Supplementary Information

Theoretical investigation on the mechanism of Ni^0(acetylide carbanion)-ate complex catalyzed C(sp^2)–F bond activation and the origin of counterion effect on reactivity

Xiao-Xia You,[#] Ling-Qi Meng,[#] Xu Liu, Li-Li Wang, Xin-Cheng Xu, Rong-Lin Zhong,[*] Zhong-Min Su[*]

State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun 130021, China. zhongrl898@jlu.edu.cn, suzhongmin@jlu.edu.cn, wangjiansen@sjtu.edu.cn

[#] These authors contributed equally to this work.

Content

1. C(sp^2)–F bond activation by $(Na^+)_3[Ni^0(CCPh)_3]^{3-}$

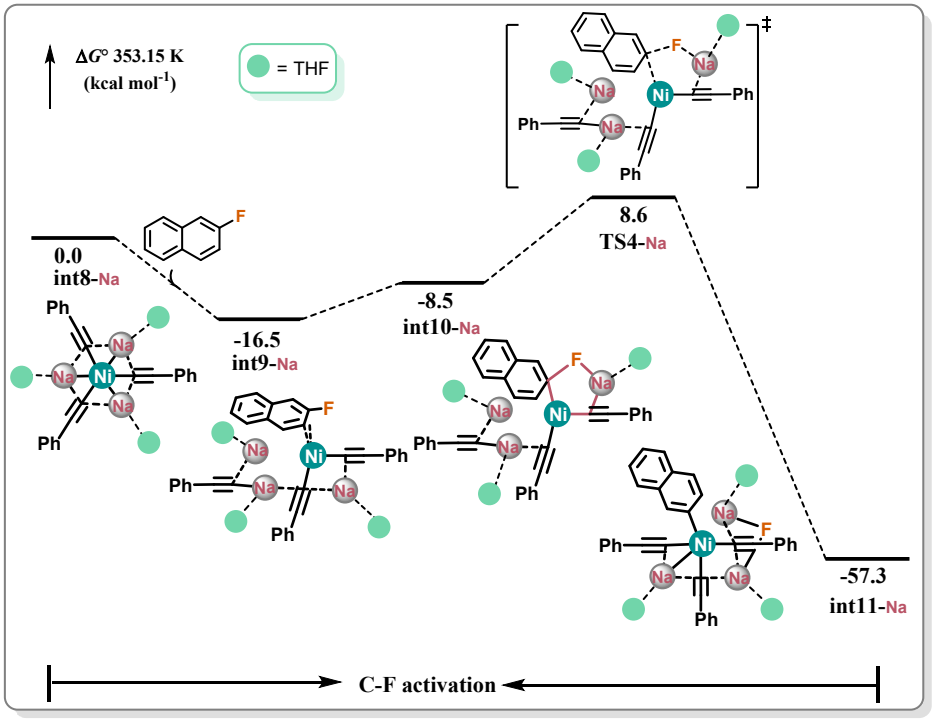


Figure S1. Gibbs energy profile of C(sp^2)–F activation by the $(Na^+)_3[Ni^0(CCPh)_3]^{3-}$ complex. The nickelate complexes is stabilized by solvent (THF) where solvent effect is simulated by PCM model.

The Gibbs energy profile for the Ni^0-mediated C(sp^2)–F bond activation, beginning from $(Na^+)_3[Ni^0(CCPh)_3]^{3-}$ complex is shown in Figure S1. The reaction initiates through η^2-coordination of fluoronaphthalene (**int1**) to the $(Na^+)_3[Ni^0(CCPh)_3]^{3-}$ (**int8-Na**), forming adduct **int9-Na** with a binding energy of -16.5 kcal mol^{-1}. Subsequent isomerization from **int9-Na** to **int10-Na** is endothermic (8.0 kcal mol^{-1}), wherein the C(sp^2)–F bond approaches the Ni^0-center that is essential for C(sp^2)–F bond activation. C(sp^2)–F bond cleavage then proceeds via **TS4-Na** to afford a complex, **int11-Na**, the $\Delta G^{o\ddagger}$ is 25.1 kcal mol^{-1} and ΔG^o is -57.3 kcal mol^{-1} relative to **int9-Na**.

2. C(sp^2)–F bond activation by$(K^+)_3[Ni^0(CCPh)_3]^{3-}$

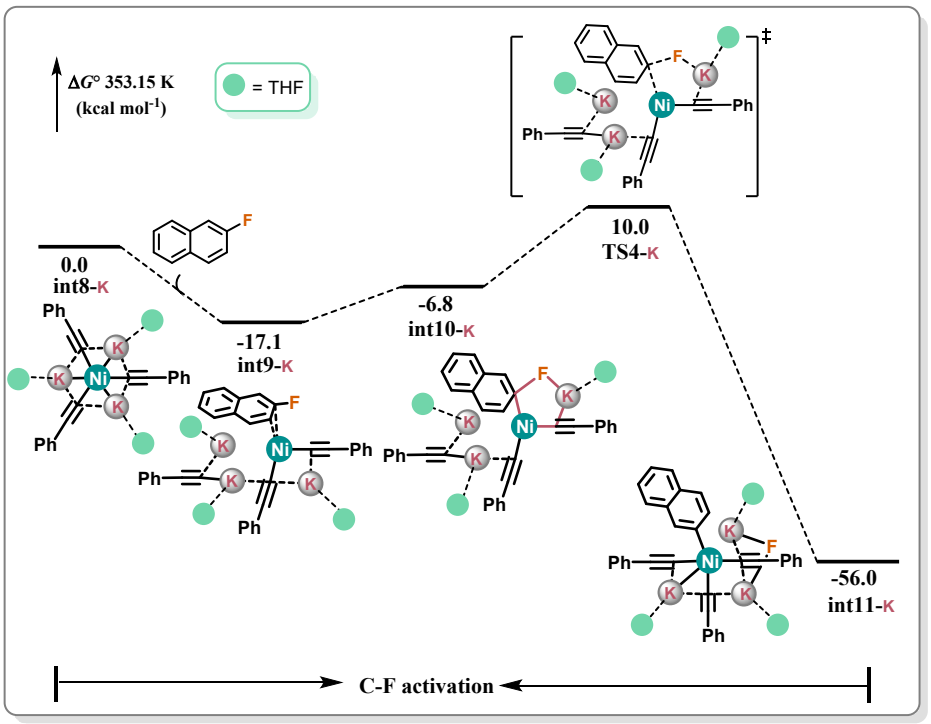


Figure S2. Gibbs energy profile of C(sp^2)–F activation by the$(K^+)_3[Ni^0(CCPh)_3]^{3-}$ complex. The nickelate complexes is stabilized by solvent (THF) where solvent effect is simulated by PCM model.

The Gibbs energy profile for the Ni^0-mediated C(sp^2)–F bond activation, beginning from $(K^+)_3[Ni^0(CCPh)_3]^{3-}$ complex is shown in Figure S2. The reaction initiates through η^2-coordination of fluoronaphthalene (**int1**) to the $(K^+)_3[Ni^0(CCPh)_3]^{3-}$ (**int8-K**), forming adduct **int9-K** with a binding energy of -17.1 kcal mol^{-1}. Subsequent isomerization from **int9-K** to **int10-K** is endothermic (10.3 kcal mol^{-1}), wherein the C(sp^2)−F bond approaches the Ni^0-center that is essential for C(sp^2)−F bond activation. C(sp^2)−F bond cleavage then proceeds via **TS4-K** to afford a complex, **int11-K**, the $\Delta G^{o‡}$ is 27.1 kcal mol^{-1} and $\Delta G°$ is -56.0 kcal mol^{-1} relative to **int9-K**.

3. C(sp²)–OMe and C(sp²)–NMe₂ bond activation

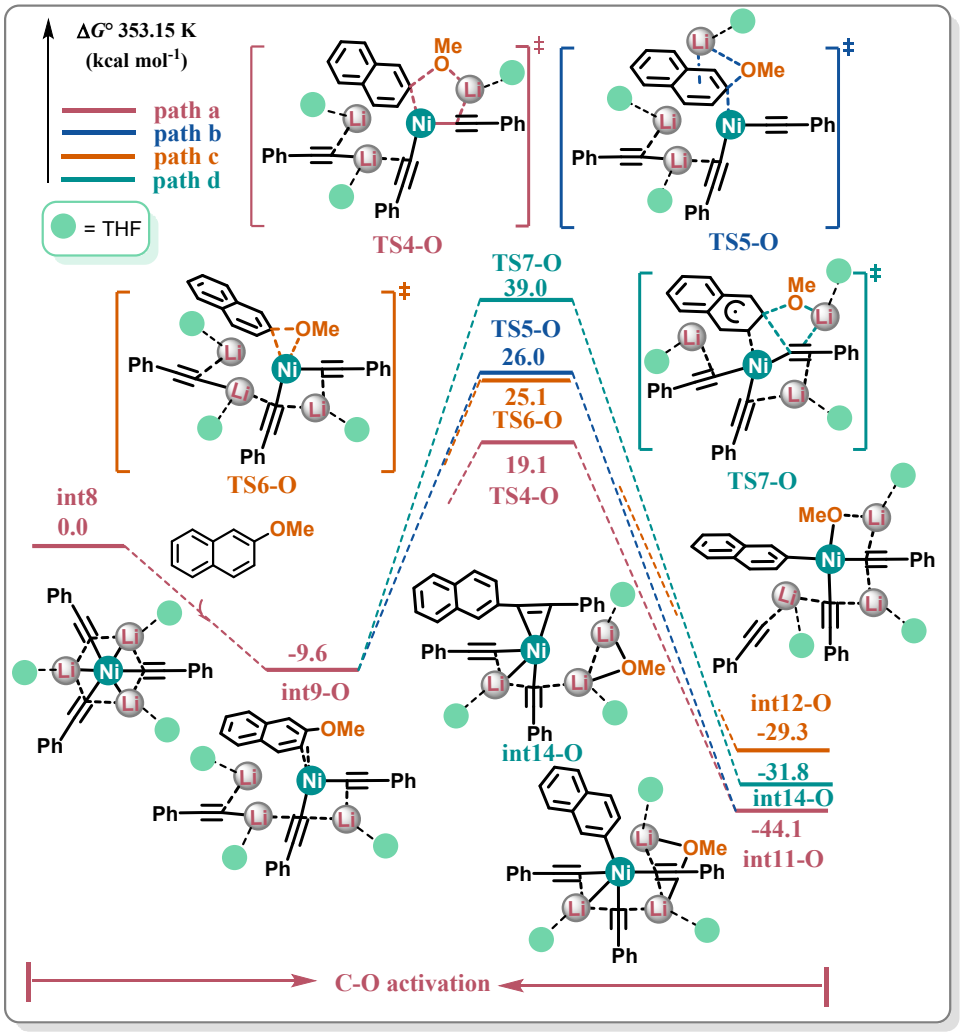


Figure S3. Gibbs energy profile of C(sp²)–OMe activation by the $(Li^+)_3[Ni^0(CCPh)_3]^{3-}$ complex. The nickelate complexes is stabilized by solvent (THF) where solvent effect is simulated by PCM model.

