Here is one of my favorite stretches for "between the shoulders" tightness:

Stand in a doorway and grasp the molding on the far side, keeping your arms 90 degrees from your side (parallel to the floor). Put your feet on the threshold, bend your knees slightly, look down, hunch your upper back, push hard with your toes and pull hard with your arms, as if trying to pull the molding off the doorframe. You will immediately feel a great stretch between your shoulders.