Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Thermally Regulated Molybdate-based Ionic Liquids Toward Molecular Oxygen Activation for One-pot Oxidative Cascade Catalysis

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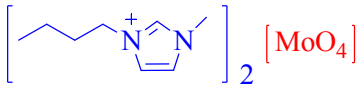
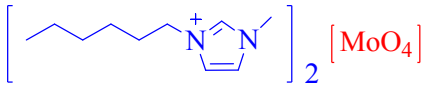
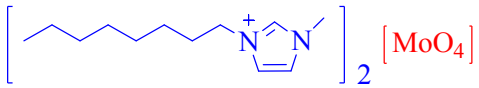
Characterization results



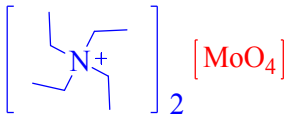
[Bmim]$_2$[MoO$_4$]: ^{1}H NMR (400 MHz, D_2O): δ = 8.67 (s, 2 H), 7.42 (s, 2 H), 7.38 (s, 2 H), 4.15 (t, *J* = 7.2 Hz, 4 H), 3.84 (s, 6 H), 1.76-1.83 (m, 4 H), 1.23-1.29 (m, 4 H), 0.87 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (101 MHz, D_2O): δ = 136.0, 123.6, 122.3, 49.3, 35.8, 31.4, 18.9, 12.9 ppm. ESI-MS: 139.1217 for [Bmim] (calculated: 139.1235), 161.9016 for [MoO_4] (calculated: 161.8851). Elemental analysis (%), calculated: C 43.84, H 6.90, N 12.78, Mo 21.89, found: C 44.24, H 7.20, N 11.89, Mo 20.75.



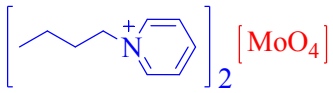
[Hmim]$_2$[MoO$_4$]: ^{1} H NMR (400 MHz, D_2O): δ = 8.80 (s, 2 H), 7.55 (s, 2 H), 7.52 (s, 2 H), 4.24-4.27 (m, 4 H), 3.96 (s, 6 H), 1.91-1.92 (m, 4 H), 1.34 (s, 12 H), 0.88-0.89 (m, 6 H) ppm. ^{13}C NMR (101 MHz, D_2O): δ 135.9, 123.6, 122.3, 49.6, 35.7, 30.4, 29.2, 25.1, 21.8, 13.3 ppm. ESI-MS: 167.1567 for [Hmim] (calculated: 167.1548), 161.9016 for [MoO_4] (calculated: 161.8851). Elemental analysis (%), calculated: C 48.58, H 7.75, N 11.33, Mo 19.40, found: C 49.16, H 8.18, N 10.49, Mo 18.52.



[Omim]$_2$[MoO$_4$]: ^{1}H NMR (400 MHz, D_2O): δ = 8.85 (s, 2 H), 7.54-7.55 (m, 4 H), 4.24-4.28 (m, 4 H), 3.97-3.98 (m, 6 H), 1.90-1.93 (m, 4 H), 1.28-1.34 (m, 20 H), 0.86-0.88 (m, 6 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 136.0, 123.7, 122.2, 49.6, 35.8, 31.3, 29.4, 28.5, 28.4, 25.6, 22.2, 13.6 ppm. ESI-MS: 195.1858 for [Omim] (calculated: 195.1861), 161.9016 for [MoO_4] (calculated: 161.8851). Elemental analysis (%), calculated: C 52.35, H 8.42, N 10.18, Mo 17.43, found: C 54.02, H 9.73, N 9.81, Mo 16.75.



$[N_{2222}]_2[MoO_4]$: slight yellow solid, ^{1}H NMR (400 MHz, D_2O): δ = 3.18 (q, *J* = 6.8, 16 H), 1.17 (t, *J* = 6.8 Hz, 24 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 52.1, 6.8 ppm. ESI-MS: 130.1613 for $[N_{2222}]$ (calculated: 130.1596), 161.9016 for $[MoO_4]$ (calculated: 161.8851). Elemental analysis (%), calculated: C 45.71, H 9.59, N 6.66, Mo 22.82, found: C 46.44, H 10.21, N 6.29, Mo 21.93.



$[Bpy]_2[MoO_4]$: slight yellow solid, ^{1}H NMR (400 MHz, D_2O): δ = 8.92-8.93 (m, 4 H), 8.59-8.63 (m, 2 H), 8.13-8.15 (m, 4 H), 4.68 (t, *J* = 8.8 Hz, 4 H), 2.02 – 2.06 (m, 4 H), 1.435-1.44 (m, 4 H), 0.97 (t, *J* = 7.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 145.6, 144.3, 128.3, 61.8, 32.6, 18.8, 12.8 ppm. ESI-MS: 136.1137 for [Bpy] (calculated: 136.1126), 161.9016 for $[MoO_4]$ (calculated: 161.8851). Elemental analysis (%), calculated: C 50.00, H 6.53, N 6.48, Mo 22.19, found: C 51.18, H 7.31, N 6.08, Mo 21.66.

Flavone: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24-8.26 (m, 1 H), 7.93-7.96 (m, 2 H), 7.69-7.74 (m, 1 H), 7.58-7.60 (m, 1 H), 7.54-7.55 (m, 3 H), 7.42-7.46 (m, 1 H), 6.86 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =178.5, 163.5, 156.3, 133.8, 131.8, 131.6, 129.1, 126.3, 125.7, 124.0, 118.1, 107.6 ppm.

Benzyl benzoate: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.09 (m, 2 H), 7.52-7.56 (m, 1 H), 7.32-7.46 (m, 7 H), 5.39 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 136.1, 133.1, 130.2, 129.8, 128.7, 128.4, 128.3, 128.2, 66.7 ppm.

***N*-benzylideneaniline:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 7.92-7.94 (m, 2 H), 7.49-7.55 (m, 6 H), 7.11-7.13 (m, 2 H) ppm.

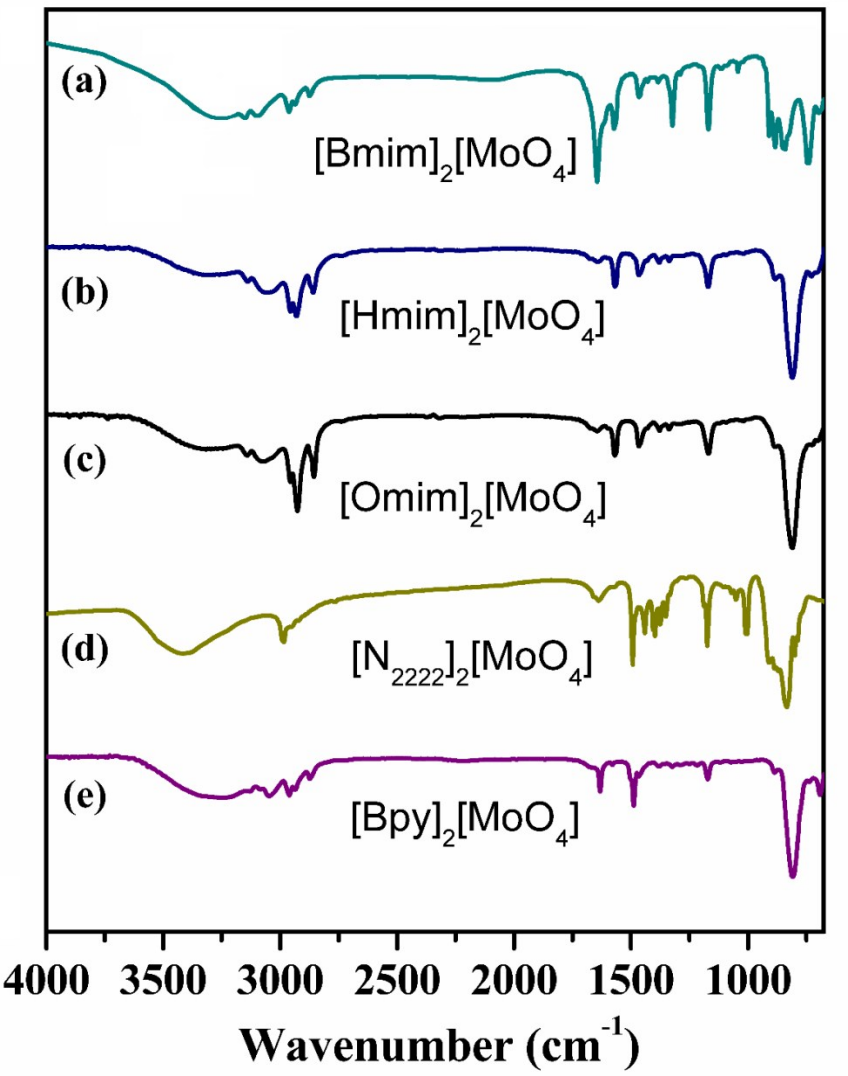


Figure S1. FT-IR spectra of five Mo-ILs catalysts.

