Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Detection of a Transient $Fe^{V}(O)(OH)$ Species Involved in Olefin Oxidation by a Bio-Inspired Non-Haem Iron Catalyst

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General Considerations: All commercially-available reagents were used as received without purification. Synthetic procedures for $[Fe^{II}(TPA)(CH_3CN)_2](OTf)_2$ (TPA = Tris(2-methylpyridyl)amine) and $[Fe^{II}(TPA)(CH_3CN)_2](OTf)_2$ (TPA* = tris(3,5-dimethyl-4-methoxypyridyl-2-methyl)amine) have been reported and were synthesized according to published procedures.[1, 2]

Reactive Transmission-Mode Desorption Electrospray Ionization Mass Spectrometry. A microdroplet spray containing acetonitrile (MeCN) and hydrogen peroxide (H_2O_2) impacts (velocity of the droplets = approximately 50–100 m/s) a polyether ether ketone (PEEK) mesh (71 µm strand diameter, 56% open area) on which the Fe(TPA) was deposited (5 µL of 1 mM solution in MeCN). The secondary micro-droplets were analysed using an Orbitrap mass spectrometer.

Electrospray Ionization Mass Spectrometry. Experiments were carried out at -40 ^{o}C using a mixing tee. 0.7 mM Fe^{II}(TPA)/MeCN and 7 mM $H_2{}^{16}O_2$/MeCN solutions were infused into separate inlets of the mixing tee. The mixing tee was immersed in a dry ice/acetone bath. After mixing, the resulting solution was infused directly into an ESI source with 60 psi nebulizing gas. Based on the flow rates and lengths of tubing, the reaction time was estimated to be approximately 4 seconds.

Mass spectra of postulated species are simulated with Qualbrowser Thermo Xcalibur (version 3.0.63) using a Lorentzian output style and a resolution of 2 ppm (FWHM).