The Gibbs energy profile for the Ni^0-mediated C(sp²)–OMe bond activation, beginning from complex **int8** is shown in Figure S3. The activation of the C(sp²)–OMe bond proceeds preferentially via an inner-sphere Ni^0-mediated S_NAr ($\Delta G^{o\ddagger}$ is 28.7 kcal mol^{-1}), which is markedly more favorable than outer-sphere S_NAr ($\Delta G^{o\ddagger}$ is 35.6 kcal mol^{-1}), carbon anion attack S_NAr ($\Delta G^{o\ddagger}$ is 48.6 kcal mol^{-1}), and concerted OA ($\Delta G^{o\ddagger}$ is 34.7 kcal mol^{-1}). The energy barrier is 28.7 kcal mol^{-1} which is higher than C(sp²)–F bond activation.

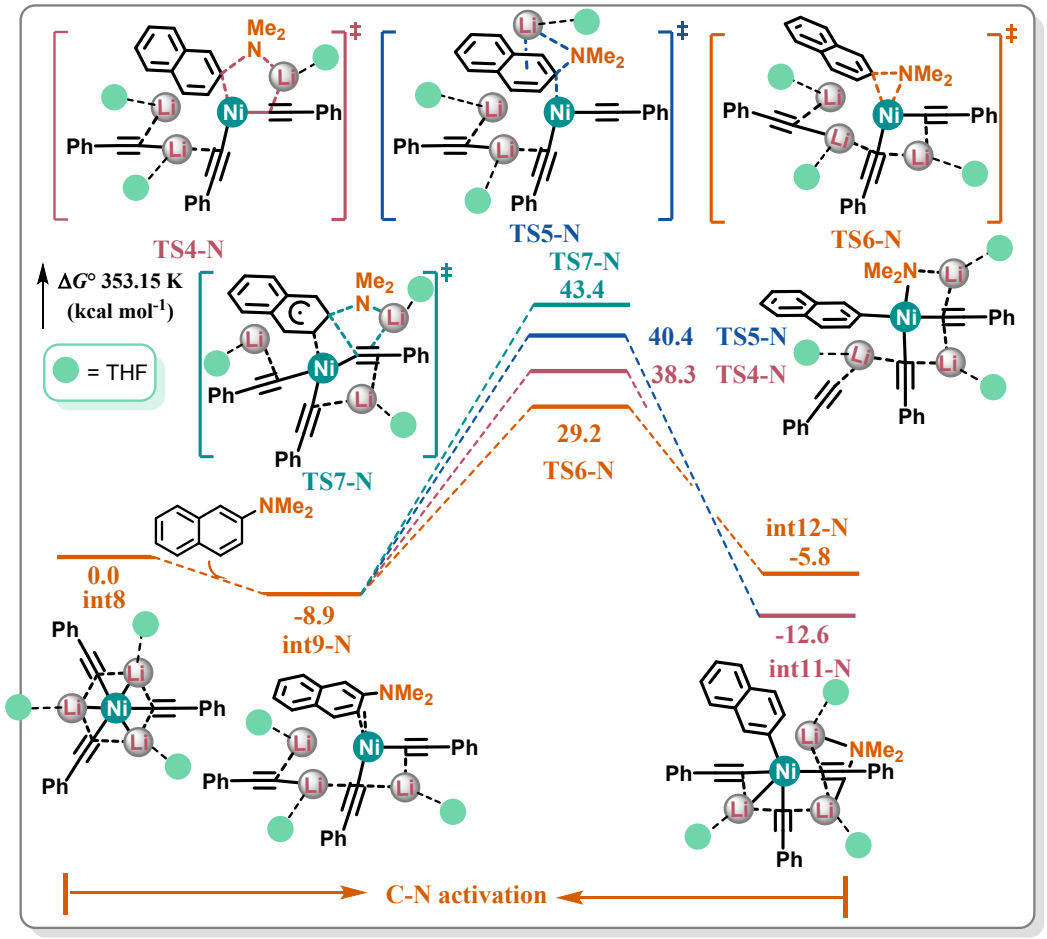


Figure S4. Gibbs energy profile of C(sp^2)–NMe_2 activation by the $(Li^+)_3[Ni^0(CCPh)_3]^{3-}$ complex. The nickelate complexes is stabilized by solvent (THF) where solvent effect is simulated by PCM model.

The Gibbs energy profile for the Ni^0-mediated C(sp^2)–NMe_2 bond activation, beginning from complex **int8** is shown in Figure S4. Initial C(sp^2)–NMe_2 bond cleavage necessitates an isomerization step to form **int9-N**, during which the substrate coordinates to the Ni^0 center. This reorganization is exothermic, with a reaction energy of -8.9 kcal mol^{-1}. Inspired by analogous inner-sphere S_NAr mechanisms proposed for C(sp^2)–F activation, we computationally evaluated a similar pathway for the C(sp^2)–NMe_2 bond. The results indicate that, from **int9-N**, the system undergoes C(sp^2)–NMe_2 activation via the transition state **TS4-N**, yielding the product complex **int11-N**. The $\Delta G^{\circ\ddagger}$ is 47.2 kcal mol^{-1} and ΔG° is -12.6 kcal mol^{-1} relative to **int9-N**. Notably, an alternative concerted oxidative addition pathway was also identified. This route

proceeds through a three-membered ring transition state (**TS6-N**), directly inserting the C(sp^2)–NMe_2 bond into the Ni^0 center to form the Ni^{II}–nitrogen complex **int12-N**. The Gibbs free activation energy ($\Delta G^{o‡}$) is 38.1 kcal mol^{-1} and the Gibbs free reaction energy (ΔG^o) is -5.8 kcal mol^{-1} relative to **int9-N**. Therefore, under these conditions, the C(sp^2)–NMe_2 bond cannot be activated.

4. C(sp^2)–F bond activation by $Ni^0(cod)_2$

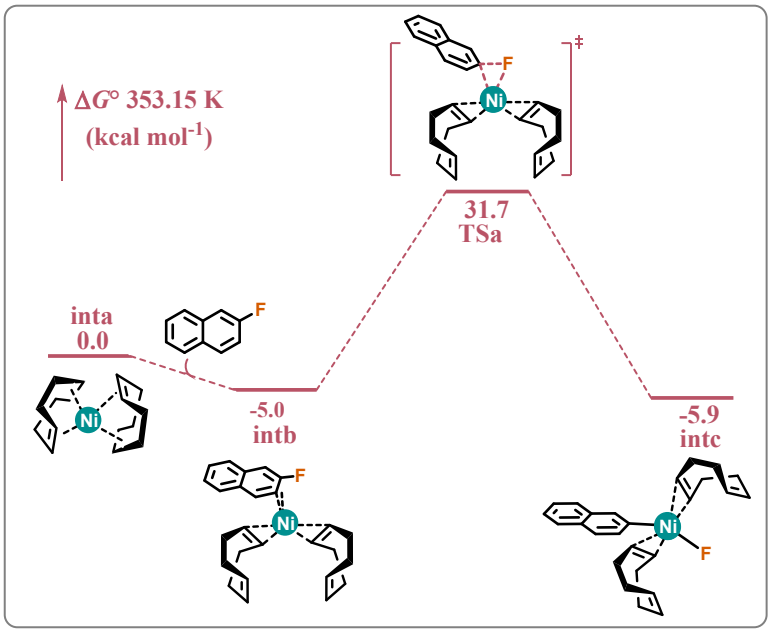


Figure S5. Gibbs energy profile of $Ni^0(cod)_2$ catalyzed C(sp^2)–F bond activation.

The Gibbs energy profile for the $Ni^0(cod)_2$ catalyzed C(sp^2)–F bond activation is shown in Figure S5. The $\Delta G^{o‡}$ of the concerted oxidative addition of C(sp^2)–F bond to Ni^0-center via **TSa**, which forms the Ni^{II}-fluoride intermediate, is 36.7 kcal mol^{-1} and ΔG^o is -5.9 kcal mol^{-1} relative to **inta**. The barrier (36.7 kcal mol^{-1}) of this elementary step is significantly higher than that of the inner-sphere Ni^0-mediated nucleophilic aromatic substitution (21.7 kcal mol^{-1}) for C(sp^2)–F bond activation.

5. Benchmark calculatons of solvent modes, functionals and basis sets

Table S1. Relative single point energies of the transition states for Ni^0(acetylide carbanion)-ate C–F bond activation by employing different solvent models. (All energy terms are in kcal mol^{-1} unit)

Solvent model	TS4	TS5	TS6	TS7
PCM [a]/ kcal mol^{-1}	0.0	10.0	10.6	35.2
SMD [b]/ kcal mol^{-1}	0.0	7.8	12.5	34.5

[a] Potential energy relative to TS4 in PCM model.

[b] Potential energy relative to TS4 in SMD model.

We calculations on the single point energies of the transition states for Ni^0(acetylide carbanion)-ate complex catalyzed C(sp^2)−F bond activation by employing PCM and SMD solvation model. As shown in Table S1, solvent effect with both PCM and SMD model on the relative energies among the four transition states is tiny and the energy of TS4 is more stable than others does not change.

Table S2. Benchmark calculations on the relative single-point energy among the TS4, TS5, TS6 and TS7 by employing different functionals.

Functional	TS4	TS5	TS6	TS7
ωB97XD	0.0	10.0	10.6	35.2
M06	0.0	12.2	19.8	35.7
B3LYP-GD3	0.0	15.0	17.2	37.5
B3PW91	0.0	13.0	18.1	39.1
B3PW91-GD3	0.0	11.8	14.7	29.3
PBE0	0.0	11.9	16.1	34.7
PBE0-GD3	0.0	11.4	14.4	29.5

All energy terms are in kcal mol^{-1} unit.

