Supporting Information

Aerobic oxidative dehydrogenation of amines to nitriles catalyzed by Co@CsETS-10 catalyst

Chaojie Zhu,*[a] Huili Liu,[c] Yuanfeng Wu,*[b] Rong Meng,[a] Lulu Ma,[a] Xiaodong Wang[a] and Cheng Wang*[a]

[a] School of Chemical and Materials Engineering, Chaohu University, Hefei, Anhui 238024, P. R. China.

[b] College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo, Henan 454003, P. R. China.

[c] School of Biological and Environmental Engineering, Chaohu University, Hefei, Anhui 238024, P. R. China.

Correspondence to: Dr. Zhu, chaojiezhu@chu.edu.cn; Dr. Wu, wuyuanfeng2015@gmail.com; Dr. Wang, wangcheng@chu.edu.cn.

Supporting Online Material

1. Chemicals and Methods

Chemicals: All used chemicals were commercially available and were used as received without any further purification.

Methods

Prepare of KETS-10, RbETS-10 and CsETS-10 samples: The NaKETS-10 zeolite was synthesized according to our previous work.[S1] The METS-10 (M = K, Rb, and Cs) samples were obtained by cation-exchanged treatment of the as-synthesized NaKETS-10.[S2] Typically, 2.0 g as-synthesized ETS-10 was added into an aqueous solution (20 mL, 0.25 mol/L) of the potassium nitrate, rubidium nitrate and cesium nitrate, respectively. The mixture was stirred at 50 °C for 16 h. Then, the suspension was filtrated; the obtained solid was thoroughly washed with deionized water to remove the residual nitrate. The final solid was dried at 100 °C for 8 h, and calcined at 200 °C for 2 h. The resulting materials were named KETS-10, RbETS-10 and CsETS-10, respectively.

Prepare of M@ETS-10 catalyst (M=Fe, Co, Ni, Cu, and Zn): The catalysts with different metal loading was prepared through an incipient wetness impregnation method. An aqueous solution containing the desired amount of water-soluble metal salt was first introduced into the powdered support. After impregnation, the samples were opened to the atmosphere for 10 h and further dried at 100 °C for 12 h. Then, the dried samples were calcined from 100 to 350 °C with a heating rate of 2 $°C\cdot min^{-1}$ and kept for 4 h at 350 °C.

Prepare of Co@CsETS-10 catalyst absorbed 2a sample: The Co@CsETS-10 catalyst absorbed **2a** sample (catalyst-**2a**) was obtained on a Bruker TENSOR 27 infrared spectroscope equipped with a reactor cell. The Co@CsETS-10 sample was evacuated to 10^{-2} Pa at 350 ºC for 4 h, and then the temperature was decreased to 75 ºC (reaction temperature). The **2a** was introduced into the reactor cell by He flow (35 mL/min) for 5 min and subsequently evacuated at 75 °C for 120 min to eliminate physisorbed **2a**.

Analysis of products: The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (60~90 °C), dichloromethane and ethyl acetate as eluents. Compounds described in the literature were characterized by comparing their ^{1}H NMR spectra with the reported data. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Advance III (300 MHz, 400 MHz, and 600 MHz) instruments at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the deuterated chloroform ($CDCl_3$) (0 ppm) unless otherwise stated. Data for ^{1}H NMR were reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sex = sextet, m = multiplet, ovrlp = overlap), coupling constants (*J*, in Hz), and integration. All GC analyses were performed on an Agilent Technologies 7890B GC system with an FID detector.

^{1}H NMR and IR experiments

^{1}H NMR experiment: The ^{1}H magic angle spinning (MAS) NMR spectra of the pyrrole adsorbed catalyst samples were collected on Bruker AVANCE III 400-WB spectrometer.[S3] Pre-analyzed Co@CsETS-10 sample was outgassed at 350 °C for 15 h under dynamic vacuum up to a final pressure of 10^{-3} Pa. Then, the sample was cooling down to room temperature, and it was exposed to pyrrole vapor for 5 min and subsequently evacuated at 65 °C for 60 min to eliminate physisorbed pyrrole. The evacuated sample was immediately transferred into the rotors in a glove box. Then ^{1}H MAS NMR spectra were recorded at 399.9 MHz under room temperature, using a VT CP-MAS Varian probe with 5 mm silicon nitride rotors spinning at 13 kHz. The p/2 rad pulses of 6 ms and a recycle delay of 5 s were used.

IR experiment: IR spectra of the $BnNH_2$ (**1a**) chemisorbed Co@CsETS-10 sample (catalyst-**1a**) were obtained on a Bruker TENSOR 27 infrared spectroscope equipped with a reactor cell. Prior to measurement, the Co@CsETS-10 sample was evacuated to 10^{-2} Pa at 350 ºC for 5 h, and then the temperature was decreased to 75 ºC (reaction temperature). The **1a** was introduced into the reactor cell by He flow (35 mL/min) for 20 s. Immediately, the spectrum (catalyst-**1a**-0 min) was obtained in the absorbance mode and was shown after subtraction of a background spectrum for the Co@CsETS-10 sample, which was also obtained at 75 ºC. After the catalyst-**1a** sample was treated at 75 °C for 20 min, the spectrum of catalyst-**1a**-20 min was obtained. For comparison, the IR spectrum of pure benzonitrile (**2a**) was also recorded at 75 ºC.

Density functional theory calculation

The CP2K2023.1 code was applied for geometric optimization and energy at the level of Perdew–Burke–Ernzerh (PBE) method equipped with DZVP-MOLOPT-SR-GTH basic sets. A 400 R y plane wave cutoff for the auxiliary grid was set. A Broyden mixing method was applied to accelerate the convergence to the requested total energy threshold value of 10^{-6} Hartree for the total energy difference between two consecutive SCF iteration steps. Atomic coordinates have also been provided in the end of the document. [S4]

Activity test

The typical experimental procedure for aerobic oxidative dehydrogenation of amines reaction was as follows: Under air atmosphere, catalyst (10 mg), amines (0.3 mmol), toluene (as internal standard, 0.2 mmol) and cyclohexane (1.5 mL) were placed into a tube (10 mL). The mixture was heated to 75 °C and kept for 3 h with stirring (400 rpm) by a stir bar, the whole reaction process was reflow using a serpentine condensing tube. The reaction temperature and stirring rate in the tube were controlled using an IKA stirrer (model of RTC Basic). When the reaction was finished and cooled to room temperature, the catalyst was separated by centrifugation and filtration to obtain the liquid phase. The liquid products were analyzed by an Agilent 7890B chromatograph. The amine conversion and product selectivity were calculated as follows.

$$Amine\ \text{conversion} = \frac{\text{Molar of reacted amine}}{\text{Molar of initial amine}} \times 100$$

$$\text{Product } i \text{ selectivity} = \frac{\text{Molar of product } i}{\text{Sum of product moles}} \times 100$$

$$\text{Product } i \text{ yield} = \text{Amines conversion} \times \text{Product } i \text{ selectivity} \times 100$$

The scale-up experiments: The scale-up experiment was performed in a 250 mL flask. 11.35 g **1a**, 100 mL cyclohexane and 2.5 g Co@CsETS-10 were charged into flask. The reaction mixture was heated to 75 °C for 11.5 h under a stirring rate of 500 rpm. The reaction products were analyzed with an Agilent 7890B GC installation.

2. Figures and Tables

Figures

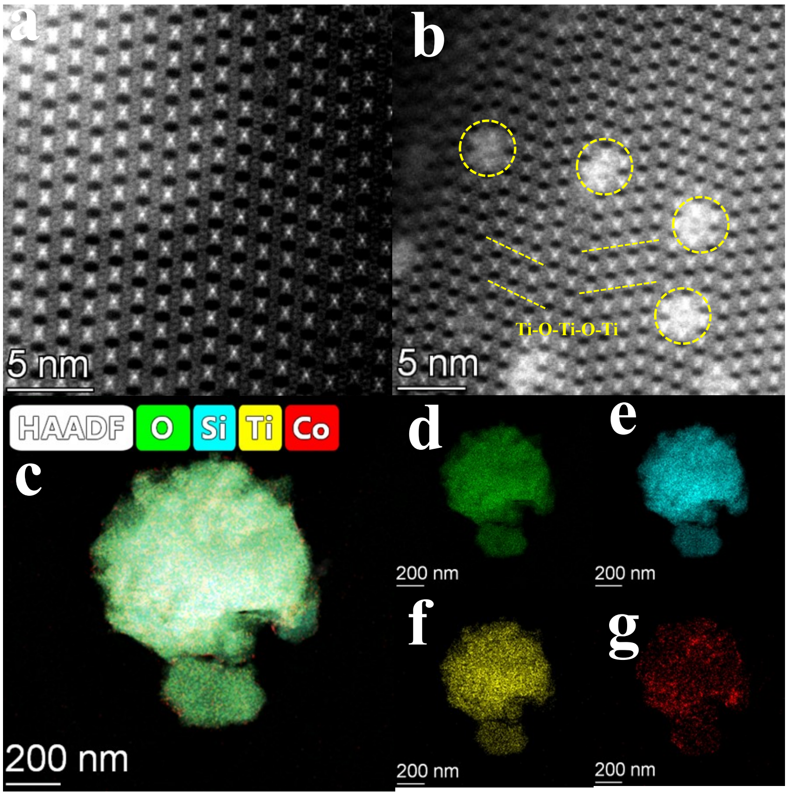


Fig. S1 The STEM of (a) CsETS-10, (b) 1.0 wt.% Co@CsETS-10 images and High-resolution HAADF-STEM of (c)~(g) 1.0 wt.% Co@CsETS-10 images.

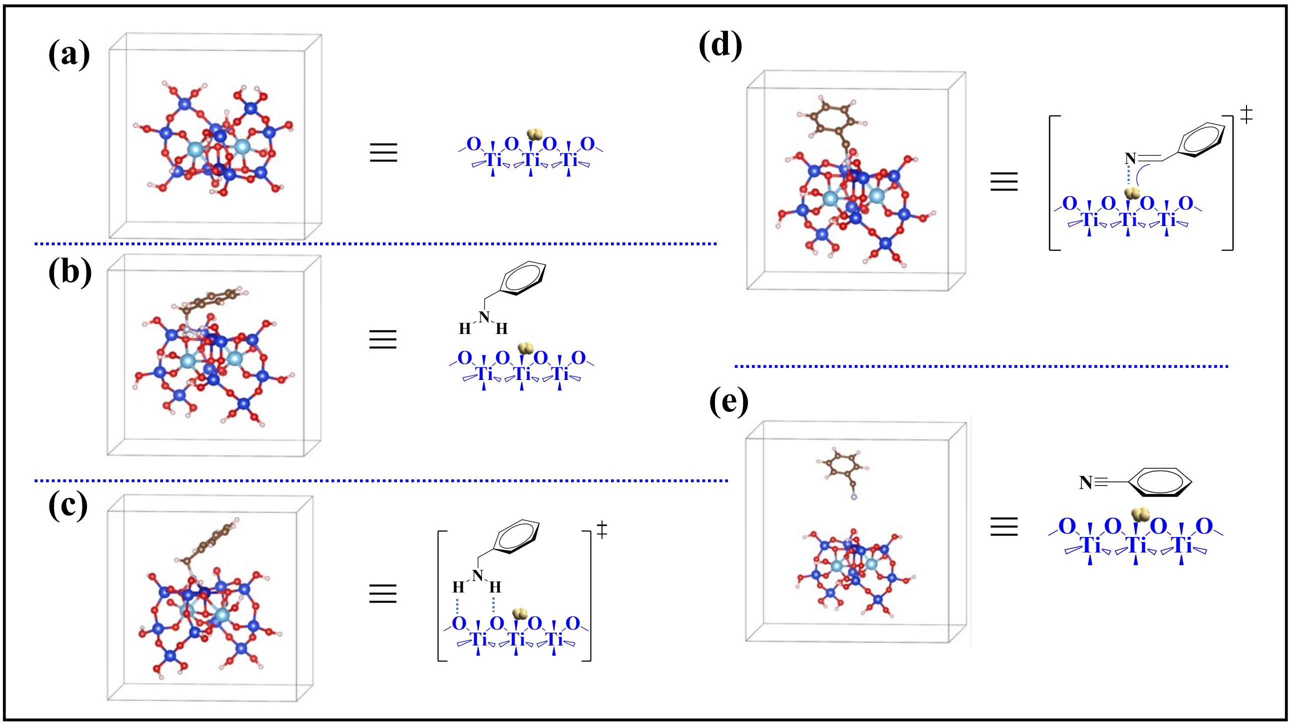


Fig. S2 The DFT calculations of optimized structure (a) ~ (e). The corresponding cartesian coordinates are shown in Table S8-S12.

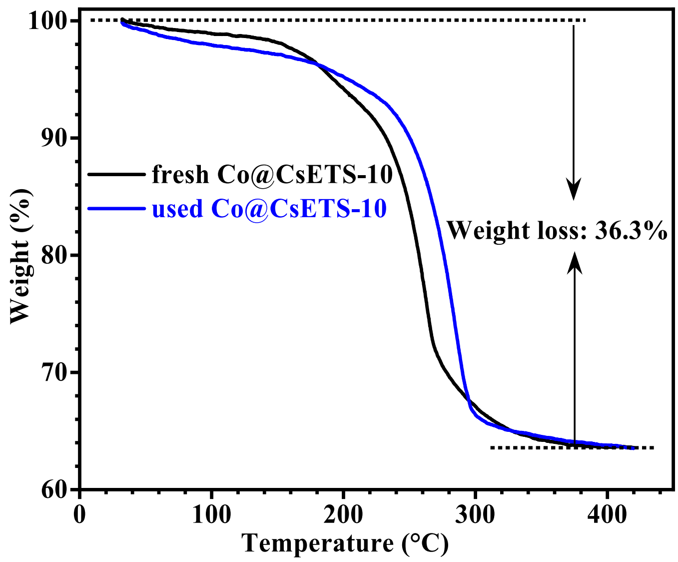
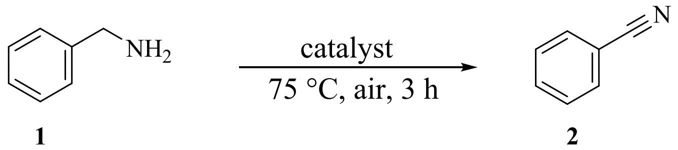


Fig. S3 The TGA diagrams of fresh and used Co@CsETS-10 catalyst.

Discussion: Both the fresh and used catalysts exhibit similar weight loss behavior in the temperature range from room temperature to 420°C. This is primarily attributed to the loss of water adsorbed within the pores of the catalysts during the heating process. Compared to the fresh catalyst, the used catalyst shows a faster weight loss in the range from room temperature to 200°C, which is likely due to slight modifications in the pore structure of the catalyst during the reaction process. In the subsequent weight loss process, the weight loss curves of the two catalysts are nearly parallel. Furthermore, the total weight loss ratios are identical (36.3%), indicating that the textural properties of the used catalyst remain well-preserved.

Tables

Table S1 The screening of solvents.[a]



Entry	Solvent	Conversion (%)[b]	Yield (%)[b]
1	EtOH	75	75
2	DCE	81	81
3	1, 4-dioxane	93	93
4	DMF	45	45
5	DMSO	51	51
6	H_2O	100	84
7	cyclohexane	100	100
8	no	31	31

[a] Reaction conditions: **1a** (0.3 mmol), solvent (1.5 mL), 1.0wt.%Co@CsETS-10 (10 mg), at 75 °C for 3 h. [b] Conversion and yield determined by GC, toluene as internal standard.

Discussion: Although the reaction can proceed in a variety of solvents with different properties, the conversion of the substrate varies significantly (Table S1, entries 1-7). When water (entry 6) and cyclohexane (entry 7) were employed as solvents, complete conversion of the substrate was achieved. However, in water, the product yield was only 84%, with 16% of the substrate being converted into an amide byproduct. In contrast, in cyclohexane, all converted amine was transformed into the desired nitrile product. Additionally, under neat conditions (without solvent), the substrate conversion rate was only 31%. Therefore, cyclohexane was selected as the optimal reaction solvent.

Table S2. General properties of support and catalyst.

Sample	S_{BET} [a] ($m^2 \cdot g^{-1}$)	$V_{micro.}$ [b] ($cm^3 \cdot g^{-1}$)	$V_{meso.}$ [c] ($cm^3 \cdot g^{-1}$)	$S_{ext.}$ [d] ($m^2 \cdot g^{-1}$)	Co loading [e] (wt. %)	Co valence state [f]
NaKETS-10	335	0.12	0.13	97	-	-
KETS-10	336	0.12	0.13	97	-	-
RbETS-10	333	0.12	0.13	97	-	-
CsETS-10	333	0.12	0.12	95	-	-
0.5wt.%Co@CsETS-10	329	0.12	0.12	93	0.471	+2 (95.5%) [g]
0.75wt.%Co@CsETS-10	322	0.12	0.12	92	0.725	+2 (96.3%)
1.0wt.%Co@CsETS-10	324	0.12	0.11	89	0.976	+2 (94.7%)
1.25wt.%Co@CsETS-10	309	0.11	0.11	87	1.229	+2 (93.2%)

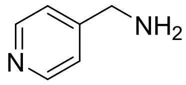
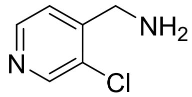
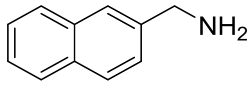
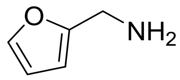
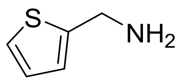
[a] BET surface area, [b] Microporous pore volume, [c] Mesoporous pore volume, [d] External surface area, including outer and mesoporous surface area, [e] Measured by ICP-OES, [f] Measured by XPS, [g] The percentage of Co^{2+}, obtained by fitting the XPS data with software Thermo Avantage.

Table S3 Reported results for homogeneous catalytic dehydrogenation of amines to nitriles.

catalyst	reaction conditions	Yield (%)	references
$NiSO_4/K_2S_2O_8$/NaOH	at room temperature for 5~24 h, CH_2Cl_2 as solvent.	84 ~ 96%	[S1]
$[RhH(PPr^i{}_3)_3]$	at 110°C for 24 h with N_2 stream, toluene as solvent.	27%	[S2]
Ru complex	at 100°C for 24~36 h with N_2 balloon, DMF as solvent, Cs_2CO_3 as base.	70 ~ >99%	[S3]
$HRu(bmpi)(PPh_3)_2$	at 110°C for 24 h, PhMe as solvent.	16 ~ 81%	[S4]
$[Ru(benzene)Cl_2]_2$	reflux for 24 h, toluene as solvent, HMTA as an additive.	71 ~ 94%	[S5]
$Ru(COD)Cl_2$	reflux for 24 h, toluene as solvent, HMTA as an additive.	70 ~ 92%	[S6]
$RuCl_3 \cdot nH_2O$	refiux at 115°C for 24 h, toluene as solvent, HMTA derivative as base, Nbenzylhexamet-hylenetetramine as ligand.	42 ~ 91%	[S7]
$[Cp^*Co(tBuPPH)I]^+I^-$	at 110°C for 40 h with Ar atmosphere, PhMe as solvent, *t*-BuOK as base.	35 ~ 89%	[S8]
Co@CsETS-10	at 75 °C for 3 h, cyclohexane as solvent.	81 ~ 100%	This work

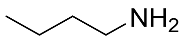
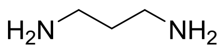
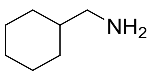
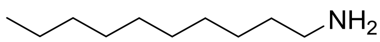
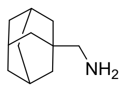
Discussion: Numerous homogeneous catalytic systems, including both transition metals (Ni and Co) and noble metals (Rh and Ru)[S1-8], have successfully realized the reaction of dehydrogenation of amines to nitriles, achieving moderate to good product yields. For transition metal catalysts, the addition of external bases such as NaOH[S1] and *t*-BuOK[S8] is essential to ensure optimal yields. In the case of noble metal catalysts, apart from their high cost, prolonged reaction times, additional additives[S5-7], organic ligands[S7], and bases[S3,S7] are also requisite. In summary, while homogeneous catalysts have enabled the dehydrogenation of primary amines to nitriles, the majority of these systems are complex, complicating subsequent operations such as product purification and thereby limiting industrial scalability. The Co@CsETS-10 catalyst reported in this work operates under milder reaction conditions, obviating the need for bases, ligands, and additives. This reaction system simplified operational procedures, and afforded high product yields (81 ~ >99%), possessing obvious advantages compared with the homogeneous catalytic systems.

Table S4. The substrate scope of heterocyclic primary amines.[a]

Entry	Substrate	Conversion[b] (%)	Yield[b] (%)
1		43	43
2		36	36
3		49	49
4		64	64
5		58	58

[a] Reaction conditions: **1a** (0.3 mmol), cyclohexane (1.5 mL), Co@CsETS-10 (10 mg), at 75 °C for 3 h. [b] Conversion and yield determined by GC, toluene as internal standard.

Table S5. The substrate scope of aliphatic primary amines.[a]

Entry	Substrate	Conversion[b] (%)	Yield[b] (%)
1		59	59
2		53	53
3		61	61
4		67	67
5		63	63

[a] Reaction conditions: **1a** (0.3 mmol), cyclohexane (1.5 mL), Co@CsETS-10 (10 mg), at 75 °C for 3 h. [b] Conversion and yield determined by GC, toluene as internal standard.

