Electronic supplementary information (ESI)

Directed *ortho* C-H borylation catalyzed using Cp*Rh(III)-NHC complexes

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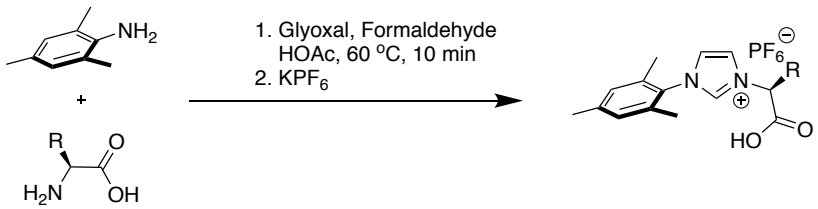
1. General Remarks

Unless indicated otherwise, all reactions requiring an inert atmosphere were conducted in an argon-filled Braun glove box. All solvents were distilled and degassed prior to use. $[RhCp^*Cl_2]_2$ was purchased from Strem Chemicals. Bis(pinacolato)diboron (B_2pin_2) was purchased from Fluorochem. Pinacolborane (HBpin) was purchased from Sigma-Aldrich. Other chemicals were used as received unless otherwise noted. Several starting materials were synthesized according to modified literature procedures (*vide infra*). Silica gel chromatography was performed with Sigma-Aldrich's silica gel high-purity grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size. Products were visualized using a 254 nm UV lamp on TLC plates unless otherwise noted. NMR spectra were acquired on 400 MHz Bruker instruments at the Ecole Nationale Supérieure de Chimie de Rennes. Chemicals shifts were reported relative to residual solvent peaks ($CDCl_3$ = 7.26 ppm for ^1H and 77.2 ppm for ^{13}C; Benzene-d_6 = 7.16 ppm for ^1H). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, br = broad, h = heptets. NMR yields were determined by ^1H NMR spectroscopy with 1,3,5-trimethybenzene as an internal standard unless otherwise noted. Mass spectrometric analyses were performed at Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Gas Phase Chromatography analysis was conducted on SHIMADZU GCMS-QP2010 SE with SH-RXi-5ms column equipped with QP5000 detector. Optical rotations were recorded on a Perkin Elmer 341 polarimeter.

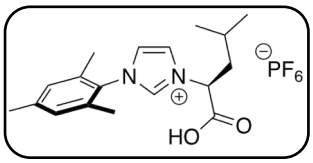
2. Preparation of Cp*RhCl/NHC complexes

2.1. Preparation of the imidazolium salts

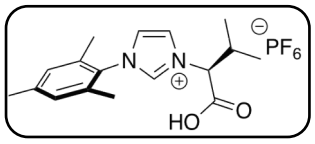


The imidazolium salts **2a.PF$_6$**, **2b.PF$_6$** and **2c.PF$_6$** were prepared according to the reported procedure by our laboratory.[1] Mixture A: In a round-bottomed flask were placed 2,4,6-trimethylaniline (4.0 mmol), a corresponding *L*-amino acid (4.0 mmol) and HOAc (18.0 mmol). The mixture was stirred at 60 °C for 5 min. Mixture B: In another round-bottomed flask were placed glyoxal (4.0 mmol), formaldehyde (4.0 mmol) and HOAc (18.0 mmol). The mixture was stirred at 60 °C for 5 min. Then B was added into A. The combined mixture was stirred at 60 °C for 10 min. After cooled down, the mixture was evaporated to remove HOAc. Then H_2O (20 mL) and CH_2Cl_2 (20 mL) were added. The aqueous layer was extracted by CH_2Cl_2 (20 mL x 2). To the combined organic layer was added brine (20 mL) was added. Then the organic layer was separated.

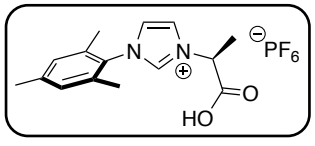
Then KPF_6 (4.0 mmol) and water (50 mL) was added to the organic layer. The mixture was stirred at room temperature for 1 h. Then organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. Then imidazolium-PF_6 salts were isolated by flash column chromatography on silica gel (CH_2Cl_2: EtOH = 9:1).



Imidazolium salt **2a.PF$_6$**[1] (pale yellow solid, 52 % yield) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.73 (br. s, 1H), 9.02 (s, 1H), 7.82 (s, 1H), 7.26 (s, 1H), 7.00 (s, 2H), 5.46-5.42 (m, 1H), 2.33 (s, 3H), 2.16- 2.04 (m, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.48-1.39 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 141.0, 136.4, 134.3, 130.9, 129.7, 123.6, 122.9, 63.6, 41.7, 25.1, 22.9, 21.0, 17.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.4 (h, *J* = 732.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.9 (d, *J* = 732.0 Hz).



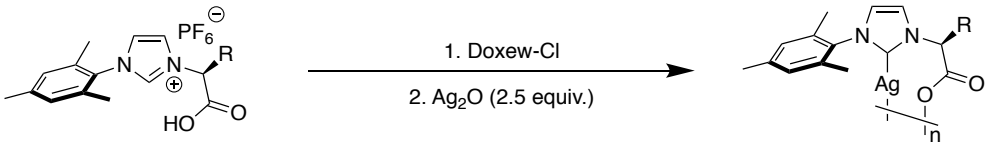
Imidazolium salt **2b.PF$_6$**[1] (pale yellow solid, 46 % yield) ^{1}H- NMR (400 MHz, $CDCl_3$): δ 9.31 (br. s, 1H), 7.88 (s, 1H), 7.11 (s, 1H), 6.91 (s, 1H), 6.90 (s, 1H), 4.84 (m, 1H, *J* = 6.8 Hz), 2.45-2.40 (m, 1H), 2.24 (s, 3H), 1.93 (s, 6H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 141.0, 137.0, 134.4, 134.1, 131.0, 129.7, 129.6, 124.4, 121.6, 72.2, 32.2, 21.1, 19.7, 18.2, 17.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.4 (h, *J* = 732.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.9 (d, *J* = 732.1 Hz).



Imidazolium salt **2c.PF$_6$** (pale yellow solid, 42 % yield) ^{1}H- NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 7.76 (s, 1H), 7.18 (s, 1H), 6.98 (s, 2H), 5.37 (br. s, 1H), 2.32 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.85 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 141.4, 136.5, 134.6, 130.7, 129.9, 123.4, 123.1, 29.8, 21.2, 17.9, 17.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.4 (h, *J* = 712.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.9 (d, *J* = 713.0 Hz). HRMS (ESI) calcd

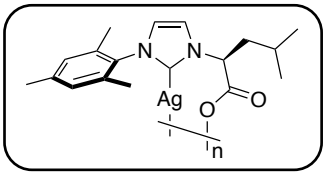
for $C_{15}H_{19}N_2O_2^+$ (M – PF_6^+): *m/z* 259.1441 found 259.1440 (0 ppm). $[\alpha]_D^{20}$ = +11.2 (*c* = 2.5 x 10^{-3}, chloroform).

2.2. Preparation of Ag.NHC intermediate complexes

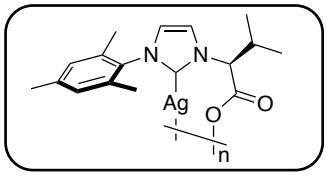


The pure imidazolium-PF_6 was loaded on the ion exchange resin Dowex® 1x2 chloride form (10 mL/ 1.0 mmol) with Milli Q water/Acetone = 2/1.5 as an eluent. After removal of acetone and water under reduced pressure, the residue was dissolved in CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the desired **2a.Cl**, **2b.Cl,** or **2c.Cl** salts.

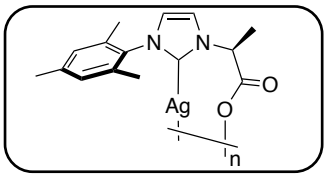
In a flame-dried round-bottomed flask were placed Ag_2O (2.5 equiv.), **2a.Cl**, **2b.Cl,** or **2c.Cl** (1 equiv.), CH_2Cl_2 (0.077 M), and 4 Å molecular sieves. The mixture was stirred at room temperature for 24 h under Ar excluding from the light. Next, CH_2Cl_2 was removed under reduce pressure. Then, acetone was added, and the mixture was filtered through a celite pad using acetone as eluent. The filtered solution was concentrated. Then pentane was added to induce precipitation. The precipitate was washed twice with pentane. The desired silver intermediate complex was obtained upon the removal of solvent under vacuum.



Ag.2a (light brown solid, 99 % yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (br. s, 1H), 6.90 (s, 2H), 6.88 (s, 1H), 5.24 (br. s, 1H), 2.33 (s, 3H), 2.05 (br. s, 2H), 1.93 (s, 3H), 1.84 (br. s, 3H), 1.28 (br. s, 1H), 0.95 (br. s, 3H), 0.89 (s, 3H).

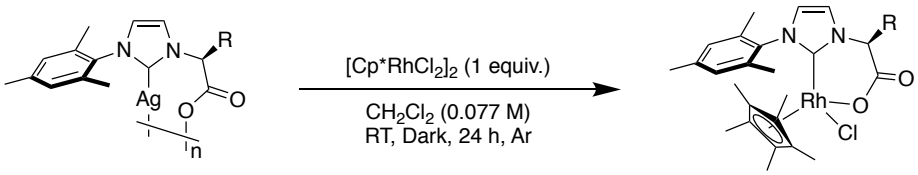


Ag.2b (light brown solid, 97 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (br. s, 1H), 6.92 (s, 2H), 6.88 (br. s, 1H), 4.81 (br. s, 1H), 2.48 (br. s, 1H), 2.32 (s, 3H), 1.95 (br. s, 6H), 1.11 (br. s, 3H), 0.82 (s, 3H).

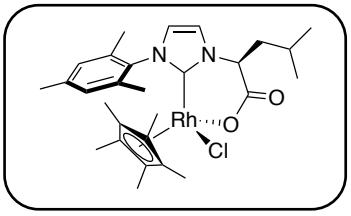


Ag.2c (light brown solid, 90 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 6.91 (s, 2H), 6.84 (s, 1H), 5.24 (s, 1H), 2.32 (s, 3H), 2.02 – 1.84 (m, 7H), 1.77 (d, *J* = 7.2 Hz, 3H).

2.3. Preparation of Cp*RhCl/NHC complexes



In a dry round-bottomed flask were placed an equivalence of silver complex **Ag.2a, Ag.2b** or **Ag.2c** (which is considered as a dimer), $[RhCp^*Cl_2]_2$ (1 equiv.) and CH_2Cl_2 (0.077 M). The mixture was stirred for 24 h under Ar atmosphere excluding from the light. Next, CH_2Cl_2 was removed under reduce pressure. Then, acetone was added, and the mixture was filtered through a celite pad using acetone as eluent. The filtered solution was concentrated. Then pentane was added to induce precipitation. The precipitate was washed twice with pentane. After removal of volatility, the complex was obtained after crystallization in bilayer of acetone and cyclohexane.



Complex 3a (red solid, 92% yield, 9:1 d.r.). **For major diastereomer**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 1.7 Hz, 1H, NC<u>H</u>$_{Heterocycle}$), 7.01 (s, 1H, $CH_{Mesityl}$), 6.96 (s, 1H, $CH_{Mesityl}$), 6.78 (d, J = 1.9 Hz, 1H, NC<u>H</u>$_{Heterocycle}$), 4.80 (dd, J = 9.3, 5.0 Hz, 1H, NC<u>H</u>CH_2), 2.43 (s, 3H, *o*-$CH_{3Mesityl}$), 2.34 (s, 3H, *o*-$CH_{3Mesityl}$), 2.02 – 1.96 (m, 1H, CHC<u>H$_2$</u>CH), 1.96 (s, 3H, *p*-$CH_{3Mesityl}$), 1.84 – 1.74 (m, 1H, CHC<u>H$_2$</u>CH), 1.60 – 1.49 (m, 1H, <u>C</u>H$(CH_3)_2$), 1.31 (s, 15H, Cp*), 1.00 (d, J = 6.5 Hz, 3H, CH(C<u>H$_3$</u>)$_2$), 0.95 (d, J = 6.5 Hz, 3H, CH(C<u>H$_3$</u>)$_2$). **For minor diastereomer**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 1.7 Hz, 1H, NC<u>H</u>$_{Heterocycle}$), 6.98 (s, 1H, $CH_{Mesityl}$), 6.96 (s, 1H, $CH_{Mesityl}$), 6.78 (d, J = 1.9 Hz, 1H, NC<u>H</u>$_{Heterocycle}$), 4.60 (t, J = 7.9 Hz, 1H, NC<u>H</u>CH_2), 2.34 (s, 3H, *o*-$CH_{3Mesityl}$), 2.27 (s, 3H, *o*-$CH_{3Mesityl}$), 2.06 (s, 3H, *p*-$CH_{3Mesityl}$), 2.02 – 1.96 (m, 1H, CHC<u>H$_2$</u>CH), 1.84 – 1.74 (m, 1H, CHC<u>H$_2$</u>CH), 1.60 – 1.49 (m, 1H, <u>C</u>H$(CH_3)_2$), 1.31 (s, 15H, Cp*), 1.00 (d, J = 6.5 Hz, 3H, CH(C<u>H$_3$</u>)$_2$), 0.95 (d, J = 6.5 Hz, 3H, CH(C<u>H$_3$</u>)$_2$). **For both diastereomers**; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 170.7 (d, J = 54.7 Hz), 139.7, 139.6, 138.6, 138.1, 136.6, 136.5, 130.3, 130.1, 128.6, 124.0, 123.4, 96.7 (d, J = 7.8 Hz, minor diastereomer), 96.4 (d, J = 7.6 Hz, major diastereomer), 64.7, 45.7, 31.1, 27.0, 25.1, 24.8, 23.3, 22.9, 22.7, 21.9, 21.2, 21.1, 20.0, 19.9, 18.9, 18.3, 9.2. HRMS (ESI) calcd for $C_{28}H_{39}N_2O_2{}^{35}ClRh^+$ (M + H^+): *m/z* 573.1750, found 573.1753 (1 ppm). The crystallization in bilayer of acetone and cyclohexane provides the crystal which suitable for X-ray crystallography.

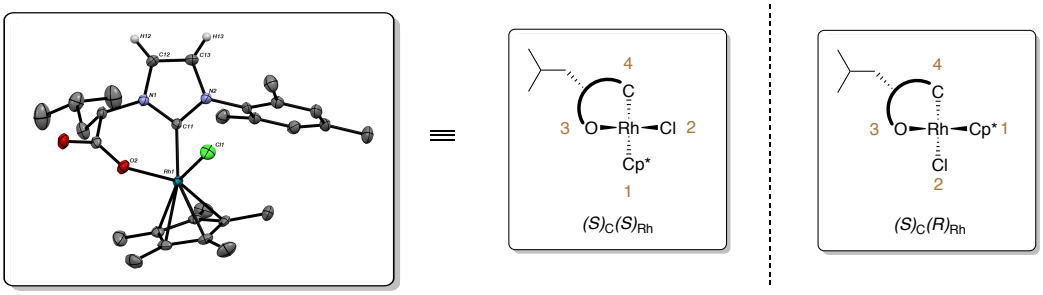
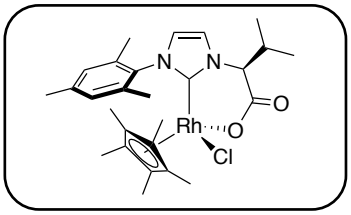


Fig. S1 The absolute configuration of **Crystal.3a** (left) and its corresponding diastereomer (right).[2]



Complex 3b (red solid, 82% yield, 9:1 d.r.). **For major diastereomer**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.99 (d, *J* = 1.9 Hz, 1H), 6.95 (s, 1H), 6.78 (d, *J* = 1.9 Hz, 1H), 4.18 (d, *J* = 9.6 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H), 2.21 (td, *J* = 6.8, 2.7 Hz, 1H), 1.98 (s, 3H), 1.32 (s, 15H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.7 Hz, 3H). **For minor diastereomer**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 7.00 – 6.97 (m, 2H), 6.75 (d, *J* = 2.0 Hz, 1H), 4.10 (d, *J* = 10.5 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 2.26 – 2.18 (m, 1H), 2.11 (s, 3H), 1.26 (s, 15H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H). **For both diastereomers**; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 170.1 (d, $J_{Rh\text{-}C}$ = 55.0 Hz), 169.9, 139.7, 138.2, 136.6, 136.5, 130.3, 128.4, 125.3, 123.8, 96.2 (d, $J_{Rh\text{-}C}$ = 7.7 Hz), 73.9, 34.7, 29.8, 21.1, 20.2, 20.1, 19.7, 18.5, 9.2. HRMS (ESI) calcd for $C_{27}H_{36}N_2O_2{}^{35}ClNaRh^+$ (M + Na^+): *m/z* 581.1413, found 581.1414 (0 ppm). The crystallization in bilayer of acetone and cyclohexane provides the crystal which suitable for X-ray crystallography.

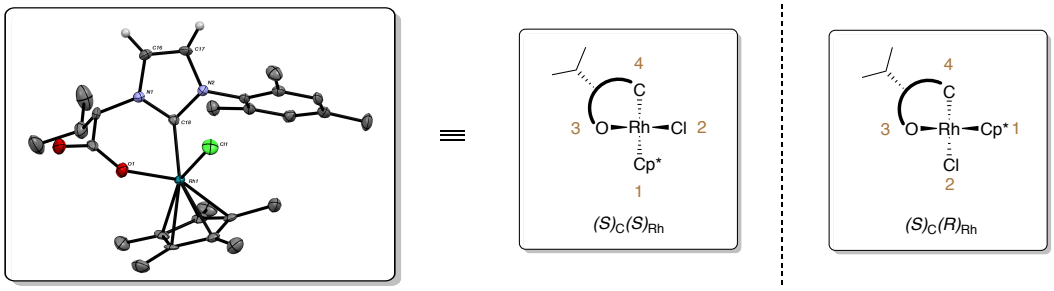
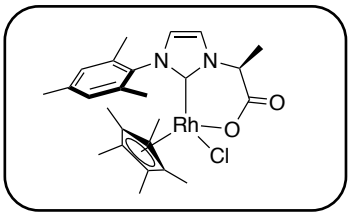


Fig. S2 The absolute configuration of **Crystal.3b** (left) and its corresponding diastereomer (right).[2]



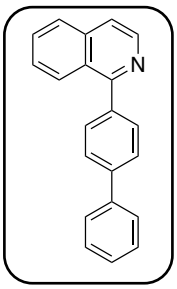
Complex 3c (red solid, 94% yield, 7.5:2.5 d.r.). **For major diastereomer**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 2.0 Hz, 1H), 7.01 (s, 1H), 7.00 (s, 1H), 6.75 (d, J = 2.0 Hz, 1H), 5.19 (q, J = 7.0 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.09 (s, 3H), 1.66 (d, J = 7.1 Hz, 3H), 1.26 (s, 14H). **For minor diastereomer**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 2.0 Hz, 1H), 7.00 (s, 1H), 6.95 (s, 1H), 6.80 (d, J = 2.0 Hz, 1H), 4.72 (q, J = 7.2 Hz, 1H), 2.34 (s, 3H), 2.26 (s, 3H), 2.07 (s, 3H), 1.84 (d, J = 7.2 Hz, 3H). **For major diastereomer**; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 169.5(d, $J_{Rh\text{-}C}$ = 54.5 Hz), 139.9, 137.9, 136.9, 136.0, 130.1, 129.1, 123.3, 120.8, 97.0 (d, $J_{Rh\text{-}C}$ = 7.0 Hz) , 59.2, 21.2, 19.2, 18.4, 18.2, 9.1. **For minor diastereomer**; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 169.0 (d, $J_{Rh\text{-}C}$ = 54.5 Hz), 139.6, 138.6, 136.5, 135.7, 130.1, 128.5, 124.7, 121.8, 96.7 (d, $J_{Rh\text{-}C}$ = 8.1 Hz), 62.2, 21.8, 21.2, 19.8, 18.8, 9.2. HRMS (ESI) calcd for $C_{25}H_{33}N_2O_2{}^{35}ClRh^+$ (M + H^+): *m/z* 531.1280, found 531.1282 (0 ppm).

3. Preparation of Substrates

Except compound **4a** (CAS: 1008-89-5) and **4q** (CAS: 2116-65-6) which are purchased from Alfa Aesar, other substrates were synthesized according to procedure reported in the literature.

3.1. Preparation of 2-arylpyridines and 1-arylisoquinolines[3]

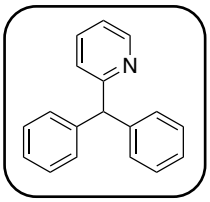
To a solution of 2-bromopyridines (2 mmol) (or 2,4-dibromopyridine (1 mmol) for **4l**) in toluene (7 mL), ethanol (1.5 mL), and H_2O (7 mL) was added Na_2CO_3 (14.8 mmol) followed by $Pd(PPh_3)_4$ (0.06 mmol) and corresponding boronic acid (2.6 mmol) under argon in a 50 mL Schlenk tube. The reaction mixture was refluxed at 120 ^oC for 12 h, and then cooled to room temperature. To the reaction mixture was added aqueous NH_4Cl (15 mL), extracted by EtOAc for three times, dried over $MgSO_4$, and evaporated in vacuum to afford the crude product, which was further purified by flash chromatography on silica gel with *n*-pentane/EtOAc to give the corresponding substrates. Compounds **4b** (CAS: 5957-90-4), **4c** (CAS: 4357-28-2)**, 4d** (CAS: 98061-21-3)**, 4e** (CAS: 4385-61-9)**, 4f** (CAS: 203065-88-7)**, 4g** (CAS: 10273-89-9)**, 4h** (CAS: 4373-61-9)**, 4i** (CAS: 76759-26-7)**, 4j** (CAS: 3475-21-6)**, 4k** (CAS: 940289-80-5)**, 4l** (CAS: 15827-72-2)**, 4m** (CAS: 3297-72-1)**, 4n** (CAS: 36710-74-4)**,** and **4q** (CAS: 525598-48-5) were previously reported.



Compound 4o

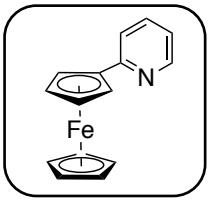
Yellow off-white solid (70 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.7 Hz, 1H), 8.21 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.90 (d, *J* = 8.3 Hz,1H), 7.85 – 7.76 (m, 4H), 7.73 – 7.68 (m, 3H), 7.66 (dd, *J* = 5.7, 0.9 Hz, 1H), 7.57 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.43 – 7.38 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 142.4, 141.5, 140.8, 138.6, 137.0, 130.5, 130.1, 129.0, 127.6, 127.6, 127.3, 127.2, 127.1, 126.8, 120.0. HRMS (ESI) calcd for $C_{21}H_{16}NO$ ($M + H^+$): *m/z* 282.12772, found 282.1278 (0 ppm).

3.2. Preparation of Compound **4r** (CAS: 3678-70-4)



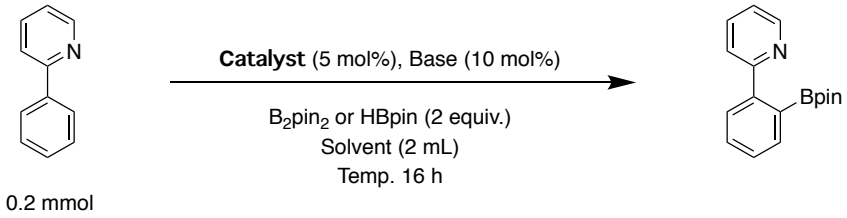
Compound 4r was prepared according to the reported procedure[4] and obtained as off-white solid (0.820 g) Yield: 74%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 7.60 (td, J = 7.7, 1.9 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.27 – 7.18 (m, 6H), 7.14 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.11 (dt, J = 7.8, 1.1 Hz, 1H), 5.74 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 149.6, 142.8, 136.5, 129.5, 128.5, 126.6, 123.8, 121.5, 59.5.

3.3. Preparation of Compound **4s** (CAS: 12216-00-1)



Compound 4s was prepared according to the reported procedure[5] and obtained as red solid. Yield: 21%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.56 (ddd, J = 8.0, 7.4, 1.9 Hz, 1H), 7.40 (ddd, J = 8.0, 1.3, 1.1 Hz, 1H), 7.06 (ddd, J = 7.4, 4.9, 1.2 Hz, 1H), 4.94 – 4.90 (m, 2H), 4.41 – 4.37 (m, 2H), 4.05 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 149.4, 136.0, 120.6, 120.2, 83.8, 70.0, 69.7, 67.3. Analytical data for this compound were consistent with previously reported data.[6]

4. Optimization Study



The studies were carried out on 0.2 mmol scale. Except indicated otherwise, the optimization studies were carried out as followed. In a glove box, in a dry Schlenk tube was placed catalyst (5 mol% of rhodium). Corresponding base (10 mol%) and solvent (2 mL) were added respectively. Next, the mixture was stirred for 10 min followed by the addition of B_2pin_2 (2 equiv. based on boron). The mixture was stirred for another 10 min, and the 2-phenylpyridine (0.2 mmol, 1 equiv.) was added afterward. The tube was closed with septum and sealed with parafilm. Outside the glovebox, the mixture was stirred at indicated temperature for 16h. After cooled down, the mixture was concentrated under reduce pressure and dried under vacuum. The residue was analyzed by ^{1}H-NMR spectroscopy, and the NMR yield was calculated using 1,3,5-trimethylbenzene as an internal standard.

Table S1 Optimization studies

Entry	Catalyst	Base	Borylating agent	Solvent	Temperature (°C)	% Yield
1	**3a**	KOAc	B_2pin_2	toluene	80	0
2	**3a**	K_2CO_3	B_2pin_2	toluene	80	8
3	**3a**	NaO^{t}Bu	B_2pin_2	toluene	80	12
4	**3a**	NaO^{i}Pr	B_2pin_2	toluene	80	61
5	**3a**	NaOEt	B_2pin_2	toluene	80	66
6	**3a**	NaOMe	B_2pin_2	toluene	80	71
7	**3a**	NaHMDS	B_2pin_2	toluene	80	43
8	**3a**	NaOMe	B_2pin_2	*m*-Xylene	80	n.r.
9	**3a**	NaOMe	B_2pin_2	MTBE	80	71
10	**3a**	NaOMe	B_2pin_2	THF	80	34
11	**3a**	NaOMe	B_2pin_2	*n*-octane	80	9
12	**3a**	NaOMe	B_2pin_2	benzene	80	86
13	**3a**	NaOMe	B_2pin_2	benzene	70	43
14	**3a**	NaOMe	B_2pin_2	benzene	r.t.	n.r.
15	**3a**	NaOMe	HBpin	benzene	80	20
16	**3b**	NaOMe	B_2pin_2	benzene	80	80
17	**3c**	NaOMe	B_2pin_2	benzene	80	54
18	$[RhCp^*Cl_2]_2$ + IMes (5 mol%)	NaOMe	B_2pin_2	benzene	80	29
19	$[RhCp^*Cl_2]_2$	NaOMe	B_2pin_2	benzene	80	25
20	$[RhCp^*Cl_2]_2$	-	B_2pin_2	benzene	80	n.r.
21	$[RhCp^*Cl_2]_2$	NaOMe	HBpin	benzene	80	8
22	**2a** (5 mol%)	NaOMe	B_2pin_2	benzene	80	n.r.
23	**3a**	-	B_2pin_2	benzene	80	n.r.
24	-	NaOMe	B_2pin_2	benzene	80	n.r.

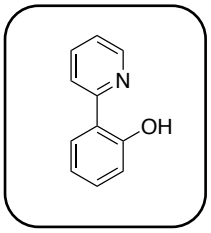
5. Catalytic C-H Borylation

General procedure for C-H borylation

In a glove box, in a dry Schlenk tube was placed **3a** (5 mol%). Then NaOMe (10 mol%) and C_6H_6 were added respectively. Next, the mixture was stirred for 10 min followed by the addition of B_2pin_2 (2 equiv.). The mixture was stirred for another 10 min, and the substrate (1 equiv.) was added afterward. The tube was closed with a septum and sealed with parafilm. Outside the glove box, the mixture was stirred at 80 °C for 16h. After cooled down, the mixture was concentrated under reduce pressure and dried under vacuum. To the residue were added 1,3,5-trimethylbenzene (as an internal standard) and 2 mL of $CDCl_3$. Then the aliquot was analyzed by ^1H NMR which reveal the NMR yield.

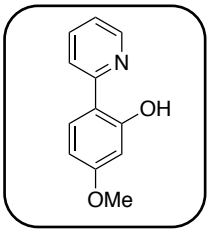
To the crude residue was added acetone (10 mL). Next, Oxone® (2 equiv.) in 2 mL of water was added dropwise within 2-4 min. Upon the complete addition, the mixture was vigorously stirred for 2 hours. Then an aqueous solution of $NaHSO_3$ (ca. 25 mL) was added until the formed precipitates dissolved. Then the aqueous layer was extracted by EtOAc (3x30 mL). The combined organic layer was washed with brine then water. After the removal of solvents, the crude residue was purified by column chromatography on silica gel using pentane/ethylacetate as eluent.

Compound **6a**



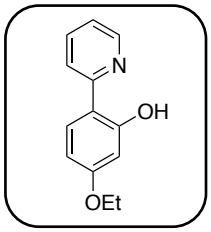
Yellow oil (77 % isolated yield, 86 % NMR yield as borylated product) ^1H NMR (400 MHz, $CDCl_3$) δ 14.24 (s, 1H), 8.50 (ddd, J = 5.1, 1.9, 1.0 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.31 (ddd, J = 8.2, 7.2, 1.6 Hz, 1H), 7.23 (ddd, J = 7.4, 5.0, 1.1 Hz, 1H), 7.04 (dd, J = 8.3, 1.3 Hz, 1H), 6.91 (ddd, J = 7.8, 7.1, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 158.0, 145.9, 137.9, 131.6, 126.2, 121.6, 119.1, 118.9, 118.9, 118.7. Analytical data for this compound were consistent with previously reported data.[7]

Compound **6b**



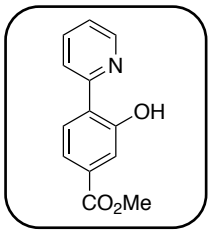
Yellow oil (67 % isolated yield, 75 % NMR yield as borylated product). ^1H NMR (400 MHz, $CDCl_3$) δ 14.72 (s, 1H), 8.43 (ddd, J = 5.0, 1.8, 1.4 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.68 (d, J = 8.8 Hz, 1H), 7.18 – 7.10 (m, 1H), 6.55 (d, J = 2.7 Hz, 1H), 6.48 (dd, J = 8.8, 2.7 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 162.0, 157.9, 145.6, 137.7, 127.2, 120.6, 118.3, 112.2, 106.7, 102.2, 55.4. Analytical data for this compound were consistent with previously reported data.[7]

Compound **6c**



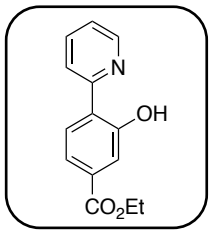
Yellow oil (64 % isolated yield, 77 % NMR yield as borylated product). ^1H NMR (400 MHz, $CDCl_3$) δ 14.70 (s, 1H), 8.42 (ddd, J = 5.1, 1.5, 1.3 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.67 (d, J = 8.8 Hz, 1H), 7.17 – 7.10 (m, 1H), 6.53 (d, J = 2.6 Hz, 1H), 6.47 (dd, J = 8.8, 2.6 Hz, 1H), 4.06 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 161.8, 158.0, 145.6, 137.7, 127.2, 120.5, 118.3, 112.0, 107.1, 102.7, 63.6, 14.9. Analytical data for this compound were consistent with previously reported data.[8]

Compound **6d**



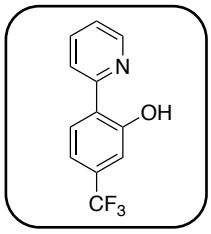
Off-white solid (70 % isolated yield, 81 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.41 (s, 1H), 8.51 (ddd, *J* = 5.0, 1.8, 0.9 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.53 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.28 (ddd, *J* = 7.5, 5.0, 1.1 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 159.9, 156.9, 146.1, 138.1, 132.6, 126.2, 122.6, 122.5, 119.9, 119.8, 119.6, 52.3. Analytical data for this compound were consistent with previously reported data.[9]

Compound **6e**



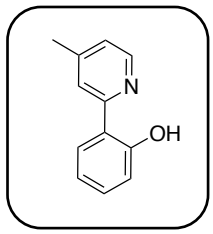
Off-white solid (67 % isolated yield, 80 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.40 (s, 1H), 8.51 (ddd, *J* = 5.1, 1.9, 0.9 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.54 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.28 (ddd, *J* = 7.5, 5.0, 1.1 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 159.8, 156.9, 146.1, 138.1, 132.9, 126.1, 122.5, 119.9, 119.8, 119.6, 61.2, 14.4. Analytical data for this compound were consistent with previously reported data.[7]

Compound **6f**



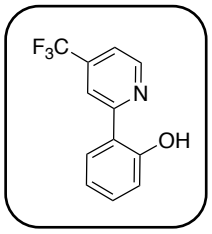
Yellow solid (44 % isolated yield, 60 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.63 (s, 1H), 8.52 (ddd, *J* = 5.1, 1.8, 1.0 Hz, 1H), 7.91 (dt, *J* = 8.3, 1.2 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.31 (ddd, *J* = 7.3, 5.0, 1.3 Hz, 1H), 7.28 (s, 1H), 7.11 (ddd, *J* = 8.3, 1.9, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 156.6, 146.1, 138.2, 133.0 (q, *J* = 32.7 Hz), 126.7, 123.9 (q, *J* = 273.7 Hz), 122.6, 121.6, 119.6, 115.9 (q, *J* = 3.9 Hz), 115.1 (q, *J* = 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2. Analytical data for this compound were consistent with previously reported data.[10]

Compound **6j**



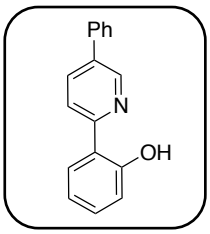
Off-white solid (40 % isolated yield, 45 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.56 (s, 1H), 8.35 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.72 (s, 1H), 7.30 (ddd, *J* = 8.3, 7.2, 1.6 Hz, 1H), 7.06 (ddd, *J* = 5.1, 1.5, 0.7 Hz, 1H), 7.02 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.90 (ddd, *J* = 7.9, 7.2, 1.3 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.7, 149.1, 145.6, 131.4, 126.1, 122.8, 119.7, 118.9, 118.7, 118.7, 21.8. Analytical data for this compound were consistent with previously reported data.[10]

Compound **6k**



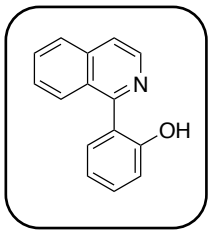
Yellow solid (40 % isolated yield, 48 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.59 (s, 1H), 8.70 (d, *J* = 5.2 Hz, 1H), 8.11 (s, 1H), 7.82 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.46 (dd, *J* = 5.3, 1.5 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.06 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.96 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 159.4, 147.4, 140.1 (q, *J* = 34.0 Hz), 132.7, 126.5, 122.8 (q, *J* = 274.7 Hz), 119.4, 119.0, 118.1, 117.0 (q, *J* = 3.4 Hz), 115.2 (q, *J* = 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1. HRMS (ESI) calcd for $C_{12}H_8NOF_3Na^+$ (M + Na^+): *m/z* 262.04502, found 262.0452 (1 ppm).

Compound **6l**



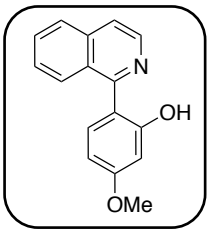
Pale yellow solid (45 % isolated yield, 56 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.29 (s, 1H), 8.76 (dd, J = 2.4, 0.9 Hz, 1H), 8.05 (dd, J = 8.6, 2.4 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.84 (dd, J = 8.0, 1.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.56 – 7.47 (m, 2H), 7.47 – 7.40 (m, 1H), 7.33 (ddd, J = 8.3, 7.2, 1.6 Hz, 1H), 7.05 (dd, J = 8.3, 1.3 Hz, 1H), 6.94 (ddd, J = 8.0, 7.2, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 156.7, 144.3, 137.2, 136.1, 134.6, 131.6, 129.4, 128.5, 127.0, 126.3, 119.2, 119.0, 118.8, 118.8. HRMS (ESI) calcd for $C_{17}H_{14}NO^+$ (M + H^+): *m/z* 248.10699, found 248.1067 (1 ppm).

Compound **6m**



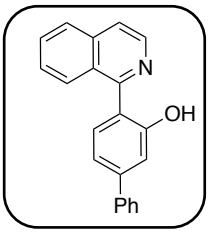
Yellow solid (46 % isolated yield, 51 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.91 (s, 1H), 8.51 – 8.42 (m, 2H), 7.89 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.67 – 7.58 (m, 2H), 7.39 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.02 (td, *J* = 7.6, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 157.9, 139.4, 138.0, 131.7, 131.1, 130.6, 127.8, 127.7, 127.5, 126.3, 121.4, 120.3, 118.8, 118.2. Analytical data for this compound were consistent with previously reported data.[10]

Compound **6n**



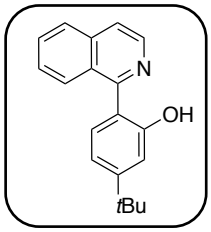
Yellow solid (60 % isolated yield, 76 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.53 (s, 1H), 8.42 (dd, *J* = 21.7, 7.1 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.65 (m, 2H), 7.63 - 7.51 (m, 2H), 6.71 (d, *J* = 2.6 Hz, 1H), 6.58 (dd, *J* = 8.7, 2.7 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 160.2, 158.8, 139.0, 138.0, 132.7, 130.5, 127.8, 127.5, 127.4, 126.0, 119.4, 114.3, 106.0, 102.5, 55.5. HRMS (ESI) calcd for $C_{16}H_{14}NO_2^+$ (M + H^+): *m/z* 252.1019, found 252.1018 (0 ppm).

