**Submitted to Dalton Transactions**
**Supplementary Materials**

# $sp\text{-}sp^3$ Coupling Reactions of Alkynylsilver Cations, $RC{\equiv}CAg_2^+$ (R = Me and Ph) with Allyliodide.

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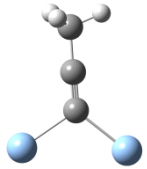
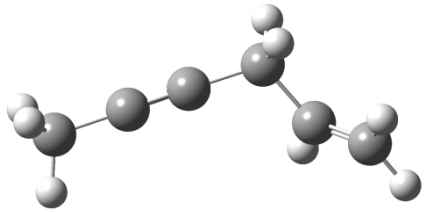


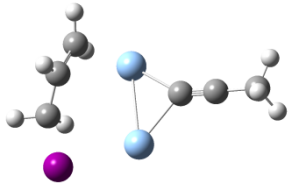
| | | | |
|---|---|---|---|
| C | -0.02997000 | 0.73867900 | -0.00117300 |
| Ag | 1.75713600 | -0.35263200 | 0.00005900 |
| Ag | -1.60940800 | -0.66375100 | 0.00004900 |
| C | -0.27727300 | 1.95490400 | 0.00011200 |
| C | -0.54782800 | 3.38415000 | 0.00093500 |
| H | 0.39935500 | 3.93565500 | -0.06679900 |
| H | -1.16081600 | 3.67261200 | -0.86068500 |
| H | -1.05133900 | 3.69533400 | 0.92313200 |

HF = -409.85568796 Hartrees



| | | | |
|---|---|---|---|
| C | -3.10776600 | -0.42556300 | 0.06084700 |
| H | -3.16099900 | -1.51082600 | -0.09078600 |
| H | -3.70690000 | 0.05061300 | -0.72517100 |
| H | -3.58302900 | -0.20133600 | 1.02386800 |
| C | -1.72226700 | 0.04402300 | 0.03283900 |
| C | -0.57493500 | 0.43404300 | 0.01571600 |
| C | 0.82203900 | 0.88840400 | -0.01813900 |
| H | 1.11236000 | 1.28450800 | 0.96431000 |
| H | 0.90641000 | 1.72804300 | -0.72587200 |
| C | 1.78707300 | -0.20527500 | -0.42885000 |
| H | 1.57651000 | -0.68411600 | -1.38509100 |
| C | 2.84120800 | -0.59332900 | 0.29329900 |
| H | 3.07314500 | -0.14382100 | 1.25752100 |
| H | 3.51039200 | -1.37688000 | -0.05305100 |

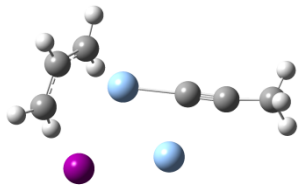
HF = -233.37484778 Hartrees



**A**

| | | | |
|---|---|---|---|
| Ag | -1.14421000 | 1.41832400 | -0.03459200 |
| Ag | -0.43148500 | -1.31628700 | 0.01829800 |
| I | 2.34629400 | -0.72738500 | -0.03659000 |
| C | 0.36315800 | 3.20160200 | 0.12476700 |
| C | 1.16616400 | 2.21792300 | -0.38347700 |
| C | 2.14588700 | 1.45603800 | 0.44944400 |
| H | -0.12213000 | 3.91207600 | -0.54235100 |
| H | 0.35627200 | 3.44005900 | 1.18755700 |
| H | 1.26062700 | 2.11572200 | -1.46424700 |
| H | 3.16331500 | 1.79730100 | 0.24253600 |
| H | 1.94610600 | 1.49057100 | 1.51958000 |
| C | -2.33966100 | -0.31467800 | 0.00730800 |
| C | -3.45707500 | -0.83929200 | 0.02538300 |
| C | -4.78768600 | -1.43177400 | 0.04532200 |
| H | -5.54790200 | -0.64062500 | 0.01961100 |
| H | -4.94861300 | -2.07753800 | -0.82562400 |
| H | -4.94828900 | -2.02082400 | 0.95555500 |

