Supporting Information

The SET-Induced Biaryl Cross-Coupling: A $S_{RN}1$ Reaction

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1. Gaussian 09, Revision C.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, N. J.; 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.

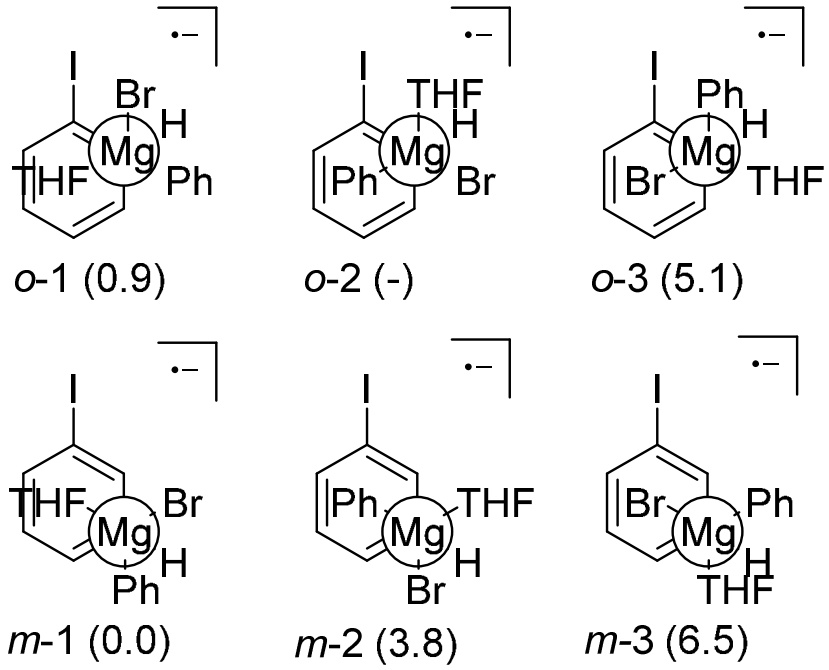

Figure S1. Different conformations of the Mg-π-radical anions depicted as Newman projections looking down the Mg-C(3) coordinating bond. The ΔG values reported in parentheses are relative to the lowest energy conformer (*m*-1). The lowest energy conformers for the Mg coordinated at the *ortho*- and *meta*-positions (*o*-1 and *m*-1) are shown in Figure 1 of the main text. No minimum was found corresponding to conformer *o*-2 at this level of theory.

