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Electronic supplementary information (ESI)

One-pot synthesis of imidazolinium salts *via* ring opening of tetrahydrofuran

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1. General Information

NMR spectra were recorded on Bruker DRX400 and 500 MHz NMR spectrometers. Chemical Shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent for ^1H NMR. Spectra are reported as follows: chemical shift (ppm), integration, multiplicity and coupling constant (Hz). (Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), and multiplet (m)). High resolution mass spectra were recorded at Center for Mass Spectrometry, Nanjing University. The imidazolinium salts were detected by electrospray ionization mass spectral (ESI-MS) measurements on an LCQ System (FinneganMAT, USA) using a mixing solution of methanol and water (1:1) as mobile phase. Compounds are named according to their entry number in Tables 2 and 3. All commercial chemicals were used as obtained without further purification.

X-ray diffraction measurements for complex $[HgI_2(IM1)_2][Hg_2I_6]\cdot 2H_2O$ were performed on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo-K*a* radiation (λ= 0.71075 Å) at 200 K. The structure was solved by direct method using SIR92 program and refined by the full-matrix least-square technique on F^2 with SHELXL-2016/6 program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms except for the ones of water molecules were generated geometrically and refined using a riding model. Details of the crystal parameters, data collection and refinements are summarized in Table S1. Selected bond lengths and angles are listed in Table S2.

CCDC 1028664.

2. Experimental Procedures and Compound Characterizations

2.1 General Procedure for the Preparation of DiSchiff-Base

To diamine (15 mmol) in dry 120 mL ethanol was added the corresponding aldehyde (30 mmol). The reaction mixture was stirred and refluxed for 24 hours. The solid products were directly filtered and rinsed with cold ethanol and heptanes, which were further purified by recrystallization in the ethanol. For *N*,*N'*-dibenzylideneethane-1,2-diamine, the solid products were obtained by distilling the ethanol off, which were further purified by recrystallization in the petroleum ether (60 ~ 90 ℃).

***N*,*N'*-Dibenzylideneethane-1,2-diamine**

Prepared according to the above general procedure in 91% yield as a yellow solid.

***N*,*N'*-Di(4-methylbenzylidene)ethane-1,2-diamine**

Prepared according to the above general procedure in 92% yield as a white solid.

***N*,*N'*-Bis(4-cyanobenzylidene)ethane-1,2-diamine**

Prepared according to the above general procedure in 87% yield as a white solid.

***N,N'*-Bis(4-hydroxybenzylidene)ethane-1,2-diamine**

Prepared according to the above general procedure in 95% yield as a white solid.

***N,N'*-Bis(4-methoxybenzylidene)ethane-1,2-diamine**

Prepared according to the above general procedure in 83% yield as a yellow solid.

***N,N'*-Bis(4-dimethylaminobenzylidene)ethane-1,2-diamine**

Prepared according to the above general procedure in 92% yield as a light yellow solid.

2.2 Procedure for the Preparation of TetrahydrodiSchiff-Base

The above-mentioned dischiff-base (20 mmol) was dissolved in a mixture of methanol (15 mL) and dichloromethane (10 mL). Then, the $NaBH_4$ (92 mmol) was added gradually over 1 h. The mixture was stirred until TLC showed the reaction to be complete. After the completion of the reaction, the solvent was distilled off under reduced pressure and the residue diluted with water and extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4, filtered to remove inorganic salt and distilled to give the expected compound.

***N,N'*-Bis[4-(oxazolin-2-yl)benzyl]ethane-1,2-diamine (**DAM1**)**

10 mmol of DAM**7** is heated with 30 mmol of amino alcohol and 1 mmol of $ZnCl_2$ catalyst in the chlorobenzene (100 ml) under reflux. The mixture was stirred until TLC showed the reaction to be complete. After the completion of the reaction, the solvent was distilled off under reduced pressure and the residue diluted with water and extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4, filtered to remove inorganic salt and distilled to give a yellow solid with 37% yield.

***N,N'*-Dibenzylethane-1,2-diamine (**DAM5**)**

Prepared according to the above general procedure in 88% yield as a yellow liquid.

***N,N'*-Bis(4-methylbenzyl)ethane-1,2-diamine (**DAM6**)**

Prepared according to the above general procedure in 84% yield as a yellow solid.

***N,N'*-Bis(4-cyanobenzyl)ethane-1,2-diamine (**DAM7**)**

Prepared according to the above general procedure in 81% yield as a yellow solid.

***N,N'*-Bis(4-hydroxybenzyl)ethane-1,2-diamine (**DAM8**)**

Prepared according to the above general procedure in 91% yield as a white solid.

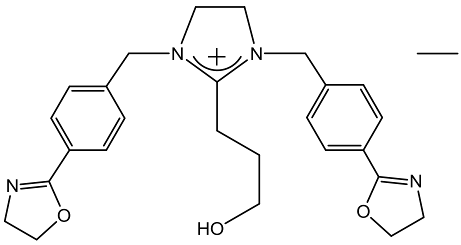
***N,N'*-Bis(4-methoxybenzyl)ethane-1,2-diamine (**DAM9**)**

Prepared according to the above general procedure in 91% yield as a white solid.

***N,N'*-Bis(4-dimethylaminobenzyl)ethane-1,2-diamine (**DAM10**)**

Prepared according to the above general procedure in 91% yield as a white solid.

Imidazolinium and tetrahydropyrimidinium Salts:



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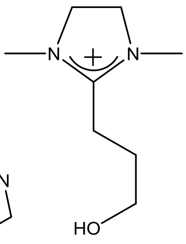

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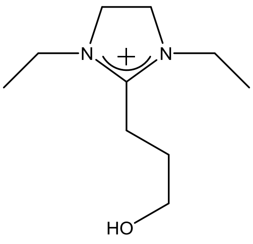

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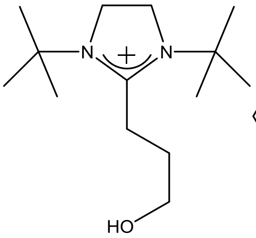

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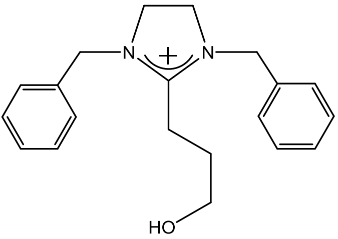

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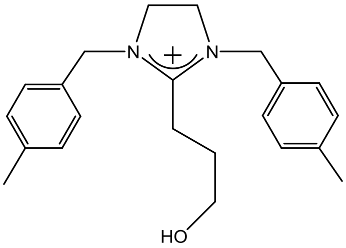

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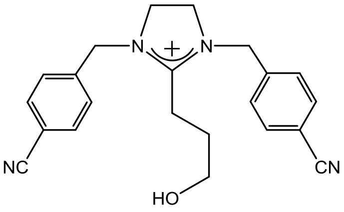

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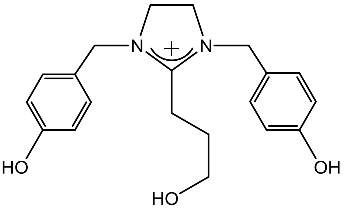

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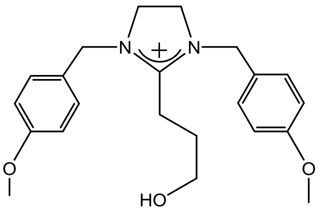

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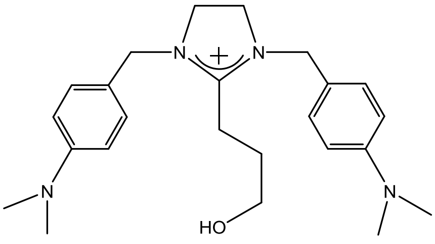

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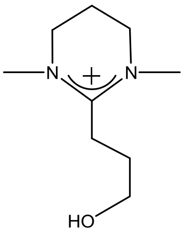

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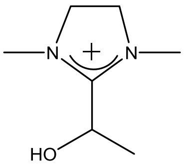

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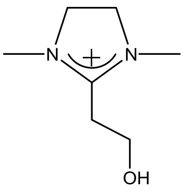

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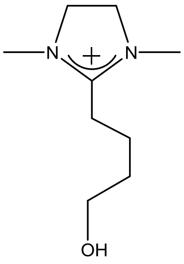

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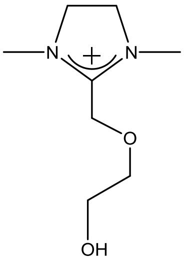

IM15

2.3 General Procedure for the Preparation of Imidazolinium Salts

0.2 mmol DAM and 0.4 mmol HgI_2 were dissolved in the corresponding cyclic ether and then, the mixture was sealed in the pressure-resistant 30 ml Teflon-lined autoclave and heated at 100 ℃ for 12 hours. It is worth mentioning that the reactions in different gas atmosphere were carried out in the 50 ml glass Schlenk tube at 80 ℃ for safety.

IM1

Prepared according to the above general procedure in 55% yield as a yellow solid. ESI-MS: m/z = 447.3. HRMS (EI) m/z calcd for $C_{26}H_{31}N_4O_3$ $[M]^+$: 447.2391; found: 447.2394.

^{1}H NMR (500 MHz, DMSO): 7.92 (d, *J* = 10.5 Hz, 4H), 7.52 (d, *J* = 10.5 Hz, 4H), 4.84 (s, 4H), 4.42 (t, *J* = 12.0 Hz, 4H), 3.98 (t, *J* = 12.0 Hz, 1H), 3.72 (s, 4H), 3.48 – 3.52 (m, 2H), 2.91 (t, *J* = 9.0 Hz, 2H), 1.66 – 1.73 (m, 2H). ^{13}C NMR (500 MHz, DMSO): 169.19, 162.59, 137.40, 128.21, 128.07, 127.33, 67.48, 59.22, 54.43, 49.66, 47.49, 28.68, 20.39.

IM2

Prepared according to the above general procedure in 78% yield as a yellow solid. ESI-MS: m/z 157.17. HRMS (EI) m/z calcd for $C_8H_{17}N_2O$ $[M]^+$: 157.1335; found: 157.1335. ^{1}H NMR (400 MHz, DMSO): 3.80 (s, 4H), 3.48 (t, *J* = 5.8 Hz, 2H), 3.09 (s, 6H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.71 – 1.64 (m, 2H). ^{13}C NMR (500 MHz, DMSO): 167.88, 59.07, 49.20, 33.58, 27.42, 19.86.

IM3

Prepared according to the above general procedure in 66% yield as a yellow solid. ESI-MS: m/z = 185.33. HRMS (EI) m/z calcd for $C_{10}H_{21}N_2O$ $[M]^+$: 185.1648; found: 185.1649. ^{1}H NMR (400 MHz, DMSO): 3.83 (s, 4H), 3.46 – 3.52 (m, 6H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.62 – 1.69 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (500 MHz, DMSO): 167.01, 59.13, 46.21, 41.00, 28.35, 19.80, 12.82.

IM5

Prepared according to the above general procedure in 74% yield as a yellow solid. ESI-MS: 309.42. HRMS (EI) m/z calcd for $C_{20}H_{25}N_2O$ $[M]^+$: 309.1961; found: 309.1963. ^{1}H NMR (500 MHz, DMSO): δ7.39 – 7.46 (m, 10H), 4.78 (s, 4H), 3.71 (s, 4H), 3.54 (t, *J* = 5.5 Hz, 2H), 2.94 (t, *J* = 7.8 Hz, 2H), 1.75 (m, 2H). ^{13}C NMR (500 MHz, DMSO): 168.60, 133.69, 128.85, 128.20, 127.87, 59.19, 49.90, 47.24, 28.71, 20.34.

IM6

Prepared according to the above general procedure in 53% yield as a yellow solid. ESI-MS: 337.50. HRMS (EI) m/z calcd for $C_{22}H_{29}N_2O$ $[M]^+$: 337.2274; found: 337.2278. ^1H NMR (400 MHz, DMSO): δ 7.23 – 7.30 (m, 8H), 4.70 (s, 4H), 3.66 (s, 4H), 3.54 (m, 2H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.32 (s, 6H), 1.71 – 1.79 (m, 2H). ^{13}C NMR (500 MHz, DMSO): 168.24, 137.47, 130.56, 129.37, 127.92, 59.17, 49.64, 47.07, 28.73, 20.82, 20.29.

IM8

Prepared according to the above general procedure in 41% yield as a yellow solid. ESI-MS: m/z =341.25. HRMS (EI) m/z calcd for $C_{20}H_{25}N_2O_3$ $[M]^+$: 341.1860; found: 341.1860. ^1H NMR (400 MHz, DMSO): 7.19 (d, *J* = 8.6 Hz, 4H), 6.79 (d, *J* = 8.5 Hz, 4H), 4.60 (s, 4H), 3.61 (s, 4H), 3.54 (t, *J* = 5.7 Hz, 2H), 2.92 (t, *J* = 8.0 Hz, 2H), 1.71 – 1.79 (m, 2H). ^{13}C NMR (500 MHz, DMSO): 167.81, 157.35, 129.65, 123.59, 115.57, 59.26, 49.47, 46.85, 28.80, 20.26.

IM9

Prepared according to the above general procedure in 51% yield as a yellow solid. ESI-MS: m/z =369.33. HRMS (EI) m/z calcd for $C_{22}H_{29}N_2O_3$ $[M]^+$: 369.2173; found: 369.2176. ^1H NMR (400 MHz, DMSO): 7.32 (d, *J* = 8.7 Hz, 4H), 6.97 (d, *J* = 8.7 Hz, 4H), 4.66 (s, 4H), 3.75 (s, 6H), 3.63 (s, 4H), 3.55 (t, *J* = 5.7 Hz, 2H), 2.94 (t, *J* = 7.8 Hz, 2H), 1.71 – 1.82 (m, 2H). ^{13}C NMR (500 MHz, DMSO): 167.91, 159.07, 129.59, 125.37, 114.21, 59.22, 55.29, 49.35, 46.91, 28.78, 20.78, 20.30.

