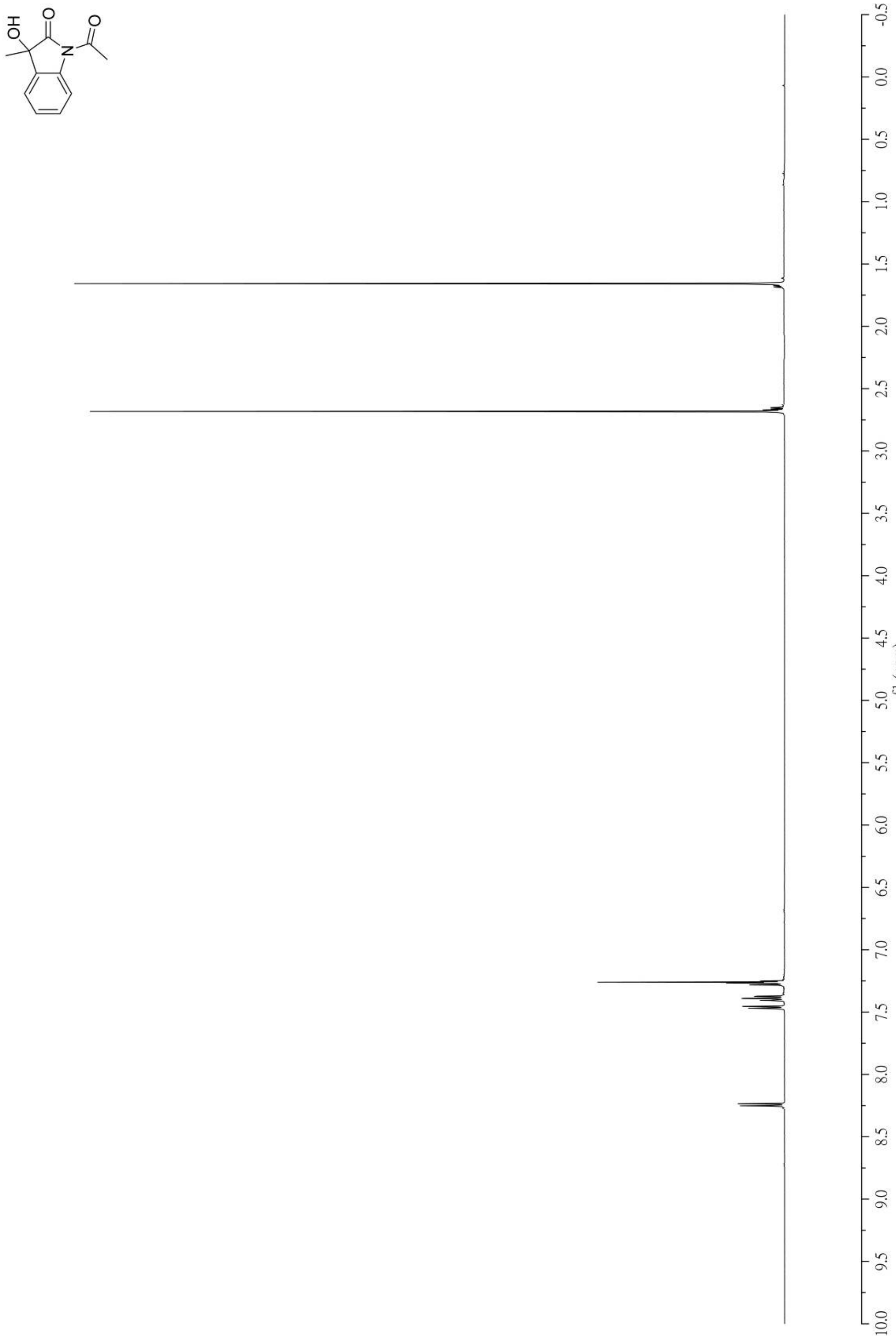
^{13}C NMR spectrum of **12** in $CDCl_3$ at 23 °C



^{1}H NMR spectrum of **13** in $CDCl_3$ at 23 °C



^{13}C NMR spectrum of **13** in CDCl$_3$ at 23 °C



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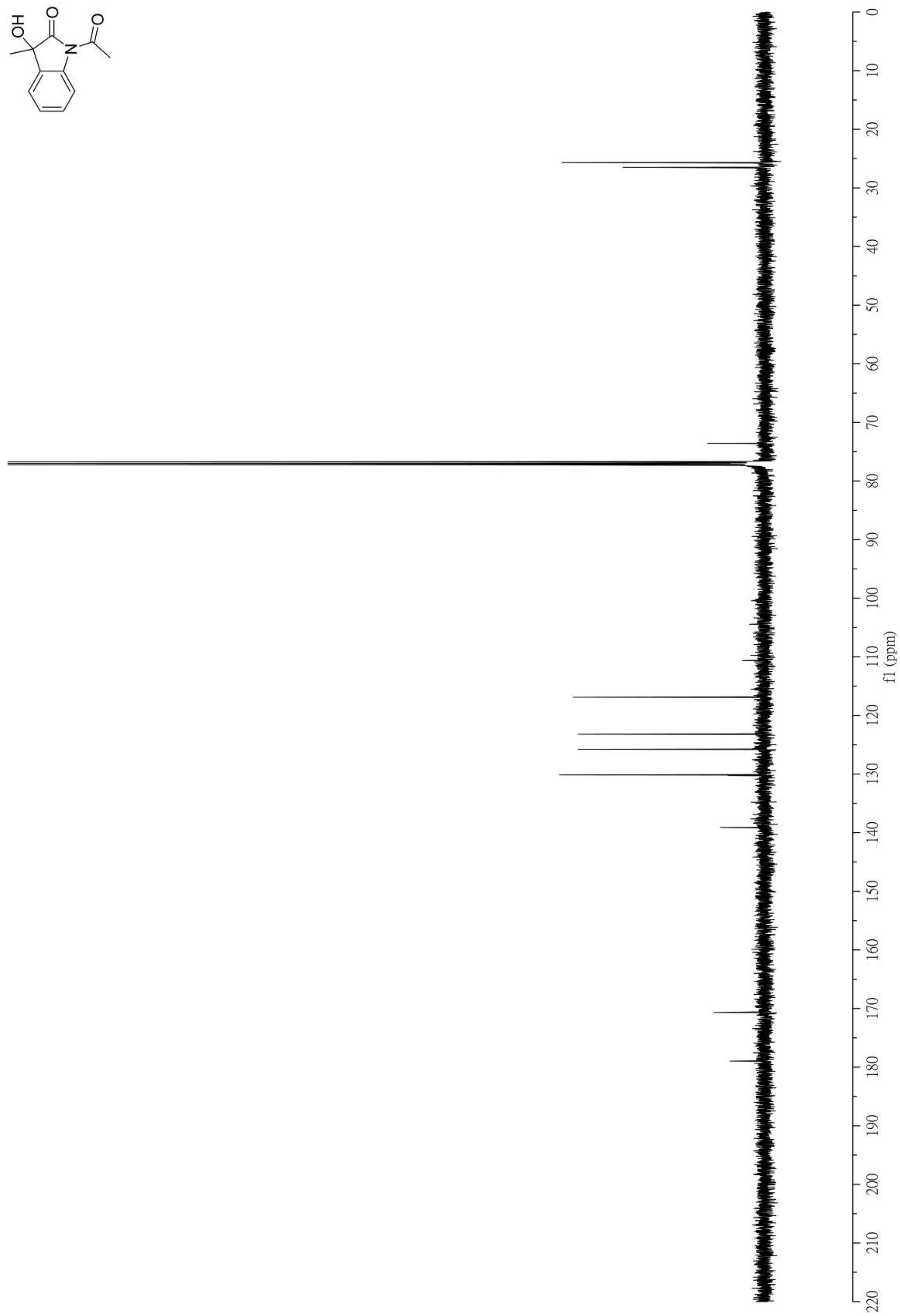

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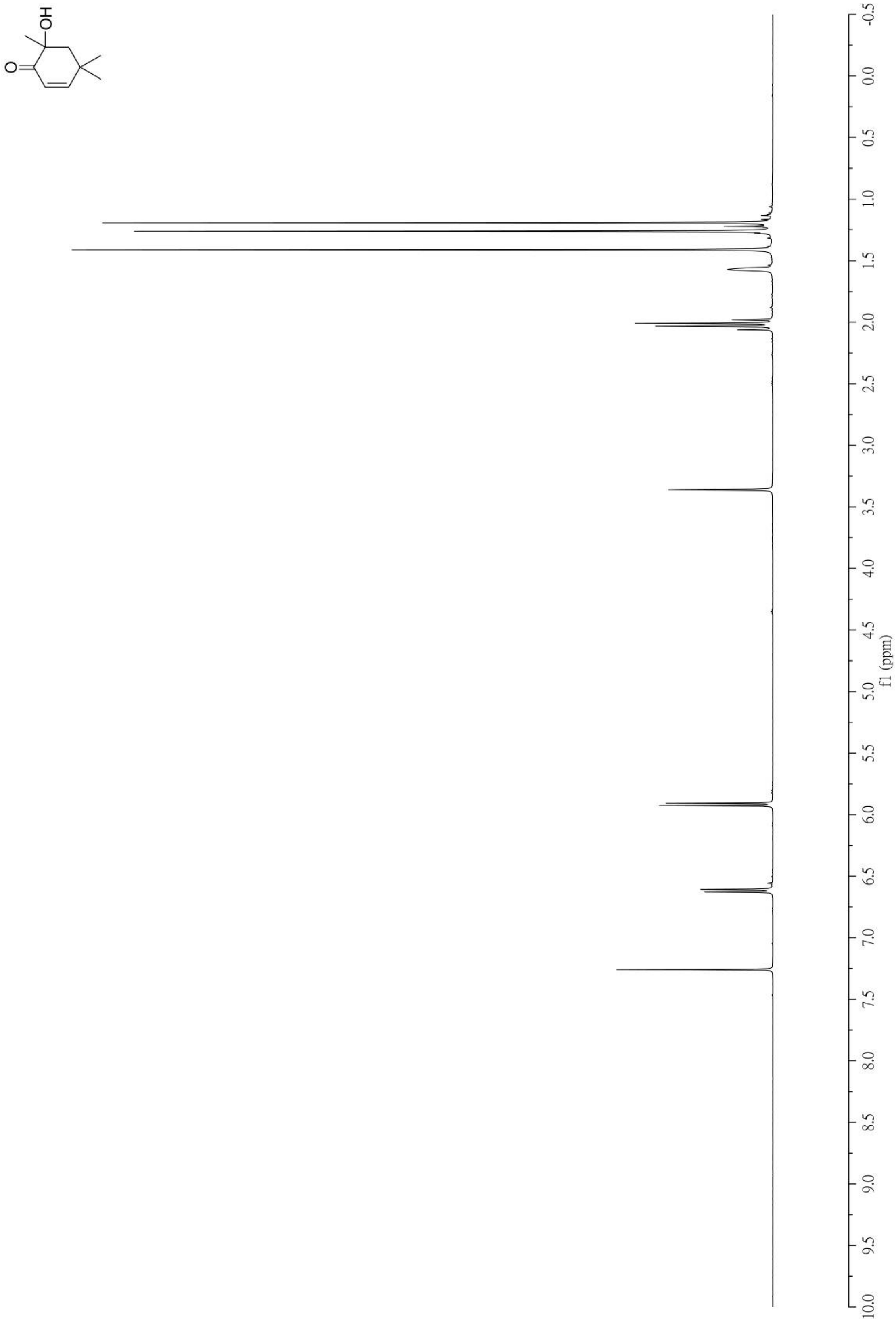

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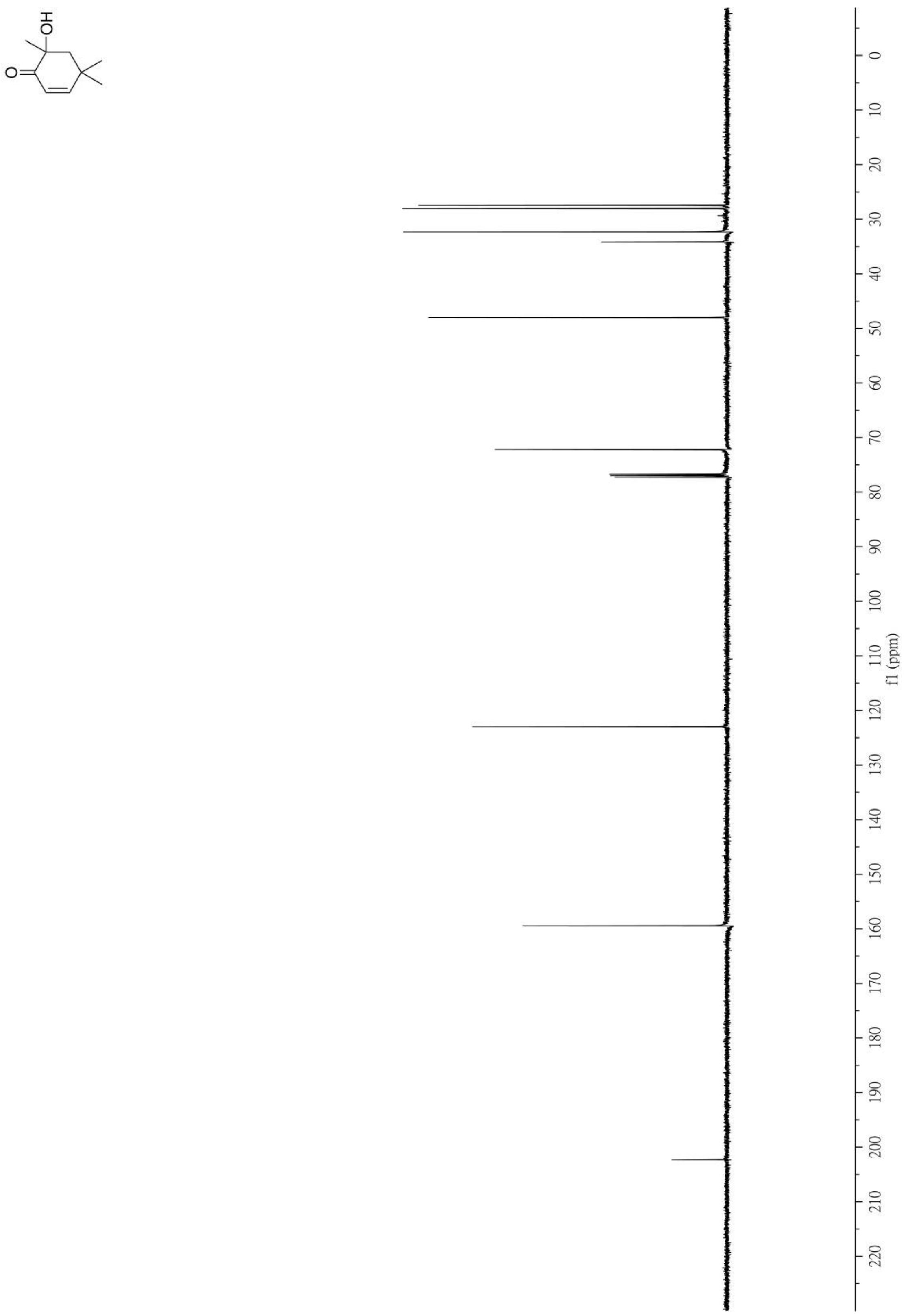

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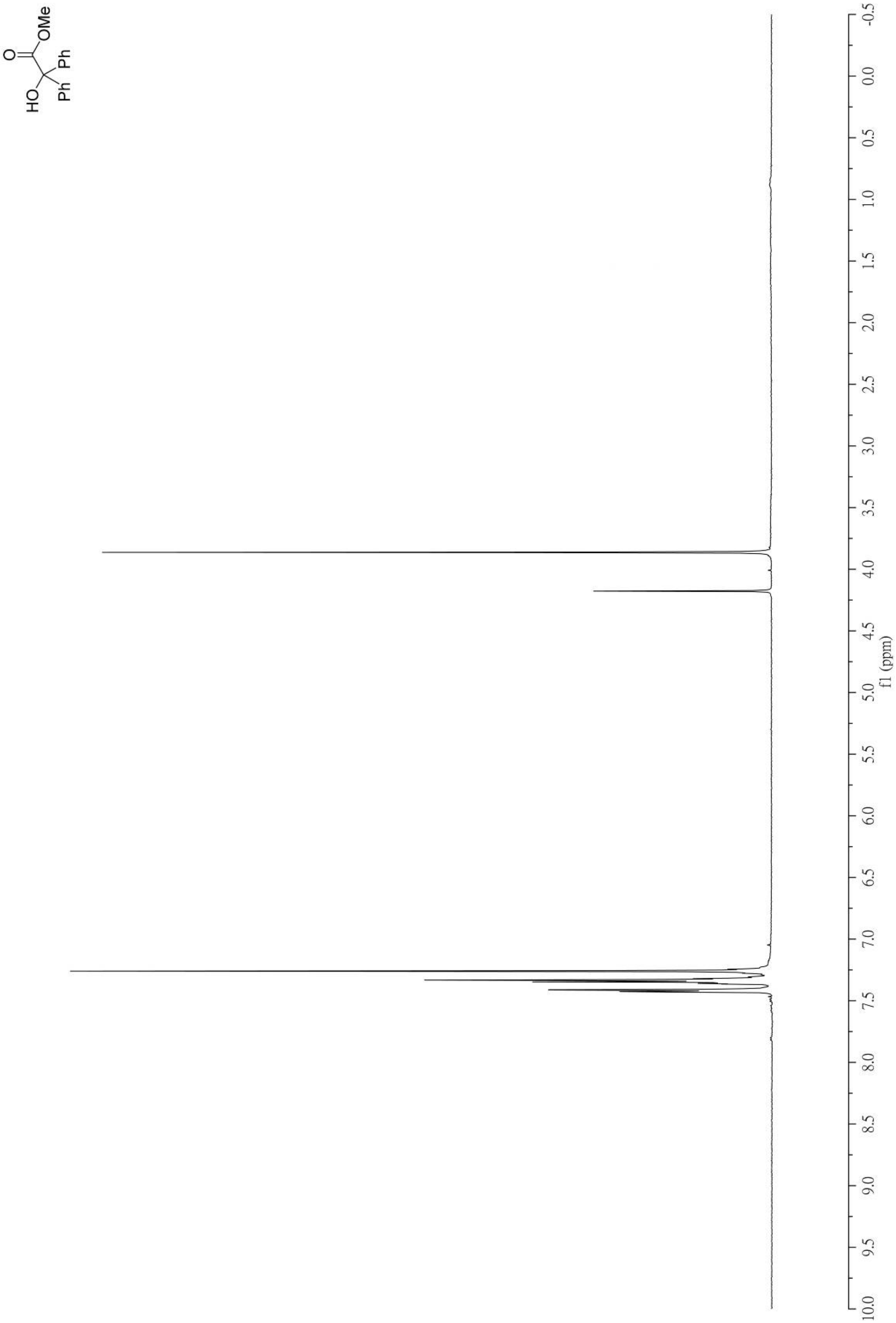

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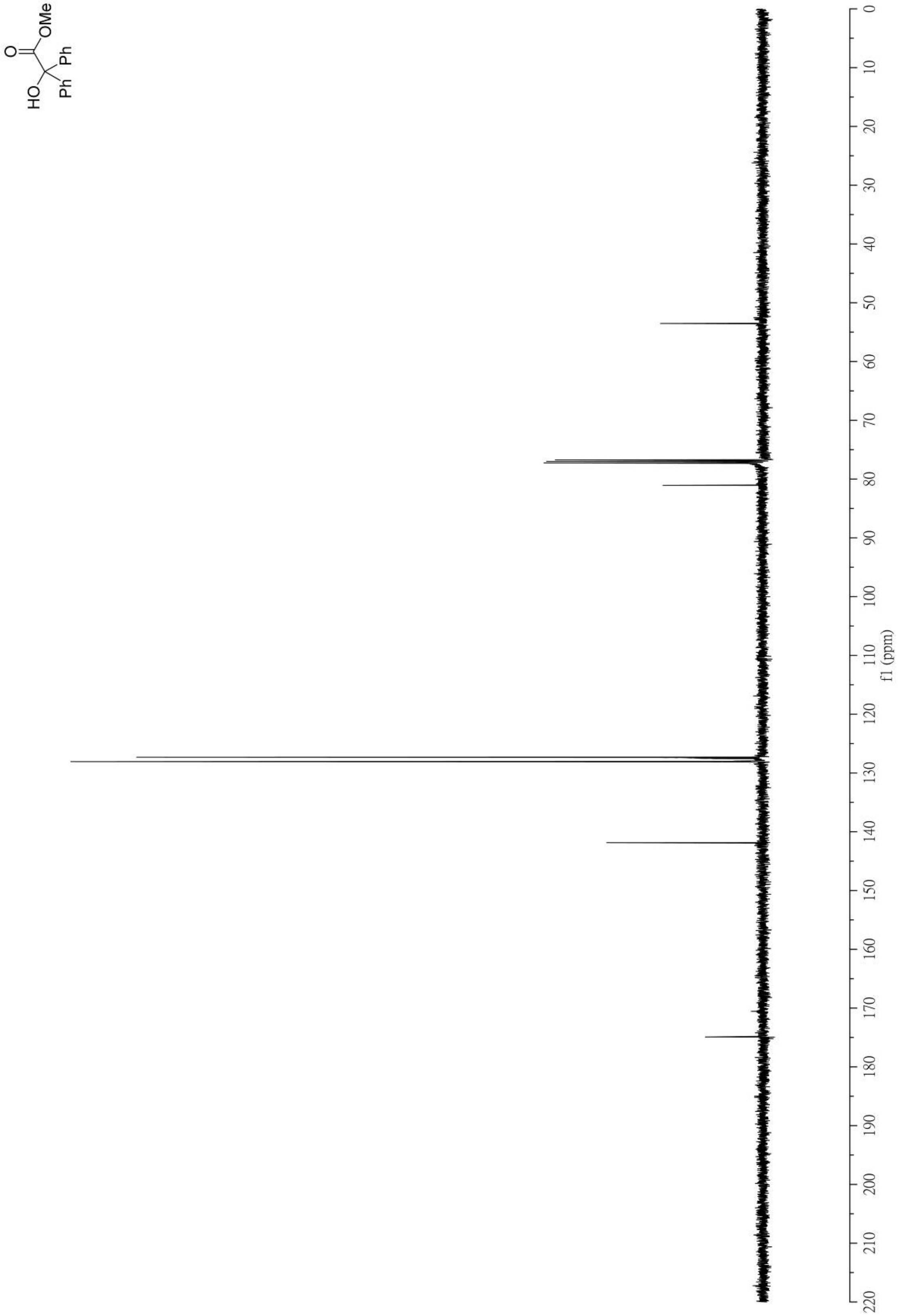
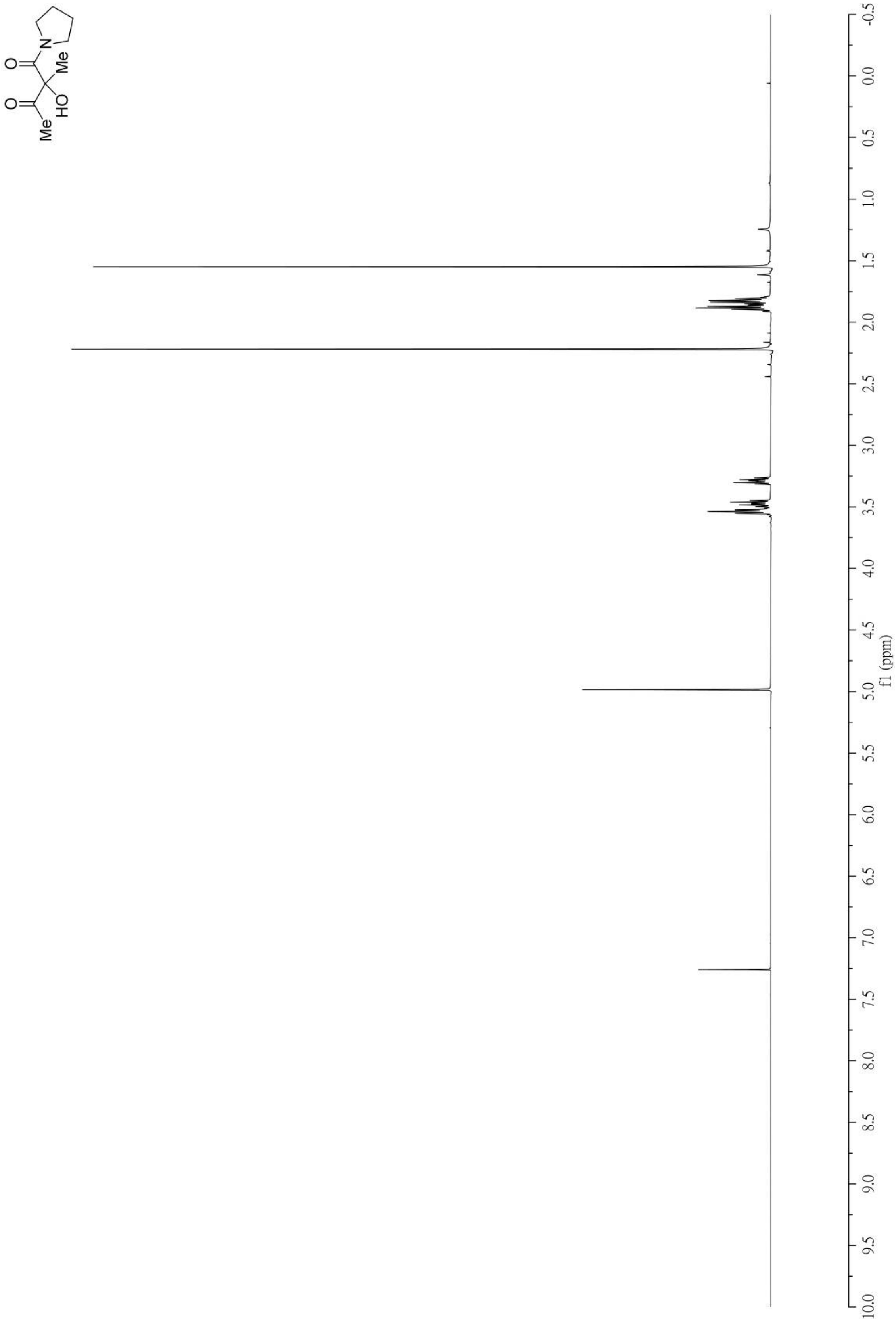


