Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Photolysis of Tp'Rh(CNneopentyl)(PhNCNneopentyl) in the presence of ketones and esters: kinetic and thermodynamic selectivity for activation of different aliphatic C-H bonds

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1. ^{1}H NMR spectra of photolysis experiments

General Comments: Most photolysis experiments yielded more than one C-H activated product. Additionally, all photolysis experiments were accompanied by *o*-, *m*-, and *p*-carbodiimide C-H activation products (amounts vary from reaction to reaction). As a result, the ^{1}H NMR spectrum (0-8 ppm) is crowded with many overlapping peaks, making the assignment of any C-H activated products difficult. For this reason, only the hydride resonances will be reported.
NOTE: * denotes *o*-, *m*-, and *p*-carbodiimide C-H activated products.

Activation of diethyl ketone

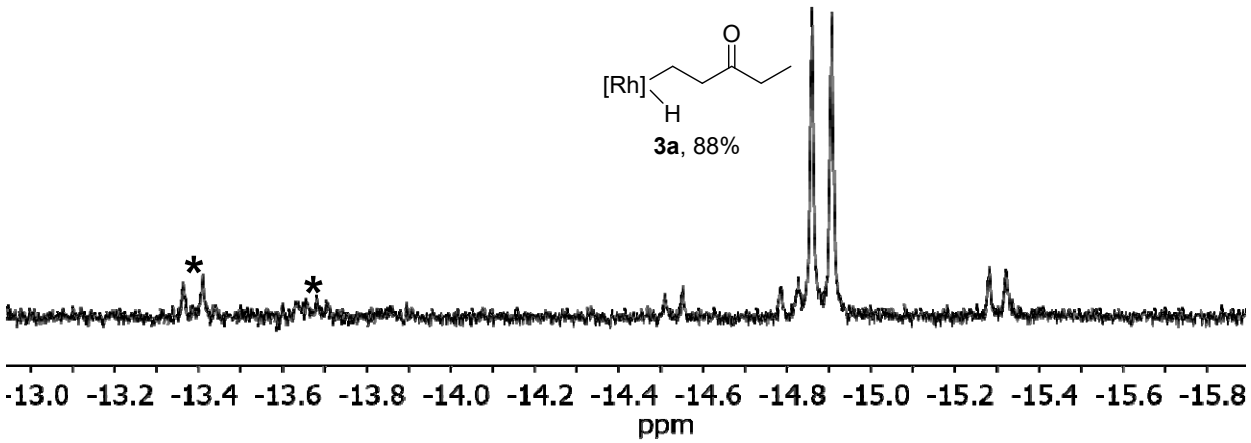


Figure S1. ^{1}H NMR of hydride region for C-H activated diethyl ketone, **3a** δ -14.89 (J_{Rh-H} = 24.0 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.39). Products at δ -14.53, and -15.31 are assigned to diastereomers arising from α-CH_2 activation. The doublet at δ -14.81 is assigned to activation of an acetone impurity.

Activation of ethyl methyl ketone

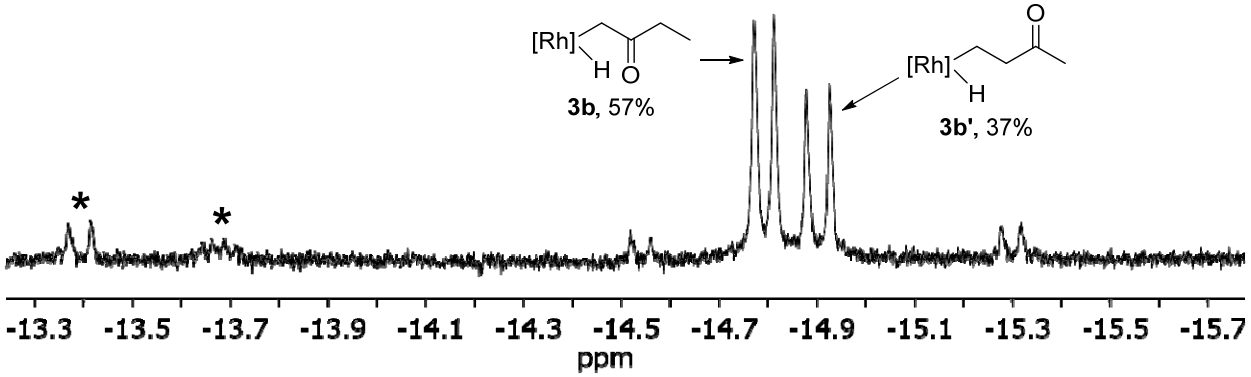


Figure S2. ^{1}H NMR of hydride region for C-H activated ethyl methyl ketone, **3b** δ -14.79 (J_{Rh-H} = 20.5 Hz) and **3b'** δ -14.90 (J_{Rh-H} = 24.0 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.39 and -13.68). Products at δ -15.28 and -14.54 are assigned to diastereomers from α-keto CH_2 activation.

Activation of cyclopentanone

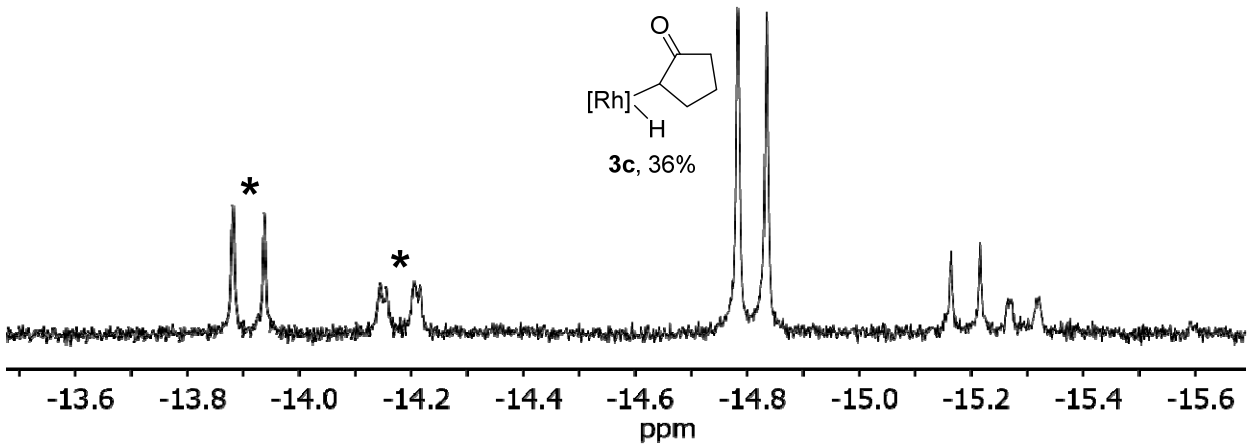


Figure S3. ^{1}H NMR of hydride region for C-H activated cyclopentanone, **3c** δ -14.82 (J_{Rh-H} = 20.4 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.90, -14.17, -14.18). Products at δ -15.19 (J_{Rh-H} = 20.9 Hz) and -15.29 (J_{Rh-H} = 23.2 Hz) were not assigned, but likely arise from β-keto C-H activation. The chemical shifts for these minor products are in the region seen for similar β-derivatives with chlorocyclopentane.[1]

Activation of cyclopropyl methyl ketone

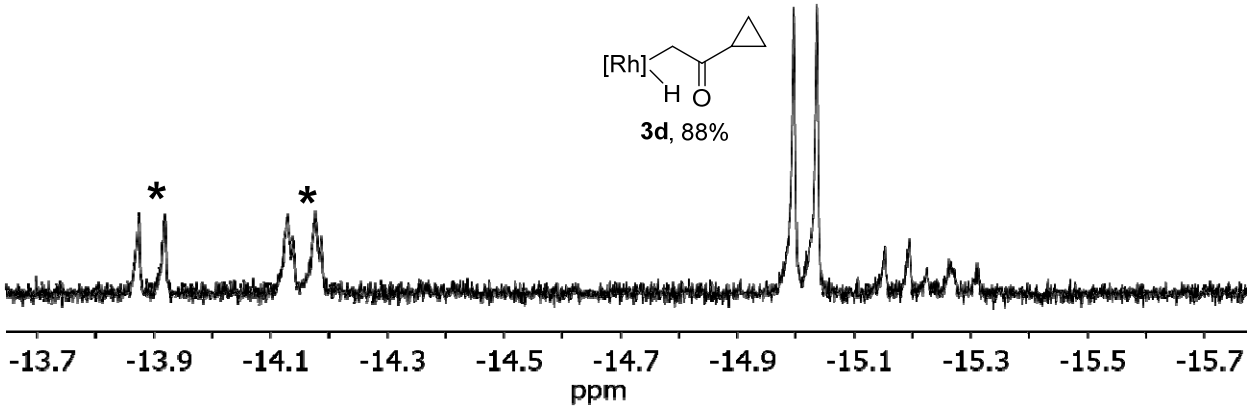


Figure S4. ^{1}H NMR of hydride region for C-H activated cyclopropyl methyl ketone, **3d** δ -15.02 (J_{Rh-H} = 19.5 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.90, -14.15, -14.16). Product at δ -15.17 was not assigned, but likely arise from cyclopropyl C-H activation.

[1] A. J. Vetter, R. D. Rieth, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* 2009, **131**, 10742–10752.

Activation of 4-phenyl-2-butanone

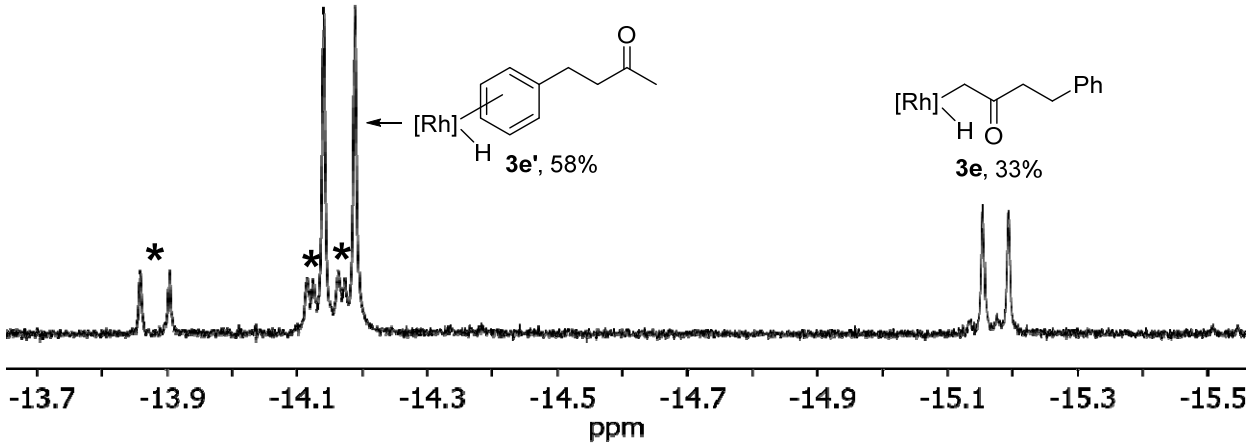


Figure S5. ^{1}H NMR of hydride region for C-H activated 4-phenyl-2-butanone, **3e** δ -15.17 (J_{Rh-H} = 19.5 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.88, -14.12, -14.17). The product at δ -14.17 (J_{Rh-H} = 24.0 Hz) was assigned to an arene C-H activation product.

