Supporting Information

Intramolecular C-H Activation of a Bisphenolate(benzene) Ligated Titanium Dibenzyl Complex. Competing Pathways Involving α-Hydrogen Abstraction and σ-Bond Metathesis.

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Table S1. The thermal decomposition of **1** at 368 K.

Run A1 (3220)					Run A2 (3238)				
seconds	Fp	tBu	[**1**]	ln[**1**]	seconds	Fp	tBu	[**1**]	ln[**1**]
0	1.00	15.95	100.00	4.61	0	1.00	12.95	100.00	4.61
2400	1.00	14.95	93.75	4.54					
4800	1.00	13.48	84.52	4.44					
7200	1.00	12.61	79.10	4.37					
9600	1.00	11.52	72.25	4.28					
12000	1.00	10.83	67.92	4.22					
14400	1.00	10.55	66.16	4.19					
16800	1.00	9.60	60.20	4.10					
19200	1.00	9.54	59.82	4.09	19200	1.00	8.03	62.01	4.13
					21600	1.00	7.74	59.80	4.09
					24000	1.00	7.30	56.41	4.03
					26400	1.00	6.95	53.72	3.98
					28800	1.00	6.70	51.78	3.95
					31200	1.00	6.36	49.17	3.90
					33600	1.00	6.00	46.37	3.84
					36000	1.00	5.74	44.37	3.79
76840	1.00	2.75	17.22	2.85					
79240	1.00	2.51	15.71	2.75					
	k_{obs}	2.22E-05							

Table S2. The thermal decomposition of **1** at 368 K.

Run B1 (3221)					Run B2 (3239)				
seconds	Fp	tBu	[**1**]	ln[**1**]	seconds	Fp	tBu	[**1**]	ln[**1**]
0	1.00	15.20	100.00	4.61	0	1.00	13.19	100.00	4.61
2400	1.00	13.82	90.93	4.51					
4800	1.00	13.24	87.12	4.47					
7200	1.00	12.73	83.79	4.43					
9600	1.00	11.63	76.51	4.34					
12000	1.00	10.97	72.22	4.28					
14400	1.00	10.10	66.49	4.20					
16800	1.00	10.02	65.93	4.19					
19200	1.00	9.508	62.55	4.14	19200	1.00	7.81	59.20	4.08
					21600	1.00	7.41	56.20	4.03
					24000	1.00	7.05	53.46	3.98
					26400	1.00	6.73	50.99	3.93
					28800	1.00	6.43	48.73	3.89
					31200	1.00	6.16	46.74	3.84
					33600	1.00	5.84	44.31	3.79
					36000	1.00	5.57	42.20	3.74
76840	1.00	2.45	16.14	2.78					
79240	1.00	2.38	15.68	2.75					
	k_{obs}	2.32E-05							

Table S3. The thermal decomposition of **1** at 378 K.

		Run A (2183)		
seconds	Fp	tBu	[**1**]	ln[**1**]
0	1.00	6.17	100.00	4.61
1200	1.00	5.54	89.74	4.50
2400	1.00	5.05	81.75	4.40
3600	1.00	4.59	74.44	4.31
4800	1.00	4.25	68.83	4.23
6000	1.00	4.00	64.88	4.17
7200	1.00	3.66	59.23	4.08
8400	1.00	3.37	54.58	4.00
9600	1.00	3.13	50.71	3.93
10800	1.00	2.98	48.34	3.88
12000	1.00	2.70	43.80	3.78
13200	1.00	2.51	40.61	3.70
14400	1.00	2.31	37.37	3.62
15600	1.00	2.15	34.76	3.55
	k_{obs}	6.59E-05		

Table S4. The thermal decomposition of **1** at 378 K.

		Run B (2184)		
seconds	Fp	tBu	[**1**]	ln[**1**]
0	1.00	9.39	100.00	4.61
1200	1.00	8.50	90.53	4.51
2400	1.00	7.73	82.40	4.41
3600	1.00	7.10	75.67	4.33
4800	1.00	6.59	70.24	4.25
6000	1.00	6.10	64.99	4.17
7200	1.00	5.60	59.71	4.09
8400	1.00	5.25	55.92	4.02
9600	1.00	4.82	51.32	3.94
10800	1.00	4.51	48.01	3.87
12000	1.00	4.14	44.11	3.79
13200	1.00	3.83	40.80	3.71
14400	1.00	3.53	37.58	3.63
15600	1.00	3.24	34.51	3.54
	k_{obs}	6.65E-05		

Table S5. The thermal decomposition of **1** at 388 K.

