Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

for

Discovery and Mechanistic Study of a Photoredox-Catalyzed Indoline Dehydrogenation for the Synthesis of Elbasvir

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Reaction Progress Studies

Kinetic Isotope Effect Studies

Materials and Methods

Analytical:

For high-throughput experimentation and scale-ups:
HPLC analysis was performed on a Waters Acquity UPLC-MS equipped with a 1.7uM 2.1x50 mm Acquity BEH C18 column using acetonitrile:water (10 mM pH 3.5 NH_4CO_2H buffer), monitored at 210 nm.

For kinetic studies:
All solvents were purified according to the method of Grubbs[1] or purchased as anhydrous, high purity solvents in Sure/Seal bottles. Thin-layer chromatography (TLC) was performed on Silicycle 250 µm silica gel plates. HPLC analysis was performed on an Agilent 1260 Infinty HPLC using a Zorbax-Rx Sil 5 um 4.6 x 250 mm column. 1H and 13C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz) instrument, and are internally referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS.

High-throughput Experimentation Using Parallel Photoredox Screening Platform:
The aluminum vial rack (Analytical Sales and Services, Inc. P# 96960) is designed to hold 96- 8x30 mm vials (Analytical Sales and Services, Inc. P# 84001) containing parylene coated stir dowels (P# 13257) and stirred via a V&P Scientific (710E-2HM-1) tumble stirrer equipped with a 96- 465 nm (DigiKey Part No: 754-1488-ND, 120 mW) LED array. Reagents were dosed to each of the 96- vials as solutions via an Eppendorf pipette in a nitrogen filled glovebox. After sealing the vials using the aluminum vial rack cover equipped with silicone and PFA mats, the reactor was placed on top of the LED array and stirred via tumble stirring. During the course of the reaction the temperature of the vial rack elevates slightly from room temperature due to the absorption of light from the LED array and generally stabilizes at ~30 °C. After the allocated time, the reactions were quenched with 500 µl of 2 mM biphenyl as internal standard in 7:3 acetonitrile:DMSO, then a 10 µl aliquot was diluted into 700 µl of ACN for UPLC-MS analysis.

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[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

Screening and Flow Reactor Design:

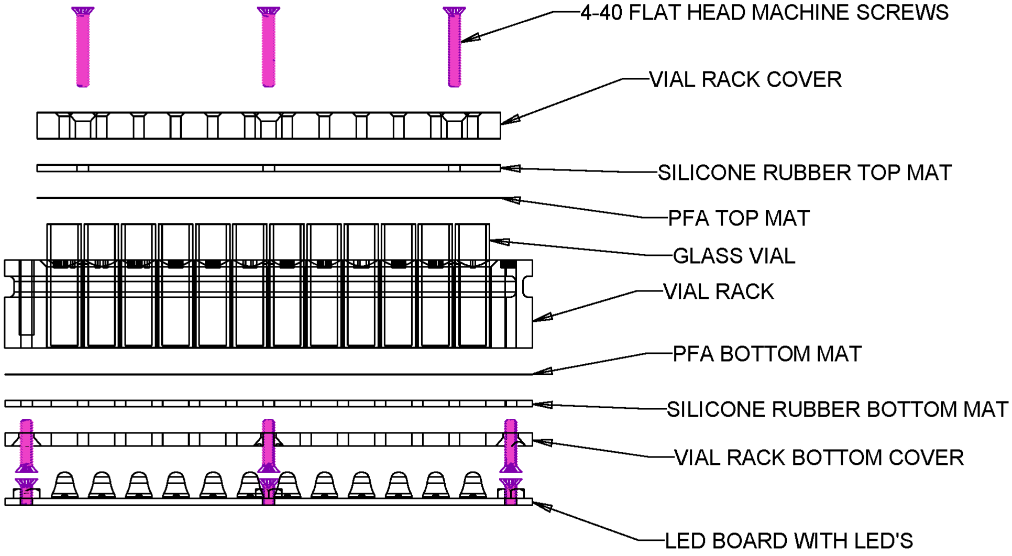


Figure S1. Screening reactor schematic

LED array and controller Design:

The LED array was manufactured by Design to Prototype LLC, Web: www.DesignToPrototype.com, Email: DesignToPrototype@Gmail.com

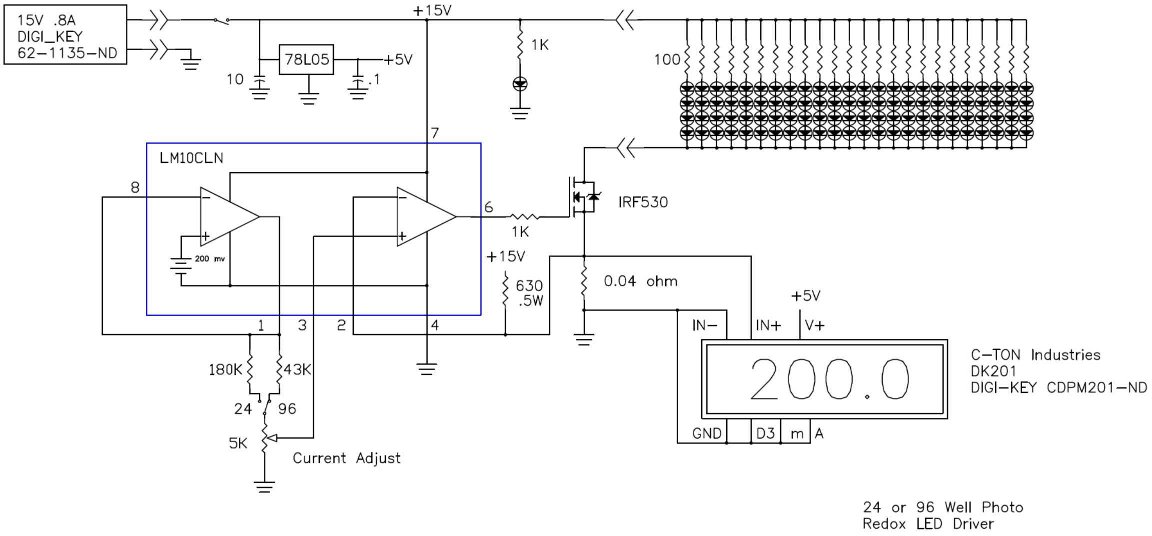


Figure S2. LED Driver – Schematic Diagram

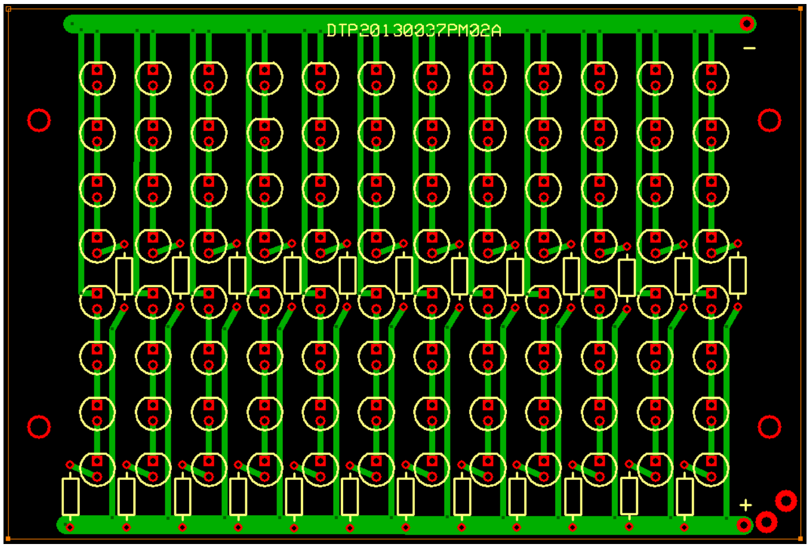


Figure S3. LED Array - Printed Circuit Board – Artwork

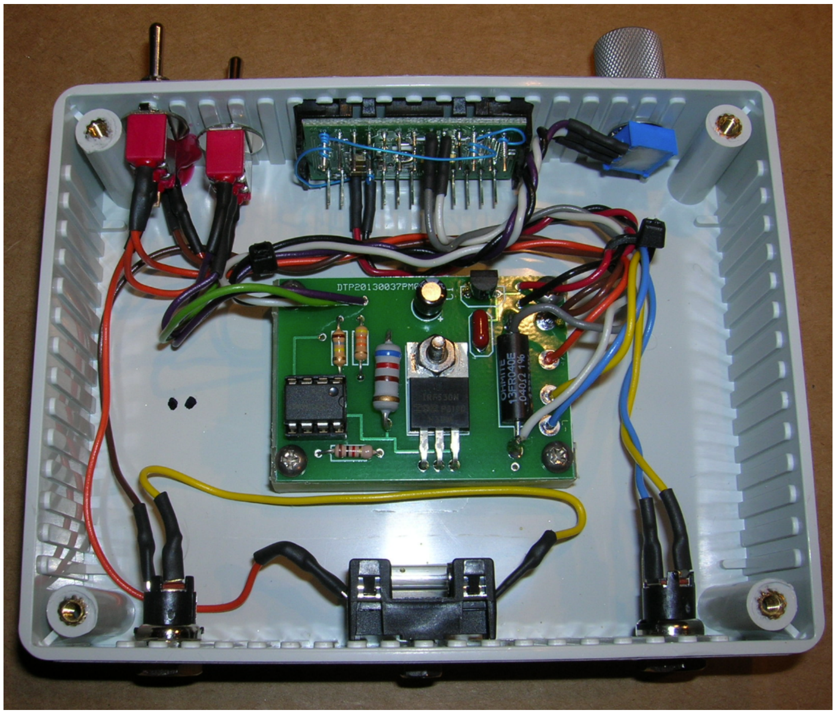


Figure S4. LED Driver – Interior View

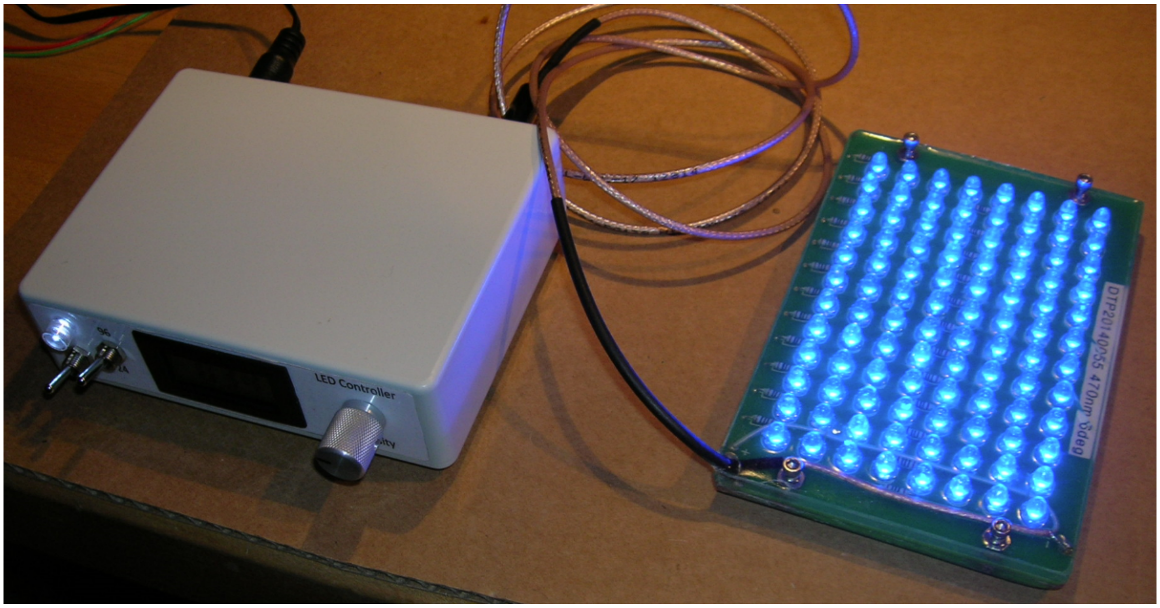


Figure S5. LED Driver – Exterior View

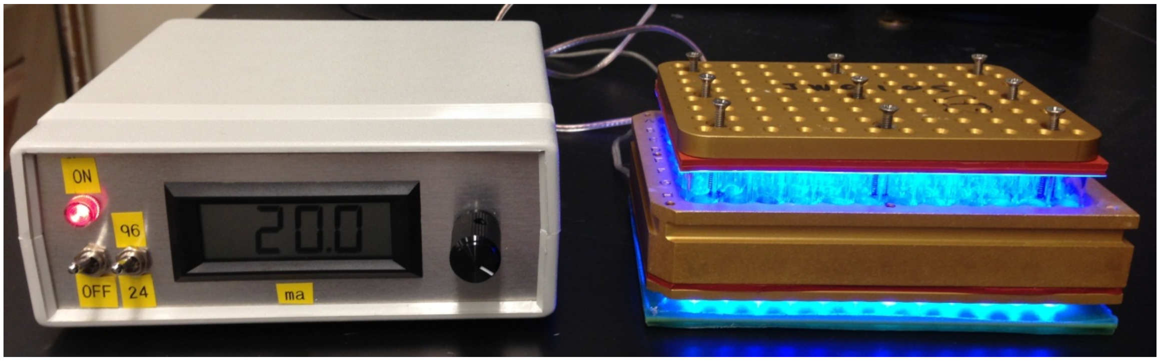


Figure S6. LED Driver – Exterior View

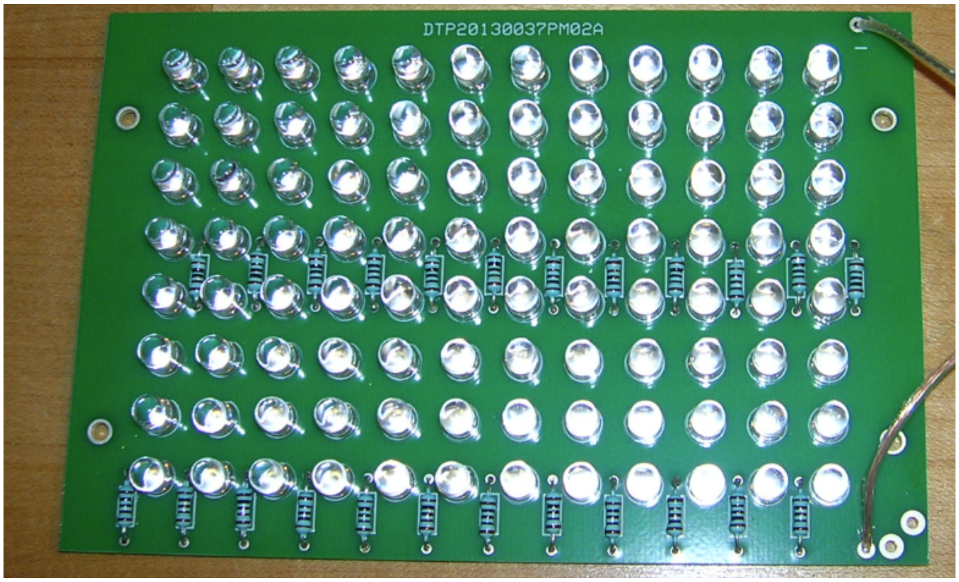
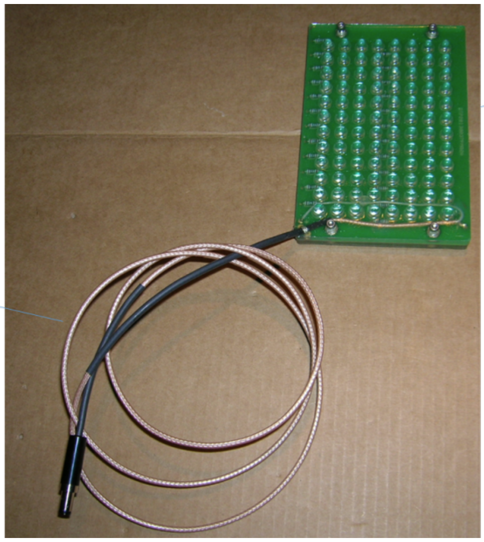


Figure S7. LED Array - Printed Circuit Board – Prior to Potting


Potting Compound:
Mouser Electronics
Part. No.: 590-832C-375ML

Interconnect Cable:
Mouser Electronics
Part. No.: 566-83264-100

Figure S8. LED Array - Printed Circuit Board – Epoxy Potted

High-throughput Experimentation Data:

Table S1. Identification of a photoredox-mediated dehydrogenation via high-throughput experimentation. Reactions performed on 2.5 μmol scale (0.1 M with respect to **1**) using 465 nm LEDs, 1 mol% photocatalyst, 2-5 equiv. oxidant at 30 ^{o}C. (all oxidants used 2 equiv. but $MeNO_2$, for which 5 equiv. was used)

Prod-to-IS-Ratio	Assay Yield	Photocatalyst	Oxidant	Solvent
2.3	12.5	$Ru(bpy)_3(PF_6)$	$CBrCl_3$	Acetonitrile
0.5	2.8	$Ru(Phen)_3Cl_2$	$CBrCl_3$	Acetonitrile
0.1	0.5	$Ru(dip)_3Cl_2$	$CBrCl_3$	Acetonitrile
0.0	0.0	$Ir(ppy)_3$	$CBrCl_3$	Acetonitrile
0.2	1.1	$Ir(dF\text{-}ppy)_3$	$CBrCl_3$	Acetonitrile
0.0	0.0	$Ir(ppy_2)(dtbbpy)(PF_6)$	$CBrCl_3$	Acetonitrile
0.1	0.8	$Ir(df\text{-}CF_3\text{-}ppy)_2(dtbbpy)(PF_6)$	$CBrCl_3$	Acetonitrile
0.4	2.4	Fluorescein	$CBrCl_3$	Acetonitrile
0.0	0.3	Eosin Y	$CBrCl_3$	Acetonitrile
0.9	4.8	Eosin B	$CBrCl_3$	Acetonitrile
0.1	0.6	Rose Bengal	$CBrCl_3$	Acetonitrile
0.1	0.5	none	$CBrCl_3$	Acetonitrile
0.2	1.0	$Ru(bpy)_3(PF_6)$	$CBrCl_3$	DMA
0.0	0.0	$Ru(Phen)_3Cl_2$	$CBrCl_3$	DMA
0.0	0.0	$Ru(dip)_3Cl_2$	$CBrCl_3$	DMA
0.0	0.0	$Ir(ppy)_3$	$CBrCl_3$	DMA
0.0	0.0	$Ir(dF\text{-}ppy)_3$	$CBrCl_3$	DMA
0.0	0.0	$Ir(ppy_2)(dtbbpy)(PF_6)$	$CBrCl_3$	DMA
0.0	0.0	$Ir(df\text{-}CF_3\text{-}ppy)_2(dtbbpy)(PF_6)$	$CBrCl_3$	DMA
0.5	3.0	Fluorescein	$CBrCl_3$	DMA
0.1	0.7	Eosin Y	$CBrCl_3$	DMA
2.0	10.6	Eosin B	$CBrCl_3$	DMA
2.1	11.3	Rose Bengal	$CBrCl_3$	DMA
0.7	3.6	none	$CBrCl_3$	DMA

0.6	3.3	$Ru(bpy)_3(PF_6)$	$MeNO_2$	Acetonitrile
0.5	2.6	$Ru(Phen)_3Cl_2$	$MeNO_2$	Acetonitrile
0.8	4.4	$Ru(dip)_3Cl_2$	$MeNO_2$	Acetonitrile
0.2	1.1	$Ir(ppy)_3$	$MeNO_2$	Acetonitrile
1.6	8.5	$Ir(dF\text{-}ppy)_3$	$MeNO_2$	Acetonitrile
3.4	18.1	$Ir(ppy_2)(dtbbpy)(PF_6)$	$MeNO_2$	Acetonitrile
6.7	36.2	$Ir(df\text{-}CF_3\text{-}ppy)_2(dtbbpy)(PF_6)$	$MeNO_2$	Acetonitrile
1.5	8.0	Fluorescein	$MeNO_2$	Acetonitrile
2.0	10.9	Eosin Y	$MeNO_2$	Acetonitrile
1.8	9.5	Eosin B	$MeNO_2$	Acetonitrile
1.1	5.8	Rose Bengal	$MeNO_2$	Acetonitrile
0.4	2.2	none	$MeNO_2$	Acetonitrile
0.9	5.0	$Ru(bpy)_3(PF_6)$	$MeNO_2$	DMA
0.6	3.4	$Ru(Phen)_3Cl_2$	$MeNO_2$	DMA
0.7	4.0	$Ru(dip)_3Cl_2$	$MeNO_2$	DMA
0.3	1.5	$Ir(ppy)_3$	$MeNO_2$	DMA
2.0	10.7	$Ir(dF\text{-}ppy)_3$	$MeNO_2$	DMA
3.5	19.1	$Ir(ppy_2)(dtbbpy)(PF_6)$	$MeNO_2$	DMA
10.6	57.2	$Ir(df\text{-}CF_3\text{-}ppy)_2(dtbbpy)(PF_6)$	$MeNO_2$	DMA
2.5	13.6	Fluorescein	$MeNO_2$	DMA
1.7	9.1	Eosin Y	$MeNO_2$	DMA
2.1	11.6	Eosin B	$MeNO_2$	DMA
1.0	5.2	Rose Bengal	$MeNO_2$	DMA
0.3	1.8	none	$MeNO_2$	DMA
2.3	12.3	$Ru(bpy)_3(PF_6)$	tBPA	Acetonitrile
1.5	8.3	$Ru(Phen)_3Cl_2$	tBPA	Acetonitrile
2.2	11.9	$Ru(dip)_3Cl_2$	tBPA	Acetonitrile
6.3	34.1	$Ir(ppy)_3$	tBPA	Acetonitrile
3.6	19.7	$Ir(dF\text{-}ppy)_3$	tBPA	Acetonitrile
7.3	39.7	$Ir(ppy_2)(dtbbpy)(PF_6)$	tBPA	Acetonitrile

9.4	50.5	Ir(df-CF$_3$-ppy)$_2$(dtbbpy)(PF$_6$)	tBPA	Acetonitrile
3.2	17.5	Fluorescein	tBPA	Acetonitrile
5.0	26.8	Eosin Y	tBPA	Acetonitrile
4.5	24.2	Eosin B	tBPA	Acetonitrile
2.0	10.7	Rose Bengal	tBPA	Acetonitrile
2.6	13.9	none	tBPA	Acetonitrile
1.7	9.1	Ru(bpy)$_3$(PF$_6$)	tBPA	DMA
2.2	11.7	Ru(Phen)$_3$Cl$_2$	tBPA	DMA
1.8	9.8	Ru(dip)$_3$Cl$_2$	tBPA	DMA
4.8	25.9	Ir(ppy)$_3$	tBPA	DMA
7.0	37.8	Ir(dF-ppy)$_3$	tBPA	DMA
8.8	47.5	Ir(ppy$_2$)(dtbbpy)(PF$_6$)	tBPA	DMA
11.4	61.7	Ir(df-CF$_3$-ppy)$_2$(dtbbpy)(PF$_6$)	tBPA	DMA
3.7	20.1	Fluorescein	tBPA	DMA
2.8	15.2	Eosin Y	tBPA	DMA
3.0	16.1	Eosin B	tBPA	DMA
1.5	8.3	Rose Bengal	tBPA	DMA
1.1	5.7	none	tBPA	DMA
1.4	7.7	Ru(bpy)$_3$(PF$_6$)	K$_2$S$_2$O$_8$	Acetonitrile
0.9	4.7	Ru(Phen)$_3$Cl$_2$	K$_2$S$_2$O$_8$	Acetonitrile
1.5	8.1	Ru(dip)$_3$Cl$_2$	K$_2$S$_2$O$_8$	Acetonitrile
2.4	13.0	Ir(ppy)$_3$	K$_2$S$_2$O$_8$	Acetonitrile
2.8	15.3	Ir(dF-ppy)$_3$	K$_2$S$_2$O$_8$	Acetonitrile
2.5	13.5	Ir(ppy$_2$)(dtbbpy)(PF$_6$)	K$_2$S$_2$O$_8$	Acetonitrile
2.8	14.9	Ir(df-CF$_3$-ppy)$_2$(dtbbpy)(PF$_6$)	K$_2$S$_2$O$_8$	Acetonitrile
2.0	10.6	Fluorescein	K$_2$S$_2$O$_8$	Acetonitrile
3.8	20.7	Eosin Y	K$_2$S$_2$O$_8$	Acetonitrile
2.6	14.0	Eosin B	K$_2$S$_2$O$_8$	Acetonitrile
1.7	9.2	Rose Bengal	K$_2$S$_2$O$_8$	Acetonitrile
2.3	12.2	none	K$_2$S$_2$O$_8$	Acetonitrile

0.5	2.8	$Ru(bpy)_3(PF_6)$	$K_2S_2O_8$	DMA
0.5	2.8	$Ru(Phen)_3Cl_2$	$K_2S_2O_8$	DMA
0.6	3.1	$Ru(dip)_3Cl_2$	$K_2S_2O_8$	DMA
NA	NA	$Ir(ppy)_3$	$K_2S_2O_8$	DMA
1.1	5.9	$Ir(dF\text{-}ppy)_3$	$K_2S_2O_8$	DMA
1.3	7.3	$Ir(ppy_2)(dtbbpy)(PF_6)$	$K_2S_2O_8$	DMA
0.7	3.8	$Ir(df\text{-}CF_3\text{-}ppy)_2(dtbbpy)(PF_6)$	$K_2S_2O_8$	DMA
0.8	4.3	Fluorescein	$K_2S_2O_8$	DMA
1.3	7.1	Eosin Y	$K_2S_2O_8$	DMA
1.1	5.9	Eosin B	$K_2S_2O_8$	DMA
0.3	1.5	Rose Bengal	$K_2S_2O_8$	DMA
1.0	5.7	none	$K_2S_2O_8$	DMA

Photochemical Flow Reactor Design:
The reactor was built using an ace glass condenser wrapped with either ~62 ft of 1/8” i.d. or ~100 ft of 1/16” i.d. PFA tubing. The PFA tubing was supported in a polished aluminum housing containing 720 LEDs (440 nm, SuperBrightLEDs, NFLS-X3-UV, 0.2W). Total light output was 21W. The base is equipped with air-ports for cooling.

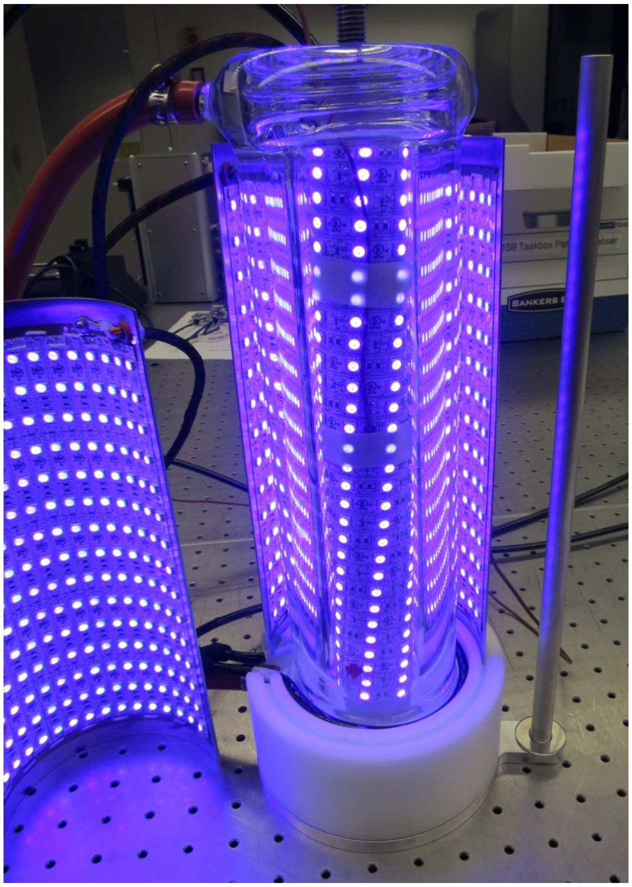


Figure S9. Reactor photo

Procedure for photochemical oxidation of (6S,12aR)-3,10-dibromo-6-phenyl-12,12a-dihydro-6H-benzo[5,6][1,3]oxazino[3,4-a]indole (1) to furnish (*S*)-3,10-dibromo-6-phenyl-6*H*-benzo[5,6][1,3]oxazino[3,4-*a*]indole (2):

(6S,12aR)-3,10-dibromo-6-phenyl-12,12a-dihydro-6H-benzo[5,6][1,3]oxazino[3,4-a]indole (**1**) (100g, 219 mmol) was added to a 1 liter jacketed round bottom flask followed by Ir[(dF-CF_3-ppy)2(dtbpy)](PF_6) (249 mg, 0.219 mmol, 0.1 mol %), N,N-dimethylacetamide (400 mL, 4 volumes) and tert-butylperoxybenzoate (82 mL, 437 mmol, 2.0 equiv). The mixture was stirred at room temperature under nitrogen atmosphere until complete dissolution was achieved, at which point the solution was sparged with nitrogen while cooling to -5°C with a glycol/water bath. The cooled reaction solution was then passed at a rate of 2.5 ml/min through a reactor consisting of 62 linear feet of 1/8” ID PFA tubing surrounded by blue LEDs (λ_{max} 440 nm, 720 LEDs, 21W output) cooled to -5°C. The internal reaction volume of the reactor was ~150 ml, providing a residence time = 60 min at 2.5 ml/min flow rate. The crude reaction stream was collected in a 1 liter jacketed round bottom flask also cooled to -5°C. The total time required to process the batch was ~5 h. Assay of reaction: 98.5% conversion, 90% AY. To this crude reaction stream was charged Na_2SO_3 aqueous solution (5.51 g, 0.2 equiv. in 24 mL of water) in 30 mins. The resulting stream was seeded with pure product (50 mg, 0.05%) and aged 20 min. To the slurry was charged Na_2SO_3 and LiOH aqueous solution (5.51 g Na_2SO_3, 0.2 equiv, 19.3 g LiOH, 2.1 equiv in 97 mL water) in 2h, water (55 mL) in additional 1 h. The product (**2**) was isolated by filtration. The isolated cake was first washed with DMA/water (60/40, v/v, 150 mLx2), water (150 mLx2), and IPA (150 mLx2). The cake was then dried under vacuum with nitrogen sweep for 15 hours yielding 85.8g, 98 NMR wt%, 84.5% IY with 99.8% ee.

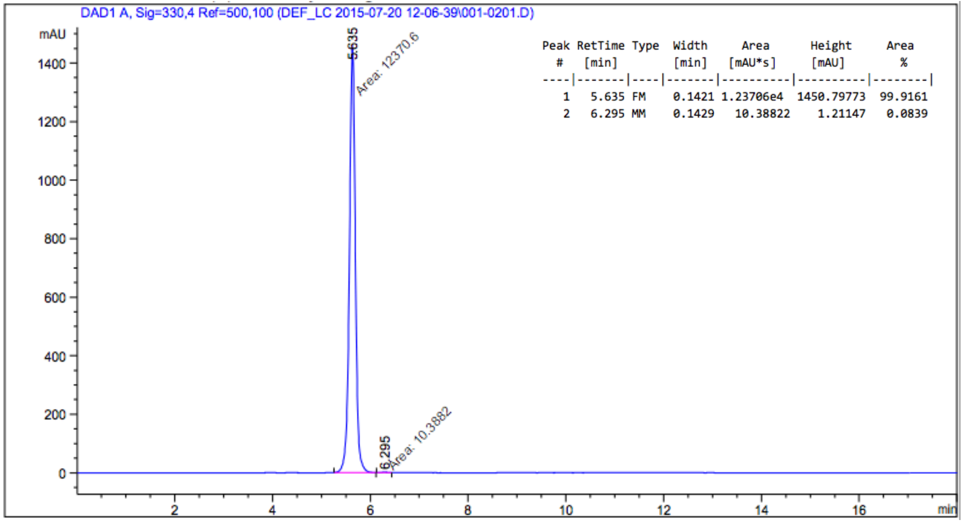
(*S*)-3,10-dibromo-6-phenyl-6*H*-benzo[5,6][1,3]oxazino[3,4-*a*]indole (2)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.22 – 7.15 (m, 3H), 7.12 (s, 1H), 7.07 (m, 2H), 6.85 (s, 1H), 6.72 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.09, 136.28, 134.05, 132.22, 130.81, 130.07, 129.08, 126.95, 126.52, 125.67, 125.22, 123.51, 122.51, 121.47, 117.11, 114.25, 111.29, 96.93, 84.61. IR (neat): 3032, 1605, 1429, 1216 cm^{-1}. HRMS calculated for $C_{21}H_{13}Br_2NO$ (M): 452.93639, found: 452.9356

HPLC Traces of Product (2) from 100g scale-up:

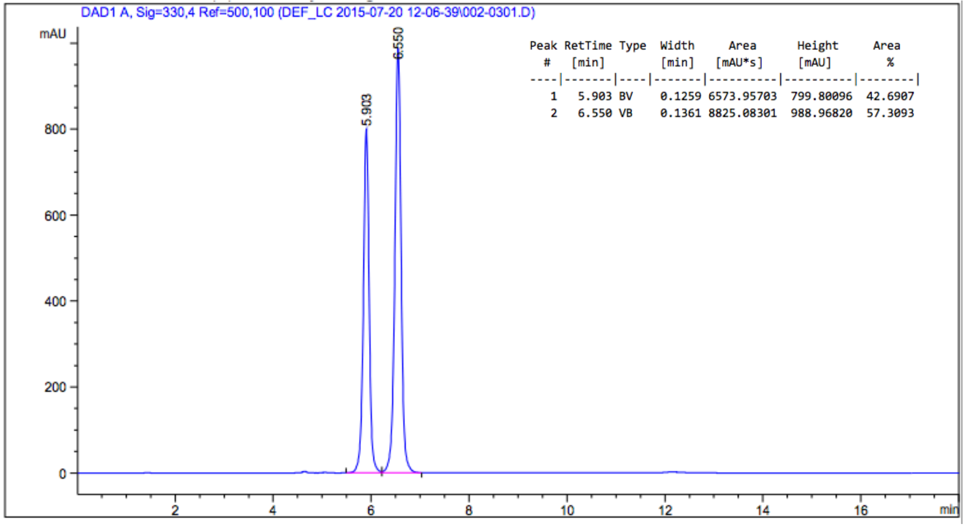
Enantiomeric ratio was determined by HPLC analysis using a HO series 1100 HPLC outfitted with a Chiracel AS-RH (150 x 4.6 mm, 5 µm) column (40 °C, 340 nm, 1 mL/min), see detailed conditions below

From scale-up:



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.635 FM    0.1421 1.23706e4 1450.79773 99.9161
   2   6.295 MM    0.1429  10.38822    1.21147  0.0839
```

Assay:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.903 BV    0.1259 6573.95703  799.80096 42.6907
   2   6.550 VB    0.1361 8825.08301  988.96820 57.3093
```

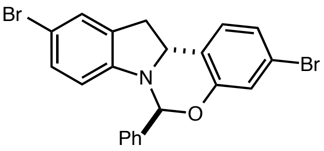
Figure S10. HPLC traces of **2** from 100 g scale-up

HPLC Conditions:

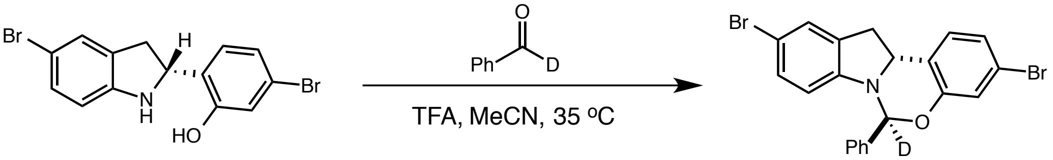
Column:	*Chiralpak AS-RH, 150 x 4.6 mm, 5 um*
Column Temperature:	*40ºC*
Injection Volume:	*5 uL*
Mobile Phase A:	*Water*
Mobile Phase B:	*MeCN*
Flow Rate:	*1.0 mL/min*
Detection:	*UV, 346 nm*

Gradient:	*Time (mins)*	*%A*	*%B*
	0.00	*25*	*75*
	10.00	*10*	*90*
	10.01	*25*	*75*
	15.00	*25*	*75*

Synthesis and characterization of starting materials



(6*S*,12a*R*)-3,10-dibromo-6-phenyl-12,12a-dihydro-6*H*-benzo[5,6][1,3]oxazino[3,4-*a*]indole[2]
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.44 (dt, *J* = 8.2, 1.2 Hz, 2H), 7.14 – 7.06 (m, 4H), 7.06 – 7.01 (m, 1H), 6.92 (s, 1H), 6.76 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.37 (s, 1H), 6.24 (d, *J* = 8.4 Hz, 1H), 6.11 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.25 (d, *J* = 8.9 Hz, 1H), 2.79 (ddt, *J* = 15.8, 9.0, 1.2 Hz, 1H), 2.40 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (126 MHz, C_6D6) δ 153.67, 148.19, 138.35, 131.64, 130.62, 129.03, 128.76, 128.61, 128.35, 127.03, 124.52, 123.99, 121.62, 120.51, 112.98, 111.28, 83.14, 55.55, 35.88. IR (neat): 3059, 2918, 1596, 1471, 1228, 931 cm^{-1}. HRMS calculated for $C_{21}H_{15}Br_2NO$ (M): 454.95204, found: 454.95193



Preparation of (6S,12aR)-3,10-dibromo-6-phenyl-12,12a-dihydro-6H-benzo[5,6][1,3]oxazino[3,4-a]indole-6-d (1a)

To a suspension of (R)-5-bromo-2-(5-bromoindolin-2-yl)phenol[3] (2.66 g., 7.21 mmol), benzaldehyde-a-d$_1$ (1.00 g, 9.37 mmol, 1.3 eq) in MeCN (10.6 mL, 4 vol) in a stirred flask under nitrogen was added TFA (0.028 mL, 0.05 eq) at 20-25 °C. The resulting solution was heated to 30-35 °C for 3 hours during which time crystallization of the product was observed. The slurry was cooled to 20-25 °C and held at this temperature for 1 hour. A 5% aqueous sodium bicarbonate solution (1.21 mL, 0.1 eq) was added to the batch followed by a slow addition of water (5.3 mL). After agitating at 20-25 °C for another 3h, the batch was filtered and washed with 8 mL (3 vol) MeCN:water (2:1) followed by 5.3 mL (2 vol) of water. The resulting solid was dried under a nitrogen sweep, providing (6S,12aR)-3,10-dibromo-6-phenyl-12,12a-dihydro-6H-benzo[5,6][1,3]oxazino[3,4-a]indole-6-d as a white solid (3.20 g., 7.21 mmol, 97% yield).

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.46 – 7.43 (m, 2H), 7.14 – 7.06 (m, 4H), 7.06 – 7.01 (m, 1H), 6.92 (s, 1H), 6.76 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.23 (d, *J* = 8.4 Hz, 1H), 6.11 (d, *J* = 8.3 Hz, 1H), 4.25 (d, *J* = 8.9 Hz, 1H), 2.79 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.40 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (126 MHz, C_6D6) δ 153.66, 148.18, 138.28, 131.63, 130.62, 129.02, 128.76, 128.62, 128.35, 127.05, 124.52, 123.99, 121.62, 120.51, 112.98, 111.28, 55.53, 35.89. IR (neat): 3060, 2249, 1597, 1590, 1476, 1262 cm^{-1}. HRMS calculated for $C_{21}H_{14}DBr_2NO$ (M): 455.95832, found: 455.9591.

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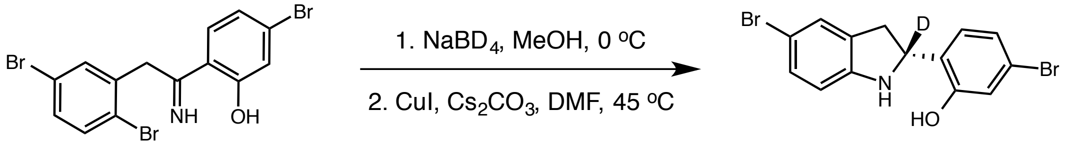
[2] For synthesis, refer to *Org. Lett.*, 2014, **16**, 2310–2313.

[3] For synthesis, refer to *Org. Lett.*, 2014, **16**, 2310–2313.



Preparation of (5-bromo-2-(5-bromoindolin-2-yl-2-*d*)phenol

To a solution of 5-bromo-2-(2-(2,5-dibromophenyl)-1-iminoethyl)phenol[4] (25.0 g., 55.8 mmol) in MeOH (250 mL) cooled to 0 °C was added sodium borodeuteride (2.50 g., 59.7 mmol), and the mixture was stirred at 0 °C for 1 hour. A 5% aqueous sodium bicarbonate solution (100 mL) and agitated for 10 minutes. At this time dichloromethane (250 mL) was added, and the resulting biphasic mixture partitioned in a separtory funnel, discarding the aqueous layer. The organic layer was further washed with 100 mL water, and again partitioned in a separtory funnel, discarding the aqueous layer. The organic layer was then slowly evaporated on a rotovap, during which the product was observed to crystallize. At this point, the batch was filtered and washed with minimal dichloromethane. The resulting solid was dried under a nitrogen sweep, providing 2-(1-amino-2-(2,5-dibromophenyl)ethyl-1-d)-5-bromophenol as a white solid (21.0 g., 46.6 mmol, 83% yield). The material was carried on crude.

Next, A 250 mL round-bottomed flask equipped with a magnetic stir bar, a thermocouple, and a nitrogen inlet was charged with the crude material (19.0 g., 42.1 mmol), copper iodide (401 mg., 2.11 mmol, 0.05 equiv) and cesium carbonate (27.5 g., 84 mmol, 2.0 equiv), and the flask was purged with nitrogen for 10 minutes. In a separate flask, DMF (95 mL, 5.0 vol) was sparged with nitrogen for 30 minutes, then added via cannula under nitrogen to the flask containing 2-(1-amino-2-(2,5-dibromophenyl)ethyl-1-d)-5-bromophenol. When addition of solvent was complete, the mixture was heated to 45 °C and stirred under nitrogen for 1 hour, monitoring for conversion by HPLC.

When conversion was complete (typically < 60 minutes), the reaction was cooled to room temperature and diluted with 20 volumes EtOAc and immediately neutralized with 25 wt% aqueous ammonium chloride with vigorous stirring. The aqueous layer will turn blue as copper is solubilized. The pH is further adjusted to pH = 7.5 with 1N HCl. The aqueous layer was cut, and back-extracted with 2 volumes EtOAc, and the combined organics washed successively with 4 volumes of 10 wt% sodium chloride and 4 volumes of water. The organics were then concentrated with a continuous solvent switch to acetonitrile (target final volume of 5 volumes acetonitrile, <5% residual EtOAc). Over this time, white crystals of 5-bromo-2-(5-bromoindolin-2-yl-2-d)phenol were observed to precipitate forming a seed bed. When the target volume was reached, 5 volumes of water was added slowly over 60 minutes with stirring. When the water addition was complete, the slurry was stirred for a further 1 hour, then the solids collected by filtration and washed with 1 volume of 1:1 acetonitrile:water, then dried via nitrogen sweep, providing 5-bromo-2-(5-bromoindolin-2-yl-2-d)phenol as a white crystalline solid (13.5 g., 36.5 mmol, 72% yield overall both 2 steps).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.48 (s, 1H), 7.20 (s, 1H), 7.14 (d, *J* = 8.3, 1H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.87 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.31 (s, 1H), 3.17 (d, *J* = 15.8 Hz, 1H), 3.00 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.70, 132.95, 130.66, 129.53, 127.98, 123.39, 122.85, 122.57, 121.02, 113.51, 37.99. IR (neat): 3276, 2910, 2144, 1597, 1573 cm^{-1}. HRMS calculated for $C_{14}H_{10}DBr_2NO$ (M): 367.92702, found: 367.92685.

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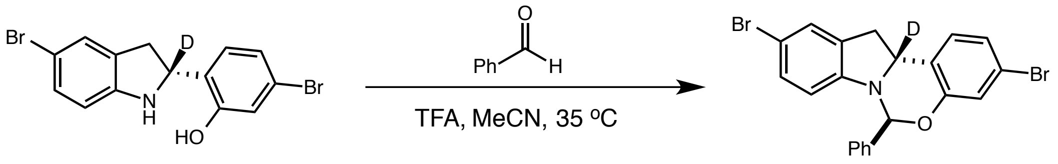
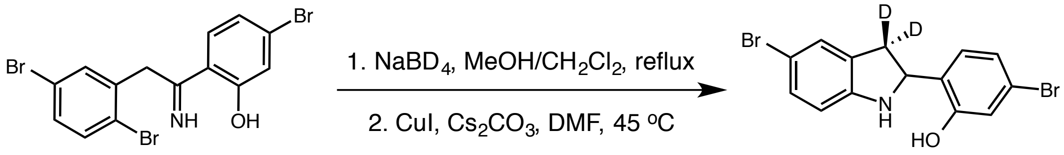
[4] For synthesis, refer to *Org. Lett.*, 2014, **16**, 2310–2313.



Preparation of 3,10-dibromo-6-phenyl-12,12a-dihydro-6H-benzo[5,6][1,3]oxazino[3,4-a]indole-12a-d (1b)

To a suspension of 5-bromo-2-(5-bromoindolin-2-yl-2-d)phenol (4.05 g, 10.9 mmol), benzaldehyde (1.51 g, 14.23 mmol, 1.3 eq) in MeCN (16.2 mL, 4 vol) in a stirred flask under nitrogen was added TFA (0.042 mL, 0.05 eq) at 20-25 °C. The resulting solution was heated to 30-35 °C for 3 hours during which time crystallization of the product was observed. The slurry was cooled to 20-25 °C and held at this temperature for 1 hour. A 5% aqueous sodium bicarbonate solution (1.84 mL, 0.1 eq) was added to the batch followed by a slow addition of water (8.1 mL). After agitating at 20-25 °C for another 3h, the batch was filtered and washed with 12.2 mL (3 vol) MeCN:water (2:1) followed by 8.1 mL (2 vol) of water. The resulting solid was dried under nitrogen, providing 3,10-dibromo-6-phenyl-12,12a-dihydro-6H-benzo[5,6][1,3]oxazino[3,4-a]indole-12a-d as a white solid (4.2 g., 9.2 mmol, 84% yield).

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.45 (dt, *J* = 8.3, 1.2 Hz, 2H), 7.14 – 7.07 (m, 4H), 7.07 – 7.01 (m, 1H), 6.92 (dt, *J* = 2.1, 1.0 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.38 (s, 1H), 6.24 (d, *J* = 8.4 Hz, 1H), 6.11 (d, *J* = 8.2 Hz, 1H), 2.79 (d, *J* = 15.8 Hz, 1H), 2.40 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (126 MHz, C_6D6) δ 153.69, 148.20, 138.34, 131.64, 130.61, 129.03, 128.76, 128.61, 128.35, 127.03, 124.52, 123.91, 121.63, 120.51, 112.97, 111.29, 83.14, 55.41, 55.23 (t, *J* = 22.9 Hz), 35.79. IR (neat): 3059, 2909, 2845, 2306, 1597, 1472 cm^{-1}. HRMS calculated for $C_{21}H_{14}DBr_2NO$ (M): 455.95832, found: 455.95789.

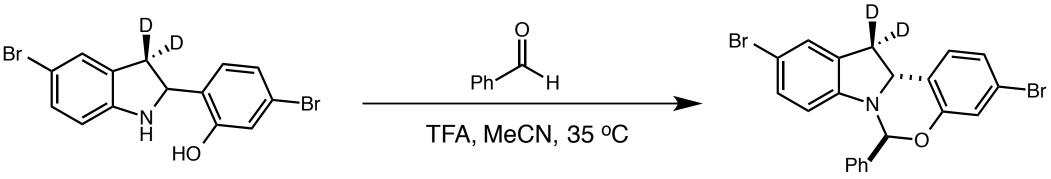


Preparation of 5-bromo-2-(5-bromoindolin-2-yl-3,3-d2)phenol

5-bromo-2-(2-(2,5-dibromophenyl)-1-iminoethyl)phenol (5g, 11.16 mmol), MeOD (50 ml), and CH_2Cl_2 (50 ml) were heated to reflux until homogeneous then stirred for 15 min. Solvent was removed *in vacuo* and the process repeated again. After stirring for an additional 15 min, $NaBH_4$ (0.845 g, 22.32 mmol) was added portionwise. The product began to crystallize after stirring for 2h. CH_2Cl_2 was removed and the methanol slurry was filtered and washed with methanol and dried under a nitrogen stream to yield the desired product as a white crystalline solid. Used in the next step without further purification.

Next, the resulting compound (3.5 g, 7.74 mmol), CuI (0.074 g, 0.387 mmol), Cs_2CO_3 (5.05 g, 15.49 mmol) were added to a flask followed by DMF (20 mL) in a glovebox. The suspension was removed from the box and stirred at 45 °C for 1h. EtOAc and NH_4Cl (sat) were added and the mixture separated. The aq layer was extracted twice with EtOAc then the combined organics were washed with brine and water followed by concentration in vacuo. Acetonitrile (20 mL) was added to the residue followed by the slow addition of water. After stirring for 10 min the mixture was filtered, washed with 1:1 ACN:water then dried under nitrogen stream to yield the desired product as a white solid (2.3g, 60% overall yield for both steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.37 – 7.23 (m, 2H), 7.10 (d, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.96 – 6.88 (m, 1H), 6.75 (dd, *J* = 8.3, 1.4 Hz, 1H), 4.95 (s, 1H), 4.42 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.55, 147.38, 132.66, 130.54, 129.41, 127.88, 123.40, 122.73, 122.41, 120.88, 113.85, 113.30, 64.99. IR (neat): 3275, 2876, 1873, 1598, 1576 cm^{-1}. HRMS calculated for $C_{21}H_{14}DBr_2NO$ (M): 368.93329, found: 368.93368.



Preparation of 3,10-dibromo-6-phenyl-12,12a-dihydro-6H-benzo[5,6][1,3]oxazino[3,4-a]indole-12,12-d2 (1c)

5-bromo-2-(5-bromoindolin-2-yl-3,3-d2)phenol (2 g, 5.39 mmol), acetonitrile (5 vol) were added to a flask followed by benzaldehyde (0.765 ml, 7.55 mmol) and TFA (0.021 ml, 0.269 mmol). The mixture was heated to 35 °C for 30 min then cooled to 0 °C. NaHCO3 (sat aq, 5 mL) was added followed by water (10 mL) and stirred for 5 min. The solids were filtered, washed with 2:1 ACN:water, water and dried under nitrogen stream to yield the desired product as a white crystaline solid (2.35 g, 95% yield). Optical resolution was conducted by prep SCF on a Chiralpak IA (2x25 cm) column. Conditions: 70 mL/min, 25% IPA, 220 nm, 100 bar, 23 mg/mL, 1 mL/inj.

^{1}H NMR (501 MHz, Benzene-*d*$_6$) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.12 (m, 2H), 7.09 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.04 (m, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.38 (s, 1H), 6.25 (d, *J* = 8.5 Hz, 1H), 6.11 (d, *J* = 8.2 Hz, 1H), 4.25 (s, 1H). ^{13}C NMR (126 MHz, C_6D6) δ 153.67, 148.24, 138.36, 130.64, 129.03, 128.81, 128.61, 128.25, 128.16, 124.52, 123.97, 121.61, 120.52, 112.97, 111.28, 83.15, 55.42. IR (neat): 3059.81, 3031.07, 2916.82, 1597.55 (s), 1569.86, 1470.63 (s) cm^{-1}. HRMS calculated for $C_{21}H_{13}D_2Br_2NO$ (M): 456.96459, found: 456.96459.