TP11

Prepared according to the above general procedure in 82% yield as a yellow solid. ESI-MS: m/z= 171.25. HRMS (EI) m/z calcd for $C_9H_{19}N_2O$ $[M]^+$: 171.1492; found: 171.1491. ^1H NMR (400 MHz, DMSO): 4.75 (t, *J* = 5.0 Hz, 1H), 3.50 (dd, J_1 = 11.0, J_2 = 5.4 Hz, 2H), 3.42 (t, *J* = 5.8 Hz, 4H), 3.21 (s, 6H), 2.69 (t, *J* = 8.2 Hz, 2H), 1.96 – 2.02 (m, 2H), 1.65 – 1.72 (m, 2H). ^{13}C NMR (500 MHz, DMSO): 163.83, 59.05, 47.95, 40.33, 27.60, 25.07, 18.59.

IM14

Prepared according to the above general procedure in 63% yield as a yellow solid. ESI-MS: m/z= 171.33. HRMS (EI) m/z calcd for $C_9H_{19}N_2O$ $[M]^+$: 171.1492; found: 171.1491. ^1H NMR (400 MHz, DMSO): 3.81 (s, 4H), 3.45 (t, *J* = 5.6 Hz, 2H), 3.09 (s, 6H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.53 – 1.57 (m, 4H). ^{13}C NMR (500 MHz, DMSO): 167.99, 59.86, 49.37, 33.43, 31.24, 22.48, 21.43.

2.4 General procedure for the catalysed aza-Diels-Alder reaction in acetonitrile

N-Benzylideneaniline (0.2 mmol) and the imidazolinium salt catalyst in Table 6 (0.02 mmol, 10 mol%) were placed into a Schlenk flask under nitrogen. The reaction mixture was dissolved in dry acetonitrile (2 ml) and Danishefsky's diene (0.2 mmol) was added. After 18 h stirring at room temperature, the mixture was distilled off under reduced pressure. TLC (PE-EtOAc, 1:2) gave the desired product.

3. References

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(4) Kouznetsov, V. V.; Amado, D. F.; Bahsas, A.; Amaro-Luis J. **2006**, *43*, 447.
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4. Tables and Schemes

Crystal data of $[HgI_2(IM1)_2][Hg_2I_6]\cdot 2H_2O$ are listed in Tables S1 and S2.

Table S1. Crystal data and refinement results for complex $[HgI_2(IM1)_2][Hg_2I_6]\cdot 2H_2O^a$

Compound	$[HgI_2(IM1)_2][Hg_2I_6]\cdot 2H_2O$
Empirical formula	$C_{52}H_{66}Hg_3I_8N_8O_8$
Formula weight	2548.09
Crystal system	monoclinic
Space group	$C2/c$
a /Å	16.055(6)
b /Å	20.351(9)
c /Å	22.103(7)
β / °	96.976(12)
V (Å^3)	7168(5)
Z	4
Dc (g cm^{-3})	2.361
μ (mm^{-1})	9.905
F(000)	4648
$2\theta_{max}$ / °	50
Reflns. collected	24896
Independent reflns.	6280
R_{int}	0.0646
Parameters refined	389
Goodness-of-fit	1.166
R_1, wR_2[a] ($I > 2\sigma(I)$)	0.0912, 0.2039
R_1, wR_2[a] (all data)	0.1109, 0.2116

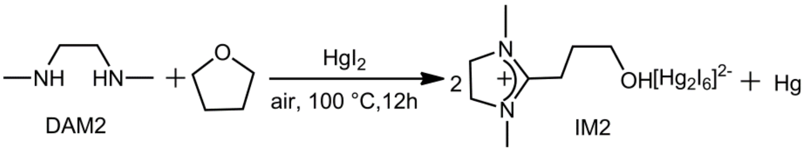
^{a} $R_1 = \Sigma||Fo| - |Fc||/|Fo|$; $wR_2 = [\Sigma w(\Sigma Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$.

Table S2. Selected bond lengths [Å] and angles [°] for $[HgI_2(IM1)_2][Hg_2I_6]\cdot 2H_2O^a$

Hg(1)-I(1)	2.687(2)	Hg(1)-I(2)	2.7278(19)
Hg(1)-I(3)	2.9232(18)	Hg(1)-I(3)$^{\#1}$	2.933(2)
Hg(2)-N(201)	2.46(4)	Hg(2)-N(101)$^{\#2}$	2.60(3)
Hg(2)-I(5)	2.652(4)	Hg(2)-I(4)	2.677(4)
N(1)-C(3)	1.29(2)	N(2)-C(3)	1.31(3)
I(1)-Hg(1)-I(2)	117.83(7)	I(1)-Hg(1)-I(3)	111.42(7)
I(2)-Hg(1)-I(3)	112.80(6)	I(1)-Hg(1)-I(3)$^{\#1}$	114.24(6)
I(2)-Hg(1)-I(3)$^{\#1}$	107.91(6)	I(3)-Hg(1)-I(3)$^{\#1}$	89.07(5)
N(201)-Hg(2)-N(101)$^{\#2}$	107.9(9)	N(201)-Hg(2)-I(5)	101.5(11)
N(101)$^{\#2}$-Hg(2)-I(5)	106.4(4)	N(201)-Hg(2)-I(4)	103.7(10)
N(101)$^{\#2}$-Hg(2)-I(4)	102.0(5)	I(5)-Hg(2)-I(4)	133.52(15)

^{a} Symmetry transformation used to generate equivalent atoms: #1 -x+1/2, -y+3/2, -z+1; #2 x, -y+1, z-1/2.

Table S3. Synthesis of Imidazolinium Salt (IM2)[a,b]

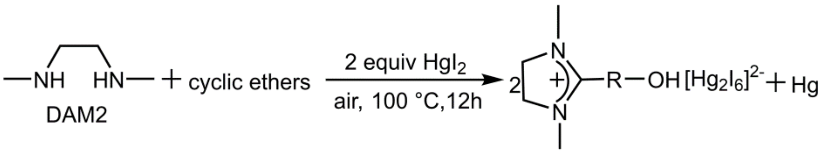


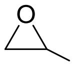
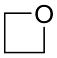
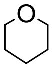
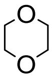
Entry	$n(HgI_2)$/mmol	Yield (%)
1	0.05	31
2	0.1	45
3	0.2	53
4	0.4	78

[a] Reactions were carried out with DAM2 (0.2 mmol), THF (8 mL) and HgI_2 with different amount at 100 °C for 12 hours.

[b] Yield determined by ^{1}H NMR spectroscopy.

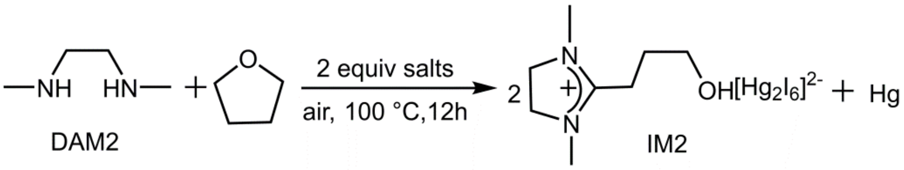
Table S4. Synthesis of imidazolinium salts using cyclic ethers[a,b]



Entry	Cyclic ethers	Product	Yield (%)
1		IM12	0
2		IM13	0
3		IM14	63
4		IM15	trace

[a] Reactions were carried out with DAM2 (0.2 mmol), cyclic ethers (8 mL) and HgI_2(0.4 mmol) at 100 ^{o}C for 12 hours.
[b] Yield determined by ^{1}H NMR spectroscopy.

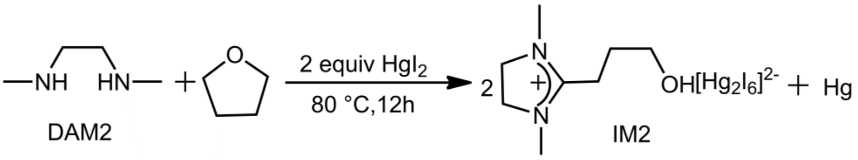
Table S5. Synthesis of imidazolinium salt (IM2) using various salts[a,b]



Entry	Salts	Yield (%)
1	NaCl	1.5
2	NaBr	2
3	$NaNO_2$	2
4	$NaNO_3$	2
5	NaOAc	0
6	$NaBF_4$	2
7	$NaClO_4$	1.5
8	NaEtBr	2

[a] Reactions were carried out with DAM2 (0.2 mmol), THF (8 mL) and various salts (0.4 mmol) at 100 °C for 12 hours.
[b] Yield determined by ^{1}H NMR spectroscopy.

Table S6. Synthesis of imidazolinium salt (IM2) under different gas atmospheres[a,b]

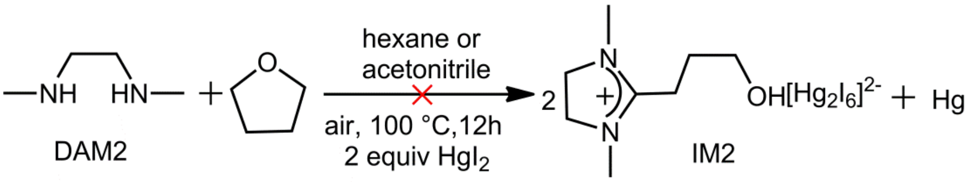


Entry	Atmosphere	Yield (%)
1	air	29
2	Ar	3
3	N_2	3
4	O_2	5
5	CO_2	3
6	O_2/CO_2 (V/V=1:1)	65
7	O_2/HOAc	18

[a] Reactions were carried out with DAM2 (0.2 mmol), THF (8 mL) and HgI_2 (0.4 mmol) in a 50 ml glass Schlenk tube at 80 °C in different atmosphere for 12 hours.

[b] Yield determined by ^1H NMR spectroscopy.

Scheme S1. Synthesis of imidazolinium salt (IM2) with 1:5 ratio of DAM2 and THF



5. ESI-MS and NMR spectra of the synthesized compounds

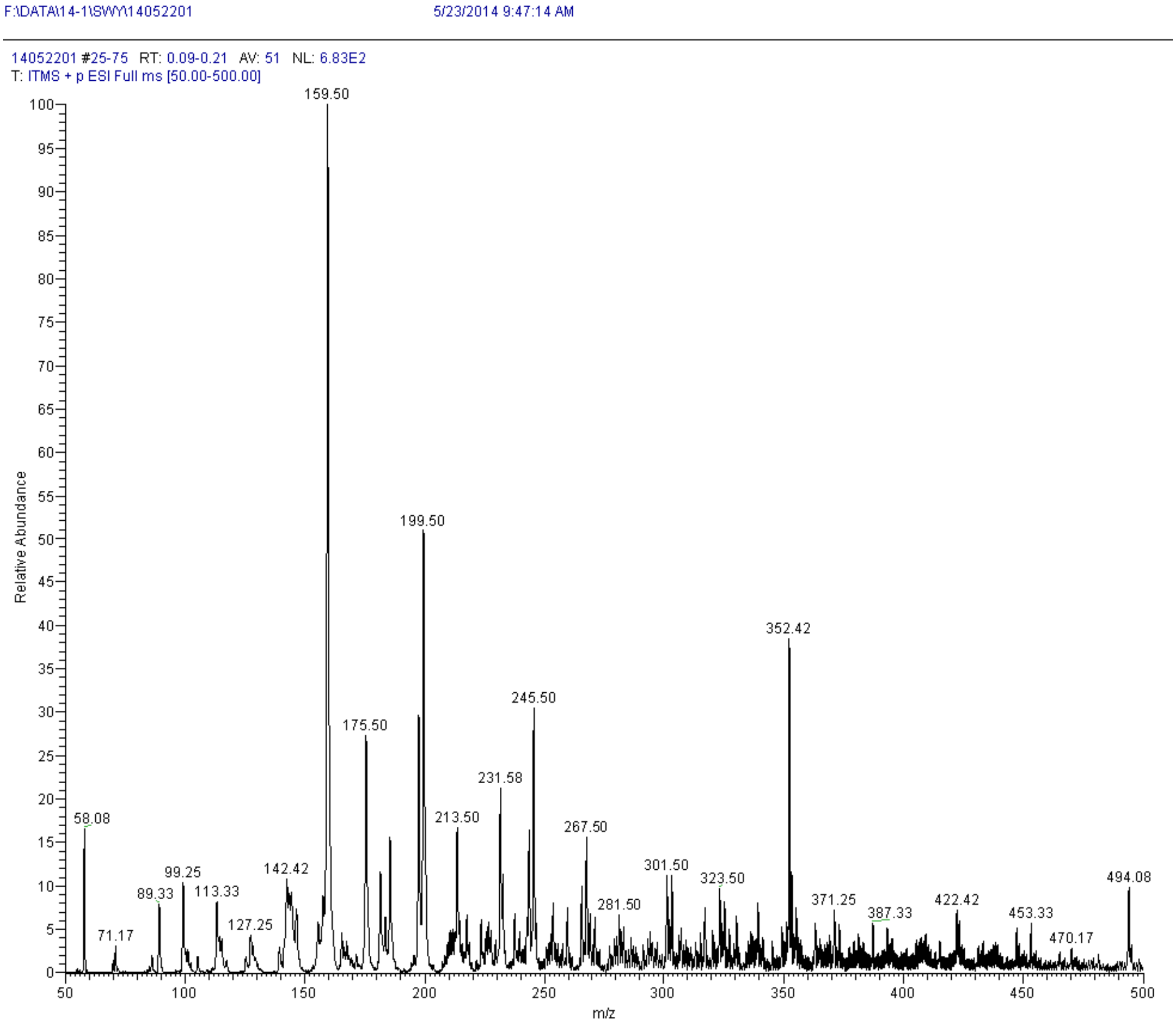


Fig. S1 ESI-MS spectrum of the reaction solution which come from the direct reaction of DAM2 and THF without any other reagents, showing the peak of imidazolidine IM 2+H^{+} (m/z = 159.50).

