Supporting Information

Cobalt nanoparticles supported on microporous nitrogen-doped carbon for efficient catalytic transfer hydrogenation reaction between nitroarenes and N-heterocycles

Xiaomei Lu[a,#], Jingzhong Qin[a,#], Chensheng Xian[a], Jiabao Nie[a], Xun Li[a], Jie He[a,*], Bing Liu[a,*]

[a]*Key Laboratory of Catalysis and Materials Sciences of the Ministry of Education, South-Central Minzu University, Wuhan 430074, P. R. China.*

[#]These authors contributed equally to this work.

*Corresponding authors. Email addresses: jiehe@scuec.edu.cn (Jie He); liubing@mail.scuec.edu.cn (Bing Liu).

1. Supporting Figures

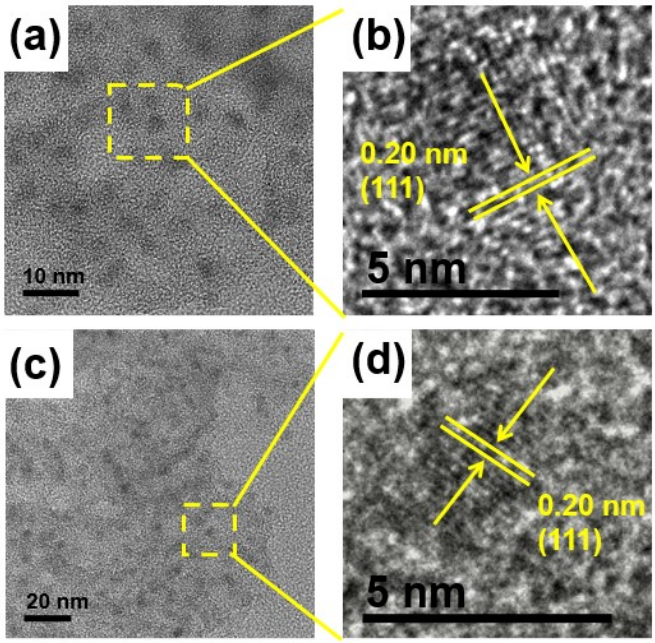


Figure S1. TEM images of the Co/mNC-500 sample.

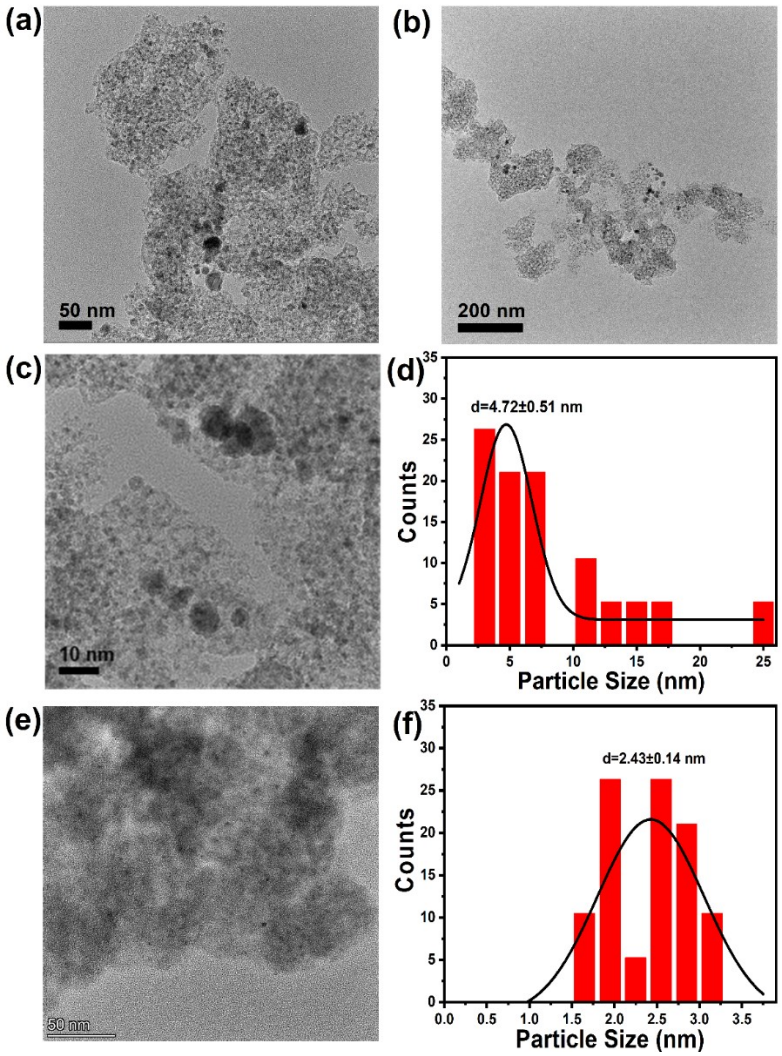


Figure S2. (a-c) TEM images and (d) particle size distribution of the Co/mNC-600 sample. (e) TEM image and (f) particle size distribution of the Co/mNC-400 sample.

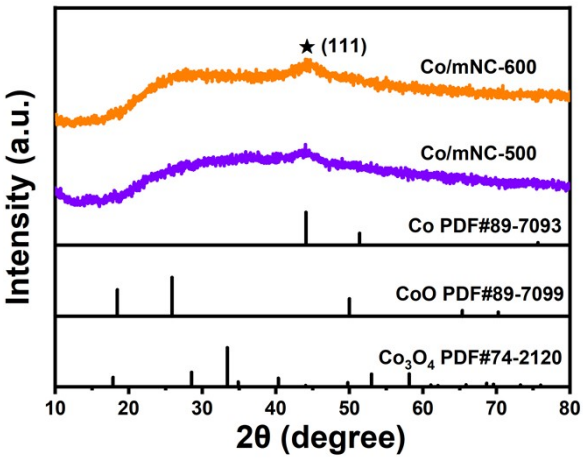


Figure S3. XRD patterns of the Co/mNC-500 sample and standard PDF data of Co^0, CoO, and Co_3O_4.

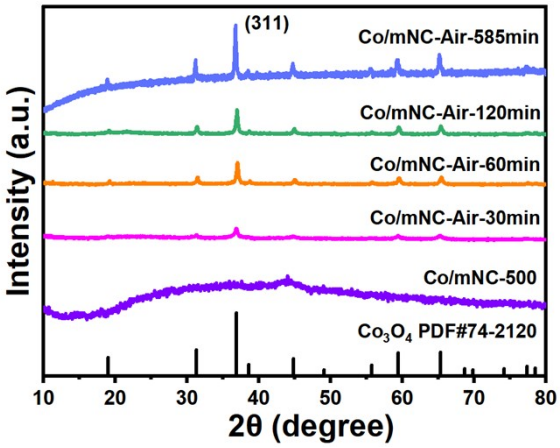


Figure S4. XRD patterns of Co/mNC-500 and Co/mNC-500-Air-x min.

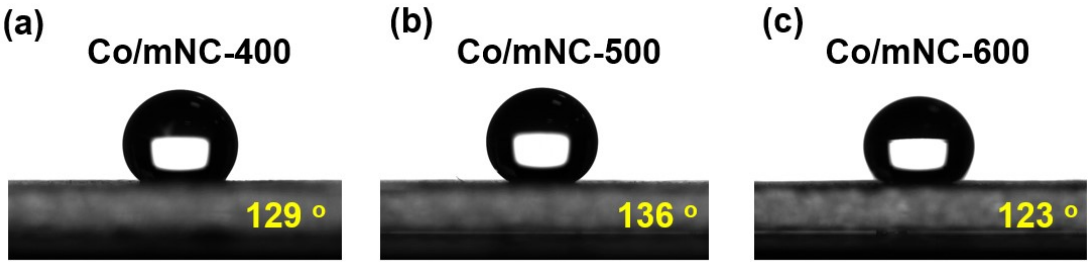


Figure S5. Water contact angle tests for (a) Co/mNC-400, (b) Co/mNC-500, and (c) Co/mNC-600 catalysts.

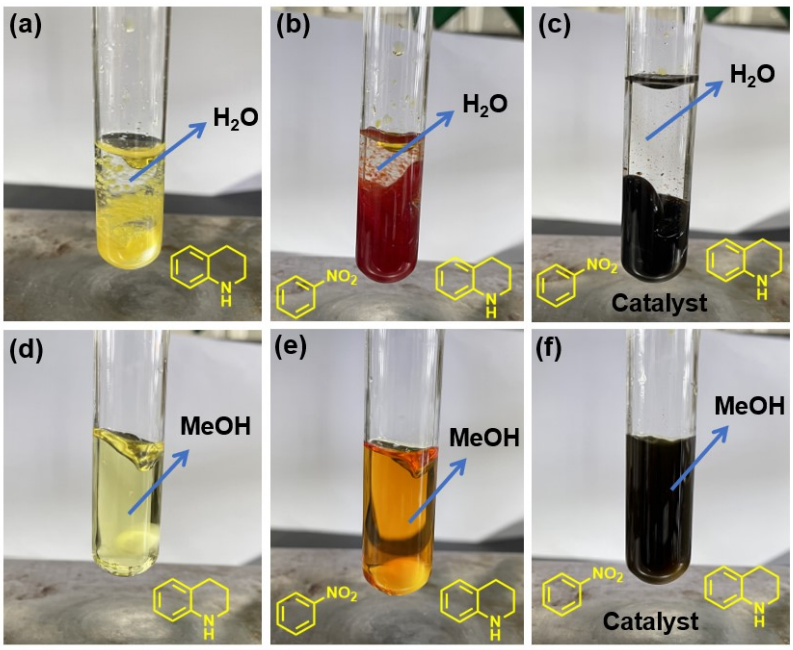


Figure S6. Photographs of substrates and catalysts in (a-c) water and (d-f) MeOH.

