Electronic Supplementary Information (ESI)

Synthesis, structure and catalytic activity of manganese (II) complexes derived from bis(imidazole)methane-based ligands

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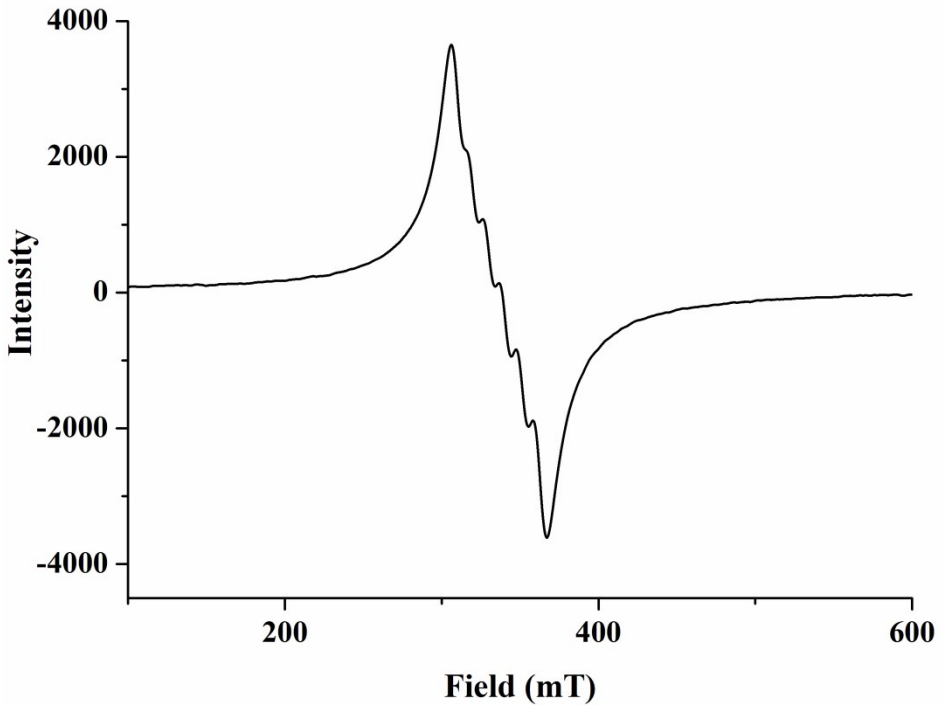


Figure S1. X-band EPR spectrum of **[Mn]-1** in methanol.

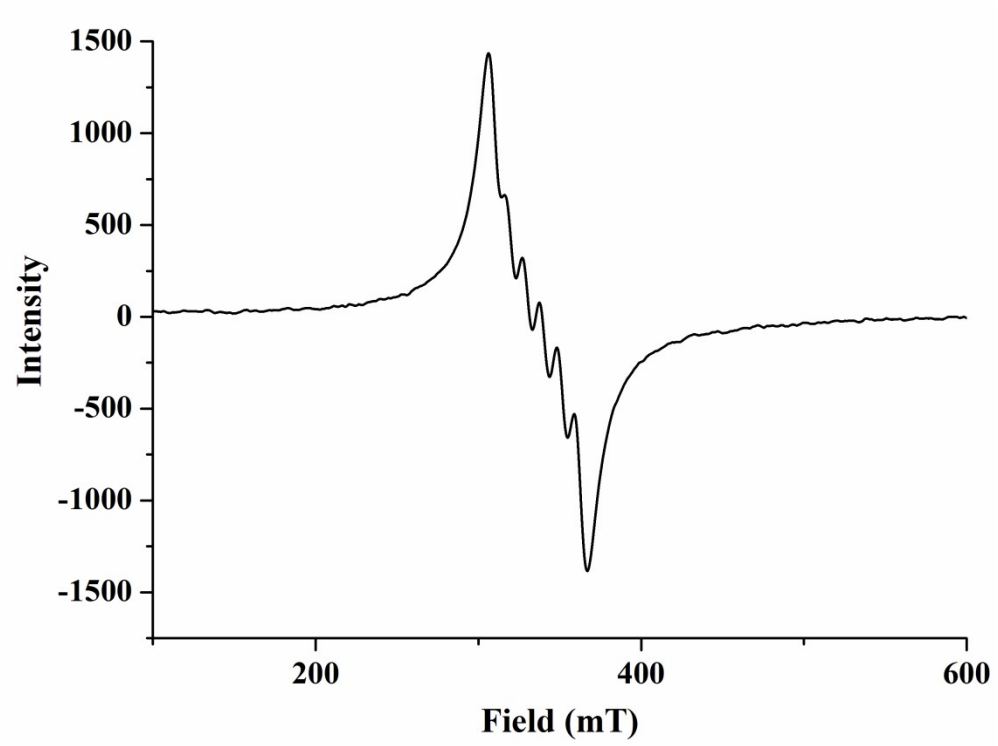


Figure S2. X-band EPR spectrum of **[Mn]-2** in methanol.

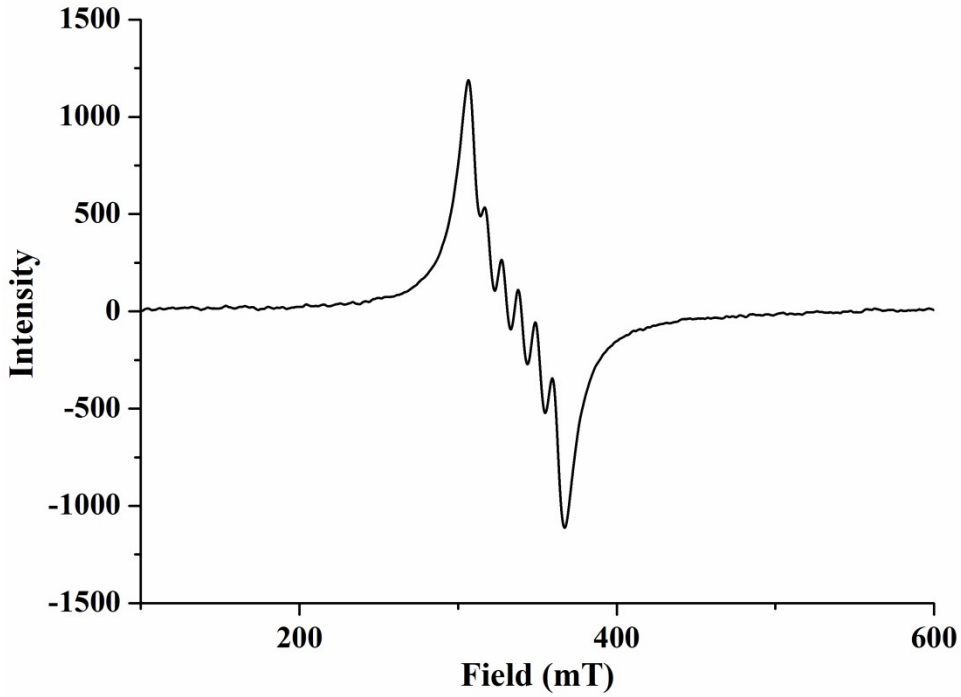
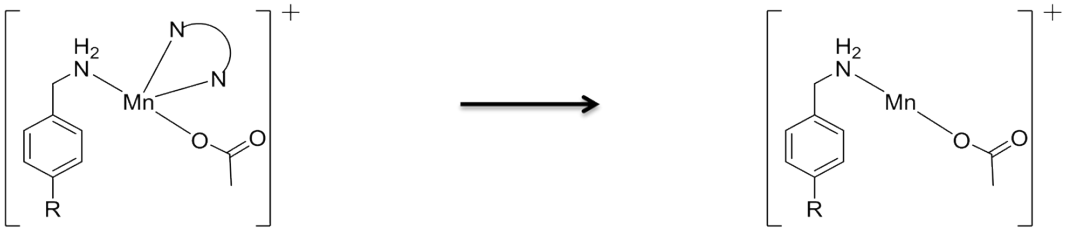
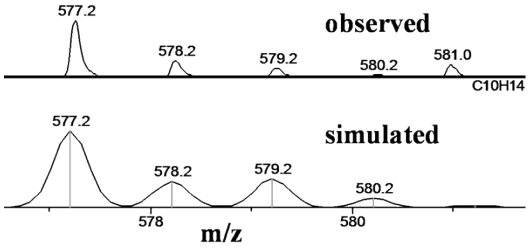


Figure S3. X-band EPR spectrum of **[Mn]-3** in methanol.

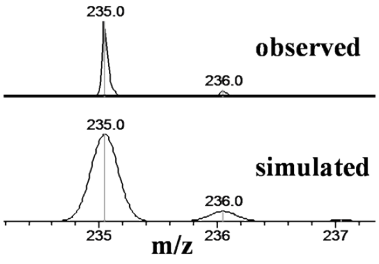
Controlled experiments for identification of catalytic species and intermediates.

Controlled experiments are performed by stirring the complex **[Mn]-3** with amines {benzyl amine (**1a**) or *p*-methyl benzyl amine (**1e**)} (cat/amine = 1:5 molar ratio) at 60 °C for 5 hours. Reaction aliquots are analyzed by ESI-MS analysis, which inferred the presence of several amine coordinated Mn(II) species (Figure S4). Moreover, the organic components of the crude reaction mixture are extracted in diethyl ether and analyzed by NMR in $CDCl_3$ (Figure S5).

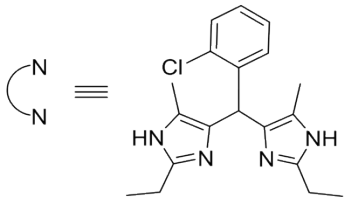




R=CH_3, m/z =577



R=CH_3, m/z =235



L3

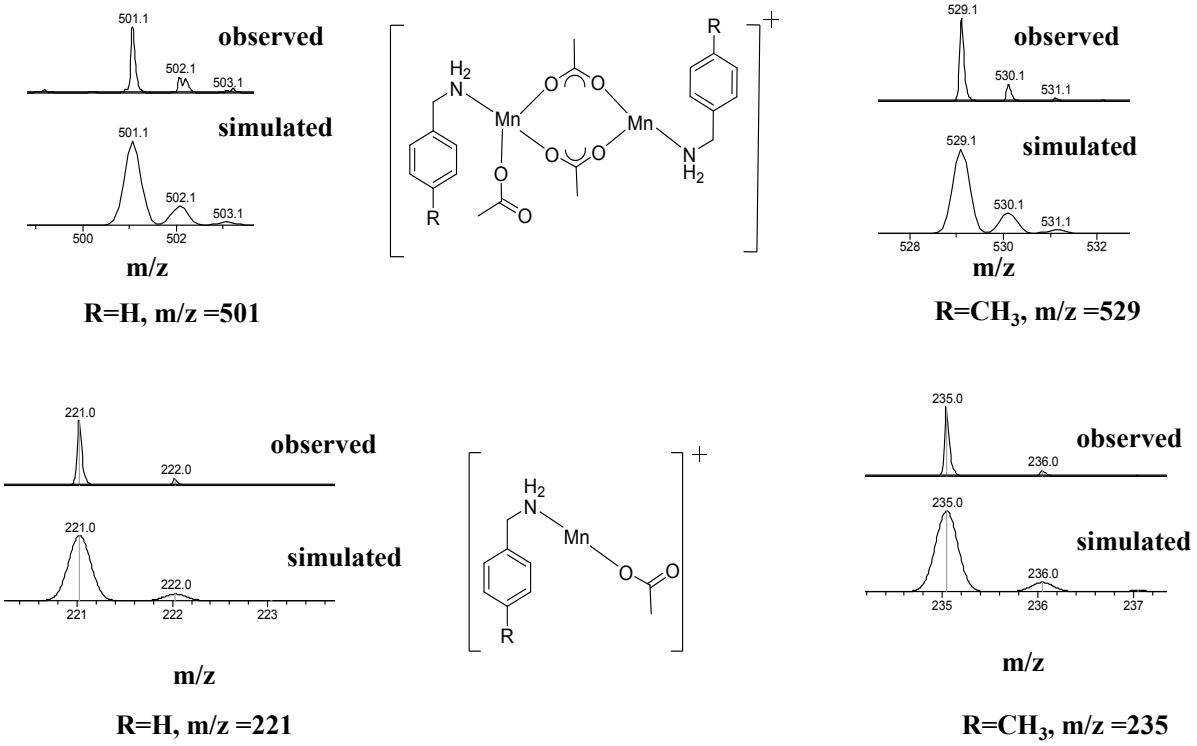


Figure S4. ESI-MS analysis of controlled experiments.