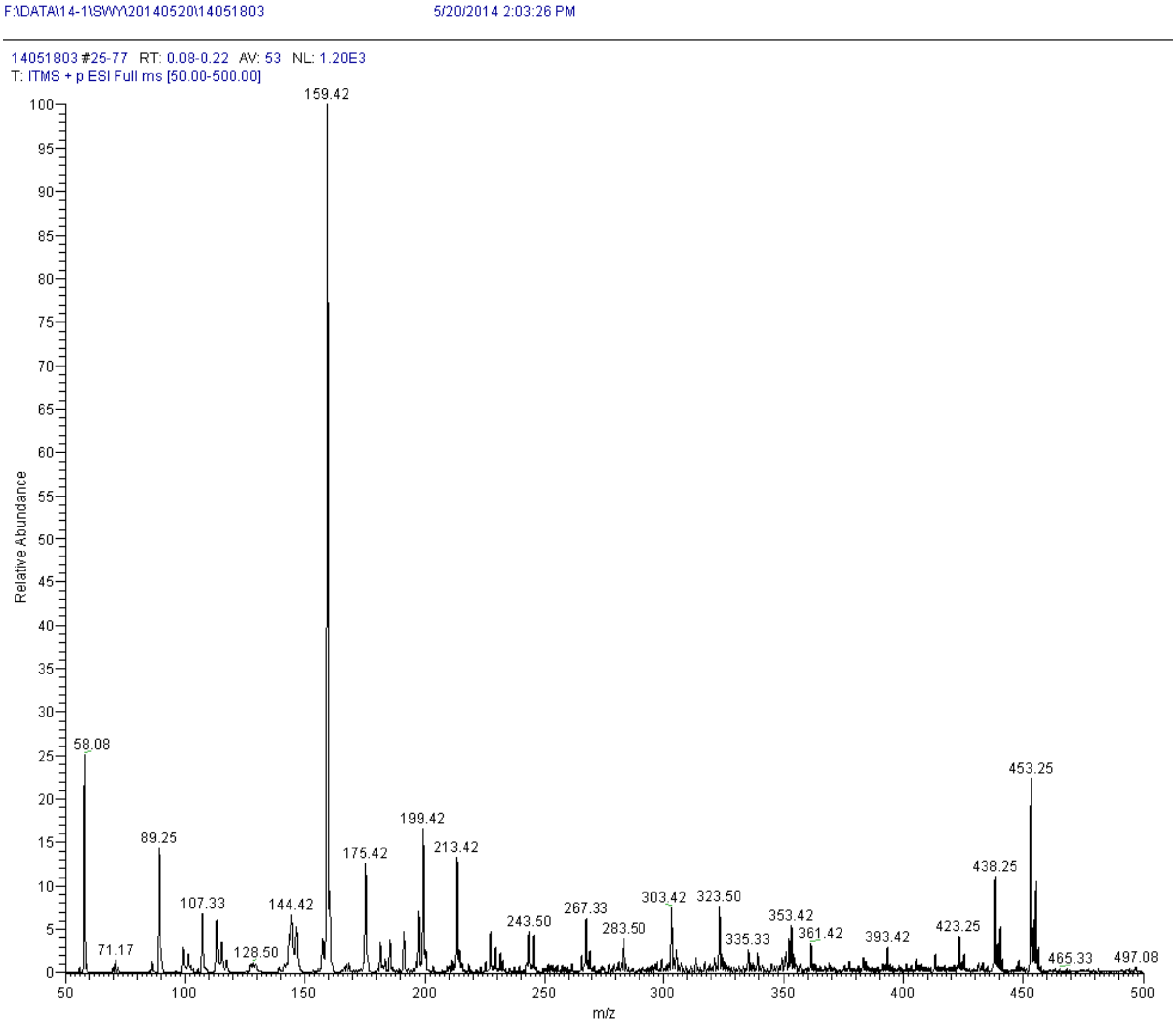


Fig. S2 ESI-MS spectrum of the reaction solution which come from the reaction of DAM2 and THF in the presence of NaOAc, showing the peak of imidazolidine IM 2+H^{+} (m/z = 159.42).

ESI-MS and NMR Spectra of the synthesized imidazolinium salts

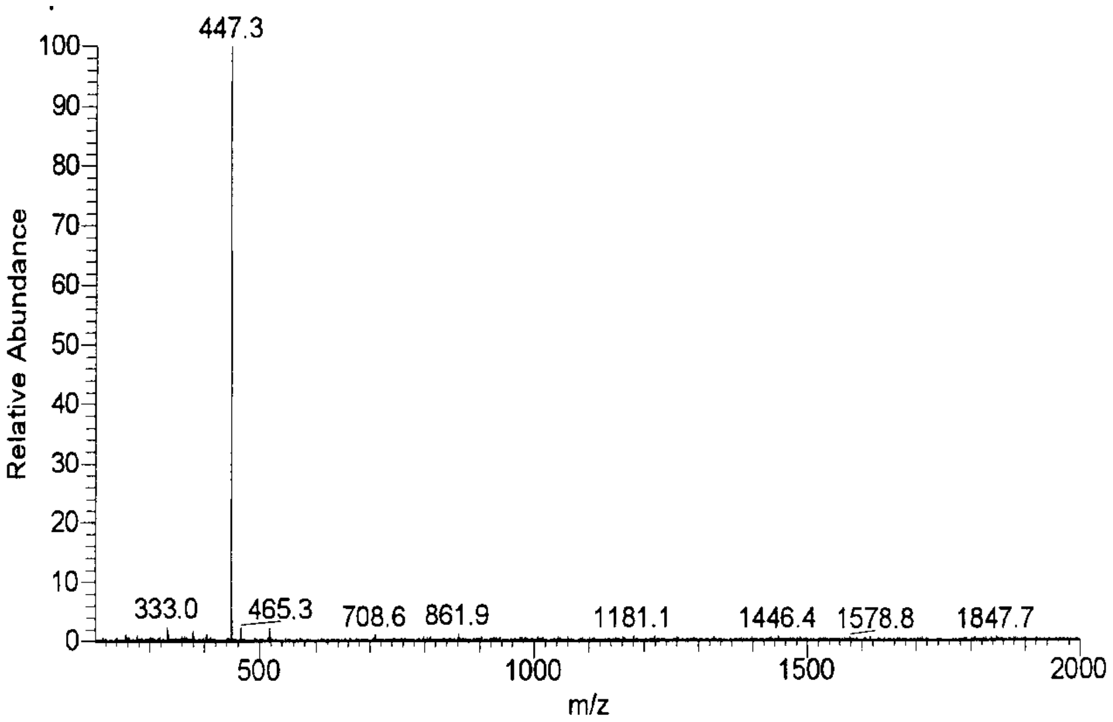


Fig. S3 ESI-MS spectrum of IM1.

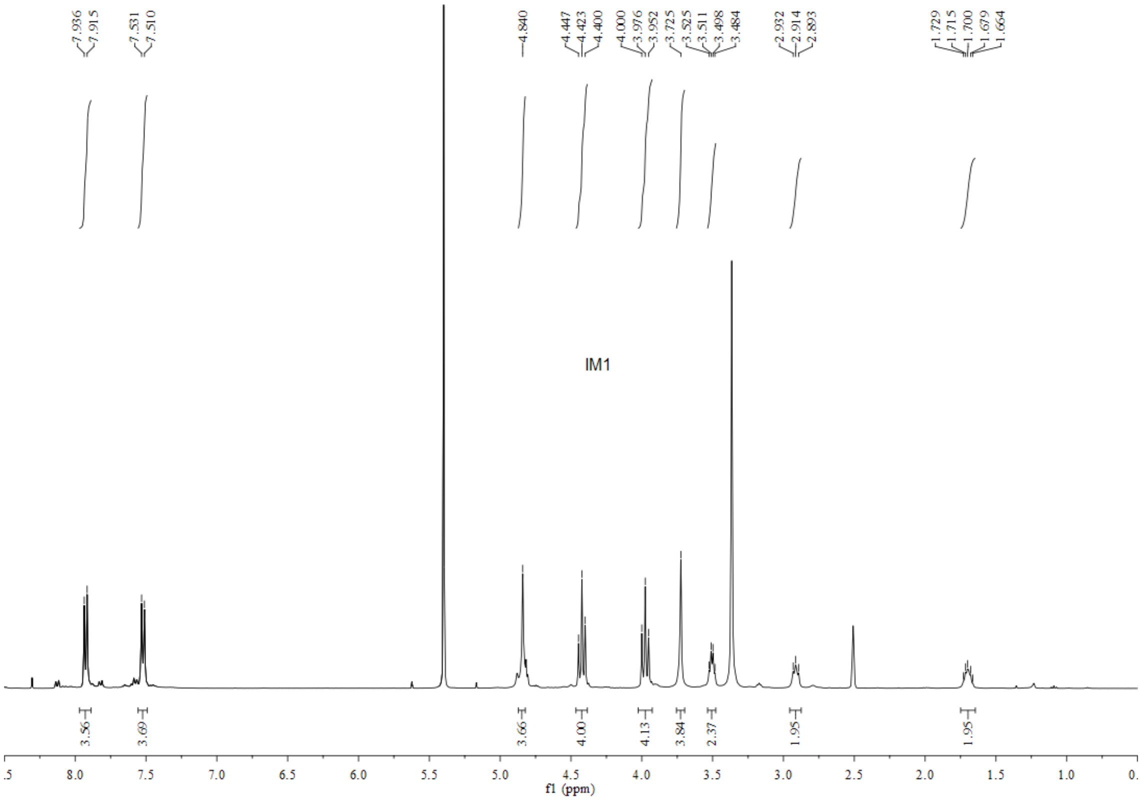


Fig. S4 ^{1}H NMR spectrum of IM1.

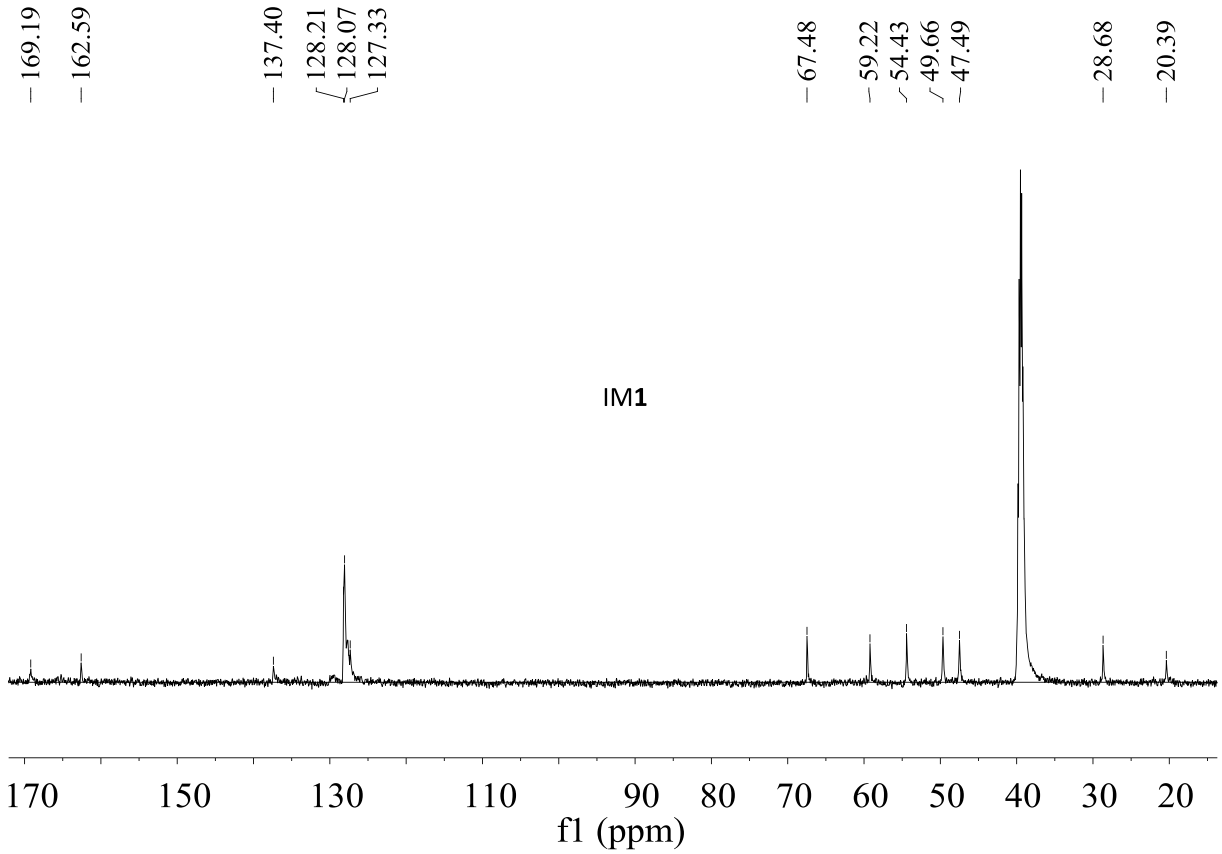


Fig. S5 ^{13}C NMR spectrum of IM1.