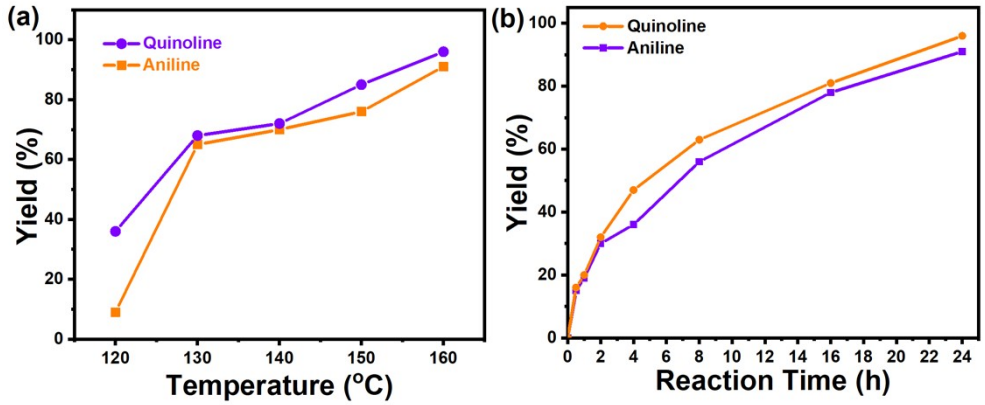


Figure S7. Temperature and time course of the catalytic transfer hydrogenation between nitrobenzene and 1,2,3,4-tetrahydroquinoline. Conditions: nitrobenzene (0.4 mmol), 1,2,3,4-tetrahydroquinoline (0.6 mmol), catalyst (20 mg), solvent (10 mL), N_2 (1 Mpa), 24 h.

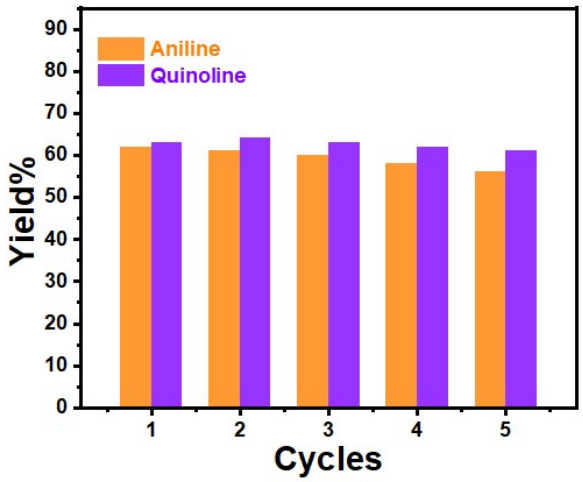


Figure S8. Recycled tests for the Co/mNC-500 catalyst. Conditions: nitrobenzene (0.4 mmol), 1,2,3,4-tetrahydroquinoline (0.6 mmol), catalyst (20 mg), solvent (10 mL), N_2 (1 Mpa), 8 h.

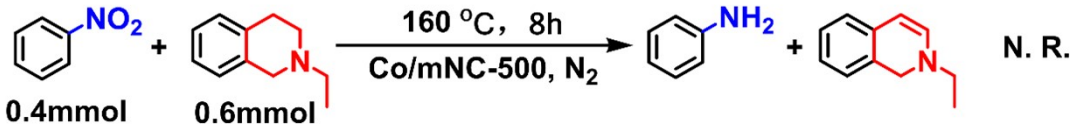


Figure S9. Conditions: nitrobenzene (0.4 mmol), 2-ethyl-1,2,3,4-tetrahydroquinoline (0.6 mmol), catalyst (20 mg), solvent (10 mL), N_2 (1 Mpa), 160 ℃, 8 h.

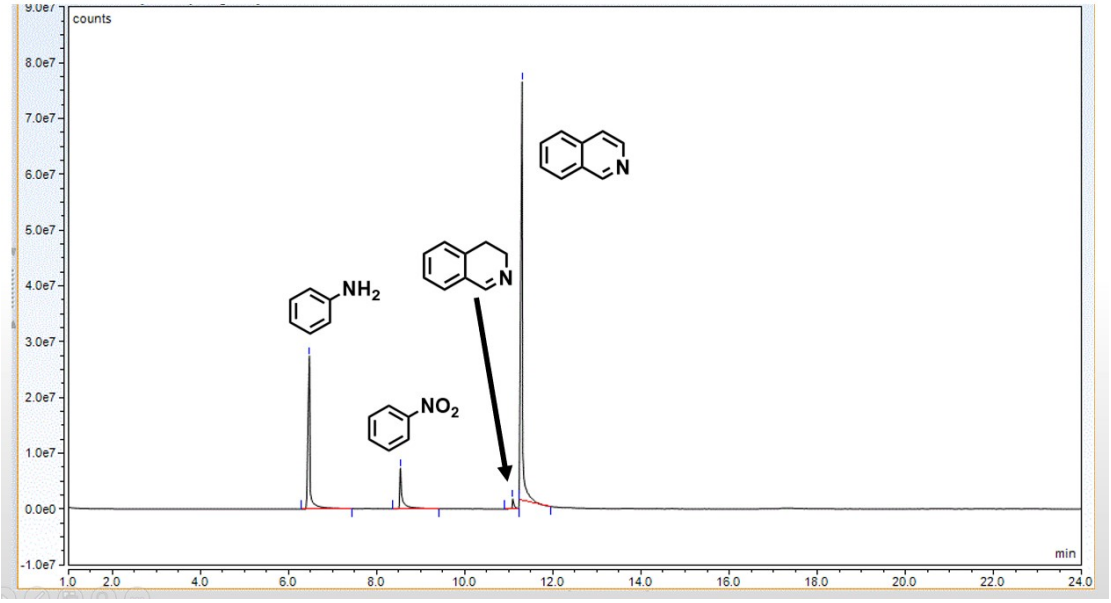


Figure S10. GC-MS spectrum of the intermediate generated from the catalytic transfer hydrogenation between nitrobenzene and 1,2,3,4-tetrahydroisoquinoline.

2. Supporting Tables

Table S1. Elemental analysis of Co/mNC-400, Co/mNC-500, and Co/mNC-600.[a]

Catalyst	C (wt%)	N (wt%)	O (wt%)	Co[a] (wt%)	Co[b] (wt%)	Co[c] (wt%)
Co/mNC-400	71.45	5.16	17.14	6.09	11.30	12.40
Co/mNC-500	76.84	4.67	10.22	8.27	14.08	13.62
Co/mNC-600	77.78	3.36	9.10	9.75	21.06	15.60

[a] Elemental analysis by XPS.

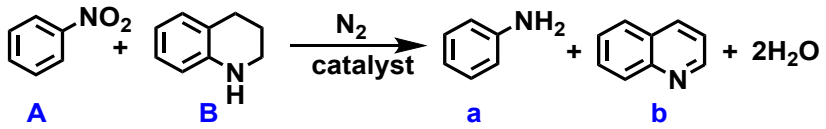
[b] Elemental analysis by ICP-AES.

[c] Theoretical composition calculated from the recipe.

Table S2. Pore structure of Co/mNC-500 and Co/mNC-600.

Catalyst	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Co/mNC-500	532.93	0.48	3.62
Co/mNC-600	616.89	0.65	0.52

Table S3. Control experiment of the catalytic transfer hydrogenation between nitrobenzene and 1,2,3,4-tetrahydroquinoline.



A B a b

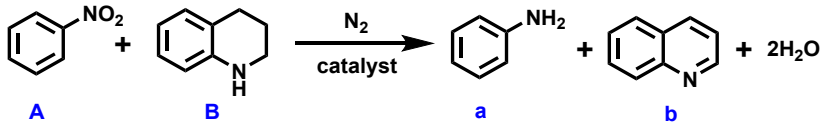
Entry	Catalyst	Yield of a (%)	Yield of b (%)
1	Co/mNC-500	36	43
2	Co_3O_4/mNC-Air-30 min	34	39
3	Co_3O_4/mNC-Air-60 min	26	31
4	Co_3O_4/mNC-Air-120 min	20	20
5	Co_3O_4/mNC-Air-585 min	0	0

Reaction conditions: nitrobenzene (0.4 mmol), 1,2,3,4-tetrahydroquinoline (0.6 mmol), Catalyst (20 mg), H_2O (10 mL), N_2 (1 Mpa), 4 h, 160 ^oC.

Table S4. Analysis on the content of Co^0 species based on XPS data.[a]

Catalyst	Co (at.%)	Co^0 (at.%)	Co^0 $2p_{3/2}$ (at.%)	Co^0 $2p_{1/2}$ (at.%)
Co/mNC-400	1.37	0.64	0.49	0.15
Co/mNC-500	1.87	1.07	0.82	0.25
Co/mNC-600	2.22	0.88	0.61	0.27

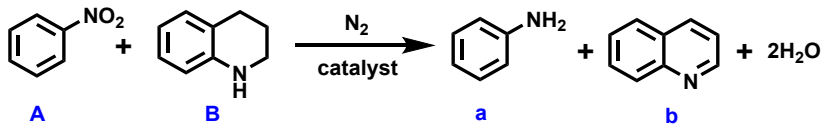
Table S5. Optimization of solvent for catalytic transfer hydrogenation between nitrobenzene and 1,2,3,4-tetrahydroquinoline.[a]



Entry	Solvent	Con. of A (%)	Con. of B (%)	Yield of a (%)	Yield of b (%)
1	H_2O	36	44	36	43
2	CH_3OH	19	12	19	12
3	CH_3CH_2OH	9	6	9	6
4	Toluene	9	6	5	6
5	THF	7	6	6	6
6	CH_3CN	7	18	7	18
7	DMF	8	9	8	9

[a]Reaction conditions: nitrobenzene (0.4 mmol), 1,2,3,4-tetrahydroquinoline (0.6 mmol), Co/mNC-500 (20 mg), solvent (10 mL), N_2 (1 Mpa), 160 ℃, 4 h.

Table S6. Activity data of catalytic transfer hydrogenation between nitrobenzene and 1,2,3,4-tetrahydroquinoline at different temperatures.[a]

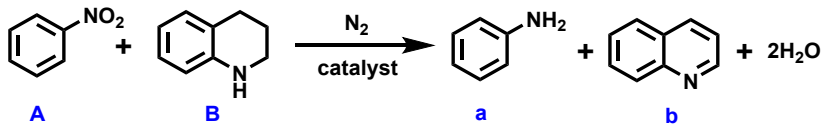


A B a b

Entry	Temperature (°C)	Con. of A (%)	Con. of B (%)	Yield of a (%)	Yield of b (%)
1	120	9	36	9	36
2	130	65	68	65	68
3	140	71	70	70	70
4	150	75	87	75	85
5	160	91	96	91	96

[a]Reaction conditions: nitrobenzene (0.4 mmol), 1,2,3,4-tetrahydroquinoline (0.6 mmol), Co/mNC-500 (20 mg), H_2O (10 mL), N_2 (1 Mpa), 24 h.

