Electronic Supporting Information

Belonging to

Construction of Pincer-Type symmetrical Ruthenium(II) complexes bearing a Pyridyl-2,6-Pyrazolyl Arms: Catalytic Behaviour in Transfer Hydrogenation of Ketones

Zhu Zhu, Jie Zhang, Haiyan Fu, Maolin Yuan, Xueli Zheng, Hua Chen and Ruixiang Li*

Prof. Ruixiang Li
Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry,
Sichuan University, Chengdu, Sichuan 610064, PR China
Fax: (+) 86-28-85412904;
E-mail: liruixiang@scu.edu.cn

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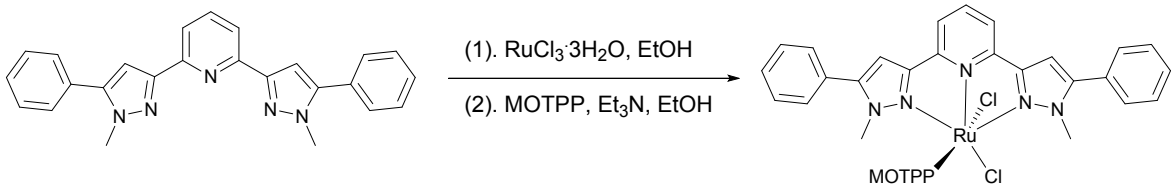
General consideration

1. Synthesis of complex **1**

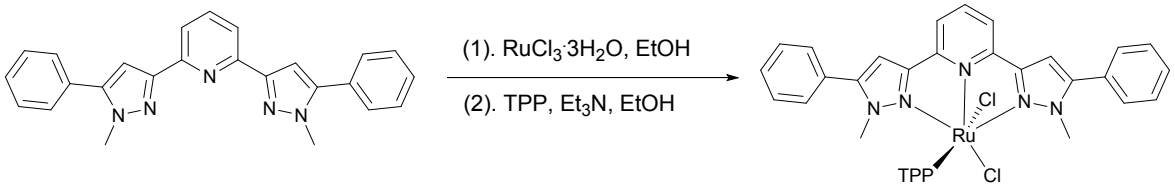


L1 **1**

MOTPP = tri(*p*-methoxyphenyl)phosphine

Under nitrogen atmosphere, a mixture of $RuCl_3 \cdot 3H_2O$ (143 mg, 0.55 mmol) and **L1** (215, 0.55 mmol) in EtOH (30 mL) was refuxed for 5 h. The color of the solution changed from black brown to red-brown slowly and further generated the red-brown precipitates. After being cooled to room temperature, the red-brown precipitates were filtered, washed with EtOH and Et_2O, and dried under vacuum. Without purification, this compound was used in the following synthesis. An EtOH (15 mL) slurry of precipitates and MOTPP (194 mg, 0.55 mmol) was treated with excess Et_3N (1 mL). After refluxed 6 h, the red-orange solution was cooled to room temperature and the solvent was removed under vacuum to give a solid red substance. Yield (306 mg, 61%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25°C,TMS, ppm): δ 7.53 (t, ^3J(H,H)=7.2 Hz, 4H, phenyl), 7.48 (dd, ^3J(H,H)=11.3, 7.4 Hz, 3H, 4-pyridyl, phenyl), 7.44 (d, ^3J(H,H)=7.1 Hz, 4H, phenyl), 7.33 (d, ^3J(H,H)=7.8 Hz, 2H, 3,5-pyridyl), 7.07 (t, ^3J(H,H)= 9.0 Hz, 6H, phenyl), 6.85 (s, 2H, pyrazolyl), 6.67 (d, ^3J(H,H)=8.0 Hz, 6H, phenyl), 4.17 (s, 6H, NCH_3), 3.75 (s, 9H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 160.0 (phenyl C), 155.9 (pyridyl C), 152.1 (pyrazolyl C), 147.8 (pyridyl CH), 134.7 (phenyl C), 131.7 (pyrazolyl C),129.3 (phenyl C), 129.2 (phenyl CH), 128.9 (phenyl CH), 125.7 (phenyl CH), 125.2 (pyridyl CH), 116.7 (phenyl CH), 113.1 (phenyl CH), 104.6 (pyrazolyl CH), 55.2 (s, OCH_3), 39.7 (s, NCH_3). ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, ppm): δ 39.9. Anal. Calcd for $C_{46}H_{42}Cl_2N_5O_3PRu$ (930.84): C, 60.33; H, 4.62; N, 7.65. Found: C, 60.36; H, 4.58; N, 7.62. HRMS (ESI) m/z: Calcd for $C_{46}H_{42}Cl_2N_5O_3PRuNa$ $[M+Na]^+$: 938.1344. found: 938.1338. $C_{46}H_{42}Cl_2N_5O_3PRu$ (915.1446).

2. Synthesis of complex **2**



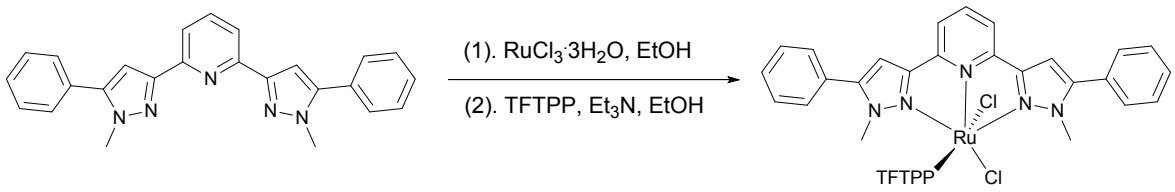
L1 **2**

TPP = triphenylphosphine

Under nitrogen atmosphere, a mixture of $RuCl_3 \cdot 3H_2O$ (143 mg, 0.55 mmol) and **L1** (215 mg, 0.55 mmol) in EtOH (30 mL) was refluxed for 5 h. The color of the solution changed from black brown to red-brown slowly and further generated the red-brown precipitates. After being cooled to room temperature, the precipitates were filtered, washed with EtOH and Et_2O, and dried under vacuum. Without purification, this compound was used in the following synthesis. An EtOH (15 mL) slurry of red-brown precipitates and TPP (144 mg, 0.55 mmol) was treated with excess Et_3N (1 mL). The solid substance slowly dissolved and the color of the solution changed to red-orange. After refluxed 6 h, the red-orange solution was cooled to room temperature and the solvent was

removed under vacuum to give a solid red substance. The solid was extracted with CH_2Cl_2 (20 mL) and filtered through Celite. The volume of the filtrate was reduced to approximately 10 mL under vacuum and Et_2O (30 mL) was carefully layered and allowed to slowly diffuse into the CH_2Cl_2 solution. After 12 h, some red crystals were obtained. The crystals were filtered, washed with Et_2O, and dried under vacuum. Yield (308 mg, 68%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25°C, TMS, ppm): δ 7.54 (d, ^3J(H,H)= 6.6 Hz, 3H, phenyl), 7.50 (d, ^3J(H,H)= 3.9 Hz, 3H, 4-pyridyl, phenyl), 7.48 (s, 1H, phenyl), 7.45–7.41 (m, 6H, phenyl), 7.30 (d, ^3J(H,H)= 7.6 Hz, 4H, phenyl), 7.23 (d, ^3J(H,H)= 7.3 Hz, 2H, 3,5-pyridyl), 7.17 (dd, ^3J(H,H)= 7.5, 3.3 Hz, 9H, phenyl), 6.84 (s, 2H, pyrazolyl), 4.16 (s, 6H, NCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C,TMS, ppm): δ=155.7 (pyridyl C), 152.1 (pyrazolyl C), 147.6 (pyridyl CH), 137.9 (phenyl C), 133.9 (pyrazolyl C), 133.3 (phenyl CH), 132.0 (phenyl CH), 129.3 (phenyl C), 128.9 (phenyl CH), 128.2 (phenyl CH), 127.5 (phenyl CH), 125.3 (pyridyl CH), 116.9(phenyl CH), 104.8 (pyrazolyl CH), 39.7 (s, NCH_3). ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, ppm): δ 43.9. Anal. Calcd for $C_{43}H_{36}Cl_2N_5PRu$ (840.76): C, 62.55; H, 4.39; N, 8.48. found: C, 62.47; H, 4.35; N 8.41. HRMS (ESI) m/z: Calcd for $C_{43}H_{36}Cl_2N_5PRuNa$ $[M+Na]^+$: 848.1027. found: 848.1021. $C_{43}H_{36}Cl_2N_5PRu$ (825.1129).

3. Synthesis of complex **3**

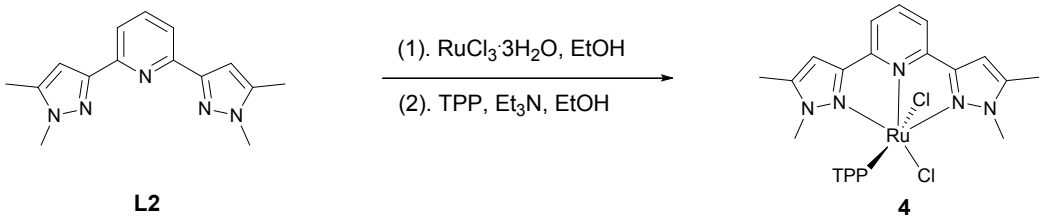


L1 **3**

TFTPP = tri(p-trifluoromethylphenyl)phosphine

Under nitrogen atmosphere, a mixture of $RuCl_3 \cdot 3H_2O$ (143 mg, 0.55 mmol) and **L1** (215 mg, 0.55 mmol) in EtOH (30 mL) was refluxed for 5 h. The solid substance slowly dissolved and the color of the solution changed to red-orange. After being cooled to room temperature, the precipitates were filtered, washed with EtOH and Et_2O, and dried under vacuum. Without purification, this compound was used in the following synthesis. An EtOH (15 mL) slurry of red-brown precipitates and TFTPP (256 mg, 0.55 mmol) was treated with excess Et_3N (1 mL). The solid substance slowly dissolved and the color of the solution changed to red-orange. After refluxed 6 h, the red-orange solution was cooled to room temperature and the solvent was removed under vacuum to give a solid red substance. Yield (413 mg, 73%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25°C, TMS, ppm): δ 7.54 (d, ^3J(H,H)= 6.6 Hz, 2H, phenyl), 7.50 (dd, ^3J(H,H)= 14.1, 8.7 Hz, 5H, 4-pyridyl, phenyl), 7.46 (d, ^3J(H,H)= 7.3 Hz, 6H, phenyl), 7.43 (t, ^3J(H,H)= 8.7 Hz, 6H, phenyl), 7.37 (d, ^3J(H,H)= 6.7 Hz, 4H, phenyl), 7.32 (d, ^3J(H,H)= 7.8 Hz, 2H, 3,5-pyridyl), 6.86 (s, 2H, pyrazolyl), 4.19 (s, 6H, NCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 155.3 (pyridyl C), 151.9 (pyrazolyl C), 148.6 (pyridyl CH), 137.7 (pyrazoly C), 137.3 (phenyl C), 133.4 (phenyl CH), 132.8 (phenyl CH), 131.7 (phenyl C), 131.4 (phenyl C), 129.7 (phenyl CH), 129.1 (phenyl CH), 128.7 (phenyl CH), 124.7 (s, CF_3), 117.3 (pyridy CH), 105.1 (pyrazolyl CH), 39.9 (s, NCH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, ppm): δ 45.8. Anal. Calcd for $C_{46}H_{33}Cl_2N_5F_9PRu$ (1044.76): C, 53.65; H, 3.23; N, 6.80. found: C, 53.89; H, 3.29; N 6.81. HRMS (ESI) m/z: Calcd for $C_{46}H_{33}Cl_2N_5F_9PRuNa$ $[M+Na]^+$: 1052.0648. found: 1052.0641. $C_{46}H_{33}Cl_2N_5F_9PRu$ (1029.0750).

4. Synthesis of complex **4**



L2 **4**

TPP = triphenylphosphine

Under nitrogen atmosphere, a mixture of $RuCl_3 \cdot 3H_2O$ (143 mg, 0.55 mmol) and **L2** (146 mg, 0.55 mmol) in EtOH (30 mL) was refluxed for 5 h. The solid substance slowly dissolved and the color of the solution changed to red-orange. After being cooled to room temperature, the precipitates were filtered, washed with EtOH and Et_2O, and dried under vacuum. Without purification, this compound was used in the following synthesis. An EtOH (15 mL) slurry of red-brown precipitates and TPP (144 mg, 0.55 mmol) was treated with excess Et_3N (1 mL). The solid substance slowly dissolved and the color of the solution changed to red-orange. After refluxed 6 h, the red-orange solution was cooled to room temperature and the solvent was removed under vacuum to give a solid red substance. The solid was extracted with CH_2Cl_2 (20 mL) and filtered through Celite. The volume of the filtrate was reduced to approximately 10 mL under vacuum and Et_2O (30 mL) was carefully layered and allowed to slowly diffuse into the CH_2Cl_2 solution. After 12 h, some red crystals were obtained. The crystals were filtered, washed with Et_2O, and dried under vacuum. Yield (246 mg, 64%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25°C, TMS, ppm): δ 7.36 (t, ^3J(H,H)=7.8 Hz, 1H, 4-pyridyl), 7.26–7.22 (m, 3H, phenyl), 7.17 (d, ^3J(H,H)=7.8 Hz, 2H, 3,5-pyridyl), 7.09 (dd, ^3J(H,H)=7.9, 2.8 Hz 12H, phenyl), 6.55 (s, 2H, pyrazolyl), 4.01 (s, 6H, NCH_3), 2.33 (s, 6H, CCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 155.9 (pyridyl C), 151.2 (pyrazolyl C), 142.4 (pyridyl CH), 134.2 (pyrazolyl C), 133.4 (phenyl C), 131.9 (phenyl CH), 128.8 (phenyl CH), 127.4 (phenyl CH), 116.3 (pyridy CH), 104.5 (pyrazolyl CH), 37.3 (s, NCH_3), 12.3 (s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$, 25°C, ppm): δ 44.1. Anal. Calcd for $C_{33}H_{32}Cl_2N_5PRu$ (716.62): C, 56.49; H, 4.60; N, 9.98. found: C, 56.38; H, 4.67; N 9.69. HRMS (ESI) m/z: Calcd for $C_{33}H_{32}Cl_2N_5PRuNa$ $[M+Na]^+$: 724.0714. found: 724.0709. $C_{33}H_{32}Cl_2N_5PRu$ (701.0816).

Crystal structure

The single crystal X-ray diffraction of **2**, **4** were carried at 293.15 K and were shown as follow:

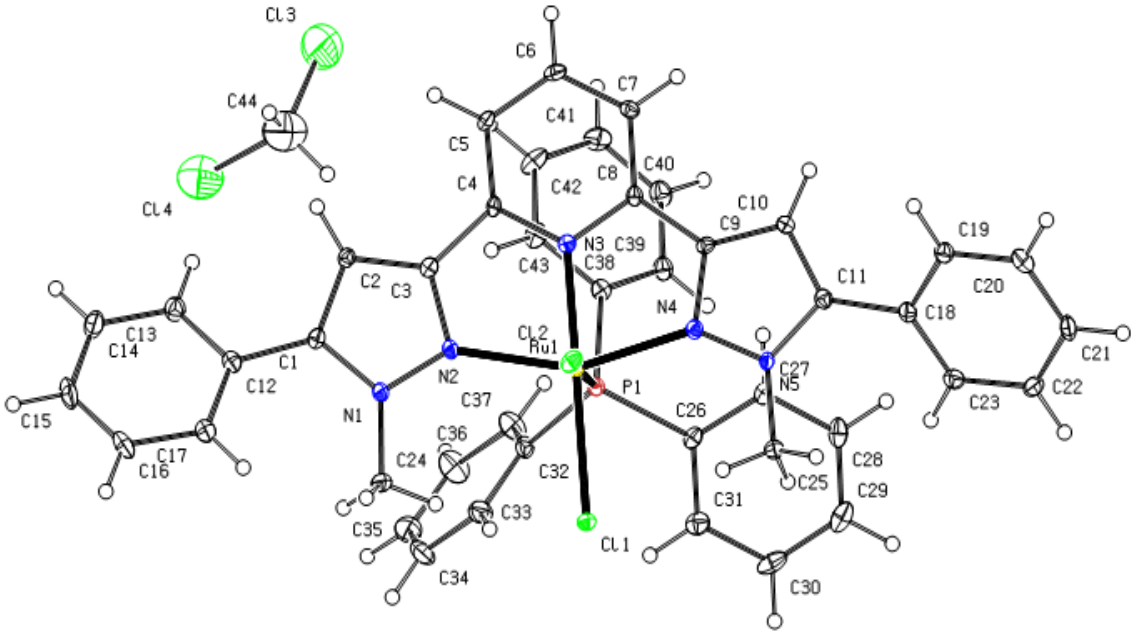


Figure 1. The molecular structure of complex **2**. Selected bond lengths [Å]: Ru1-Cl1 = 2.4558(9), Ru1-Cl2 = 2.4681(10), Ru1-P1 = 2.2958(11), Ru1-N2 = 2.117(3), Ru1-N3 = 1.989(3), Ru1-N4 = 2.081(3); angles [°]: Cl1-Ru1-Cl2 = 87.55(3), P1-Ru1-Cl1 = 87.15(3), P1-Ru1-Cl2 = 171.77(4), N3-Ru1-Cl1 = 178.53(10), N3-Ru1-P1 = 94.31(9), N4-Ru1-N2 = 153.96(12), N3-Ru1-Cl2 = 91.00(9).