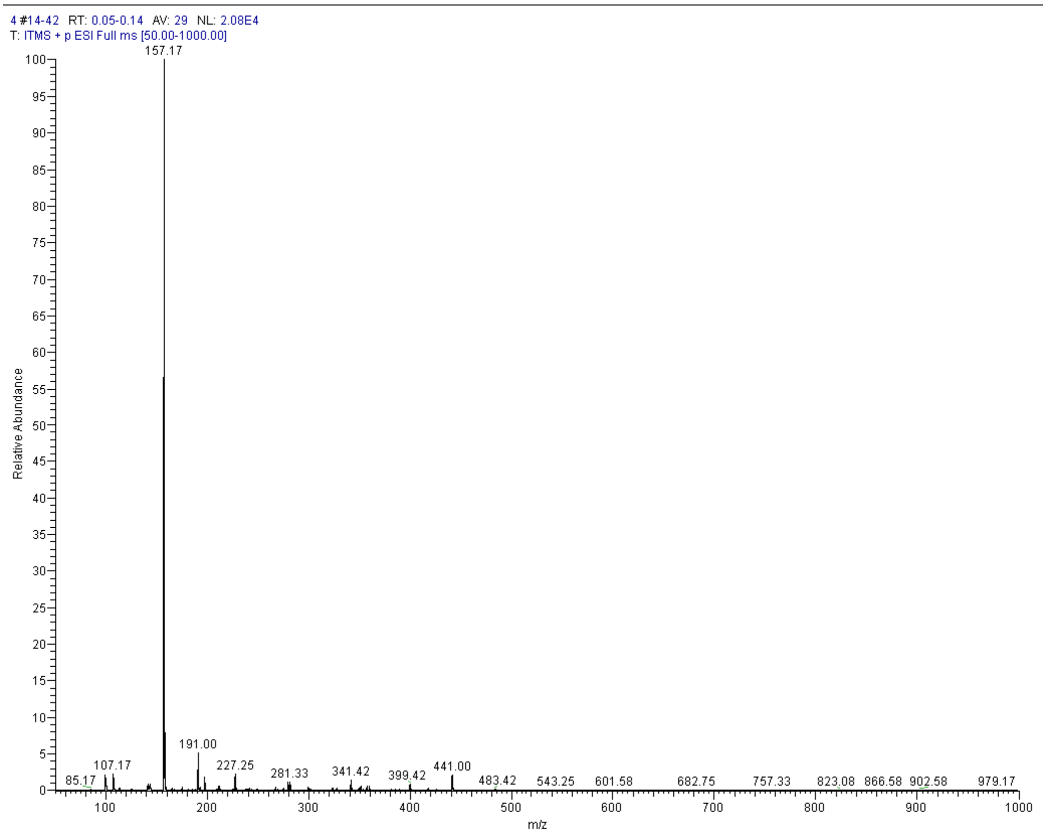


Fig. S6 ESI-MS spectrum of IM2.

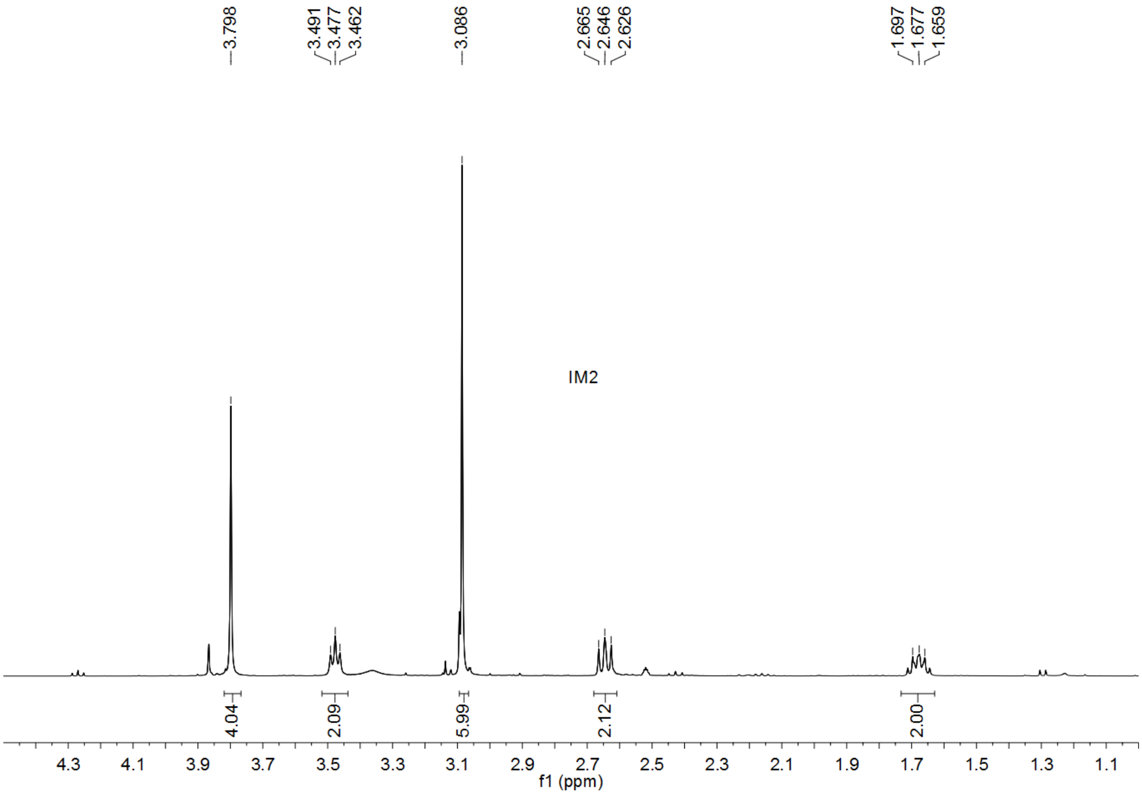


Fig. S7 ^{1}H NMR spectrum of IM2.

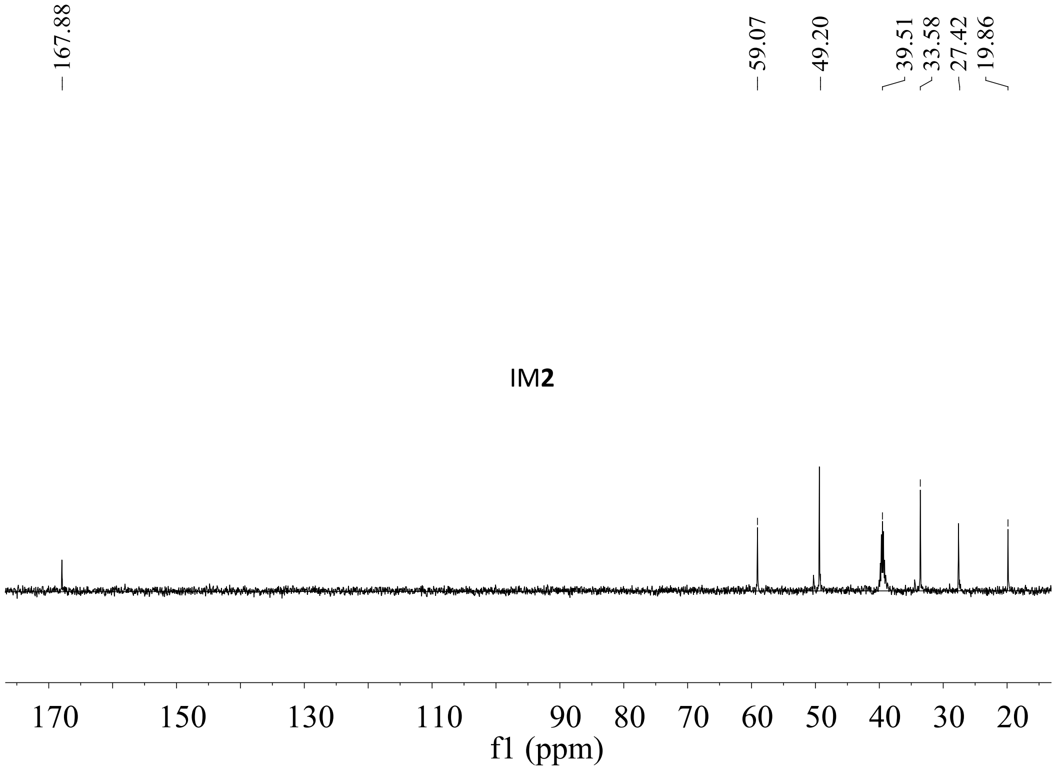


Fig. S8 ^{13}C NMR spectrum of IM2.

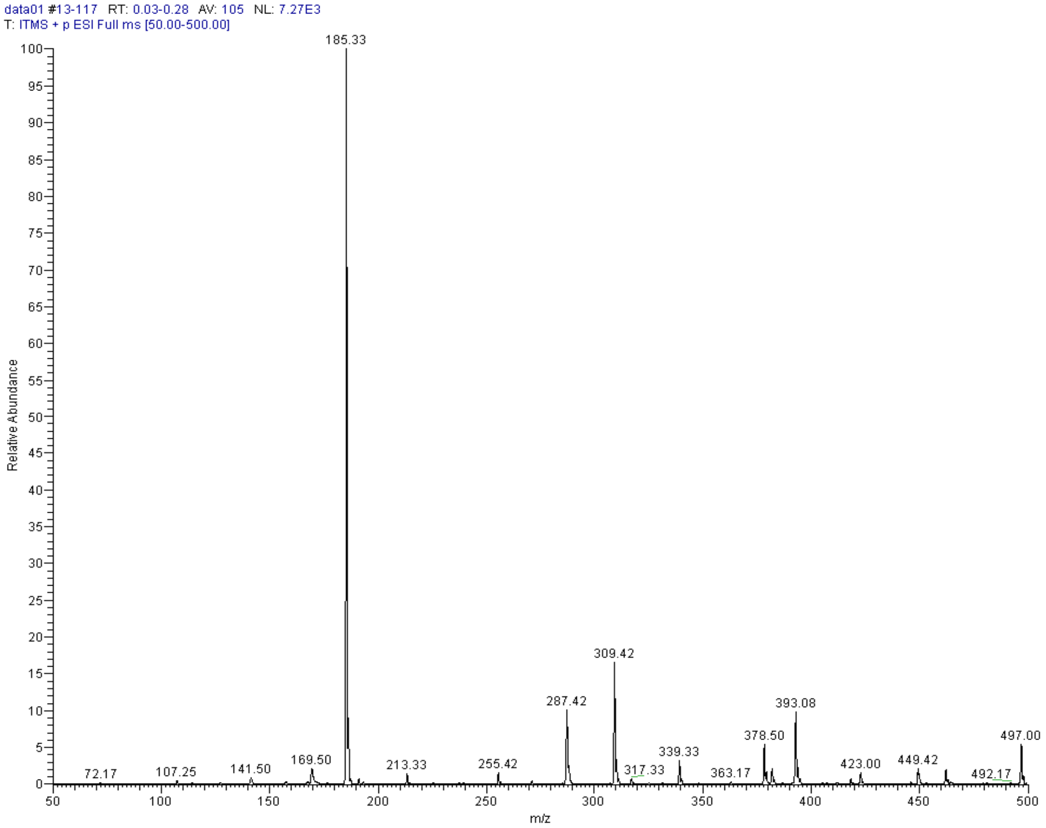


Fig. S9 ESI-MS spectrum of IM3.

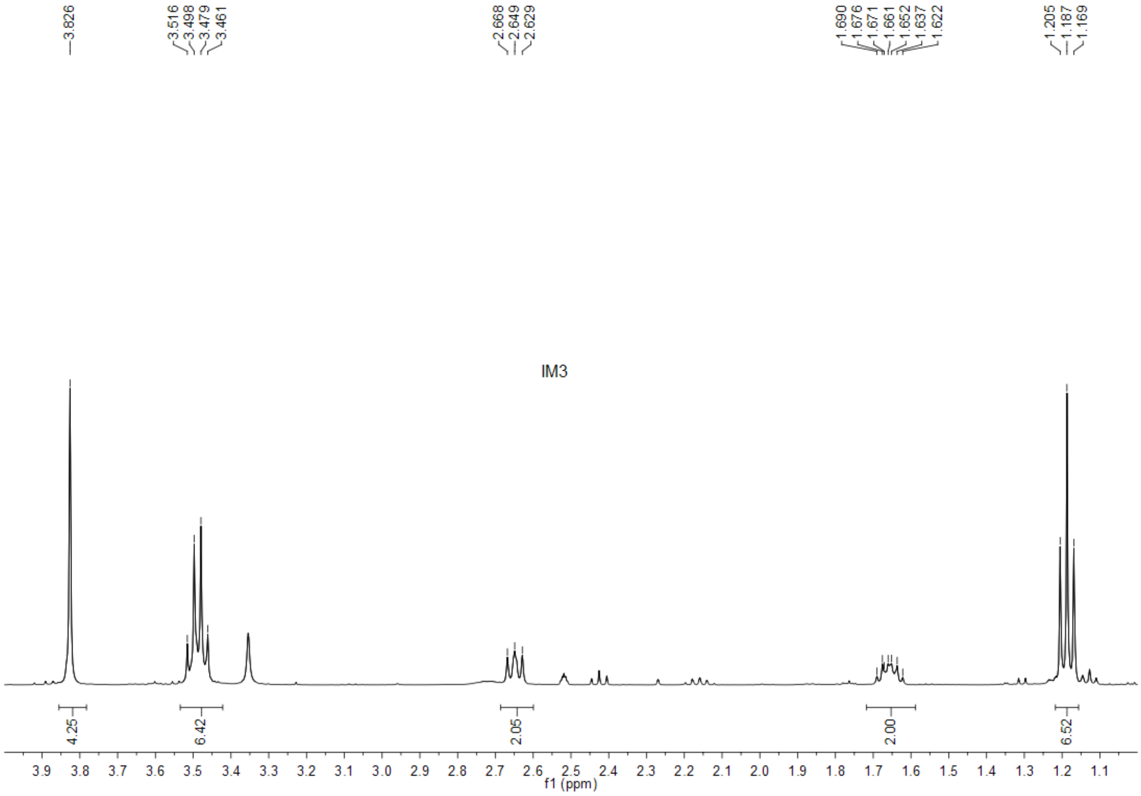


Fig. S10 ^{1}H NMR spectrum of IM3.

