Energy Materials

Supplementary Materials

Conjugated-engineering covalent organic framework for synergistic artificial photosynthesis of hydrogen peroxide and high-value chemicals

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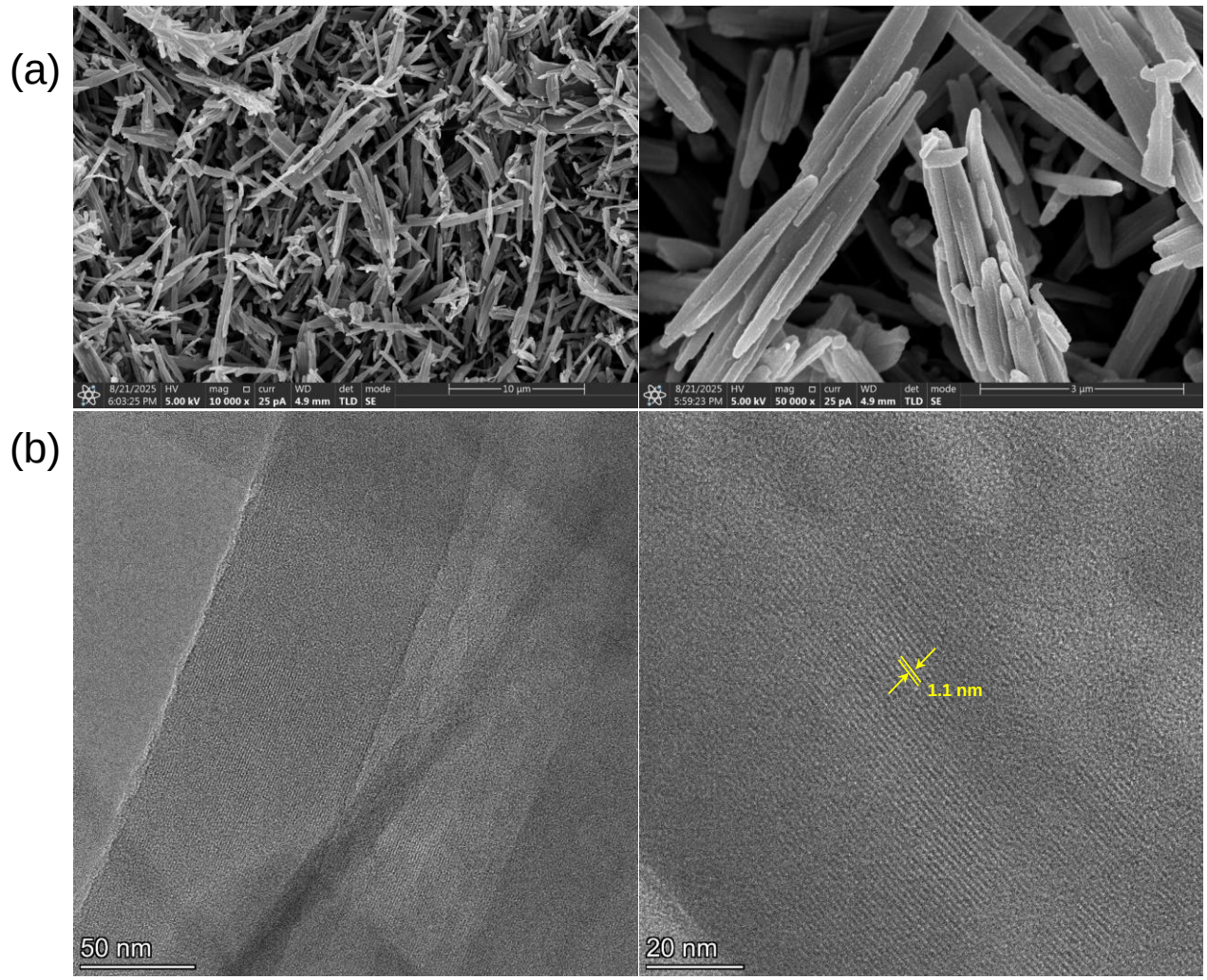
1. General information

Reactions were monitored by thin layer chromatography (TLC), and column chromatography purifications were carried out using silica gel. Column chromatography was performed on silica gel (300-400 mesh). ^{1}H NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm; ^{13}C NMR: $CDCl_3$ at 77.00 ppm, DMSO-d_6 at 30.92 ppm). Data for ^{1}H and ^{13}C NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; m = multiplet; br = broad), coupling constant (Hz), integration.

Powder x-ray powder diffraction (PXRD) patterns were measurement on a Rigaku RINT smart lab se powder diffraction system, equipped with Cu Kα radiation (λ = 1.54 Å). Fourier-transform infrared Spectrometer (FTIR) data were collected using a Bruker VERTEX 70 spectrophotometer with KBr disks. Solid-state ^{13}C CP-TOSS NMR spectra were performed on a Bruker 500 MHz spectrometer. UV-vis diffuse reflectance spectrophotometry (DRS) was recorded using Shimadzu UV-2600 UV-visible spectrum with $BaSO_4$ as reference. Nitrogen adsorption-desorption isotherm measurement was performed on a Quantanchrome autosorb IQ system. The isotherms were collected at 77 K under a liquid nitrogen bath. The specific surface areas were calculated utilizing the BrunauerEmmett-Teller (BET) method and pore diameter was determined from the adsorption branch by using the Non-Localized Density Functional Theory (NLDFT) method. Structural modeling of **TANB-Py-COF** The process of simulating COF structure was performed by the Materials Studio software. The triclinic lattice with P1 symmetry group was set as the initial eclipsed COF structure. After the smallest asymmetric fragment was filled into the blank cell, the Forcite tools package was employed to optimize the cell geometry including energy minimization. The cell optimized from the Universal force fields was subsequently refined using the Pawley refinement method in Reflex tools.

2. SEM and TEM of TANB-Py-COF



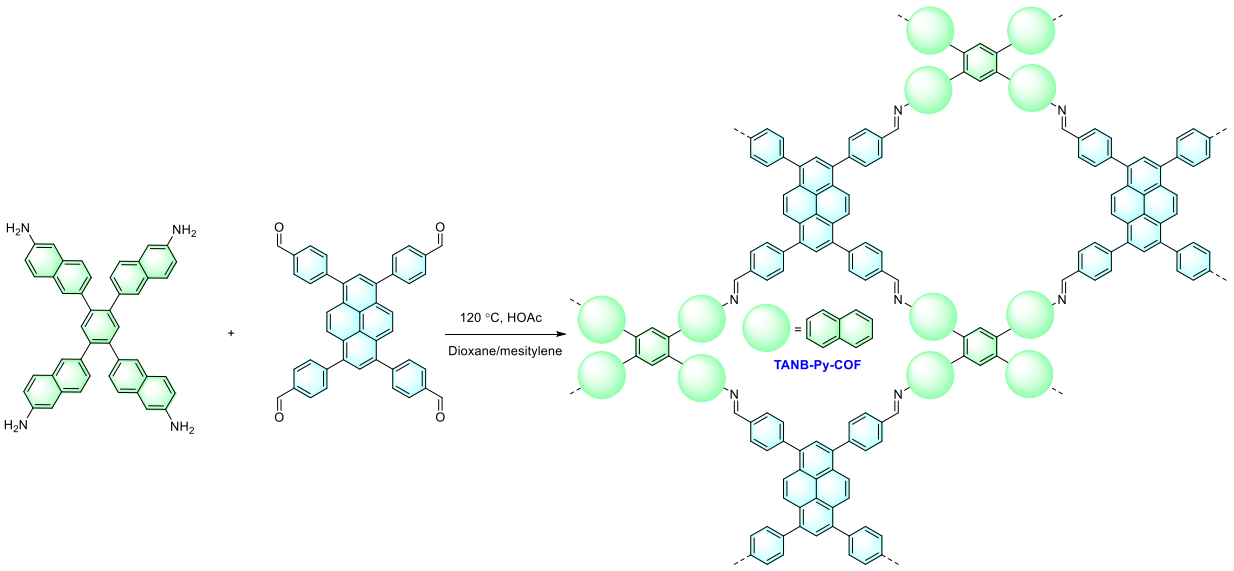
Supplementary Figure 1. SEM (a) and TEM (b) images of **TANB-Py-COF.**

