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铁催化芳基格氏试剂的联芳交叉偶联的反应机理

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Reaction Mechanism for the Iron-Catalyzed Biaryl Cross-Coupling of Aryl Grignard Reagents

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Table S1 The calculated values of electronic energy Δ*E*, zero-point energy correction ΔZPE, relative enthalpy Δ*H*, relative entropy Δ*S*, Gibbs free energy ΔG_g and Gibbs free energy in solution THF, ΔG_{sol}, (298 K) for the overall catalytic cycles

	$\triangle E$	$\triangle$ZPE	$\triangle H$	$\triangle S$	$\triangle G_g$	$\triangle G_{sol}$
CA+R_1	0.0	0.0	0.0	0.0	0.0	0.0
2	−194.86	3.89	−191.29	−202.44	−130.93	−102.81
TS_1	−88.75	−1.93	−90.29	−188.96	−33.95	−33.91
3	−334.50	2.21	−330.98	−182.14	−276.68	−209.52
4+P_2	−219.34	−2.25	−220.91	−37.75	−209.66	−265.46
5	−304.52	0.39	−300.85	−187.53	−244.94	−246.48
TS_2	−299.65	−0.16	−298.78	−217.91	−233.82	−225.70
6	−327.85	−0.06	−324.56	−188.99	−268.21	−265.50
TS_3	−231.38	−1.66	−232.66	−235.05	−162.58	−182.52
P_1	−228.50	5.07	−223.43	−28.76	−214.86	−279.08
7	−478.91	4.40	−470.71	−344.70	−367.94	−256.24
TS_4	−423.70	5.37	−417.37	−400.05	−298.09	−251.37
8	−466.42	4.34	−458.52	−347.54	−354.90	−248.50

The unit of relative entropy Δ*S* is J mol^{-1} K^{-1} and all other energy units are kJ mol^{-1}.

The full optimized geometries:

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Molecule CA

Fe	0.00000000	0.00000000	2.39143900
Mg	0.00000000	1.80703100	0.64199400
Mg	0.00000000	−1.80703100	0.64199400
Br	0.00000000	−3.42084500	−1.10836100
Br	0.00000000	3.42084500	−1.10836100

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Molecule R1
C -2.43269000 -0.39722900 0.06258200
C -1.68006100 0.77226000 0.06810700
C -0.29244700 0.69870800 -0.01148100
C 0.38882900 -0.52752200 -0.09408900
C -0.40606900 -1.68779300 -0.10913700
C -1.79061000 -1.63199800 -0.02673500
H -3.51338500 -0.34030500 0.12070700
H -2.15931300 1.74045100 0.13605100
H 0.08404600 -2.64860800 -0.21165300
Cl 0.60142500 2.21999400 0.01874800
C 1.85691900 -0.60188900 -0.17813600
H 2.35150500 0.27713600 -0.57704500
C 2.60777000 -1.63761500 0.20677600
H 2.18751900 -2.52972700 0.65824400
H 3.68495300 -1.61229600 0.09406200
H -2.36941200 -2.54808600 -0.04640200
21
Molecule 2
Fe -0.22599900 -0.80855000 -0.04218800
Mg 2.19780300 -0.13650200 -0.20441100
Mg -0.42584500 1.69799200 -0.27804900
Br -1.15323900 3.96895000 -0.21581700
Br 4.58083200 -0.14123000 -0.08717100
Cl -2.23562900 -3.01635200 -1.70262500
C -1.58389600 -2.36833800 -0.19657800
C -2.27011100 -1.31459100 0.47977500
C -0.34587000 -2.90845900 0.23469300
C -1.57469700 -0.76202500 1.59458000
C 0.29510000 -2.35537000 1.35988200
H 0.10898700 -3.70896600 -0.33285800
C -0.32944400 -1.27168900 2.02494500
H -2.00914800 0.07869300 2.12046900
H 1.23650200 -2.75768900 1.71094400
C -3.59384400 -0.82662200 0.06639400
H -3.85455600 -0.98345600 -0.97394200
C -4.47861700 -0.23932600 0.87695000
H -4.29814500 -0.09511100 1.93648000
H -5.43002100 0.11030000 0.49559000
H 0.18706100 -0.77303200 2.83508500
21
Molecule TS1

