Supplementary Information

Discovery of a Synthesis Method for a Difluoroglycine Derivative Based on a Path Generated by Quantum Chemical Calculations

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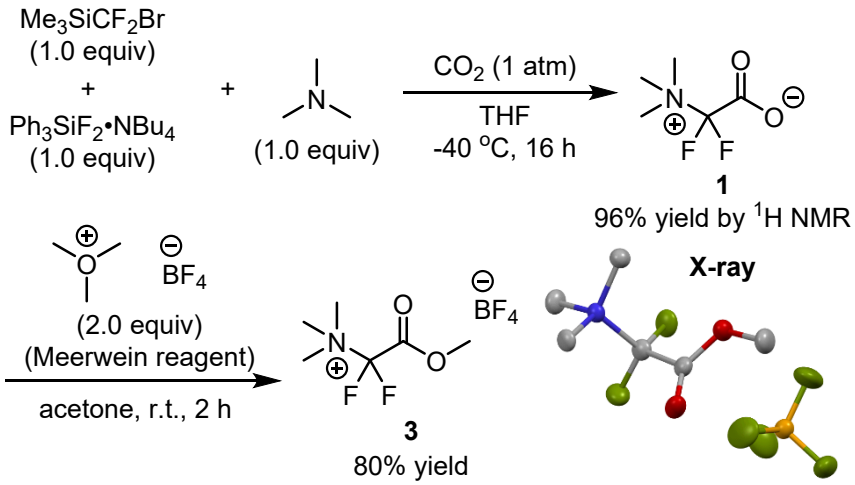
(A) General

All manipulations were carried out under an atmosphere of nitrogen unless otherwise noted. Infrared (IR) spectra were recorded on a JASCO FT/IR 4600 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ESZ-400S spectrometer, operating at 400 MHz (^{1}H), 100 MHz (^{13}C), and, 396 MHz (^{19}F). Chemical shifts in DMSO-d_6 were reported in the scale relative to DMSO-d_6 (2.50 ppm) for ^{1}H NMR and to $CDCl_3$ (39.52 ppm) for ^{13}C NMR as internal references. Chemical shifts for ^{19}F NMR in DMSO-d_6 was reported in the scale relative to trifluoroacetic acid (-78.50 ppm). ESI mass spectra were measured on a Thermo Scientific Exactive. Dry THF was purified under argon using the Ultimate Solvent System (GlassContour: Nikko Hansen & Co.,Ltd.). A cylinder of CO_2 was purchased from Hokkaido Air Water, Inc.

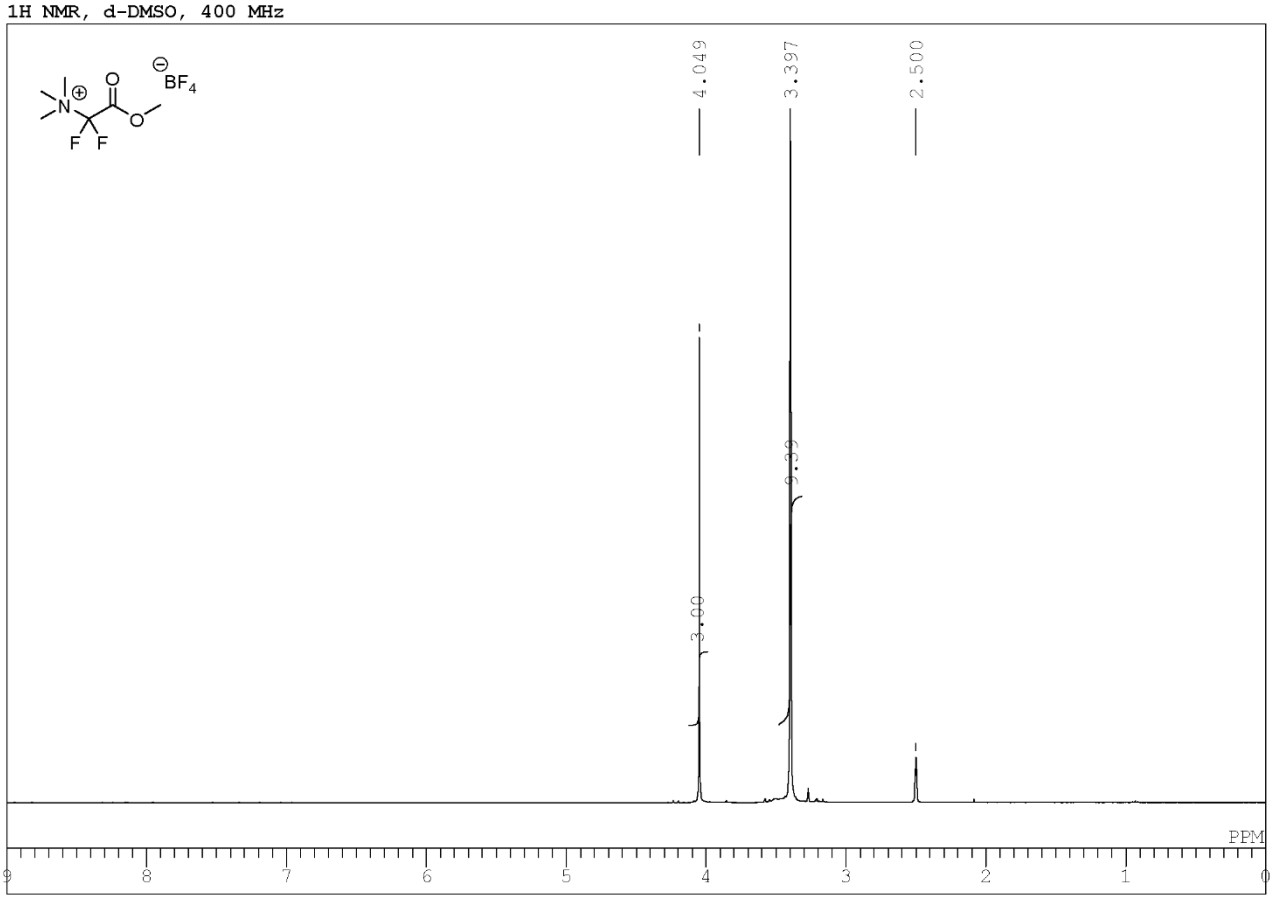
(B) The Synthesis of Difluoroglycine Derivative



