

Anion Dependent Switch in C-X Reductive Elimination Diastereoselectivity

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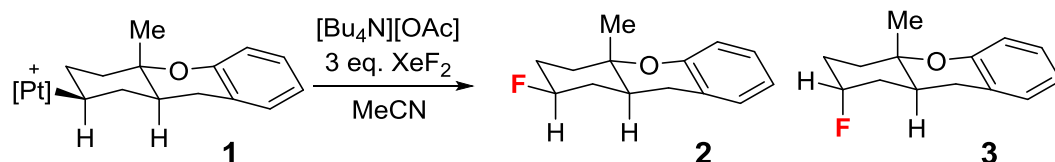
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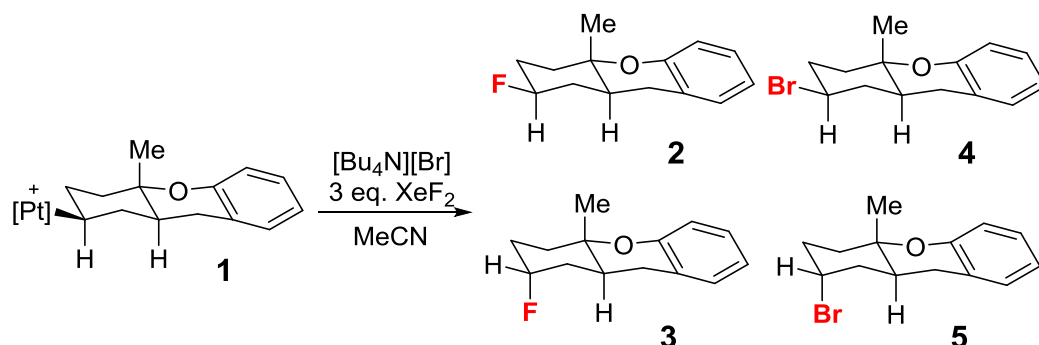
Supporting Information

All air and moisture sensitive procedures were performed using an MBraun glovebox or standard Schlenk line techniques. Commercially available reagents were used without further purification. Acetonitrile was distilled from CaH₂. NMR spectra were collected on a Bruker 600 MHz Avance spectrometer and referenced to residual solvent peaks. Compounds **1**,¹ **2**,² **4**³ and **5**³ have been reported. New compounds were isolated by prep tlc, using 20:1 hexanes:ethyl acetate. HRMS was performed by Dr. Mee-Kyung Chung at the University of North Carolina at Chapel Hill.

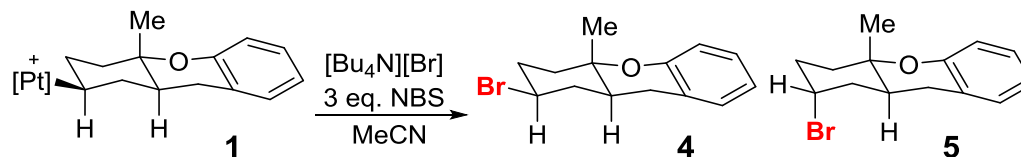
Procedure for Oxidation Reactions



Reactions in Table 1: XeF₂ (4 mg, 0.24 mmol) was added to a stirring solution of **1** (8 mg, 0.08 mmol) and tetrabutylammonium acetate in CD₃CN (0.7 mL). The reaction mixtures were immediately (<5 minutes) analyzed by NMR and yields and ratios were determined by ¹⁹F NMR using 1-fluoro-3,5-dimethoxybenzene as internal standard.



Reactions in Table 2: XeF₂ (4 mg, 0.24 mmol) was added to a stirring solution of **1** (8 mg, 0.08 mmol) and tetrabutylammonium bromide in CD₃CN (0.7 mL). The reaction mixtures were immediately (<5 minutes) analyzed by NMR and yields and ratios were determined by ¹H NMR using 4-methylanisole as internal standard.