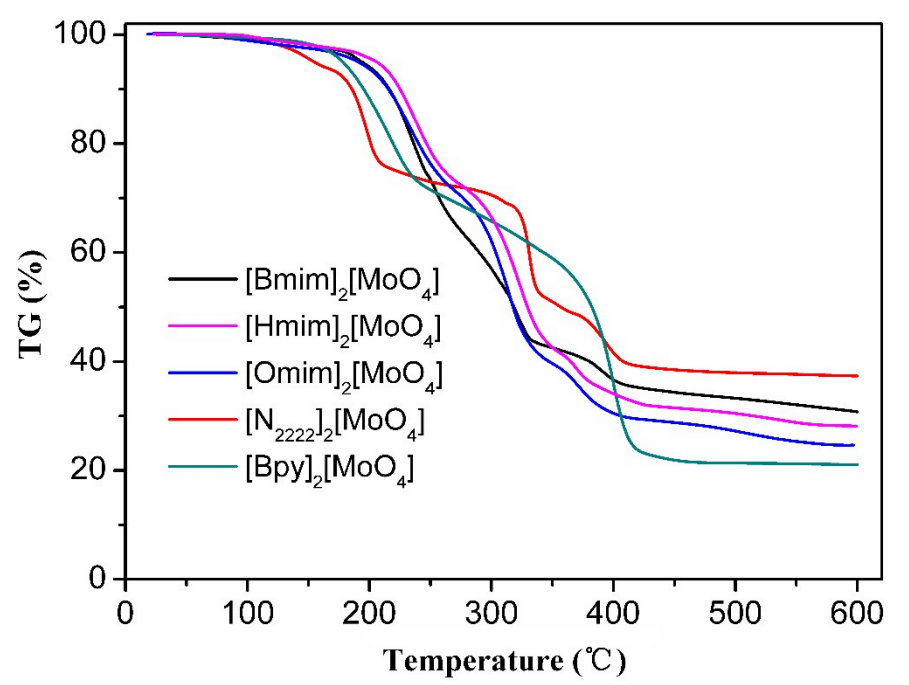


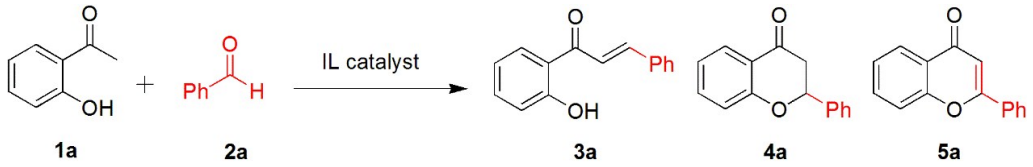
Figure S2. TG curves of five Mo-ILs catalysts.

Table S1. Thermal properties of five Mo-ILs.

Mo-ILs	T_m (°C)	T_d (°C)
$[Bmim]_2[MoO_4]$	NA[a]	200
$[Hmim]_2[MoO_4]$	NA[a]	207
$[Omim]_2[MoO_4]$	NA[a]	221
$[N_{2222}]_2[MoO_4]$	69	173
$[Bpy]_2[MoO_4]$	47	175

[a] NA: not available.

Table S2. Aerobic oxidative tandem reactions for synthesis of flavone using the Mo-IL $[Bmim]_2[MoO_4]$ catalyst under different reaction conditions.[a]



1a 2a 3a 4a 5a

Entry	Catalyst loading	Temperature (°C)	Solvent	Time (h)	Yield (%)		
					3a	**4a**	**5a**
1	0.6	110	*n*-HeOH	21	n.d.	17	65
2	0.6	120	*n*-HeOH	11	1	n.d.	82
3	0.6	130	*n*-HeOH	8	n.d.	6	88
4	0.2	140	*n*-HeOH	6	14	37	43
5	0.4	140	*n*-HeOH	4	n.d.	7	87
6	**0.6**	**140**	***n*-HeOH**	**3**	**n.d.**	**n.d.**	**98**
7	0.6	140	Glycol	3	8	30	34
8	0.6	140	DMSO	3	5	12	79
9	0.6	140	DMF	3	1	1	85
10	0.6	140	DMAC	3	7	15	70
11	0.6	140	*n*-BuOH	3	n.d.	3	91
12	0.6	140	THFA[b]	3	n.d.	4	94

[a] Reaction conditions: **1a** (2.0 mmol), **2a** (2.0 mmol), $[Bmim]_2[MoO_4]$ as catalyst, solvent (1 mL), under an air atmosphere, determined by GC and GC-MS analysis.
[b] THFA (tetrahydrofurfuryl alcohol).

4a 5a

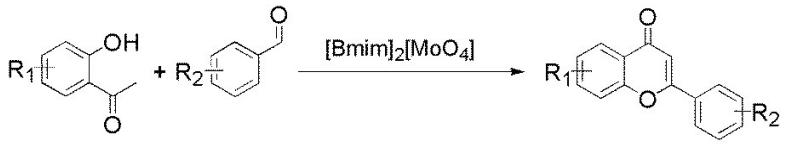
Yield = 89%

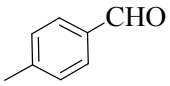
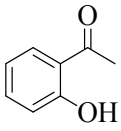
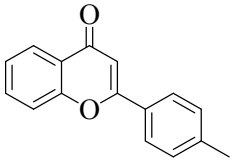
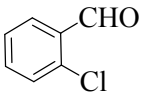
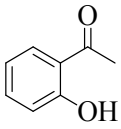
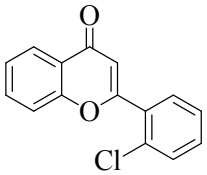
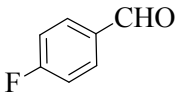
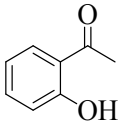
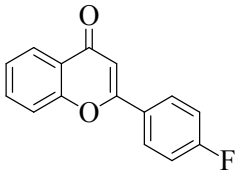
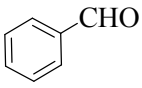
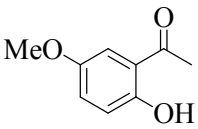
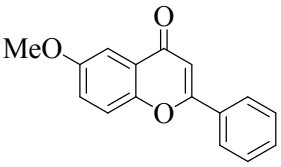
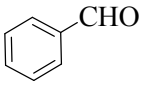
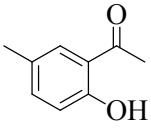
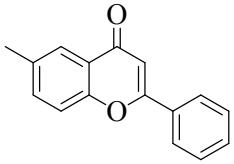
Scheme S1. The direct oxidative dehydrogenation of **4a** by $[Bmim]_2[MoO_4]$.

Table S3. The Raman frequencies of various molybdenum species calculated at B3LYP/6-31+G(d)/LANL2DZ level. For comparison, the experimental peak of Mo-IL $[Bmim]_2[MoO_4]$ is at 890 cm^{-1}. The neutral carbene after 2-H migration is labeled as $[Bmim_{-H}]$ in the Table.

Species	Raman / cm^{-1}
$[MoO_4]^{2-}$	868.95
$[Bmim]_2[MoO_4]$	885.72
$[HMoO_4]^-$	949.15
$[Bmim][Bmim_{-H}][HMoO_4]$	944.31
H_2MoO_4	1022.05

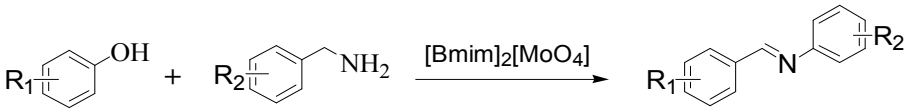
Table S4. Synthesis of various flavone derivatives via selective aerobic cascade oxidation catalyzed by Mo-IL $[Bmim]_2[MoO_4]$.[a]

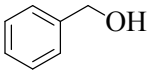
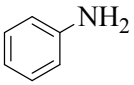
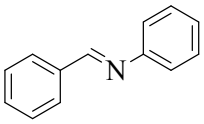
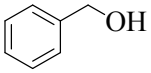
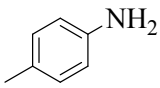
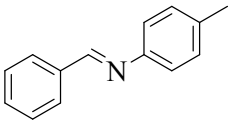
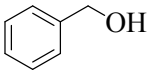
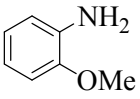
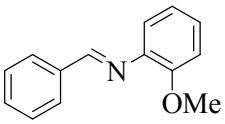
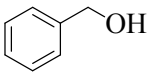
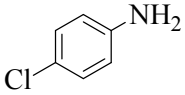
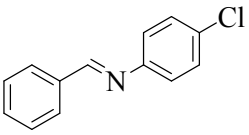
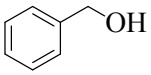
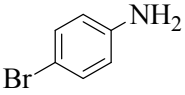
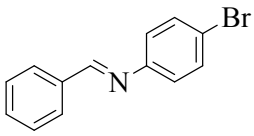
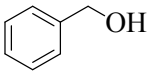
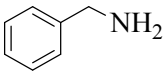
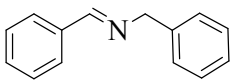


Entry	Aldehyde	Ketone	Products	Time (h)	Yield[b] (%)
1				3	87
2				3	75
3				3	50
4				5	66
5				6	76

[a] Reaction conditions: aldehyde (2.0 mmol), ketone (3.0 mmol), $[Bmim]_2[MoO_4]$ (0.6 mmol), *n*-hexanol (1 mL), 140 °C, under an air atmosphere, determined by GC-MS analysis. [b] GC yield.

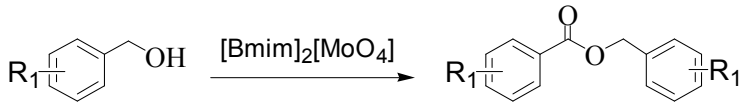
Table S5. Synthesis of various imine derivatives via selective aerobic cascade oxidation catalyzed by Mo-IL $[Bmim]_2[MoO_4]$.[a]

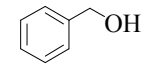
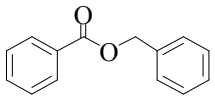
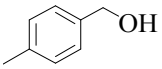
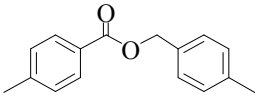
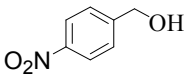
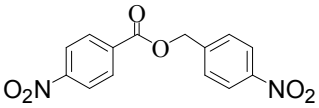
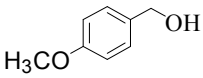
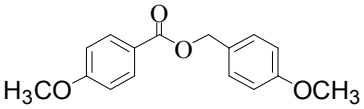


Entry	Alcohol	Amine	Product	Time (h)	Yield[b] (%)
1				12	91
2				6	89
3				6	60
4				6	59
5				8	63
6				6	78

[a] Reaction conditions: alcohol (2.0 mmol), amine (2.0 mmol), $[Bmim]_2[MoO_4]$ (0.6 mmol), 100 °C, under an air atmosphere, determined by GC-MS analysis. [b] GC yield.