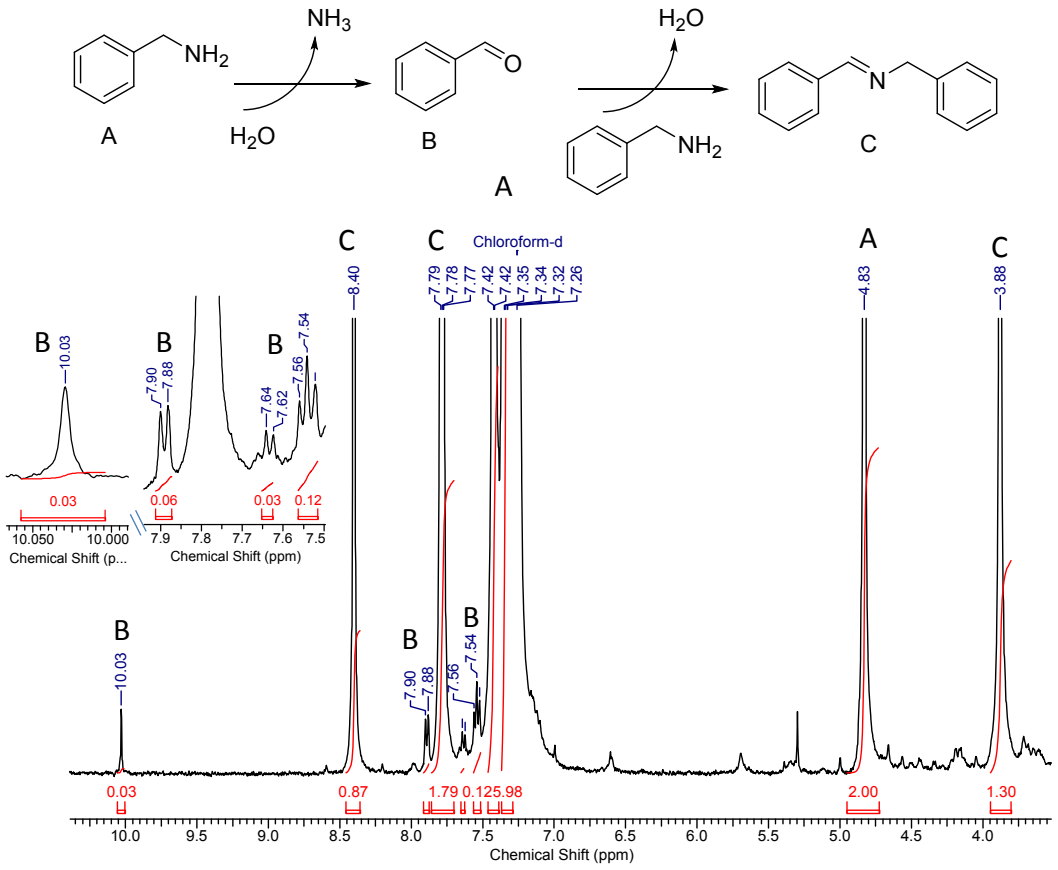


Figure S5. [1]H NMR spectra of the crude reaction mixture, showing the formation of aldehyde intermediate during the oxidative coupling of benzylamine (**1a**) to (**2a)**.

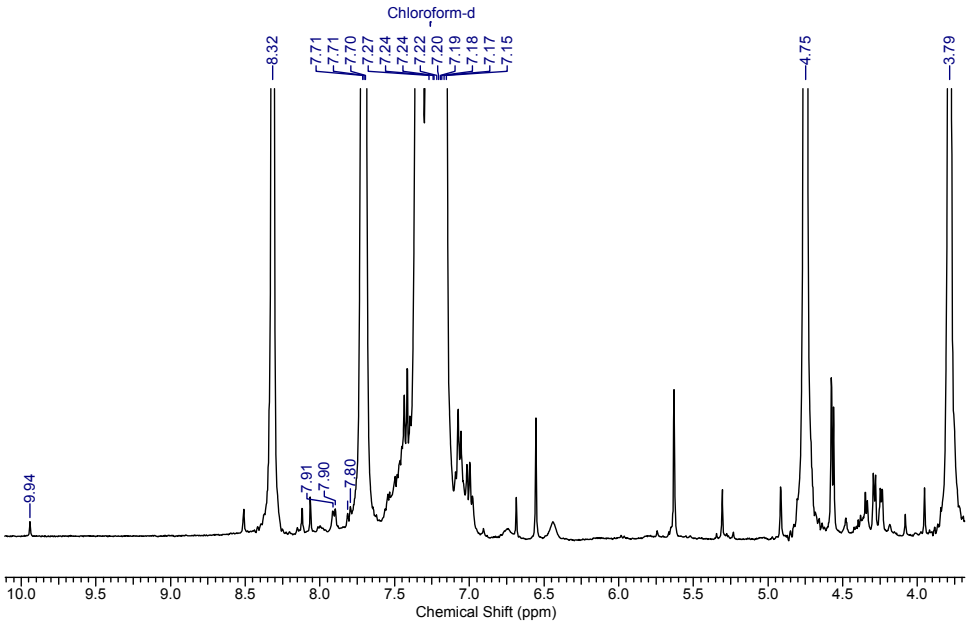


Figure S6. [1]H NMR spectra of the crude reaction mixture performed in water, showing the formation of aldehyde intermediate during the oxidative coupling of benzylamine (**1a**) to (**2a)**.

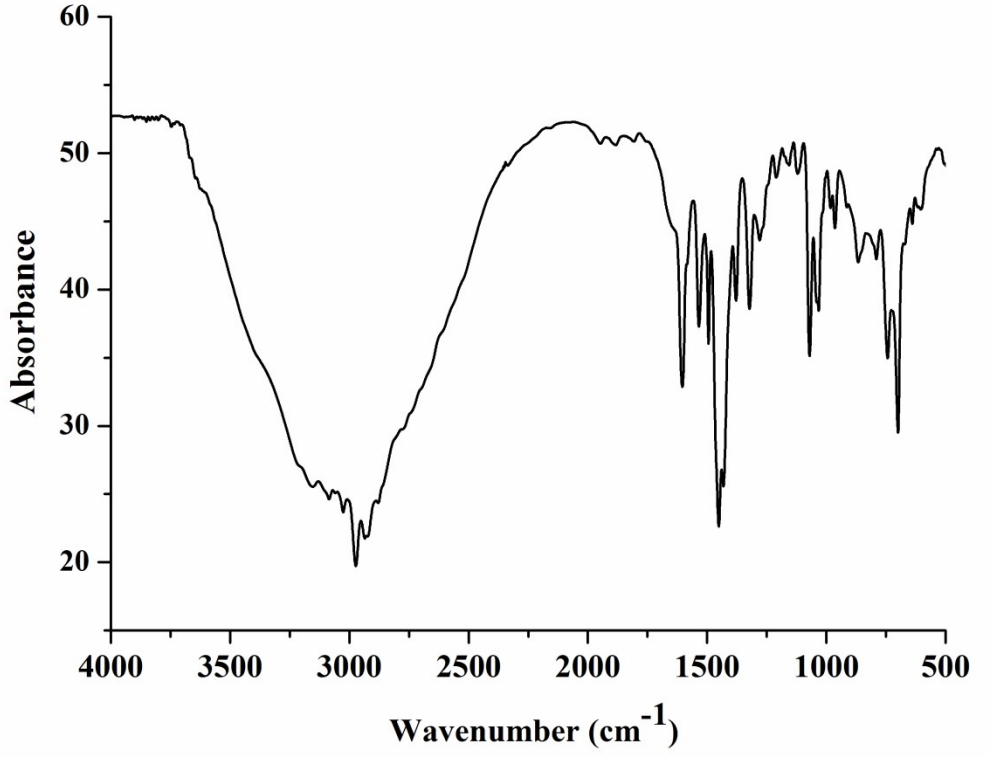


Figure S7. FT-IR spectrum of ligand **L1** in KBr pellet.

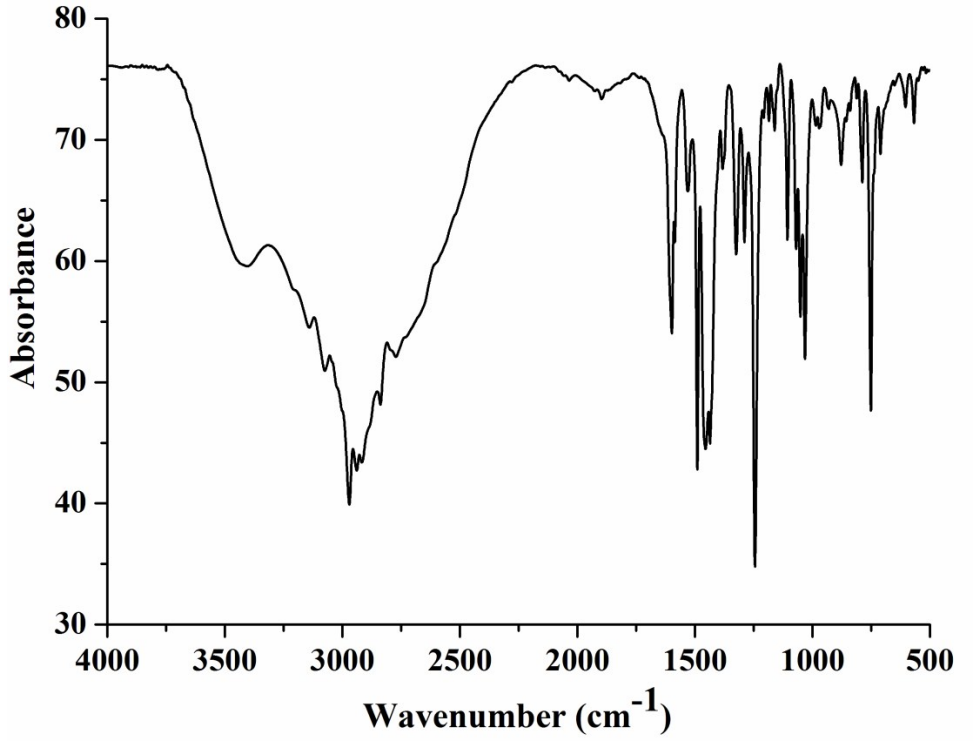


Figure S8. FT-IR spectrum of ligand **L2** in KBr pellet.

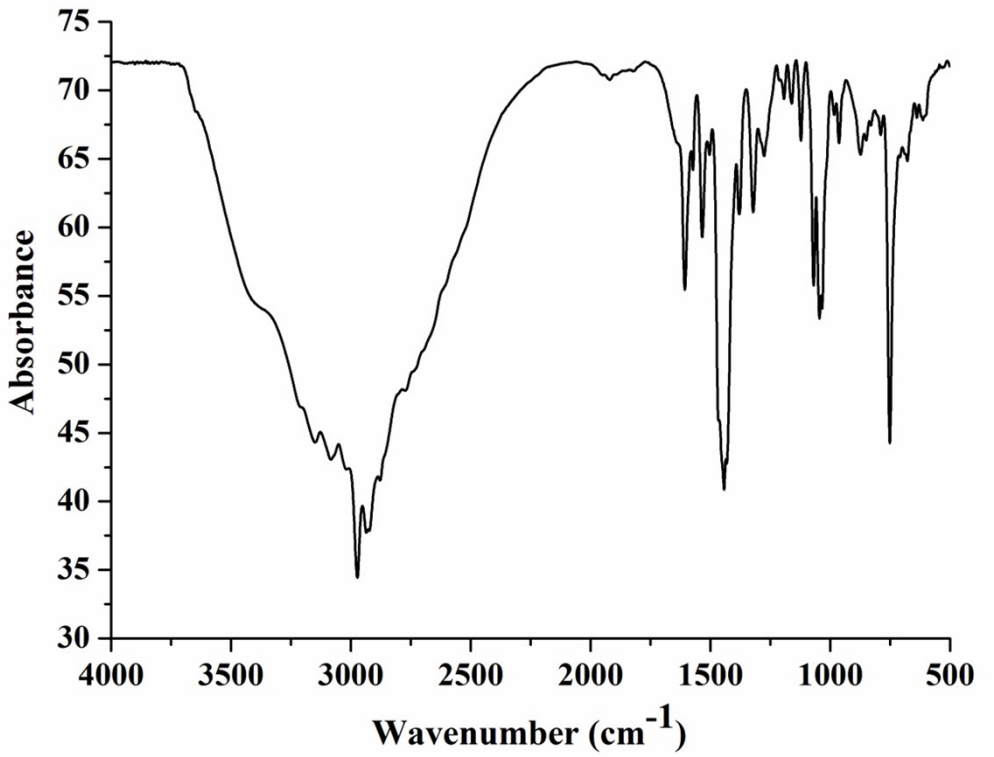


Figure S9. FT-IR spectrum of ligand **L3** in KBr pellet.

