

Supporting Information

Base-promoted Protodeboronation of 2,6-Disubstituted Arylboronic Acids

Jerome Lozada, Zhibo Liu, and David M Perrin*

Department of Chemistry, University of British Columbia, 2036 Main Mall Vancouver, British Columbia, CANADA V6T 1Z1

Email: jlozada@chem.ubc.ca ; dperrin@chem.ubc.ca

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General Experimental Procedures

HPLC Analysis

20 mM solutions of the 35 compounds listed in Table 1 were prepared by dissolution through either acetonitrile (ACN) or tetrahydrofuran (THF). These solutions were mixed with a basic solution of 200mM KOH, or KOD, at a 1:1 ratio (100 μ L organic solution with 100 μ L base solution) in a small eppendorf test tube. The resulting mixture was allowed to sit at varying time points and was quenched using a solution of \geq 1M HC (50 μ L). To prevent HPLC blockage, each sample was centrifuged down for a few minutes and transferred into a mass spec vial which was subsequently entered into the HPLC. Screening was performed at $t_1 = 30$ minutes, see Fig 1, while later studies were performed at $t_n = 0 - 30$ min using successful targets (**1**, **12**, **22**, **23**, **31**, **34**).

A standard curve UV analysis showed desired max wavelength to be used in HPLC analysis. Since the products may be volatile, no attention was given to the new peaks produced in the HPLC as difficulties in quantifying the products arose, however these new peaks were confirmed by EI-MS to be the corresponding products.

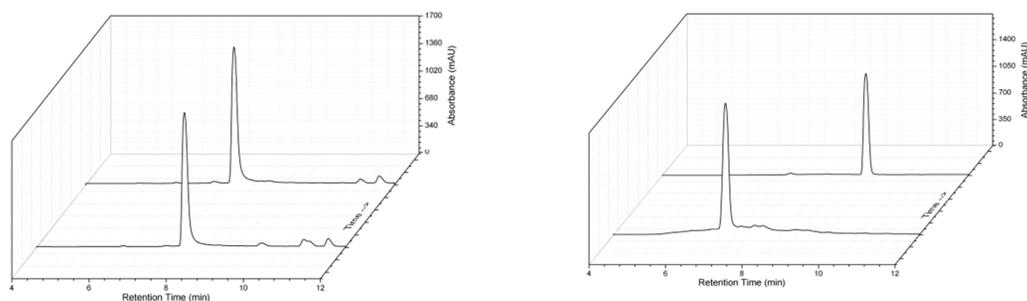


Fig S0 left; No reaction after incubation at 30 minutes; right, disappearance of starting material

NMR Analysis

20 mM solutions of **1** and **33** were prepared using a solution of 4 mM trifluoroethanol (TFE) in ACN and 4 mM TFE in THF respectively to serve as a fluoride reference. The boronic acid solutions were then mixed at a 1:1 ratio (250 μ L organic with 250 μ L base) and incubated at specific time intervals and was quenched with \geq 1M HCl (100 μ L).

FIG S1. Deboronation Kinetics of **1** A; HPLC trace, B; UV trace for extinction coefficients C; Concentration loss over time D; first order rate extrapolation

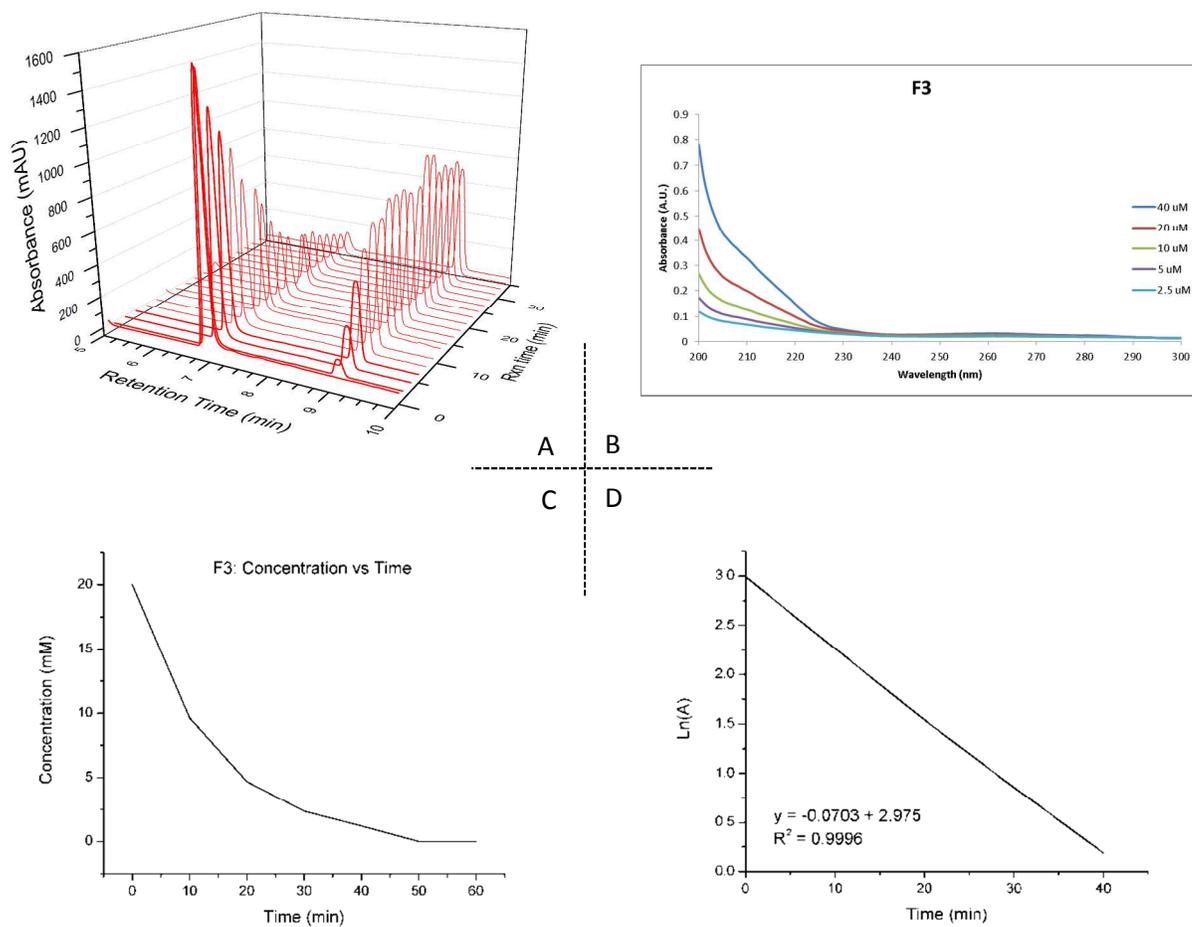


FIG S2. Deboronation Kinetics of **12** A; HPLC trace, B; UV trace for extinction coefficients C; Concentration loss over time D; first order rate extrapolation

