Supplementary data for article:

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# STRUCTURAL CHEMISTRY

# SUPPLEMENTARY DATA

associated with the paper

# Mechanistic investigation and DFT calculation of the new reaction between *S*-methylisothiosemicarbazide and methyl acetoacetate

# Contents:

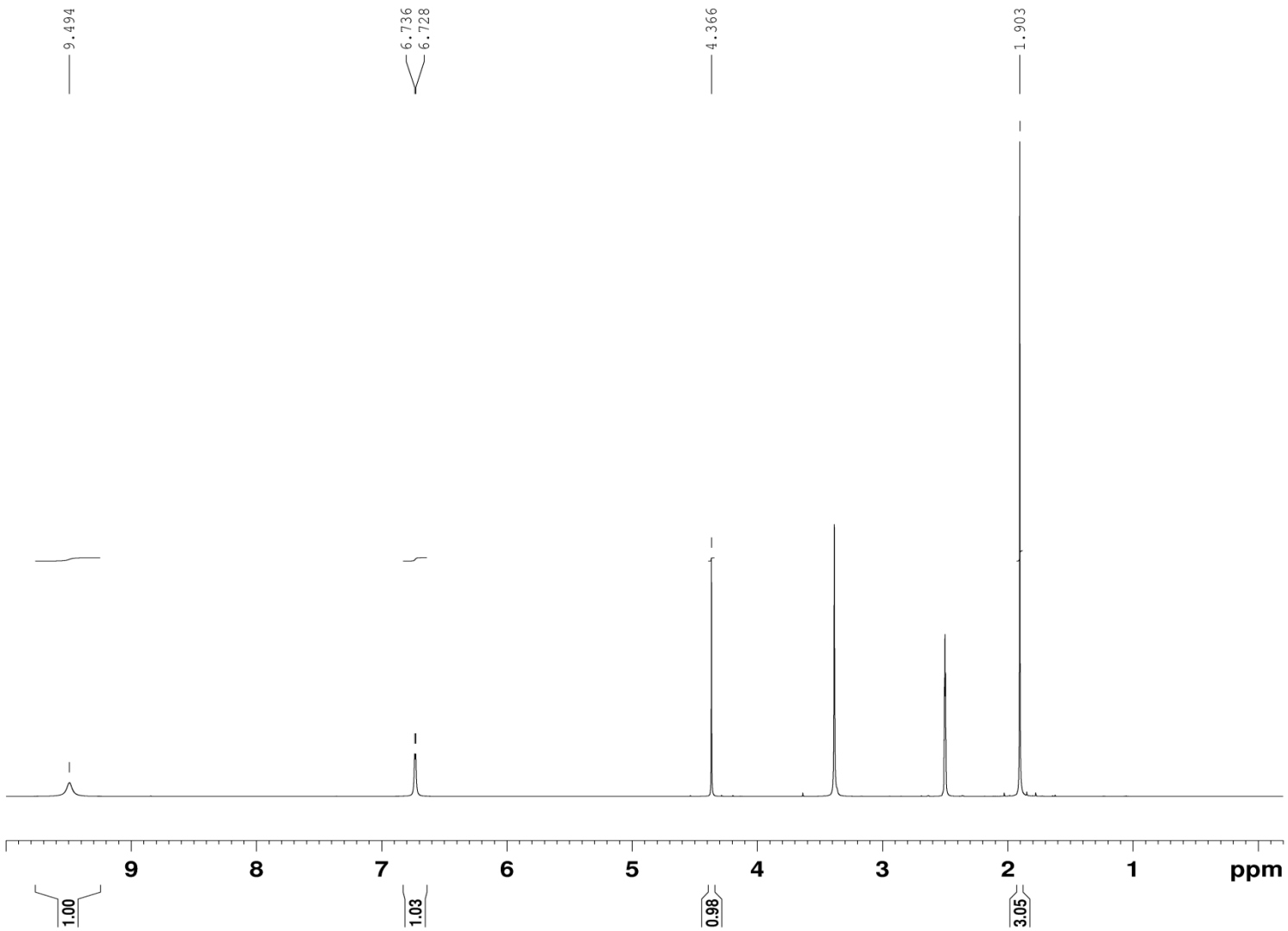



**Fig. S1.** $^{1}$H NMR spectrum of **16**.

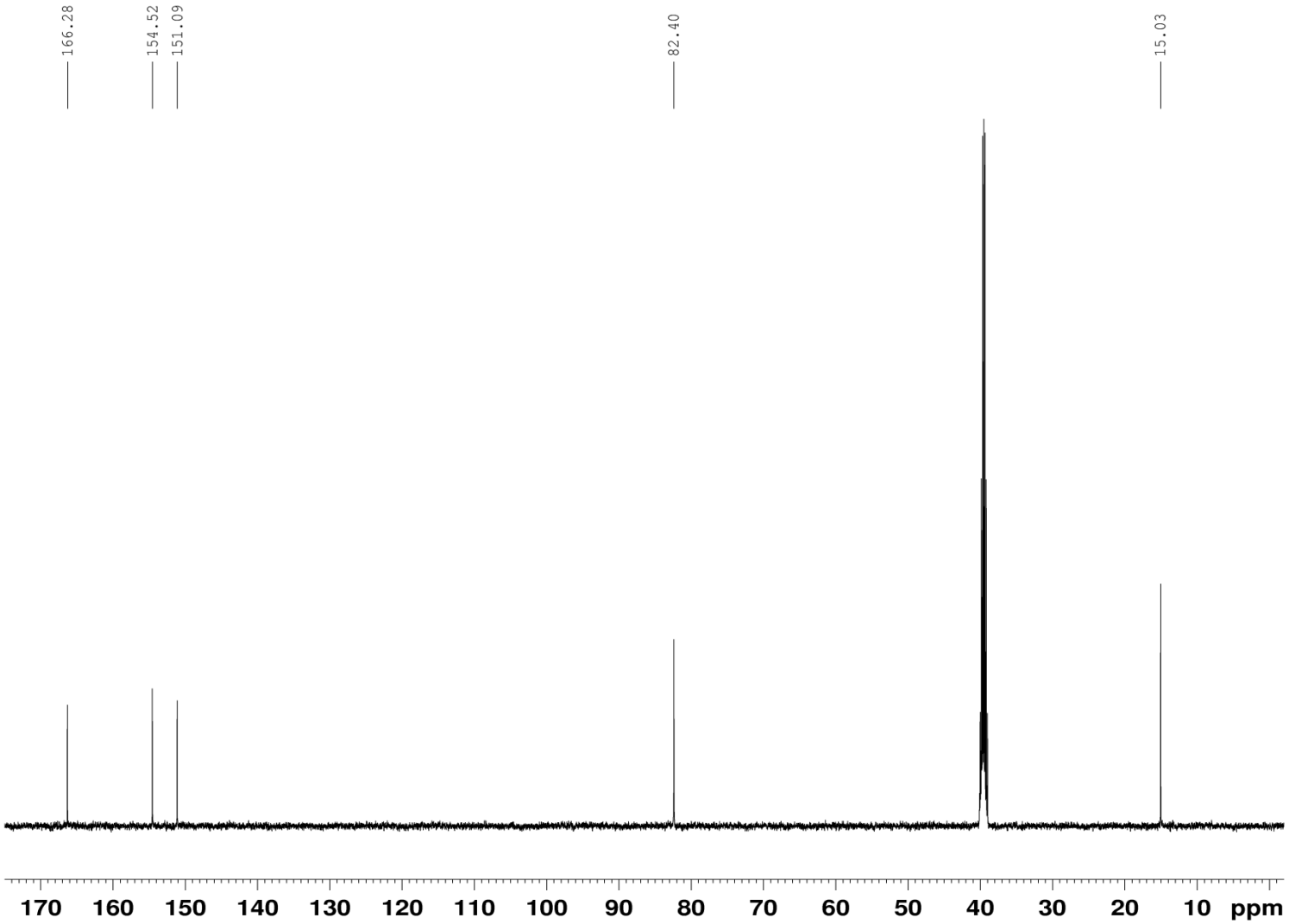



**Fig. S2.** $^{13}$C NMR spectrum of **16**.

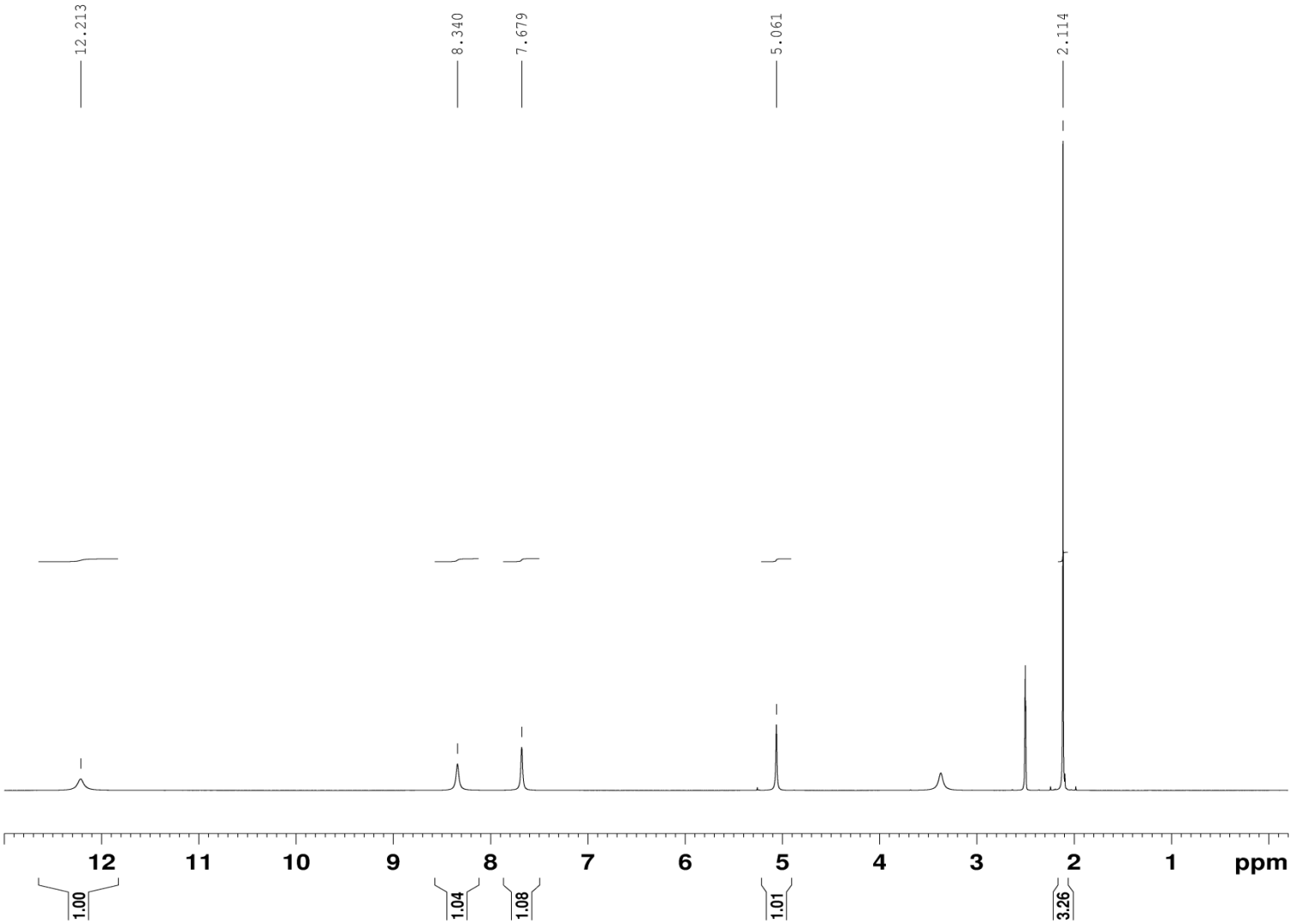



**Fig. S3.** $^{1}$H NMR spectrum of **1**.

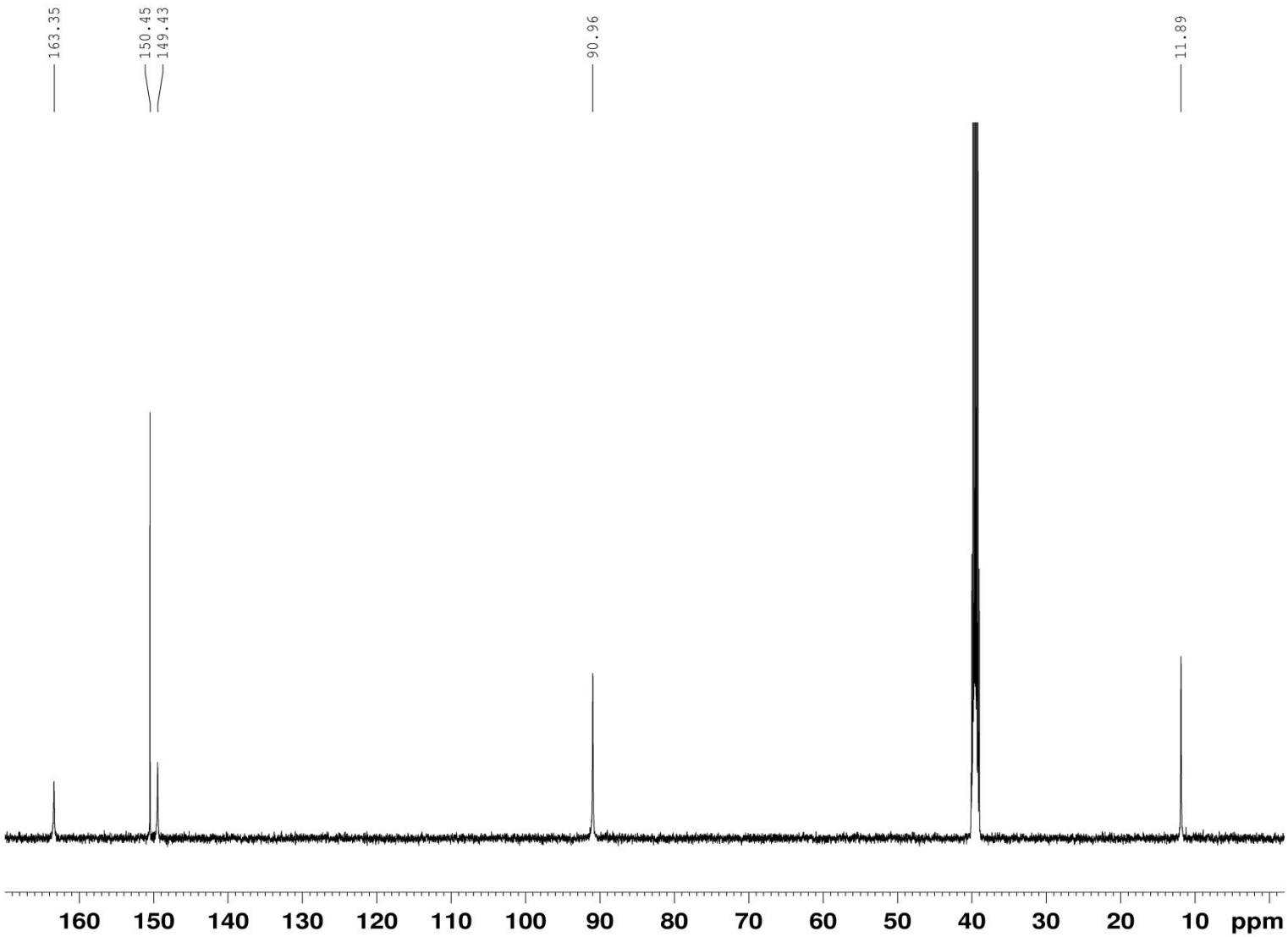



**Fig. S4.** $^{13}$C NMR spectrum of **1**.

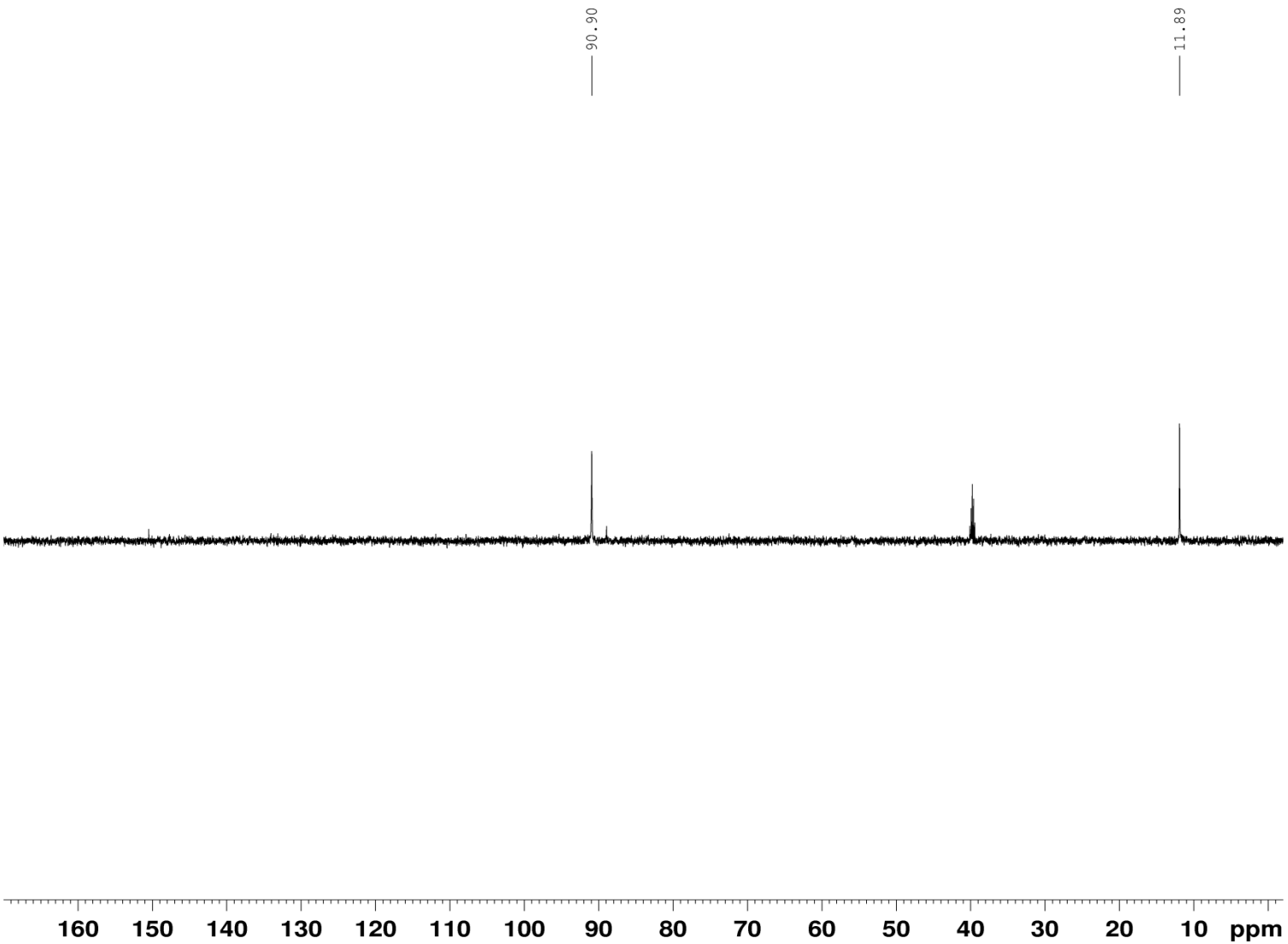



**Fig. S5.** DEPT spectrum of **1**.

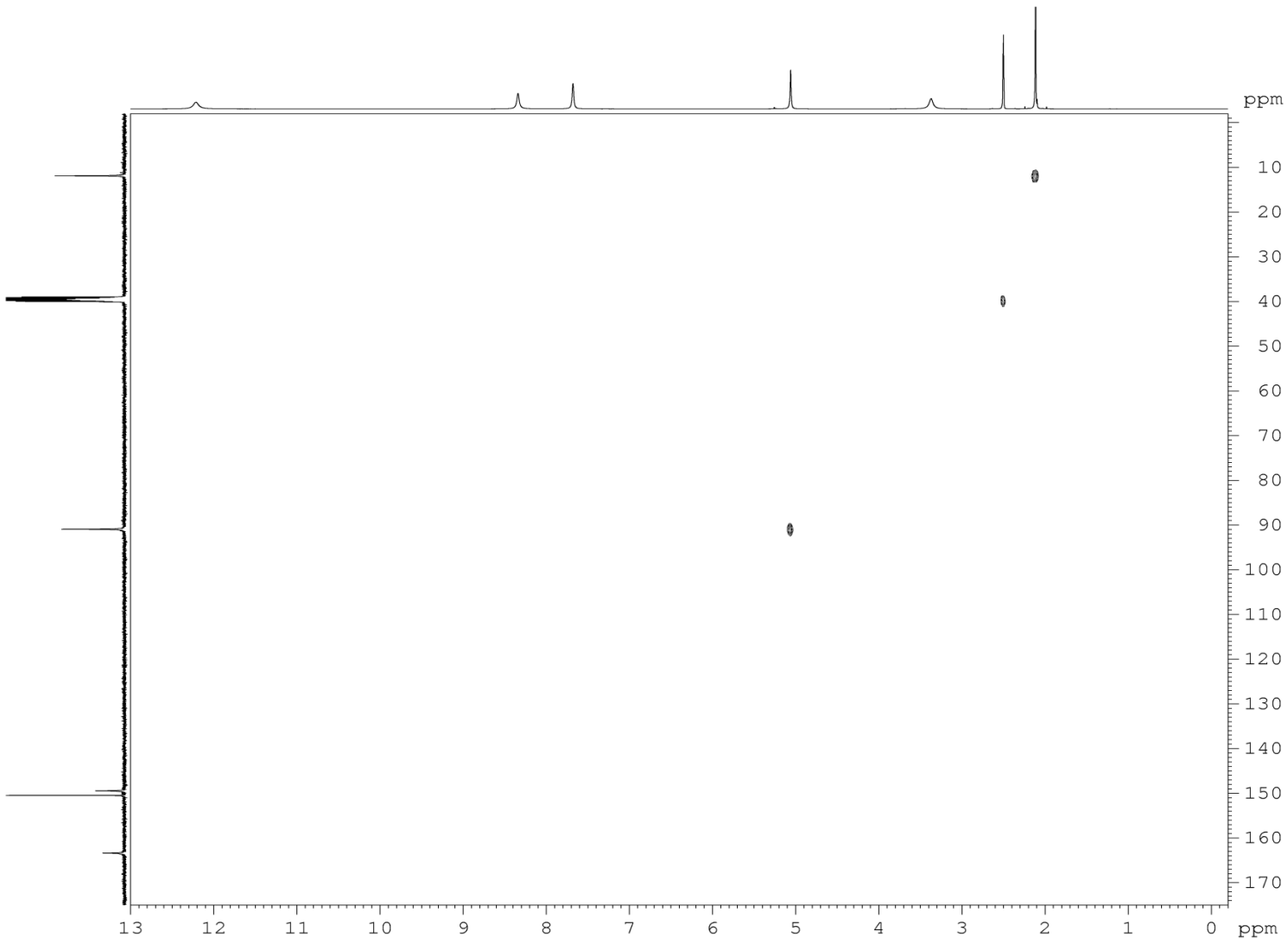



**Fig. S6.** HSQC spectrum of **1**.

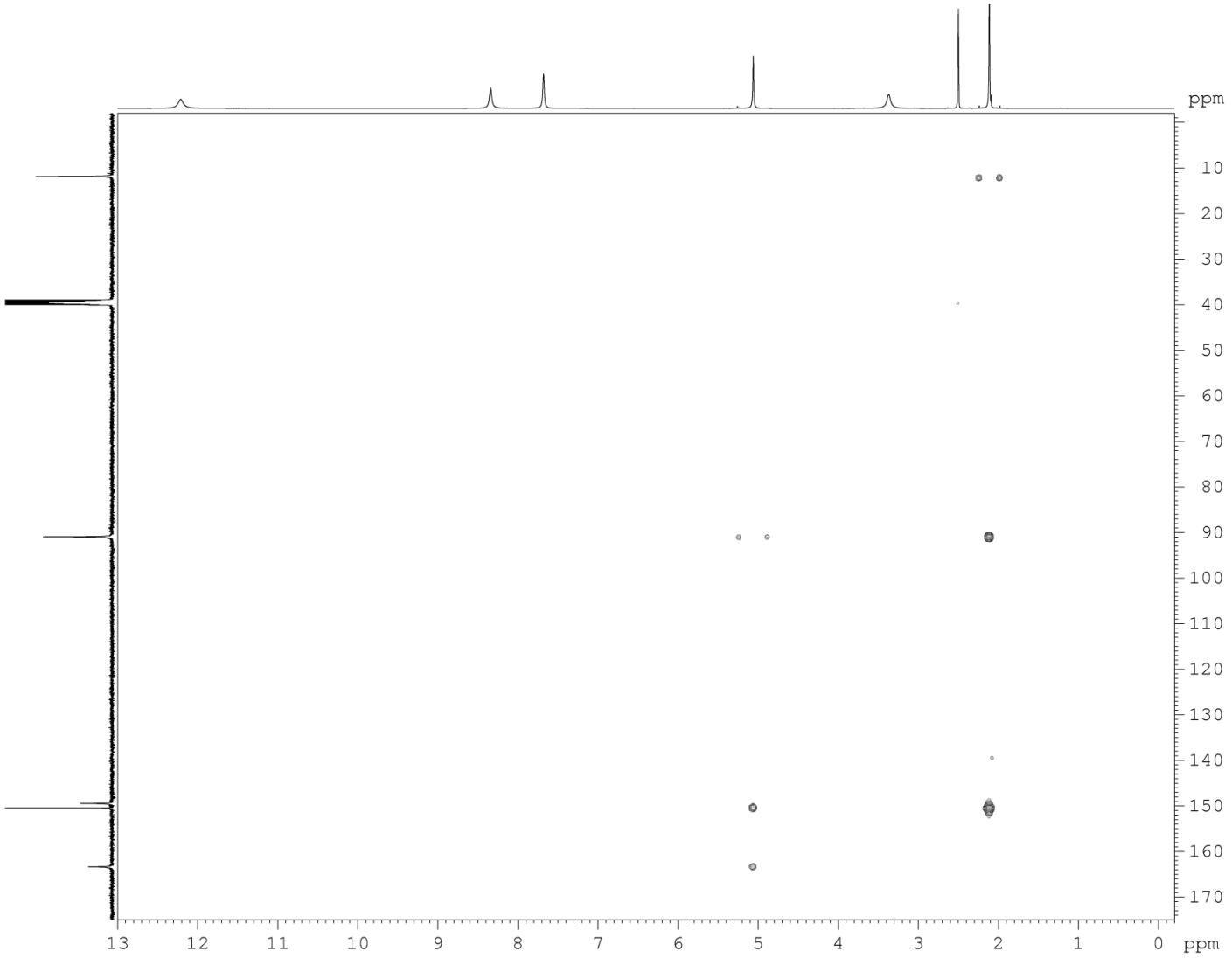



