Supporting Information

Imidazoline Synthesis: Mechanistic Investigations Show that Fe Catalysts Promote a New Multicomponent Redox Reaction

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Table of contents

Materials and methods

General

All solvents and reagents were of reagent grade quality and used as received except for dichloromethane and acetonitrile that were distilled under argon and over CaH_2 and thf over Na/benzophenone, respectively. Standard inert atmosphere techniques and a glove box Braun were used in handling all air and moisture sensitive reagents. Lewis acids and iron salts were kept under a positive pressure of argon (glovebox). Complexes **1a,b** were prepared according to published methods.[1–3] Literature procedures were used to prepare *m*-phenylene dipropionic acid,[4] 2-picolylamino-N,N-bis-2-methylene-4,6-dichlorophenol[5] and *para*-toluenesulfonyliminoiodobenzene (ArI=NTs).[6] All compounds gave good analytical data consistent with their purported structures.

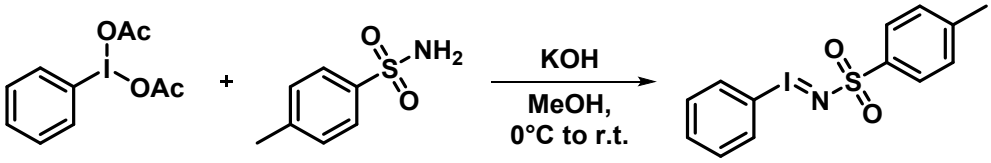
Physical measurements

NMR spectra were recorded on Bruker Avance III 400 MHz at 400 or 500 MHz (^{1}H) and at 100, 125 MHz (^{13}C), and 370, 470.6 MHz (^{19}F). Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (^{1}H: δ = 7.26 ppm and ^{13}C: δ = 77.16 ppm), CD_3CN (^{1}H: δ = 1.94 ppm and ^{13}C: δ = 118.26 ppm) and DMSO-d_6 (^{1}H: δ = 2.50 ppm) as the internal standard. All ^{13}C spectra were measured with complete proton decoupling. Coupling constants (*J*) are measured in hertz and are given with 0.5 Hz accuracy and the chemical shifts (δ) are measured in ppm. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet. HSQC, COSY, DEPT, and/or NOESY experiments were used to further characterize organic molecules. UV-Visible spectra were obtained with a spectrometer Hewlett Packard HP 89090A. ESI-MS were recorded on a LCQ Finnigan-Thermoquest equiped with an octupolar analyzer and an ion trap.

Chromatography. Reactions were monitored by thin layer chromatography (TLC) using commercial plastic silica gel plates (Merck, Kieselgel 60 F254), using ultraviolet light ($\lambda = 254$ nm) as the visualizing agent. TLC spots were viewed under ultraviolet light (light ($\lambda = 254$ nm). Products were purified by silica gel (Merck Kieselgel 60, 0.063-0.200 nm) for flash column chromatography.

Syntheses

Synthesis of nitrene precursor (tosylimino)iodobenzene (PhI=NTs)[6]

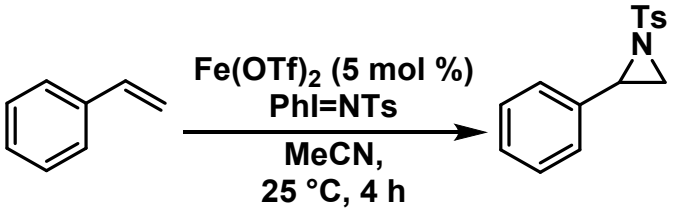


Iodobenzene diacetate (12.8 g, 40 mmol) was poured in 160 mL of methanol. The resulting white slurry was stirred and cooled at 0 °C. Then, *p*-toluenesulphonamide (6.84 g, 40 mmol) and KOH (5.6 g, 100 mmol) were added and the mixture was stirred for 1 h in an ice bath. The mixture was then thawed to room temperature and stirred for 3 h. The solution was left at 6 °C for several days to obtain yellow crystals. The crystals was filtered off and washed with cold methanol. Light yellow crystals were obtained (4.78 g, 32 %).

^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 2.33 (s, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.81 (t, *J* = 7.2 Hz, 2H), 8.21 (t, *J* = 7.8 Hz, 1H), 8.44 (d, *J* = 5.5 Hz, 2H).

The purity of PhI=NTs was checked regularly in the sulfimidation of thioanisole[7,8] and the catalytic efficiencies were corrected for the presence of advantitious tosylamine.

Bulk synthesis of 1-tosyl-2-phenylaziridine 2



$Fe(OTf)_2$ (65.8 mg, 0.186 mmol) was dissolved in 36 mL of acetonitrile. Then, styrene (4.25 mL, 37.2 mmol) was added to the solution. After 5 minutes of stirring, PhI=NTs (1.39 g, 3.72 mmol) was added, and the mixture was stirred for 3 hours at room temperature (red solution). The catalyst was eliminated upon filtration over silica gel (acetonitrile 100 %). The acetonitrile solution was evaporated to give a colorless oil. The aziridine was purified upon a column chromatography over silica gel using a hexane / EtOAc gradient: 100/0, 95/5, 90/10, 50/50 and 0/100). The aziridine **2** was obtained as a white crystalline product (631 mg, 62 %).

^{1}H NMR (400 MHz, CD_3CN, 298K) δ 2.43 (s, 3H), 2.51 (d, *J* = 4.5 Hz, 1H), 2.93 (d, *J* = 7.3 Hz, 1H), 3.73 (dd, *J* = 4.5 and 7.2 Hz, 1H), 7.21-7.34 (m, 5H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H).

ESI-MS m/z for $C_{15}H_{15}NO_2S$ $[M+H]^+$ calcd 274.1, found : 274.1.

Synthesis of 2-(methyl)-4-phenyl-1-tosyl-4,5-dihydro-1H-imidazole 3 from 2

2 (10 mg, 36.7 µmol) was dissolved in 1.7 mL of acetonitrile. The Lewis acid (5.3 µmol) was added to the solution. The colorless solution was stirred under argon in a thermostated bath regulated at 25°C for 18 h. The solution was then deposited on a silica plate and eluted with acetonitrile to remove the catalyst. The resulting solution was evaporated to dryness leaving an oil which was analyzed by NMR.

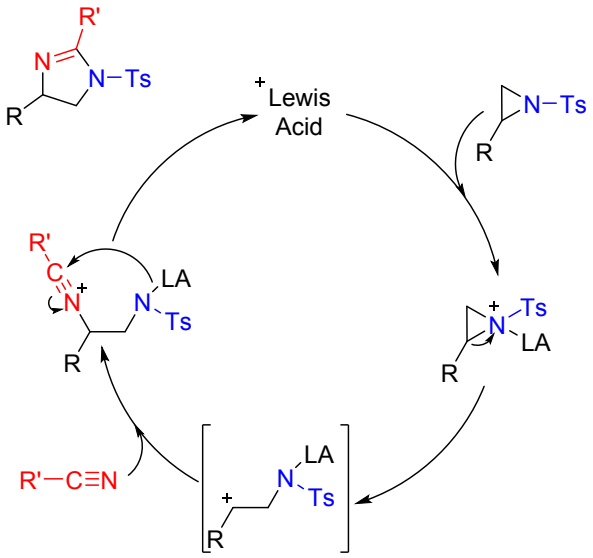
The imidazoline was purified upon a column chromatography over silica gel using a hexane / EtOAc 50/50 eluent. Aziridine **2**, imidazoline **3** and tosylamine were eluted successively with R_f = 0.2, 0.5 and 0.6.

Synthesis of aziridine 2 and imidazoline 3 from styrene

In a typical experiment, **1b** (3.00 mg, 2.6 µmol) was dissolved in 1.7 mL of acetonitrile and 61 µL of styrene (532 µmol) were added. The blue solution was transferred on PhI=NTs (19.84 mg, 53.2 µmol). The mixture was stirred under argon in a thermostated bath regulated at 25°C for 5 h. The solution was then deposited on a silica column and eluted with acetonitrile to remove the catalyst. The resulting solution was evaporated to dryness leaving a colorless oil which was analyzed by NMR.

Synthesis of aziridine 2 and imidazoline 3 from styrene by a telescoping reaction

In a typical experiment, **1b** (3.00 mg, 2.6 µmol) was dissolved in 1.7 mL of acetonitrile and 61 µL of styrene (532 µmol) were added. The blue solution was transferred on PhI=NTs (19.84 mg, 53.2 µmol). The mixture was stirred under argon in a thermostated bath regulated at 25°C for 5 h. Then, the Lewis acid (7.98 µmol) was added to the solution. The mixture was stirred overnight (13 h) and the solution was then deposited on a silica column and eluted with acetonitrile to remove the catalyst. The resulting solution was evaporated to dryness leaving a colorless oil which was analyzed by NMR.