Table S7. Activity data of catalytic transfer hydrogenation between nitrobenzene and 1,2,3,4-tetrahydroquinoline over reaction time.[a]

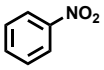
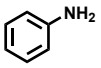


A B a b

Entry	Time (h)	Con. of A (%)	Con. of B (%)	Yield of a (%)	Yield of b (%)
1	0.5	15	16	15	16
2	1	19	20	19	20
3	2	30	32	30	32
4	4	36	44	36	43
5	8	62	63	62	63
6	16	83	83	78	81
7	24	91	96	91	96

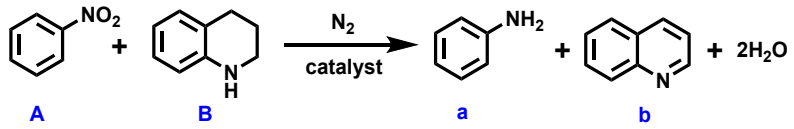
[a]Reaction conditions: nitrobenzene (0.4 mmol), 1,2,3,4-tetrahydroquinoline (0.6 mmol), Co/mNC-500 (20 mg), H_2O (10 mL), N_2 (1 Mpa), 160 °C.

Table S8. The results of reduction of nitrobenzene and dehydrogenation of 1,2,3,4-tetrahydroquinoline[a]

Entry	Substrate	Product	Atomsphere	Y(a) (%)	Y(b) (%)
1			H_2	95	95
2			N_2	11	11

[a] Reaction conditions: 0.4 mmol of nitrobenzene, 0.6mmol 1,2,3,4-tetrahydroquinoline, Co/mNC catalyst (20 mg), 160 ℃, 24 h, solvent (10 mL);

Table S9. catalytic transfer hydrogenation performance between nitrobenzene and 1,2,3,4-tetrahydroquinoline in this work and previous studies.



A B a b

Entry	Catalyst	Yield of a (%)	Yield of b (%)
1[a]	Co/mNC-500 (Catalyst in this work)	91	96
2[b]	Co-N-C-900 (Catalyst in Ref S1)	99	98
3[b]	Co/mNC-500	100	96
4[c]	Ni@NCF-700 (50.13wt%) (Catalyst in Ref S2)	97	96
5[c]	Co/mNC-500	71	65

[a]Optimized conditions in this work: nitrobenzene (0.4 mmol), 1,2,3,4-tetrahydroquinoline (0.6 mmol), Co/mNC-500 (20 mg), H_2O (10 mL), N_2 (1 Mpa), 24 h, 160 °C;
[b]Conditions in Ref. S1: nitrobenzene (0.125 mmol), 1,2,3,4-tetrahydroquinoline (0.188 mmol), Co/mNC-500 (50 mg), H_2O (2 mL), N_2 (1 Mpa), 24 h, 145 °C;
[c]Conditions in Ref. S2: nitrobenzene (0.5 mmol), 1,2,3,4-tetrahydroquinoline (0.75 mmol), Co/mNC-500 (50 mg), H_2O (2 mL), N_2 (1 Mpa) , 24 h, 145 °C.

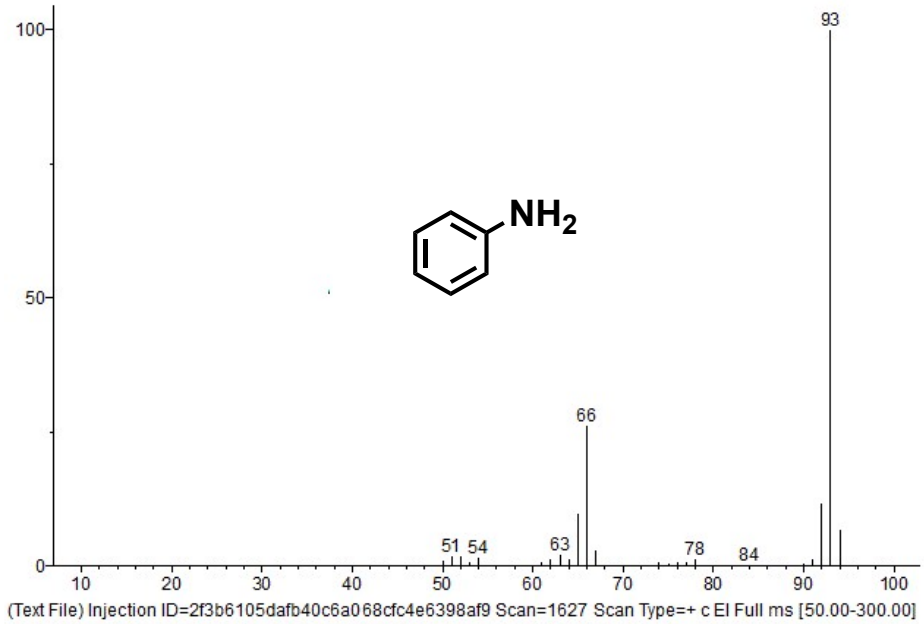
Refer

[S1] D. Xu, R. R. Liu, J. F. Li, H. C. Zhao, J. T. Ma, Z. P. Dong, *Appl. Catal. B,* 2021, **299**, 120681.

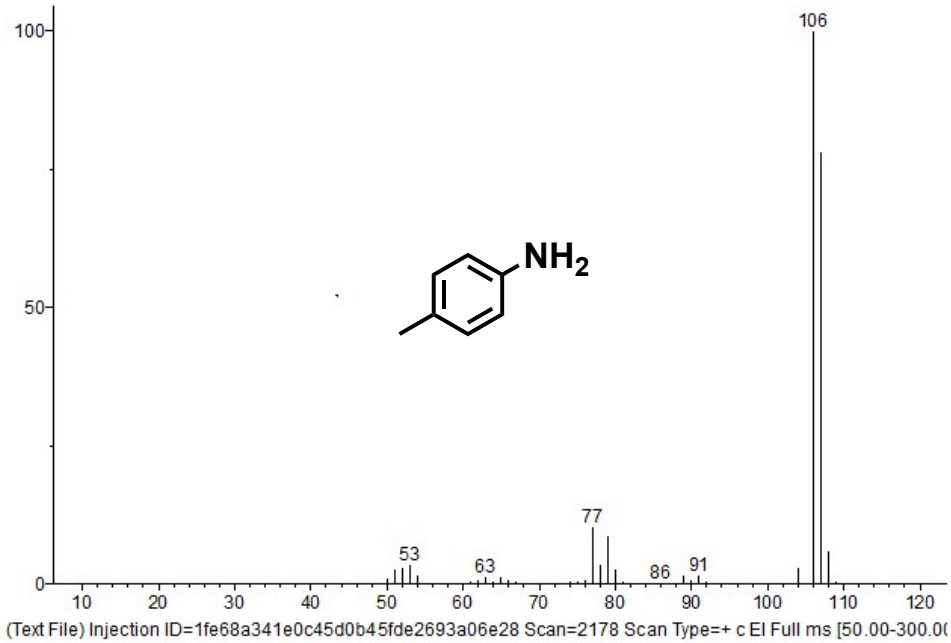
[S2] S. F. Pang, Y. J. Zhang, Q. Su, F. F. Liu, X. Xie, Z. Y. Duan, F. Zhou, P. Zhang, ; Y. B. Wang, *Green Chem.,* 2020, **22**, 1996.