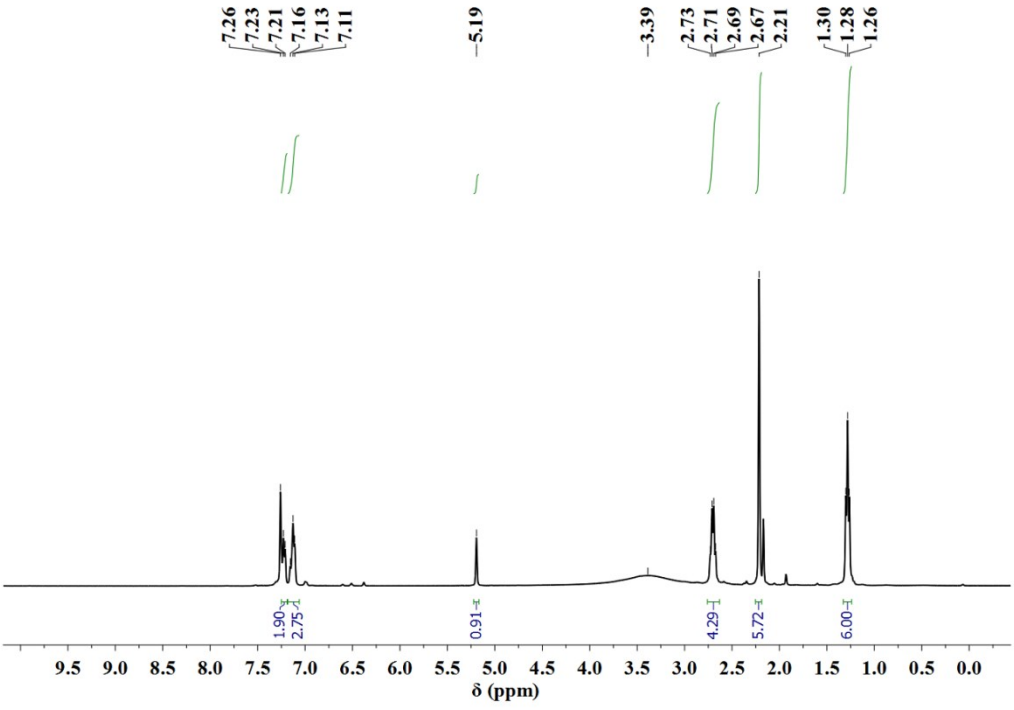


Figure S10. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

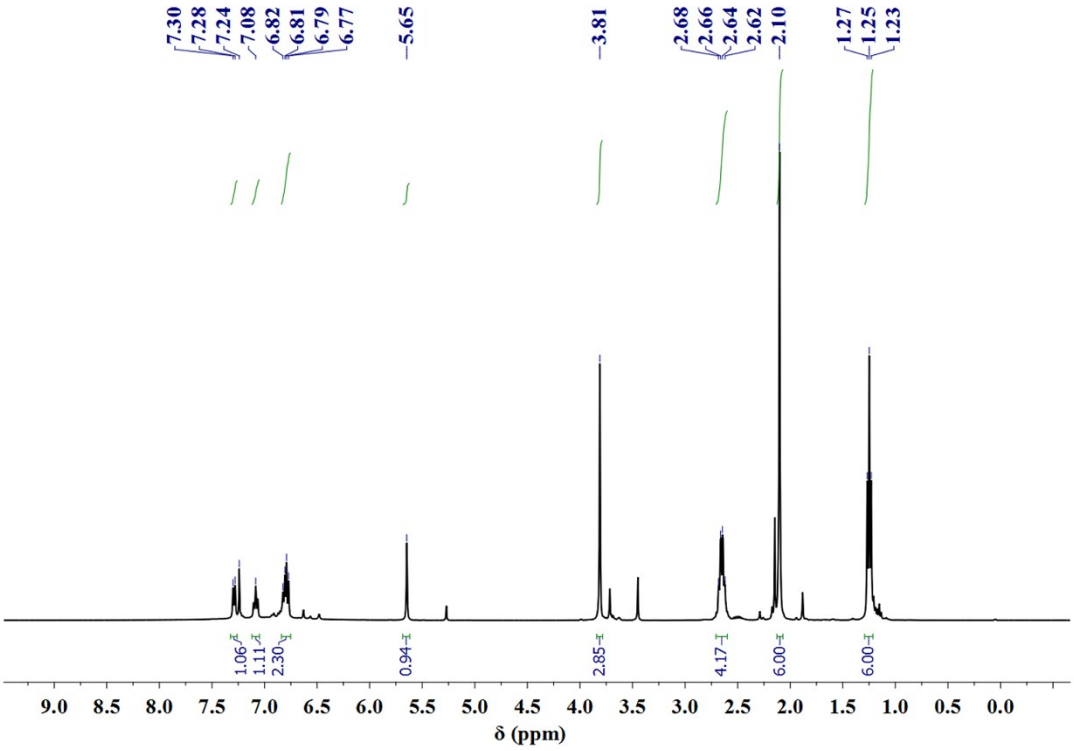


Figure S11. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

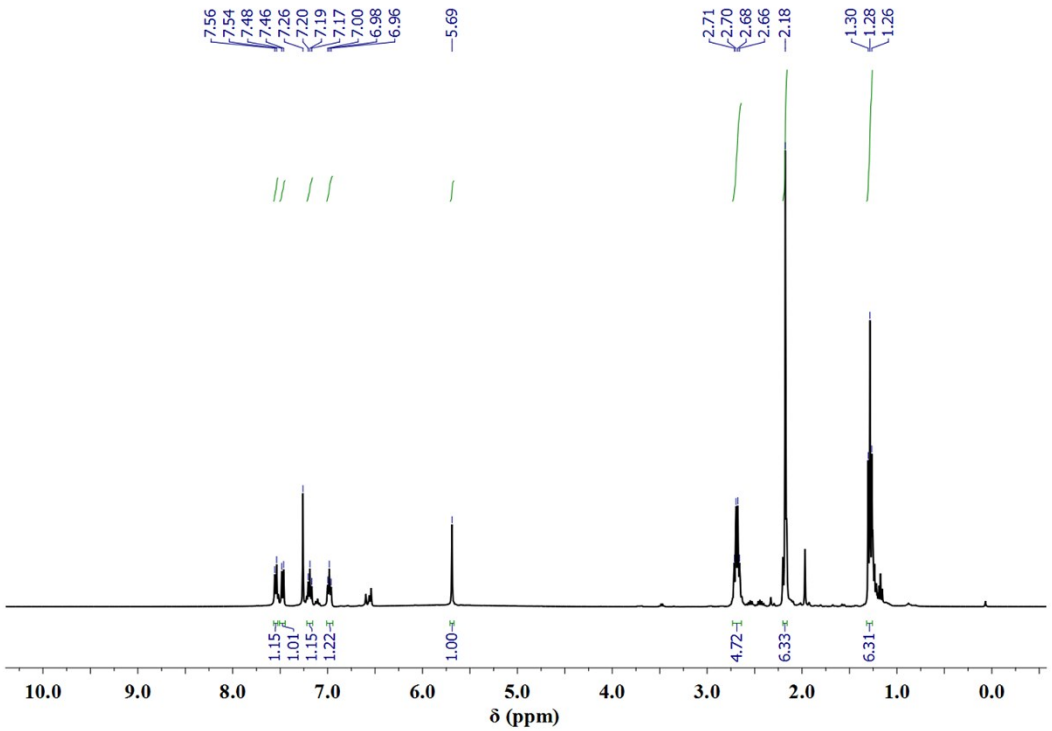


Figure S12. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

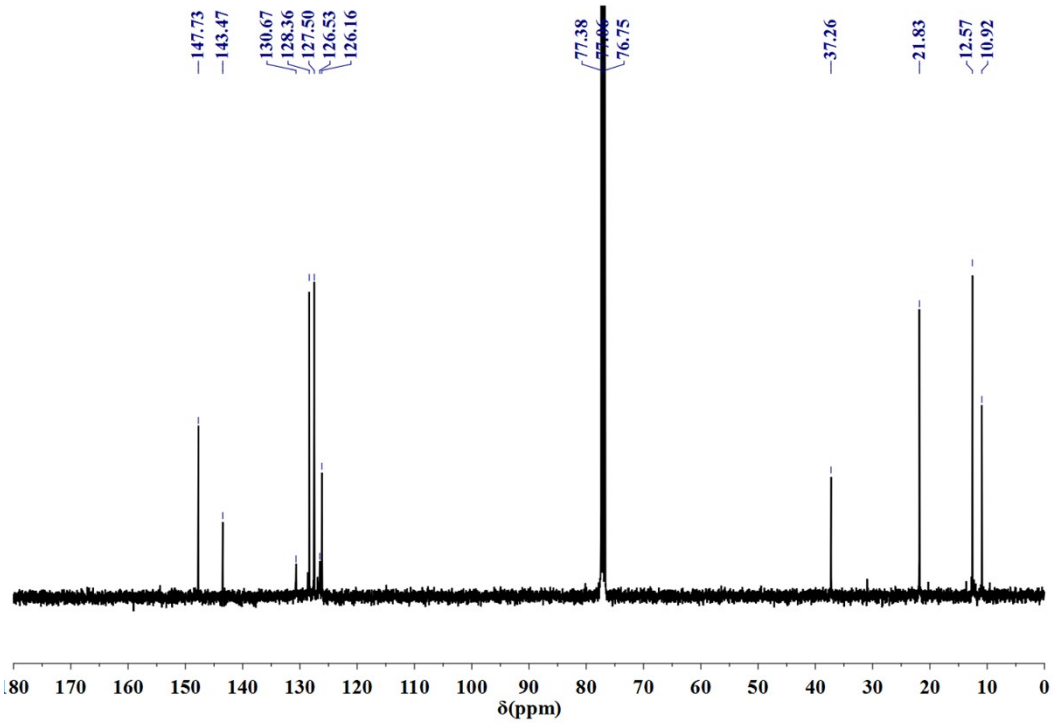


Figure S13. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

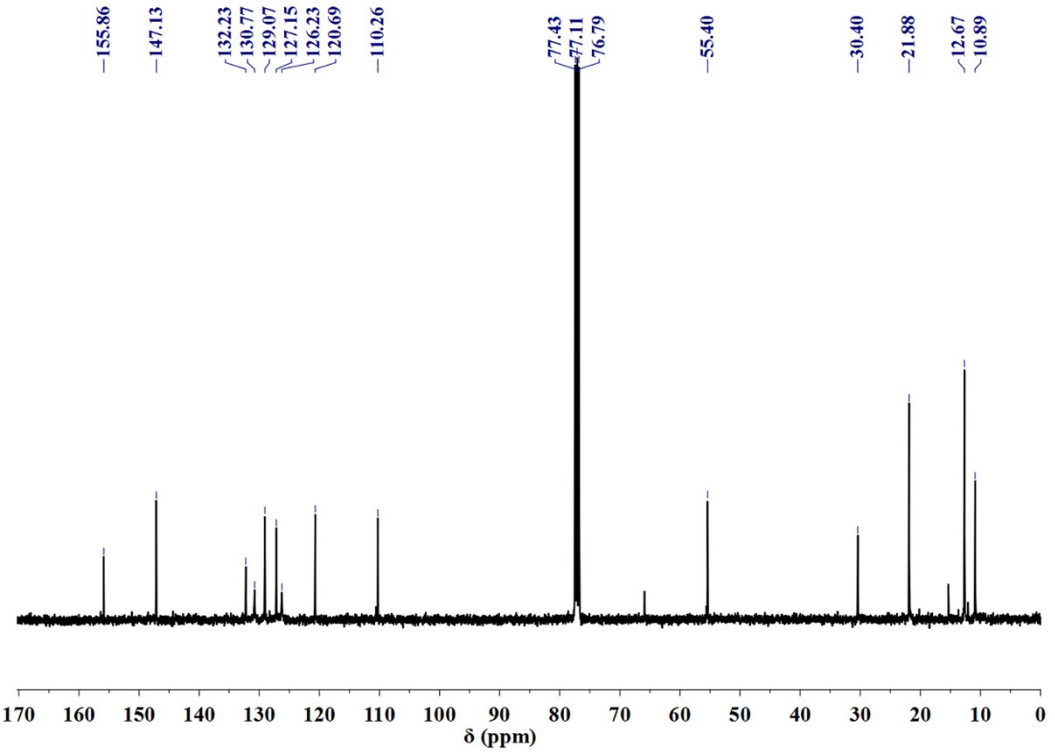


Figure S14. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

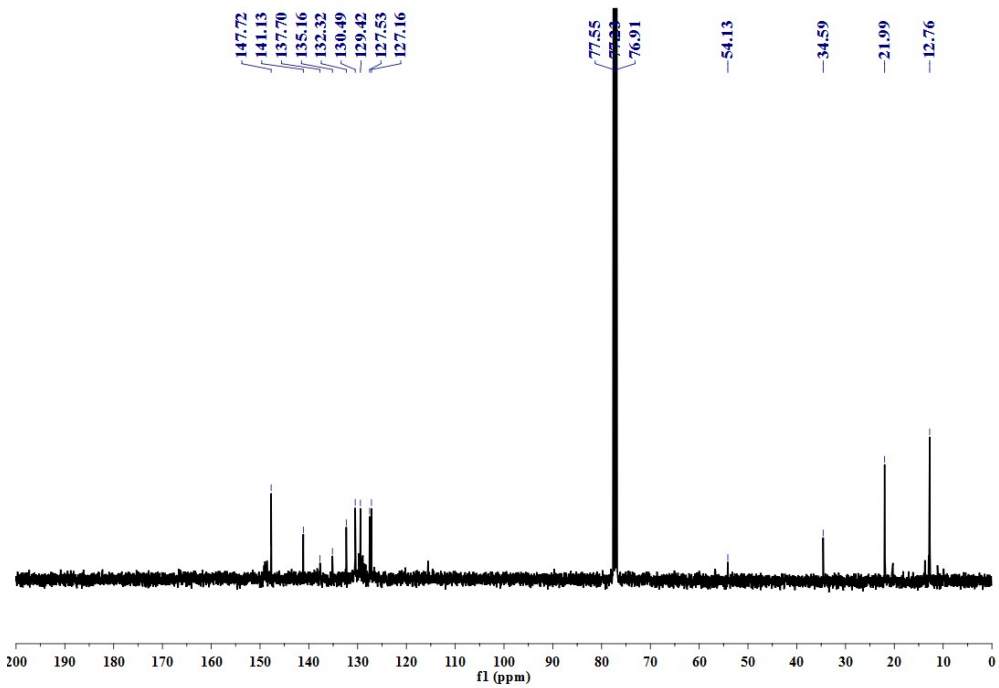


Figure S15. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

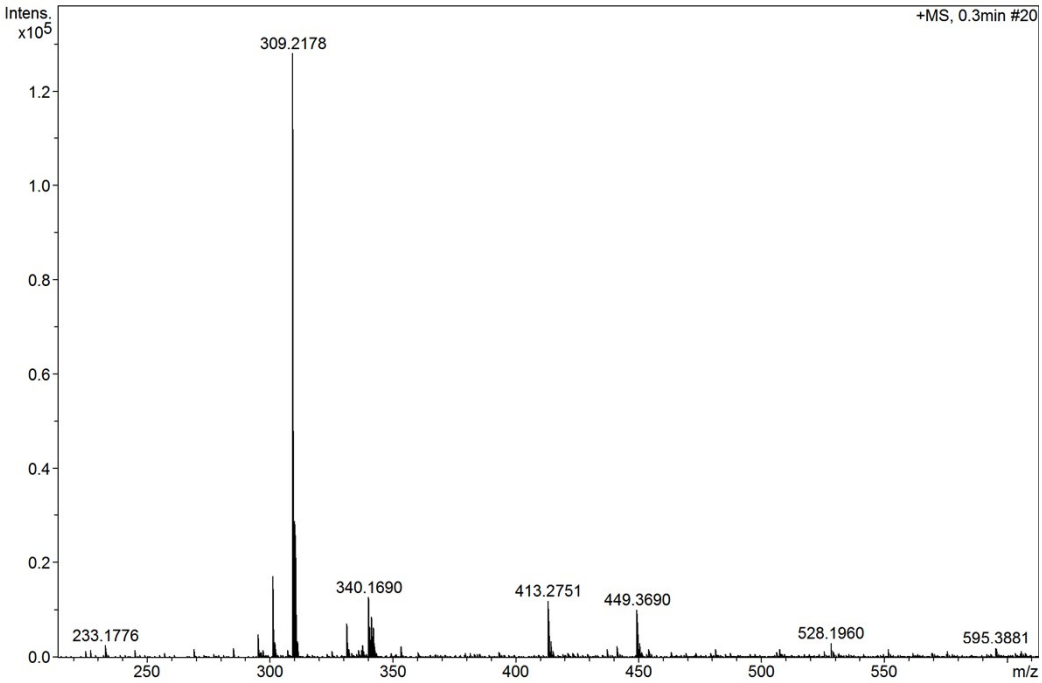


Figure S16. ESI-mass spectrum of **L1** in methanol.