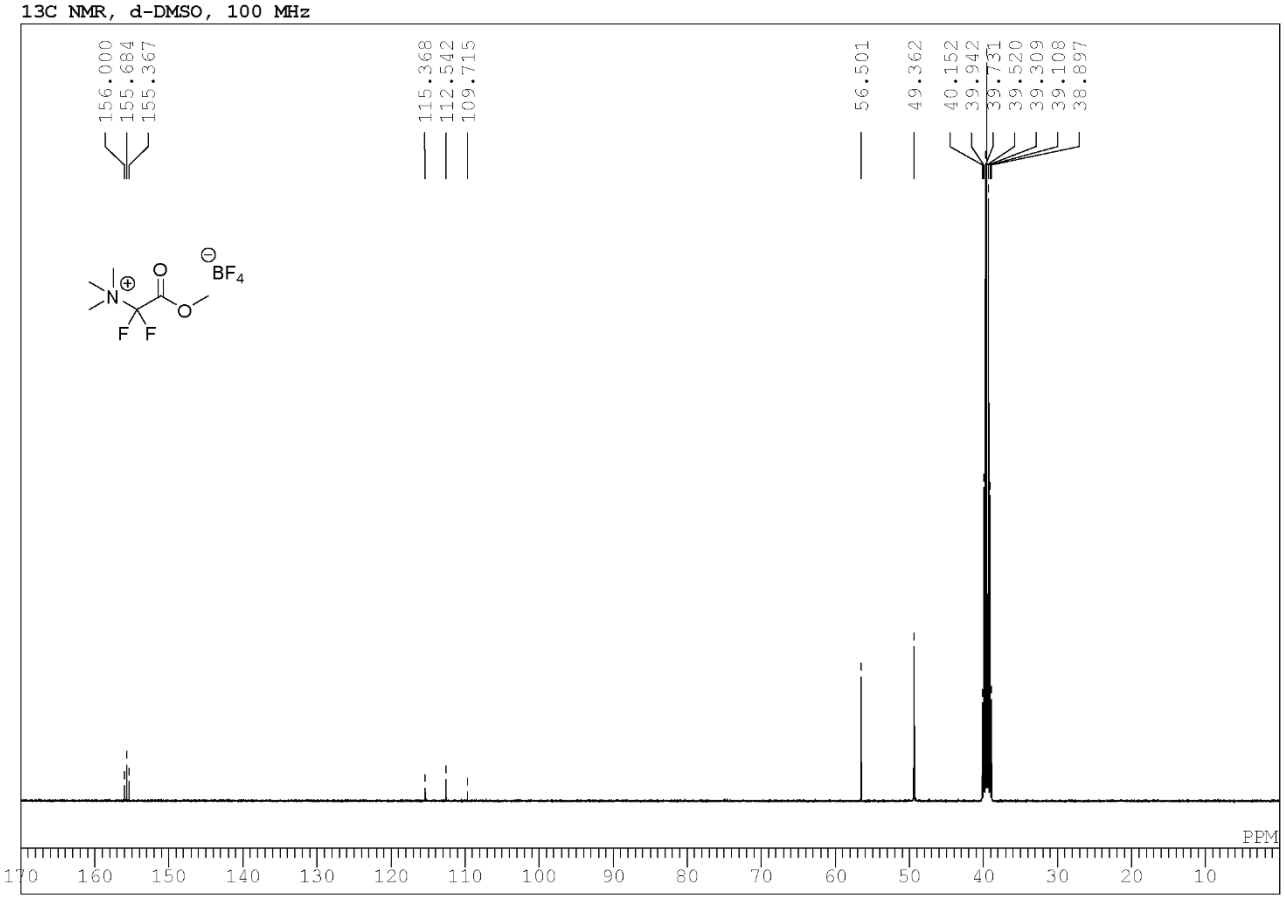
In an oven-dried round-bottom flask was placed TBAT (539.9 mg, 1.0 mmol, 1 equiv). The flask was evacuated and backfilled with CO_2 (3 times) followed by the addition of THF (10 mL). The mixture was stirred at room temperature until TBAT was completely dissolved. After adding trimethylamine (2 M in THF, 500 μL, 1.0 mmol, 1 equiv) at 0 °C, the solution was cooled to −40 °C, and then Me_3SiCF_2Br (156 μL, 1.0 mmol, 1 equiv) was added dropwise. After the resulting slurry was stirred at −40 °C for 20 h, the precipitate was isolated by filtration, washed with hexane, and dried under vacuum. The approximate yield of carboxylate **1** was 96%, as determined by ^{1}H NMR spectroscopy using pyridine as an internal standard. The solids were then treated with the Meerwein reagent (295.8 mg, 2.0 mmol, 2 equiv) in acetone (1.5 mL) for 2 h. After the solvent was removed under vacuum, the resulting solids were washed with a small amount of MeOH to afford methyl carboxylate **3** after filtration (1st crop: 176.6 mg, 2nd and 3rd crops: 28.2 mg, 0.803 mmol, 80% yield).

White solids; IR (ATR): 3068, 2977, 1787, 1483, 1343 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.05 (s, 3H), 3.40 (s, 9H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 155.7 (J_{CF} = 31.6 Hz), 112.5 (J_{CF} = 282.7 Hz), 56.5, 49.4 ppm; ^{19}F NMR (376 MHz, DMSO-d_6) δ: −105.4 (CF_2), −151.4 (BF_4) ppm (internal reference: CF_3CO_2H in DMSO-d_6 = −78.5 ppm); HRMS (ESI) *m/z* calcd. for $C_6H_{12}F_2NO_2^+$ [M-BF_4^-]$^+$: 168.0831, found: 168.0833; calcd. for BF_4^- [M-$C_6H_{12}F_2NO_2^+$]: 87.0035, found: 87.0030.