3. Supporting Mass Spectrometry

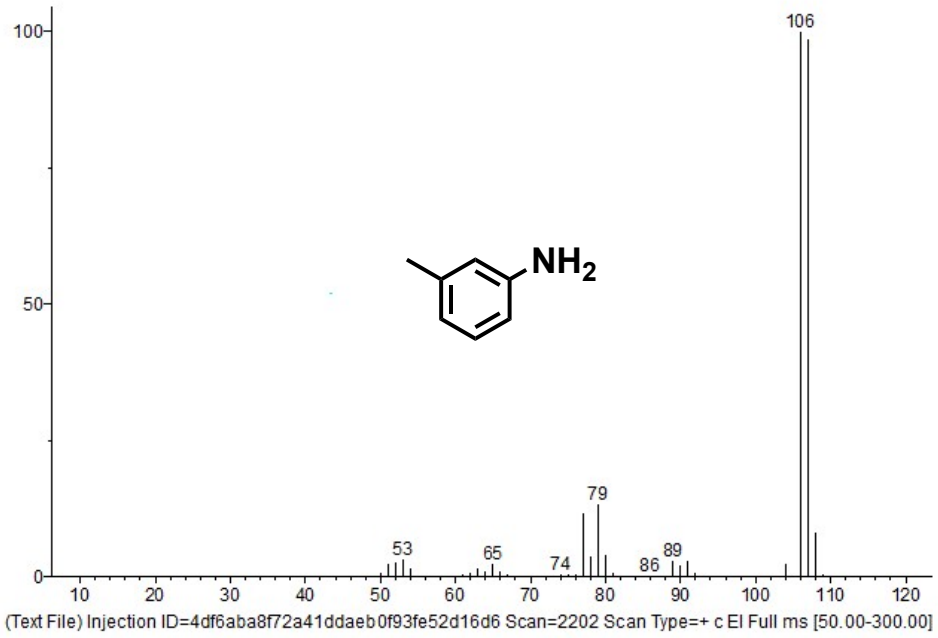
3a: Aniline



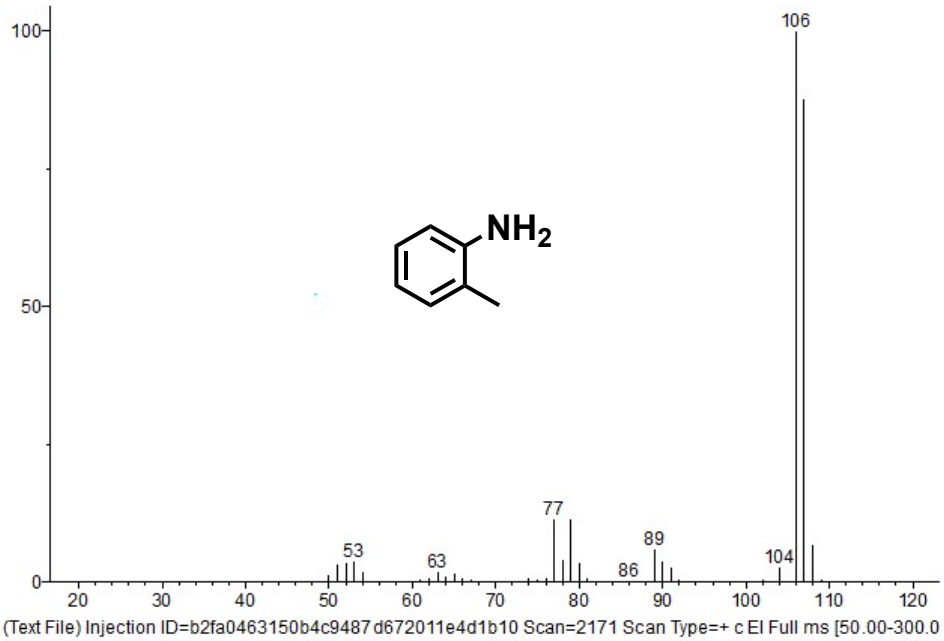
3b: 4-Toluidine



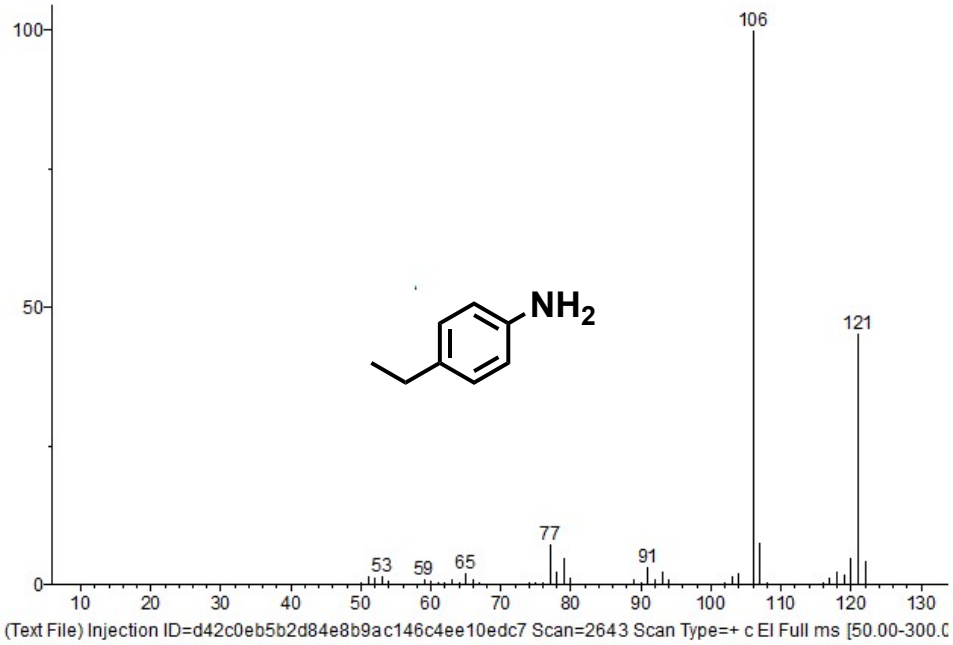
3c: 3-Toluidine



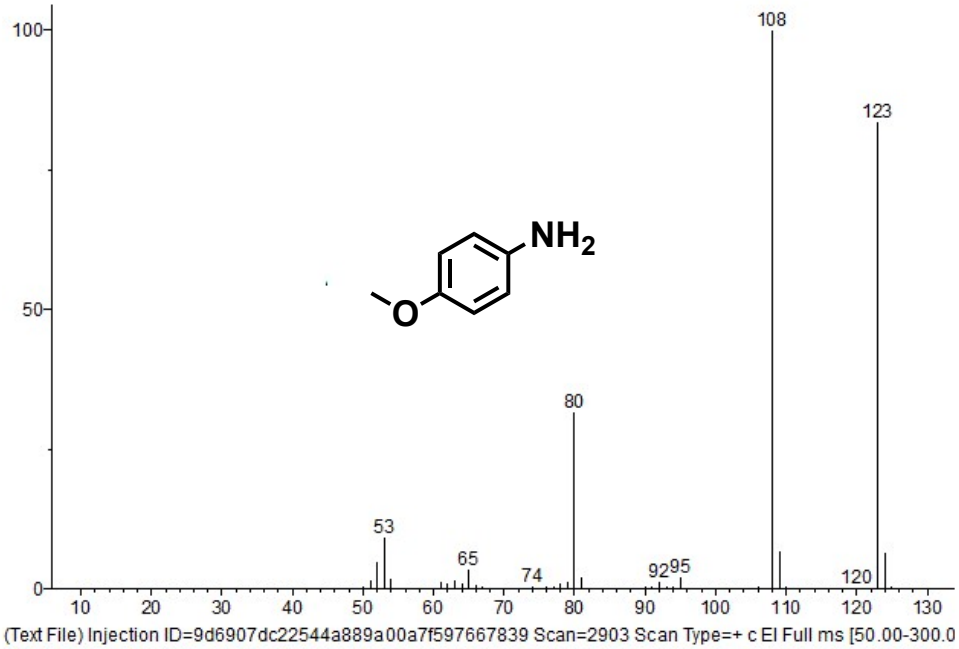
3d: 2-Toluidine



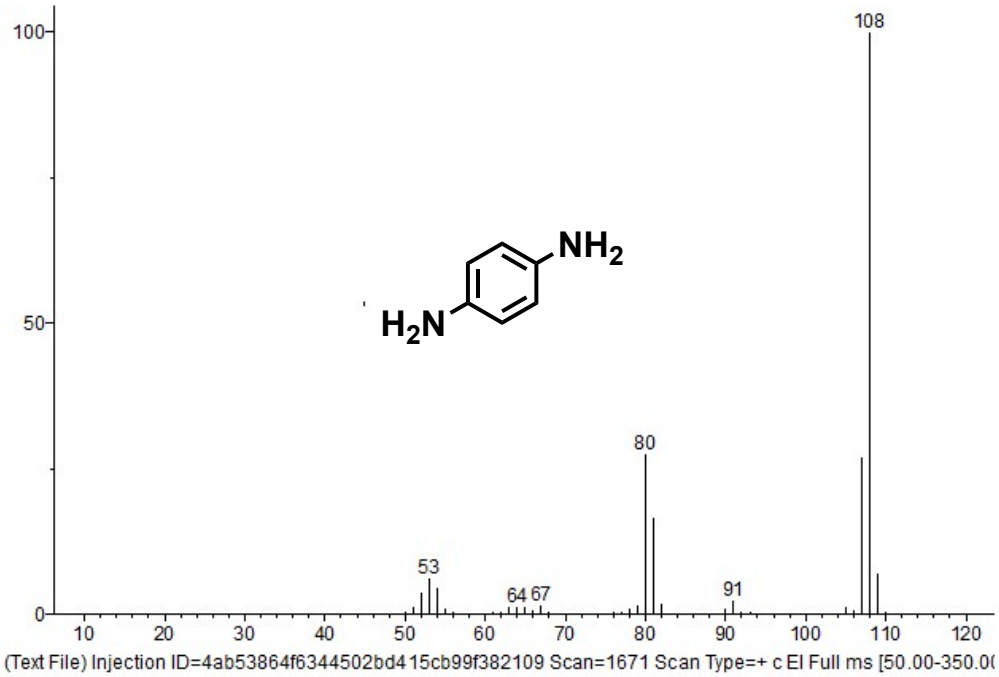
3e: 4-Ethylaniline



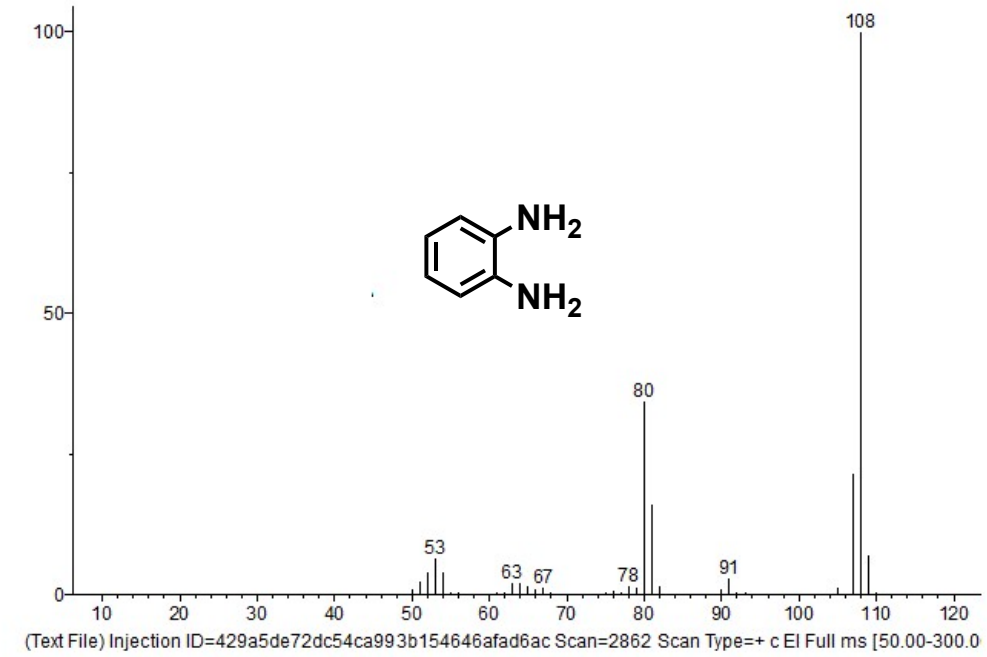