Table S6. Reaction condition reoptimization for the heterocyclic and aliphatic primary amines.[a]

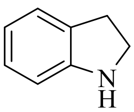
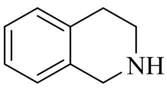
1ah **2ah**

1al **2al**

Entry	Temperature (°C)	Time (h)	Conversion[b] (%)		Yield[b] (%)	
			1af	**1aj**	**2af**	**2aj**
1	75	3	78	74	78	74
2	75	5	84	87	84	84
3	75	7	89	93	89	93
4	75	9	91	94	91	94
5	95	3	85	83	85	83
6	95	4	97	94	97	94
7	95	5	100	100	100	100

[a] Reaction conditions: **1** (0.3 mmol), cyclohexane (1.5 mL), Co@CsETS-10 (15 mg), at 95 °C for 6 h. [b] Conversion and yield determined by GC, toluene as internal standard.

Table S7. Substrate scope of cyclic amines.[a]

Entry	cyclic amines	Temperature (°C)	Time (h)	Yield (%)[b]
1		75 (standard)	3 (standard)	not detected
2		75 (standard)	10	not detected
3		100	10	not detected
4		75 (standard)	3 (standard)	not detected
5		75 (standard)	10	not detected
6		100	10	not detected

[a] Reaction condition: cyclic amines (0.3 mmol), cyclohexane (1.5 mL), Co@CsETS-10 (10 mg). [b] determined by GC, toluene as internal standard.

Table S8. The cartesian coordinate for the optimized structure (a) in Fig. S2.

Ti	8.20611379	5.93535839	5.76596665
Ti	5.58831844	8.56455755	5.88615829
Si	3.24151882	6.70466392	7.21266977
Si	3.75051263	6.24856798	4.43935638
Si	5.90631255	4.07046853	4.35186601
Si	10.10130561	8.25686639	4.46845867
Si	7.93511806	10.42436650	4.55975972
Si	6.38120784	3.59836774	7.13076840
Si	10.52650682	7.72296203	7.24307052
Si	7.42611014	10.88046244	7.33296021
Si	4.32701191	4.60075980	9.13836113
Si	9.53141150	9.77856932	9.27006949
O	6.56141061	12.16255834	7.68636540
O	4.56901826	10.17146444	5.86306840
O	4.52001575	7.65055913	7.12616736
O	1.94851309	7.56336515	7.54736030
O	3.05630571	6.03155687	5.81626762
O	4.69461542	7.52226627	4.59236220
O	2.64160504	6.43756355	3.33205774
O	7.76970636	11.54376052	3.46895991
O	7.19151345	5.00606080	4.47366660
O	5.75981311	3.33466876	5.71875657
O	4.61511336	4.96635917	4.08596530
O	9.14490985	6.98505933	4.52766533
O	6.60750572	6.95756598	5.90936109
O	6.65650823	9.47845718	4.64626213
O	9.22801088	9.56566527	4.22495628
O	8.12021826	11.09745944	5.95616188
O	7.26981584	4.91495735	7.02896682
O	9.20130790	6.85106456	7.08176589
O	6.48190856	9.60676415	7.18006730
O	5.22071494	3.74685720	8.17046277
O	10.82501001	8.36126488	5.85476959
O	10.37151098	8.86905903	8.30496563
O	8.53501773	10.69146688	8.44025885
O	3.40691641	5.58526990	8.30345547
O	6.05790701	2.83256240	3.01266638
H	5.90151392	1.95476543	3.36856969
O	11.36060800	8.11805888	3.14795960
H	12.22931579	8.30156425	3.51296619
O	3.27540564	3.45916505	10.10765674
H	3.73700589	3.20026470	10.90856267
O	5.39091116	5.59046371	10.25076890
H	5.33510588	5.24026231	11.14286298
O	8.55220813	8.71826905	10.39506662
H	8.91011557	8.77765919	11.28385810
O	10.68141797	10.83206682	10.22746731
H	10.94690939	10.37206141	11.02725827
O	9.87270721	4.86685811	5.73206572
H	9.77971252	4.14806525	5.10256978
O	11.92241500	6.65536502	7.75346158
H	12.69170641	7.19965701	7.93686815
O	7.43181204	2.18375901	7.62485822
H	6.88101367	1.41136260	7.77156936
Co	7.40351422	7.70976579	4.42676702
H	1.42190548	8.35255678	7.40056447
H	3.76250921	10.68716222	5.93535839
H	2.03831809	6.99016846	2.82976790
H	7.21241573	12.13996243	2.96336748
H	5.78380628	12.70226340	7.52626043

Table S9. The cartesian coordinate for the optimized structure (b) in Fig. S2.

H	6.87793135	2.74317491	4.82553229
H	11.77052359	7.64687578	4.75242236
H	3.89062905	3.53127516	12.16471950
H	5.27411965	6.57977696	12.12372546
H	8.14642871	9.64647242	12.26172318
H	11.17972539	10.84967379	12.43863026
H	9.91742379	4.57958261	6.10102720
H	13.12042590	7.52447678	8.75862778
H	7.12382271	1.73227525	9.25931781
H	1.45782510	7.82728164	9.81743157
H	3.54981870	10.80507892	7.15082163
H	2.13052391	7.36577794	4.87852423
H	6.82082834	12.24057014	4.70082993
H	5.88973003	12.84597575	8.95673163
O	6.77242855	12.77107269	9.35442632
O	4.50723075	10.72567119	7.00742996
O	4.35652079	8.38727599	8.64822668
O	1.75062927	7.82407442	8.89182926
O	3.24612457	6.49697250	7.16452519
O	5.22872297	7.90217011	5.98412421
O	3.02112385	7.13007678	4.57913069
O	7.72443207	11.88878236	4.67023018
O	7.33272905	5.87397094	5.91212222
O	6.00513146	3.76868198	7.12912920
O	4.80512273	5.33827853	5.28422237
O	9.04032332	7.66947207	6.06522302
O	7.09091960	7.67477855	7.70712769
O	7.00362503	9.63307501	5.99272537
O	9.59502577	10.25657223	5.51912173
O	8.18332626	11.66867993	7.32182452
O	7.64393097	5.16468072	8.66413156
O	9.67441893	7.19337555	8.82092065
O	6.62182064	10.11826836	8.80902479
O	5.36873250	4.06457674	9.66962268
O	11.09313058	8.85466930	7.31382106
O	10.77012027	9.39597433	9.90912877
O	8.82202859	11.28027159	9.90573204
O	3.55642264	6.09878215	9.82813201
O	6.70783232	3.66118196	4.56512099
O	11.24351982	8.45518148	4.65732843
O	3.47672335	4.15437877	11.54832189
O	5.61252459	5.87147806	11.55632535
O	8.82143088	9.23548237	11.70062088
O	10.61551792	11.28858119	11.78443124
O	9.98652470	5.08627888	6.92652066
O	12.28242430	7.30067147	9.19523182
O	7.54612549	2.57828032	9.04162079
Si	3.24933179	7.18047380	8.65652171
Si	4.07672042	6.72057371	5.76222865
Si	6.21241962	4.65428157	5.76222865
Si	10.24673191	8.80517613	5.90942525
Si	8.12362832	10.86777998	5.89102749
Si	6.64392127	3.88608063	8.65872302
Si	10.96073091	8.19186911	8.82482762
Si	7.59932152	11.43647755	8.85192859
Si	4.51943275	5.05298216	10.65282367
Si	9.74222237	10.28217163	10.82652353
Ti	8.73702281	6.20087364	7.62662659
Ti	5.51681837	9.31077904	7.58623026
Co	7.15122982	7.75447785	6.00532098
N	5.47411867	9.73526855	5.04771941
H	5.23222175	8.86927670	5.48532935
H	6.39103235	10.01027268	5.33712685
C	5.45032697	9.56977624	3.58722649
H	4.46982296	9.27367739	3.27773022
H	5.70742900	10.49688012	3.11892933

C	6.46672263	8.48817207	3.17652800
C	6.07122925	7.15246898	3.09983182
C	7.78273050	8.84388139	2.88123095
C	6.99162713	6.17257726	2.72842172
H	5.03382634	6.87227499	3.33352119
C	8.70331789	7.86397509	2.50872748
H	8.09463218	9.89657690	2.94142455
C	8.30802862	6.52847610	2.43252696
H	6.68003159	5.11967766	2.66862174
H	9.74072081	8.14467932	2.27551920
H	9.03363191	5.75577048	2.13962074

Table S10. The cartesian coordinate for the optimized structure (c) in Fig. S2.

H	6.7926540966	2.9818772590	5.8560845363
H	11.9486608282	7.8591269826	5.8939856658
H	4.1550297567	3.7084246519	13.2181001352
H	6.6664745134	6.4361573037	12.2292096149
H	8.3511100343	9.8920448136	13.3528121028
H	11.4520470604	11.1077811133	13.5821280898
H	10.1111180318	4.9085178793	7.2267394444
H	13.4079474719	7.9595509908	10.1551960235
H	7.3583195384	2.0212894619	10.4489001049
H	1.6422463687	7.9212398722	10.9279779048
H	3.8351533180	11.1304435613	8.3812318111
H	2.3889033216	7.5844439248	6.0633474055
H	7.5725511950	12.9842110147	6.1034124700
H	6.1495716705	13.1166191042	10.1221533316
O	7.0353659500	13.0340149100	10.5095112900
O	4.7701699700	10.9886141600	8.1625113600
O	4.6194610000	8.6502084800	9.8033178800
O	2.0135612500	8.0870058300	10.0469172200
O	3.5090660700	6.7599120100	8.3196093700
O	5.4916638600	8.1651092700	7.1392068200
O	3.2840599100	7.3930165500	5.7342059200
O	7.9873639100	12.1517073900	5.8253140000
O	7.5956686100	6.1369121200	7.0672205600
O	6.2680612500	4.0316084200	8.2842204000
O	5.0680686500	5.6012140900	6.4393118300
O	9.3032655800	7.9324151000	7.2203159800
O	7.3538666600	7.9377166500	8.8622099900
O	7.2665648100	9.8960119000	7.1478161700
O	9.8579646000	10.5195102200	6.6742112000
O	8.4462574700	11.9316100600	8.4769188400
O	7.9068589200	5.4276072600	9.8192074200
O	9.9373669900	7.4563179500	9.9760184500
O	6.8847627100	10.3812168400	9.9641164000
O	5.6316640000	4.3275133500	10.8247192900
O	11.3560673400	9.1176207600	8.4689136600
O	11.0330656100	9.6589073300	11.0642103100
O	9.0849656400	11.5432074600	11.0608118900
O	3.8193652400	6.3617068300	10.9832068900
O	6.9707656100	3.9241123500	5.7202194900
O	11.5064591200	8.7181166300	5.8124150800
O	3.7396607600	4.4173073800	12.7034158000
O	5.8754597000	6.1344199400	12.7114058800
O	9.0843614800	9.4984108800	12.8557107000
O	10.8784597700	11.5515147300	12.9395083900
O	10.2494635500	5.3492168500	8.0816136600
O	12.5453662200	7.5636176600	10.3503138000
O	7.8090597000	2.8412069300	10.1967199400
Si	3.5122681500	7.4434190200	9.8116100400
Si	4.3396570700	6.9835134900	6.9173121000
Si	6.4753653800	4.9172086400	6.9173121000
Si	10.5096623300	9.0681094400	7.0645169200
Si	8.3865659600	11.1307137800	7.0461200900
Si	6.9068600500	4.1490127900	9.8138152400

Si	11.2236645700	8.4548064000	9.9799153200
Si	7.8622564400	11.6994143300	10.0070121200
Si	4.7823590000	5.3159122500	11.8079072700
Si	10.0051694200	10.5451117100	11.9816047200
Ti	8.9999596200	6.4638107200	8.7817201100
Ti	5.7797599600	9.5737200600	8.7413165700
Co	7.4141623300	8.0174060200	7.1604130100
N	7.0165613200	8.9825143600	6.0488097600
H	5.4055443654	8.7415853882	6.3228393258
C	6.9346667500	9.4758151100	4.6664197300
H	6.7561019729	10.5413654940	4.5133960071
C	6.3049606300	8.3925169900	3.7711075500
C	4.9219664400	8.3534124000	3.5913080400
C	7.1171699000	7.4504122300	3.1401175900
C	4.3512570300	7.3721124400	2.7810169900
H	4.2892746687	9.1039569213	4.0560115843
C	6.5465662300	6.4693086200	2.3287088300
H	8.1929245025	7.4811833843	3.2954007411
C	5.1638590100	6.4299170600	2.1493171300
H	3.2728233842	7.3415972695	2.6503992651
H	7.1836377383	5.7393464284	1.8353241993
H	4.7189769098	5.6708779800	1.5095138597

Table S11. The cartesian coordinate for the optimized structure (d) in Fig. S2.

H	7.14086827	3.00611378	5.98061463
H	12.03345718	7.90981933	5.90751066
H	4.15355913	3.79421687	13.31981518
H	5.53706686	6.84271283	13.27880748
H	8.40935809	9.90940926	13.41681388
H	11.44265930	11.11261904	13.59371340
H	10.18036217	4.84251873	7.25611276
H	13.38335824	7.78741549	9.91371393
H	7.38676345	1.99520973	10.41441571
H	1.72076776	8.09020791	10.97251317
H	3.81276473	11.06801655	8.30590993
H	2.39346022	7.62871644	6.03361500
H	7.08375957	12.50351269	5.85591496
H	6.15266573	13.10891627	10.11181965
O	7.03536595	13.03401491	10.50951129
O	4.77016997	10.98861416	8.16251136
O	4.61946100	8.65020848	9.80331788
O	2.01356125	8.08700583	10.04691722
O	3.50906607	6.75991201	8.31960937
O	5.49166386	8.16510927	7.13920682
O	3.28405991	7.39301655	5.73420592
O	7.98736391	12.15170739	5.82531400
O	7.59566861	6.13691212	7.06722056
O	6.26806125	4.03160842	8.28422040
O	5.06806865	5.60121409	6.43931183
O	9.30326558	7.93241510	7.22031598
O	7.35386666	7.93771665	8.86220999
O	7.26656481	9.89601190	7.14781617
O	9.85796460	10.51951022	6.67421120
O	8.44625747	11.93161006	8.47691884
O	7.90685892	5.42760726	9.81920742
O	9.93736699	7.45631795	9.97601845
O	6.88476271	10.38121684	9.96411640
O	5.63166400	4.32751335	10.82471929
O	11.35606734	9.11762076	8.46891366
O	11.03306561	9.65890733	11.06421031
O	9.08496564	11.54320746	11.06081189
O	3.81936524	6.36170683	10.98320689
O	6.97076561	3.92411235	5.72021949
O	11.50645912	8.71811663	5.81241508
O	3.73966076	4.41730738	12.70341580
O	5.87545970	6.13441994	12.71140588

O	**9.08436148**	**9.49841088**	**12.85571070**
O	**10.87845977**	**11.55151473**	**12.93950839**
O	**10.24946355**	**5.34921685**	**8.08161366**
O	**12.54536622**	**7.56361766**	**10.35031380**
O	**7.80905970**	**2.84120693**	**10.19671994**
Si	**3.51226815**	**7.44341902**	**9.81161004**
Si	**4.33965707**	**6.98351349**	**6.91731210**
Si	**6.47536538**	**4.91720864**	**6.91731210**
Si	**10.50966233**	**9.06810944**	**7.06451692**
Si	**8.38656596**	**11.13071378**	**7.04612009**
Si	**6.90686005**	**4.14901279**	**9.81381524**
Si	**11.22366457**	**8.45480640**	**9.97991532**
Si	**7.86225644**	**11.69941433**	**10.00701212**
Si	**4.78235900**	**5.31591225**	**11.80790727**
Si	**10.00516942**	**10.54511171**	**11.98160472**
Ti	**8.99995962**	**6.46381072**	**8.78172011**
Ti	**5.77975996**	**9.57372006**	**8.74131657**
Co	**7.41416233**	**8.01740602**	**7.16041301**
N	**7.01656132**	**8.98251436**	**6.04880976**
C	**6.93466675**	**9.47581511**	**4.66641973**
C	**6.30496063**	**8.39251699**	**3.77110755**
C	**4.92196644**	**8.35341240**	**3.59130804**
C	**7.11716990**	**7.45041223**	**3.14011759**
C	**4.35125703**	**7.37211244**	**2.78101699**
H	**4.28186868**	**9.09581041**	**4.08971399**
C	**6.54656623**	**6.46930862**	**2.32870883**
H	**8.20715915**	**7.48111892**	**3.28150731**
C	**5.16385901**	**6.42991706**	**2.14931713**
H	**3.26116205**	**7.34090732**	**2.63980852**
H	**7.18716242**	**5.72682000**	**1.83090705**
H	**4.71375606**	**5.65620821**	**1.51041260**

Table S12. The cartesian coordinate for the optimized structure (e) in Fig. S2.

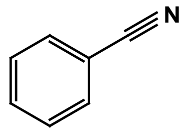
H	**9.75874611**	**5.62399550**	**10.69279380**
H	**14.65134008**	**10.52769504**	**10.61969229**
H	**6.77142881**	**6.41208426**	**18.03198986**
H	**8.15494704**	**9.46058389**	**17.99098467**
H	**11.02724235**	**12.52728772**	**18.12899072**
H	**14.06052776**	**13.73049296**	**18.30588660**
H	**12.79823518**	**7.46038102**	**11.96828696**
H	**16.00123650**	**10.40528968**	**14.62589490**
H	**10.00463484**	**4.61308342**	**15.12658123**
H	**4.33863750**	**10.70808939**	**15.68468704**
H	**6.43063422**	**13.68588762**	**13.01808888**
H	**5.01133816**	**10.24657765**	**10.74577917**
H	**9.70163174**	**15.12139457**	**10.56809003**
H	**8.77053333**	**15.72679058**	**14.82398493**
O	**9.65324318**	**15.65187882**	**15.22169049**
O	**7.38803209**	**13.60648075**	**12.87469276**
O	**7.23733397**	**11.26808680**	**14.51549006**
O	**4.63142999**	**10.70489603**	**14.75908039**
O	**6.12693957**	**9.37778027**	**13.03177761**
O	**8.10952810**	**10.78298080**	**11.85139370**
O	**5.90193988**	**10.01087919**	**10.44639657**
O	**10.60523064**	**14.76959611**	**10.53747852**
O	**10.21354569**	**8.75479027**	**11.77939055**
O	**8.88594177**	**6.64949127**	**12.99638623**
O	**7.68592989**	**8.21907867**	**11.15147830**
O	**11.92113913**	**10.55029264**	**11.93248878**
O	**9.97174527**	**10.55558101**	**13.57438443**
O	**9.88444653**	**12.51388374**	**11.85997713**
O	**12.47582784**	**13.13738224**	**11.38638350**
O	**11.06413888**	**14.54947799**	**13.18908620**
O	**10.52474576**	**8.04547784**	**14.53139584**
O	**12.55523470**	**10.07419721**	**14.68819593**
O	**9.50264675**	**12.99909143**	**14.67627676**
O	**8.24952746**	**6.94539576**	**15.53687717**
O	**13.97394092**	**11.73549710**	**13.18109263**
O	**13.65094372**	**12.27678183**	**15.77637919**
O	**11.70283126**	**14.16108810**	**15.77298243**
O	**6.43724468**	**8.97958655**	**15.69538581**
O	**9.58864374**	**6.54199503**	**10.43238239**
O	**14.12433394**	**11.33598130**	**10.52458304**

O	6.35753272	7.03519630	17.41558998
O	8.49334153	8.75228846	17.42358355
O	11.70224141	12.11627988	17.56789495
O	13.49634033	14.16938676	17.65169523
O	12.86732973	7.96708797	12.79378075
O	15.16323369	10.18149005	15.06249029
O	10.42693131	5.45907980	14.90888356
Si	6.13013293	10.06128139	14.52378873
Si	6.95753866	9.60139684	11.62948568
Si	9.09324577	7.53508938	11.62948568
Si	13.12753774	11.68598985	11.77668535
Si	11.00444135	13.74859545	11.75827776
Si	9.52473586	6.76689302	14.52598544
Si	13.84152834	11.07268163	14.69208085
Si	10.48014042	14.31727799	14.71919390
Si	7.40023602	7.93379159	16.52008634
Si	12.62302750	13.16299014	16.69378887
Ti	11.61783093	9.08169272	13.49387921
Ti	8.39764242	12.19157810	13.45348422
Co	10.03203265	10.63529298	11.87258785
N	10.07793975	11.45968841	6.57238281
C	9.99603108	11.95299137	5.18998327
C	9.36632892	10.86968969	4.29468304
C	7.98333953	10.83059645	4.11487855
C	10.17854077	9.92758740	3.66367912
C	7.41264334	9.84927889	3.30457865
H	7.34324369	11.57298151	4.61328682
C	9.60794628	8.94649358	2.85228087
H	11.26853427	9.95828027	3.80508193
C	8.22524165	8.90709524	2.67288318
H	6.32252779	9.81807752	3.16337924
H	10.24853027	8.20398648	2.35448279
H	7.77514058	8.13338678	2.03398740

Table S13. The Co loading of fresh and used Co@CsETS-10 catalyst.

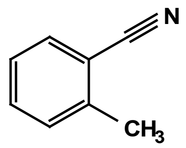
catalyst	cycle number	Co loading (%)
fresh Co@CsETS-10	-	0.976
used Co@CsETS-10	10	0.971

3. Analytical data



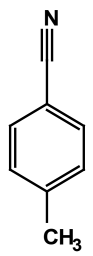
(2a) benzonitrile: light yellow liquid was obtained in 100%; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.63 – 7.57 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H).