Scheme S1. Proposed mechanism involving a nucleophilic opening of an aziridine by a Lewis acid.

Table S1. Influence of reaction time on imidazoline formation[a]

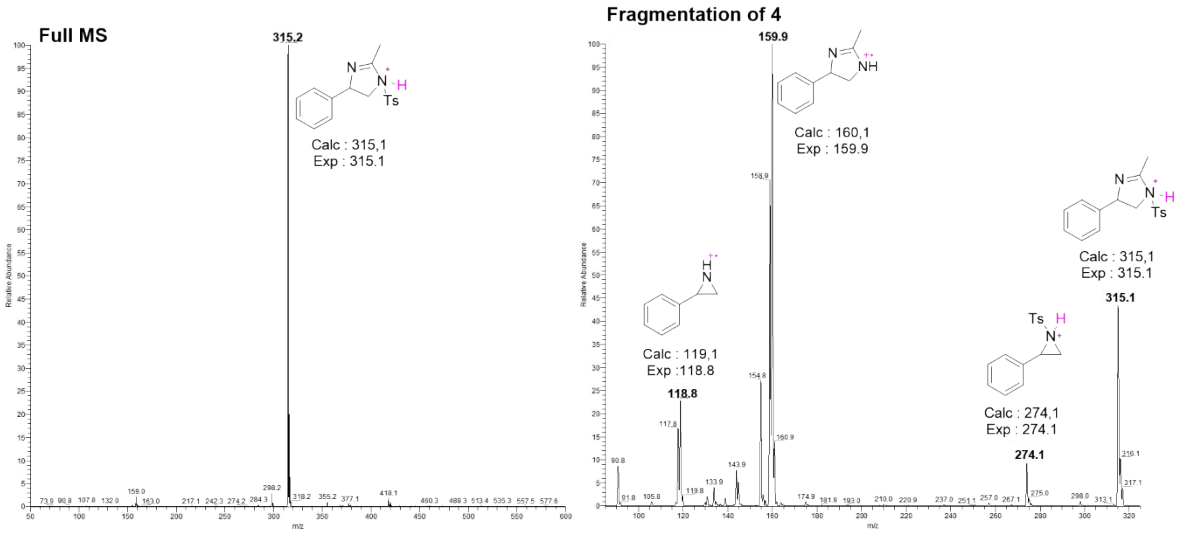
Entry	Reaction Time (h)	Conversion[b] (%)	**2**[b] (%)	**3**[b] (%)
1	1	100	86	14
2	4	100	86	14
3	8	100	86	14
4	24	100	85	15

[a] Reaction conditions: **1b**/PhI=NTs/styrene molar ratio = 0.05/1/10, acetonitrile, 25 °C [b] Yield based on ^{1}H NMR analysis of the reaction mixture, uncertainty $\pm$ 3 %.

Table S2. Influence of nitrile nature on imidazoline formation[a]

Entry	DCM	RCN	R	Conv.[b] (%)	**2**[b] (%)	**3**[b] (%)
1	50	50	Me	100	85	15
2	50	50	Ph	100	87	13
3	50	50	^{t}Bu	100	86	14

[a] Reaction conditions: **1**/PhI=NTs/styrene molar ratio = 0.05/1/10, 25 °C, reaction time 5 h.
[b] Yield based on ^{1}H NMR analysis of the reaction mixture, uncertainty $\pm$ 3 %.



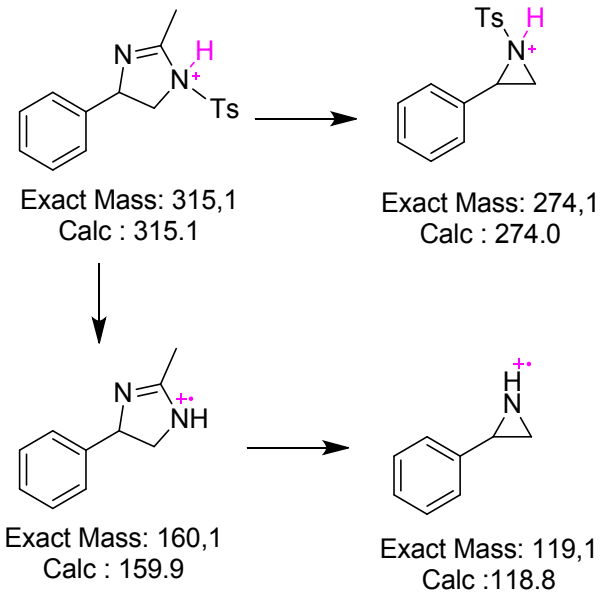


Figure S1. MS fragmentation of the $^{14}N/^{14}N$ imidazoline.

Reaction performed in $CH_3C^{14}N$:

ESI-MS: calculed for $C_{17}H_{18}N_2O_2S$ $[M + H]^+$: 315.1; found : 315.2.

Fragmentation of 4 (^{15}N)

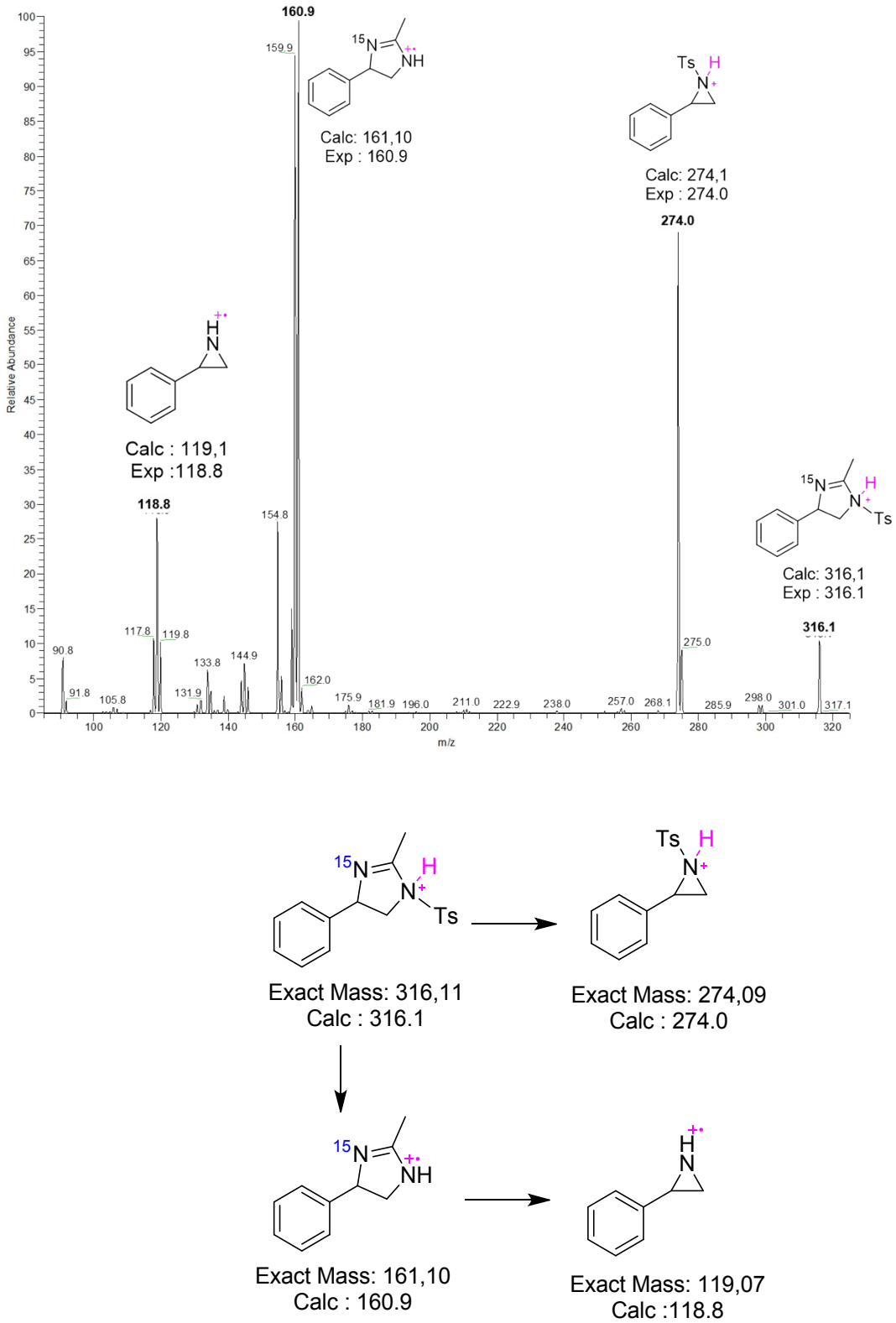
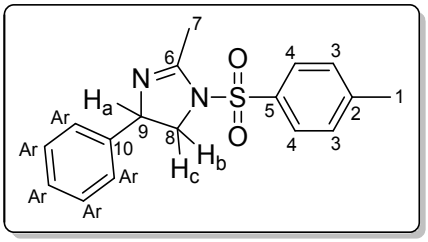


Figure S2. MS fragmentation of the ^{14}N/^{15}N imidazoline.