3. Experimental procedures

3.1 Synthesis of 1,2,4,5-tetrakis(6-aminonaphthyl)-benzene (TANB)

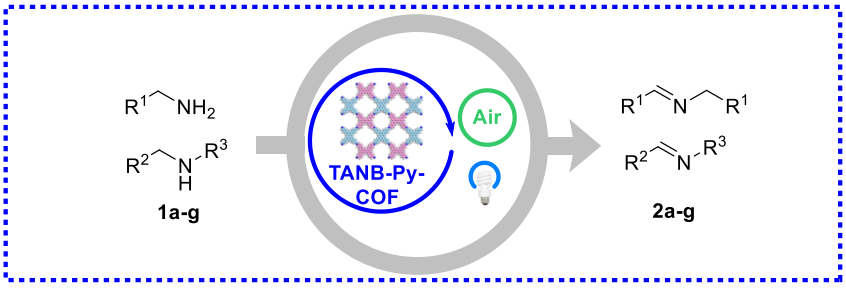
Under a nitrogen atmosphere, 1,2,4,5-tetrabromobenzene (0.94 g, 2.4 mmol), 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (3.10 g, 11.5 mmol), $Pd(PPh_3)_4$ (277.4 mg, 0.24 mmol) and potassium carbonate (1.59 g, 11.5 mmol) were added to 5.0 mL dioxane and 1.0 mL water in a 50 mL round bottom flask. The mixture was stirred under reflux for 3 days. After cooling to room temperature, 30 mL of water were added. The precipitate was filtered, washed with water and methanol. The solid was dissolved in acetone and filtered through a short silica gel plug. The solvent was removed to afford the product with a yield of 78%.

3.2 Synthesis of TANB-Py-COF



1,2,4,5-tetrakis(6-aminonaphthyl)-benzene (TANB) (12.84 mg, 20 μmol) and 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetrabenzaldehyde (Py-CHO) (12.4 mg, 20 μmol) and CH_3COOH (0.1 mL, 6 M) were mixed in a mixture of solvents containing 0.25 mL of dioxane and 0.75 mL of mesitylene in a seal tube. The mixture was ultrasonicated for 10 min and then flash frozen at 77 K (liquid N_2 bath) and degassed through three freeze-pump-thaw cycles. The mixture was then heated at 120 °C for 72 h under an N_2 atmosphere. The resulting solid product was recovered by filtration, washed with methanol and DCM, and subjected to Soxhlet extraction using THF for 24 hours. After drying under vacuum for 6 hours, a yellow solid was obtained with a yield of 85%. This material was designated as **TANB-Py-COF**.

3.3 General experimental procedure of artificial synthesis



Under air atmosphere, **TANB-Py-COF** (2.4 mg, 0.002 mmol based on the repeating unit) and **1** (0.1 mmol) were mixed in acetonitrile (5.0 mL) in a reaction tube. The resulting mixture was stirred under blue LED irradiation (410 nm) at room temperature. Upon completion, the residual was filtered through celite pad and filtrate was concentrated. The concentration of H_2O_2 was determined by a UV spectrophotometer after removal of the photocatalyst by filtration with a 0.1 μm filter in the dark. The mixture was purified by silica gel flash chromatography to afford the desired product **2**. The oxidations of thioethers followed a similar procedure.

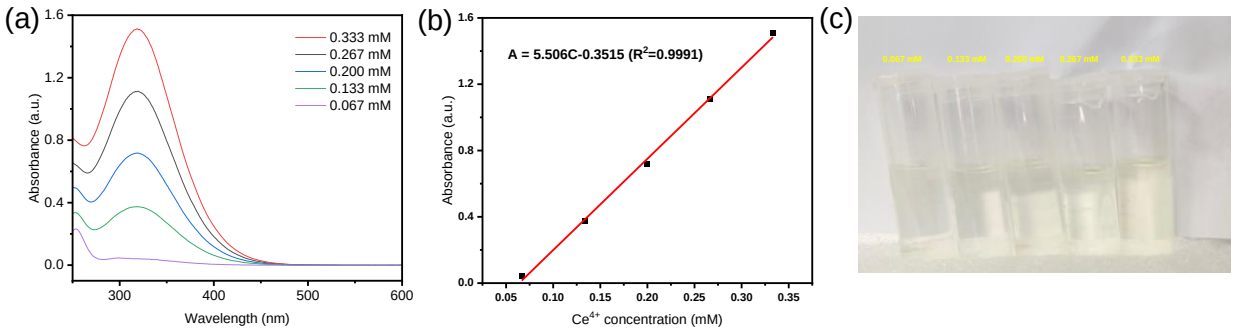
A 1.0 mM $Ce(SO_4)_2$ solution was prepared by dissolving 33.2 mg of $Ce(SO_4)_2$ in 100 mL of 0.5 M H_2SO_4 to give a clear, yellow solution. For the standard curve, 1 mL $Ce(SO_4)_2$ (1.0 mM) were mixed with 1 mL of aqueous H_2O_2 at known concentrations (0.1, 0.2, 0.3, and 0.4 mM), followed by the addition of 1 mL of deionized water. The sample was mixed with pre-prepared $Ce(SO_4)_2$ solution and the concentrations of H_2O_2 was determined by a UV-vis spectrometer, in which the yellow Ce^{4+} reacted with H_2O_2 to generate achromatous Ce^{3+} (Eq. S1).

$$2Ce^{4+} + H_2O_2 = 2Ce^{3+} + 2H^+ + O_2 \text{ (Eq. S1)}$$

The concentration of produced H_2O_2 can be calculated by Eq. S2:

$$c(H_2O_2) = 1/2 \times c(Ce^{4+}) \text{ (Eq. S2)}$$

By adding known concentration of H_2O_2 solution into the $Ce(SO_4)_2$ solution, the change of absorption intensity at about 317 nm was measured with the UV-vis spectrometer. The linear relationship between Ce^{4+} concentration and the absorption intensity were established as follows. The H_2O_2 concentration was quantified by UV-vis spectroscopy using a mixture composed of 1 mL $Ce(SO_4)_2$ solution, 2 mL H_2O, and 10 μL of the reaction solution.



Supplementary Figure 2 (a) UV–vis spectra of $Ce(SO_4)_2$ solutions at various concentrations in the presence of H_2O_2. (b) Standard curve. (c) Original pictures of filtered solutions.