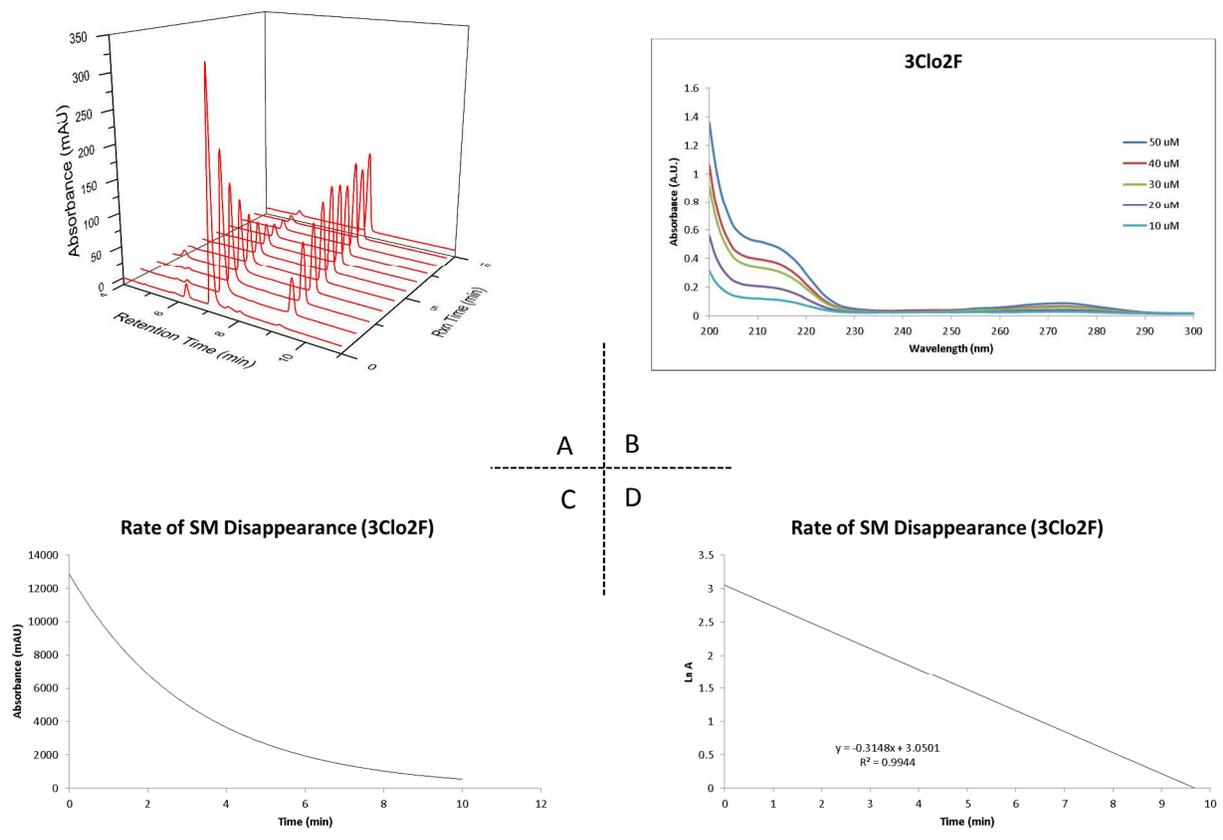


FIG S3. Deboronation Kinetics of **23** A; HPLC trace, B; UV trace for extinction coefficients C; Concentration loss over time first order rate extrapolation

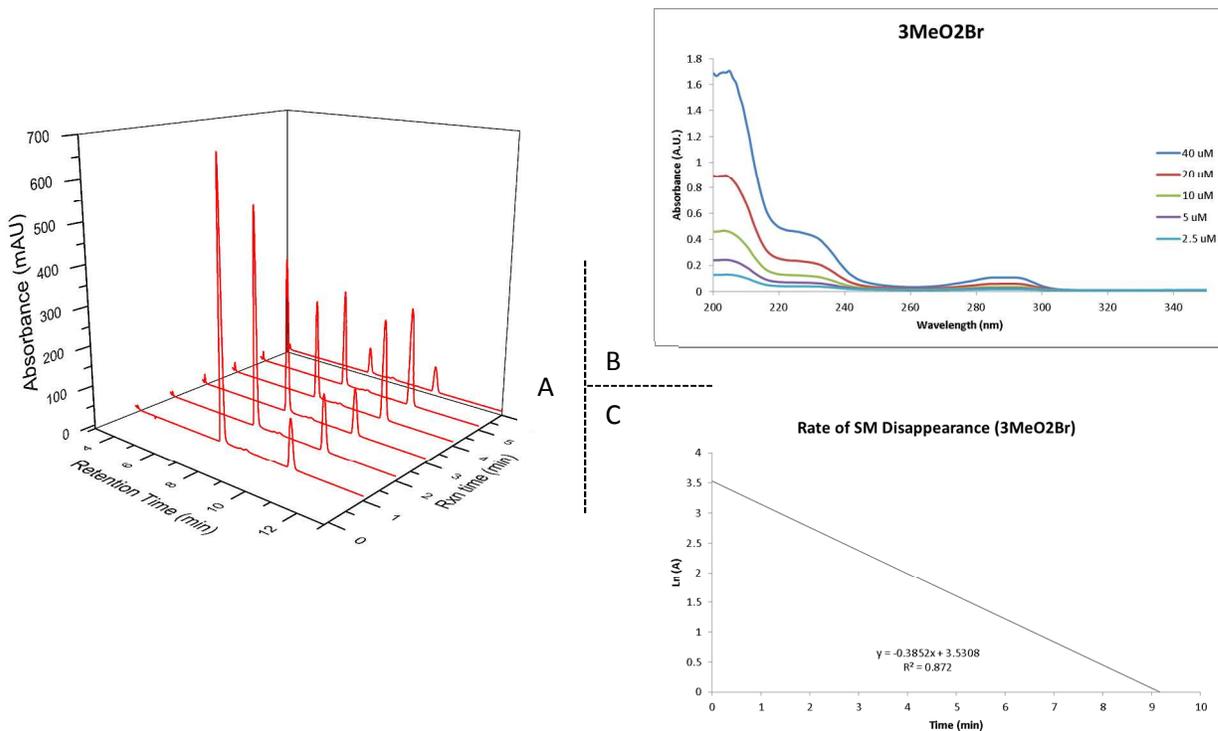


FIG S4. Deboronation Kinetics of **22** A; HPLC trace, B; UV trace for extinction coefficients C; Concentration loss over time D; first order rate extrapolation