Reaction performed in $CH_3C^{15}N$:

ESI-MS: calcd for $C_{17}H_{19}N^{15}NO_2S$ $[M + H]^+$: 316.1; found : 316.1.

NMR characterization of 3 in CD_3CN.



^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 2.32 (d, *J* = 1.6 Hz, 3H, CH_3), 2.44 (s, 3H, $^{Ts}CH_3$), 3.45 (dd, *J* = 10.1 and 7.5 Hz, 1H, ^{B}CH), 4.17 (t, *J* = 10.1 Hz, 1H, ^{C}CH), 4.96 (dt, *J* = 1.6, 7.7 and 10.1 Hz, 1H, ^{A}CH), 6.96–6.99 (m, 2H, ^{Ar}CH), 7.21–7.26 (m, 3H, ^{Ar}CH), 7.41 (d, *J* = 8.4 Hz, 2H, ^{Ts}CH), 7.77 (d, J = 8.4 Hz, 2H, ^{Ts}CH).

^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 16.1 ($^{7}CH_3$), 20.6 ($^{1}CH_3$), 55.4 ($^{8}CH_2$), 66.5 (^{9}CH), 126.3 (^{Ar}CH), 127.3 (^{Ar}CH), 127.4 (^{4}CH), 128.5 (^{Ar}CH), 130.2 (^{3}CH), 134.8 (^{5}C), 142.5 (^{2}C), 145.2 (^{10}C), 155.6 (^{6}C).

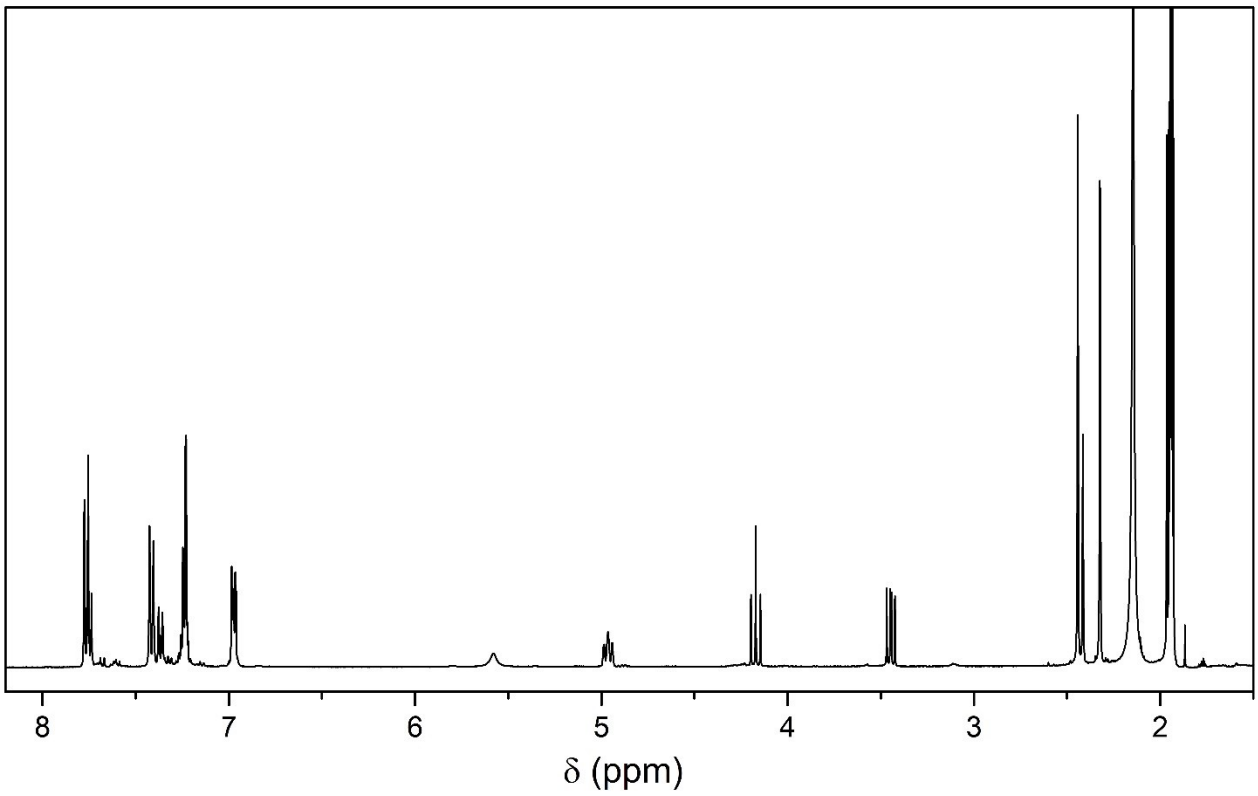


Figure S3. ^{1}H NMR of imidazoline **3** in CD_3CN.

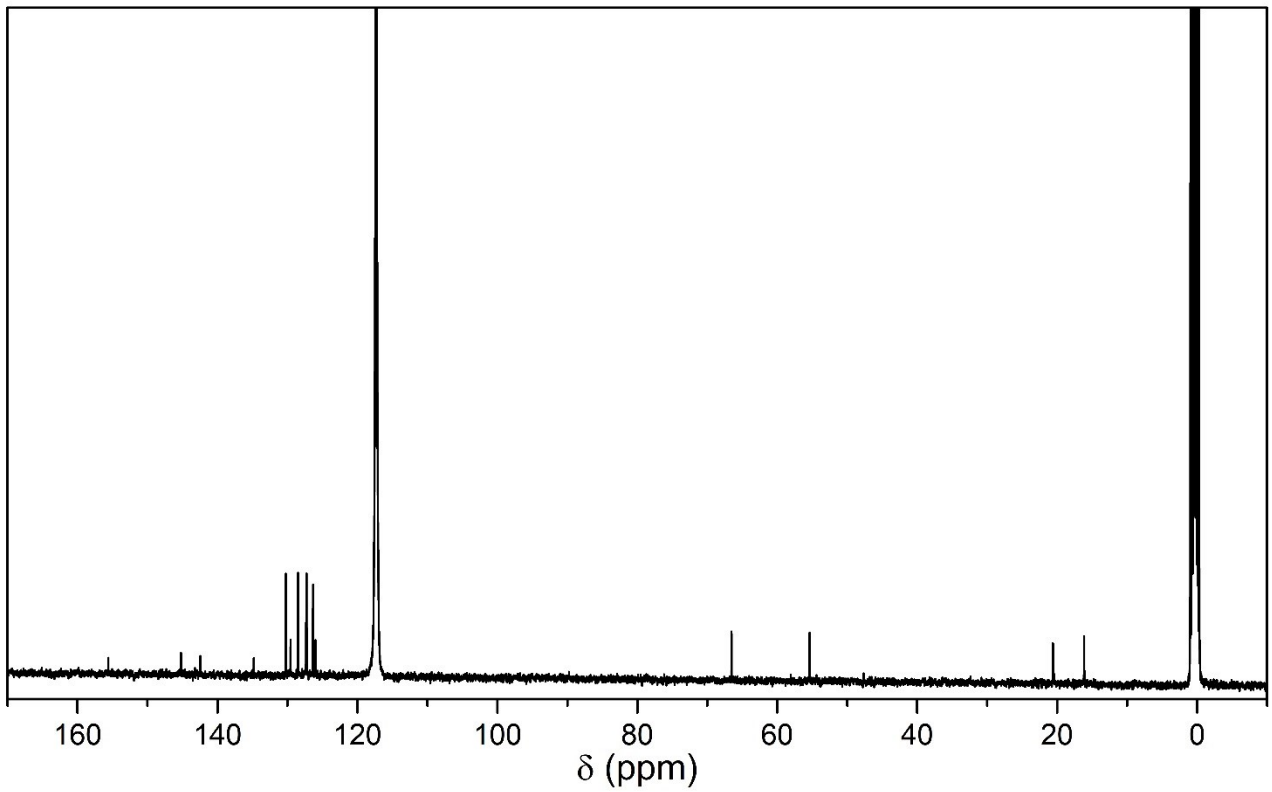


Figure S4. ^{13}C NMR of imidazoline **3** in CD_3CN.