The yields of **2g**, **4e** and **4f** was detected by effective carbon number (ECN) concept**.** The response factors (R_f) of standard compounds were determined with GC-MS using the following formula (Eq. S3 and Eq. S4)

$$R_f = (A_c/A_{is}) \times (C_{is}/C_c) \text{ (Eq. S3)}$$

$$Cc = (A_c/A_{is}) \times (C_{is} \times ECN_{is}/ECN_c) \text{ (Eq. S4)}$$

where C_c is the carbon moles of the model compound, C_{is} is the carbon moles of the internal standard (biphenyl), A_c is the area of the model compound, A_{is} is the area of the internal standard, R_f is the response factor of the

compound, ECN_{is} is the effective carbon number of the internal standard and ECN_c is the effective carbon number of the compound.

3.4 Photocurrents and photoelectrochemical measurements

5 mg of catalysts were dispersed in 0.5 mL ethanol, and 20 μL Nafion solution (5 wt%) was added. The mixture was ultrasonically treated to form homogenous catalyst ink. Then the catalyst ink was dipped on a polished FTO glass and dried in air. Photocurrent measurements were conducted with a Chi600e electrochemical workstation in a standard three-electrode system under irradiation of 410nm blue-LED. The photocatalyst composites was used as the working electrode, Pt foil was used as the counter electrode, Ag/AgCl electrode was used as the reference electrode, and 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte.

4. Fractional atomic coordinated for unit cell of TANB-Py-COF

Supplementary Table 1 Fractional atomic coordinated for unit cell of TANB-Py-COF calculated using the Materials Studio modeling program after performing the Pawley Refinement

Space group	**P1**		
Calculated cell parameters	**a = 25.9 Å, b = 4.9 Å, c = 27.4 Å, α = 90°, β = 90°, γ = 90°, R_{wp} = 5.23% and R_p = 4.11%**		
Atoms	x	y	z
C1	0.47403	0.51294	0.54821
C2	0.55535	0.47207	0.50298
C3	0.52953	0.48118	0.45761
C4	0.44226	0.498	0.4119
C5	0.44168	0.50747	0.59426
C6	0.39831	0.6767	0.60069
C7	0.3679	0.66286	0.64359
C8	0.38136	0.48094	0.68105
C9	0.42406	0.31255	0.67458
C10	0.45314	0.32446	0.63162
C11	0.32423	0.82735	0.65002
C12	0.29443	0.81038	0.69275

C13	0.30801	0.63173	0.73024
C14	0.35181	0.46922	0.72425
C15	0.60374	0.29204	0.40712
C16	0.6359	0.29468	0.36541
C17	0.62657	0.48063	0.32747
C18	0.58463	0.65696	0.33159
C19	0.55305	0.65289	0.37312
C20	0.67723	0.11412	0.36087
C21	0.70879	0.11801	0.31928
C22	0.70055	0.3047	0.28178
C23	0.65901	0.48564	0.28593
N24	0.27295	0.56461	0.23592
C25	0.23469	0.71605	0.22168
C26	0.20372	0.65496	0.17725
N27	0.27923	0.6238	0.77534
C28	0.23186	0.53657	0.77828
C29	0.20316	0.528	0.82544
C30	0.16506	0.33217	0.83265
C31	0.13604	0.3244	0.87594
C32	0.14241	0.52058	0.91223
C33	0.18144	0.71404	0.90532
C34	0.21177	0.71685	0.86266
C35	0.21645	0.4451	0.1451
C36	0.18646	0.39735	0.10322
C37	0.14273	0.55575	0.09295
C38	0.13056	0.76723	0.12478
C39	0.1605	0.815	0.16643
C40	0.11097	0.5149	0.95863
C41	0.11167	0.51437	0.04737
C42	0.13754	0.52355	0.00225

C43	0.02659	0.51772	0.91623
C44	0.97477	0.47642	0.00431
C45	0.9466	0.49073	0.9611
C46	0.94787	0.45278	0.04953
C47	0.97705	0.42712	0.09254
C48	0.5292	0.48753	0.54818
C49	0.44826	0.52383	0.50281
C50	0.47447	0.50787	0.45757
C51	0.56205	0.47342	0.41177
C52	0.56137	0.49153	0.59398
C53	0.6031	0.313	0.60066
C54	0.63367	0.32381	0.64332
C55	0.62262	0.51553	0.67985
C56	0.58101	0.69131	0.67324
C57	0.55129	0.67969	0.63072
C58	0.67461	0.14378	0.65057
C59	0.70414	0.15362	0.69344
C60	0.69387	0.34579	0.72944
C61	0.65294	0.52633	0.72257
C62	0.40028	0.67422	0.40466
C63	0.36867	0.65285	0.36285
C64	0.37913	0.45428	0.32753
C65	0.42116	0.28129	0.33452
C66	0.45173	0.30178	0.3764
C67	0.32645	0.82484	0.3559
C68	0.29478	0.79976	0.31462
C69	0.30493	0.60232	0.27886
C70	0.3474	0.43098	0.28588
N71	0.73245	0.29543	0.23854
C72	0.76236	0.49205	0.22441

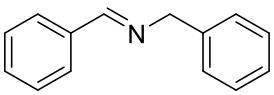
C73	0.79617	0.47044	0.18035
N74	0.72368	0.34936	0.7738
C75	0.76051	0.52301	0.78132
C76	0.79215	0.52491	0.82675
C77	0.83127	0.72016	0.83086
C78	0.86497	0.73798	0.87057
C79	0.85756	0.52573	0.91214
C80	0.81469	0.32772	0.90628
C81	0.78408	0.33487	0.86414
C82	0.78911	0.27057	0.14476
C83	0.82095	0.26083	0.10312
C84	0.86114	0.44767	0.09638
C85	0.86794	0.64742	0.132
C86	0.836	0.65811	0.1734
C87	0.89177	0.48323	0.96171
C88	0.89272	0.44816	0.05024
C89	0.86599	0.46025	0.00556
C90	0.97408	0.50684	0.91705
C91	0.02891	0.4879	0.00351
C92	0.05583	0.50519	0.95935
C93	0.05699	0.48397	0.04793
C94	0.0297	0.44498	0.09185
H95	0.59722	0.4626	0.50312
H96	0.38826	0.81952	0.57237
H97	0.43478	0.16961	0.70257
H98	0.48546	0.19306	0.62773
H99	0.31318	0.96914	0.62196
H100	0.26103	0.93922	0.69705
H101	0.36262	0.33265	0.75328
H102	0.61115	0.14812	0.43599

H103	0.5766	0.80098	0.30295
H104	0.52154	0.79127	0.37506
H105	0.68501	-0.03125	0.38931
H106	0.74016	-0.02422	0.31638
H107	0.65163	0.62621	0.25656
H108	0.22427	0.89331	0.24213
H109	0.21334	0.45438	0.74604
H110	0.15813	0.18181	0.80495
H111	0.10854	0.16343	0.88116
H112	0.188	0.86565	0.93294
H113	0.24045	0.87229	0.85805
H114	0.24934	0.31739	0.15244
H115	0.19686	0.23388	0.0792
H116	0.09822	0.89803	0.11696
H117	0.14984	0.97864	0.19038
H118	0.17923	0.54143	0.00188
H119	0.04451	0.53924	0.88095
H120	0.9586	0.39061	0.12723
H121	0.40643	0.53113	0.50261
H122	0.61144	0.16378	0.57299
H123	0.57168	0.83914	0.70076
H124	0.51953	0.81523	0.62681
H125	0.6835	-0.00688	0.62335
H126	0.7353	0.01202	0.69845
H127	0.64466	0.67317	0.75064
H128	0.39237	0.82843	0.43151
H129	0.42994	0.12633	0.30805
H130	0.48291	0.16291	0.38143
H131	0.31767	0.97892	0.3825
H132	0.26253	0.93529	0.3115