Table S6. Synthesis of various benzyl benzoate derivatives via selective aerobic cascade oxidation catalyzed by Mo-IL $[Bmim]_2[MoO_4]$.[a]



Entry	Alcohol	Product	Yield[b] (%)
1			78
2			79
3			60
4			62

[a] Reaction conditions: alcohol (10.0 mmol), $[Bmim]_2[MoO_4]$ (0.6 mmol), 110 °C, 48 h, under an air atmosphere, determined by GC-MS analysis. [b] GC yield.

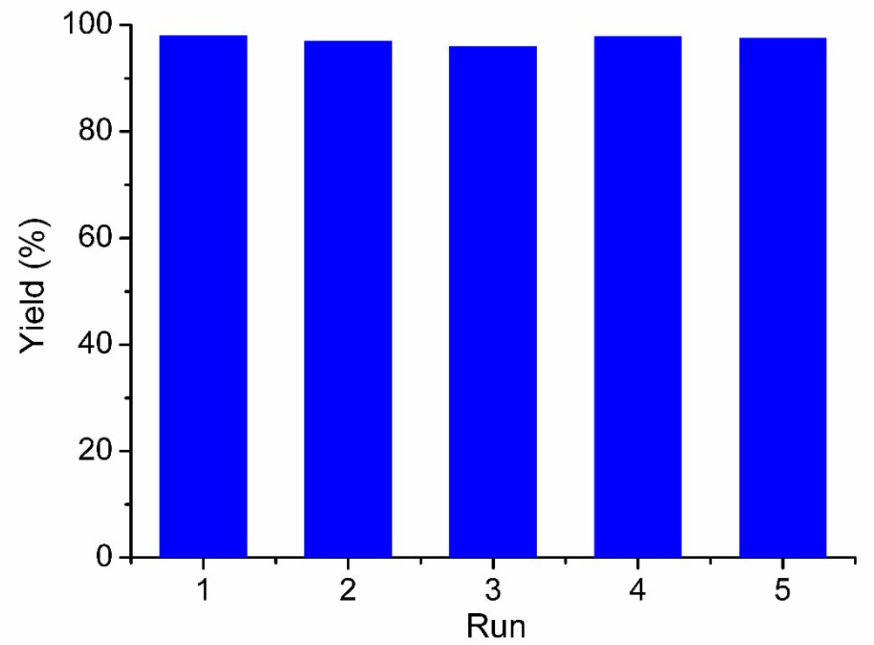


Figure S3. The recycle test of the Mo-based IL $[Bmim]_2[MoO_4]$ catalyst.

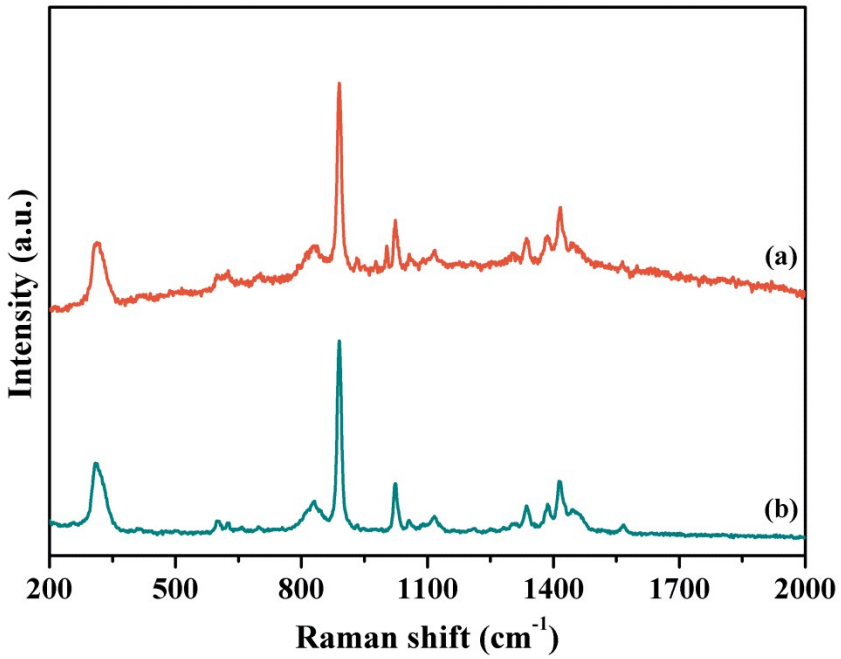


Figure S4. Raman spectra of (a) reused $[Bmim]_2[MoO_4]$ and (b) fresh $[Bmim]_2[MoO_4]$.

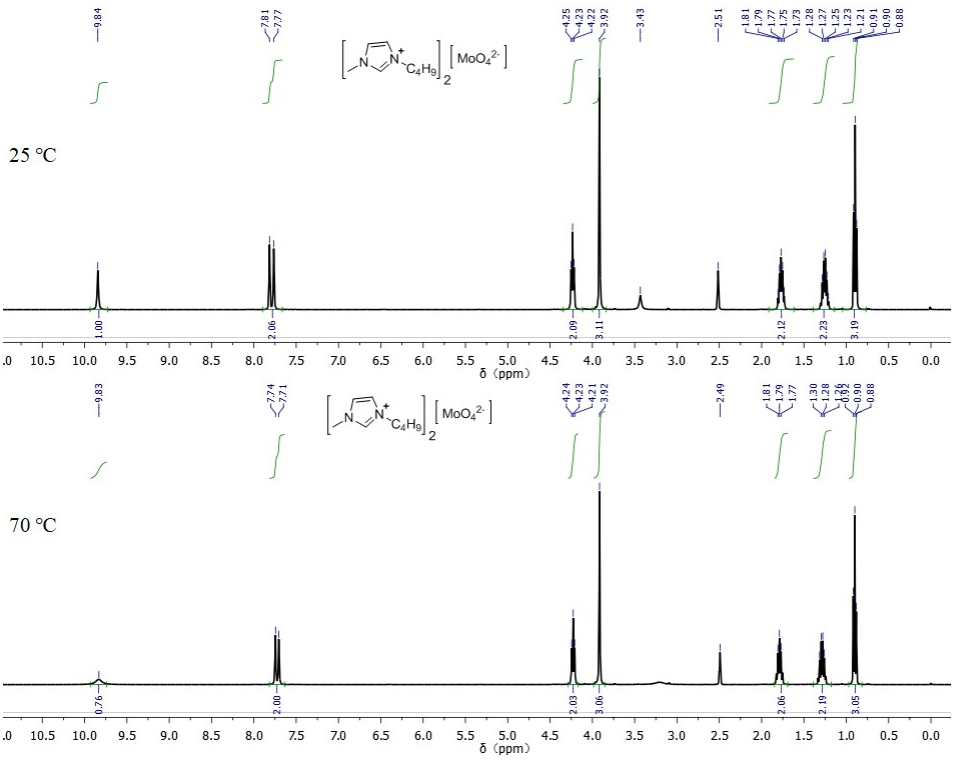


Figure S5. ^{1}H NMR spectra of $[Bmim]_2[MoO_4]$ at 25 ˚C and 70 ˚C.