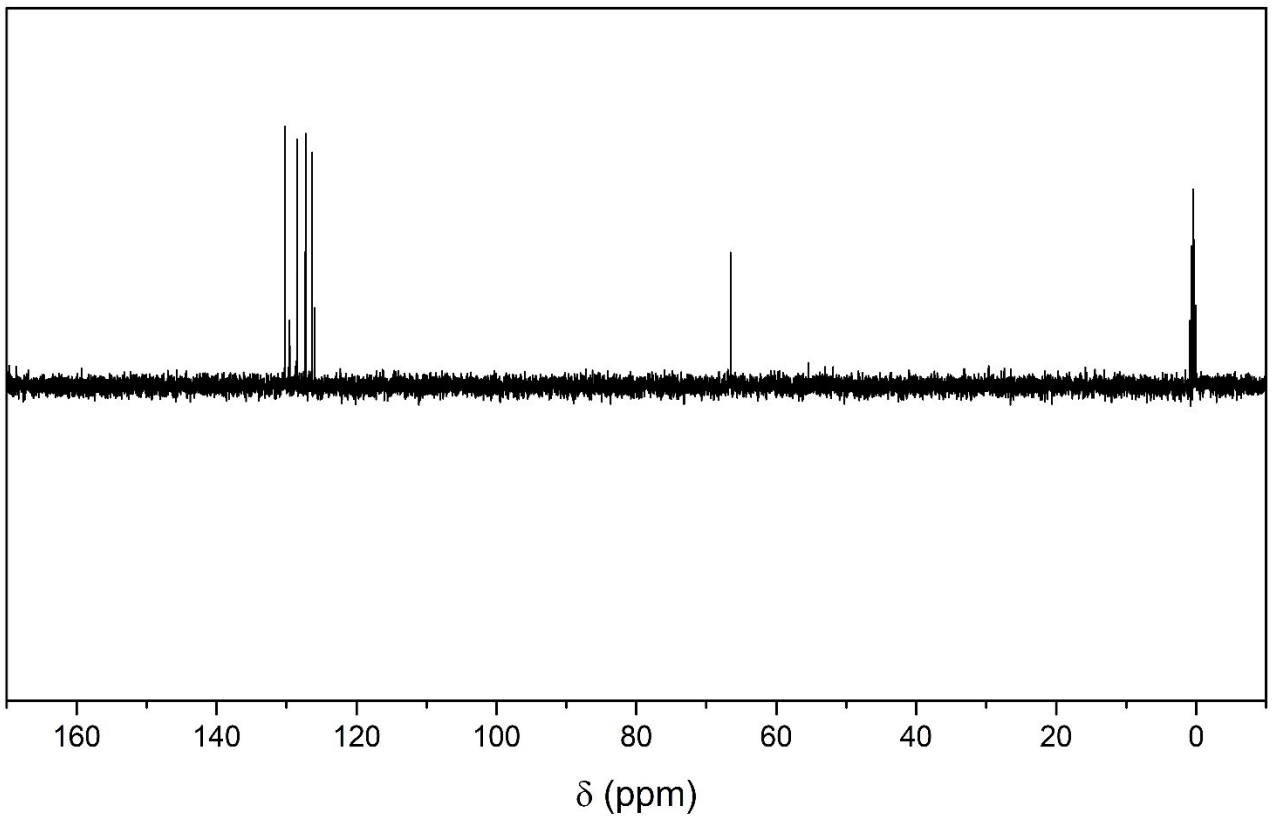


Figure S5. DEPT 90 NMR of imidazoline **3** in CD_3CN.

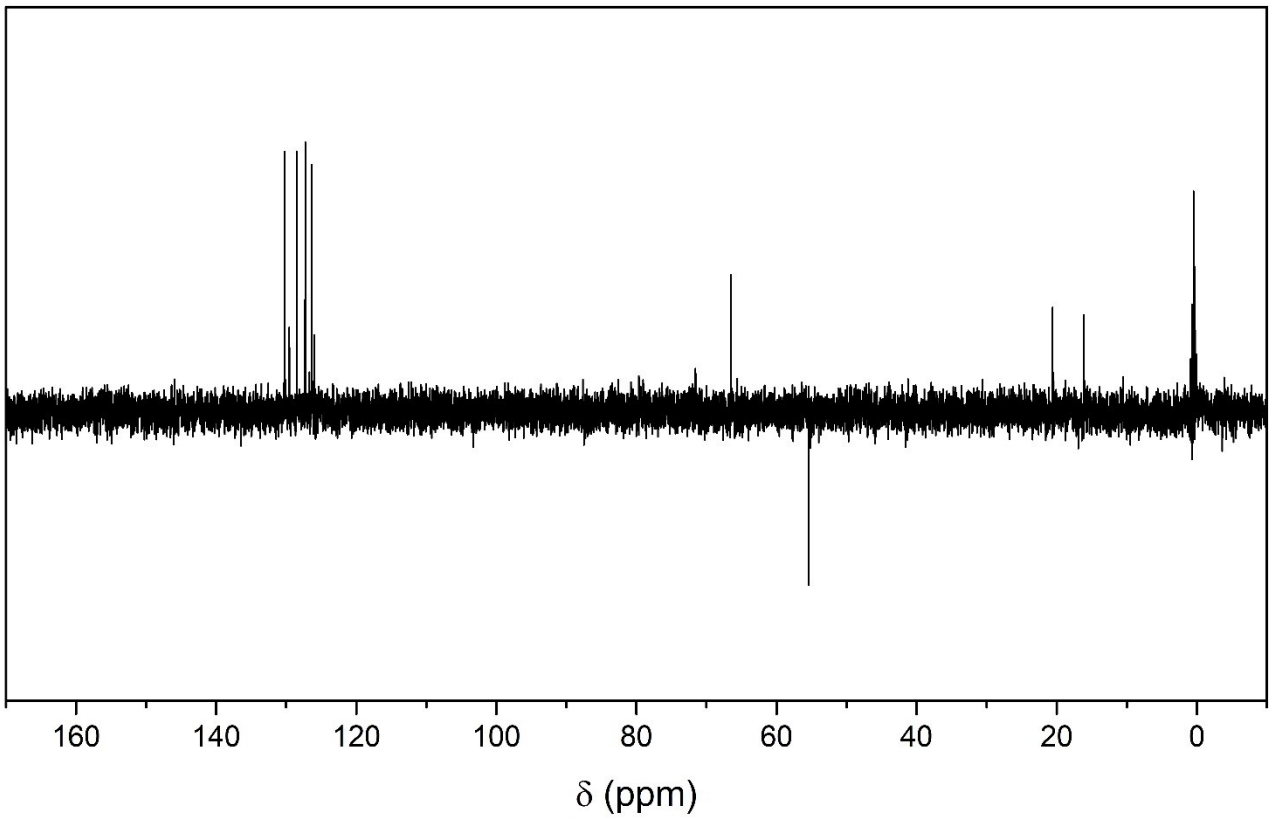


Figure S6. DEPT 135 NMR of imidazoline **3** in CD_3CN.