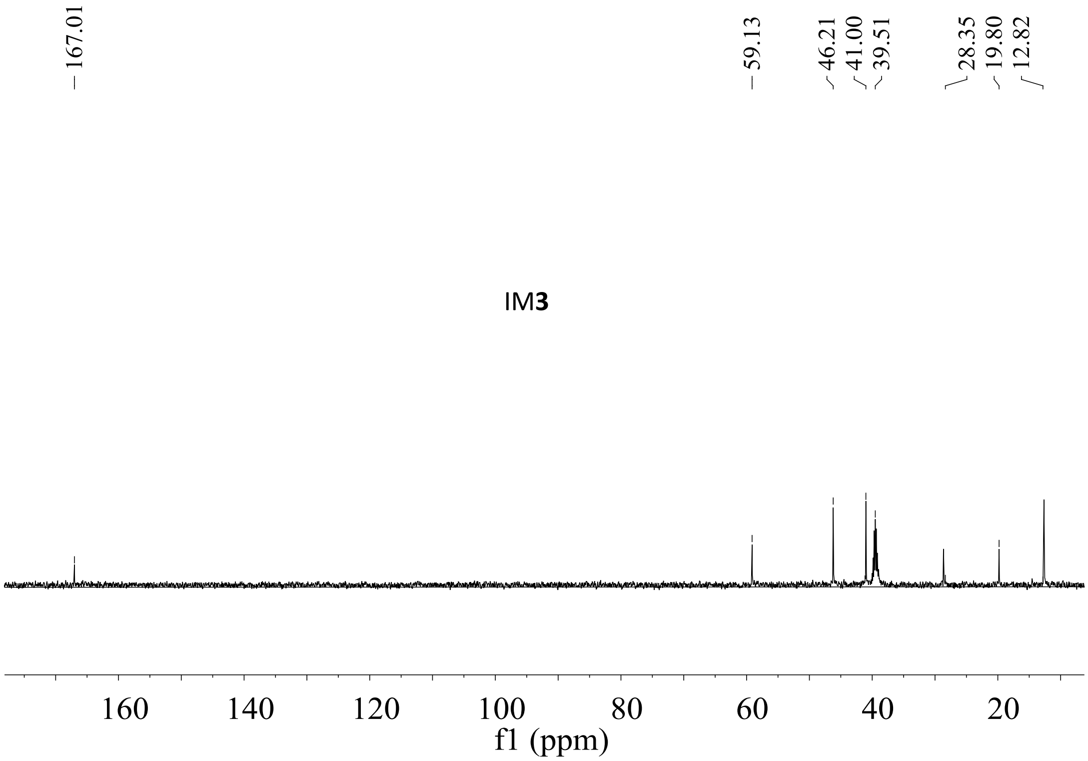


Fig. S11 ^{13}C NMR spectrum of IM3.

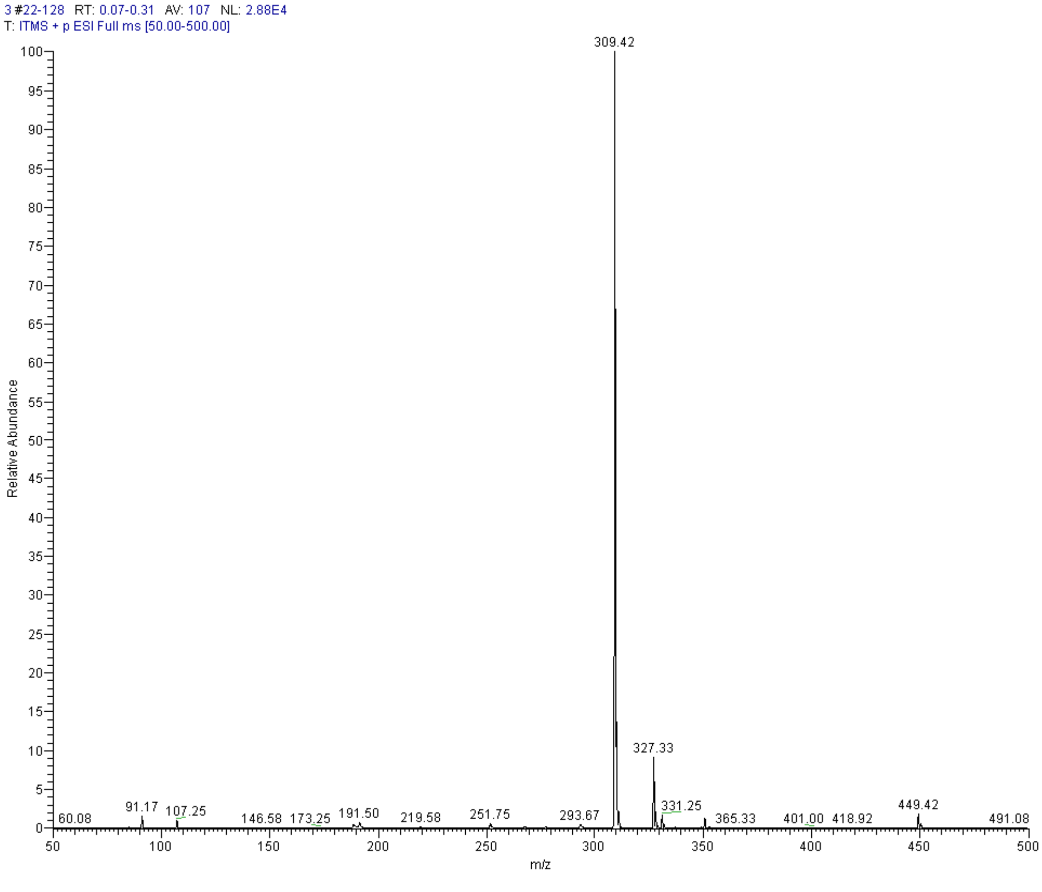


Fig. S12 ESI-MS spectrum of IM5.

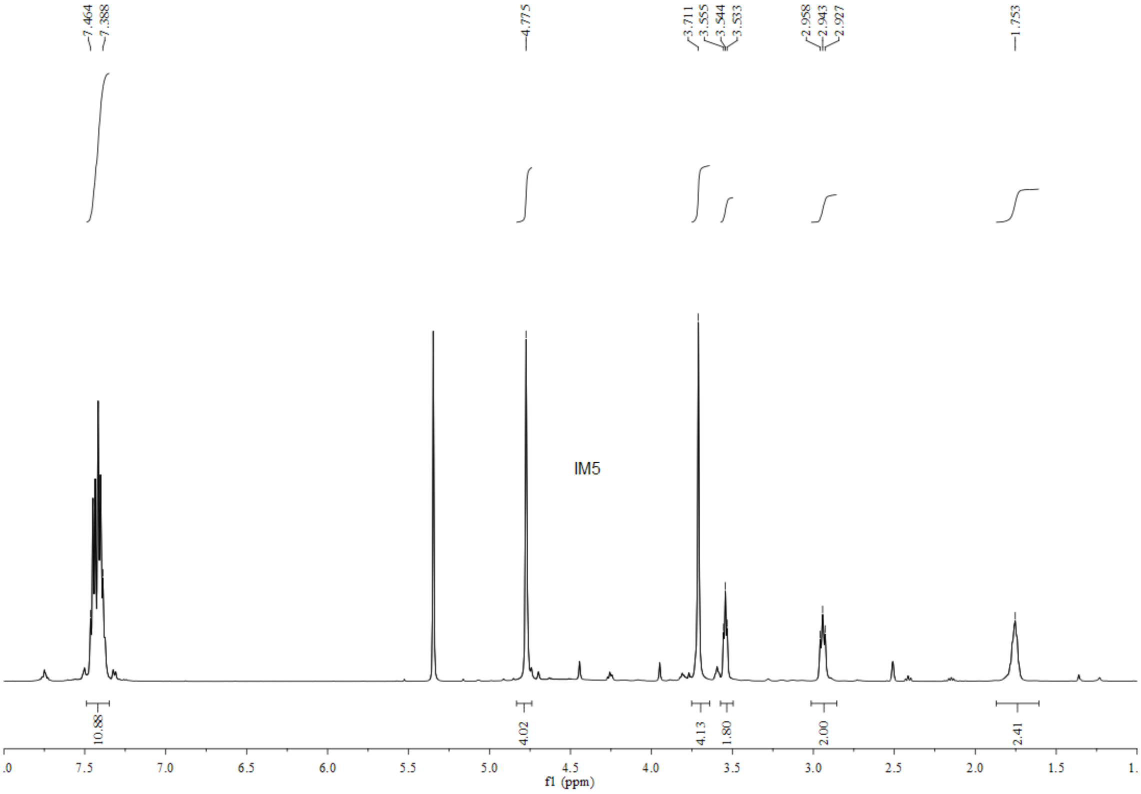


Fig. S13 ^{1}H NMR spectrum of IM5.

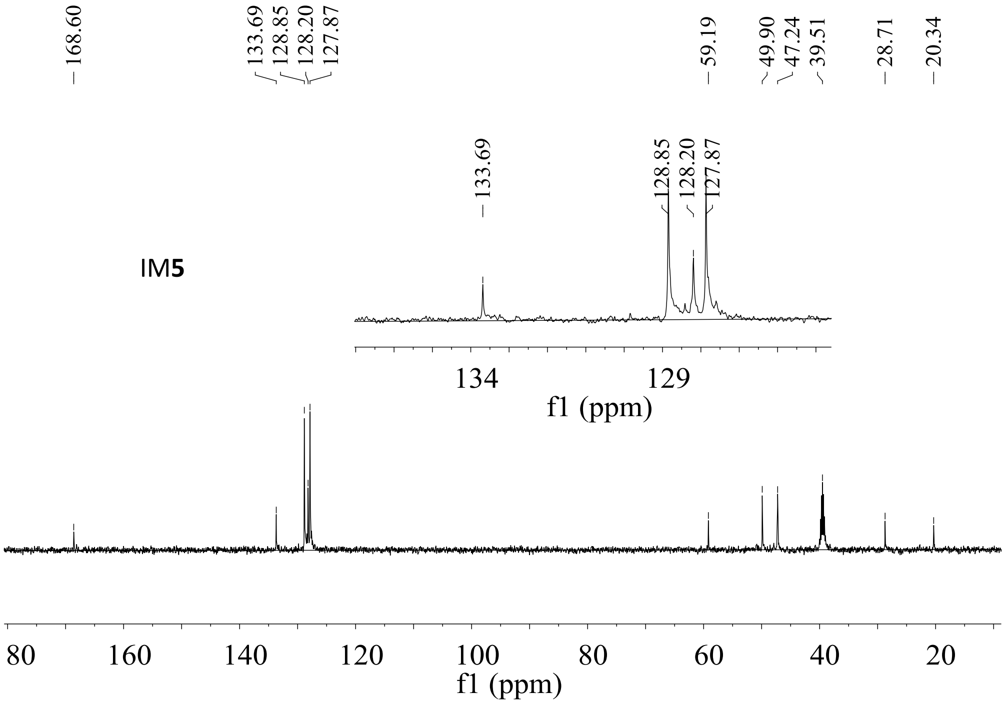


Fig. S14 ^{13}C NMR spectrum of IM5.

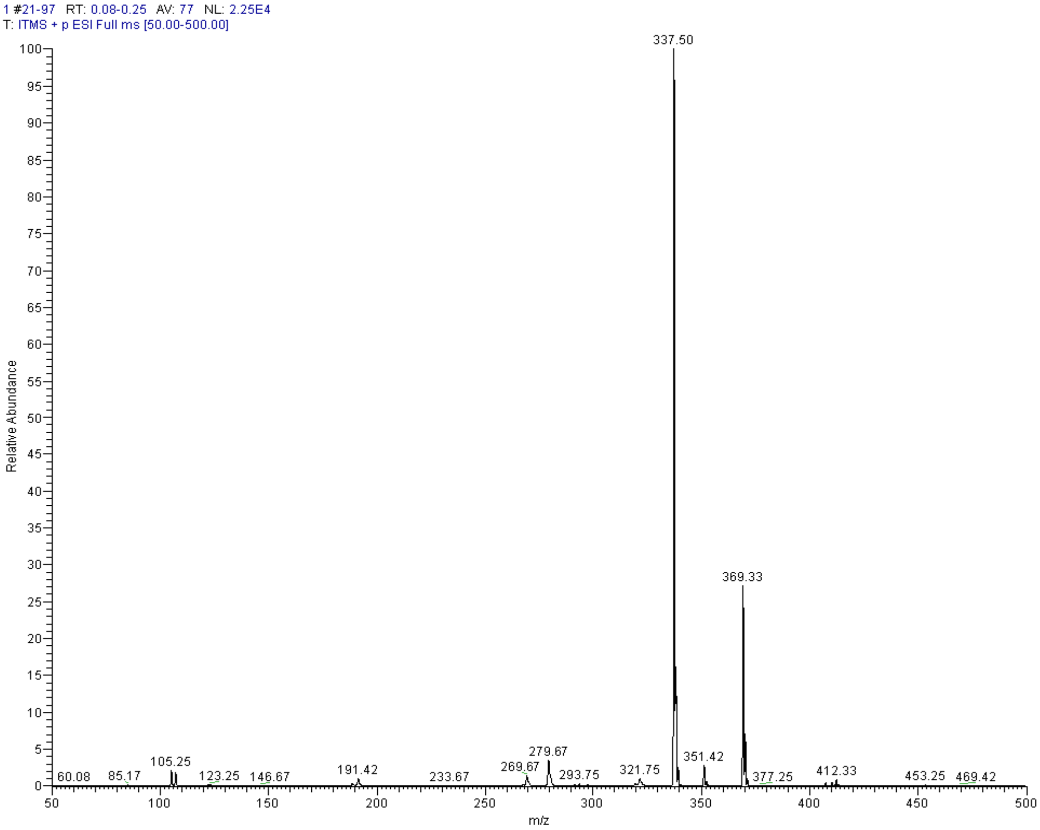


Fig. S15 ESI-MS spectrum of IM6.

