Nickel(II) and Nickel(0) Complexes as Precursors of Nickel Nanoparticles for the Catalytic Hydrogenation of Benzonitrile

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Supporting Information

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Synthesis of [(TEEDA)$NiCl_2$] (1)

The synthesis was carried out using a previously reported methodology with some modifications.[1] Inside the glovebox, a Schlenk flask equipped with a stirring bar was charged with [$Ni(COD)_2$] (120 mg, 0.43 mmol), TEEDA (100 mg, 0.58 mmol) and chlorobenzene (0.4 mL, 4 mmol). The resulting mixture was stirred for 48 h at room temperature. After the reaction time, hexanes (5.0 mL) were added to the reaction mixture and the precipitation of a purple solid was observed, the mixture was stirred for 30 min. The resulting solid was filtered and washed with hexanes (3 x 2 mL). After this, the solid was dissolved in toluene and filtered. The filtrate was recovered, the solvent was evaporated, and the resulting solid was dried under high vacuum for 4 h. The complex was recovered as a purple solid in 47% yield (61.2 mg, 0.2 mmol) and characterized by single crystal XRD upon comparison with the reported lattice parameters.

Synthesis of [(TMEDA)NiCl(*o*-tolyl)] (2)

This synthesis was carried out using a previously reported methodology.[2] Inside the glovebox, a Schlenk flask equipped with a stirring bar was charged with [$Ni(COD)_2$] (100 mg, 0.36 mmol), TMEDA (51.5 mg, 0.44 mmol) and *o*-chlorotoluene (2.0 mL, 17.1 mmol). The resulting mixture was stirred for 66 h at room temperature. After the reaction time, the orange solid formed was suspended in hexanes (6.0 mL) and stirred for 30 min. The liquid phase was decanted, and the resulting solid was washed with hexanes (6 x 2.0 mL) and dried under high vacuum for 4 h. The complex was obtained as an orange powder in 81% yield (88.7 mg, 0.29 mmol) and characterized by ^{1}H-NMR (300 MHz, CD_2Cl_2): 7.38 (br, 1H, Ar *CH*), 6.68-6.58 (m, 3 H, Ar *CH*), 3.43 (s, 3H, Ar *CH_3*), 2.64-2.41 (3 br s, 11 H, N-*CH_3*, N-*CH_2*), 2.18 (br, 2H, N-*CH_2*), 1.83 (br, 3H, N-*CH_3*).

Synthesis of [(bpy)$NiCl_2$] (3)

This synthesis was carried out using a previously reported methodology.[3] Inside the glovebox, a Schlenk Flask equipped with a stirring bar was charged with $NiCl_2 \bullet H_2O$ (152.0 mg, 0.64 mmol), 2,2'-bipyridine (100 mg, 0.64 mmol) and 4.0 mL of EtOH. The resulting solution was stirred for 6 h at room temperature. After the reaction time, the pale green solid formed was filtered, washed with anhydrous ethanol (4 x 3.0 mL) and dried under high vacuum. The complex was obtained as a pale green powder in 23% yield (42.8 mg, 0.15 mmol). Elemental Analysis Calculated for $C_{10}H_8Cl_2N_2Ni$: C, 42.03; H, 2.82; N, 9.80. Found: C, 42.04; H, 2.95; N, 9.58.

Synthesis of [(phen)$NiCl_2$] (4)

This synthesis was carried out using a previously reported methodology.[4] Inside the glovebox, a Schlenk flask was charged with $NiCl_2$ (77.7 mg, 0.6 mmol), 1,10-phenantroline (108.1 mg, 0.6 mmol) and EtOH (5.0 mL). The resulting mixture was stirred for 15 h at room temperature. After the reaction time, the solvent was evaporated and the resulting pale green solid was suspended in anhydrous THF (5.0 mL), filtered and dried under high vacuum. The complex was obtained as a pale green powder in a 83% yield (155 mg, 0.72 mmol). Elemental Analysis calculated for $C_{12}H_8Cl_2N_2Ni$: C, 46.52; H, 2.60; N, 9.04. Found: C, 46.98; H, 2.67; N, 9.03.

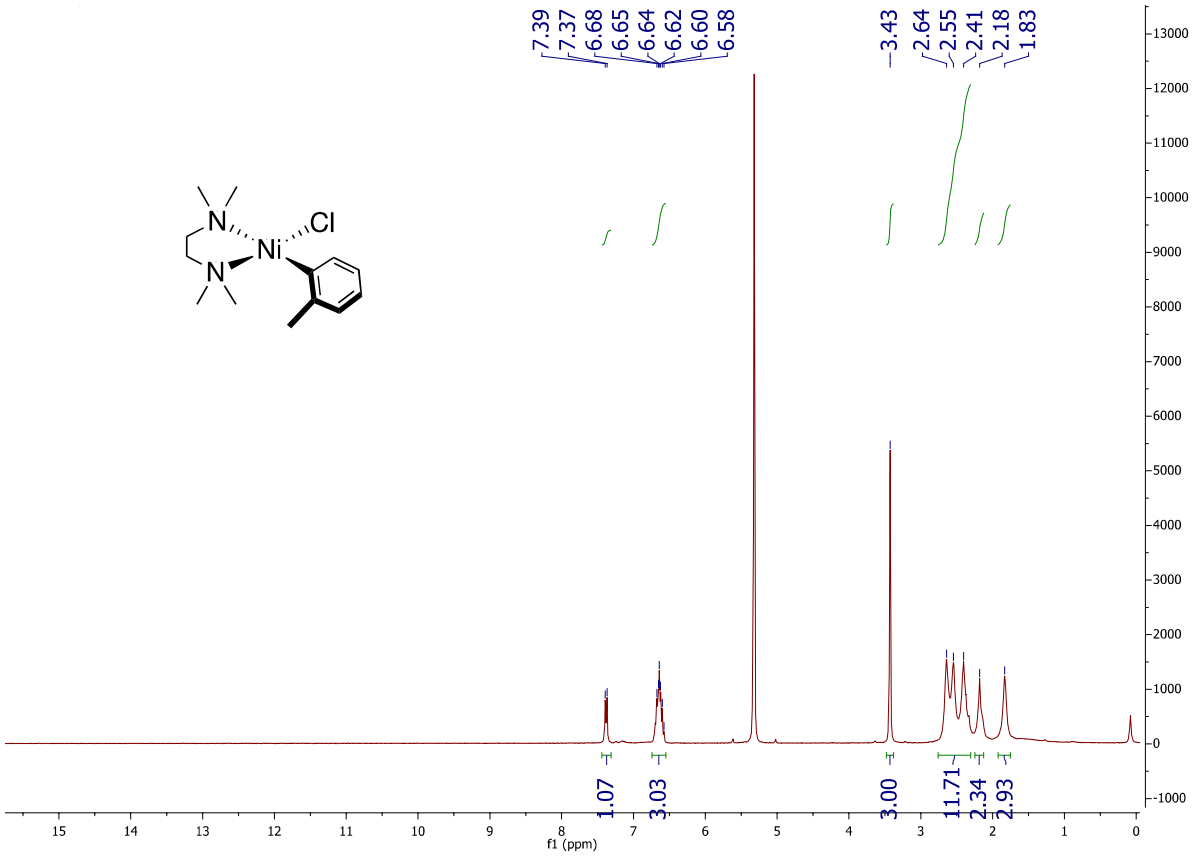
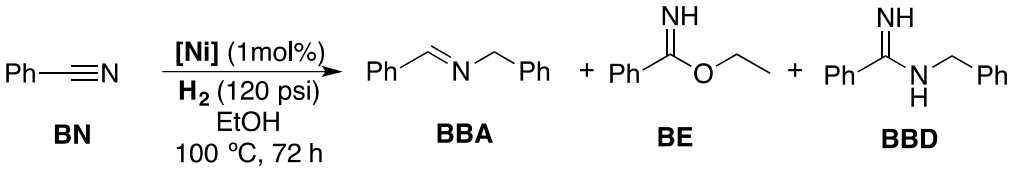


Figure S1. ^{1}H-NMR (400 MHz, CD_2Cl_2) spectrum of complex [(TMEDA)NiCl(*o*-tolyl)] (2)

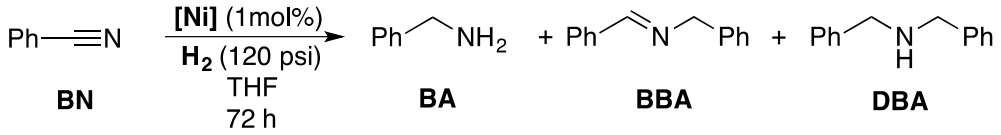
Table S1. Hydrogenation of benzonitrile in the presence of complexes 3 and 4 in EtOH[a]

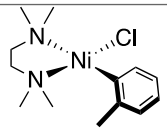
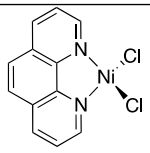


Entry	Complex	Conversion(%)[b]	BBA (%)	BE(%)	BBD(%)
1	**3**	61	54	n.d.	7
2	**4**	18	16	2	n.d.

[a]Reaction conditions: **BN** (1.55 mmol), **[Ni]** (0.0155 mmol), EtOH (5.0 mL), n.d. = no detected. [b]Determined by GC-MS.