Compound **6o**



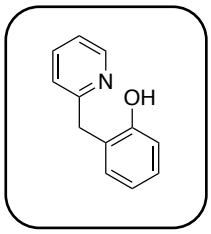
Off-white solid (64 % isolated yield, 81 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.52 (d, *J* = 8.6 Hz, 1H), 8.48 (d, *J* = 5.7 Hz, 1H), 7.89 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.69 (m, 3H), 7.66 – 7.61 (m, 2H), 7.52 – 7.45 (m, 3H), 7.43 – 7.37 (m, 1H), 7.28 (dd, *J* = 8.1, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 158.4, 143.9, 140.4, 139.3, 138.0, 132.0, 130.7, 128.9, 127.9, 127.8, 127.7, 127.5, 127.2, 126.3, 120.3, 120.2, 117.6, 116.6. HRMS (ESI) calcd for $C_{21}H_{16}NO^+$ (M + H^+): *m/z* 298.12264, found 298.1229 (1 ppm).

Compound **6p**



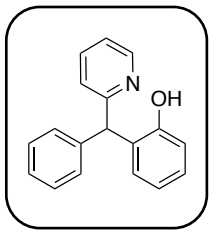
Yellow off-white solid (41 % isolated yield, 54 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.50 (d, *J* = 8.5 Hz, 1H), 8.44 (d, *J* = 5.7 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.63 – 7.57 (m, 2H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.05 (dd, *J* = 8.3, 2.0 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 157.8, 155.0, 139.3, 138.0, 131.3, 130.6, 128.0, 127.5, 127.4, 126.3, 119.9, 118.6, 116.2, 115.3, 35.0, 31.3. HRMS (ESI) calcd for $C_{19}H_{20}NO^+$ (M + H^+): *m/z* 278.15394, found 278.1540 (0 ppm).

Compound **6q**



Off-white solid (33 % isolated yield, 37 % NMR yield as borylated product) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 8.50 – 8.44 (m, 1H), 7.69 (tdd, *J* = 7.7, 1.8, 0.6 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.13 (m, 3H), 7.03 – 6.97 (m, 1H), 6.85 – 6.77 (m, 1H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 156.7, 147.8, 138.4, 130.3, 128.8, 126.3, 122.9, 122.0, 120.1, 118.6, 41.8. Analytical data for this compound were consistent with previously reported data.[11]

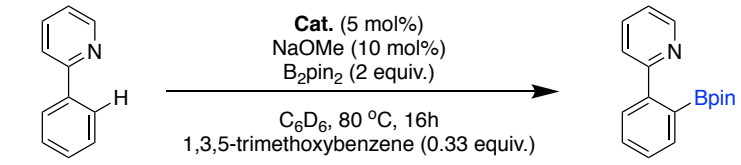
Compound **6r**



White solid (7 % isolated yield, 12 % NMR yield as borylated product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H), 8.50 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.27 – 7.09 (m, 7H), 6.96 – 6.88 (m, 3H), 6.83 (td, *J* = 7.4, 1.3 Hz, 1H), 5.27 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 156.7, 148.3, 141.4, 138.6, 132.1, 129.6, 128.3, 127.8, 127.8, 126.6, 124.8, 122.7, 119.9, 119.8, 59.3. HRMS (ESI) calcd for $C_{18}H_{16}NO^+$ (M + H^+): *m/z* 262.12264, found 262.1227 (0 ppm).

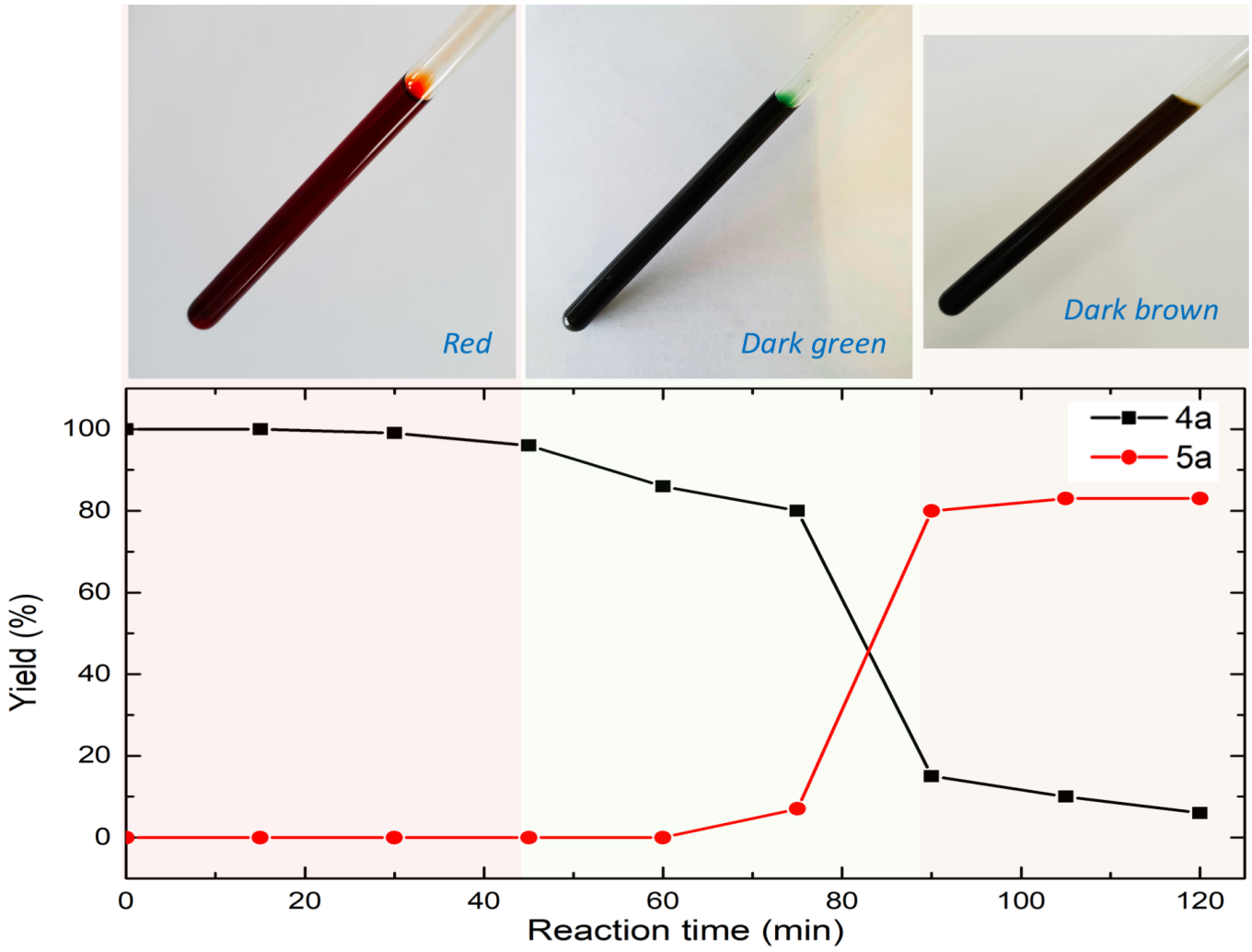
6. Preliminary Mechanistic Study

6.1. Kinetic study for **3a**-catalyzed C-H borylation of **4a**



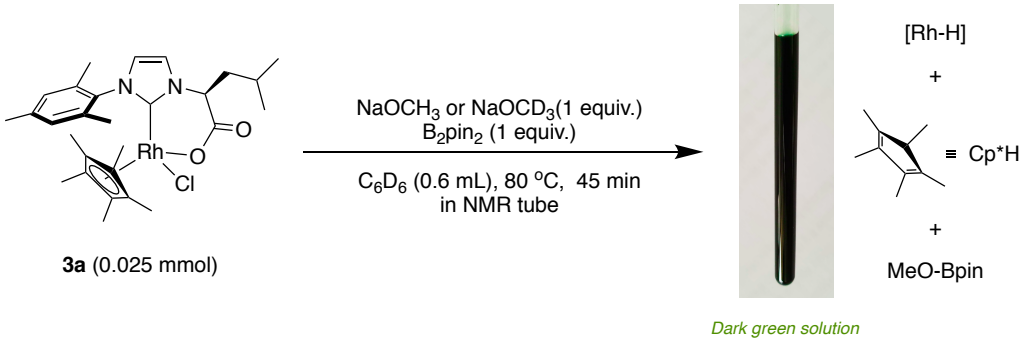
4a (1.0 mmol) **5a**

In a glove box, in a dry Schlenk tube was placed **3a** (5 mol%). Then NaOMe (10 mol%) and C_6D_6 (10 mL) were added respectively. Next, the mixture was stirred for 10 min followed by the addition of B_2pin_2 (2.0 mmol). The mixture was stirred for another 10 min. Then **4a** (1.0 mmol) and 1,3,5-trimethoxybenzene (56 mg) was added afterward. The tube was closed with a septum and sealed with parafilm. Outside the glove box, the mixture was stirred at 80 °C. Under the argon flow, the aliquot (ca. 0.5 mL) was taken after 15, 30, 45, 60, 75, 90, 105 and 120 minutes. The study was monitored by ^{1}H-NMR method, and the yield was calculated versus 1,3,5-trimethoxybenzene. The kinetic plot is shown below.



Scheme S1 Kinetic plot of **3a**-catalyzed C-H borylation of **4a**

6.2. Stoichiometric experiments



3a (0.025 mmol)

In a glove box, in a dry J. Young valve NMR tube was placed a red dispersion of **3a** (0.025 mmol in 0.6 mL of C_6D_6). Then an equivalent of $NaOCH_3$ or $NaOCD_3$ and B_2pin_2 (1 equiv.) were added respectively. The tube was sealed. Outside the glove box, the mixture was allowed to react at 80 °C for 45 minutes then subjected to NMR analysis. After NMR analysis, in the glovebox, the residue was sampled and subjected to the GCMS analysis.

In ^{1}H NMR spectra, a signal at 3.51 ppm was observed corresponding to $\underline{CH_3}OBpin$.[12] This signal disappeared when $NaOCD_3$ was used. In ^{11}B NMR spectra, a signal at 22.7 ppm for $CH_3O\underline{B}pin$ was observed in both cases. Furthermore, key signals at 1.81 and 1.74 ppm were observed which refer to Cp*H.[13] This compound was also detected in GCMS analysis; GCMS (EI): *m/z* 136 (50), 121 (100), 105 (50).

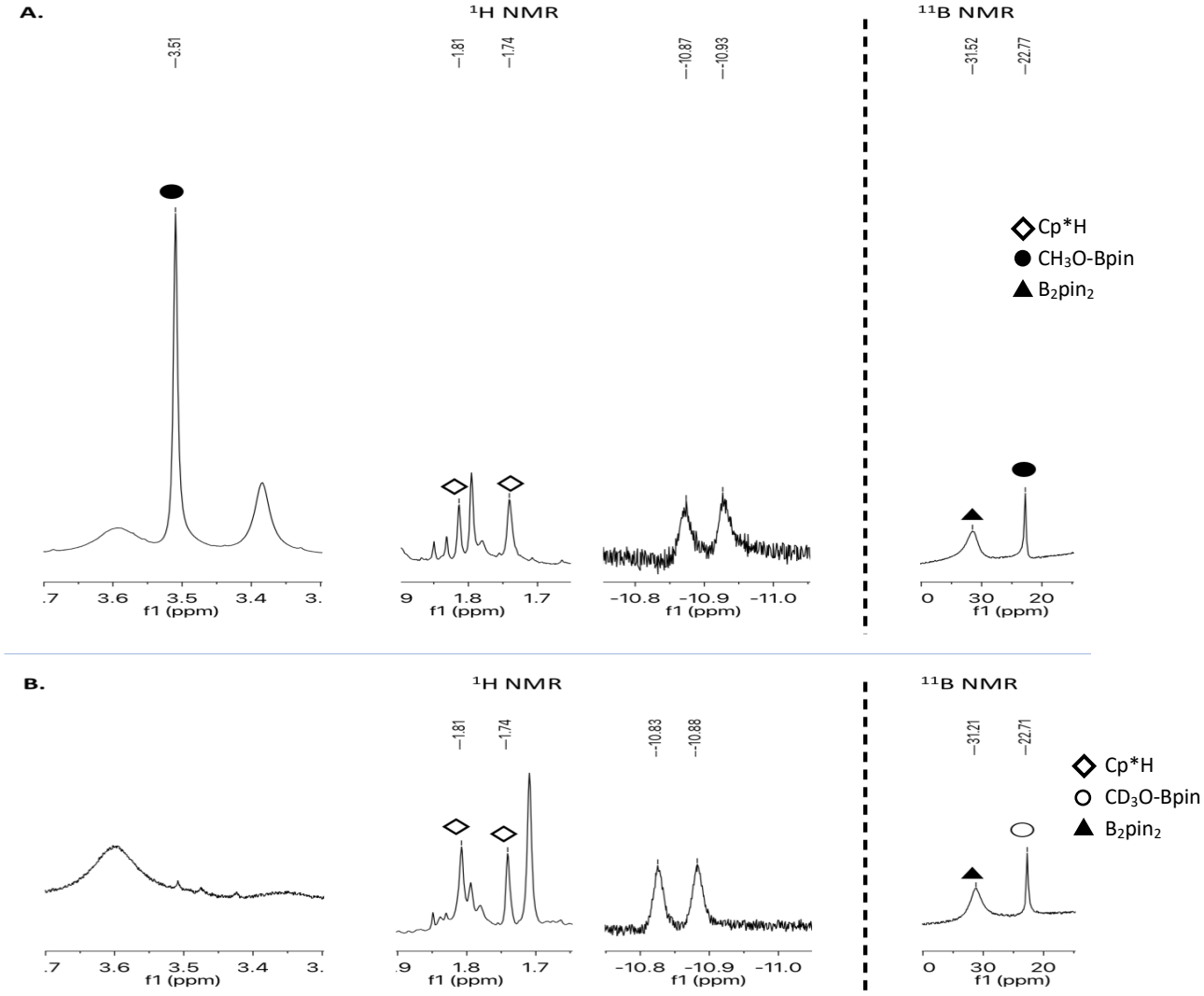
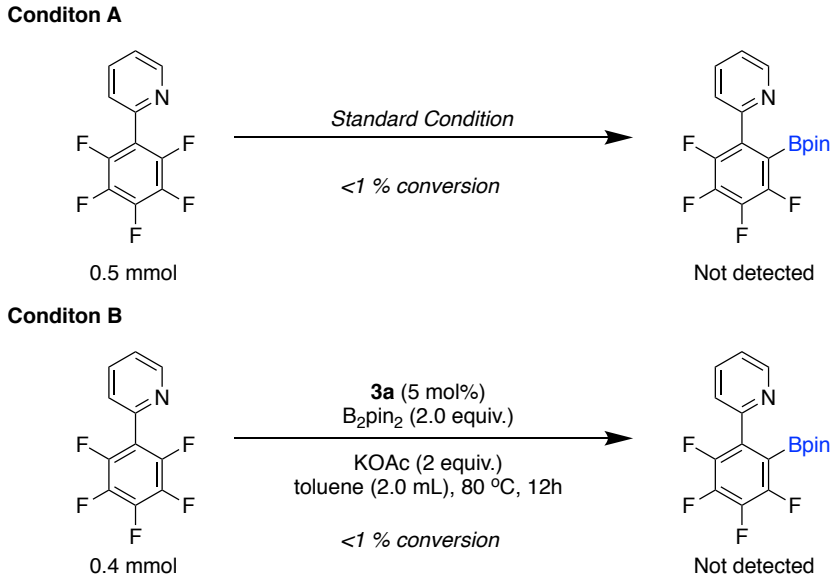


Fig. S3 Spectra of stoichiometric reaction with A) $NaOCH_3$ and B) $NaOCD_3$

6.3. Catalytic C-F borylation with **3a**



Scheme S2: Catalytic C-F borylation with **3a**

Condition A: Standard condition

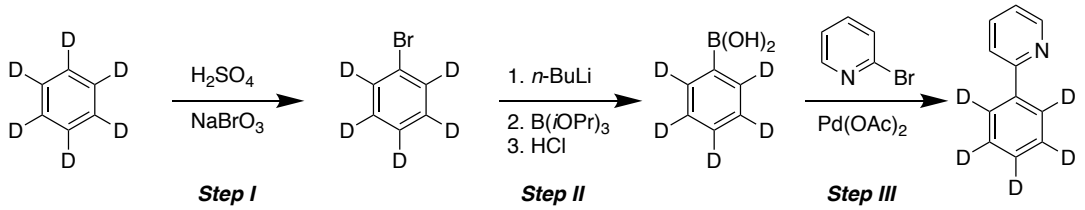
In a glove box, in a dry Schlenk tube was placed **3a** (5 mol%). Then NaOMe (10 mol%) and C_6H_6 were added respectively. Next, the mixture was stirred for 10 min followed by the addition of B_2pin_2 (2 equiv.). The mixture was stirred for another 10 min, and 2-(pentafluorophenyl)-pyridine[14] (0.5 mmol) was added afterward. The tube was closed with a septum and sealed with parafilm. Outside the glove box, the mixture was stirred at 80 °C for 16h. After cooled down, the mixture was concentrated under reduce pressure and dried under vacuum. To the residue were added fluorobenzene (as an internal standard) and 2 mL of $CDCl_3$. Then the aliquot was analyzed by ^{19}F NMR. The *ortho* functionalized product was *not detected* in the spectrum.

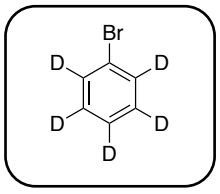
Condition B: Reported condition[15]

The procedure was followed the one reported in the literature.[13] In a glove box, a dry Schlenk tube was charged with 2-(pentafluorophenyl)-pyridine (0.4 mmol, 1.0 equiv), B_2pin_2 (0.8 mmol, 2.0 equiv.), followed by addition of KOAc (0.8 mmol, 2.0 equiv) and **3a** (5 mol%). Toluene (2 mL) was then added. The Schlenk tube was sealed and heated to 80 °C (oil bath) for 12h. After cooled down, the mixture was concentrated under reduce pressure and dried under vacuum. To the residue were added fluorobenzene (as an internal standard) and 2 mL of $CDCl_3$. Then the aliquot was analyzed by ^{19}F NMR. The *ortho* functionalized product was *not detected* in the spectrum.

6.4. H/D kinetic isotope effect Study

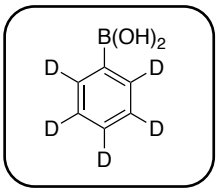
a. Synthesis of 2-pentadeuteriophenylpyridine



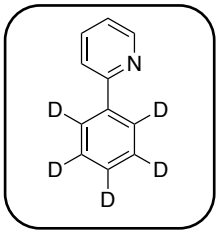


Step I: The reported procedure was applied.[16] To a vigorously stirred solution of sulfuric acid (16.65 g, 9.05 mL) in H_2O (33.3 mL), deuteriobenzene (4.21 g, 4.43 mL, 50 mmol) was added in one portion at 0 °C. Thereafter, $NaBrO_3$ (8.30 g, 55.0 mmol) added in two portions with an interval of 1 h at the same temperature. The reaction mixture was stirred for an additional 10 h at ambient temperature, poured into ice- cold water (100 mL) and extracted with n-pentane (3 × 40 mL). The combined extracts were washed with ice-cold water (2 × 50 mL), sat. aq. $NaHCO_3$ solution (2 × 50 mL), brine (40 mL), and dried. *n*-Pentane was carefully evaporated, and the residue was distilled at 45 °C under reduce pressure (0.1 Torr) into a cold (–78 °C) trap to give 6.614 g (70 %) of pure 1-bromopentadeuteriobenzene as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) *no signal*. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.0 (t, *J* = 25.3 Hz), 129.5 (t, *J* = 24.5 Hz), 126.2 (t, *J* = 24.5 Hz), 122.0.



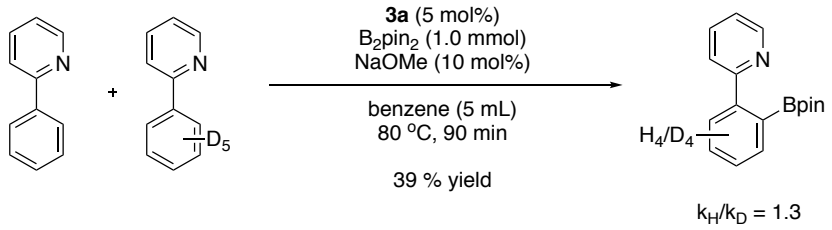
Step II: The reported procedure was applied.[16] A two-neck 500 mL flask fitted with a magnetic stirring bar, and low-temperature thermometer was charged with bromobenzene-d_5 (8.1 mL, 40.0 mmol) under nitrogen atmosphere. Dry THF (100 mL) was added, and the solution was cooled to -78°C. To this solution was added n-butyllithium (25.0 mL, 1.6 M, 40.0 mmol) using a slow addition pump over 30 min. The solution was stirred at -78°C for 2 h whereupon triisopropyl borate (6.3 g, 60.0 mmol) dissolved in 10 mL of dry THF was added drop wise to the reaction system. The solution was allowed to warm to room temperature overnight. After that the reaction was quenched with dilute HCl (20%, 70 mL), and the reaction mixture was stirred for 3 h at room temperature. The resulted biphasic solution was extracted with Et_2O (2 X 50 mL). The ethereal solution was washed twice with H_2O and concentrated by rotary evaporation. To the crude product (viscous liquid), n-hexane 75 ml was added. The white (d_5-phenyl)boronic acid solid precipitated in pentane was filtered, dried and used without further purification (80% isolated yield).



Step III: The reported procedure was applied.[17] A mixture of 2-bromopyridine (500 mg, 3.16 mmol), pentadeuteriophenylboronic acid (600 mg, 4.74 mmol), K_2CO_3 (873 mg, 6.32 mmol), $Pd(OAc)_2$ (10 mg, 0.04 mmol), distilled water (12 mL) and ethanol (36 mL) was stirred at 80 °C in air for 1 h. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (4 × 15 mL). The solvent was concentrated under vacuum, and the product was isolated by column chromatography on a short silica gel column to give 2-phenylpyridine-d_5 in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.69 (m, 1H), 7.78 – 7.71 (m, 2H), 7.23 (ddd, J = 6.1, 4.8, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 149.8, 139.4, 136.8, 128.4 (t, J = 24.2 Hz), 126.6 (t, J = 24.2 Hz), 122.2, 120.7. HRMS (ESI) calcd for $C_{11}H_5D_5N^+$ (M + H^+): *m/z* 161.11216, found 161.1122 (0 ppm).

b. Kinetic isotopic effect study



In a glove box, in a dry Schlenk tube was placed **3a** (5 mol%). Then NaOMe (10 mol%) and C_6D_6 were added respectively. Next, the mixture was stirred for 10 min followed by the addition of B_2Pin_2 (2 equiv.). The mixture was stirred for another 10 min, and an equimolar of 2-phenylpyridine (0.25 mmol) and 2-phenylpyridine-d_5 (0.25 mmol) and 1,3,5-trimethoxybezene (28 mg) were added. The tube was closed with a septum and sealed with parafilm. Outside the glove box, the mixture was stirred at 80 °C for 90 minutes. Then the aliquot was taken and analyzed by ^{1}H-NMR. *Integration of the peaks at 7.96 ppm revealed the k_H/k_D. At 90 min; the NMR yield is 39 % and k_H/k_D = 1.3.*

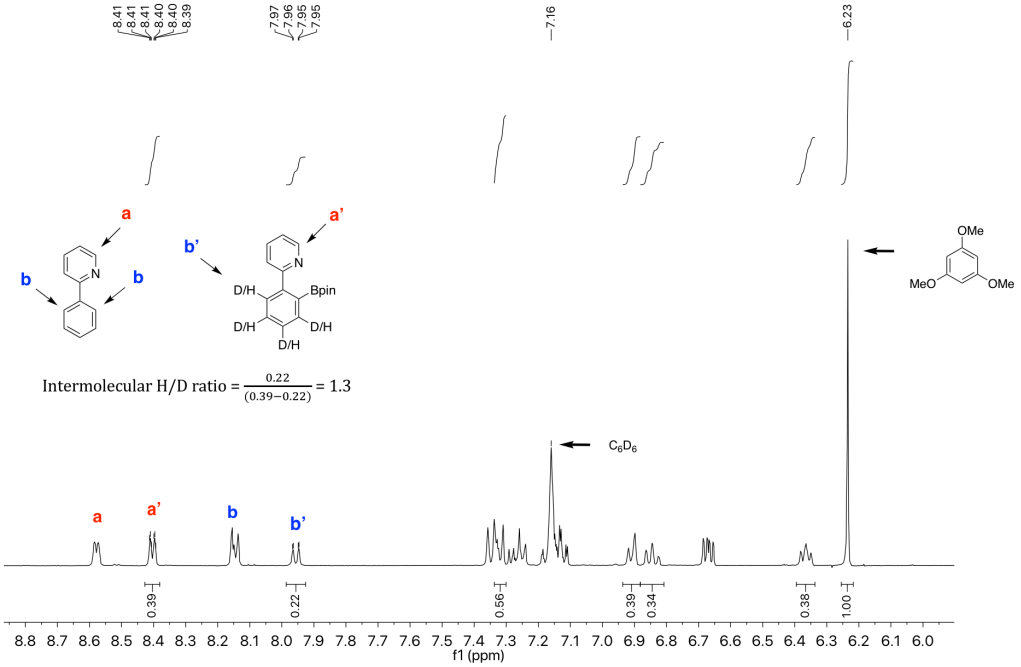
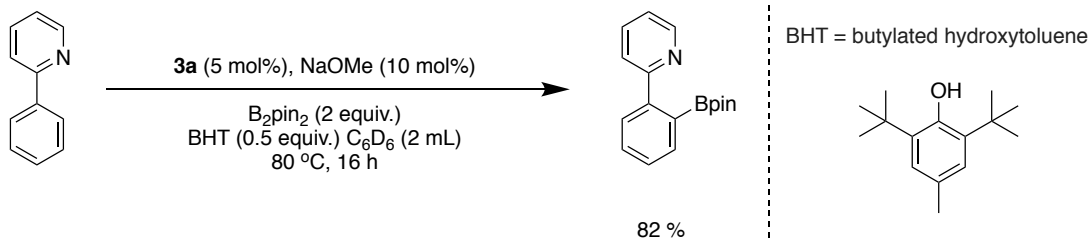


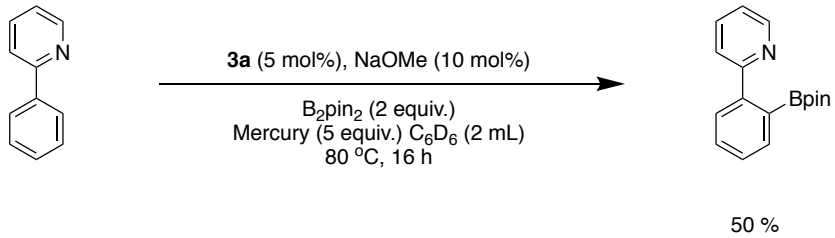
Fig. S4 The spectra for H/D kinetic isotope effect experiment

6.5. Radical scavenger experiment



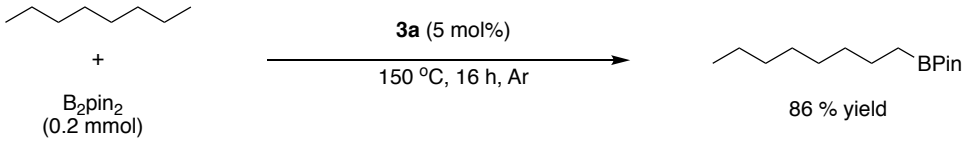
In a glove box, in a dry Schlenk tube was placed **3a** (5 mol%). Then NaOMe (10 mol%) and C_6D_6 were added respectively. Next, the mixture was stirred for 10 min followed by the addition of B_2pin_2 (2 equiv.). The mixture was stirred for another 10 min, and an equimolar of 2-phenylpyridine (0.20 mmol), BHT (0.5 equiv.) and 1,3,5-trimethoxybezene (28 mg) were added. The tube was closed with septum and sealed with parafilm. Outside the glove box, the mixture was stirred at 80 °C for 16 hours. Then the aliquot was taken and analyzed by ^{1}H-NMR. The NMR yield is 82 % which showed that the radical reaction is likely non-operative.

6.6. Mercury poisoning test



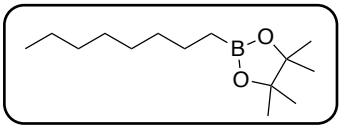
In a glove box, in a dry Schlenk tube was placed **3a** (5 mol%). Then NaOMe (10 mol%) and C_6D_6 were added respectively. Next, the mixture was stirred for 10 min followed by the addition of B_2pin_2 (2 equiv.). The mixture was stirred for another 10 min, and an equimolar of 2-phenylpyridine (0.20 mmol), mercury (5 equiv.) and 1,3,5-trimethoxybezene (28 mg) were added. The tube was closed with septum and sealed with parafilm. Outside the glove box, the mixture was stirred at 80 °C for 16 hours. Then the aliquot was taken and analyzed by ^{1}H-NMR. The NMR yield is 50 % which showed that the nanocatalysis is likely non-operative.

7. C-H Borylation of *n*-Octane



Inside the glovebox, to a dry Schlenk tube were added **3a** (5 mol%), B_2pin_2 (0.2 mmol). Then *n*-Octane (2 mL) was added, and the tube was closed with septum and sealed with parafilm. Outside the glovebox, the resulting biphasic solid-liquid mixture was stirred at 150 °C for 16h. After cooled down, the volatiles were remove. The crude residue was subjected to silica gel chromatography using dichlomethane as eluent. After removal of solvent, 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane was obtained as colorless oil.

4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 – 1.33 (m, 2H), 1.27 – 1.24 (m, 10H), 1.24 (s, 12H), 0.92 – 0.80 (m, 3H), 0.76 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.96, 32.59, 32.05, 29.53, 29.41, 24.96, 24.16, 22.83, 14.27. GCMS (EI): *m/z* 240 (2), 225 (58), 183 (7), 154 (14), 111 (17), 129.1 (100). Analytical data for this compound were consistent with previously reported data.[18,19]

8. References

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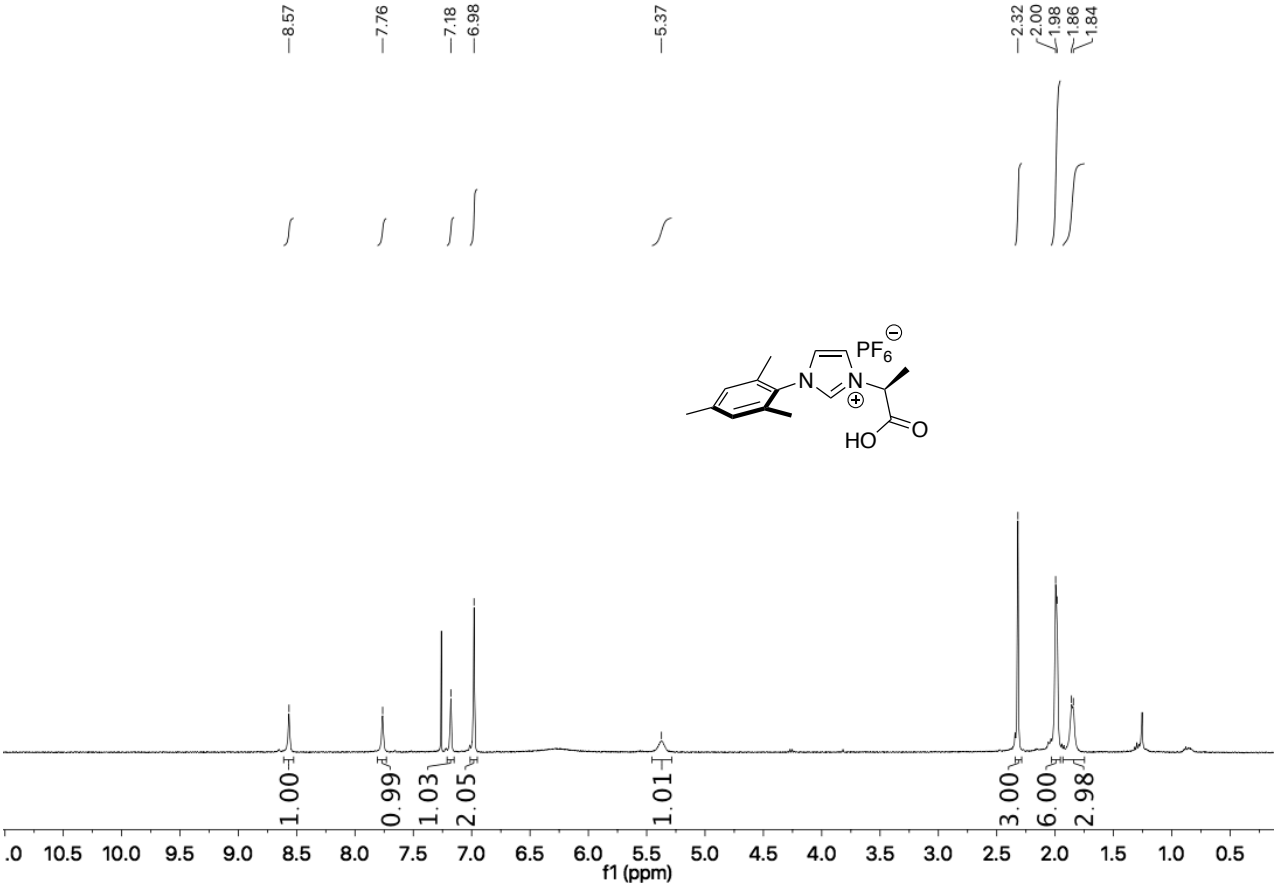
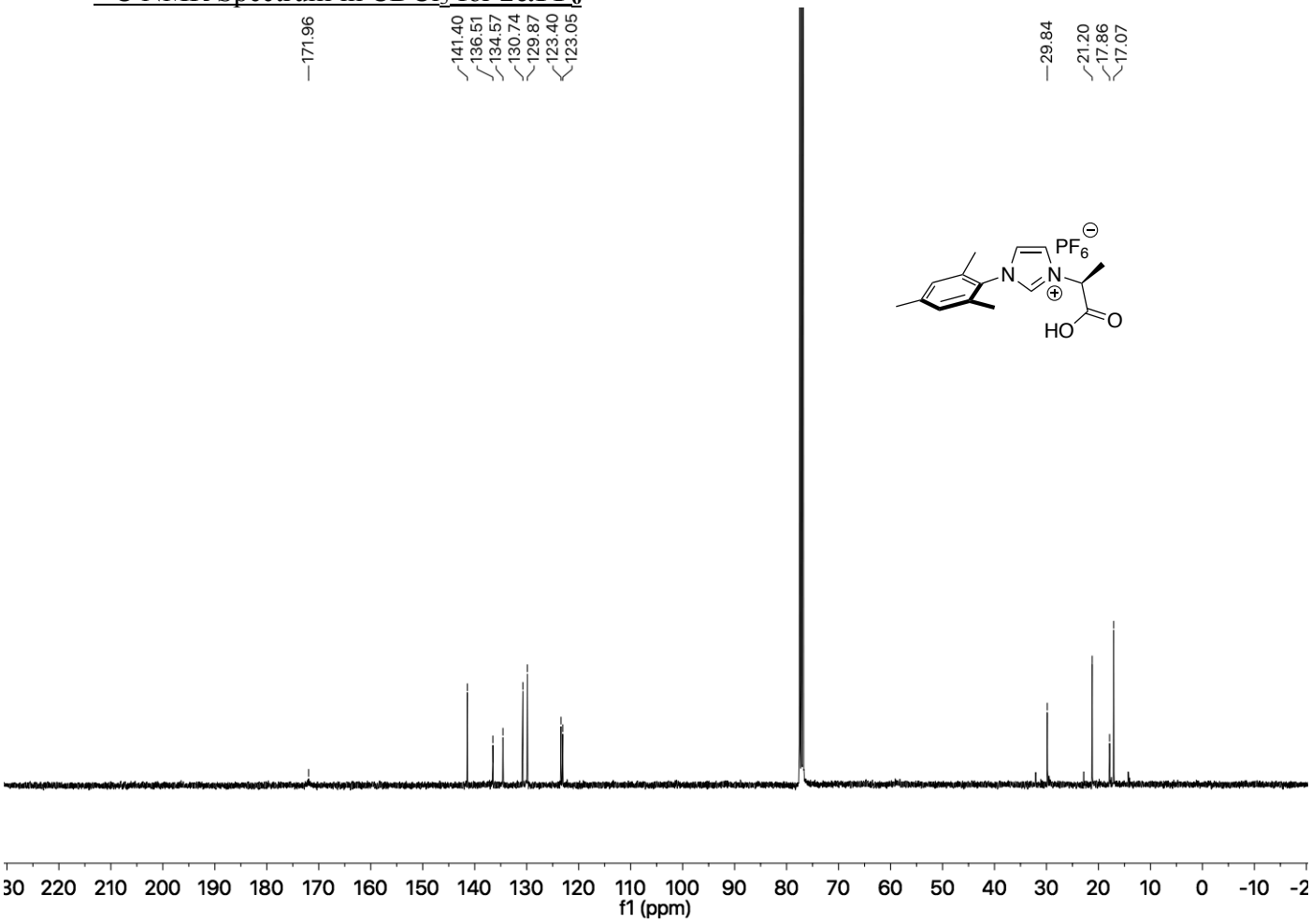
9. Spectroscopic Data

