Rate-Driving Force Relationships in the Multisite PCET Activation of Ketones

Guanqi Qiu and Robert R. Knowles*

Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

Supporting Information

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1. General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified and stored according to the method of Grubbs.[2] All luminescence quantities were measured using steady-state Stern–Volmer experiments on an Agilent Cary Eclipse fluorescence spectrophotometer. Stern–Volmer fluorescence quenching experiments were run with freshly prepared 3 x 10^{-6} M solutions of Ir(III) photocatalyst in acetonitrile at ambient temperature (22–24 ºC) under an argon atmosphere. All solutions were degassed with argon before luminescence measurement. The irradiation and emission wavelengths depend on the specific photocatalyst used. In all Stern–Volmer experiments, the fluorescence intensity was measured three times for each sample. Time-resolved luminescence experiments were used qualitatively to identify the nature (static or dynamic) of the relevant steady-state quenching experiments. These experiments were conducted using time-correlated single-photon counting with Horiba DeltaFlex.

2. Extended Description of Experimental Method for Obtaining K_A and k_{PCET}

2.1. Supplementary Explanation of the Experimental Method

S_0 and A_0 are the initial concentrations used to prepare the solutions for luminescence quenching measurements. In a typical set of Stern-Volmer experiments, we keep the initial ketone concentration constant and vary the initial acid concentration to obtain a value for k_{obs} using equation 2. For the values used in key equation 8, S_0 is the initial ketone concentration, and we take A_0 as the average value of all the initial acid concentrations that lead to the corresponding k_{obs}. Conceptually, this average value can be thought of as an approximation for the point of tangency with equation 5. For example, in a luminescence quenching experiment in which the initial ketone concentration is fixed at 0.050M and the initial acid concentration is varied at 0.0010, 0.0015, 0.0020, 0.0025, 0.0030 M, S_0= 0.050 M, A_0= 0.0020 M, and the slope from equation 2 gives the corresponding k_{obs} for S_0= 0.050 M, A_0= 0.0020 M. In practice, if the chosen value of S_0 is significantly higher than A_0, the range of A_0 can be broader. If S_0 and A_0 are similar, $\Delta A_0/A_0$ needs to be small. More generally, the key is that $\Delta A_0/(S_0+A_0)$ should be kept small. Whether appropriate intervals of A_0 around the average value A_0 were chosen is assessed by the linearity of the plot of equation 2. If curvature is observed within one quenching data set, we would reduce the interval of variance in the A_0.

It is important to note that the magnitude of x should not be insignificant with respect to A_0 and S_0, otherwise equation 3a will collapse into $K_A = x/S_0A_0$ so that k_{obs} will be constant and curvature will not be captured. As seen in the main text Figure 2c, the four different slopes indicate that the variation in x as a result of the variation in A_0 displays four different sensitivities (as reflected in each value of k_{obs}). Thus x/S_0A_0 appears to be constant within each linear Stern-Volmer quenching data set, but it is not a constant between any two of the four linear data sets. The fact that four different slopes are obtained rather than a single slope for all four data sets indicates that x is not negligible compared to A_0.

When the changes in the concentration for either the acid or ketone become too large, the resulting changes in I_0/I should deviate from linearity. This is observed experimentally. In Figure S.2.1.1, data are presented for the PCET activation of ketone **1** with *p*-TsOH and photoreductant **7**. At a fixed A_0 = 0.003M, we varied the S_0 over between 0.040 and 0.104M. Indeed, non-linear quenching behavior was observed. Notably, the ketone alone does not quench the luminescence of **7** under these conditions. As such, this behavior can be taken as a evidence of the reaction occurring through a H-bond complex of the ketone & acid.

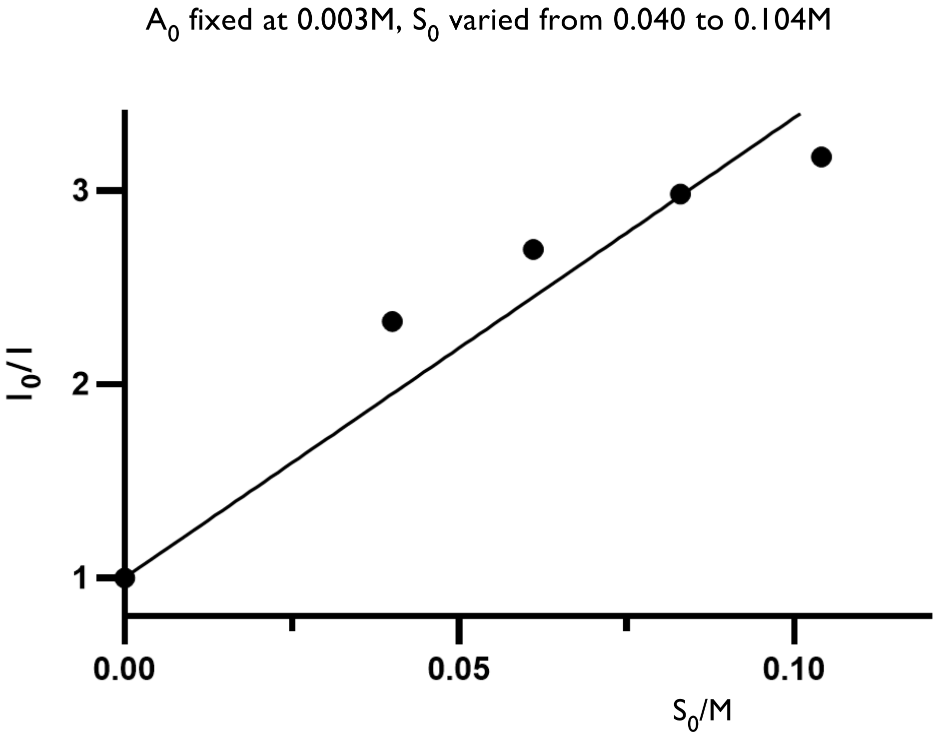


Figure S.2.1.1. Non-linear luminescence quenching data for fixed [*p*-TsOH]$_0$ and varying [ketone **1**]$_0$ from 13 to 35 equivalence

2.2. Treatment of Competitive non-PCET Quenching

In all equations below, I_0 is the luminescence intensity in the absence of any quencher and I is the luminescence intensity in the presence of a quencher.

As mentioned in the main text, some ketones and acids undergo non-PCET luminescence quenching in the presence of the *Ir (III)-based photoreductant. The luminescence intensity relationships are defined by equations S1a and S1b as follows:

$$\frac{I_0}{I} = 1 + k'_{SV} S_0 \qquad \text{(S1a)}$$

$$\frac{I_0}{I} = 1 + k''_{SV} A_0 \qquad \text{(S1b)}$$

Although the effect of this non-PCET quenching is significantly smaller than that of PCET quenching, it important to consider in some cases to obtain precise values of K_A and k_{PCET} owing to the wide concentration ranges examined for both species. We took the non-PCET quenching into account in all cases. The results show that non-PCET quenching is insignificant compared to the PCET quenching in most cases. Moreover, the non-PCET rate constant (if there was one) is very small compared to the PCET rate constant, in all cases.

The nature of non-PCET quenching by each ketone or acid was determined qualitatively using time-resolved luminescence experiments. A constant lifetime of the excited-state *Ir(III) luminescence, regardless of the quencher concentration, suggests static quenching, whereas a decreasing lifetime with increasing concentration of the quencher indicates dynamic quenching.

If the non-PCET luminescence quenching by both ketone and acid was found to be dynamic, equation 2 in the main text is modified to equation S2,

$$\frac{I_0}{I} = 1 + k'_{SV} S_0 + k''_{SV} A_0 + k_{obs} \tau_0 S_0 A_0 \qquad \text{(S2)}$$

and equation 4 in the main text is modified to equation S3.

$$\frac{I_0}{I} = 1 + k'_{SV} S_0 + k''_{SV} A_0 + k_{\mathrm{PCET}}\, \tau_0 (\mathrm{x}) \qquad \text{(S3)}$$

A linear plot leads to the second order rate constant $k_{obs}\tau_0$by equation S4a.

$$\frac{I_0}{I(1+k'_{SV} S_0)} = 1 + \frac{(k''_{SV} + k_{obs}\tau_0 S_0)\, A_0}{1+k'_{SV} S_0} \qquad \text{(S4a)}$$

K'$_{\mathrm{SV}}$ and *k''*$_{\mathrm{SV}}$ are obtained by independent Stern–Volmer analysis of the steady-state luminescence quenching according to equation S1a or S1b. According to equation S4a, for each combination of ketone and acid concentrations, the concentration of ketone is held constant and the concentration of acid is varied. The term $\frac{I_0}{I(1+k'_{SV}\,S_0)}$is extrapolated from the luminescence intensity changes upon variation in the concertation of acid. The slope is $\frac{k''_{SV}+k_{obs}\tau_0 S_0}{1+k'_{SV}\,S_0}$ and the $k_{\mathrm{obs\,SV}}$ could be calculated accordingly. It is equally viable to keep the concentration of acid constant and vary the concentration of ketone. The linear Stern–Volmer plot becomes equation S4b,

$$\frac{I_0}{I(1+k''_{SV}\,A_0)} = 1 + \frac{(k'_{SV}+k_{obs}\tau_0 A_0)\,S_0}{1+k''_{SV}\,A_0} \qquad \text{(S4b)}$$

and the slope is given by $\frac{k'_{SV}+k_{obs}\tau_0 A_0}{1+k''_{SV}A_0}$.

If the non-PCET luminescence quenching by ketone was found to be static and that by acid was dynamic, equation 2 in the main text is modified to equation S5.

$$\frac{I_0}{I(1+k'_{SV}\,S_0)} = 1 + (k''_{SV} + k_{obs}\tau_0 S_0)A_0 \qquad \text{(S5)}$$

As shown in equation S5, the concentration of ketone is held constant, while that of the acid is varied. The Stern–Volmer slope gives $(k''_{SV} + k_{obs}\tau_0 S_0)$, and $k_{\mathrm{obs\,SV}}$ is then known.

The $k_{\mathrm{obs\,SV}}$ obtained from equations S4a, S4b, or S5 is then substituted into equation 3a from the main text, just as that from equation 2 is substituted into equation 3a. Whatever modification for equation 2 is required, the identical modification must be made for equation 4, as well, leading to equations 6 and 7, and thus equation 8 anyway. For example, if the non-PCET quenching by ketone is static and that by acid is dynamic:

$$\frac{I_0}{I} = (1 + +k''_{SV}A_0 + k_{obs}\,\tau_0 S_0 A_0)(1 + k'_{SV}S_0)$$

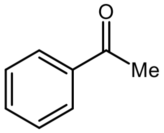
$$= (1 + k''_{SV}A_0 + \mathrm{k_{PCET}}\,\tau_0(\mathrm{x}))(1 + k'_{SV}S_0)$$

$$k_{obs}\tau_0\, S_0 A_0 = k_{\mathrm{PCET}}\,\tau_0(\mathrm{x})$$

An identical expression to the scenario in which there is no non-PCET quenching, is obtained.

3. Computational Evaluation of Ketyl O–H Bond Dissociation Free Energy

All calculations were performed using DFT at the UB3LYP/6-311+G(d,p) level of theory as implemented in the *Gaussian 16* suite.[3] Frequency calculations were performed at the same level of theory in order to derive thermal corrections at 295 K. Acetonitrile solvent was simulated using the CPCM model.



1

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C                     1.9058   -2.33612  -1.40567
C                     2.10663  -0.95661  -1.2624
C                     1.52453  -0.27171  -0.18723
C                     0.74161  -0.96633   0.74468
H                     0.96954  -4.08403  -0.58315
H                     2.35024  -2.85906  -2.22659
H                     1.67787   0.78158  -0.07784
H                     0.29716  -0.44339   1.5656
C                     2.96698  -0.19329  -2.28648
O                     3.14732   1.04546  -2.15783
C                     3.60665  -0.94592  -3.46799
H                     4.57635  -1.29777  -3.18376
H                     2.98994  -1.778    -3.73672
H                     3.6981   -0.28493  -4.30443
H                    -0.057    -2.8762    1.31295

Sum of electronic and zero-point Energies=           -384.872161
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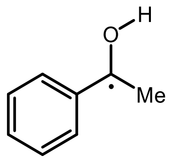

1-ketyl

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Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                     1.51036  -2.37982  -0.04072
C                     2.23289  -1.17941  -0.07087
C                     1.55477   0.04697  -0.06285
C                     0.15413   0.07295  -0.02467
C                    -0.56839  -1.12745   0.00549
H                     2.02812  -3.31619  -0.04684
H                     3.3023   -1.19925  -0.10003
H                    -0.36362   1.00932  -0.01854
H                    -1.63781  -1.10762   0.03464
C                     2.34876   1.3661   -0.09599
C                     3.88361   1.35457   0.0293
H                     4.1661    0.80366   0.90199
H                     4.30873   0.89268  -0.83721
H                     4.24241   2.35937   0.11015
O                     1.66311   2.61018   0.06847
H                     2.30358   3.32224   0.13453
C                     0.10972  -2.35384  -0.00253
H                    -0.44194  -3.27037   0.02049

Sum of electronic and zero-point Energies=           -385.426592
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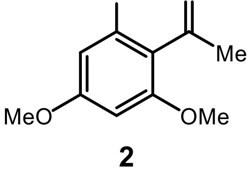

2

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Symbolic Z-Matrix:
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C                     1.50746  -2.36044  -0.04844
C                     2.22134  -1.15465  -0.02935
C                     1.54163   0.0595    0.13729
C                     0.14805   0.06786   0.28484
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```
C                    -0.56583  -1.13793   0.26574
H                     2.02643  -3.28747  -0.17567
H                    -1.62987  -1.13155   0.3784
C                     2.32612   1.38455   0.15827
O                     1.71577   2.4748    0.3079
C                     3.85753   1.37536  -0.00387
H                     4.31764   1.29498   0.9588
H                     4.14719   0.54136  -0.60839
H                     4.17179   2.28337  -0.47469
O                    -0.61458  -3.58248   0.07963
C                    -0.99829  -3.88803  -1.26361
H                    -1.54336  -4.80868  -1.27819
H                    -1.61556  -3.10201  -1.64578
H                    -0.12308  -3.98204  -1.87195
O                    -0.54553   1.30678   0.45488
O                     3.64337  -1.16317  -0.17991
C                     4.03048  -2.27777  -0.9878
H                     5.09452  -2.28416  -1.10046
H                     3.71622  -3.18578  -0.51699
H                     3.57038  -2.19739  -1.95048
C                    -1.86092   1.19606  -0.09503
H                    -2.37989   2.12309   0.0322
H                    -1.79336   0.9653   -1.13767
H                    -2.39375   0.41693   0.4089

Sum of electronic and zero-point Energies=          -728.442637
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Sum of electronic and thermal Free Energies=        -728.486297
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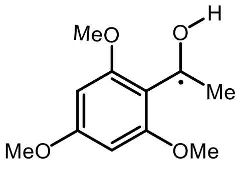

2-ketyl

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Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                     0.12376  -2.32588   0.47287
C                     1.5045   -2.35494   0.23492
C                     2.20602  -1.15873   0.03275
C                     1.52679   0.06654   0.06853
C                     0.14604   0.0956    0.30649
C                    -0.55547  -1.10061   0.50866
H                     2.02311  -3.29046   0.2076
H                    -1.6097   -1.07842   0.69034
```

```
C                     2.29769   1.38106  -0.15363
C                     3.83464   1.37573  -0.25024
H                     4.24389   0.87566   0.6026
H                     4.13424   0.86457  -1.14123
H                     4.19369   2.38328  -0.27923
O                     1.63337   2.63299   0.03677
H                     2.27123   3.34725  -0.03073
O                    -0.59208  -3.54651   0.67917
C                     0.04506  -4.60122  -0.04645
H                     1.05121  -4.71497   0.29945
H                    -0.49056  -5.51456   0.10791
H                     0.05129  -4.36334  -1.08965
O                    -0.54705   1.34588   0.343
O                     3.61494  -1.18838  -0.21006
C                    -1.89484   1.15673  -0.09583
H                    -2.38528   0.45808   0.54935
H                    -2.41345   2.09225  -0.06851
H                    -1.89429   0.77833  -1.09668
C                     3.95872  -2.40754  -0.87367
H                     5.01295  -2.42973  -1.05535
H                     3.68544  -3.23842  -0.25734
H                     3.43499  -2.4667   -1.80486

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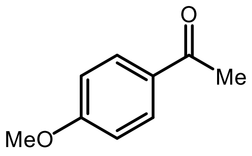

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C                     2.21951  -1.17652  -0.03428
C                     1.53778   0.04606   0.0327
C                     0.13715   0.06593   0.07481
C                    -0.58175  -1.13677   0.04994
H                     2.02112  -3.31268  -0.11029
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```
H                    3.28891  -1.19169  -0.06643
H                   -0.38336   0.99939   0.12595
H                   -1.65116  -1.1216    0.08209
C                    2.32777   1.3677    0.06003
O                    1.71561   2.46552   0.12017
C                    3.86692   1.34587   0.01375
H                    4.25314   1.3022    1.01066
H                    4.19514   0.48719  -0.53384
H                    4.2219    2.23304  -0.46772
O                   -0.63359  -3.58659  -0.04241
C                   -0.91787  -3.94407  -1.39751
H                   -1.46676  -4.86236  -1.41649
H                   -1.49927  -3.17148  -1.85573
H                   -0.00028  -4.06586  -1.93426

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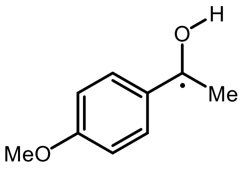

3-ketyl

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C                    1.49232  -2.40816   0.28814
C                    2.21086  -1.21956   0.10145
C                    1.53174   0.00298   0.01136
C                    0.13409   0.03692   0.10797
C                   -0.58445  -1.15168   0.29466
H                    2.01084  -3.34159   0.35693
H                    3.278    -1.24547   0.02769
H                   -0.38444   0.97036   0.03918
H                   -1.65159  -1.12577   0.36842
C                    2.32134   1.30914  -0.1938
C                    3.86023   1.30621  -0.13538
H                    4.18165   0.84837   0.77674
H                    4.24767   0.75533  -0.96683
H                    4.22059   2.31291  -0.17545
O                    1.64153   2.5656   -0.12997
H                    2.28311   3.27878  -0.1666
O                   -0.63853  -3.58708   0.57525
```

```
C                     0.06803  -4.67167  -0.03248
H                     1.03432  -4.76461   0.41756
H                    -0.48059  -5.57919   0.11006
H                     0.17903  -4.48276  -1.07981

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Sum of electronic and thermal Enthalpies=            -499.939225
Sum of electronic and thermal Free Energies=         -499.9895
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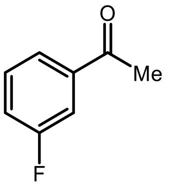

4

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C                     1.12287  -3.03074  -0.47376
C                     1.9058   -2.33612  -1.40567
C                     2.10663  -0.95661  -1.2624
C                     1.52453  -0.27171  -0.18723
C                     0.74161  -0.96633   0.74468
H                     2.35024  -2.85906  -2.22659
H                     1.67787   0.78158  -0.07784
H                     0.29716  -0.44339   1.5656
C                     2.96698  -0.19329  -2.28648
O                     3.14732   1.04546  -2.15783
C                     3.60665  -0.94592  -3.46799
H                     4.57635  -1.29777  -3.18376
H                     2.98994  -1.778    -3.73672
H                     3.6981   -0.28493  -4.30443
H                    -0.057    -2.8762    1.31295
F                     0.92941  -4.35966  -0.61177

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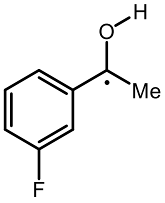

4-ketyl

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C                     2.23289  -1.17941  -0.07087
C                     1.55477   0.04697  -0.06285
C                     0.15413   0.07295  -0.02467
C                    -0.56839  -1.12745   0.00549
H                     3.3023   -1.19925  -0.10003
H                    -0.36362   1.00932  -0.01854
H                    -1.63781  -1.10762   0.03464
C                     2.34876   1.3661   -0.09599
C                     3.88361   1.35457   0.0293
H                     4.1661    0.80366   0.90199
H                     4.30873   0.89268  -0.83721
H                     4.24241   2.35937   0.11015
O                     1.66311   2.61018   0.06847
H                     2.30358   3.32224   0.13453
C                     0.10972  -2.35384  -0.00253
H                    -0.44194  -3.27037   0.02049
F                     2.1636   -3.56122  -0.04844

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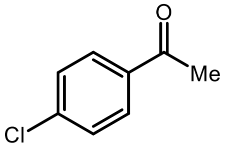

5

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C                     1.54272  -2.34229   0.00168
C                     2.24026  -1.13454   0.00168
C                     1.54261   0.07397   0.00048
C                     0.14778   0.07389   0.
```

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C                    -0.54982  -1.13431   0.001
H                     2.09223  -3.2948    0.00299
H                     3.33994  -1.13446   0.00231
H                    -0.40234   1.02617  -0.00095
H                    -1.64942  -1.13413   0.00082
C                     2.31311   1.40736   0.0004
O                     1.74159   2.49348  -0.00064
C                     3.84842   1.28729   0.00175
H                     4.16395   0.7571    0.87596
H                     4.16541   0.75614  -0.87134
H                     4.28266   2.26522   0.00158
Cl                   -0.73236  -3.86654   0.0024

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Sum of electronic and thermal Energies=              -844.495379
Sum of electronic and thermal Enthalpies=            -844.494435
Sum of electronic and thermal Free Energies=         -844.539859
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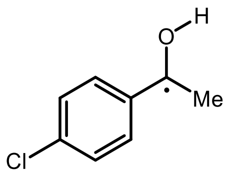
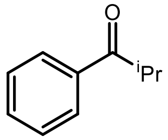


5-ketyl

```
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                     0.10972  -2.35384  -0.00254
C                     1.51037  -2.37982  -0.04047
C                     2.2329   -1.17942  -0.07065
C                     1.55478   0.04696  -0.06291
C                     0.15414   0.07295  -0.02499
C                    -0.56839  -1.12745   0.0052
H                     2.02813  -3.3162   -0.04638
H                     3.30232  -1.19926  -0.09961
H                    -0.36362   1.00932  -0.01908
H                    -1.63782  -1.10761   0.03415
C                     2.34877   1.36608  -0.09607
C                     3.8836    1.35458   0.0295
H                     4.16593   0.80378   0.90232
H                     4.30889   0.89258  -0.83686
H                     4.24239   2.35939   0.11029
O                     1.6631    2.61019   0.06811
H                     2.30355   3.32226   0.13419
Cl                   -0.79769  -3.86141   0.03537

Sum of electronic and zero-point Energies=           -845.060397
Sum of electronic and thermal Energies=              -845.050404
```

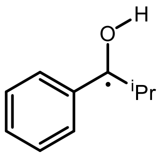
```
Sum of electronic and thermal Enthalpies=            -845.049459
Sum of electronic and thermal Free Energies=         -845.097809
```



10

```
Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
C                      1.51036  -2.37982  -0.04072
C                      2.23289  -1.17941  -0.07087
C                      1.55477   0.04697  -0.06285
C                      0.15413   0.07295  -0.02467
C                     -0.56839  -1.12745   0.00549
H                      2.02812  -3.31619  -0.04684
H                      3.3023   -1.19925  -0.10003
H                     -0.36362   1.00932  -0.01854
H                     -1.63781  -1.10762   0.03464
C                      2.34876   1.3661   -0.09599
C                      3.88361   1.35457   0.0293
O                      1.66311   2.61018   0.06847
C                      0.10972  -2.35384  -0.00253
H                     -0.44194  -3.27037   0.02049
C                      4.29019   0.56167   1.28532
H                      3.46996   0.53605   1.97196
H                      4.55348  -0.43732   1.00676
H                      5.12961   1.03538   1.74994
C                      4.49547   0.6898   -1.21782
H                      4.72031  -0.33387  -1.00227
H                      3.79712   0.73883  -2.02701
H                      5.39411   1.20253  -1.49067
H                      4.24241   2.35937   0.11015

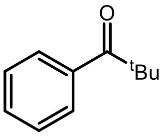
Sum of electronic and zero-point Energies=           -463.456820
Sum of electronic and thermal Energies=              -463.446216
Sum of electronic and thermal Enthalpies=            -463.445272
Sum of electronic and thermal Free Energies=         -463.493536
```



10-ketyl

```
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
C                     1.51036  -2.37982  -0.04072
C                     2.23289  -1.17941  -0.07087
C                     1.55477   0.04697  -0.06285
C                     0.15413   0.07295  -0.02467
C                    -0.56839  -1.12745   0.00549
H                     2.02812  -3.31619  -0.04684
H                     3.3023   -1.19925  -0.10003
H                    -0.36362   1.00932  -0.01854
H                    -1.63781  -1.10762   0.03464
C                     2.34876   1.3661   -0.09599
C                     3.88361   1.35457   0.0293
O                     1.66311   2.61018   0.06847
H                     2.30358   3.32224   0.13453
C                     0.10972  -2.35384  -0.00253
H                    -0.44194  -3.27037   0.02049
C                     4.29019   0.56167   1.28532
H                     3.46996   0.53605   1.97196
H                     4.55348  -0.43732   1.00676
H                     5.12961   1.03538   1.74994
C                     4.49547   0.6898   -1.21782
H                     4.72031  -0.33387  -1.00227
H                     3.79712   0.73883  -2.02701
H                     5.39411   1.20253  -1.49067
H                     4.24241   2.35937   0.11015

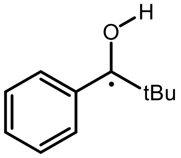
Sum of electronic and zero-point Energies=           -464.012300
Sum of electronic and thermal Energies=              -464.001135
Sum of electronic and thermal Enthalpies=            -464.000191
Sum of electronic and thermal Free Energies=         -464.049617
```



11

```
Charge =  0 Multiplicity = 1
Symbolic Z-Matrix:
C                     1.51036  -2.37982  -0.04072
C                     2.23289  -1.17941  -0.07087
C                     1.55477   0.04697  -0.06285
C                     0.15413   0.07295  -0.02467
C                    -0.56839  -1.12745   0.00549
H                     2.02812  -3.31619  -0.04684
H                     3.3023   -1.19925  -0.10003
H                    -0.36362   1.00932  -0.01854
H                    -1.63781  -1.10762   0.03464
C                     2.34876   1.3661   -0.09599
C                     3.88361   1.35457   0.0293
O                     1.66311   2.61018   0.06847
C                     0.10972  -2.35384  -0.00253
H                    -0.44194  -3.27037   0.02049
C                     4.40002   2.80073   0.14567
H                     5.46959   2.7962    0.17561
H                     4.06928   3.3667   -0.70002
H                     4.01999   3.2441    1.04228
C                     4.29019   0.56167   1.28532
H                     3.46996   0.53605   1.97196
H                     4.55348  -0.43732   1.00676
H                     5.12961   1.03538   1.74994
C                     4.49547   0.6898   -1.21782
H                     4.72031  -0.33387  -1.00227
H                     3.79712   0.73883  -2.02701
H                     5.39411   1.20253  -1.49067

Sum of electronic and zero-point Energies=           -502.751192
Sum of electronic and thermal Energies=              -502.739189
Sum of electronic and thermal Enthalpies=            -502.738245
Sum of electronic and thermal Free Energies=         -502.789261
```



11-ketyl

```
Charge =  0 Multiplicity = 2
```

```
Symbolic Z-Matrix:
C                     1.51036  -2.37982  -0.04072
C                     2.23289  -1.17941  -0.07087
C                     1.55477   0.04697  -0.06285
C                     0.15413   0.07295  -0.02467
C                    -0.56839  -1.12745   0.00549
H                     2.02812  -3.31619  -0.04684
H                     3.3023   -1.19925  -0.10003
H                    -0.36362   1.00932  -0.01854
H                    -1.63781  -1.10762   0.03464
C                     2.34876   1.3661   -0.09599
C                     3.88361   1.35457   0.0293
O                     1.66311   2.61018   0.06847
H                     2.30358   3.32224   0.13453
C                     0.10972  -2.35384  -0.00253
H                    -0.44194  -3.27037   0.02049
C                     4.40002   2.80073   0.14567
H                     5.46959   2.7962    0.17561
H                     4.06928   3.3667   -0.70002
H                     4.01999   3.2441    1.04228
C                     4.29019   0.56167   1.28532
H                     3.46996   0.53605   1.97196
H                     4.55348  -0.43732   1.00676
H                     5.12961   1.03538   1.74994
C                     4.49547   0.6898   -1.21782
H                     4.72031  -0.33387  -1.00227
H                     3.79712   0.73883  -2.02701
H                     5.39411   1.20253  -1.49067

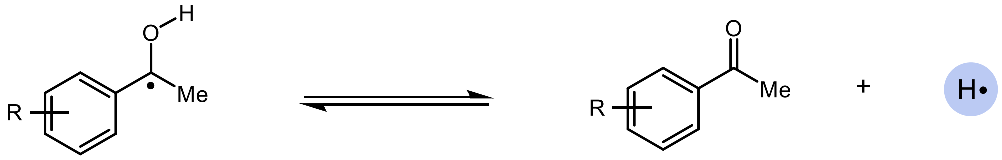
Sum of electronic and zero-point Energies=          -503.303927
Sum of electronic and thermal Energies=             -503.291543
Sum of electronic and thermal Enthalpies=           -503.290598
Sum of electronic and thermal Free Energies=        -503.342278
```

Hydrogen Atom

```
Charge =  0 Multiplicity = 2
Symbolic Z-Matrix:
H                     0.22062  -0.15394   1.12464