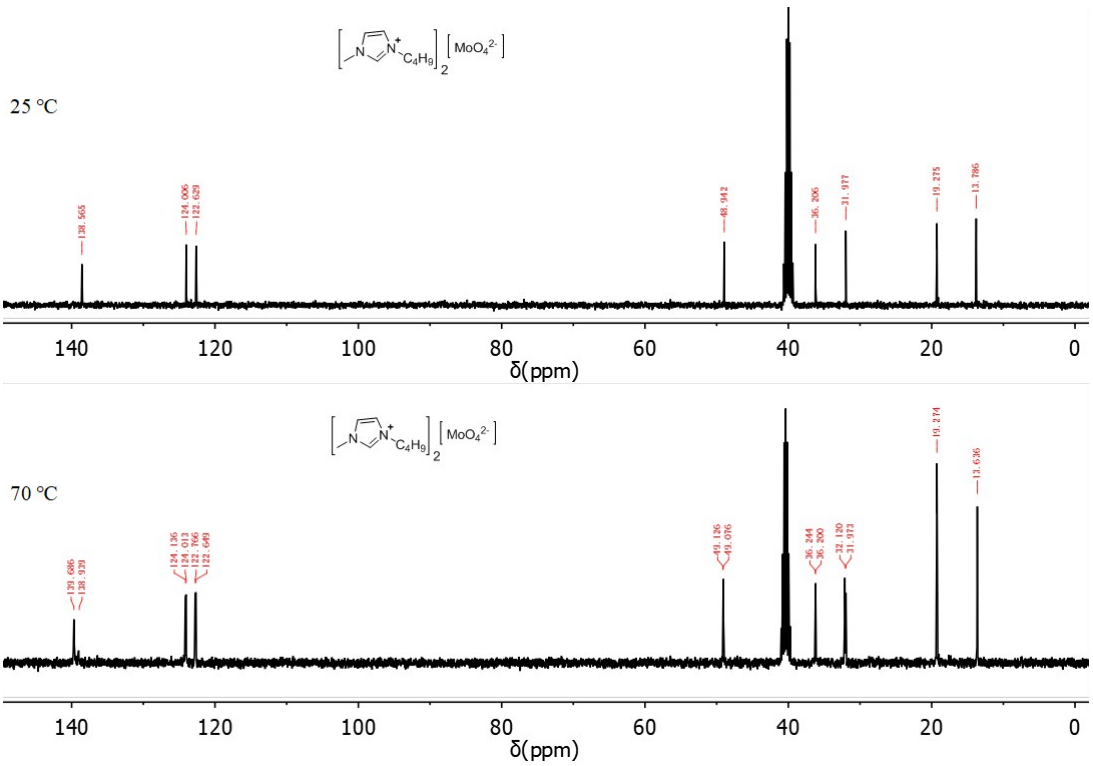


Figure S6. ^{13}C NMR spectra of $[Bmim]_2[MoO_4]$ at 25 ˚C and 70 ˚C

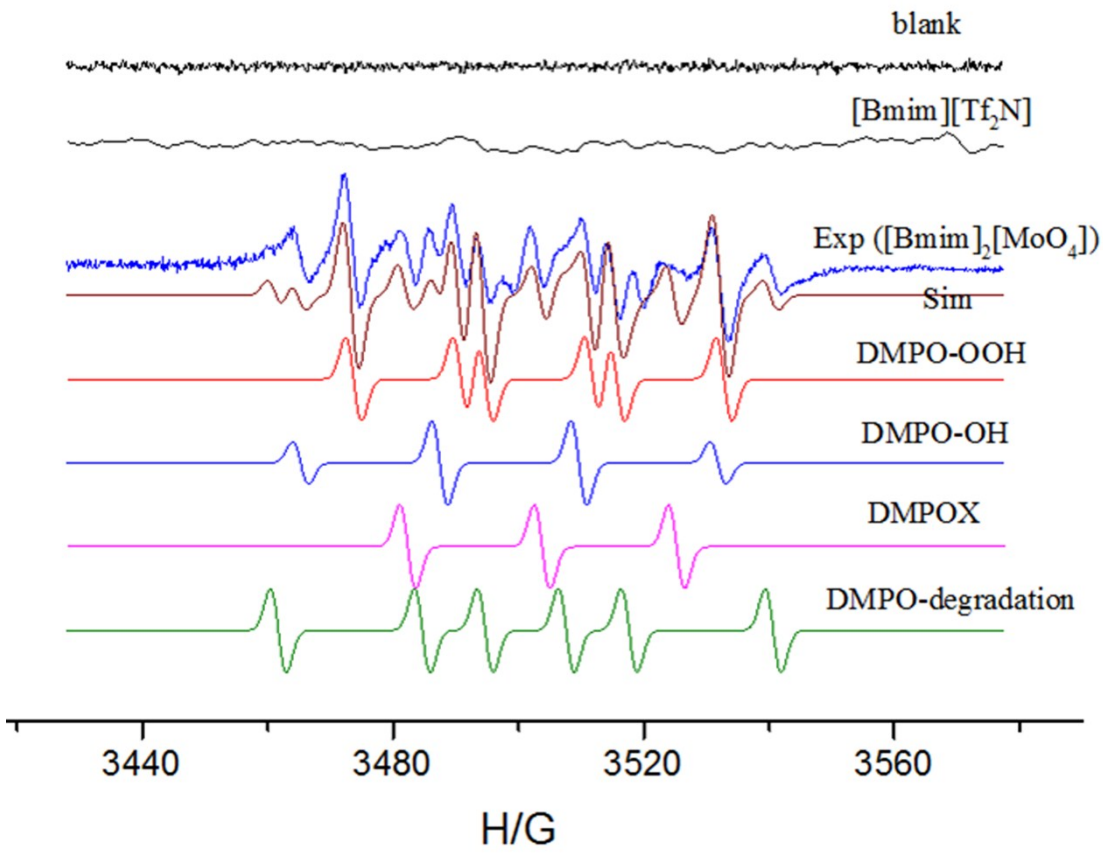
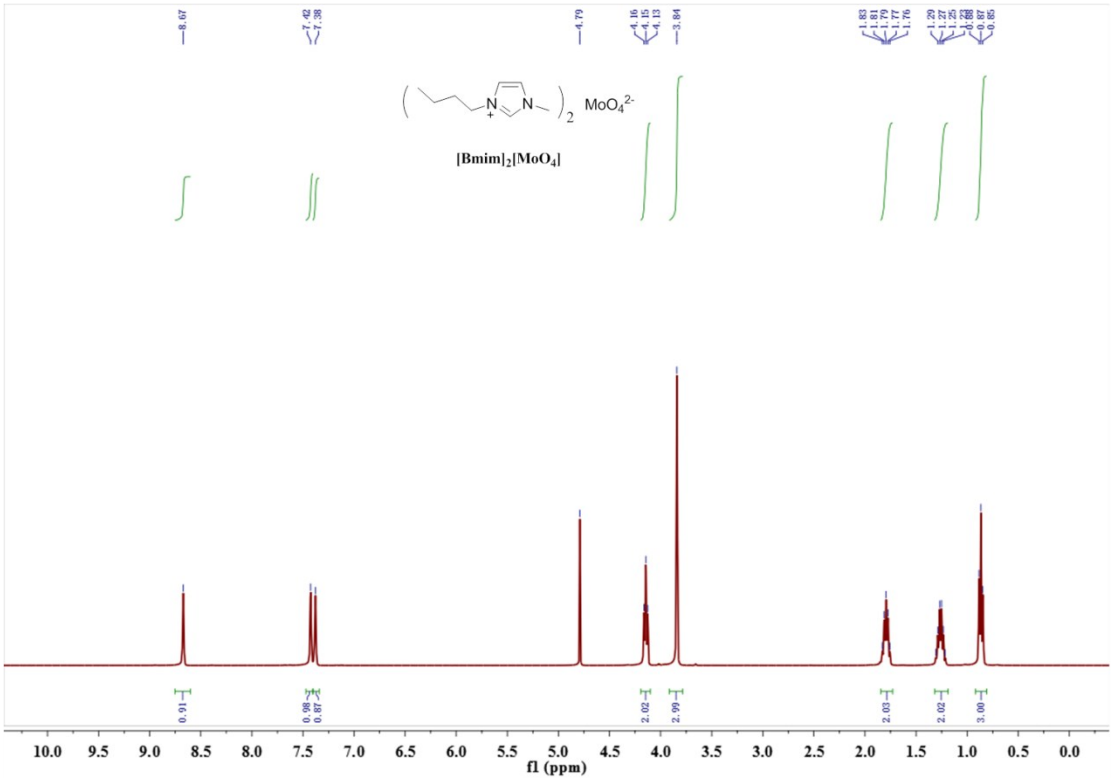
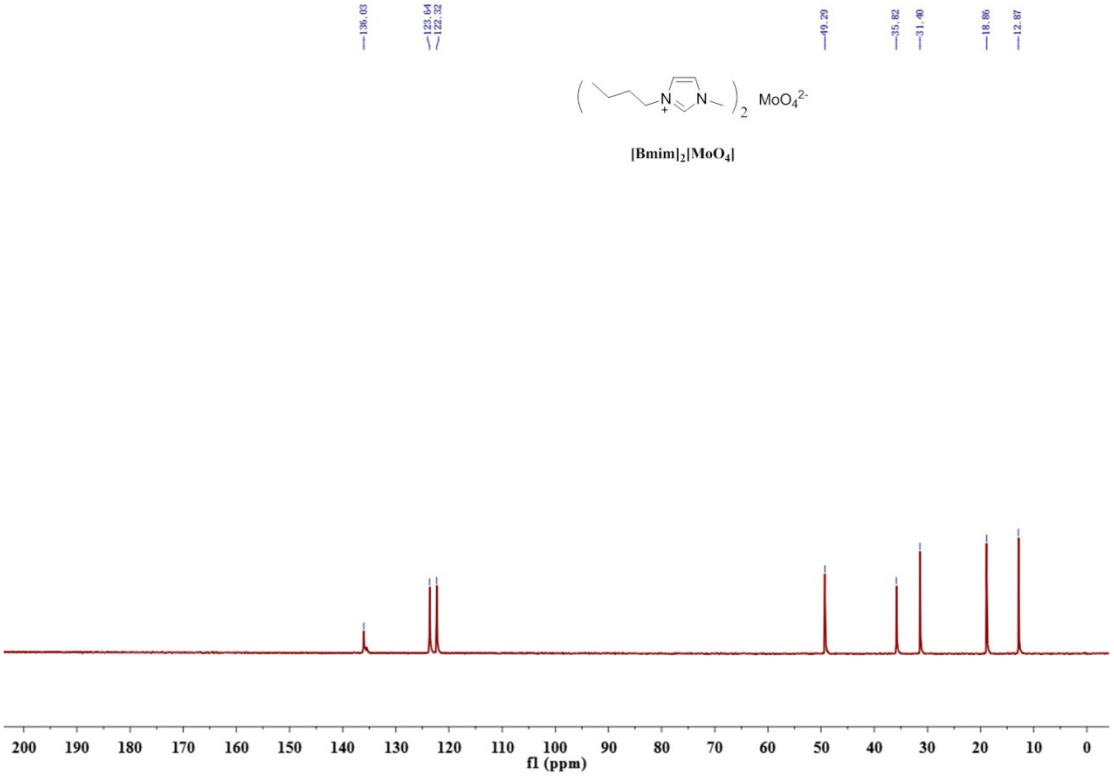


Figure S7. EPR spectra of experimental (black line: no catalyst, [Bmim][Tf_2N]; blue line: $[Bmim]_2[MoO_4]$) and simulated spectrum (wine red line). The simulated spectrum of $[Bmim]_2[MoO_4]$ (wine red line) was composed of DMPO-OOH (red line), DMPO-OH (blue line), DMPOX (pink line) and DMPO-degradation (green line) radicals in a ratio roughly 1:0.3:0.2:0.2. Detection conditions: 70 ˚C, DMPO 10 μL, Mo-IL catalyst 25 mg, *n*-hexanol 30 mL, 1 mL of the solution was collected and detected by room-temperature EPR.