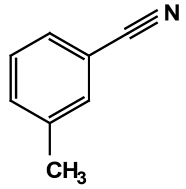
(2b) 2-methylbenzonitrile: light yellow liquid was obtained in 96%; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.12 (m, 2H), 2.47 (s, 3H).



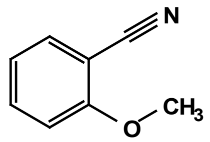
(2c) 4-methylbenzonitrile: colorless oily liquid was obtained in 100%; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 3H).



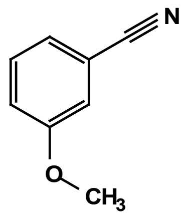
(2d) 3-methylbenzonitrile: light yellow liquid was obtained in 100%; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.22 (m, 4H), 2.31 (s, 3H).



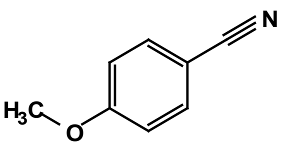
(2e) 2-methoxybenzonitrile: light yellow liquid was obtained in 97%; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (td, *J* = 7.4, 1.8 Hz, 2H), 7.00 – 6.84 (m, 2H), 3.86 (s, 3H).



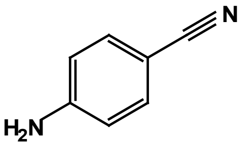
(2f) 3-methoxybenzonitrile: colorless oily liquid was obtained in 99%; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 -7.25 (m, 1H), 7.21 -7.13 (m, 1H), 7.10 -7.02 (m, 2H), 3.76 (s, 3H).



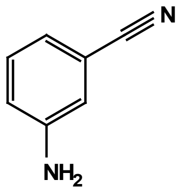
(2g) 4-methoxybenzonitrile: light grey powder was obtained in 100%, m.p. 57-60 °C; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.46 (m, 2H), 6.94 – 6.87 (m, 2H), 3.79 (s, 3H).



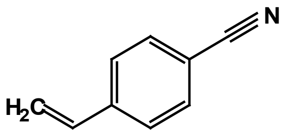
(2h) 4-aminobenzonitrile: orange crystal was obtained in 100%, m.p. 83-85 °C; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 2H), 4.13 (s, 2H).



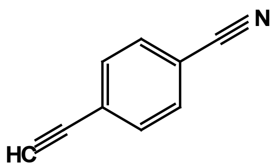
(2i) 3-aminobenzonitrile：brown solid was obtained in 96%, m.p. 49-52 °C; [S13]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 1.9 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.91 (s, 2H).



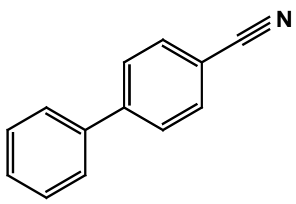
(2j) 4-vinylbenzonitrile: light yellow liquid was obtained in 100%; [S14]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H).



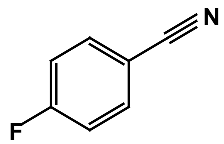
(2k) 4-ethynylbenzonitrile: yellow solid was obtained in 100%, m.p. 156-159 °C; [S14]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 (q, *J* = 8.2 Hz, 4H), 3.23 (s, 1H).



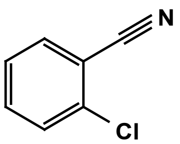
(2l) [1,1'-biphenyl]-4-carbonitrile: orange crystal was obtained in 99%, m.p. 85-87 °C; [S13]

¹H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.59 (dd, *J* = 7.3, 1.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43 (tt, *J* = 7.4, 1.3 Hz, 1H).



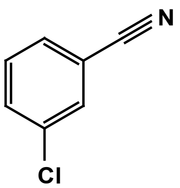
(2m) 4-fluorobenzonitrile: white solid was obtained in 100%, 33-35 °C; [S13]

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 2H), 7.22 – 7.15 (m, 2H).



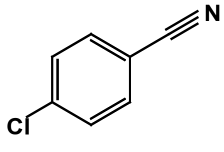
(2n) 2-chlorobenzonitrile: light yellow solid was obtained in 94%, m.p. 43-46 °C; [S13]

¹H NMR (600 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.56 (td, *J* = 7.8, 1.6 Hz, 1H), 7.52 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.39 (td, *J* = 7.6, 1.3 Hz, 1H).



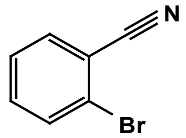
(2o) 3-chlorobenzonitrile: yellow viscous liquid was obtained in 98%; [S13]

¹H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 1.5 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H).



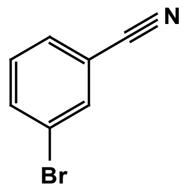
(2p) 4-chlorobenzonitrile：yellow solid was obtained in 100%, m.p. 90-93 °C; [S13]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 – 7.59 (m, 2H), 7.49 – 7.45 (m, 2H).



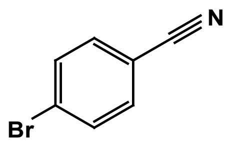
(2q) 2-bromobenzonitrile：yellow solid was obtained in 96%, 53-56 °C; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.69 – 7.54 (m, 2H), 7.46-7.30 (m, 2H).



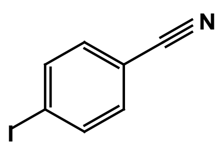
(2r) 3-bromobenzonitrile: light yellow crystal was obtained in 100%, m.p. 38-40 °C; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H).



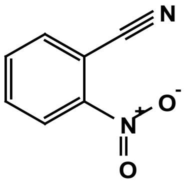
(2s) 4-bromobenzonitrile: light yellow powder was obtained in 100%, m.p. 110-115 °C; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H).



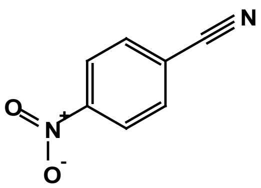
(2t) 4-iodobenzonitrile: dark yellow powder was obtained in 100%, 124-128 °C; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H).



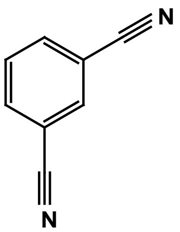
(2u)2-nitrobenzonitrile: yellow crystal was obtained in 94%, m.p. 107-109 °C; [S15]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.40 – 8.18 (m, 1H), 7.97 – 7.65 (m, 3H).



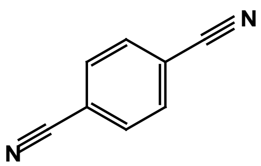
(2v) 4-nitrobenzonitrile: yellow powder was obtained in 100%; [S13]

^{1}H NMR (400 MHz, Chloroform-d) δ 8.35 – 8.24 (m, 2H), 7.90 – 7.78 (m, 2H).



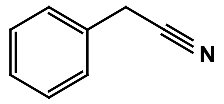
(2w) isophthalonitrile: reddish brown powder was obtained in 100%, 163-165 °C; [S15]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H).



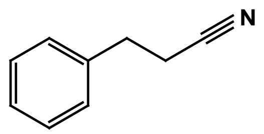
(2x) terephthalonitrile: light yellow powder was obtained in 100%, 223-225 °C; [S15]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 (s, 4H).



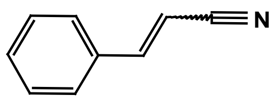
(2y) 2-phenylacetonitrile: colorless oily liquid was obtained in 100%; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.27 (q, *J* = 7.4, 6.7 Hz, 5H), 3.67 (s, 2H).



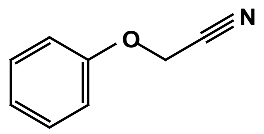
(2z) 3-phenylpropanenitrile： light yellow liquid was obtained in 100%; [S13]

^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 -7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 7.25 – 7.19 (m, 2H), 2.94 (t, J = 7.4 Hz, 2H), 2.60 (t, J = 7.4 Hz, 2H).



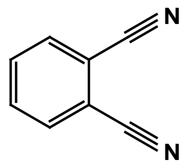
(2aa) 3-phenylacrylonitrile: light yellow liquid was obtained in 100%; [S15]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 6H), 5.81 (d, *J* = 16.7 Hz, 1H).



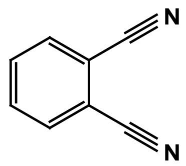
(2ab) 2-phenoxyacetonitrile: colorless liquid was obtained in 100%; [S16]

^{1}H NMR (300 MHz, Chloroform-d) δ 7.28 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 8.1 Hz, 2H), 4.69 (s, 2H).



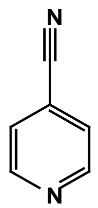
(2ac) 1,2-dicyano benzene: white powder was obtained in 100%, 138-140 °C; [S13]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.82 – 7.75 (m, 2H).



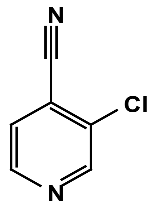
(2ad) 1,2-dicyano benzene: white powder was obtained in 100%, 138-140 °C; [S13]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.82 – 7.76 (m, 2H).



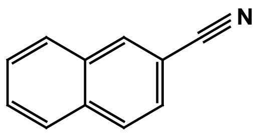
(2ae) isonicotinonitrile：white powder was obtained in 87%, 76-79 °C; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (dd, *J* = 4.4 Hz, 1.8 Hz, 2H), δ 7.56 (dd, *J* = 4.4 Hz, 1.8 Hz, 2H).



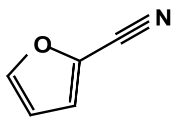
(2af) 3-chloroisonicotinonitrile: light yellow solid was obtained in 83%, 71-73 °C; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 8.69 (d, *J* = 4.9 Hz, 1H), 7.58 (d, *J* = 4.9 Hz, 1H).



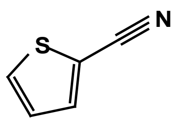
(2ag)2-naphthonitrile: white powder was obtained in 94%, 63-67 °C; [S15]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.82 (t, J = 7.5 Hz, 3H), 7.63 – 7.44 (m, 3H).



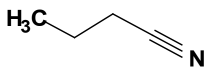
(2ah) furan-2-carbonitrile: light yellow liquid was obtained in 100%; [S13]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 (d, J = 1.7 Hz, 1H), 7.04 (d, J = 3.6 Hz, 1H), 6.56 – 6.39 (m, 1H).



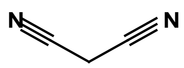
(2ai) thiophene-2-carbonitrile: colorless liquid was obtained in 91%; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, J = 3.8, 1.2 Hz, 1H), 7.55 (dd, J = 5.1, 1.2 Hz, 1H), 7.07 (dd, J = 5.1, 3.8 Hz, 1H).



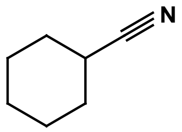
(2aj) Butyronitrile: colorless liquid was obtained in 100%; [S14]

^{1}H NMR (400 MHz, Chloroform-d) δ 2.26 (t, J = 7.1 Hz, 2H), 1.64 (h, J = 7.3 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H).



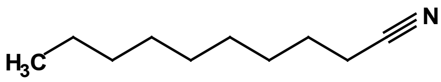
(2ak) malononitrile: colorless crystal was obtained in 98%, m.p. 30-32 °C; [S16]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.53 (s, 2H).



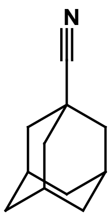
(2al) cyclohexanecarbonitrile: pink crystal was obtained in 100%; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.73 – 2.52 (m, 1H), δ 1.95 – 1.80 (m, 2H), δ 1.79 – 1.61 (m, 4H), δ 1.60 – 1.33 (m, 4H).



(2am) decanenitrile: pink crystal was obtained in 97%; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.33 (t, *J* = 7.2 Hz, 2H), 1.73 – 1.60 (m, 2H), 1.53 – 1.39 (m, 2H), 1.38 -1.18 (m, 10H), δ 0.88 (t, *J* = 6.8 Hz, 3H).



(2an) 1-Adamantanecarbonitrile： pink crystal was obtained in 100%; [S13]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.04 (s, 9H), 1.73 (s, 6H).

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4. References

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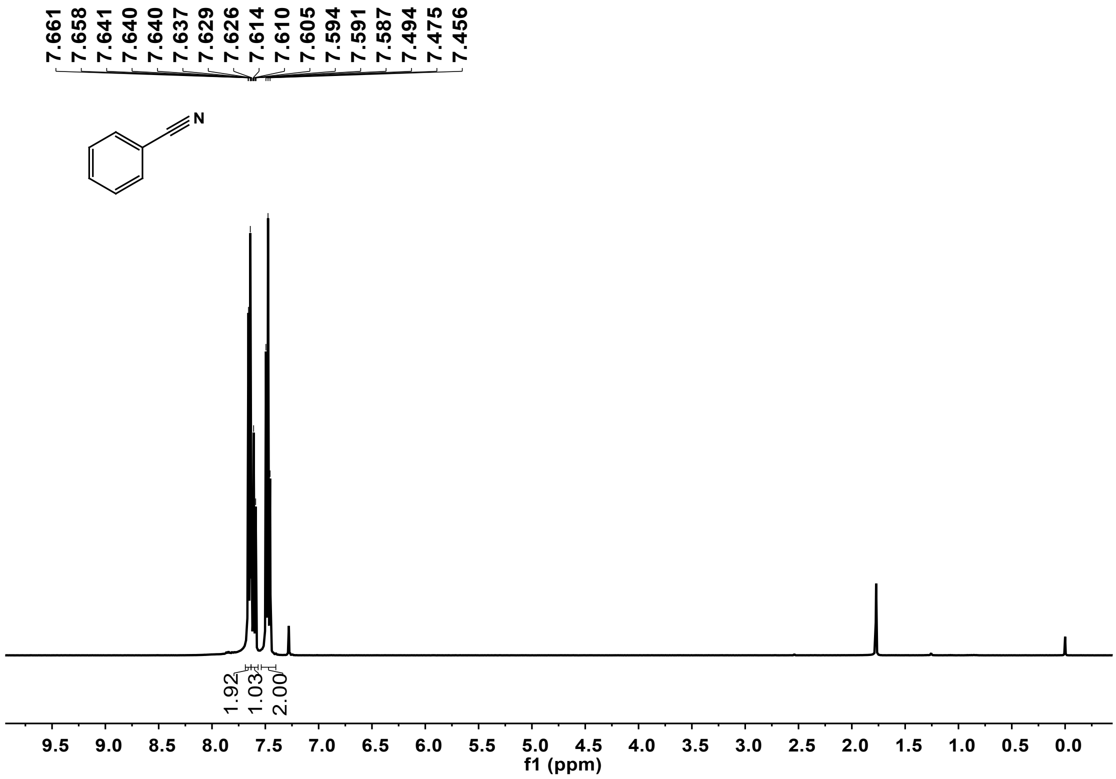
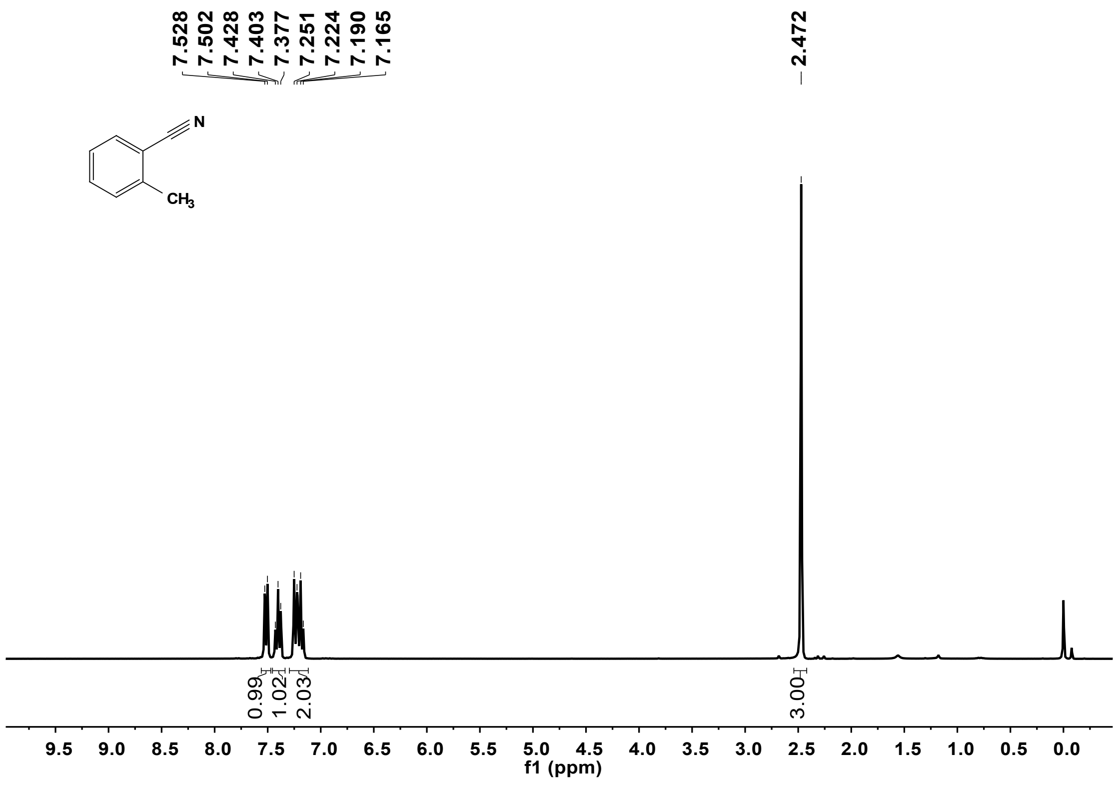
[16] D. L. J. Broere, *Phys. Sci. Rev.*, 2018, **3**, 20170029-20170048.