Sum of electronic and zero-point Energies=            -0.502177
Sum of electronic and thermal Energies=               -0.500761
Sum of electronic and thermal Enthalpies=             -0.499817
Sum of electronic and thermal Free Energies=          -0.512831
```

Scheme S1. Thermochemistry of $\mathrm{BDFE_{O-H}}$



$$\mathrm{BDFE_{O-H}} = \Delta G^{\circ}(\text{ketone}) + \Delta G^{\circ}(\text{H atom}) - \Delta G^{\circ}(\text{ketyl})$$

Table S1. Calculation of $\mathrm{BDFE_{O-H}}$

	ΔG^{o}(ketyl)	ΔG^{o}(ketone)	ΔG^{o}(H•)	BDFE (au)	BDFE (kcal/mol)
PhCOMe	-385.461103	-384.905171	-0.512831	0.043101	27.0
2,4,6-$(OMe)_3$-PhCOMe	-729.031085	-728.486297	-0.512831	0.034318	21.5
p-OMe-PhCOMe	-499.989588	-499.437269	-0.512831	0.039488	24.8
m-F-PhCOMe	-484.740631	-484.183068	-0.512831	0.047093	29.6
p-Cl-PhCOMe	-845.097809	-844.539859	-0.512831	0.045119	28.3
PhCOiPr	-464.049617	-463.493536	-0.512831	0.04325	27.1
PhCO^{t}Bu	-503.342278	-502.789261	-0.512831	0.040186	25.2

4. Independent Verification of the Method in Different Systems Reported

4.1. Wenger measured the equilibrium constant (K_A) for hydrogen bonding between pyridine and phenol in MeCN *via* NMR titration.[4] As verification of the accuracy of our method, we measured the K_A of 4-chlorophenol and pyridine in MeCN using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as the photooxidant. The solution was irradiated at 375 nm, and fluorescence was measured at 475nm. Neither the phenol nor pyridine alone quenched the luminescence of *Ir(III). Initial pyridine concentration is denoted as A_0. Initial phenol concentration is denoted as S_0.

1. For this experiment, A_0 is fixed at 0.151 M, while S_0 is varied from 0.0050 to 0.0300 M.

Table S4.1.1. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.151 M pyridine, and variable [4-chlorophenol]. See **Figure S4.1.1.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.004938	0.000748	979	979	979	979	1.109295
0.009877	0.001495	905	905	900	903.3333	1.202214
0.014815	0.002243	824	821	820	821.6667	1.321704
0.019753	0.002991	767	767	767	767	1.415906
0.024691	0.003738	714	714	710	712.6667	1.523854
0.029630	0.004486	659	662	662	661	1.642965

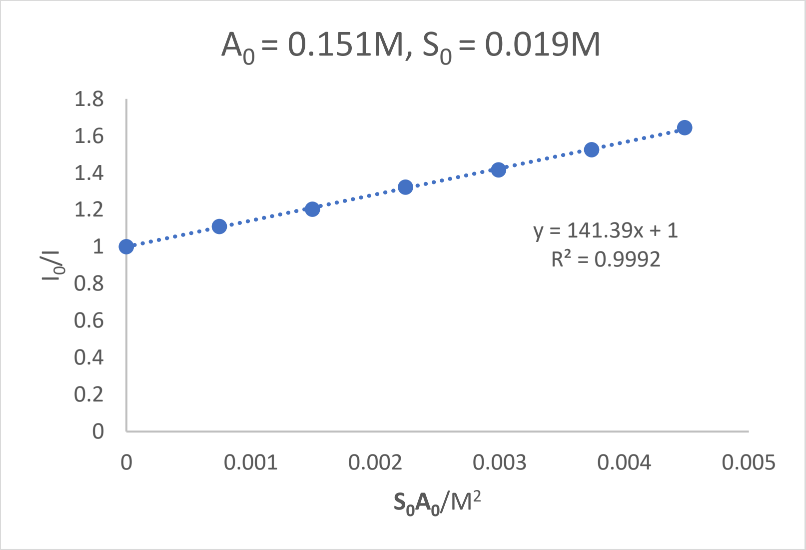


Figure S4.1.1. Stern-Volmer plot of luminescence data in **Table S4.1.1.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs\,1}\,\tau_0\,\mathrm{S_0A_0}$$

$$k_{obs\,1}\,\tau_0 = 141.4$$

2. For this experiment, A_0 fixed at 0.296 M, while S_0 is varied from 0.010 to 0.030 M.

Table S4.1.2. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.296 M pyridine, and variable [4-chlorophenol]. See **Figure S4.1.2.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.009756	0.002884	894	895	893	894	1.353468
0.014634	0.004326	789	792	790	790.3333	1.531
0.019512	0.005768	714	714	716	714.6667	1.693097
0.02439	0.00721	647	647	647	647	1.87017
0.029268	0.008652	590	588	588	588.6667	2.055493

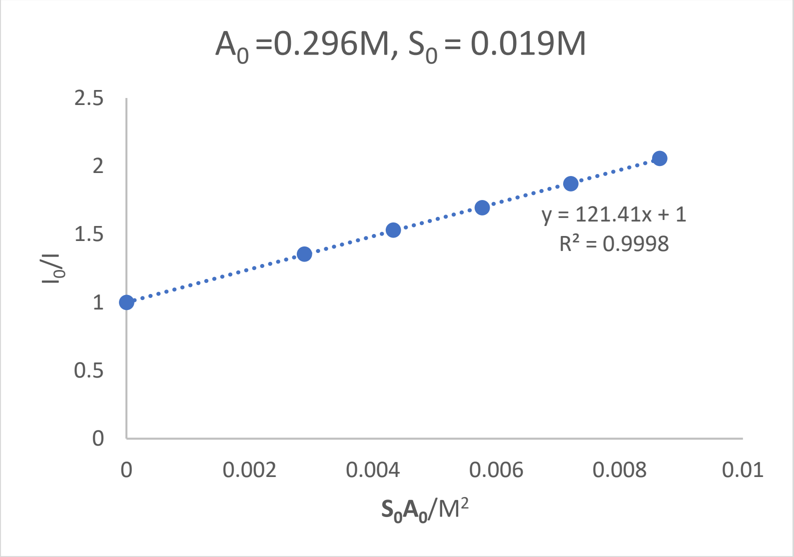


Figure S4.1.2. Stern-Volmer plot of luminescence data in **Table S4.1.2.**

I_0 was extrapolated from the five data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0\ \mathrm{S_0A_0}$$

$$k_{obs\ 2}\ \tau_0 = 121.4$$

3. For this experiment, A_0 fixed at 0.449 M, while S_0 is varied from 0.010 to 0.030 M.

Table S4.1.3. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.4487 M pyridine, and variable [4-chlorophenol]. See **Figure S4.1.3.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.009639	0.004325	990	990	988	989.3333	1.453504
0.014458	0.006487	857	843	853	851	1.689777
0.019277	0.00865	755	755	756	755.3333	1.903795
0.024096	0.010812	674	672	672	672.6667	2.13776
0.028916	0.012974	610	602	599	603.6667	2.382109

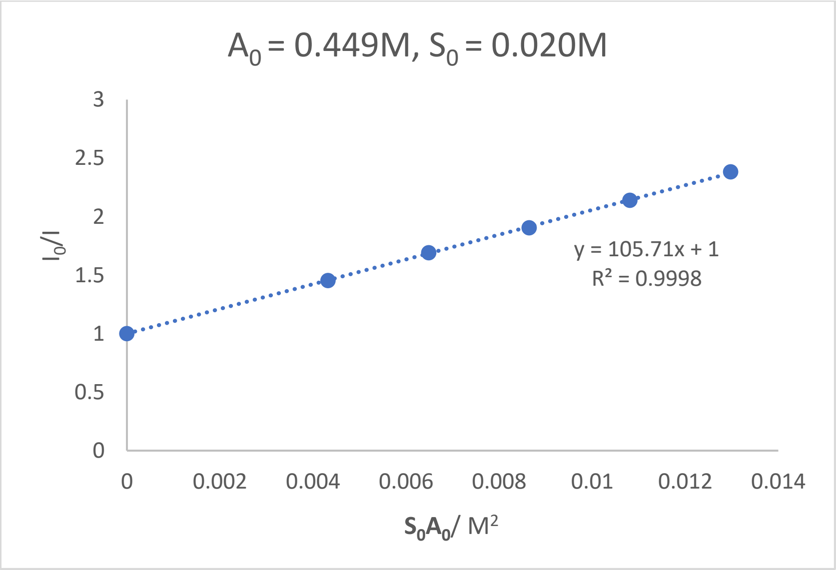


Figure S4.1.3. Stern-Volmer plot of luminescence data in **Table S4.1.3.**

I_0 was extrapolated from the five data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, \mathrm{S_0A_0}$$

$$k_{obs\,3}\,\tau_0 = 105.7$$

4. For this experiment, A_0 fixed at 0.591 M, while S_0 is varied from 0.010 to 0.030 M.

Table S4.1.4. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.591 M pyridine, and variable [4-chlorophenol]. See **Figure S4.1.4.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.009524	0.00563	950	950	950	950	1.527368
0.014286	0.008445	803	805	803	803.6667	1.805475
0.019048	0.01126	704	704	702	703.3333	2.063033
0.02381	0.014075	627	622	625	624.6667	2.322839
0.028571	0.016891	561	560	560	560.3333	2.58953

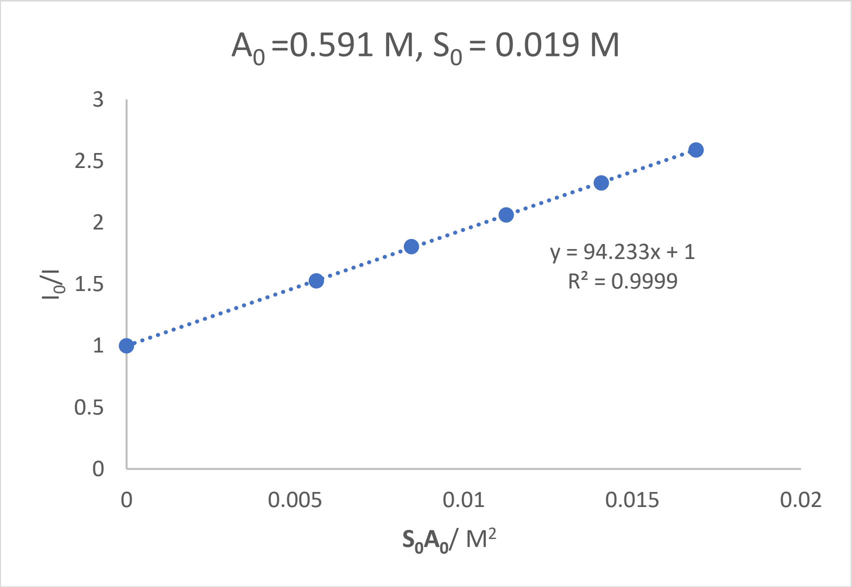


Figure S4.1.4. Stern-Volmer plot of luminescence data in **Table S4.1.4.**

I_0 was extrapolated from the five data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0\, \mathrm{S_0A_0}$$

$$k_{obs\,4}\,\tau_0 = 94.2$$

$$S_0 + A_0 = \frac{S_0A_0\, k_{obs}\,\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table S4.1.5. Luminescence quenching data of **Figure 4.1.1-4.1.4**

	A_0 (M)	**S_0 (M)**	**S_0A_0 (M^2)**	**S_0+A_0 (M)**	**$k_{obs}\tau_0$**
1	0.151	0.019	0.00288	0.170	141
2	0.296	0.019	0.00562	0.315	121
3	0.449	0.019	0.00853	0.468	106
4	0.591	0.019	0.0112	0.610	94.2

Table S4.1.6. Six sets of values of K_A obtained, upon substituting the Information of any two experiments shown in **Table S4.1.5** into equation 8

into equation 8	**K_A/M^{-1}**
1&2	1.45
1&3	1.43
1&4	1.43
2&3	1.41
2&4	1.42
3&4	1.44
average	1.4±0.1

This value of K_A is within the error reported by Wenger (1.5±0.1 M^{-1}).[4]

4.2. Wenger measured the equilibrium constant (K_A) for hydrogen bonding between pyridine and phenol in MeCN *via* NMR titration.[4] As verification of the accuracy of our method, we measured the K_A of 4-methylphenol and pyridine in MeCN using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as the photooxidant. The solution was irradiated at 375 nm, and fluorescence was measured at 475nm. Neither the phenol nor pyridine alone quenched the luminescence of *Ir(III).

1. For this experiment, A_0 fixed at 0.303 M, while S_0 is varied from 0.030 to 0.160 M.

Table S4.2.1. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.303 M pyridine, and variable [4-chlorophenol]. See **Figure S4.2.1.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.026488	0.007999	158	159	158	158.3333	2.576842
0.052976	0.015999	98	98	98	98	4.163265
0.079463	0.023998	69	69	69	69	5.913043
0.105951	0.031997	53.8	53.8	53.9	53.83333	7.578947
0.132439	0.039997	44.3	44.2	44.2	44.23333	9.223813
0.158927	0.047996	37.6	37.5	37.5	37.53333	10.87034

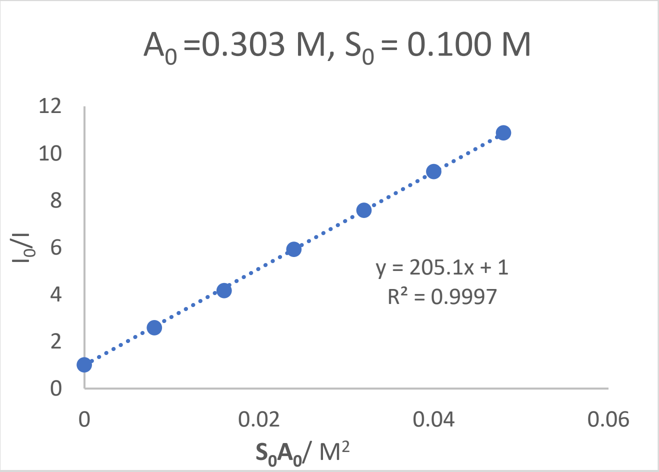


Figure S4.2.1. Stern-Volmer plot of luminescence data in **Table S4.2.1.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, S_0A_0$$

$$k_{obs\,1}\,\tau_0 = 205.1$$

2. For this experiment, A_0 fixed at 0.449 M, while S_0 is varied from 0.030 to 0.160 M.

Table S4.2.2. Luminescence quenching data with $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, 0.449 M pyridine, and variable [4-chlorophenol]. See **Figure S4.2.2.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.026169	0.011742	130	129	129	129.3333	3.023196
0.052337	0.023485	75	75	75.1	75.03333	5.211017
0.078506	0.035227	51.9	51.8	52.1	51.93333	7.528883
0.104675	0.04697	40.3	40.3	40.4	40.33333	9.694215
0.130843	0.058712	32.9	32.5	33	32.8	11.92073
0.157012	0.070454	27.6	27.6	27.7	27.63333	14.14958

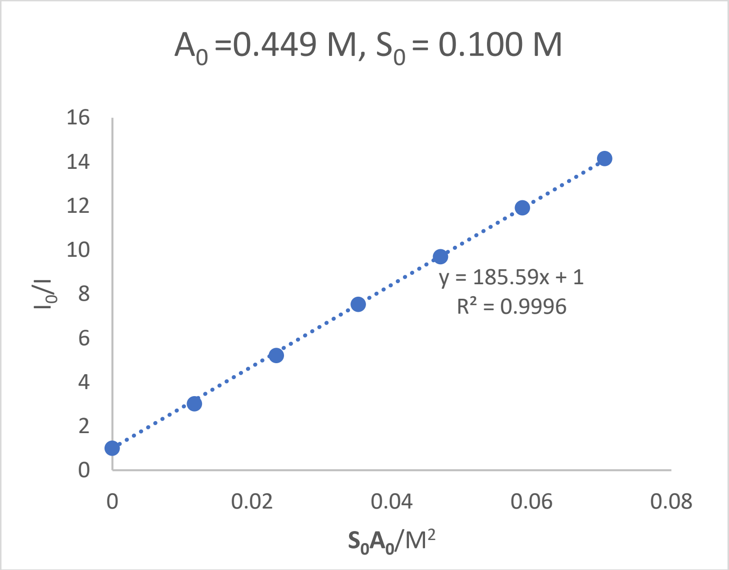


Figure S4.2.2. Stern-Volmer plot of luminescence data in **Table S4.2.2.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, S_0A_0$$

$$k_{obs\,2}\,\tau_0 = 185.6$$

3. For this experiment, A_0 fixed at 0.591 M, while S_0 is varied from 0.030 to 0.160 M.

Table S4.2.3. Luminescence quenching data with $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, 0.591 M pyridine, and variable [4-chlorophenol]. See **Figure S4.2.3.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0				0	1
0.025857	0.015286	111	111	111	111	3.414414
0.051714	0.030572	62.4	62.4	62.4	62.4	6.073718
0.077571	0.045858	43	43.6	43	43.2	8.773148
0.103429	0.061144	33.4	33.4	33.4	33.4	11.34731
0.129286	0.07643	27	27	26.9	26.97	14.05439
0.155143	0.091716	22.7	22.7	22.7	22.7	16.69604

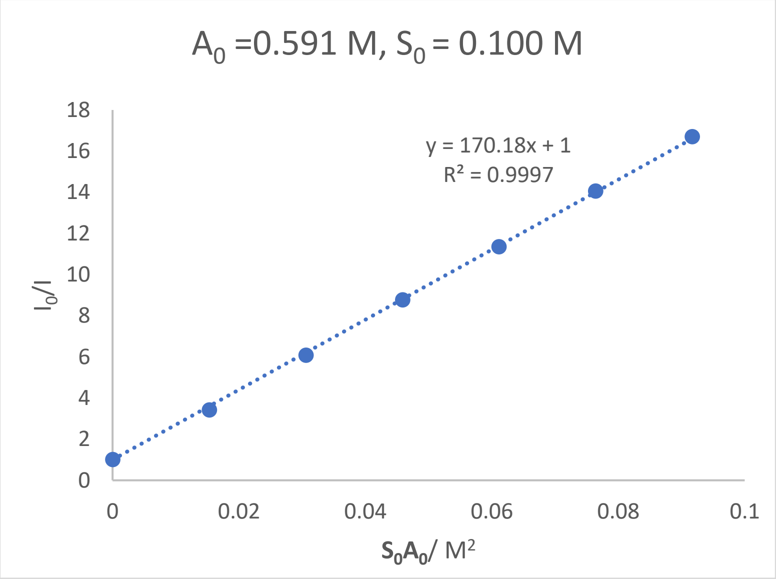


Figure S4.2.3. Stern-Volmer plot of luminescence data in **Table S4.2.3.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, S_0A_0$$

$$k_{obs\,3}\,\tau_0 = 170.2$$

4. For this experiment, A_0 fixed at 0.730 M, while S_0 is varied from 0.030 to 0.160 M.

Table S4.2.4. Luminescence quenching data with $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, 0.730 M pyridine, and variable [4-chlorophenol]. See **Figure S4.2.4.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.025553	0.018661	101	100	100	100.3333	3.747508
0.051106	0.037321	55	55	55	55	6.836364
0.076659	0.055982	38.4	38.7	38.2	38.43333	9.783174
0.102212	0.074642	29.5	29.6	29.3	29.46667	12.76018
0.127765	0.093303	24.1	23.9	24	24	15.66667
0.153318	0.111963	20.3	20.3	20.2	20.26667	18.55263

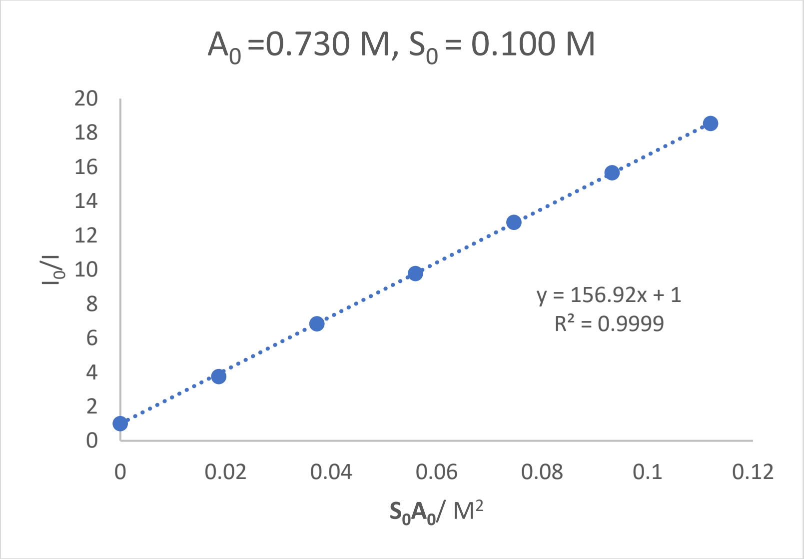


Figure S4.2.4. Stern-Volmer plot of luminescence data in **Table S4.2.4.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, S_0A_0$$

$$k_{obs\,4}\,\tau_0 = 156.9$$

$$S_0 + A_0 = \frac{S_0 A\, k_{obs}\, \tau_0}{k_{PCET} \tau_0} + \frac{k_{PCET} \tau_0}{k_{obs} \tau_0} - \frac{1}{K_A} \quad (8)$$

Table S4.2.5. Luminescence quenching data of **Figure 4.2.1-4.2.4**

	A_0 (M)	S_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.303	0.104	0.0315	0.407	205
2	0.449	0.104	0.0467	0.553	186
3	0.591	0.104	0.0615	0.695	170
4	0.730	0.104	0.0760	0.834	157

Table S4.2.6. Six sets of values of K_A obtained, upon substituting the Information of any two experiments shown in **Table S4.2.5** into equation 8

into equation 8	K_A/M^{-1}
1&2	1.09
1&3	1.06
1&4	1.07
2&3	1.03
2&4	1.06
3&4	1.09
average	1.1±0.1

This value of K_A is within the error reported by Wenger (1.1±0.1 M^{-1}). [4]

4.3. Linschitz measured the equilibrium constant (K_A) for hydrogen bonding between pyridine and phenol in PhCN *via* spectroscopic methods and saturation kinetics.[5] As verification of the accuracy of our method, we measured the K_A of 4-methylphenol and pyridine in PhCN using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as the photooxidant. The solution was irradiated at 383 nm, and fluorescence was measured at 475nm. Neither the phenol nor pyridine alone quenched the luminescence of *Ir(III).

1. For this experiment, A_0 fixed at 0.153 M, while S_0 is varied from 0.0076 to 0.0457 M.

Table S4.3.1. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.153 M pyridine, and variable [4-chlorophenol]. See **Figure S4.3.1.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00763	0.001169	193	193	193	193	1.606218
0.015259	0.002339	146.5	146	146	146.1667	2.120867
0.022889	0.003508	115	115	115	115	2.695652
0.030519	0.004677	95.7	95.8	95.8	95.76667	3.237034
0.038148	0.005847	81	81.2	81.2	81.13333	3.820871
0.045778	0.007016	70.8	70.8	71	70.86667	4.374412

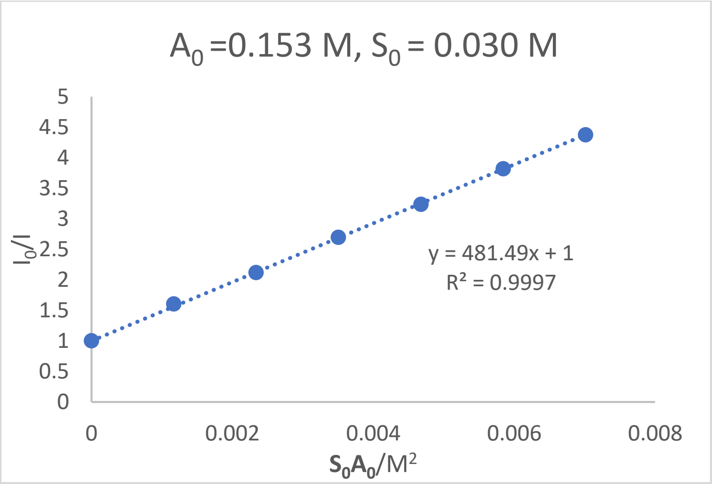


Figure S4.3.1. Stern-Volmer plot of luminescence data in **Table S4.3.1.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, S_0A_0$$

$$k_{obs\,1}\,\tau_0 = 481.5$$

2. For this experiment, A_0 fixed at 0.184 M, while S_0 is varied from 0.0076 to 0.0457 M.

Table S4.3.2. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.184 M pyridine, and variable [4-chlorophenol]. See **Figure S4.3.2.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.007611	0.001396	186	186	186	186	1.66129
0.015222	0.002793	133	133	133	133	2.323308
0.022833	0.004189	105	105	104	104.6667	2.952229
0.030443	0.005585	87	87	86.3	86.76667	3.561275
0.038054	0.006982	74.3	74.2	74.4	74.3	4.158816
0.045665	0.008378	63.6	63.7	64.2	63.83333	4.840731

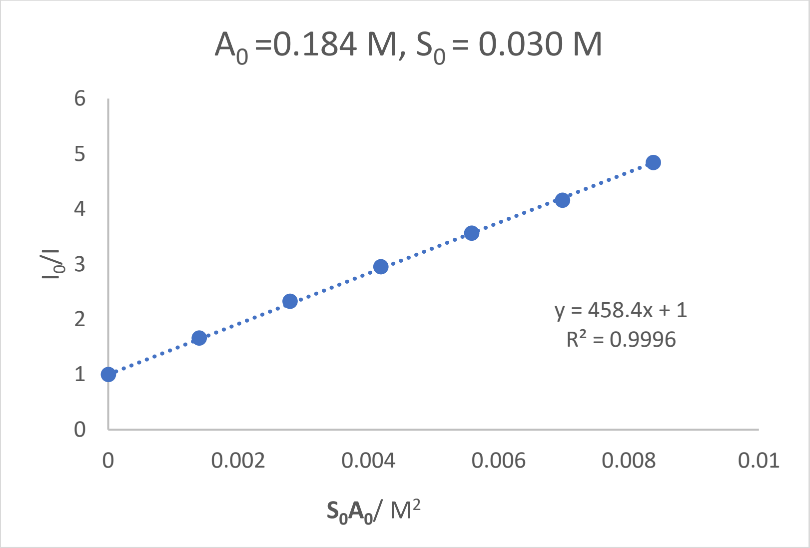


Figure S4.3.2. Stern-Volmer plot of luminescence data in **Table S4.3.2.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, S_0A_0$$

$$k_{obs\,2}\,\tau_0 = 458.4$$

3. For this experiment, A_0 fixed at 0.214 M, while S_0 is varied from 0.0076 to 0.0457 M.

Table S4.3.3. Luminescence quenching data with $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$, 0.214 M pyridine, and variable [4-chlorophenol]. See **Figure S4.3.3.**

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.007592	0.001621	174	174	174	174	1.764368
0.015184	0.003242	127	126	126	126.3333	2.430079
0.022776	0.004863	97.5	97.5	97.4	97.46667	3.149795
0.030369	0.006484	80.4	80.5	80.4	80.43333	3.816826
0.037961	0.008105	68	68	68	68	4.514706
0.045553	0.009726	58.6	58.3	58.4	58.43333	5.253851

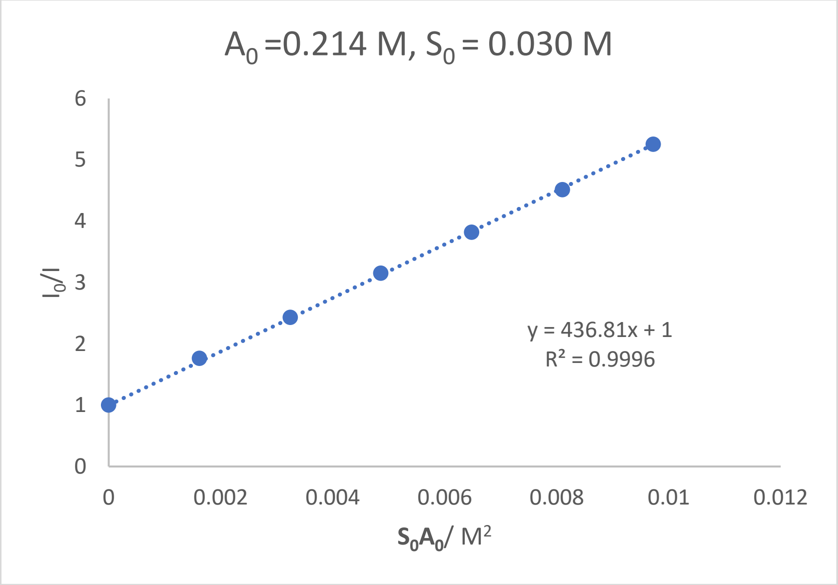


Figure S4.3.3. Stern-Volmer plot of luminescence data in **Table S4.3.3.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, S_0A_0$$

$$k_{obs\,3}\,\tau_0 = 436.8$$

4. For this experiment, A_0 fixed at 0.273 M, while S_0 is varied from 0.0076 to 0.0457 M.

Table S4.3.4. Luminescence quenching data with [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$, 0.2732 M pyridine, and variable [4-chlorophenol]. See **Figure S4.3.4.**

S_0/M	**S_0A_0/M^2**	**I/au 1**	**I/au 2**	**I/au 3**	**I/au avg.**	**I_0/I**
0	0					1
0.007555	0.002064	162	163	163	162.6667	1.865779
0.01511	0.004128	112	112	111	111.6667	2.71791
0.022665	0.006192	86.5	86.5	86.4	86.46667	3.510023
0.03022	0.008256	71.1	71.1	71.3	71.16667	4.264637
0.037775	0.010319	59.4	59.4	59.3	59.36667	5.112296
0.04533	0.012383	51.2	51.3	51.3	51.26667	5.920026

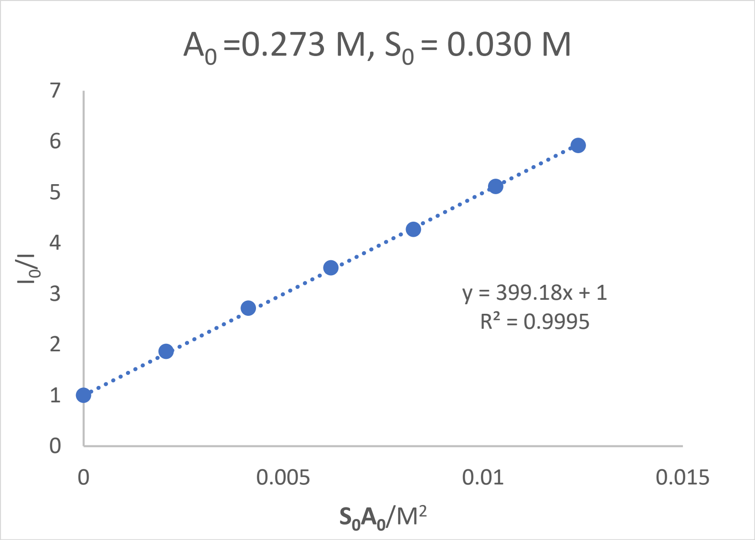


Figure S4.3.4. Stern-Volmer plot of luminescence data in **Table S4.3.4.**

I_0 was extrapolated from the six data points.

The linear Stern–Volmer quenching equation is:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0\, S_0A_0$$

$$k_{obs\,4}\tau_0 = 399.2$$

$$S_0 + A_0 = \frac{S_0 A_0\ k_{obs}\ \tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

	A_0 (M)	**S_0 (M)**	**S_0A_0 (M^2)**	**S_0+A_0 (M)**	**$k_{obs}\tau_0$**
1	0.153	0.030	0.00460	0.183	482
2	0.184	0.030	0.00551	0.214	458
3	0.214	0.030	0.00641	0.244	437
4	0.273	0.030	0.00820	0.303	399

into equation 8	**K_A/M^{-1}**
1&2	2.67
1&3	2.49
1&4	2.58
2&3	2.62
2&4	2.62
3&4	2.62
average	2.6±0.1

This value of K_A is within the error reported by Linschitz (2.8±0.2 M^{-1} *via* spectroscopic measurement; 2.6±0.3 M^{-1} *via* saturation kinetics).[5]

5. Generation of Data Points in the Main Rate-Driving Force Correlation

pK_a Values (in MeCN) of Acids Employed in this Study [6-9]

$(PhO)_2P(O)OH$: 13

p-TsOH: 8.6

NEt_3HBF_4: 18.8

NMe_3HBF_4: 17.6

Effective BDFE Equation [10-12] 'BDFE' (kcal/mol) = $1.37pK_a + 23.06E^0 + 54.9$

Table S5. Kinetic and H-bonding equilibrium data for ketone MS-PCET reactions

Entry	Ketone	acid	reductant	$BDFE_{O-H}$ (kcal/mol)	$BDFE_{O-H}$– 'BDFE' (kcal/mol)	K_A (M^{-1})	$\Delta G°_{H\text{-}bond}$ (kcal/mol)	$\Delta G°'_{PCET}$ (kcal/mol)	$\ln[k'_{PCET}(M^{-1}s^{-1})]$ (effective)[a]	$\ln[k'_{PCET}(M^{-1}s^{-1})]$ (actual)[b]
1	**1**	$(PhO)_2P(O)OH$	**6**	27.1	–3.1	6.3	–1.1	–2.0	19.92	19.95
2	**2**	$(PhO)_2P(O)OH$	**6**	21.5	2.4	92	–2.7	5.1	17.97	17.97
3	**3**	$(PhO)_2P(O)OH$	**6**	24.8	–0.8	17	–1.5	0.7	19.35	19.35
4	**4**	$(PhO)_2P(O)OH$	**6**	29.6	–5.6	2.1	–0.4	–5.2	21.16	21.27