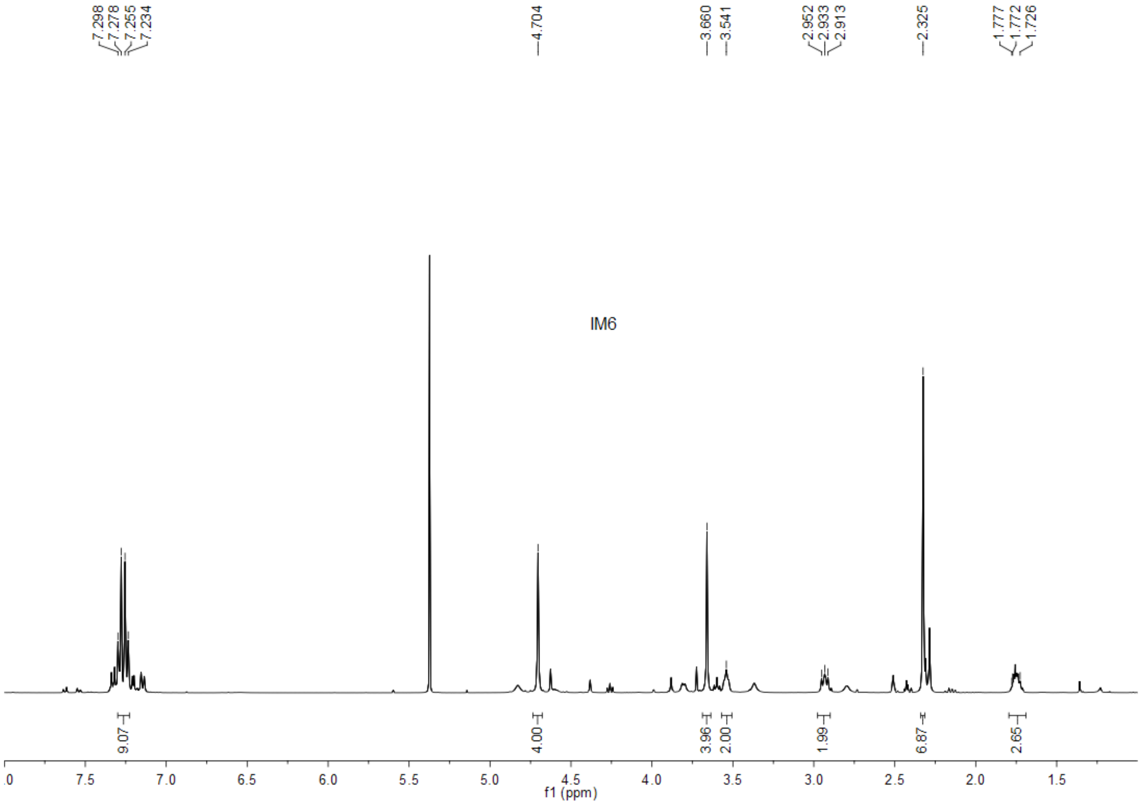


Fig. S16 ^{1}H NMR spectrum of IM6.

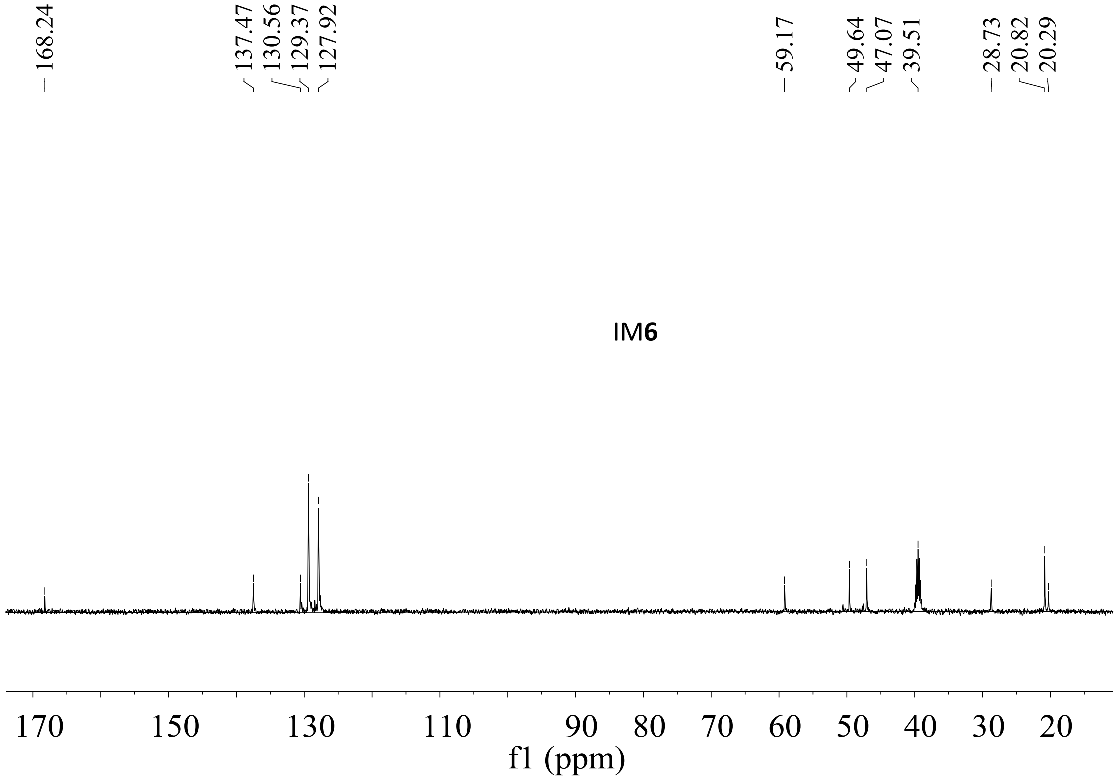


Fig. S17 ^{13}C NMR spectrum of IM6.

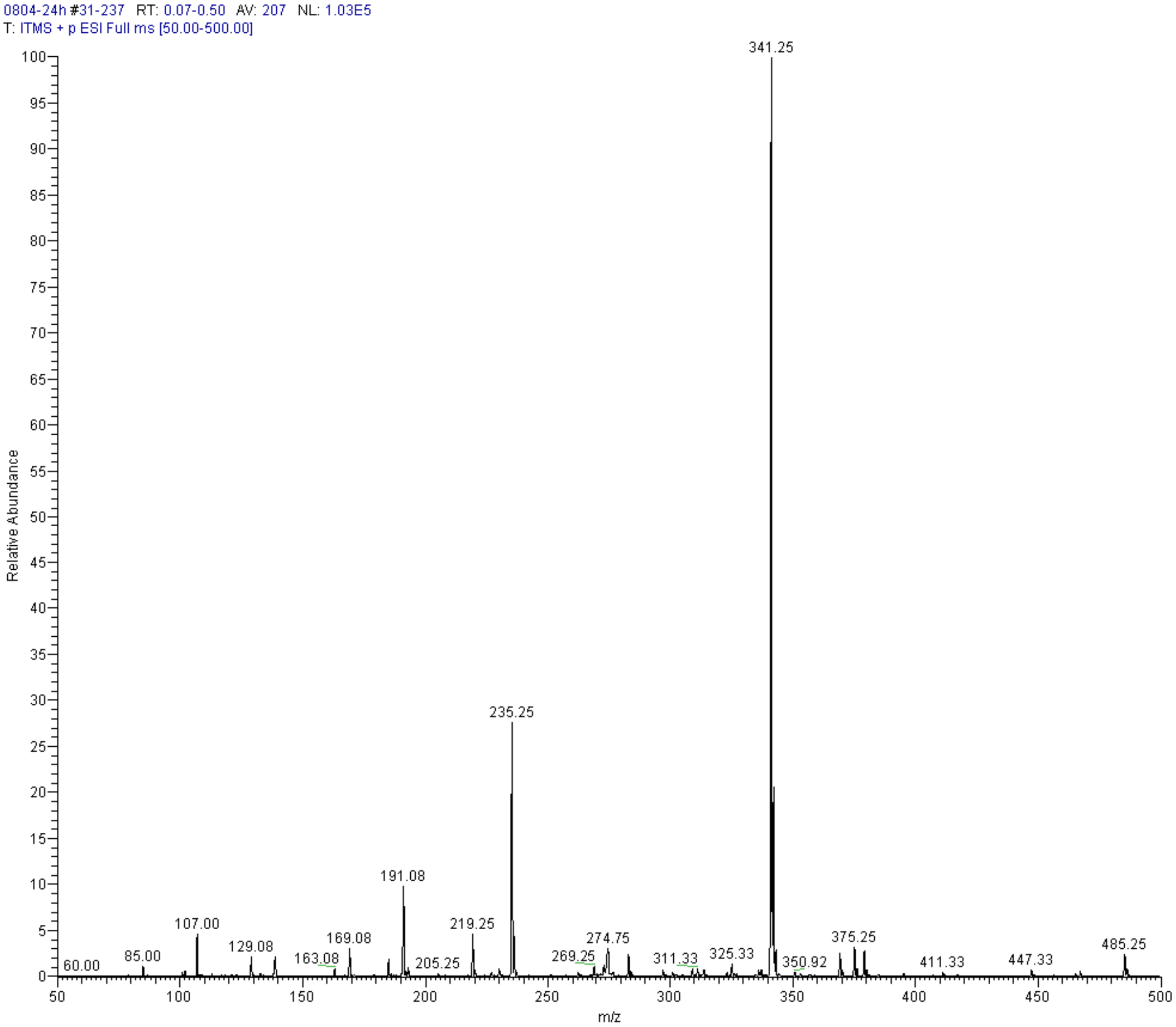


Fig. S18 ESI-MS spectrum of IM8.

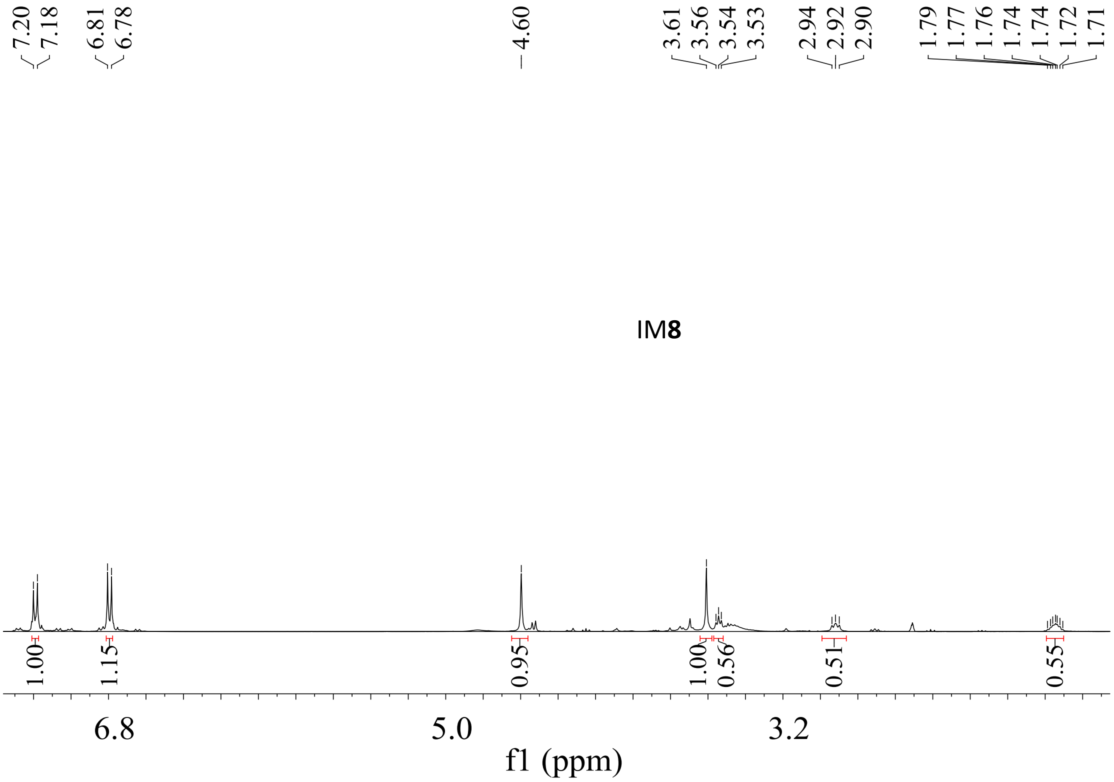


Fig. S19 ^{1}H NMR spectrum of IM8.

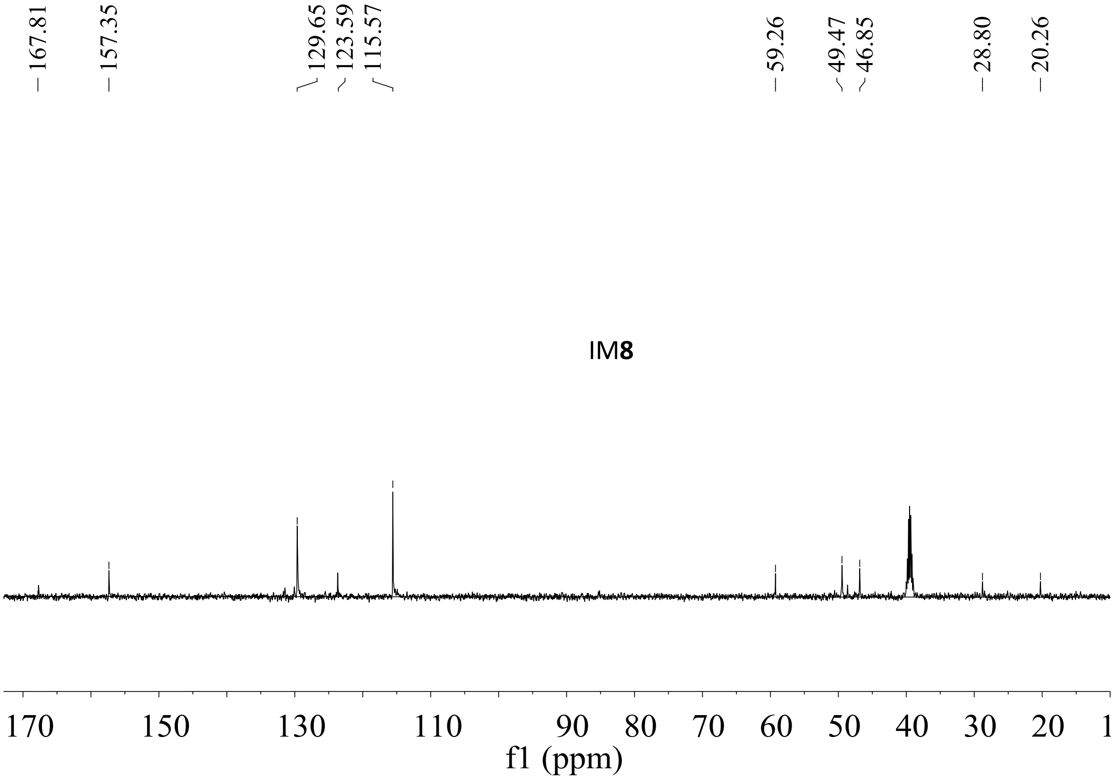


Fig. S20 ^{13}C NMR spectrum of IM8.