Table 1

Crystal and results of structure refinement for complex **2**

Empirical formula	$C_{43}H_{36}Cl_2N_5PRu.CH_2Cl_2$
Formula weight	910.63
Temperature/K	142.95(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.2141(3)
b/Å	11.6147(4)
c/Å	17.2905(6)
α/°	73.605(3)
β/°	81.162(3)
γ/°	84.055(3)
Volume/Å^3	1940.55(11)
Z	2
Dc/gcm^{-3}	1.558

Absorption coefficient /mm $^{-1}$	0.762		
F(000)	928.0		
Crystal size/mm^3	0.28 × 0.12 × 0.1		
θrange for data collection /°	5.958-52.746		
Data/restraints/parameters	7931/0/498		
Goodness-of-fit on F^2	1.042		
Final R indexes [I>=2σ(I)]	R_1=0.0473, wR_2 = 0.1211		
Final R indexes [all data]	R_1=0.0657, wR_2 = 0.1305		
Largest diff.peak/hole/e Å^{-3}	0.97/-1.78		
Bond lengths/Å		Bond angles/°	
Ru1-Cl1	2.4558(9)	Cl1-Ru1-Cl2	87.55(3)
Ru1-Cl2	2.4681(10)	P1-Ru1-Cl1	87.15(3)
Ru1-P1	2.2958(11)	P1-Ru1-Cl2	171.77(4)
Ru1-N2	2.117(3)	N3-Ru1-Cl1	178.53(10)
Ru1-N3	1.989(3)	N3-Ru1-P1	94.31(9)
Ru1-N4	2.081(3)	N4-Ru1-N2	153.96(12)
		N3-Ru1-Cl2	91.00(9)

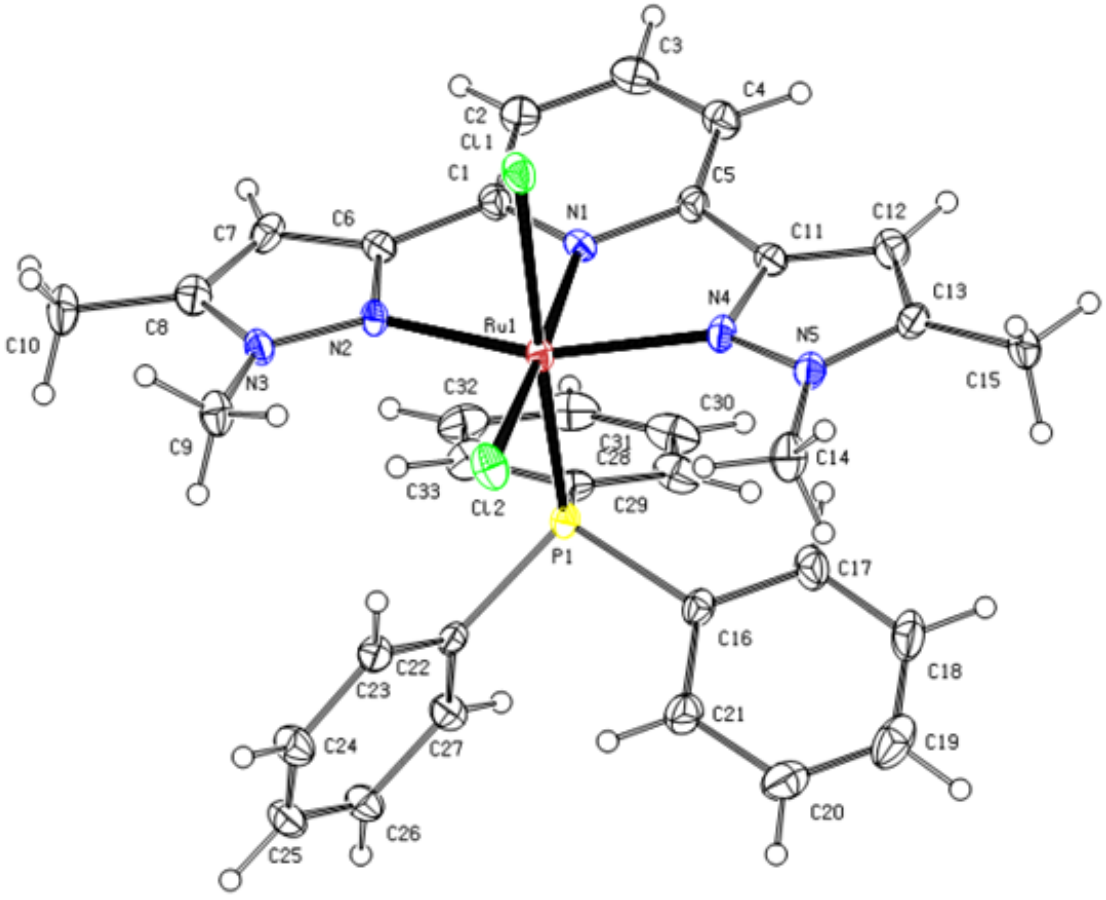


Figure 2. The molecular structure of complex **4**. Selected bond lengths [Å]: Ru1-Cl1 = 2.4646(17), Ru1-Cl2 = 2.4550(17), Ru1-P1 = 2.2760(17), Ru1-N1 = 1.999(5), Ru1-N2 = 2.106(5), Ru1-N4 = 2.085(5); angles [°]: Cl1-Ru1-Cl2 = 87.72(6), P1-Ru1-Cl1 = 178.28(6), P1-Ru1-Cl2 = 93.19(6), N1-Ru1-Cl2 = 172.87(16), N1-Ru1-P1 = 93.88(16), N4-Ru1-N2 = 154.9 (2), N1-Ru1-Cl1 = 85. 18(16)

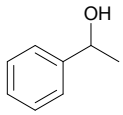
Table 2

Crystal and results of structure refinement for complex **4**

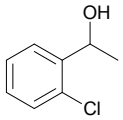
Empirical formula	$C_{33}H_{32}Cl_2N_5PRu$

Formula weight		701.57	
Temperature/K		140.00(10)	
Crystal system		orthorhombic	
Space group		$P2_12_12_1$	
a/Å		12.4349(4)	
b/Å		14.1604(4)	
c/Å		21.7232(8)	
α/°		90	
β/°		90	
γ/°		90	
Volume/Å^3		3825.1(2)	
Z		4	
Dc/gcm^{-3}		1.218	
Absorption coefficient /mm^{-1}		0.617	
F(000)		1432.0	
Crystal size/mm^3		0.3 × 0.25 × 0.25	
*θ*range for data collection /°		5.752-52.746	
Data/restraints/parameters		6784/0/383	
Goodness-of-fit on F^2		1.059	
Final *R* indexes [$I>=2\sigma(I)$]		R_1=0.0446, wR_2 = 0.1213	
Final *R* indexes [all data]		R_1=0.0532, wR_2 = 0.1266	
Largest diff.peak/hole/e Å^{-3}		0.64/-0.45	
Bond lengths/Å		Bond angles/°	
Ru1-Cl1	2.4646(17)	Cl1-Ru1-Cl2	87.72(6)
Ru1-Cl2	2.4550(17)	P1-Ru1-Cl1	178.28(6)
Ru1-P1	2.2760(17)	P1-Ru1-Cl2	93.19(6)
Ru1-N1	1.999(5)	N1-Ru1-Cl2	172.87(16)
Ru1-N2	2.106(5)	N1-Ru1-P1	93.88(16)
Ru1-N4	2.085(5)	N4-Ru1-N2	154.9 (2)
		N1-Ru1-Cl1	85.18(16)

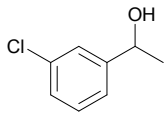
Further details of the crystal structure investigation(s) can be free obtained from the Cambridge Crystallographic Data Centre. The deposition numbers of complexes **2**, **4** are CCDC 999183, CCDC 999184 respectively.



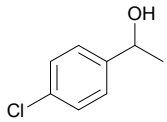
1-Phenylethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.39-7.33 (m, 4H, phenyl), 7.28 (d, ^{3}J (H,H) = 6.7 Hz, 1H, phenyl), 4.90 (q, J = 6.5 Hz, 1H, OCH), 1.72 (s, 1H), 1.50 (d, ^{3}J (H,H) = 6.5 Hz, 3H, CH_3). EI-MS: m/z 122.5 (M, 30%), 120.8 (50), 103.9 (100). MS (ESI) m/z: Calcd for $C_8H_{10}ONa$ $[M+Na]^+$: 145.0629. found: 145.04. $C_8H_{10}O$ (122.07).



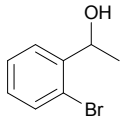
1-(2-chlorophenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.60 (d, ^{3}J (H,H) = 7.8 Hz, 1H, phenyl), 7.31 (dd, ^{3}J (H,H) = 13.6, 7.6 Hz, 2H, phenyl), 7.20 (t, ^{3}J (H,H) = 8.4 Hz, 1H, phenyl), 5.30 (q, ^{3}J (H,H) = 6.4 Hz, 1H, OCH), 1.72 (s, 1H), 1.50 (d, ^{3}J (H,H) = 6.4 Hz, 3H, CH_3). EI-MS: m/z: 156.03 (M, 100.0%), 158.03 (32), 157.04 (8.8), 159.03 (2.8). MS (ESI) m/z: Calcd for C_8H_9ClONa $[M+Na]^+$: 179.0240. found: 179.01. C_8H_9ClO (156.03).



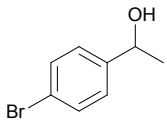
1-(3-chlorophenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.36 (s, 1H, phenyl), 7.28-7.21 (m, 3H, phenyl), 4.85 (q, ^{3}J (H,H) = 6.5 Hz, 1H, OCH), 2.23 (s, 1H), 1.46 (d, ^{3}J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for C_8H_9ClONa $[M+Na]^+$: 179.0240. found: 179.01. C_8H_9ClO (156.03).



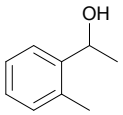
1-(4-chlorophenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.33-7.27 (m, 4H, phenyl), 4.86 (q, ^{3}J (H,H) = 6.4 Hz, 1H, OCH), 1.96 (s, 1H), 1.46 (d, ^{3}J (H,H) = 7.4 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for C_8H_9ClONa $[M+Na]^+$: 179.0240. found: 179.01. C_8H_9ClO (156.03).



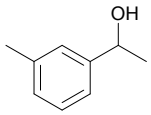
1-(2-bromophenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.60 (d, ^{3}J (H,H) = 6.3 Hz, 1H, phenyl), 7.52 (d, ^{3}J (H,H) = 8.0 Hz, 1H, phenyl), 7.35 (t, ^{3}J (H,H) = 7.5 Hz, 1H, phenyl), 7.13 (t, ^{3}J (H,H) = 7.6 Hz, 1H, phenyl), 5.25 (q, ^{3}J (H,H) = 6.4 Hz, 1H, OCH), 1.65 (s, 1H), 1.49 (d, ^{3}J (H,H) = 6.4 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for C_8H_9BrONa $[M+Na]^+$: 222.9734. found: 222.96. C_8H_9BrO (199.98).



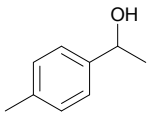
1-(4-bromophenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.44 (d, ^3J (H,H) = 8.4 Hz, 2H, phenyl), 7.21 (d, ^3J (H,H) = 8.3 Hz, 2H, phenyl), 4.82 (q, ^3J (H,H) = 6.4 Hz, 1H, OCH), 1.44 (d, ^3J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for C_8H_9BrONa $[M+Na]^+$: 222.9734. found: 222.96. C_8H_9BrO (199.98).



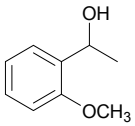
1-(o-tolyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.52 (d, ^3J (H,H) = 7.6 Hz, 1H, phenyl), 7.23 (d, ^3J (H,H) = 7.5 Hz, 1H, phenyl), 7.20-7.10 (m, 2H, phenyl), 5.14 (q, ^3J (H,H) = 6.4 Hz, 1H, OCH), 2.35 (s, 3H, CH_3), 1.63 (s, 1H), 1.47 (d, ^3J (H,H) = 6.4 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_{12}ONa$ $[M+Na]^+$: 159.0786. found: 159.08. $C_9H_{12}O$ (136.09).



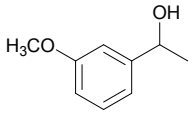
1-(m-tolyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.23 (d, ^3J (H,H) = 7.5 Hz, 1H, phenyl), 7.20-7.15 (m, 2H, phenyl), 7.09 (d, ^3J (H,H) = 7.4 Hz, 1H, phenyl), 4.87 (q, ^3J (H,H) = 6.5 Hz, 1H, OCH), 2.36 (s, 3H, CH_3), 1.69 (s, 1H), 1.49 (d, ^3J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_{12}ONa$ $[M+Na]^+$: 159.0786. found: 159.08. $C_9H_{12}O$ (136.09).



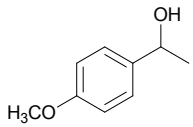
1-(p-tolyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.25 (d, ^3J (H,H) = 8.1 Hz, 2H, phenyl), 7.15 (d, ^3J (H,H) = 7.9 Hz, 2H, phenyl), 4.85 (q, ^3J (H,H) = 6.4 Hz, 1H, OCH), 2.34 (s, 3H, CH_3), 1.87 (s, 1H), 1.47 (d, ^3J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_{12}ONa$ $[M+Na]^+$: 159.0786. found: 159.08. $C_9H_{12}O$ (136.09).



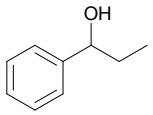
1-(2-methoxyphenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.34 (d, ^3J (H,H) = 7.5 Hz, 1H, phenyl), 7.26-7.22 (m, 1H, phenyl), 6.97 (t, ^3J (H,H) = 7.5 Hz, 1H, phenyl), 6.89 (d, ^3J (H,H) = 8.2 Hz, 1H, phenyl), 5.10 (q, ^3J (H,H) = 6.5 Hz, 1H,OCH), 3.87 (s, 3H, OCH_3), 1.51 (d, ^3J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_{12}O_2Na$ $[M+Na]^+$: 175.0735. found: 175.06. $C_9H_{12}O_2$ (152.08).



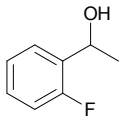
1-(3-methoxyphenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.23 (dd, ^3J (H,H) = 10.4, 5.7 Hz, 1H, phenyl), 6.91 (d, ^3J (H,H) = 6.3 Hz, 2H, phenyl), 6.79 (d, ^3J (H,H) = 8.3 Hz, 1H, phenyl), 4.81 (q, ^3J (H,H) = 6.5 Hz, 1H, OCH), 3.78 (s, 3H, OCH_3), 1.45 (d, ^3J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_{12}O_2Na$ $[M+Na]^+$: 175.0735. found: 175.06. $C_9H_{12}O_2$ (152.08).



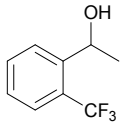
1-(4-methoxyphenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.31 (d, ^{3}J (H,H) = 8.6 Hz, 2H, phenyl), 6.89 (d, ^{3}J (H,H) = 8.6 Hz, 2H, phenyl), 4.87 (q, ^{3}J (H,H) = 6.4 Hz, 1H, OCH), 3.81 (s, 3H, OCH_3), 1.55 (s, 1H), 1.49 (d, ^{3}J (H,H) = 6.4 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_{12}O_2Na$ $[M+Na]^+$: 175.0735. found: 175.06. $C_9H_{12}O_2$ (152.08).



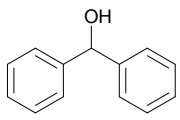
1-phenylpropan-1-ol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.36-7.30 (m, 4H, phenyl), 7.28 -7.24 (m, 1H, phenyl), 4.56 (t, ^{3}J (H,H) = 6.6 Hz, 1H, OCH), 2.00 (s, 1H), 1.77 (dd, ^{3}J (H,H) = 24.3, 6.8 Hz, 2H, CH_2), 0.90 (t, ^{3}J (H,H) = 7.4 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_{12}ONa$ $[M+Na]^+$: 159.0786. found: 159.07. $C_9H_{12}O$ (136.09).