5	**5**	$(PhO)_2P(O)OH$	**6**	28.3	–4.4	6.2	–1.1	–3.3	20.52	20.58
6	**1**	$(PhO)_2P(O)OH$	**9**	27.1	–4.9	6.3	–1.1	–3.8	20.58	20.63
7	**2**	$(PhO)_2P(O)OH$	**8**	21.5	–1.4	92	–2.7	1.3	19.19	19.19
8	**3**	$(PhO)_2P(O)OH$	**8**	24.8	–4.6	17	–1.5	–3.1	20.47	20.47
9	**1**	$(PhO)_2P(O)OH$	**7**	27.1	1.7	6.3	–1.1	2.9	18.69	18.69
10	**2**	$(PhO)_2P(O)OH$	**7**	21.5	7.2	92	–2.7	10.2	16.86	16.86
11	**3**	$(PhO)_2P(O)OH$	**7**	24.8	4.0	17	–1.5	5.5	17.94	17.94
12	**4**	$(PhO)_2P(O)OH$	**7**	29.6	–0.8	2.1	–0.4	–0.3	19.8	19.79
13	**5**	$(PhO)_2P(O)OH$	**7**	28.3	0.5	6.2	–1.1	1.6	19.05	19.05
14	**3**	NEt_3HBF_4	**8**	24.8	3.6	17	–1.7	5.3	18.47	18.47
15	**3**	NMe_3HBF_4	**8**	24.8	1.8	16	–1.6	3.4	18.69	18.69
16	**3**	*p*-TsOH	**7**	24.8	–2.0	21	–1.8	–0.2	19.7	19.7
17	**5**	*p*-TsOH	**7**	28.3	–5.4	15	–1.6	–3.7	20.66	20.72
18	**5**	*p*-TsOH	**6**	28.3	–10.3	15	–1.6	–8.5	21.8	22.15
19	**1**	*p*-TsOH	**7**	27.1	–4.2	15	–1.6	–2.7	20.21	20.24
20	**3**	*p*-TsOH	**6**	24.8	–6.9	21	–1.8	–5.1	20.93	21.01

[a] $\ln[k_{PCET}(M^{-1}s^{-1})]$ (effective) was obtained by the experimental method described above. The data points generation described below are in the column "$\ln[k_{PCET}(M^{-1}s^{-1})]$ (effective)".

[b] $\ln[k'_{PCET}(M^{-1}s^{-1})]$ (actual) takes the diffusion rate limit ($k_{diff} = 10^{10.2}\ M^{-1}s^{-1}$ in MeCN) into consideration, in the relationship $k_{PCET}(effective) = \frac{k_{PCET} \times k_{diff}}{k_{PCET} + k_{diff}}$.

5.1. Entry 1.

Non-PCET quenching of reductant by acetophenone alone (without acid) is given by the following equation:

$$I_0/I = 1 + k'_{SV}\, S_0$$

The solution was irradiated at 375nm, and fluorescence was measured at 518nm.

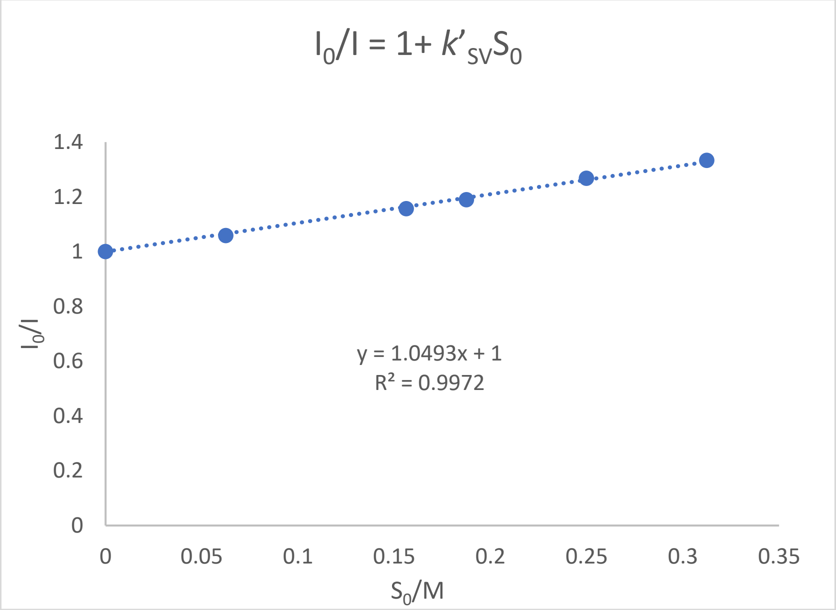


Figure S5.1. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$$k'_{SV} = 1.05$$

Time-resolved luminescence suggests that the non-PCET quenching by acetophenone is static, while $(PhO)_2P(O)OH$ does not quench the luminescence intensity. Therefore, the following equation is used:

$$\frac{I_0/I}{1 + k_{SV}{}' S_0} = 1 + k_{obs}\tau_0 S_0 A_0$$

$\frac{I_0/I}{1+k_{SV}{}'S_0}$ was plotted against S_0A_0 with vertical intercept of 1 in all four experiments. Each slope provides the corresponding $k_{obs}\tau_0$. Given that acetophenone does not dynamically quench the excited state of the reductant, in each of the four luminescence quenching experiments the concentration of ketone was held constant, while the concentration of acid was varied. Determination of k_{SV}' was not needed, as $\frac{I_0/I}{1+k_{SV}'S_0}$ could be extrapolated, and the slope gives the corresponding $k_{obs}\tau_0$.

Table. S5.1.1. S_0 fixed at 0.040 M, A_0 varied from 0.0020 to 0.0060 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}'\ S_0)$
0	0					1
0.002	0.00008	729	730	730	729.6667	1.330745
0.003	0.00012	649	650	647	648.6667	1.496917
0.004	0.00016	587	586	587	586.6667	1.655114
0.005	0.0002	531	529	530	530	1.832075
0.006	0.00024	487	487	486	486.6667	1.995205

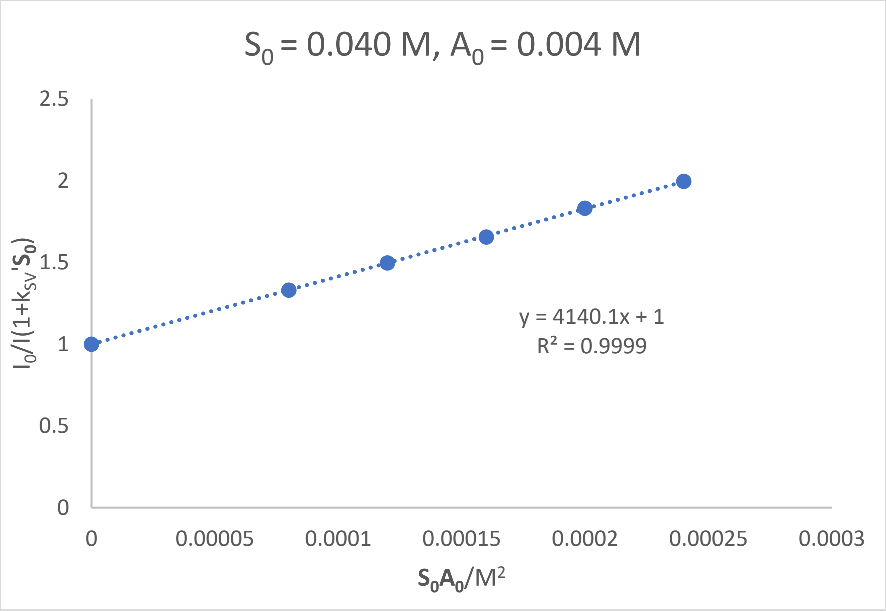


Figure S5.1.1. Stern-Volmer plot of luminescence data in **Table S5.1.1**

$k_{obs}\tau_0$ = 4140

Table S5.1.2. S_0 **fixed at 0.061 M,** A_0 **varied from 0.002 to 0.006 M**

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}'\,S_0)$
0	0					1
0.002	0.0001228	568	566	566	566.6667	1.473529
0.003	0.0001842	487	490	488	488.3333	1.709898
0.004	0.0002456	438	438	438	438	1.906393
0.005	0.000307	388	388	388	388	2.152062
0.006	0.0003684	348	348	350	348.6667	2.394837

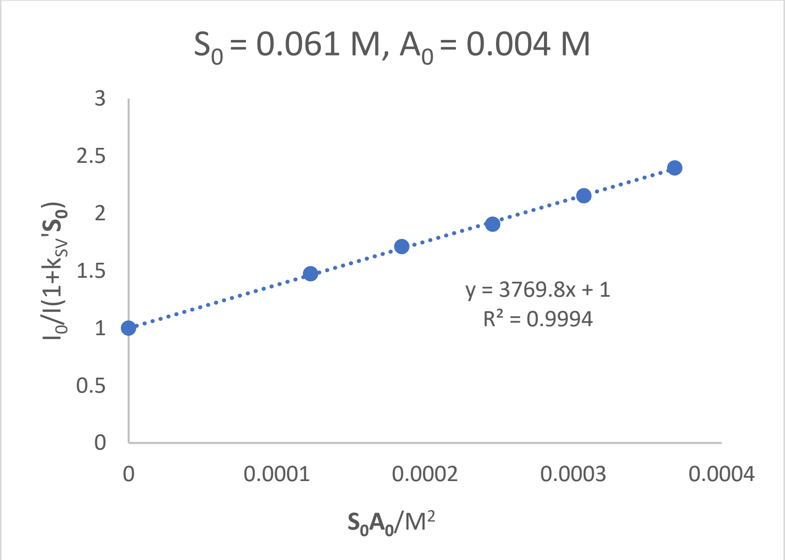


Figure S5.1.2. Stern-Volmer plot of luminescence data in **Table S5.1.2**

$$k_{obs}\tau_0 = 3770$$

Table S5.1.3. S_0 **fixed at 0.083 M,** A_0 **varied from 0.002 to 0.006 M**

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}'\,S_0)$
0	0					1
0.002	0.00016572	404	404	405	404.3333	1.57296
0.003	0.00024858	340	340	340	340	1.870588
0.004	0.00033144	294	297	297	296	2.148649
0.005	0.0004143	262	262	263	262.3333	2.424396
0.006	0.00049716	235	236	236	235.6667	2.698727

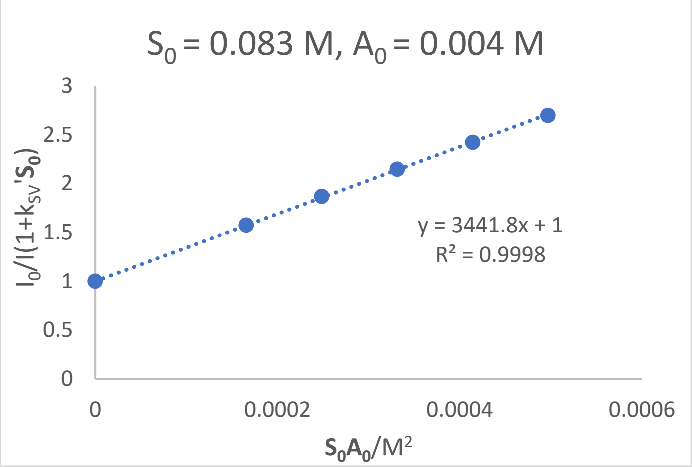


Figure S5.1.3. Stern-Volmer plot of luminescence data in **Table S5.1.3**

$k_{obs}\tau_0$ = 3442

Table S5.1.4. S_0 fixed at 0.104 M, A_0 varied from 0.002 to 0.006 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}'\ S_0)$
0	0					1
0.002	0.0002074	344	347	346	345.6667	1.672131
0.003	0.0003111	287	287	288	287.3333	2.011601
0.004	0.0004148	249	248	251	249.3333	2.318182
0.005	0.0005185	219	218	220	219	2.639269
0.006	0.0006222	196	196	195	195.6667	2.954003

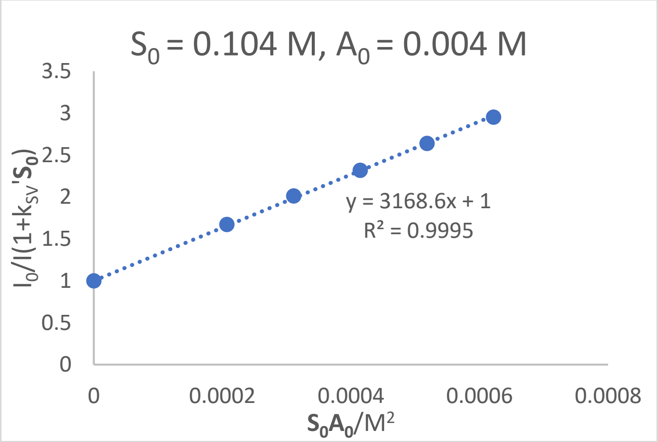


Figure S5.1.4. Stern-Volmer plot of luminescence data in **Table S5.1.4**

$k_{obs}\tau_0$ = 3169

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\, \tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.1.5. Solutions to Key Equation 8 and Entry 1 in Table S5.

	S_0 (M)	A_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.040	0.0040	0.00016	0.044	4140
2	0.061	0.0040	0.000244	0.065	3770
3	0.083	0.0040	0.000332	0.087	3440
4	0.104	0.0040	0.000416	0.108	3170

	K_A/M^{-1}	$k_{PCET}\tau_0$/M^{-1}
1&2	5.8	888
1&3	6.1	859
1&4	6.2	848
2&3	6.4	833
2&4	6.4	829
3&4	6.5	826
average	6.2	847

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = $-RT\ln K_A$ = -1.09

$\ln[k_{PCET}(M^{-1}s^{-1})] = \ln[k_{PCET}\tau_0/\tau_0]$ = 19.91

τ_0 = 1.9 μs

error in $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.05

error in $\ln[k_{PCET}(M^{-1}s^{-1})]$ = 0.05

5.2. Entry 2.

The solution was irradiated at 375nm, and fluorescence was measured at 518nm. Neither the ketone nor the acid quenches reductant **6** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 S_0 A_0$$

In all the four experiments, $\frac{I_0}{I}$ is plotted against S_0A_0 , each slope provides the corresponding $k_{obs}\tau_0$.

Table S5.2.1. S_0 fixed at 0.010 M, A_0 varied from 0.0075 to 0.0125 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0075	0.000075	691	689	691	690.3333	1.344278
0.00875	0.0000875	662	665	662	663	1.399698
0.01	0.0001	639	639	643	640.3333	1.449245
0.01125	0.0001125	618	618	620	618.6667	1.5
0.0125	0.000125	589	591	594	591.3333	1.569335

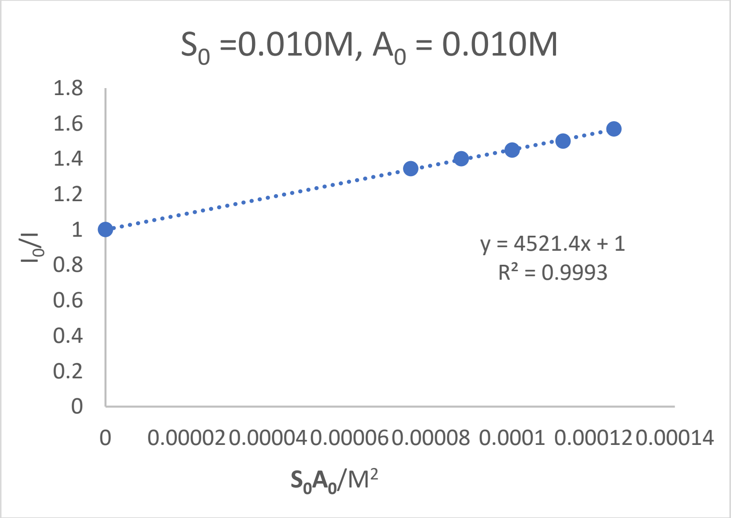


Figure S5.2.1. Stern-Volmer plot of luminescence data in **Table S5.2.1**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 4521

Table S5.2.2. S_0 fixed at 0.040 M, A_0 varied from 0.0018 to 0.0037 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001875	0.000075	745	745	743	744.3333	1.179579
0.0025	0.0001	708	710	710	709.3333	1.237782
0.003125	0.000125	683	683	686	684	1.283626
0.00375	0.00015	652	648	656	652	1.346626

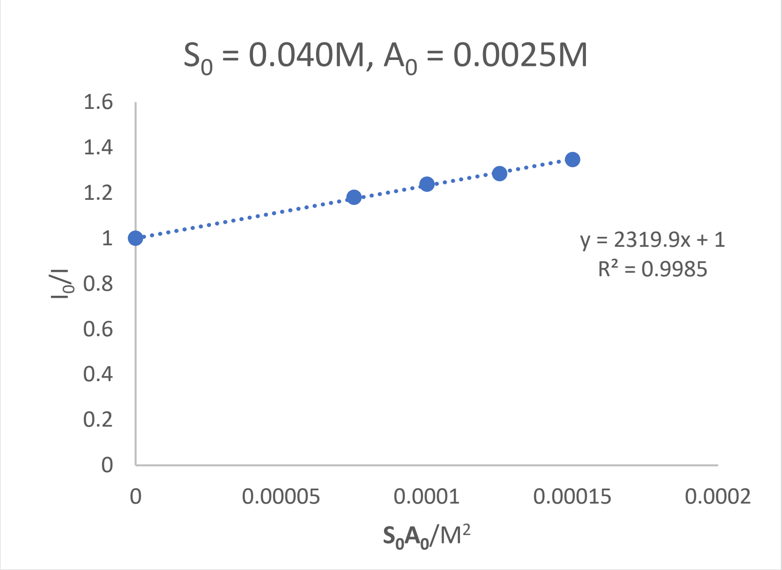


Figure S5.2.2. Stern-Volmer plot of luminescence data in **Table S5.2.2**

I_0 was extrapolated from the four data points.

$k_{obs}\tau_0$ = 2320

Table S5.2.3. S_0 fixed at 0.0625 M, A_0 varied from 0.0004 to 0.0024 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0004	0.000025	597	599	598	598	1.041806
0.0008	0.00005	576	577	577	576.6667	1.080347
0.0012	0.000075	560	558	558	558.6667	1.115155
0.0016	0.0001	537	536	535	536	1.162313
0.0024	0.00015	499	500	504	501	1.243513

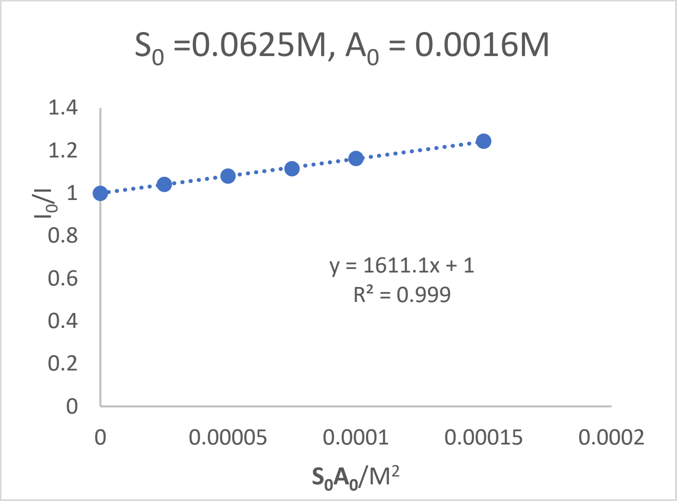


Figure S5.2.3. Stern-Volmer plot of luminescence data in **Table S5.2.3**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 1611

Table S5.2.4. S_0 fixed at 0.156 M, A_0 varied from 0.0004 to 0.0024 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0004	0.0000625	763	764	764	763.6667	1.04234
0.0008	0.000125	728	731	730	729.6667	1.090909
0.0012	0.0001875	705	704	705	704.6667	1.129612
0.0016	0.00025	671	676	678	675	1.179259
0.002	0.0003125	649	650	651	650	1.224615
0.0024	0.000375	628	628	629	628.3333	1.266844

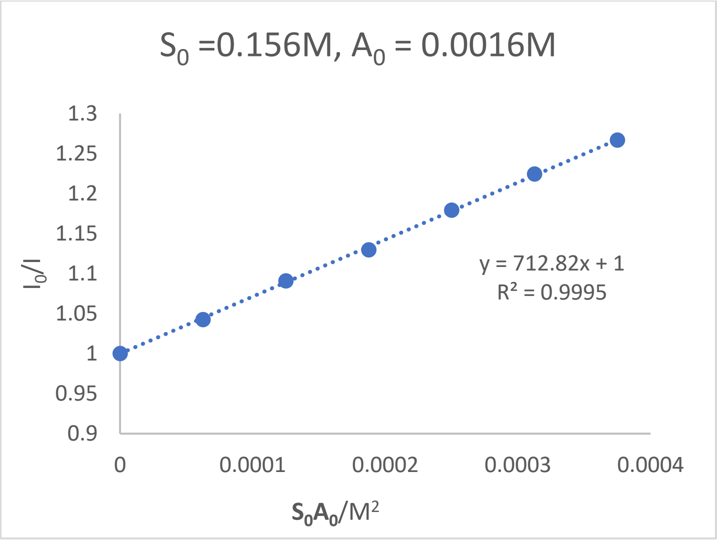


Figure S5.2.4. Stern-Volmer plot of luminescence data in **Table S5.2.4**

I_0 was extrapolated from the six data points.

$k_{obs}\tau_0$ = 713

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\,\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.2.5. Solutions to Key Equation 8 and Entry 2 in Table S5.

entry	S_0 (M)	A_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.01	0.01	0.0001	0.02	5690
2	0.025	0.004	0.0001	0.029	3820
3	0.0625	0.0016	0.0001	0.0641	1780
4	0.15625	0.00064	0.0001	0.15689	763

	K_A/M^{-1}	$k_{PCET}\tau_0$/M^{-1}
1&2	101	118
1&3	102	116
1&4	94	122
2&3	92	119
2&4	89	119
3&4	88	120
average	94	119

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = $-RT\ln K_A$= -2.69

$\ln[k_{PCET}(M^{-1}s^{-1})] = \ln[k_{PCET}\tau_0/\tau_0]$= 17.95

τ_0 = 1.9us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.05

error of $\ln[k_{PCET}(M^{-1}s^{-1})]$ = 0.02

5.3. Entry 3.

Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$$I_0/I = 1 + k'_{SV}\,\mathbf{S_0}$$

The solution was irradiated at 375nm, and fluorescence was measured at 518nm.

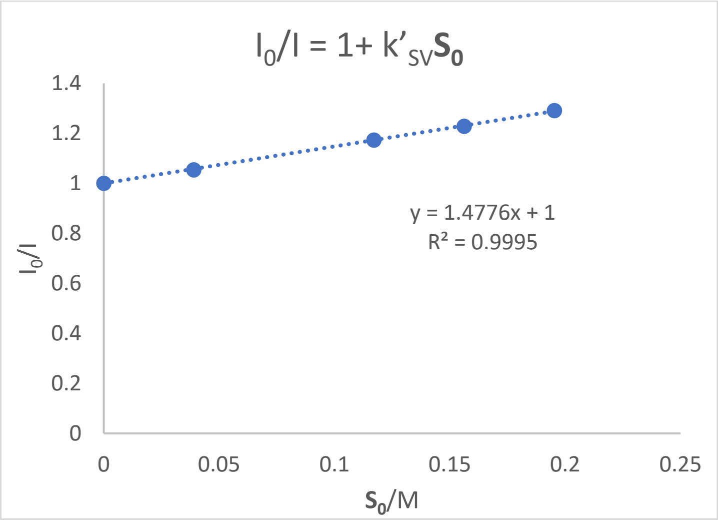


Figure S5.3. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$$k'_{SV} = 1.48$$

Time-resolved luminescence suggests that the non-PCET quenching by ketone is static, while $(PhO)_2P(O)OH$ does not quench the luminescence intensity. Therefore, the following equation is used:

$$\frac{I_0/I}{1 + k_{SV}{'}S_0} = 1 + k_{obs}\tau_0 \mathrm{S_0 A_0}$$

$\frac{I_0/I}{1+k_{SV}{'}S_0}$ was plotted against $\mathrm{S_0A_0}$ with vertical intercept of 1 in all four experiments. Each slope provides the corresponding $k_{\text{obs SV}}$. Given that acetophenone does not dynamically quench the excited state of the reductant, in each of the four luminescence quenching experiments the concentration of ketone was held constant, while the concentration of acid was varied. Determination of $k_{SV}{'}$ was not needed, as $\frac{I_0}{1+k_{SV}{'}S_0}$ could be extrapolated, and the slope gives the corresponding $k_{obs}\tau_0$.

Table S5.3.1. A_0 fixed at 0.0100 M, S_0 varied from 0.0075 to 0.0125 M

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I	$I_0/I(1+k_{SV}'\ S_0)$
0	0	893	888	895	892	1	1
0.0075	0.000075	611	615	615	613.6667	1.453558	1.437622
0.00875	8.75E-05	586	586	586	586	1.522184	1.50275
0.01125	0.000113	532	531	531	531.3333	1.678795	1.651338
0.0125	0.000125	519	510	510	513	1.738791	1.70725

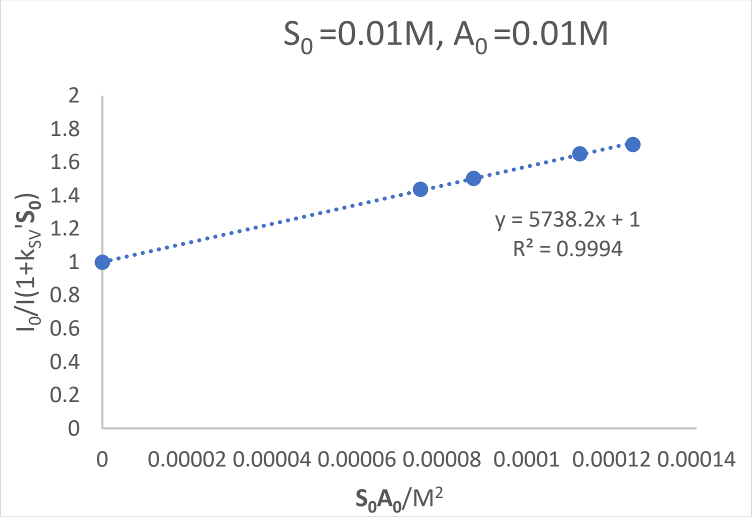


Figure S5.3.1. Stern-Volmer plot of luminescence data in **Table S5.3.1**

$k_{obs}\tau_0$ = 5738

Table S5.3.2. S_0 **fixed at 0.025 M,** A_0 **varied from 0.0020 to 0.0070 M**

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}'\ S_0)$
0	0					1
0.002	0.00005	617	618	619	618	1.273463
0.003	0.000075	562	564	562	562.6667	1.398697
0.004	0.0001	516	511	514	513.6667	1.532122
0.005	0.000125	476	474	474	474.6667	1.658006
0.006	0.00015	443	443	443	443	1.776524
0.007	0.000175	413	411	411	411.6667	1.911741

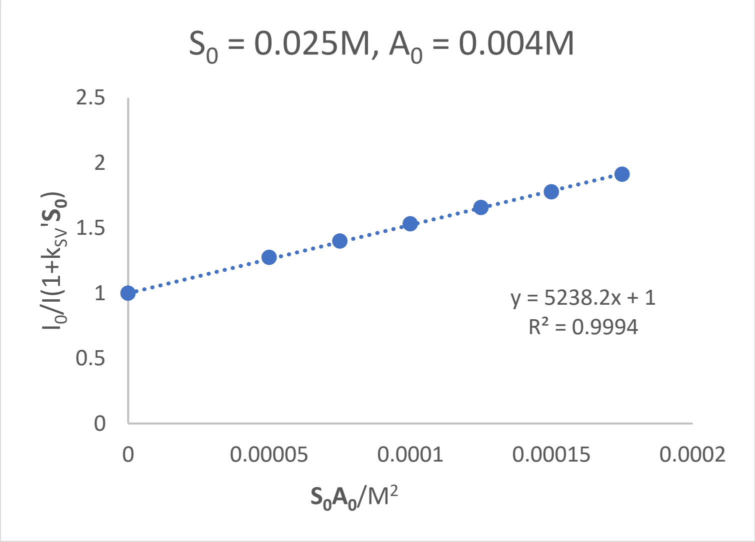


Figure S5.3.2. Stern-Volmer plot of luminescence data in **Table S5.3.2**

$\frac{I_0}{1+k_{SV}'S_0}$ was extrapolated from the six data points.

$k_{obs}\tau_0$ = 5238

Table S5.3.3. A_0 fixed at 0.0016 M, S_0 varied from 0.047 to 0.078 M

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I	$I_0/I(1+k_{SV}'\ S_0)$
0	0	892	893	891	892	1	1
0.046875	0.000075	647	648	648	647.6667	1.377252	1.288016
0.054688	8.75E-05	616	616	616	616	1.448052	1.339762
0.0625	0.0001	594	589	585	589.3333	1.513575	1.385582
0.070313	0.000113	562	561	562	561.6667	1.588131	1.438626
0.078125	0.000125	539	541	537	539	1.654917	1.483606

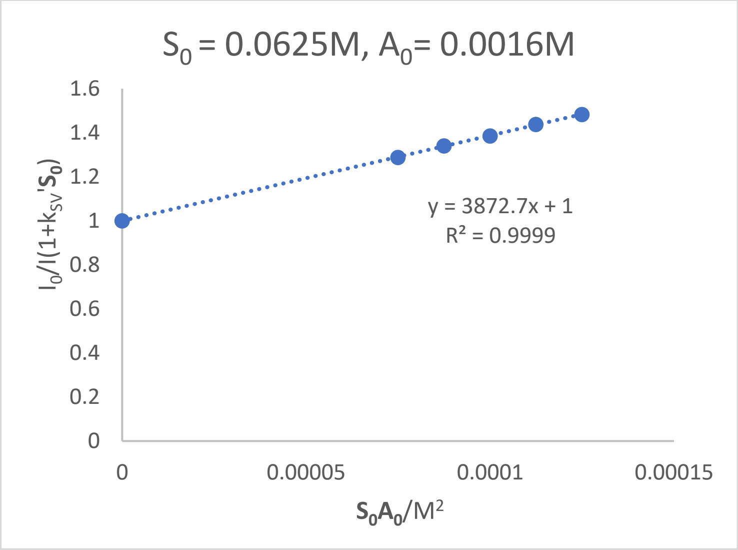


Figure S5.3.3. Stern-Volmer plot of luminescence data in **Table S5.3.3**

$k_{obs}\tau_0$ = 3873

Table S5.3.4. S_0 fixed at 0.156 M, A_0 varied from 0.0015 to 0.0035 M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}'\ S_0)$
0	0					1
0.0015	0.0002344	368	368	368	368	1.513587
0.002	0.0003125	326	328	328	327.3333	1.701629
0.0025	0.0003906	293	291	291	291.6667	1.909714
0.003	0.0004688	266	264	264	264.6667	2.104534
0.0035	0.0005469	244	244	242	243.3333	2.289041

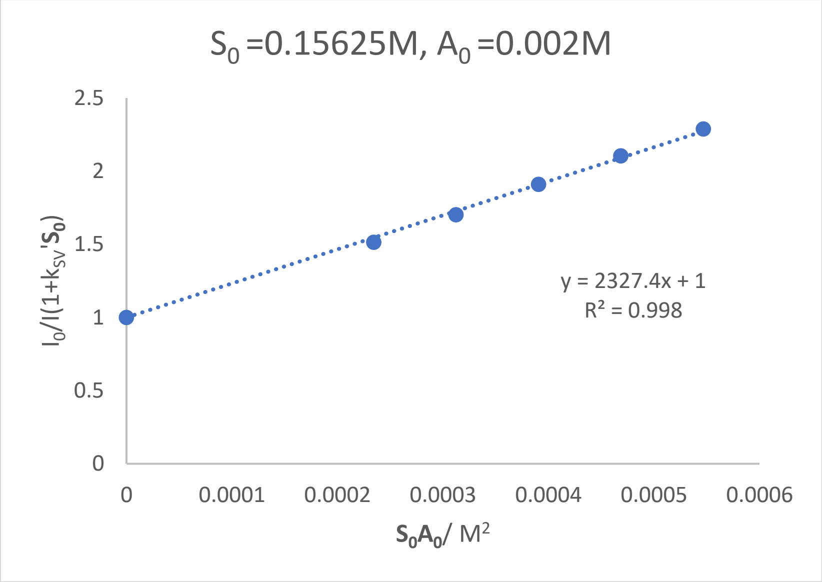


Figure S5.3.4. Stern-Volmer plot of luminescence data in **Table S5.3.4**

$\frac{I_0}{1+k_{SV}'S_0}$ was extrapolated from the five data points.

$$k_{obs}\tau_0 = 2327$$

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\,\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.3.5. Solutions to Key Equation 8 and Entry 3 in Table S5.

	S_0 (M)	A_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.010	0.010	0.0001	0.02	5740
2	0.025	0.004	0.0001	0.029	5240
3	0.0625	0.0016	0.0001	0.0641	3870
4	0.156	0.00064	0.0001	0.157	2330

	K_A/M^{-1}	$k_{PCET}\tau_0/M^{-1}$
1&2	13.1	546
1&3	13.6	530
1&4	13.3	538
2&3	13.8	526
2&4	13.4	538
3&4	13.1	543
average	13.4	536

$\Delta G^{\circ}_{\text{H-bond}}$ (kcal/mol) = $-RT\ln K_A$ = -1.54

$\ln[k_{PCET}(M^{-1}s^{-1})] = \ln[k_{PCET}\tau_0/\tau_0]$ = 19.46

τ_0 = 1.9us

error of $\Delta G^{\circ}_{\text{H-bond}}$ (kcal/mol) = 0.02

error of $\ln[k_{PCET}(M^{-1}s^{-1})]$ = 0.02

5.4. Entry 4.

Non-PCET quenching of reductant by ketone alone (without acid) is given by **Figure S5.4.** The solution was irradiated at 370nm, and fluorescence was measured at 518nm.

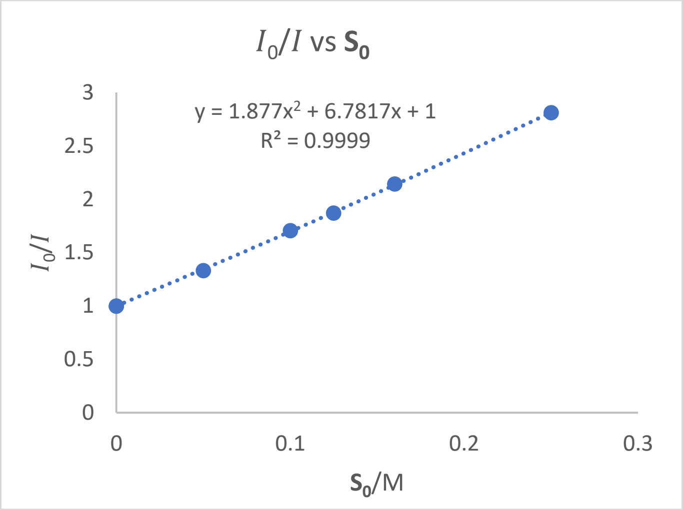


Figure S5.4. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

A quadratic relationship gives the best fitting, indicating two quenching mechanisms, one dynamic with rate constant $k'_{d\,SV}$, and one static with constant K'_{sSV}. Therefore,

$$\frac{I_0}{I} = (1 + k'_{d\,SV}S_0)(1 + K_{sSV}{}'S_0)$$

From the sready-state quenching data, $k'_{d\,SV}$ and $K_{sSV}{}'$ are indistinguishably 6.50 and 0.29. Time-resolved luminescence data (lifetime of reductant **6** *Ir (III) reduces from 1.9us to 1.2us upon adding 0.05M of ketone) suggest that $k'_{d\,SV}$= 6.5

Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + \frac{k_{obs}\tau_0 S_0 A_0}{1+k'_{d\,SV}S_0}$$

The easiest way is to keep **S₀** fixed and vary **A₀** in each of the four Stern–Volmer analysis. In this way, the static $K_{sSV}{}'$ is automatically taken into consideration, and only the dynamic $k'_{d\,SV}$ requires treatment. Here the I_0 is not directly measured but extrapolated by the data points. In each Stern–Volmer plot, **S₀** is fixed and **A₀** is varied, and I_0/I is plotted against **S₀A₀**. The slope represents $\frac{k_{obs}\tau_0}{1+k'_{d\,SV}S_0}$, and the corresponding $k_{obs}\tau_0$ is obtained thereafter.

Table S5.4.1. S_0 fixed at 0.025M. A_0 varied from 0.003 to 0.006M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.003	0.000075	473	467	471	470.3333	1.371368
0.004	0.0001	427	426	424	425.6667	1.51527
0.005	0.000125	405	398	399	400.6667	1.609817
0.006	0.00015	373	373	373	373	1.729223

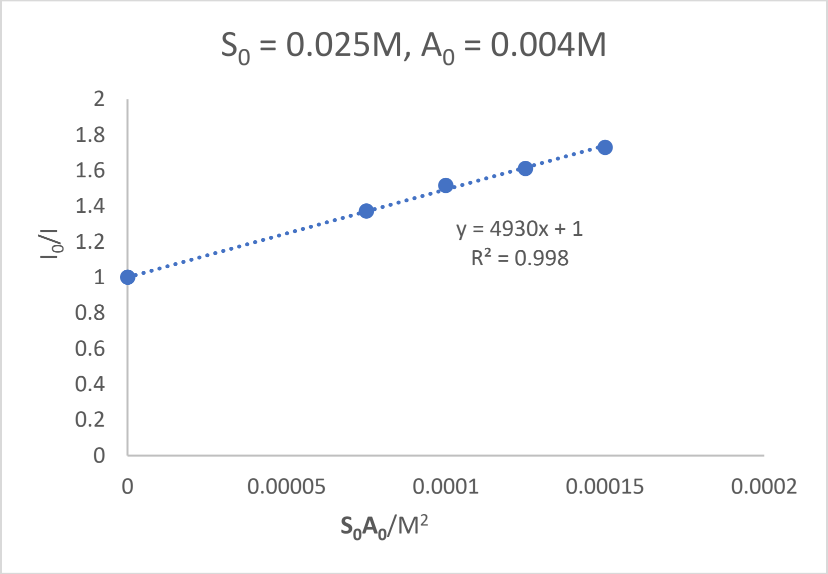


Figure S5.4.1. Stern-Volmer plot of luminescence data in **Table S5.4.1.**

$k_{obs}\tau_0$ = 4930 × $(1 + k'_{d\,SV}S_0)$

= 4930 × $(1 + 6.5 \times 0.025)$

= 5731

Table S5.4.2. S_0 fixed at 0.04M. A_0 varied from 0.000625 to 0.0025M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.000625	0.000025	516	519	519	518	1.11583
0.00125	0.00005	475	476	477	476	1.214286
0.001875	0.000075	450	450	451	450.3333	1.327905
0.0025	0.0001	410	413	416	413	1.447942