Figure S11. ^{1}H and ^{13}C NMR Spectra of **1**

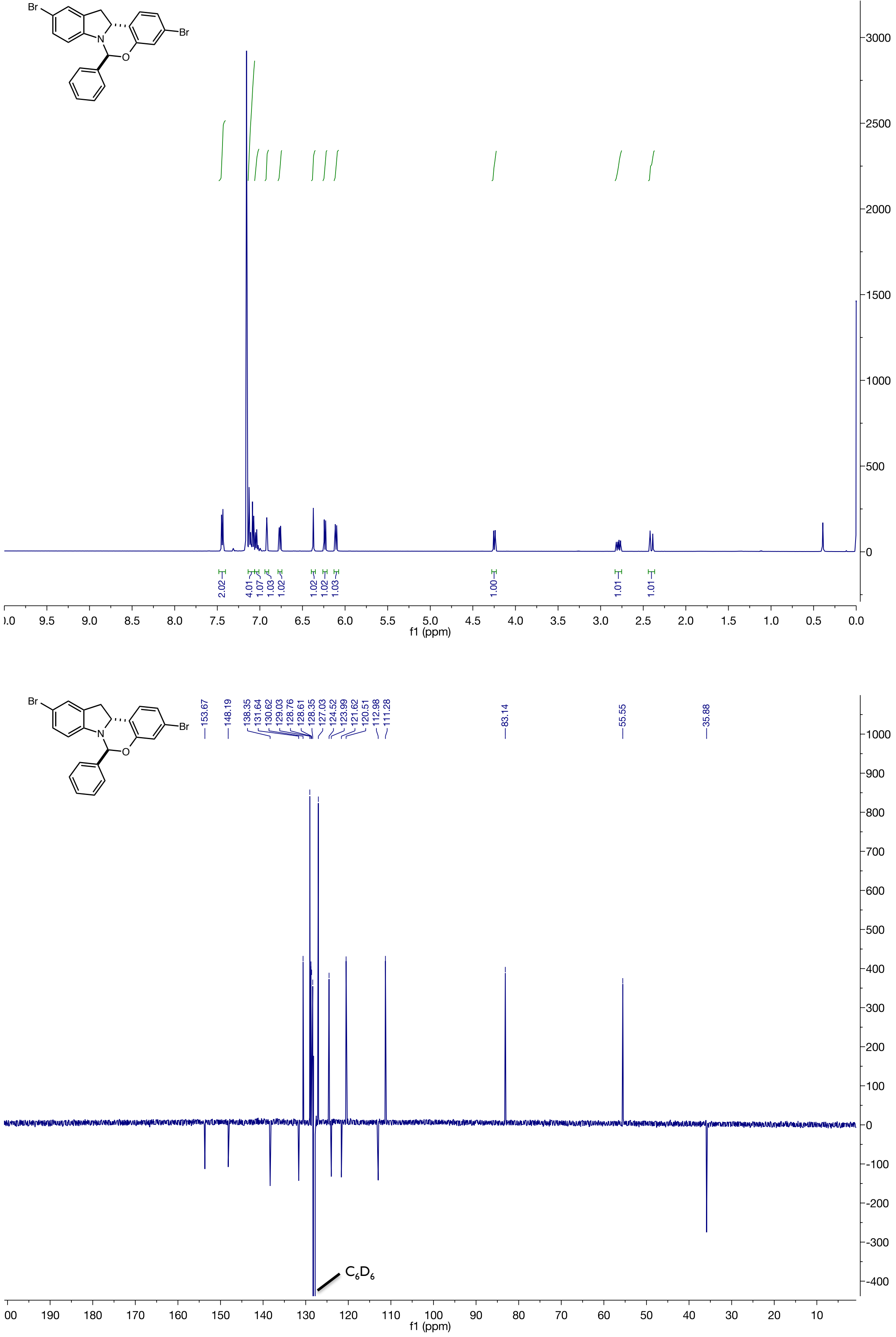
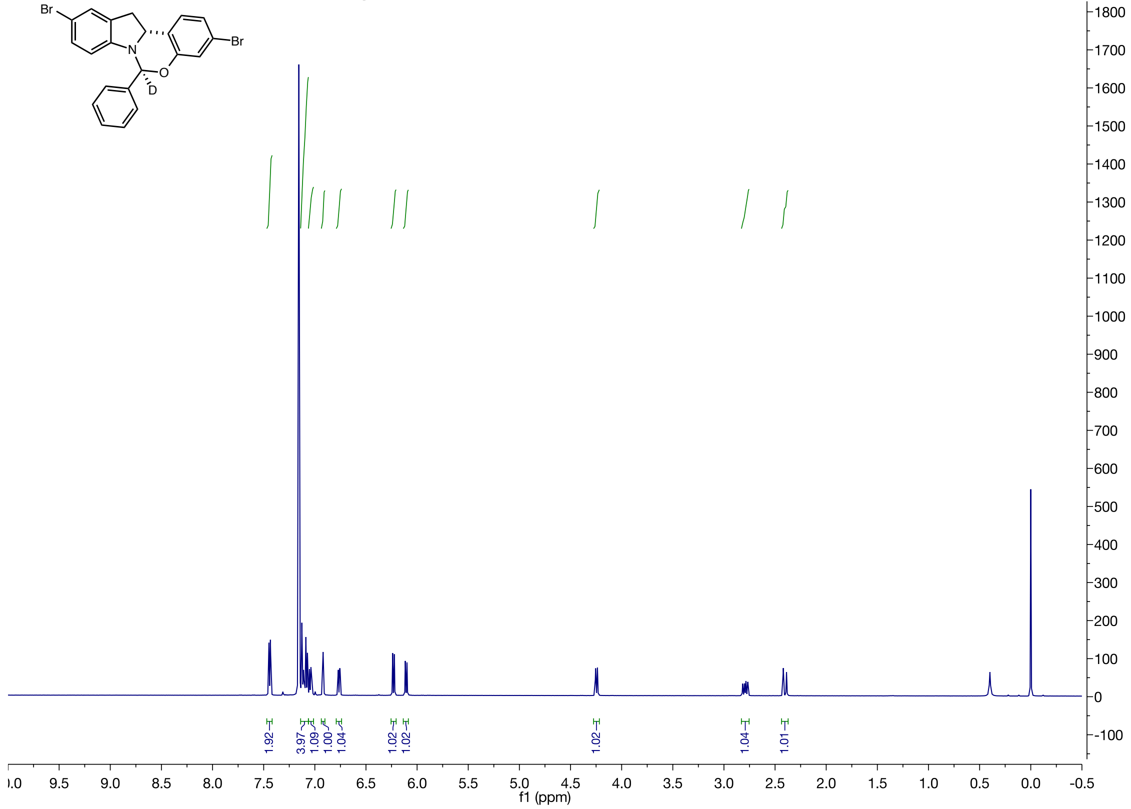
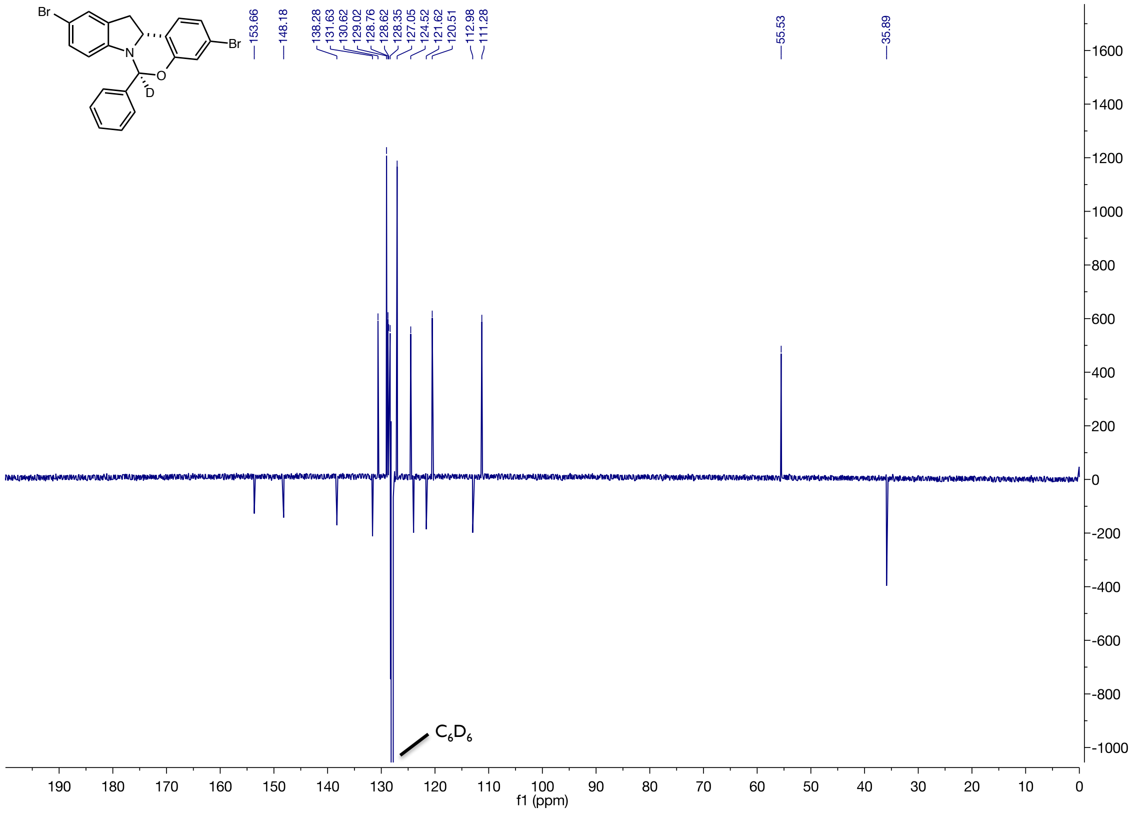


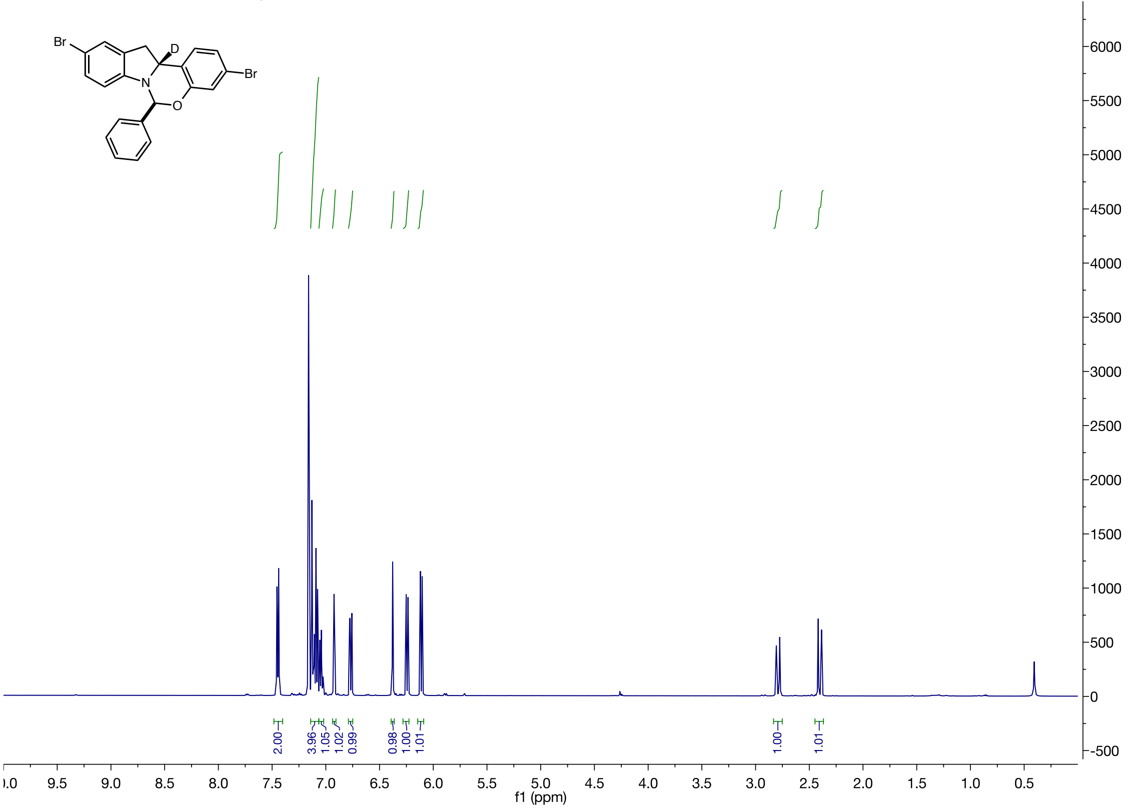
Figure S12. ^{1}H and ^{13}C NMR Spectra of **1a**





Figure

S13. ^{1}H and ^{13}C NMR Spectra of **1b**



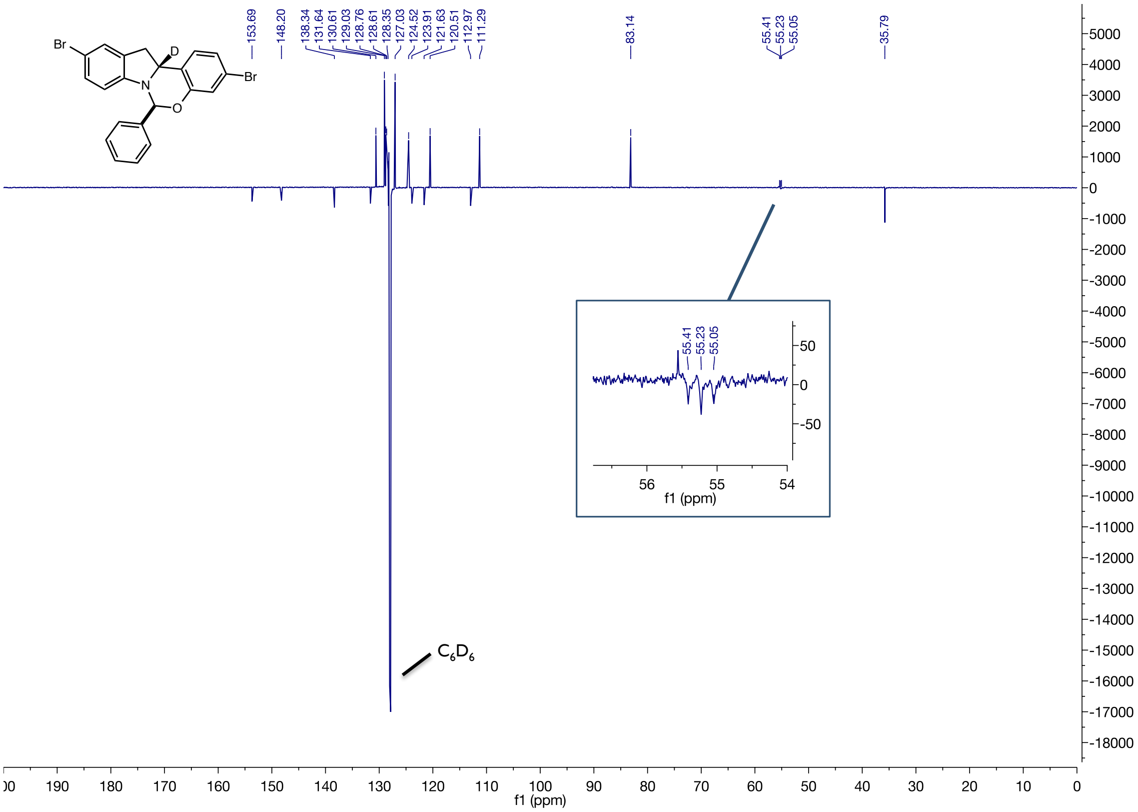
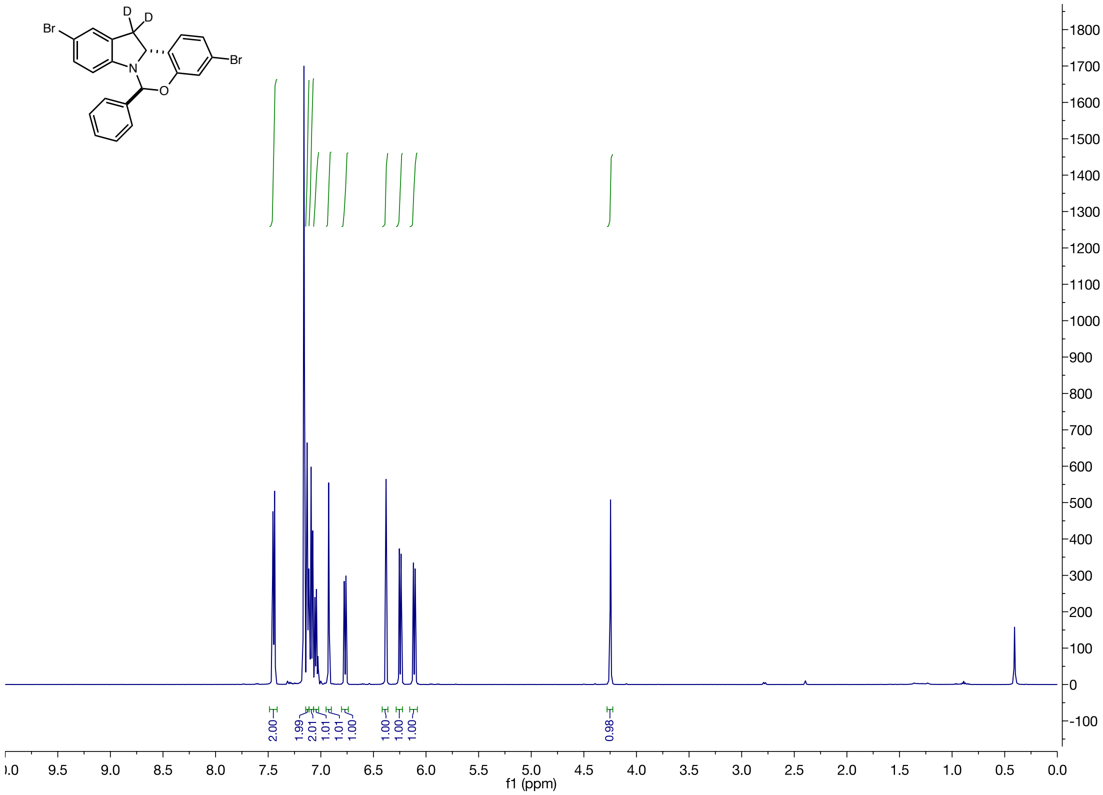


Figure S14. ^{1}H and ^{13}C NMR Spectra of **1c**



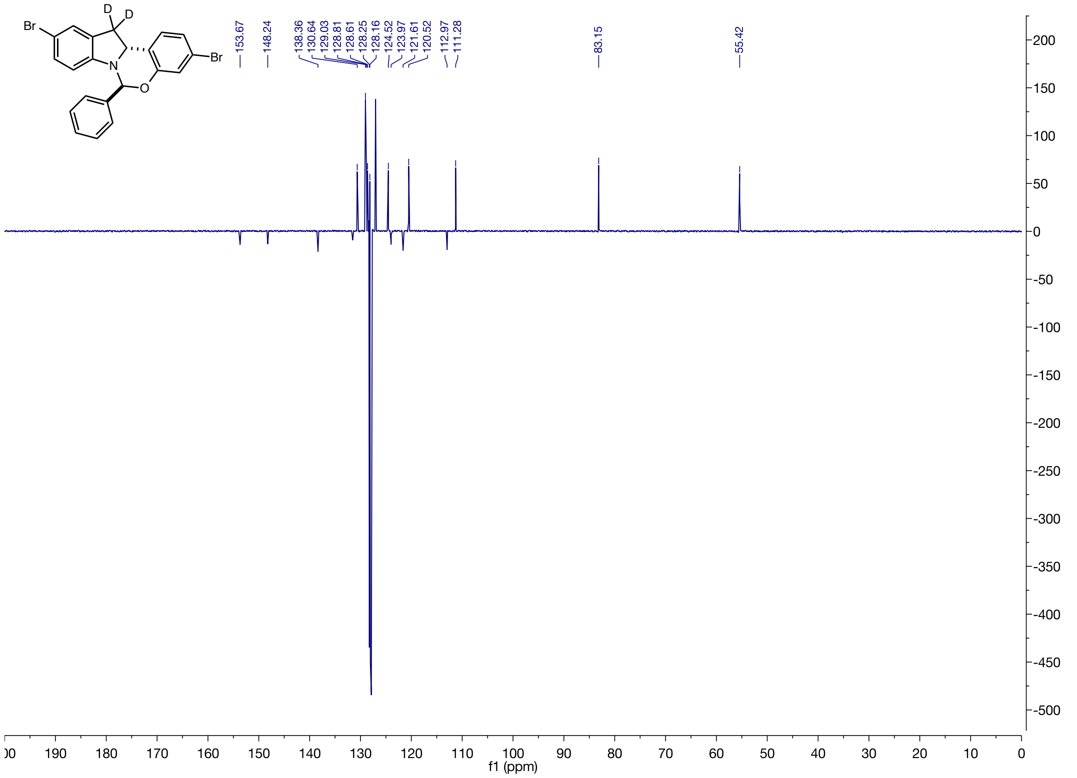
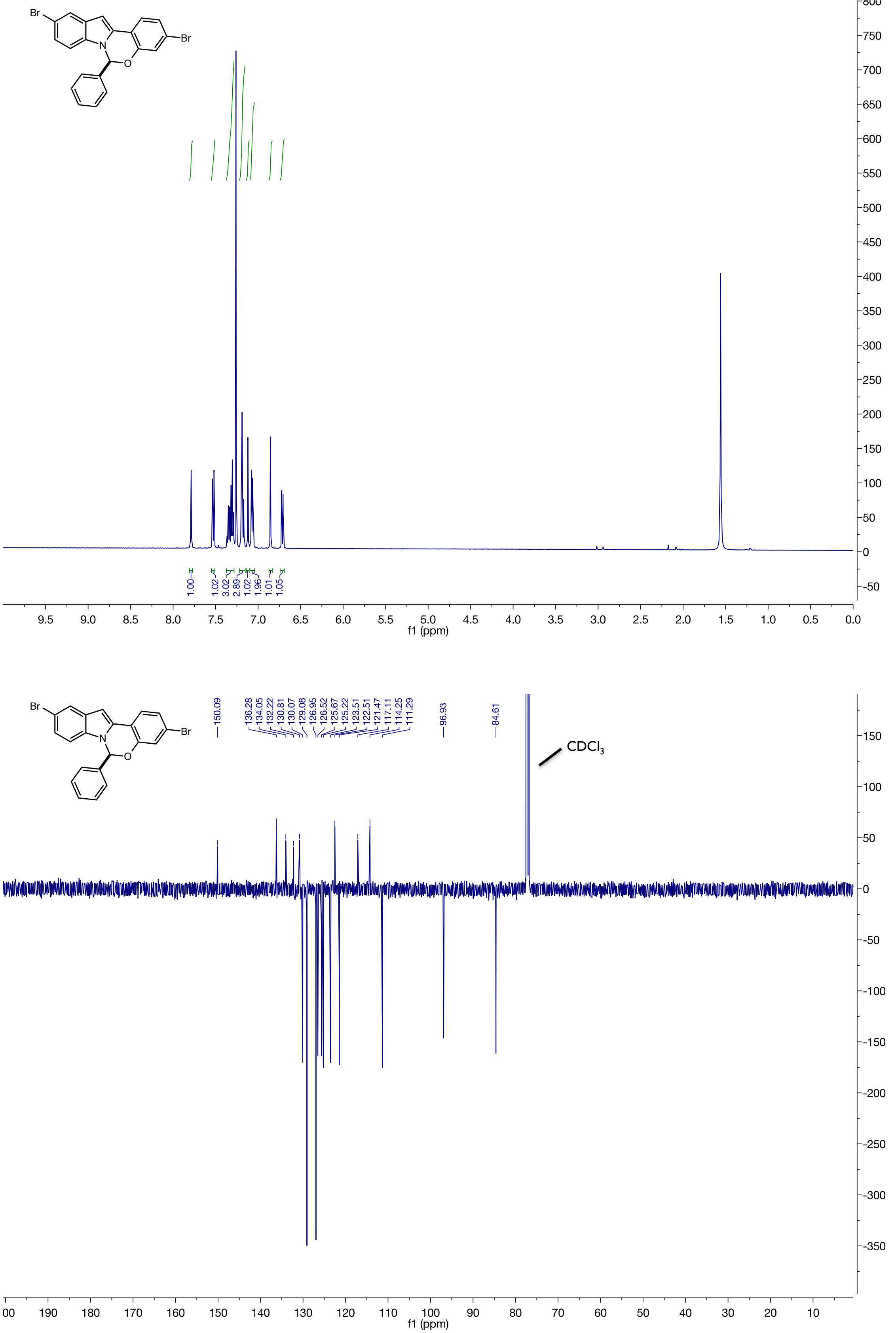
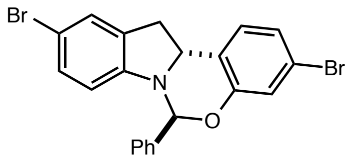


Figure S15. ^{1}H and ^{13}C NMR Spectra of **2**



Cyclic Voltammetry Studies

Estimating the reduction potential of **1** in MeCN:



$E_p \sim 0.855$ V vs $Cp_2Fe^{0/+}$ in MeCN

$E_{inf} \sim 0.787$ V vs $Cp_2Fe^{0/+}$ in MeCN

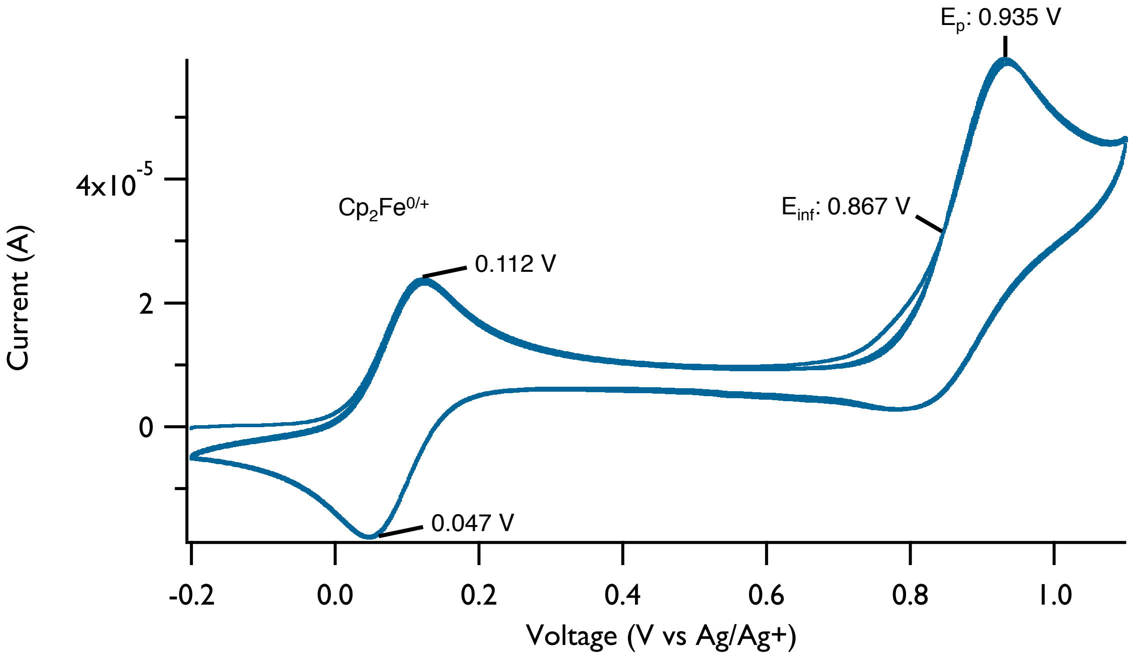
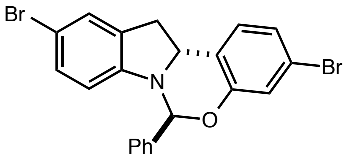


Figure S16. Cyclic voltammogram of **1** and $FeCp_2^+$ vs. Ag/Ag^+ in MeCN at 0.100 Vs^{-1}. *Conditions:* 1 mM 1, 1 mM $FeCp_2^+$ and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag^+ MeCN reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Estimating the reduction potential of **1** in DMA:



E_p ~ 0.670 V vs $Cp_2Fe^{0/+}$ in DMA

E_{inf} ~ 0.613 V vs $Cp_2Fe^{0/+}$ in DMA

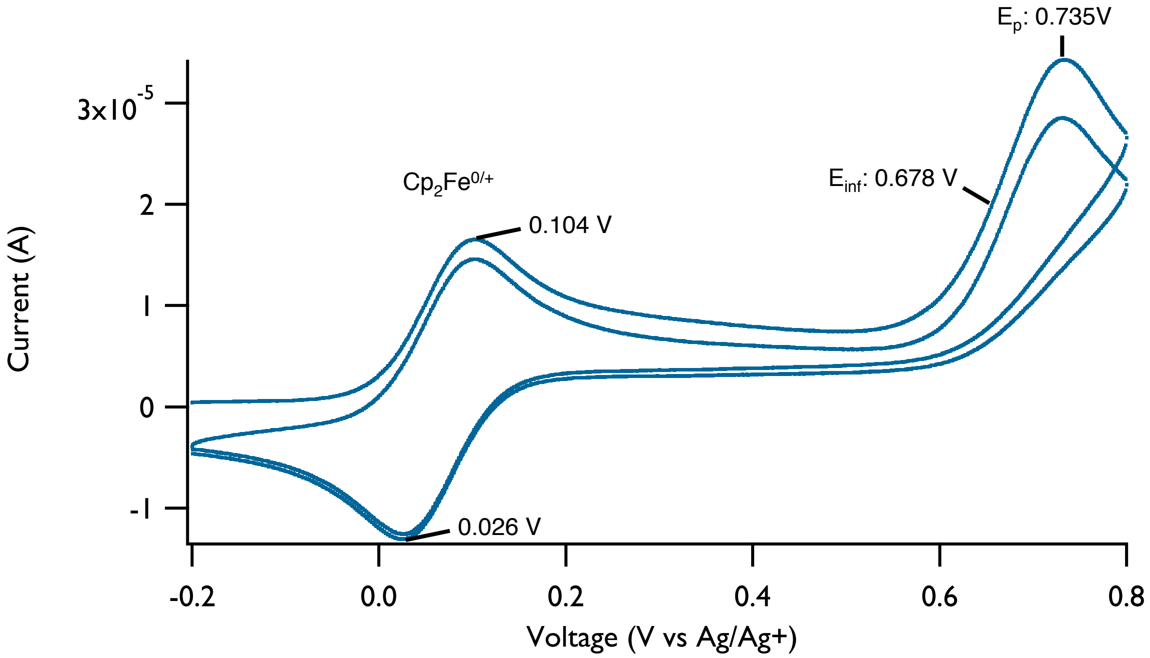
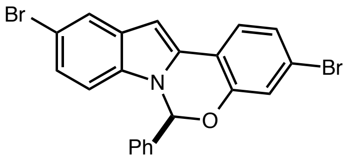


Figure S17. Cyclic voltammogram of **1** and $FeCp_2^+$ vs. Ag/Ag^+ in MeCN at 0.100 Vs^{-1}. *Conditions:* 1 mM 1, 1 mM $FeCp_2^+$ and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag^+ MeCN reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Estimating the reduction potential of **2** in DMA:



$E_p \sim 0.948$ V vs $Cp_2Fe^{0/+}$ in DMA

$E_{inf} \sim 0.886$ V vs $Cp_2Fe^{0/+}$ in DMA

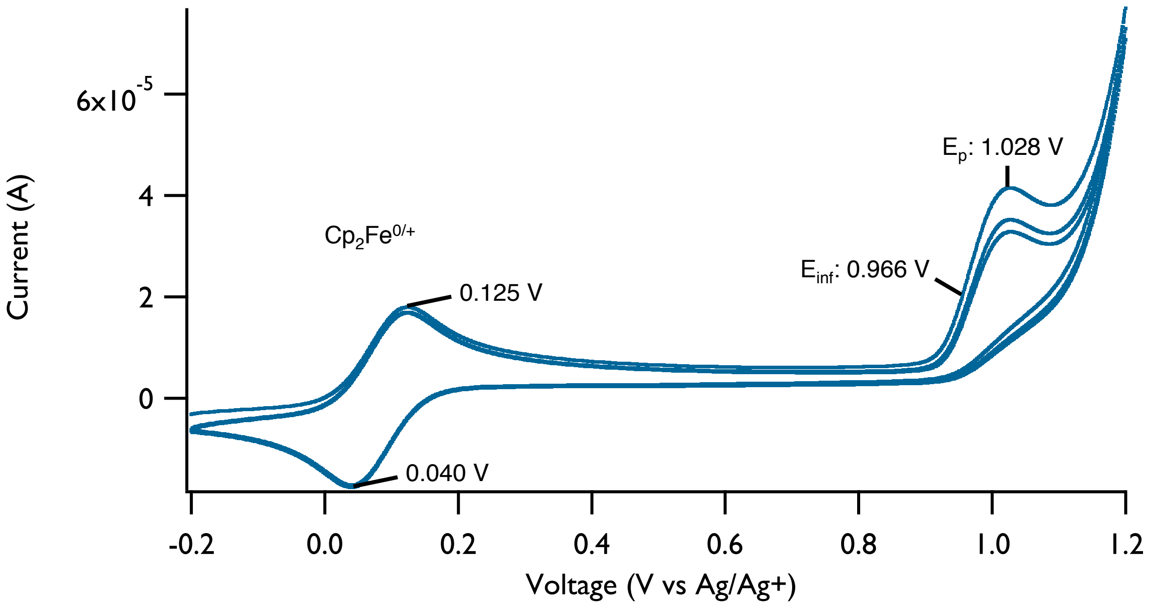
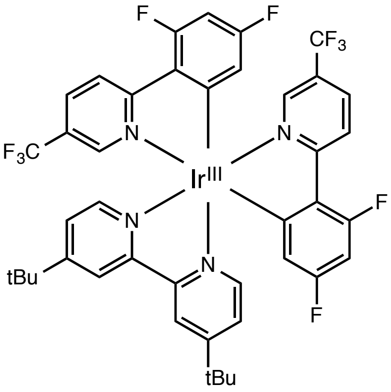


Figure S18. Cyclic voltammogram of **2** and $FeCp_2^+$ vs. Ag/Ag^+ in DMA at 0.100 Vs^{-1}. *Conditions:* 1 mM product, 1 mM $FeCp_2^+$ and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag^+ MeCN reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Estimating the ground and excited state reduction potentials of Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6) in DMA:



$E_{1/2}'(Ir^{III/II})$ = ~ –1.72 V vs $Cp_2Fe^{0/+}$ in DMA

$E_{1/2}'(Ir^{III*/II})$ = ~ 0.86 V vs $Cp_2Fe^{0/+}$ in DMA

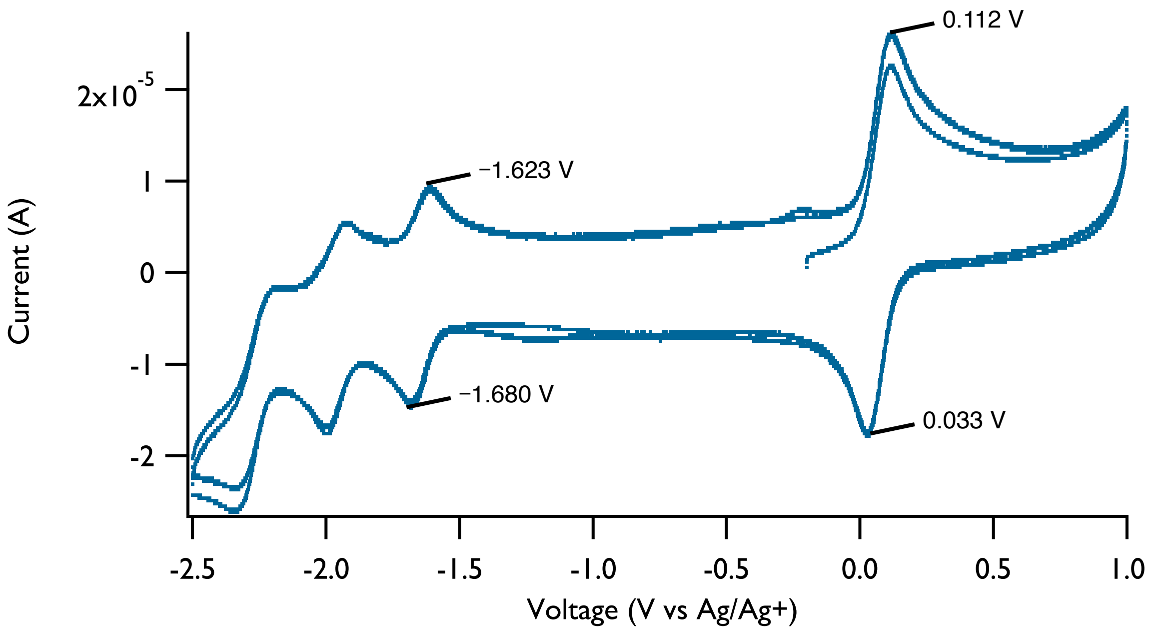


Figure S19. Cyclic voltammogram of Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6) and $FeCp_2^+$ vs. Ag/Ag^+ in DMA at 0.100 Vs^{-1}.

Conditions: 0.5 mM Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6), 1 mM $FeCp_2^+$ and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag^+ MeCN reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Calculation of excited state reduction potential for the $Ir^{III*/II}$ couple:

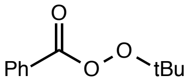
Wavelength of emission maxima of photocatalyst in DMA: 480 nm

$$E = h\text{v} = \text{hc}/\lambda = \frac{4.1357\bullet10^{-15}\ \text{eVs} \bullet 3\bullet10^{8}\ \text{m/s} \bullet 10^{9}\ \text{nm/m}}{480\ \text{nm}} = 2.58\ \text{V}$$

$E\ [\text{Ir}^{\text{III/III}*}] = 2.58\ \text{V}$

$E\ [\text{Ir}^{\text{III*/II}}] = E\ [\text{Ir}^{\text{III/II}}] - E\ [\text{Ir}^{\text{III/III}*}] = (-1.72\ \text{V vs}\ \text{Cp}_2\text{Fe}^{+/0}) - (-2.58\ \text{V}) = 0.86\ \text{V vs}\ \text{Cp}_2\text{Fe}^{+/0}$

Estimating the reduction potential of BzOOtBu in DMA:



$E_p \sim -1.938$ V vs $Cp_2Fe^{0/+}$ in DMA

$E_{inf} \sim -1.806$ V vs $Cp_2Fe^{0/+}$ in DMA

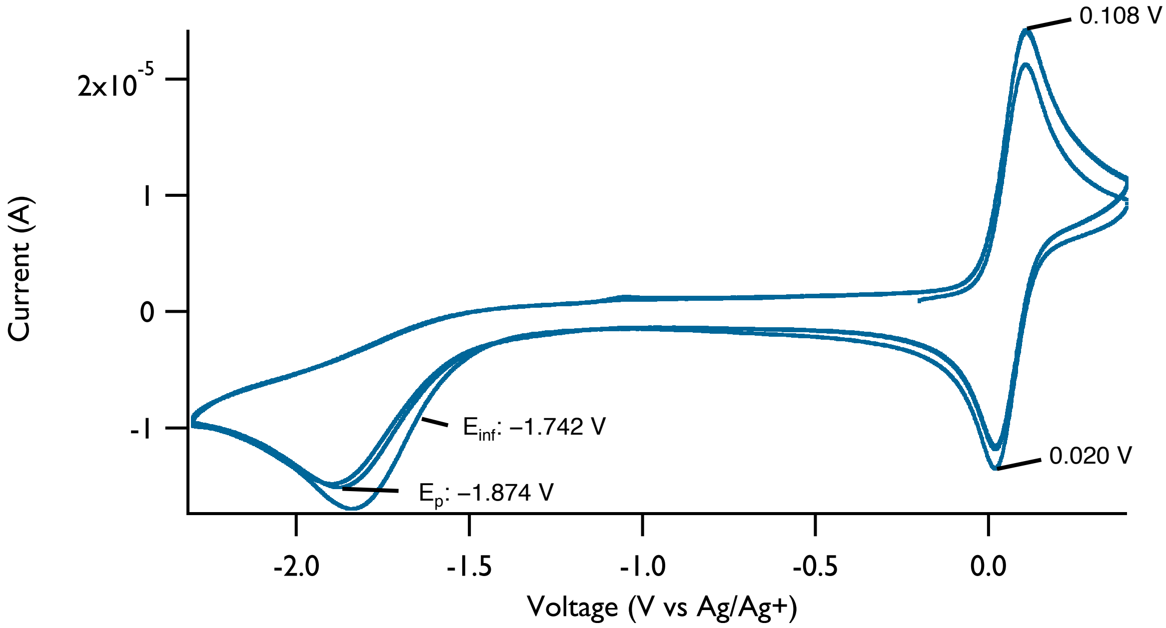
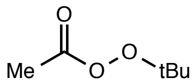


Figure S20. Cyclic voltammogram of BzOOtBu and $FeCp_2^+$ vs. Ag/Ag^+ in DMA at 0.100 Vs^{-1}. *Conditions:* 1 mM perester, 1 mM $FeCp_2^+$ and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag^+ MeCN reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Estimating the reduction potential of AcOOtBu in DMA:



E_p ~ –1.982 V vs $Cp_2Fe^{0/+}$ in DMA

E_{inf} ~ –1.844 V vs $Cp_2Fe^{0/+}$ in DMA

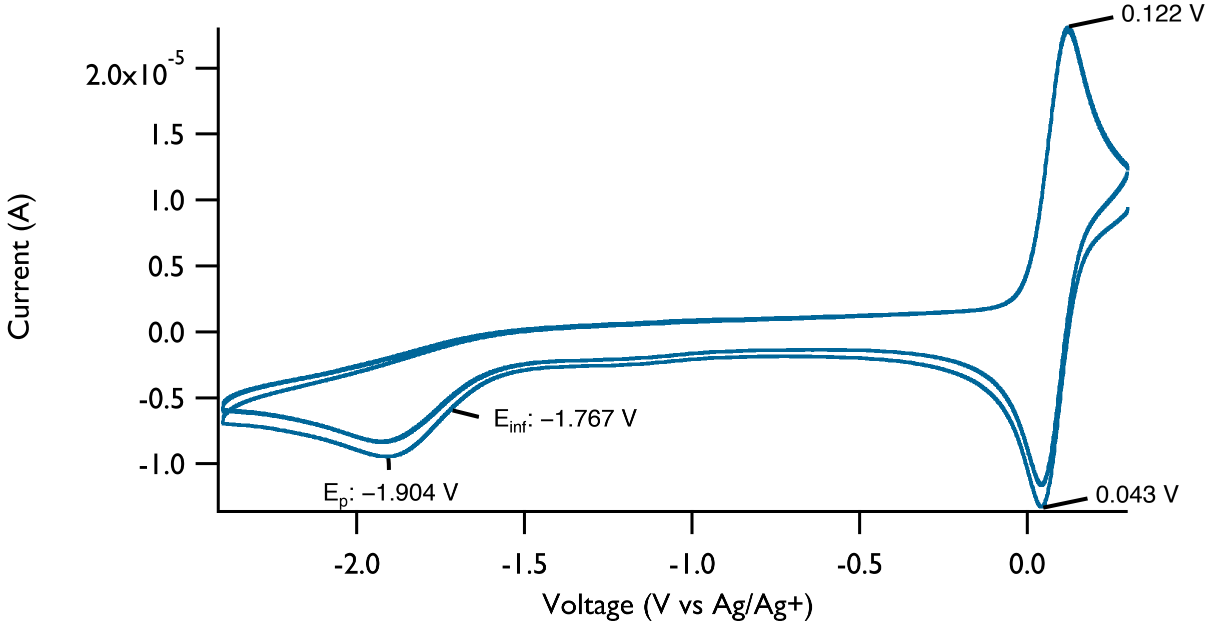
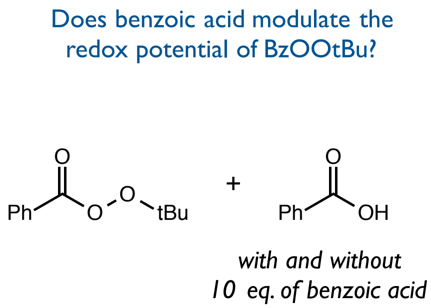


Figure S21. Cyclic voltammogram of AcOOtBu and $FeCp_2^+$ vs. Ag/Ag^+ in DMA at 0.100 Vs^{-1}. *Conditions:* 1 mM AcOOtBu, 1 mM $FeCp_2^+$ and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag^+ MeCN reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Investigating the effect of benzoic acid (pK_a 21.5 in MeCN) on the redox potential of BzOOtBu in DMA:



We questioned whether the benzoic acid formed in the reaction could be acting as a PCET reagent and modulating the redox potential of the perester. No significant Pourbaix-type change in the reduction potential of the perester is observed when benzoic acid is added to a solution of perester.

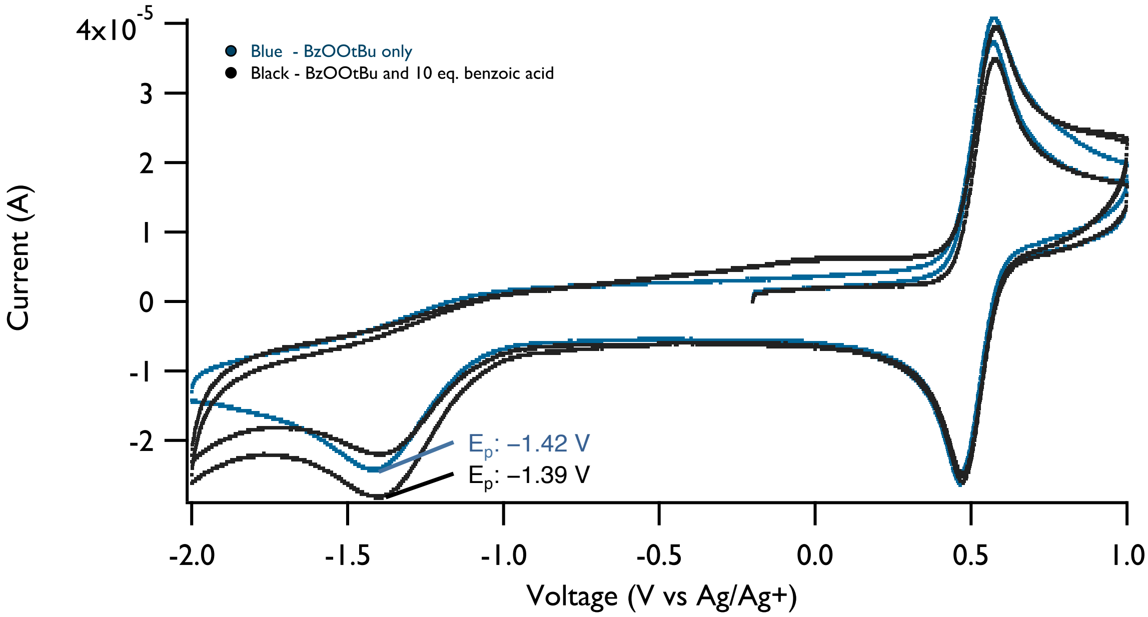
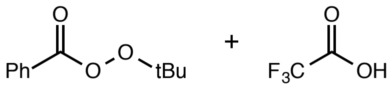


Figure S22. Superimposed cyclic voltammogram of BzOOtBu and $FeCp_2^+$ vs. Ag/Ag^+ in DMA at 0.100 Vs^{-1} with and without 10 mM benzoic acid.

Conditions: 1 mM BzOOtBu, 1 mM $FeCp_2^+$, 10 mM benzoic acid and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag^+ MeCN reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Investigating the effect of trifluoroacid acid (pK_a 12.5 in MeCN) on the redox potential of BzOOtBu:

Does triflouroacidic acid modulate the redox potential of BzOOtBu and AcOOtBu?



with and without 10 eq. of benzoic acid

Trifluoroacetic acid was found to modulate the reduction potential of perester, as shown in Figure S23.

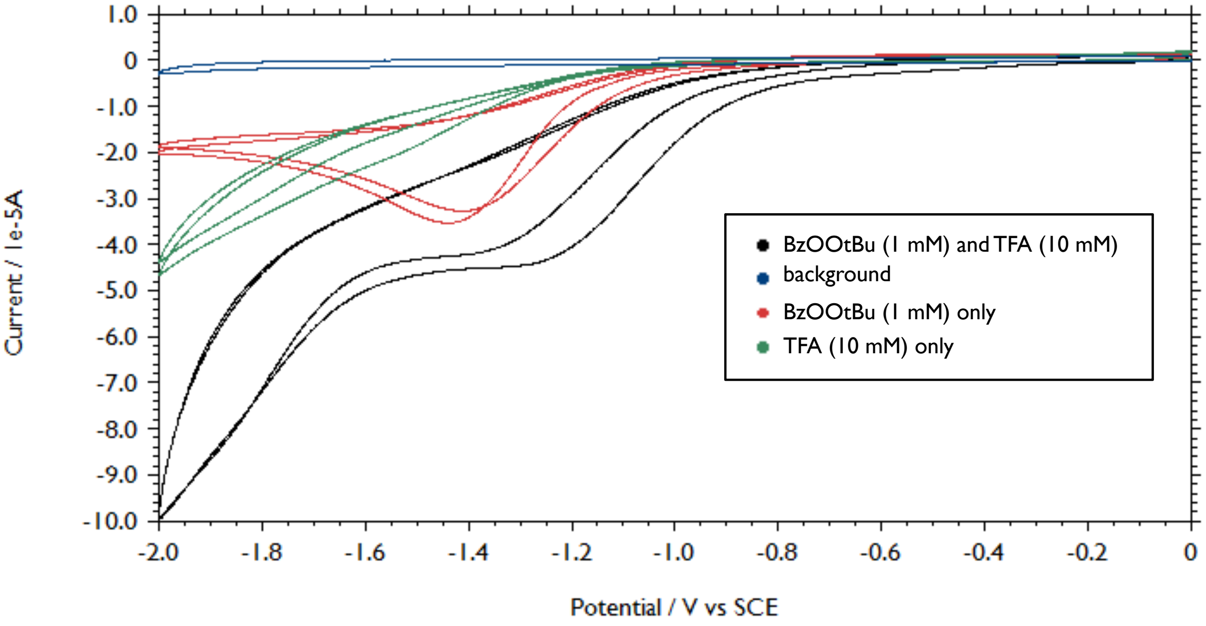
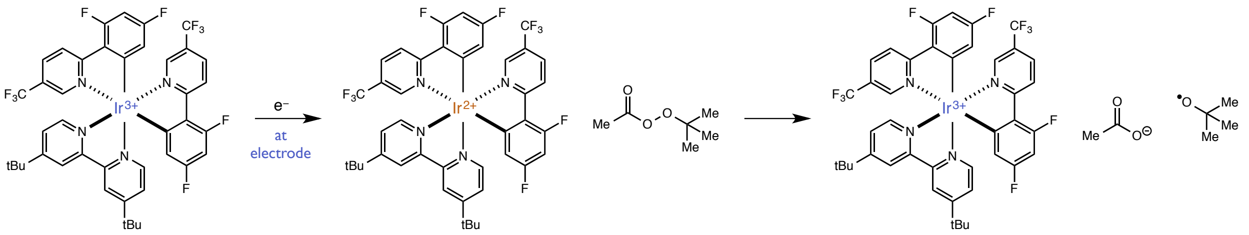


Figure S23. Cyclic voltammogram of BzOOtBu and $FeCp_2^+$ vs. SCE in MeCN at 0.100 Vs^{-1}. *Conditions:* 1 mM BzOOtBu, 10 mM TFA and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, SCE reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

Investigating the feasibility between an electron transfer between the Ir redox catalyst and perester using cyclic voltammetry:



Cyclic voltammogram were collected of a solution containing both Ir catalyst and perester. In the presence of perester, the Ir catalyst becomes a catalytic peak (blue line, Figure S24) where the return wave disappears. The new oxidation wave observed at approximately −0.5 V vs Ag/Ag$^+$ corresponds to the oxidation of tBuO$^-$ to tBuO-radical.[5]

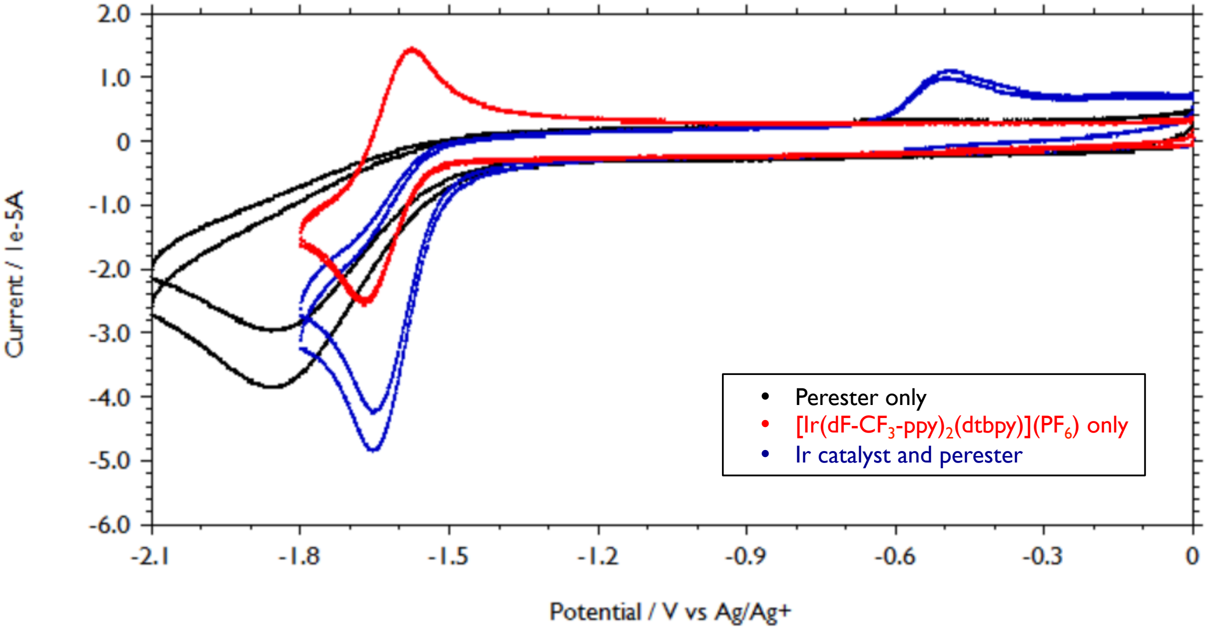


Figure S24. Overlaid cyclic voltammogram of AcOOtBu and [Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) independently and together in solution in DMA at 0.500 Vs^{-1}. *Conditions:* 1 mM AcOOtBu, 1 mM Ir catalyst and 0.1 M tetrabutylammonium hexafluorophosphate. A glassy working electrode, Ag/Ag$^+$ reference electrode and platinum mesh counter electrode were used. The experiment was conducted at 23 °C.

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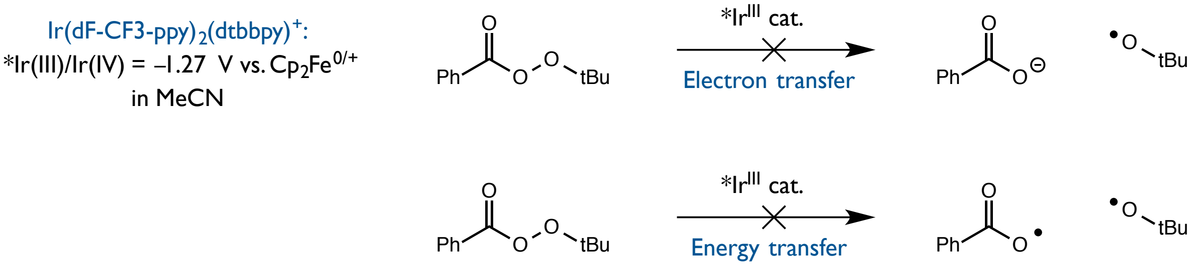
[5] R. Baron, A. Darchen and D. Hauchard, *Electrochimica Acta*, 2006, **51**, 1336–1341.

Investigating possible reaction pathways – Stern-Volmer Studies of *Ir(dF-CF_3-ppy)$_2$(dtbbpy)$^+$ and BzOOtBu:

To assess the feasibility of electron or energy transfer by photoexcited *Ir^{III} photocatalyst to perester, a Stern-Volmer luminescence quenching study was undertaken. No significant quenching was observed (Figure S25) in the same concentration range that compound **1** is found to quench.



Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 2.05 * 10^{-5} M [Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6)] in DMA at room temperature under an inert atmosphere. The solutions were irradiated at 440 nm and luminescence was measured at 480 nm.

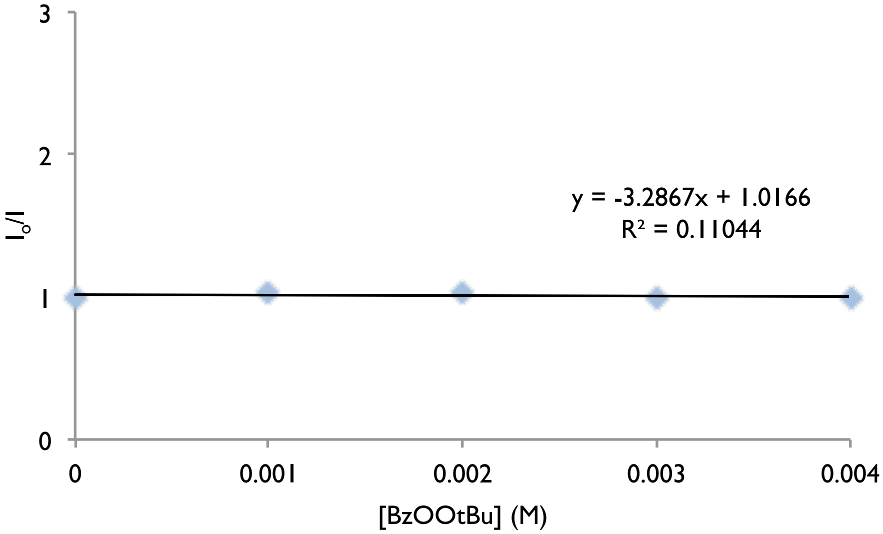


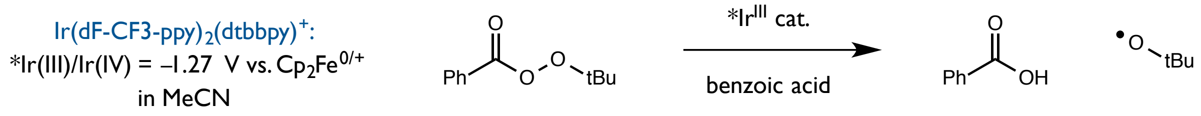
Figure S25. Stern-Volmer plot of Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6) with BzOOtBu. Average of two runs.