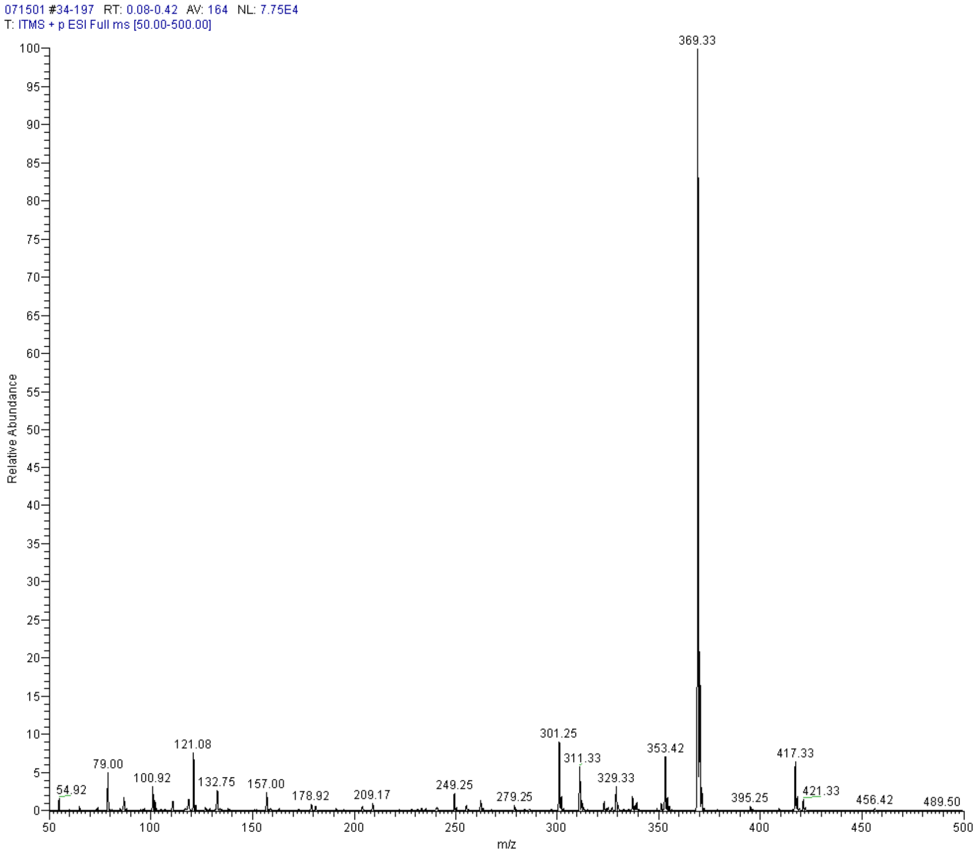


Fig. S21 ESI-MS spectrum of IM9.

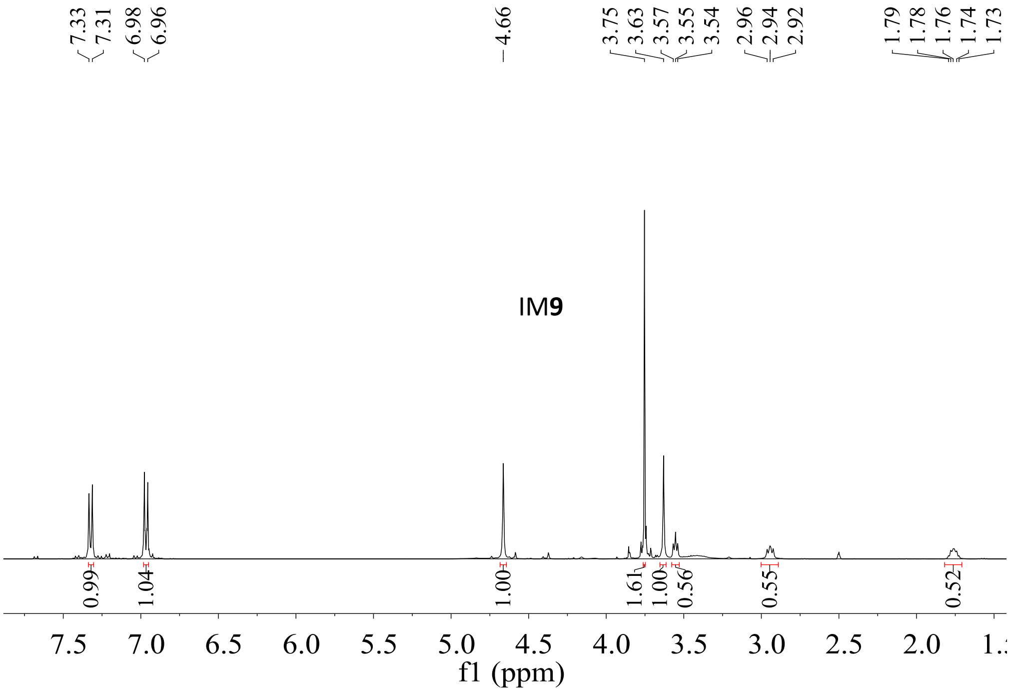


Fig. S22 ^{1}H NMR spectrum of IM9.

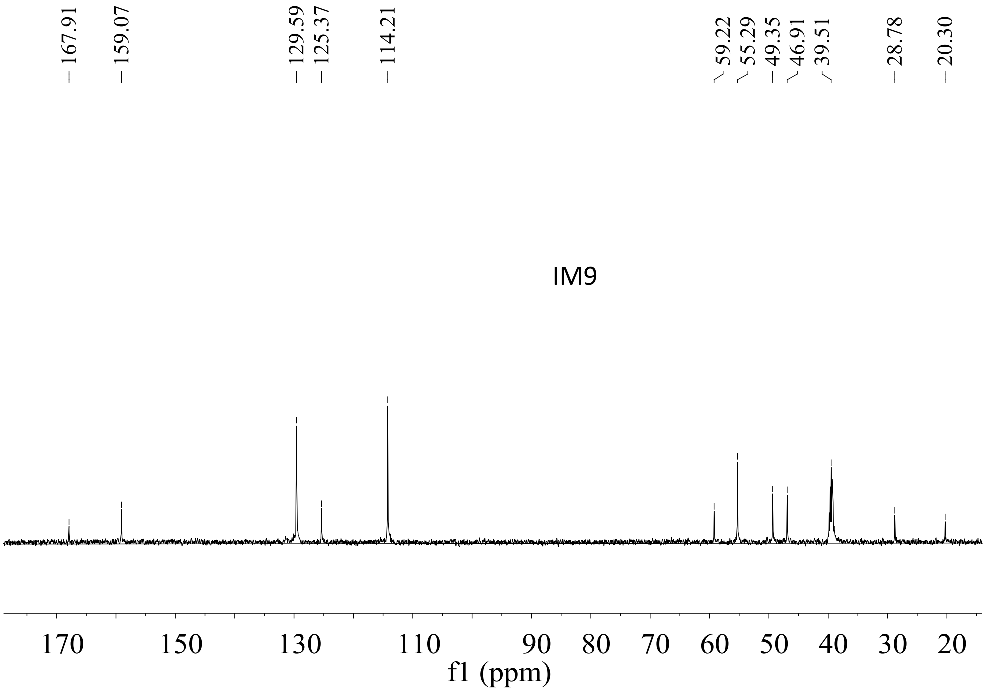


Fig. S23 ^{13}C NMR spectrum of IM9.

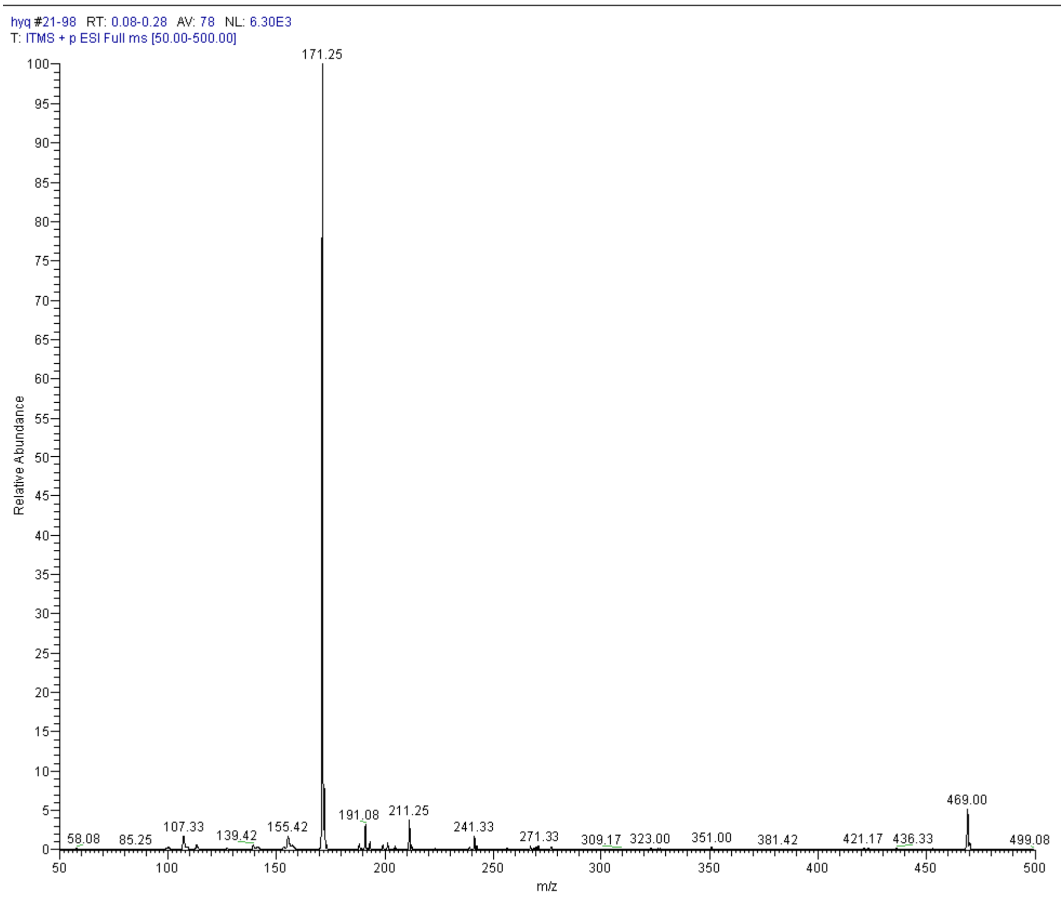


Fig. S24 ESI-MS spectrum of TP11.

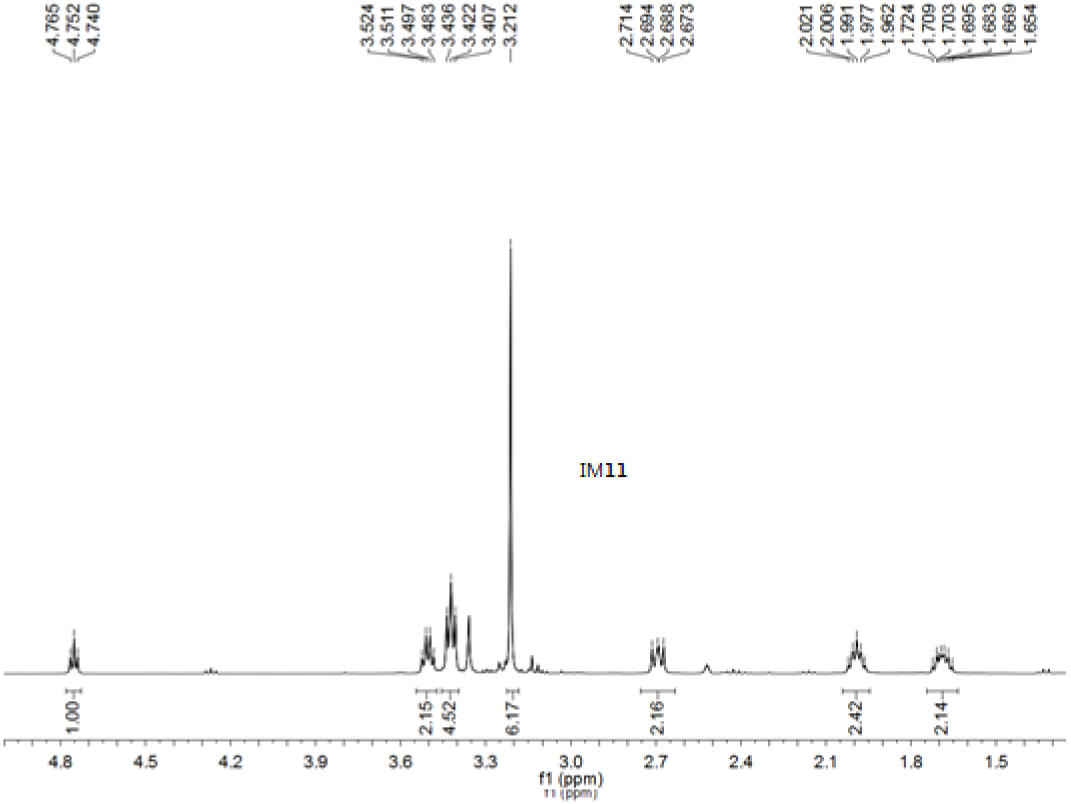


Fig. S25 ^{1}H NMR spectrum of TP11.