5. ^{1}H NMR spectra of these compounds

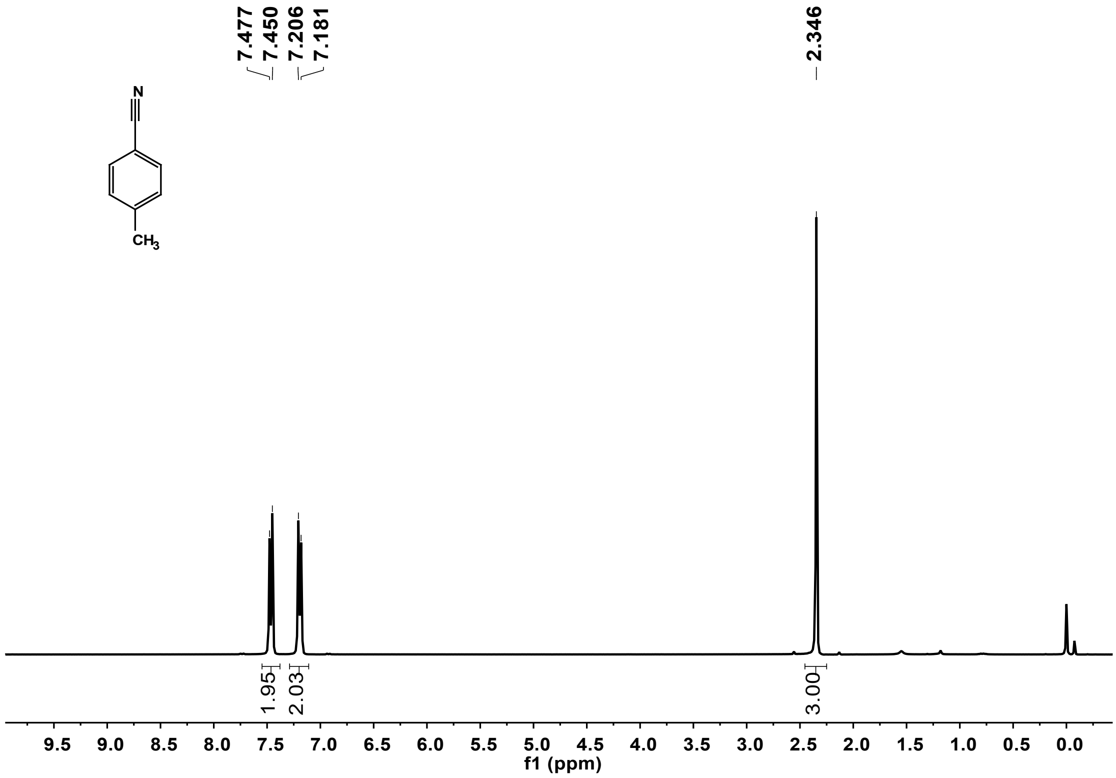
2a



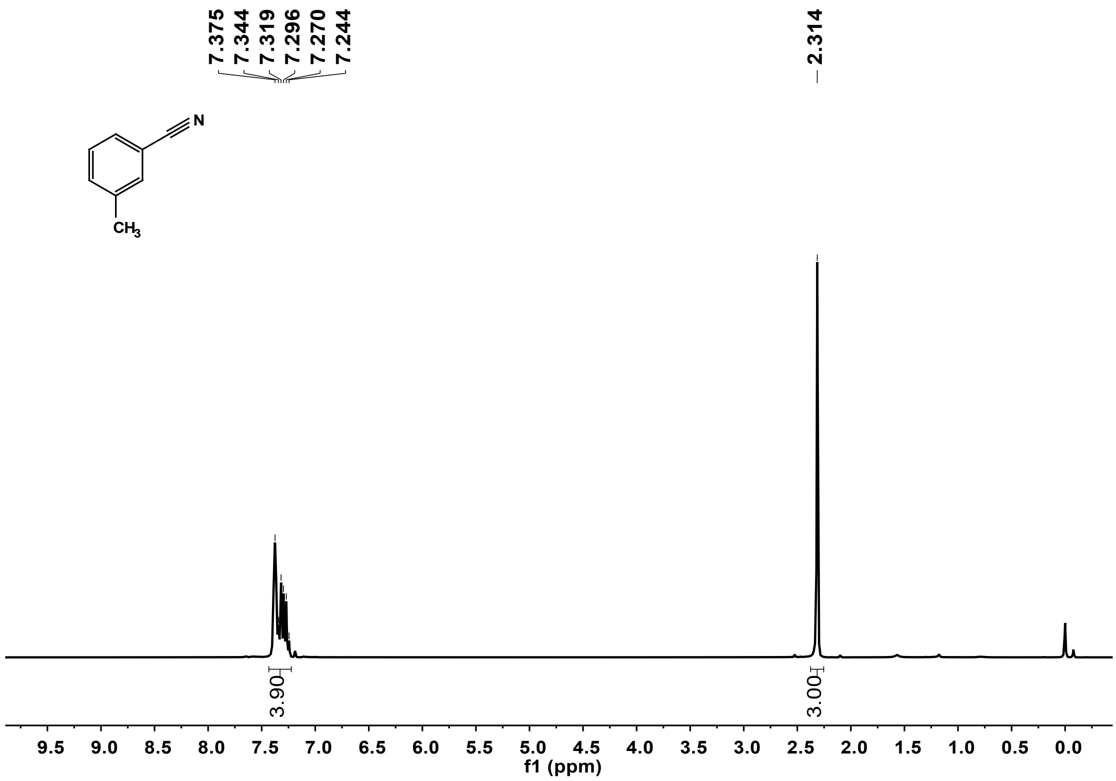
2b



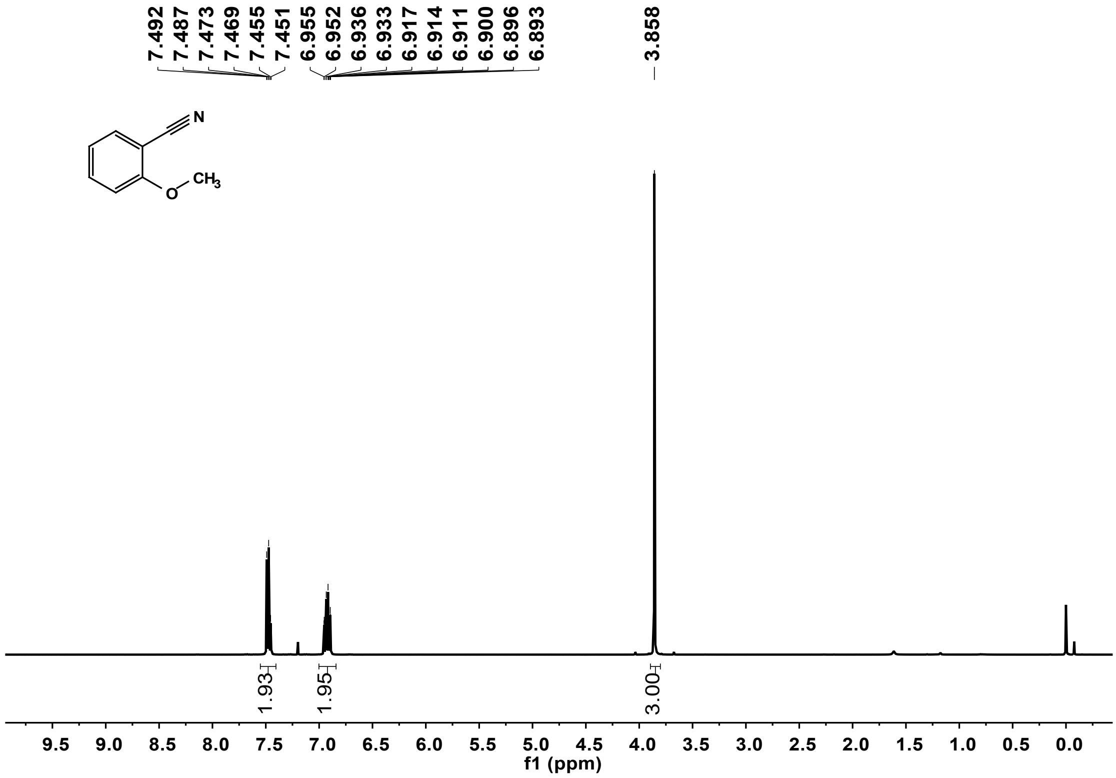
2c


7.477
7.450
7.206
7.181
2.346
N
CH3
1.95
2.03
3.00
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 0.5 0.0
f1 (ppm)

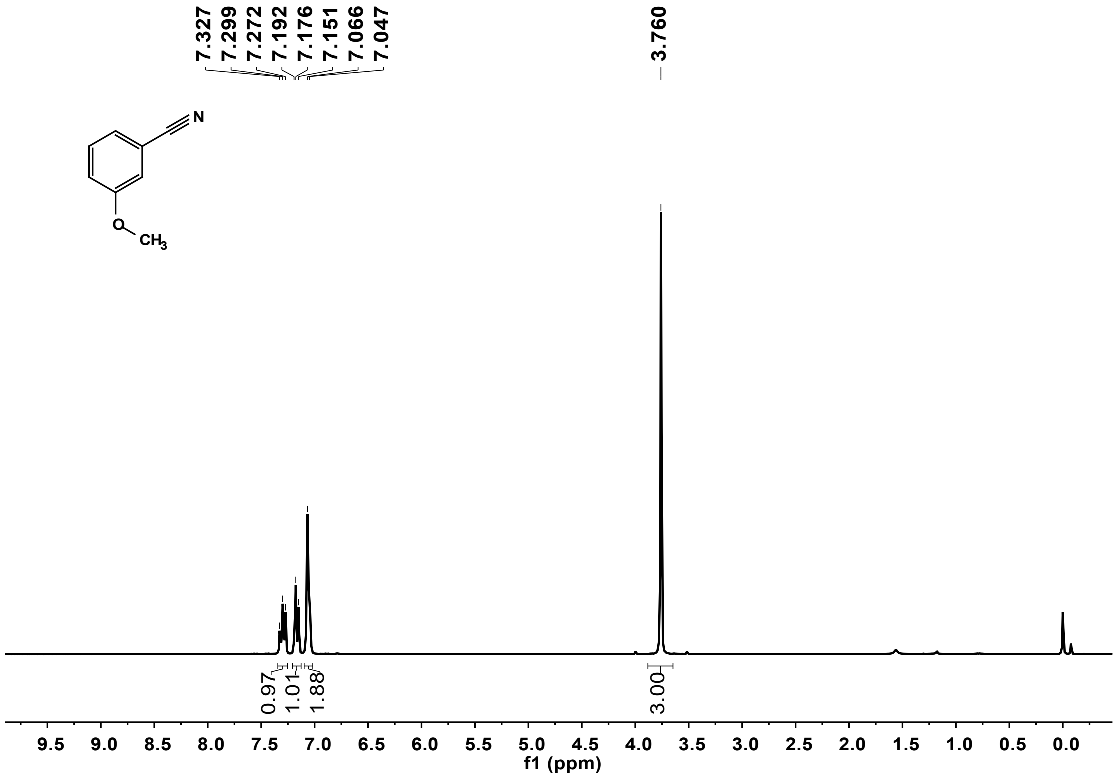
2d


7.375
7.344
7.319
7.296
7.270
7.244
2.314
N
CH3
3.90
3.00
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 0.5 0.0
f1 (ppm)

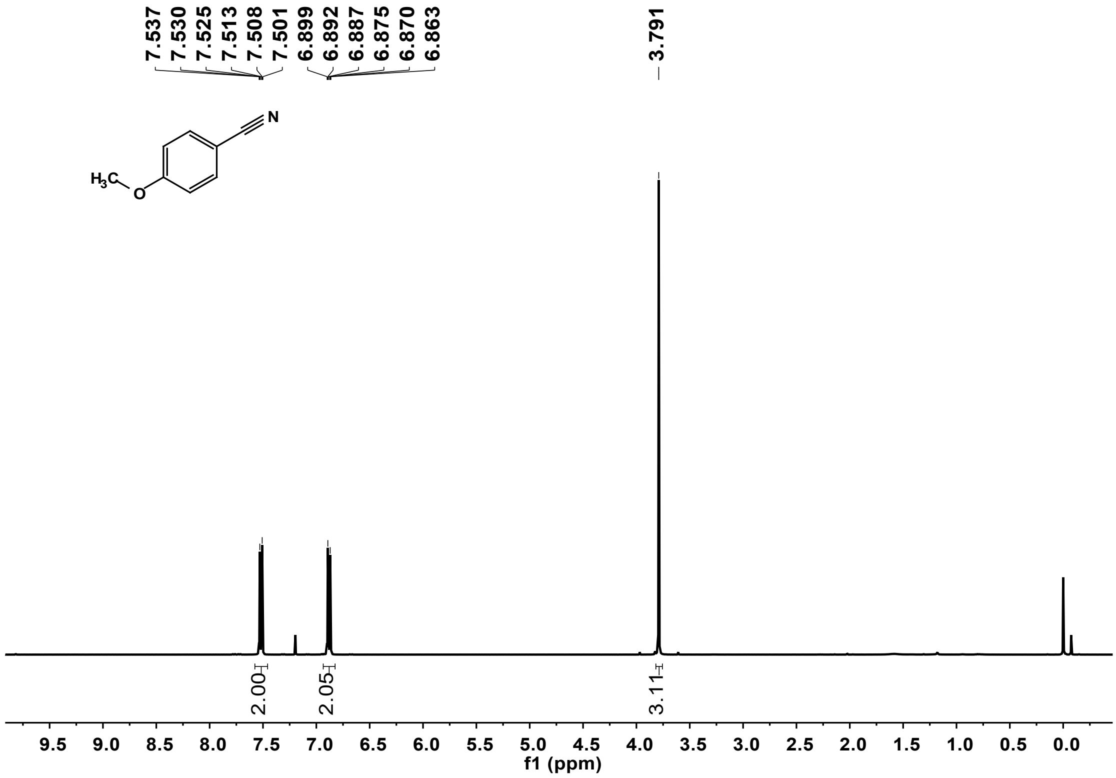
2e


7.492
7.487
7.473
7.469
7.455
7.451
6.955
6.952
6.936
6.933
6.917
6.914
6.911
6.900
6.896
6.893
3.858
N
O
CH3
1.93
1.95
3.00
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 0.5 0.0
f1 (ppm)

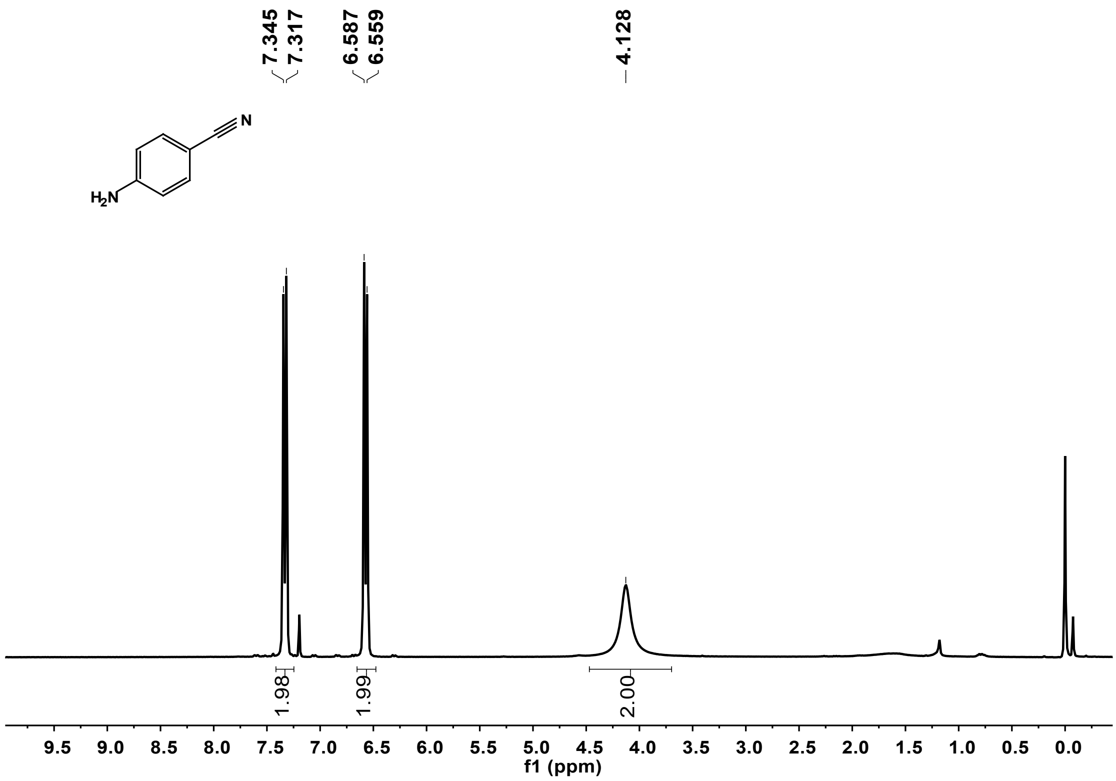
2f


7.327
7.299
7.272
7.192
7.176
7.151
7.066
7.047
3.760
N
O
CH3
0.97
1.01
1.88
3.00
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 0.5 0.0
f1 (ppm)

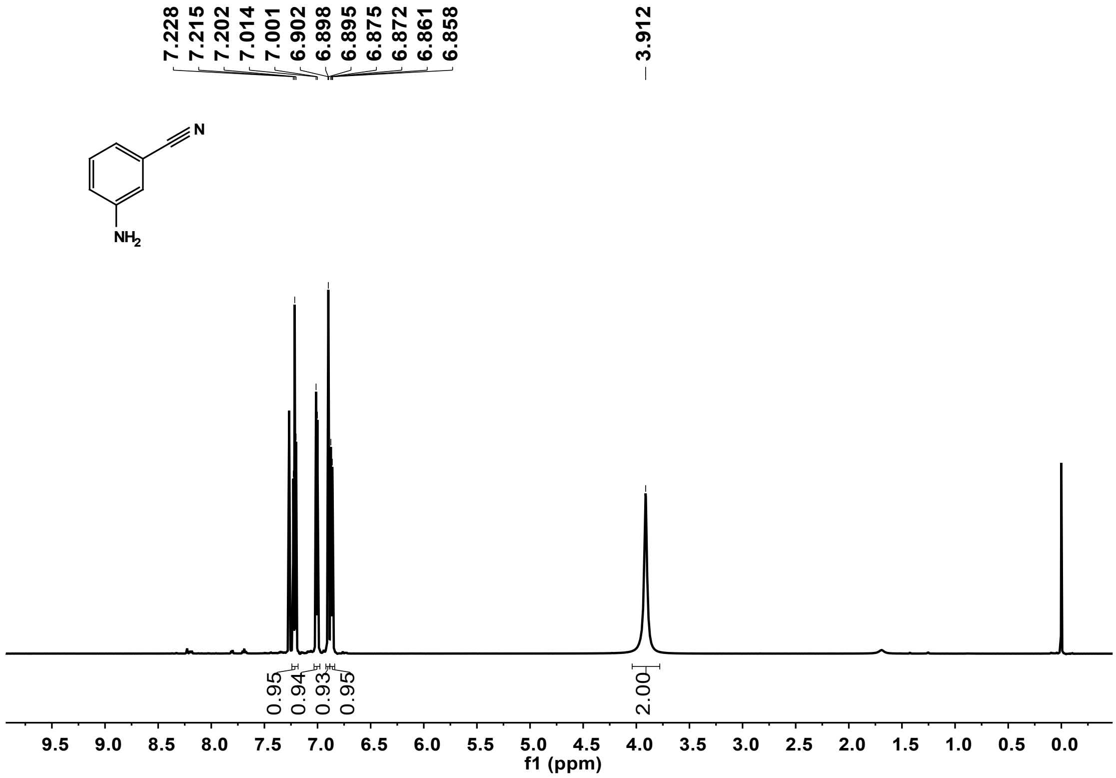
2g


7.537
7.530
7.525
7.513
7.508
7.501
6.899
6.892
6.887
6.875
6.870
6.863
3.791
N
H3C
O
2.00
2.05
3.11
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 0.5 0.0
f1 (ppm)

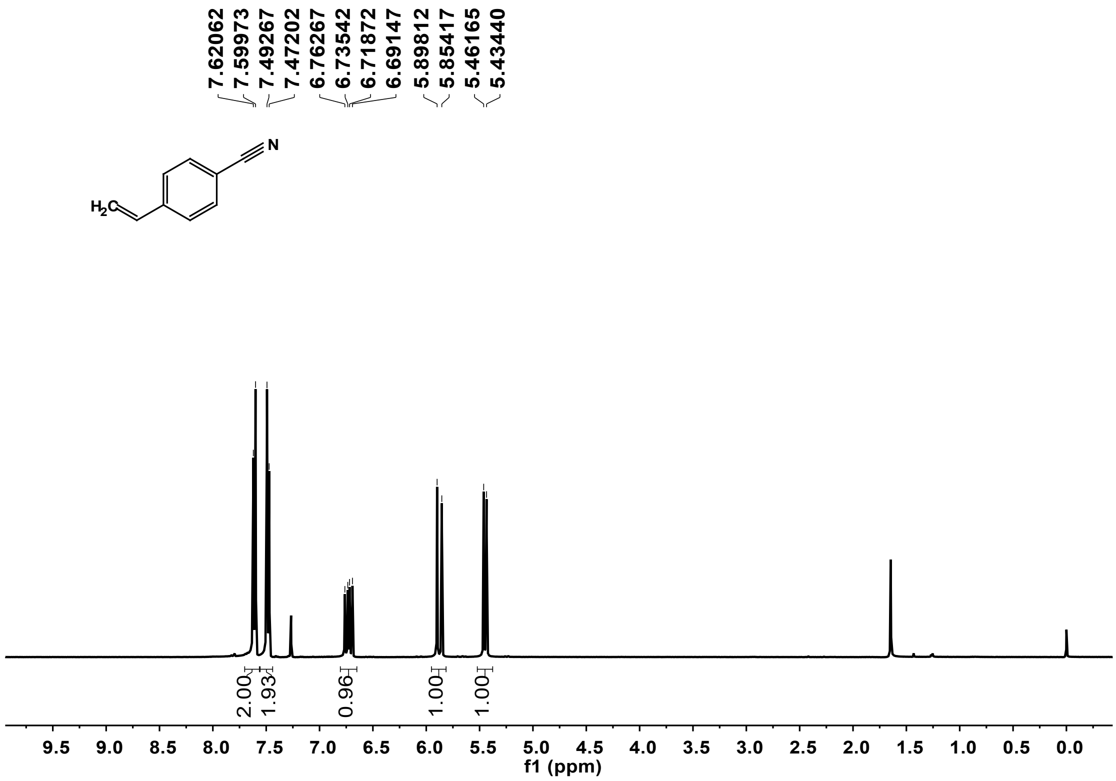
2h


7.345
7.317
6.587
6.559
4.128
N
H2N
1.98
1.99
2.00
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 0.5 0.0
f1 (ppm)

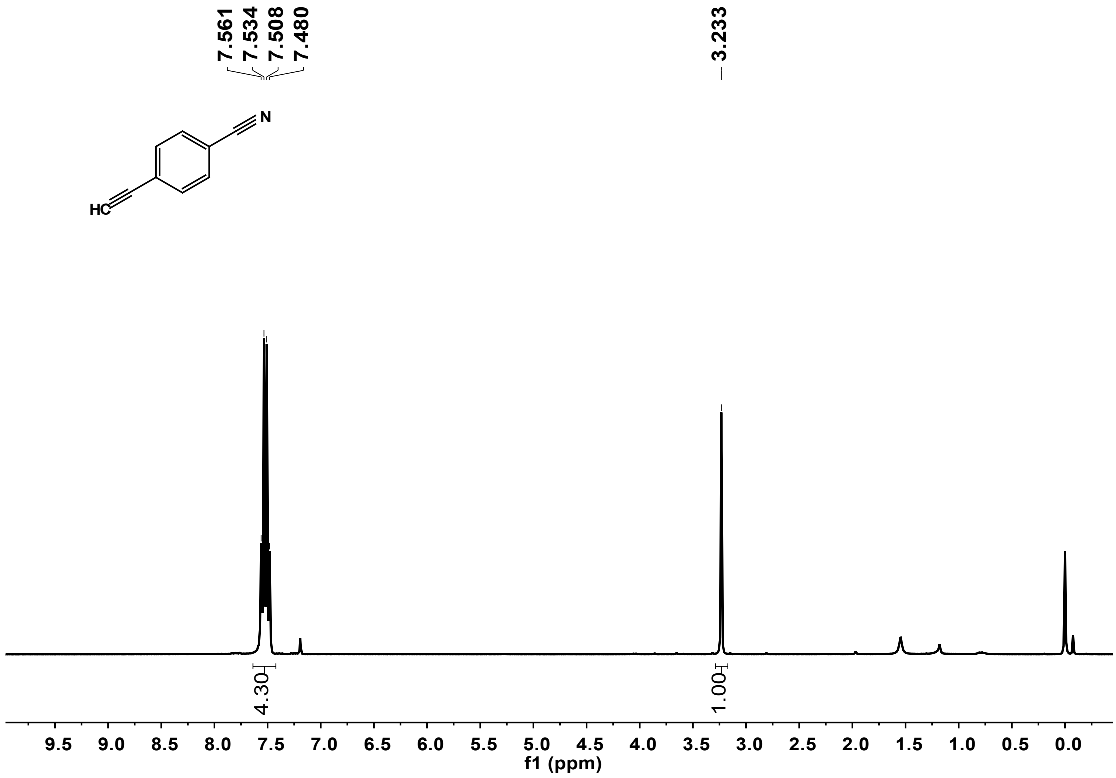
2i


7.228
7.215
7.202
7.014
7.001
6.902
6.898
6.895
6.875
6.872
6.861
6.858
3.912
N
NH2
0.95
0.94
0.93
0.95
2.00
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 0.5 0.0
f1 (ppm)