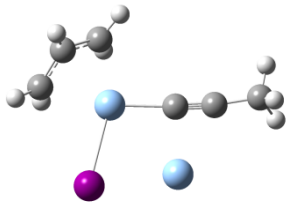
HF = -538.63769204 Hartrees



**TS (A–B)**

| | | | |
|---|---|---|---|
| Ag | 0.12425100 | 1.36741100 | -0.16372000 |
| Ag | -1.31892500 | -1.15043700 | 0.10382500 |
| I | 1.51369100 | -1.49404100 | -0.05084100 |
| C | 1.39167600 | 3.25595600 | 0.46749800 |
| C | 2.20069000 | 2.33334100 | -0.19456600 |
| C | 2.71440500 | 1.15856000 | 0.42949500 |
| H | 1.08227500 | 4.17057700 | -0.02971400 |
| H | 1.21116100 | 3.19446300 | 1.53916400 |
| H | 2.48005700 | 2.52257400 | -1.23003300 |
| H | 3.50735400 | 0.60672700 | -0.05979800 |
| H | 2.59377300 | 1.00001100 | 1.49741700 |
| C | -1.91728900 | 1.02208700 | -0.06721100 |
| C | -3.13170900 | 0.78415900 | -0.02086700 |
| C | -4.59231200 | 0.68927100 | 0.00968200 |
| H | -5.02282200 | 1.69396400 | -0.08225300 |
| H | -4.97285800 | 0.08314600 | -0.81970700 |
| H | -4.94765500 | 0.25473000 | 0.95039300 |

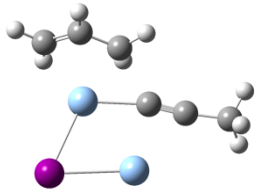
HF = -538.60362489 Hartrees



**B**

| | | | |
|---|---|---|---|
| Ag | 1.01566800 | 0.76954900 | -0.00289900 |
| Ag | -1.94092500 | -0.42582100 | -0.01250400 |
| I | 0.44641800 | -1.95294300 | 0.00196200 |
| C | 2.29304300 | 2.67701300 | 0.18064700 |
| C | 3.08327500 | 1.67854300 | -0.42456500 |
| C | 3.31614200 | 0.46218500 | 0.23304400 |
| H | 1.95559500 | 3.53643700 | -0.39034700 |
| H | 2.21367700 | 2.75055800 | 1.26435900 |
| H | 3.30967800 | 1.75813100 | -1.48672200 |
| H | 3.77254400 | -0.37220200 | -0.29052800 |
| H | 3.27310400 | 0.39050400 | 1.31939600 |
| C | -0.88682400 | 1.59872400 | 0.00956600 |
| C | -1.98405400 | 2.16983100 | 0.01159300 |
| C | -3.18750800 | 3.00829700 | 0.01546200 |
| H | -2.89812700 | 4.06584900 | 0.02848800 |
| H | -3.79760800 | 2.83677600 | -0.87795900 |
| H | -3.80639900 | 2.81714400 | 0.89876200 |