Activation of 4-chloro-2-butanone

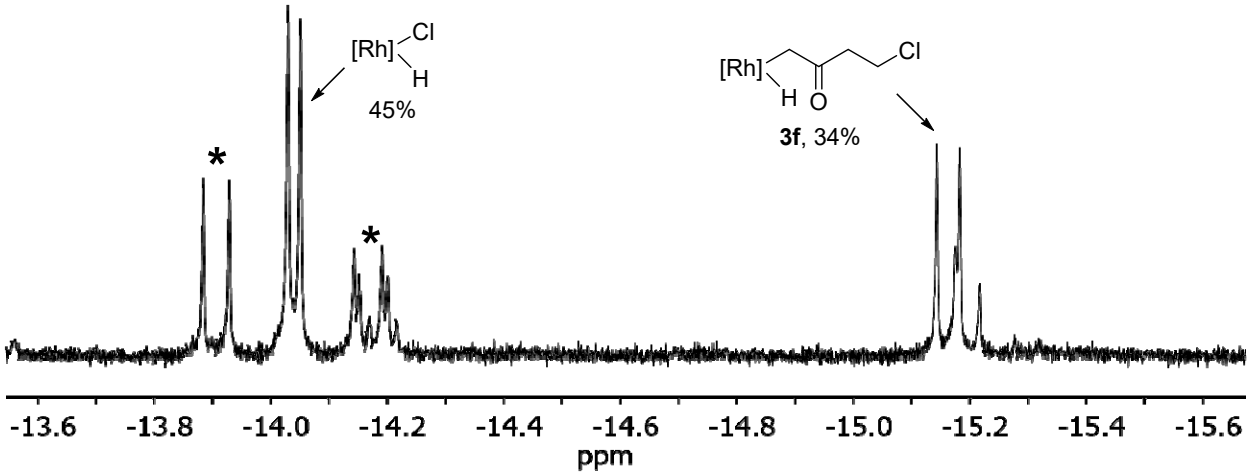
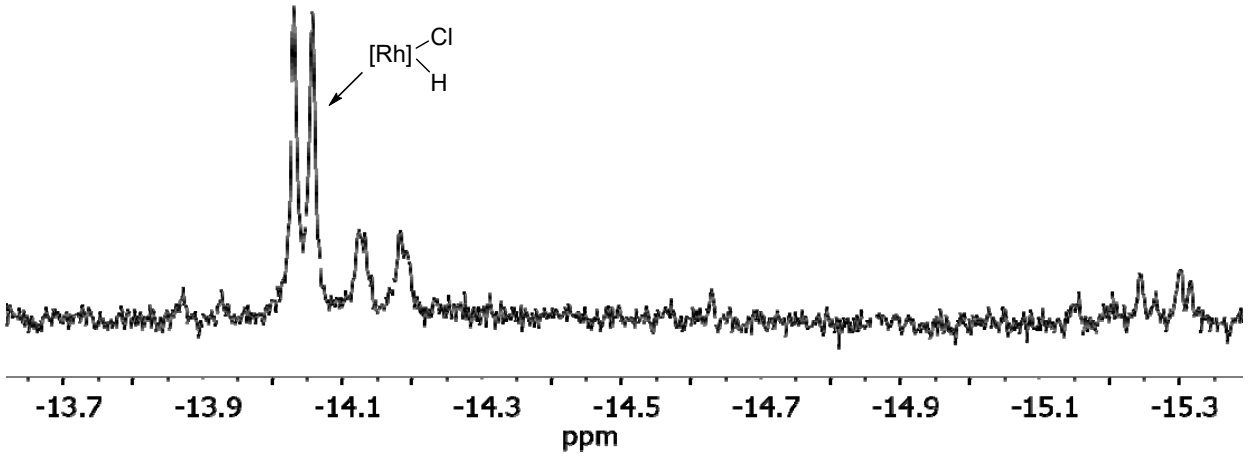


Figure S6. ^{1}H NMR of hydride region for C-H activated 4-chloro-2-butanone, **3f** δ -15.16 (J_{Rh-H} = 19.5 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.91, -14.15, -14.20). Product at δ -14.04 (J_{Rh-H} = 10.5 Hz) was assigned to Tp'Rh(CNR)HCl. The hydride doublet at δ -15.19 (J_{Rh-H} = 20.8 Hz) was not visible after 5 h, and could be due to α-keto CH_2 activation that leads to β-chlorine elimination.

Formation of Tp'Rh(CNR)(H)(Cl) in C_6D_{12}:

The identity of Tp'Rh(CNR)(H)(Cl) has been previously reported in C_6D_6 from the photolysis of **1** with 2-chloropropane.[2] In order to confirm the identity of δ -14.04 (J_{Rh-H} = 10.5 Hz) in the activation of 4-chloro-2-butanone, activation of 2-chloropropane in C_6D_{12} was performed. Indeed, the chemical shift of Tp'Rh(CNR)(H)(Cl) generated from photolysis of **1** with 2-chloropropane is shifted in C_6D_{12}.



Activation of methyl acetate

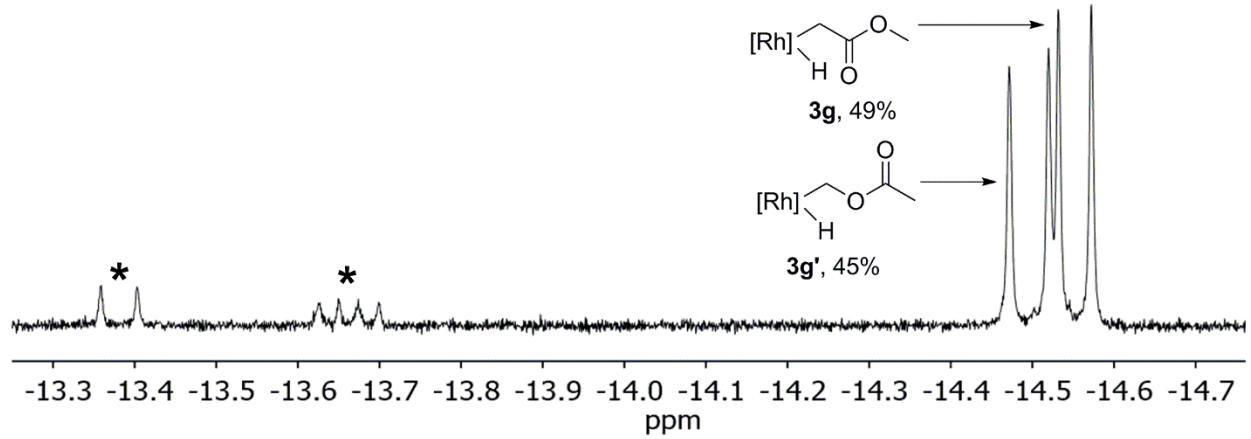


Figure S7. ^{1}H NMR of hydride region for C-H activated methyl acetate, **3g** δ -14.55 (J_{Rh-H} = 20.2 Hz) and **3g'** δ -14.50 (J_{Rh-H} = 24.1 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.39, -13.64, and -13.69).

[2] A. J. Vetter, W. D. Jones, *Polyhedron* **2004**, *23*, 413-417.

Activation of methyl butyrate

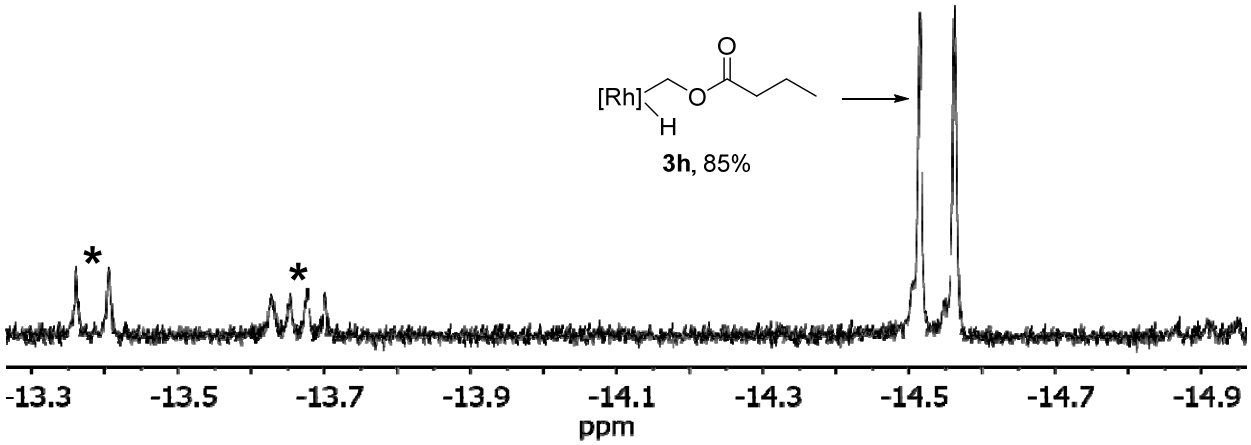


Figure S8. ^{1}H NMR of hydride region for C-H activated methyl butyrate, **3h** δ -14.54 (J_{Rh-H} = 23.9 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.39, -13.64, and -13.69).

Activation of dimethyl carbonate

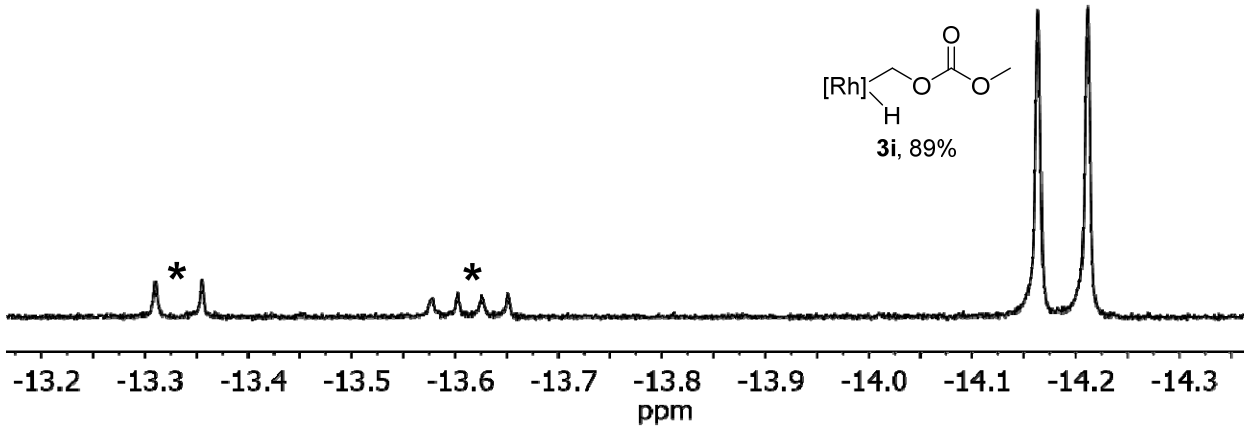


Figure S9. ^{1}H NMR of hydride region for C-H activated dimethyl carbonate, **3i** δ -14.24 (J_{Rh-H} = 24.1 Hz). Small quantities of *o*-, *m*-, and *p*-carbodiimide activation products were observed (δ -13.39, -13.64, and -13.69).

2. Plots of the reductive elimination of Tp'Rh(CNneopentyl)(R)(H) complexes

Note: All hydride integrations were measured relative to hexamethyldisiloxane as an internal standard.