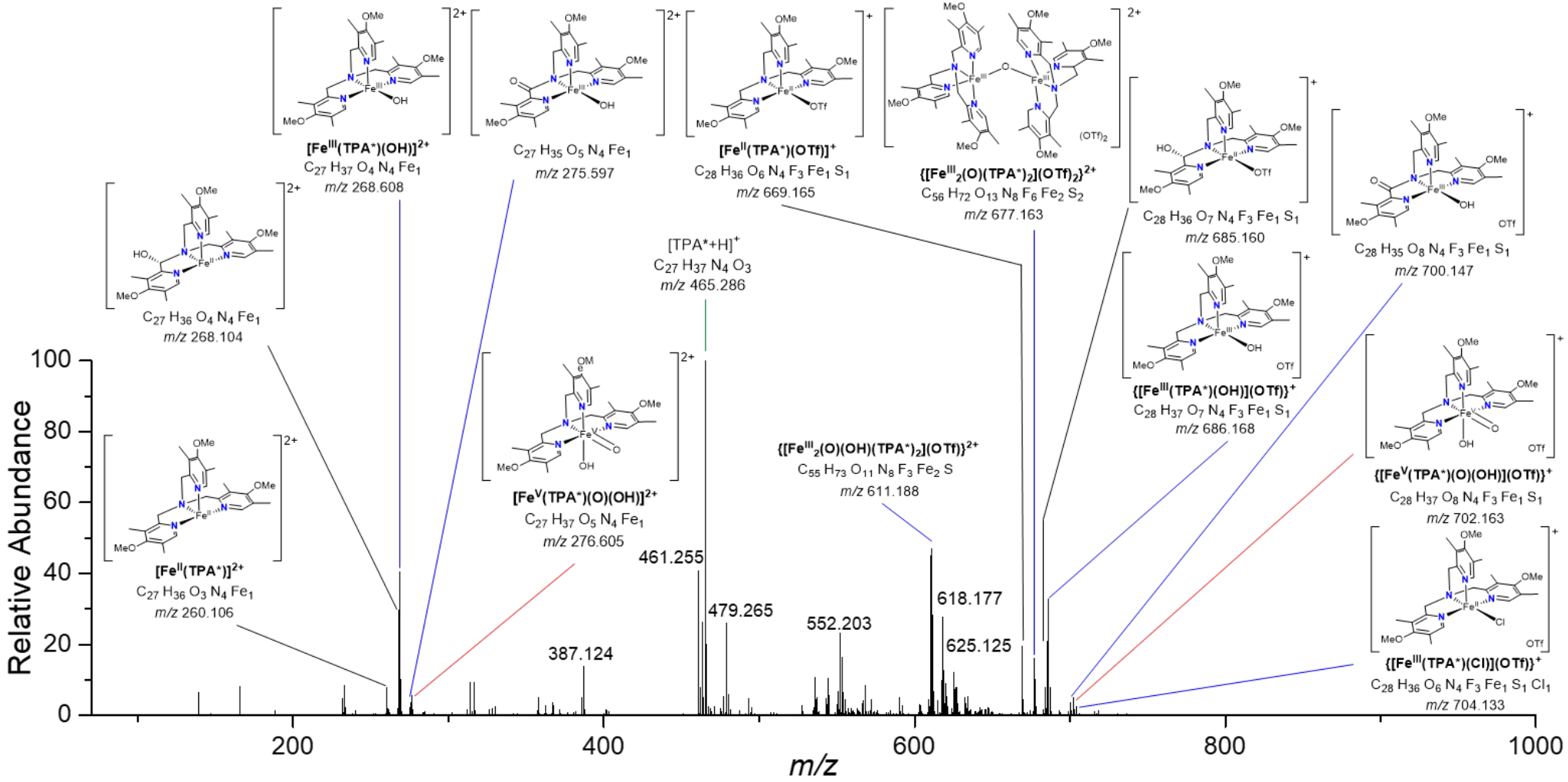


Figure S1. Full *r*TM[1]-DESI-MS spectrum of the reaction of Fe^{II}(TPA*) with droplets composed of 15 mM 90% $H_2{}^{16}O_2$ in $H_2{}^{16}O$. Postulated iron species are shown with their formulae and *m/z* ratios. Black lines: ferrous species; blue lines: ferric species; red lines: Fe^{V} species.

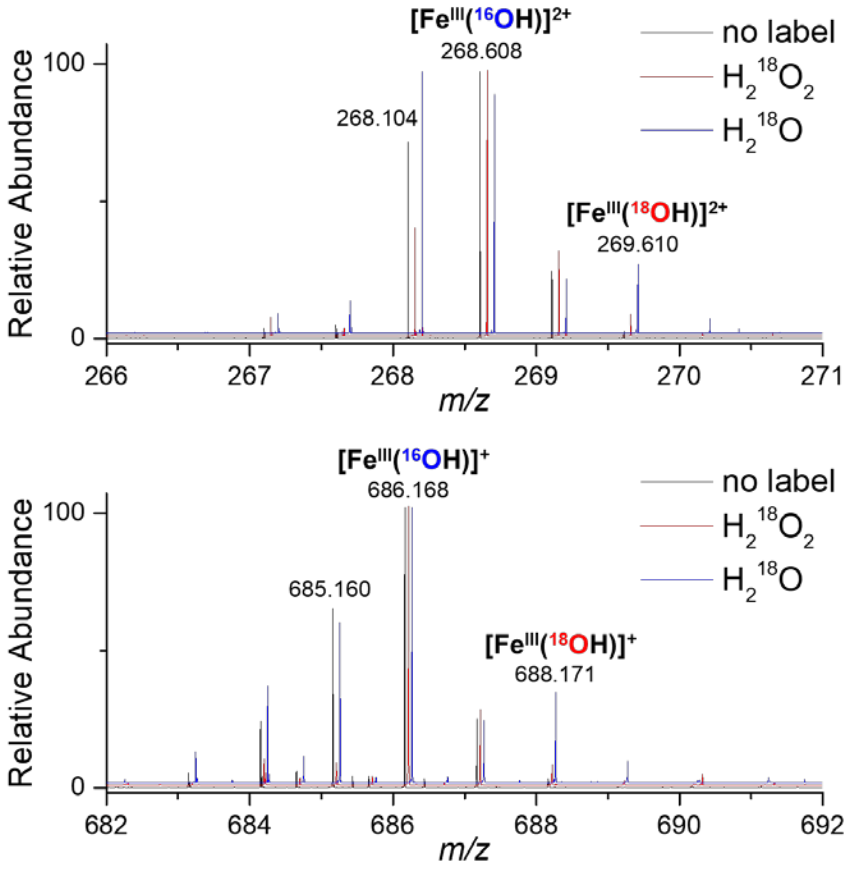
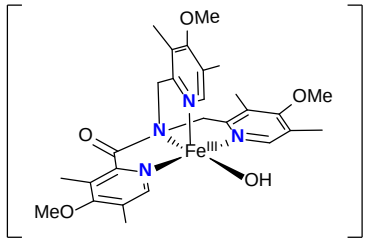
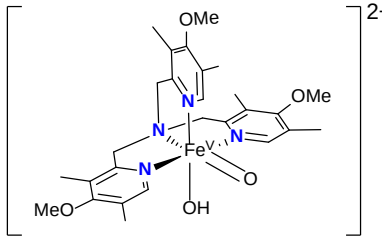
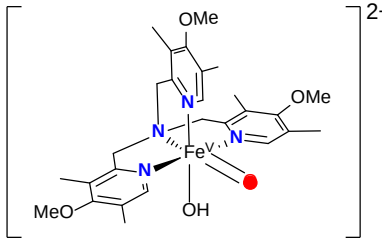


