Supporting Information for

Is the Formation of *N*-heterocyclic carbenes (NHCs) a Feasible Mechanism for the Distillation of Imidazolium Ionic Liquids?

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Summary

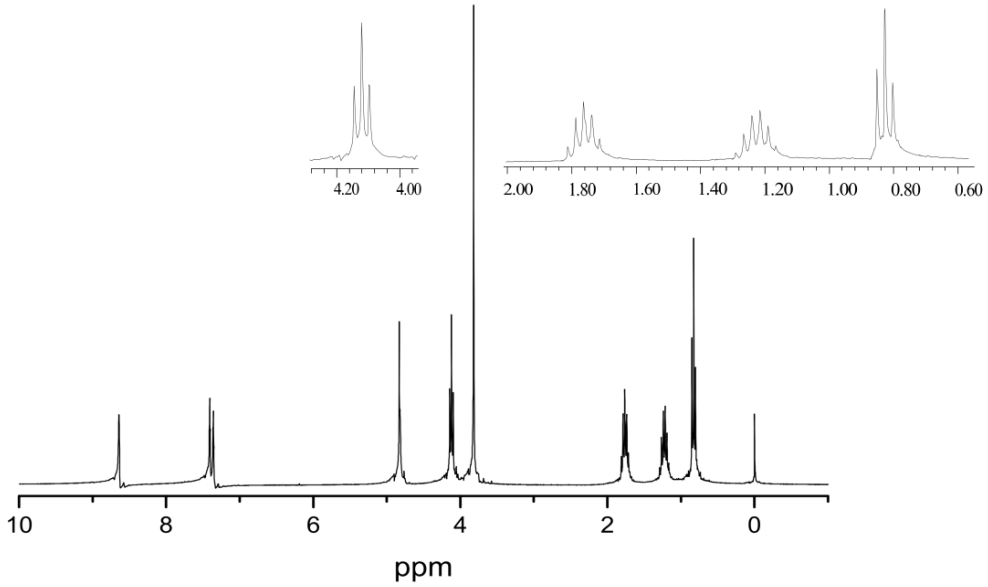

Figure S1. ^{1}H NMR (D_2O, 300 MHz) spectrum of **1a**. A sealed TMSP capillary was used as internal reference.

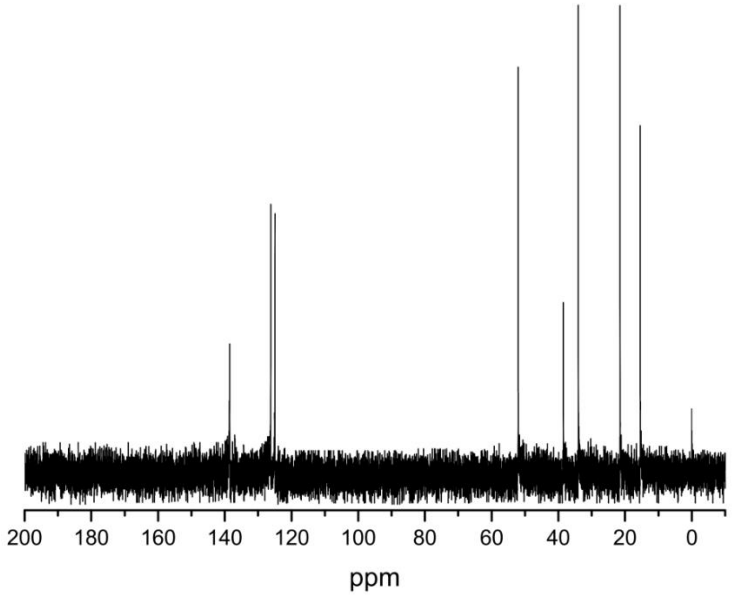

Figure S2. ^{13}C NMR (D_2O, 75 MHz) spectrum of **1a**. A sealed TMSP capillary was used as internal reference.