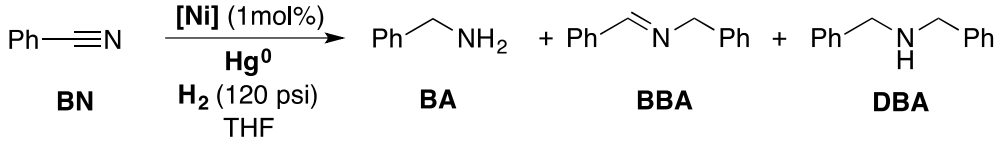
Table S2. Temperature dependent experiments of the hydrogenation of benzonitrile in the presence of complexes 2-4[a]



Entrada	Complex	T (°C)	Conv (%)[b]	BA (%)	BBA (%)	DBA (%)
1		100	82	18	59	5
2		120	82	21	56	5
3		140	>99	39	29	31
4		160	>99	42	19	38
5		100	6	n.d.	6	n.d.
6		120	30	3	25	2
7		140	95	14	68	13
8		160	98	26	49	23
9		100	20	1	19	n.d.
10		120	43	8	33	2
11		140	46	2	36	8
12		160	87	2	73	12

[a]Reaction conditions: **BN** (1.55 mmol), **[Ni]** (0.0155 mmol), THF (5.0 mL), n.d. = no detected. [b]Determined by GC-MS.

Table S3. Mercury drop test for the catalytic hydrogenation of benzonitrile with complexes 2-4[a].



Entry	Complex	Temperature (ºC)	Time (h)	Conversión(%)	BA (%)	BBA(%)	DBA(%)
1	**1**	100	72	>1	n.d.	n.d.	n.d.
2	**2**	160	72	43	n.d.	37	6
3	**3**	160	72	<1	n.d.	n.d.	n.d.
4	**4**	160	72	<1	n.d.	n.d.	n.d.
5	**5**	80	24	17	14	3	n.d.

[a]Reaction conditions: **BN** (1.55 mmol), **[Ni]** (0.0155 mmol), THF (5.0 mL), 1 Hg^0 drop, n.d. = no detected.
[b]Determined by GC-MS.

Figure S2. TEM images of the Ni-Np's after hydrogenation process with precatalyst 2 and distribution histogram generated from the micrographs

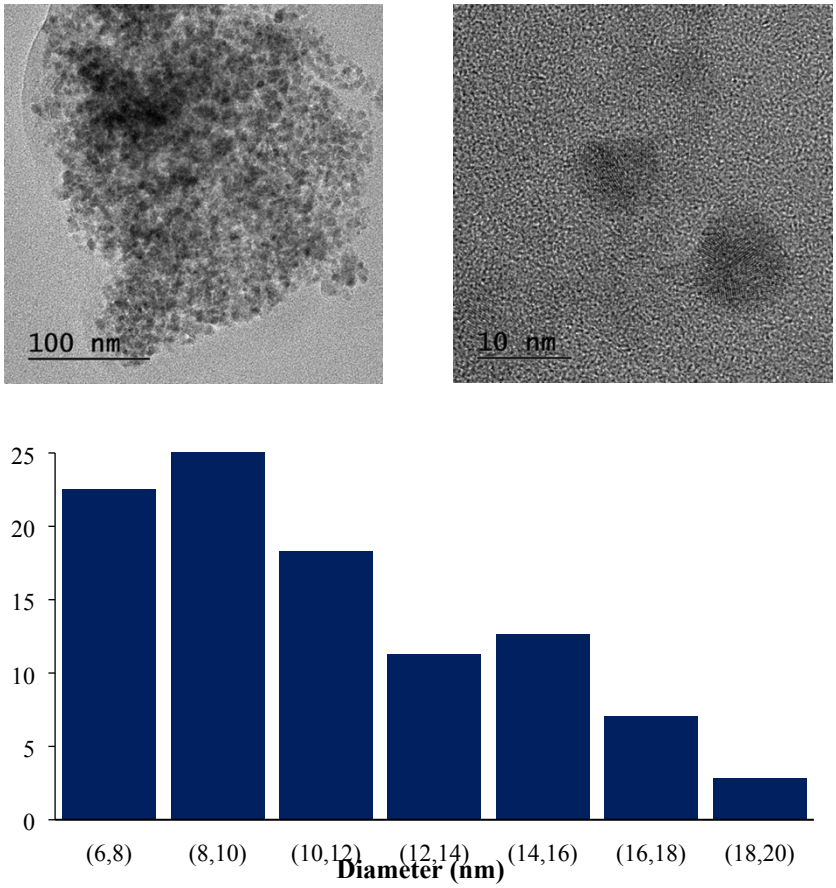
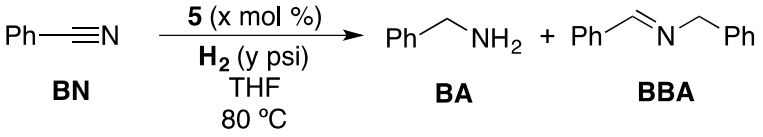


Table S4. Optimization of the reaction conditions in the hydrogenation of benzonitrile

with complex 5[a]



Entry	H_2(psi)	Time(h)	5 (mol%)	Conversion(%)[b]	BA(%)	BBA(%)
1	60	24	1	31	25	6
2	120	12	1	75	66	9
3	120	24	0.5	57	31	26
4[c]	120	24	1	85	51	34

[a]Reaction conditions: **BN** (1.55 mmol), THF (5.0 mL). [b]Determined by GC-MS.[c]3.0 mL of THF were used.

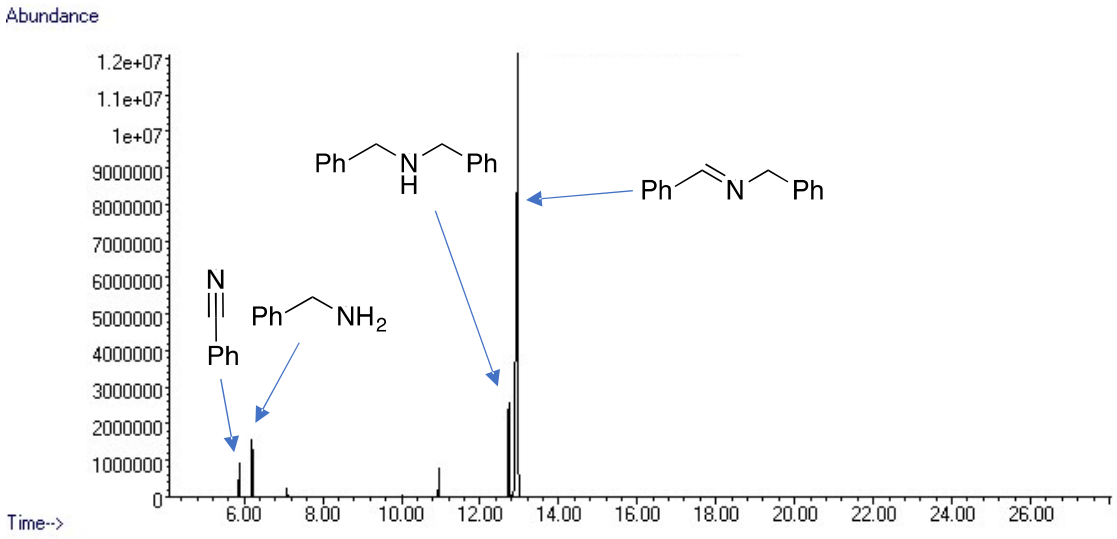


Figure S3. GC trace from the catalytic hydrogenation of benzonitrile with complex 1 under optimized conditions

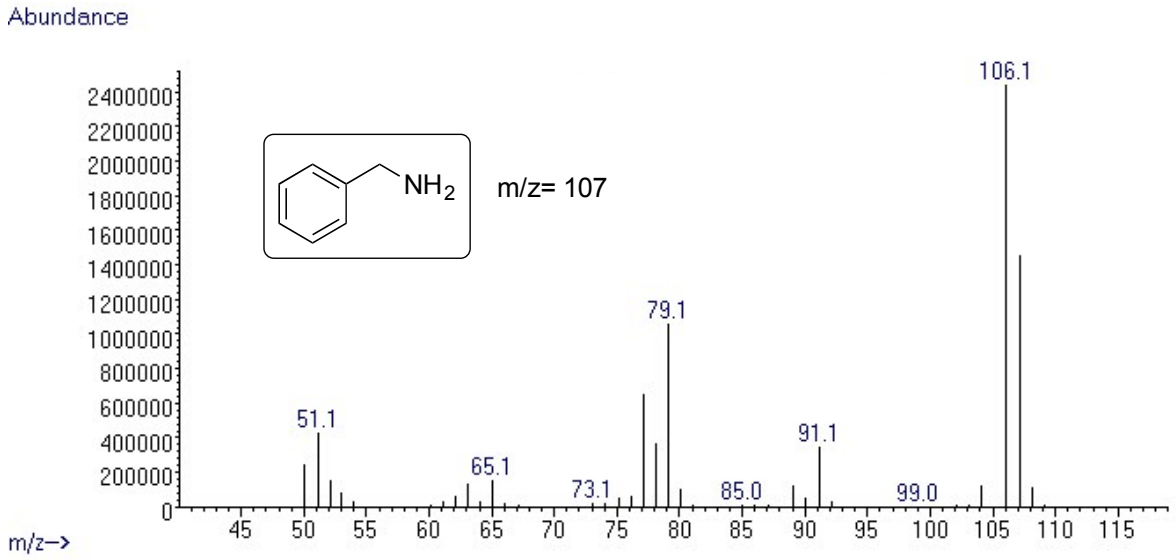


Figure S4. MS for Benzylamine (BA)