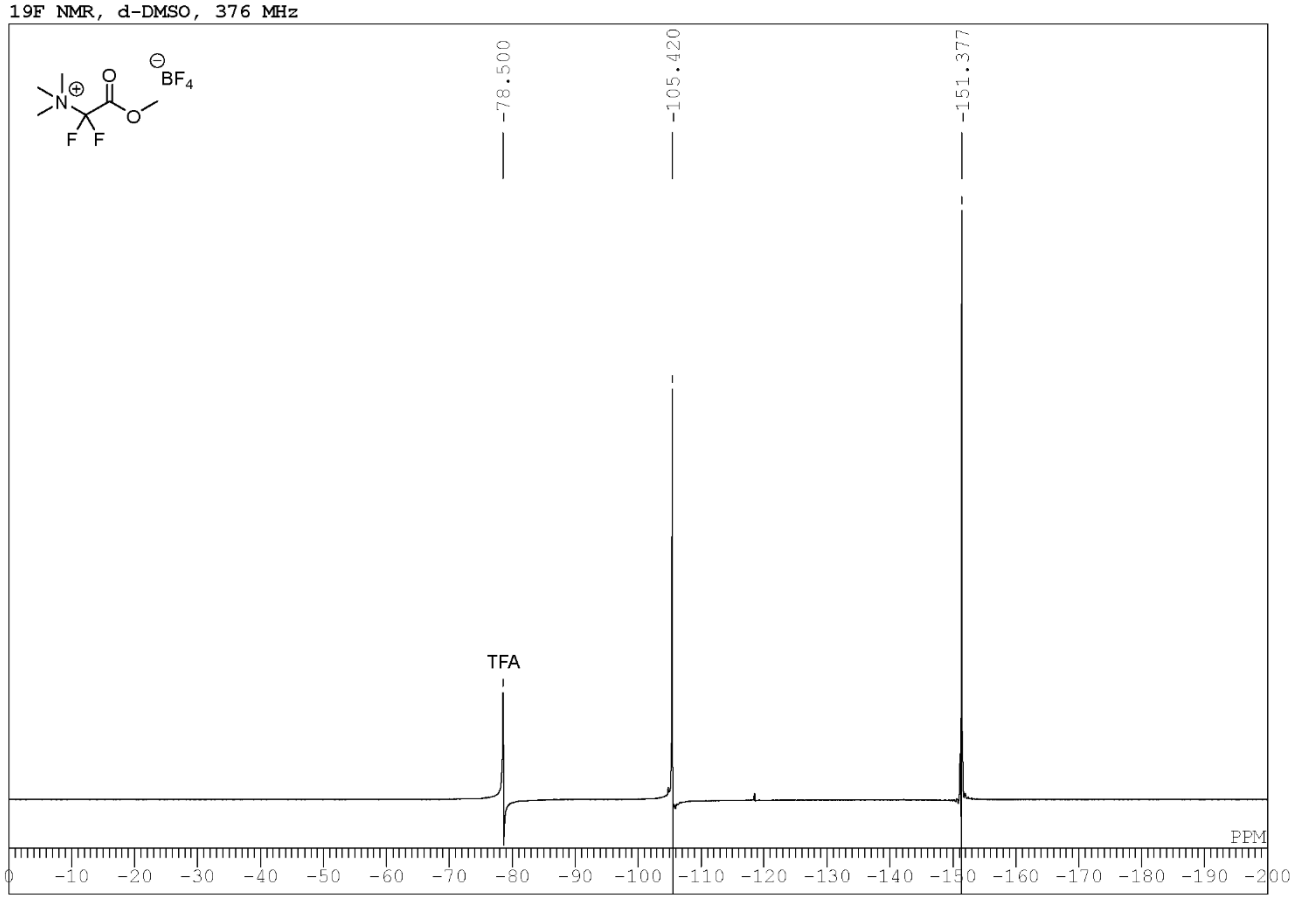
1H NMR, d-DMSO, 400 MHz



13C NMR, d-DMSO, 100 MHz



19F NMR, d-DMSO, 376 MHz



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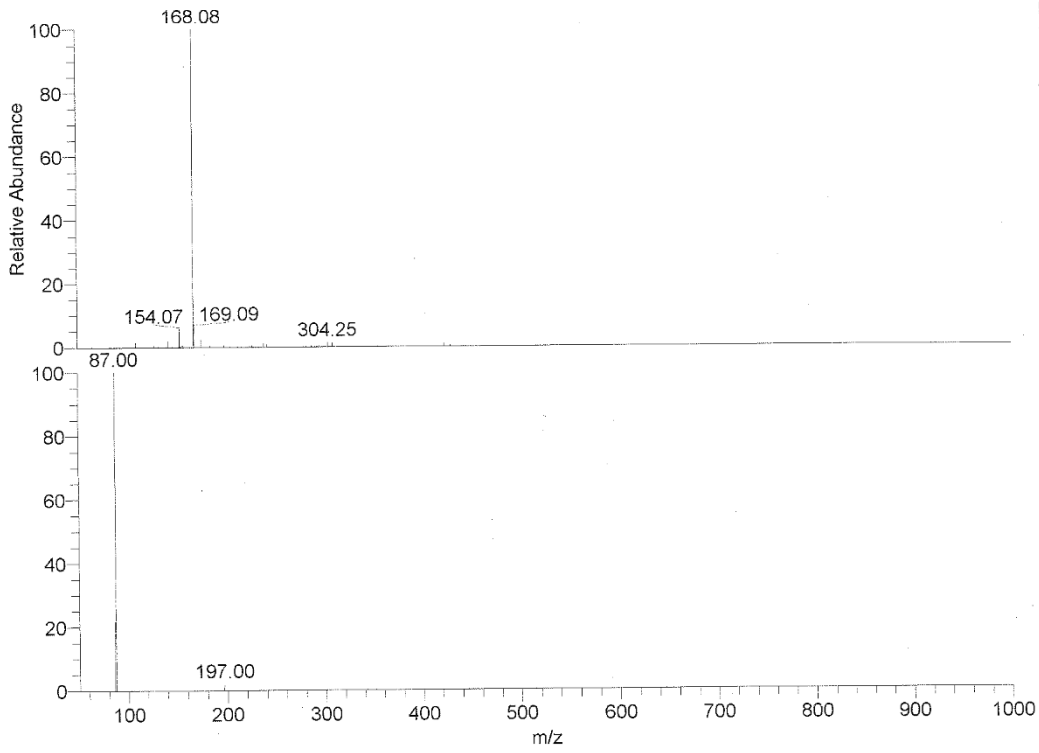
Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : MeOH



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Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

Instrument : Exactive

Mobile phase solvent : MeOH
Sample solvent : MeOH

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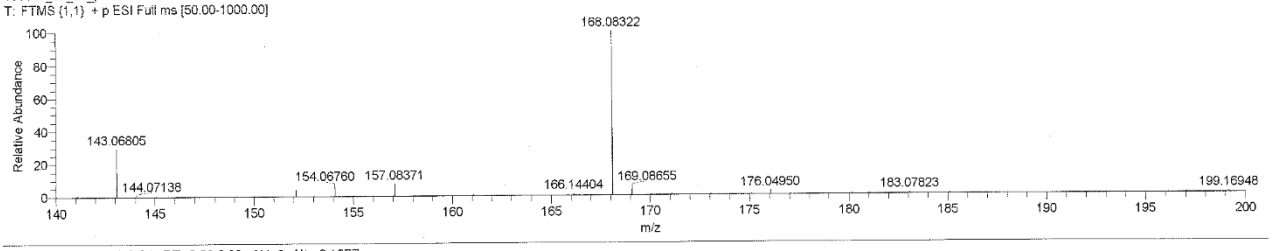