Fe	-0.44150300	-0.52235500	-0.00618500
Mg	2.07663700	-1.12766400	-0.19803600
Mg	0.73392700	1.67571900	-0.12513400
Br	1.19725000	4.00018200	-0.00803700
Br	4.18034600	-2.23498000	-0.29193400
Cl	-1.34540500	-1.62822600	1.90529800
C	-2.24171100	-0.53853500	0.42565200
C	-3.31194200	-1.10071800	-0.33115000
C	-2.10019000	0.86281800	0.66724000
C	-4.10721100	-0.17567000	-1.00086600
C	-3.00225100	1.73716200	0.00084100
H	-1.61783300	1.21939500	1.56907500
C	-3.96099000	1.21957900	-0.84168600
H	-4.85583900	-0.54401700	-1.69328000
H	-2.95717200	2.80178800	0.20253400
C	-3.48201200	-2.55490700	-0.45148700
H	-2.63345400	-3.15447900	-0.13901400
C	-4.58873900	-3.18123300	-0.86299200
H	-5.49313000	-2.65132000	-1.14097200
H	-4.62358800	-4.26221800	-0.91936100
H	-4.64038600	1.88221000	-1.36451100

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Molecule 3

Fe	0.25998700	-1.49542400	-0.31805900
Mg	-2.23390100	-0.80140800	-0.08035500
Mg	0.30721800	1.02905000	-0.20092800
Br	0.38831400	3.36750500	-0.55627900
Br	-4.38492200	0.08705800	0.33448800
Cl	-1.35728400	-3.04247500	-0.33022900
C	1.83167300	-0.57383300	0.50757400
C	1.78700500	-0.20780900	1.87351700
C	3.11475800	-0.69446900	-0.10560000
C	2.94439300	0.01678900	2.61746900
H	0.82806800	-0.12421900	2.38016400
C	4.26688600	-0.42938100	0.64690100
C	4.18522500	-0.08706800	1.99333100
H	2.87650300	0.28316900	3.66596900
H	5.24020100	-0.47570800	0.17176800
C	3.20399100	-1.09606200	-1.52245700
H	2.28855000	-0.96130400	-2.09953300
C	4.26198700	-1.62288800	-2.14630100
H	5.20102000	-1.81708400	-1.64014900
H	4.21326900	-1.88849900	-3.19522500

H	5.09250300	0.11364500	2.55191300
18			
Molecule 4			
Fe	0.87212000	2.18614400	-0.28289300
Mg	-1.11905800	0.77019000	-0.09162300
Br	-3.08482300	-0.56116400	0.08174900
C	1.33816000	-0.17504000	-1.81541700
C	1.80121500	-1.46102700	-2.08268100
H	0.98992100	0.43219400	-2.64840400
C	2.24818900	-1.76835100	0.26775600
C	2.25979800	-2.25849600	-1.03365600
H	1.80991100	-1.83729600	-3.09984600
H	2.63060600	-2.38896800	1.07067800
C	1.75758700	0.03421600	1.93959000
H	1.74171500	1.12035500	2.03471000
C	1.73764400	-0.68250900	3.06836300
H	1.72307400	-1.76690100	3.06746200
H	1.72497600	-0.19771900	4.03706100
H	2.63107800	-3.25780000	-1.23068200
C	1.77927300	-0.47734100	0.55513900
C	1.32331700	0.36436000	-0.50534500
3			
Molecule P2			
Mg	0.00000000	0.00000000	-0.69375300
Cl	0.00000000	0.00000000	-2.88562500
Br	0.00000000	0.00000000	1.63944700
13			
Molecule R2			
Mg	0.72792400	-0.00028900	-0.00001100
Br	3.08433800	0.00005500	-0.00003400
C	-1.35077400	-0.00029800	0.00024700
C	-2.09211900	-1.19845500	0.00014900
C	-2.09158500	1.19818900	0.00015000
C	-3.48792200	-1.20387900	-0.00006300
H	-1.58387500	-2.16001500	0.00027800
C	-3.48739900	1.20424100	-0.00006300
H	-1.58294200	2.15954300	0.00027800
C	-4.18928000	0.00034000	-0.00018800
H	-4.02636300	-2.14607200	-0.00012900
H	-4.02541000	2.14668000	-0.00013000
H	-5.27386200	0.00057000	-0.00037600
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Molecule 5			