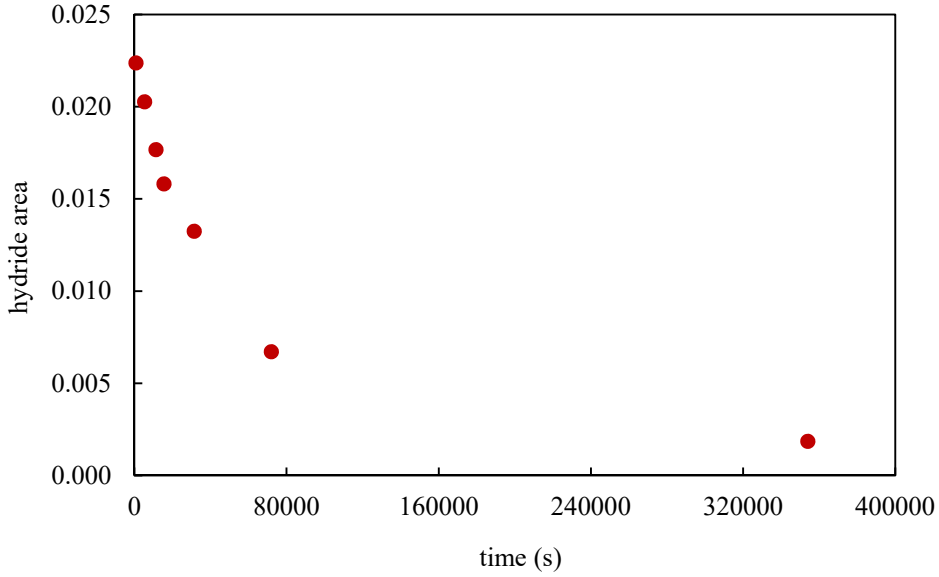


Figure S10. Reductive elimination of diethyl ketone (**2a**) from **3a** at room temperature (24 °C) in C_6D_6.

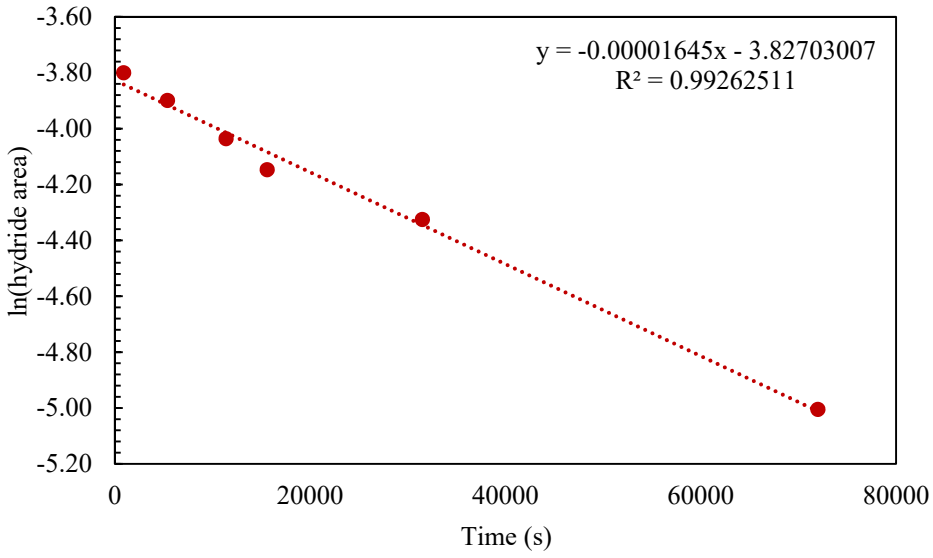


Figure S11. Kinetic data for the reductive elimination of diethyl ketone (**2a**) from **3a** at room temperature (24 °C) in C_6D_6.

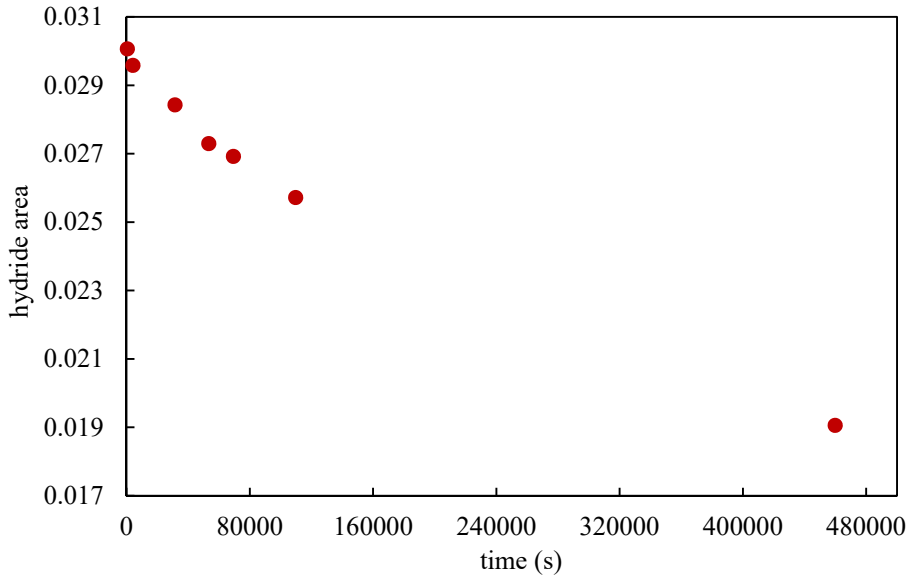


Figure S12. Reductive elimination of ethyl methyl ketone (**2b**) from **3b** at room temperature (24 °C) in C_6D_6.

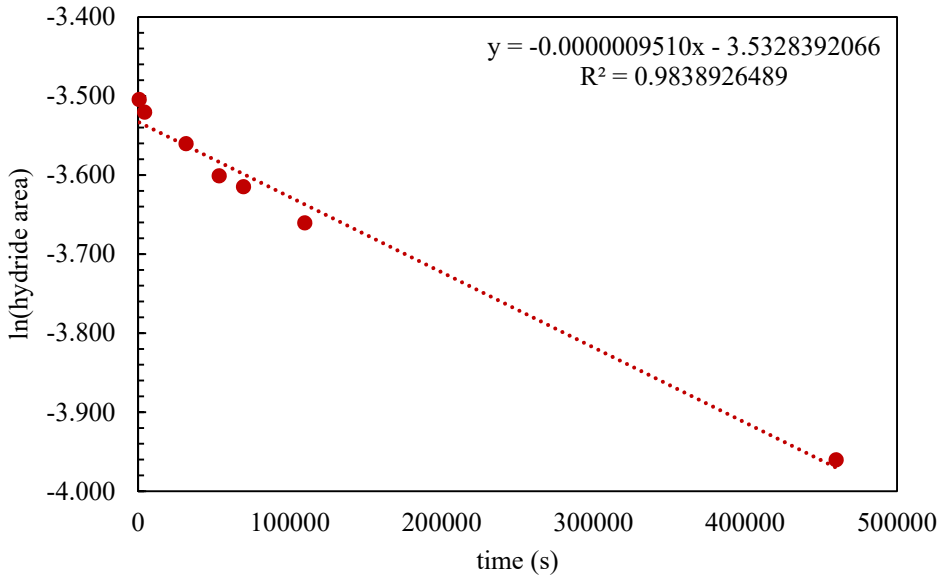


Figure S13. Kinetic data for the reductive elimination of ethyl methyl ketone (**2b**) from **3b** at room temperature (24 °C) in C_6D_6.

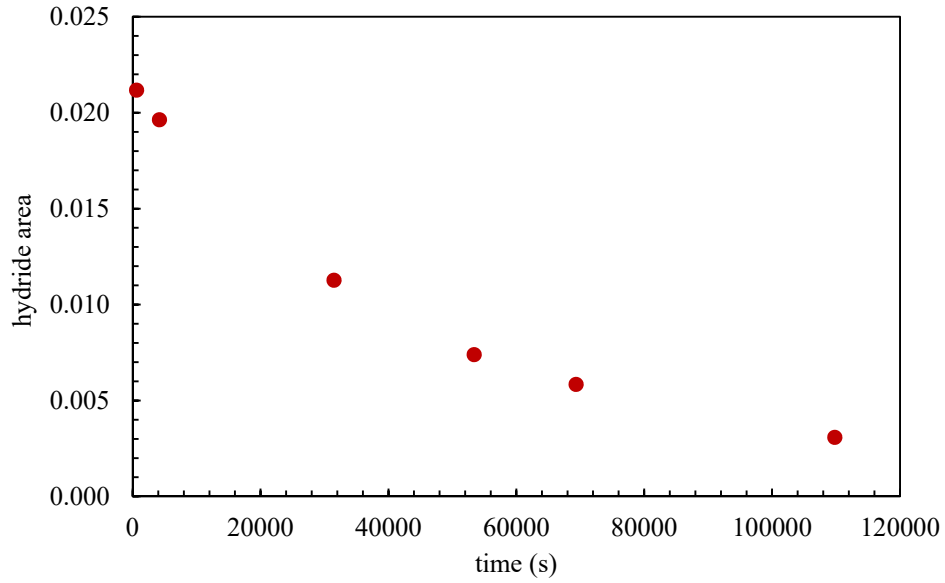


Figure S14. Reductive elimination of ethyl methyl ketone (**2b'**) from **3b'** at room temperature (24 °C) in C_6D_6.

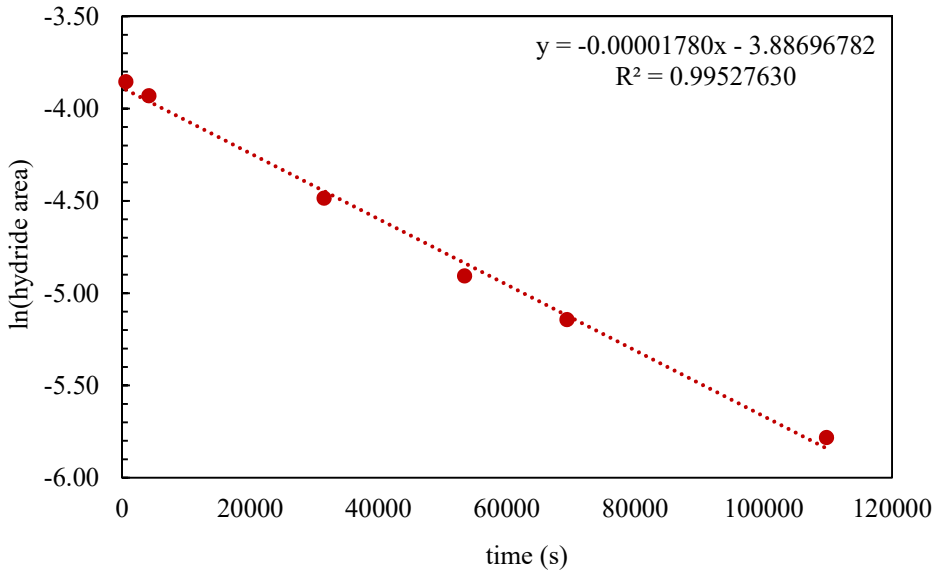


Figure S15. Kinetic data for the reductive elimination of ethyl methyl ketone (**2b'**) from **3b'** at room temperature (24 °C) in C_6D_6.

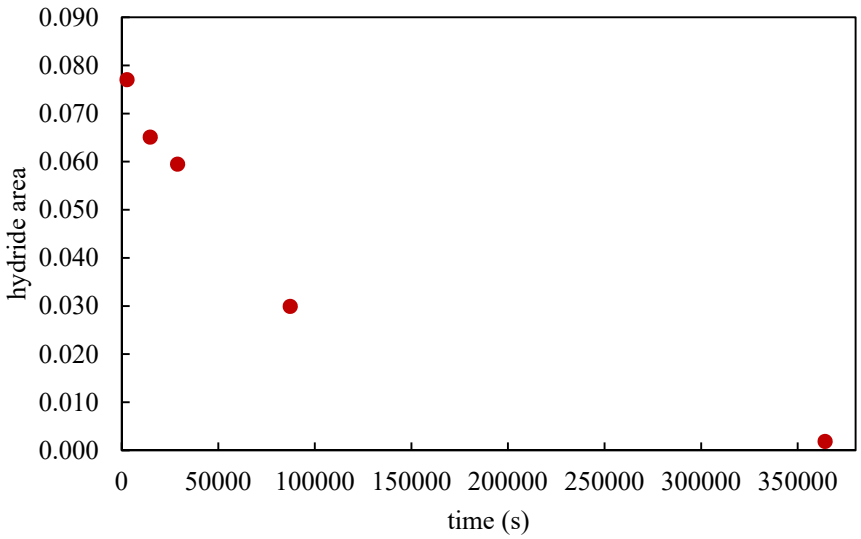


Figure S16. Reductive elimination of cyclopentanone (**2c**) from **3c** at 40 °C in C_6D_{12}.