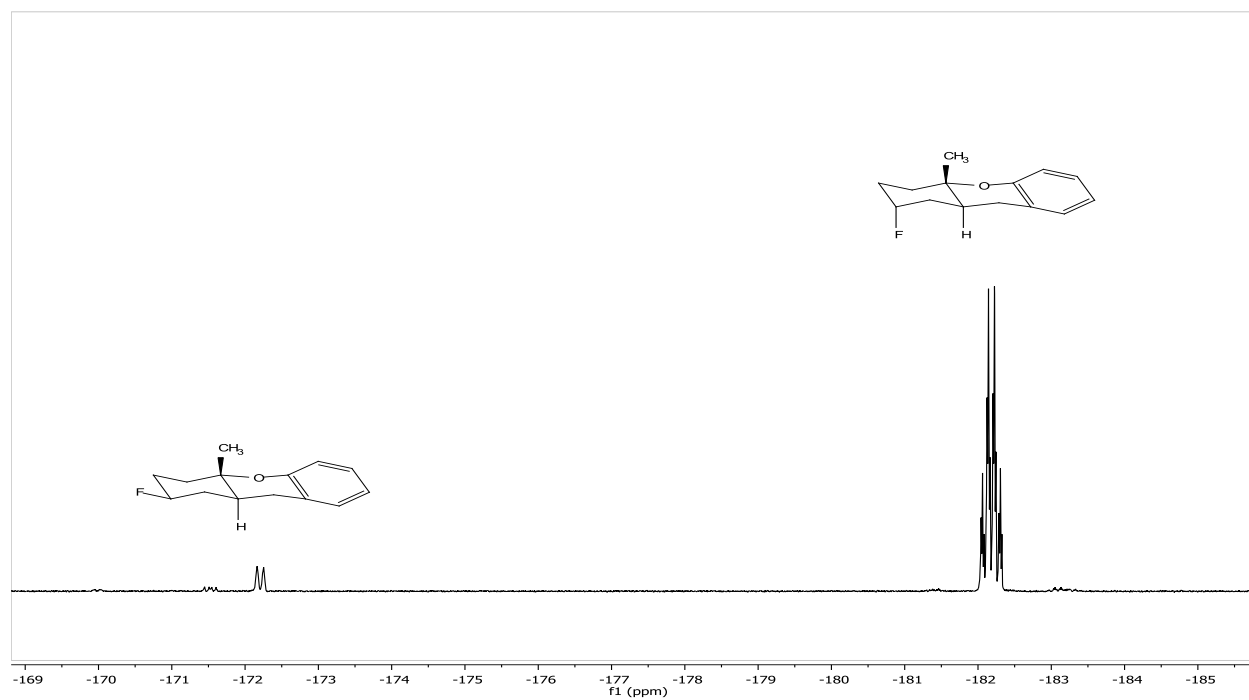
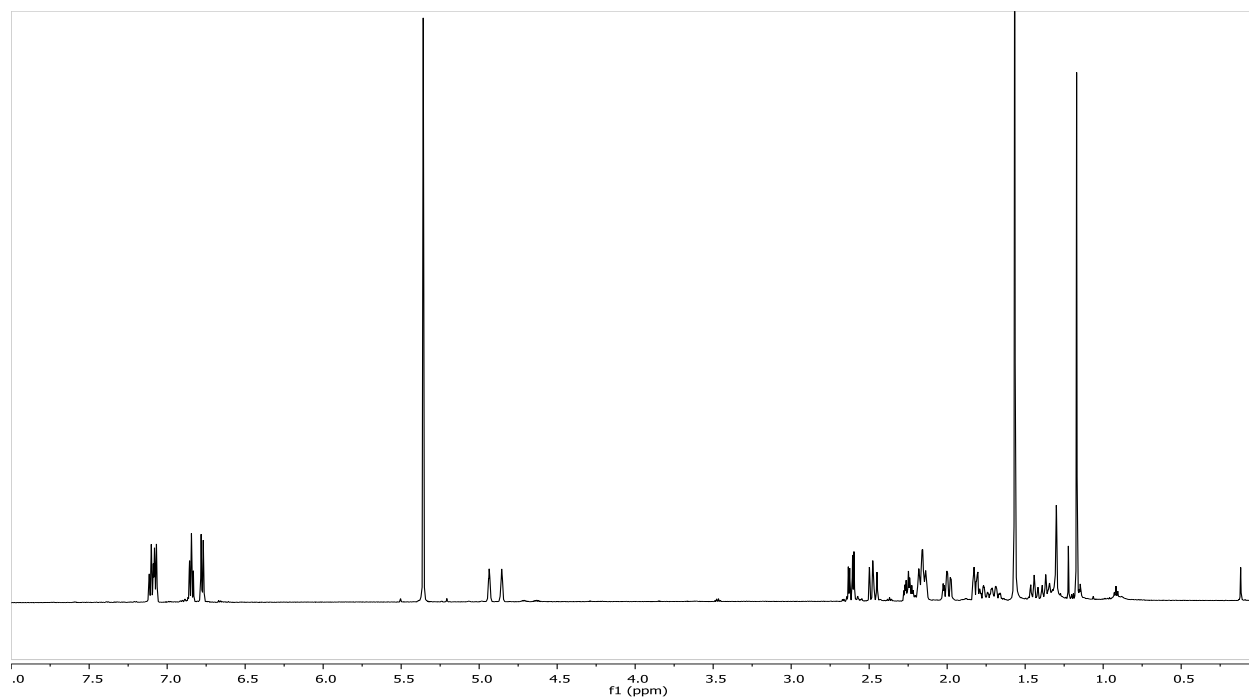


