Electronic Supplementary Material (ESI)

Supporting Information

Heterogeneous cobalt catalysts for selective oxygenation of alcohols to aldehydes, esters and nitriles

Fei Mao[a], Zhengliang Qi[a], Haipeng Fan[a], Dejun Sui[a], Rizhi Chen[a] and Jun Huang[a]*

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009 (P. R. China), Fax: (+86) 25-83172261; E-mail: junhuang@njtech.edu.cn

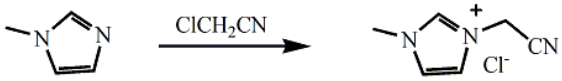
Experimental section

General Methods and Reagents

All reagents were purchased from Aladdin Reagent Company, Sigma-Aldrich Company and Alfa-Aesar Company and used without further purification. ^{1}H-NMR spectra were measured with a Bruker AVANCE 400D spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal reference. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKa radiations. X-ray diffraction (XRD) patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu Kα radiation source at 40 Kv and 20 mA, from 5^{o}C to 80^{o}C with a scan rate of 0.5 ^{o}C/min. The base pressure was about $3x10^{-9}$ mbar. SEM images were performed on a HITACHI S-4800 field-emission scanning electron microscope and TEM images were obtained using a JEOL JEM-2010 (200 kV) TEM instrument. BET surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed at 150 ^{o}C to vacuum of 10^{-3} Torr before analysis. The amount of Co was measured using a Jarrell-Ash 1100 ICP-AES spectrometer (Inductively Coupled Plasma-Atomic Emission Spectrometry).

The synthesis of [MCNIm]Cl

The ionic liquid [MCNIm]Cl was synthesized as following:



A mixture of 1-methylimidazole (8.21 g, 100 mmol) and $ClCH_2CN$ (9.06 g, 120 mmol) was stirred at room temperature for 24 hours, the solid could be formed in the process of reaction. The formed solid was then washed with diethyl ether (3*50 mL) and dried under vacuum for 24 hours. Finally, the [MCNIm]Cl was synthesized with 96% yield (15.1 g).

Procedure for the preparation of the Co@NC catalyst

The tyipcal procedure for the preparation of the catalysts is described as follows: A mixture of $Co(OAc)_2.4H_2O$ (0.249 g, 1.0 mmol) and [MCNIm]Cl (0.772 g, 3.0 mmol) in methanol was stirred for 30 minutes at room temperature. Then, the activated carbon powder (0.75 g) was added and the whole reaction mixture was stirred at 50 ^{o}C for 5 hours. The reaction mixture was cooled to room temperature and methanol was removed slowely under vacuum. The remaining solid sample obtained was dried at 60 ^{o}C for 12 hours. The dried sample was grinded to a powder. Then, the grinded powder was pyrolyzed at 500^{o}C -800 ^{o}C for 2-3 hours under nitrogen atmosphere. The Co@NC (800-2h) catalyst was pyrolyzed at 800 ^{o}C for 2 hours.

ICP-AES analysis of Co@NC (800-2h): Co = 5.95

XPS data of Co@NC (800-2h) (Atom%): C = 92.47, N = 2.86, O = 4.28, Co = 0.39

Characterization of the Co@NC (800-2h) catalyst

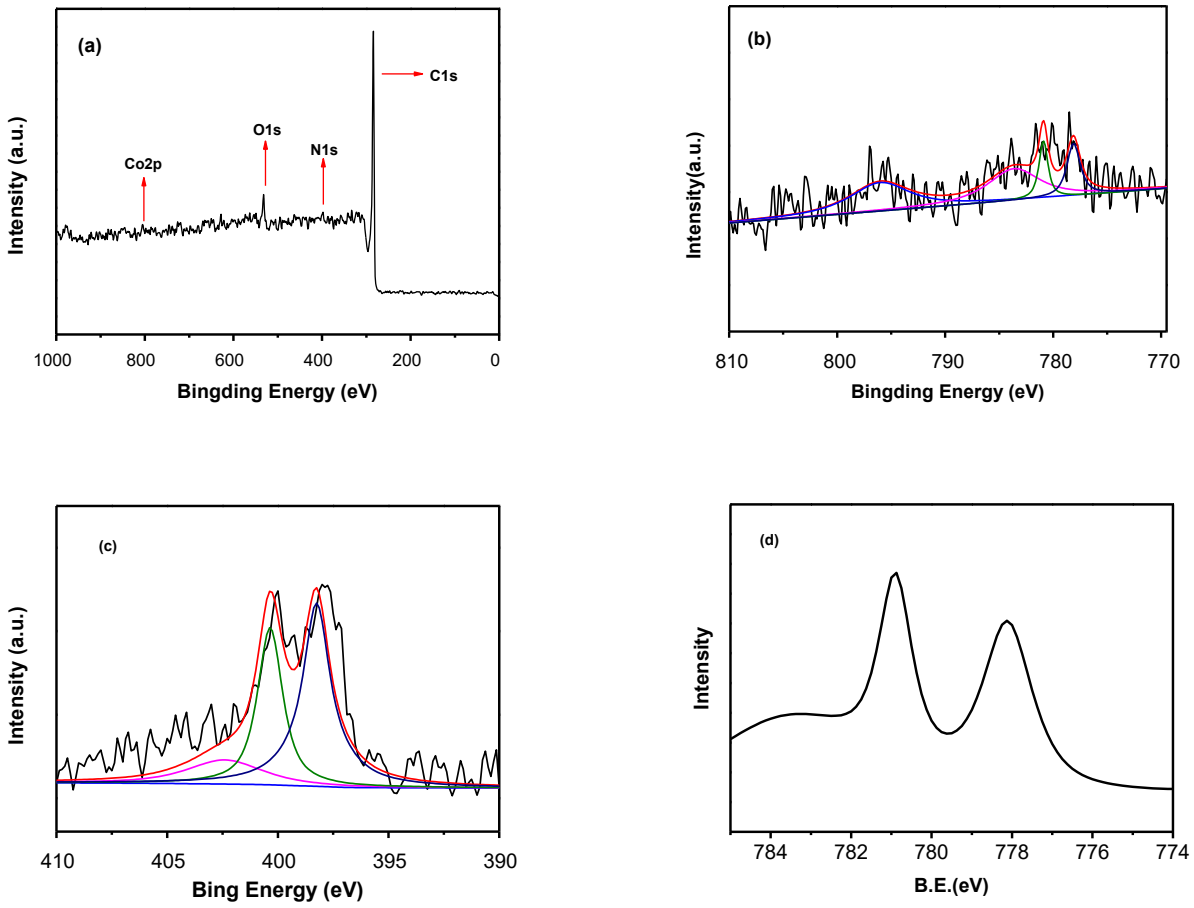


Figure S1. (a) XPS survey spectrum for Co@NC (800-2h). High-resolution XPS survey spectra of (b) Co 2p:780.91 eV is CoO, 778.12 eV is Co and (c) N 1s for Co@NC (800-2h):398.3 eV is pyridine-type nitrogen, 400.4 eV is pyrrole-type nitrogen,402.4 eV is carbon nitrogen. (d) A close look at the XPS spectrum of Co 2p in Co@NC (800-2h).

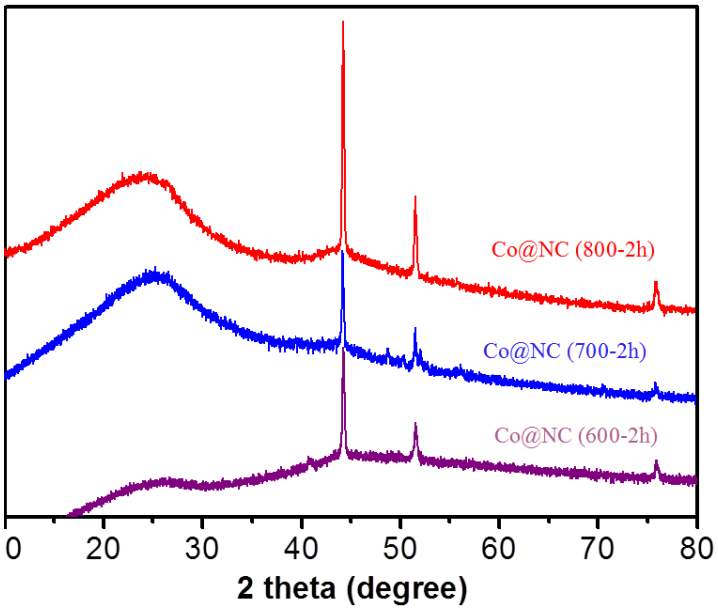


Figure S2A. XRD powder pattern of the active cobalt catalyst. The powder XRD patterns show weak broad peak at ~25° assigned to carbon from the organic moiety and three sharp characteristic peaks for metallic β-Co at 2θ = 44.38° (111), 51.60° (200) and 75.68° (220) (associated with standard JCPDS card no. 00-043-0806), while no peak assignable to CoO (standard JCPDS card no.00-071-1178) or Co_3O_4 species.

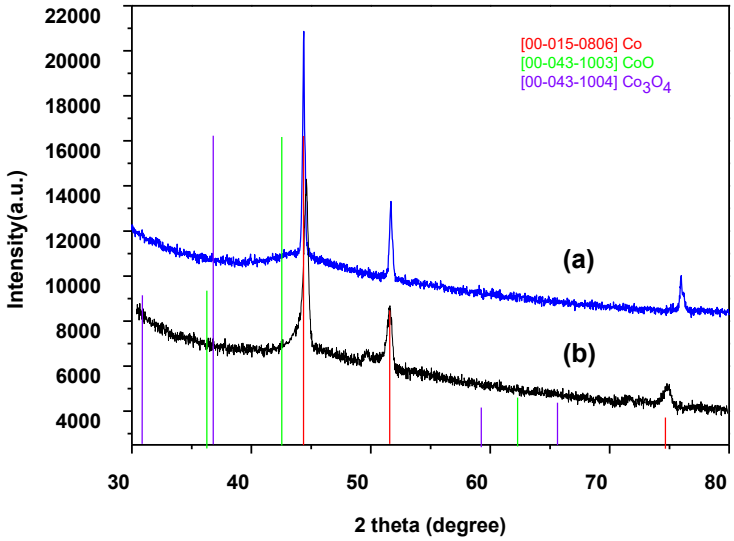


Figure S2B. The peak locations of Co@NC(800-2h) comparing with standard of Co/CoO/Co_3O_4 :(a) Co@NC(800-2h), (b) recycled Co@NC (800-2h).

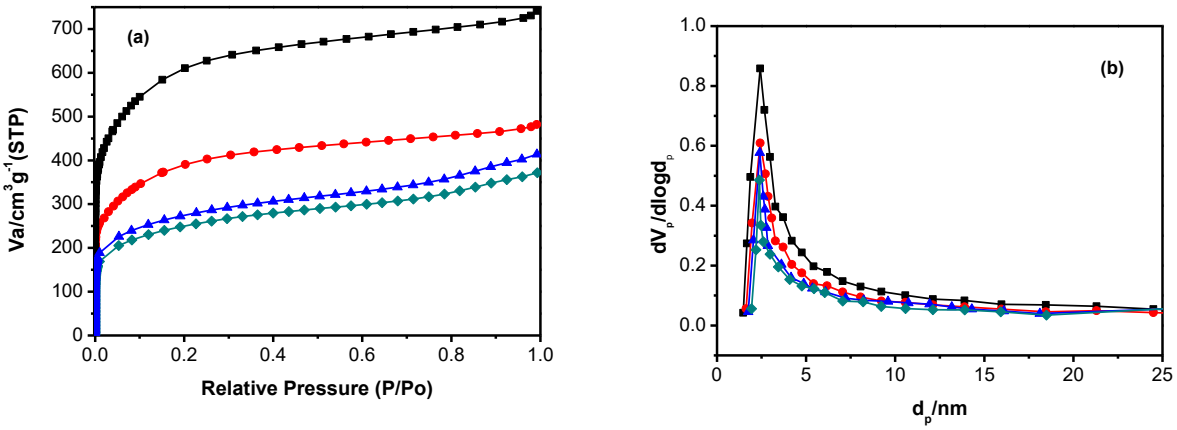


Figure S3. Nitrogen adsorption-desorption isotherms at 77 K (a) and corresponding pore size distribution curves (b) of AC(■), Co@NC (800) (●), Co@NC (700) (▲),and Co@NC (600) (◆).

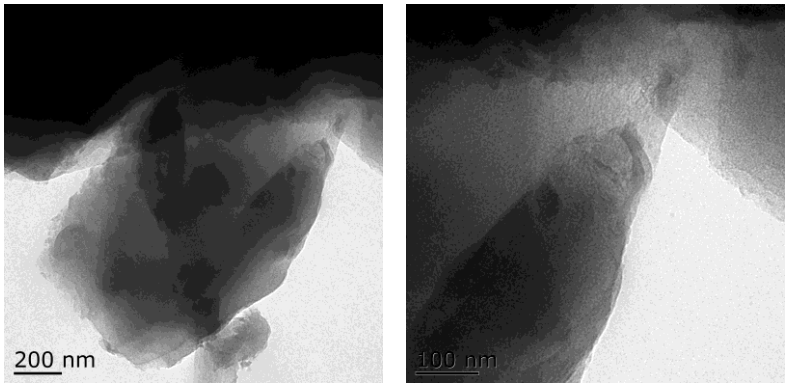


Figure S4. TEM images for Co@NC (800-2h).

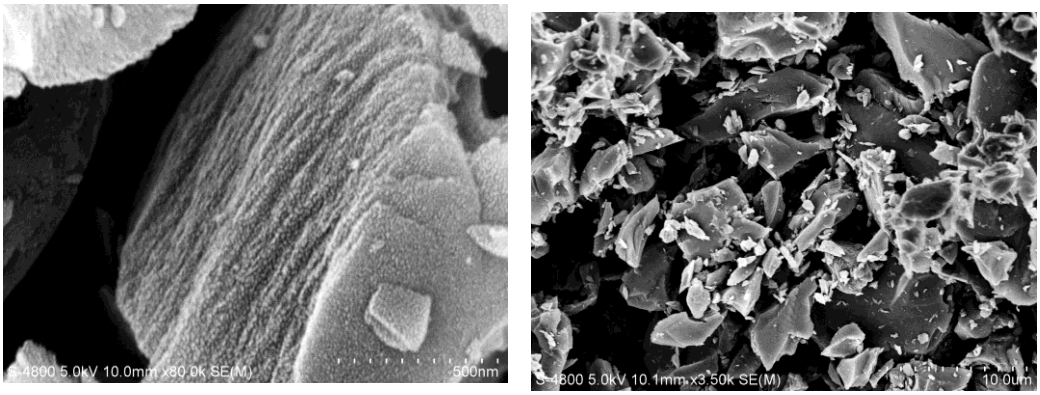
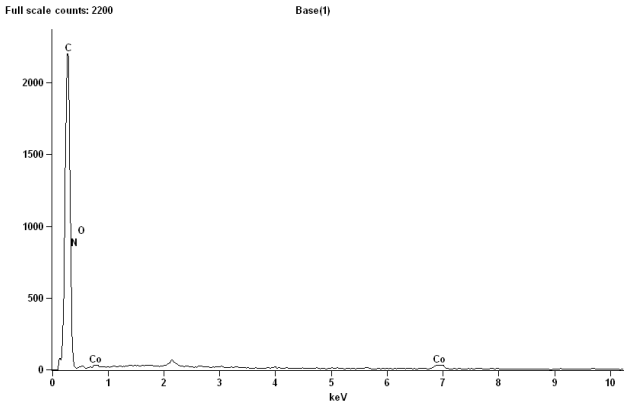


Figure S5. SEM images for Co@NC (800-2h)



Element Line	Weight %	Atom %
C K	85.84	89.05
N K	11.05	9.83
O K	0.80	0.63
CoK	2.3	0.49

Figure S6. EDX analysis for the Co@NC (800-2h)

Typical procedure for oxidative esterification of benzyl alcohol with methanol over Co catalyst (Table 1)

Benzyl alcohol (1.0 mmol), methanol (4.0 mL), K_2CO_3 (0.2 mmol) and Co catalyst containing Co 3.0 mol % were added into the oven dried Schlenk tube. Then, the Schlenk tube was evacuated, refilled with 1 bar O_2 and closed with septum. The Schlenk tube was stirred under 1 bar of O_2 at 60 ^{0}C for 20 h. After the reaction mixture was cooled to room temperature, the sample was analyzed by GC.

Typical procedure for the oxidative esterification of alcohols with methanol (Table 2)

Alcohols (1.0 mmol), methanol (4.0 mL), K_2CO_3 (0.2 mmol) and Co@NC(800-2h) catalyst containing Co 3.0 mol % were added into a Schlenk tube. Then, the Schlenk tube was evacuated, refilled with 1 bar O_2 and closed with septum. The Schlenk tube was stirred under 1 bar of O_2 at 60 ^{o}C for 20 h. After the reaction mixture was cooled to room temperature, the catalyst was separated and a sample of the liquid mixture was subjected to GC for analysis. The pure product was obtained by flash column chromatography (hexane and ethyl acetate).

Typical procedure for the oxygenation of alcohols to aldehydes (Table 3)

Alcohols (1.0 mmol), ethanol (2.0 mL), and Co@NC(800-2h) catalyst containing Co 5.0 mol % were added into a Schlenk tube. Then, the Schlenk tube was evacuated, refilled with 1 bar O_2 and closed with septum. The Schlenk tube was stirred under 1 bar of O_2 at 80 ^{o}C for 30 h. After the reaction mixture was cooled to room temperature, the catalyst was separated and a sample of the liquid mixture was subjected to GC for analysis (comparing with the commercial products). The pure product was obtained by flash column chromatography (hexane and ethyl acetate).

Typical procedure for the ammoxidation of alcohols to nitriles (Table 4)

Reactions were performed in a 30 mL stainless steel autoclave equipped with a stirring bar. Alcohols (1.0 mmol), *t*-amyl alcohol (2.0 mL), 200 µl of aq. NH_3 (30% NH_3 basis) and Co@NC(800-2h) catalyst containing Co 5.0 mol % were added into the autoclave. Then, the

autoclave was purged with O_2 three times, and pressurized to 5 bar O_2 and heated to 130 ^{o}C for 24 h. After the reaction mixture was cooled to room temperature, the catalyst was separated and a sample of the liquid mixture was subjected to GC for analysis (comparing with the commercial products). The pure product was obtained by flash column chromatography (hexane and ethyl acetate).

Recycling Procedure

Oxidative esterification of alcohols with methanol

Benzyl alcohol (1.0 mmol), methanol (4.0 mL), K_2CO_3 (0.2 mmol) and Co catalyst containing Co 3.0 mol % were added into the oven dried Schlenk tube. Then, the Schlenk tube was evacuated, refilled with 1 bar O_2 and closed with septum. The Schlenk tube was stirred under 1 bar of O_2 at 60 ^{0}C for 20 h. After the reaction mixture was cooled to room temperature, the sample was analyzed by GC. The catalyst Co@NC (800-2h) was was separated and washed with methanol. The recovered Co@NC (800-2h) was used again for the reaction under the same action conditions.

Oxygenation of alcohols to aldehydes

Benzyl alcohol (1.0 mmol), **ethanol** (2.0 mL), and Co@NC(800-2h) catalyst containing Co 5.0 mol % were added into the oven dried Schlenk tube. Then, the Schlenk tube was evacuated, refilled with 1 bar O_2 and closed with septum. The Schlenk tube was stirred under 1 bar of O_2 at 80 ^{o}C for 30 h. After the reaction mixture was cooled to room temperature, the sample was analyzed by GC. The catalyst Co@NC (800-2h) was separated and washed with ethanol. The recovered Co@NC (800-2h) was used again for the reaction under the same action conditions.

Ammoxidation of alcohols to nitriles

Reactions were performed in a 30 mL stainless steel autoclave equipped with a stirring bar. Benzyl alcohol (1.0 mmol), **t**-amyl alcohol (2.0 mL), 200 µl of aq. NH_3 (30% NH_3 basis) and Co@NC(800-2h) catalyst containing Co 5.0 mol % were added into the autoclave. Then, the autoclave was purged with O_2 three times, and pressurized to 5 bar O_2 and heated to 130 ^{o}C for 24 h. After the reaction mixture was cooled to room temperature, the sample was analyzed by GC. The catalyst Co@NC (800-2h) was separated and washed with *t*-amyl alcohol. The recovered Co@NC (800-2h) was used again for the reaction under the same action conditions.