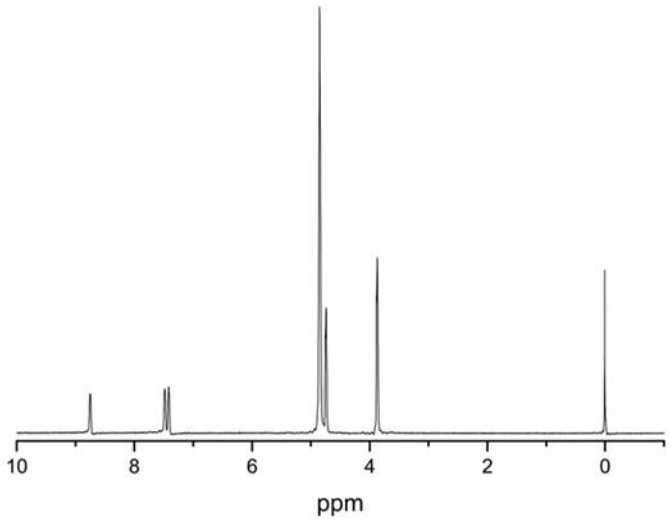

Figure S3. ^{1}H NMR (D_2O, 300 MHz) spectrum of **1b**. A sealed TMSP capillary was used as internal reference.

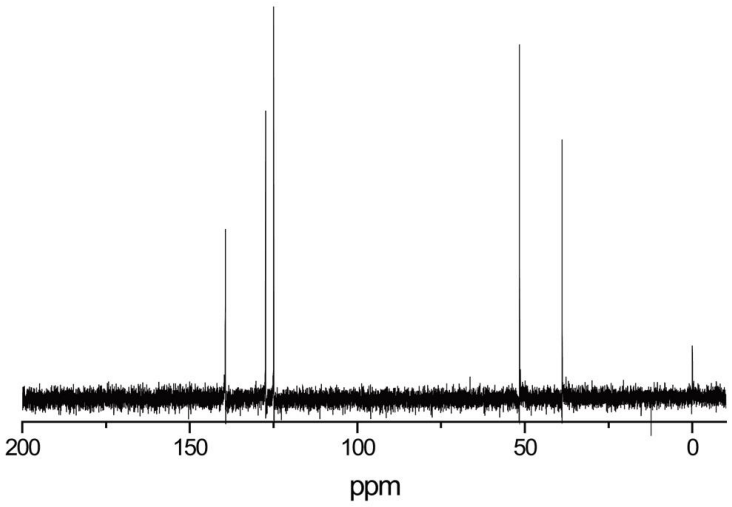

Figure S4. ^{13}C NMR (D_2O, 75 MHz) spectrum of **1b**. A sealed TMSP capillary was used as internal reference.

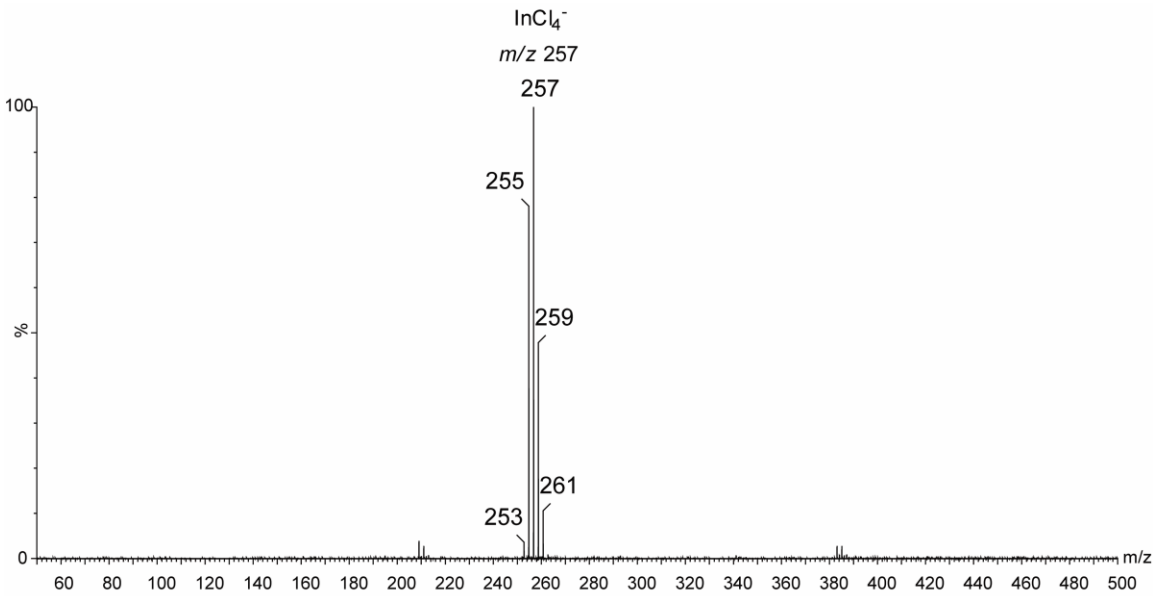

Figure S5. ESI(-)-MS of **1a**.

