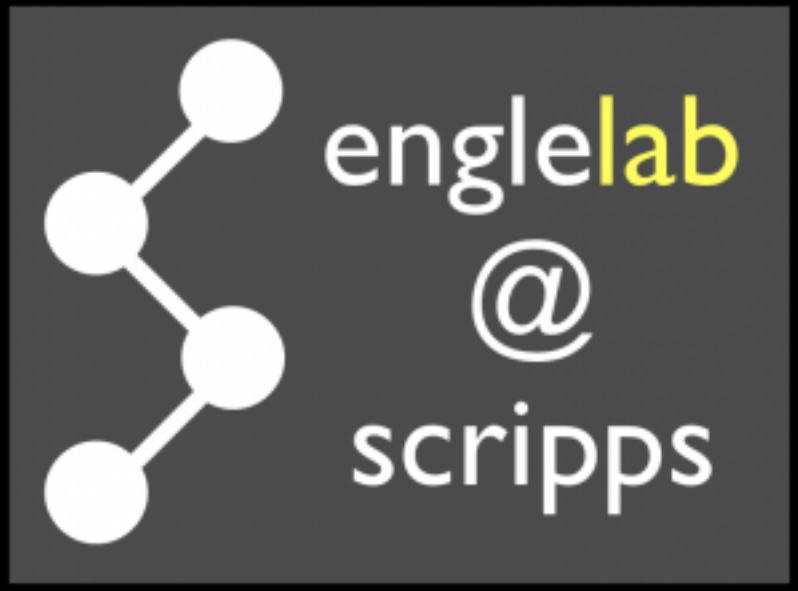


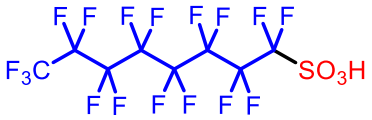
Long-Lit: *Depolymerisation of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)*

Engle Lab Group Meeting
05/18/17
Miriam L. O'Duill

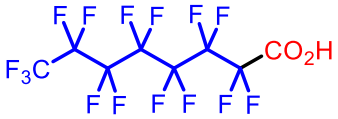
Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)

What are PFASs?

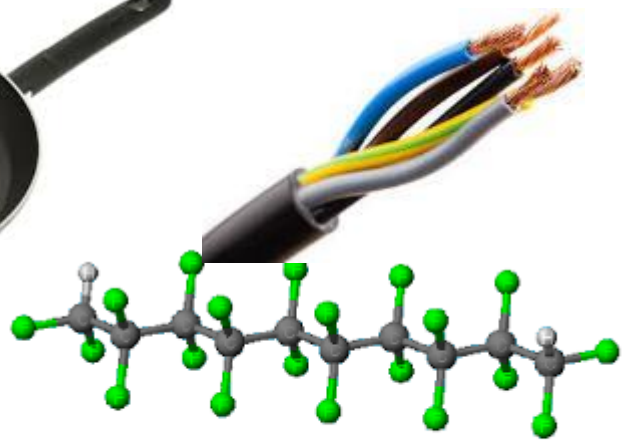
Fluorosurfactants: fluorinated tail, hydrophilic head; lipophobic, hydrophobic



Perfluorooctanesulfonic acid (PFOS)

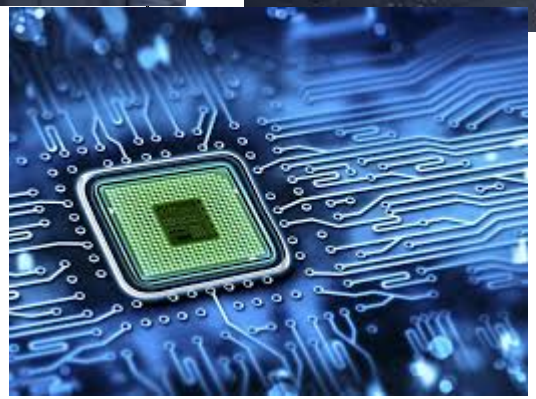


Perfluorooctanoic acid (PFOA, C8)



Uses

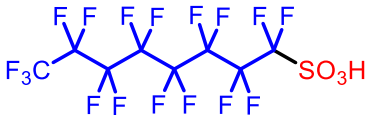
- Emulsifier in Teflon production
- Textile impregnating agents
- Fire-fighting foams
- Insulation of electric wires
- Semiconductor coatings
- Hydraulic fluids in aircrafts



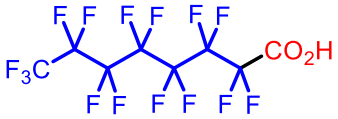
Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)

What are PFASs?