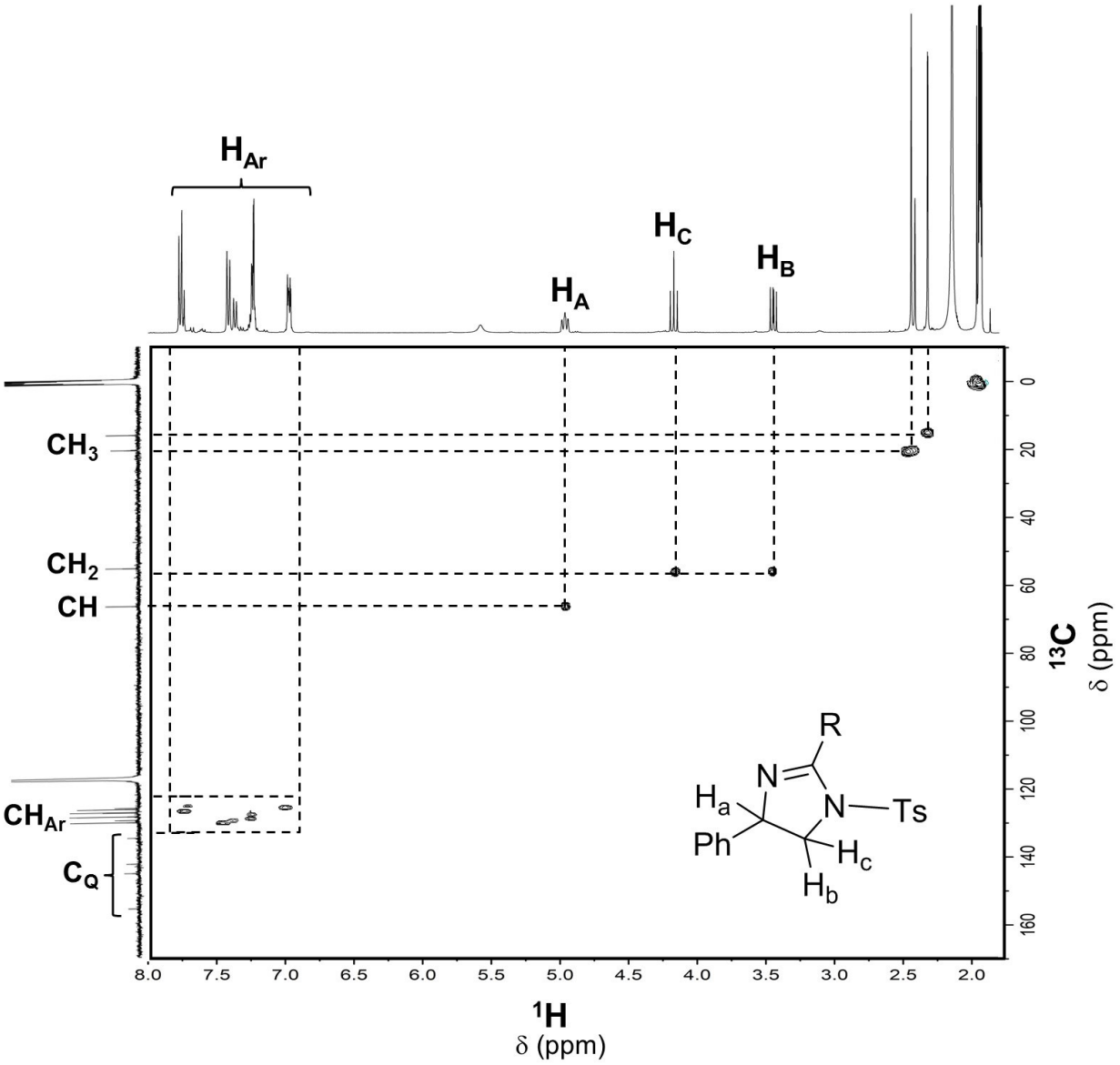


Figure S7. ^{1}H-^{13}C HSQC NMR of imidazoline **3** in CD_3CN.

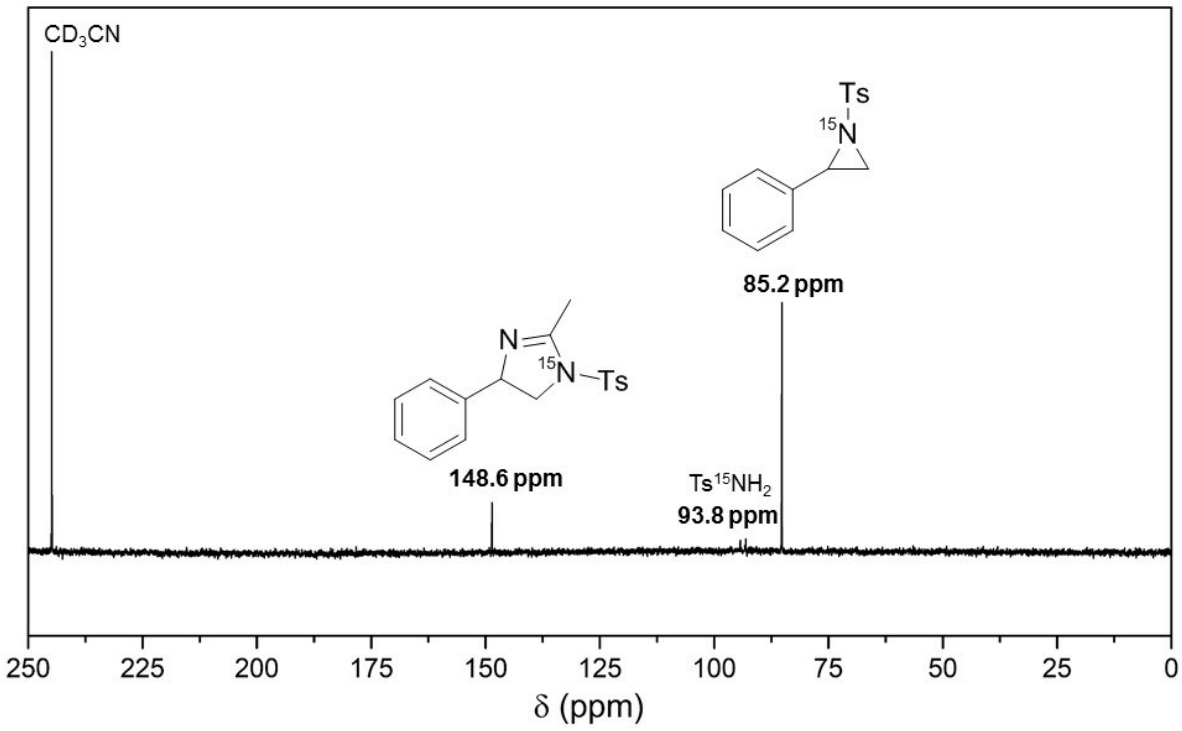
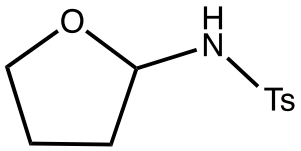


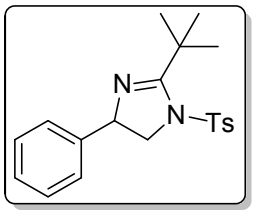
Figure S8. ^{15}N NMR of the crude reaction after separation of the catalyst.



Scheme S2. Product of THF amination **4**: 2-tosylaminotetrahydrofuran.

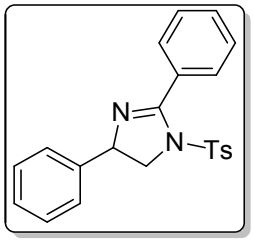
Characterization of imidazolines in CD_3CN.

2-(*tert*-butyl)-4-phenyl-1-tosyl-4,5-dihydro-*1H*-imidazole



^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 1.48 (s, 9H, CH3), 2.40 (s, 3H, CH3), 3.53 (dd, *J* = 3.0 and 8.1 Hz, 1H, CH), 4.16 (dd, *J* = 1.8 and 9.2 Hz, CH), 4.68-4.73 (m, 1H, CH), 7.03-7.06 (m, 2H, ^{Ar}CH), 7.20-7.36 (m, 5H, ^{Ar}CH), 7.72 (d, *J* = 8.4 Hz, 2H, ^{Ar}CH).
ESI - MS : calcd for $C_{20}H_{24}N_2O_2S$ $[M + H]^+$: 357.2; found : 357.2.

2,4-diphenyl-1-tosyl-4,5-dihydro-*1H*-imidazole



^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 2.42 (s, 3H, CH3), 3.71-3.76 (m, 1H, CH), 4.43 (dd, *J* = 1.5 and 10.0 Hz, CH), 4.99 (dd, *J* = 2.1 and 7.8 Hz, 1H, CH), 6.94-6.97 (m, 2H, ^{Ar}CH), 7.26-7.53 (m, 10H, ^{Ar}CH), 7.75 (d, *J* = 8.4 Hz, 2H, ^{Ar}CH).
ESI - MS : calcd for $C_{22}H_{20}N_2O_2S$ $[M + H]^+$: 377.1; found : 377.2.

Computational procedures

Calculations were done in the DFT framework with Orca 3.0.2.[9] The B3LYP[10,11] functional with Grimme 3[12,13] dispersion terms (noted B3LYP-D3) was employed with the LANL2DZ pseudopotential for Fe and 6-31G* for other atoms (basis set noted BS1). Numerical harmonic frequencies were calculated to characterize the nature of stationary points, minimum or transition state (TS) and to derive thermodynamics parameters. Tight parameters were used for electronic convergence (Grid4 and TightSCF criteria). Single-points were calculated from these geometries using B3LYP-D3 and a larger basis set, LANL2DZ for Fe and 6-311G** for other atoms, noted BS2, using a solvent continuum model (COSMO)[14] with standard parameters for acetonitrile. No automatic IRC is available in Orca 3.0, but for each TS, points on each side of the TS maximum were extracted from the animation of the imaginary mode using Chemcraft[15] utilities and submitted to geometry optimizations in order to check the connections between all minima and TSs.