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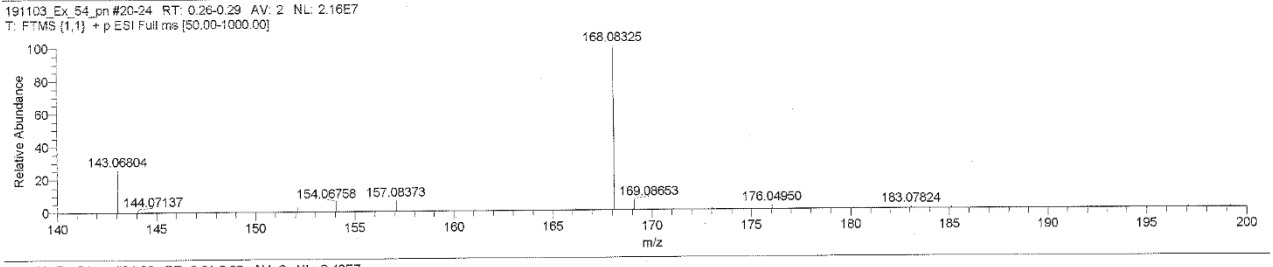

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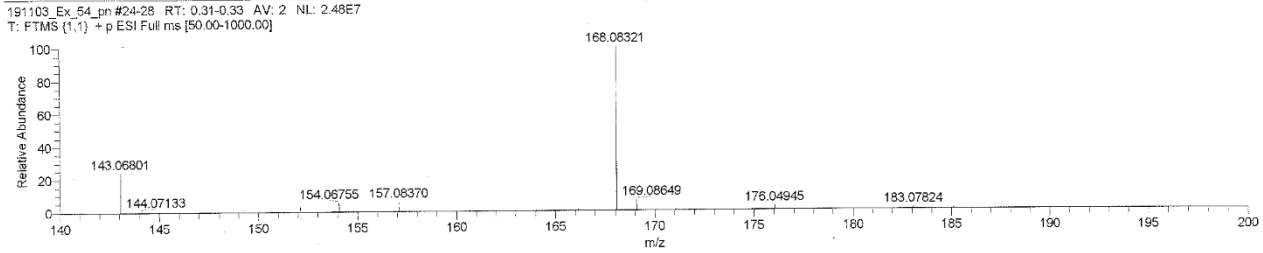

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Instrumental Analysis Division, Global Facility Center, Creative Research Institution, Hokkaido University

Instrument : Exactive

Neg
Mobile phase solvent : MeOH
Sample solvent : MeOH

191103_Ex_54_pn #16-19 RT: 0.20-0.23 AV: 2 NL: 8.11E6
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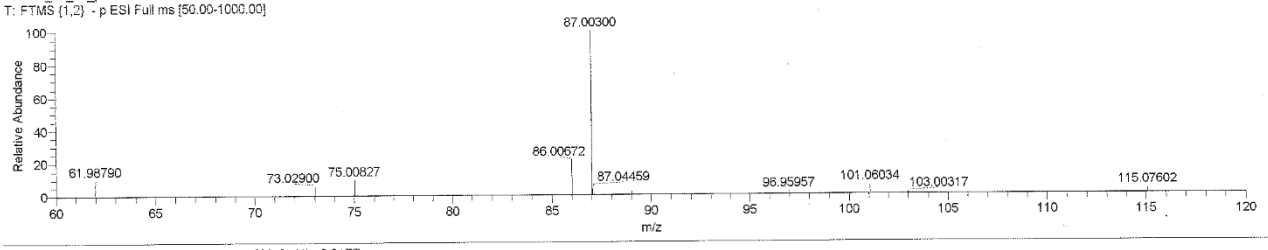

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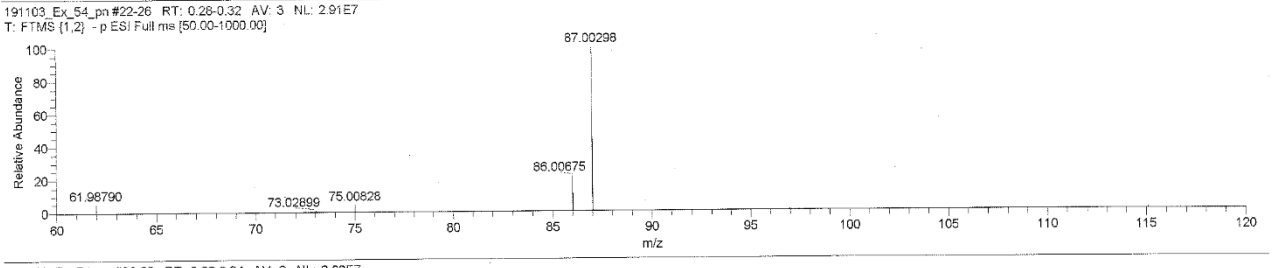

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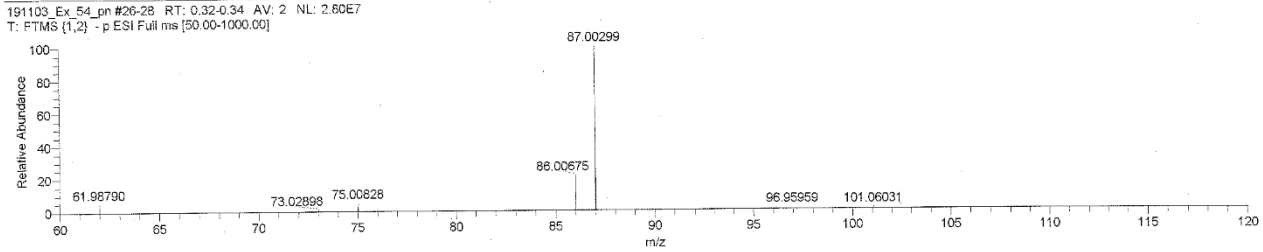

(C) Data for Single Crystal X-ray Structural Analysis

Polymorph	Compound **3**
CCDC Name	CCDC 1971834
Empirical Formula	$C_6H_{12}BF_6NO_2$
Formula Weight	254.98
Crystal System	Orthorhombic
Crystal Size / mm	0.75 × 0.09 × 0.08
a / Å	7.2137(2)
b / Å	11.1355(3)
c / Å	13.0859(3)
α / °	90
β / °	90
γ / °	90
V / Å^3	1051.17(5)
Space Group	$P2_12_12_1$
Z value	4
D_{calc} / g cm^{-3}	1.621
Temperature / K	293
$2\theta_{max}$ / °	10.432 to 152.24
μ (CuK_α) / mm^{-1}	1.643
No. of Reflections Measured	1899
No. of Observations (All reflections)	3624
Residuals: R_1 (I > 2.00σ(I))	0.0610
Residuals: wR_2 (All reflections)	0.1651
Goodness of Fit Indicator (*GOF*)	1.064
Maximum peak in Final Diff. Map / Å^3	0.507
Minimum peak in Final Diff. Map / Å^3	-0.412