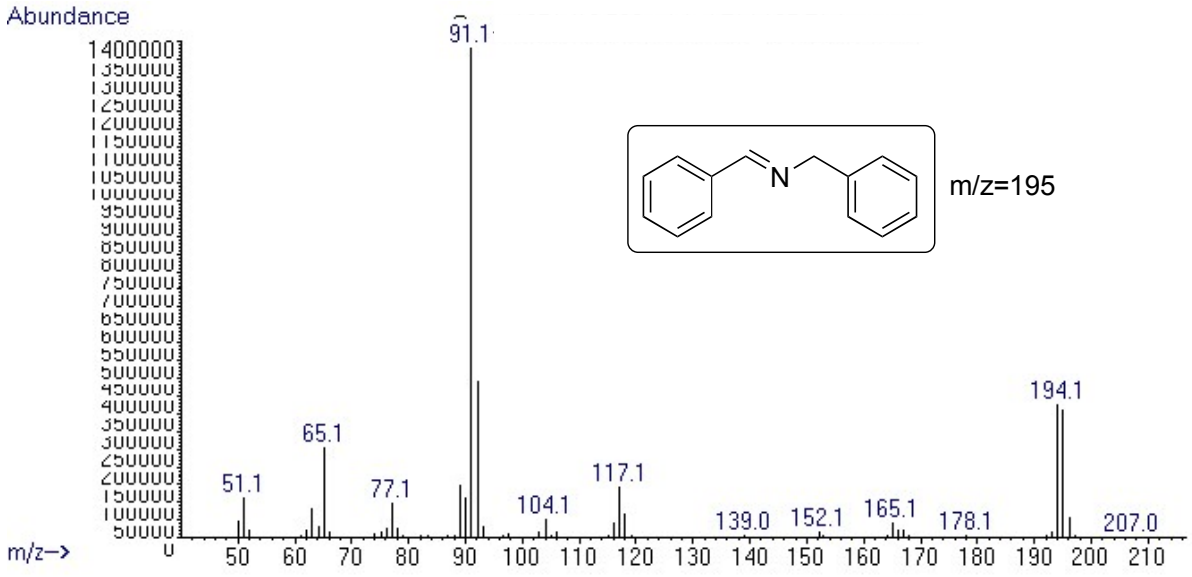


Figure S5. MS for *N*-benzylidenebenzylamine

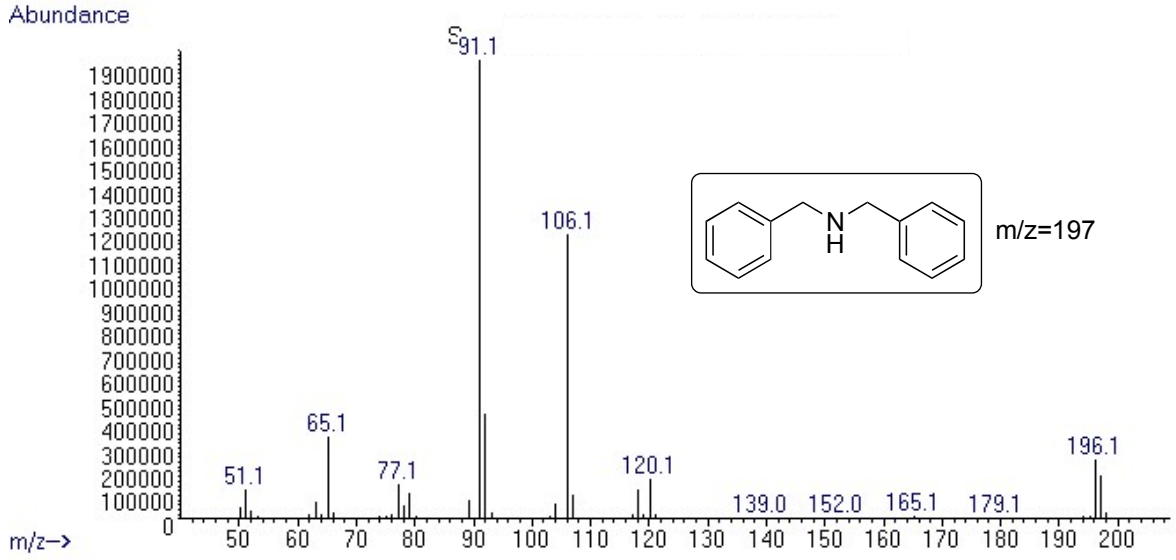


Figure S6. MS for dibenzylamine

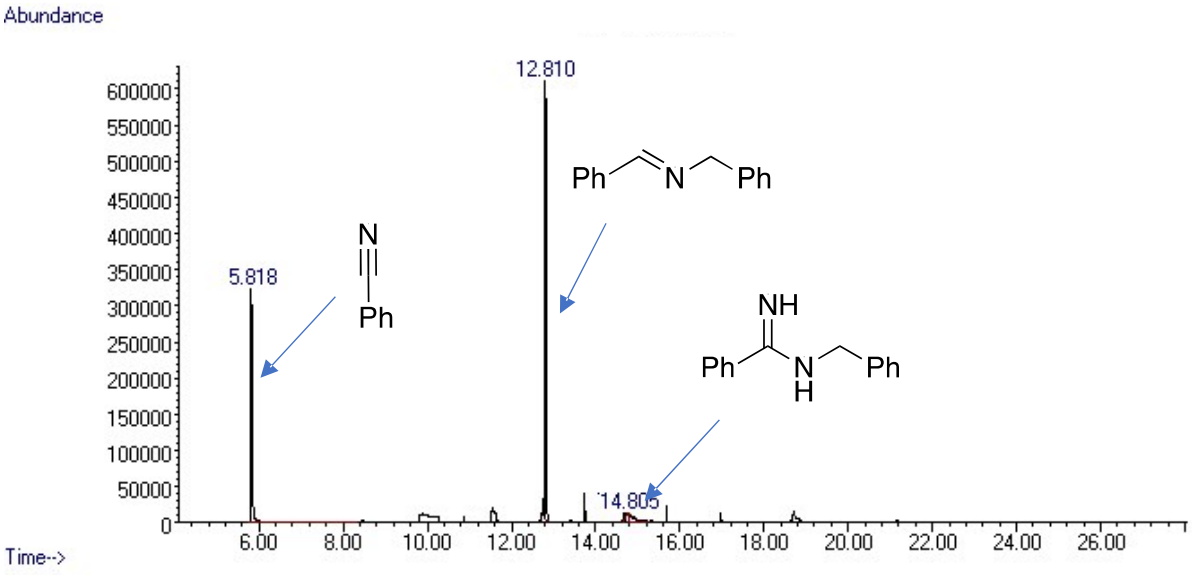


Figure S7. GC Trace for the hydrogenation of benzonitrile with complex 3 in EtOH at 100 ºC

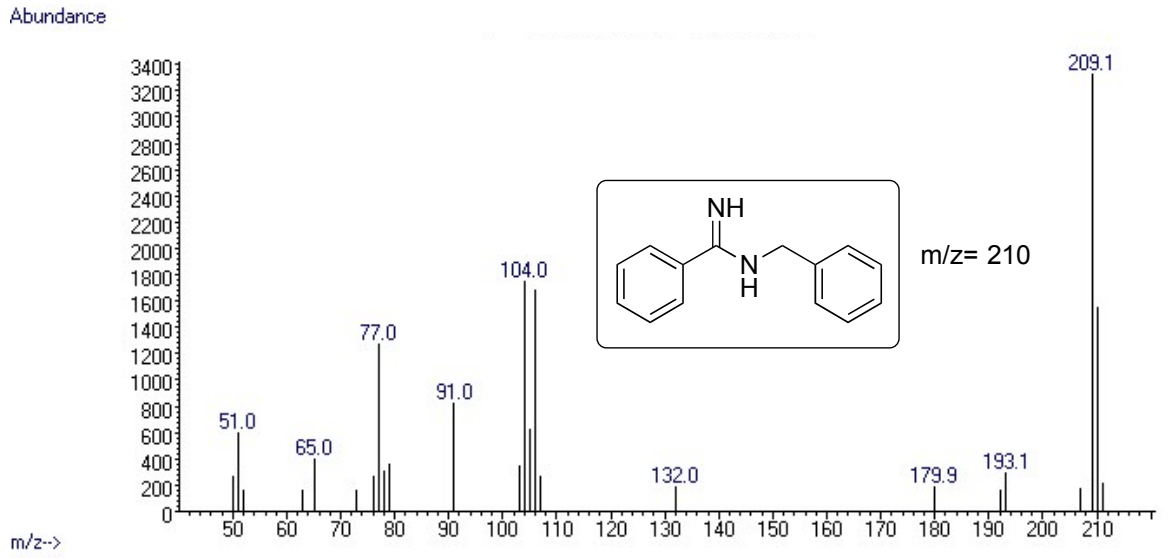


Figure S8. MS for *N*-benzylbenzimidamide

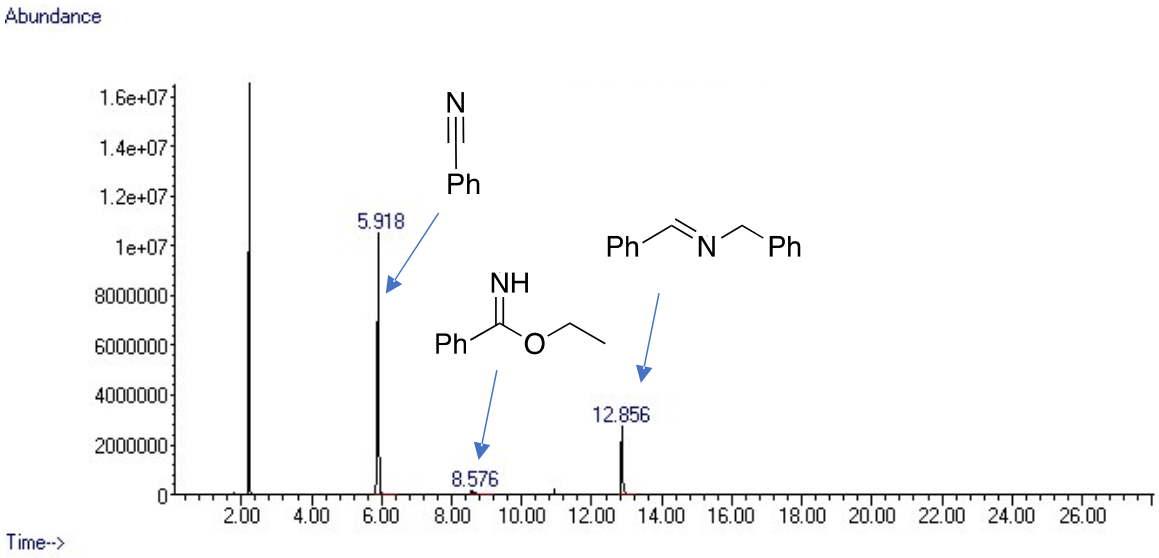


Figure S9. GC trace for the hydrogenation of benzonitrile with complex 4 in EtOH at 100 ºC