Fluorosurfactants: fluorinated tail, hydrophilic head; lipophobic, hydrophobic



Perfluorooctanesulfonic acid (PFOS)



Perfluorooctanoic acid (PFOA, C8)

Uses

- Emulsifier in Teflon production
- Textile impregnating agents
- Fire-fighting foams
- Insulation of electric wires
- Semiconductor coatings
- Hydraulic fluids in aircrafts

Disadvantages

- Stable, non-biodegradable (half-life >97 years)
- Persistent organic pollutants: bioaccumulative, toxic
- Health implications: carcinogens, brain, immune system, hormone levels, fertility
- Now listed under the Stockholm Convention on Persistent Organic Chemicals, US (EPA): voluntary phase-out since 2006

Current Remediation

- Barriers
- Pump-and-treat technologies (*e.g.* ex-situ filtration through activated carbon)
- Chemical oxidation (activation necessary)

Challenge

- PFCs (Perfluorinated Compounds) very stable towards oxidation (C–F BDE ≈ 552 kJ/mol)
- Activation required

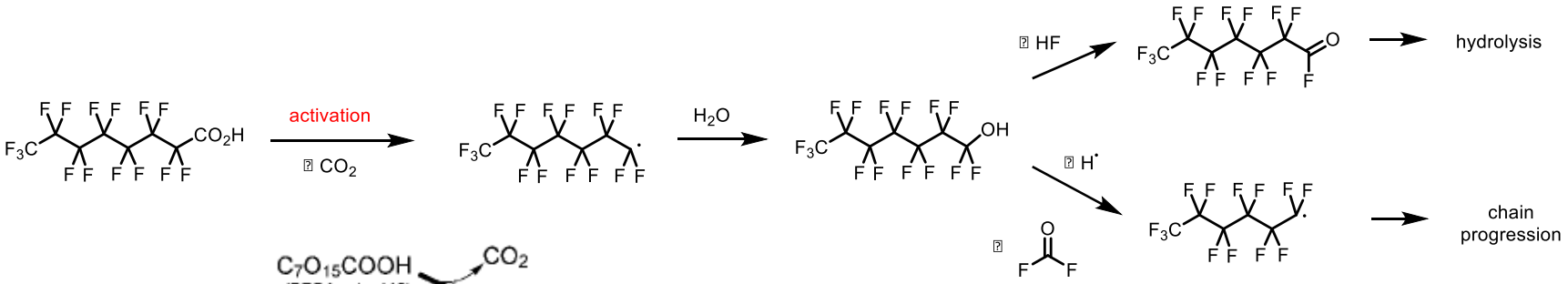
Opportunity

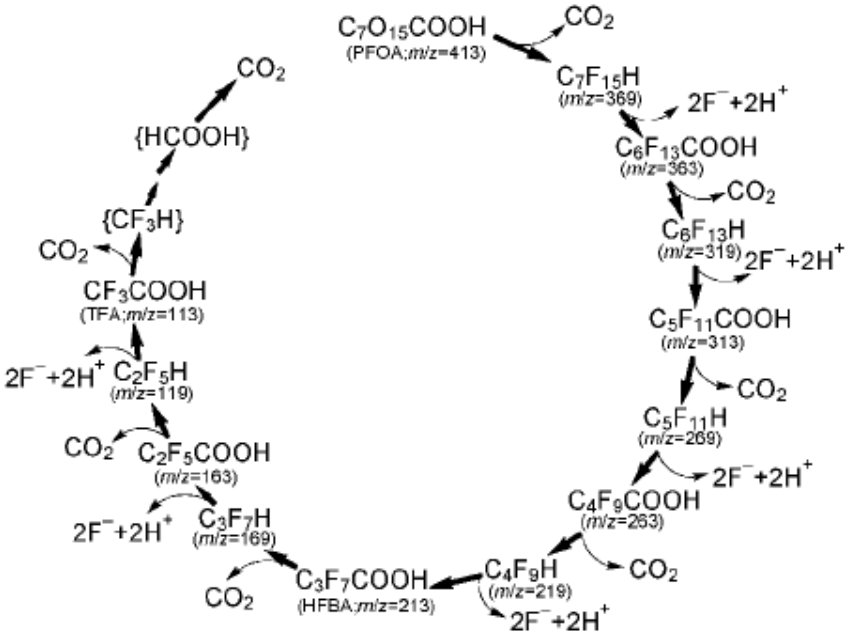
- Chemical depolymerisation of PFASs to small fluorinated building blocks: recycling