3f: 4-Methoxyaniline



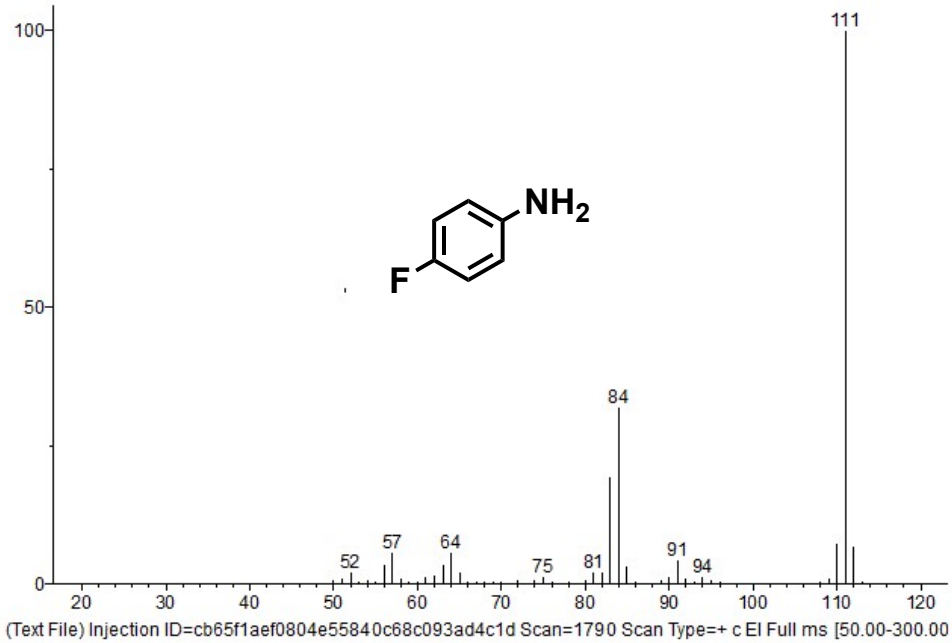
3g: 1,4-Benzenediamine



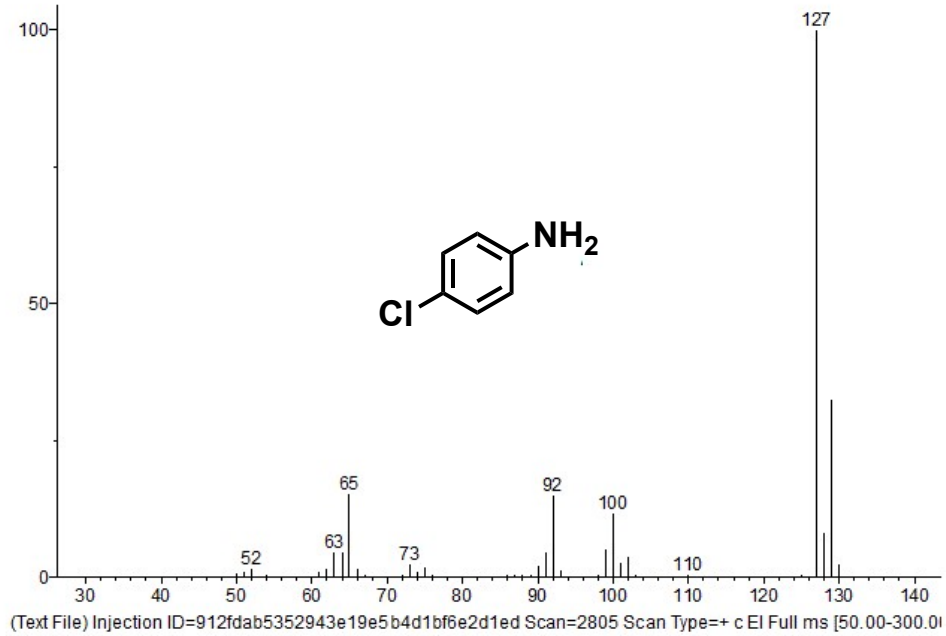
3h: 1,2-Benzenediamine



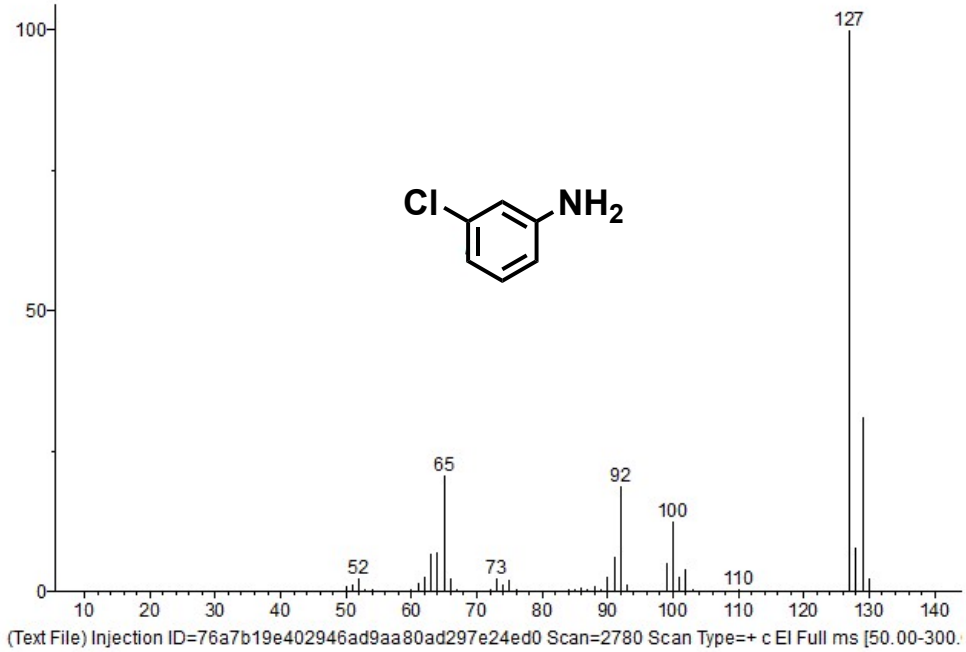
3i: 4-Fluoroaniline



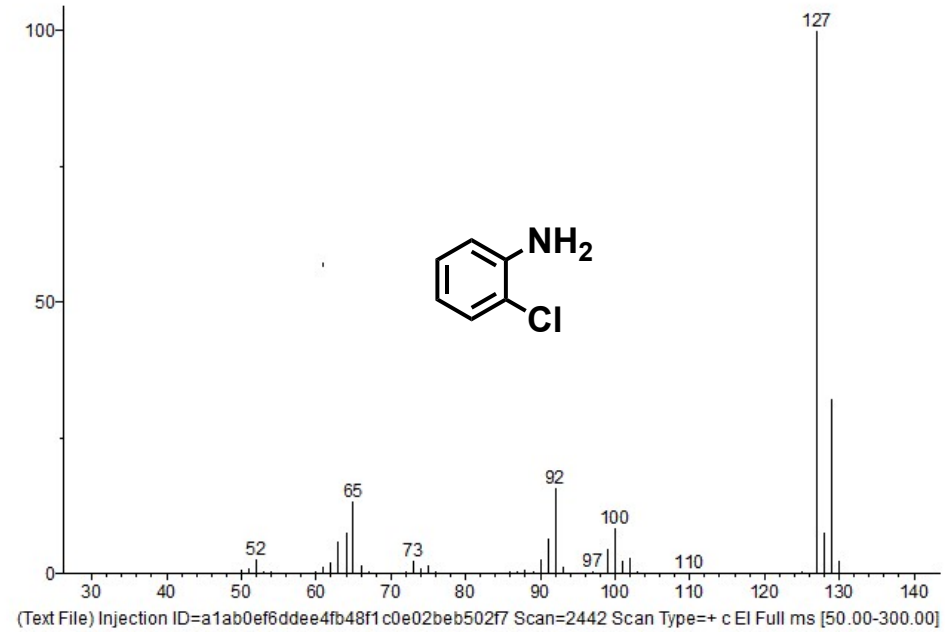
3j: 4-Chloroaniline



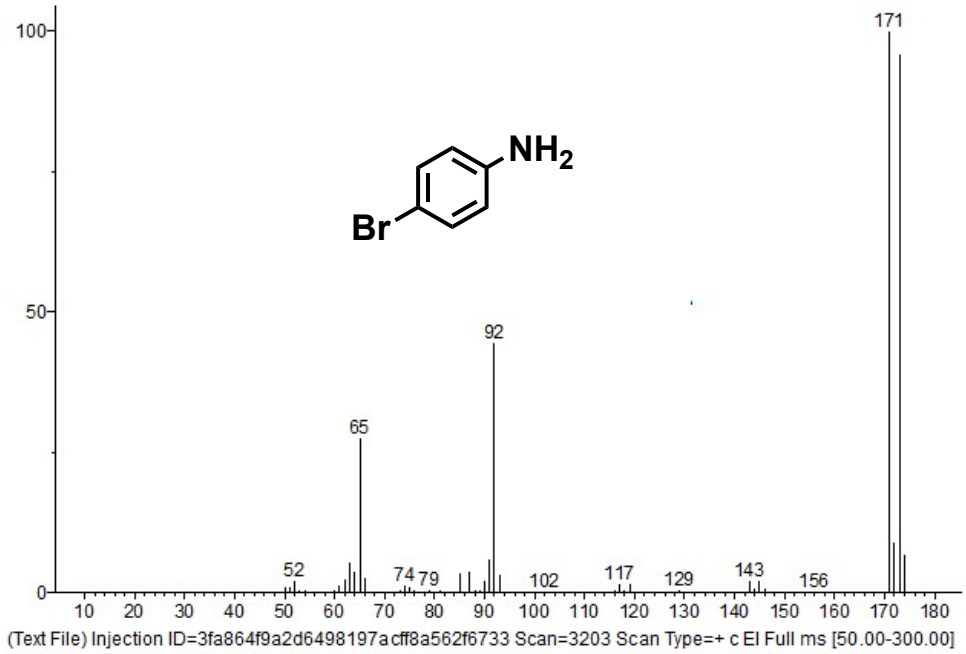
3k: 3-Chloroaniline