Run A (2146)					
seconds	Fp	tBu	normalized	[**1**]	ln[**1**]
0	0.54	3.16	5.84	100.00	4.61
600	0.54	2.98	5.49	94.09	4.54
1200	0.53	2.52	4.72	80.92	4.39
1800	0.54	2.19	4.08	69.84	4.25
2400	0.53	1.93	3.63	62.10	4.13
3000	0.54	1.72	3.21	54.91	4.01
3600	0.54	1.54	2.87	49.14	3.89
4200	0.54	1.41	2.63	45.03	3.81
4800	0.53	1.27	2.38	40.74	3.71
5400	0.54	1.13	2.12	36.24	3.59
6000	0.54	0.99	1.85	31.76	3.46
6600	0.53	0.88	1.65	28.18	3.34
7200	0.53	0.82	1.53	26.26	3.27
7800	0.53	0.73	1.36	23.36	3.15
8400	0.53	0.64	1.20	20.55	3.02
9000	0.53	0.56	1.06	18.11	2.90
9600	0.53	0.50	0.94	16.03	2.77
10200	0.53	0.45	0.85	14.54	2.68
10800	0.53	0.41	0.77	13.12	2.57
11400	0.53	0.36	0.68	11.72	2.46
		k_{obs}	1.89E-04		

Table S6. The thermal decomposition of **1** at 388 K.

		Run B (2150)			
seconds	Fp	tBu	normalized	[**1**]	ln[**1**]
0	1.00	7.48		100.00	4.61
600	1.00	6.36		85.08	4.44
1200	1.00	5.58		74.54	4.31
1800	1.00	4.90		65.54	4.18
2400	1.00	4.39		58.69	4.07
3000	1.00	3.95		52.87	3.97
3600	1.00	3.62		48.37	3.88
4200	1.00	3.30		44.06	3.79
4800	1.00	2.99		40.04	3.69
5400	1.00	2.70		36.08	3.59
6000	1.00	2.44		32.68	3.49
6600	1.00	2.24		29.92	3.40
7200	1.00	2.01		26.88	3.29
7800	1.00	1.94		25.92	3.26
8400	1.00	1.79		23.95	3.18
9000	1.00	1.61		21.55	3.07
9600	1.00	1.46		19.46	2.97
10200	1.00	1.33		17.83	2.88
10800	1.00	1.20		16.09	2.78
11400	1.00	1.09		14.52	2.68
12000	1.00	0.99		13.23	2.58
		k_{obs}	1.60E-04		

Table S7. The thermal decomposition of **1** at 398 K.

		Run A (2168)		
seconds	Fp	tBu	[**1**]	ln[**1**]
0	1.00	7.72	100.00	4.61
300	1.00	5.63	72.93	4.29
600	1.00	4.52	58.63	4.07
900	1.00	4.01	51.90	3.95
1200	1.00	3.68	47.70	3.86
1500	1.00	3.34	43.22	3.77
1800	1.00	3.04	39.40	3.67
2100	1.00	2.71	35.16	3.56
2400	1.00	2.47	31.98	3.46
2700	1.00	2.13	27.61	3.32
3000	1.00	2.14	27.69	3.32
3300	1.00	1.93	24.99	3.22
3600	1.00	1.73	22.44	3.11
3900	1.00	1.53	19.89	2.99
4200	1.00	1.38	17.85	2.88
4500	1.00	1.16	15.09	2.71
4800	1.00	1.04	13.45	2.60
5100	1.00	0.93	11.99	2.48
5400	1.00	0.83	10.82	2.38
	k_{obs}	3.67E-04		

Table S8. The thermal decomposition of **1** at 398 K.

		Run B (2181)		
seconds	Fp	tBu	[**1**]	ln[**1**]
0	1.00	4.27	100.00	4.61
300	1.00	3.26	76.54	4.34
600	1.00	2.49	58.32	4.07
900	1.00	2.01	47.07	3.85
1200	1.00	1.77	41.49	3.73
1500	1.00	1.57	36.78	3.60
1800	1.00	1.41	33.07	3.50
2100	1.00	1.27	29.80	3.39
2400	1.00	1.15	26.85	3.29
2700	1.00	1.03	24.10	3.18
3000	1.00	0.93	21.69	3.08
3300	1.00	0.82	19.29	2.96
3600	1.00	0.74	17.39	2.86
3900	1.00	0.67	15.75	2.76
4200	1.00	0.61	14.37	2.66
4500	1.00	0.56	13.03	2.57
4800	1.00	0.51	12.04	2.49
	k_{obs}	4.06E-04		

Table S9. The thermal decomposition of **1** at 398 K.