California Environmental Contaminant Biomonitoring Program, March 2015 Meeting of the Scientific Guidance Panel; Z. Wang, J. C. DeWitt, C. P. Higgins, I. T. Cousins, *Environ. Sci. Technol.* **2017**, *51*, 2508; N. Törneman, Remedial methods and strategies for PFOS and PFOA. Presentation at 4th Joint Nordic Meeting on Remediation of Contaminated Sites, 18–21 September 2012, in Oslo, Norway.

Decomposition Mechanism

Proposed Radical Decomposition Mechanism:





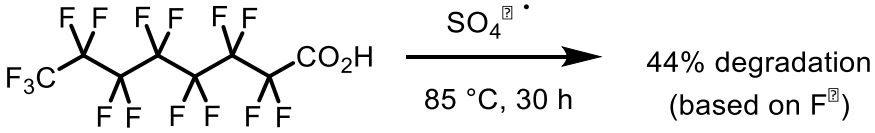
Activation Modes

- Persulfate radicals
- Photocatalysis/UV
- Heat/Plasma
- Electrochemistry
- Utrasound
- Microbial

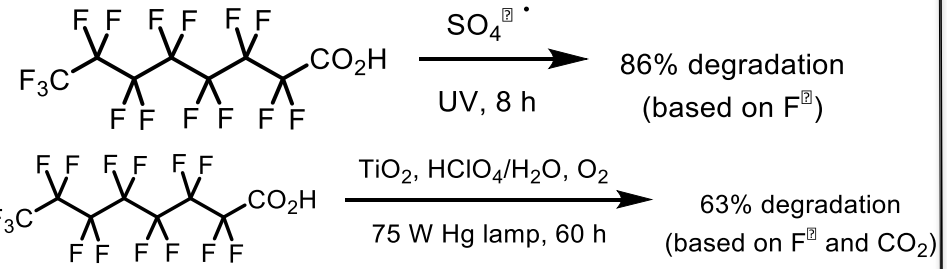
J. Niu, H. Lin, C. Gong, X. Sun, *Environ. Sci. Technol.* **2013**, *47*, 14341; R. R. Giri, H. Ozaki, X. Guo, R. Takanami, S. Taniguchi, *Int. J. Environ. Sci. Tech.* **2014**, *11*, 1277; Y. Bo, L. Yingying, Y. Gang, D. Shubo, Z. Qiongfang, Z. Hong, *Progress in Chem.* **2014**, *26*, 1265.

Oxidative Decomposition of PFCs: Activation Modes

Persulfate Activation

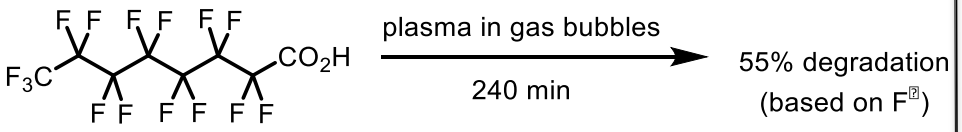


Photocatalytic Activation

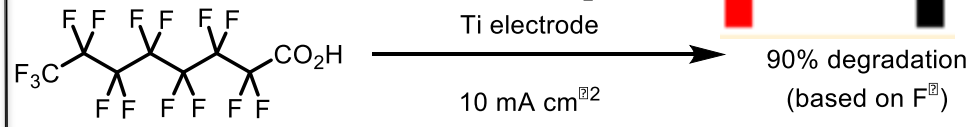


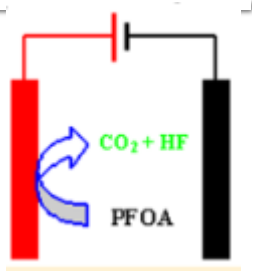
Other photocatalysts used: ZnO, InO_2H,

Plasma Activation



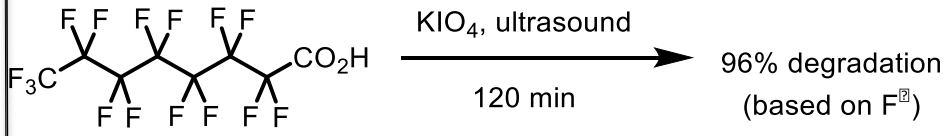
Electrochemical Activation





Other anodes used: SnO_2, PbO_2, boron-doped diamond, Ti/SnO_2–Sn-Bi, Ti/SnO_2–Sb, Ti/SnO_2–Sb/PbO_2, Ti/SnO_2–Sb/MnO_2