(D) Computational Details

To obtain the 30 reactant candidates in Figure 1, we performed an automated search by the single component artificial force induced reaction (SC-AFIR)[1] method starting from α,α-difluoroglycine. SC-AFIR is a method to search for many structures and reaction paths for their interconversions by inducing structural deformations systematically by applying artificial forces between fragments automatically defined in the system. In the search, the model collision energy parameter γ, which defines the strength of the artificial force, was set as 1000 kJ/mol, the maximum number of fragment pairs to

which the artificial force is applied was set as 2 (SC-AFIR2), and the NoBondRearrange option with which the search from local minima having a different bond connectivity pattern from the initial structure is omitted was used to limit the search area.[2] All obtained AFIR paths were reoptimized by the LUP[3,4] method until the highest energy point converged to the first-order saddle point or the number of iterations exceeded 300. As the result, 288 equilibrium (EQ) structures, 309 transition state (TS) structures, and 380 LUP path top (PT) structures, were obtained, where PT is the highest energy structure along a LUP path and regarded as an approximate TS structure. The initial SC-AFIR2 search took 8 h using 28 nodes, wherein each node contained two Intel Xeon (Gold6148) CPUs (i.e., 40 CPU-cores per node). All the reactants, i.e., R1-30 in Figure 1, were already obtained by the initial SC-AFIR2 search. Although further path refinement calculations took 44 h, this would not be required if the purpose was primarily to know the possible new reactions. In this study, the additional calculations were conducted to obtain accurate energetics as well.

The reaction path network for CF_3^- + NH_3 + CO_2 shown in Figure 4 (a) and (b) were obtained by the SC-AFIR method combined with the kinetics-based navigation approach. In the search, γ was set as 200 kJ/mol, and the maximum number of fragment pairs to which the artificial force is applied was set as 1 (SC-AFIR1). The kinetics-based navigation is an approach to decide an EQ to which the SC-AFIR procedure is applied next, where the decision is made based on the so-called traffic volume evaluated by the rete constant matrix contraction (RCMC) method. The traffic volume is an index representing the total population influx and outflow that occur in each EQ under given conditions such as initial populations, reaction temperature, and reaction time. Therefore, an EQ having a large traffic volume can be regarded as one contributing to the kinetics significantly, and the kinetics-based navigation preferentially choose such EQs. Further details on the kinetics-based navigation is available in Ref. 5. The search was initiated from 100 initial structures generated by randomly giving mutual positions and orientations between CF_3^- and a NH_3---CO_2 complex, where the most stable NH_3---CO_2 complex prepared separately was used assuming that the reagents for in situ generation of CF_2 was added after mixing NH_3 and CO_2. In the kinetics-based navigation, the initial population 1/100 was given to the 100 initial structures. Three reaction temperatures, 200, 250, and 300 K, were considered, and the highest traffic volume among those obtained with these three temperatures was regarded as the traffic volume of each EQ. The reaction time was set as 1 hour. The search was terminated when a list of EQs with the 3N largest traffic volume values was not updated in the last 10N path calculations, where N was the number of atoms and 11 in this system. All obtained AFIR paths were reoptimized by the LUP method until the number of iterations exceeded 30. Then, LUP paths for transitions taking more than 10^{-10} second were further optimized by the LUP method until the highest energy point converged to the first-order saddle point or the number of iterations exceeded 60. It is known that such an approximate treatment of fast processes affects little on the overall kinetics taking the longer timescale.[6] As the result, 460 EQ structures, 119 TS structures, and 1020 PT structures, were obtained. Population of each EQ after the reaction time of 1 hour was regarded as the yield of each EQ, and the product yield discussed in the main text was obtained by summing yields of all EQs having the corresponding bond connectivity pattern.

The reaction path network for CF_2Br^- + NH_3 + CO_2 shown in Figure 4 (c) and (d) were obtained by the same calculation as had done for CF_3^- + NH_3 + CO_2. As the result, 425 EQ structures, 178 TS structures, and 795 PT structures, were obtained.

The reaction path network for CF_2Br^- + NMe_3 + CO_2 shown in Figure 4 (e) and (f) were also obtained by the same calculation as had done for CF_3^- + NH_3 + CO_2, where N = 20 in this case. As the result, 839 EQ structures, 188 TS structures, and 2654 PT structures, were obtained.

1. S. Maeda, Y. Harabuchi, M. Takagi, K. Saita, K. Suzuki, T. Ichino, Y. Sumiya, K. Sugiyama and Y. Ono, Implementation and performance of the artificial force induced reaction method in the GRRM17 program. *J. Comput. Chem.* 2018, **39**, 233-251.
2. For these options, see website of the AFIR method: https://afir.sci.hokudai.ac.jp/
3. C. Choi and R. Elber, Reaction path study of helix formation in tetrapeptides: effect of side chains. *J. Chem. Phys.* 1991, **94**, 751-760.
4. P. Y. Ayala and H. B. Schlegel, A combined method for determining reaction paths, minima, and transition state geometries. *J. Chem. Phys.* 1997, **107**, 375-384.
5. Y. Sumiya and S. Maeda, A reaction path network for wohler's urea synthesis. *Chem. Lett.* 2019, **48**, 47-50.
6. S. Maeda, K. Sugiyama, Y. Sumiya, M. Takagi and K. Saita, Global reaction route mapping for surface adsorbed molecules: a case study for H_2O on Cu(111) surface. *Chem. Lett.* 2018, **47**, 396-399.

(E) Predicted Reactant Candidates

Coordinates of difluoroglycine and obtained 30 reactants with the lowest energy shown in Figure 1. Electronic energies on minima at the wB97XD/6-31+G* Int(Grid=FineGrid) level are indicated in atomic units. The indices of minima, R1, R2, … R30, correspond to those in Figure 1.

difluoroglycine

Energy = -482.793203469575 Hartree

C	-0.400412817137	-0.358246729151	0.768814519728
O	-0.565971386999	0.683907656513	1.574867643848
O	-0.286744406301	-1.504359768219	1.124832827093
C	-0.313379782600	0.055116002438	-0.713700941301
F	1.016478055913	0.413591241203	-0.919707073391
F	-1.013078175109	1.189552787468	-0.956993867132
N	-0.756809206676	-0.974227357103	-1.537426793681
H	-0.565530052945	0.354727093862	2.488966630282
H	-0.414616817502	-1.879732602779	-1.236200027428
H	-0.561278039854	-0.797899206184	-2.516382059488