The product data.

Methyl benzoate (Table 2, entry 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 132.7, 130.0, 129.4, 128.2, 51.9.

K. J. Jong, P. Y. Dae, K. D. Heon, K. Y. Jin, K. H. Kyun, L. S. Gyeong, C. S. Dong, L. W. Song, Y. Y. Jin, *Bull. Korean Chem. Soc.* **2004**, *25*, 501-505.

Methyl-4-methoxybenzoate (Table 2, entry 2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70-4.09 (m, 6H), 6.93 (d, *J* = 8.7Hz, 2H), 8.01 (d, *J* = 8.7Hz, 2H) ; ^{13}C NMR (100 MHz; $CDCl_3$) δ 166.8, 163.5, 131.6, 122.8, 113.7, 55.4, 51.7.

T. Mamoru, Y. Ken, S. Toshiaki, C. Naoto, *Chem. Commun.* **2011**, *47*, 2946-2948.

Methyl-3-methoxybenzoate (Table 2, entry 3)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (d, *J* = 26.0Hz, 6H), 7.11 (t, *J* = 1.9Hz, 1H), 7.36 (t, *J* = 7.8Hz, 1H), 7.63 (t, *J* = 26.6Hz, 2H) ; ^{13}C NMR (75 MHz; $CDCl_3$) δ 167.8, 160.4, 132.2, 130.2, 122.8, 120.3, 114.8, 56.2, 52.9.

T. Mamoru, Y. Ken, S. Toshiaki, C. Naoto, *Chem. Commun.* **2011**, *47*, 2946-2948.

Methyl 4-methylbenzoate (Table 2, entry 4)

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.95 (d, *J* = 4.1Hz, 3H), 7.27 (d, *J* = 6.4Hz, 2H), 7.80-7.98 (m, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.1, 143.5, 129.6, 129.1, 127.5, 51.9, 21.6.

W. J. Eun, K. H. Kyun, K. J. Jong, Y. H. Seup, K. M.Jung, K. S. Beom, C. H. A., L. S. Gyeong, Y. Y. Jin, *Tetrahedron* **2007,** *63*, 12720–12730.

Methyl 3-methylbenzoate (Table 2, entry 5)

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.93 (s, 3H), 7.35-7.40 (m, 2H), 7.87 (t, *J* = 8.0Hz, 2H) ; ^{13}C NMR (75 MHz; $CDCl_3$) δ 167.5, 138.3, 133.9, 130.3, 130.3, 128.4, 126.9, 52.2, 21.4.

P. Koos, U. Gross, A. Polyzos, M. O'Brien, I. Baxendale, S. V. Ley, *Org. Biomol. Chem.* **2011**, *9*, 6903-6908.

Methyl 2-methylbenzoate (Table 2, entry 6)

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (s, 3H), 3.92 (s, 3H), 7.25 (d, *J* = 6.0Hz, 2H), 7.42 (t, *J* = 7.4Hz, 1H), 7.93 (d, *J* = 7.7Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 167.7, 139.9, 131.7, 131.4, 130.3, 129.2, 125.4, 51.5, 21.5.

W. X. Feng, C. Darcelli, *Eur. J. Org. Chem.* **2009**, *8*, 1144-1147.

Methyl 4-nitrobenzoate (Table 2, entry 7)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98 (s, 3H), 8.24 (s, 4H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 165.4, 150.7, 135.7, 130.9, 123.7, 53.0.

W. J. Eun, K. H. Kyun, K. J. Jong, Y. H. Seup, K. M.Jung, K. S. Beom, C. H. A., L. S. Gyeong, Y. Y. Jin, *Tetrahedron* **2007,** *63*, 12720–12730.

Methyl 4-fluorobenzoate (Table 2, entry 8)

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.95 (s, 3H), 7.12-7.17 (m, 2H), 8.07-8.11 (m,2H); ^{13}C NMR (75

MHz; $CDCl_3$) δ 166.3, 166.0, 132.3, 126.6, 115.7, 52.4.
C. Liu, J. Wang, L. k. Meng, Y. Deng, Y. Li, A. W. Lei, *Angew. Chem., Int. Ed.* **2011**, *50*, 5144-5148.

Methyl 4-chlorobenzoate (Table 2, entry 9)
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (t, *J* = 7.5Hz, 3H),7.43 (d, *J* = 8.5Hz, 2H), 7.99 (d, *J* = 8.5Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 166.5, 139.6, 131.2, 128.9, 52.5.
R, Lerebours,C. Wolf, *J. Am. Chem. Soc.* **2006**, *128*, 13052-13053 .

Methyl 4-bromobenzoate (Table 2, entry 10)
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.94 (t, *J* = 8.3Hz, 3H) 7.60 (d, *J* = 8.2Hz, 2H), 7.92 (d, *J* = 8.2Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 166.5, 132.0, 131.3, 129.3, 128.3, 52.7.
R, Lerebours,C. Wolf, *J. Am. Chem. Soc.* **2006**, *128*, 13052-13053 .

Methyl 2-fluorobenzoate (Table 2, entry 11)
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (t, *J* = 7.6Hz, 3H), 7.14-7.25 (m, 2H), 7.52-7.57 (m, 1H), 7.94-7.98 (m, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 164.9, 163.0, 160.9, 134.5, 132.2, 124.0, 118.7, 117.0, 77.3, 52.3.
V. L. Rendina, J. S. Kingsbury, *J. Org. Chem.* **2012**, *77*, 1181-1185.

Methyl 2-chlorobenzoate (Table 2, entry 12)
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.97 (s, 3H), 7.31-7.36 (m, 1H), 7.43-7.50 (m, 2H), 7.85-7.87 (m, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 166.1, 133.6, 132.4, 131.3, 131.0, 30.1, 126.5, 52.3.
P. Dawar, M. B. Raju, R. A. Ramakrishna, *Tetrahedron Letters* **2011**, *52*, 4262-4265.

Methyl 2-bromobenzoate (Table 2, entry 13)
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (t, J = 7.8Hz, 3H), 7.29-7.39 (m, 2H),7.68 (d, J = 7.3Hz, 1H), 7.80 (d, J = 5.5Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 166.6, 134.3, 132.5, 132.2, 131.3, 127.1, 121.6, 52.4.
H. Shin-ichi; N. Tomoya, T. Norihiro, M. Tsuyoshi, I. Akichika, *Org. Lett.* **2010**, *12*, 3645-3647.

Methyl 3,4-methylenedioxybenzoate (Table 2, entry 14)
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 3H), 6.07 (s, 2H), 6.87 (d, J = 8.2Hz, 1H), 7.51 (d, J = 1.5H,1H), 7.68-7.70 (m, 1H); ^{13}C NMR (75 MHz; CDCl3) δ 166.7, 153.2, 146.8, 125.1, 124.7, 109.3, 108.2, 101.0, 52.5.
J. Wielens, S. J. Headey, J. J. Deadman, D. I. Rhodes, M. W. Parker, D. K. Chalmers, M. J. Scanlon, *ChemMedChem* **2011**, *6*, 258-261.

Methyl 1-naphthalenecarboxylate (Table 2, entry 15)
^{1}H NMR (400 MHz, CDCl3): δ 4.04 (s, 3H), 7.51-7.67 (m, 3H), 7.91 (d, J = 8.0Hz, 1H), 8.05 (d, J = 8.1Hz, 1H), 8.22 (d, J = 7.0Hz, 1H), 8.94 (d, J = 8.6Hz, 1H) ; ^{13}C NMR (75 MHz; CDCl3) δ 168.5, 134.1, 133.7, 131.6, 130.5, 128.8, 128.4, 127.5, 126.1, 124.8, 52.4.
H. Shin-ichi; N. Tomoya, T. Norihiro, M. Tsuyoshi, I. Akichika, *Org. Lett.* **2010**, *12*, 3645-3647.

Methyl 3-phenyl-2-propenoate (Table 2, entry 16)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.47 (d, J = 16.1Hz, 1H), 7.41 (d, J = 2.8Hz, 3H), 7.54 (s, 2H), 7.72 (d, J = 16.0Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 168.0, 145.3, 134.8, 130.7, 129.3, 128.5, 118.2, 52.2.

C. Liu, J. Wang, L. k. Meng, Y. Deng, Y. Li, A. W. Lei, *Angew. Chem., Int. Ed.* **2011**, *50*, 5144-5148.

Methyl 2-furancarboxylate (Table 2, entry 17)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 6.46-6.58 (m, 1H), 7.20 (d, J = 32.2Hz, 1H), 7.58 (d, J = 7.9Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 159.4, 146.5, 144.8, 118.2, 112.1, 52.1.

C. Liu, J. Wang, L. k. Meng, Y. Deng, Y. Li, A. W. Lei, *Angew. Chem., Int. Ed.* **2011**, *50*, 5144-5148.

Methyl 3-pyridinecarboxylate (Table 2, entry 18)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (s, 3H), 7.14-7.25 (m, 2H), 7.52-7.57 (m, 1H), 7.94-7.98 (m, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 165.6, 153.3, 150.8, 136.9, 125.9, 123.2, 52.3.

K. Luba, G. Dmitri, R. B. Karola, *J. Org. Chem.* **2010**, 695, 260–266.

Methyl 2-pyridinecarboxylate (Table 2, entry 19)

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (s, 3H), 7.54 (t, J = 5.0Hz, 1H), 7.90 (t, J= 8.0Hz, 1H),8.17 (d, J = 7.8Hz, 1H), 8.79 (d, J = 4.5Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 165.6, 149.7, 147.9, 137.2, 127.1, 125.8, 52.7.

H. Shin-ichi; N. Tomoya, T. Norihiro, M. Tsuyoshi, I. Akichika, *Org. Lett.* **2010**, *12*, 3645-3647.

Benzaldehyde (Table 3, entry 1)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (t, J = 7.6Hz, 2H), 7.64 (t, J = 7.5Hz, 1H), 7.90 (d, J = 6.8Hz, 2H), 10.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 192.3, 135.5, 133.3, 128.6, 128.0.

L. Masataka, M. Katsuhiko, T. Hideo, *Tetrahedron* **2013**, *69*, 2961-2970.

4-Methylbenzaldehyde (Table 3, entry 2)

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.36 (d, J = 8.0Hz, 2H), 7.80 (d, J = 8.1Hz, 2H), 9.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 191.9, 145.5, 134.1, 129.8, 129.6, 21.2.

B. Jiang, S. J. Tu, P. Kaur, W. Wever, G. G. Li, *J. Am. Chem. Soc.* **2009**, *131*, 11660-11661.

3-Methylbenzaldehyde (Table 3, entry 3)

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.40-7.45 (m, 2H), 7.68 (d, J = 6.4Hz, 2H), 9.99 (s, 1H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 192.1, 139.1, 135.5, 130.0, 129.2, 21.3.

H. Takuya, O. Masato, K. Taichi, M.Keiji, *Org. Lett.***2007**, *9*, 4805-4808.

4-Nitrobenzaldhyde (Table 3, entry 4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.7Hz, 2H), 8.42 (d, J = 8.6Hz, 2H), 10.20 (s, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 190.3, 151.1, 139.9, 130.4, 124.2.

L. Masataka, M. Katsuhiko, T. Hideo, *Tetrahedron* **2013**, *69*, 2961-2970.

4-F1uorobenzaldehyde (Table 3, entry 5)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (t, J = 8.6Hz, 2H), 7.92-7.95 (m, 2H), 9.99 (s, 1H) ; ^{13}C NMR

(100 MHz, $CDCl_3$): *δ* 192.3, 167.3, 138.1, 133.2, 129.6.
F. Takeru, K. H. Martin, R. Tobias, *Angew. Chem., Int. Ed.* **2008**, 47, 5993-5996.

4-Chlorobenzaldehyde (Table 3, entry 6)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 10.2Hz, 2H), 7.84 (d, J = 8.4Hz,2H), 10.01 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 190.3, 140.3, 134.1, 130.2, 128.9.
L. Masataka, M. Katsuhiko, T. Hideo, *Tetrahedron* **2013**, *69*, 2961-2970.

4-Bromobenzaldehyde (Table 3, entry 7)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4Hz, 2H), 7.77 (d, J = 1.7Hz,2H), 10.01 (s, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 191.0, 135.1, 132.4, 130.9, 129.7.
L. Masataka, M. Katsuhiko, T. Hideo, *Tetrahedron* **2013**, *69*, 2961-2970.

4-Methoxybenzaldehyde (Table 3, entry 8)
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 3H), 7.00 (d, J = 8.8Hz, 2H), 7.82-7.85 (m, 2H), 9.88 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 190.7, 164.5, 131.9, 129.9, 114.2, 55.5.
L. Masataka, M. Katsuhiko, T. Hideo, *Tetrahedron* **2013**, *69*, 2961-2970.

2-Methoxybenzaldehyde (Table 3, entry 9)
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.93 (s, 3H), 6.99 (m, 2H), 7.54-7.82 (m, 1H), 7.83 (d, J = 1.8Hz, 1H), 10.48 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 160.2, 137.9, 130.1, 123.6, 121.6, 112.1, 55.6.
N. P. G. Laura, C. G. Deysi, L. R. Leticia, *Molecules* **2009**, *14*, 4065-4078.

Benzophenone (Table 3, entry 10)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (m, 4H), 7.62 (m, 2H), 7.85 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 196.7, 137.5, 132.3, 129.9, 128.2.
L. Masataka, M. Katsuhiko, T. Hideo, *Tetrahedron* **2013**, *69*, 2961-2970.

Cinnamaldehyde (Table 3, entry 11)
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.72-6.77 (m, 1H), 7.44-7.52 (m, 4H), 7.58-7.60 (m, 2H), 9.73 (d, J = 7.7Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.5, 152.6, 133.81, 131.1, 128.9, 128.4, 128.3.
N. Jiang, A. J. Ragauskas, *Org. Lett.* **2005**, *7* , 3689–3692.

Furfuraldehyde (Table 3, entry 12)
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60-6.61 (m, 1H), 7.25 (d, J = 3.7Hz, 1H), 7.69 (t, J = 0.8Hz ,1H), 9.66 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 177.8, 153.6, 148. 1, 121.6, 113.1.
D. Alexander, *Org. Lett.* **2005**, *7*, 2913-2915.

2-Pyridinecarboxaldehyde (Table 3, entry 13)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.53 (m, 1H), 7.85-7.89 (m, 1H), 7.95 (d, J = 7.8Hz, 1H), 8.78 (d, J = 4.7Hz, 1H), 10.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3. 152.7, 7 150.2, 137.2, 128.0, 121.8.
V. Subbarayan, A. Muneer, T. Punniyamurthy, *Org. Lett.* **2004**, *6*, 4821-4824.

Benzonitrile (Table 4, entry 1)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.61 (m, 5H); ^{13}CNMR ($CDCl_3$, 100 MHz) : δ132.15, 131.34, 128.49, 118.12, 111.57.

E. C. Wang, K. S. Huang, H. M. Chen, C. C. Wu, G. J. Lin, *J. Chin. Chem. Soc.* **2004**, *51*, 619-627.

1-Cyanonaphthalene(Table 4, entry 2)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (t, J = 7.4Hz, 1H), 7.64-7.67 (m, 1H),7,71-7.74 (m, 1H), 7.93-7.96 (m, 2H), 8.10 (d, J = 8.4Hz, 1H), 8.27 (d, J = 8.4Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 133.2, 132.9, 132.6, 132.3, 128.6, 128.5, 127.5, 125.1, 124.9, 117.8, 110.1.

M. Hatsuda, M. Seki, *Tetrahedron*,**2005**, *61*, 2005, 9908–9917.

4-Methylbenzonitrile(Table 4, entry 3)

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.30 (d, J = 8.0Hz, 2H), 7.57 (d, J = 8.2Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.30, 131.50, 129.44, 118.65, 108.79, 21.29.

E. C. Wang, K. S. Huang, H. M. Chen, C. C. Wu, G. J. Lin, *J. Chin. Chem. Soc.* **2004**, *51*, 619-627.

3-Methylbenzonitrile(Table 4, entry 4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.37-7.40 (m, 1H), 7.44 (d, J = 7.7Hz, 1H), 7.49 (d, J = 5.2Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2, 134.1, 132.7, 129.5, 119.3, 112.2, 20.8.

M. Takashi, K. Tomoko, S. Masanori, H. Kiminori, S. Masami, F. Tsutomu, *Heterocycles* **2011***, 83*, 163-169.

2-Methylbenzonitrile (Table 4, entry 5)

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (s, 3H), 7.28-7.31 (m, 1H), 7.34 (d, J = 7.8Hz, 1H), 7.49-7.53 (m, 1H), 7.61 (d, J = 7.8Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.9, 132.6, 132.5, 130.2, 126.2, 118.1, 112.7, 20.4.

O. Grossman, D. Gelman, *Org. Lett.* **2006**, *8* , 1189–1191.

4-Nitrobenzonitrile (Table 4, entry 6)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, J = 8.8Hz, 2H), 8.39 (d, J = 8.8Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2, 133.4,124.5, 118.6, 116.3.

E. C. Wang, K. S. Huang, H. M. Chen, C. C. Wu, G. J. Lin, *J. Chin. Chem. Soc.* **2004**, *51*, 619-627.

4-Fluorobenzonitrile (Table 4, entry 7)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19-7.23 (m, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ167.6, 162.5, 134.8, 134.6, 118.0, 117.1, 116.6, 108.6, 108.5.

S. Enthaler, *Eur. J. Org. Chem.* **2011**, *25,* 4760–4763.

4-Chlorobenzonitrile (Table 4, entry 8)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J = 8.5Hz, 2H), 7.63 (d, J = 8.5Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 139.6, 133.3, 130.0 , 118.0, 110.8.

M. Hatsuda, M. Seki, *Tetrahedron*,**2005**, *61*, 2005, 9908–9917.

4-Bromobenzonitrile (Table 4, entry 9)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.5Hz, 2H), 7.67 (d, J = 8.5Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 133.4, 132.7, 128.1, 118.1, 111.2.
S. Enthaler, *Eur. J. Org. Chem.* **2011**, *25,* 4760–4763.

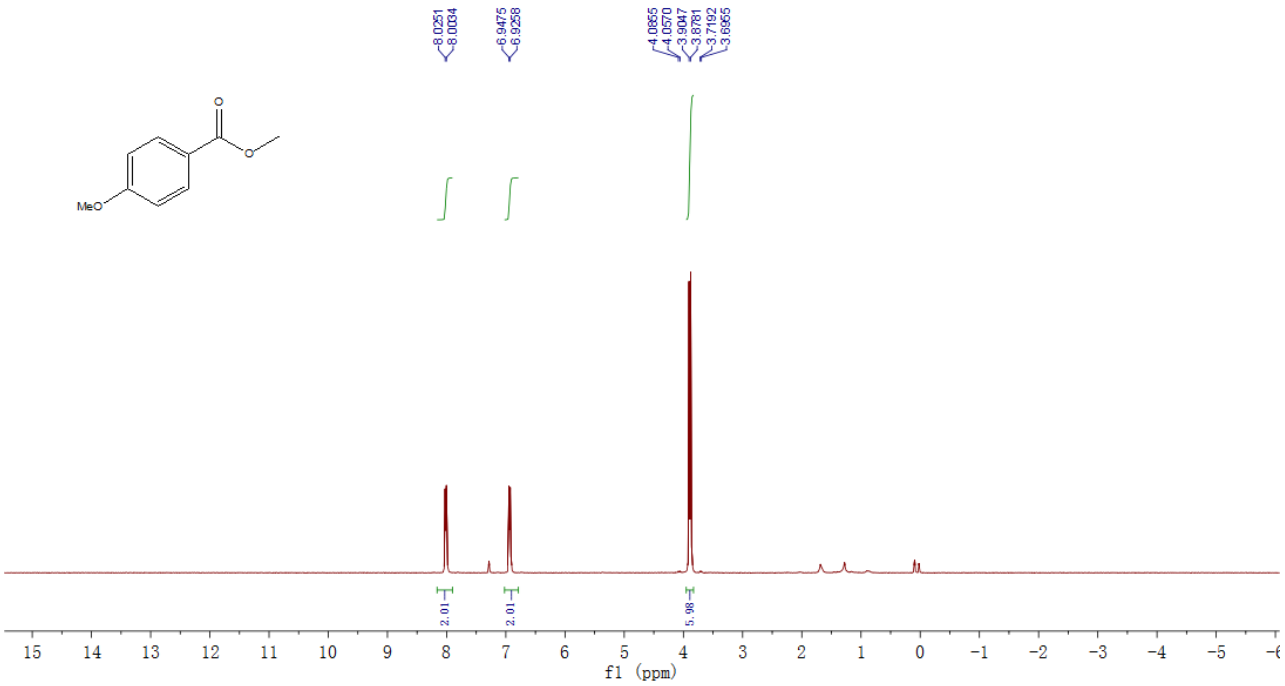
2-Chlorobenzonitrile (Table 4, entry 10)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.43 (m, 1H), 7.54-7.60 (m, 2H), 7.70-7.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 136.8, 134.02, 133.96, 130.1, 116.0, 113.4.
J. T. Zhang, Z. T. Wang, Y. Wang, C. F. Wan, X. Q. Zheng, Z. Y. Wang, *Green Chem.* **2009**, *11*, 1973–1978.

