SUPPORTING INFORMATION

Aryl Carbamates:
Mechanisms of Orthosodiations and Snieckus-Fries Rearrangements

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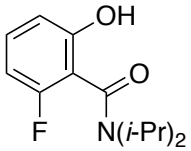
I. Spectroscopic studies

II. Rate studies

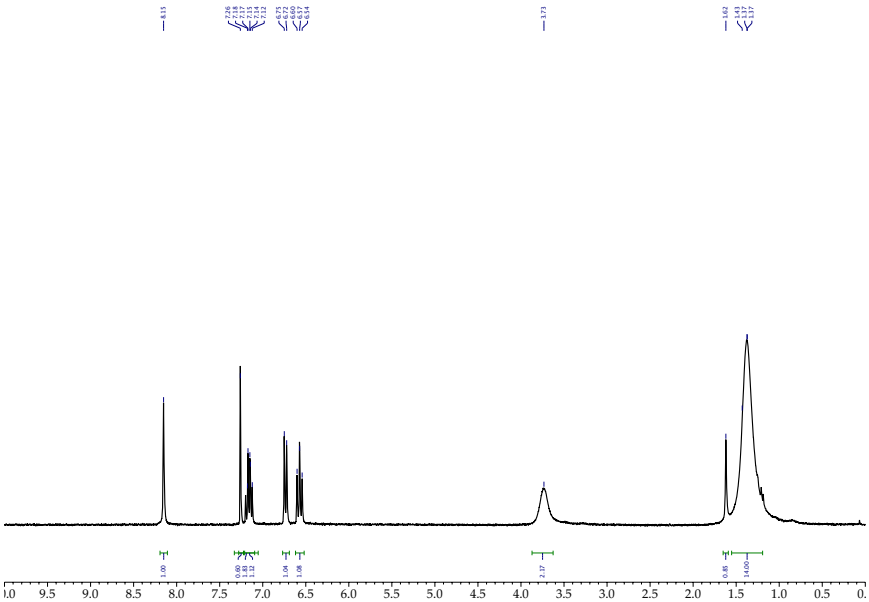
III. Calculations

I. Spectroscopic Studies

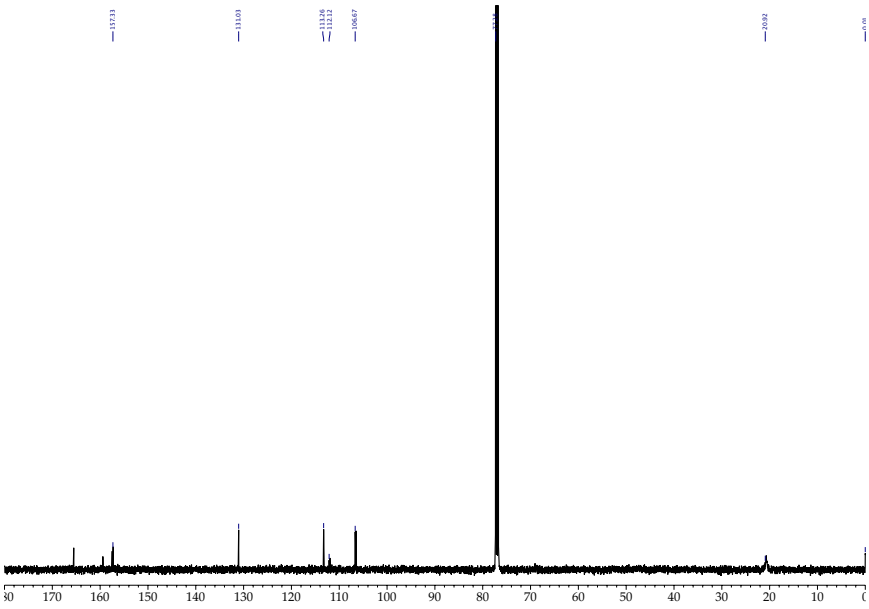


4e

(A)



(B)



(C)

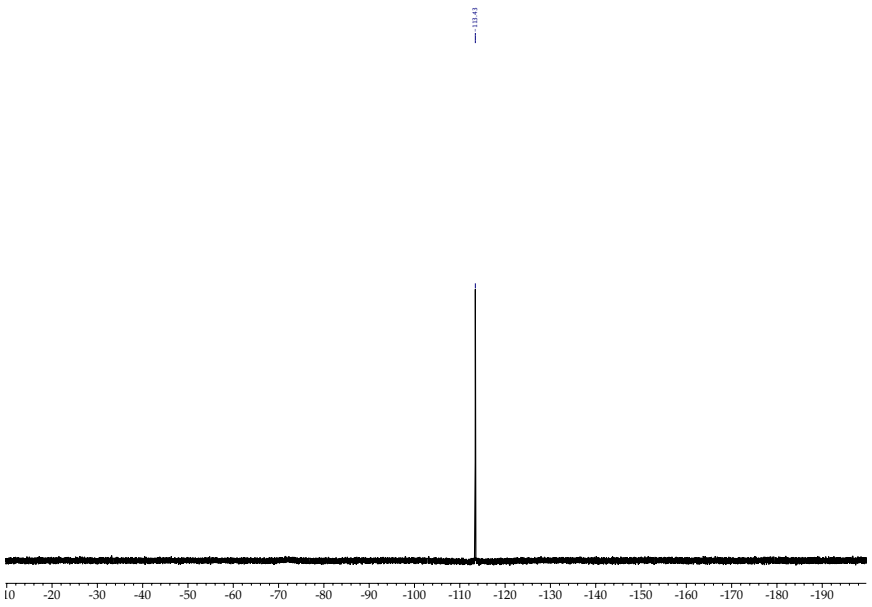
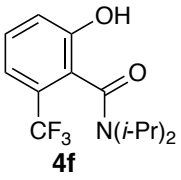
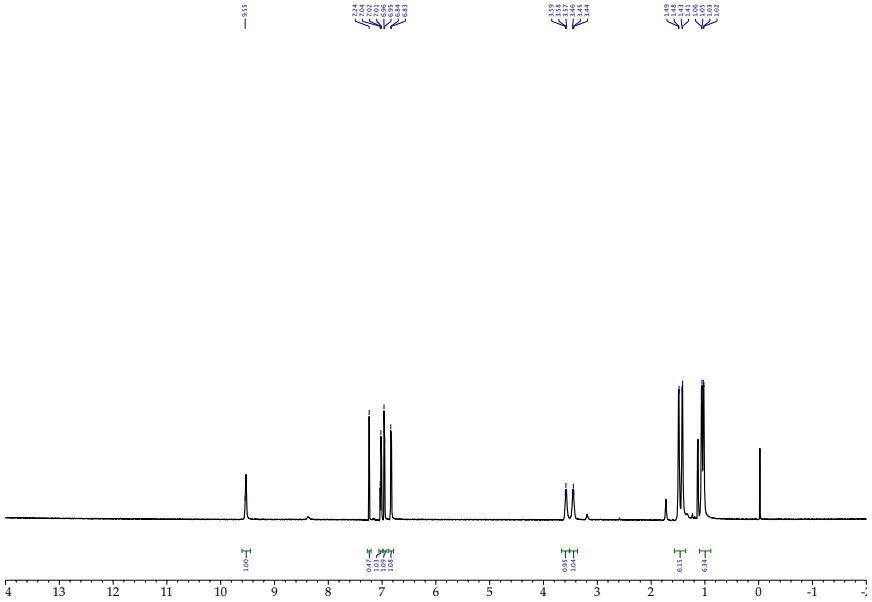


Figure S1. NMR spectra of 2-fluoro-6-hydroxy-*N*,*N*-diisopropylbenzamide (**4e**): (A) ^{1}H NMR spectrum (THF-d_8, 500 MHz) (B) ^{13}C{^{1}H} NMR spectrum ($CDCl_3$,125.8 MHz); (C) ^{19}F NMR spectrum ($CDCl_3$, 470.33 MHz).



4f

(A)



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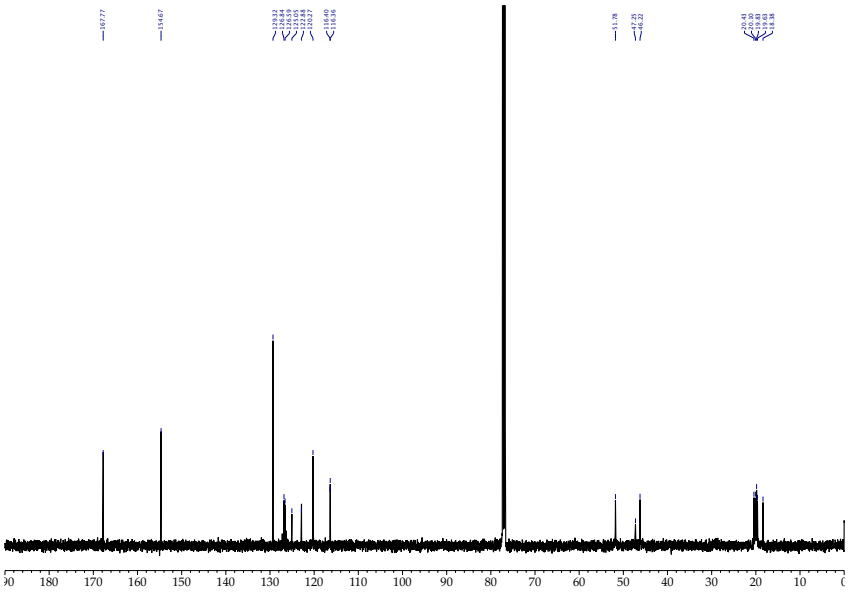


Figure S2. NMR spectra of 2-hydroxy-*N*,*N*-diisopropyl-6-(trifluoromethyl)benzamide (**4f**): (A) ^{1}H NMR spectrum ($CDCl_3$, 500 Mz) (B) $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125.8 Mz).

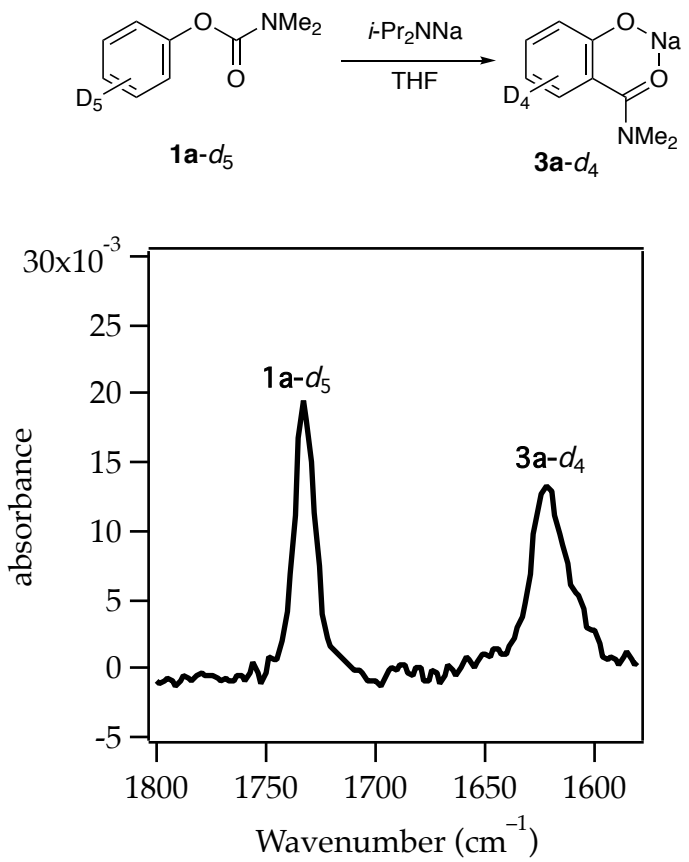


Figure S3. IR spectrum of the metalation-rearrangement of 0.010 M phenyl-d_5 dimethylcarbamate (**1a**-d_5) with 0.10 M NaDA in 6.15 M THF in hexane at –78 °C after 10 minutes.

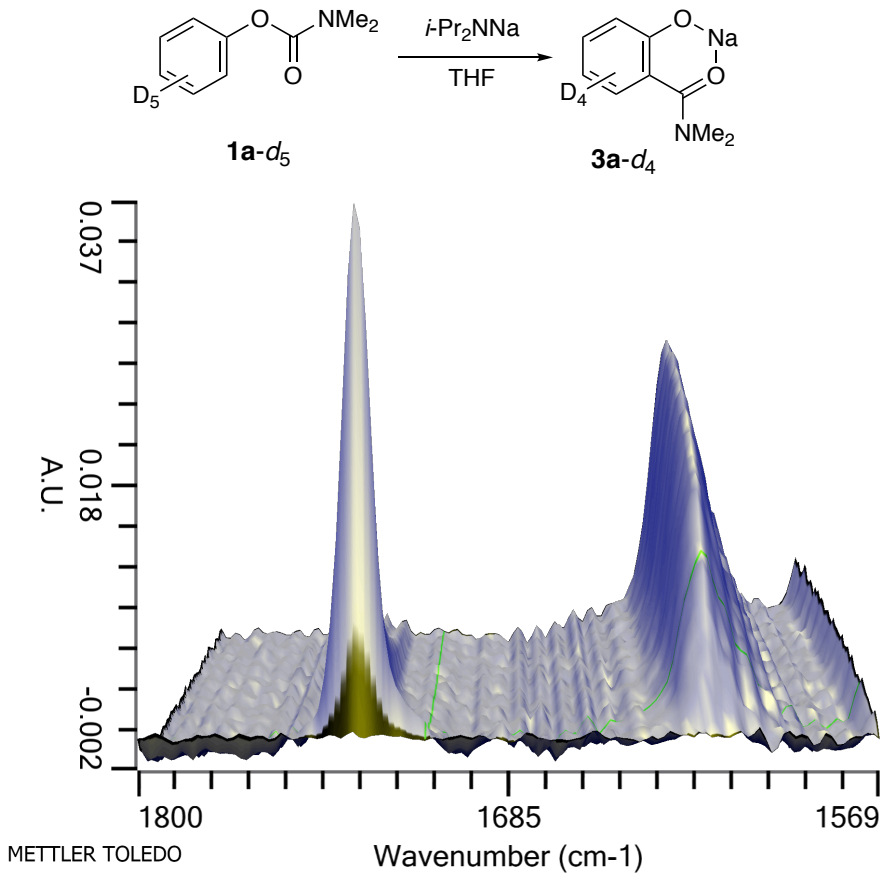
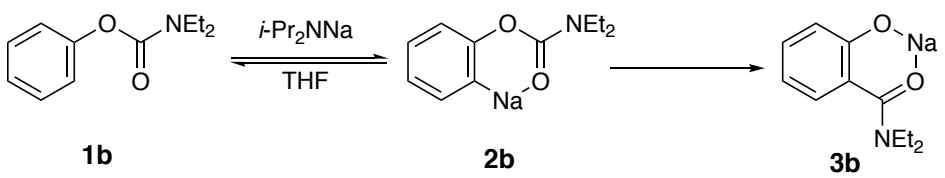


Figure S4. The metalation-rearrangement of 0.010 M phenyl-d_5 dimethylcarbamate (**1a**-d_5) with 0.10 M NaDA in 6.15 M THF in hexane at –78 °C monitored by in situ IR.



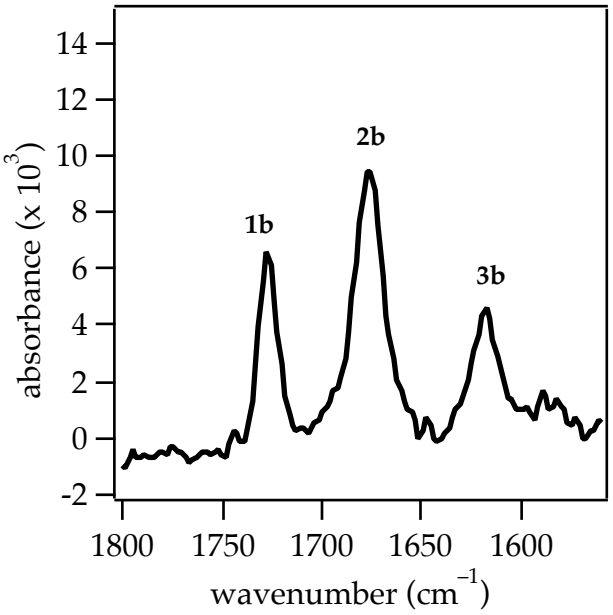


Figure S5. IR spectrum for the metalation and rearrangement of 0.010 M phenyl diethylcarbamate **1b** with 0.15 M NaDA in 6.80 M THF in hexane at –50 °C.