H133	0.35528	0.27725	0.2589
H134	0.76527	0.67131	0.24668
H135	0.76974	0.66782	0.75302
H136	0.83643	0.86503	0.80188
H137	0.90341	0.94796	0.8715
H138	0.80783	0.17569	0.93369
H139	0.75394	0.18628	0.86034
H140	0.75872	0.12306	0.14879
H141	0.81436	0.10612	0.07614
H142	0.89737	0.79964	0.12735
H143	0.84226	0.81513	0.20011
H144	0.82416	0.46494	0.00578
H145	0.95452	0.50853	0.88228
H146	0.0499	0.42286	0.12612

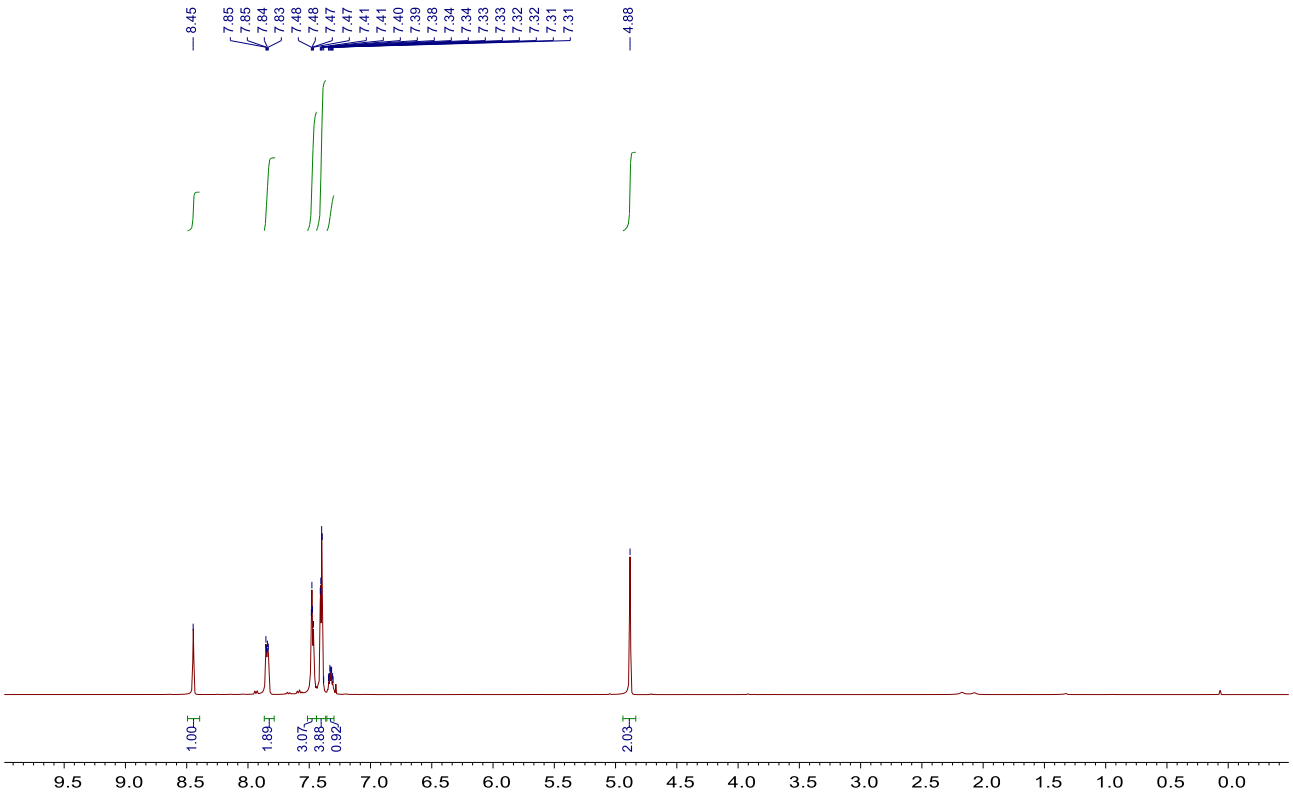
5. Spectral data of products

(*E*)-N-Benzyl-1-phenylmethanimine

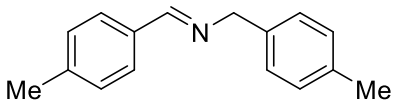


2a

99% yield, 19.2 mg. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 7.87 – 7.79 (m, 2H), 7.51 – 7.44 (m, 3H), 7.44 – 7.37 (m, 4H), 7.36 – 7.30 (m, 1H), 4.88 (s, 2H).It’s known compound.