2-Bromobenzonitrile (Table 4, entry 11)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.52 (m, 2H), 7.68-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 134.6, 134.4, 133.2, 127.6, 125.1, 117.0, 115.7.
S. Chiba, L. Zhang, G. Y. Ang, B. W. Q. Hui, *Org. Lett.* **2010**, *12*, 2052–2055.

4-Methoxybenzonitrile (Table 4, entry 12)
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (s, 3H), 6.98 (d, J = 8.9Hz, 2H), 7.61 (d, J = 8.9Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.9, 134.0, 119.2, 114.8, 104.0, 55.6.
M. Hatsuda, M. Seki, *Tetrahedron*,**2005**, *61*, 2005, 9908–9917.

3-Methoxybenzonitrile (Table 4, entry 13)
^{1}H NMR (500 MHz, $CDCl_3$): δ3.87 (s, 3H), 7.15-7.17 (m, 2H), 7.26 (d, J = 7.9Hz, 1H), 7.39-7.42 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 160.1, 130.3, 122.5, 119.2, 118.1, 126.5, 52.6.
A. V. Ushkov, V. V. Grushin, *J. Am. Chem. Soc.* **2011**, *133,* 10999–11005.

Cinnamonitrile (Table 4, entry 14)
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.72-5.77 (m, 1H), 7.44-7.52 (m, 4H), 7.58-7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*150.6, 133.6, 131.3, 129.2, 127.4, 118.2, 96.4
