Combined Inorganic Bases Promoted N-Addition/[2,3]-
Sigmatropic Rearrangement to Construct Homoallyl Sulfur-
Containing Pyrazolones

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Supporting Material

A. X-ray Structures of 3a........................................................................................................S2-S3

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A. X-Ray of 3a

Crystal of compound 3a was obtained by dissolving product in $n$-Hexane and Ethyl acetate (v/v 5:1) and allowing the solvent to slowly evaporate at room temperature. The single crystal X-ray diffraction study at room temperature revealed that compound 3a ($C_{28}H_{26}N_{2}OS$) crystallizes as the centrosymmetric monoclinic space group Pbca ($Z = 8$) and the crystal structure consists of one crystallographically independent formula unit in the unit cell (Figure S1).

Figure S1. X-ray crystallography structure of 3a. Drawn with ellipsoids at 30% probability and hydrogen atoms omitted for clarity.
### Table S1. X-ray crystallography data of 3a

| Property                        | Value                              |
|---------------------------------|------------------------------------|
| Moiety formula                  | **C_{28}H_{26}N_{2}O_{5}S**        |
| Mr                              | 438.57                             |
| Dx                              | 1.219 g/cm\(^3\)                  |
| Wavelength                      | 0.71000                            |
| Cell                            | a = 12.3067 (3) alpha = 90         |
|                                 | b = 18.4393 (4) beta = 90          |
|                                 | c = 21.0597 (5) gamma = 90        |
| Temperature                     | 293 K                              |
| Volume                          | 4779.00 (19)                       |
| Space group                     | Pbca                               |
| Hall group                      | -P 2ac 2ab                         |
| Z                               | 8                                  |
| Mu                              | 0.158/mm\(^{-1}\)                 |
| F000/F000'                      | 1856.0/1857.64                     |
| T\(_{\text{min}}\), T\(_{\text{max}}\), T\(_{\text{min'}}\) | 0.940, 0.947, 0.939               |
| Data completeness               | 0.999                              |
| Theta (max)                     | 25.998                             |
| R (reflections)                 | 0.0669 (3339)                      |
| wR\(_2\) (reflections)         | 0.2060 (4705)                      |
| S                               | 1.057                              |
| Npar                            | 317                                |
B. NMR Spectra

![NMR Spectra Image]

CDCl₃, 600 MHz

![NMR Spectra Image]

CDCl₃, 150 MHz
3n
CDCl₃, 600MHz

3n
CDCl₃, 150MHz
$^{3r}$

CDCl$_3$, 600MHz

$^{3r}$

CDCl$_3$, 150MHz

ppm
CDCl₃, 600MHz

3s

CDCl₃, 150MHz
3aa
CDCl₃, 600MHz

CDCl₃, 150MHz

S24
3ac

CDCl₃, 600MHz
CDCl$_3$, 600MHz

CDCl$_3$, 150MHz
Ph

3af

CDCl$_3$, 600MHz
Ph\[N\[N\[Ph\[3ag\]

CDCl₃, 600MHz

-110
-120
-130
-140
-150
-160
-170
-180
-190 ppm
3ah

CDCl₃, 600MHz

3ah

CDCl₃, 150MHz

S34
CDCl₃, 600MHz

3ah
CDCl₃, 600 MHz

CDCl₃, 150 MHz
Ph
N
O
Ph

CDCl₃, 600 MHz

Ph
N
O
Ph

CDCl₃, 150 MHz
CDCl₃, 600 MHz

CDCl₃, 150 MHz
CDCl$_3$, 600 MHz

CDCl$_3$, 150 MHz