We calculated the relative energy for Ni^0(acetylide carbanion)-ate complex catalyzed C(sp^2)−F bond activations by employing seven DFT functionals, as shown in Table S2. All results show the single-point energy of **TS4** is lower than that of **TS5**,

TS6 and **TS7**. It indicates that the **TS4** is more stable than other three analogues, which is independent on the DFT functionals.

Table S3. Benchmark calculations on the relative single-point energy among the TS4, TS5, TS6 and TS7 by employing different basis sets.

Functional	TS4	TS5	TS6	TS7
SDD + 2f/6-311G(d)	0.0	10.0	10.6	35.2
SDD + 2f/6-311G(d, p)	0.0	10.1	10.7	35.4
SDD + 2f/6-311+G(d)	0.0	10.8	11.4	34.0
SDD + 2f/6-311+G(d, p)	0.0	10.8	11.5	34.2
SDD + 2f/6-311+G(2d, p)	0.0	10.5	11.5	34.0
SDD + 2f/def2tzvp	0.0	10.1	11.9	35.7
SDD + 2f/def2qzvpp	0.0	10.1	12.1	35.4
LANL2DZ + 2f/6-311G(d)	0.0	9.8	10.9	35.6
def2tzvp	0.0	10.1	12.2	35.6

All energy terms are in kcal mol^{-1} unit.

We calculated the relative energy for (Ni^0(acetylide carbanion)-ate complex catalyzed C(sp^2)−F bond activations by employing nine combinations of basis sets, as shown in Table S3. All results show the single-point energy of **TS4** is lower than that of **TS5**, **TS6** and **TS7**. It indicates that the **TS4** is more stable than other three analogues, which is independent on the basis sets.

6. C(sp^2)–Cl bond activation

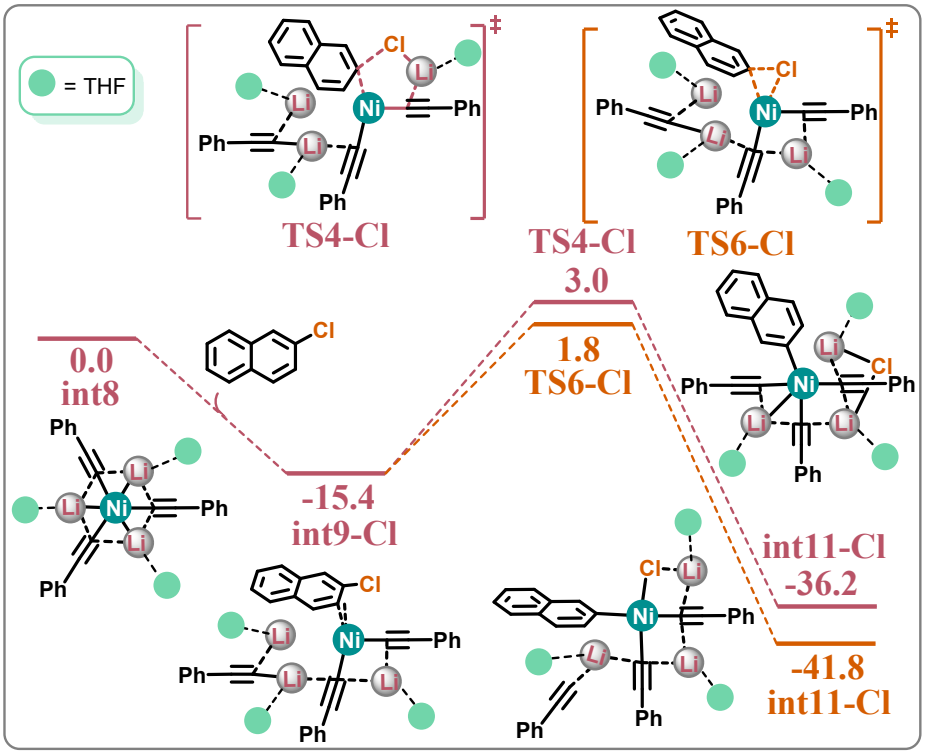


Figure S6. Gibbs energy profile of C(sp^2)–Cl activation by the $(Li^+)_3[Ni^0(CCPh)_3]^{3-}$ complex. The nickelate complexes is stabilized by solvent (THF) where solvent effect is simulated by PCM model.

The Gibbs energy profile for the Ni^0-mediated C(sp^2)–Cl bond activation, beginning from complex **int8** is shown in Figure S6. This process exhibits an activation free energy ($\Delta G^{o\ddagger}$) of 18.4 kcal mol^{-1} and is highly exergonic, with a reaction free energy (ΔG^o) of 36.2 kcal mol^{-1} relative to intermediate int9-Cl. In contrast, the activation energy ($\Delta G^{o\ddagger}$) of the concerted oxidation addition pathway is 17.2 kcal mol^{-1}, suggesting both S_NAr and concerted oxidation addition patheays are plausible for C(sp^2)–Cl bond activation. The activation energy for this step is lower than that for the corresponding C(sp^2)–F bond activation (21.7 kcal mol^{-1}), indicating C(sp^2)–Cl bond activation is more favorable because the bond dissociation energy of C(sp^2)–Cl bond is smaller

7. Implicit and explicit solvent

Table S4. Gibbs free energy of TS4, TS5, TS6, and TS7 under gas phase, PCM, SMD and explicit solvation.

$\Delta G^{o\ddagger}$	gas phase	PCM	SMD	explicit solvation [a]
TS4	30.7	21.7	25.5	18.8
TS5	40.7	32.6	34.9	28.0
TS6	48.1	35.3	36.4	34.6
TS7	69.4	60.8	63.9	54.9

[a] In explicit solvation model, THF is involved via a Li···O interaction to stabilize the nickelate complexes.

To clarify the influence of solvent molecules on the C(sp^2)–F activation, To clarify the influence of solvent molecules on the C(sp^2)–F activation, we added calculations for all four possible pathways using gas phase model, other implicit solvent model (SMD), and explicit solvent model in which THF is involved via a Li···O interaction to stabilize the nickelate complexes. As shown in Table S4, the activation energies calculated with solvent model are much lower than those calculated in gas phase, which is consistent with the experimental result that the presence of a Lewis donor is crucial for the stability of this complex and nickelate complexes. On the other hand, computational results show that the inner-sphere Ni^0-mediated nucleophilic aromatic substitution (S_NAr) for C(sp^2)–F bond activation is more favorable compared to the outer-sphere mechanism, the carbon anion attack S_NAr pathway, and the concerted oxidative addition of the C(sp^2)–F bond to the Ni^0 center, which is independent on the solvent model.

Table S5. Gibbs free energy of TS4, TS4-Na and TS4-K under PCM and explicit solvation.

	PCM	explicit solvation
TS4	21.7	18.8
TS4-Na	25.1	22.3
TS4-K	27.1	26.2

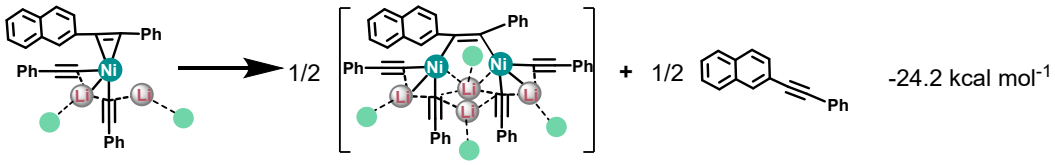
To clarify the influence of explicit solvent molecules on the C(sp^2)–F activation, we conducted additional calculations within a solvation model. As shown in Table S5, the inclusion of explicit THF molecules decreases the activation energy which suggests that Li···O interactions stabilize the transition states more than the pre-intermediates. In the explicit solvent model with Na^+ and K^+ counterion, the activation energy for C(sp^2)–F bond becomes 22.3 and 26.2 kcal mol^{-1}, respectively, which is also larger than that (18.6 kcal mol^{-1}) with Li^+ counterion. This trend is consistent with the results with PCM model, indicating that the counterion effect on reactivity is not dependent on solvent model for computation.

Table S6. Gibbs free energy of TS4, TS4-O and TS4-N under PCM and explicit solvation.

	PCM	explicit solvation
TS4	21.7	18.8
TS4-O	28.7	21.4
TS4-N	47.2	42.6

To clarify the influence of solvent molecules, we conducted additional calculations within a solvation model where THF is involved via a Li···O interaction to stabilize the nickelate complexes. As shown in Table S6, the activation energy becomes lower when THF molecules is involved. Nevertheless, in the explicit solvent model, the barriers for C(sp^2)–OMe and C(sp^2)–NMe_2 activation are also larger than

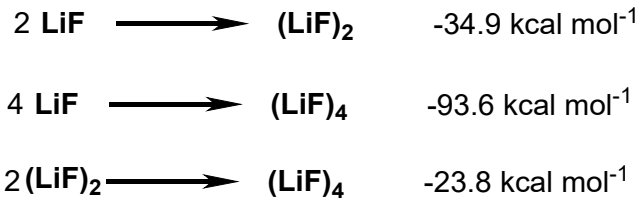
that for C(sp^2)–F bond activation, which is consistent with in the results within the implicit solvent model.



Scheme S1. Plausible conversion. The number on the right-hand side represents the Gibbs energy of reaction.

The int16 is more stable than int15 by 24.2 kcal mol^{-1}, as shown in Scheme S1.

8. LiF energy



Scheme S2. Plausible conversion. The number on the right-hand side represents the Gibbs energy of reaction.

Specifically, we calculated the energies of the dimer $(LiF)_2$ and tetramer $(LiF)_4$ of LiF. The energy decreases by 34.9 kcal mol^{-1} from the LiF monomer to the dimer $(LiF)_2$, and decreases 23.8 kcal mol^{-1} from the dimer $(LiF)_2$ to the tetramer $(LiF)_4$, as shown in Scheme S2. These results clearly indicate that the self-aggregation of LiF under the reaction conditions must be taken into account. We considered the lattice energy of LiF by using an approach as following: the energy per formula unit obtained from the more stable tetramer ($G_{tetramer}/4$) was then used as the reference energy for a "LiF molecule" in our energy profile.