**Fig. S7.** HMBC spectrum of **1**.

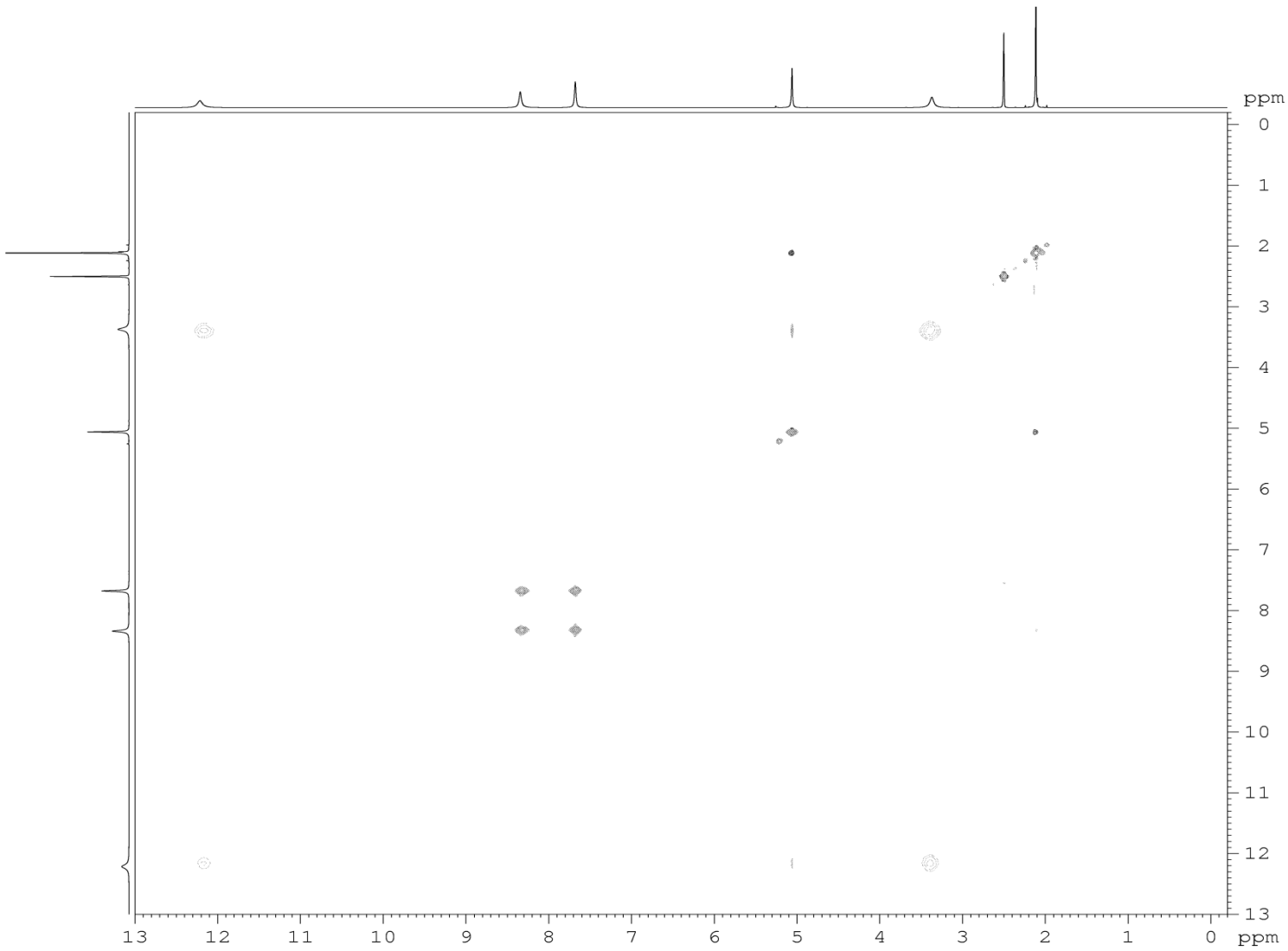



**Fig. S8.** NOESY spectrum of **1**.

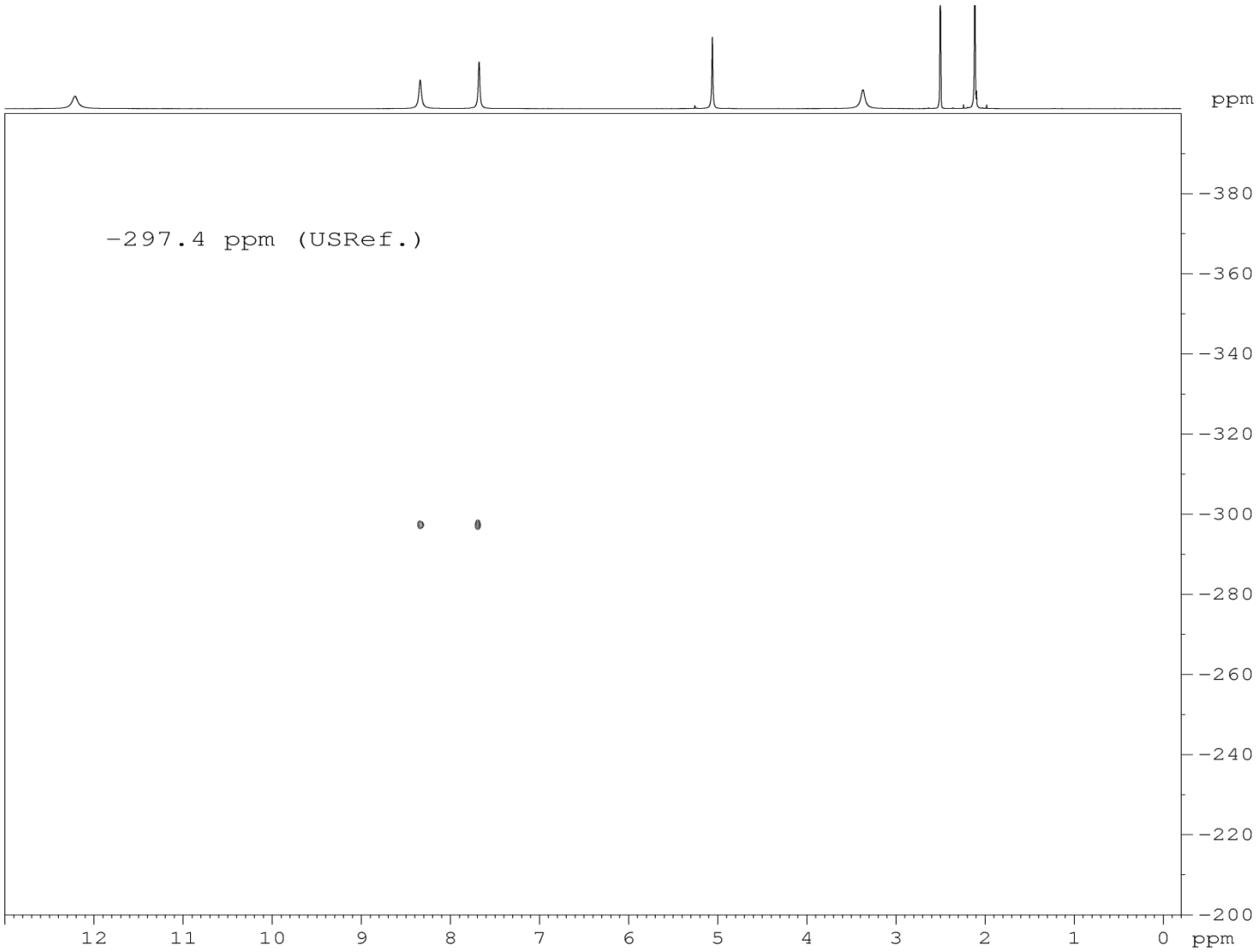



**Fig. S9.** $^{1}H$-$^{15}N$ HSQC spectrum of **1**.

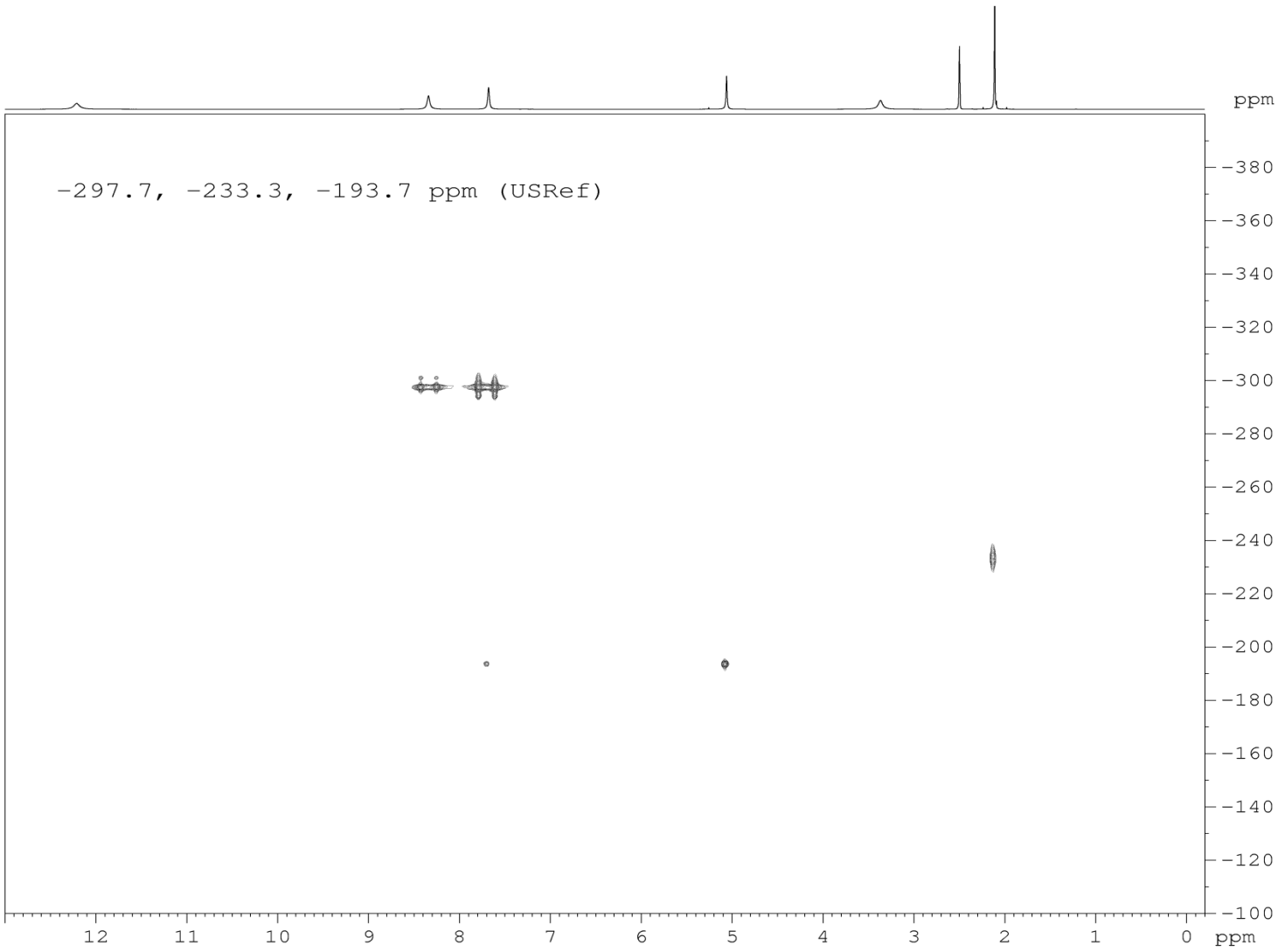



**Fig. S10.** $^{1}H$-$^{15}N$ HMBC spectrum of **1**.

# Experimental and calculated geometrical parameters of MOPC (1)

**Table S1.** Experimental and calculated bond lengths (Å) in **1**.

| Bond length | Experimental | Calculated |
|---|---|---|
| O2—C7 | 1.220 (2) | 1.225 |
| C6—C3 | 1.487 (2) | 1.490 |
| C6—H4D | 0.96 | 1.089 |
| C6—H4E | 0.96 | 1.093 |
| C6—H4F | 0.96 | 1.093 |
| C7—N3 | 1.320 (2) | 1.344 |
| C7—N1 | 1.408 (2) | 1.411 |
| N1—N2 | 1.368 (2) | 1.385 |
| N1—C5 | 1.400 (2) | 1.418 |
| N2—C3 | 1.334 (2) | 1.364 |
| N2—H2 | 0.88 (2) | 1.013 |
| C3—C4 | 1.367 (2) | 1.372 |
| O1—C5 | 1.247 (2) | 1.239 |
| C4—C5 | 1.407 (2) | 1.435 |
