Supporting Information For:

Nickel-catalyzed Cross-coupling Reaction of Aryl Fluorides and Chlorides with Grignard Reagents under Nickel/Magnesium Bimetallic Cooperation

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1. Experimental details

General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in oven-dried reaction vessels under argon or nitrogen atmosphere. Flash chromatography was performed as described by Still et al.,¹ employing Kanto Silica gel 60 (spherical, neutral, 140-325 mesh). ¹H, ¹³C and ³¹P nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA-500 (500 MHz) or ECX-400 (400 MHz) NMR spectrometers. ¹H NMR and ¹³C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CDCl₃ (77.0 ppm), respectively. ³¹P NMR spectra are reported in ppm and are referenced to an external standard (85% H₃PO₄: 0.0 ppm). Gas chromatographic (GC) analysis was performed on a Shimadzu GC-14B instrument equipped with an FID detector and a capillary column, HR-1 (25 m x 0.25 mm i.d., 0.25 μm film). IR spectra were recorded on a React IR 1000 Reaction Analysis System equipped with DuraSample IR (ASI Applied System) and reported in cm⁻¹. Recycle preparative gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 machine equipped with GPC columns (JAIGEL 1H and 2H) and an RI detector RI-5HC using chloroform as eluent (flow rate: 3.5 mL/min).

Materials. Unless otherwise noted, commercial reagents were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after distillation or recrystallization just before use. Anhydrous diethyl ether was purchased from KANTO Chemical Co. and distilled over Na/benzophenone under argon atmosphere. The water content was determined with a Karl-Fischer moisture titrator (MKC-210, Kyoto Electronics Company) to be less than 20 ppm. Ni(acac)₂ was purchased from Aldrich Inc., and used as

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¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2924.

received. MeMgBr (1M in THF) was purchased from Tokyo Kasei Co., and titrated before use. All other Grignard reagents were prepared from corresponding halides and magnesium turnings in anhydrous diethyl ether, and titrated prior to use. 4-Methylphenyltrifluoromethanesulfonate,² 4-*tert*-butyl-1-chlorocyclohexene,³ 1-bromocyclooctene⁴, 1-cyclooctenyltrifluoromethanesulfonate⁵, and 1-ethyl-4-propylthiobenzene⁶ were prepared following the literature procedures. 2-Fluoroanisole was prepared by methylation of 2-fluorophenol with NaH and MeI.

1-(2-Diphenylphosphinophenyl)ethanol (Ligand 2): To a cooled (0 °C) suspension of LiAlH₄ (228 mg, 6 mmol) in THF (15 mL) was added 2-diphenylphosphinoacetophenone⁷ (1.22 g, 4 mmol) portionwise over 10 min. After 30 min stirring at 0 °C, the reaction mixture was diluted with 15 mL of THF, treated successively with water (0.3 mL), 15% aqueous NaOH (0.3 mL), and water (0.9 mL). The mixture was filtered through a pad of Celite® while washing with 15 mL of Et₂O and 3 mL of CH₂Cl₂. The organic solution was concentrated under reduced pressure and purified by silica gel chromatography (10% EtOAc/hexane) to afford the titled compound as a viscous, colorless oil which solidified upon standing (0.92 g, 75% yield); IR (neat): cm⁻¹ 3325, 3053, 2973, 1584, 1476, 1434, 1372, 1308, 1196, 1088, 1067, 1054, 1038, 1001, 893, 765, 695; ¹H NMR (400 MHz, CDCl₃): δ 7.63 (ddd, *J* = 7.8, 1.4 Hz, *J*_{HP} = 4.1 Hz, 1H), 7.39 (ddd, *J* = 7.8, 7.6, 1.4 Hz, 1H), 7.35-7.32 (m, 6H), 7.28-7.24 (m, 4H), 7.16 (ddd, *J* = 7.8, 7.6, 1.4 Hz, 1H), 6.89 (ddd, *J* = 7.8, 1.4 Hz, *J*_{HP} = 4.6 Hz, 1H), 5.63 (dq, *J*_{HP} = 6.4 Hz, *J*_{HH} = 6.4 Hz, 1H), 2.00 (br s, 1H), 1.33 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 150.1 (*J*_{CP} = 21.9 Hz), 136.8 (*J*_{CP} = 9.5 Hz), 136.2 (*J*_{CP} = 9.5 Hz), 134.1 (2C, *J*_{CP} = 19.1 Hz), 133.8 (*J*_{CP} = 14.3 Hz), 133.7 (2C, *J*_{CP} = 19.1 Hz), 133.5, 129.6, 128.9, 128.8, 128.61 (2C, *J*_{CP} = 6.7 Hz), 128.57 (2C, *J*_{CP} = 7.6 Hz), 127.6, 125.5 (*J*_{CP} = 4.8 Hz), 67.5 (*J*_{CP} = 25.8 Hz), 24.4; ³¹P NMR (162 MHz, CDCl₃): δ -17.2; Anal. Calcd for C₂₀H₁₉OP: C, 78.41; H, 6.25. Found: C, 78.26; H, 6.32.

A typical procedure for Ni/2-catalyzed cross-coupling of Grignard reagent with aryl fluorides and related electrophiles (Table 1). In a Schlenk tube were placed the

² Frantz, D. E.; Weaver, D. G.; Carey, J. P.; Kress, M. H.; Dolling, U. H. *Org. Lett.* **2002**, *4*, 4717-4718.

³ Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838-7845.

⁴ Bandodakar, D. S.; Nagendrappa, G. *Synthesis* **1990**, 843-844.

⁵ Scheiper, B.; Bonnekessel, M.; Krause, H.; Fürstner, A. *J. Org. Chem.* **2004**, *69*, 3943-3949.

⁶ Cabiddu, M. G.; Cabiddu, S.; Cadoni, E.; De Montis, S.; Fattouoni, C.; Melis, S. *Tetrahedron* **2004**, *60*, 3915.

