Supporting Information

When Weaker Can Be Tougher: On the Role of Oxidation State (I) in P- vs. N-Ligand Derived Ni-Catalyzed Trifluoromethylthiolation of Aryl halides

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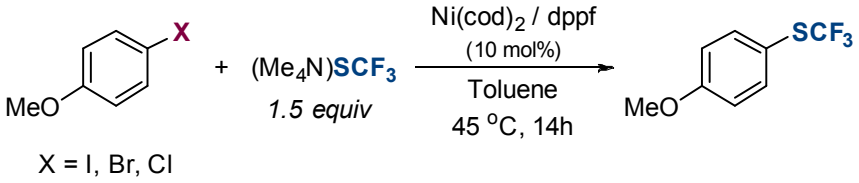
Contents

1. General Information

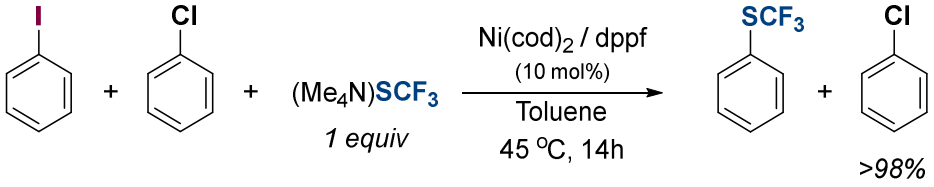
^{1}H, ^{13}C and ^{19}F NMR spectra were recorded either on V-NMRS 400 or Varian Mercury 300 spectrometer. ^{1}H spectra are referenced to residual solvent signals; $CDCl_3$ 7.26 ppm; benzene-d_6 7.16 ppm and THF-d_8 1.73 ppm. Chemical shifts (δ) of ^{19}F NMR spectra are reported in ppm relative to trifluorotoluene (-63.18 ppm). Chemical shifts (δ) of ^{31}P NMR spectra are given in ppm relative to trimethyl phosphate (2.36 ppm). Coupling constants (*J*) are reported in Hz and coupling patterns are described as br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

$Ni(cod)_2$, dppf, and anhydrous benzene were purchased from Sigma Aldrich. Toluene, THF and hexane were dried by solvent purification system (Innovative Technology PS-MD-5). Unless otherwise stated, all starting materials were commercially available and used as received. $(Me_4N)SCF_3$,[1] (dppf)Ni(cod),[2] (dppf)NiCl[2] and $(dme)_2NiI_2$[3] were prepared according to their corresponding literature procedures.

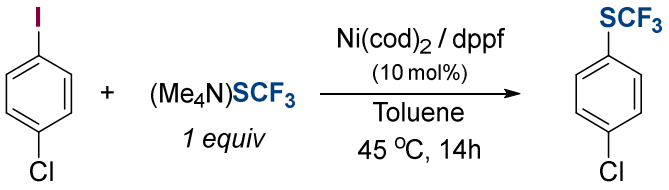
1.1. Trifluoromethylthiolation with dppf / $Ni(cod)_2$ catalyst



In an argon filled glovebox, a mixture of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol), and $(Me_4N)SCF_3$ (26 mg, 0.15 mmol) in dry toluene (0.5 mL) was stirred at room temperature for 5 min, followed by the addition of aryl halide (0.1 mmol). The suspension was stirred at 45 °C for 12-15 h. Subsequently a known amount of trifluorotoluene was added as an internal standard and conversion to the trifluoromethylthiolated product was determined by quantitative ^{19}F NMR analysis.



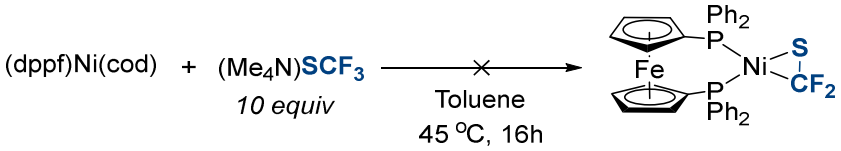
In an argon filled glovebox, a mixture of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol), and $(Me_4N)SCF_3$ (18 mg, 0.1 mmol) in dry toluene (0.5 mL) was stirred at room temperature for 5 min, followed by the addition of chlorobenzene and iodobenzene (0.1 mmol each). The suspension was stirred at 45 °C for 12-15 h. Subsequently a known amount of mesitylene was added as an internal standard and conversion to the trifluoromethylthiolated product as well as the amount of remaining starting materials was determined by calibrated GC/MS analysis. The yield of the formed product was further verified by ^{19}F NMR analysis using trifluorotoluene as internal standard.



In an argon filled glovebox, a mixture of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), dppf (5.5 mg, 0.01 mmol), and $(Me_4N)SCF_3$ (18 mg, 0.1 mmol) in dry toluene (0.5 mL) was stirred at room temperature for 5 min, followed by the addition of aryl halide (24 mg, 0.1 mmol). The suspension was stirred at 45 °C for 12-15 h. Subsequently a known amount of trifluorotoluene was added as an internal standard and conversion to the trifluoromethylthiolated products was determined by quantitative ^{19}F NMR and GC/MS analyses.

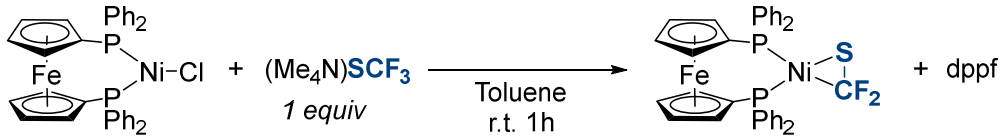
1.2. Studies into SCF_2 formation

Thermal decomposition of $(Me_4N)SCF_3$ under catalytically relevant conditions:



In an argon filled glovebox, a mixture of (dppf)Ni(cod) (7.2 mg, 0.01 mmol) and $(Me_4N)SCF_3$ (18 mg, 0.1 mmol) in dry toluene (0.7 mL) was stirred at 45 °C for 16 h. The mixture was subsequently analyzed by ^{19}F and ^{31}P NMR and no conversion to (dppf)Ni(SCF_2) as well as to any other F- or P-containing species was observed.

Reaction between (dppf)NiCl and $(Me_4N)SCF_3$:

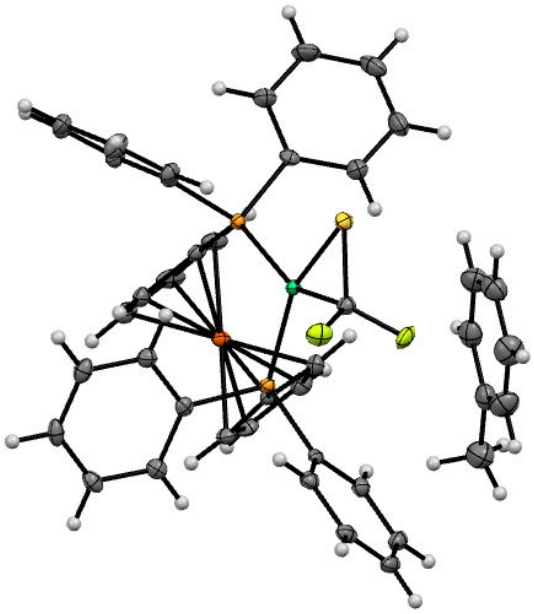


^{31}P NMR:	50%	50%	(of introduced P)
^{19}F NMR:	30%		(of introduced F)

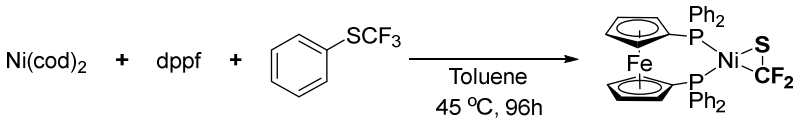
In an argon filled glovebox, a mixture of (dppf)NiCl (20 mg, 0.031 mmol) and $(Me_4N)SCF_3$ (5.4 mg, 0.031 mmol) in dry toluene (1.5 mL) was stirred at room temperature for 1 h, after which the solution had turned orange and a green precipitate had formed. A known amount of trifluorotoluene and triethyl phosphate were subsequently added and the formed species were quantified by ^{19}F and ^{31}P NMR analysis.
After 30 minutes the solution phase was also orange, along with a dark red precipitate. ^{31}P NMR analysis revealed there to be only (dppf)Ni(SCF_2) present and no free ligand, suggesting that it is likely formed *via* the decomposition of the dark red precipitate. On a preparative scale it is however difficult to isolate the material at the time when there would not be any unreacted starting material or free dppf impurity present.

Crystals suitable for X-ray analysis were grown from the reaction mixture in toluene that was filtered through celite after 30 minutes running time. Slow diffusion of hexane through gas phase was used to induce crystal formation.

All the ellipsoids are drawn at 50% probability.