S. Enthaler, *Eur. J. Org. Chem.* **2011**, *25,* 4760–4763.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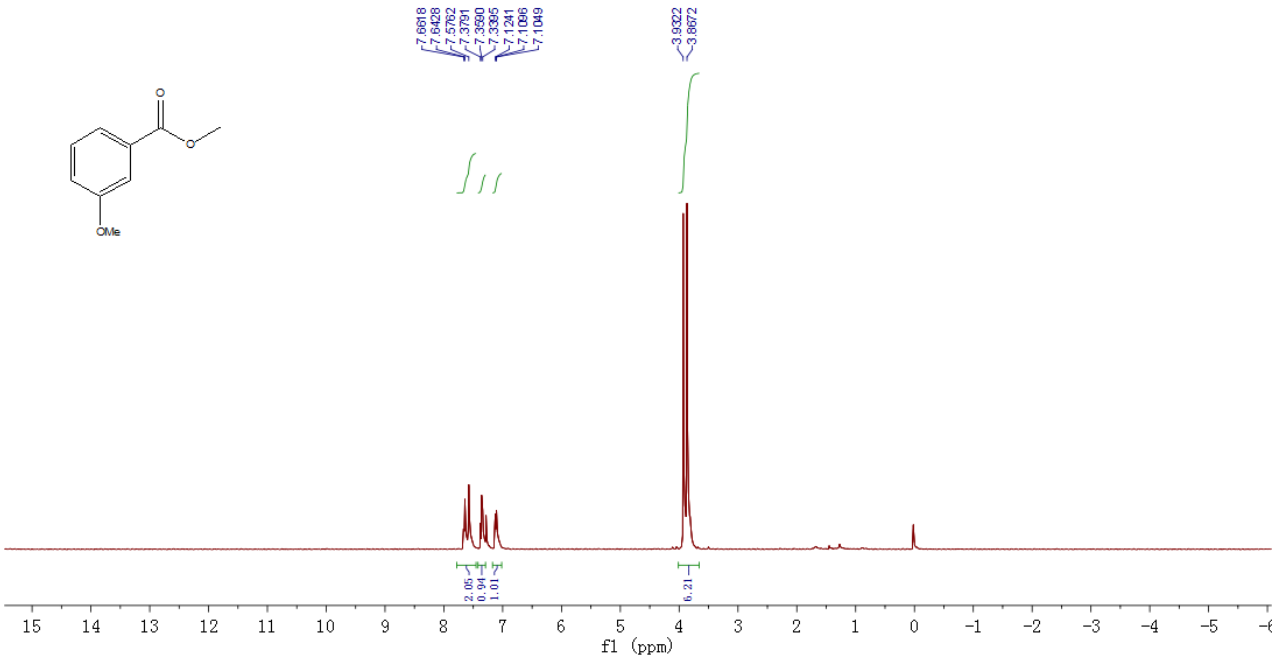
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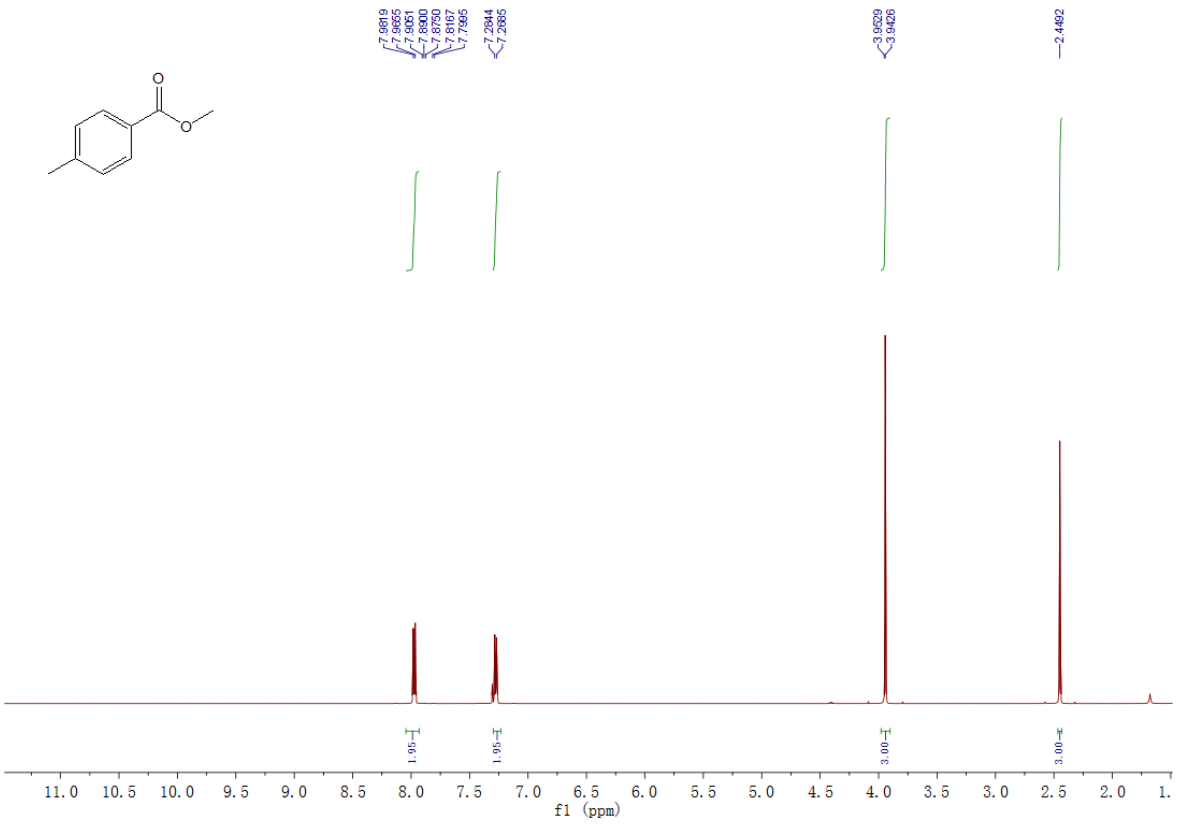
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1.95
3.00
3.00
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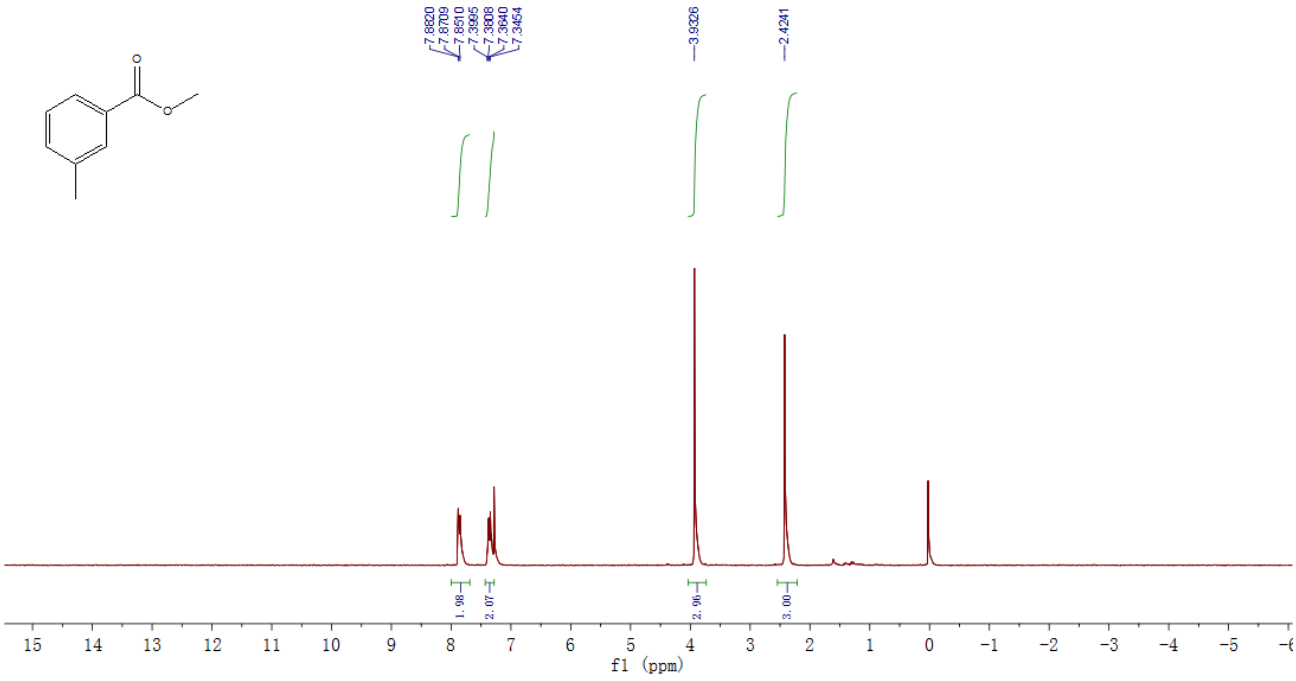
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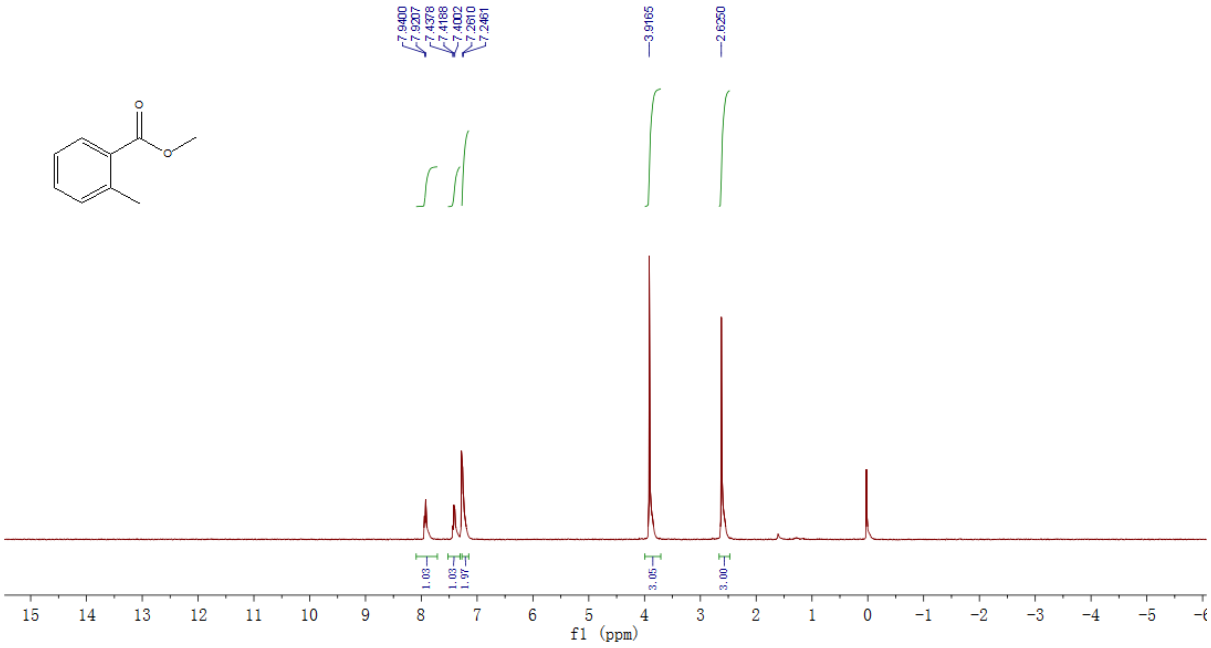
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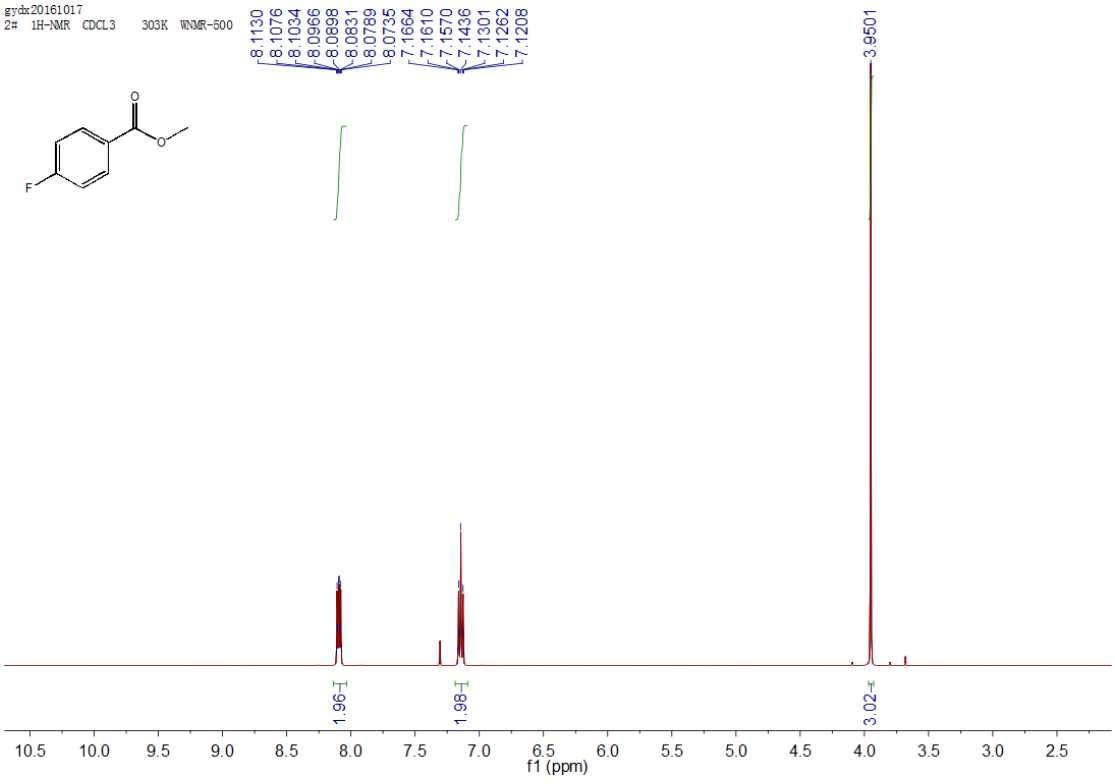
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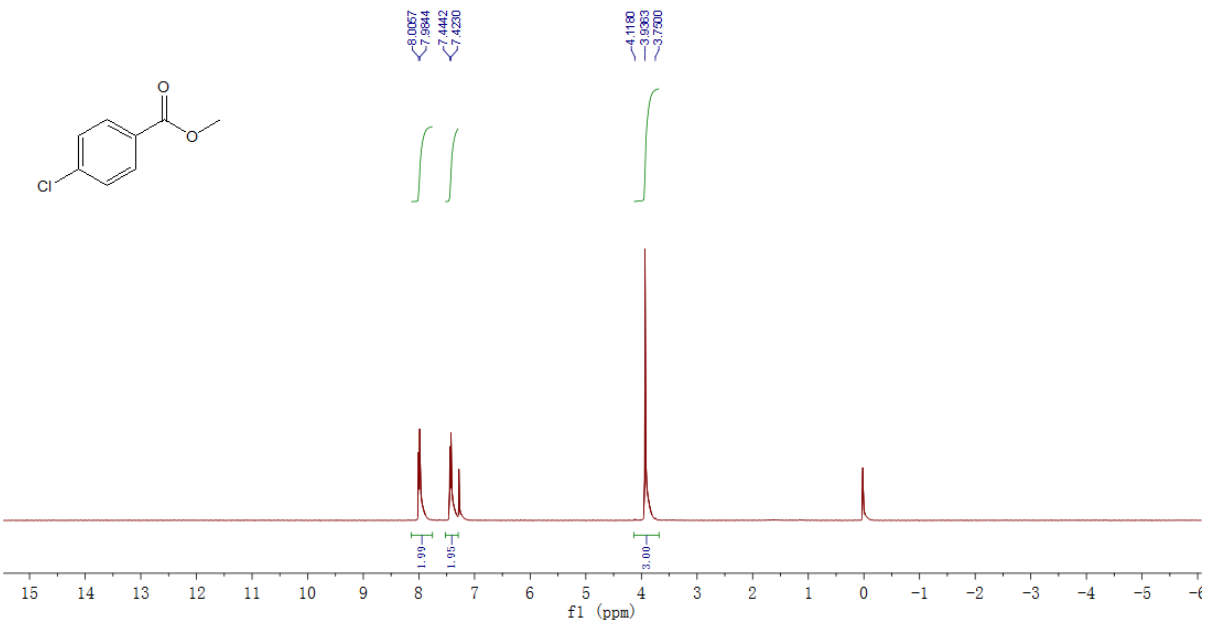
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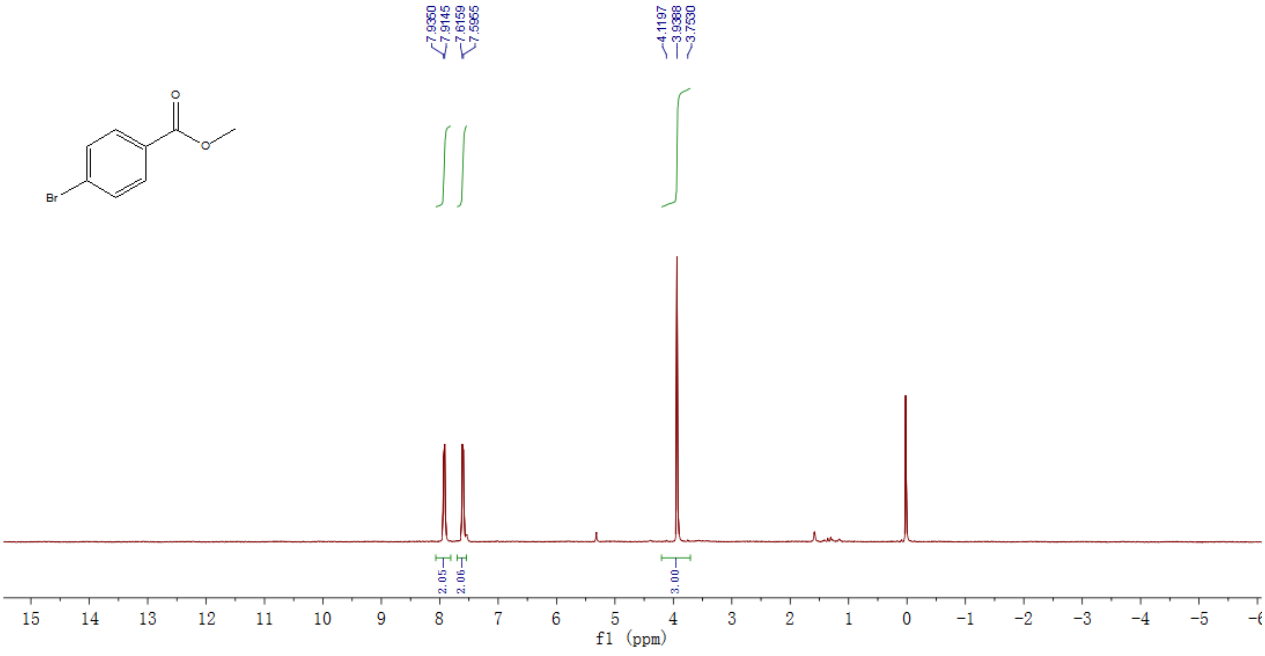
f1 (ppm)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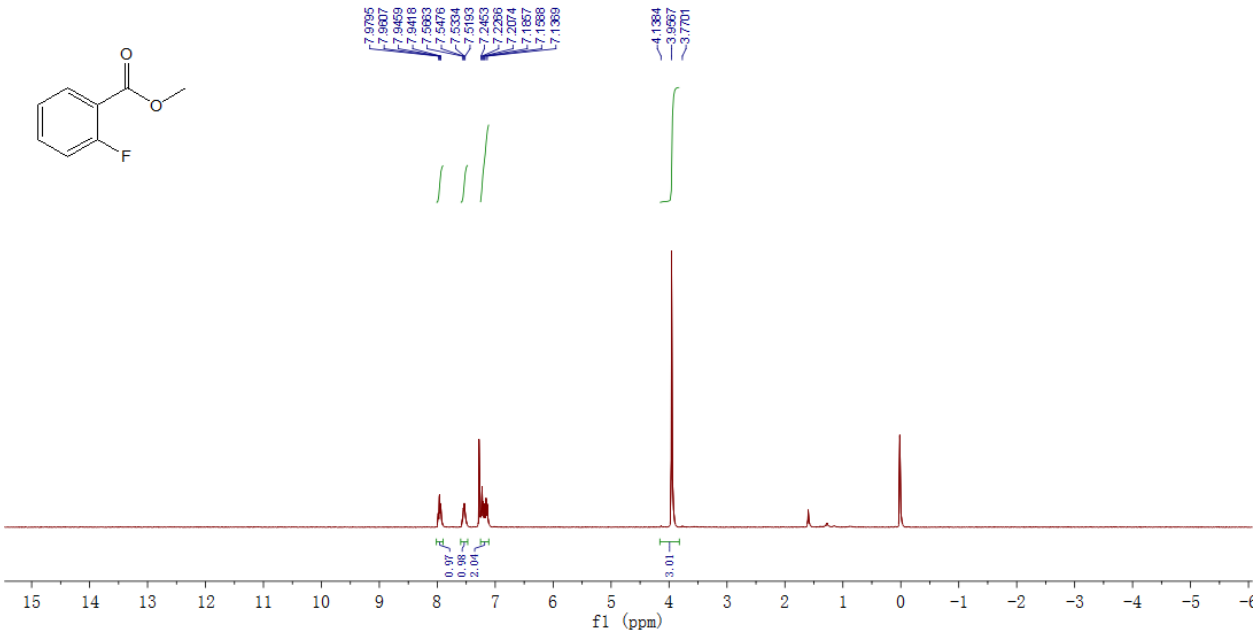
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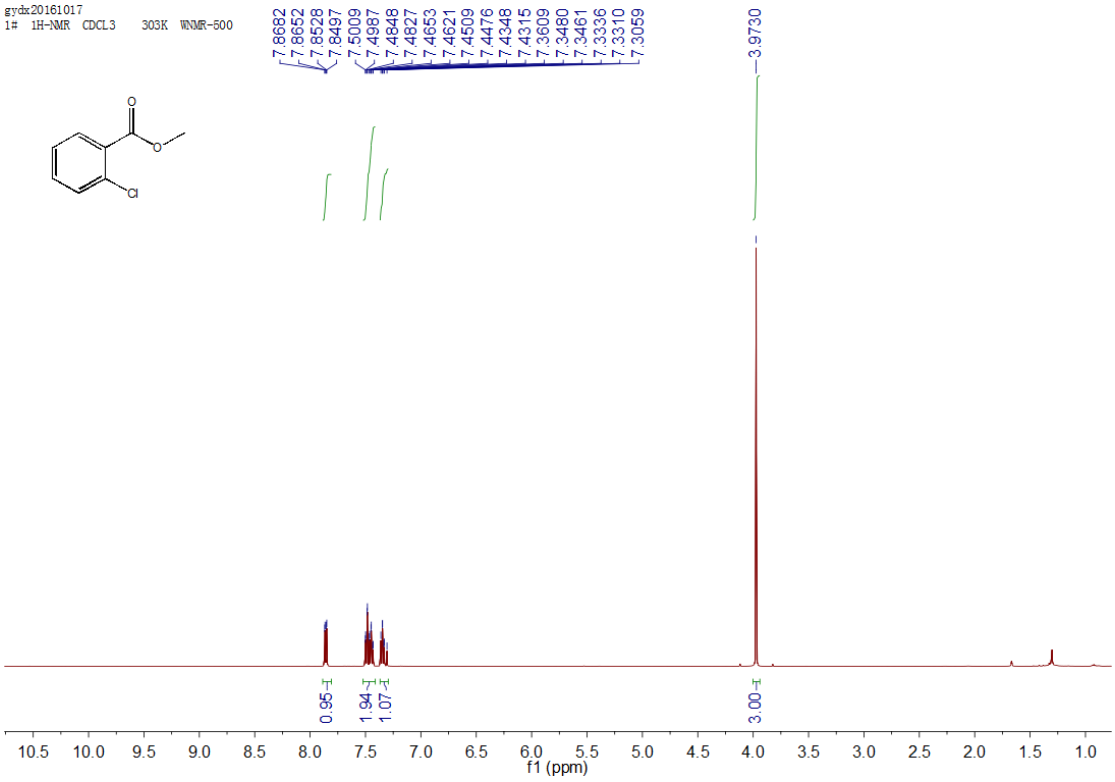
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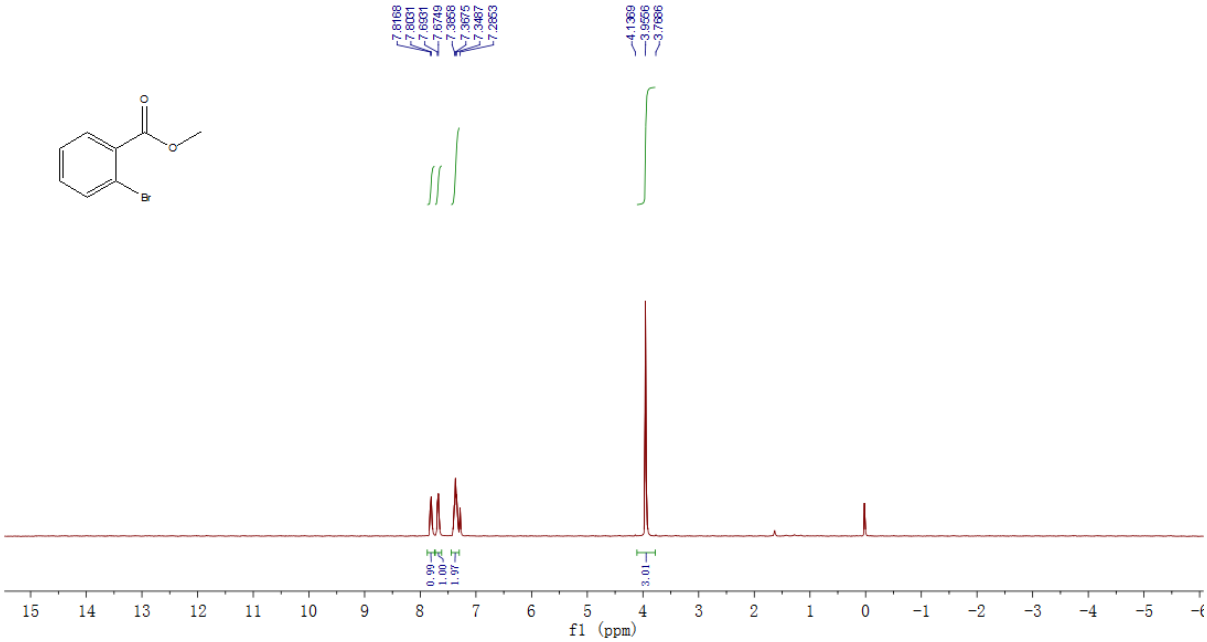