9. Cartesian coordinates

18

int1, E(ωB97XD /BSII)= -485.070422 au

C	-3.016633	1.224025	0.000330
C	-1.641700	1.228234	0.000150
C	-0.918622	2.447912	0.000238
C	-1.641497	3.683758	0.000518
C	-3.059531	3.645348	0.000699
C	-3.730459	2.445010	0.000606
H	1.050058	1.546176	-0.000155
H	-3.559760	0.282763	0.000260
H	-1.087847	0.291926	-0.000063
C	0.499729	2.484135	0.000057
C	-0.923275	4.905857	0.000608
H	-3.609134	4.583861	0.000911
H	-4.817294	2.431189	0.000747
C	0.446021	4.879514	0.000424
C	1.180607	3.677663	0.000147
H	2.264830	3.722962	0.000012
H	-1.444654	5.858309	0.000819
F	1.133648	6.035175	0.000507

14

LiCCPh, E(ωB97XD /BSII)= -315.327162 au

C	1.099519	6.269259	-0.133884
C	1.711404	7.340911	-0.088158
C	2.417548	8.577727	-0.036092
C	3.706762	8.698220	-0.590338
C	1.844910	9.712368	0.570956
C	4.393254	9.906625	-0.537985
H	4.156831	7.828526	-1.060716
C	2.536560	10.917952	0.620090
H	0.850873	9.629231	1.001265
C	3.813308	11.022551	0.066695
H	5.387938	9.978864	-0.971893
H	2.076677	11.782463	1.093396
H	4.351949	11.966041	0.106340
Li	0.154951	4.615189	-0.204681

32

int2, E(ωB97XD /BSII)= -800.4018439 au

C	0.392091	1.541512	-3.268236
C	0.575658	0.524715	-2.573493
Li	0.369899	2.866093	-1.901224
C	0.755266	-0.683168	-1.826244
C	1.912753	-0.888871	-1.053075
C	-0.235939	-1.681970	-1.818794
C	2.071538	-2.048503	-0.301915
H	2.682442	-0.122270	-1.048991
C	-0.070621	-2.841002	-1.068565
H	-1.138148	-1.525946	-2.401968
C	1.081922	-3.031607	-0.305553
H	2.972470	-2.184546	0.291661
H	-0.851157	-3.598010	-1.072779
H	1.207637	-3.938627	0.280709
F	0.002282	2.993500	-0.044391
C	-2.657559	-1.197805	0.860386
C	-1.495636	-1.304686	1.586297
C	-0.521951	-0.276468	1.554000
C	-0.780318	0.873623	0.743548
C	-1.980348	0.961479	-0.001422
C	-2.898642	-0.059626	0.058581
H	0.873559	-1.244716	2.887761
H	-3.392196	-1.997709	0.890014
H	-1.299179	-2.187724	2.188259
C	0.687839	-0.357300	2.289420
C	0.221839	1.861959	0.742582
H	-2.166279	1.830809	-0.622692
H	-3.815579	0.006505	-0.520136
C	1.387582	1.798850	1.446401
C	1.617684	0.653119	2.242709
H	2.106693	2.609403	1.389236
H	2.542547	0.578900	2.806457
H	2.542547	0.578900	2.806457

32

TS1, E(ωB97XD /BSII)= -800.3564686 au

C	6.730059	12.002205	10.838751
C	7.055246	10.816414	10.650020
Li	6.218281	13.788915	10.139890
C	7.225591	9.416905	10.571672
C	8.469091	8.815956	10.292928
C	6.103841	8.591104	10.812038
C	8.583708	7.431897	10.250710
H	9.333683	9.448706	10.113794
C	6.235077	7.209134	10.774161
H	5.150590	9.056067	11.048432
C	7.470719	6.623064	10.490018
H	9.547817	6.978669	10.033446

H	5.368067	6.583226	10.970622
H	7.567017	5.540831	10.458429
F	5.536939	13.963587	11.786935
C	3.057036	9.809512	13.294140
C	4.198715	9.887322	14.061366
C	5.185635	10.878611	13.824324
C	4.966326	11.788535	12.746778
C	3.792979	11.693898	11.977888
C	2.843228	10.727286	12.245372
H	6.503357	10.302908	15.447750
H	2.316520	9.040049	13.498669
H	4.361385	9.181908	14.873396
C	6.349170	10.997564	14.627154
C	6.053826	12.680414	12.388019
H	3.638808	12.394199	11.161822
H	1.938085	10.670220	11.646559
C	7.062262	12.928820	13.337168
C	7.233529	12.034616	14.397197
H	7.794184	13.703999	13.134030
H	8.091775	12.166753	15.052221

32

int3, E(ωB97XD /BSII)= -800.4732 au

C	0.882891	-0.300442	0.322299
C	1.169771	-1.023513	-0.619184
Li	-0.914968	0.496983	-1.090659
C	1.551089	-1.887661	-1.687487
C	2.736257	-2.638404	-1.579702
C	0.748380	-1.988610	-2.839990
C	3.112537	-3.487469	-2.613084
H	3.347016	-2.550865	-0.685478
C	1.144764	-2.844208	-3.863467
H	-0.157867	-1.378719	-2.911762
C	2.317200	-3.592665	-3.755772
H	4.027156	-4.068332	-2.527722
H	0.529385	-2.922384	-4.755849
H	2.614935	-4.257481	-4.562853
F	-1.476995	-0.021924	-2.492887
C	-3.662248	0.873365	2.372576
C	-2.745977	1.712657	2.963427
C	-1.364438	1.620244	2.657815
C	-0.931746	0.632862	1.718473
C	-1.894421	-0.246995	1.157181
C	-3.231474	-0.119795	1.466685
H	-0.743879	3.217875	3.977099
H	-4.718394	0.964971	2.609975
H	-3.071702	2.467969	3.674940
C	-0.406518	2.477423	3.255866
C	0.461593	0.581777	1.358773
H	-1.565562	-1.052509	0.501218
H	-3.952913	-0.796098	1.017630
C	1.361211	1.444298	1.970651
C	0.926680	2.379756	2.928927
H	2.408721	1.399442	1.688679
H	1.652974	3.040158	3.394169

16

LiCHCHPh, E(ωB97XD /BSII)= -316.5369118 au

C	5.169213	10.685285	14.073651
C	4.277872	9.674391	13.929303
C	2.800862	9.725768	13.894516
C	2.067808	10.918791	14.018096
C	2.072690	8.535358	13.730763
C	0.678468	10.918653	13.979421
H	2.600364	11.857629	14.146334
C	0.680737	8.529820	13.691341
H	2.615985	7.596447	13.632650
C	-0.026656	9.724102	13.815684
H	0.138126	11.857835	14.077758
H	0.147264	7.590422	13.563196
H	-1.113499	9.726575	13.785754
H	4.647484	8.645545	13.817432
H	4.689275	11.672132	14.177018
Li	7.105404	10.380095	14.090940

34

int4, E(ωB97XD /BSII)= -801.6147225 au

C	0.494235	1.973329	-1.763745
C	-0.020648	0.720799	-1.707282
Li	-0.445688	3.354289	-0.700986
C	0.640657	-0.583249	-1.918349
C	2.017020	-0.718806	-2.168943
C	-0.110802	-1.765348	-1.799558
C	2.609525	-1.970554	-2.290334
H	2.627245	0.176666	-2.256370
C	0.478349	-3.021644	-1.915963
H	-1.177512	-1.686816	-1.597718
C	1.846445	-3.133722	-2.160890
H	3.678195	-2.042836	-2.482776
H	-0.133186	-3.916658	-1.818004

H	2.312934	-4.111699	-2.252210
F	-0.527974	3.216318	1.295769
C	-2.730749	-1.296479	1.181171
C	-1.384581	-1.523729	1.347065
C	-0.476308	-0.445726	1.489140
C	-0.998385	0.884695	1.450259
C	-2.388984	1.097872	1.290804
C	-3.237150	0.023349	1.157799
H	1.305672	-1.659799	1.614896
H	-3.412764	-2.134183	1.064389
H	-0.991345	-2.536575	1.349910
C	0.920096	-0.644640	1.627419
C	-0.052142	1.923111	1.520579
H	-2.777058	2.112165	1.283996
H	-4.303974	0.187831	1.033554
C	1.289659	1.746942	1.677333
C	1.778724	0.422150	1.739791
H	1.956793	2.602028	1.692282
H	2.847646	0.258845	1.834703
H	1.550121	1.989413	-2.084543
H	-1.068492	0.588506	-1.403499

34

TS2, E(ωB97XD /BSII)= -801.5835251 au

C	6.175892	12.525930	10.410696
C	5.930079	11.204868	10.176651
Li	4.596298	13.718668	10.749515
C	6.832344	10.214031	9.582207
C	8.220457	10.420008	9.485849
C	6.319380	8.994354	9.105410
C	9.051755	9.455496	8.928903
H	8.646619	11.340626	9.875545
C	7.149499	8.030456	8.542268
H	5.249137	8.808858	9.180093
C	8.522911	8.255630	8.448162
H	10.122989	9.636710	8.873472
H	6.724127	7.098039	8.177731
H	9.174936	7.503726	8.010822
F	5.721858	14.462809	12.209293
C	2.615177	10.722512	13.350429
C	3.889391	10.188330	13.401516
C	5.034128	10.984791	13.163926
C	4.823037	12.360213	12.853537
C	3.522528	12.900953	12.843877
C	2.422325	12.090155	13.090093
H	6.531741	9.450420	13.481271
H	1.755255	10.084469	13.537095
H	4.028574	9.134824	13.633414
C	6.368476	10.499731	13.254525
C	5.983695	13.086557	12.395992
H	3.383962	13.978667	12.735052
H	1.423128	12.516239	13.108063
C	7.262093	12.720580	12.838865
C	7.437119	11.380035	13.195012
H	8.091737	13.407002	12.715236
H	8.441982	11.015521	13.390845
H	7.185259	12.888425	10.169383
H	4.950016	10.798077	10.448538

34

int5, E(ωB97XD /BSII)= -801.7153341 au

C	1.041761	0.051897	0.097834
C	0.646176	-0.934975	-0.737716
Li	0.259825	0.898739	-2.461593
C	1.211762	-1.247257	-2.058312
C	2.347725	-0.601258	-2.591878
C	0.551147	-2.193254	-2.867666
C	2.788602	-0.885807	-3.880678
H	2.888966	0.132046	-1.999969
C	1.000302	-2.479433	-4.153001
H	-0.325886	-2.703579	-2.475169
C	2.118842	-1.824129	-4.666918
H	3.659611	-0.367946	-4.271805
H	0.471715	-3.212303	-4.756539
H	2.465352	-2.039978	-5.673521
F	0.270623	2.462673	-2.631833
C	-3.643363	0.113140	2.491392
C	-2.684577	0.309933	3.455443
C	-1.311447	0.410289	3.113475
C	-0.915356	0.261752	1.743973
C	-1.938651	0.107980	0.772823
C	-3.264401	0.035586	1.133993
H	-0.652928	0.790015	5.137905
H	-4.692395	0.045185	2.766537
H	-2.967260	0.409941	4.501013
C	-0.334617	0.684086	4.103389
C	0.483200	0.341981	1.421672
H	-1.675982	0.092321	-0.278875
H	-4.026709	-0.064117	0.365883
C	1.386219	0.678957	2.419796