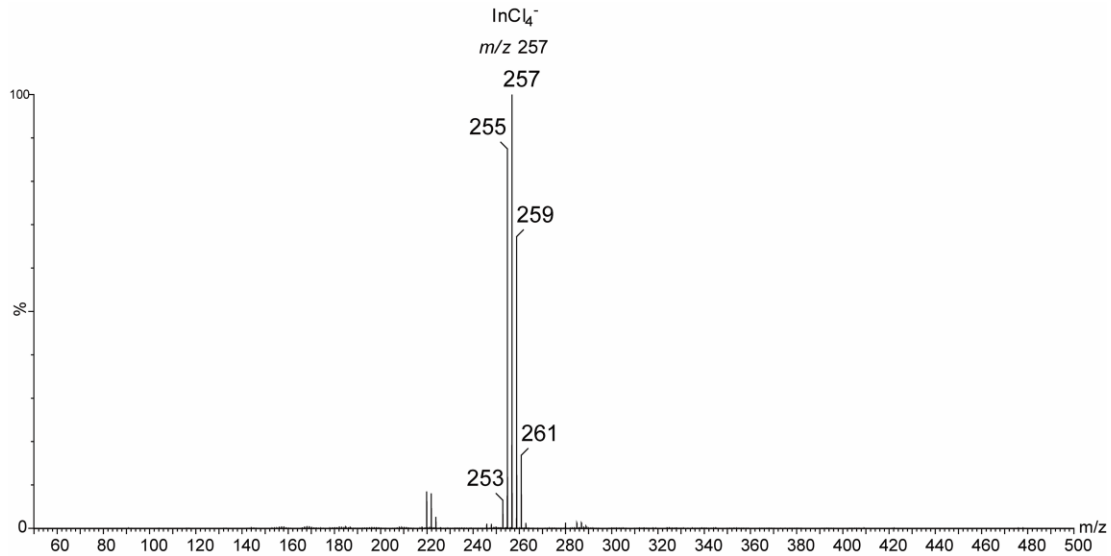

Figure S6. APCI(-)-MS of **1a**.