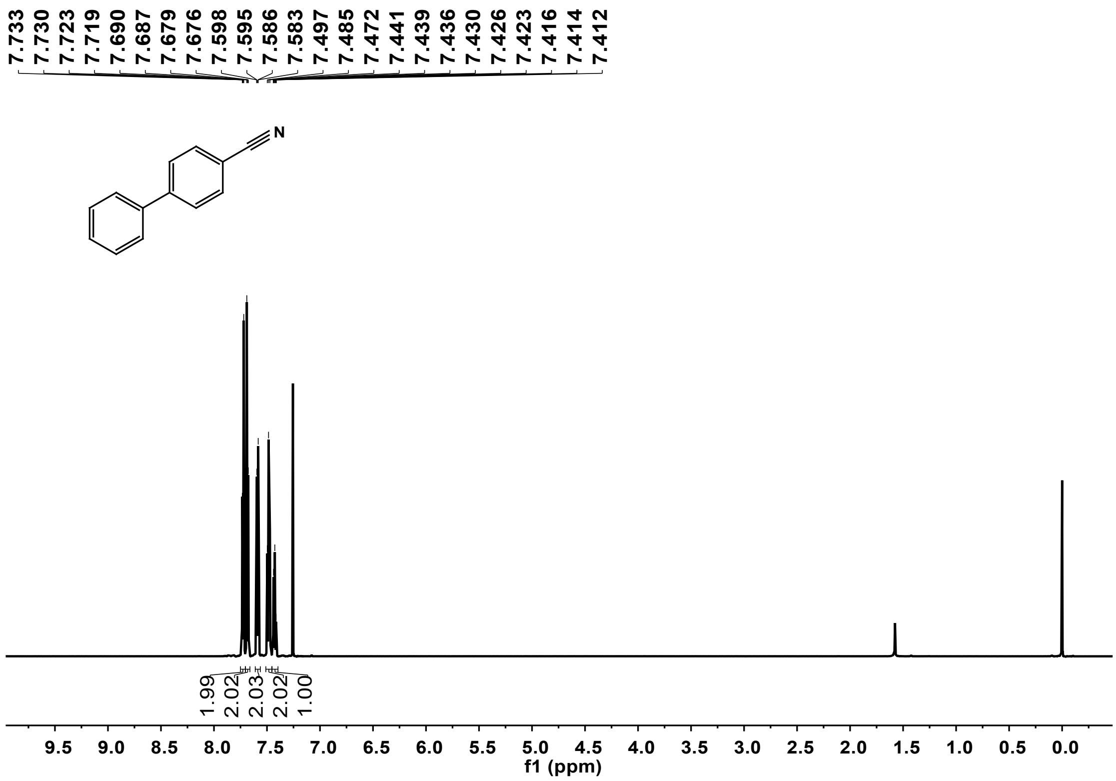
2j


7.62062
7.59973
7.49267
7.47202
6.76267
6.73542
6.71872
6.69147
5.89812
5.85417
5.46165
5.43440
N
H2C
2.00
1.93
0.96
1.00
1.00
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 0.5 0.0
f1 (ppm)

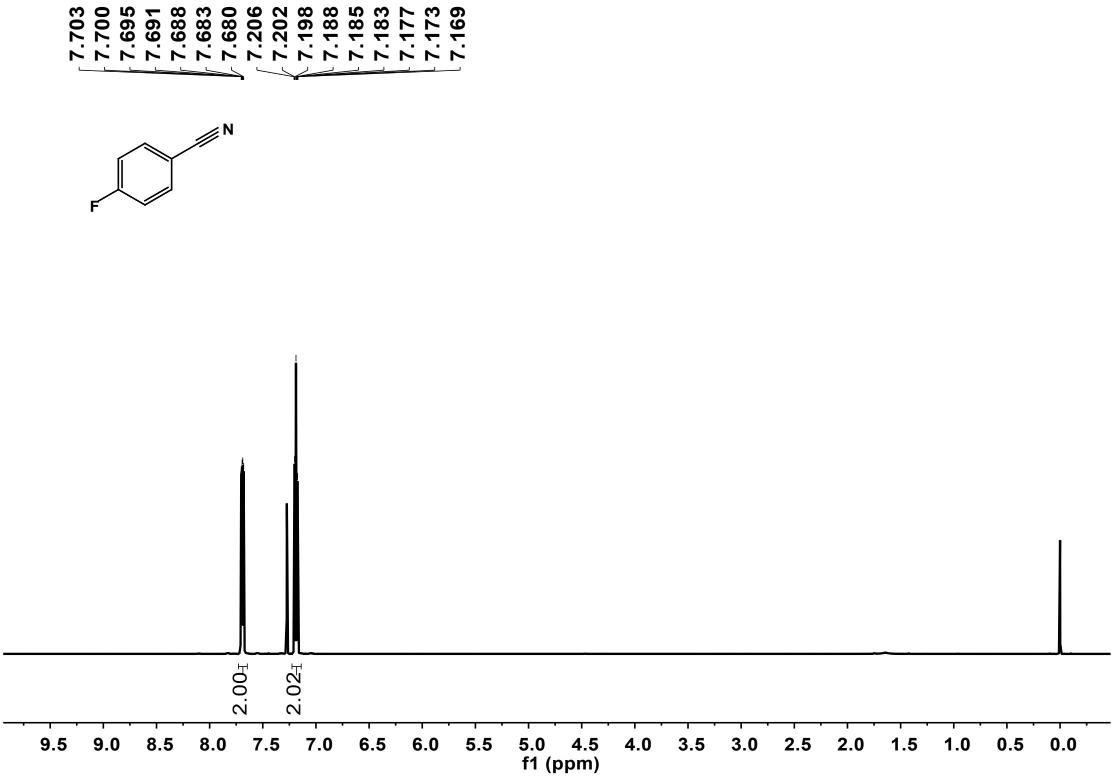
2k


7.561
7.534
7.508
7.480
3.233
N
HC
4.30
1.00
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 0.5 0.0
f1 (ppm)

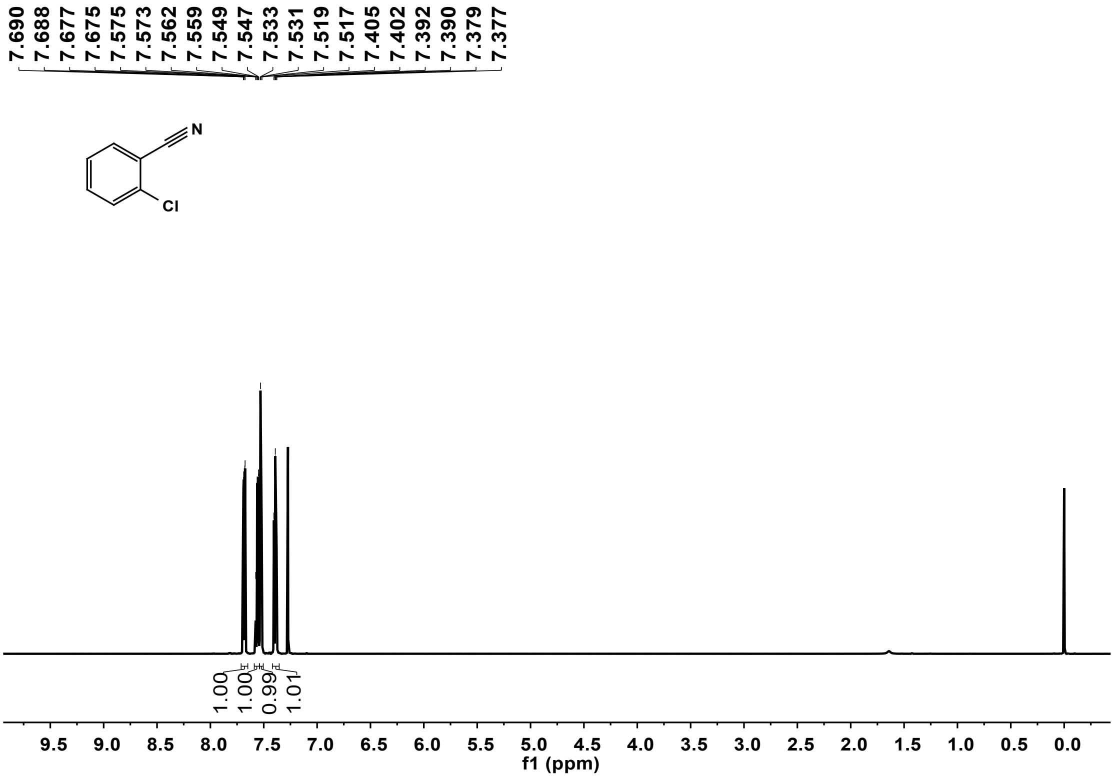
2l


7.733
7.730
7.723
7.719
7.690
7.687
7.679
7.676
7.598
7.595
7.586
7.583
7.497
7.485
7.472
7.441
7.439
7.436
7.430
7.426
7.423
7.416
7.414
7.412
N
1.99
2.02
2.03
2.02
1.00
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 0.5 0.0
f1 (ppm)

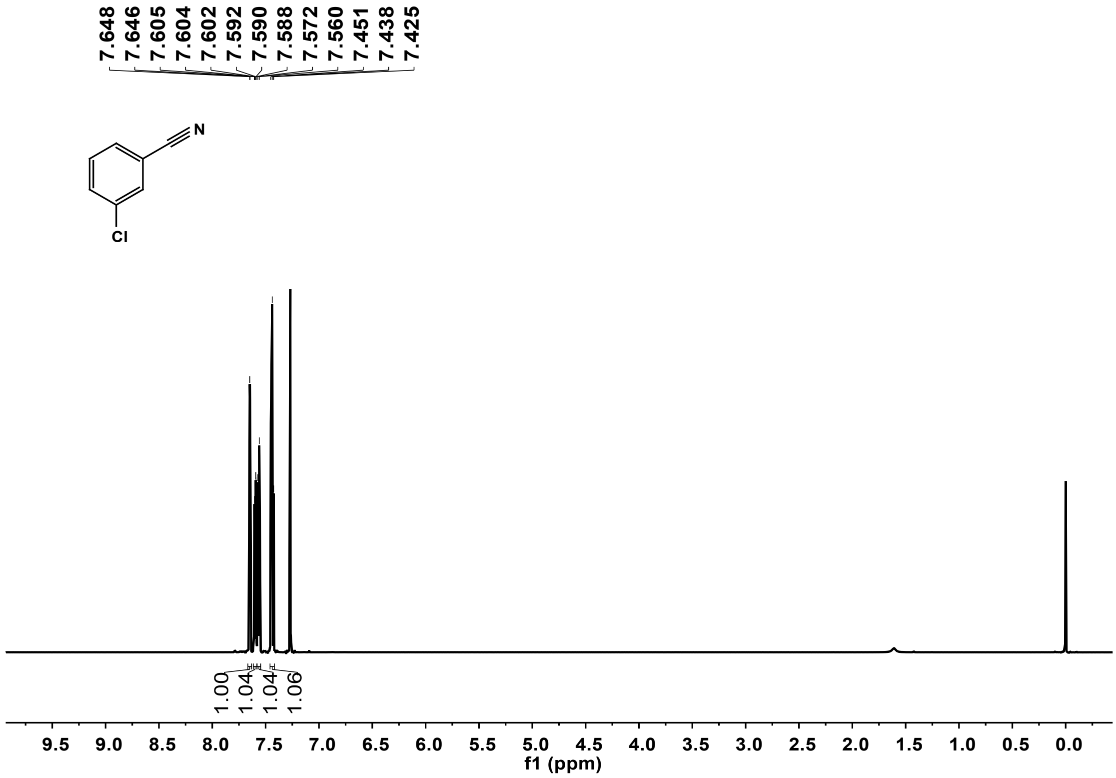
2m


7.703
7.700
7.695
7.691
7.688
7.683
7.680
7.206
7.202
7.198
7.188
7.185
7.183
7.177
7.173
7.169
N
F
2.00
2.02
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 0.5 0.0
f1 (ppm)

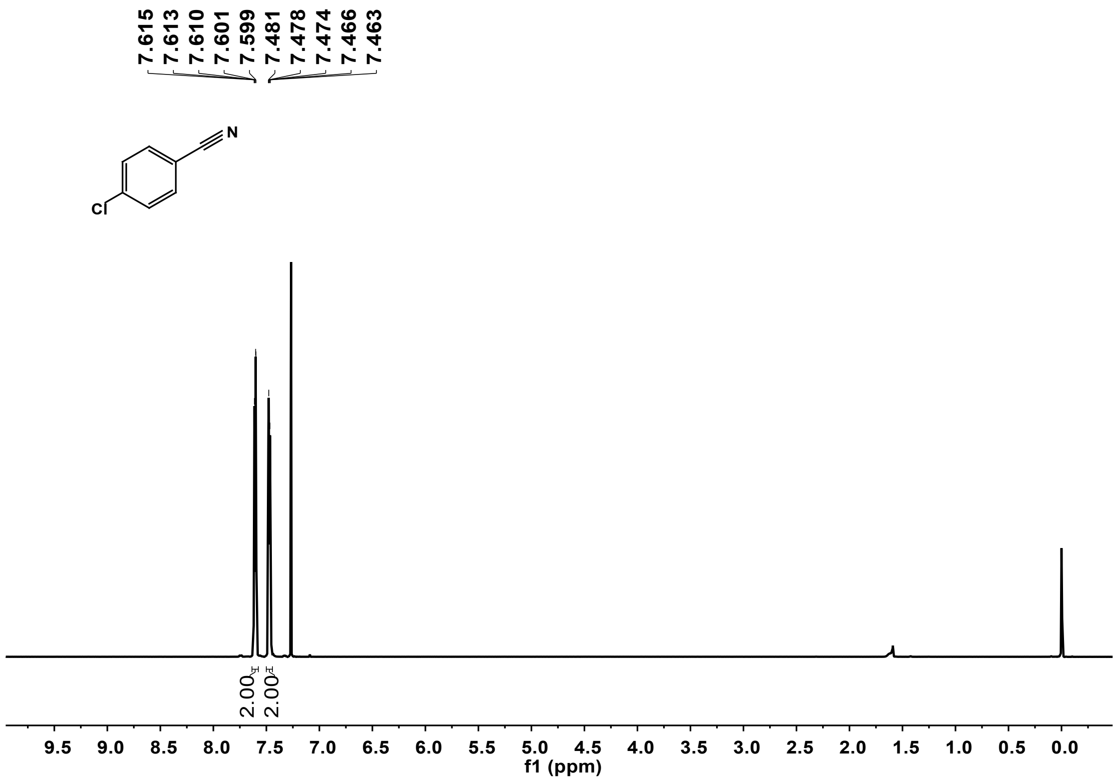
2n


7.690
7.688
7.677
7.675
7.575
7.573
7.562
7.559
7.549
7.547
7.533
7.531
7.519
7.517
7.405
7.402
7.392
7.390
7.379
7.377
N
Cl
1.00
1.00
0.99
1.01
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 0.5 0.0
f1 (ppm)

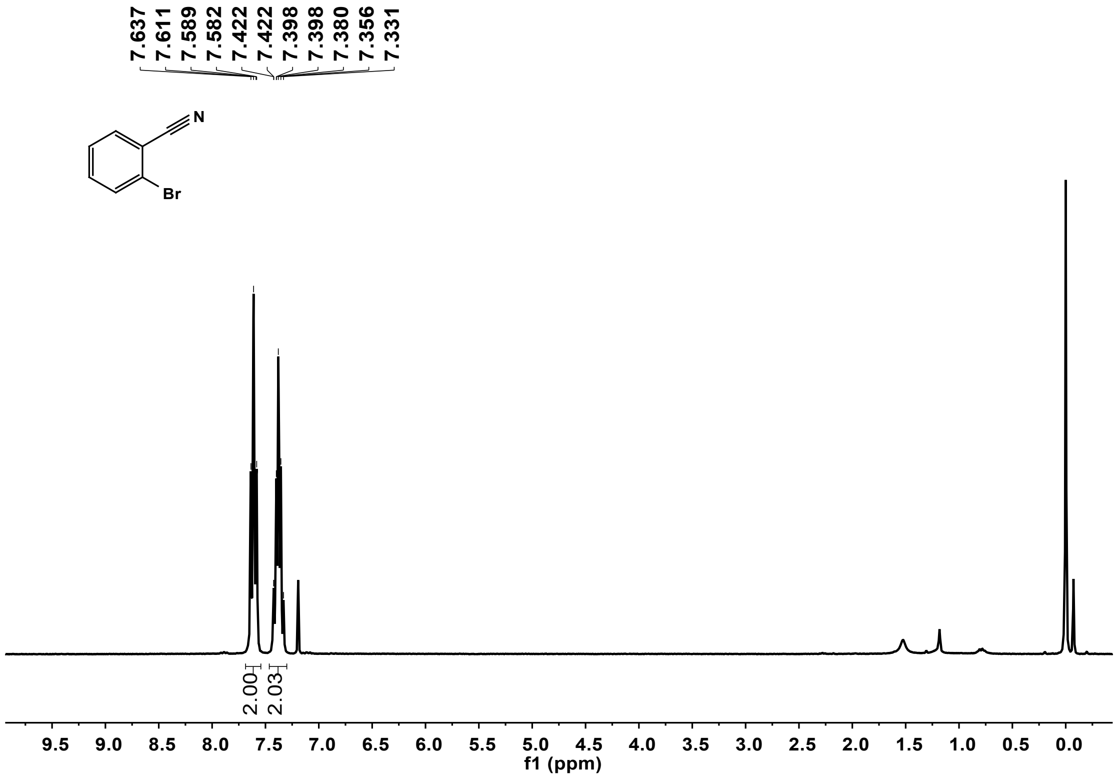
2o


7.648
7.646
7.605
7.604
7.602
7.592
7.590
7.588
7.572
7.560
7.451
7.438
7.425
N
Cl
1.00
1.04
1.04
1.06
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 0.5 0.0
f1 (ppm)

2p

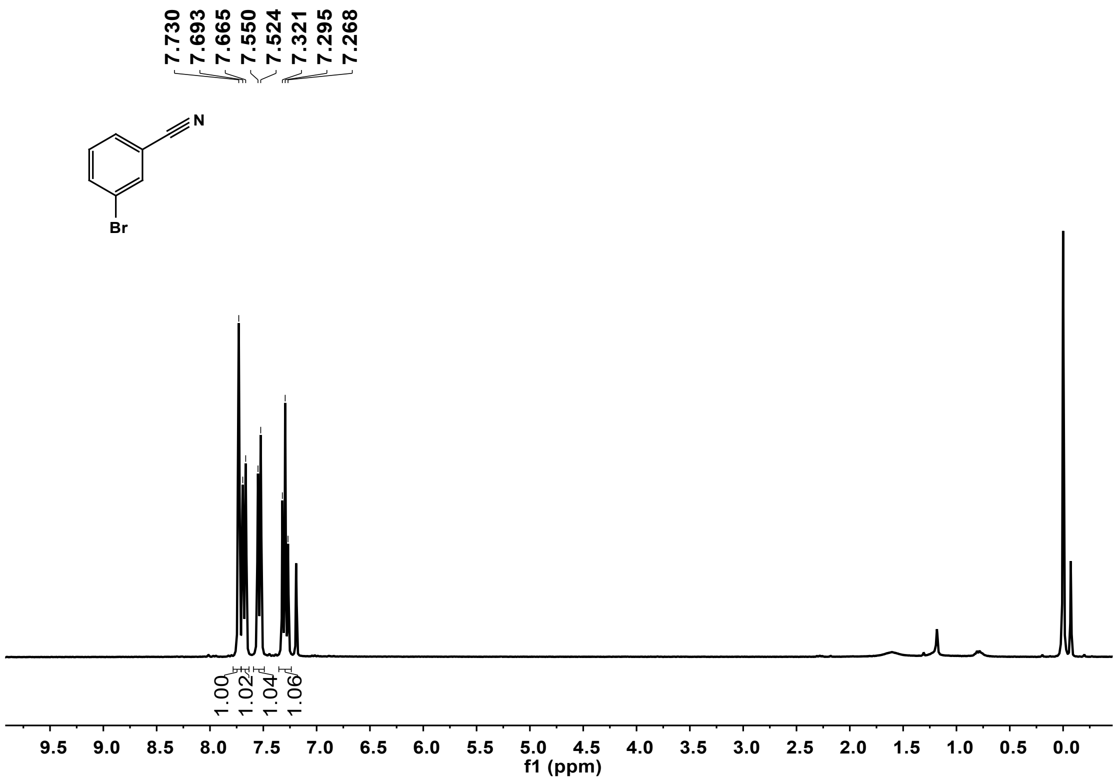

7.615
7.613
7.610
7.601
7.599
7.481
7.478
7.474
7.466
7.463
N
Cl
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2q