*Formation of **(dppf)Ni(SCF_2)** via oxidative addtion:*

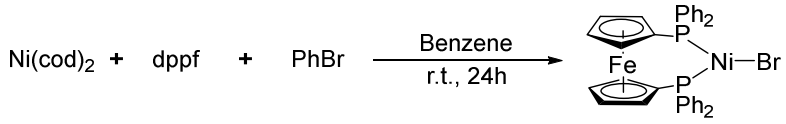


Inside an argon filled glovebox, $Ni(cod)_2$ (138 mg, 0.5 mmol), dppf (282 mg, 0.505 mmol) and benzene (10 mL) were added to a vial. The solution was stirred for 10 min at room temperature, and then phenyl trifluoromethyl sulfide (1 mL) was added. The solution was stirred at 45 °C for 96 hours, followed by the isolation of the solid material by filtration. The obtained dark green solid was subsequently recrystallized from benzene/hexane to yield 70 mg of pale orange solid (20% yield). ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 7.95 (m, 8H), 7.02 (br, 12H), 4.37 (br, 2H), 4.02 (br, 2H), 3.86 (br, 2H), 3.77 (br, 2H). ^{19}F NMR (282 MHz, C_6D_6) δ (ppm) -44.75 (dd, J = 37.6, 23.0 Hz). ^{31}P NMR (121 MHz, C_6D_6) δ (ppm) 30.82 (t, J = 23.0 Hz), 22.10 (t, J = 37.6 Hz).

2. Synthetic procedures

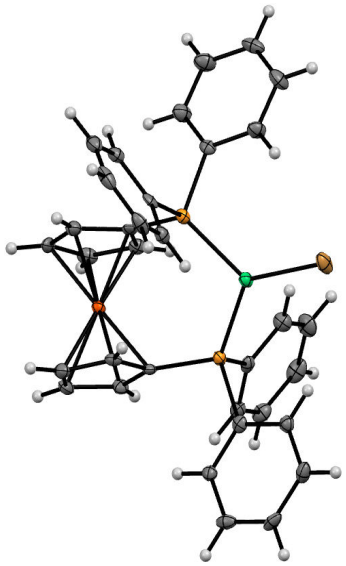
2.1. Preparation of $Ni^{(I)}$ I- and Br-complexes

*Preparation of **(dppf)$Ni^{(I)}$Br** via oxidative addition:*

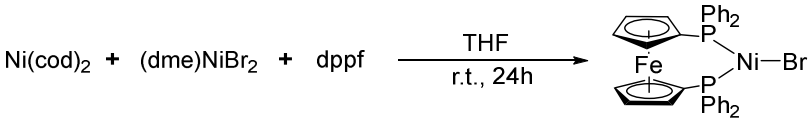


Inside an argon filled glovebox, $Ni(cod)_2$ (138 mg, 0.5 mmol), dppf (282 mg, 0.505 mmol), and benzene (10 mL) were added to a 20 mL vial. The solution was stirred at room temperature for 5 minutes, after which 1 mL of bromobenzene was added. Additional stirring for 24 hours, yielded an orange suspension. After filtration and washing with hexane, orange powder (231 mg) was collected, 67% yield. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane through gas phase into a moderately concentrated solution of the title compound in benzene (400 µL saturated solution + 100 µL benzene) at room temperature.

All the ellipsoids are drawn at 50% probability. C_6H_6 is omitted for clarity.

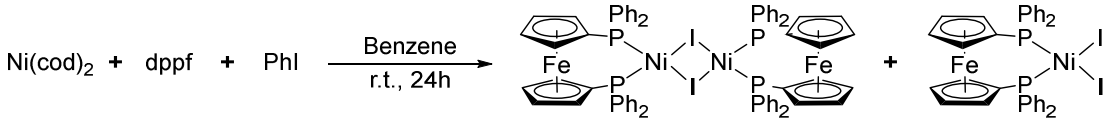


*Preparation of **(dppf)$Ni^{(I)}$Br** via comproportionation:*



Inside an argon filled glovebox, $Ni(cod)_2$ (55 mg, 0.2 mmol), dppf (222 mg, 0.4 mmol), $(dme)NiBr_2$ (61 mg, 0.2 mmol) and THF (10 mL) were added to a 20 mL vial. The solution was stirred at room temperature for 24 hours, after which an orange suspension had formed. After filtration and washing with hexane, orange powder (174 mg) was collected, 63% yield. Paramagnetic ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 12.7 (br), 4.5 (br), 1.3 (br).

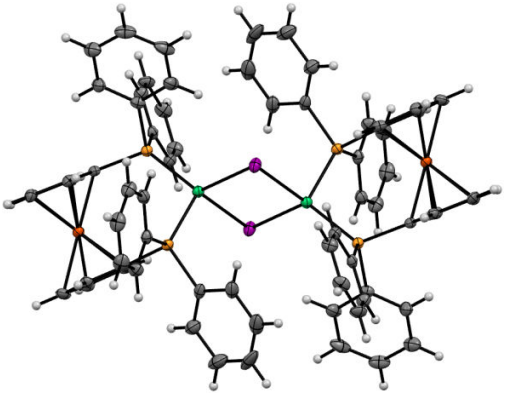
*Preparation of **(dppf)Ni$^{(I)}$I** via oxidative addition:*



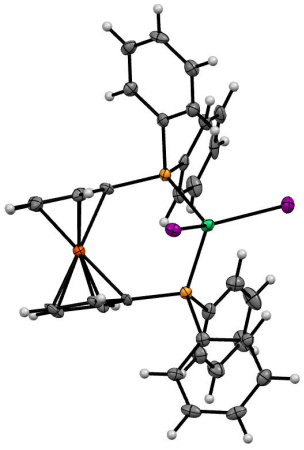
Inside an argon filled glovebox, $Ni(cod)_2$ (138 mg, 0.5 mmol), dppf (282 mg, 0.505 mmol), and benzene (10 mL) were added to a 20 mL vial. The solution was stirred at room temperature for 5 minutes, after which 1 mL of iodobenzene was added. Additional stirring for 24 hours, yielded an orange suspension had formed. After filtration and washing with hexane, orange-purplish powder (231 mg) was collected, 67% yield. ^{1}H NMR analysis indicated the isolated material to be a mixture of (dppf)Ni$^{(I)}$I and (dppf)Ni$^{(II)}I_2$. The latter is not observed when the reaction is run on a more dilute NMR experiment scale (0.01 mmol in 0.7 mL), suggesting that its (NiI_2) isolation may be associated with its poor solubility in benzene.

^{1}H NMR spectrum of (dppf)Ni$^{(II)}I_2$ contains characteristic signals at 19.8 and -2.8 ppm (as determined after mixing $(dme)_2NiI_2$ and dppf in THF-d_8 or C_6D_6 for 1h).

Attempt to grow single crystal of the isolated impure material from THF yielded a dimeric (dppf)Ni$^{(I)}$I, whereas crystallization from benzene yielded (dppf)Ni$^{(II)}I_2$. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane through gas phase into a solution of the isolated material at room temperature.

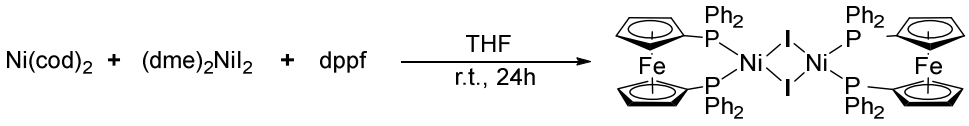


All the ellipsoids are drawn at 50% probability. THF is omitted for clarity.



All the ellipsoids are drawn at 50% probability. C_6H_6 is omitted for clarity.

*Preparation of **(dppf)Ni$^{(I)}$I** via comproportionation:*



Inside an argon filled glovebox, $Ni(cod)_2$ (55 mg, 0.2 mmol), dppf (222 mg, 0.4 mmol), $(dme)_2NiI_2$ (98 mg, 0.2 mmol) and THF (10 mL) were added to a 20 mL vial. The solution was stirred at room temperature for 24 hours, after which the reaction mixture had turned greenish-purple. After filtration and washing with hexane, dark greenish orange powder (168 mg) was collected, 57% yield. Paramagnetic ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 12.8 (br), 4.4 (br).