Figure S2. Mass spectra (rTM[1]-DESI-MS) of reaction mixtures of Fe^{II}(TPA*) with spray mixtures containing isotopically labelled H_2O and H_2O_2. Shown are the regions where ligand degradation products were expected.

			
m/z	275.597	276.605	277.607
Formula	$C_{27}H_{35}FeN_4O_5$	$C_{27}H_{37}FeN_4O_5$	$C_{27}H_{37}FeN_4O_4$ [18]O
unlabeled	0.39	0.61	0.00
labeled peroxide	0.18	0.29	0.53
labeled water	0.40	0.48	0.12

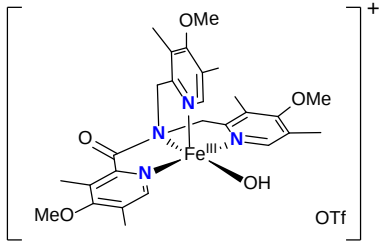
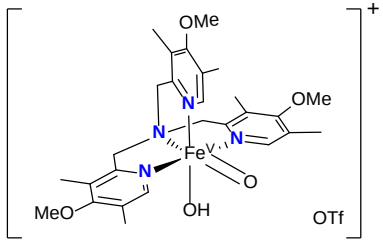
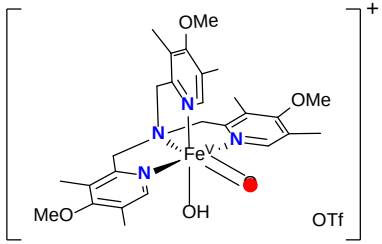
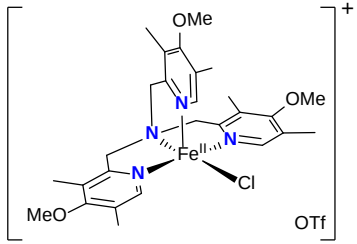
				
m/z	700.147	702.162	704.167	704.134
Formula	$C_{28}H_{35}F_3FeN_4O_8S$	$C_{28}H_{37}F_3FeN_4O_8S$	$C_{28}H_{37}F_3FeN_4O_7$ [18]O S	$C_{28}H_{36}F_3FeN_4O_6SCl$
unlabeled	0.33	0.46	0.00	0.21
labeled peroxide	0.17	0.09	0.74	0.00
labeled water	0.29	0.48	0.23	-*

Figure S3. Parameters used for simulated spectra of Fe^{II}(TPA*) reactions with H_2O_2 in the presence of water. Values shown are normalized. *Not fit due to low intensity.