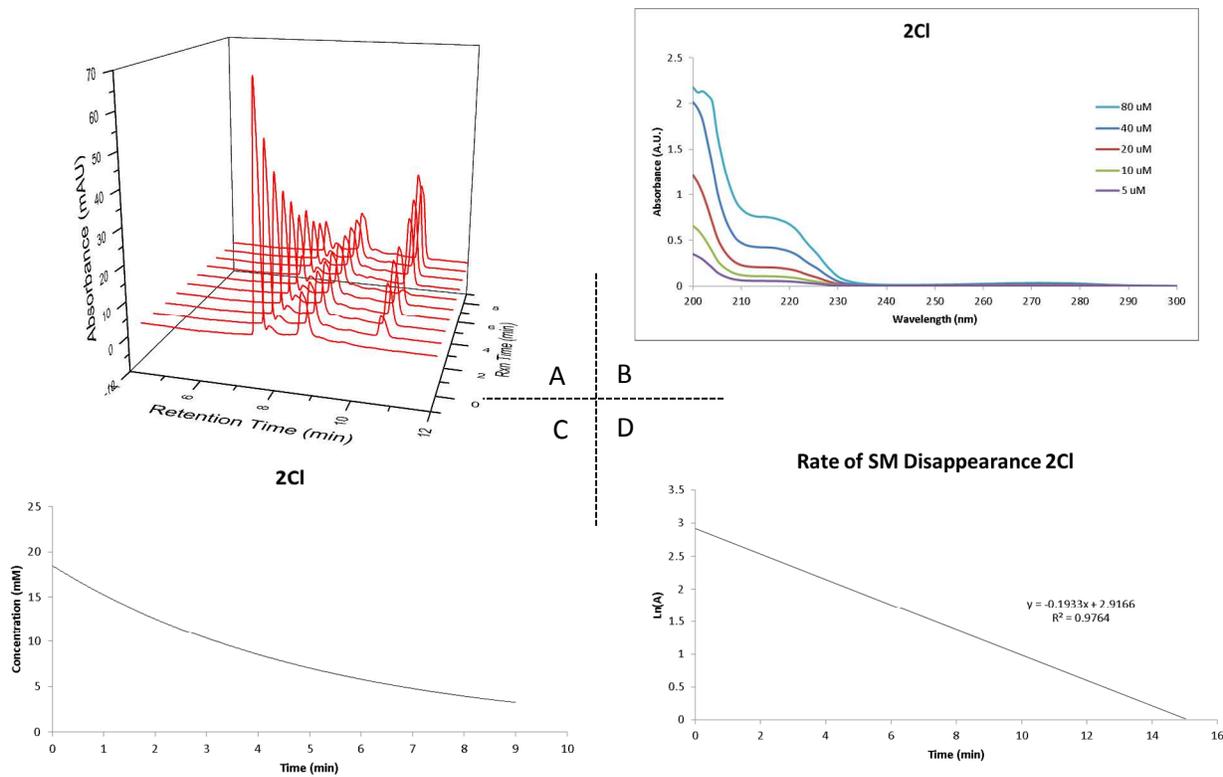


FIG S6. Deboronation Kinetics of **31** A; HPLC trace, B; UV trace for extinction coefficients C; Concentration loss over time D; first order rate extrapolation

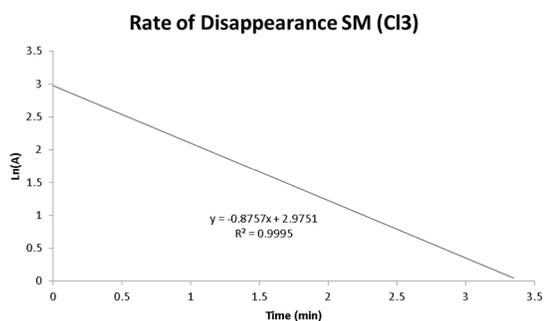
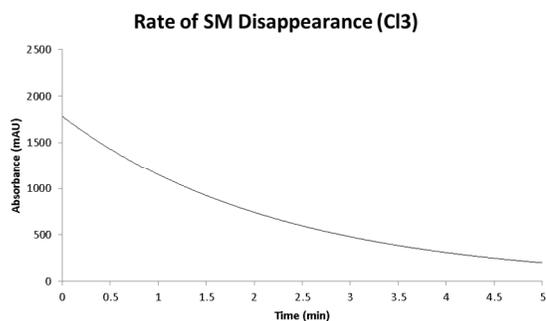
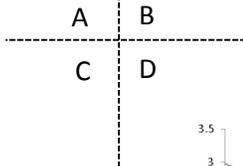
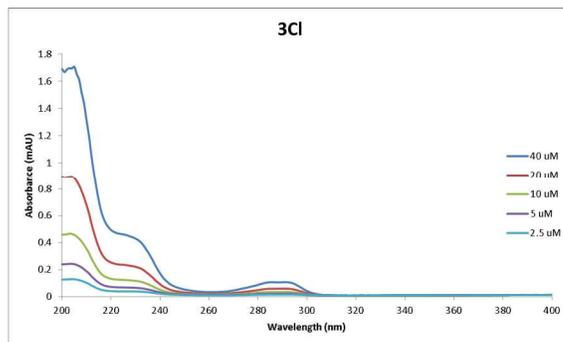
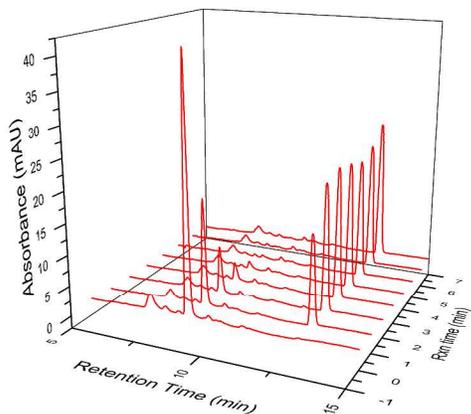
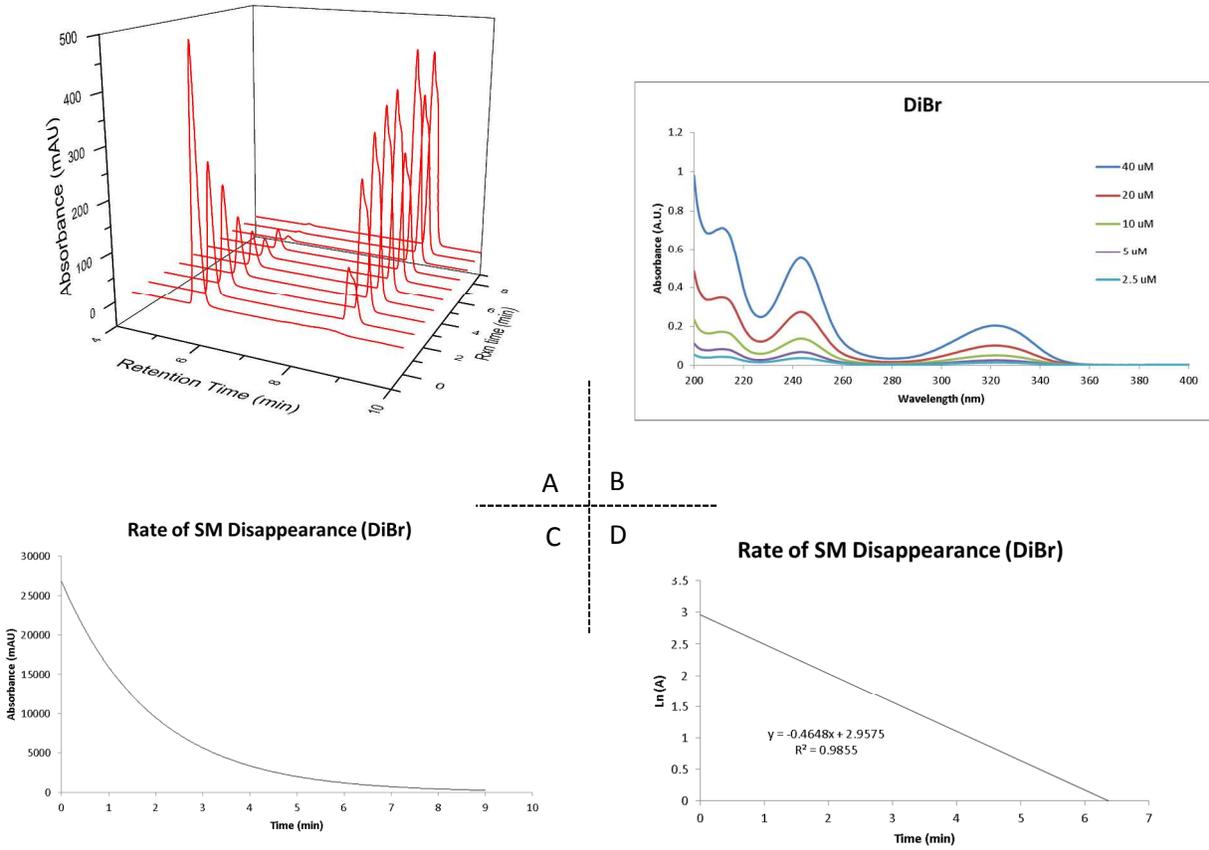