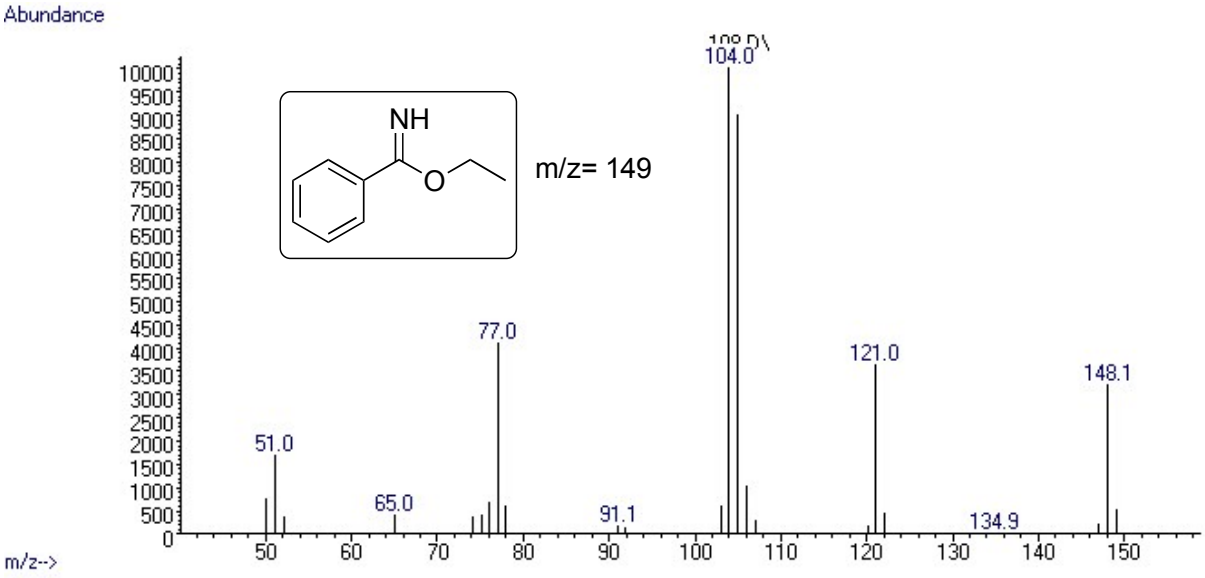


Figure S10. MS for ethyl benzimidate

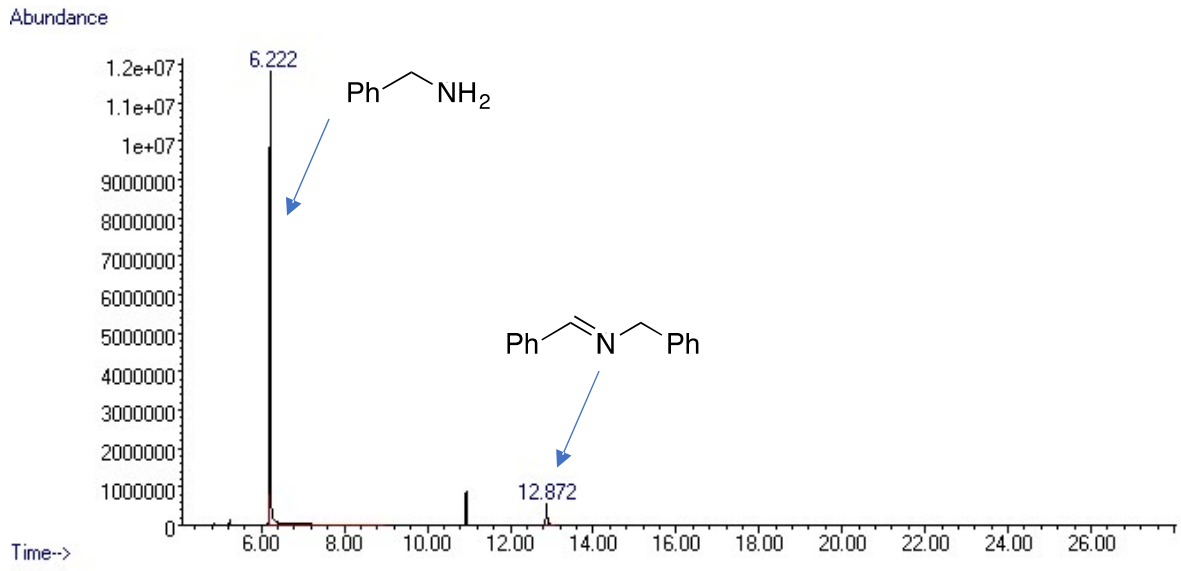


Figure S11. GC trace of the hydrogenation of benzonitrile with complex 5 under optimized conditions

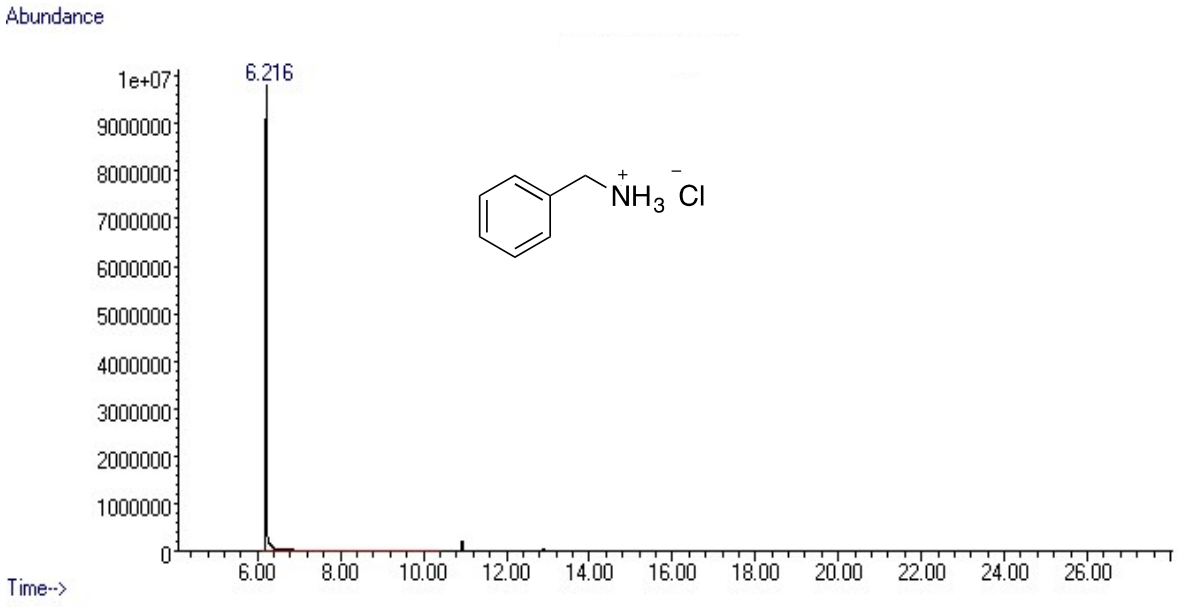


Figure S12. GC of a MeOH/THF(1:1) solution of benzylamine hydrochloride

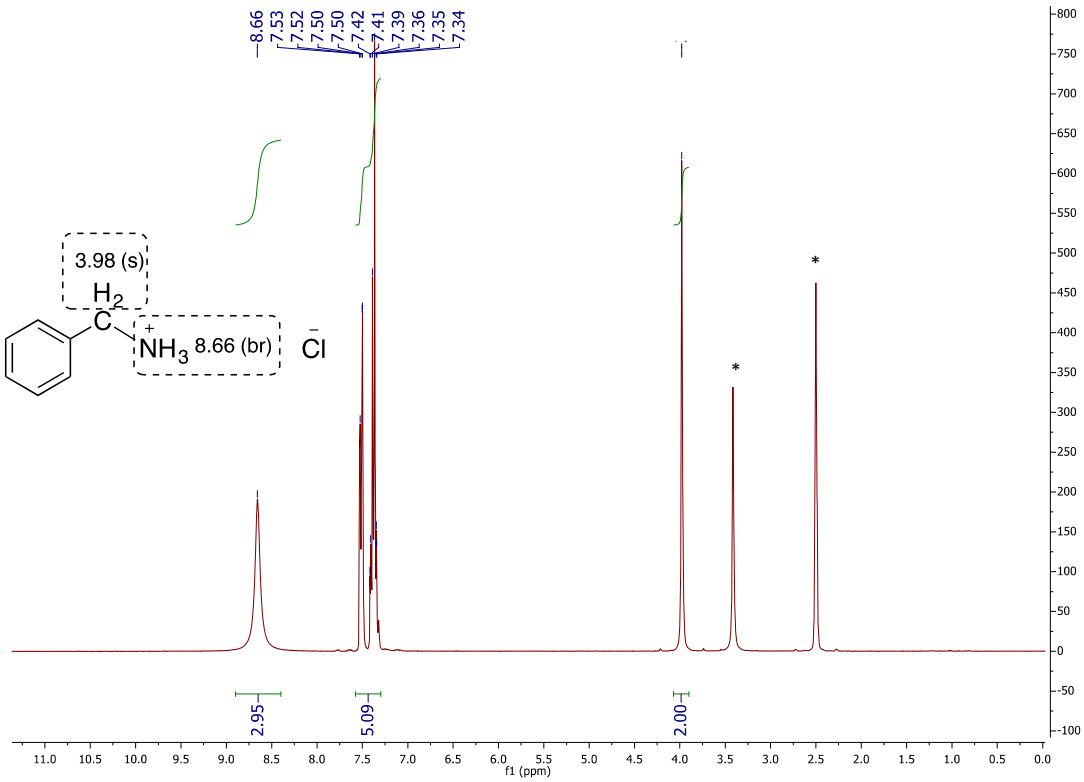


Figure S13. ^{1}H-NMR (400 MHz, DMSO-*d*$_6$) spectrum of benzylamine hydrochloride