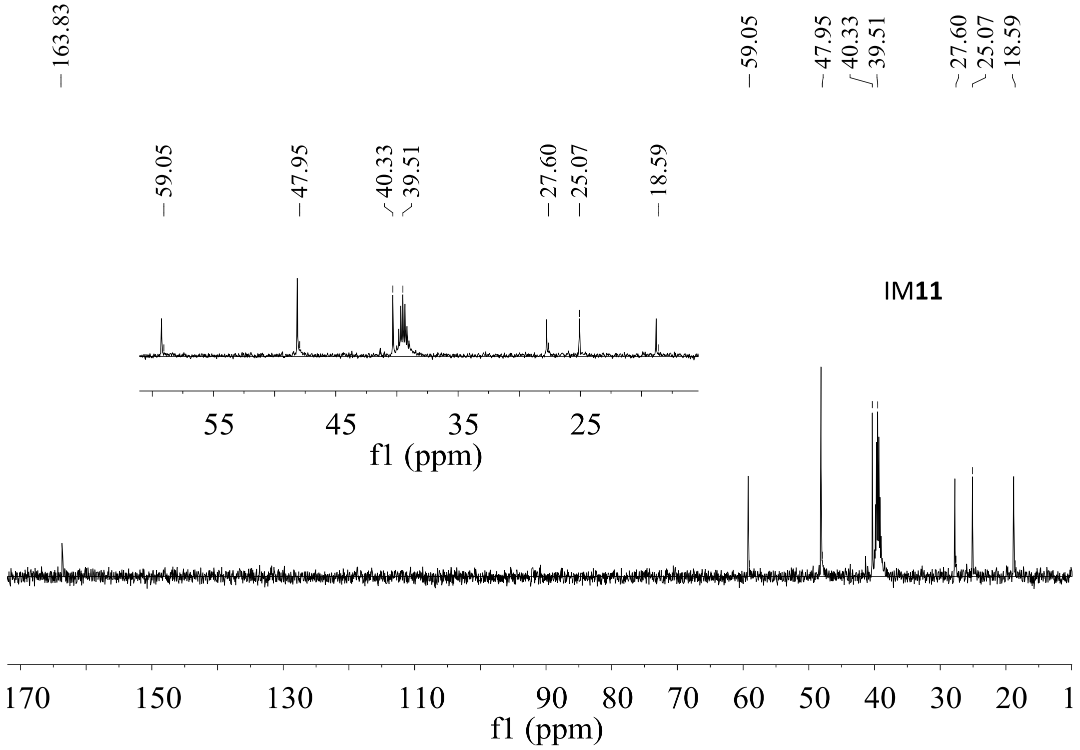


Fig. S26 ^{13}C NMR spectrum of TP11.

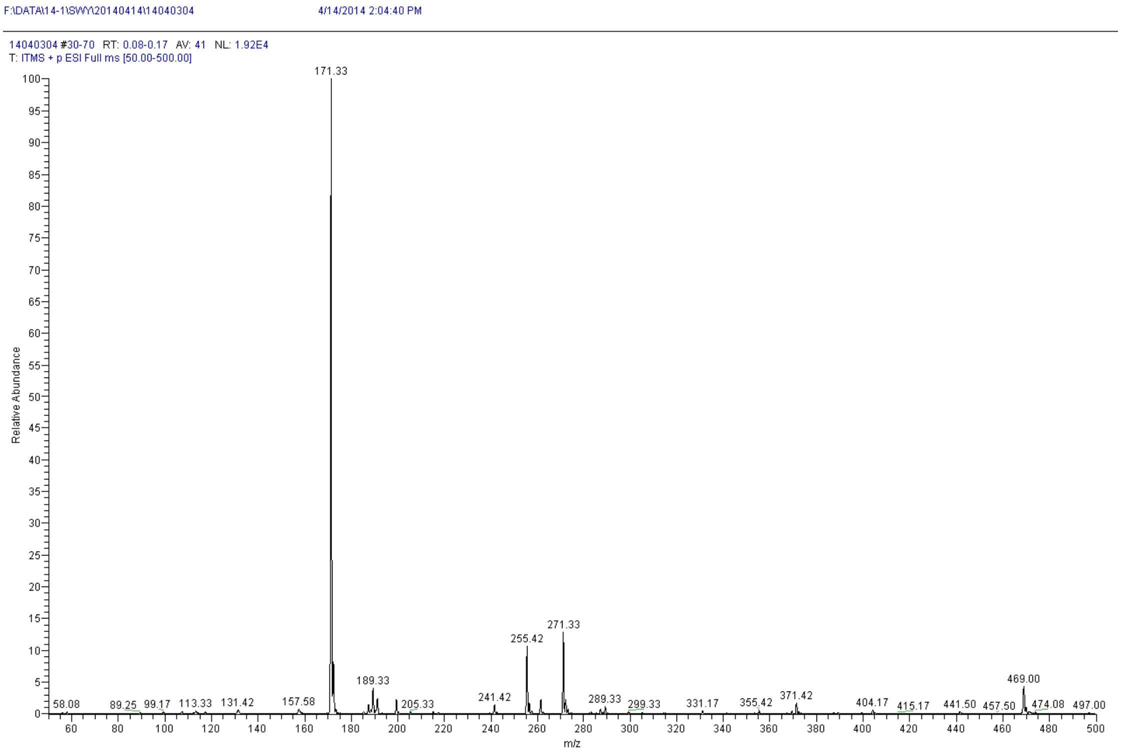


Fig. S27 ESI-MS spectrum of IM14.

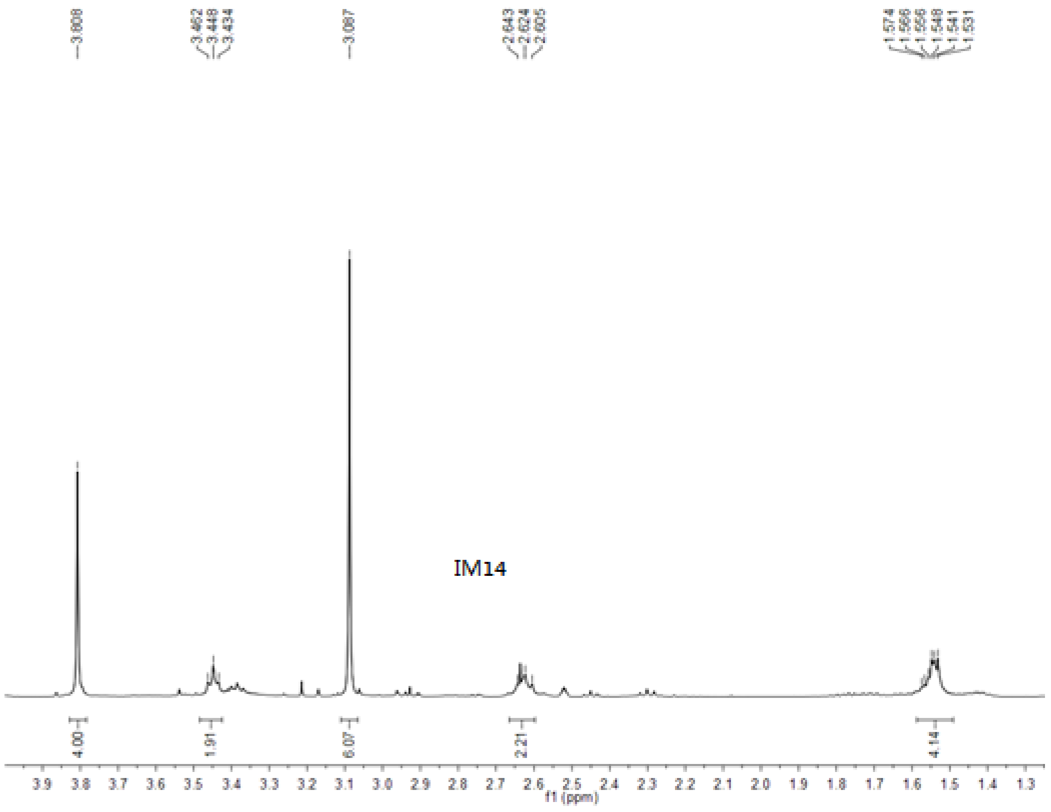


Fig. S28 ^{1}H NMR spectrum of IM14.

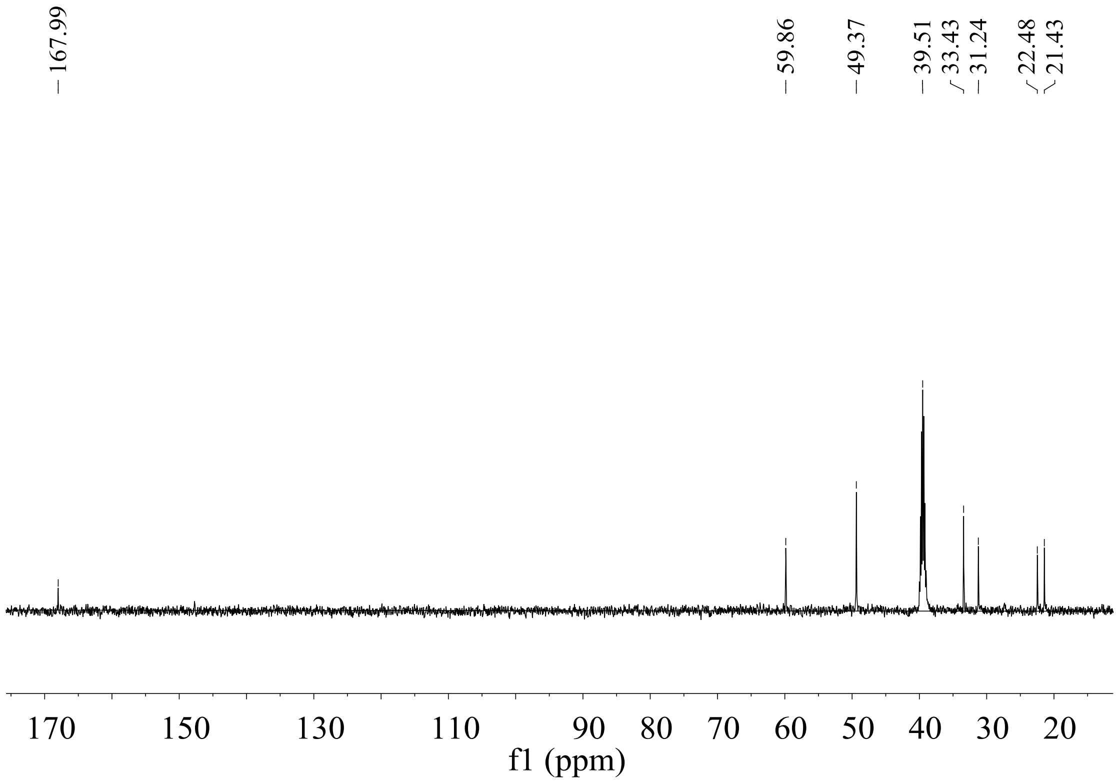


Fig. S29 ^{13}C NMR spectrum of IM14.

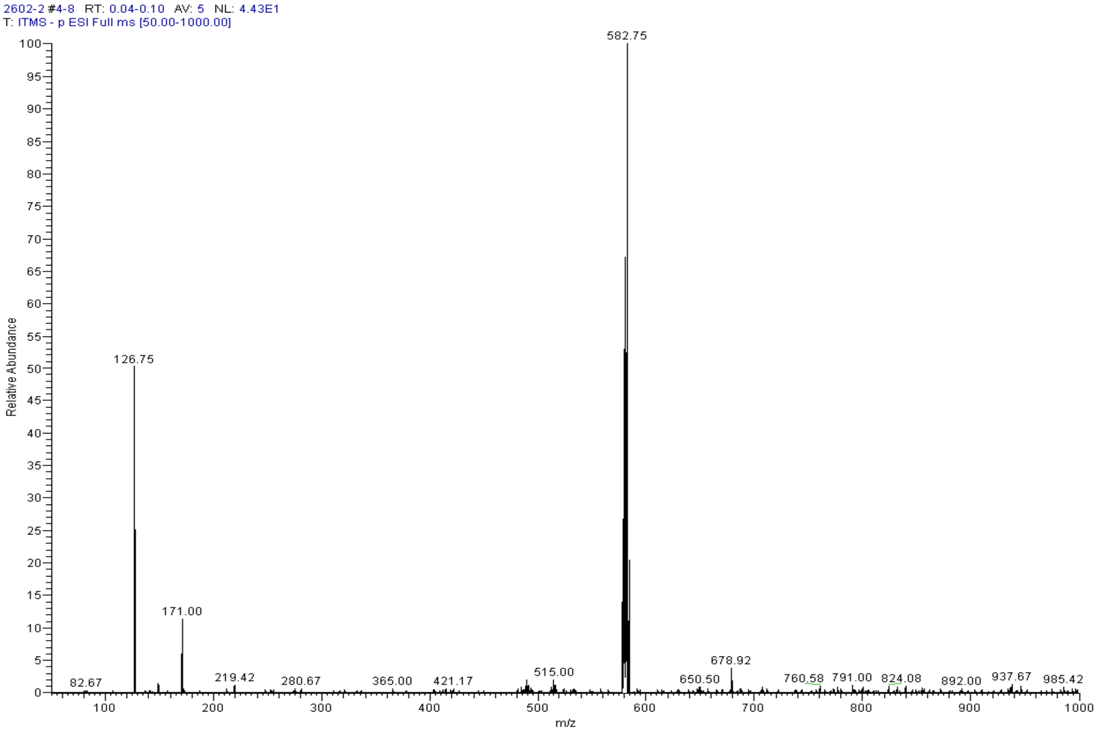


Fig. S30 ESI-MS spectrum of the synthesized imidazolinium salts, showing the peak (m/z = 582.75) of counter anions $[Hg_2I_6]^{2-}$.