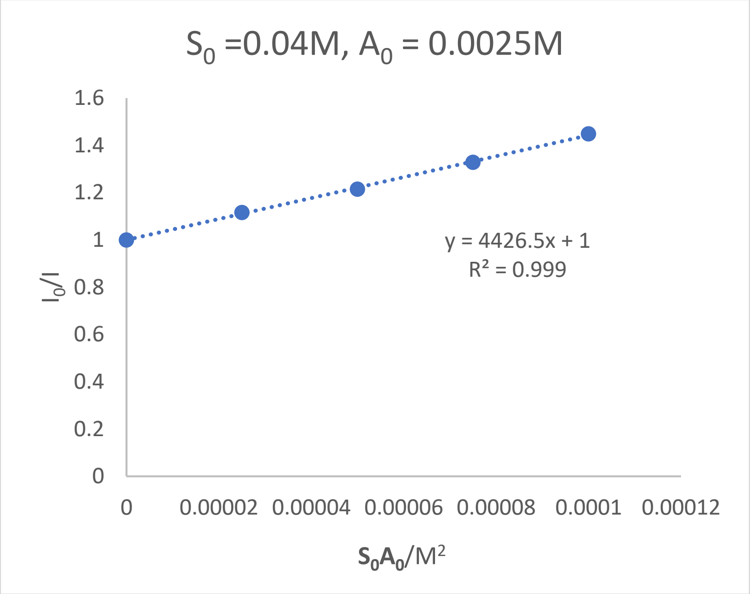


Figure S5.4.2. Stern-Volmer plot of luminescence data in **Table S5.4.2.**

$k_{obs}\tau_0$ = 4426 × $(1 + k'_{d\,SV}S_0)$

= 4426 × $(1 + 6.5\ \times 0.04)$

= 5577

Table S5.4.3. S_0 fixed at 0.0625M. A_0 varied from 0.0004 to 0.002M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0004	0.000025	460	459	459	459.3333	1.092888
0.0008	0.00005	420	421	422	421	1.192399
0.0012	0.000075	391	392	390	391	1.283887
0.002	0.000125	340	337	341	339.3333	1.479371

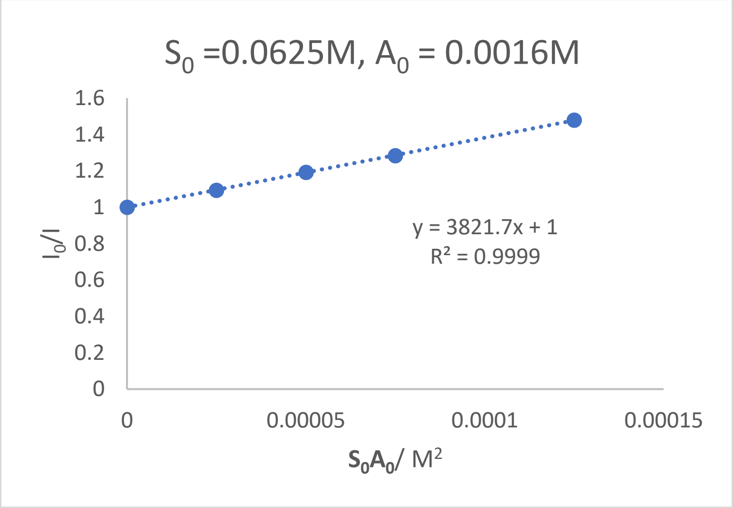


Figure S5.4.3. Stern-Volmer plot of luminescence data in **Table S5.4.3.**

$k_{obs}\tau_0$ = 3822 × $(1 + k'_{d\,SV} S_0)$

= 3822 × $(1 + 6.5 \times 0.0625)$

= 5375

Table S5.4.4. S_0 fixed at 0.156M. A_0 varied from 0.00016 to 0.0016M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00016	0.000025	312	310	310	310.6667	1.049356
0.00032	0.00005	295	293	294	294	1.108844
0.00048	0.000075	280	276	278	278	1.172662
0.00064	0.0001	263	265	265	264.3333	1.233291
0.0016	0.00025	207	208	209	208	1.567308

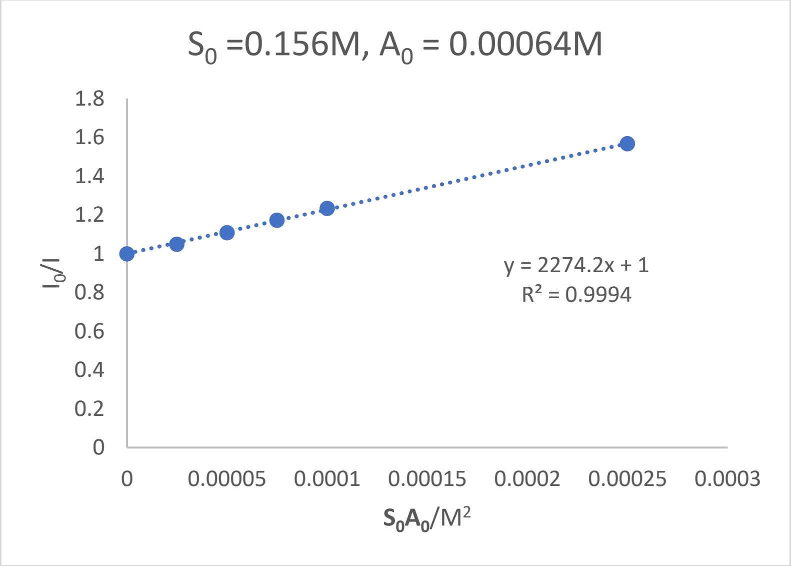


Figure S5.4.4. Stern-Volmer plot of luminescence data in **Table S5.4.4.**

$k_{obs}\tau_0$ = 2274 × $(1 + k'_{d\,SV} S_0)$

= 2274 × $(1 + 6.5 \times 0.156)$

= 4583

$$S_0 + A_0 = \frac{S_0 A_0\ k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \qquad (8)$$

Table 5.4.5. Solutions to Key Equation 8 and Entry 4 in Table S5.

	S_0 (M)	**A_0 (M)**	**S_0A_0 (M^2)**	**S_0+A_0 (M)**	**$k_{obs}\tau_0$**
1	0.025	0.004	0.0001	0.029	5730
2	0.040	0.0025	0.0001	0.0425	5580
3	0.0625	0.0016	0.0001	0.0641	5370
4	0.156	0.00064	0.0001	0.157	4580

	K_A/M^{-1}	**$k_{PCET}\tau_0/M^{-1}$**
1&2	2.17	2803
1&3	1.99	3038
1&4	2.08	2927
2&3	1.95	3085
2&4	2.06	2942
3&4	2.11	2887
average	2.06	2947

$\Delta G^\circ_{\text{H-bond}}$ (kcal/mol) = $-RT\ln K_A$ = -0.43

$\ln[k_{PCET}(M^{-1}s^{-1})] = \ln[k_{PCET}\tau_0/\tau_0]$ = 21.16

τ_0 = 1.9us

error of $\Delta G^\circ_{\text{H-bond}}$ (kcal/mol) = 0.03   error of $\ln[k_{PCET}(M^{-1}s^{-1})]$ = 0.03

5.5. Entry 5.

In all experiments, the solution was irradiated at wavelength 375nm that gives highest emission intensity at 518nm. Steady-state fluorescence quenching data of reductant **6** *Ir (III) by ketone is plotted in **Figure. S5.5**

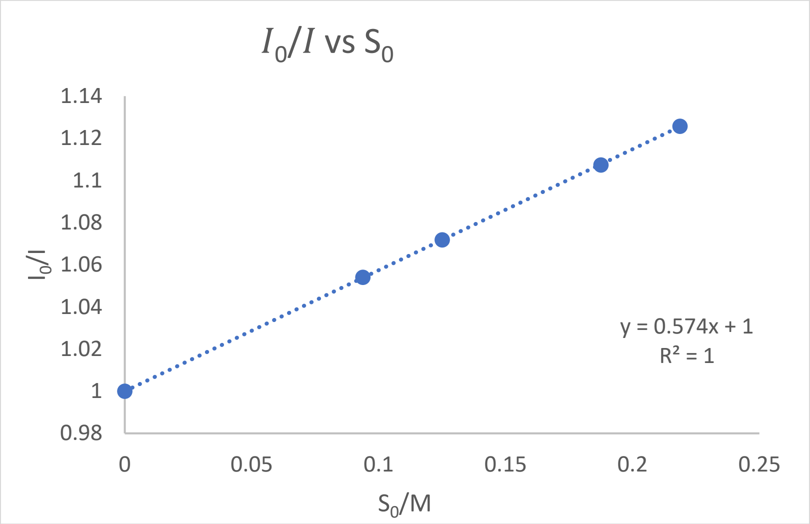


Figure S5.5. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$k'_{SV} = 0.574$

Time-resolved fluorometry suggest that the quenching of *Ir (III) by ketone is dynamic. Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + \frac{k_{obs}\tau_0 S_0 A_0}{1 + k'_{d\,SV} S_0}$$

Table S5.5.1. S_0 fixed at 0.025M. **A_0 varied from** 0.002 to 0.007M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.002	0.00005	576	577	574	575.6667	1.398379
0.003	0.000075	510	509	511	510	1.578431
0.004	0.0001	452	452	453	452.3333	1.779661
0.006	0.00015	362	361	360	361	2.229917
0.007	0.000175	334	331	329	331.3333	2.429577

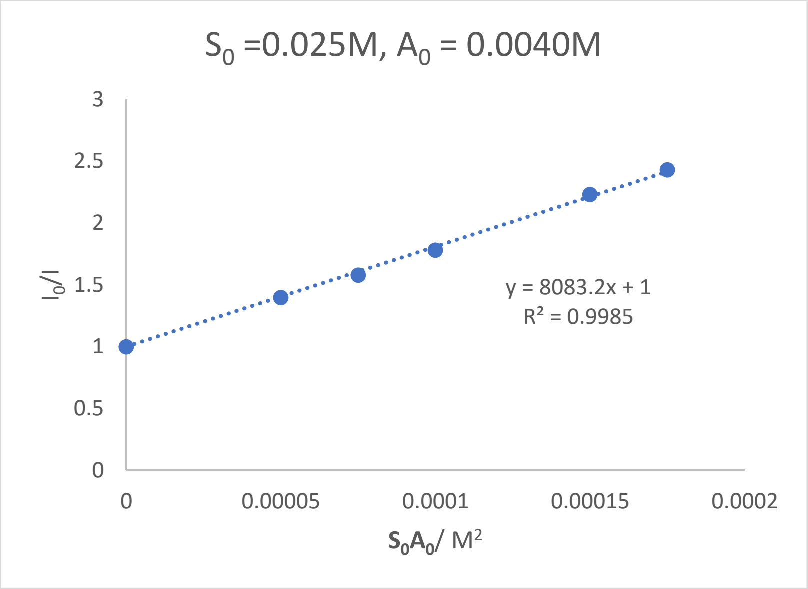


Figure S5.5.1. Stern-Volmer plot of luminescence data in **Table S5.5.1.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 8083 × $(1 + k'_{d\,SV} S_0)$

= 8083 × $(1 + 0.574 \times 0.025)$

= 8198

Table S5.5.2. S_0 fixed at 0.0625M**. A_0 varied from** 0.0008 to 0.0024M

A_0/M	**S_0A_0/ M^2**	**I/au 1**	**I/au 2**	**I/au 3**	**I/au avg.**	**I_0/I**
0	0					1
0.0008	0.00005	559	559	560	559.3333	1.346246
0.0012	0.000075	503	502	503	502.6667	1.498011
0.0016	0.0001	449	448	446	447.6667	1.682055
0.002	0.000125	411	411	411	411	1.832117
0.0024	0.00015	380	379	379	379.3333	1.985062

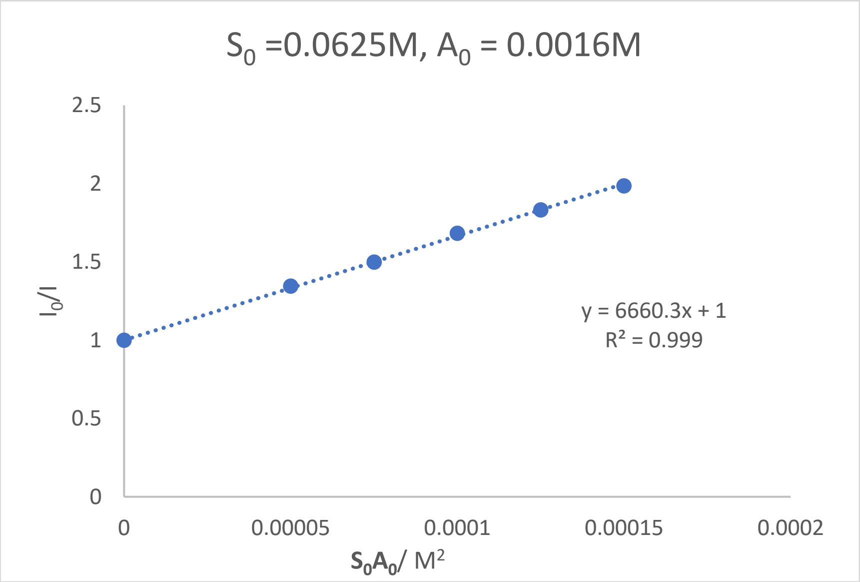


Figure S5.5.2. Stern-Volmer plot of luminescence data in **Table S5.5.2.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 6660 × $(1 + k'_{d\,SV}S_0)$

= 6660 × $(1 + 0.574 \times 0.0625)$

= 6899

Table S5.5.3. S_0 fixed at 0.100M. A_0 varied from 0.0008 to 0.0027M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0008	0.00008	450	451	450	450.3333	1.414508
0.0012	0.00012	387	388	389	388	1.641753
0.0016	0.00016	337	335	335	335.6667	1.897716
0.0024	0.00024	271	270	270	270.3333	2.35635
0.002732	0.000273	249	250	249	249.3333	2.554813

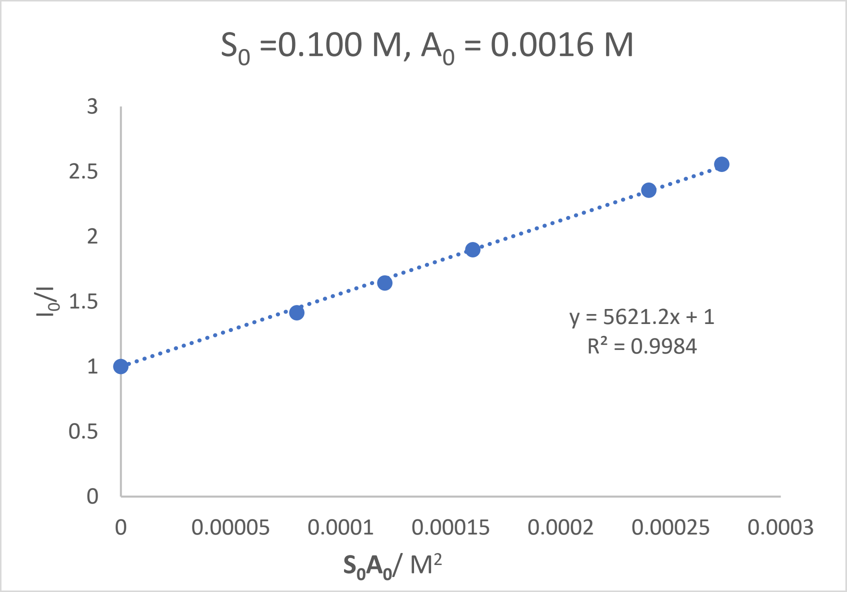


Figure S5.5.3. Stern-Volmer plot of luminescence data in **Table S5.5.3.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 5621 × $(1 + k'_{d\,SV}S_0)$

= 5621 × $(1 + 0.574 \times 0.1)$

= 5944

Table S5.5.4. S_0 **fixed at 0.156M.** A_0 **varied from 0.0008 to 0.0024M**

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0008	0.000125	352	352	350	351.3333	1.593928
0.0012	0.000188	305	304	304	304.3333	1.840088
0.0016	0.00025	271	268	269	269.3333	2.079208
0.002	0.000313	236	234	236	235.3333	2.379603
0.0024	0.000375	211	208	208	209	2.679426

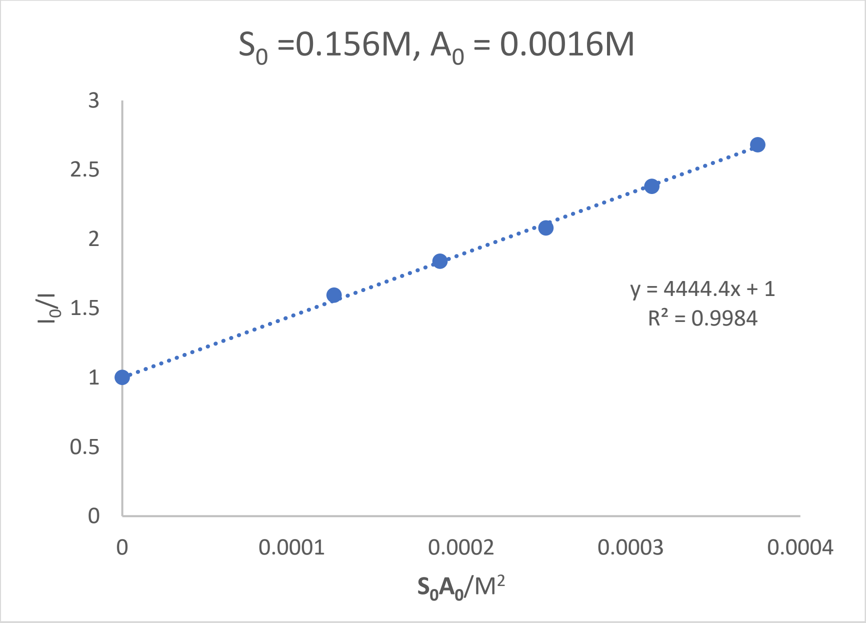


Figure S5.5.4. Stern-Volmer plot of luminescence data in **Table S5.5.4.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 4444 × $(1 + k'_{d\,SV}S_0)$

= 4444 × $(1 + 0.574 \times 0.15625)$

= 484

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\,\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (5)$$

Table 5.5.5. Solutions to Key Equation 8 and Entry 5 in Table S5.

	S_0 (M)	**A_0 (M)**	**S_0A_0 (M^2)**	**S_0+A_0 (M)**	**$k_{obs}\tau_0$**
1	0.025	0.004	0.0001	0.029	8200
2	0.0625	0.0016	0.0001	0.0641	6900
3	0.100	0.0016	0.00016	0.102	5940
4	0.156	0.0016	0.00025	0.158	4840

	K_A/M^{-1}	**$k_{PCET}\tau_0$/M^{-1}**
1&2	6.3	1532
1&3	6.2	1568
1&4	6.4	1522
2&3	5.9	1613
2&4	5.8	1595
3&4	6.4	1526
average	6.2	1559

$\Delta G^\circ_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.08

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{PCET}\tau_0/\tau_0$]= 20.53

τ_0 = 1.9us

error of $\Delta G^\circ_{\text{H-bond}}$ (kcal/mol) = 0.03

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.02

5.6. Entry 6.

Reductant **9** *Ir (III) was measured to display maximum emission at 500nm, with lifetime τ_0= 1.82us.

$E_{1/2}$(Ir(IV)/*Ir(III)) = -2.21V (vs Fc+/Fc).

In all experiments, the solution was irradiated at 370nm and fluorescence was measured at 500nm.

Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$$I_0/I = 1 + k'_{SV}S_0$$

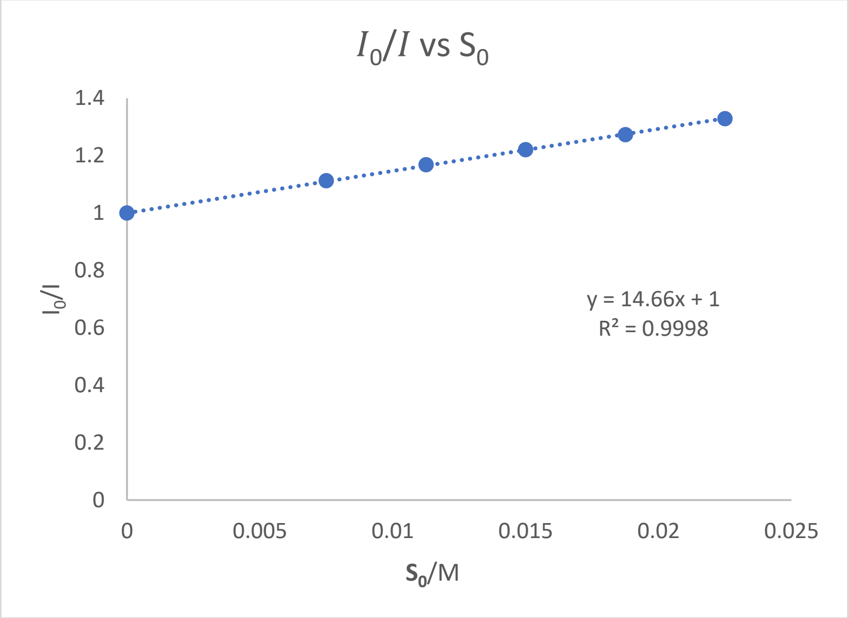


Figure S5.6. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$$k'_{d\,SV} = 14.66$$

The luminescence of *Ir (III) is not affected by $(PhO)_2P(O)OH$ and is dynamically quenched by ketone. Therefore, the following equation is used

$$\frac{I_0}{I} = 1 + \frac{k_{obs}\tau_0 S_0 A_0}{1 + k'_{d\,SV}S_0}$$

Table S5.6.1. Luminescence quenching data with S_0 = 0.0168M, A_0=0.003M. S_0 fixed at 0.0168M. A_0 varied from 0.0015 to 0.0045M.

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0015	0.0000252	407	407	407	407	1.174447
0.00225	0.0000378	382	382	383	382.3333	1.250218
0.003	0.0000504	361	362	362	361.6667	1.321659
0.00375	0.000063	342	342	342	342	1.397661
0.0045	0.0000756	320	321	320	320.3333	1.492196

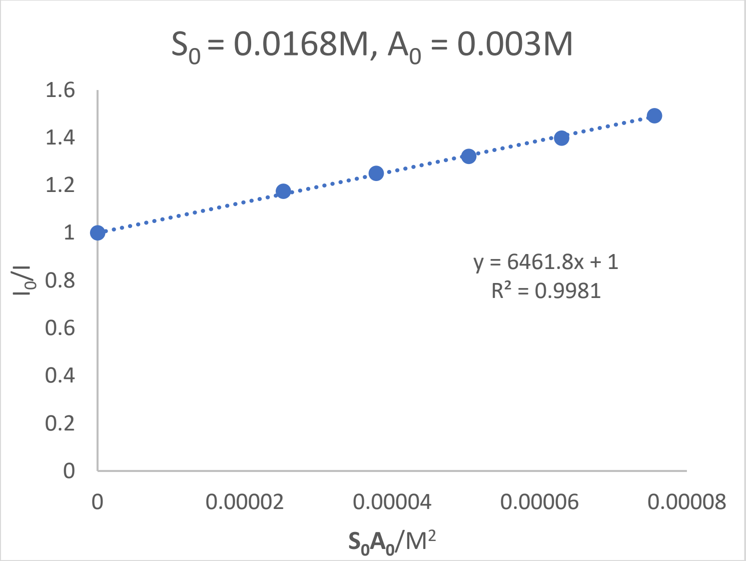


Figure S5.6.1. Stern-Volmer plot of luminescence data in **Table S5.6.1.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 6461.8 × $(1 + k'_{d\,SV}S_0)$

= 6461.8 × $(1 + 14.66 \times 0.0168)$

= 8053

Substitute K_A= 6.3 (from entry 1), $k_{obs}\tau_0$ = 8053 into the equation

$$S_0 + A_0 = \frac{S_0A_0\,k_{obs}\,\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.0168 + 0.003 = \frac{0.0168 \times 0.003 \times 8053}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{8053} - \frac{1}{6.3}$$

$$k_{\mathrm{PCET}}\tau_0 = 145$$

Table S5.6.2. Luminescence quenching data with S_0 = 0.028M, A_0=0.003M. S_0 fixed at 0.028M. A_0 varied from 0.0015 to 0.0045M.

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0015	0.0000417	248	248	249	248.3333	1.26443
0.00225	0.00006255	228	228	228	228	1.377193
0.003	0.0000834	209	209	208	208.6667	1.504792
0.00375	0.00010425	191	191	193	191.6667	1.638261
0.0045	0.0001251	177	177	177	177	1.774011

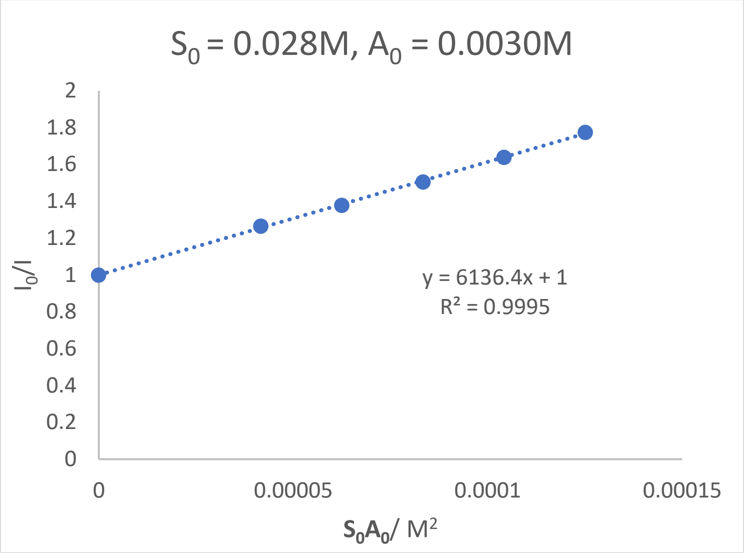


Figure S5.6.2. Stern-Volmer plot of luminescence data in **Table S5.6.2.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 6136.4 × $(1 + k'_{d\,SV}S_0)$

= 6136.4 × $(1 + 14.66\ \times 0.028)$

= 8637

Substitute K_A= 6.3 (from **entry 1**), $k_{obs\,SV}$ = 8053 into the equation

$$S_0 + A_0 = \frac{S_0A_0\,k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.0278 + 0.003 = \frac{0.0278\times0.003\times8637}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{8637} - \frac{1}{6.3}$$

$$k_{\mathrm{PCET}}\tau_0 = 1656$$

$k_{\mathrm{PCET}}\tau_0\ average$ = (1656 + 1456)/2= 1560

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.09 (same as in entry 1)

ln[k_{PCET}(M^{-1}s^{-1})] = ln[k_{PCET} τ_0/τ_0]= 20.58

τ_0 = 1.82us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.05

error of ln[k_{PCET} (M^{-1}s^{-1})] = 0.10

5.7. Entry 7.

Reductant **8** *Ir (III) was measured to display maximum emission at 491nm, with lifetime τ_0= 1.61us.

$E_{1/2}$(Ir(IV)/*Ir(III)) = -2.28V (vs Fc+/Fc).

Ketone does not quench the luminescence of reductant **8** *Ir (III). Non-PCET quenching of reductant by acid alone (without ketone) is given by the following equation:

$$\frac{I_0}{I} = 1 + k''_{d\,SV}\,\mathbf{A_0}$$

In all experiments, the solution was irradiated at wavelength (370nm) that gives highest emission intensity at 491nm.

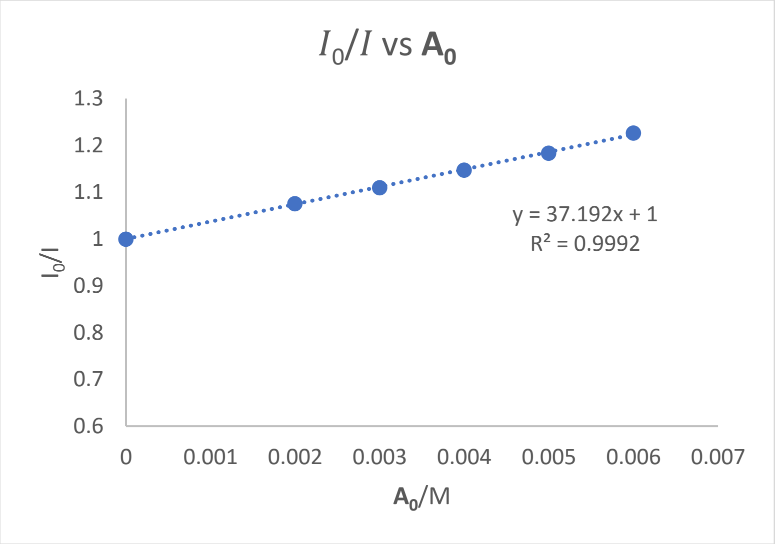


Figure S5.7. Stern-Volmer plot of luminescence data of non-PCET quenching by acid alone

$$k''_{d\,SV} = 37.2$$

Time-resolved luminescence suggests that the non-PCET quenching by acid is dynamic, therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + (k''_{SV} + k_{obs}\,\tau_0 S_0)A_0$$

Table S5.7.1. Luminescence quenching data with S_0= 0.025M, A_0= 0.0023M. S_0 fixed at 0.025M. A_0 varied from 0.0015 to 0.003M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0015	9.375E-05	500	501	493	498	1.449799
0.002	0.000125	454	454	455	454.3333	1.589142
0.0025	0.0001563	409	407	413	409.6667	1.762408
0.003	0.0001875	374	378	376	376	1.920213

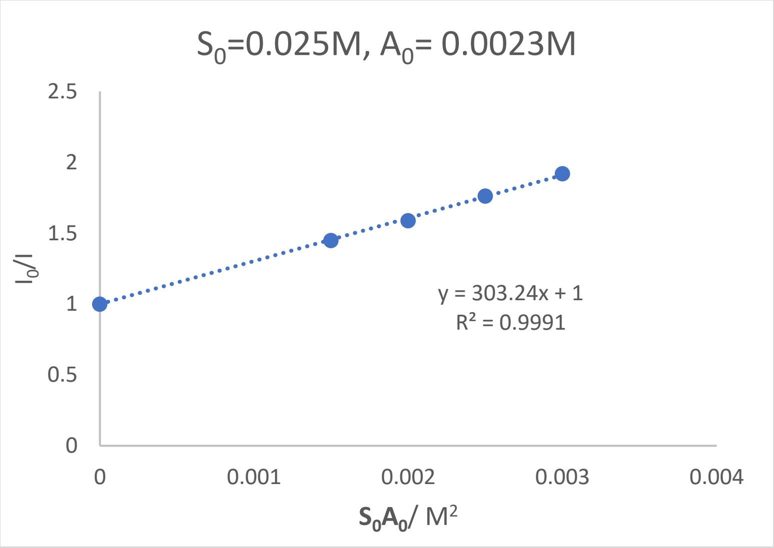


Figure S5.7.1. Stern-Volmer plot of luminescence data in **Table S5.7.1.**

I_0 was extrapolated from the four data points.

$\frac{I_0}{I}$ $against\ \mathrm{A}_0$ is plotted to fit $\frac{I_0}{I} = 1 + (k''_{SV} + k_{obs}\tau_0\mathrm{S}_0)\mathrm{A}_0$ in which $k''_{d\,SV} = 37.2$ refers to the dynamic quenching of reductant by acid alone

$$k''_{SV} + k_{obs}\tau_0 S_0 = 303.24$$

$$37.2 + k_{obs}\tau_0 \times 0.025 = 303.24,\ k_{obs}\tau_0 = 9200$$

Substitute S_0= 0.025, A_0= 0.0023, K_A= 92 (from **entry 2**), $k_{obs}\tau_0$ = 9200 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.025 + 0.00225 = \frac{0.025 \times 0.00225 \times 9200}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{9200} - \frac{1}{92}$$

$$k_{\mathrm{PCET}}\tau_0 = 337$$

Table S5.7.2. Luminescence quenching data with S_0= 0.050M, A_0= 0,0010M. S_0 fixed at 0.050M. A_0 varied from 0.00025 to 0.0015M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00025	0.0000125	542	543	540	541.6667	1.085538
0.0005	0.000025	505	500	507	504	1.166667
0.00075	0.0000375	470	468	466	468	1.25641
0.001	0.00005	441	438	440	439.6667	1.337377
0.0015	0.000075	400	402	398	400	1.47

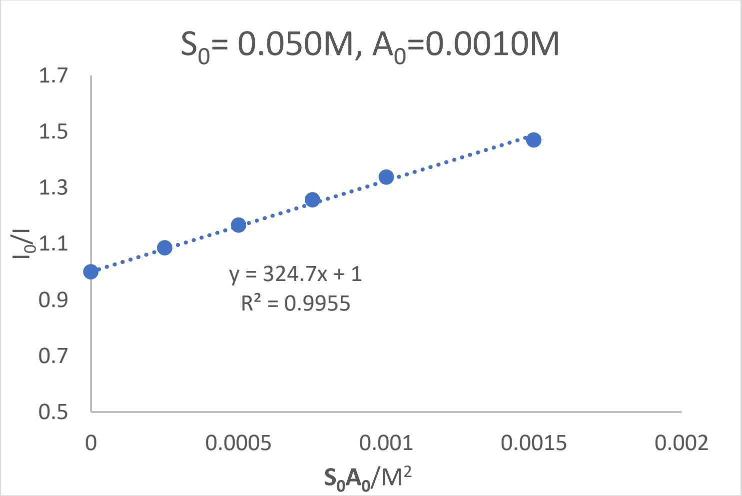


Figure S5.7.2. Stern-Volmer plot of luminescence data in **Table S5.7.2.**

I_0 was extrapolated from the five data points.

$\frac{I_0}{I}$ *against* A_0 is plotted to fit $\frac{I_0}{I} = 1 + (k''_{SV} + k_{obs}\tau_0\mathrm{S}_0)\mathrm{A}_0$ in which $k''_{d\,SV} = 37.2$ refers to the dynamic quenching of reductant **8** *Ir (III) by $(PhO)_2P(O)OH$

$$k''_{SV} + k_{obs}\tau_0 S_0 = 324.7$$

$$37.2 + k_{obs}\tau_0 \times 0.05 = 324.7,\ k_{obs}\tau_0 = 5745$$

Substitute S_0=0.050, A_0=0.0010, K_A= 92, $k_{obs}\tau_0$ = 5745 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.05 + 0.001 = \frac{0.05 \times 0.001 \times 5745}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{5745} - \frac{1}{92}$$

$$k_{\mathrm{PCET}}\tau_0 = 351$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (337+351)/2 = 344

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -2.68 (same as in entry 2)

ln[k_{PCET}($\mathrm{M^{-1}s^{-1}}$)] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 19.03

τ_0 = 1.61us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.04 (same as in entry 2)

error of ln[k_{PCET}($\mathrm{M^{-1}s^{-1}}$)] = 0.03

5.8. Entry 8.

Ketone does not quench luminescence of reductant **8** *Ir (III). Time-resolved luminescence suggests that the non-PCET quenching by acid is dynamic, therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + (k''_{SV} + k_{obs}\tau_0 S_0)A_0$$

$$k''_{d\,SV} = 37.2\ (\textbf{entry 7})$$

In all experiments, the solution was irradiated at 365nm, and fluorescence was measured at 491nm.

Table S5.8.1. Luminescence quenching data with S_0= 0.0250M, A_0= 0.0016M. S_0 fixed at 0.025M. A_0 varied from 0.0004 to 0.0024M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0						1
0.0004	0.00001	596	600	600	598.6667	1.150891
0.0012	0.00003	470	471	473	471.3333	1.46181
0.0016	0.00004	436	435	434	435	1.583908
0.0024	0.00006	362	363	365	363.3333	1.89633

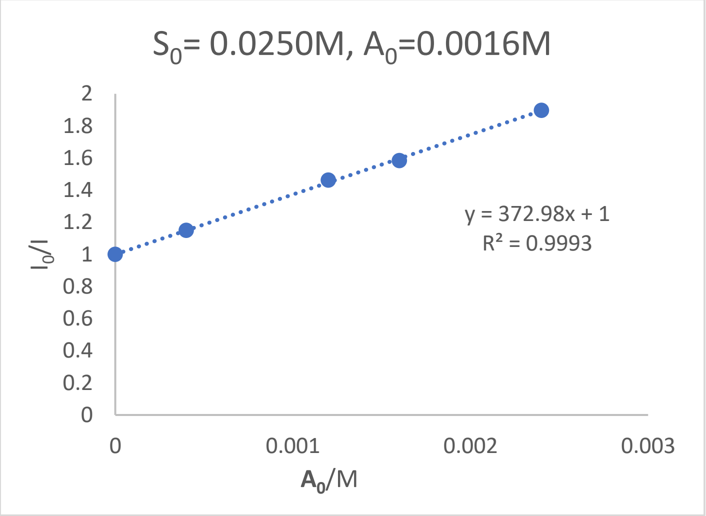


Figure S5.8.1. Stern-Volmer plot of luminescence data in **Table S5.8.1.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 372.98$$

$$37.2 + k_{obs}\tau_0 \times 0.05 = 372.98,\ \ k_{obs}\tau_0 = 13422$$

Substitute S_0=0.025, A_0=0.0016, K_A= 13.4 (from **entry 3**), $k_{obs}\tau_0$ = 13422 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\ k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.025 + 0.0016 = \frac{0.025 \times 0.0016 \times 13422}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{13422} - \frac{1}{13.4}$$

$$k_{\mathrm{PCET}}\tau_0 = 1353$$

Table S5.8.2. Luminescence quenching data with S_0= 0.100M, A_0= 0,0016M. S_0 fixed at 0.025M. A_0 varied from 0.0004 to 0.0006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0						1
0.0004	0.00004	434	431	431	432	1.331019
0.0008	0.00008	348	350	351	349.6667	1.644423
0.0012	0.00012	291	291	290	290.6667	1.978211
0.0016	0.00016	249	250	250	249.6667	2.303071
0.002	0.0002	216	217	214	215.6667	2.666151
0.0006	0.00006	383	383	383	383	1.501305

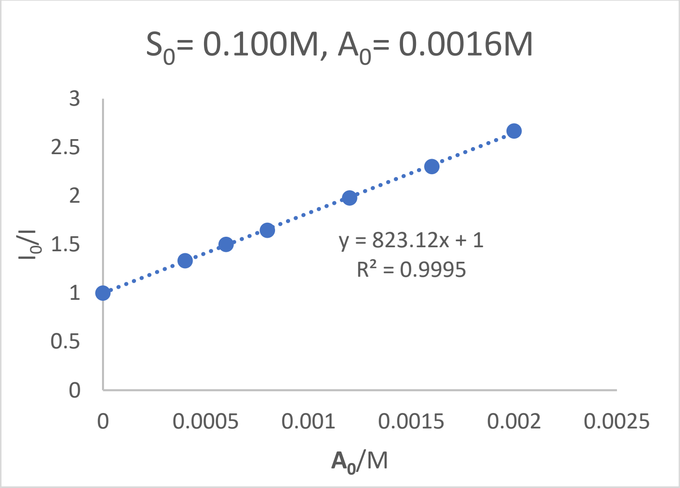


Figure S5.8.2. Stern-Volmer plot of luminescence data in **Table S5.8.2.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 823.12$$

$$37.2 + k_{obs}\tau_0 \times 0.1 = 823.12,\ k_{obs}\tau_0 = 7856$$

Substitute S_0=0.100, A_0=0.0016, K_A= 13.4 (from entry 3), $k_{obs\ SV}$ = 7856 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\ k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.1 + 0.0016 = \frac{0.1 \times 0.0016 \times 7856}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{7856} - \frac{1}{13.4}$$

$$k_{\mathrm{PCET}}\tau_0 = 1377$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (1353+1377)/2 = 1365

$\Delta G^\circ_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.54 (same as in entry 3)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 20.56