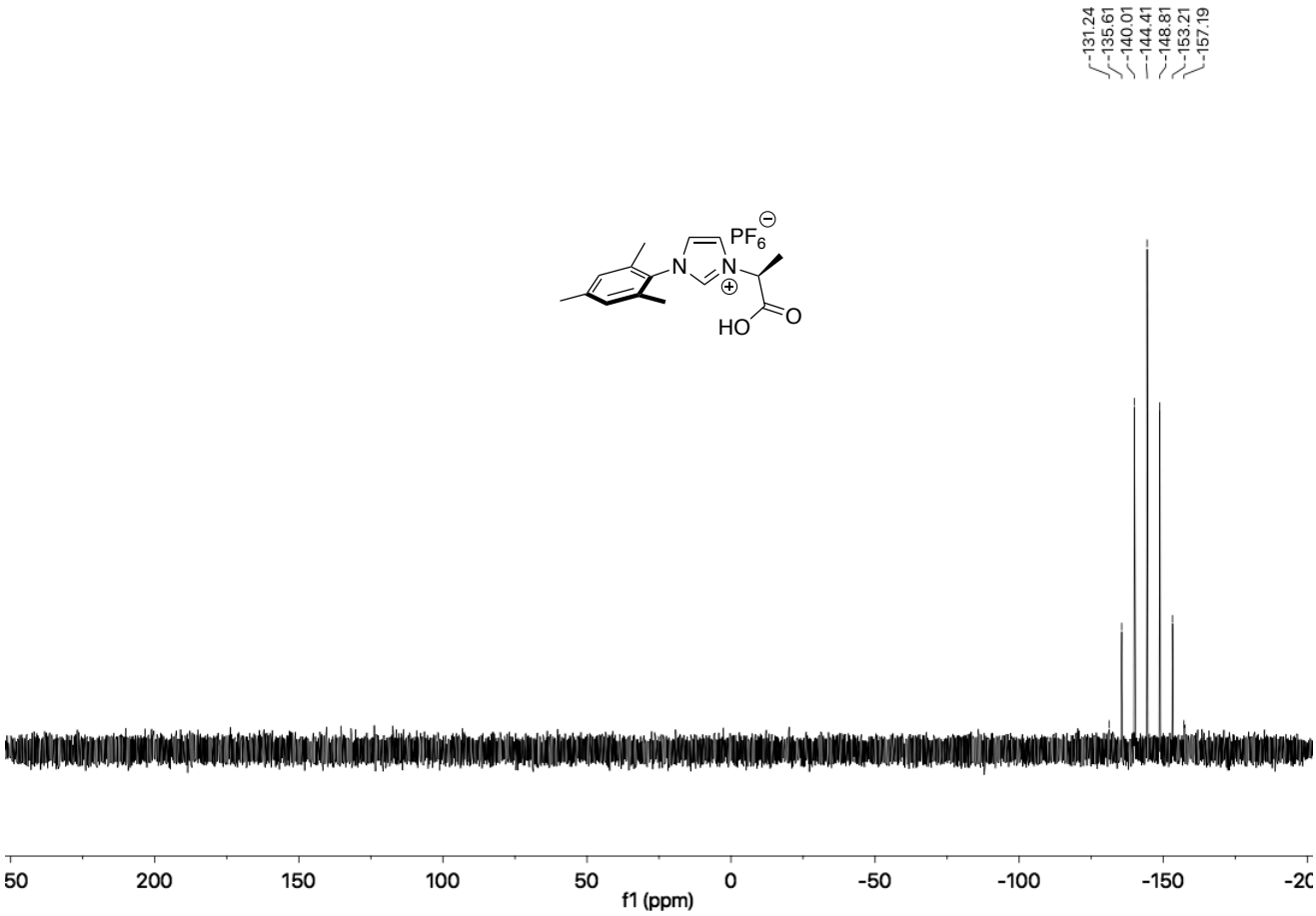
^{1}H NMR Spectrum in $CDCl_3$ for **2c.PF_6**



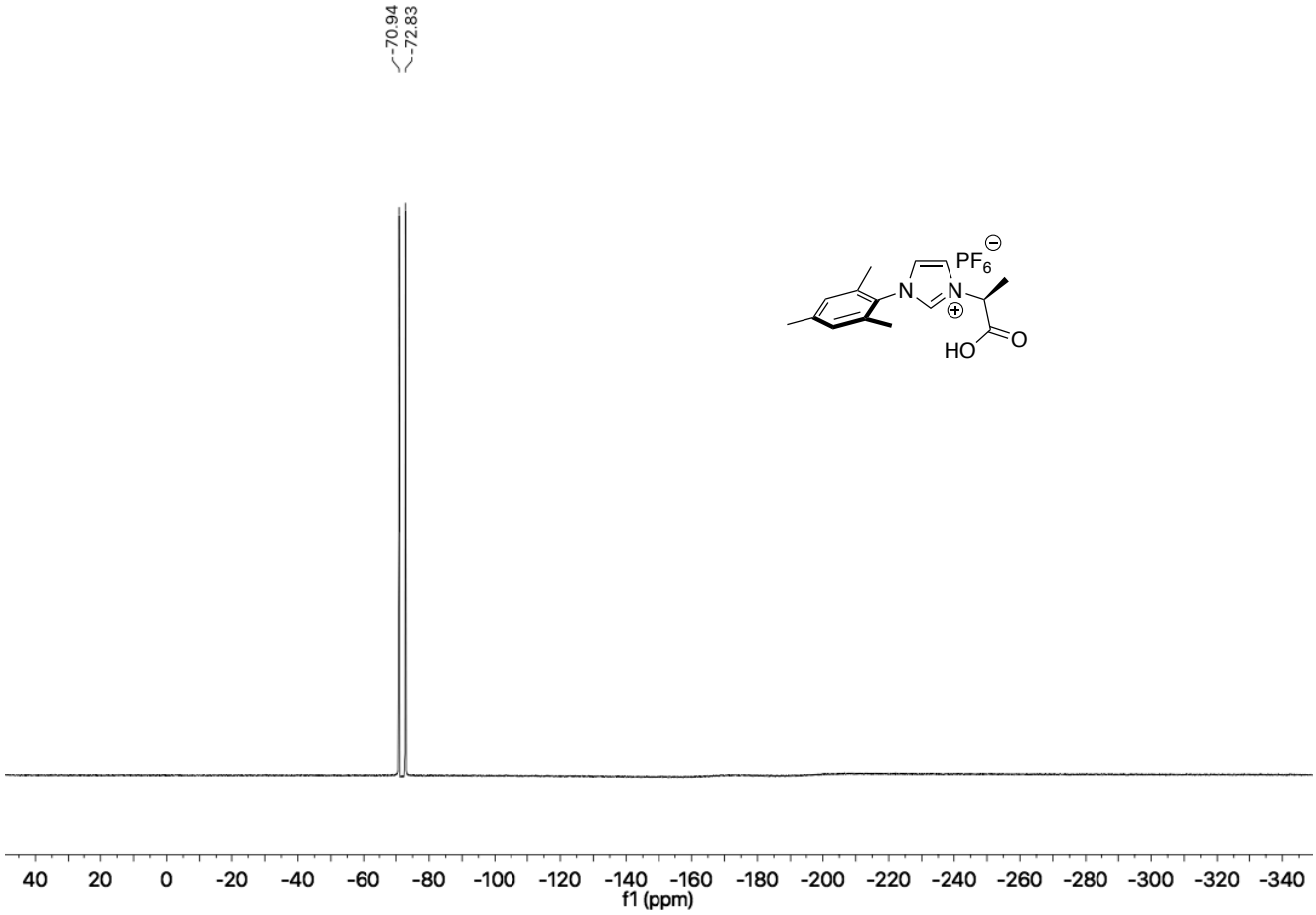
^{13}C NMR Spectrum in $CDCl_3$ for **2c.PF_6**



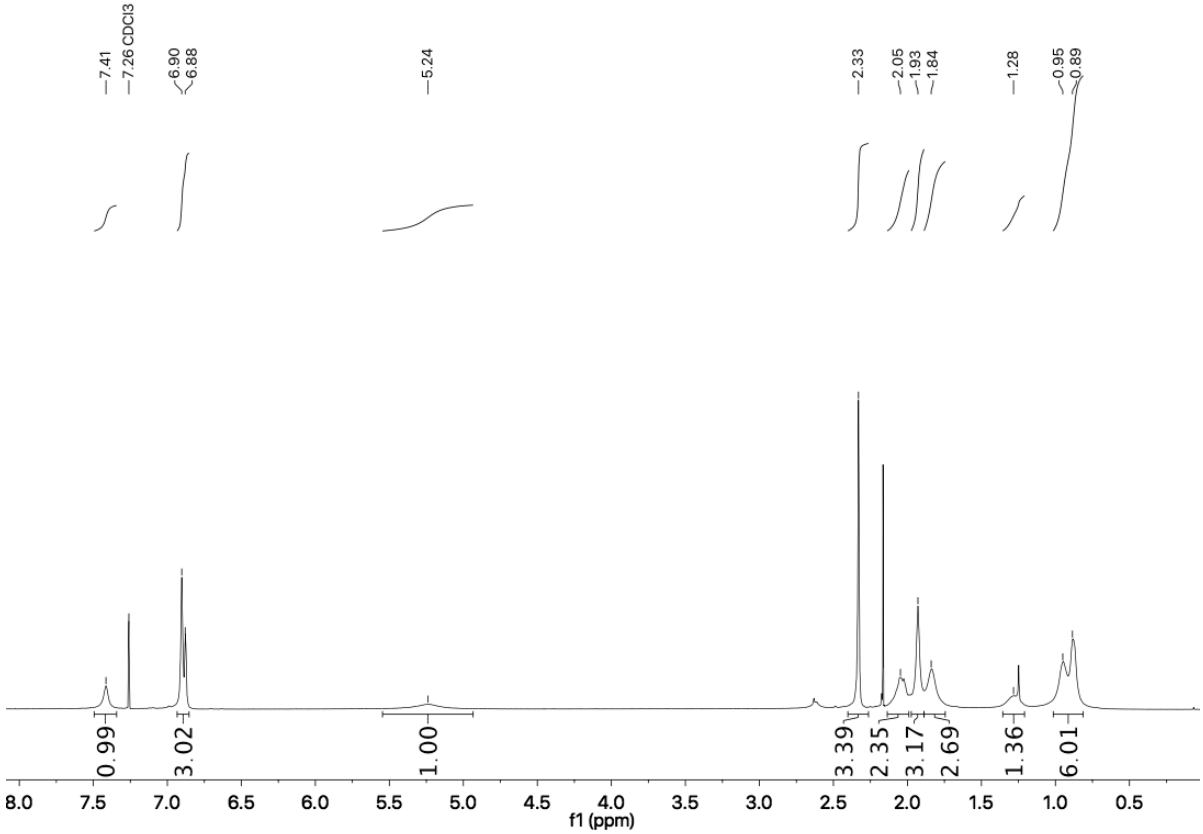
^{31}P NMR Spectrum in $CDCl_3$ for **2c.PF_6**



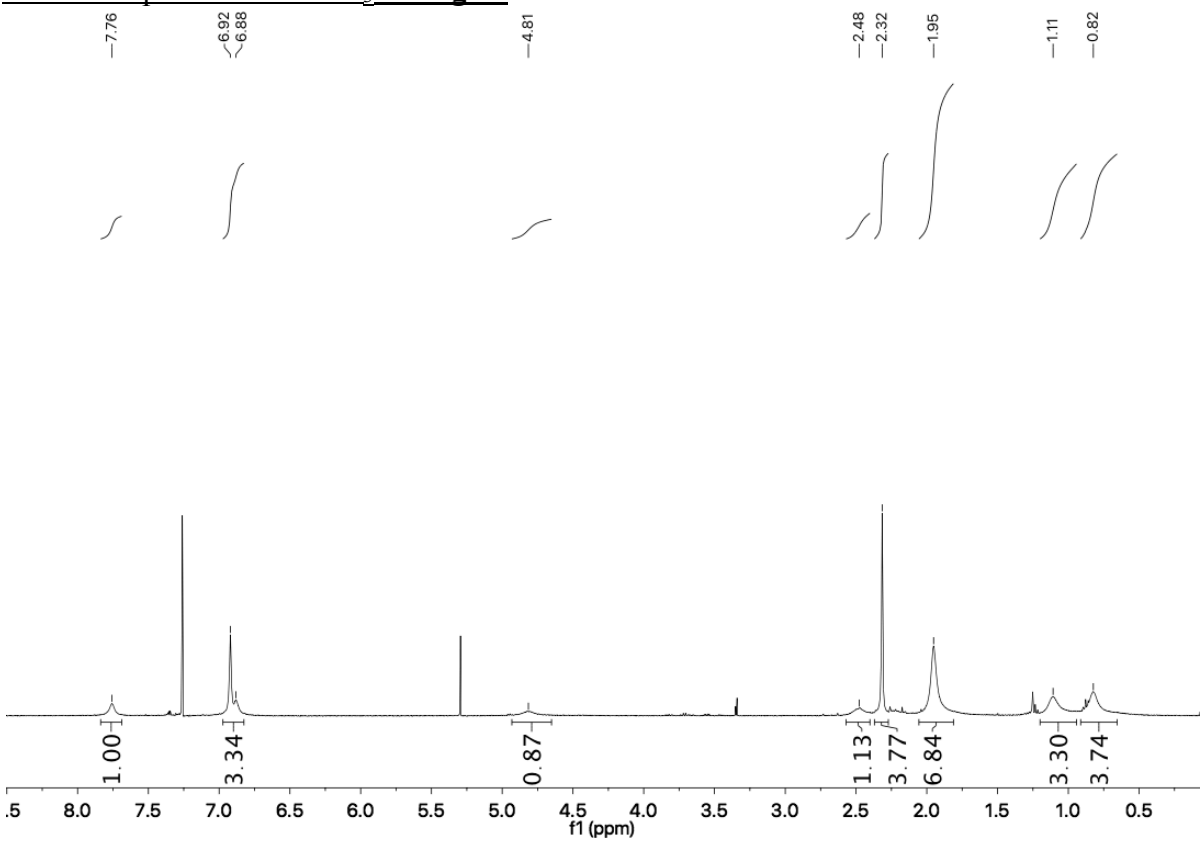
^{19}F NMR Spectrum in $CDCl_3$ for **2c.PF_6**



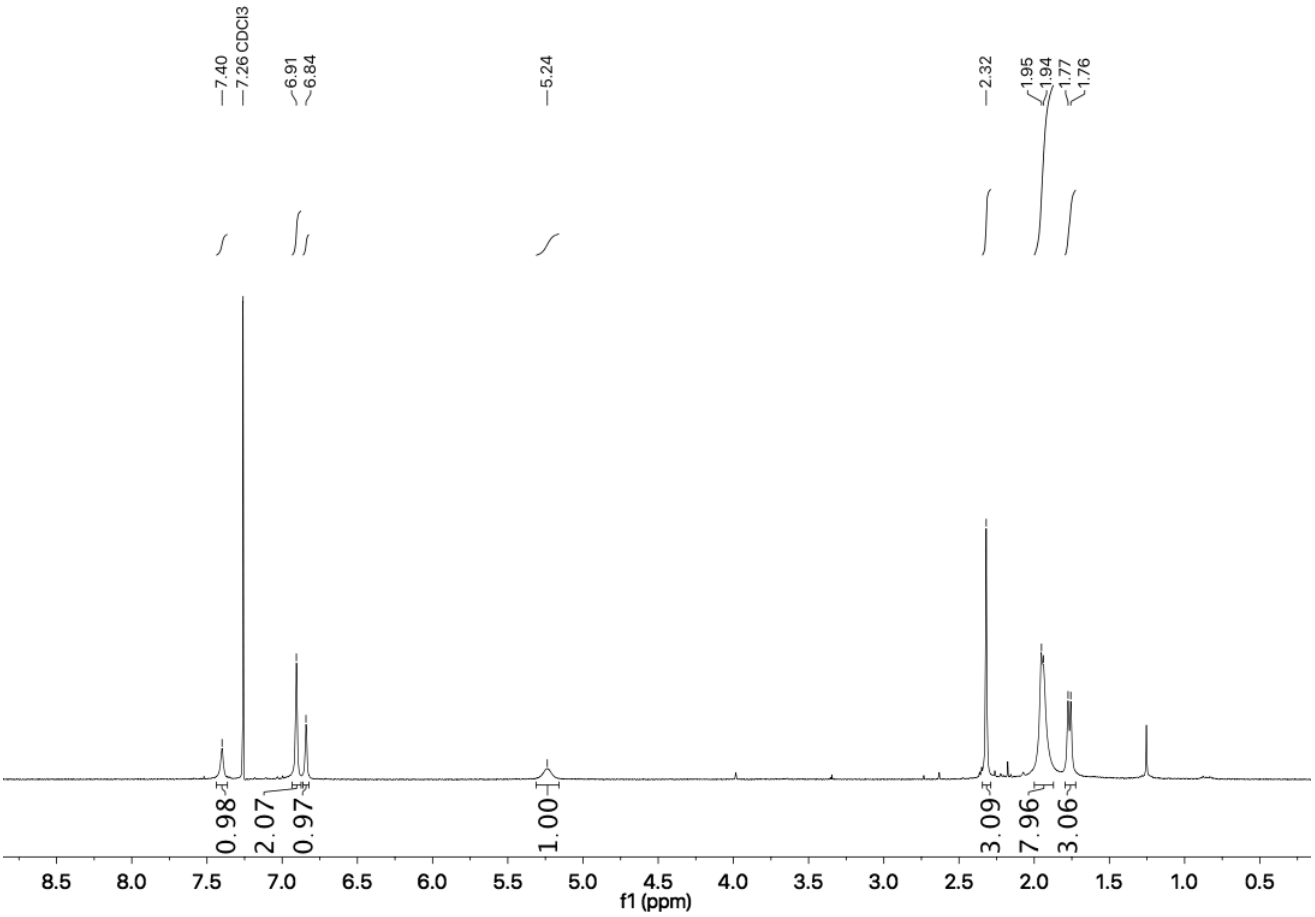
^{1}H NMR Spectrum in $CDCl_3$ for **Ag.2a**



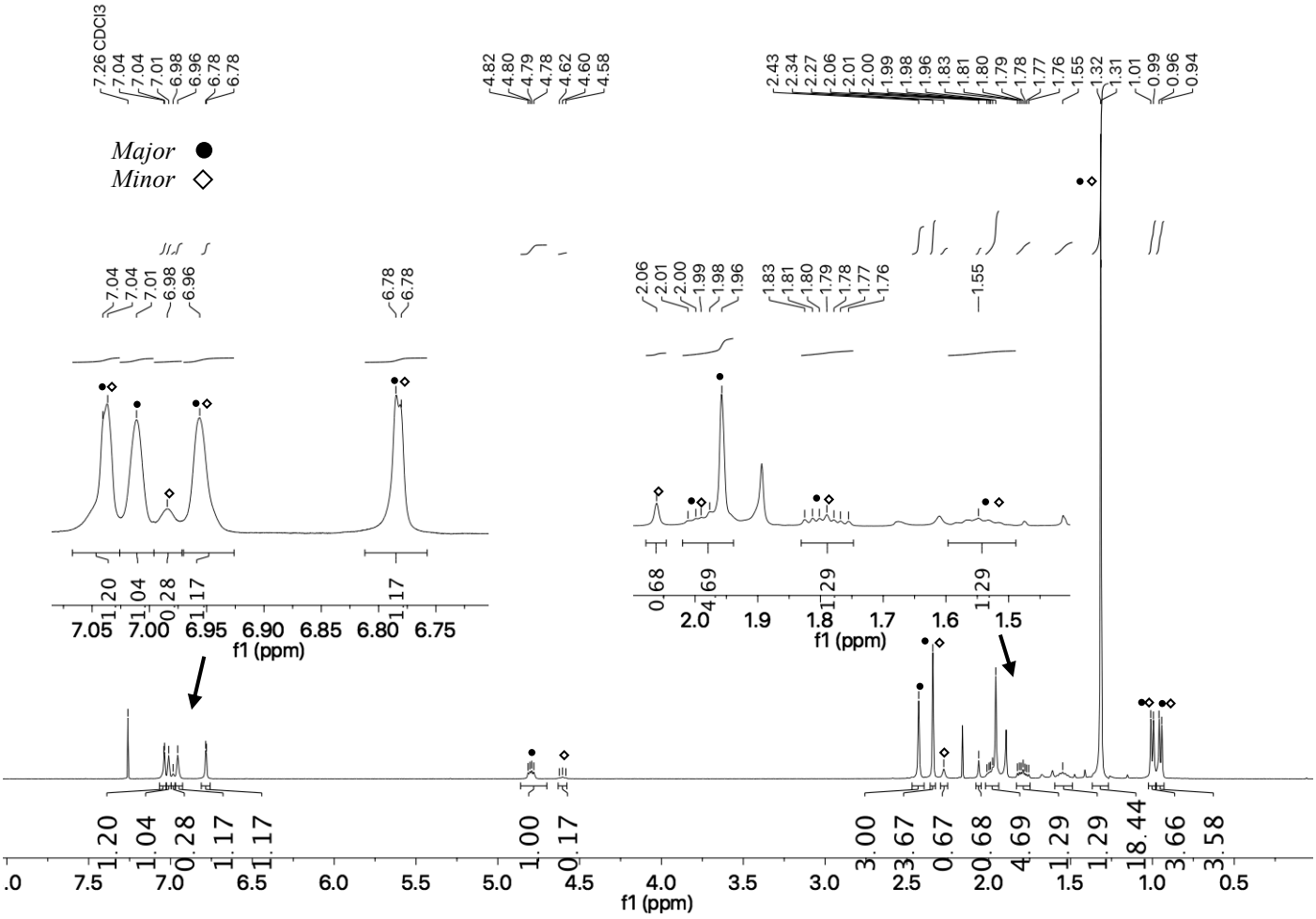
^{1}H NMR Spectrum in $CDCl_3$ for **Ag.2b**



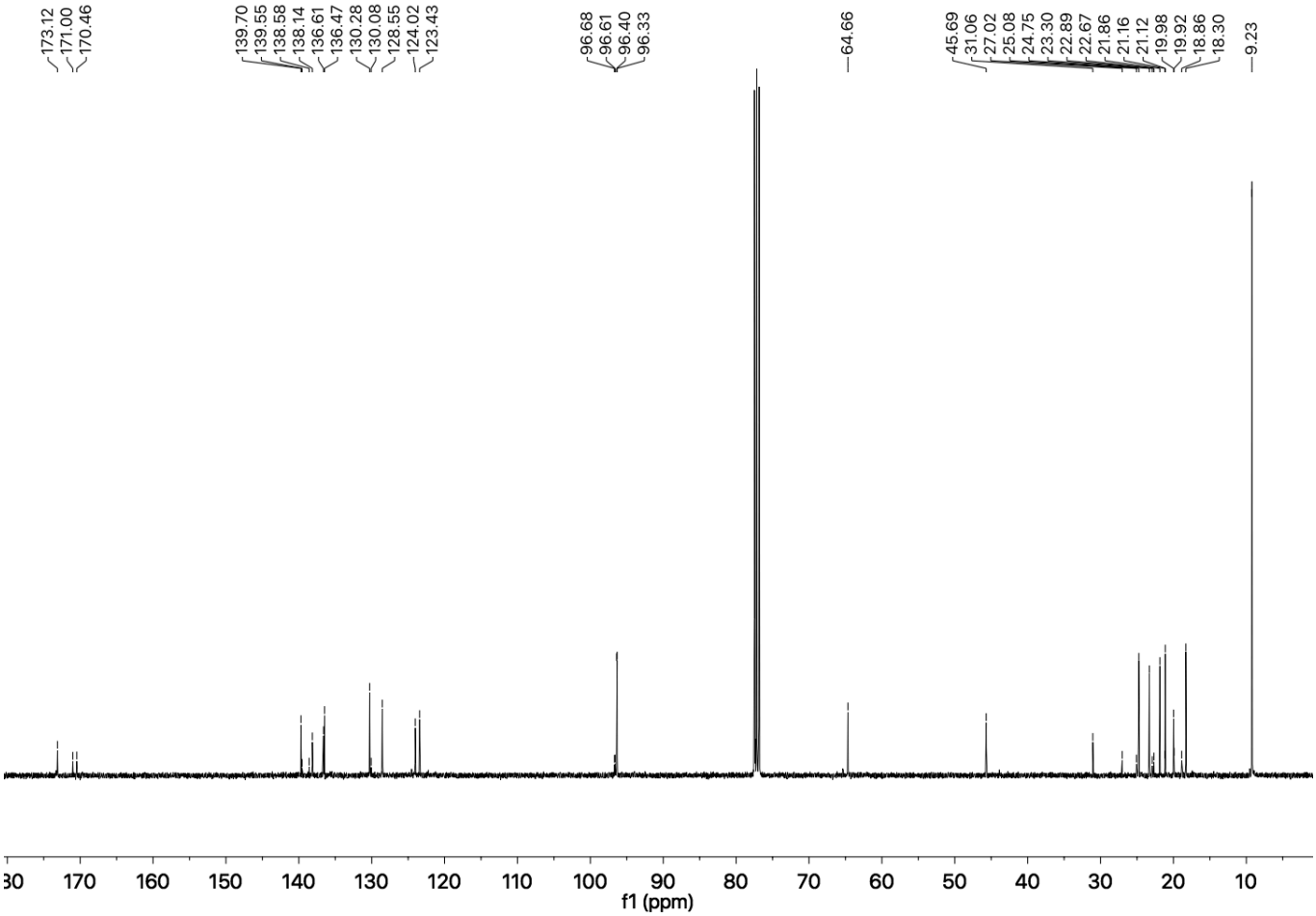
^{1}H NMR Spectrum in $CDCl_3$ for **Ag.2c**



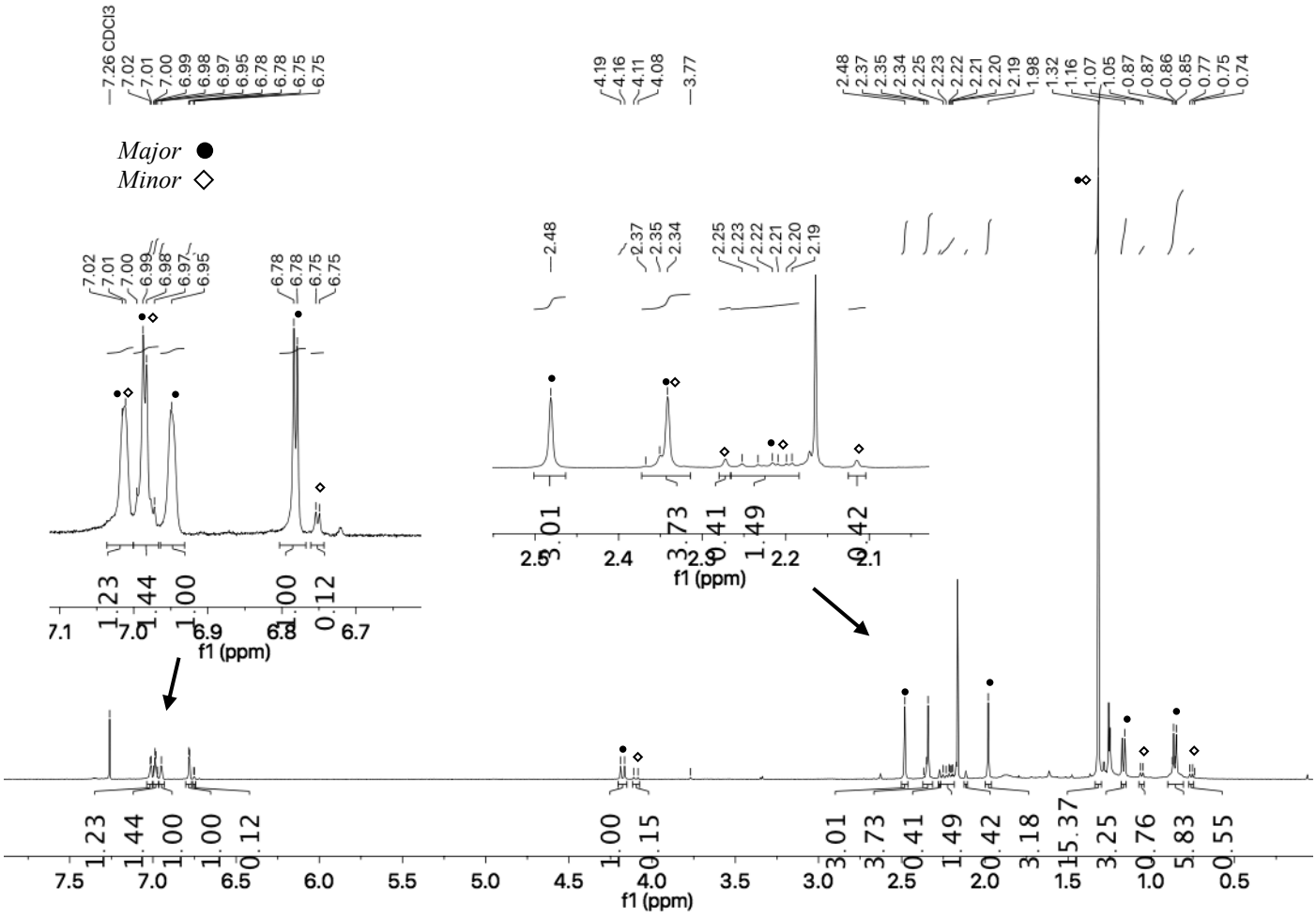
^{1}H NMR Spectrum in $CDCl_3$ for **3a** (Mixture of 2 diastereomers)



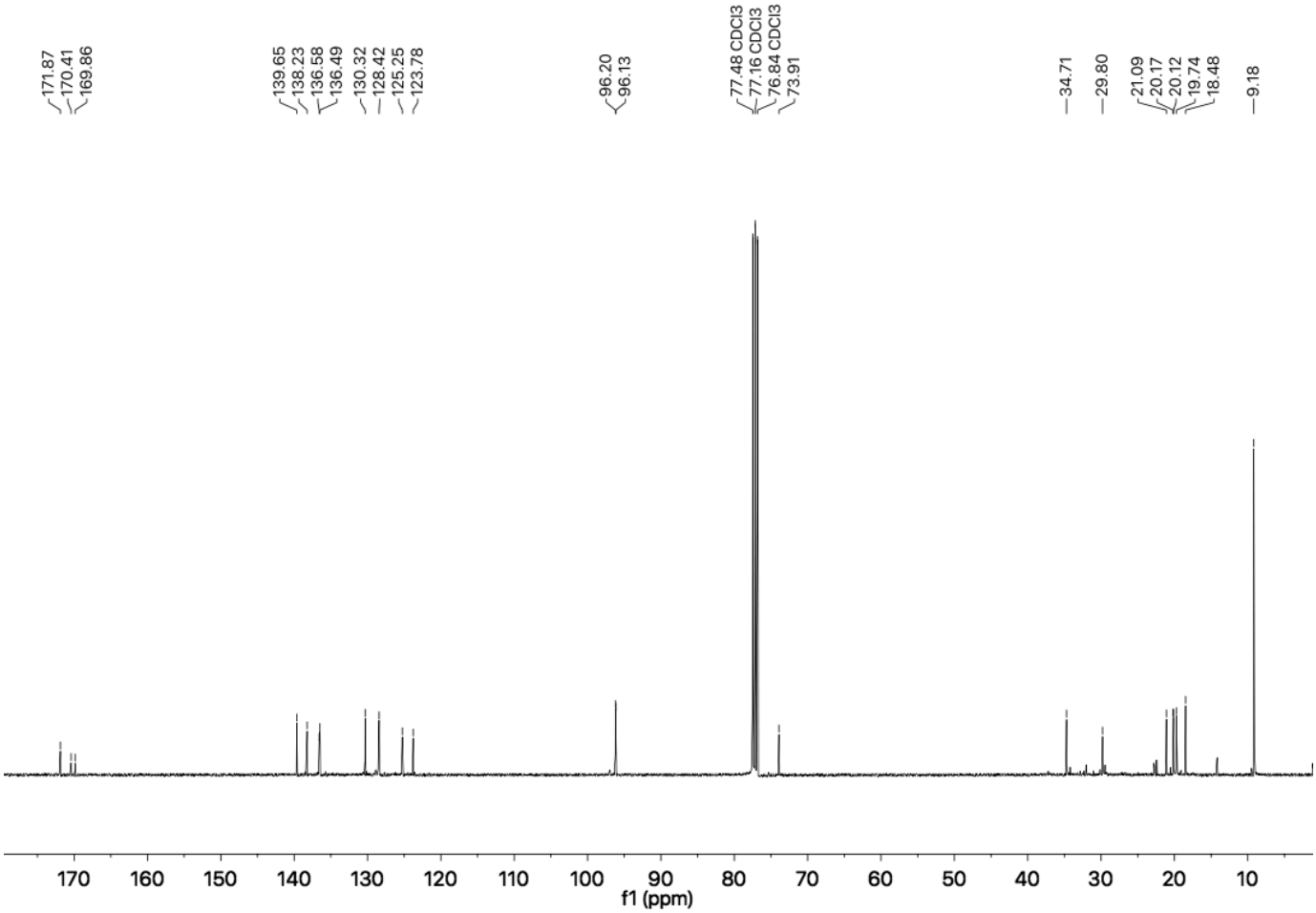
^{13}C NMR Spectrum in $CDCl_3$ for **3a**



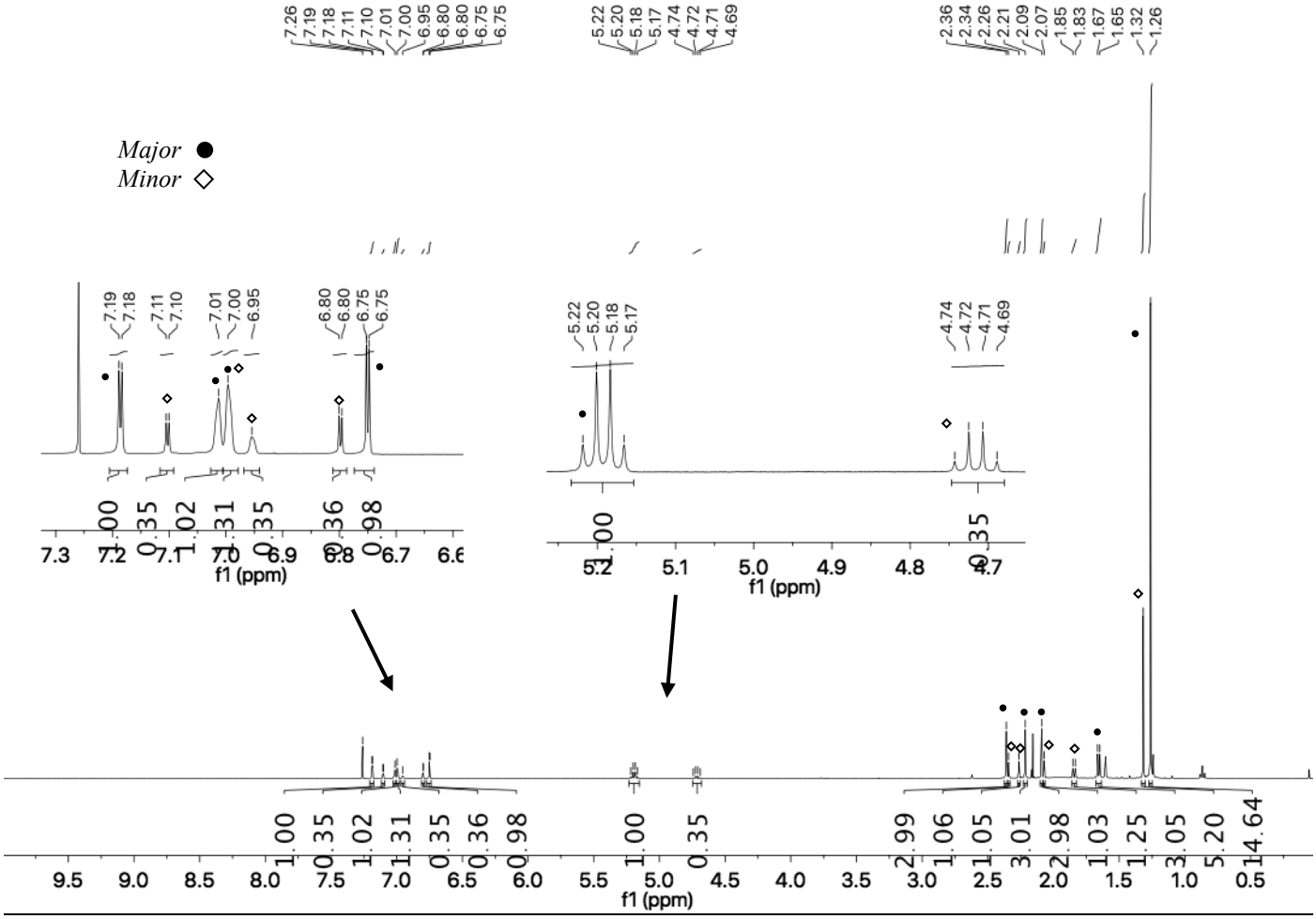
^{1}H NMR Spectrum in $CDCl_3$ for **3b** (Mixture of 2 diastereomers)