C	0.986038	0.842362	3.758846
H	2.439571	0.776154	2.166725
H	1.728578	1.079796	4.515535
H	1.902121	0.664179	-0.174319
H	-0.180783	-1.573095	-0.430080

18

$LiCH_2CH_2Ph$, E(ωB97XD /BSII)= -317.7557518 au

C	0.414927	-0.326928	0.065878
H	0.955175	-1.140750	0.572812
H	-0.540212	-0.219294	0.601874
C	1.225510	0.985873	0.151707
H	2.151154	0.846835	-0.435361
H	0.668676	1.760221	-0.406124
Li	1.696206	1.693514	1.965952
C	0.123056	-0.755682	-1.354441
C	-1.021960	-0.305857	-2.023713
C	1.020437	-1.563655	-2.063805
C	-1.262284	-0.645591	-3.353453
H	-1.732727	0.322945	-1.489473
C	0.787352	-1.907836	-3.393698
H	1.916584	-1.924538	-1.561129
C	-0.357187	-1.449679	-4.046057
H	-2.161156	-0.286060	-3.850015
H	1.498373	-2.539749	-3.921847
H	-0.543481	-1.719136	-5.082894

36

int6, E(ωB97XD /BSII)= -802.8345383 au

C	0.256770	1.474153	-2.055225
C	-0.324815	0.045340	-1.953498
Li	-0.892126	2.918917	-1.275360
C	0.717184	-1.041893	-2.076643
C	1.281273	-1.628205	-0.936564
C	1.196188	-1.452501	-3.327678
C	2.290176	-2.584660	-1.038390
H	0.919386	-1.322832	0.043255
C	2.201101	-2.410355	-3.437534
H	0.772696	-1.005305	-4.225608
C	2.755454	-2.982267	-2.291172
H	2.711613	-3.025864	-0.136890
H	2.552428	-2.715892	-4.421084
H	3.539634	-3.731068	-2.374962
F	-1.224472	3.183112	0.631557
C	-2.353993	-1.545330	1.932600
C	-1.066142	-1.321178	2.358129
C	-0.448717	-0.058077	2.176193
C	-1.201350	0.973359	1.531272
C	-2.533075	0.727224	1.118184
C	-3.094612	-0.511900	1.314407
H	1.446743	-0.592240	3.068675
H	-2.808674	-2.522359	2.069455
H	-0.496494	-2.115938	2.833059
C	0.884346	0.202340	2.585802
C	-0.530074	2.193000	1.322103
H	-3.100687	1.521212	0.643439
H	-4.112948	-0.702082	0.987544
C	0.749474	2.456069	1.712348
C	1.466634	1.427998	2.366188
H	1.201045	3.418725	1.498325
H	2.490624	1.614037	2.674875
H	1.156657	1.507853	-1.409576
H	-0.849317	-0.102075	-0.997533
H	0.648935	1.610774	-3.076553
H	-1.085459	-0.096212	-2.736200

36

TS3, E(ωB97XD /BSII)= -802.8078653 au

C	6.607941	12.289182	10.470327
C	6.702335	10.825601	10.873128
Li	5.545028	13.954856	10.231592
C	7.569290	10.012796	9.941623
C	8.963015	10.022671	10.078356
C	7.013392	9.267940	8.895975
C	9.776194	9.314895	9.196966
H	9.408875	10.593932	10.890941
C	7.822027	8.558168	8.009141
H	5.930807	9.241040	8.781582
C	9.208091	8.579686	8.155734
H	10.856208	9.331584	9.325050
H	7.368128	7.981792	7.206073
H	9.840964	8.024061	7.468179
F	5.303150	14.331748	11.902020
C	2.956494	10.257227	13.752496
C	4.166237	10.352248	14.400876
C	5.154328	11.289283	13.999724
C	4.856340	12.137414	12.886574
C	3.608185	12.017616	12.238634
C	2.669559	11.100075	12.657183
H	6.611066	10.763447	15.518333

H	2.218472	9.530036	14.081847
H	4.386467	9.702127	15.244975
C	6.395727	11.411682	14.673866
C	5.875302	13.039348	12.430720
H	3.384917	12.665850	11.393784
H	1.713723	11.022347	12.145886
C	7.034626	13.222523	13.178409
C	7.298955	12.369881	14.263266
H	7.754187	13.975917	12.873498
H	8.240823	12.488887	14.794506
H	7.607782	12.756155	10.481751
H	7.105601	10.767928	11.891576
H	6.268935	12.302572	9.397844
H	5.693474	10.395190	10.917646

36

int7, E(ωB97XD /BSII)= -802.950906 au

C	0.815990	0.275760	-0.430338
C	1.211106	-1.212837	-0.551402
Li	-0.756453	2.876302	1.460847
C	1.671129	-1.549278	-1.946195
C	3.008952	-1.383970	-2.318951
C	0.755856	-1.976493	-2.913810
C	3.423554	-1.640834	-3.624114
H	3.732734	-1.052669	-1.576496
C	1.164863	-2.234504	-4.220422
H	-0.288499	-2.113011	-2.637603
C	2.501622	-2.066750	-4.579436
H	4.468266	-1.510432	-3.894962
H	0.439992	-2.569542	-4.958056
H	2.823529	-2.268983	-5.597613
F	-0.909204	4.171425	0.577569
C	-3.712030	-0.297335	2.113279
C	-2.857454	0.302816	3.004440
C	-1.519939	0.607374	2.637238
C	-1.061698	0.284121	1.314884
C	-1.981605	-0.326057	0.418777
C	-3.268238	-0.611040	0.808370
H	-0.994566	1.506669	4.538843
H	-4.733492	-0.524919	2.404912
H	-3.192742	0.557219	4.006956
C	-0.635501	1.252128	3.544761
C	0.283923	0.614272	0.936942
H	-1.665319	-0.564917	-0.590888
H	-3.954409	-1.074968	0.105275
C	1.103848	1.239517	1.861707
C	0.651654	1.561923	3.163865
H	2.115109	1.512552	1.571336
H	1.320981	2.069371	3.852686
H	1.694224	0.894306	-0.644730
H	2.003224	-1.425339	0.177253
H	0.082021	0.524153	-1.205583
H	0.356521	-1.841180	-0.272112

43

int8, E(ωB97XD /BSII)= -1117.0148778 au

Ni	6.909366	10.066369	14.048811
C	7.652240	9.313071	15.585809
C	5.058999	10.305524	14.023684
C	7.743200	9.685507	12.423612
C	8.154070	9.121706	11.381448
C	3.819733	10.121171	13.968351
C	8.011211	8.519964	16.488518
Li	8.782110	8.625195	13.933230
Li	5.553170	9.374007	15.859205
Li	5.663599	9.824034	12.052303
C	2.398661	10.011238	13.916502
C	1.580407	11.155196	14.032717
C	1.771575	8.758104	13.747969
C	0.195166	11.043843	13.981770
H	2.052139	12.125103	14.162732
C	0.385477	8.656822	13.698213
H	2.390404	7.868552	13.657055
C	-0.411167	9.797338	13.814607
H	-0.417021	11.937840	14.073318
H	-0.076745	7.681219	13.567688
H	-1.494095	9.715462	13.775396
C	8.465092	7.697472	17.561708
C	8.167603	6.318294	17.597746
C	9.225525	8.242632	18.618227
C	8.613013	5.521334	18.646785
H	7.582337	5.885380	16.789937
C	9.666459	7.437629	19.662935
H	9.460527	9.303117	18.600980
C	9.364434	6.074674	19.685121
H	8.372274	4.460924	18.654517
H	10.251127	7.877692	20.467231
H	9.711265	5.449688	20.503703
C	8.669034	8.567237	10.172472
C	9.480650	9.337385	9.312328

C	8.382342	7.235712	9.802612
C	9.980906	8.793272	8.134379
H	9.707905	10.363603	9.586890
C	8.887240	6.700400	8.622559
H	7.758117	6.631230	10.456412
C	9.688857	7.474353	7.781503
H	10.604395	9.403863	7.485669
H	8.653795	5.672073	8.356982
H	10.082148	7.053642	6.859928

61

int9, E(ωB97XD /BSII)= -1602.1241908 au

C	-0.630382	-1.691478	2.322564
C	-1.214955	-0.172920	-0.724009
C	1.788054	-0.573811	0.813067
C	2.337139	-0.623840	-0.303363
C	-1.009851	0.397676	-1.806454
C	-1.541554	-2.506868	2.089889
Li	-0.000095	-1.702085	0.251723
Li	0.636160	1.002808	-0.277571
C	-0.751525	1.123949	-3.012519
C	-1.587655	2.191721	-3.388186
C	0.371678	0.824878	-3.804925
C	-1.299603	2.943661	-4.522032
H	-2.454264	2.422770	-2.775810
C	0.654592	1.586189	-4.934586
H	1.021479	0.002028	-3.524993
C	-0.175828	2.647172	-5.296599
H	-1.953311	3.765531	-4.803026
H	1.532801	1.345967	-5.527543
H	0.048581	3.239985	-6.179526
C	-2.589812	-3.462482	1.901442
C	-2.926887	-4.374457	2.919361
C	-3.309086	-3.505185	0.689882
C	-3.949903	-5.297461	2.726620
H	-2.375699	-4.345952	3.854712
C	-4.332878	-4.429724	0.508208
H	-3.055084	-2.804269	-0.103236
C	-4.657538	-5.330034	1.523993
H	-4.197263	-5.996162	3.521964
H	-4.878169	-4.448326	-0.432142
H	-5.456296	-6.052616	1.379199
C	2.934129	-0.583744	-1.601934
C	3.549399	0.596092	-2.067376
C	2.853304	-1.686445	-2.475046
C	4.041507	0.674847	-3.365814
H	3.622713	1.448635	-1.397716
C	3.349817	-1.601493	-3.772155
H	2.389442	-2.604537	-2.124528
C	3.940084	-0.420008	-4.225651
H	4.503322	1.596585	-3.709972
H	3.272246	-2.460050	-4.434086
H	4.323436	-0.355880	-5.240471
Ni	0.621131	-0.277907	2.274593
C	-0.070199	1.058366	3.517363
F	0.176489	0.735726	4.830690
C	1.017517	1.589911	2.730991
C	-1.420672	1.477236	3.242995
C	0.684666	2.450139	1.606015
H	2.004618	1.694205	3.179631
C	-1.728580	2.224954	2.138543
H	-2.189516	1.160116	3.944727
C	-0.680821	2.719524	1.268899
C	1.692594	2.953556	0.750785
H	-2.757994	2.513316	1.933702
C	-0.971364	3.434498	0.090697
C	1.376174	3.643737	-0.416385
H	2.730837	2.749904	1.002345
C	0.034238	3.883176	-0.754823
H	-2.013579	3.605232	-0.169489
H	2.171466	3.985653	-1.073591
H	-0.214916	4.390973	-1.681028
Li	-1.777338	-0.136691	1.307164