| C4—H4 | 0.93 | 1.077 |
| N3—H3A | 0.86 (3) | 1.016 |
| N3—H3B | 0.85 (3) | 1.007 |

**Table S2.** Experimental and calculated bond angles (°) in **1**.

| Bond angle | Experimental | Calculated |
|---|---|---|
| C3—C6—H4D | 109.5 | 110.1 |
| C3—C6—H4E | 109.5 | 110.7 |
| H4D—C6—H4E | 109.5 | 108.8 |
| C3—C6—H4F | 109.5 | 110.8 |
| H4D—C6—H4F | 109.5 | 108.6 |
| H4E—C6—H4F | 109.5 | 107.8 |
| O2—C7—N3 | 127.0 (2) | 126.6 |
| O2—C7—N1 | 118.5 (2) | 119.7 |
| N3—C7—N1 | 114.4 (2) | 113.7 |
| N2—N1—C5 | 109.2 (1) | 109.3 |
| N2—N1—C7 | 120.1 (1) | 118.9 |
| C5—N1—C7 | 130.6 (2) | 131.6 |
| C3—N2—N1 | 108.4 (1) | 108.0 |
| C3—N2—H2 | 127.9 (1) | 125.7 |
| N1—N2—H2 | 123.0 (1) | 116.4 |
| N2—C3—C4 | 109.4 (2) | 109.4 |
| N2—C3—C6 | 120.2 (2) | 120.4 |
| C4—C3—C6 | 130.3 (2) | 130.1 |
| C3—C4—C5 | 108.4 (2) | 108.6 |
| C3—C4—H4 | 125.8 | 126.7 |
| C5—C4—H4 | 125.8 | 124.6 |