3. Crystallographic data

	(dppf)Ni(SCF$_2$)	**(dppf)Ni$^{(I)}$Br**	**[(dppf)Ni$^{(I)}$I]$_2$**	**(dppf)Ni$^{(II)}$I$_2$**
Chemical formula	$C_{34}H_{28}F_2FeNiP_2S$,C_7H_8	$C_{34}H_{28}BrFeNiP_2$,C_6H_6	$C_{68}H_{56}Fe_2I_2Ni_2P_4$,$C_4H_8O$	$C_{34}H_{28}FeI_2NiP_2$,C_6H_6
M_r	787.27	771.08	1552.03	944.97
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, C2/c	Triclinic, $P\bar{1}$
a, b, c (Å)	11.2326(10) 11.3360(10) 16.1197(14)	9.6075(11) 10.9191(13) 17.624(2)	23.6771(5) 13.9547(3) 19.1841(4)	8.9532(2) 10.0303(3) 20.4331(11)
α, β, γ (°)	78.1070(10) 72.5100(10) 67.2790(10)	96.565(2) 105.405(2) 103.759(2)	90 90.394(2) 90	91.917(3) 99.127(4) 94.971(2)
V (Å^3)	1796.3(3)	1699.9(3)	6338.4(2)	1802.83(12)
Z	2	2	4	2
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	1.116	2.278	2.153	2.754
Crystal size (mm)	0.30 x 0.30 x 0.21	0.18 x 0.15 x 0.04	0.06 x 0.05 x 0.04	0.07 x 0.05 x 0.03
Total/unique reflections	22492, 7576	19061, 6202	41356, 7243	9996, *twinned crystal*
R_{int}	0.0529	0.0622	0.060	*twinned crystal*
$R(F^2 > 2\sigma(F^2))$	0.0345	0.0383	0.0395	0.0415
$wR_2(F^2)$	0.0849	0.0872	0.0798	0.0878
GoF	1.028	1.009	1.017	1.071
No. of reflections	7576	6202	7243	9996
No. of parameters	443	406	397	416
No. of restraints	0	0	30	0
$\Delta>_{max}$, $\Delta>_{min}$ (e Å^{-3})	0.424, -0.467	0.933, -0.374	1.098, -0.435	3.023, -0.982
CCDC Number	1528670	1528671	1528182	1528181

3.1. Structural details of (dppf)Ni$^{(I)}$Br

To investigate a possible electronic exchange between the Ni-center and the ferrocene ligand (e.g. whether it is truly Ni$^{(I)}$/Fe$^{(II)}$ and not Ni$^{(0)}$/Fe$^{(III)}$), we performed calculations of the spin density in (dppf)Ni$^{(I)}$Br complex. The obtained results indicate that the unpaired electron in this complex is localized predominantly on the Ni center (Figure S1).

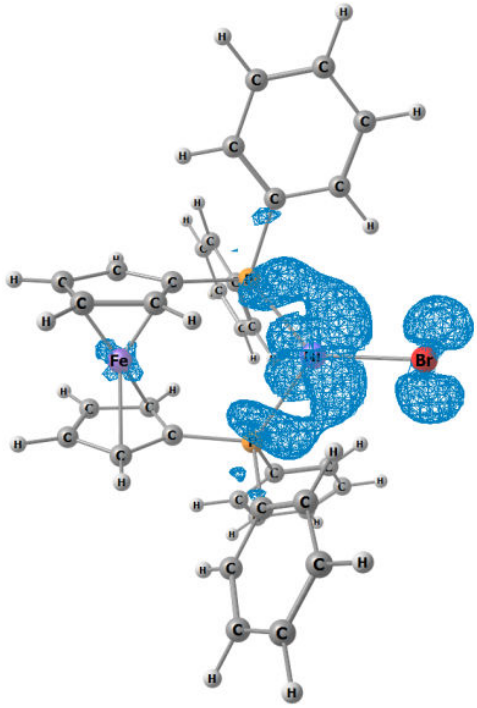


Figure S1. Spin density analysis for (dppf)Ni$^{(I)}$Br, calculated at CPCM (Toluene) M06L/def2TZVP // ωB97XD/6-31G(d) SDD level of theory.

Furthermore, we also compared the average C-Fe distances in the ferrocene moieties of the obtained crystal structures with the corresponding distances in Fe$^{(II)}$ (CCDC 1154857) and Fe$^{(III)}$ (CCDC 194434, 170258, 138350 and 1194362) ferrocenes. The data, shown in the Table S1 indicate that the ferrocene units in our Ni$^{(I)}$ complexes are more similar to Fe$^{(II)}$ ferrocene.

Table S1. Comparison of average C-Fe distances in Fe$^{(II)}$ and Fe$^{(III)}$ ferrocenes and (dppf)Ni complexes.

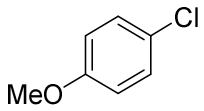
Complex	Average C-Fe distance (Å)
Fe$^{(II)}$ ferrocene	2.045
Fe$^{(III)}$ ferrocene	2.065
(dppf)Ni$^{(I)}$Br	2.041
(dppf)Ni$^{(I)}$I dimer	2.042
(dppf)Ni$^{(0)}$(cod)	2.044

4. Computational details

All calculations were performed using Gaussian 09 software.[4] Structural optimizations and frequency calculations were performed with ωB97XD method along with 6-31G(d) basis set and the SDD ECP on Ni and Fe atoms. Single point energy calculations were performed with M06 and M06L methods and def2-TZVP basis set. Solvent effects of toluene and THF were included using the CPCM solvation model. Frequency calculations were performed to confirm whether the structure is a minimum or a transition state. Intrinsic reaction coordinate (IRC) analysis was used to confirm that the obtained transition states connect the correct minima. Energies of all structures are corrected to 1M standard state with the addition of a constant of 1.89 kcal/mol.[5] Both singlet and triplet spin states were considered for $Ni^{(II)}$ complexes, with the lowest energy ones reported herein.

Energetic and thermal data for computed structures

MeO-Ph-Cl

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Zero-point correction=                           0.125560 (Hartree/Particle)
 Thermal correction to Energy=                    0.133511
 Thermal correction to Enthalpy=                  0.134456
 Thermal correction to Gibbs Free Energy=         0.092354
 Sum of electronic and zero-point Energies=           -806.101249
 Sum of electronic and thermal Energies=              -806.093298
 Sum of electronic and thermal Enthalpies=            -806.092353
 Sum of electronic and thermal Free Energies=         -806.134455

CPCM (Toluene) M06L/def2TZVP E = -806.457700124
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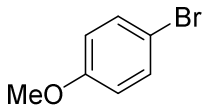
MeO-Ph-Br

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Zero-point correction=                           0.125022 (Hartree/Particle)
 Thermal correction to Energy=                    0.133254
 Thermal correction to Enthalpy=                  0.134199
 Thermal correction to Gibbs Free Energy=         0.090526
 Sum of electronic and zero-point Energies=          -2917.353822
 Sum of electronic and thermal Energies=             -2917.345589
 Sum of electronic and thermal Enthalpies=           -2917.344645
 Sum of electronic and thermal Free Energies=        -2917.388318

CPCM (Toluene) M06L/def2TZVP E = -2920.31216203
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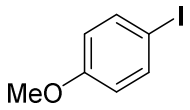
MeO-Ph-I

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CPCM (Toluene) M06L/def2TZVP E = -644.124891465
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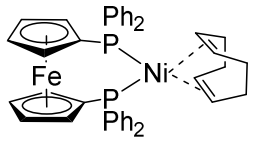
[(dppf)Ni$^{(0)}$(cod)]

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 Sum of electronic and thermal Enthalpies=           -2600.838030
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CPCM (Toluene) M06L/def2TZVP E = -5079.72044133
CPCM (Toluene) M06/def2TZVP E = -5078.57741291
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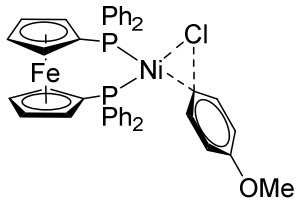
TS-OA-ArCl

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Zero-point correction=                           0.650568 (Hartree/Particle)
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 Thermal correction to Enthalpy=                  0.693642
 Thermal correction to Gibbs Free Energy=         0.572084
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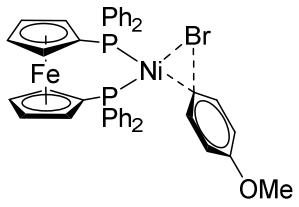
CPCM (Toluene) M06L/def2TZVP E = -5574.03756636
```

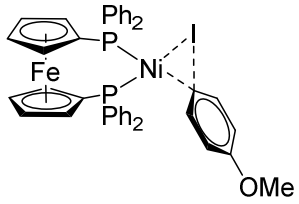
TS-OA-ArBr




```
Zero-point correction=                           0.650998 (Hartree/Particle)
 Thermal correction to Energy=                    0.692166
 Thermal correction to Enthalpy=                  0.693110
 Thermal correction to Gibbs Free Energy=         0.575356
 Sum of electronic and zero-point Energies=          -5206.448728
 Sum of electronic and thermal Energies=             -5206.407560
 Sum of electronic and thermal Enthalpies=           -5206.406616
 Sum of electronic and thermal Free Energies=        -5206.524370

CPCM (Toluene) M06L/def2TZVP E = -7687.89995235
```

TS-OA-ArI



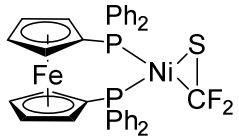

```
 Zero-point correction=                           0.651107 (Hartree/Particle)
 Thermal correction to Energy=                    0.692317
 Thermal correction to Enthalpy=                  0.693262
 Thermal correction to Gibbs Free Energy=         0.575259
 Sum of electronic and zero-point Energies=          -2646.446733
 Sum of electronic and thermal Energies=             -2646.405523
 Sum of electronic and thermal Enthalpies=           -2646.404578
 Sum of electronic and thermal Free Energies=        -2646.522581