Ultrasound Activation



Lower pH (acid catalysis) increases efficiency
Effect of atmosphere: N_2 > air > O_2
Effect of added anions: Br^- > none ≥ Cl^- > SO_4^{2-}

C. S. Liu, C. P. Higgins, F. Wang, K. Shih, *Separation and Purification Technology* **2012**, *91*, 46; Y. Qian, X. Guo, Y. Zhang, Y. Peng, P. Sun, C.-H. Huang, J. Niu, X. Zhou, J. C. Crittenden, *Environ. Sci. Technol.* **2016**, *50*, 772; R. Dillert, D. Bahnemann, H. Hidaka, *Chemosphere* **2007**, *67*, 785; K. Yasuoka, K. Sasaki, R. Hayashi, *Plasma Sources Sci. Technol.* **2011**, *20*, 034009; J. Niu, H. Lin, C. Gong, X. Sun, *Environ. Sci. Technol.* **2013**, *47*, 14341; Y.-C. Lee, M.-J. Chen, C.-P. Huang, J. Kuo, S.-L. Lo, *Ultrasonics Sonochemistry* 2016, 31, 499.

Oxidative Decomposition of PFCs: Summary

Table 1 Summary of representative reports for PFOA oxidative degradation

technique	C_0 (μM)	power (W)	vol (mL)	k	$\tau_{1/2}$ (min)	product	energy [a] (kJ/μmol)	ref
persulfate-H_2O(85 ℃)	0.5	—	40	0.0915 h^{-1}	720	93.5% DA[b], 43.6% F^-	—	14
alkaline-O_3	12	85	1000	0.0175 min^{-1}	39.6	90% DA	202	20
alkaline-O_3-H_2O_2	12	85	1000	0.0716 min^{-1}	9.68	99% DA	49.36	20
photolysis by VUV	50×10^3	23	1000	0.017 min^{-1}	41	90% PF acids, 10% F^-	1	23
photolysis with persulfate	1.35×10^3	200	22	0.69 h^{-1}	58	85% PF acids, 12% F^-	50	26
photocatalysis by In_2O_3	72.5	23	100	5.89 h^{-1}	7.1	99% DA, 71% F^-	2.7	33
electrolysis by BDD	8×10^3	—	300	0.0693 h^{-1}	540	55% DA, 2.2% F^-	—	42
electrolysis by BDD	114	—	40	0.0428 min^{-1}	15	97.5% DA, 60% F^-	—	46
electrolysis by Ti/SnO_2-Sb-Bi	120.7	3.3	25	1.93 h^{-1}	45	93.3% DA, 63.8% F^-	5.9	52
electrolysis by Ti/SnO_2-Sb/Ce-PbO_2	241.5	—	100	0.037 min^{-1}	18.7	96.7% DA, 81.7% F^-	5.5	55
sonolysis	20	150	600	0.018 min^{-1}	39	95% F^-	67	67
plasma	120.7	15	50	0.99 h^{-1}	60	55% F^-	25.7	74
microwave with persulfate	253.8	70	50	0.67 h^{-1}	28	99.3% DR, 74.3% F^-	19	80
mechanochemistry by ball milling	0.2 g[c]	750	—	1.69 h^{-1}	29	96.7% F^-	5.4	86

a Energy value required to reduce PFOA to 50% of its initial concentration and energy per μmole for the same process.

b DA means degradation rate of PFOA, and F^- represents defluorination rate.

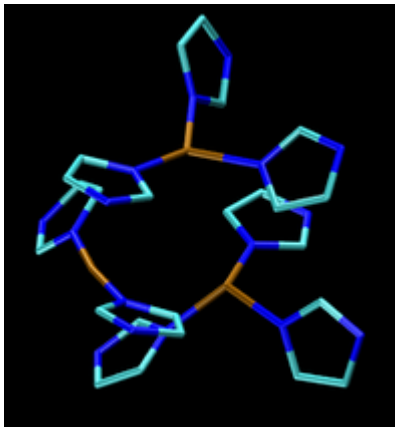
c The degradation objective is pure PFOA solid.