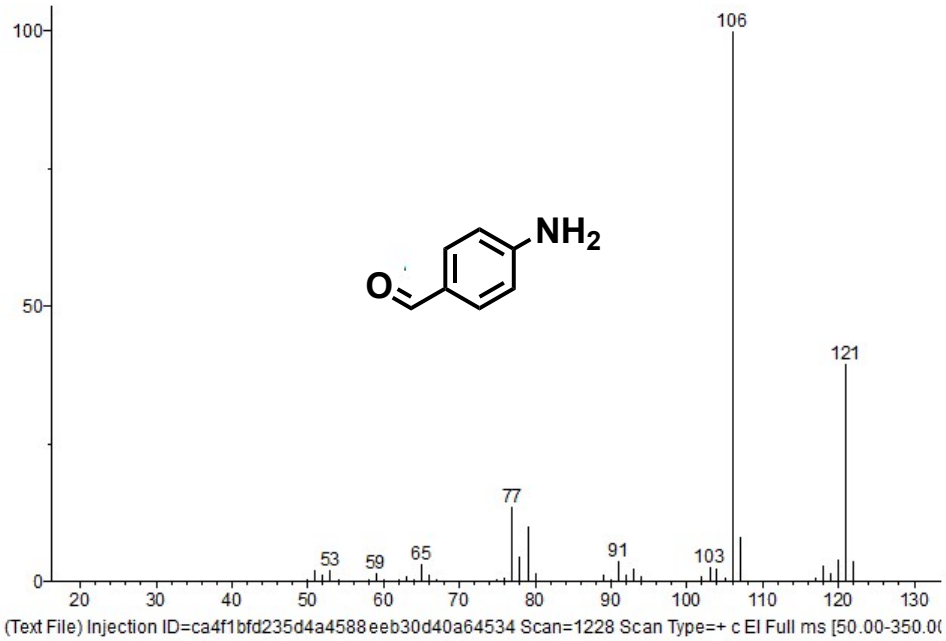
3l: 2-Chloroaniline



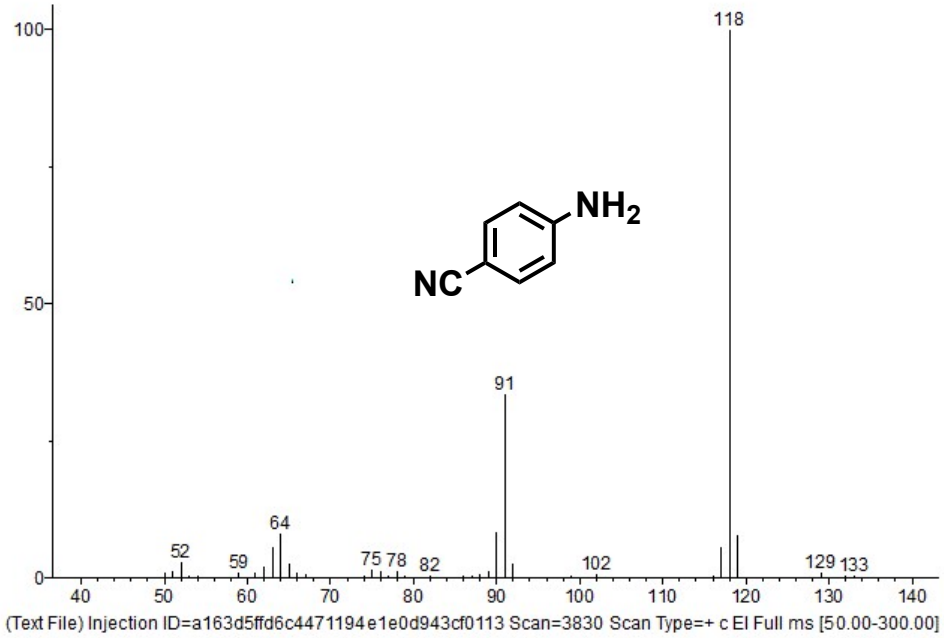
3m: 4-Bromoaniline



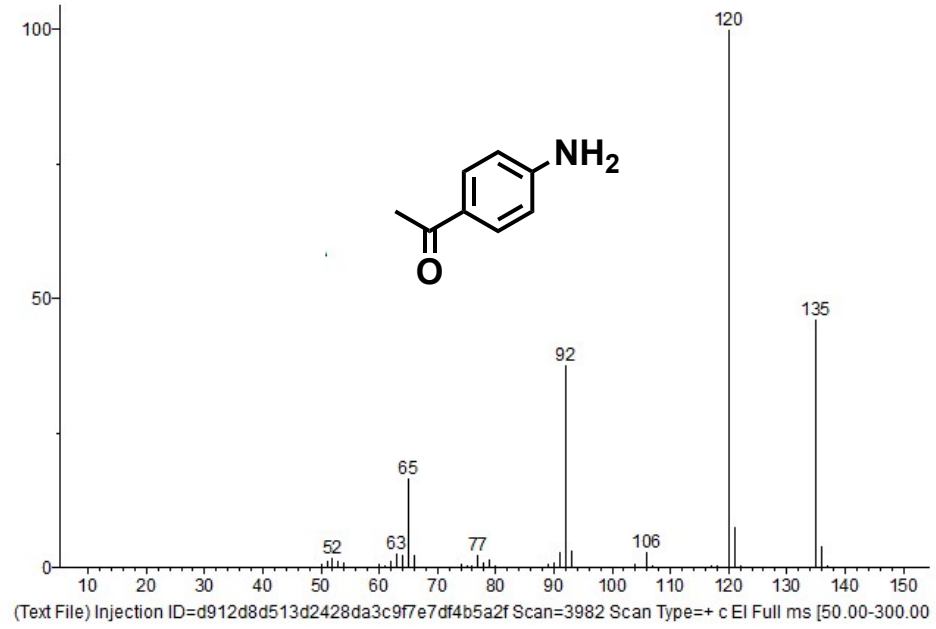
3n: 4-Aminobenzaldehyde



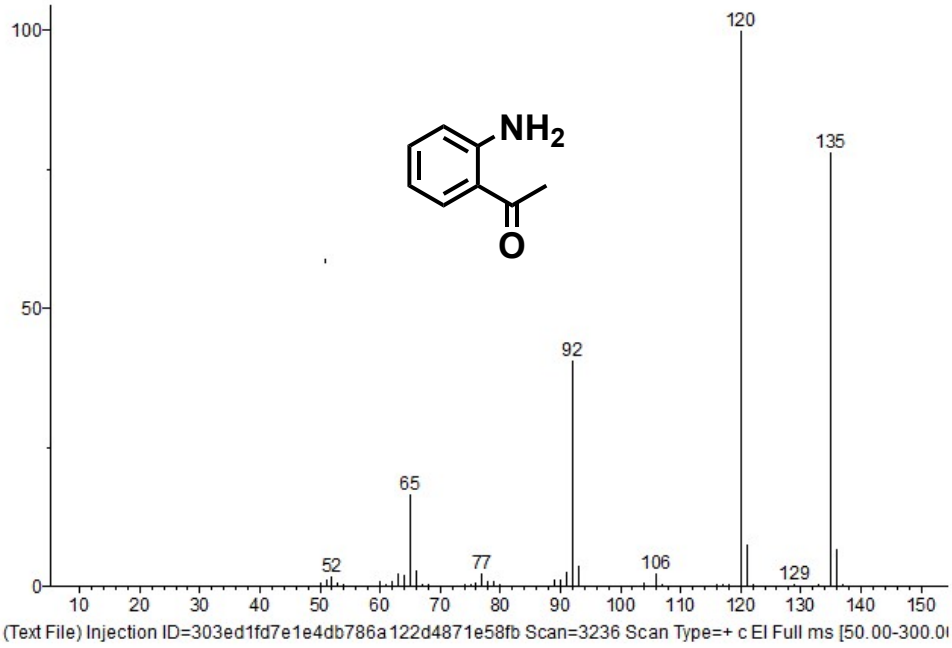
3o:4-Aminobenzonitrile



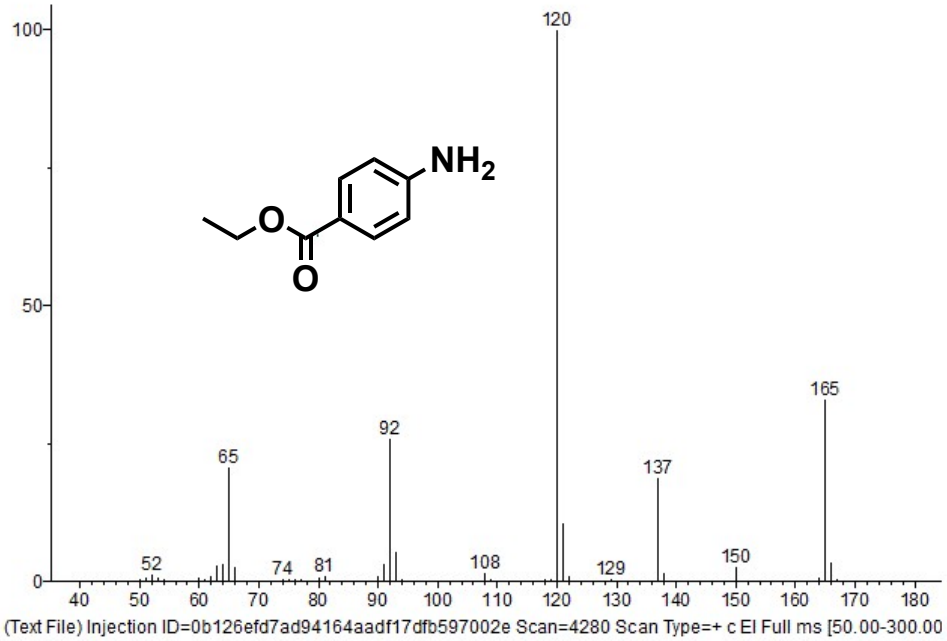
3p: 4-Aminoacetophenone



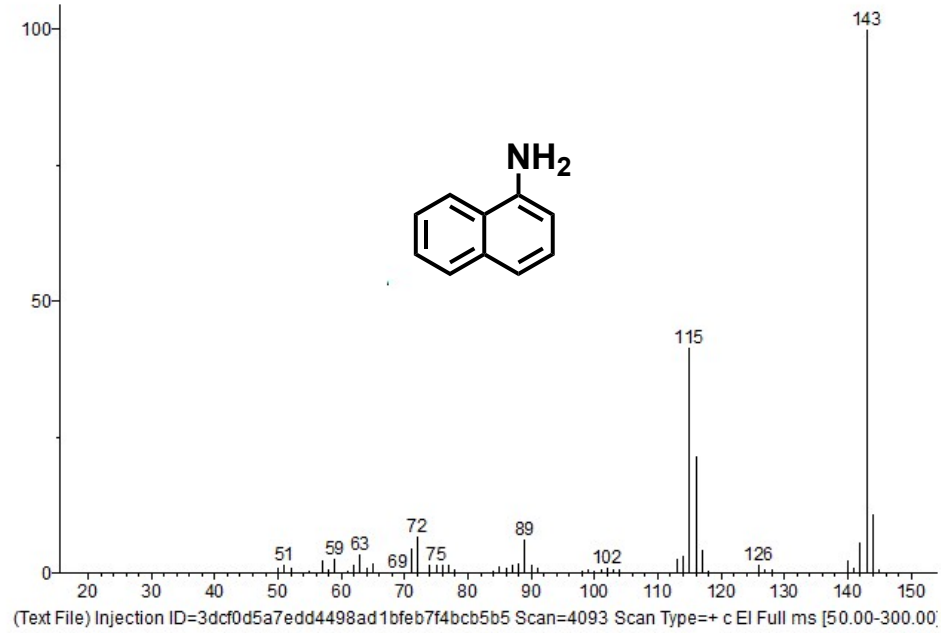