CPCM (Toluene) M06L/def2TZVP E = -5411.72153315
```

1,5-cyclooctadiene

```
Zero-point correction=                           0.183361 (Hartree/Particle)
 Thermal correction to Energy=                    0.190701
 Thermal correction to Enthalpy=                  0.191646
 Thermal correction to Gibbs Free Energy=         0.151915
 Sum of electronic and zero-point Energies=           -311.745607
 Sum of electronic and thermal Energies=              -311.738266
 Sum of electronic and thermal Enthalpies=            -311.737322
 Sum of electronic and thermal Free Energies=         -311.777053
CPCM (Toluene) M06L/def2TZVP E = -312.0931233
CPCM (Toluene) M06/def2TZVP E = -311.885770491
CPCM (THF) M06/def2TZVP E = -311.886489619
```

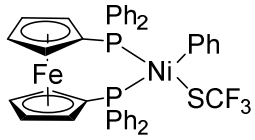
(dppf)Ni (SCF_2)




```
Zero-point correction=                           0.540297 (Hartree/Particle)
 Thermal correction to Energy=                    0.577186
 Thermal correction to Enthalpy=                  0.578130
 Thermal correction to Gibbs Free Energy=         0.468722
 Sum of electronic and zero-point Energies=          -2925.008081
 Sum of electronic and thermal Energies=             -2924.971193
 Sum of electronic and thermal Enthalpies=           -2924.970249
 Sum of electronic and thermal Free Energies=        -2925.079656

CPCM (Toluene) M06L/def2TZVP E = -5403.69208574
```

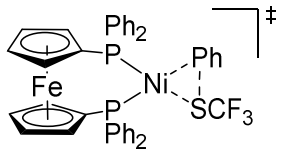
(dppf)Ni(Ph)(SCF_3)




```
Zero-point correction=                           0.635991 (Hartree/Particle)
 Thermal correction to Energy=                    0.679119
 Thermal correction to Enthalpy=                  0.680063
 Thermal correction to Gibbs Free Energy=         0.557839
 Sum of electronic and zero-point Energies=          -3256.282808
 Sum of electronic and thermal Energies=             -3256.239680
 Sum of electronic and thermal Enthalpies=           -3256.238735
 Sum of electronic and thermal Free Energies=        -3256.360960

CPCM (Toluene) M06/def2TZVP E = -5734.08229759
```

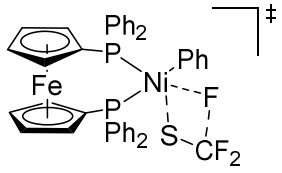
TS-RE-PhSCF$_3$




```
Zero-point correction=                           0.635105 (Hartree/Particle)
 Thermal correction to Energy=                    0.677832
 Thermal correction to Enthalpy=                  0.678776
 Thermal correction to Gibbs Free Energy=         0.557630
 Sum of electronic and zero-point Energies=          -3256.255528
 Sum of electronic and thermal Energies=             -3256.212802
 Sum of electronic and thermal Enthalpies=           -3256.211857
 Sum of electronic and thermal Free Energies=        -3256.333004

CPCM (Toluene) M06/def2TZVP E = -5734.05622609
```

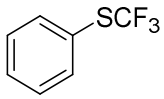
TS-βF-elim-PhSCF$_3$




```
 Zero-point correction=                           0.634900 (Hartree/Particle)
 Thermal correction to Energy=                    0.677967
 Thermal correction to Enthalpy=                  0.678911
 Thermal correction to Gibbs Free Energy=         0.557817
 Sum of electronic and zero-point Energies=          -3256.253080
 Sum of electronic and thermal Energies=             -3256.210014
 Sum of electronic and thermal Enthalpies=           -3256.209069
 Sum of electronic and thermal Free Energies=        -3256.330164

CPCM (Toluene) M06/def2TZVP E = -5734.04455539
```

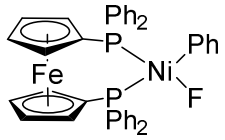
PhSCF$_3$




```
Zero-point correction=                           0.108184 (Hartree/Particle)
 Thermal correction to Energy=                    0.117609
 Thermal correction to Enthalpy=                  0.118553
 Thermal correction to Gibbs Free Energy=         0.071274
 Sum of electronic and zero-point Energies=           -967.159310
 Sum of electronic and thermal Energies=              -967.149886
 Sum of electronic and thermal Enthalpies=            -967.148942
 Sum of electronic and thermal Free Energies=         -967.196220

CPCM (Toluene) M06/def2TZVP E = -967.397178728
CPCM (THF) M06/def2TZVP E = -967.398135792
```

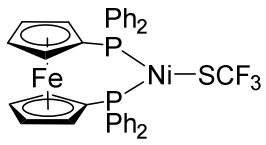
(dppf)Ni(Ph)(F)




```
Zero-point correction=                           0.620929 (Hartree/Particle)
 Thermal correction to Energy=                    0.659966
 Thermal correction to Enthalpy=                  0.660910
 Thermal correction to Gibbs Free Energy=         0.547259
 Sum of electronic and zero-point Energies=          -2620.399423
 Sum of electronic and thermal Energies=             -2620.360387
 Sum of electronic and thermal Enthalpies=           -2620.359443
 Sum of electronic and thermal Free Energies=        -2620.473093

CPCM (Toluene) M06/def2TZVP E = -5098.07454855
```

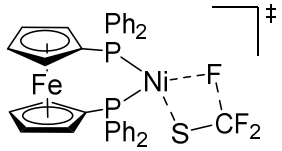
(dppf)Ni(SCF$_3$)




```
Zero-point correction=                           0.543054 (Hartree/Particle)
 Thermal correction to Energy=                    0.581734
 Thermal correction to Enthalpy=                  0.582678
 Thermal correction to Gibbs Free Energy=         0.467024
 Sum of electronic and zero-point Energies=          -3024.844392
 Sum of electronic and thermal Energies=             -3024.805712
 Sum of electronic and thermal Enthalpies=           -3024.804768
 Sum of electronic and thermal Free Energies=        -3024.920421

CPCM (Toluene) M06/def2TZVP E = -5502.5638082
```

TS-βF-elim-Ni$^{(I)}$SCF$_3$




```
Zero-point correction=                           0.540907 (Hartree/Particle)
 Thermal correction to Energy=                    0.579795
 Thermal correction to Enthalpy=                  0.580739
 Thermal correction to Gibbs Free Energy=         0.463477
 Sum of electronic and zero-point Energies=          -3024.808429
 Sum of electronic and thermal Energies=             -3024.769541
 Sum of electronic and thermal Enthalpies=           -3024.768596
 Sum of electronic and thermal Free Energies=        -3024.885859

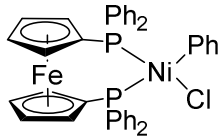
CPCM (Toluene) M06/def2TZVP E = -5502.5273849
```

SCF$_2$


```
 Zero-point correction=                           0.011698 (Hartree/Particle)
 Thermal correction to Energy=                    0.015249
 Thermal correction to Enthalpy=                  0.016193
 Thermal correction to Gibbs Free Energy=        -0.015171
 Sum of electronic and zero-point Energies=           -635.844412
 Sum of electronic and thermal Energies=              -635.840861
 Sum of electronic and thermal Enthalpies=            -635.839917
 Sum of electronic and thermal Free Energies=         -635.871281

CPCM (Toluene) M06/def2TZVP E = -635.97015519
CPCM (THF) M06/def2TZVP E = -635.970566068
```

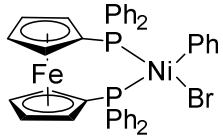
(dppf)Ni(Ph)(Cl)




```
Zero-point correction=                           0.620308 (Hartree/Particle)
 Thermal correction to Energy=                    0.659080
 Thermal correction to Enthalpy=                  0.660024
 Thermal correction to Gibbs Free Energy=         0.547509
 Sum of electronic and zero-point Energies=          -2980.774640
 Sum of electronic and thermal Energies=             -2980.735868
 Sum of electronic and thermal Enthalpies=           -2980.734924
 Sum of electronic and thermal Free Energies=        -2980.847439

CPCM (Toluene) M06L/def2TZVP E = -5459.53062821
```

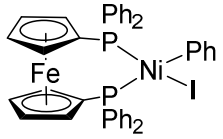
(dppf)Ni(Ph)(Br)




```
Zero-point correction=                           0.619667 (Hartree/Particle)
 Thermal correction to Energy=                    0.658672
 Thermal correction to Enthalpy=                  0.659616
 Thermal correction to Gibbs Free Energy=         0.546416
 Sum of electronic and zero-point Energies=          -5092.035957
 Sum of electronic and thermal Energies=             -5091.996951
 Sum of electronic and thermal Enthalpies=           -5091.996007
 Sum of electronic and thermal Free Energies=        -5092.109207

CPCM (Toluene) M06L/def2TZVP E = -7573.38748299
```

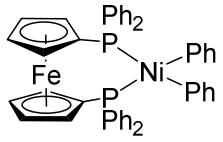
(dppf)Ni(Ph)(I)