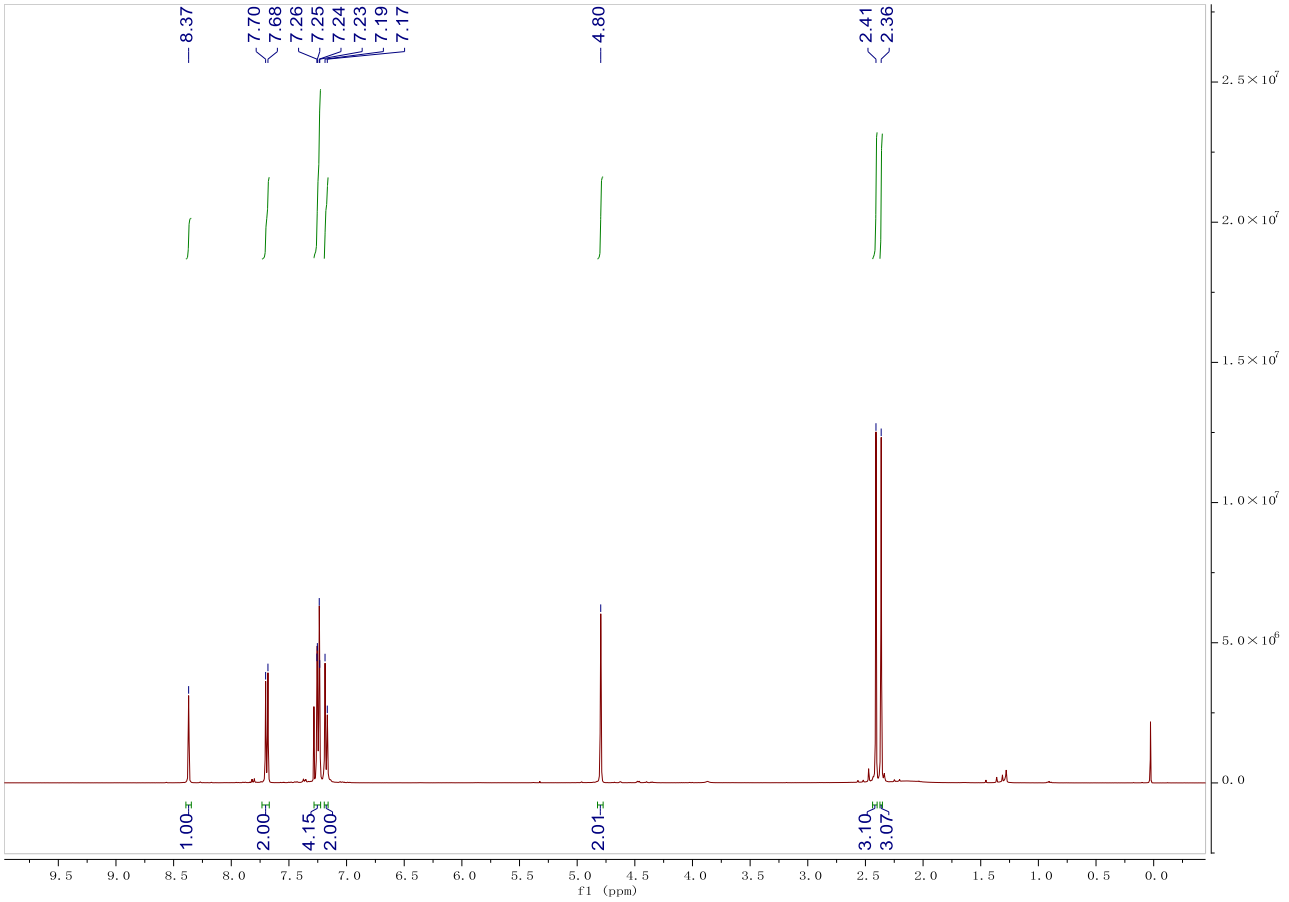

8.45
7.85
7.85
7.84
7.83
7.48
7.48
7.47
7.47
7.41
7.41
7.40
7.39
7.38
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
4.88
1.00
1.89
3.07
3.88
0.92
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

(*E*)-N-(4-Methylbenzyl)-1-(4-methylphenyl)methanimine

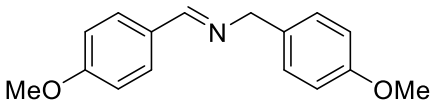


2b

99% yield, 22.0 mg. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 2H), 4.80 (s, 2H), 2.41 (s, 3H), 2.36 (s, 3H). It's known compound.

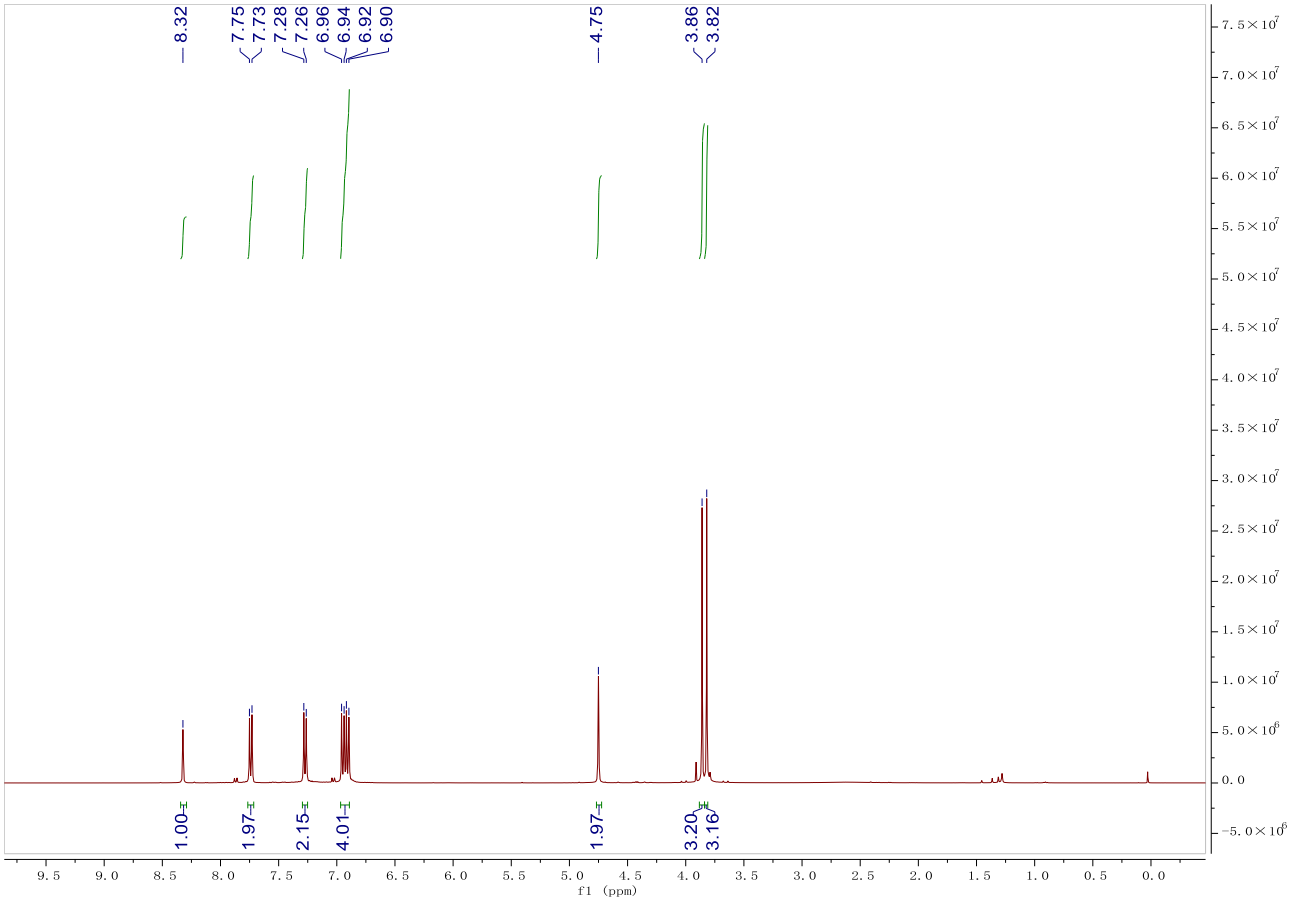


(*E*)-N-(4-Methoxybenzyl)-1-(4-methoxyphenyl)methanimine

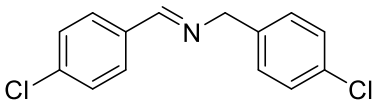


2c

99% yield, 25.4 mg. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.89 (m, 4H), 4.75 (s, 2H), 3.86 (s, 3H), 3.82 (s, 3H). It's known compound.