Y. Bo, L. Yingying, Y. Gang, D. Shubo, Z. Qiongfang, Z. Hong, *Progress in Chem.* **2014**, *26*, 1265.

Microbial Degradation of PFCs

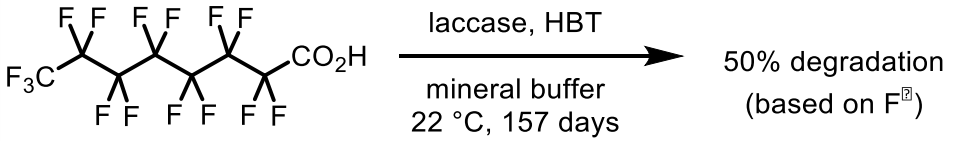
Experimental Set-ups: Microbial Cultures, Activated Sludge, Soil and Sediment

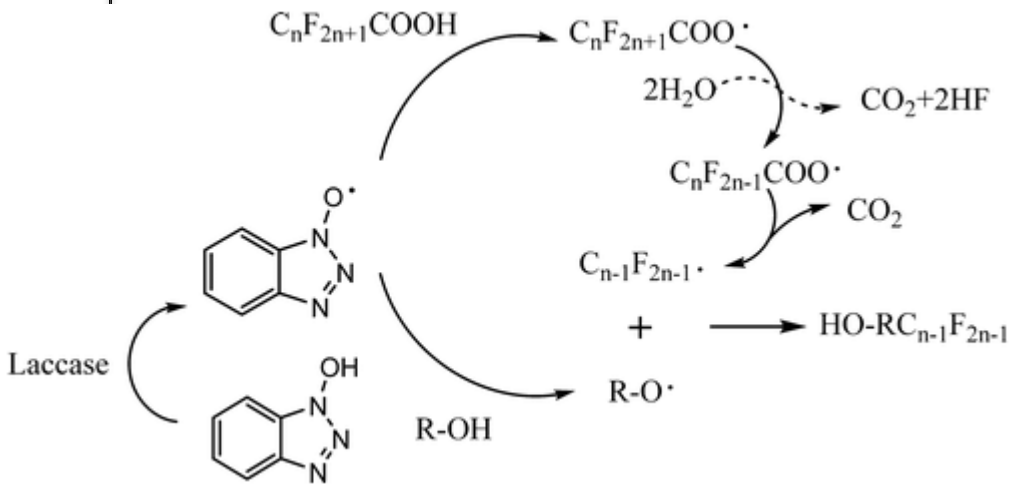
Laccases: Copper-based oxidase enzymes;
Laccase from *Pleurotus ostreatus* (Oyster mushroom): degradation/depolymerisation of lignin