```
Zero-point correction=                           0.619840 (Hartree/Particle)
 Thermal correction to Energy=                    0.659836
 Thermal correction to Enthalpy=                  0.660780
 Thermal correction to Gibbs Free Energy=         0.543574
 Sum of electronic and zero-point Energies=          -2532.033234
 Sum of electronic and thermal Energies=             -2531.993239
 Sum of electronic and thermal Enthalpies=           -2531.992295
 Sum of electronic and thermal Free Energies=        -2532.109501

CPCM (Toluene) M06L/def2TZVP E = -5297.20322026
```

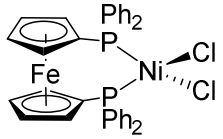
(dppf)Ni(Ph)$_2$




```
Zero-point correction=                           0.710525 (Hartree/Particle)
 Thermal correction to Energy=                    0.752431
 Thermal correction to Enthalpy=                  0.753375
 Thermal correction to Gibbs Free Energy=         0.634654
 Sum of electronic and zero-point Energies=          -2752.027634
 Sum of electronic and thermal Energies=             -2751.985728
 Sum of electronic and thermal Enthalpies=           -2751.984783
 Sum of electronic and thermal Free Energies=        -2752.103505

CPCM (Toluene) M06L/def2TZVP E = -5230.96728508
```

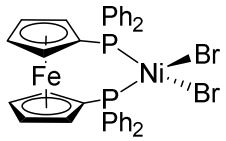
(dppf)Ni(Cl)$_2$




```
Zero-point correction=                           0.530181 (Hartree/Particle)
 Thermal correction to Energy=                    0.566395
 Thermal correction to Enthalpy=                  0.567339
 Thermal correction to Gibbs Free Energy=         0.458453
 Sum of electronic and zero-point Energies=          -3209.568649
 Sum of electronic and thermal Energies=             -3209.532435
 Sum of electronic and thermal Enthalpies=           -3209.531491
 Sum of electronic and thermal Free Energies=        -3209.640377

CPCM (Toluene) M06L/def2TZVP E = -5688.11609826
```

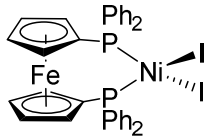
(dppf)Ni(Br)$_2$




```
Zero-point correction=                           0.529653 (Hartree/Particle)
 Thermal correction to Energy=                    0.566355
 Thermal correction to Enthalpy=                  0.567299
 Thermal correction to Gibbs Free Energy=         0.456116
 Sum of electronic and zero-point Energies=          -7432.085825
 Sum of electronic and thermal Energies=             -7432.049123
 Sum of electronic and thermal Enthalpies=           -7432.048179
 Sum of electronic and thermal Free Energies=        -7432.159363

CPCM (Toluene) M06L/def2TZVP E = -9915.82440917
```

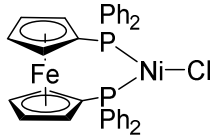
(dppf)Ni(I)$_2$




```
Zero-point correction=                           0.529459 (Hartree/Particle)
 Thermal correction to Energy=                    0.566372
 Thermal correction to Enthalpy=                  0.567317
 Thermal correction to Gibbs Free Energy=         0.453669
 Sum of electronic and zero-point Energies=          -2312.071896
 Sum of electronic and thermal Energies=             -2312.034983
 Sum of electronic and thermal Enthalpies=           -2312.034039
 Sum of electronic and thermal Free Energies=        -2312.147687

CPCM (Toluene) M06L/def2TZVP E = -5363.45083194
```

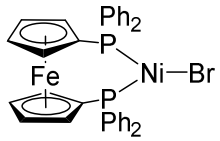
(dppf)NiCl




```
Zero-point correction=                           0.527940 (Hartree/Particle)
 Thermal correction to Energy=                    0.562598
 Thermal correction to Enthalpy=                  0.563542
 Thermal correction to Gibbs Free Energy=         0.455804
 Sum of electronic and zero-point Energies=          -2749.342480
 Sum of electronic and thermal Energies=             -2749.307822
 Sum of electronic and thermal Enthalpies=           -2749.306878
 Sum of electronic and thermal Free Energies=        -2749.414616

CPCM (Toluene) M06L/def2TZVP E = -5227.85718500
```

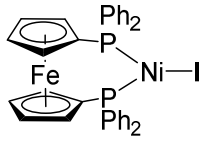
(dppf)NiBr




```
Zero-point correction=                           0.527769 (Hartree/Particle)
 Thermal correction to Energy=                    0.562598
 Thermal correction to Enthalpy=                  0.563543
 Thermal correction to Gibbs Free Energy=         0.454749
 Sum of electronic and zero-point Energies=          -4860.602976
 Sum of electronic and thermal Energies=             -4860.568147
 Sum of electronic and thermal Enthalpies=           -4860.567202
 Sum of electronic and thermal Free Energies=        -4860.675996

CPCM (Toluene) M06L/def2TZVP E = -7341.71262698
```

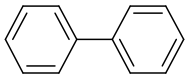
(dppf)NiI




```
Zero-point correction=                           0.527389 (Hartree/Particle)
 Thermal correction to Energy=                    0.562338
 Thermal correction to Enthalpy=                  0.563282
 Thermal correction to Gibbs Free Energy=         0.454906
 Sum of electronic and zero-point Energies=          -2300.600091
 Sum of electronic and thermal Energies=             -2300.565141
 Sum of electronic and thermal Enthalpies=           -2300.564197
 Sum of electronic and thermal Free Energies=        -2300.672574

CPCM (Toluene) M06L/def2TZVP E = -5065.52607106
```

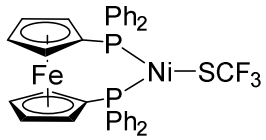
Ph-Ph



```
Zero-point correction=                           0.184206 (Hartree/Particle)
 Thermal correction to Energy=                    0.192989
 Thermal correction to Enthalpy=                  0.193933
 Thermal correction to Gibbs Free Energy=         0.150365
 Sum of electronic and zero-point Energies=           -462.953471
 Sum of electronic and thermal Energies=              -462.944689
 Sum of electronic and thermal Enthalpies=            -462.943744
 Sum of electronic and thermal Free Energies=         -462.987312

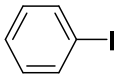
CPCM (Toluene) M06L/def2TZVP E = -463.400094216
```

TS-OA-PhI-(dppf)Ni(SCF_3)



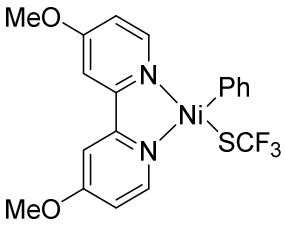

```
Zero-point correction=                           0.637088 (Hartree/Particle)
 Thermal correction to Energy=                    0.682119
 Thermal correction to Enthalpy=                  0.683063
 Thermal correction to Gibbs Free Energy=         0.556454
 Sum of electronic and zero-point Energies=          -3267.712570
 Sum of electronic and thermal Energies=             -3267.667540
 Sum of electronic and thermal Enthalpies=           -3267.666596
 Sum of electronic and thermal Free Energies=        -3267.793204
CPCM (Toluene) M06/def2TZVP E = -6031.84687603
```

Ph-I



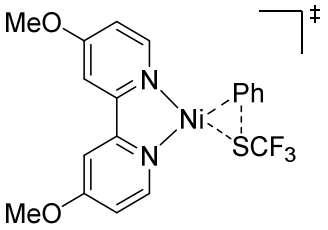
```
Zero-point correction=                           0.091513 (Hartree/Particle)
 Thermal correction to Energy=                    0.097310
 Thermal correction to Enthalpy=                  0.098254
 Thermal correction to Gibbs Free Energy=         0.060505
 Sum of electronic and zero-point Energies=          -242.888371
 Sum of electronic and thermal Energies=             -242.882573
 Sum of electronic and thermal Enthalpies=           -242.881629
 Sum of electronic and thermal Free Energies=        -242.919379
CPCM (Toluene) M06/def2TZVP E = -529.309413
CPCM (THF) M06/def2TZVP E = -529.310339402
```

(dmbpy)Ni(Ph)(SCF$_3$)



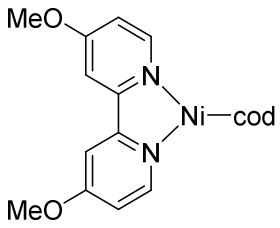

```
Zero-point correction=                           0.338518 (Hartree/Particle)
 Thermal correction to Energy=                    0.363609
 Thermal correction to Enthalpy=                  0.364553
 Thermal correction to Gibbs Free Energy=         0.282062
 Sum of electronic and zero-point Energies=         -1862.130925
 Sum of electronic and thermal Energies=            -1862.105834
 Sum of electronic and thermal Enthalpies=          -1862.104889
 Sum of electronic and thermal Free Energies=       -1862.187381
CPCM (THF) M06/def2TZVP E = -3199.99227758
```

TS-RE-(dmbpy)Ni(Ph)(SCF$_3$)



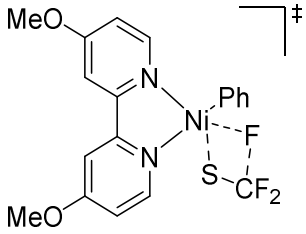