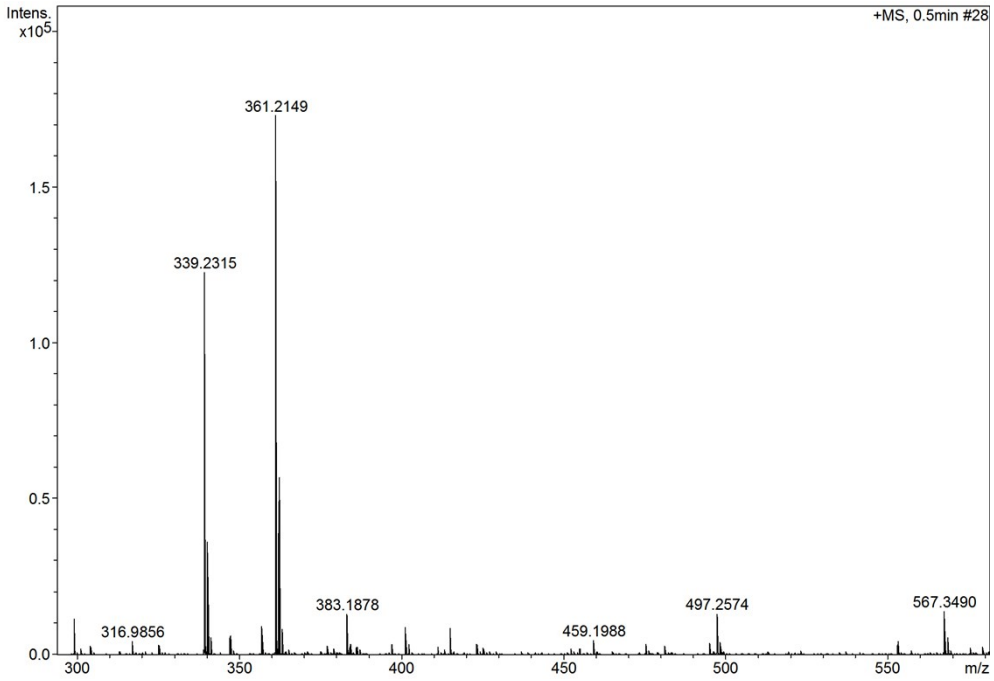


Figure S17. ESI-mass spectrum of **L2** in methanol.

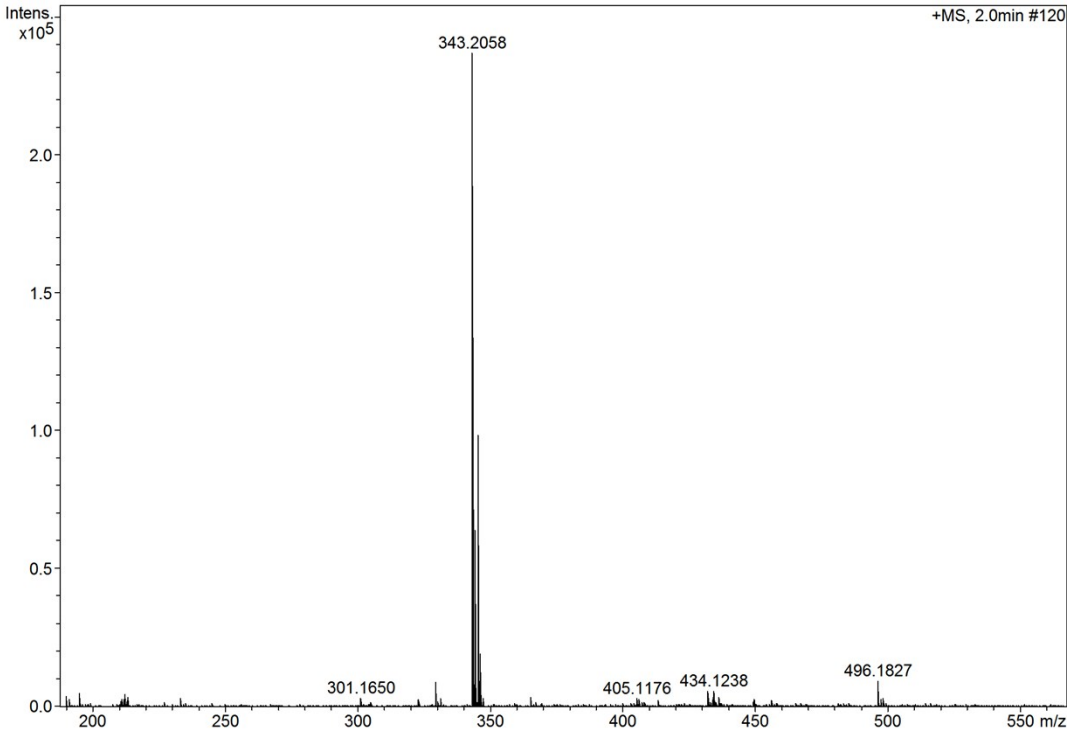


Figure S18. ESI-mass spectrum of **L3** in methanol.

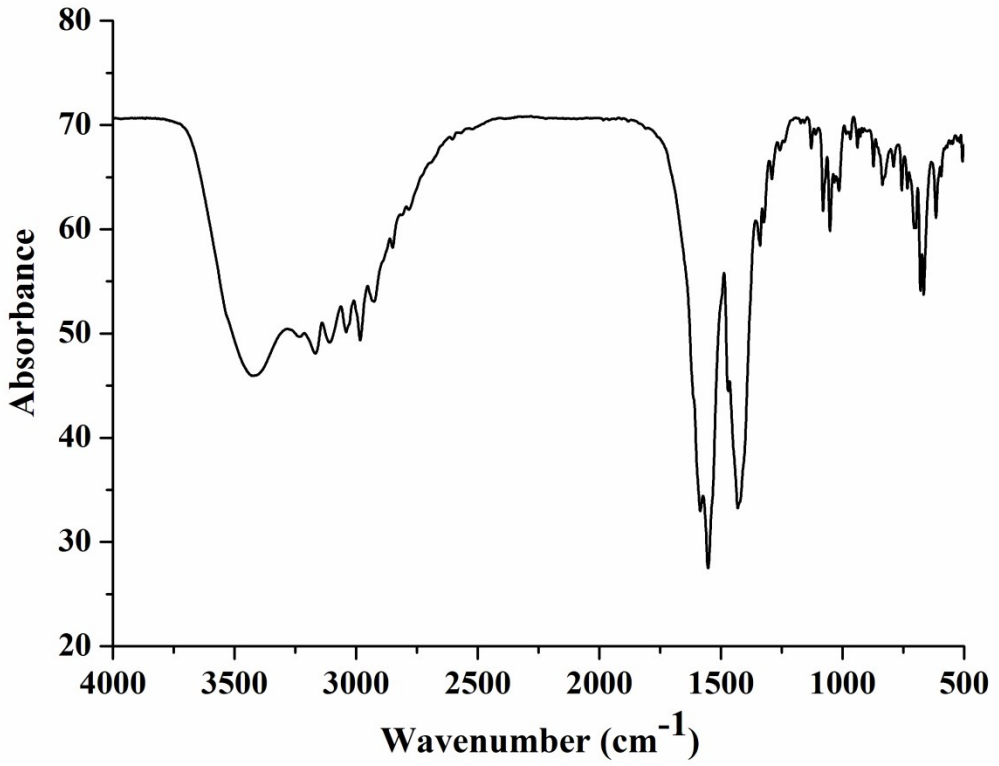


Figure S19. FT-IR spectrum of **[Mn]-1** in KBr pellet.

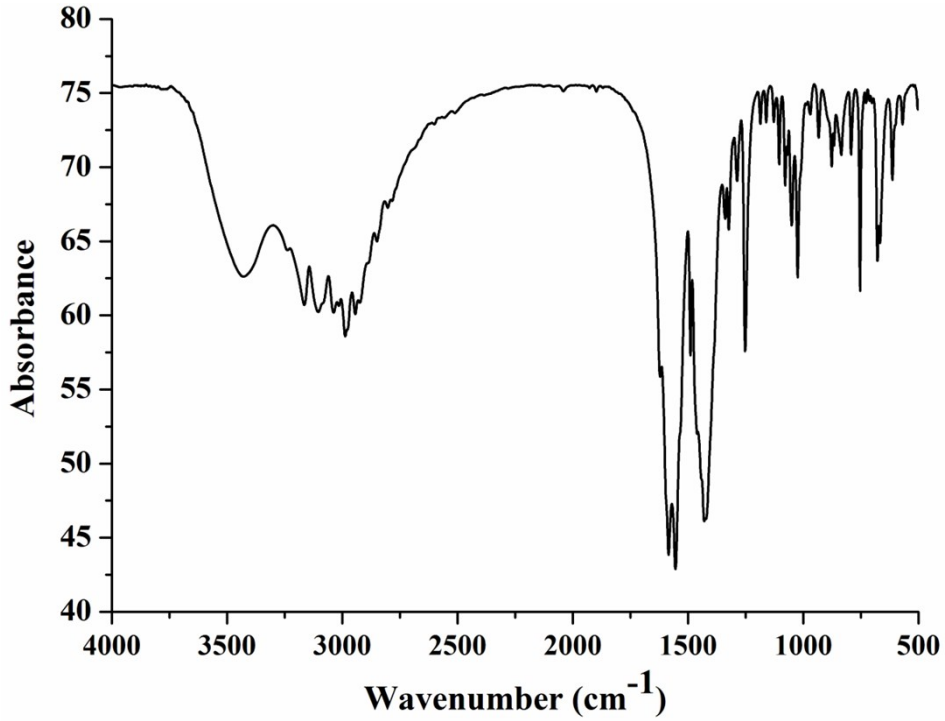


Figure S20. FT-IR spectrum of **[Mn]-2** in KBr pellet.

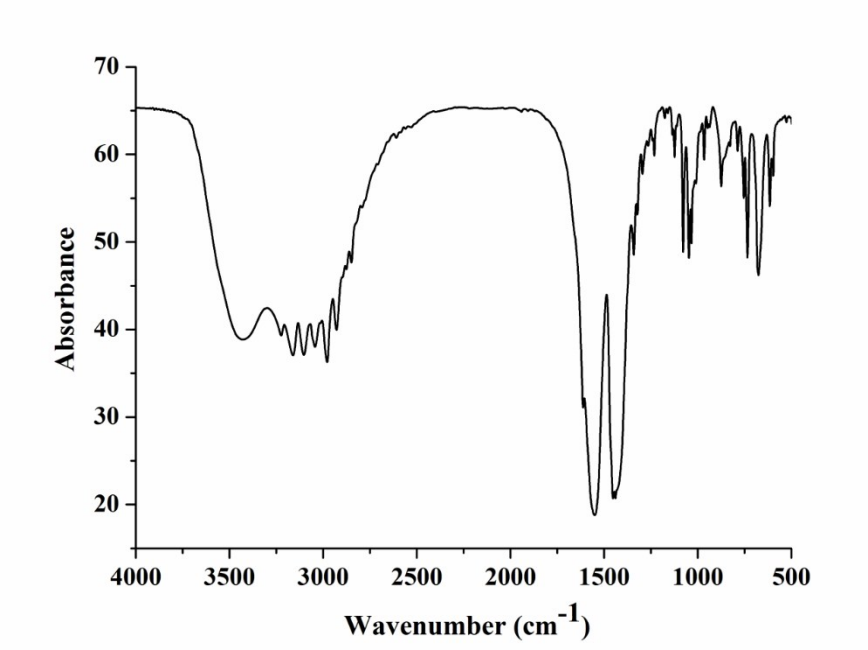


Figure S21. FT-IR spectrum of **[Mn]-3** in KBr pellet.