^{13}C NMR spectrum of **16** in $CDCl_3$ at 23 °C



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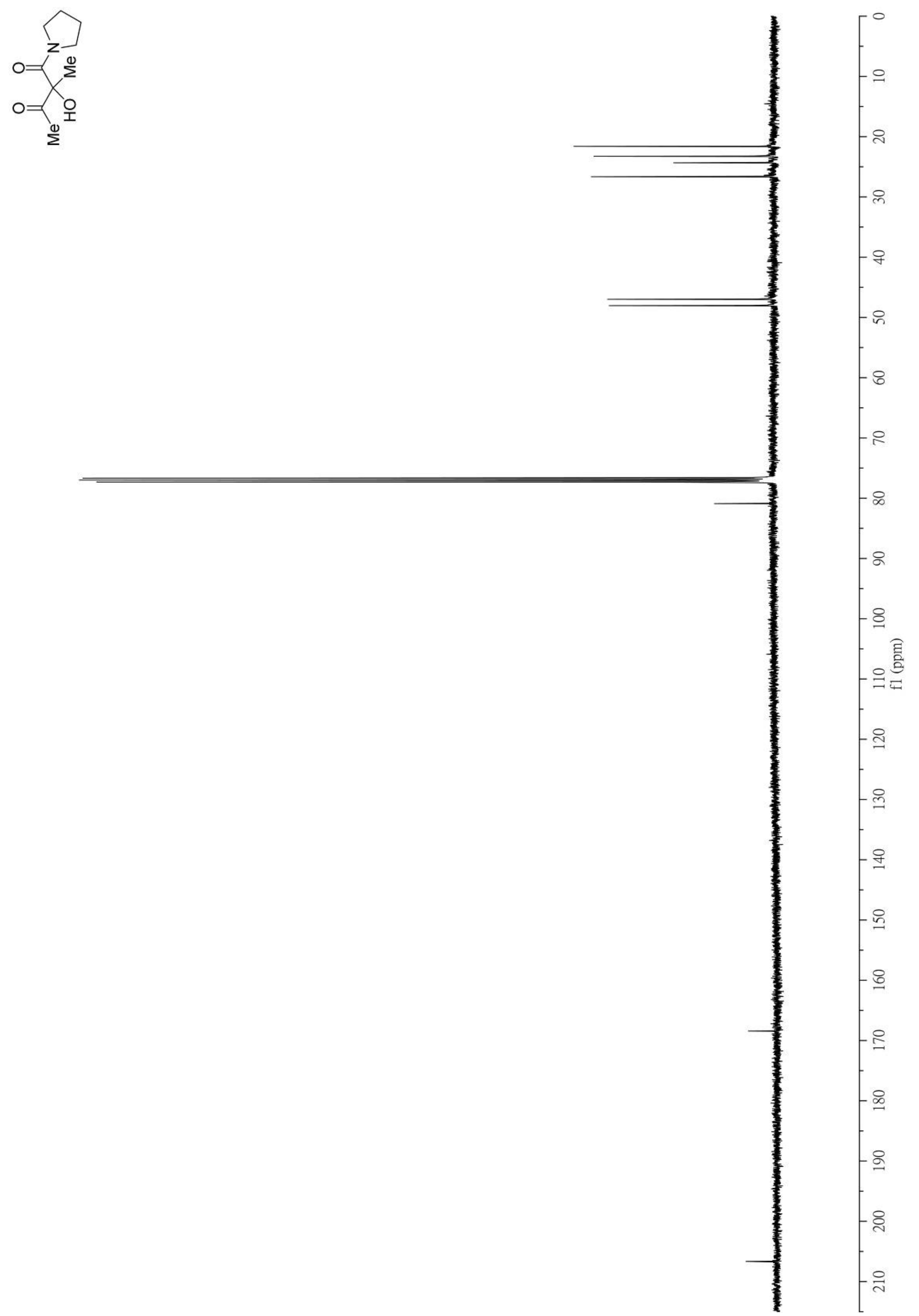

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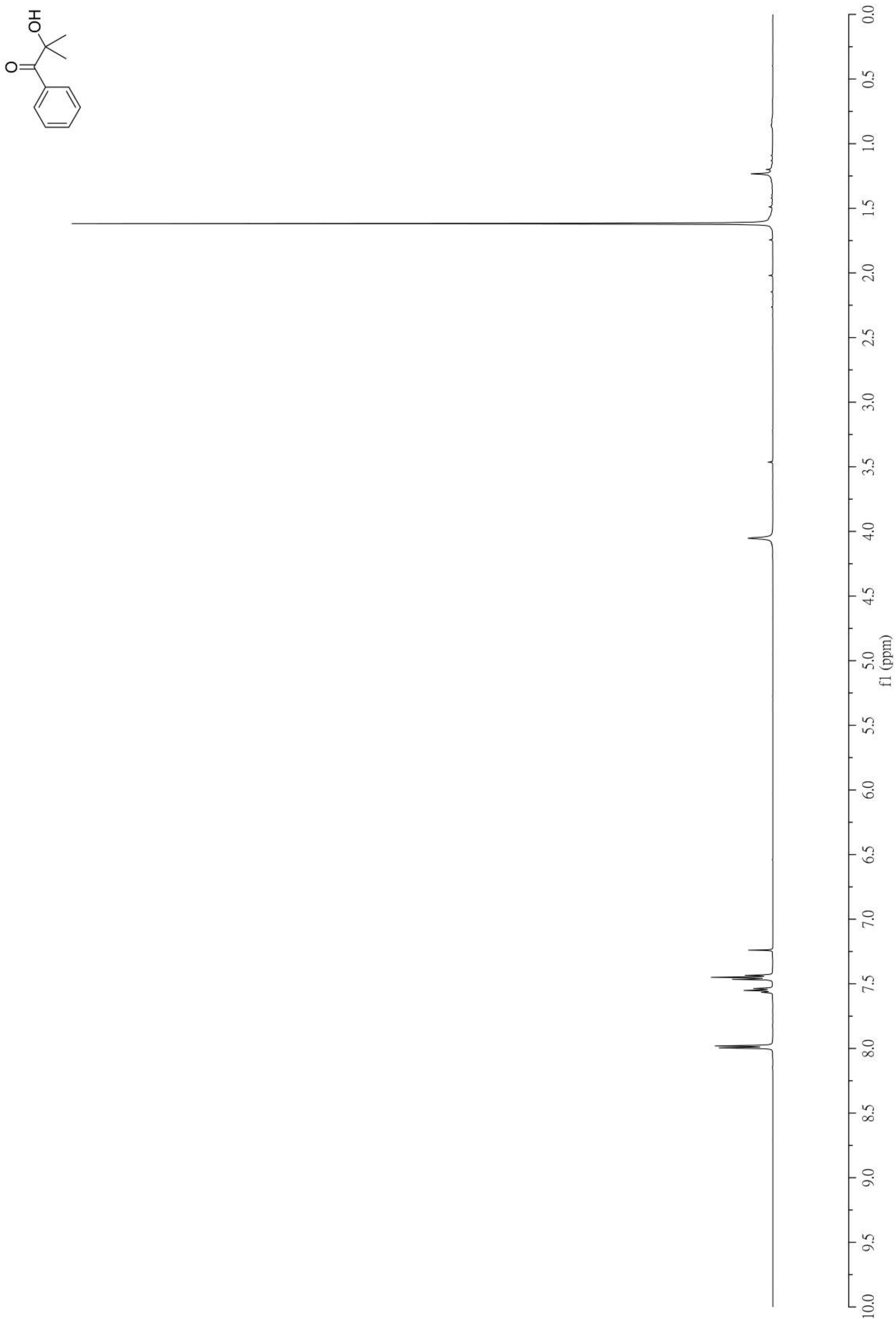

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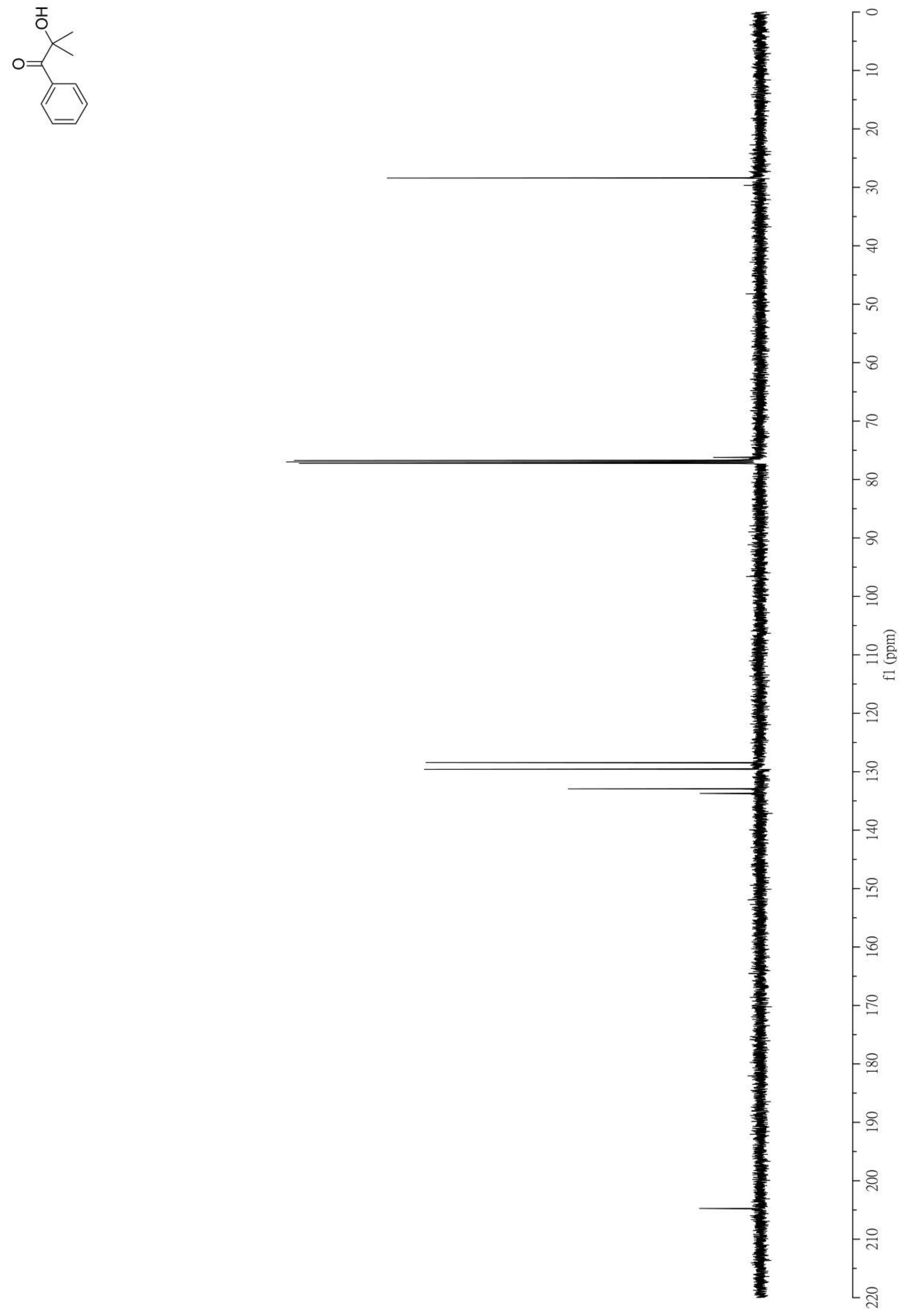
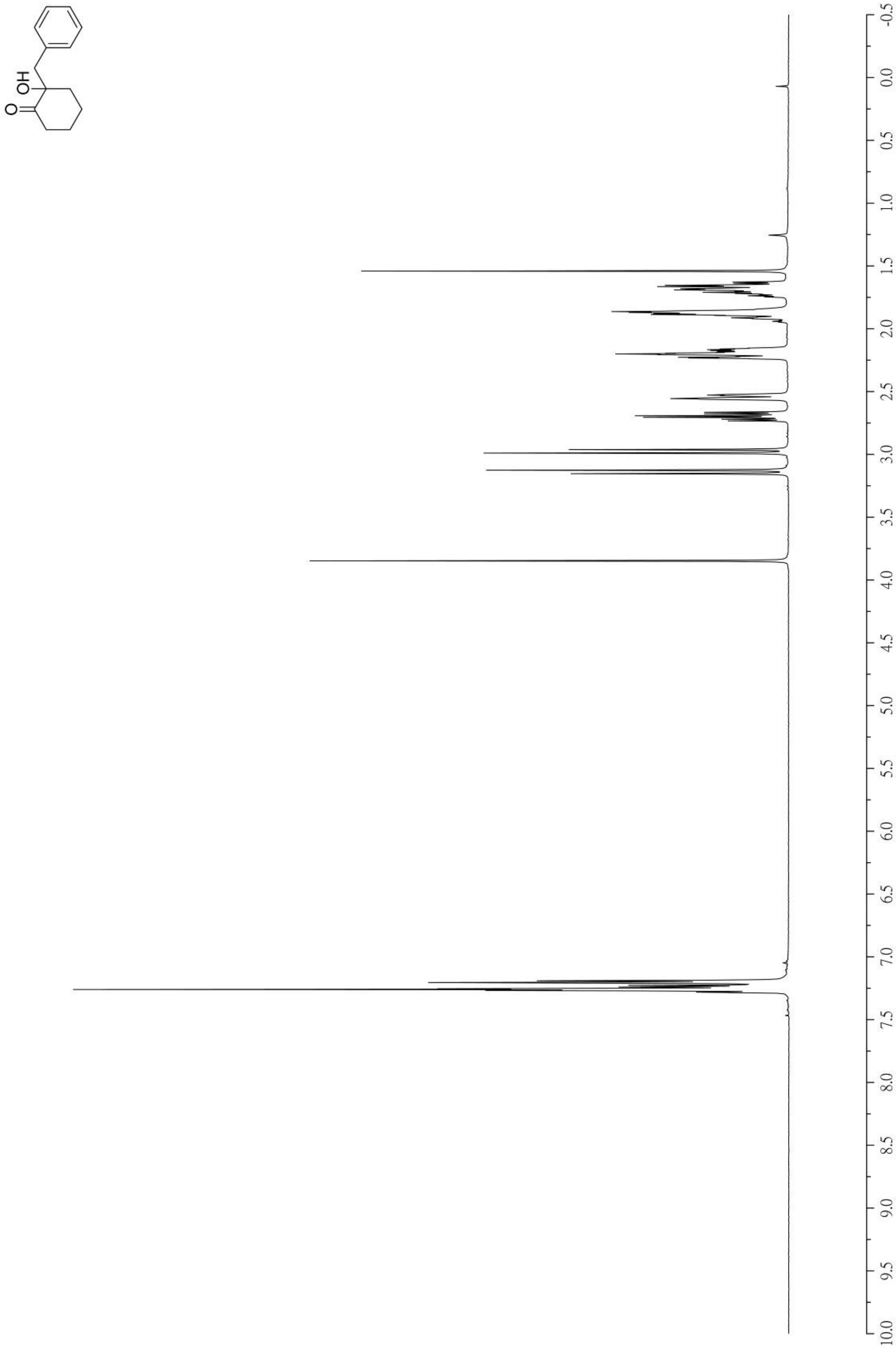


^{13}C NMR spectrum of **18** in $CDCl_3$ at 23 °C



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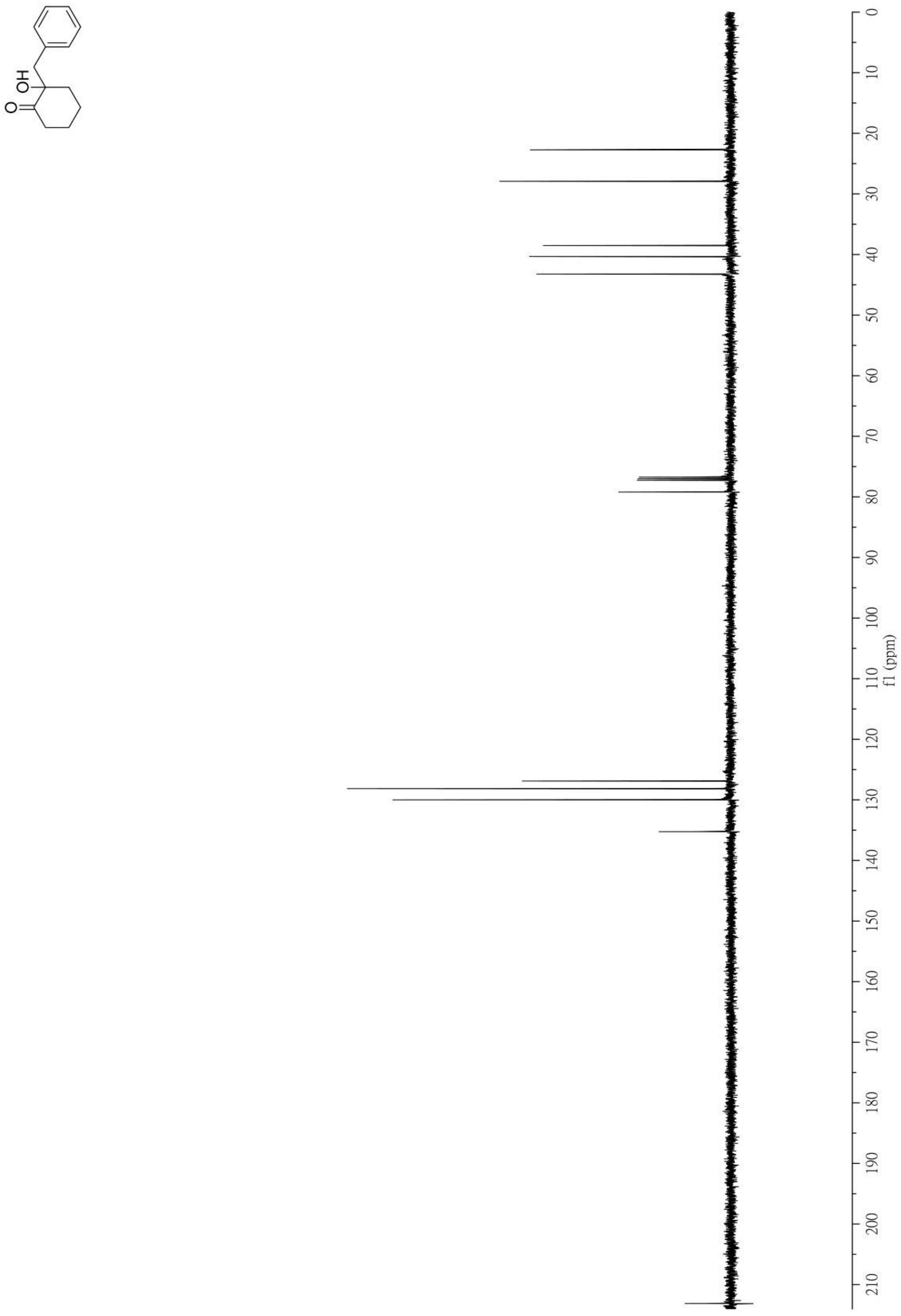