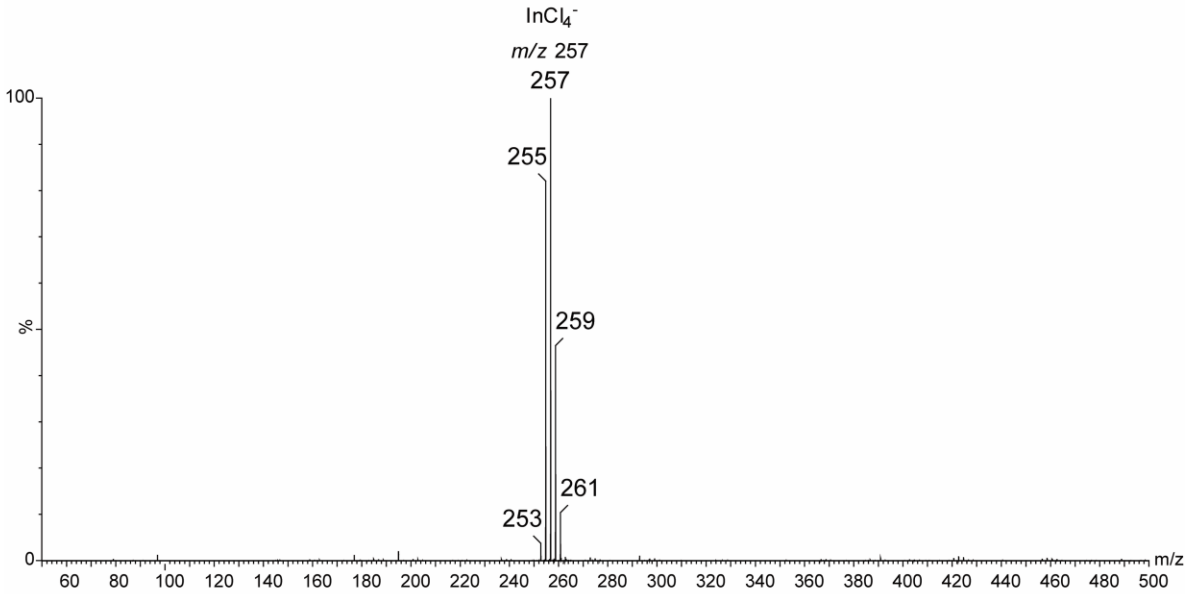

Figure S7. ESI(-)-MS of **1b**.

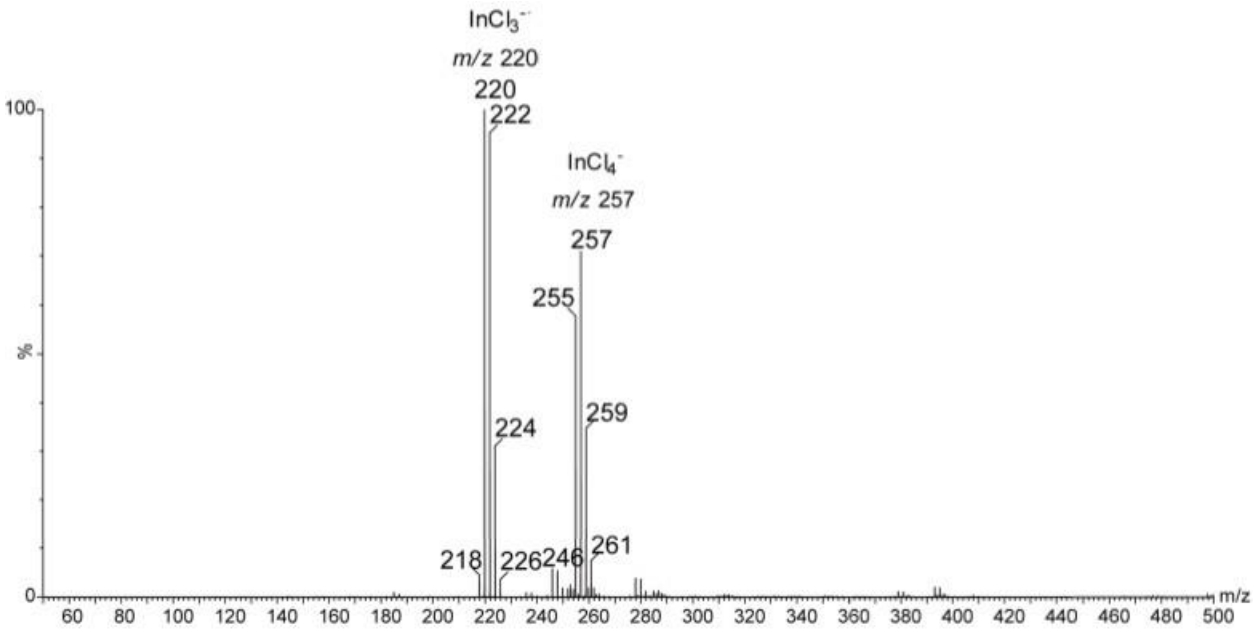

Figure S8. APCI(-)-MS of **1b**. $InCl_3$ was detected as an anion radical.

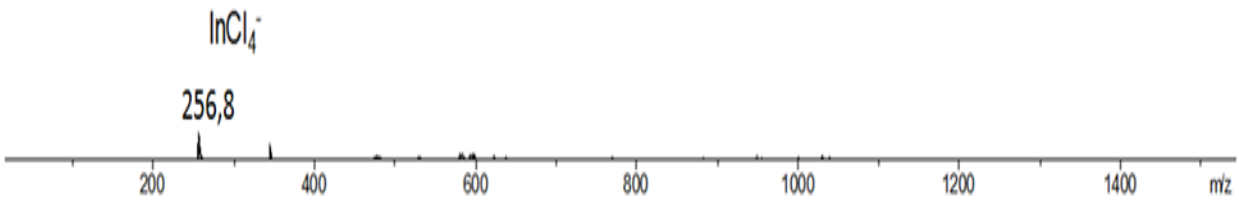

Figure S9. APTDI(-)-MS of **1b**.