		Run C (2182)		
seconds	Fp	tBu	[**1**]	ln[**1**]
0	1.00	5.39	100.00	4.61
300	1.00	4.24	78.56	4.36
600	1.00	3.60	66.71	4.20
900	1.00	3.15	58.47	4.07
1200	1.00	2.77	51.47	3.94
1500	1.00	2.46	45.63	3.82
1800	1.00	2.16	40.19	3.69
2100	1.00	1.89	35.14	3.56
2400	1.00	1.65	30.65	3.42
2700	1.00	1.45	26.85	3.29
3000	1.00	1.24	23.00	3.14
3300	1.00	1.08	20.04	3.00
3600	1.00	0.94	17.47	2.86
3900	1.00	0.81	15.18	2.72
4200	1.00	0.73	13.60	2.61
4500	1.00	0.64	12.00	2.49
4800	1.00	0.58	10.74	2.37
	k_{obs}	4.53E-04		

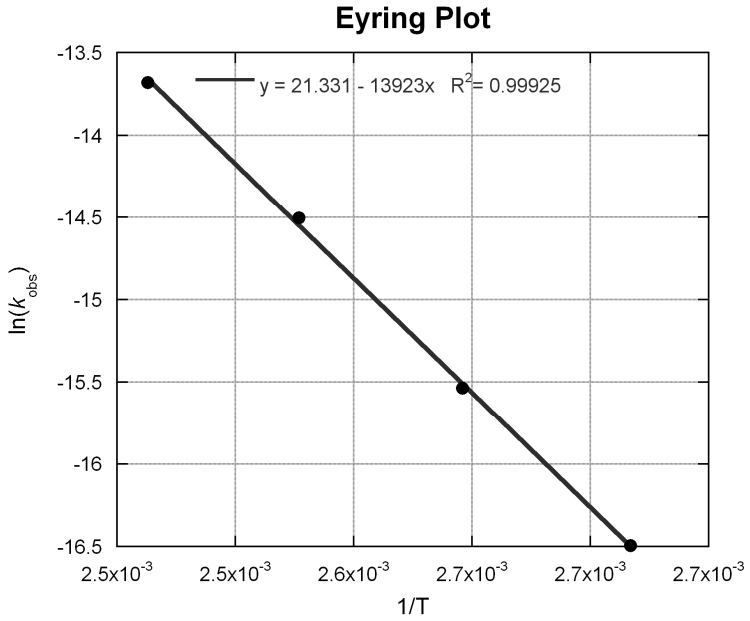

Figure S1. The Eyring plot for the formation of **2**.

Table S10. The thermal decomposition of **1-*d*$_3$** at 388 K.

Run A (2190)					
seconds	Fp	tBu	normalized	[**1-*d*$_3$**]	ln[**1-*d*$_3$**]
0	0.56	4.73	8.43	100.00	4.61
600	0.55	3.56	6.44	76.37	4.34
1200	0.55	3.08	5.63	66.74	4.20
1800	0.54	2.67	4.90	58.12	4.06
2400	0.55	2.51	4.59	54.40	4.00
3000	0.56	2.32	4.18	49.56	3.90
3600	0.55	2.13	3.84	45.56	3.82
4200	0.55	1.97	3.56	42.21	3.74
4800	0.55	1.81	3.31	39.19	3.67
5400	0.55	1.67	3.01	35.73	3.58
6000	0.54	1.48	2.76	32.74	3.49
6600	0.54	1.38	2.54	30.08	3.40
7200	0.55	1.28	2.32	27.47	3.31
7800	0.55	1.17	2.12	25.18	3.23
8400	0.55	1.07	1.93	22.85	3.13
9000	0.55	0.96	1.76	20.85	3.04
9600	0.55	0.90	1.62	19.23	2.96
10200	0.55	0.81	1.48	17.54	2.86
10800	0.55	0.75	1.36	16.13	2.78
		k_{obs}	1.53E-04		

Table S11. The thermal decomposition of **1-*d*$_3$** at 388 K.