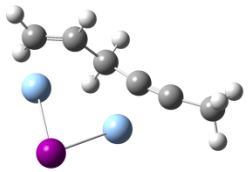
HF = -538.61845569 Hartrees



**TS (B–C)**

| | | | |
|---|---|---|---|
| Ag | -0.47761000 | 1.06397700 | -0.08674900 |
| Ag | 0.25343600 | -1.73893900 | 0.04861700 |
| I | 2.16746500 | 0.30012400 | -0.00618200 |
| C | -2.80853000 | 1.40481800 | 0.17670000 |
| C | -2.21131300 | 2.63066400 | -0.33144900 |
| C | -1.43319900 | 3.46425600 | 0.43022300 |
| H | -3.56497500 | 0.93086600 | -0.43569100 |
| H | -2.92226700 | 1.28057900 | 1.24983700 |
| H | -2.36667900 | 2.86219900 | -1.38387700 |
| H | -1.00756300 | 4.36801700 | 0.00425200 |
| H | -1.30125300 | 3.31483600 | 1.50064400 |
| C | -1.83742500 | -0.62706300 | -0.02115600 |
| C | -2.37957700 | -1.73853400 | -0.01753600 |
| C | -3.16657400 | -2.97531900 | -0.02512800 |
| H | -4.23592200 | -2.73120800 | -0.05694900 |
| H | -2.93699800 | -3.58906400 | -0.90295100 |
| H | -2.98408000 | -3.57252000 | 0.87465100 |

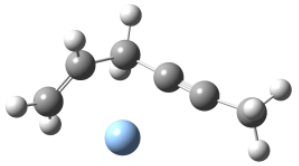
HF = -538.60077277 Hartrees



**C**

| | | | |
|---|---|---|---|
| Ag | -0.81157100 | 1.44224600 | 0.08411000 |
| Ag | 0.77215700 | -1.08810000 | -0.07257200 |
| I | -1.94258100 | -1.02641500 | -0.01818200 |
| C | 2.42122000 | 1.73830400 | -0.51612600 |
| C | 1.42487400 | 2.45201400 | 0.38059500 |
| C | 0.53213400 | 3.38550400 | -0.05809100 |
| H | 3.38320800 | 2.26516300 | -0.40625300 |
| H | 2.13538500 | 1.83873200 | -1.56967500 |
| H | 1.56280400 | 2.31156900 | 1.45294700 |
| H | 0.00434100 | 4.02202300 | 0.64980900 |
| H | 0.46363400 | 3.65740600 | -1.11085600 |
| C | 2.68129900 | 0.31848300 | -0.19003600 |
| C | 3.14578200 | -0.79401500 | 0.05292200 |
| C | 3.93034400 | -2.00180600 | 0.35066100 |
| H | 4.99087400 | -1.72883500 | 0.40645500 |
| H | 3.64144100 | -2.44252900 | 1.31036100 |
| H | 3.81359800 | -2.75931900 | -0.43099200 |

HF = -538.70129418 Hartrees



**D**

| | | | |
|---|---|---|---|
| C | 3.23157600 | 0.20090300 | 0.00195600 |
| H | 3.41714400 | -0.38637900 | 0.90727600 |
| H | 3.93221700 | 1.04404500 | -0.00344900 |
| H | 3.44746600 | -0.42335700 | -0.87136200 |
| C | 1.85968000 | 0.72126100 | -0.03306500 |
| C | 0.79475200 | 1.32665700 | -0.07289100 |
| C | -0.49046000 | 2.05390000 | -0.11056400 |
| H | -0.40711100 | 2.98129900 | 0.47020700 |
| H | -0.72879100 | 2.33487800 | -1.14387800 |
| C | -1.59284800 | 1.16893800 | 0.47012500 |
| H | -1.68089800 | 1.16179300 | 1.55690100 |
| C | -2.44629300 | 0.42583800 | -0.27781500 |
| H | -3.22937300 | -0.16597300 | 0.18931400 |
| H | -2.46027500 | 0.49179900 | -1.36544500 |
| Ag | -0.22189000 | -0.90261900 | 0.00838200 |