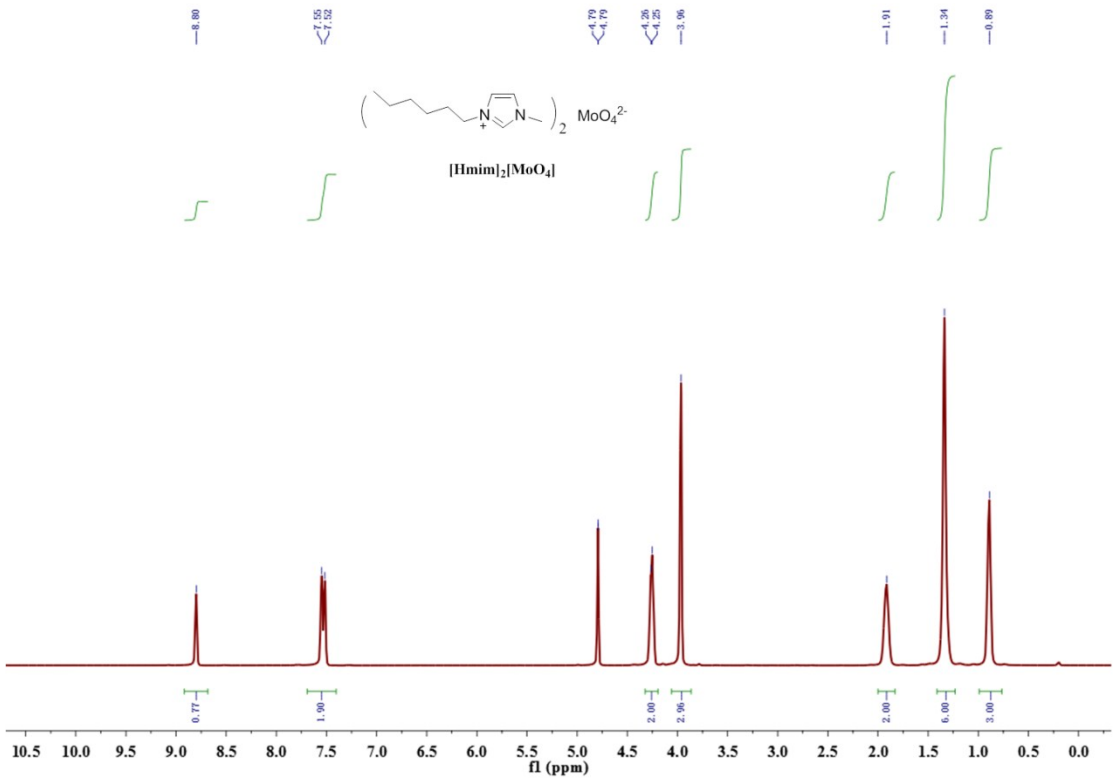
NMR spectra of Mo-ILs

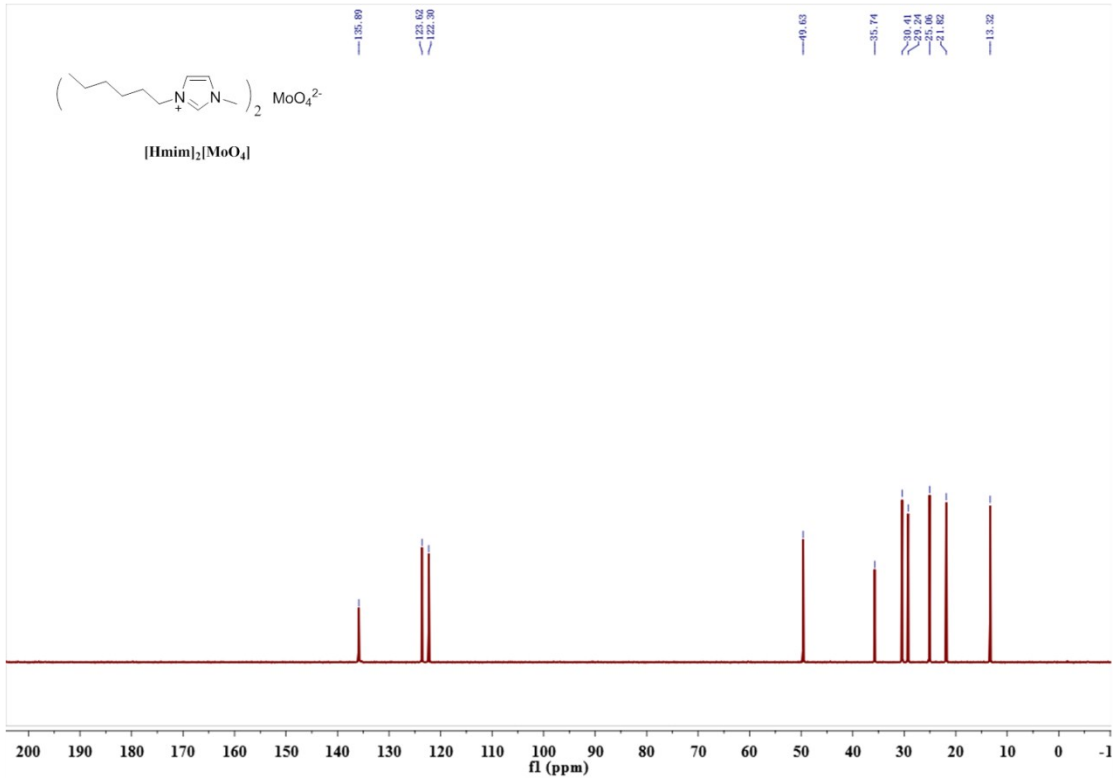


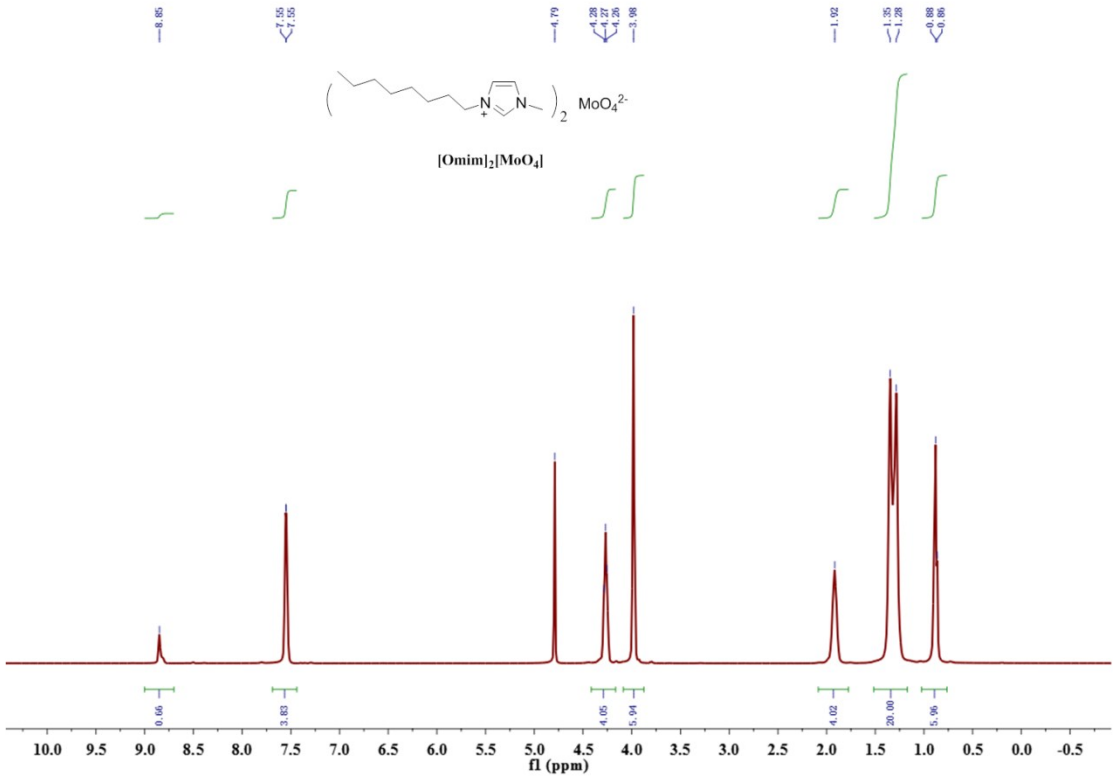
$[Bmim]_2[MoO_4]$

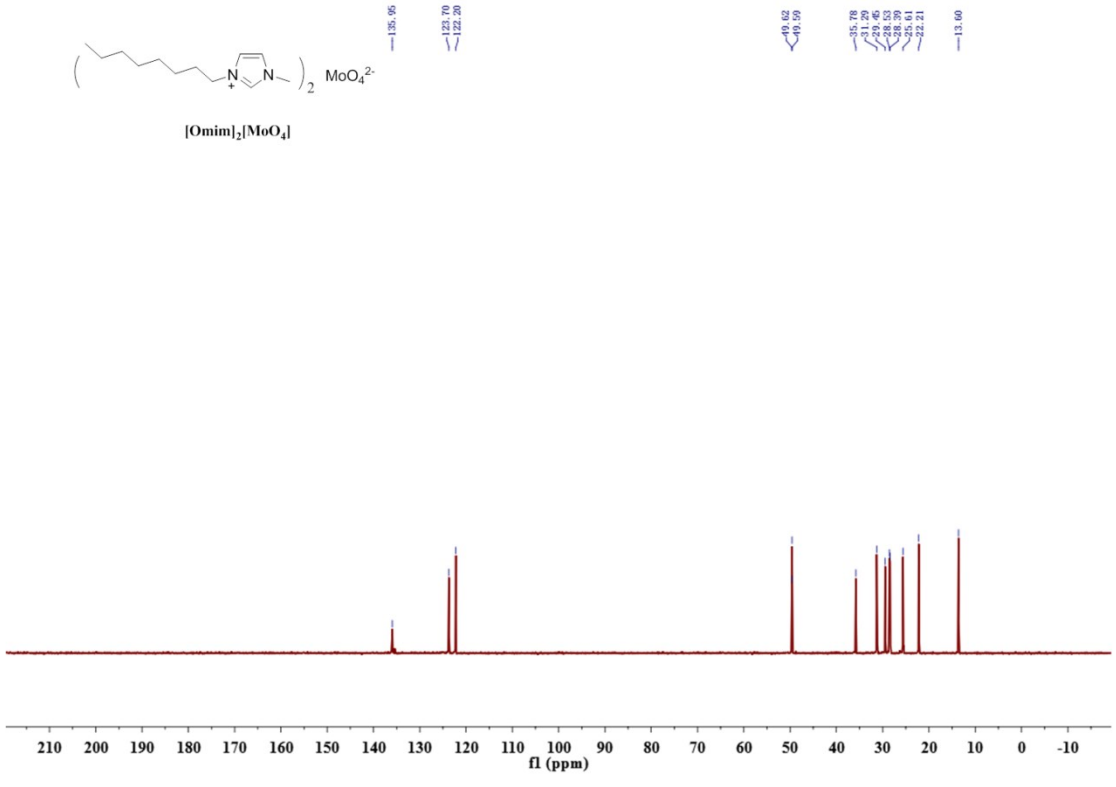


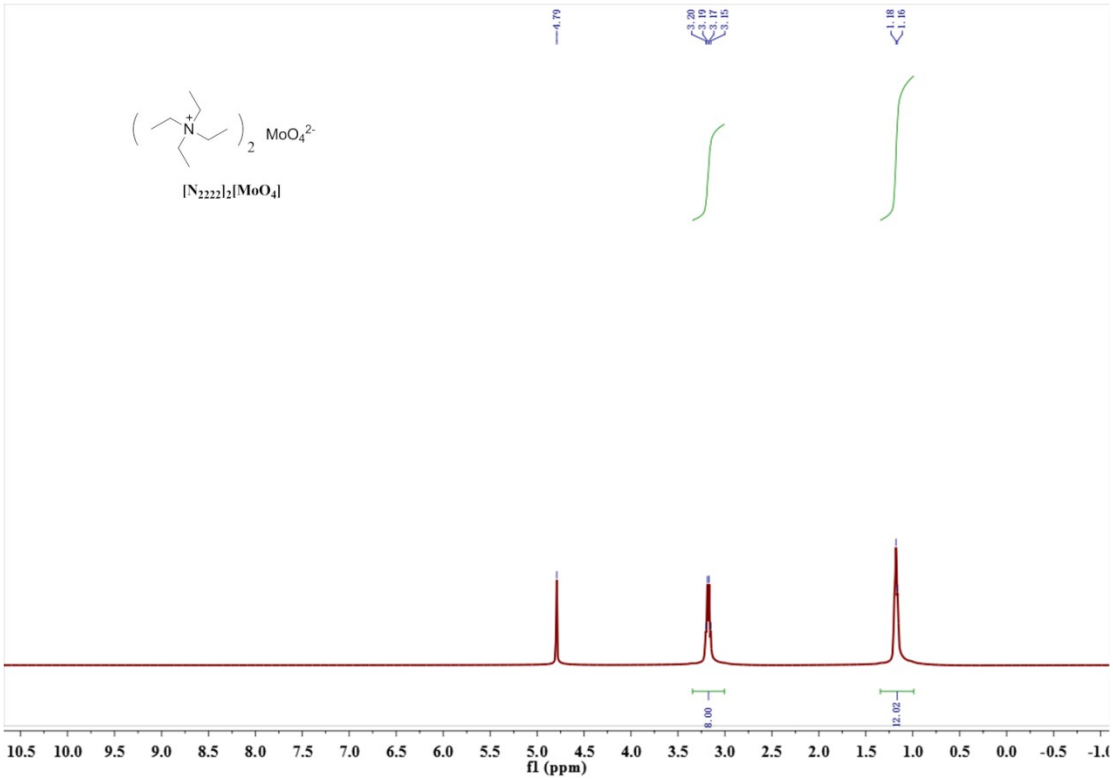
$[Bmim]_2[MoO_4]$