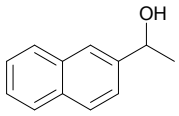
1-(2-fluorophenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.49 (t, ^{3}J (H,H) = 8.4 Hz, 1H, phenyl), 7.26-7.21 (m, 1H, phenyl), 7.15 (t, ^{3}J (H,H) = 7.4 Hz, 1H, phenyl), 7.05-6.99 (m, 1H, phenyl), 5.21 (q, ^{3}J (H,H) = 6.5 Hz, 1H, OCH), 1.76 (s, 1H), 1.52 (d, ^{3}J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for C_8H_9FONa $[M+Na]^+$: 163.0535. found: 163.03. C_8H_9FO (140.06).



1-(2-(trifluoromethyl)phenyl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.83 (d, ^{3}J (H,H) = 7.8 Hz, 1H, phenyl), 7.60 (t, ^{3}J (H,H) = 8.7 Hz, 2H, phenyl), 7.37 (t, ^{3}J (H,H) = 7.6 Hz, 1H, phenyl), 5.34 (q, ^{3}J (H,H) = 6.2 Hz, 1H, OCH), 1.72 (s, 1H), 1.50 (d, ^{3}J (H,H) = 6.3 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_9H_9F_3ONa$ $[M+Na]^+$: 213.0503. found: 213.04. $C_9H_9F_3O$ (152.08).

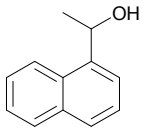


Diphenylmethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.40-7.32 (m, 8H, phenyl), 7.29 - 7.26 (m, 2H, phenyl), 5.85 (s, 1H, OCH). MS (ESI) m/z: Calcd for $C_{13}H_{12}ONa$ $[M+Na]^+$: 207.0786. found: 207.07. $C_{13}H_{12}O$ (184.09).

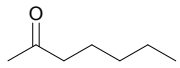


1-(naphthalen-2-yl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 7.84 (dd, ^{3}J (H,H) = 9.3, 4.5 Hz, 4H, naphthalen-2-yl), 7.53-7.46 (m, 3H, naphthalen-2-yl), 5.08 (q, ^{3}J (H,H) = 6.5 Hz, 1H, OCH),

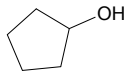
1.73 (s, 1H), 1.59 (d, ^3J (H,H) = 6.5 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_{12}H_{12}ONa$ $[M+Na]^+$: 195.0786. found: 195.06. $C_{12}H_{12}O$ (172.09).



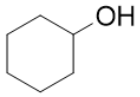
1-(naphthalen-1-yl)ethanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 8.12 (d, ^3J (H,H) = 8.3 Hz, 1H, naphthalen-2-yl), 7.87 (d, ^3J (H,H) = 9.3 Hz, 1H, naphthalen-2-yl), 7.78 (d, ^3J (H,H) = 8.2 Hz, 1H, naphthalen-2-yl), 7.68 (d, ^3J (H,H) = 7.1, 1H, naphthalen-2-yl), 7.54-7.46 (m, 3H,naphthalen-2-yl), 5.67 (d, ^3J (H,H) = 12.9, 1H, OCH), 1.68 (s, 3H,CH_3). MS (ESI) m/z: Calcd for $C_{12}H_{12}ONa$ $[M+Na]^+$: 195.0786. found: 195.06. $C_{12}H_{12}O$ (172.09).



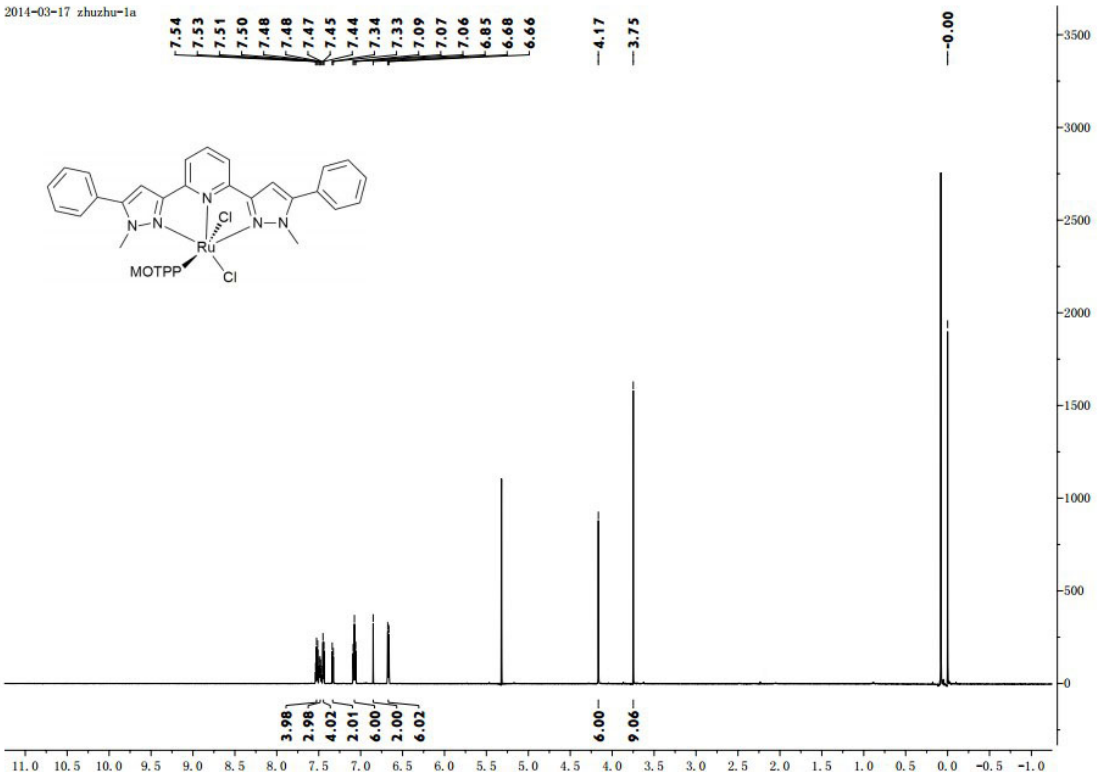
heptan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 3.78 (dd,^3J (H,H) = 11.8, 5.9 Hz, 1H, OCH), 1.91 (s, 1H), 1.49 -1.37 (m, 3H, CH_3), 1.32 (d, ^3J (H,H) = 17.2 Hz, 5H, CH_2), 1.18 (d, ^3J (H,H) = 6.2 Hz, 3H, CH_2), 0.89 (t, ^3J (H,H) = 6.6 Hz, 3H, CH_3). MS (ESI) m/z: Calcd for $C_7H_{16}ONa$ $[M+Na]^+$: 139.1099. found: 139.10. $C_7H_{16}O$ (116.12).



Cyclopentanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 4.30 (s, 1H, OCH), 2.81-2.68 (m, 1H), 1.76 (s, 4H,CH_2), 1.55 (s, 4H,CH_2). MS (ESI) m/z: Calcd for $C_5H_{10}ONa$ $[M+Na]^+$: 109.0629. found: 109.05. $C_5H_{10}O$ (86.07).



