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Electronic Supplementary Informationfor:

New Insights into Mechanism of Iron-Catalyzed Cross-Coupling Reactions

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Experimental section

Synthesis of iron(III) alkoxide:

Ferric chloride (1.625 g, 0.01 mole) was added to toluene (100 ml) in a vessel. Ethanol (or methanol) (50 ml) and sodium alkoxide solution (25 cc, 0.03 mole) (which was prepared by dissolution of metal sodium in distilled ethanol or methanol) was added dropwise to the reaction vessel and stirred for 8 hours. The reaction mixture was filtered to remove preticipated sodium chloride. Removal of solvents in high vacuum gave a crude product which was crystallized from fresh ethanol. The reaction was done in nitrogen atmosphere due to moisture sensitivity.

Cross-coupling of phenyl magnesium bromide with cyclohexyl bromide in the presence iron(III) alkoxide:

A round bottomed flask (50 mL) was sealed with a rubber septum, then evacuated and refilled with nitrogen four times. The flask was charged with dry tetrahydrofuran (THF) (30 mL), dodecane (0.225

mL, as the internal standard), phenyl magnesium bromide (1.2 mmol). An aliquot (0.5 mL) was taken from the mixture, quenched with saturated NH_4Cl (0.5 mL), filtered through a small silica plug, diluted with diethyl ether and analyzed by GC. A mixture of iron(III) alkoxide (0.05 mmol) and cyclohexyl bromide (0.1 mmol, 0.5M in THF) was added to the reaction vessel. After stirring for 5 min, an aliquot (0.5 mL) was collected and analyzed as mentioned. The procedure was repeated by adding cyclohexyl bromide (0.5M in THF) in portions of 0.2 mL (yield <%73). After addition a total of nine portions, two extra portions of 1 or 2 equivalents of cyclohexyl bromide (1 mmol or 2 mmol) were added to react with any remaining Grignard reagent.

Theoretical section

Atomic Transfer Possibility

(**Starting Materials)**

Fe(OMe)DME+MeBr, multip=4

File:AT_2.7_f_ts4f_cofu_ts_8_fQRC_f_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -446.673649 au

G_therm : -446.56467 au

Solution phase energy: -446.711545 au

File: AT_2.7_f_ts4f_cofu_ts_8_fQRC_f.out

Low frequencies 11.10 25.57 25.85 27.11 39.16

Fe1	-6.0097301567	-0.1332860656	-0.9218149730
O2	-7.6437481176	0.5132197459	-0.6886903956
C3	-8.8560402152	0.0656731705	-0.1640582643
H4	-9.6152188365	0.8613409154	-0.2504347203
H5	-8.7797499560	-0.1998927590	0.9032180332
H6	-9.2474126288	-0.8174811674	-0.6978091667
O16	-4.1703820681	-0.8286843014	-1.3243857042
C17	-3.8021975051	-1.3083359188	-2.6257749949
H18	-4.7122355318	-1.3429073927	-3.2245025937

H19	-3.3702719607	-2.3123852772	-2.5371836938
H20	-3.0773496965	-0.6244960791	-3.0834479811
C21	-3.0638355585	-0.7424668338	-0.4124436366
H22	-2.3308150009	-0.0181706915	-0.7871206833
H23	-2.5995235136	-1.7304967723	-0.3104425225
H24	-3.4618429137	-0.4181179028	0.5486895378
C16	-5.1927577381	-0.5469242292	4.6954597502
H17	-6.1171644593	-0.3486865461	5.2339793812
Br18	-5.6028507422	-0.3246650689	2.7260199748
H21	-4.4188269530	0.1744709684	4.9499858183
H25	-4.8543627341	-1.5704824197	4.8438714570

Atomic Transfer Possibility

(Transition state)

Fe(OMe)MeBrDME, multip=4

File:AT_2.7_f_ts4f_cofu_ts_8_dsol.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -446.669754 au