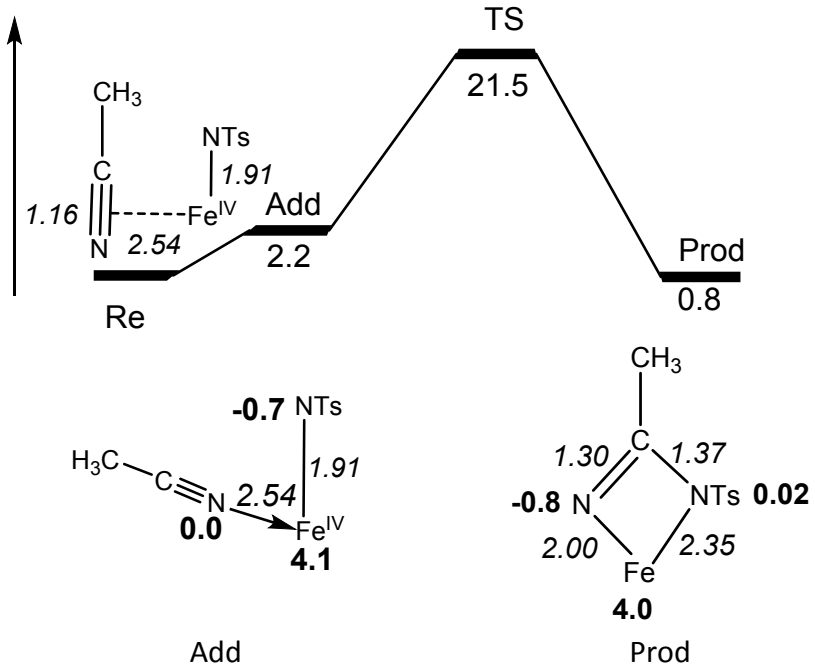


Figure S9. Enthalpies (kcal mol^{-1}) of formation of the metallacycle from acetonitrile and the [Fe^{IV}NTs] species in quintet state. Calculations with B3LYP-D3/BS2-COSMO//B3LYP-D3-BS1. Some selected bond distances (Å) are shown in italics and Mulliken spin densities on Fe and N (acetonitrile and NTs) are given in bold for the adduct (Add) and the final metallacycle (Prod).

Table S3. Energetics (Hartree) for the formation of the metallacycle from reaction of acetonitrile with the [Fe^{IV}NTs] active species calculated at the B3LYP-D3/BS2_COSMO//B3LYP-D3/BS1 level on the quintet state: electronic energy, enthalpy and free energy.

	E_{el}	H	G
Re	-5141.60585	-5141.09011	-5141.21657
Add	-5141.60454	-5141.08659	-5141.19384
TS	-5141.57215	-5141.05582	-5141.15927
Prod	-5141.61348	-5141.08877	-5141.19754

Table S4. Energetics (Hartree) for the pathway of formation of the imidazoline from reaction of acetonitrile with the intermediate species in aziridination mechanism with the Fe^{IV} model of active species calculated at the B3LYP-D3/BS2_COSMO//B3LYP-D3/BS1 level on the quintet state: electronic energy, enthalpy and free energy.

	E_{el}	H	G
Int0	-5408.91016	-5411.25864	-5411.39054
TS1	-5408.74159	-5411.23213	-5411.34667
Int1	-5408.77226	-5411.25675	-5411.36912
TS2	-5408.76861	-5411.24771	-5411.36147
Pdt	-5408.83568	-5411.31312	-5411.42015

Table S5. Selected distances (Å) in the key-species of the formation pathway of imidazoline from the Fe^{IV} model of active species calculated at the B3LYP-D3/BS2_COSMO//B3LYP-D3/BS1 level on the quintet state.

	Fe-N	C_α(styr)-N	CN (CH_3CN)
Int0	2.04	-	1.14
TS1	1.65	2.07	1.16
Int1	2.12	1.44	1.15
TS2	2.16	1.45	1.18
Pdt	-	1.46	1.27

Table S6. Mulliken spin densities and charges (Q) for selected atoms in the formation pathway of imidazoline from the Fe^{IV} model of active species calculated at the B3LYP-D3/BS2_COSMO//B3LYP-D3/BS1 level on the quintet state.

	Spin densities				Q		
	Fe	NTs	C_α(styr)	N(CH_3CN)	Cα(styr)	N(CH_3CN)	C(CH_3CN)
Int0	4.14	0.13	-0.76	0.00	-0.15	-0.15	-0.12
TS1	3.89	0.06	-0.17	-0.01	0.04	-0.04	-0.16
Int1	3.78	0.03	0.00	0.00	0.11	0.13	-0.09
TS2	3.76	0.00	0.00	0.00	0.1	0.00	0.14
Pdt	3.75	0.00	0.00	0.00	0.05	-0.17	-0.02

Cartesian coordinates

^{5}Int0

C	-2.207671	1.325539	0.742402
C	-1.789468	-0.102301	0.584306
N	-0.330873	-0.231834	0.563655
Fe	1.130580	1.188927	0.722871
O	2.805380	0.985877	-0.168748
O	0.792956	1.657034	2.535825
N	1.680378	3.641472	0.653010
N	0.409016	2.022345	-1.241010
C	3.156270	3.719297	0.497708
H	3.590430	3.206790	1.370636
H	3.470627	4.780593	0.558822
C	3.710465	3.110674	-0.763627
C	4.479402	3.877430	-1.645543
H	4.645172	4.939539	-1.450452
C	5.060610	3.287604	-2.769422
C	4.889542	1.925688	-3.023495
H	5.348607	1.461295	-3.896394
C	4.125390	1.160983	-2.144050
C	3.513123	1.719742	-0.989393
C	1.274993	4.307112	1.921260
H	1.554063	5.378989	1.879356
H	0.174883	4.249322	1.964541
C	1.842387	3.686573	3.166706
C	2.590819	4.425526	4.087523
H	2.842845	5.470440	3.892022
C	3.021679	3.821554	5.270675
C	2.720129	2.484610	5.540246
H	3.066815	2.015363	6.461164
C	1.977849	1.745313	4.617940
C	1.515246	2.329300	3.410041
C	0.966342	4.262252	-0.470317
H	1.518160	5.130588	-0.876514
H	0.008418	4.655795	-0.088322
C	0.629416	3.301549	-1.583548
C	0.470134	3.745449	-2.902528
H	0.663093	4.791463	-3.150900
C	0.076178	2.838446	-3.882858
H	-0.055613	3.165708	-4.917570
C	-0.137649	1.506523	-3.519440
H	-0.437910	0.756258	-4.252722
C	0.045613	1.141622	-2.188767
H	-0.094783	0.114457	-1.844896
Cl	6.020921	4.255183	-3.865775
Cl	3.924510	-0.541953	-2.474527
Cl	3.954537	4.745074	6.428233
Cl	1.602115	0.084109	4.951834
S	0.362901	-1.488799	1.348738
O	-0.397048	-1.963915	2.510935
O	1.750800	-0.957131	1.516845
C	0.486827	-2.869519	0.201393
C	1.394271	-2.788136	-0.862732
C	1.474318	-3.851967	-1.764490
C	0.658526	-4.979458	-1.599469
C	-0.237427	-5.048954	-0.526542
C	-0.326435	-3.991393	0.385271
H	2.033388	-1.909592	-0.972375
H	2.182460	-3.800574	-2.595831
H	-0.862328	-5.934978	-0.386509
H	-0.999790	-4.032586	1.243548
H	0.732366	-5.811818	-2.304733
C	-3.696105	1.489955	-1.272299
C	-4.624757	2.208130	-2.017427
C	-5.026665	3.491710	-1.617443
C	-4.466306	4.058100	-0.460095
C	-3.535257	3.351107	0.289993
C	-3.124500	2.031569	-0.078986
H	-2.189983	-0.674467	1.445477
H	-2.235650	-0.554451	-0.319643
H	-1.792005	1.838483	1.616377
H	-3.392236	0.498408	-1.614383
H	-5.050699	1.761903	-2.920833
H	-5.763162	4.046797	-2.203903
H	-4.778490	5.055477	-0.136758
H	-3.110599	3.795114	1.195439

^{5}TS1

C	-2.830378	1.416736	0.344989
C	-2.118235	0.113255	-0.122921
N	-0.980007	-0.167807	0.714878
Fe	0.658645	1.214342	0.925780
O	2.567334	0.775548	0.532196
O	0.309979	1.752078	2.799089
N	1.169650	3.523928	0.599671
N	0.506419	1.625624	-1.356607
C	2.652199	3.646959	0.625528
H	2.968659	3.355996	1.638719
H	2.924566	4.713935	0.491455
C	3.414218	2.821638	-0.379683
C	4.235877	3.461454	-1.314451
H	4.248924	4.552900	-1.369752
C	5.044986	2.720818	-2.175084
C	5.070070	1.327209	-2.085620
H	5.719461	0.740611	-2.735885
C	4.253077	0.689985	-1.155478
C	3.365164	1.392382	-0.286362
C	0.559481	4.325371	1.694464
H	0.715881	5.406124	1.499687
H	-0.527236	4.131026	1.647520
C	1.063517	3.996582	3.074407
C	1.648316	4.979644	3.880676
H	1.785931	5.994905	3.501500
C	2.069881	4.671151	5.173907
C	1.924882	3.373167	5.669148
H	2.274222	3.118926	6.670210