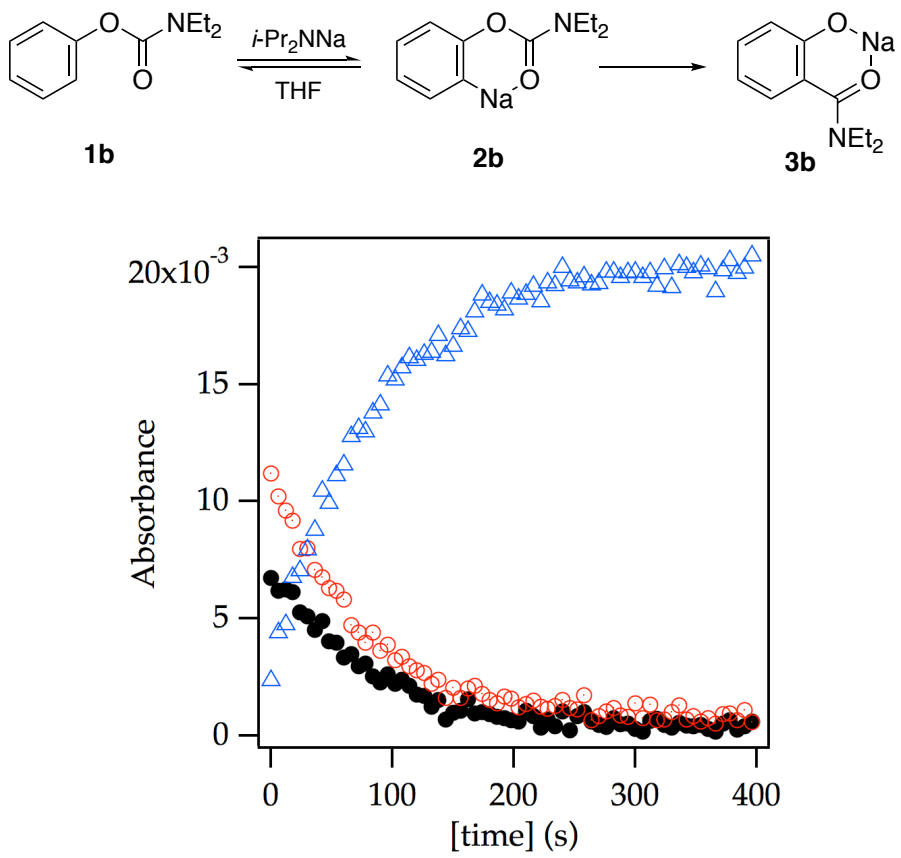
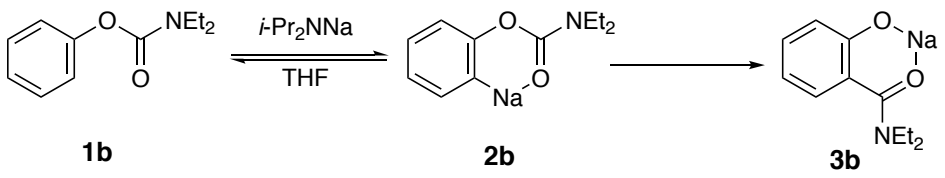


Figure S6. Rearrangement of an equilibrium mixture of phenyl diethylcarbamate **1b (**black**)** and arylsodium **2b** (red) (0.10 M total concentration) generated with 0.15 M NaDA in 6.80 M THF in hexane at –50 °C to give phenolate **3b** (blue).



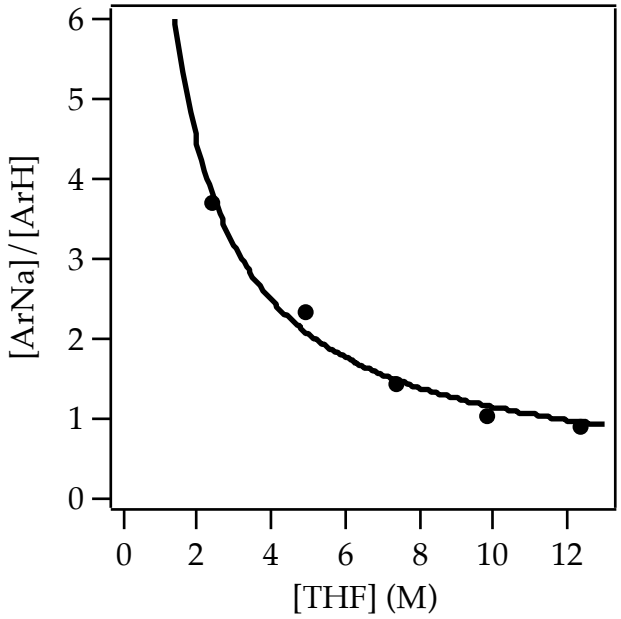


Figure S7. Plot of [ArNa]/[ArH] versus [THF] in hexane for the sodiation of phenyl diethylcarbamate **1b** (ArH) to give arylsodium **2b** (ArNa) with 0.10 M NaDA at –50 °C. The curve depicts the result of an unweighted least-squares fit to $y = ax^b$ ($a = 8.1 \pm 0.7$, $b = -0.85 \pm 0.07$). Each point is the average value of the [ArNa]/[ArH] ratio obtained from taking the average value from all points from plots analogous to those in Figure S6.

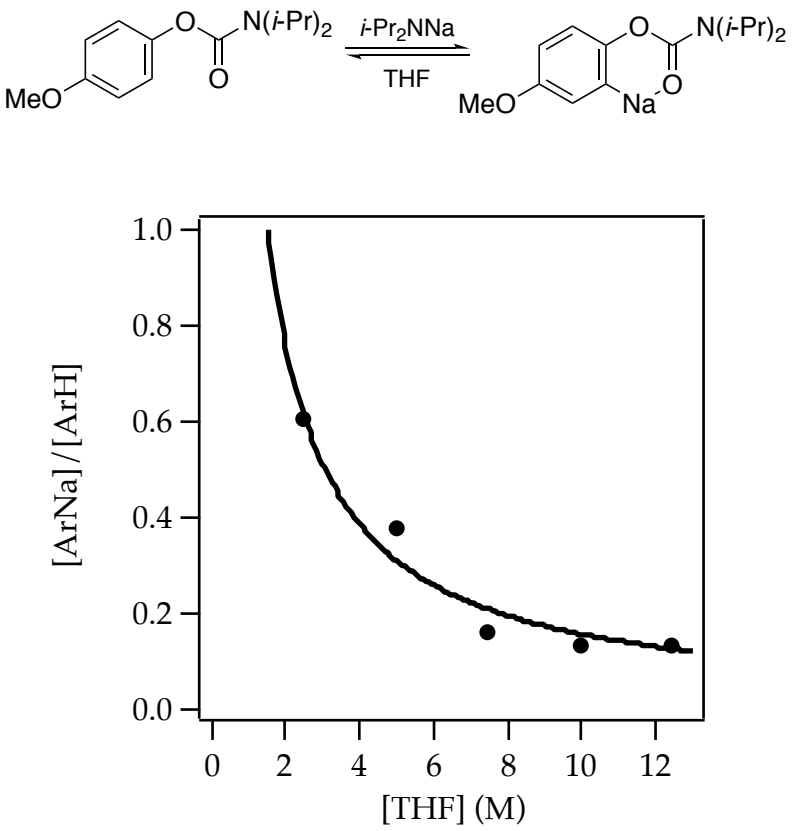


Figure S8. Plot of [ArNa]/[ArH] versus [THF] in hexane for the sodiation of 0.010 M 4-methoxyphenyl diisopropylcarbamate with 0.10 M NaDA containing 0.10 M diisopropylamine at –78 °C. The curve depicts the result of an unweighted least-squares fit to $y = ax^b$ ($a = 1.5 \pm 0.3$, $b = -0.98 \pm 0.13$).

II. Rate Studies

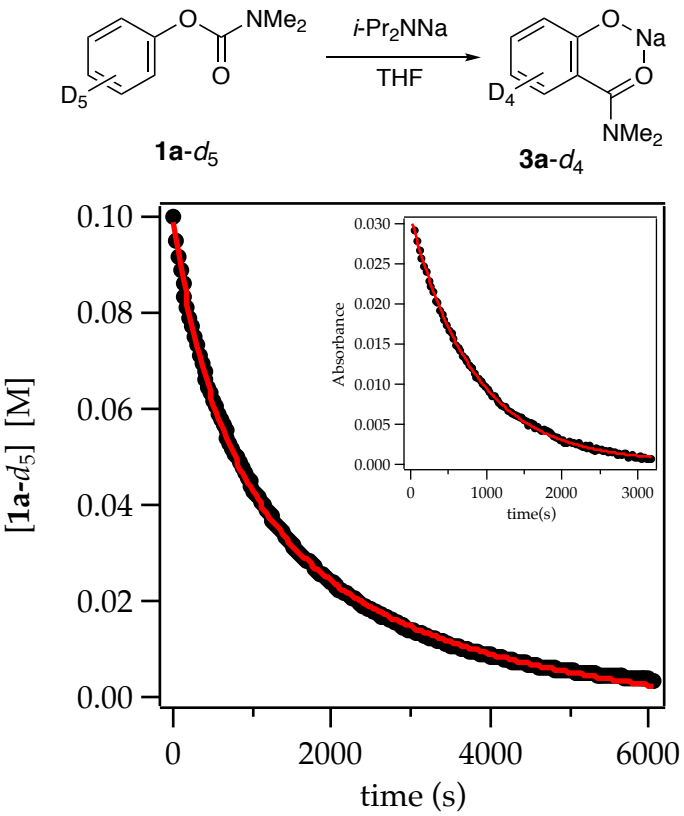


Figure S9. Plot of phenyl-d_5-dimethylcarbamate (**1a**-d_5) concentration versus time for the metalation of 0.10 M **1a**-d_5 with 0.10 M NaDA in 7.50 M THF in hexane at –78 °C. The curve depicts the result of an unweighted least-squares fit to the second-order function, $y = a/(1+bx) + c$ ($a = 0.1128 \pm 0.0002$, $b = -0.00010 \pm 0.00001$, $c = 0.014 \pm 0.001$). Insert: plot of phenyl-d_5-dimethylcarbamate (**1a**-d_5) concentration versus time for the metalation of 0.010 M **1a**-d_5 with 0.10 M NaDA in 7.50 M THF in hexane at –78 °C. $y = ae^{bx} + c$ ($a = 0.034 \pm 0.001$, $b = 0.0012 \pm 0.0005$, $c = 00028 \pm 0.0001$).

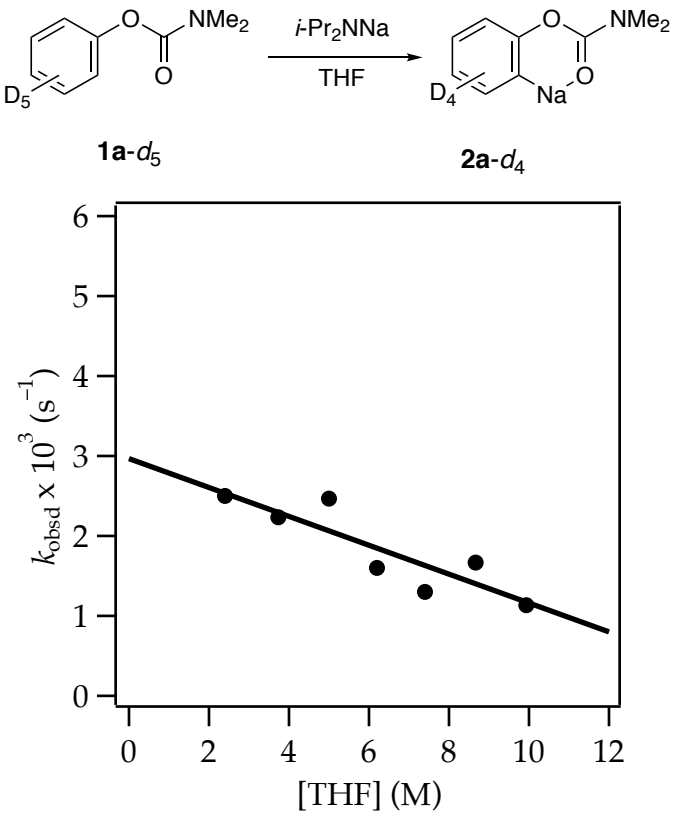


Figure S10. Plot of k_{obsd} versus [THF] in hexane cosolvent for the orthosodiation of phenyl-d_5 dimethylcarbamate **1a**-d_5 (0.010 M) by NaDA (0.10 M) at –78 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k$[THF] + k' (k = –0.00018 ± 0.00004, k' = 0.0029 ± 0.0003)

[THF] (M)	k_{obsd} x 10^3 (s^{-1})
2.40	2.50
3.72	2.22
5.01	2.48
6.20	1.60
7.44	1.32
8.68	1.67
9.94	1.13

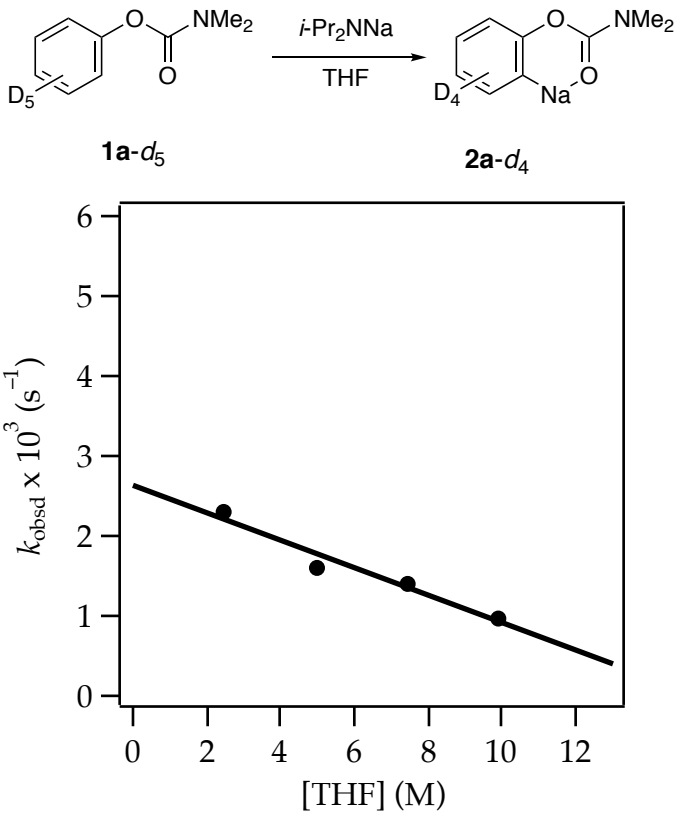


Figure S11. Plot of k_{obsd} versus [THF] in 2,5-dimethyltetrahydrofuran cosolvent for the orthosodiation of phenyl-d_5 dimethylcarbamate **1a**-d_5 (0.010 M) by NaDA (0.10 M) at –78 °C. The curve depicts the result of an unweighted least–squares fit to $k_{obsd} = k$[THF] + k' (k = –0.00017 ± 0.00003, k' = 0.0026 ± 0.0002)

[THF] (M)	k_{obsd} x 10^3 (s^{-1})
2.40	2.42
5.01	1.62
7.44	1.60
9.94	1.02

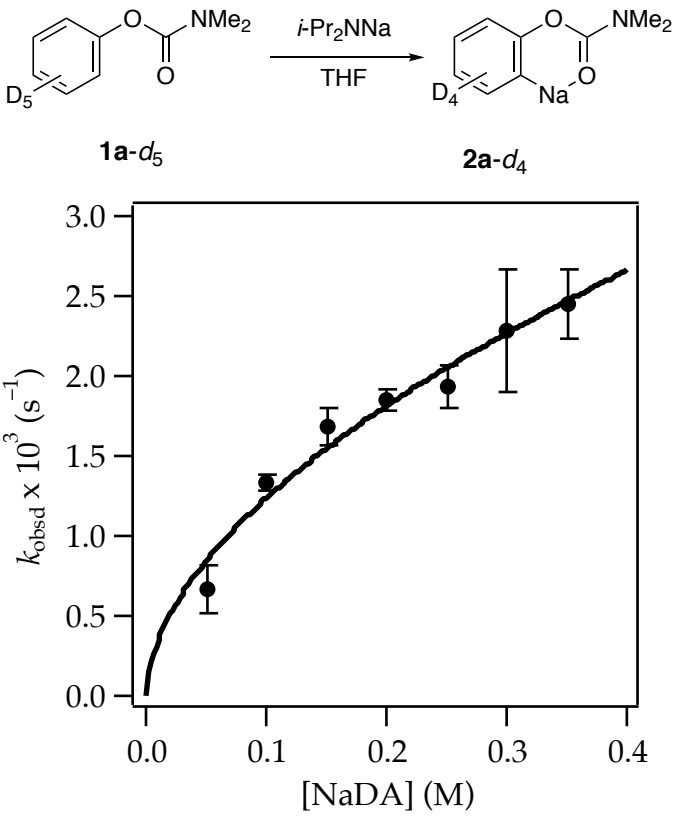


Figure S12. Plot of k_{obsd} versus [NaDA] in 6.2 M THF in hexane cosolvent for the orthosodiation of carbamate **1**-d_5 (0.010 M) by NaDA at –78 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{NaDA}]^n$ ($k = 0.0044 \pm 0.0004$, $n = 0.55 \pm 0.06$).