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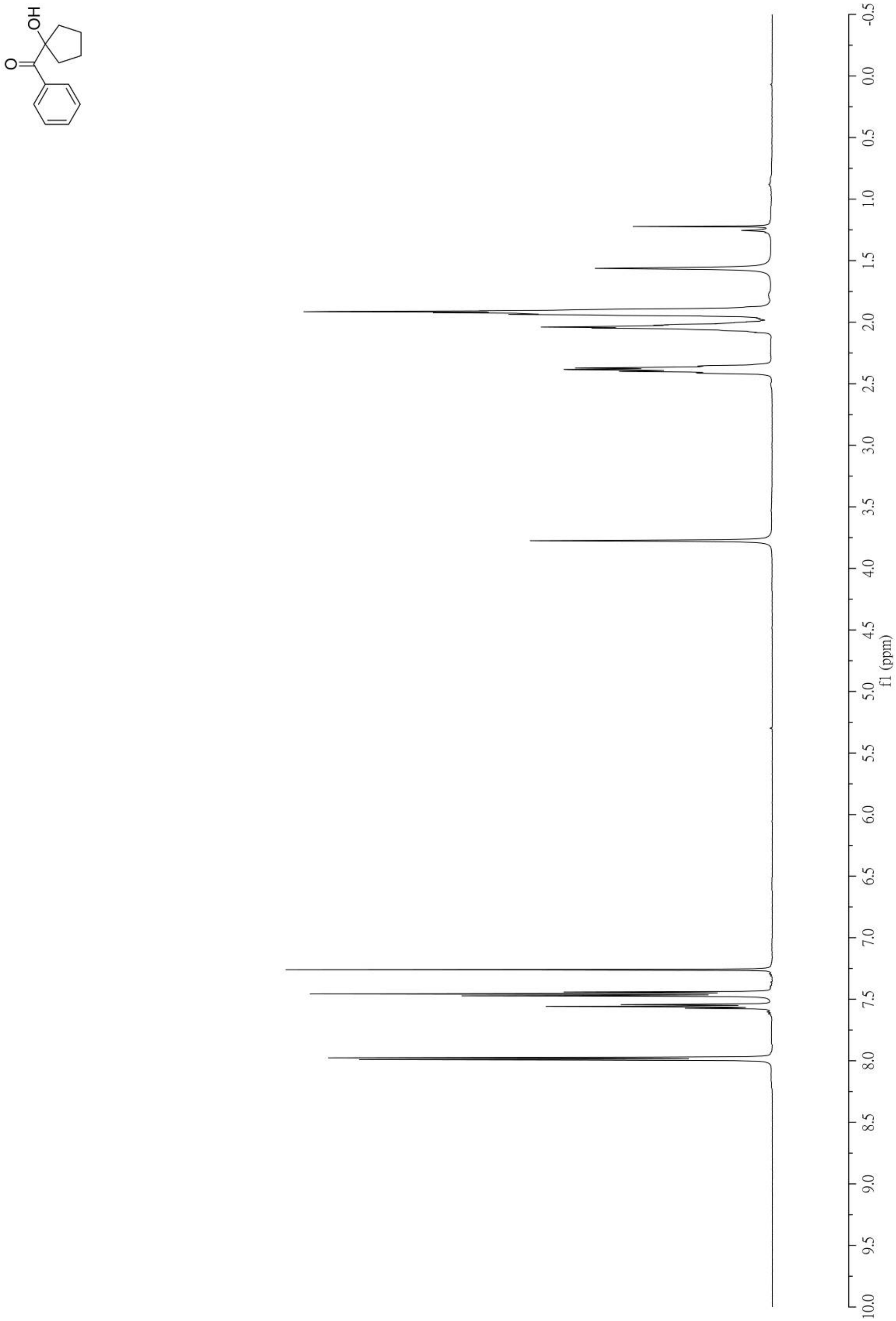

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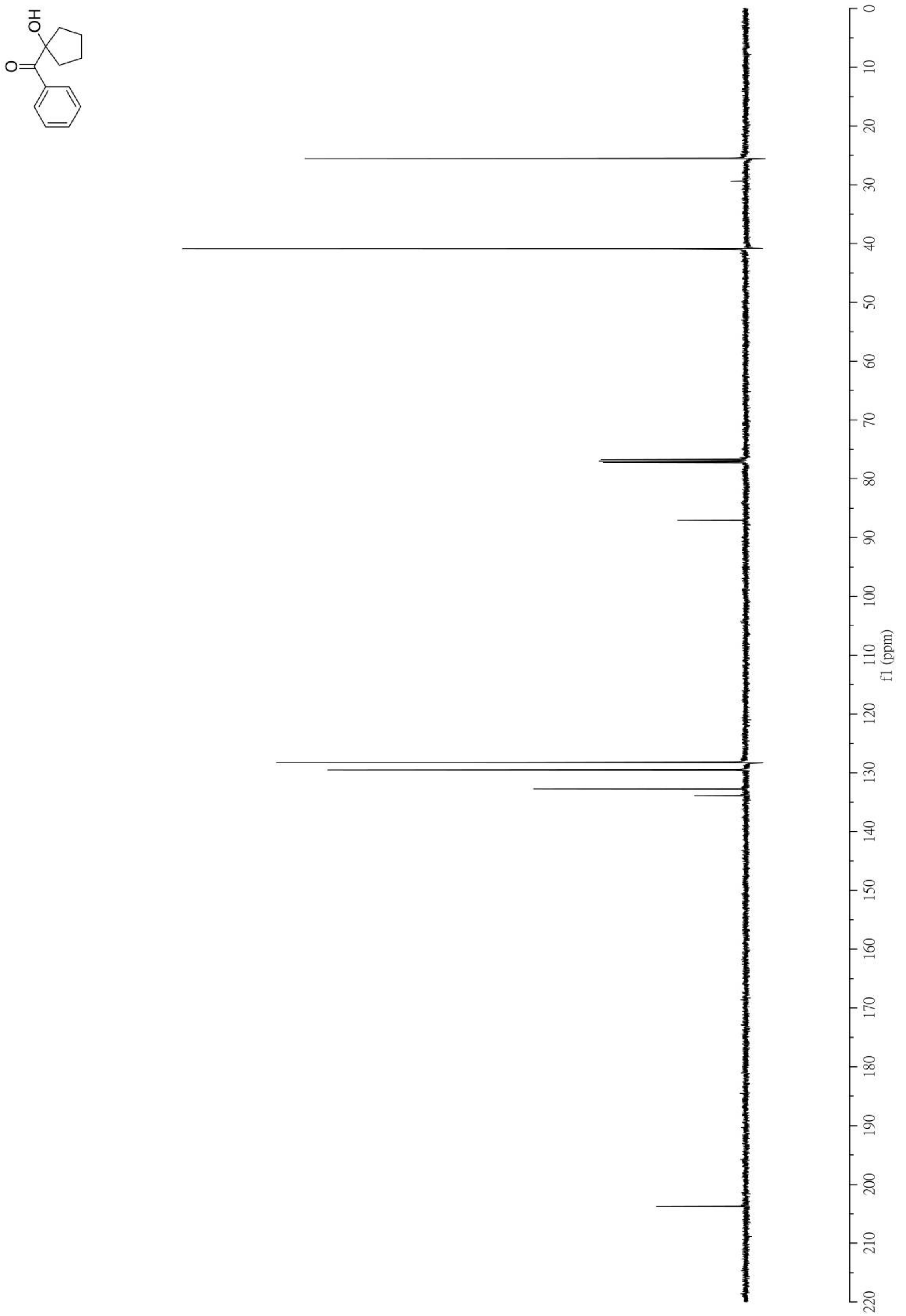

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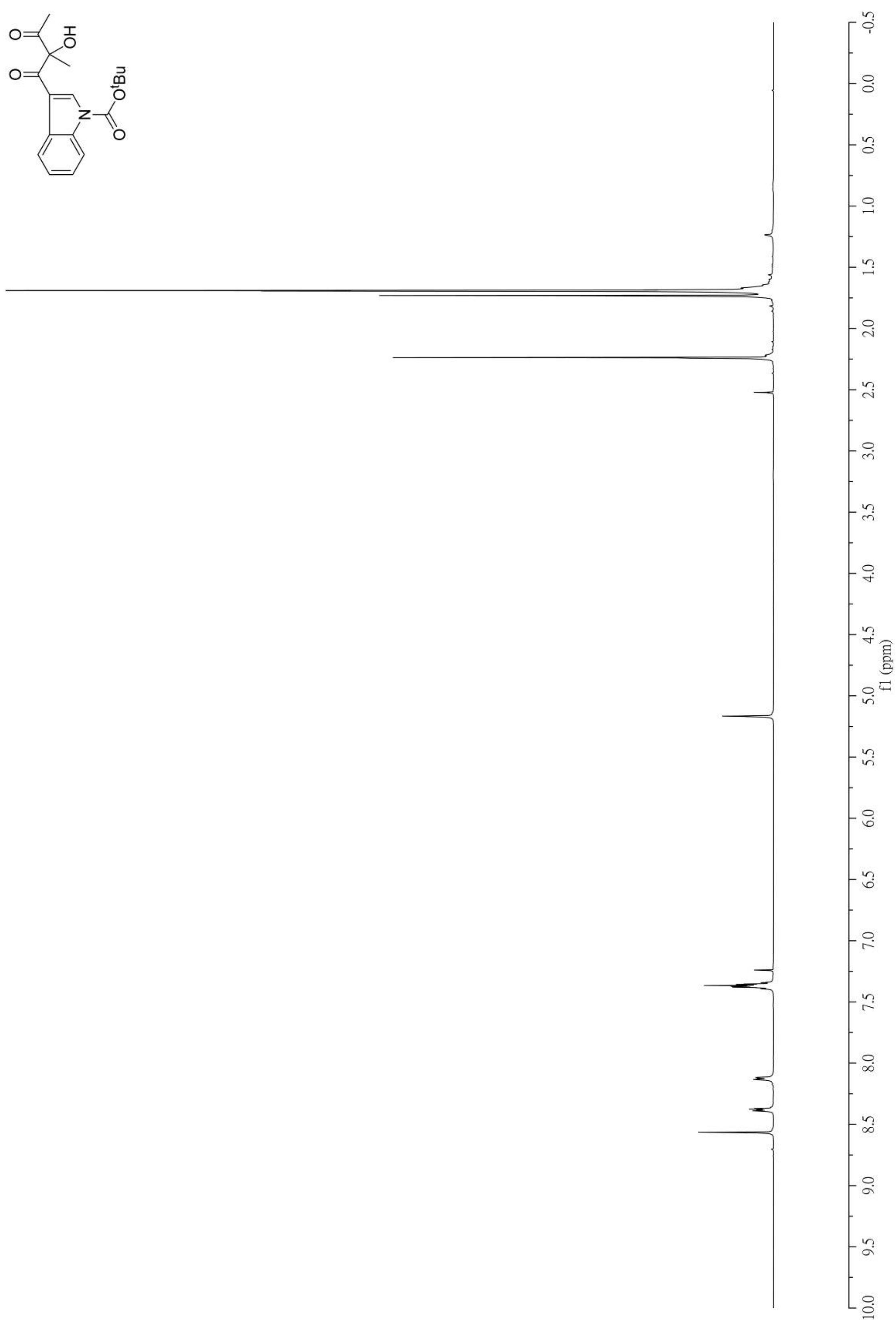

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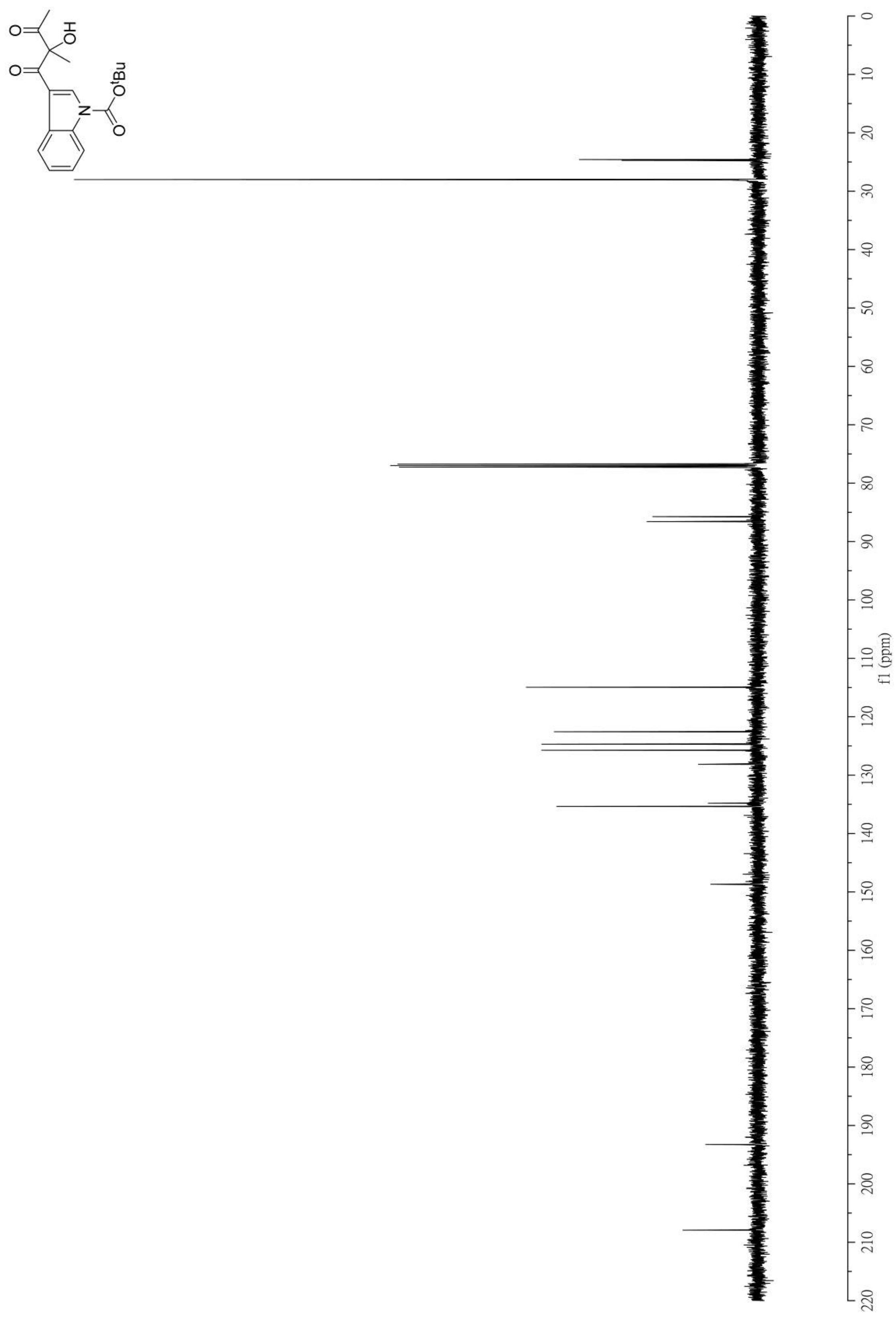

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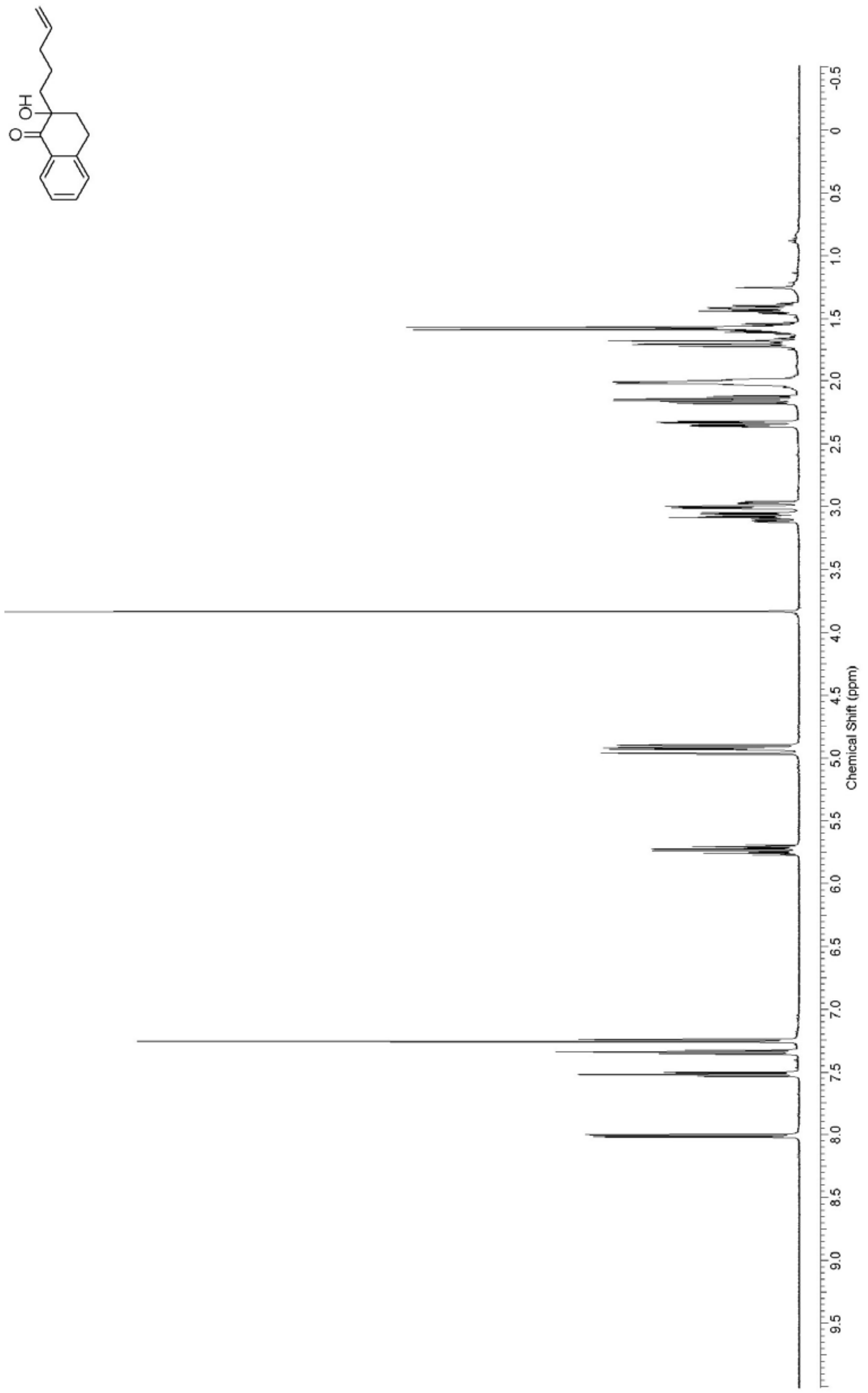

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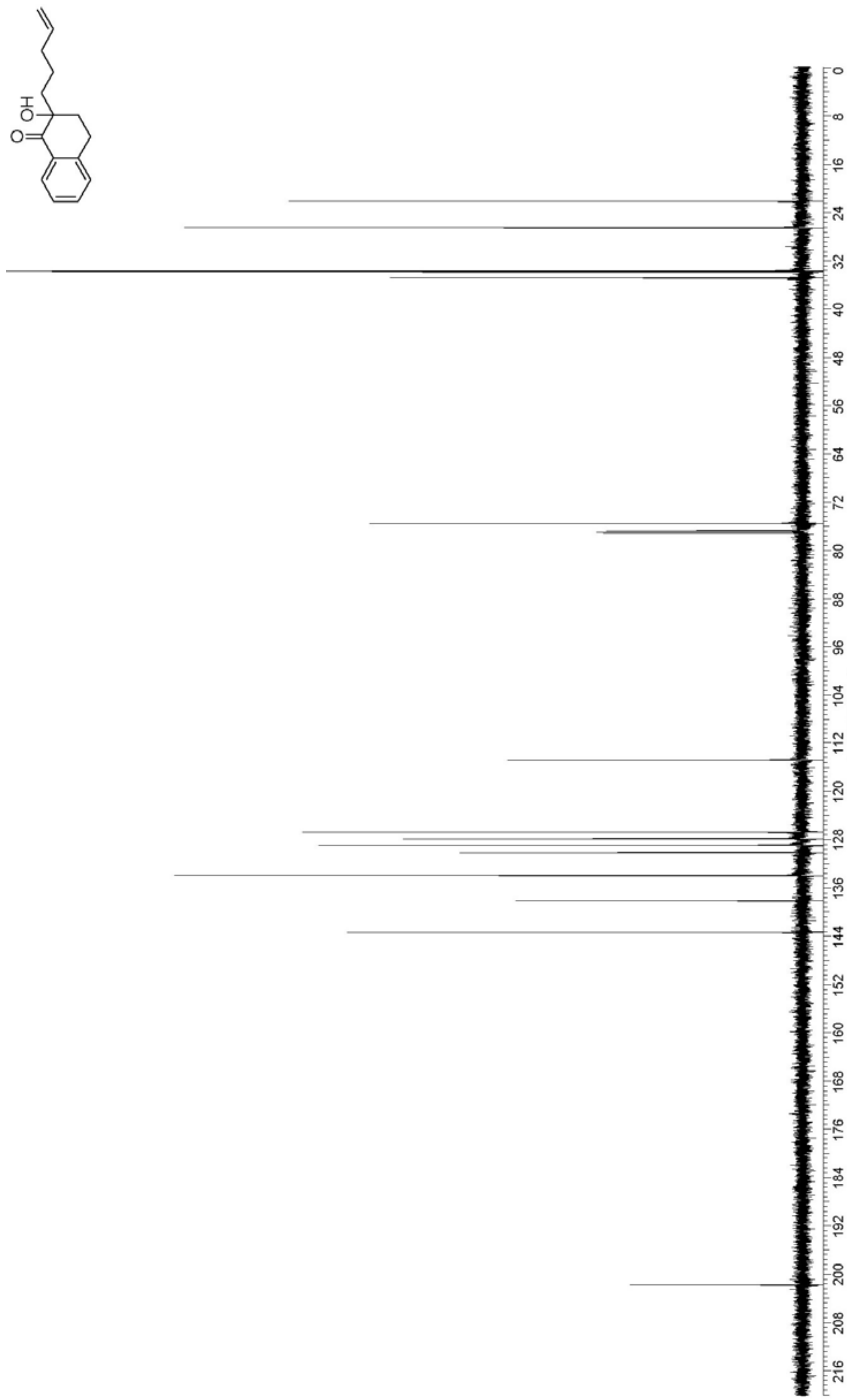

