[Electronic Supporting Information to accompany]

# Epoxidation of the commercially relevant divinylbenzene with [*tetrakis*-(pentafluorophenyl)porphyrinato]iron(III) chloride and its derivatives

Kainan Zhang,<sup>a</sup> Ying Yu,<sup>b</sup> SonBinh T. Nguyen,<sup>a</sup> Joseph T. Hupp,<sup>a</sup> Linda J. Broadbelt,<sup>b</sup> Omar K. Farha<sup>a,c,\*</sup>

<sup>a</sup> Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA.

<sup>b</sup> Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3120, USA.

<sup>c</sup> Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia.

#### **Table of Contents**

S1. Materials and methods.	S1
S2. Instrument and characterization.	S1
S3. General procedures for product quantification and reagent preparation.	S2
S4. Synthesis of (TPFPP)FeCl and epoxidation of DVB using (TPFPP)FeCl.	S3
S5. Procedures for the functionalization of fluorinated Fe-porphyrin.	S15
S6. Epoxidation of DVB using functionalized Fe-porphyrin.	S18
S7. Computational details.	S25
S8. References.	S35
S9. NMR spectra.	S36

**S1. Material and methods.** Compounds  $\mathbf{1}$ , <sup>S1</sup>  $\mathbf{3}$ , <sup>S2</sup> and  $\mathbf{4}^{S3}$  were synthesized according to literature procedures. Styrene, divinylbenzene (DVB), FeCl<sub>2</sub>·2H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> (50%), and *N*-Methyl-2-pyrrolidone were obtained from Sigma Aldrich Chemicals Co. (Milwaukee,WI) and used as received. Divinylbenzene monoxide (DVBMO), ethylvinylbenzene oxide (EVBO), and divinylbenzene dioxide (DVBDO) were gifts from Dow Chemical Company (Midland, MI), [*tetrakis*-(pentafluorophenyl)porphyrin (Frontier Scientific, Logan, Utah), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, Acros Organics part of Thermo Fisher Scientific, Waltham, MA), Chloroform-*d* and benzene-*d*<sub>6</sub> (Cambridge Isotope Laboratories, Andover, MA), acetonitrile (Fisher Scientific, Waltham, MA), and MeOH (EMD, Gibbstown, NJ) were obtained from commercial sources and used as received.

**S2. Instrument and characterization**. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on an Agilent 400 MR DD2 spectrometer (400 MHz for <sup>1</sup>H, 376 MHz for <sup>19</sup>F) (Agilent Technologies, Santa Clara, CA). <sup>1</sup>H and <sup>19</sup>F chemical shifts are referenced to the residual proton resonance of solvent on the  $\delta$  scale.

Matrix-assisted laser desorption-ionization time-of-flight (MALDI-ToF) mass spectra were obtained on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer (Bruker Daltonics, Billerica, MA) in positive ionization mode with  $\alpha$ -Cyano-4-hydroxycinnamic acid (CHCA) as a matrix.

Microwaved reactions were carried out using a Biotage Initiator microwave reactor (Biotage, LLC, Charlotte, NC).

UV-vis spectra were carried out using a Varian Gary 500 UV-Vis-NIR spectrophotometer.

GC-MS analysis in Figure S7, S10, S15, S31, S34, and S37 were carried out on a Shimadzu QP-2010 GC-MS equipped with an MS detector and a Phenomenex ZB-624 column (30 m × 250  $\mu$ m diameter × 1.4  $\mu$ m film thickness). Analysis parameters were as followed: initial temperature = 60 °C, initial time = 1 minutes, ramp = 10 °C/min, ramp to 150 °C, then a slow ramp = 2 °C/min, ramp to 180 °C, hold for 5 min, final ramp = 10 °C/min to 250 °C, final time = 15 minutes, total flow = 78 mL/min, purge flow: 3 mL/min. Elution times (min) = 18.5 (DVBMO *meta*), 18.9 (DVBMO *para*), 16.8 (EVBO *meta*), 17.2 (EVBO *para*), 27.8 (DVBDO *meta*), 28.4 (DVBDO *para*). Product concentrations were calculated based on calibration curves constructed from five solutions of known compounds with a concentration range from 0 to 7 mM.

GC analysis in Figure S18, S21, S24 and S40 were carried out on an Agilent Technologies 7820A GC system equipped with an FID detector and an Agilent J&W GC HP-5 capillary column ( $30 \text{ m} \times 320 \mu \text{m} \times 0.25 \mu \text{m}$  film thickness). Analysis parameters were as followed: initial temperature = 75 °C, initial time = 5 minutes, ramp = 6 °C/min, final temperature = 200 °C, final time = 5 minutes, flow rate = 6.5 mL/min. Elution times (min) = 4.814 (DVB *meta*), 5.128 min (DVB *para*), 4.026 (EVB *meta*), 4.201 (EVB *para*), 9.730 (DVBMO *meta*), 9.945 (DVBMO *para*), 8.947 (EVBO *meta*), 9.170 (EVBO *para*), 14.047 (DVBDO *meta*), 14.191 (DVBDO *para*), 11.435, and 11.626 (benzaldehyde derivatives). Product concentrations were calculated based on calibration curves constructed from five solutions of known compounds with a concentration range from 6 mM to 0.1 mM.

#### S3. General procedures for product quantification and reagent preparation

**General procedure for monitoring reactions by NMR**: Before the addition of  $H_2O_2$  into the reaction mixture, one drop of the mixture was taken using a disposable glass pipet and dropped into another glass pipet that has been prepacked with a cotton plug.  $C_6D_6$  (~ 0.5 mL) was then added into the pipet to rinse the content into an NMR tube. An NMR spectrum of this solution was then acquired and used as a reference for the reaction at 0 h (Caution: the reaction vial should be tightly sealed by a cap, and the screw top of the vial should be wrapped by Teflon tape to ensure a good seal so that the solvent evaporation is negligible, and the vial should be tightly sealed immediately after the sample drop was taken). Following the above mentioned method for sample preparation, progress of all the reactions were monitored by NMR spectroscopy until the ratio of the alkene resonances to those for the dichloromethane internal standard stops decreasing.

General procedure for quantifying the products for epoxidation of styrene. The normalized alkene concentration and the overall epoxide yields were determined by NMR integration of the resonances at 5.01, 5.54, and 6.52 ppm (for alkenes of styrene), 2.27, 2.55, and 3.40 ppm (for epoxides of styrene oxide), 9.19 ppm (for phenylacetylaldehhyde), 9.57 ppm (for benzaldehyde), 4.00 ppm and 3.56 ppm (for methanol ring opening derivatives), relative to the resonances for dichloromethane (4.27 ppm). All integrated peak areas were normalized against the 4.27 ppm resonance for dichloromethane (assigned as 1500 for all NMR spectra). Using Figure S2 as an example, the yield of styrene oxide was calculated using the following method: Styrene oxide yield = 56.17 (the epoxide integration at 2.55 ppm)/69.85(the alkene integration at 5.54 ppm)  $\times 100\% = 80\%$ .

General procedure for quantifying the total epoxide yield for the epoxidation of DVB. The normalized alkene concentration and the overall epoxide yields were determined by NMR integration of the resonances at 5.02, 5.56, and 6.52 ppm (for alkenes of DVB and EVB), 2.26, 2.55, 3.40 ppm (for epoxides DVBDO, DVBMO and EVBO), 4.02 ppm and 3.60 ppm (for methanol ring opening derivatives), relative to the resonances for dichloromethane (4.29 ppm). All integrated peak areas were normalized against the 4.29 ppm resonance for dichloromethane (assigned as 1500 for all NMR spectra). Using Figure S5 as an example, the yield of styrene oxide was calculated using the following method: Total epoxide yield = 118.79 (the epoxide integration at 2.55 ppm)/158.13 (the alkene integration at 5.56 ppm)  $\times 100\% = 75\%$ .

General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR. The following calculation was carried out using the data shown in Figures S6 and S7. Based upon GC calibration, the ratio of EVBO, DVBMO, DVBDO in the final product mixture (Figure S7) is 0.476:0.195:2.774. The ratio of the epoxide groups from EVBO, DVBMO, and DVBDO in the final product is then 0.476:0.195:( $2.774 \times 2$ )= 0.476:0.195:5.548. For simplification, the normalized concentrations of DVB and EVB in the starting material are set at 80 and 20 mol%, respectively. The normalized concentration of alkene from DVB and EVB are then 160 and 20 mol%, respectively, making the total normalized concentration of alkene in the starting material = (160 + 20) = 180 mol%. Since the total epoxide yield is 75% based on the NMR data summarized in Figure S64, the total normalized concentration of epoxide in the final product should be  $180 \times 0.75 = 135$  mol%.

The normalized concentration of epoxide from EVBO =  $(135 \times 0.475)/(0.475 + 0.195 + 5.548) = 10.3 \text{ mol}\%$ 

The normalized concentration of epoxide from DVBMO =  $(135 \times 0.195)/(0.475 + 0.195 + 5.548) = 4.23 \text{ mol}\%$ 

The normalized concentration of epoxide from DVBDO =  $(135 \times 5.548)/(0.475 + 0.195 + 5.548) = 120 \text{ mol}\%$ 

The normalized concentration of EVBO, DVBMO, DVBDO and should then be 10.3, 4.23, and (120/2) = 60 mol%, respectively.

The product yields for EVBO (based on EVB), DVBMO (based on DVB), and DVBDO (based on DVB), should be 10.3/20 = 52%, 4.23/80 = 5%, and 60/80 = 75%, respectively.

**General procedure for calculating the turnover number**: The turnover number is calculated based on the conversion of the total number of alkene and the catalyst charged. Using Figure S23 as an example, the total conversion of alkene is 97%, the total turnover number = 0.339 mmol (the amount of starting material charged) × 1.8 (1 mol% of starting material contains 1.8 mol% of alkene due to the 20% EVB impurity) × 97% (total alkene conversion) / 0.94  $\mu$ mol (amount of catalyst charged) = 630.

General procedure for the preparation of  $H_2O_2$  solution:  $H_2O_2$  solution was prepared by mixing 50 wt%  $H_2O_2$ and acetonitrile with a volume ratio of 1 to 9 in order to perform slow addition at an appropriate rate. (Caution: the  $H_2O_2$  solution should be kept in the refrigerator all the time through the reaction to minimize the decomposition unless when it is being added to the reaction vial.)