C	1.346068	2.394216	4.863148
C	0.880520	2.664552	3.545107
C	0.615354	3.950308	-0.688778
H	1.083816	4.890694	-1.042451
H	-0.456673	4.175538	-0.542079
C	0.724643	2.888230	-1.757312
C	0.987707	3.204642	-3.095568
H	1.173974	4.241458	-3.384720
C	1.041835	2.178078	-4.036053
H	1.260293	2.400381	-5.083848
C	0.841440	0.862729	-3.608370
H	0.898641	0.021374	-4.301207
C	0.581591	0.636051	-2.258315
H	0.442589	-0.378566	-1.875330
Cl	6.041379	3.534091	-3.368665
Cl	4.326910	-1.057244	-1.034216
Cl	2.794223	5.912962	6.177929
Cl	1.206743	0.765965	5.491361
S	-0.884877	-1.708009	1.331784
O	-2.249102	-2.191813	1.653501
O	0.128663	-1.657401	2.393429
C	-0.246495	-2.785246	0.035582
C	1.057038	-2.579991	-0.434849
C	1.562893	-3.441628	-1.411414
C	0.787300	-4.504671	-1.890332
C	-0.505925	-4.707541	-1.397910
C	-1.030910	-3.845773	-0.428412
H	1.675956	-1.763700	-0.052929
H	2.572552	-3.273916	-1.793140
H	-1.109350	-5.541983	-1.764610
H	-2.030865	-3.993042	-0.016462
H	1.196920	-5.181148	-2.645238
C	-4.640212	1.034839	-1.425539
C	-5.813292	1.438660	-2.074839
C	-6.499919	2.576536	-1.646850
C	-6.013091	3.309427	-0.558053
C	-4.839177	2.912243	0.082854
C	-4.138364	1.771506	-0.343621
H	-2.854252	-0.706920	-0.092691
H	-1.832865	0.300626	-1.172008
H	-2.122841	2.254399	0.203403
H	-4.123228	0.141609	-1.778821
H	-6.191263	0.854141	-2.917706
H	-7.412700	2.893950	-2.157837
H	-6.548975	4.195551	-0.208172
H	-4.460056	3.491801	0.929398
C	-2.376293	0.716761	2.630285
N	-2.963571	1.292828	1.787671
C	-1.983134	0.165534	3.902816
H	-2.302001	0.854158	4.702301
H	-0.884716	0.074567	3.915277
H	-2.444785	-0.827209	4.011773

[5]Int1

C	-2.880931	1.330937	0.386420
C	-2.123152	0.187460	-0.363969
N	-0.848825	-0.103796	0.235736
Fe	0.656634	1.315987	0.662772
O	2.570777	0.877354	0.313933
O	0.150077	1.839075	2.534313
N	1.228312	3.649296	0.419303
N	0.553130	1.833986	-1.601321
C	2.707534	3.745692	0.541861
H	2.953487	3.423393	1.565142
H	3.001488	4.812100	0.455411
C	3.534520	2.939745	-0.428234
C	4.490953	3.594682	-1.213403
H	4.557260	4.685414	-1.189333
C	5.381707	2.870187	-2.004520
C	5.329769	1.474631	-2.018147
H	6.027847	0.898748	-2.626170
C	4.378225	0.821695	-1.239724
C	3.437825	1.509252	-0.412671
C	0.562870	4.424064	1.500696
H	0.737320	5.509340	1.350070
H	-0.520778	4.240256	1.388137
C	0.990610	4.044492	2.891270
C	1.600279	4.979654	3.733979
H	1.795399	5.994887	3.380504
C	1.984515	4.621998	5.025768
C	1.773579	3.319279	5.481843
H	2.098048	3.021751	6.479349
C	1.168549	2.389677	4.637756
C	0.736893	2.706063	3.317113
C	0.762022	4.134087	-0.882518
H	1.307626	5.046976	-1.194480
H	-0.297764	4.429276	-0.776944
C	0.835983	3.091365	-1.972181
C	1.109856	3.427186	-3.303742
H	1.350751	4.459433	-3.568309
C	1.093028	2.423769	-4.270795
H	1.310470	2.660677	-5.315767
C	0.818134	1.111958	-3.874578
H	0.812196	0.288576	-4.591229
C	0.561450	0.864158	-2.526915
H	0.360621	-0.146272	-2.159551
Cl	6.588514	3.703781	-2.969094
Cl	4.358511	-0.932447	-1.245700
Cl	2.754592	5.801335	6.070752
Cl	0.980861	0.745064	5.220013
S	-0.688147	-1.536325	1.016181
O	-2.003238	-2.009204	1.532878
O	0.413391	-1.373955	1.974503
C	-0.156587	-2.758222	-0.200505
C	1.122749	-2.628758	-0.757034
C	1.546392	-3.570374	-1.697529
C	0.708099	-4.629980	-2.067909

C	-0.561115	-4.753492	-1.493859
C	-1.000503	-3.815358	-0.552206
H	1.781986	-1.809431	-0.459054
H	2.541653	-3.472053	-2.138109
H	-1.213162	-5.584951	-1.774564
H	-1.979306	-3.900272	-0.076866
H	1.050580	-5.365918	-2.800389
C	-4.933422	0.973972	-1.108927
C	-6.173157	1.401771	-1.598250
C	-6.752991	2.578865	-1.120372
C	-6.086032	3.334592	-0.149371
C	-4.842735	2.916271	0.327056
C	-4.252005	1.732174	-0.146585
H	-2.779107	-0.697882	-0.389918
H	-2.010337	0.565176	-1.397105
H	-2.218734	2.214345	0.377101
H	-4.503801	0.047913	-1.493800
H	-6.689258	0.803541	-2.353556
H	-7.718981	2.913142	-1.508338
H	-6.534616	4.253926	0.236210
H	-4.322200	3.520001	1.076774
C	-2.633618	0.478454	2.782246
N	-2.938687	0.956226	1.778112
C	-2.304391	-0.088490	4.061712
H	-2.961653	0.324373	4.842196
H	-1.248999	0.172748	4.272738
H	-2.404367	-1.181600	3.978261

^{5}TS2

C	-2.859944	1.414987	0.337360
C	-2.125563	0.121772	-0.123556
N	-0.997498	-0.150255	0.731279
Fe	0.653280	1.225262	0.941612
O	2.562782	0.778657	0.549282
O	0.324183	1.767995	2.817550
N	1.178161	3.532465	0.611858
N	0.505311	1.635700	-1.340811
C	2.661095	3.649896	0.625688
H	2.982764	3.364157	1.638667
H	2.936323	4.715138	0.483711
C	3.416864	2.815433	-0.376565
C	4.242132	3.446225	-1.314201
H	4.258195	4.537170	-1.377774
C	5.053383	2.697418	-2.165671
C	5.077206	1.304752	-2.063394
H	5.729323	0.711844	-2.705171
C	4.256173	0.676407	-1.130650
C	3.364601	1.386983	-0.271755
C	0.582709	4.337904	1.711615
H	0.743501	5.417651	1.514858
H	-0.505307	4.149026	1.675905
C	1.099589	4.005831	3.085642
C	1.704716	4.982584	3.884545
H	1.848930	5.996246	3.503579
C	2.138783	4.669785	5.172507
C	1.984320	3.373768	5.670503
H	2.341344	3.116071	6.667984
C	1.384864	2.401475	4.871655
C	0.910268	2.675474	3.557635
C	0.613287	3.959623	-0.671209
H	1.076419	4.901940	-1.026974
H	-0.458237	4.181631	-0.515931
C	0.718574	2.899202	-1.741535
C	0.975223	3.217514	-3.080527
H	1.156695	4.255253	-3.369396
C	1.029413	2.191979	-4.022106
H	1.242800	2.415786	-5.070613
C	0.835860	0.875687	-3.594402
H	0.894018	0.034857	-4.287788
C	0.581393	0.647170	-2.243643
H	0.447910	-0.368450	-1.861525
Cl	6.055535	3.499647	-3.361931
Cl	4.333626	-1.069328	-0.990247
Cl	2.890892	5.903739	6.165894
Cl	1.227588	0.775803	5.502054
S	-0.894211	-1.698570	1.331156
O	-2.257656	-2.191304	1.644747
O	0.116943	-1.652406	2.393651
C	-0.251203	-2.762843	0.025809
C	1.055213	-2.556056	-0.435707
C	1.565143	-3.410854	-1.416356
C	0.791225	-4.469669	-1.907025
C	-0.504580	-4.675143	-1.422524
C	-1.033941	-3.819668	-0.449874
H	1.673754	-1.744286	-0.043449
H	2.576773	-3.240779	-1.791684
H	-1.106557	-5.506866	-1.797708
H	-2.035729	-3.970007	-0.043572
H	1.204330	-5.141117	-2.664541
C	-4.653188	1.000033	-1.442853
C	-5.828383	1.384136	-2.100354
C	-6.531690	2.515804	-1.683020
C	-6.059541	3.262555	-0.597126
C	-4.883619	2.885056	0.051944
C	-4.166574	1.750377	-0.363385
H	-2.852716	-0.706526	-0.106602
H	-1.826850	0.315711	-1.167604
H	-2.163617	2.263171	0.203782
H	-4.122854	0.111333	-1.787672
H	-6.194754	0.789217	-2.941056
H	-7.446520	2.817572	-2.199750
H	-6.608482	4.143982	-0.255849
H	-4.516360	3.474915	0.896648
C	-2.422532	0.710712	2.623136
N	-3.006475	1.287229	1.778405
C	-2.019655	0.176725	3.899700
H	-2.514411	0.757674	4.695879