| C7—N3—H3A | 120.7 (2) | 119.7 |
| C7—N3—H3B | 118.6 (2) | 118.5 |
| H3A—N3—H3B | 121 (2) | 121.7 |
| O1—C5—N1 | 121.8 (2) | 123.1 |
| O1—C5—C4 | 133.7 (2) | 132.5 |
| N1—C5—C4 | 104.5 (2) | 104.3 |

**Table S3.** Experimental and calculated dihedral angles (°) in **1**.

| Torsion angle | Experimental | Calculated |
|---|---|---|
| O2—C7—N1—N2 | 1.1 (2) | 5.4 |
| N3—C7—N1—N2 | −178.3 (2) | −175.2 |
| O2—C7—N1—C5 | 176.0 (2) | 179.5 |
| N3—C7—N1—C5 | −3.4 (3) | −1.2 |
| C5—N1—N2—C3 | 1.7 (2) | 5.9 |
| C7—N1—N2—C3 | 177.6 (2) | 178.7 |
| N1—N2—C3—C4 | −1.2 (2) | −5.8 |
| N1—N2—C3—C6 | 179.2 (2) | 175.2 |
| N2—C3—C4—C5 | 0.3 (2) | 3.5 |
| C6—C3—C4—C5 | 179.7 (2) | 177.6 |
| N2—N1—C5—O1 | 177.8 (2) | 175.6 |
| C7—N1—C5—O1 | 2.5 (3) | 1.1 |
| N2—N1—C5—C4 | −1.5 (2) | −3.6 |
| C7—N1—C5—C4 | −176.8 (2) | −178.2 |
| C3—C4—C5—O1 | −178.5 (2) | −179.0 |
| C3—C4—C5—N1 | 0.7 (2) | 0.2 |