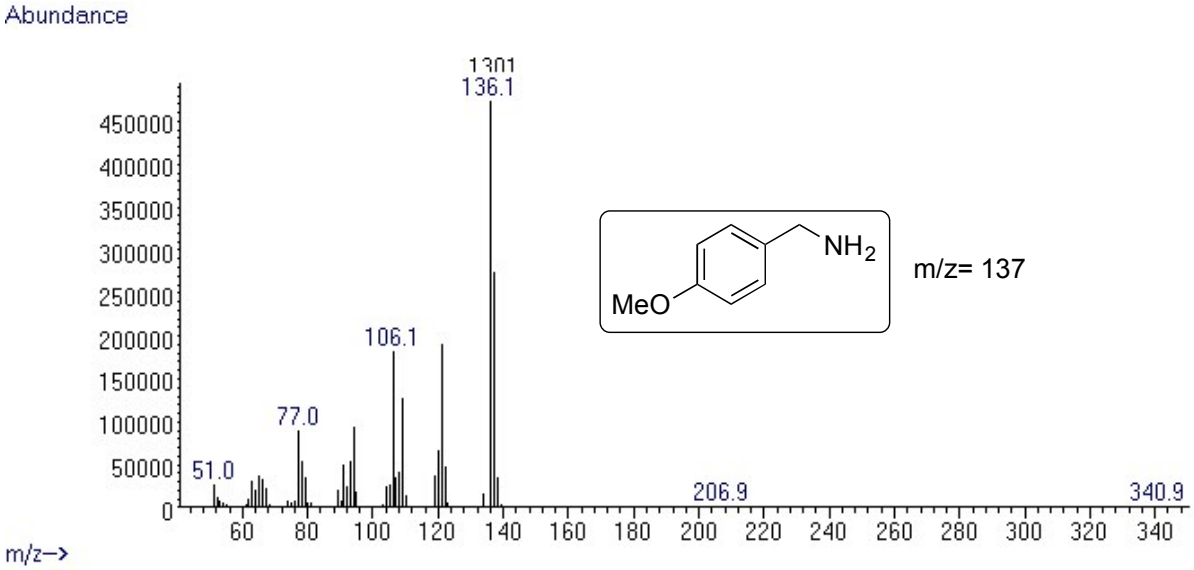


Figure S14. MS for (4-methoxyphenyl)methanamine

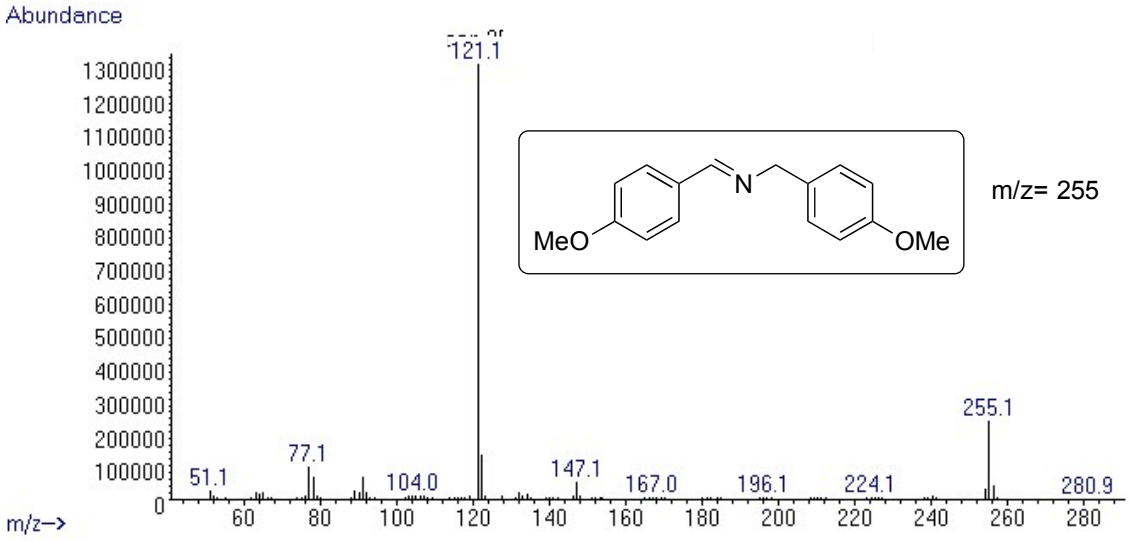


Figure S15. MS for (*E*)-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine

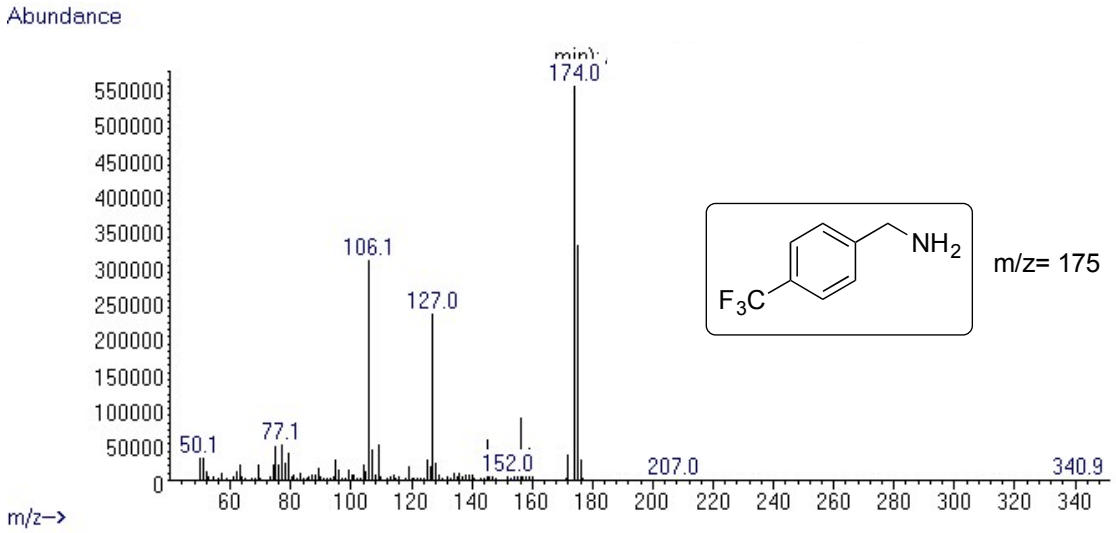


Figure S16. MS for (4-(trifluoromethyl)phenyl)methanamine

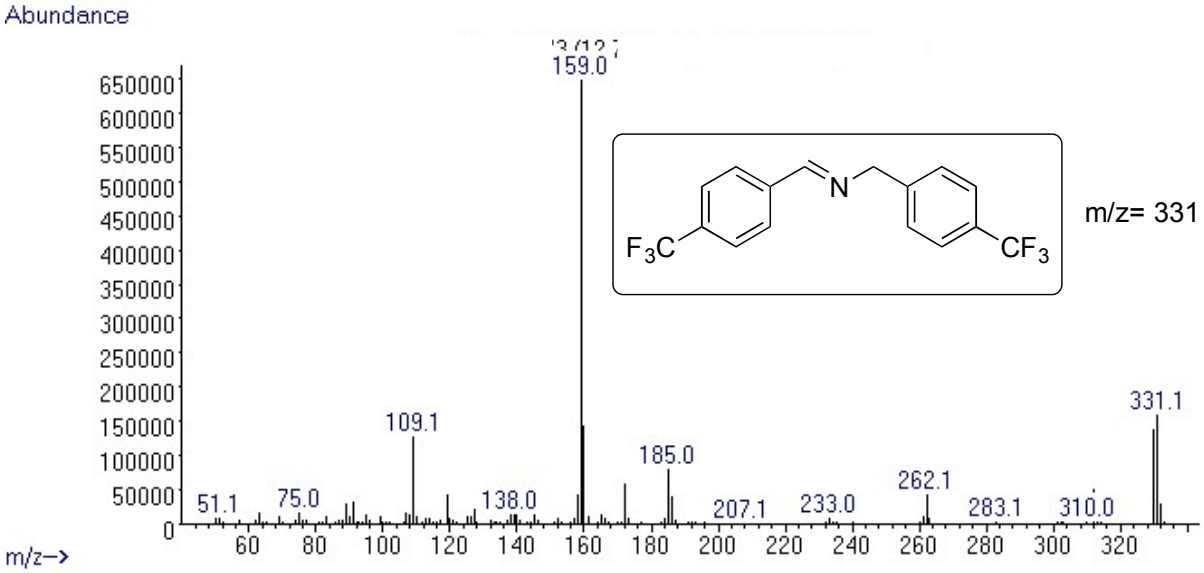


Figure S17. MS for (*E*)-*N*-(4-(trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)phenyl)methanimine