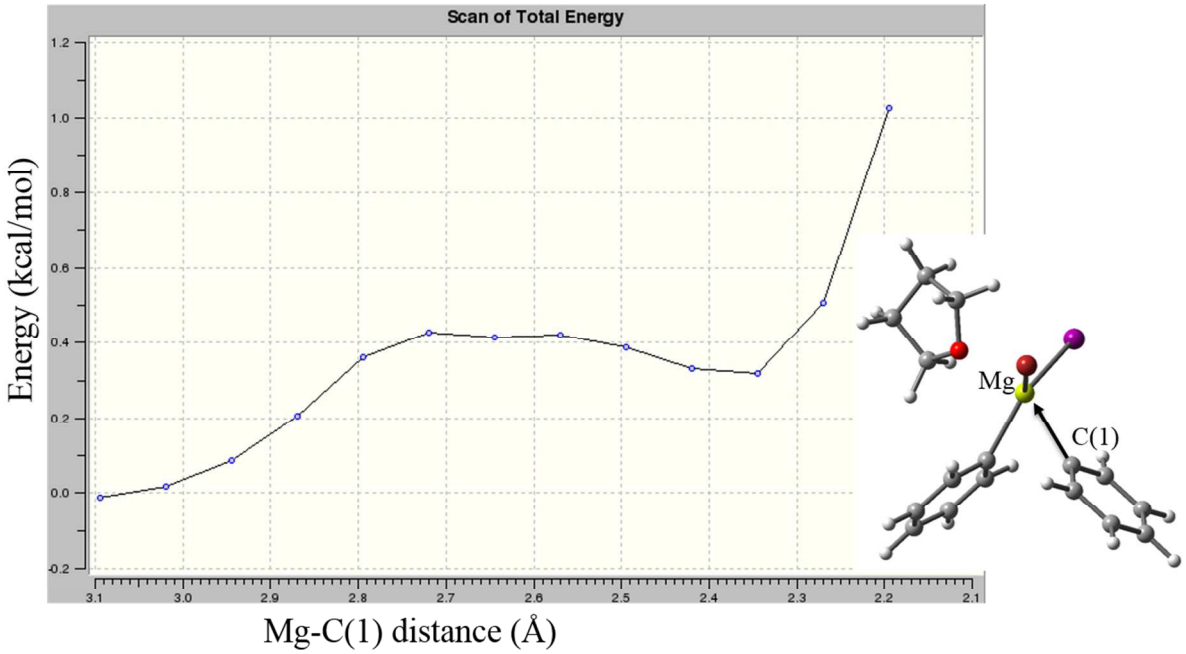

Figure S2. Relaxed energy scan that demonstrates that the PES around the TS for delocalization of the radical is very flat. It also illustrates how close in energy the delocalized radical (the minimum around ~2.3Å) is to the TS.

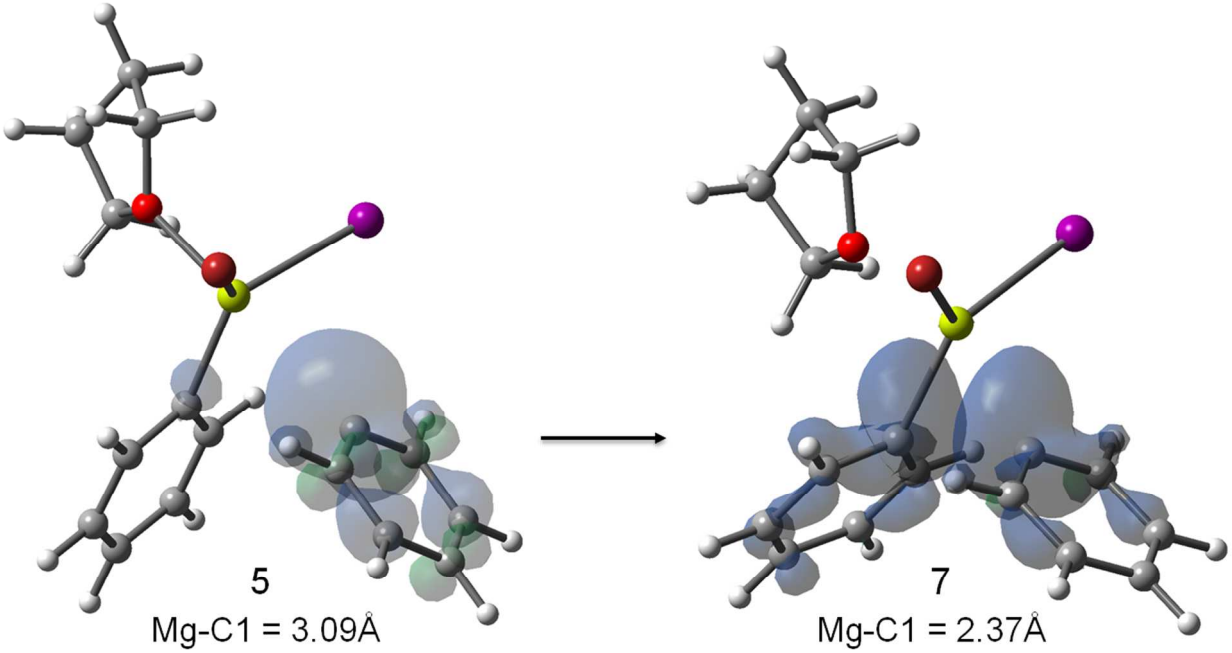

Figure S3. Spin plots illustrating how the radical delocalizes from the caged Mg-radical ion pair where the SOMO is located almost entirely on the aryl group previously associated with the halide to the MgPh2 radical anion where the SOMO is located on both aryl groups.