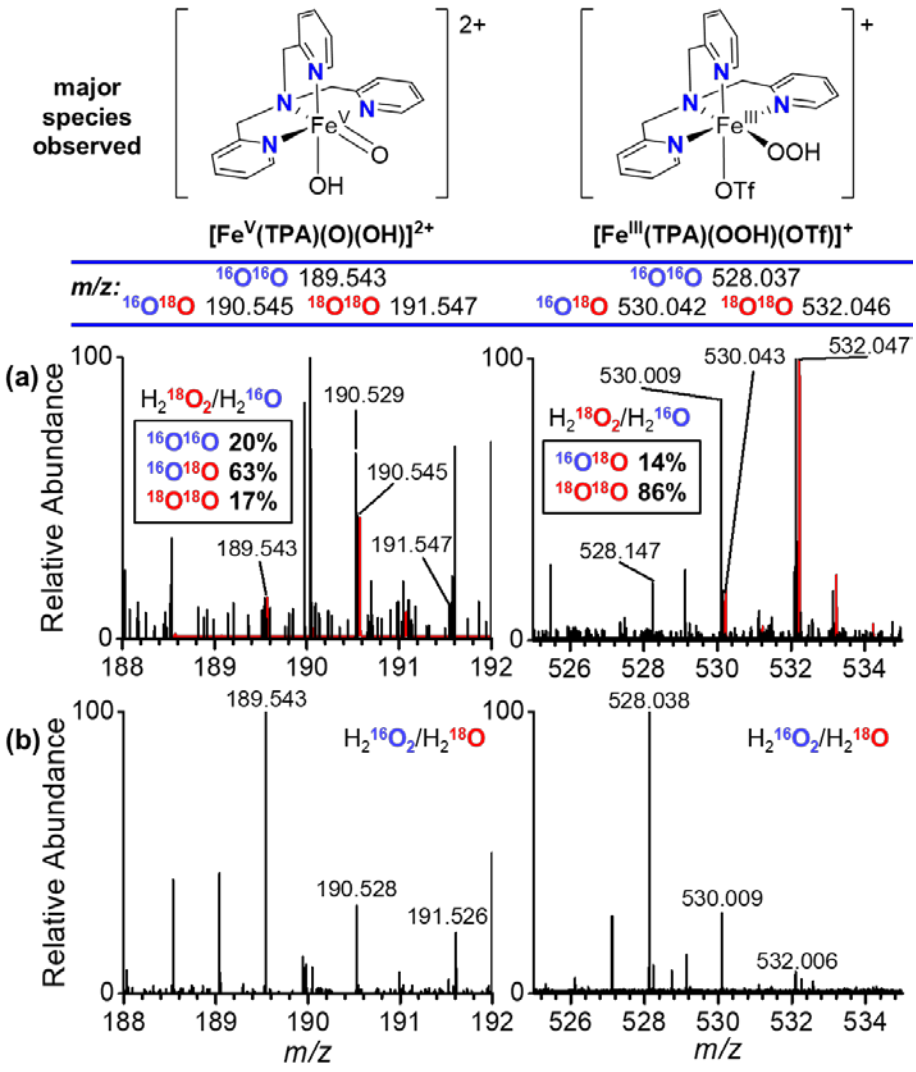


Figure S4. *r*TM[1]-DESI MS spectra of reaction mixtures of Fe(TPA) with spray mixtures containing isotopically labelled H_2O and H_2O_2. (a) 1 µM $H_2{}^{18}O_2$ (90% ^{18}O-enriched) in H_2O. (b) 9 µM 30% $H_2{}^{16}O_2$.in $H_2{}^{18}O$. *m/z* ratios shown on top are theoretical *m/z* ratios of corresponding ions with certain oxygen isotope compositions. Offset red traces are simulated spectra of the corresponding mixtures. Simulated spectra were computed using Thermo Xcalibur.