		Run B (2191)			
seconds	Fp	tBu	normalized	[**1-*d*$_3$**]	ln[**1-*d*$_3$**]
0	0.56	4.15	7.42	100.00	4.61
600	0.55	3.11	5.64	76.05	4.33
1200	0.55	2.66	4.84	65.25	4.18
1800	0.55	2.39	4.36	58.79	4.07
2400	0.54	2.19	4.02	54.13	3.99
3000	0.55	2.01	3.67	49.42	3.90
3600	0.55	1.86	3.39	45.68	3.82
4200	0.55	1.71	3.12	42.09	3.74
4800	0.55	1.57	2.87	38.61	3.65
5400	0.55	1.44	2.64	35.54	3.57
6000	0.53	1.29	2.43	32.77	3.49
6600	0.54	1.20	2.21	29.75	3.39
7200	0.54	1.09	2.01	27.07	3.30
7800	0.53	0.97	1.85	24.88	3.21
8400	0.55	0.92	1.68	22.61	3.12
9000	0.54	0.83	1.55	20.92	3.04
9600	0.55	0.75	1.37	18.44	2.91
10200	0.55	0.68	1.25	16.89	2.83
10800	0.55	0.63	1.15	15.51	2.74
		k_{obs}	1.56E-04		

Table S12. The thermal decomposition of **1-*d*$_4$** at 388 K.

Run A (3120)					
seconds	Fp	tBu	normalized	[**1-*d*$_4$**]	ln[**1-*d*$_4$**]
0	1.00	6.38		100.00	4.61
600	1.00	5.94		93.16	4.53
1200	1.00	5.54		86.80	4.46
1800	1.00	5.32		83.40	4.42
2400	1.00	5.04		79.06	4.37
3000	1.00	4.85		76.05	4.33
3600	1.00	4.78		74.93	4.32
4200	1.00	4.55		71.32	4.27
4800	1.00	4.40		69.01	4.23
5400	1.00	4.14		64.96	4.17
6000	1.00	3.94		61.69	4.12
6600	1.00	3.77		59.14	4.08
7200	1.00	3.48		54.62	4.00
7800	1.00	3.32		52.10	3.95
8400	1.00	3.12		48.91	3.89
9000	1.00	2.95		46.27	3.83
9600	1.00	2.77		43.35	3.77
10200	1.00	2.57		40.35	3.70
10800	1.00	2.39		37.51	3.62
11400	1.00	2.24		35.09	3.56
12000	1.00	2.05		32.17	3.47
12600	1.00	1.95		30.57	3.42
13200	1.00	1.76		27.54	3.32
13800	1.00	1.60		25.08	3.22
14400	1.00	1.50		23.52	3.16
15000	1.00	1.38		21.58	3.07
15600	1.00	1.27		19.92	2.99
16200	1.00	1.17		18.40	2.91
		k_{obs}	1.02E-04		

Table S13. The thermal decomposition of **1-*d*$_4$** at 388 K.

		Run B (3296)			
seconds	Fp	tBu	normalized	[**1-*d*$_4$**]	ln[**1-*d*$_4$**]
0	1.00	25.96		100.00	4.61
600	1.00	20.97		80.78	4.39
1200	1.00	19.33		74.45	4.31
1800	1.00	22.99		88.57	4.48
2400	1.00	22.44		86.43	4.46
3000	1.00	21.97		84.64	4.44
3600	1.00	20.67		79.65	4.38
4200	1.00	20.89		80.48	4.39
4800	1.00	15.15		58.36	4.07
5400	1.00	15.25		58.74	4.07
6000	1.00	14.63		56.38	4.03
6600	1.00	13.73		52.88	3.97
7200	1.00	12.87		49.59	3.90
7800	1.00	12.76		49.16	3.90
8400	1.00	12.24		47.15	3.85
9000	1.00	11.22		43.21	3.77
9600	1.00	10.65		41.03	3.71
10200	1.00	9.97		38.39	3.65
10800	1.00	8.91		34.34	3.54
11400	1.00	8.74		33.66	3.52
12000	1.00	8.10		31.21	3.44
12600	1.00	7.58		29.20	3.37
13200	1.00	7.24		27.89	3.33
13800	1.00	6.69		25.78	3.25
		k_{obs}	9.61E-05		

Table S14. The thermal decomposition of **1-*d*$_4$** at 388 K.