#### S4. Synthesis of Fepor-2a and epoxidation of DVB using Fepor-2a

**Synthesis of Fepor-2a**: Into a 20 mL microwave vial equipped with a magnetic stir bar, *tetrakis*-(pentafluorophenyl)porphyrin (100 mg, 0.103 mmol), FeCl<sub>2</sub>•4H<sub>2</sub>O (82 mg, 0.412 mmol), and *N*-Methyl-2-pyrrolidone (18 mL) were added. The microwave vial was crimp-capped and then the reaction mixture was heated in a microwave reactor at 170 °C for 20 min. The reaction mixture was poured in to a 500 mL beaker, LiCl (100 mg) was then added and the mixture was stirred for 1 h in air. Water (100 mL) was added to precipitate the product from the mixture and the product was isolated by filtration. After being washed by water (50 mL) and suction-dried for 1 h, the crude product was purified by silica gel column chromatography (using DCM/hexane = 1/3 to collect the unmetallated free base porphyin and followed by DCM/hexane = 3/2 to obtain a black-green fraction) to obtain a black product (40 mg, 36.7%) (The product is tailing on TLC, so only the top part of the tailing spot is the right product). MALDI-ToF MS: m/z 1027.5 (1027.9 calcd for [M-Cl]<sup>+</sup>). UV-vis (MeOH): [ $\lambda$  max in nm ( $\epsilon \times 10^4$  /M<sup>-1</sup>cm<sup>-1</sup>)] 406 (8.25), 589 (0.772).

**Procedure for the epoxidation reaction of styrene using Fepor-2a**: Into a 1.5 dram glass vial equipped with a magnetic stir bar, **Fepor-2a** (2.0 mg, 0.00188 mmol), styrene (19.6 mg, 22  $\mu$ L, 0.188 mmol), methanol (0.40 mL), and dichloromethane (0.14 mL) were added. An NMR sample was measured using the "General procedure for monitoring reactions by NMR". And then, an aliquot of H<sub>2</sub>O<sub>2</sub> solution (6.5  $\mu$ L 0.0095 mmol, 0.05 equiv) was added into the reaction mixture by a micropipette every 20 min. Progress of the reaction was monitored by NMR using the general procedure. Finally, a total of 1.6 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of styrene oxide (based on styrene) is 80%.





Figure S1. a): 0 h; b): 12 h. Styrene oxide yield = 56.17 (the epoxide integration at 2.55 ppm)/69.85(the alkene integration at 5.54 ppm)  $\times$  100% = 80%. See Figure S2 for reaction profile.



Figure S2. Plots of normalized styrene and product concentrations vs. time for the epoxidation of styrene using Fepor-2a.

Procedure epoxidation reaction for the of styrene with in situ formed [tetrakis-(pentafluorophenyl)porphyrinatoliron(III) nitrate: A catalyst stock solution was prepared by the following described procedure: Into a 1.5 drum glass vial equipped with a magnetic stir bar, Fepor-2a (12.5 mg, 0.0118 mmol) and AgNO<sub>3</sub> (2.0 mg, 0.012 mmol), acetonitrile (0.9 mL) and dichloromethane (0.3 mL) were added. The catalyst stock solution was kept at room temperature for 10 h before being used.

Follow the "Procedure for the epoxidation reaction of styrene using **Fepor-2a**". The catalyst stock solution (0.19 mL, 0.00188 mmol), styrene (19.6 mg, 22  $\mu$ L, 0.188 mmol), methanol (0.3 mL), and dichloromethane (0.1 mL) were used. An NMR sample was measured using the "General procedure for monitoring reactions by NMR". And then, an aliquot of H<sub>2</sub>O<sub>2</sub> solution (6.5  $\mu$ L 0.0095 mmol, 0.05 equiv) was added into the reaction mixture by a micropipette every 20 min. Progress of the reaction was monitored by NMR using the general procedure. Finally, a total of 1.2 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of styrene oxide (based on styrene) is 81%.

a)



Figure S3. a): 0 h; b): 8 h. Styrene oxide yield = 60.56 (the epoxide integration at 2.55 ppm)/74.61(the alkene integration at 5.54 ppm) × 100% = 81%. See Figure S4 for reaction profile.



Figure S4. Plots of normalized styrene and product concentrations vs. time for the epoxidation of styrene using in situ formed (TPFPP)Fe<sup>+</sup>NO<sub>3</sub><sup>-</sup>.

**Procedure for the epoxidation reaction of divinylbenzene (DVB) using Fepor-2a**: Into a 1.5 dram glass vial equipped with a magnetic stir bar, **Fepor-2a** (3.0 mg, 0.0028 mmol), DVB (36.6 mg, 40  $\mu$ L, 0.28 mmol), methanol (0.54 mL), and dichloromethane (0.18 mL) were added. An NMR sample was measured using the "General procedure for monitoring reactions by NMR". And then, an aliquot of H<sub>2</sub>O<sub>2</sub> solution (15  $\mu$ L 0.022 mmol, 0.078 equiv) was added into the reaction mixture by a micropipette every 20 min. Progress of the reaction was monitored by NMR using the general procedure. Finally, a total of 3.4 equiv of H<sub>2</sub>O<sub>2</sub> was added. Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the





**Figure S5.** a): 0 h; b): 15 h. Total epoxide yield = 118.79 (the epoxide integration at 2.55 ppm)/158.13 (the alkene integration at 5.56 ppm)  $\times$  100% = 75%. See Figure S6 for reaction profile.



Figure S6. Plots of normalized alkene and product concentrations *vs.* time for the epoxidation of DVB using Fepor-2a.



**Figure S7.** GC trace for the epoxidation of DVB using (TPFPP)FeCl at 15 h. Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 75, 5, and 52%, respectively.

**Procedure for the epoxidation reaction of divinylbenzene (DVB) using Fepor-2a and imidazole**: Follow the "Procedure for the epoxidation reaction of divinylbenzene (DVB) using **Fepor-2a**". **Fepor-2a** (3.0 mg, 0.0028 mmol), DVB (36.6 mg, 40  $\mu$ L, 0.28 mmol), imidazole (3.8 mg, 0.0559 mmol), methanol (0.54 mL), and dichloromethane (0.18 mL) were used. An aliquot of H<sub>2</sub>O<sub>2</sub> solution (15  $\mu$ L 0.022 mmol, 0.078 equiv) was added into the reaction mixture by a micropipette every 20 min. Finally, a total of 3.2 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 53, 27, and 82%, respectively.



**Figure S8.** a): 0 h; b): 14 h. Total epoxide yield = 72.87 (the epoxide integration at 2.55 ppm)/107.93 (the alkene integration at 5.56 ppm)  $\times$  100% = 68%. See Figure S9 for reaction profile.



Figure S9. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2a with imidazole as additive.



**Figure S10.** GC trace for the epoxidation of DVB using **Fepor-2a** at 15 h. Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 53, 27, and 82%, respectively.

Procedure for the epoxidation reaction of divinylbenzene (DVB) with acetonitrile and dichloromethane as solvents: Follow the "Procedures for the epoxidation reaction of divinylbenzene (DVB) using Fepor-2a". Fepor-2a (1.5 mg, 0.0014 mmol), DVB (18.3 mg, 20  $\mu$ L, 0.14 mmol), acetonitrile (0.27 mL), and dichloromethane (0.09 mL) were used. An aliquot of H<sub>2</sub>O<sub>2</sub> solution (7.5  $\mu$ L 0.011 mmol, 0.078 equiv) was added into the reaction mixture by a micropipette every 10 min. Finally, a total of 1.8 equiv of H<sub>2</sub>O<sub>2</sub> was added. The color of the solution turns from black green to dark red. See Figure 12 for the reaction profile.





Figure S11. Total epoxide yield (after 8 h) = 34.81 (the epoxide integration at 2.55 ppm)/130.71 (the alkene integration at 5.56 ppm)  $\times$  100% = 27%. See Figure S12 for reaction profile.



Figure S12. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2a with acetonitrile and dichloromethane as solvent mixture.

**Epoxidation reaction with high turnover numbers (turnover number = 441)**: Follow the "Procedures for the epoxidation the reaction of divinylbenzene (DVB) using **Fepor-2a**". **Fepor-2a** (1.0 mg, 0.00094 mmol), DVB (30.6 mg, 33.5  $\mu$ L, 0.235 mmol), methanol (0.50 mL), and dichloromethane (0.17 mL) were used. And then, an aliquot of H<sub>2</sub>O<sub>2</sub> solution (5  $\mu$ L 0.0074 mmol, 0.032 equiv) was added into the reaction mixture by a micropipette every 10 min (Slower and more distributed H<sub>2</sub>O<sub>2</sub> addition extends the catalyst lifetime). Finally a total of 2.7 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 70, 4, and 37%, respectively.





Figure S13. Total epoxide yield = 103.29 (the epoxide integration at 2.55 ppm)/150.69 (the alkene integration at 5.56 ppm) × 100% = 69%. See Figure S14 for reaction profile.



Figure S14. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2a (turnover number = 441).



**Figure S15.** GC trace for the epoxidation of DVB using **Fepor-2a** at 14 h (turnover number = 441). Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 70, 4, and 37%, respectively.

**Epoxidation reaction with high turnover numbers (turnover number = 529)**: Follow the "Procedures for the epoxidation reaction of divinylbenzene (DVB) using **Fepor-2a**". **Fepor-2a** (1.0 mg, 0.00094 mmol), DVB (36.7 mg, 40.1  $\mu$ L, 0.282 mmol), methanol (0.60 mL), and dichloromethane (0.20 mL) were used. An aliquot of H<sub>2</sub>O<sub>2</sub> solution (5  $\mu$ L 0.0074 mmol, 0.030 equiv) was added into the reaction mixture by a micropipette every 10 min (Slower and more distributed H<sub>2</sub>O<sub>2</sub> addition extends the catalyst lifetime). Finally, a total of 2.5 equiv of H<sub>2</sub>O<sub>2</sub> was added. The

calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 66, 6, and 42%, respectively.



Figure S16. Total epoxide yield = 104.19 (the epoxide integration at 2.55 ppm)/157.55 (the alkene integration at 5.56 ppm) × 100% = 66%. See Figure S17 for reaction profile.



Figure S17. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2a (turnover number = 529).



**Figure S18.** GC trace for the epoxidation of DVB using **Fepor-2a** at 14 h (turnover number = 529). Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 66, 6, and 42%, respectively.