61

int10, E(ωB97XD /BSII)= -1602.110892 au

C	7.543828	10.114491	14.202650
C	5.312541	7.733811	13.701566
C	6.873180	10.541136	11.377860
C	7.105319	9.982844	10.289148
C	4.905013	7.631020	12.530603
C	8.287099	9.369931	14.860803
C	4.396457	7.739951	11.198274
C	3.271853	8.560842	10.946028
C	5.053239	7.157749	10.097290
C	2.854784	8.814877	9.637268
H	2.734670	8.990681	11.788295
C	4.634558	7.418623	8.796630
H	5.920670	6.528501	10.271771
C	3.541660	8.252833	8.557508

H	1.986962	9.447691	9.466444	Li	5.828389	9.199238	15.081934
H	5.192173	6.998979	7.964314	Li	4.803471	10.462363	10.946180
H	3.227379	8.463688	7.539389	Li	7.028890	8.675981	12.660814
C	9.162007	8.527546	15.616109	61			
C	10.332735	9.038819	16.204988	TS4, E(ωB97XD /BSII)= -1602.0832201 au			
C	8.857898	7.161342	15.780615	C	8.768238	10.206713	13.605339
C	11.172405	8.204384	16.936280	C	5.639768	7.951361	13.403231
H	10.569259	10.091427	16.080150	C	7.135774	10.368831	11.114950
C	9.704910	6.335527	16.512974	C	6.559059	9.733364	10.218707
H	7.951315	6.763059	15.329171	C	4.463846	7.895526	13.012974
C	10.864287	6.852317	17.093503	C	9.547520	9.453339	14.203185
H	12.073830	8.612573	17.386500	Li	6.868289	12.342367	10.381690
H	9.457597	5.283581	16.631788	Li	7.552154	8.406973	13.852661
H	11.523680	6.205068	17.665785	Li	5.371797	9.800619	12.389297
C	7.376281	9.363523	9.030353	C	3.117054	7.932632	12.523994
C	8.126994	8.175133	8.956000	C	2.046228	8.230744	13.387996
C	6.841234	9.892235	7.840421	C	2.850836	7.738904	11.154113
C	8.311599	7.526348	7.739504	C	0.751156	8.338251	12.891435
H	8.558874	7.763703	9.864866	H	2.250940	8.395535	14.441108
C	7.031641	9.241789	6.626107	C	1.552984	7.855138	10.665729
H	6.269477	10.815508	7.883869	H	3.669998	7.500270	10.483151
C	7.760409	8.052364	6.569607	C	0.499146	8.155774	11.529998
H	8.890445	6.606949	7.703498	H	-0.065869	8.572271	13.569551
H	6.607633	9.663994	5.718541	H	1.368804	7.709272	9.604437
H	7.905468	7.543969	5.620206	H	-0.513766	8.246374	11.146063
Ni	6.250989	10.963999	13.097609	C	10.452050	8.587893	14.897137
F	3.767267	11.736874	11.797528	C	11.343360	7.762431	14.184619
C	4.700343	12.763934	18.010924	C	10.452047	8.527604	16.304241
C	5.011887	13.536418	16.900411	C	12.205098	6.905407	14.861506
C	4.898970	13.018346	15.599302	H	11.350973	7.812015	13.099293
C	4.467341	11.673239	15.427104	C	11.315872	7.666496	16.973507
C	4.108984	10.919357	16.562646	H	9.770898	9.168267	16.857595
C	4.237416	11.452110	17.839646	C	12.194057	6.852683	16.256273
H	5.517232	14.832121	14.566742	H	12.889280	6.275754	14.298396
H	4.801341	13.179521	19.009659	H	11.305157	7.631365	18.059900
H	5.348156	14.563391	17.029565	H	12.867600	6.180990	16.781966
C	5.176208	13.808714	14.425777	C	5.882814	8.865122	9.307608
C	4.467880	11.102246	14.096778	C	4.855565	9.349844	8.477141
H	3.697931	9.916057	16.429594	C	6.177868	7.488614	9.294542
H	3.967450	10.852648	18.705507	C	4.142794	8.480995	7.657241
C	4.663029	11.942644	12.947016	H	4.611998	10.409209	8.497288
C	5.003159	13.328294	13.161464	C	5.456538	6.625672	8.476156
H	5.173274	13.956658	12.291918	H	6.956006	7.111622	9.950602
H	3.909816	10.173442	13.953368	C	4.438298	7.116848	7.656047

H	3.348659	8.868047	7.024383
H	5.683925	5.563161	8.484211
H	3.875160	6.437921	7.021480
Ni	7.457244	11.246042	12.705044
F	6.176574	13.591108	11.268058
C	2.518357	11.974217	16.370339
C	3.813795	12.425856	16.335798
C	4.552280	12.441734	15.120493
C	3.914721	11.992276	13.910223
C	2.568867	11.530101	13.983364
C	1.894636	11.521342	15.178116
H	6.343890	13.301277	15.960428
H	1.966767	11.960041	17.306279
H	4.301612	12.772637	17.244411
C	5.886108	12.891900	15.061757
C	4.645688	11.976563	12.704508
H	2.087725	11.169282	13.077590
H	0.868254	11.164044	15.212707
C	5.996217	12.361907	12.678845
C	6.613086	12.861041	13.876588
H	7.582847	13.359859	13.828707
H	4.147392	11.676351	11.780008

61

TS5, E(ωB97XD /BSII)= -1602.0672071 au

C	8.720735	10.341937	13.310074
C	5.486623	8.365994	14.201769
C	6.541618	9.949626	11.312357
C	5.769392	9.100381	10.852420
C	4.254599	8.485506	14.299034
C	9.520897	9.659423	13.961488
Li	5.002437	14.321097	12.129045
Li	7.385247	8.652544	13.496550
Li	5.044646	9.983330	12.885779
C	2.842089	8.721594	14.318410
C	2.173854	9.056610	15.510534
C	2.106404	8.702087	13.114321
C	0.819892	9.374755	15.496055
H	2.738246	9.082332	16.437524
C	0.755021	9.038012	13.107096
H	2.603136	8.411365	12.191496
C	0.106497	9.378764	14.295442
H	0.318976	9.631041	16.426602
H	0.205425	9.021141	12.169198
H	-0.949616	9.636020	14.287896
C	10.480707	8.915873	14.715296
C	11.797746	8.755756	14.244635
C	10.124715	8.320288	15.941142
C	12.725194	8.024429	14.979520
H	12.076345	9.211496	13.298901
C	11.056853	7.584927	16.666527
H	9.112467	8.448621	16.316672
C	12.360064	7.434525	16.190723
H	13.738983	7.911403	14.603244
H	10.765024	7.130084	17.609873
H	13.086876	6.861044	16.760186
C	4.779559	8.178642	10.392051
C	3.864923	8.555877	9.389592
C	4.638019	6.915021	10.997666
C	2.837503	7.696372	9.012512
H	3.972631	9.530252	8.921049
C	3.604634	6.064599	10.617713
H	5.316827	6.635742	11.796936
C	2.700658	6.449914	9.626454
H	2.137935	8.001901	8.238301
H	3.499511	5.099218	11.105780
H	1.892745	5.783661	9.335428
Ni	7.301879	11.215611	12.405746
F	5.830719	13.313452	10.922356
C	3.416951	13.229073	16.695871
C	4.684595	13.526331	16.262506
C	5.104152	13.196040	14.945177
C	4.176651	12.550633	14.043650
C	2.868593	12.253421	14.533552
C	2.509833	12.581030	15.816289
H	7.091928	14.015322	15.136667
H	3.108413	13.473931	17.707984
H	5.398245	14.008875	16.927300
C	6.405275	13.487717	14.476366
C	4.582186	12.220542	12.728644
H	2.170696	11.725087	13.887763
H	1.514856	12.321636	16.167792
C	5.939266	12.425599	12.265237
C	6.831569	13.138584	13.197927
H	7.789937	13.512535	12.829901
H	3.867145	11.757816	12.044381