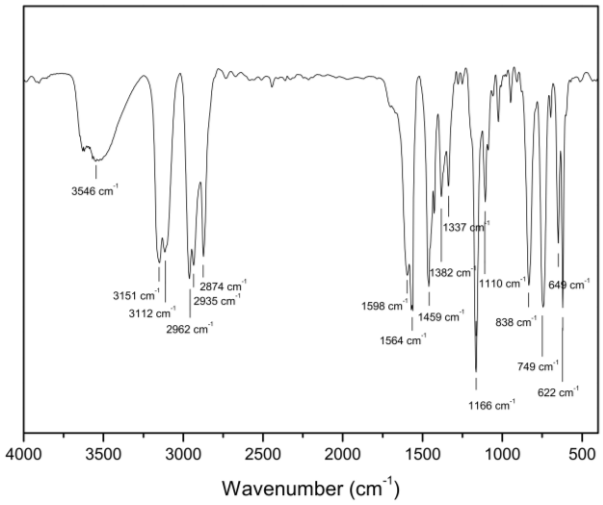

Figure S10. FTIR spectrum of **1a.**

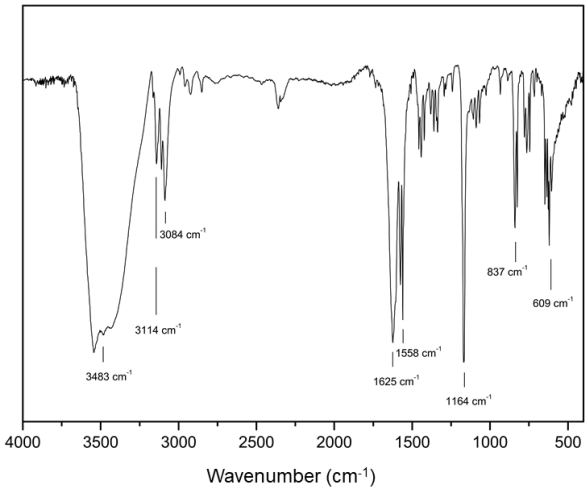

Figure S11. FTIR spectrum of **1b.**

Table S1. Cartesian coordinates for the optimized ion pair (**1a**).

B3LYP/6-31+G(d),

(with the LANL2DZ basis set for In)

Standard Orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.036203	1.443506	-0.720169
2	6	2.496904	2.649748	-0.924390
3	7	1.704406	2.957144	0.013806
4	6	1.793373	1.708012	0.935028
5	7	2.609713	0.932257	0.356627
6	6	0.906311	4.179376	0.187283
7	6	3.009312	-0.386928	0.867482
8	6	4.002578	-1.025138	-0.094620
9	6	4.416584	-2.391885	0.434655
10	6	5.409851	-3.030095	-0.527447
11	1	3.755006	0.959571	-1.397760
12	1	2.713076	3.290038	-1.792317
13	1	1.256334	1.533694	1.894179
14	1	0.320733	4.109867	1.131230
15	1	1.584269	5.060723	0.235946
16	1	0.210004	4.292885	-0.673554
17	1	3.485107	-0.268676	1.866684
18	1	2.110641	-1.037269	0.958124
19	1	3.526784	-1.143389	-1.093821
20	1	4.901249	-0.374796	-0.185262
21	1	4.892379	-2.273633	1.433857
22	1	3.517913	-3.042226	0.525297
23	1	5.712404	-4.028906	-0.140656

24	1	4.934056	-3.148347	-1.526649
25	1	6.308521	-2.379754	-0.618089
26	49	1.964564	-0.407309	-0.035532
27	17	2.840405	-1.358562	2.092406
28	17	2.561241	-1.914118	-1.925929
29	17	0.512316	-0.195728	0.107292
30	17	-2.968927	1.839172	-0.415895

Table S2. Cartesian coordinates for the optimized NHC (from **1a**).