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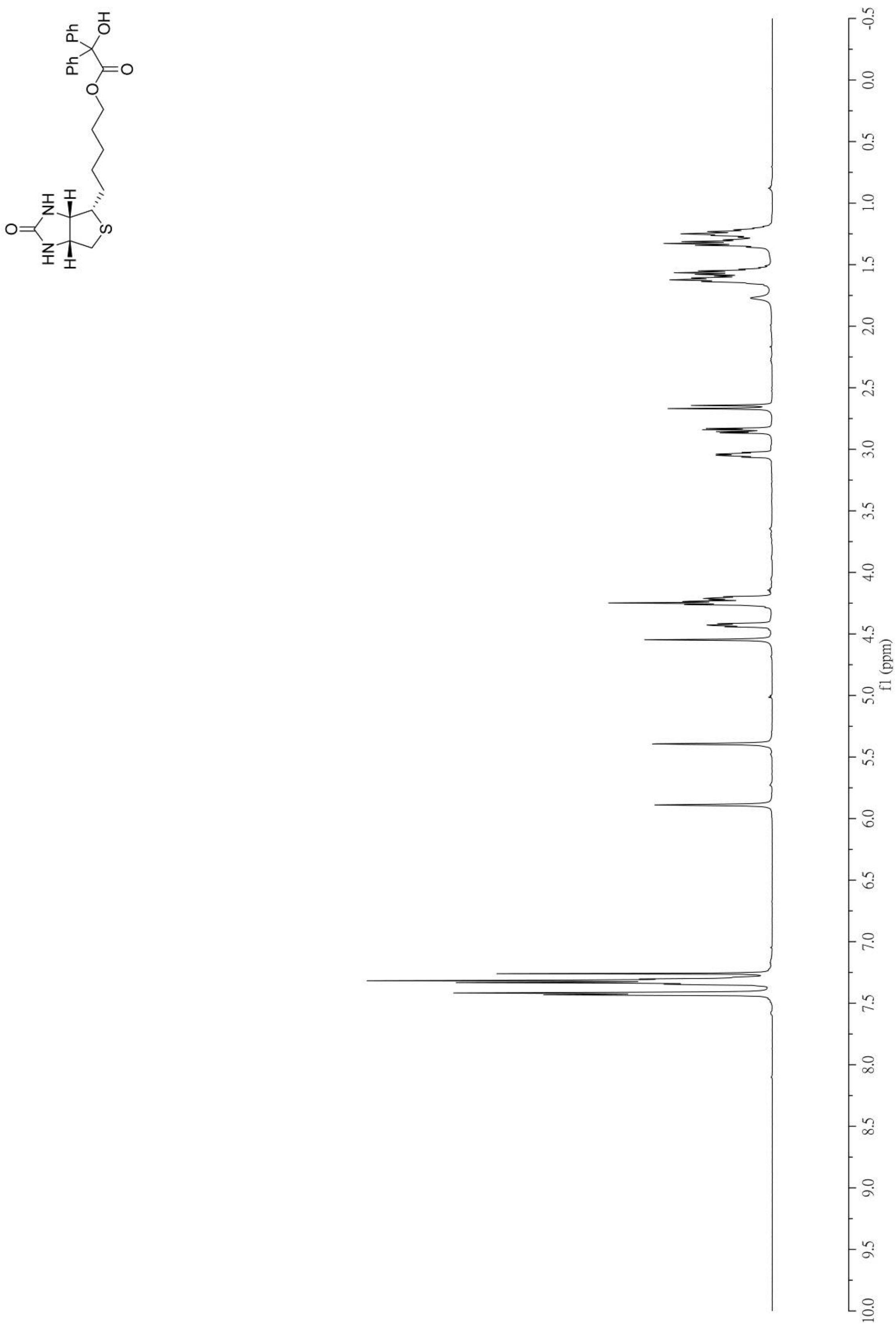

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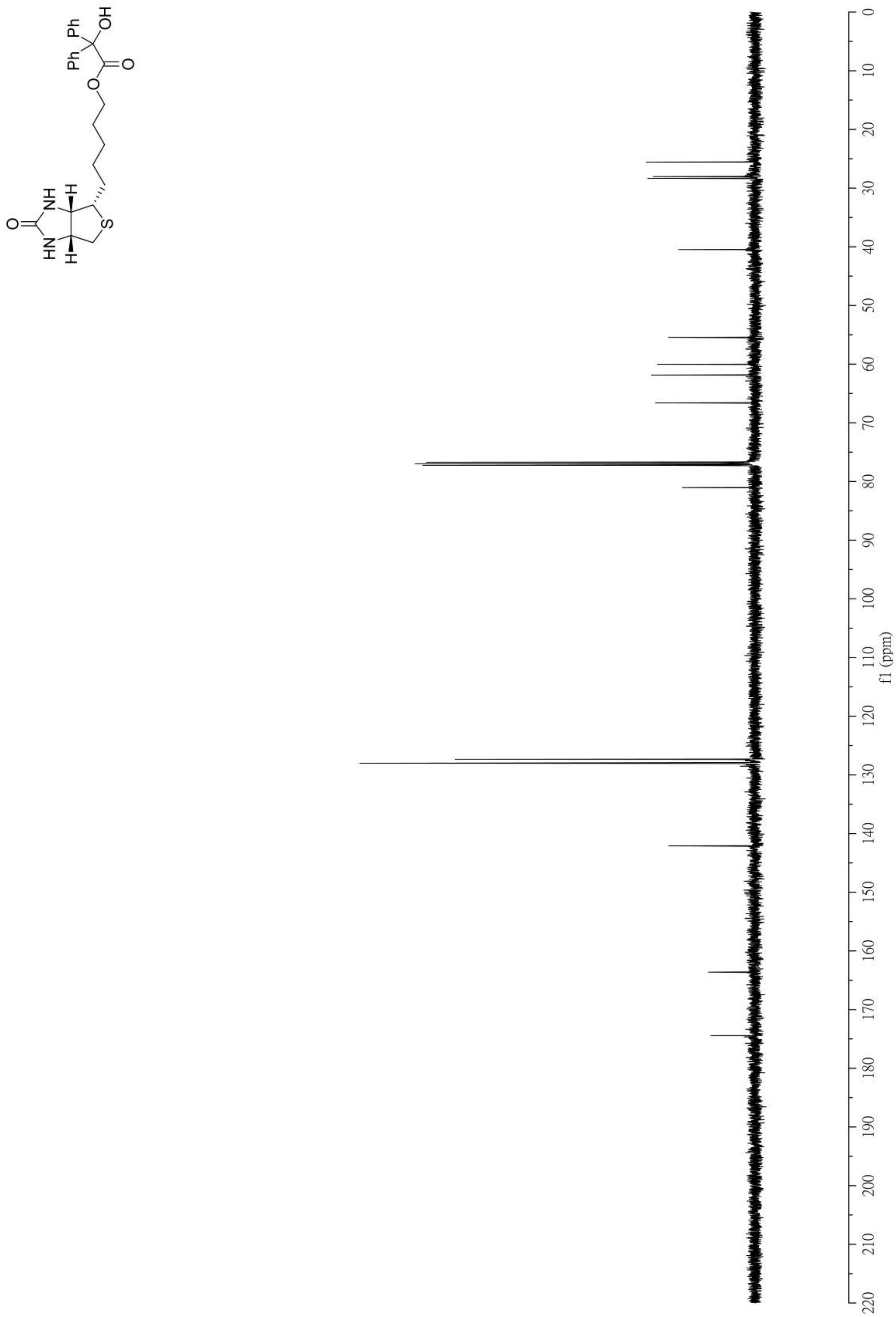

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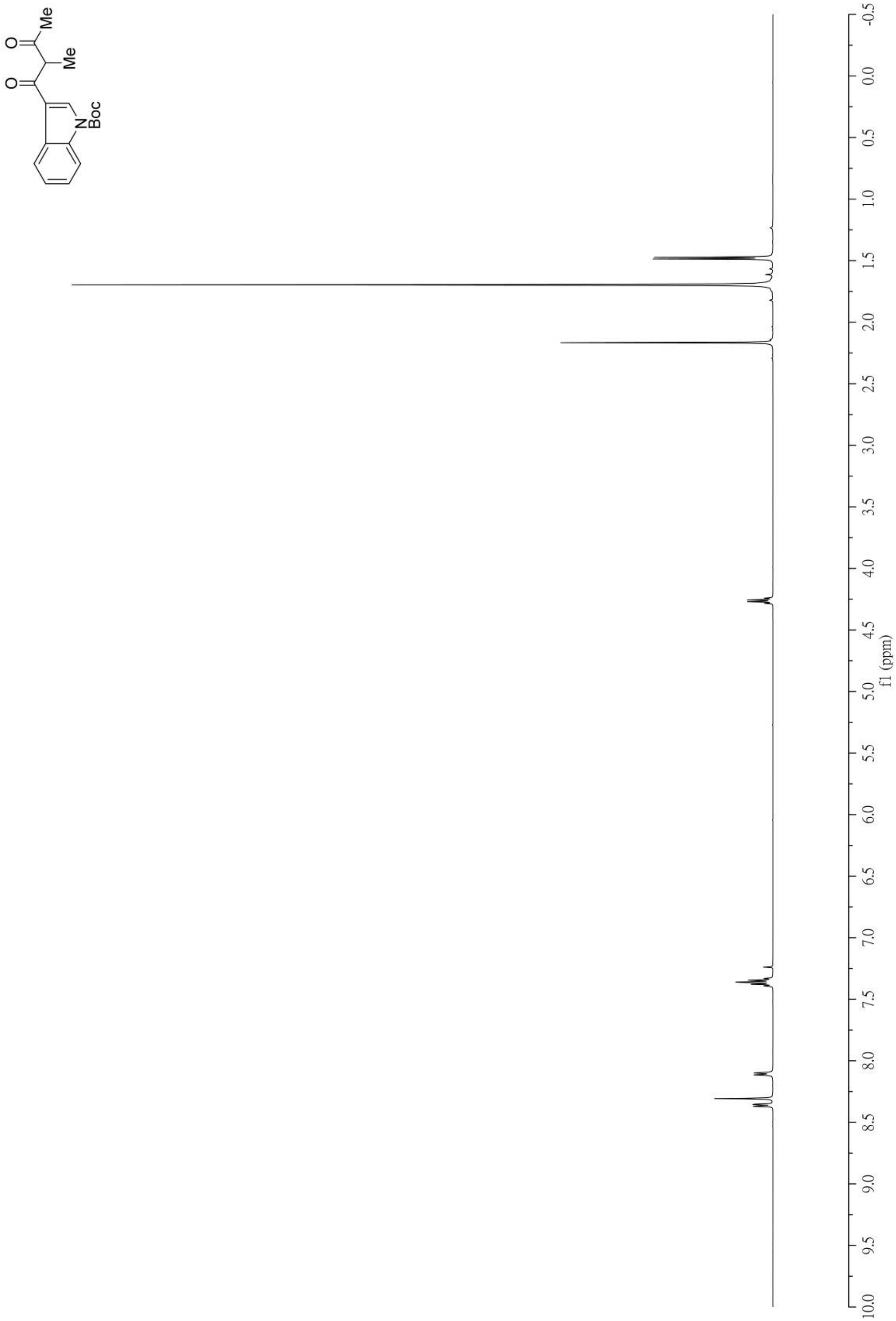

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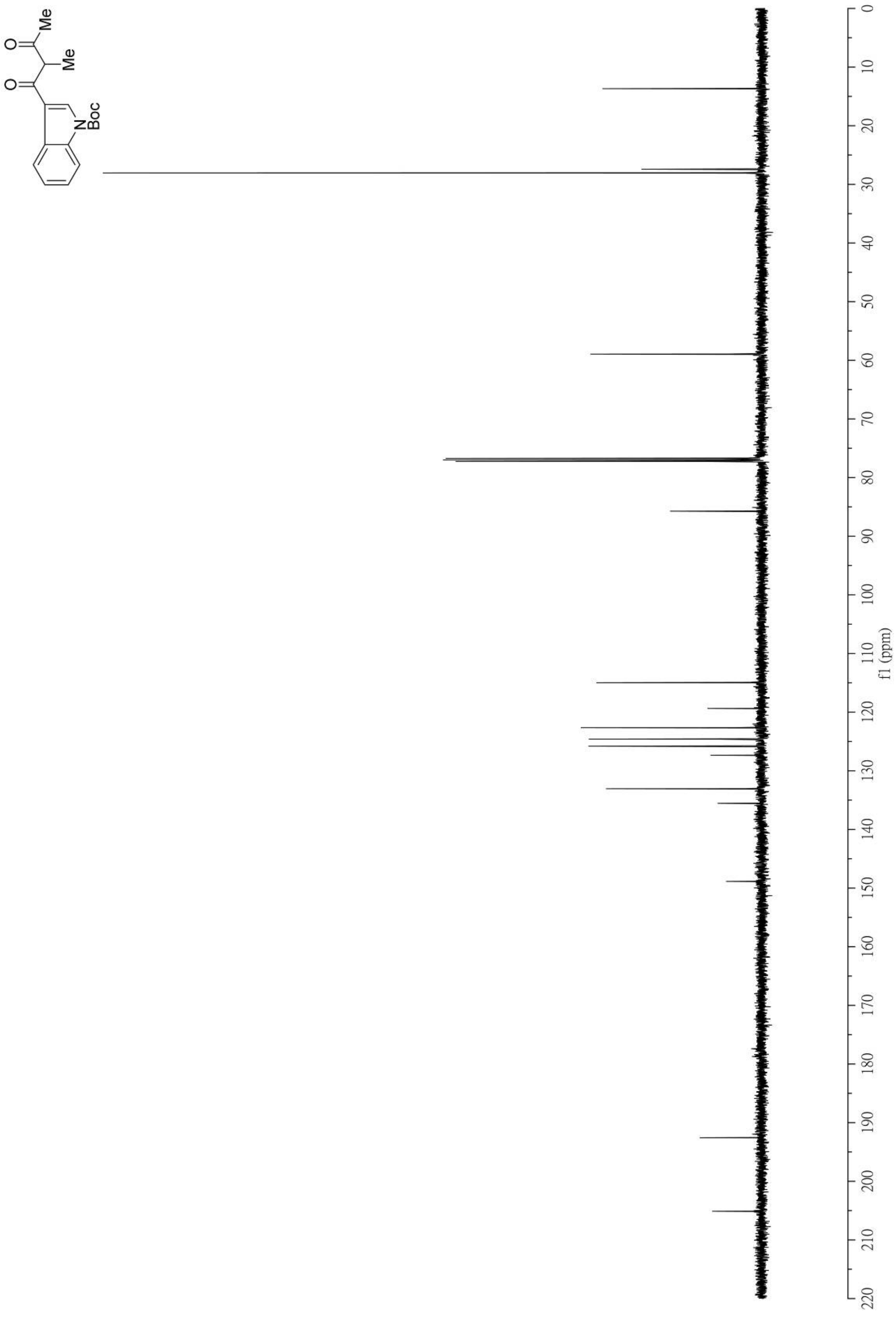

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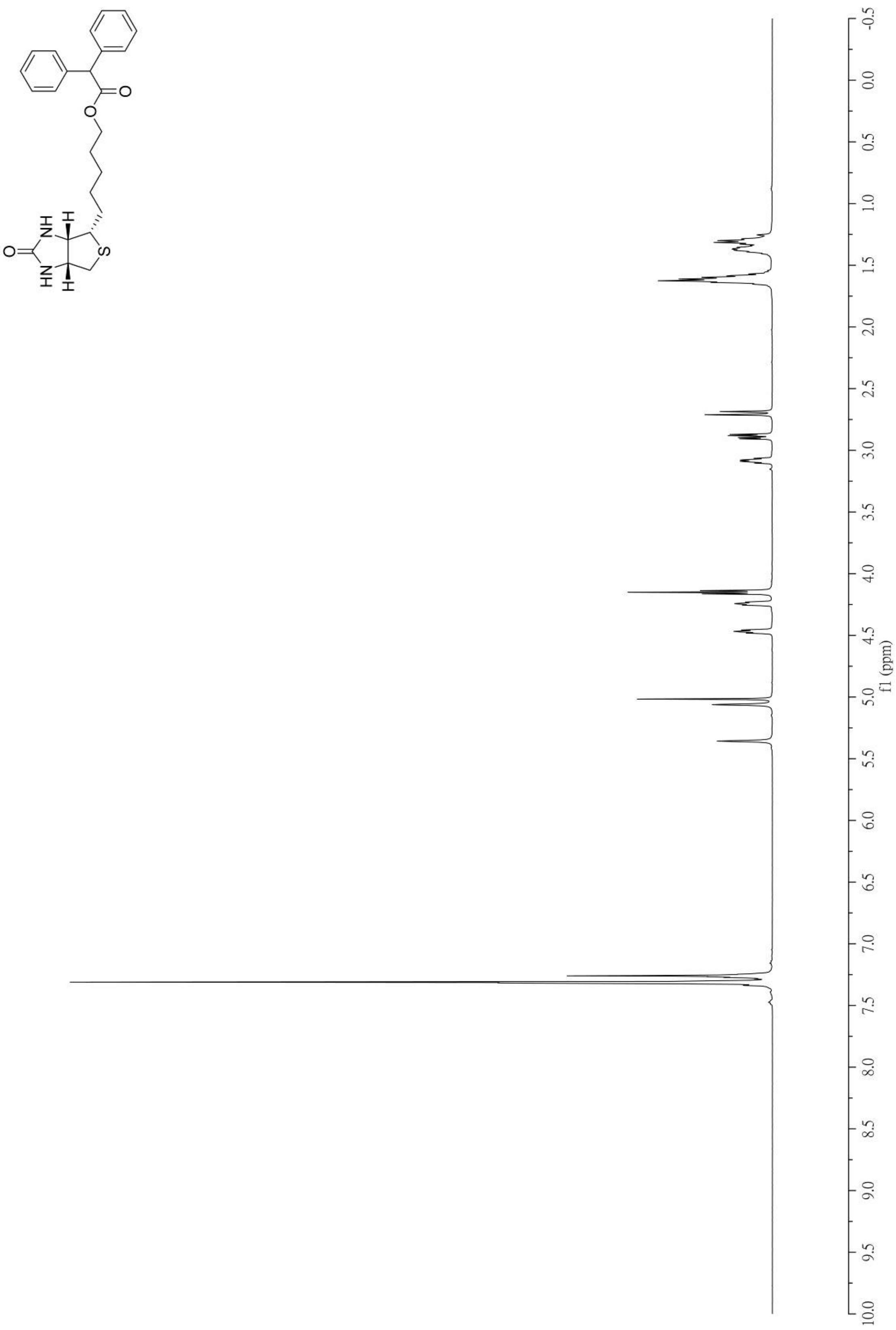

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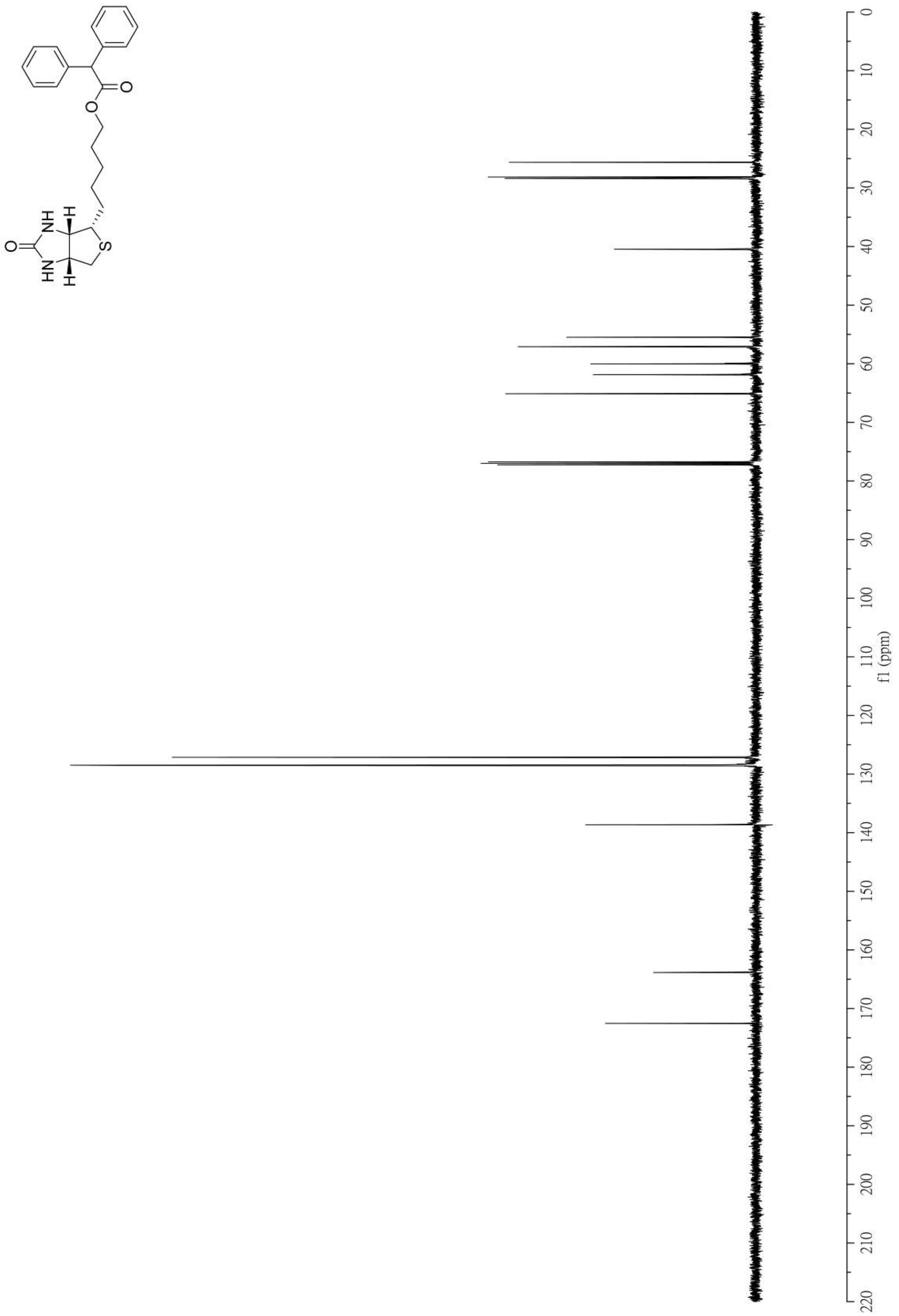