**Table S4.** Hydrogen-bond geometry (Å, °)

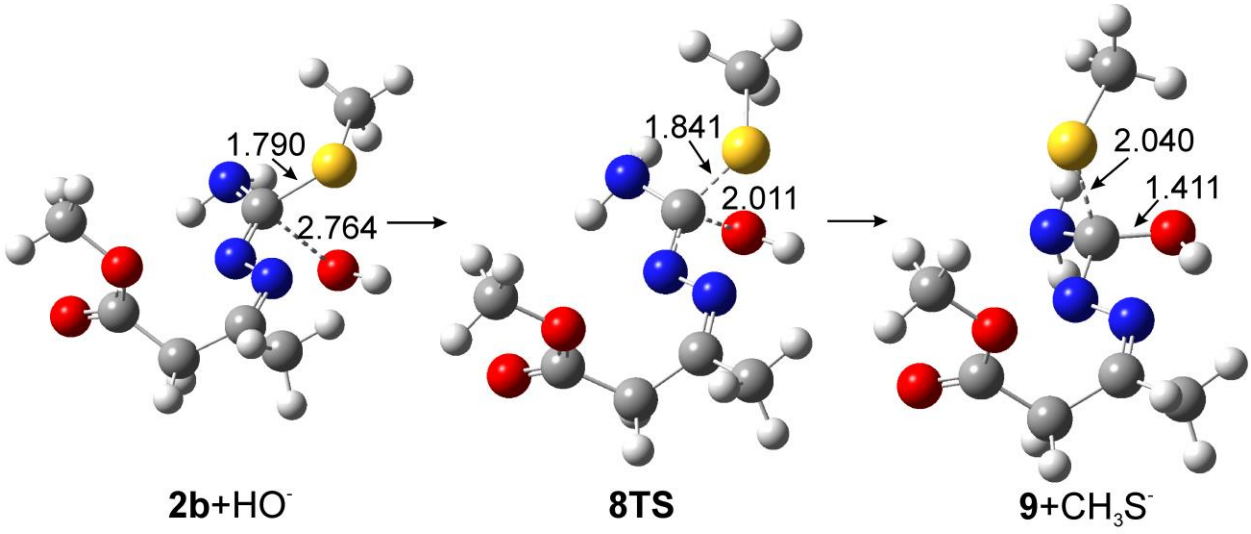
| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*A*···O1 | 0.86 (3) | 2.03 (2) | 2.701 (2) | 135 (2) |
| N3—H3*B*···O2$^{i}$ | 0.85 (3) | 2.09 (3) | 2.930 (2) | 168 (2) |
| N2—H2···O1$^{ii}$ | 0.88 (2) | 1.83 (2) | 2.711 (2) | 172 (2) |

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*−1, *y*, *z*.

**Table S5.** Crystal data and refinement parameters

| | |
|---|---|
| Molecular formula | $C_5H_7N_3O_2$ |
| CCDC No. | 902014 |
| $M$ (g mol$^{-1}$) | 141.14 |
| Color / habit | translucent pale pink / prism |
| Crystal size (mm) | 0.29 × 0.24 × 0.08 |
| Temperature (K) | 298(2) |
| Crystal system | triclinic |
| Space group | $P$ −1 |
| $a$ (Å) | 6.0099(8) |
| $b$ (Å) | 7.3248(9) |
| $c$ (Å) | 7.602(1) |
| $\alpha$ (°) | 90.11(1) |
| $\beta$ (°) | 100.81(1) |
| $\gamma$ (°) | 107.28(1) |
| $V$ (Å$^3$) | 313.30(7) |
| $Z$ | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.496 |
| $F$(0 0 0) | 148 |
| $\theta$ range (°) | 5.9–66.9 |
| Data collection limits | $-7 \le h \le 7$, $-7 \le k \le 8$, $-9 \le l \le 9$ |
| $\mu$ (mm$^{-1}$) | 1.01 |
| $T_{min}$ / $T_{max}$ | 0.891 / 1 |
| Reflections collected | 1676 |
| Independent reflections | 1120 |
| $R_{int}$ | 0.021 |
| Data [$F_o > 4\sigma F_o$] | 934 |
| Restraints / parameters | 0 / 104 |
| Goodness-of-fit on $F^2$ | 1.07 |
| $R$ / $wR$ [$F_o > 4\sigma F_o$] | 0.039 / 0.102 |
| $R$ / $wR$ [all data] | 0.047 / 0.11 |
| $\Delta\rho_{min}$ / $\Delta\rho_{max}$ (e Å$^{-3}$) | −0.16 / 0.18 |