[NaDA] (M)	k_{obsd1}x10^3 (s^{-1})	k_{obsd2}x10^3 (s^{-1})	k_{obsd}(avg)x10^3 (s^{-1})
0.05	0.77	0.56	0.67
0.10	1.37	1.30	1.34
0.15	1.76	1.6	1.68
0.20	1.80	1.89	1.85
0.25	2.04	1.84	1.94
0.30	2.56	2.01	2.29
0.35	2.60	2.30	2.45

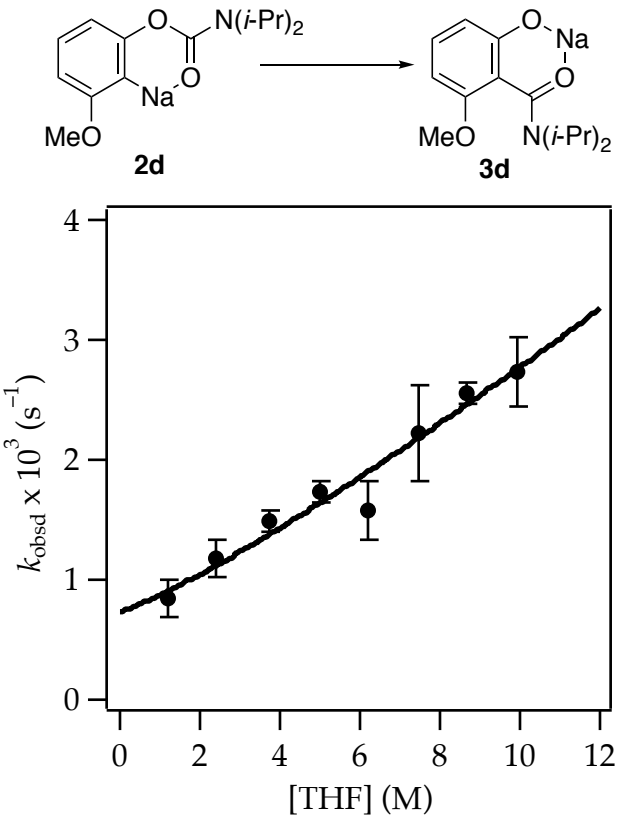


Figure S13. Plot of k_{obsd} versus [THF] in hexane cosolvent for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-methoxyphenyl)sodium **2d** (0.010 M) by NaDA (0.10 M) at –15 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{THF}]^n + k'$ (k = 0.00014 ± 0.00014, k' = 0.00074 ± 0.00028, n = 1.17 ± 0.39)

[THF] (M)	k_{obsd1} x 10^3 (s^{-1})	k_{obsd2} x 10^3 (s^{-1})	k_{obsd}(avg) x 10^3 (s^{-1})
1.20	0.72	0.95	0.84
2.40	1.07	1.28	1.18
3.72	1.43	1.54	1.49
5.01	1.66	1.81	1.73
6.20	1.76	1.42	1.59
7.44	1.94	2.05	2.00
8.68	2.40	2.63	2.52
9.94	2.94	2.79	2.86

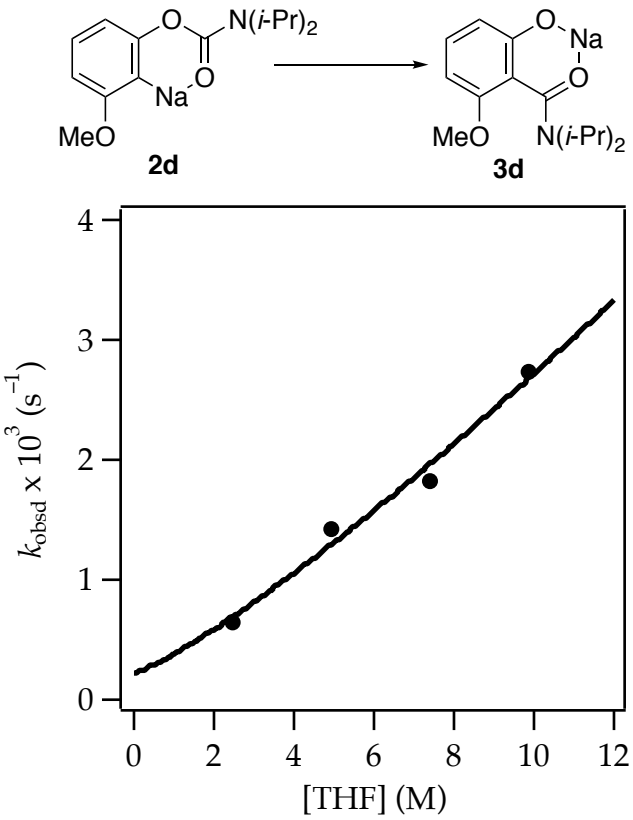


Figure S14. Plot of k_{obsd} versus [THF] in 2,5-dimethyltetrahydrofuran cosolvent for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-methoxyphenyl)sodium **2d** (0.010 M) by NaDA (0.10 M) at –15 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{THF}]^n + k'$ ($k = 0.00016 \pm 0.0003$, $k' = 0.00022 \pm 0.0007$, $n = 1.19 \pm 0.75$)

[THF] (M)	k_{obsd} x 10^3(s^{-1})
2.46	0.65
4.93	1.43
7.40	1.82
9.86	2.74

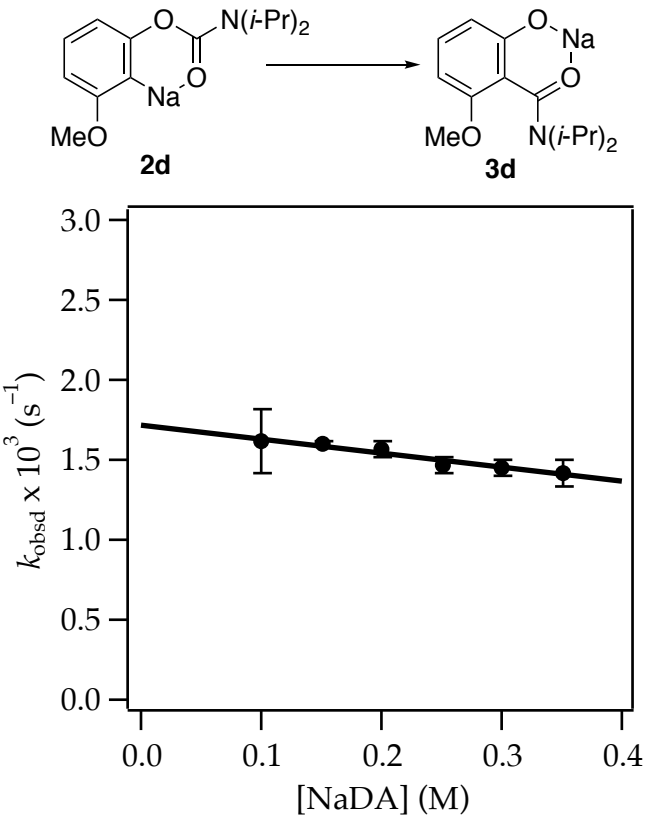


Figure S15. Plot of k_{obsd} versus [NaDA] in 6.2 M THF in hexane cosolvent for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-methoxyphenyl)sodium **2d** (0.010 M) at –15 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{NaDA}] + k'$ ($k = -0.00087 \pm 0.00014$, $k' = 0.0017 \pm 0.0001$)

[NaDA] (M)	k_{obsd1}x10^3 (s^{-1})	k_{obsd2}x10^3 (s^{-1})	k_{obsd}(avg)x10^3 (s^{-1})
0.10	1.76	1.47	1.62
0.15	1.61	1.58	1.60
0.20	1.53	1.61	1.57
0.25	1.50	1.43	1.47
0.30	1.41	1.49	1.45
0.35	1.36	1.48	1.42

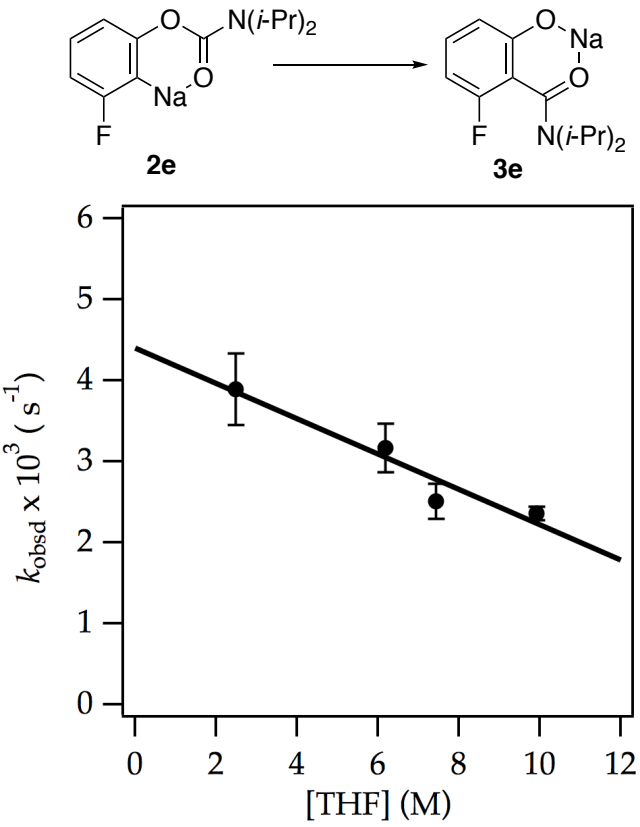


Figure S16. Plot of k_{obsd} versus [THF] in hexane cosolvent for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium **2e** (0.010 M) at 0 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k$[THF]+ k' (k = –0.00022 ± 0.00004, k' = 0.0044 ± 0.0003)

[THF] (M)	k_{obsd1} x 10^3(s^{-1})	k_{obsd2} x 10^3(s^{-1})	k_{obsd}(avg) x 10^3 (s^{-1})
2.48	4.58	3.20	3.89
6.18	3.38	2.95	3.17
7.44	2.66	2.35	2.51
9.92	2.42	2.30	2.36

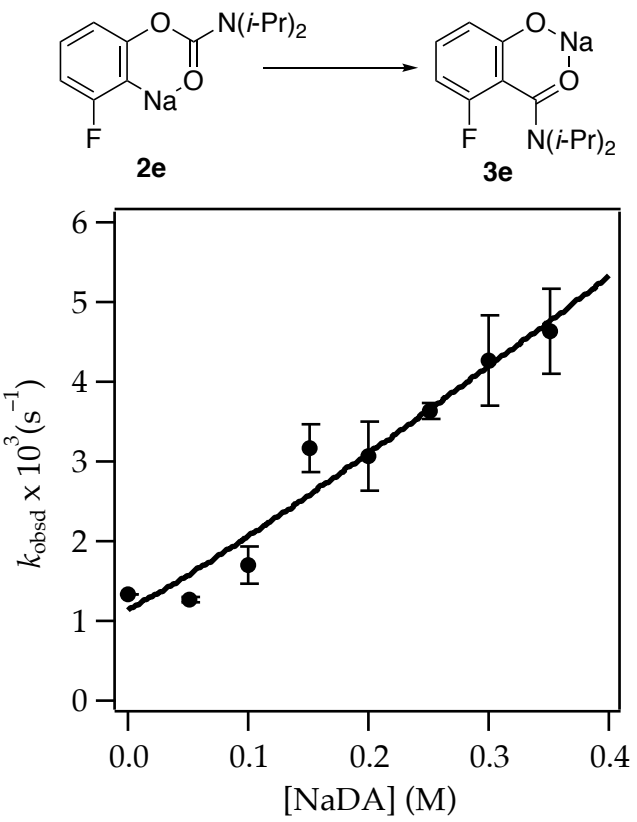


Figure S17. Plot of k_{obsd} versus [NaDA] in 4.2 M THF/hexane for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium **2e** (0.010 M) at 0 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{NaDA}]^n + k'$ (k = 0.012 ± 0.004, k' = 0.0012 ± 0.0004, n = 1.15 ± 0.30)

[NaDA] (M)	k_{obsd1}x10^3 (s^{-1})	k_{obsd2}x10^3 (s^{-1})	k_{obsd}(avg)x10^3 (s^{-1})
0.0	1.40	1.60	1.50
0.05	1.25	1.29	1.27
0.10	1.86	1.51	1.69
0.15	3.38	2.95	3.17
0.20	3.35	2.76	3.06
0.25	3.69	3.55	3.62
0.30	3.86	4.66	4.26
0.35	5.01	4.25	4.63

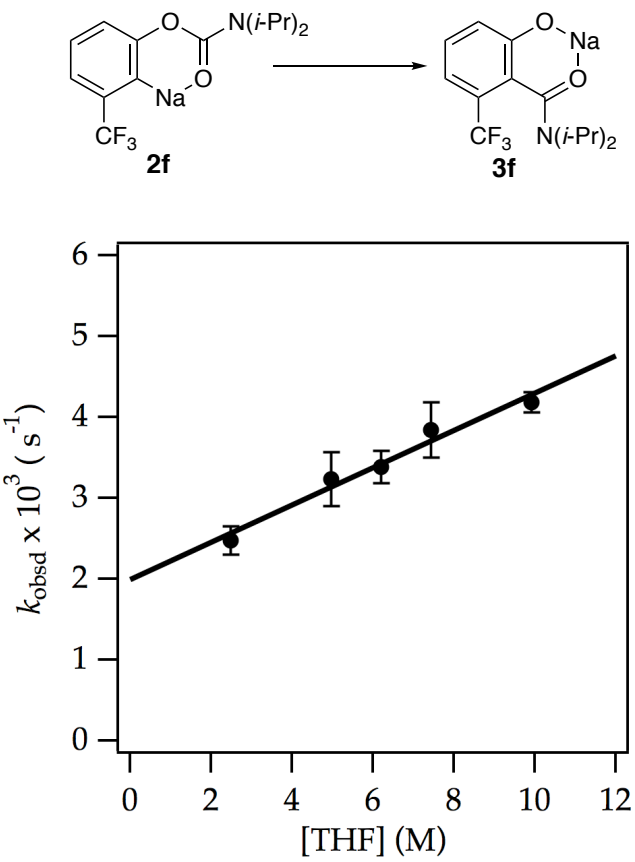


Figure S18. Plot of k_{obsd} versus [THF] in hexane cosolvent for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-(trifluoromethyl)phenyl)sodium **2f** (0.010 M) at –30 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{THF}] + k'$ ($k = 0.0023 \pm 0.0002$, $k' = 0.0020 \pm 0.0002$).

[THF] (M)	k_{obsd1} x 10^3 (s^{-1})	k_{obsd2} x 10^3 (s^{-1})	k_{obsd}(avg) x 10^3 (s^{-1})
2.48	2.35	2.60	2.48
4.96	3.00	3.47	3.24
6.20	3.20	3.68	3.44
7.44	3.60	4.08	3.84
9.92	4.27	4.09	4.18

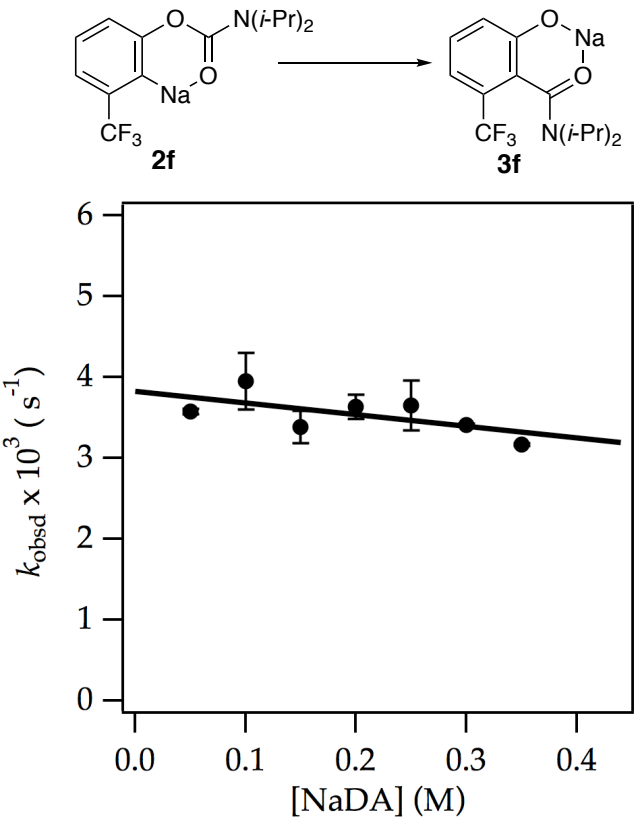


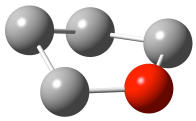
Figure S19. Plot of k_{obsd} versus [NaDA] in 6.2 M THF/hexane for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-(trifluoromethyl)phenyl)sodium **2f** (0.010 M) at –30°C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{NaDA}] + k'$ (k = –0.0014 ± 0.0008, k' = 0.0038 ± 0.0002).

[NaDA] (M)	k_{obsd1}x10^3 (s^{-1})	k_{obsd2}x10^3 (s^{-1})	k_{obsd}(avg)x10^3 (s^{-1})
0.05	3.60	3.55	3.58
0.10	4.20	3.70	3.92
0.15	3.24	3.52	3.38
0.20	3.53	3.74	3.64
0.25	3.43	3.87	3.65
0.30	3.40	3.42	3.41
0.35	3.18	3.16	3.17

III. Computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory. $G_{M06\text{-}2X}$ is derived from a M06-2X SP calculation corresponding to the optimized geometry and includes a thermal correction from the geometry optimization calculation.

Table S-1. Geometric coordinates and thermally corrected M06-2X energies for THF.

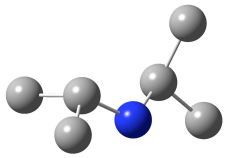


G = -145737.157

$G_{M06\text{-}2X}$ = -145728.9988

Atom	**X**	**Y**	**Z**
C	-1.1655770	-0.4304460	-0.1316510
H	-0.7966490	1.1557780	1.3100440
H	-1.3434230	1.7616460	-0.2642560
H	-1.5359580	-0.4831270	-1.1673560
C	0.7339430	0.9965910	-0.2269410
H	0.7973310	1.1548800	-1.3102840
H	-1.9488020	-0.8230080	0.5275430
H	1.3443500	1.7610810	0.2638280
C	1.1652710	-0.4309590	0.1320600
C	-0.7333840	0.9970250	0.2267570
H	1.9488890	-0.8240060	-0.5263660
H	1.5347420	-0.4835500	1.1681130
O	-0.0002500	-1.2516200	-0.0003270

Table S-2. Geometric coordinates and thermally corrected M06-2X energies for diisopropylamine.