⁷ Coote, S. J.; Dawson, G. J.; Frost, C. G.; Williams, J. M. J. *Synlett* **1993**, 509-510.

electrophile (1 mmol) and the catalyst (1.2 mL of a 8.3-mM solution prepared from Ni(acac)₂ (12.8 mg, 0.05 mmol), **2** (15.3 mg, 0.05 mmol) and Et₂O (6.0 mL) just before use, 1 mol%). To this was added PhMgBr (0.77 mL of a 1.44-M Et₂O solution, 1.1 mmol) at room temperature. The reaction was quenched by the addition of MeOH (0.5 mL) at 0 °C. After aqueous workup, the reaction mixture was filtered through a pad of Florisil®, concentrated *in vacuo*, and purified with silica gel chromatography or gel permeation chromatography.

4-Methylbiphenyl (Table 1, entries 1-6):⁸ The typical procedure was employed using 4-fluorotoluene (111 mg, 1.01 mmol). After 1 h at room temperature, workup and gel permeation chromatography afforded the titled compound as a white solid (159 mg, 94%); ¹H NMR (500 MHz, CDCl₃): δ 7.58-7.56 (m, 2H), 7.50-7.48 (m, 2H), 7.44-7.40 (m, 2H), 7.33-7.30 (m, 1H), 7.25-7.24 (m, 2H), 2.39 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 141.1, 138.2, 136.8, 129.4 (2C), 128.6 (2C), 126.9 (5C), 21.0.

For the reactions of the corresponding aryl chloride, bromide, iodide, triflate and sulfide, the product yields were determined by GC using *n*-tridecane (184 mg, 1 mmol) as an internal standard.

Comparison with other catalytic systems. Our new catalytic system was compared with other representative systems (Ni/dppp (1,3-bis(diphenylphosphino)propane) by Tamao,⁹ Mongin,¹⁰ Ni/P(OAr)₃ (Ar = 2,4-di(*tert*-butyl)phenyl) by Dankwardt,¹¹ and Ni/*N*-heterocyclic carbene (NHC) by Herrmann¹²). The cross-coupling reaction between 4-fluorotoluene and PhMgBr was employed as a benchmark test. Table S1 summarizes the results (entries 1-4) and the literature data (entries 5-7). While our system (1 mol% catalyst loading, 1 h reaction at rt) gave the cross-coupling product in nearly quantitative yield (entry 1), dppp, P(OAr)₃ and NHC were found to be less effective under the same conditions except for the solvent (THF instead of Et₂O, entries 2-4). Note that these systems were entirely ineffective in Et₂O; only 1-3 % of the cross-coupling product was detected after 1 h reaction. In addition, the use of P(OAr)₃ produced large amount of an undesirable homo-coupling product (entry 3). After all, our catalytic system proved to be

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⁸ Rao, M. S. C.; Rao, G. S. K. *Synthesis* **1987**, 231-233.

⁹ Saeki, T.; Takashima, Y.; Tamao, K. *Synlett* **2005**, 1771.

¹⁰ Mongin, F.; Mojovic, B.; Guillaumet, B.; Trécourt, F.; Quéguiner, G. *J. Org. Chem.* **2002**, 67, 8991.

¹¹ Dankwardt, J. W. *J. Organomet. Chem.* **2005**, 690, 932.

the best in terms of reactivity and selectivity.

Table S1. Comparison of the ligand **2** with others in Ni-catalyzed cross-coupling reaction of 4-fluorotoluene and PhMgBr

entry	Ni catalyst	x	solvent	conditions	yield (%)		
					II	III	I
1 ^a	Ni(acac) ₂ / 2	1	Et ₂ O	rt, 1 h	94	-	-
2	Ni(acac) ₂ /dppp	1	THF	rt, 1 h	28	1	60
3	Ni(acac) ₂ /P(OAr) ₃	1	THF	rt, 1 h	54	24	12
4	Ni(acac) ₂ /IPr•HBF ₄	1	THF	rt, 1 h	9	1	91
5 ^b	Ni(acac) ₂ /dppp	5	THF	rt, 18 h	59	-	-
6 ^c	Ni(acac) ₂ /P(OAr) ₃	5	THF	80 °C, 15 h	79	-	-
7 ^d	Ni(acac) ₂ /IPr•HBF ₄	5	THF	rt, 18 h	92	-	-

^a Isolated yield (see the main text). Yields for entries 2-4 indicate those determined by GC using *n*-tridecane as an internal standard. ^b Ref 10. ^c Ref 11. ^d Ref 12.

2-Phenylpyridine (Table 1, entry 7): The typical procedure was employed using 2-fluoropyridine (99 mg, 1.02 mmol), 0.24 mL of the catalyst solution (0.2 mol%) and 0.96 mL of additional Et₂O. After 2 h at room temperature, workup and silica gel chromatography (0-10% EtOAc/hexane) afforded the titled compound as a colorless oil (151 mg, 96%), which was identical to authentic material (Aldrich); ¹H NMR (500 MHz, CDCl₃): δ 8.70-8.68 (m, 1H), 7.99-7.97 (m, 2H), 7.77-7.71 (m, 2H), 7.49-7.45 (m, 2H), 7.43-7.40 (m, 1H), 7.24-7.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 157.4, 149.6, 139.3, 136.7, 128.9, 128.7 (2C), 126.9 (2C), 122.1, 120.6.

4-Methoxybiphenyl (Table 1, entry 8):¹³ The typical procedure was employed using 4-fluoroanisole (126 mg, 1.00 mmol). After 1 h at room temperature, workup and silica gel

¹² Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2001**, 40, 3387.

¹³ Darses, S.; Jeffery, T.; Brayer, J. L.; Demoute, J. P.; Genet, J. P. *Bull. Soc. Chim. Fr.* **1996**, 133, 1095-1102.

chromatography (0-5% EtOAc/hexane) afforded the coupling product as a white solid (171 mg, 93% yield); ¹H NMR (500 MHz, CDCl₃): δ 7.56-7.52 (m, 4H), 7.43-7.40 (m, 2H), 7.32-7.28 (m, 1H), 6.99-6.96 (m, 2H), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.1, 140.8, 133.7, 128.7 (2C), 128.1 (2C), 126.7 (2C), 126.6 (2C), 114.1, 55.3.