Cartesian coordinates, energies, and frequency analysis of important stationary points

*Energies are reported in hartrees. Computational methods: **A** = M06/SDD level for Br and I and M06/6-31+g(d) for all other atoms, **B** = M06/aug-cc-pVTZ-PP level for I and M06/6-311++g(2d,2p) level for all other atoms

Ortho-isomer of Mg-π-RA (**o-1**)

Electronic energy calculated with method A ($E_{ele,A}$)	=	-920.198642581
Zero point energy correction (ZPE_{corr})	=	0.294760
Gibbs free energy correction (ΔG_{corr})	=	0.236798
Electronic energy calculated with method B ($E_{ele,B}$)	=	-3765.44296363
Eele,B + ΔGcorr (ΔG_B)	=	-3765.206166
Number of imaginary frequencies (Nimag)	=	0

Mg	0.86819600	-0.38071300	1.25285600
C	1.51321700	-0.92679200	3.24144200
C	2.52417000	-0.28195700	3.98459100
C	0.91810800	-2.02583800	3.89556200
C	2.91953200	-0.69011800	5.26136200
H	3.03526500	0.58769100	3.55371600
C	1.28966200	-2.45165500	5.17436700
H	0.12399400	-2.58302600	3.38660000
C	2.29852500	-1.78291000	5.86601700
H	3.71183100	-0.15324400	5.78835500
H	0.79089600	-3.30820700	5.63352300
H	2.59703800	-2.10767600	6.86404300
Br	-0.78282600	-2.01888600	0.19656400
O	2.52714100	-0.67865500	0.01257100
C	3.88354500	-0.57031100	0.49153000
C	2.50598900	-0.85759300	-1.41642600
C	4.75162900	-0.94057400	-0.69710400
H	4.04451900	0.47088000	0.80967800
H	3.98960800	-1.23454200	1.35743200
C	3.89860200	-0.47090500	-1.87218300
H	2.27711600	-1.91308400	-1.62772500
H	1.70325200	-0.23035700	-1.82370800
H	4.90128100	-2.02890500	-0.74415900
H	5.73660000	-0.46117900	-0.65356700
H	4.17062300	-0.93925700	-2.82532700
H	3.97172300	0.62087900	-1.98507100
C	0.76633100	2.17360300	-0.53870400
C	1.98506200	2.65043300	-0.94183300
C	2.98504800	2.94673800	0.02678600
C	2.62966500	2.86894000	1.40046800
C	1.40159400	2.39497700	1.79322200
C	0.43880000	1.84588300	0.83869000
H	2.18791700	2.82233400	-2.00050800

H	3.95875700	3.32109300	-0.28784500
H	3.33983600	3.20554400	2.15925800
H	1.14331300	2.37349200	2.85392100
H	-0.61932500	1.89070600	1.12276200
I	-0.76015500	1.85429700	-2.02007100

<u>*Meta*-isomer of Mg-π-RA (**m-1**)</u>

$E_{ele,A}$	=	-920.200298399
ZPE_{corr}	=	0.294667
ΔG_{corr}	=	0.236921
$E_{ele,B}$	=	-3765.44446092
ΔG_B	=	-3765.207540
Nimag	=	0