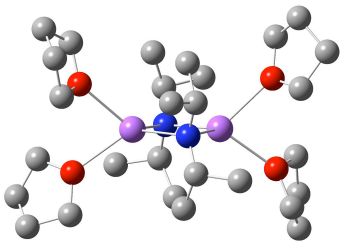


G = -183263.5852

$\mathbf{G_{M06\text{-}2X}}$ = -183280.0771

Atom	X	Y	Z
C	-2.3326560	-0.9422780	0.4466450
H	-2.0463390	-1.6573420	1.2287260
H	-3.2784570	-0.4797340	0.7488170
H	-2.4984340	-1.5018680	-0.4810530
C	-1.2461340	0.1181580	0.2403730
H	-1.1181040	0.6553470	1.1994030
C	-1.6851130	1.1418170	-0.8142190
H	-0.9439240	1.9365860	-0.9509170
H	-1.8333940	0.6471290	-1.7808350
H	-2.6256340	1.6188720	-0.5151540
N	-0.0141350	-0.5639690	-0.1834440
H	0.1153940	-1.3929040	0.3973890
C	1.2400150	0.2049250	-0.1653040
H	1.0711530	1.1036560	-0.7717820
C	2.3240050	-0.6280580	-0.8585730
H	2.0037950	-0.9103990	-1.8659910
H	3.2666320	-0.0732190	-0.9283170
H	2.5241710	-1.5507690	-0.2967610
C	1.6992260	0.6504500	1.2361930
H	0.9435680	1.2638740	1.7387130
H	1.9010200	-0.2230170	1.8709720
H	2.6214450	1.2414940	1.1802080

Table S-3. Geometric coordinates and thermally corrected M06-2X energies for NaDA ground-state $A_2(THF)_4$.



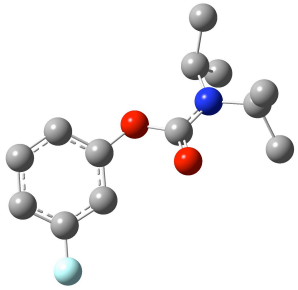
G = -1152417.329

$\mathbf{G_{M06\text{-}2X}}$ = -1152415.563

Atom	X	Y	Z	Atom	X	Y	Z
Na	-1.4745010	-0.0632710	-0.0235120	H	-1.6880690	-2.8019560	-3.0002740
Na	1.5318880	-0.0837150	-0.0153470	H	-1.2901530	-4.3272000	-2.1901370
N	0.0480430	-1.1761660	-1.6084690	H	-2.0883350	-3.0173860	-1.2853010
C	0.1694240	-0.6602420	-2.9692230	N	0.0436240	0.9620520	1.6283840
H	-0.4391800	-1.2515570	-3.6856630	C	0.1629600	0.3853700	2.9640200
C	1.6173190	-0.7046300	-3.5272920	H	-0.6048770	0.7831280	3.6620500
H	1.6660960	-0.4095990	-4.5863350	C	1.5227050	0.6404950	3.6656670
H	2.2667120	-0.0262920	-2.9563270	H	1.5496610	0.1956660	4.6704000
H	2.0364470	-1.7149110	-3.4483130	H	2.3433580	0.2066400	3.0763150
C	-0.3591310	0.7771420	-3.0699780	H	1.7276340	1.7111730	3.7780880
H	0.1590080	1.4365080	-2.3605390	C	-0.0808510	-1.1279190	2.9182160
H	-0.2204570	1.1961090	-4.0758830	H	-0.0389550	-1.5743730	3.9205700
H	-1.4296400	0.8116060	-2.8348000	H	-1.0667210	-1.3524080	2.4933100
C	0.0271220	-2.6365720	-1.6314440	H	0.6699010	-1.6337420	2.2966250
H	0.7700500	-3.0423870	-2.3523090	C	0.1180760	2.4186890	1.6539680
C	0.4062580	-3.2286650	-0.2668280	H	1.0966840	2.7865630	2.0449150
H	0.3735860	-4.3267510	-0.2805270	C	-0.9440190	3.1314560	2.5304000
H	1.4159540	-2.9220130	0.0308580	H	-0.8438370	4.2238800	2.4653710
H	-0.2902890	-2.8883490	0.5107590	H	-1.9551740	2.8575990	2.2008830
C	-1.3387470	-3.2360300	-2.0563500	H	-0.8583860	2.8609410	3.5879860

C	0.0185850	2.9789940	0.2279000	H	-5.2225710	-0.8558490	-0.4101070
H	-0.9483170	2.7203850	-0.2233340	H	-3.9887420	-1.6012620	-1.4539740
H	0.1102680	4.0736640	0.2192520	C	-5.0889850	-3.0243470	-0.1740300
H	0.8112090	2.5716710	-0.4093050	C	-4.9638820	-3.0982440	1.3553370
O	3.2577980	1.5416510	-0.6638420	C	-3.6126820	-2.4178520	1.5911700
C	3.9857410	2.0219660	0.4919400	H	-3.5447420	-1.9016160	2.5538340
H	3.2579640	2.3311640	1.2515300	H	-2.7854400	-3.1364570	1.5218640
H	4.5765230	1.1930680	0.8925230	H	-5.7700750	-2.5292250	1.8340020
C	4.8326480	3.2018480	0.0024160	H	-4.9913180	-4.1199540	1.7458670
C	3.9941480	3.7343840	-1.1697470	H	-4.4982270	-3.8189740	-0.6439690
C	3.4510790	2.4390760	-1.7742680	H	-6.1200620	-3.1081090	-0.5312060
H	2.4928980	2.5597860	-2.2872250	O	-3.3798430	1.4669330	-0.5936400
H	4.1689420	1.9945590	-2.4785430	C	-4.2223680	1.8421640	0.5128200
H	3.1698500	4.3540500	-0.7984710	H	-5.1178640	1.2037760	0.5261900
H	4.5722940	4.3244270	-1.8874770	H	-3.6599370	1.6727060	1.4339750
H	5.8100450	2.8557700	-0.3553700	C	-4.5910330	3.3033560	0.2651240
H	5.0034250	3.9449820	0.7871290	C	-4.7116000	3.3327290	-1.2666450
O	3.5270160	-1.3789260	0.5680030	C	-3.5995450	2.3670140	-1.7022990
C	4.4239670	-1.7202000	-0.4966710	H	-3.8647470	1.7802710	-2.5886700
H	3.9520080	-1.4221720	-1.4344730	H	-2.6598550	2.8935520	-1.9058840
H	5.3660330	-1.1612940	-0.3774660	H	-5.6935320	2.9562590	-1.5771100
C	4.6503900	-3.2324120	-0.3525370	H	-4.5843960	4.3318020	-1.6940450
C	4.4582220	-3.4859690	1.1678370	H	-3.7808030	3.9593460	0.6029010
C	3.9634930	-2.1266860	1.7108940	H	-5.5108880	3.5999960	0.7785850
H	3.1175580	-2.1988930	2.3971970	C	-4.4738530	-1.6560670	-0.4757560
H	4.7769180	-1.5813150	2.2134040				
H	3.7189100	-4.2727580	1.3412860				
H	5.3871050	-3.7911540	1.6592860				
H	5.6388130	-3.5342260	-0.7121630				
H	3.9006430	-3.7803170	-0.9305790				
O	-3.4695290	-1.4404060	0.5393580				

Table S-4. Geometric coordinates and thermally corrected M06-2X energies for 3-fluorophenyl diisopropylcarbamate.



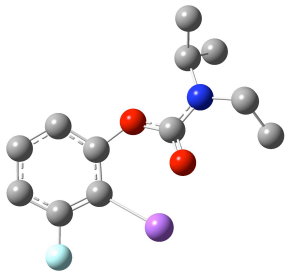
G = -508746.7771

$\mathbf{G_{M06\text{-}2X}}$ = -508700.2475

Atom	X	Y	Z	Atom	X	Y	Z
C	-2.9524340	-0.9709310	-0.2504140	H	-4.1214990	1.6351330	-0.6509490
N	-1.8856020	0.0307630	0.0142560	H	-3.3530630	3.1367540	-0.1267450
C	-0.5933780	-0.3297560	-0.2211350	C	-2.9321600	1.2804520	1.9053350
O	0.2812190	0.7094580	0.0632640	H	-2.2685390	0.7775560	2.6162160
C	1.6508650	0.5293680	-0.0629300	H	-3.1381160	2.2879590	2.2840150
C	2.3132630	-0.5903840	0.4418090	H	-3.8839740	0.7376560	1.8813100
C	3.6985540	-0.6187020	0.3392580	H	-3.8806410	-0.4553860	0.0126320
C	4.4371000	0.4140060	-0.2272670	C	-3.0437160	-1.3492670	-1.7359620
C	3.7461210	1.5232730	-0.7161220	H	-2.1409340	-1.8704890	-2.0605450
C	2.3549980	1.5873630	-0.6400900	H	-3.9047730	-2.0083190	-1.8967300
H	1.8064000	2.4438670	-1.0171750	H	-3.1774350	-0.4581560	-2.3587830
H	4.2973240	2.3455120	-1.1629970	C	-2.8400280	-2.2010480	0.6619080
H	5.5177490	0.3383470	-0.2787730	H	-3.7062300	-2.8546320	0.5071090
F	4.3517820	-1.6977390	0.8206930	H	-1.9332050	-2.7678240	0.4417940
H	1.7795130	-1.4227760	0.8785760	H	-2.8221320	-1.9051930	1.7165020
O	-0.2179210	-1.4122670	-0.6336090				
C	-2.2772800	1.3687060	0.5188180				
H	-1.3489250	1.9255680	0.6288610				
C	-3.1531780	2.1233230	-0.4927490				

H	-2.6470920	2.2028000	-1.4603350

Table S-5. Geometric coordinates and thermally corrected M06-2X energies for (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium.

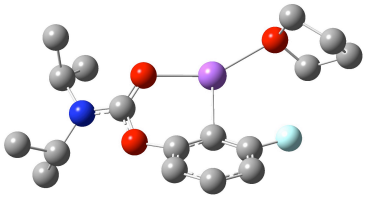


G = -610230.6687

$\mathbf{G_{M06\text{-}2X}}$ = -610155.4525

Atom	X	Y	Z	Atom	X	Y	Z
C	-3.1052200	-0.8348830	-0.1790620	H	-3.3242800	3.2740170	-0.4461120
N	-2.0013440	0.1347620	0.0295560	C	-3.0778620	1.5893940	1.7530240
C	-0.7076250	-0.2636270	-0.1658570	H	-2.4736350	1.1202150	2.5363280
O	0.1618970	0.7405570	0.0056760	H	-3.2458280	2.6353210	2.0333530
C	1.5965330	0.6765640	-0.0592310	H	-4.0567100	1.0960570	1.7308310
C	2.3261430	-0.4502240	0.2874450	H	-4.0116830	-0.2561480	0.0187140
C	3.6929520	-0.2453170	0.2029680	C	-3.1988930	-1.3311400	-1.6299320
C	4.3343690	0.9409930	-0.1423430	H	-2.3272350	-1.9320990	-1.8960450
C	3.5279780	2.0373690	-0.4614310	H	-4.0988210	-1.9451170	-1.7530200
C	2.1396450	1.9138130	-0.4263580	H	-3.2657090	-0.4884980	-2.3260870
H	1.4930170	2.7510820	-0.6736550	C	-3.0861670	-1.9878780	0.8362430
H	3.9814600	2.9853370	-0.7386380	H	-3.9962850	-2.5896860	0.7301590
H	5.4184910	1.0027390	-0.1687430	H	-2.2225310	-2.6361220	0.6741440
F	4.5124720	-1.3234460	0.4737920	H	-3.0491210	-1.6048800	1.8615520
Na	1.3765630	-2.5220000	0.1443670	H	-2.5883780	2.2082290	-1.6581250
O	-0.4208220	-1.4304290	-0.4788260	H	-4.1258920	1.7630820	-0.8885610
C	-2.3564210	1.5273500	0.3984550				
H	-1.4083000	2.0487360	0.5083960				
C	-3.1474650	2.2269860	-0.7169790				

Table S-6. Geometric coordinates and thermally corrected M06-2X energies for (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium(THF).



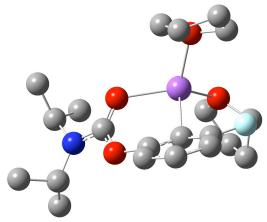
G = -755968.1463

$\mathbf{G_{M06\text{-}2X}}$ = -755895.2321

Atom	X	Y	Z	Atom	X	Y	Z
C	-3.5453420	-1.8025800	-0.2281390	C	5.1170860	-0.8312510	-0.7638610
N	-3.0692770	-0.4214090	0.0311110	C	3.9658240	-1.7432610	-1.1832370
C	-1.7680310	-0.0956340	-0.2380900	H	3.2844000	-1.2823630	-1.9068810
O	-1.5188620	1.2069790	-0.0387620	H	4.3243110	-2.6955010	-1.5971720
C	-0.2237170	1.8290630	-0.0893900	H	4.7699460	0.2044540	-0.7037630
C	0.9170110	1.2098410	0.4020070	H	5.9671570	-0.8870680	-1.4503510
C	2.0233700	2.0349740	0.3154220	H	6.0326680	-2.2723550	0.5932190
C	2.0652030	3.3458700	-0.1515760	H	5.9633050	-0.6301060	1.2645940
C	0.8664590	3.8976400	-0.6120310	C	-4.0474700	0.5755220	0.5299800
C	-0.3006230	3.1339690	-0.5884220	H	-3.4802930	1.4934180	0.6679740
H	-1.2455940	3.5375050	-0.9417410	C	-5.1495010	0.8576940	-0.5023510
H	0.8427640	4.9172210	-0.9876740	H	-4.7139930	1.1833860	-1.4526160
H	2.9939610	3.9095260	-0.1609460	H	-5.7753410	-0.0218710	-0.6940420
F	3.2502880	1.5113250	0.7269910	H	-5.8072670	1.6547050	-0.1372740
Na	1.1252470	-1.0975520	0.1326480	C	-4.6190470	0.1757600	1.8984600
O	-0.9475780	-0.9329050	-0.6420280	H	-3.8144270	0.0203880	2.6245180
O	3.2223790	-2.0141630	0.0308040	H	-5.2673240	0.9751260	2.2748210
C	4.0319890	-1.6560960	1.1884220	H	-5.2218320	-0.7385650	1.8505970
H	3.5920710	-0.7649790	1.6483950	H	-4.6075350	-1.7753590	0.0313340
H	4.0021260	-2.4929230	1.8931940	C	-3.4582160	-2.1955220	-1.7106570
C	5.4306710	-1.3571610	0.6452290	H	-2.4191520	-2.2514220	-2.0408120

H	-3.9274340	-3.1748400	-1.8618490
H	-3.9839530	-1.4672170	-2.3371540
C	-2.8898050	-2.8420470	0.6939540
H	-3.3840110	-3.8127140	0.5692690
H	-1.8307330	-2.9618160	0.4559060
H	-2.9818730	-2.5456100	1.7442030

Table S-7. Geometric coordinates and thermally corrected M06-2X energies for (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium(THF)$_2$.



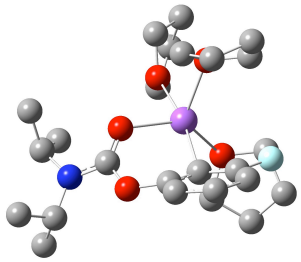
G = -901701.5728

$\mathbf{G_{M06\text{-}2X}}$ = -901632.5294

Atom	X	Y	Z	Atom	X	Y	Z
C	3.6939400	-0.1773490	1.4520910	H	-4.7223380	2.1548270	2.7704940
N	3.1278980	0.3643230	0.1929430	H	-4.9464170	2.3085230	1.0187220
C	1.7904000	0.6468820	0.1210370	H	-2.5709800	2.8314200	0.6883530
O	1.4580170	1.2511670	-1.0308300	H	-2.9130680	3.7071110	2.1984220
C	0.1013640	1.4755090	-1.4528440	O	-1.4701840	-2.9597700	0.4371970
C	-0.8697660	0.4935140	-1.3199000	C	-2.2909510	-3.1478190	-0.7410760
C	-2.0742660	0.9033290	-1.8582280	H	-3.1831040	-3.7317070	-0.4699920
C	-2.3534980	2.1063760	-2.5034530	H	-2.5928750	-2.1603550	-1.0967380
C	-1.3082550	3.0292940	-2.6084800	C	-1.3952150	-3.9086290	-1.7122370
C	-0.0572210	2.7197300	-2.0720300	C	-0.6451560	-4.8611300	-0.7659240
H	0.7723790	3.4187690	-2.1359160	C	-0.4958300	-4.0240930	0.5184060
H	-1.4684620	3.9828170	-3.1049750	H	-0.6781000	-4.6096770	1.4272820
H	-3.3417050	2.3150540	-2.9043590	H	0.4967290	-3.5637150	0.5972540
F	-3.1657180	0.0333140	-1.7309500	H	-1.2472500	-5.7560640	-0.5714570
Na	-0.9640300	-0.7129520	0.7336420	H	0.3215370	-5.1886720	-1.1599100
O	1.0066070	0.3896810	1.0447960	H	-0.7043710	-3.2091630	-2.1961870
O	-2.4626520	0.4249420	2.0940070	H	-1.9604580	-4.4319980	-2.4892870
C	-1.9795850	1.7384290	2.4588060	C	4.0556270	0.6465990	-0.9285050
H	-2.0506090	1.8560650	3.5502170	H	3.4267810	1.0094570	-1.7388050
H	-0.9299370	1.8000050	2.1592900	C	5.0543360	1.7598230	-0.5776630

C	-2.8947140	2.7186790	1.7287370	H	4.5265050	2.6687910	-0.2712960
C	-4.2463600	1.9896920	1.7964060	H	5.7356290	1.4685160	0.2306930
C	-3.8368850	0.5190300	1.6340070				
H	-4.4494990	-0.1663520	2.2301630				
H	-3.8657600	0.2078620	0.5844080				
H	5.3614460	-0.4002460	-2.3043970				
H	5.4223600	-1.0614280	-0.6679580				
H	4.7663330	-0.2593080	1.2530950				
C	3.5318240	0.7826380	2.6404240				
H	2.4795320	0.9029820	2.9047950				
H	4.0689900	0.3884670	3.5111090				
H	3.9472120	1.7677280	2.4027050				
C	3.1907050	-1.5932880	1.7730340				
H	3.7500550	-2.0028750	2.6225300				
H	2.1301180	-1.5786420	2.0331620				
H	3.3349180	-2.2616030	0.9170750				
H	5.6684380	2.0002620	-1.4530680				
C	4.7537170	-0.6295220	-1.4217780				
H	4.0168960	-1.3888100	-1.7038870				

Table S-8. Geometric coordinates and thermally corrected M06-2X energies for (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium(THF)$_3$.