B3LYP/6-31+G(d)

Standard Orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.485051	0.387708	0.432550
2	6	1.335694	-0.688584	0.541528
3	7	2.517480	-0.339823	-0.064771
4	6	1.139243	1.428374	-0.275214
5	1	0.671004	2.370080	-0.494128
6	1	3.212371	1.472226	-1.094974
7	6	2.410885	0.978694	-0.578057
8	6	3.714979	-1.181462	-0.161269
9	1	3.980221	-1.373812	-1.215941
10	1	4.575386	-0.706574	0.342934
11	1	3.535793	-2.162429	0.328569
12	6	0.913287	0.420874	0.911692
13	6	1.873938	-0.090356	-0.172278
14	6	3.321187	-0.078799	0.336600
15	6	4.291417	-0.570023	-0.733954

16	1	0.985940	-0.222701	1.825176
17	1	1.171109	1.457826	1.220162
18	1	1.588304	-1.121522	-0.469532
19	1	1.785421	0.521782	-1.089901
20	1	3.606184	0.941729	0.658746
21	1	3.409210	-0.719576	1.238213
22	1	4.064569	-1.596854	-1.045379
23	1	4.264457	0.058934	-1.630527
24	1	5.323131	-0.566609	-0.362155

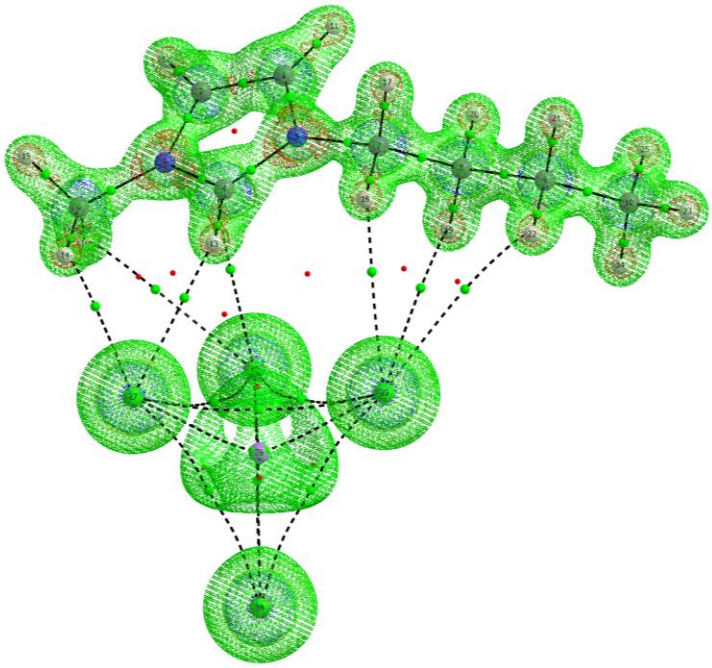

Figure S12. Three-dimensional map of the electronic density for optimized Ion Pair. M06-2X/6-311++G(2d,2p)//B3LYP/6-31+G(d) (with the LANL2DZ basis set for In).

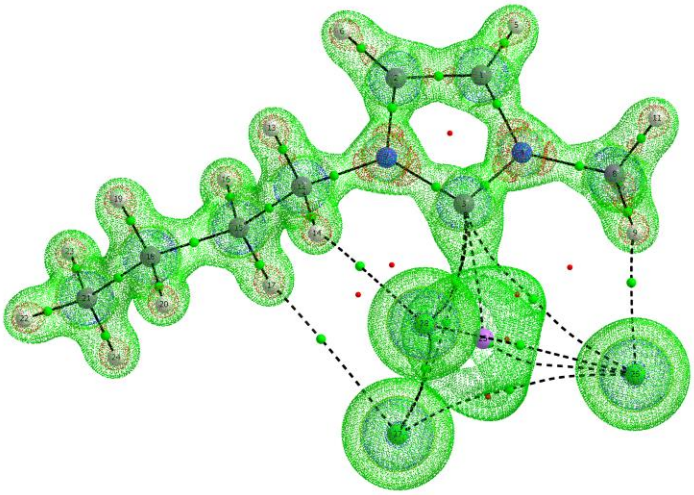

Figure S13. Three-dimensional map of electronic density for optimized complexed NHC. M06-2X/311++G(2d, 2p)//B3LYP/6-31+G(d) (with the LANL2DZ basis set for In).