3q: 2-Aminoacetophenone



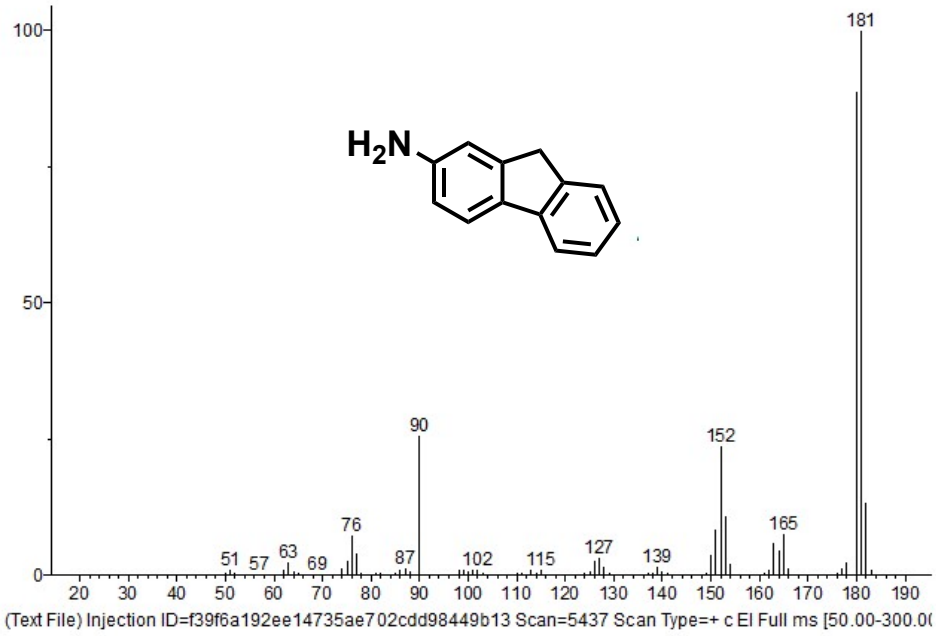
3r: Ethyl para-aminobenzoate



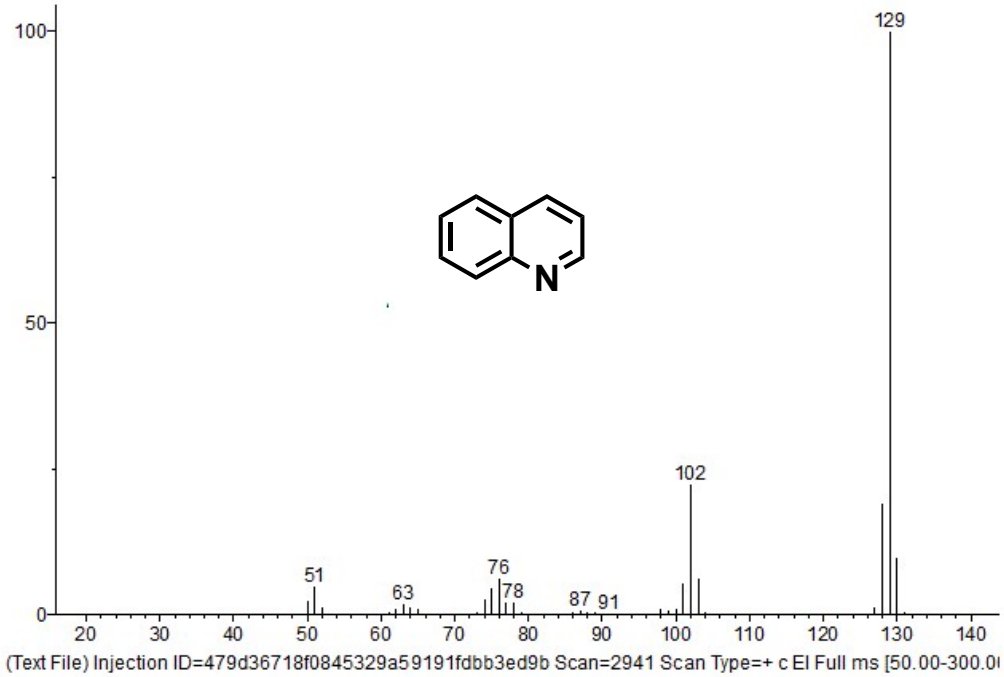
3s: 1-aminonaphthalene



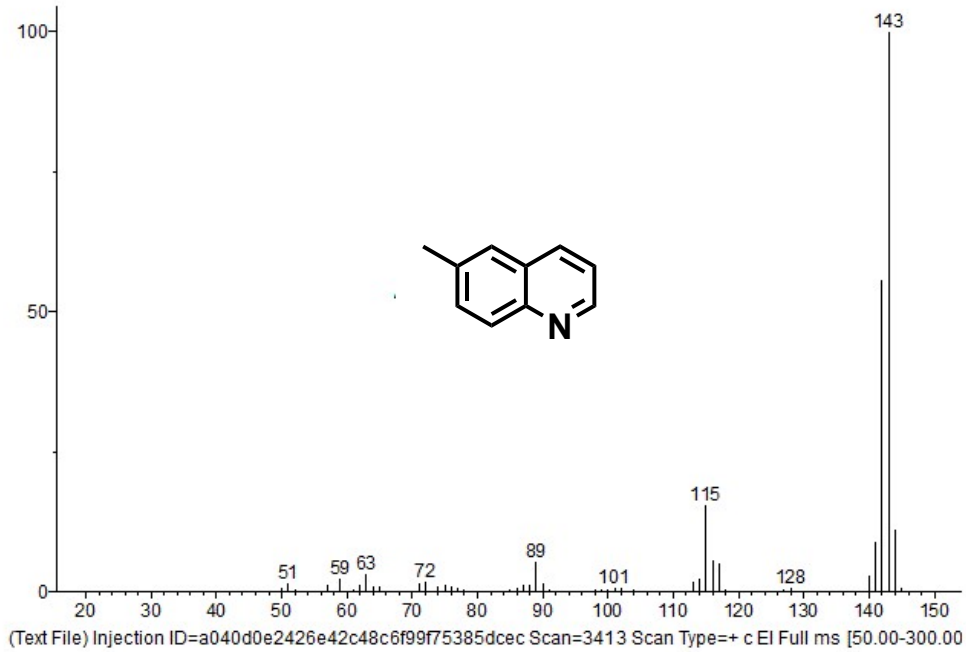
3t: 2-Aminofluorene



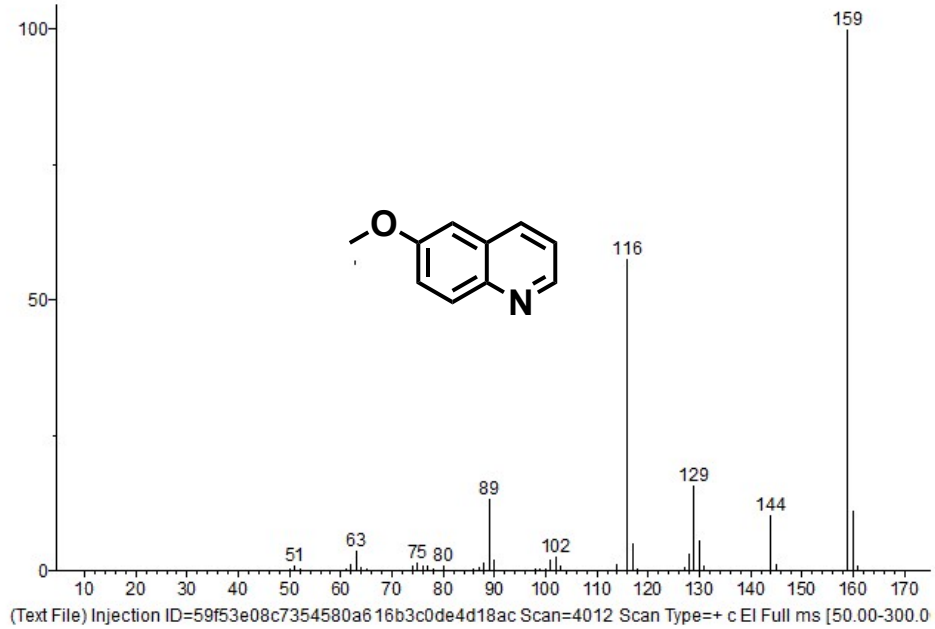
4a: quinoline



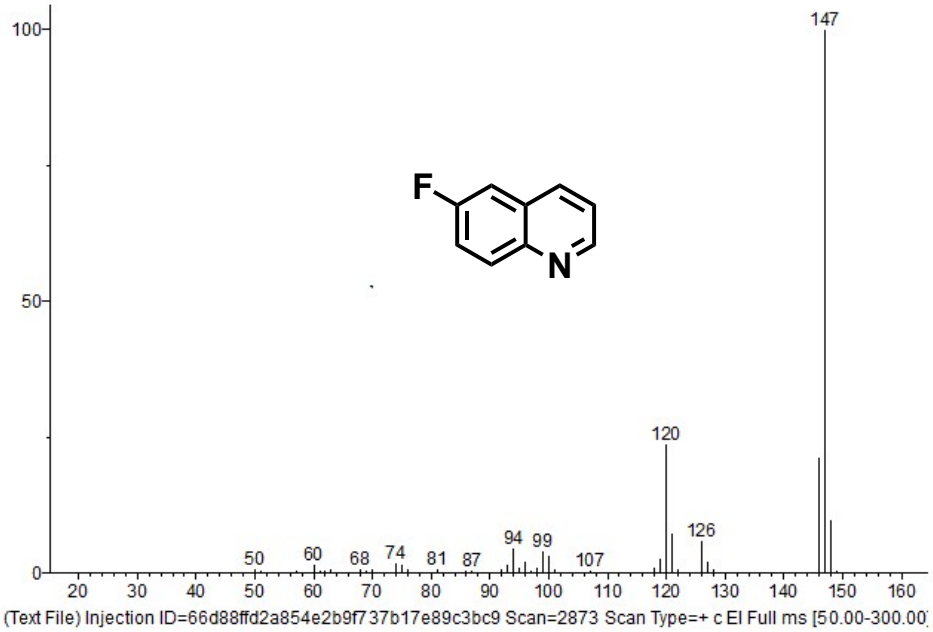
4b: 6-Methylquinoline



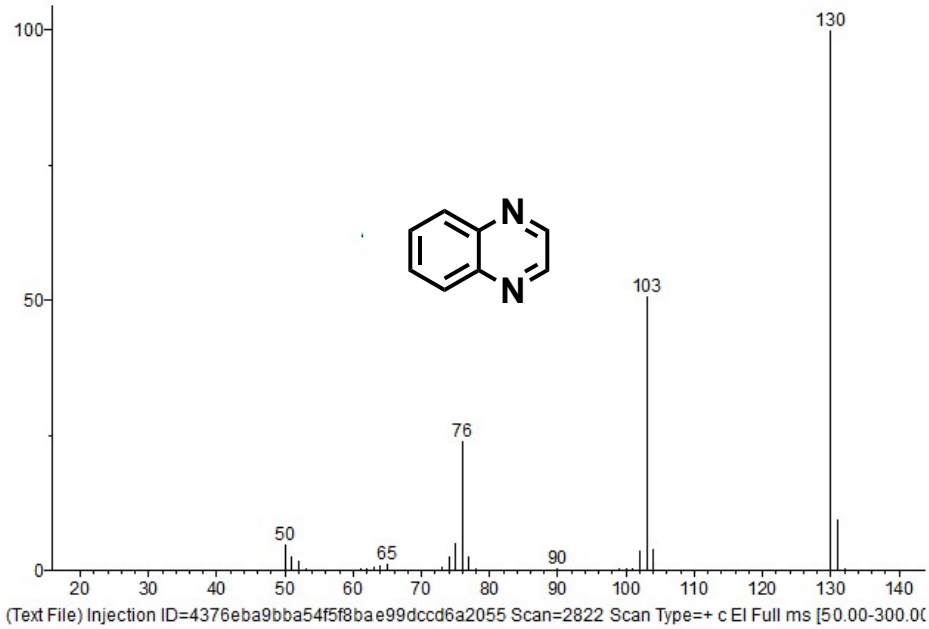