4-(*N,N*-Dimethylamino)biphenyl (Table 1, entry 9):¹⁴ The typical procedure was employed using 4-fluoro-*N,N*-dimethylaniline (140 mg, 1.01 mmol). After 5 h at room temperature, workup and silica gel chromatography (0-5% EtOAc/hexane) afforded the coupling product as a white solid (172 mg, 87% yield); ¹H NMR (500 MHz, CDCl₃): δ 7.56-7.53 (m, 2H), 7.52-7.49 (m, 2H), 7.40-7.37 (m, 2H), 7.26-7.23 (m, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.00 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 141.2, 129.2, 128.6 (2C), 127.7 (2C), 126.3 (2C), 126.0, 112.8 (2C), 40.6 (2C).

2-Methoxybiphenyl (Table 1. Entry 10):¹⁵ The typical procedure was employed using 2-fluoroanisole (126 mg, 1.00 mmol). After 9 h at room temperature, workup and silica gel chromatography (0-2% EtOAc/hexane) afforded the coupling product as a colorless oil (171 mg, 93% yield); ¹H NMR (500 MHz, CDCl₃): δ 7.53-7.51 (m, 2H), 7.42-7.38 (m, 2H), 7.33-7.29 (m, 3H), 7.04-7.01 (m, 1H), 6.99-6.97 (m, 1H), 3.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.4, 138.5, 130.9, 130.7, 129.5 (2C), 128.6, 127.9 (2C), 126.9, 120.8, 111.2, 55.5.

2-Methylbiphenyl (Table 1, entry 11):¹⁶ The typical procedure was employed using 2-fluorotoluene (111 mg, 1.01 mmol). After 5 h at room temperature, workup and gel permeation chromatography afforded the titled compound as a colorless oil (163 mg, 96% yield); ¹H NMR (500 MHz, CDCl₃): δ 7.42-7.39 (m, 2H), 7.35-7.31 (m, 3H), 7.27-7.22 (m, 4H), 2.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 141.90, 141.86, 135.2, 130.2, 129.7, 129.1 (2C), 128.0 (2C), 127.2, 126.7, 125.7, 20.4.

1-Phenylnaphtalene (Table 1, entry 12):¹⁷ The typical procedure was employed using 2-fluoronaphtalene (146 mg, 1.00 mmol). After 1 h at room temperature, workup and gel

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¹⁴ Chen, Q.-Y.; Li, Z.-T. *J. Fluorine Chem.* **1994**, 66, 59.

¹⁵ Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc.* **1993**, 115, 9276-9282.

¹⁶ Mowley, M. E.; DeShong, P. *J. Org. Chem.* **1999**, 64, 3266-3270.

¹⁷ Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, 67, 5553-5566.

permeation chromatography afforded the titled compound as a colorless oil (198 mg, 97% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.91-7.89 (m, 2H), 7.86-7.84 (m, 1H), 7.54-7.40 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3): δ 140.7, 140.2, 133.7, 131.6, 130.1 (2C), 128.2 (3C), 127.6, 127.2, 126.9, 126.0 (2C), 125.7, 125.4.

4-Methoxy-4'-methylbiphenyl (Table 1, entries 13 and 14):¹⁸ The typical procedure was employed using 4-fluoroanisole (125 mg, 0.99 mmol) and 4-methylphenylmagnesium bromide (0.83 mL of a 1.45-M Et_2O solution, 1.2 mmol). After 12 h at room temperature, workup and silica gel chromatography (0-5% EtOAc /hexane) afforded the coupling product as a white solid (191 mg, 97% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.49-7.45 (m, 2H), 7.44-7.40 (m, 2H), 7.20 (d, J = 7.8 Hz, 2H), 6.95-6.92 (m, 2H), 3.83 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 137.9, 136.3, 133.7, 129.4 (2C), 127.9 (2C), 126.5 (2C), 114.1 (2C), 55.3, 21.0.

The titled compound was also obtained by an alternative procedure: To a suspension of $\text{Ni}(\text{acac})_2$ (6.4 mg, 0.025 mmol), **2** (7.7 mg, 0.025 mmol) and 4-fluorotoluene (110 mg, 1.00 mmol) in Et_2O (0.3 mL) was added 4-methoxyphenylmagnesium bromide (1.69 mL of 0.89-M Et_2O /benzene (ca. 2:1) solution, 1.5 mmol). After 12 h at room temperature, workup and silica gel chromatography (0-5% EtOAc /hexane) afforded the coupling product as a white solid (187 mg, 94% yield).

4-Methoxy-2'-methylbiphenyl (Table 1, entry 15):¹⁹ To a suspension of $\text{Ni}(\text{acac})_2$ (12.8 mg, 0.05 mmol), **2** (15.3 mg, 0.05 mmol) and 4-fluoroanisole (126 mg, 1.00 mmol) in Et_2O (1.0 mL) was added 2-methylphenylmagnesium bromide (0.97 mL of a 1.55-M Et_2O solution, 1.5 mmol). The Schlenk tube was sealed with a teflon stopcock and warmed at 40 °C. After 48 h, workup and silica gel chromatography (0-5% EtOAc /hexane) afforded the coupling product as a white solid (54 mg, 27% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.27-7.20 (m, 6H), 6.96-6.93 (m, 2H), 3.84 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.4, 141.5, 135.4, 134.3, 130.3, 130.2 (2C), 129.9, 126.9, 125.7, 113.4 (2C), 55.2, 20.5.

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¹⁸ Ueda, M.; Saitoh, A.; Oh-tani, S.; Miyaura, N. *Tetrahedron* **1998**, *54*, 13079-13086.

¹⁹ Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434-5444.