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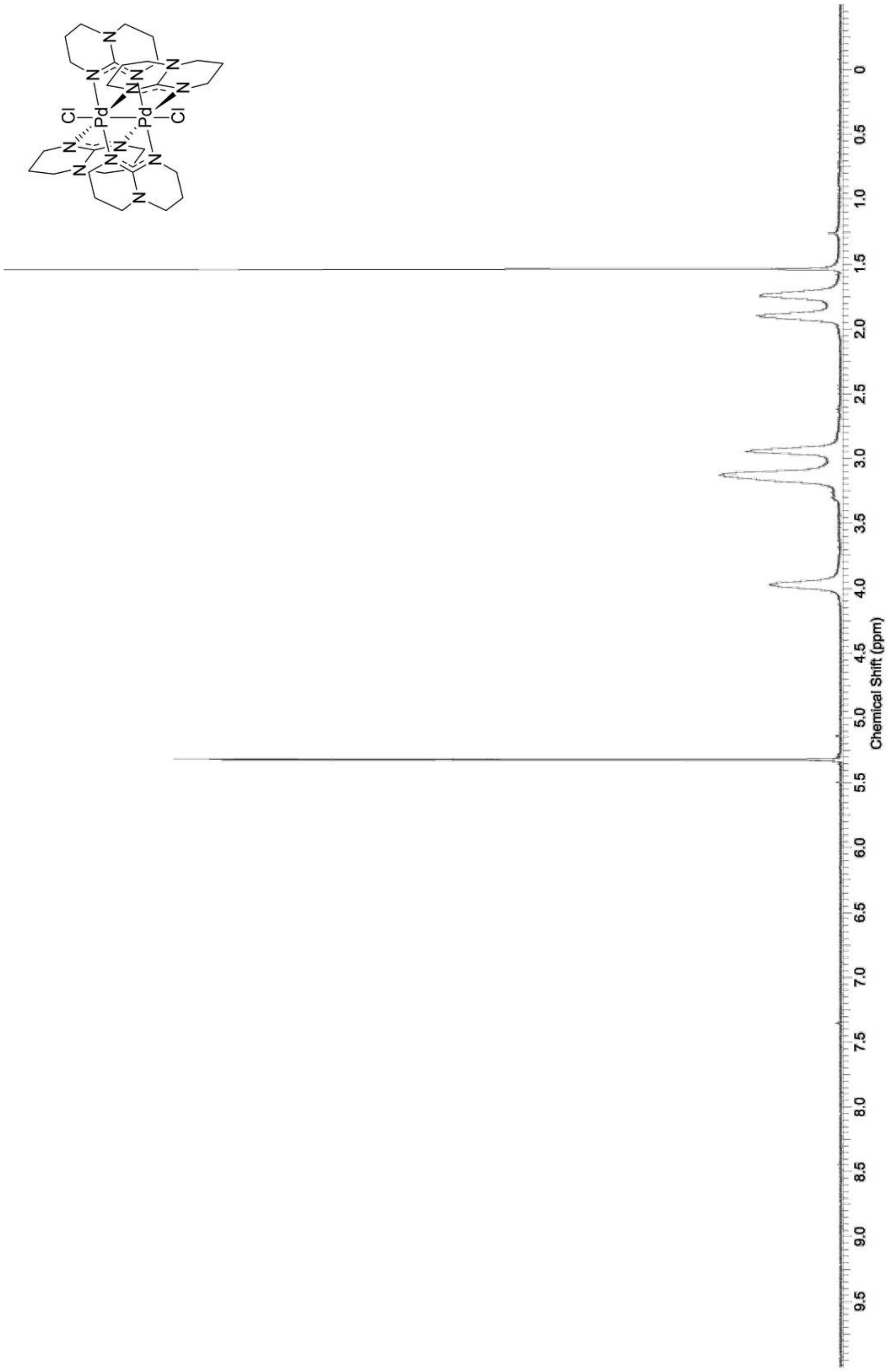
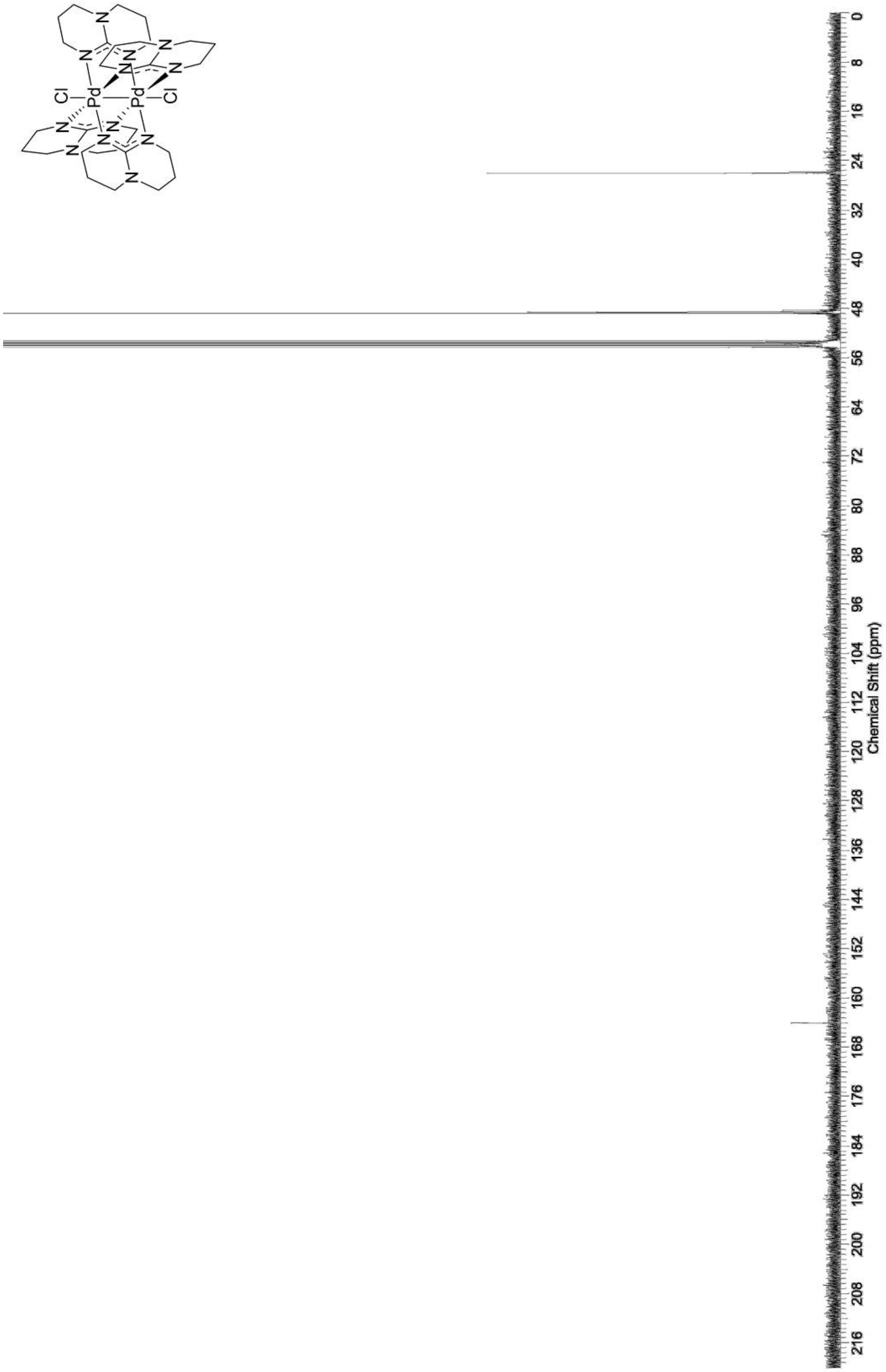


^{1}H NMR spectrum of **S3** in CD_2Cl_2 at 23 °C



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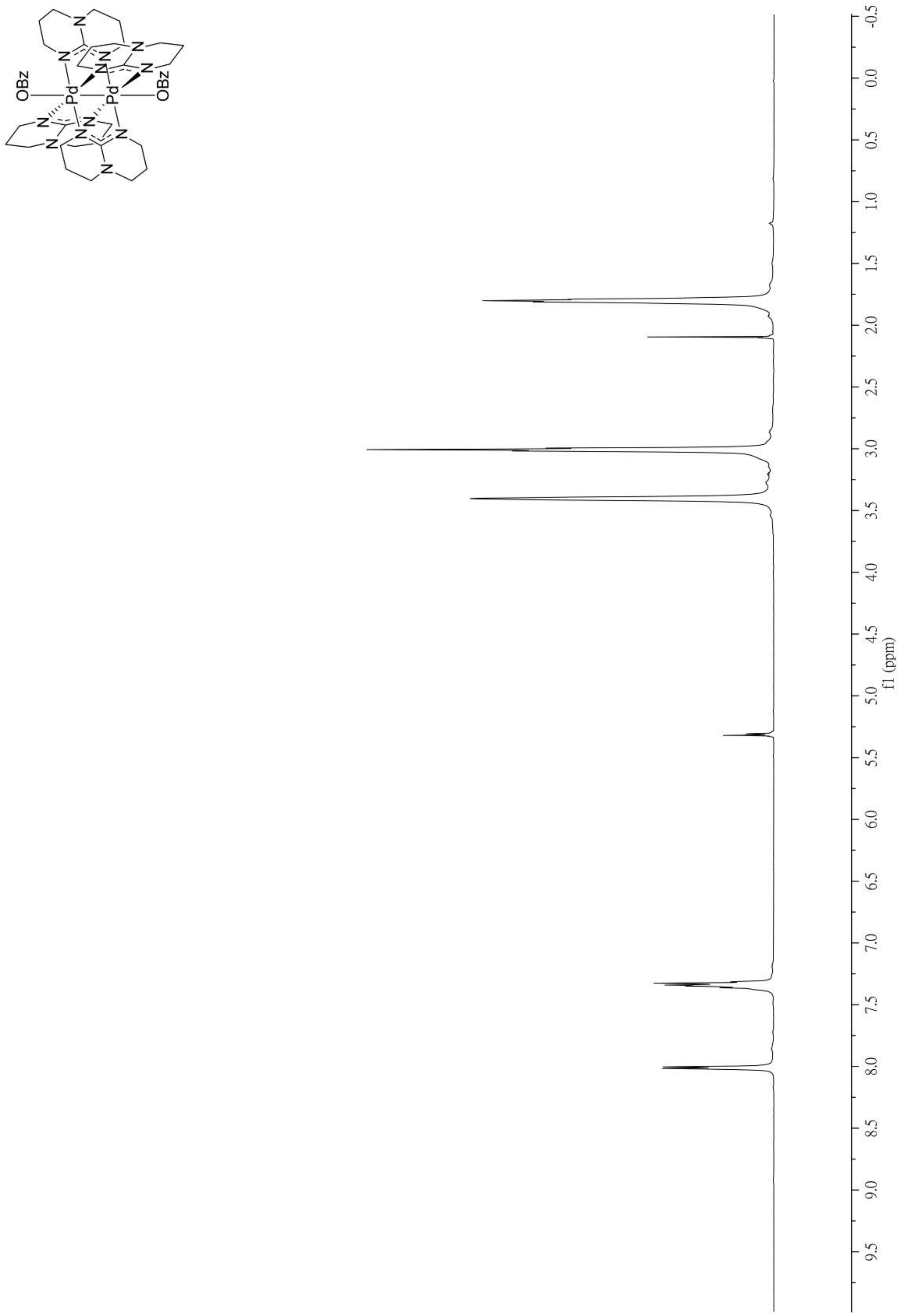

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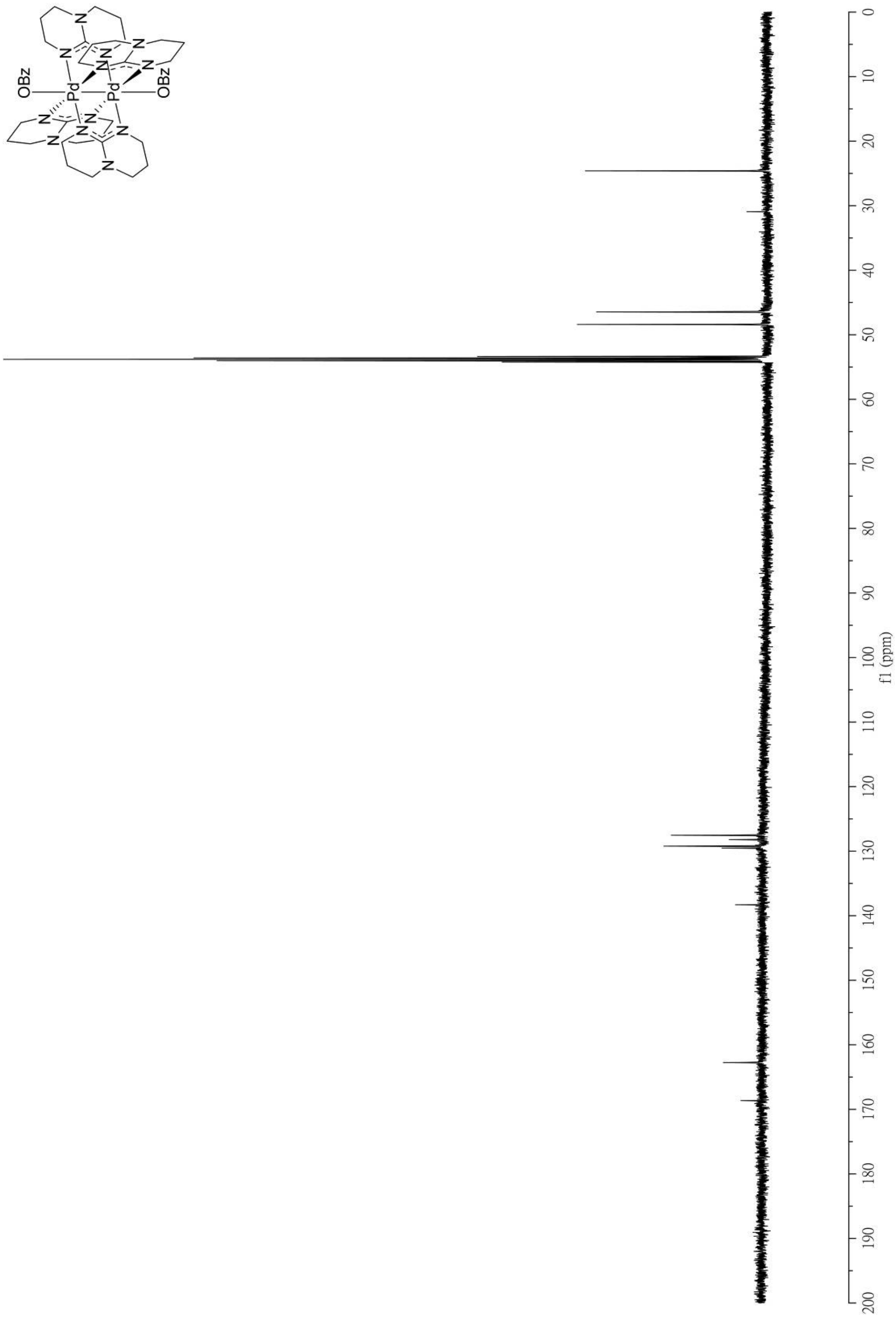

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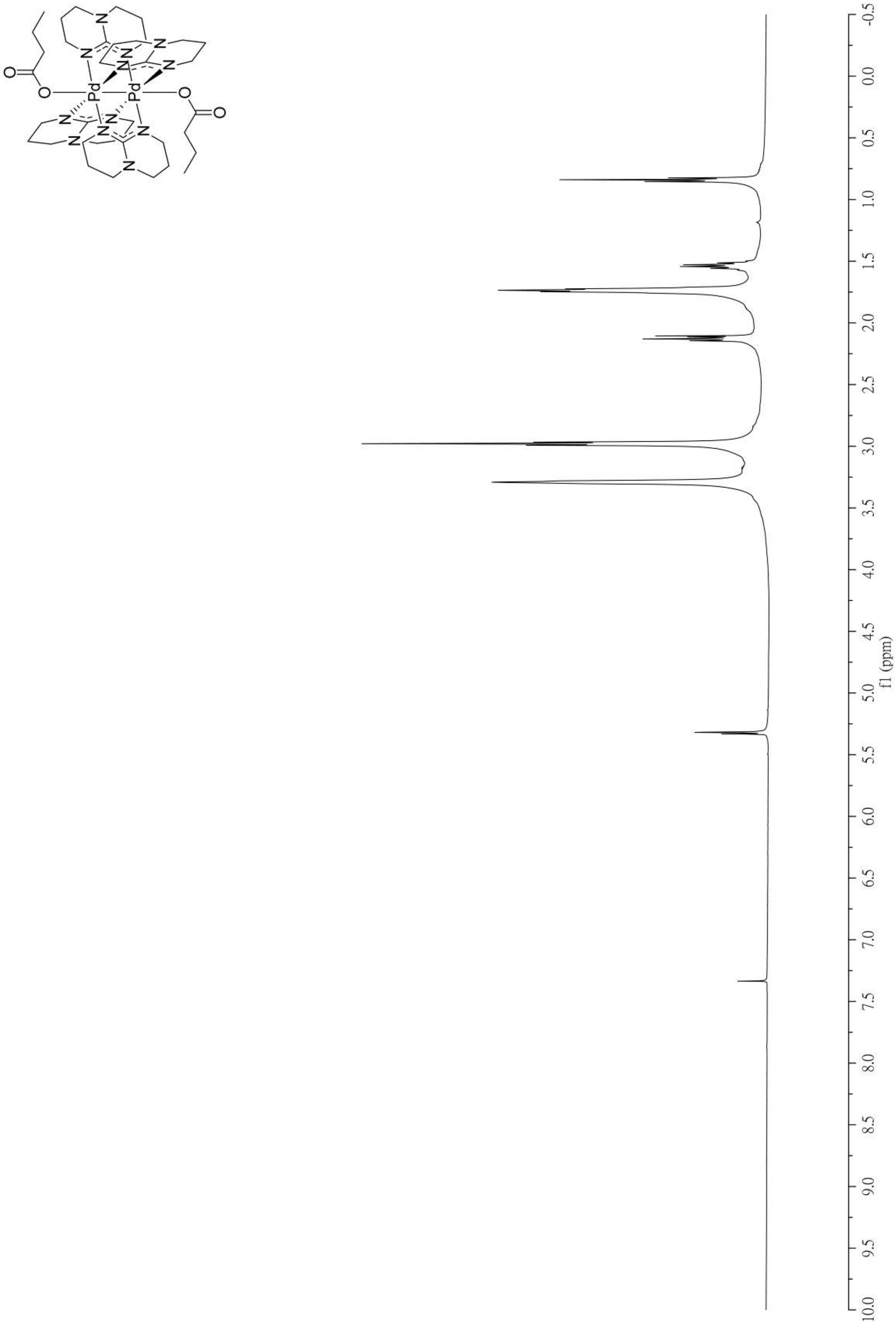

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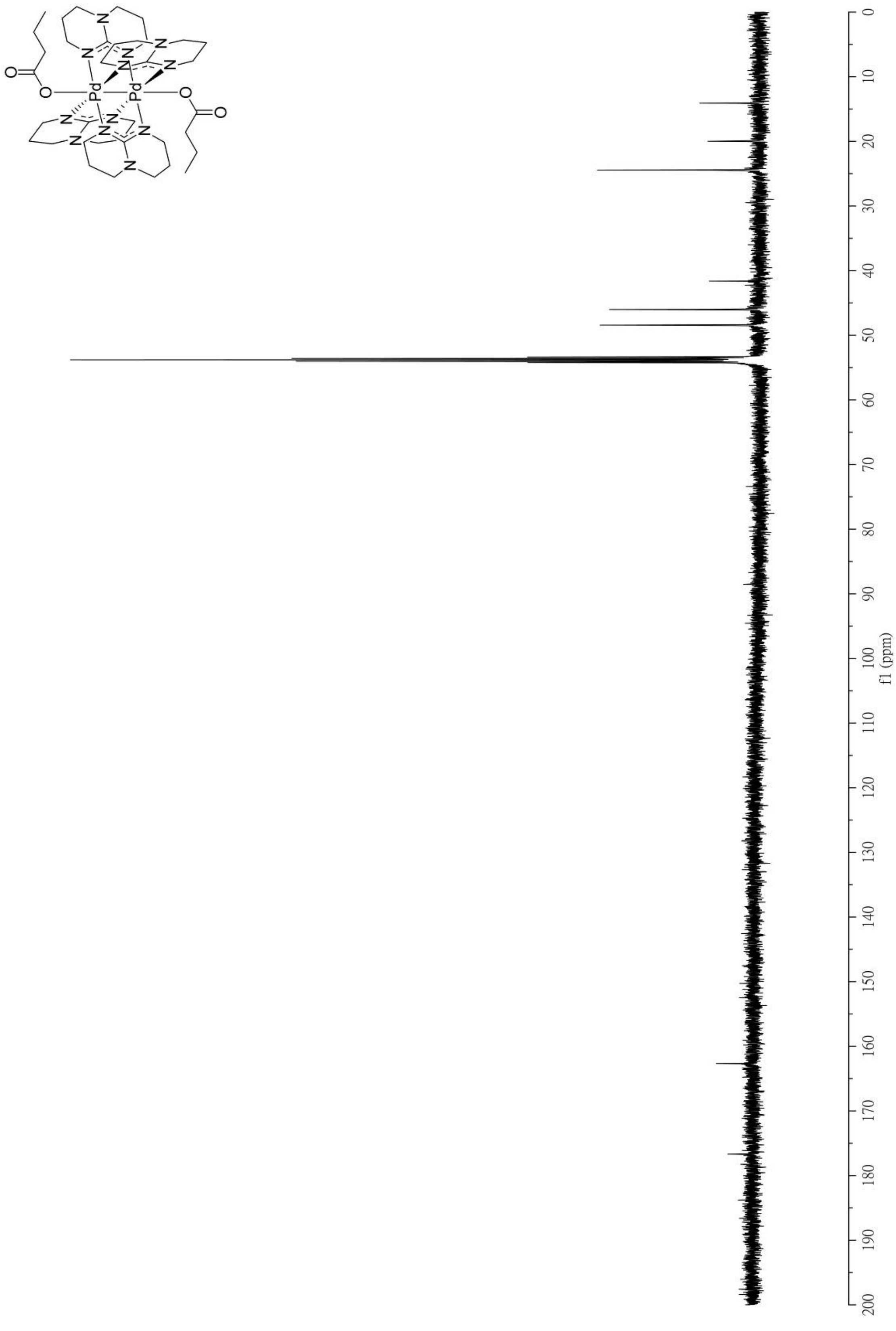