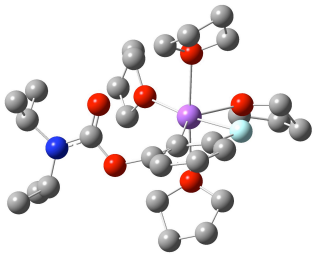
G = -1047429.616

$\mathbf{G_{M06\text{-}2X}}$ = -1047365.692

Atom	X	Y	Z	Atom	X	Y	Z
Na	-0.8435660	0.3738920	-0.0203080	H	5.3205420	1.6745040	1.7365030
C	-0.0912770	-1.8696960	0.6372180	O	1.3307510	0.2811050	-0.8945670
C	1.1470050	-2.3309380	0.2089050	C	1.4629610	-3.6408310	-0.1661150
O	2.3010780	-1.4746440	0.2084760	C	0.4504690	-4.6005520	-0.1148840
C	2.2719140	-0.2174470	-0.2685210	C	-0.8328370	-4.2259700	0.2942070
N	3.4311930	0.4649390	-0.0097520	C	-1.0254200	-2.8878870	0.6337150
C	3.6198050	1.8191890	-0.5846770	F	-2.3419430	-2.5608790	0.9945820
H	4.6272770	2.1077360	-0.2708780	H	-1.6478950	-4.9430760	0.3454820
C	3.6127090	1.8204690	-2.1210750	H	0.6592620	-5.6313450	-0.3894500
H	2.6269950	1.5514920	-2.5055440	H	2.4705990	-3.9007280	-0.4797100
H	3.8730170	2.8191290	-2.4916120	O	-2.0159050	-0.2520870	-2.0516800
H	4.3480570	1.1104100	-2.5147900	C	-1.1096210	-0.8117390	-3.0340430
C	2.6527270	2.8589020	0.0034620	H	-1.2014560	-0.2363820	-3.9676000
H	2.9404120	3.8614950	-0.3364380	H	-0.0949300	-0.7080050	-2.6442240
H	1.6247790	2.6662460	-0.3118460	C	-1.5596760	-2.2584300	-3.2257640
H	2.6932410	2.8490390	1.0984430	C	-3.0823770	-2.1377080	-3.0567570
C	4.5487560	-0.1392100	0.7524330	C	-3.2012380	-1.0808430	-1.9517660
H	4.1746660	-1.1001860	1.0997530	H	-4.0835420	-0.4396700	-2.0631570
C	5.7703270	-0.4078290	-0.1400330	H	-3.2129690	-1.5428350	-0.9592810
H	5.4952880	-1.0422120	-0.9889810	H	-3.5453230	-1.7824470	-3.9856530

H	6.2103640	0.5176420	-0.5302710	H	-3.5619070	-3.0804670	-2.7770320
H	6.5477850	-0.9243130	0.4347450	O	-1.9031160	0.9092220	2.1479390
C	4.9082930	0.6916540	1.9933330	C	-3.2014540	0.3211840	2.3869650
H	4.0283690	0.8427860	2.6272000				
H	5.6666840	0.1639000	2.5827730				
H	-3.9131190	1.1286110	2.6110670				
H	-3.5228710	-0.1946920	1.4772960				
C	-3.0283510	-0.6361120	3.5685760				
C	-1.8834380	0.0210360	4.3537590				
C	-0.9992520	0.5543960	3.2252630				
H	-0.4346800	1.4529140	3.4983080				
H	-0.3131060	-0.2150370	2.8506940				
H	-2.2600500	0.8422860	4.9762900				
H	-1.3486300	-0.6807710	5.0010500				
H	-2.7234690	-1.6168190	3.1944900				
H	-3.9473420	-0.7494000	4.1524340				
O	-1.1905090	2.6920180	-0.5264460				
C	-1.4335610	3.7408100	0.4342960				
H	-1.7302360	3.2482450	1.3627090				
H	-0.5021750	4.2963190	0.6068170				
C	-2.5336840	4.6500390	-0.1671070				
C	-2.9678800	3.9005770	-1.4435030				
C	-1.7077160	3.1119280	-1.7964430				
H	-1.8880310	2.2091520	-2.3826340				
H	-0.9711090	3.7466190	-2.3142040				
H	-3.7873280	3.2064110	-1.2253670				
H	-3.2919610	4.5715880	-2.2450960				
H	-2.1244070	5.6342080	-0.4195040				
H	-3.3640520	4.8081900	0.5273120				
H	-1.1357960	-2.8913530	-2.4393140				
H	-1.2640790	-2.6634980	-4.1987950				

Table S-9. Geometric coordinates and thermally corrected M06-2X energies for (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium(THF)$_4$.



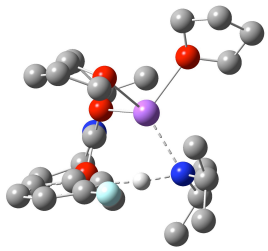
G = -1193154.211

$\mathbf{G_{M06\text{-}2X}}$ = -1193095.198

Atom	X	Y	Z	Atom	X	Y	Z
Na	1.3415090	-0.0741230	-0.1271510	H	-6.0814010	-0.6270290	2.8082420
C	-0.2547780	1.6941250	0.5405250	C	-4.0373360	-2.2244970	1.8110160
C	-1.5676610	2.1220910	0.7080940	H	-2.9740000	-2.4189000	1.6338460
O	-2.6036670	1.1455910	0.8686560	H	-4.2490760	-2.4133500	2.8700470
C	-3.0977360	0.5400280	-0.2413320	H	-4.6195420	-2.9470730	1.2270200
N	-4.0140300	-0.4393210	0.0647880	O	-2.7809760	0.8410890	-1.3847230
C	-4.6829910	-1.1598760	-1.0430470	C	-1.9889410	3.4476320	0.8389170
H	-5.3625860	-1.8603990	-0.5477100	C	-1.0266250	4.4596290	0.8004710
C	-5.5432700	-0.2339180	-1.9175390	C	0.3205590	4.1223290	0.6383310
H	-4.9167040	0.4945210	-2.4353700	C	0.6112360	2.7665870	0.5202060
H	-6.0895680	-0.8244970	-2.6628500	F	1.9938130	2.4635180	0.3669160
H	-6.2764910	0.3057950	-1.3082530	H	1.1012430	4.8779400	0.6112880
C	-3.6983390	-1.9944950	-1.8774010	H	-1.3214300	5.5010260	0.8999850
H	-4.2433800	-2.5787470	-2.6287930	H	-3.0421730	3.6807340	0.9711900
H	-2.9849220	-1.3426460	-2.3855040	O	3.7515280	-0.4235610	-0.1118220
H	-3.1443310	-2.6919340	-1.2388120	C	4.7448590	0.6114150	0.0113120
C	-4.3873540	-0.7706320	1.4551760	H	5.2898570	0.7123840	-0.9392300
H	-3.7763720	-0.1224430	2.0807550	H	4.2230170	1.5474930	0.2199400
C	-5.8604950	-0.4451130	1.7498650	C	5.6763280	0.1467520	1.1303720
H	-6.0729450	0.6066720	1.5324890	C	5.6918570	-1.3736680	0.9055100

H	-6.5481630	-1.0629480	1.1602910	C	4.2504280	-1.6552740	0.4543180
C	0.1213630	-0.5050300	4.2343800	H	4.1887550	-2.4433470	-0.3047440
C	0.1702590	-1.1197140	2.8356230	H	3.5992660	-1.9233070	1.2938190
H	0.0524690	-2.2085900	2.8303820	H	6.4029580	-1.6312200	0.1116190
H	-0.5793520	-0.6633160	2.1777010	H	5.9666680	-1.9418720	1.7994180
H	0.5834120	-1.1753150	4.9701360	H	5.2426260	0.3868180	2.1080920
H	-0.9013730	-0.2910130	4.5597160	H	6.6685940	0.6047050	1.0734060
H	0.3730920	1.5403500	3.5569970	O	1.4852500	-0.8132280	2.3174620
H	1.3815480	1.1578450	4.9718270	C	2.0608440	0.2766880	3.0774100
O	0.8626760	-2.3094190	-0.8148320	H	2.9378780	-0.1086990	3.6171670
C	0.6862870	-3.5047000	-0.0391520	H	2.3803280	1.0571310	2.3820080
H	1.2983990	-3.3960270	0.8600130	C	0.9698300	0.7599380	4.0389170
H	-0.3655080	-3.5939700	0.2661950	H	1.9012460	2.0800860	-4.9109630
C	1.1108830	-4.6902310	-0.9445690	H	2.2721750	3.4789650	-3.8853410
C	1.5513050	-4.0085130	-2.2595970	H	0.1939890	3.1589900	-2.5948180
C	0.8047290	-2.6756220	-2.2010760	H	-0.3551860	2.8080050	-4.2466840
H	1.2585400	-1.8597430	-2.7657430				
H	-0.2444810	-2.7917480	-2.5152470				
H	2.6320140	-3.8271560	-2.2600540				
H	1.3048440	-4.5974240	-3.1484070				
H	0.2638250	-5.3616420	-1.1188330				
H	1.9132590	-5.2849780	-0.4982060				
O	1.3984220	0.6063870	-2.4946090				
C	2.4346710	1.5399030	-2.8710380				
H	2.7512110	2.0835070	-1.9735170				
H	3.2873050	0.9747910	-3.2646000				
C	1.8062390	2.4884320	-3.8970220				
C	0.3348990	2.4972030	-3.4563490				
C	0.1221920	1.0449440	-3.0345420				
H	-0.6429240	0.9263130	-2.2655560				
H	-0.1246590	0.4108530	-3.8991840				

Table S-10. Geometric coordinates and thermally corrected M06-2X transition state energies for the metalation of 3-fluorophenyl diisopropylcarbamate by $NaDA(THF)_2$.



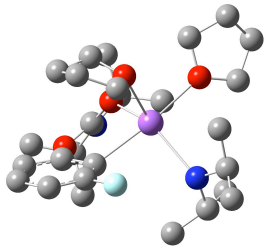
G = -1084939.711

$\mathbf{G_{M06\text{-}2X}}$ = -1084904.799

Atom	X	Y	Z	Atom	X	Y	Z
Na	-0.9917930	0.4305190	-0.0720100	H	4.7421790	-1.2383840	-0.2177940
C	0.3452710	-1.8858850	0.8563100	O	1.0457530	0.4814930	-1.1593700
C	1.5663100	-1.8592540	0.1846970	C	2.1185800	-2.9372740	-0.5123170
O	2.4049250	-0.7039520	0.2304160	C	1.4166300	-4.1417430	-0.5537080
C	2.1380050	0.3329300	-0.6017190	C	0.1787160	-4.2389250	0.0837960
N	3.1865790	1.1858770	-0.7452220	C	-0.2989390	-3.1130130	0.7476580
C	3.0053610	2.3961150	-1.6011400	F	-1.5419300	-3.2468110	1.3240060
H	3.9547910	2.9310730	-1.5068390	H	-0.4011250	-5.1571710	0.0761880
C	2.8281580	2.0357810	-3.0834010	H	1.8313800	-4.9983660	-1.0778060
H	1.8911730	1.4975850	-3.2416720	H	3.0806580	-2.8342470	-1.0052340
H	2.8112130	2.9498750	-3.6882270	N	-0.7689570	0.2132600	2.3028130
H	3.6564800	1.4111870	-3.4361870	C	-2.0501980	-0.0660340	2.9600230
C	1.9135120	3.3486300	-1.0935920	H	-2.3856000	0.8458070	3.4972580
H	1.9623510	4.2829040	-1.6658010	C	-2.0168580	-1.1968090	4.0160560
H	0.9151340	2.9235560	-1.2124280	H	-2.9985300	-1.3272790	4.4934980
H	2.0669140	3.5898140	-0.0368280	H	-1.7326230	-2.1466600	3.5512750
C	4.5391880	0.9407380	-0.1610820	H	-1.2951060	-0.9736310	4.8091250
H	5.1393840	1.7660610	-0.5549500	C	-3.1370520	-0.3779340	1.9184120
C	4.5647800	1.0591230	1.3687470	H	-2.8739280	-1.2718510	1.3442380
H	4.1219300	2.0056140	1.6950440	H	-4.1054540	-0.5704460	2.3976090

H	4.0180290	0.2422350	1.8433730	H	-3.2743330	0.4642120	1.2259030
H	5.6031690	1.0285940	1.7193290	C	0.1824560	0.8554000	3.2221440
C	5.2013770	-0.3526850	-0.6599650	H	-3.1383930	-3.8325660	-2.6656220
H	5.1396010	-0.4294970	-1.7511770	H	-0.7781720	-3.1383540	-2.7068690
H	6.2615140	-0.3445540	-0.3814460	H	-1.2834340	-2.7766740	-4.3725180
H	1.3531110	1.8645050	1.6824680	H	1.5041450	2.6151850	3.2812690
O	-2.0623800	2.4417170	-0.6885300	H	0.8984680	-0.9741470	4.1973750
C	-2.3919160	3.4212610	0.3238550	H	1.9357350	-0.4102610	2.8847100
H	-2.2663600	2.9294500	1.2924810	H	1.9575660	0.4289040	4.4471710
H	-1.6828290	4.2556360	0.2614800	C	0.8024760	2.1184750	2.5959450
C	-3.8443480	3.8740600	0.0480200	H	0.0206340	2.8377150	2.3255140
C	-4.3410560	2.8721340	-1.0129780	C	1.3088650	-0.0789170	3.7197910
C	-3.0448270	2.5069170	-1.7334930				
H	-3.0558930	1.5303180	-2.2224040				
H	-2.7643310	3.2791350	-2.4668020				
H	-4.7636900	1.9808260	-0.5356990				
H	-5.0971890	3.2957030	-1.6812330				
H	-3.8593540	4.8934590	-0.3528020				
H	-4.4576030	3.8659330	0.9535250				
O	-2.0950860	-0.8069530	-1.8328320				
C	-1.2901540	-1.0566340	-3.0106850				
H	-1.6661220	-0.4323180	-3.8348130				
H	-0.2638600	-0.7647240	-2.7801650				
C	-1.4646140	-2.5429290	-3.3187410				
C	-2.9179620	-2.7831130	-2.8825030				
C	-3.0263980	-1.9008250	-1.6347690				
H	-4.0263600	-1.4799720	-1.4853210				
H	-2.7349910	-2.4457630	-0.7312760				
H	-3.6124040	-2.4435240	-3.6605330				
H	-0.1816680	-0.9071600	1.6347830				
H	-0.3603530	1.1979330	4.1221120				

Table S-11. Geometric coordinates and thermally corrected M06-2X energies for IRC of the metalation of 3-fluorophenyl diisopropylcarbamate by NaDA(THF)$_2$.