1-Phenyl-4-*tert*-butylcyclohex-1-ene (Table 1, entry 17):²⁰ The typical procedure was followed using 1-chloro-4-*tert*-butylcyclohex-1-ene (173 mg, 1.00 mmol), 60 μ L of a 8.3-mM catalyst solution, and 1.2 mL of additional Et₂O. After 3 h at room temperature, workup and ¹H NMR analysis of the crude product showed, upon comparison with the integration of an internal standard (bromoform, 253 mg, 1.0 mmol), that 1-phenylcyclooctene was obtained in 95% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.40-7.38 (m, 2H), 7.33-7.28 (m, 2H), 7.22-7.18 (m, 1H), 6.13-6.11 (m, 1H), 2.54-2.49 (m, 1H), 2.45-2.37 (m, 1H), 2.27-2.21 (m, 1H), 2.00-1.93 (m, 2H), 1.39-1.22 (m, 2H), 0.91 (s, 9H).

1-Phenylcyclooctene (Table 1, entries 18 and 19):⁵ The typical procedure was followed using 1-bromocyclooctene (188 mg, 0.99 mmol), 60 μ L of a 8.3-mM catalyst solution, and 1.2 mL of additional Et₂O. After 5 h at room temperature, workup and ¹H NMR analysis of the crude product showed, upon comparison with the integration of an internal standard (tetrachloroethane, 84 mg, 0.5 mmol), that 1-phenylcyclooctene was obtained in 100% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.42-7.39 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.19 (m, 1H), 6.00 (t, *J* = 8.3 Hz, 1H), 2.64-2.61 (m, 2H), 2.31-2.27 (m, 2H), 1.66-1.51 (m, 8H).

1-cyclooctenyltrifluoromethanesulfonate was subjected to the same reaction conditions to afford the titled compound in 17% yield with 83% recovery of the starting material. Catalyst loading of 1 mol% afforded 88% yield (7% recovery) after 5 h.

Competition experiments between aryl fluoride and sulfide (eq 2). To a stirred mixture of 4-fluorotoluene (110 mg, 1.00 mmol), 1-ethyl-4-propylthiobenzene (181 mg, 1.00 mmol), *n*-tridecane (internal standard; 92.2 mg, 0.5 mmol) and 1.31 mL of a 7.6-mM catalyst solution (1 mol%) was added PhMgBr (0.691 mL of a 1.49-M Et₂O solution, 1.03 mmol) at 25 °C. The reaction was monitored by GC after 2 h and 4 h to determine the product composition; 2 h: 4-methylbiphenyl (52%), 4-ethylbiphenyl (0%), 4-fluorotoluene (30%), 1-ethyl-4-propylthiobenzene (100%); 4 h: 4-methylbiphenyl (60%), 4-ethylbiphenyl (0%), 4-fluorotoluene (26%), 1-ethyl-4-propylthiobenzene (100%). The reaction using NiCl₂(dppp) (5 mol%) as the catalyst was similarly carried out at reflux for 22 h to afford 4-methylbiphenyl and 4-ethylbiphenyl in 4% and 34% yields, respectively.

A typical procedure for Ni/2-catalyzed arylation of aryl polyfluorides and

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²⁰ Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095-4112.

polychlorides (Table 2). To a cooled (ca. 15 °C) suspension of Ni(acac)₂, **2** and the polyhalide in Et₂O was added the Grignard reagent over 10 min (Since the initial arylation takes place rather violently, the Grignard reagent must be slowly added to the cooled suspension of the catalyst and the halide). After 20 min of the Grignard addition, the reaction mixture was allowed to room temperature or warmed at 45 °C. The reaction was quenched by the addition of MeOH (0.5 mL) at 0 °C. After aqueous workup, the reaction mixture was filtered through a pad of Florisil®, concentrated *in vacuo*, and purified with silica gel chromatography or gel permeation chromatography.

***p*-Terphenyl:** The typical procedure was employed using 1,4-difluorobenzene (118 mg, 1.03 mmol), Ni(acac)₂/**2** (0.6 mL of a 8.3-mM Et₂O solution, 0.5 mol%), and PhMgBr (1.46 mL of a 1.44-M Et₂O solution, 2.1 mmol). After 1 h at room temperature, workup and concentration afforded a pale-yellow solid. Washing of the solid with hexane (1 mL for five times) afforded the title compound as a white solid (220 mg, 92% yield), which was identical to authentic material (TCI); ¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 4H), 7.64 (d, *J* = 7.8 Hz, 4H), 7.47-7.44 (m, 4H), 7.37-7.33 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 140.7 (2C), 140.1 (2C), 128.8 (4C), 127.5 (4C), 127.3 (2C), 127.0 (4C).

***m*-Terphenyl:**²¹ The typical procedure was employed using 1,3-difluorobenzene (115 mg, 1.01 mmol), Ni(acac)₂/**2** (1.2 mL of a 8.3-mM Et₂O solution, 1 mol%), and PhMgBr (1.47 mL of a 1.44-M Et₂O solution, 2.1 mmol). After 2 h at room temperature, workup and gel permeation chromatography afforded the title compound as a white solid (213 mg, 92% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.79 (t, *J* = 1.8 Hz, 1H), 7.62-7.60 (m, 4H), 7.55-7.52 (m, 2H), 7.47-7.45 (m, 1H), 7.43-7.39 (m, 4H), 7.34-7.30 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 141.7 (2C), 141.1 (2C), 129.1, 128.7 (4C), 127.3 (2C), 127.2 (4C), 126.1 (3C).

***o*-Terphenyl:**²² The typical procedure was employed using 1,2-difluorobenzene (116 mg, 1.02 mmol), Ni(acac)₂ (12.8 mg, 0.05 mmol), **2** (15.3 mg, 0.05 mmol), Et₂O (0.3 mL) and PhMgBr (1.77 mL of a 1.44-M Et₂O solution, 2.5 mmol). After 48 h at room temperature, workup and gel permeation chromatography afforded the title compound as a colorless

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²¹ Tiecco, M.; Testaferri, L.; Tingoli, M.; Wenkert, E. *Tetrahedron* **1983**, *39*, 2289-2294.

²² Sahoo, A. K.; Oda, T.; Nakao, Y.; Hiyama, T. *Adv. Synth. Catal.* **2004**, *346*, 1715-1727.

solid (197 mg, 85% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.44-7.41 (m, 4H), 7.22-7.19 (m, 6H), 7.15-7.13 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 141.4, 140.4, 130.5, 129.9, 127.8, 127.4, 126.4.