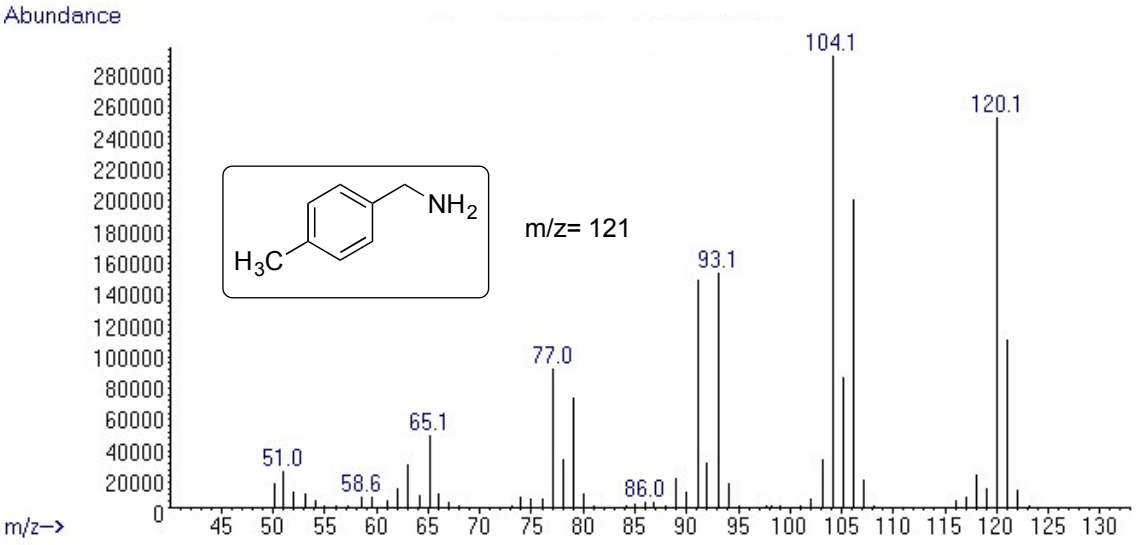


Figure S18. MS for *p*-tolylmethanamine

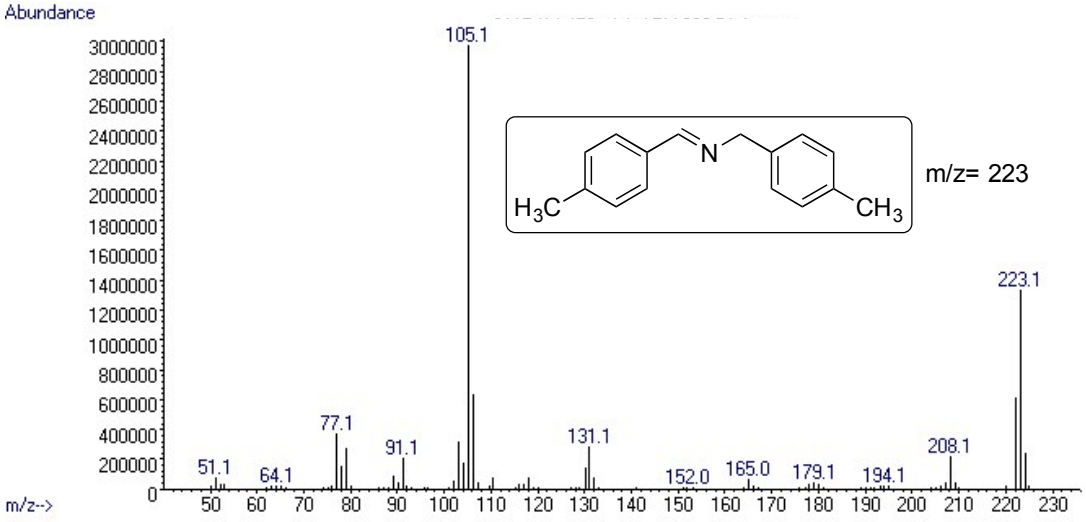


Figure S19. MS for (*E*)-*N*-(4-methylbenzyl)-1-(*p*-tolyl)methanimine

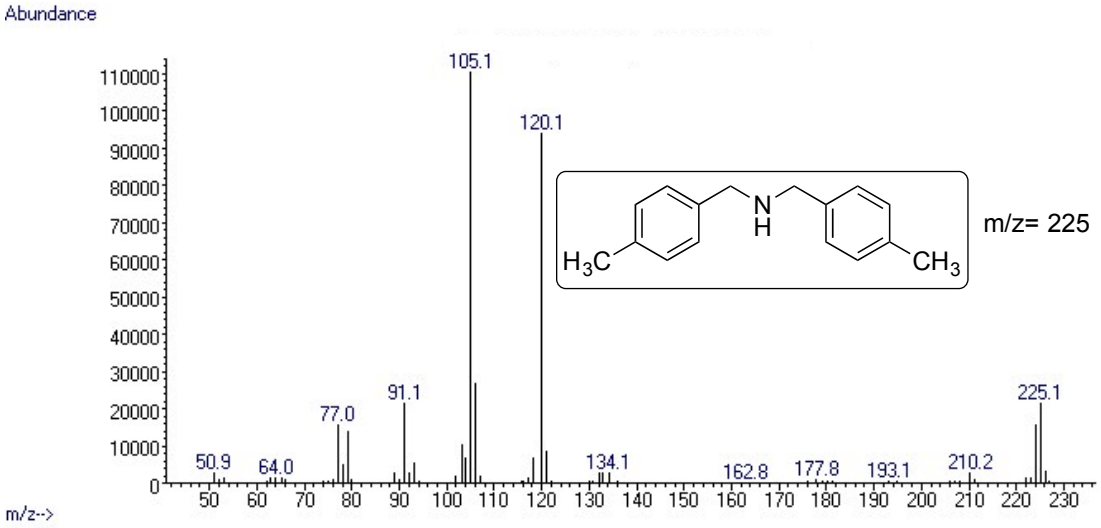


Figure S20. MS for bis(4-methylbenzyl)amine

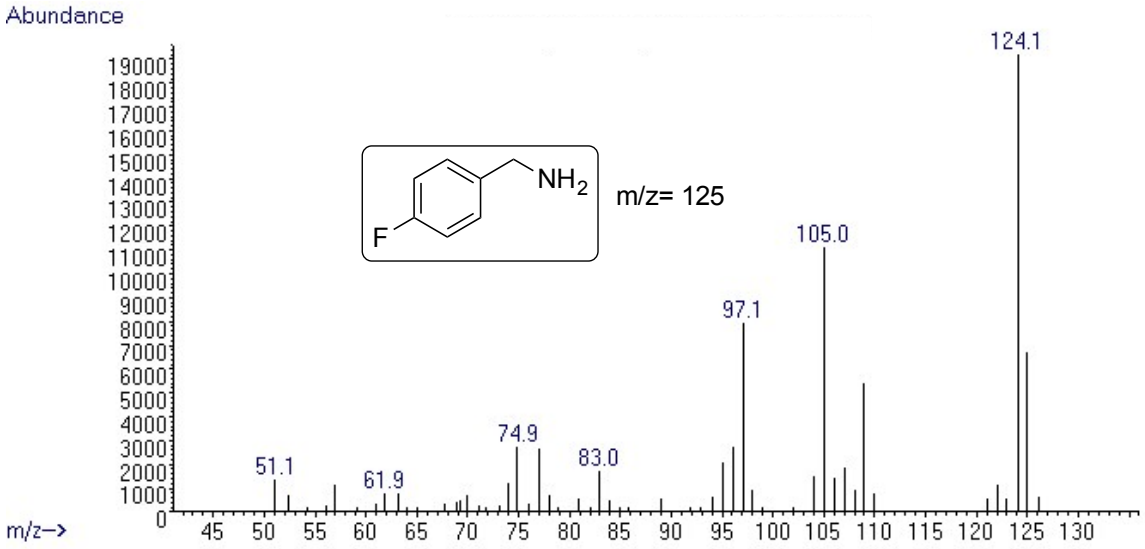


Figure S21. MS for (4-fluorophenyl)methanamine

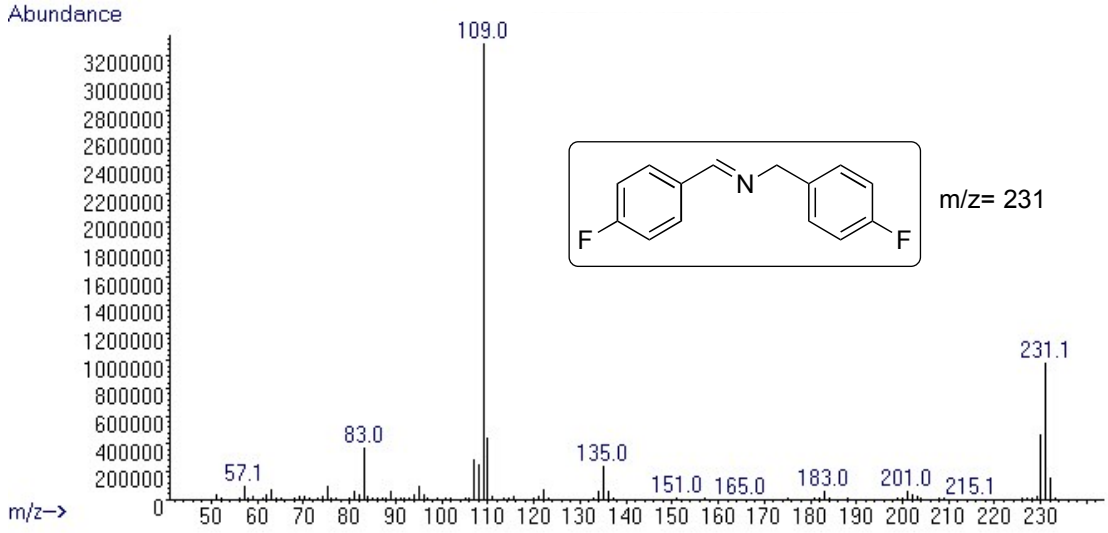


Figure S22. MS for (*E*)-*N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine

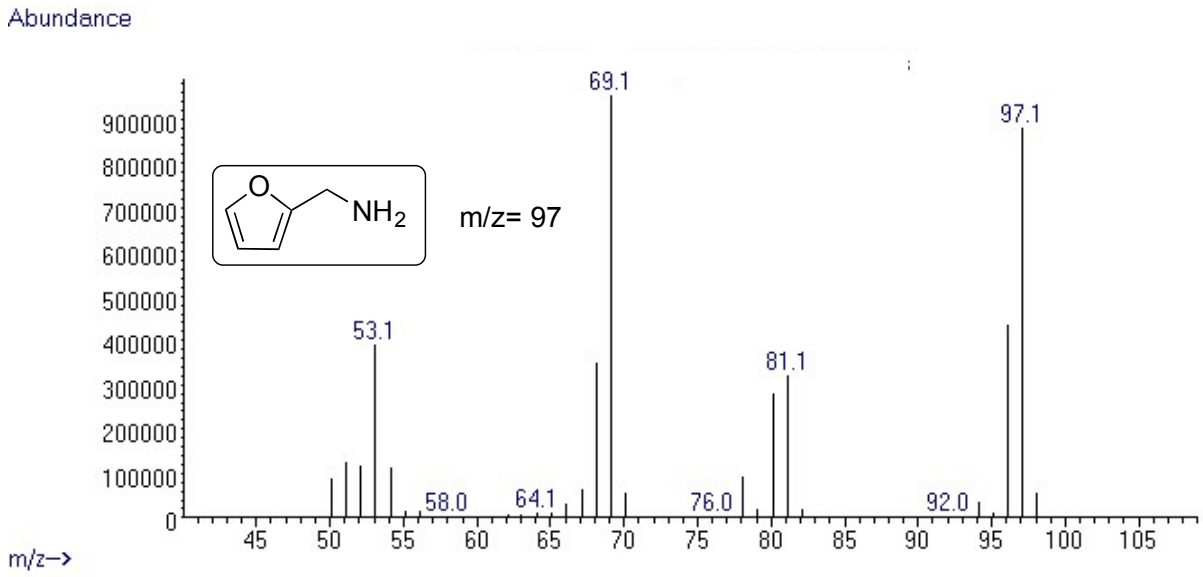


Figure S23. MS for furan-2-ylmethanamine

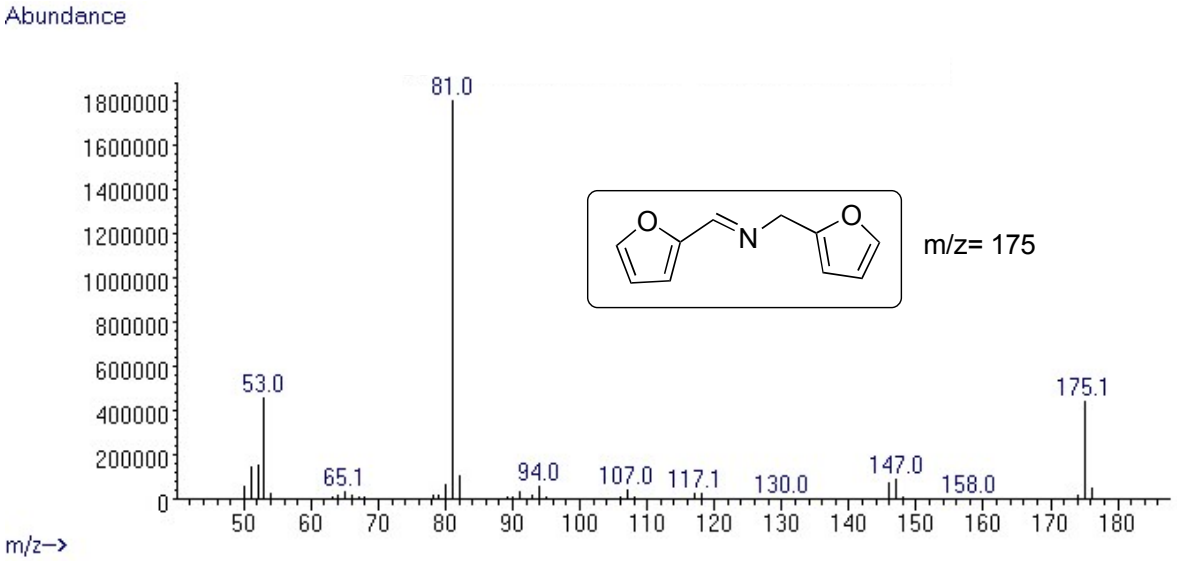


Figure S24. MS for (*E*)-1-(furan-2-yl)-*N*-(furan-2-ylmethyl)methanimine

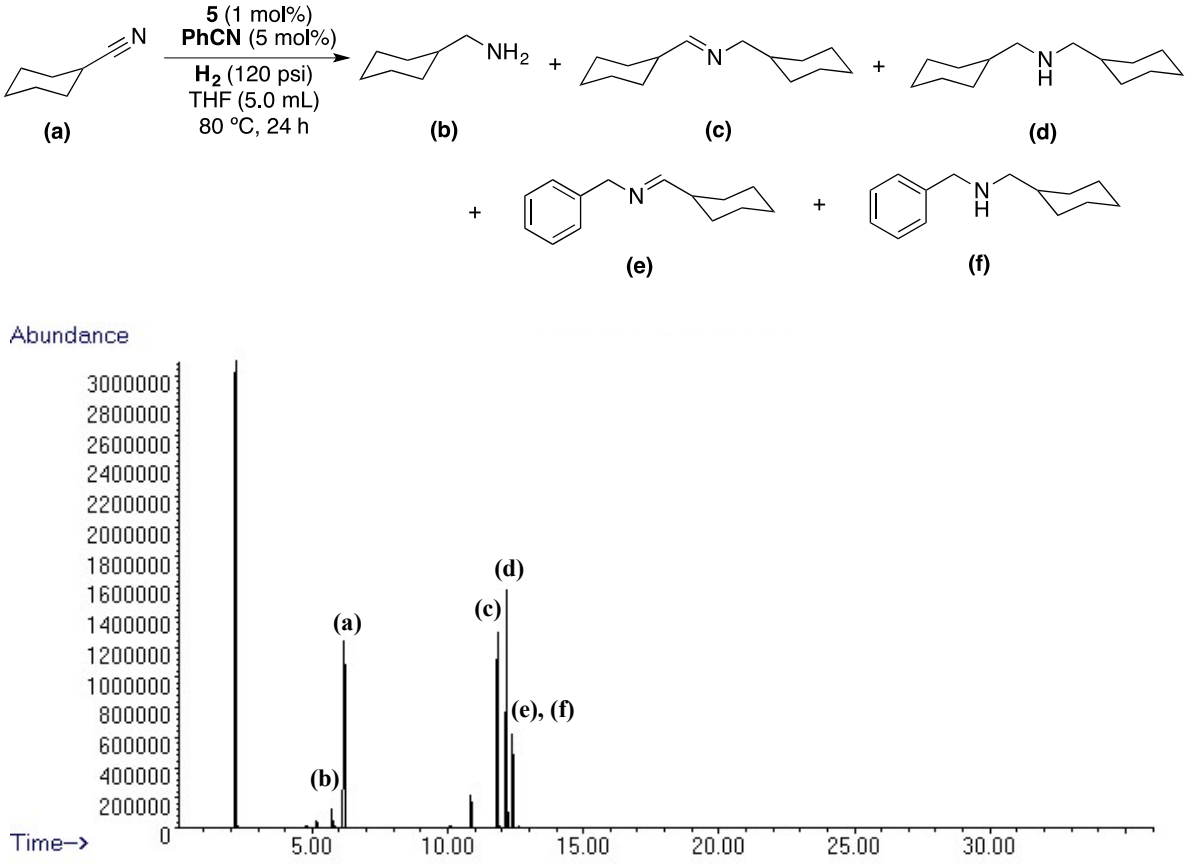


Figure S25. GC for the hydrogenation of cyclohexylcarbonitrile with complex 5 in the presence of sub-stoichiometric amouts of PhCN