61

TS6, E(ωB97XD /BSII)= -1602.066354 au

C	6.791099	9.420748	13.793725

C	6.409505	10.780636	10.581453	C	6.350684	12.636045	13.837427
C	9.426309	10.479059	12.158602	C	7.697088	14.480292	12.190739
C	9.873345	10.326574	11.005443	H	9.484605	13.326785	12.665192
C	6.658454	11.499014	9.601447	C	5.647226	13.658728	13.247005
C	5.895796	8.611991	13.477439	H	5.890240	11.981954	14.576442
Li	7.569378	9.305182	11.693282	C	6.279589	14.590422	12.375614
Li	8.224591	11.956891	11.112689	C	8.340254	15.436435	11.358069
C	7.061838	12.382957	8.548898	H	4.588926	13.787178	13.471812
C	6.685145	13.739109	8.587926	C	5.569814	15.626601	11.726094
C	7.909351	11.931983	7.519662	C	7.620555	16.433536	10.738734
C	7.141662	14.617348	7.611259	H	9.416822	15.366914	11.216933
H	6.056036	14.097096	9.397757	C	6.222144	16.533310	10.916959
C	8.358550	12.820162	6.548874	H	4.494719	15.699097	11.878109
H	8.229759	10.894748	7.507092	H	8.133407	17.151998	10.104399
C	7.975263	14.162097	6.588509	H	5.667055	17.325666	10.422614
H	6.852449	15.663480	7.660607	Li	5.690364	10.846121	12.526716
H	9.022656	12.461864	5.767264	61			
H	8.332599	14.852892	5.829117	TS7, E(ωB97XD /BSII)= -1602.0270811 au			
C	4.848022	7.666443	13.227954	C	5.175778	10.297106	13.546358
C	4.411650	6.795078	14.243591	C	3.321825	12.612355	13.408865
C	4.232425	7.595182	11.962116	C	6.642074	11.341710	11.659417
C	3.392003	5.881884	13.995608	C	7.875259	10.890980	11.576080
H	4.883641	6.847468	15.220218	C	4.177369	12.735841	14.307276
C	3.208265	6.683130	11.725877	C	5.520287	9.409186	14.331897
H	4.566529	8.261804	11.168909	Li	7.807959	12.244724	10.120560
C	2.785363	5.822685	12.739776	Li	2.123069	13.390974	12.032979
H	3.066667	5.213404	14.788636	Li	6.500717	9.246755	12.275455
H	2.741798	6.641777	10.744917	C	5.084373	12.844793	15.406774
H	1.987651	5.108859	12.552305	C	6.470042	12.937714	15.175539
C	10.372823	10.279685	9.665125	C	4.616141	12.830132	16.731781
C	11.070614	11.378913	9.126625	C	7.359798	13.003825	16.242026
C	10.117439	9.173603	8.831643	H	6.828104	12.926619	14.149766
C	11.478443	11.376990	7.797059	C	5.512562	12.908576	17.794398
H	11.283547	12.232163	9.765288	H	3.549144	12.743281	16.914090
C	10.534483	9.174839	7.504441	C	6.885447	12.992908	17.555897
H	9.585667	8.316670	9.236786	H	8.427823	13.062950	16.047563
C	11.210988	10.278058	6.979859	H	5.137701	12.892405	18.814643
H	12.005396	12.238761	7.396438	H	7.582006	13.046214	18.388549
H	10.327697	8.312947	6.875350	C	6.038303	8.624510	15.408076
H	11.531671	10.278141	5.941524	C	6.437295	9.284516	16.586511
Ni	8.325876	10.661942	13.687082	C	6.248021	7.240168	15.299725
C	7.746386	12.423281	13.547146	C	7.044626	8.573337	17.615221
F	8.450698	12.030001	15.115295	H	6.277233	10.354940	16.669194
C	8.405231	13.400300	12.788498	C	6.857965	6.536207	16.334109

H	5.935140	6.721776	14.396400	Li	0.982908	0.125494	1.989200
C	7.262655	7.198911	17.493049	Li	-2.244277	-0.843002	0.042259
H	7.352039	9.096932	18.517183	C	-0.619576	-3.085573	2.185726
H	7.020213	5.466040	16.233448	C	-1.432903	-2.972518	3.328773
H	7.741212	6.647352	18.298183	C	0.042441	-4.302450	1.938042
C	8.592790	9.878848	12.341500	C	-1.579819	-4.049513	4.197692
C	9.161304	8.758079	11.690580	H	-1.937708	-2.030867	3.531275
C	8.691015	9.941073	13.753027	C	-0.111448	-5.374236	2.811566
C	9.773931	7.740221	12.422157	H	0.672456	-4.389402	1.057663
H	9.125101	8.710292	10.604153	C	-0.921611	-5.252888	3.941609
C	9.312718	8.924439	14.470486	H	-2.208486	-3.948070	5.078355
H	8.231420	10.776311	14.273975	H	0.404797	-6.309088	2.609787
C	9.852835	7.816880	13.813046	H	-1.037914	-6.092597	4.621445
H	10.198532	6.887160	11.897950	C	4.414848	0.926499	0.613289
H	9.334703	8.978021	15.555562	C	5.047404	2.013648	-0.022816
H	10.324124	7.020075	14.381502	C	5.140755	0.175398	1.554304
Ni	4.989096	11.689296	12.369862	C	6.366034	2.335855	0.280683
F	7.012449	13.403093	9.133102	H	4.489673	2.592122	-0.755679
C	1.390194	15.156788	10.421337	C	6.458959	0.505381	1.853236
C	2.638023	15.540791	10.898808	H	4.658940	-0.667344	2.042678
C	3.754942	14.677939	10.819093	C	7.075884	1.584844	1.219347
C	3.588574	13.381513	10.229734	H	6.841725	3.176916	-0.217326
C	2.312690	13.021579	9.727122	H	7.008286	-0.082765	2.584007
C	1.230256	13.886761	9.821230	H	8.105620	1.839814	1.455817
H	5.100043	15.923324	11.984048	C	-4.288360	0.966083	-1.687104
H	0.542833	15.831475	10.501618	C	-5.076846	1.963594	-1.083145
H	2.760832	16.511915	11.373186	C	-4.890771	0.100736	-2.619810
C	5.012002	14.990155	11.432379	C	-6.425247	2.085959	-1.402835
C	4.663035	12.441456	10.331988	H	-4.613675	2.639640	-0.370026
H	2.188686	12.034258	9.288082	C	-6.239964	0.230917	-2.934916
H	0.259386	13.588043	9.434916	H	-4.282943	-0.659959	-3.102893
C	5.974341	12.867644	10.644019	C	-7.012896	1.221148	-2.327427
C	6.046551	14.102715	11.409584	H	-7.020324	2.863354	-0.930271
H	6.977673	14.349860	11.915121	H	-6.689053	-0.441527	-3.661498
H	4.525304	11.470948	9.853687	H	-8.066269	1.320751	-2.575563
61				Ni	0.065869	0.550041	-0.509069
int11, E(ωB97XD /BSII)= -1602.1928963 au				F	0.990259	1.726325	2.571490
C	1.875181	0.507017	-0.052594	C	0.402976	2.354751	-1.057312
C	-0.229160	-1.076277	0.467658	C	1.344964	2.725324	-2.005036
C	-1.696915	0.786799	-1.077270	C	-0.205565	3.405107	-0.301363
C	-2.904550	0.826851	-1.344949	C	1.722091	4.075636	-2.221368
C	-0.459913	-1.980403	1.286146	H	1.855745	1.953552	-2.577525
C	3.051007	0.632015	0.304594	C	0.160734	4.729846	-0.457731
Li	1.504405	2.470887	1.116598	H	-0.980103	3.148746	0.419901

C	1.134148	5.104763	-1.417159
C	2.705102	4.441435	-3.180625
H	-0.311170	5.503676	0.146098
C	1.544870	6.450020	-1.606530
C	3.084051	5.753741	-3.338730
H	3.153491	3.659681	-3.790431
C	2.497683	6.769765	-2.545257
H	1.090463	7.227088	-0.994908
H	3.837077	6.017595	-4.077298
H	2.804375	7.803615	-2.681877

61

int12, E(ωB97XD /BSII)= -1602.1602285 au

C	-1.229685	-1.933050	2.129756
C	-2.663827	-0.517935	-0.602693
C	0.605012	-0.555929	0.843126
C	1.252443	-0.788305	-0.188257
C	-2.114214	0.064945	-1.555890
C	-1.699877	-3.062257	1.944783
Li	-1.074642	-1.847284	-0.021759
Li	-0.366621	0.966612	-0.364336
C	-1.326016	0.861933	-2.452988
C	-1.167283	2.242952	-2.185692
C	-0.555232	0.281544	-3.480204
C	-0.240183	3.003250	-2.897585
H	-1.757427	2.703423	-1.394569
C	0.349238	1.053996	-4.198368
H	-0.652785	-0.780778	-3.680852
C	0.518474	2.409559	-3.905045
H	-0.105265	4.050668	-2.641500
H	0.956023	0.584717	-4.966911
H	1.250135	2.996703	-4.453020
C	-2.217806	-4.386640	1.775592
C	-1.662117	-5.471934	2.476632
C	-3.285593	-4.624788	0.888994
C	-2.165567	-6.756146	2.294645
H	-0.839117	-5.291020	3.161625
C	-3.780108	-5.913349	0.710599
H	-3.721445	-3.789759	0.344016
C	-3.223317	-6.982852	1.412699
H	-1.729301	-7.585657	2.845193
H	-4.605397	-6.081631	0.023521
H	-3.612488	-7.988028	1.274274
C	2.042798	-0.868023	-1.379733
C	2.766398	0.260351	-1.811185
C	2.067098	-2.030058	-2.171492
C	3.485952	0.223909	-3.000117
H	2.741692	1.165915	-1.211126
C	2.783355	-2.056732	-3.364013
H	1.525191	-2.912058	-1.838794
C	3.494925	-0.931348	-3.783145
H	4.035039	1.105117	-3.321211
H	2.791564	-2.961698	-3.965987
H	4.056306	-0.956510	-4.713366
Ni	-0.738637	-0.081190	1.996148
C	-0.407996	1.811567	1.622530
F	-2.438394	0.319165	2.727750
C	0.789152	2.349510	1.153528
C	-1.537859	2.693072	1.612141
C	0.897928	3.661708	0.610713
H	1.689336	1.735728	1.154510
C	-1.470987	3.973736	1.109066
H	-2.474628	2.314275	2.006084
C	-0.267077	4.486601	0.558919
C	2.107662	4.148408	0.051428
H	-2.358955	4.604651	1.102147
C	-0.182629	5.759073	-0.061152
C	2.158566	5.383982	-0.552921
H	2.996394	3.521968	0.103455
C	1.001553	6.196987	-0.611587
H	-1.072469	6.384248	-0.098797
H	3.089881	5.742669	-0.984054
H	1.053453	7.172774	-1.087879
Li	-3.138619	-0.717149	1.487267

2

LiF, E(ωB97XD /BSII)= -107.4720023 au

Li	6.834584	12.340823	10.733644
F	6.320267	13.638342	11.424670

59

int13, E(ωB97XD /BSII)= -1494.6657377 au

C	1.752085	0.289164	0.646557
C	0.455216	-2.261374	0.572290
C	-1.399509	-0.719399	-0.966006
C	-2.498864	-0.971611	-1.482243
C	0.592823	-3.412981	1.017703
C	2.772285	0.712051	1.211290
Li	2.082337	-1.453773	1.603616
Li	-1.456692	-2.585611	-0.206272
C	0.774353	-4.753973	1.493867