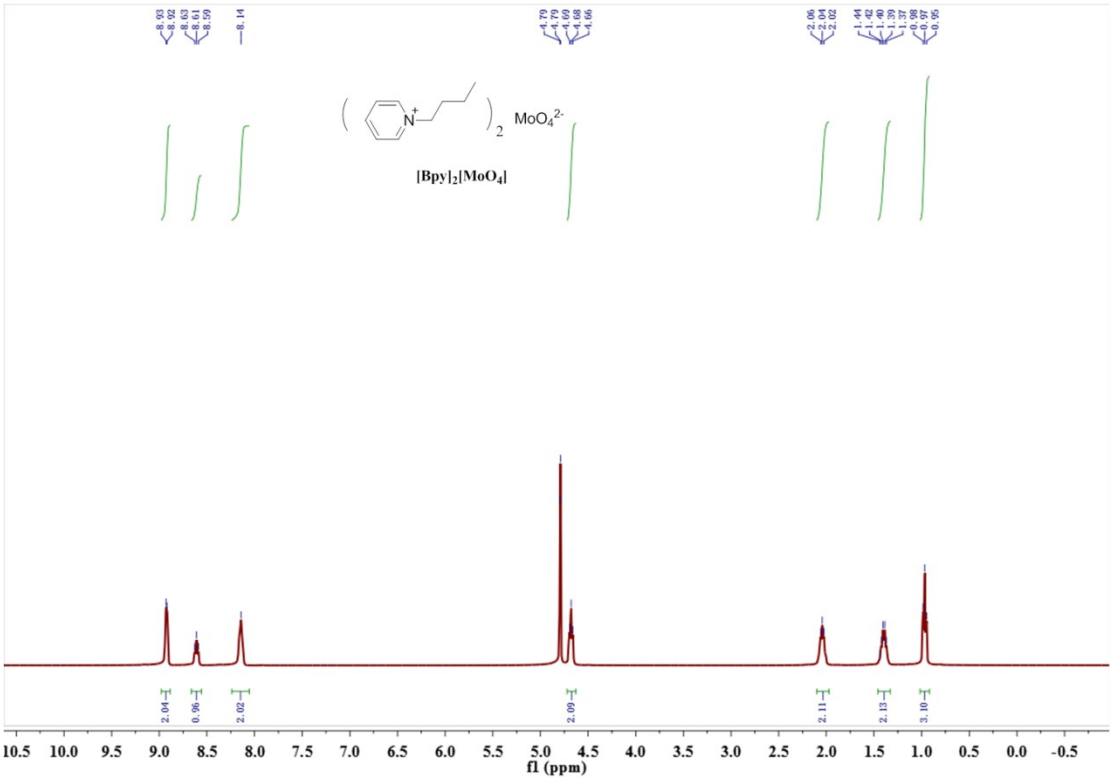

8.80
7.55
7.52
4.79
4.79
4.26
4.25
3.96
1.91
1.34
0.89
MoO4 2-
[Hmim]2[MoO4]
0.77
1.90
2.00
2.96
2.00
6.00
3.00
fl (ppm)

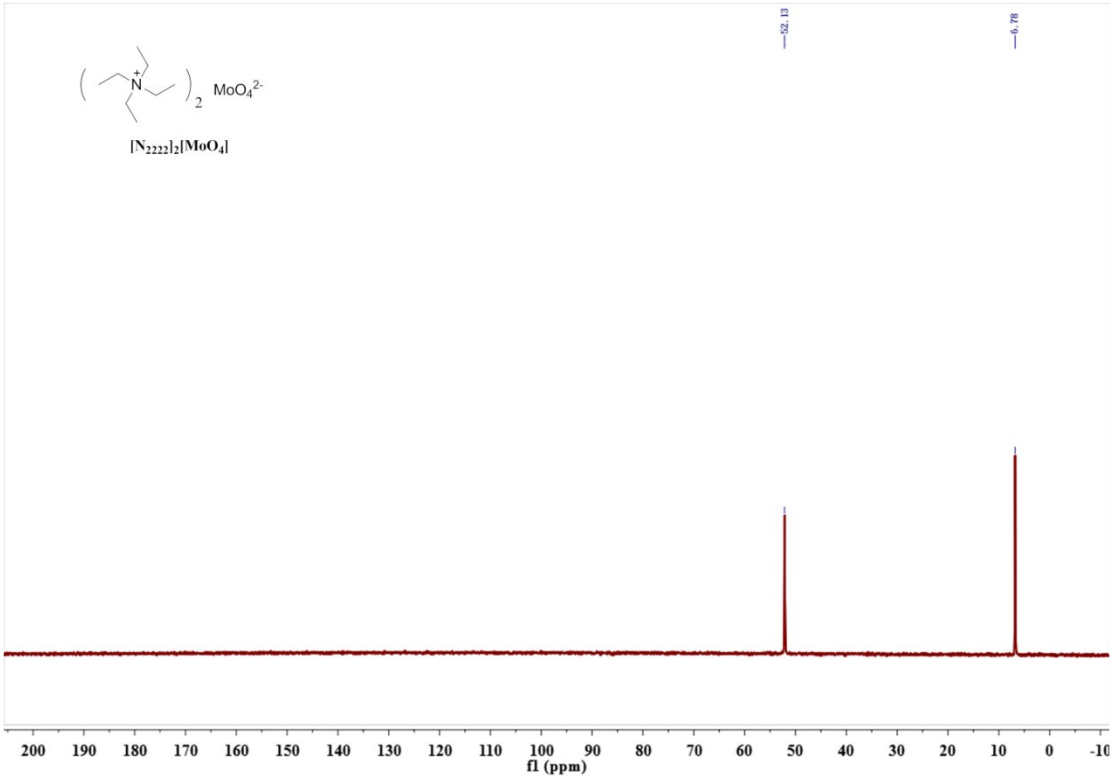

135.89
123.62
122.30
49.63
35.74
30.41
29.24
25.06
21.82
13.32
MoO4 2-
[Hmim]2[MoO4]
fl (ppm)