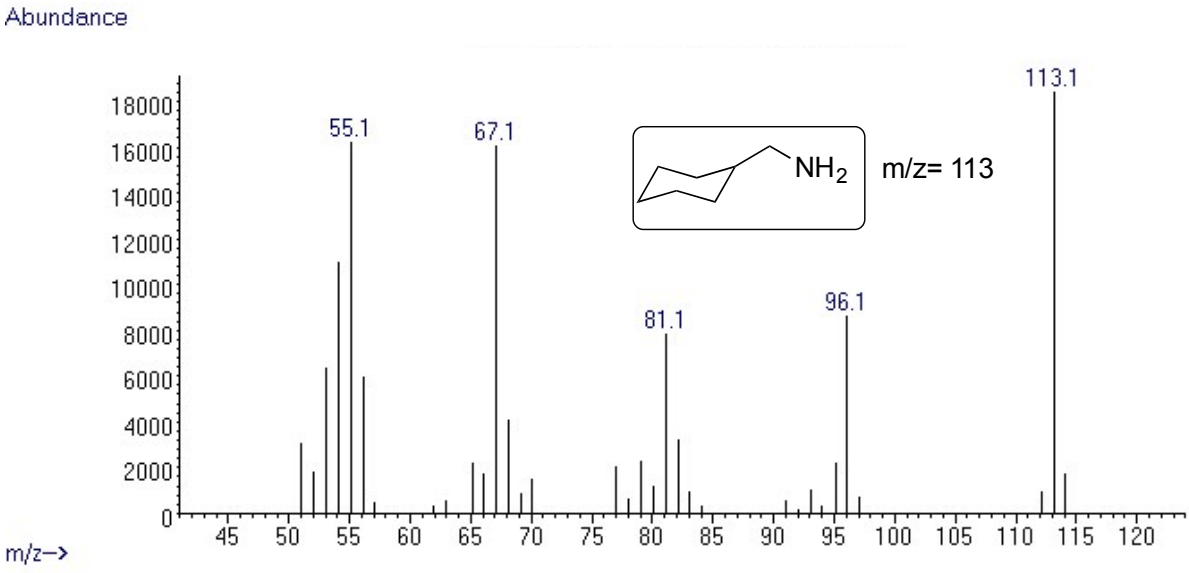


Figure S26. MS for cyclohexylmethanamine

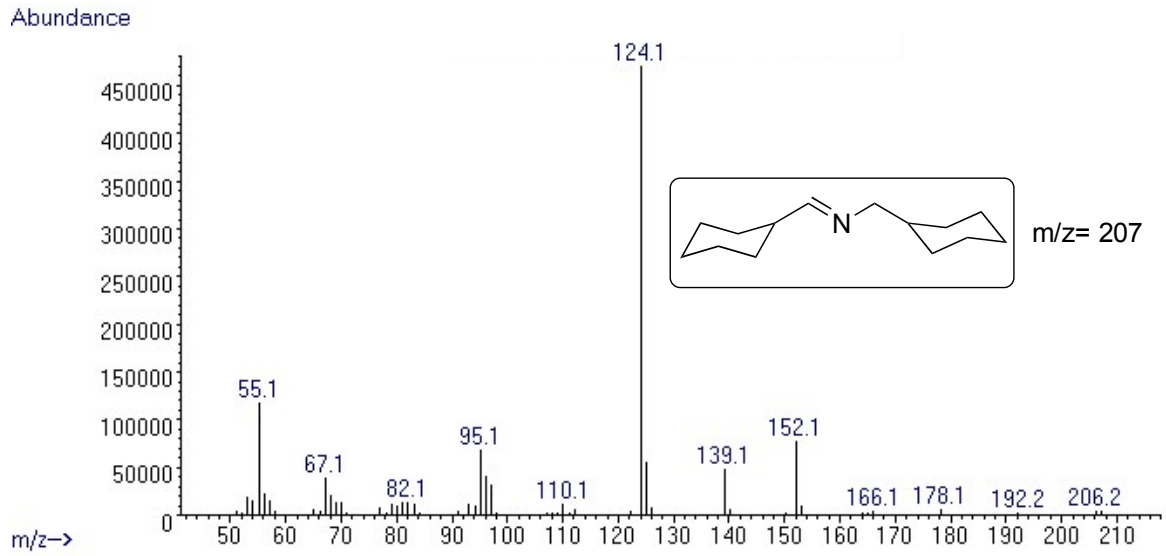


Figure S27. MS for (*E*)-1-cyclohexyl-*N*-(cyclohexylmethyl)methanimine

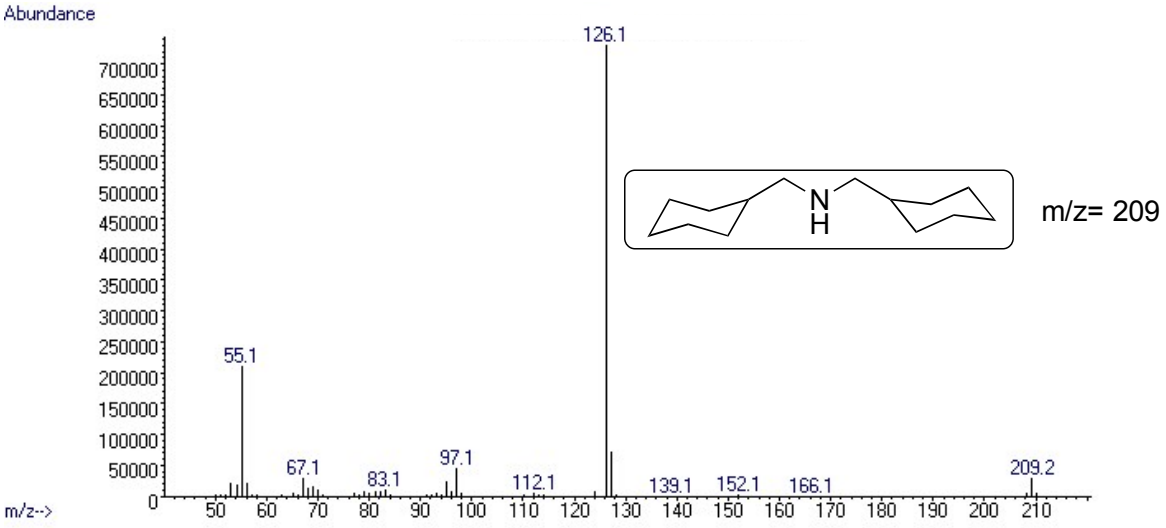


Figure S28. MS for bis(cyclohexylmethyl)amine

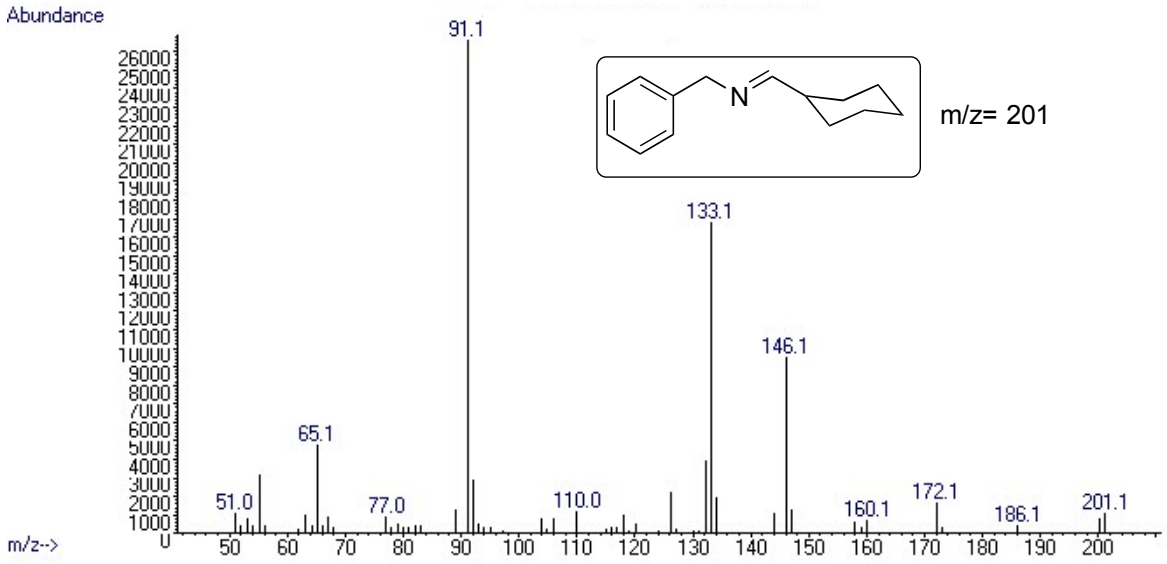


Figure S29. MS for (*E*)-*N*-benzyl-1-cyclohexylmethanimine

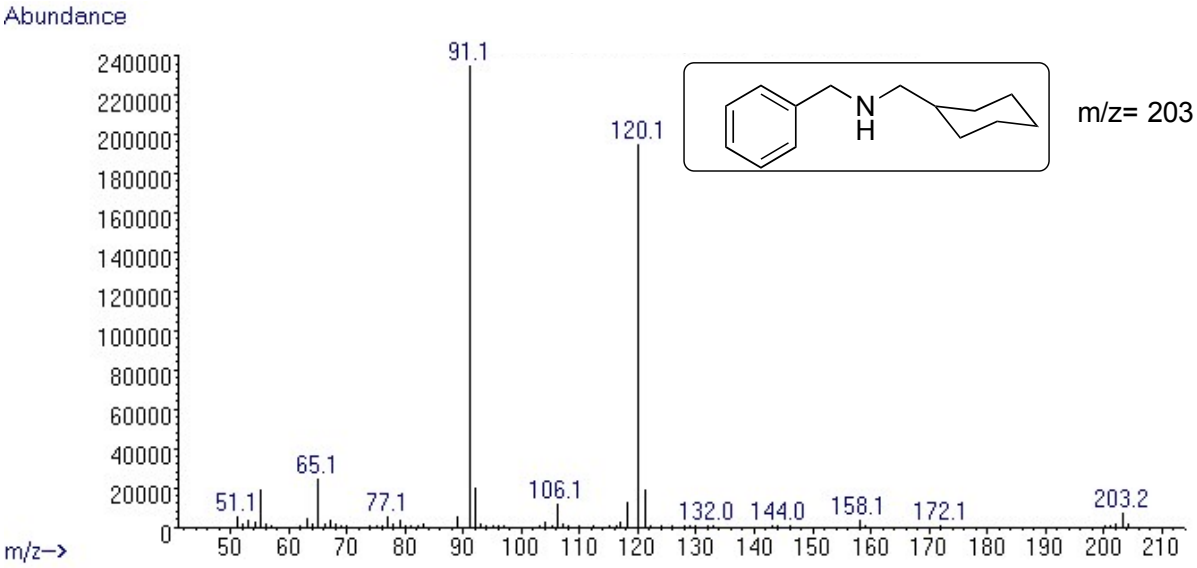


Figure S30. MS for *N*-benzyl-1-cyclohexylmethanamine

References

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[2] J. Magano and S. Monfette, Development of an Air-Stable, Broadly Applicable Nickel Source for Nickel-Catalyzed Cross-Coupling, *ACS Catal.*, 2015, **5**, 3120-3123.

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