$\tau_{0\ [\mathrm{Irppy3}]}$ = 1.61us

error of $\Delta G^\circ_{\text{H-bond}}$ (kcal/mol) = 0.01 (same as in entry 3)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.01 (same as in entry 3)

5.9. Entry 9.

Reductant **7** *Ir (III) was measured to display maximum emission at 491nm, with lifetime τ_0= 2.02us.

$E_{1/2}$(Ir(IV)/*Ir(III)) = -1.92V (vs Fc+/Fc).

Acid does not quench the luminescence of reductant **7** *Ir (III). Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$$I_0/I = 1 + k'_{SV}S_0$$

In all experiments, the solution was irradiated at wavelength (370nm) that gives highest emission intensity at 491nm.

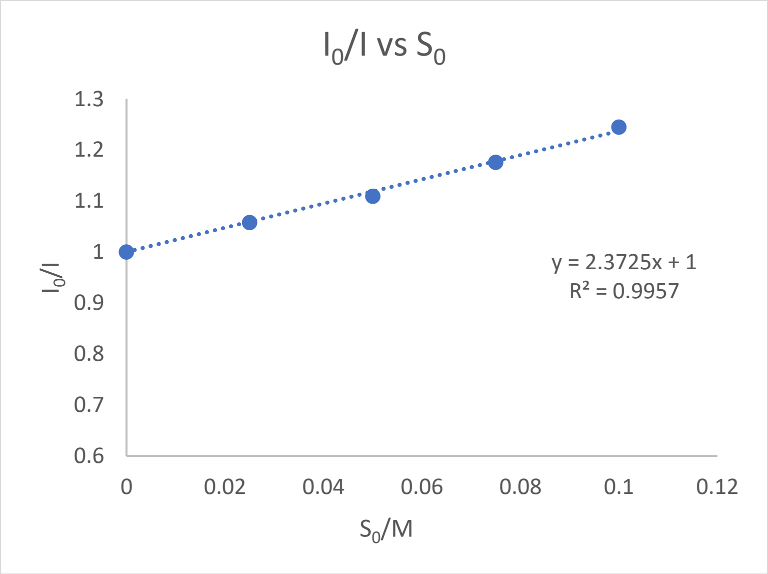


Figure S5.9. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

A_0= 0, S_0 is varied from 0 to 0.10M.

$$k'_{SV} = 2.37$$

Time-resolved luminescence suggests that the non-PCET quenching by ketone is static. Therefore, the following equation is used:

$$\frac{I_0/I}{1 + k_{SV}'S_0} = 1 + k_{obs}\tau_0 S_0 A_0$$

Table S5.9.1. Luminescence quenching data with S_0= 0.0250M, A_0= 0.004M. A_0 fixed at 0.004M. S_0 varied from 0.0218 to 0.0312M

S_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I	$I_0/I(1+k_{SV}'\ S_0)$
0	0					1	1
0.021875	8.75E-05	405	403	403	403.6667	1.21387283	1.153923
0.025	0.0001	401	392	393	395.3333	1.23946037	1.169992
0.028125	0.000113	387	387	382	385.3333	1.2716263	1.192004
0.03125	0.000125	376	372	377	375	1.30666667	1.216388

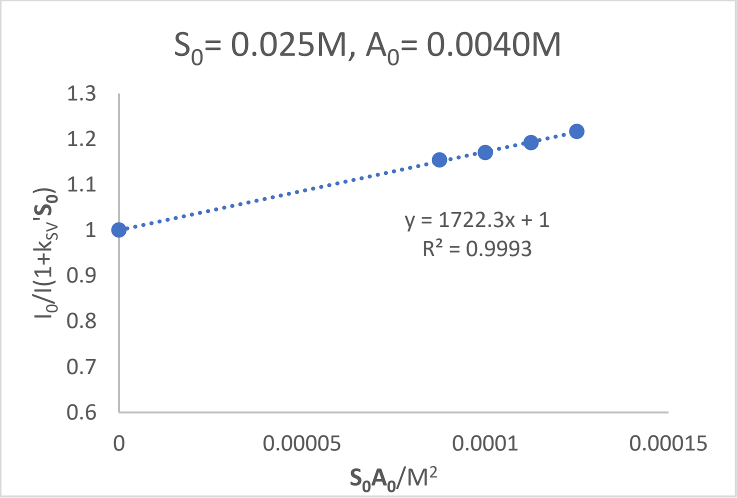


Figure S5.9.1. Stern-Volmer plot of luminescence data in **Table S5.9.1.**

I_0 was extrapolated from the four data points.

$$k_{obs}\tau_0 = 1722$$

Substitute S_0= 0.025, A_0= 0.004, K_A= 6.3 (from **entry 1**), $k_{obs\ SV}$ = 1722 into the equation

$$S_0 + A_0 = \frac{S_0A_0\ k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.025 + 0.004 = \frac{0.025 \times 0.004 \times 1722}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{1722} - \frac{1}{6.3}$$

$$k_{\mathrm{PCET}}\tau_0 = 322$$

Table S5.9.2. Luminescence quenching data with S_0= 0.050M, A_0= 0.0015M. S_0 fixed at 0.050M. A_0 varied from 0.0005 to 0.0025M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}' S_0)$
0	0					1
0.0005	0.000025	175	175	174	174.6667	1.03625954
0.001	0.00005	167	167	168	167.3333	1.08167331
0.0015	0.000075	161	160	160	160.3333	1.12889813
0.002	0.0001	155	154	154	154.3333	1.17278618
0.0025	0.000125	150	150	149	149.6667	1.20935412

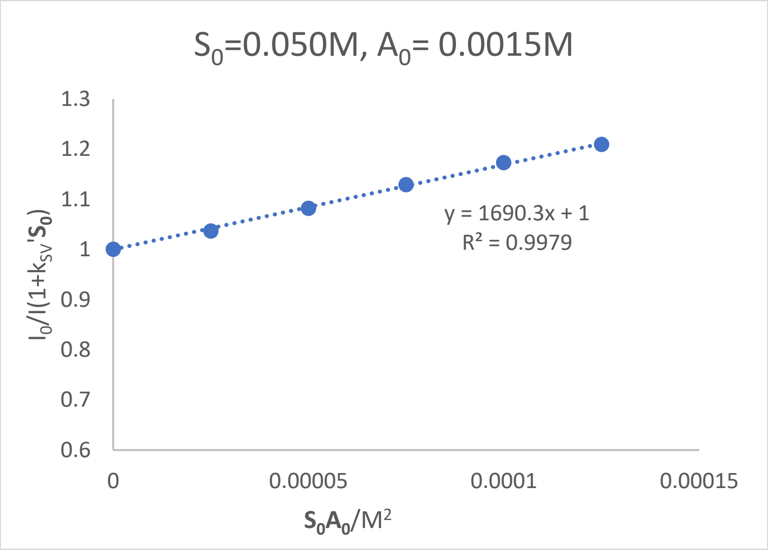


Figure S5.9.2. Stern-Volmer plot of luminescence data in **Table S5.9.2.**

$\frac{I_0}{1+k_{SV}'S_0}$ was extrapolated from the five data points.

$$k_{obs}\tau_0 = 1690$$

Substitute S= 0.05, A= 0.0015, K_A= 6.3 (from entry 1), $k_{obs}\tau_0$ = 1690 into the equation

$$S_0 + A_0 = \frac{S_0A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.05 + 0.0015 = \frac{0.05 \times 0.0015 \times 1690}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{1690} - \frac{1}{6.3}$$

$$k_{\mathrm{PCET}}\tau_0 = 354$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (322+354)/2 = 338

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.09 (same as in entry1)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\mathrm{pcet}}\tau_0/\tau_0$]= 18.93

τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.05 (same as in entry1)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.06

5.10. Entry 10.

Neither ketone nor acid quenches the luminescence of reductant **7** *Ir (III). Therefore, the following equation is used:

$$I_0/I = 1 + k_{obsSV}\mathrm{S_0A_0}$$

In all experiments, the solution was irradiated at 370nm, and fluorescence was measured at 491nm.

Table S5.10.1. Luminescence quenching data with S_0= 0.050M, A_0= 0.0020M. S_0 fixed at 0.050M. A_0 varied from 0.0005 to 0.003M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0005	0.000025	611	608	611	610	1.014754
0.001	0.00005	604	598	602	601.333333	1.029379
0.0015	0.000075	592	592	592	592	1.045608
0.002	0.0001	586	584	582	584	1.059932
0.0025	0.000125	576	576	574	575.333333	1.075898
0.003	0.00015	568	567	569	568	1.089789

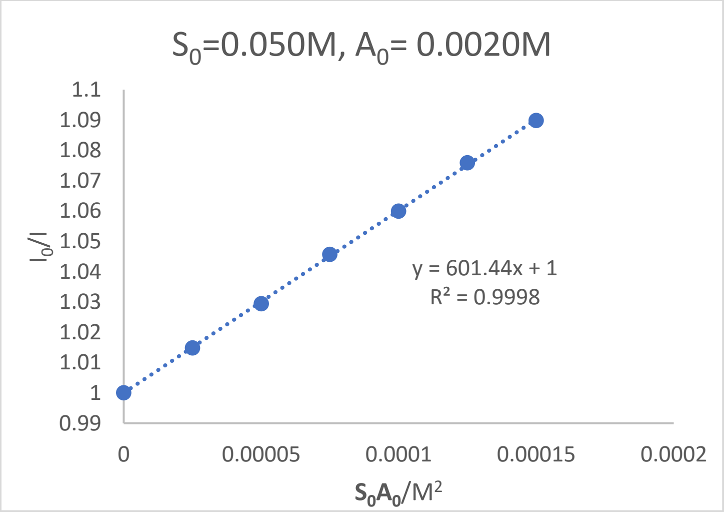


Figure S5.10.1. Stern-Volmer plot of luminescence data in **Table S5.10.1.**

I_0 was extrapolated from the six data points.

$k_{obs}\tau_0$ = 601

Substitute S_0= 0.05, A_0= 0.002, K_A= 92 (from **entry 2**), $k_{obs}\tau_0$= 601 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.05 + 0.002 = \frac{0.05 \times 0.002 \times 601}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{601} - \frac{1}{92}$$

$$k_{\mathrm{PCET}}\tau_0 = 37$$

Table S5.10.2. Luminescence quenching data with S_0= 0.0625M, A_0= 0.0030M. S_0 fixed at 0.0625M. A_0 varied from 0.001 to 0.005M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.0000625	430	440	433	434.3333	1.03607061
0.002	0.000125	419	422	421	420.6667	1.06973059
0.003	0.0001875	405	406	405	405.3333	1.11019737
0.004	0.00025	388	389	387	388	1.15979381
0.005	0.0003125	376	377	377	376.6667	1.19469027

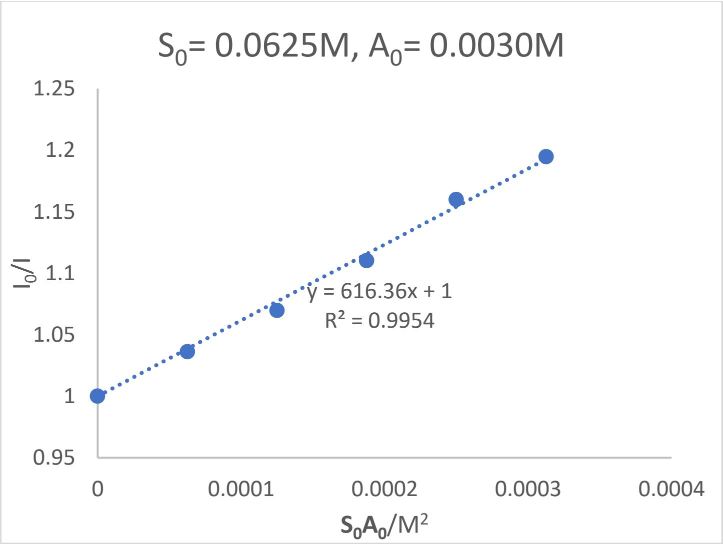


Figure S5.10.2. Stern-Volmer plot of luminescence data in **Table S5.10.2.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 616

Substitute S_0= 0.0625, A_0= 0.003, K_A= 92 (from **entry 2**), $k_{obs}\tau_0$ = 616 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.0625 + 0.003 = \frac{0.0625 \times 0.003 \times 616}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{616} - \frac{1}{92}$$

$$k_{\mathrm{PCET}}\tau_0 = 45$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (37+45)/2 = 41

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -2.68 (same as in entry 2)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 16.83

τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.04 (same as in entry 2)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.08

5.11. Entry 11.

Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$$I_0/I = 1 + k'_{SV}S_0$$

In all experiments, The solution was irradiated at 365nm, and fluorescence was measured at 491nm.

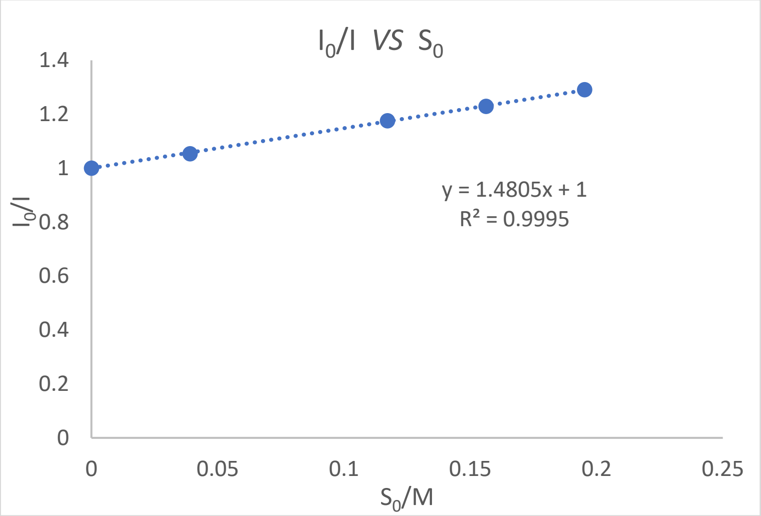


Figure S5.11. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$$k'_{SV} = 1.48$$

Time-resolved luminescence suggests that the non-PCET quenching by ketone is static, while $(PhO)_2P(O)OH$ does not quench the luminescence intensity. Therefore, the following equation is used:

$$\frac{I_0/I}{1 + k_{SV}{}'S_0} = 1 + k_{obs}\tau_0 \mathrm{S}_0 \mathrm{A}_0$$

Table S5.11.1. Luminescence quenching data with S_0= 0.0390M, A_0= 0.006M. S_0 fixed at 0.0390M. A_0 varied from 0.0040 to 0.0125M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	$I_0/I(1+k_{SV}'\ S_0)$
0	0					1
0.004	0.00025	324	323	323	323.3333	1.280412371
0.005	0.000313	304	304	304	304	1.361842105
0.0075	0.000469	265	264	262	263.6667	1.570164349
0.01	0.000625	237	234	235	235.3333	1.759206799
0.0125	0.000781	214	214	213	213.6667	1.937597504

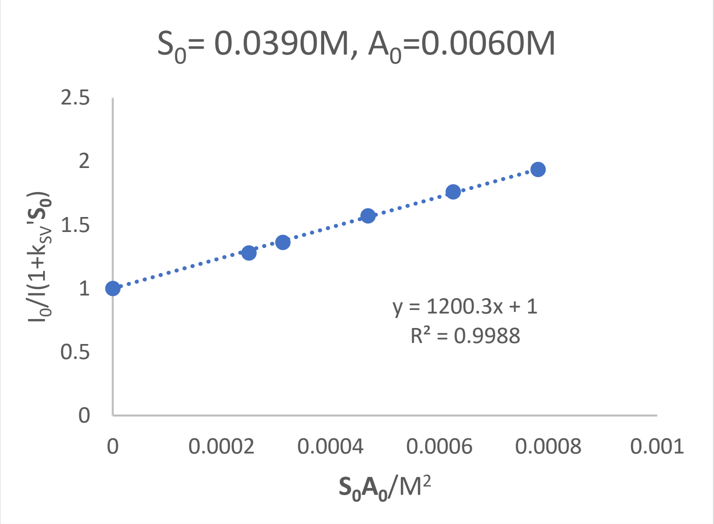


Figure S5.11.1. Stern-Volmer plot of luminescence data in **Table S5.11.1.**

$\frac{I_0}{1+k_{SV}'S_0}$ was extrapolated from the five data points.

$$k_{obs}\tau_0 = 1200$$

Substitute S_0= 0.039, A_0= 0.006, K_A= 13.4 (from **entry 3**), $k_{obs\ SV}$ = 1200 into the equation

$$S_0 + A_0 = \frac{S_0A_0\ k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.039 + 0.006 = \frac{0.039 \times 0.006 \times 1200}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{1200} - \frac{1}{13.4}$$

$$k_{\mathrm{PCET}}\tau_0 = 142$$

Table S5.11.2. Luminescence quenching data with S_0= 0.0156, A_0= 0.010. A_0 fixed at 0.0100M. S_0 varied from 0 to 0.0219M

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I	$\frac{I_0/I}{1+k_{SV}'S_0}$
0	0	517	516	515	516	1	1
0.009375	9.38E-05	436	436	436	436	1.183486	1.166858505
0.0125	0.000125	408	410	410	409.3333	1.260586	1.237081766
0.015625	0.000156	390	387	387	388	1.329897	1.299044598
0.01875	0.000188	368	369	369	368.6667	1.399638	1.360853997
0.021875	0.000219	351	351	351	351	1.470085	1.422778098

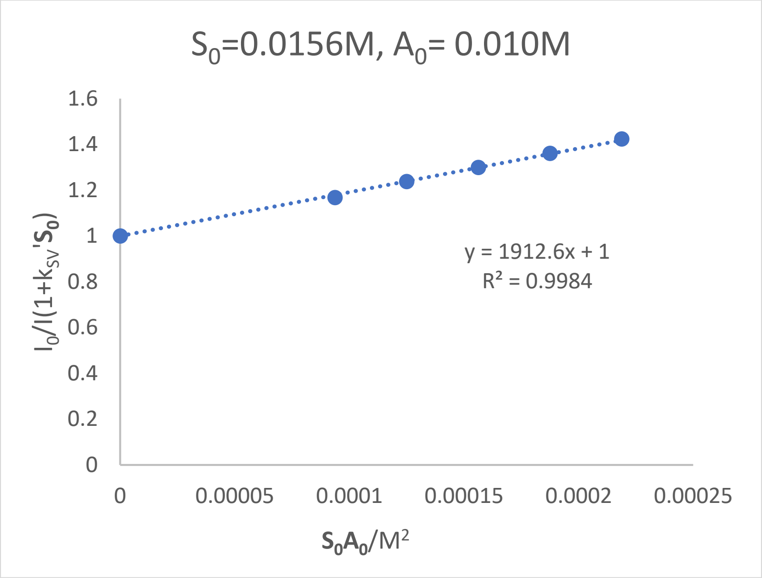


Figure S5.11.2. Stern-Volmer plot of luminescence data in **Table S5.11.2.**

$$k_{obs}\tau_0 = 1913$$

Substitute S_0= 0.015625, A_0= 0.01, K_A= 13.4 (from **entry 3**), $k_{obs}\tau_0$ = 1913 into the equation

$$S_0 + A_0 = \frac{S_0A_0\,k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.015625 + 0.01 = \frac{0.015625 \times 0.01 \times 1913}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{1913} - \frac{1}{13.4}$$

$$k_{\mathrm{PCET}}\tau_0 = 188$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (142+188)/2 = 165

$\Delta G^{\circ}_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.54 (same as in entry 3)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 18.28

τ_0 = 2.02us

error of $\Delta G^{\circ}_{\text{H-bond}}$ (kcal/mol) = 0.01 (same as in entry 3)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.09

5.12. Entry 12.

Neither ketone nor acid quenches the luminescence of reductant **7** *Ir (III). Therefore, the following equation is used:

$$I_0/I = 1 + k_{obs}\tau_0 \mathrm{S}_0\mathrm{A}_0$$

In all experiments, the solution was irradiated at 370nm, and fluorescence was measured at 491nm.

Table S5.12.1. Luminescence quenching data with S_0= 0.0625M, A_0= 0.0060M. S_0 fixed at 0.0625M. A_0 varied from 0.003 to 0.0125M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.003	0.000188	274	271	269	271.3333	1.253071
0.004	0.00025	249	248	247	248	1.370968
0.005	0.000313	234	234	232	233.3333	1.457143
0.0075	0.000469	200	199	198	199	1.708543
0.01	0.000625	180	178	179	179	1.899441
0.0125	0.000781	161	160	160	160.3333	2.120582

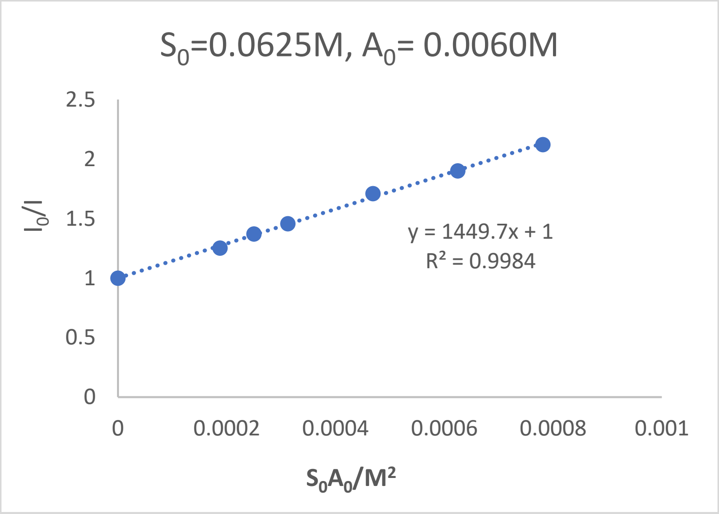


Figure S5.12.1. Stern-Volmer plot of luminescence data in **Table S5.12.1.**

I_0 was extrapolated from the six data points.

$k_{obs}\tau_0$ = 1450

Substitute S_0= 0.0625, A_0= 0.006, K_A= 2.06 (from **entry 4**), $k_{obs}\tau_0$ = 1450 into the equation

$$S_0 + A_0 = \frac{S_0A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.0625 + 0.006 = \frac{0.0625 \times 0.006 \times 1450}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{1450} - \frac{1}{2.06}$$

$$k_{\mathrm{PCET}}\tau_0 = 803$$

Table S5.12.1. Luminescence quenching data with S_0= 0.025M, A_0= 0.0060M. S_0 fixed at 0.025M. A_0 varied from 0.004 to 0.010M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.004	0.0001	853	853	855	853.6667	1.156189
0.005	0.000125	815	812	802	809.6667	1.21902
0.006	0.00015	784	789	785	786	1.255725
0.008	0.0002	731	734	730	731.6667	1.348975
0.01	0.00025	685	686	691	687.3333	1.435984

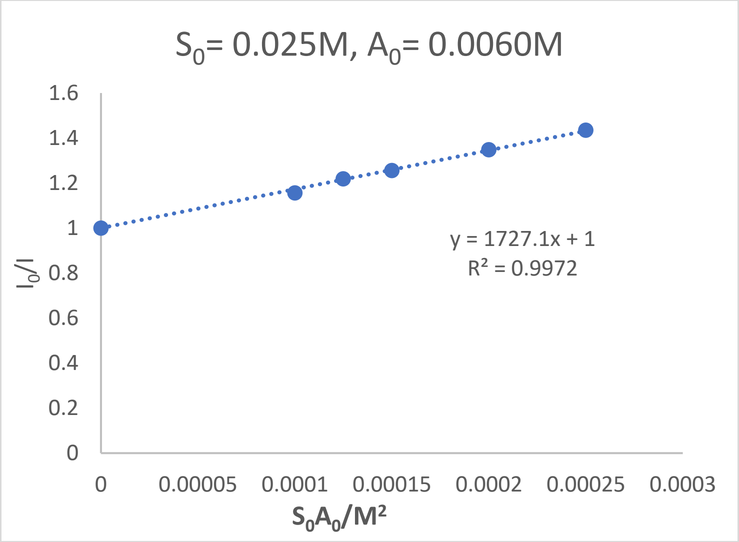


Figure S5.12.2. Stern-Volmer plot of luminescence data in **Table S5.12.2.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 1727

Substitute S_0= 0.025, A_0= 0.006, K_A= 2.06 (from **entry 4**), $k_{obs}\tau_0$ = 1727 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.025 + 0.006 = \frac{0.025 \times 0.006 \times 1727}{k_{PCET\ SV}} + \frac{k_{PCET\ SV}}{1727} - \frac{1}{2.06}$$

$$k_{\mathrm{PCET}}\tau_0 = 793$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (803+793)/2 = 798

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -0.43 (same as in entry 4)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 19.79

τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.03 (same as in entry 4)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.03 (same as in entry 4)

5.13. Entry 13.

Neither ketone nor acid quenches the luminescence of reductant **7** *Ir (III). Therefore, the following equation is used:

$$I_0/I = 1 + k_{obs}\tau_0 \mathrm{S}_0 \mathrm{A}_0$$

In all experiments, the solution was irradiated at 370nm, and fluorescence was measured at 491nm.

Table S5.13.1. Luminescence quenching data with S_0= 0.050M, A_0= 0.0040M. S_0 fixed at 0.050M. A_0 varied from 0.002 to 0.006M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.002	0.0001	590	590	590	590	1.211864
0.003	0.00015	545	542	540	542.3333	1.318377
0.004	0.0002	501	499	500	500	1.43
0.005	0.00025	464	464	467	465	1.537634
0.006	0.0003	432	431	431	431.3333	1.657651

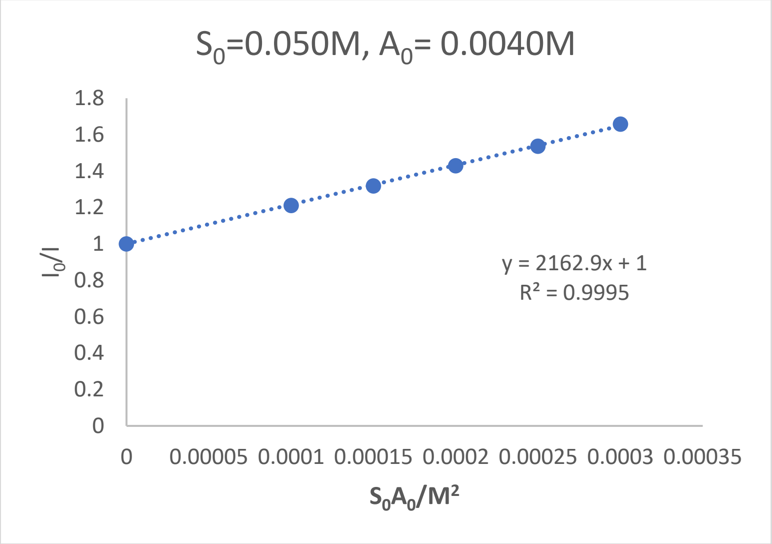


Figure S5.13.1. Stern-Volmer plot of luminescence data in **Table S5.13.1.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$= 2163

Substitute S_0= 0.05, A_0= 0.00, K_A= 6.2 (from **entry 5**), $k_{obs\ SV}$ = 2163 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.05 + 0.004 = \frac{0.05 \times 0.004 \times 2163}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{2163} - \frac{1}{6.2}$$

$$k_{\mathrm{PCET}}\tau_0 = 463$$

Table S5.13.2. Luminescence quenching data with S_0= 0.100M, A_0= 0.0040M. S_0 fixed at 0.100M. A_0 is varied from 0.002 to 0.006M

A_0/M	S_0A_0/ M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.002	0.0002	500	500	501	500.3333	1.295137
0.003	0.0003	438	438	439	438.3333	1.478327
0.004	0.0004	394	394	392	393.3333	1.647458
0.005	0.0005	359	358	358	358.3333	1.808372
0.005825	0.000583	333	333	332	332.6667	1.947896

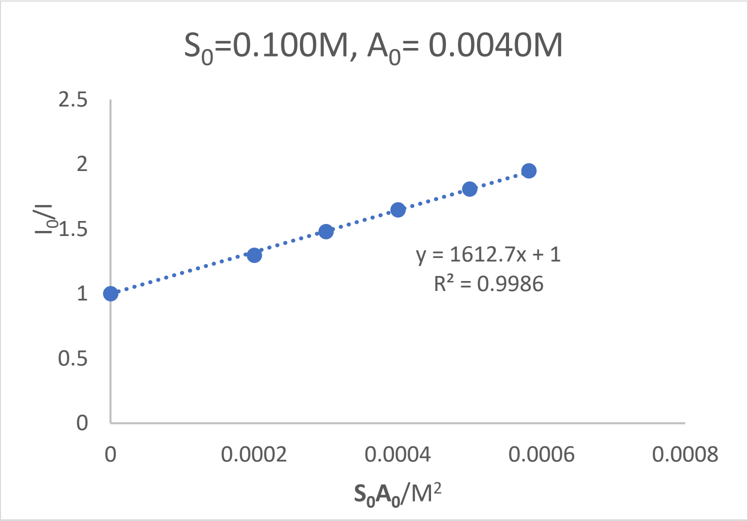


Figure S5.13.2. Stern-Volmer plot of luminescence data in **Table S5.13.2.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 1613

Substitute S_0= 0.100, A_0= 0.00, K_A= 6.2 (from **entry 5**), $k_{obs}\tau_0$ = 1613 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.10 + 0.004 = \frac{0.10 \times 0.004 \times 1613}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{1613} - \frac{1}{6.2}$$

$$k_{\mathrm{PCET}}\tau_0 = 425$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (463+425)/2 = 444

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.08 (same as in entry 5)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 19.209

τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.02 (same as in entry 5)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.04

5.14. Entry 14.

Neither ketone nor acid quenches the luminescence of reductant **8** *Ir (III). Therefore, the following equation is used:

$$I_0/I = 1 + k_{obs}\tau_0 \mathrm{S}_0\mathrm{A}_0$$

In all experiments, the solution was irradiated at 365nm, and fluorescence was measured at 491nm.

Table S5.14.1. S_0 fixed at 0.100 M, A_0 varied from 0.002 to 0.005M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
	0					1
0.002132	0.000213247	566	570	568	568	1.223592
0.002666	0.000266559	545	544	545	544.6667	1.27601
0.003732	0.000373182	505	502	502	503	1.38171
0.004265	0.000426494	481	478	483	480.6667	1.445908
0.004798	0.000479806	459	459	459	459	1.514161

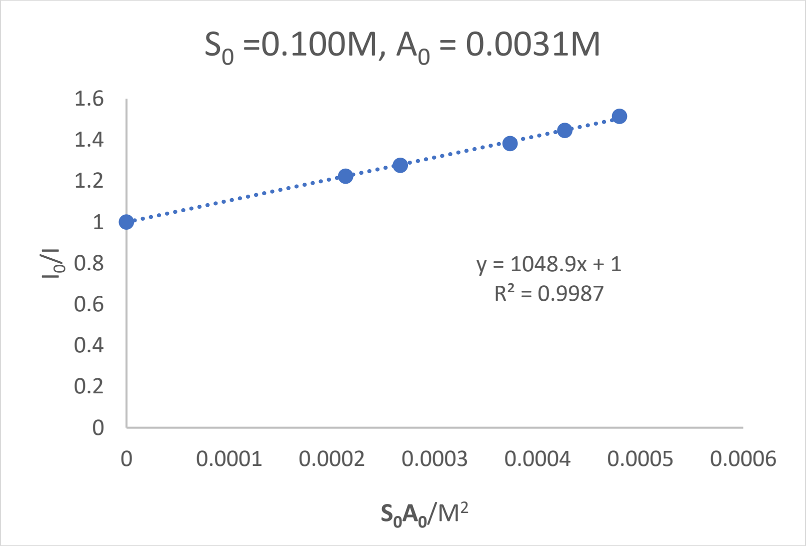


Figure S5.14.1. Stern-Volmer plot of luminescence data in **Table S5.14.1.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 1049

Table S5.14.2. S_0 fixed at 0.040M. A_0 varied from 0.004 to 0.011M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.004372	0.000174863	916	917	917	916.6667	1.293818
0.005464	0.000218578	863	865	862	863.3333	1.373745
0.006557	0.000262294	828	830	829	829	1.430639
0.00765	0.000306009	798	783	790	790.3333	1.500633
0.009836	0.000393441	722	726	722	723.3333	1.639631
0.010929	0.000437156	698	698	697	697.6667	1.699952

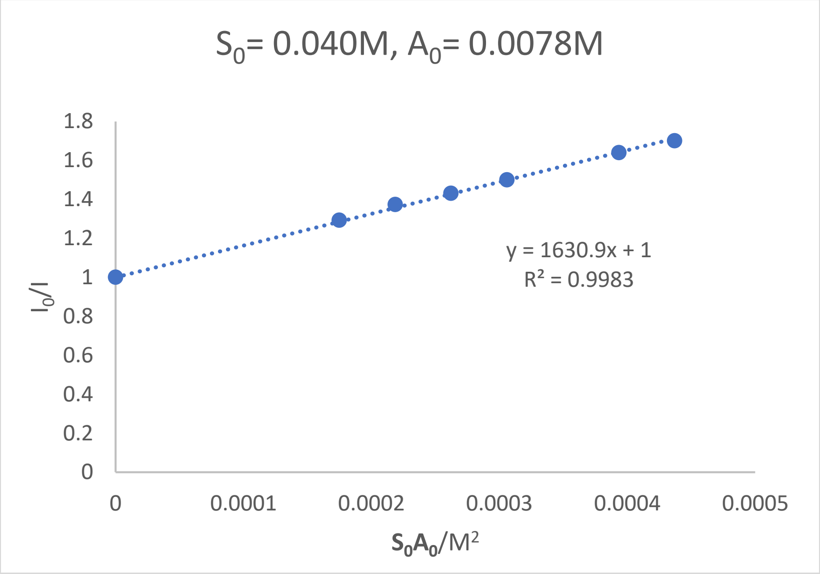


Figure S5.14.2. Stern-Volmer plot of luminescence data in **Table S5.14.2.**