Mg	1.54053500	0.09655700	2.10444300
C	2.82173400	-0.00599400	3.83924500
C	3.95553300	0.80930200	4.04318400
C	2.55829400	-0.91352500	4.88645700
C	4.76365300	0.73237400	5.18062500
H	4.22903000	1.54876000	3.28069500
C	3.34827600	-1.00955300	6.03576900
H	1.69463800	-1.58291100	4.81000700
C	4.46052500	-0.18280900	6.18823900
H	5.62983600	1.39000400	5.28328900
H	3.09576600	-1.73067100	6.81626200
H	5.08269100	-0.24804200	7.08210500
Br	-0.27349000	-1.66912300	1.78640200
O	2.78575400	-0.34279100	0.48830800
C	4.17793200	0.02894200	0.45587500
C	2.38599200	-0.92104600	-0.77290700
C	4.74762800	-0.72891400	-0.72559400
H	4.23678500	1.11996000	0.30870500
H	4.61183100	-0.23384400	1.42831300
C	3.57120600	-0.70963400	-1.69763900
H	2.16966900	-1.98482600	-0.59982200
H	1.46678900	-0.42061900	-1.10357100
H	4.99496000	-1.76121700	-0.43822300
H	5.65212600	-0.25675000	-1.12653300
H	3.63199700	-1.48031900	-2.47493600
H	3.49822900	0.27095800	-2.19212500
C	1.29353100	2.45959600	-0.82459600
C	2.50807100	3.11272300	-0.49661700
C	2.70207300	3.41650500	0.88494100
C	1.82246000	2.98639000	1.84637900
C	0.69068700	2.13358800	1.51869800
C	0.38521500	2.01698800	0.09743100

H	3.19652500	3.46399000	-1.26190300
H	3.57446400	4.00638600	1.17566900
H	1.99900100	3.24756800	2.89163700
H	-0.17118000	2.15219500	2.19707300
H	-0.54366700	1.53687700	-0.21231800
I	0.86506700	2.18341900	-2.92331900

Intramolecular electron transfer TS (**2**)

$E_{ele,A}$	=	-920.198412795
ZPE_{corr}	=	0.294489
ΔG_{corr}	=	0.239314
$E_{ele,B}$	=	-3765.44202040
ΔG_B	=	-3765.202706
Nimag	=	1 (-79.94)

Mg	0.96672300	-0.58580600	1.42412900
C	1.07308500	-0.69138700	3.57674200
C	1.50831400	0.35087900	4.42204900
C	0.70736700	-1.87646400	4.24855000
C	1.58044600	0.23252200	5.81274300
H	1.80613000	1.30938100	3.98038200
C	0.76675700	-2.02039200	5.63814100
H	0.35675400	-2.73415200	3.66434500
C	1.20619000	-0.96064200	6.43027600
H	1.92424300	1.07465500	6.41786100
H	0.46752900	-2.96149400	6.10490600
H	1.25476000	-1.06217400	7.51555800
Br	0.11717400	-2.69199400	0.25697700
O	2.94722200	-0.58630400	0.76077100
C	4.03834800	-0.10026300	1.56499700
C	3.39776500	-0.90053800	-0.57391000
C	5.28199800	-0.54346800	0.82215200
H	3.96378400	0.99905900	1.62110600
H	3.92213000	-0.52334900	2.56963200
C	4.83374800	-0.40883200	-0.63047500
H	3.31436300	-1.98861100	-0.70536300
H	2.72845200	-0.40242200	-1.28742100
H	5.51746100	-1.59123100	1.05814600
H	6.15655600	0.07003400	1.06835000
H	5.44304800	-0.98880100	-1.33328100
H	4.86474800	0.64670300	-0.93811100
C	0.90567800	1.59448700	-0.77106400
C	2.03387200	2.37601900	-0.79151900
C	2.48106100	2.99375000	0.40458800
C	1.61512200	2.98685700	1.53304900
C	0.45699000	2.24697900	1.52843900
C	0.14590700	1.33435200	0.43724200

H	2.57854500	2.53248500	-1.72497900
H	3.42358800	3.54098200	0.42045900
H	1.86286600	3.59534500	2.40531200
H	-0.22258400	2.29232000	2.38212000
H	-0.89064800	1.00152700	0.33439700
I	0.09907300	0.89377000	-2.66274800

Mg Ion-Radical Cage (**5**)