G_therm : -446.55834 au

Solution phase energy: -446.706767 au

File: AT_2.7_f_ts4f_cofu_ts_8.out

Low Frequencies	-164.90	23.31	30.66	34.93	45.26	56.08
Fe1	-6.0113752476	-0.2126609496	-0.4351435529			
O2	-7.6857132474	0.2404422913	-0.8473892142			
C3	-8.9490805991	0.1382597064	-0.2584271808			
H4	-9.6965678587	0.6304429364	-0.9024686898			
H5	-8.9907251612	0.6230755972	0.7294004906			
H6	-9.2645131994	-0.9102941188	-0.1280969627			

O16	-4.1117815939	-0.7194222149	-1.0402710146
C17	-3.8673643069	-1.0421673512	-2.4176448726
H18	-4.8041408617	-0.8954403106	-2.9557698620
H19	-3.5452753231	-2.0867620530	-2.5038729282
H20	-3.0952941322	-0.3773396545	-2.8227527952
C21	-2.9443861907	-0.8583318267	-0.2136376900
H22	-2.1629152475	-0.1741039098	-0.5641285843
H23	-2.5836147276	-1.8926764102	-0.2564769879
H24	-3.2436581482	-0.6076223457	0.8032748938
C16	-4.9292464182	-0.4995822097	4.3963279521
H17	-5.8331707723	-0.4452449311	4.9958639478
Br18	-5.6940512263	-0.2992077210	2.2975888580
H21	-4.2590629157	0.3461955902	4.5218287484
H25	-4.4386022929	-1.4687305380	4.4168063189

Atomic Transfer Possibility

(Product)

Fe(OMe)DMEBr-----Me, multip=4

File:AT_2.7_f_ts4f_cofu_ts_8_bQRC_f_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -446.697626 au

G_therm : -446.590144 au

Solution phase energy: -446.734826 au

File: AT_2.7_f_ts4f_cofu_ts_8_bQRC_f.out

Low frequencies 29.24 40.47 48.80 57.18

Fe1	-6.1279633181	-0.2827772447	-0.0431628761
O2	-6.9508057710	-0.4499500568	-1.6234136088
C3	-8.2263516437	-0.3847996848	-2.1990500110

H4	-8.1579086635	0.0160432992	-3.2212431129
H5	-8.9053507824	0.2669139901	-1.6284045728
H6	-8.6845777143	-1.3837802939	-2.2585660273
O16	-4.1262667955	-0.7145312895	-0.5092188790
C17	-3.7691073839	-1.0263553376	-1.8659961018
H18	-4.6917630195	-0.9875922301	-2.4454079550
H19	-3.3291769416	-2.0296257585	-1.9107822496
H20	-3.0491795397	-0.2880302291	-2.2385864004
C21	-3.0138438834	-0.7288282910	0.3997875174
H22	-2.2773241012	0.0236044538	0.0938670889
H23	-2.5526552646	-1.7232035887	0.4021708917
H24	-3.4013992675	-0.4962346317	1.3914189385
C16	-2.6974357200	-1.3303220839	4.1872240501
H17	-3.7365494375	-1.0410999754	4.0853520686
Br18	-6.2732759484	0.1945354408	2.3180458769
H21	-1.9508758415	-0.5881796633	4.4434931409
H25	-2.4141165986	-2.3738855038	4.1190976367

Oxidative Addition possibility with one coordinate solvent

(Starting Materials)

Fe(OMe)DME+MeBr, multip=4

File:merge_scan6_TS_TSu_01_1solf_bQRC_03_f_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -446.676543 au