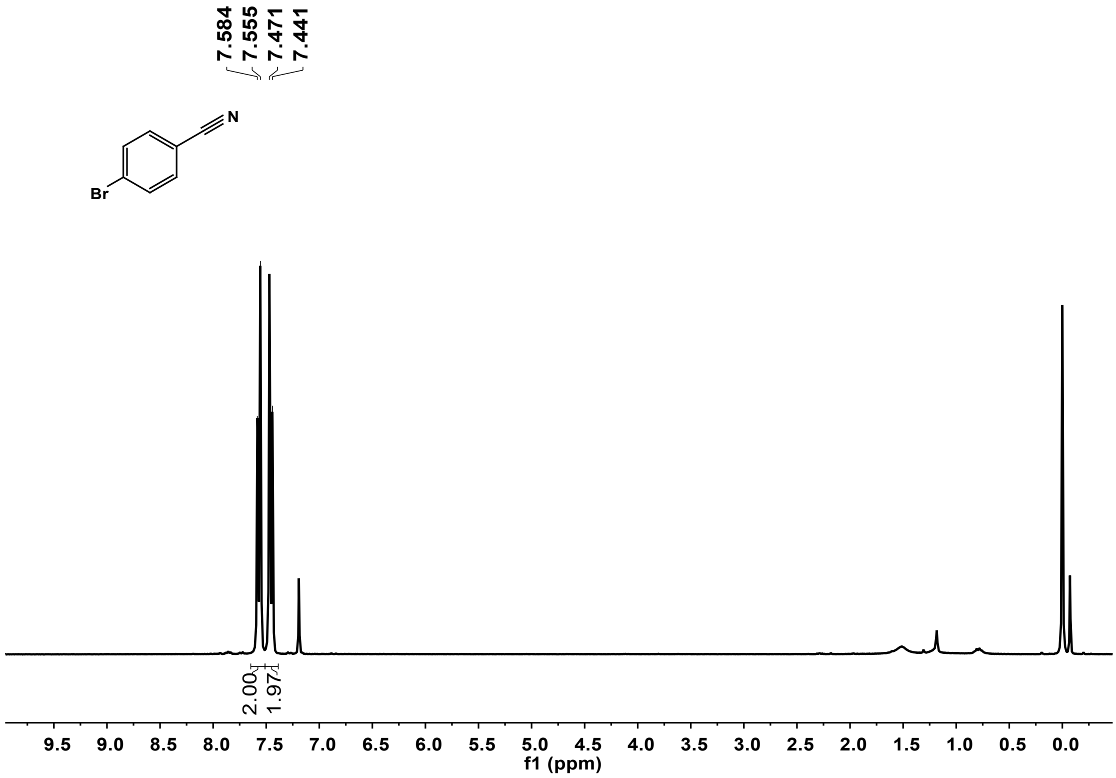
7.637
7.611
7.589
7.582
7.422
7.422
7.398
7.398
7.380
7.356
7.331
N
Br
2.00
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2r

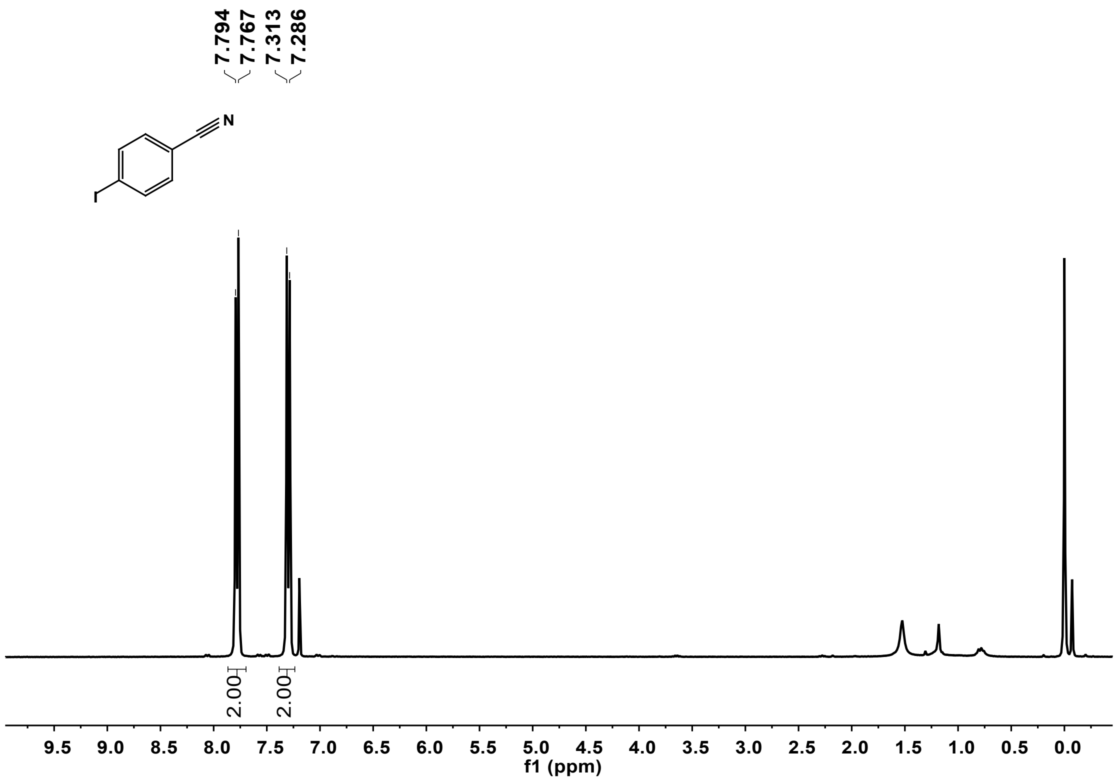


7.730
7.693
7.665
7.550
7.524
7.321
7.295
7.268
N
Br
1.00
1.02
1.04
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

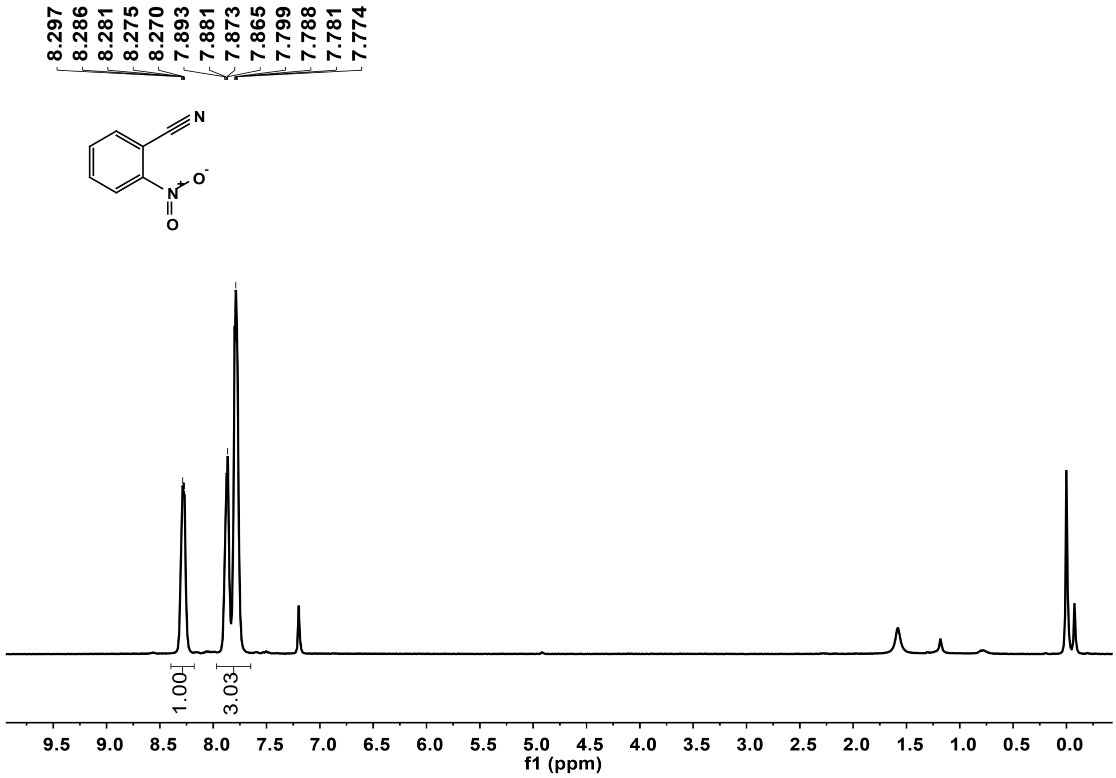
2s


7.584
7.555
7.471
7.441
N
Br
2.00
1.97
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 0.5 0.0
f1 (ppm)

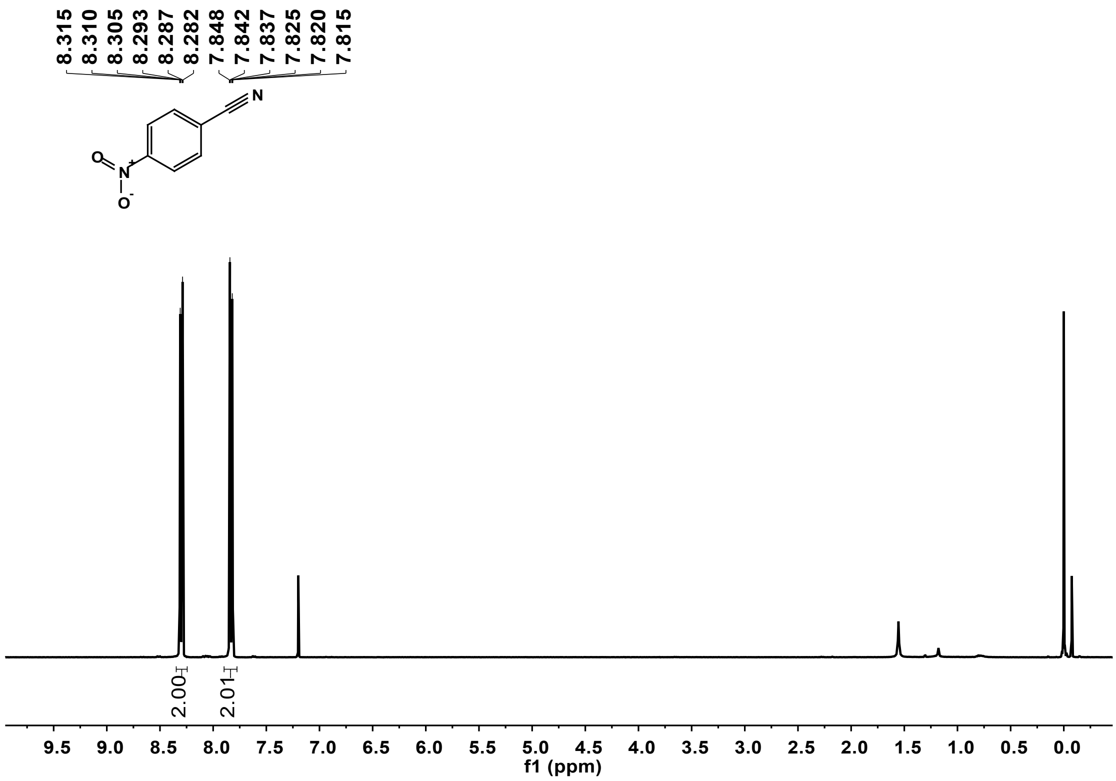
2t


7.794
7.767
7.313
7.286
N
I
2.00
2.00
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 0.5 0.0
f1 (ppm)

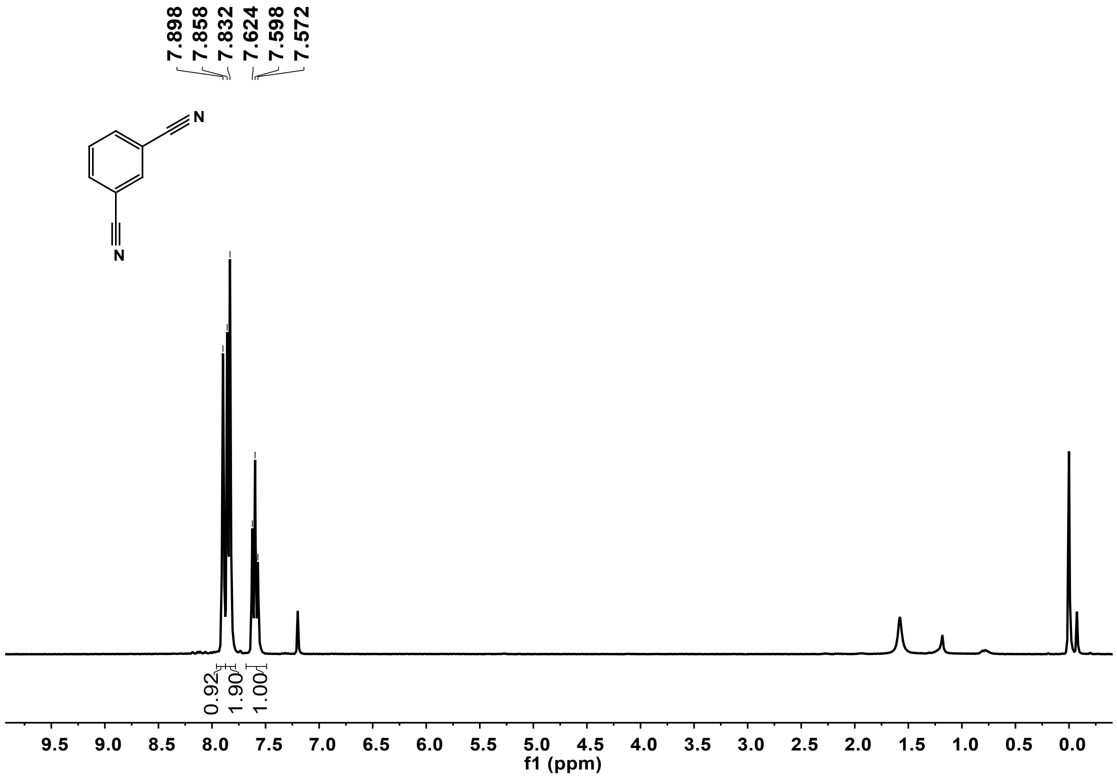
2u


8.297
8.286
8.281
8.275
8.270
7.893
7.881
7.873
7.865
7.799
7.788
7.781
7.774
N
N
O
O
1.00
3.03
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 0.5 0.0
f1 (ppm)

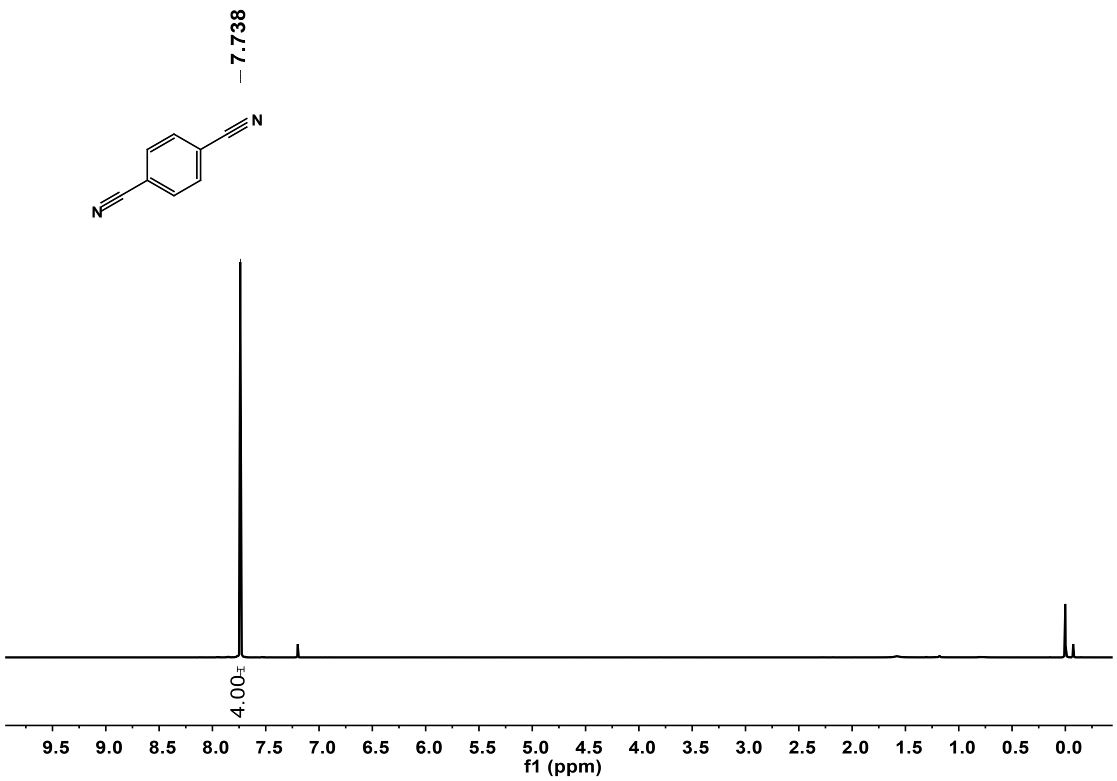
2v


8.315
8.310
8.305
8.293
8.287
8.282
7.848
7.842
7.837
7.825
7.820
7.815
N
O
N
O
2.00
2.01
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 0.5 0.0
f1 (ppm)

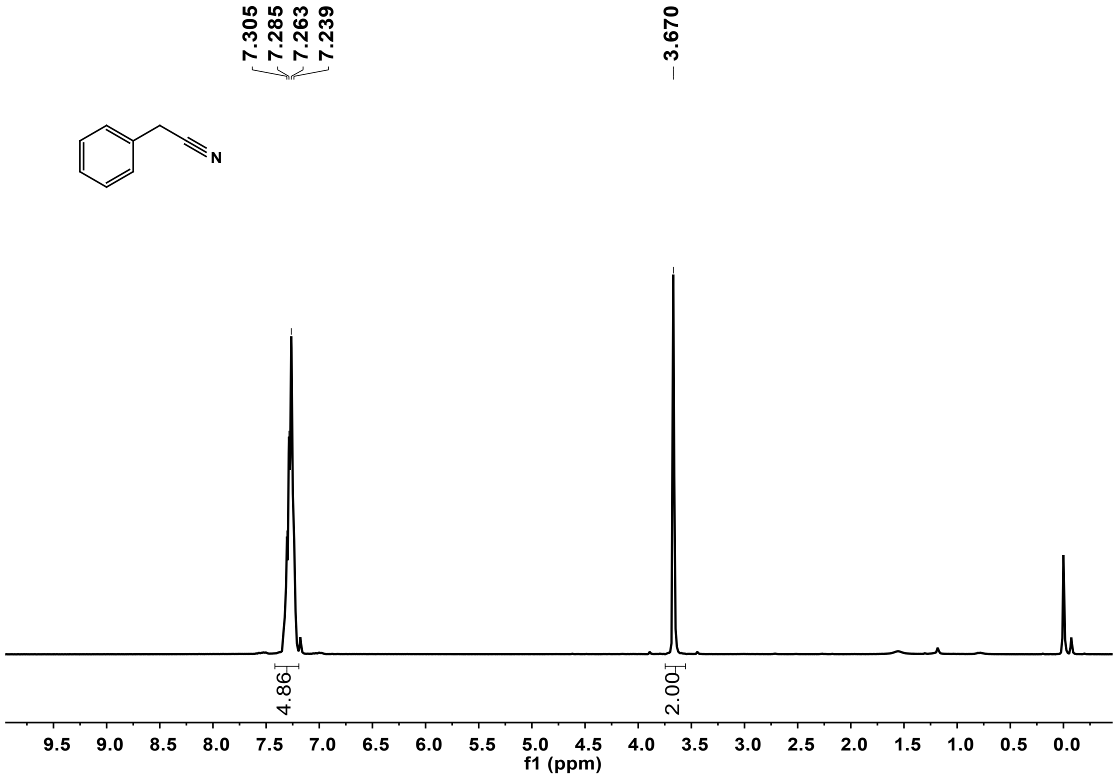
2w


7.898
7.858
7.832
7.624
7.598
7.572
N
N
0.92
1.90
1.00
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 0.5 0.0
f1 (ppm)