C	4.40816600	1.21746500	-0.99558200
C	3.13503000	0.74273800	-1.30572200
C	1.97909600	1.19812000	-0.62663100
C	2.15378500	2.17830100	0.39850100
C	3.44502700	2.62854400	0.70969900
C	4.55886300	2.15964800	0.01955100
H	5.27255900	0.84080000	-1.53011400
H	3.04237900	-0.00637900	-2.08739000
H	3.57787300	3.34438700	1.51314500
Mg	1.26101100	-0.92217300	0.12396000
Br	2.42524900	-2.90023400	-0.54538300
Fe	0.28425300	0.96559800	-1.48898000
Mg	-1.77911800	-0.17912900	-0.02878200
Br	-0.46344800	-1.05916400	2.00421800
C	-3.84587400	0.03784300	-0.33285700
C	-4.77314200	-0.27080100	0.68216400
C	-4.38456200	0.50385200	-1.54823700
C	-6.14997900	-0.12564100	0.49959000
H	-4.42632500	-0.63817200	1.64564600
C	-5.75887900	0.65353500	-1.74493100
H	-3.72607700	0.75840600	-2.37688000
C	-6.64648800	0.33823600	-0.71755700
H	-6.83391100	-0.37534700	1.30474300
H	-6.13654900	1.01369900	-2.69687900
H	-7.71526500	0.45180800	-0.86444000
C	0.97673900	2.73432200	1.09434600
H	0.11891600	2.06994000	1.17235200
C	0.87035100	3.96108500	1.61445800
H	-0.03689400	4.27745200	2.11493100
H	1.67164000	4.68929900	1.55120800
H	5.54651200	2.51963500	0.28503400

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Molecule TS2

C	3.53020400	2.27829400	-1.42446400
C	2.34050500	1.56280700	-1.52817900
C	1.37890100	1.55650000	-0.49049800
C	1.66789200	2.31321000	0.68663100
C	2.88274800	3.00851400	0.78382200
C	3.80112400	2.99711700	-0.26018600
H	4.24903200	2.25764600	-2.23557700
H	2.16132700	0.98797100	-2.43284600
H	3.11623400	3.55288800	1.69210200
Mg	1.28952800	-0.81616600	-0.07580900

Br	2.99824500	-2.19773000	-1.02326100
Fe	-0.41479700	1.02448500	-0.85435400
Mg	-1.72064900	-0.96016600	0.37065500
Br	-0.05043500	-2.07846000	1.86095100
C	-3.63044900	-0.30317300	-0.22359300
C	-4.59279600	0.21869600	0.66508600
C	-3.98161300	-0.31139900	-1.58945600
C	-5.82943900	0.69127900	0.22434900
H	-4.38838000	0.25622200	1.73286800
C	-5.21614500	0.15948900	-2.04345500
H	-3.28726600	-0.70365500	-2.33070400
C	-6.14389500	0.66288600	-1.13436100
H	-6.54843800	1.07976500	0.93872400
H	-5.45299500	0.13167400	-3.10233600
H	-7.10422300	1.02978300	-1.48018700
C	0.66425700	2.37496900	1.76569600
H	-0.04935500	1.54976700	1.78235300
C	0.53165400	3.32565900	2.69630600
H	-0.24604300	3.26523100	3.44793700
H	1.18082700	4.19334300	2.73739700
H	4.73640000	3.53628800	-0.16000800

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Molecule 6

C	-1.92562100	2.68568000	-2.29598400
C	-1.40000800	1.44302000	-1.95285000
C	-1.22477100	1.05359800	-0.60557100
C	-1.55761600	2.01229500	0.39267500
C	-2.06660300	3.27200500	0.03675500
C	-2.26068200	3.60416000	-1.29845400
H	-2.06480900	2.94398100	-3.34013900
H	-1.12113400	0.75999900	-2.75287400
H	-2.32998500	3.97815800	0.81661400
Mg	0.93037600	1.29924300	0.15902600
Br	2.58286100	3.01118800	0.26897100
Fe	-0.68959000	-0.78345900	-0.25551300
Mg	1.95627400	-1.53249800	-0.18091100
Br	3.59744200	-3.25220600	-0.27115700
C	-2.43002300	-1.47435200	0.02188100
C	-3.52992600	-1.50869700	-0.85242300
C	-2.48215100	-2.26715500	1.18225400
C	-4.62554200	-2.32709500	-0.58702300
H	-3.53590000	-0.88941800	-1.74474700
C	-3.57802800	-3.09267100	1.45139500

H	-1.65788500	-2.25300900	1.89835800
C	-4.65024100	-3.12102300	0.56329100
H	-5.46606300	-2.34697600	-1.27308700
H	-3.59599100	-3.70145700	2.34916500
H	-5.50701900	-3.75354900	0.76732700
C	-1.31653200	1.64852400	1.81220500
H	-1.65578700	0.65771200	2.10987100
C	-0.70613500	2.42622100	2.71681100
H	-0.33848500	3.41649800	2.46780300
H	-0.56017900	2.09137500	3.73738600
H	-2.66455300	4.57427900	-1.56300200