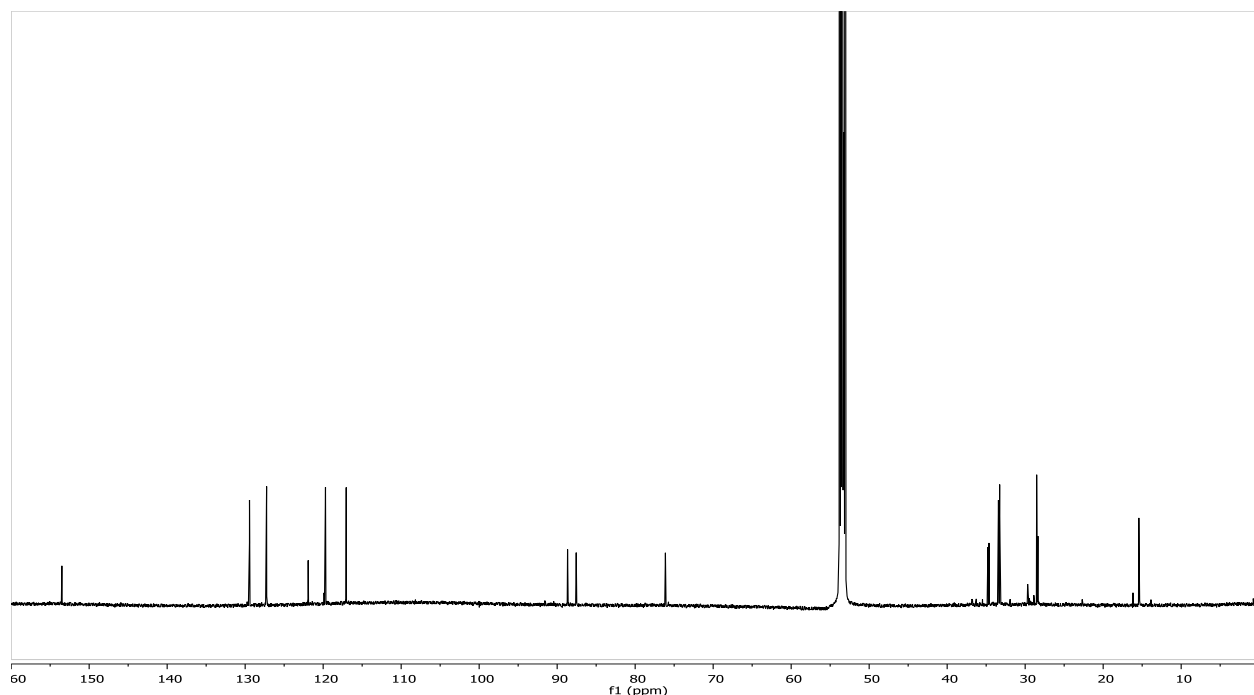
Reactions in Table 3: N-bromosuccinimide (4.2 mg, 0.24 mmol) was added to a stirring solution of **1** (8 mg, 0.08 mmol) and tetrabutylammonium bromide in CD₃CN (0.7 mL). The reaction mixtures were immediately (<5 minutes) analyzed by NMR and yields were determined by ¹H NMR using 4-methylanisole as internal standard, the ratio of diastereomers was determined by integration using gcms.