FIG S5. Deboronation Kinetics of **34** A; HPLC trace, B; UV trace for extinction coefficients C; Concentration loss over time D; first order rate extrapolation



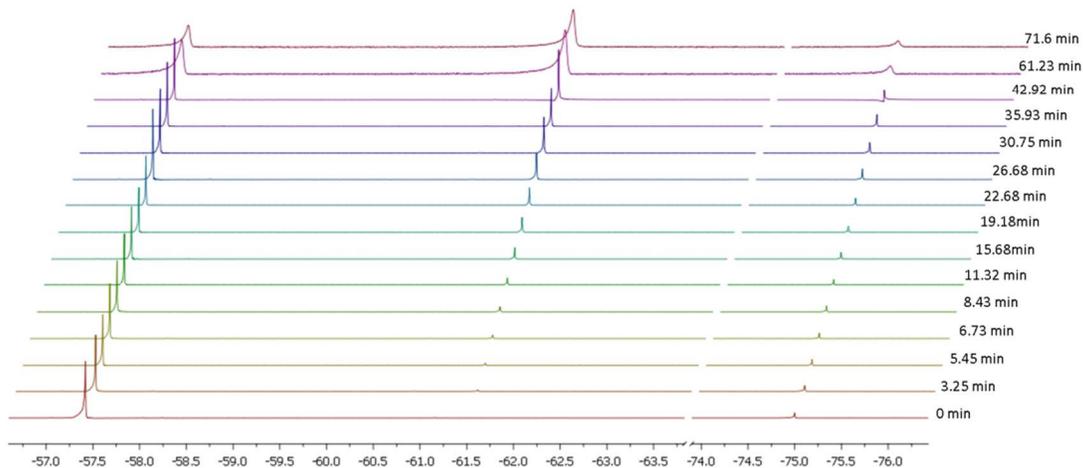


FIG S7A. Deboronation Kinetics of 33 NMR traces at various time points. TFE is used as a reference t -75 ppm. Starting material, 2,6-bistrifluoromethylphenylboronic acid appears at -57.2 ppm and the product, 1,3-bistrifluorobenzene, appears at -61.5 ppm.

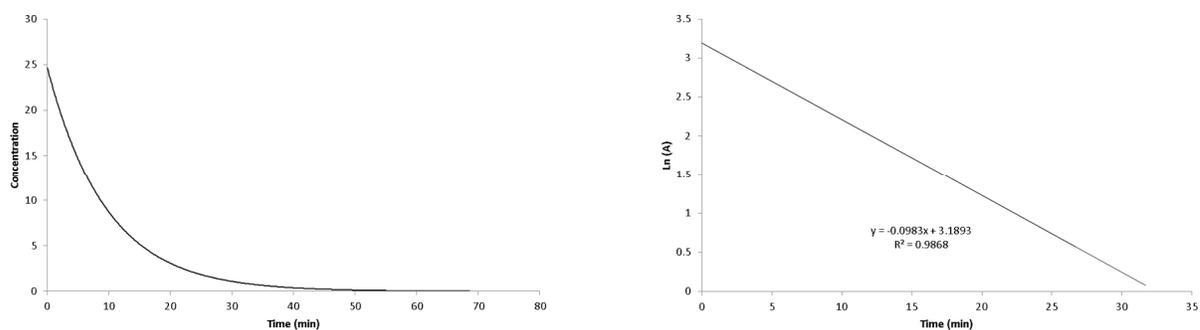
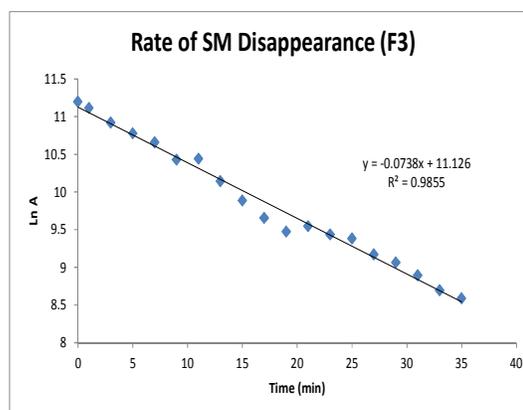
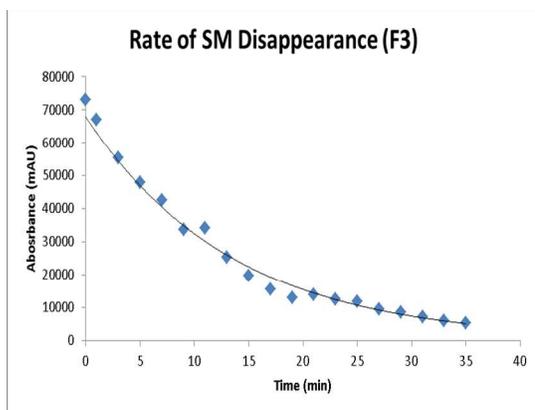
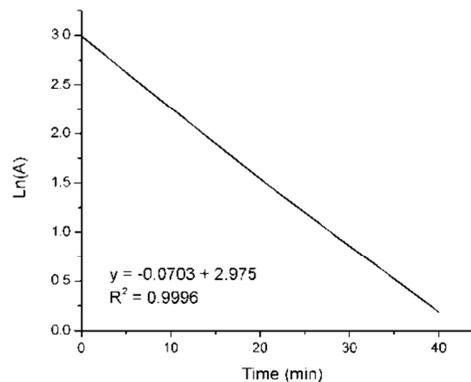
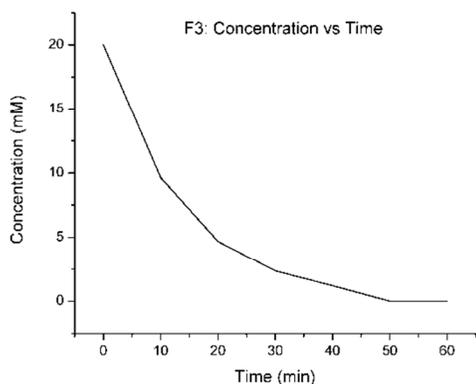


FIG S7B left; Concentration loss over time, Right; first order extrapolation to obtain kinetic rate.

Fig S8. Comparison of HPLC analysis (top) vs NMR analysis (bottom) of **1**. Graphs on the left are concentration losses and the right shows extrapolation to first order rate kinetics. The comparison of rates show agreeable values at 0.0738 min^{-1} and 0.0703 min^{-1}



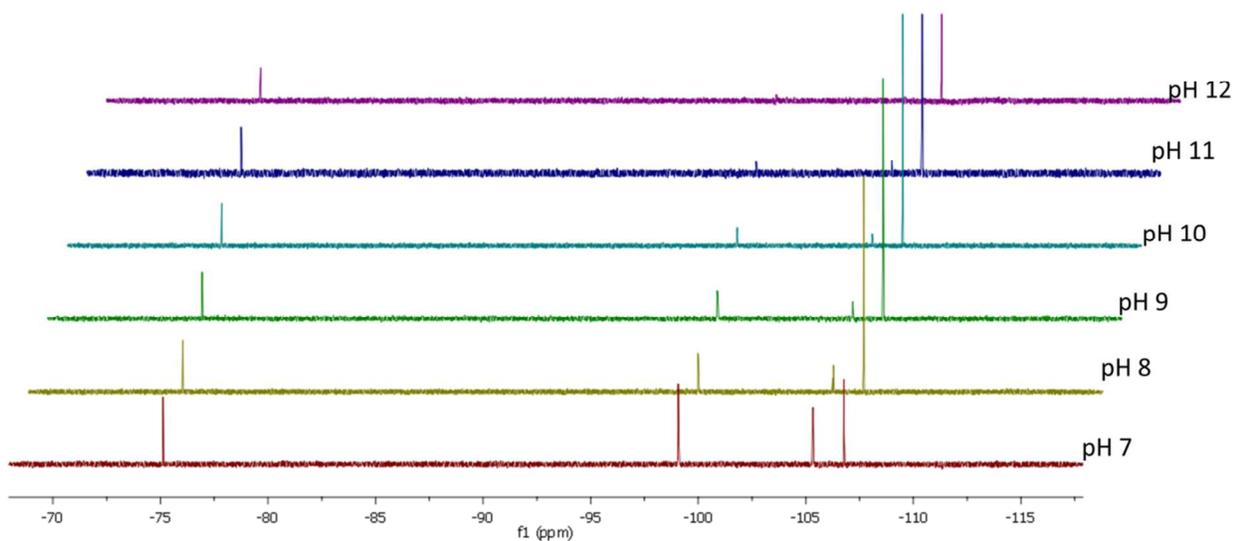


Fig S9A. NMR of **1** stabilities at pH 7-12 under 5 minutes.