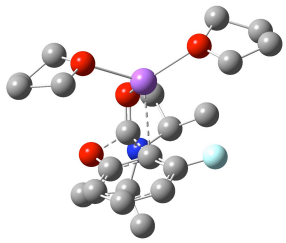
G = -1084952.837

$\mathbf{G_{M06\text{-}2X}}$ = -1084918.7

Atom	X	Y	Z	Atom	X	Y	Z
Na	0.7798150	-0.1537630	-0.1081950	H	-5.2097420	1.0082350	0.1068350
C	-0.4810880	1.8675080	0.4647900	O	-1.4547160	-0.6651030	-0.7639290
C	-1.8066930	2.0544060	0.0977340	C	-2.4035410	3.2685880	-0.2603600
O	-2.7582960	0.9802560	0.1518680	C	-1.6109650	4.4184700	-0.2511840
C	-2.4450190	-0.2984280	-0.1233770	C	-0.2610540	4.3246780	0.1017360
N	-3.3883560	-1.1698280	0.3524470	C	0.2155760	3.0575120	0.4281280
C	-3.3052820	-2.5979900	-0.0534630	F	1.5911390	3.0081750	0.7357400
H	-4.2028980	-3.0532140	0.3763550	H	0.3867350	5.1969930	0.1202800
C	-3.3944530	-2.7954660	-1.5744140	H	-2.0422570	5.3806680	-0.5148330
H	-2.5147000	-2.3881730	-2.0763140	H	-3.4554960	3.3139850	-0.5302730
H	-3.4659510	-3.8653230	-1.8040310	N	2.4734900	0.2068360	1.9277040
H	-4.2858850	-2.3022870	-1.9773350	C	3.9195550	-0.0421160	1.7377970
C	-2.0952370	-3.3191210	0.5605850	H	4.1236360	-1.0263830	2.1816580
H	-2.1599410	-4.3942690	0.3521080	C	4.8149360	0.9993990	2.4332030
H	-1.1607340	-2.9360160	0.1446830	H	5.8755280	0.7373560	2.3357750
H	-2.0775090	-3.1862180	1.6482750	H	4.6704370	1.9888440	1.9807120
C	-4.5347460	-0.7512100	1.2068400	H	4.5907690	1.0823000	3.5022200
H	-4.9956510	-1.6984430	1.5050650	C	4.2447150	-0.1210700	0.2426030
C	-4.1091830	-0.0541080	2.5081560	H	4.0302890	0.8358650	-0.2486610
H	-3.3491940	-0.6443930	3.0315890	H	5.3066590	-0.3441110	0.0829010

H	-3.7078440	0.9436970	2.3260300	H	3.6464780	-0.8964590	-0.2468980
H	-4.9802440	0.0382370	3.1677820	C	1.9770160	-0.1162070	3.2891350
C	-5.5987290	0.0410760	0.4315620	H	2.8031810	-0.0359930	4.0155260
H	-5.9317470	-0.5154360	-0.4517470	C	0.8894050	0.8747790	3.7124420
H	-6.4724690	0.2158130	1.0705270	H	1.2963080	1.8891200	3.8006030
H	0.0837820	0.9099030	2.9711530	H	2.2777090	1.1897330	1.7263670
H	0.4710400	0.5915480	4.6852740	H	2.0671190	2.6455020	-4.4536330
C	1.4673750	-1.5622930	3.3349660	H	1.7702170	3.8575220	-3.1943960
H	2.2324000	-2.2659220	2.9863730	H	-0.3631070	2.8173160	-2.5893050
H	1.1915530	-1.8466330	4.3579310	H	-0.3754000	2.6120490	-4.3560650
H	0.5832900	-1.6777310	2.6959010	H	3.2902570	1.5504840	-2.7170670
O	1.4599470	-2.3967610	-0.7171660	H	2.3181450	2.3210720	-1.4345610
C	1.9672790	-3.5366660	0.0077940				
H	2.9295970	-3.2595950	0.4567280				
H	1.2682270	-3.7829140	0.8133660				
C	2.1243570	-4.6659290	-1.0193790				
C	2.3293560	-3.8898160	-2.3297970				
C	1.3956000	-2.6973490	-2.1288830				
H	1.6903840	-1.7943340	-2.6676300				
H	0.3600100	-2.9501280	-2.3949830				
H	3.3686230	-3.5511260	-2.4180970				
H	2.0829020	-4.4732910	-3.2221410				
H	1.2075960	-5.2646490	-1.0741980				
H	2.9523970	-5.3382760	-0.7756420				
O	1.4334590	0.6919240	-2.3481780				
C	0.2931460	0.8579070	-3.2222150				
H	0.4895180	0.3356790	-4.1718410				
H	-0.5667280	0.4027340	-2.7271040				
C	0.1622580	2.3635450	-3.4352810				
C	1.6342490	2.8047040	-3.4585020				
C	2.2804010	1.8656810	-2.4287160				

Table S-12. Geometric coordinates and thermally corrected M06-2X transition state energies for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium(THF)$_2$.



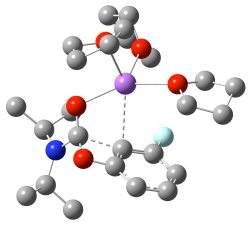
G = -901674.2413

$\mathbf{G_{M06\text{-}2X}}$ = -901611.0134

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.2049540	-0.7066010	-0.5101800	C	-0.8420810	4.7138580	-0.9852720
C	-0.5130510	-0.2292820	1.2046220	C	0.3285090	3.9813370	-0.3154450
C	0.2599860	-0.1586140	2.3407360	H	1.2120710	4.6150000	-0.1796500
C	0.0335320	0.7913550	3.3507960	H	0.0368220	3.5625720	0.6551970
C	-1.0230370	1.6912470	3.1923990	H	-0.4745760	5.5317860	-1.6164140
C	-1.8458970	1.6734270	2.0508920	H	-1.5341600	5.1385810	-0.2519730
C	-1.5462950	0.7001980	1.1007950	H	-2.1127690	2.9555650	-1.2497810
O	-2.1619130	0.4324390	-0.0838740	H	-2.0611570	4.0031970	-2.6854280
H	-2.6743190	2.3665130	1.9379070	O	3.3707640	0.1235010	-0.3816640
H	-1.2146770	2.4219840	3.9744210	C	4.0899380	-0.0625280	0.8687870
H	0.6607980	0.8055000	4.2372520	H	4.5825760	0.8800670	1.1319340
F	1.3166400	-1.0242510	2.5151900	H	3.3518490	-0.3106910	1.6361520
O	-0.3876900	-0.4129140	-1.4279350	C	5.0878420	-1.2066980	0.6271510
Na	1.1858360	0.7710860	-0.4661690	C	4.4811550	-1.9430110	-0.5788310
O	0.6780060	2.8828790	-1.1936710	C	3.8845050	-0.7866240	-1.3762360
C	-0.2457040	2.8332000	-2.3138440	H	4.6479570	-0.2758980	-1.9807440
H	0.2321660	3.3035200	-3.1850320	H	3.0533660	-1.0744440	-2.0271500
H	-0.4513980	1.7802570	-2.5219860	H	5.2184560	-2.5143760	-1.1506370
C	-1.4731410	3.6108630	-1.8499910	H	3.6866390	-2.6258270	-0.2577970

N	-1.8933080	-1.9207730	-0.5704860	H	5.1993600	-1.8460410	1.5072980
C	-1.1727260	-3.0711430	-1.1729500				
H	-1.7270860	-3.9541930	-0.8369670				
C	0.2642040	-3.2557470	-0.6550960				
H	0.6438470	-4.2324630	-0.9796600				
H	0.9264240	-2.4808380	-1.0485580				
H	0.2986860	-3.2166690	0.4384200				
C	-1.2268020	-3.0536280	-2.7088530				
H	-0.6939980	-2.1809220	-3.0921210				
H	-0.7705320	-3.9638760	-3.1202460				
H	-2.2646250	-3.0050030	-3.0569900				
C	-3.1892060	-2.2097810	0.0888470				
H	-3.3613860	-3.2659480	-0.1442510				
C	-3.1894800	-2.1155710	1.6250340				
H	-2.3354830	-2.6502740	2.0535330				
H	-3.1566140	-1.0835110	1.9796190				
H	-4.1087680	-2.5722100	2.0126670				
C	-4.3739220	-1.4496530	-0.5329060				
H	-4.3757990	-1.5713530	-1.6214910				
H	-5.3170380	-1.8519600	-0.1410610				
H	-4.3278750	-0.3832080	-0.3084110				
H	6.0768590	-0.8100010	0.3709210				

Table S-13. Geometric coordinates and thermally corrected M06-2X transition state energies for the Fries rearrangement of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium(THF)$_3$.



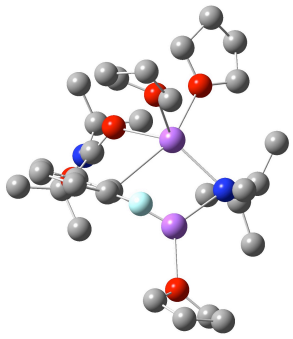
G = -1047403.025

$\mathbf{G_{M06\text{-}2X}}$ = -1047340.918

Atom	X	Y	Z	Atom	X	Y	Z
Na	-0.9255160	-0.4291210	0.1832280	H	4.1313580	-2.8025380	1.3549160
C	1.1378210	1.2152750	-0.6097510	C	4.4419490	0.3220820	0.2119210
C	0.5432930	1.8141530	-1.6932330	H	5.2060090	-0.3793250	-0.1404700
C	0.2911490	3.1948460	-1.7539450	C	4.4621920	1.4964430	-0.7834240
C	0.6460950	3.9846590	-0.6569380	H	4.1351560	1.1750410	-1.7780390
C	1.2314030	3.4278910	0.4950930	H	3.8221250	2.3224890	-0.4668720
C	1.4564300	2.0540070	0.4569990	H	5.4864330	1.8811060	-0.8680540
O	2.0457400	1.2529440	1.3850270	C	4.8998930	0.7519780	1.6168010
C	1.9262960	-0.0464070	0.5751310	H	4.2467240	1.5169160	2.0378900
O	1.0776910	-0.8819520	0.9921730	H	4.9021710	-0.1073320	2.2962070
N	3.2046000	-0.4939280	0.2086840	H	5.9217110	1.1497600	1.5636920
C	3.2986950	-1.8366190	-0.4130860	H	1.5129920	4.0430520	1.3444430
H	4.2693370	-1.8439320	-0.9211800	H	0.4655730	5.0563860	-0.6973750
C	2.2535780	-2.1022570	-1.5090550	H	-0.1576100	3.6297550	-2.6425070
H	2.5278090	-3.0134160	-2.0559200	F	0.1346090	1.0562080	-2.7731830
H	1.2594310	-2.2430790	-1.0797560	O	-1.9516640	-1.4972640	2.0393390
H	2.2094220	-1.2715970	-2.2210080	C	-3.1464680	-1.0107190	2.6681770
C	3.3223460	-2.9628420	0.6333470	H	-3.6298720	-0.3369610	1.9571470
H	2.3760130	-2.9854270	1.1781660	H	-3.8198720	-1.8565090	2.8729530
H	3.4833650	-3.9364140	0.1509330	C	-2.6962010	-0.3301910	3.9830500

O	-2.6550820	1.1469930	-0.0565390	H	-3.3292860	-0.6422590	4.8196170
C	-3.2358660	1.2580380	-1.3740010	H	-2.7606840	0.7598590	3.9131700
H	-2.4351920	1.3937920	-2.1131770	H	-1.0123660	-1.1550120	5.1694280
H	-3.7539390	0.3187790	-1.5837920				
C	-4.1472510	2.4804870	-1.3011160				
C	-3.3366230	3.4167760	-0.3900200				
C	-2.6663780	2.4440020	0.5927250				
H	-1.6380570	2.7306230	0.8323290				
H	-3.2365220	2.3416590	1.5247290				
H	-2.5726690	3.9430770	-0.9707160				
H	-3.9531650	4.1631730	0.1198130				
H	-5.1035900	2.2147630	-0.8346980				
H	-4.3540870	2.9110160	-2.2856880				
O	-1.8099270	-1.8583270	-1.4468110				
C	-2.3451850	-3.1371030	-1.0774330				
H	-2.3639300	-3.1767590	0.0136830				
H	-3.3739420	-3.2325930	-1.4607470				
C	-1.4073220	-4.1442150	-1.7475570				
C	-1.0170660	-3.4306230	-3.0675820				
C	-1.4228370	-1.9549140	-2.8316360				
H	-0.6212370	-1.2327080	-2.9891650				
H	-2.2793820	-1.6741420	-3.4611540				
H	0.0524610	-3.5267130	-3.2708990				
H	-1.5559730	-3.8471200	-3.9243720				
H	-1.8828410	-5.1158370	-1.9122550				
H	-0.5237720	-4.2996390	-1.1204890				
C	-1.2248080	-0.7937490	4.1587060				
C	-1.0641550	-1.8931430	3.1032160				
H	-0.0623130	-1.9547860	2.6777900				
H	-1.3800090	-2.8748730	3.4898480				
H	-0.5307310	0.0234140	3.9400820				

Table S-14. Geometric coordinates and thermally corrected M06-2X energies for the mixed dimer of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium (A) and NaDA (B) solvated by THF. Short hand can be written as $AB(THF)_3$.



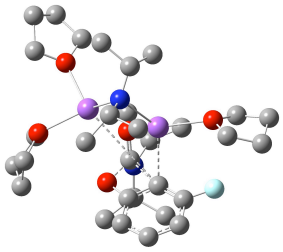
G = -1332160.164

$\mathbf{G_{M06\text{-}2X}}$ = -1332101.49

Atom	X	Y	Z	Atom	X	Y	Z
Na	0.5273120	-0.9542630	0.1111280	C	-1.6980680	1.4262710	1.9179350
Na	-2.2818820	0.2074380	-0.6532100	C	-0.8156970	1.5151330	0.8594560
N	-1.2742530	-1.7433790	-1.4215260	C	0.1689990	2.4639680	1.1200270
C	-0.8349650	-1.7543650	-2.8115010	O	1.1285830	2.8056250	0.1184600
H	-0.4177800	-2.7433920	-3.1056610	C	2.0744250	1.9128310	-0.2464350
C	-1.9651740	-1.4571380	-3.8328100	N	2.9197740	2.4167070	-1.1940150
H	-1.6333510	-1.5918940	-4.8729340	C	4.1859590	1.6893770	-1.4836910
H	-2.8268180	-2.1161370	-3.6739770	H	4.7273530	2.3579500	-2.1602590
H	-2.3089470	-0.4175380	-3.7219520	C	5.0655150	1.5172720	-0.2360890
C	0.2934400	-0.7351930	-3.0285450	H	4.5938140	0.8512400	0.4894910
H	1.1889930	-1.0027900	-2.4562520	H	6.0337620	1.0910420	-0.5238030
H	0.5819110	-0.6637100	-4.0856780	H	5.2505570	2.4834550	0.2464250
H	-0.0245310	0.2666980	-2.7033210	C	3.9651520	0.3678300	-2.2316180
C	-2.0177360	-2.9552720	-1.0892820	H	4.9329300	-0.0367410	-2.5539020
H	-2.6492300	-3.2907760	-1.9385110	H	3.4721870	-0.3694310	-1.5944980
C	-1.1159510	-4.1663630	-0.7425950	H	3.3500670	0.5251800	-3.1239360
H	-0.5274400	-3.9574840	0.1620900	C	2.6895210	3.7161130	-1.8857350

H	-1.6988300	-5.0832420	-0.5691250	H	3.4523910	3.7285840	-2.6708900
H	-0.4138850	-4.3719170	-1.5588000	C	1.3349990	3.7920080	-2.6063040
C	-2.9893930	-2.7023180	0.0752450	H	1.1852640	2.9100760	-3.2384040
H	-2.4591810	-2.2845400	0.9412090	H	0.5027710	3.8611810	-1.9040810
H	-3.7732220	-1.9877640	-0.2127340	H	1.3198540	4.6792180	-3.2503440
H	-3.4876590	-3.6241740	0.4032330	C	2.9500330	4.9323540	-0.9837680
F	-2.7611380	0.4994830	1.7780330	H	3.9449210	4.8742770	-0.5279720
H	2.9040110	5.8529280	-1.5776260	H	1.2951370	-0.4994610	5.5492110
H	2.2056710	4.9992170	-0.1874710	H	0.5402730	-2.7668500	4.9578130
O	2.1778560	0.7857520	0.2442470	H	-1.0051970	-1.9704680	5.3196620
C	0.2788810	3.2369380	2.2806440	O	2.4425470	-2.4401490	-0.3149620
C	-0.6769370	3.0733880	3.2860260	C	2.6251710	-3.5097440	-1.2594490
C	-1.7055400	2.1436380	3.1101880	H	1.9314110	-4.3293930	-1.0292850
H	-2.4771890	1.9914860	3.8598330	H	2.3856740	-3.1227520	-2.2533930
H	-0.6256680	3.6692960	4.1932420	C	4.0782760	-3.9493800	-1.0887500
H	1.0844580	3.9585340	2.3863580	C	4.2634900	-3.7978190	0.4296580
O	-4.4189290	0.9990740	-1.1635140	C	3.4173940	-2.5541730	0.7459830
C	-5.3120820	0.4900210	-2.1627030	H	2.8852480	-2.6259250	1.6990400
H	-5.6351000	1.3083670	-2.8252620	H	4.0176720	-1.6371080	0.7478020
H	-4.7616450	-0.2472880	-2.7514790	H	3.8642670	-4.6780190	0.9474780
C	-6.4856660	-0.0796570	-1.3630480	H	5.3089080	-3.6776610	0.7300780
C	-6.5946540	0.8975850	-0.1658180	H	4.7478610	-3.2694740	-1.6288830
C	-5.2317350	1.6352760	-0.1566390	H	4.2581520	-4.9671280	-1.4486630
H	-5.3506360	2.6977270	-0.4090320	C	-0.1268480	-1.9460600	4.6671520
H	-4.6880280	1.5520860	0.7854270	C	0.6171660	-0.6016590	4.6960750
H	-7.4166280	1.6073240	-0.3022040	C	1.3652470	-0.6021990	3.3552910
H	-6.7734260	0.3641910	0.7719640	H	1.4156230	0.3827520	2.8862870
H	-6.2398340	-1.0884880	-1.0157690	H	2.3846840	-0.9962440	3.4582870
H	-7.4063890	-0.1385450	-1.9512800	H	-0.0977850	0.2267120	4.7260200
O	0.6340170	-1.4980010	2.4788290	H	-1.3921780	-1.4730510	2.9563850
C	-0.4905120	-2.0554320	3.1876590	H	-0.6322480	-3.0815110	2.8356100

Table S-15. Geometric coordinates and thermally corrected M06-2X transition state energies for Fries rearrangement of the mixed dimer of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium (A) and NaDA (B) solvated by 3THF. Short hand can be written as $[AB(THF)_3]^{‡}$.