Table S2. Results from Stern-Volmer quenching experiments with BzOOtBu

Experiment	Vial	[BzOOtBu] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
Run 1	1	0	572.77	584.30	584.06	580.38	1.00
	2	0.001	570.03	569.75	562.66	567.48	1.02
	3	0.002	576.30	584.73	576.44	579.16	1.00
	4	0.003	615.16	611.07	605.23	610.49	0.95
	5	0.004	582.71	581.69	566.51	576.97	1.01
Experiment	Vial	[BzOOtBu] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
Run 2	1	0	710.33	717.73	710.00	712.69	1.00
	2	0.001	688.00	696.90	672.40	685.77	1.04
	3	0.002	682.75	683.60	684.70	683.69	1.04
	4	0.003	685.54	684.75	685.18	685.16	1.04
	5	0.004	715.40	714.96	714.59	714.99	1.00

Stern-Volmer studies of *Ir(dF-CF$_3$-ppy)$_2$(dtbbpy)$^+$, BzOOtBu and benzoic acid:

To assess the feasibility of a PCET-mediated reduction of perester with the *Ir^{III} photocatalyst and benzoic acid was not occurring, we studied the effect of benzoic acid on the quenching rate. No significant quenching was observed (Figure S26).



Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 2.05 * 10^{-5} M Ir(dF-CF$_3$-ppy)$_2$(dtbbpy)(PF$_6$) in DMA at room temperature under an inert atmosphere. The solutions were irradiated at 440 nm and luminescence was measured at 480 nm.

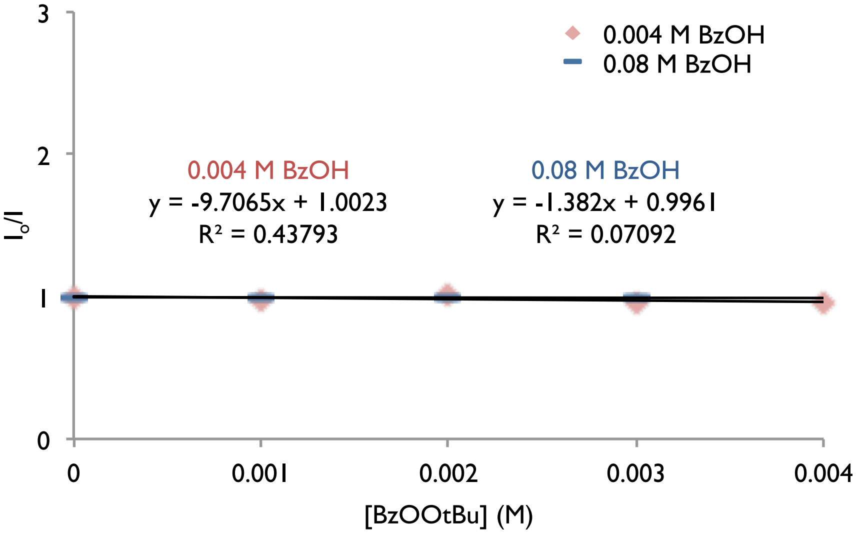
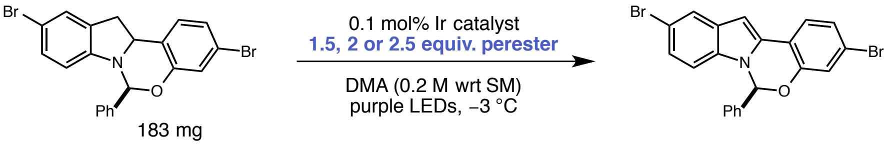


Figure S26. Stern-Volmer plot of Ir(dF-CF$_3$-ppy)$_2$(dtbbpy)(PF$_6$) with BzOOtBu and benzoic acid (0.004 M or 0.08 M).

Table S3. Results from Stern-Volmer experiments with BzOOtBu

Experiment	Vial	[BzOOtBu] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
[BzOH] = 0.004 M	1	0	618.32	620.48	609.00	615.94	1.00
	2	0.001	633.41	623.74	630.91	629.35	0.98
	3	0.002	613.33	605.24	605.69	608.08	1.01
	4	0.003	648.32	631.78	637.10	639.07	0.96
	5	0.004	639.87	641.85	645.28	642.33	0.96
Experiment	Vial	[BzOOtBu] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
[BzOH] = 0.08 M	1	0	630.76	627.53	632.09	630.13	1.00
	2	0.001	637.06	640.71	639.57	639.11	0.99
	3	0.002	630.97	635.23	626.09	630.76	1.00
	4	0.003	636.07	633.46	637.93	635.82	0.99

Determination of kinetic order of perester and starting material using Blackmond's different excess experiment



Blackmond's different excess experiment was used to determine the kinetic order of perester and starting material. Each experiment was repeated thrice.

Standard reaction conditions / General reaction set-up:

A 2 mL volumetric flask was charged with **1** (1 equiv., 0.4 mmol, 183 mg), tert-butyl perbenzoate (2 eq, 0.8 mmol, 152 μL), Ir[(dF-CF_3-ppy)$_2$(dtbpy)]PF_6 (0.1 mol%, 0.4 μmol), Ph_2O (1 eq, 0.4 mmol, 63 uL) and DMA. The solution was then transferred to a 12.5 cm culture tube and sparged with argon in the dark for 60 min. The vials were immersed in a −3 °C Cryocool bath, which was lined with four purple (402 nm) LED strips (see picture of an example set-up at end of kinetic section in SI). The reaction was stirred by continuous sparging. Aliquots were taken with 5−15 minute intervals and pushed through a plug of Celite with 50:50 IPA:hexanes. Samples were analyzed on an Agilent 1260 Infinty HPLC using a Zorbax-Rx Sil 5 um 4.6 x 250 mm column using a 20 minute method with 1% IPA in hexanes as the eluent. UV-absorbances were measured at 230 nm. Starting material conversions and yields were tracked as a function of time from peak areas relative to Ph_2O as an internal standard.

Data analysis: The concentration of **1** was plotted against time and data points between 20% and 80% conversion were used to fit a 5th order polynomial.

$$[\mathbf{1}] = f(t) = a + bt + ct^2 + dt^3 + et^4 + ft^5$$

The derivative of this polynomial was calculated and d[**1**]/dt was plotted as a function of [**1**]. To validate this approach, the same raw data was fit to a second order exponential function given below.

$$[\mathbf{1}] = f(t) = y_0 + A_1 e^{-y_1 t} + A_2 e^{-y_2 t}$$

The derivative of the second order exponential function was also calculated and plotted as a function of [**1**]. Both methods produced essentially identical graphical rate equations, indicating that the method of fitting does not impact the underlying kinetic data. A representative example is shown below in Figure S27:

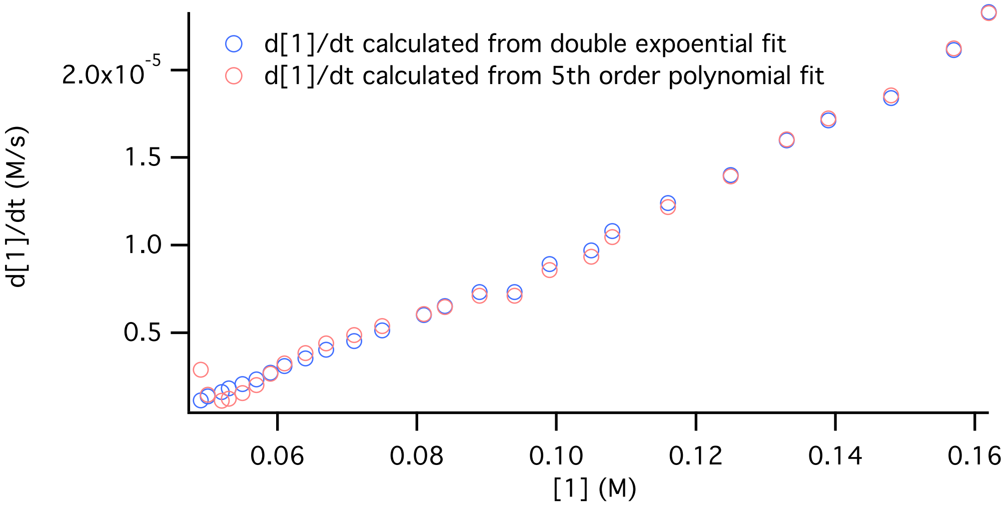


Figure S27. Example of a reaction progress profile for a reaction obtained using two different fitting functions. *Specific conditions:* 0.2 M **1**, 0.3 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM Ir[Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

Next, the normalized rate (d[**1**]/dt / [perester]) was plotted against [**1**] (see Figure S28 for a summary of all results). For the different excess experiment, each experiment was run in triplicate.

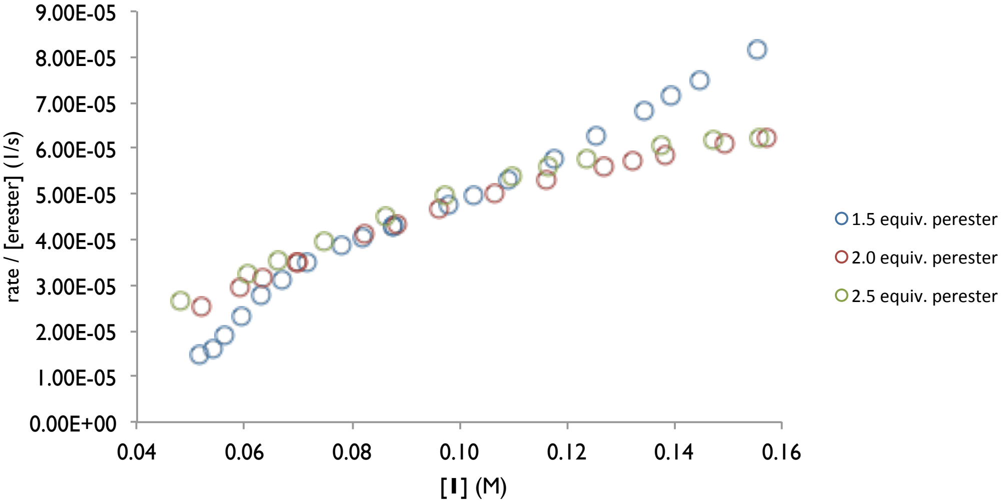


Figure S28. Relative rate (corrected for [perester]) as a function of starting material concentration ([**1**]) at different concentrations of perester. Each plot is an average of three independent runs.

Table S4. Relative rate (corrected for [perester]) as a function of starting material concentration ([**1**]) at different concentrations of perester. Each entry is an average of three runs.

1.5 equiv. of BzOOtBu used

Time (s)	Mean [**1**] (M)	Mean -d[**1**]/dt (M/s)	Mean [perester] (M)	Normalized rate: -d[**1**]/dt / [perester] (1/s)
2100.00	1.63E-01	2.27E-05	2.68E-01	8.47E-05
2460.00	1.55E-01	2.08E-05	2.59E-01	8.03E-05
3000.00	1.45E-01	1.83E-05	2.47E-01	7.40E-05
3300.00	1.40E-01	1.71E-05	2.42E-01	7.07E-05
3600.00	1.35E-01	1.60E-05	2.36E-01	6.76E-05
4200.00	1.26E-01	1.41E-05	2.28E-01	6.20E-05
4800.00	1.18E-01	1.26E-05	2.20E-01	5.72E-05
5520.00	1.09E-01	1.11E-05	2.12E-01	5.24E-05
6120.00	1.03E-01	1.01E-05	2.06E-01	4.91E-05
6600.00	9.80E-02	9.42E-06	2.01E-01	4.68E-05
7800.00	8.76E-02	8.06E-06	1.90E-01	4.23E-05
7800.00	8.76E-02	8.06E-06	1.90E-01	4.23E-05
8520.00	8.20E-02	7.36E-06	1.84E-01	4.00E-05
9060.00	7.82E-02	6.87E-06	1.80E-01	3.82E-05
10080.00	7.16E-02	5.97E-06	1.72E-01	3.47E-05
10920.00	6.69E-02	5.21E-06	1.66E-01	3.14E-05
11700.00	6.31E-02	4.51E-06	1.61E-01	2.79E-05
12600.00	5.95E-02	3.71E-06	1.57E-01	2.36E-05
13500.00	5.64E-02	3.00E-06	1.54E-01	1.95E-05
14400.00	5.40E-02	2.47E-06	1.52E-01	1.63E-05
15420.00	5.16E-02	2.23E-06	1.49E-01	1.50E-05
16260.00	4.97E-02	2.50E-06	1.47E-01	1.71E-05
17100.00	4.73E-02	3.36E-06	1.42E-01	2.36E-05
18000.00	4.35E-02	5.13E-06	1.33E-01	3.85E-05

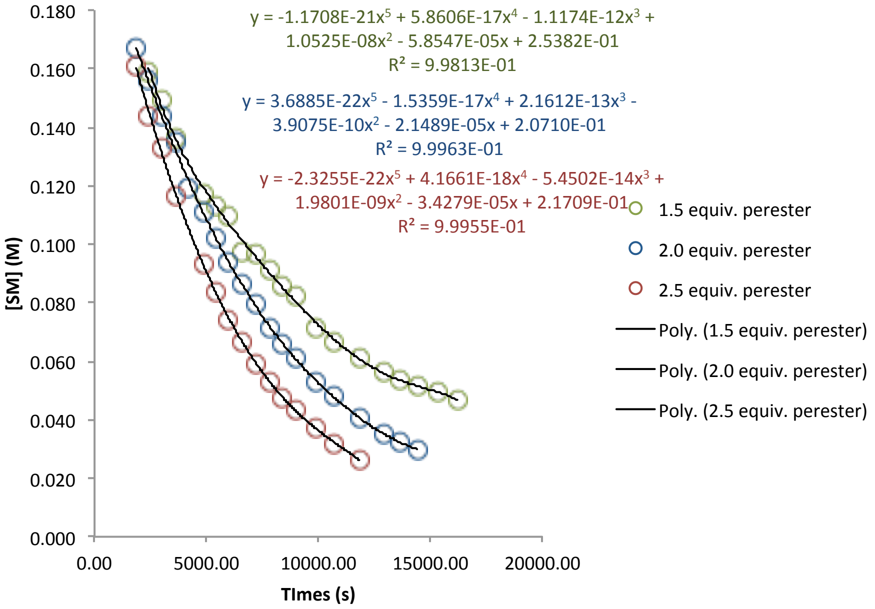
2.0 equiv. of BzOOtBu used

Time (s)	Mean [**1**] (M)	Mean -d[**1**]/dt (M/s)	Mean [perester] (M)	Normalized rate: -d[**1**]/dt / [perester] (1/s)
2100.00	1.57E-01	2.19E-05	3.64E-01	6.01E-05
2460.00	1.50E-01	2.15E-05	3.57E-01	6.02E-05
3000.00	1.39E-01	2.10E-05	3.50E-01	6.00E-05
3300.00	1.33E-01	2.00E-05	3.39E-01	5.90E-05
3600.00	1.27E-01	1.93E-05	3.33E-01	5.81E-05
4200.00	1.16E-01	1.87E-05	3.27E-01	5.71E-05
4800.00	1.06E-01	1.72E-05	3.16E-01	5.45E-05
5520.00	9.57E-02	1.57E-05	3.06E-01	5.13E-05
6120.00	8.78E-02	1.39E-05	2.96E-01	4.71E-05
6600.00	8.21E-02	1.25E-05	2.88E-01	4.35E-05
7800.00	6.98E-02	1.14E-05	2.82E-01	4.06E-05
7800.00	6.98E-02	9.14E-06	2.70E-01	3.39E-05
8520.00	6.36E-02	9.14E-06	2.70E-01	3.39E-05
9060.00	5.94E-02	8.04E-06	2.64E-01	3.05E-05
10080.00	5.25E-02	7.36E-06	2.59E-01	2.84E-05
10920.00	4.74E-02	6.37E-06	2.52E-01	2.52E-05
11700.00	4.31E-02	5.75E-06	2.47E-01	2.32E-05
12600.00	3.87E-02	5.23E-06	2.43E-01	2.15E-05
13500.00	3.51E-02	4.53E-06	2.39E-01	1.90E-05
14400.00	3.26E-02	3.49E-06	2.35E-01	1.48E-05

2.5 equiv. of BzOOtBu used

Time (s)	Mean [**1**] (M)	Mean -d[**1**]/dt (M/s)	Mean [perester] (M)	Normalized rate: -d[**1**]/dt / [perester] (1/s)
1800.00	1.56E-01	2.88E-05	4.56E-01	6.32E-05
2100.00	1.47E-01	2.78E-05	4.47E-01	6.22E-05
2460.00	1.38E-01	2.66E-05	4.38E-01	6.07E-05
3000.00	1.24E-01	2.45E-05	4.24E-01	5.78E-05
3300.00	1.17E-01	2.33E-05	4.17E-01	5.59E-05
3600.00	1.10E-01	2.21E-05	4.10E-01	5.38E-05
4200.00	9.73E-02	1.96E-05	3.97E-01	4.94E-05
4800.00	8.63E-02	1.73E-05	3.86E-01	4.48E-05
5520.00	7.47E-02	1.48E-05	3.75E-01	3.95E-05
6120.00	6.64E-02	1.30E-05	3.66E-01	3.55E-05
6600.00	6.05E-02	1.17E-05	3.60E-01	3.26E-05
7800.00	4.79E-02	9.32E-06	3.48E-01	2.68E-05
7800.00	4.79E-02	9.32E-06	3.48E-01	2.68E-05
8520.00	4.16E-02	8.20E-06	3.42E-01	2.40E-05
9060.00	3.74E-02	7.40E-06	3.37E-01	2.19E-05
10080.00	3.07E-02	5.63E-06	3.31E-01	1.70E-05

Raw data - Run 1:



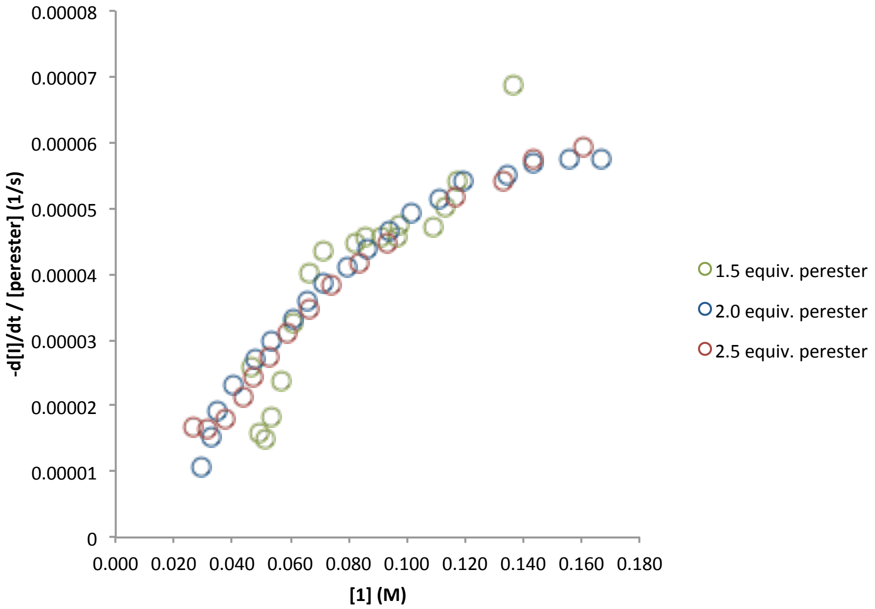


Figure S29. Kinetics plots for different excess experiment. *Top*: Starting material (**1**) conversion versus time. *Middle*: [**1**] versus time fitted to a 5th order polynomial using only data points between 20 and 80% conversion. *Bottom*: Normalized reaction progress profiles with respect to perester concentration at different perester loadings ((rate/[perester]) versus [1])

Table S5. Results from kinetic run using 1.5 equiv. perester: 0.2 M 1, 0.3 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 ^{o}C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	42.375	0	57.625	1.36	0%	0.200	0.300
300.00	42.14	1.687	56.173	1.33	2%	0.196	0.296
630.00	41.63	3.933	54.437	1.31	4%	0.192	0.292
1200.00	41.614	8.3887	49.9973	1.20	12%	0.177	0.277
1500.00	40.813	10.61	48.577	1.19	12%	0.175	0.275
1860.00	40.396	13.435	46.169	1.14	16%	0.168	0.268
2400.00	39.829	17.077	43.094	1.08	20%	0.159	0.259
3000.00	39.131	21.16	39.709	1.01	25%	0.149	0.249
3600.00	39.153	24.489	36.358	0.93	32%	0.137	0.237
4860.00	38.4	30.955	30.645	0.80	41%	0.117	0.217
5400.00	37.428	33.817	28.755	0.77	44%	0.113	0.213
6000.00	36.762	35.918	27.32	0.74	45%	0.109	0.209
6600.00	37.265	38.08	24.655	0.66	51%	0.097	0.197
7200.00	36.389	39.695	23.916	0.66	52%	0.097	0.197
7800.00	36.08	41.488	22.432	0.62	54%	0.091	0.191
8400.00	35.747	43.405	20.848	0.58	57%	0.086	0.186
9000.00	35.676	44.424	19.9	0.56	59%	0.082	0.182
9900.00	35.809	46.845	17.346	0.48	64%	0.071	0.171
10680.00	35.48	48.426	16.094	0.45	67%	0.067	0.167
11820.00	35.216	50.24	14.544	0.41	70%	0.061	0.161
12900.00	35.063	51.457	13.48	0.38	72%	0.057	0.157
13680.00	35.128	52.077	12.795	0.36	73%	0.054	0.154
14400.00	35.114	52.583	12.303	0.35	74%	0.052	0.152
15300.00	34.907	53.4	11.693	0.33	75%	0.049	0.149
16200.00	34.946	53.917	11.137	0.32	77%	0.047	0.147
17100.00	34.879	54.341	10.78	0.31	77%	0.045	0.145
18000.00	34.859	54.684	10.457	0.30	78%	0.044	0.144
18900.00	34.717	55.067	10.216	0.29	78%	0.043	0.143
19800.00	34.78	55.244	9.976	0.29	79%	0.042	0.142

Table S6. Results from kinetic run using 2 equiv. perester: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM Ir[Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	42.359	0	57.641	1.360773389	0%	0.200	0.400
300.00	41.83	1.462	56.708	1.355677743	0%	0.199	0.399
630.00	41.575	3.258	55.167	1.32692724	2%	0.195	0.395
1200.00	41.504	7.464	51.032	1.229568234	10%	0.181	0.381
1500.00	41.572	9.736	48.692	1.171269123	14%	0.172	0.372
1860.00	40.736	13.003	46.261	1.135629419	17%	0.167	0.367
2400.00	40.218	17.165	42.617	1.059649908	22%	0.156	0.356
3000.00	39.441	22.059	38.5	0.976141579	28%	0.143	0.343
3600.00	38.462	26.327	35.211	0.915475014	33%	0.135	0.335
4200.00	38.491	30.23	31.279	0.812631524	40%	0.119	0.319
4860.00	37.654	33.86	28.486	0.756519892	44%	0.111	0.311
5400.00	37.122	37.164	25.714	0.692688971	49%	0.102	0.302
6000.00	36.678	39.914	23.408	0.638202737	53%	0.094	0.294
6600.00	36.274	42.403	21.323	0.587831505	57%	0.086	0.286
7200.00	36.089	44.44	19.471	0.53952728	60%	0.079	0.279
7800.00	36.261	46.129	17.61	0.485645735	64%	0.071	0.271
8400.00	35.324	48.888	15.788	0.44694825	67%	0.066	0.266
9000.00	35.172	50.198	14.63	0.415955874	69%	0.061	0.261
9900.00	35.084	52.225	12.691	0.361731844	73%	0.053	0.253
10680.00	34.742	53.955	11.303	0.325341086	76%	0.048	0.248
11820.00	34.543	55.941	9.516	0.275482732	80%	0.040	0.240
12900.00	34.727	57.01	8.263	0.237941659	83%	0.035	0.235
13680.00	34.409	57.939	7.652	0.222383679	84%	0.033	0.233
14400.00	34.468	58.578	6.954	0.20175235	85%	0.030	0.230
15300.00	34.483	59.203	6.314	0.183104718	87%	0.027	0.227
16200.00	34.244	60.021	5.735	0.167474594	88%	0.025	0.225
17100.00	34.056	60.654	5.29	0.155332394	89%	0.023	0.223
18000.00	34.195	60.681	5.124	0.149846469	89%	0.022	0.222
18900.00	34.272	61.293	4.435	0.129405929	90%	0.019	0.219
19800.00	34.78	61.76	3.46	0.099482461	93%	0.015	0.215

Table S7. Results from kinetic run using 2.5 equiv. perester: 0.2 M 1, 0.5 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM Ir[Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	41.893	0	58.107	1.387033633	0%	0.200	0.500
300.00	41.766	1.51	56.724	1.358138199	2%	0.196	0.496
630.00	41.323	3.55	55.127	1.334051255	4%	0.192	0.492
1200.00	41.358	8.546	50.096	1.211277141	13%	0.175	0.475
1500.00	40.577	11.391	48.032	1.18372477	15%	0.171	0.471
1860.00	40.074	15.299	44.627	1.113614813	20%	0.161	0.461
2400.00	39.832	20.502	39.666	0.995832496	28%	0.144	0.444
3000.00	38.531	25.938	35.531	0.922140614	34%	0.133	0.433
3600.00	37.857	31.588	30.555	0.807116253	42%	0.116	0.416
4860.00	36.915	39.228	23.857	0.646268455	53%	0.093	0.393
5400.00	36.244	42.709	21.047	0.580703013	58%	0.084	0.384
6000.00	35.83	45.709	18.461	0.515238627	63%	0.074	0.374
6600.00	35.5	48.179	16.321	0.459746479	67%	0.066	0.366
7200.00	35.551	49.878	14.571	0.409861889	70%	0.059	0.359
7800.00	35.239	51.812	12.949	0.367462187	74%	0.053	0.353
8400.00	34.904	53.662	11.434	0.327584231	76%	0.047	0.347
9000.00	34.863	54.624	10.513	0.301551788	78%	0.043	0.343
9900.00	34.538	56.529	8.933	0.258642654	81%	0.037	0.337
10680.00	34.44	58.01	7.55	0.219221835	84%	0.032	0.332
11820.00	33.952	59.834	6.214	0.183023091	87%	0.026	0.326
12900.00	34.286	60.885	4.829	0.14084466	90%	0.020	0.320
13680.00	34.364	61.397	4.239	0.123355838	91%	0.018	0.318
14400.00	34.259	62.159	3.582	0.104556467	92%	0.015	0.315
15300.00	34.336	62.68	2.984	0.086905871	94%	0.013	0.313
16200.00	34.337	63.277	2.386	0.069487725	95%	0.010	0.310
17100.00	34.432	63.488	2.08	0.060408922	96%	0.009	0.309
18000.00	34.339	63.826	1.835	0.053437782	96%	0.008	0.308
18900.00	34.277	64.148	1.575	0.045949179	97%	0.007	0.307
19800.00	34.953	64.331	0.716	0.020484651	99%	0.003	0.303

Raw data - Run 2:

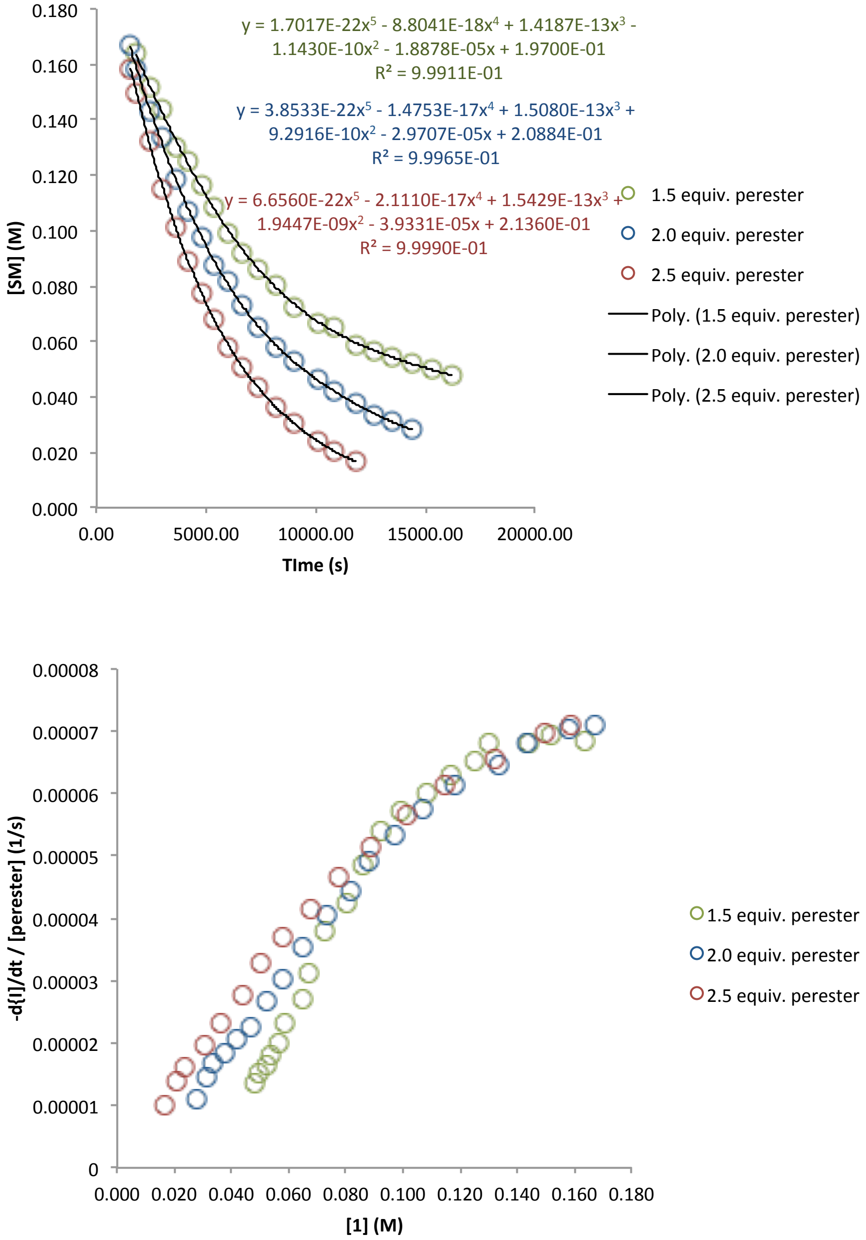


Figure S30. Kinetics plots for different excess experiment. *Top*: Starting material (**1**) conversion versus time. *Middle*: [Starting material] versus time fitted to a 5th order polynomial using only data points between 20 and 80% conversion. *Bottom*: Normalized reaction progress profiles with respect to perester concentration at different perester loadings ((rate/[perester]) versus [1])

Table S8. Results from kinetic run using 1.5 equiv. perester: 0.2 M 1, 0.3 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	42.809	0	57.191	1.33595739	0%	0.200	0.300
300.00	42.317	2.2	55.483	1.31112792	2%	0.196	0.296
600.00	42.181	4.334	53.485	1.26798796	5%	0.190	0.290
900.00	41.548	7.069	51.383	1.23671416	7%	0.185	0.285
1230.00	40.631	9.743	49.626	1.22138269	9%	0.183	0.283
1530.00	40.635	12.583	46.782	1.15127353	14%	0.172	0.272
1800.00	40.461	15.215	44.324	1.09547465	18%	0.164	0.264
2400.00	39.806	19.906	40.288	1.01210873	24%	0.152	0.252
3000.00	38.621	24.266	37.113	0.96095389	28%	0.144	0.244
3600.00	38.413	28.205	33.382	0.86902871	35%	0.130	0.230
4200.00	37.278	31.624	31.098	0.83421857	38%	0.125	0.225
4800.00	36.767	34.589	28.644	0.77906819	42%	0.117	0.217
5400.00	36.549	36.98	26.471	0.72426058	46%	0.108	0.208
6000.00	36.579	39.124	24.297	0.66423358	50%	0.099	0.199
6600.00	36.328	41.343	22.329	0.61464986	54%	0.092	0.192
7380.00	35.757	43.707	20.536	0.57432111	57%	0.086	0.186
8220.00	35.499	45.487	19.014	0.53562072	60%	0.080	0.180
9000.00	35.538	47.198	17.264	0.48578986	64%	0.073	0.173
10080.00	35.352	48.824	15.824	0.44761258	66%	0.067	0.167
10800.00	35.11	49.628	15.262	0.43469097	67%	0.065	0.165
11820.00	35.114	51.085	13.801	0.39303412	71%	0.059	0.159
12660.00	34.978	51.747	13.275	0.37952427	72%	0.057	0.157
13500.00	35.002	52.357	12.641	0.36115079	73%	0.054	0.154
14400.00	34.84	53.051	12.109	0.34756028	74%	0.052	0.152
15300.00	34.958	53.434	11.608	0.33205561	75%	0.050	0.150
16200.00	34.81	54.061	11.129	0.31970698	76%	0.048	0.148
17100.00	34.873	54.234	10.893	0.312362	77%	0.047	0.147
18000.00	34.87	54.652	10.478	0.30048753	78%	0.045	0.145
18900.00	34.789	54.897	10.314	0.29647302	78%	0.044	0.144
19800.00	34.604	55.319	10.077	0.29120911	78%	0.044	0.144

Table S9. Results from kinetic run using 2.0 equiv. perester: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	42.468	0	57.532	1.35471414	0%	0.200	0.400
300.00	42.423	2.2	55.377	1.30535323	4%	0.193	0.393
600.00	42.207	4.603	53.19	1.2602175	7%	0.186	0.386
900.00	41.635	7.256	51.109	1.22754894	9%	0.181	0.381
1230.00	40.993	10.98	48.027	1.17159027	14%	0.173	0.373
1530.00	40.322	14.096	45.582	1.13044988	17%	0.167	0.367
1800.00	40.176	16.768	43.056	1.07168459	21%	0.158	0.358
2400.00	39.521	22.188	38.291	0.96887731	28%	0.143	0.343
3000.00	38.121	27.405	34.474	0.90433095	33%	0.134	0.334
3600.00	37.983	31.57	30.447	0.80159545	41%	0.118	0.318
4200.00	37.239	35.788	26.973	0.72432128	47%	0.107	0.307
4800.00	36.723	39.03	24.247	0.66026741	51%	0.097	0.297
5400.00	36.513	41.786	21.701	0.59433626	56%	0.088	0.288
6000.00	36.044	44.043	19.913	0.55246366	59%	0.082	0.282
6600.00	35.871	46.287	17.842	0.49739344	63%	0.073	0.273
7380.00	35.402	48.963	15.635	0.44164172	67%	0.065	0.265
8220.00	35.348	50.737	13.915	0.39365735	71%	0.058	0.258
9000.00	35.122	52.365	12.513	0.35627242	74%	0.053	0.253
10080.00	34.843	54.174	10.983	0.31521396	77%	0.047	0.247
10800.00	34.858	55.254	9.888	0.28366516	79%	0.042	0.242
11820.00	34.779	56.349	8.872	0.25509647	81%	0.038	0.238
12660.00	34.81	57.254	7.936	0.22798047	83%	0.034	0.234
13500.00	35.294	57.27	7.436	0.21068737	84%	0.031	0.231
14400.00	34.531	58.877	6.592	0.19090093	86%	0.028	0.228
15300.00							
16200.00	34.543	59.942	5.515	0.15965608	88%	0.024	0.224
17100.00	34.762	60.258	4.98	0.14325988	89%	0.021	0.221
18000.00	34.552	60.854	4.594	0.13295902	90%	0.020	0.220
18900.00	34.405	61.371	4.224	0.12277285	91%	0.018	0.218
19800.00	34.467	61.632	3.901	0.11318072	92%	0.017	0.217

Table S10. Results from kinetic run using 2.5 equiv. perester: 0.2 M 1, 0.5 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	42.386	0	57.614	1.35926957	0%	0.200	0.500
300.00	42.181	2.044	55.775	1.3222778	3%	0.195	0.495
600.00	42.015	4.902	53.083	1.26342973	7%	0.186	0.486
900.00	41.38	8.138	50.482	1.21996133	10%	0.180	0.480
1230.00	40.78	12.308	46.912	1.15036783	15%	0.169	0.469
1530.00	40.27	16.365	43.365	1.07685622	21%	0.158	0.458
1800.00	39.717	19.882	40.401	1.01722184	25%	0.150	0.450
2400.00	38.629	26.601	34.77	0.90010096	34%	0.132	0.432
3000.00	37.704	32.85	29.446	0.78097815	43%	0.115	0.415
3600.00	36.942	37.65	25.408	0.68778085	49%	0.101	0.401
4200.00	36.064	42.137	21.799	0.60445319	56%	0.089	0.389
4800.00	35.736	45.509	18.755	0.52482091	61%	0.077	0.377
5400.00	35.44	48.192	16.368	0.46185102	66%	0.068	0.368
6000.00	35.262	50.79	13.948	0.39555329	71%	0.058	0.358
6600.00	35.214	52.693	12.093	0.34341455	75%	0.051	0.351
7380.00	34.491	55.235	10.274	0.29787481	78%	0.044	0.344
8220.00	34.662	56.843	8.495	0.24508107	82%	0.036	0.336
9000.00	34.483	58.35	7.167	0.20784155	85%	0.031	0.331
10080.00	35.024	59.3	5.676	0.1620603	88%	0.024	0.324
10800.00	34.52	60.63	4.85	0.14049826	90%	0.021	0.321
11820.00	34.432	61.651	3.917	0.11376046	92%	0.017	0.317
12660.00	34.614	62.052	3.334	0.09631941	93%	0.014	0.314
13500.00	34.628	62.571	2.801	0.0808883	94%	0.012	0.312
14400.00	34.727	62.823	2.45	0.07055029	95%	0.010	0.310
15300.00	34.76	63.103	2.137	0.06147871	95%	0.009	0.309
16200.00	35.084	63.074	1.842	0.05250257	96%	0.008	0.308
17100.00	34.923	63.446	1.631	0.04670275	97%	0.007	0.107
18000.00	35.079	63.866	1.055	0.03007497	98%	0.004	0.104
18900.00	35.171	63.903	0.926	0.02632851	98%	0.004	0.104
19800.00	35.058	63.953	0.989	0.02821039	98%	0.004	0.104

Raw data - Run 3:

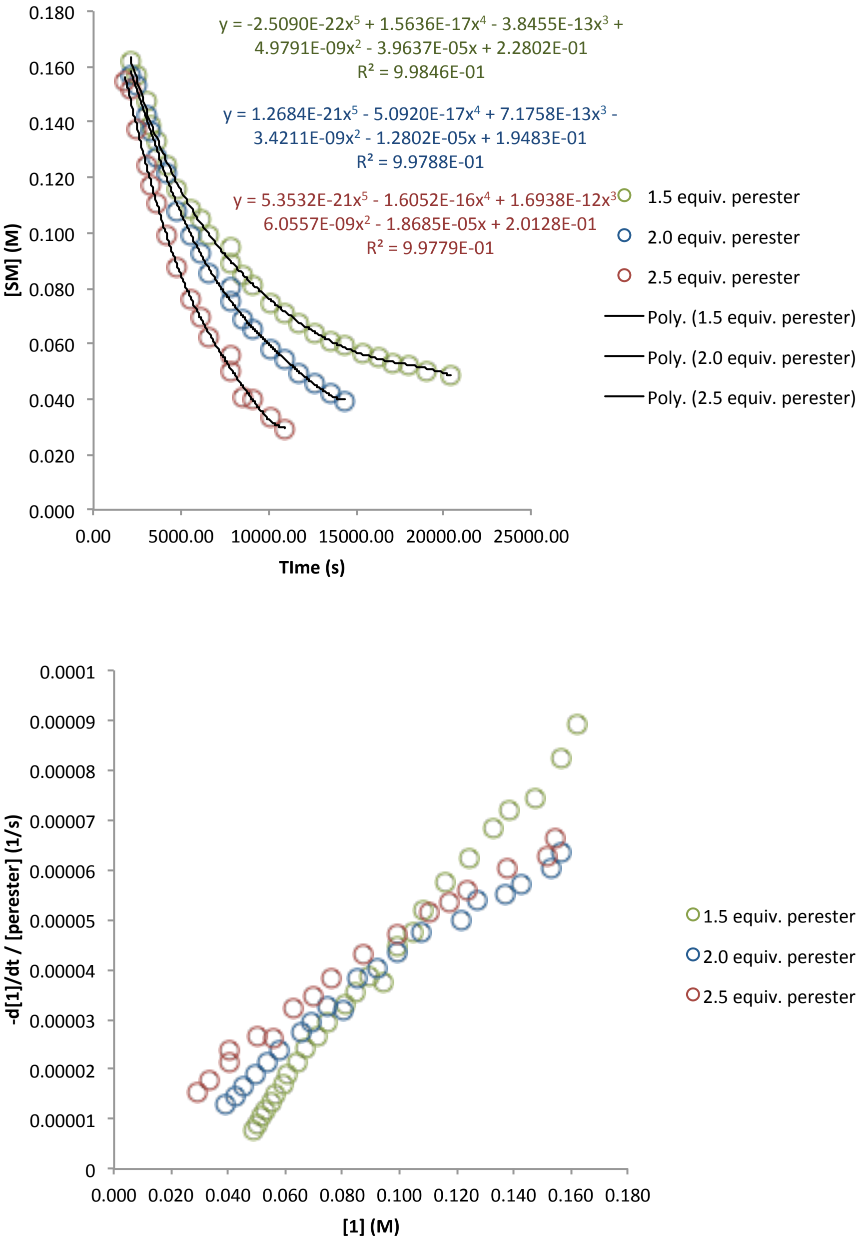


Figure S31. Kinetics plots for different excess experiment. *Top*: Starting material (1) conversion versus time. *Middle*: [Starting material] versus time fitted to a 5th order polynomial using only data points between 20 and 80% conversion. *Bottom*: Normalized reaction progress profiles with respect to perester concentration at different perester loadings ((rate/[perester]) versus [1])

Table S11. Results from kinetic run using 1.5 equiv. perester: 0.2 M 1, 0.3 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	Yield	[SM] (M)	[Peracid] (M)
0.00	42.83	0	57.17	1.33481205	0%	0%	0.200	0.300
300.00	42.745	2.05	55.205	1.29149608	3%	2%	0.194	0.294
600.00	42.228	4.508	53.264	1.26134318	6%	5%	0.189	0.289
900.00	41.906	6.989	51.105	1.21951511	9%	7%	0.183	0.283
1200.00	41.396	9.585	49.019	1.18414823	11%	10%	0.177	0.277
1500.00	41.135	12.009	46.856	1.13907864	15%	13%	0.171	0.271
1800.00	40.752	14.44	44.808	1.09952886	18%	16%	0.165	0.265
2100.00	40.038	16.681	43.281	1.08099805	19%	19%	0.162	0.262
2460.00	39.421	19.334	41.245	1.04626975	22%	22%	0.157	0.257
3000.00	38.807	22.905	38.288	0.98662612	26%	26%	0.148	0.248
3300.00	39.049	24.804	36.147	0.92568312	31%	28%	0.139	0.239
3600.00	38.843	26.622	34.535	0.88909199	33%	30%	0.133	0.233
4200.00	38.465	29.555	31.98	0.83140517	38%	34%	0.125	0.225
4800.00	38.162	32.34	29.498	0.77296787	42%	38%	0.116	0.216
5520.00	37.643	35.112	27.245	0.72377334	46%	42%	0.108	0.208
6120.00	37.06	36.972	25.968	0.70070157	48%	44%	0.105	0.205
6600.00	36.93	38.557	24.513	0.66376929	50%	46%	0.099	0.199
7800.00	36.721	40.129	23.15	0.63042945	53%	49%	0.094	0.194
7800.00	36.498	41.741	21.761	0.59622445	55%	51%	0.089	0.189
8520.00	36.272	43.297	20.431	0.56327195	58%	53%	0.084	0.184
9060.00	36.21	44.26	19.53	0.53935377	60%	54%	0.081	0.181
10080.00	36.003	46.031	17.966	0.49901397	63%	57%	0.075	0.175
10920.00	35.894	47.091	17.015	0.47403466	64%	58%	0.071	0.171
11700.00	35.831	48.114	16.055	0.44807569	66%	60%	0.067	0.167
12600.00	35.715	49.032	15.253	0.42707546	68%	61%	0.064	0.164
13500.00	35.658	49.802	14.54	0.40776263	69%	62%	0.061	0.161
14400.00	35.394	50.562	14.044	0.39679042	70%	64%	0.059	0.159
15420.00	35.398	51.244	13.358	0.37736595	72%	64%	0.057	0.157
16260.00	35.417	51.578	13.005	0.36719654	72%	65%	0.055	0.155
17100.00	35.468	51.932	12.6	0.3552498	73%	65%	0.053	0.153
18000.00	35.302	52.474	12.224	0.34626933	74%	66%	0.052	0.152
19080.00	35.247	52.908	11.845	0.33605697	75%	67%	0.050	0.150
20400.00	35.222	53.323	11.455	0.32522287	76%	67%	0.049	0.149

Table S12. Results from kinetic run using 2.0 equiv. perester: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 ^oC using purple LEDs

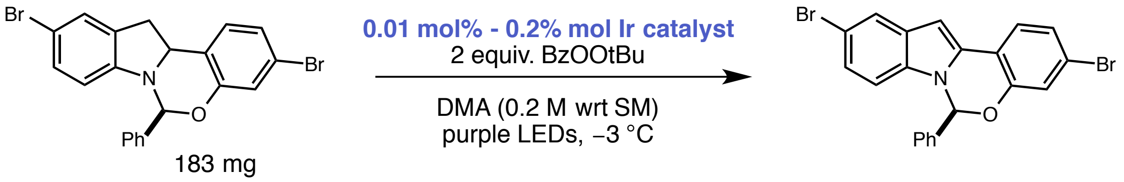
Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	42.432	0	57.568	1.35671192	0%	0.200	0.400
300.00	42.161	2.046	55.793	1.32333199	2%	0.195	0.395
600.00	41.841	4.318	53.841	1.28680003	5%	0.190	0.390
900.00	40.618	8.61	50.772	1.24998769	8%	0.184	0.384
1200.00	41.166	9.583	49.251	1.19639994	12%	0.176	0.376
1500.00	40.687	12.377	46.936	1.15358714	15%	0.170	0.370
1800.00	40.354	15.135	44.511	1.10301333	19%	0.163	0.363
2100.00	39.911	17.706	42.383	1.06193781	22%	0.157	0.357
2460.00	38.867	20.688	40.445	1.04059999	23%	0.153	0.353
3000.00	38.216	24.776	37.008	0.9683902	29%	0.143	0.343
3300.00	37.872	26.942	35.186	0.92907689	32%	0.137	0.337
3600.00	38.095	29.031	32.874	0.86294789	36%	0.127	0.327
4200.00	37.124	32.26	30.616	0.82469561	39%	0.122	0.322
4800.00	37.241	35.48	27.279	0.73249913	46%	0.108	0.308
5520.00	36.782	38.493	24.725	0.6722038	50%	0.099	0.299
6120.00	36.438	40.708	22.854	0.62720237	54%	0.092	0.292
6600.00	36.551	42.251	21.198	0.57995677	57%	0.085	0.285
7800.00	36.065	44.229	19.706	0.54640233	60%	0.081	0.281
7800.00	35.838	45.902	18.26	0.50951504	62%	0.075	0.275
8520.00	35.581	47.725	16.694	0.46918299	65%	0.069	0.269
9060.00	35.429	48.844	15.727	0.44390189	67%	0.065	0.265
10080.00	35.312	50.748	13.94	0.39476665	71%	0.058	0.258
10920.00	35.067	52.068	12.865	0.36686914	73%	0.054	0.254
11700.00	35.086	53.117	11.797	0.33623098	75%	0.050	0.250
12600.00	34.901	54.286	10.813	0.3098192	77%	0.046	0.246
13500.00	34.81	55.18	10.01	0.28756105	79%	0.042	0.242
14400.00	34.759	56.016	9.225	0.26539889	80%	0.039	0.239
15420.00	34.685	56.946	8.369	0.24128586	82%	0.036	0.236
16260.00	34.685	57.416	7.899	0.22773533	83%	0.034	0.234
17100.00	34.693	57.979	7.328	0.21122417	84%	0.031	0.231
18000.00	34.586	58.592	6.822	0.19724744	85%	0.029	0.229
19080.00	34.589	59.162	6.249	0.18066437	87%	0.027	0.227
20400.00	34.613	59.664	5.723	0.1653425	88%	0.024	0.224

Table S13. Results from kinetic run using 2.5 equiv. perester: 0.2 M 1, 0.5 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph_2O	Area of PDT	Area of SM	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	[Peracid] (M)
0.00	42.103	0	57.897	1.37512766	0%	0.200	0.500
300.00	42.214	2.209	55.577	1.31655375	4%	0.191	0.491
600.00	41.927	4.646	53.427	1.27428626	7%	0.185	0.485
900.00	41.475	7.486	51.039	1.23059675	11%	0.179	0.479
1200.00	41.046	10.732	48.222	1.17482824	15%	0.171	0.471
1500.00	40.521	13.985	45.494	1.12272649	18%	0.163	0.463
1800.00	40.09	17.333	42.577	1.06203542	23%	0.154	0.454
2100.00	38.887	20.579	40.534	1.04235349	24%	0.152	0.452
2460.00	39.086	23.973	36.941	0.94512102	31%	0.137	0.437
3000.00	38.224	29.156	32.62	0.85339054	38%	0.124	0.424
3300.00	37.815	31.724	30.461	0.80552691	41%	0.117	0.417
3600.00	37.381	34.163	28.456	0.76124234	45%	0.111	0.411
4200.00	36.754	38.114	25.132	0.68378952	50%	0.099	0.399
4800.00	36.327	41.783	21.89	0.6025821	56%	0.088	0.388
5520.00	35.982	45.119	18.899	0.52523484	62%	0.076	0.376
6120.00	35.532	47.446	17.022	0.47906113	65%	0.070	0.370
6600.00	35.407	49.334	15.259	0.43095998	69%	0.063	0.363
7800.00	35.329	51.067	13.604	0.38506609	72%	0.056	0.356
7800.00	35.071	52.808	12.121	0.34561318	75%	0.050	0.350
8520.00	35.838	54.206	9.956	0.27780568	80%	0.040	0.340
9060.00	34.769	55.608	9.623	0.27676954	80%	0.040	0.340
10080.00	34.586	57.425	7.989	0.23098942	83%	0.034	0.334
10920.00	34.557	58.547	6.896	0.19955436	85%	0.029	0.329
11700.00	34.557	59.499	5.944	0.17200567	87%	0.025	0.325
12600.00	34.772	60.111	5.117	0.14715863	89%	0.021	0.321
13500.00	34.717	60.899	4.384	0.12627819	91%	0.018	0.318
14400.00	34.514	61.591	3.895	0.11285276	92%	0.016	0.316
15420.00	34.488	62.391	3.121	0.09049524	93%	0.013	0.313
16260.00	34.569	62.63	2.801	0.08102635	94%	0.012	0.312
17100.00	34.623	62.972	2.405	0.0694625	95%	0.010	0.310
18000.00	34.719	63.221	2.06	0.05933351	96%	0.009	0.309
19080.00	34.647	63.612	1.741	0.05024966	96%	0.007	0.307
20400.00	35.224	63.634	1.142	0.03242108	98%	0.005	0.305

Ir-photocatalyst loading studies

Standard reactions were run, side by side, at different catalyst loadings. Conversion was monitored by HPLC, concentration of [**1**] was plotted as a function of time and fitted to a 6th order polynomial. The derivative of this equation was calculated and used to calculate reaction rate. To capture the induction periods observed at low catalyst concentrations, all data points from 0% to 95% conversion were included in the analysis. Graphical rate equations were produced using the entire range of conversion to capture the induction periods. The result is listed in the Figure S32 below and data from each individual kinetic run is listed below.



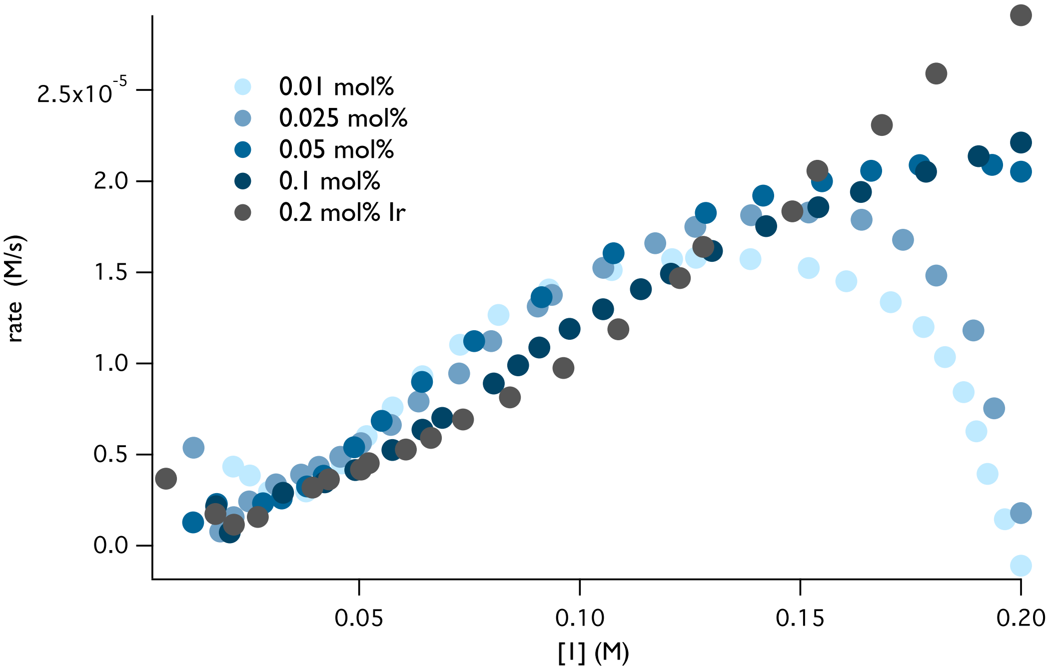


Figure S32. Reaction progress profiles with different photocatalyst loadings – Rate versus starting material (**1**) concentration.