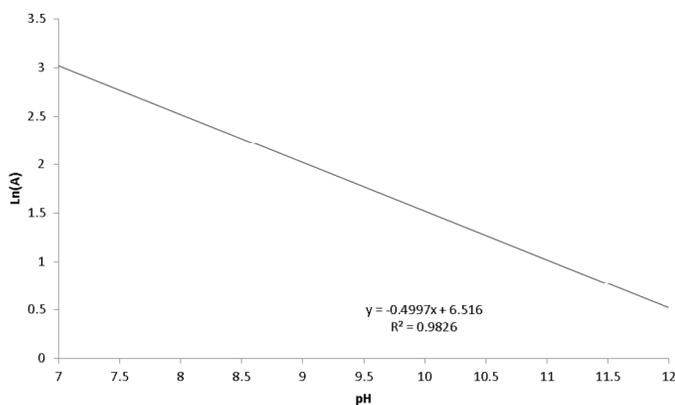


Fig S9B. A linear trend for this disappearance with $k_{\text{obs}} = 0.500 \text{ min}^{-1}$ is observed for the disappearance of **1** when incubated under different pH

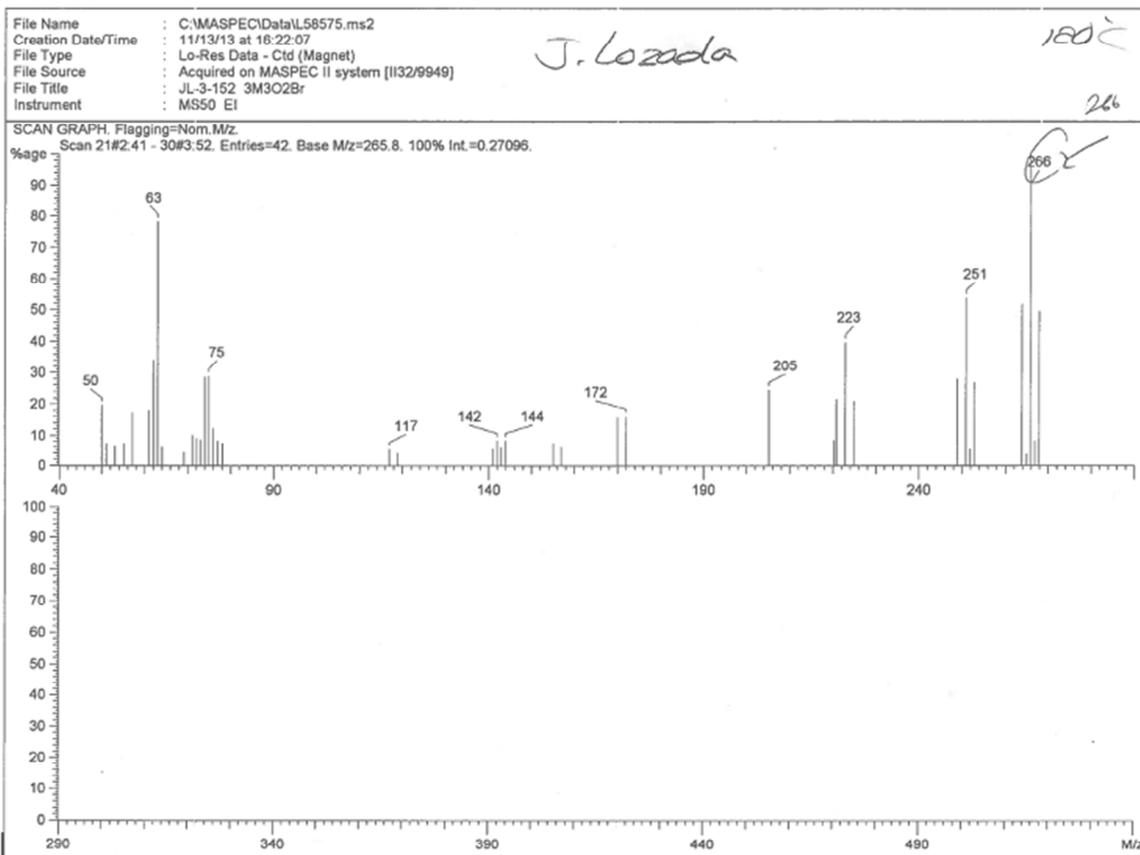