2x

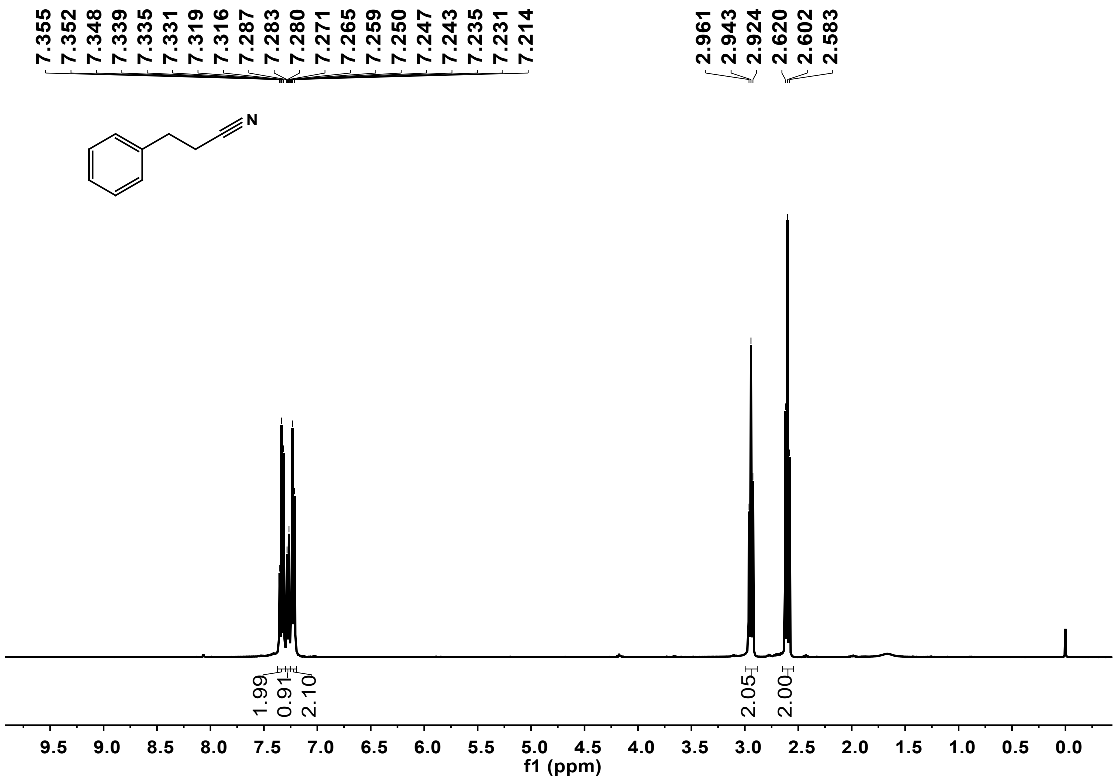

7.738
N
N
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2y



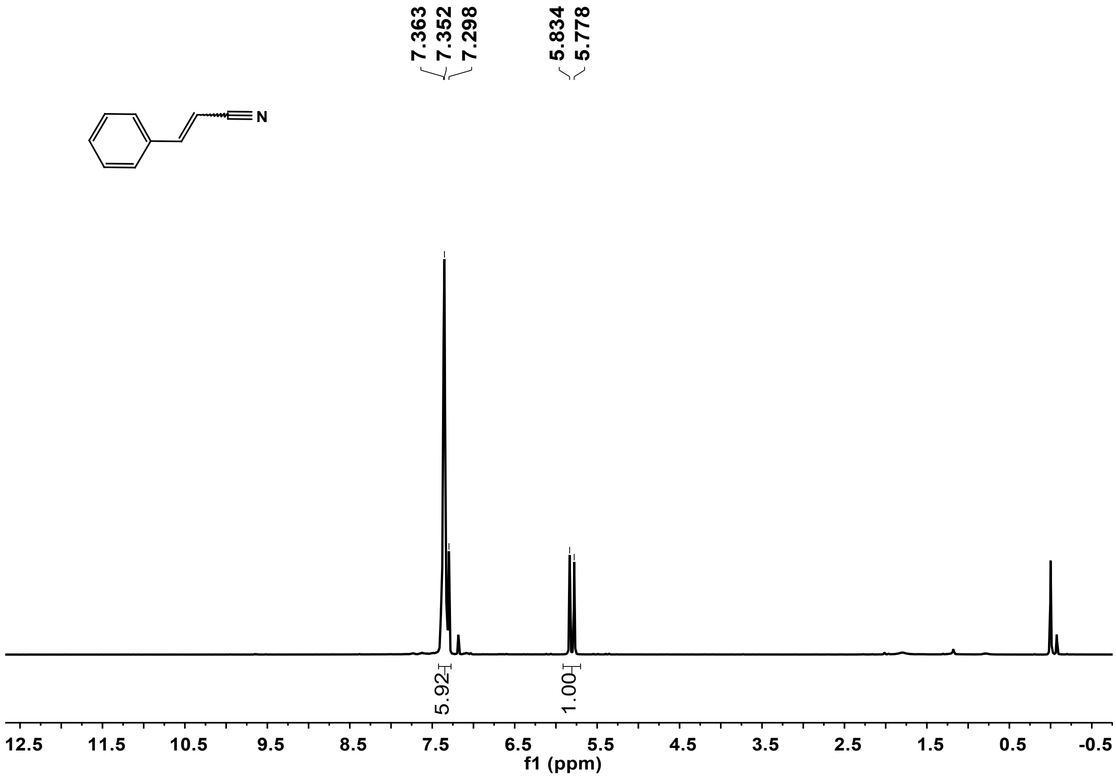
7.305
7.285
7.263
7.239
3.670
N
4.86
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2z

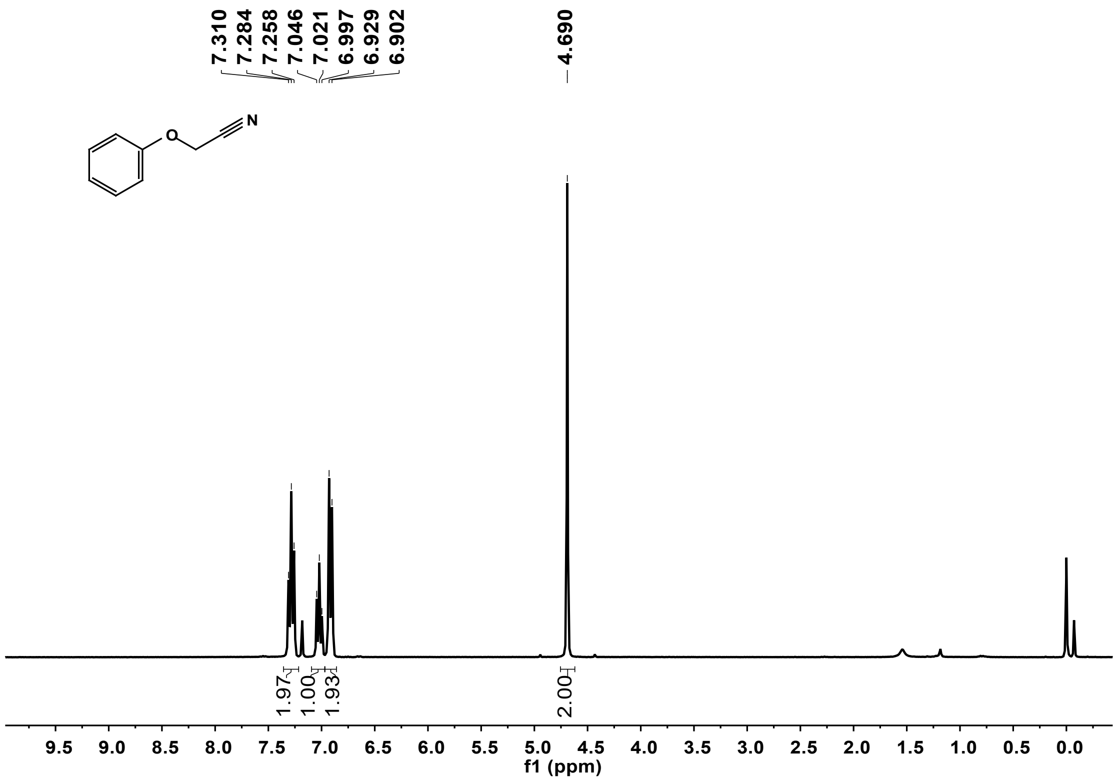


7.355
7.352
7.348
7.339
7.335
7.331
7.319
7.316
7.287
7.283
7.280
7.271
7.265
7.259
7.250
7.247
7.243
7.235
7.231
7.214
2.961
2.943
2.924
2.620
2.602
2.583
N
1.99
0.91
2.10
2.05
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

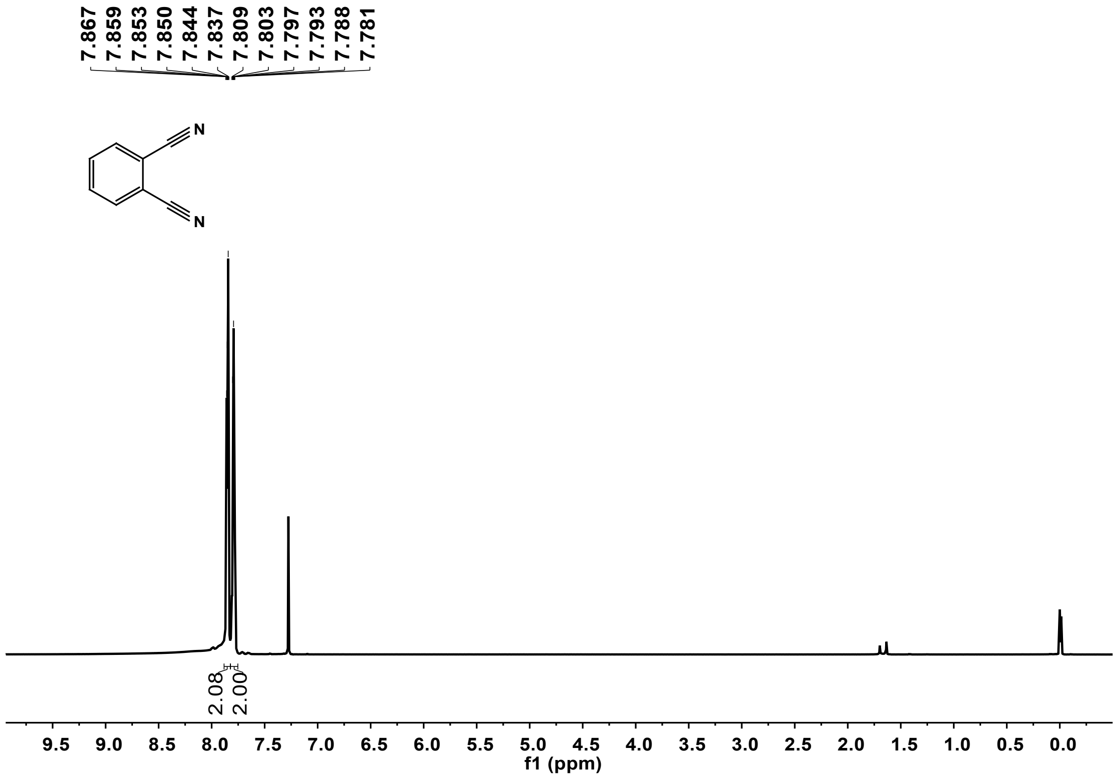
2aa


7.363
7.352
7.298
5.834
5.778
N
5.92
1.00
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

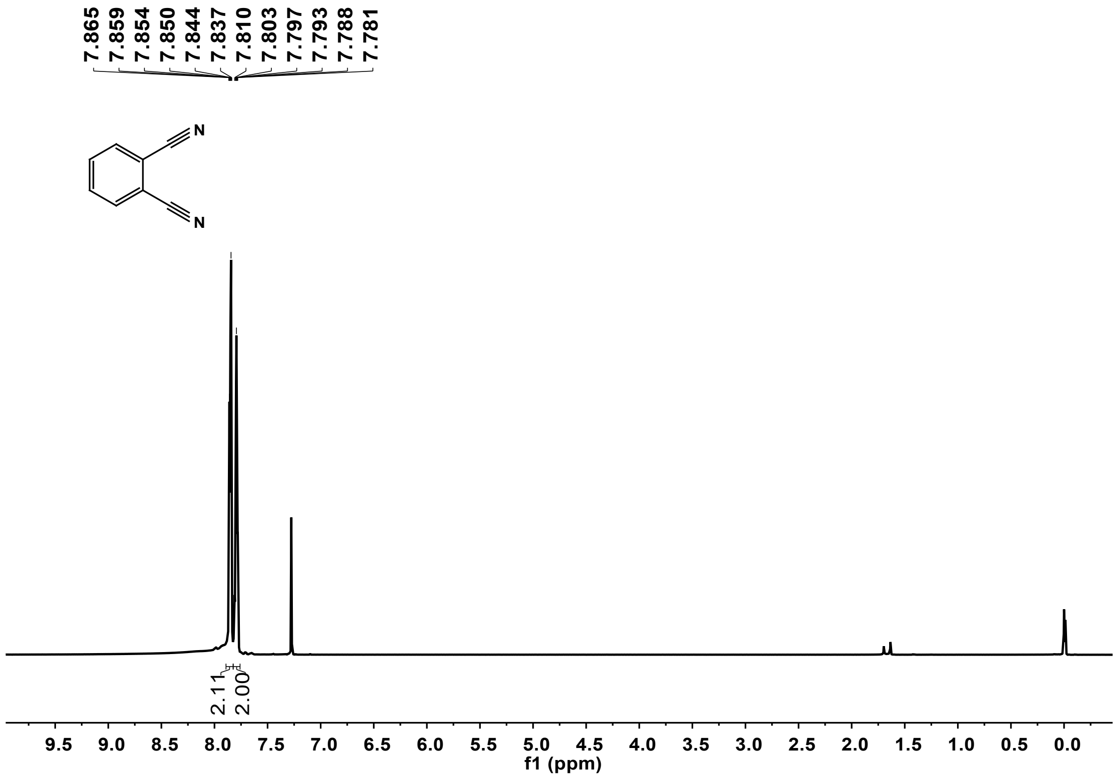
2ab


7.310
7.284
7.258
7.046
7.021
6.997
6.929
6.902
4.690
O
N
1.97
1.00
1.93
2.00
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 0.5 0.0
f1 (ppm)

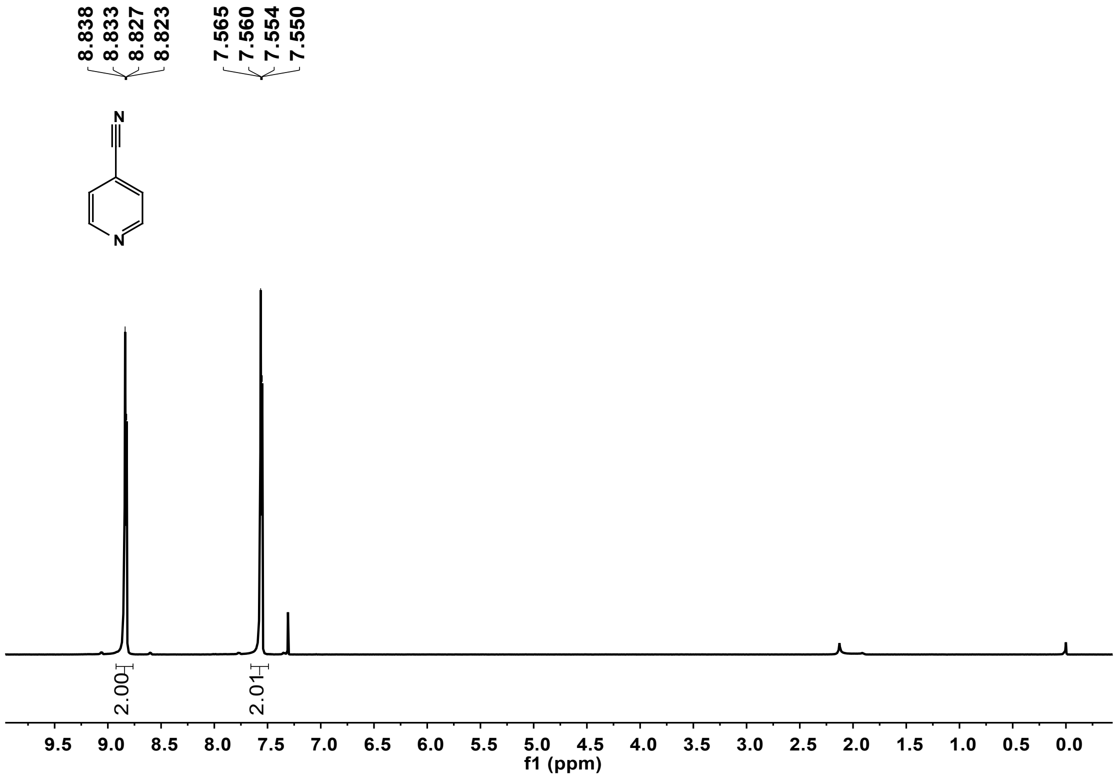
2ac


7.867
7.859
7.853
7.850
7.844
7.837
7.809
7.803
7.797
7.793
7.788
7.781
N
N
2.08
2.00
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 0.5 0.0
f1 (ppm)

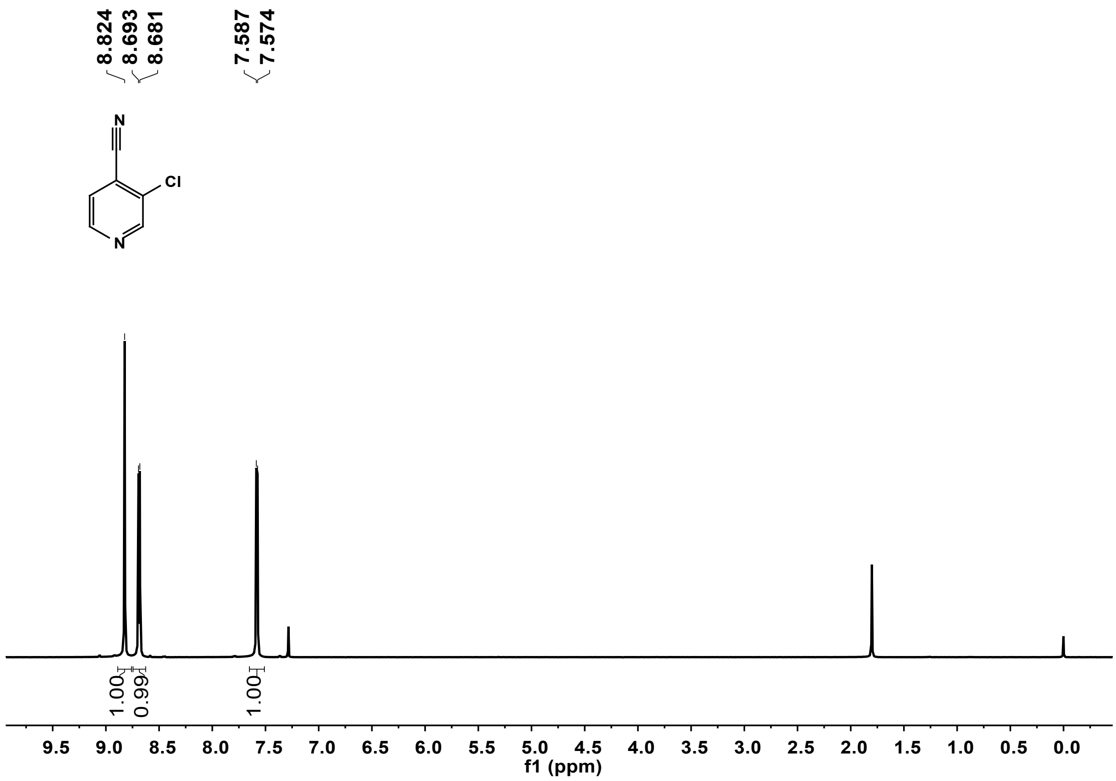
2ad


7.865
7.859
7.854
7.850
7.844
7.837
7.810
7.803
7.797
7.793
7.788
7.781
N
N
2.11
2.00
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 0.5 0.0
f1 (ppm)

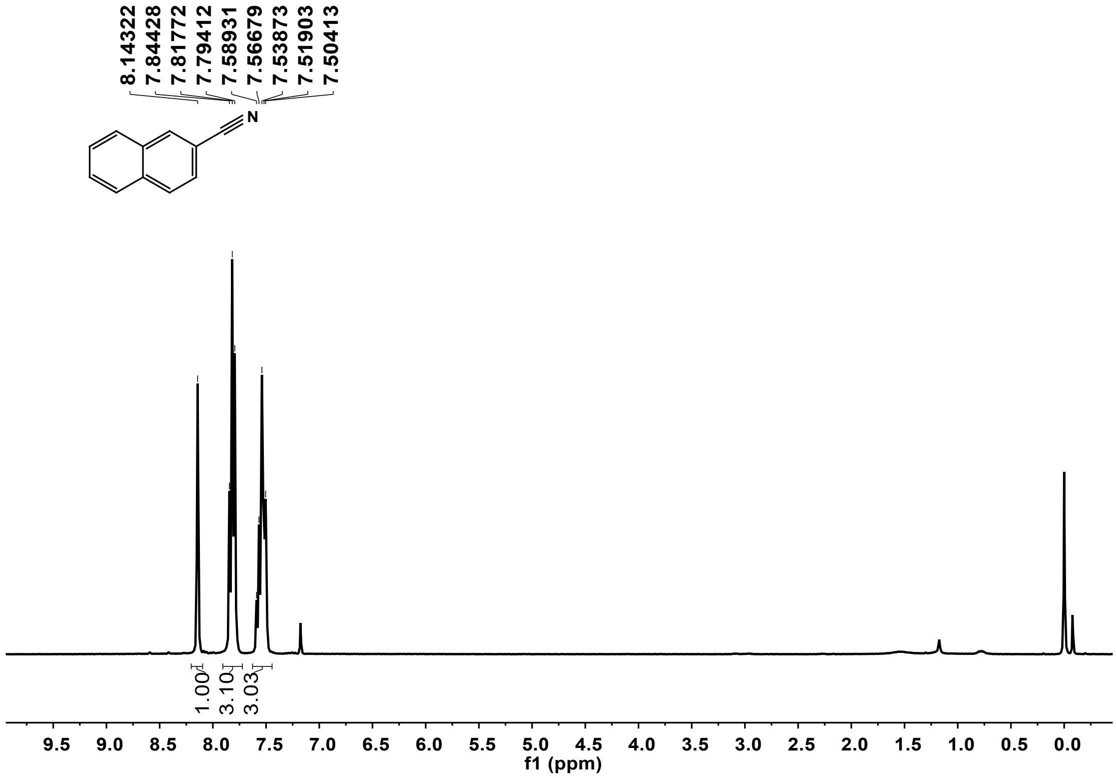
2ae


8.838
8.833
8.827
8.823
7.565
7.560
7.554
7.550
N
N
2.00
2.01
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 0.5 0.0
f1 (ppm)