**Epoxidation reaction with high turnover numbers (turnover number = 598)**: Follow the "Procedures for the epoxidation reaction of divinylbenzene (DVB) using **Fepor-2a**". **Fepor-2a** (1.0 mg, 0.00094 mmol), DVB (44.1 mg, 48  $\mu$ L, 0.339 mmol), methanol (0.72 mL), and dichloromethane (0.24 mL) were used. And then, an aliquot of H<sub>2</sub>O<sub>2</sub> solution (5  $\mu$ L 0.0074 mmol, 0.021 equiv) was added into the reaction mixture by a micropipette every 10 min. Finally, a total of 1.8 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 49, 17, and 42%, respectively.



Figure S19. Total epoxide yield = 88.93 (the epoxide integration at 2.55 ppm)/155.78 (the alkene integration at 5.56 ppm) × 100% = 57%. See Figure S20 for reaction profile.



Figure S20. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using (TPFPP)FeCl (turnover number = 598).



**Figure S21.** GC trace for the epoxidation of DVB using **Fepor-2a** at 14 h (turnover number = 598). Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 49, 17, and 42%, respectively.

**Epoxidation reaction of divinylbenzene (DVB) at 0** °C with the highest turnover numbers (turnover number = 630): Into a 1.5 dram glass vial equipped with a magnetic stir bar, Fepor-2a (1.0 mg, 0.00094 mmol), DVB (44.1 mg, 48  $\mu$ L, 0.339 mmol), methanol (0.72 mL), and dichloromethane (0.24 mL) were used. An NMR sample was measured using the "General procedure for monitoring reactions by NMR". And then, an aliquot of H<sub>2</sub>O<sub>2</sub> solution (5  $\mu$ L, 0.0074 mmol, 0.021 equiv) was added into the reaction mixture by a micropipette every 10 min. Progress of the reaction was monitored by NMR using the general procedure. Finally, a total of 1.8 equiv of H<sub>2</sub>O<sub>2</sub> was added. Follow the "General procedure for quantifying the products distribution from DVB epoxidation", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 80, trace by GC, and 5%, respectively.





Figure S22. Total epoxide yield = 116.16 (the epoxide integration at 2.55 ppm)/148.37 (the alkene integration at 5.56 ppm)  $\times$  100% = 78%. See Figure S23 for reaction profile.



**Figure S23**. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using **Fepor-2a** (turnover number = 630).



**Figure S24.** GC trace for the epoxidation of DVB using **Fepor-2a** at 13 h (turnover number = 630). Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 76, 8, and 65%, respectively.

 Table 1.
 Optimization of Reaction conditions.

Catalyst loading (mol%) (relative to substrate)	Reaction time (h)	H <sub>2</sub> O <sub>2</sub> (equiv) (relative to substrate)	DVB conversion (%) (based on DVB)	DVBMO yield (%) (based on DVB)	DVBDO yield (%) (based on DVB)	Ring open by MeOH (%) (based on alkene)	Turnover number
1 <sup>a</sup>	15	3.4	100	5	75	12	176

1 (with imidazole) <sup>a</sup>	14	3.2	100	27	53	0	154
1 (using MeCN instead of MeOH) <sup>a</sup>	8	1.8	Alkene	e conversion: 68%	6; epoxide yield:	26%	122
0.4 <sup>b</sup>	14	2.7	100	4	70	13	441
0.33 <sup>c</sup>	14	2.5	100	6	66	12	529
0.28 <sup>d</sup>	14	1.8	100	17	49	21	598
0.28	14	1.8	100	8	76	7	630

#### S5. Procedures for functionalization of fluorinated Fe-porphyrin.





Synthesis of free base porphyrin 2: Into a 1000 mL round bottom flask, Compound 1 (1.70 g, 4.87 mmol) and pyrrole (0.24 mL, 4.87 mmol) were dissolved in dichloromethane (487 mL) and purged with N<sub>2</sub> for 5 min. BF<sub>3</sub>·OEt<sub>2</sub> (0.60 mL, 0.69 g, 4.87 mmol) was then added dropwise to the reaction mixture. After the reaction mixture was stirred at r.t. for 1 h and 30 min, DDQ (1.10 g, 4.84 mmol) was added and the mixture was continued to be stirred for another hour. Then, triethylamine (0.4 mL) was added. The mixture was then stirred for 30 min and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (dichloromethane/hexanes = 1/1) to afford a purple product. The product was then dissolved in MeOH/dichloromethane (30/30 mL) and using a rotary evaporator the solvent was concentrated down to 5 mL (mostly MeOH). The mixture was filtered and a purple solid product was collected which was then suction-dried for 1 h to afford 250 mg product (yield = 13%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  8.81 (s, 8H), 7.28 (d, *J* = 8.9 Hz, 8H), 6.85 (d, *J* = 8.7 Hz, 8H), -3.12 (s, 2H). <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -137.04 (dd, *J* = 23.8, 9.4 Hz, 8F), -153.80 (dd, *J* = 23.7, 9.3 Hz, 8F). MALDI-ToF MS: m/z 1586.3 (1585.8 calcd for [M·]<sup>+</sup>).

Synthesis of Fepor-2b: Into a 20 mL microwave vial, porphyrin 2 (100 mg, 0.0630 mmol), FeCl<sub>2</sub>•4H<sub>2</sub>O (50.1 mg, 0.252 mmol), and *N*-Methyl-2-pyrrolidone (18 mL) were added. The microwave vial was crimp-capped and then the reaction mixture was heated in a microwave reactor at 170 °C for 20 min. The reaction mixture was poured in to a 500 mL beaker, LiCl (80 mg in 20 mL water) was then added and the mixture was stirred for 1 h in air. Water (50 mL) was added to precipitate the product from the mixture and the crude product was isolated by filtration. The crude product was then purified by silica gel column chromatography (using MeOH/DCM = 1/5) to obtain a black product (71 mg, yield = 67.2%). MALDI-ToF MS: m/z 1639.1 (may be redo this) (1639.7 calcd for [M-Cl]<sup>+</sup>). UV-vis (MeOH): [ $\lambda$  max in nm ( $\epsilon \times 10^4$  /M<sup>-1</sup>cm<sup>-1</sup>)] 408 (4.53), 588 (0.427).



Figure 26. The synthetic route of Fe-porphyrin 9.

**Synthesis of free base porphyrin 5**: Into a 1000 mL round bottom flask, compound **3** (0.985 g, 3.85 mmol) and **4** (1.20 g, 3.85 mmol) were dissolved in dichloromethane (770 mL) and purged with N<sub>2</sub> for 5 min. Trifluoroacetic acid (1.18 mL, 15.4 mmol) was then added dropwise to the reaction mixture. After the reaction mixture was stirred at r.t. for 5 min, DDQ (1.70 g, 7.49 mmol) was added and the mixture was continued to be stirred for 30 min. Then triethylamine (2.1 mL) was added. The mixture was then stirred for 30 min and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (dichloromethane/hexanes = 1/2) to afford a purple product. The product was then suction-dried for 1 h to afford 110 mg product (yield = 5.2%). <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.93 (s 4H), 8.91 (s, 4H), -2.91 (s, 2H). <sup>19</sup>FNMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -132.66 (dd, *J* = 24.2, 10.5 Hz, 4F), -135.60 (dd, *J* = 23.7, 10.5 Hz, 4F), -136.53 (dd, *J* = 23.2, 6.9 Hz, 4F), -151.28 (t, *J* = 20.8 Hz, 2F), -161.36 (dd, *J* = 21.9, 17.4 Hz, 4F). MALDI-TOF MS: m/z 1095.6 (1095.9 calcd for [M·]<sup>+</sup>).

Synthesis of Fepor-2c: Into a 20 mL microwave vial, porphyrin 5 (87 mg, 0.0794 mmol), FeCl<sub>2</sub>•4H<sub>2</sub>O (64.0 mg, 0.318 mmol), and *N*-Methyl-2-pyrrolidone (18 mL) were added. The microwave vial was crimp-capped and then the reaction mixture was heated in a microwave reactor at 170 °C for 20 min. The reaction mixture was poured in to a 500 mL beaker, LiCl (70 mg) was then added and the mixture was stirred for 1 h in air. Water (100 mL) was added to precipitate the product from the mixture and the crude product was isolated by filtration. The crude product was then purified by silica gel column chromatography (using dichloromethane/hexanes = 1/1 to separate the unreacted starting material, and then using MeOH/ dichloromethane = 1/40 to obtain a black fraction) to obtain a black product (58 mg, yield = 62%). MALDI-ToF MS: m/z 1149.6 (1149.8 calcd for [M-Cl]<sup>+</sup>). UV-vis (MeOH): [ $\lambda$  max in nm ( $\epsilon \times 10^4$  /M<sup>-1</sup>cm<sup>-1</sup>)] 404 (7.14), 565 (0.591), 586 (0.499), 657 (0.155).



Figure 27. The synthetic route for Fepor-2d.

**Synthesis of 6**: Into a 100 mL round bottom flask, aldehyde **3** (1.92 g, 7.50 mmol), ethynyltrimethylsilane (12 mL, 8.34 g, 84.9 mmol), (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (105 mg, 0.150 mmol) and dry triethylamine (30 mL) were added. N<sub>2</sub> was bubbled through the mixture for 10 min, followed by addition of CuI (57 mg, 0.30 mmol). The reaction mixture was refluxed for 10 h, and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (using dichloromethane/hexanes = 1/5) to give a pure product (1.78 g, 87%). <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.27 (s, 1H), 0.29 (s, 9H). <sup>19</sup>FNMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -135.32 – -135.44 (m, 2F), -145.87 (td, *J* = 15.8, 3.4 Hz, 2F). GC-MS (EI): m/z 274 (calcd m/z 274 for [M·]<sup>+</sup>)

Synthesis of free base porphyrin 7: Into a 2000 mL round bottom flask, aldehyde 6 (0.878 g, 3.20 mmol) and 4 (1.0 g, 3.2 mmol) were dissolved in dichloromethane (770 mL) and purged with N<sub>2</sub> for 5 min. trifluoroacetic acid (0.98 mL, 1.46 g, 12.8 mmol) was then added dropwise to the reaction mixture. After the reaction mixture was stirred at r.t. for 30 min, DDQ (1.40 g, 6.17 mmol) was added and the mixture was continued to be stirred for 30 min. Then triethylamine (1.8 mL) was added. The mixture was then stirred for 30 min and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (using dichloromethane/hexanes = 1/6) to afford a purple product. The product was then washed by MeOH (5 mL). The mixture was filtered and a purple solid product was collected which was then suction-dried for 1 h to afford 290 mg product (yield = 8%). <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.89 (s, 8H), -2.93 (s, 2H). <sup>19</sup>FNMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -136.36 (dd, *J* = 23.3, 12.6 Hz, 4F), -137.68 (dd, *J* = 23.2, 12.6 Hz, 4F), -151.43 (t, *J* = 20.9 Hz, 2F), -161.45 (dt, *J* = 22.9, 7.6 Hz, 4F). MALDI-ToF MS: m/z 1129.9 (1130.1 calcd for [M·]<sup>+</sup>).