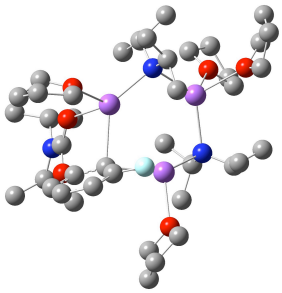
G = -1616908.716

$\mathbf{G_{M06\text{-}2X}}$ = -1616853.939

Atom	X	Y	Z	Atom	X	Y	Z
Na	-1.2195340	-1.1815950	0.0902800	C	0.6507770	-3.7304380	0.5983710
C	-2.1129410	1.3510210	0.3397770	H	0.0050990	-4.5132110	1.0510850
C	-1.3218650	1.9386620	1.3220160	C	0.2726630	-3.6868120	-0.8928620
O	-0.0854610	2.1389680	0.7567980	H	0.5396540	-4.6172910	-1.4111110
C	-0.3664770	1.5534340	-0.5856940	H	-0.8065780	-3.5347040	-1.0240120
O	0.1751300	0.4271330	-0.7995360	H	0.7994450	-2.8640710	-1.3999880
Na	1.7890970	-0.6140910	0.4696310	C	2.1055460	-4.2482180	0.7348350
N	0.4358600	-2.4308440	1.2278170	H	2.4235420	-4.2464690	1.7839910
C	0.2650520	-2.5679980	2.6714800	H	2.2228310	-5.2732800	0.3524430
H	0.9142510	-3.3693910	3.0806080	H	2.7869770	-3.5919160	0.1763690
C	0.6804410	-1.2787870	3.3965380	O	3.2512480	1.0798260	1.3175340
H	1.7540840	-1.0899790	3.2609850	C	3.5634250	2.0680390	0.3045040
H	0.1251560	-0.4152690	3.0015230	H	4.4290020	1.7160730	-0.2658140
H	0.4836170	-1.3298470	4.4756300	H	2.7050760	2.1513590	-0.3715570
C	-1.1799960	-2.9421150	3.0883680	C	3.8198690	3.3811000	1.0524190
H	-1.8677120	-2.1115620	2.8685770	C	2.9461290	3.2125070	2.3041860
H	-1.5265890	-3.8229440	2.5347400	C	3.1207300	1.7247490	2.6036860
H	-1.2629550	-3.1670530	4.1619560	H	4.0304280	1.5349920	3.1916770

H	5.6660910	-0.9277610	-2.8851510	H	2.2688470	1.2783100	3.1224540
H	5.3293050	-2.5957450	-3.3881550	H	3.2547200	3.8491600	3.1392430
H	5.5080350	-3.4025940	-1.0773490	H	1.8992660	3.4209610	2.0641730
H	6.8184300	-2.2093910	-1.1263940	H	3.5525940	4.2567120	0.4529100
N	-0.3369540	2.5159390	-1.5947830	H	4.8774680	3.4700770	1.3297490
C	-0.8145900	3.9209110	-1.4734130	O	3.6885510	-1.1786970	-0.8857100
H	-0.3817720	4.3988800	-2.3606070	C	4.9472900	-1.4773510	-0.2400710
C	-0.2594240	4.7199120	-0.2857990	H	5.4594900	-0.5314820	-0.0239680
H	-0.4195240	5.7858770	-0.4906530	H	4.7397450	-1.9847710	0.7071850
H	-0.7559240	4.4819600	0.6559680	C	5.7370990	-2.3414730	-1.2288670
H	0.8141280	4.5507140	-0.1639290	C	5.1882880	-1.8677130	-2.5836650
C	-2.3426910	4.0780240	-1.5829330	C	3.7132830	-1.6364420	-2.2534470
H	-2.8517760	3.6727990	-0.7059040	H	3.2344300	-0.8745400	-2.8752940
H	-2.5980700	5.1414610	-1.6679140	H	3.1356300	-2.5673180	-2.3309950
H	-2.7342070	3.5683290	-2.4700010	H	-4.1428990	-1.8952450	1.1002530
C	-0.3064380	2.0171340	-3.0000390	C	-5.5198010	-2.4800820	-0.5149300
H	-0.6010930	2.8829200	-3.6019870	C	-5.0805550	-2.7340210	-1.9658350
C	1.1155250	1.6332370	-3.4347750	C	-3.7193180	-2.0403490	-1.9996190
H	1.8074130	2.4672270	-3.2703000	H	-3.0268370	-2.4608560	-2.7354010
H	1.4643950	0.7718810	-2.8613250	H	-3.8242040	-0.9635330	-2.1749170
H	1.1319000	1.3805700	-4.5028620	H	-4.9679300	-3.8084160	-2.1543190
C	-1.3230510	0.9096900	-3.3251450	H	-5.7767950	-2.3266870	-2.7052410
H	-2.3176330	1.1634300	-2.9454450	H	-5.9276890	-1.4696260	-0.4158160
H	-1.3903200	0.7889210	-4.4133040	H	-6.2673770	-3.1942170	-0.1567740
H	-1.0213600	-0.0457670	-2.8917190	H	-4.9723460	1.2191700	2.2052600
C	-1.7340720	2.2834520	2.6043780	H	-3.4617830	2.2508750	3.8963660
C	-3.0767170	2.0045770	2.9102220	H	-1.0713340	2.7474850	3.3285850
C	-3.9316710	1.4237250	1.9709130	C	-4.1978180	-2.5868700	0.2541170
C	-3.4225290	1.1154400	0.7002460	H	-4.0106410	-3.6042030	0.6177770
F	-4.2968680	0.5530780	-0.2011200				
O	-3.1517680	-2.2501670	-0.6897410				

Table S-16. Geometric coordinates and thermally corrected M06-2X energies for the mixed trimer of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium (A) and NaDA (B) solvated by 4THF. Short hand can be written as $AB_2(THF)_4$.



G = -1762660.62

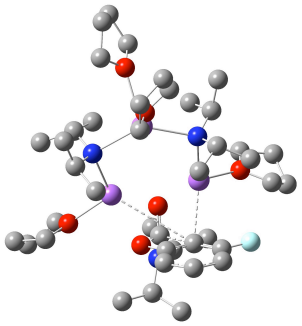
$\mathbf{G_{M06\text{-}2X}}$ = -1762611.102

Atom	X	Y	Z	Atom	X	Y	Z
Na	2.6408840	0.1663530	-0.0566700	H	4.0458080	2.1962410	3.0212170
Na	-0.9042850	-0.7846730	-1.5424050	C	2.1556620	3.8154170	0.5979430
O	-2.2289210	-2.2085100	-0.2821290	H	1.0996810	4.0715320	0.4379480
C	-2.8436060	-2.0038180	0.7696070	H	2.7068920	4.7604640	0.6883520
O	-3.6093310	-0.9131010	0.9870630	H	2.5168880	3.3032820	-0.3034350
C	-3.6407030	0.1506600	0.0358160	C	1.4695110	0.9497040	2.9248070
C	-4.9225140	0.4211980	-0.4543850	H	2.3831670	0.9667160	3.5604180
C	-5.0957470	1.5207210	-1.2990500	C	0.3457510	1.5504170	3.8135050
C	-3.9947180	2.3154000	-1.6313010	H	-0.6422780	1.3646530	3.3654620
C	-2.7674730	1.9415650	-1.0883930	H	0.3364190	1.1050130	4.8190190
F	-1.6856620	2.7756520	-1.4259150	H	0.4637540	2.6333800	3.9313800
Na	-0.4658970	2.0366430	0.7206080	C	1.1486150	-0.5340320	2.6813560
C	-2.4883060	0.8838360	-0.2430610	H	0.9008380	-1.0528840	3.6176270
N	1.6757000	1.6387980	1.6539650	H	0.2871720	-0.6334090	2.0051850
C	2.3440770	2.9274210	1.8384310	H	1.9972320	-1.0556030	2.2236340
H	1.9092300	3.4995610	2.6863170	O	-1.6650570	3.9267270	1.5875420
C	3.8609890	2.8221120	2.1406330	C	-1.9495690	5.1114170	0.8133380
H	4.3874610	2.3743010	1.2876860	H	-1.3117080	5.9328090	1.1684820

H	4.3046890	3.8077680	2.3438880	H	-1.7082030	4.8958350	-0.2298750
C	-2.0721210	-4.1169980	1.6988670	C	-3.4307870	5.4116550	1.0477170
H	-1.6170390	-4.0571850	0.7105140	C	-3.6214410	4.9349870	2.4957030
C	-0.9408820	-4.1940570	2.7335810	C	-2.7234770	3.6940420	2.5444010
H	-1.3183210	-4.2698550	3.7604370	H	-2.2705140	3.5228840	3.5257420
H	-0.3299230	-5.0839370	2.5438240	H	-3.2675970	2.7897410	2.2430940
H	-0.2934600	-3.3141010	2.6681960	H	-3.2646550	5.6968530	3.1991700
C	-2.9753380	-5.3582430	1.7293900	H	-4.6620670	4.7047740	2.7434140
H	-2.3764250	-6.2565540	1.5415180	H	-4.0487360	4.8159540	0.3663460
H	-3.4683790	-5.4912390	2.6997340	H	-3.6740760	6.4687020	0.9019970
H	-3.7486070	-5.2971110	0.9563450	H	-4.0865950	3.1812550	-2.2812560
C	-3.6040870	-2.6257660	3.0870480	H	-6.0813210	1.7607890	-1.6887290
H	-3.3708690	-3.5028490	3.6972990	H	-5.7643590	-0.2035390	-0.1683330
C	-3.1034140	-1.4005730	3.8666780	N	-2.8539860	-2.8640580	1.8271270
H	1.3624080	-2.6942110	-3.0328130	H	-2.0185260	-1.4438270	4.0053350
C	1.3682690	-3.0678660	-0.9423060	H	-3.3472370	-0.4710910	3.3484220
H	1.6760060	-4.1179930	-1.0367830	H	-3.5741060	-1.3793590	4.8567980
H	1.7840480	-2.6745850	-0.0051440	C	-5.1280450	-2.6183420	2.8908730
H	0.2758270	-3.0503630	-0.8457900	H	-5.4570730	-3.5138940	2.3531140
C	3.3636910	-2.4591640	-2.3427600	H	-5.6235050	-2.6088380	3.8688630
H	3.9261010	-2.1026740	-1.4689630	H	-5.4543980	-1.7382800	2.3332660
H	3.5969600	-3.5233300	-2.4917630	N	1.4453830	-0.8389860	-1.9607460
H	3.7364000	-1.9165470	-3.2191860	C	1.7683750	0.0042570	-3.1116440
O	-2.2509000	-1.1661170	-3.4879950	H	2.8685140	0.1412030	-3.2364810
C	-2.8026560	-0.1926710	-4.4043080	C	1.2008270	1.4144340	-2.8843300
H	-3.0382660	0.7082840	-3.8289600	H	1.5380120	1.8324610	-1.9270490
H	-2.0459380	0.0557430	-5.1568430	H	1.5081270	2.1077970	-3.6790050
C	-4.0620040	-0.8316190	-5.0155030	H	0.1027710	1.4108160	-2.8606900
C	-4.4222390	-1.9184110	-3.9894440	C	1.2692610	-0.5090890	-4.4859340
C	-3.0388980	-2.3703690	-3.5271650	H	0.1881960	-0.6981010	-4.4572960
H	-3.0185670	-2.8037520	-2.5252460	H	1.4742590	0.2245700	-5.2777710

H	-2.5934710	-3.0806760	-4.2405860	H	1.7584460	-1.4454490	-4.7764810
H	-4.9731300	-1.4842740	-3.1474090	C	1.8428910	-2.2324010	-2.1419740
H	-5.0167480	-2.7337200	-4.4140000				
H	-3.8325390	-1.2871660	-5.9859790				
H	-4.8617210	-0.1008310	-5.1689880				
O	4.7323730	1.0763130	-1.0307690				
C	4.8869430	2.1645320	-1.9540110				
H	3.8913320	2.4404360	-2.3045080				
H	5.3298910	3.0235630	-1.4291220				
C	5.8220890	1.6490940	-3.0733380				
C	6.4276310	0.3476500	-2.4822750				
C	5.9914130	0.3952740	-1.0129380				
H	5.8262430	-0.5791910	-0.5510130				
H	6.7112740	0.9670970	-0.4043190				
H	5.9954490	-0.5311170	-2.9695230				
H	7.5155940	0.2961160	-2.5902350				
H	6.5913210	2.3901560	-3.3124290				
H	5.2646900	1.4409850	-3.9906050				
O	4.3237040	-1.4910090	1.2859670				
C	4.3417050	-2.9230140	1.4443790				
H	3.3895150	-3.2554220	1.8822270				
H	4.4407910	-3.3707870	0.4527870				
C	5.5097590	-3.2151190	2.3843170				
C	5.4465590	-2.0076320	3.3324320				
C	5.0268420	-0.8711380	2.3899120				
H	4.3639380	-0.1409940	2.8604020				
H	5.8957440	-0.3389400	1.9830020				
H	4.6824830	-2.1701770	4.1017060				
H	6.3943520	-1.8000860	3.8382290				
H	6.4552800	-3.2208130	1.8284670				
H	5.4087550	-4.1769130	2.8965630				

Table S-17. Geometric coordinates and thermally corrected M06-2X transition state energies for the Fries rearrangement of the mixed trimer of (2-((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium (A) and NaDA (B) solvated by 4THF. Short hand can be written as $[AB_2(THF)_4]^{‡}$.



G = -1762632.3

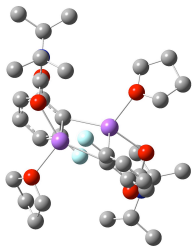
$\mathbf{G_{M06\text{-}2X}}$ = -1762585.133

Atom	X	Y	Z	Atom	X	Y	Z
Na	-2.5145160	0.0283270	-0.0213370	H	-3.9980690	-2.3076530	1.2890120
Na	1.0189560	1.7736990	-0.3127390	H	-3.9680020	-3.7673240	0.2902620
C	2.7693470	0.9706990	1.6262820	C	-1.3726960	-2.4645050	2.2081880
C	2.3872390	-0.2163750	2.2384280	H	-1.7351190	-1.4396220	2.3627700
O	2.4681030	-1.2065390	1.2738650	H	-1.6289170	-3.0511620	3.1002180
C	2.9836670	-0.3789240	0.1484280	H	-0.2770600	-2.4127410	2.1541520
O	2.1455070	-0.1765920	-0.7826040	O	1.8615610	-4.0041310	-0.6530820
Na	0.7040830	-1.9507560	-0.3015550	C	1.7027480	-5.0687890	0.3121510
N	-1.6141220	-2.2740600	-0.2245430	H	2.4312690	-4.9214280	1.1202410
C	-2.0868560	-2.8308070	-1.4904930	H	0.6930930	-5.0034760	0.7285480
H	-3.1950720	-2.7670280	-1.5924800	C	1.9665980	-6.3666630	-0.4539940
C	-1.7408450	-4.3196030	-1.7448720	C	2.9900780	-5.9114690	-1.5062790
H	-2.0808520	-4.6390620	-2.7393960	C	2.4844910	-4.5084470	-1.8533700
H	-0.6540000	-4.4712910	-1.6876870	H	3.2785360	-3.8148580	-2.1447010
H	-2.2084670	-4.9852720	-1.0111760	H	1.7330210	-4.5403680	-2.6540050
C	-1.5212240	-2.0069960	-2.6590030	H	3.9933550	-5.8603000	-1.0666790
H	-1.7134990	-0.9365810	-2.5277300	H	3.0351030	-6.5674100	-2.3808660