1,3,5-Triphenylbenzene:²³ The typical procedure was employed using 1,3,5-trifluorobenzene (135 mg, 1.02 mmol), $\text{Ni}(\text{acac})_2$ (6.4 mg, 0.025 mmol), **2** (7.7 mg, 0.025 mmol), Et_2O (0.6 mL) and PhMgBr (2.5 mL of a 1.44-M Et_2O solution, 3.6 mmol). After 2 h at room temperature, workup and concentration afforded a pale-yellow solid. Washing of the solid with hexane (1 mL for five times) and Et_2O (1 mL for 3 times) afforded the title compound as a white solid (277 mg, 88% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.78 (s, 3H), 7.71-7.68 (m, 6H), 7.49-7.46 (m, 6H), 7.40-7.37 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 142.3 (3C), 141.1 (3C), 128.8 (6C), 127.5 (3C), 127.2 (6C), 125.1 (3C).

1,3,5-Tris(4-methylphenyl)benzene:²³ The typical procedure was employed using 1,3,5-trichlorobenzene (182 mg, 1.00 mmol), $\text{Ni}(\text{acac})_2$ (6.4 mg, 0.025 mmol), **2** (7.7 mg, 0.025 mmol), Et_2O (0.6 mL) and 4-methylphenylmagnesium bromide (2.4 mL of a 1.45-M Et_2O solution, 3.5 mmol). After 2 h at room temperature, workup and silica gel chromatography (0-10% toluene/hexane) afforded the titled compound as a white solid (315 mg, 91% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.73 (s, 3H), 7.59 (d, J = 8.0 Hz, 6H), 7.28 (d, J = 8.2 Hz, 6H), 2.42 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 142.1 (3C), 138.4 (3C), 137.3 (3C), 129.5 (6C), 127.2 (6C), 124.6 (3C), 21.1 (3C).

1-Methoxy-2,4,6-tris(4-methylphenyl)benzene: The typical procedure was employed using 2,4,6-trichloroanisole (106 mg, 0.50 mmol), $\text{Ni}(\text{acac})_2$ (6.4 mg, 0.025 mmol), **2** (7.7 mg, 0.025 mmol), Et_2O (0.8 mL) and 4-methylphenylmagnesium bromide (1.21 mL of a 1.45-M Et_2O solution, 1.75 mmol). After 20 h at room temperature, workup and gel permeation chromatography afforded the titled compound as a white solid (150 mg, 80% yield); IR (powder): cm^{-1} 3025, 2917, 1513, 1463, 1422, 1393, 1310, 1227, 1173, 1115, 1073, 1003, 949, 890, 826, 810, 789, 780, 756, 723, 702; ^1H NMR (500 MHz, CDCl_3): δ 7.55 (d, J = 8.1 Hz, 4H), 7.52 (s, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.1 Hz, 4H),

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²³ Cheng, K. J.; Ding, Z. B.; Wu, S. H. *Synth. Commun.* **1997**, 27, 11.

7.22 (d, $J = 8.3$ Hz, 2H), 3.20 (s, 3H), 2.40 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 154.2, 137.7, 137.0, 136.9 (3C), 135.8 (4C), 129.5 (2C), 129.2 (4C), 128.9 (4C), 128.5 (2C), 126.8 (2C), 60.5, 21.2, 21.1 (2C); Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{O}$: C, 88.85; H, 6.92. Found: C, 88.74; H, 6.91.

1,2,4-Triphenylbenzene: ²⁴ The typical procedure was employed using 1,2,4-trichlorobenzene (91 mg, 0.50 mmol), $\text{Ni}(\text{acac})_2$ (6.4 mg, 0.025 mmol), **2** (7.7 mg, 0.025 mmol), Et_2O (0.6 mL) and PhMgBr (1.39 mL of a 1.44-M Et_2O solution, 2.0 mmol). After 48 h at 45 °C, workup and gel permeation chromatography afforded the titled compound as a white solid (136 mg, 89% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.66-7.60 (m, 4H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.42-7.39 (m, 2H), 7.33-7.30 (m, 1H), 7.20-7.15 (m, 10 H); ^{13}C NMR (125 MHz, CDCl_3): δ 141.4, 141.1, 140.9, 140.5, 140.3, 139.5, 131.1, 129.86 (2C), 129.82 (2C), 129.4, 128.8 (2C), 127.90 (2C), 127.87 (2C), 127.4, 127.1 (2C), 126.55, 126.48, 126.1.

1-Chloro-2,6-bis(4-methylphenyl)benzene: The typical procedure was employed using 1,2,3-trichlorobenzene (91 mg, 0.50 mmol), $\text{Ni}(\text{acac})_2$ (6.4 mg, 0.025 mmol), **2** (7.7 mg, 0.025 mmol), Et_2O (0.8 mL) and PhMgBr (1.21 mL of a 1.44-M Et_2O solution, 1.74 mmol). After 24 h at room temperature, workup and gel permeation chromatography afforded the titled compound as a pale-yellow solid (128 mg, 87% yield); IR (powder): cm^{-1} 3025, 2948, 2919, 2856, 1914, 1611, 1513, 1476, 1453, 1418, 1387, 1306, 1260, 1214, 1185, 1115, 1042, 1028, 1019, 973, 949, 841, 789, 760, 743, 731, 718; ^1H NMR (500 MHz, CDCl_3): δ 7.35 (d, $J = 8.0$ Hz, 4H), 7.30-7.27 (m, 3H), 7.23 (d, $J = 7.8$ Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 141.5 (2C), 137.2 (4C), 131.0, 130.6 (2C), 129.4 (4C), 128.7 (4C), 126.3, 21.2 (2C); Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}$: C, 82.04; H, 6.07. Found: C, 82.03; H, 5.85.