Figure S10. Mass Spectrum of **23** product peak

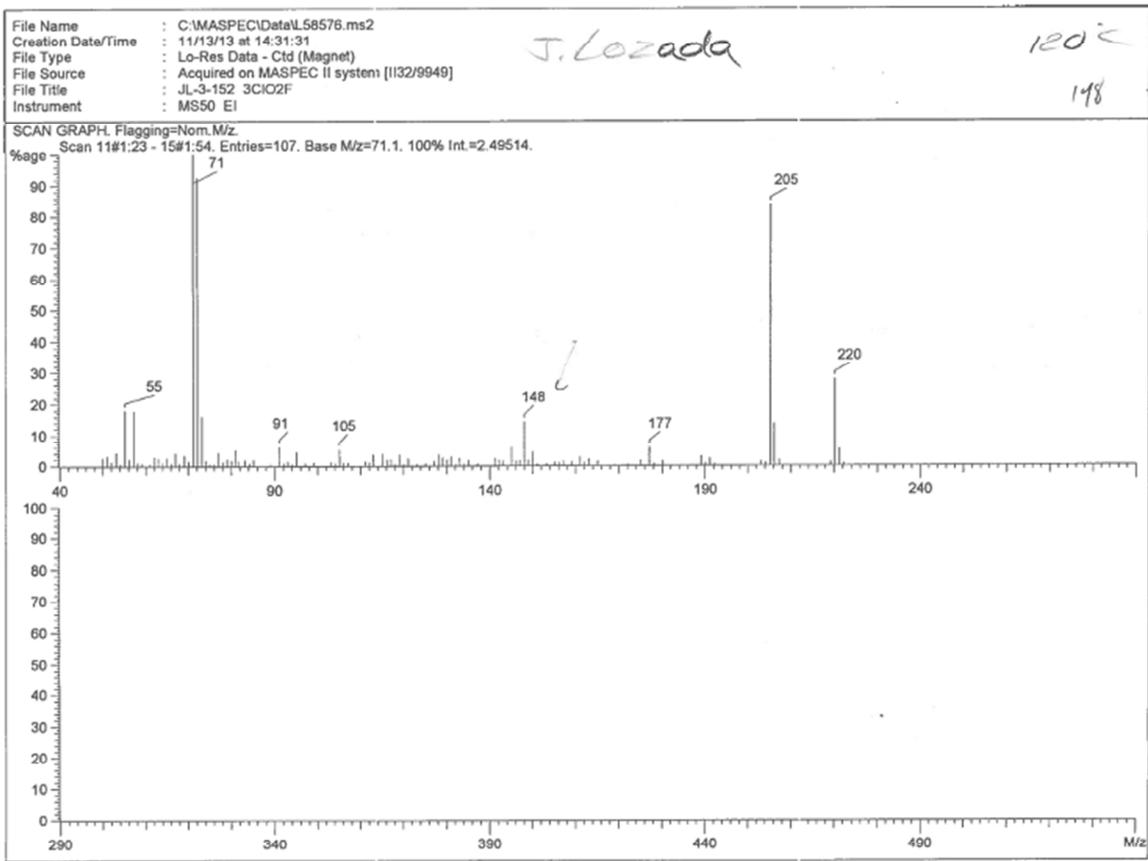


Figure S10. Mass Spectrum of **12** product peak

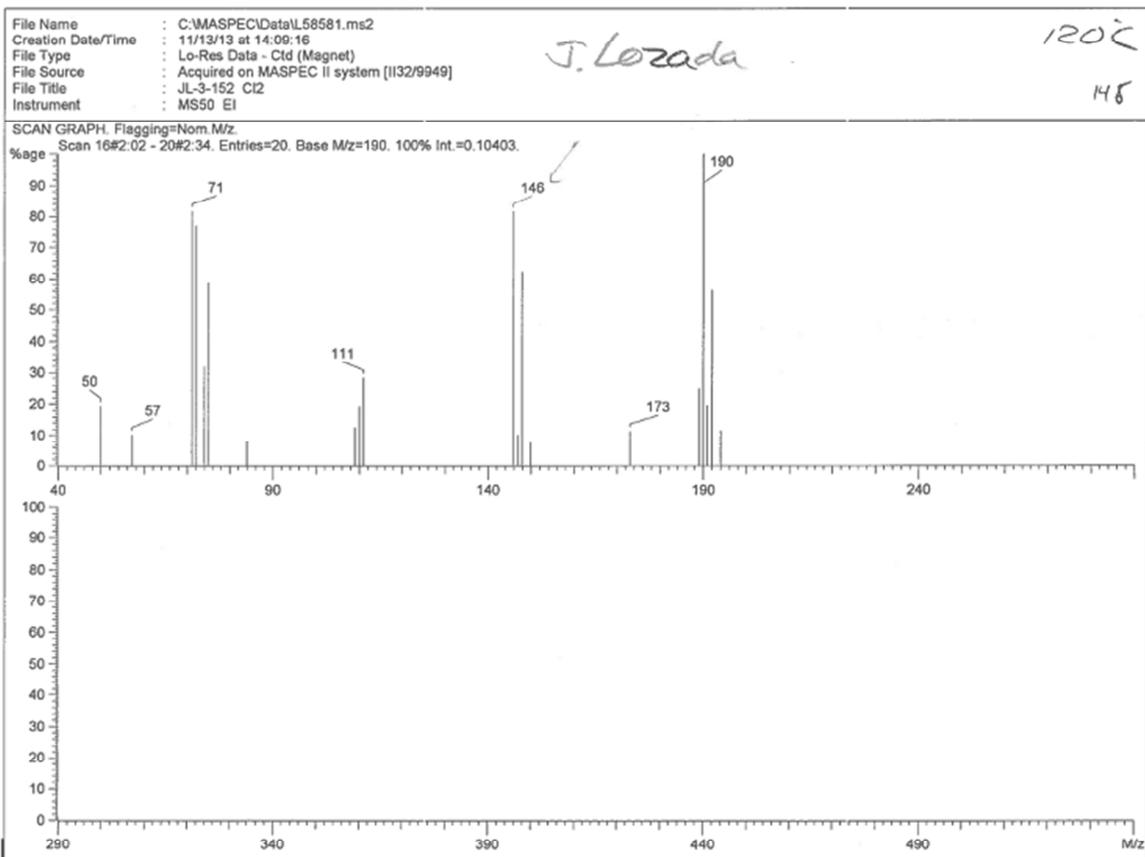


Figure S12. Mass Spectrum of **22** product peak