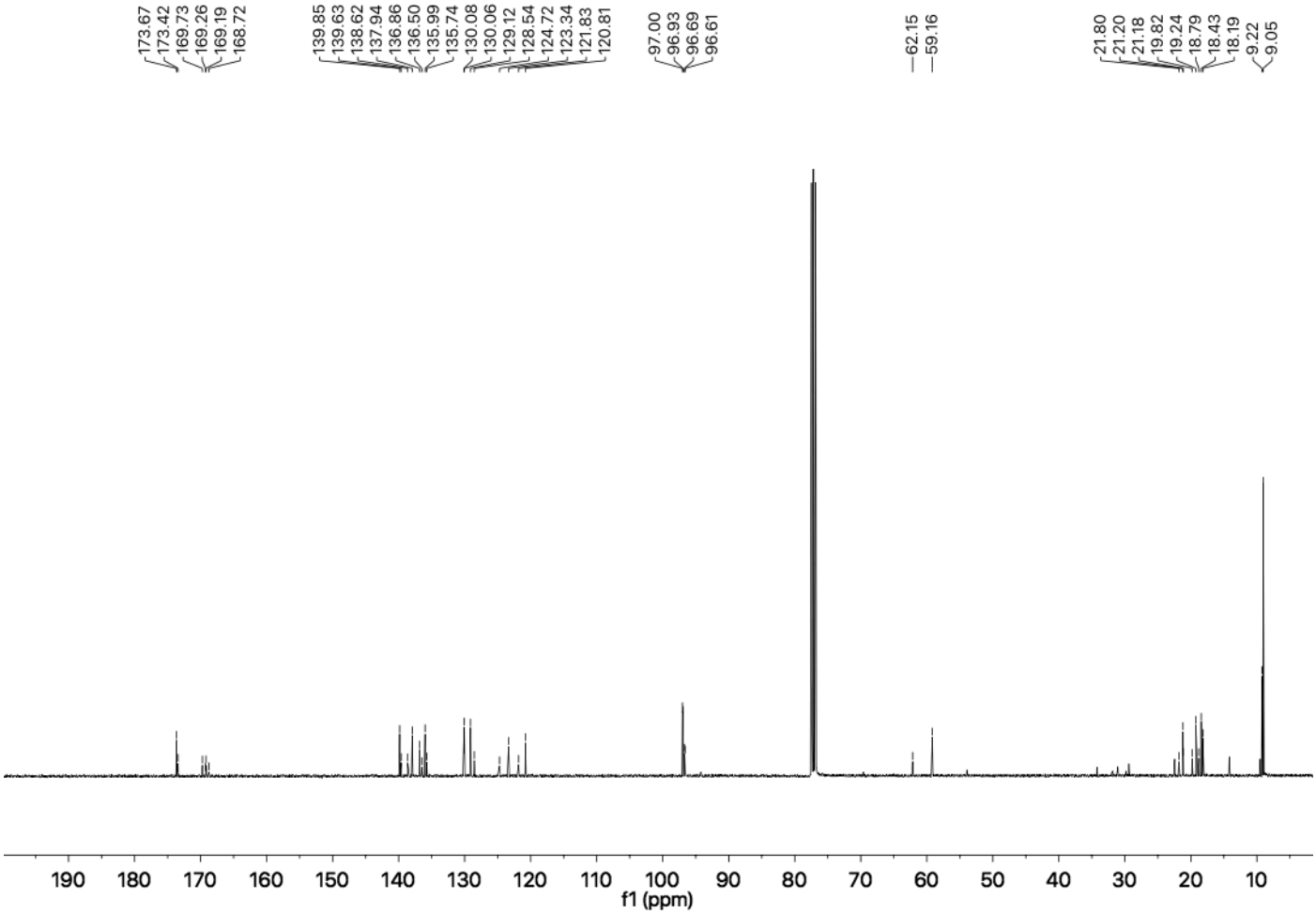
^{13}C NMR Spectrum in $CDCl_3$ for **3b**



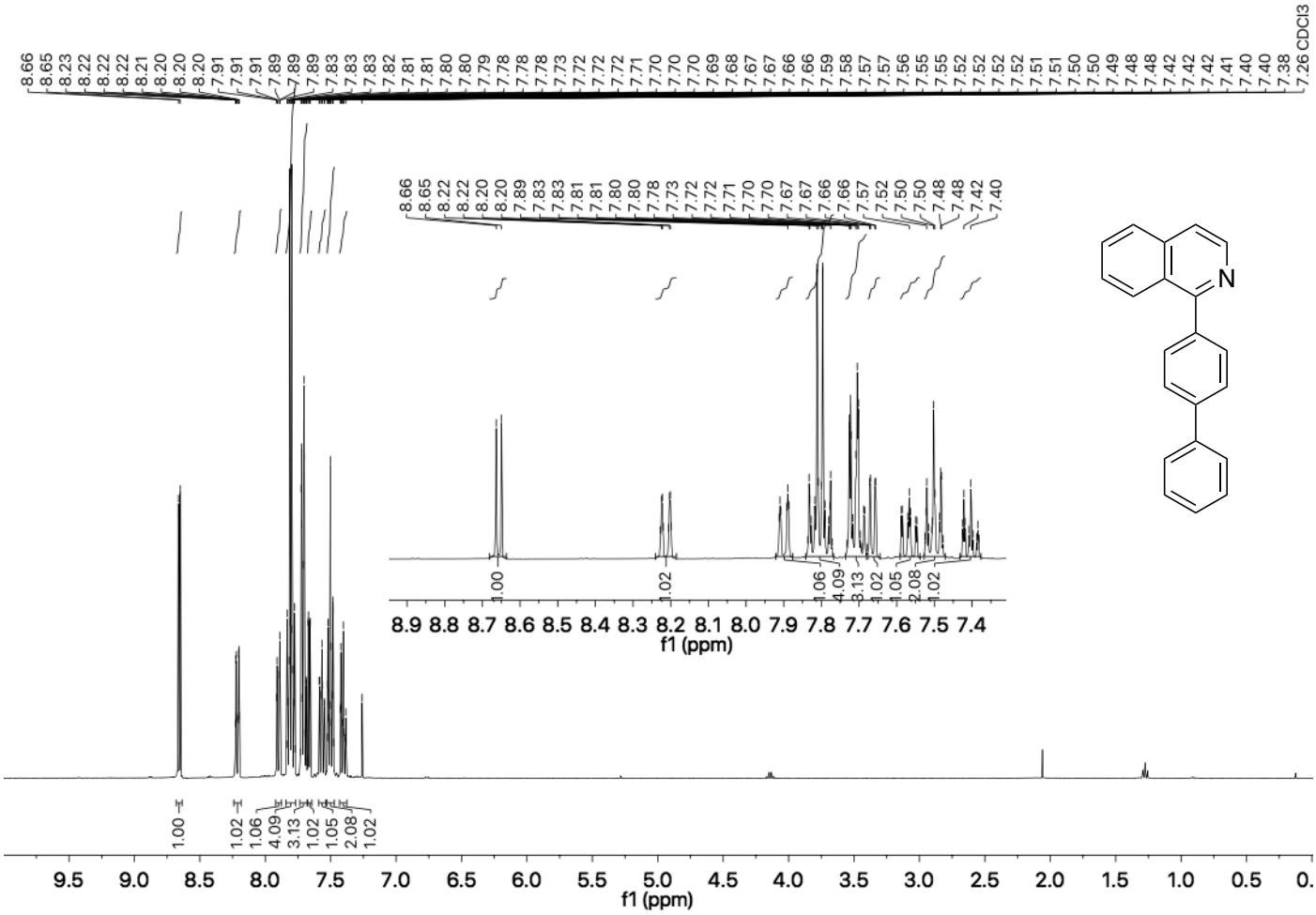
^{1}H NMR Spectrum in $CDCl_3$ for **3c** (Mixture of 2 diastereomers)



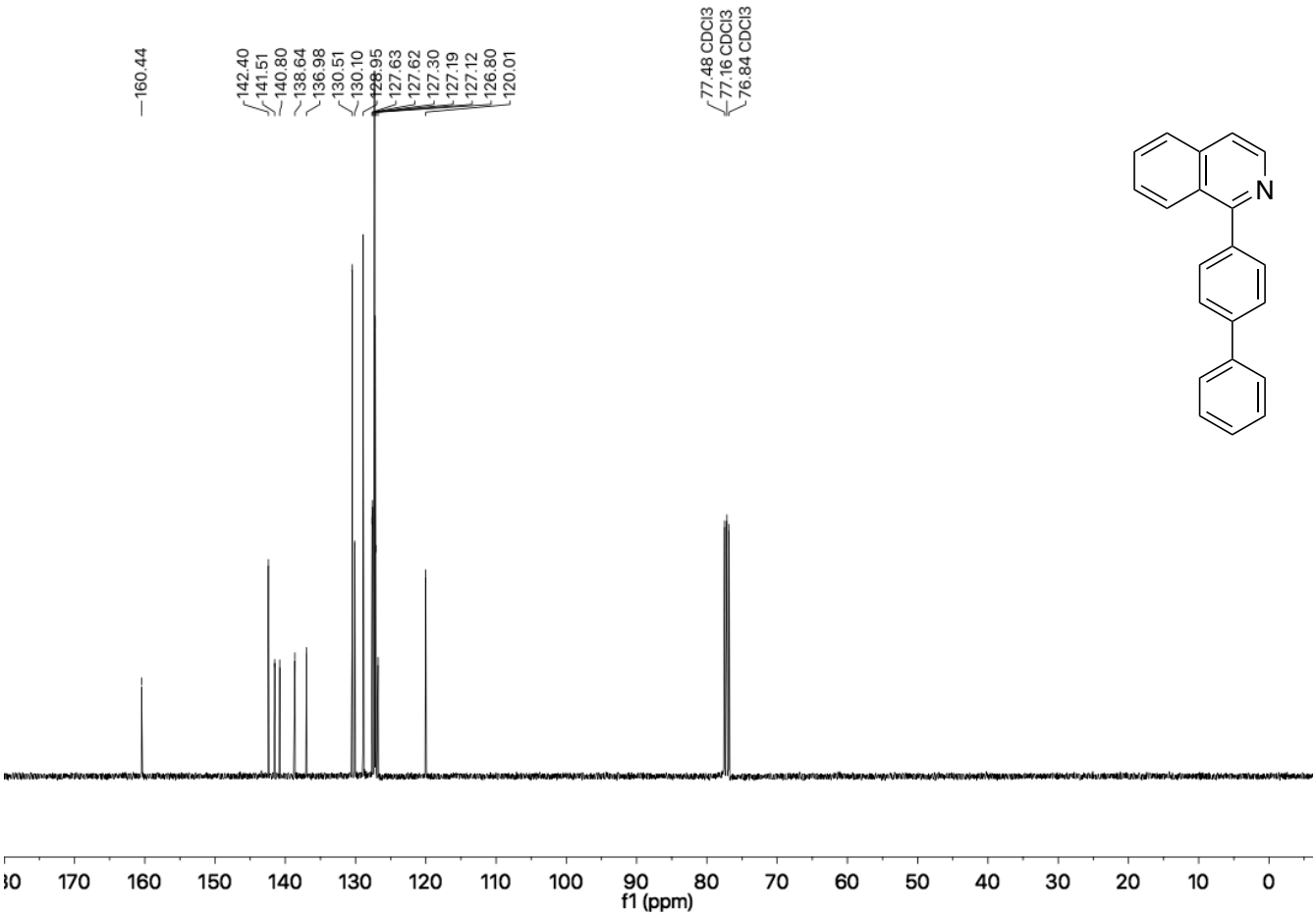
^{13}C NMR Spectrum in $CDCl_3$ for **3c**



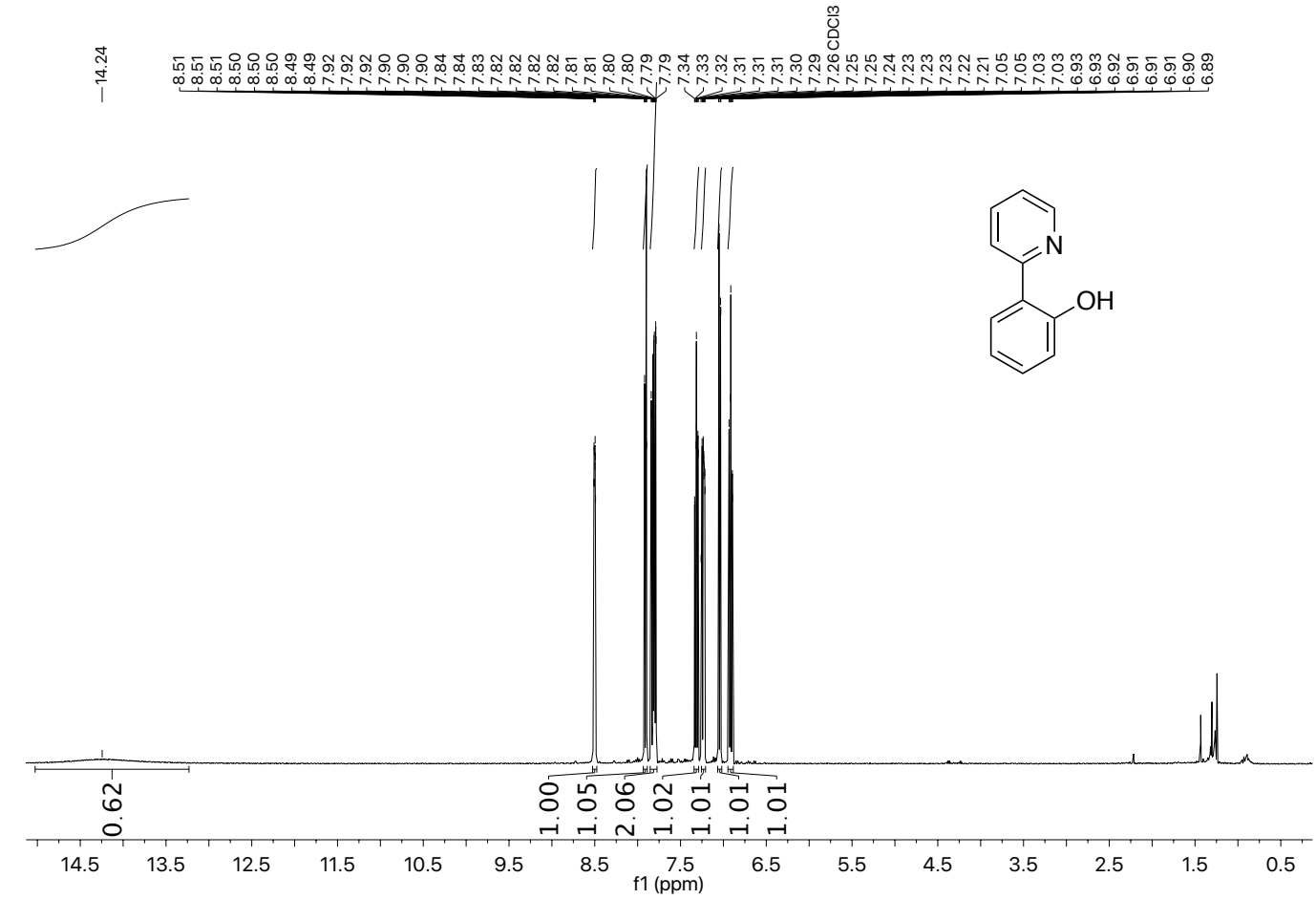
^{1}H NMR Spectrum in $CDCl_3$ for **4o**



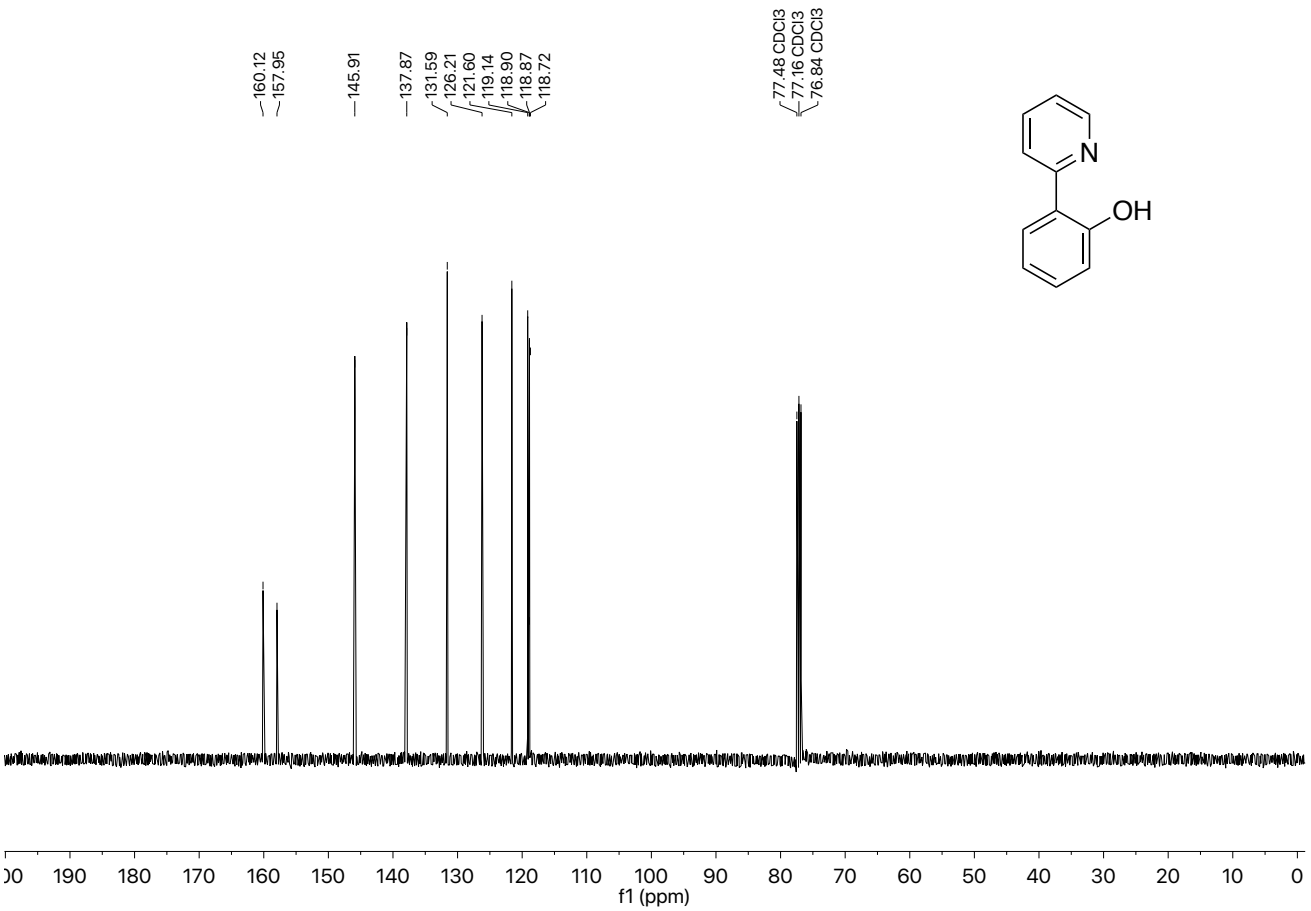
^{13}C NMR Spectrum in $CDCl_3$ for **4o**



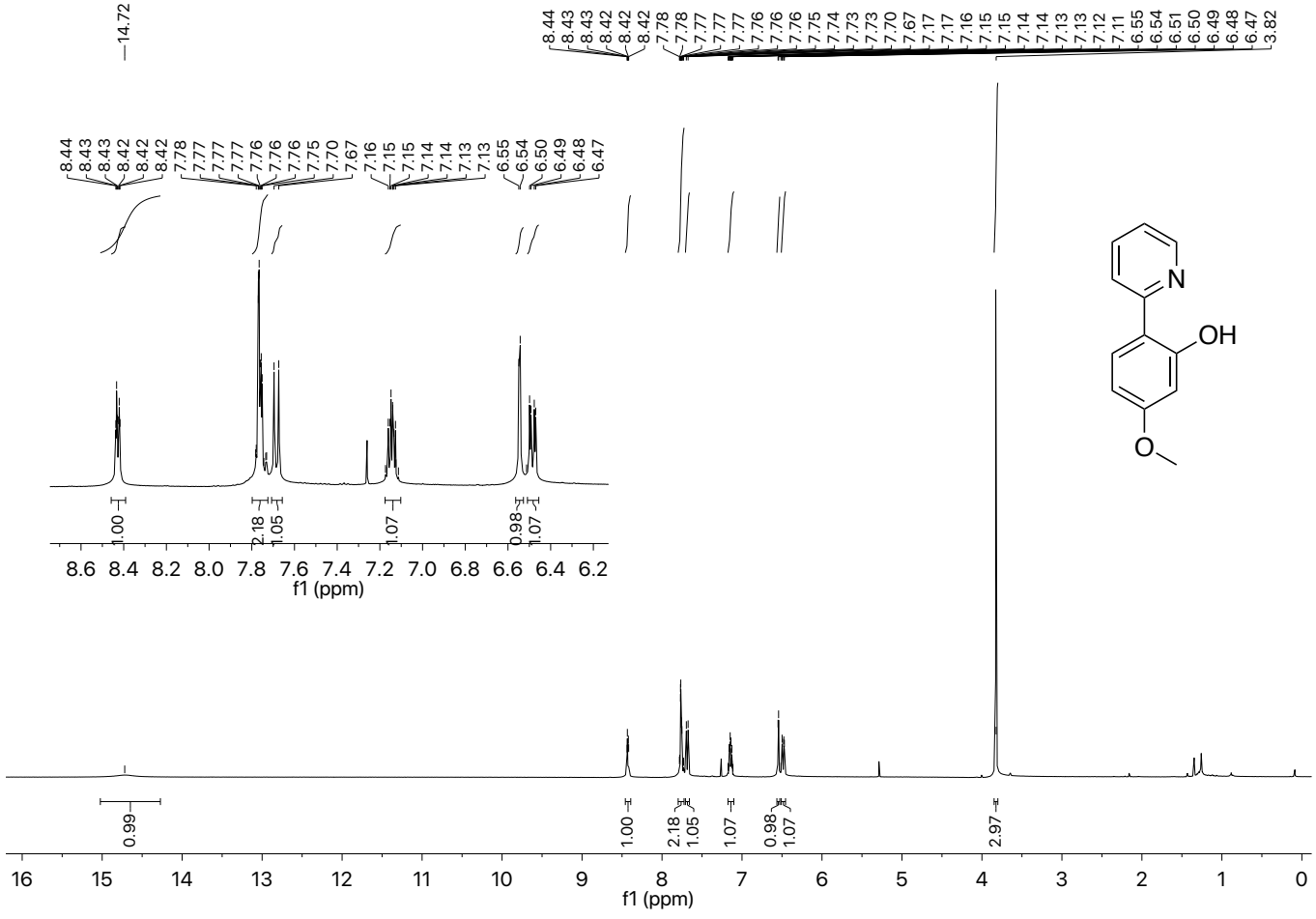
^{1}H NMR Spectrum in $CDCl_3$ for **6a**



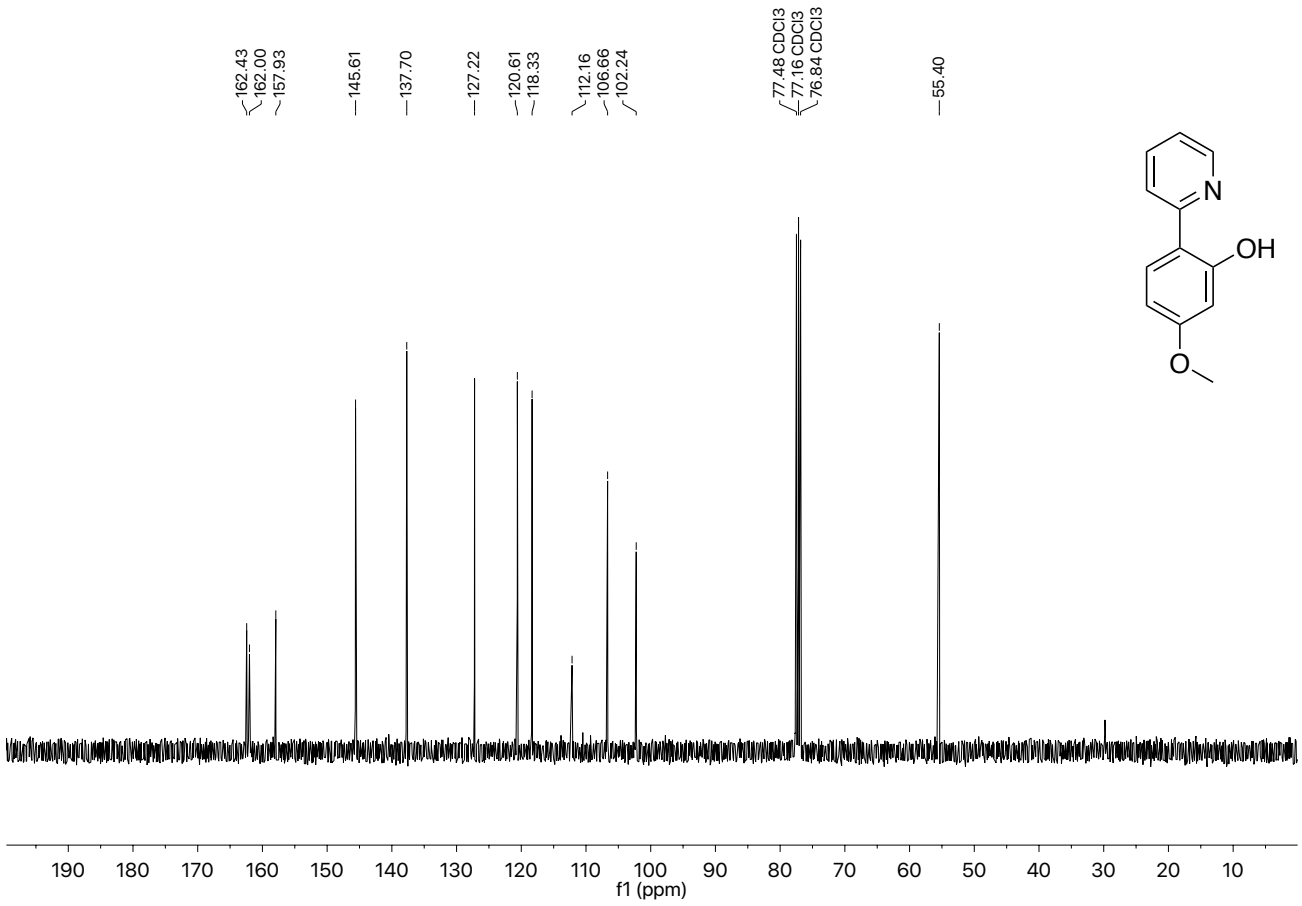
^{13}C NMR Spectrum in $CDCl_3$ for **6a**



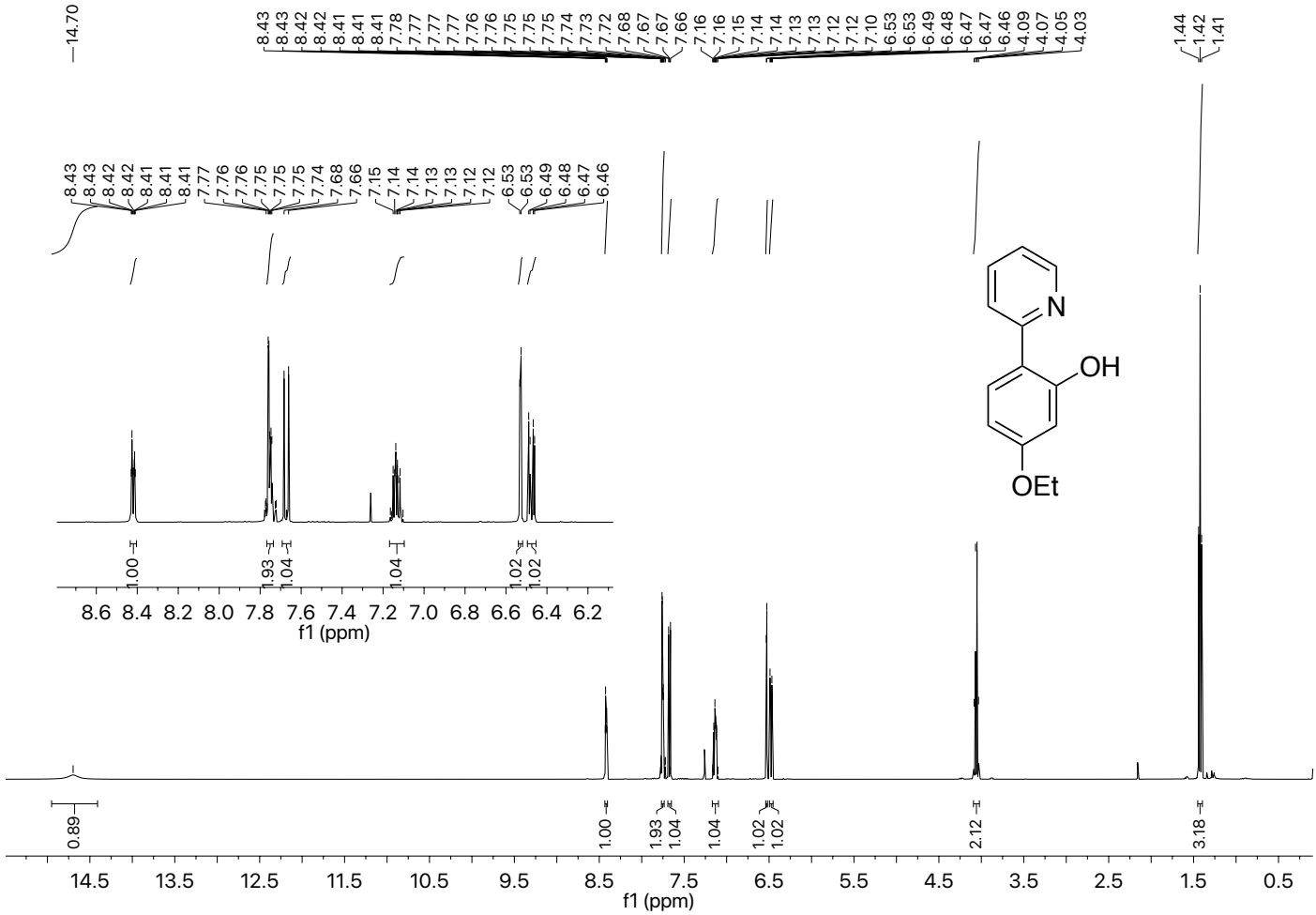
^{1}H NMR Spectrum in $CDCl_3$ for **6b**



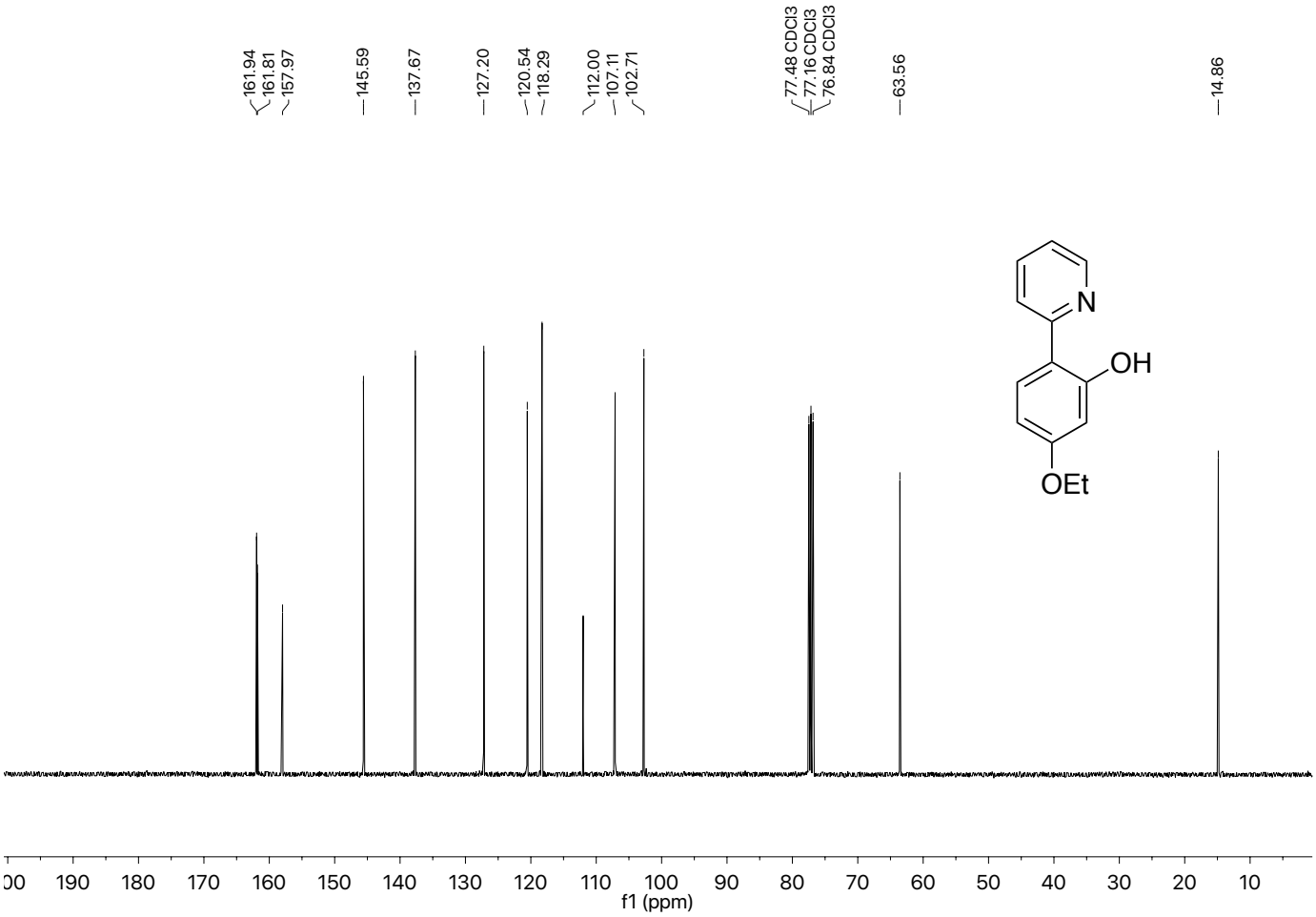
^{13}C NMR Spectrum in $CDCl_3$ for **6b**



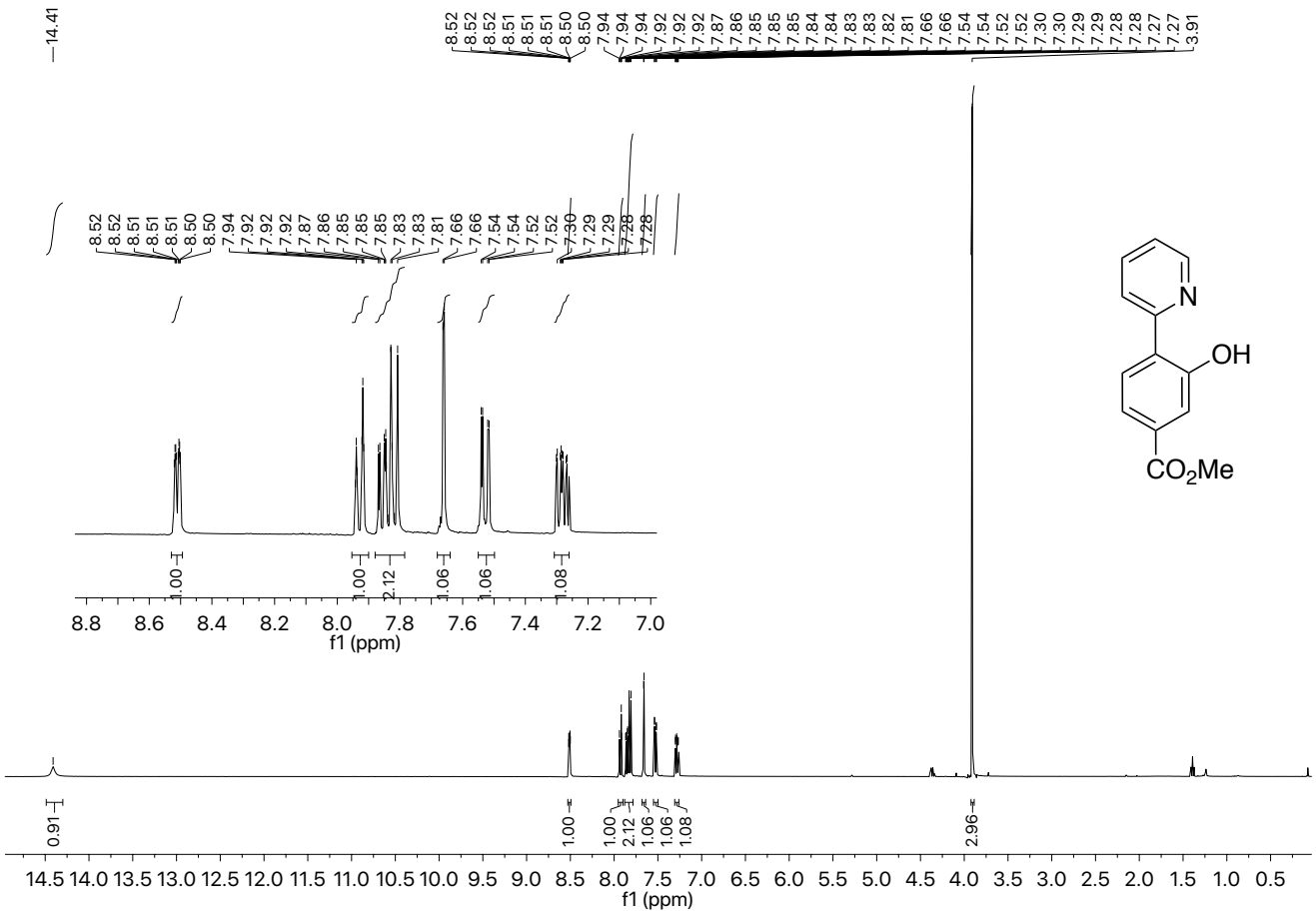
^{1}H NMR Spectrum in $CDCl_3$ for **6c**