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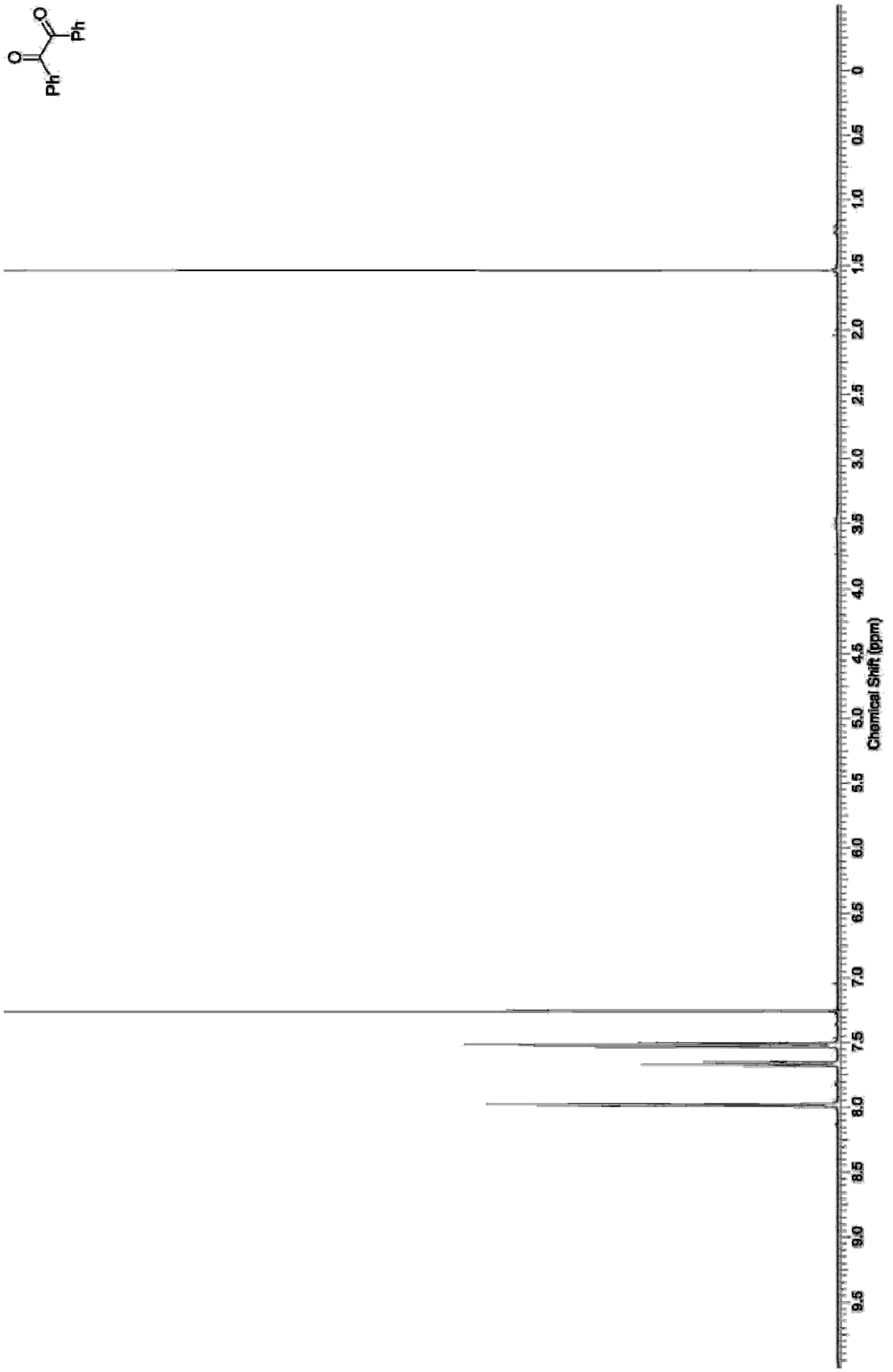

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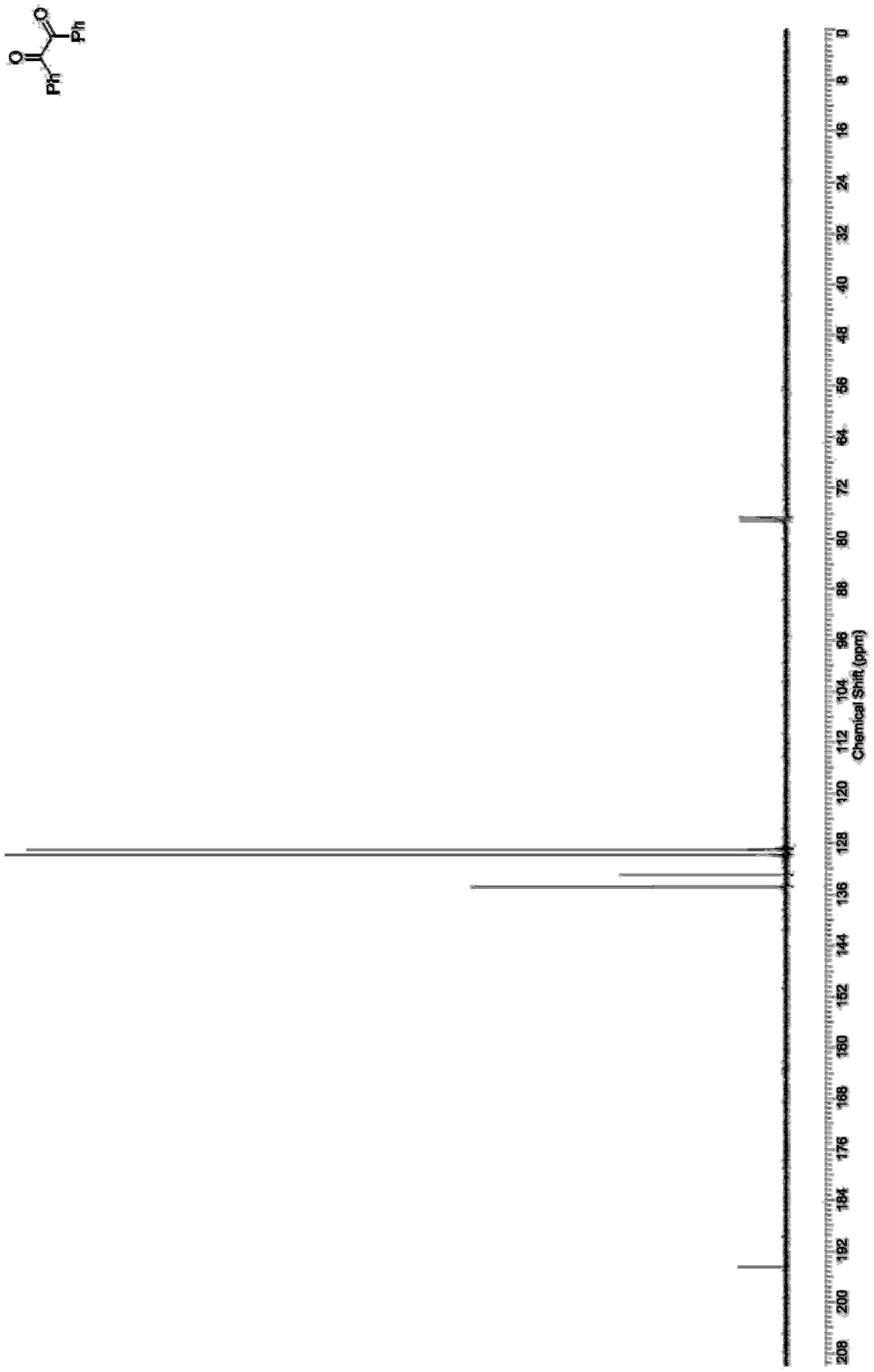
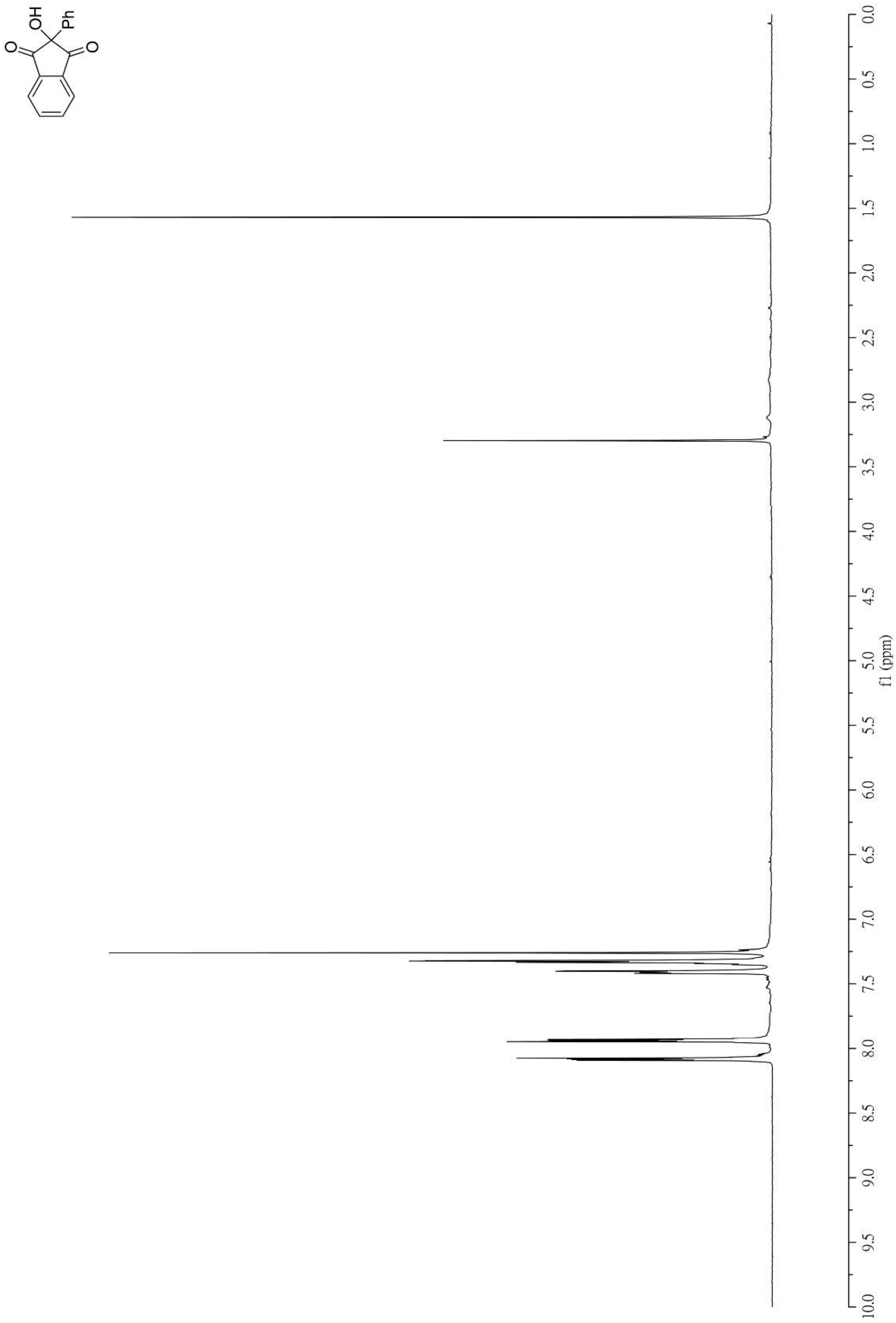
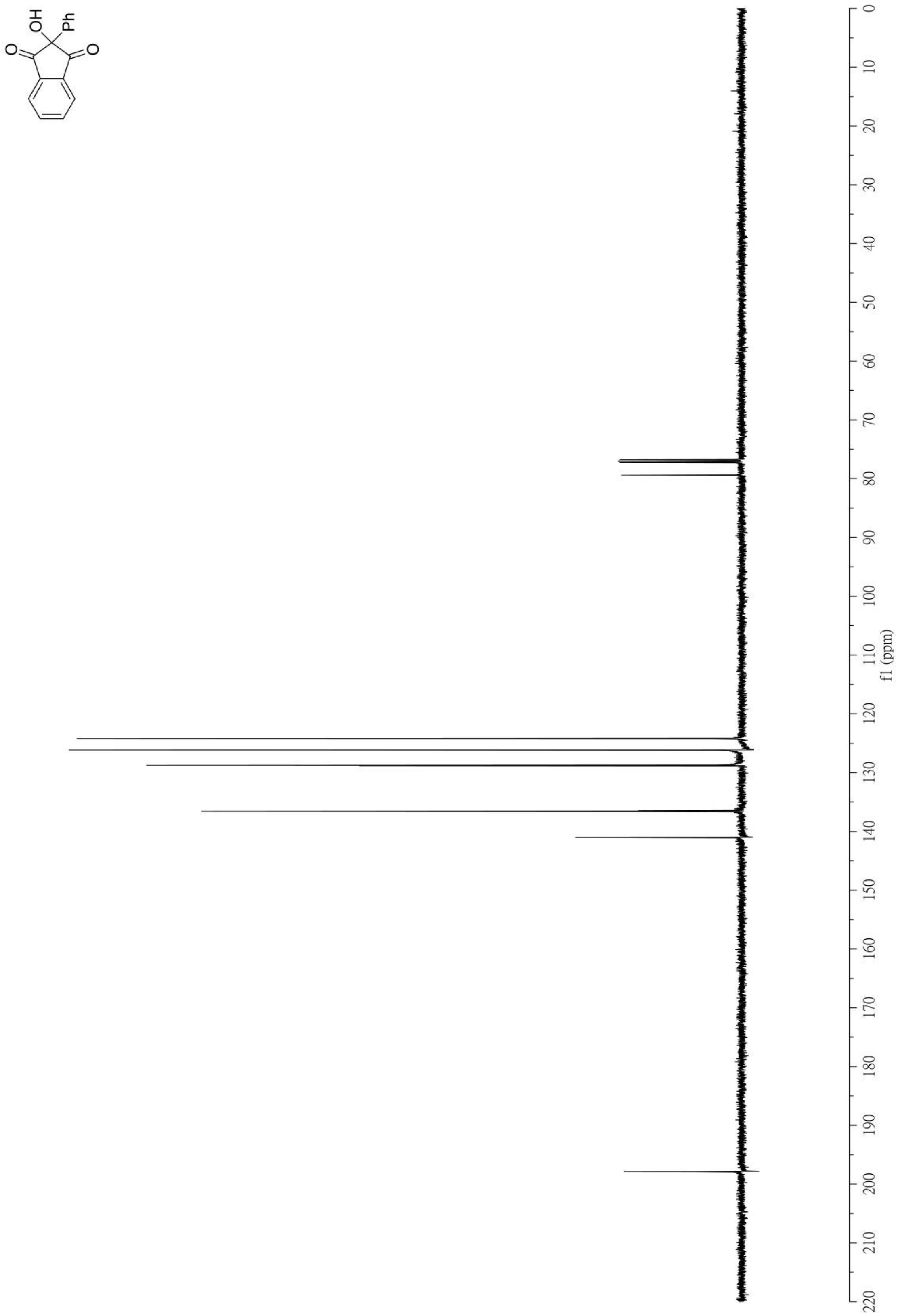


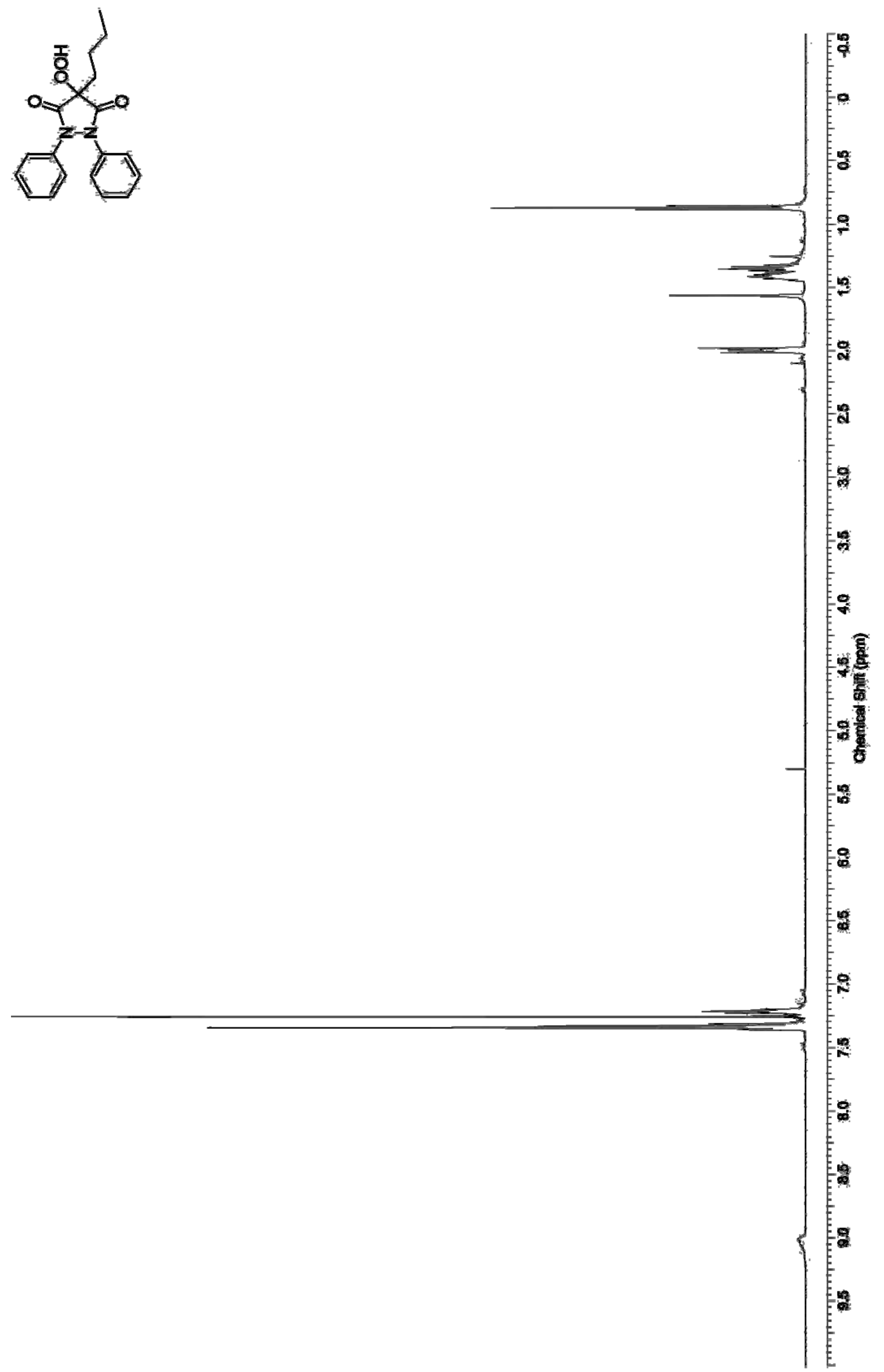
^{13}C NMR spectrum of **S5** in CDCl$_3$ at 23 °C



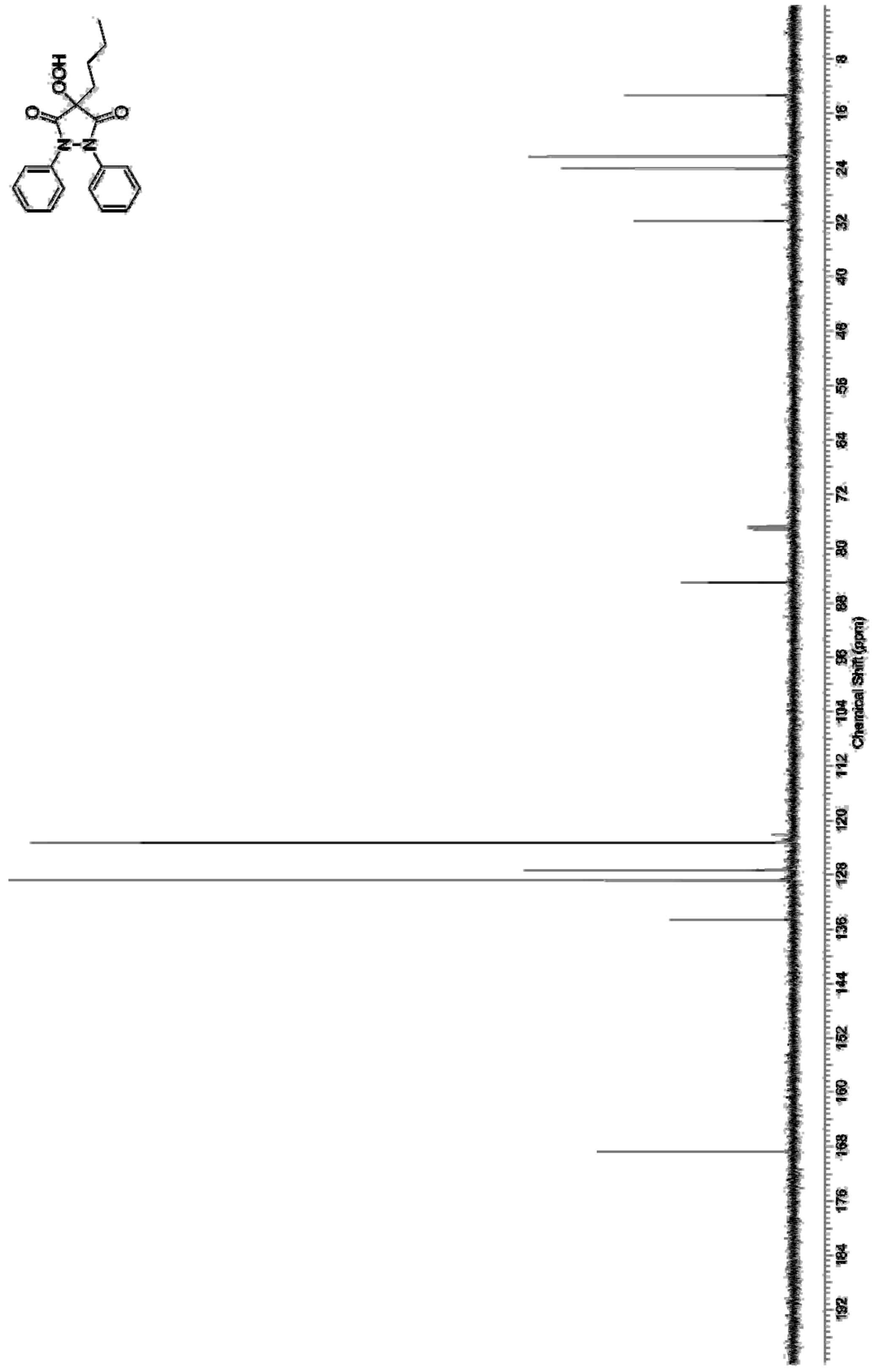
^{1}H NMR spectrum of **S6** in $CDCl_3$ at 23 °C