Characterization

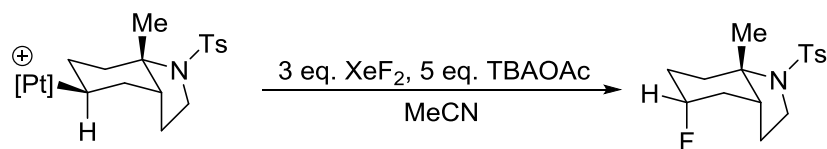


¹H NMR (600 MHz, CD₂Cl₂): δ 7.11-7.06 (m, 2H), 6.84 (m, 1H), 6.77 (m, 1H), 4.90 (dm, 1H, *J*_{H-F} = 48 Hz), 2.62 (dd, 1H, *J* = 16.8 Hz, 5.4 Hz), 2.47 (dd, 1H, *J* = 16.8 Hz, 13.2 Hz), 2.25 (m, 1H), 2.15 (m, 2H), 2.00 (m, 1H), 1.83-1.65 (m, 2H), 1.46-1.33 (m, 1H), 1.17 (s, 3H) ppm. ¹³C NMR (152 MHz, CD₂Cl₂): δ 153.5, 129.5, 127.3, 121.9, 119.7, 117.1, 87.6 (d, *J*_{C-F} = 168 Hz), 76.1, 34.7 (d, *J*_{C-F} = 21.1 Hz), 33.4, 33.3, 28.5, 28.4 (d, *J*_{C-F} = 21.1 Hz), 15.4 ppm. ¹⁹F NMR (565 MHz, CD₂Cl₂): -182.2 ppm. HRMS (EI) C₁₄H₁₈FO [M + H]⁺/*z* calc. 221.1336 found 221.1331.