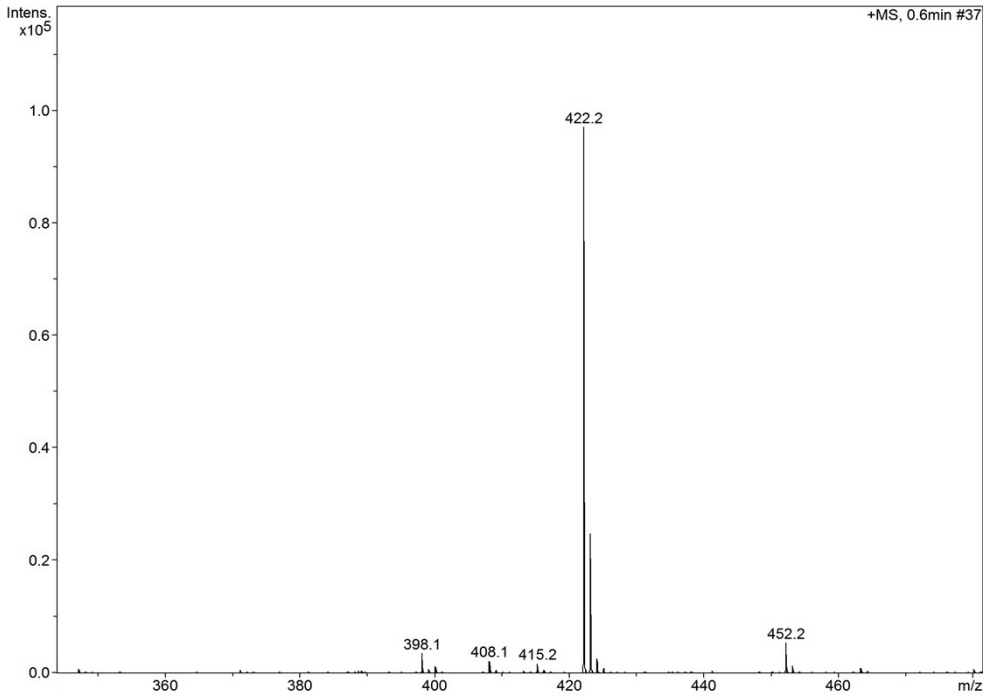


Figure S22. ESI-mass spectrum of [**Mn]-1** in methanol.

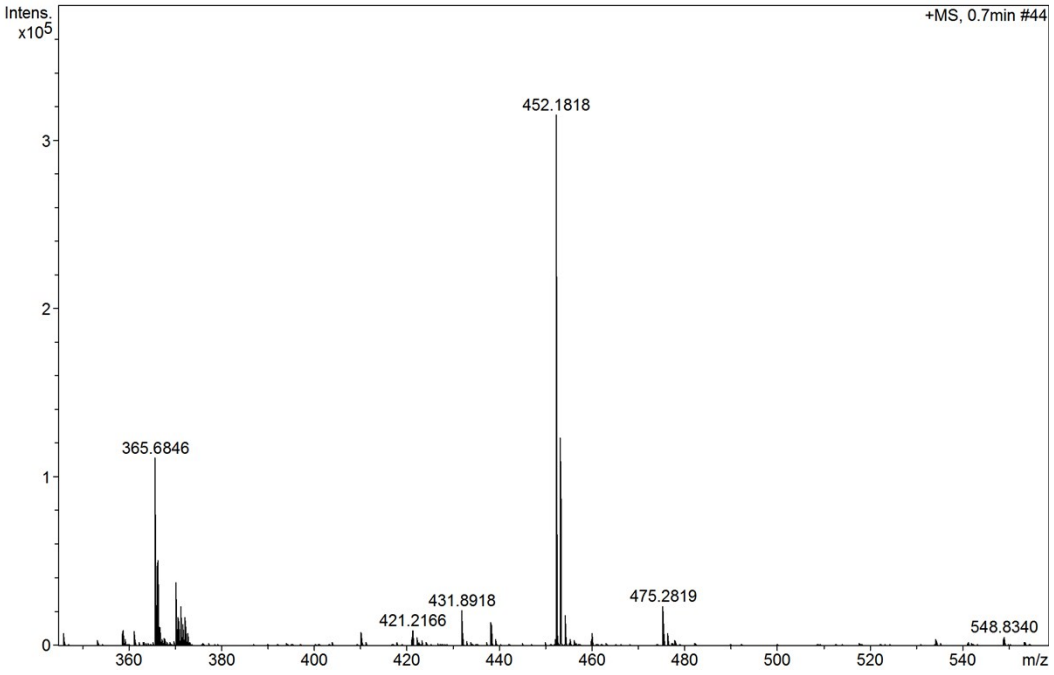


Figure S23. ESI-mass spectrum of **[Mn]-2** in methanol.

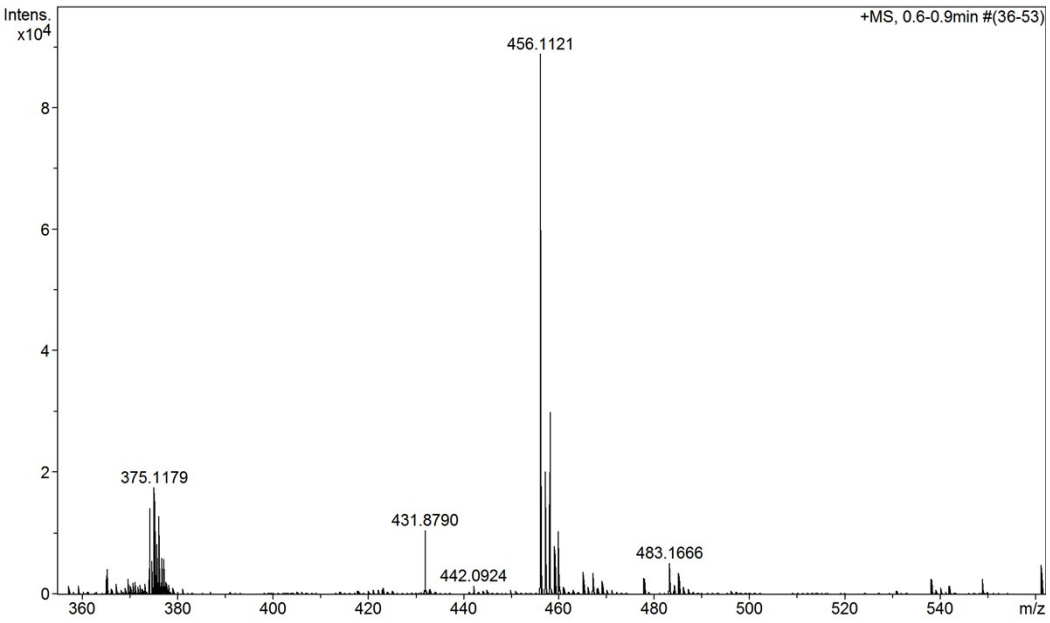
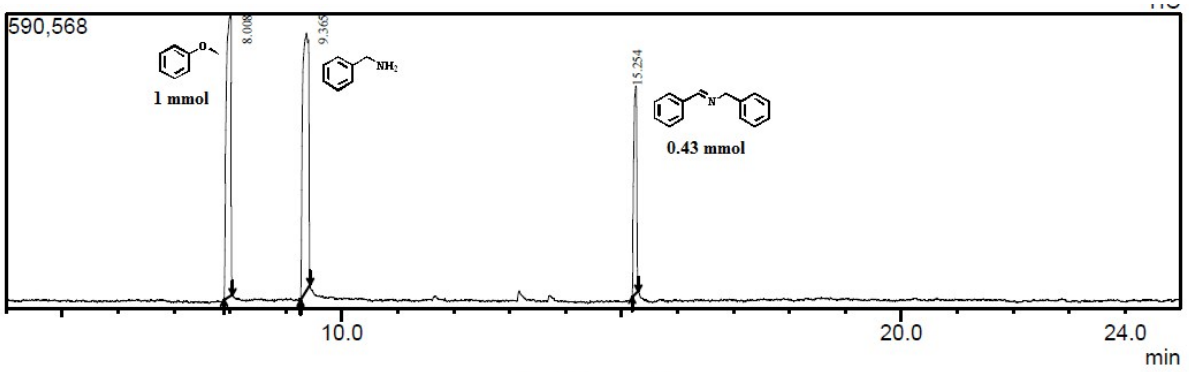


Figure S24. ESI-mass spectrum of **[Mn]-3** in methanol.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	8.008	3370288	38.56	564756	37.78	5.97	Anisole
2	9.365	3848502	44.03	515031	34.45	7.47	Benzylamine
3	15.254	1521863	17.41	415105	27.77	3.67	Benzenemethanamine, N-(phenylmethylene)-
		8740653	100.00	1494892	100.00		

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BG Mode:Calc. from Peak Group 1 - Event 1 Scan

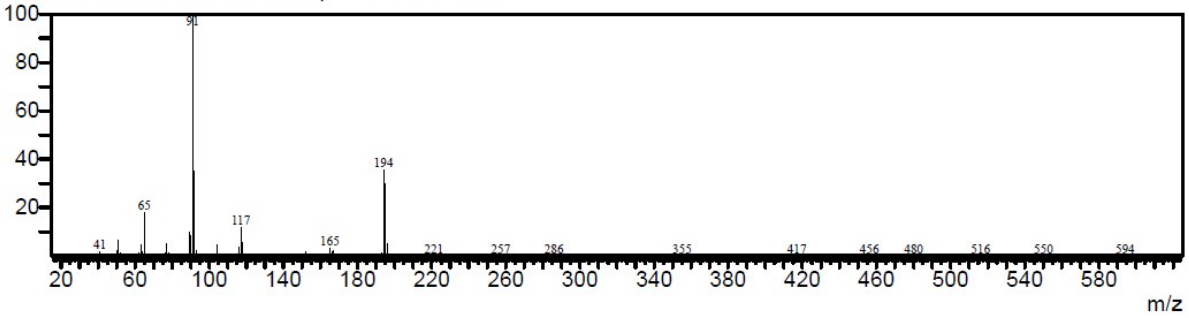
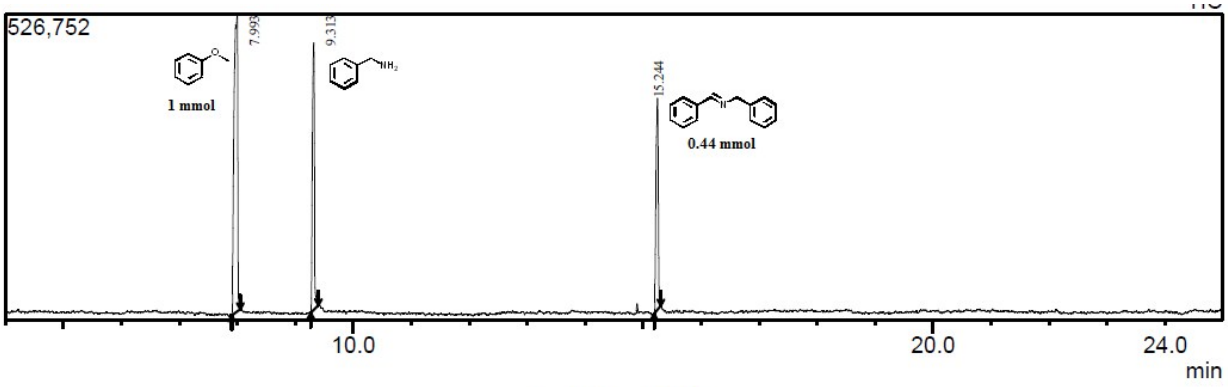


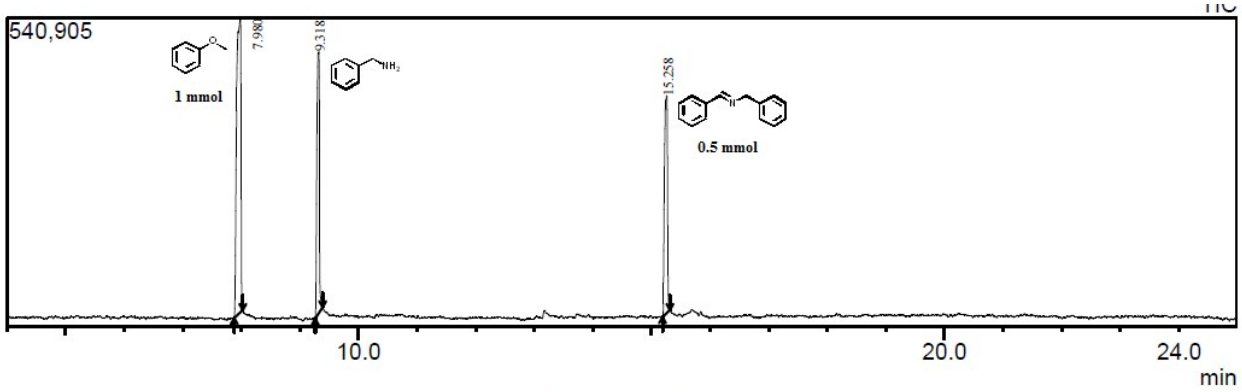
Figure S25. GC-MS for entry 1 of table 1.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.993	2149273	51.00	511712	38.33	4.20	Anisole
2	9.313	1118631	26.55	459559	34.43	2.43	Benzylamine
3	15.244	946022	22.45	363664	27.24	2.60	Benzenemethanamine, N-(phenylmethylene)-
		4213926	100.00	1334935	100.00		

Figure S26. GC-MS for entry 2 of table 1.