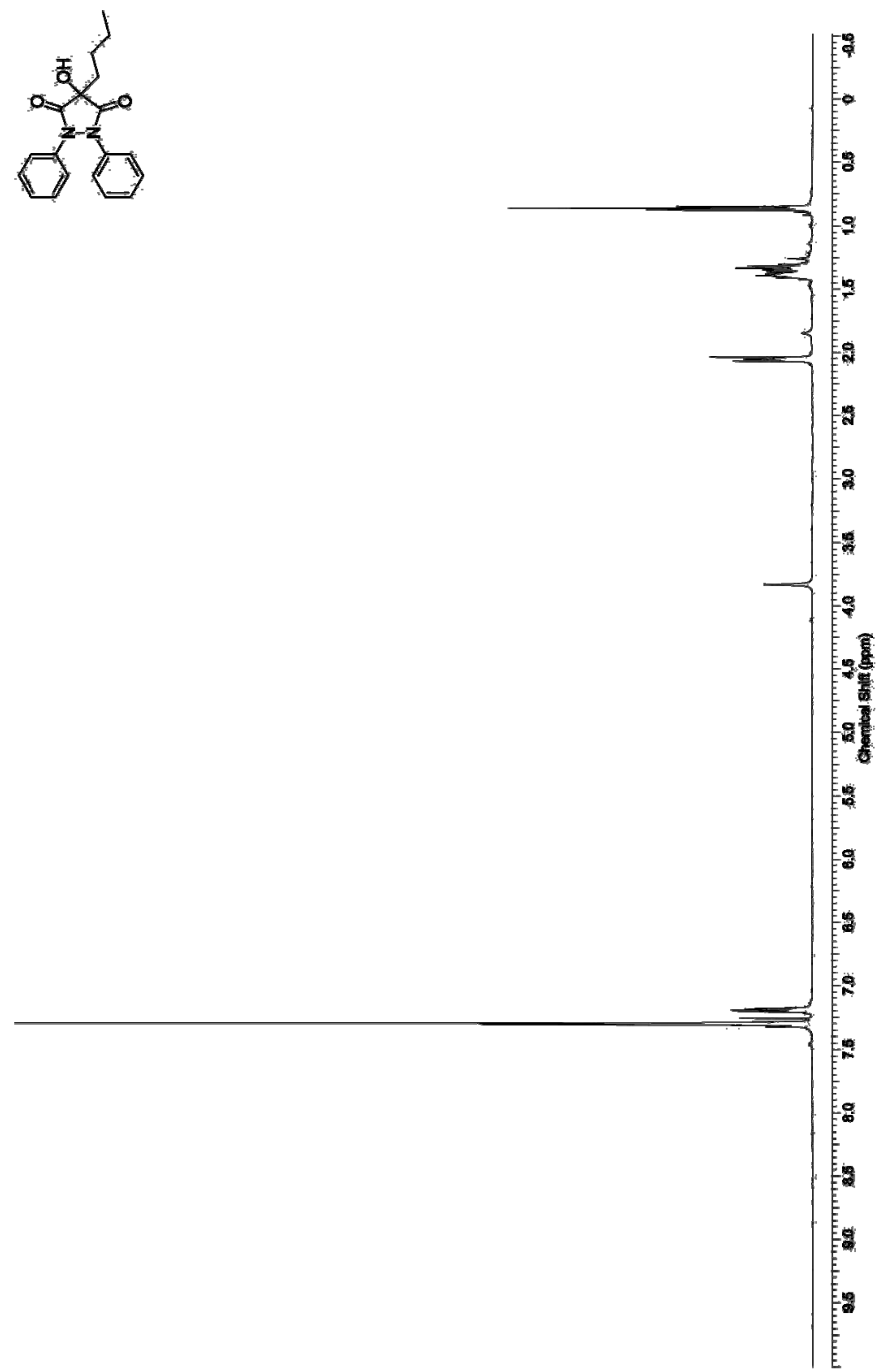
^{13}C NMR spectrum of **S6** in $CDCl_3$ at 23 °C



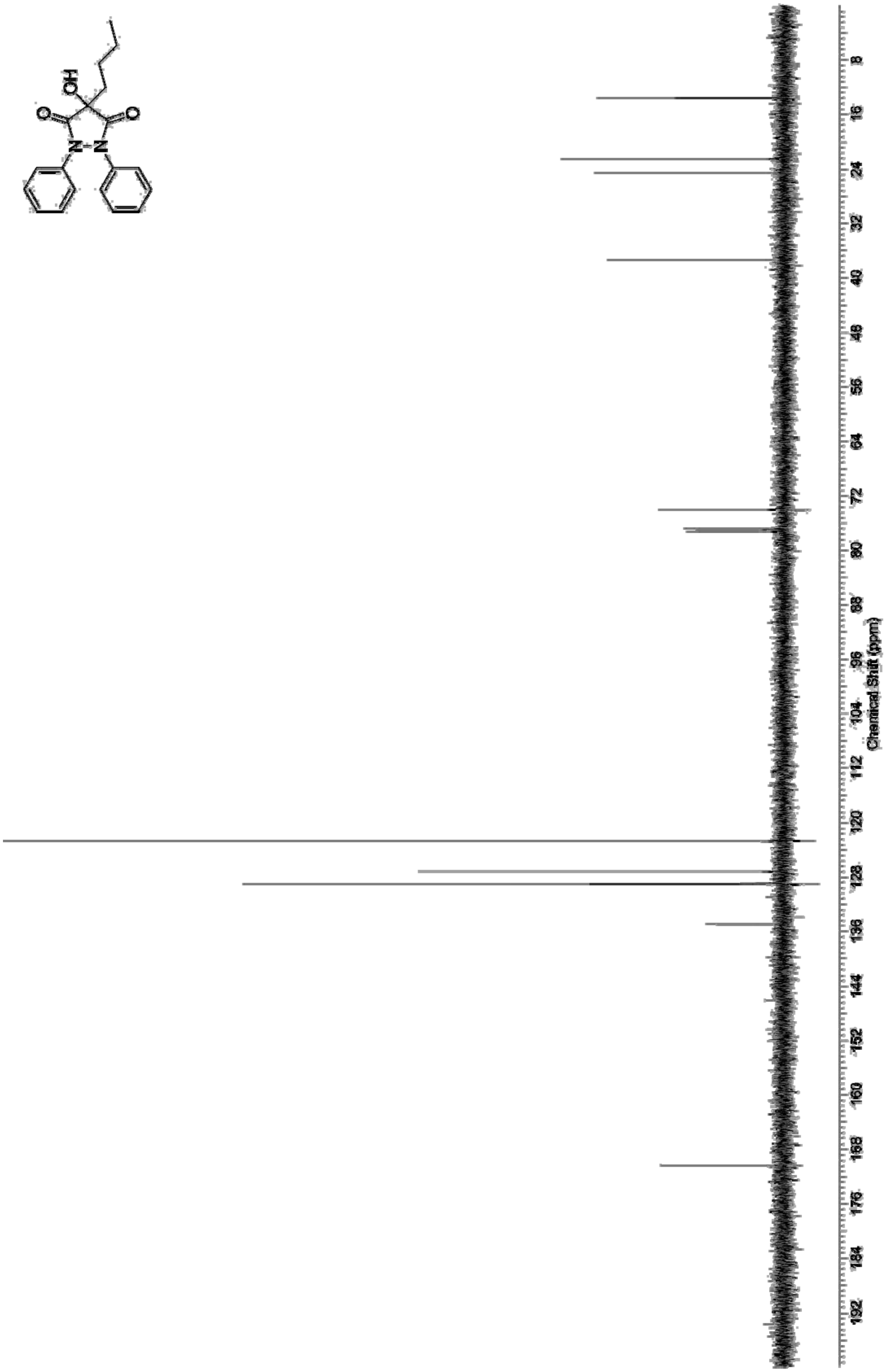
^{1}H NMR spectrum of **S7** in $CDCl_3$ at 23 °C



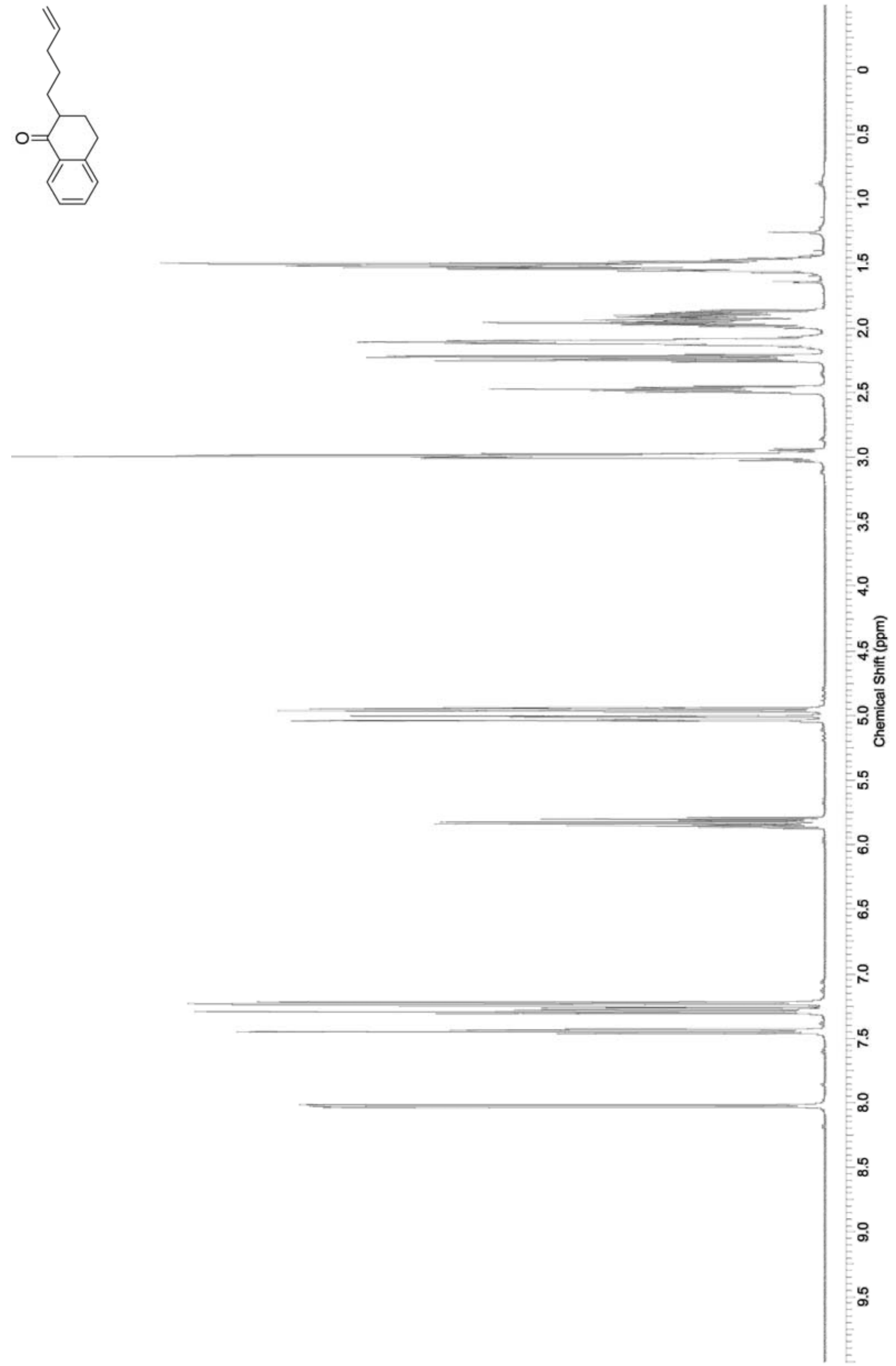
^{13}C NMR spectrum of **S7** in CDCl$_3$ at 23°C



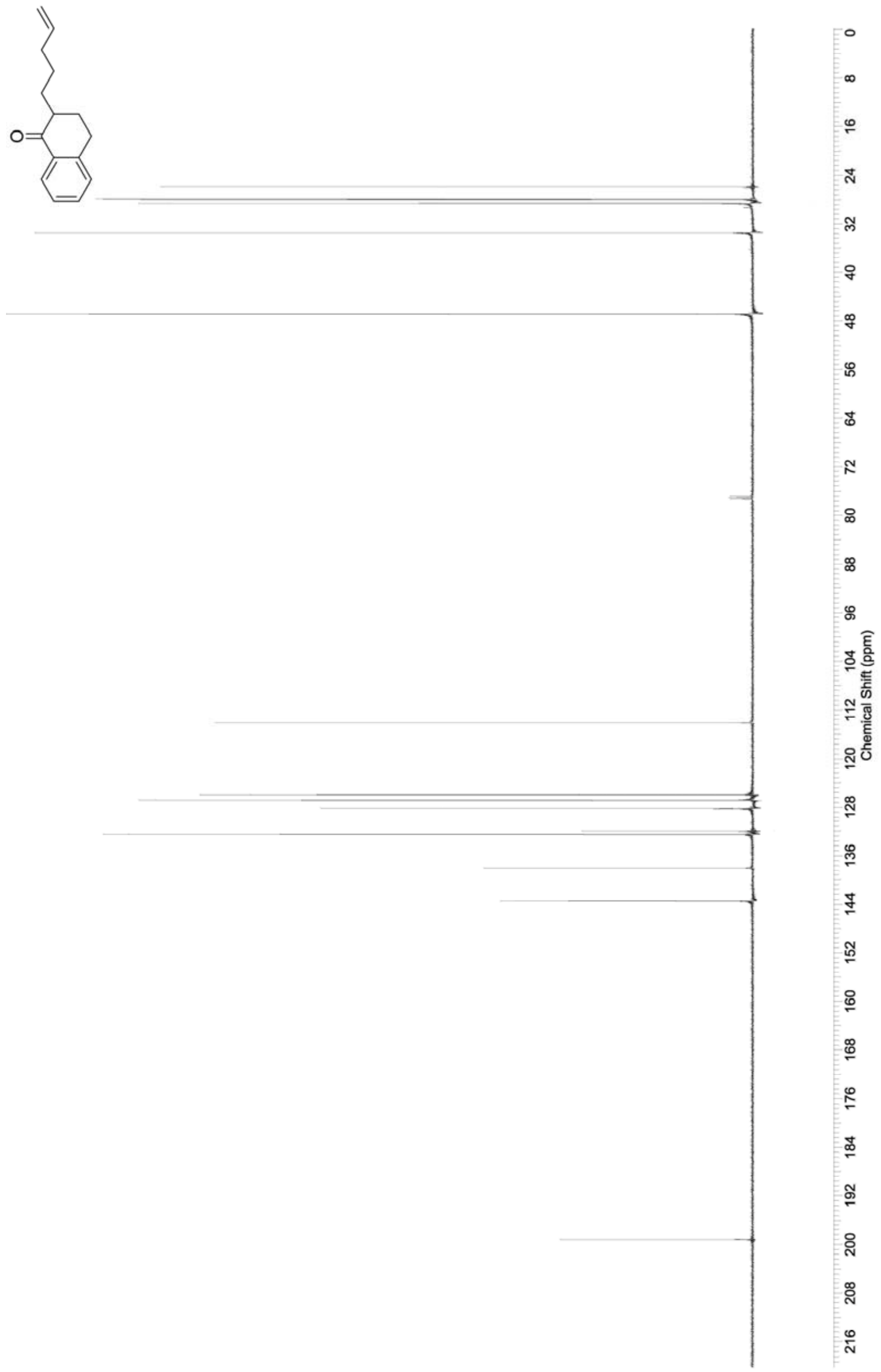
^{1}H NMR spectrum of **S8** in CDCl$_3$ at 23 °C



^{13}C NMR spectrum of **S8** in CDCl$_3$ at 23 °C



^{1}H NMR spectrum of **S10** in $CDCl_3$ at 23 °C



^{13}C NMR spectrum of **S10** in CDCl$_3$ at 23 °C

X-ray Crystallographic data of $Pd_2hpp_4(OBz)_2$ (24) (CCDC 784627)

X-Ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S8, and geometric parameters are shown in Table S9. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

Table S8. Experimental details

	$Pd_2hpp_4(OBz)_2$
Crystal data	
Chemical formula	$C_{46}H_{66}Cl_8N_{12}O_4Pd_2$
M_r	1347.51
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, *b*, *c* (Å)	20.6200 (17), 20.3363 (16), 25.951 (2)
V (Å^3)	10882.1 (15)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.11
Crystal size (mm)	0.40 × 0.16 × 0.10
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*

T_{min}, T_{max}	0.665, 0.897
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	341623, 12050, 10466
R_{int}	0.048
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.054, 1.05
No. of reflections	12050
No. of parameters	649
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.65, -0.58

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Table S9. Selected geometric parameters (Å, º)

Pd1—N7	2.0228 (14)	C16—H16B	0.9900
Pd1—N1	2.0376 (15)	C21—C22	1.515 (2)
Pd1—N4	2.0405 (15)	C21—H21A	0.9900
Pd1—N10	2.0522 (14)	C21—H21B	0.9900
Pd1—O1	2.1805 (12)	C22—C23	1.506 (3)
Pd1—Pd2	2.3991 (2)	C22—H22A	0.9900
Pd2—N3	2.0257 (15)	C22—H22B	0.9900
Pd2—N12	2.0261 (14)	C23—H23A	0.9900
Pd2—N6	2.0373 (15)	C23—H23B	0.9900
Pd2—N9	2.0462 (14)	C24—C25	1.509 (3)
Pd2—O3	2.1854 (12)	C24—H24A	0.9900
O1—C41	1.281 (2)	C24—H24B	0.9900
O2—C41	1.234 (2)	C25—C26	1.515 (2)
O3—C51	1.277 (2)	C25—H25A	0.9900
O4—C51	1.239 (2)	C25—H25B	0.9900

N1—C7	1.329 (2)	C26—H26A	0.9900
N1—C1	1.457 (2)	C26—H26B	0.9900
N2—C7	1.369 (2)	C31—C32	1.517 (2)
N2—C3	1.453 (2)	C31—H31A	0.9900
N2—C4	1.458 (2)	C31—H31B	0.9900
N3—C7	1.334 (2)	C32—C33	1.511 (3)
N3—C6	1.452 (2)	C32—H32A	0.9900
N4—C17	1.332 (2)	C32—H32B	0.9900
N4—C11	1.458 (2)	C33—H33A	0.9900
N5—C17	1.371 (2)	C33—H33B	0.9900
N5—C13	1.459 (2)	C34—C35	1.505 (3)
N5—C14	1.460 (2)	C34—H34A	0.9900
N6—C17	1.333 (2)	C34—H34B	0.9900
N6—C16	1.453 (2)	C35—C36	1.509 (3)
N7—C27	1.335 (2)	C35—H35A	0.9900
N7—C21	1.467 (2)	C35—H35B	0.9900
N8—C27	1.364 (2)	C36—H36A	0.9900
N8—C24	1.457 (2)	C36—H36B	0.9900
N8—C23	1.460 (2)	C41—C42	1.518 (3)
N9—C27	1.357 (2)	C42—C43	1.388 (3)
N9—C26	1.460 (2)	C42—C47	1.390 (3)
N10—C37	1.362 (2)	C43—C44	1.396 (3)
N10—C31	1.464 (2)	C43—H43A	0.9500
N11—C37	1.366 (2)	C44—C45	1.375 (4)
N11—C33	1.457 (2)	C44—H44A	0.9500
N11—C34	1.460 (2)	C45—C46	1.380 (4)
N12—C37	1.333 (2)	C45—H45A	0.9500
N12—C36	1.466 (2)	C46—C47	1.386 (3)
C1—C2	1.519 (3)	C46—H46A	0.9500

C1—H1A	0.9900	C47—H47A	0.9500
C1—H1B	0.9900	C51—C52	1.517 (2)
C2—C3	1.511 (3)	C52—C53	1.392 (3)
C2—H2A	0.9900	C52—C57	1.393 (3)
C2—H2B	0.9900	C53—C54	1.390 (3)
C3—H3A	0.9900	C53—H53A	0.9500
C3—H3B	0.9900	C54—C55	1.385 (3)
C4—C5	1.510 (3)	C54—H54A	0.9500
C4—H4A	0.9900	C55—C56	1.390 (3)
C4—H4B	0.9900	C55—H55A	0.9500
C5—C6	1.520 (3)	C56—C57	1.389 (3)
C5—H5A	0.9900	C56—H56A	0.9500
C5—H5B	0.9900	C57—H57A	0.9500
C6—H6A	0.9900	C1S—Cl1S	1.763 (2)
C6—H6B	0.9900	C1S—Cl2S	1.769 (2)
C11—C12	1.520 (3)	C1S—H1SA	0.9900
C11—H11A	0.9900	C1S—H1SB	0.9900
C11—H11B	0.9900	C2S—Cl4S	1.759 (3)
C12—C13	1.511 (3)	C2S—Cl3S	1.766 (2)
C12—H12A	0.9900	C2S—H2SA	0.9900
C12—H12B	0.9900	C2S—H2SB	0.9900
C13—H13A	0.9900	C3S—Cl5S	1.771 (2)
C13—H13B	0.9900	C3S—Cl6S	1.773 (2)
C14—C15	1.515 (3)	C3S—H3SA	0.9900
C14—H14A	0.9900	C3S—H3SB	0.9900
C14—H14B	0.9900	C4S—Cl7S	1.763 (2)
C15—C16	1.517 (3)	C4S—Cl8S	1.772 (2)
C15—H15A	0.9900	C4S—H4SA	0.9900
C15—H15B	0.9900	C4S—H4SB	0.9900

C16—H16A	0.9900		
N7—Pd1—N1	173.79 (6)	N6—C17—N5	119.63 (16)
N7—Pd1—N4	88.03 (6)	N7—C21—C22	111.19 (15)
N1—Pd1—N4	89.74 (6)	N7—C21—H21A	109.4
N7—Pd1—N10	93.73 (6)	C22—C21—H21A	109.4
N1—Pd1—N10	87.76 (6)	N7—C21—H21B	109.4
N4—Pd1—N10	172.49 (6)	C22—C21—H21B	109.4
N7—Pd1—O1	96.09 (5)	H21A—C21—H21B	108.0
N1—Pd1—O1	89.74 (5)	C23—C22—C21	108.12 (15)
N4—Pd1—O1	91.11 (5)	C23—C22—H22A	110.1
N10—Pd1—O1	95.96 (5)	C21—C22—H22A	110.1
N7—Pd1—Pd2	86.75 (4)	C23—C22—H22B	110.1
N1—Pd1—Pd2	87.32 (4)	C21—C22—H22B	110.1
N4—Pd1—Pd2	86.09 (4)	H22A—C22—H22B	108.4
N10—Pd1—Pd2	86.72 (4)	N8—C23—C22	109.82 (15)
O1—Pd1—Pd2	175.94 (3)	N8—C23—H23A	109.7
N3—Pd2—N12	87.60 (6)	C22—C23—H23A	109.7
N3—Pd2—N6	89.86 (6)	N8—C23—H23B	109.7
N12—Pd2—N6	174.34 (6)	C22—C23—H23B	109.7
N3—Pd2—N9	173.14 (6)	H23A—C23—H23B	108.2
N12—Pd2—N9	93.04 (6)	N8—C24—C25	110.48 (15)
N6—Pd2—N9	88.88 (6)	N8—C24—H24A	109.6
N3—Pd2—O3	89.81 (5)	C25—C24—H24A	109.6
N12—Pd2—O3	96.78 (5)	N8—C24—H24B	109.6
N6—Pd2—O3	88.27 (5)	C25—C24—H24B	109.6
N9—Pd2—O3	96.89 (5)	H24A—C24—H24B	108.1
N3—Pd2—Pd1	86.39 (4)	C24—C25—C26	107.53 (15)
N12—Pd2—Pd1	87.28 (4)	C24—C25—H25A	110.2