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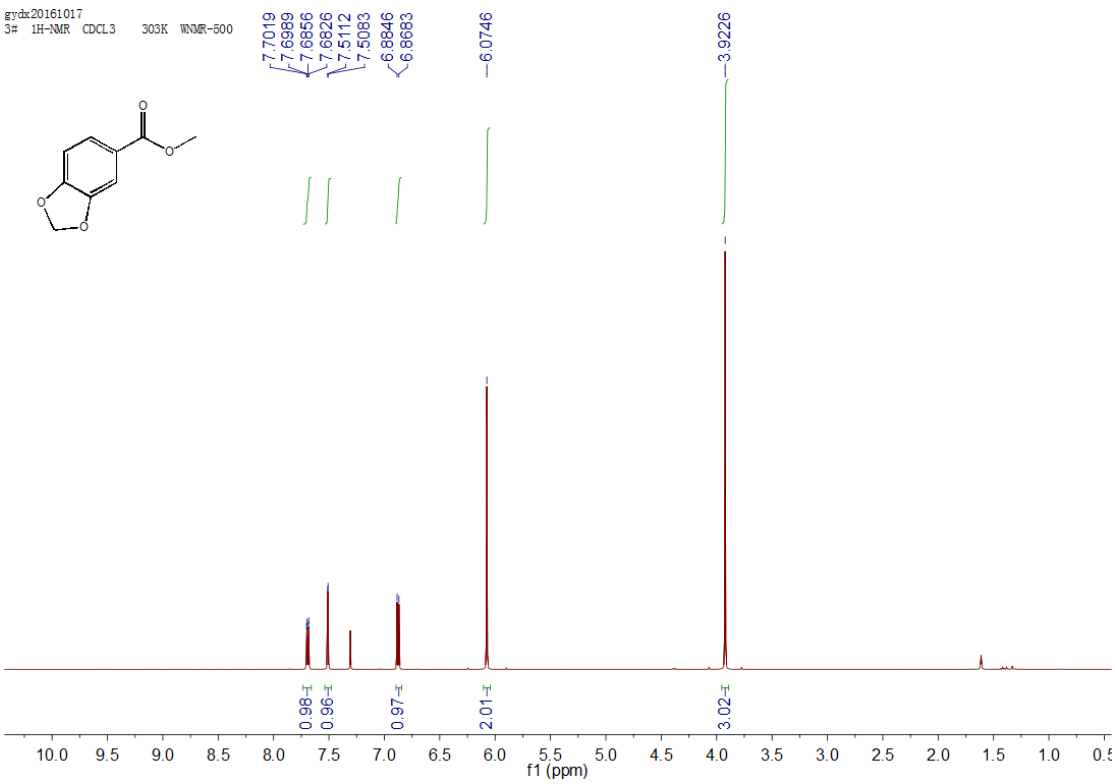
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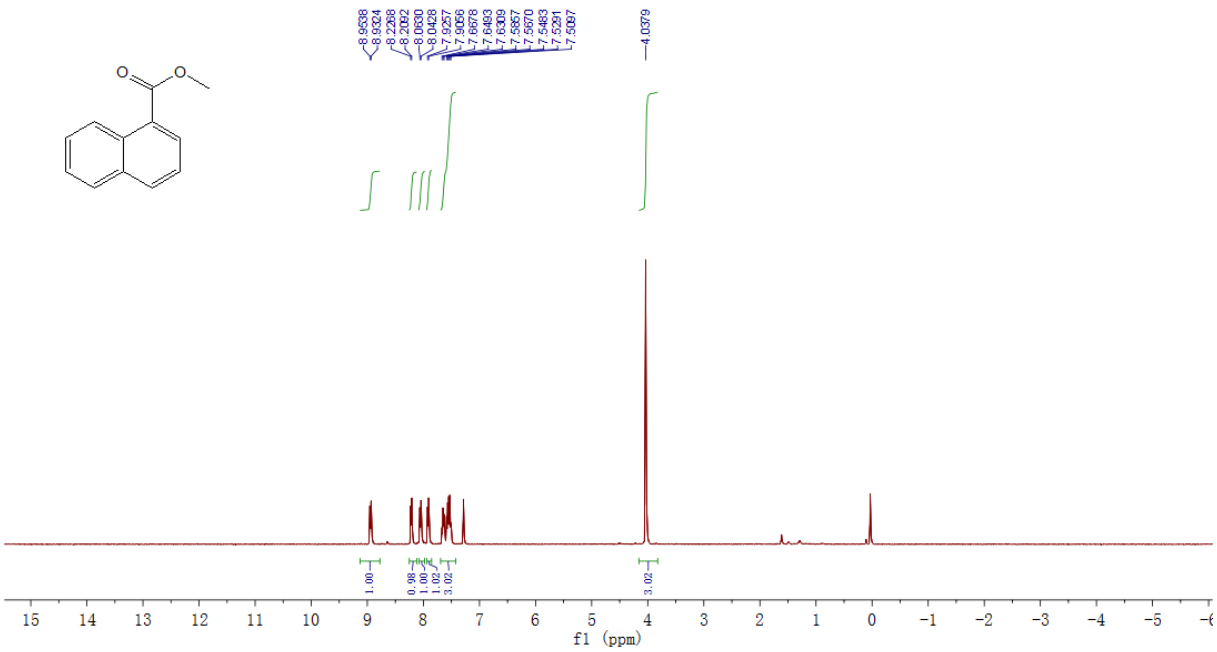
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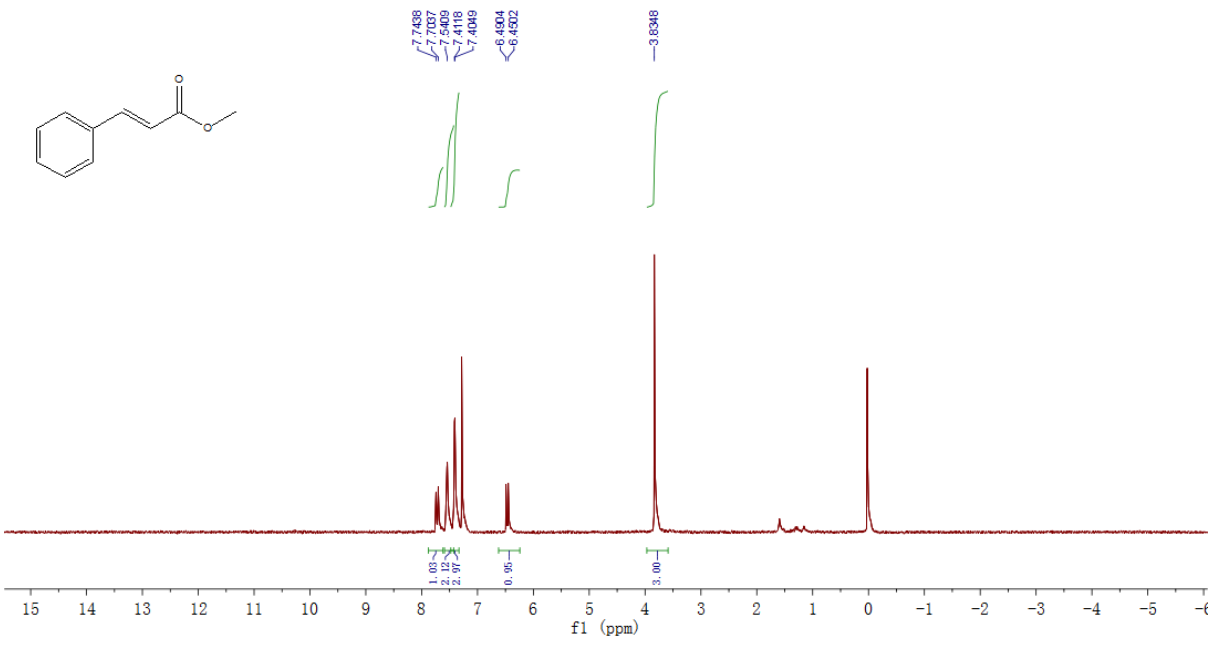
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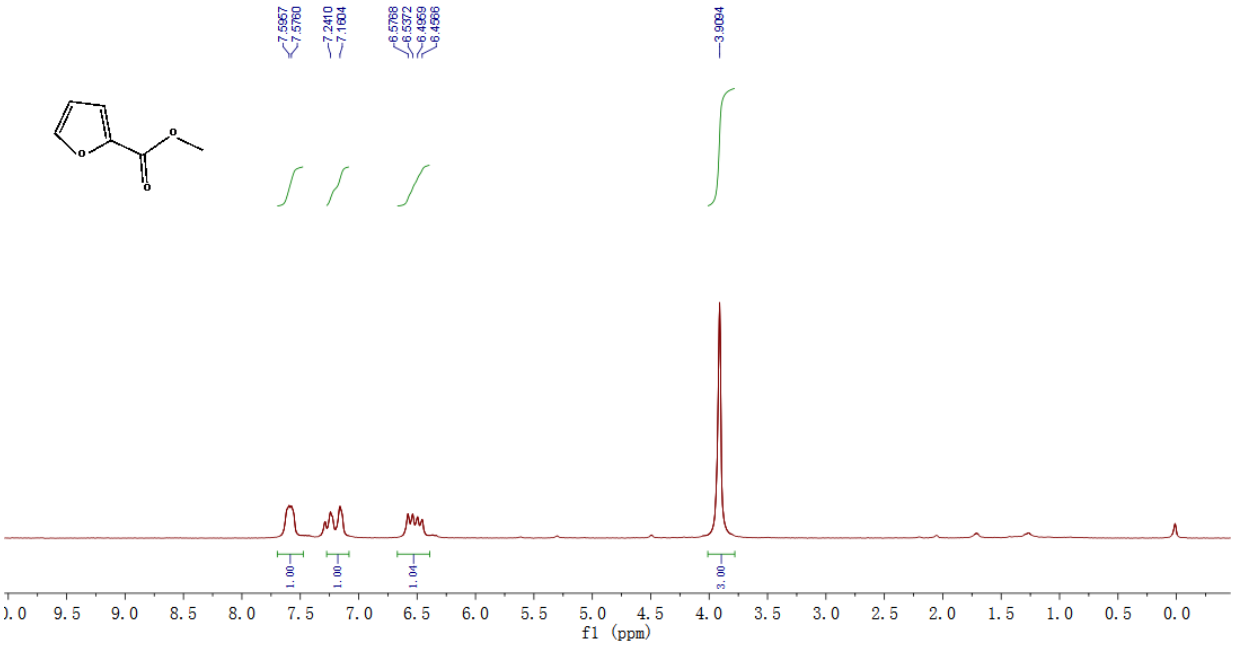
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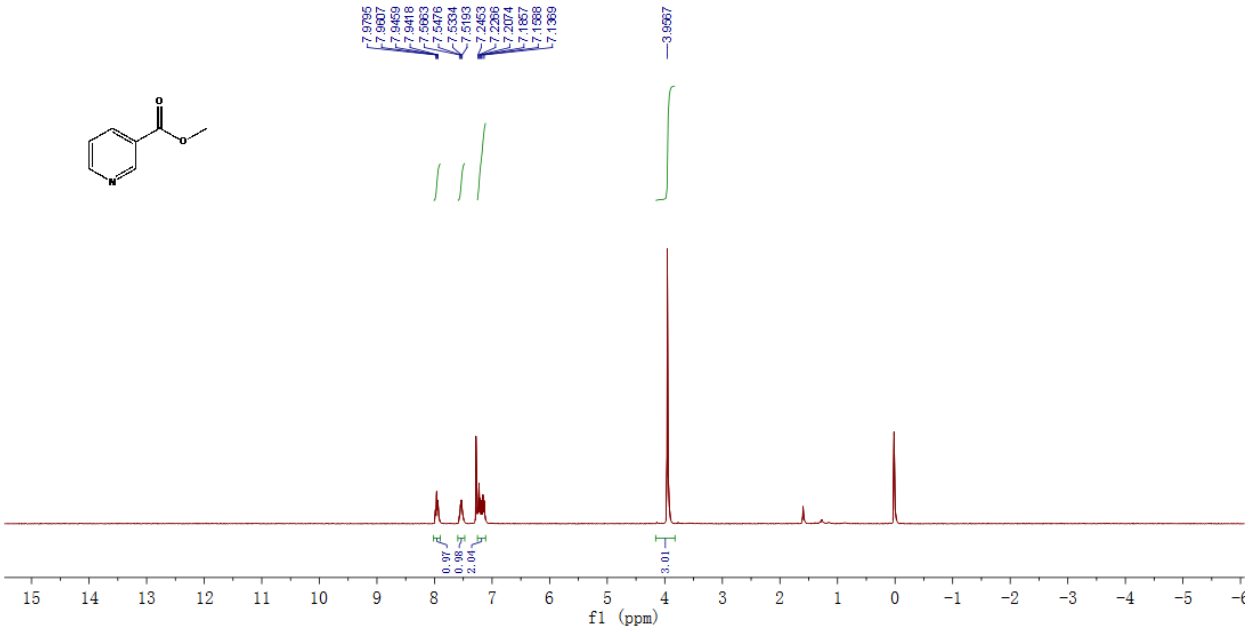
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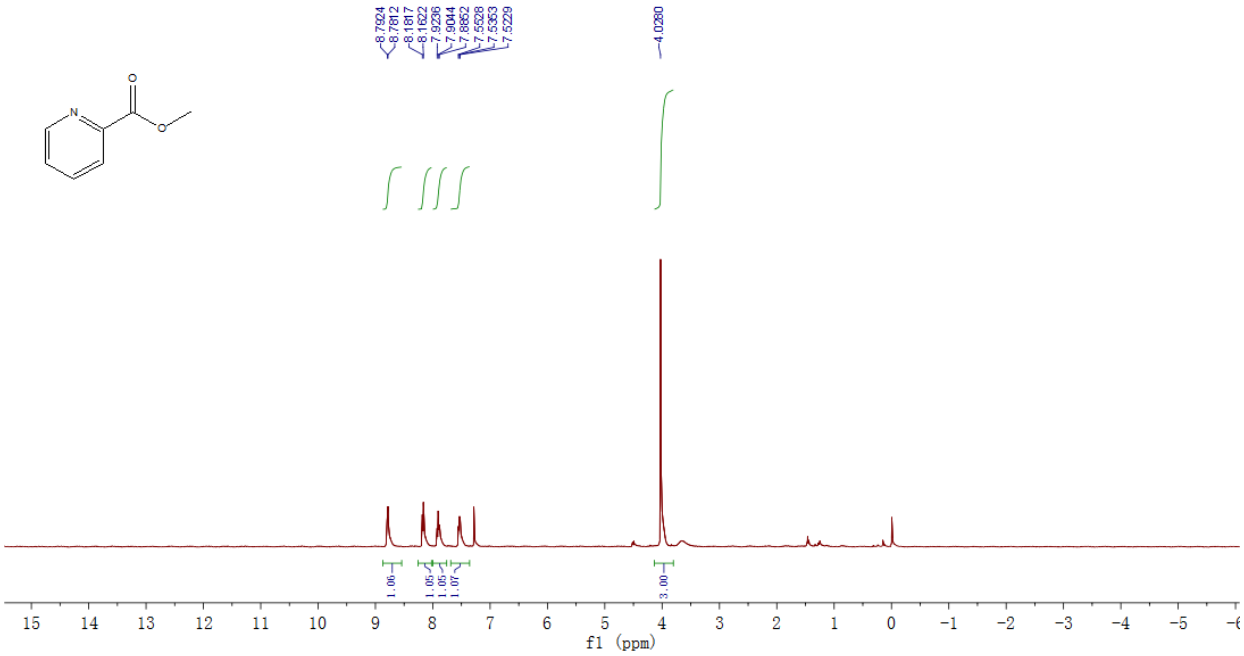
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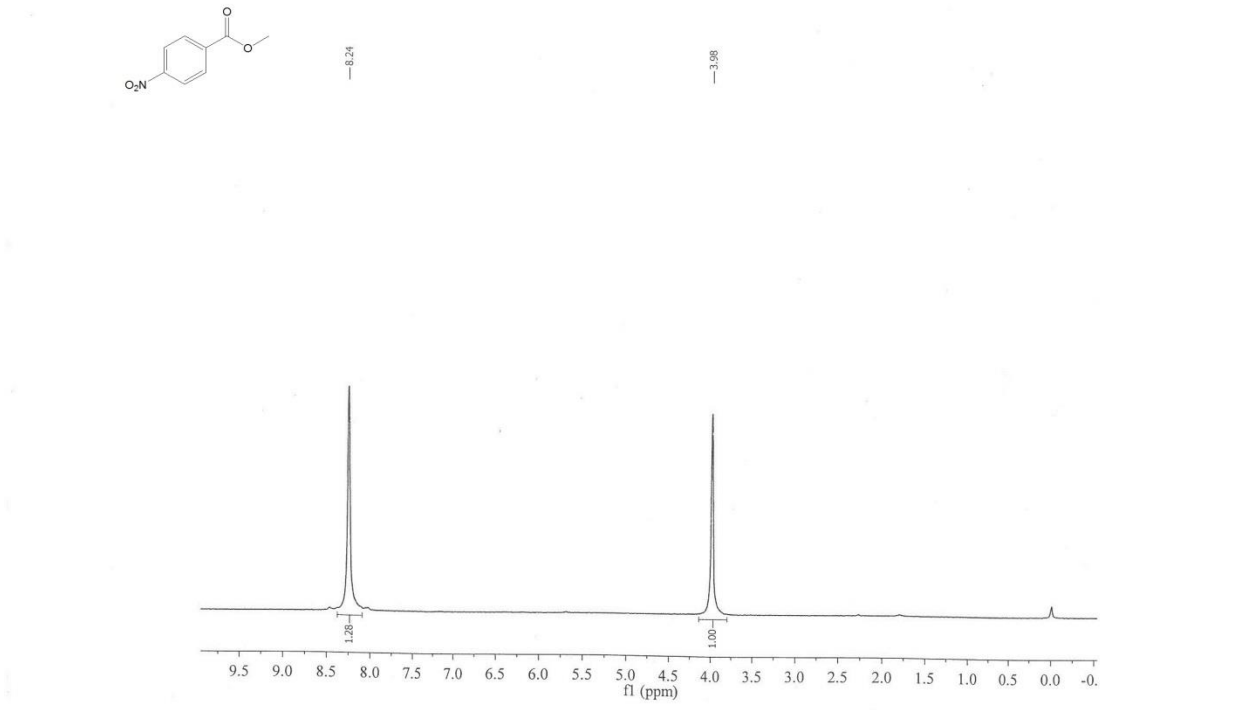
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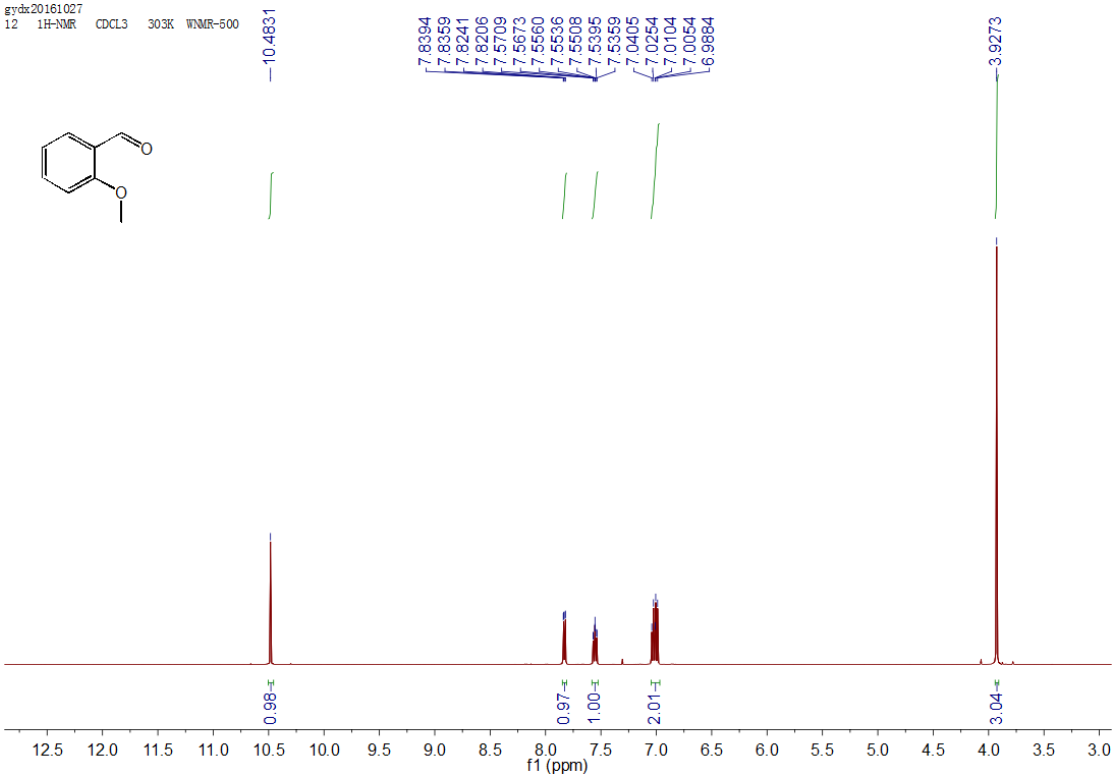
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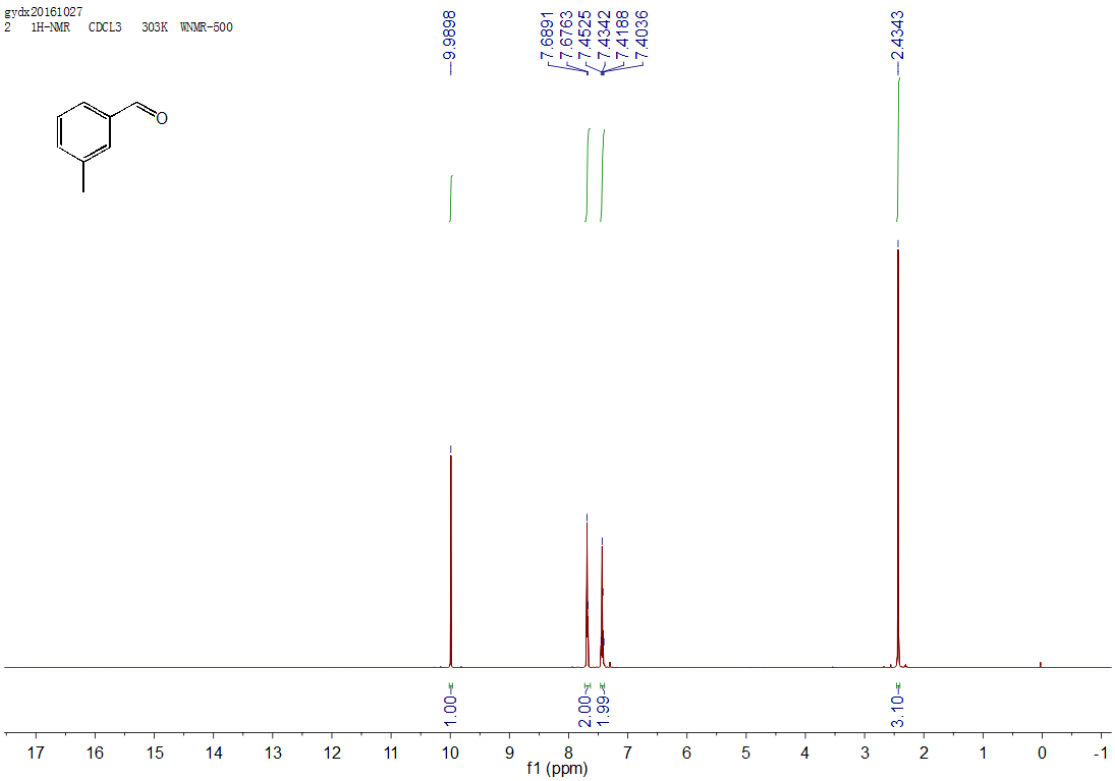
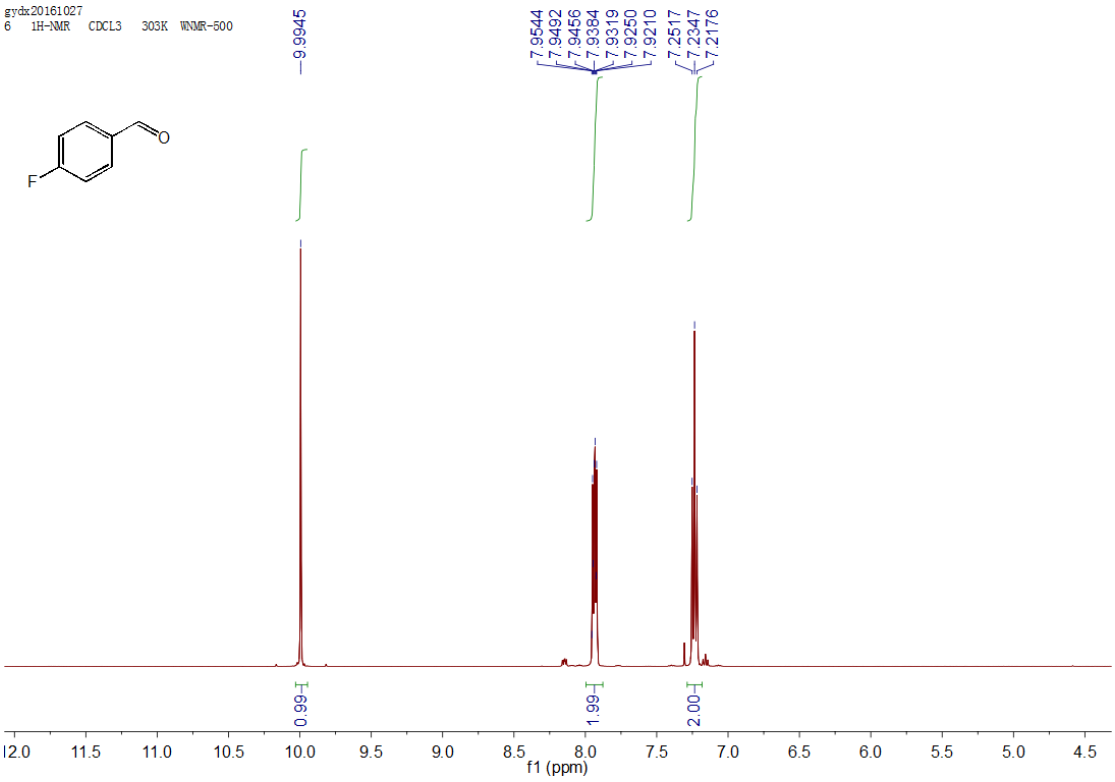
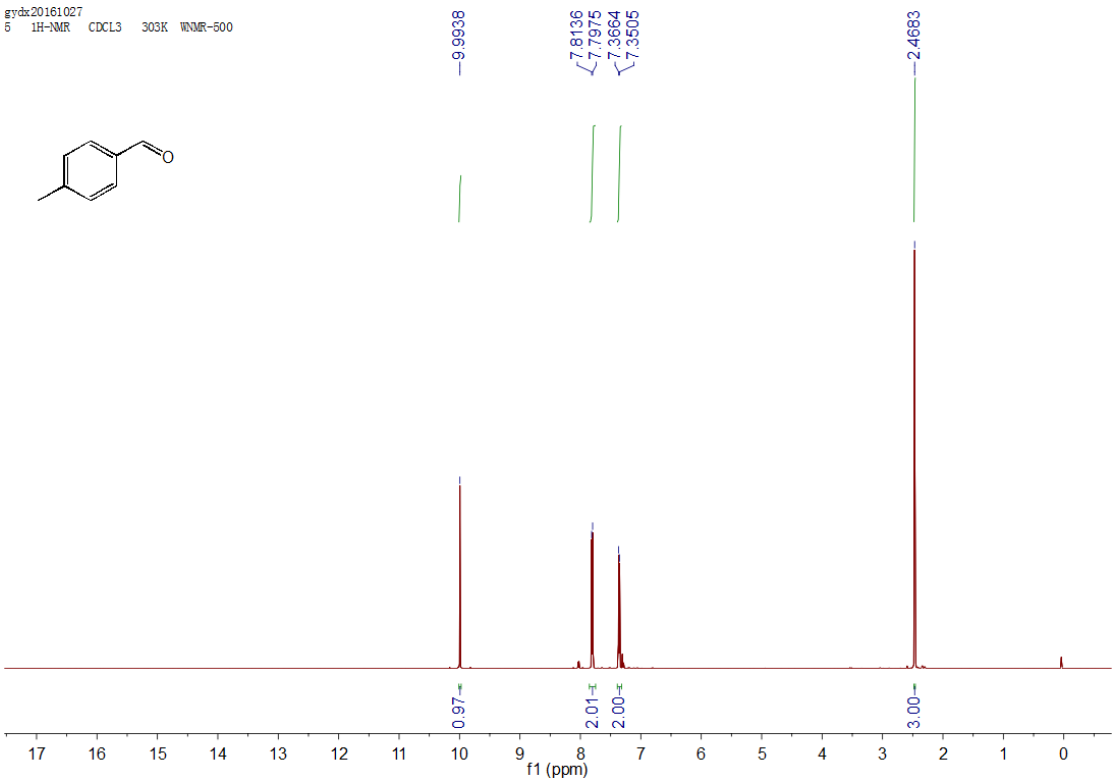
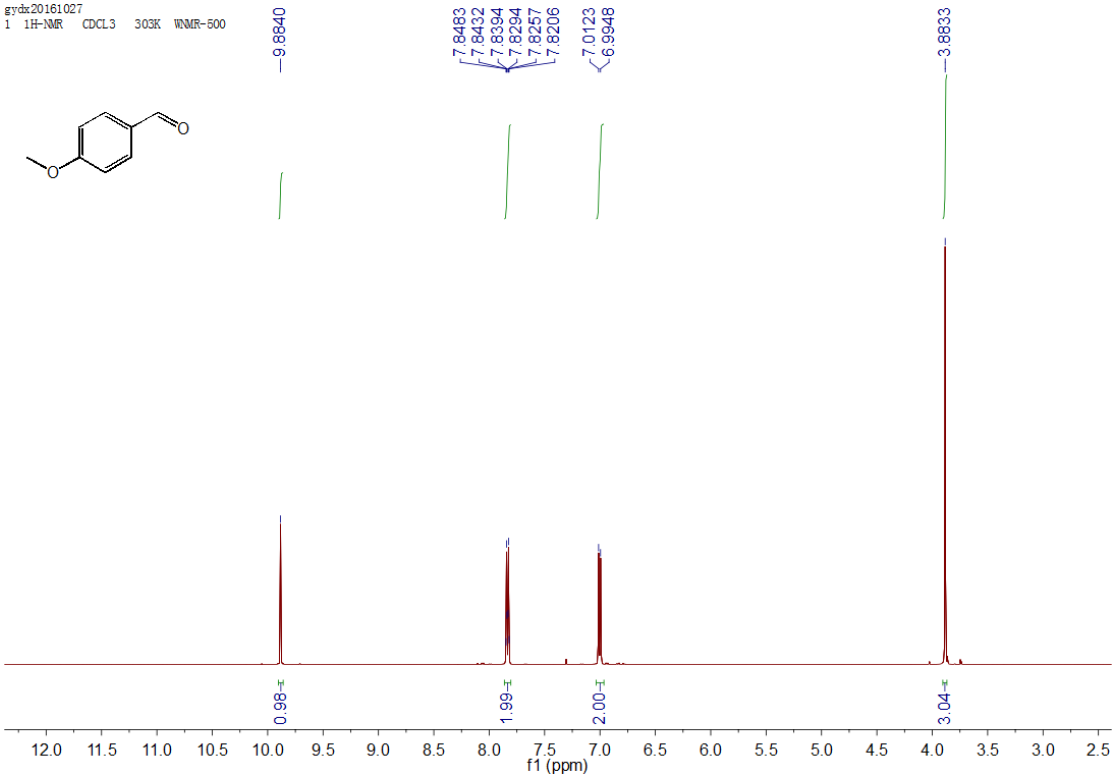
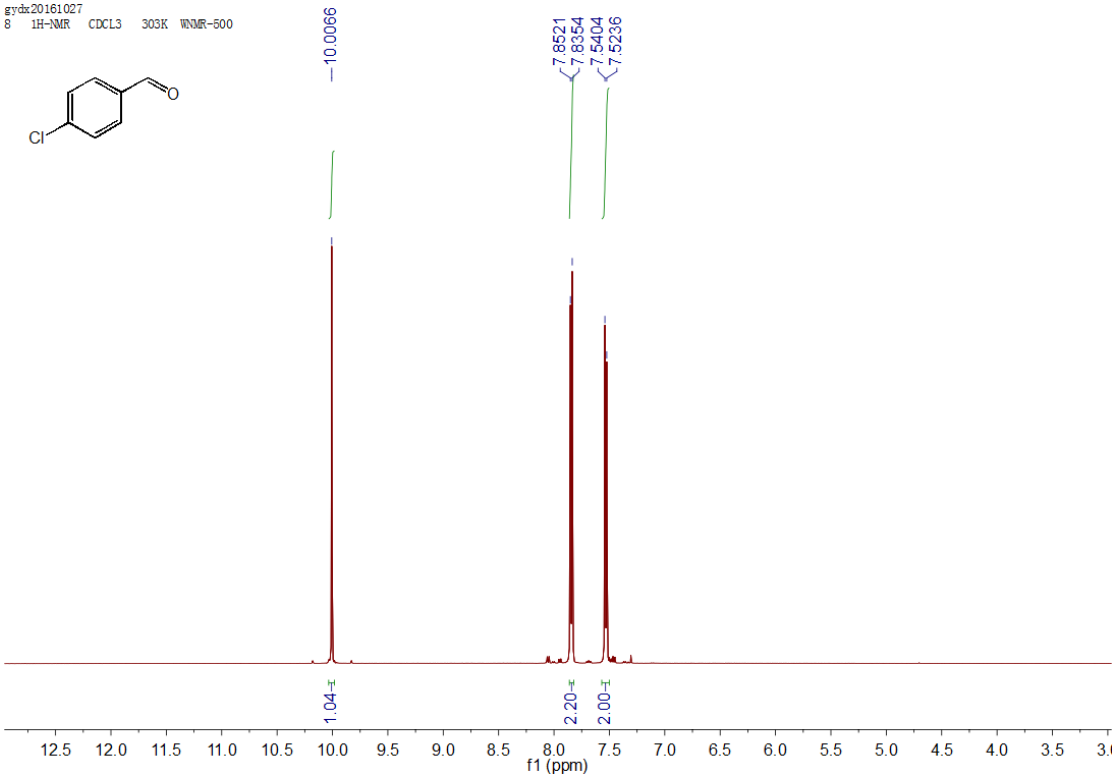
7.5536
7.5508
7.5395
7.5359
7.0405
7.0254
7.0104
7.0054
6.9884
3.9273
O
O
0.98
0.97
1.00
2.01
3.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
f1 (ppm)