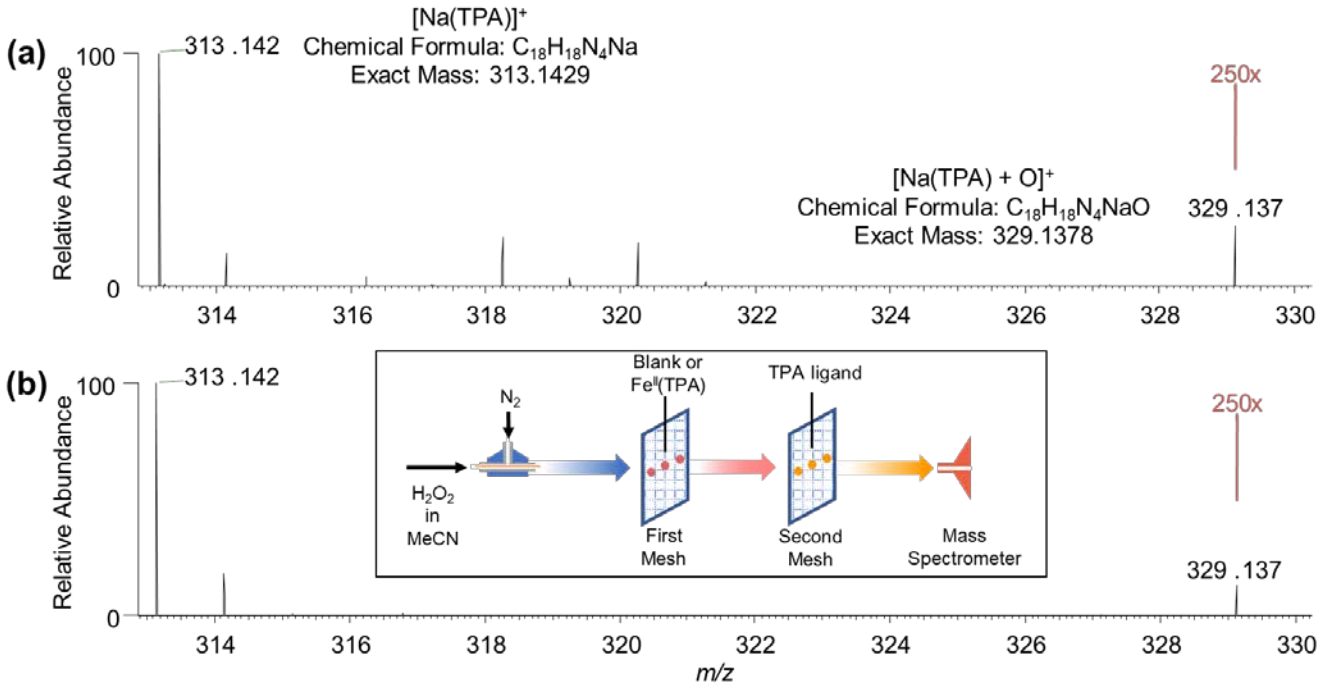


Figure S5. Representative *r*TM^2-DESI mass spectra of reaction between H_2O_2 (9.7 mM in MeCN, sprayed at 15 µL/min with 200 psi N_2) and (a) free TPA ligand (5 µL of 10^{-4} M spotted) with blank first mesh, and (b) free TPA ligand with Fe(TPA) (5 µL of 10^{-4} M spotted) on first mesh. Inset: schematic diagram of the *r*TM^2-DESI MS setup. No catalyst-induced ligand oxidation was observed under either condition.

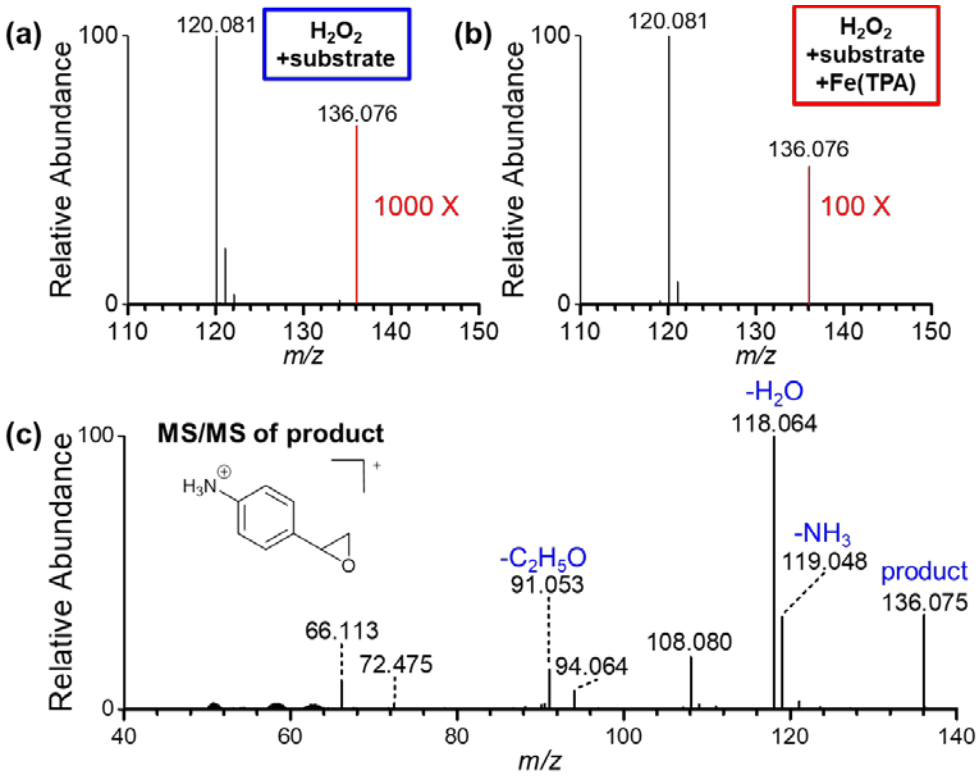


Figure S6. Mass spectra (*r*TM[1]-DESI) of a solution containing H_2O_2 (9.6 mM in MeCN) and 4-vinylaniline (1 mM) directed towards (a) bare mesh and (b) Fe(TPA) deposited on the mesh. (c) MS/MS spectrum of the product peak at *m/z* 136.075.

References

1. W. N. Oloo, A. J. Fielding and L. Que, Jr., *J. Am. Chem. Soc.*, 2013, **135**, 6438-6441.
2. W. N. Oloo, K. K. Meier, Y. Wang, S. Shaik, E. Münck and L. Que, Jr., *Nat. Comm.*, 2014, **5**, 3046.