```
Zero-point correction=                           0.335985 (Hartree/Particle)
 Thermal correction to Energy=                    0.361540
 Thermal correction to Enthalpy=                  0.362484
 Thermal correction to Gibbs Free Energy=         0.278418
 Sum of electronic and zero-point Energies=         -1862.067215
 Sum of electronic and thermal Energies=            -1862.041660
 Sum of electronic and thermal Enthalpies=          -1862.040716
 Sum of electronic and thermal Free Energies=       -1862.124782
CPCM (THF) M06/def2TZVP E = -3199.93580732
```

(dmbpy)Ni(cod)



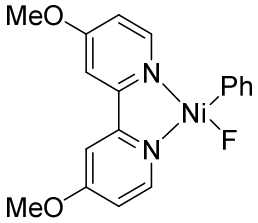

```
Zero-point correction=                           0.411979 (Hartree/Particle)
 Thermal correction to Energy=                    0.435055
 Thermal correction to Enthalpy=                  0.435999
 Thermal correction to Gibbs Free Energy=         0.359302
 Sum of electronic and zero-point Energies=          -1206.691394
 Sum of electronic and thermal Energies=             -1206.668319
 Sum of electronic and thermal Enthalpies=           -1206.667374
 Sum of electronic and thermal Free Energies=        -1206.744072
CPCM (THF) M06/def2TZVP E = -2544.45197474
```

TS-βF-elim-(dmbpy)Ni(Ph)(SCF$_3$)



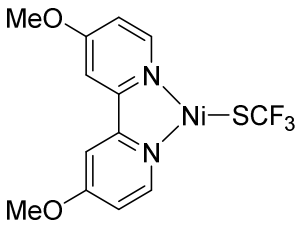

```
Zero-point correction=                           0.336813 (Hartree/Particle)
 Thermal correction to Energy=                    0.362610
 Thermal correction to Enthalpy=                  0.363554
 Thermal correction to Gibbs Free Energy=         0.278627
 Sum of electronic and zero-point Energies=          -1862.098271
 Sum of electronic and thermal Energies=             -1862.072474
 Sum of electronic and thermal Enthalpies=           -1862.071529
 Sum of electronic and thermal Free Energies=        -1862.156457
CPCM (THF) M06/def2TZVP E = -3199.95069403
```

(dmbpy)Ni(Ph)(F)



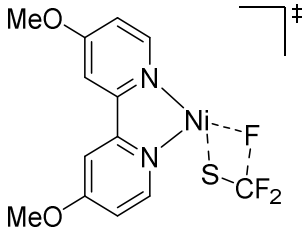

```
Zero-point correction=                           0.323499 (Hartree/Particle)
 Thermal correction to Energy=                    0.345305
 Thermal correction to Enthalpy=                  0.346249
 Thermal correction to Gibbs Free Energy=         0.270156
 Sum of electronic and zero-point Energies=          -1226.242231
 Sum of electronic and thermal Energies=             -1226.220425
 Sum of electronic and thermal Enthalpies=           -1226.219481
 Sum of electronic and thermal Free Energies=        -1226.295573
CPCM (THF) M06/def2TZVP E = -2563.98163656
```

(dmbpy)Ni(SCF$_3$)



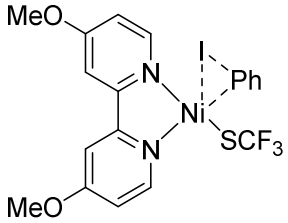

```
Zero-point correction=                           0.245467 (Hartree/Particle)
 Thermal correction to Energy=                    0.266804
 Thermal correction to Enthalpy=                  0.267748
 Thermal correction to Gibbs Free Energy=         0.190353
 Sum of electronic and zero-point Energies=          -1630.677349
 Sum of electronic and thermal Energies=             -1630.656012
 Sum of electronic and thermal Enthalpies=           -1630.655068
 Sum of electronic and thermal Free Energies=        -1630.732463
CPCM (THF) M06/def2TZVP E = -2968.46411812
```

TS-βF-elim-(dmbpy)Ni(SCF$_3$)



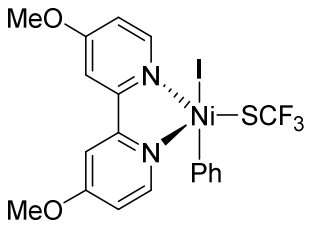

```
Zero-point correction=                           0.242945 (Hartree/Particle)
 Thermal correction to Energy=                    0.264596
 Thermal correction to Enthalpy=                  0.265540
 Thermal correction to Gibbs Free Energy=         0.186795
 Sum of electronic and zero-point Energies=          -1630.639163
 Sum of electronic and thermal Energies=             -1630.617512
 Sum of electronic and thermal Enthalpies=           -1630.616568
 Sum of electronic and thermal Free Energies=        -1630.695314
CPCM (THF) M06/def2TZVP E = -2968.42300663
```

TS-OA-PhI-(dmbpy)Ni(SCF$_3$)



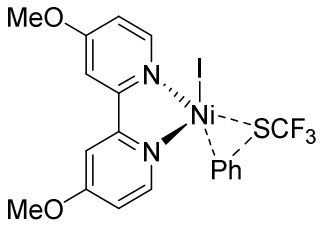

```
Zero-point correction=                           0.336942 (Hartree/Particle)
 Thermal correction to Energy=                    0.365276
 Thermal correction to Enthalpy=                  0.366220
 Thermal correction to Gibbs Free Energy=         0.272716
 Sum of electronic and zero-point Energies=          -1873.572800
 Sum of electronic and thermal Energies=             -1873.544466
 Sum of electronic and thermal Enthalpies=           -1873.543522
 Sum of electronic and thermal Free Energies=        -1873.637026
CPCM (THF) M06/def2TZVP E = -3497.77267139
```

(dmbpy)Ni(I)(SCF$_3$)(Ph)



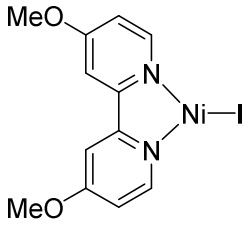

```
Zero-point correction=                           0.338628 (Hartree/Particle)
 Thermal correction to Energy=                    0.367167
 Thermal correction to Enthalpy=                  0.368111
 Thermal correction to Gibbs Free Energy=         0.274753
 Sum of electronic and zero-point Energies=          -1873.590197
 Sum of electronic and thermal Energies=             -1873.561658
 Sum of electronic and thermal Enthalpies=           -1873.560714
 Sum of electronic and thermal Free Energies=        -1873.654072
CPCM (THF) M06/def2TZVP E = -3497.78070392
```

TS-RE-(dmbpy)Ni(I)(Ph-SCF$_3$)



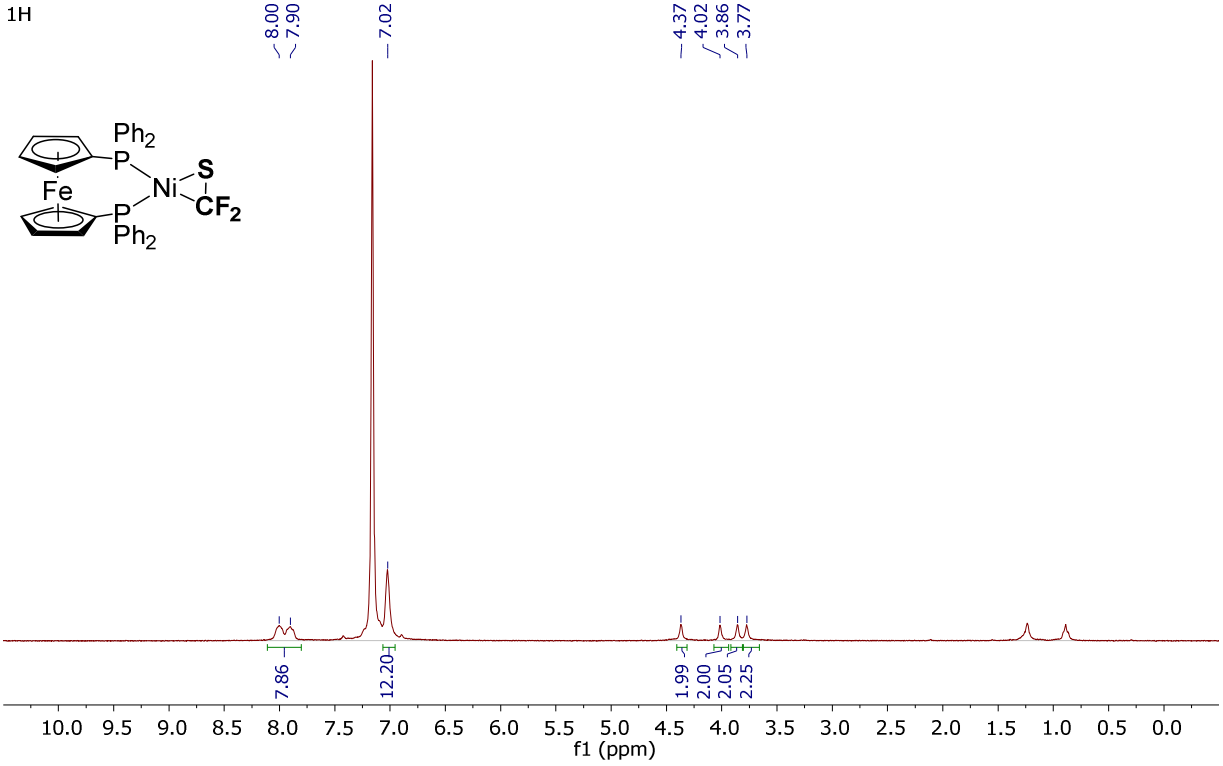