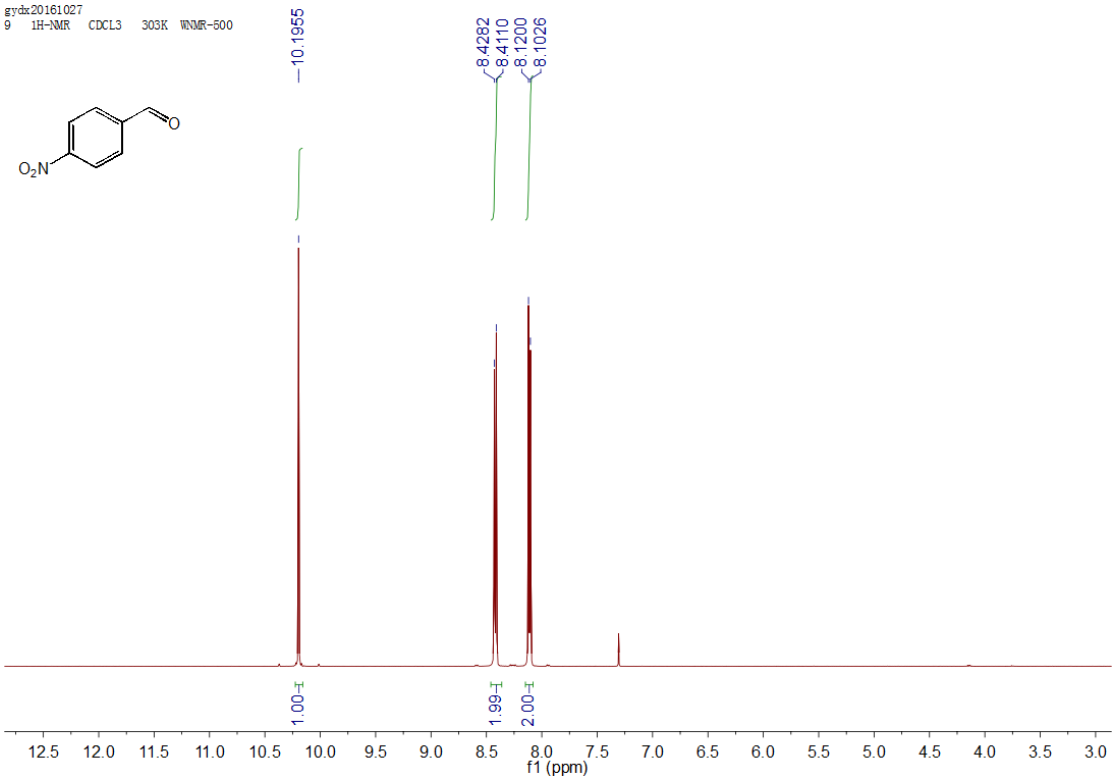

gydx20161027
2 1H-NMR CDCL3 303K WNMR-500
9.9898
7.6891
7.6763
7.4525
7.4342
7.4188
7.4036
2.4343
O
1.00
2.00
1.99
3.10
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

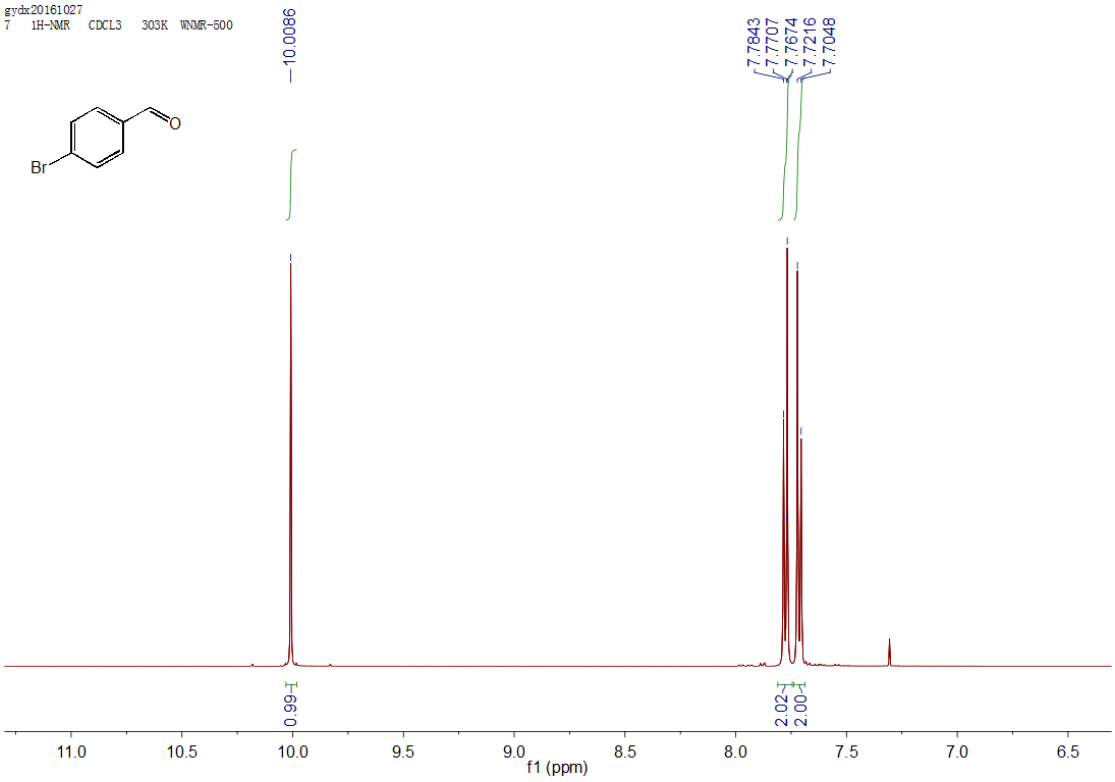

gydx20161027
6 1H-NMR CDCL3 303K WNMR-500
9.9945
7.9544
7.9492
7.9456
7.9384
7.9319
7.9250
7.9210
7.2517
7.2347
7.2176
O
F
0.99
1.99
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5
f1 (ppm)

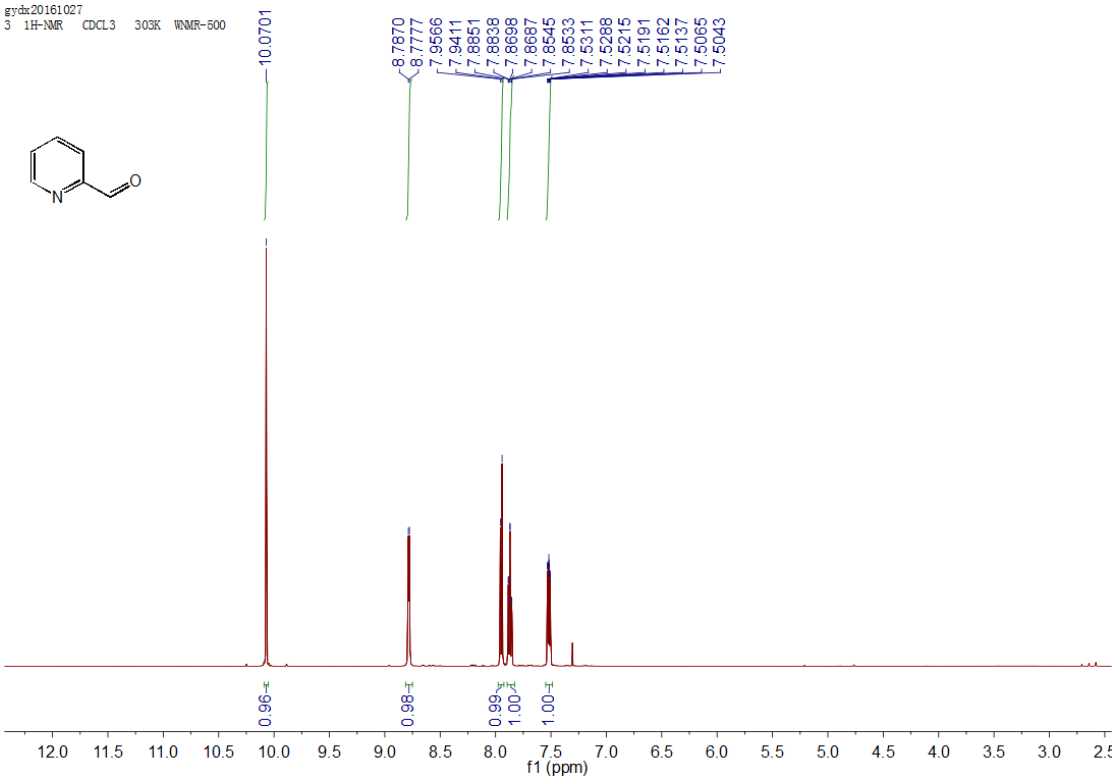

gydx20161027
5 1H-NMR CDCL3 303K WNMR-500
9.9938
7.8136
7.7975
7.3664
7.3505
2.4683
O
0.97
2.01
2.00
3.00
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

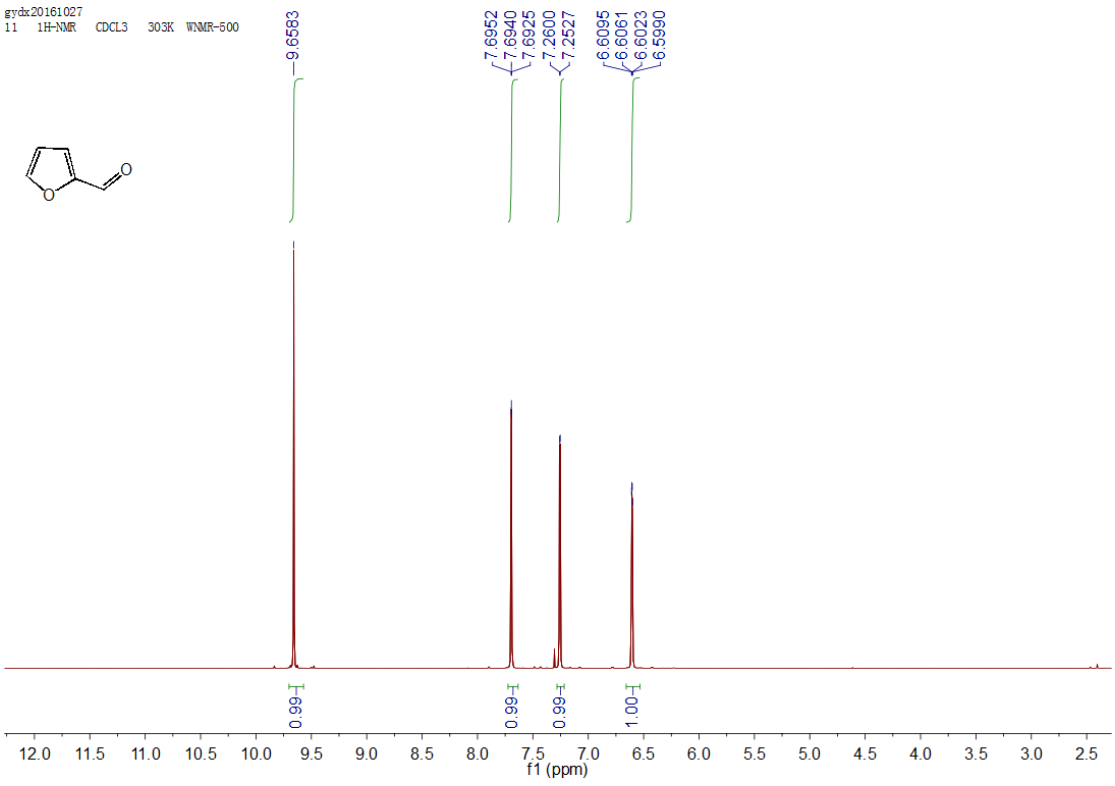

gydx20161027
1 1H-NMR CDCL3 303K WNMR-500
9.8840
7.8483
7.8432
7.8394
7.8294
7.8257
7.8206
7.0123
6.9948
3.8833
O
O
0.98
1.99
2.00
3.04
f1 (ppm)

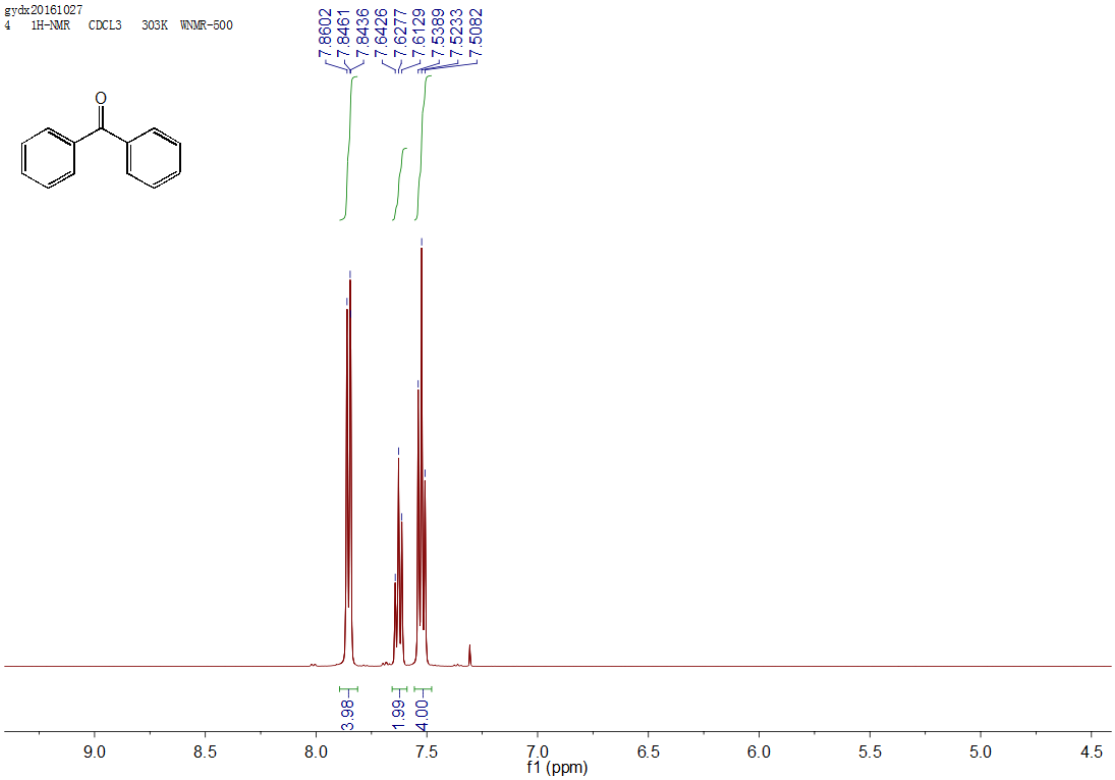

gydx20161027
8 1H-NMR CDCL3 303K WNMR-500
10.0066
7.8521
7.8354
7.5404
7.5236
O
Cl
1.04
2.20
2.00
f1 (ppm)

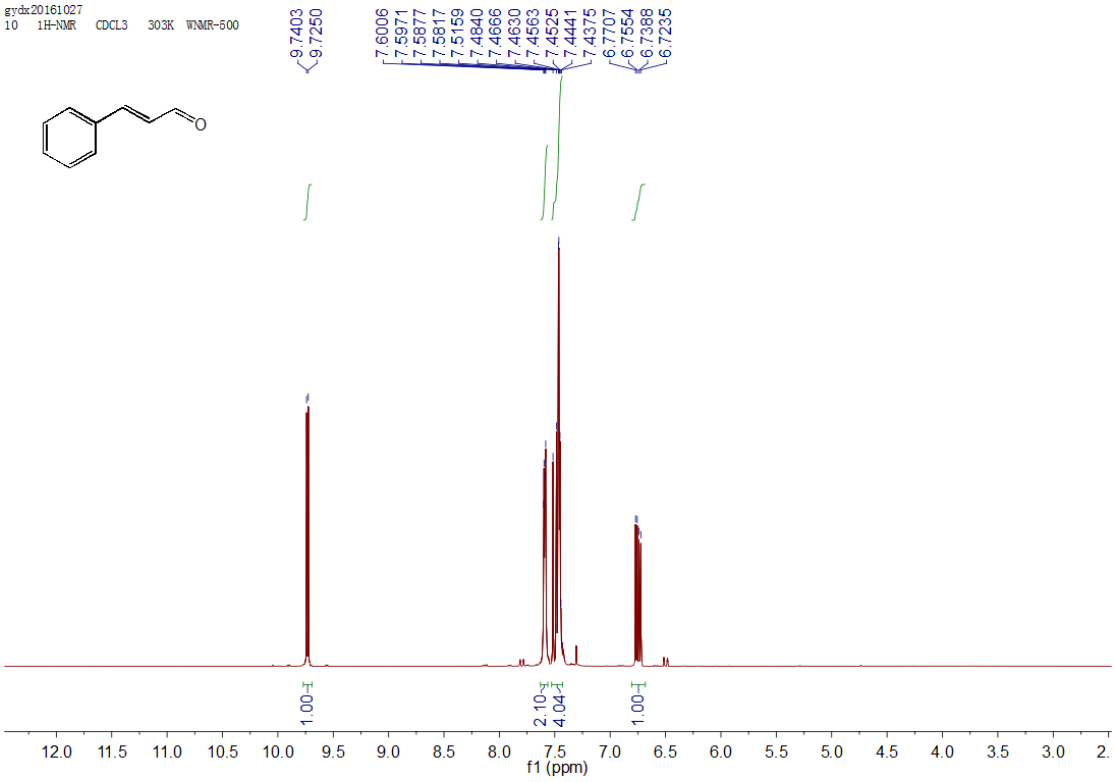

gydx20161027
9 1H-NMR CDCL3 303K WNMR-500
10.1955
8.4282
8.4110
8.1200
8.1026
O
O2N
1.00
1.99
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
f1 (ppm)