Run C (3297)					
seconds	Fp	tBu	normalized	[**1-*d*$_4$**]	ln[**1-*d*$_4$**]
0	1.00	12.13		100.00	4.61
600	1.00	10.78		88.89	4.49
1200	1.00	12.29		101.37	4.62
1800	1.00	12.61		103.98	4.64
2400	1.00	12.12		99.89	4.60
3000	1.00	11.43		94.24	4.55
3600	1.00	10.96		90.40	4.50
4200	1.00	10.77		88.77	4.49
4800	1.00	8.41		69.34	4.24
5400	1.00	8.10		66.79	4.20
6000	1.00	8.02		66.13	4.19
6600	1.00	7.49		61.78	4.12
7200	1.00	7.19		59.31	4.08
7800	1.00	6.76		55.72	4.02
8400	1.00	6.51		53.65	3.98
9000	1.00	6.29		51.86	3.95
9600	1.00	5.89		48.59	3.88
10200	1.00	5.58		45.97	3.83
10800	1.00	5.34		44.06	3.79
11400	1.00	5.01		41.31	3.72
12000	1.00	4.66		38.46	3.65
12600	1.00	4.48		36.94	3.61
13200	1.00	4.18		34.47	3.54
13800	1.00	3.92		32.32	3.48
		k_{obs}	8.81E-05		

Table S15. The thermal decomposition of **1-*d*$_{10}$** at 388 K.

Run A (3171)					
seconds	Fp	tBu	normalized	[**1-*d*$_{10}$**]	ln[**1-*d*$_{10}$**]
0	0.31	1.50	4.88	100.00	4.61
600	0.31	1.64	5.24	107.40	4.68
1200	0.30	1.19	3.94	80.74	4.39
1800	0.31	1.14	3.62	74.18	4.31
2400	0.31	1.03	3.30	67.66	4.21
3000	0.31	0.95	3.04	62.34	4.13
3600	0.31	0.86	2.75	56.48	4.03
4200	0.31	0.78	2.51	51.57	3.94
4800	0.31	0.91	2.94	60.25	4.10
5400	0.31	0.65	2.09	42.85	3.76
6000	0.31	0.59	1.90	39.06	3.67
6600	0.31	0.55	1.78	36.41	3.59
7200	0.31	0.49	1.57	32.10	3.47
7800	0.31	0.45	1.46	29.90	3.40
8400	0.31	0.40	1.29	26.49	3.28
9000	0.31	0.36	1.17	23.90	3.17
9600	0.31	0.32	1.03	21.09	3.05
10200	0.30	0.31	1.00	20.61	3.03
10800	0.31	0.27	0.90	18.38	2.91
11400	0.31	0.25	0.82	16.72	2.82
12000	0.31	0.24	0.75	15.45	2.74
12600	0.31	0.21	0.67	13.78	2.62
		k_{obs}	1.60E-04		

Table S16. The thermal decomposition of **1-*d*$_{10}$** at 388 K.

Run B (3172)					
seconds	Fp	tBu	normalized	[**1-*d*$_{10}$**]	ln[**1-*d*$_{10}$**]
0	0.30	1.90	6.24	100.00	4.61
600	0.30	1.75	5.75	92.14	4.52
1200	0.31	1.54	4.94	79.10	4.37
1800	0.31	1.45	4.64	74.36	4.31
2400	0.31	1.35	4.36	69.89	4.25
3000	0.31	1.22	3.92	62.82	4.14
3600	0.31	1.09	3.53	56.52	4.03
4200	0.31	1.03	3.30	52.82	3.97
4800	0.31	0.93	3.00	48.12	3.87
5400	0.31	0.84	2.70	43.25	3.77
6000	0.31	0.78	2.51	40.16	3.69
6600	0.31	0.71	2.28	36.48	3.60
7200	0.31	0.65	2.10	33.66	3.52
7800	0.31	0.58	1.84	29.49	3.38
8400	0.31	0.51	1.65	26.39	3.27
9000	0.31	0.47	1.51	24.13	3.18
9600	0.31	0.43	1.38	22.14	3.10
10200	0.31	0.39	1.27	20.29	3.01
10800	0.31	0.36	1.14	18.30	2.91
11400	0.31	0.33	1.04	16.73	2.82
12000	0.31	0.30	0.96	15.40	2.73
12600	0.31	0.28	0.89	14.22	2.65
		k_{obs}	1.56E-04		

Table S17. The thermal decomposition of **1-*d*$_{14}$** at 388 K.