Ir loading: 0.01 mol%

Table S14. Results from kinetic run under the following conditions: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.02 μM $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{SM}/A_{STD}	% conv.	% yield	[SM] (M)	d[SM]/dt (M/s)
0	42.008	0	57.992	1.38	0%	0%	0.200	
600	41.997	1.09	56.913	1.36	2%	1%	0.196	1.45E-06
1200	42.136	1.906	55.958	1.33	4%	2%	0.192	3.93E-06
1800	41.998	2.957	55.045	1.31	5%	3%	0.190	6.28E-06
2400	41.799	4.251	53.95	1.29	7%	5%	0.187	8.43E-06
3000	41.654	5.802	52.544	1.26	9%	6%	0.183	1.03E-05
3600	41.2	8.207	50.593	1.23	11%	9%	0.178	1.20E-05
4200	40.848	11.083	48.069	1.18	15%	12%	0.170	1.34E-05
4860	40.263	15.156	44.581	1.11	20%	17%	0.160	1.45E-05
5460	39.729	18.613	41.658	1.05	24%	21%	0.152	1.52E-05
6180	39.138	23.398	37.464	0.96	31%	27%	0.139	1.57E-05
6900	38.233	28.427	33.34	0.87	37%	33%	0.126	1.58E-05
7200	38.133	30.037	31.83	0.83	40%	35%	0.121	1.57E-05
8100	37.301	35.084	27.615	0.74	46%	42%	0.107	1.51E-05
9000	36.918	39.377	23.705	0.64	53%	47%	0.093	1.41E-05
9900	36.543	42.869	20.588	0.56	59%	52%	0.082	1.27E-05
10800	35.996	45.896	18.108	0.50	64%	57%	0.073	1.10E-05
11700	35.765	48.349	15.886	0.44	68%	60%	0.064	9.30E-06
12600	35.686	50.13	14.184	0.40	71%	63%	0.058	7.59E-06
13500	35.237	52.182	12.581	0.36	74%	66%	0.052	6.01E-06
14520	35.096	53.742	11.162	0.32	77%	68%	0.046	4.51E-06
16200	35.029	55.785	9.186	0.26	81%	71%	0.038	2.98E-06
18600	34.749	58.161	7.09	0.20	85%	74%	0.030	2.97E-06
20160	34.827	59.111	6.062	0.17	87%	76%	0.025	3.85E-06
21900	34.545	60.331	5.124	0.15	89%	78%	0.021	4.33E-06
25500	34.725	61.455	3.82	0.11	92%	79%	0.016	

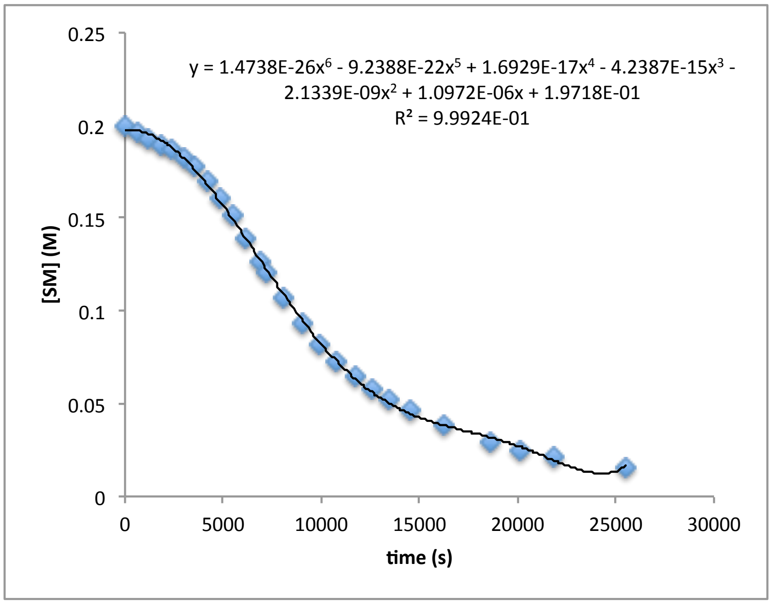


Figure S33. Concentration of starting material (1) versus time with a 0.01 mol% Ir catalyst loading. The plot is fitted to a 6th order polynomial.

Ir loading: 0.025 mol%

Table S15. Results from kinetic run under the following conditions: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.05 μM $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{SM}/A_{STD}	% conv.	% yield	[SM] (M)	d[SM]/dt (M/s)
0	42.243	0	57.757	1.367256113	0%	0%	0.2	1.7917E-06
600	42.188	1.884	55.928	1.325685029	3%	2%	0.19391905	7.54322E-06
1200	41.873	3.962	54.165	1.293554319	5%	4%	0.18921902	1.18108E-05
1800	41.671	6.83	51.499	1.235847472	10%	7%	0.18077776	1.48226E-05
2400	40.865	10.725	48.41	1.184632326	13%	12%	0.17328609	1.67851E-05
3000	40.167	14.839	44.994	1.120173277	18%	16%	0.16385712	1.78841E-05
3600	39.582	19.319	41.099	1.038325501	24%	22%	0.15188457	1.82856E-05
4200	39.12	23.751	37.129	0.949105317	31%	27%	0.13883358	1.81372E-05
4860	38.324	28.62	33.056	0.862540445	37%	33%	0.12617101	1.74928E-05
5460	37.712	32.101	30.187	0.800461392	41%	38%	0.11709019	1.65915E-05
6180	37.279	35.879	26.842	0.720030044	47%	43%	0.10532482	1.52518E-05
6900	36.859	39.535	23.606	0.640440598	53%	48%	0.09368261	1.37594E-05
7200	36.629	40.717	22.654	0.618471703	55%	49%	0.09046903	1.31197E-05
8100	36.328	43.818	19.854	0.54652059	60%	54%	0.07994414	1.12204E-05
9000	36.02	46.091	17.889	0.496640755	64%	57%	0.0726478	9.45344E-06
9900	35.536	49.046	15.418	0.433869878	68%	61%	0.06346578	7.90784E-06
10800	35.228	51	13.772	0.390939026	71%	64%	0.05718592	6.62836E-06
11700	35.205	52.664	12.131	0.344581736	75%	67%	0.05040486	5.62302E-06
12600	35.059	53.977	10.964	0.312729969	77%	69%	0.04574563	4.87064E-06
13500	35.093	55.105	9.802	0.279314963	80%	70%	0.04085774	4.32843E-06
14520	34.825	56.405	8.77	0.251830581	82%	72%	0.03683737	3.89586E-06
16200	34.861	57.713	7.426	0.213017412	84%	74%	0.03115984	3.36906E-06
18600	34.502	59.584	5.914	0.171410353	87%	77%	0.02507363	2.42536E-06
20160	34.607	60.291	5.102	0.147426821	89%	78%	0.02156536	1.56526E-06
21900	34.519	61.108	4.373	0.126683855	91%	79%	0.01853111	7.73088E-07
25500	34.666	62.371	2.963	0.085472798	94%	80%	0.01250282	5.37465E-06

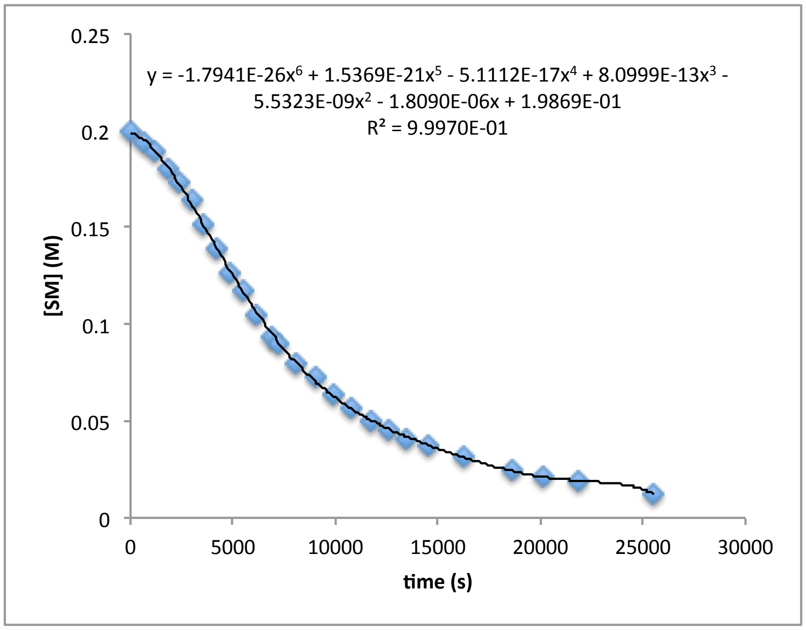


Figure S34. Concentration of starting material (1) versus time with a 0.025 mol% Ir catalyst loading. The plot is fitted to a 6th order polynomial.

Ir loading: 0.05 mol%

Table S16. Results from kinetic run under the following conditions: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.1 μM $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{SM}/A_{STD}	% conv.	% yield	[SM] (M)	d[SM]/dt (M/s)
0	42.671	0.125	57.204	1.34	0%	0%	0.2	0.000020521
600	42.068	3.39	54.542	1.30	3%	4%	0.19342634	2.0891E-05
1200	42.186	7.749	50.065	1.19	11%	8%	0.17705259	2.08867E-05
1800	41.183	12.989	45.828	1.11	17%	14%	0.16601577	2.05687E-05
2400	40.369	17.721	41.91	1.04	23%	20%	0.15488383	1.99927E-05
3000	39.735	22.554	37.711	0.95	29%	25%	0.14158957	1.92092E-05
3600	39.021	27.346	33.633	0.86	36%	31%	0.12858894	1.82642E-05
4800	37.77	34.969	27.261	0.72	46%	41%	0.10767905	1.60505E-05
6000	36.859	40.573	22.568	0.61	54%	49%	0.09134524	1.36312E-05
7200	36.651	44.661	18.688	0.51	62%	54%	0.07607	1.12228E-05
8400	36.225	48.168	15.607	0.43	68%	59%	0.06427579	8.9842E-06
9720	36.041	50.643	13.316	0.37	72%	63%	0.05512053	6.84538E-06
10800	35.67	52.648	11.682	0.33	76%	66%	0.04885967	5.40342E-06
12360	35.187	54.918	9.895	0.28	79%	69%	0.04195367	3.84275E-06
13200	35.338	55.618	9.044	0.26	81%	70%	0.03818168	3.25039E-06
14640	35.329	56.982	7.689	0.22	84%	72%	0.03246945	2.59314E-06
15900	35.511	57.768	6.721	0.19	86%	72%	0.02823628	2.32172E-06
21300	35.364	60.423	4.213	0.12	91%	76%	0.01777324	2.28938E-06
24840	35.319	61.747	2.934	0.08	94%	78%	0.01239333	1.28247E-06
28500	35.325	62.519	2.156	0.06	95%	79%	0.00910548	-7.66444E-07
32640	36.413	60.204	3.383	0.09	93%	74%	0.0138606	0.005244684

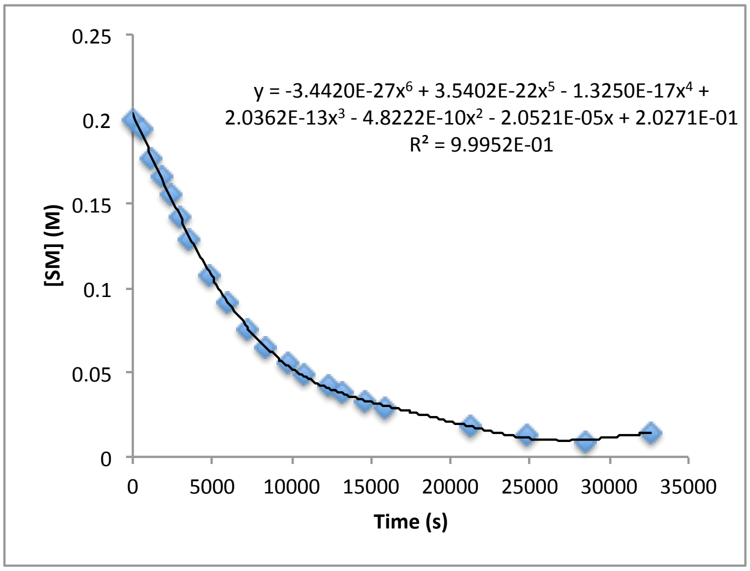


Figure S35. Concentration of starting material (1) versus time with a 0.05 mol% Ir catalyst loading. The plot is fitted to a 6th order polynomial.

Ir loading: 0.1 mol%

Table S17. Results from kinetic run under the following conditions: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{SM}/A_{STD}	% conv.	% yield	[SM] (M)	d[SM]/dt (M/s)
0	42.31	0	57.69	1.36	0%	0%	0.2	0.000022114
630	41.563	4.493	53.944	1.30	5%	5%	0.19037449	2.13711E-05
1230	40.841	9.464	49.695	1.22	11%	10%	0.17847969	2.05179E-05
1920	40.047	15.256	44.697	1.12	18%	17%	0.16371213	1.94035E-05
2400	39.541	18.923	41.536	1.05	23%	21%	0.15408115	1.85664E-05
2970	39.15	22.89	37.96	0.97	29%	26%	0.14222205	1.75274E-05
3690	38.533	27.32	34.147	0.89	35%	32%	0.12998469	1.61747E-05
4350	38.051	30.643	31.306	0.82	40%	36%	0.12067964	1.49231E-05
4800	37.651	33.13	29.219	0.78	43%	39%	0.1138312	1.4076E-05
5400	37.403	35.754	26.843	0.72	47%	43%	0.10526818	1.29672E-05
6000	37.125	38.146	24.729	0.67	51%	46%	0.09770405	1.18939E-05
6600	36.689	40.589	22.722	0.62	55%	49%	0.09084126	1.08671E-05
7200	36.517	42.069	21.414	0.59	57%	51%	0.0860152	9.89589E-06
7860	36.294	43.789	19.917	0.55	60%	54%	0.08049364	8.89983E-06
9300	35.873	47.292	16.835	0.47	66%	59%	0.06883636	7.01749E-06
9900	35.603	48.774	15.623	0.44	68%	61%	0.06436508	6.35652E-06
11100	35.556	50.498	13.946	0.39	71%	63%	0.05753197	5.25145E-06
12780	35.278	52.911	11.811	0.33	75%	67%	0.04910833	4.15636E-06
14520	35.291	54.553	10.156	0.29	79%	69%	0.04221154	3.48062E-06
18000	35.043	57.128	7.829	0.22	84%	73%	0.03277008	2.90643E-06
21900	43.408	51.381	5.211	0.12	91%	53%	0.01760856	2.16116E-06
25200	35.061	59.989	4.95	0.14	90%	76%	0.02070873	7.3301E-07
28800	35.28	60.996	3.724	0.11	92%	77%	0.01548295	-8.7241E-07
34800	35.258	62.162	2.58	0.07	95%	78%	0.01073333	7.01051E-06

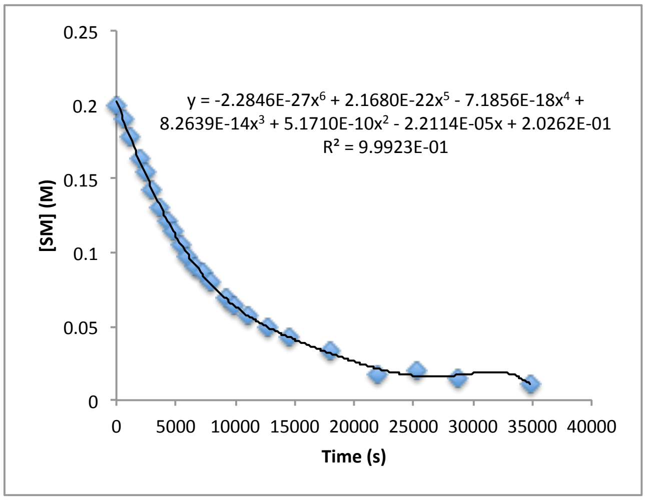


Figure S36. Concentration of starting material (**1**) versus time with a 0.1 mol% Ir catalyst loading. The plot is fitted to a 6th order polynomial.

Ir loading: 0.2 mol%

Table S18. Results from kinetic run under the following conditions: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.4 μM $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{SM}/A_{STD}	% conv.	% yield	[SM] (M)	d[SM]/dt (M/s)
0	42.696	0	57.304	1.34	0%	0%	0.200	0.000029104
600	42.197	6.599	51.204	1.21	10%	7%	0.181	2.59114E-05
1200	40.842	12.989	46.169	1.13	16%	14%	0.168	2.30762E-05
1800	40.373	17.939	41.688	1.03	23%	20%	0.154	2.05657E-05
2400	38.94	22.332	38.728	0.99	26%	26%	0.148	1.83493E-05
3000	40.217	25.243	34.54	0.86	36%	28%	0.128	1.63983E-05
3600	39.102	28.701	32.197	0.82	39%	33%	0.123	1.46859E-05
4800	37.952	34.352	27.696	0.73	46%	40%	0.109	1.18783E-05
6000	37.5	38.27	24.23	0.65	52%	45%	0.096	9.74719E-06
7200	37.196	41.786	21.018	0.57	58%	50%	0.084	8.13912E-06
8400	37.097	44.59	18.313	0.49	63%	53%	0.074	6.92517E-06
9720	36.517	47.242	16.241	0.44	67%	58%	0.066	5.91864E-06
10800	36.269	48.979	14.752	0.41	70%	60%	0.061	5.27453E-06
12360	36.636	50.534	12.83	0.35	74%	61%	0.052	4.52656E-06
13200	35.977	51.855	12.168	0.34	75%	64%	0.050	4.18025E-06
14640	36.74	52.623	10.637	0.29	78%	64%	0.043	3.63804E-06
15900	36.352	54.035	9.613	0.26	80%	66%	0.039	3.19419E-06
21300	35.963	57.514	6.523	0.18	86%	71%	0.027	1.57214E-06
24840	36.133	58.63	5.237	0.14	89%	72%	0.022	1.14643E-06
28500	36.177	59.591	4.232	0.12	91%	73%	0.017	1.73898E-06
32640	35.913	62.583	1.504	0.04	97%	78%	0.006	3.6741E-06

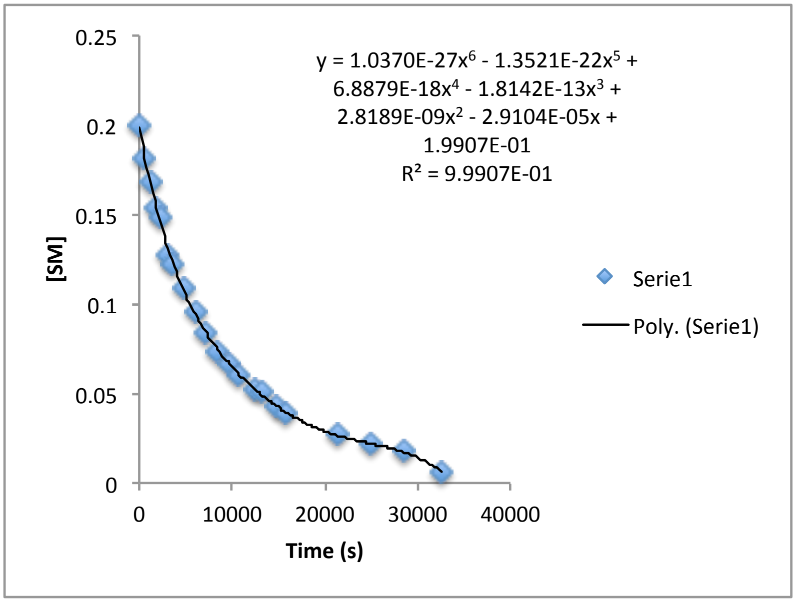
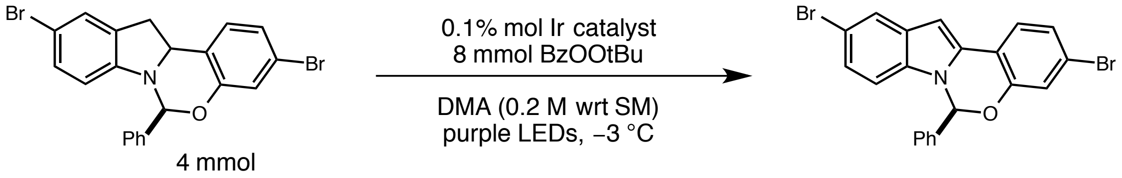


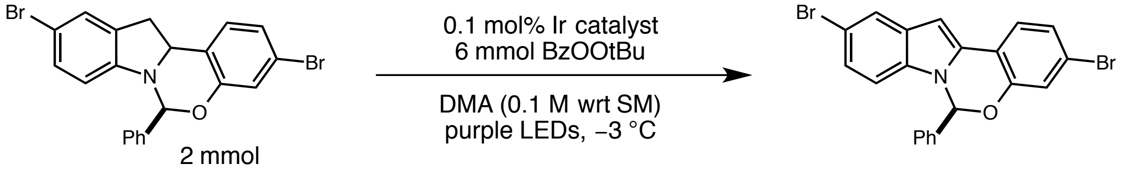
Figure S37. Concentration of starting material (**1**) versus time with a 0.2 mol% Ir catalyst loading. The plot is fitted to a 6th order polynomial.

Blackmond's Same Excess Experiment

Standard reaction conditions:



Reaction conditions that mimic 50% conversion:



Blackmond's same excess experiment was run to verify that there was no kinetically significant catalyst decomposition occurring during the reaction. Two reactions were set up side by side: the first reaction was run in accordance with standard reaction conditions, while the second experiment simulates a reaction that has reached 50% conversion. The first reaction uses 1 equiv. of starting material and 2 equiv. of perester, whereas the second reaction is charged with 0.5 equiv. of starting material and 1.5 equiv. of perester. Catalyst concentration and the internal standard (diphenyl ether) concentrations are kept constant at 0.1 mol% and 1 equiv. respectively.

Conversion was monitored by HPLC and the concentration of [1] was plotted as a function of time and fitted to a 6th order polynomial. The derivative of this equation was calculated and used to calculate reaction rate. Graphical rate equations were produced using the entire range of conversion to capture the induction periods. The result is listed in Figure S38 below and data from each individual kinetic run is listed below.

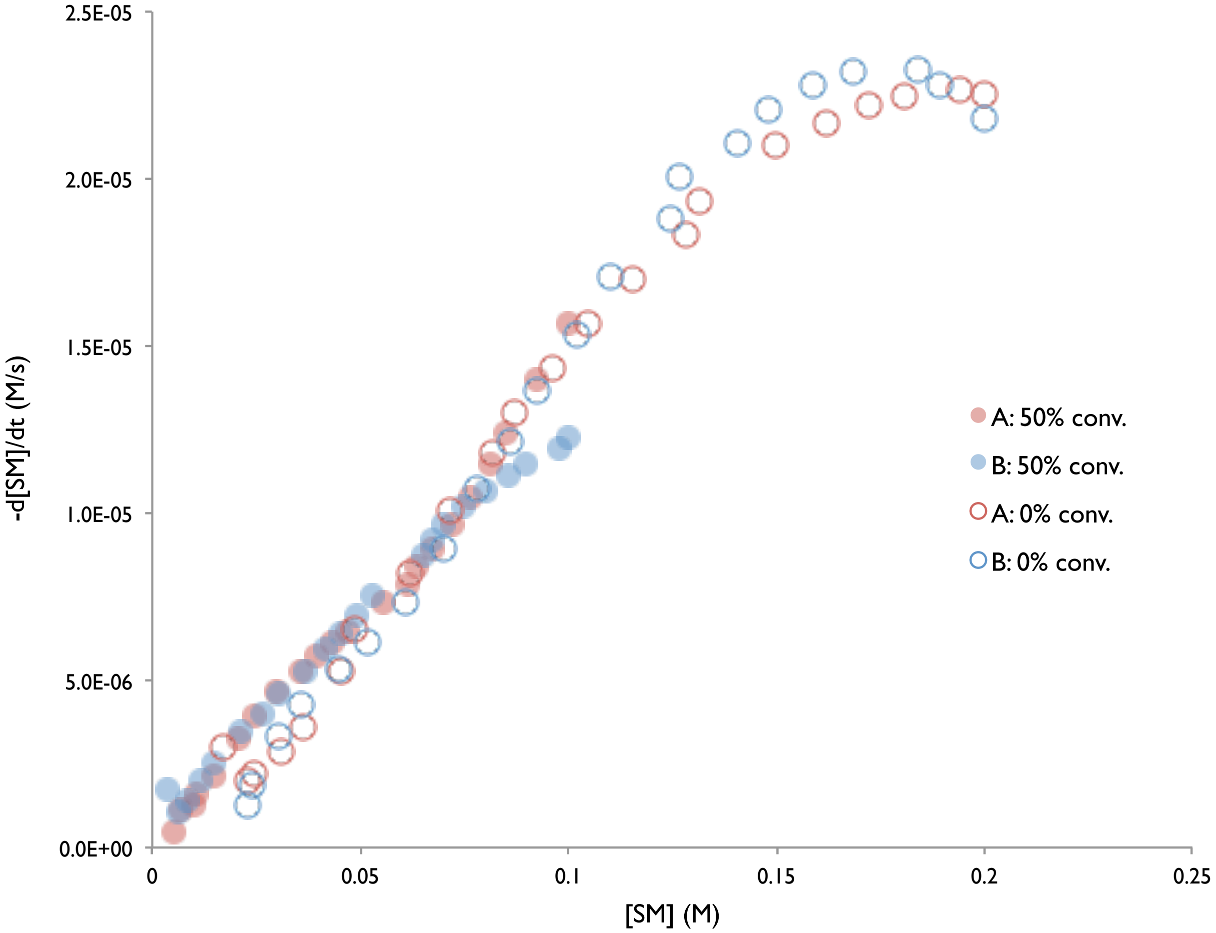


Figure S38. Reaction progress profiles from the same excess experiment: Comparison of –d[**1**]/dt versus starting material (**1**) concentration for four reactions carried out at the same excess.

Same excess experiment, run A: “50% conversion”

Table S19. Results from kinetic run under the following conditions: 0.1 M 1, 0.3 M BzOOtBu, 0.2 M Ph2O, 0.2 μM Ir[Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 °C using purple LEDs

time (s)	Ph$_2$O (A$_{230nm}$)	PDT (A$_{230nm}$)	SM (A$_{230nm}$)	A$_{PDT}$/A$_{STD}$	A$_{SM}$/A$_{STD}$	% conv.	[PDT] (M)	[SM] (M)	-d[SM]/dt (M/s)
0	59.503	0	40.497	0.000	0.681	0%	0.0000	0.1000	1.56E-05
450	59.06	3.779	37.162	0.064	0.629	8%	0.0057	0.0925	1.40E-05
990	58.466	7.688	33.846	0.131	0.579	15%	0.0117	0.0851	1.24E-05
1350	58.163	9.7	32.137	0.167	0.553	19%	0.0148	0.0812	1.15E-05
1800	57.697	12.249	30.053	0.212	0.521	23%	0.0189	0.0765	1.05E-05
2250	56.945	15.02	28.036	0.264	0.492	28%	0.0235	0.0723	9.65E-06
2730	56.773	17.265	25.962	0.304	0.457	33%	0.0271	0.0672	8.92E-06
3132	56.574	18.918	24.508	0.334	0.433	36%	0.0298	0.0637	8.40E-06
3600	54.817	22.171	23.012	0.404	0.420	38%	0.0360	0.0617	7.88E-06
4200	55.797	23.015	21.189	0.412	0.380	44%	0.0367	0.0558	7.32E-06
5400	55.008	27.354	17.638	0.497	0.321	53%	0.0443	0.0471	6.46E-06
6000	54.947	28.977	16.076	0.527	0.293	57%	0.0469	0.0430	6.10E-06
6600	54.569	30.731	14.7	0.563	0.269	60%	0.0501	0.0396	5.76E-06
7500	53.856	33.119	13.025	0.615	0.242	64%	0.0547	0.0355	5.26E-06
8580	53.766	35.365	10.868	0.658	0.202	70%	0.0585	0.0297	4.66E-06
9780	53.718	37.28	9.003	0.694	0.168	75%	0.0618	0.0246	3.96E-06
10980	53.682	38.79	7.528	0.723	0.140	79%	0.0643	0.0206	3.25E-06
13200	53.268	41.283	5.448	0.775	0.102	85%	0.0690	0.0150	2.11E-06
14640	53.967	42.239	3.794	0.783	0.070	90%	0.0697	0.0103	1.60E-06
16500	53.921	42.447	3.633	0.787	0.067	90%	0.0701	0.0099	1.26E-06
18180	53.894	43.558	2.549	0.808	0.047	93%	0.0719	0.0069	1.14E-06
20400	54.174	43.964	1.863	0.812	0.034	95%	0.0722	0.0051	4.84E-07

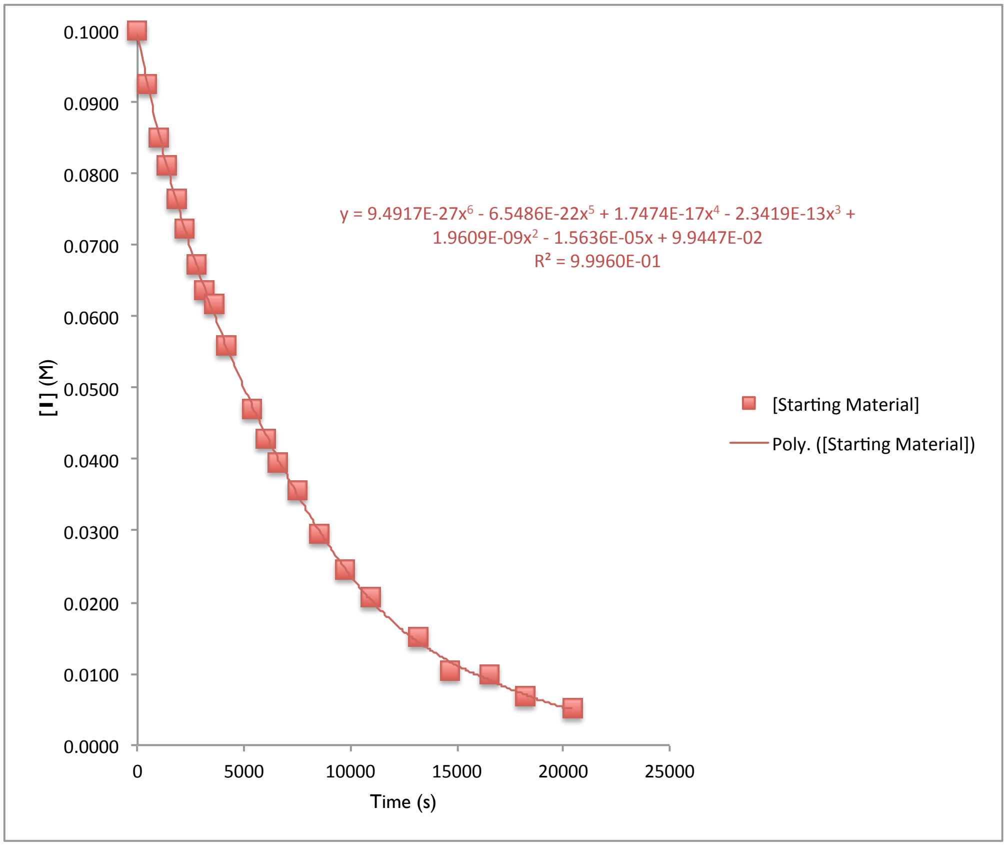


Figure S39. Concentration of starting material (**1**) versus time.

Same excess experiment, run A: “0% conversion” / standard reaction set-up

Table S20. Results from kinetic run under the following conditions: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM Ir[Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{PDT}/A_{STD}	A_{SM}/A_{STD}	% conv.	[PDT] (M)	[SM] (M)	-d[SM]/dt (M/s)
0	42.884	0	57.116	0.000	1.332	0%	0.000	0.200	2.25E-05
450	41.872	4.015	54.113	0.096	1.292	3%	0.009	0.194	2.27E-05
990	41.218	9.227	49.555	0.224	1.202	10%	0.020	0.181	2.25E-05
1350	40.678	12.622	46.701	0.310	1.148	14%	0.028	0.172	2.22E-05
1800	40.082	16.682	43.236	0.416	1.079	19%	0.037	0.162	2.16E-05
2250	39.807	20.539	39.654	0.516	0.996	25%	0.046	0.150	2.10E-05
3132	38.858	27.164	33.979	0.699	0.874	34%	0.062	0.131	1.93E-05
3600	37.96	29.765	32.376	0.784	0.853	36%	0.070	0.128	1.84E-05
4200	37.812	33.094	29.094	0.875	0.769	42%	0.078	0.116	1.70E-05
4800	37.265	36.784	25.951	0.987	0.696	48%	0.088	0.105	1.57E-05
5400	36.788	39.65	23.562	1.078	0.640	52%	0.096	0.096	1.43E-05
6000	36.807	41.813	21.379	1.136	0.581	56%	0.101	0.087	1.30E-05
6600	36.242	44.066	19.692	1.216	0.543	59%	0.108	0.082	1.18E-05
7500	36.093	46.728	17.18	1.295	0.476	64%	0.115	0.071	1.00E-05
8580	35.83	49.434	14.736	1.380	0.411	69%	0.123	0.062	8.22E-06
9780	35.847	52.611	11.542	1.468	0.322	76%	0.131	0.048	6.57E-06
10980	35.533	53.689	10.778	1.511	0.303	77%	0.134	0.046	5.27E-06
13200	35.049	56.488	8.463	1.612	0.241	82%	0.143	0.036	3.60E-06
14640	35.236	57.449	7.315	1.630	0.208	84%	0.145	0.031	2.87E-06
16500	35.59	58.652	5.758	1.648	0.162	88%	0.147	0.024	2.21E-06
18180	34.991	59.639	5.37	1.704	0.153	88%	0.152	0.023	2.00E-06
20400	35.481	60.487	4.032	1.705	0.114	91%	0.152	0.017	3.01E-06

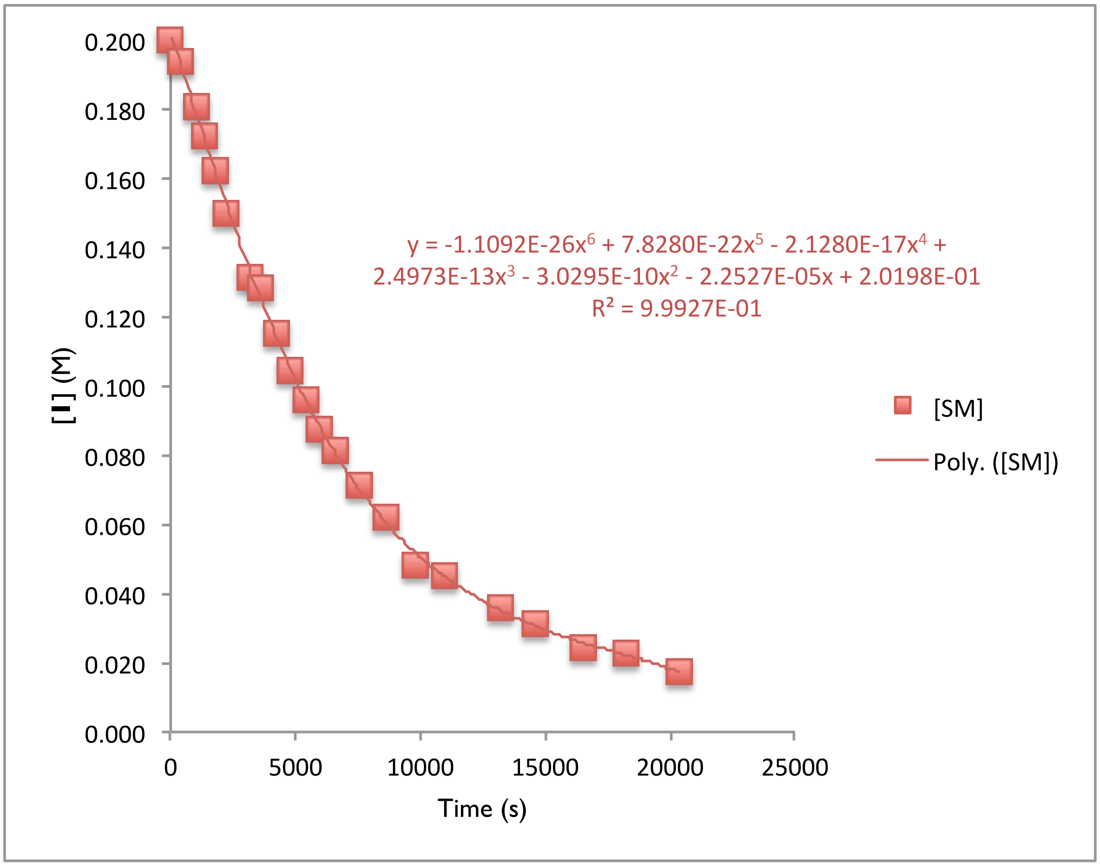


Figure S40. Concentration of starting material (**1**) versus time

Same excess experiment, run B: “50% conversion”

Table S21. Results from kinetic run under the following conditions: 0.1 M 1, 0.3 M BzOOtBu, 0.2 M Ph2O, 0.2 μM Ir[Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 °C using purple LEDs

time (s)	Ph$_2$O (A$_{230nm}$)	PDT (A$_{230nm}$)	SM (A$_{230nm}$)	A$_{PDT}$/A$_{STD}$	A$_{SM}$/A$_{STD}$	% conv.	[PDT] (M)	[SM] (M)	-d[SM]/dt (M/s)
0	60.5	0	39.5	0.000	0.653	0%	0.000	0.100	1.23E-05
450	58.604	3.92	37.476	0.067	0.639	2%	0.006	0.098	1.19E-05
990	58.096	7.824	34.08	0.135	0.587	10%	0.012	0.090	1.15E-05
1350	57.941	9.872	32.387	0.170	0.559	14%	0.015	0.086	1.11E-05
1800	57.46	12.471	30.069	0.217	0.523	20%	0.019	0.080	1.07E-05
2250	56.996	15.092	27.912	0.265	0.490	25%	0.024	0.075	1.02E-05
2730	56.797	17.173	26.031	0.302	0.458	30%	0.027	0.070	9.66E-06
3132	56.243	19.11	24.647	0.340	0.438	33%	0.030	0.067	9.23E-06
3600	55.962	20.654	23.838	0.369	0.426	35%	0.033	0.065	8.73E-06
4800	55.404	25.479	19.116	0.460	0.345	47%	0.041	0.053	7.50E-06
5400	54.88	27.566	17.554	0.502	0.320	51%	0.045	0.049	6.94E-06
6000	54.551	29.259	16.189	0.536	0.297	55%	0.048	0.045	6.41E-06
6600	54.334	30.943	14.723	0.569	0.271	58%	0.051	0.042	5.92E-06
7500	53.857	33.243	12.9	0.617	0.240	63%	0.055	0.037	5.27E-06
8580	53.822	35.511	10.667	0.660	0.198	70%	0.059	0.030	4.60E-06
9780	53.308	37.477	9.215	0.703	0.173	74%	0.063	0.026	3.97E-06
10980	53.14	39.514	7.346	0.744	0.138	79%	0.066	0.021	3.44E-06
13200	52.935	41.915	5.15	0.792	0.097	85%	0.070	0.015	2.56E-06
14640	53.628	42.27	4.102	0.788	0.076	88%	0.070	0.012	2.01E-06
16500	53.511	43.534	2.955	0.814	0.055	92%	0.072	0.008	1.37E-06
18180	53.524	44.231	2.245	0.826	0.042	94%	0.074	0.006	1.06E-06
20400	53.762	44.929	1.309	0.836	0.024	96%	0.074	0.004	1.75E-06

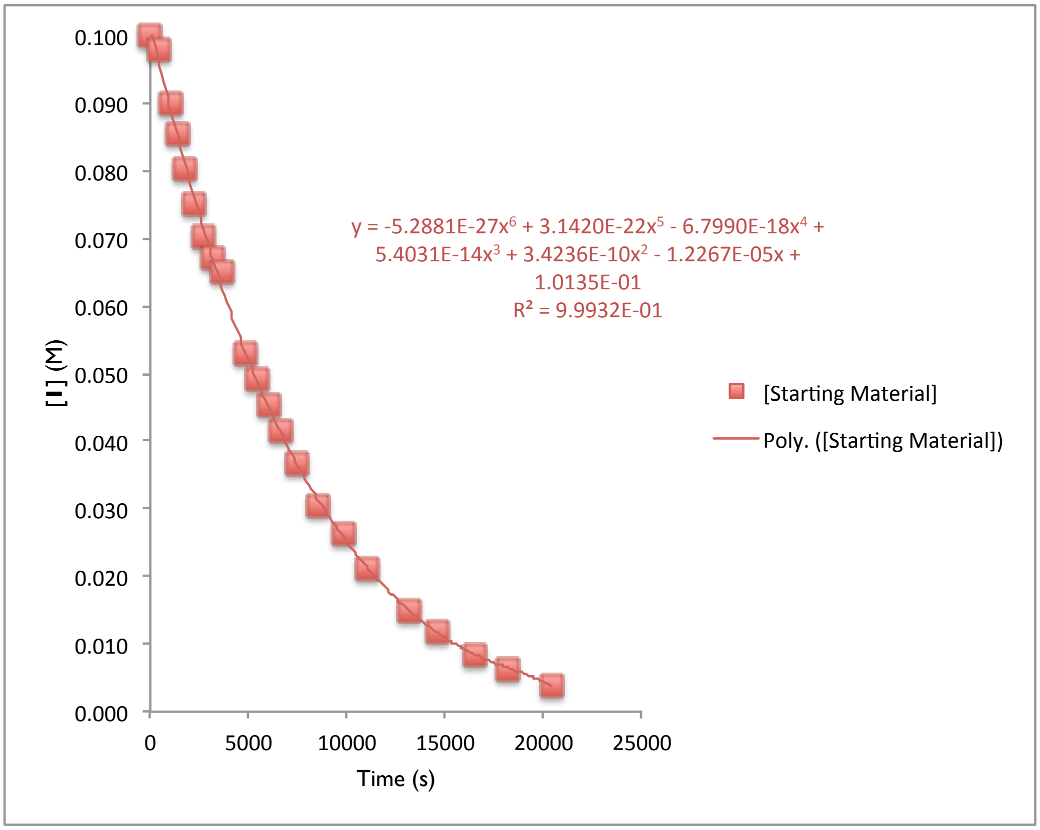


Figure S41. Concentration of starting material (**1**) versus time.

Same excess experiment, run B: “0% conversion” / standard reaction set-up

Table S22. Results from kinetic run under the following conditions: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM Ir[Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 °C using purple LEDs

time (s)	Ph$_2$O (A$_{230nm}$)	PDT (A$_{230nm}$)	SM (A$_{230nm}$)	A$_{PDT}$/A$_{STD}$	A$_{SM}$/A$_{STD}$	% conv.	[PDT] (M)	[SM] (M)	-d[SM]/dt (M/s)
0	42.46	0	57.54	0.000	1.355	0%	0.000	0.200	2.18E-05
450	42.01	4.029	53.961	0.096	1.284	5%	0.009	0.190	2.28E-05
990	40.381	9.257	50.362	0.229	1.247	8%	0.020	0.184	2.33E-05
1350	40.731	12.704	46.565	0.312	1.143	16%	0.028	0.169	2.32E-05
1800	40.03	16.872	43.099	0.421	1.077	21%	0.038	0.159	2.28E-05
2250	39.587	20.703	39.71	0.523	1.003	26%	0.047	0.148	2.21E-05
2730	38.613	24.652	36.735	0.638	0.951	30%	0.057	0.140	2.10E-05
3132	39.315	26.925	33.76	0.685	0.859	37%	0.061	0.127	2.00E-05
3600	38.097	29.689	32.214	0.779	0.846	38%	0.069	0.125	1.88E-05
4200	38.038	33.631	28.339	0.884	0.745	45%	0.079	0.110	1.71E-05
4800	37.341	36.878	25.781	0.988	0.690	49%	0.088	0.102	1.53E-05
5400	37.197	39.483	23.32	1.061	0.627	54%	0.094	0.093	1.37E-05
6000	36.572	42.135	21.295	1.152	0.582	57%	0.103	0.086	1.21E-05
6600	36.485	44.237	19.277	1.212	0.528	61%	0.108	0.078	1.07E-05
7500	36.093	46.728	17.179	1.295	0.476	65%	0.115	0.070	8.93E-06
8580	35.83	49.434	14.736	1.380	0.411	70%	0.123	0.061	7.32E-06
9780	35.847	51.611	12.542	1.440	0.350	74%	0.128	0.052	6.12E-06
10980	35.533	53.689	10.778	1.511	0.303	78%	0.134	0.045	5.34E-06
13200	35.049	56.488	8.463	1.612	0.241	82%	0.143	0.036	4.24E-06
14640	35.236	57.449	7.315	1.630	0.208	85%	0.145	0.031	3.30E-06
16500	35.59	58.652	5.758	1.648	0.162	88%	0.147	0.024	1.85E-06
18180	34.991	59.639	5.37	1.704	0.153	89%	0.152	0.023	1.24E-06
20400	35.481	60.487	4.032	1.705	0.114	92%	0.152	0.017	5.32E-06

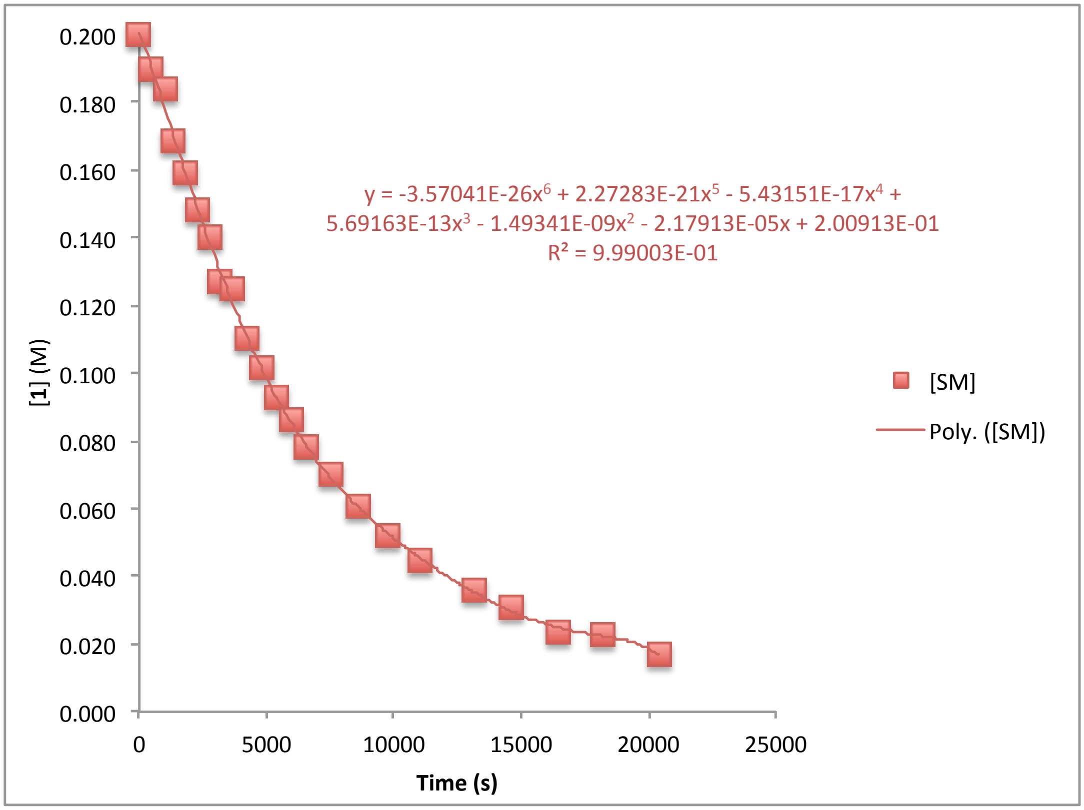
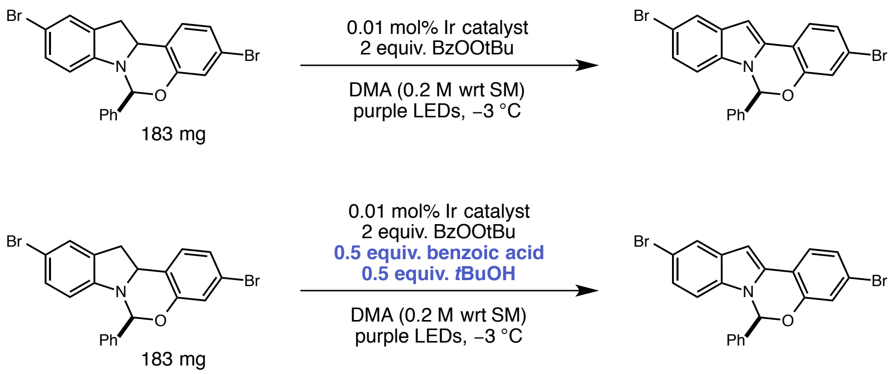


Figure S42. Concentration of starting material (**1**) versus time.

The effect of adding benzoic acid and tBuOH on reaction rate



Two reaction vials, were run side by side, following the standard reaction step up. In one reaction, additional benzoic acid and tert-butanol was added. The result is listed in the Figure S43 below.

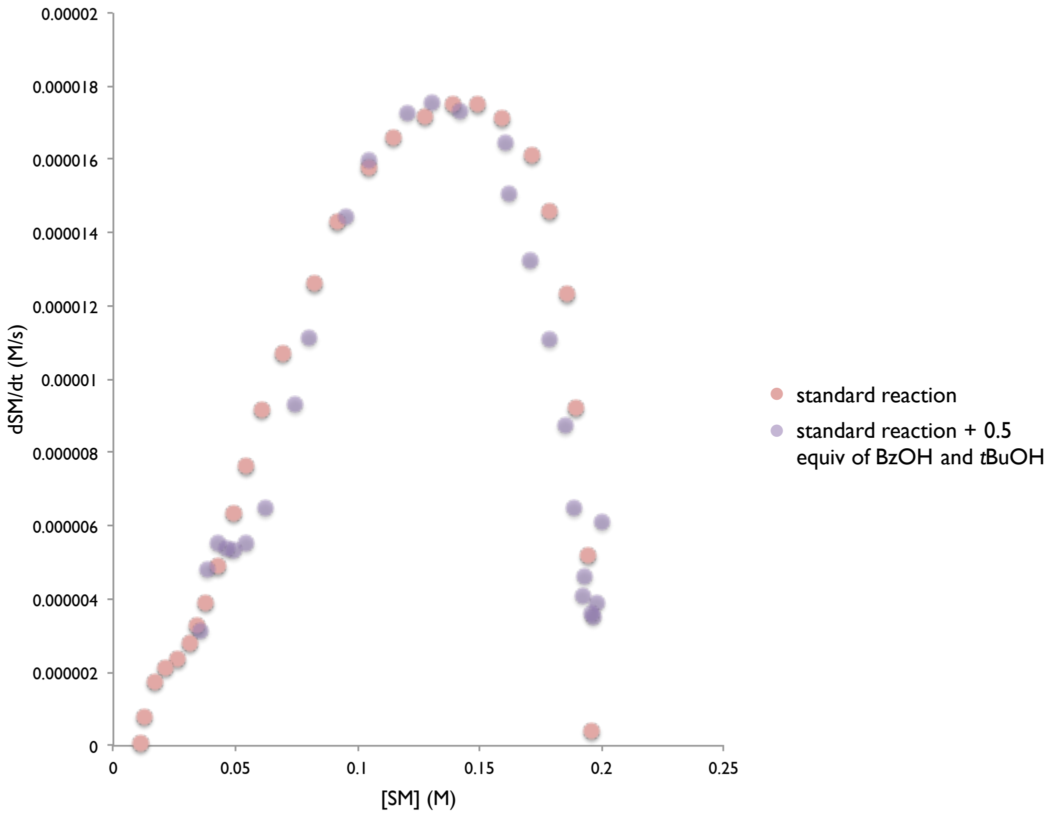
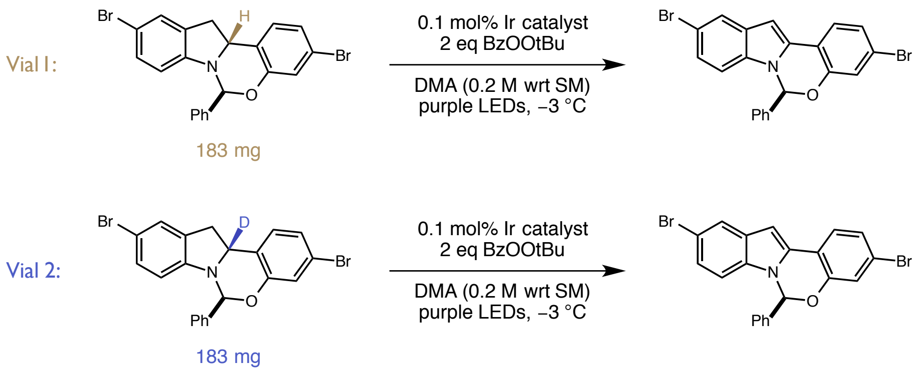


Figure S43. Reaction progress profiles with and without benzoic acid and t-butanol added. Standard reaction: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.02 μM Ir[Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 ^{o}C using purple LEDs. Reaction with BzOH and tBuOH: 0.2 M 1, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.02 μM Ir[Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6), 0.1 M benzoic acid and 0.1 M tBuOH in DMA at -3 ^{o}C using purple LEDs.

Direct KIE between reactions run in parallel with compound 1 and 1b



Two reactions, one with deuterated substrate and one with protiated substrate, were run side-by-side in separate vials under standard conditions. The experiment was run three times (Figure S44). The following pages outline how the data was analyzed.

Standard reaction conditions / General reaction set-up:

A 2 mL volumetric flask was charged with starting material (1 eq, 0.4 mmol, 183 mg), BzOOtBu (2 eq, 0.8 mmol, 152 μL), Ir[(dF-CF$_3$-ppy)$_2$(dtbpy)]PF$_6$ (0.1 mol%, 0.4 μmol), Ph$_2$O (1 eq, 0.4 mmol, 63 uL) and DMA. The solution was then transferred to a 12.5 cm culture tube and sparged with argon in the dark for 60 min. The vials were immersed in a –3 ^{o}C Cryocool bath, which was lined with four purple (402 nm) LED strips (see picture of an example set-up at end of kinetic section in SI). The reaction was stirred by continuous sparging. Aliquots were taken with 10–15 minute intervals and pushed through a plug of celite with 50:50 IPA:hexanes. Samples were analyzed on an Agilent 1260 Infinty HPLC using a Zorbax-Rx Sil 5 um 4.6 x 250 mm column using a 20 minute method with 1% IPA in hexanes as the eluent. UV-absorbances were measured at 230 nm. Starting material conversions and yields were tracked as a function of time from peak areas relative to Ph$_2$O as an internal standard.

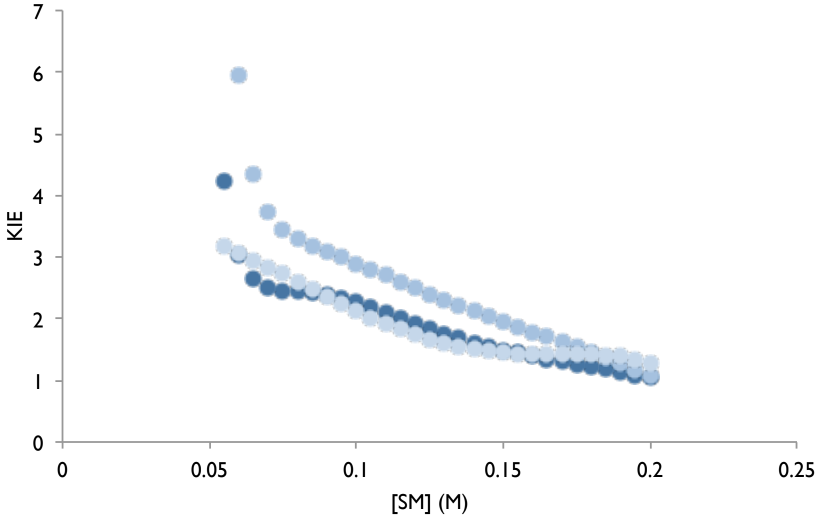


Figure S44. Overlay of three KIE runs

Summary of results (3 runs):

Run 1:

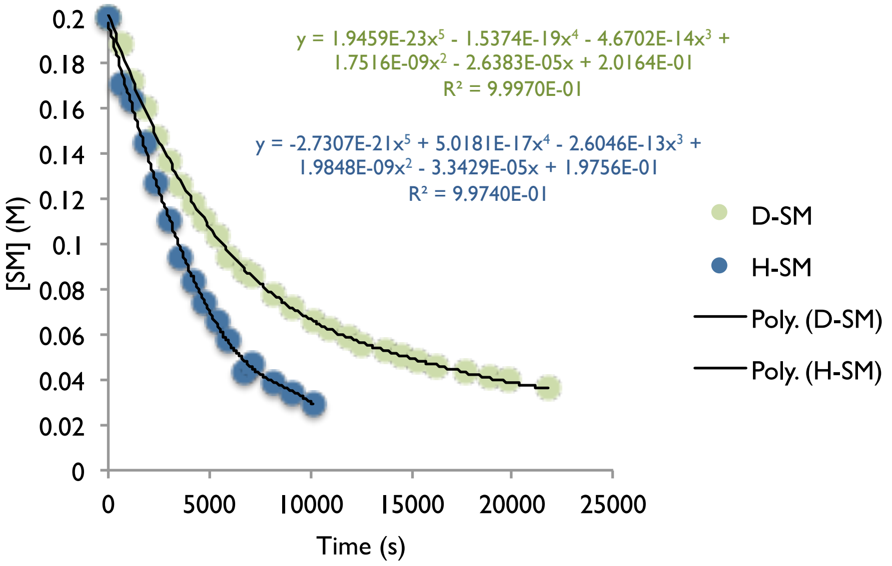


Figure S45. Starting material concentration as a function of time for both protiated (**1**) and deuterated substrates (**1b**). Data points between 0% and 80% conversion were used.