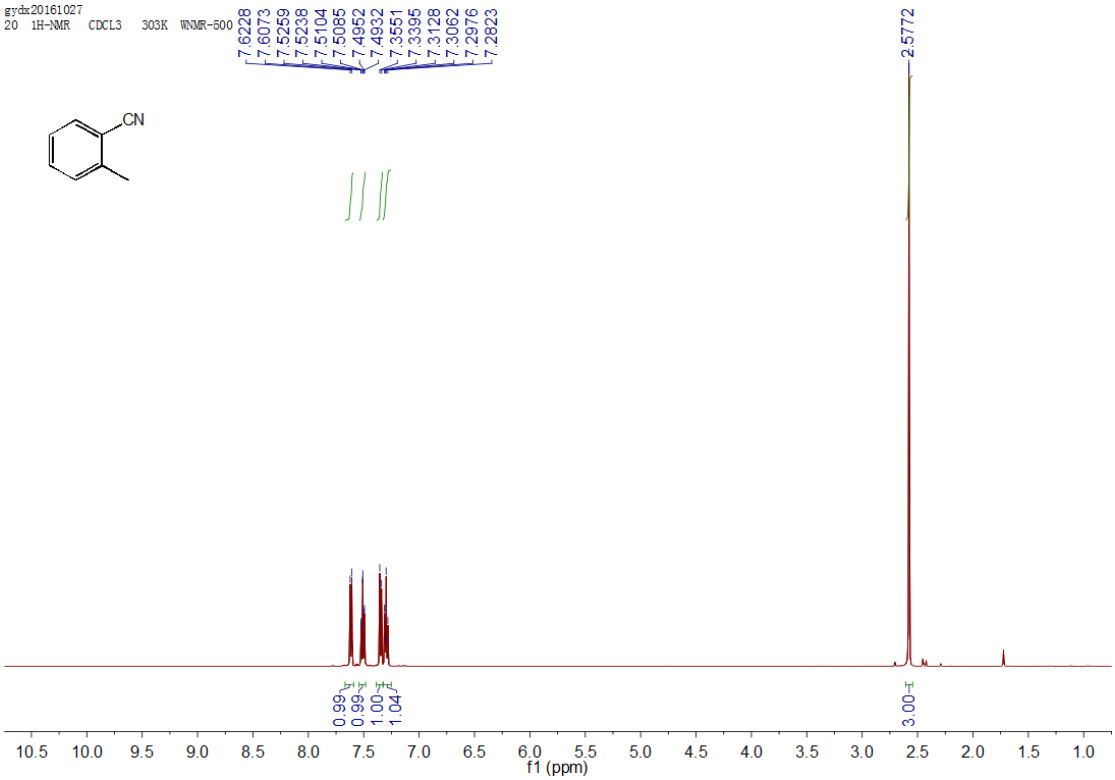

gydx20161027
7 1H-NMR CDCL3 303K WNMR-500
10.0086
7.7843
7.7707
7.7674
7.7216
7.7048
O
Br
0.99
2.02
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5
f1 (ppm)

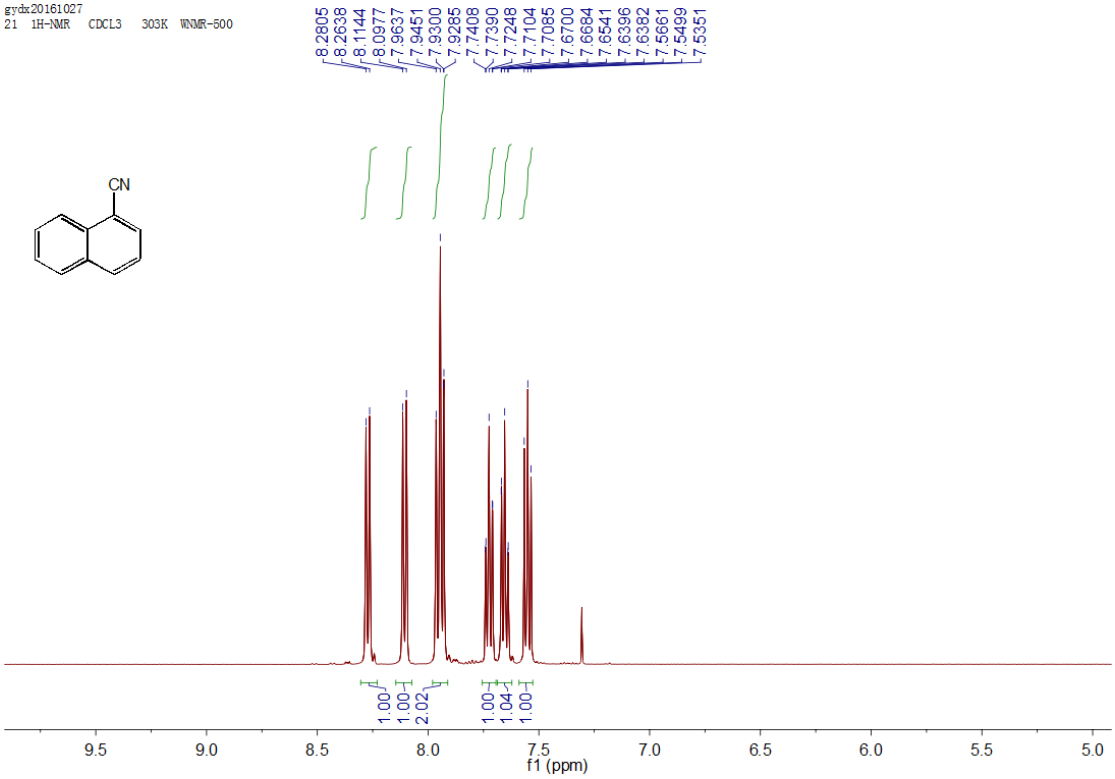

gydx20161027
3 1H-NMR CDCL3 303K WNMR-500
10.0701
8.7870
8.7777
7.9566
7.9411
7.8851
7.8838
7.8698
7.8687
7.8545
7.8533
7.5311
7.5288
7.5215
7.5191
7.5162
7.5137
7.5065
7.5043
O
N
0.96
0.98
0.99
1.00
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)

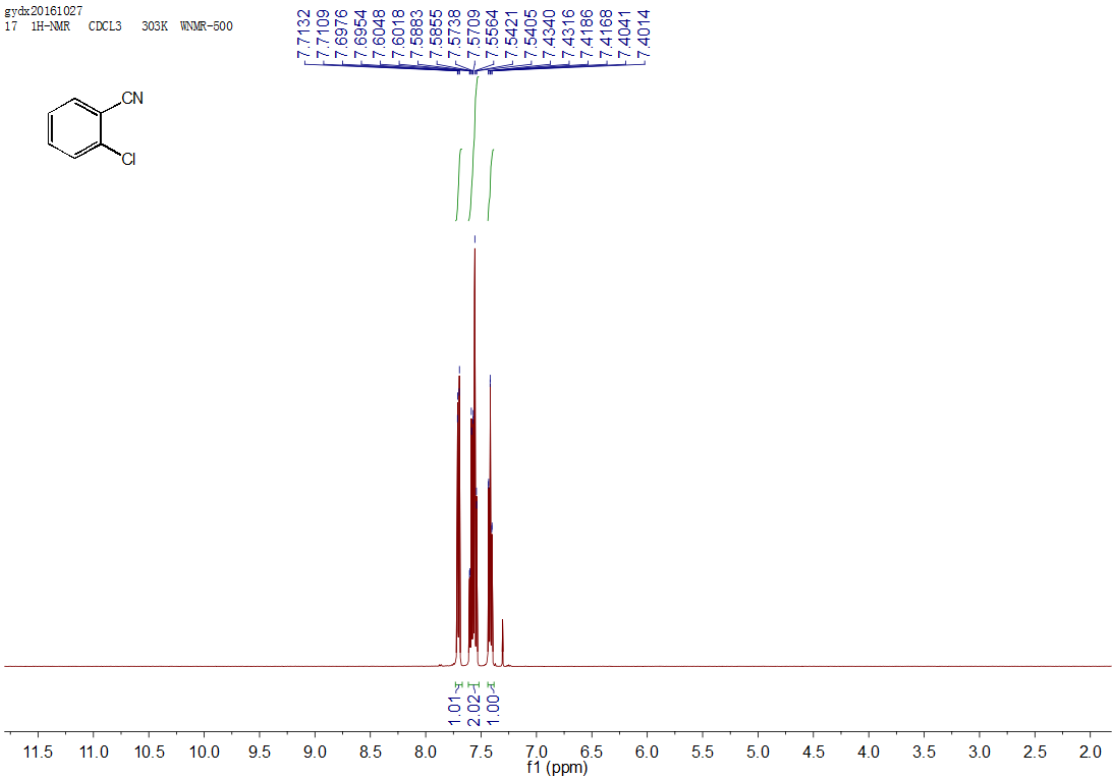

gydx20161027
11 1H-NMR CDCL3 303K WNMR-500
9.6583
7.6952
7.6940
7.6925
7.2600
7.2527
6.6095
6.6061
6.6023
6.5990
O
O
0.99
0.99
0.99
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
f1 (ppm)

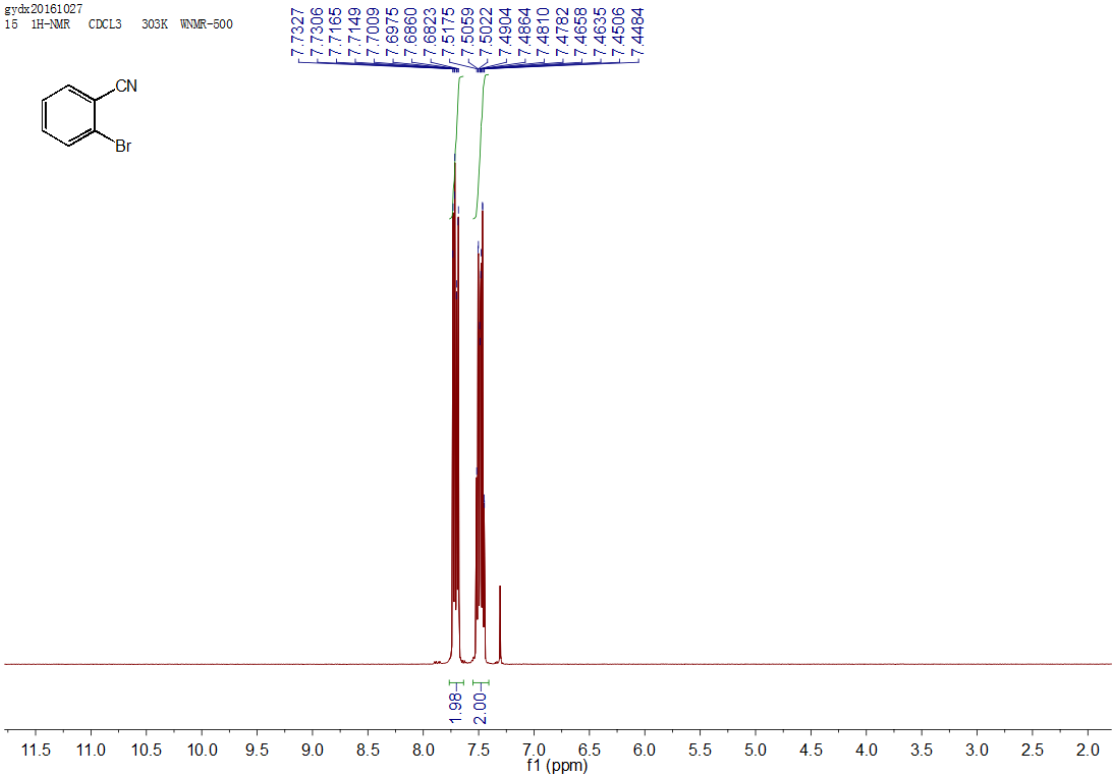

gydx20161027
4 1H-NMR CDCL3 303K WNMR-600
7.8602
7.8461
7.8436
7.6426
7.6277
7.6129
7.5389
7.5233
7.5082
O
3.98
1.99
4.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)

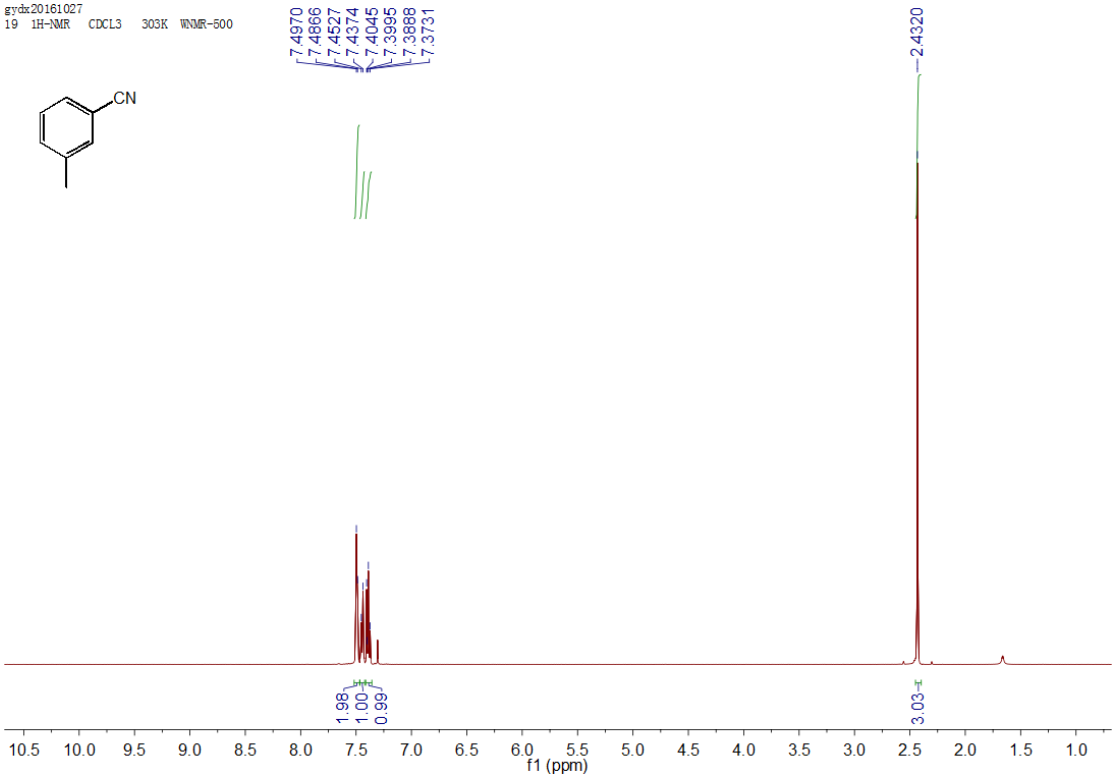

gydx20161027
10 1H-NMR CDCL3 303K WNMR-600
9.7403
9.7250
7.6006
7.5971
7.5877
7.5817
7.5159
7.4840
7.4666
7.4630
7.4563
7.4525
7.4441
7.4375
6.7707
6.7554
6.7388
6.7235
O
1.00
2.10
4.04
1.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f1 (ppm)

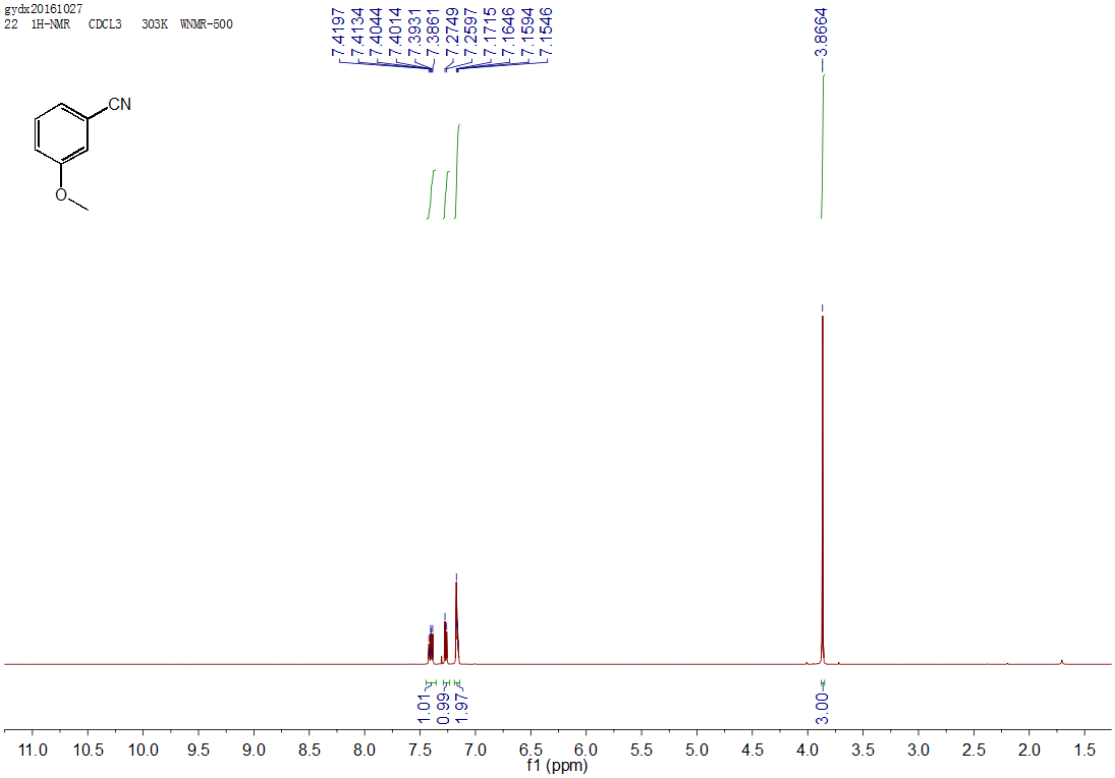

gydx20161027
20 1H-NMR CDCL3 303K WNMR-600
7.6228
7.6073
7.5259
7.5238
7.5104
7.5085
7.4952
7.4932
7.3551
7.3395
7.3128
7.3062
7.2976
7.2823
2.5772
CN
0.99
0.99
1.00
1.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

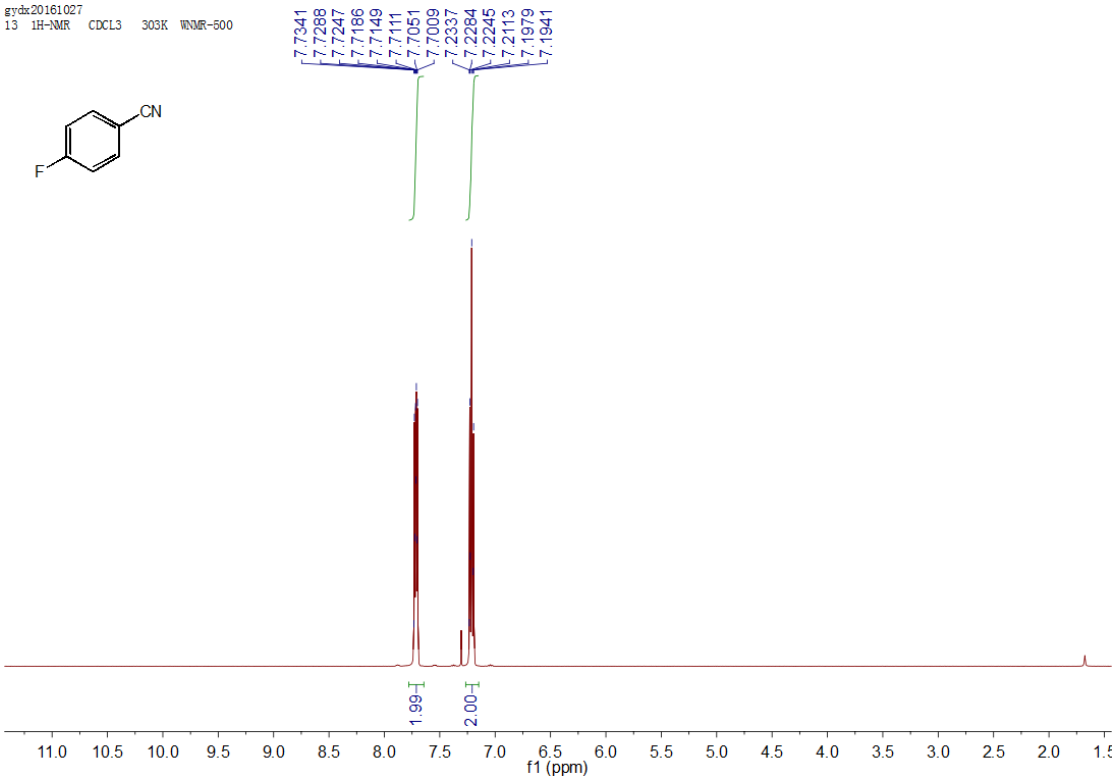

gydx20161027
21 1H-NMR CDCL3 303K WNMR-600
8.2805
8.2638
8.1144
8.0977
7.9637
7.9451
7.9300
7.9285
7.7408
7.7390
7.7248
7.7104
7.7085
7.6700
7.6684
7.6541
7.6396
7.6382
7.5661
7.5499
7.5351
CN
1.00
1.00
2.02
1.00
1.04
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
f1 (ppm)