1,2,4,5-Tetraphenylbenzene: ²⁵ The typical procedure was employed using 1,2,4,5-tetrachlorobenzene (108 mg, 0.50 mmol), $\text{Ni}(\text{acac})_2$ (9.7 mg, 0.038 mmol), **2** (11.6 mg, 0.038 mmol), Et_2O (0.5 mL) and PhMgBr (1.91 mL of a 1.44-M Et_2O solution, 2.75 mmol). After 96 h at 45 °C, workup and gel permeation chromatography afforded the titled

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²⁴ Ozelov, O. V.; Patrick, B. O.; Ladipo, F. T. *J. Am. Chem. Soc.* **2000**, *122*, 6423-6431.

²⁵ Yang, J.; Verkade, J. G. *Organometallics* **2000**, *19*, 893-900.

compound as a white solid (110 mg, 58% yield); ^1H NMR (500 MHz, CDCl_3): δ 7.53 (s, 2H), 7.24-7.21 (m, 20H); ^{13}C NMR (125 MHz, CDCl_3): δ 140.9 (4C), 139.6 (4C), 133.0 (2C), 129.9 (8C), 128.0 (8C), 126.6 (4C).

2. Computational details

Methods.

All calculations were performed with a Gaussian 03 package.²⁶ The density functional theory (DFT) method was employed using the B3LYP hybrid functional.²⁷ Structures were optimized with a basis set consisting of the LANL2DZ basis set including a double-zeta valence basis set with the Hay and Wadt effective core potential (ECP) for Ni²⁸ and 6-31G(d)²⁹ for the rest. The method and basis sets used here have been applied to related systems and known to give reliable results.³⁰ Each stationary point was adequately characterized by normal coordinate analysis (no imaginary frequencies for an equilibrium structure and one imaginary frequency for a transition structure). The intrinsic reaction coordinate (IRC) analysis³¹ was carried out to confirm that stationary points are smoothly connected to each other.

Reaction pathways and energetics.

Schemes S1 and S2 show the reaction pathways for oxidative addition of vinyl fluoride (or sulfide) to the Ni/Mg bimetallic complex (**cat1**) and Ni(H₂PCH₂CH₂PH₂) (**cat2**), respectively. The latter was employed as a model of the reaction when the magnesium salt does not take part in the reaction. In this model, the reaction took place through a three-centered TS as has been accepted widely. Energy diagrams for these reactions are shown in Figure S1.

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²⁶ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

²⁷ (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G.; *Phys. Rev. B* **1988**, *37*, 785-789.

²⁸ Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 299-310.

²⁹ Hehre, W. J.; Radom, L.; Schleyer, P. v R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons, Inc.: New York, 1986. References cited therein.

³⁰ Yamanaka, M.; Inagaki, A.; Nakamura, E. *J. Comput. Chem.* **2003**, *24*, 1401-1409.

³¹ (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363-368. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*,

Scheme S1. Ni/Mg Bimetallic Synergistic Pathway for C-F Bond Cleavage

Scheme S2. Three-centered Pathways for C-F and C-S Bond Cleavage in the Absence of Mg(II) Salt

Figure S1. Energy diagrams (kcal/mol) for oxidative addition reactions described in Schemes S1 and S2. Numbers in italics represents activation energies for C-F (or C-S) bond cleavage.

Energies and Cartesian coordinates of stationary points.

vinyl fluoride

SCF Done: E(RB+HF-LYP) = -177.819638916 A.U. after 8 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.432477	0.000000
2	6	0	1.190448	-0.148818	0.000000
3	1	0	2.086043	0.461370	0.000000
4	9	0	-1.149105	-0.270942	0.000000
5	1	0	1.294846	-1.228473	0.000000
6	1	0	-0.181634	1.503627	0.000000

methyl vinyl sulfide

SCF Done: E(RB+HF-LYP) = -516.091833572 A.U. after 8 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.926338	0.443351	-0.206928
2	6	0	-2.160570	0.117166	0.184241
3	1	0	-2.993849	0.790553	0.004082
4	16	0	0.464500	-0.650511	-0.095690
5	1	0	-2.382318	-0.826468	0.674974
6	1	0	-0.725967	1.398117	-0.692462
7	6	0	1.814468	0.556011	0.170598
8	1	0	1.721278	1.051174	1.140419
9	1	0	1.833140	1.303397	-0.628393
10	1	0	2.750358	-0.007759	0.144948

cat1

SCF Done: E(RB+HF-LYP) = -1517.82046292 A.U. after 11 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	28	0	0.615159	-1.064571	-0.560189
2	15	0	-1.069692	-1.907825	0.533141
3	6	0	-2.087579	-0.365667	0.306461
4	1	0	-2.132006	-2.853979	0.469671
5	1	0	-0.896884	-1.976799	1.941888
6	6	0	-1.510395	0.931751	0.286991
7	6	0	-2.344142	2.023274	0.013831
8	6	0	-3.705967	1.868121	-0.246485
9	6	0	-4.265005	0.593500	-0.236235
10	12	0	2.714791	0.133923	-0.150829
11	17	0	4.808874	0.765989	0.246711
12	6	0	-3.456210	-0.509905	0.037971
13	6	0	-0.046902	1.232804	0.597346
14	1	0	-1.910358	3.020185	0.001122
15	1	0	-4.320272	2.738371	-0.459974
16	1	0	-5.322788	0.451380	-0.439593
17	1	0	-3.900852	-1.501633	0.045913
18	1	0	0.199239	0.825735	1.590120
19	1	0	0.072686	2.321443	0.657173
20	8	0	0.900126	0.766063	-0.382696

CP1

SCF Done: E(RB+HF-LYP) = -1695.73126957 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	1.763872	-2.744404	-0.376217
2	6	0	2.307113	-1.496167	-0.788001
3	1	0	2.676114	-1.320520	-1.797782
4	1	0	2.051936	-3.159878	0.590082
5	9	0	3.347587	-0.845127	0.112280
6	1	0	1.566774	-3.489193	-1.147799
7	28	0	0.559897	-1.258529	-0.088147
8	15	0	-1.507923	-1.741173	0.559844
9	6	0	-2.548943	-0.275460	0.176963
10	1	0	-2.315332	-2.777502	0.037972
11	1	0	-1.790577	-1.978546	1.931668
12	6	0	-2.021183	1.018783	0.385284
13	6	0	-2.798319	2.122071	0.018348
14	6	0	-4.064293	1.965518	-0.548331
15	6	0	-4.575217	0.686696	-0.760685
16	12	0	2.285220	0.845624	0.064544
17	17	0	3.551095	2.664945	-0.175038
18	6	0	-3.815505	-0.427300	-0.401072
19	6	0	-0.659825	1.249829	1.027714
20	1	0	-2.399435	3.121573	0.173935
21	1	0	-4.643529	2.840739	-0.829252
22	1	0	-5.557523	0.552132	-1.204778
23	1	0	-4.216031	-1.423783	-0.569928
24	1	0	-0.678579	0.851504	2.056939
25	1	0	-0.498573	2.332376	1.112230
26	8	0	0.412592	0.670589	0.312970