HF = -380.15715785 Hartrees

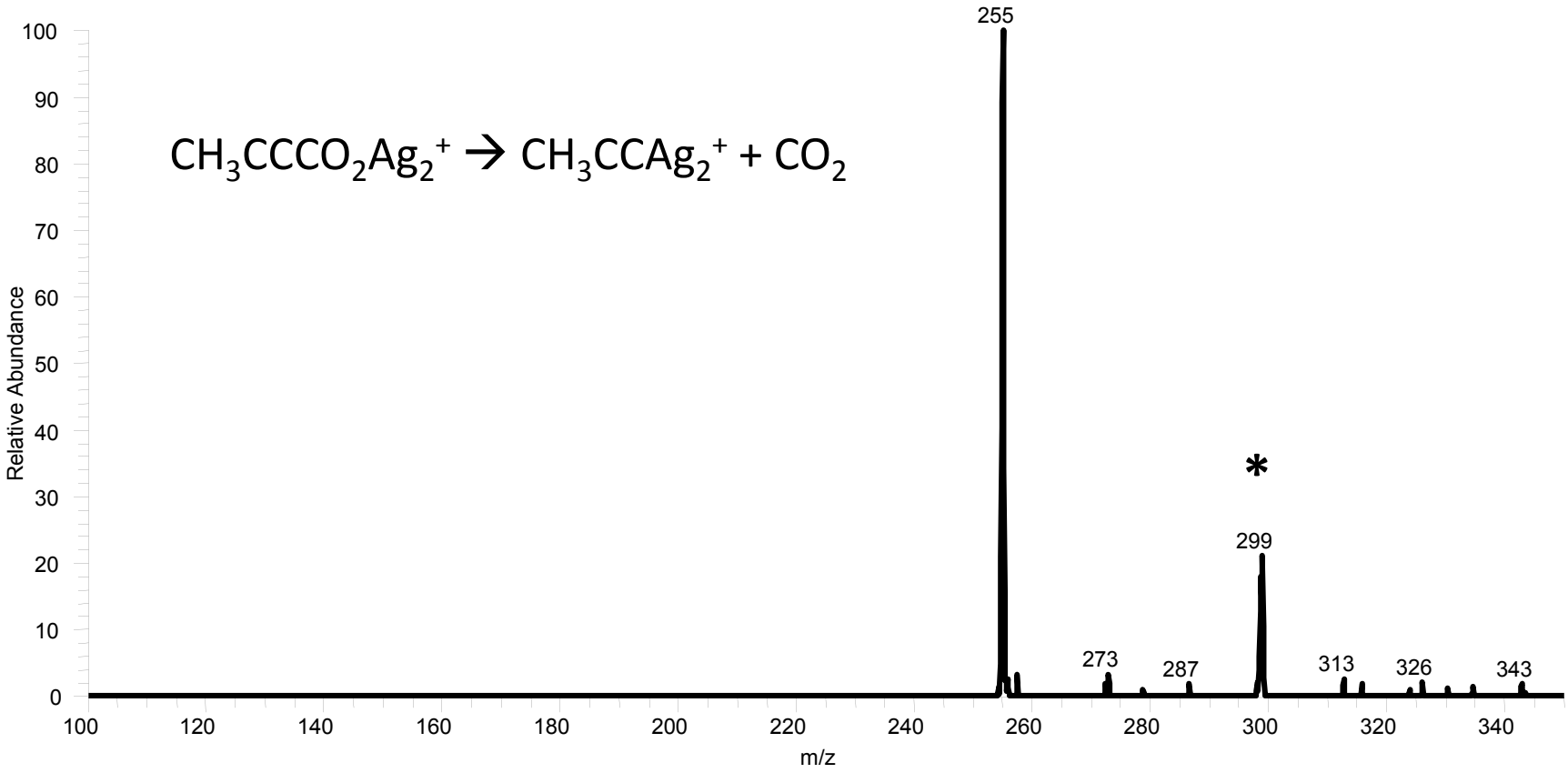



Fig. S1: CID of $CH_3CCCO_2Ag_2^+$ (m/z 299) to generate $CH_3CCAg_2^+$ method (a). An * represent the mass-selected ion