G_therm : -446.56635 au

Solution phase energy: -446.712934 au

File: merge_scan6_TS_TSu_01_1solf_bQRC_03_f.out

Low frequencies 14.22 18.54 27.92 41.73 48.22 57.32

Fe1	-6.2298928746	-0.7634871365	2.3757718611
O2	-7.4813733032	0.4706176762	2.5989315920
C3	-7.7523469804	1.7859466605	2.2335288105
H4	-6.9849447710	2.4922272484	2.5941733311
H5	-8.7163504301	2.1059711145	2.6637492064
H6	-7.8283796422	1.9160633241	1.1390640401
O7	-4.8356327062	-2.1749263056	2.1139194357
C8	-3.4336914651	-1.8616456375	2.2042972173
H9	-3.3439450112	-0.9791682866	2.8379808588
H10	-3.0330982165	-1.6534219910	1.2067501632
H11	-2.9069588328	-2.7076300982	2.6613390704
C12	-5.0987493147	-3.3584479127	1.3378320054
H13	-4.5737922133	-4.2074607580	1.7916533762
H14	-4.7670511125	-3.2084754211	0.3051796597
H15	-6.1754272075	-3.5256581973	1.3669166424
Br25	-4.0425550479	-0.9035285984	-1.8782661922
C26	-5.5093761075	0.4387330560	-1.5230265574
H27	-6.3009162137	0.2319362539	-2.2400042944
H28	-5.8364889905	0.2851753658	-0.4942884122
H29	-5.0725597766	1.4239739765	-1.6720772420

Oxidative Addition with one coordinate solvent

(Transition state)

Fe(OMe)MeBrDME, multip=4

File:merge_scan6_TS_TSu_01_1solf_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -446.649269 au

G_therm : -446.534913 au

Solution phase energy: -446.6812 au

File: merge_scan6_TS_TSu_01_1solf.out

frequencies	-134.45	30.10	38.57	41.15	52.85	61.42
Fe1	-5.4498919873	-0.3169629287	1.1642954478			
O2	-6.3974223393	0.1055933225	2.6332406010			
C3	-7.2485950323	1.0886108394	3.1299620015			
H4	-6.7527518372	2.0709012436	3.2188490204			
H5	-7.6027199260	0.8122881628	4.1387738038			
H6	-8.1443359918	1.2293027633	2.5003560625			
O7	-3.8338496053	-1.8666003615	1.4576420113			
C8	-2.9555423938	-1.5384453552	2.5403902620			
H9	-2.6086411995	-0.5180636828	2.3713011979			
H10	-2.1014048585	-2.2281581803	2.5507935758			
H11	-3.4881758366	-1.5868751951	3.4980488953			
C12	-4.3341106694	-3.2058083445	1.5557090222			
H13	-4.9222113384	-3.3316677777	2.4734390541			
H14	-3.4993001188	-3.9184047394	1.5485457649			
H15	-4.9692085277	-3.3733762840	0.6847102978			
Br25	-5.7940167549	-1.1886496497	-1.5587760724			
C26	-4.1721079751	0.0027393062	-0.9236850344			
H27	-3.8891219388	0.5345180735	-1.8293012768			
H28	-4.5036484222	0.7761809921	-0.1804947467			
H29	-3.3971457810	-0.6746064572	-0.5722790075			

Oxidative Addition with one coordinate solvent

(Product)

BrFeMe(OMe)DME, multip=4

File:merge_scan6_TS_TSu_01_1solf_fQRC_f_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -446.732884 au

G_therm : -446.615349 au

Solution phase energy: -446.767622 au

File: merge_scan6_TS_TSu_01_1solf_fQRC_f.out

frequencies	31.01	45.28	58.12	70.32	90.43	93.60
Fe1	-5.3827670273	-0.3225683500	0.6696416862			
O2	-5.5258459909	0.7716733146	2.0640815482			
C3	-5.9798670743	2.0916894073	2.2097548774			
H4	-5.2960816852	2.8091079879	1.7296493337			
H5	-6.0236328703	2.3352895879	3.2802070629			
H6	-6.9849860144	2.2343727050	1.7858683301			
O7	-4.0023415957	-1.7264349760	1.6994802027			
C8	-3.5540742988	-1.4561057032	3.0310700269			
H9	-4.0376917662	-0.5302619059	3.3402295251			
H10	-2.4622509269	-1.3403106766	3.0466845898			
H11	-3.8421073650	-2.2788356526	3.6983976083			
C12	-3.4448238633	-2.9253355073	1.1555468710			
H13	-3.7033505786	-3.7823451393	1.7906922737			
H14	-2.3524176518	-2.8372135478	1.0871845236			
H15	-3.8773864567	-3.0593187832	0.1643661715			
Br25	-6.2149855823	-1.8121239472	-1.0426090143			
C26	-4.5496558559	1.0558612608	-0.5275557603			
H27	-5.3745736064	1.6741634820	-0.8895587907			
H28	-3.8425582430	1.6085419809	0.0916677597			
H29	-4.0744860221	0.4929853834	-1.3306238116			