Cyclohexanol: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS, ppm): δ 3.61 (s, 1H, OCH), 1.92-1.66 (m, 5H, CH_2), 1.54 (s, 1H), 1.32-1.15 (m, 5H, CH_2). MS (ESI) m/z: Calcd for $C_6H_{12}ONa$ $[M+Na]^+$: 123.0786. found: 123.08. $C_6H_{12}O$ (100.09).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7.06
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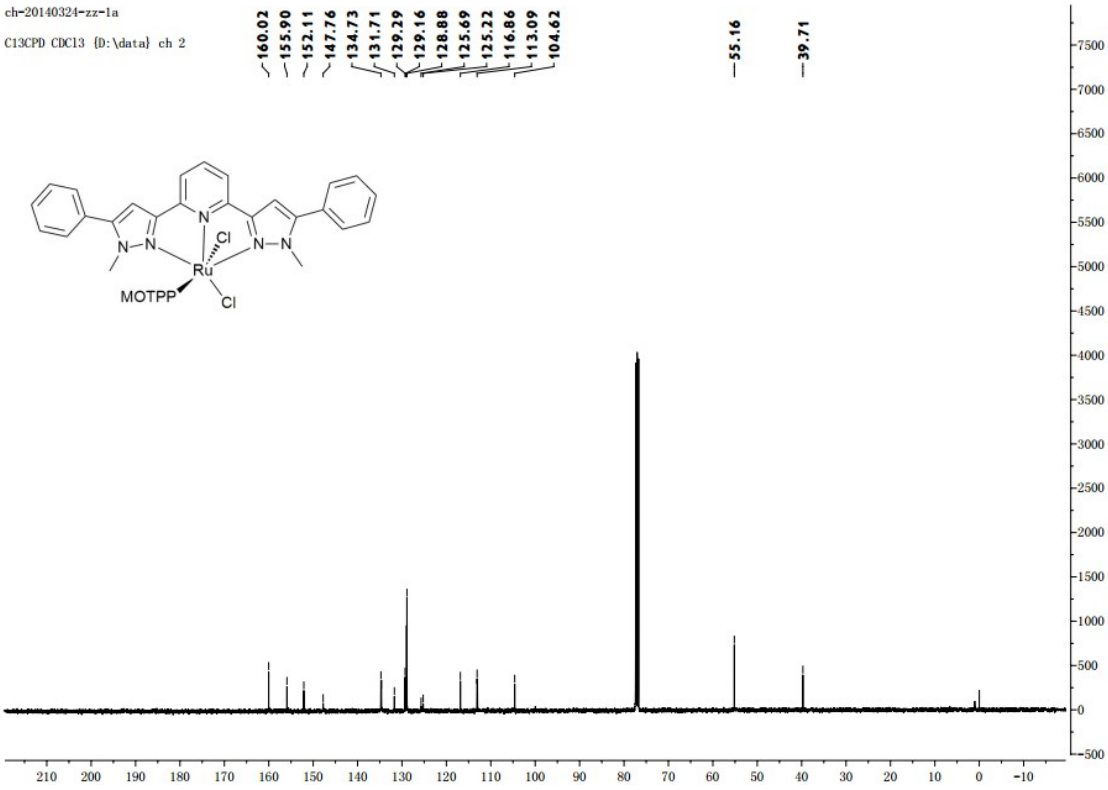
9.06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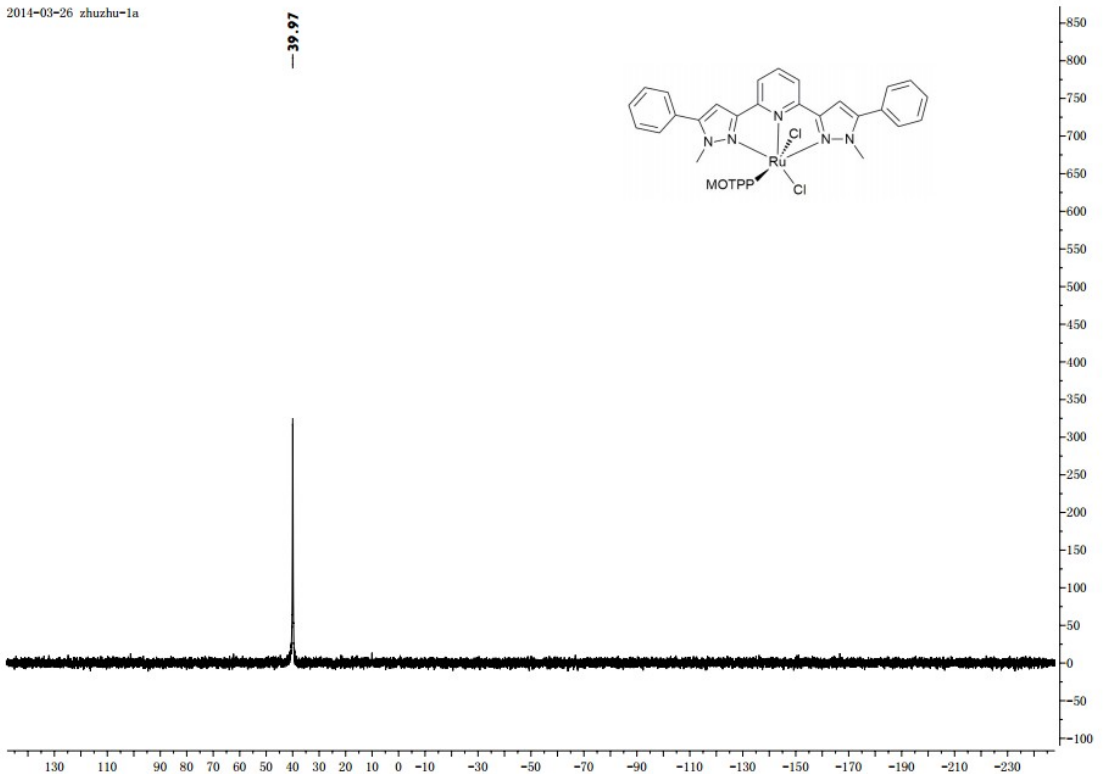
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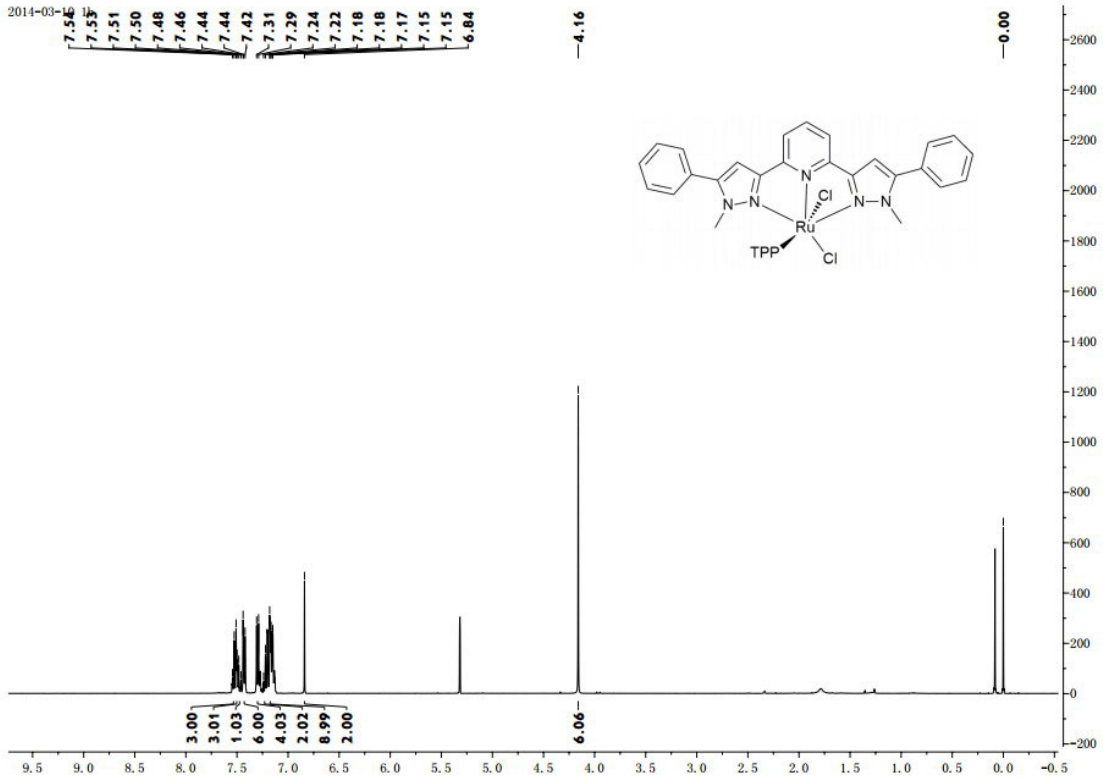