Tricopper site found in many laccases
Source: Wikipedia

Laccase-catalysed degradation of PFOA

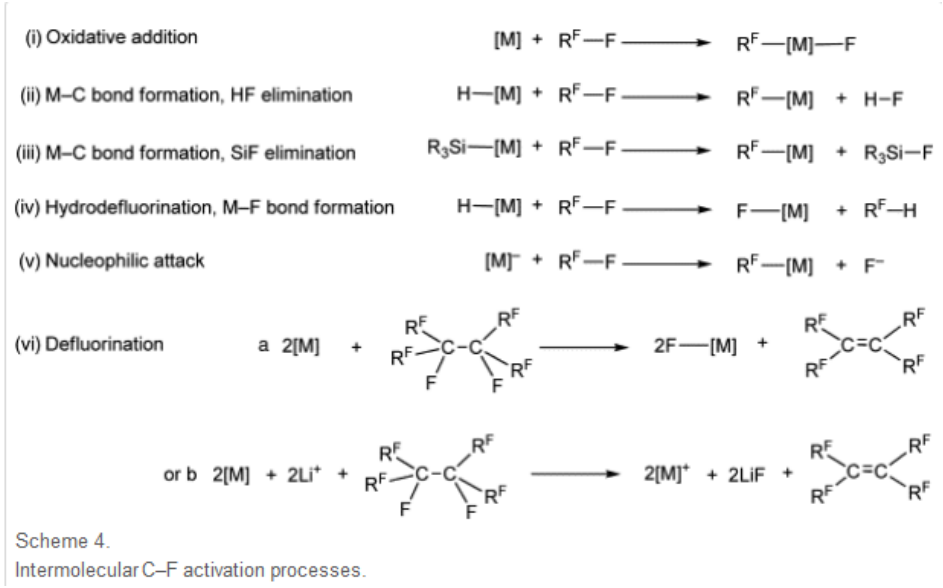




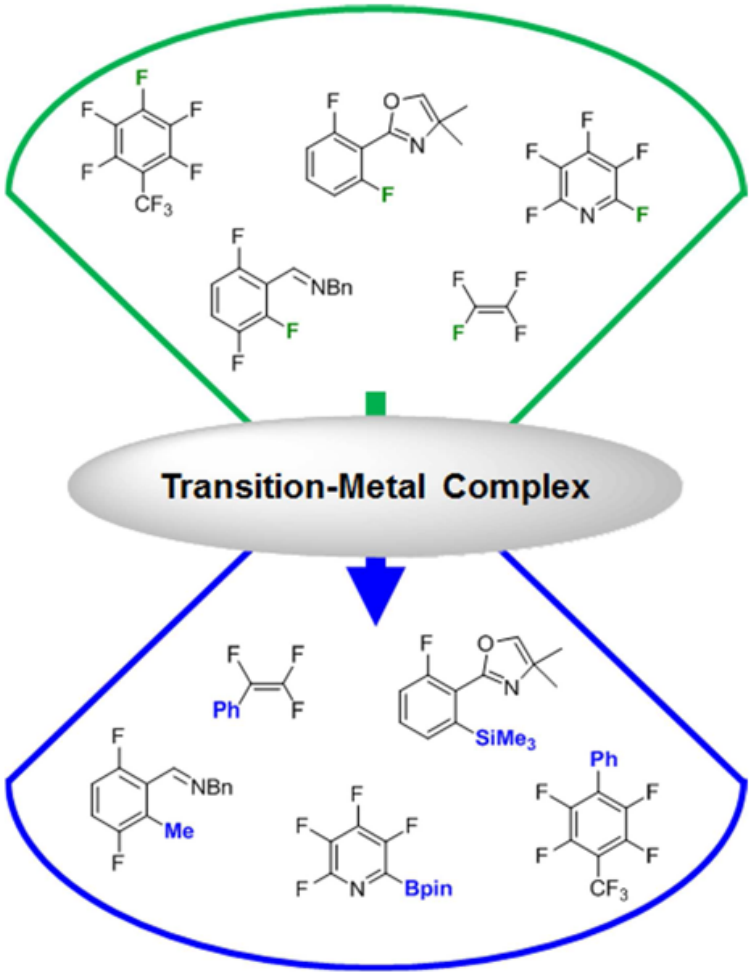
J. Liu, S. M. Avandano, *Environment International* **2013**, *61*, 98; Q. Luo, J. Lu, H. Zhang, Z. Wang, M. Feng, S.-Y. D. Chiang, D. Woodward, Q. Huang, *Environ. Sci. Technol. Lett.* **2015**, *2*, 198; ; and references therein.

Decomposition of PFCs by Transition-Metal Mediated C–F Activation?

Question: Would it be possible to degrade PFCs into synthetically useful fluorinated building-blocks by transition-metal catalysis?
Two aims: (1) recycle resistant organic pollutant, (2) cheap source of fluorinated reagents.



Scheme 4.
Intermolecular C–F activation processes.



R. N. Perutz, T. Braun, Transition Metal-mediated C–F Bond Activation in: Comprehensive Organometallic Chemistry III, **2007**, 725-758; M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3328; M. K. Whittlesey, E. Peris, *ACS Catal.* **2014**, *4*, 3152; T. A. Unzner, T. Magauer, *Tet. Lett.* **2015**, *56*, 877; T. Ahrens, J. Kohlmann, M. Ahrens, T. Braun, *Chem. Rev.* **2015**, *115*, 931.

Acknowledgements

- Engle Lab:
  Mark Boulous
  Joe Derosa
  John Gurak
  Matt Holcomb
  Zhen Liu
  Kin Yang, Ph.D
  Keary Engle, Ph.D
- Carrie Gabaldon
- NMR Facilities Staff:
  Laura Pasternack, Ph.D
  Dee-Hua Huang, Ph.D
- Other labs at TSRI for support and supplies:
  Yu Lab
  Baran Lab
  Shenvi Lab
  Boger Lab
- **DAAD** for funding