C	0.262260	-5.146876	2.744708
C	1.468986	-5.697506	0.713668
C	0.442216	-6.449552	3.199478
H	-0.274550	-4.420617	3.349374
C	1.643952	-6.997713	1.176673
H	1.864745	-5.395454	-0.251985
C	1.132335	-7.377532	2.418417
H	0.042387	-6.741456	4.166888
H	2.181893	-7.717706	0.565793
H	1.271105	-8.394027	2.776465
C	3.822084	1.520309	1.753790
C	5.011702	0.965018	2.255776
C	3.661622	2.919133	1.787421
C	6.009931	1.781393	2.779214
H	5.153792	-0.113212	2.218891
C	4.662816	3.728989	2.311963
H	2.744308	3.348640	1.394974
C	5.839081	3.165569	2.810764
H	6.925480	1.336207	3.160775
H	4.525281	4.807202	2.329957
H	6.619424	3.802375	3.219336
C	-3.775436	-0.897632	-2.126191
C	-4.371899	0.363604	-2.319060
C	-4.456858	-2.042433	-2.573848
C	-5.612946	0.466776	-2.937539
H	-3.842780	1.248641	-1.977338
C	-5.698693	-1.932001	-3.192435
H	-3.997558	-3.020522	-2.445408
C	-6.282011	-0.678046	-3.375322
H	-6.060311	1.447152	-3.080754
H	-6.211454	-2.827141	-3.535680
H	-7.251701	-0.592793	-3.858884
Ni	0.219316	-0.457281	-0.093005
C	-0.029895	1.321842	-0.724229
C	-0.724774	2.256737	0.016633
C	0.502268	1.713754	-1.982802
C	-0.917293	3.584950	-0.445413
H	-1.142824	1.980122	0.983294
C	0.335504	2.992152	-2.462913
H	1.051364	0.983402	-2.572436
C	-0.375920	3.965292	-1.714633
C	-1.630479	4.555382	0.306743
H	0.750309	3.274625	-3.429563
C	-0.569065	5.292170	-2.175379
C	-1.801619	5.835966	-0.167369
H	-2.042389	4.266279	1.272050
C	-1.265475	6.210094	-1.422185
H	-0.154603	5.574796	-3.141559
H	-2.350803	6.566382	0.422376
H	-1.405825	7.224261	-1.788332

59

TS8, E(ωB97XD /BSII)= -1494.6457511 au

C	1.488255	1.304876	0.080151
C	0.263184	-1.328203	0.073818
C	-1.582663	0.307751	-1.521831
C	-2.650125	0.062106	-2.102277
C	0.399029	-2.490335	0.490875
C	2.593213	1.549686	0.659183
Li	2.034750	-0.502237	0.890442
Li	-1.582785	-1.592841	-0.842259
C	0.561623	-3.831912	0.965957
C	0.076787	-4.206406	2.233596
C	1.208276	-4.798122	0.171876
C	0.235950	-5.511120	2.689663
H	-0.421520	-3.462710	2.849532
C	1.363183	-6.100266	0.636512
H	1.584703	-4.511654	-0.806327
C	0.878404	-6.461220	1.894495
H	-0.142551	-5.787486	3.670230
H	1.864821	-6.836651	0.014206
H	1.001264	-7.479252	2.254101
C	3.540671	2.600639	0.953465
C	4.692793	2.364212	1.720458
C	3.313732	3.903161	0.465801
C	5.590922	3.392076	1.995313
H	4.874980	1.360838	2.099381
C	4.212843	4.927039	0.741761
H	2.426110	4.097372	-0.128249
C	5.354341	4.677334	1.507131
H	6.477650	3.190185	2.591546
H	4.020842	5.926317	0.358245
H	6.055212	5.480394	1.721578
C	-3.905381	-0.058382	-2.779521
C	-4.931234	0.877138	-2.546453
C	-4.146406	-1.109688	-3.683806
C	-6.155934	0.757475	-3.195087
H	-4.747739	1.694327	-1.855026
C	-5.374165	-1.223364	-4.328852

H	-3.352420	-1.824416	-3.888008
C	-6.384474	-0.292155	-4.086421
H	-6.936818	1.489728	-3.005469
H	-5.541341	-2.039412	-5.027528
H	-7.342643	-0.381593	-4.591550
Ni	0.046718	0.445066	-0.556428
C	0.342153	2.341512	-0.902934
C	-0.277129	3.308873	-0.123279
C	0.887601	2.730872	-2.164049
C	-0.377698	4.655333	-0.546975
H	-0.672417	3.033133	0.851539
C	0.800706	4.026645	-2.604931
H	1.387619	1.977979	-2.766545
C	0.173069	5.028114	-1.815154
C	-0.994767	5.655133	0.250566
H	1.220661	4.307867	-3.568931
C	0.085402	6.379321	-2.230486
C	-1.065861	6.959085	-0.181811
H	-1.410051	5.369985	1.214942
C	-0.520367	7.325784	-1.434491
H	0.506336	6.658797	-3.194266
H	-1.540841	7.714130	0.439685
H	-0.581210	8.359165	-1.766446

59

int15, E(ωB97XD /BSII)= -1494.6720303 au

C	2.247868	1.907351	0.288469
C	0.666776	-1.246188	0.109505
C	-1.850336	0.321238	-0.328477
C	-3.068478	0.086010	-0.376853
C	0.910245	-2.411720	0.485214
C	2.990238	1.836034	1.268996
Li	1.994155	-0.089458	1.154362
Li	-1.404965	-1.612937	0.038412
C	1.247767	-3.759877	0.822115
C	1.105986	-4.233707	2.141677
C	1.728141	-4.643445	-0.165238
C	1.437827	-5.546468	2.460197
H	0.734685	-3.558789	2.908830
C	2.052140	-5.955809	0.161904
H	1.842357	-4.282149	-1.183313
C	1.910362	-6.412921	1.473268
H	1.325216	-5.895800	3.483352
H	2.420424	-6.625648	-0.610901
H	2.166737	-7.438530	1.724667
C	3.824735	1.778857	2.421327
C	5.132064	1.253519	2.341368
C	3.346156	2.218182	3.674329
C	5.926098	1.169461	3.479646
H	5.513832	0.927253	1.377561
C	4.152029	2.129663	4.803583
H	2.344736	2.634484	3.740810
C	5.442608	1.604233	4.715094
H	6.932042	0.765331	3.400418
H	3.769997	2.476061	5.760465
H	6.067703	1.537147	5.601146
C	-4.481993	0.076273	-0.593206
C	-5.031749	0.900522	-1.595431
C	-5.348239	-0.732832	0.163610
C	-6.402646	0.906236	-1.828077
H	-4.362694	1.527551	-2.178472
C	-6.719581	-0.720236	-0.074310
H	-4.935063	-1.361934	0.948807
C	-7.252884	0.097519	-1.070973
H	-6.811653	1.546880	-2.605754
H	-7.375197	-1.350125	0.522128
H	-8.323986	0.105579	-1.255954
Ni	0.005721	0.454688	-0.358626
C	1.395219	1.864381	-0.841229
C	0.037158	2.372602	-0.777950
C	1.961857	1.581101	-2.153889
C	-0.636075	2.750449	-2.015103
H	-0.272777	2.904390	0.122116
C	1.273109	1.845612	-3.290820
H	2.958871	1.150091	-2.194579
C	-0.038211	2.454029	-3.266771
C	-1.898129	3.363493	-1.991956
H	1.716824	1.617144	-4.257485
C	-0.729582	2.770766	-4.449032
C	-2.566928	3.666930	-3.170336
H	-2.361846	3.570733	-1.030358
C	-1.981567	3.367231	-4.407781
H	-0.266050	2.540453	-5.406619
H	-3.547290	4.136024	-3.130308
H	-2.503859	3.603608	-5.331354

61

TS9, E(ωB97XD /BSII)= -1602.153518 au

C	1.880965	0.577788	-0.072687
C	-0.154997	-1.267346	0.494754

C	-1.577165	0.772046	-1.144655
C	-2.779870	0.915363	-1.413081
C	-0.441608	-2.214071	1.245237
C	3.032173	0.255144	0.440168
Li	2.448671	1.796609	2.011292
Li	1.440251	-0.530163	1.894208
Li	-2.130420	-0.813105	0.029271
C	-0.720777	-3.329604	2.098628
C	-1.012937	-3.126861	3.461328
C	-0.707059	-4.643296	1.593787
C	-1.281261	-4.210566	4.291637
H	-1.020905	-2.113749	3.855653
C	-0.979895	-5.720055	2.431594
H	-0.474190	-4.802821	0.544817
C	-1.267559	-5.509227	3.780918
H	-1.501113	-4.040043	5.342335
H	-0.964226	-6.729870	2.029710
H	-1.477902	-6.353500	4.432025
C	4.267196	0.989973	0.587241
C	4.880304	1.660325	-0.497742
C	4.871619	1.117365	1.862765
C	6.013365	2.440539	-0.304122
H	4.450833	1.554025	-1.488483
C	5.993280	1.924690	2.050666
H	4.459586	0.550752	2.697774
C	6.570414	2.590268	0.969690
H	6.464723	2.947099	-1.154243
H	6.429831	2.012137	3.042748
H	7.454063	3.206285	1.112485
C	-4.145082	1.166615	-1.764026
C	-4.891994	2.145202	-1.080602
C	-4.773254	0.433445	-2.788822
C	-6.222652	2.378505	-1.412967
H	-4.409542	2.719052	-0.294270
C	-6.104267	0.673316	-3.115979
H	-4.198756	-0.315115	-3.327871
C	-6.834900	1.644517	-2.430009
H	-6.784639	3.139459	-0.877096
H	-6.573104	0.101090	-3.912704
H	-7.874401	1.829665	-2.687764
Ni	0.146400	0.297311	-0.449816
F	1.540563	0.791577	3.026689
C	1.356378	1.966576	-0.601829
C	1.831961	2.438525	-1.820778
C	0.847266	2.920140	0.345615
C	1.859065	3.819249	-2.125121
H	2.192168	1.722816	-2.555455
C	0.855688	4.264243	0.072447
H	0.399480	2.549335	1.269331
C	1.370493	4.756868	-1.159225
C	2.357655	4.306820	-3.361070
H	0.447448	4.972195	0.790987
C	1.404838	6.137944	-1.464158
C	2.375765	5.656276	-3.629074
H	2.725205	3.592924	-4.094729
C	1.897058	6.580598	-2.672439
H	1.032765	6.847521	-0.728364
H	2.758511	6.017119	-4.580144
H	1.916249	7.644029	-2.895580