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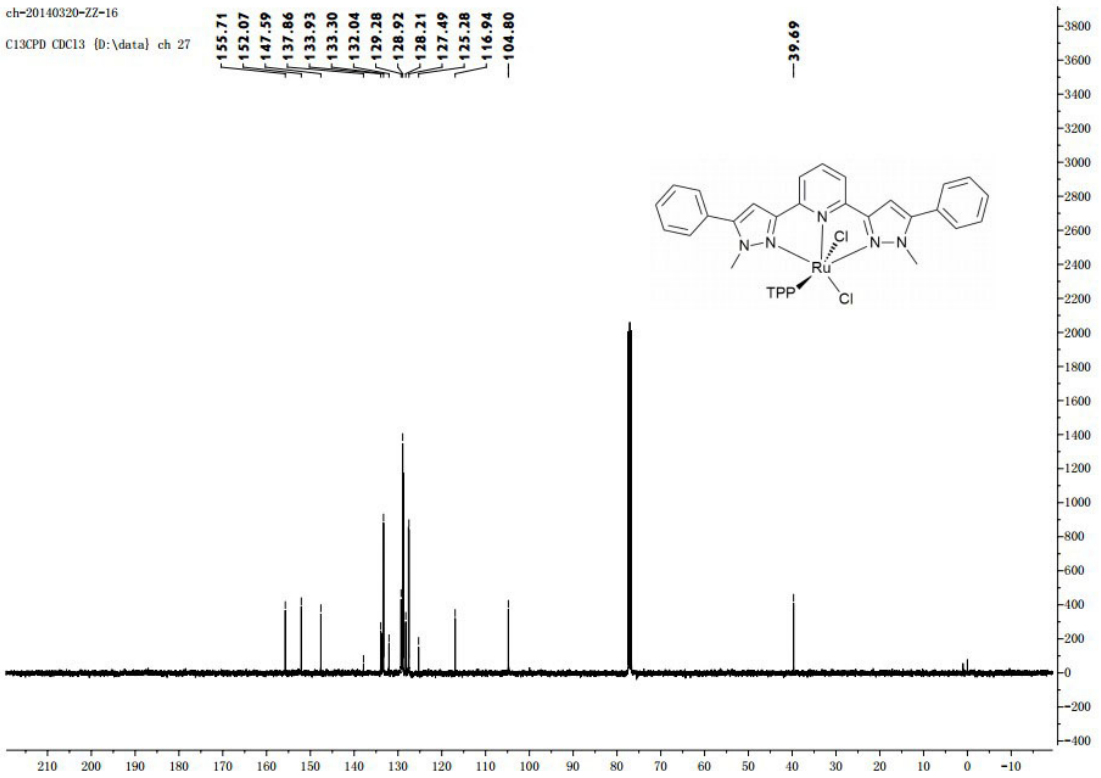
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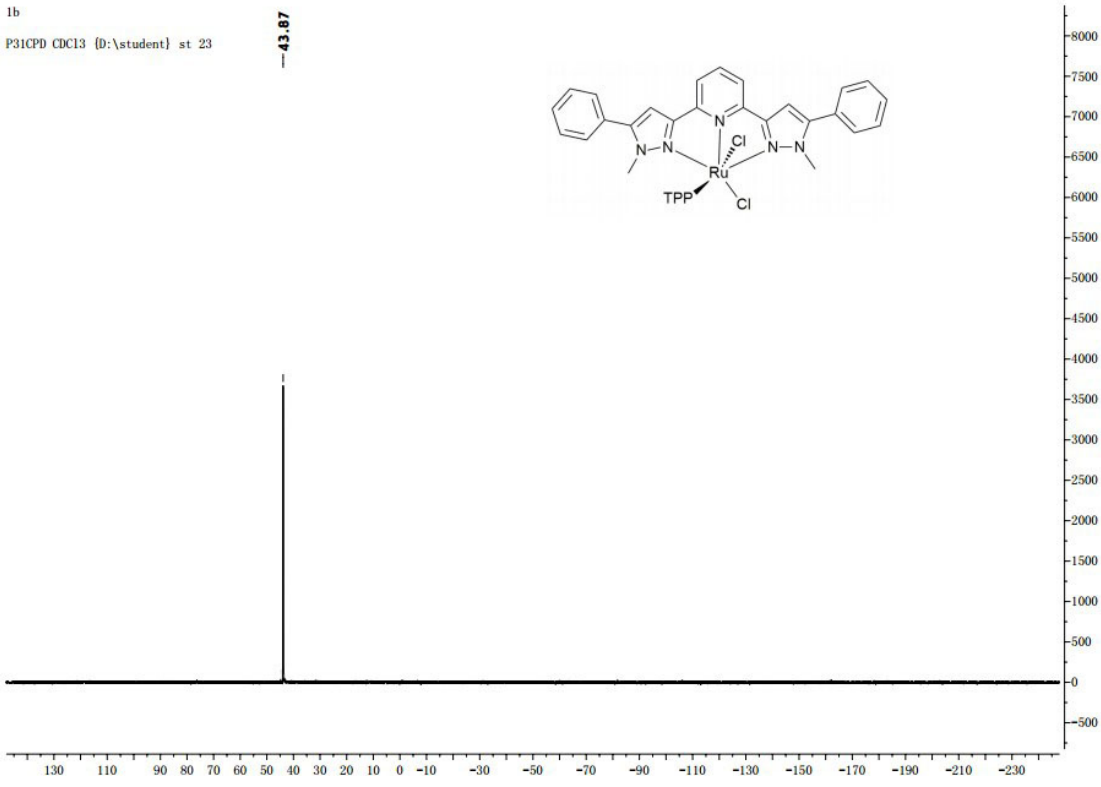
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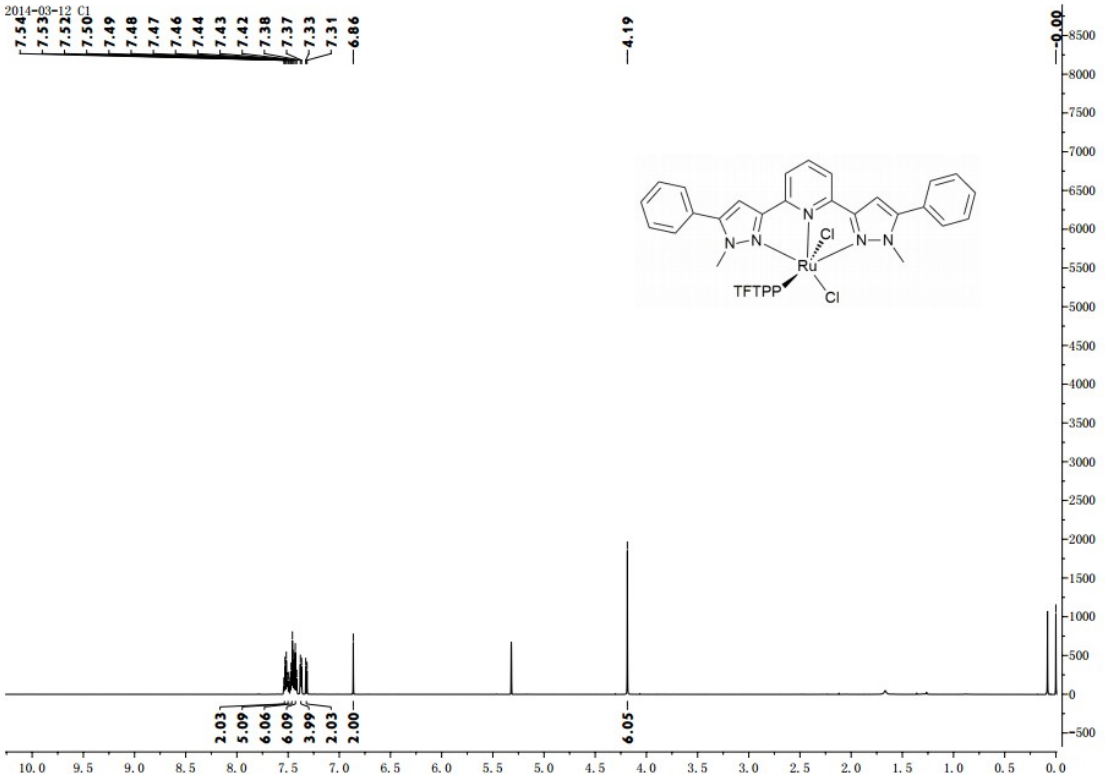
2014-03-12 C1
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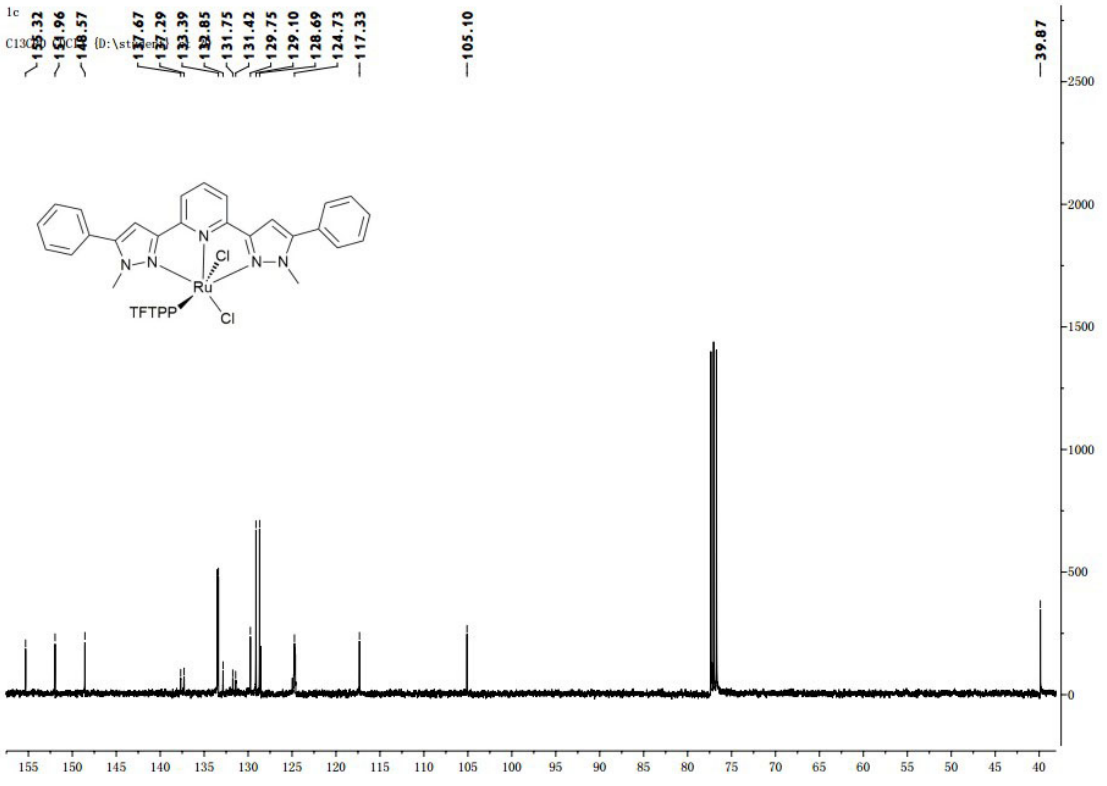
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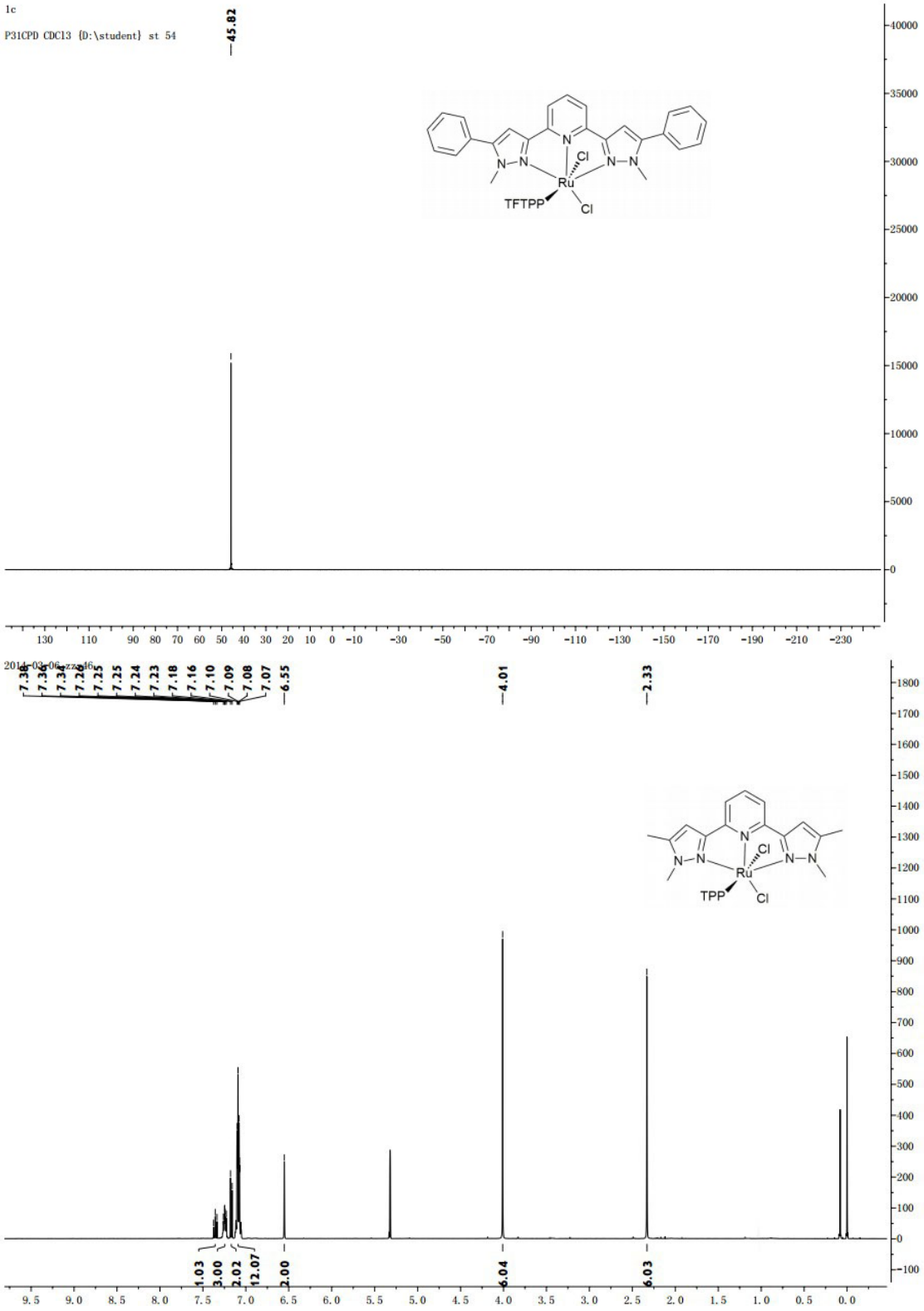
Cl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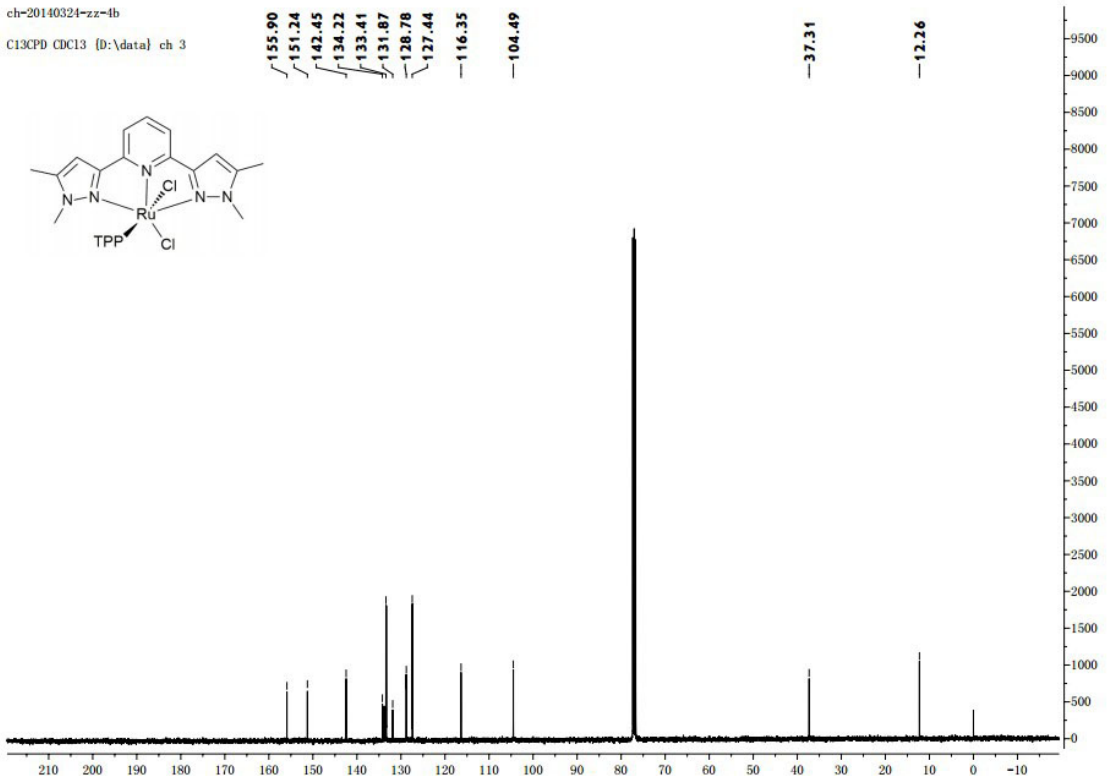
6.03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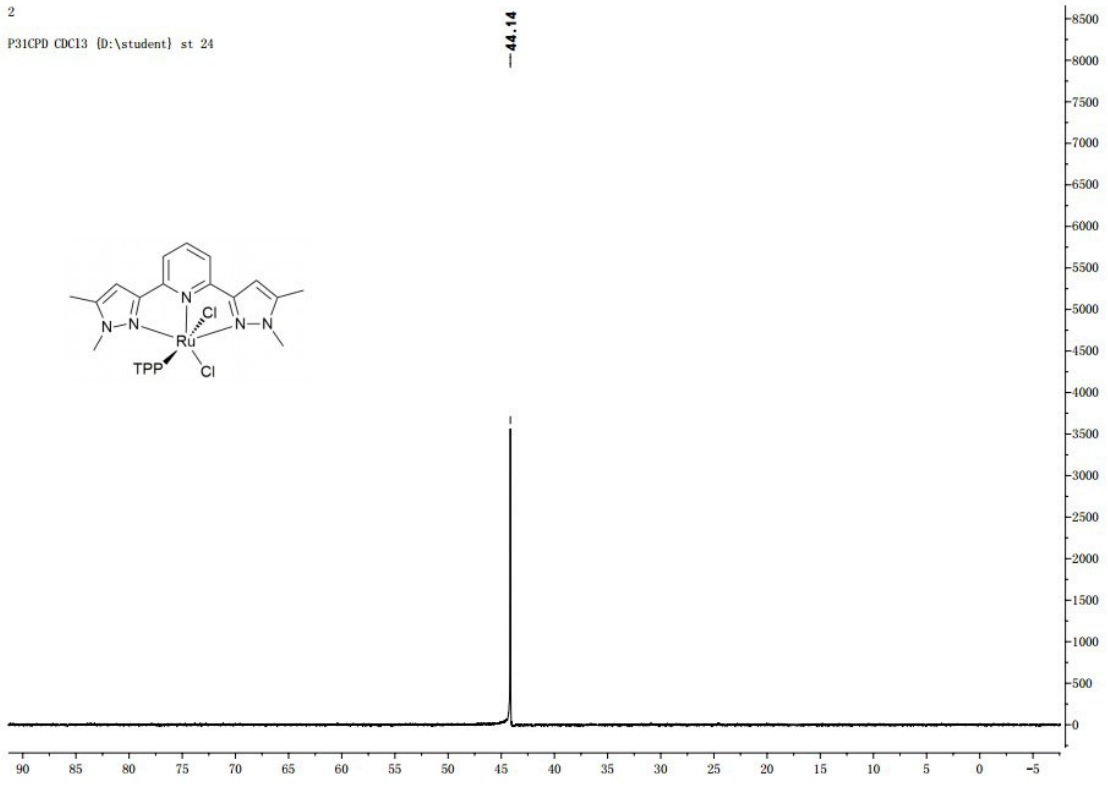
TPP
Cl