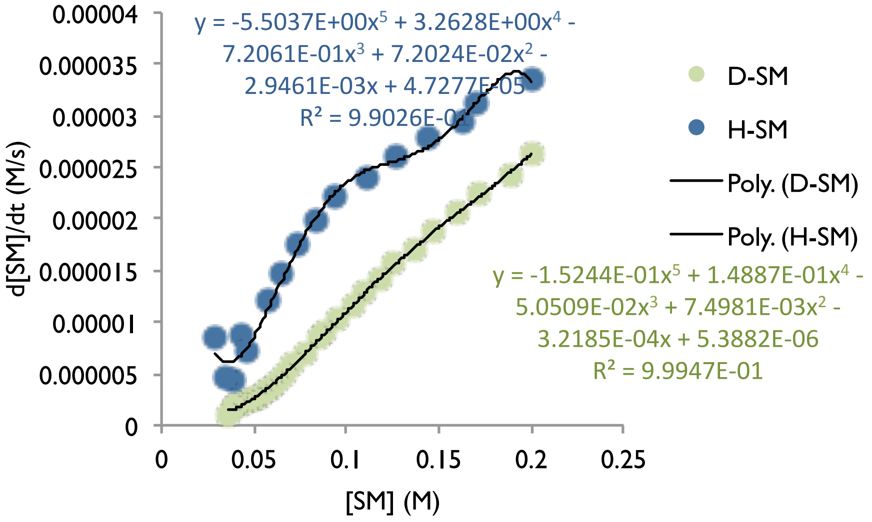


Figure S46. Graphical rate law: rate vs. starting material concentration for both protiated (**1**) and deuterated substrates (**1b**)

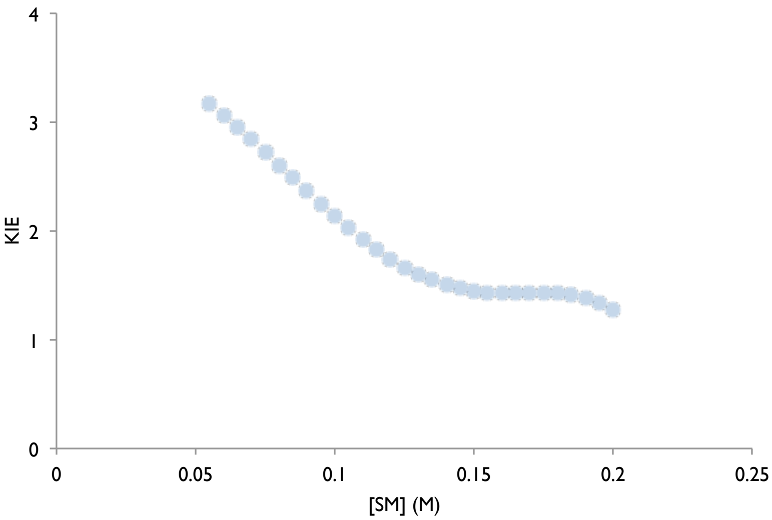


Figure S47. Kinetic isotope effect vs. starting material concentration. This figure represents the ratio between the graphical rate equations for protiated (**1**) and deuterated substrates (**1b**).

Raw data for run 1 (areas from HPLC traces at 230 nm)

Table S23. Results from kinetic run under the following conditions: 0.2 M **1**, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 ^{o}C using purple LEDs

Time (s)	Area of Ph2O	Area of Product	Area of starting material	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	dSM/dt
0	41.97	0	58.03	1.38265428	0%	0.2	0.000033429
630	43.786	4.686	51.528	1.17681451	15%	0.17022542	3.11902E-05
1200	40.217	14.296	45.487	1.13103911	18%	0.16360404	2.94721E-05
1800	39.193	21.518	39.289	1.00244942	27%	0.14500363	2.77881E-05
2400	38.306	28.082	33.612	0.87746045	37%	0.12692406	2.60809E-05
3060	37.319	34.037	28.644	0.76754468	44%	0.11102482	2.40444E-05
3600	37.313	38.436	24.251	0.64993434	53%	0.09401256	2.21934E-05
4230	36.411	42.564	21.025	0.57743539	58%	0.08352564	1.97978E-05
4800	36.143	45.388	18.469	0.51099798	63%	0.07391551	1.74273E-05
5400	35.703	48.175	16.122	0.45155869	67%	0.06531766	1.4781E-05
6000	35.442	50.344	14.214	0.4010496	71%	0.05801155	1.20796E-05
6780	36.542	52.354	11.104	0.30386952	78%	0.04395452	8.72623E-06
7200	35.067	53.607	11.326	0.32298172	77%	0.04671909	7.12701E-06
8220	34.888	55.651	9.461	0.27118207	80%	0.0392263	4.44582E-06
9180	34.869	56.923	8.208	0.23539534	83%	0.03404978	4.51755E-06
10140	34.597	58.435	6.968	0.20140475	85%	0.02913306	8.58848E-06
10980	34.721	58.922	6.357	0.18308804	87%	0.02648356	1.67883E-05
11880	34.566	59.885	5.549	0.16053347	88%	0.02322106	3.19635E-05
12600	34.417	60.548	5.035	0.14629398	89%	0.02116133	5.00733E-05
13680	34.494	60.957	4.549	0.13187801	90%	0.01907606	8.96557E-05
14520	34.899	61.093	4.008	0.1148457	92%	0.01661235	0.000132952
15300	34.482	61.751	3.767	0.1092454	92%	0.01580227	0.000184885
16200	34.461	62.117	3.422	0.09930066	93%	0.01436377	0.000261185
17700	34.417						0.000435004
18900	34.511	62.886	2.603	0.07542523	95%	0.01091021	0.000270882
19800	34.618	63.015	2.367	0.06837483	95%	0.00989037	0.000343846
21780	34.564	63.376	2.06	0.05959958	96%	0.00862104	0.000552829

Table S24. Results from kinetic run under the following conditions: 0.2 M **1-D**, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM [Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph2O	Area of Product	Area of starting material	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	dSM/dt
0	44.465	0	55.535	1.24895986	0%	0.2	0.000026383
630	43.786	4.686	51.528	1.17681451	6%	0.18844713	2.42317E-05
1200	43.101	10.572	46.327	1.07484745	14%	0.17211881	2.23818E-05
1800	42.394	15.382	42.224	0.99599	20%	0.15949111	2.05337E-05
2400	41.798	19.886	38.316	0.91669458	27%	0.14679328	1.87876E-05
3060	41.122	23.791	35.087	0.85324157	32%	0.13663235	1.69842E-05
3600	41.025	26.653	32.322	0.78786106	37%	0.12616275	1.55996E-05
4230	40.625	29.398	29.977	0.73789538	41%	0.11816159	1.40868E-05
4800	40.47	31.635	27.895	0.68927601	45%	0.11037601	1.2812E-05
5400	40.299	33.517	26.184	0.64974317	48%	0.10404548	1.15653E-05
6000	40.485	35.617	23.898	0.5902927	53%	0.09452549	1.04144E-05
6780	40.17	37.6	22.23	0.55339806	56%	0.08861743	9.05782E-06
7200	40.059	38.614	21.327	0.53238973	57%	0.0852533	8.39112E-06
8220	39.982	40.735	19.283	0.48229203	61%	0.07723099	6.95079E-06
9180	39.933	42.309	17.758	0.44469486	64%	0.07121043	5.81547E-06
10140	39.888	43.689	16.423	0.41172784	67%	0.06593132	4.87876E-06
10980	39.863	44.532	15.605	0.39146577	69%	0.06268669	4.20899E-06
11880	39.757	45.548	14.695	0.36962044	70%	0.05918852	3.63184E-06
12600	39.962	46.14	13.898	0.34778039	72%	0.0556912	3.26376E-06
13680	40.007	46.763	13.23	0.33069213	74%	0.05295481	2.84587E-06
14520	39.945	47.436	12.619	0.31590938	75%	0.05058759	2.61298E-06
15300	40.03	47.856	12.114	0.30262303	76%	0.04846001	2.4524E-06
16200	40.251	48.21	11.539	0.28667611	77%	0.04590638	2.31393E-06
17700	40.18	48.969	10.851	0.27005973	78%	0.04324554	2.1307E-06
18900	40.414	49.308	10.278	0.25431781	80%	0.04072474	1.9568E-06
19800	40.381	49.658	9.961	0.24667542	80%	0.03950094	1.76657E-06
21780	40.967	49.833	9.2	0.224571	82%	0.03596128	1.00493E-06

Results from Run 2:

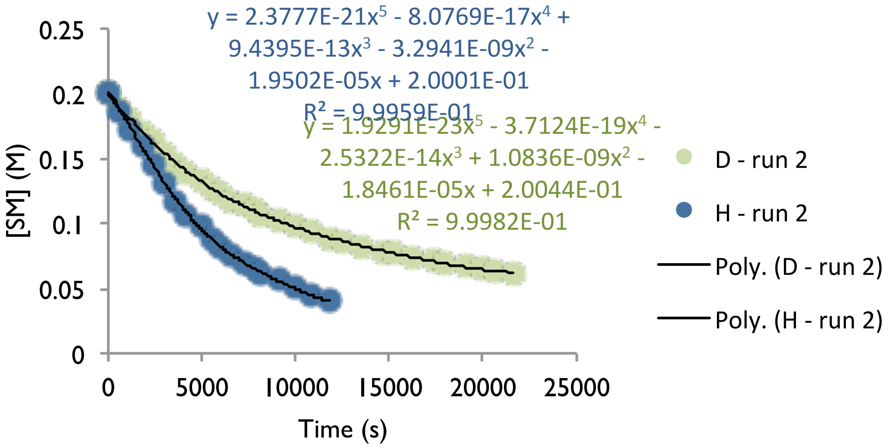


Figure S48. Starting material concentration as a function of time for both protiated (**1**) and deuterated substrates (**1b**). Data points between 0% and 80% conversion were used.

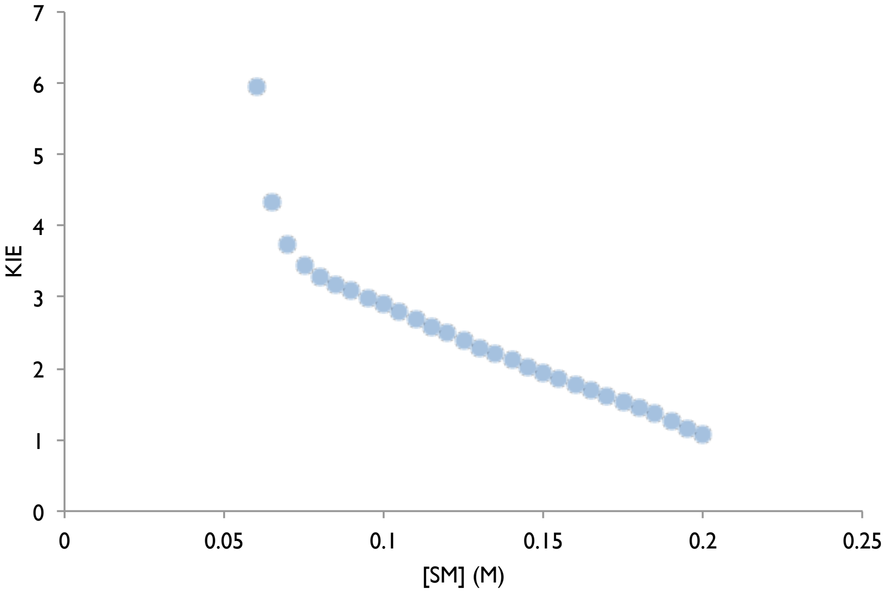


Figure S49. Kinetic isotope effect vs. starting material concentration. This figure represents the ratio between the graphical rate equations for protiated (**1**) and deuterated substrates (**1b**).

Raw data for run 2 (areas from HPLC traces at 230 nm):

Table S25. Results from kinetic run under the following conditions: 0.2 M **1**, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM [Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 ^{o}C using purple LEDs

Time (s)	Area of Ph2O	Area of Product	Area of starting	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	dSM/dt (M/s)
0	43.299	0	56.701	1.30952216	0%	0.2	0.000019502
630	42.667	5.115	52.218	1.22384981	7%	0.18691548	2.26075E-05
1200	42.057	10.604	47.339	1.12559146	14%	0.17190873	2.38636E-05
1800	40.98	15.999	43.021	1.04980478	20%	0.16033402	2.39449E-05
2400	41.566	16.002	42.432	1.02083434	27%	0.146	2.3074E-05
3000	39.716	26.147	34.137	0.85952765	34%	0.13127348	2.154E-05
3600	39.617	30.196	30.187	0.76197087	42%	0.11637388	1.95954E-05
4200	38.791	33.927	27.282	0.70330747	46%	0.10741437	1.74553E-05
4920	37.994	37.561	24.445	0.64339106	51%	0.09826349	1.48779E-05
5580	37.834	40.608	21.558	0.56980494	56%	0.08702486	1.26965E-05
6000	37.531	42.158	20.311	0.54117929	59%	0.08265294	1.14615E-05
6600	37.174	44.373	18.453	0.49639533	62%	0.0758132	9.95368E-06
7200	37.038	45.972	16.99	0.45871807	65%	0.07005885	8.77242E-06
7800	36.73	47.655	15.615	0.42512932	68%	0.06492892	7.91122E-06
8100	36.717	48.45	14.833	0.40398181	69%	0.06169912	7.58848E-06
9060	36.159	50.471	13.37	0.3697558	72%	0.05647187	6.90562E-06
9900	36.136	51.98	11.884	0.32886872	75%	0.05022729	6.45542E-06
10800	36.2489	53.085	10.6661	0.29424617	78%	0.04493947	5.58856E-06
11880	36.128	54.448	9.424	0.26085031	80%	0.03983901	2.98629E-06
12600	36.182	55.126	8.692	0.24022995	81%	0.03805331	-4.44232E-07
13560	35.935	56.153	7.912	0.22017532	83%	0.03487658	-8.27492E-06
14640	36.15	56.702	7.148	0.19773167	84%	0.03132142	-2.3377E-05
15300	35.916	57.366	6.718	0.18704756	85%	0.02962902	-3.69523E-05
16200	35.947	57.814	6.239	0.17356108	86%	0.02749271	-6.22107E-05
17400	35.867	58.511	5.622	0.15674576	88%	0.0248291	-0.000111005
18000	35.822	58.812	5.366	0.14979621	88%	0.02372827	-0.000143258
19080	35.737	59.324	4.939	0.1382041	89%	0.02189204	-0.000217213
19920	36.111	59.297	4.592	0.12716347	90%	0.02014316	-0.000291148
20700	35.896	59.669	4.435	0.12355137	90%	0.01957099	-0.000374713
21600	35.859	60.051	4.09	0.11405784	91%	0.01806718	-0.000491427

Table S26. Results from kinetic run under the following conditions: 0.2 M **1-D**, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM [Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph2O	Area of Product	Area of starting	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	dSM/dt
0	44.197	0	55.803	1.26259701	0%	0.2	0.000018461
630	43.715	4.12	52.165	1.1932975	5%	0.1890227	1.71262E-05
1200	42.775	8.508	48.717	1.13891292	10%	0.18040799	1.59721E-05
1800	42.263	12.136	45.601	1.07898162	15%	0.17091465	1.48138E-05
2400	41.357	16.059	42.584	1.0296685	18%	0.16310327	1.37146E-05
3000	41.295	18.639	40.066	0.97023853	23%	0.15368934	1.26754E-05
3600	41.035	21.18	37.785	0.92079932	27%	0.14585799	1.16967E-05
4200	40.705	23.319	35.976	0.88382263	30%	0.14000075	1.07788E-05
4920	40.413	25.603	33.984	0.84091753	33%	0.13320442	9.75757E-06
5580	40.195	27.791	32.014	0.79646722	37%	0.12616333	8.89782E-06
6000	40.345	28.621	31.034	0.76921552	39%	0.12184656	8.38832E-06
6600	40.13	30.174	29.696	0.73999502	41%	0.11721793	7.71046E-06
7200	39.625	31.665	28.71	0.72454259	43%	0.1147702	7.09028E-06
7800	39.805	32.631	27.564	0.69247582	45%	0.10969071	6.52627E-06
8160	39.888	33.2	26.912	0.67468913	47%	0.10687323	6.21408E-06
9060	39.495	34.833	25.672	0.65000633	49%	0.10296339	5.51618E-06
9900	39.439	36.179	24.382	0.61822054	51%	0.0979284	4.96546E-06
10800	39.38	37.348	23.272	0.59095988	53%	0.09361021	4.47428E-06
11880	39.296	38.705	21.999	0.55982797	56%	0.08867881	4.0046E-06
12600	39.45	39.342	21.208	0.53759189	57%	0.08515653	3.754E-06
13560	39.084	40.488	20.428	0.52266912	59%	0.08279271	3.4833E-06
14640	39.173	41.361	19.466	0.4969239	61%	0.07871457	3.24357E-06
15300	39.112	41.952	18.936	0.48414809	62%	0.07669083	3.11867E-06
16200	39.094	42.66	18.246	0.46672124	63%	0.07393036	2.95891E-06
17400	39.071	43.503	17.426	0.44600855	65%	0.07064939	2.73258E-06
18000	39.077	43.874	17.049	0.43629245	65%	0.06911033	2.59921E-06
19080	39.039	44.59	16.371	0.41934988	67%	0.06642656	2.29735E-06
19920	38.893	45.169	15.938	0.40979096	68%	0.06491239	1.98451E-06
20700	38.984	45.473	15.543	0.39870203	68%	0.06315587	1.61235E-06
21600	38.778	46.096	15.126	0.39006653	69%	0.06178797	1.061E-06

Run 3:

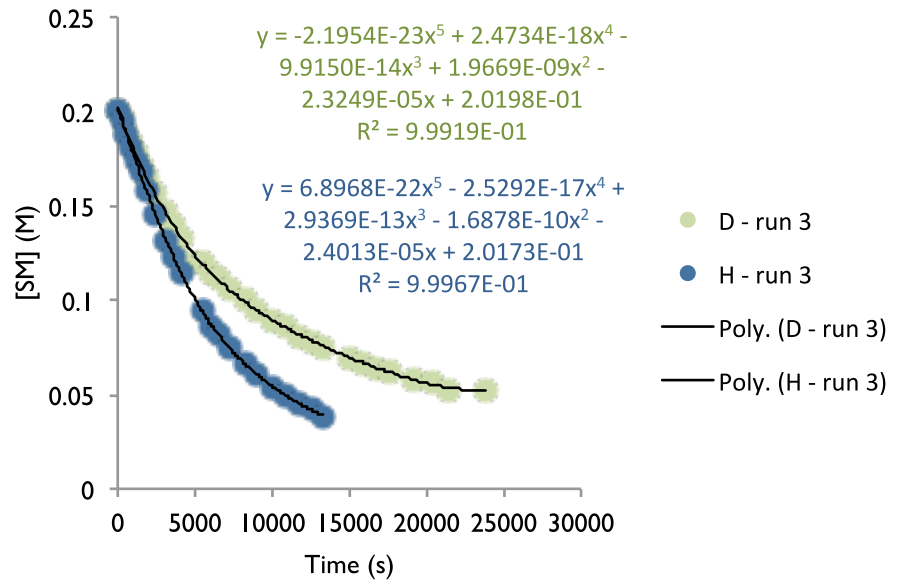


Figure S50. Starting material concentration as a function of time for both protiated (**1**) and deuterated substrates (**1b**). Data points between 0% and 80% conversion were used.

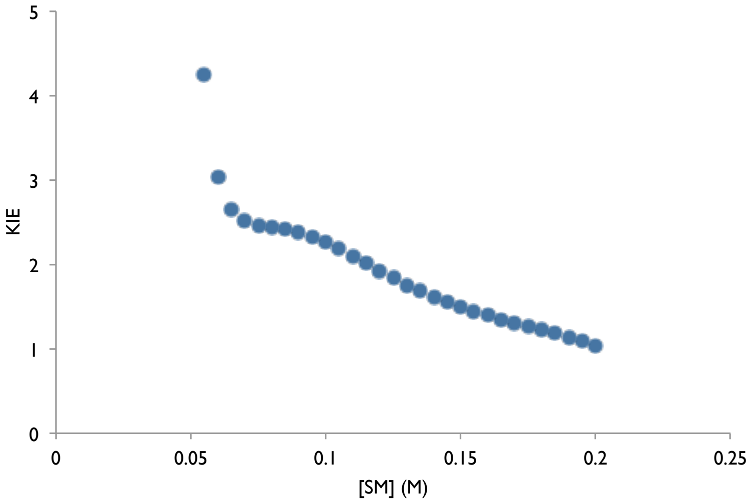


Figure S51. Kinetic isotope effect vs. starting material concentration. This figure represents the ratio between the graphical rate equations for protiated (**1**) and deuterated substrates (**1b**).

Raw data for run 3 (areas from HPLC traces at 230 nm):

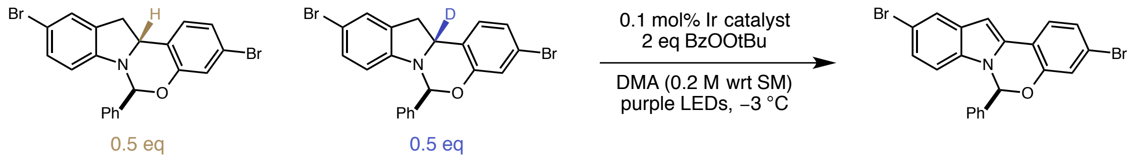
Table S27. Results from kinetic run under the following conditions: 0.2 M **1**, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM [Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 ^{o}C using purple LEDs

Time (s)	Area of Ph2O	Area of Product	Area of starting material	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	dSM/dt
0	43.344	0	56.656	1.307124	0%	0.2	0.000024013
330	42.877	2.449	54.674	1.275136	2%	0.195106	2.4032E-05
600	42.957	4.448	52.595	1.224364	6%	0.187337	2.39198E-05
900	42.651	6.934	50.415	1.182036	10%	0.18086	2.36746E-05
1200	42.197	9.916	47.887	1.134844	13%	0.17364	2.3317E-05
1500	41.643	12.571	45.786	1.099489	16%	0.16823	2.28609E-05
1830	41.65	15.458	42.892	1.02982	21%	0.15757	2.22615E-05
2400	40.998	20.031	38.971	0.950559	27%	0.145443	2.10323E-05
3030	40.428	24.837	34.735	0.859182	34%	0.131461	1.94704E-05
3600	39.663	28.595	31.742	0.800292	39%	0.122451	1.79504E-05
4200	38.801	32.282	28.917	0.745264	43%	0.114031	1.6311E-05
							0.000024013
5520	38.217	38.263	23.52	0.615433	53%	0.094166	1.28442E-05
6120	38.107	40.326	21.567	0.565959	57%	0.086596	1.14312E-05
6600	37.825	42.067	20.108	0.531606	59%	0.08134	1.04036E-05
7200	37.511	43.997	18.492	0.492975	62%	0.075429	9.26234E-06
8220	37.39	46.589	16.021	0.428484	67%	0.065561	7.70157E-06
9060	37.051	48.411	14.538	0.392378	70%	0.060037	6.75191E-06
10020	36.836	50.109	13.055	0.354409	73%	0.054227	5.95109E-06
10800	36.823	51.215	11.962	0.324851	75%	0.049705	5.41809E-06
11820	36.523	52.695	10.782	0.295211	77%	0.04517	4.66422E-06
12660	36.526	53.487	9.987	0.273422	79%	0.041836	3.76795E-06
13380	37.104	53.592	9.304	0.250755	81%	0.038367	2.60863E-06
15000	36.349	55.608	8.043	0.221272	83%	0.033856	-2.2976E-06
15960	36.414	56.172	7.414	0.203603	84%	0.031153	-7.48595E-06
16800	36.424	56.61	6.966	0.191248	85%	0.029262	-1.39853E-05
17640	36.169	57.337	6.494	0.179546	86%	0.027472	-2.27768E-05
19200	36.397	57.772	5.831	0.160206	88%	0.024513	-4.68696E-05
20400	36.402	58.196	5.402	0.148398	89%	0.022706	-7.411E-05
21480	36.382	58.577	5.041	0.138558	89%	0.0212	-0.00010671
23820	35.173	60.435	4.392	0.124869	90%	0.019106	-0.000210702
40260	35.399	62.823	1.778	0.050227	96%	0.007685	-0.00384834

Table S28. Results from kinetic run under the following conditions: 0.2 M **1-D**, 0.4 M BzOOtBu, 0.2 M Ph2O, 0.2 μM [Ir(dF-CF$_3$-ppy)$_2$(dtbpy)](PF$_6$) in DMA at -3 °C using purple LEDs

Time (s)	Area of Ph2O	Area of Product	Area of starting material	A_{SM}/A_{Ph2O}	Conversion	[SM] (M)	dSM/dt
0	44.751	0	55.249	1.234587	0%	0.2	0.000023249
330	44.539	1.681	53.78	1.207481	2%	0.195609	2.19829E-05
600	44.383	3.874	51.743	1.165829	6%	0.188861	2.09937E-05
900	43.921	6.217	49.862	1.135266	8%	0.18391	1.99424E-05
1200	43.728	8.325	47.947	1.096483	11%	0.177627	1.89399E-05
1500	43.688	10.188	46.124	1.055759	14%	0.17103	1.79847E-05
1830	43.472	12.323	44.205	1.016861	18%	0.164729	1.69869E-05
2400	43.046	15.482	41.472	0.963434	22%	0.156074	1.53881E-05
3030	42.556	18.698	38.746	0.910471	26%	0.147494	1.37945E-05
3600	42.296	21.188	36.516	0.863344	30%	0.13986	1.24991E-05
4200	41.944	23.522	34.534	0.823336	33%	0.133378	1.12752E-05
4860	39.751	30.966	29.283	0.736661	40%	0.119337	1.00819E-05
5520	41.466	27.688	30.846	0.743887	40%	0.120508	9.03569E-06
6120	41.453	29.206	29.341	0.707814	43%	0.114664	8.20112E-06
6600	41.087	30.621	28.292	0.688588	44%	0.111549	7.60676E-06
7200	41.102	31.992	26.906	0.654615	47%	0.106046	6.94768E-06
8220	40.643	34.313	25.044	0.616195	50%	0.099822	6.01751E-06
9060	40.629	35.743	23.628	0.581555	53%	0.09421	5.40649E-06
10020	40.229	37.54	22.231	0.552611	55%	0.089522	4.84985E-06
10800	39.96	38.721	21.319	0.533509	57%	0.086427	4.48885E-06
11820	40.016	39.973	20.011	0.500075	59%	0.081011	4.1133E-06
12660	39.978	40.843	19.179	0.479739	61%	0.077716	3.86587E-06
13380	39.956	41.624	18.42	0.461007	63%	0.074682	3.68506E-06
15000	39.686	43.247	17.067	0.430051	65%	0.069667	3.33446E-06
15960	39.71	43.968	16.322	0.41103	67%	0.066586	3.1337E-06
16800	39.768	44.504	15.728	0.395494	68%	0.064069	2.94585E-06
17640	39.55	45.314	15.136	0.382705	69%	0.061997	2.73653E-06
19200	39.645	46.104	14.251	0.359465	71%	0.058232	2.26346E-06
20400	39.645	46.651	13.704	0.345668	72%	0.055997	1.8039E-06
21480	40.422	46.501	13.077	0.323512	74%	0.052408	1.30735E-06
23820	38.302	49.329	12.369	0.322934	74%	0.052314	-5.93797E-08
40260	38.139	52	9.861	0.258554	79%	0.041885	-1.02277E-05

The intermolecular competition KIE with compound 1 and 1b



A vial was charged with 50:50 mixture of deuterated and protiated starting material and the reaction was run, under standard conditions, to partial conversion. A small aliquot was taken, pushed through a celite plug and shot on the HPLC to determine the degree of conversion. To quench the reaction, water and DCM was added and the organic layer was washed several times with 10% LiCl. The organic solution was dried on $NaSO_4$ and concentrated in vacuo. To remove any remaining DMA, the crude mixture was purified on neutral alumina with 10% ethyl acetate in hexanes (a very broad band was collected to ensure that all the starting material was recovered). Next, a H NMR spectrum in C_6H_6 was collected. To determine the intermolecular competition KIE, the equation 1 was used (see derivation below). A sample calculation is included below.

Table S29. Summary of all intermolecular competition KIE experiments

Run	Perester used	conv. (%)**	$(D/H)_{initial}$*	$(D/H)_{final}$*	KIE
1a	BzOOtBu	80	0.887	1.325	1.28
1b	BzOOtBu	43	0.887	1.083	1.42
2	BzOOtBu	84	0.96	1.63	1.33
3	BzOOtBu	61	0.96	1.44	1.54
4	BzOOtBu	91	0.96	2.125	1.38
				mean KIE	1.39
				std dev	0.08
5	AcOOtBu	51	0.96	1.27	1.47
6	AcOOtBu	39	0.96	1.13	1.38
7	AcOOtBu	73	0.96	1.56	1.45
				mean KIE	1.43
				std dev	0.04

* determined by ^1H NMR
** determined by HPLC using Ph_2O as an internal standard

Derivation of intermolecular competition KIE equation for radical chains[6]

The rates for an intermolecular competition experiment can be expressed as follows, where a, b and c denote concentrations.

$$-\frac{da_H}{dt} = k_H \times a_H \times f(b, c \ldots)$$

$$-\frac{da_D}{dt} = k_D \times a_D \times f(b, c \ldots)$$

Therefore, we can write

$$\frac{1}{k_H} \times \frac{da_H}{a_H} = \frac{1}{k_D} \times \frac{da_D}{a_D}$$

Integrating this expression with the initial conditions $a_H = a_H^0$ *and* $a_D = a_D^0$*, we obtain the following term:*

$$\frac{k_H}{k_D} = \frac{\log\left(\frac{a_H}{a_H^0}\right)}{\log\left(\frac{a_D}{a_D^0}\right)}$$

where a_H *and* a_D *represent the concentration of remaining H- and D-labeled starting material molecules at any given level of conversion. The measured ratio between the deuterated and protiated substrate is now a direct function of the ratio of rate constants. Note that this calculation only holds when the reaction is first order with respect to a.*

This analysis hold true in a radical chain reaction as well. Assuming the chains are sufficiently long, the majority of starting material is consumed during the propagation steps. We can write out the rate law for the propagation steps of the reported reaction:

$$-\frac{d[SM]_H}{dt} = k_H [SM]_H [tBuO\,\cdot]$$

$$-\frac{d[SM]_D}{dt} = k_D [SM]_D [tBuO\,\cdot]$$

Since the two reactions occur in the same reaction vial, the [tBuO•] is identical and we can rearrange both expressions and write

$$\frac{1}{k_H} \times \frac{d[SM]_H}{[SM]_H} = \frac{1}{k_D} \times \frac{d[SM]_D}{[SM]_D}$$

---

[6] L. Melander, W. H. Saunders Jr., *Reaction Rates of Isotopic Molecules*, John Wiley and Sons Inc., New York, 1980, pp 95.

Integrating this expression with the initial conditions $[\boldsymbol{SM}]_{\boldsymbol{H}} = [\boldsymbol{SM}]_{\boldsymbol{H}}^{\boldsymbol{0}}$ *and* $[\boldsymbol{SM}]_{\boldsymbol{D}} = [\boldsymbol{SM}]_{\boldsymbol{D}}^{\boldsymbol{0}}$*, we obtain the following term:*

$$\frac{\boldsymbol{k_H}}{\boldsymbol{k_D}} = \frac{\mathbf{log}\left(\frac{[\boldsymbol{SM}]_{\boldsymbol{H}}}{[\boldsymbol{SM}]_{\boldsymbol{H}}^{\boldsymbol{0}}}\right)}{\mathbf{log}\left(\frac{[\boldsymbol{SM}]_{\boldsymbol{D}}}{[\boldsymbol{SM}]_{\boldsymbol{D}}^{\boldsymbol{0}}}\right)} \qquad (1)$$

Sample calculation (from Run 3)

For simplicity, it is assumed the reaction has 100 molecules. Of these, 49 molecules are deuterated and 51 are protiated (see initial ^{1}H NMR spectrum).

$$\boldsymbol{Initial\ \#\ H\ molecules = \ a_H^0 = 51}$$

$$\boldsymbol{Initial\ \#\ D\ molecules = \ a_D^0 = 49}$$

After 61% conversion, the recovered starting material has been isotopically enriched. According to the ^{1}H NMR, 59% of the recovered starting material is deuterated. With this at hand, we can now calculate the intermolecular competition KIE.

$$\#\ \boldsymbol{Remaining\ H\ moleulces = \ a_H = (1 - \%\ conv)(\%\ H\ of\ recovered\ SM)}$$
$$= (\mathbf{1} - 0.61)(0.41) = 16.0$$

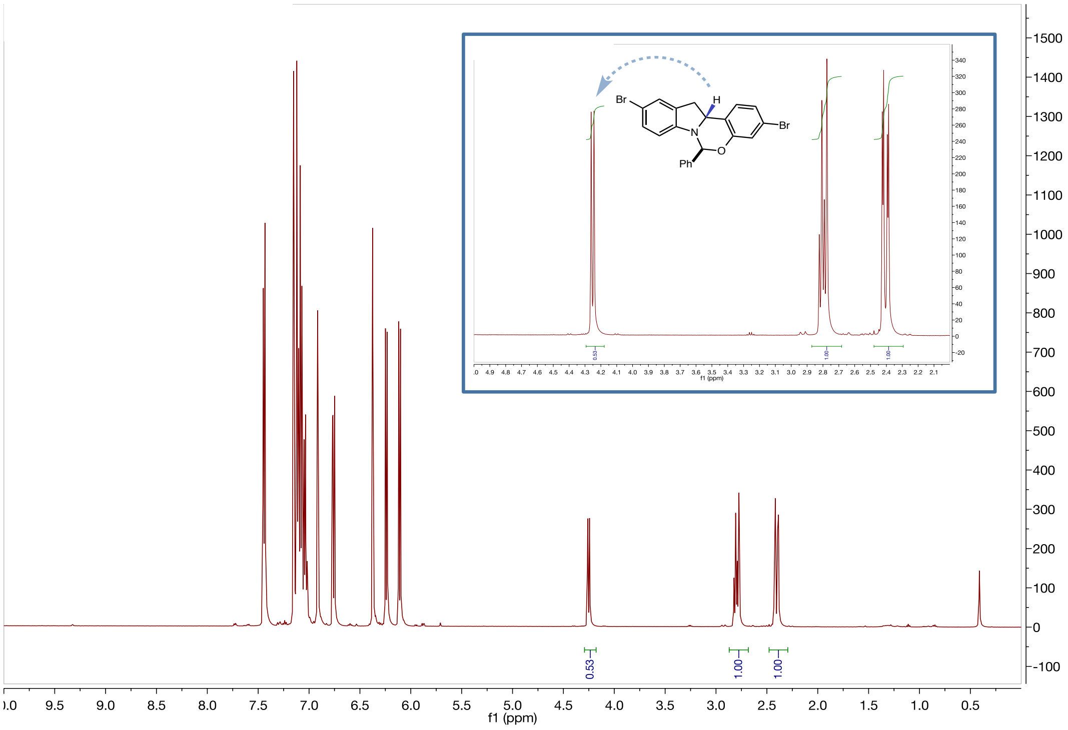
$$\#\ Remaining\ D\ moleulces = \ a_D = (1 - \%\ conv)(\%\ D\ of\ recovered\ SM)$$
$$= (1 - 0.61)(0.59) = 23.0$$

Thus,

$$\frac{k_H}{k_D} = \frac{\log\left(\frac{[SM]_H}{[SM]_H^0}\right)}{\log\left(\frac{[SM]_D}{[SM]_D^0}\right)} = \frac{\log\left(\frac{[16.06]_H}{[51]_H^0}\right)}{\log\left(\frac{[23.12]_D}{[49]_D^0}\right)} = 1.54$$

NMR Spectra from Intermolecular KIE experiment (see Table S29 for summary)

At 0% conversion – H = 53%



At 80% conversion – H = 43%

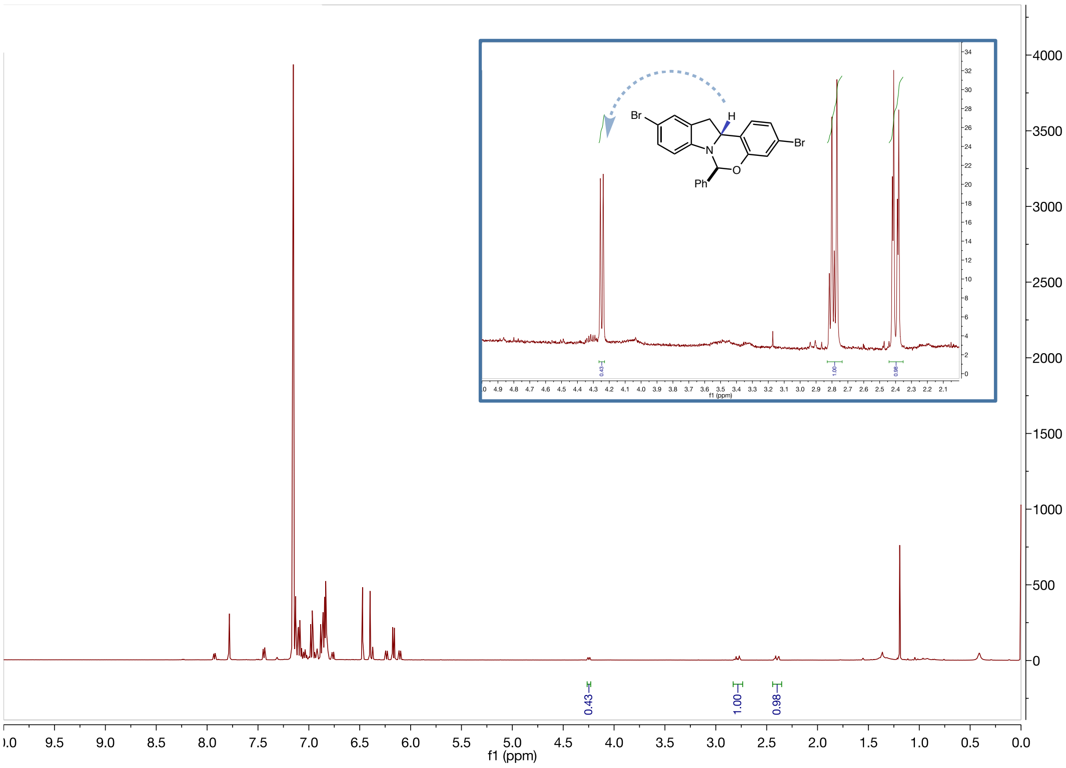
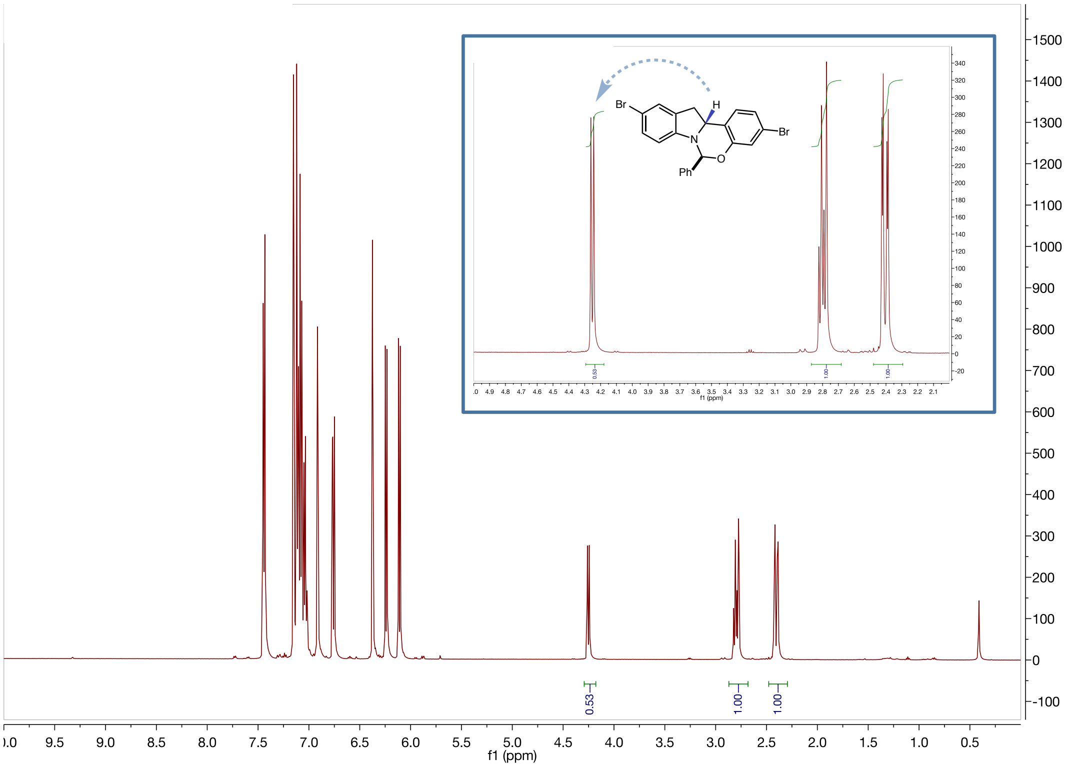


Figure S52. Crude NMR spectra from intermolecular KIE experiment, run 1a.

At 0% conversion – H = 53%



At 43% conversion – H = 48%

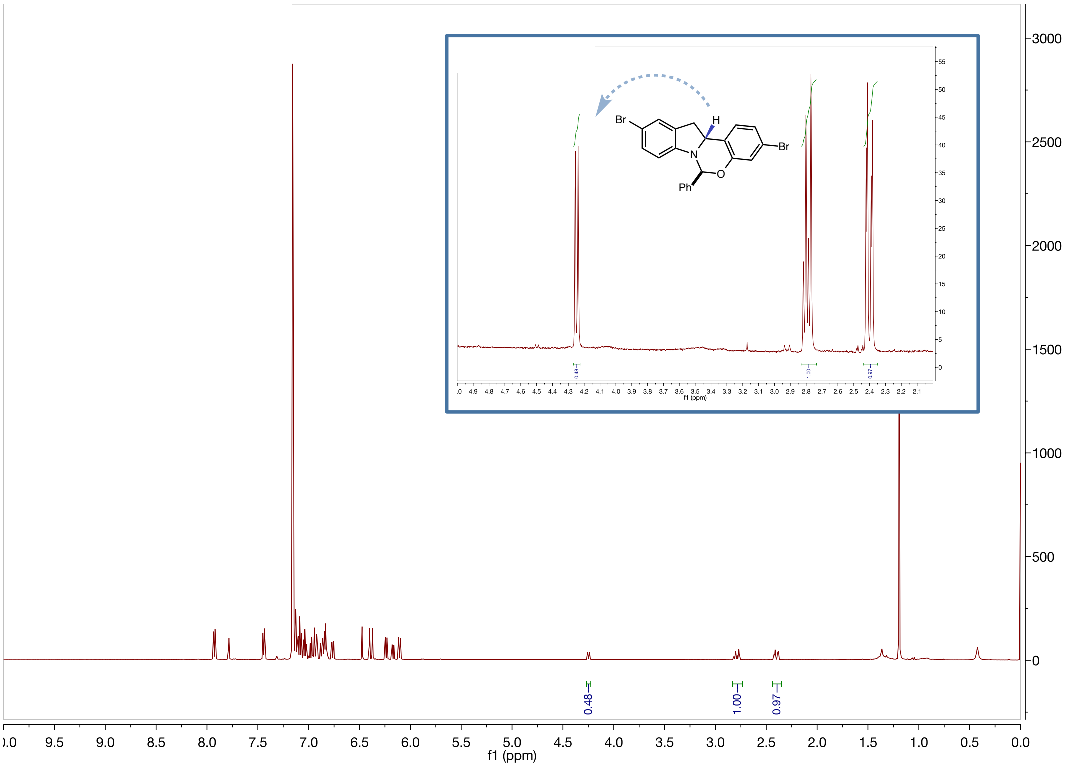
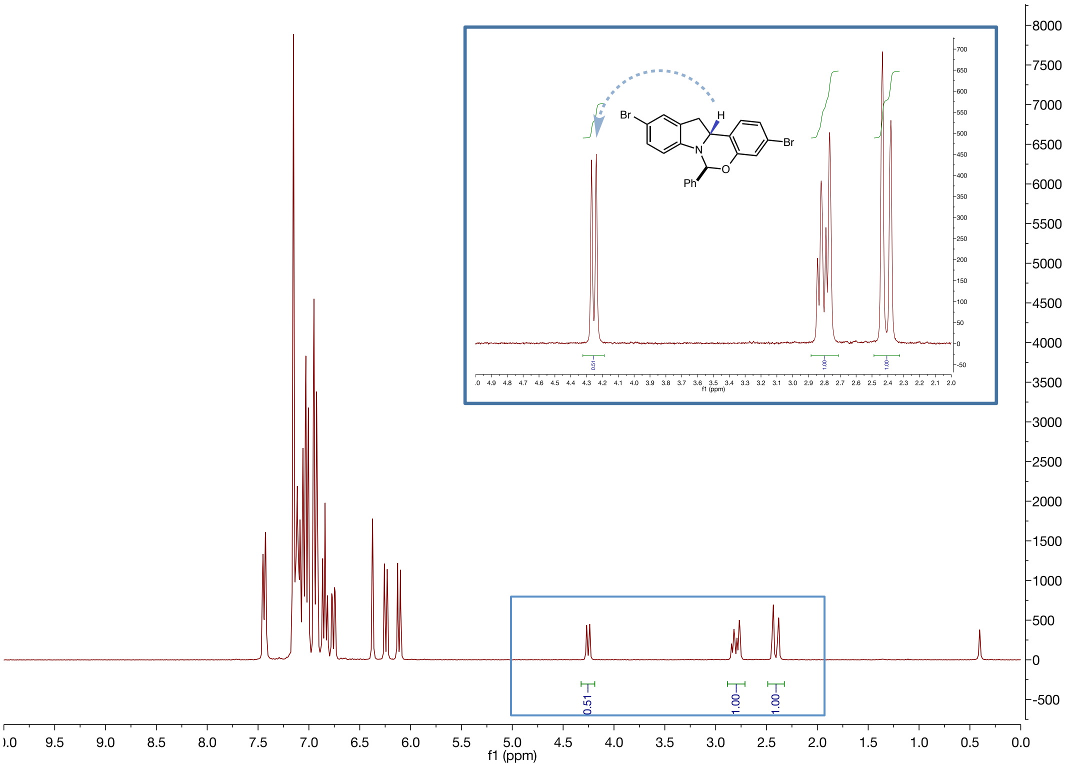


Figure S53. Crude NMR spectra from intermolecular KIE experiment, run 1b.

At 0% conversion – H = 51%



At 84% conversion – H = 38%

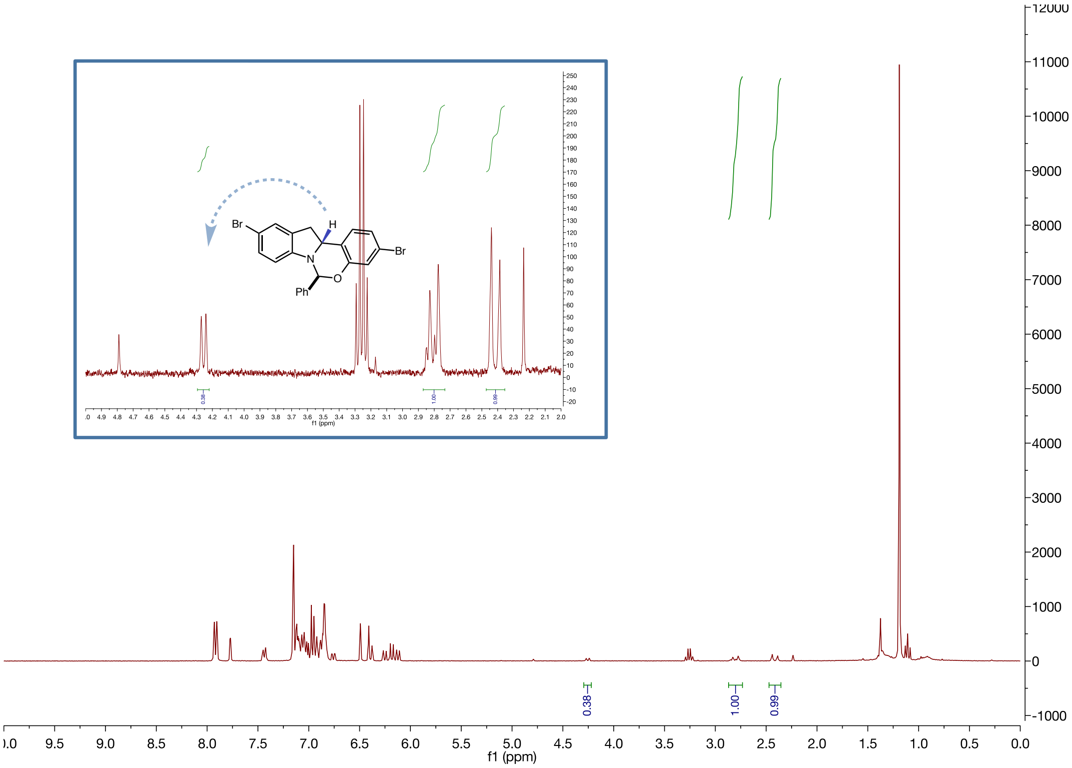
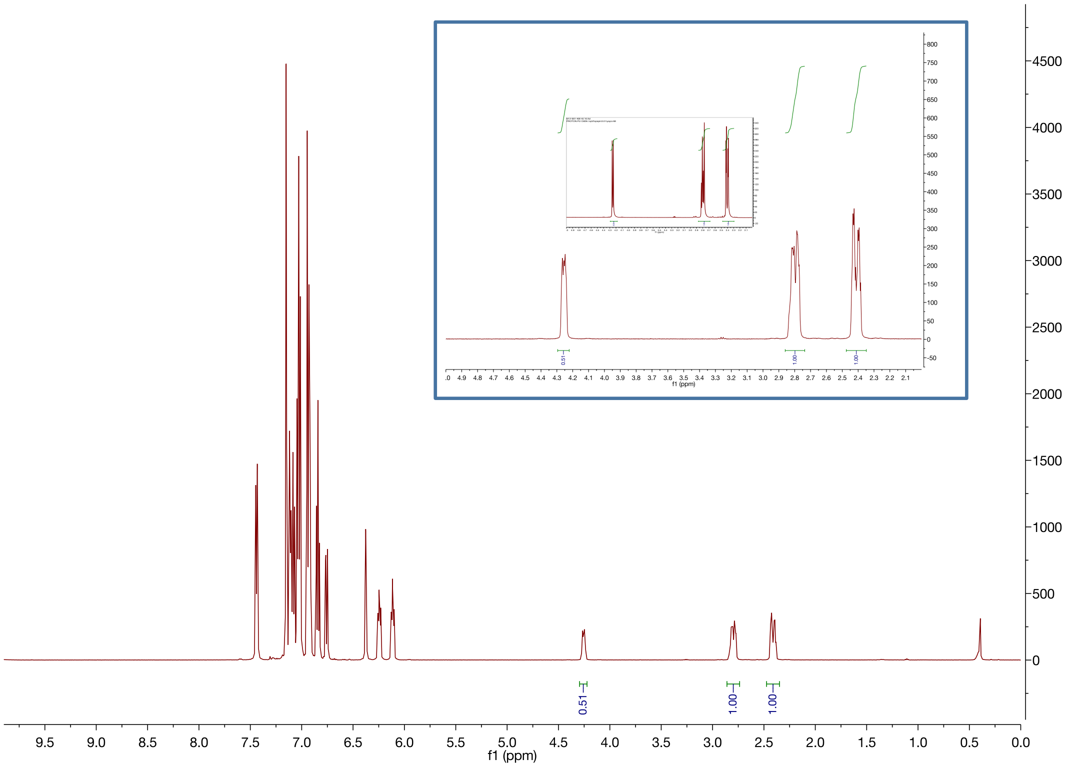


Figure S54. Crude NMR spectra from intermolecular KIE experiment, run 2.

At 0% conversion – H = 51%



At 61% conversion – H = 41%

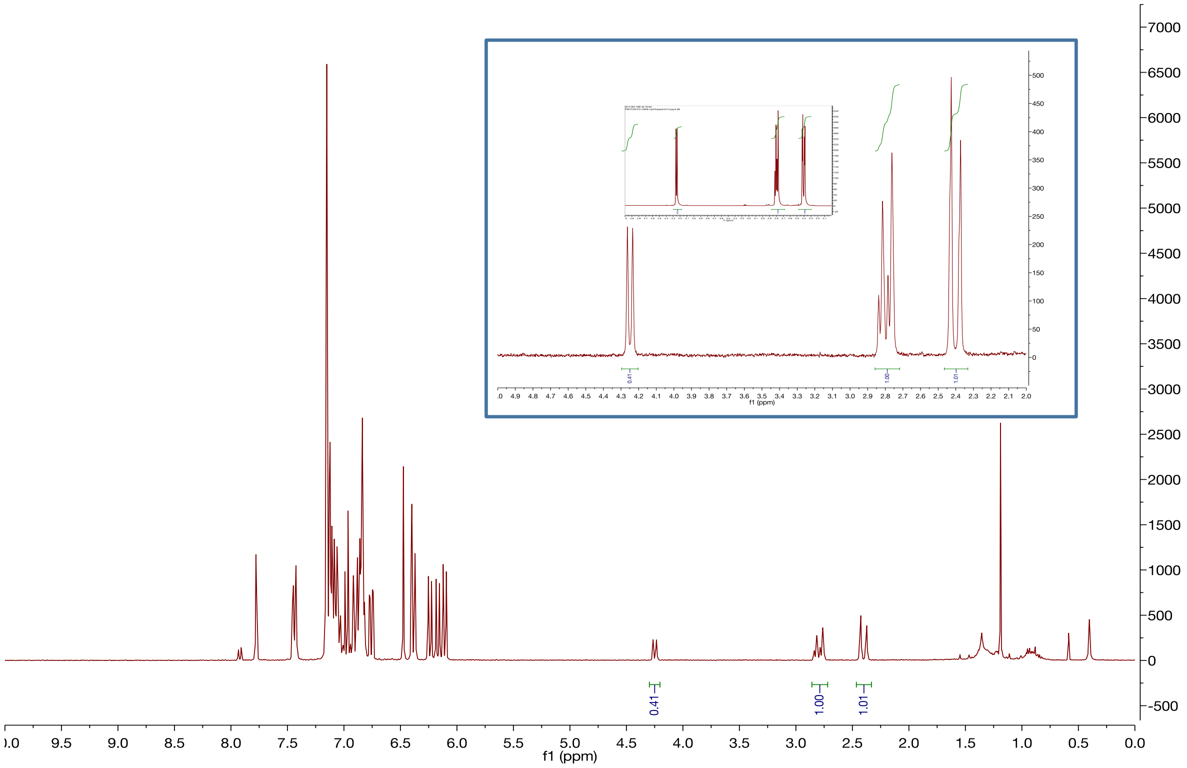


Figure S55. Crude NMR spectra from intermolecular KIE experiment, run 3.