Peak Report TIC

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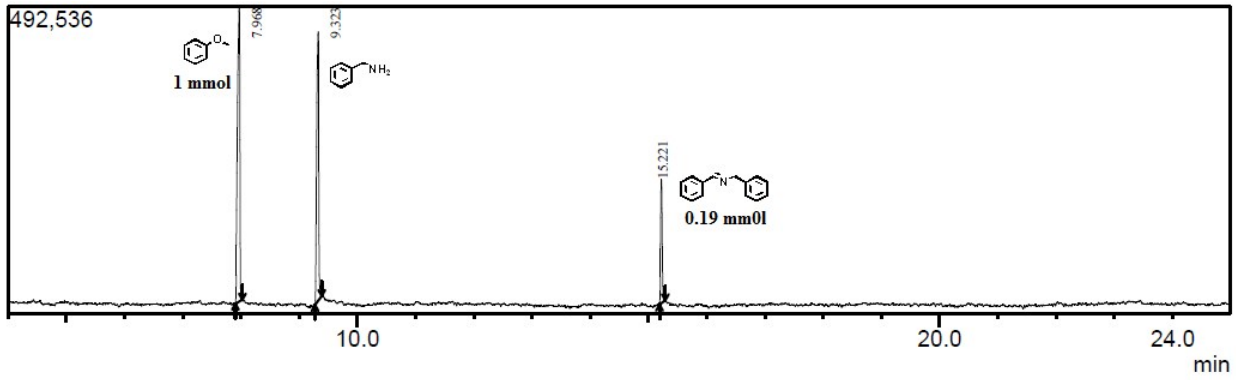
1	7.980	2631633	49.31	515312	38.08	5.11	Anisole
2	9.318	1386012	25.97	457271	33.79	3.03	Benzylamine
3	15.258	1319630	24.72	380572	28.12	3.47	Benzenemethanamine, N-(phenylmethylene)-
		5337275	100.00	1353155	100.00		

Figure S27. GC-MS for entry 3 of table 1.



Peak Report TIC

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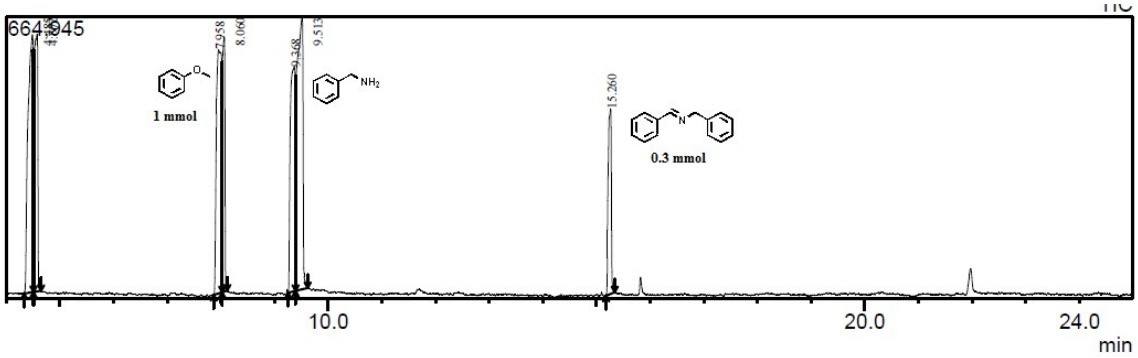
1	7.968	1339667	50.34	472608	42.90	2.83	Anisole
2	9.323	1120622	39.60	430797	39.10	2.60	Benzylamine
3	15.221	369349	10.05	198321	18.00	1.86	Benzenemethanamine, N-(phenylmethylene)-
		2829638	100.00	1101726	100.00		

Figure S28. GC-MS for entry 4 of table 1.



Peak Report TIC

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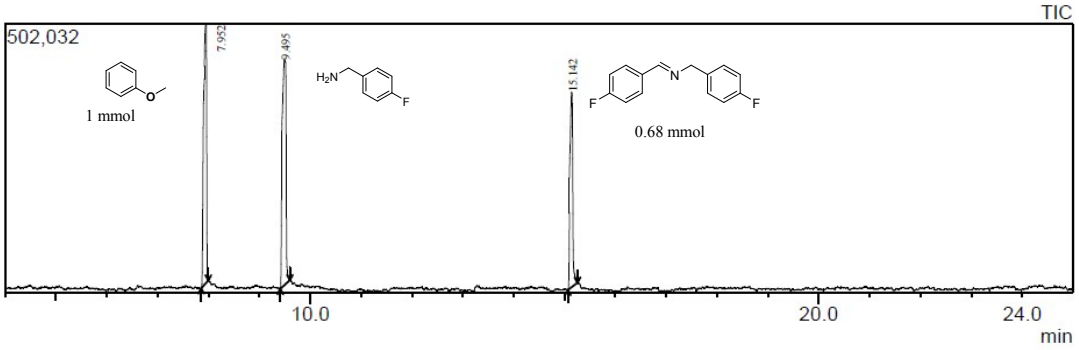
1	4.485	4097302	17.84	606808	15.19	6.75	Toluene
2	4.572	2947741	12.84	606441	15.18	4.86	Toluene
3	7.958	3966564	17.27	573962	14.37	6.91	Anisole
4	8.060	1893529	8.25	600514	15.03	3.15	Anisole
5	9.368	3437438	14.97	528561	13.23	6.50	Benzylamine
6	9.513	4889465	21.29	642594	16.08	7.61	Benzylamine
7	15.260	1732596	7.54	436289	10.92	3.97	Benzenemethanamine, N-(phenylmethylene)-
		2964635	100.00	3995169	100.00		

Figure S29. GC-MS for entry 5 of table1.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.952	2038162	36.07	483315	38.09	4.22	Anisole
2	9.495	2214996	39.20	420976	33.18	5.26	Benzenemethanamine, 4-fluoro-
3	15.142	1397085	24.73	364527	28.73	3.83	4-fluoro-benzenemethanamine, N-(4-fluorophenylm
		5650243	100.00	1268818	100.00		

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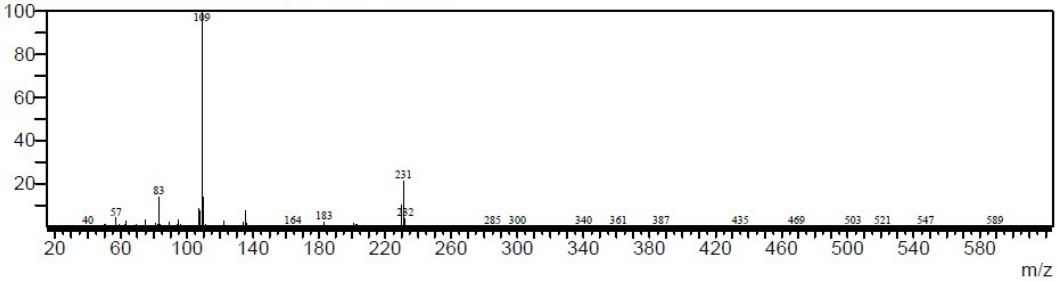
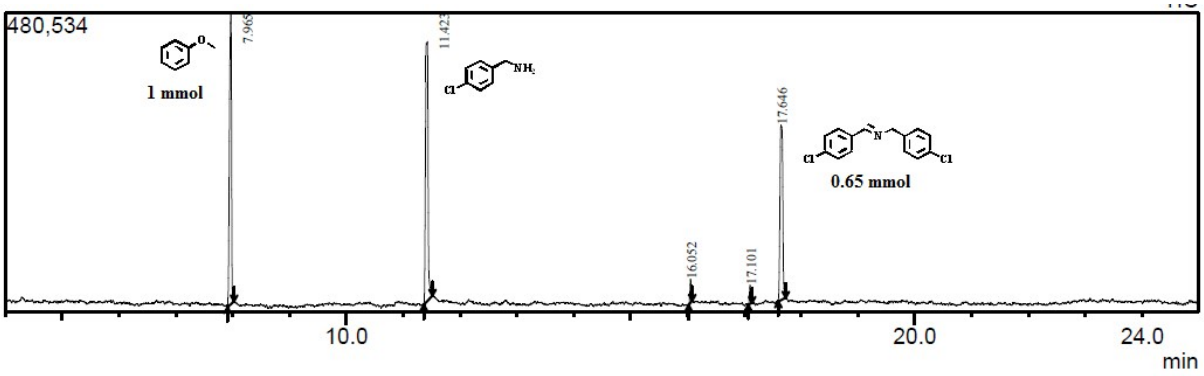


Figure S30. GC-MS for **2b**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.965	1134986	32.14	467878	37.95	2.43	Anisole
2	11.423	1379599	30.05	416382	33.78	3.31	Benzenemethanamine, 3-chloro-
3	16.052	58112	1.65	38012	3.08	1.53	Hexadecanoic acid, methyl ester
4	17.101	43896	1.24	29562	2.40	1.48	Methyl stearate
5	17.646	915129	20.91	280930	22.79	3.26	4-Chloro-benzenemethanamine, N-(4-chloro-pheny
		3531722	100.00	1232764	100.00		

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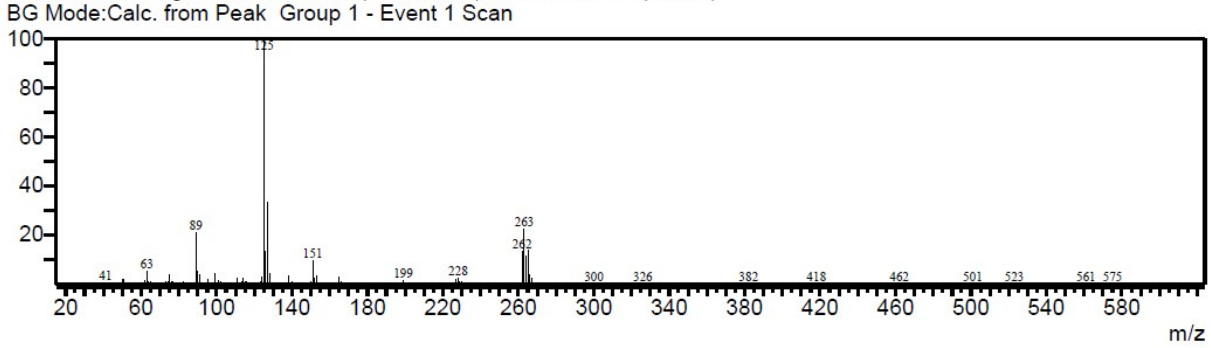
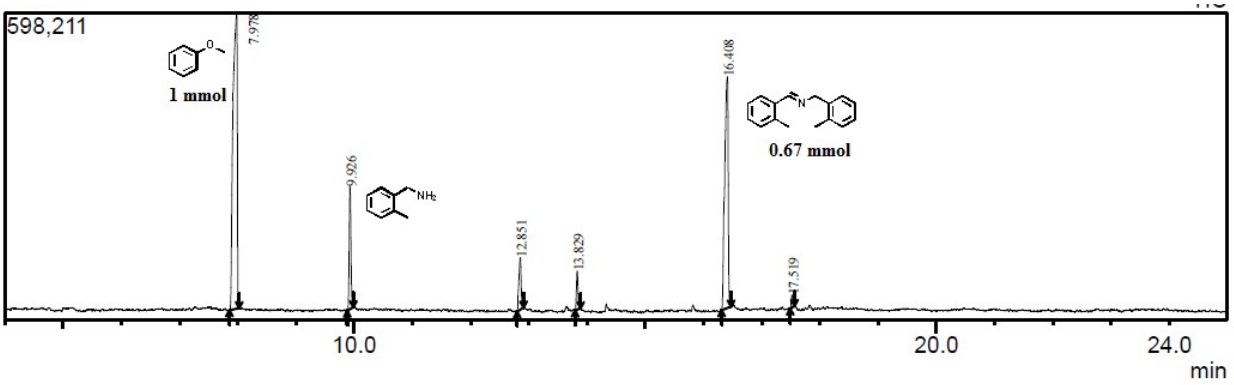


Figure S31. GC-MS for **2c**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.978	2898033	50.64	575974	39.36	5.03	Anisole
2	9.926	464986	8.13	238440	16.30	1.95	Benzaldehyde, 2-methyl-
3	12.851	262294	4.58	100606	6.88	2.61	Benzamide, 2-methyl-
4	13.829	139270	2.43	74572	5.10	1.87	Acetamide, N-(2-phenylethyl)-
5	16.408	1910122	33.38	449658	30.73	4.25	2-Methyl-benzenemethanamine, N-(2-methyl-phen
6	17.519	48001	0.84	23967	1.64	2.00	Benzeneethanamine, N-benzoyl-
		5722706	100.00	1463217	100.00		

Line#:5 R.Time:16.410(Scan#:2483)
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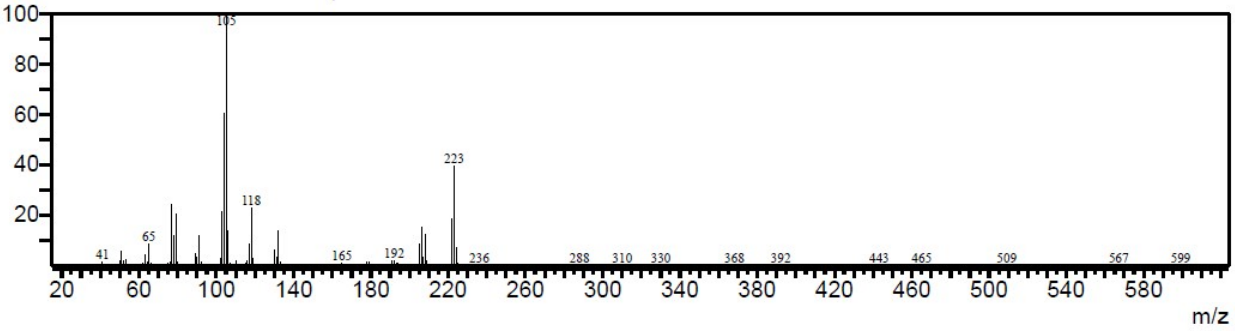
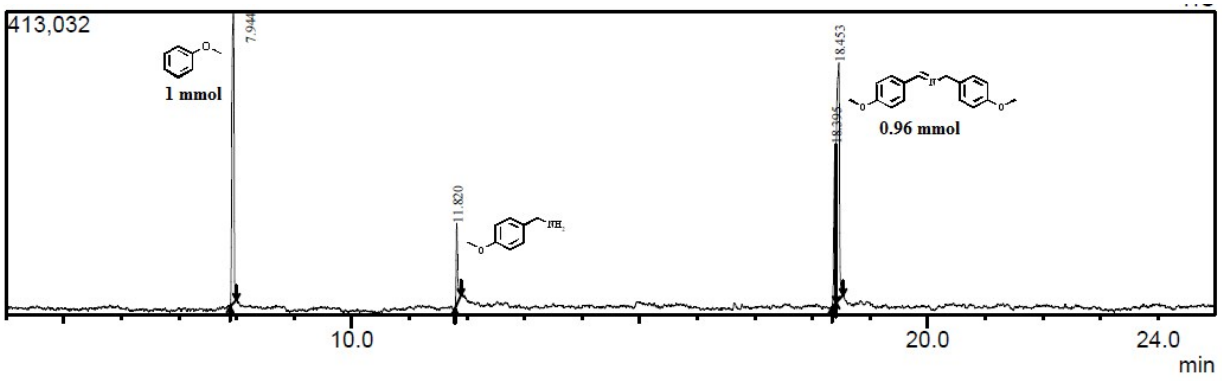