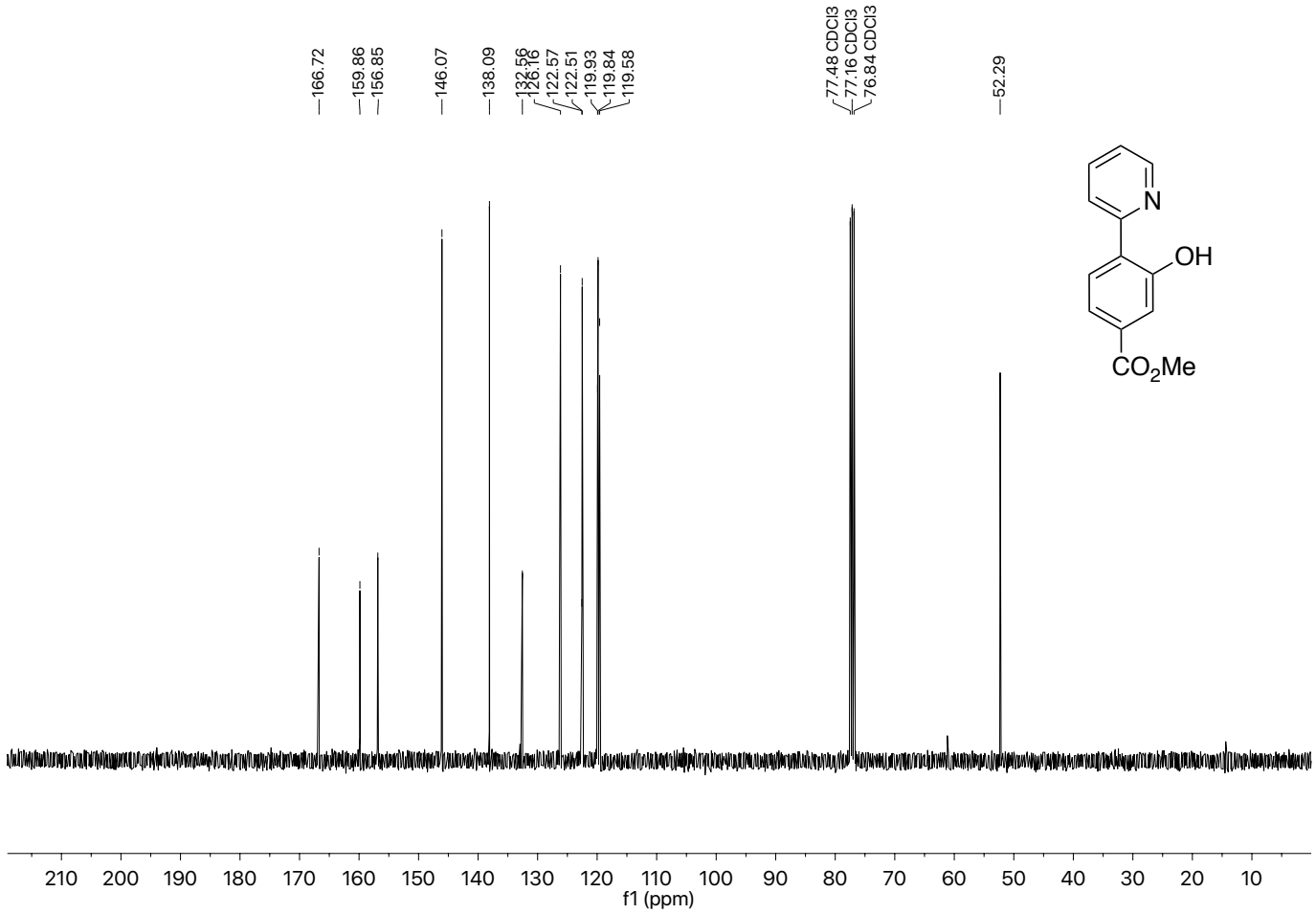
^{13}C NMR Spectrum in $CDCl_3$ for **6c**



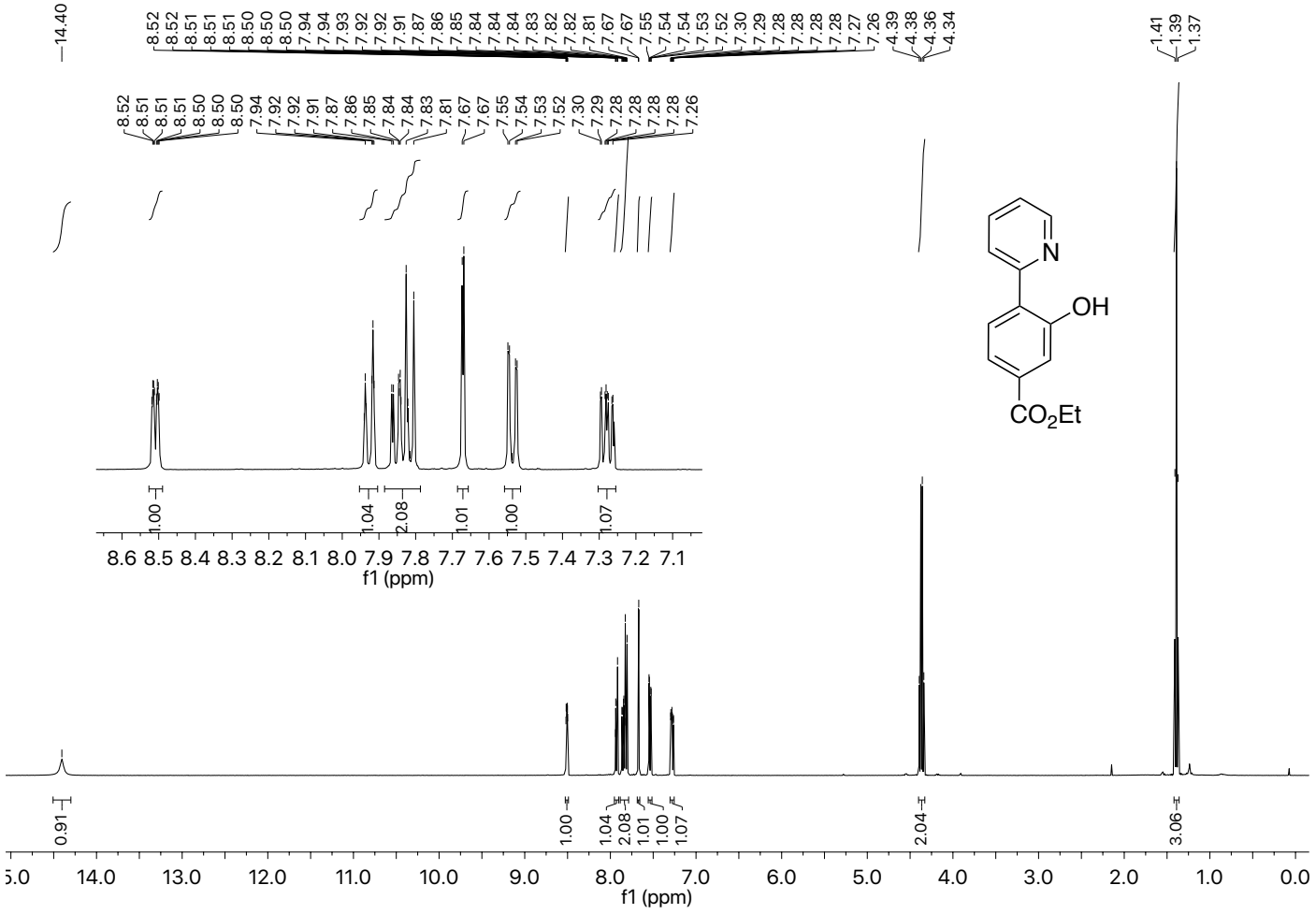
^{1}H NMR Spectrum in $CDCl_3$ for **6d**



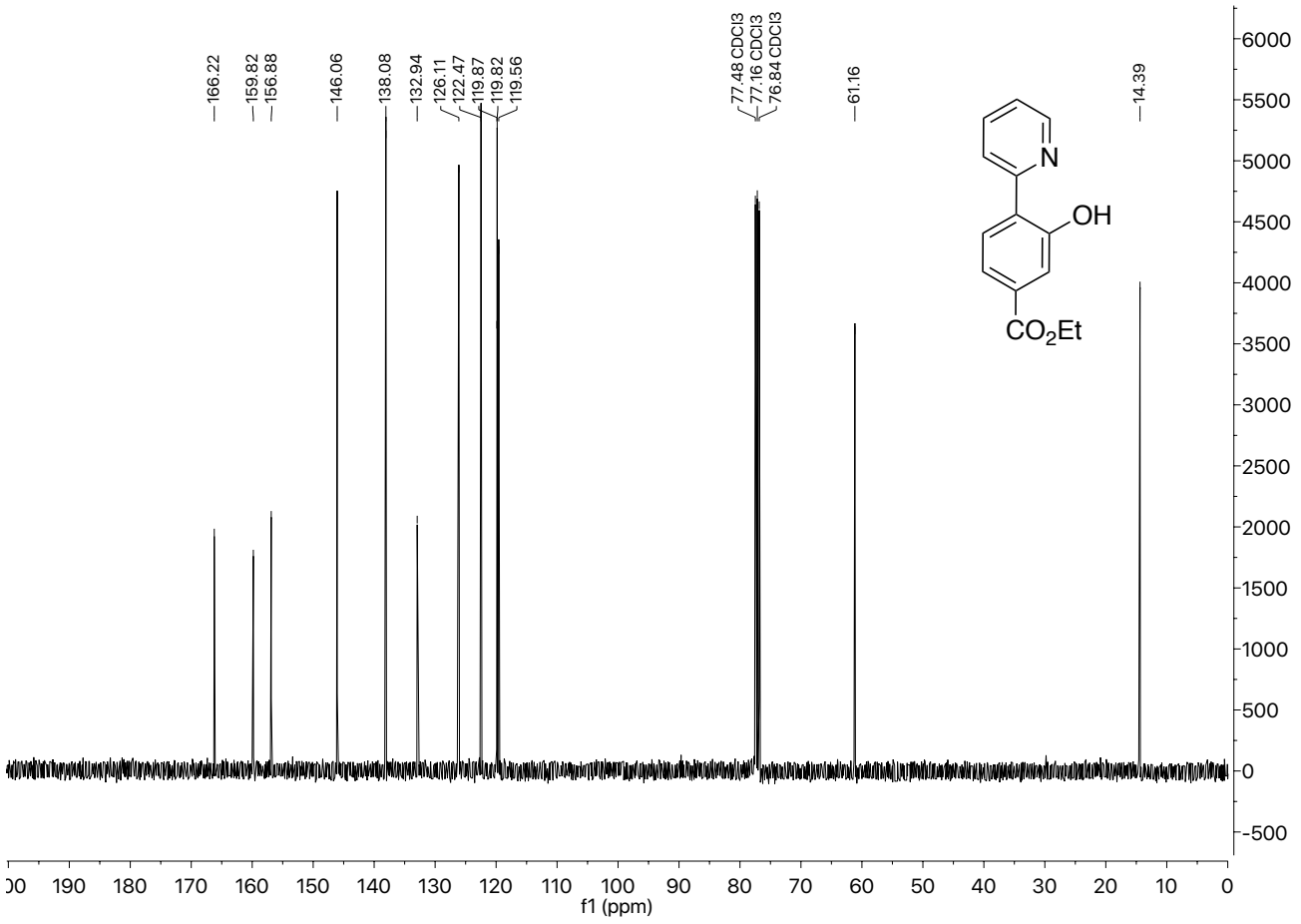
^{13}C NMR Spectrum in $CDCl_3$ for **6d**



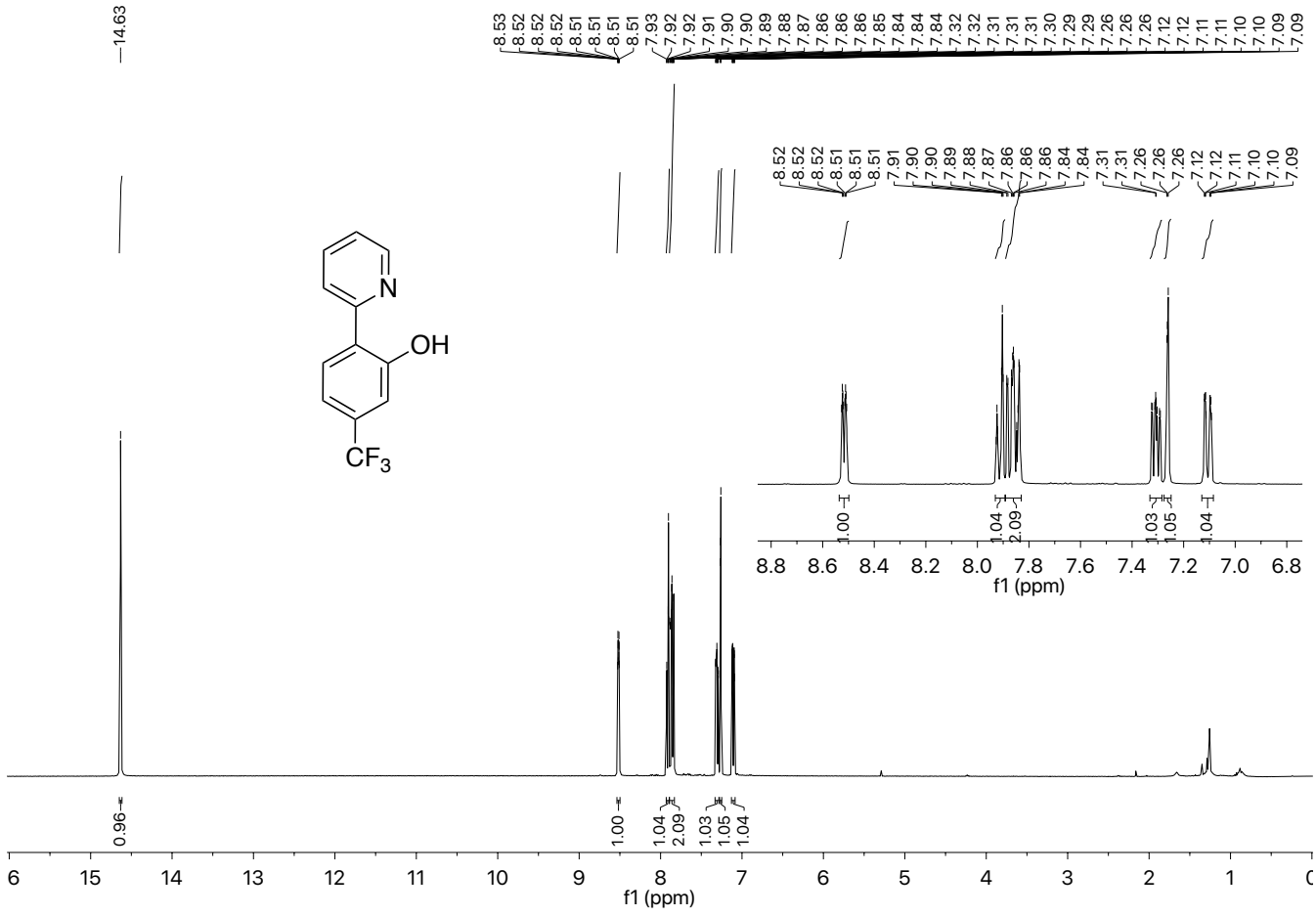
^{1}H NMR Spectrum in $CDCl_3$ for **6e**



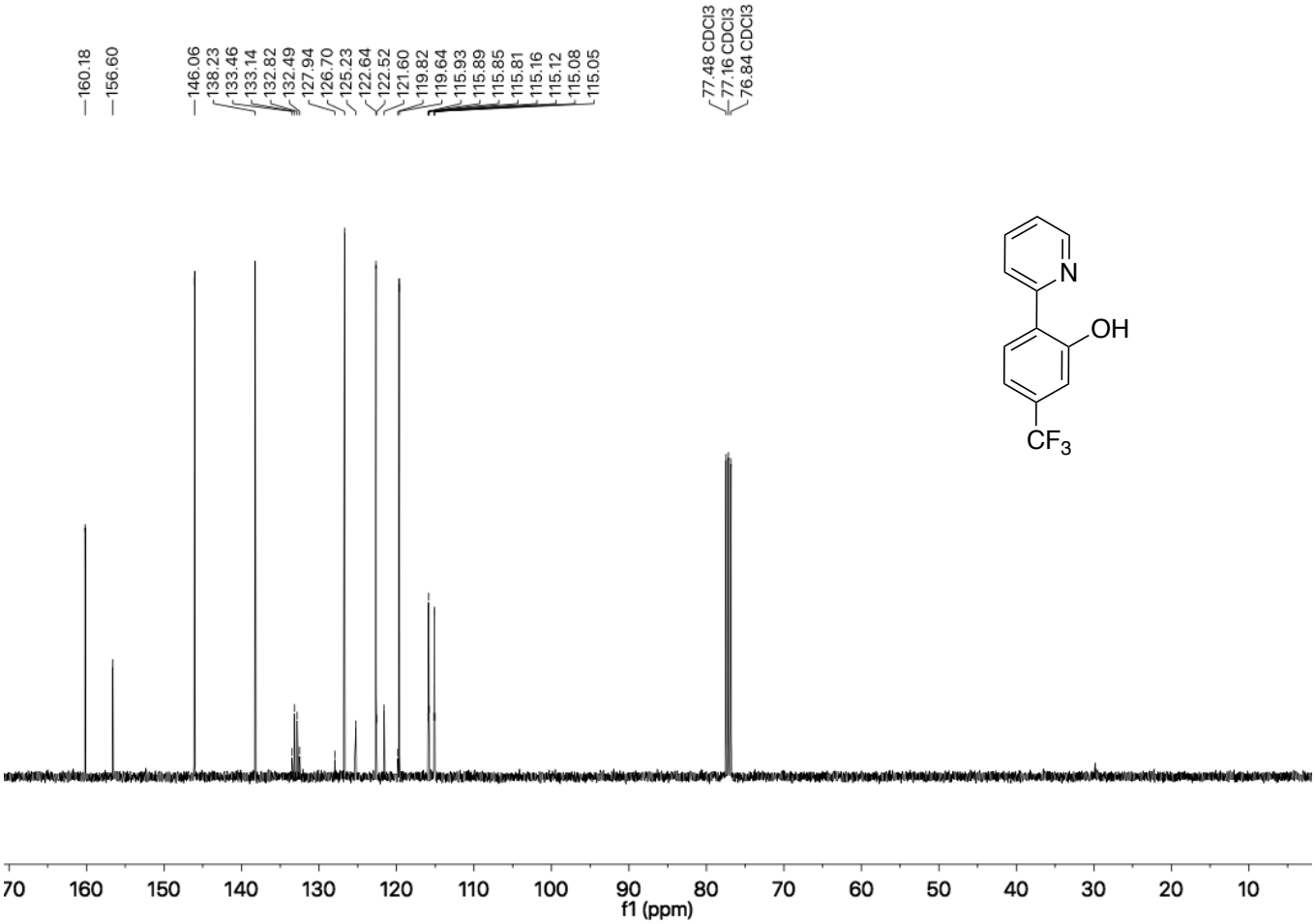
^{13}C NMR Spectrum in $CDCl_3$ for **6e**



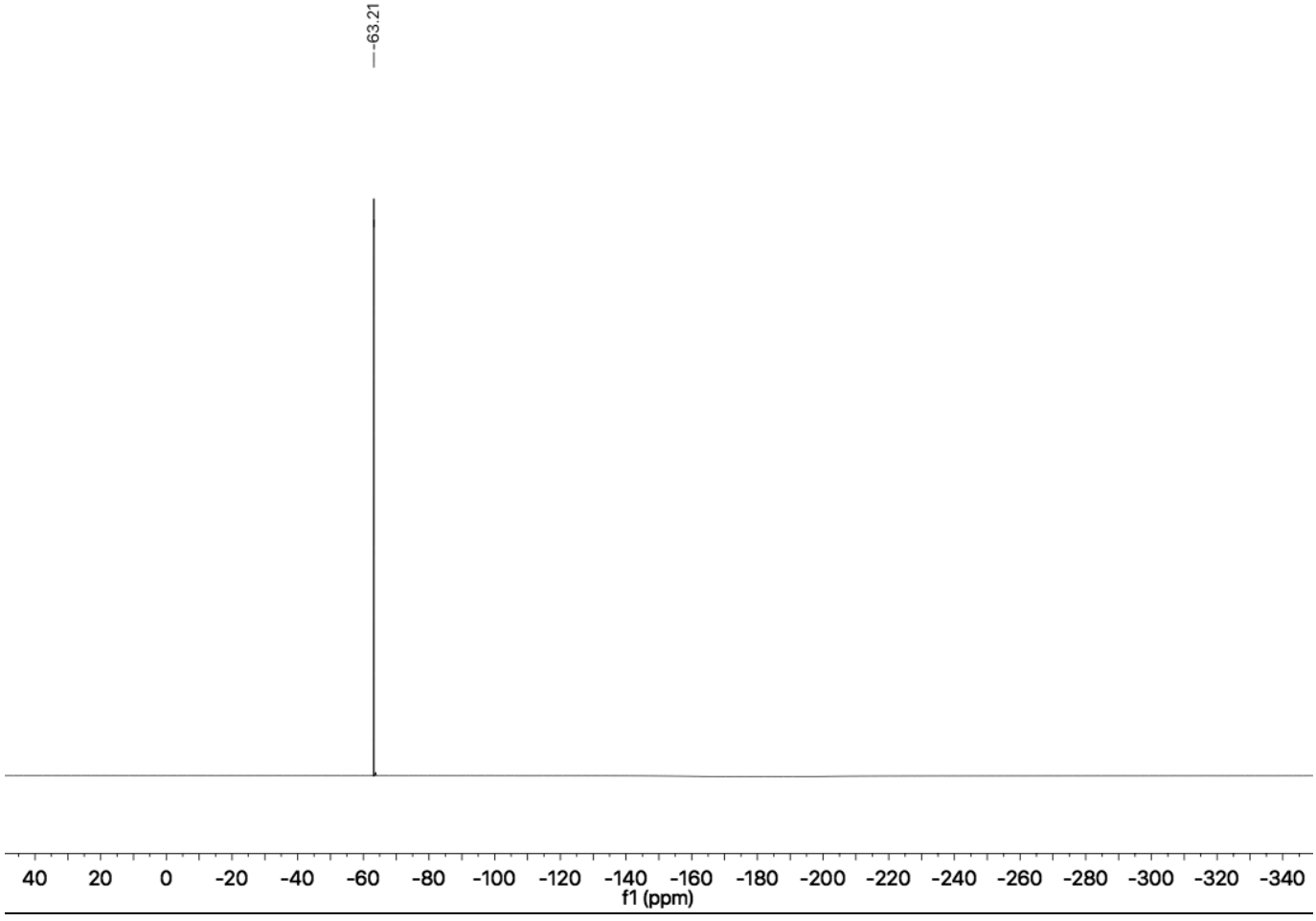
^{1}H NMR Spectrum in $CDCl_3$ for **6f**



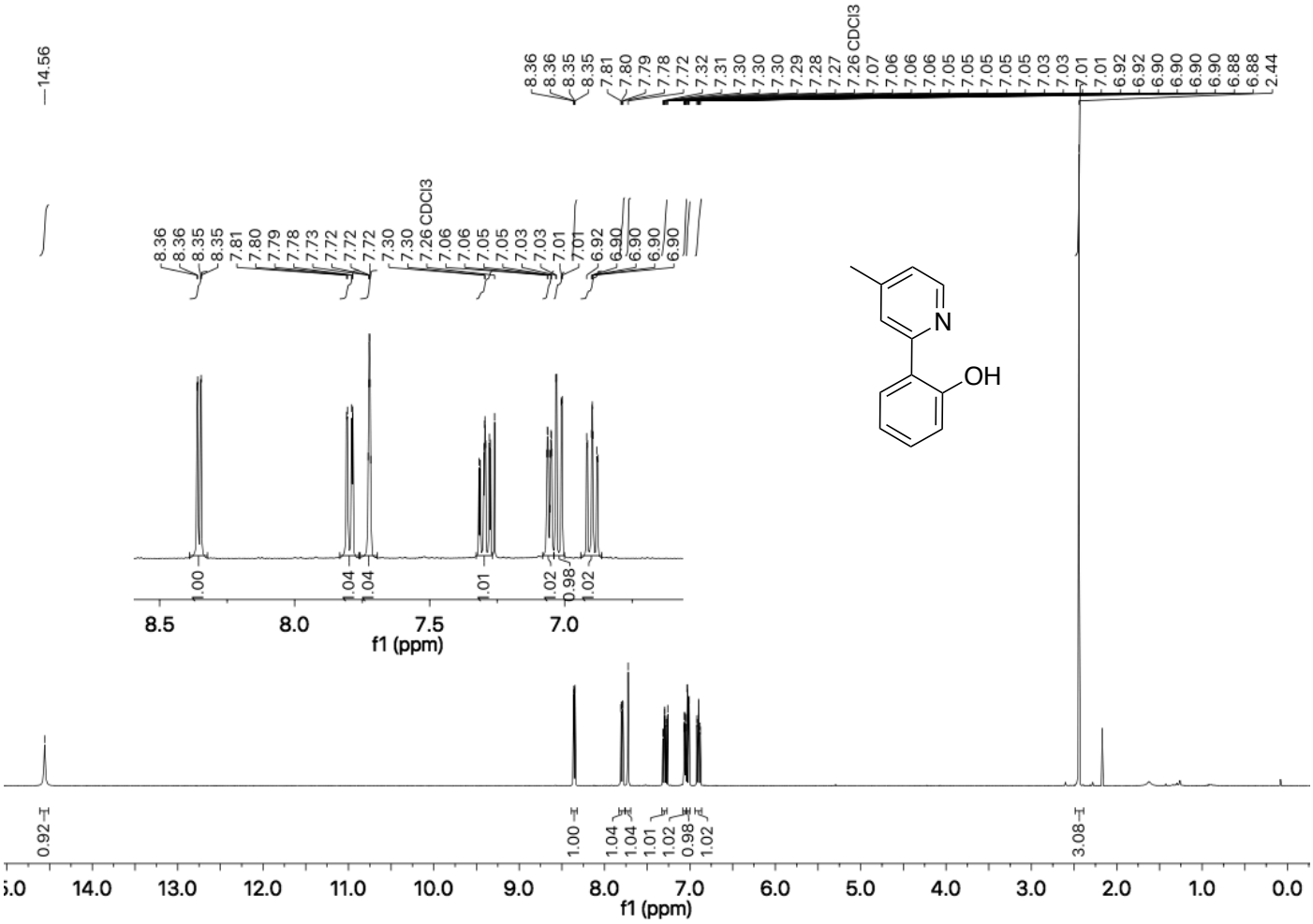
^{13}C NMR Spectrum in $CDCl_3$ for **6f**



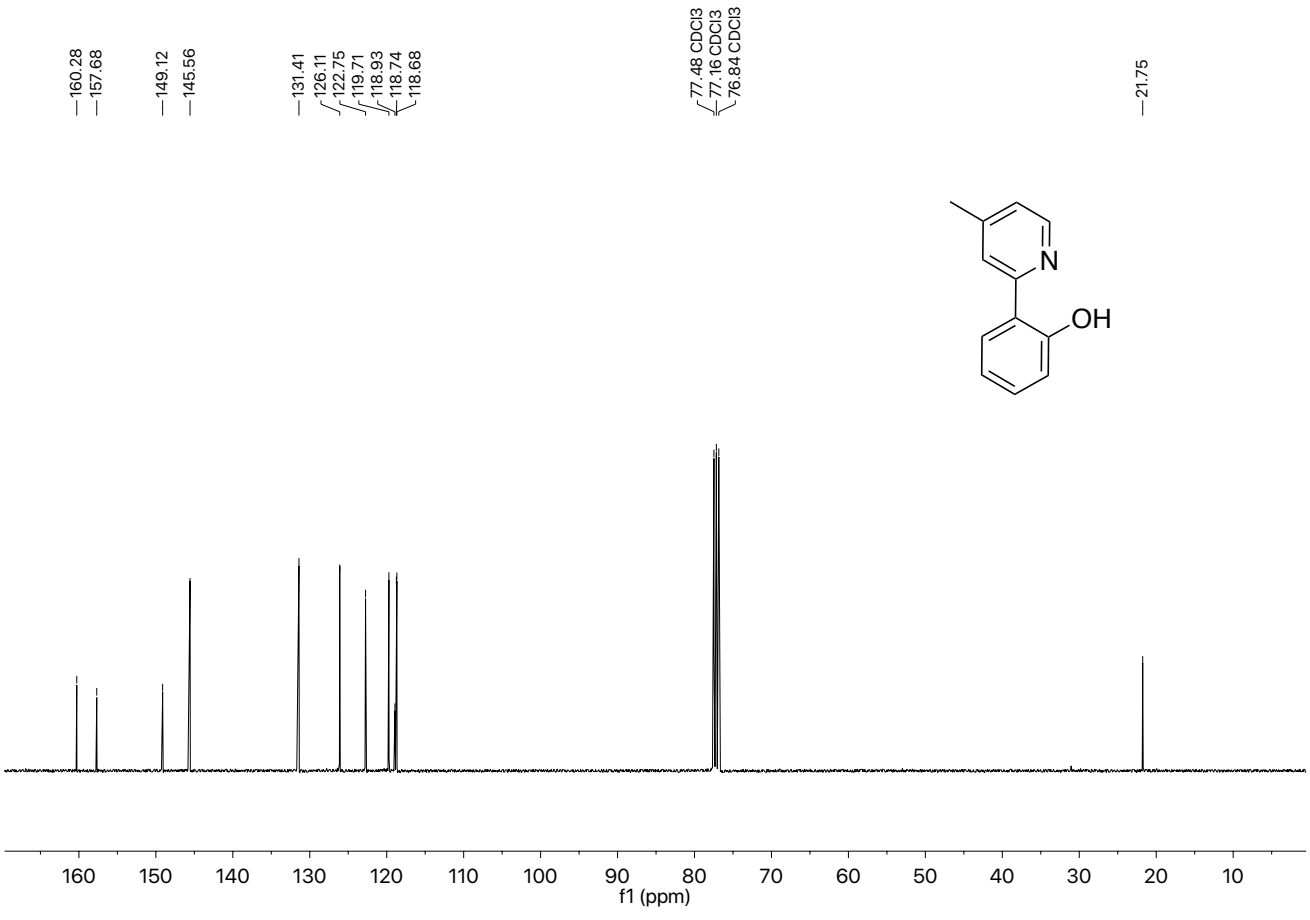
^{19}F NMR Spectrum in $CDCl_3$ for **6f**



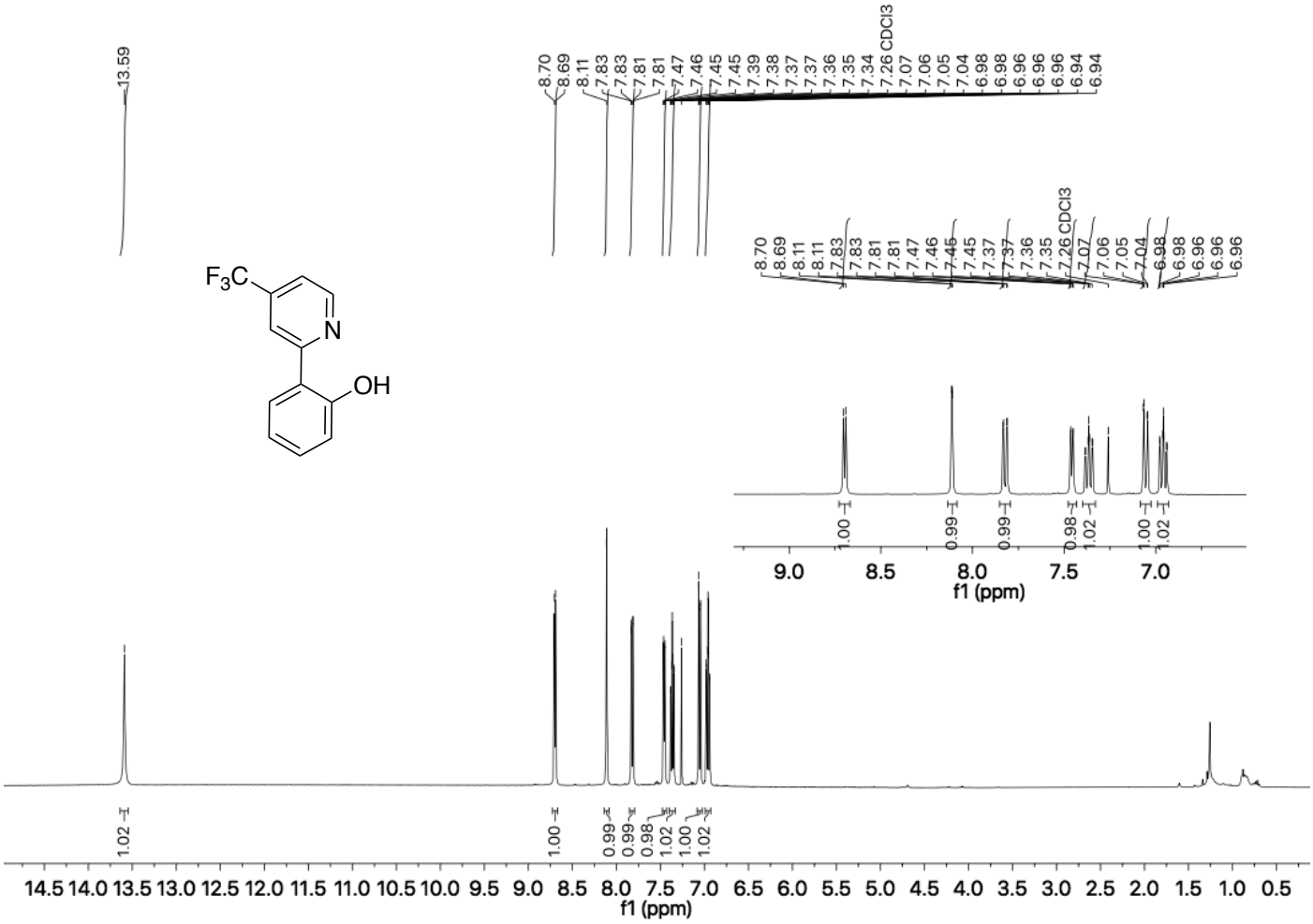
^{1}H NMR Spectrum in $CDCl_3$ for **6j**



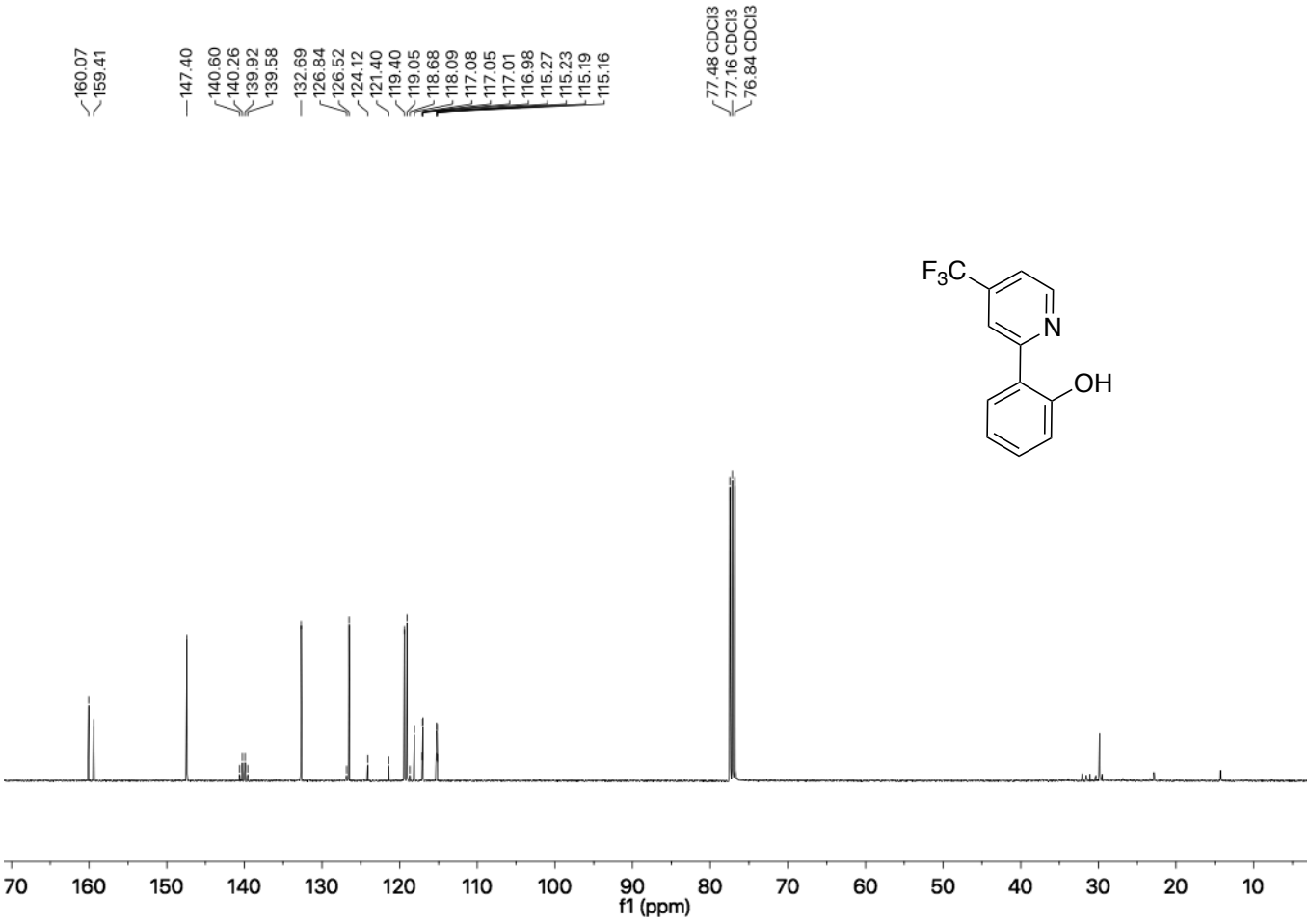
^{13}C NMR Spectrum in $CDCl_3$ for **6j**