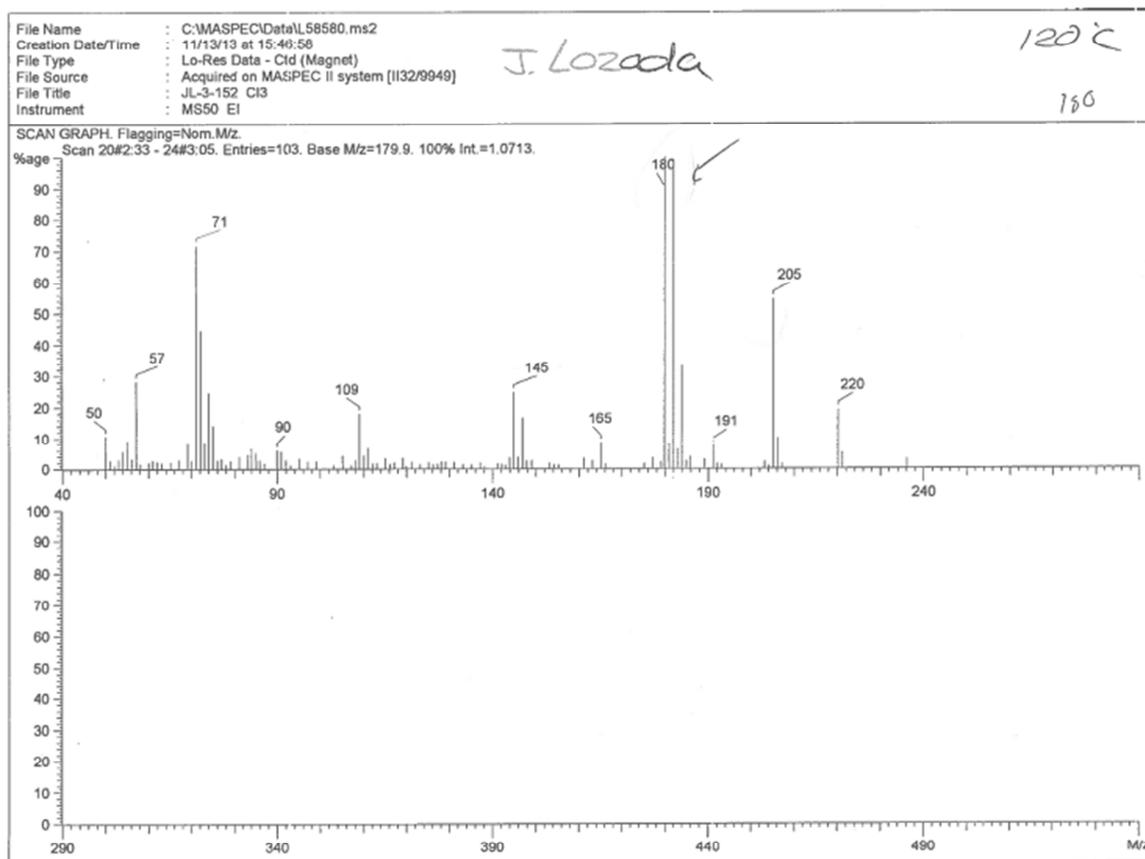


Figure S13. Mass Spectrum of **31** product peak

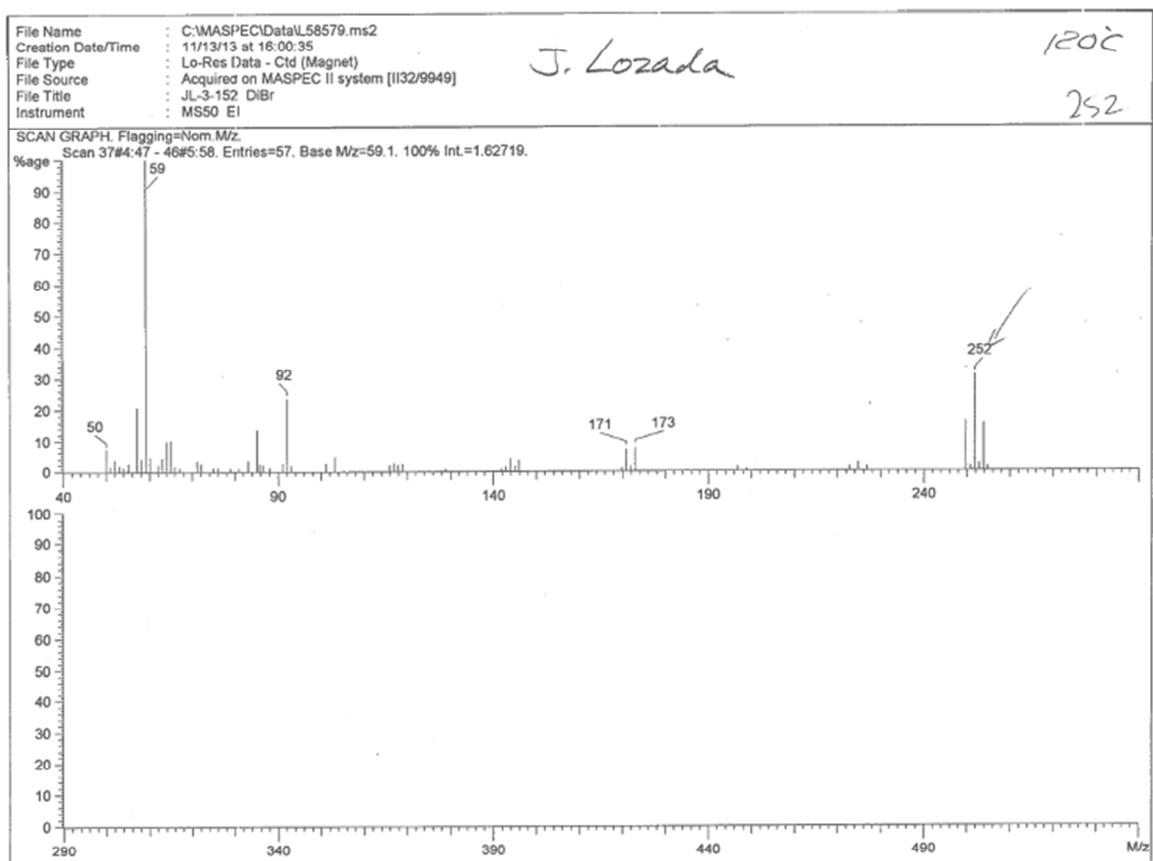


Figure S14. Mass Spectrum of **34** product peak

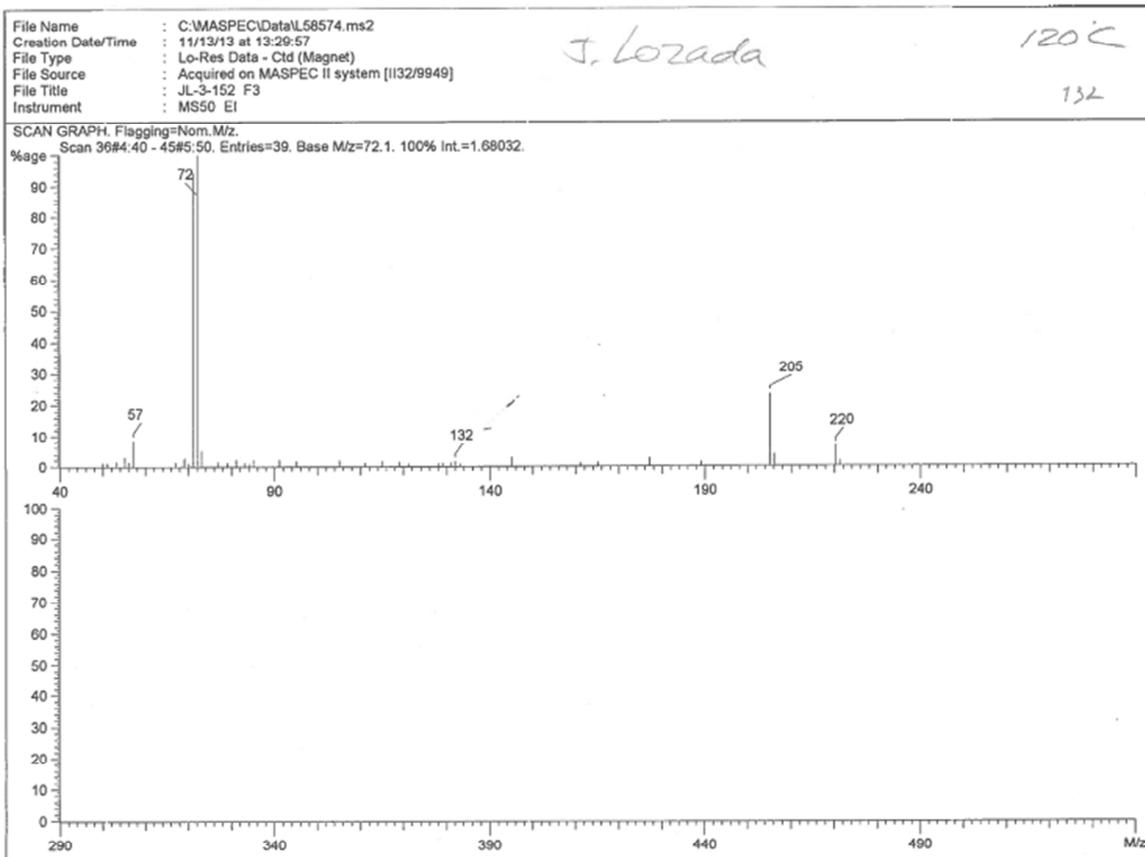
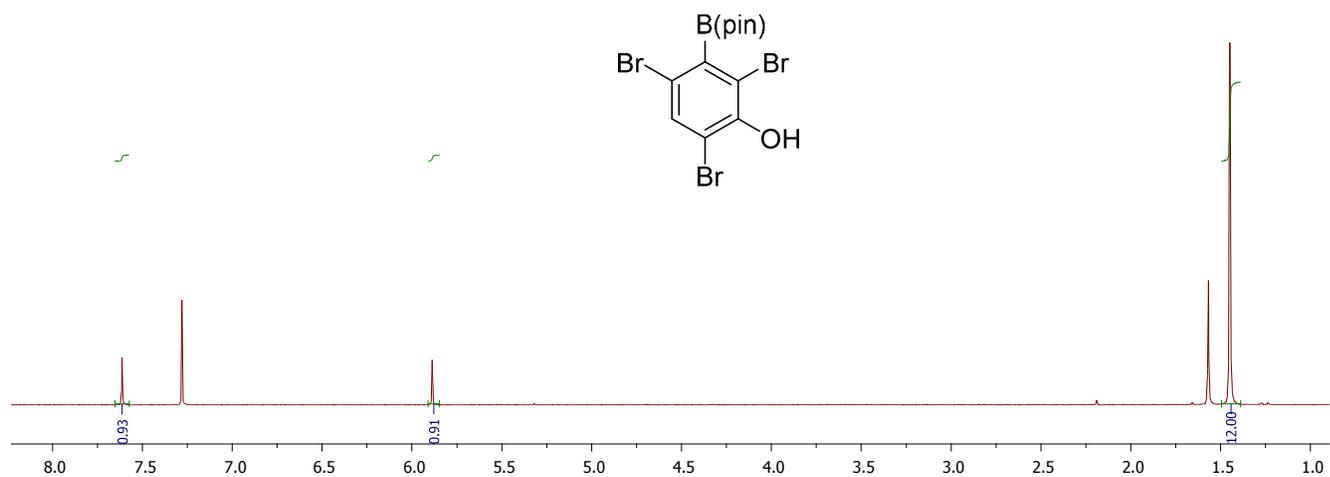