Synthesis of free base porphyrin 8: Into a solution of porphyrin 7 (200 mg, 0.177 mmol) in chloroform (22.5 mL) and THF (7.5 mL), TBAF (1M of THF solution) was added. The reaction mixture was stirred at r.t. and monitored by TLC. After 2 h, aqueous NaHCO<sub>3</sub> (10 %, 20 mL) was added to quench the reaction. The organic phase was separated and the aqueous phase was washed by dichloromethane (20 mL × 3) to give crude product mixture. The crude product was purified by silica gel column chromatography (using dichloromethane/hexanes = 1/1) to give pure product (170 mg, yield = 97%). <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.92 (s, 4H), 8.90 (s, 4H), 3.90 (s, 2H), -2.93 (s, 2H). <sup>19</sup>FNMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -136.20 (dd, *J* = 23.1, 12.6 Hz, 4F), -136.54 (dd, *J* = 23.3, 7.9 Hz, 4F), -137.08 (dd, *J* = 23.0, 12.6 Hz, 4F), -151.32 (t, *J* = 20.9 Hz, 2F), -161.40 (dt, *J* = 22.6, 7.4 Hz, 4F). MALDI-ToF MS: m/z 986.0 (986.1 calcd for [M·]<sup>+</sup>).

Synthesis of Fepor-2d: Into a 20 mL microwave vial, porphyrin 8 (160 mg, 0.162 mmol), FeCl<sub>2</sub>•4H<sub>2</sub>O (484 mg, 2.43 mmol), and *N*-Methyl-2-pyrrolidone (18 mL) were added. The microwave vial was crimp-capped and then the reaction mixture was heated in a microwave reactor at 170 °C for 30 min. The reaction mixture was poured in to a

500 mL beaker, LiCl (160 mg) was then added and the mixture was stirred for 1 h in air. Water (200 mL) was added to precipitate the product from the mixture and the crude product was isolated by filtration. The crude product was then purified by silica gel column chromatography (using dichloromethane/hexanes = 1/1 to separate the unreacted starting material, and then using MeOH/ dichloromethane = 1/25 to obtain a black fraction) to obtain a black product (117 mg, yield = 67%). MALDI-ToF MS: m/z 1040.0 (1040.0 calcd for [M-Cl]<sup>+</sup>). UV-vis (MeOH): [ $\lambda$  max in nm ( $\epsilon \times 10^4$  /M<sup>-1</sup>cm<sup>-1</sup>)] 407 (8.90), 586 (0.813).



Figure 28. The synthetic route for Fepor-2e.

Synthesis of aldehyde 9: Into a 500 mL round bottom flask, aldehyde 4 (2.65 g, 10.3 mmol), 4-ethoxycarbonylphenylboronic acid (2.40g, 12.4 mmol) and 1,4-dioxane (100 mL) were combined, the mixture was purged with N<sub>2</sub> for 10 min, then, K<sub>3</sub>PO<sub>4</sub> (4.15 g, 19.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (15.5 mg, 0.0134 mmol) were added, the reaction mixture were stirred and refluxed for 12 h. And then water (~50 mL) was added to the reaction mixture. The reaction mixture was extracted by EtOAc (100 mL × 5). The organic phase was combined, dried over NaSO<sub>4</sub> and then concentrated under vacuum to afford the crude product. Purification by silica gel chromatography (using EtOAc/hexanes = 1/10) gave pure product (500 mg, yield = 15%). <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.37 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). <sup>19</sup>FNMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -141.97~-142.11 (m, 2F), -144.96 (td, *J* = 16.6, 4.3 Hz, 2F). GC-MS (EI): m/z 326 (calcd m/z 326 for [M·]<sup>+</sup>)

Synthesis of free base porphyrin 10: Into a 500 mL round bottom flask, aldehyde 9 (509 mg, 1.56 mmol) and pyrrole (104 mg, 1.56 mmol, 108  $\mu$ L) were dissolved in dichloromethane (160 mL) and purged with N<sub>2</sub> for 15 min. BF<sub>3</sub>·OEt<sub>2</sub> (221 mg, 1.56 mmol, 192  $\mu$ L) was then added to the reaction mixture. The reaction mixture was stirred at room temperature for 3 h. And then DDQ (708 mg, 3.12 mmol) was added. The reaction mixture was filtered with silica gel and then triethyl amine (220  $\mu$ L, 1.56 mmol) was added. The crude reaction mixture was filtered with silica gel and then concentrated under vacuum. Purification by silica gel chromatography using pure DCM gave the product. The product was then washed by MeOH (5 mL). The mixture was filtered and a purple solid product was collected which was then suction-dried for 1 h to afford 200 mg product (yield = 34%). <sup>1</sup>HNMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  8.97 (s, 8H), 8.28 (d, *J* = 8.4 Hz, 8H), 7.54 (d, *J* = 8.1 Hz, 8H), 4.18 (q, *J* = 7.1 Hz, 8H), 1.07 (t, *J* = 7.1 Hz, 12H), -2.99 (s, 2H). <sup>19</sup>FNMR (375 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -137.37 (dd, *J* = 25.2, 13.2 Hz, 8F), -143.08 (dd, *J* = 25.5, 13.5 Hz, 8F). MALDI-ToF MS: m/z 1494.5 (1494.3 calcd for [M·]<sup>+</sup>).

Synthesis of Fepor-2e: Into a 20 mL microwave vial, porphyrin 10 (80.0 mg, 0.0535 mmol), FeCl<sub>2</sub>•4H<sub>2</sub>O (53.0 mg, 0.266 mmol), and *N*-Methyl-2-pyrrolidone (13 mL) were added. The microwave vial was crimp-capped and then the reaction mixture was heated in a microwave reactor at 170 °C for 30 min. The reaction mixture was poured in to a 500 mL beaker, LiCl (100 mg) was then added and the mixture was stirred for 1 h in air. Water (100 mL) was added to precipitate the product from the mixture and the crude product was isolated by filtration. The crude product was then purified by natural alumina column chromatography (using EtOAc/dichloromethane = 1/50 to separate the unreacted starting material, and then using EtOAc/dichloromethane = 1/10 to obtain a black green fraction) to obtain a black product (23 mg, yield = 27%). MALDI-ToF MS: m/z 1548.9 (1548.2 calcd for [M-Cl]<sup>+</sup>). UV-vis (MeOH): [ $\lambda$  max in nm ( $\varepsilon \times 10^4$  /M<sup>-1</sup>cm<sup>-1</sup>)] 391 (10.0), 504 (0.704).

# S6. Epoxidation of DVB using functionalized Fe-porphyrin

Procedure for the epoxidation reaction of divinylbenzene (DVB) with Fepor-2b: Follow the procedure similar to the "Procedure for epoxidation reaction of divinylbenzene (DVB) using Fepor-2a". Fepor-2b (2.5 mg, 0.0015 mmol), DVB (19.5 mg, 21.5  $\mu$ L, 0.150 mmol), methanol (0.3 mL), and dichloromethane (0.1 mL) were used. An



aliquot of  $H_2O_2$  solution (8.0  $\mu$ L, 0.0117 mmol, 0.078 equiv) was added every 20 min. Finally, a total of 2.1 equiv of  $H_2O_2$  was added. The calculated yield of total number epoxide based on total number of alkene is 46% after 10 h.

Figure S29. Total epoxide yield = 80.00 (the epoxide integration at 2.55 ppm)/174.02 (the alkene integration at 5.56 ppm) × 100% = 46%. See Figure S30 for reaction profile.



Figure S30. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2b.



Figure S31. GC trace for the epoxidation of DVB using Fepor-2b at 9.3 h. Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 3, 28, and 26%, respectively.

**Procedure for the epoxidation reaction of divinylbenzene (DVB) with Fepor-2c**: Follow a similar procedure to the "Procedures for epoxidation reaction of divinylbenzene (DVB) using **Fepor-2a**". **Fepor-2c** (1.8 mg, 0.0015 mmol), DVB (20.0 mg, 22  $\mu$ L, 0.154 mmol), methanol (0.33 mL), and dichloromethane (0.11 mL) were used. An aliquot of H<sub>2</sub>O<sub>2</sub> solution (8.5  $\mu$ L, 0.08 equiv) was added every 20 min. Finally, a total of 3.1 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of total number epoxide based on total number of alkene is 61% after 10 h. The calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 38, 43, and 74%, respectively.



Figure S32. Total epoxide yield = 104.10 (the epoxide integration at 2.55 ppm)/169.53 (the alkene integration at 5.56 ppm) × 100% = 61% (after 10 h). See Figure S33 for reaction profile.



S20

Figure S33. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2c.



**Figure S34.** GC trace for the epoxidation of DVB using **Fepor-2c** at 10 h. Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 38, 43, and 74%, respectively.

**Procedure for the epoxidation reaction of divinylbenzene (DVB) with Fepor-2d**: Follow a similar procedure to the "Procedure for epoxidation reaction of divinylbenzene (DVB) using **Fepor-2a**". **Fepor-2d** (1.7 mg, 0.0015 mmol), DVB (20.0 mg, 22  $\mu$ L, 0.154 mmol), methanol (0.33 mL), and dichloromethane (0.11 mL) were used. An aliquot of H<sub>2</sub>O<sub>2</sub> solution (8.5  $\mu$ L, 0.08 equiv) was added every 20 min. Finally, a total of 2.8 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of total number epoxide based on total number of alkene is 35% after 12 h. The calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 35, 3, and 21%, respectively.



Figure S35. Total epoxide yield = 48.16 (the epoxide integration at 2.55 ppm)/132.58 (the alkene integration at 5.56 ppm) × 100% = 36% (after 12 h). See Figure S36 for reaction profile.