I_0 was extrapolated from the six data points.

$k_{obs}\tau_0$ = 1631

Table S5.14.3. S_0 **is fixed at 0.0625M.** A_0 **is varied from 0.002 to 0.014M**

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.002798	0.000174863	745	745	739	743	1.238223
0.004197	0.000262294	686	674	671	677	1.358936
0.005596	0.000349725	622	616	620	619.3333	1.485468
0.008393	0.000524588	530	534	534	532.6667	1.727159
0.011191	0.00069945	470	470	473	471	1.953291
0.013989	0.000874313	416	416	422	418	2.200957

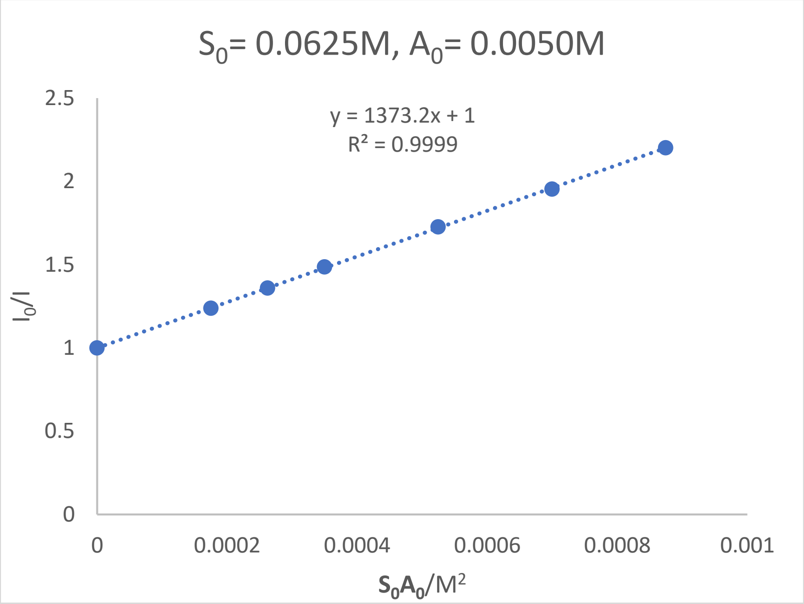


Figure S5.14.3. Stern-Volmer plot of luminescence data in **Table S5.14.3.**

I_0 was extrapolated from the six data points.

$k_{obs}\tau_0$ = 1373

Table S5.14.4. S_0 fixed at 0.156M. A_0 varied from 0.002 to 0.009M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001791	0.00027978	431	429	422	427.3333	1.214509
0.002686	0.00041967	397	387	390	391.3333	1.326235
0.003581	0.00055956	351	351	353	351.6667	1.475829
0.007162	0.00111912	276	276	277	276.3333	1.878166
0.008953	0.0013989	248	248	244	246.6667	2.104054

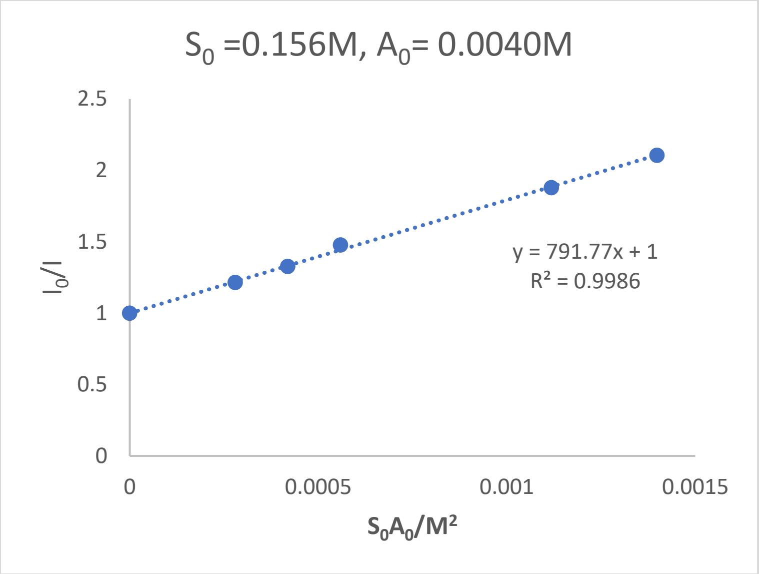


Figure S5.14.4. Stern-Volmer plot of luminescence data in **Table S5.14.4.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 792

$$S_0 + A_0 = \frac{S_0 A_0 \; k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.14.5. Solutions to Key Equation 8 and Entry 14 in Table S5.

	S_0 (M)	**A_0 (M)**	**S_0A_0 (M^2)**	**S_0+A_0 (M)**	**$k_{obs}\tau_0$**
1	0.100	0.0031	0.00031	0.103	1050
2	0.040	0.0078	0.00031	0.0478	1630
3	0.0625	0.0050	0.00031	0.0675	1370
4	0.156	0.0040	0.00062	0.160	790

	K_A/M^{-1}	**$k_{PCET}\tau_0$/M^{-1}**
1&2	17.5	166.0
1&3	18.9	161.5
1&4	14.0	181.0
2&3	16.2	174.0
2&4	16.3	173.0
3&4	16.1	175.0
average	16.5	172

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.66

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{PCET}\tau_0/\tau_0$]= 18.47

τ_0 = 1.61us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.05

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.04

5.15. Entry 15.

Neither ketone nor acid quenches the luminescence of reductant **8** *Ir (III). Therefore, the following equation is used:

$$I_0/I = 1 + k_{obs}\tau_0\mathrm{S}_0\mathrm{A}_0$$

In all experiments, the solution was irradiated at 365nm, and fluorescence was measured at 491nm.

Table S5.15.1. S_0 fixed at 0.100M. A_0 varied from 0.0015 to 0.003M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001563	0.000156	690	689	690	689.6667	1.20783
0.001875	0.000188	666	668	668	667.3333	1.248252
0.002188	0.000219	648	645	650	647.6667	1.286155
0.002813	0.000281	614	614	614	614	1.356678
0.003125	0.000313	593	593	600	595.3333	1.399216

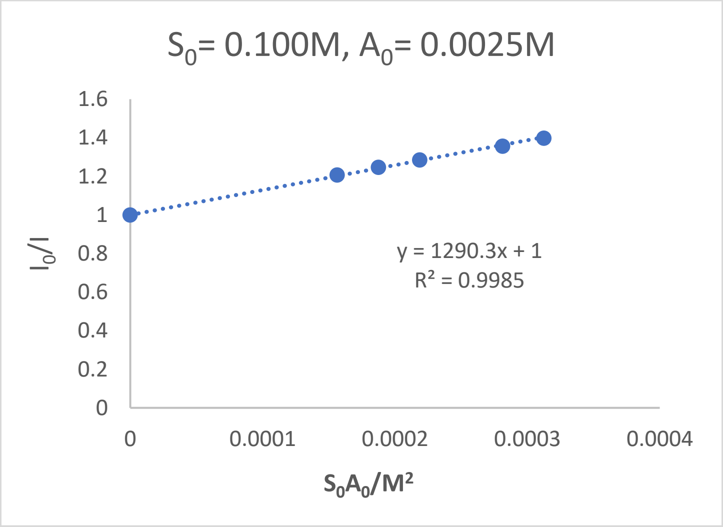


Figure S5.15.1. Stern-Volmer plot of luminescence data in **Table S5.15.1.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 1290

Table S5.15.2. S_0 fixed at 0.0312M. A_0 varied from 0.005 to 0.009M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.005	0.000156	989	964	952	968.3333	1.331153
0.006	0.000188	935	913	912	920	1.401087
0.007	0.000219	884	884	875	881	1.46311
0.008	0.00025	837	837	838	837.3333	1.539411
0.009	0.000281	808	805	803	805.3333	1.600579

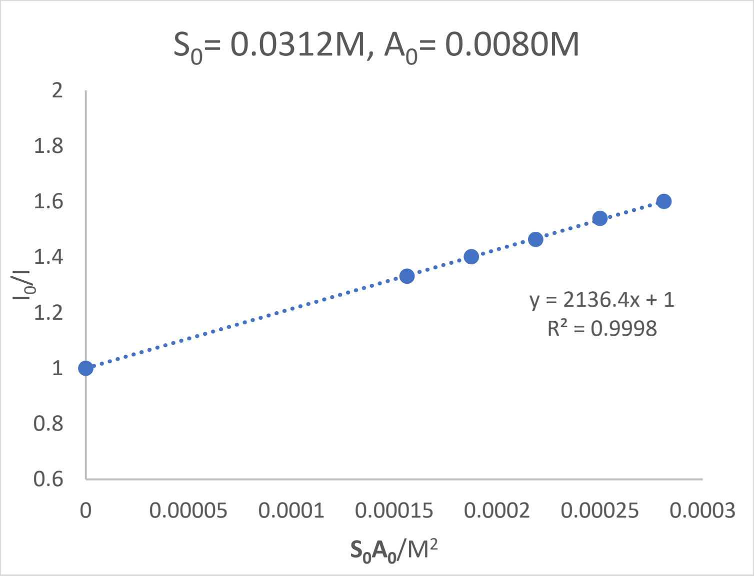


Figure S5.15.2. Stern-Volmer plot of luminescence data in **Table S5.15.2.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 2136

Table S5.15.3. S_0 fixed at 0.0625M. A_0 varied from 0.003 to 0.005M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.003	0.000188	792	777	780	783	1.319285
0.0035	0.000219	750	751	748	749.6667	1.377946
0.004	0.00025	722	727	726	725	1.424828
0.0045	0.000281	697	700	700	699	1.477825
0.005	0.000313	680	682	680	680.6667	1.51763

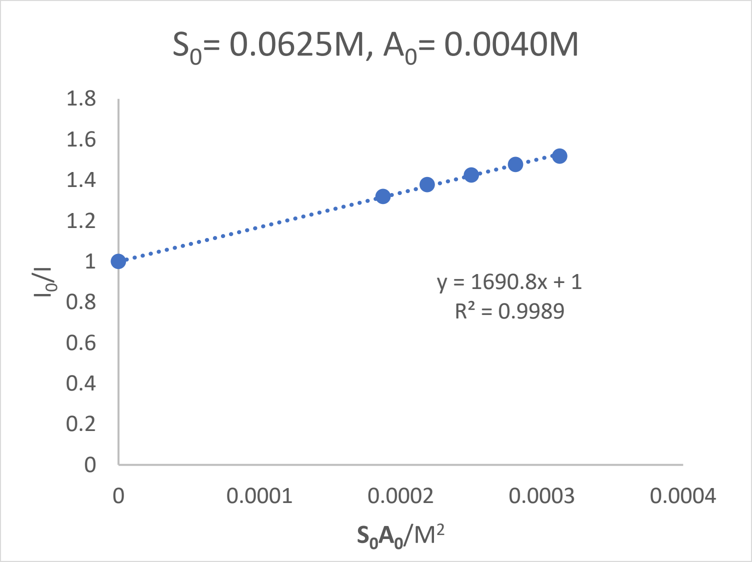


Figure S5.15.3. Stern-Volmer plot of luminescence data in **Table S5.15.3.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 1691

Table S5.15.4. S_0 is fixed at 0.156M. A_0 is varied from 0.001 to 0.002M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000156	573	573	573	573	1.144852
0.0012	0.000188	554	553	558	555	1.181982
0.0014	0.000219	543	541	541	541.6667	1.211077
0.0018	0.000281	516	516	516	516	1.271318
0.002	0.000313	502	502	504	502.6667	1.30504

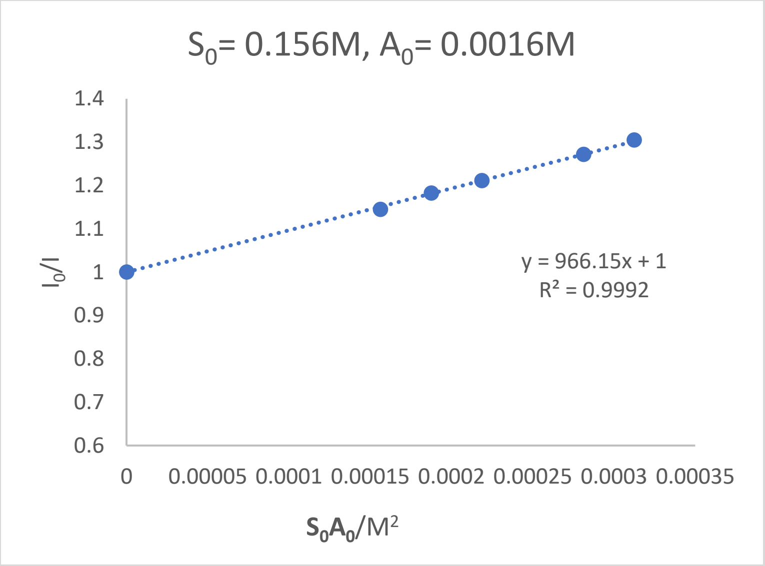


Figure S5.15.4. Stern-Volmer plot of luminescence data in **Table S5.15.4.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 966

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.15.5. Solutions to Key Equation 8 and Entry 15 in Table S5.

	S_0 (M)	**A_0 (M)**	**S_0A_0 (M^2)**	**S_0+A_0 (M)**	$\boldsymbol{k_{obs}\tau_0}$
1	0.100	0.0025	0.00025	0.103	1290
2	0.0312	0.0080	0.00025	0.0393	2140
3	0.0625	0.0040	0.00025	0.0665	1690
4	0.156	0.0016	0.00025	0.158	970

	K_A/M^{-1}	**$k_{PCET}\tau_0/M^{-1}$**
1&2	16.0	211.7
1&3	18.0	202.8
1&4	16.1	211.5
2&3	14.7	224.6
2&4	16.0	211.6
3&4	17.1	207.9
average	16.3	212

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = $-RT\ln K_A$= -1.65

$\ln[k_{PCET}(M^{-1}s^{-1})] = \ln[k_{PCET}\tau_0/\tau_0]$= 18.68

τ_0 = 1.61us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.04

error of $\ln[k_{PCET}(M^{-1}s^{-1})]$ = 0.05

5.16. Entry 16.

Ketone does not quench the luminescence of reductant **7** *Ir (III). Non-PCET quenching of reductant by acid alone (without ketone) is given by the following equation:

$$\frac{I_0}{I} = 1 + k''_{d\,SV}\,\mathbf{A_0}$$

In all experiments, the solution was irradiated at wavelength (365nm) that gives highest emission intensity at 491nm.

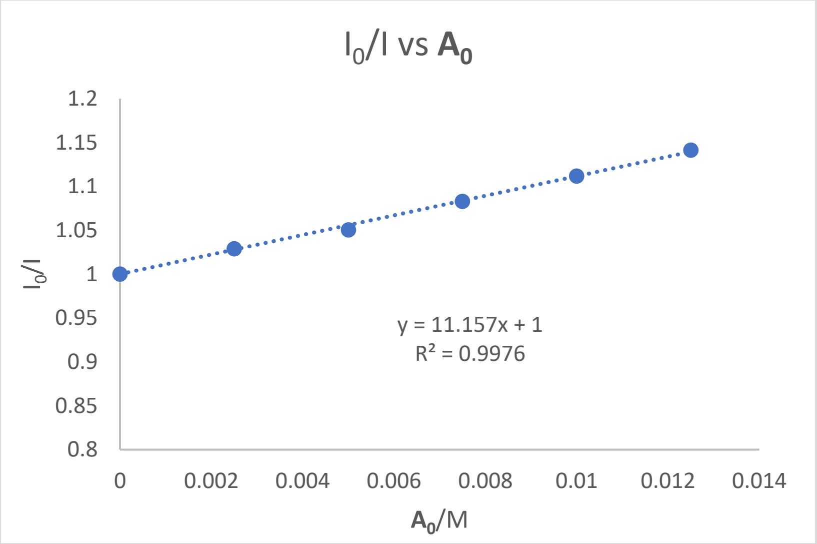


Figure S5.16. Stern-Volmer plot of luminescence data of non-PCET quenching by acid alone

$$k''_{d\,SV} = 11.2$$

Time-resolved luminescence suggests that the non-PCET quenching by acid is dynamic, therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + (k''_{SV} + k_{obs}\tau_0 \mathrm{S}_0)\mathrm{A}_0$$

Table S5.16.1. S_0 fixed at 0.040M. $\mathbf{A_0}$ varied from 0.000625 to 0.00313M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.000625	0.000025	362	363	363	362.6667	1.227022
0.00125	0.00005	304	301	303	302.6667	1.470264
0.001875	0.000075	263	264	262	263	1.692015
0.0025	0.0001	236	235	235	235.3333	1.890935
0.003125	0.000125	210	209	209	209.3333	2.125796

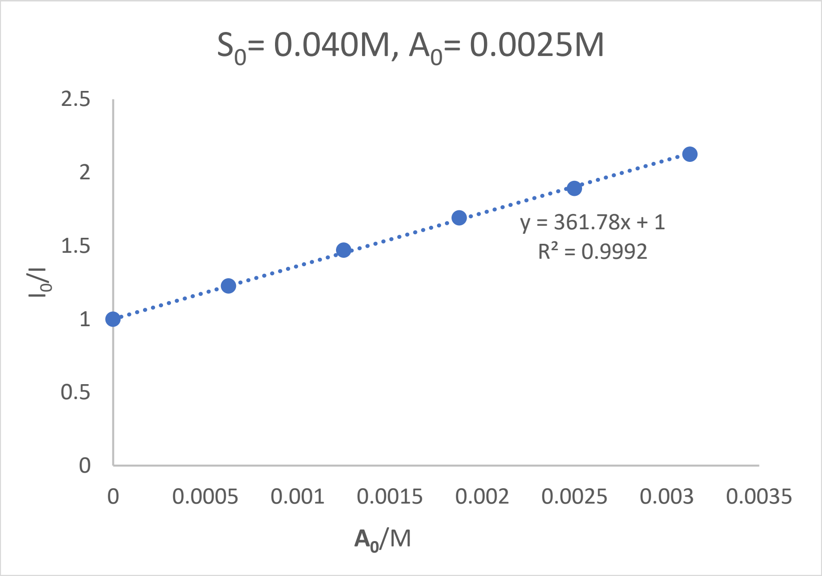


Figure S5.16.1. Stern-Volmer plot of luminescence data in **Table S5.16.1.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 361.78$$

$$11.2 + k_{obs}\tau_0 \times 0.04 = 361.78,\ k_{obs}\tau_0 = 8765$$

Table S5.16.2. S_0 fixed at 0.0625M. A_0 varied from 0.0008 to 0.0024M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0008	0.00005	290	292	295	292.3333	1.323831
0.0012	0.000075	257	257	257	257	1.505837
0.0016	0.0001	226	226	225	225.6667	1.714919
0.002	0.000125	203	204	203	203.3333	1.903279
0.0024	0.00015	184	186	185	185	2.091892

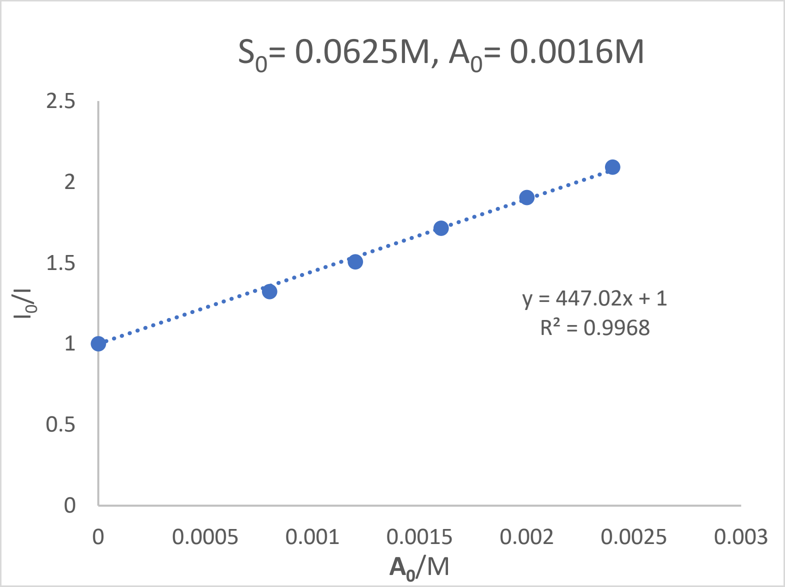


Figure S5.16.2. Stern-Volmer plot of luminescence data in **Table S5.16.2.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 447.02$$

$$11.2 + k_{obs}\tau_0 \times 0.0625 = 447.02,\ k_{obs}\tau_0 = 6973$$

Table S5.16.3. S_0 fixed at 0.050M. A_0 varied from 0.001 to 0.003M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.00005	289	284	287	286.6667	1.39186
0.0015	0.000075	247	248	248	247.6667	1.611036
0.002	0.0001	223	223	222	222.6667	1.791916
0.0025	0.000125	198	198	199	198.3333	2.011765
0.003	0.00015	181	181	180	180.6667	2.208487

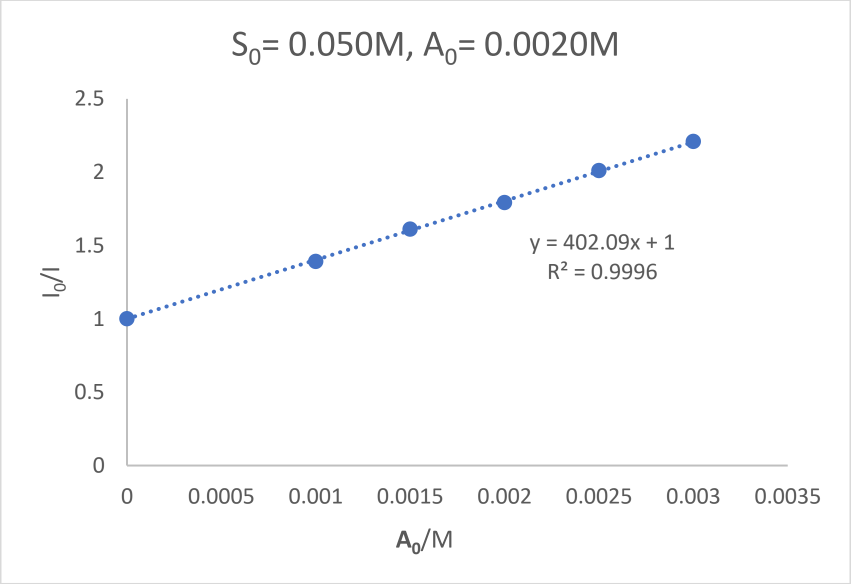


Figure S5.16.3. Stern-Volmer plot of luminescence data in **Table S5.16.3.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 402.09$$

$$11.2 + k_{obs}\tau_0 \times 0.05 = 402.09,\ k_{obs}\tau_0 = 7820$$

Table S5.16.4. S_0 fixed at 0.025M. A_0 varied from 0.001 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	364	362	364	363.3333	1.312844
0.002	0.00005	301	301	299	300.3333	1.588235
0.003	0.000075	268	263	265	265.3333	1.797739
0.004	0.0001	230	231	232	231	2.064935
0.006	0.00015	186	186	185	185.6667	2.56912

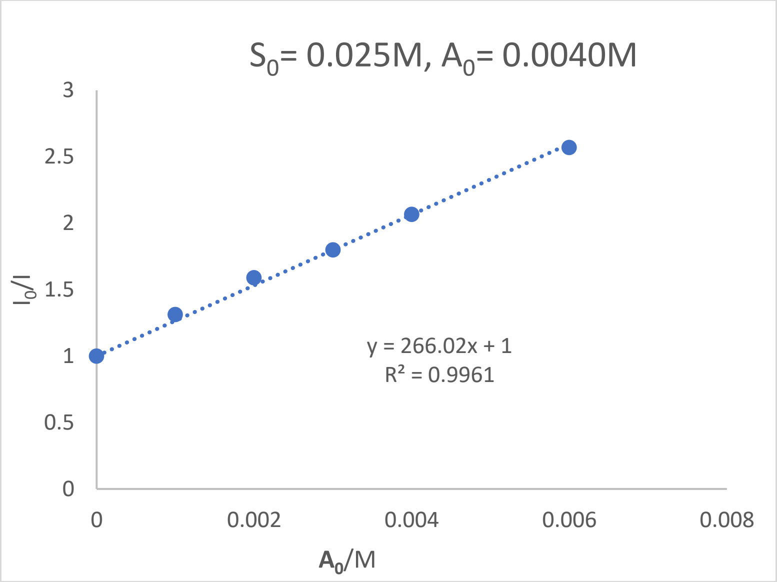


Figure S5.16.4. Stern-Volmer plot of luminescence data in **Table S5.16.4.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 266.02$$

$$11.2 + k_{obs}\tau_0 \times 0.025 = 266.02,\ k_{obs}\tau_0 = 10193$$

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.16.5. Solutions to Key Equation 8 and Entry 16 in Table S5.

	S_0 (M)	A_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.040	0.0025	0.0001	0.0425	8770
2	0.0625	0.0016	0.0001	0.0641	6970
3	0.050	0.0020	0.0001	0.052	7820
4	0.025	0.0040	0.0001	0.029	10200

	K_A/M^{-1}	$k_{PCET}\tau_0/M^{-1}$
1&2	22.9	745.0
1&3	26.0	699.0
1&4	18.0	855.0
2&3	20.2	786.0
2&4	20.3	784.0
3&4	20.4	783.0
average	21.3	775

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = $-RT\ln K_A$ = -1.81

$\ln[k_{PCET}(M^{-1}s^{-1})] = \ln[k_{PCET}\tau_0/\tau_0]$ = 19.77

τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.16

error of $\ln[k_{PCET}(M^{-1}s^{-1})]$ = 0.13

5.17. Entry 17.

Ketone does not quench the luminescence of reductant **7** *Ir (III). Non-PCET quenching of reductant by acid alone (without ketone) is given by the following equation:

$$\frac{I_0}{I} = 1 + k''_{d\,SV}\mathrm{A}_0$$

In all experiments, the solution was irradiated at wavelength (365nm) that gives highest emission intensity at 491nm. Time-resolved luminescence suggests that the non-PCET quenching by acid is dynamic, $k''_{d\,SV} = 11.2$ **(entry 16)**. Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + (k''_{SV} + k_{obs}\tau_0\mathrm{S}_0)\mathrm{A}_0$$

Table S5.17.1. S_0 is fixed at 0.0625M. A_0 is varied from 0.001 to 0.002M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.0000625	501	500	501	500.6667	1.963382
0.0012	0.000075	452	456	461	456.3333	2.154127
0.0014	0.0000875	413	421	420	418	2.351675
0.0016	0.0001	388	390	390	389.3333	2.524829
0.002	0.000125	338	338	338	338	2.908284

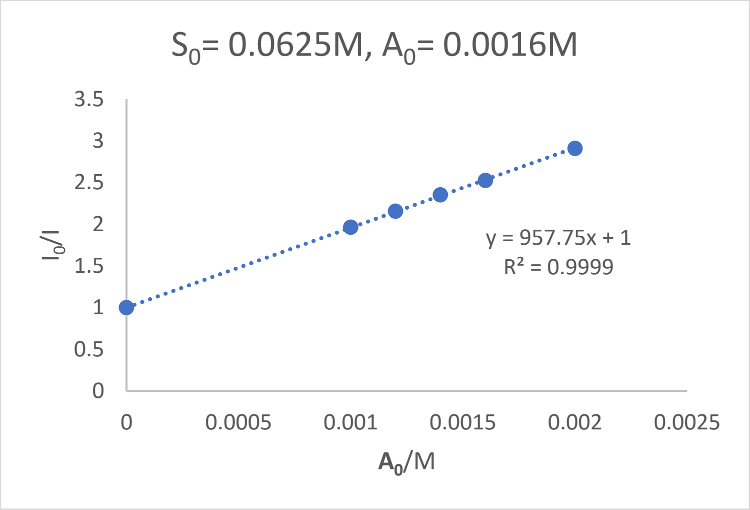


Figure S5.17.1. Stern-Volmer plot of luminescence data in **Table S5.17.1.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 957.75$$

$$11.2 + k_{obs}\tau_0 \times 0.0625 = 957.75,\ k_{obs}\tau_0 = 15145$$

Table S5.17.2. S_0 is fixed at 0.100M. A_0 is varied from 0.000625 to 0.00125M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.000625	0.0000625	540	538	538	538.6667	1.732054
0.00075	0.000075	493	492	496	493.6667	1.889939
0.000875	0.0000875	455	455	452	454	2.055066
0.001	0.0001	424	419	422	421.6667	2.212648
0.001125	0.0001125	394	392	396	394	2.36802
0.00125	0.000125	372	373	370	371.6667	2.510314

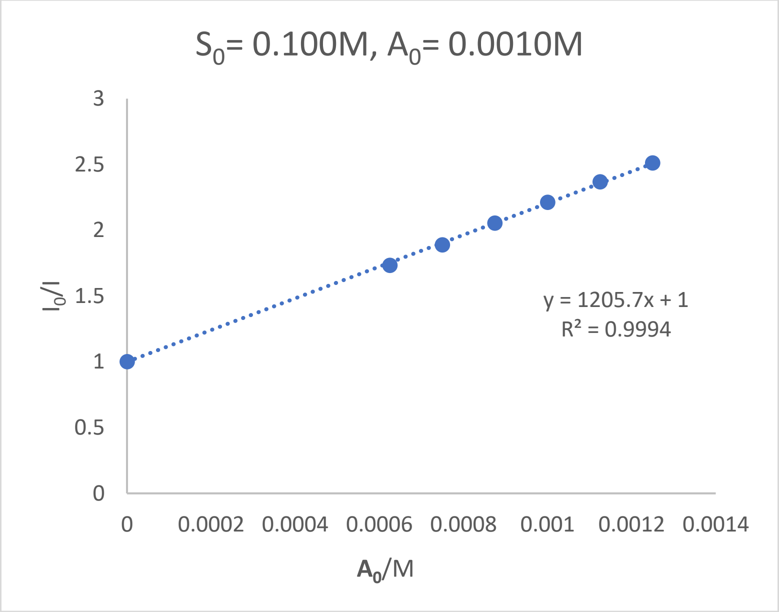


Figure S5.17.2. Stern-Volmer plot of luminescence data in **Table S5.17.2.**

I_0 was extrapolated from the six data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 1205.7$$

$$11.2 + k_{obs}\tau_0 \times 0.1 = 1205.7,\ k_{obs}\tau_0 = 11950$$

Table S5.17.3. S_0 is fixed at 0.125M. A_0 is varied from 0.0004 to 0.0012M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0004	0.00005	598	602	598	599.3333	1.510011
0.0006	0.000075	509	507	509	508.3333	1.780328
0.0008	0.0001	446	446	443	445	2.033708
0.001	0.000125	395	393	395	394.3333	2.295013
0.0012	0.00015	353	351	353	352.3333	2.56859

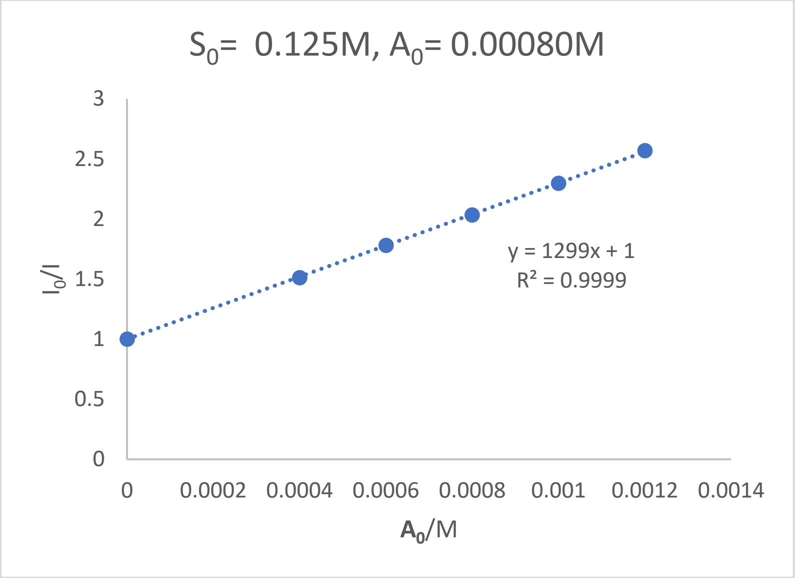


Figure S5.17.3. Stern-Volmer plot of luminescence data in **Table S5.17.3.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 1299$$

$$11.2 + k_{obs}\tau_0 \times 0.125 = 1299,\ k_{obs}\tau_0 = 10300$$

Table S5.17.4. S_0 fixed at 0.156M. A_0 varied from 0.00016 to 0.00096M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00016	0.000025	624	621	619	621.3333	1.252146
0.00048	0.000075	463	463	464	463.3333	1.679137
0.00064	0.0001	413	411	411	411.6667	1.889879
0.00096	0.00015	332	334	332	332.6667	2.338677

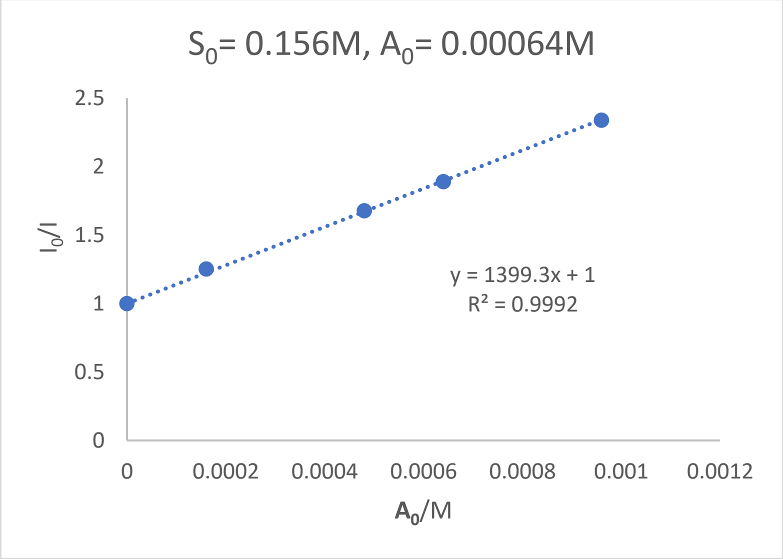


Figure S5.17.4. Stern-Volmer plot of luminescence data in **Table S5.17.4.**

I_0 was extrapolated from the four data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 1399$$

$$11.2 + k_{obs}\tau_0 \times 0.15625 = 1399,\ k_{obs}\tau_0 = 8883$$

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.17.5. Solutions to Key Equation 8 and Entry 17 in Table S5.

	S_0 (M)	A_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.0625	0.0016	0.0001	0.0641	15100
2	0.100	0.0010	0.0001	0.101	11900
3	0.125	0.00080	0.0001	0.126	10300
4	0.156	0.00064	0.0001	0.157	8880

	K_A/M^{-1}	$k_{PCET}\tau_0$/M^{-1}
1&2	14.0	2042
1&3	14.6	1994
1&4	14.5	2000
2&3	16.2	1927
2&4	15.2	1973
3&4	14.3	2012
average	14.8	1991

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = $-RT\ln K_A$= -1.60

$\ln[k_{PCET}(M^{-1}s^{-1})] = \ln[k_{PCET}\tau_0/\tau_0]$= 20.71

τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.06

error of $\ln[k_{PCET}(M^{-1}s^{-1})]$ = 0.06

5.18. Entry 18.

Non-PCET quenching of reductant by acid alone (without ketone) is given by the following equation:

$$\frac{I_0}{I} = 1 + k''_{d\,SV}\mathrm{A}_0$$

Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$$\mathrm{I_0/I = 1+}\ k'_{\mathrm{SV}}\mathrm{S_0}$$

Time-resolved fluorometry suggest that both ketone and acid dynamically quench reductant **6** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + \frac{(k''_{SV} + k_{obs}\tau_0\mathrm{S}_0)\mathrm{A}_0}{1 + k'_{d\,SV}\mathrm{S}_0}$$

$k'_{d\,SV} = 0.574$ (see **entry 5**)

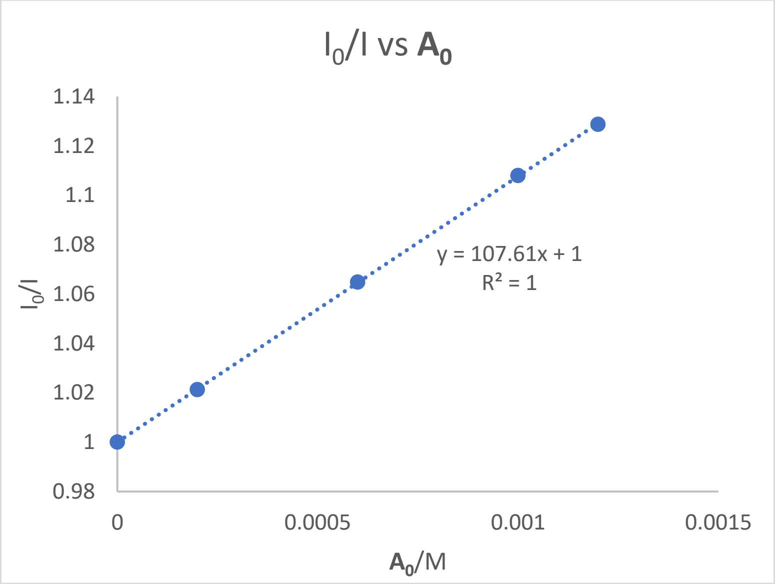


Figure S5.18. Stern-Volmer plot of luminescence data of non-PCET quenching by acid alone

$$k''_{d\,SV} = 107.6$$

Table S5.18.1. S_0 = 0.0625M, A_0 = 0.0008M. S_0 fixed at 0.0625M. A_0 varied from 0.0004 to 0.0012M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0004	0.000025	377	377	377	377	2.466844
0.0006	0.0000375	300	301	297	299.3333	3.106904
0.0008	0.00005	246	246	245	245.6667	3.785617
0.001	0.0000625	208	208	209	208.3333	4.464
0.0012	0.000075	179	180	180	179.6667	5.176252

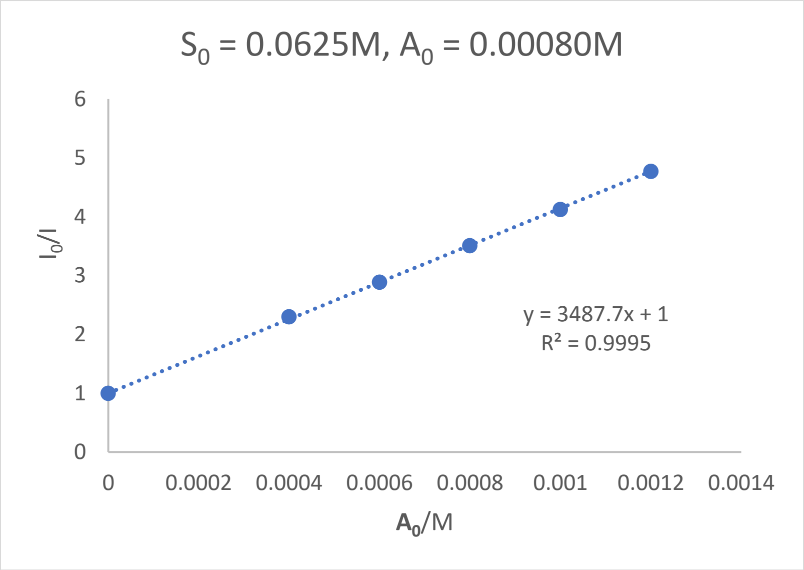


Figure S5.18.1. Stern-Volmer plot of luminescence data in **Table S5.18.1.**

I_0 was extrapolated from the five data points.

$$\frac{k''_{SV} + k_{obs}\tau_0 S_0}{1 + k'_{d\,SV} S_0} = 3488$$

$$k''_{SV} + k_{obs}\tau_0 S_0 = 3488 \times (1 + 0.574 \times 0.0625) = 3613$$

$$107.6 + 0.0625\, k_{obs}\tau_0 = 3613$$

$$k_{obs}\tau_0 = 56086$$

Substitute S_0= 0.0625, A_0= 0.0008, K_A= 14.8 (from **entry 16**), $k_{obs}\tau_0$ = 56086 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.0625 + 0.0008 = \frac{0.0625 \times 0.0008 \times 56086}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{56086} - \frac{1}{14.8}$$

$$k_{\mathrm{PCET}}\tau_0 = 7318$$

Table S5.18.2. S_0 = 0.100M, A_0 = 0.0005M. S_0 fixed at 0.100M. A_0 varied from 0.0001 to 0.00075M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00009375	9.375E-06	870	870	870	870	1.351724
0.0001875	1.875E-05	727	723	726	725.3333	1.621324
0.000375	0.0000375	540	542	542	541.3333	2.172414
0.0005625	5.625E-05	421	423	421	421.6667	2.788933
0.00075	0.000075	348	348	350	348.6667	3.372849

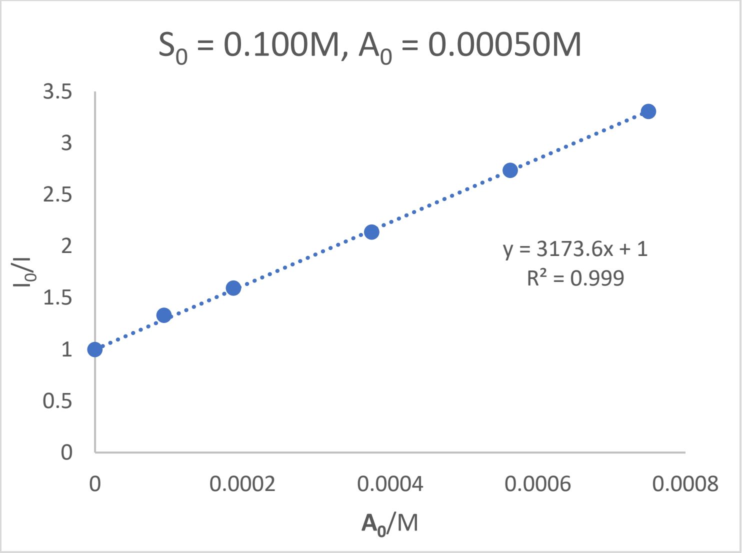


Figure S5.18.2. Stern-Volmer plot of luminescence data in **Table S5.18.2.**

I_0 was extrapolated from the five data points.

$$\frac{k''_{SV} + k_{obs}\tau_0 S_0}{1 + k'_{d\,SV} S_0} = 3174$$