Figure S32. GC-MS for **2d**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.944	1062736	37.15	396510	37.87	2.58	Anisole
2	11.820	202455	7.09	110937	10.60	1.82	3-Methoxybenzylamine
3	18.395	570371	19.97	216678	20.70	2.63	Benzene, (3-iodo-1-methoxybutyl)-
4	18.453	1021230	35.80	322808	30.83	3.29	Benzenemethanamine, 4-methoxy-N-[(4-methoxy
		2856792	100.00	1046933	100.00		

Line#:4 R.Time:18.455(Scan#:2892)
MassPeaks:373
RawMode:Averaged 18.450-18.460(2891-2893) BasePeak:121(86612)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

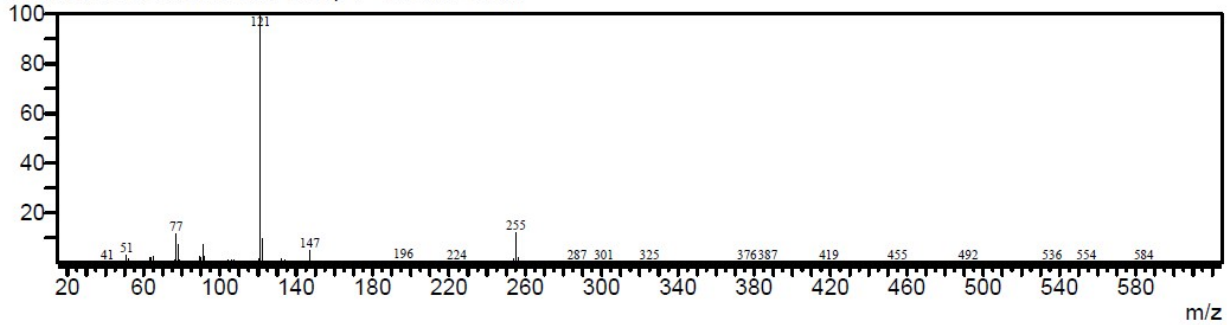
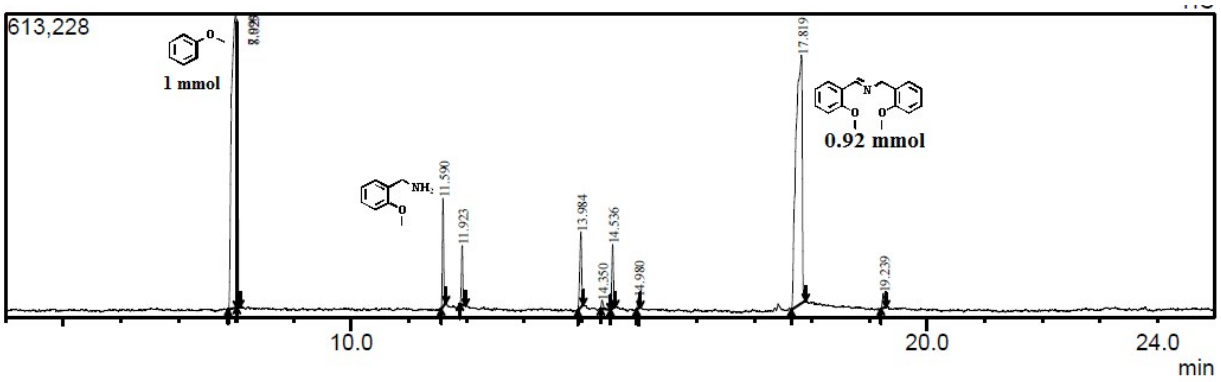


Figure S33. GC-MS for **2e**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.990	3879809	40.63	592556	25.15	6.04	Anisole
2	8.025	867488	9.12	577049	24.49	1.50	Anisole
3	11.590	333851	3.51	218903	9.29	1.53	2-Methoxybenzylamine
4	11.923	200655	2.11	118635	5.03	1.69	o-Methoxybenzonitrile
5	13.984	330993	3.48	152350	6.47	2.17	2-Methoxybenzamide
6	14.350	34012	0.36	16145	0.69	2.11	2-Methoxybenzylamine
7	14.536	240995	2.53	128926	5.47	1.87	2-Methoxybenzylamine, N-acetyl-
8	14.980	41307	0.43	21972	0.93	1.88	2-Methoxybenzylamine
9	17.819	3514568	37.10	500387	21.24	7.62	2 Methoxy-Benzenemethanamine, N-(2-methoxyp
10	19.239	70046	0.74	29315	1.24	2.39	Benzaldehyde, 4-methoxy-
		9513724	100.00	2356238	100.00		

Line#:9 R.Time:17.820(Scan#:2765)
MassPeaks:359
RawMode:Averaged 17.815-17.825(2764-2766) BasePeak:91(86569)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

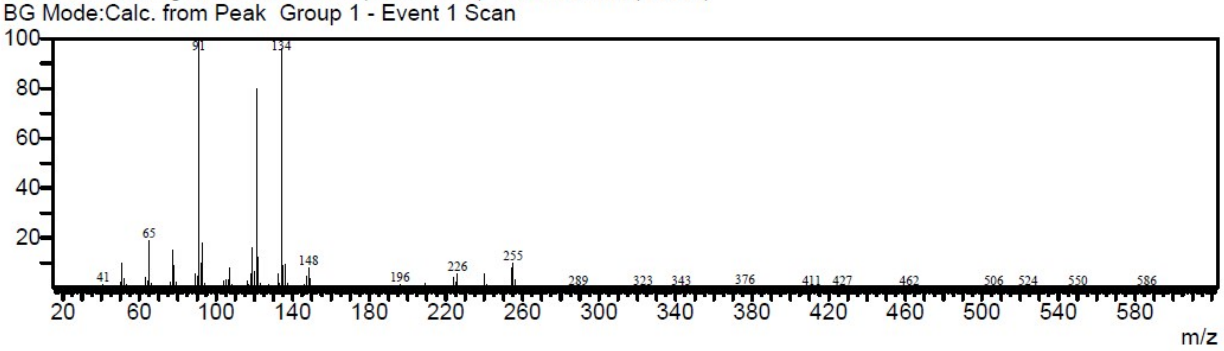
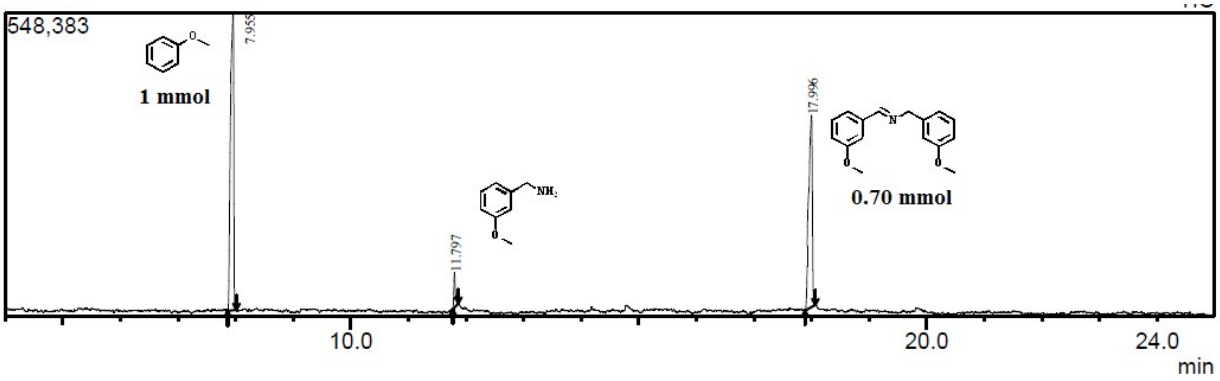


Figure S34. GC-MS for **2f**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.955	2144263	56.95	539324	56.69	3.98	Anisole
2	11.797	119206	3.17	63964	6.72	1.86	3-Methoxybenzylamine
3	17.996	1501539	39.88	348030	36.58	4.31	3-Methoxy-benzenemethanamine, N-(3-methoxy-ph
		3765008	100.00	951318	100.00		

Line#:3 R.Time:17.995(Scan#:2800)
MassPeaks:364
RawMode:Averaged 17.990-18.000(2799-2801) BasePeak:122(59586)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

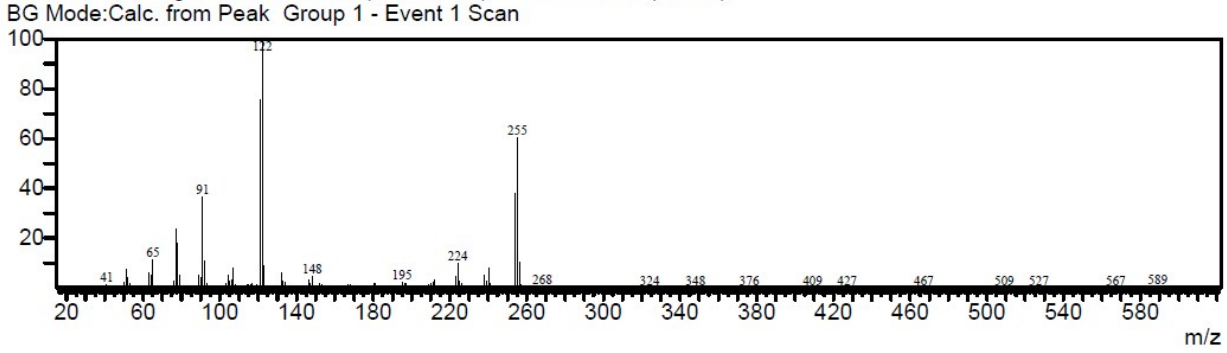
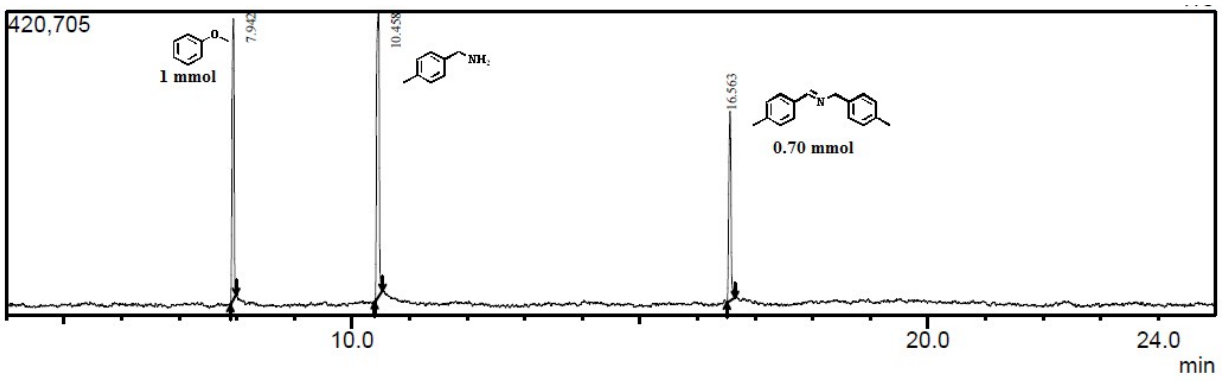


Figure S35. GC-MS for **2g**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.942	962121	32.52	388306	37.15	2.48	Anisole
2	10.458	1319416	44.60	394686	37.76	3.34	Benzenemethanamine, 3-methyl-
3	16.563	676689	22.87	262214	25.09	2.58	4-Methyl-benzenemethanamine, (N-4-methyl-phen
		2958226	100.00	1045206	100.00		