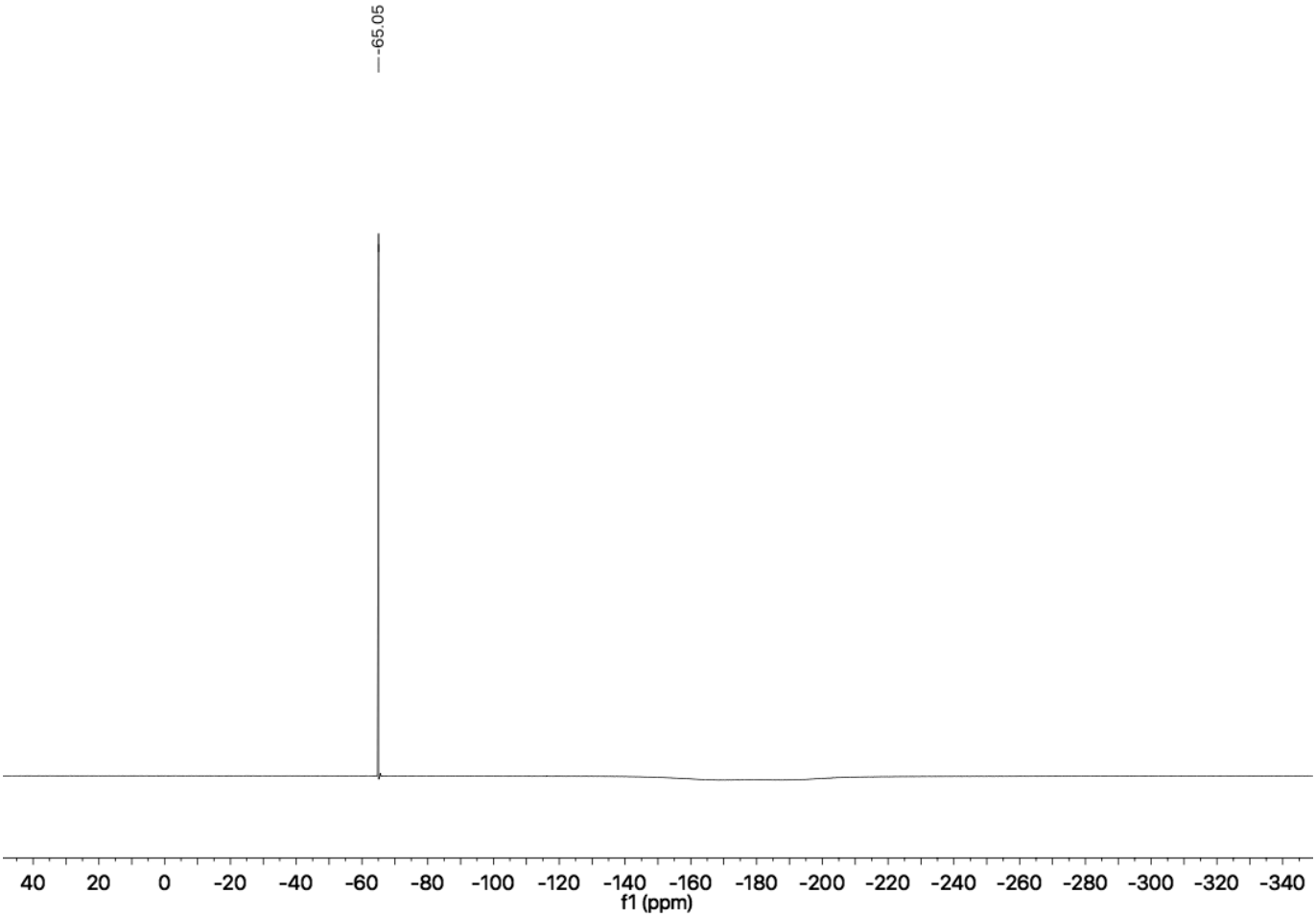
^{1}H NMR Spectrum in $CDCl_3$ for **6k**



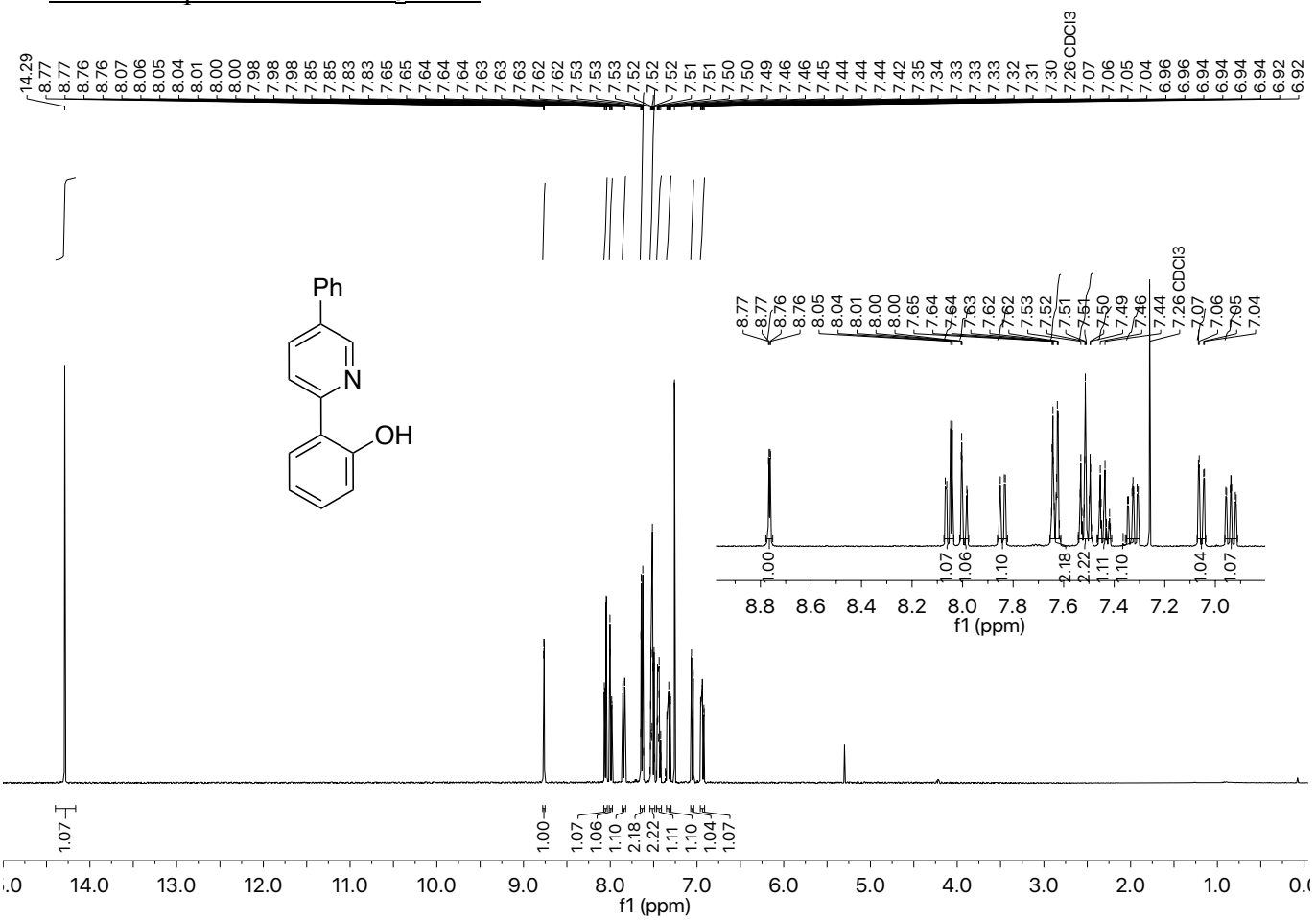
^{13}C NMR Spectrum in $CDCl_3$ for **6k**



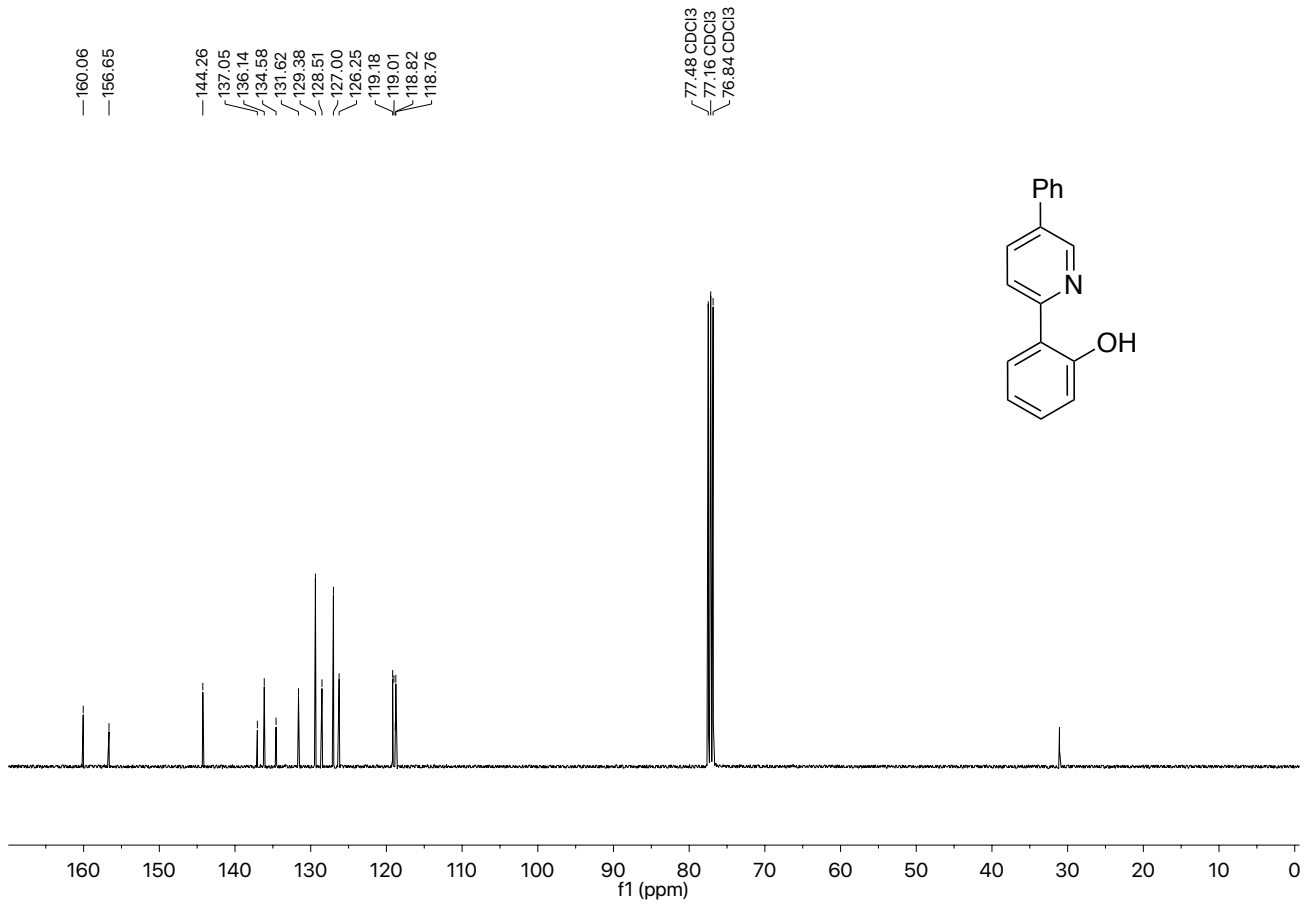
^{19}F NMR Spectrum in $CDCl_3$ for **6k**



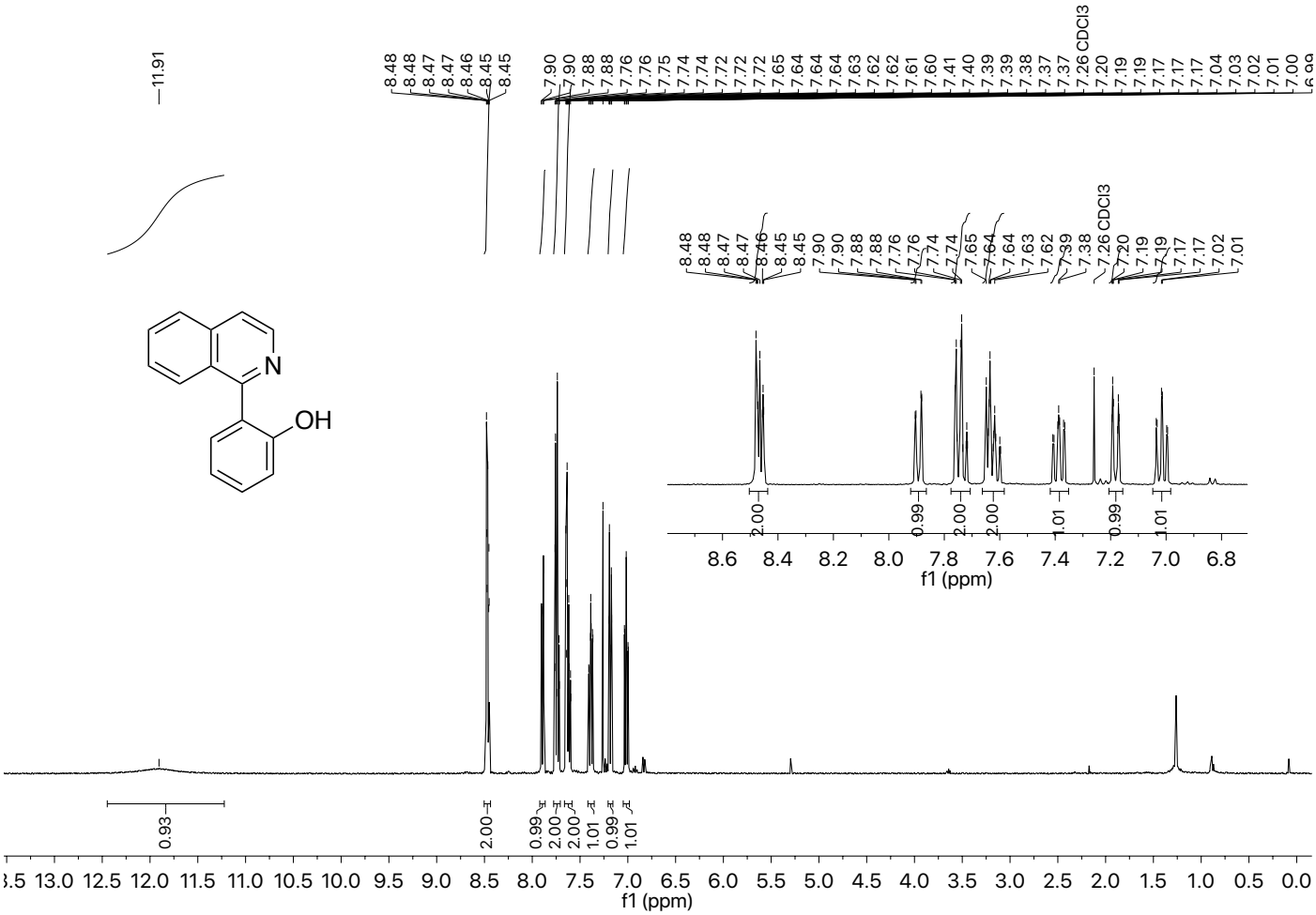
^{1}H NMR Spectrum in $CDCl_3$ for **6l**



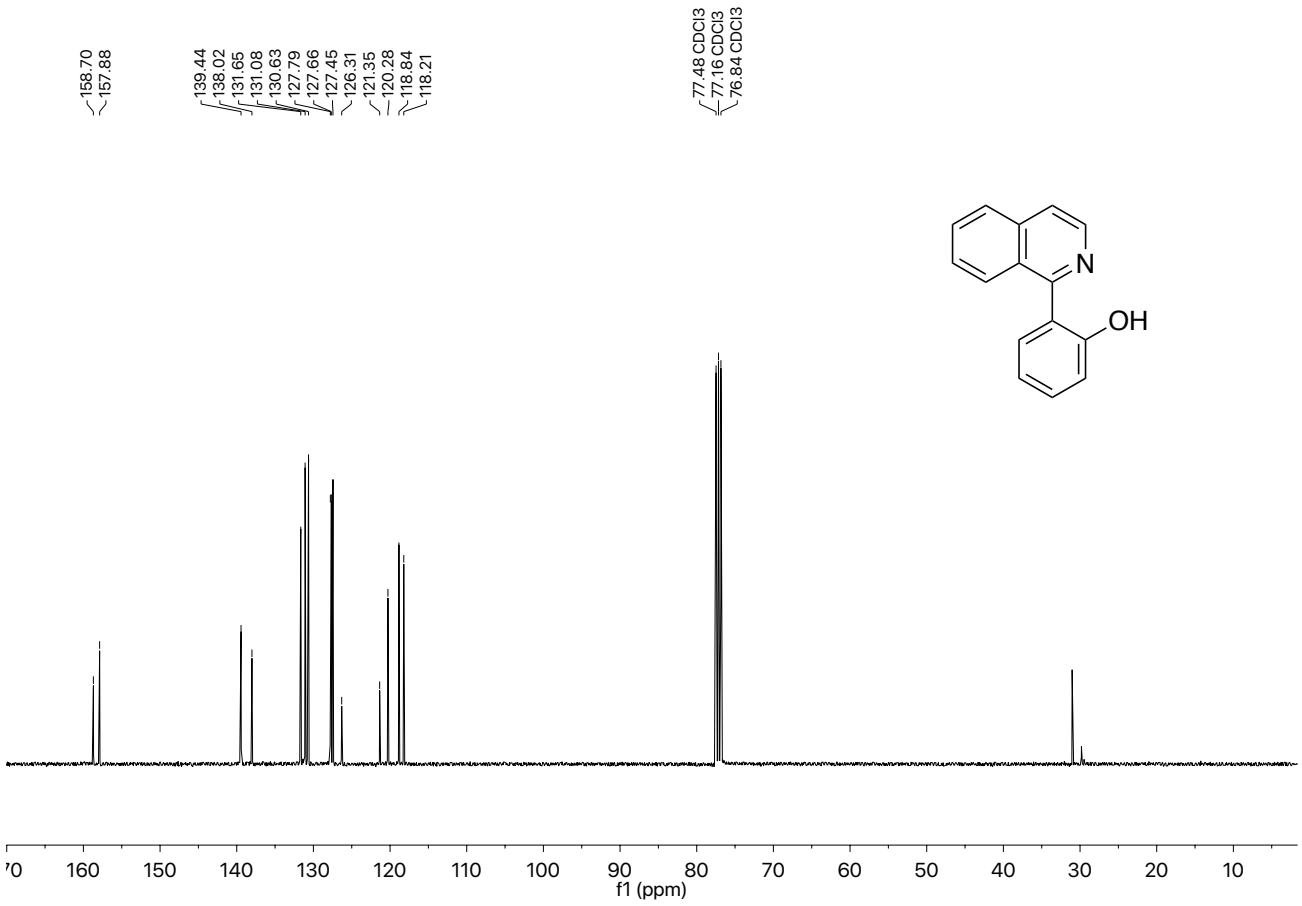
^{13}C NMR Spectrum in $CDCl_3$ for **6l**



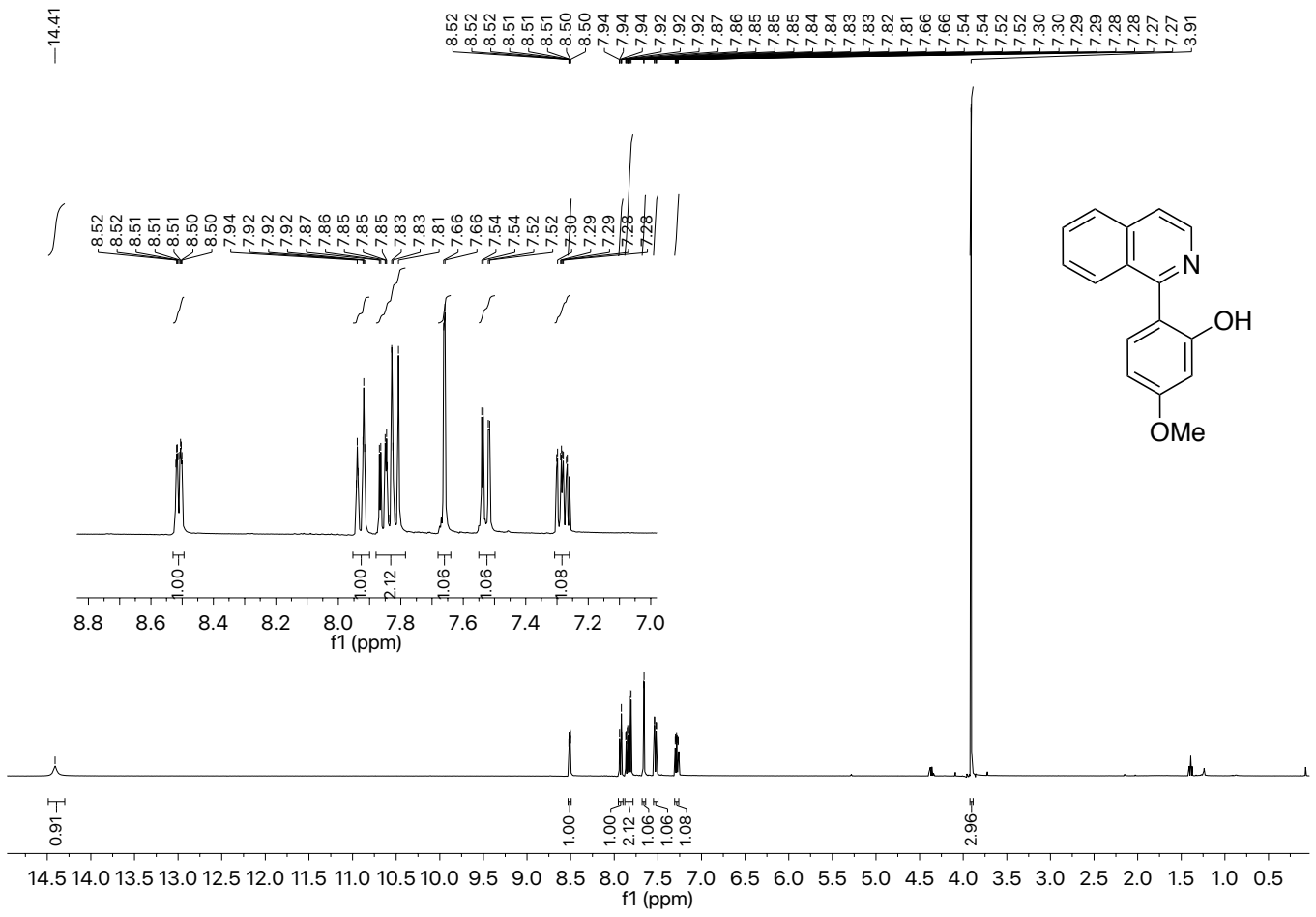
^{1}H NMR Spectrum in $CDCl_3$ for **6m**



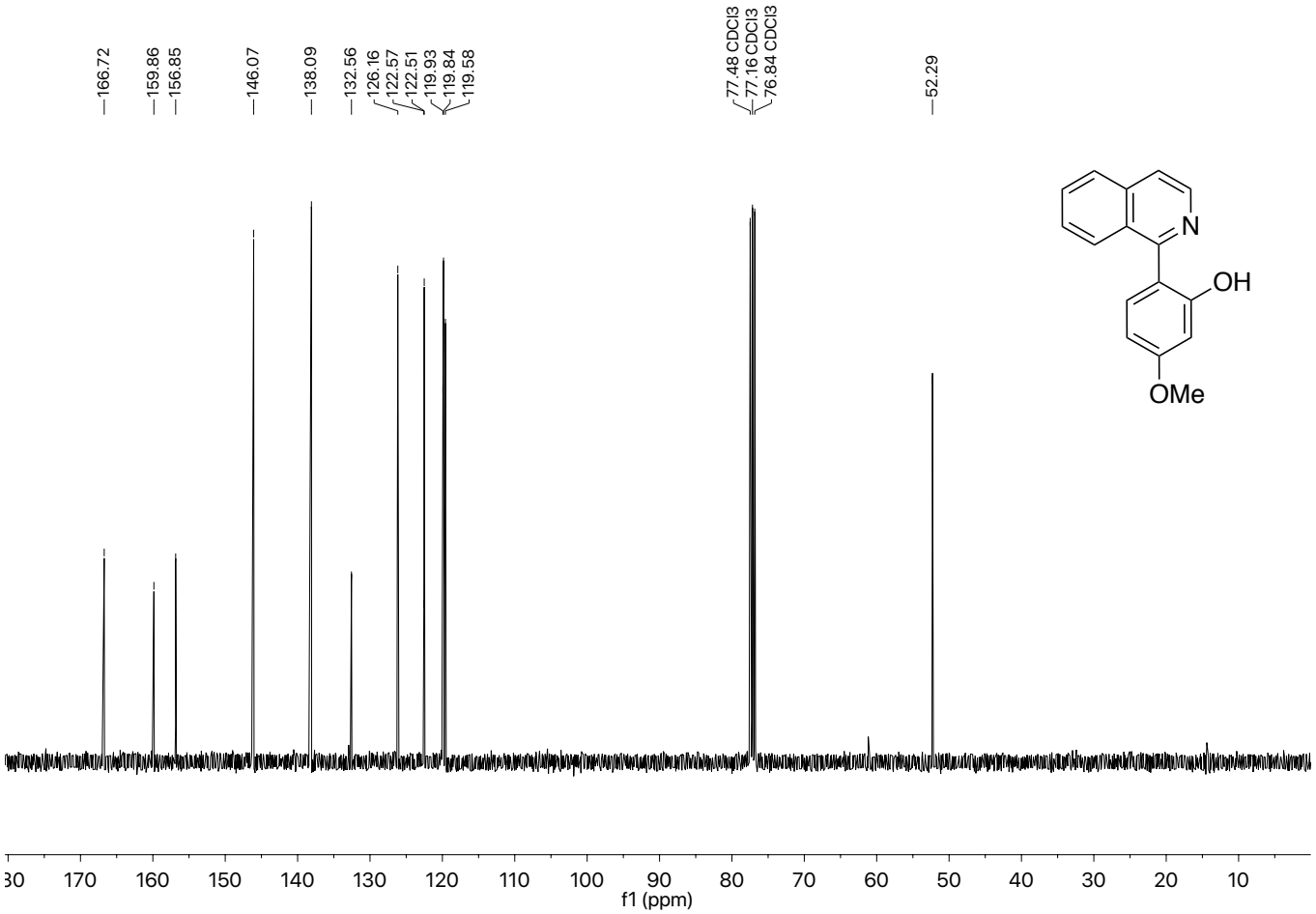
^{13}C NMR Spectrum in $CDCl_3$ for **6m**



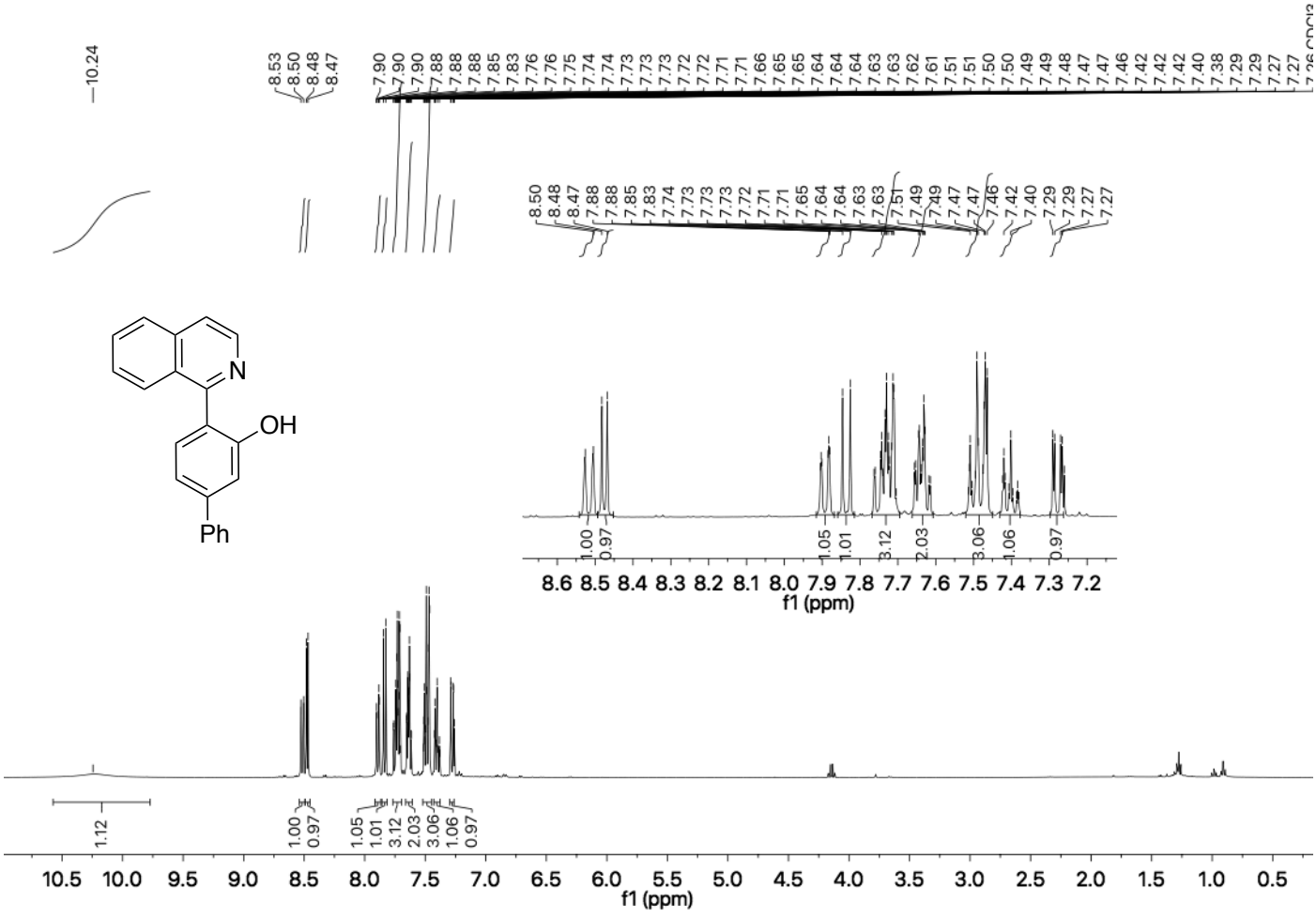
^{1}H NMR Spectrum in $CDCl_3$ for **6n**



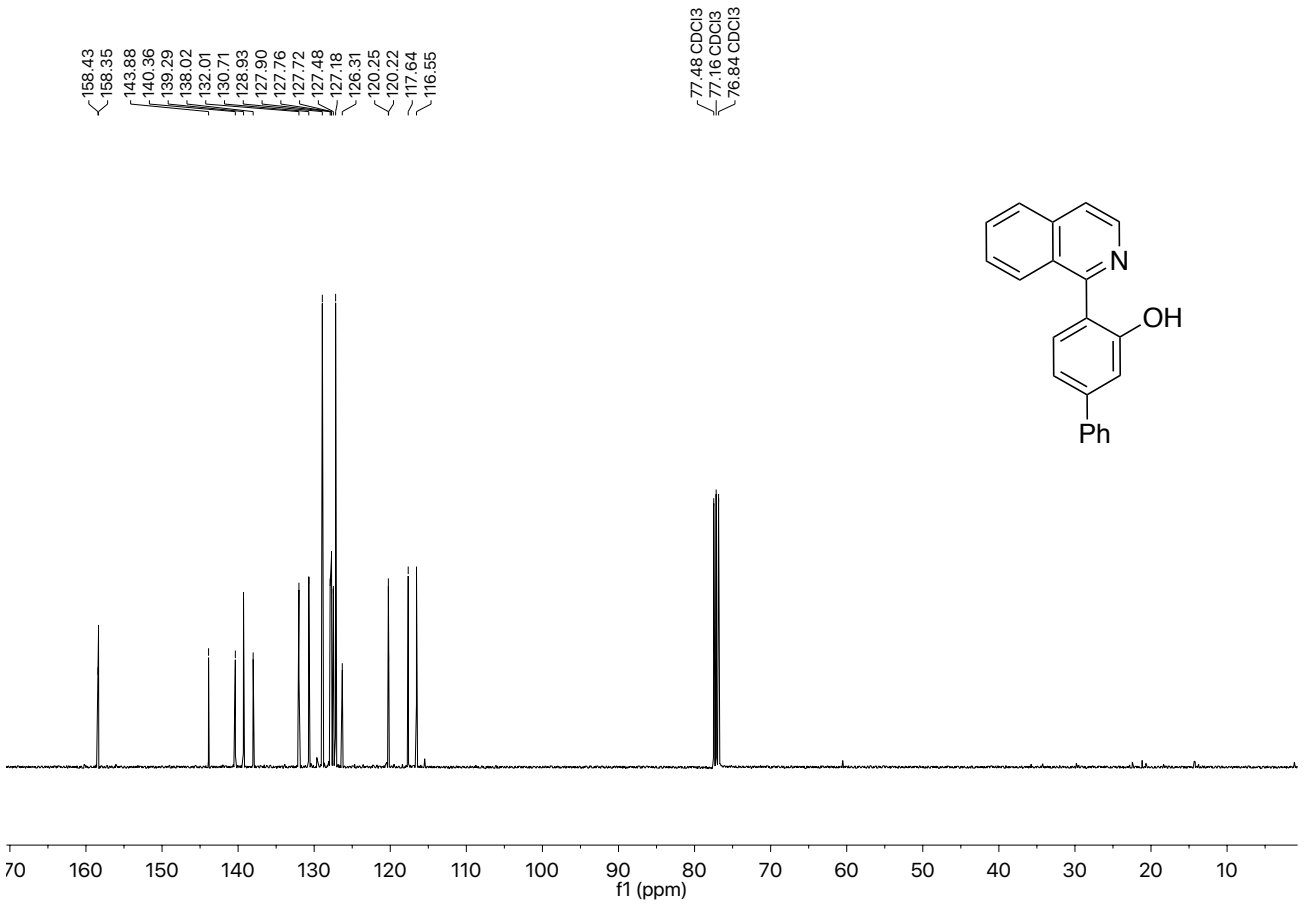
^{13}C NMR Spectrum in $CDCl_3$ for **6n**



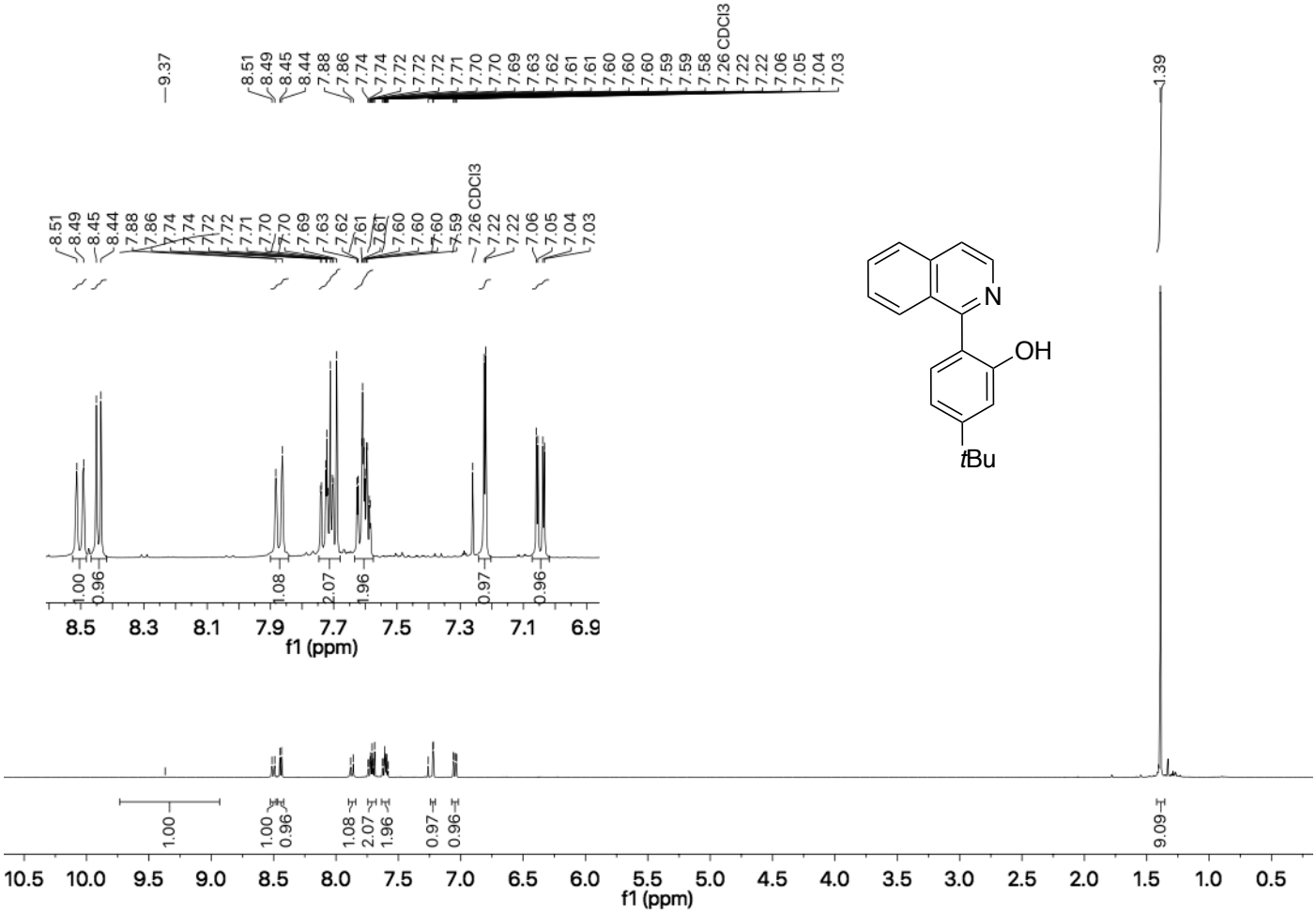
^{1}H NMR Spectrum in $CDCl_3$ for **6o**