```
Zero-point correction=                           0.338029 (Hartree/Particle)
 Thermal correction to Energy=                    0.366007
 Thermal correction to Enthalpy=                  0.366951
 Thermal correction to Gibbs Free Energy=         0.275230
 Sum of electronic and zero-point Energies=          -1873.582866
 Sum of electronic and thermal Energies=             -1873.554889
 Sum of electronic and thermal Enthalpies=           -1873.553945
 Sum of electronic and thermal Free Energies=        -1873.645665
CPCM (THF) M06/def2TZVP E = -3497.77016884
```

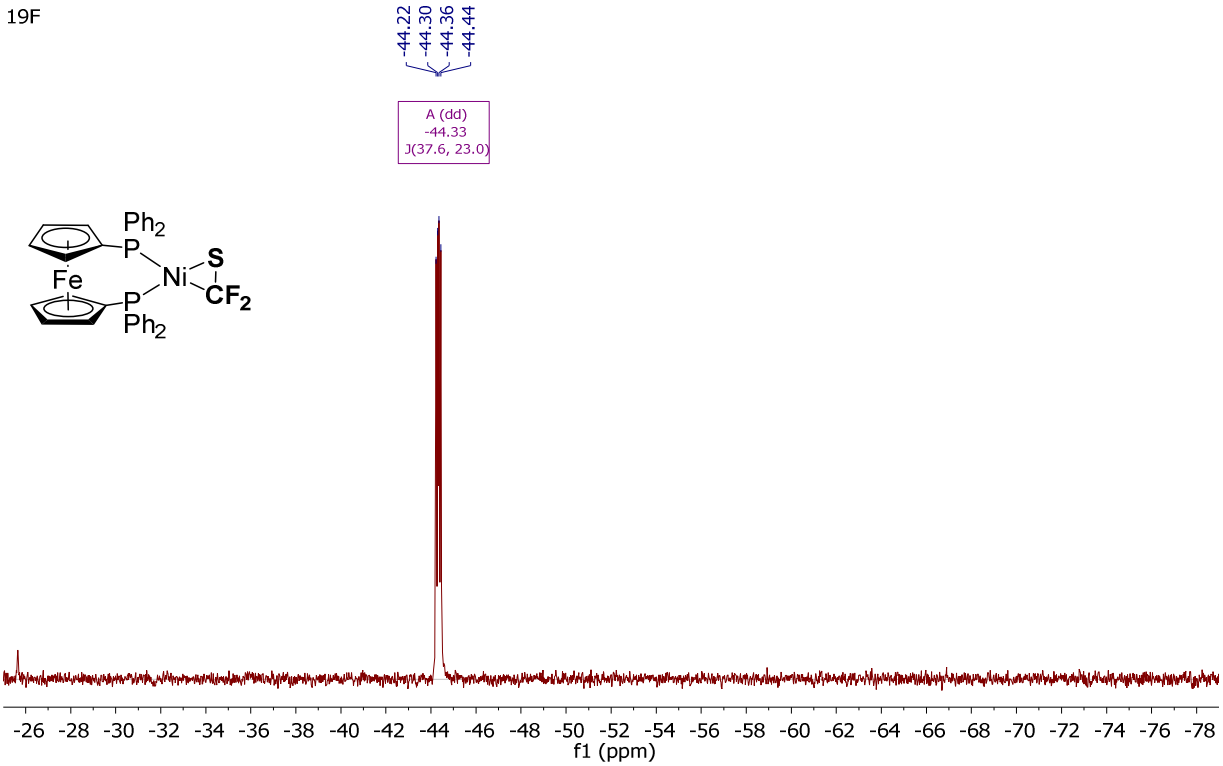
(dmbpy)Ni(I)

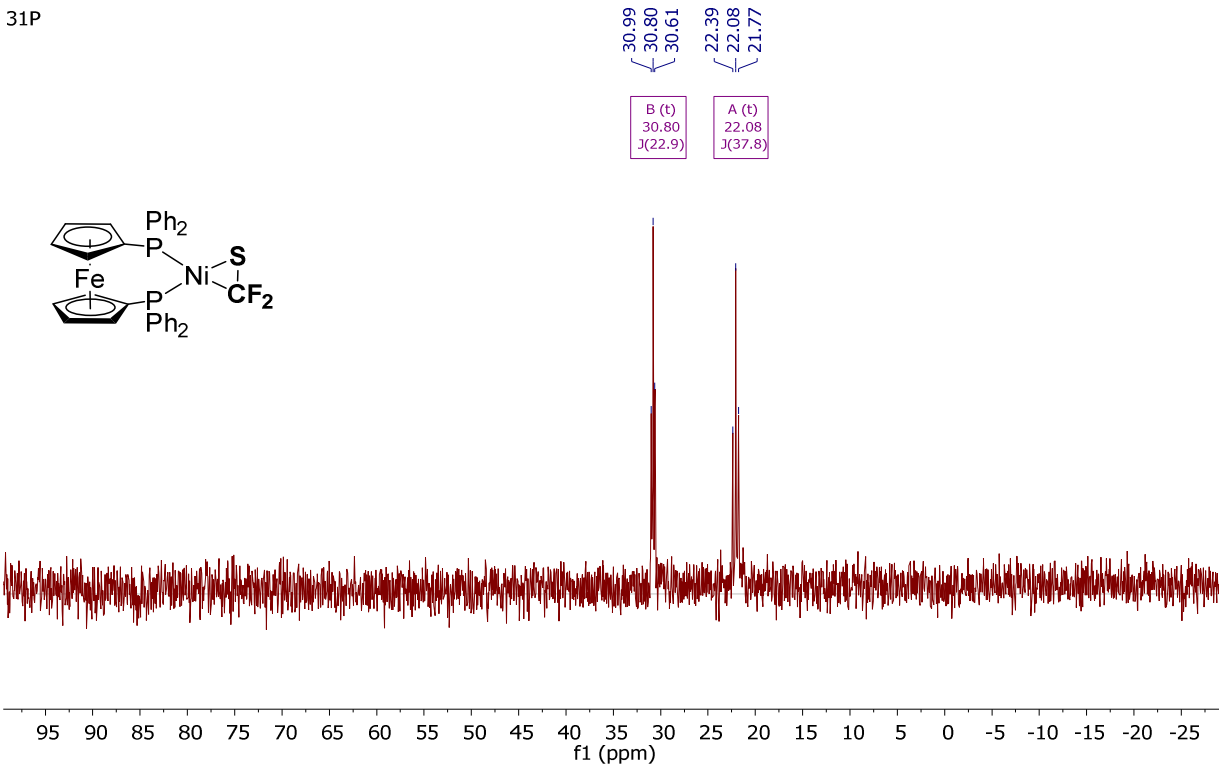


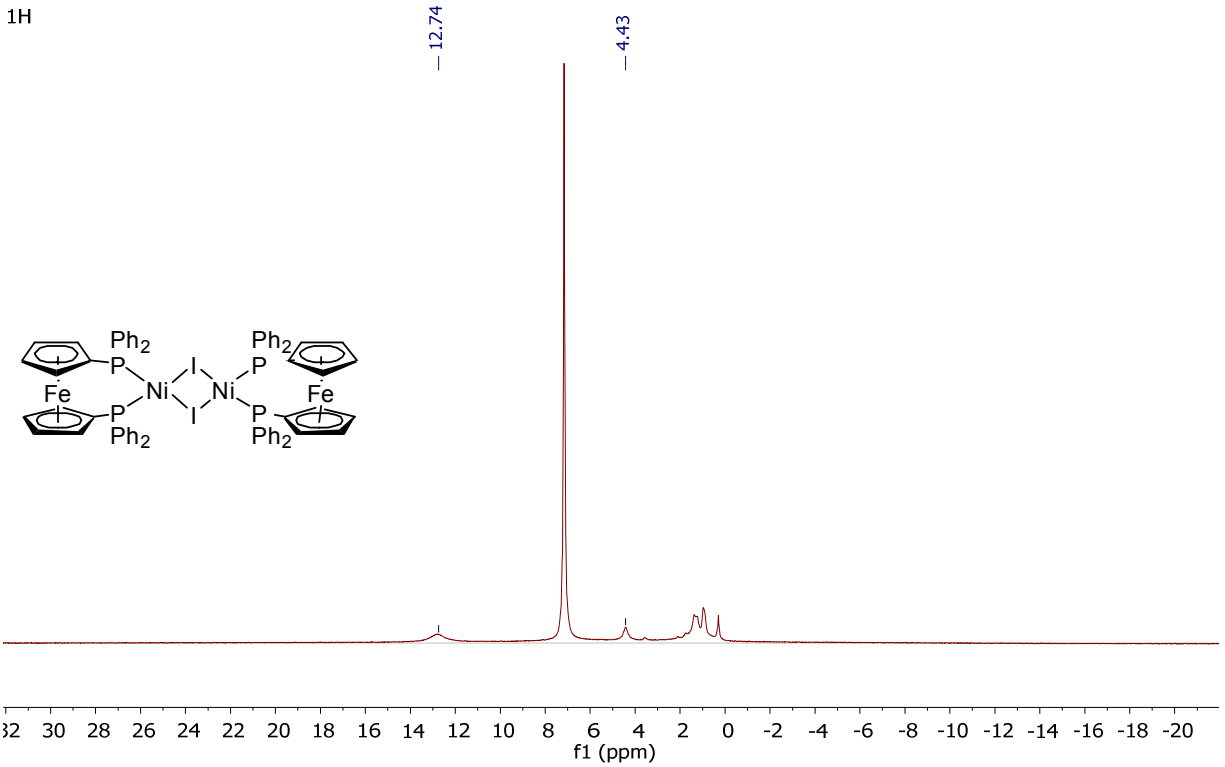