## Mechanism B: Elementary steps in the conversion of methyl acetoacetate *S*-methylisothiosemicarbazone (2b) into 1



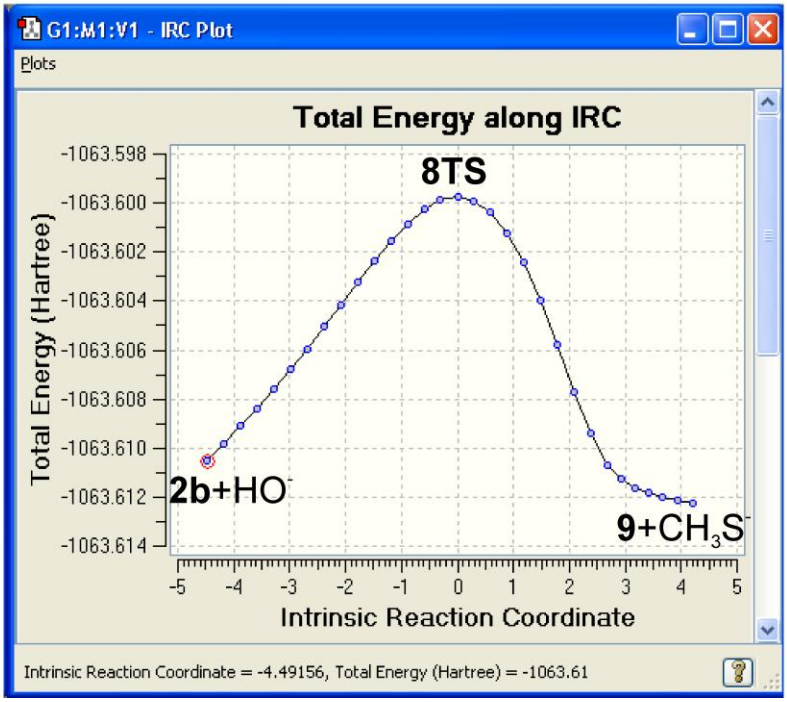




**Fig. S11.** Optimized geometries of the participants in step 1 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

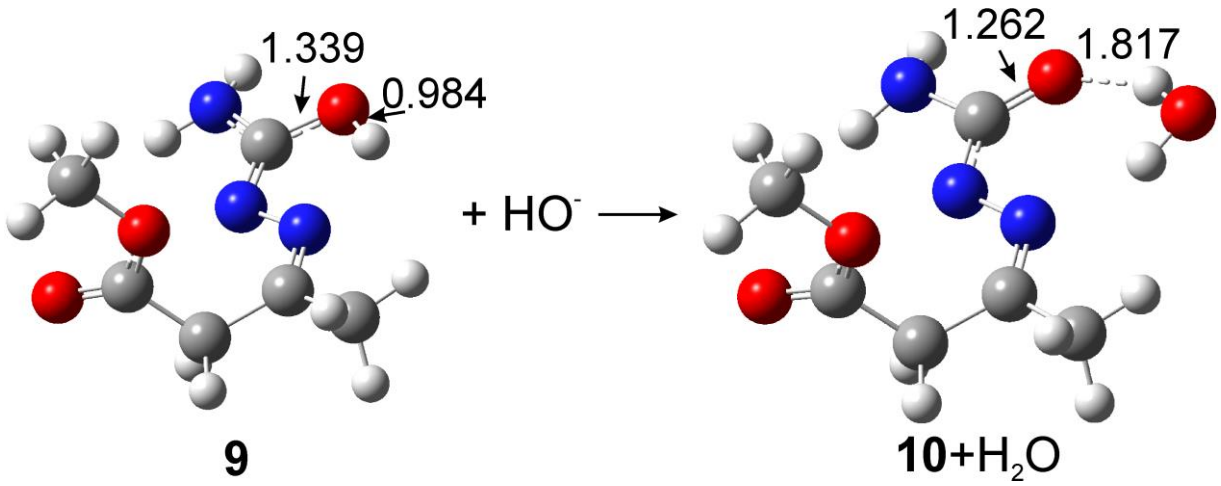



**Fig. S12.** Optimized geometries of the participants in step 2 with crucial intramolecular distances (Å).

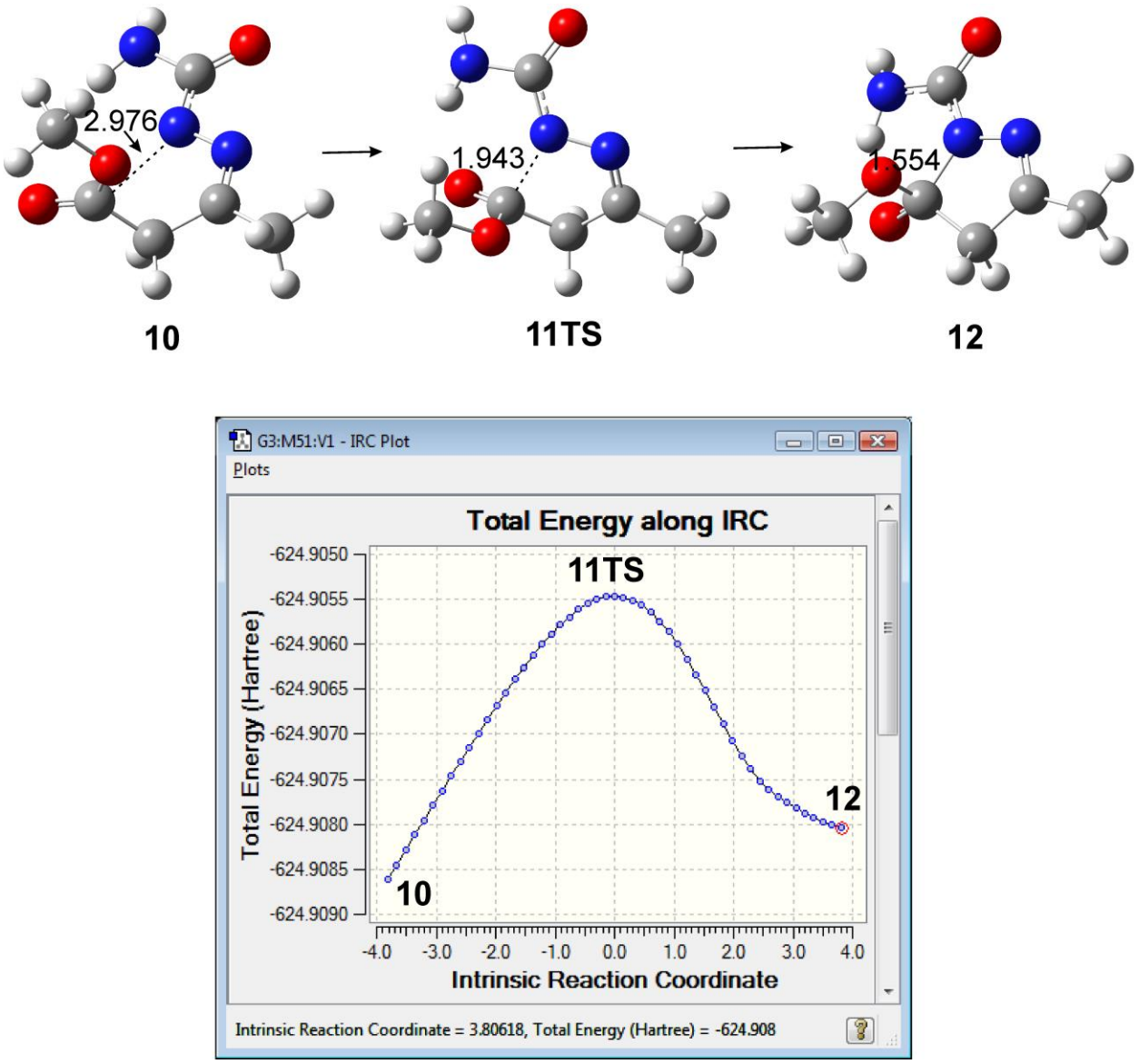
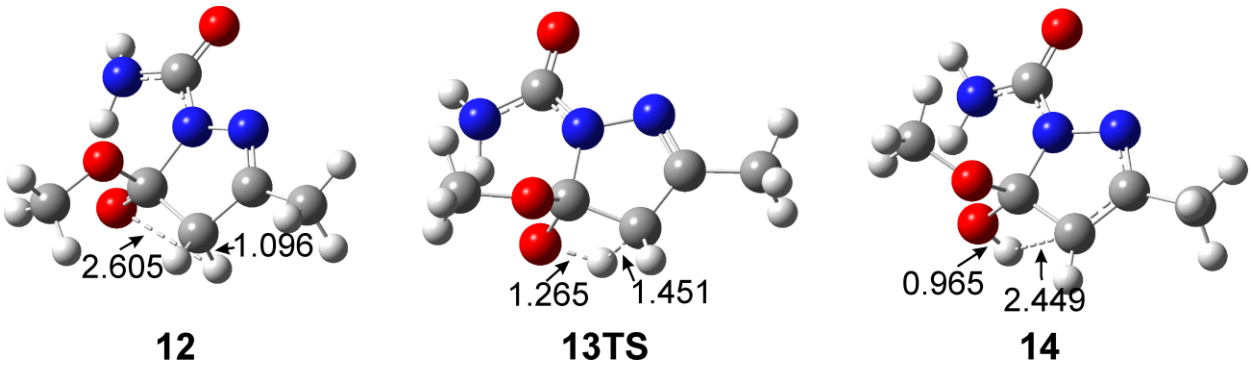



**Fig. S13.** Optimized geometries of the participants in step 3 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.



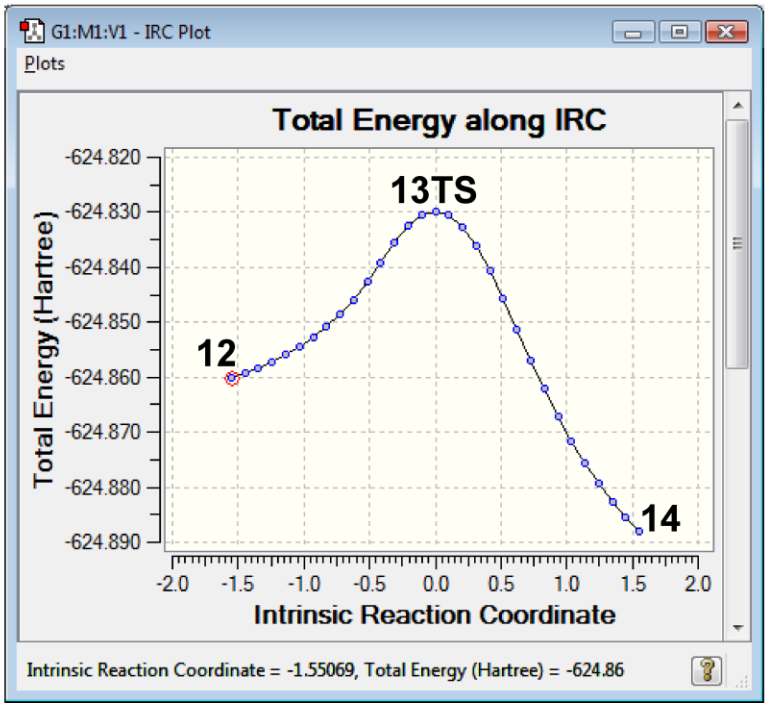




**Fig. S14.** Optimized geometries of the participants in step 4 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

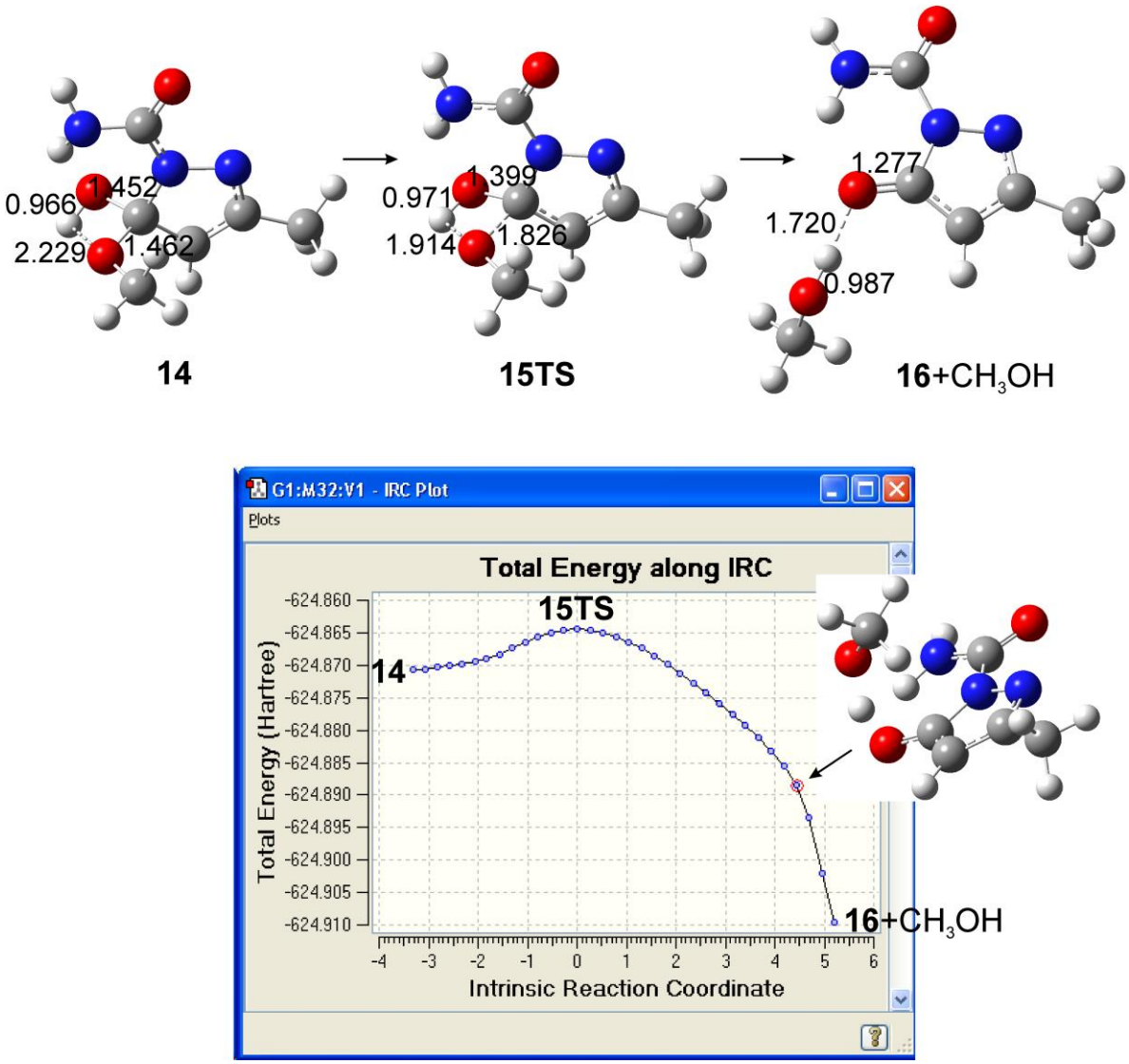



**Fig. S15.** Optimized geometries of the participants in step 5 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

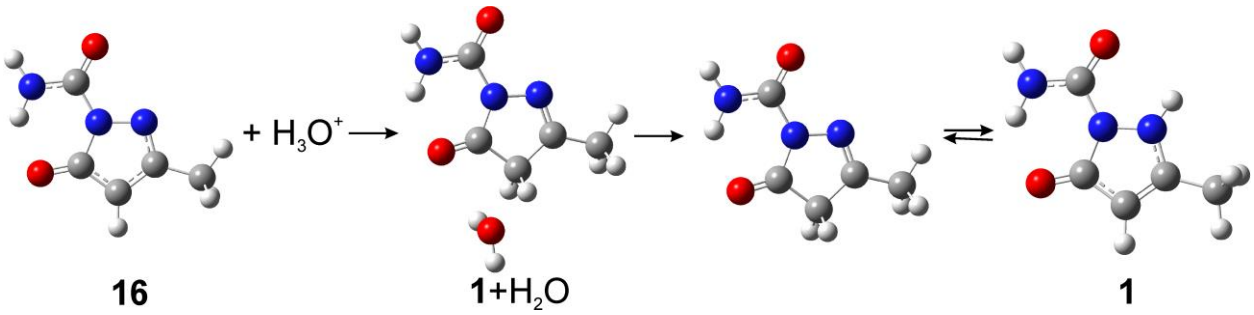
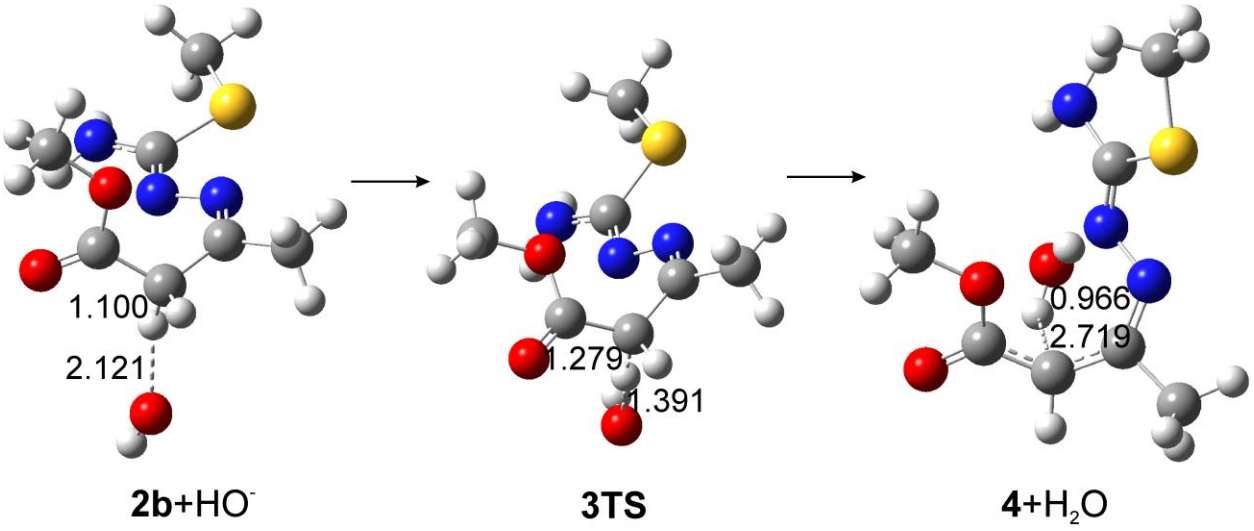