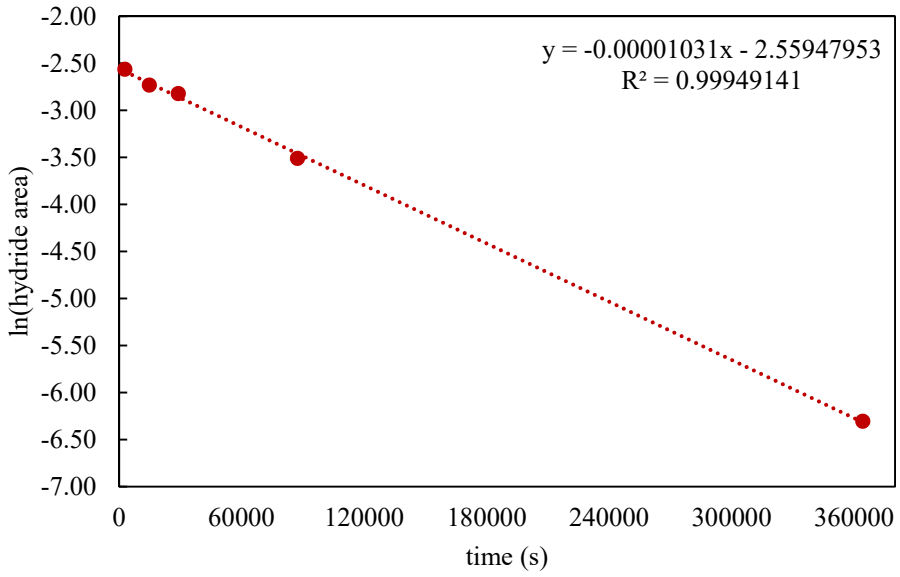


Figure S17. Kinetic data for the reductive elimination of cyclopentanone (**2c**) from **3c** at 40 °C in C_6D_{12}.

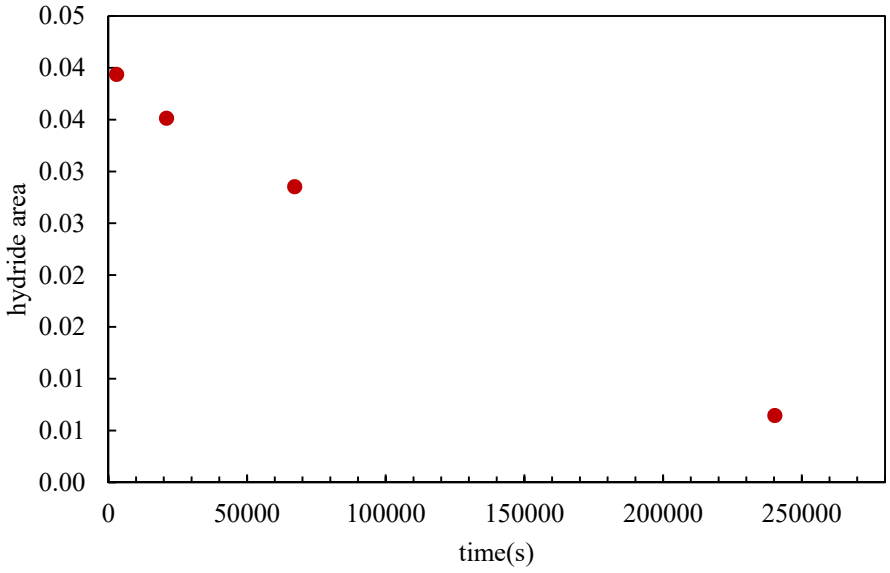


Figure S18. Reductive elimination of cyclopropyl methyl ketone (**2d**) from **3d** at 70 °C in C_6D_{12}.

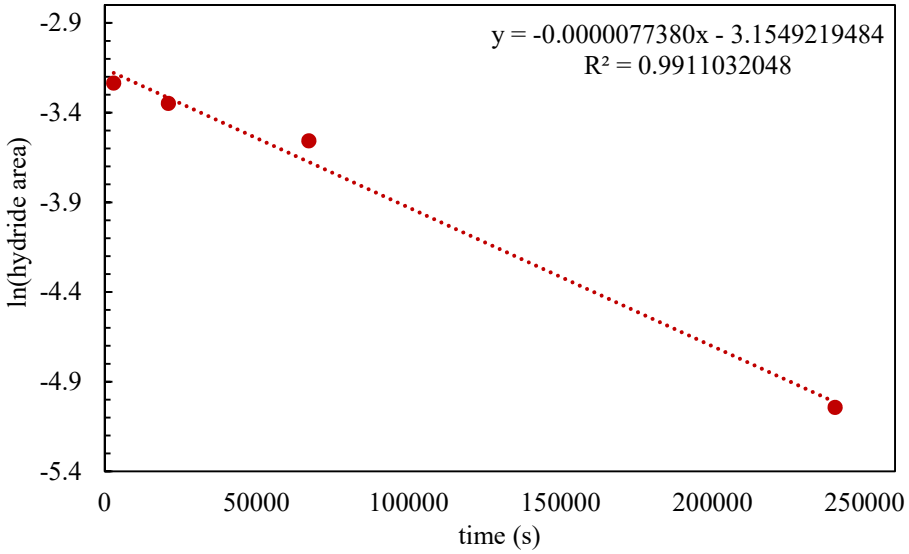


Figure S19. Kinetic data for the reductive elimination of cyclopropyl methyl ketone (**2d**) from **3d** at 70 °C in C_6D_{12}.

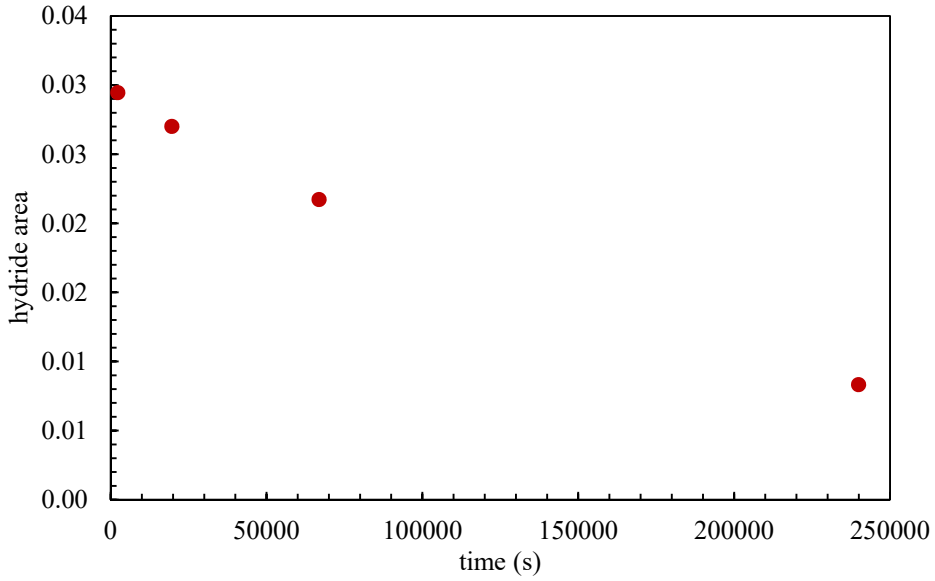


Figure S20. Reductive elimination of 4-phenyl-2-butanone (**2e**) from **3e** at 70 °C in C_6D_{12}.

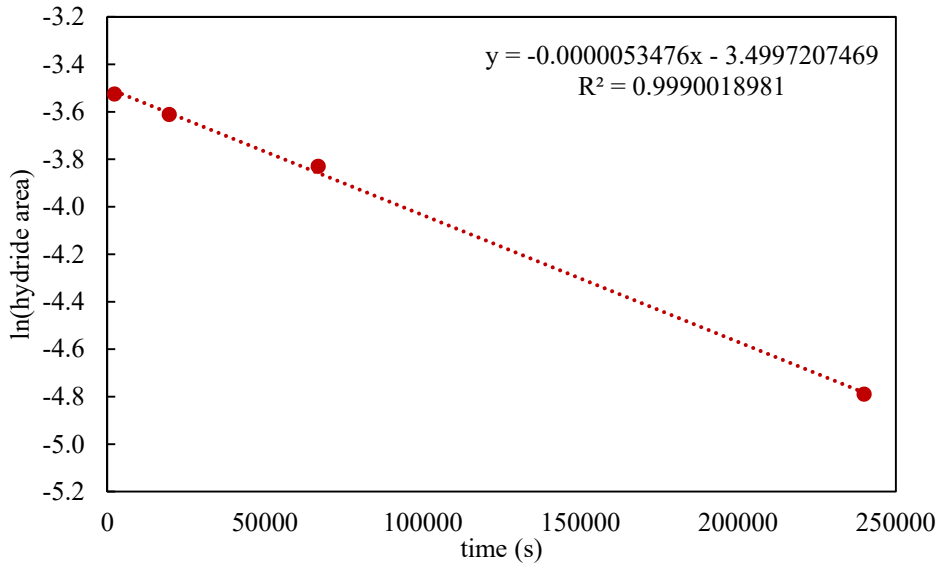


Figure S21. Kinetic data for the reductive elimination of 4-phenyl-2-butanone (**2e**) from **3e** at 70 °C in C_6D_{12}.

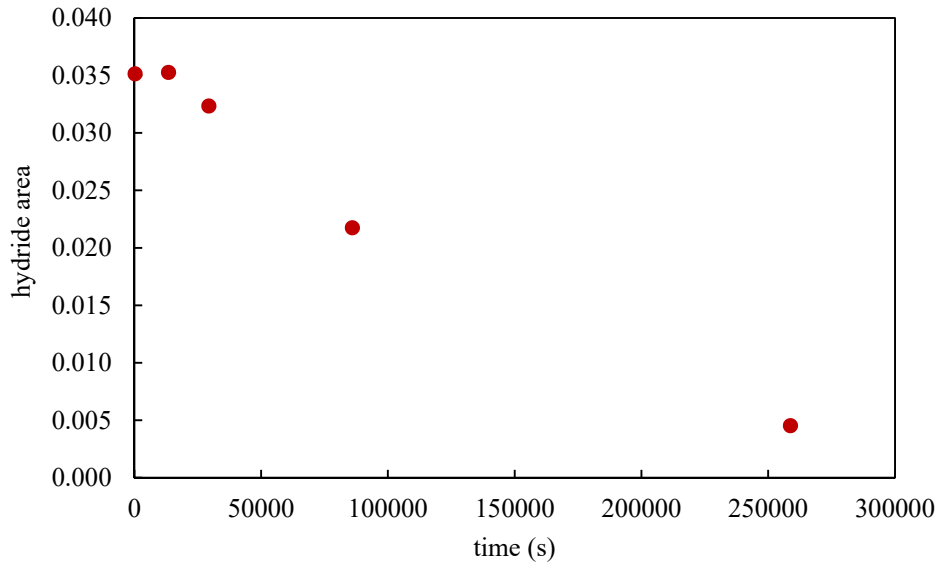


Figure S22. Reductive elimination of 4-chloro-2-butanone (**2f**) from **3f** at room temperature (24 °C) in C_6D_{12}.