TS1

SCF Done: E(RB+HF-LYP) = -1695.72106962 A.U. after 11 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.232259	-3.132380	-0.277289
2	6	0	2.181431	-1.928492	-0.884131
3	1	0	2.601003	-1.630889	-1.836533
4	1	0	2.061956	-3.256941	0.796707
5	9	0	3.610704	0.091832	-0.638088
6	1	0	2.509076	-4.048679	-0.803072
7	28	0	0.664147	-1.578145	0.010366
8	15	0	-1.532313	-1.904155	0.704911
9	6	0	-2.423463	-0.394948	0.184569
10	1	0	-2.329610	-2.926641	0.147151
11	1	0	-1.905759	-2.088599	2.060527
12	6	0	-1.755822	0.836248	0.351799
13	6	0	-2.373952	2.000769	-0.112620
14	6	0	-3.623449	1.951502	-0.734223
15	6	0	-4.274409	0.729475	-0.900591
16	12	0	2.325200	1.209268	-0.109426
17	17	0	2.148676	3.434979	0.228753
18	6	0	-3.672597	-0.444352	-0.444343
19	6	0	-0.403819	0.911145	1.038485
20	1	0	-1.864032	2.952986	0.008467
21	1	0	-4.083998	2.867556	-1.093250
22	1	0	-5.245558	0.685641	-1.385314
23	1	0	-4.179399	-1.396579	-0.578268
24	1	0	-0.469055	0.461632	2.042430
25	1	0	-0.132013	1.963800	1.177160
26	8	0	0.647833	0.282617	0.304655

PD1

SCF Done: E(RB+HF-LYP) = -1695.72757792 A.U. after 10 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.731363	-2.767866	-0.492487
2	6	0	2.812838	-1.465996	-0.381505

3	1	0	3.505891	-0.645020	-0.551824
4	1	0	1.726319	-3.245416	-0.202980
5	9	0	3.479964	1.273684	-0.801932
6	1	0	3.419545	-3.539405	-0.829805
7	28	0	1.037829	-1.576291	0.107145
8	15	0	-1.161356	-2.278123	0.384576
9	6	0	-2.214302	-0.822168	0.061782
10	1	0	-1.729407	-3.252740	-0.464223
11	1	0	-1.628304	-2.803719	1.615398
12	6	0	-1.724318	0.432692	0.477649
13	6	0	-2.464028	1.578067	0.165992
14	6	0	-3.666838	1.482954	-0.536564
15	6	0	-4.146340	0.237344	-0.941973
16	12	0	1.871702	1.721780	-0.182506
17	17	0	0.848821	3.714127	0.159854
18	6	0	-3.417101	-0.915454	-0.648161
19	6	0	-0.422882	0.555595	1.248589
20	1	0	-2.077016	2.549785	0.459907
21	1	0	-4.224251	2.384676	-0.773802
22	1	0	-5.080516	0.160155	-1.490974
23	1	0	-3.786714	-1.884584	-0.973323
24	1	0	-0.437501	-0.089133	2.140125
25	1	0	-0.320448	1.587190	1.601531
26	8	0	0.731638	0.241313	0.458912

cat2

SCF Done: E(RB+HF-LYP) = -933.012093936 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	28	0	0.000103	-1.226142	0.000029
2	15	0	1.628453	0.108967	0.056835
3	15	0	-1.628464	0.108731	-0.056930
4	6	0	0.706464	1.723111	-0.307923
5	6	0	-0.706768	1.723004	0.308041
6	1	0	2.285814	0.474288	1.269083
7	1	0	2.766938	0.337670	-0.773064
8	1	0	-2.285756	0.474121	-1.269190
9	1	0	-2.767087	0.337104	0.772874
10	1	0	1.277941	2.592733	0.036639
11	1	0	0.637131	1.790732	-1.400542
12	1	0	-1.278345	2.592547	-0.036560
13	1	0	-0.637526	1.790616	1.400663

CP2

SCF Done: E(RB+HF-LYP) = -1110.88718376 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	28	0	0.545777	-0.234770	-0.150018
2	15	0	-0.700531	1.571947	-0.111048
3	15	0	-1.261899	-1.487421	0.079865
4	6	0	-2.500819	1.020142	-0.228689
5	6	0	-2.687723	-0.324028	0.497864
6	1	0	-0.752349	2.366150	1.066432
7	1	0	-0.725383	2.659101	-1.024869
8	1	0	-1.807861	-2.158407	-1.048581
9	1	0	-1.525701	-2.527529	1.010353
10	6	0	2.464007	0.190602	-0.307748
11	9	0	2.915185	0.873383	0.806016
12	6	0	2.284172	-1.194367	-0.233017
13	1	0	2.744699	0.713379	-1.220584
14	1	0	2.492267	-1.722057	0.695504
15	1	0	2.351269	-1.781768	-1.146756
16	1	0	-3.186131	1.779014	0.162342
17	1	0	-2.719508	0.902131	-1.297381

