A novel method, Spin-State-Selective (S<sup>3</sup>) HMBC, for accurate measurement of homonuclear coupling constants is introduced. As characteristic for S<sup>3</sup> techniques, S<sup>3</sup> HMBC yields independent subspectra corresponding to particular passive spin states and thus allows determination of coupling constants between detected spins and homonuclear coupling partners along with relative signs. In the presented S<sup>3</sup> HMBC experiment, spin-state selection occurs via large one-bond coupling constants ensuring high editing accuracy and unequivocal sign determination of the homonuclear long-range relative to the associated one-bond coupling constant. The sensitivity of the new experiment is comparable to that of regular edited HMBC and the accuracy of the J/RDC measurement is as usual for E.COSY and S<sup>3</sup>-type experiments independent of the size of the homonuclear coupling constant of interest. The merits of the method are demonstrated by an application to strychnine where thirteen J<sub>HH</sub> coupling constants not previously reported could be measured.