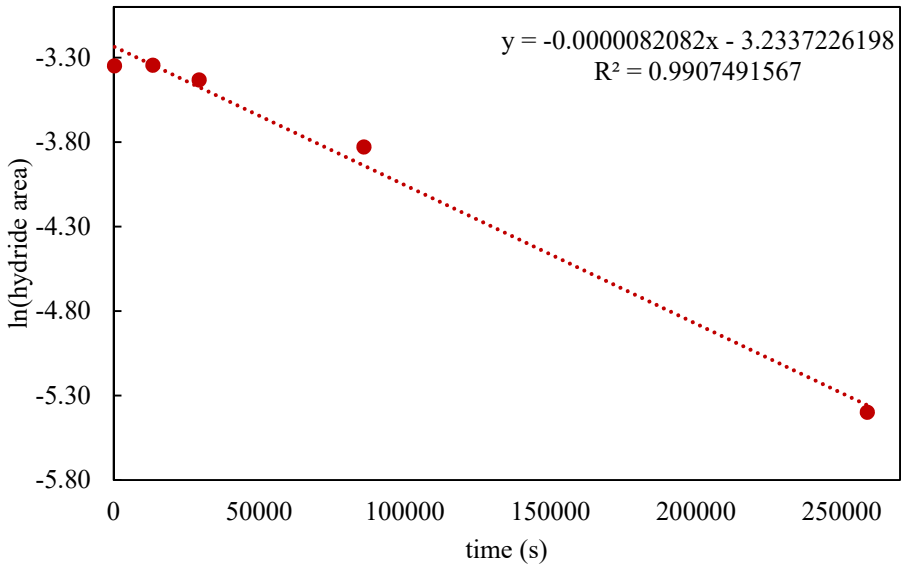


Figure S23. Kinetic data for the reductive elimination of 4-chloro-2-butanone (**2f**) from **3f** at room temperature (24 °C) in C_6D_{12}.

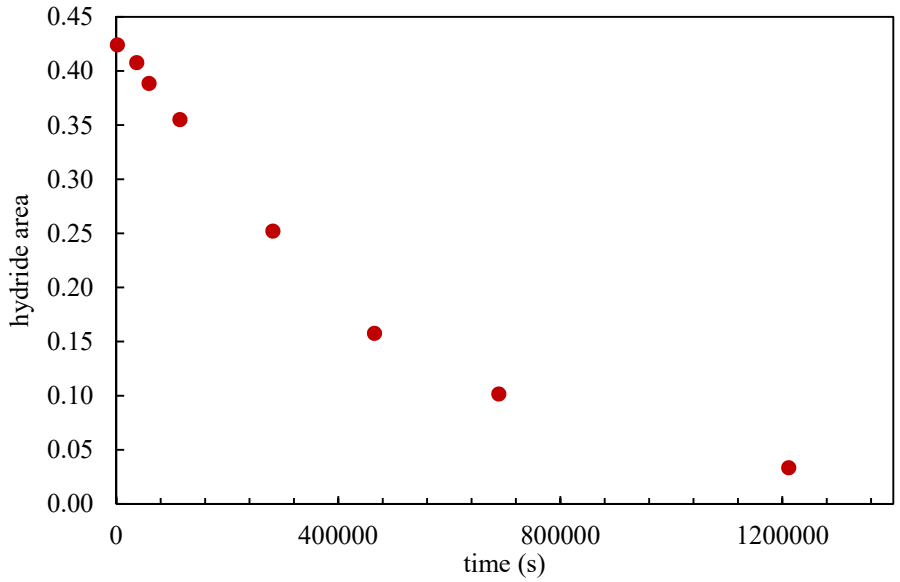


Figure S24. Reductive elimination of methyl acetate (**2g**) from **3g** at 60 °C in C_6D_6.

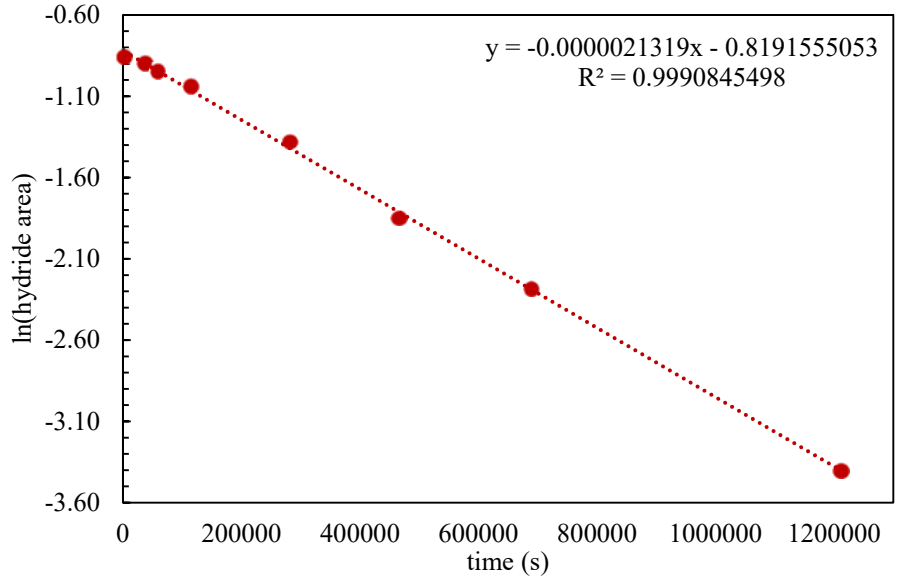


Figure S25. Kinetic data for the reductive elimination of methyl acetate (**2g**) from **3g** at 60 °C in C_6D_6.

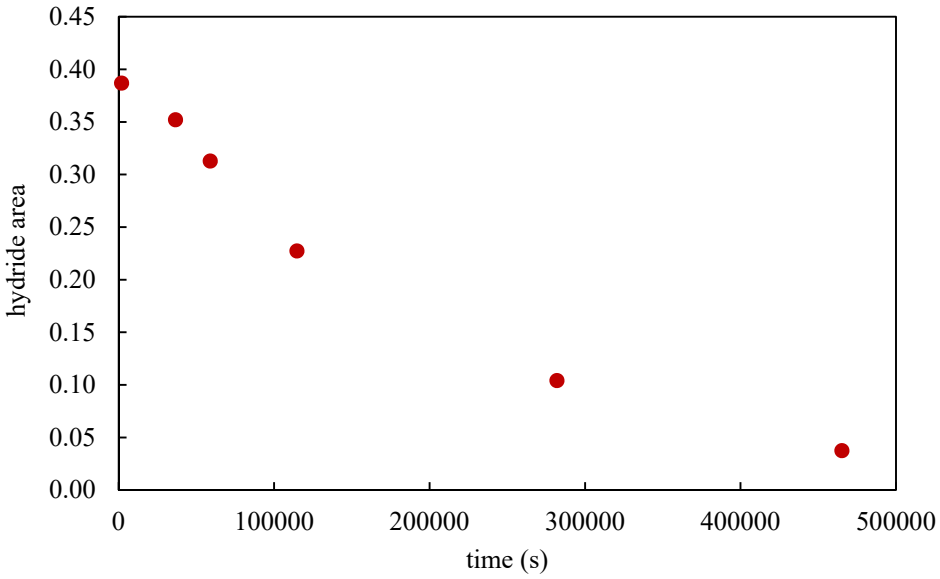


Figure S26. Reductive elimination of methyl acetate (**2g'**) from **3g'** at 60 °C in C_6D_6.

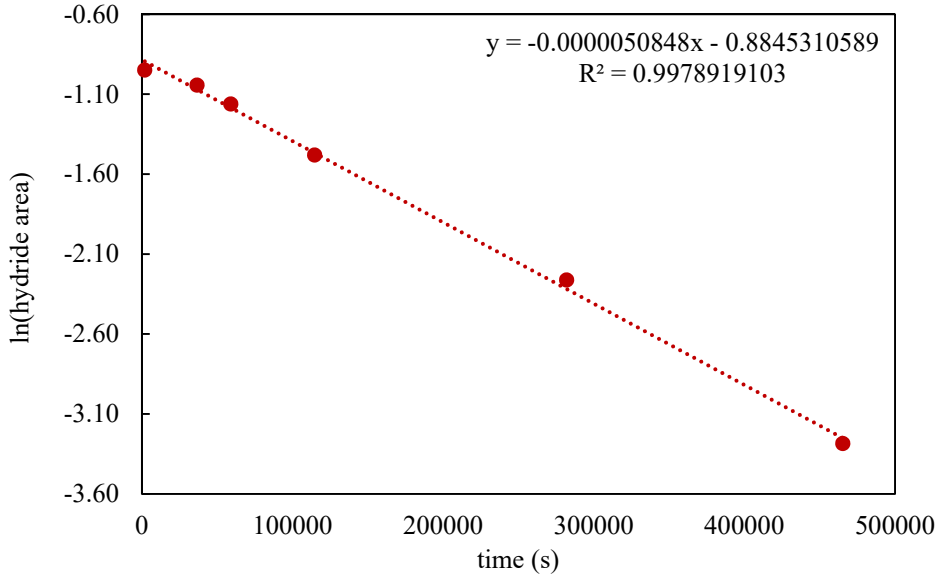


Figure S27. Kinetic data for the reductive elimination of methyl acetate (**2g'**) from **3g'** at 60 °C in C_6D_6.

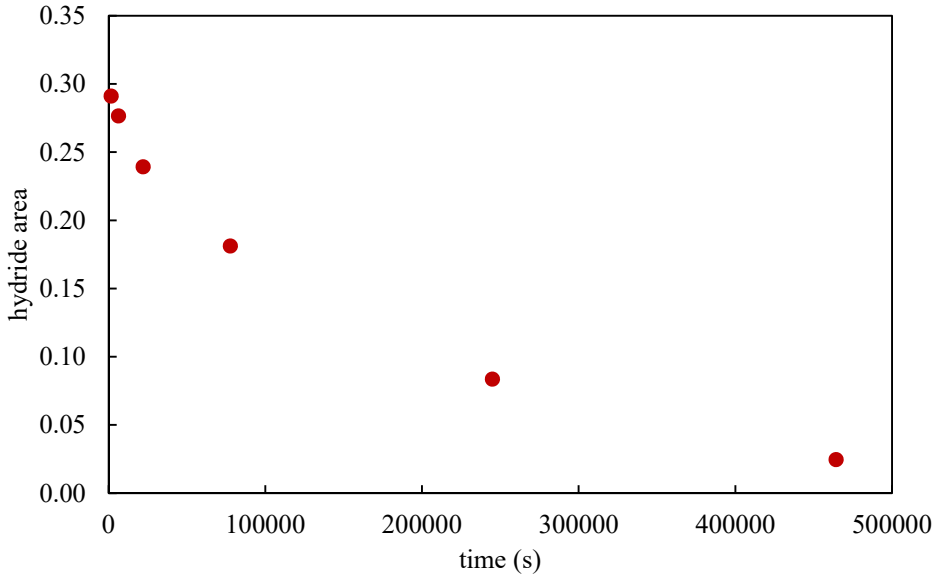


Figure S28. Reductive elimination of methyl butyrate (**2h**) from **3h** at 60 °C in C_6D_6.