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Molecule 7

C	-2.85401600	-3.68829300	-1.81723800
C	-2.03799900	-2.56694200	-1.67938200
C	-1.92656400	-1.85797300	-0.46166300
C	-2.73518700	-2.30872400	0.61825000
C	-3.56870300	-3.42643200	0.47131100
C	-3.61995900	-4.11888000	-0.73512800
H	-2.89742400	-4.21812600	-2.76227400
H	-1.46679000	-2.24540300	-2.55187700
H	-4.16177800	-3.76344300	1.31434400
Mg	-2.77859000	0.25750200	-0.02701800
Br	-4.80762800	1.48019200	-0.31973300
Mg	2.93539300	-0.37644700	-0.06178300
Br	0.92540500	-0.92896200	1.37015800
Fe	-0.44907000	-0.59102000	-0.69346400
Cl	1.42066600	0.47721700	-1.78136700
Mg	-0.24670200	1.94810700	-0.35060600
Br	0.60971800	4.05514200	0.32016200
C	4.99693800	-0.64077800	-0.05630400
C	5.66151600	-1.27252400	1.01336200
C	5.80348500	-0.20185100	-1.12485000
C	7.04529000	-1.45668800	1.02043000
H	5.09861900	-1.63499800	1.87071400
C	7.18812300	-0.37971600	-1.12903600
H	5.35467500	0.29534100	-1.98189800
C	7.81252200	-1.00933000	-0.05375800
H	7.52368700	-1.94714100	1.86220200
H	7.77829400	-0.02682500	-1.96874200
H	8.88818700	-1.14918000	-0.05242500
C	-2.71226900	-1.54520200	1.89616200
H	-1.73232700	-1.35852100	2.32711800

C	-3.79859400	-1.05729200	2.51129700
H	-3.71584300	-0.50022600	3.43775500
H	-4.79767300	-1.19720500	2.11150000
H	-4.25814400	-4.98969500	-0.83150200

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Molecule TS4

C	-3.14165600	2.76441600	-0.31393100
C	-2.38942800	1.62179400	-0.56505100
C	-1.34290800	1.19043200	0.28482900
C	-1.06230700	2.02676200	1.40576900
C	-1.83551500	3.17447300	1.66116900
C	-2.87113400	3.54086500	0.81340900
H	-3.94143500	3.04491700	-0.99074100
H	-2.64306900	1.03205500	-1.44274100
H	-1.61928400	3.77092300	2.54057900
Mg	0.83488300	1.78955800	-0.34998100
Br	1.75136600	3.85690700	-1.13035100
Mg	-1.00604600	-3.02982800	0.08056900
Br	0.38699600	-2.00415100	1.84035900
Fe	-0.49462100	-0.47398900	-0.35270100
Cl	0.43402500	-2.47712100	-1.71734100
Mg	2.08481800	-0.97156400	-0.41792100
Br	4.37315600	-1.61187800	-0.27607100
C	-2.68230400	-1.84053500	-0.35907100
C	-3.58891300	-1.46194400	0.65708900
C	-3.17685400	-1.81929400	-1.68378100
C	-4.89372300	-1.06744100	0.37298900
H	-3.26282300	-1.45052400	1.69371900
C	-4.48065300	-1.42154200	-1.98076100
H	-2.52774400	-2.10743600	-2.50745100
C	-5.33988200	-1.04424000	-0.94927100
H	-5.56108200	-0.77110000	1.17525900
H	-4.82624300	-1.40648100	-3.00914100
H	-6.35427200	-0.73297900	-1.17435100
C	0.09810300	1.72190000	2.28173900
H	0.21774100	0.68660900	2.58351900
C	1.00712400	2.62309800	2.68065900
H	1.83608400	2.33684600	3.31803900
H	0.95675600	3.66444800	2.37923900
H	-3.45960200	4.42635600	1.02457900