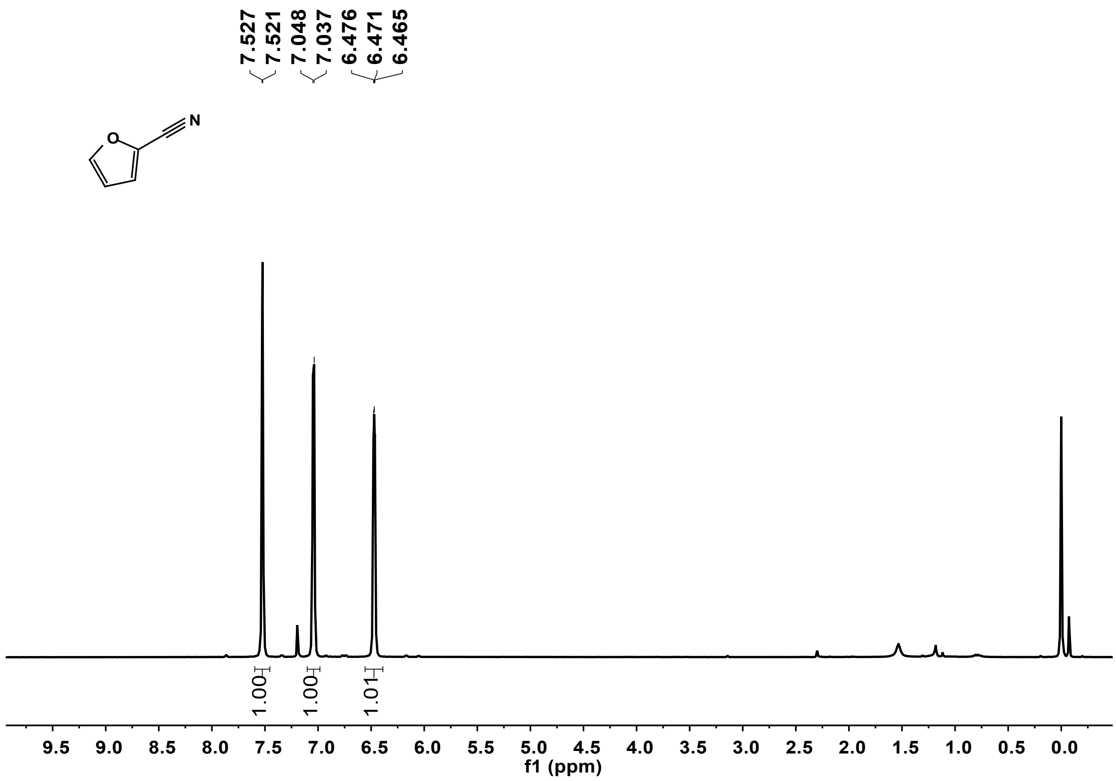
2af


8.824
8.693
8.681
7.587
7.574
N
Cl
N
1.00
0.99
1.00
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 0.5 0.0
f1 (ppm)

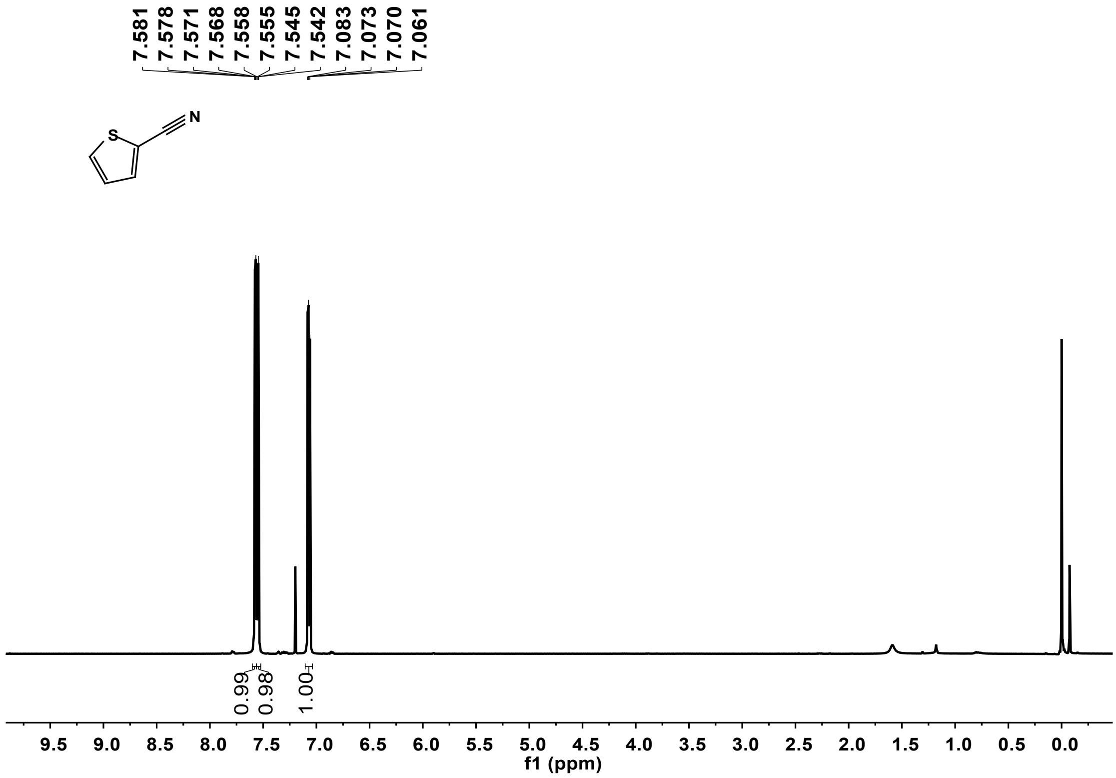
2ag


8.14322
7.84428
7.81772
7.79412
7.58931
7.56679
7.53873
7.51903
7.50413
N
1.00
3.10
3.03
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
0.5
0.0
f1 (ppm)

2ah

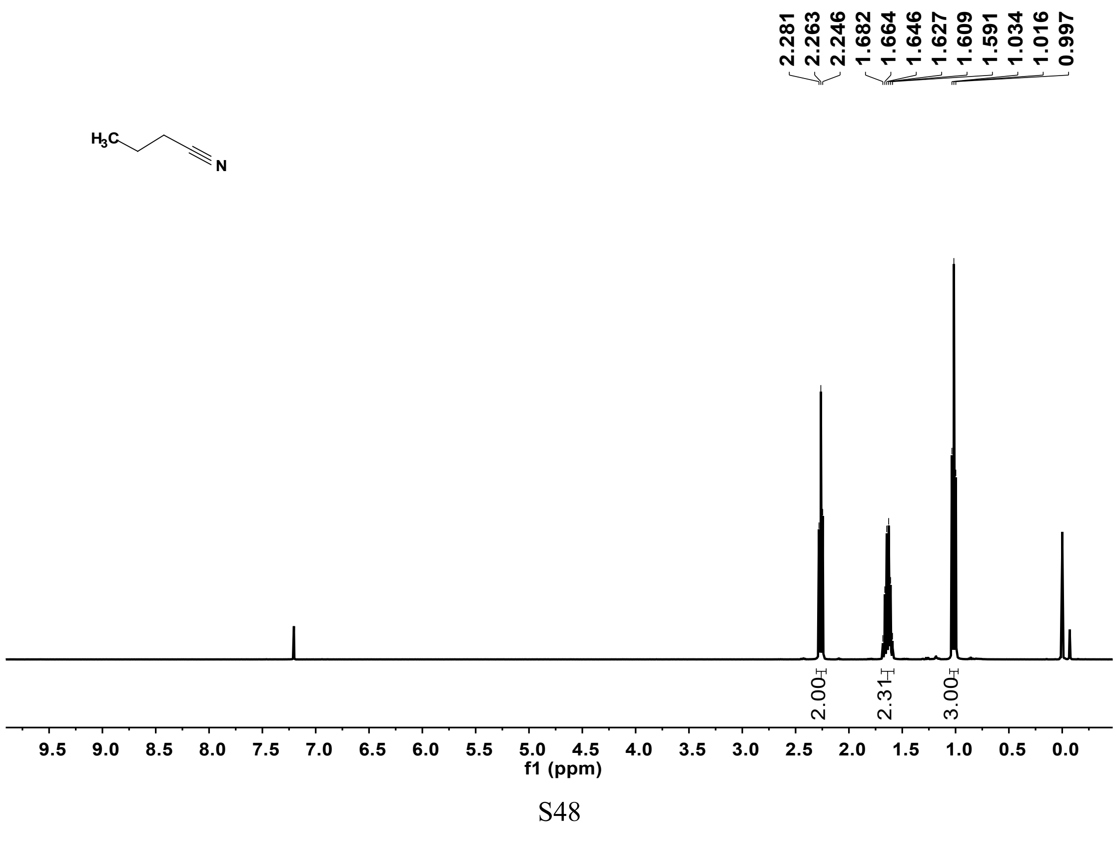

7.527
7.521
7.048
7.037
6.476
6.471
6.465
O
N
1.00
1.00
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2ai



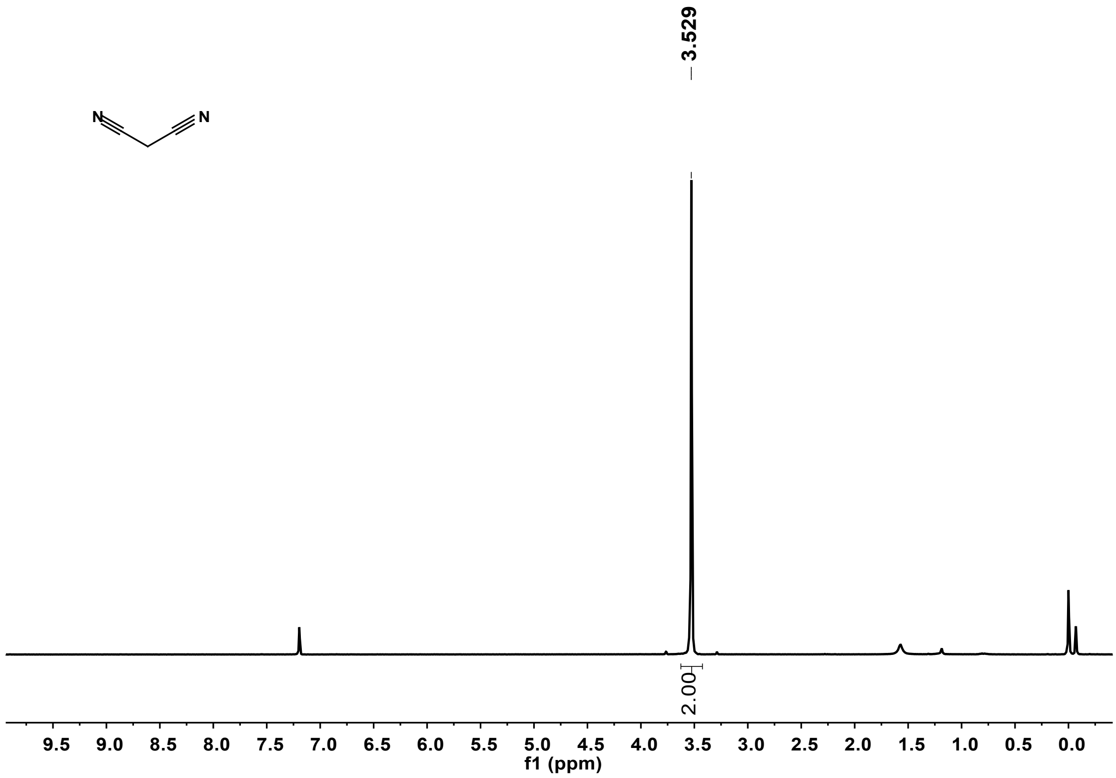
7.581
7.578
7.571
7.568
7.558
7.555
7.545
7.542
7.083
7.073
7.070
7.061
S
N
0.99
0.98
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2aj

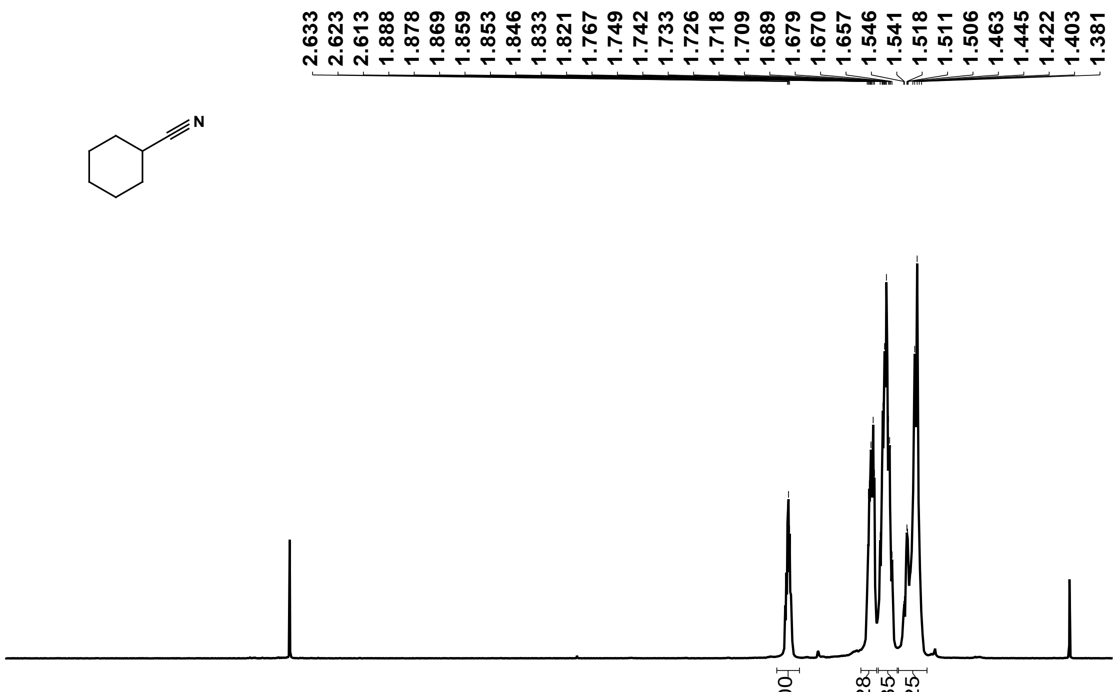


2.281
2.263
2.246
1.682
1.664
1.646
1.627
1.609
1.591
1.034
1.016
0.997
H_3C
N
2.00
2.31
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

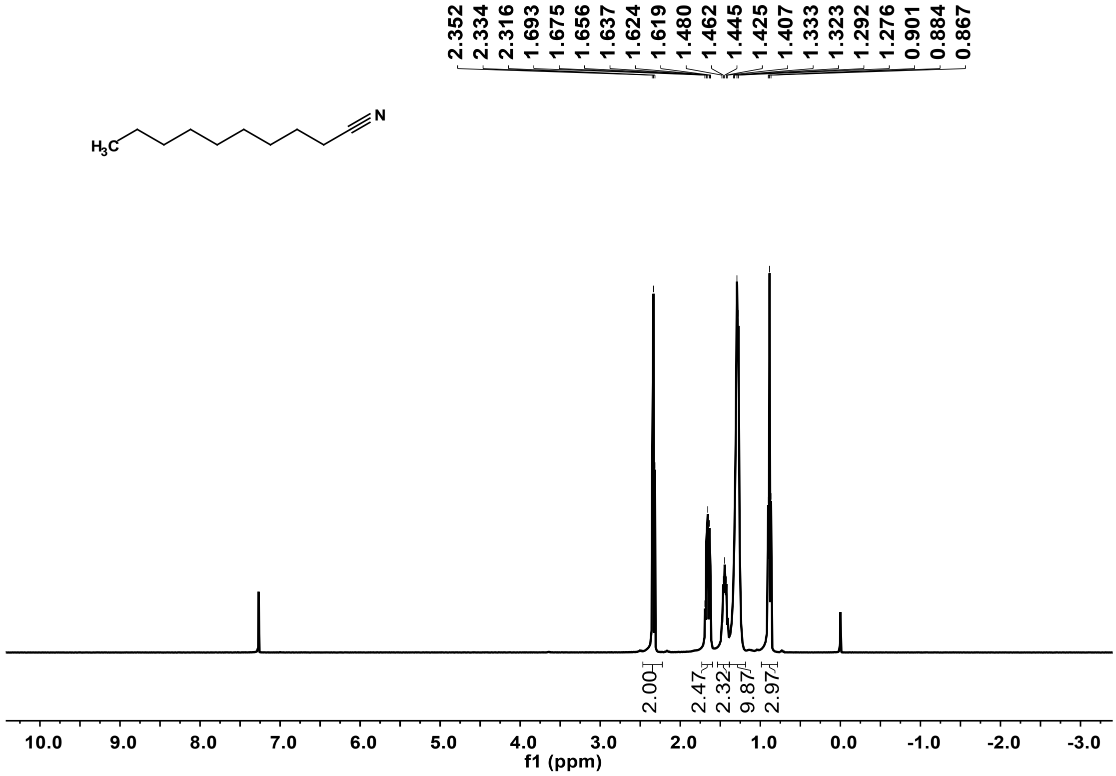
2ak


3.529
N
N
2.00
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 0.5 0.0
f1 (ppm)

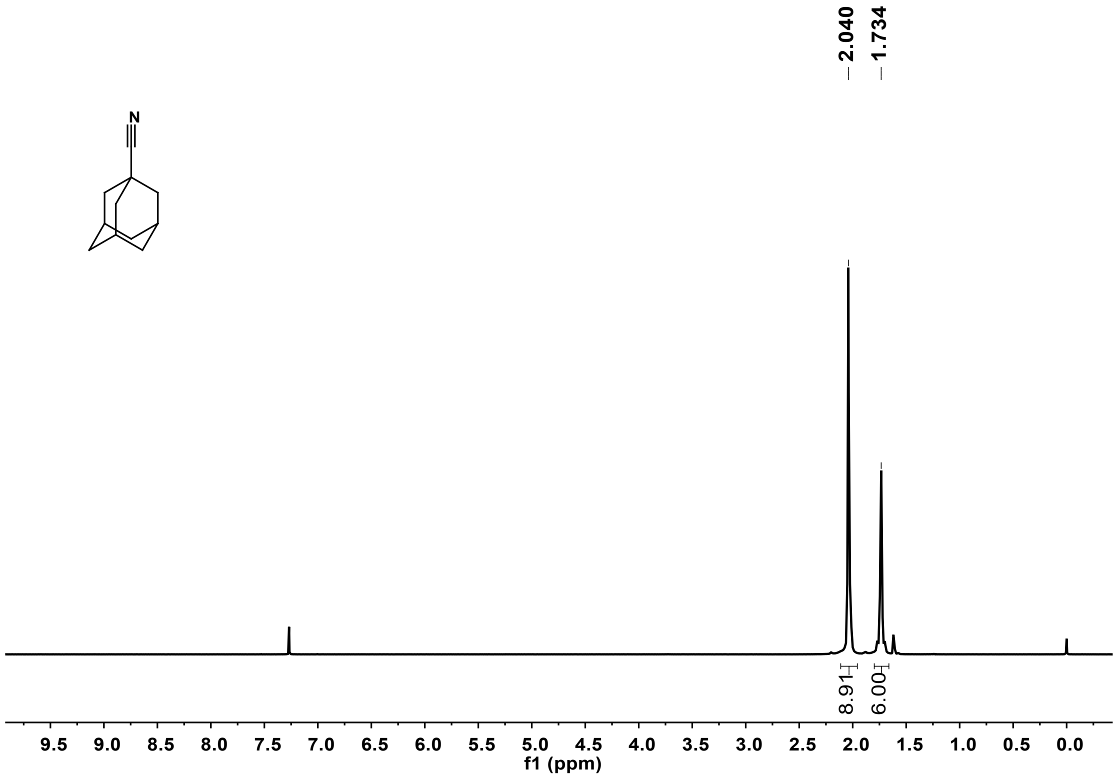
2al


2.633 2.623 2.613 1.888 1.878 1.869 1.859 1.853 1.846 1.833 1.821 1.767 1.749 1.742 1.733 1.726 1.718 1.709 1.689 1.679 1.670 1.657 1.546 1.541 1.518 1.511 1.506 1.463 1.445 1.422 1.403 1.381
N
1.00
2.28 4.35 4.25
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 0.5 0.0
f1 (ppm)

2am


2.352
2.334
2.316
1.693
1.675
1.656
1.637
1.624
1.619
1.480
1.462
1.445
1.425
1.407
1.333
1.323
1.292
1.276
0.901
0.884
0.867
H_3C
N
2.00
2.47
2.32
9.87
2.97
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0 -3.0
f1 (ppm)

2an


2.040
1.734
N
8.91
6.00
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 0.5 0.0
f1 (ppm)