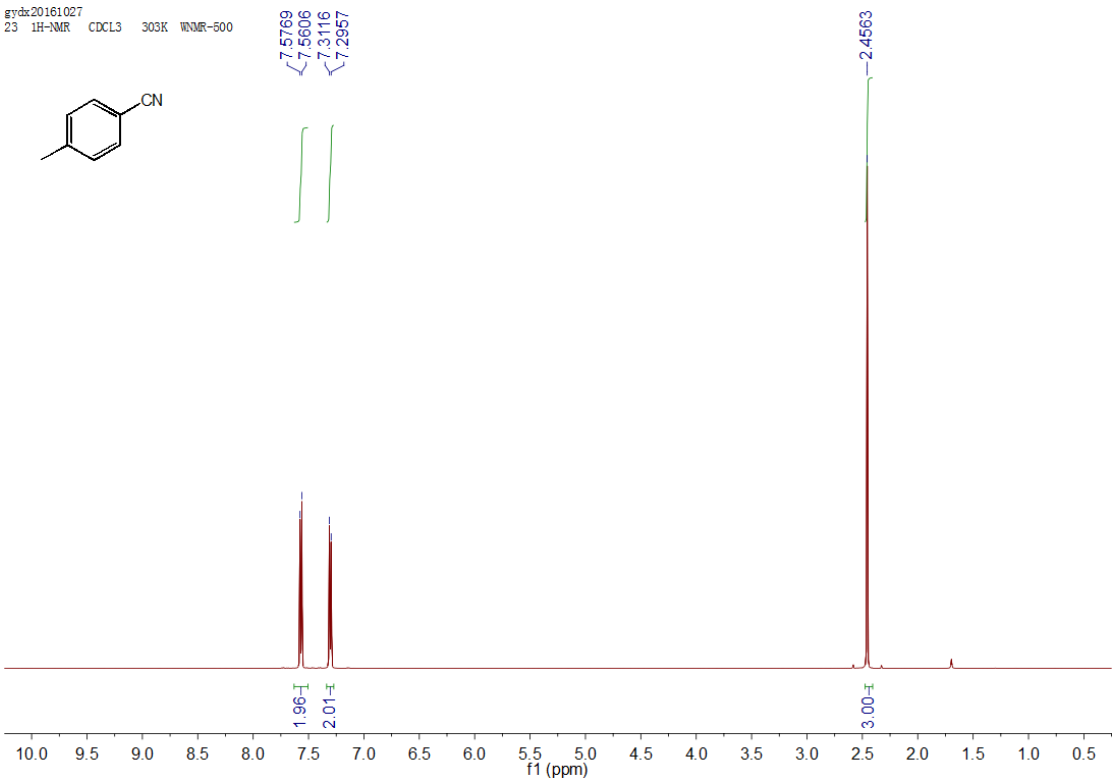

gydx20161027
17 1H-NMR CDCL3 303K WNMR-500
7.7132
7.7109
7.6976
7.6954
7.6048
7.6018
7.5883
7.5855
7.5738
7.5709
7.5564
7.5421
7.5405
7.4340
7.4316
7.4186
7.4168
7.4041
7.4014
CN
Cl
1.01
2.02
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)

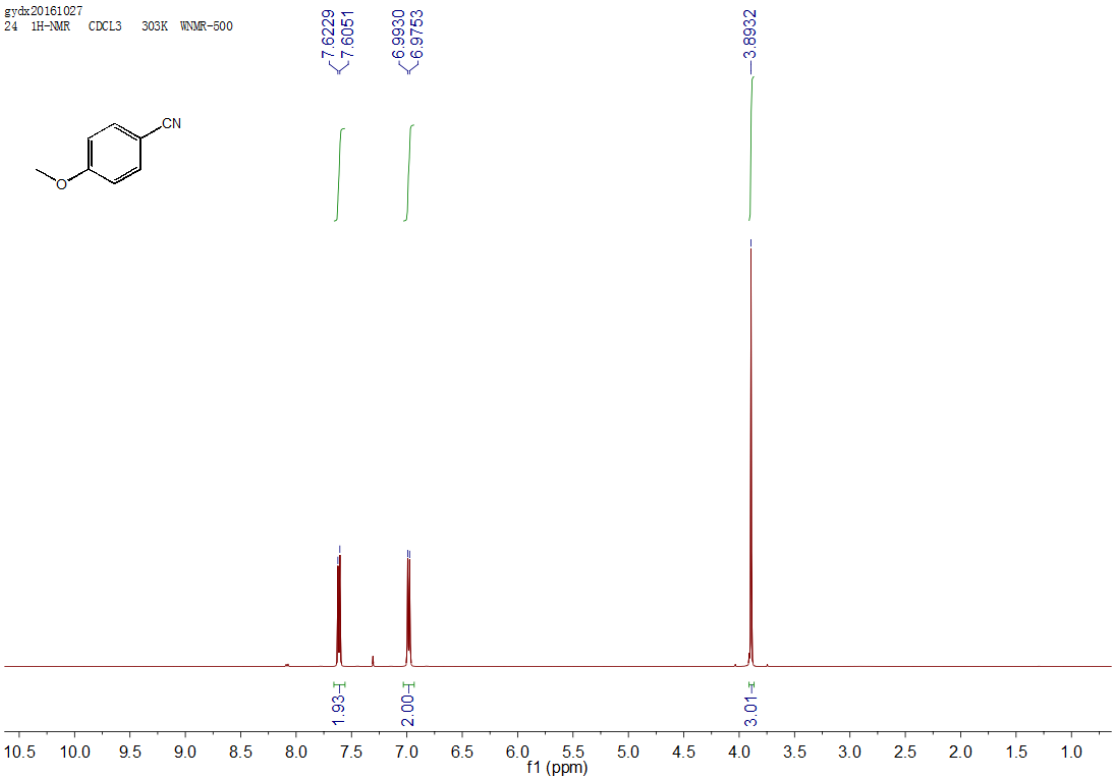

gydx20161027
15 1H-NMR CDCL3 303K WNMR-500
7.7327
7.7306
7.7165
7.7149
7.7009
7.6975
7.6860
7.6823
7.5175
7.5059
7.5022
7.4904
7.4864
7.4810
7.4782
7.4658
7.4635
7.4506
7.4484
CN
Br
1.98
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)

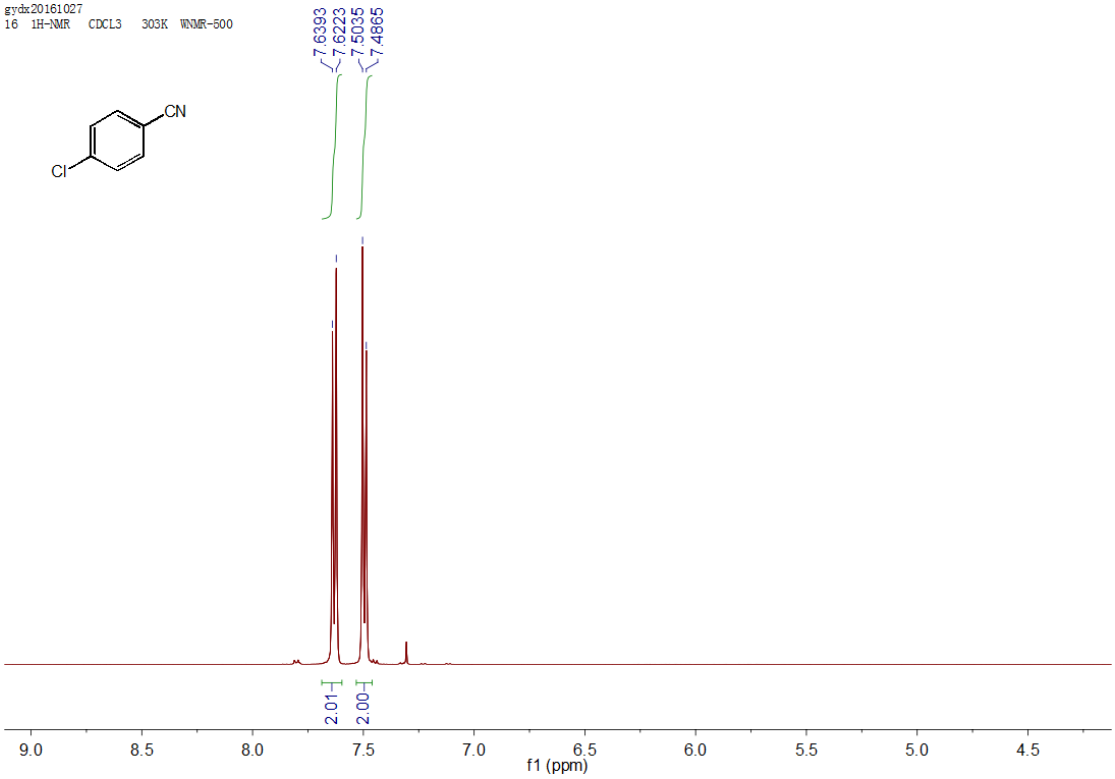

gydx20161027
19 1H-NMR CDCL3 303K WNMR-600
7.4970
7.4866
7.4527
7.4374
7.4045
7.3995
7.3888
7.3731
2.4320
CN
1.98
1.00
0.99
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

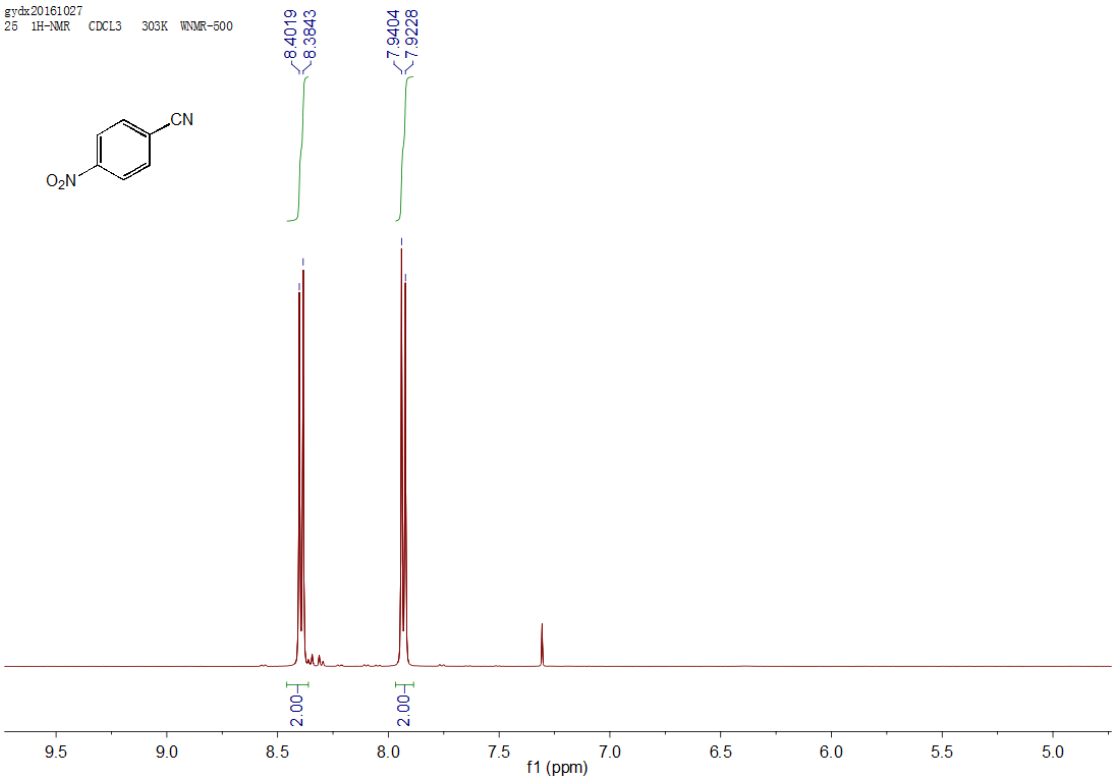

gydx20161027
22 1H-NMR CDCL3 303K WNMR-600
7.4197
7.4134
7.4044
7.4014
7.3931
7.3861
7.2749
7.2597
7.1715
7.1646
7.1594
7.1546
3.8664
CN
O
1.01
0.99
1.97
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

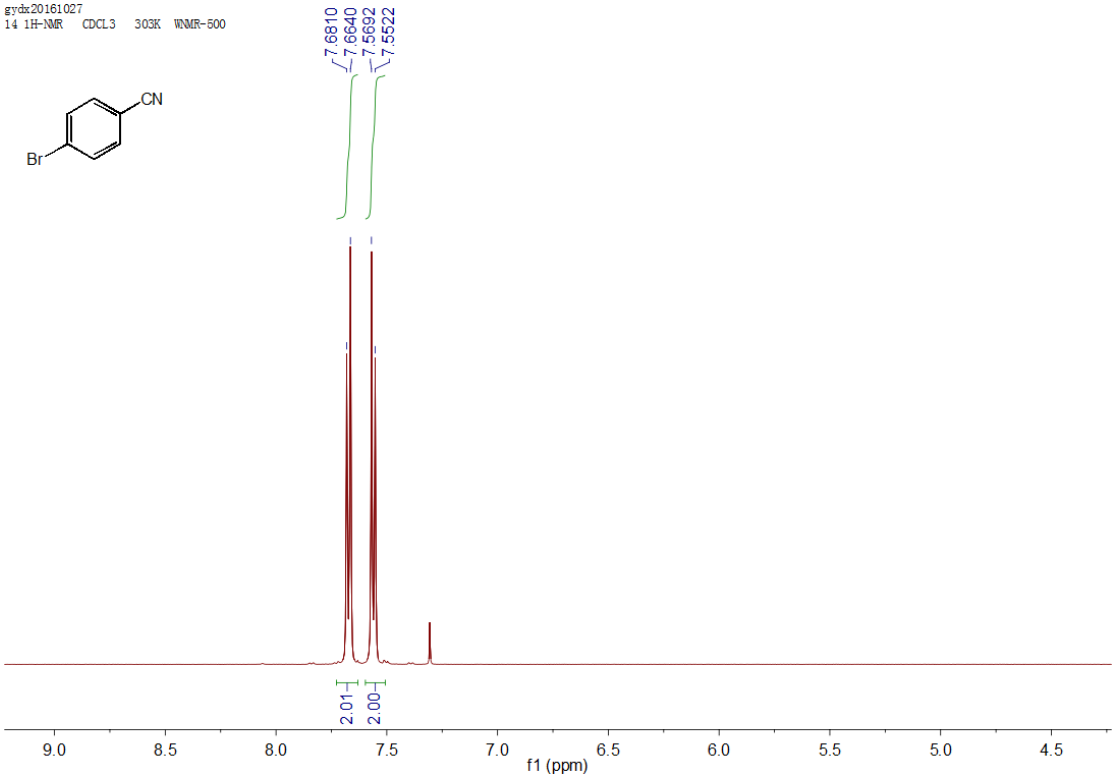

gydx20161027
13 1H-NMR CDCL3 303K WNMR-500
7.7341
7.7288
7.7247
7.7186
7.7149
7.7111
7.7051
7.7009
7.2337
7.2284
7.2245
7.2113
7.1979
7.1941
CN
F
1.99
2.00
f1 (ppm)

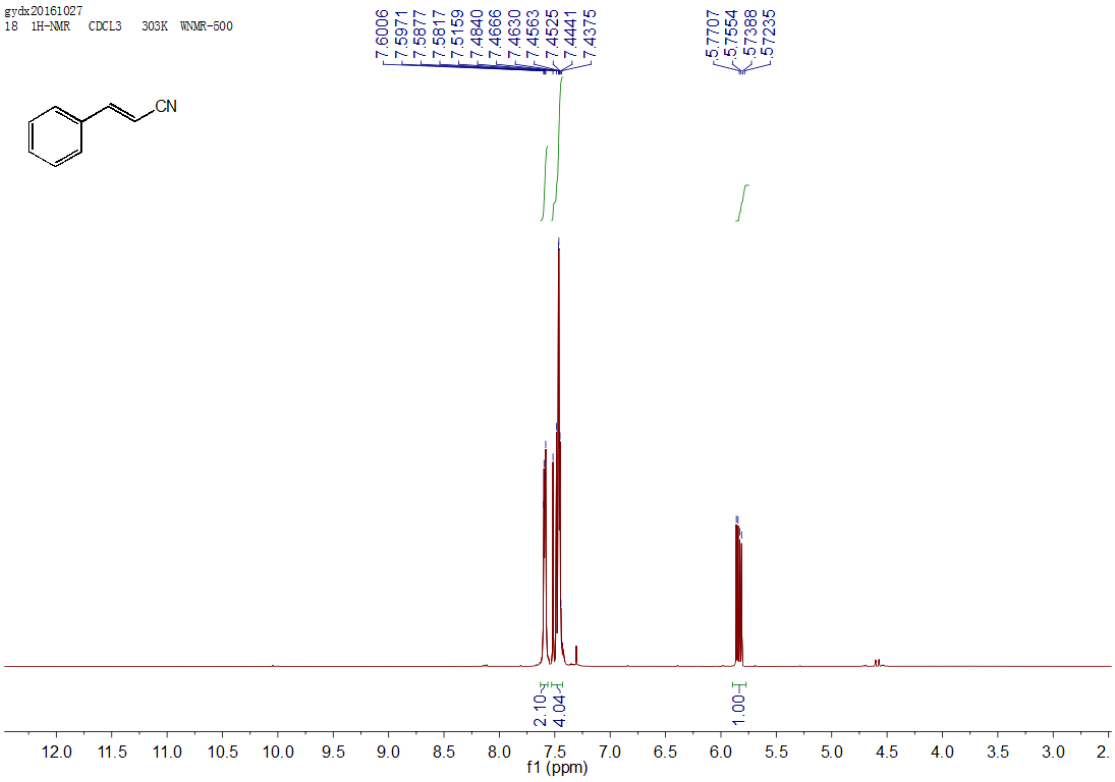

gydx20161027
23 1H-NMR CDCL3 303K WNMR-500
7.5769
7.5606
7.3116
7.2957
2.4563
CN
1.96
2.01
3.00
f1 (ppm)


gydx20161027
24 1H-NMR CDCL3 303K WNMR-600
7.6229
7.6051
6.9930
6.9753
3.8932
CN
O
1.93
2.00
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


gydx20161027
16 1H-NMR CDCL3 303K WNMR-600
7.6393
7.6223
7.5035
7.4865
CN
Cl
2.01
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5
f1 (ppm)


gydx20161027
26 1H-NMR CDCL3 303K WNMR-500
CN
O2N
8.4019
8.3843
7.9404
7.9228
2.00
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)


gydx20161027
14 1H-NMR CDCL3 303K WNMR-500
CN
Br
7.6810
7.6640
7.5692
7.5522
2.01
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)


gydx20161027
18 1H-NMR CDCL3 303K WNMR-600
CN
7.6006
7.5971
7.5877
7.5817
7.5159
7.4840
7.4666
7.4630
7.4563
7.4525
7.4441
7.4375
5.7707
5.7554
5.7388
5.7235
2.10
4.04
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.
f1 (ppm)