8.85
7.55
7.55
4.79
4.28
4.27
4.26
3.98
1.92
1.35
1.28
0.88
0.86
MoO4 2-
[Omim]2[MoO4]
0.66
3.83
4.05
5.94
4.02
20.00
5.96
10.0 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 -0.5
f1 (ppm)

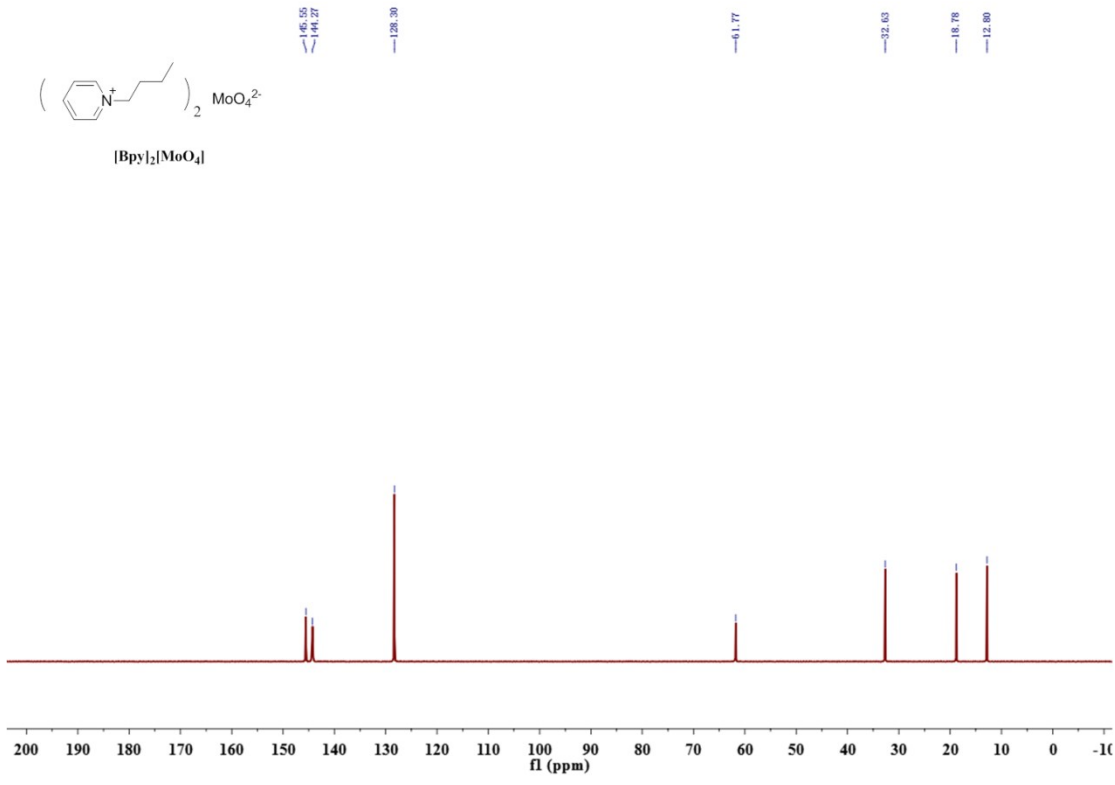

135.95
123.70
122.20
49.62
49.59
35.78
31.20
29.45
28.53
28.39
26.54
22.21
13.60
MoO4 2-
[Omim]2[MoO4]
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4.79
3.20
3.19
3.17
3.15
1.18
1.16
MoO4 2-
2
[N2222]2[MoO4]
8.00
12.02
10.5 10.0 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 -0.5
f1 (ppm)


8.93
8.92
8.63
8.61
8.59
8.14
4.79
4.79
4.69
4.68
4.66
2.06
2.04
2.02
1.44
1.42
1.40
1.39
1.37
0.98
0.97
0.95
MoO4 2-
2
[Bpy]2[MoO4]
2.04
0.96
2.02
2.09
2.11
2.13
3.10
10.5 10.0 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 -0.5
f1 (ppm)