Oxidative Addition possibility with two coordinate solvent

(**Starting Materials)**

Fe(OMe)DME2+MeBr, multip=4

File:merge_scan6_TS_TSuf_01_bQRC_f_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -601.702919 au

G_therm : -601.515412 au

Solution phase energy: -601.746294 au

File: merge_scan6_TS_TSuf_01_bQRC_f.out

Low frequencies 10.68 24.46

Fe1	-5.4224480816	-0.6145688036	2.0586947062
O2	-6.4268133086	0.7892441590	2.5362956764
C3	-7.7912189155	1.0232851393	2.7195784163
H4	-8.3691933091	0.9090322379	1.7865682742
H5	-7.9507130811	2.0575862960	3.0706038722
H6	-8.2405023295	0.3499545995	3.4679982871
O7	-4.0883307634	-2.0618791398	1.6373267190
C8	-2.8171570839	-2.0149478825	2.3083710520
H9	-2.5613277457	-0.9605940516	2.4175708403
H10	-2.0707182472	-2.5301782248	1.6917686627
H11	-2.8883404904	-2.4949781089	3.2912618342
C12	-4.5307631116	-3.3927474072	1.3303921444
H13	-4.7336097138	-3.9501036175	2.2520169787
H14	-3.7572832494	-3.9010679415	0.7426664479
H15	-5.4412009351	-3.2967857228	0.7389802278
O16	-2.6864750298	1.4737151182	1.9942689821
C17	-3.4194674402	2.3923486409	2.7968641745
H18	-4.4446733206	2.0199809509	2.8586002458

H19	-3.4183301945	3.3959548912	2.3420273427
H20	-2.9858265536	2.4678750462	3.8071549800
C21	-1.3569179235	1.8935949218	1.7777391907
H22	-0.7958929007	1.9824709015	2.7229090392
H23	-1.3178043635	2.8679780007	1.2639211712
H24	-0.8722465929	1.1422551099	1.1468197237
Br25	-5.5888302006	-0.8782775222	-1.6756540112
C26	-4.1842248361	0.4854972509	-1.2169570002
H27	-4.2614832759	1.2847710760	-1.9519044931
H28	-4.3923955392	0.8372554225	-0.2069395003
H29	-3.2211024013	-0.0173977601	-1.2738476661

Oxidative Addition possibility with two coordinate solvent

(Trasition state)

Fe(OMe)MeBrDME2, multip=4

File:merge_scan6_TS_TSuf_01_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -601.678867 au

G_therm : -601.4931 au

Solution phase energy: -601.719059 au

File: merge_scan6_TS_TSuf_01.out

Low frequencies -259.28 18.45 32.94 36.59 48.43 51.99

Fe1	-5.2602050000000	-0.2089290000000	1.1951030000000
O2	-6.1134610000000	0.4307460000000	2.6710130000000
C3	-7.3416700000000	1.0140050000000	2.9793510000000
H4	-7.4497680000000	2.0246410000000	2.5465450000000
H5	-7.4522990000000	1.1170730000000	4.0737770000000
H6	-8.1996540000000	0.4165100000000	2.6245840000000

O7	-3.8650540000000	-1.9481050000000	1.4081230000000
C8	-2.9445150000000	-1.7599240000000	2.4935000000000
H9	-2.6060370000000	-0.7235320000000	2.4521540000000
H10	-2.0955910000000	-2.4480100000000	2.3810150000000
H11	-3.4443720000000	-1.9462080000000	3.4526620000000
C12	-4.4094990000000	-3.2716700000000	1.3889750000000
H13	-4.9790930000000	-3.4655400000000	2.3070310000000
H14	-3.6005990000000	-4.0081410000000	1.2966980000000
H15	-5.0692610000000	-3.3357760000000	0.5235160000000
O16	-2.5680880000000	1.6065000000000	2.2159940000000
C17	-3.3174350000000	2.2729850000000	3.2253750000000
H18	-4.2652810000000	1.7372280000000	3.3244660000000
H19	-3.5163180000000	3.3167920000000	2.9379440000000
H20	-2.7736430000000	2.2732920000000	4.1839400000000
C21	-1.3458970000000	2.2532270000000	1.9318780000000
H22	-0.6915230000000	2.2982220000000	2.8177910000000
H23	-1.5074390000000	3.2817460000000	1.5711000000000
H24	-0.8431640000000	1.6778820000000	1.1491480000000
Br25	-5.9477180000000	-1.2034500000000	-1.4417150000000
C26	-4.1904470000000	-0.0759830000000	-1.0276990000000
H27	-3.9639940000000	0.3594700000000	-1.9982150000000
H28	-4.4012900000000	0.7708400000000	-0.3278880000000
H29	-3.4214060000000	-0.7677360000000	-0.6884990000000