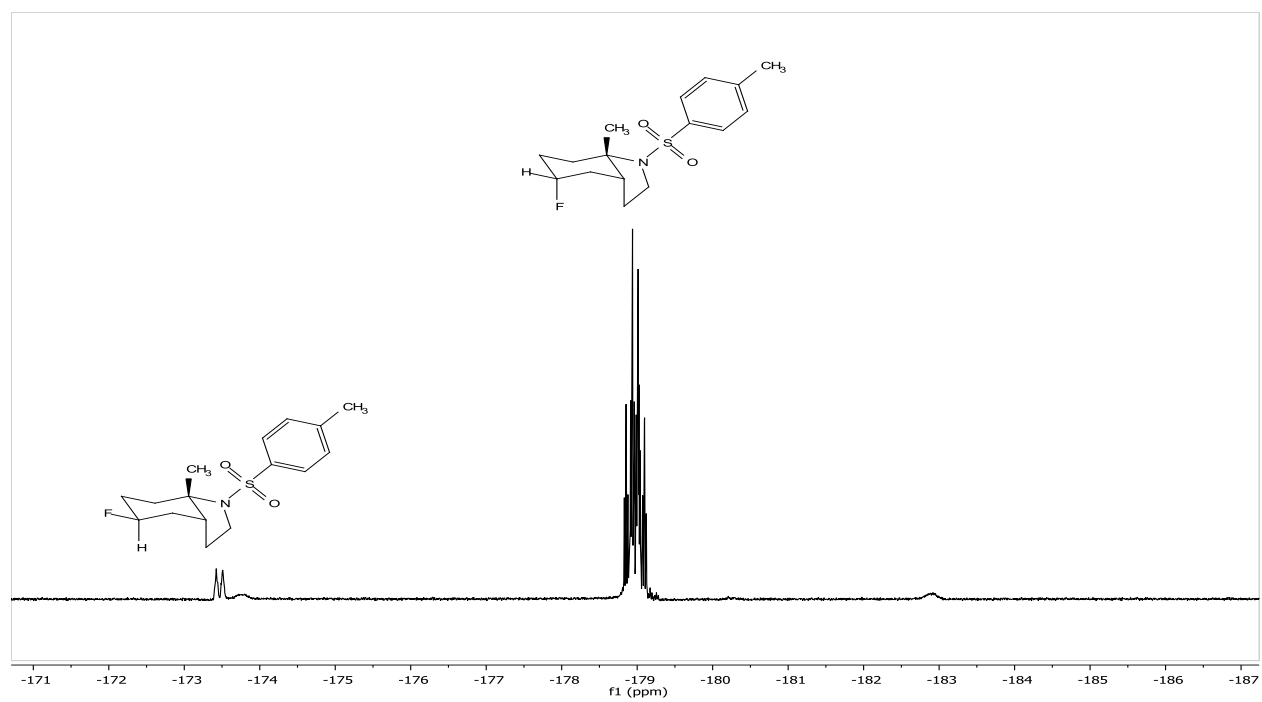
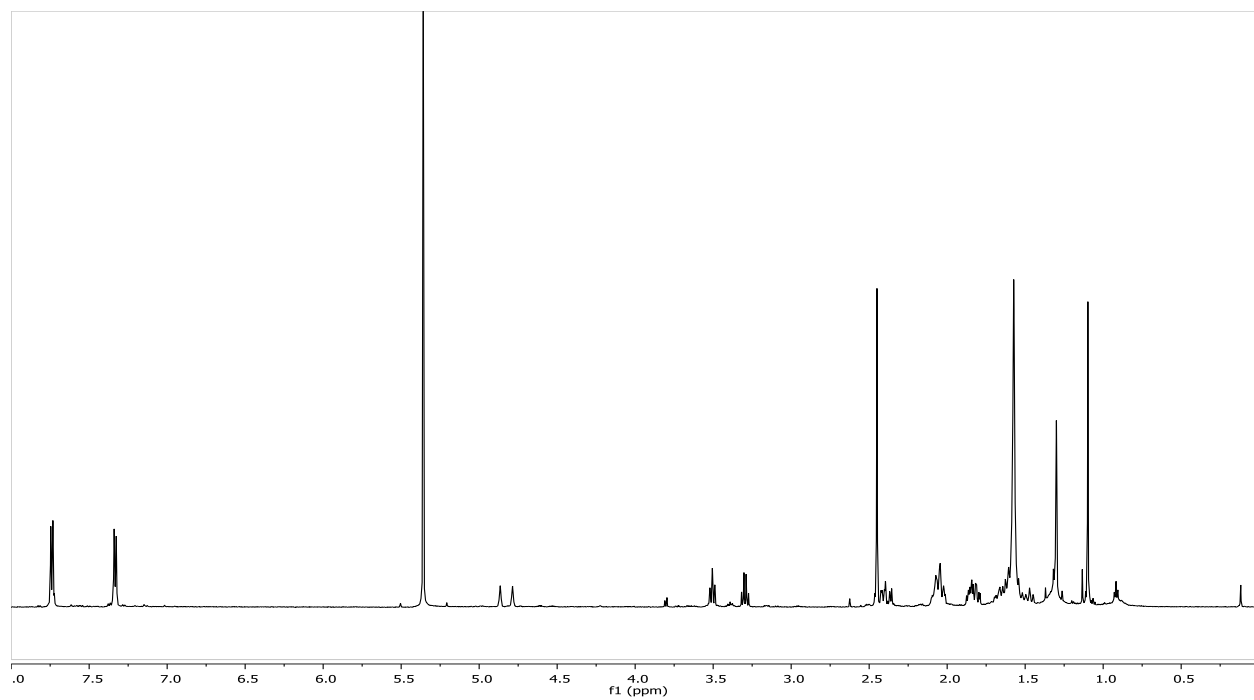