**Fig. S16.** Optimized geometries of the participants in step 6.

## Mechanism A: Elementary steps in the hypothetical conversion of methyl acetoacetate *S*-methylisothiosemicarbazone (2b) into 3-aminopyrazole derivative 7



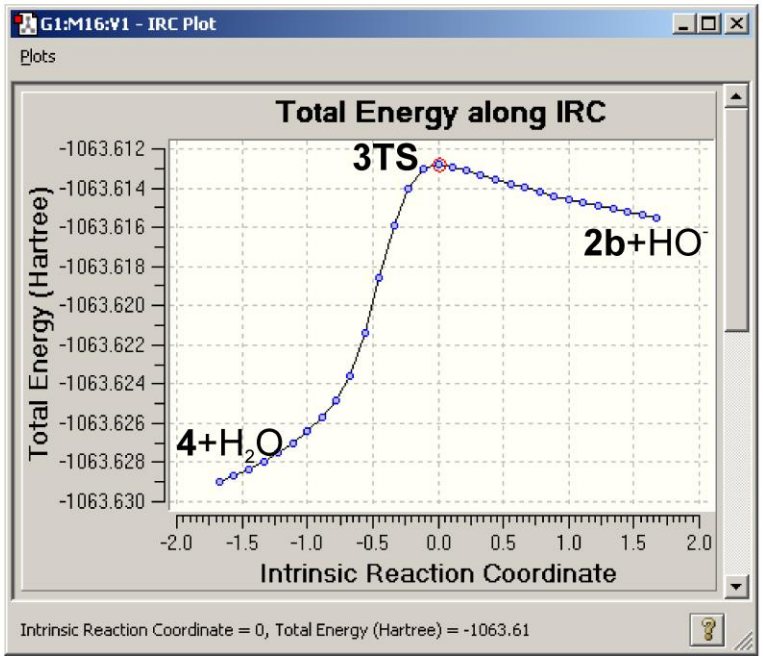




**Fig. S17.** Optimized geometries of the participants in step 1 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

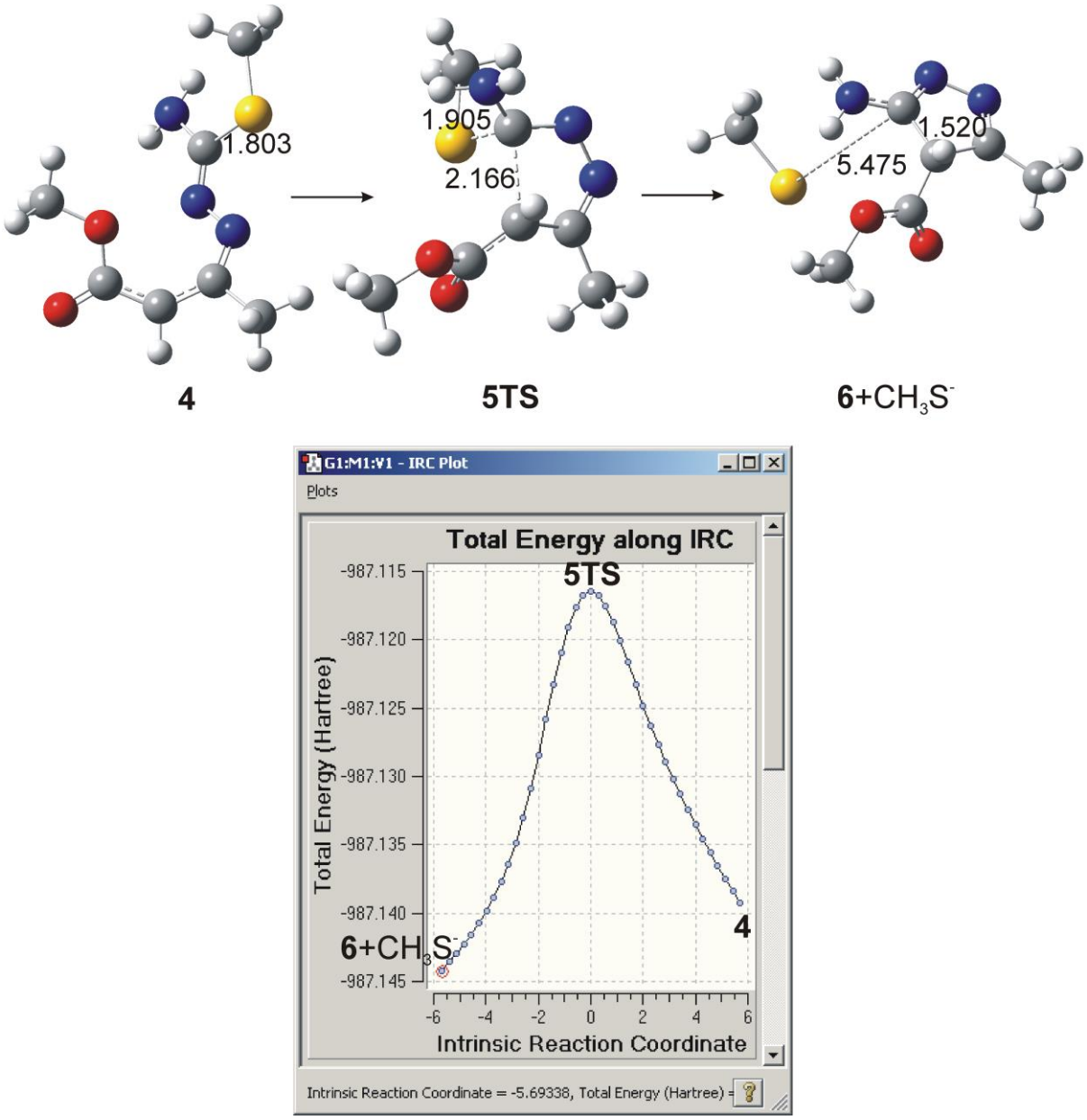



**Fig. S18.** Optimized geometries of the participants in step 2 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

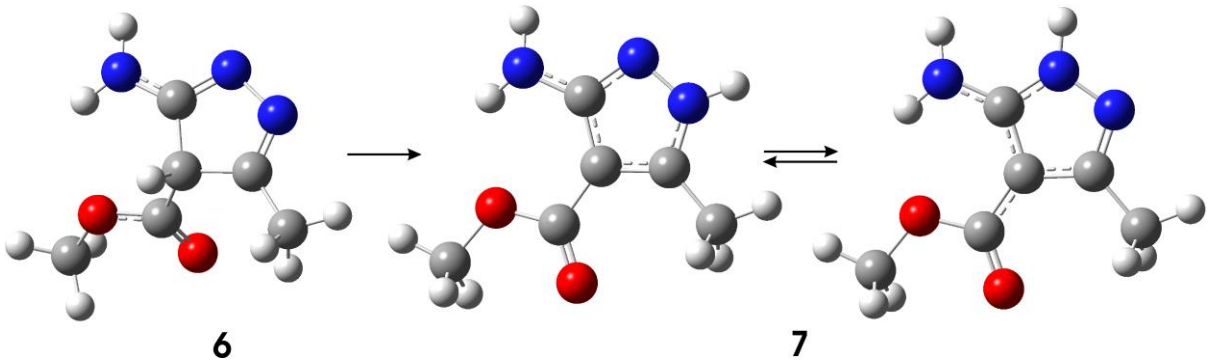
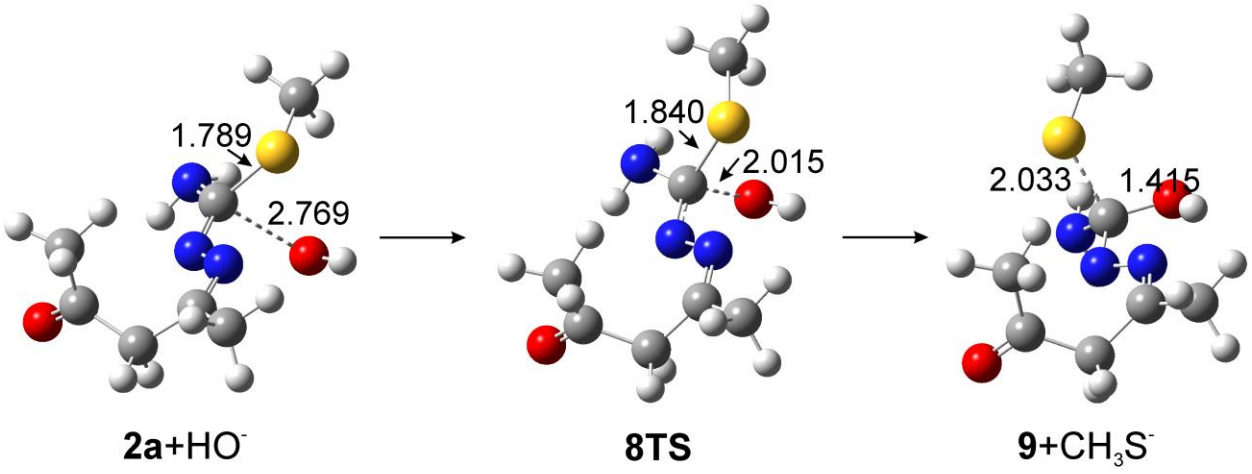



**Fig. S19.** Optimized geometries of the participants in step 3.

# Mechanism B: Elementary steps in the hypothetical conversion of acetylacetone mono-*S*-methylisothiosemicarbazone (2a) into 1