2
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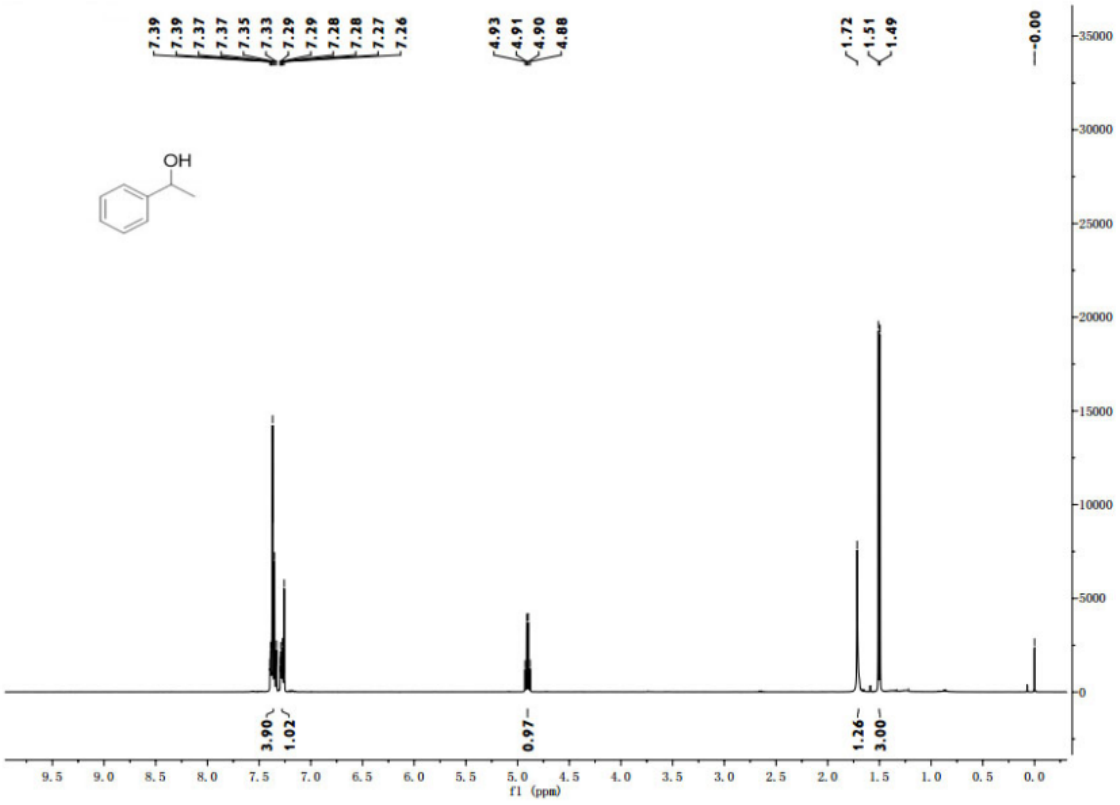
TPP
Cl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7.26
4.93
4.91
4.90
4.88
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1.49
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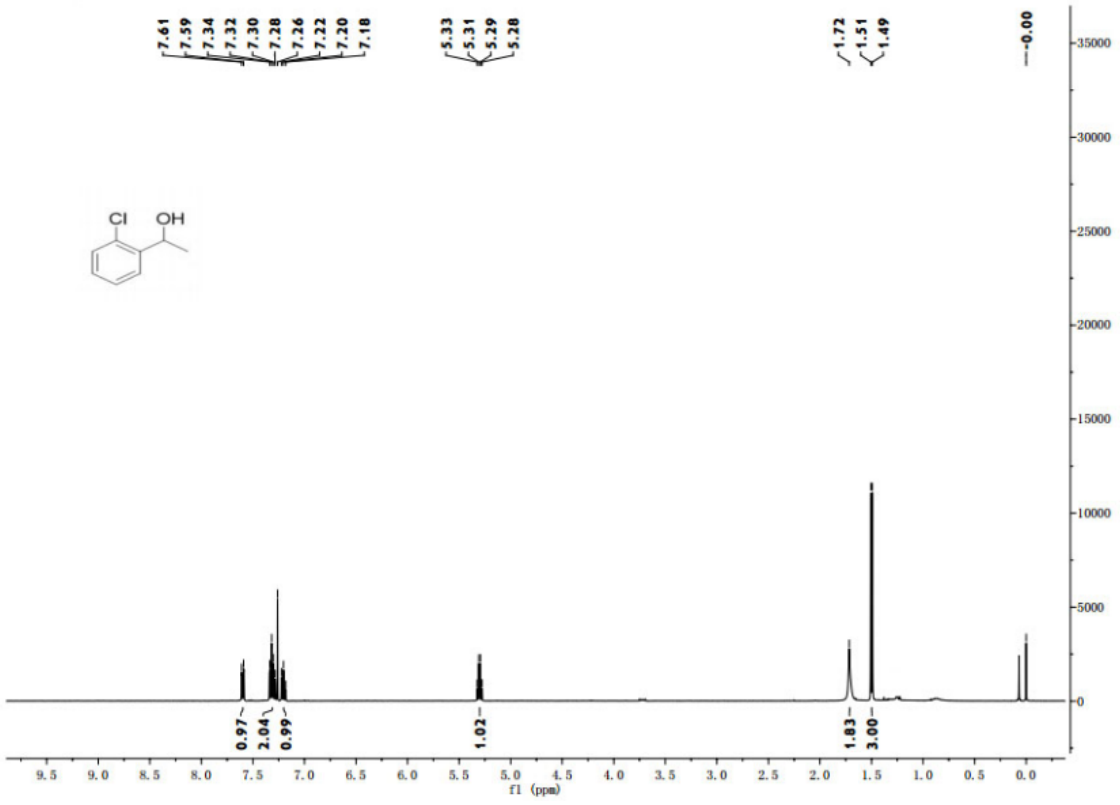
OH
3.90
1.02
0.97
1.26
3.00
f1 (ppm)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5.31
5.29
5.28
1.72
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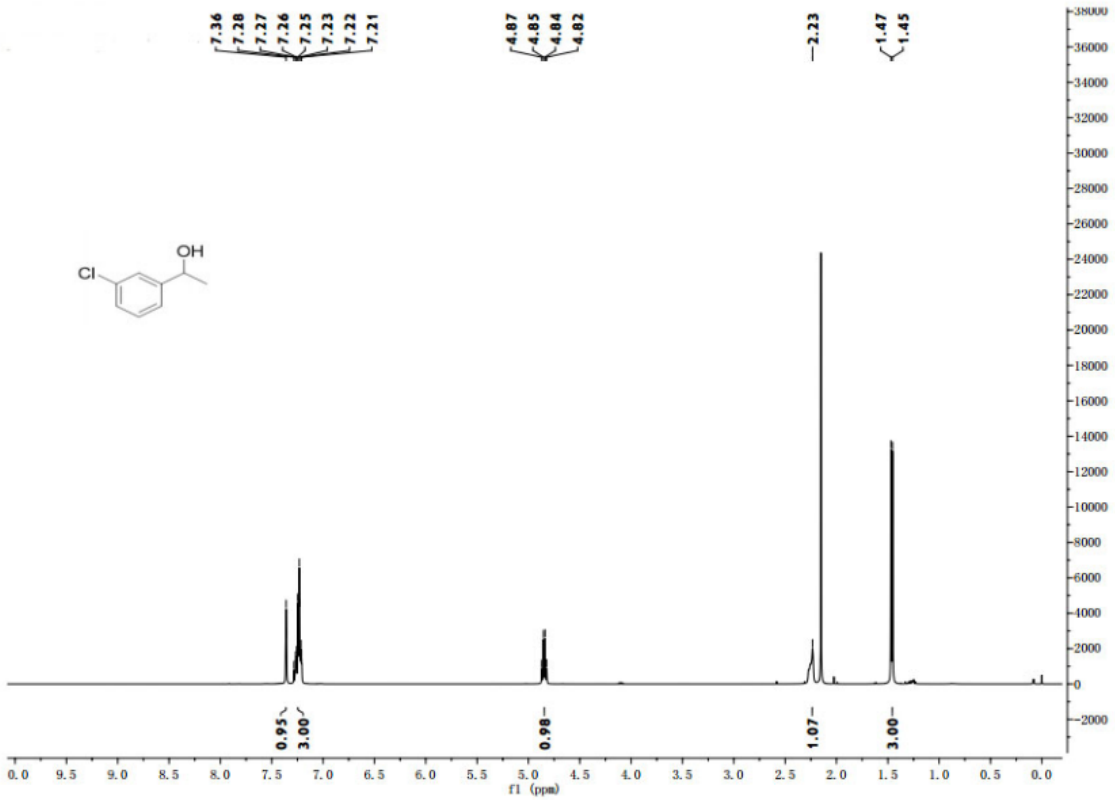
1.49
0.00
Cl
OH
0.97
2.04
0.99
1.02
1.83
3.00
f1 (ppm)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7.22
7.21
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4.85
4.84
4.82
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1.47
1.45
OH
Cl
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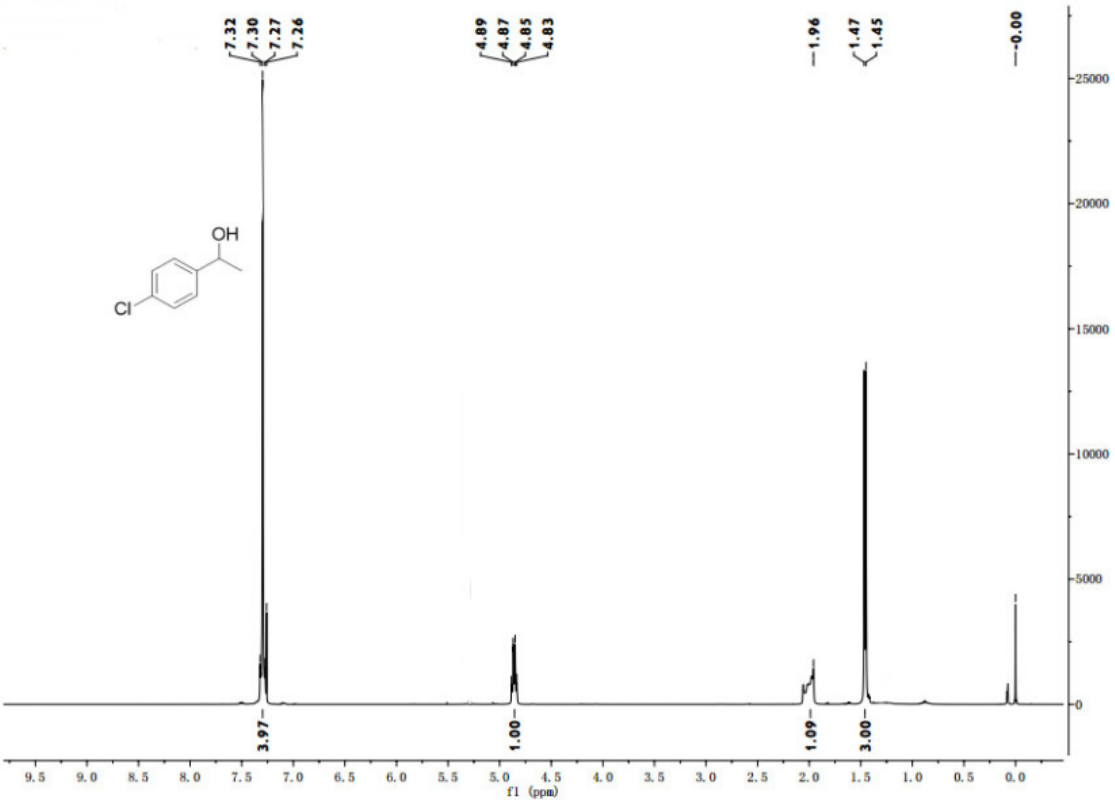
3.00
0.98
1.07
3.00
f1 (ppm)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4.87
4.85
4.83
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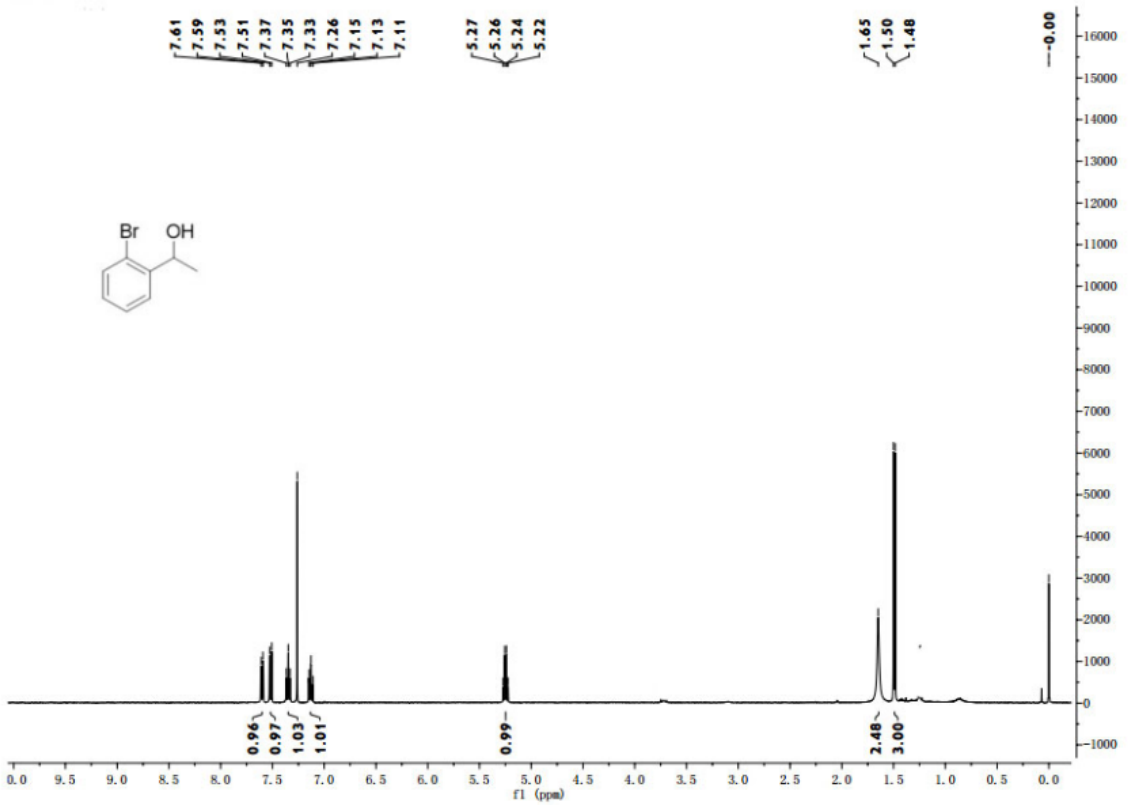
1.47
1.45
0.00
OH
Cl
3.97
1.00
1.09
3.00
f1 (ppm)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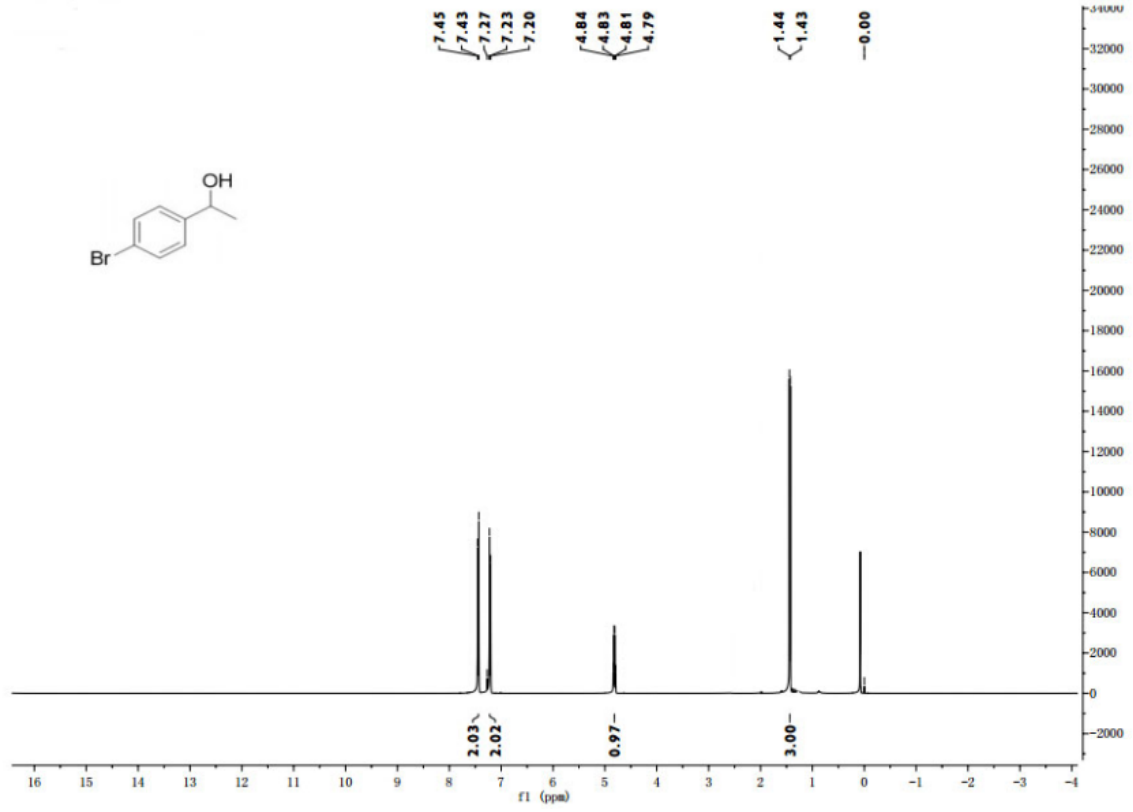
7.11
5.27
5.26
5.24
5.22
1.65
1.50
1.48
0.00
Br
OH
0.96
0.97
1.03
1.01
0.99
2.48
3.00
f1 (ppm)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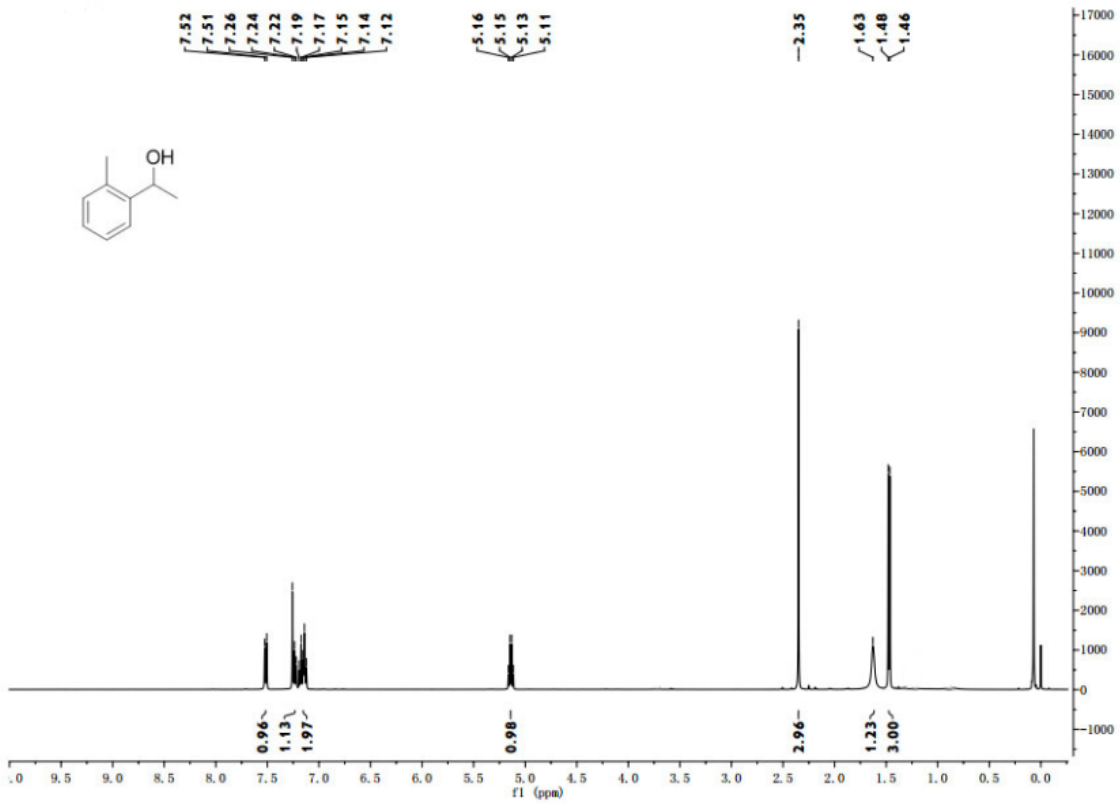
1.43
0.00
OH
Br
2.03
2.02
0.97
3.00
f1 (ppm)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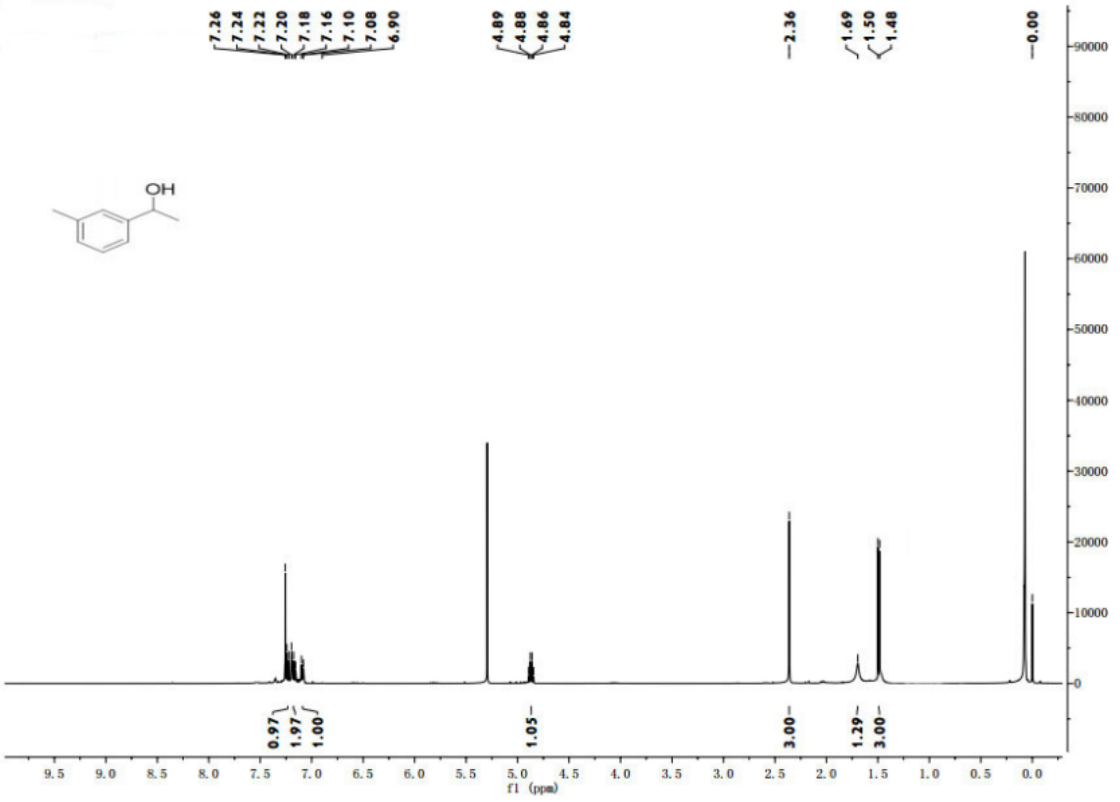
7.12
5.16
5.15
5.13
5.11
2.35
1.63
1.48
1.46
OH
0.96
1.13
1.97
0.98
2.96
1.23
3.00