H	-0.923948	0.280539	3.981304
H	-2.303550	-0.885238	3.941872

^{5}Prod

C	-4.504991	-0.367127	-0.451043
C	-3.221192	-1.182605	-0.128992
N	-2.166946	-0.217635	-0.523080
Fe	1.766330	1.724445	0.742823
O	3.087005	0.384648	1.164422
O	0.241820	2.579492	1.615998
N	3.192395	3.317185	1.631348
N	2.482999	2.749729	-1.028364
C	3.953523	2.641412	2.720731
H	3.204914	2.207756	3.402090
H	4.529778	3.386783	3.304113
C	4.889155	1.571619	2.213634
C	6.262943	1.665029	2.473153
H	6.652347	2.505139	3.053325
C	7.146808	0.701971	1.986535
C	6.667864	-0.372031	1.231531
H	7.349748	-1.124209	0.833113
C	5.302209	-0.465827	0.970999
C	4.356156	0.488927	1.446559
C	2.336286	4.421994	2.138211
H	2.984193	5.226916	2.539635
H	1.805453	4.833488	1.261966
C	1.324284	4.024034	3.183512
C	1.369747	4.579680	4.467441
H	2.168134	5.276087	4.734249
C	0.400370	4.247297	5.415433
C	-0.630313	3.361647	5.089309
H	-1.385373	3.087669	5.827051
C	-0.680193	2.818103	3.807241
C	0.293059	3.111958	2.813613
C	4.051850	3.793436	0.544575
H	4.961300	3.170043	0.531160
H	4.398112	4.832390	0.713385
C	3.440029	3.674442	-0.838154
C	3.939288	4.428271	-1.910129
H	4.708504	5.182741	-1.729047
C	3.460534	4.185850	-3.196527
H	3.850923	4.754980	-4.044337
C	2.480241	3.205226	-3.383022
H	2.079597	2.973414	-4.372133
C	2.012538	2.519820	-2.264928
H	1.241085	1.749152	-2.342657
Cl	8.866494	0.855436	2.300876
Cl	4.715698	-1.793851	-0.004737
Cl	0.480193	4.932342	7.028072
Cl	-1.965935	1.701504	3.406198
S	-0.595635	-0.596514	-0.028695
O	-0.559690	-1.008742	1.371441
O	0.281012	0.512905	-0.489636
C	-0.255485	-2.024302	-1.055454
C	-0.222884	-1.881403	-2.447329
C	0.027856	-3.007050	-3.231518
C	0.243405	-4.252215	-2.625526
C	0.221357	-4.373920	-1.233051
C	-0.025693	-3.253336	-0.433332
H	-0.407808	-0.908842	-2.907684
H	0.054784	-2.913647	-4.320056
H	0.401360	-5.342920	-0.760987
H	-0.044845	-3.320696	0.655963
H	0.435361	-5.130990	-3.246179
C	-6.655202	-1.537431	0.197049
C	-7.691372	-1.804377	1.097320
C	-7.737819	-1.137584	2.325223
C	-6.743846	-0.205288	2.645158
C	-5.706697	0.057223	1.745944
C	-5.649030	-0.612329	0.513834
H	-3.145379	-1.417845	0.945502
H	-3.146606	-2.114257	-0.706646
H	-4.856759	-0.640607	-1.463794
H	-6.635550	-2.050588	-0.769559
H	-8.467642	-2.527402	0.831901
H	-8.547739	-1.341093	3.030828
H	-6.777270	0.324532	3.600806
H	-4.938884	0.794449	1.994486
C	-2.791188	1.082499	-0.549521
N	-4.063417	1.028312	-0.506860
C	-2.013174	2.348138	-0.688233
H	-1.367488	2.521776	0.188725
H	-2.736142	3.166804	-0.792145
H	-1.363226	2.313107	-1.575918

^{5}[FeII]

Fe	0.494498	-1.455562	0.013910
O	2.439642	-1.620650	-0.042574
O	-0.882425	-1.759709	1.354730
N	0.730053	0.712166	0.860411
N	0.463795	-0.211301	-1.806075
C	2.099883	0.799468	1.431499
H	2.158681	0.038609	2.212010
H	2.227665	1.778147	1.915596
C	3.202821	0.589794	0.428339
C	4.128237	1.601553	0.190402
H	4.032869	2.550529	0.703195
C	5.175590	1.403272	-0.695060
C	5.325263	0.186665	-1.345521
H	6.143317	0.026940	-2.032965
C	4.405268	-0.821803	-1.111264
C	3.309978	-0.667205	-0.226405
C	-0.296404	0.940809	1.915381
H	-0.139517	1.925568	2.376921
H	-1.260210	0.962259	1.401532
C	-0.350855	-0.110185	2.988807
C	-0.158027	0.229672	4.323138
H	0.095318	1.247516	4.592156

C	-0.288982	-0.730509	5.315444
C	-0.623452	-2.037187	4.988398
H	-0.728089	-2.788070	5.758499
C	-0.819160	-2.374557	3.657868
C	-0.691712	-1.434522	2.610770
C	0.537829	1.661134	-0.248702
H	1.138878	2.566622	-0.112796
H	-0.509484	1.976540	-0.241692
C	0.811613	1.071143	-1.614521
C	1.344479	1.841149	-2.644159
H	1.645219	2.862242	-2.450339
C	1.516628	1.275656	-3.897559
H	1.947768	1.854062	-4.704626
C	1.145395	-0.048994	-4.094366
H	1.271813	-0.536175	-5.051295
C	0.629962	-0.752036	-3.020088
H	0.352220	-1.793826	-3.115781
Cl	6.325667	2.688633	-1.004752
Cl	4.595711	-2.337952	-1.959004
Cl	-0.039053	-0.287757	6.992838
Cl	-1.241491	-4.023032	3.256388
N	0.081174	-3.421268	-0.874894
C	-0.189720	-4.505002	-1.132473
C	-0.533176	-5.882856	-1.433465
H	-0.904819	-6.370661	-0.531483
H	0.348285	-6.414813	-1.792982
H	-1.307535	-5.921973	-2.200070

Imidazoline

C	-4.736508	-0.549657	-0.333134
C	-3.494575	-1.378971	0.091025
N	-2.396064	-0.571799	-0.483982
S	-0.805922	-0.916038	0.054614
O	-0.939800	-1.630226	1.325913
O	-0.009763	0.306513	-0.059067
C	-0.168091	-2.083742	-1.150515
C	0.566439	-1.605659	-2.242023
C	1.118184	-2.525148	-3.137726
C	0.942871	-3.898496	-2.931893
C	0.219348	-4.360988	-1.826601
C	-0.339703	-3.452789	-0.924065
H	0.732492	-0.533376	-2.362266
H	1.701378	-2.165909	-3.989606
H	0.104457	-5.433807	-1.651144
H	-0.871848	-3.794872	-0.034321
H	1.386166	-4.613028	-3.629783
C	-6.901711	-1.507005	0.586685
C	-7.902829	-1.572063	1.562557
C	-7.877076	-0.697467	2.654091
C	-6.847423	0.245314	2.758943
C	-5.847278	0.306339	1.784125
C	-5.859678	-0.572076	0.688394
H	-3.391080	-1.422597	1.186196
H	-3.500605	-2.403760	-0.307696
H	-5.131435	-0.950168	-1.286137
H	-6.940606	-2.187157	-0.270523
H	-8.708305	-2.305296	1.463775
H	-8.659245	-0.746304	3.416860
H	-6.821484	0.936687	3.605960
H	-5.049638	1.049197	1.863427
C	-2.939627	0.731137	-0.724534
N	-4.211861	0.789103	-0.624418
C	-2.105239	1.903783	-1.134914
H	-1.437834	2.227700	-0.324430
H	-2.789219	2.714293	-1.414683
H	-1.461353	1.647330	-1.990162

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