```
Zero-point correction=                           0.228570 (Hartree/Particle)
 Thermal correction to Energy=                    0.244779
 Thermal correction to Enthalpy=                  0.245723
 Thermal correction to Gibbs Free Energy=         0.180999
 Sum of electronic and zero-point Energies=          -906.436669
 Sum of electronic and thermal Energies=             -906.420460
 Sum of electronic and thermal Enthalpies=           -906.419516
 Sum of electronic and thermal Free Energies=        -906.484240
CPCM (THF) M06/def2TZVP E = -2530.39541558
```

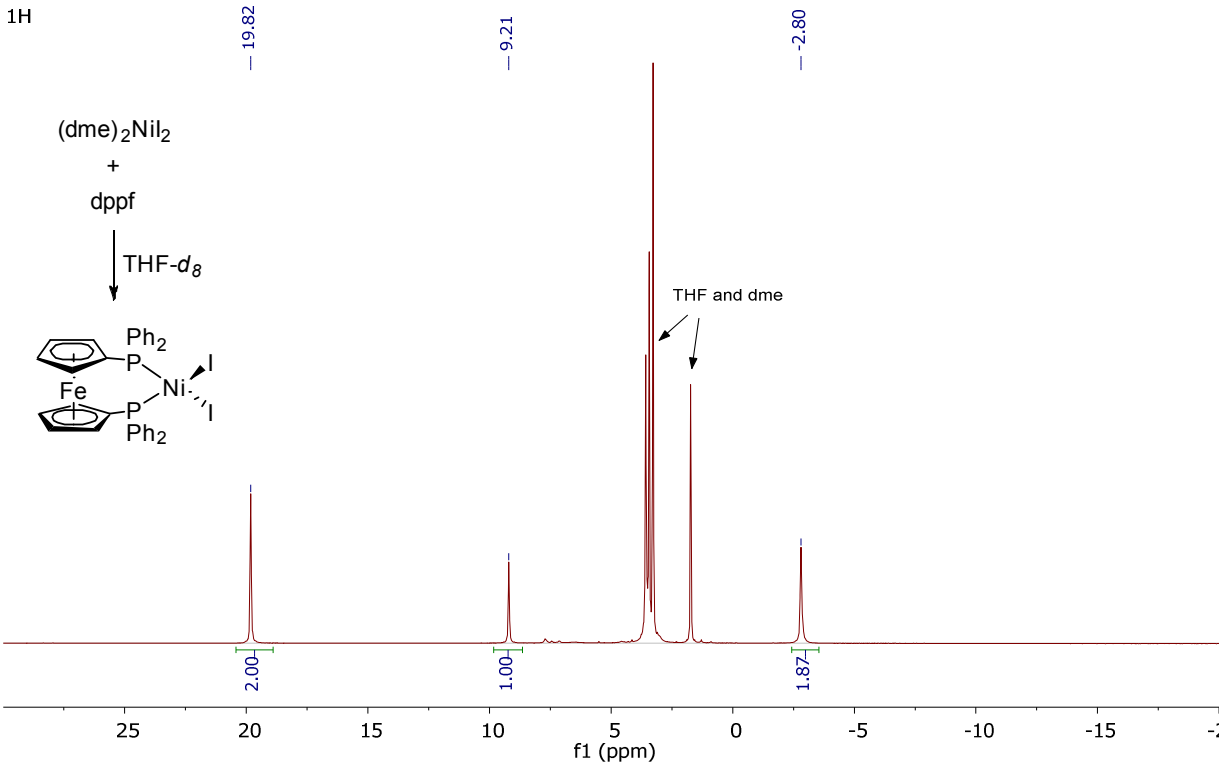
5. NMR spectra

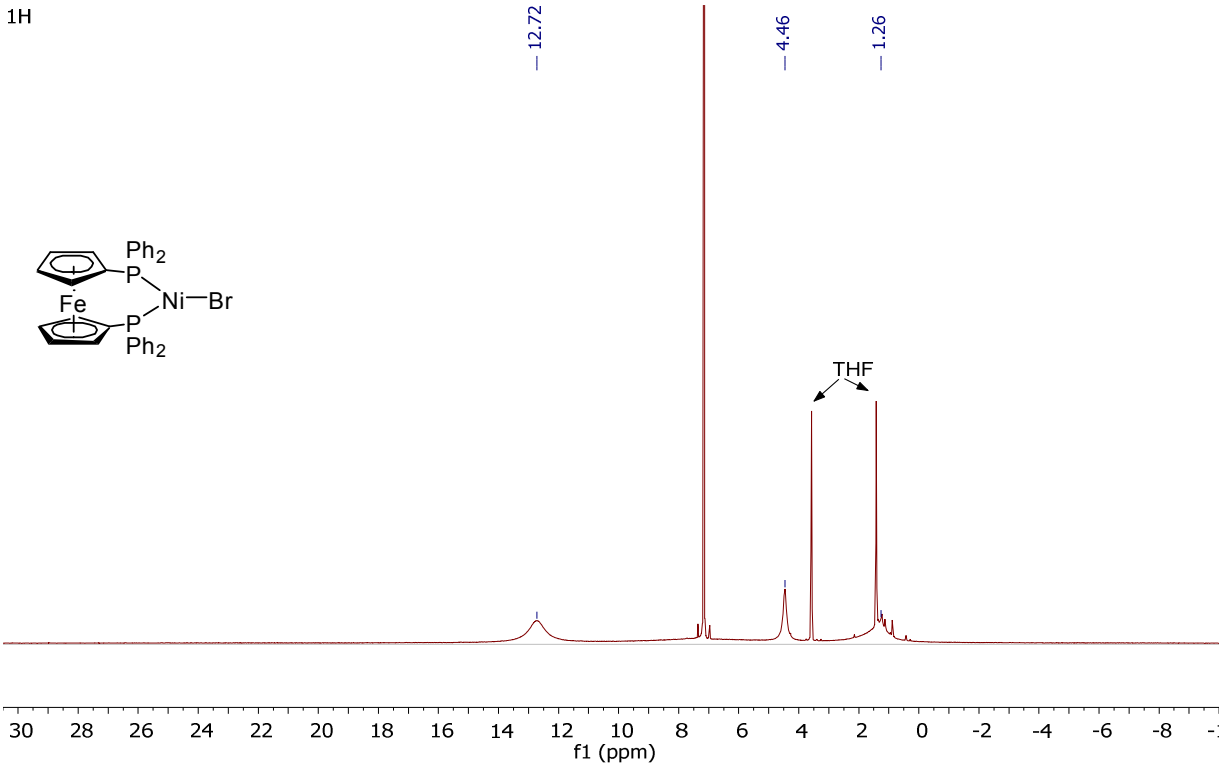





31P
30.99
30.80
30.61
22.39
22.08
21.77
B (t)
30.80
J(22.9)
A (t)
22.08
J(37.8)
Ph2
P
Fe
Ni
S
CF2
P
Ph2
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)


1H
12.74
4.43
Ph2
P
Fe
Ni
I
Ni
I
P
Ph2
32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20
f1 (ppm)


1H
19.82
9.21
-2.80
(dme)2NiI2
+
dppf
THF-d8
Ph2
P
Fe
Ni
I
I
P
Ph2
THF and dme
2.00
1.00
1.87
25
20
15
10
5
0
-5
-10
-15
f1 (ppm)


1H
12.72
4.46
1.26
Ph2
P
Fe
Ni—Br
P
Ph2
THF
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
f1 (ppm)

6. References

(1) Yin, G.; Kalvet, I.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2015,** *54*, 6809-6813.
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(4) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
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