$E_{ele,A}$	=	-920.244252638
ZPE_{corr}	=	0.297320
ΔG_{corr}	=	0.237141
$E_{ele,B}$	=	-3765.47675165
ΔG_B	=	-3765.206166
Nimag	=	0

Mg	0.21279200	-0.51745900	0.72228300
C	2.17569400	-1.01974200	0.02390900
C	2.56308500	-0.91192200	-1.32666600
C	3.16994300	-1.51443500	0.89122200
C	3.83360600	-1.26976600	-1.78576100
H	1.84499000	-0.52476800	-2.05943400
C	4.44741300	-1.87996900	0.45702900
H	2.94706500	-1.61746400	1.95979300
C	4.78532200	-1.75844300	-0.89045700
H	4.08469000	-1.16455600	-2.84366800
H	5.18266500	-2.25787600	1.17102400
H	5.78082400	-2.03835400	-1.23852300
Br	-0.24776400	-0.13554700	3.19478300
O	-0.78999200	-2.36363200	0.57869300
C	-0.49707800	-3.25039200	-0.52146100
C	-2.14323600	-2.56337500	1.03785300
C	-1.63549200	-4.25229700	-0.52897200
H	-0.47097800	-2.65533400	-1.44836100
H	0.49564500	-3.68191800	-0.35040300
C	-2.80176400	-3.39847600	-0.04215800
H	-2.09821300	-3.08437600	2.00550300
H	-2.60352100	-1.57947900	1.18896900
H	-1.43653500	-5.06872600	0.18039900
H	-1.79529700	-4.69066100	-1.52082300
H	-3.64740000	-3.98314300	0.33818200
H	-3.16326100	-2.74900700	-0.85223400
C	1.87931900	2.08622400	0.86937700
C	2.03348900	2.90378700	-0.22611700
C	2.87351500	4.01281800	-0.07065700
C	3.51218400	4.24333800	1.14873200
C	3.32190400	3.37555100	2.22527100
C	2.48586500	2.26110700	2.09203300

H	1.52487400	2.70184600	-1.16903300
H	3.02781600	4.69671900	-0.90574100
H	4.16614500	5.10781700	1.26069800
H	3.82438500	3.56345400	3.17470000
H	2.31582000	1.56820700	2.91639000
I	-1.41424900	0.75996100	-1.17759600

Delocalization TS (**6**)

$E_{ele,A}$	=	-920.243528987
ZPE_{corr}	=	0.296493
ΔG_{corr}	=	0.238085
$E_{ele,B}$	=	-3765.47590935
ΔG_B	=	-3765.237824
Nimag	=	1 (-43.30)

Mg	0.28418300	-0.19789900	0.77525000
C	2.23265900	-0.82254700	0.06804700
C	2.69662800	-0.70844000	-1.25538100
C	3.04475400	-1.58111200	0.93327600
C	3.86536100	-1.32971900	-1.70112400
H	2.12323600	-0.11662200	-1.97768400
C	4.21859400	-2.20996500	0.50932200
H	2.75098700	-1.70227200	1.98238100
C	4.63286400	-2.08885900	-0.81691600
H	4.18208000	-1.21973900	-2.74043900
H	4.81206500	-2.79649700	1.21401000
H	5.54819000	-2.57526700	-1.15685000
Br	-0.20776200	0.06461100	3.26164200
O	-0.61033100	-2.12203600	0.60117900
C	-0.28164800	-2.96511400	-0.52233900
C	-1.95207800	-2.39724900	1.05614800
C	-1.35821100	-4.03280600	-0.53732600
H	-0.30647500	-2.35300400	-1.43822100
H	0.73855500	-3.33847700	-0.37656800
C	-2.56831500	-3.25450800	-0.03150800
H	-1.88014800	-2.92422400	2.01884500
H	-2.46407800	-1.44012000	1.21436500
H	-1.10599200	-4.84574800	0.15921600
H	-1.49893700	-4.46623300	-1.53436200
H	-3.37687000	-3.89160800	0.34556100
H	-2.97195500	-2.61562400	-0.83040700
C	1.98667800	1.91918000	0.78093900
C	1.90882900	2.83337700	-0.24827300
C	2.60777000	4.03664900	-0.09358800
C	3.35872700	4.26836600	1.05892800
C	3.42243100	3.30455300	2.06639900
C	2.73310500	2.09549000	1.92720600