Figure S36. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2d.



Figure S37. GC trace for the epoxidation of DVB using Fepor-2d at 12 h. Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 35, 3, and 21%, respectively.

**Procedure for the epoxidation reaction of divinylbenzene (DVB) with** *in situ* **formed** [*tetrakis*-(**pentafluorophenyl**)**porphyrinato**]**iron(III) nitrate**: A catalyst stock solution was prepared by the following described procedure: Into a 1.5 dram glass vial of which the top screw part was wrapped by Teflon tape to ensure a good seal, **Fepor-2a** (12.5 mg, 0.0118 mmol) and AgNO<sub>3</sub> (2.0 mg, 0.012 mmol), acetonitrile (0.9 mL) and dichloromethane (0.3 mL) were added. The catalyst stock solution was kept at room temperature for 10 h before being used.

Follow a similar procedure to the "Procedures for epoxidation reaction of divinylbenzene (DVB) using **Fepor-2a**". The catalyst stock solution (0.19 mL, 0.00188 mmol), DVB (24.3 mg, 27  $\mu$ L, 0.188 mmol), methanol (0.3 mL), and dichloromethane (0.1 mL) were used. An aliquot of H<sub>2</sub>O<sub>2</sub> solution (9.5  $\mu$ L, 0.075 equiv) was added every 20 min. Finally, a total of 2.0 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of total number epoxide based on total number of alkene is 52% after 6 h. The calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 29, 43, and 66%, respectively.

a)



 $5.56 \text{ ppm}) \times 100\% = 52\%$  (after 6 h). See Figure S39 for reaction profile.







S23

Figure S40. GC DVB trace for the epoxidation of using in situ formed [tetrakis-(pentafluorophenyl)porphyrinato]iron(III) nitrate. Follow the "General procedure for quantifying the products distribution from the epoxidation of DVB using GC and NMR", the calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 29, 43, and 66%, respectively.

**Procedure for the epoxidation reaction of divinylbenzene (DVB) with Fepor-2e**: Follow a similar procedure to the "Procedure for epoxidation reaction of divinylbenzene (DVB) using **Fepor-2a**". **Fepor-2e** (3.0 mg, 0.0019 mmol), DVB (24.6 mg, 27  $\mu$ L, 0.189 mmol), methanol (0.40 mL), and dichloromethane (0.14 mL) were used. An aliquot of H<sub>2</sub>O<sub>2</sub> solution (10  $\mu$ L, 0.078 equiv) was added every 20 min. Finally, a total of 2.5 equiv of H<sub>2</sub>O<sub>2</sub> was added. The calculated yield of total number epoxide based on total number of alkene is 77% after 12 h. The calculated yield of DVBDO (based on DVB), DVBMO (based on DVB), and EVBO (Based on EVB) are 69, 0, and 62%, respectively.



Figure S41. Total epoxide yield = [120.64 (the epoxide integration at 2.55 ppm)-15.4 (baseline integration next to the epoxide peak)]/136.20 (the alkene integration at 5.56 ppm) × 100% = 77% (after 10 h). See Figure S44 for reaction profile. DVBDO yield = [96.44 (the epoxide integration of DVBDO at 2.52 ppm)-15.4 (baseline integration next to the epoxide peak)]/[136.20 (the alkene integration at 5.56 ppm) × 0.89 (the fraction of alkene from DVB in the total alkene)] = 63%; EVBO yield = [120.64 (the epoxide integration at 2.55 ppm)-96.44 (the epoxide integration of DVBDO at 2.52 ppm)-15.4 (baseline integration next to the epoxide integration of DVBDO at 2.52 ppm)-15.4 (baseline integration at 2.55 ppm)-96.44 (the epoxide integration at 5.56 ppm) × 0.11 (the fraction of alkene from EVB in the total alkene)] = 62%. See Figure S42 for reaction profile.



Figure S42. Plots of normalized alkene and product concentrations vs. time for the epoxidation of DVB using Fepor-2e.

# **S7.** Computational details

All calculations were performed using the unrestricted B3LYP functional in Gaussian09.<sup>S4</sup> The pseudo potential basis set, LANL2DZ, was used for Fe and F; 6-31G(d) was used for all other elements, including C, H, O, N. All geometries were fully optimized without symmetry constraints in gas phase at 0 K. Transition states were verified by IRC calculations.

## Energies

 Table 2.
 Absolute energy with ZPE corrections (in Hartree) obtained from QM calculations

Species	Gas phase energies (with ZPE included)
<sup>4</sup> Fepor-1-HOOH + MeOH (isolated)	-2302.426429
<sup>6</sup> Fepor-1-TS <sub>rxn1</sub>	-2302.409636
<sup>4</sup> Fepor-2a-HOOH + MeOH (isolated)	-4287.539825
<sup>6</sup> Fepor-2a-TS <sub>rxn1</sub>	-4287.532716
<sup>4</sup> Fepor-1-HOOH	-2186.763494
<sup>2</sup> Fepor-1-TS <sub>rxn2</sub>	-2186.744115
<sup>4</sup> Fepor-2a-HOOH	-4171.87689
<sup>6</sup> Fepor-2a-TS <sub>rxn2</sub>	-4171.841356

All species carry one positive charge;

Superscripts stand for spin multiplicities;

All three possible spin states (S=1/2, S=3/2, S=5/2) were considered;

Under the assumption that spin crossover is much faster than reactions 1 and 2, the energies of reactants and TS were chosen as the lowest among all three spin states.

<sup>4</sup> Fepor-	1-HOOH
Fe	0.02504700 -0.00384300 -0.04722400
Ν	0.25387000 -2.01139300 -0.07643500
Ν	$-1.96734500 \ -0.23298300 \ -0.15378400$
Ν	-0.20207400 1.99093200 -0.14224800
Ν	2.02147300 0.21425200 -0.11038500
С	1.43146800 -2.71775100 0.05780600
С	1.17533200 -4.13088600 0.01321100
Н	1.91841900 -4.90622600 0.11821400

С	-0.16043000 -4.28104400 -0.21326200
Н	-0.70770600 -5.20189900 -0.34384300
С	-0.73026200 -2.96141000 -0.23865800
С	-2.10888300 -2.69695400 -0.39059000
Ĉ	-2 66879100 -1 40663000 -0 31463000
C	-4.08593000 -1.15104300 -0.28845100
н	-4 85712500 -1 90001300 -0 38449900
n C	4 24000200 0 19810200 0 10025400
	-4.24090500 0.18810500 -0.10055400 5 16222600 0.74642200 0.02742800
п	-3.10233000 $0.74043200$ $-0.03742800$
C	-2.91885600 0.75058100 -0.02029800
C	-2.66321100 2.13269000 0.08650900
C	-1.37/29700 2.69748500 -0.02184100
C	-1.1200/200 4.1125//00 -0.0/023100
Н	-1.86438700 4.88821100 0.02277400
С	0.21682400 4.26065000 -0.27930000
Η	0.76803200 5.17991000 -0.40443600
С	0.78579000 2.93785200 -0.28861400
С	2.16482800 2.67283000 -0.39920000
С	2.72439600 1.38232600 -0.28223500
С	4.14047000 1.12985800 -0.22902400
Н	4.91223300 1.87799400 -0.32675100
C	4 29452700 -0 20650600 -0 01740900
н	5 21575800 -0 76238200 0 06686500
C	2 97259300 -0.76951200 0.05130500
C C	2.77257500 -0.70751200 0.05150500
C	2.71718400 -2.14987800 0.10889500
C	-3.03441800 -3.84498300 -0.00927400
C	-3.20828900 -4.83010400 0.37220300
C H	-4.08678100 -5.89752400 0.15684000
H	-4.22218800 -6.64842100 0.92981200
C	-4.79220800 -5.99260400 -1.04510200
Н	-5.47123000 -6.82325300 -1.21359100
С	-4.62368000 -5.01496800 -2.02833900
Н	-5.16545300 -5.08572600 -2.96698600
С	-3.75879900 -3.94298800 -1.81015900
С	-3.83055300 3.04020900 0.27687400
С	-4.58285400 2.96900900 1.46208300
С	-5.67465500 3.81454200 1.65702100
Н	-6.23906000 3.75913700 2.58337000
С	-6.04152400 4.72733800 0.66537500
н	-6.89629500 5.38028400 0.81545400
C	-5.30836600 4.79546600 -0.52167900
й	-5 59627500 5 49458900 -1 30142000
C	-4 20578700 3 96326300 -0 71418300
C C	2 00718400 2 81658400 0 61324300
C	2 25640000 4 81558200 0 26248400
C	5.23049900 4.81338300 0.30248400
C H	4.14080900 5.87537200 0.15257100
H	4.26449200 6.63108500 0.92066500
C	4.86674700 5.95626400 -1.03814100
H	5.55032900 6.78400200 -1.20253300
С	4.71289700 4.97015700 -2.01533200
Н	5.27074200 5.03138500 -2.94521100
С	3.84201000 3.90192800 -1.80236700
С	3.88424300 -3.05838400 0.36482300
С	4.63492400 -2.99144400 1.55103700
С	5.72574800 -3.83848000 1.74586500
Н	6.28865100 -3.78545200 2.67323100