Figure S15. Mass Spectrum of **1** product peak

Fig S11. ^1H NMR Spectrum of **35**



300 MHz, CDCl_3 , δ 1.47 ppm, (s, 12H); δ 5.91 ppm, (s, 1H), δ 7.64 ppm, (s, 1H)

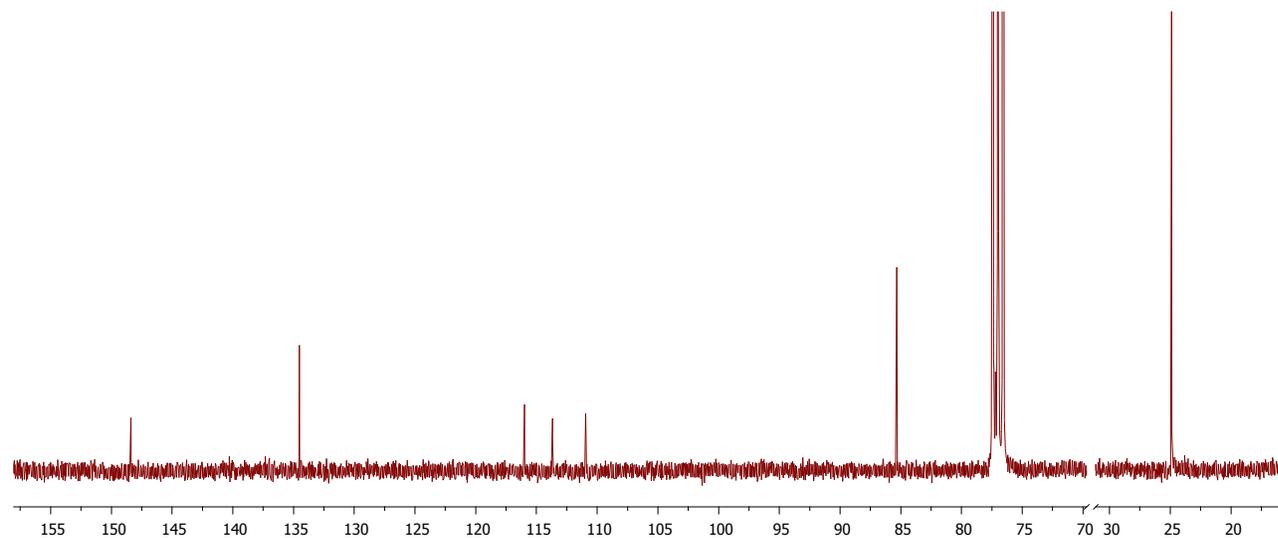


Fig S12. ^{13}C NMR Spectrum of **35**; 24.894 ppm, 77.028 ppm, 85.307 ppm, 110.930 ppm, 113.488 ppm, 116.066 ppm, 134.554 ppm, 148.415 ppm

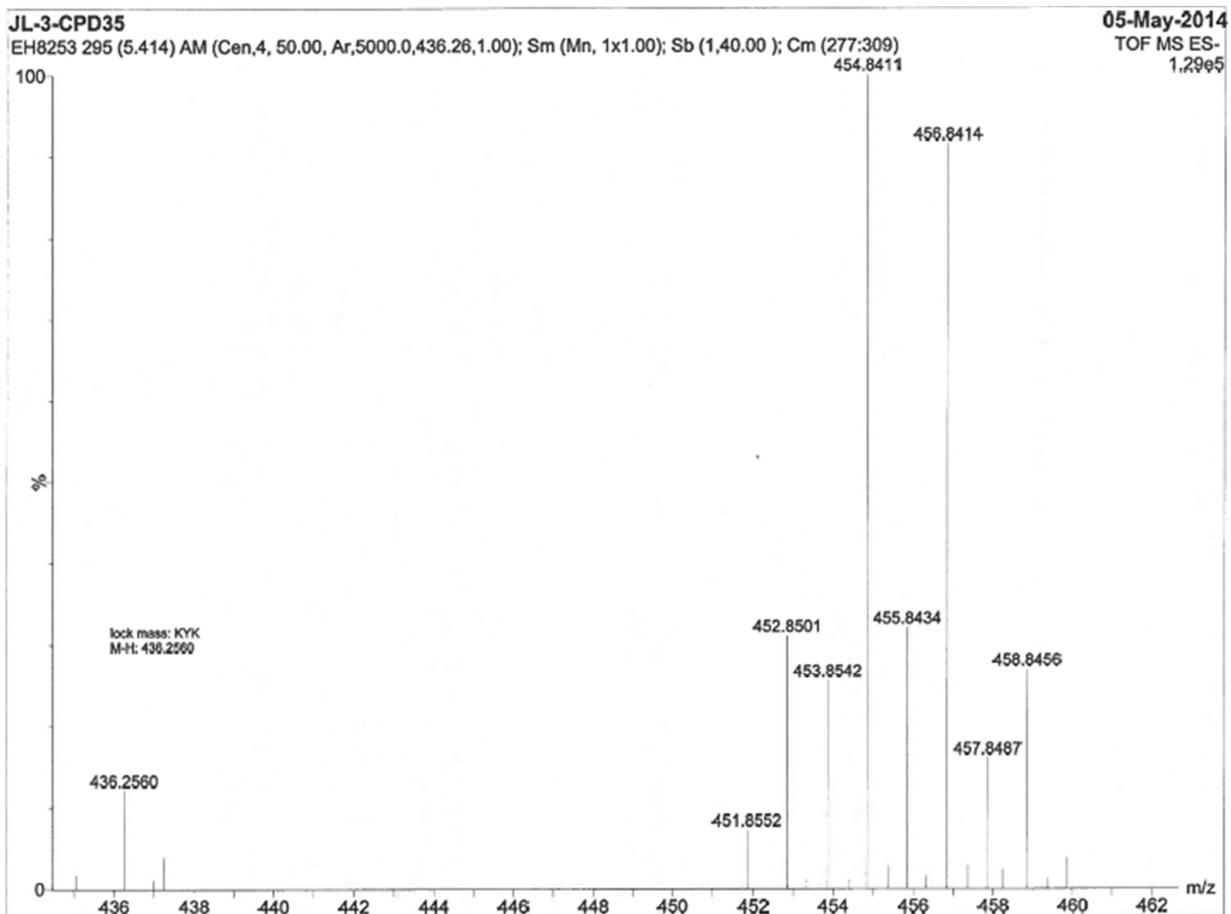


Fig S13: High Resolution Mass Spectra of compound **35**. HRMS (ESI-TOF) m/z: [M + Na]⁺ Calcd for C₁₂H₁₄BBr₃NaO₃ 451.8544; Found 451.8552