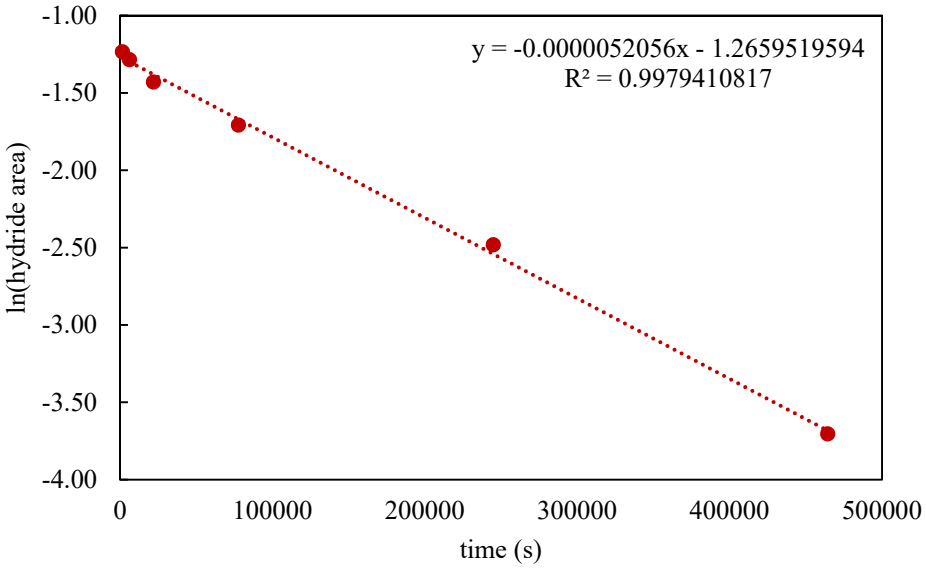


Figure S29. Kinetic data for the reductive elimination of methyl butyrate (**2h**) from **3h** at 60 °C in C_6D_6.

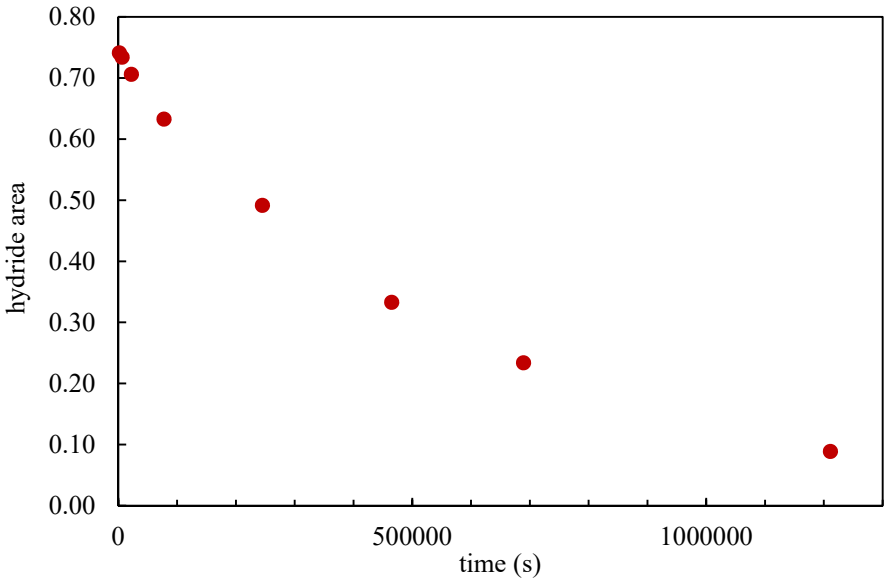


Figure S30. Reductive elimination of dimethyl carbonate (**2i**) from **3i** at 60 °C in C_6D_6.

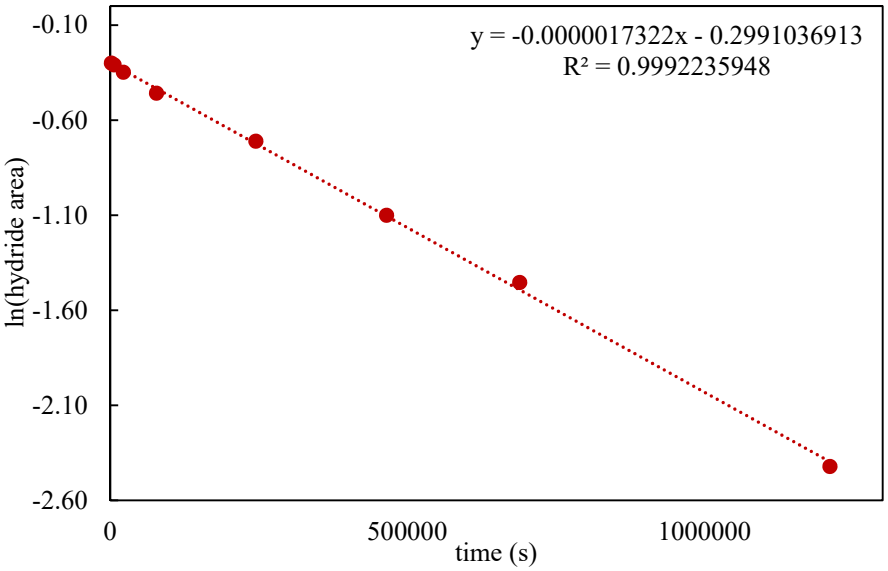
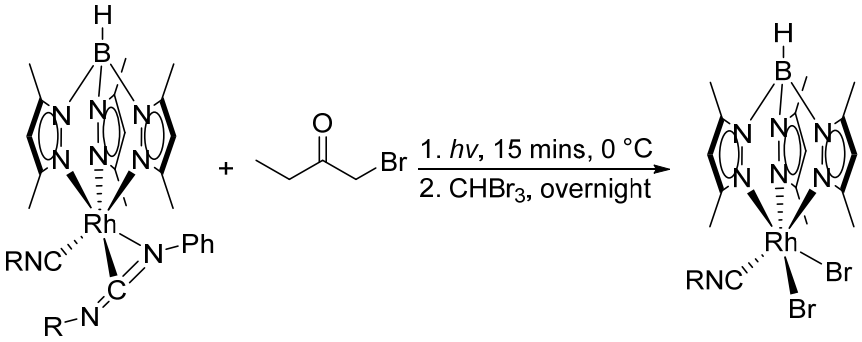


Figure S31. Kinetic data for the reductive elimination of dimethyl carbonate (**2i**) from **3i** at 60 °C in C_6D_6.

3. Activation of Substrates Bearing C-Br Bonds

Activation of 1-bromo-2-butanone

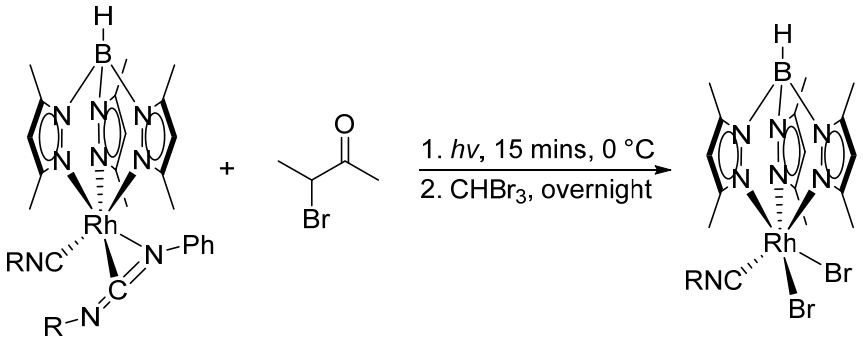


1, R = neopentyl **5**, 64%

The reaction was setup in a nitrogen filled glovebox. To an oven-dried 1-dram vial was added **1** (35.0 mg, 0.050 mmol). Next, 1.0 mL of 1-bromo-2-butanone was added and the reaction mixture was capped. The sample was removed from the glovebox and irradiated at 0 °C for 15 min. After 15 min, the reaction mixture was removed from the ice bath and brought inside the glovebox. Bromoform (0.25 mL, 2.8 mmol) and a Teflon-coated stir-bar were added and the reaction mixture was stirred overnight. The reaction was concentrated *in vacuo* and the resulting residue was purified by column chromatography (7:3 hexane: ethyl acetate, $R_f = 0.47$) to afford **5** as a yellow solid (21 mg, 67% yield).

^{1}H NMR (400 MHz; C_6D_6): δ 5.57 (s, 1H), 5.51 (s, 2H), 3.29 (s, 3H), 2.77 (s, 2H), 2.76 (s, 6H), 2.12 (s, 3H), 2.03 (s, 6H), 0.86 (s, 1H), 0.85 (s, 9H).

Activation of 3-bromo-2-butanone



1, R = neopentyl 76%

The reaction was setup in a nitrogen filled glovebox. To an oven-dried 1-dram vial was added **1** (35.0 mg, 0.050 mmol). Next, 1.0 mL of 3-bromo-2-butanone was added and the reaction mixture was capped. The sample was removed from the glovebox and irradiated at 0 °C for 15 min. After 15 min, the reaction mixture was removed from the ice bath and brought inside the glovebox. Bromoform (0.25 mL, 2.8 mmol) and a Teflon-coated stir-bar were added and the reaction mixture was stirred overnight. The reaction was concentrated *in vacuo* and the resulting residue was purified by column chromatography (7:3 hexane: ethyl acetate, $R_f = 0.49$) to afford **5** as a yellow solid (25 mg, 76% yield).

^{1}H NMR (400 MHz; C_6D_6): δ 5.57 (s, 1H), 5.51 (s, 2H), 3.29 (s, 3H), 2.77 (s, 2H), 2.76 (s, 6H), 2.12 (s, 3H), 2.03 (s, 6H), 0.86 (s, 1H), 0.85 (s, 9H).