N6—Pd2—Pd1	87.51 (4)	C26—C25—H25A	110.2
N9—Pd2—Pd1	86.82 (4)	C24—C25—H25B	110.2
O3—Pd2—Pd1	174.33 (3)	C26—C25—H25B	110.2
C41—O1—Pd1	134.11 (12)	H25A—C25—H25B	108.5
C51—O3—Pd2	136.39 (11)	N9—C26—C25	109.35 (15)
C7—N1—C1	118.94 (15)	N9—C26—H26A	109.8
C7—N1—Pd1	117.05 (12)	C25—C26—H26A	109.8
C1—N1—Pd1	122.96 (12)	N9—C26—H26B	109.8
C7—N2—C3	122.83 (16)	C25—C26—H26B	109.8
C7—N2—C4	123.40 (16)	H26A—C26—H26B	108.3
C3—N2—C4	113.43 (15)	N7—C27—N9	118.43 (15)
C7—N3—C6	117.43 (15)	N7—C27—N8	120.45 (16)
C7—N3—Pd2	119.90 (12)	N9—C27—N8	121.02 (16)
C6—N3—Pd2	121.36 (12)	N10—C31—C32	109.23 (15)
C17—N4—C11	118.85 (15)	N10—C31—H31A	109.8
C17—N4—Pd1	119.76 (12)	C32—C31—H31A	109.8
C11—N4—Pd1	121.38 (11)	N10—C31—H31B	109.8
C17—N5—C13	123.14 (15)	C32—C31—H31B	109.8
C17—N5—C14	123.27 (15)	H31A—C31—H31B	108.3
C13—N5—C14	113.10 (15)	C33—C32—C31	107.25 (15)
C17—N6—C16	118.25 (15)	C33—C32—H32A	110.3
C17—N6—Pd2	117.82 (12)	C31—C32—H32A	110.3
C16—N6—Pd2	123.78 (12)	C33—C32—H32B	110.3
C27—N7—C21	119.32 (15)	C31—C32—H32B	110.3
C27—N7—Pd1	119.48 (12)	H32A—C32—H32B	108.5
C21—N7—Pd1	116.36 (11)	N11—C33—C32	110.75 (15)
C27—N8—C24	123.26 (15)	N11—C33—H33A	109.5
C27—N8—C23	122.74 (15)	C32—C33—H33A	109.5
C24—N8—C23	114.00 (15)	N11—C33—H33B	109.5

C27—N9—C26	116.65 (14)	C32—C33—H33B	109.5
C27—N9—Pd2	111.73 (11)	H33A—C33—H33B	108.1
C26—N9—Pd2	115.41 (11)	N11—C34—C35	110.05 (15)
C37—N10—C31	115.84 (14)	N11—C34—H34A	109.6
C37—N10—Pd1	111.58 (11)	C35—C34—H34A	109.6
C31—N10—Pd1	115.23 (11)	N11—C34—H34B	109.6
C37—N11—C33	123.48 (15)	C35—C34—H34B	109.6
C37—N11—C34	122.52 (15)	H34A—C34—H34B	108.2
C33—N11—C34	113.61 (15)	C34—C35—C36	107.71 (16)
C37—N12—C36	119.12 (15)	C34—C35—H35A	110.2
C37—N12—Pd2	118.92 (12)	C36—C35—H35A	110.2
C36—N12—Pd2	116.46 (11)	C34—C35—H35B	110.2
N1—C1—C2	109.34 (15)	C36—C35—H35B	110.2
N1—C1—H1A	109.8	H35A—C35—H35B	108.5
C2—C1—H1A	109.8	N12—C36—C35	112.17 (15)
N1—C1—H1B	109.8	N12—C36—H36A	109.2
C2—C1—H1B	109.8	C35—C36—H36A	109.2
H1A—C1—H1B	108.3	N12—C36—H36B	109.2
C3—C2—C1	107.89 (16)	C35—C36—H36B	109.2
C3—C2—H2A	110.1	H36A—C36—H36B	107.9
C1—C2—H2A	110.1	N12—C37—N10	118.75 (15)
C3—C2—H2B	110.1	N12—C37—N11	120.81 (16)
C1—C2—H2B	110.1	N10—C37—N11	120.41 (16)
H2A—C2—H2B	108.4	O2—C41—O1	127.10 (17)
N2—C3—C2	111.71 (16)	O2—C41—C42	118.82 (17)
N2—C3—H3A	109.3	O1—C41—C42	114.09 (16)
C2—C3—H3A	109.3	C43—C42—C47	119.05 (19)
N2—C3—H3B	109.3	C43—C42—C41	121.63 (18)
C2—C3—H3B	109.3	C47—C42—C41	119.32 (19)

H3A—C3—H3B	107.9	C42—C43—C44	120.3 (2)
N2—C4—C5	113.17 (16)	C42—C43—H43A	119.9
N2—C4—H4A	108.9	C44—C43—H43A	119.9
C5—C4—H4A	108.9	C45—C44—C43	119.9 (2)
N2—C4—H4B	108.9	C45—C44—H44A	120.1
C5—C4—H4B	108.9	C43—C44—H44A	120.1
H4A—C4—H4B	107.8	C44—C45—C46	120.4 (2)
C4—C5—C6	110.39 (16)	C44—C45—H45A	119.8
C4—C5—H5A	109.6	C46—C45—H45A	119.8
C6—C5—H5A	109.6	C45—C46—C47	120.0 (2)
C4—C5—H5B	109.6	C45—C46—H46A	120.0
C6—C5—H5B	109.6	C47—C46—H46A	120.0
H5A—C5—H5B	108.1	C46—C47—C42	120.5 (2)
N3—C6—C5	108.30 (16)	C46—C47—H47A	119.8
N3—C6—H6A	110.0	C42—C47—H47A	119.8
C5—C6—H6A	110.0	O4—C51—O3	127.09 (17)
N3—C6—H6B	110.0	O4—C51—C52	118.74 (16)
C5—C6—H6B	110.0	O3—C51—C52	114.16 (15)
H6A—C6—H6B	108.4	C53—C52—C57	118.97 (17)
N1—C7—N3	120.10 (16)	C53—C52—C51	121.03 (16)
N1—C7—N2	120.84 (17)	C57—C52—C51	119.97 (17)
N3—C7—N2	119.05 (16)	C54—C53—C52	120.43 (18)
N4—C11—C12	108.91 (15)	C54—C53—H53A	119.8
N4—C11—H11A	109.9	C52—C53—H53A	119.8
C12—C11—H11A	109.9	C55—C54—C53	120.20 (19)
N4—C11—H11B	109.9	C55—C54—H54A	119.9
C12—C11—H11B	109.9	C53—C54—H54A	119.9
H11A—C11—H11B	108.3	C54—C55—C56	119.84 (18)
C13—C12—C11	108.51 (15)	C54—C55—H55A	120.1

C13—C12—H12A	110.0	C56—C55—H55A	120.1
C11—C12—H12A	110.0	C57—C56—C55	119.89 (18)
C13—C12—H12B	110.0	C57—C56—H56A	120.1
C11—C12—H12B	110.0	C55—C56—H56A	120.1
H12A—C12—H12B	108.4	C56—C57—C52	120.66 (18)
N5—C13—C12	111.73 (15)	C56—C57—H57A	119.7
N5—C13—H13A	109.3	C52—C57—H57A	119.7
C12—C13—H13A	109.3	Cl1S—C1S—Cl2S	111.27 (12)
N5—C13—H13B	109.3	Cl1S—C1S—H1SA	109.4
C12—C13—H13B	109.3	Cl2S—C1S—H1SA	109.4
H13A—C13—H13B	107.9	Cl1S—C1S—H1SB	109.4
N5—C14—C15	112.58 (15)	Cl2S—C1S—H1SB	109.4
N5—C14—H14A	109.1	H1SA—C1S—H1SB	108.0
C15—C14—H14A	109.1	Cl4S—C2S—Cl3S	111.41 (12)
N5—C14—H14B	109.1	Cl4S—C2S—H2SA	109.3
C15—C14—H14B	109.1	Cl3S—C2S—H2SA	109.3
H14A—C14—H14B	107.8	Cl4S—C2S—H2SB	109.3
C14—C15—C16	108.69 (16)	Cl3S—C2S—H2SB	109.3
C14—C15—H15A	110.0	H2SA—C2S—H2SB	108.0
C16—C15—H15A	110.0	Cl5S—C3S—Cl6S	110.25 (11)
C14—C15—H15B	110.0	Cl5S—C3S—H3SA	109.6
C16—C15—H15B	110.0	Cl6S—C3S—H3SA	109.6
H15A—C15—H15B	108.3	Cl5S—C3S—H3SB	109.6
N6—C16—C15	109.26 (15)	Cl6S—C3S—H3SB	109.6
N6—C16—H16A	109.8	H3SA—C3S—H3SB	108.1
C15—C16—H16A	109.8	Cl7S—C4S—Cl8S	110.74 (11)
N6—C16—H16B	109.8	Cl7S—C4S—H4SA	109.5
C15—C16—H16B	109.8	Cl8S—C4S—H4SA	109.5
H16A—C16—H16B	108.3	Cl7S—C4S—H4SB	109.5

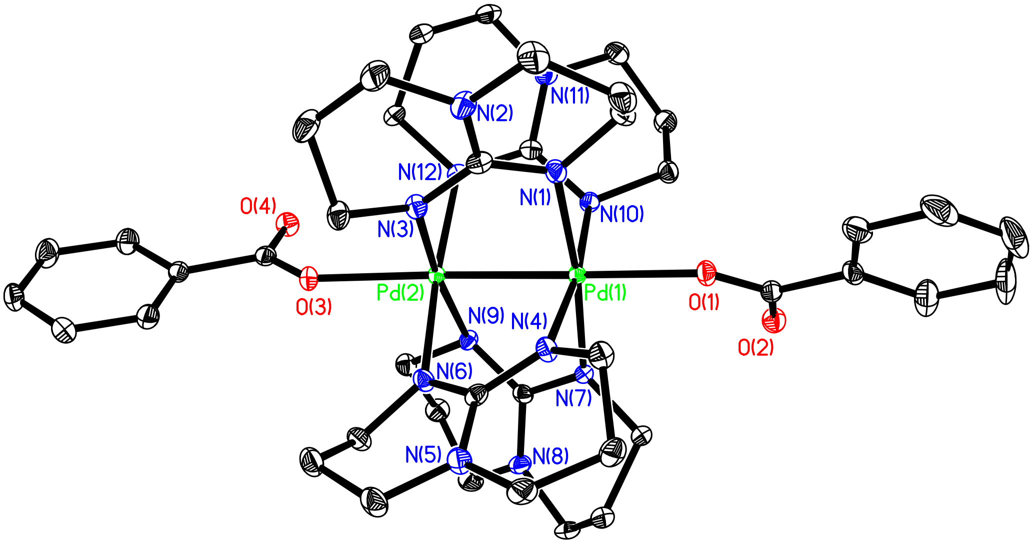
N4—C17—N6	119.79 (16)	Cl8S—C4S—H4SB	109.5
N4—C17—N5	120.56 (16)	H4SA—C4S—H4SB	108.1
N7—Pd1—Pd2—N3	156.36 (6)	C6—N3—C7—N2	-18.9 (2)
N1—Pd1—Pd2—N3	-21.80 (6)	Pd2—N3—C7—N2	173.97 (12)
N4—Pd1—Pd2—N3	68.12 (6)	C3—N2—C7—N1	-7.6 (3)
N10—Pd1—Pd2—N3	-109.70 (6)	C4—N2—C7—N1	165.24 (18)
N7—Pd1—Pd2—N12	-115.87 (6)	C3—N2—C7—N3	172.84 (17)
N1—Pd1—Pd2—N12	65.96 (6)	C4—N2—C7—N3	-14.3 (3)
N4—Pd1—Pd2—N12	155.88 (6)	C17—N4—C11—C12	45.6 (2)
N10—Pd1—Pd2—N12	-21.94 (6)	Pd1—N4—C11—C12	-135.10 (13)
N7—Pd1—Pd2—N6	66.35 (6)	N4—C11—C12—C13	-60.40 (19)
N1—Pd1—Pd2—N6	-111.82 (6)	C17—N5—C13—C12	-12.5 (3)
N4—Pd1—Pd2—N6	-21.90 (6)	C14—N5—C13—C12	175.38 (16)
N10—Pd1—Pd2—N6	160.28 (6)	C11—C12—C13—N5	44.3 (2)
N7—Pd1—Pd2—N9	-22.67 (6)	C17—N5—C14—C15	0.2 (3)
N1—Pd1—Pd2—N9	159.17 (6)	C13—N5—C14—C15	172.30 (17)
N4—Pd1—Pd2—N9	-110.92 (6)	N5—C14—C15—C16	36.6 (2)
N10—Pd1—Pd2—N9	71.26 (6)	C17—N6—C16—C15	48.3 (2)
N7—Pd1—O1—C41	36.54 (16)	Pd2—N6—C16—C15	-127.21 (14)
N1—Pd1—O1—C41	-145.59 (16)	C14—C15—C16—N6	-59.8 (2)
N4—Pd1—O1—C41	124.68 (16)	C11—N4—C17—N6	169.32 (16)
N10—Pd1—O1—C41	-57.87 (16)	Pd1—N4—C17—N6	-10.0 (2)
N3—Pd2—O3—C51	119.33 (17)	C11—N4—C17—N5	-12.2 (3)
N12—Pd2—O3—C51	31.78 (17)	Pd1—N4—C17—N5	168.42 (13)
N6—Pd2—O3—C51	-150.80 (17)	C16—N6—C17—N4	168.30 (16)
N9—Pd2—O3—C51	-62.14 (17)	Pd2—N6—C17—N4	-16.0 (2)
N4—Pd1—N1—C7	-57.20 (14)	C16—N6—C17—N5	-10.2 (2)
N10—Pd1—N1—C7	115.71 (14)	Pd2—N6—C17—N5	165.58 (13)

O1—Pd1—N1—C7	-148.31 (13)	C13—N5—C17—N4	-5.6 (3)
Pd2—Pd1—N1—C7	28.89 (13)	C14—N5—C17—N4	165.77 (17)
N4—Pd1—N1—C1	110.92 (14)	C13—N5—C17—N6	172.88 (17)
N10—Pd1—N1—C1	-76.16 (14)	C14—N5—C17—N6	-15.8 (3)
O1—Pd1—N1—C1	19.82 (14)	C27—N7—C21—C22	-27.0 (2)
Pd2—Pd1—N1—C1	-162.98 (14)	Pd1—N7—C21—C22	128.23 (13)
N12—Pd2—N3—C7	-65.53 (14)	N7—C21—C22—C23	57.5 (2)
N6—Pd2—N3—C7	109.41 (14)	C27—N8—C23—C22	16.4 (2)
O3—Pd2—N3—C7	-162.33 (14)	C24—N8—C23—C22	-163.51 (16)
Pd1—Pd2—N3—C7	21.89 (13)	C21—C22—C23—N8	-51.2 (2)
N12—Pd2—N3—C6	127.82 (14)	C27—N8—C24—C25	10.6 (2)
N6—Pd2—N3—C6	-57.24 (14)	C23—N8—C24—C25	-169.51 (16)
O3—Pd2—N3—C6	31.02 (14)	N8—C24—C25—C26	-47.2 (2)
Pd1—Pd2—N3—C6	-144.76 (13)	C27—N9—C26—C25	-43.4 (2)
N7—Pd1—N4—C17	-62.63 (14)	Pd2—N9—C26—C25	-177.54 (11)
N1—Pd1—N4—C17	111.57 (14)	C24—C25—C26—N9	64.32 (19)
O1—Pd1—N4—C17	-158.69 (14)	C21—N7—C27—N9	172.86 (15)
Pd2—Pd1—N4—C17	24.24 (13)	Pd1—N7—C27—N9	18.4 (2)
N7—Pd1—N4—C11	118.03 (14)	C21—N7—C27—N8	-10.7 (2)
N1—Pd1—N4—C11	-67.76 (14)	Pd1—N7—C27—N8	-165.20 (12)
O1—Pd1—N4—C11	21.97 (14)	C26—N9—C27—N7	-178.90 (15)
Pd2—Pd1—N4—C11	-155.10 (13)	Pd2—N9—C27—N7	-43.11 (19)
N3—Pd2—N6—C17	-59.24 (13)	C26—N9—C27—N8	4.7 (2)
N9—Pd2—N6—C17	114.02 (13)	Pd2—N9—C27—N8	140.49 (14)
O3—Pd2—N6—C17	-149.05 (13)	C24—N8—C27—N7	-163.37 (16)
Pd1—Pd2—N6—C17	27.16 (13)	C23—N8—C27—N7	16.7 (3)
N3—Pd2—N6—C16	116.26 (14)	C24—N8—C27—N9	13.0 (3)
N9—Pd2—N6—C16	-70.48 (14)	C23—N8—C27—N9	-166.94 (17)
O3—Pd2—N6—C16	26.45 (14)	C37—N10—C31—C32	-45.3 (2)

Pd1—Pd2—N6—C16	-157.34 (14)	Pd1—N10—C31—C32	-178.11 (11)
N4—Pd1—N7—C27	96.73 (13)	N10—C31—C32—C33	65.42 (19)
N10—Pd1—N7—C27	-75.95 (13)	C37—N11—C33—C32	4.6 (3)
O1—Pd1—N7—C27	-172.36 (13)	C34—N11—C33—C32	-168.28 (16)
Pd2—Pd1—N7—C27	10.55 (12)	C31—C32—C33—N11	-44.4 (2)
N4—Pd1—N7—C21	-58.49 (12)	C37—N11—C34—C35	19.8 (3)
N10—Pd1—N7—C21	128.83 (12)	C33—N11—C34—C35	-167.19 (16)
O1—Pd1—N7—C21	32.42 (12)	N11—C34—C35—C36	-52.0 (2)
Pd2—Pd1—N7—C21	-144.67 (12)	C37—N12—C36—C35	-26.8 (2)
N12—Pd2—N9—C27	127.08 (12)	Pd2—N12—C36—C35	126.79 (14)
N6—Pd2—N9—C27	-47.59 (12)	C34—C35—C36—N12	56.7 (2)
O3—Pd2—N9—C27	-135.71 (12)	C36—N12—C37—N10	173.06 (15)
Pd1—Pd2—N9—C27	39.98 (11)	Pd2—N12—C37—N10	20.1 (2)
N12—Pd2—N9—C26	-96.54 (12)	C36—N12—C37—N11	-8.9 (2)
N6—Pd2—N9—C26	88.78 (12)	Pd2—N12—C37—N11	-161.88 (13)
O3—Pd2—N9—C26	0.67 (12)	C31—N10—C37—N12	-178.43 (15)
Pd1—Pd2—N9—C26	176.36 (12)	Pd1—N10—C37—N12	-43.94 (19)
N7—Pd1—N10—C37	126.04 (12)	C31—N10—C37—N11	3.6 (2)
N1—Pd1—N10—C37	-47.93 (12)	Pd1—N10—C37—N11	138.04 (14)
O1—Pd1—N10—C37	-137.43 (12)	C33—N11—C37—N12	-159.55 (17)
Pd2—Pd1—N10—C37	39.52 (11)	C34—N11—C37—N12	12.7 (3)
N7—Pd1—N10—C31	-99.18 (12)	C33—N11—C37—N10	18.4 (3)
N1—Pd1—N10—C31	86.86 (12)	C34—N11—C37—N10	-169.28 (17)
O1—Pd1—N10—C31	-2.65 (12)	Pd1—O1—C41—O2	-4.5 (3)
Pd2—Pd1—N10—C31	174.30 (12)	Pd1—O1—C41—C42	175.05 (11)
N3—Pd2—N12—C37	95.58 (13)	O2—C41—C42—C43	173.84 (18)
N9—Pd2—N12—C37	-77.58 (13)	O1—C41—C42—C43	-5.8 (3)
O3—Pd2—N12—C37	-174.90 (13)	O2—C41—C42—C47	-6.9 (3)
Pd1—Pd2—N12—C37	9.08 (12)	O1—C41—C42—C47	173.44 (17)

N3—Pd2—N12—C36	-58.07 (12)	C47—C42—C43—C44	1.3 (3)
N9—Pd2—N12—C36	128.77 (12)	C41—C42—C43—C44	-179.51 (18)
O3—Pd2—N12—C36	31.45 (13)	C42—C43—C44—C45	-0.7 (3)
Pd1—Pd2—N12—C36	-144.57 (12)	C43—C44—C45—C46	-0.2 (3)
C7—N1—C1—C2	42.9 (2)	C44—C45—C46—C47	0.6 (4)
Pd1—N1—C1—C2	-125.05 (14)	C45—C46—C47—C42	-0.1 (3)
N1—C1—C2—C3	-60.5 (2)	C43—C42—C47—C46	-0.9 (3)
C7—N2—C3—C2	-13.4 (3)	C41—C42—C47—C46	179.90 (19)
C4—N2—C3—C2	173.06 (17)	Pd2—O3—C51—O4	1.0 (3)
C1—C2—C3—N2	46.0 (2)	Pd2—O3—C51—C52	-178.55 (11)
C7—N2—C4—C5	7.6 (3)	O4—C51—C52—C53	173.52 (17)
C3—N2—C4—C5	-178.90 (18)	O3—C51—C52—C53	-6.9 (2)
N2—C4—C5—C6	28.2 (2)	O4—C51—C52—C57	-8.3 (3)
C7—N3—C6—C5	54.4 (2)	O3—C51—C52—C57	171.35 (16)
Pd2—N3—C6—C5	-138.64 (13)	C57—C52—C53—C54	0.2 (3)
C4—C5—C6—N3	-57.1 (2)	C51—C52—C53—C54	178.48 (17)
C1—N1—C7—N3	171.28 (16)	C52—C53—C54—C55	-0.7 (3)
Pd1—N1—C7—N3	-20.1 (2)	C53—C54—C55—C56	0.6 (3)
C1—N1—C7—N2	-8.2 (3)	C54—C55—C56—C57	0.0 (3)
Pd1—N1—C7—N2	160.38 (13)	C55—C56—C57—C52	-0.4 (3)
C6—N3—C7—N1	161.60 (16)	C53—C52—C57—C56	0.3 (3)
Pd2—N3—C7—N1	-5.6 (2)	C51—C52—C57—C56	-177.97 (17)

Figure S10. X-ray structure of 24



The x-ray structure of **24** with hydrogens and the atomic labeling scheme. The nonhydrogen atoms are depicted with 50% probability ellipsoids.