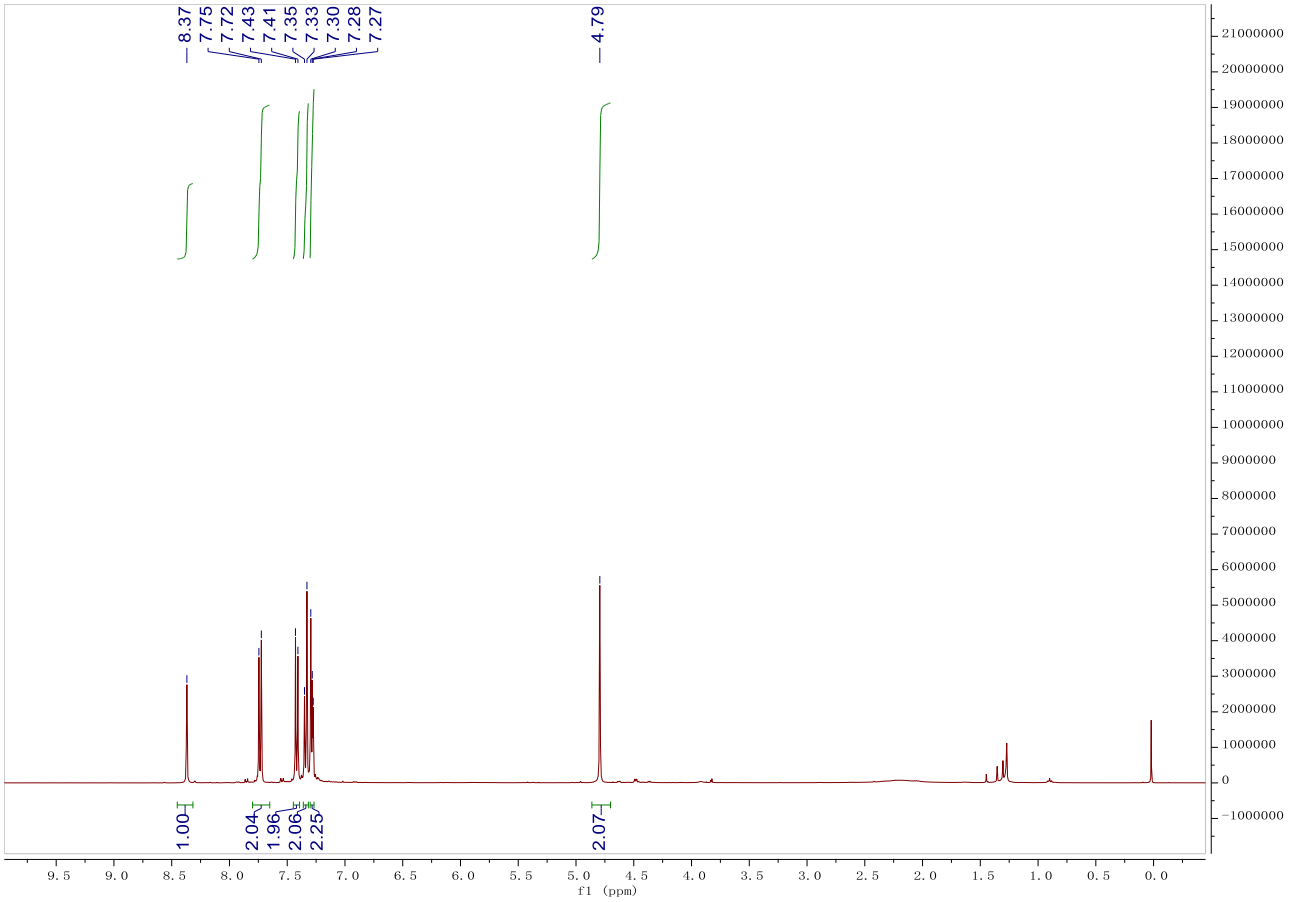


(*E*)-N-(4-Chlorobenzyl)-1-(4-chlorophenyl)methanimine

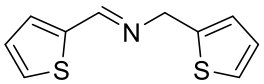


2d

99% yield, 26.1 mg,^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.79 (s, 2H). It's known compound.



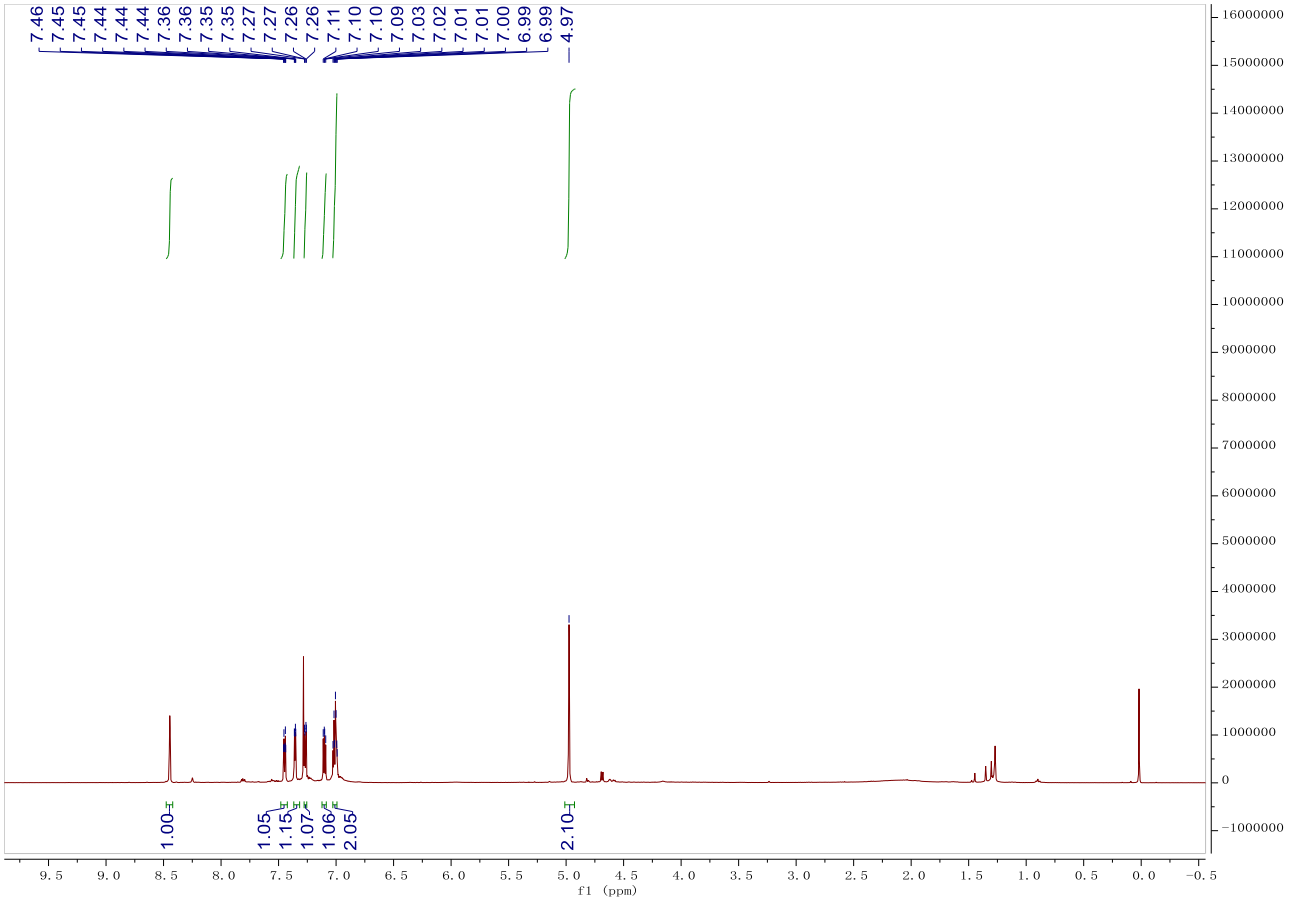
(*E*)-1-(Thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine



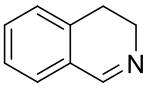
2e

99% yield, 20.6 mg, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 7.45 (dt, *J* = 5.1, 1.1 Hz, 1H), 7.36 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.27 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.03 – 6.99 (m, 2H), 4.97 (s, 2H).

It's known compound.