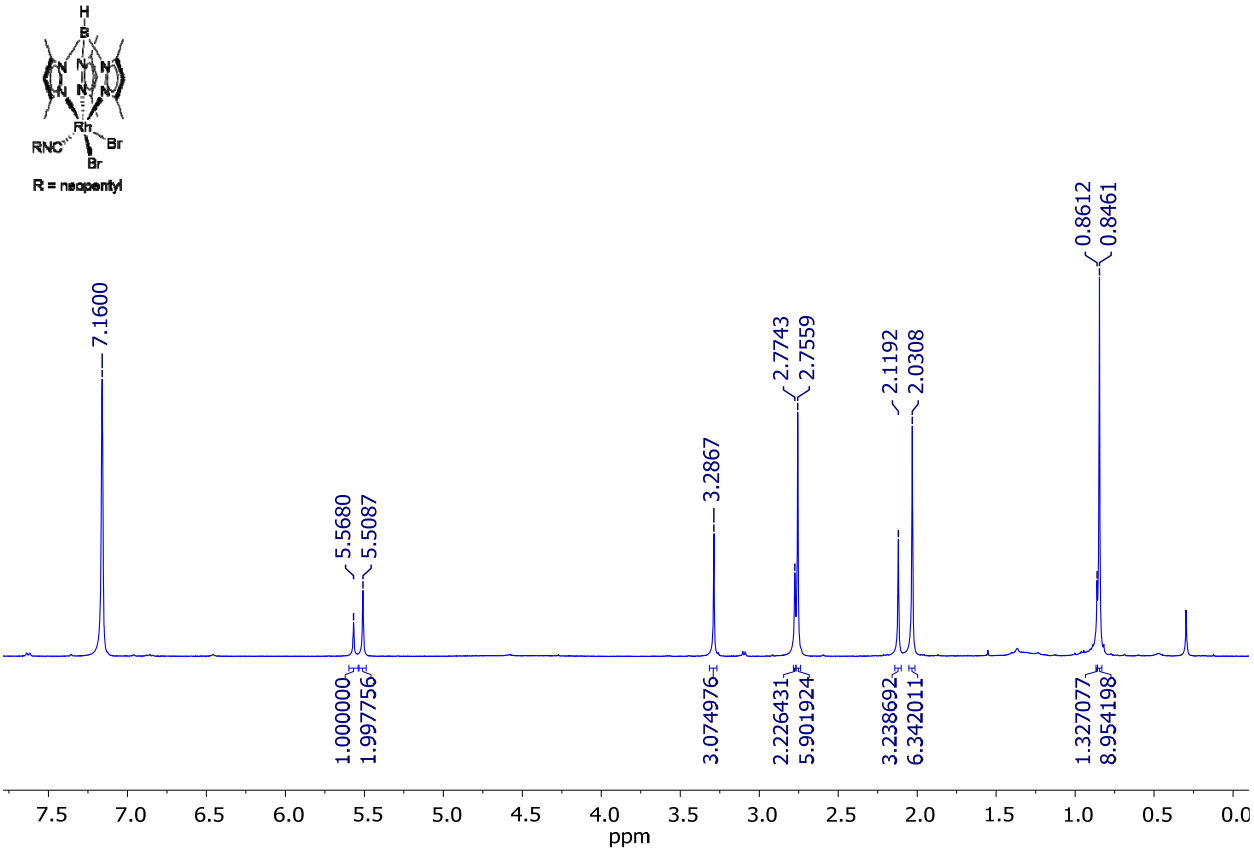
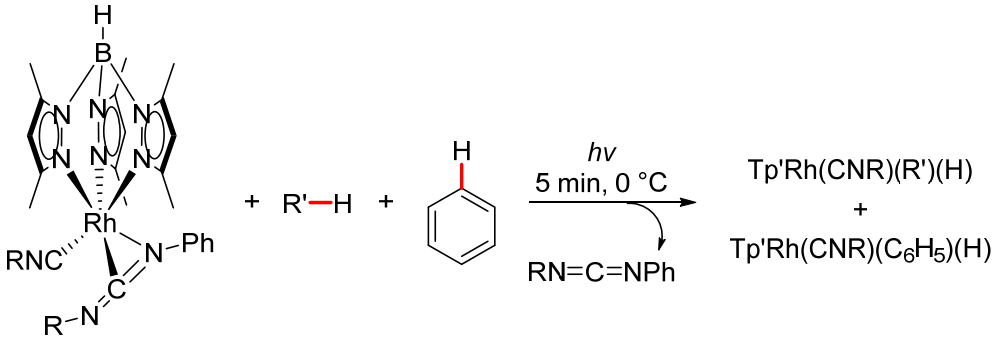


Figure S32. ^{1}H NMR analysis of Tp'Rh(CNneopentyl)Br$_2$.

4. Summary of Kinetic and Thermodynamic Selectivity



Reactions were setup in a nitrogen filled glovebox. To an oven-dried 5 mm J Young NMR tube was added **1** (6.9 mg, 0.010 mmol). Next, benzene (0.25 mL) and substrate (0.25 mL) were added and the NMR tube was capped. The sample was removed from the glovebox and irradiated at 0 °C for 5 minutes. After 5 minutes, the reaction was removed from the ice bath and the integrated area ratio (benzene: substrate) was determined by ^{1}H NMR spectroscopy.

Table S1. Kinetic Selectivity Data[a]

entry	benzene: substrate	integrated area ratio (I_2/I_1)	substrate ratio (n_1/n_2)[b]	k_1/k_2[c]
1	benzene: **2a**	1.63	0.84	1.37(7)
2	benzene: **2b**	1.97	1.00	1.97(10)
3	benzene: **2b'**	1.77	1.00	1.67(9)
4	benzene: **2c**	20.64	1.01	20.85(104)
5	benzene: **2d**	11.15	0.90	10.06(50)
6	benzene: **2e**	4.09	0.60	2.44(12)
7	benzene: **2f**	-	-	-
8	benzene: **2g**	5.42	1.13	6.11(31)
9	benzene: **2g'**	7.51	1.13	7.51(38)
10	benzene: **2h**	22.09	0.79	17.36(87)
11	benzene: **2i**	3.03	1.06	3.21(15)

[a]Each sample was irradiated for 5 minutes at 0 °C. [b]The substrate ratio was determined from added amounts in mmol. [c]Errors in rate ratio estimated at 5% for proton NMR integrations.

NOTE: Attempts to obtain kinetic selectivity data for 4-chloro-2-butanone were unsuccessful.

Table S2. Summary of Thermodynamic Data (All values are in kcal/mol)

Data for plot of M-R vs R-H bond strengths-Tp'Rh(CNneopenthyl)(R)(H)

D_{rel}(R-H) = [ΔH(Rh-R) -ΔH(Rh-Ph)] = ΔG° + RT ln(6/#H) + [ΔH(R-H)-ΔH(Ph-H)]

ΔG° ≈ ΔH° - RT ln(6/#H)

ΔS° ≈ R ln(6/#H)

ΔG° = [ΔH(Rh-R) + ΔH(Ph-H)] – [ΔH(R-H) + ΔH(Rh-Ph)] – RT ln(6/#H)

ΔG° = [ΔH(Rh-R) – ΔH(Rh-Ph)] – [ΔH(R-H) – ΔH(Ph-H)] – RT ln(6/#H)

Product	***D*(R-H)**[a]	**$\Delta\Delta G_{oa}^{\ddagger}$ vs PhH**[b]	**$\Delta G_{re}^{\ddagger}$**	**T_{re}(R-H) (K)**	**ΔG° vs PhH**	**# H**	**D_{rel}(M-R)**
phenyl	112.9	0	27.61	303	0	6	0
$CH_2C(=O)CH_3$	96.0	0.71	27.71	343	0.21	6	-17.1
3a	98.34	0.17	23.88	297	3.97	6	-18.1
3b	91.34	0.31	25.57	297	2.42	3	-23.7
3b'	98.94	0.37	23.84	297	4.21	3	-17.8
3c	85.34	1.65	25.49	313	3.67	4	-30.8
3d	91.22	1.25	28.19	343	0.27	3	-21.5
3e	90.22	0.48	28.45	343	-0.76	3	-21.5
3f	90.67	-	24.29	298	-	3	-
3g	93.59	0.98	28.21	333	0.08	3	-19.0
3g'	95.95	1.09	27.63	333	0.77	3	-17.3
3h	94.63	1.55	27.61	333	1.25	3	-19.1
3i	96.83	0.63	28.34	333	-0.40	6	-15.7

[a]All hydrocarbon C-H bond strengths were calculated using B3LYP/6-311g.

5. Gaussian Input

```
%mem=1500mb
%chk=/scratch/aolivare/diethylketone.chk
%NProcShared=12
#n B3LYP/6-311g opt freq scf=(maxcycles=10000) nosymm

diethylketone

0 1
 C                  0.08620690   -0.09852217    0.00000000
 O                  0.71324555    0.99252716    0.00210835
 C                  0.85356407   -1.43372364    0.00000000
 H                  0.15663780   -2.24562923   -0.00176057
 H                  1.46993096   -1.49086305   -0.87276969
 C                 -1.45379093   -0.09852092   -0.00258904
 H                 -1.80898766   -0.60215948   -0.87727953
 H                 -1.81192521   -0.60368694    0.87002034
 C                 -1.96712476    1.35340478   -0.00218280
 H                 -1.61194137    1.85719497    0.87242579
 H                 -1.60914647    1.85853922   -0.87487446
 H                 -3.03712338    1.35322509   -0.00389446
 C                  1.73686620   -1.51814950    1.25866978
 H                  2.09672591   -2.51903889    1.37538060
 H                  2.56670399   -0.85029271    1.15749397
 H                  1.16089132   -1.24377638    2.11766473
```

6. X, Y, Z Coordinates Used for BDE (DFT) Calculations

Substrate **2a**

```
C                  0.08620690   -0.09852217    0.00000000
O                  0.71324555    0.99252716    0.00210835
C                  0.85356407   -1.43372364    0.00000000
H                  0.15663780   -2.24562923   -0.00176057
H                  1.46993096   -1.49086305   -0.87276969
C                 -1.45379093   -0.09852092   -0.00258904
H                 -1.80898766   -0.60215948   -0.87727953
H                 -1.81192521   -0.60368694    0.87002034
C                 -1.96712476    1.35340478   -0.00218280
H                 -1.61194137    1.85719497    0.87242579
H                 -1.60914647    1.85853922   -0.87487446
H                 -3.03712338    1.35322509   -0.00389446
C                  1.73686620   -1.51814950    1.25866978
H                  2.09672591   -2.51903889    1.37538060
H                  2.56670399   -0.85029271    1.15749397
```

H	1.16089132	-1.24377638	2.11766473

Substrate **2b'**

C	1.83497538	-0.44334975	0.00000000
O	2.46201404	0.64769958	0.00210835
C	0.29497756	-0.44334850	-0.00258904
H	-0.06021918	-0.94698707	-0.87727953
H	-0.06315673	-0.94851452	0.87002034
H	-0.06168945	0.56545702	-0.00230678
C	2.60233255	-1.77855122	0.00000000
H	2.34105017	-2.34008676	0.87253043
H	2.34441077	-2.33815538	-0.87476828
C	4.11695525	-1.50014916	0.00322082
H	4.37486127	-0.94046022	0.87793951
H	4.65011834	-2.42785446	0.00331974
H	4.37825342	-0.93869768	-0.86935897

Substrate **2b'**

Same coordinates as **2b** above.

Substrate **2c**

C	-0.91059599	-0.06622516	0.00000000
C	0.61126201	-0.06622516	0.00000000
C	1.08003501	1.38163984	0.00000000
C	-1.37980199	1.37809484	-0.10359000
H	-1.30255799	-0.66867016	-0.85750800
H	-1.30071099	-0.53663616	0.93750400
H	0.99988901	-0.60082316	-0.90328000
H	1.00462901	-0.60695716	0.89683700
H	1.62697001	1.61333284	0.94858800
H	1.79199601	1.56481584	-0.84321600
H	-2.03217999	1.63989684	0.76707400
H	-1.99154799	1.52571684	-1.02879300
C	-0.14770499	2.27120784	-0.13318600
O	-0.14442610	3.52404496	-0.25133398

Substrate **2d**

C	-0.62913904	-0.44701986	0.00000000
C	0.87197596	-0.44701986	0.00000000
C	0.12139096	0.85295514	0.00000000
H	-1.16573504	-0.75689486	-0.91385800
H	-1.16573504	-0.75689486	0.91385800
H	1.40853696	-0.75678686	-0.91388800
H	1.40853696	-0.75678686	0.91388800
H	0.12116796	1.47248314	0.91394400
C	0.12107992	1.71704808	-1.27473263
O	0.12119782	2.97252663	-1.18903462
C	0.12062305	1.04240066	-2.65909193
H	0.99409341	0.43249541	-2.75891734

H	-0.75320951	0.43295694	-2.75856560
H	0.12066780	1.79300135	-3.42165249

Substrate **2e**

C	0.72847679	-0.54635761	0.00000000
O	1.35551722	0.54469069	-0.00211561
C	-0.81152321	-0.54635761	0.00000000
H	-1.16818956	-0.04348018	-0.87453039
H	-1.16818956	-1.55516186	0.00176083
H	-1.16819007	-0.04043076	0.87276960
C	1.49583396	-1.88155657	0.00258904
H	1.23616436	-2.44047020	0.87728170
H	1.23629725	-2.44378195	-0.87001816
C	3.01045975	-1.60315301	0.00217656
H	3.26999144	-1.04090193	0.87476869
H	3.27013420	-1.04426453	-0.87253073
C	3.77781624	-2.93835228	0.00480827
C	4.12616980	-3.54503952	-1.20227574
C	4.12467821	-3.54111614	1.21390324
C	4.82063703	-4.75455702	-1.20016997
H	3.85189049	-3.06996503	-2.15533234
C	4.82022093	-4.75050649	1.21618267
H	3.85035613	-3.06299951	2.16536575
C	5.16810905	-5.35734508	0.00942760
H	5.09469767	-5.23313008	-2.15156636
H	5.09393306	-5.22532015	2.16965416
H	5.71572272	-6.31097688	0.01083793