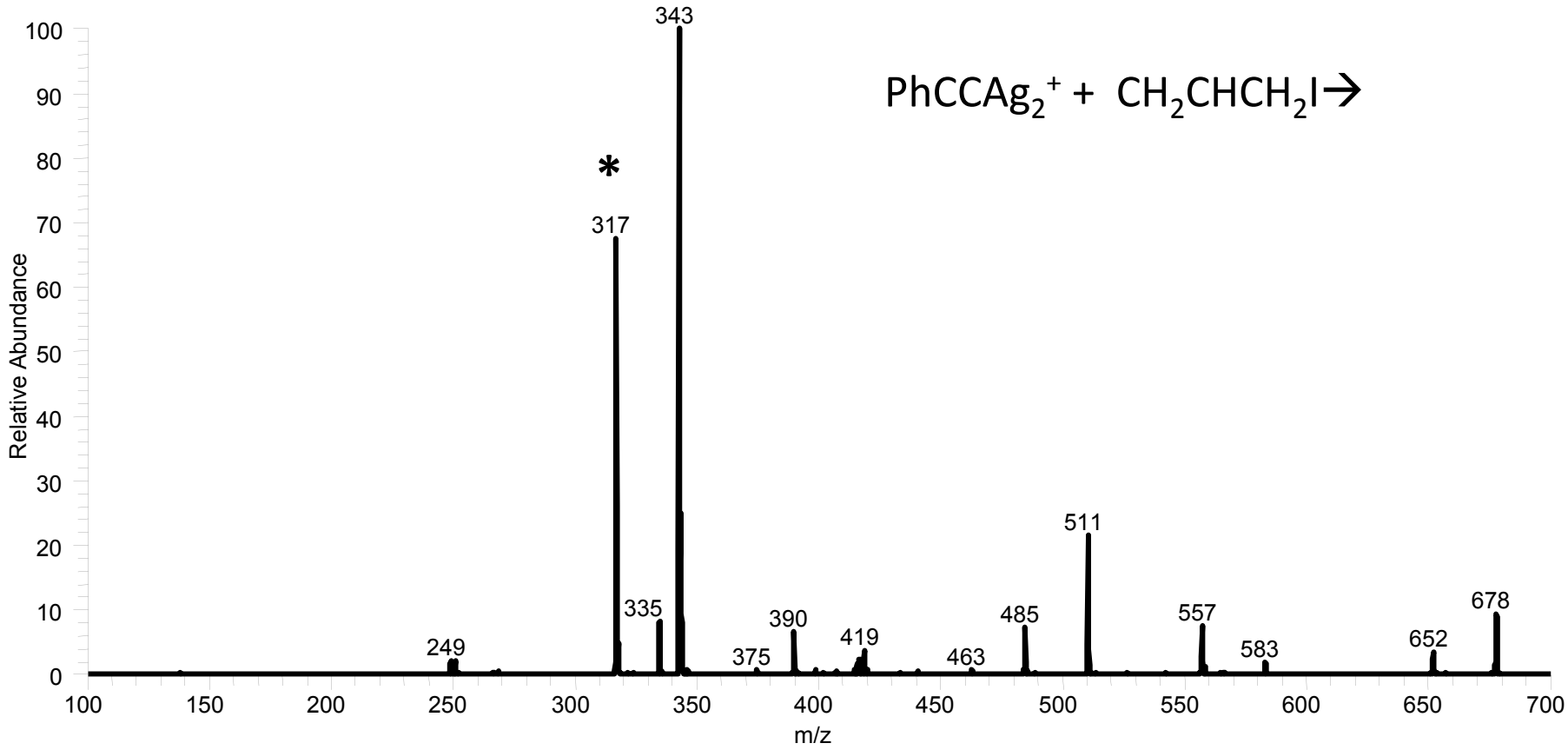



Fig. S2: IMR of $PhCCAg_2^+$ prepared via method (b) with allyl iodide. An * represent the mass-selected ion