$k''_{SV} + k_{obs}\tau_0 S_0$ = 3174 × (1+ 0.574 × 0.10) = 3356

107.6 + 0.1 $k_{obs}\tau_0$= 3356

$k_{obs}\tau_0$ = 32486

Substitute S_0= 0.1000, A_0= 0.0005, K_A= 14.8 (from entry 16), $k_{obs}\tau_0$ = 32486 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.10 + 0.0005 = \frac{0.10 \times 0.0005 \times 32486}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{32486} - \frac{1}{14.8}$$

$$k_{\mathrm{PCET}}\tau_0 = 5450$$

Average the two values of $k_{\mathrm{PCET}}\tau_0$ = (7318+5450)/2 = 6384

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.60 (same as in **entry 17**)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 21.94

τ_0 = 1.9us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.06 (same as in **entry 17**)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.16

5.19. Entry 19.

Time-resolved fluorometry suggests that acid, but not ketone, dynamically quenches reductant **7** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + (k''_{SV} + k_{obs}\tau_0 \mathrm{S}_0)\mathrm{A}_0$$

$$k''_{d\,SV} = 11.2 \text{ (see } \textbf{Entry 16}\text{)}$$

In all experiments, the solution was irradiated at 365nm, and fluorescence was measured at 491nm

Table S5.19.1. S_0 fixed at 0.040M. A_0 varied from 0.002 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.002	0.00008	373	373	370	372	1.897849
0.003	0.00012	305	303	303	303.6667	2.324918
0.004	0.00016	256	256	257	256.3333	2.754226
0.005	0.0002	220	220	221	220.3333	3.204236
0.006	0.00024	192	191	191	191.3333	3.689895

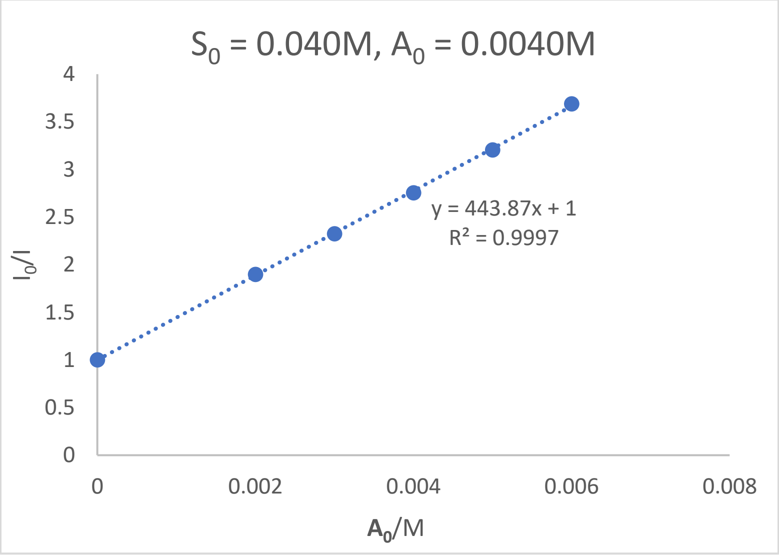


Figure S5.19.1. Stern-Volmer plot of luminescence data in **Table S5.19.1.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 443.9$$

$$11.2 + k_{obs}\tau_0 \times 0.04 = 443.9,\ k_{obs}\tau_0 = 10814$$

Table S5.19.2. S_0 fixed at 0.061M. A_0 varied from 0.003 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.003	0.000184	231	231	231	231	2.69697
0.004	0.000246	191	191	191	191	3.26178
0.005	0.000307	164	164	165	164.3333	3.791075
0.006	0.000368	140	140	142	140.6667	4.42891

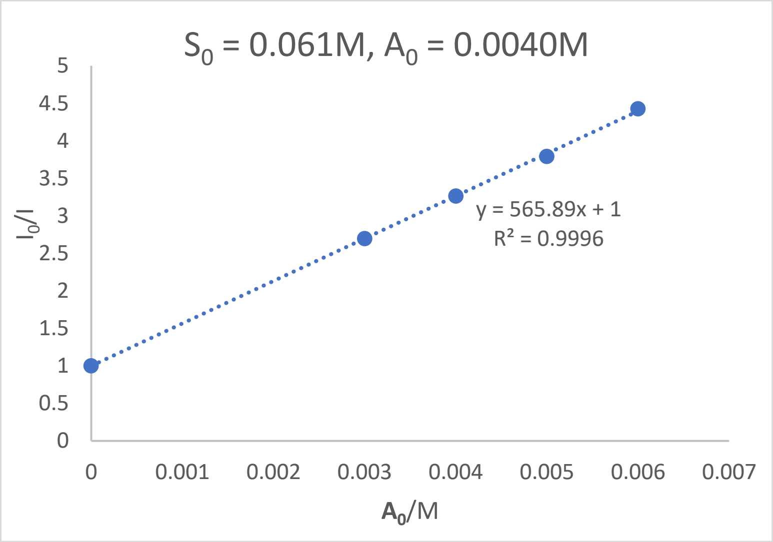


Figure S5.19.2. Stern-Volmer plot of luminescence data in **Table S5.19.2.**

I_0 was extrapolated from the four data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 565.9$$

$$11.2 + k_{obs}\tau_0 \times 0.0614 = 565.9,\ k_{obs}\tau_0 = 9035$$

Table S5.19.3. S_0 **fixed at 0.083M.** A_0 **varied from 0.003 to 0.006M**

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.003	0.000249	192	192	193	192.3333	2.984402
0.004	0.000331	157	158	160	158.3333	3.625263
0.005	0.000414	135	133	134	134	4.283582
0.006	0.000497	115	115	115	115	4.991304

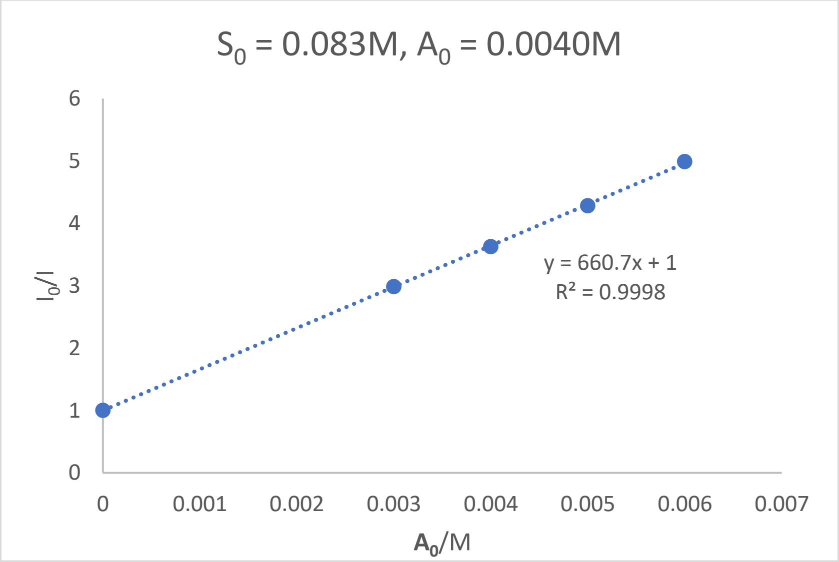


Figure S5.19.3. Stern-Volmer plot of luminescence data in **Table S5.19.3.**

I_0 was extrapolated from the four data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 660.7$$

$$11.2 + k_{obs}\tau_0 \times 0.0614 = 660.7,\ k_{obs}\tau_0 = 7836$$

Table S5.19.4. S_0 fixed at 0.104M. A_0 varied from 0.003 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.003	0.000311	170	170	170	170	3.176471
0.004	0.000415	138	138	139	138.3333	3.903614
0.005	0.000519	117	116	117	116.6667	4.628571
0.006	0.000622	101	100	100	100.3333	5.38206

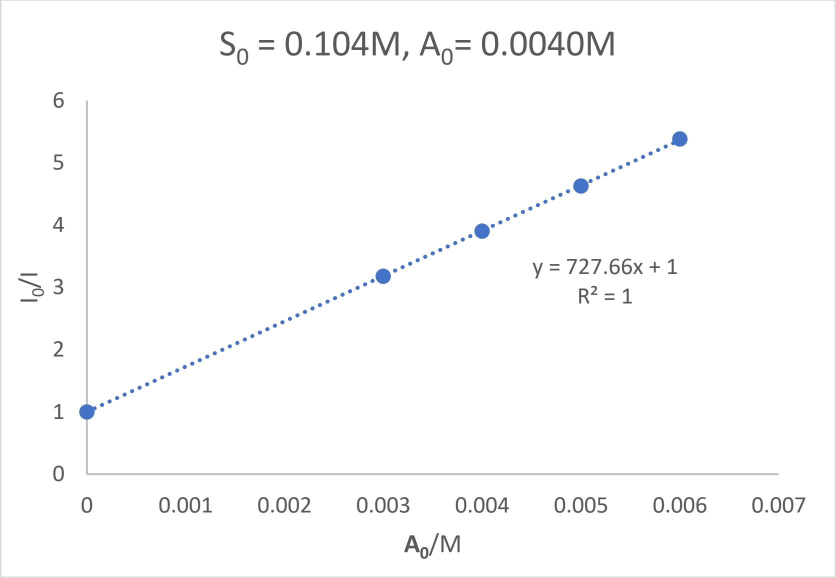


Figure S5.19.4. Stern-Volmer plot of luminescence data in **Table S5.19.4.**

I_0 was extrapolated from the four data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 727.7$$

$$11.2 + k_{obs}\tau_0 \times 0.0614 = 727.7,\ k_{obs}\tau_0 = 6910$$

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A} \quad (8)$$

Table 5.19.5. Solutions to Key Equation 8 and Entry 19 in Table S5.

	S_0 (M)	**A_0 (M)**	**S_0A_0 (M^2)**	**S_0+A_0 (M)**	**$k_{obs}\tau_0$**
1	0.04	0.004	0.00016	0.044	10814
2	0.061	0.004	0.000244	0.065	9035
3	0.083	0.004	0.000332	0.087	7836
4	0.104	0.004	0.000416	0.108	6910

	K_A/M^{-1}	**$k_{PCET}\tau_0$/M^{-1}**
1&2	15.6	1152
1&3	14.8	1193
1&4	14.6	1201
2&3	13.7	1236
2&4	13.8	1227
3&4	14.1	1218
average	14.4	1205

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.58

ln[k k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{PCET}\tau_0/\tau_0$]= 20.21

τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.03

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.03

5.20. Entry 20.

Non-PCET quenching of reductant by acid alone (without ketone) is given by the following equation:

$$\frac{I_0}{I} = 1 + k''_{d\,SV}\mathrm{A}_0$$

$$k''_{d\,SV} = 107.6\ (\textbf{entry 18})$$

Therefore, the following equation is used:

$$\frac{I_0}{I} = \ 1 + (k''_{SV} + k_{obs}\tau_0\mathrm{S}_0)\mathrm{A}_0$$

The solution was irradiated at 375nm, and fluorescence was measured at 518nm.

Table S5.20.1. S_0= 0.0357M, A_0= 0.0006M. S_0 fixed at 0.0357M. A_0 varied from 0.0001 to 0.0009M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.000145	5.16998E-06	411	412	410	411	1.175182
0.000435	1.55099E-05	320	321	321	320.6667	1.506237
0.00058	2.06799E-05	288	289	290	289	1.67128
0.000725	2.58499E-05	262	264	262	262.6667	1.838832
0.00087	3.10199E-05	240	240	241	240.3333	2.009709

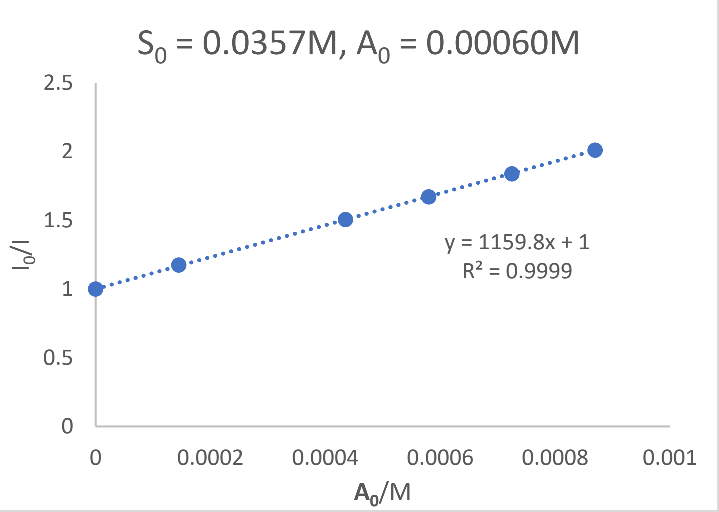


Figure S5.20.1. Stern-Volmer plot of luminescence data in **Table S5.20.1.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 1160$$

$$107.6 + k_{obs}\tau_0 \times 0.0357 = 1160,\ k_{obs}\tau_0 = 29480$$

Table S5.20.2. Repeat S_0= 0.0357M, A_0= 0.0006M. S_0 fixed at 0.0357M. A_0 varied from 0.0001 to 0.0009M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00029	1.034E-05	325	324	324	324.3333	1.31038
0.000435	1.55099E-05	290	292	290	290.6667	1.462156
0.00058	2.06799E-05	263	265	263	263.6667	1.611884
0.000725	2.58499E-05	240	240	242	240.6667	1.765928
0.00087	3.10199E-05	221	220	220	220.3333	1.928896

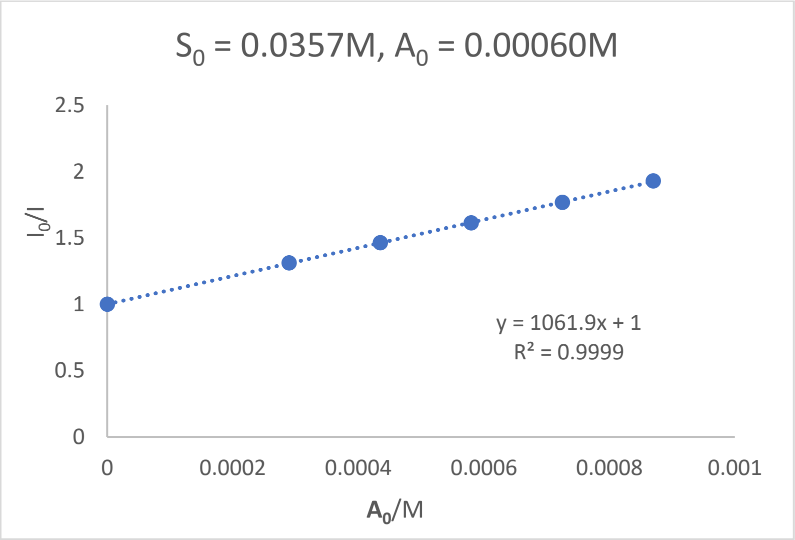


Figure S5.20.2. Stern-Volmer plot of luminescence data in **Table S5.20.2.**

I_0 was extrapolated from the five data points.

$$k''_{SV} + k_{obs}\tau_0 S_0 = 1062$$

$$107.6 + k_{obs}\tau_0 \times 0.0357 = 1062,\ k_{obs}\tau_0 = 26720$$

Average $k_{obs}\tau_0$ = (29480 + 26720)/2 = 28100

Substitute S_0= 0.0357, A_0= 0.0006, K_A= 21.3 (from **entry 16**), $k_{obs}\tau_0$= 28100 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.0357 + 0.0006 = \frac{0.0357 \times 0.0006 \times 28100}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{28100} - \frac{1}{21.3}$$

$$k_{\mathrm{PCET}}\tau_0 = 2300$$

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -1.81 (same as entry 16)

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{\text{PCET}}\tau_0/\tau_0$]= 20.93

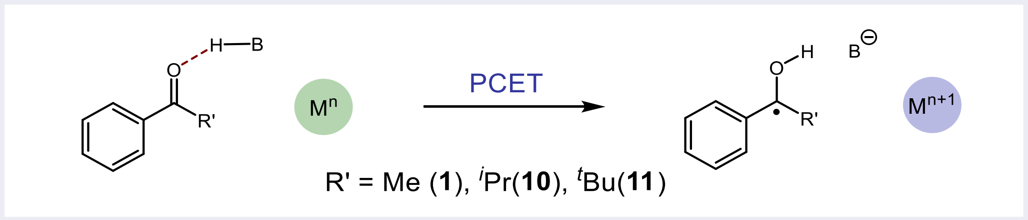
τ_0 = 2.02us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.16 (same as entry 16)

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.13 (same as entry 16)

6. Brønsted Slopes of Bulkier Ketone-Acid Adduct

We used $(PhO)_2P(O)OH$ as the Bronsted acid in all experiments. In each series, i.e. same acid and ketone, driving force was varied by the reduction potential of the photo reductant only.



6.1. Series of iso-propyl phenyl ketone

In the four data points, same ketone and acid were used in all. Four photocatalyst are used as the reductant. Iso-propyl phenyl ketone does not affect the luminescence of reductant **6** *Ir (III) or reductant **7** *Ir (III), and dynamically quench reductant **8** *Ir (III) and reductant **9** *Ir (III).

*6.1.1.1a Reductant **6** Experiment 1a*

Neither ketone nor acid quench the luminescence of reductant **6** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0\ S_0A_0$$

The solution was irradiated at 375nm and fluorescence was measured at 518nm.

Table S6.1.1.1a. S_0 fixed at 0.025 M, A_0 varied from 0.001 to 0.006 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	503	503	503	503	1.059642
0.002	0.00005	476	475	475	475.3333	1.121318
0.004	0.0001	431	431	430	430.6667	1.237616
0.005	0.000125	413	415	415	414.3333	1.286404
0.006	0.00015	400	400	400	400	1.3325

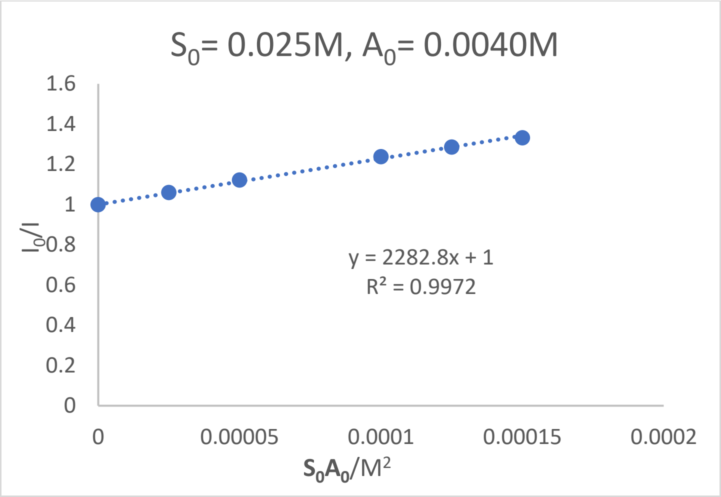


Figure S6.1.1.1a. Stern-Volmer plot of luminescence data in **Table S6.1.1.1a.**

I_0 was extrapolated from the five data points.

$$k_{obs}\tau_0 = 2283$$

*6.1.1.1b Reductant **6** Experiment 1b*

The solution was irradiated at 375nm and fluorescence was measured at 518nm.

Table S6.1.1.1b. Repeat- S_0 fixed at 0.0250 M, A_0 varied from 0.001 to 0.006 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	460	458	458	458.6667	1.059593
0.002	0.00005	433	434	434	433.6667	1.120676
0.003	0.000075	416	413	413	414	1.173913
0.004	0.0001	396	395	395	395.3333	1.229342
0.005	0.000125	376	376	375	375.6667	1.2937
0.006	0.00015	358	359	356	357.6667	1.358807

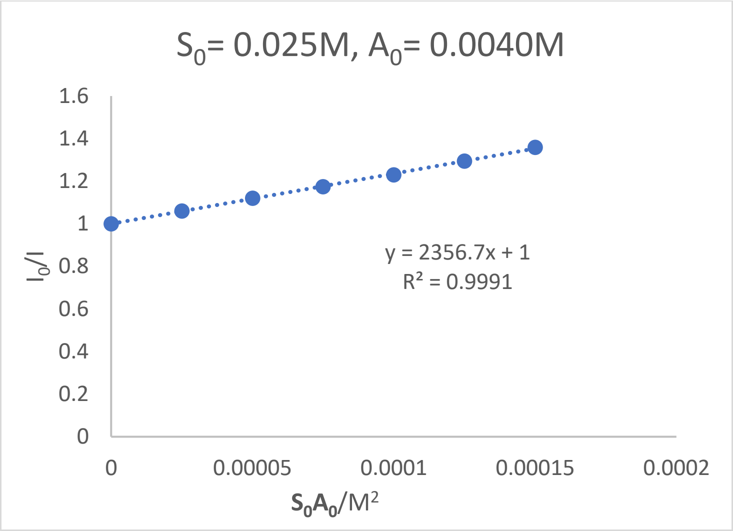


Figure S6.1.1.1b. Stern-Volmer plot of luminescence data in **Table S6.1.1.1b.**

I_0 was extrapolated from the six data points.

$$k_{obs}\tau_0 = 2357$$

$k_{obs}\tau_0$ $average$ = (2283+2357)/2 = 2320 ± 37

*6.1.1.2. Reductant **6** Experiment 2*

The solution was irradiated at 375nm and fluorescence was measured at 518nm.

Table S6.1.1.2. S_0 fixed at 0.050 M, A_0 varied from 0.003 to 0.006 M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.003	0.00015	184	185	184	184.3333	1.323689
0.004	0.0002	171	172	170	171	1.426901
0.005	0.00025	160	159	159	159.3333	1.531381
0.006	0.0003	150	148	148	148.6667	1.641256

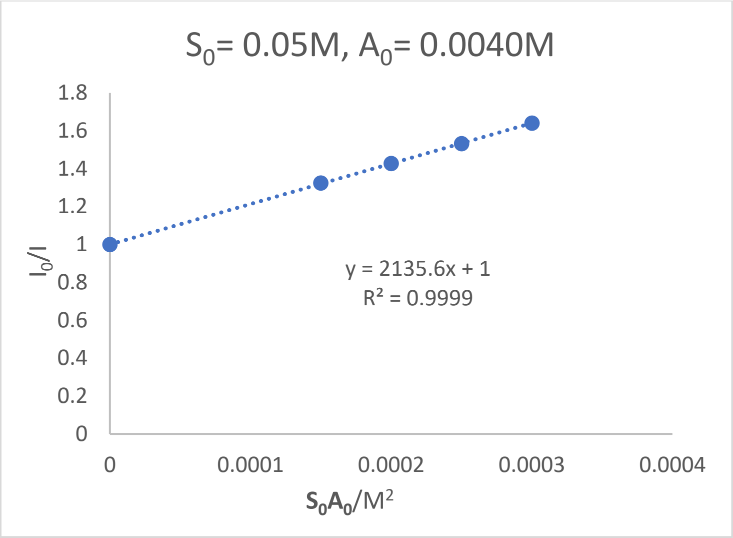


Figure S6.1.1.2. Stern-Volmer plot of luminescence data in Table S6.1.1.2.

I_0 was extrapolated from the four data points.

$$k_{obs}\tau_0 = 2136$$

*6.1.1.3. Reductant **6** Experiment 3*

The solution was irradiated at 375nm and fluorescence was measured at 518nm.

Table S6.1.1.3. S_0 fixed at 0.100 M, A_0 varied from 0.0005 to 0.0025M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0005	0.00005	472	473	473	472.6667	1.100141
0.001	0.0001	441	442	443	442	1.176471
0.0015	0.00015	409	409	410	409.3333	1.270358
0.002	0.0002	383	383	378	381.3333	1.363636
0.0025	0.00025	352	352	356	353.3333	1.471698

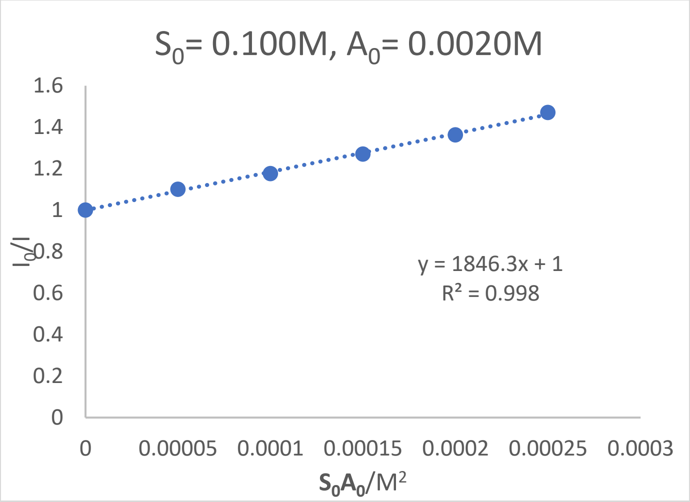


Figure S6.1.1.3. Stern-Volmer plot of luminescence data in Table S6.1.1.3.

I_0 was extrapolated from the five data points.

$$k_{obs}\tau_0 = 1846$$

Table S6.1.1.4. Solutions to Key Equation 8

	S_0 (M)	A_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.025	0.0040	0.0001	0.029	2320
2	0.050	0.0040	0.0002	0.054	2140
3	0.100	0.0020	0.0002	0.10	1850

	K_A/M^{-1}	$k_{PCET}\tau_0$/M^{-1}
1&2	3.9	665
1&3	3.9	658
2&3	4.0	654
avg	3.9	659

$\Delta G°_{H\text{-bond}}$ (kcal/mol) = -RTlnK_A= -0.806

ln[k_{PCET}(M^{-1}s^{-1})] = ln[$k_{PCET}\tau_0/\tau_0$]= 19.664

τ_0 = 1.9 us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.01

error of $\ln[k_{\text{PCET}}$ (M^{-1}s^{-1})] = 0.01

6.1.2. Reductant **9**

In all experiments, the solution was irradiated at 370nm and fluorescence was measured at 500nm.

The luminescence of *Ir (III) is not affected by $(PhO)_2P(O)OH$ and is dynamically quenched by iso-propyl phenyl ketone. Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + \frac{k_{obs}\tau_0 \mathrm{S}_0 \mathrm{A}_0}{1 + k'_{d\,SV}\mathrm{S}_0}$$

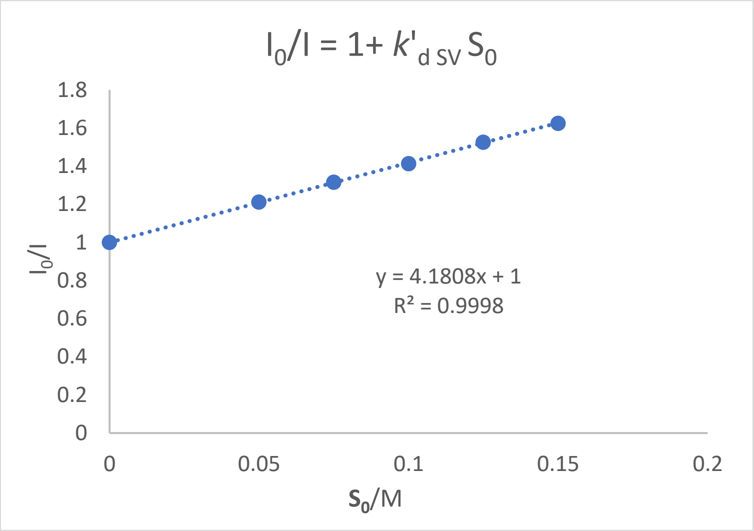


Figure S6.1.2. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$$\frac{I_0}{I} = 1 + k'_{d\,SV}\mathrm{S}_0$$

$$k'_{d\,SV} = 4.2$$

6.1.2.1 Reductant **9** *Experiment 1*

Table S6.1.2.1. S_0 fixed at 0.025M, A_0 varied from 0.001 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	796	796	796	796	1.129397
0.003	0.000075	660	662	662	661.3333	1.359375
0.004	0.0001	613	613	613	613	1.466558
0.005	0.000125	566	568	566	566.6667	1.586471
0.006	0.00015	530	530	528	529.3333	1.698363

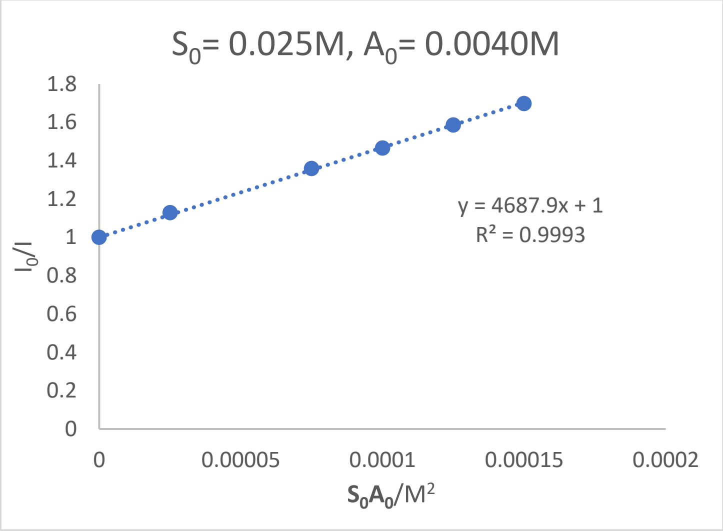


Figure S6.1.2.1. Stern-Volmer plot of luminescence data in **Table S6.1.2.1.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 4688 × $(1 + k'_{d\,SV}S_0)$

= 4688 × $(1 + 4.2 \times 0.025)$

= 5180

6.1.2.2 Reductant **9** *Experiment 2*

Table S6.1.2.2. Repeat- S_0 fixed at 0.025M, A_0 varied from 0.001 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	636	635	633	634.6667	1.136029
0.002	0.00005	571	570	568	569.6667	1.265652
0.004	0.0001	475	474	475	474.6667	1.518961
0.005	0.000125	438	434	437	436.3333	1.652406
0.006	0.00015	405	403	405	404.3333	1.783182

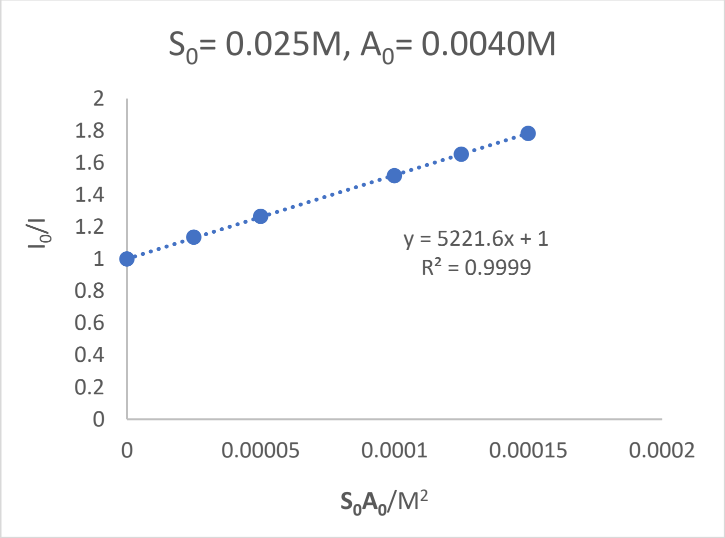


Figure S6.1.2.2. Stern-Volmer plot of luminescence data in **Table S6.1.2.2.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 5222 × $(1 + k'_{d\,SV}S_0)$

= 5222 × $(1 + 4.2 \times 0.025)$

= 5770

$k_{obs}\tau_0$ $average$ = (5180+5770)/2 = 5475 ± 295

Substitute S_0= 0.025, A_0= 0.004, K_A= 3.9, $k_{obs}\tau_0$ = 5475 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\ k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.025 + 0.004 = \frac{0.025 \times 0.004 \times 5475}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{5475} - \frac{1}{3.9}$$

$$k_{PCET\ SV} = 1542 \pm 83$$

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{PCET}\tau_0/\tau_0$]= 20.56

τ_0 = 1.82us

error of ln[k_{PCET} ($M^{-1}s^{-1}$)] = 0.05

6.1.3. Reductant **8**

Non-PCET quenching of reductant by acid alone (without ketone) is given by the following equation:

$$\frac{I_0}{I} = 1 + k''_{d\,SV}\mathrm{A}_0$$

$k''_{d\,SV}$ = 37.2 (**Entry 6** in **Table S5**)

Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$I_0/I = 1 + k'_{SV}\,S_0$

Time-resolved fluorometry suggest that both ketone and acid dynamically quench reductant **8** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + \frac{(k''_{SV} + k_{obs}\tau_0\mathrm{S}_0)\mathrm{A}_0}{1 + k'_{d\,SV}\mathrm{S}_0}$$

In all experiments, the solution was irradiated at 370nm and fluorescence was measured at 491nm.

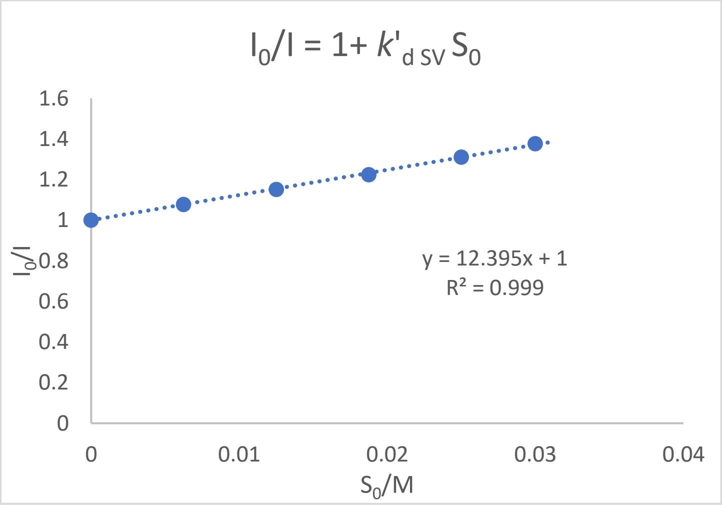


Figure S6.1.3. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$k'_{d\,SV}$=12.4

6.1.3.1. Reductant **8** *Experiment 1*

Table S6.1.3.1. S_0 fixed at 0.025M, A_0 varied from 0.001 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	325	326	325	325.3333	1.3125
0.002	0.00005	267	269	268	268	1.593284
0.003	0.000075	233	233	234	233.3333	1.83
0.004	0.0001	205	205	207	205.6667	2.076175
0.005	0.000125	180	180	182	180.6667	2.363469
0.006	0.00015	161	161	160	160.6667	2.657676

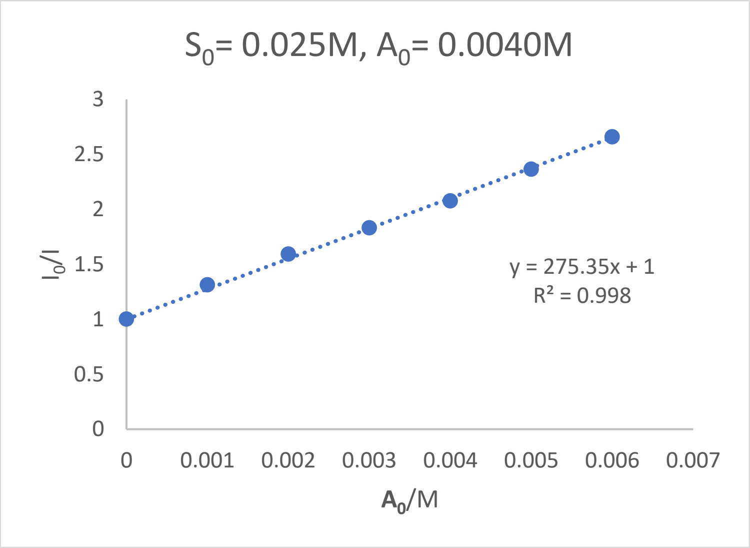


Figure S6.1.3.1. Stern-Volmer plot of luminescence data in **Table S6.1.3.1.**

I_0 was extrapolated from the six data points.

$$\frac{k''_{SV} + k_{obs}\tau_0 S_0}{1 + k'_{d\,SV} S_0} = 275.35$$

$$k''_{SV} + k_{obs}\tau_0 S_0 = 275 \times (1 + 12.4 \times 0.025) = 361$$

$$37.2 + 0.025\, k_{obs}\tau_0 = 361$$

$$k_{obs}\tau_0 = 12952$$

6.1.3.2. Reductant **8** *Experiment 2*

Table S6.1.3.2. Repeat- S_0 fixed at 0.025M, A_0 varied from 0.001 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	250	248	250	249.3333	1.287433
0.002	0.00005	199	199	200	199.3333	1.610368
0.003	0.000075	166	167	168	167	1.922156
0.005	0.000125	125	126	124	125	2.568
0.006	0.00015	111	111	111	111	2.891892

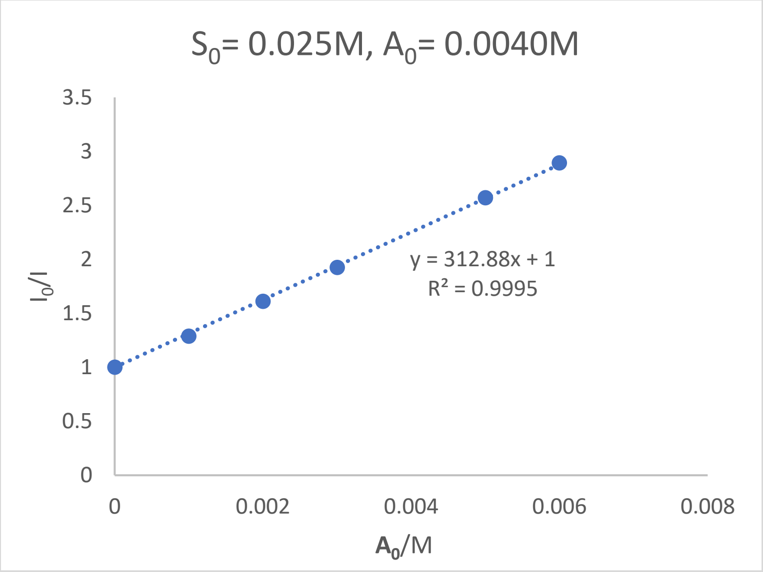


Figure S6.1.3.2. Stern-Volmer plot of luminescence data in **Table S6.1.3.2.**

I_0 was extrapolated from the five data points.