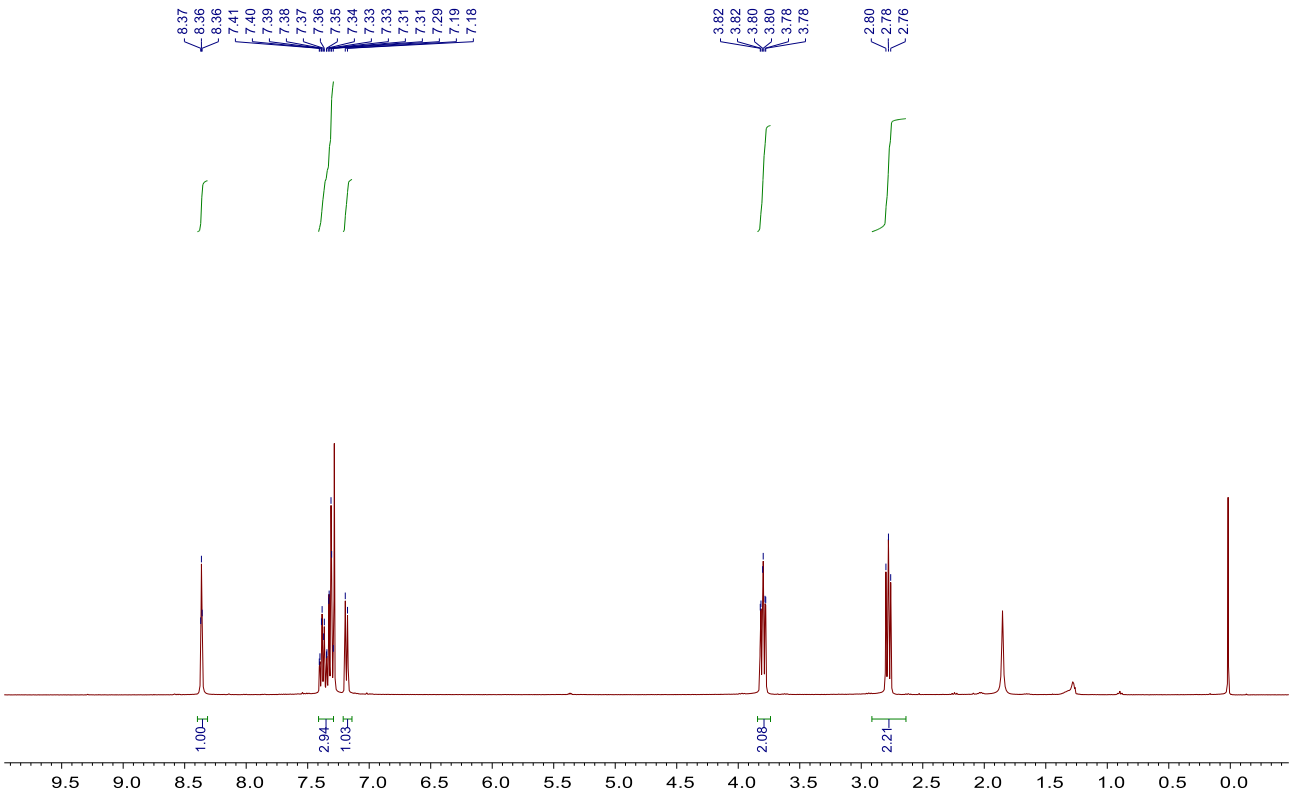


3,4-Dihydroisoquinoline

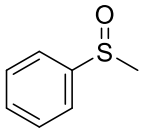


2f

74% yield, 9.6 mg, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (t, *J* = 2.3 Hz, 1H), 7.41 – 7.29 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 1H), 3.84 – 3.74 (m, 2H), 2.91 – 2.64 (m, 2H). It's known compound.



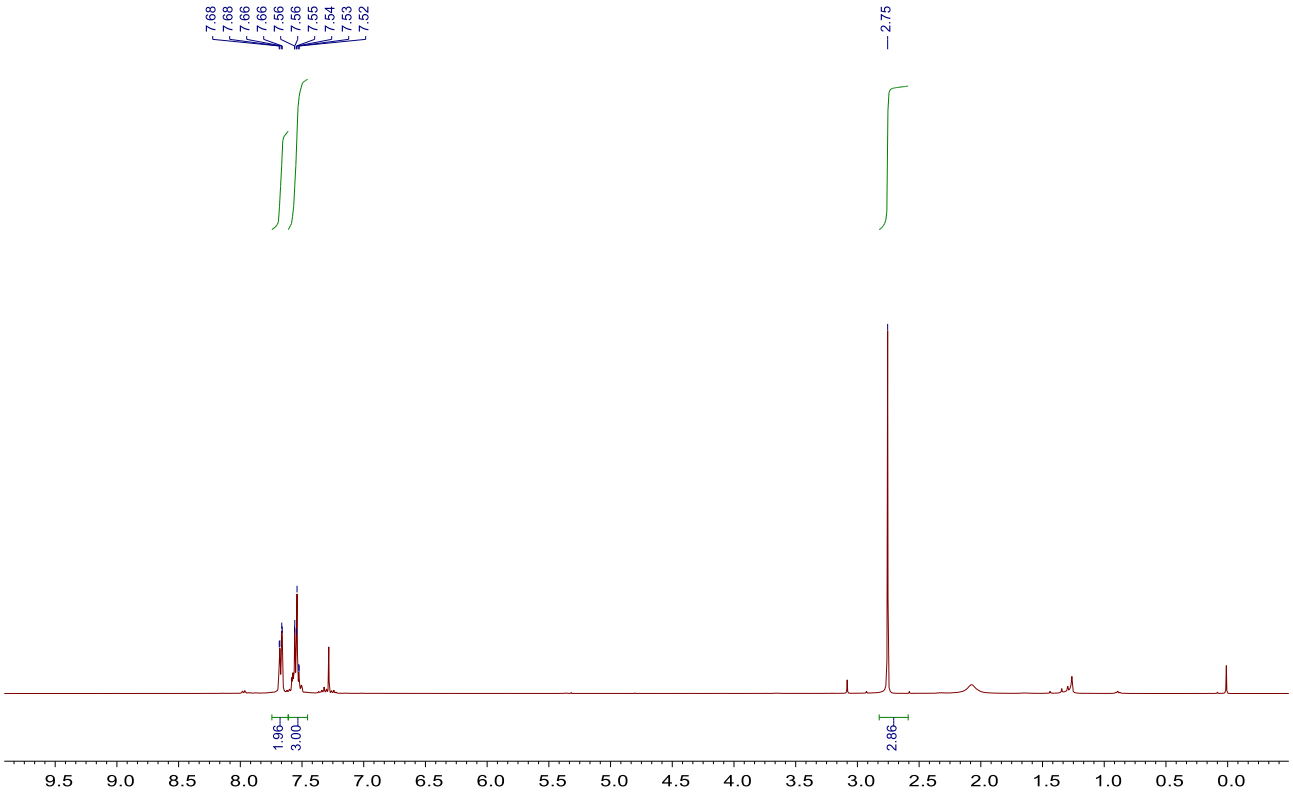
(Methylsulfinyl)benzene



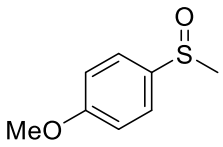
4a

93% yield, 13.0 mg, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.61 (m, 2H), 7.61 – 7.46 (m, 3H), 2.75 (s, 3H).

It's known compound.