R1

Energy = -482.814626163586 Hartree

C	0.054775062131	-0.730481675845	2.049854523032
O	-0.374468264226	0.348864468401	2.153452105640
O	0.493324770614	-1.807304812088	1.991696067817

C	-0.356568476754	0.391760378657	-1.198872709965
F	0.990211514201	0.376242456575	-1.002678979730
F	-0.528228915711	0.547438634315	-2.562689091529
N	-0.904250203855	-0.802453340200	-0.700015677631
H	-0.782893952661	1.271769489361	-0.715945019863
H	-1.917112216418	-0.798948651573	-0.749964879150
H	-0.536131946529	-1.614457829578	-1.187765480095

R2

Energy = -482.797075448367 Hartree

C	-0.389298812330	0.091190687955	2.428223389531
O	-0.133290114593	-0.814515535074	1.735452266404
O	-0.631358259388	0.959244847267	3.160179808045
C	-0.100730461892	-1.355349059588	-1.480321168011
F	0.165442315955	-2.279387041424	-2.410417121644
F	-0.962446175435	1.557112380791	0.177942519148
N	-0.483528691829	-0.193719958377	-1.753415838156
H	-0.801326480480	0.951247625138	-0.557188431882
H	0.051744715584	-1.724644727998	-0.471068576937
H	-0.576550664838	-0.008750100618	-2.752315987964

R3

Energy = -482.794810441895 Hartree

C	-0.099328785630	-1.591755468299	1.880463185072
O	-1.060769994497	1.010764647324	0.000234372758
O	0.347509505268	-1.575699815881	2.922269912006
C	-1.381297942188	0.131896812838	-0.767188356172
F	1.524111388048	0.828087643771	-0.093400710416
F	-2.675240837503	-0.166338201329	-0.952824107697
N	-0.588313041126	-0.631214980947	-1.524603326483
H	0.624963197129	1.100399590284	0.096837286874
H	0.413730302051	-0.538101412090	-1.409503776766
H	-0.966706420734	-1.385609697627	-2.075213620657

R4

Energy = -482.797213060850 Hartree

C	-0.137616486102	-1.402367452271	-0.124622638376
O	0.303423435204	0.879461376724	0.705939737763
O	0.190877538026	-2.559630211884	0.025673726107
C	0.525383145977	-0.296270821448	0.731710088231
F	1.423103608121	-0.794455807170	1.556628620070

F	-1.475270226104	1.974834028480	-0.919206794542
N	-1.054442047026	-0.932188017707	-0.988913007284
H	-0.807520169427	1.868669076050	-0.255126538405
H	-1.303019710453	0.048837468936	-1.077863241079
H	-1.526261717455	-1.604460521675	-1.577149093969

R5

Energy = -482.781378055004 Hartree

C	-0.561501393410	-0.067347068459	2.001343652035
O	-1.164932591453	-1.008439656546	1.327350568849
O	-0.585940350595	0.144446491021	3.167630090295
C	0.066670227202	-0.017245780929	-1.912010248594
F	0.313642049238	0.038033013044	-3.224432080595
F	0.173667833782	0.730601100516	1.157158400616
N	-0.653463928073	-0.894206339510	-1.379795171047
H	0.560002886696	0.781350122461	-1.366827699000
H	-0.971486371676	-0.956389073158	0.349097445071
H	-1.038000990925	-1.568373690412	-2.042444099097

R6

Energy = -482.778812795010 Hartree

C	0.501569957861	-0.828706972148	2.653968070911
O	-1.383211854247	-0.575175848335	0.120163514731
O	1.286759227254	-0.838164122086	3.468705631164
C	-0.558017283453	-0.018686222385	-0.789463302188
F	0.635061040323	-0.752274601388	-0.823886850449
F	-0.132799855675	1.223936805914	-0.403890575700
N	-1.191094361357	0.074951978009	-2.032496124781
H	-0.881170401896	-0.724879291237	0.939400565475
H	-1.574941201250	-0.818660913143	-2.316303496659
H	-0.563497896808	0.440088304823	-2.739126573997

R7

Energy = -482.776326585774 Hartree

C	-0.540183932677	-0.597043050686	0.838955660570
O	-1.196003796297	0.415672616183	1.395362951353
O	-0.221297438725	-1.612315689170	1.411177797862
C	0.435584266609	-1.121876741821	-1.133331667116
F	0.715244404812	-0.930521177453	-2.400581137496
F	-1.311573525307	1.954999412899	-1.789638418796
N	-0.288907843501	-0.287675445271	-0.524085525707

H	-1.363450991730	0.187643290373	2.323609019054
H	0.882372795842	-2.027062303451	-0.722941790402
H	-0.973126568244	1.200608206444	-1.321456030780

R8

Energy = -482.765214428561 Hartree

C	0.808980017438	-1.761679259423	1.679575351247
O	-0.478597585198	1.116568112910	0.849941459184
O	1.362309509356	-1.485764454857	2.629451767236
C	-0.302555122050	1.296606115979	-0.302748973293
F	0.828609037604	1.084894246519	-0.948528826837
F	-1.134801745369	1.904698067607	-1.123709539721
N	-1.147121143155	-0.983458719510	-1.143882991366
H	-2.131432773103	-1.072410521716	-0.906454649126
H	-0.631886978217	-1.628553757055	-0.549825876340
H	-1.034845846509	-1.288470712412	-2.106746862492

R9

Energy = -482.773952835216 Hartree

C	-0.851727089433	-0.462508740591	1.124719955388
O	-1.184303962233	0.525433916037	1.945373422534
O	-0.903229604140	-1.640092185930	1.373414611051
C	-0.374048863563	0.032509988358	-0.230077966745
F	0.835916124882	-0.082774918021	-3.684697986057
F	-0.368059968260	1.344999919865	-0.369763572402
N	-0.007805673752	-0.712303023042	-1.168126358914
H	-1.478574359933	0.136661307429	2.786387057823
H	-0.070298813779	-1.695996510475	-0.903702446807
H	0.540789580992	-0.263500635599	-2.796455857339

R10

Energy = -482.760308196684 Hartree

C	0.399429503567	-0.214519900336	2.118443816533
O	0.582257405049	0.366660669275	3.108153621117
O	0.235893771410	-0.840428773398	1.146350108469
C	-0.639188824116	-1.391255623135	-1.896944528381
F	-1.398222273130	1.188141352187	-1.519047574379
F	-0.681612827025	1.992187115930	0.840440750007
N	-0.286908288119	-2.496185458801	-1.987282477225
H	-0.968756828698	1.757799590282	-0.035013780105
H	0.029720120398	-3.445456958323	-2.027200353270