At 0% conversion – H = 51%
At 91% conversion – H = 32%

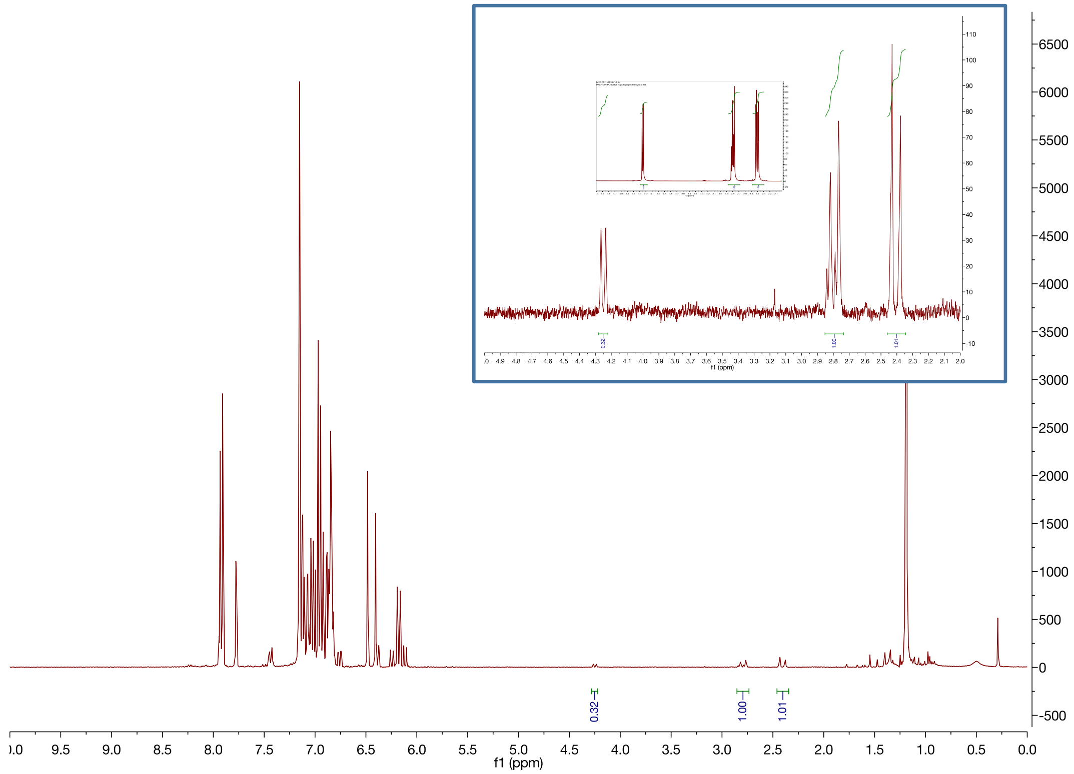
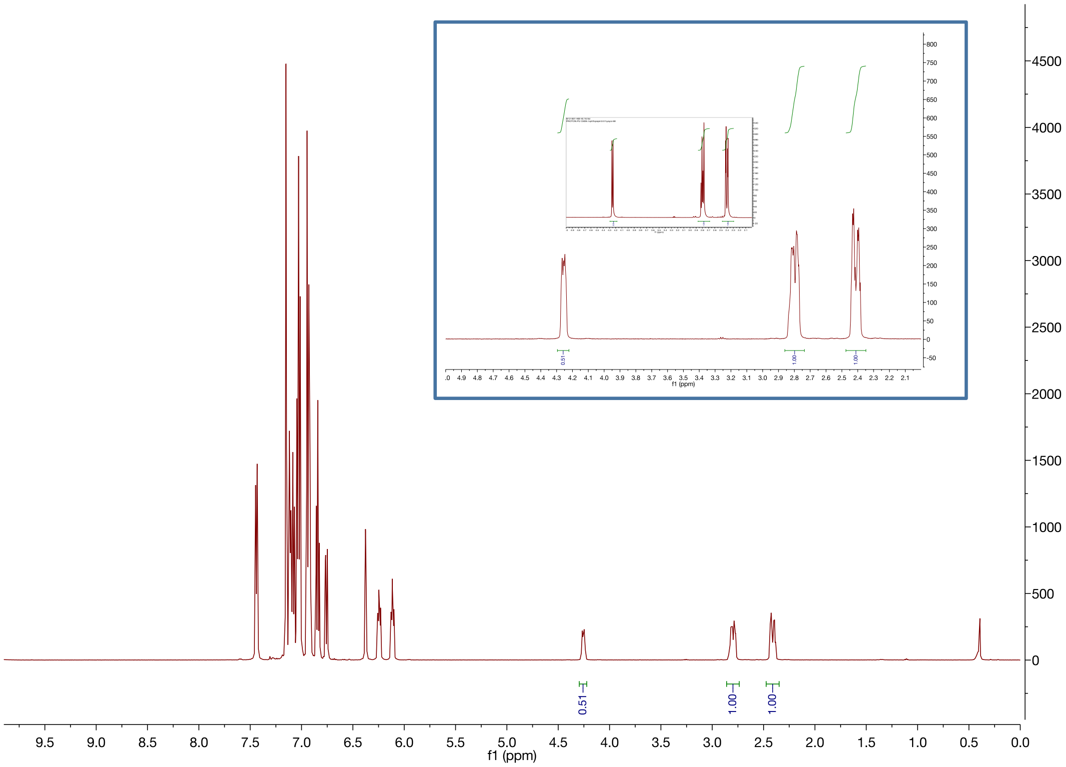


Figure S56. Crude NMR spectra from intermolecular KIE experiment, run 4.

At 0% conversion – H = 51%



At 51% conversion – H = 44%

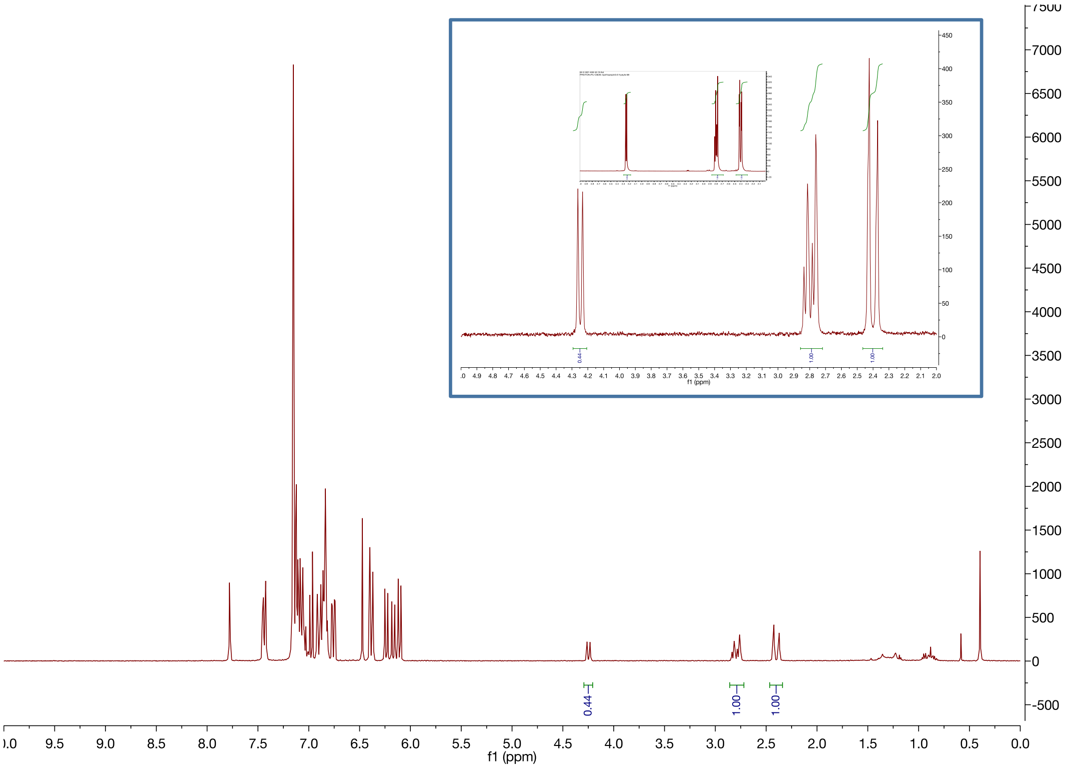


Figure S57. Crude NMR spectra from intermolecular KIE experiment, run 5.

At 0% conversion – H% = 51%
At 39% conversion – H = 46%

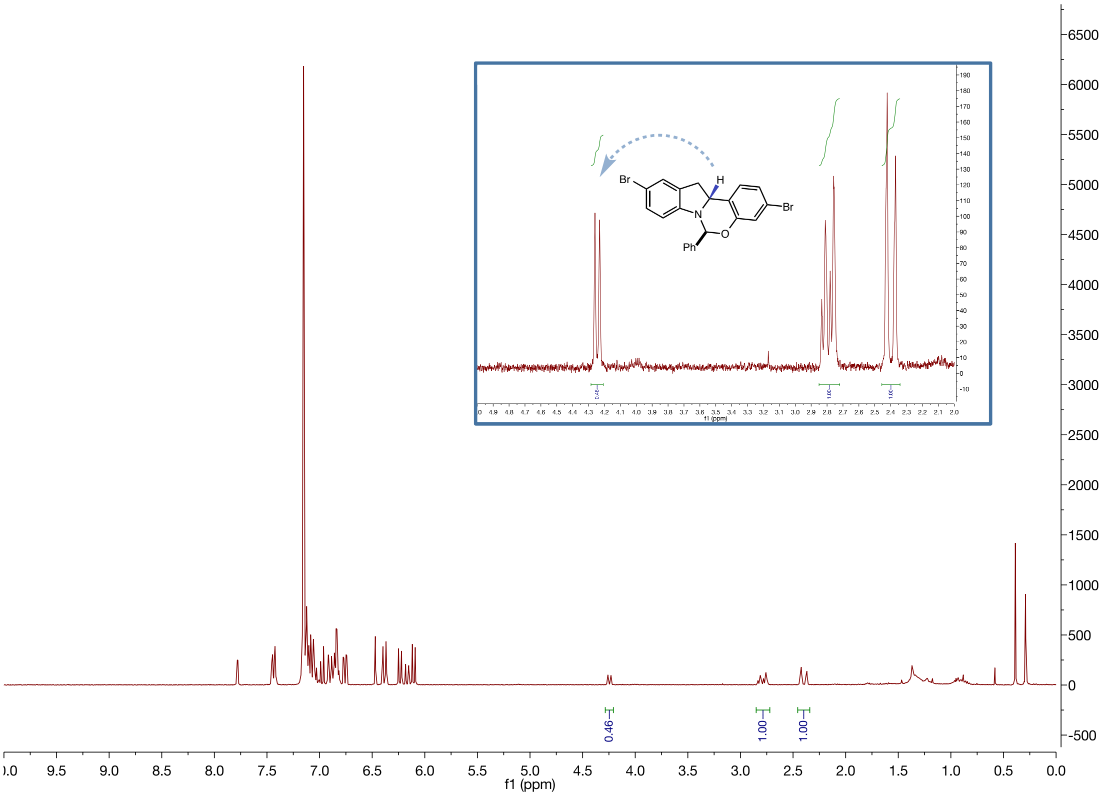


Figure S58. Crude NMR spectra from intermolecular KIE experiment, run 6.

At 0% conversion – H% = 51%
At 73% conversion – H = 39%

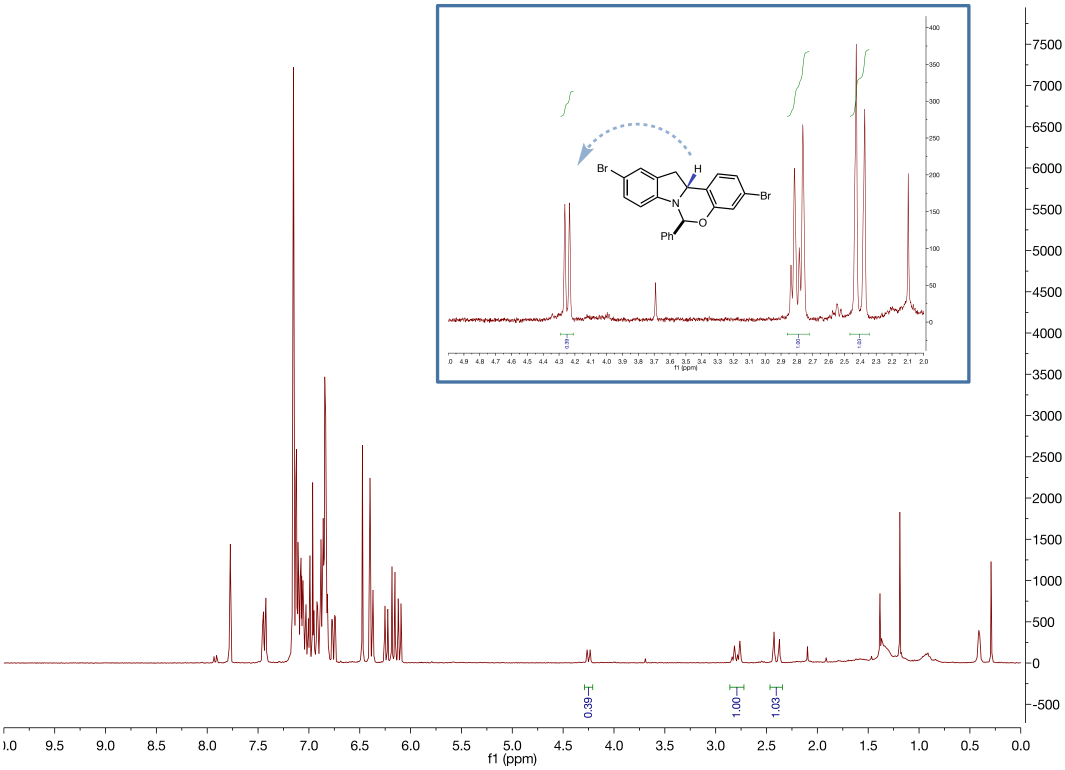
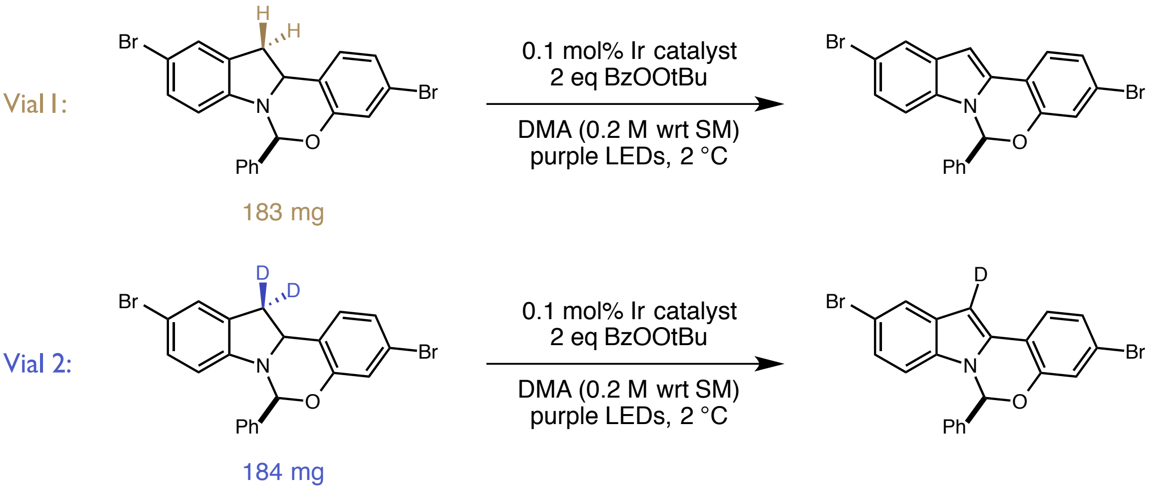


Figure S59. Crude NMR spectra from intermolecular KIE experiment, run 7.

Direct KIE between reactions run in parallel with 1 and 1c



Two reactions, one with deuterated substrate **1c** and one with protiated substrate **1**, were run side-by-side in separate vials under identical conditions. The experiment was run three times. The following pages outline how the data was analyzed.

Standard reaction conditions / General reaction set-up:

A 2 mL volumetric flask was charged with starting material (1 eq, 0.4 mmol, 183 mg), BzOOtBu (2 eq, 0.8 mmol, 152 μL), Ir[(dF-CF$_3$-ppy)$_2$(dtbpy)]PF$_6$ (0.1 mol%, 0.4 μmol), Ph$_2$O (1 eq, 0.4 mmol, 63 uL) and DMA. The solution was then transferred to a 12.5 cm culture tube and sparged with argon in the dark for 60 min. The vials were immersed in a 2 ^{o}C Cryocool bath, which was lined with four purple (402 nm) LED strips (see picture of an example set-up at end of kinetic section in SI). The reaction was stirred by continuous sparging. Aliquots were taken with 5–15 minute intervals and pushed through a plug of celite with 50:50 IPA:hexanes. Samples were analyzed on an Agilent 1260 Infinty HPLC using a Zorbax-Rx Sil 5 um 4.6 x 250 mm column using a 20 minute method with 1% IPA in hexanes as the eluent. UV-absorbances were measured at 230 nm. Starting material conversions and yields were tracked as a function of time from peak areas relative to Ph$_2$O as an internal standard.

Summary of results (3 runs):

Table S30. Results from kinetic run under the following conditions: 0.2 M **1**, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at 2 °C using purple LEDs

Protiated substrate (**1**)								
	Run 1		Run 2		Run 3		*Mean of 3 runs*	
Time (s)	Conversion	[**1**] (M)	Conversion	[**1**] (M)	Conversion	[**1**] (M)	Conversion	[**1**] (M)
0	0%	0.200	0%	0.200	0%	0.200	0%	0.200
300	2%	0.195	3%	0.193	0%	0.200	2%	0.196
600	5%	0.190	5%	0.190	3%	0.194	4%	0.191
900	8%	0.183	8%	0.184	8%	0.184	8%	0.184
1200	10%	0.180	11%	0.177	8%	0.184	10%	0.180
1500	14%	0.173	15%	0.171	11%	0.178	13%	0.174
1800	17%	0.165	20%	0.161	14%	0.172	17%	0.166
2400	24%	0.151	26%	0.147	21%	0.158	24%	0.152
3000	30%	0.141	35%	0.130	29%	0.143	31%	0.138
3600	40%	0.119	40%	0.121	33%	0.134	38%	0.125
4200	46%	0.107	47%	0.106	40%	0.120	44%	0.111
4800	52%	0.097	54%	0.092	45%	0.110	50%	0.100
5400	56%	0.087	57%	0.086	49%	0.103	54%	0.092
6000	61%	0.078	62%	0.076	55%	0.091	59%	0.082
6600	63%	0.073	65%	0.069	56%	0.088	62%	0.077
7200	67%	0.067	69%	0.063	60%	0.079	65%	0.070
8100	70%	0.059	73%	0.055	65%	0.070	69%	0.061
9000	74%	0.052	76%	0.048	68%	0.063	73%	0.054
9900	78%	0.045	79%	0.042	71%	0.057	76%	0.048
10800	80%	0.040	81%	0.037	75%	0.051	79%	0.043
11880	83%	0.035	83%	0.033	77%	0.046	81%	0.038
12600	84%	0.031	85%	0.029	79%	0.042	83%	0.034
13500	86%	0.028	87%	0.026	81%	0.037	85%	0.030
14400	88%	0.025	88%	0.023	83%	0.034	86%	0.027
15300	89%	0.022	89%	0.022	85%	0.031	88%	0.025

Table S31. Results from kinetic run under the following conditions: 0.2 M **1c**, 0.4 M BzOOtBu, 0.2 M Ph_2O, 0.2 μM $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at 2 ^{o}C using purple LEDs

Deuterated substrate (**1c**)								
	Run 1		Run 2		Run 3		*Mean of 3 runs*	
Time (s)	Conversion	[**1c**] (M)	Conversion	[**1c**] (M)	Conversion	[**1c**] (M)	Conversion	[**1**] (M)
0	0%	0.200	0%	0.200	0%	0.200	0%	0.200
300	2%	0.196	1%	0.198	3%	0.194	2%	0.196
600	4%	0.191	4%	0.193	4%	0.193	4%	0.192
900	9%	0.183	9%	0.183	8%	0.185	8%	0.184
1200	12%	0.176	13%	0.175	10%	0.180	12%	0.177
1500	18%	0.164	19%	0.163	12%	0.176	16%	0.168
1800	24%	0.152	26%	0.147	17%	0.166	22%	0.155
2400	36%	0.128	37%	0.126	24%	0.151	32%	0.135
3000	44%	0.111	46%	0.108	35%	0.130	42%	0.116
3600	51%	0.098	52%	0.096	43%	0.114	49%	0.103
4200	58%	0.083	58%	0.085	47%	0.105	54%	0.091
4800	61%	0.077	64%	0.072	53%	0.094	59%	0.081
5400	67%	0.067	67%	0.065	57%	0.086	64%	0.073
6000	70%	0.060	71%	0.059	63%	0.074	68%	0.064
6600	72%	0.055	72%	0.055	66%	0.068	70%	0.059
7200	75%	0.051	75%	0.050	67%	0.065	72%	0.055
8100	77%	0.045	78%	0.044	73%	0.055	76%	0.048
9000	80%	0.040	80%	0.040	75%	0.050	78%	0.043
9900	82%	0.035	82%	0.036	77%	0.046	81%	0.039
10800	83%	0.034	83%	0.033	79%	0.042	82%	0.036
11880	85%	0.030	85%	0.031	81%	0.038	84%	0.033
12600	86%	0.028	86%	0.028	82%	0.035	85%	0.030
13500	87%	0.026	87%	0.026	84%	0.032	86%	0.028
14400	88%	0.024	88%	0.025	85%	0.029	87%	0.026
15300	89%	0.023	88%	0.023	86%	0.028	88%	0.025

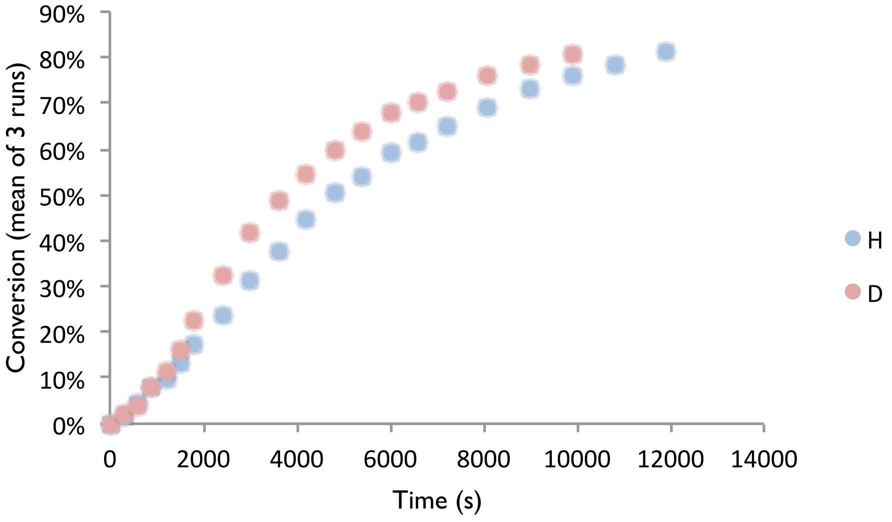


Figure S60. Starting material conversion for **1** and **1c** vs. time. Average of 3 runs.

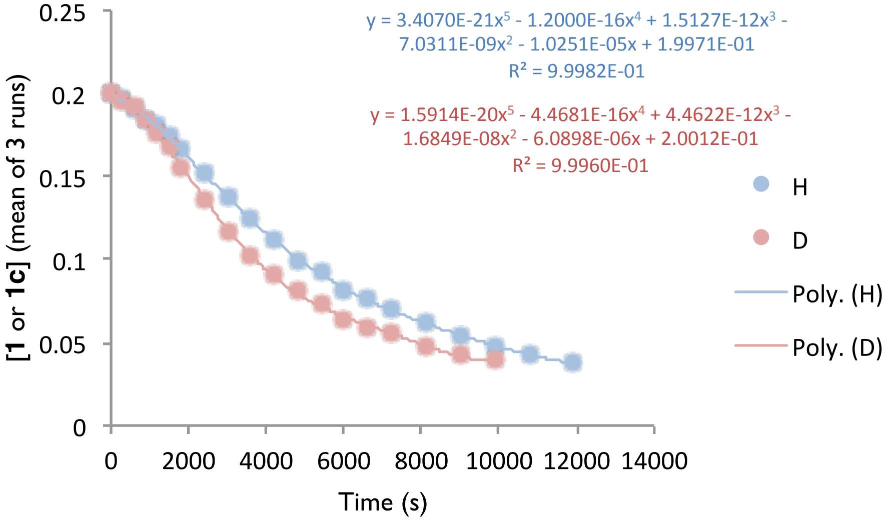


Figure S61. Concentration of starting material conversion for **1** and **1c** vs. time. Average of 3 runs. Data fitted to 5th order polynomial.

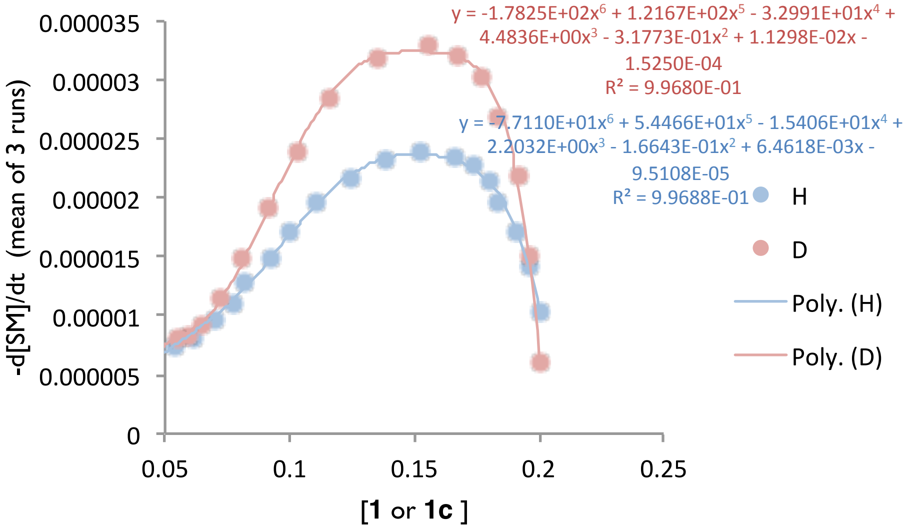


Figure S62. –d[1]/dt or –d[1c]/dt vs.[1] or [1c]. Graphical rate equations for **1** and **1c** obtained from Figure S61. Data fitted to 6th order polynomial.

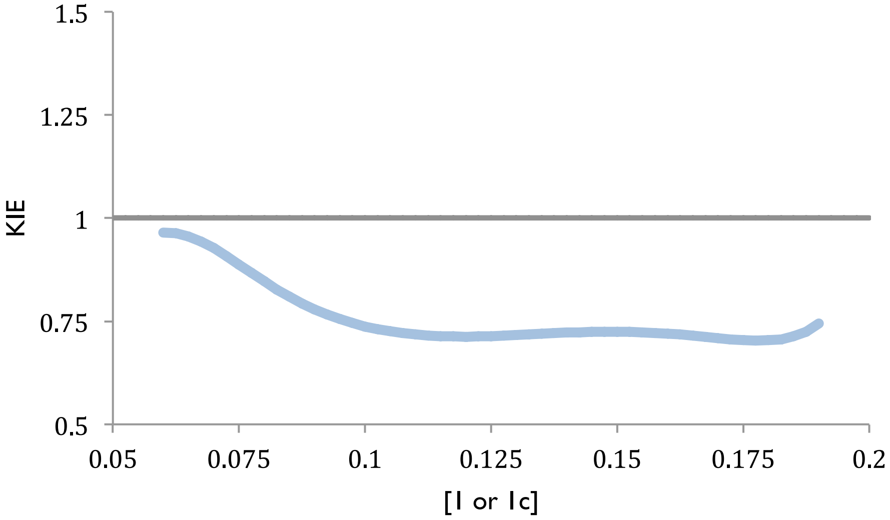
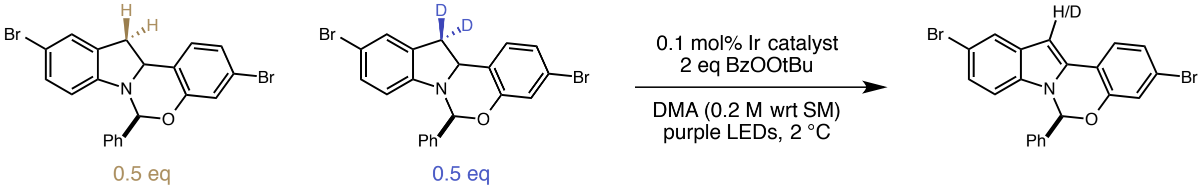


Figure S63. Kinetic isotope effect vs. starting material concentration. This figure represents the ratio between the graphical rate equations for protiated (**1**) and deuterated substrates (**1b**) as a function of starting material.

The intermolecular competition KIE with 1c and 1



A vial was charged with 50:50 mixture of deuterated and protiated starting material (**1** and **1c**) and the reaction was run, under standard conditions, to partial conversion. A small aliquot was taken, pushed through a celite plug and shot on the HPLC to determine the degree of conversion. To quench the reaction, water and DCM was added and the organic layer was washed several times with 10% LiCl. The organic solution was dried on $NaSO_4$ and concentrated *in vacuo*. To remove any remaining DMA, the crude mixture was purified on neutral alumina with 10% ethyl acetate in hexanes (a very broad band was collected to ensure that all the starting material was recovered). Next, a H NMR spectrum in C_6H_6 was collected and the degree of enrichment in the recovered starting material was measured.

No significant isotopic enrichment was observed.

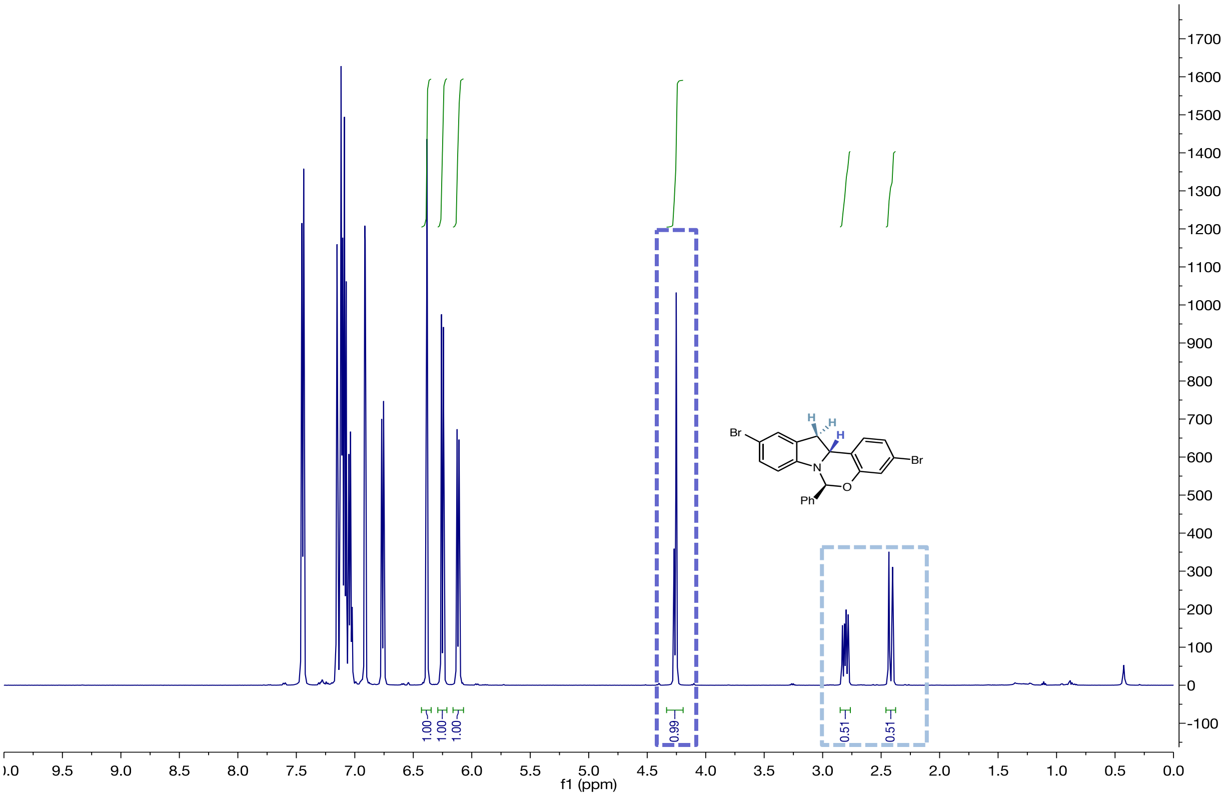
Table S32. Summary of all intermolecular competition KIE experiments

Run	Perester used	conv. (%)**	$(D/H)_{initial}$*	$(D/H)_{final}$*	KIE
1a	BzOOtBu	47	0.96	0.96	1.00
1b	BzOOtBu	55	0.96	0.96	1.00
2a	BzOOtBu	34	1.00	0.98	0.95
2b	BzOOtBu	44	1.00	0.98	0.97
				mean KIE	0.98
				std dev	0.02

* determined by ^1H NMR

** determined by HPLC using Ph_2O as an internal standard

At 0% conversion:



At 47% conversion:

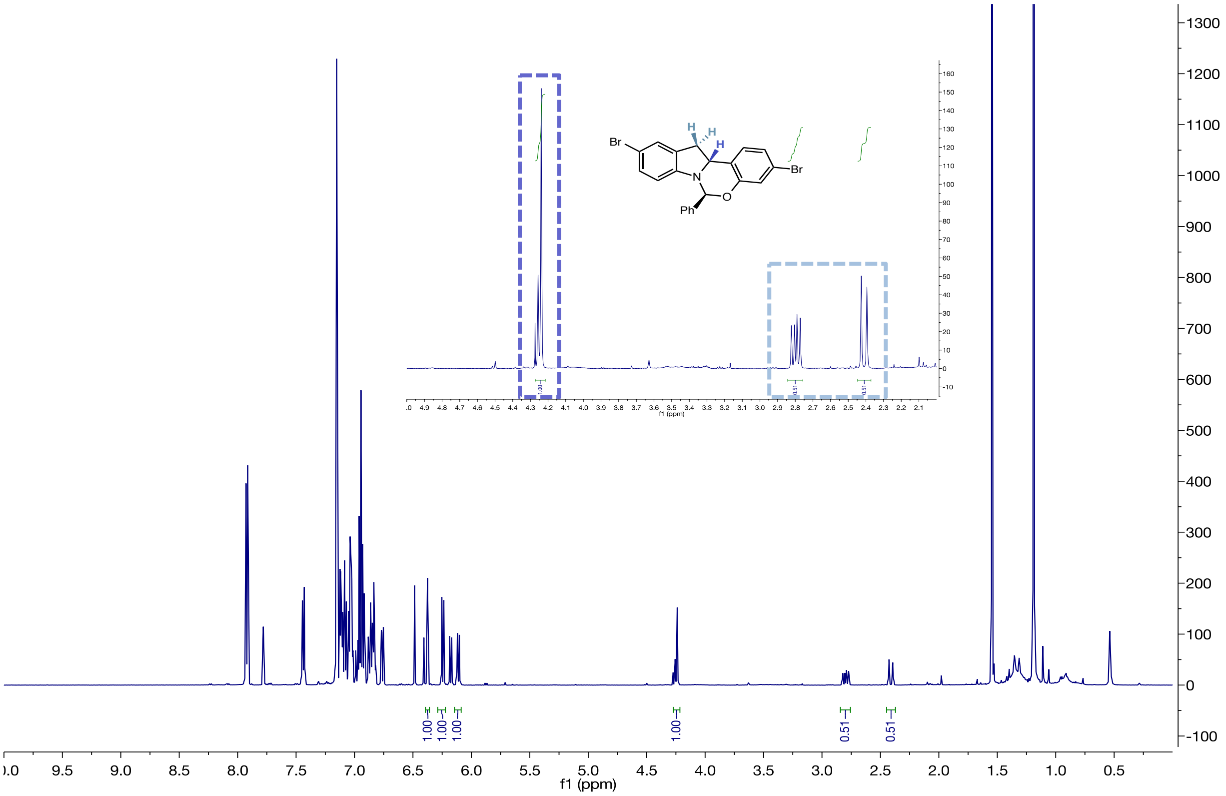
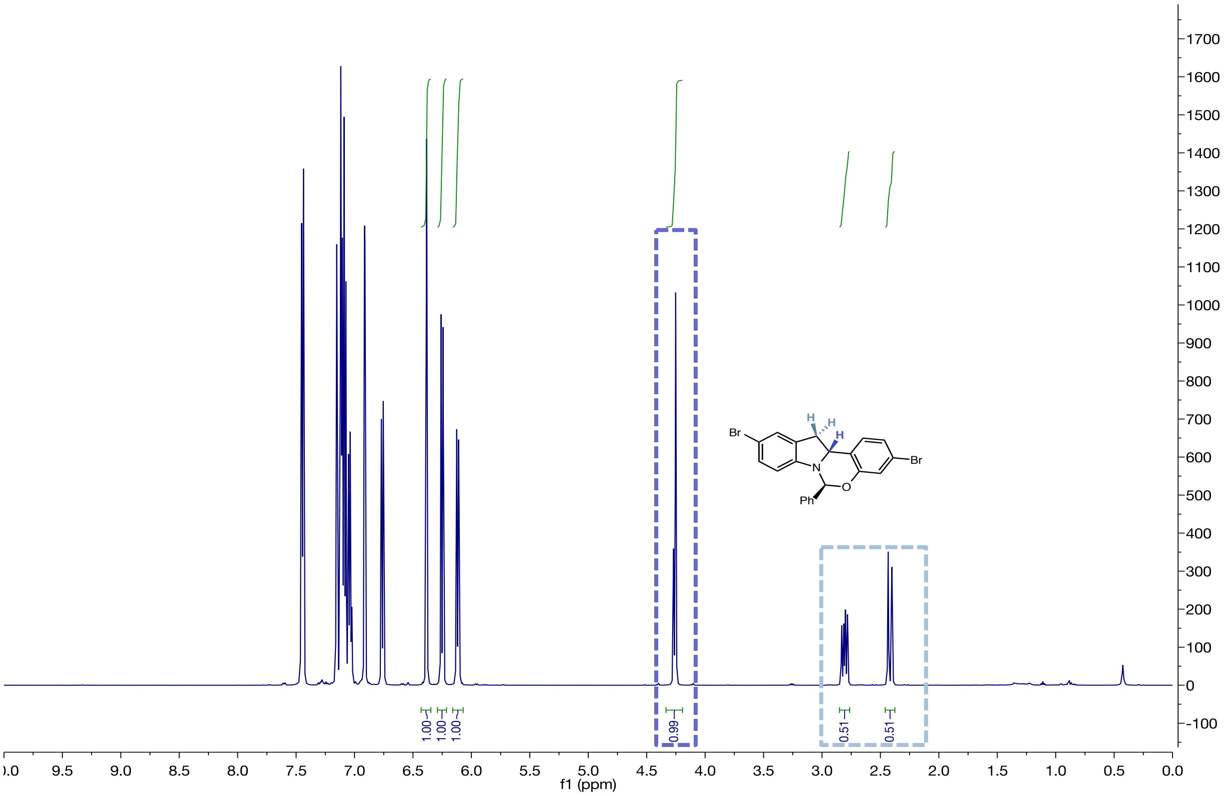


Figure S64. Crude NMR spectra from intermolecular KIE experiment with **1** and **1c**, run 1a.

At 0% conversion:



At 55% conversion:

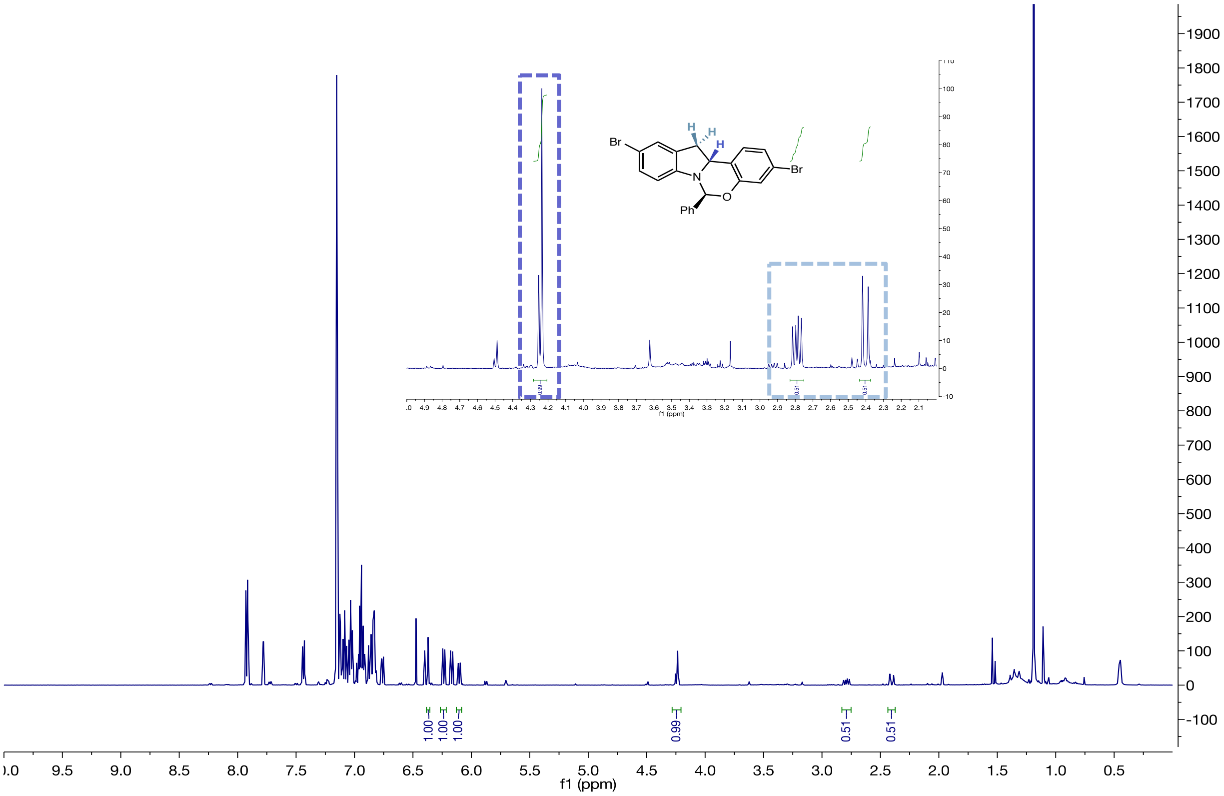
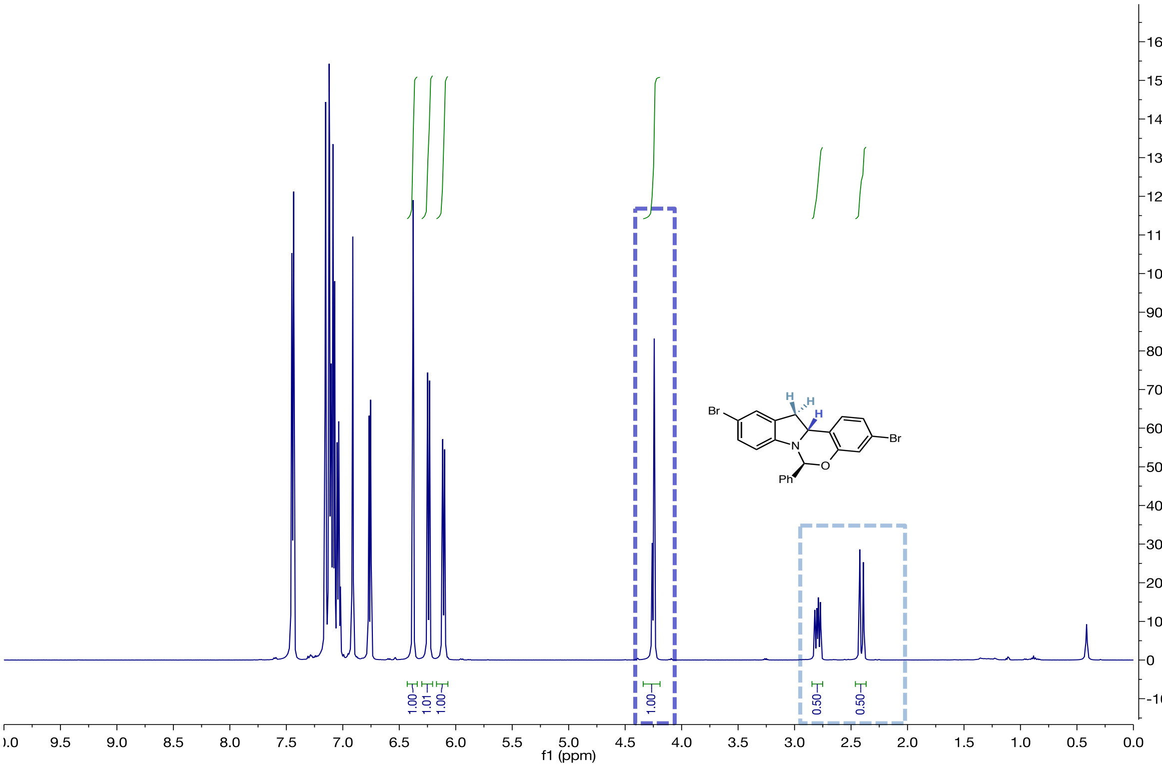


Figure S65. Crude NMR spectra from intermolecular KIE experiment with **1** and **1c**, run 1b.

At 0% conversion:



At 34% conversion:

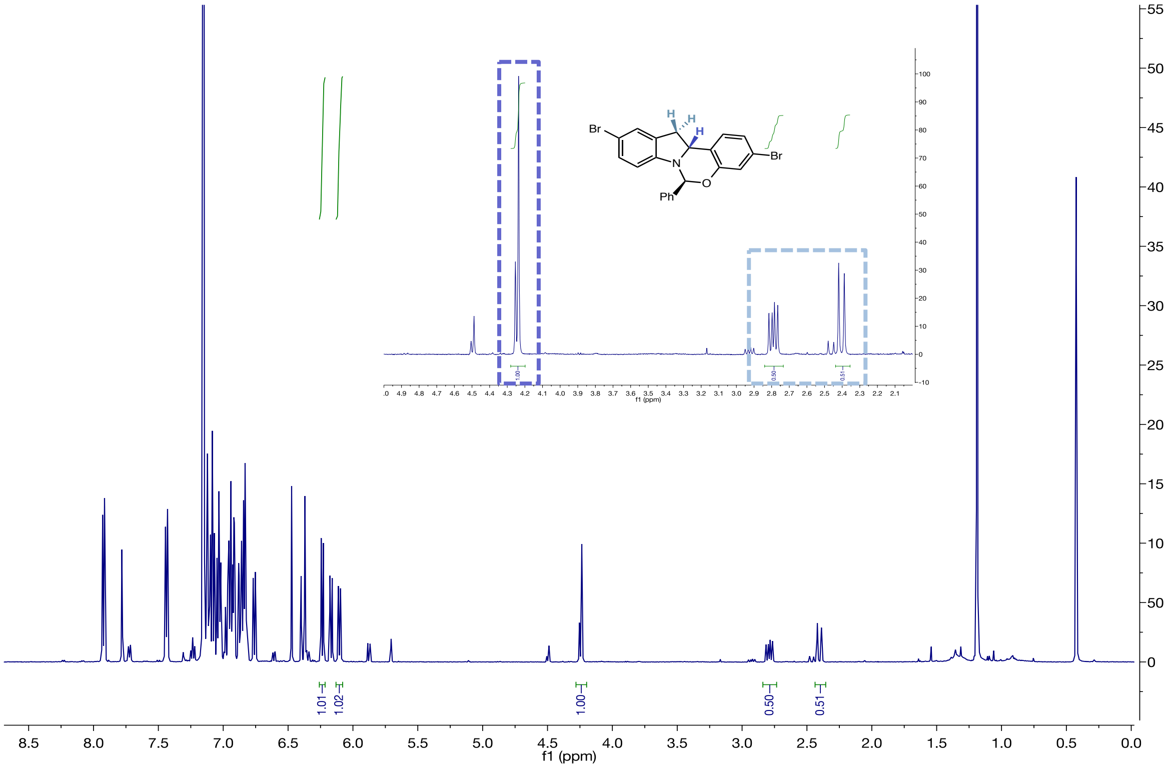
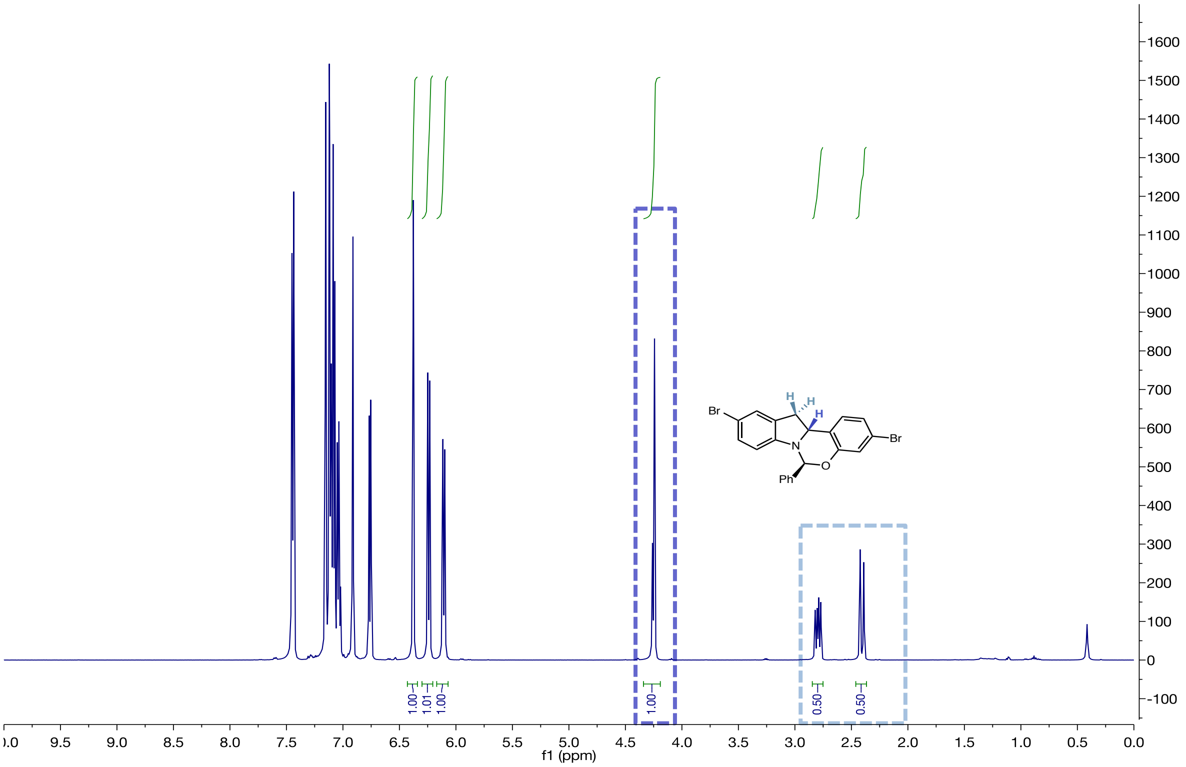


Figure S66. Crude NMR spectra from intermolecular KIE experiment with **1** and **1c**, run 2a.

At 0% conversion:



At 44% conversion:

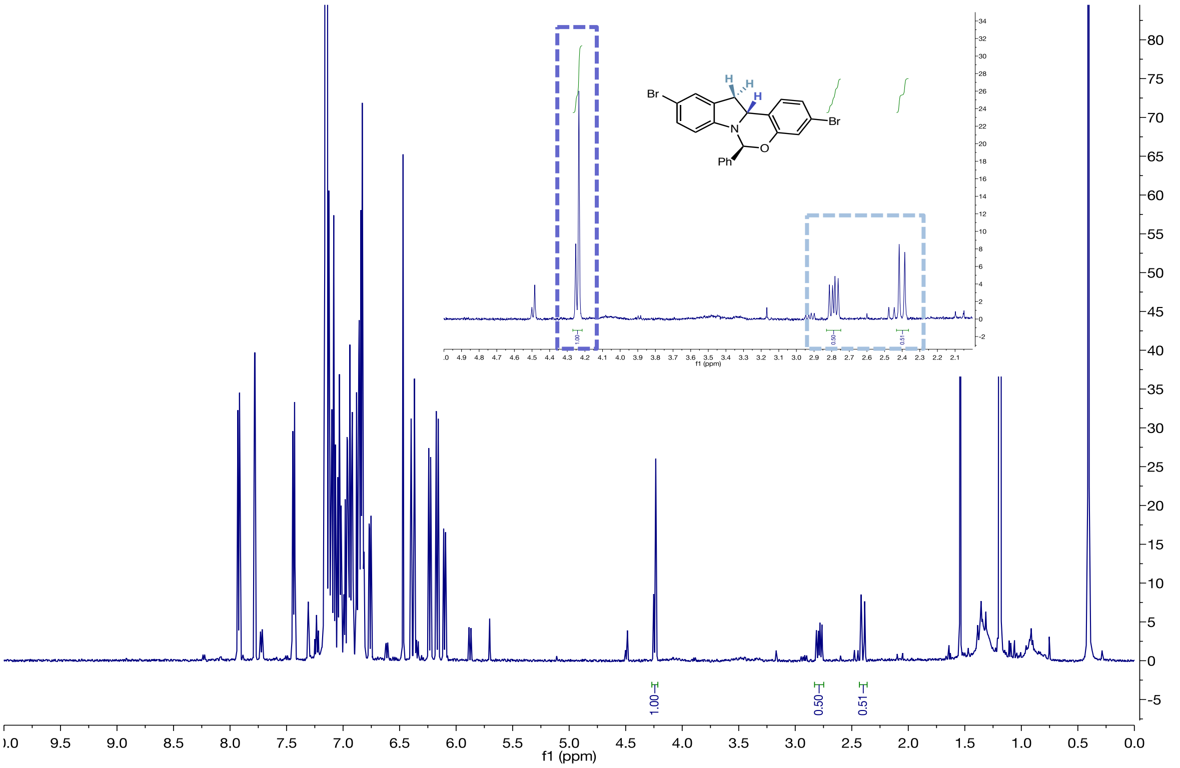
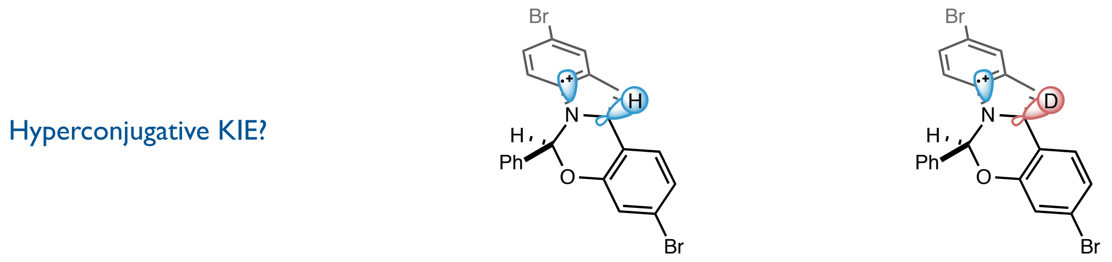


Figure S67. Crude NMR spectra from intermolecular KIE experiment with **1** and **1c**, run 2b.