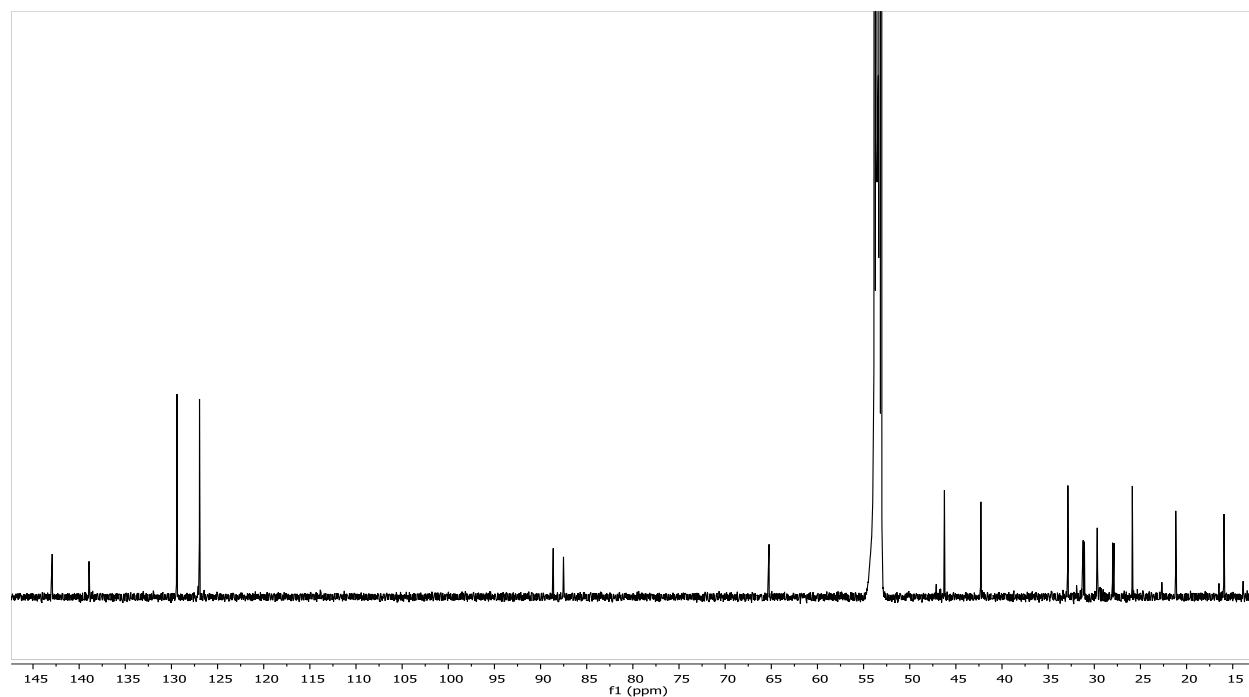


Compound from reference 19: The stereoretentive fluorinated product has been reported previously² from reaction of the Pt organometallic with XeF₂. Addition of 5 equivalents of tetrabutylammonium acetate to the reaction yielded the stereoinvertive product characterized below.



¹H NMR (600 MHz, CD₂Cl₂): δ 7.74 (d, 2H, *J* = 7.8 Hz), 7.33 (d, 2H, *J* = 7.8 Hz), 4.82 (dm, 1H, *J*_{H-F} = 47 Hz), 3.51 (m, 1H), 3.29 (m, 1H), 2.45 (s, 3H), 2.39 (m, 3H), 2.05 (m, 3H), 1.83 (m, 2H), 1.58 (m, 1H) 1.10 (s, 3H) ppm. ¹³C NMR (152 MHz, CD₂Cl₂): δ 142.9, 138.9, 129.4, 127.0, 88.1 (d, *J*_{C-F} = 168.7 Hz), 65.2, 46.2, 42.3, 32.9, 31.1 (d, *J*_{C-F} = 21.3 Hz), 27.9 (d, *J*_{C-F} = 22.8 Hz), 25.9, 21.2, 16.0 ppm. ¹⁹F NMR (565MHz, CD₂Cl₂): - 179.0 ppm. HRMS (EI) C₁₆H₂₂FNO₂S [M + H]⁺/*z* calc. 312.1428 found 312. 1325.





- (1) Koh, J. H.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 3459.
- (2) Zhao, S.-B.; Becker, J. J.; Gagné, M. R. *Organometallics* **2011**, *30*, 3926.
- (3) Geier, M. J.; Gagné, M. R. *Organometallics* **2013**, *32*, 380.