H	-0.4308440	-2.1350210	-2.7450910	H	1.0485760	-6.7162030	-0.9403380
H	-1.9580860	-2.3154870	-3.6181020	H	2.3363570	-7.1668420	0.1942290
C	-1.9783320	-3.0798090	0.9364680	N	4.3033580	-0.6924240	-0.1572450
H	-1.5621020	-4.1124360	0.8797420	C	5.3011220	-1.2535430	0.7955440
C	-3.5003360	-3.2760810	1.1512790	H	6.1211950	-1.5490770	0.1316200
H	-3.7041810	-3.8988180	2.0339100	C	4.8789280	-2.5524820	1.5019890
C	4.4250010	-0.6980410	-2.6697680	H	5.7857240	-3.0708110	1.8388880
H	4.6151600	-1.7775560	-2.6485610	H	4.2485540	-2.3734030	2.3739550
H	3.3566360	-0.5357730	-2.8219190	H	4.3352720	-3.2079840	0.8154250
H	4.9760940	-0.2747360	-3.5193810	C	5.8856450	-0.2342960	1.7901890
C	4.7453150	1.4841030	-1.3951980	H	5.1459270	0.0854940	2.5266850
H	5.0935970	1.9362980	-0.4615410	H	6.7271340	-0.6907210	2.3259100
H	5.3504510	1.8857530	-2.2179560	H	6.2592690	0.6569190	1.2746100
H	3.7100560	1.7906720	-1.5525710	C	4.8948940	-0.0438120	-1.3619020
H	2.5161780	2.8056090	-3.5031720	H	5.9677350	-0.2441450	-1.2769500
C	-0.5532570	4.1446210	1.3531280	C	1.9782980	3.6719190	-3.1004970
H	-0.7797090	4.6804980	2.2853610	O	1.9359630	3.5287140	-1.6631950
H	0.5057810	3.8519960	1.3998790	C	2.4889150	4.7082980	-1.0441800
H	-0.6683310	4.8598670	0.5303970	H	1.6822250	5.4247500	-0.8323230
C	-1.2457280	1.9629660	2.3679640	H	2.9436650	4.3982230	-0.1025230
H	-1.3559220	2.4873790	3.3262410	C	3.4655820	5.2649800	-2.0761340
H	-1.9638240	1.1353070	2.3555190	C	2.7101090	4.9960700	-3.3886880
H	-0.2367310	1.5325600	2.3435040	H	1.9886550	5.7985300	-3.5803670
C	-1.6362290	2.9866390	-1.2509360	H	3.3684660	4.9239590	-4.2595690
H	-0.9568290	3.8644140	-1.3492260	H	4.4061900	4.7032040	-2.0466320
C	-3.0689820	3.5755980	-1.2964800	H	3.6907790	6.3241620	-1.9181750
H	-3.2357720	4.1489830	-2.2192230	H	0.9560940	3.6615250	-3.4916090
H	-3.8141540	2.7693140	-1.2515640	C	2.0514970	-0.3838030	3.5754530
H	-4.6910540	1.3091140	-2.9846370	C	2.1112520	0.7756400	4.3667080
C	-4.8092200	0.2264140	-2.8821400	C	2.4862050	2.0062370	3.8232460
O	-4.6207580	-0.0955230	-1.4863760	C	2.8053180	2.0674890	2.4605860

C	-5.6762790	-0.9798720	-1.0740960	F	3.1406080	3.3038730	1.9551130
C	-6.8814700	-0.5472860	-1.9049050	H	2.5221780	2.9050980	4.4314360
C	-6.2251790	-0.2579880	-3.2667160	C	-1.4778260	2.9097530	1.1814040
H	-6.1678820	-1.1764840	-3.8611210	H	-2.5091670	3.3076200	1.3080960
H	-6.7712770	0.4846400	-3.8559170				
H	-7.3230200	0.3642000	-1.4844130				
H	-7.6612370	-1.3135190	-1.9580660				
H	-5.7905900	-0.8624840	0.0045730				
H	-5.3986690	-2.0221840	-1.2899690				
H	-4.0316120	-0.2656260	-3.4777540				
H	-3.2589670	4.2513500	-0.4554510				
C	-1.4174860	2.1540920	-2.5240290				
H	-1.5675240	2.7553980	-3.4308830				
H	-0.4055530	1.7307640	-2.5666160				
H	-2.1195690	1.3120720	-2.5662600				
O	-4.3915090	0.3437020	1.7727850				
C	-4.5360390	-0.0048420	3.1551900				
H	-4.2345320	-1.0477480	3.2683700				
H	-3.8744540	0.6259920	3.7682250				
C	-6.0129570	0.2672770	3.4696170				
C	-6.3630120	1.4530260	2.5308400				
C	-5.1324160	1.5645820	1.6000130				
H	-5.3729640	1.6433770	0.5384130				
H	-4.4959850	2.4143690	1.8797920				
H	-7.2790400	1.2525300	1.9669380				
H	-6.5178120	2.3836810	3.0853010				
H	-6.1748720	0.4982090	4.5267940				
H	-6.6176310	-0.6113750	3.2226820				
H	1.8595980	0.7158500	5.4223020				
H	1.7675510	-1.3449330	3.9931630				
N	-1.3272320	2.1761340	-0.0748220				

Table S-18. Geometric coordinates and thermally corrected M06-2X energies for THF disolvated ((diisopropylcarbamoyl)oxy)-6-fluorophenyl)sodium dimer.



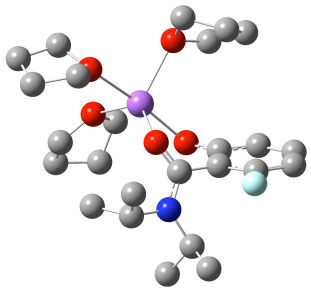
G = -1511953.511

$\mathbf{G_{M06\text{-}2X}}$ = -1511823.242

Atom	X	Y	Z	Atom	X	Y	Z
Na	-0.9069720	-1.3265440	1.0700400	H	-7.5948480	0.3193010	-0.7278810
C	-0.8306290	-0.8821260	-1.5339540	H	-7.3656990	0.5833800	-2.4599320
C	-2.0554260	-1.3186270	-2.0370560	C	-5.5696990	2.2651180	-1.1515420
O	-3.2661330	-0.6577770	-1.6710970	H	-4.5602900	2.6709990	-1.0254290
C	-3.6793280	-0.6453090	-0.3828110	H	-6.0173310	2.7282640	-2.0382910
N	-4.8222390	0.0767150	-0.2037440	H	-6.1702060	2.5657300	-0.2852800
C	-5.4030860	0.1960520	1.1590050	O	-3.1006110	-1.2406590	0.5290020
H	-6.3169210	0.7788790	1.0104220	C	-2.2393410	-2.3281090	-2.9865270
C	-5.8271650	-1.1568780	1.7498730	C	-1.1116600	-2.9697140	-3.5037960
H	-4.9582120	-1.7833970	1.9580120	C	0.1584440	-2.5987260	-3.0551970
H	-6.3738290	-0.9923950	2.6857690	C	0.2165120	-1.5894240	-2.0976010
H	-6.4882990	-1.6931230	1.0601650	F	1.5106270	-1.2620110	-1.6549730
C	-4.5049790	1.0014190	2.1095420	H	1.0607480	-3.0695200	-3.4350410
H	-5.0193990	1.1474170	3.0669230	H	-1.2214820	-3.7499510	-4.2521140
H	-3.5600150	0.4903920	2.3023920	H	-3.2389460	-2.5916280	-3.3207190
H	-4.2842140	1.9892640	1.6904990	Na	0.4593550	0.9526160	-0.4215600
C	-5.5207480	0.7402680	-1.3294330	C	0.9974490	0.1831760	1.9828710
H	-4.9167110	0.5318150	-2.2101490	C	2.3101350	0.5995000	2.2005590
C	-6.9134780	0.1369510	-1.5668680	O	3.3374870	0.2701250	1.2562890
H	-6.8442140	-0.9444860	-1.7234620	C	3.3968900	0.9117000	0.0690790

H	4.9061300	-0.9966630	0.6222470	N	4.4287060	0.4948100	-0.7138390
C	5.1079000	-1.8207170	-1.3376640	C	4.6857820	1.1765520	-2.0080190
H	4.0492190	-2.0729400	-1.4515400	H	5.5303010	0.6278010	-2.4342860
H	5.5123550	-1.5812240	-2.3282790	C	3.5266420	1.0634790	-3.0111050
H	5.6423480	-2.7051690	-0.9720030	H	2.7098130	1.7371940	-2.7432500
C	6.7486780	-0.2564220	-0.1591300	H	3.8848570	1.3353370	-4.0113150
H	6.8408380	0.5419550	0.5845850	H	3.1298300	0.0456860	-3.0457030
H	7.3298860	-1.1176140	0.1898540	C	5.1390190	2.6300450	-1.8085530
H	7.2057500	0.0897180	-1.0935010	H	5.4014320	3.0750460	-2.7755920
O	2.6009960	1.7990060	-0.2633370	H	4.3389960	3.2240610	-1.3600330
C	2.7873640	1.2453320	3.3443610	H	6.0195580	2.6821430	-1.1591550
C	1.8928900	1.5037420	4.3853070	C	5.2792210	-0.6614290	-0.3436140
C	0.5590520	1.1064810	4.2623960	C	-0.1365250	-4.4353850	0.4277030
C	0.2017120	0.4779430	3.0745060	H	-0.5766480	-5.3926860	0.7469570
F	-1.1445840	0.0622170	2.9997680	H	-0.7257330	-4.0297120	-0.3982350
H	-0.1656450	1.2743700	5.0538290	C	1.3528740	-4.5742420	0.1243180
H	2.2346330	1.9994090	5.2899010	C	1.9664200	-4.5453710	1.5369100
H	3.8344560	1.5250790	3.4209710	C	0.9891950	-3.6531950	2.3341330
O	-0.4764390	3.0875460	-0.3386780	H	0.6981090	-4.1085720	3.2885650
C	-1.0925330	3.8381110	-1.4055370	H	1.3853700	-2.6516800	2.5252390
H	-0.6092750	3.5548990	-2.3496590	H	1.9994140	-5.5553520	1.9608660
H	-2.1516560	3.5641680	-1.4672700	H	2.9851350	-4.1472040	1.5463930
C	-0.8731080	5.3223740	-1.0749500	H	1.6857120	-3.7124120	-0.4631200
C	0.3740040	5.2814190	-0.1767730	H	1.5920050	-5.4876100	-0.4294610
C	0.1513320	3.9876230	0.6029100	O	-0.1906980	-3.4891490	1.5097010
H	1.0692600	3.5097430	0.9506900				
H	-0.5222970	4.1434740	1.4570820				
H	1.2845160	5.2041180	-0.7825400				
H	0.4666550	6.1565430	0.4735930				
H	-1.7282070	5.7219090	-0.5170650				
H	-0.7427740	5.9335150	-1.9731150				

Table S-19. Geometric coordinates and thermally corrected M06-2X energies for THF trisolvated sodium 2-(diisopropylcarbamoyl)-3-fluorophenolate monomer.



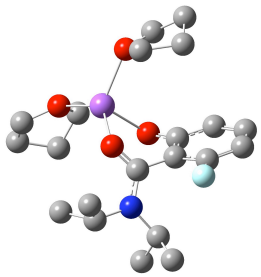
G = -1047464.614

$\mathbf{G_{M06\text{-}2X}}$ = -1047399.605

Atom	X	Y	Z	Atom	X	Y	Z
Na	1.2425970	-0.4931810	-0.0909040	C	-1.7076600	3.0150760	0.9251730
O	-0.4759420	0.5495220	1.0382720	H	-2.4282590	3.7930960	0.6580940
C	-1.5804350	0.5918340	0.4518250	C	-0.3496910	3.4629130	0.3600950
C	-2.1906310	-0.6633110	-0.0888760	H	-0.0916070	4.4494640	0.7645860
C	-1.4840040	-1.4075250	-1.1073200	H	0.4369420	2.7551110	0.6260770
C	-2.1369880	-2.5965890	-1.5731610	H	-0.3899650	3.5447270	-0.7314370
C	-3.3307760	-3.0452290	-1.0316910	C	-1.7088810	2.9183970	2.4579790
C	-3.9794470	-2.3469320	-0.0001200	H	-2.7085690	2.6668910	2.8269720
C	-3.3800500	-1.1752600	0.4294300	H	-1.0129850	2.1518510	2.8036460
F	-3.9925970	-0.4732260	1.4320090	H	-1.4161090	3.8822700	2.8913680
H	-4.9006990	-2.6903170	0.4561050	O	1.8613940	-2.7046040	0.5201220
H	-3.7786970	-3.9621240	-1.4099140	C	1.2396590	-3.7616630	-0.2490820
H	-1.6481690	-3.1452670	-2.3742660	H	0.7295890	-3.2777490	-1.0846470
O	-0.3469610	-1.0239540	-1.5755330	H	2.0222600	-4.4287000	-0.6354050
N	-2.2341690	1.7808950	0.2888760	C	0.2769880	-4.5037830	0.7104520
C	-3.4377710	1.9259060	-0.5661810	C	0.3736750	-3.6971120	2.0237340
H	-3.6532330	0.9244060	-0.9362840	C	1.7552260	-3.0558130	1.9054720
C	-3.1522020	2.8084040	-1.7915700	H	1.8885330	-2.1383850	2.4837970
H	-2.3060850	2.4137790	-2.3635220	H	2.5526710	-3.7672630	2.1760320

H	-4.0304930	2.8230710	-2.4470110	H	-0.3930650	-2.9155680	2.0495960
H	-2.9321010	3.8466810	-1.5162080	H	0.2654240	-4.3190230	2.9180030
C	-4.6637330	2.4087920	0.2227650	H	0.6054410	-5.5377110	0.8635690
H	-4.5423240	3.4314500	0.5994480	H	-0.7427510	-4.5247140	0.3190910
H	-5.5434420	2.4059560	-0.4309860	O	2.6802190	0.2450550	-1.8650570
H	-4.8593900	1.7421980	1.0650840	C	2.3654530	-0.4795130	-3.0858920
H	3.9715000	1.6122990	-4.0094000				
H	2.5987600	2.7349280	-4.0437730				
H	0.9925940	0.8652170	-4.0768200				
H	2.2670790	0.2564600	-5.1514140				
O	2.7925580	0.3006390	1.5131900				
C	4.2135060	0.3104940	1.3219820				
H	4.6709630	-0.4659370	1.9525920				
H	4.3973100	0.0669130	0.2736620				
C	4.6906300	1.7225790	1.7441640				
C	3.4634160	2.3284990	2.4780130				
C	2.5301940	1.1239480	2.6544800				
H	2.7696120	0.5679250	3.5754120				
H	1.4649000	1.3586210	2.6444330				
H	3.7256850	2.7951700	3.4322670				
H	2.9785340	3.0876680	1.8559980				
H	4.9708360	2.3278560	0.8769640				
H	5.5675080	1.6601650	2.3959100				
H	3.2444480	-1.0763100	-3.3661390				
H	1.5143210	-1.1306250	-2.8756320				
C	2.0520320	0.5911020	-4.1319520				
C	2.9370880	1.7610670	-3.6764800				
C	2.8444720	1.6466680	-2.1525030				
H	3.7408800	2.0053490	-1.6340190				
H	1.9755850	2.1969810	-1.7644760				

Table S-20. Geometric coordinates and thermally corrected M06-2X energies for THF disolvated sodium 2-(diisopropylcarbamoyl)-3-fluorophenolate monomer.



G = -901735.3669

$\mathbf{G_{M06\text{-}2X}}$ = -901666.5004

Atom	X	Y	Z	Atom	X	Y	Z
Na	1.7040040	-0.0802110	0.6269930	C	-2.0958340	2.5023060	1.3701790
O	-0.3787300	0.3545800	1.3545250	H	-2.8850330	3.1900410	1.0541080
C	-1.2389130	0.3809210	0.4425120	C	-0.7898980	3.3124930	1.4053770
C	-1.3169820	-0.7460640	-0.5427340	H	-0.9186540	4.1840270	2.0586150
C	-0.1910290	-1.0058120	-1.4129530	H	0.0331430	2.7066290	1.7884340
C	-0.3354410	-2.1213540	-2.3011940	H	-0.5252530	3.6724990	0.4055880
C	-1.4551670	-2.9369760	-2.2866310	C	-2.4934560	1.9705140	2.7549170
C	-2.5223580	-2.7076460	-1.4021590	H	-3.4535650	1.4463720	2.7067200
C	-2.4100520	-1.6115730	-0.5629740	H	-1.7398760	1.2815290	3.1406530
F	-3.4333430	-1.3638970	0.3105920	H	-2.5952070	2.8079230	3.4553940
H	-3.3993760	-3.3430470	-1.3589560	O	2.1425450	-2.2193580	1.3735530
H	-1.5116990	-3.7804240	-2.9719110	C	2.5774450	-3.1297650	0.3307100
H	0.4839540	-2.3098070	-2.9900150	H	2.3189950	-2.6852530	-0.6379530
O	0.8751850	-0.2818850	-1.3914190	H	3.6658320	-3.2344880	0.3980260
N	-2.0972490	1.4325040	0.3367380	C	1.8263460	-4.4444480	0.5702200
C	-3.0139810	1.6064790	-0.8169120	C	0.5457020	-3.9676420	1.2734040
H	-2.8487440	0.7365260	-1.4516280	C	1.0686300	-2.8209940	2.1371810
C	-2.6442310	2.8467420	-1.6452680	H	0.3247410	-2.0437540	2.3328090
H	-1.6003470	2.7968010	-1.9715930	H	1.4751790	-3.1840610	3.0917970

H	-3.2790840	2.8941970	-2.5372590	H	-0.1762290	-3.5932400	0.5405070
H	-2.7907770	3.7801720	-1.0893290				
C	-4.4900940	1.6063200	-0.3940090				
H	-4.7452770	2.4697310	0.2316550				
H	-5.1258640	1.6515620	-1.2856120				
H	-4.7289060	0.6912030	0.1522330				
H	4.6982970	0.9019820	-1.5245030				
H	2.9401400	0.6256970	-1.7679260				
C	3.5620240	2.7480740	-1.7678410				
C	4.1891110	3.4898880	-0.5760640				
C	3.7487010	2.6336300	0.6221170				
H	4.5216250	2.5519590	1.3948790				
H	2.8336180	3.0229970	1.0867990				
H	5.2817910	3.4929210	-0.6637190				
H	3.8572480	4.5285710	-0.4865530				
H	2.5044690	3.0130710	-1.8804120				
H	4.0694350	2.9502300	-2.7159460				
H	0.0635070	-4.7503960	1.8671550				
H	2.4043120	-5.1044150	1.2283530				
H	1.6284460	-4.9803870	-0.3624520				
O	3.4614190	1.3168760	0.1024010				
C	3.6882440	1.2917010	-1.3311890				