Investigating the presence of a hyperconjugative KIE during single-electron oxidation of starting material

We postulated that a slight hyperconjugative KIE might be observed during electron transfer from starting material. To evaluate this hypothesis, we performed Stern-Volmer on the indoline starting material and its deuterated isotopologue. No significant hyperconjugative KIE was observed (Figure S68).



Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 1.98 * 10^{-5} M Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6) in DMA at room temperature under an inert atmosphere. The solutions were irradiated at 440 nm and luminescence was measured at 480 nm.

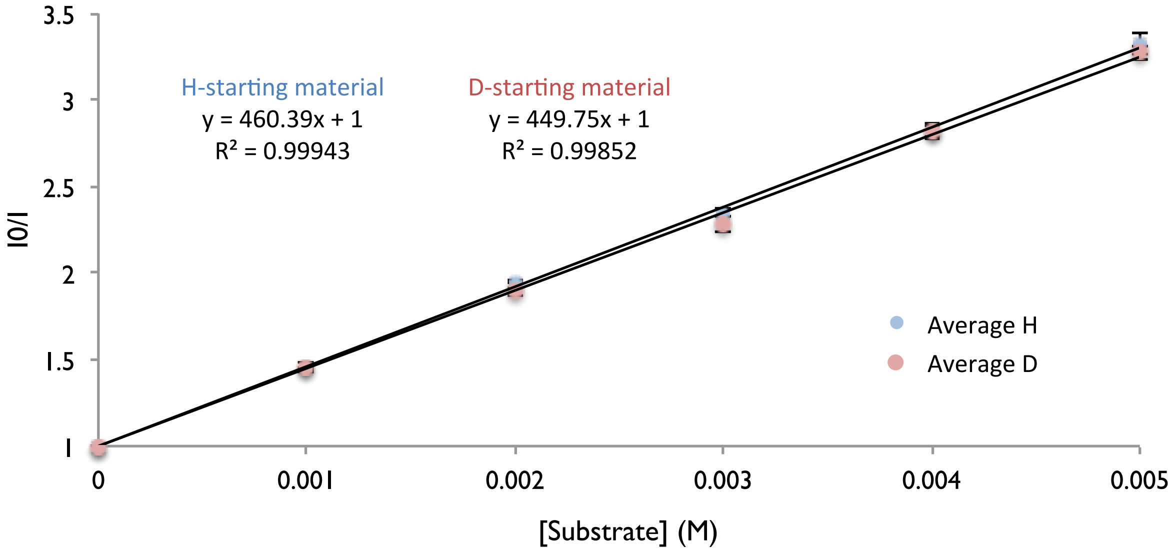


Figure S68. Stern-Volmer plot of Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6) with the starting material and D-labeled starting material.

Table S33. Results from Stern-Volmer experiments with H-starting material

Experiment	Vial	[H-SM] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
H-SM Run 1	1	0	588.95	585.13	593.06	589.04	1.00
	2	0.001	412.67	410.40	412.14	411.74	1.43
	3	0.002	296.60	294.79	296.37	295.92	1.99
	4	0.003	245.13	246.60	247.85	246.52	2.39
	5	0.004	204.68	204.36	203.40	204.15	2.89
	6	0.004	171.06	172.49	171.29	171.61	3.43
Experiment	Vial	[H-SM] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
H-SM Run 2	1	0	565.92	567.08	566.19	566.40	1.00
	2	0.001	398.04	396.16	396.91	397.04	1.43
	3	0.002	300.52	296.56	295.09	297.39	1.90
	4	0.003	245.23	245.48	245.50	245.40	2.31
	5	0.004	204.51	205.58	205.15	205.08	2.76
	6	0.004	176.91	175.93	175.00	175.95	3.22
Experiment	Vial	[H-SM] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
H-SM Run 3	1	0	581.12	580.69	587.68	583.16	1.00
	2	0.001	383.01	388.38	386.73	386.04	1.51
	3	0.002	299.69	305.39	305.13	303.40	1.92
	4	0.003	249.87	245.11	248.02	247.67	2.35
	5	0.004	205.66	206.28	206.08	206.01	2.83
	6	0.004	176.05	176.05	173.56	175.22	3.33

Table S34. Results from Stern-Volmer experiments with D-starting material

Experiment	Vial	[D-SM] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
D-SM Run 1	1	0	580.80	578.95	587.52	582.42	1.00
	2	0.001	408.19	410.08	403.72	407.33	1.43
	3	0.002	297.85	301.51	300.71	300.02	1.94
	4	0.003	252.96	248.21	249.77	250.31	2.33
	5	0.004	203.46	204.74	203.88	204.03	2.85
	6	0.004	180.21	181.19	178.11	179.84	3.24
Experiment	Vial	[D-SM] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
D-SM Run 2	1	0	570.73	580.66	570.89	574.09	1.00
	2	0.001	394.25	397.90	396.21	396.12	1.45
	3	0.002	310.27	313.41	313.74	312.47	1.84
	4	0.003	230.56	230.56	323.85	261.66	2.19
	5	0.004	211.55	210.08	207.85	209.83	2.74
	6	0.004	178.36	177.65	177.89	177.97	3.23
Experiment	Vial	[D-SM] (M)	I (@ 480 nm)	I (@ 480 nm)	I (@ 480 nm)	Mean	I0/I
D-SM Run 3	1	0	587.00	586.13	588.89	587.34	1.00
	2	0.001	399.99	402.89	397.35	400.08	1.47
	3	0.002	301.25	305.81	304.12	303.73	1.93
	4	0.003	252.77	251.88	252.26	252.30	2.33
	5	0.004	204.79	204.62	207.23	205.54	2.86
	6	0.004	174.77	174.15	176.28	175.07	3.35

Table S35. Summary of calculations for the hyperconjugative KIE

Substrate	Run	Slope (1/M)	Error in slope	Mean slope and error (1/M)	KIE
H-SM	1	478	5	460 ± 4	**1.02 ± 0.02**
	2	442	2		
	3	461	4		
Substrate	Run	Slope (1/M)	Error in slope	Mean slope and error (1/M)	
D-SM	1	453	4	450 ± 5	
	2	432	8		
	3	464	4		

CHEMICAL ACTINOMETRY

Synthesis of potassium ferrioxolate

A round-bottomed flask was charged with 20 mL water and 12 g potassium oxalate and heated. Next, 8 mL of $FeCl_3$ (0.4 g/mL) was added to the hot oxalate solution. The solution was stirred in water at 70 ^{o}C for 1 hour. The round bottom flask was carefully wrapped in aluminum foil to minimize light exposure. The reaction was then let cool to room temperature and then cooled on an ice bath. Large, emerald green crystals formed. The aqueous supernatant was removed and the crystals were recrystallized from warm water three times. After recrystallization, the crystals were left in a vac-oven (50 ^{o}C) until a constant mass was reached. *Note*: at every step of the synthesis, great precaution was made to minimize light exposure, usually by wrapping all glassware in aluminum foil and working in a dark hood.

Solutions needed

0.05 M sulfuric acid stock solution

In a 100 mL volumetric flask, 0.281 mL of concentrated sulfuric acid (17.8 M) was added to 90 mL deionized water. Then, water was added until the 100 mL graduation mark was reached.

Ferrioxolate solution

A 0.15 M solution of potassium ferrioxolate was prepared by dissolving potassium ferrioxolate ($K_3FeC_2O_4$*$3H_2O$, MW 491.243) (1.842 g, 3.75 mmol) with the 0.05 M sulfuric acid solution prepared in a 25 mL volumetric flask. Make every precaution to prepare and store the solution in the dark.

Developer solution:

225 g of sodium acetate trihydrate was dissolved in 1 liter of 0.5 M sulfuric acid. 10 g of 1,10-phenantroline was added to this solution. Store in the dark.

Typical Experiment: Measuring Photon Flux

A 1cm x 1cm quartz cuvette was charged with 3 mL of 0.15 M aqueous potassium ferrioxalate solution. Two sides of the cuvette were coated with black electrical tape to ensure a minimum pathway of the light of 1 cm. To stir the ferrioxolate, the solution was continually sparged with N_2. While stirring, the solution was irradiated with a purple LED (402 nm) at room temperature. 10 μL aliquots of the solution were taken at different time points between 1 and 6 minutes of irradiation. This aliquot was immediately added to 5 mL of a developer solution of sodium acetate and 1,10-phenanthroline and the flask was quickly wrapped in aluminum foil. Concurrently, a "blank" sample was prepared by diluting 10 uL of the stock solution (kept in the dark) into 5 uL of developer solution. The solutions were left in the dark for 30 min - 1 hr, becoming bright red. The solutions were transferred to a cuvette and the absorbance spectrum of the $Fe(phen)_3^{2+}$ complex was obtained. The absorbance at 510 nm (ε = 11,100 M^{-1} cm^{-1}) was measured for every sample. To ensure high quality data, check that the absorbance is linear to the irradiation time.

DATA ANALYSIS

To calculate photon flux from your chemical actinometry data, first determine the number of Fe^{2+} ions produced by ferrioxolate photo-degradation:

$$moles\ Fe^{2+} = \frac{\Delta A_{510\ nm}\ V_1\ V_3}{\varepsilon_{510\ nm}\ l\ V_2}$$

ΔA = difference in absorbance at 510 nm between sample and 'blank'
l = path length of cuvette (1 cm)
$\varepsilon_{510\ nm}$= Extinction coefficient of $Fe(phen)_3$ complex at 510 (ε = 11,100 M^{-1} cm^{-1})
V_1 = total volume of irradiated solution (3 mL)
V_2 = volume of aliquot taken from V_1 (10 uL)
V_3 = the volume that V_2 is diluted into (5 mL)

Now, the photon flux can be determined:

$$photon\ flux = \frac{moles\ of\ Fe^{2+}}{\emptyset_{405\ nm} \times t \times F}$$

$\emptyset_{405\ nm}$ = 1.14 (reported literature value)
t = time of irradiation (seconds)
F = mean fraction of light absorbed by the ferrioxalate solution (F ~ 1 at 402 nm at 0.15 M ferrioxolate)[7].

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[7] C. G. Hatchard, and C. A. Parker, *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences,* 1956, **235**, 518-536.

Results

Run1: 8.33 x 10^{-8} einstein / s through 3 mL solvent

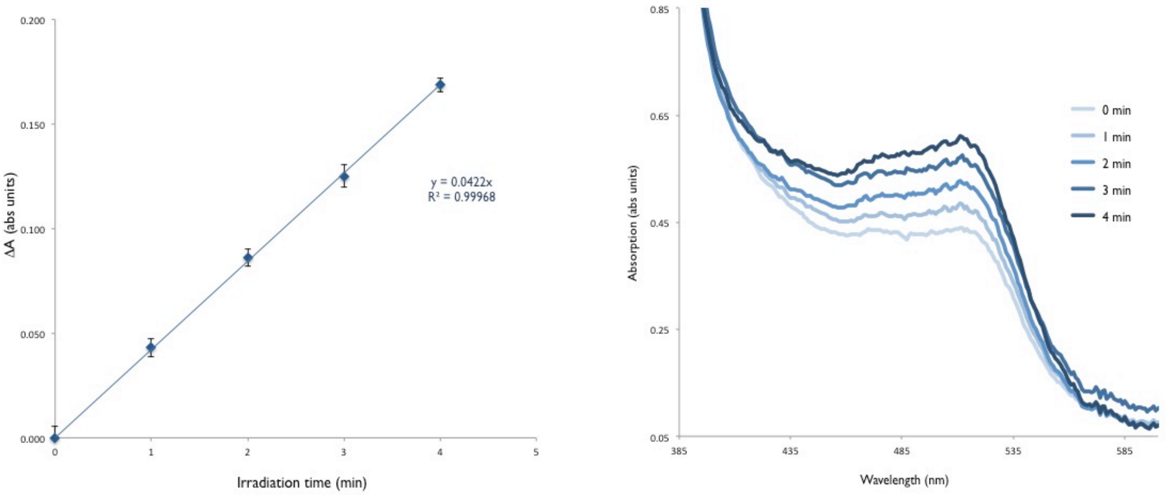

Figure S69. Summary of photon flux determination, run 1

Table S36. Summary of photon flux determination, run 1

Time of irr (min)	0	0	1	2	3	4	5
Absorbance at 510	0.43837	0.42473	0.48211	0.52624	0.56861	0.60616	0.68074
	0.44093	0.44316	0.48003	0.52199	0.56051	0.60719	0.68006
	0.44123	0.44193	0.48254	0.52487	0.56137	0.60773	0.68233
Mean Absorbance		0.438	0.482	0.524	0.563	0.607	0.681

Run2: 9.40 x 10^{-8} einstein / s through 3 mL solvent

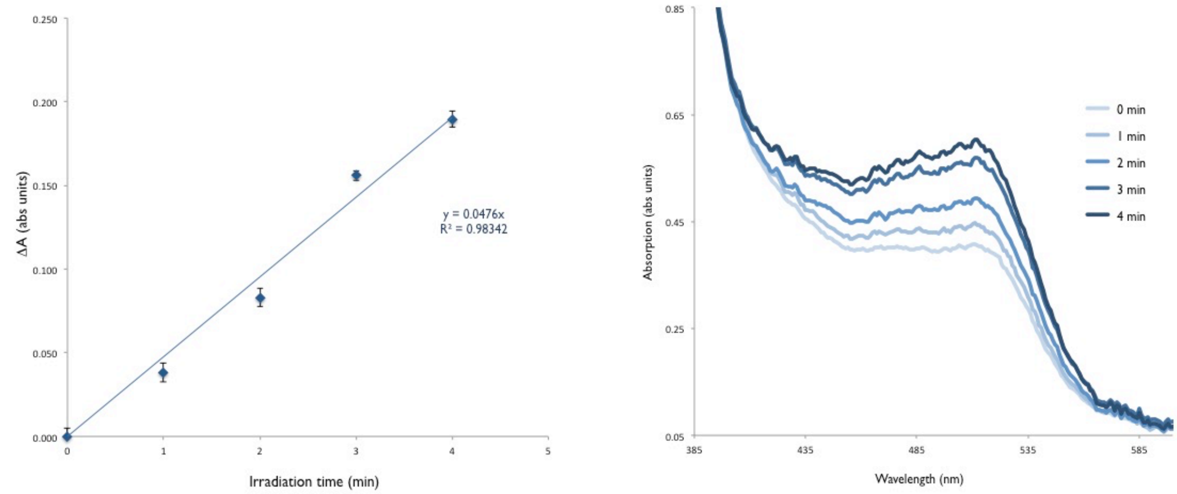

Figure S70. Summary of photon flux determination, run 1

Table S37. Summary of photon flux determination, run 2

Time of irr (min)	0	0	1	2	3	4	5
Absorbance at 510	0.4082		0.44575	0.49228	0.5644	0.59855	0.69951
	0.40694		0.44618	0.48915	0.56394	0.59616	0.70051
	0.40978		0.44746	0.49191	0.56416	0.59829	0.69959
Mean A		0.408	0.446	0.491	0.564	0.598	0.700

Run3: 9.60 x 10^{-8} einstein / s through 3 mL solvent

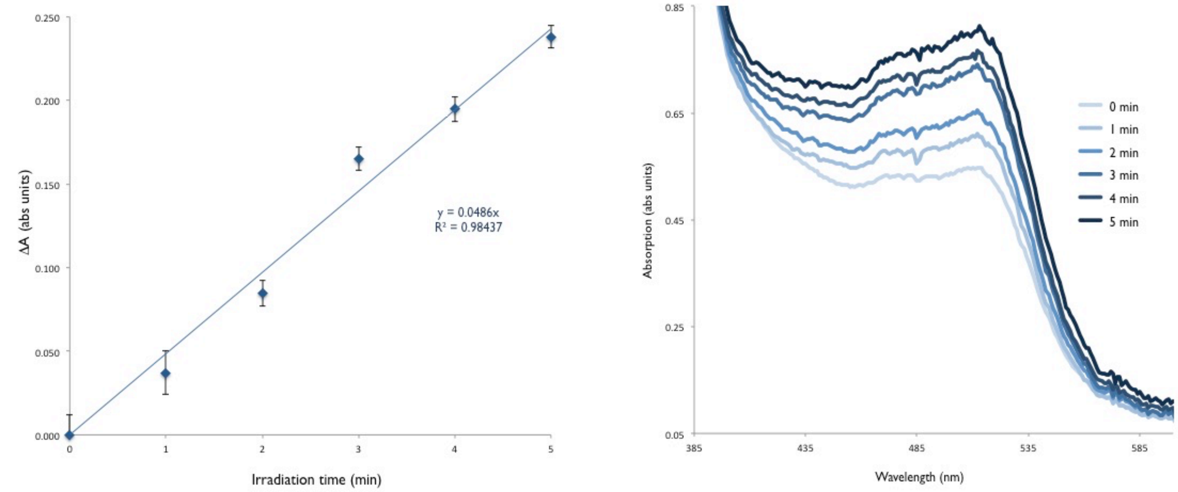

Figure S71. Summary of photon flux determination, run 1

Table S38. Summary of photon flux determination, run 3

Time of irr (min)	0	0	1	2	3	4	5
Absorbance at 510	0.54585	0.57323	0.60572	0.64636	0.72979	0.75534	0.79919
	0.55538	0.57638	0.59363	0.65146	0.72614	0.76082	0.8009
	0.54958	0.57732	0.60096	0.64492	0.7283	0.75695	0.80251
Mean A		0.563	0.600	0.648	0.728	0.758	0.801

EMISSION SPECTRUM OF PURPLE LEDs USED FOR KINETICS:

The emission band of the light source was determined (402 nm), using a UVN-SR fiber optic spectrometer (EPP2000, StellarNet Inc.) The emission spectrum of the LEDs was measured at 9 V. See Figure S72 for results.

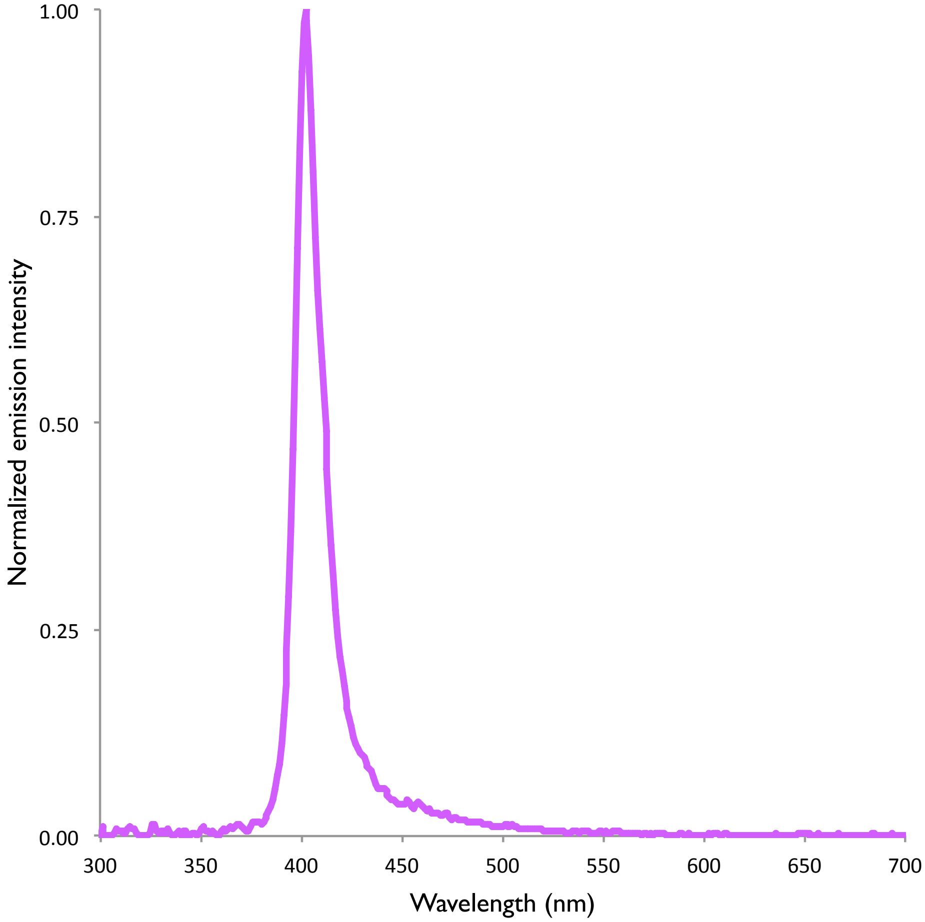

Figure S72. Normalized emission spectrum of purple LEDs. The maximum emission wavelength is 402 nm and 70% of the photon output was found to be between 395 nm and 416 nm.

QUANTUM YIELD DETERMINATION

To estimate the quantum yield of the reaction, we used the below equation:

$$\text{Quantum Yield} = \frac{\text{Reaction yield}}{\text{Photons absorbed by sample}}$$

which, as the reaction time approaches 0, can be expressed as:

$$\text{Quantum Yield} = \frac{d[P]/dt \text{ or } -d[SM]/dt}{\text{Photons absorbed by sample per unit time}}$$

A 1cm x 1cm quartz cuvette was charged with a solution containing 1 (0.375 M, 1 equiv.), BzOOtBu (0.75 M, 1 equiv.), 0.1 mol% Ir[(dF-CF_3-ppy)$_2$(dtbpy)]PF_6 and Ph_2O (1 equiv., used as an internal standard) in DMA. Two sides of the cuvette were coated with black electrical tape to ensure a minimum pathway of the light of 1 cm. For stirring, the solution was continually sparged with N_2. While stirring, the solution was irradiated with a purple LED (402 nm) at room temperature.

Aliquots were taken with 10–15 minute intervals and pushed through a plug of Celite with 50:50 IPA:hexanes. Samples were analyzed on an Agilent 1260 Infinty HPLC using a Zorbax-Rx Sil 5 um 4.6 x 250 mm column using a 20 minute method with 1% IPA in hexanes as the eluent. UV-absorbances were measured at 230 nm. Starting material conversions and yields were tracked as a function of time from peak areas relative to Ph_2O as an internal standard.

Data analysis: The concentration of 1 was plotted against time and data points from 0 50% conversion were used to fit a 6th order polynomial. The derivative of the polynomial used to calculate rate and divided by the number of photons passing through the sample per unit time. The experiment was repeated twice and the data was averaged.

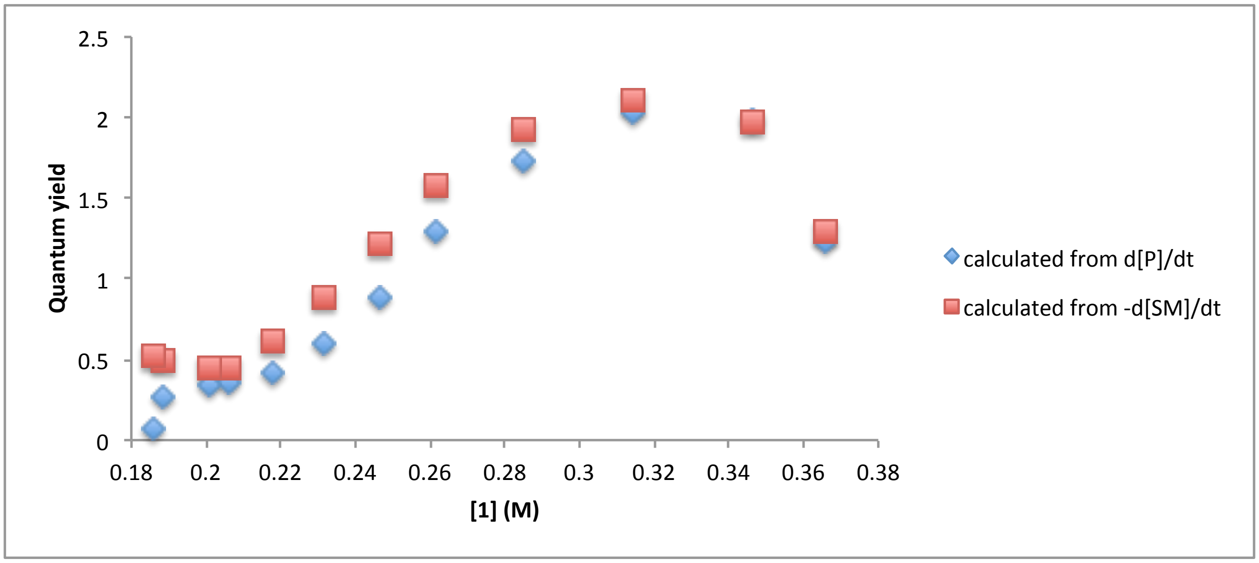

Figure S73. Quantum yield as a function of starting material concentration. Average of two runs.

Run 1:

Table S39. Results from kinetic run for quantum yield determination, run 1. Conditions: 0.375 M 1 (1 equiv), 0.7 M BzOOtBu, 0.375 M Ph_2O, 0.1 mol% $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{PDT}/A_{STD}	A_{SM}/A_{STD}	% yield	% conv.	[PDT] (M)	[SM] (M)
0	42.465	0	57.535	0.000	1.355	0%	0%	0.000	0.375
450	41.996	2.172	55.832	0.052	1.329	2%	2%	0.009	0.368
900	41.501	6.848	51.651	0.165	1.245	7%	8%	0.028	0.344
1350	40.252	14.475	45.273	0.360	1.125	16%	17%	0.060	0.311
1800	39.499	20.713	39.788	0.524	1.007	23%	26%	0.088	0.279
2250	38.913	25.221	35.866	0.648	0.922	29%	32%	0.108	0.255
2700	38.409	27.86	33.731	0.725	0.878	32%	35%	0.121	0.243
3150	38.238	29.886	31.876	0.782	0.834	35%	38%	0.130	0.231
3690	38.29	32.087	29.623	0.838	0.774	37%	43%	0.140	0.214
4380	38.299	33.845	27.856	0.884	0.727	39%	46%	0.147	0.201
4860	38.079	34.881	27.04	0.916	0.710	41%	48%	0.153	0.197
5460	38.611	36.193	25.196	0.937	0.653	42%	52%	0.156	0.181
6060	38.177	36.652	25.171	0.960	0.659	43%	51%	0.160	0.182
7980	38.137	38.922	22.941	1.021	0.602	45%	56%	0.170	0.166
8820	38.291	39.556	22.153	1.033	0.579	46%	57%	0.172	0.160
9840	38.489	39.868	21.643	1.036	0.562	46%	58%	0.173	0.156
11220	38.482	41.111	20.407	1.068	0.530	48%	61%	0.178	0.147
13080	39.169	42.278	18.553	1.079	0.474	48%	65%	0.180	0.131
15960	39.488	43.315	17.197	1.097	0.435	49%	68%	0.183	0.121
19320	39.387	45.565	15.048	1.157	0.382	51%	72%	0.193	0.106

d[P]/dt (M/s)	Yield per second in 3 mL vial (mol/s)	Photon flux (mol/s)	Quantum yield from product yield	[SM] (M)	-d[SM]/dt (M/s)	SM consumed per second in 3 mL vial (mol/s)	Photon flux (mol/s)	Quantum yield from starting material conversion
1.42E-05	4.27E-08	9.11E-08	0.47	0.375	1.96E-05	5.89E-08	9.11E-08	0.65
4.22E-05	1.27E-07	9.11E-08	1.39	0.368	4.61E-05	1.38E-07	9.11E-08	1.52
5.46E-05	1.64E-07	9.11E-08	1.80	0.344	5.84E-05	1.75E-07	9.11E-08	1.92
5.63E-05	1.69E-07	9.11E-08	1.85	0.311	6.08E-05	1.82E-07	9.11E-08	2.00
5.13E-05	1.54E-07	9.11E-08	1.69	0.279	5.68E-05	1.71E-07	9.11E-08	1.87
4.26E-05	1.28E-07	9.11E-08	1.40	0.255	4.92E-05	1.48E-07	9.11E-08	1.62
3.26E-05	9.79E-08	9.11E-08	1.07	0.243	4.01E-05	1.20E-07	9.11E-08	1.32
2.31E-05	6.93E-08	9.11E-08	0.76	0.231	3.11E-05	9.32E-08	9.11E-08	1.02
1.37E-05	4.11E-08	9.11E-08	0.45	0.214	2.17E-05	6.50E-08	9.11E-08	0.71
6.21E-06	1.86E-08	9.11E-08	0.20	0.201	1.34E-05	4.01E-08	9.11E-08	0.44
4.01E-06	1.20E-08	9.11E-08	0.13	0.197	1.02E-05	3.06E-08	9.11E-08	0.34
4.00E-06	1.20E-08	9.11E-08	0.13	0.181	8.74E-06	2.62E-08	9.11E-08	0.29

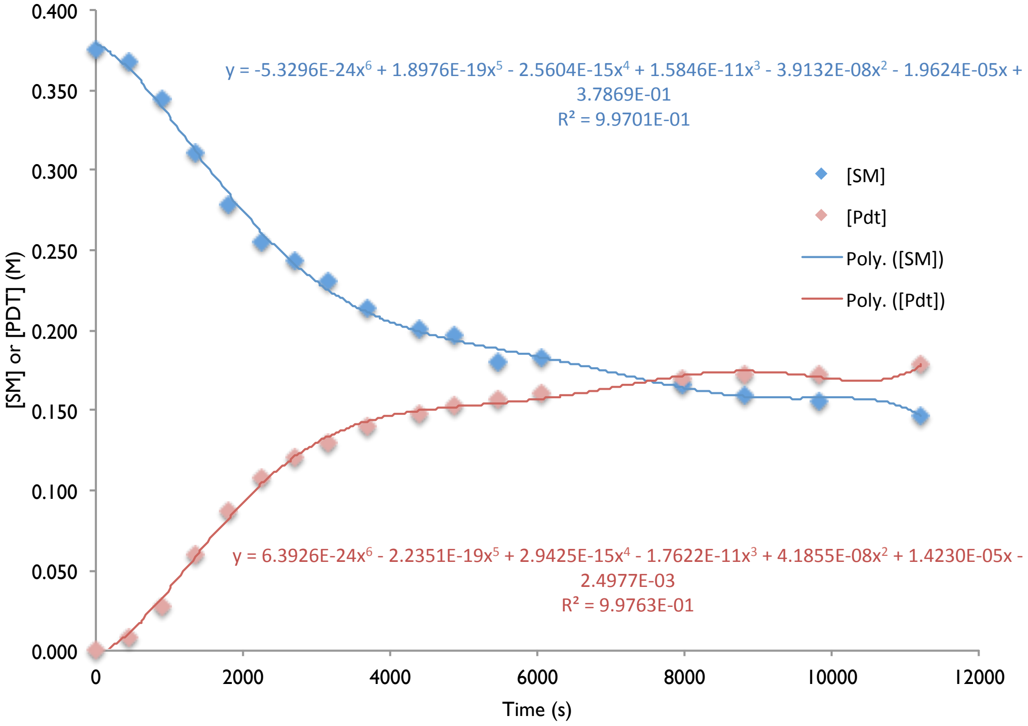

Figure S74. Concentration of starting material (**1**) or product (**2**) versus time. The plot is fitted to a 6th order polynomial.

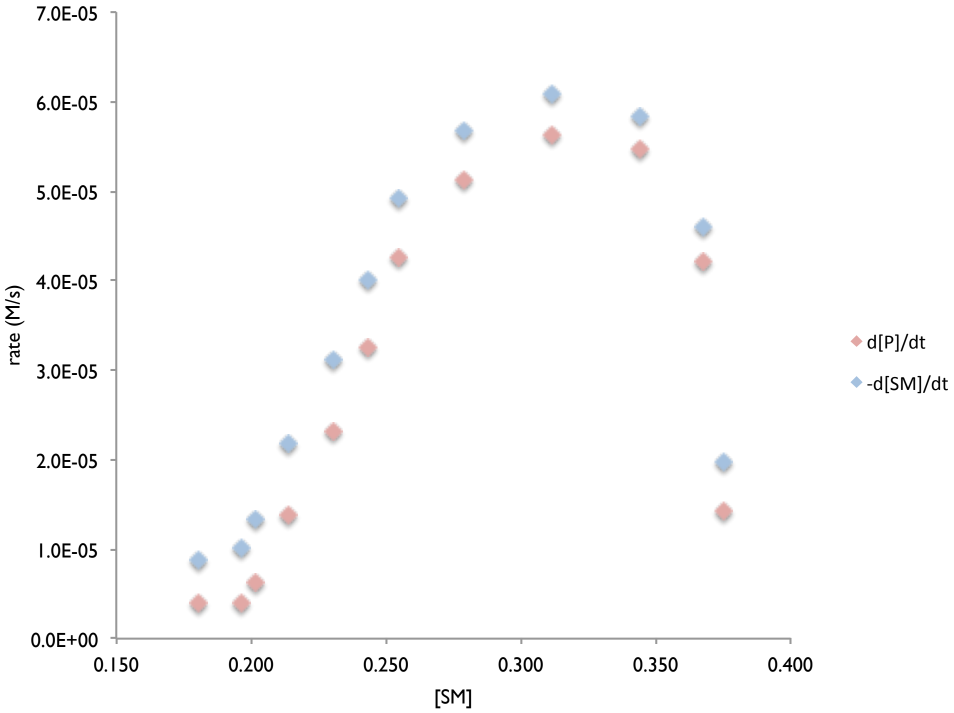

Figure S75. Reaction progress profiles: d[P]/dt and –d[SM]/dt as a function of starting material (**1**) concentration

Run 2:

Table S40. Results from kinetic run for quantum yield determination, run 2. Conditions: 0.375 M 1 (1 equiv), 0.7 M BzOOtBu, 0.375 M Ph_2O, 0.1 mol% [Ir(dF-CF_3-ppy)$_2$(dtbpy)](PF_6) in DMA at -3 °C using purple LEDs

time (s)	Ph_2O (A_{230nm})	PDT (A_{230nm})	SM (A_{230nm})	A_{PDT}/A_{STD}	A_{SM}/A_{STD}	% yield	% conv.	[PDT] (M)	[SM] (M)
0	42.333	0	57.667	0.000	1.362	0%	0%	0.000	0.375
450	42.212	1.947	55.841	0.046	1.323	2%	3%	0.008	0.364
900	41.491	6.048	52.461	0.146	1.264	6%	7%	0.024	0.348
1350	40.323	13.11	46.567	0.325	1.155	14%	15%	0.054	0.318
1800	39.187	19.405	41.408	0.495	1.057	22%	22%	0.083	0.291
2250	38.823	23.446	37.731	0.604	0.972	27%	29%	0.101	0.268
2700	38.584	26.339	35.077	0.683	0.909	30%	33%	0.114	0.250
3150	38.615	28.781	32.604	0.745	0.844	33%	38%	0.124	0.232
3690	38.329	30.736	30.935	0.802	0.807	36%	41%	0.134	0.222
4380	38.095	32.686	29.219	0.858	0.767	38%	44%	0.143	0.211
4860	38.06	33.535	28.405	0.881	0.746	39%	45%	0.147	0.205
5460	38.201	34.592	27.207	0.906	0.712	40%	48%	0.151	0.196
6060	37.968	35.859	26.173	0.944	0.689	42%	49%	0.158	0.190
7980	39.01	38.61	22.38	0.990	0.574	44%	58%	0.165	0.158
8820	38.236	38.861	22.903	1.016	0.599	45%	56%	0.170	0.165
9840	38.201	39.636	22.163	1.038	0.580	46%	57%	0.173	0.160
11220	38.631	40	21.369	1.035	0.553	46%	59%	0.173	0.152
13080	38.798	41.36	19.842	1.066	0.511	47%	62%	0.178	0.141
15960	39.319	42.755	17.926	1.087	0.456	48%	67%	0.181	0.126
19320	39.796	44.096	16.108	1.108	0.405	49%	70%	0.185	0.111
22500	40.443	44.488	15.069	1.100	0.373	49%	73%	0.184	0.103

d[P]/dt (M/s)	Yield per second in 3 mL vial (mol/s)	Photon flux (mol/s)	Quantum yield from product yield	[SM] (M)	-d[SM]/dt (M/s)	SM consumed per second in 3 mL vial (mol/s)	Photon flux (mol/s)	Quantum yield from starting material conversion
-1.53E-06		9.11E-08	0.00	0.375	-1.20E-05	-3.60E-08	9.11E-08	-3.95E-01
3.64E-05	1.09E-07	9.11E-08	1.20	0.364	3.53E-05	1.06E-07	9.11E-08	1.16E+00
5.33E-05	1.60E-07	9.11E-08	1.75	0.348	5.73E-05	1.72E-07	9.11E-08	1.89E+00
5.62E-05	1.69E-07	9.11E-08	1.85	0.318	6.25E-05	1.87E-07	9.11E-08	2.06E+00
5.09E-05	1.53E-07	9.11E-08	1.67	0.291	5.76E-05	1.73E-07	9.11E-08	1.89E+00
4.14E-05	1.24E-07	9.11E-08	1.36	0.268	4.77E-05	1.43E-07	9.11E-08	1.57E+00
3.09E-05	9.27E-08	9.11E-08	1.02	0.250	3.66E-05	1.10E-07	9.11E-08	1.20E+00
2.14E-05	6.43E-08	9.11E-08	0.71	0.232	2.66E-05	7.97E-08	9.11E-08	8.75E-01
1.30E-05	3.90E-08	9.11E-08	0.43	0.222	1.80E-05	5.40E-08	9.11E-08	5.92E-01
7.68E-06	2.30E-08	9.11E-08	0.25	0.211	1.33E-05	3.99E-08	9.11E-08	4.38E-01
7.01E-06	2.10E-08	9.11E-08	0.23	0.205	1.35E-05	4.04E-08	9.11E-08	4.44E-01

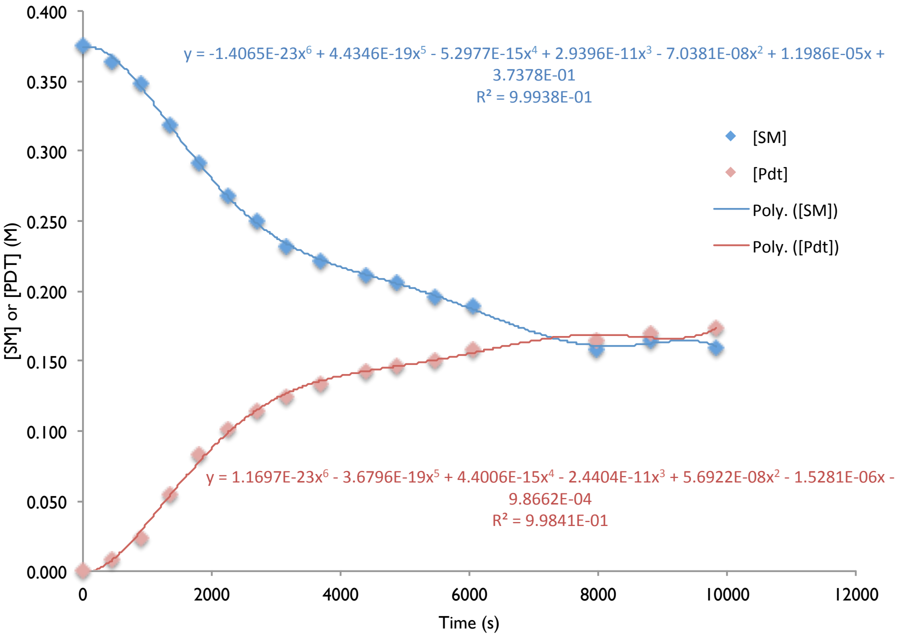

Figure S76. Concentration of starting material (**1**) versus time. The plot is fitted to a 6th order polynomial.

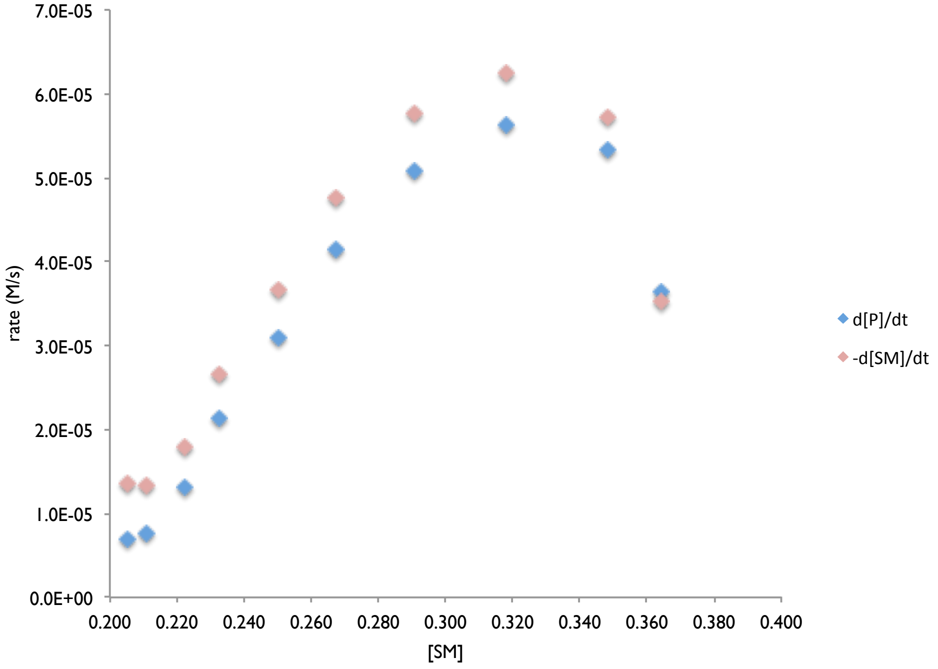

Figure S77. Reaction progress profiles: d[P]/dt and –d[SM]/dt as a function of starting material (**1**) concentration

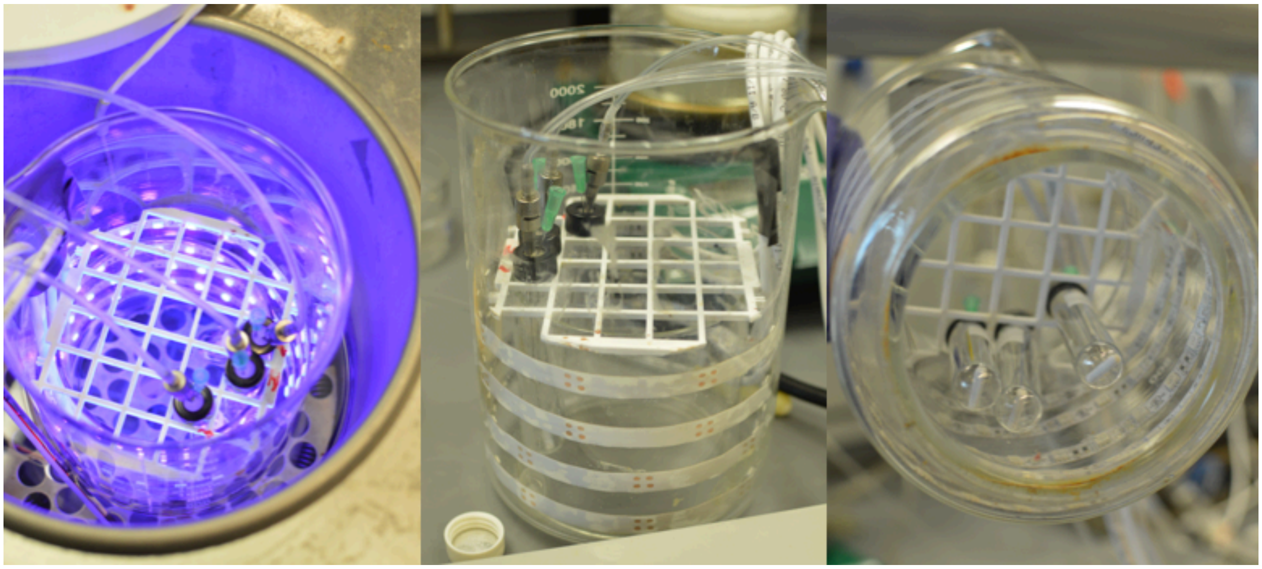

Figure S78. Picture of kinetic reaction set-up for Cryocool (four strips of purple LEDs were used in this study, unless stated otherwise).

DFT COMPUTATIONAL INFORMATION

All calculations used DFT methodology[8] as implemented in the Gaussian 09 series of computer programs.[9] We employed the unrestricted B3LYP functional.[10], [11],[12],[13],[14] All-electron, valence triple-ζ plus polarization and diffuse function 6-311+G(d,p) basis sets were used.[15] [161718] Calculations were performed in the gas phase.17 All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis. Mulliken population analyses were performed as implemented by Gaussian 09.

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[8] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, University Press, Oxford, 1989.

[9] Gaussian 09, Revision C.01, Frisch, M. J. T., 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, Jr., J. A.; 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, N. J.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford, CT.

[10] R. G. Parr, W. Yang, *Annu. Rev. Phys. Chem.,* 1995, **46**, 701.

[11] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623.

[12] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

[13] A. D. Becke, *Phys. Rev. A,* 1988, **38**, 3098.

[14] A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.

[15] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.

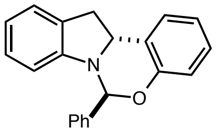
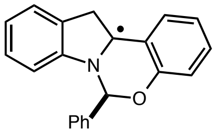
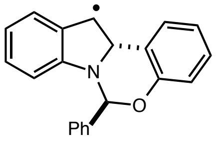
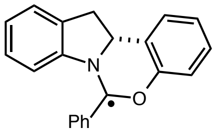
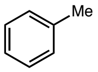
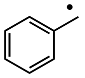
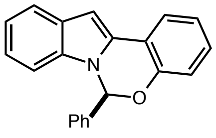
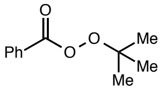
[16] P. C. Hariharan, J. A. Pople, *Mol. Phys.*,1974, **27**, 209.

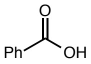
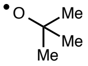
[17] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

[18] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.,* 1980, **72**, 650.

Calculation of bond dissociation energies (BDE)

Table S41: Thermodynamic parameters. Geometries and frequencies were optimized and calculated with UB3LP/6-311+g(d,p) in the gas phase.

Entry	Molecule	Uncorrected Electronic energies (E_h)	H (E_h)	G (E_h)	S (cal K^{-1} mol^{-1})
1		-940.6755124	-940.333121	-940.397367	135.217
2		-940.050076	-939.720996	-939.784877	134.448
3		-940.0336067	-939.704986	-939.769253	135.26
4		-940.0447197	-939.71543	-939.77939	134.615
5		-271.6388134	-271.504325	-271.542004	79.303
6		-270.9872381	-270.866464	-270.902789	76.452
7	H•	-0.50215593	-0.499795	-0.51281	27.392
8		-939.4833427	-939.164243	-939.226528	131.09
9		-653.3834909	-653.196916	-653.196916	120.286

10		-420.9481521	-420.865029	-420.824871	84.52
11		-233.0787462	-232.986733	-232.949651	78.046

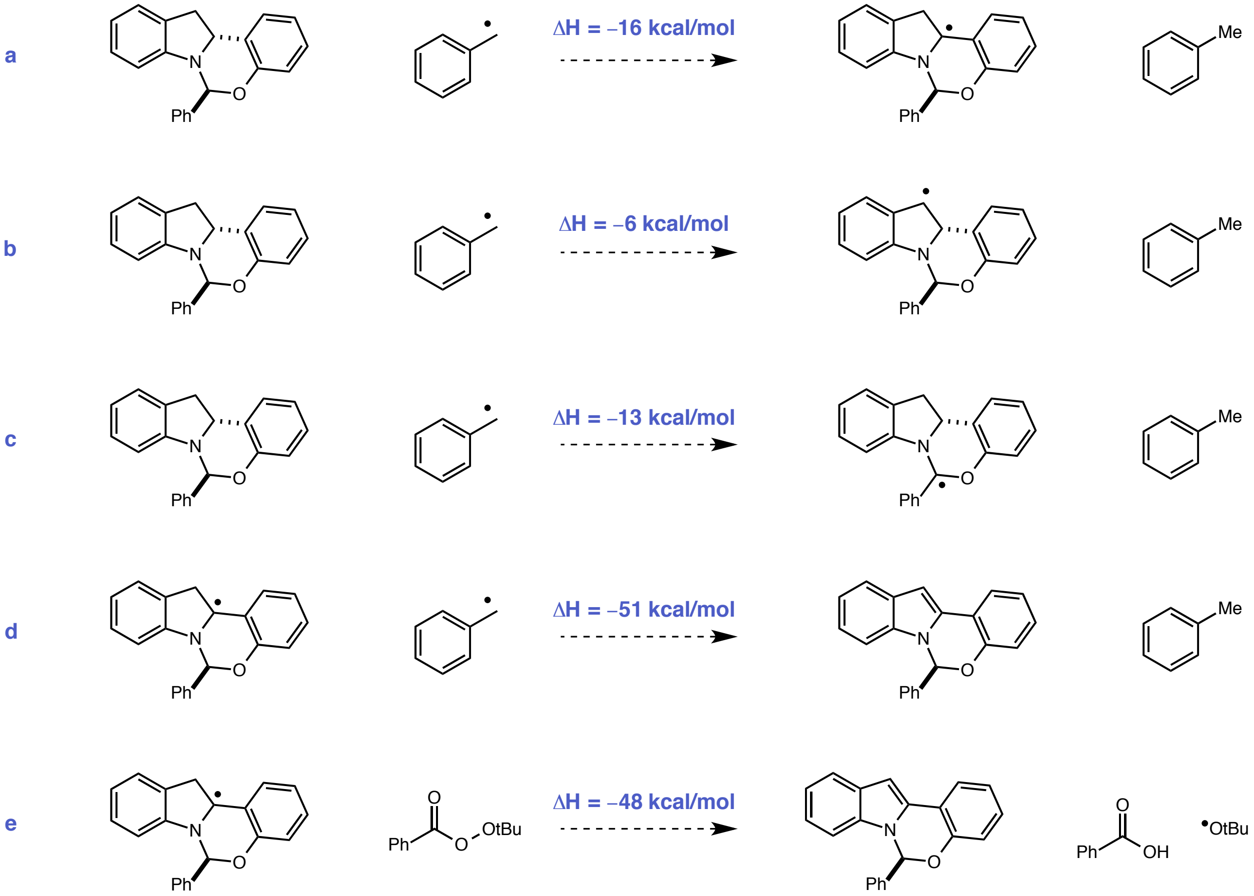
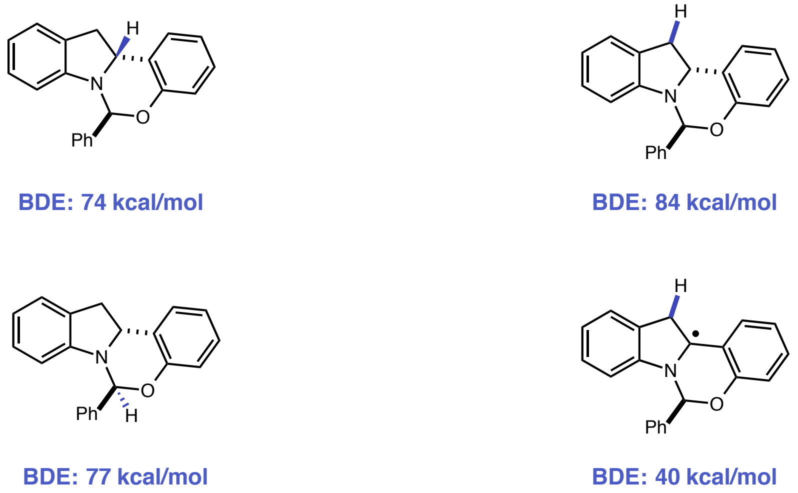


Figure S79. Isodesmic reactions used for BDE calculations. Explicit calculations are shown below in table S42.

Table S42. DFT estimations of the energetics of reactions depicted in Figure S79. Energies are provided in kcal/mol using a conversion factor of 627.51 kcal/mol per hartree. Entropies are provided in e.u.

Reaction from Figure S79	Entries for D	DE (kcal/mol)	DG (kcal/mol)	DH (kcal/mol)	DS (e.u.)
a	=(5+2)-(6+1)	-16.402	-16.770	-16.150	2.082
b	=(5+3)-(6+1)	-6.0678	-6.966	-6.103	2.894
c	=(5+4)-(6+1)	-13.041	-13.327	-12.657	2.249
d	=(8+5)-(6+2)	-53.239	-50.744	-50.896	-0.507
e	=(8+10+11)-(2+9)	-48.114	-60.553	-48.948	38.922

The calculated C-H bond strengths of compound 1 were referenced against the benzylic C-H bond dissociation energy of toluene, which has been determined experimentally (BDE = 89.8 ± 0.6 kcal/mol)[19]. A summary of the results is given in Figure S80.



BDE: 74 kcal/mol

BDE: 84 kcal/mol

BDE: 77 kcal/mol

BDE: 40 kcal/mol

corrected BDE = BDE ($PhCH_2$-H, experimental) + ΔH (calculated by DFT)

Figure S80. Corrected BDE's of C-H bonds in starting material 1.

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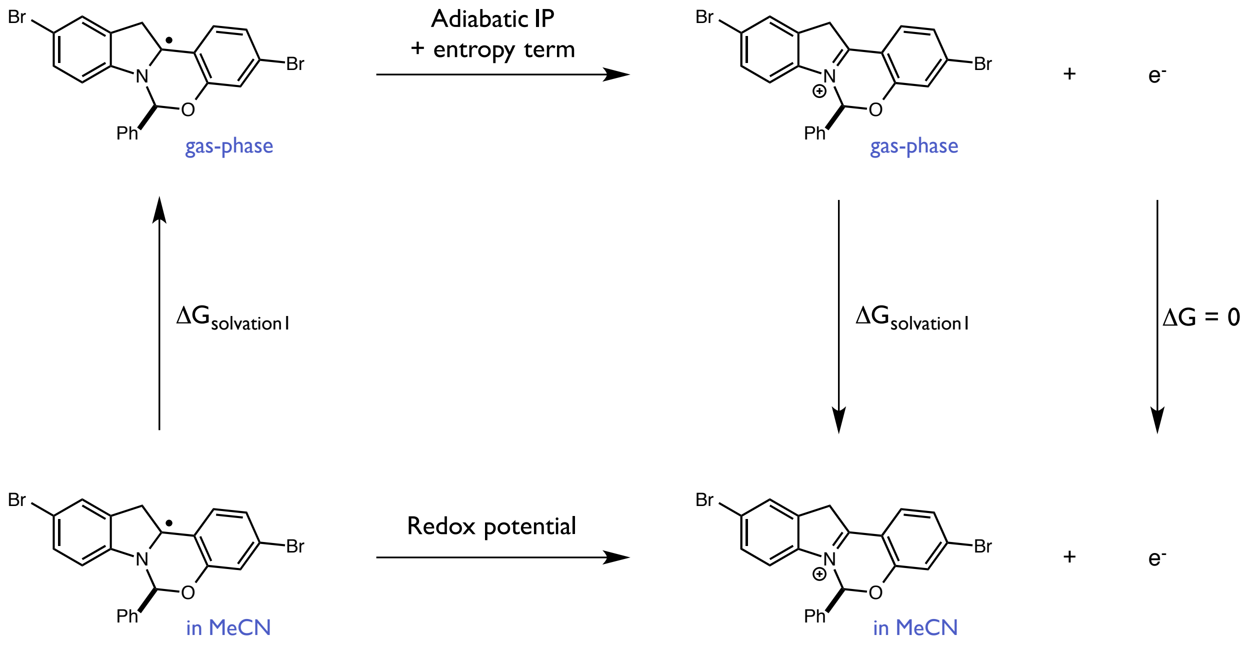
[19] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.,* 2003, **36**, 255–263.