Oxidative Addition with two coordinate solvent

(**Product)**

BrFeMe(OMe)DME2, multip=4

File:merge_scan6_TS_TSuf_01_fQRC_f_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -601.770784 au

G_therm : -601.576966 au

Solution phase energy: -601.823097 au

File: merge_scan6_TS_TSuf_01_fQRC_f.out

frequencies	32.43	46.17	47.33	71.64	81.61	86.03
Fe1	-5.3930783185	-0.1038775648	0.9827996714			
O2	-6.5836591914	-0.1611074071	2.3219962721			
C3	-7.9492081504	0.1259479307	2.4248705457			
H4	-8.1760584861	1.1800277942	2.1981076980			
H5	-8.2775158976	-0.0674329815	3.4567290963			
H6	-8.5574015106	-0.5010726612	1.7539098387			
O7	-4.3266457825	-1.8618054674	1.9788408890			
C8	-4.3061913240	-1.8052635617	3.4058539134			
H9	-4.0452008584	-0.7827228530	3.6772705693			
H10	-3.5516732478	-2.5034354860	3.7927827830			
H11	-5.2913796388	-2.0503912429	3.8186750875			
C12	-4.6236801348	-3.1748949624	1.4984344096			
H13	-5.6206270628	-3.4917520646	1.8343717794			
H14	-3.8725151286	-3.8861753435	1.8669185346			
H15	-4.5907689372	-3.1260120310	0.4101123370			
O16	-3.6276724486	1.0049662149	1.8659243869			
C17	-3.7726071006	2.3795118269	2.2129230028			
H18	-4.7917864967	2.5119753681	2.5779080851			
H19	-3.6020715267	3.0256449890	1.3415382951			
H20	-3.0605499792	2.6449584061	3.0057163413			
C21	-2.3011103543	0.6749892273	1.4414653683			
H22	-1.5895453322	0.8949881764	2.2487643766			

H23	-2.0297086289	1.2411754816	0.5424538813
H24	-2.3015536572	-0.3898919514	1.2143436249
Br25	-4.4259182923	-0.7781522145	-1.2003166244
C26	-6.3115131268	1.4671020662	0.1153047280
H27	-6.6271265786	2.1306197767	0.9225105399
H28	-5.5794852909	1.9294176607	-0.5465193266
H29	-7.1576019780	1.0654332411	-0.4460399160

DME

File:DME_thf_dsol2.out

Method: UDFT(b3lyp-d3)/lacvp*

SCF energy: -155.022481 au

G_therm : -154.967463 au

Solution phase energy: -155.029916 au

File: DME_thf_f.out

Low frequencies	231.77	259.07	416.73	959.99	1139.56	1174.76
O1	-1.0411830000000	2.0879526666667	0.0857000000000			
C3	-2.1531150633115	1.2489949355357	-0.1330624555437			
H4	-3.0954542939025	1.8413729033421	-0.0189846846077			
H5	-2.1023172022821	0.8244577166134	-1.1670432808686			
H6	-2.1439400181584	0.4154048356097	0.6132431011332			
C6	0.1001658103221	1.2756493149131	-0.0742567376085			
H7	1.0210063165811	1.8900671081210	0.0884459283108			
H8	0.0717890289967	0.4416150286330	0.6710688205644			
H9	0.1134118745574	0.8506678631640	-1.1092175714213			