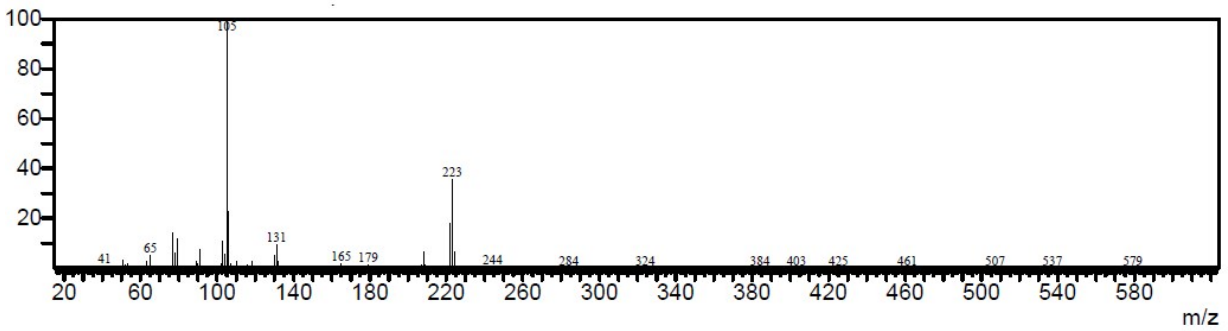
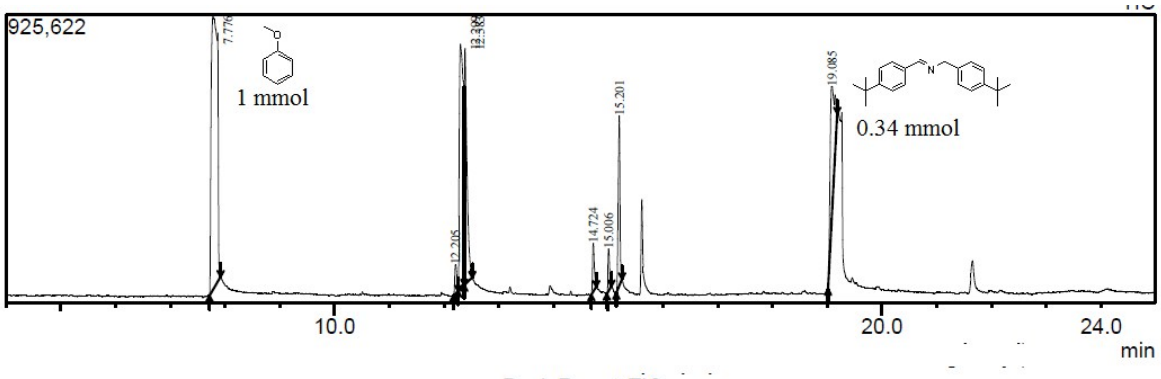


Figure S36. GC-MS for **2h**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.776	6928931	38.77	883968	23.50	7.84	Anisole
2	12.205	229780	1.29	91813	2.44	2.50	4-t-Butylbenzonitrile
3	12.299	4025532	22.52	784086	20.84	5.13	benzenamine, 4-(2-methylbutyl)-
4	12.383	2479627	13.87	755904	20.10	3.28	Benzenamine, 4-(cyclopropylmethyl)-
5	14.724	343215	1.92	155984	4.15	2.20	4-t-Butylbenzamide
6	15.006	275254	1.54	134292	3.57	2.05	3,4-Dihydrocoumarin, 7,8-dimethyl-
7	15.201	1300314	7.28	544827	14.48	2.39	4-tert-Butylbenzylamine, N-acetyl-
8	19.085	2290466	12.82	410696	10.92	5.58	4-(tert-butyl)benzyl)-1-(4-(tert-butyl)phenyl))-
		17873119	100.00	3761570	100.00		

Line#:8 R.Time:19.085(Scan#:3018)
MassPeaks:342
RawMode:Averaged 19.080-19.090(3017-3019) BasePeak:147(89990)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

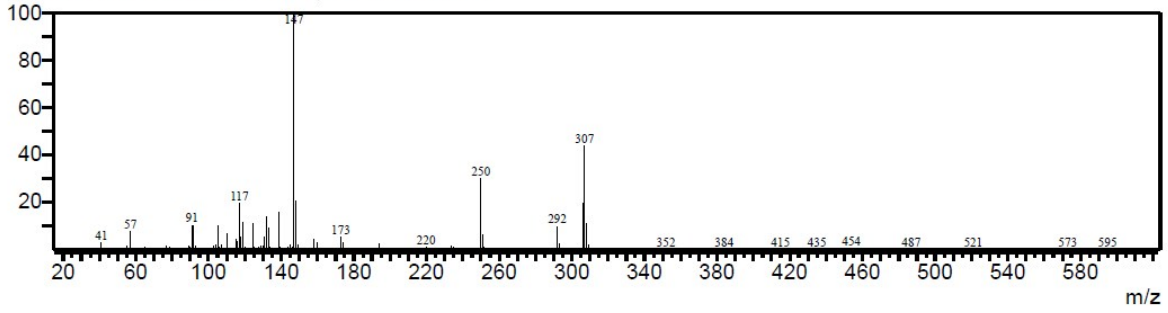
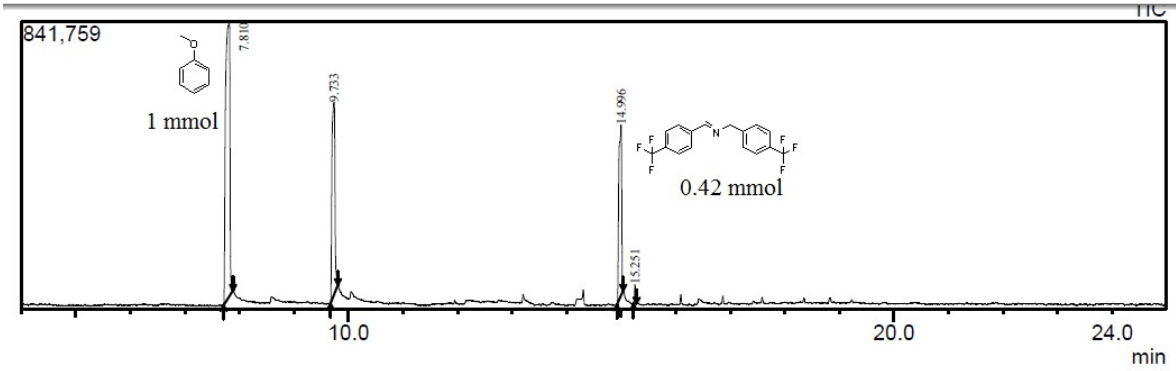


Figure S37. GC-MS for **2i**.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.810	4502289	52.65	803758	41.85	5.60	Anisole
2	9.733	2104840	24.62	562242	29.27	3.74	Benzenemethanamine, 3-(trifluoromethyl)-
3	14.996	1874426	21.92	498585	25.96	3.76	Benzeneacetic acid, 3-(trifluoromethyl)-
4	15.251	69294	0.81	56057	2.92	1.24	4-(trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)
		8550849	100.00	1920642	100.00		

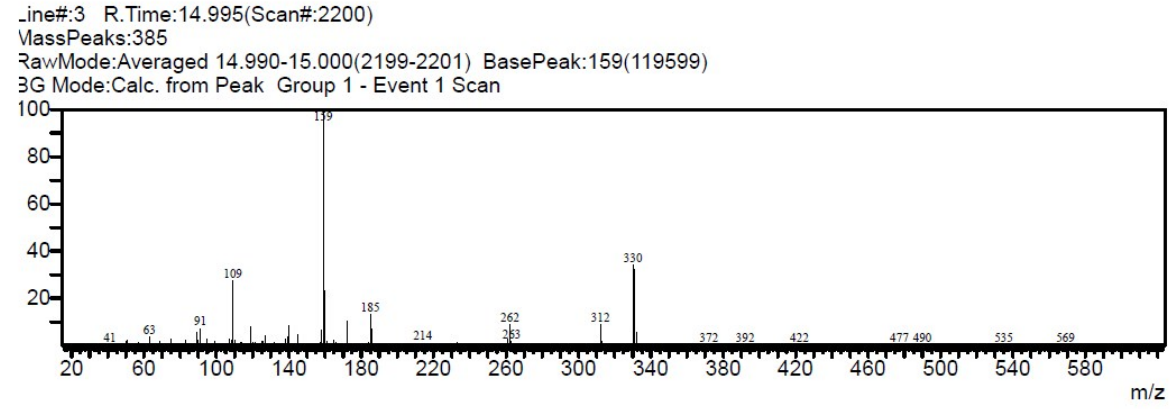


Figure S38. GC-MS for **2j**.

Table S1. Crystallographic data for complexes **[Mn]-1** and **[Mn]-2**.

	[Mn]-1	**[Mn]-2**
Formulae	$C_{23}H_{30}MnN_4O_4$	$C_{24}H_{32}MnN_4O_5$
Molecular weight	481.45	511.47
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Temperature/K	293	293
Wavelength	0.71073	0.71073
a/Å	8.8681(13)	9.1830(5)
b/Å	9.0206(14)	9.2736(5)
c/Å	16.558(2)	16.6245(10)
α/°	79.765(13)	82.388(5)

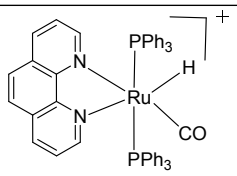
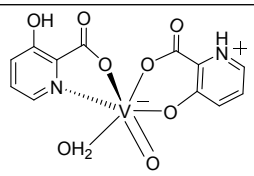
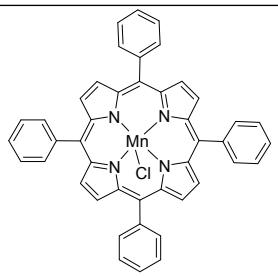
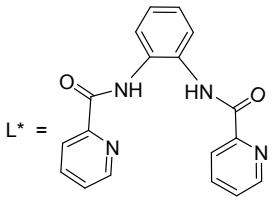
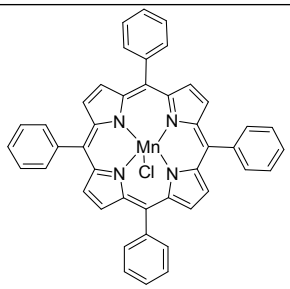
β/°	77.487(13)	75.759(5)
γ/°	68.120(14)	67.089(5)
V/ Å^3	1193.1(3)	1262.91(13)
Z	2	2
Density/gcm^{-1}	1.340	1.354
Absorption Coefficient	0.589	0.563
Absorption Correction	Multi-scan	Multi-scan
F(000)	506	538.88
Total no of reflections	4310	5752
Reflections, $I>2\sigma(I)$	2735	4683
Max. 2θ/°	25.25	28.89
Ranges (h, k, l)	-10≤ h ≤10	-21≤ h ≤33
	-10≤ k ≤10	-8≤ k ≤153
	-19≤ l ≤17	-9≤ l ≤10
Complete to 2θ(%)	99.8	99.8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goof (F^2)	1.111	1.062
R indices [$I>2\sigma(I)$]	0.0768	0.0563
R Indices (all data)	0.1149	0.0698

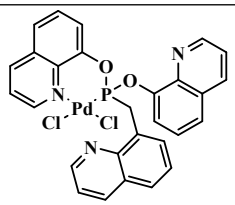
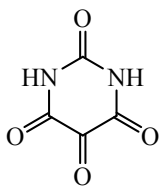
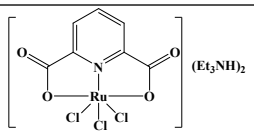
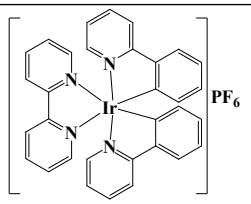
Table S2. Selected bond parameters of complexes **[Mn]-1** and **[Mn]-2**.

	[Mn]-1	**[Mn]-2**
Bond lengths (Å)		
Mn1-N1	2.158(4)	2.156(2)
Mn1-N3	2.164(4)	2.175(2)
Mn1-O1	2.178(4)	2.141(2)

Mn1-O3	2.060(4)	2.073(2)
Bond angles (°)		
O3-Mn1-N3	127.79(16)	107.40(9)
O3-Mn1-N1	111.64(15)	129.66(10)
N3-Mn1-N1	86.14(15)	87.93(8)
O3-Mn1-O1	97.76(15)	95.14(9)
N3-Mn1-O1	130.29(14)	99.18(8)
N1-Mn1-O1	95.28(15)	130.25(8)
O3-Mn1-O1	103.09(15)	95.25(10)
N1-Mn1-O1	89.80(14)	130.11(9)
O2-Mn1-O1	57.68(13)	56.99(8)

Table S3. Comparative chart showing the literature available catalysts explored for oxidative coupling of benzylamines

Catalysts	Substrate	Solvent	Air/O_2	T (°C)	t (h)	TON	TOF (h^{-1})	Ref.
CuCl	Benzyl amine	Solvent Free	air	100	18	200	11.11	S1
$CuBr_2$ + TEMPO	Benzyl amine	CH_3CN/H_2O	air	25	12	40	3.33	S2
	Benzyl amine	TEMPO (20%) in Toluene	O_2 (1 atm)	90	24	49	2.04	S3
	Benzyl amine	Ionic liquid	O_2 (1 atm)	120	6	40	6.66	S4
$CuPF_6^-$	Benzyl amine	CH_3CN	O_2 (1 atm)	rt	3	14.20	4.73	S5
	Benzyl amine	dioxane	O_2 (6 atm)	130	3	10000	3333	S6
CoL^* 	Benzyl amine	water	air	40	12	128	10.66	S7
	Benzyl amine	Toluene/ t-BuOOH	air	rt	0.25	3333	13333	S8

Au/Al_2O_3	Benzyl amine	Toluene	O_2 (1 atm)	100	24	-	-	S9
PI/CB-Pt	Dibenzylamine	$CDCl_3/H_2O$	O_2 (1 atm)	30	16	176	11	S10
Nb_2O_5	Benzyl amine	Benzene	O_2 (1 atm)	irradiation	50	13.29	0.26	S11
	Benzyl amine	Solvent Free	air	80	6	100	16.7	S12
CuCl + 	Benzyl amine	CH_3CN	air	30	3	30.4	10.13	S13
	Benzyl amine	Solvent free	air	100	10	100	10	S14
	N,N- dimethyl benzylamine	CH_3CN	air	80	1.5	82	54.66	S15

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