H	-1.133954388542	0.265487104374	-1.670828724235

R11

Energy = -482.765849885398 Hartree

C	0.691261994700	-1.306963296442	-0.235805425021
O	-1.509144166900	2.105491194794	1.483979057983
O	0.394316124756	-0.395186932180	0.653198148064
C	-2.363572777764	2.794582787315	1.193969810115
F	1.777480800617	-1.971149697613	0.129072175333
F	-1.722875066649	0.223264821264	-0.972176454965
N	0.049922438348	-1.544362540295	-1.303861436426
H	-0.413292637551	0.085022622073	0.362120218981
H	0.438081629694	-2.293282284925	-1.866617022392
H	-1.203520968366	-0.514987556006	-1.366808213069

R12

Energy = -482.762355318733 Hartree

C	-0.551295903810	-0.245049708697	2.331024414277
O	-0.741327122415	-1.077557865248	1.529619823546
O	-0.382148765227	0.527125077023	3.178142403620
C	-0.204762771659	-0.021546441771	-1.722197690143
F	-0.063018192460	0.133445281103	-3.040928711974
F	0.099345829973	1.511363524468	0.410043452971
N	-0.581062781376	-1.246295016604	-1.465621302741
H	0.021400499861	1.046361459043	-0.465231448617
H	-0.724558479905	-1.496400676918	-0.492090654709
H	-0.733914942207	-1.949016514357	-2.185689427710

R13

Energy = -482.764317151512 Hartree

C	-1.395414041104	-0.309922280105	1.375814057524
O	-2.117869229846	-0.325084205208	2.494887796226
O	-0.272449785029	-0.747827196699	1.282006193404
C	0.764378251252	-0.110641483798	-2.470570775056
F	1.995099288622	-0.607264260972	-2.377969011082
F	0.582993589562	0.303525425232	-3.705969031398
N	-0.097122955104	-0.029191409806	-1.583596111743
H	-1.584693337315	-0.741676174387	3.193985580778
H	0.216216109713	-0.400973030805	-0.683775000391
H	-1.952480519862	0.151483734534	0.552257160318

R14

Energy = -482.760568478488 Hartree

C	-0.816981391116	-1.160596524877	1.423057298049
O	-0.808010134806	0.127867944959	1.697256413723
O	-1.047551017002	-2.041370579930	2.198773568165
C	-0.501179154897	-1.471449676102	-0.003707225114
F	0.253377680349	0.379864172193	-2.721477120118
F	-0.208027584064	1.599478651864	-0.508797091937
N	-0.251811445992	-1.673309378459	-1.113332869924
H	-0.594355600348	0.691400060973	0.919169351736
H	0.130507814934	-0.523791330117	-2.430369162909
H	-0.017311796291	1.254335777531	-1.383502303125

R15

Energy = -482.762198666521 Hartree

C	0.350766125307	-0.231720807310	1.016233445062
O	-0.732995526138	0.316004195673	1.331621673749
O	1.372106566208	-0.483675804199	1.623165685770
C	0.412900729125	-0.700438353550	-0.498949984281
F	1.507289013152	-1.268974179745	-0.902899474859
F	-2.553857804915	0.601846615464	-0.231235442088
N	-0.520647855375	-0.573751501032	-1.372462214257
H	-1.881966999624	0.551784516203	0.531710606661
H	-1.425517017168	-0.120238256902	-1.097046769795
H	-0.389419859772	-0.908407306561	-2.323066667429

R16

Energy = -482.753221614938 Hartree

C	0.572463353152	-0.711661517260	-0.534380180783
O	-0.734373857390	1.051203403213	0.972638706836
O	1.088032887577	-1.418438115369	0.268365960751
C	-0.833094472349	-0.898106096797	-1.058065762162
F	1.218610784967	0.294994377622	-1.124665897248
F	-1.224500793983	0.074729995583	-1.876465297370
N	-1.589472858339	-1.856556581199	-0.798978272448
H	-1.005235260275	1.905960868493	0.617008855152
H	-1.132873366188	-2.502442142191	-0.154718036930
H	-0.220899046407	1.242744926012	1.766330782913

R17

Energy = -482.736998341643 Hartree

C	0.150379167545	2.533544693338	1.099753803691
O	-1.569674077547	-2.373467214714	0.272759304340
O	-0.665485979621	3.320683381372	1.055391715433
C	0.514277429716	-0.049384280226	-1.290633294425
F	1.222381642640	-1.165256437937	-1.089483466574
F	1.312937106833	0.837716684259	-1.845623271057
N	-0.675040725964	0.158019537744	-1.018301639842
H	-2.218100924021	-2.483638294107	0.977626936865
H	-0.819607008171	-2.933653881356	0.505014400593
H	-1.113409260634	-0.662135070402	-0.589433630499

R18

Energy = -482.748315896604 Hartree

C	-0.217277764187	-1.913727146999	0.819647475506
O	-0.013641585634	-1.065231846257	1.760174238379
O	-0.248899031223	1.201364645610	0.336141227727
C	-0.488213064179	1.076411391976	-0.846151952591
F	-0.133442893058	-3.119354396966	1.368023462537
F	-0.620592313953	2.167402893742	-1.618106890688
N	-0.650083039152	-0.048747512112	-1.539477453088
H	-0.074803658190	-0.155985766825	1.354870064980
H	-0.566062401116	-0.935984552884	-1.030536930974
H	-0.848326878510	-0.023718591227	-2.527512383266

R19

Energy = -482.737619100570 Hartree

C	-0.601052960466	0.091671279171	1.121788797195
O	-1.716230549422	-0.646528521721	1.078785091981
O	0.102925637823	0.218958314390	2.090947671802
C	0.539771797652	0.504150866590	-0.837538751711
F	1.437805114130	-0.446811522183	-0.693082589776
F	0.786806001508	1.172466374703	-1.932363302533
N	-0.421634647358	0.760579968357	-0.095225023681
H	-1.826152353691	-1.048240296563	1.955118591010
H	-0.814660358274	-1.968828286027	-2.324512986746
H	-1.348920311129	-1.454989058662	-2.286846639016

R20

Energy = -482.741700046415 Hartree

C	0.652082911649	-0.055649567707	0.609476787050
O	-2.449652283058	-0.223567168914	0.929676327933

O	1.826578254132	-0.158161327432	0.845186483213
C	0.379474404293	-0.352585349838	-1.689894259755
F	-0.142755539142	-0.927249809139	-2.744220243942
F	1.260826632474	0.541271639640	-2.074861150640
N	0.028205635680	-0.626890343549	-0.528560030573
H	-3.282828122157	-0.631868194862	1.189540694180
H	-0.078340474278	0.419048347049	1.278738460225
H	-2.054934048803	-0.801919107239	0.261987790860