Run A (3086)					
seconds	Fp	tBu	normalized	[**1-*d*$_{14}$**]	ln[**1-*d*$_{14}$**]
0	1.00	18.88		100.00	4.61
600	1.00	18.04		95.52	4.56
1200	1.00	16.23		85.97	4.45
1800	1.00	16.80		88.95	4.49
2400	1.00	16.40		86.85	4.46
3000	1.00	15.57		82.47	4.41
3600	1.00	15.71		83.20	4.42
4200	1.00	14.19		75.17	4.32
4800	1.00	13.98		74.05	4.30
5400	1.00	13.50		71.51	4.27
6000	1.00	12.14		64.31	4.16
6600	1.00	11.94		63.24	4.15
7200	1.00	11.63		61.57	4.12
7800	1.00	10.63		56.27	4.03
8400	1.00	10.12		53.62	3.98
9000	1.00	9.70		51.36	3.94
9600	1.00	9.00		47.66	3.86
10200	1.00	8.46		44.79	3.80
10800	1.00	7.94		42.06	3.74
11400	1.00	7.17		37.99	3.64
		k_{obs}	8.04E-05		

Table S18. The thermal decomposition of **1-*d*$_{14}$** at 388 K.

		Run B (3087)			
seconds	Fp	tBu	normalized	[**1-*d*$_{14}$**]	ln[**1-*d*$_{14}$**]
0	1.00	15.27		100.00	4.61
600	1.00	14.95		97.86	4.58
1200	1.00	13.91		91.05	4.51
1800	1.00	13.52		88.48	4.48
2400	1.00	13.21		86.49	4.46
3000	1.00	12.56		82.21	4.41
3600	1.00	12.14		79.45	4.38
4200	1.00	11.81		77.34	4.35
4800	1.00	11.41		74.72	4.31
5400	1.00	10.74		70.31	4.25
6000	1.00	10.25		67.09	4.21
6600	1.00	9.71		63.57	4.15
7200	1.00	9.41		61.60	4.12
7800	1.00	8.76		57.33	4.05
8400	1.00	8.37		54.78	4.00
9000	1.00	8.43		55.22	4.01
9600	1.00	7.44		48.72	3.89
10200	1.00	7.12		46.65	3.84
10800	1.00	6.68		43.71	3.78
11400	1.00	6.18		40.45	3.70
		k_{obs}	7.67E-05		

Rate Equations

$1.64(2) \times 10^{-4} = k_{obs}(\mathbf{1}, \mathbf{1\text{-}d_{10}}) = k_{\alpha H} + k_{\sigma H}$

$1.55(2) \times 10^{-4} = k_{obs}(\mathbf{1\text{-}d_3}) = k_{\alpha H} + k_{\sigma D}$

$8.65(5) \times 10^{-5} = k_{obs}(\mathbf{1\text{-}d_4}, \mathbf{1\text{-}d_{14}}) = k_{\alpha D} + k_{\sigma H}$

$k_{\alpha H} = 1.3\ k_{\sigma D}$

$k_{\sigma H} = 4.4\ k_{\alpha D}$

$1.55(2) \times 10^{-4} = 1.3\ k_{\sigma D} + k_{\sigma D}$

$k_{\sigma D} = 6.74(2) \times 10^{-5}$

$8.65(5) \times 10^{-5} = k_{\alpha D} + 4.4\ k_{\alpha D}$

$k_{\alpha D} = 1.60(5) \times 10^{-5}$

$1.64(2) \times 10^{-4} = 1.3\ k_{\sigma D} + 4.4\ k_{\alpha D}$

$1.64(2) \times 10^{-4} = 1.58 \times 10^{-4}$ *(check)*

$k_{\alpha H} = 8.75(2) \times 10^{-5}$

$k_{\alpha D} = 1.60(5) \times 10^{-5}$

KIE (α-abstraction) = 5.5(3)

$k_{\sigma H} = 7.04(5) \times 10^{-5}$

$k_{\sigma D} = 6.74(2) \times 10^{-5}$

KIE (σ-bond metathesis) = 1.0(1)