H	1.31049200	2.63963800	-1.13997700
H	2.55898500	4.79346100	-0.87737500
H	3.89940300	5.20781000	1.17272300
H	4.01166000	3.49137200	2.96484900
H	2.77417900	1.33218200	2.70450500
I	-1.52997500	0.93987100	-1.05346600

$MgPh_2$ radical anion (**7**)

$E_{ele,A}$	=	-920.243730694
ZPE_{corr}	=	0.296835
ΔG_{corr}	=	0.239347
$E_{ele,B}$	=	-3765.47614000
ΔG_B	=	-3765.236793
Nimag	=	0

Mg	0.23902700	0.04720500	0.81288400
C	2.22856600	-0.60419300	0.06331700
C	2.62317600	-0.58929100	-1.28040000
C	2.97155600	-1.39243400	0.95401000
C	3.67657900	-1.38406700	-1.73563700
H	2.09023200	0.03933100	-2.00004200
C	4.02904600	-2.18908700	0.50933100
H	2.70875400	-1.41590200	2.01657500
C	4.38224300	-2.19029100	-0.84055700
H	3.95165600	-1.37275000	-2.79188900
H	4.57956800	-2.81081100	1.21779300
H	5.21006000	-2.80732700	-1.19107100
Br	-0.33590200	0.02718900	3.29806100
O	-0.51861700	-1.95573200	0.55731400
C	-0.14746900	-2.78271700	-0.56105000
C	-1.83726300	-2.31555000	1.02553400
C	-1.09550000	-3.96310900	-0.50146500
H	-0.28378100	-2.20457000	-1.48989400
H	0.91400000	-3.03510000	-0.45230000
C	-2.37267700	-3.29690500	-0.00069800
H	-1.72572700	-2.76178200	2.02374400
H	-2.43513800	-1.39944700	1.11358100
H	-0.73741500	-4.70854300	0.22360400
H	-1.20985000	-4.45516700	-1.47450800
H	-3.09676900	-3.99779600	0.43110100
H	-2.86347400	-2.75471300	-0.82196900
C	1.91700600	1.72490400	0.79656000
C	1.93721100	2.64181900	-0.25114000
C	2.64043300	3.84131400	-0.11182600
C	3.34784400	4.10539200	1.06090500
C	3.35144400	3.16808100	2.09448200
C	2.64922300	1.96890900	1.95574900

H	1.38522400	2.44405200	-1.17296200
H	2.63479600	4.57036100	-0.92365400
H	3.90038300	5.03919900	1.16720500
H	3.90454400	3.37032200	3.01306900
H	2.66059700	1.24129000	2.76960100
I	-1.60274700	0.99598600	-1.12187000

Coupling TS (**8**)

$E_{ele,A}$	=	-920.242750143
ZPE_{corr}	=	0.296353
ΔG_{corr}	=	0.239705
$E_{ele,B}$	=	-3765.47539058
ΔG_B	=	-3765.235686
Nimag	=	1 (-192.58)