$$\frac{k''_{SV} + k_{obs}\tau_0 S_0}{1 + k'_{d\,SV} S_0} = 313$$

$$k''_{SV} + k_{obs}\tau_0 S_0 = 313 \times (1 + 12.4 \times 0.025) = 410$$

$$37.2 + 0.025\, k_{obs}\tau_0 = 410$$

$$k_{obs\,2}\,\tau_0 = 14913$$

$k_{obs}\tau_0\ average$ = (12952+14913)/2 = 13933 ± 980

Substitute S_0= 0.025, A_0= 0.004, K_A= 3.9, $k_{obs}\tau_0$ = 13933 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\ k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$0.025 + 0.004 = \frac{0.025 \times 0.004 \times 13933}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{13933} - \frac{1}{3.9}$$

$$k_{\mathrm{PCET}}\tau_0 = 3972 \pm 280$$

$\ln[k_{\mathrm{PCET}}(\mathrm{M}^{-1}\mathrm{s}^{-1})] = \ln[k_{\mathrm{PCET}}\tau_0/\tau_0] = 21.63$

$\tau_0 = 1.61$us

error of $\ln[k_{\mathrm{PCET}}(\mathrm{M}^{-1}\mathrm{s}^{-1})] = 0.07$

6.1.4.1 Reductant **7** *Experiment 1*

Neither ketone nor acid quenches the luminescence of reductant **7** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0 \, \mathrm{S_0A_0}$$

In all experiments, the solution was irradiated at 370nm and fluorescence was measured at 491nm.

Table S6.1.4.1. S_0 fixed at 0.100M, A_0 varied from 0.005 to 0.015M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.005	0.0005	335	335	337	335.6667	1.129096
0.0075	0.00075	316	318	318	317.3333	1.194328
0.01	0.001	301	301	302	301.3333	1.257743
0.0125	0.00125	288	286	287	287	1.320557
0.015	0.0015	272	272	273	272.3333	1.391677

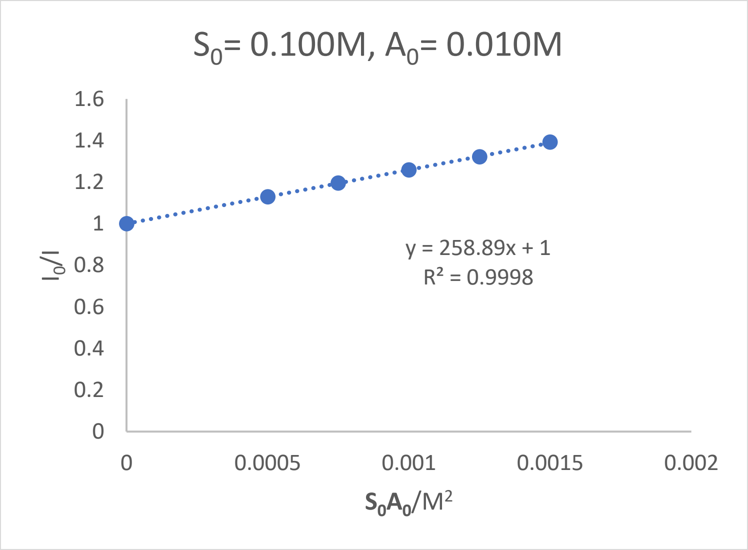


Figure S6.1.4.1. Stern-Volmer plot of luminescence data in **Table S6.1.4.1.**

I_0 was extrapolated from the fiver data points.

$$k_{obs}\tau_0 = 259$$

6.1.4.2. Reductant **7** *Experiment 2*

Table S6.1.4.2. Repeat- S_0 fixed at 0.100M, A_0 varied from 0.005 to 0.015M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.005	0.0005	448	448	446	447.3333	1.140089
0.0075	0.00075	421	422	422	421.6667	1.209486
0.01	0.001	398	398	396	397.3333	1.283557
0.0125	0.00125	375	376	377	376	1.356383
0.015	0.0015	354	356	354	354.6667	1.43797

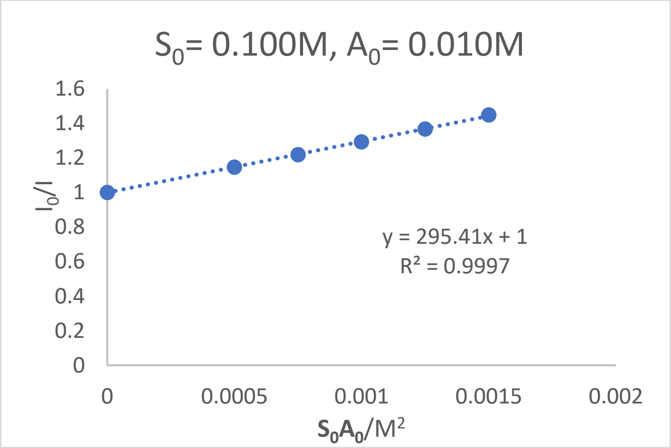


Figure S6.1.4.2. Stern-Volmer plot of luminescence data in **Table S6.1.4.2.**

I_0 was extrapolated from the fiver data points.

$$k_{obs}\tau_0 = 295$$

$k_{obs}\tau_0$ *average* = (259+295)/2 = 277 ± 18

Substitute S_0= 0.1, A_0= 0.01, K_A= 3.9, $k_{obs}\tau_0$ = 273 into the equation

$$S_0 + A_0 = \frac{S_0A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$k_{\mathrm{PCET}}\tau_0 = 99 \pm 5$$

τ_0 = 2.02us

error of ln[k_{PCET}(M^{-1}s^{-1})] = 0.09

6.2. ***Series of tert-butyl phenyl ketone***

6.2.1.1. Reductant **6** *Experiment 1*

Neither ketone nor acid quenches the luminescence of reductant **6** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + k_{obs}\tau_0\, \mathrm{S_0A_0}$$

In all experiments, the solution was irradiated at 375nm and fluorescence was measured at 518nm.

Table S6.2.1.1. S_0 fixed at 0.025M, A_0 varied from 0.001 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	695	695	694	694.6667	1.068138
0.003	0.000075	616	615	614	615	1.206504
0.004	0.0001	582	582	580	581.3333	1.276376
0.005	0.000125	552	553	551	552	1.344203
0.006	0.00015	523	525	525	524.3333	1.41513

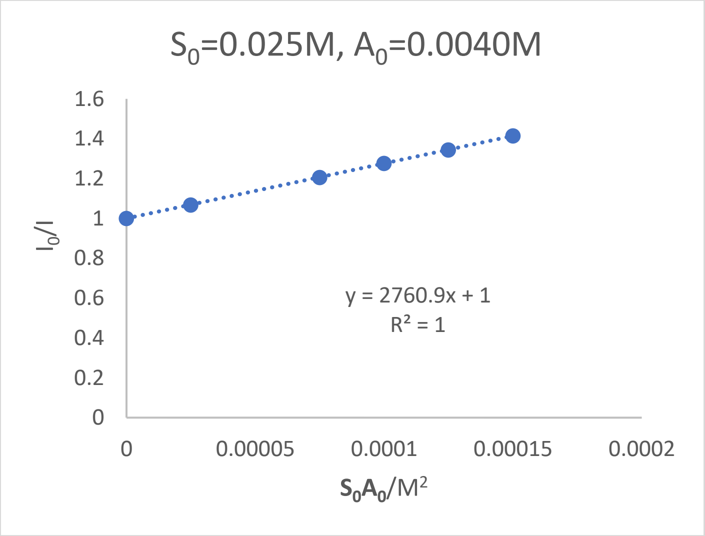


Figure S6.2.1.1. Stern-Volmer plot of luminescence data in **Table S6.2.1.1.**

I_0 was extrapolated from the fiver data points.

$$k_{obs}\tau_0 = 2761$$

6.2.1.2. Reductant **6** *Experiment 2*

Table S6.2.1.2. S_0 fixed at 0.100M, A_0 varied from 0.0005 to 0.00125M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0005	0.00005	612	614	614	613.3333	1.115217
0.00075	0.000075	580	579	580	579.6667	1.179988
0.001	0.0001	555	554	556	555	1.232432
0.00125	0.000125	524	526	524	524.6667	1.303685

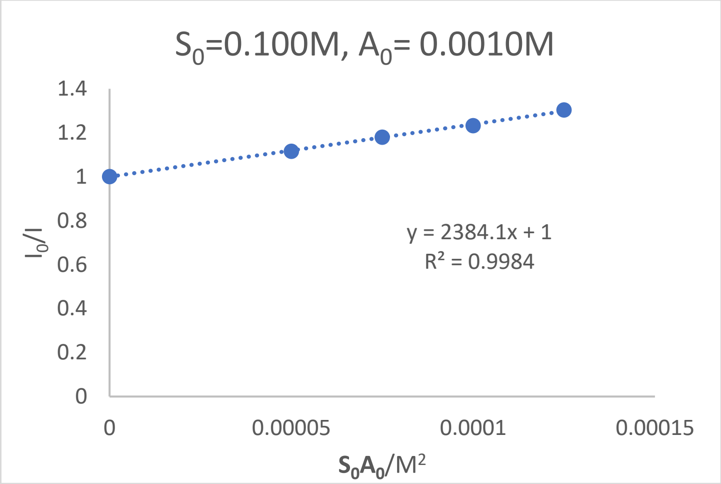


Figure S6.2.1.2. Stern-Volmer plot of luminescence data in **Table S6.2.1.2.**

I_0 was extrapolated from the four data points.

$$k_{obs}\tau_0 = 2384$$

6.2.1.3. Reductant **6** *Experiment 3*

Table S6.2.1.3. S_0 fixed at 0.156M, A_0varied from 0.00016 to 0.00080M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00016	0.000025	608	606	606	606.6667	1.053297
0.00032	0.00005	576	576	576	576	1.109375
0.00064	0.0001	527	528	528	527.6667	1.210992
0.0008	0.000125	506	503	503	504	1.267857

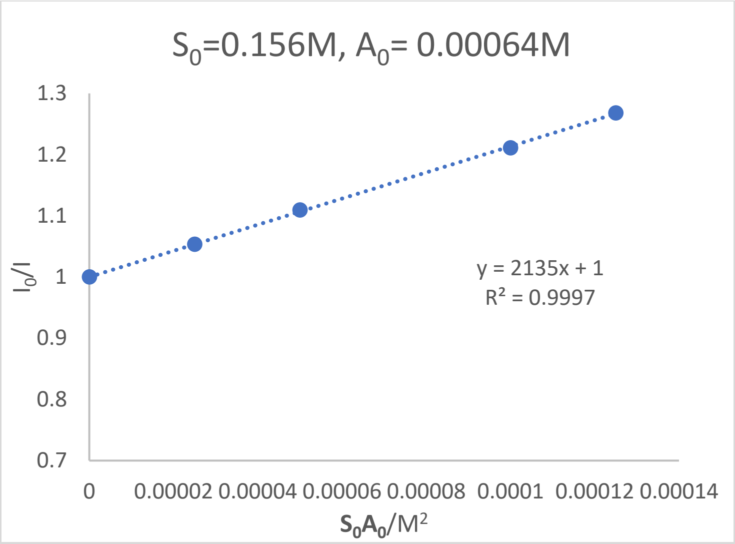


Figure S6.2.1.3. Stern-Volmer plot of luminescence data in **Table S6.2.1.3.**

I_0 was extrapolated from the four data points.

$$k_{obs}\tau_0 = 2135$$

Table S6.2.1.4. Solutions to Key Equation 8

	S_0 (M)	A_0 (M)	S_0A_0 (M^2)	S_0+A_0 (M)	$k_{obs}\tau_0$
1	0.025	0.004	0.0001	0.029	2760
2	0.100	0.001	0.0001	0.101	2380
3	0.156	0.00064	0.0001	0.157	2140

	K_A/M^{-1}	$k_{PCET}\tau_0/M^{-1}$
1&2	2.5	1205
1&3	2.7	1120
2&3	2.6	1142
avg	2.6	1156

$\Delta G°_{\text{H-bond}}$ (kcal/mol) = -RTlnK_A= -0.57

ln[k_{PCET}($M^{-1}s^{-1}$)] = ln[$k_{PCET}\tau_0/\tau_0$]= 20.23

τ_0 = 1.9 us

error of $\Delta G°_{\text{H-bond}}$ (kcal/mol) = 0.02

error of ln[k_{PCET}($M^{-1}s^{-1}$)] = 0.03

6.2.2. *Reductant **9***

The time-resolved fluorometry suggest that reductant **9** *Ir (III) is dynamically quenched by ketone. Acid does not quench the luminescence intensity of reductant **9** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + \frac{k_{obs}\tau_0 \mathrm{S}_0 \mathrm{A}_0}{1 + k'_{d\,SV}\mathrm{S}_0}$$

Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$$\frac{I_0}{I} = 1 + k'_{d\,SV}\mathrm{S}_0$$

In all experiments, the solution was irradiated at 370nm and fluorescence was measured at 500nm.

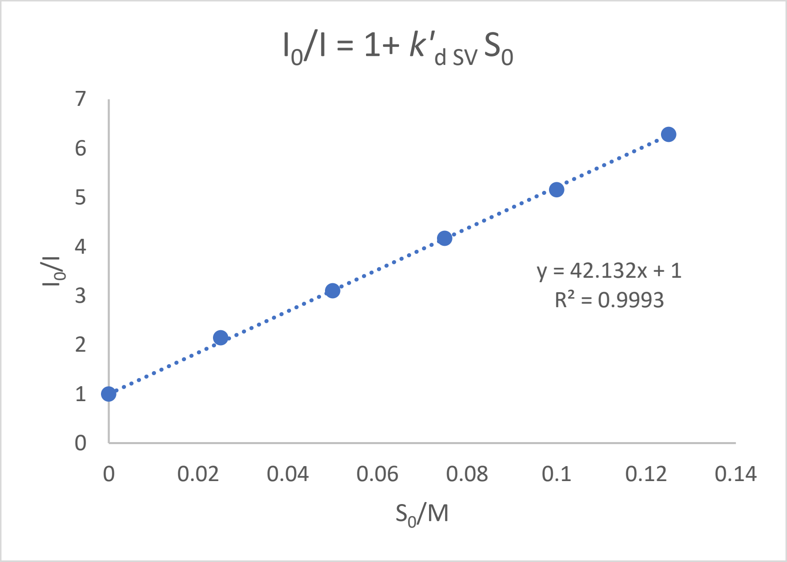


Figure S6.2.2. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

$$k'_{d\,SV} = 42.1$$

6.2.2.1. *Reductant **9** Experiment 1*

Table S6.2.2.1. S_0 fixed at 0.025M, A_0 varied from 0.001 to 0.006M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.001	0.000025	635	635	632	634	1.124606
0.002	0.00005	579	575	579	577.6667	1.234276
0.003	0.000075	527	523	534	528	1.350379
0.005	0.000125	452	451	454	452.3333	1.576271
0.006	0.00015	414	411	414	413	1.726392

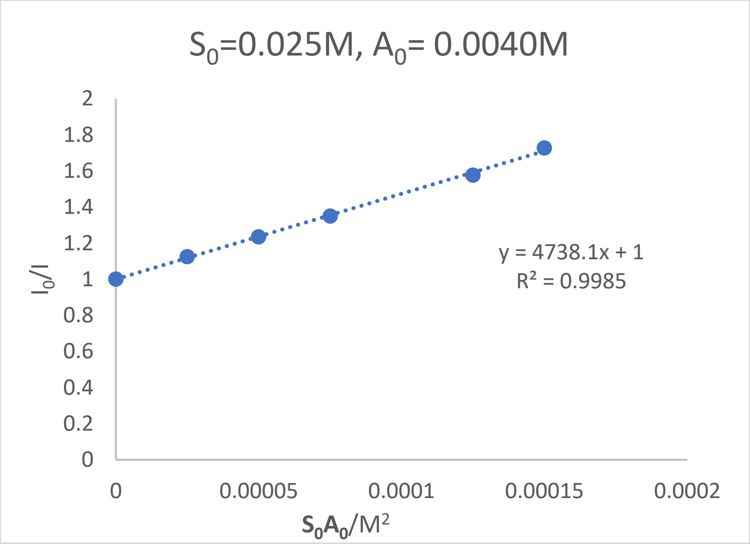


Figure S6.2.2.1. Stern-Volmer plot of luminescence data in **Table S6.2.2.1.**

I_0 was extrapolated from the five data points.

$k_{obs}\tau_0$ = 4738 × $(1 + k'_{d\,SV}S_0)$

= 4738 × $(1 + 42.1 \times 0.025)$

= 9725

Substitute S_0= 0.025, A_0= 0.004, K_A= 2.6, $k_{obs}\tau_0$= 9725 into the equation

$$S_0 + A_0 = \frac{S_0A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$k_{\mathrm{PCET}}\tau_0 = 4020$$

6.2.2.2. *Reductant **9** Experiment 2*

Table S6.2.2.2. S_0 fixed at 0.020M, A_0 varied from 0.00125 to 0.0075M

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00125	0.000025	547	539	540	542	1.380074
0.0025	0.00005	435	433	436	434.6667	1.720859
0.00375	0.000075	344	348	348	346.6667	2.157692
0.005	0.0001	286	290	290	288.6667	2.591224
0.00625	0.000125	249	249	250	249.3333	3

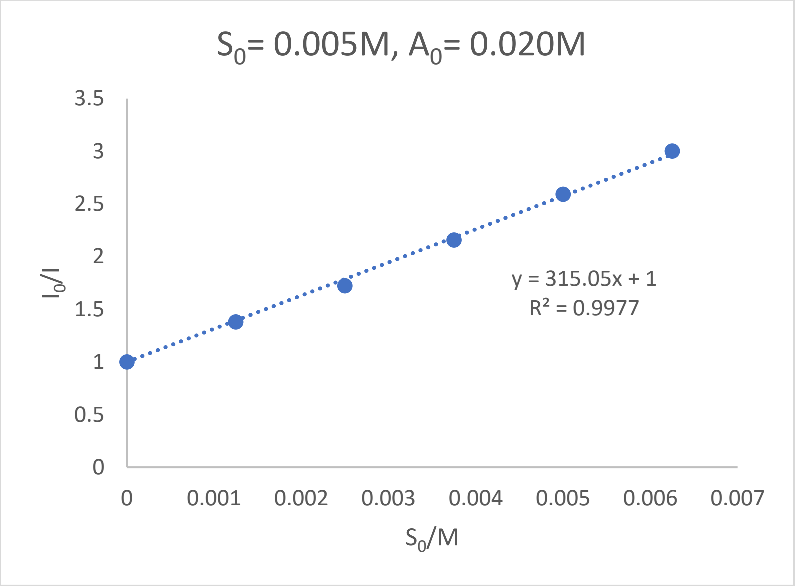


Figure S6.2.2.2. Stern-Volmer plot of luminescence data in **Table S6.2.2.2.**

I_0 was extrapolated from the five data points.

$$k'_{SV} + k_{obs}\tau_0 A_0 = 315$$

$$42.1 + k_{obs}\tau_0 \times 0.02 = 315$$

$$k_{obs}\tau_0 = 13645$$

Substitute S_0= 0.020, A_0= 0.005, K_A= 2.6, $k_{obs}\tau_0$ = 13645 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$k_{\text{PCET}}\tau_0 = 5586$$

$$k_{\text{PCET}}\tau_0\ average = (4020+5586)/2 = 4803 \pm 783$$

$$\ln[k_{\text{PCET}}(\text{M}^{-1}\text{s}^{-1})] = \ln[k_{\text{PCET}}\tau_0/\tau_0] = 21.68$$

$$\tau_0 = 1.82\text{us}$$

$$\text{error of } \ln[k_{\text{PCET}}(\text{M}^{-1}\text{s}^{-1})] = 0.16$$

6.2.3. *Reductant **8***

Non-PCET quenching of reductant by acid alone (without ketone) is given by the following equation:

$$\frac{I_0}{I} = 1 + k''_{d\,SV}\text{A}_0$$

$k''_{d\,SV} = 37.2$ (**entry 6** in **Table S5**)

Non-PCET quenching of reductant by ketone alone (without acid) is given by the following equation:

$$I_0/I = 1 + k'_{SV}S_0$$

Time-resolved fluorometry suggest that both ketone and acid dynamically quench reductant **8** *Ir (III). Therefore, the following equation is used:

$$\frac{I_0}{I} = 1 + \frac{(k''_{SV} + k_{obs}\tau_0\text{S}_0)\text{A}_0}{1 + k'_{d\,SV}\text{S}_0}$$

In all experiments, the solution was irradiated at 370nm and fluorescence was measured at 491nm.

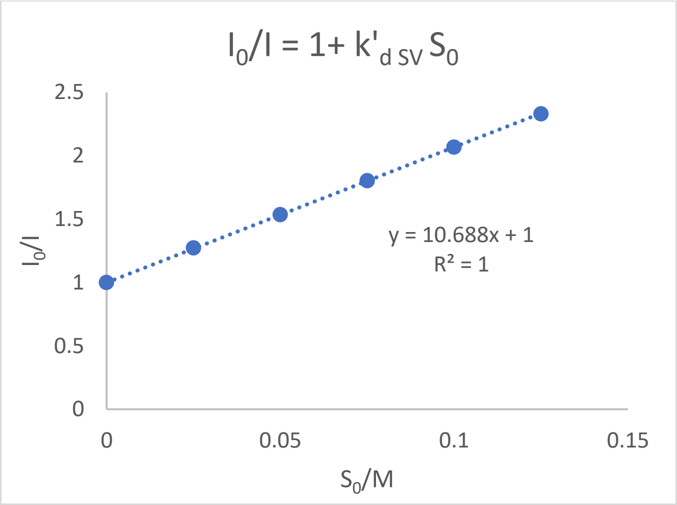


Figure S6.2.3. Stern-Volmer plot of luminescence data of non-PCET quenching by ketone alone

I_0 was extrapolated from the five data points.

$$k'_{d\,SV} = 10.7$$

6.2.3.1 *Reductant **8** Experiment 1*

Table S6.2.3.1. S_0 fixed at 0.025M, A_0 varied from 0.0004 to 0.0025M

A_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.0004	0.00001	369	369	369	369	1.236249
0.0008	0.00002	304	304	304	304	1.503289
0.0012	0.00003	262	265	267	264.6667	1.7267
0.0016	0.00004	229	231	230	230	1.984081
0.002	0.00005	203	203	203	203	2.251232
0.0025	0.00006	177	177	177	177	2.581921

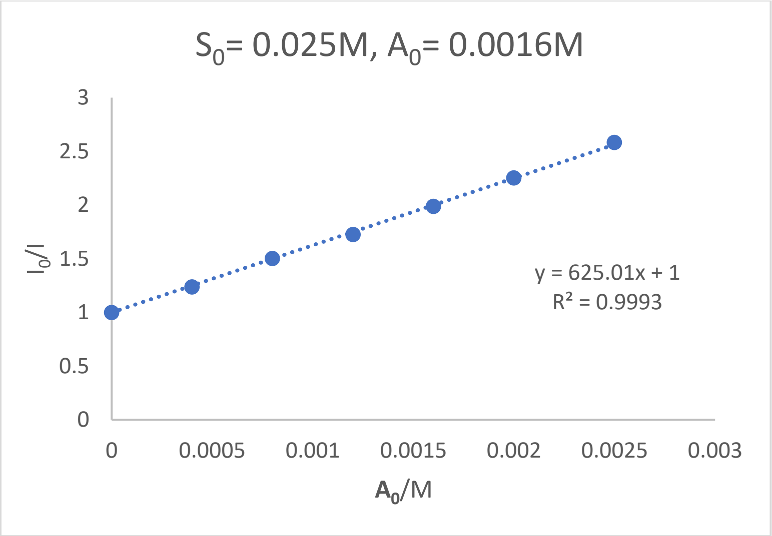


Figure S6.2.3.1. Stern-Volmer plot of luminescence data in **Table S6.2.3.1.**

I_0 was extrapolated from the six data points.

$$\frac{k''_{SV} + k_{obs}\tau_0 S_0}{1 + k'_{d\,SV} S_0} = 625$$

$$k''_{SV} + k_{obs}\tau_0 S_0 = 625 \times (1 + 10.7 \times 0.025) = 792.2$$

$$37.2 + 0.025\, k_{obs}\tau_0 = 792.2$$

$$k_{obs}\tau_0 = 30200$$

Substitute S_0= 0.025, A_0= 0.0016, K_A= 2.6, $k_{obs}\tau_0$= 30200 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$k_{\mathrm{PCET}}\tau_0 = 12415$$

6.2.3.2. *Reductant **8** Experiment 2*

Table S6.2.3.2. A_0 fixed at 0.0002M, S_0 varied from 0.00625 to 0.0375M

S_0/M	S_0A_0/M^2	I/au 1	I/au 2	I/au 3	I/au avg.	I_0/I
0	0					1
0.00625	0.0000125	394	394	395	394.3333	1.468301
0.0125	0.000025	304	302	302	302.6667	1.912996
0.01875	0.0000375	248	248	248	248	2.334677
0.025	0.00005	208	205	208	207	2.797101
0.03125	0.0000625	180	180	178	179.3333	3.228625
0.0375	0.000075	154	154	156	154.6667	3.743534

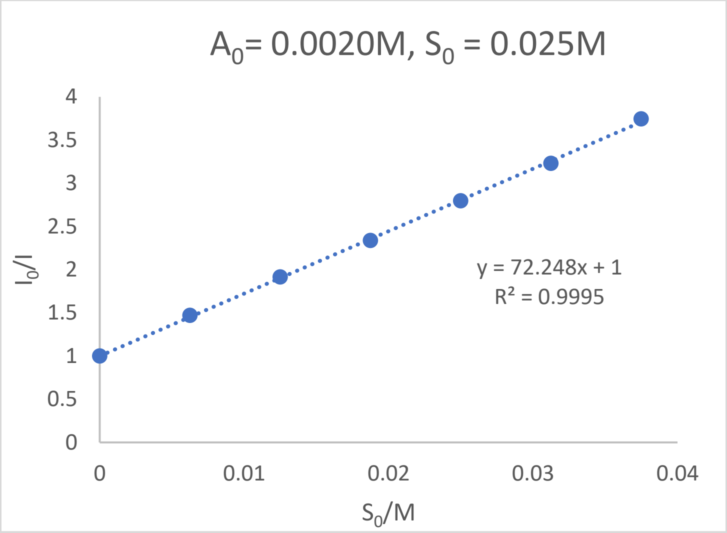


Figure S6.2.3.2. Stern-Volmer plot of luminescence data in **Table S6.2.3.2.**

I_0 was extrapolated from the six data points.

$$\frac{k''_{SV} + k_{obs}\tau_0 A_0}{1 + k'_{d\,SV} A_0} = 72.2$$

$k''_{SV} + k_{obs}\tau_0 A_0$ = 72.2 × (1+ 37.2 × 0.002) = 77.4

10.7 + 0.002 $k_{obs}\tau_0$ = 77.4 $k_{obs}\tau_0$ = 33330

Substitute S_0= 0.025, A_0= 0.002, K_A= 2.6, $k_{obs}\tau_0$ = 33330 into the equation

$$S_0 + A_0 = \frac{S_0 A_0\, k_{obs}\tau_0}{k_{PCET}\tau_0} + \frac{k_{PCET}\tau_0}{k_{obs}\tau_0} - \frac{1}{K_A}$$

$$k_{\mathrm{PCET}}\tau_0 = 13715$$

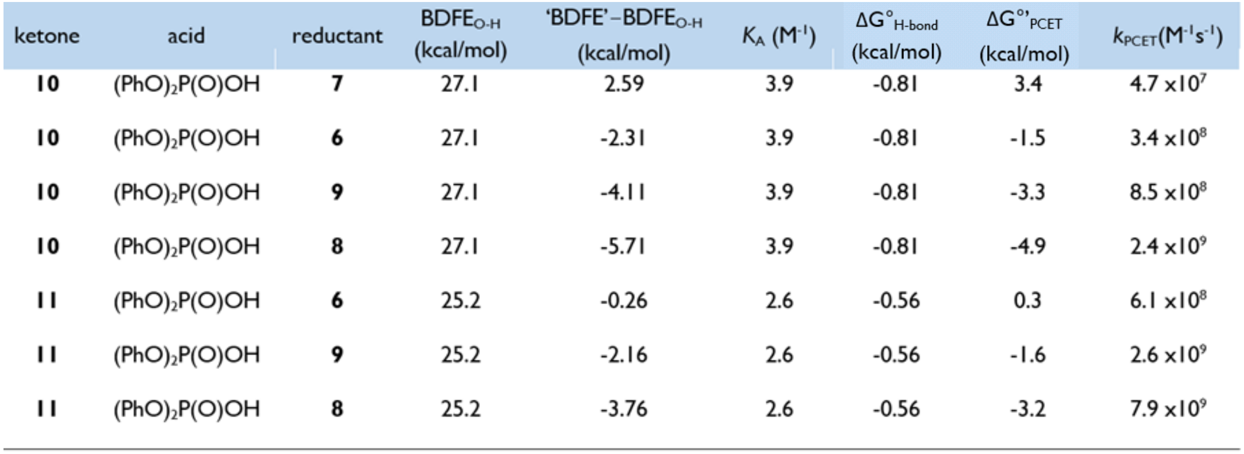
$$k_{\mathrm{PCET}}\tau_0\ average = (12415+13715)/2 = 13065 \pm 650$$

ln[k_{PCET}(M^{-1}s^{-1})] = ln[$k_{\mathrm{PCET}}\tau_0/\tau_0$]= 22.82

τ_0 = 1.61us

error of ln[k_{PCET}(M^{-1}s^{-1})] = 0.05

Table S6. Kinetic and H-bonding equilibrium data for ketone 10 and 11 MS-PCET reactions



ketone	acid	reductant	BDFE$_{\mathrm{O\text{-}H}}$ (kcal/mol)	'BDFE'−BDFE$_{\mathrm{O\text{-}H}}$ (kcal/mol)	K_A (M^{-1})	ΔG°$_{\mathrm{H\text{-}bond}}$ (kcal/mol)	ΔG°'$_{\mathrm{PCET}}$ (kcal/mol)	k_{PCET}(M^{-1}s^{-1})
10	(PhO)$_2$P(O)OH	**7**	27.1	2.59	3.9	-0.81	3.4	4.7 x10^7
10	(PhO)$_2$P(O)OH	**6**	27.1	-2.31	3.9	-0.81	-1.5	3.4 x10^8
10	(PhO)$_2$P(O)OH	**9**	27.1	-4.11	3.9	-0.81	-3.3	8.5 x10^8
10	(PhO)$_2$P(O)OH	**8**	27.1	-5.71	3.9	-0.81	-4.9	2.4 x10^9
11	(PhO)$_2$P(O)OH	**6**	25.2	-0.26	2.6	-0.56	0.3	6.1 x10^8
11	(PhO)$_2$P(O)OH	**9**	25.2	-2.16	2.6	-0.56	-1.6	2.6 x10^9
11	(PhO)$_2$P(O)OH	**8**	25.2	-3.76	2.6	-0.56	-3.2	7.9 x10^9

7. Miscellaneous Rate-Driving Force Correlation Plots

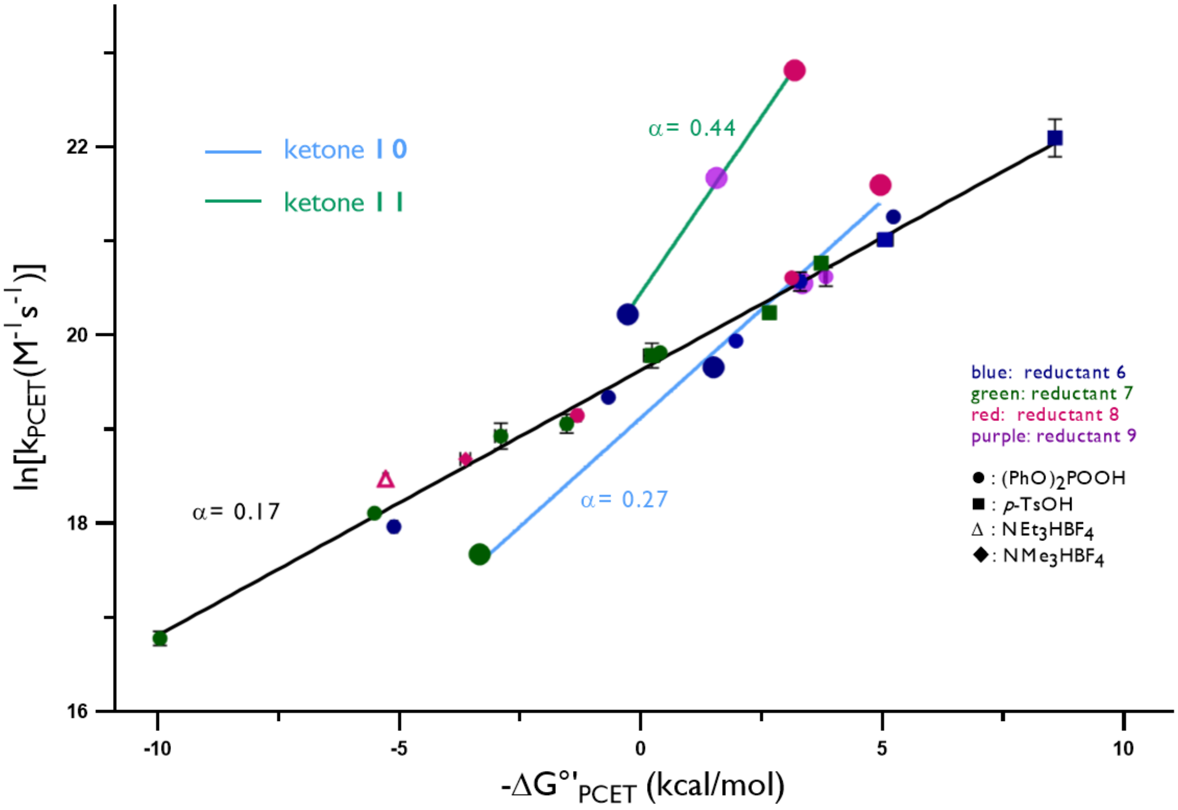


Figure S7.1. Superimposed plot of rate-driving force relationship for the data presented in Table S5 and S6

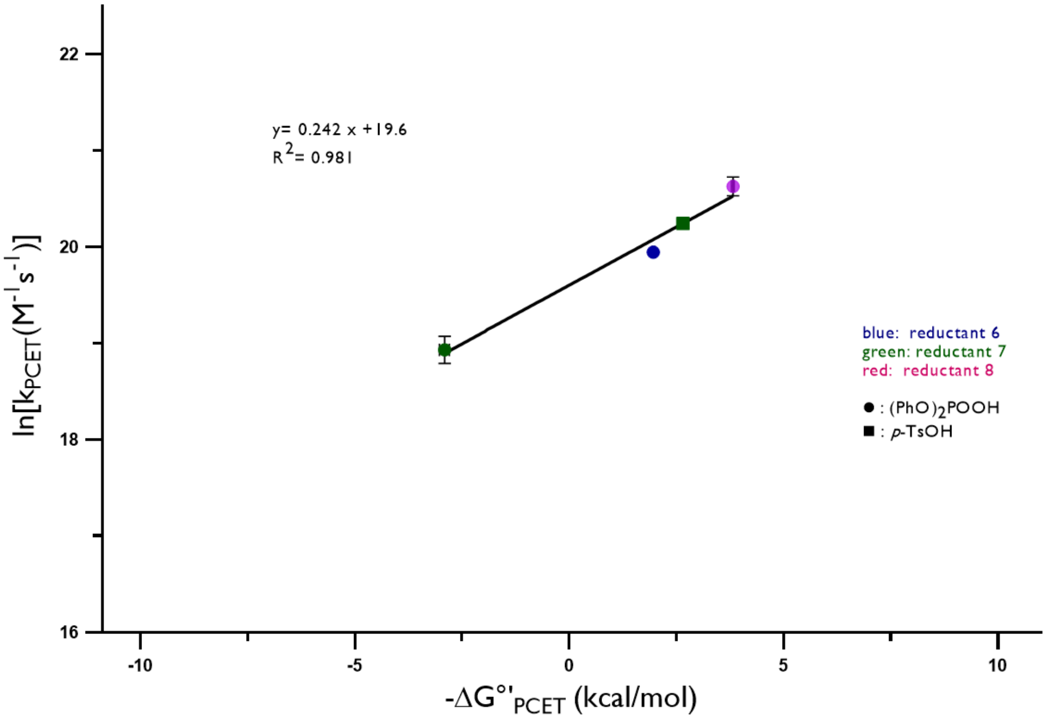


Figure S7.2. Plot of rate-driving force relationship for data of ketone **1** presented in Table S5

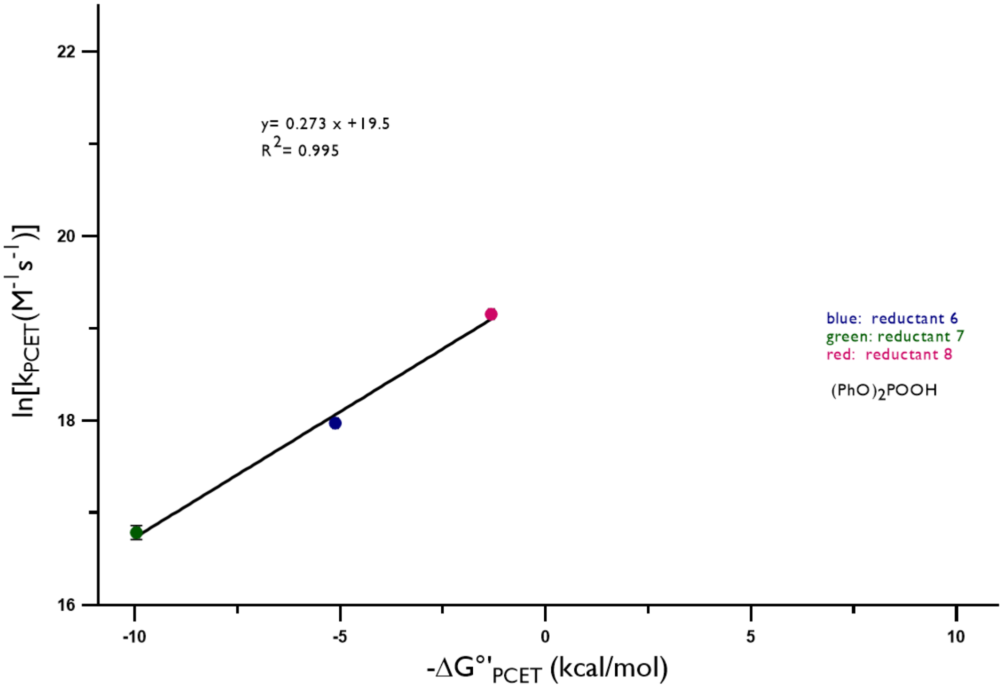


Figure S7.3. Plot of rate-driving force relationship for data of ketone **2** with $(PhO)_2POOH$ presented in Table S5

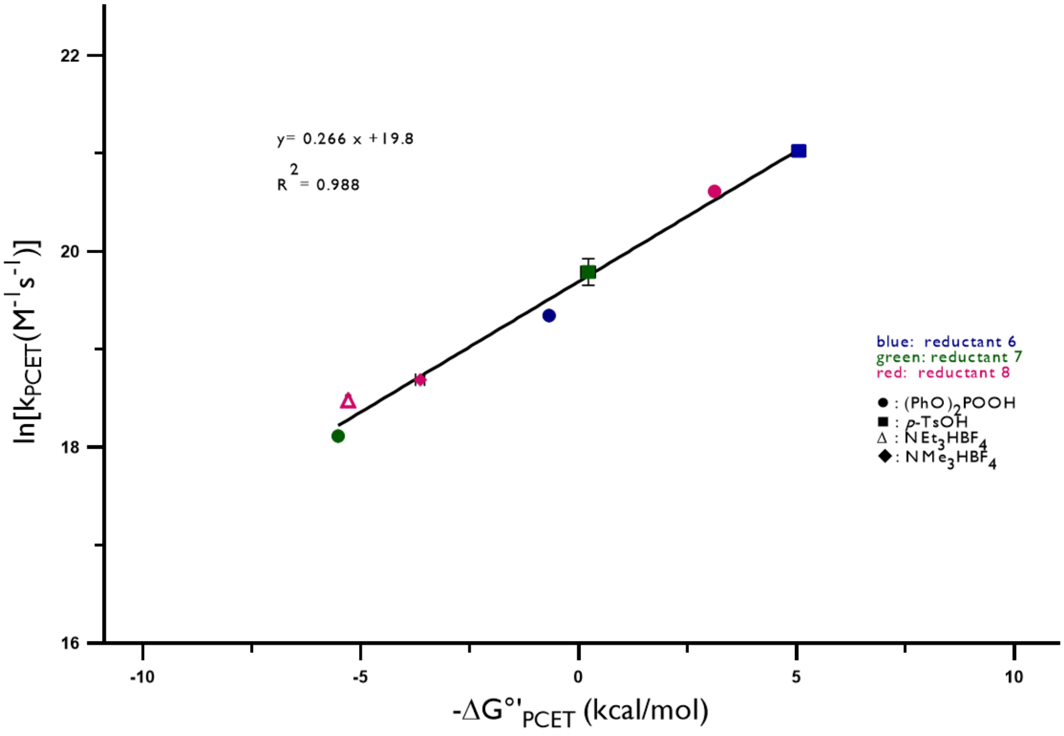


Figure S7.4. Plot of rate-driving force relationship for data of ketone **3** presented in Table S5

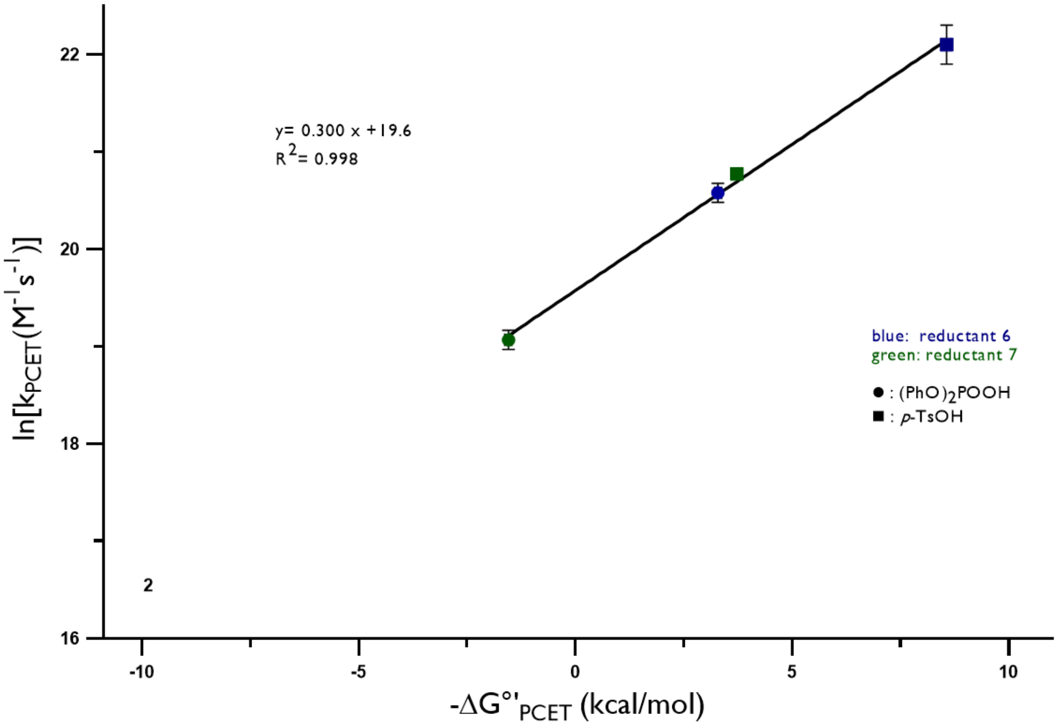


Figure S7.5. Plot of rate-driving force relationship for data of ketone **5** presented in Table S5

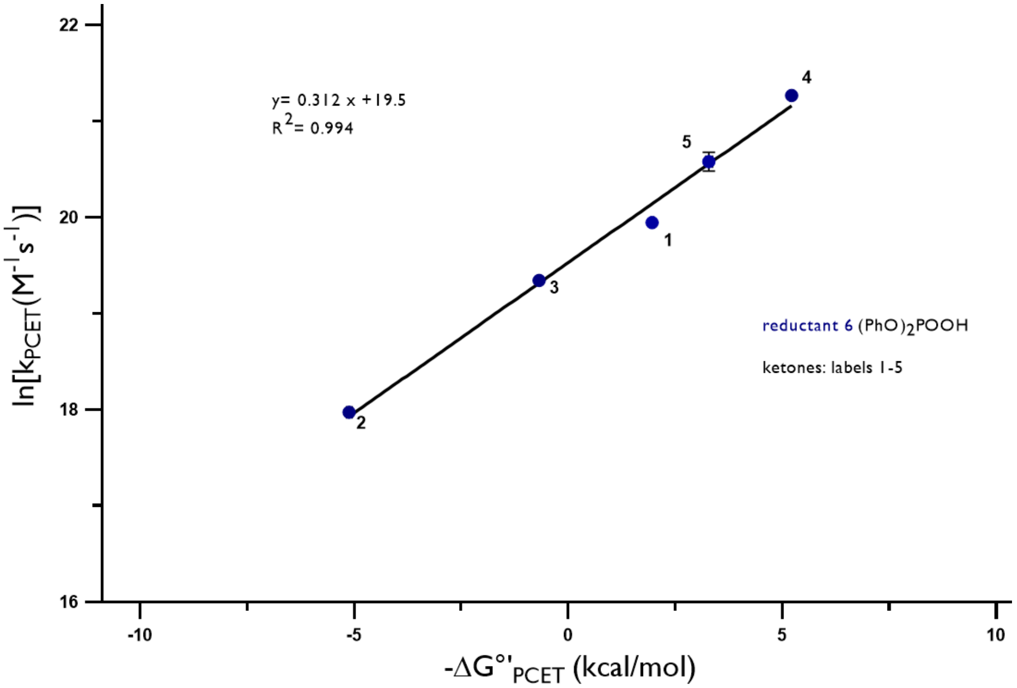


Figure S7.6. Plot of rate-driving force relationship for data of reductant **6** with (PhO)$_2$POOH presented in Table S5

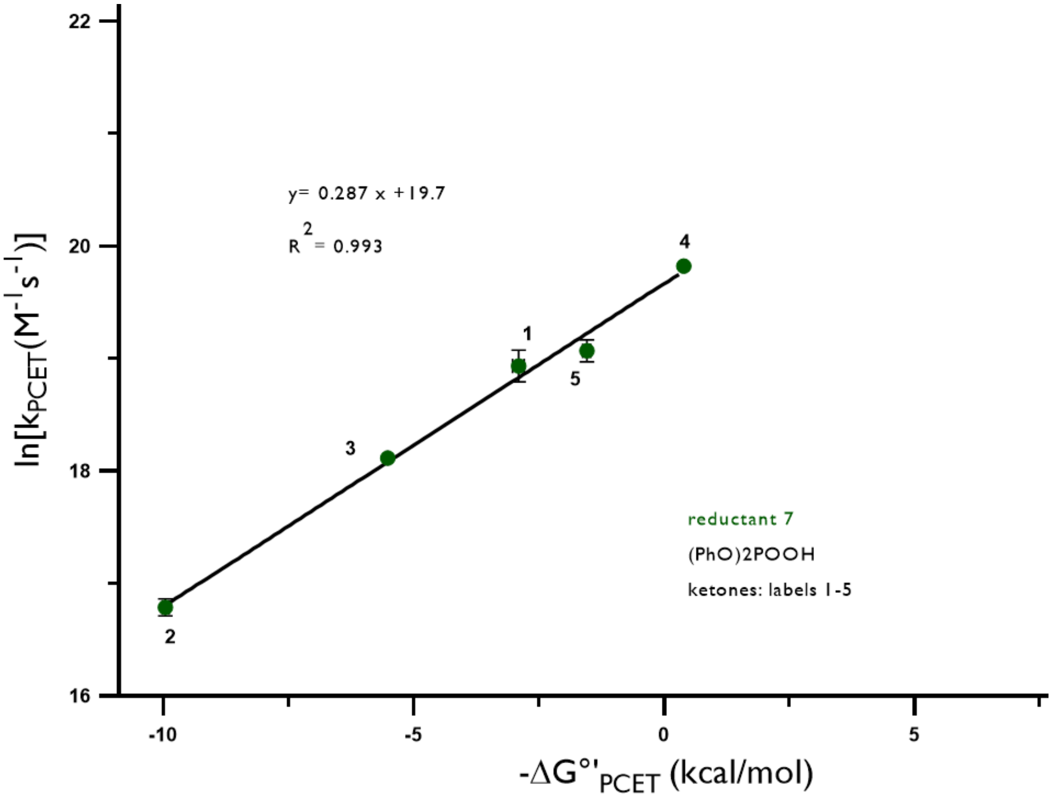


Figure S7.7. Plot of rate-driving force relationship for data of reductant **7** with (PhO)$_2$POOH presented in Table S5

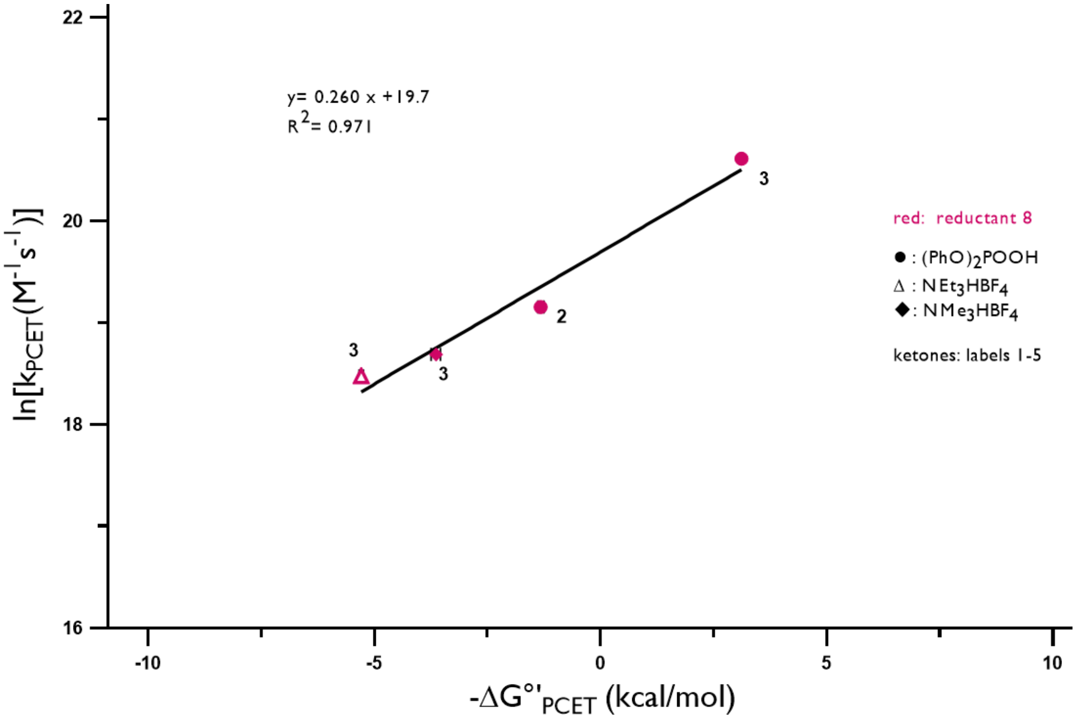


Figure S7.8. Plot of rate-driving force relationship for data of reductant **8** presented in Table S5

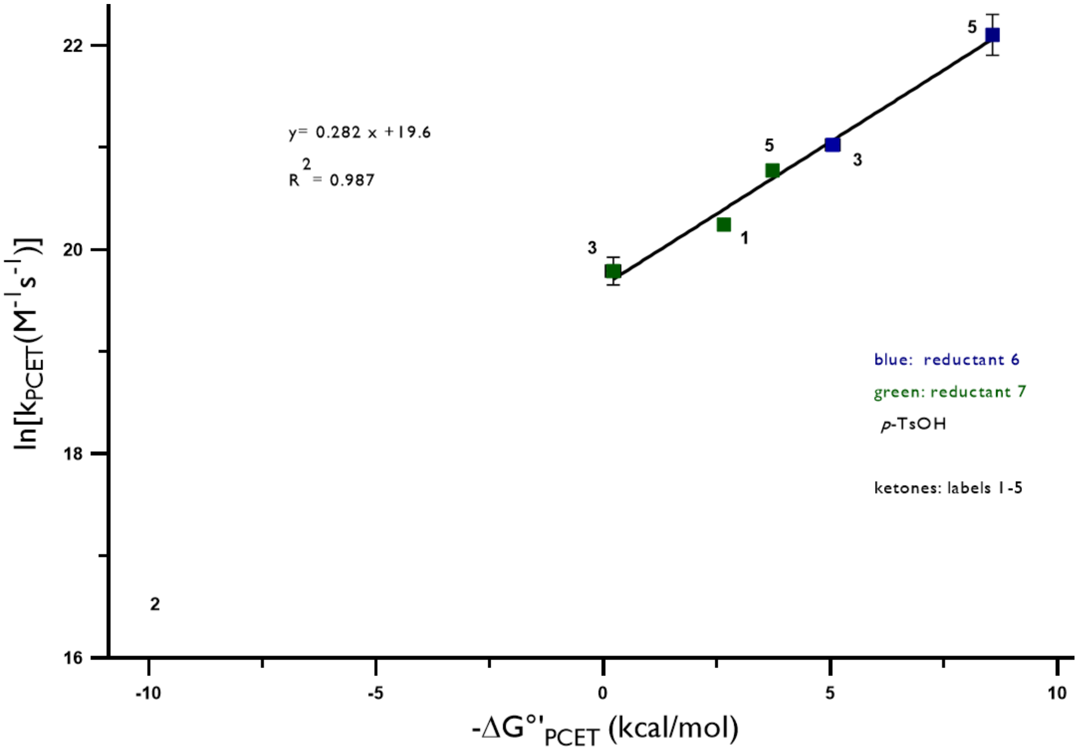


Figure S7.9. Plot of rate-driving force relationship for data with $(PhO)_2POOH$ presented in Table S5

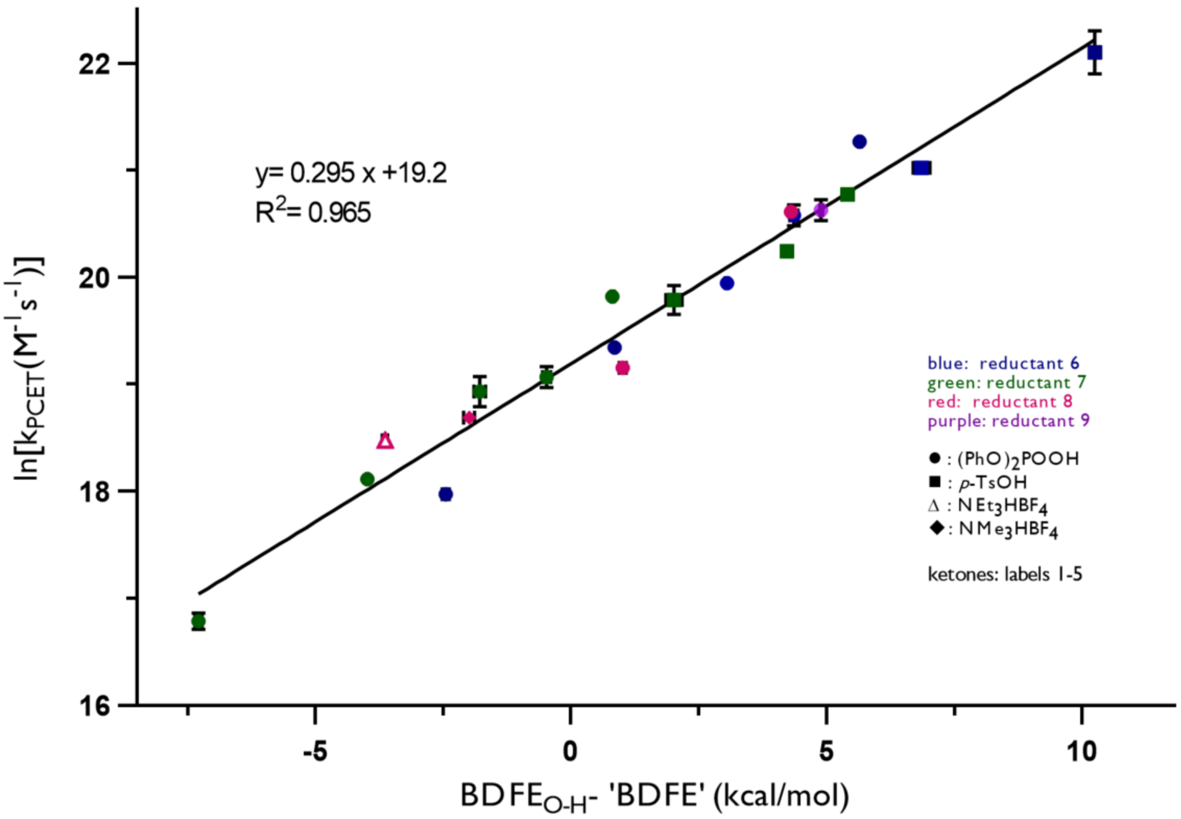


Figure S.7.10. Rate-driving force plot that excludes any energetic contribution from either the precursor (K_A) or successor H-bonding to the overall driving force.

8. H/D Kinetic Isotope Effects (KIE)

The H/D equilibrium isotope effect was assumed to be unity. $(PhO)_2P(O)OH$ or $(PhO)_2P(O)OD$, and photoreductant **6** were used for ketone **1**, **10** and **11.** The H/D KIE value for acetophenone is taken from our previous study.[13]

*8.1. KIE for ketone **10***

Trial 1

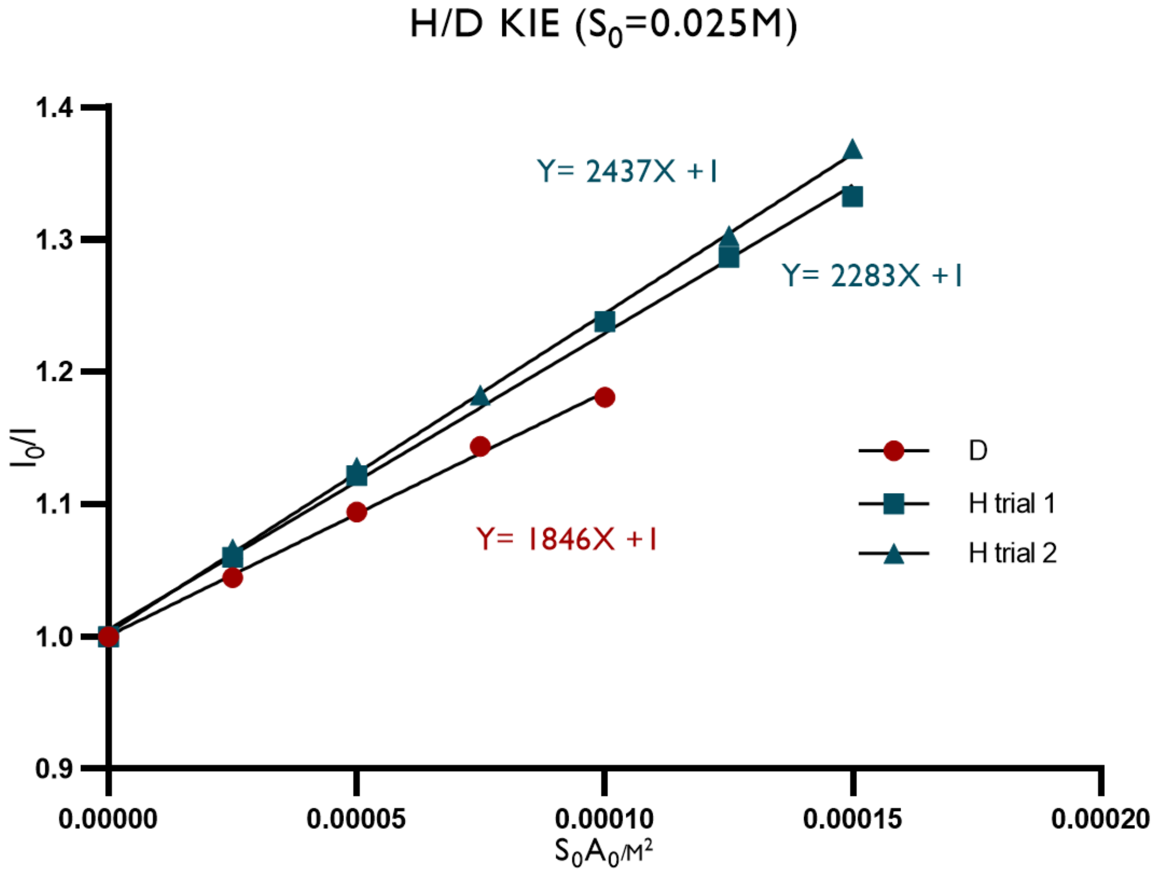


Figure S8.1.1. Superimposed Stern-Volmer plot of luminescence data of quenching by ketone **10** and $(PhO)_2P(O)OD$ (or $(PhO)_2P(O)OH$). S_0 fixed at 0.025M, A_0 varied from 0.001 to 0.004M for $(PhO)_2P(O)OD$ and varied from 0.001 to 0.006M for $(PhO)_2P(O)OH$

k_H/k_D = 2320 (from **6.1.1.1**) /1846 = 1.26

Trial 2

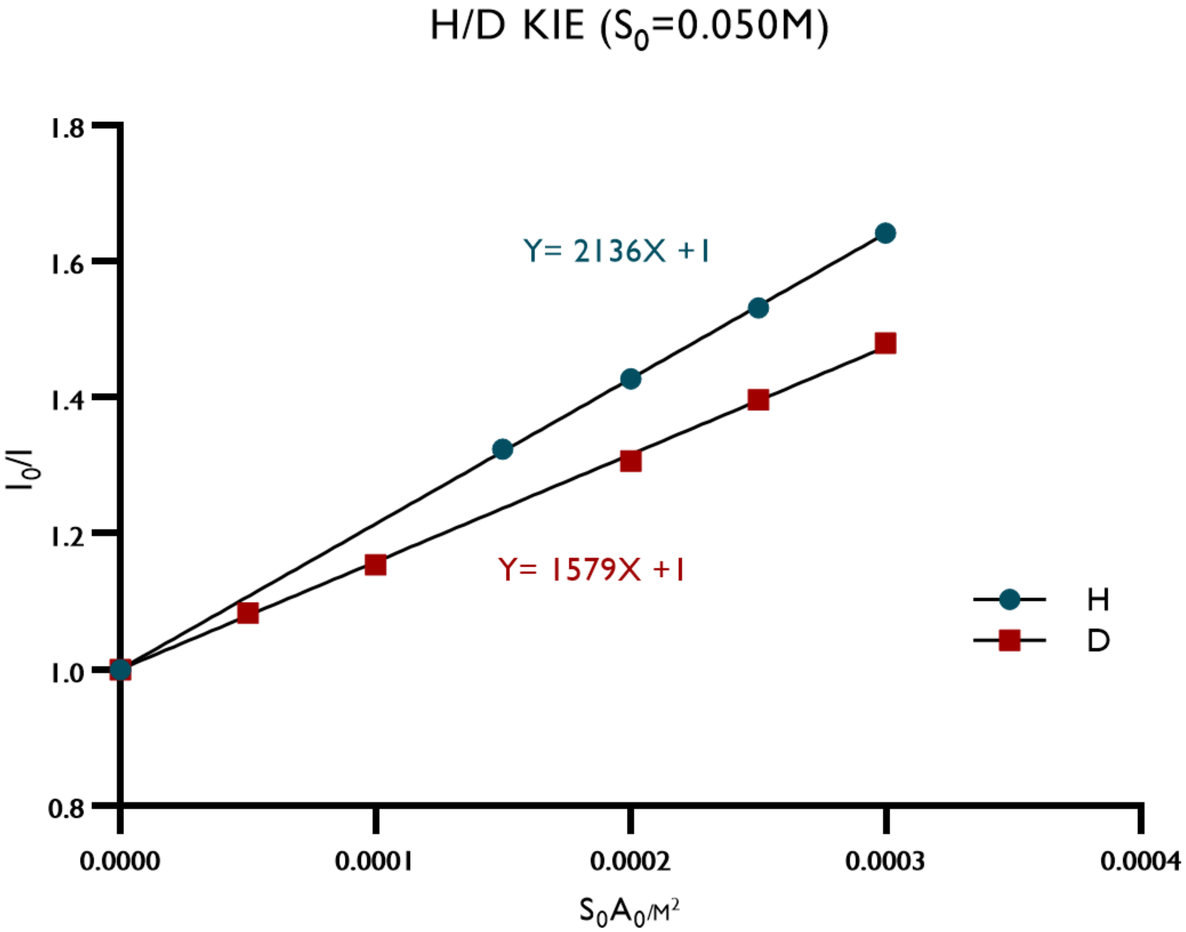


Figure S8.1.2. Superimposed Stern-Volmer plot of luminescence data of quenching by ketone **10** and $(PhO)_2P(O)OD$ (or $(PhO)_2P(O)OH$). S_0 fixed at 0.05M, A_0 varied from 0.001 to 0.006M

k_H/k_D = 2136 (from **6.1.1.2**) /1579 = 1.35

KIE (ketone **10**) = (1.26+1.35)/2 = 1.30 ± 0.05

*8.2. KIE for ketone **11***

Protiated reference

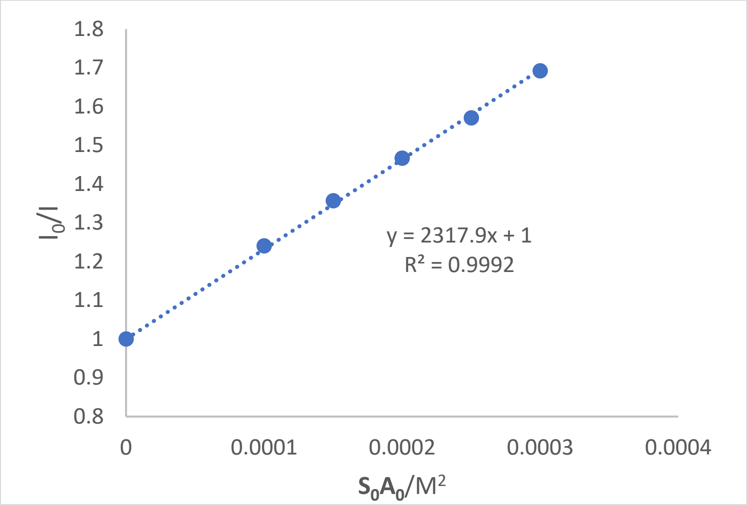


Figure S8.2.1. Stern-Volmer plot of luminescence data of quenching by ketone **11** and $(PhO)_2P(O)OH$. [acid] fixed at 0.004M, [acid] varied from 0.0125 to 0.075M

Trial 1

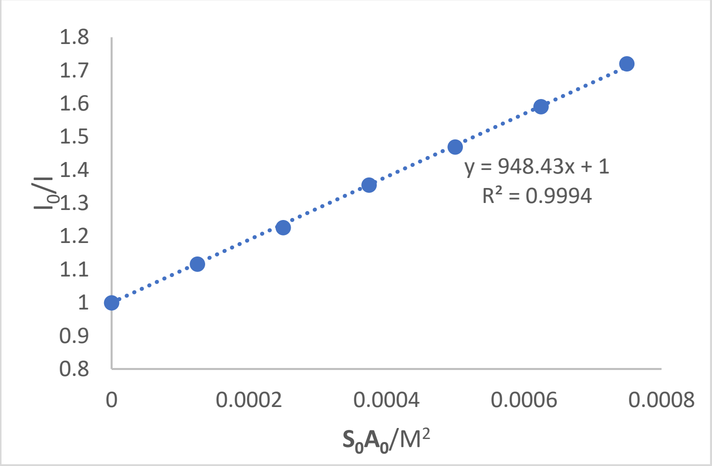


Figure S8.2.2. Stern-Volmer plot of luminescence data of quenching by ketone **11** and $(PhO)_2P(O)OD$. [acid] fixed at 0.01M, [acid] varied from 0.0125 to 0.075M

k_H/k_D = 2318 /948 = 2.45

Trial 2

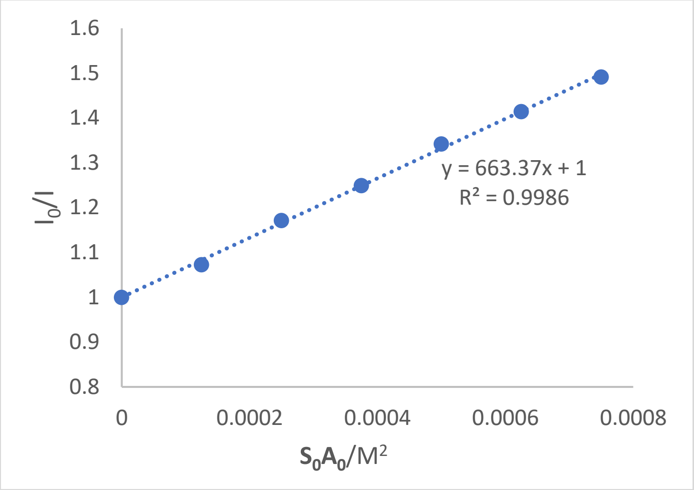


Figure S8.2.3. Stern-Volmer plot of luminescence data of quenching by ketone **11** and $(PhO)_2P(O)OD$. [acid] fixed at 0.010M, [acid] varied from 0.0125 to 0.075M

k_H/k_D = 2318 /663 = 3.50

KIE (ketone **11**) = (2.45+3.50)/2 = 3.0 ± 0.5

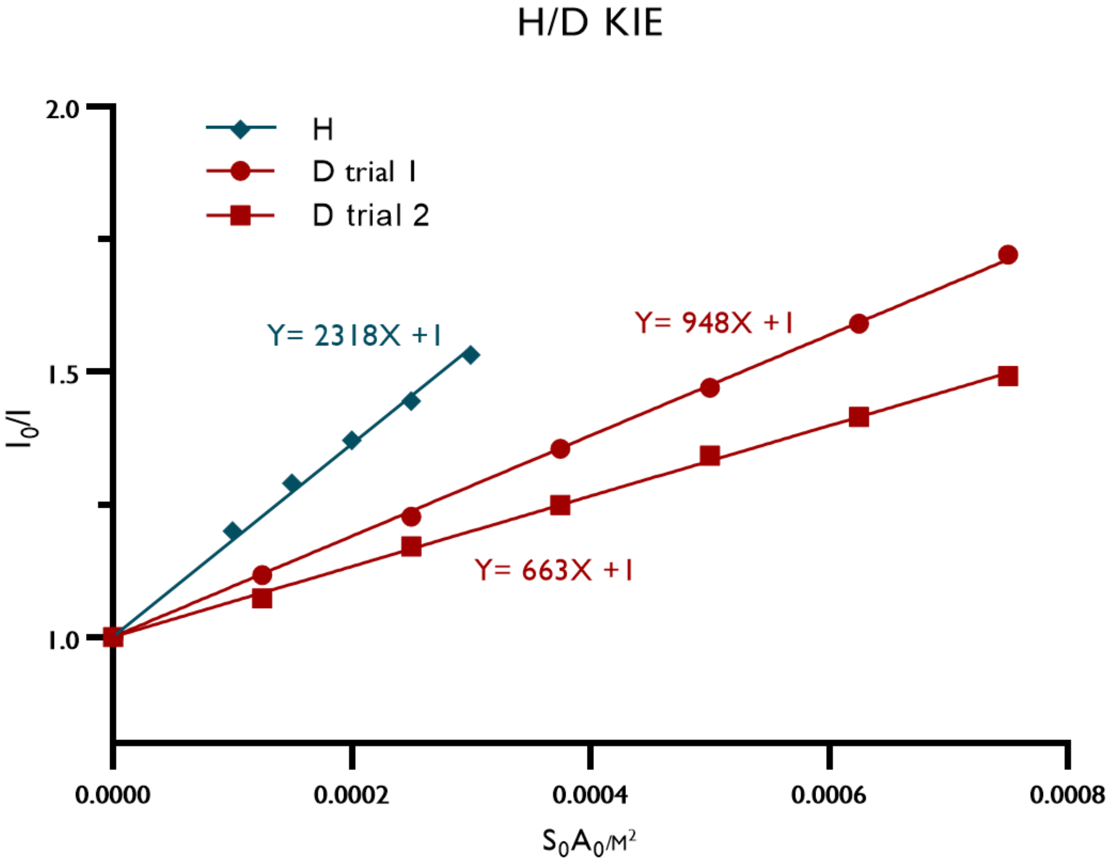


Figure S8.2.4. Superimposed plot of Figure **S8.2.1-3**.

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