4c: 6-Methoxyquinoline



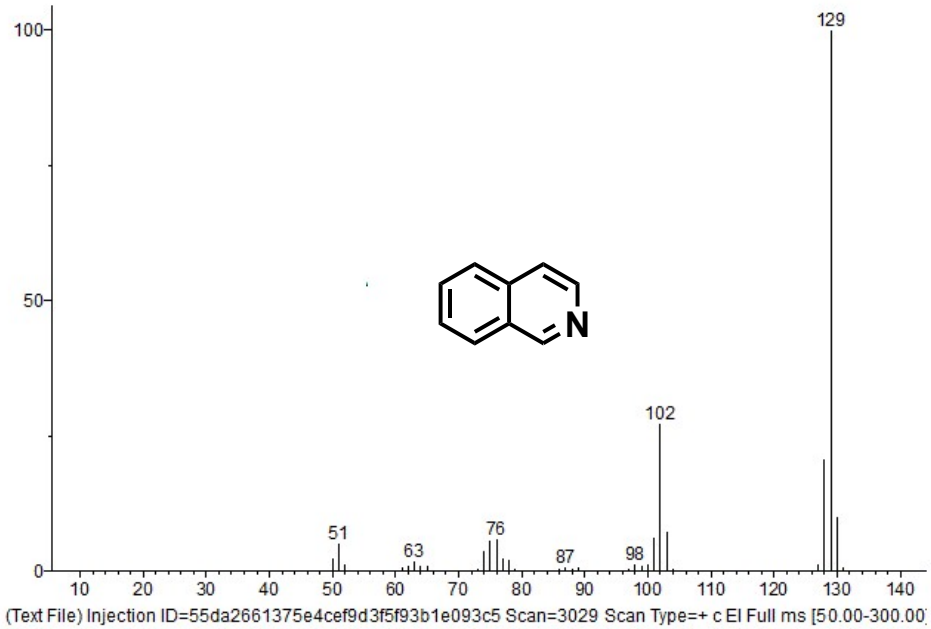
4d: 6-Fluoroquinoline



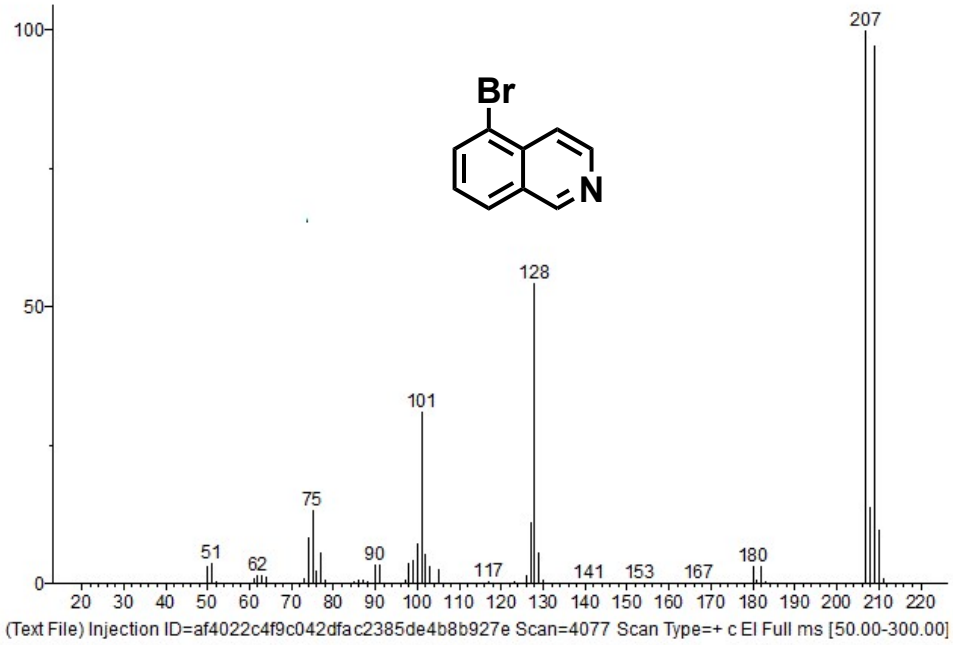
4e: Quinoxaline



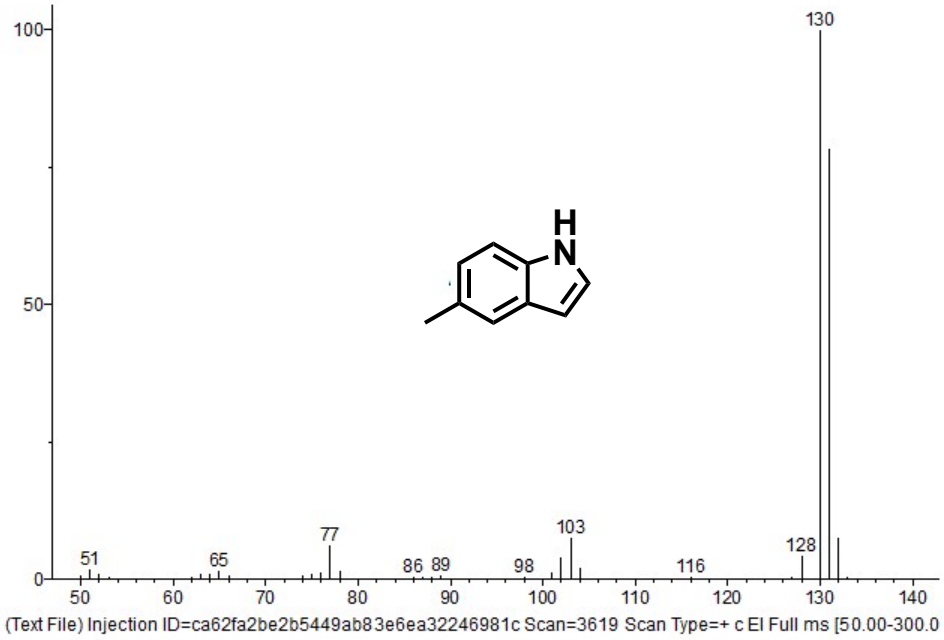
4f: Isoquinoline



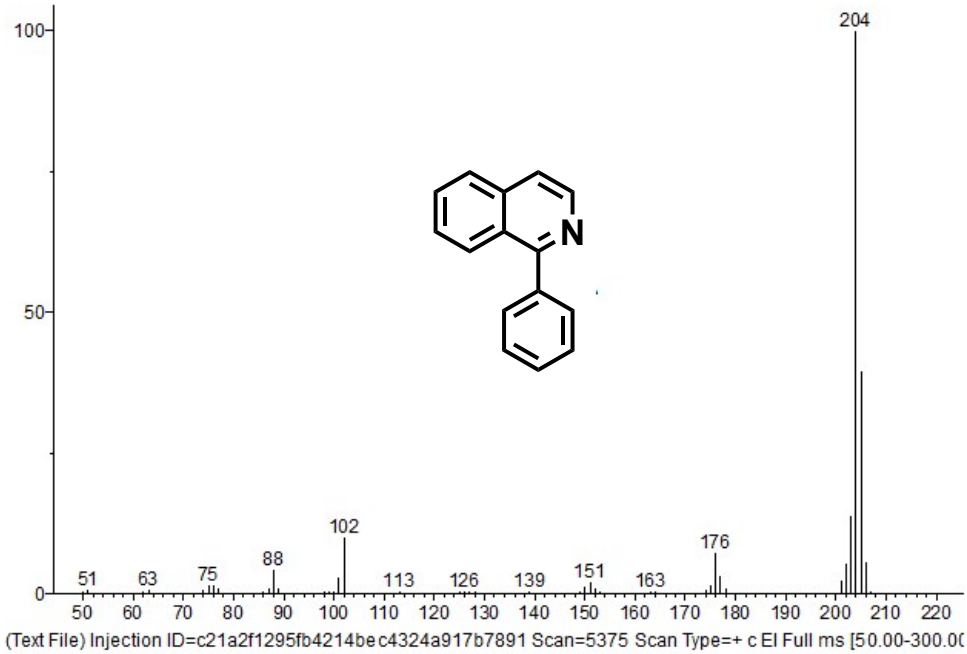
4g: 5-Bromoisoquinoline



4h: 5-Methylindole



4i: 1-Phenylisoquinoline



4j: 1-Methylisoquinoline