Mg	0.25681200	-0.02063400	0.76134400
C	2.21768500	-0.63584300	0.00757700
C	2.62909500	-0.67416600	-1.34250400
C	2.96496200	-1.41773000	0.91833300
C	3.68320800	-1.47877300	-1.76554000
H	2.09528400	-0.07996300	-2.09012300
C	4.02069700	-2.22453500	0.50118200
H	2.69525300	-1.41989300	1.97964000
C	4.38891600	-2.26234000	-0.84661200
H	3.95653500	-1.50231300	-2.82234600
H	4.55793300	-2.83517200	1.22962400
H	5.21804300	-2.88900200	-1.17561200
Br	-0.27266200	0.09048500	3.23791700
O	-0.54476400	-1.99604100	0.55203100
C	-0.18344100	-2.82948000	-0.56579900
C	-1.86356600	-2.34238700	1.02773400
C	-1.15080000	-3.99425600	-0.50728900
H	-0.30889400	-2.24906900	-1.49460600
H	0.87447600	-3.09574000	-0.45523100
C	-2.41664400	-3.30868000	-0.00294300
H	-1.74997100	-2.79887300	2.02135400
H	-2.44845400	-1.41923800	1.12890500
H	-0.80417000	-4.74736800	0.21538300
H	-1.27448800	-4.48211800	-1.48123700
H	-3.15310700	-3.99919400	0.42446600
H	-2.89691000	-2.75262700	-0.82119600
C	2.18539600	1.46450800	0.65446700
C	2.14105700	2.42790300	-0.35157600
C	2.77402600	3.65989200	-0.17272100
C	3.47355100	3.92162300	1.00523600
C	3.53551900	2.94889200	2.00390800
C	2.90179200	1.71905000	1.82216500

H	1.59354900	2.23795300	-1.27804200
H	2.71551500	4.41891900	-0.95452200
H	3.96978700	4.88228100	1.14484600
H	4.07815100	3.15031900	2.92899000
H	2.95845900	0.96465400	2.61012000
I	-1.55850800	1.02666900	-1.10480600

MgBrI Biaryl radical anion (**9**)

$E_{ele,A}$	=	-920.309005753
ZPE_{corr}	=	0.298850
ΔG_{corr}	=	0.243754
$E_{ele,B}$	=	-3765.54313484
ΔG_B	=	-3765.299381
Nimag	=	0

Mg	0.19577000	-0.16018900	0.18990500
C	2.46624000	-0.14632400	-0.32595100
C	2.44653600	-0.53971800	-1.72513800
C	2.82541500	-1.21247100	0.59586000
C	2.76101700	-1.81716400	-2.13104600
H	2.20778000	0.20199500	-2.48673600
C	3.12524500	-2.48752900	0.16046900
H	2.84248000	-1.01410300	1.66761400
C	3.11646700	-2.82676500	-1.20760500
H	2.73751600	-2.04628500	-3.19833000
H	3.37324800	-3.24767900	0.90386700
H	3.37694300	-3.83003200	-1.54187200
Br	-0.38868700	0.35390100	2.57332400
O	-0.60754900	-2.08360000	0.07812900
C	-0.38885100	-2.95898100	-1.05469900
C	-1.91783100	-2.32964500	0.64825600
C	-1.44496500	-4.03517100	-0.92021200
H	-0.52247100	-2.36871600	-1.97552700
H	0.64763300	-3.31161700	-1.00288600
C	-2.61293800	-3.24683200	-0.33851000
H	-1.76700200	-2.79870200	1.63052600
H	-2.42139800	-1.36608600	0.79265600
H	-1.11541400	-4.81479800	-0.21800700
H	-1.67339200	-4.51135500	-1.88065900
H	-3.37111900	-3.87392200	0.14447100
H	-3.10179800	-2.65554300	-1.12594100
C	2.48597200	1.25797400	0.07727600
C	2.07897700	2.30588700	-0.79593300
C	2.03827400	3.62823000	-0.38140000
C	2.42225400	3.99359200	0.91347100
C	2.86973100	2.98846200	1.77563700
C	2.91405900	1.66343400	1.37188600

H	1.74492300	2.07253900	-1.80609300
H	1.69055300	4.38823800	-1.08234600
H	2.37680000	5.03207400	1.23887500
H	3.19369600	3.24238000	2.78598500
H	3.28191600	0.92072500	2.07803400
I	-1.44277200	0.82900100	-1.82516900