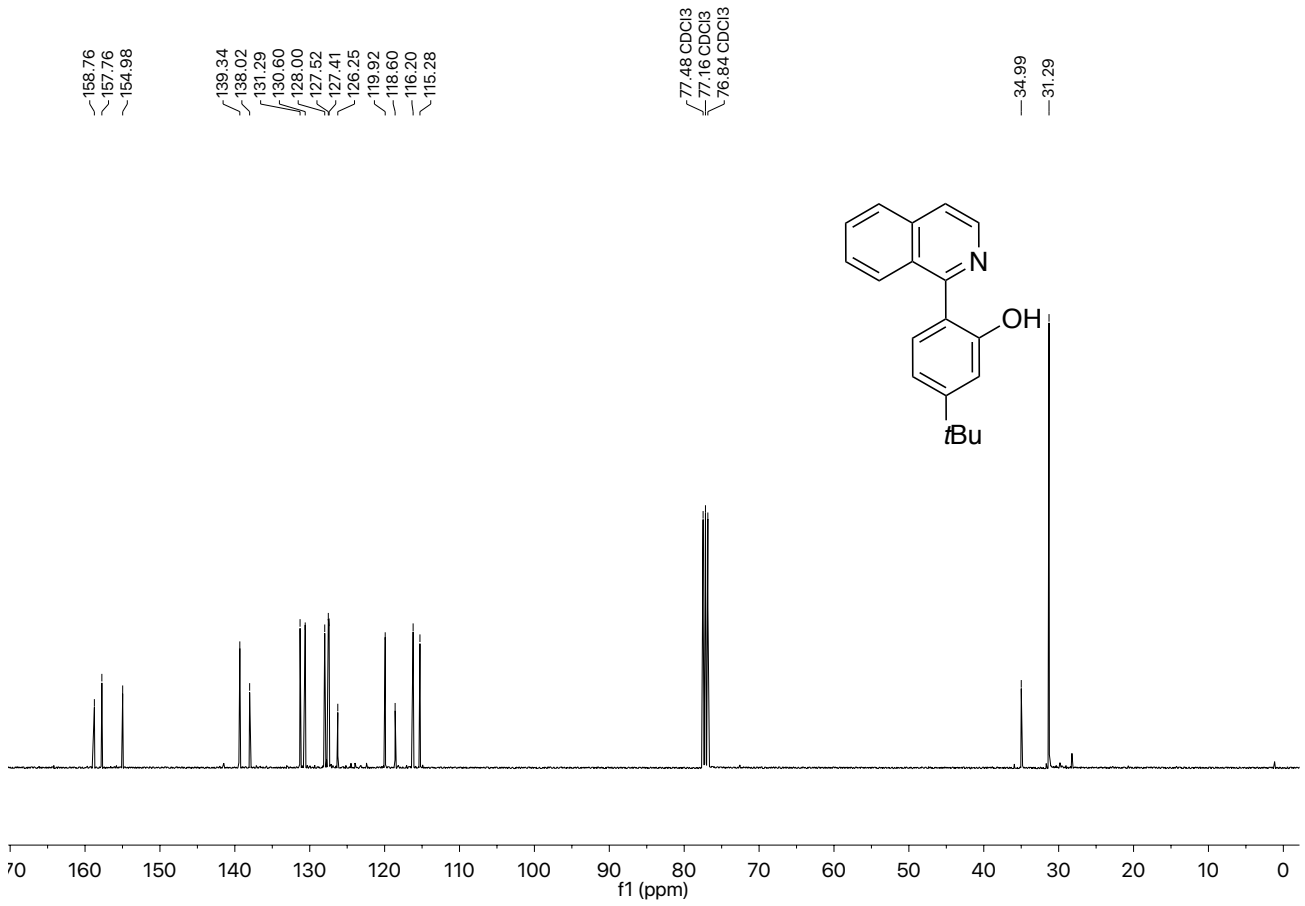
^{13}C NMR Spectrum in $CDCl_3$ for **6o**



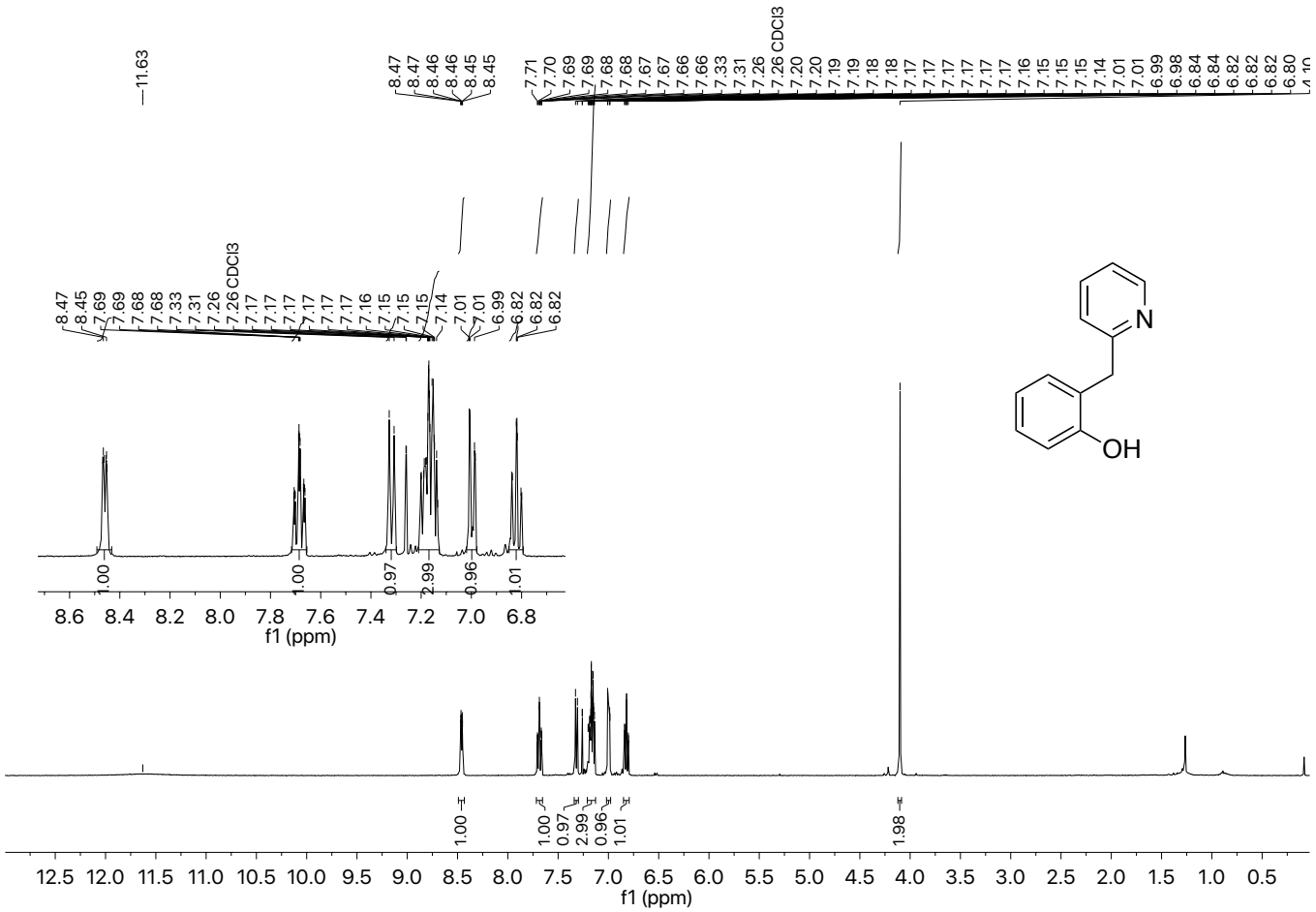
^{1}H NMR Spectrum in $CDCl_3$ for **6q**



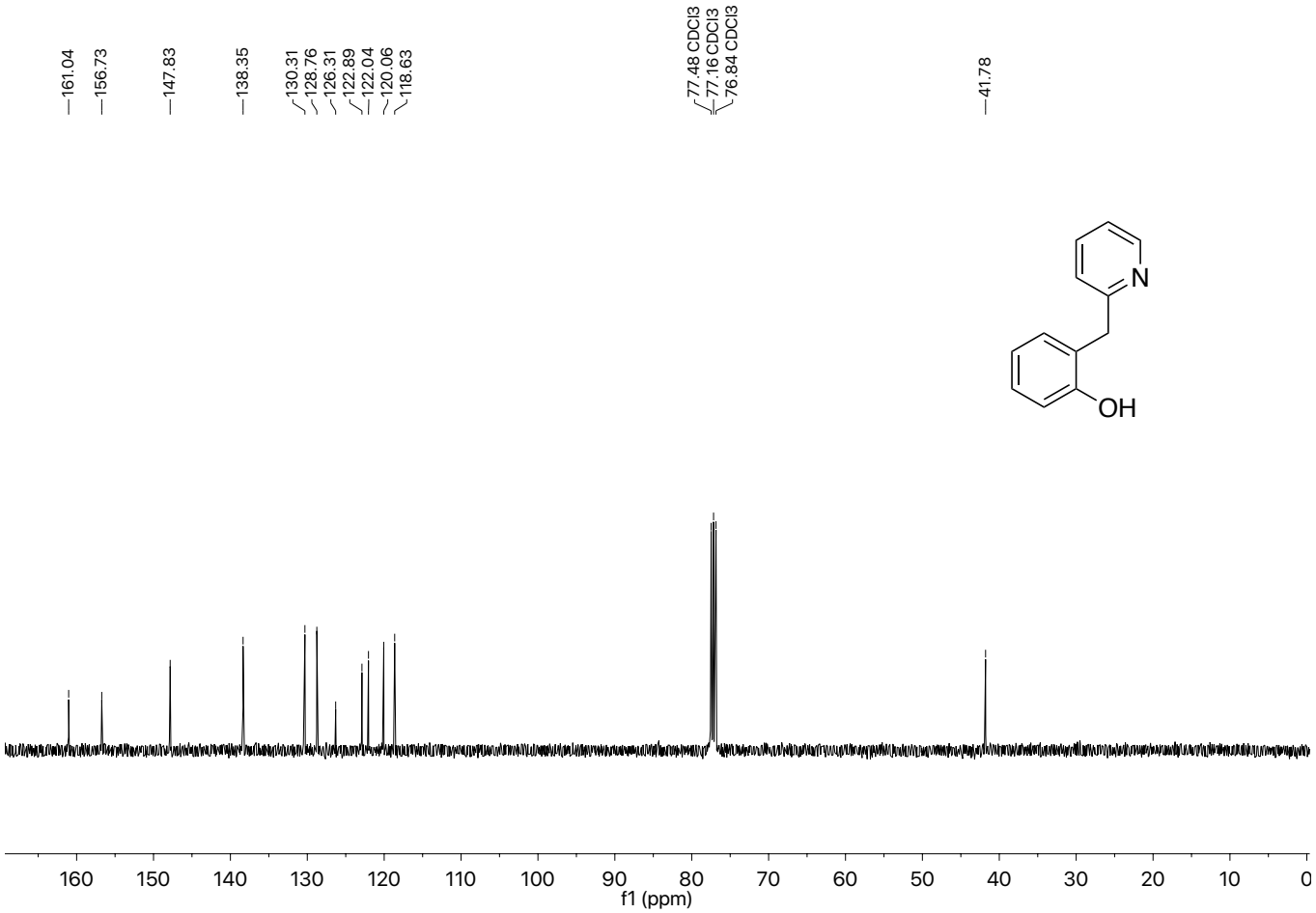
^{13}C NMR Spectrum in $CDCl_3$ for **6q**



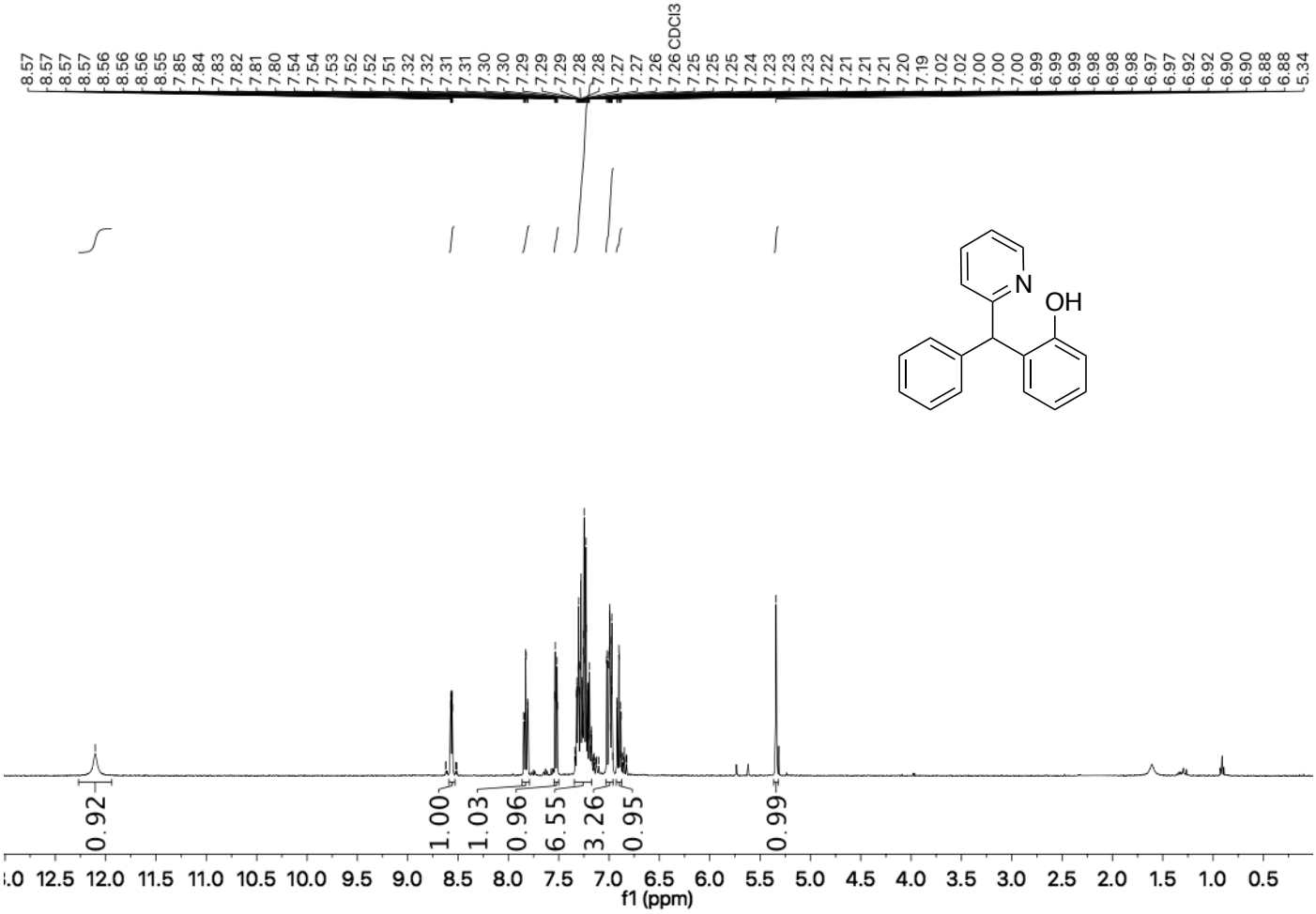
^{1}H NMR Spectrum in $CDCl_3$ for **6r**



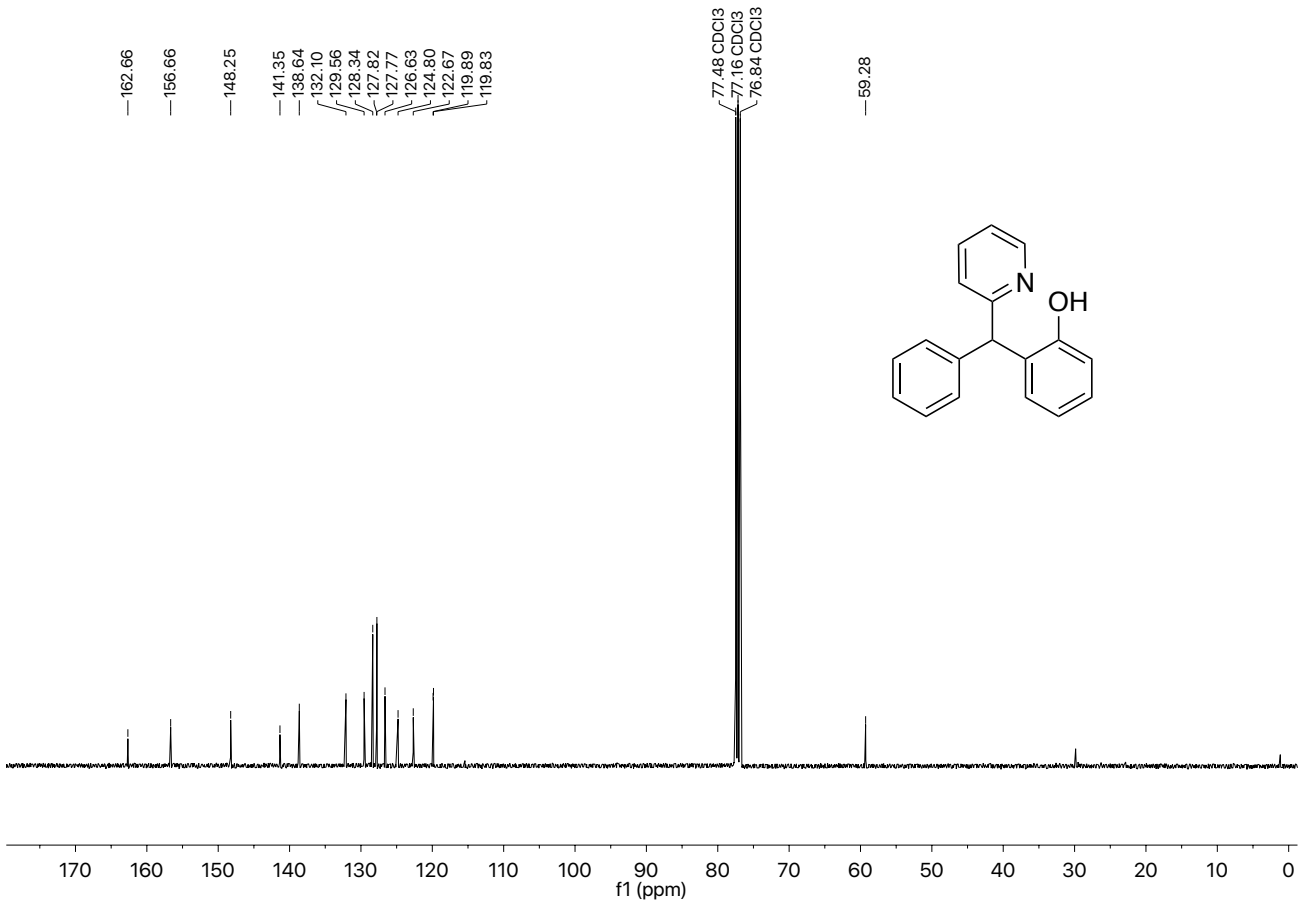
^{13}C NMR Spectrum in $CDCl_3$ for **6r**



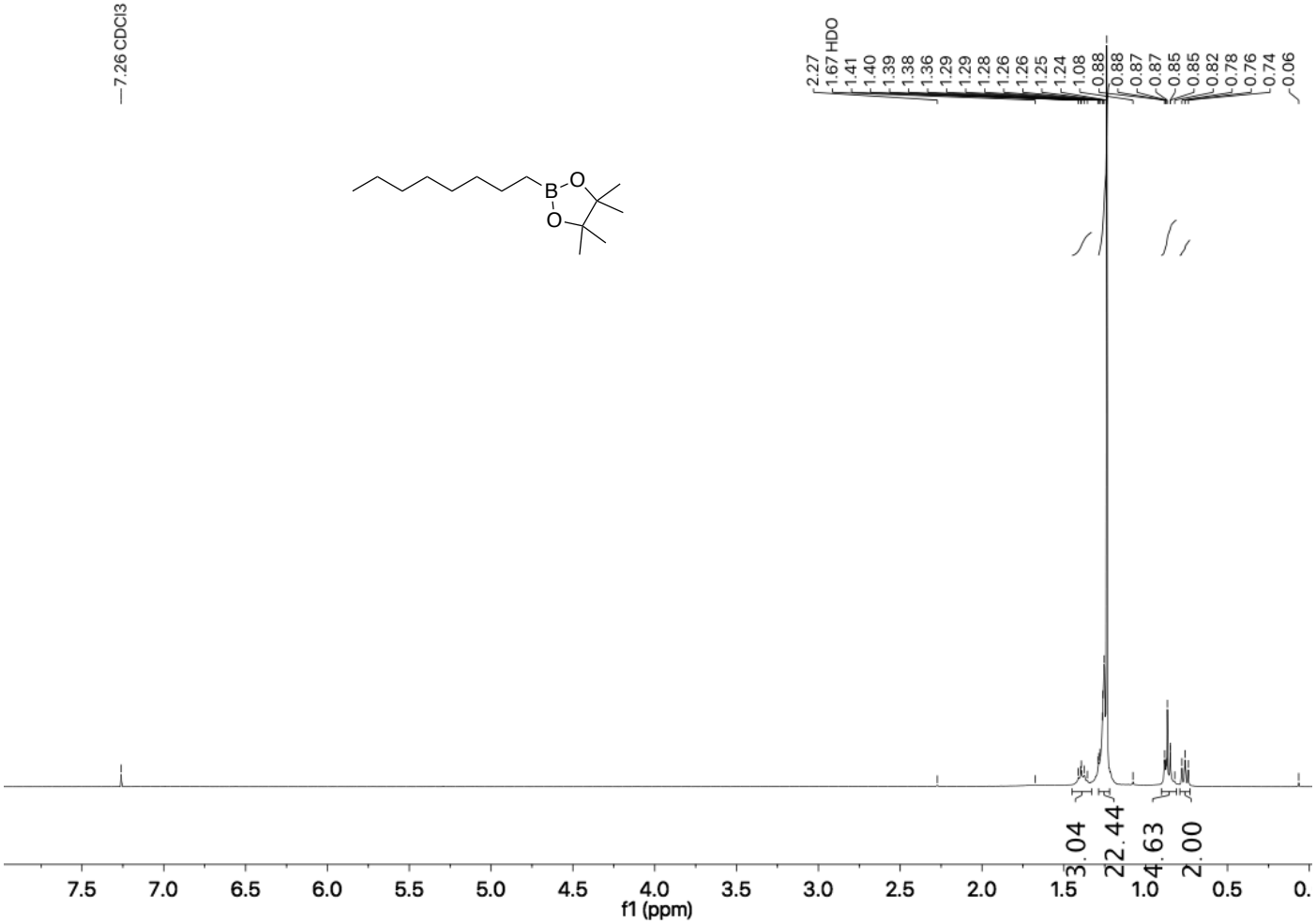
^{1}H NMR Spectrum in $CDCl_3$ for **6s**



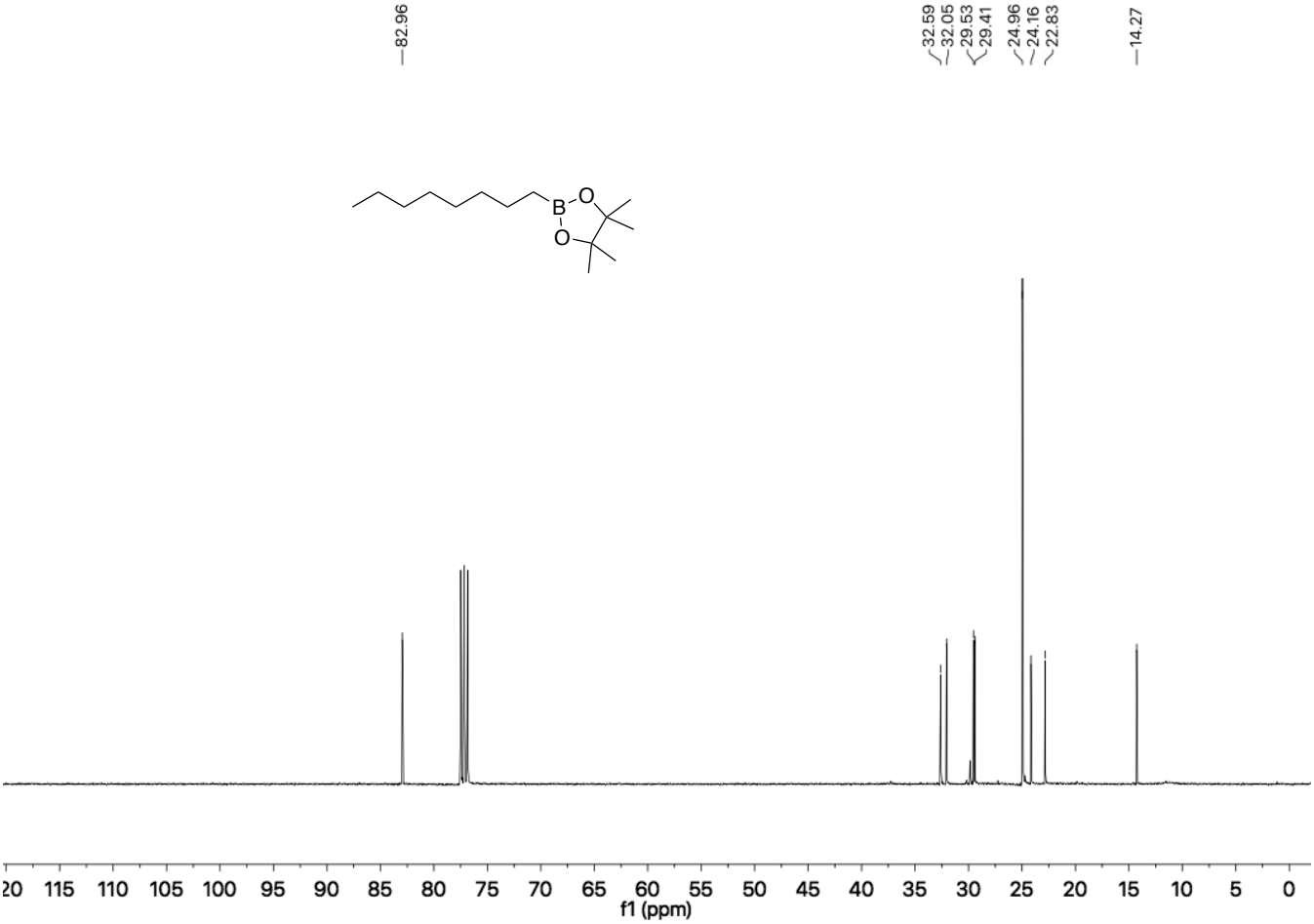
^{13}C NMR Spectrum in $CDCl_3$ for **6s**



^{1}H NMR Spectrum in $CDCl_3$ for 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane

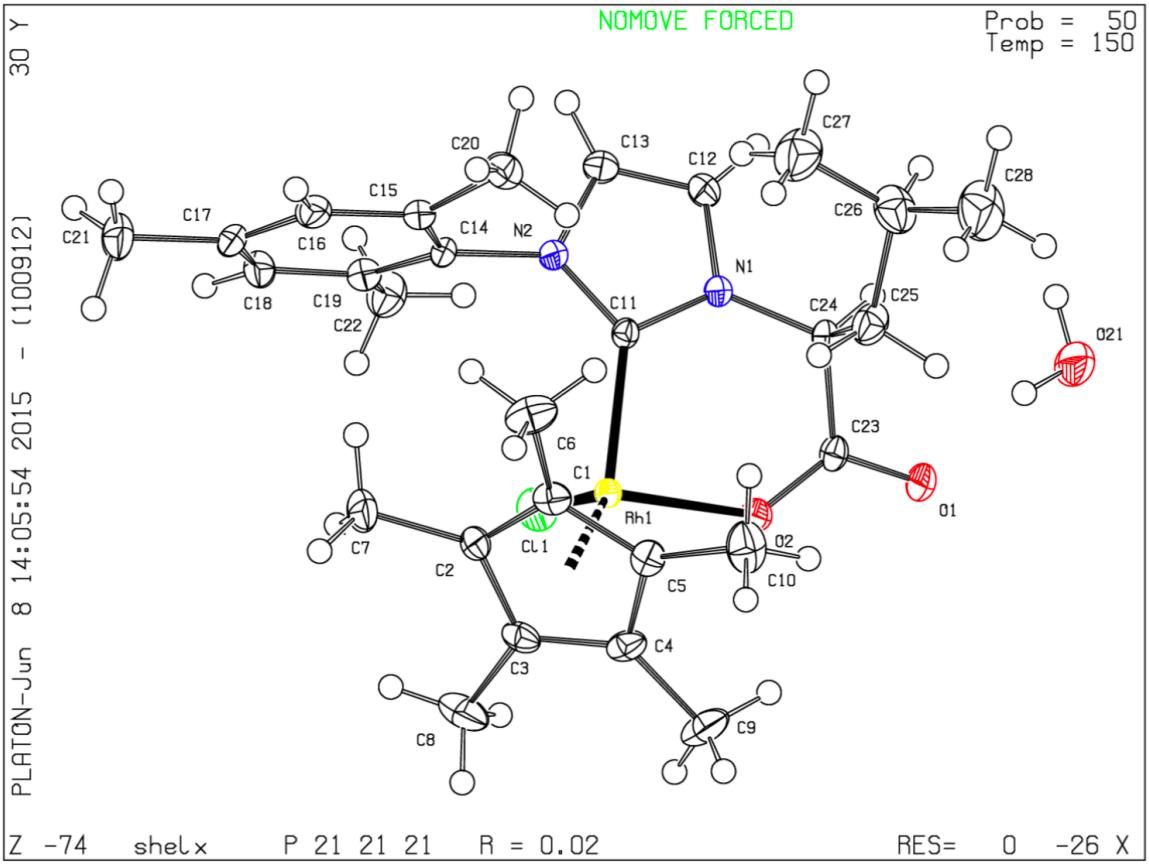


^{13}C NMR Spectrum in $CDCl_3$ for 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane



10. Crystallographic Data

- ORTEP of **3a**; CCDC nº 1405507



Empirical formula	C28 H40 Cl N2 O3 Rh
Formula weight	590.98
Temperature	150(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 10.05640(10) A alpha = 90 deg. b = 15.75740(10) A beta = 90 deg. c = 17.17330(10) A gamma = 90 deg.
Volume	2721.33(4) A^3
Z, Calculated density	4, 1.442 Mg/m^3
Absorption coefficient	6.224 mm^-1
F(000)	1232
Crystal size	0.301 x 0.271 x 0.121 mm
Theta range for data collection	3.807 to 70.631 deg.
Limiting indices	-12<=h<=12, -18<=k<=19, -21<=l<=19
Reflections collected / unique	32210 / 5224 [R(int) = 0.0409]
Completeness to theta = 67.684	100.0 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.43986
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5224 / 0 / 330
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0211, wR2 = 0.0555
R indices (all data)	R1 = 0.0211, wR2 = 0.0556
Absolute structure parameter	-0.009(3)
Extinction coefficient	0.00115(8)
Largest diff. peak and hole	0.496 and -0.737 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for jj086_cu_150k. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Rh(1)	4941(1)	9110(1)	1508(1)	13(1)
Cl(1)	3440(1)	9088(1)	417(1)	25(1)
O(1)	5216(2)	6422(1)	1463(1)	24(1)
O(2)	4678(2)	7776(1)	1497(1)	20(1)
N(1)	6946(2)	8141(2)	543(2)	16(1)
N(2)	6942(3)	9425(2)	130(2)	18(1)
C(1)	5753(3)	10026(2)	2335(2)	19(1)
C(2)	4612(3)	10366(2)	1952(2)	18(1)
C(3)	3475(3)	9860(2)	2173(2)	20(1)
C(4)	3918(3)	9183(2)	2635(2)	20(1)
C(5)	5350(3)	9269(2)	2731(2)	19(1)
C(6)	7068(4)	10449(2)	2400(2)	30(1)
C(7)	4555(4)	11185(2)	1517(2)	30(1)
C(8)	2070(3)	10045(3)	1944(2)	34(1)
C(9)	3099(4)	8482(2)	2960(2)	33(1)
C(10)	6171(4)	8744(2)	3271(2)	32(1)
C(11)	6454(3)	8925(2)	710(2)	14(1)
C(12)	7704(3)	8150(2)	-126(2)	23(1)
C(13)	7716(3)	8956(2)	-382(2)	24(1)
C(14)	6840(3)	10334(2)	54(2)	18(1)
C(15)	7801(3)	10835(2)	422(2)	19(1)
C(16)	7707(3)	11712(2)	345(2)	23(1)
C(17)	6725(4)	12093(2)	-109(2)	25(1)
C(18)	5856(3)	11567(2)	-514(2)	25(1)
C(19)	5897(3)	10686(2)	-453(2)	21(1)
C(20)	8970(3)	10445(2)	835(2)	25(1)
C(21)	6639(4)	13046(2)	-182(2)	34(1)
C(22)	5025(4)	10158(2)	-978(2)	29(1)
C(23)	5474(3)	7179(2)	1345(2)	16(1)
C(24)	6867(3)	7373(2)	1033(2)	18(1)
C(25)	7848(3)	7390(2)	1718(2)	26(1)
C(26)	9348(3)	7350(2)	1511(2)	34(1)
C(27)	9913(4)	8218(3)	1328(3)	47(1)
C(28)	10122(5)	6970(3)	2181(3)	52(1)
O(21)	6218(3)	4982(2)	702(2)	37(1)

Table 3. Bond lengths [A] and angles [deg] for jj086_cu_150k.