С	6.09307100 -4.74949000 0.75294500
Ĉ	5 36171400 -4 81368400 -0 43538800
ч	5 64980700 5 51131200 1 21639400
C II	4 26060500 - 2 07040200 - 0 62774400
C H	4.20009300 -3.97940200 -0.02774400
Н	6.946/0/00 -5.40389200 0.90298600
Н	-2.66955600 -4.76128000 1.31249900
Н	-3.62753600 -3.18577000 -2.57783200
Н	-3.64515100 4.01146600 -1.64328600
Н	-4.29734700 2.25985100 2.23387600
Н	3.70157100 -4.02469700 -1.55788800
н	4 35232800 -2 28338400 2 32507200
н	2 70133000 / 7/9/1/00 1 29377900
и П	2.70135000 4.74941400 1.29577900
п	0.01191400 0.10406200 0.24051400
0	-0.01181400 -0.10406300 2.34051400
0	-1.13247800 0.58134900 2.96511600
Н	-0.22485000 -1.03395500 2.54511900
Н	-0.65836400 1.07800900 3.65783000
<sup>4</sup> Fepor	-2a-HOOH
Fe	0.01759500 -0.01263100 -0.00885900
N	0.24981300 -1.97381500 -0.13845700
N	1.02421700 - 0.24861700 - 0.10808100
IN N	-1.93431700 -0.24801700 -0.19808100
IN N	-0.20/41500 1.93/88200 -0.19221200
N	1.9//15800 0.21430000 -0.13896400
С	1.43468200 -2.68088800 0.01336100
С	1.20039400 -4.08300900 -0.15959000
Н	1.95684300 -4.85171500 -0.09887800
С	-0.12061500 -4.23543600 -0.45530000
Н	-0.64564500 -5.15369300 -0.67373900
C	-0.71719700 -2.93427400 -0.41055200
Č	-2 08333300 -2 69548800 -0 53548600
C	-2.00333300 -2.09340000 -0.33340000
C	-2.04001000 -1.43070300 -0.30222100
C	-4.04834000 -1.18618500 -0.25267900
Н	-4.81859600 -1.93763600 -0.34593700
С	-4.20514000 0.13812100 0.02004400
Н	-5.12940100 0.67244900 0.18341400
С	-2.89783000 0.72531000 0.02058800
С	-2.65504600 2.09114700 0.13376800
Č	-1 39219200 2 64523800 -0 06544300
Č	
с u	1.01162100 / 21600200 0.20700100
п	-1.91103100 4.81000800 -0.20700100
C	0.1/210800 4.19594700 -0.51678600
Н	0.70292900 5.11164500 -0.73203800
С	0.76621800 2.89376000 -0.44584800
С	2.13562200 2.65457500 -0.52154800
С	2.68715100 1.39431900 -0.30438100
С	4.09164200 1.15296700 -0.15281500
Н	4.86362700 1.90375300 -0.23658800
C	4 24279900 -0 16770100 0 14045100
й	5 16290200 _0 60021000 0.14045100
C	2.10270200 - 0.07721700 0.33300300 2.02652400 0.75607600 0.11425200
	2.73033400 -0.73097000 0.11433200
C	2.69404100 -2.12343700 0.22862700
С	-2.99721200 -3.84888800 -0.79556900
С	-3.35301000 -4.74737500 0.21505400
С	-4.20719100 -5.82208400 -0.01823500
С	-4.73055000 -6.01533000 -1.29708600

C	-4.39697700 -5.13580000 -2.32721200
С	-3.54015600 -4.06890900 -2.06550400
С	-3.78888300 3.01120800 0.44718700
С	-3.92843600 3.54216200 1.73346600
С	-4.96673800 4.40521400 2.07164000
С	-5.90332200 4.75967900 1.10002900
С	-5.79211000 4.24994000 -0.19385600
С	-4.74197700 3.38781300 -0.50358100
С	3.05705800 3.80359000 -0.77551100
С	3.39494100 4.71245400 0.23186700
С	4.25591700 5.78280800 0.00323400
С	4.80451400 5.96085000 -1.26718600
С	4.48900200 5.07069800 -2.29386500
С	3.62482800 4.00855500 -2.03701900
С	3.83292500 -3.04189100 0.53183500
С	3.99006000 -3.57733100 1.81390100
С	5.03432200 -4.44024300 2.13465600
С	5.95836600 -4.78917900 1.14925900
С	5.82952600 -4.27425700 -0.14103200
С	4.77420000 -3.41264800 -0.43330200
0	0.07448100 0.01536300 2.22835400
0	-1.15587000 0.58296700 2.74908300
Η	0.06580400 -0.87464800 2.63370300
Н	-0.79945200 1.33781400 3.25822900
F	3.10543500 -3.24707000 2.78196500
F	5.15666600 -4.93171800 3.37602200
F	6.96692600 -5.61673700 1.44151700
F	6.71502800 -4.61156700 -1.08907500
F	4.66515900 -2.93091200 -1.68840200
F	2.87884600 4.55424900 1.47023100
F	4.56054600 6.63581200 0.99226400
F	5.63261400 6.98463400 -1.49989400
F	5.01412300 5.24152400 -3.51516100
F	3.33089500 3.15965600 -3.04269700
F	-3.03106700 3.20901200 2.69101000
F	-5.07136100 4.89209100 3.31661500
F	-6.90638700 5.58774500 1.40917600
F	-6.68911800 4.59269900 -1.12886800
F	-4.65022700 2.91130900 -1.76203400
F	-2.86175700 -4.57369700 1.46151700
F	-4.52961000 -6.66453400 0.97409000
F	-5.55189800 -7.04340800 -1.53454500
F	-4.89784200 -5.32133300 -3.55651900
F	-3.22843200 -3.23074000 -3.07482500

# MeOH

0
0
0
)

<sup>6</sup>Fepor-1-TS<sub>rxn1</sub>

Fe	-0.05797100	-0.18115800	0.01788500
Ν	-0.02708700	0.08320900	2.07358400

Ν	2.04027300 0.02269300 0.05251900
Ν	0.02451800 0.42264200 -1.96963800
Ν	-2.03055700 0.45035500 0.04385300
С	-1.12169700 0.23992700 2.89970900
Ċ	-0 70330500 0 18424700 4 27774100
с ц	1 36017800 0 2820/200 5 12800100
n C	-1.50017800 0.2820+200 5.12899100
U U	0.04319000 0.00204000 4.28200400
H	1.2989/300 -0.06629200 5.13862400
C	1.06877700 -0.07975200 2.90638000
С	2.38778400 -0.30972300 2.49908100
С	2.80906000 -0.30532100 1.15016400
С	4.12480800 -0.69687900 0.70899500
Η	4.94186900 -0.98399800 1.35572800
С	4.14914400 -0.55332200 -0.66098700
H	4.98349100 -0.73051600 -1.32434500
C	2 84681700 -0.09985600 -1.06167500
C C	2.64061700 0.09905000 1.00107500
C	1 1 20 2 6000 0 40 2 40 500 2 70 20 600
C	1.13980900 0.40849300 -2.79200000
C	0.74696400 0.71676800 -4.14377500
Н	1.41991400 0.79982300 -4.98405000
С	-0.60338400 0.88804900 -4.14104600
Н	-1.24154500 1.12434400 -4.97918500
С	-1.05160200 0.71135800 -2.78355200
С	-2.39629200 0.82148500 -2.38126000
С	-2.82927600 0.70843400 -1.05404400
С	-4.18929300 0.93128800 -0.62363900
Н	-5.01391100 1.17129700 -1.27812100
С	-4.20449000 0.81957200 0.73095800
Н	-5.04378800 0.95054700 1.39758800
С	-2.85422800 0.52624300 1.14967500
Ċ	-2 45402700 0 41951900 2 48895400
Ĉ	3 41975800 -0 58288300 3 54628600
C	3 32881600 -1 72179200 4 36412000
C C	4 29594900 1 97695100 5 33716400
	4.27374700 -1.97095100 5.35710400
п	4.21304200 -2.80438700 3.93832300
C	5.36516600 -1.09562600 5.51163400
H	6.11523600 -1.29224400 6.27218800
C	5.46424100 0.04166300 4.70684000
Н	6.28774800 0.73668600 4.84386300
С	4.50176500 0.29499100 3.72899700
С	3.50889100 0.02639200 -3.45546000
С	3.43106900 -0.95534900 -4.45878300
С	4.42325600 -1.05687300 -5.43512000
Н	4.34877200 -1.82286400 -6.20196100
С	5.50593700 -0.17481300 -5.42825900
Н	6.27565900 -0.25018200 -6.19077900
C	5.59149900 0.80863200 -4.44009000
н	6 42482800 1 50539100 -4 43549700
C	4 60369700 0 90720900 -3 45946300
C	-3 42580100 1 11287800 -3 43049500
C C	A 34847100 0 12734000 - 3.43047500 A 34847100 0 12734000 - 3.81380700
Č	5 31100300 0 307/0200 / 78782/00
	-3.31103300 0.37/49200 -4./8/82400
п	-0.01383900 -0.37073200 -3.0773800
U H	-5.300/0200 1.65690/00 -5.38824200
H	-6.11/18600 1.86/50500 -6.14472500
C	-4.45546900 2.64559100 -5.01074100