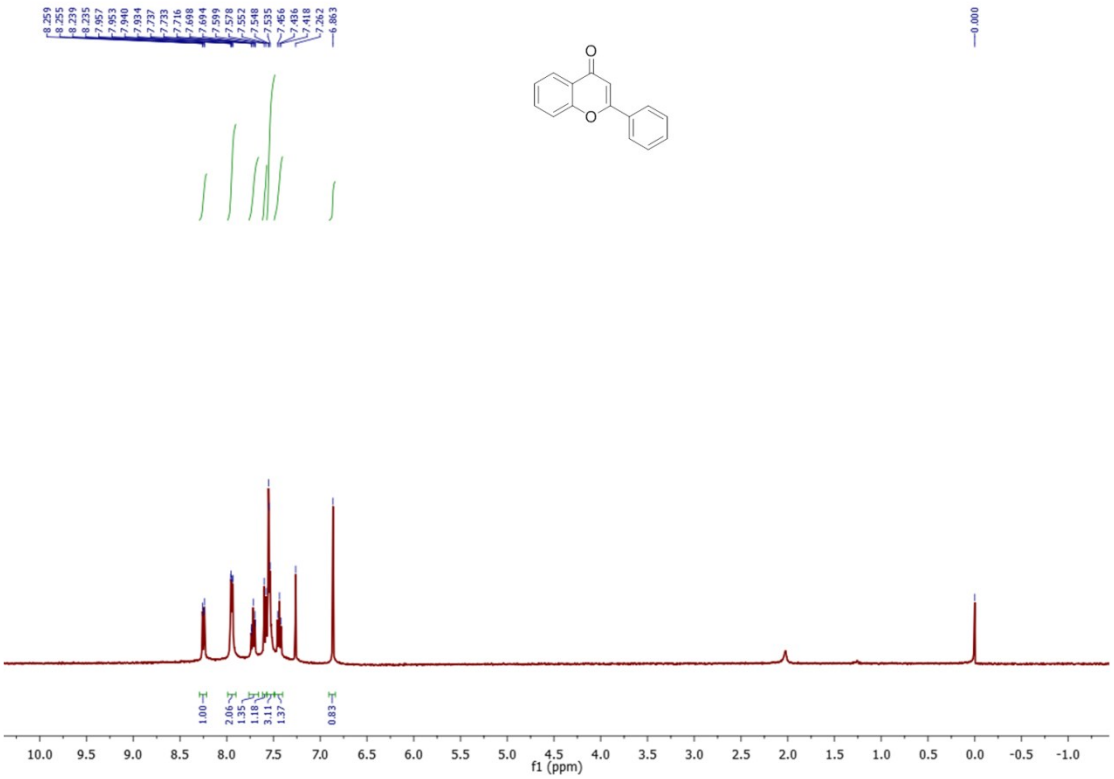


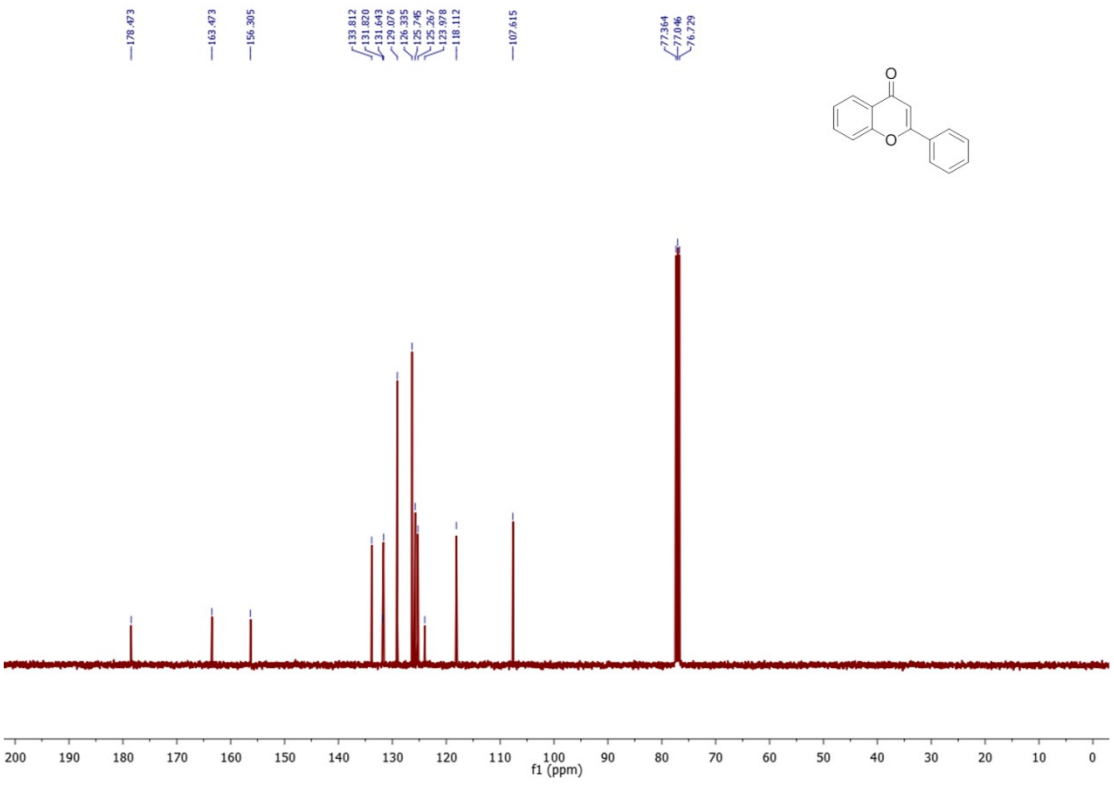
$[N_{2222}]_2[MoO_4]$

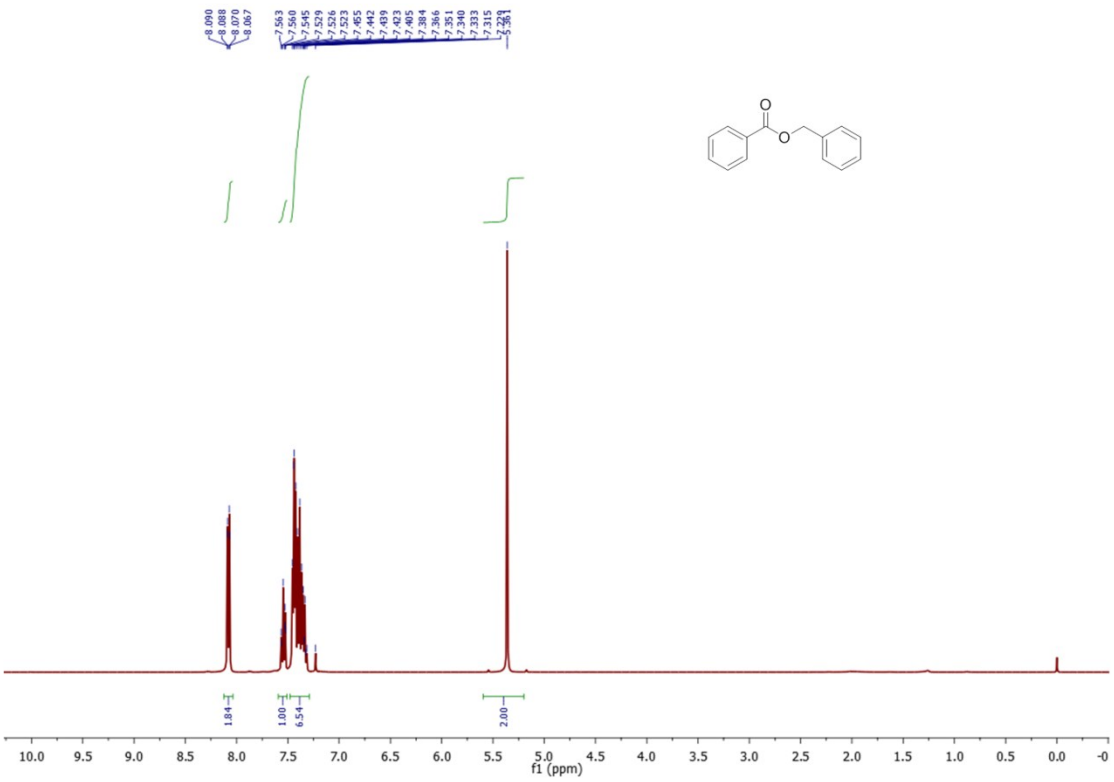


$[Bpy]_2[MoO_4]$

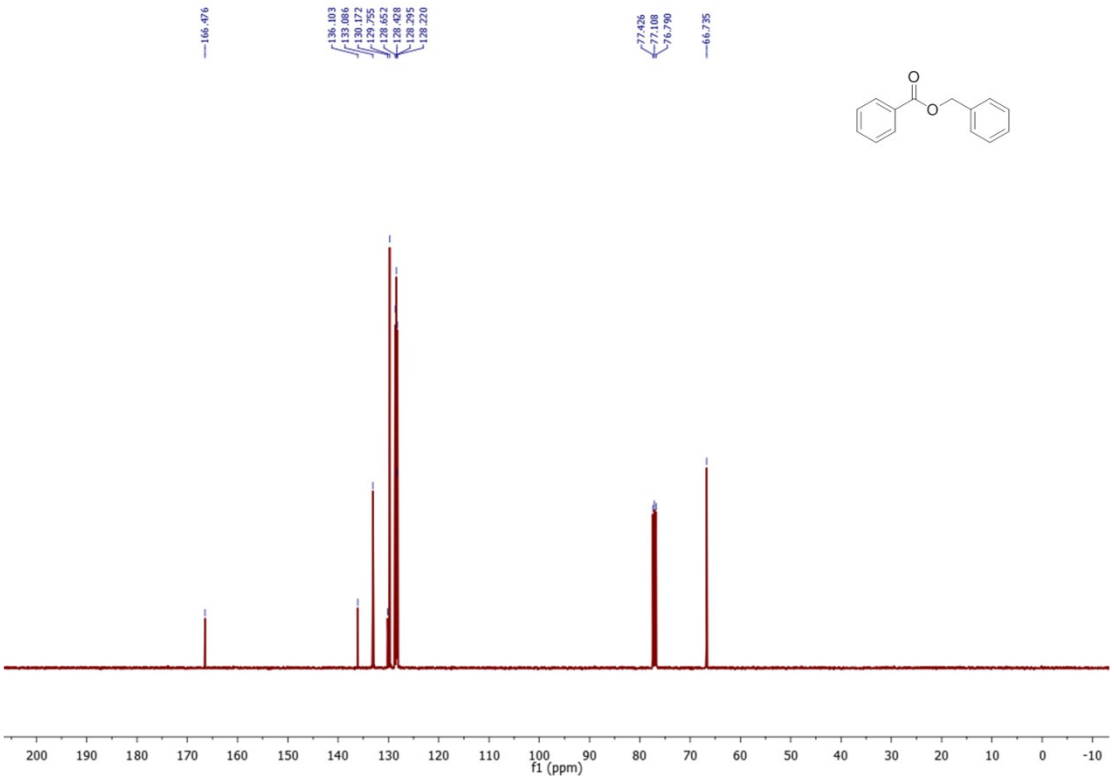
NMR spectra of products

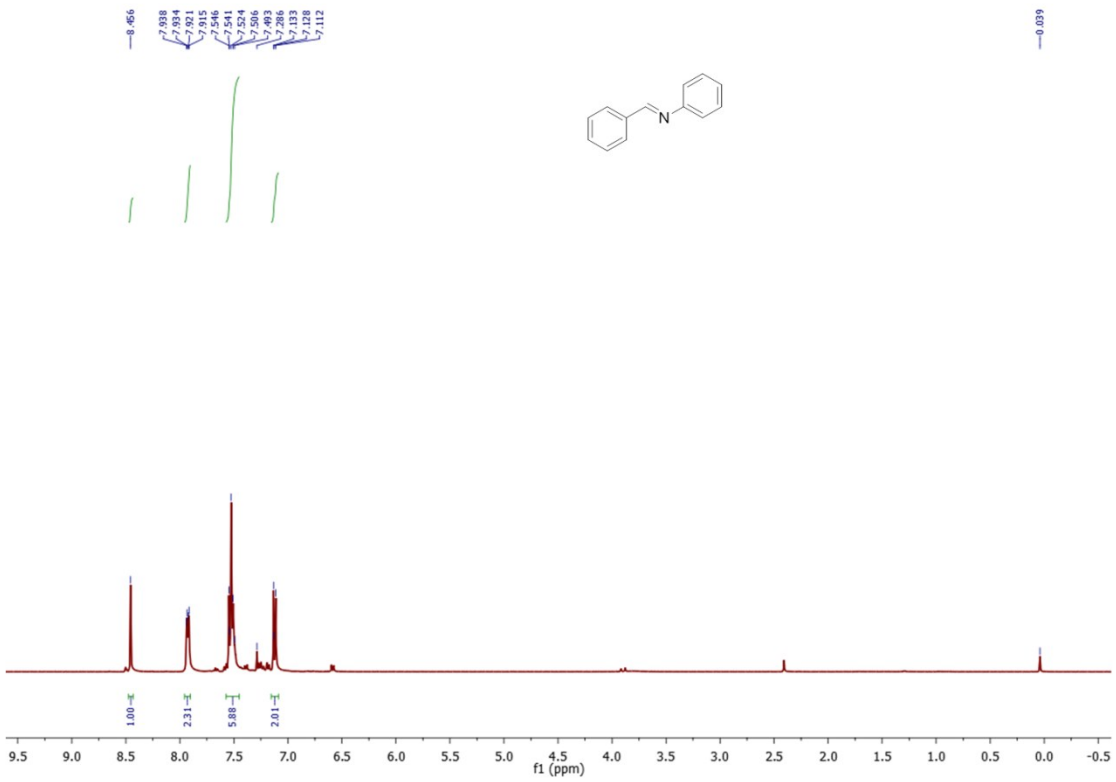






^{13}C NMR spectra of benzyl benzoate

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7.921
7.915
7.546
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7.524
7.506
7.493
7.286
7.133
7.128
7.112
0.039
N
1.00
2.31
5.88
2.01
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
-0.5
f1 (ppm)