Rh(1)-C(11)	2.068(3)
Rh(1)-O(2)	2.1191(19)
Rh(1)-C(2)	2.147(3)
Rh(1)-C(5)	2.156(3)
Rh(1)-C(1)	2.184(3)
Rh(1)-C(4)	2.195(3)
Rh(1)-C(3)	2.208(3)
Rh(1)-Cl(1)	2.4065(7)
O(1)-C(23)	1.237(4)
O(2)-C(23)	1.262(4)
N(1)-C(11)	1.362(4)
N(1)-C(12)	1.378(4)
N(1)-C(24)	1.476(4)
N(2)-C(11)	1.361(4)
N(2)-C(13)	1.387(4)
N(2)-C(14)	1.442(4)
C(1)-C(2)	1.428(4)
C(1)-C(5)	1.431(4)
C(1)-C(6)	1.485(4)
C(2)-C(3)	1.444(4)
C(2)-C(7)	1.492(4)
C(3)-C(4)	1.403(5)
C(3)-C(8)	1.496(5)
C(4)-C(5)	1.456(4)
C(4)-C(9)	1.487(4)
C(5)-C(10)	1.492(5)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(12)-C(13)	1.345(5)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(19)	1.401(4)
C(14)-C(15)	1.399(5)
C(15)-C(16)	1.392(4)
C(15)-C(20)	1.504(4)
C(16)-C(17)	1.394(5)
C(16)-H(16)	0.9500
C(17)-C(18)	1.391(5)
C(17)-C(21)	1.510(4)
C(18)-C(19)	1.393(5)
C(18)-H(18)	0.9500
C(19)-C(22)	1.508(5)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800

C(22)-H(22C)	0.9800
C(23)-C(24)	1.532(4)
C(24)-C(25)	1.536(4)
C(24)-H(24)	1.0000
C(25)-C(26)	1.550(5)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(28)	1.514(6)
C(26)-C(27)	1.514(5)
C(26)-H(26)	1.0000
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
O(21)-H(21D)	0.87(6)
O(21)-H(21E)	0.89(6)

C(11)-Rh(1)-O(2)	86.93(10)
C(11)-Rh(1)-C(2)	118.60(11)
O(2)-Rh(1)-C(2)	153.95(10)
C(11)-Rh(1)-C(5)	121.44(12)
O(2)-Rh(1)-C(5)	98.50(10)
C(2)-Rh(1)-C(5)	64.88(11)
C(11)-Rh(1)-C(1)	104.41(11)
O(2)-Rh(1)-C(1)	135.07(11)
C(2)-Rh(1)-C(1)	38.48(12)
C(5)-Rh(1)-C(1)	38.50(12)
C(11)-Rh(1)-C(4)	159.45(12)
O(2)-Rh(1)-C(4)	90.05(10)
C(2)-Rh(1)-C(4)	64.28(12)
C(5)-Rh(1)-C(4)	39.09(12)
C(1)-Rh(1)-C(4)	64.34(12)
C(11)-Rh(1)-C(3)	155.41(12)
O(2)-Rh(1)-C(3)	116.90(10)
C(2)-Rh(1)-C(3)	38.70(12)
C(5)-Rh(1)-C(3)	63.94(11)
C(1)-Rh(1)-C(3)	63.85(12)
C(4)-Rh(1)-C(3)	37.15(12)
C(11)-Rh(1)-Cl(1)	86.79(8)
O(2)-Rh(1)-Cl(1)	84.30(6)
C(2)-Rh(1)-Cl(1)	101.14(9)
C(5)-Rh(1)-Cl(1)	151.66(8)
C(1)-Rh(1)-Cl(1)	138.66(9)
C(4)-Rh(1)-Cl(1)	113.14(9)
C(3)-Rh(1)-Cl(1)	89.51(8)
C(23)-O(2)-Rh(1)	131.46(19)
C(11)-N(1)-C(12)	111.6(2)
C(11)-N(1)-C(24)	127.2(2)
C(12)-N(1)-C(24)	120.9(2)
C(11)-N(2)-C(13)	111.0(3)
C(11)-N(2)-C(14)	128.0(3)
C(13)-N(2)-C(14)	120.7(3)
C(2)-C(1)-C(5)	107.7(3)
C(2)-C(1)-C(6)	125.5(3)
C(5)-C(1)-C(6)	126.2(3)
C(2)-C(1)-Rh(1)	69.39(16)
C(5)-C(1)-Rh(1)	69.69(16)
C(6)-C(1)-Rh(1)	132.7(2)
C(1)-C(2)-C(3)	107.9(3)
C(1)-C(2)-C(7)	125.9(3)
C(3)-C(2)-C(7)	125.3(3)
C(1)-C(2)-Rh(1)	72.14(17)
C(3)-C(2)-Rh(1)	72.93(17)
C(7)-C(2)-Rh(1)	128.7(2)

C(4)-C(3)-C(2)	108.5(3)
C(4)-C(3)-C(8)	126.6(3)
C(2)-C(3)-C(8)	124.9(3)
C(4)-C(3)-Rh(1)	70.92(17)
C(2)-C(3)-Rh(1)	68.38(16)
C(8)-C(3)-Rh(1)	126.8(2)
C(3)-C(4)-C(5)	107.9(3)
C(3)-C(4)-C(9)	127.1(3)
C(5)-C(4)-C(9)	125.1(3)
C(3)-C(4)-Rh(1)	71.93(17)
C(5)-C(4)-Rh(1)	68.98(16)
C(9)-C(4)-Rh(1)	123.5(2)
C(1)-C(5)-C(4)	107.7(3)
C(1)-C(5)-C(10)	126.9(3)
C(4)-C(5)-C(10)	124.5(3)
C(1)-C(5)-Rh(1)	71.81(17)
C(4)-C(5)-Rh(1)	71.92(17)
C(10)-C(5)-Rh(1)	130.3(2)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-N(2)	103.8(2)
N(1)-C(11)-Rh(1)	122.3(2)
N(2)-C(11)-Rh(1)	132.0(2)
C(13)-C(12)-N(1)	106.6(3)
C(13)-C(12)-H(12)	126.7
N(1)-C(12)-H(12)	126.7
C(12)-C(13)-N(2)	106.9(3)
C(12)-C(13)-H(13)	126.5
N(2)-C(13)-H(13)	126.5
C(19)-C(14)-C(15)	121.6(3)
C(19)-C(14)-N(2)	119.9(3)
C(15)-C(14)-N(2)	118.0(3)
C(16)-C(15)-C(14)	118.1(3)
C(16)-C(15)-C(20)	120.2(3)
C(14)-C(15)-C(20)	121.5(3)
C(15)-C(16)-C(17)	121.9(3)
C(15)-C(16)-H(16)	119.1
C(17)-C(16)-H(16)	119.1

C(18)-C(17)-C(16)	118.0(3)
C(18)-C(17)-C(21)	121.0(3)
C(16)-C(17)-C(21)	121.0(3)
C(17)-C(18)-C(19)	122.5(3)
C(17)-C(18)-H(18)	118.8
C(19)-C(18)-H(18)	118.8
C(18)-C(19)-C(14)	117.5(3)
C(18)-C(19)-C(22)	119.2(3)
C(14)-C(19)-C(22)	123.1(3)
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(17)-C(21)-H(21A)	109.5
C(17)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(17)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(1)-C(23)-O(2)	123.5(3)
O(1)-C(23)-C(24)	116.2(3)
O(2)-C(23)-C(24)	120.3(2)
N(1)-C(24)-C(23)	114.4(2)
N(1)-C(24)-C(25)	112.8(2)
C(23)-C(24)-C(25)	108.8(2)
N(1)-C(24)-H(24)	106.8
C(23)-C(24)-H(24)	106.8
C(25)-C(24)-H(24)	106.8
C(24)-C(25)-C(26)	116.7(3)
C(24)-C(25)-H(25A)	108.1
C(26)-C(25)-H(25A)	108.1
C(24)-C(25)-H(25B)	108.1
C(26)-C(25)-H(25B)	108.1
H(25A)-C(25)-H(25B)	107.3
C(28)-C(26)-C(27)	108.8(3)
C(28)-C(26)-C(25)	110.1(3)
C(27)-C(26)-C(25)	112.1(3)
C(28)-C(26)-H(26)	108.6
C(27)-C(26)-H(26)	108.6
C(25)-C(26)-H(26)	108.6
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
H(21D)-O(21)-H(21E)	104(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for jj086_cu_150k. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Rh(1)	14(1)	10(1)	14(1)	-2(1)	0(1)	-1(1)
Cl(1)	24(1)	26(1)	23(1)	-4(1)	-8(1)	-1(1)
O(1)	25(1)	13(1)	33(1)	3(1)	4(1)	-2(1)
O(2)	19(1)	12(1)	30(1)	-2(1)	5(1)	-2(1)
N(1)	17(1)	12(1)	19(1)	0(1)	2(1)	1(1)
N(2)	20(1)	14(1)	20(1)	1(1)	6(1)	1(1)
C(1)	21(2)	19(1)	16(1)	-8(1)	2(1)	-3(1)
C(2)	24(2)	11(1)	20(1)	-5(1)	4(1)	1(1)
C(3)	19(2)	21(2)	21(2)	-8(1)	4(1)	2(1)
C(4)	25(2)	20(2)	16(1)	-5(1)	7(1)	-6(1)
C(5)	24(2)	17(1)	14(1)	-3(1)	-1(1)	-1(1)
C(6)	27(2)	38(2)	26(2)	-5(2)	1(1)	-13(2)
C(7)	40(2)	16(2)	33(2)	2(1)	8(2)	8(1)
C(8)	18(2)	39(2)	44(2)	-10(2)	4(2)	5(2)
C(9)	41(2)	29(2)	29(2)	0(2)	14(2)	-14(2)
C(10)	45(2)	30(2)	22(2)	0(1)	-8(2)	7(2)
C(11)	16(1)	11(1)	15(1)	0(1)	0(1)	0(1)
C(12)	26(2)	18(2)	24(2)	0(1)	7(1)	5(1)
C(13)	29(2)	22(2)	21(2)	1(1)	10(1)	5(1)
C(14)	21(1)	13(1)	19(1)	4(1)	6(1)	2(1)
C(15)	19(1)	19(1)	20(1)	3(1)	5(1)	2(1)
C(16)	23(2)	18(2)	28(2)	-2(1)	7(1)	-3(1)
C(17)	30(2)	16(2)	28(2)	7(1)	13(1)	3(1)
C(18)	28(2)	23(2)	25(2)	7(1)	4(1)	8(1)
C(19)	21(1)	21(2)	21(1)	2(1)	4(1)	1(1)
C(20)	21(2)	25(2)	29(2)	0(1)	1(1)	3(1)
C(21)	45(2)	17(2)	40(2)	5(1)	7(2)	5(2)
C(22)	31(2)	29(2)	28(2)	5(1)	-5(2)	-2(2)
C(23)	21(1)	12(1)	16(1)	-1(1)	-2(1)	-2(1)
C(24)	20(2)	11(1)	21(1)	2(1)	1(1)	1(1)
C(25)	25(2)	27(2)	27(2)	8(1)	-5(1)	-3(1)
C(26)	26(2)	30(2)	45(2)	0(2)	-8(2)	2(1)
C(27)	32(2)	43(2)	64(3)	15(2)	-6(2)	-8(2)
C(28)	33(2)	48(2)	74(3)	19(2)	-17(2)	2(2)
O(21)	46(2)	20(1)	43(2)	0(1)	14(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for jj086_cu_150k.

	x	y	z	U(eq)
H(6A)	7105	10776	2885	45
H(6B)	7194	10831	1956	45
H(6C)	7772	10019	2401	45
H(7A)	4331	11646	1877	44
H(7B)	3875	11149	1110	44
H(7C)	5422	11299	1278	44
H(8A)	2045	10557	1620	51
H(8B)	1711	9565	1649	51
H(8C)	1533	10136	2413	51
H(9A)	2189	8525	2760	49
H(9B)	3086	8523	3529	49
H(9C)	3482	7935	2806	49
H(10A)	7116	8834	3158	48
H(10B)	5951	8143	3200	48
H(10C)	5985	8910	3810	48
H(12)	8135	7678	-360	27
H(13)	8168	9166	-828	29
H(16)	8331	12062	610	27
H(18)	5209	11818	-845	30
H(20A)	9633	10264	452	38
H(20B)	8672	9953	1137	38
H(20C)	9367	10865	1187	38
H(21A)	6445	13198	-724	51
H(21B)	7487	13300	-26	51
H(21C)	5928	13259	156	51
H(22A)	4090	10299	-882	44
H(22B)	5174	9555	-870	44
H(22C)	5245	10278	-1523	44
H(24)	7128	6883	695	21
H(25A)	7641	6906	2064	31
H(25B)	7689	7916	2019	31
H(26)	9462	6979	1044	40
H(27A)	9417	8471	895	70
H(27B)	9835	8584	1788	70
H(27C)	10851	8163	1184	70
H(28A)	9764	6407	2304	77
H(28B)	11061	6917	2035	77
H(28C)	10044	7338	2639	77
H(21D)	6000(50)	5460(40)	920(30)	50
H(21E)	6850(50)	5130(30)	370(30)	50

Table 6. Torsion angles [deg] for jj086_cu_150k.

C(5)-C(1)-C(2)-C(3)	5.3(3)
C(6)-C(1)-C(2)-C(3)	-166.9(3)
Rh(1)-C(1)-C(2)-C(3)	64.6(2)
C(5)-C(1)-C(2)-C(7)	175.4(3)
C(6)-C(1)-C(2)-C(7)	3.2(5)
Rh(1)-C(1)-C(2)-C(7)	-125.3(3)
C(5)-C(1)-C(2)-Rh(1)	-59.4(2)
C(6)-C(1)-C(2)-Rh(1)	128.5(3)
C(1)-C(2)-C(3)-C(4)	-4.3(3)
C(7)-C(2)-C(3)-C(4)	-174.5(3)
Rh(1)-C(2)-C(3)-C(4)	59.8(2)
C(1)-C(2)-C(3)-C(8)	175.3(3)
C(7)-C(2)-C(3)-C(8)	5.1(5)
Rh(1)-C(2)-C(3)-C(8)	-120.6(3)
C(1)-C(2)-C(3)-Rh(1)	-64.1(2)
C(7)-C(2)-C(3)-Rh(1)	125.7(3)
C(2)-C(3)-C(4)-C(5)	1.7(3)
C(8)-C(3)-C(4)-C(5)	-177.9(3)
Rh(1)-C(3)-C(4)-C(5)	59.9(2)
C(2)-C(3)-C(4)-C(9)	-177.0(3)
C(8)-C(3)-C(4)-C(9)	3.4(5)
Rh(1)-C(3)-C(4)-C(9)	-118.8(3)
C(2)-C(3)-C(4)-Rh(1)	-58.2(2)
C(8)-C(3)-C(4)-Rh(1)	122.2(3)
C(2)-C(1)-C(5)-C(4)	-4.2(3)
C(6)-C(1)-C(5)-C(4)	167.9(3)
Rh(1)-C(1)-C(5)-C(4)	-63.4(2)
C(2)-C(1)-C(5)-C(10)	-173.6(3)
C(6)-C(1)-C(5)-C(10)	-1.5(5)
Rh(1)-C(1)-C(5)-C(10)	127.2(3)
C(2)-C(1)-C(5)-Rh(1)	59.2(2)
C(6)-C(1)-C(5)-Rh(1)	-128.7(3)
C(3)-C(4)-C(5)-C(1)	1.5(3)
C(9)-C(4)-C(5)-C(1)	-179.7(3)
Rh(1)-C(4)-C(5)-C(1)	63.3(2)
C(3)-C(4)-C(5)-C(10)	171.3(3)
C(9)-C(4)-C(5)-C(10)	-10.0(5)
Rh(1)-C(4)-C(5)-C(10)	-126.9(3)
C(3)-C(4)-C(5)-Rh(1)	-61.8(2)
C(9)-C(4)-C(5)-Rh(1)	117.0(3)
C(12)-N(1)-C(11)-N(2)	-0.7(3)
C(24)-N(1)-C(11)-N(2)	172.0(3)
C(12)-N(1)-C(11)-Rh(1)	165.5(2)
C(24)-N(1)-C(11)-Rh(1)	-21.9(4)
C(13)-N(2)-C(11)-N(1)	0.0(3)
C(14)-N(2)-C(11)-N(1)	-173.8(3)
C(13)-N(2)-C(11)-Rh(1)	-164.2(2)
C(14)-N(2)-C(11)-Rh(1)	22.0(5)
C(11)-N(1)-C(12)-C(13)	1.1(4)
C(24)-N(1)-C(12)-C(13)	-172.1(3)
N(1)-C(12)-C(13)-N(2)	-1.0(4)
C(11)-N(2)-C(13)-C(12)	0.6(4)
C(14)-N(2)-C(13)-C(12)	174.9(3)
C(11)-N(2)-C(14)-C(19)	-101.2(4)
C(13)-N(2)-C(14)-C(19)	85.5(4)
C(11)-N(2)-C(14)-C(15)	86.3(4)
C(13)-N(2)-C(14)-C(15)	-87.0(4)
C(19)-C(14)-C(15)-C(16)	7.3(4)
N(2)-C(14)-C(15)-C(16)	179.7(3)
C(19)-C(14)-C(15)-C(20)	-167.7(3)
N(2)-C(14)-C(15)-C(20)	4.7(4)
C(14)-C(15)-C(16)-C(17)	-2.6(5)
C(20)-C(15)-C(16)-C(17)	172.4(3)

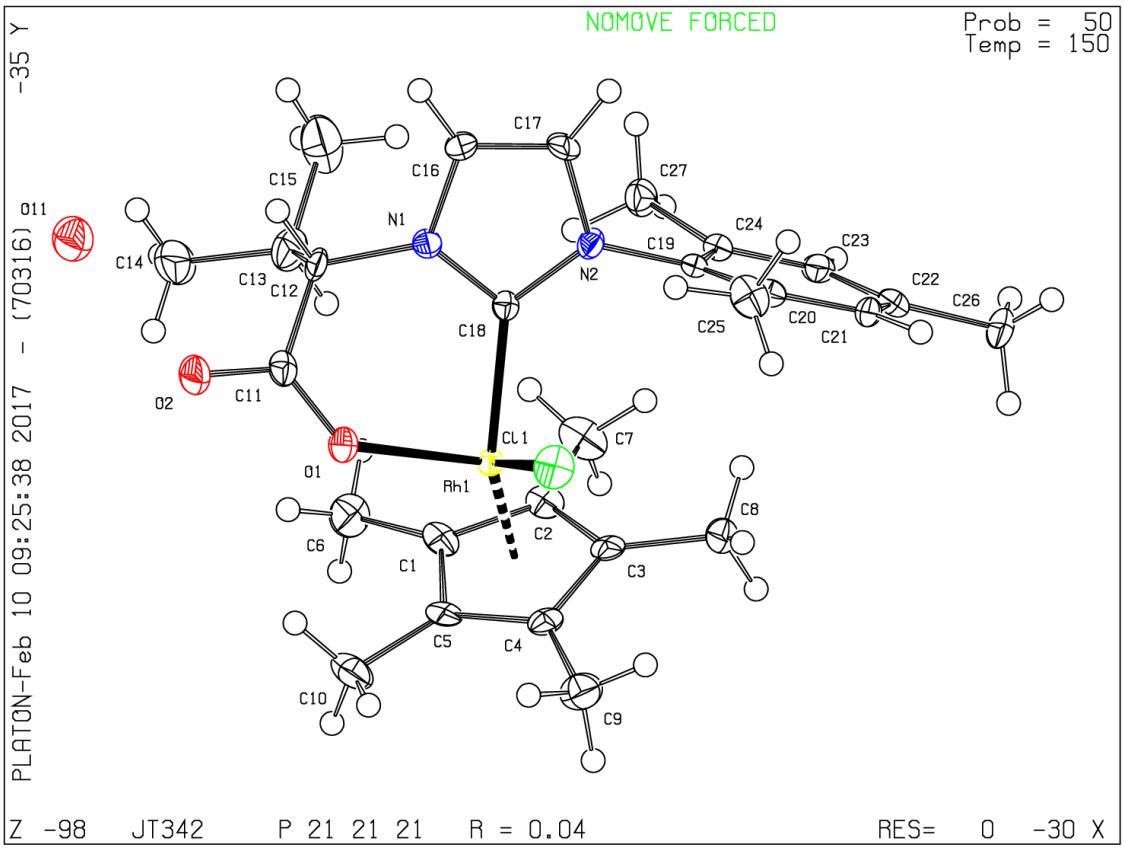
C(15)-C(16)-C(17)-C(18)	-2.4(5)
C(15)-C(16)-C(17)-C(21)	179.8(3)
C(16)-C(17)-C(18)-C(19)	2.9(5)
C(21)-C(17)-C(18)-C(19)	-179.2(3)
C(17)-C(18)-C(19)-C(14)	1.5(5)
C(17)-C(18)-C(19)-C(22)	-173.2(3)
C(15)-C(14)-C(19)-C(18)	-6.8(4)
N(2)-C(14)-C(19)-C(18)	-179.0(3)
C(15)-C(14)-C(19)-C(22)	167.8(3)
N(2)-C(14)-C(19)-C(22)	-4.5(5)
Rh(1)-O(2)-C(23)-O(1)	170.2(2)
Rh(1)-O(2)-C(23)-C(24)	-7.0(4)
C(11)-N(1)-C(24)-C(23)	49.1(4)
C(12)-N(1)-C(24)-C(23)	-138.8(3)
C(11)-N(1)-C(24)-C(25)	-75.9(4)
C(12)-N(1)-C(24)-C(25)	96.1(3)
O(1)-C(23)-C(24)-N(1)	150.7(3)
O(2)-C(23)-C(24)-N(1)	-32.0(4)
O(1)-C(23)-C(24)-C(25)	-82.2(3)
O(2)-C(23)-C(24)-C(25)	95.2(3)
N(1)-C(24)-C(25)-C(26)	-66.9(4)
C(23)-C(24)-C(25)-C(26)	165.1(3)
C(24)-C(25)-C(26)-C(28)	-153.6(3)
C(24)-C(25)-C(26)-C(27)	85.1(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for jj086_cu_150k [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

- ORTEP of **3b**; CCDC nº 1818181



(C_{27} H_{36} Cl N_2 O_2 Rh, O); *M* = 574.94. D8 VENTURE Bruker AXS diffractometer [*], Mo-Kα radiation (λ = 0.71073 Å), *T* = 150(2) K; orthorhombic *P* 2_1 2_1 2_1 (I.T.#19), a = 9.8757(4), b = 15.8497(5), c = 17.3332(7) Å, *V* = 2713.11(18) $Å^3$. *Z* = 4, *d* = 1.408 $g.cm^{-3}$, μ = 0.757 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program [1], and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*) [2]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 6134 unique intensities and 317 parameters converged at $\omega R(F^2)$ = 0.0832 ($R(F)$ = 0.0393) for 5055 observed reflections with $I > 2\sigma(I)$.

[1] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8

[2] Sheldrick G.M., Acta Cryst. C71 (2015) 3-8

Structural data

Empirical formula	C_{27} H_{36} Cl N_2 O_3 Rh
Extended formula	C_{27} H_{36} Cl N_2 O_2 Rh, O
Formula weight	574.94
Temperature	150(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, *P* 2_1 2_1 2_1
Unit cell dimensions	a = 9.8757(4) Å, α = 90 °
	b = 15.8497(5) Å, β = 90 °
	c = 17.3332(7) Å, γ = 90 °
Volume	2713.11(18) $Å^3$
Z, Calculated density	4, 1.408 ($g.cm^{-3}$)
Absorption coefficient	0.757 mm^{-1}
F(000)	1192
Crystal size	0.520 x 0.340 x 0.080 mm
Crystal color	red
Theta range for data collection	2.350 to 27.484 °
h_min, h_max	-12, 12
k_min, k_max	-16, 20
l_min, l_max	-22, 22
Reflections collected / unique	18101 / 6134 [R(int)[a] = 0.0717]
Reflections [I>2σ]	5055
Completeness to theta_max	0.997
Absorption correction type	multi-scan
Max. and min. transmission	0.941 , 0.759
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6134 / 0 / 317
Flack parameter	-0.02(3)
[b]Goodness-of-fit	1.034
Final *R* indices [I>2σ]	$R1^c$ = 0.0393, $wR2^d$ = 0.0832
R indices (all data)	$R1^c$ = 0.0570, $wR2^d$ = 0.0899
Largest diff. peak and hole	0.800 and -0.946 $e^-.Å^{-3}$

[a] $R_{int} = \sum |F_o^2 - < F_o^2>| / \sum[F_o^2]$

[b] $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

[c] $R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

[d] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

$w = 1 / [\sigma(F_o^2) + aP^2 + bP]$ where $P = [2F_c^2 + MAX(F_o^2, 0)] /3$

Table 2. Atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters ($Å^2$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	occ.	U(eq)
Rh1	0.50248(5)	0.58883(2)	0.35296(2)	1	0.01181(10)
Cl1	0.35664(16)	0.59925(10)	0.46351(8)	1	0.0245(3)
C1	0.5343(6)	0.5682(3)	0.2305(3)	1	0.0188(14)
C2	0.5706(6)	0.4917(3)	0.2716(3)	1	0.0190(12)
C3	0.4549(6)	0.4642(3)	0.3127(3)	1	0.0165(12)
C4	0.3419(6)	0.5190(3)	0.2922(3)	1	0.0176(12)
C5	0.3920(6)	0.5824(3)	0.2435(3)	1	0.0169(12)
C6	0.6222(7)	0.6168(4)	0.1763(3)	1	0.0291(15)
H6A	0.602555	0.599635	0.123169	1	0.044
H6B	0.717557	0.605376	0.188004	1	0.044
H6C	0.604230	0.677267	0.182196	1	0.044
C7	0.7001(7)	0.4431(4)	0.2636(3)	1	0.0295(15)
H7A	0.715766	0.409876	0.310410	1	0.044
H7B	0.775515	0.482490	0.256035	1	0.044
H7C	0.693805	0.405255	0.219032	1	0.044

C8	0.4453(6)	0.3850(3)	0.3591(4)	1	0.0274(13)
H8A	0.414970	0.338652	0.325898	1	0.041
H8B	0.380283	0.392975	0.401173	1	0.041
H8C	0.534421	0.371355	0.380654	1	0.041
C9	0.1989(6)	0.5107(4)	0.3186(4)	1	0.0288(14)
H9A	0.161403	0.566816	0.328832	1	0.043
H9B	0.195939	0.476899	0.365938	1	0.043
H9C	0.145306	0.482836	0.278402	1	0.043
C10	0.3152(7)	0.6548(4)	0.2100(3)	1	0.0296(15)
H10A	0.301339	0.645320	0.154688	1	0.044
H10B	0.366712	0.707021	0.217567	1	0.044
H10C	0.227187	0.659666	0.235727	1	0.044
C11	0.5776(6)	0.7785(3)	0.3638(3)	1	0.0177(11)
C12	0.7154(6)	0.7545(3)	0.3960(3)	1	0.0177(12)
H12	0.748102	0.803610	0.426978	1	0.021
C13	0.8225(6)	0.7382(4)	0.3328(3)	1	0.0278(14)
H13	0.790729	0.689840	0.300383	1	0.033
C14	0.8388(8)	0.8145(4)	0.2809(4)	1	0.0429(19)
H14A	0.751335	0.828507	0.257398	1	0.064
H14B	0.904688	0.801831	0.240217	1	0.064
H14C	0.870847	0.862534	0.311432	1	0.064
C15	0.9612(7)	0.7155(4)	0.3658(4)	1	0.045(2)
H15A	1.025571	0.706965	0.323489	1	0.068
H15B	0.953955	0.663531	0.396167	1	0.068
H15C	0.993104	0.761461	0.398981	1	0.068
C16	0.7863(6)	0.6798(3)	0.5166(3)	1	0.0215(13)
H16	0.833391	0.725871	0.539215	1	0.026
C17	0.7798(6)	0.6007(3)	0.5434(3)	1	0.0220(12)
H17	0.821576	0.579721	0.588870	1	0.026
C18	0.6553(6)	0.6049(3)	0.4321(3)	1	0.0133(11)
C19	0.6874(6)	0.4646(3)	0.4982(3)	1	0.0147(11)
C20	0.5921(6)	0.4294(3)	0.5496(3)	1	0.0181(12)
C21	0.5867(6)	0.3417(3)	0.5532(3)	1	0.0196(12)
H21	0.522202	0.316210	0.586456	1	0.024
C22	0.6711(6)	0.2902(3)	0.5105(3)	1	0.0209(13)
C23	0.7698(6)	0.3280(3)	0.4650(3)	1	0.0195(12)
H23	0.831220	0.293285	0.437249	1	0.023
C24	0.7816(5)	0.4155(3)	0.4589(3)	1	0.0177(11)
C25	0.5040(8)	0.4820(3)	0.6021(3)	1	0.0262(11)
H25A	0.409073	0.465629	0.595470	1	0.039
H25B	0.514855	0.541810	0.589206	1	0.039
H25C	0.531110	0.472692	0.655870	1	0.039
C26	0.6585(7)	0.1952(3)	0.5134(4)	1	0.0286(15)
H26A	0.645994	0.177135	0.567014	1	0.043
H26B	0.740924	0.169454	0.492518	1	0.043
H26C	0.580316	0.177391	0.482610	1	0.043
C27	0.9000(6)	0.4551(3)	0.4171(3)	1	0.0227(13)
H27A	0.868172	0.503308	0.386720	1	0.034
H27B	0.941478	0.413363	0.382788	1	0.034
H27C	0.967170	0.474397	0.454867	1	0.034
N1	0.7101(5)	0.6812(3)	0.4487(2)	1	0.0166(10)
N2	0.7003(5)	0.5550(2)	0.4920(2)	1	0.0169(10)
O1	0.4916(5)	0.72183(18)	0.34851(19)	1	0.0216(7)
O2	0.5557(4)	0.8546(2)	0.3520(2)	1	0.0293(10)
O11	0.6324(5)	1.0007(3)	0.4298(2)	1	0.0344(11)

Table 3. Bond lengths [Å]

Rh1	- C18	= 2.056(5)
Rh1	- O1	= 2.112(3)
Rh1	- C3	= 2.146(5)

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Rh1  - C1       = 2.170(5)
Rh1  - C5       = 2.191(5)
Rh1  - C2       = 2.193(5)
Rh1  - C4       = 2.202(5)
Rh1  - Cl1      = 2.4029(14)
C1   - C5       = 1.441(9)
C1   - C2       = 1.451(8)
C1   - C6       = 1.493(7)
C2   - C3       = 1.415(8)
C2   - C7       = 1.500(8)
C3   - C4       = 1.458(8)
C3   - C8       = 1.494(7)
C4   - C5       = 1.403(7)
C4   - C9       = 1.490(8)
C5   - C10      = 1.493(7)
C6   - H6A      = 0.9800
C6   - H6B      = 0.9800
C6   - H6C      = 0.9800
C7   - H7A      = 0.9800
C7   - H7B      = 0.9800
C7   - H7C      = 0.9800
C8   - H8A      = 0.9800
C8   - H8B      = 0.9800
C8   - H8C      = 0.9800
C9   - H9A      = 0.9800
C9   - H9B      = 0.9800
C9   - H9C      = 0.9800
C10  - H10A     = 0.9800
C10  - H10B     = 0.9800
C10  - H10C     = 0.9800
C11  - O2       = 1.242(6)
C11  - O1       = 1.265(6)
C11  - C12      = 1.520(8)
C12  - N1       = 1.478(6)
C12  - C13      = 1.544(8)
C12  - H12      = 1.0000
C13  - C14      = 1.516(8)
C13  - C15      = 1.528(9)
C13  - H13      = 1.0000
C14  - H14A     = 0.9800
C14  - H14B     = 0.9800
C14  - H14C     = 0.9800
C15  - H15A     = 0.9800
C15  - H15B     = 0.9800
C15  - H15C     = 0.9800
C16  - C17      = 1.339(7)
C16  - N1       = 1.397(7)
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C16	- H16	=	0.9500
C17	- N2	=	1.391(6)
C17	- H17	=	0.9500
C18	- N1	=	1.356(6)
C18	- N2	=	1.378(6)
C19	- C24	=	1.391(7)
C19	- C20	=	1.411(7)
C19	- N2	=	1.442(6)
C20	- C21	=	1.392(7)
C20	- C25	=	1.511(8)
C21	- C22	=	1.383(8)
C21	- H21	=	0.9500
C22	- C23	=	1.389(8)
C22	- C26	=	1.511(7)
C23	- C24	=	1.395(7)
C23	- H23	=	0.9500
C24	- C27	=	1.512(7)
C25	- H25A	=	0.9800
C25	- H25B	=	0.9800
C25	- H25C	=	0.9800
C26	- H26A	=	0.9800
C26	- H26B	=	0.9800
C26	- H26C	=	0.9800
C27	- H27A	=	0.9800
C27	- H27B	=	0.9800
C27	- H27C	=	0.9800

Table 4. Angles [°]

C18	- Rh1	- O1	=	86.47(18)
C18	- Rh1	- C3	=	119.40(2)
O1	- Rh1	- C3	=	153.54(19)
C18	- Rh1	- C1	=	124.40(2)
O1	- Rh1	- C1	=	96.99(16)
C3	- Rh1	- C1	=	64.90(2)
C18	- Rh1	- C5	=	161.70(2)
O1	- Rh1	- C5	=	89.39(17)
C3	- Rh1	- C5	=	64.30(2)
C1	- Rh1	- C5	=	38.60(2)
C18	- Rh1	- C2	=	106.90(2)
O1	- Rh1	- C2	=	133.84(18)
C3	- Rh1	- C2	=	38.00(2)
C1	- Rh1	- C2	=	38.90(2)
C5	- Rh1	- C2	=	64.10(2)
C18	- Rh1	- C4	=	155.50(2)
O1	- Rh1	- C4	=	116.59(18)
C3	- Rh1	- C4	=	39.10(2)

C1	- Rh1	- C4	=	64.00(2)
C5	- Rh1	- C4	=	37.24(19)
C2	- Rh1	- C4	=	63.90(2)
C18	- Rh1	- Cl1	=	84.21(15)
O1	- Rh1	- Cl1	=	85.99(11)
C3	- Rh1	- Cl1	=	101.02(15)
C1	- Rh1	- Cl1	=	151.29(16)
C5	- Rh1	- Cl1	=	113.27(16)
C2	- Rh1	- Cl1	=	138.14(16)
C4	- Rh1	- Cl1	=	89.09(15)
C5	- C1	- C2	=	107.10(5)
C5	- C1	- C6	=	125.80(5)
C2	- C1	- C6	=	126.60(5)
C5	- C1	- Rh1	=	71.50(3)
C2	- C1	- Rh1	=	71.40(3)
C6	- C1	- Rh1	=	128.50(4)
C3	- C2	- C1	=	107.80(5)
C3	- C2	- C7	=	125.20(5)
C1	- C2	- C7	=	126.40(5)
C3	- C2	- Rh1	=	69.20(3)
C1	- C2	- Rh1	=	69.70(3)
C7	- C2	- Rh1	=	133.00(4)
C2	- C3	- C4	=	108.20(5)
C2	- C3	- C8	=	125.50(5)
C4	- C3	- C8	=	125.70(5)
C2	- C3	- Rh1	=	72.80(3)
C4	- C3	- Rh1	=	72.50(3)
C8	- C3	- Rh1	=	127.80(4)
C5	- C4	- C3	=	107.70(5)
C5	- C4	- C9	=	125.60(5)
C3	- C4	- C9	=	126.70(5)
C5	- C4	- Rh1	=	71.00(3)
C3	- C4	- Rh1	=	68.40(3)
C9	- C4	- Rh1	=	125.50(4)
C4	- C5	- C1	=	109.00(5)
C4	- C5	- C10	=	127.30(6)
C1	- C5	- C10	=	123.70(5)
C4	- C5	- Rh1	=	71.80(3)
C1	- C5	- Rh1	=	69.90(3)
C10	- C5	- Rh1	=	123.60(4)
C1	- C6	- H6A	=	109.50
C1	- C6	- H6B	=	109.50
H6A	- C6	- H6B	=	109.50
C1	- C6	- H6C	=	109.50
H6A	- C6	- H6C	=	109.50
H6B	- C6	- H6C	=	109.50
C2	- C7	- H7A	=	109.50

C2	- C7	- H7B	=	109.50
H7A	- C7	- H7B	=	109.50
C2	- C7	- H7C	=	109.50
H7A	- C7	- H7C	=	109.50
H7B	- C7	- H7C	=	109.50
C3	- C8	- H8A	=	109.50
C3	- C8	- H8B	=	109.50
H8A	- C8	- H8B	=	109.50
C3	- C8	- H8C	=	109.50
H8A	- C8	- H8C	=	109.50
H8B	- C8	- H8C	=	109.50

Table 5. Torsion angles [°]

C5	- C1	- C2	- C3	=	-4.10(6)
C6	- C1	- C2	- C3	=	-176.40(5)
Rh1	- C1	- C2	- C3	=	58.90(4)
C5	- C1	- C2	- C7	=	167.90(5)
C6	- C1	- C2	- C7	=	-4.50(9)
Rh1	- C1	- C2	- C7	=	-129.10(6)
C5	- C1	- C2	- Rh1	=	-63.00(3)
C6	- C1	- C2	- Rh1	=	124.60(5)
C1	- C2	- C3	- C4	=	5.00(6)
C7	- C2	- C3	- C4	=	-167.00(5)
Rh1	- C2	- C3	- C4	=	64.30(3)
C1	- C2	- C3	- C8	=	176.20(5)
C7	- C2	- C3	- C8	=	4.20(9)
Rh1	- C2	- C3	- C8	=	-124.50(5)
C1	- C2	- C3	- Rh1	=	-59.30(3)
C7	- C2	- C3	- Rh1	=	128.70(5)
C2	- C3	- C4	- C5	=	-4.10(6)
C8	- C3	- C4	- C5	=	-175.30(5)
Rh1	- C3	- C4	- C5	=	60.40(3)
C2	- C3	- C4	- C9	=	176.70(5)
C8	- C3	- C4	- C9	=	5.50(8)
Rh1	- C3	- C4	- C9	=	-118.90(5)
C2	- C3	- C4	- Rh1	=	-64.50(4)
C8	- C3	- C4	- Rh1	=	124.30(5)
C3	- C4	- C5	- C1	=	1.60(6)
C9	- C4	- C5	- C1	=	-179.20(5)
Rh1	- C4	- C5	- C1	=	60.30(4)
C3	- C4	- C5	- C10	=	-177.60(5)
C9	- C4	- C5	- C10	=	1.70(8)
Rh1	- C4	- C5	- C10	=	-118.90(5)
C3	- C4	- C5	- Rh1	=	-58.70(3)

C9	- C4	- C5	- Rh1	= 120.50(5)
C2	- C1	- C5	- C4	= 1.50(6)
C6	- C1	- C5	- C4	= 174.00(5)
Rh1	- C1	- C5	- C4	= -61.50(3)
C2	- C1	- C5	- C10	= -179.30(5)
C6	- C1	- C5	- C10	= -6.90(8)
Rh1	- C1	- C5	- C10	= 117.70(5)
C2	- C1	- C5	- Rh1	= 63.00(3)
C6	- C1	- C5	- Rh1	= -124.60(5)
O2	- C11	- C12	- N1	= 146.00(5)
O1	- C11	- C12	- N1	= -35.50(7)
O2	- C11	- C12	- C13	= -88.80(6)
O1	- C11	- C12	- C13	= 89.70(6)
N1	- C12	- C13	- C14	= -175.80(5)
C11	- C12	- C13	- C14	= 57.10(6)
N1	- C12	- C13	- C15	= -53.90(6)
C11	- C12	- C13	- C15	= 179.00(5)
N1	- C16	- C17	- N2	= 0.00(7)
C24	- C19	- C20	- C21	= -6.60(8)
N2	- C19	- C20	- C21	= -179.20(5)
C24	- C19	- C20	- C25	= 170.00(5)
N2	- C19	- C20	- C25	= -2.60(8)
C19	- C20	- C21	- C22	= 1.30(8)
C25	- C20	- C21	- C22	= -175.50(5)
C20	- C21	- C22	- C23	= 3.30(8)
C20	- C21	- C22	- C26	= -177.40(5)
C21	- C22	- C23	- C24	= -2.90(8)
C26	- C22	- C23	- C24	= 177.90(6)
C20	- C19	- C24	- C23	= 7.00(8)
N2	- C19	- C24	- C23	= 179.80(5)
C20	- C19	- C24	- C27	= -167.50(5)
N2	- C19	- C24	- C27	= 5.30(7)
C22	- C23	- C24	- C19	= -2.10(8)
C22	- C23	- C24	- C27	= 172.40(5)
N2	- C18	- N1	- C16	= -0.30(6)
Rh1	- C18	- N1	- C16	= 164.90(4)
N2	- C18	- N1	- C12	= 167.90(5)
Rh1	- C18	- N1	- C12	= -26.80(7)
C17	- C16	- N1	- C18	= 0.20(7)
C17	- C16	- N1	- C12	= -168.70(5)
C11	- C12	- N1	- C18	= 53.90(7)
C13	- C12	- N1	- C18	= -73.30(7)
C11	- C12	- N1	- C16	= -138.90(5)
C13	- C12	- N1	- C16	= 93.90(6)
N1	- C18	- N2	- C17	= 0.30(6)
Rh1	- C18	- N2	- C17	= -163.00(4)
N1	- C18	- N2	- C19	= -171.00(5)

Rh1	- C18	- N2	- C19	= 25.70(8)
C16	- C17	- N2	- C18	= -0.20(7)
C16	- C17	- N2	- C19	= 171.70(5)
C24	- C19	- N2	- C18	= 81.30(7)
C20	- C19	- N2	- C18	= -105.70(6)
C24	- C19	- N2	- C17	= -89.10(6)
C20	- C19	- N2	- C17	= 83.80(7)
O2	- C11	- O1	- Rh1	= 174.40(4)
C12	- C11	- O1	- Rh1	= -4.10(7)