Н	
	-4.49765900 3.62985100 -5.46846900
С	-3.49037500 2.37616400 -4.03921700
С	-3.50942900 0.53593000 3.54650700
С	-4.42858400 -0.50492900 3.74931000
C	-5 41450600 -0 39778400 4 73159200
н	
C	5 40677100 0 75152400 5 52025900
C	-5.4907/100 0.75155400 5.52055800
C	-4.58843700 1.79394200 5.32363200
Н	-4.65067100 2.69350600 5.92943100
С	-3.59997900 1.68744500 4.34400100
Н	-6.26520700 0.83508300 6.28345100
Н	2.49851800 -2.41020700 4.23101200
Н	4.57533700 1.18721300 3.11330400
н	4 66811300 1 68141800 -2 70009200
н	2 58440700 -1 63723100 -4 47316600
и Ц	2,80048700 2,50340200 4,18771400
п	-2.89948700 2.30340200 4.18771400
H	-4.36409600 -1.40203400 3.13932000
H	-4.30626/00 -0.85443900 -3.34959400
Н	-2.78826100 3.15018000 -3.74133500
0	-0.02402600 -2.11723200 0.13159500
0	0.23352500 -2.73719800 -1.18365800
Н	1.59943100 -2.97652000 -0.21043100
Н	-0.50930900 -3.36712200 -1.22493800
0	2 56446500 -3 22886300 -0 01072100
н	3 08393700 -2 39737400 0 22841800
C	3 16006600 3 01366600 1 16886400
	5.10700000 - 5.71500000 - 1.10880400
п	4.10/08/00 -4.21328000 -0.8309/000
H	2.54239300 -4.78202800 -1.35989100
Н	3.19539100 -3.23445100 -2.02083200
°Fepo	$r-2a-TS_{rxn1}$
Fe	0.21661000 -0.10443800 0.45874800
Ν	0.28559900 -2.12912400 0.01158800
Ν	-1.83876000 -0.17833800 0.09219400
N N	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400
N N N	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400
N N N	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 2.00661200 0.00106100
N N C	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 -2.90661300 -0.09196100
N N C C	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 -2.90661300 -0.09196100 1.05983700 -4.30146900 -0.04526400
N N C C H	-1.83876000-0.178338000.092194000.112635001.930016000.073144002.23041000-0.01172500-0.044804001.42018200-2.90661300-0.091961001.05983700-4.30146900-0.045264001.75062600-5.12947700-0.11041100
N N C C H C	-1.83876000-0.178338000.092194000.112635001.930016000.073144002.23041000-0.01172500-0.044804001.42018200-2.90661300-0.091961001.05983700-4.30146900-0.045264001.75062600-5.12947700-0.11041100-0.29214100-4.362116000.09845000
N N C H C H	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 -2.90661300 -0.09196100 1.05983700 -4.30146900 -0.04526400 1.75062600 -5.12947700 -0.11041100 -0.29214100 -4.36211600 0.09845000 -0.90246800 -5.25101700 0.16723900
N N C C H C H C	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 -2.90661300 -0.09196100 1.05983700 -4.30146900 -0.04526400 1.75062600 -5.12947700 -0.11041100 -0.29214100 -4.36211600 0.09845000 -0.90246800 -5.25101700 0.16723900 -0.77601300 -3.00416600 0.11547300
N N C C H C H C C	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 -2.90661300 -0.09196100 1.05983700 -4.30146900 -0.04526400 1.75062600 -5.12947700 -0.11041100 -0.29214100 -4.36211600 0.09845000 -0.90246800 -5.25101700 0.16723900 -0.77601300 -3.00416600 0.11547300 -2.12549400 -2.63295800 0.18809900
N N C C H C C C C C	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 -2.90661300 -0.09196100 1.05983700 -4.30146900 -0.04526400 1.75062600 -5.12947700 -0.11041100 -0.29214100 -4.36211600 0.09845000 -0.90246800 -5.25101700 0.16723900 -0.77601300 -3.00416600 0.11547300 -2.12549400 -2.63295800 0.18809900 -2.61268400 -1.31729500 0.10807100
N N C C H C C C C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ \end{array}$
N N C C H C C C C C H C C C C H	-1.83876000 -0.17833800 0.09219400 0.11263500 1.93001600 0.07314400 2.23041000 -0.01172500 -0.04480400 1.42018200 -2.90661300 -0.09196100 1.05983700 -4.30146900 -0.04526400 1.75062600 -5.12947700 -0.11041100 -0.29214100 -4.36211600 0.09845000 -0.90246800 -5.25101700 0.16723900 -0.77601300 -3.00416600 0.11547300 -2.12549400 -2.63295800 0.18809900 -2.61268400 -1.31729500 0.10807100 -4.00669000 -0.95955100 0.01603000 -4.83395500 -1.65358600 -0.03057500
N N C C H C C C C H C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -0.6466100 & 0.40015600 & 0.05838400 \\ \end{array}$
N N C C H C H C C C C H C H C H C H C H	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -0.977601200 & 1.01274500 & 0.16022000 \\ \end{array}$
N N C C H C H C C C C H C H C H C C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ \hline 2.70012300 & 0.986(9700) & 0.0022020 \\ \end{array}$
N N C C H C H C C C C H C H C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.70912200 & 0.88668700 & 0.00839000 \\ \end{array}$
N N C C H C H C C C C H C H C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.70912200 & 0.88668700 & 0.00839000 \\ -2.34222900 & 2.24022600 & 0.02742700 \\ \end{array}$
N N C C H C H C C C C H C H C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.70912200 & 0.88668700 & 0.00839000 \\ -2.34222900 & 2.24022600 & 0.02742700 \\ -1.02351900 & 2.71313000 & 0.06670000 \\ \end{array}$
N N N C C H C H C C C C C H C H C C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.70912200 & 0.88668700 & 0.00839000 \\ -2.34222900 & 2.24022600 & 0.02742700 \\ -1.02351900 & 2.71313000 & 0.06670000 \\ -0.65519000 & 4.10643100 & 0.09467400 \\ \end{array}$
N N N C C H C H C C C C C H C H C C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.70912200 & 0.88668700 & 0.00839000 \\ -2.34222900 & 2.24022600 & 0.02742700 \\ -1.02351900 & 2.71313000 & 0.06670000 \\ -0.65519000 & 4.10643100 & 0.09467400 \\ -1.34356300 & 4.93894100 & 0.09787700 \\ \end{array}$
N N N C C H C H C C C C C H C H C C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.70912200 & 0.88668700 & 0.00839000 \\ -2.34222900 & 2.24022600 & 0.02742700 \\ -1.02351900 & 2.71313000 & 0.06670000 \\ -0.65519000 & 4.10643100 & 0.09467400 \\ -1.34356300 & 4.93894100 & 0.0787700 \\ 0.70432100 & 4.16093400 & 0.10546200 \\ \end{array}$
N N N C C H C H C C C C C H C H C H C H	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.34222900 & 2.24022600 & 0.02742700 \\ -1.02351900 & 2.71313000 & 0.06670000 \\ -0.65519000 & 4.10643100 & 0.09467400 \\ -1.34356300 & 4.93894100 & 0.0787700 \\ 0.70432100 & 4.16093400 & 0.10546200 \\ 1.32655100 & 5.04398300 & 0.11239300 \\ \end{array}$
N N N C C H C H C C C C C H C H C H C C C C	$\begin{array}{c} -1.83876000 & -0.17833800 & 0.09219400 \\ 0.11263500 & 1.93001600 & 0.07314400 \\ 2.23041000 & -0.01172500 & -0.04480400 \\ 1.42018200 & -2.90661300 & -0.09196100 \\ 1.05983700 & -4.30146900 & -0.04526400 \\ 1.75062600 & -5.12947700 & -0.11041100 \\ -0.29214100 & -4.36211600 & 0.09845000 \\ -0.90246800 & -5.25101700 & 0.16723900 \\ -0.77601300 & -3.00416600 & 0.11547300 \\ -2.12549400 & -2.63295800 & 0.18809900 \\ -2.61268400 & -1.31729500 & 0.10807100 \\ -4.00669000 & -0.95955100 & 0.01603000 \\ -4.83395500 & -1.65358600 & -0.03057500 \\ -4.06466100 & 0.40015600 & -0.05838400 \\ -4.94777600 & 1.01274500 & -0.16993300 \\ -2.70912200 & 0.88668700 & 0.00839000 \\ -2.34222900 & 2.24022600 & 0.02742700 \\ -1.02351900 & 2.71313000 & 0.06670000 \\ -0.65519000 & 4.10643100 & 0.09467400 \\ -1.34356300 & 4.93894100 & 0.09787700 \\ 0.70432100 & 4.16093400 & 0.10546200 \\ 1.32655100 & 5.04398300 & 0.11239300 \\ 1.8156200 & 2.80159800 & 0.8321900 \\ \end{array}$

С 2.53490700 2.43840400 0.03669100 С 3.00963300 1.12504700 -0.06364800 С 4.39748700 0.76494600 -0.22446000 Η 5.22348900 1.45927400 -0.27585600 С 4.44833700 -0.59054000 -0.31688800 Η 5.32353000 -1.20756900 -0.45923900 С 3.09436500 -1.07462500 -0.19371400 С 2.73163800 -2.42775200 -0.20562700 С -3.13847200 -3.71559800 0.38445700 С -3.73935400 -3.90380500 1.62868600 С -4.69051700 -4.88314700 1.88358300 С -5.07204100 -5.73029000 0.84210400 С -4.49861100 -5.57878200 -0.42075200 С -3.54756200 -4.58048600 -0.63560200 С -3.44716100 3.24882600 0.03394500 С -4.22309900 3.46468100 1.17622400 С -5.25872900 4.39288400 1.21371600  $-5.54317300 \ 5.14337100 \ 0.07295700$ С С -4.79163400 4.95420400 -1.08653800 С -3.76143300 4.01502500 -1.09334500 С 3.54748900 3.54109000 0.07900900 С 3.99251700 4.06069100 1.29740700 С 4.93166100 5.08624800 1.36756500 С 5.45148900 5.61821100 0.18761700 С 5.02846900 5.12221600 -1.04543800 С 4.08629600 4.09607400 -1.08501400 С 3.82874400 -3.43853800 -0.33708100 С 4.58261500 -3.84292900 0.76833700 С 5.60698500 -4.78058400 0.66244700 С 5.89703500 -5.33997300 -0.58181400 С 5.16299300 -4.95861000 -1.70467000 С 4.14368100 -4.01825100 -1.56965900 0 0.18892900 -0.43190200 2.35755200 0 -0.20802000 0.78448500 3.08933800 Η -1.23655000 -0.52200000 3.45494300 Η 0.59140500 0.94113200 3.62805200 0 -2.05689800 -0.99992100 3.81585500 Η -2.32513400 -1.72500900 3.20225500 С -3.17212500 -0.05995200 4.09217400 Η -3.97465100 -0.66605300 4.50714600 Η -2.78290600 0.63774200 4.82975600 Η -3.46091900 0.44586800 3.17169100 F 4.31625800 -3.31713800 1.98359500 F 6.31005900 -5.14839100 1.74502800 F 6.87840900 -6.24279500 -0.69763400 F 5.44133900 -5.49544300 -2.90211100 F 3.44785700 -3.66303100 -2.66889800 F -3.38096600 -3.08708500 2.67860100 F -5.23287500 -5.01542000 3.10325500 F -5.98540300 -6.68214100 1.05619300 F -4.86786400 -6.38852800 -1.42063700 F -3.01893000 -4.45491300 -1.86592800 F -3.96852400 2.74924900 2.30312900 F -5.97813500 4.56791400 2.33413200 F -6.53555100 6.04027800 0.09172900 F -5.06596000 5.67046700 -2.18581100