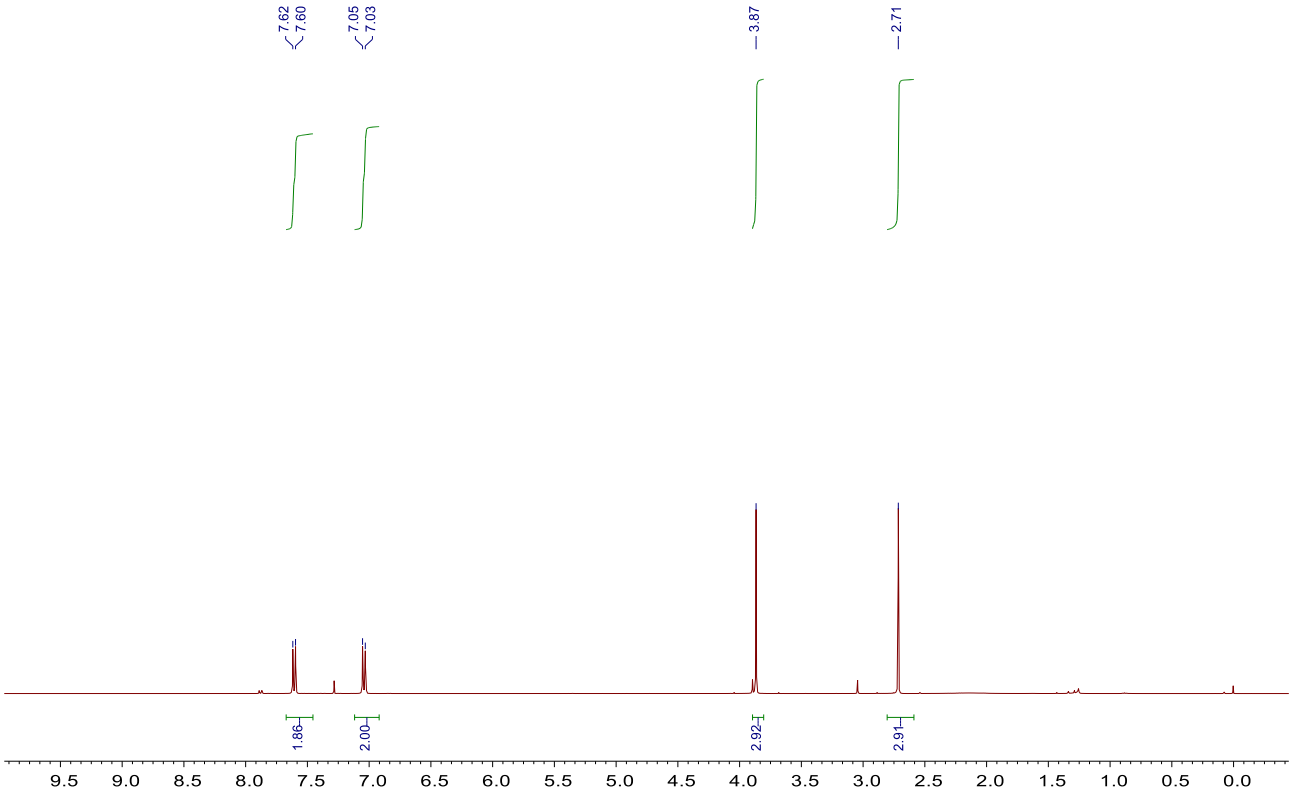


1-Methoxy-4-(methylsulfinyl)benzene

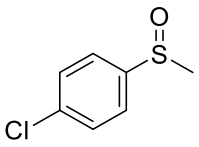


4b

96% yield, 16.3 mg, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.71 (s, 3H). It's known compound.

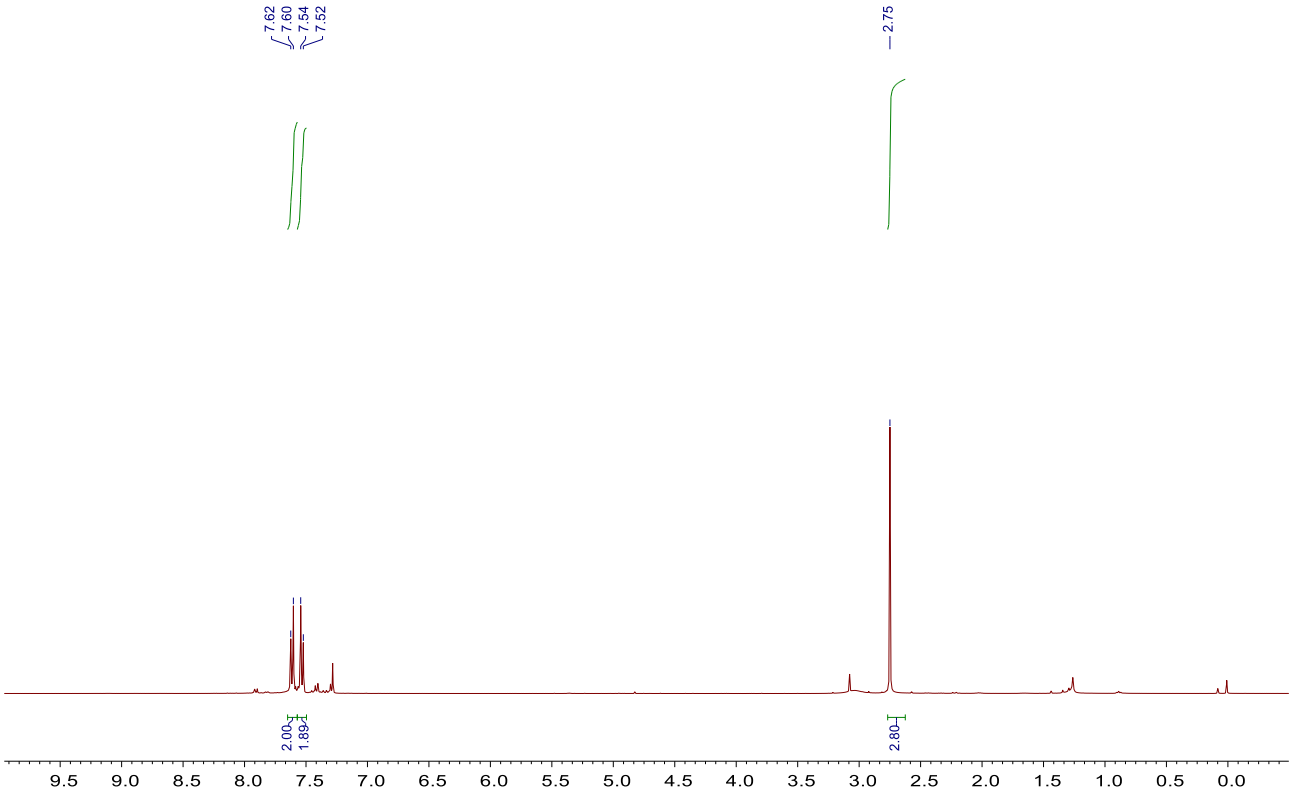


1-Chloro-4-(methylsulfinyl)benzene

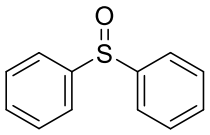


4c

94% yield, 16.0 mg, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 2.75 (s, 3H). It's known compound.



Sulfinyldibenzene



4d

92% yield, 18.5 mg, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 4H), 7.52 – 7.43 (m, 6H). It's known compound.