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Molecule 8

C	-1.77290400	-3.89697200	-1.12412200

C	-1.31713700	-2.58437800	-1.24130200
C	-0.91342600	-1.82605300	-0.11956600
C	-1.00616400	-2.45874700	1.15583000
C	-1.48119100	-3.77471000	1.26417000
C	-1.85642400	-4.49234600	0.13445200
H	-2.07559100	-4.44688700	-2.00831400
H	-1.25863000	-2.14658500	-2.23601100
H	-1.57577900	-4.23285900	2.24270100
Mg	-2.67959400	-0.36986900	-0.15967800
Br	-5.02994100	-0.73270000	-0.18935400
Mg	3.07262800	0.59928700	-0.07151900
Br	5.28483500	1.06242500	0.59096600
Fe	-0.01209500	-0.07520200	-0.19731900
Cl	1.22077700	2.09377300	-0.11750100
Mg	-1.37804500	2.31728300	-0.08555300
Br	-2.06445000	4.59060500	-0.03818200
C	1.67735100	-1.08486100	-0.59878100
C	2.35740200	-2.03333400	0.20609700
C	2.19964500	-0.91653500	-1.91382700
C	3.42941500	-2.78950400	-0.27583400
H	2.01843500	-2.20607500	1.22287600
C	3.26277000	-1.68506400	-2.40739200
H	1.73497800	-0.19781000	-2.58941600
C	3.87902100	-2.62511800	-1.58557600
H	3.91731300	-3.50586200	0.37608300
H	3.60919300	-1.53903800	-3.42481100
H	4.71126400	-3.21180900	-1.95575400
C	-0.56154300	-1.69195300	2.33331400
H	-0.55828900	-0.60310700	2.19939000
C	-0.16203800	-2.15886100	3.52099300
H	0.13626400	-1.48590800	4.31565500
H	-0.12024900	-3.22028200	3.74037700
H	-2.23170500	-5.50399700	0.23525300

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Molecule TS3

C	-2.71171500	1.19240000	-2.44366000
C	-1.91933400	0.16530800	-1.96912700
C	-1.73024000	-0.08151700	-0.56999600
C	-2.41629700	0.80822400	0.33360900
C	-3.23998400	1.82536300	-0.18238700
C	-3.39438700	2.02539800	-1.54585000
H	-2.80860400	1.34770100	-3.51248400
H	-1.41717100	-0.48343800	-2.68414300

H	-3.76699500	2.46484900	0.51650100
Mg	0.26123000	1.31309300	0.10709200
Br	0.65078300	3.65670600	0.32521300
Fe	-0.01122900	-1.08833700	-0.34097200
Mg	2.58255500	-0.76109600	-0.22044300
Br	4.94443500	-1.13057600	-0.16874700
C	-1.79050200	-1.82898700	-0.19721600
C	-2.82221200	-2.54739000	-0.82600400
C	-1.23435200	-2.34191100	0.98561100
C	-3.26500900	-3.73848200	-0.26272500
H	-3.27773000	-2.16764200	-1.73349900
C	-1.66155000	-3.54656400	1.54366700
H	-0.41564900	-1.78086700	1.49329500
C	-2.69572200	-4.23762600	0.91689200
H	-4.06005900	-4.29359200	-0.74838300
H	-1.19934800	-3.93623900	2.44359700
H	-3.05663600	-5.16819200	1.33889300
C	-2.23268100	0.68250900	1.79300100
H	-2.18598100	-0.32858100	2.18775600
C	-2.11003300	1.70795800	2.64646400
H	-2.09999600	2.74047800	2.31446100
H	-2.00156500	1.53502800	3.71090300
H	-4.03227100	2.82066000	-1.91137000

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Molecule P1

C	-2.89976200	0.59634600	0.07172700
C	-1.50692700	0.77544400	-0.00588300
C	-0.68383300	-0.37730400	0.02089200
C	-1.28842800	-1.64006000	0.07096900
C	-2.67110300	-1.79354700	0.11845900
C	-3.48321200	-0.66320200	0.12850200
H	-3.53452500	1.47650000	0.06526800
H	-0.65092100	-2.51693500	0.09871700
H	-3.10539200	-2.78585800	0.16366500
C	0.80907000	-0.33375600	0.04496900
C	1.55405700	-0.90172000	-0.99558800
C	1.49428500	0.21561600	1.13680600
C	2.94818100	-0.90745900	-0.95470000
H	1.03654400	-1.32967600	-1.84728900
C	2.88531900	0.20468100	1.18155500
H	0.93012100	0.65165700	1.95328600
C	3.61823300	-0.35364700	0.13372600
H	3.50854600	-1.34497000	-1.77362900

H	3.39879000	0.62942600	2.03713700
H	4.70186200	-0.35941600	0.16831400
C	-1.03904800	2.16989900	-0.14534200
H	-1.75930000	2.90485500	0.20918400
C	0.08425600	2.63279800	-0.70227300
H	0.85186300	1.98869800	-1.10979800
H	0.25777400	3.70105200	-0.76657400
H	-4.56189200	-0.75986400	0.17880000