F	-3.05648400 3.84815600 -2.22930500
F	3.50028500 3.55891000 2.45300100
F	5.33626400 5.56184200 2.55571000
F	6.35505100 6.60424000 0.23901800
F	5.52709000 5.63391500 -2.18059400
F	3.69066800 3.63241300 -2.28777600
<sup>2</sup> Fepor-	-1-TS <sub>rxn2</sub>
Fe	0.02859300 -0.01377700 0.07722000
Ν	0.04228500 -2.01852500 -0.08858000
Ν	-1.95484700 -0.03053700 -0.25278200
Ν	0.02120000 1.97558800 -0.22166700
Ν	2.02256400 -0.01201300 -0.10978100
С	1.12979300 -2.84759500 0.11174000
С	0.72466300 -4.22178000 0.05899300
Η	1.37429400 -5.07078700 0.20552100
С	-0.60526100 -4.23048500 -0.24296000
Η	-1.23953200 -5.08847100 -0.40362100
С	-1.03119900 -2.86184800 -0.29838000
С	-2.36433300 -2.45866000 -0.51381000
С	-2.77920100 -1.11803400 -0.43858900
С	-4.15922300 -0.71082400 -0.40926200
Η	-5.00482200 -1.37057600 -0.53058600
С	-4.16895800 0.62853200 -0.16569000
Η	-5.02265300 1.28261000 -0.07315200
С	-2.79570800 1.04170300 -0.07302900
С	-2.39701600 2.38016700 0.08947800
С	-1.06626800 2.80576700 -0.07244400
С	-0.66377900 4.18197700 -0.15552300
Н	-1.32182900 5.03170200 -0.05775400
С	0.67435700 4.18467800 -0.41026600
Н	1.31590000 5.03745900 -0.57056000
С	1.10252500 2.81215200 -0.40162700
С	2.44187000 2.40212100 -0.50539900
С	2.85141800 1.06676500 -0.32282900
С	4.22801100 0.66414900 -0.24025400
Н	5.07595100 1.31987300 -0.36652300
С	4.23452200 -0.66871300 0.04087800
Н	5.08844400 -1.31704900 0.16515300
С	2.86193900 -1.08451600 0.11297000
C	2.46191400 -2.42252300 0.27437800
C	-3.39800300 -3.49710000 -0.78382900
C	-3.71707300 -4.47433500 0.17498200
C	-4.69777700 -5.42939900 -0.09071900
H	-4.94532400 -6.16965700 0.66444900
C	-5.36230700 -5.43096000 -1.31953500
H	-6.12139700 -6.17945800 -1.52671400
C	-5.05085500 -4.46512800 -2.27930400
Н	-5.56149600 -4.46345400 -3.23781100
C	-4.08289700 -3.49765800 -2.01156800
C	-5.44815500 5.38414300 0.413/5100
C	-4.0/155600 3.32663800 1.67226600
C	-5.05582100 4.25560100 2.00901600
H	-5.52286700 4.21220100 2.98867100
C	-5.44011300 5.23637600 1.09140400
Н	-6.21204400 5.95411100 1.35320300

С	-4.83220000 5.29114100 -0.16523000
Н	-5.13589600 6.04481900 -0.88591900
С	-3.83570000 4.37511200 -0.50292500
С	3.49239700 3.42651700 -0.77119200
С	3.77557300 4.43546600 0.16504500
С	4.76858500 5.37980300 -0.09483100
Н	4.98700700 6.14647200 0.64280700
C	5 48149100 5 33742100 -1 29526600
н	6 25025500 6 07717300 -1 49816400
C II	5 20522300 / 22022100 2 22252800
С П	5.20332300 4.33332100 -2.23233800
П	5./555/500 4.50559000 -5.10950500
C	4.22415100 3.38346500 -1.97032200
C	3.51608000 -3.436/8600 0.56360400
C	4.20926600 -3.39266500 1.78538000
С	5.19637100 -4.33569300 2.07102500
Н	5.71449500 -4.29916200 3.02483800
С	5.51760700 -5.32110500 1.13480800
С	4.84472900 -5.36306100 -0.08861600
Н	5.09965200 -6.11865300 -0.82596000
С	3.84588800 -4.43191500 -0.37237600
Н	6.29105100 -6.05071100 1.35583700
Н	-3 21248700 -4 46893400 1 13688200
н	-3 84085900 -2 74906000 -2 76058300
и Ц	3 37397500 / /1181500 1 /8567700
и П	2 75062700 2 56692100 2 29224100
11	-3.73903700 2.30088100 2.38324100
H	3.33404400 -4.43977200 -1.33037000
н	3.90140400 -2.02729700 2.51548400
H	3.23126900 4.46496700 1.10462200
Н	4.00956400 2.61000/00 -2./0236300
0	-0.11786500 0.10750700 2.00924900
0	-1.36081100 1.01449100 2.92153700
Н	-0.41982300 -0.72926500 2.40343900
Η	-0.69160800 1.60859800 3.31016600
<sup>6</sup> Fenor	2 <sub>2</sub> TS
repoi-	$-2a - 1S_{rxn2}$
ге	0.00001400 -0.14302000 0.000/1100
IN N	0.01305500 -0.03909000 2.10421000
N	2.09545500 -0.09890/00 0.08358500
N	0.16932000 0.62886200 -1.94377600
N	-1.92268900 0.65448800 0.07548300
C	-1.06522300 0.10178100 2.91427100
С	-0.70220400 -0.17643200 4.29350700
Н	-1.36960800 -0.12859400 5.14117400
С	0.61354700 -0.49869800 4.29545500
Н	1.22381100 -0.76720500 5.14519600
С	1.07853600 -0.39079800 2.92030000
С	2.39338500 -0.55587000 2.50746900
С	2.86730300 -0.35011100 1.17450800
C	4.27146300 -0.33578600 0.81229400
Н	5.09735000 -0.48770400 1 49127600
C	4 33265900 -0 06468500 -0 51485400
й	5.21867900 0.0/813200 1.12235000
C	2.21007700 0.0+013200 -1.12233700 2.06405800 0.08258600 0.08408600
C	2.30 + 33000 0.00230000 - 0.304000000 - 2.60100000 0.26677300 - 2.30200000
C	2.00100900 0.300/4200 -2.29380800
C	1.20103800 0.39515000 -2.73992900
C	0.88504300 0.80327300 -4.13046700

Η	1.56222600 0.81559700 -4.97157900
С	-0.45984700 0.95392500 -4.15212700
Η	-1.08879400 1.11872000 -5.01437800
С	-0.91940300 0.86194200 -2.77387100
Ĉ	-2 23308100 1 01759200 -2 35933200
c	2.23508100 1.01735200 -2.35553200
C	-2.07973200 0.97818000 -1.00029400
C	-4.03510800 1.303/1400 -0.58439400
H	-4.83624800 1.61269600 -1.23933100
С	-4.07885400 1.15881800 0.76150900
Η	-4.92442600 1.31747300 1.41472700
С	-2.74900900 0.74821500 1.18669900
С	-2.37763000 0.48104200 2.49550400
С	3.41372100 -0.93317300 3.53420200
č	3 95681200 -2 22202900 3 56522700
c	4 01245800 - 2 60020600 4 50428200
C	4.91249800 -2.00029000 4.90498200 5.25126000 1.66016800 5.44660200
C	5.35126000 -1.66916800 5.44669300
C	4.83281100 -0.37399300 5.44065300
С	3.87681000 -0.02287800 4.48998200
С	3.68282600 0.43362100 -3.32247900
С	4.35593600 -0.71646400 -3.75032000
С	5.36014200 -0.66937600 -4.71427000
Ċ	5.71406800 0.55756100 -5.27599900
Ĉ	5 06192100 1 72346500 -4 87197500
C	4 06010800 1 64742600 3 00800300
C	2 27770400 1 25621800 - 2 40164100
C	-5.2///9400 1.25051800 -5.40104100
C	-4.2131/900 0.26424000 -3./1/26000
C	-5.19739900 0.45585400 -4.68294900
С	-5.26443600 1.67416500 -5.36019200
С	-4.35044600 2.68591600 -5.06567600
С	-3.37460000 2.46706200 -4.09564800
С	-3.42096500 0.61248600 3.56113100
С	-4.06762100 -0.51074000 4.08556300
Ĉ	-5 03693700 -0 40753200 5 08012400
č	-5 37857600 0 85186500 5 57467800
C	4 75059500 1 00215200 5 07205100
C	-4.75058500 1.99215500 5.07505100
C	-3.78397000 1.85980600 4.07837400
0	-0.41890900 -1.94000500 -0.37029900
0	-1.36760200 -2.27254600 -1.93265800
Н	0.27405100 -2.55456000 -0.67031700
Η	-2.11504900 -2.67013000 -1.44337800
F	-3.74870300 -1.73605700 3.61768100
F	-5.64108100 -1.50384100 5.55921700
F	-6 30804400 0 96541300 6 52868300
F	5.07706200 3.20211300 5.54791300
Г Г	2 19500200 2 07252500 2 60760000
г Б	-5.18577800 2.77552500 5.00707900
F	-4.16/44600 -0.92033900 -3.0/092600
F	-6.07402100 -0.51828700 -4.96465300
F	-6.20461100 1.87149300 -6.28951900
F	-4.41629400 3.85857000 -5.71122000
F	-2.50609700 3.46258700 -3.82289100
F	4.02444800 -1.91566100 -3.22696800
F	5.98205600 -1.79075600 -5.10400600
F	6 67741700 0 61677000 -6 2002/000
F	5 40400800 2 00330600 5 40711000
L. L	2.44260100 2.70550000 -3.40711000
Г Г	3.44500100 2.78528700 -3.52717600
F	3.542/3100 -3.13525000 2.66113800

- F 5.40730400 -3.84562100 4.50970900
- F 6.26802500 -2.01813600 6.35444000
- F 5.25623700 0.52260200 6.34233700
- F 3.39436900 1.23710100 4.49821900

## **S8. References**

(S1) Gryko, D. T.; Wyrostek, D.; Nowak-Krol, A.; Abramczyk, K.; Rogacki, M. K. Straightforward Transformation of Pentafluorobenzaldehyde into 4-Aryloxy-2,3,5,6-Tetrafluorobenzaldehydes. *Synthesis* **2008**, 4028-4032.

(S2) Mariaca, R.; Behrnd, N. R.; Eggli, P.; Stoeckli-Evans, H.; Hulliger, J. Synthesis and Crystal Engineering of Fluorinated Stilbenes. *Crystengcomm* **2006**, *8*, 222-232.

(S3) Littler, B. J.; Miller, M. A.; Hung, C. H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. Refined Synthesis of 5-Substituted Dipyrromethanes. *J. Org. Chem.* **1999**, *64*, 1391-1396.

(S4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P. Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.

S9. NMR spectra









-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 fl (ppm)



120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280 f1 (ppm)



			1 1	1 I							1	1 1 1	1 1 1 1				ĩ
120	100	80	60	40	20	0	-20	-40	-60	-80 f1 (ppm	)	-120	-160	-200	-240	-280	





												·	1 . 1		1 0 1 0	
120	100	80	60	40	20	0	-20	-40	-60	-80 f1 (ppm	1)	-120	-160	-200	-240	-280