18	1	0	-3.660398	-0.768376	0.263620
19	1	0	-2.650692	-0.170505	1.583556

TS2

SCF Done: E(RB+HF-LYP) = -1110.82715329 A.U. after 11 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.827782	0.342134	1.245729
2	6	0	-2.353117	0.524296	-0.002128
3	1	0	-2.705501	1.267733	-0.710115
4	1	0	-2.543930	-0.515881	1.849555
5	9	0	-2.212544	-0.926465	-0.916348
6	1	0	-3.497301	1.072575	1.694884
7	28	0	-0.603672	-0.169460	-0.183090
8	15	0	0.726287	1.567314	-0.237799
9	15	0	1.208553	-1.521430	0.256398
10	6	0	2.420955	1.020365	0.372488
11	6	0	2.703203	-0.425155	-0.074539
12	1	0	0.566327	2.766855	0.502624
13	1	0	1.493003	-1.933187	1.586025
14	1	0	1.650463	-2.717783	-0.367691
15	1	0	3.212915	1.696467	0.034975
16	1	0	2.388243	1.075133	1.467546
17	1	0	3.602417	-0.816497	0.411258
18	1	0	2.875975	-0.456924	-1.157335
19	1	0	1.090943	2.186455	-1.466372

PD2

SCF Done: E(RB+HF-LYP) = -1110.87125201 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	28	0	-0.632695	-0.467523	-0.053605
2	15	0	0.236192	1.533235	-0.166520
3	15	0	1.593436	-1.233407	0.196083
4	6	0	2.068004	1.523095	0.246295
5	6	0	2.706982	0.210643	-0.249314
6	1	0	0.206546	2.184159	-1.421562
7	1	0	-0.253930	2.588796	0.630884
8	1	0	2.097794	-1.601112	1.468871
9	1	0	2.175435	-2.291342	-0.539915
10	6	0	-2.319240	0.317470	-0.330831
11	9	0	-1.388186	-2.063772	-0.038562
12	6	0	-3.001012	1.135414	0.475704
13	1	0	-2.792672	-0.077725	-1.232578
14	1	0	-2.586832	1.536162	1.400734
15	1	0	-4.036233	1.414320	0.269919
16	1	0	2.584084	2.397141	-0.164001
17	1	0	2.139534	1.586302	1.339131
18	1	0	3.720611	0.091796	0.145404
19	1	0	2.781988	0.218946	-1.343479

CP3

SCF Done: E(RB+HF-LYP) = -1449.16156263 A.U. after 10 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.888352	-0.705896	0.670664
2	16	0	-3.076305	-0.097162	-0.534755
3	6	0	-1.263660	-1.951682	0.449203
4	1	0	-2.091489	-0.386839	1.693840
5	1	0	-1.418185	-2.489726	-0.485116
6	1	0	-0.999621	-2.573983	1.303516

7	6	0	-2.992473	1.704047	-0.262009
8	1	0	-2.016349	2.104213	-0.552697
9	1	0	-3.192450	1.952601	0.785142
10	1	0	-3.768294	2.159604	-0.883878
11	28	0	0.038477	-0.479515	0.196111
12	15	0	0.841499	1.570564	0.266611
13	15	0	2.038502	-1.243826	-0.308850
14	6	0	2.722557	1.414654	0.269772
15	6	0	3.154049	0.242236	-0.628067
16	1	0	0.673439	2.471637	-0.821923
17	1	0	0.691929	2.548870	1.286448
18	1	0	2.803970	-1.933010	0.670875
19	1	0	2.415194	-2.070917	-1.400069
20	1	0	3.206341	2.347757	-0.036373
21	1	0	3.014992	1.219250	1.308997
22	1	0	4.212053	0.000777	-0.484035
23	1	0	3.019277	0.509540	-1.683549

TS3

SCF Done: E(RB+HF-LYP) = -1449.12420749 A.U. after 10 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.004000	-1.640436	1.362636
2	6	0	1.619465	-1.475951	0.077779
3	1	0	1.757136	-2.262049	-0.662566
4	1	0	1.948607	-0.840106	2.098552
5	16	0	2.154800	0.424980	-0.984104
6	1	0	2.384520	-2.596011	1.723331
7	28	0	0.236046	-0.187164	-0.061131
8	15	0	-1.633610	-1.408872	-0.345958
9	15	0	-1.108813	1.608588	0.440652
10	6	0	-3.101845	-0.357878	0.189688
11	6	0	-2.835303	1.123222	-0.133540
12	1	0	-1.964596	-2.638707	0.279385
13	1	0	-1.403162	2.007246	1.773782
14	1	0	-1.025527	2.916723	-0.100045
15	1	0	-4.035593	-0.697286	-0.269571
16	1	0	-3.203158	-0.492555	1.273744
17	1	0	-3.603246	1.766320	0.307595
18	1	0	-2.857752	1.281875	-1.218665
19	1	0	-2.057733	-1.780182	-1.651305
20	6	0	3.045412	1.370881	0.304555
21	1	0	3.924106	1.828903	-0.159195
22	1	0	3.378481	0.681993	1.088975
23	1	0	2.417808	2.149975	0.746217

PD3

SCF Done: E(RB+HF-LYP) = -1449.14421401 A.U. after 8 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	28	0	-0.276148	0.046269	-0.021276
2	15	0	1.418634	1.440440	-0.138047
3	15	0	1.289947	-1.617807	0.231265
4	6	0	3.050529	0.553241	0.156999
5	6	0	2.933692	-0.905334	-0.326527
6	1	0	1.640854	2.094914	-1.372414
7	1	0	1.520063	2.566576	0.708069
8	1	0	1.618363	-2.097046	1.523507
9	1	0	1.257548	-2.862794	-0.435289
10	6	0	-1.401114	1.535649	-0.337820
11	16	0	-1.946648	-1.402745	0.005461
12	6	0	-1.709591	2.531795	0.500757
13	1	0	-1.840423	1.535229	-1.340315
14	1	0	-1.317290	2.587721	1.516003

15	1	0	-2.405508	3.326060	0.223161
16	1	0	3.890895	1.065499	-0.322254
17	1	0	3.228484	0.576785	1.239096
18	1	0	3.780815	-1.506841	0.017961
19	1	0	2.928474	-0.940322	-1.422612
20	6	0	-3.585330	-0.585901	-0.122770
21	1	0	-3.706316	-0.077254	-1.083853
22	1	0	-3.733446	0.136718	0.682060
23	1	0	-4.341822	-1.373060	-0.046845

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