f1 (ppm)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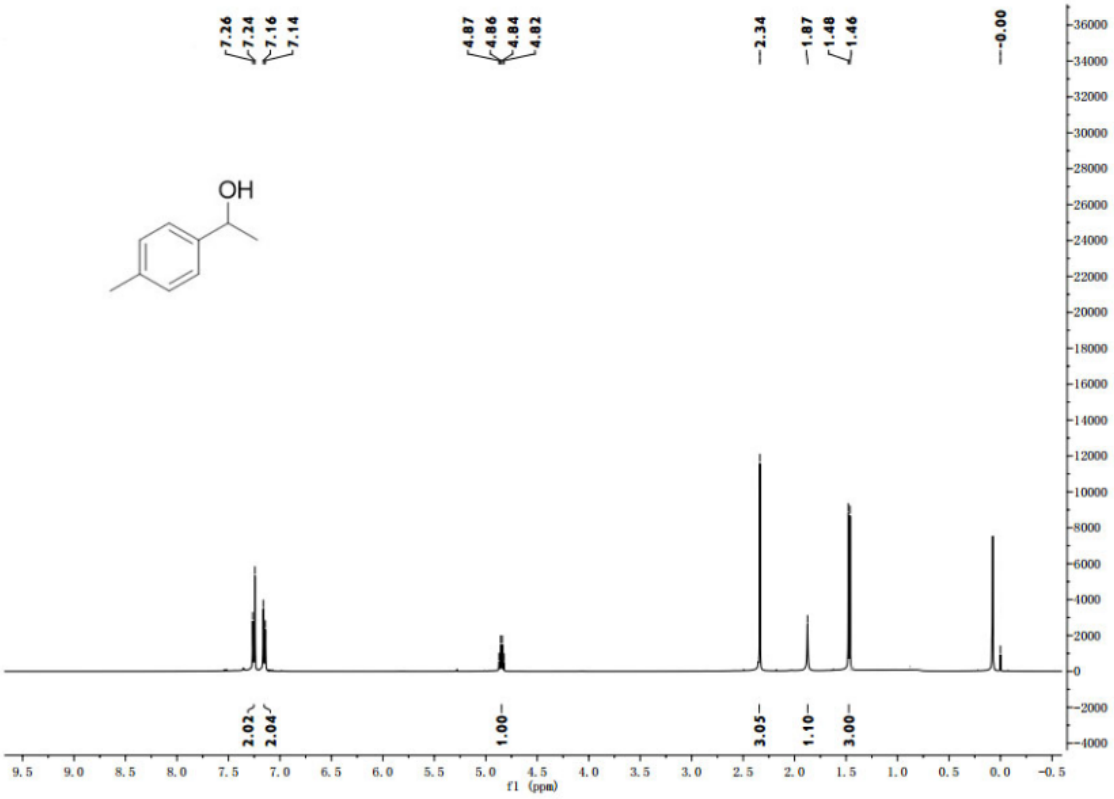
4.88
4.86
4.84
2.36
1.69
1.50
1.48
0.00
OH
0.97
1.97
1.00
1.05
3.00
1.29
3.00
f1 (ppm)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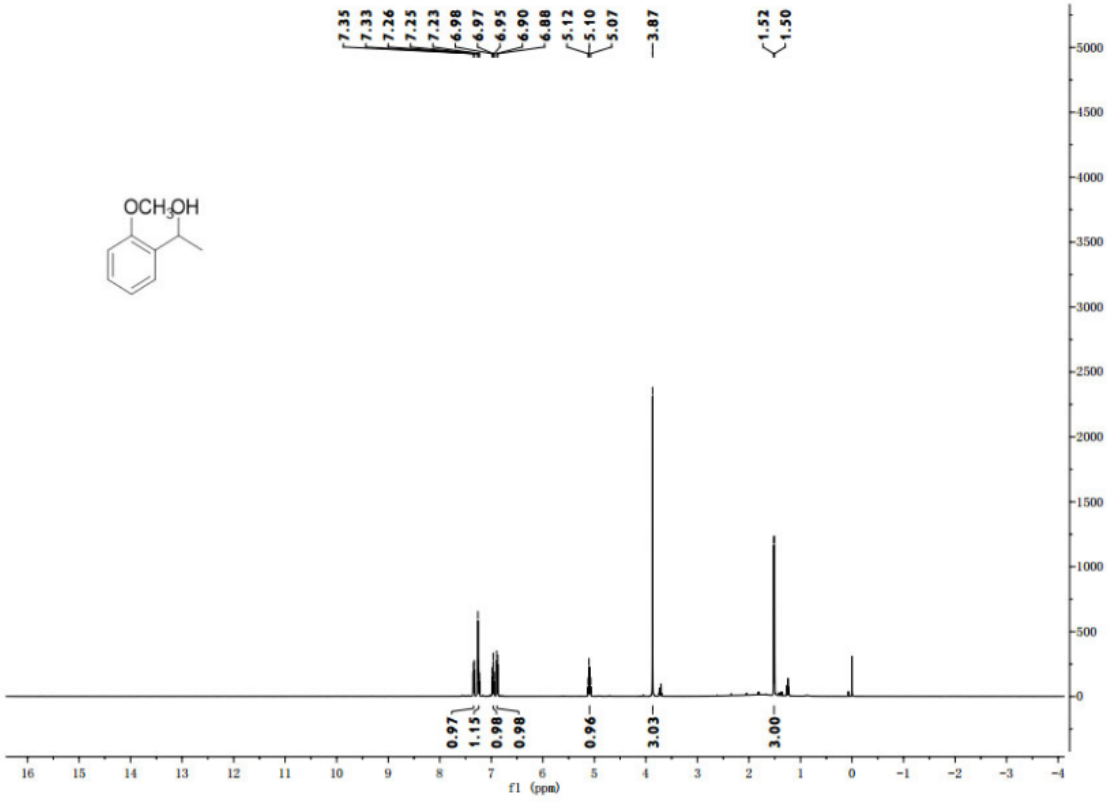
4.86
4.84
4.82
2.34
1.87
1.48
1.46
0.00
OH
2.02
2.04
1.00
3.05
1.10
3.00
f1 (ppm)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7.23
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6.97
6.95
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6.88
5.12
5.10
5.07
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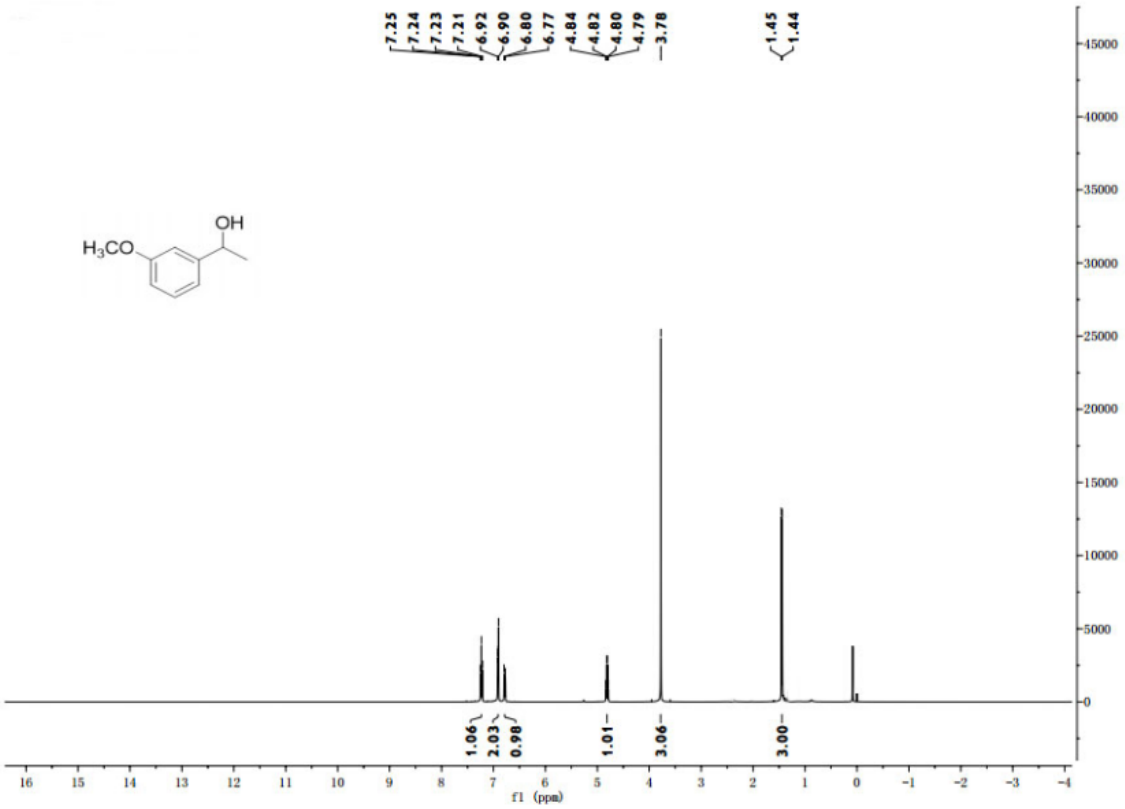
OCH3OH
0.97
1.15
0.98
0.98
0.96
3.03
3.00
f1 (ppm)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6.90
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6.77
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4.82
4.80
4.79
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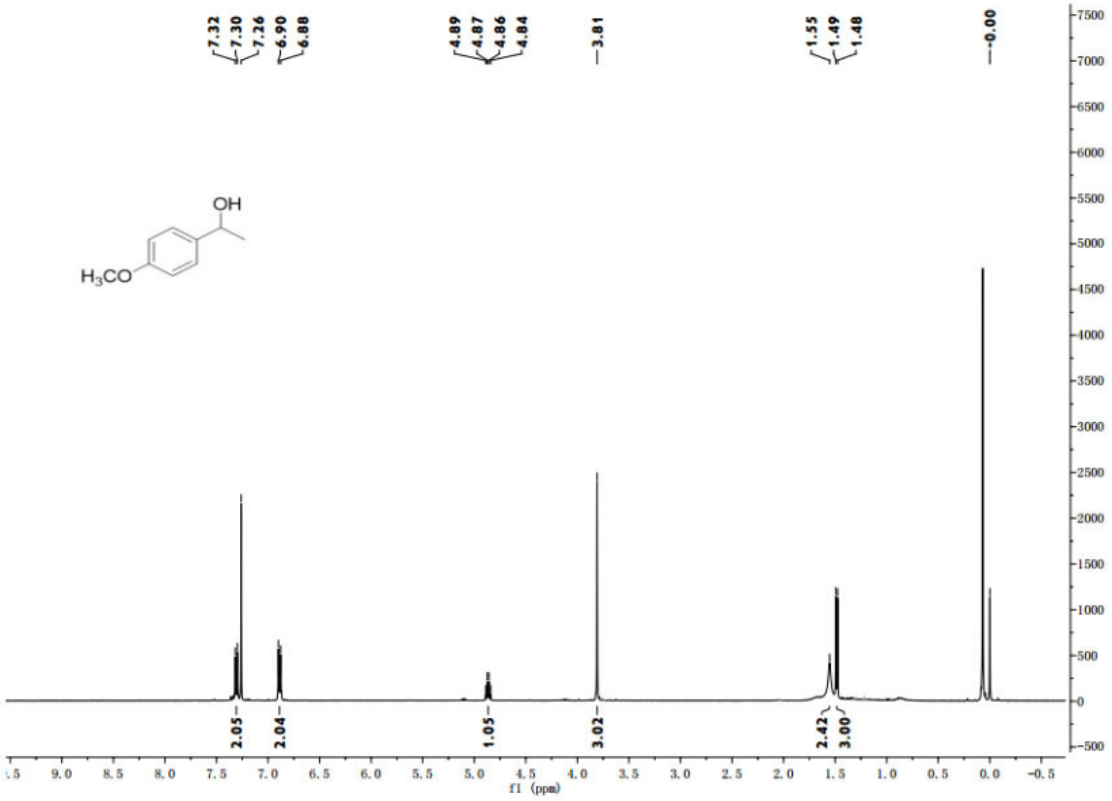
1.44
OH
H3CO
1.06
2.03
0.98
1.01
3.06
3.00
f1 (ppm)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6.88
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4.87
4.86
4.84
3.81
1.55
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1.48
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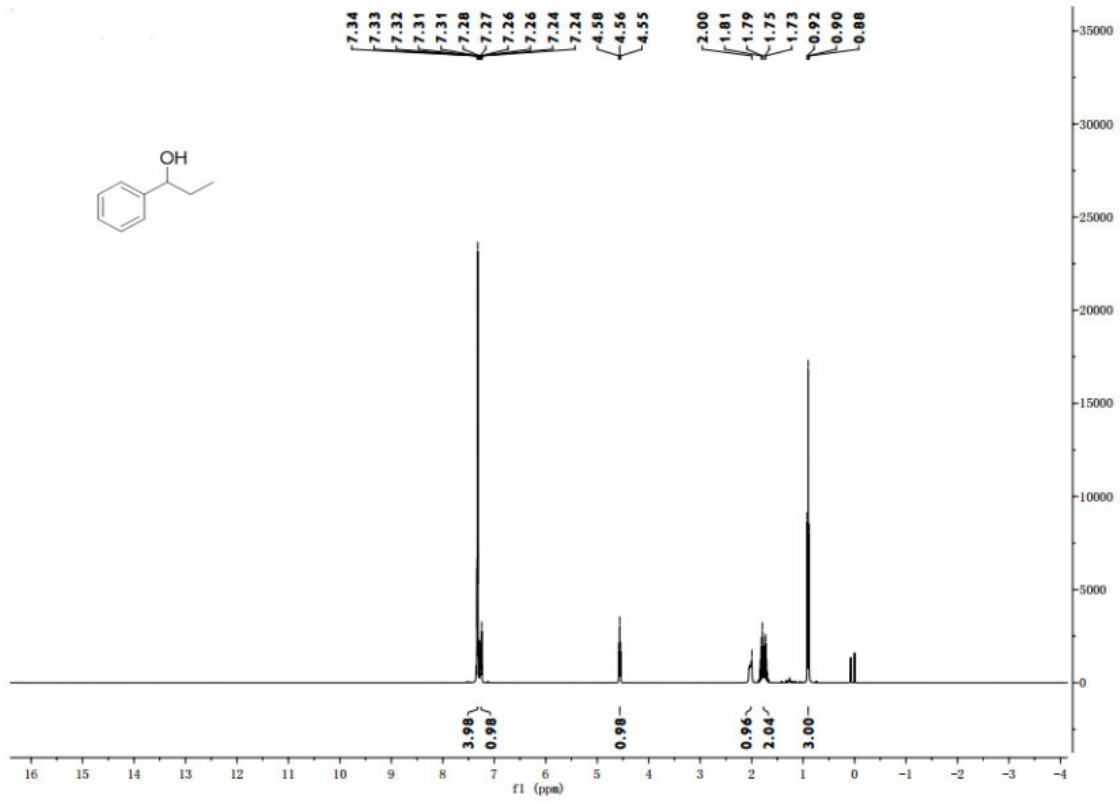
OH
H3CO
2.05
2.04
1.05
3.02
2.42
3.00
f1 (ppm)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7.31
7.31
7.28
7.27
7.26
7.26
7.24
7.24
4.58
4.56
4.55
2.00
1.81
1.79
1.75
1.73
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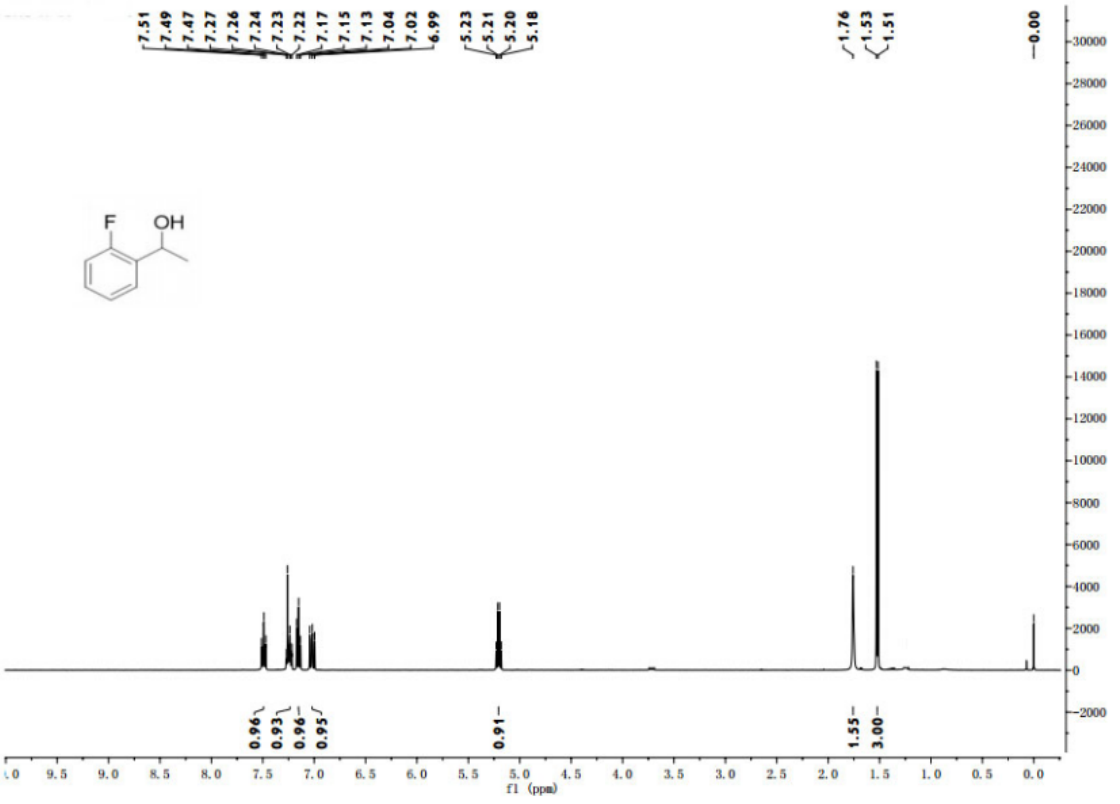
0.90
0.88
3.98
0.98
0.98
0.96
2.04
3.00
f1 (ppm)