R21

Energy = -482.744866113294 Hartree

C	-0.236101539365	0.311548010933	1.866685134741
O	-1.003477089662	0.959458237962	1.048923509189
O	-0.021612618484	0.487778670203	3.019731612721
C	-0.872449239855	-0.164608343514	-1.464368704179
F	-1.481900675882	0.153279892166	-2.608144024091
F	0.398995122825	-0.740915001259	1.207012535441
N	-0.093594844801	-1.196219667956	-1.660510293002
H	-0.991895288471	0.576330800073	0.092987401307
H	0.430771099147	-1.542391986979	-0.865529509132
H	0.009922445331	-1.661831493598	-2.559716804482

R22

Energy = -482.734701613681 Hartree

C	-0.084757338449	0.298254718212	1.484551899565
O	-1.279558976311	0.852046529661	1.223675118835
O	0.593488865186	0.031501104880	2.419084398502
C	-0.451174933706	0.376321632578	0.080031701728
F	0.887074396295	-1.891573024271	-2.394368594680
F	-0.020214864676	1.393526086421	-0.671817550821
N	-0.919470853974	-0.669295931641	-0.723081130288
H	-1.273335765182	-1.448631810581	-0.175857006947
H	0.324449888899	-1.412706829348	-1.795013323604
H	-1.637843047291	-0.347013357861	-1.370134653768

R23

Energy = -482.732778807392 Hartree

C	-1.115116946685	0.140767370471	0.866418795530
O	-1.510913748947	-0.877257369469	1.641855650147
O	-1.349699293917	1.299736217515	1.046836937013
C	0.248641567534	0.184268313896	-1.238705226295

F	1.375860262247	-1.773295005007	-2.694397543683
F	0.106279467736	1.486316966908	-1.198449245650
N	-0.365919018725	-0.407514717207	-0.210397709713
H	-2.023414880501	-0.509173123283	2.379024739031
H	1.046463892088	-0.942266076391	-2.307144212873
H	-0.273523929950	-1.419153459477	-0.207971324922

R24

Energy = -482.724978283980 Hartree

C	-1.117680748457	-0.406142208190	-0.400452239590
O	-0.796313226307	-1.215106189235	0.618531540749
O	-0.339132226429	0.397932605455	-0.898268211687
C	1.809883917121	0.081480641815	0.458639724425
F	2.599080668818	-0.111515201204	-0.558993234842
F	1.963459830752	1.333494434992	0.781806127518
N	-2.395920822321	-0.581156738913	-0.806590551773
H	0.139538771655	-1.008432044599	0.838424402255
H	-2.736065686790	-0.036590181013	-1.581710899330
H	-2.988193107172	-1.271536001131	-0.374315799187

R25

Energy = -482.724300210028 Hartree

C	-0.174337224603	-0.035529683576	2.118533289647
O	-1.248907083059	-0.365576500570	1.783283409340
O	0.850129393199	0.288148743556	2.556429991118
C	0.376397146221	0.001613051707	-0.731875370597
F	1.153500397628	-0.415005138390	-1.809587529955
F	-0.022496920493	1.283130868446	-1.124471627781
N	-0.984155066810	-0.766321430530	-1.130642476535
H	-1.685557339598	-0.526904213640	-0.428277570076
H	-0.811228869758	-1.770102025898	-1.088138930831
H	-1.314687061938	-0.511024553058	-2.068182325804

R26

Energy = -482.710546064105 Hartree

C	-0.114935572271	-0.121718425870	2.329813452850
O	-0.974595785863	-0.768002744763	1.879655154182
O	0.735726135531	0.516910365356	2.801628680052
C	0.742579966321	0.661126759105	-0.621626508054
F	1.621370034428	0.078270256649	-1.392485110702
F	0.277658396573	1.646428626729	-1.342488668541

N	-1.732900447439	-1.366776552233	-1.431642637877
H	-1.588906395881	-1.229836352719	-0.436417558856
H	-0.892780140063	-1.760020419173	-1.841296391845
H	-1.934558820549	-0.473952395032	-1.868069552678

R27

Energy = -482.718950903638 Hartree

C	0.267629918934	-0.151693042990	1.184237936626
O	-0.388915800334	-0.803753594717	1.922108839212
O	1.368342890770	0.647101883896	1.233840120413
C	0.716566700118	0.457168610064	-0.041658526583
F	1.452879908236	-0.164275999885	-0.944823542013
F	0.192479770139	1.555175536406	-0.554925828054
N	-1.635063538074	-0.948784596456	-1.107563325148
H	-2.473709486299	-0.515357212018	-0.730495946252
H	-1.619519971184	-1.906229242707	-0.766235496357
H	-1.742033021530	-0.986923223546	-2.117413373289

R28

Energy = -482.714239391937 Hartree

C	0.109791730373	1.277575712858	0.248129648913
O	-1.672019604950	-2.330960159952	0.227810072532
O	0.073657353725	2.012712501364	1.193004889552
C	0.655348437243	0.741102972679	-1.024130730209
F	1.821062440564	0.061702165495	-1.065365852924
F	0.434509267421	1.234997582583	-2.256260527555
N	-0.432163367726	0.179342574953	-0.322014257553
H	-2.634014450401	-2.391225870045	0.268414438153
H	-0.882744008097	-0.730508232603	-0.144267844794
H	-1.334770427373	-2.872310129285	0.951751022382

R29

Energy = -482.700362053186 Hartree

C	-0.579202735555	-0.530532079091	1.719258652443
O	-0.437918887803	-0.676716775350	3.032122147864
O	0.619906619231	-0.292221872710	1.252387746733
C	-0.343270623587	0.004234403062	-2.579267958675
F	0.780492433139	0.258810606127	-3.198375310343
F	-1.320812331217	-0.060852582707	-3.465618609564
N	-0.425810839646	-0.144432076340	-1.347684215645
H	-1.315436274259	-0.853807871616	3.392202227268

H	-1.366375219418	-0.337616769975	-1.009264578696
H	0.527085229922	-0.184435863359	0.281310757162

R30

Energy = -482.676595442259 Hartree

C	-0.801055085218	-1.065123076873	0.287002021833
O	-0.877370152070	0.218444931465	0.658552481230
O	0.498097397500	-1.409837679507	0.269557218240
C	0.553712361881	1.505523620391	-1.498153778290
F	1.642773831192	1.675024660379	-0.798946908107
F	-0.160901396997	2.576174175222	-1.246911409173
N	-1.841340446324	-1.742238651107	0.023083826456
H	-1.818675228722	0.446953553381	0.664761392927
H	0.591530079413	-2.319134204009	-0.039331692046
H	-1.648113989851	-2.703358211323	-0.242542294546