Substrate **2f**

C	0.01655629	-0.94362773	-0.01235276
O	0.64359495	0.14742160	-0.01024441
C	0.78391346	-2.27882920	-0.01235276
H	0.08698587	-3.09073555	-0.01235263
H	1.39895899	-2.33672801	-0.88600414
H	1.39895907	-2.33672855	0.86129852
C	-1.52344153	-0.94362648	-0.01494180
H	-1.87863897	-1.44799105	-0.88921359
H	-1.88157653	-1.44806689	0.85808695
C	-2.03677334	0.50829977	-0.01574179
H	-1.67836998	1.01283486	-0.88860568
H	-1.68184425	1.01256980	0.85869350
Cl	-3.79676986	0.50830037	-0.01924073

Substrate **2g**

C	1.58866996	-0.71422449	-0.00934971
O	2.21571039	0.37682380	-0.01146532
C	0.04866996	-0.71422449	-0.00934971
H	-0.30799639	-1.22030363	-0.88203122
H	-0.30799639	-1.21694906	0.86526857

H	-0.30799689	0.29457925	-0.01128648
C	3.87065293	-1.77102031	-0.00738602
H	4.13030372	-1.20874927	0.86515782
H	4.40381621	-2.69872380	-0.00560887
H	4.13020828	-1.21215198	-0.88214152
O	2.35602713	-2.04942346	-0.00676068

Substrate **2g'**
Same coordinates as **2g** above.

Substrate **2h**

C	1.80463568	-1.05951183	-0.01386977
O	2.43167611	0.03153851	-0.01386977
O	2.51718162	-2.29934177	-0.01386977
C	1.58631920	-3.38488088	-0.01386977
H	2.11994772	-4.31231648	-0.01582603
H	0.97253145	-3.32839367	0.86075803
H	0.96995929	-3.32618868	-0.88654134
C	0.26463568	-1.05951183	-0.01386977
H	-0.09203067	-1.56356997	-0.88772017
H	-0.09203067	-1.56425918	0.85958271
C	-0.24869792	0.39241388	-0.01329707
H	0.10945702	0.89768687	-0.88583603
H	0.10647890	0.89594527	0.86146322
C	-1.78869569	0.39241493	-0.01592135
H	-2.14684946	-0.11318219	0.85643031
H	-2.14536318	1.40122002	-0.01514960
H	-2.14387242	-0.11079232	-0.89086818

Substrate **2i**

C	1.05960260	-0.84437085	0.00000000
O	1.68664303	0.24667950	0.00000000
O	1.77214854	-2.08420079	0.00000000
O	-0.37039740	-0.84437085	0.00000000
C	0.84128612	-3.16973990	0.00002588
H	0.23887503	-3.12302936	-0.88304773
H	1.37477798	-4.09705785	0.01920544
H	0.21368621	-3.10138867	0.86393933
C	-0.84774121	-0.55505496	-1.31656341
H	-1.77800286	-1.05870128	-1.47735408
H	-0.99094002	0.50024905	-1.42013730
H	-0.13145390	-0.89023164	-2.03731932

Substrate **2a•**

C	0.08620690	-0.09852217	0.00000000
O	0.71324555	0.99252716	0.00210835
C	0.85356407	-1.43372364	0.00000000
H	0.15663780	-2.24562923	-0.00176057
H	1.46993096	-1.49086305	-0.87276969

C	-1.45379093	-0.09852092	-0.00258904
H	-1.80898766	-0.60215948	-0.87727953
H	-1.81192521	-0.60368694	0.87002034
C	-1.96712476	1.35340478	-0.00218280
H	-1.61194137	1.85719497	0.87242579
H	-1.60914647	1.85853922	-0.87487446
H	-3.03712338	1.35322509	-0.00389446
C	1.73686620	-1.51814950	1.25866978
H	2.09672591	-2.51903889	1.37538060
H	1.16089132	-1.24377638	2.11766473

Substrate **2b'•**

C	1.83497538	-0.44334975	0.00000000
O	2.46201404	0.64769958	0.00210835
C	0.29497756	-0.44334850	-0.00258904
H	-0.06021918	-0.94698707	-0.87727953
H	-0.06315673	-0.94851452	0.87002034
C	2.60233255	-1.77855122	0.00000000
H	2.34105017	-2.34008676	0.87253043
H	2.34441077	-2.33815538	-0.87476828
C	4.11695525	-1.50014916	0.00322082
H	4.37486127	-0.94046022	0.87793951
H	4.65011834	-2.42785446	0.00331974
H	4.37825342	-0.93869768	-0.86935897

Substrate **2b•**

C	1.83497538	-0.44334975	0.00000000
O	2.46201404	0.64769958	0.00210835
C	0.29497756	-0.44334850	-0.00258904
H	-0.06021918	-0.94698707	-0.87727953
H	-0.06315673	-0.94851452	0.87002034
H	-0.06168945	0.56545702	-0.00230678
C	2.60233255	-1.77855122	0.00000000
H	2.34105017	-2.34008676	0.87253043
H	2.34441077	-2.33815538	-0.87476828
C	4.11695525	-1.50014916	0.00322082
H	4.37486127	-0.94046022	0.87793951
H	4.65011834	-2.42785446	0.00331974

Substrate **2c•**

C	-0.91059599	-0.06622516	0.00000000
C	0.61126201	-0.06622516	0.00000000
C	1.08003501	1.38163984	0.00000000
C	-1.37980199	1.37809484	-0.10359000
H	-1.30255799	-0.66867016	-0.85750800
H	-1.30071099	-0.53663616	0.93750400
H	0.99988901	-0.60082316	-0.90328000
H	1.00462901	-0.60695716	0.89683700
H	1.62697001	1.61333284	0.94858800

H	-2.03217999	1.63989684	0.76707400
H	-1.99154799	1.52571684	-1.02879300
C	-0.14770499	2.27120784	-0.13318600
O	-0.14442610	3.52404496	-0.25133398

Substrate **2d•**

C	-0.62913904	-0.44701986	0.00000000
C	0.87197596	-0.44701986	0.00000000
C	0.12139096	0.85295514	0.00000000
H	-1.16573504	-0.75689486	-0.91385800
H	-1.16573504	-0.75689486	0.91385800
H	1.40853696	-0.75678686	-0.91388800
H	1.40853696	-0.75678686	0.91388800
H	0.12116796	1.47248314	0.91394400
C	0.12107992	1.71704808	-1.27473263
O	0.12119782	2.97252663	-1.18903462
C	0.12062305	1.04240066	-2.65909193
H	0.99409341	0.43249541	-2.75891734
H	-0.75320951	0.43295694	-2.75856560

Substrate **2e•**

C	0.72847679	-0.54635761	0.00000000
O	1.35551722	0.54469069	-0.00211561
C	-0.81152321	-0.54635761	0.00000000
H	-1.16818956	-0.04348018	-0.87453039
H	-1.16818956	-1.55516186	0.00176083
C	1.49583396	-1.88155657	0.00258904
H	1.23616436	-2.44047020	0.87728170
H	1.23629725	-2.44378195	-0.87001816
C	3.01045975	-1.60315301	0.00217656
H	3.26999144	-1.04090193	0.87476869
H	3.27013420	-1.04426453	-0.87253073
C	3.77781624	-2.93835228	0.00480827
C	4.12616980	-3.54503952	-1.20227574
C	4.12467821	-3.54111614	1.21390324
C	4.82063703	-4.75455702	-1.20016997
H	3.85189049	-3.06996503	-2.15533234
C	4.82022093	-4.75050649	1.21618267
H	3.85035613	-3.06299951	2.16536575
C	5.16810905	-5.35734508	0.00942760
H	5.09469767	-5.23313008	-2.15156636
H	5.09393306	-5.22532015	2.16965416
H	5.71572272	-6.31097688	0.01083793

Substrate **2f•**

C	0.01655629	-0.94362773	-0.01235276
O	0.64359495	0.14742160	-0.01024441
C	0.78391346	-2.27882920	-0.01235276
H	0.08698587	-3.09073555	-0.01235263

H	1.39895907	-2.33672855	0.86129852
C	-1.52344153	-0.94362648	-0.01494180
H	-1.87863897	-1.44799105	-0.88921359
H	-1.88157653	-1.44806689	0.85808695
C	-2.03677334	0.50829977	-0.01574179
H	-1.67836998	1.01283486	-0.88860568
H	-1.68184425	1.01256980	0.85869350
Cl	-3.79676986	0.50830037	-0.01924073

Substrate **2g•**

C	1.58866996	-0.71422449	-0.00934971
O	2.21571039	0.37682380	-0.01146532
C	0.04866996	-0.71422449	-0.00934971
H	-0.30799639	-1.22030363	-0.88203122
H	-0.30799639	-1.21694906	0.86526857
C	3.87065293	-1.77102031	-0.00738602
H	4.13030372	-1.20874927	0.86515782
H	4.40381621	-2.69872380	-0.00560887
H	4.13020828	-1.21215198	-0.88214152
O	2.35602713	-2.04942346	-0.00676068

Substrate **2g'•**

C	1.58866996	-0.71422449	-0.00934971
O	2.21571039	0.37682380	-0.01146532
C	0.04866996	-0.71422449	-0.00934971
H	-0.30799639	-1.22030363	-0.88203122
H	-0.30799639	-1.21694906	0.86526857
H	-0.30799689	0.29457925	-0.01128648
C	3.87065293	-1.77102031	-0.00738602
H	4.13030372	-1.20874927	0.86515782
H	4.40381621	-2.69872380	-0.00560887
O	2.35602713	-2.04942346	-0.00676068

Substrate **2h•**

C	1.80463568	-1.05951183	-0.01386977
O	2.43167611	0.03153851	-0.01386977
O	2.51718162	-2.29934177	-0.01386977
C	1.58631920	-3.38488088	-0.01386977
H	0.97253145	-3.32839367	0.86075803
H	0.96995929	-3.32618868	-0.88654134
C	0.26463568	-1.05951183	-0.01386977
H	-0.09203067	-1.56356997	-0.88772017
H	-0.09203067	-1.56425918	0.85958271
C	-0.24869792	0.39241388	-0.01329707
H	0.10945702	0.89768687	-0.88583603
H	0.10647890	0.89594527	0.86146322
C	-1.78869569	0.39241493	-0.01592135
H	-2.14684946	-0.11318219	0.85643031
H	-2.14536318	1.40122002	-0.01514960

H	-2.14387242	-0.11079232	-0.89086818

Substrate **2i•**

C	1.05960260	-0.84437085	0.00000000
O	1.68664303	0.24667950	0.00000000
O	1.77214854	-2.08420079	0.00000000
O	-0.37039740	-0.84437085	0.00000000
C	0.84128612	-3.16973990	0.00002588
H	0.23887503	-3.12302936	-0.88304773
H	1.37477798	-4.09705785	0.01920544
H	0.21368621	-3.10138867	0.86393933
C	-0.84774121	-0.55505496	-1.31656341
H	-1.77800286	-1.05870128	-1.47735408
H	-0.13145390	-0.89023164	-2.03731932

Hydrogen atom **H•**

H	3.43167708	-2.06521736	0.00000000