F
OH
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7.47
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7.26
7.24
7.23
7.22
7.17
7.15
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7.04
7.02
6.99
5.23
5.21
5.20
5.18
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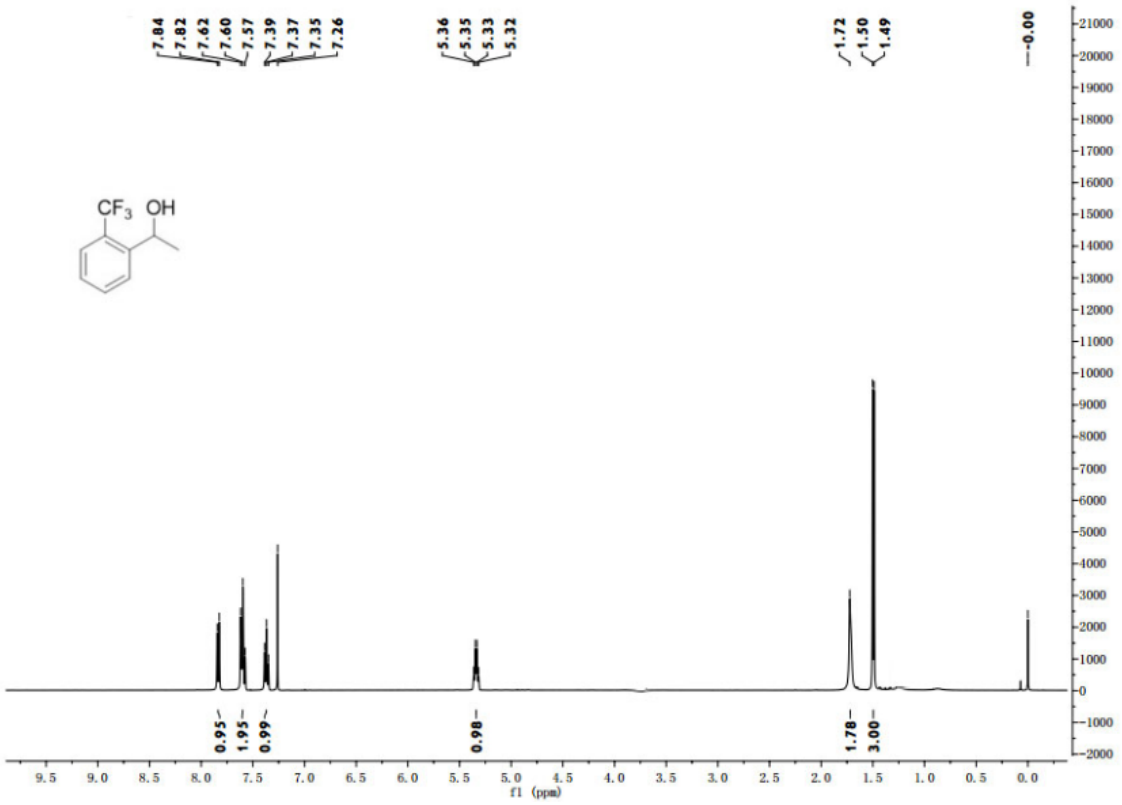
1.53
1.51
0.00
0.96
0.93
0.96
0.95
0.91
1.55
3.00
f1 (ppm)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7.35
7.26
5.36
5.35
5.33
5.32
1.72
1.50
1.49
0.00
CF3 OH
0.95
1.95
0.99
0.98
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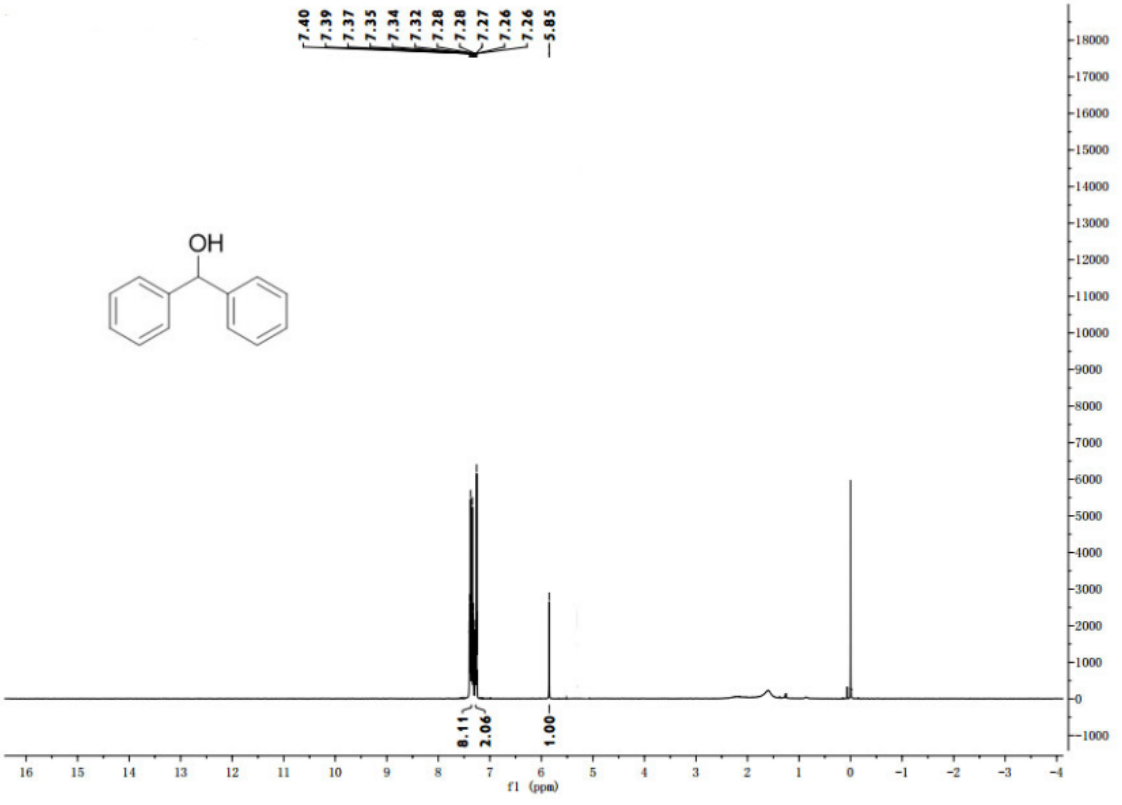
3.00
f1 (ppm)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7.28
7.27
7.26
7.26
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OH
8.11
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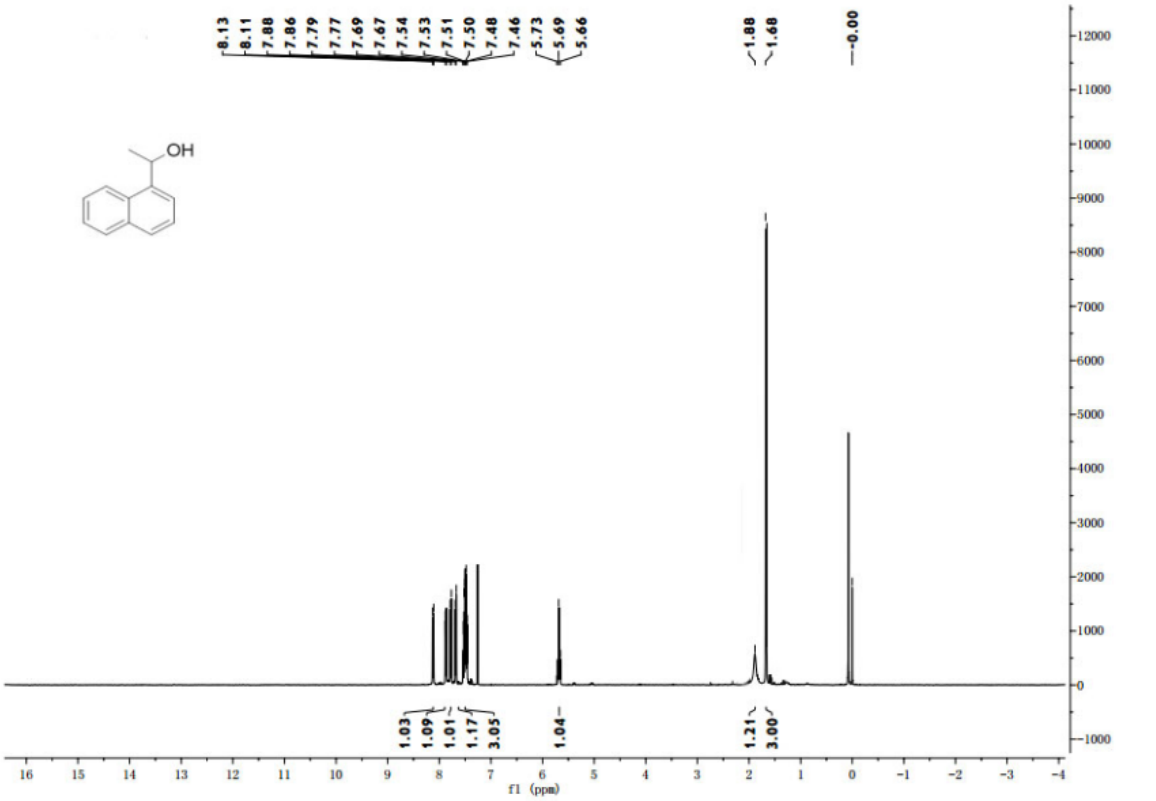
1.00
f1 (ppm)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7.67
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7.53
7.51
7.50
7.48
7.46
5.73
5.69
5.66
1.88
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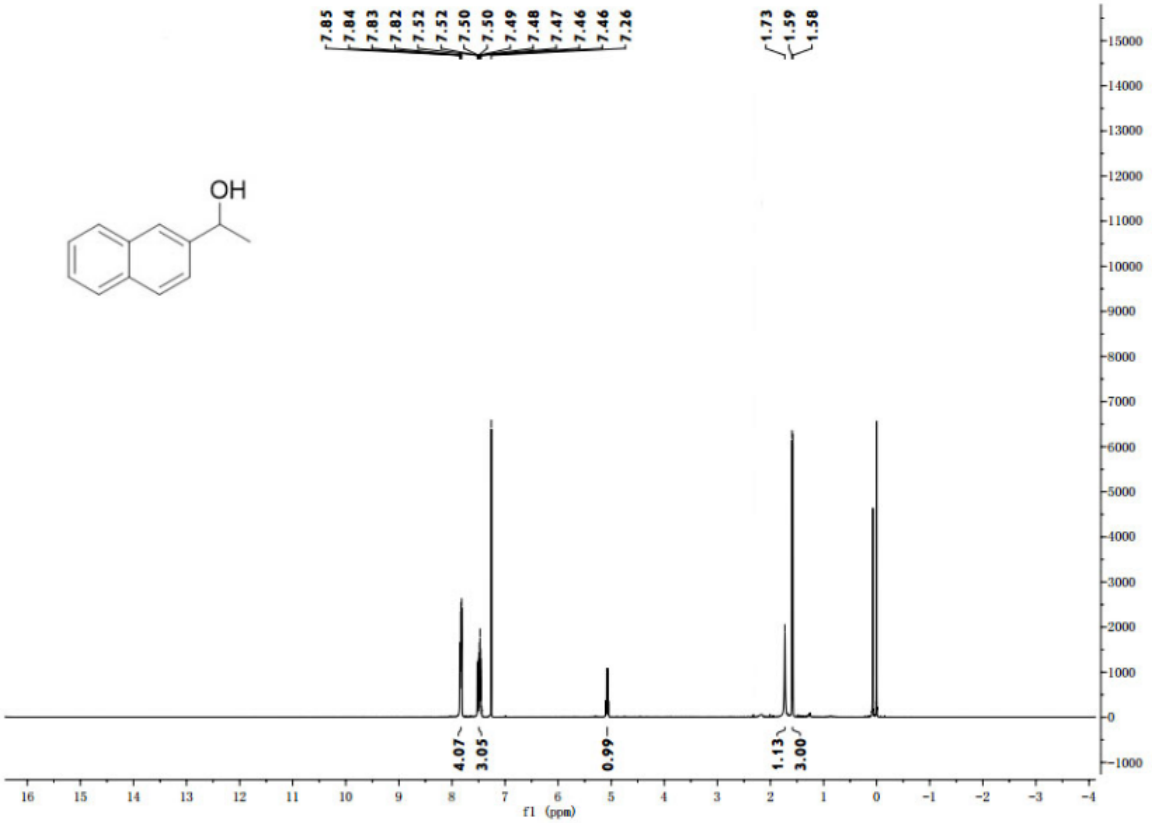
OH
1.03
1.09
1.01
1.17
3.05
1.04
1.21
3.00
f1 (ppm)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7.83
7.82
7.52
7.52
7.50
7.50
7.49
7.48
7.47
7.46
7.46
7.26
1.73
1.59
1.58
OH
4.07
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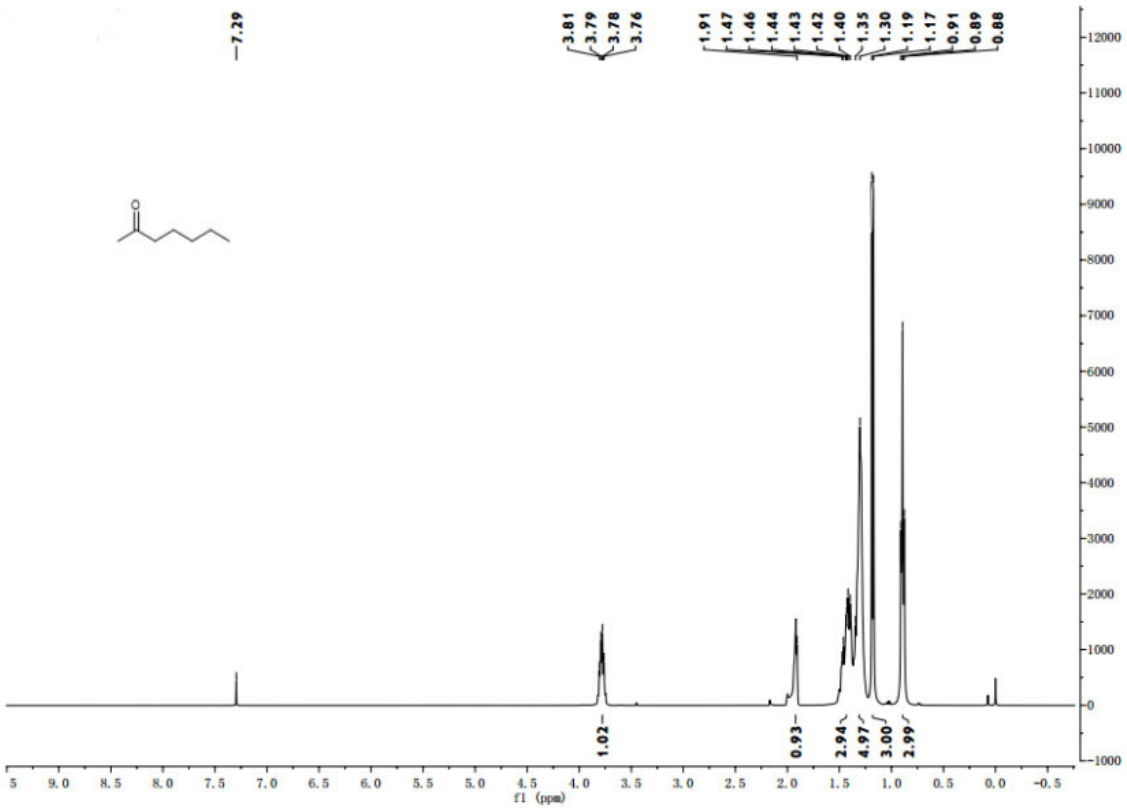
0.99
1.13
3.00
f1 (ppm)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3.76
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1.47
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1.44
1.43
1.42
1.40
1.35
1.30
1.19
1.17
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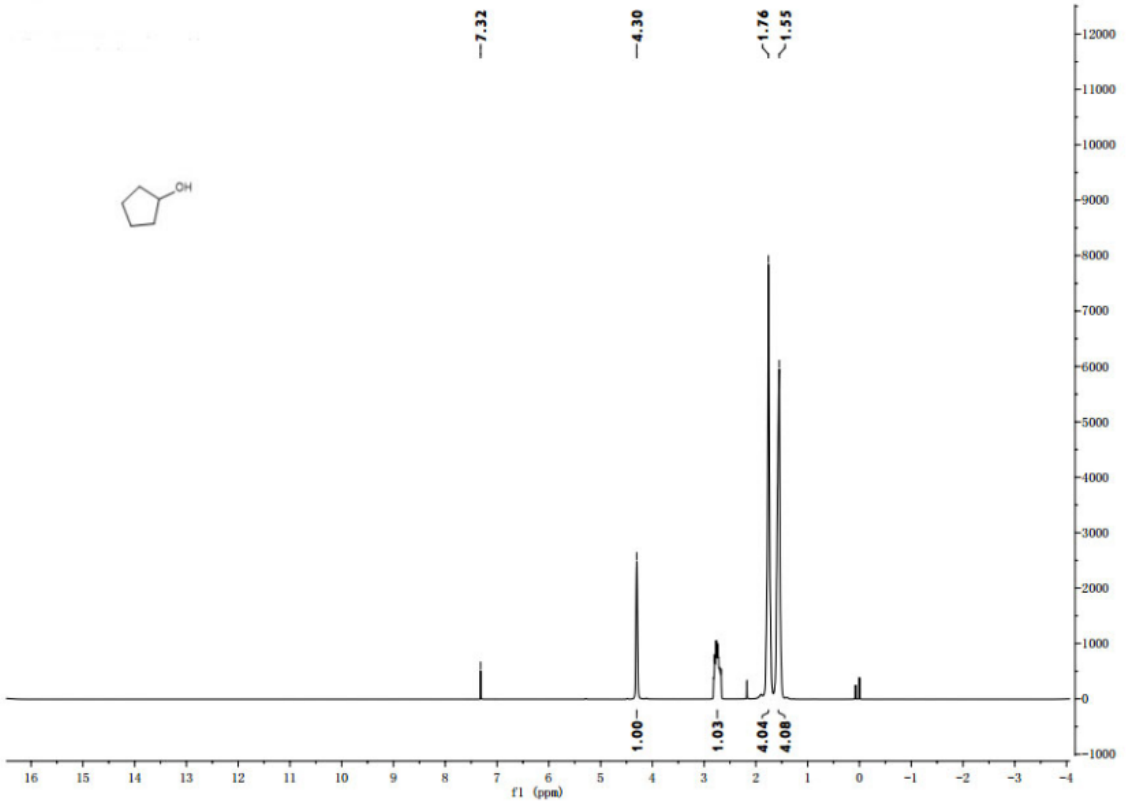
0.89
0.88
1.02
0.93
2.94
4.97
3.00
2.99
f1 (ppm)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4.08
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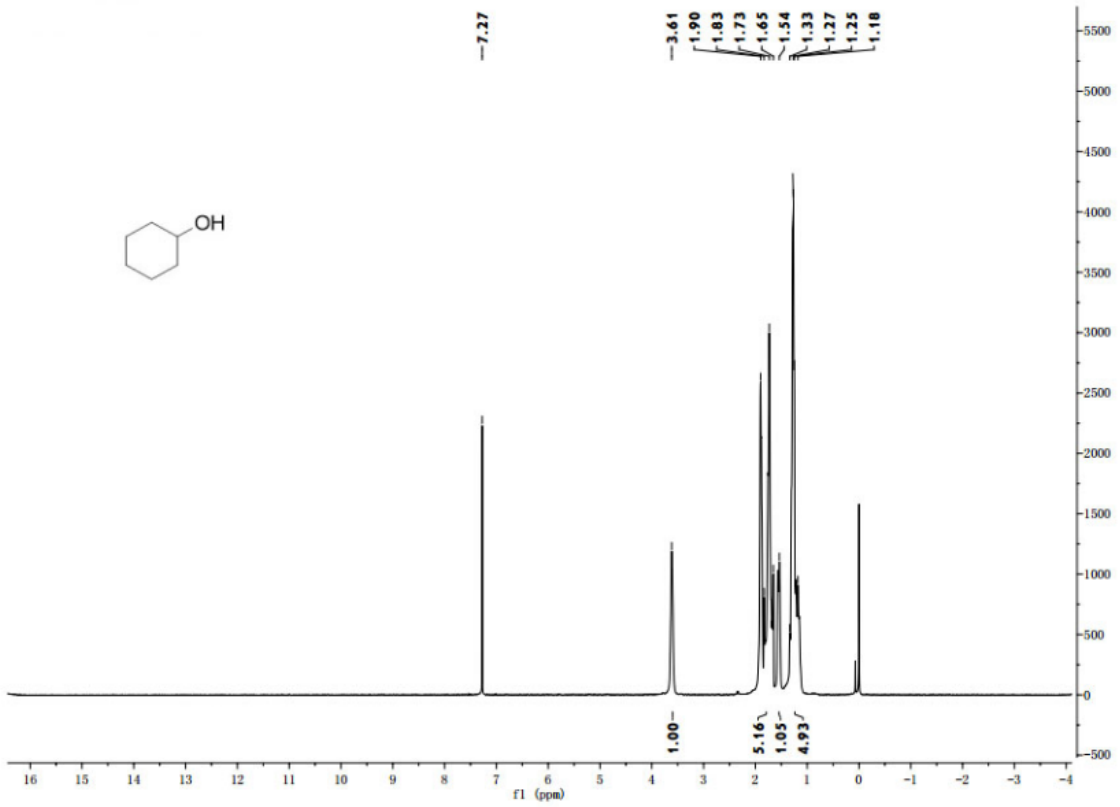
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1.33
1.27
1.25
1.18
OH
1.00
5.16
1.05
4.93
f1 (ppm)