Estimating the 6/6$^+$ redox couple using DFT



$$\boxed{E^{\circ}\ (\text{vs Fc/Fc}^{+}) = \text{IP} + \frac{1}{23.06}\left(-T\Delta S + \Delta G_{\text{solvation2}} - \Delta G_{\text{solvation1}}\right) - 3.81}$$

Figure S81. Thermodynamic cycle for calculating radical reduction potential

Following calculations principles from Batista[20] and Liu and Guo,[21] the redox potential of radical **6** was estimated using a thermodynamic cycle like the one shown above. To simplify the computation, the two Br-atoms in **6** were substituted with H-atoms.

---

[20] S. J. Konezny, M. D. Doherty, O. R. Luca, R. H. Crabtree, G. L. Soloveichik, V. S. Batista, *J. Phys. Chem. C*, 2012, ***116***, 6349–6356.

[21] Y. Fu, L. Liu, H.-Z. Yu, Y.-M. Wang, Q. X. Guo, *J. Am. Chem. Soc.* 2005, **127**, 7227–7234.

Table S43: Thermodynamic parameters. Geometries and frequencies were optimized and calculated with UB3LP/6-311+g(d,p) in the gas phase or in MeCN (CPCM solvent correction).

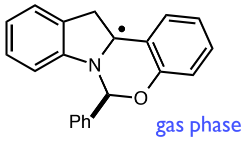
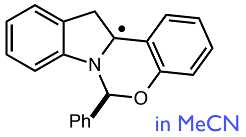
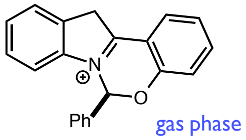
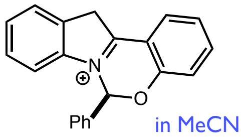
Entry	Molecule	Uncorrected Electronic energies (E_h)	H (E_h)	G (E_h)	S (cal K^{-1} mol^{-1})
1		-940.050076	-939.720996	-939.784877	134.448
2		-940.0589558	-939.730051	-939.794019	134.632
3		-939.8598096	-939.528078	-939.590655	131.705
4		-939.9216456	-939.590055	-939.65303	132.544

Table S44: Summary of results for calculations (see terms from thermodynamic cycle used).

Calculated Parameter	**Energy**
Ionization potential (in V)	5.177531587
TΔS (+entropy correction, 0.04) (in V)	-0.004552732
$\Delta G_{solv1(radical)}$ (in V)	-0.248772215
$\Delta G_{solv2(cation)}$ (in V)	-1.697349257
E_{calc} (V vs NHE)	-0.44
E_{calc} (V vs Fc/Fc$^+$)	-1.07

We found this calculation method predicted known redox potentials of radicals accurately across a large range of redox potentials. To illustrate this, Figure S82 shows calculated redox potentials versus experimental redox potentials for a number of structurally similar radicals to **6**.

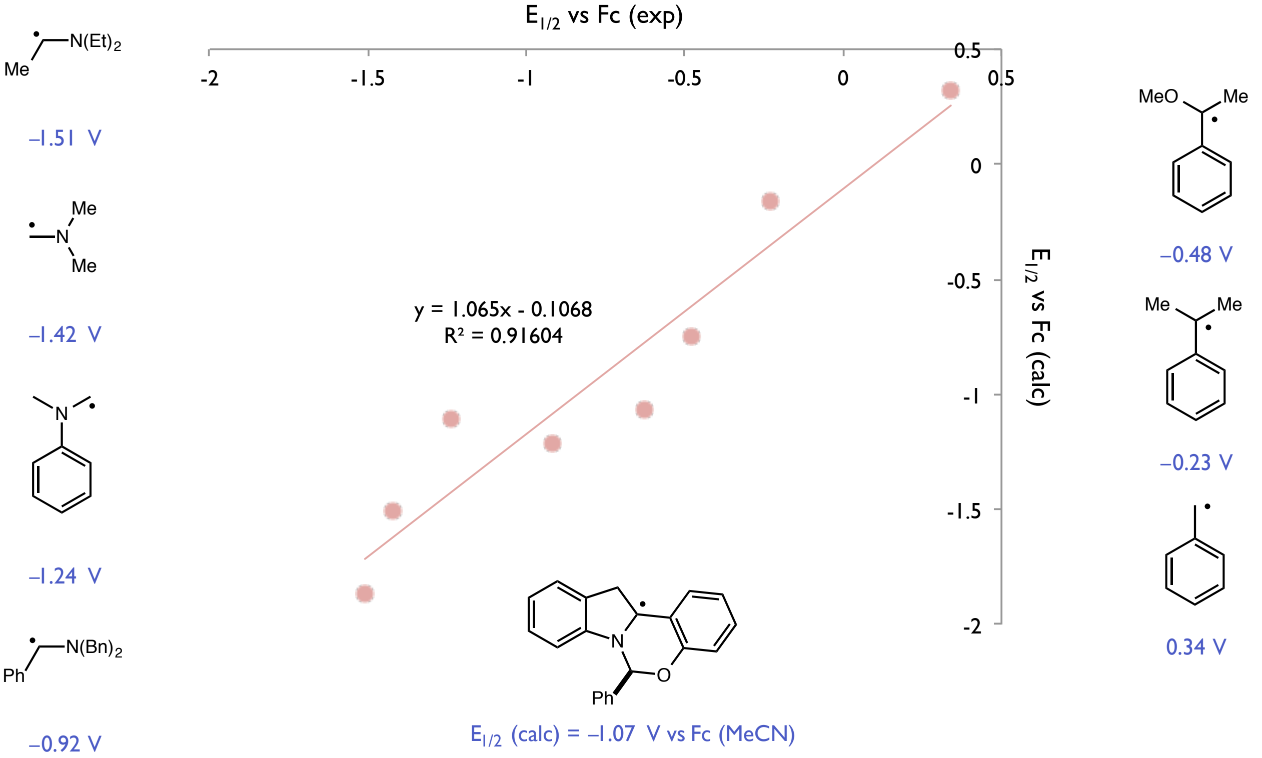


Figure S82. Calculated $E_{1/2}$ versus experimental $E_{1/2}$. The known experimental redox potentials used in the plot are shown to the left and right of the plot.[22]

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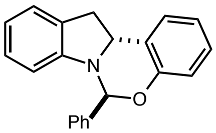
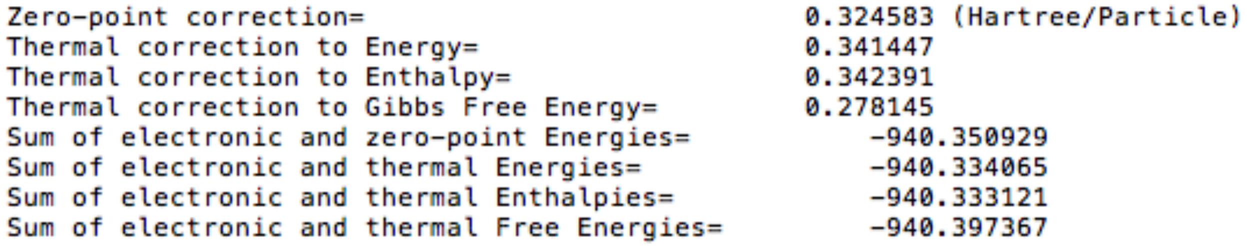
[22] Experimental redox potentials used were compiled by Fu et al. *J. Am. Chem. Soc.,* 2005, **127**, 7227–7234

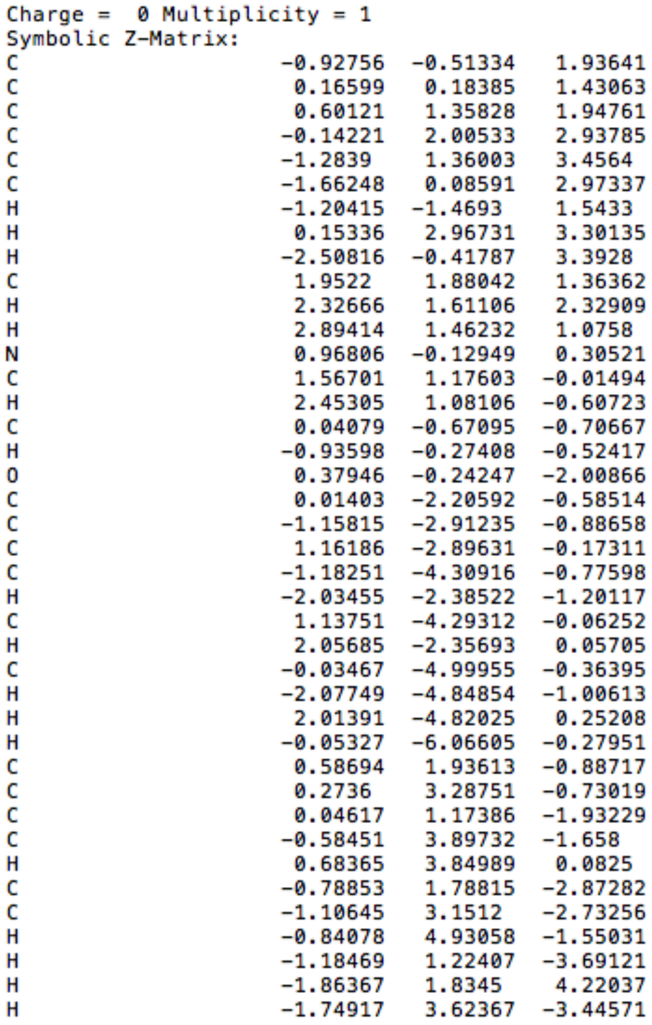
SI.1. Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points. All geometries were optimized at UB3LP/6-311+g(d,p) in gas phase and all energies and calculations were calculated at this level.



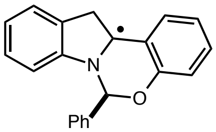
(6*S*,12a*R*)-6-phenyl-12,12a-dihydro-6*H*-benzo[5,6][1,3]oxazino[3,4-*a*]indole



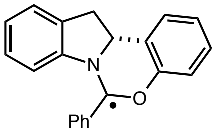
```
Zero-point correction=                           0.324583 (Hartree/Particle)
Thermal correction to Energy=                    0.341447
Thermal correction to Enthalpy=                  0.342391
Thermal correction to Gibbs Free Energy=         0.278145
Sum of electronic and zero-point Energies=           -940.350929
Sum of electronic and thermal Energies=              -940.334065
Sum of electronic and thermal Enthalpies=            -940.333121
Sum of electronic and thermal Free Energies=         -940.397367
```



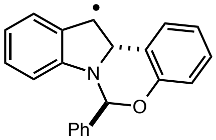
```
Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
C                    -0.92756  -0.51334   1.93641
C                     0.16599   0.18385   1.43063
C                     0.60121   1.35828   1.94761
C                    -0.14221   2.00533   2.93785
C                    -1.2839    1.36003   3.4564
C                    -1.66248   0.08591   2.97337
H                    -1.20415  -1.4693    1.5433
H                     0.15336   2.96731   3.30135
H                    -2.50816  -0.41787   3.3928
C                     1.9522    1.88042   1.36362
H                     2.32666   1.61106   2.32909
H                     2.89414   1.46232   1.0758
N                     0.96806  -0.12949   0.30521
C                     1.56701   1.17603  -0.01494
H                     2.45305   1.08106  -0.60723
C                     0.04079  -0.67095  -0.70667
H                    -0.93598  -0.27408  -0.52417
O                     0.37946  -0.24247  -2.00866
C                     0.01403  -2.20592  -0.58514
C                    -1.15815  -2.91235  -0.88658
C                     1.16186  -2.89631  -0.17311
C                    -1.18251  -4.30916  -0.77598
H                    -2.03455  -2.38522  -1.20117
C                     1.13751  -4.29312  -0.06252
H                     2.05685  -2.35693   0.05705
C                    -0.03467  -4.99955  -0.36395
H                    -2.07749  -4.84854  -1.00613
H                     2.01391  -4.82025   0.25208
H                    -0.05327  -6.06605  -0.27951
C                     0.58694   1.93613  -0.88717
C                     0.2736    3.28751  -0.73019
C                     0.04617   1.17386  -1.93229
C                    -0.58451   3.89732  -1.658
H                     0.68365   3.84989   0.0825
C                    -0.78853   1.78815  -2.87282
C                    -1.10645   3.1512   -2.73256
H                    -0.84078   4.93058  -1.55031
H                    -1.18469   1.22407  -3.69121
H                    -1.86367   1.8345    4.22037
H                    -1.74917   3.62367  -3.44571
```



```
Zero-point correction=                           0.311167 (Hartree/Particle)
Thermal correction to Energy=                    0.328136
Thermal correction to Enthalpy=                  0.329080
Thermal correction to Gibbs Free Energy=         0.265199
Sum of electronic and zero-point Energies=           -939.738909
Sum of electronic and thermal Energies=              -939.721941
Sum of electronic and thermal Enthalpies=            -939.720996
Sum of electronic and thermal Free Energies=         -939.784877
 Charge =  0 Multiplicity = 2
 Symbolic Z-Matrix:
 C                    -0.57344  -0.86756   2.36167
 C                     0.1601    0.09803   1.68092
 C                     0.54504   1.30132   2.24309
 C                     0.11686   1.61878   3.53519
 C                    -0.64637   0.67334   4.25413
 C                    -0.97963  -0.57384   3.67408
 H                    -0.82342  -1.80012   1.90043
 H                     0.36714   2.56194   3.97418
 H                    -1.54266  -1.29133   4.23364
 C                     1.44754   2.25345   1.34293
 H                     2.19246   2.03659   2.0798
 H                     2.27944   2.19403   0.67263
 N                     0.6195    0.09281   0.34545
 C                     0.74178   1.50066   0.17346
 C                    -0.18787  -0.49677  -0.71915
 H                    -1.18091  -0.09858  -0.70478
 O                     0.46489  -0.15513  -1.99923
 C                    -0.25388  -2.02396  -0.53221
 C                    -1.37149  -2.73771  -0.98546
 C                     0.80365  -2.69995   0.09116
 C                    -1.43157  -4.12745  -0.81534
 H                    -2.17894  -2.22158  -1.46141
 C                     0.74357  -4.08969   0.26128
 H                     1.65697  -2.15498   0.43723
 C                    -0.37404  -4.80344  -0.19197
 H                    -2.28489  -4.67241  -1.16141
 H                     1.55102  -4.60582   0.73724
 H                    -0.41991  -5.86453  -0.06208
 C                     0.20262   2.08779  -1.12091
 C                    -0.36859   3.35869  -1.21231
 C                     0.26911   1.26495  -2.23171
 C                    -0.65641   3.87972  -2.4848
 H                    -0.56843   3.93144  -0.33087
 C                     0.07929   1.79418  -3.51074
 C                    -0.38059   3.11617  -3.63715
 H                    -1.07835   4.85845  -2.5795
 H                     0.26536   1.19784  -4.37945
 H                    -0.97446   0.90113   5.24679
 H                    -0.52994   3.54005  -4.60819
```

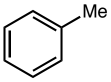


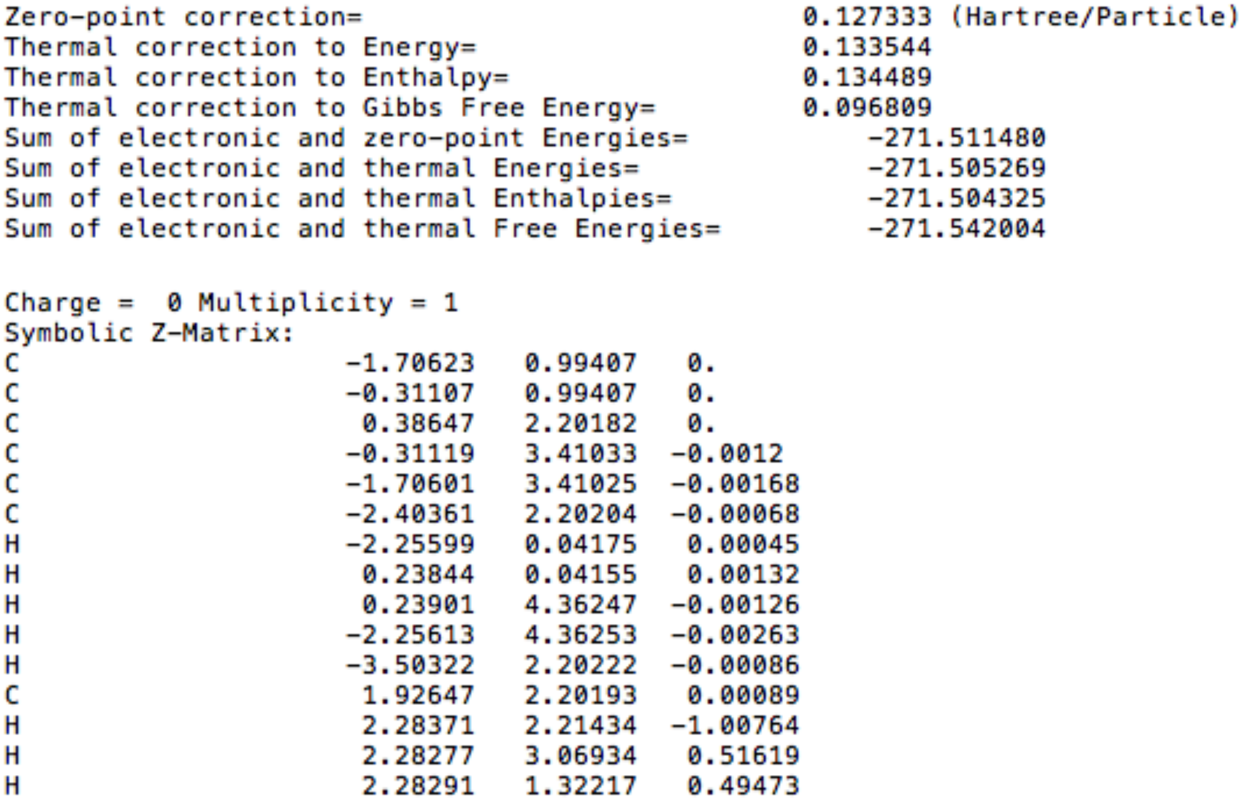
```
 Zero-point correction=                           0.311404 (Hartree/Particle)
 Thermal correction to Energy=                    0.328346
 Thermal correction to Enthalpy=                  0.329290
 Thermal correction to Gibbs Free Energy=         0.265330
 Sum of electronic and zero-point Energies=           -939.733316
 Sum of electronic and thermal Energies=              -939.716374
 Sum of electronic and thermal Enthalpies=            -939.715430
 Sum of electronic and thermal Free Energies=         -939.779390
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                    -1.20919  -0.24576   1.61838
C                     0.03281   0.31386   1.33356
C                     0.44641   1.50777   1.83961
C                    -0.42393   2.28204   2.61023
C                    -1.70443   1.76872   2.90481
C                    -2.09198   0.49627   2.42216
H                    -1.48466  -1.20579   1.23451
H                    -0.1238    3.24257   2.97385
H                    -3.05591   0.10102   2.66614
C                     1.92292   1.89329   1.47979
H                     2.13805   1.68089   2.50619
H                     2.87008   1.40632   1.37664
N                     1.06126  -0.181     0.48784
C                     1.68004   1.1021    0.13711
H                     2.60202   0.96895  -0.38931
C                     0.54831  -0.93383  -0.66438
O                     0.18884  -0.26598  -1.88559
C                     0.38581  -2.46166  -0.55986
C                    -0.8204   -3.00828  -0.10139
C                     1.44413  -3.30537  -0.92323
C                    -0.96828  -4.39861  -0.00629
H                    -1.62845  -2.3641    0.17604
C                     1.29625  -4.69569  -0.82812
H                     2.3651   -2.88801  -1.27328
C                     0.09005  -5.24231  -0.36965
H                    -1.88924  -4.81597   0.34377
H                     2.10431  -5.33988  -1.10556
H                    -0.02287  -6.30386  -0.29703
C                     0.69739   1.8628   -0.75541
C                     0.54016   3.24896  -0.63588
C                    -0.0435    1.14329  -1.70127
C                    -0.40121   3.91316  -1.43367
H                     1.13391   3.79845   0.06442
C                    -0.99949   1.80471  -2.48393
C                    -1.17939   3.18914  -2.34883
H                    -0.52741   4.97186  -1.34356
H                    -1.58938   1.25441  -3.18685
H                    -2.38502   2.34331   3.49771
H                    -1.90975   3.69389  -2.94608
```



```
Zero-point correction=                           0.310803 (Hartree/Particle)
Thermal correction to Energy=                    0.327676
Thermal correction to Enthalpy=                  0.328620
Thermal correction to Gibbs Free Energy=         0.264354
Sum of electronic and zero-point Energies=           -939.722803
Sum of electronic and thermal Energies=              -939.705931
Sum of electronic and thermal Enthalpies=            -939.704986
Sum of electronic and thermal Free Energies=         -939.769253

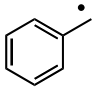
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                    -0.95352  -0.66706   2.11064
C                     0.07923   0.109     1.59321
C                     0.4145    1.31088   2.14767
C                    -0.36183   1.92377   3.12408
C                    -1.44524   1.18725   3.64674
C                    -1.72135  -0.11971   3.16164
H                    -1.16437  -1.64047   1.71958
H                    -0.14106   2.91131   3.47184
H                    -2.51877  -0.6895    3.59101
C                     1.66      1.78706   1.43769
H                     2.46901   2.36118   1.83867
N                     0.91767  -0.13958   0.38124
C                     1.56444   1.17612   0.04868
H                     2.52748   1.04817  -0.39973
C                     0.02509  -0.64008  -0.68671
H                    -0.93459  -0.17977  -0.57707
O                     0.48746  -0.27157  -1.9834
C                    -0.10673  -2.16771  -0.54333
C                    -1.29778  -2.80614  -0.91446
C                     0.96436  -2.91944  -0.04173
C                    -1.41774  -4.19629  -0.78399
H                    -2.11558  -2.23219  -1.29745
C                     0.8444   -4.30958   0.08874
H                     1.87375  -2.43198   0.24163
C                    -0.34665  -4.94801  -0.28239
H                    -2.32713  -4.68374  -1.06736
H                     1.6622   -4.88354   0.47172
H                    -0.43824  -6.00942  -0.18278
C                     0.75912   1.95093  -0.97244
C                     0.53725   3.3284   -0.92139
C                     0.27728   1.169    -2.02665
C                    -0.15589   3.94318  -1.97497
H                     0.89324   3.90629  -0.09422
C                    -0.3893    1.78468  -3.0924
C                    -0.60794   3.17386  -3.06436
H                    -0.33903   4.99714  -1.95182
H                    -0.73352   1.20192  -3.92114
H                    -2.05919   1.6126    4.41293
H                    -1.12157   3.64829  -3.8743
```





```
Zero-point correction=                           0.127333 (Hartree/Particle)
Thermal correction to Energy=                    0.133544
Thermal correction to Enthalpy=                  0.134489
Thermal correction to Gibbs Free Energy=         0.096809
Sum of electronic and zero-point Energies=          -271.511480
Sum of electronic and thermal Energies=             -271.505269
Sum of electronic and thermal Enthalpies=           -271.504325
Sum of electronic and thermal Free Energies=        -271.542004

Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
C                    -1.70623   0.99407   0.
C                    -0.31107   0.99407   0.
C                     0.38647   2.20182   0.
C                    -0.31119   3.41033  -0.0012
C                    -1.70601   3.41025  -0.00168
C                    -2.40361   2.20204  -0.00068
H                    -2.25599   0.04175   0.00045
H                     0.23844   0.04155   0.00132
H                     0.23901   4.36247  -0.00126
H                    -2.25613   4.36253  -0.00263
H                    -3.50322   2.20222  -0.00086
C                     1.92647   2.20193   0.00089
H                     2.28371   2.21434  -1.00764
H                     2.28277   3.06934   0.51619
H                     2.28291   1.32217   0.49473
```



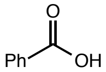
```
Zero-point correction=                           0.114137 (Hartree/Particle)
Thermal correction to Energy=                    0.119829
Thermal correction to Enthalpy=                  0.120774
Thermal correction to Gibbs Free Energy=         0.084449
Sum of electronic and zero-point Energies=          -270.873101
Sum of electronic and thermal Energies=             -270.867409
Sum of electronic and thermal Enthalpies=           -270.866464
Sum of electronic and thermal Free Energies=        -270.902789

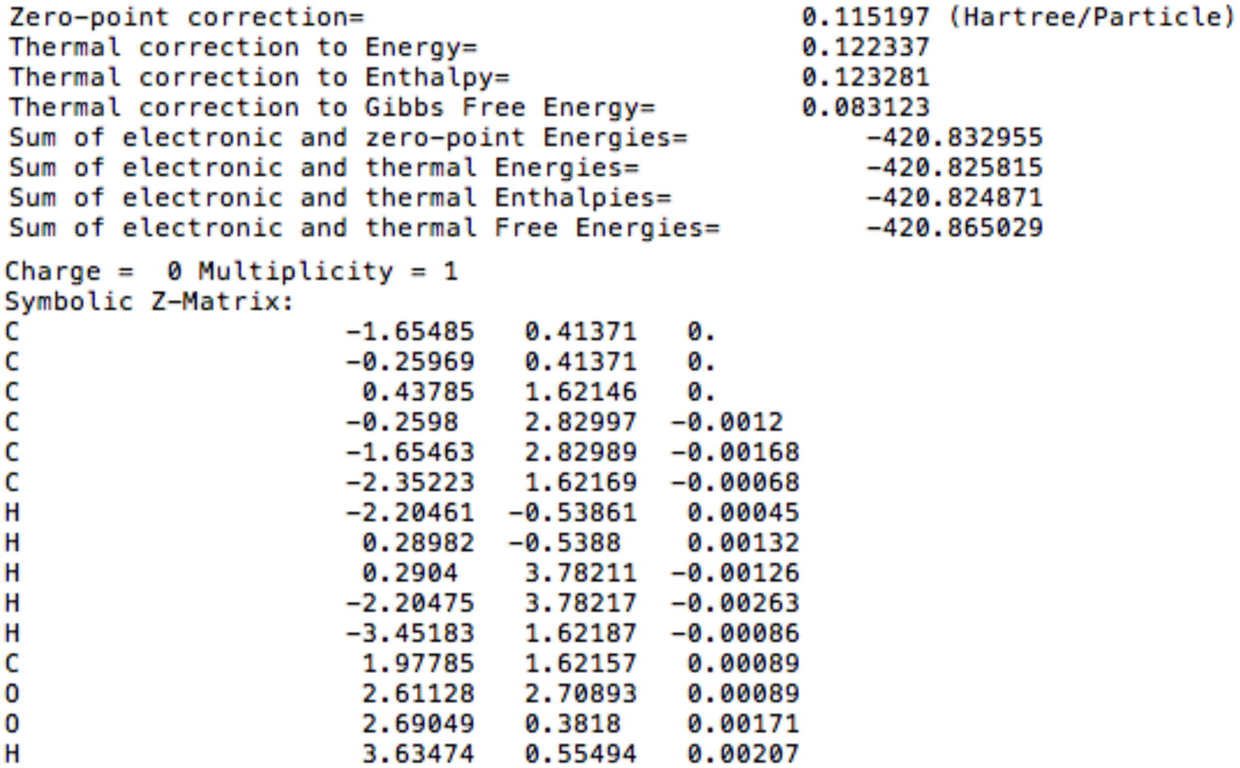
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                    -1.73646   0.99054  -0.01566
C                    -0.33698   0.99034   0.05772
C                     0.37268   2.20064   0.05745
C                    -0.33546   3.41183   0.05966
C                    -1.73494   3.41351  -0.01373
C                    -2.4355    2.2025   -0.0591
H                    -2.27095   0.06385  -0.03739
H                     0.19304   0.06249   0.11308
H                     0.19573   4.33892   0.1165
H                    -2.26826   4.3409   -0.03397
H                    -3.50349   2.20322  -0.12463
C                     1.90055   2.19952   0.25042
H                     2.43191   3.12578   0.3182
H                     2.43075   1.27249   0.31672
```

H•

```
Zero-point correction=                           0.000000 (Hartree/Particle)
Thermal correction to Energy=                    0.001416
Thermal correction to Enthalpy=                  0.002360
Thermal correction to Gibbs Free Energy=        -0.010654
Sum of electronic and zero-point Energies=             -0.502156
Sum of electronic and thermal Energies=                -0.500740
Sum of electronic and thermal Enthalpies=              -0.499795
Sum of electronic and thermal Free Energies=           -0.512810

Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
H                    -1.54303   2.0459   -0.08038
```

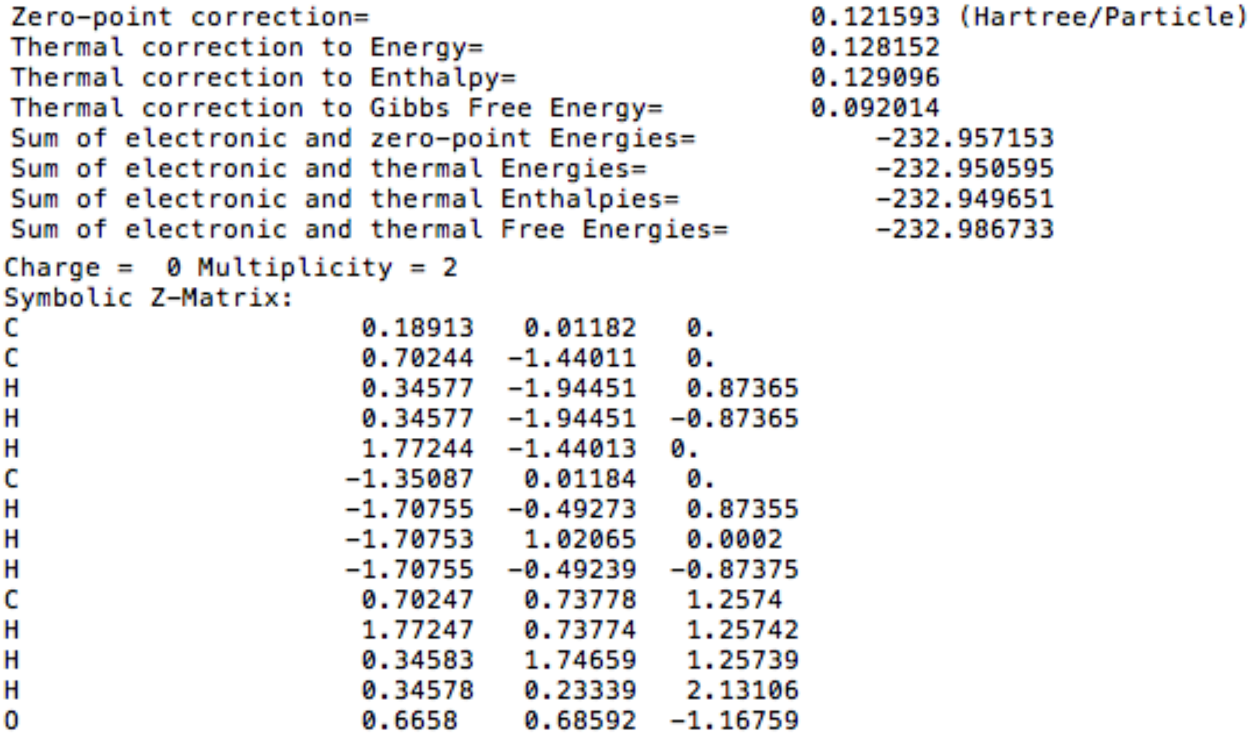




```
 Zero-point correction=                           0.115197 (Hartree/Particle)
 Thermal correction to Energy=                    0.122337
 Thermal correction to Enthalpy=                  0.123281
 Thermal correction to Gibbs Free Energy=         0.083123
 Sum of electronic and zero-point Energies=           -420.832955
 Sum of electronic and thermal Energies=              -420.825815
 Sum of electronic and thermal Enthalpies=            -420.824871
 Sum of electronic and thermal Free Energies=         -420.865029
```

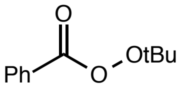
```
Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
C                    -1.65485   0.41371   0.
C                    -0.25969   0.41371   0.
C                     0.43785   1.62146   0.
C                    -0.2598    2.82997  -0.0012
C                    -1.65463   2.82989  -0.00168
C                    -2.35223   1.62169  -0.00068
H                    -2.20461  -0.53861   0.00045
H                     0.28982  -0.5388    0.00132
H                     0.2904    3.78211  -0.00126
H                    -2.20475   3.78217  -0.00263
H                    -3.45183   1.62187  -0.00086
C                     1.97785   1.62157   0.00089
O                     2.61128   2.70893   0.00089
O                     2.69049   0.3818    0.00171
H                     3.63474   0.55494   0.00207
```

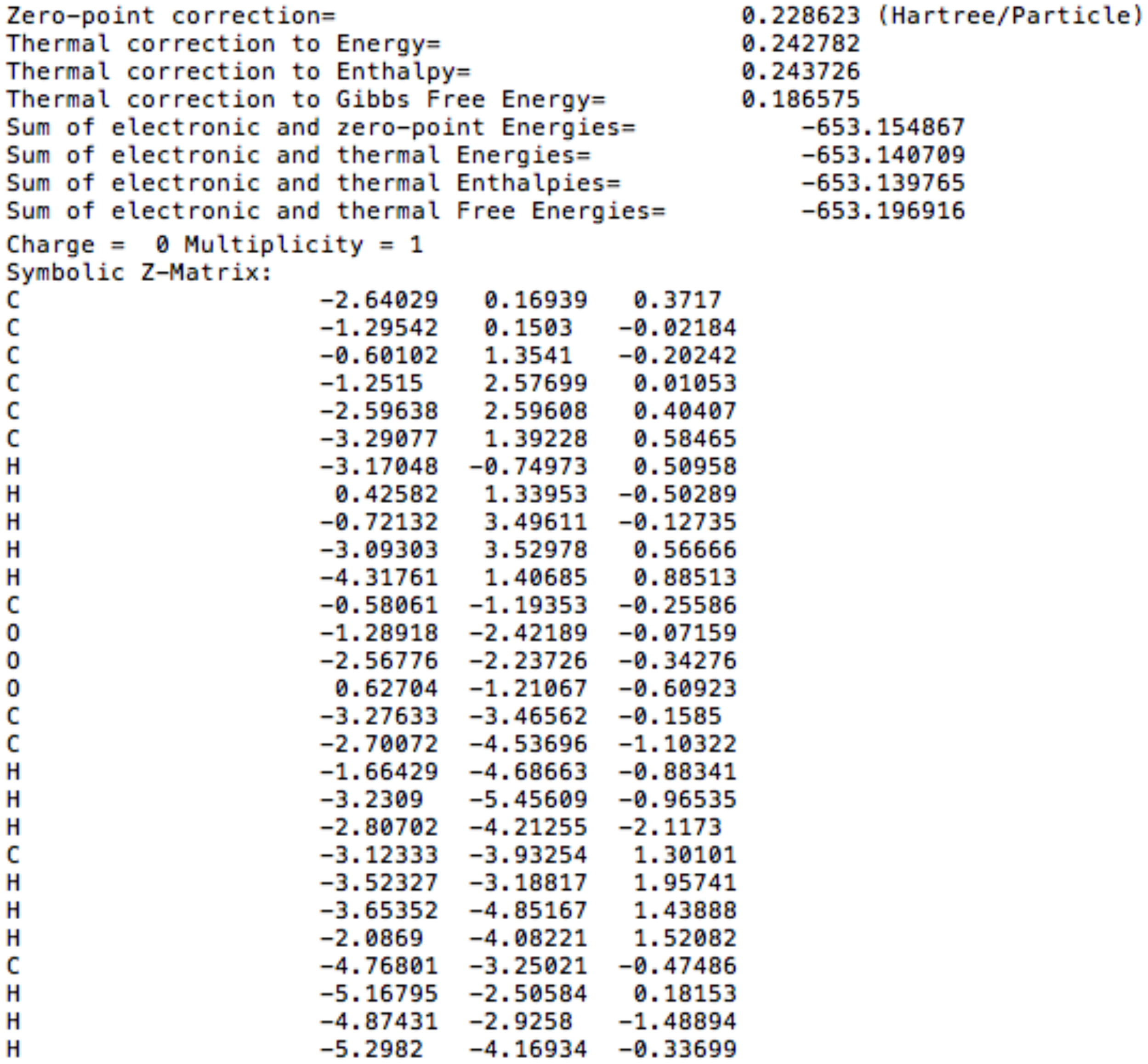
•OtBu



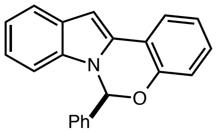
```
 Zero-point correction=                           0.121593 (Hartree/Particle)
 Thermal correction to Energy=                    0.128152
 Thermal correction to Enthalpy=                  0.129096
 Thermal correction to Gibbs Free Energy=         0.092014
 Sum of electronic and zero-point Energies=           -232.957153
 Sum of electronic and thermal Energies=              -232.950595
 Sum of electronic and thermal Enthalpies=            -232.949651
 Sum of electronic and thermal Free Energies=         -232.986733
```

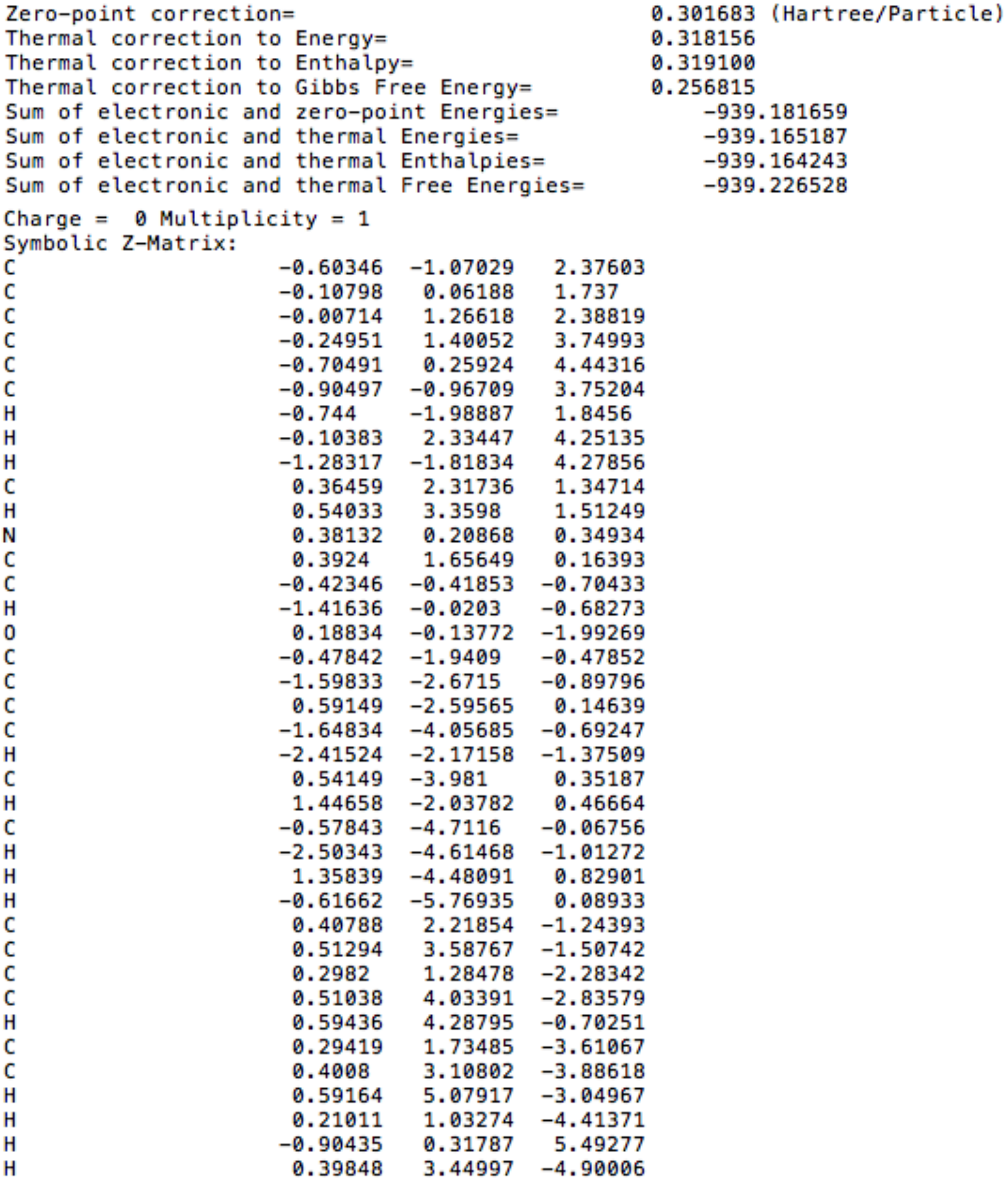
```
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                     0.18913   0.01182   0.
C                     0.70244  -1.44011   0.
H                     0.34577  -1.94451   0.87365
H                     0.34577  -1.94451  -0.87365
H                     1.77244  -1.44013  0.
C                    -1.35087   0.01184   0.
H                    -1.70755  -0.49273   0.87355
H                    -1.70753   1.02065   0.0002
H                    -1.70755  -0.49239  -0.87375
C                     0.70247   0.73778   1.2574
H                     1.77247   0.73774   1.25742
H                     0.34583   1.74659   1.25739
H                     0.34578   0.23339   2.13106
O                     0.6658    0.68592  -1.16759
```





```
Zero-point correction=                           0.228623 (Hartree/Particle)
Thermal correction to Energy=                    0.242782
Thermal correction to Enthalpy=                  0.243726
Thermal correction to Gibbs Free Energy=         0.186575
Sum of electronic and zero-point Energies=           -653.154867
Sum of electronic and thermal Energies=              -653.140709
Sum of electronic and thermal Enthalpies=            -653.139765
Sum of electronic and thermal Free Energies=         -653.196916
Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
C                    -2.64029   0.16939   0.3717
C                    -1.29542   0.1503   -0.02184
C                    -0.60102   1.3541   -0.20242
C                    -1.2515    2.57699   0.01053
C                    -2.59638   2.59608   0.40407
C                    -3.29077   1.39228   0.58465
H                    -3.17048  -0.74973   0.50958
H                     0.42582   1.33953  -0.50289
H                    -0.72132   3.49611  -0.12735
H                    -3.09303   3.52978   0.56666
H                    -4.31761   1.40685   0.88513
C                    -0.58061  -1.19353  -0.25586
O                    -1.28918  -2.42189  -0.07159
O                    -2.56776  -2.23726  -0.34276
O                     0.62704  -1.21067  -0.60923
C                    -3.27633  -3.46562  -0.1585
C                    -2.70072  -4.53696  -1.10322
H                    -1.66429  -4.68663  -0.88341
H                    -3.2309   -5.45609  -0.96535
H                    -2.80702  -4.21255  -2.1173
C                    -3.12333  -3.93254   1.30101
H                    -3.52327  -3.18817   1.95741
H                    -3.65352  -4.85167   1.43888
H                    -2.0869   -4.08221   1.52082
C                    -4.76801  -3.25021  -0.47486
H                    -5.16795  -2.50584   0.18153
H                    -4.87431  -2.9258   -1.48894
H                    -5.2982   -4.16934  -0.33699
```

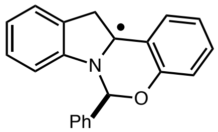




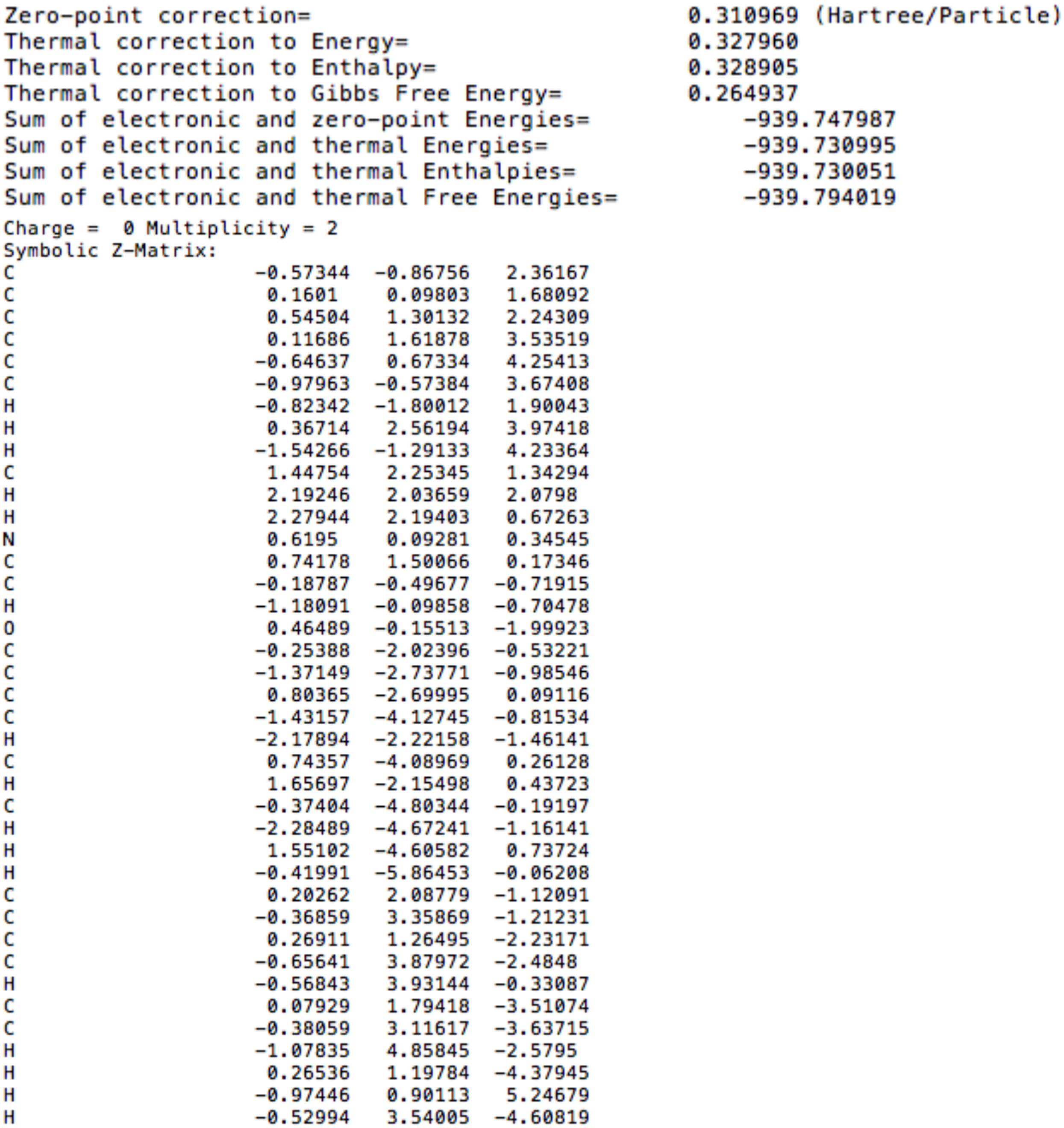
```
Zero-point correction=                           0.301683 (Hartree/Particle)
Thermal correction to Energy=                    0.318156
Thermal correction to Enthalpy=                  0.319100
Thermal correction to Gibbs Free Energy=         0.256815
Sum of electronic and zero-point Energies=           -939.181659
Sum of electronic and thermal Energies=              -939.165187
Sum of electronic and thermal Enthalpies=            -939.164243
Sum of electronic and thermal Free Energies=         -939.226528

Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
C                    -0.60346  -1.07029   2.37603
C                    -0.10798   0.06188   1.737
C                    -0.00714   1.26618   2.38819
C                    -0.24951   1.40052   3.74993
C                    -0.70491   0.25924   4.44316
C                    -0.90497  -0.96709   3.75204
H                    -0.744    -1.98887   1.8456
H                    -0.10383   2.33447   4.25135
H                    -1.28317  -1.81834   4.27856
C                     0.36459   2.31736   1.34714
H                     0.54033   3.3598    1.51249
N                     0.38132   0.20868   0.34934
C                     0.3924    1.65649   0.16393
C                    -0.42346  -0.41853  -0.70433
H                    -1.41636  -0.0203   -0.68273
O                     0.18834  -0.13772  -1.99269
C                    -0.47842  -1.9409   -0.47852
C                    -1.59833  -2.6715   -0.89796
C                     0.59149  -2.59565   0.14639
C                    -1.64834  -4.05685  -0.69247
H                    -2.41524  -2.17158  -1.37509
C                     0.54149  -3.981     0.35187
H                     1.44658  -2.03782   0.46664
C                    -0.57843  -4.7116   -0.06756
H                    -2.50343  -4.61468  -1.01272
H                     1.35839  -4.48091   0.82901
H                    -0.61662  -5.76935   0.08933
C                     0.40788   2.21854  -1.24393
C                     0.51294   3.58767  -1.50742
C                     0.2982    1.28478  -2.28342
C                     0.51038   4.03391  -2.83579
H                     0.59436   4.28795  -0.70251
C                     0.29419   1.73485  -3.61067
C                     0.4008    3.10802  -3.88618
H                     0.59164   5.07917  -3.04967
H                     0.21011   1.03274  -4.41371
H                    -0.90435   0.31787   5.49277
H                     0.39848   3.44997  -4.90006
```

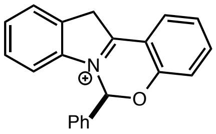
SI.2. Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points. All geometries were optimized at UB3LP/6-311+g(d,p) in MeCN (CPCM solvent correction) and all energies and calculations were calculated at this level.



in MeCN (CPCM solvent correction)



```
Zero-point correction=                           0.310969 (Hartree/Particle)
Thermal correction to Energy=                    0.327960
Thermal correction to Enthalpy=                  0.328905
Thermal correction to Gibbs Free Energy=         0.264937
Sum of electronic and zero-point Energies=           -939.747987
Sum of electronic and thermal Energies=              -939.730995
Sum of electronic and thermal Enthalpies=            -939.730051
Sum of electronic and thermal Free Energies=         -939.794019
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                    -0.57344  -0.86756   2.36167
C                     0.1601    0.09803   1.68092
C                     0.54504   1.30132   2.24309
C                     0.11686   1.61878   3.53519
C                    -0.64637   0.67334   4.25413
C                    -0.97963  -0.57384   3.67408
H                    -0.82342  -1.80012   1.90043
H                     0.36714   2.56194   3.97418
H                    -1.54266  -1.29133   4.23364
C                     1.44754   2.25345   1.34294
H                     2.19246   2.03659   2.0798
H                     2.27944   2.19403   0.67263
N                     0.6195    0.09281   0.34545
C                     0.74178   1.50066   0.17346
C                    -0.18787  -0.49677  -0.71915
H                    -1.18091  -0.09858  -0.70478
O                     0.46489  -0.15513  -1.99923
C                    -0.25388  -2.02396  -0.53221
C                    -1.37149  -2.73771  -0.98546
C                     0.80365  -2.69995   0.09116
C                    -1.43157  -4.12745  -0.81534
H                    -2.17894  -2.22158  -1.46141
C                     0.74357  -4.08969   0.26128
H                     1.65697  -2.15498   0.43723
C                    -0.37404  -4.80344  -0.19197
H                    -2.28489  -4.67241  -1.16141
H                     1.55102  -4.60582   0.73724
H                    -0.41991  -5.86453  -0.06208
C                     0.20262   2.08779  -1.12091
C                    -0.36859   3.35869  -1.21231
C                     0.26911   1.26495  -2.23171
C                    -0.65641   3.87972  -2.4848
H                    -0.56843   3.93144  -0.33087
C                     0.07929   1.79418  -3.51074
C                    -0.38059   3.11617  -3.63715
H                    -1.07835   4.85845  -2.5795
H                     0.26536   1.19784  -4.37945
H                    -0.97446   0.90113   5.24679
H                    -0.52994   3.54005  -4.60819
```



in MeCN (CPCM solvent correction)

```
Zero-point correction=                           0.313893 (Hartree/Particle)
Thermal correction to Energy=                    0.330647
Thermal correction to Enthalpy=                  0.331591
Thermal correction to Gibbs Free Energy=         0.268615
Sum of electronic and zero-point Energies=          -939.607752
Sum of electronic and thermal Energies=             -939.590999
Sum of electronic and thermal Enthalpies=           -939.590055
Sum of electronic and thermal Free Energies=        -939.653030
Charge =  1 Multiplicity = 1
Symbolic Z-Matrix:
C                    -0.57344  -0.86756   2.36167
C                     0.1601    0.09803   1.68092
C                     0.54504   1.30132   2.24309
C                     0.11686   1.61878   3.53519
C                    -0.64637   0.67334   4.25413
C                    -0.97963  -0.57384   3.67408
H                    -0.82342  -1.80012   1.90043
H                     0.36714   2.56194   3.97418
H                    -1.54266  -1.29133   4.23364
C                     1.44754   2.25345   1.34294
H                     2.19246   2.03659   2.0798
H                     2.27944   2.19403   0.67263
N                     0.6195    0.09281   0.34545
C                     0.74178   1.50066   0.17346
C                    -0.18787  -0.49677  -0.71915
H                    -1.18091  -0.09858  -0.70478
O                     0.46489  -0.15513  -1.99923
C                    -0.25388  -2.02396  -0.53221
C                    -1.37149  -2.73771  -0.98546
C                     0.80365  -2.69995   0.09116
C                    -1.43157  -4.12745  -0.81534
H                    -2.17894  -2.22158  -1.46141
C                     0.74357  -4.08969   0.26128
H                     1.65697  -2.15498   0.43723
C                    -0.37404  -4.80344  -0.19197
H                    -2.28489  -4.67241  -1.16141
H                     1.55102  -4.60582   0.73724
H                    -0.41991  -5.86453  -0.06208
C                     0.20262   2.08779  -1.12091
C                    -0.36859   3.35869  -1.21231
C                     0.26911   1.26495  -2.23171
C                    -0.65641   3.87972  -2.4848
H                    -0.56843   3.93144  -0.33087
C                     0.07929   1.79418  -3.51074
C                    -0.38059   3.11617  -3.63715
H                    -1.07835   4.85845  -2.5795
H                     0.26536   1.19784  -4.37945
H                    -0.97446   0.90113   5.24679
H                    -0.52994   3.54005  -4.60819
```

Process mass intensity (PMI): $KMnO_4$ vs. photocatalytic oxidation protocol

The photo-mediated process reported herein compares favorably with the use of permanganate as a stoichiometric oxidant from a processing perspective. Due to the simple workup and direct crystallization of the product from the reaction media, the photo-mediated process reduces the step PMI by >60%. For a comparative breakdown of the PMI's for both protocols, see Table S45.

Table S45. Comparison of PMI's for both oxidation protocols.

	$KMnO_4$	*Photo-oxidation*
Step Yield	85%	85%
Step PMI Substrates, Reagents	1.8	2.5
Step PMI Solvents	33.2	9.2
Step PMI Water	14.0	8.2
Total Step PMI	49	19.9