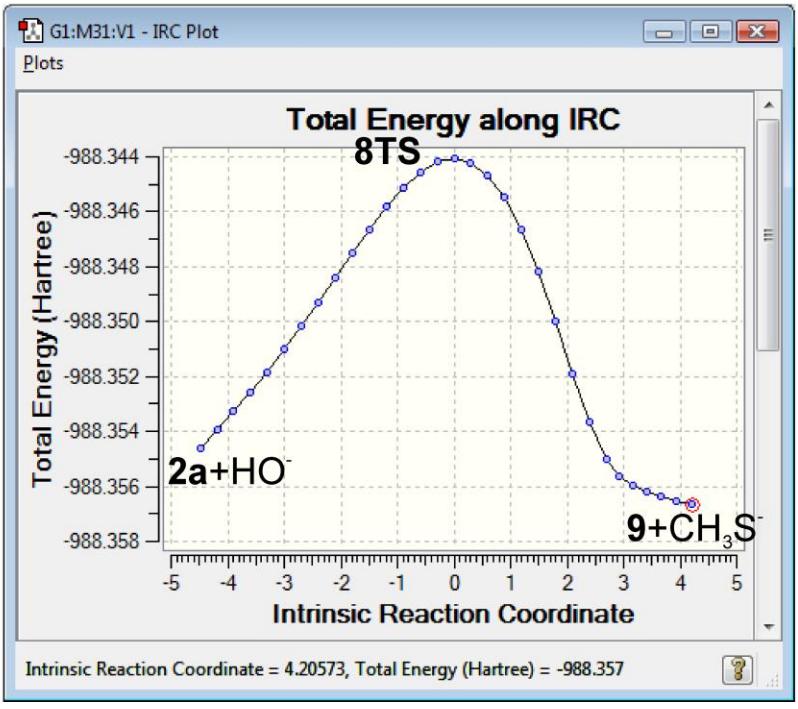




**Fig. S20.** Optimized geometries of the participants in step 1 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

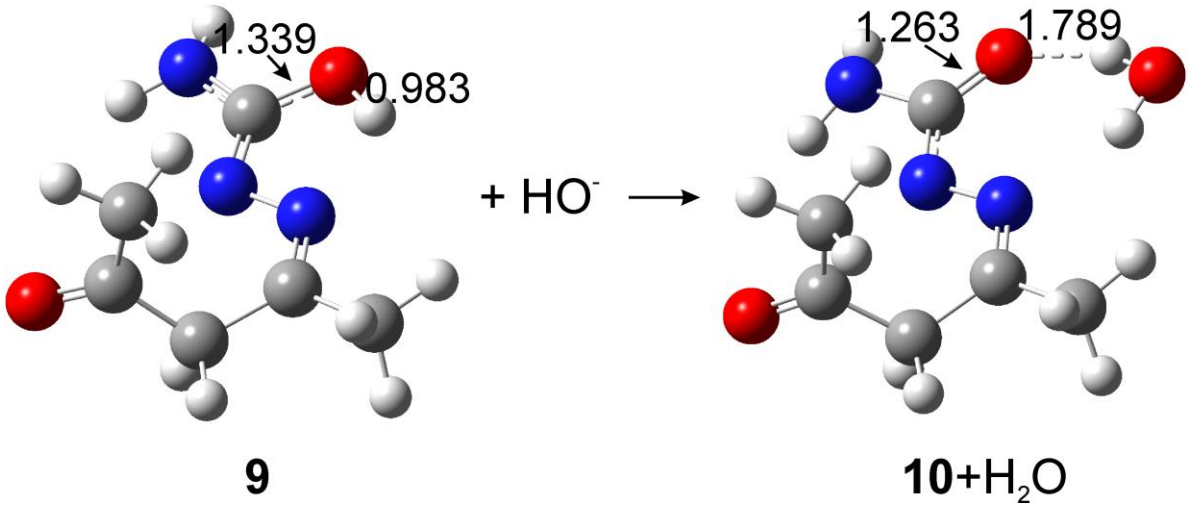



**Fig. S21.** Optimized geometries of the participants in step 2 with crucial intramolecular distances.

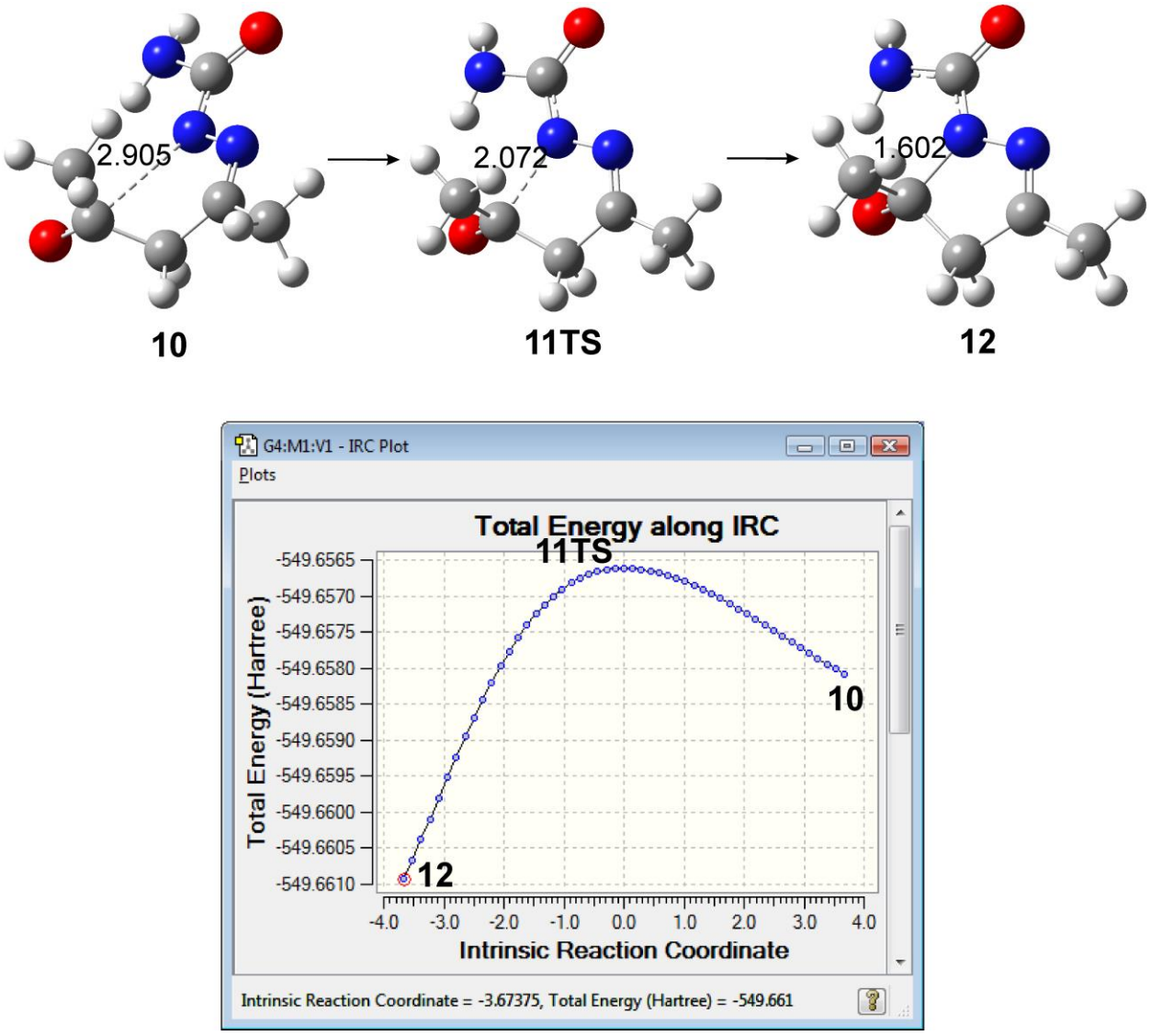
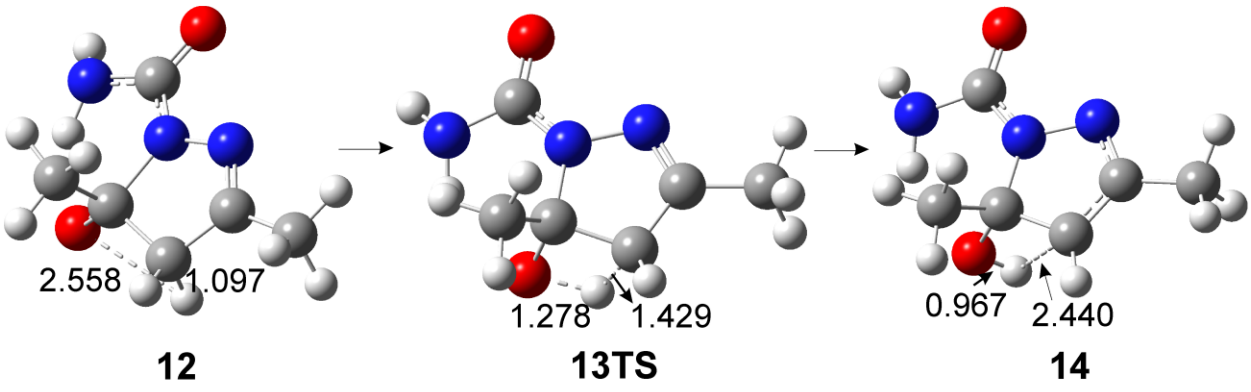



**Fig. S22.** Optimized geometries of the participants in step 3 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.



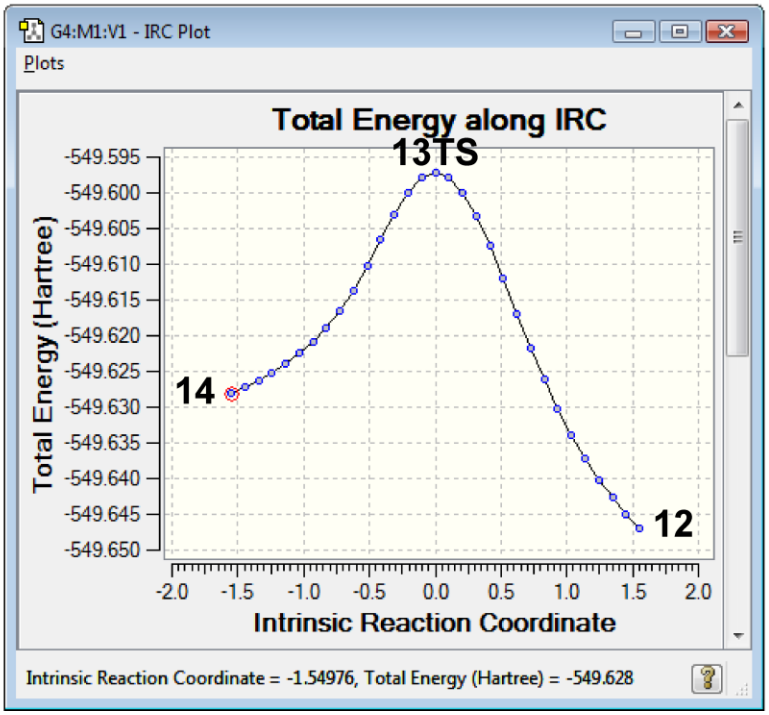




**Fig. S23.** Optimized geometries of the participants in step 4 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

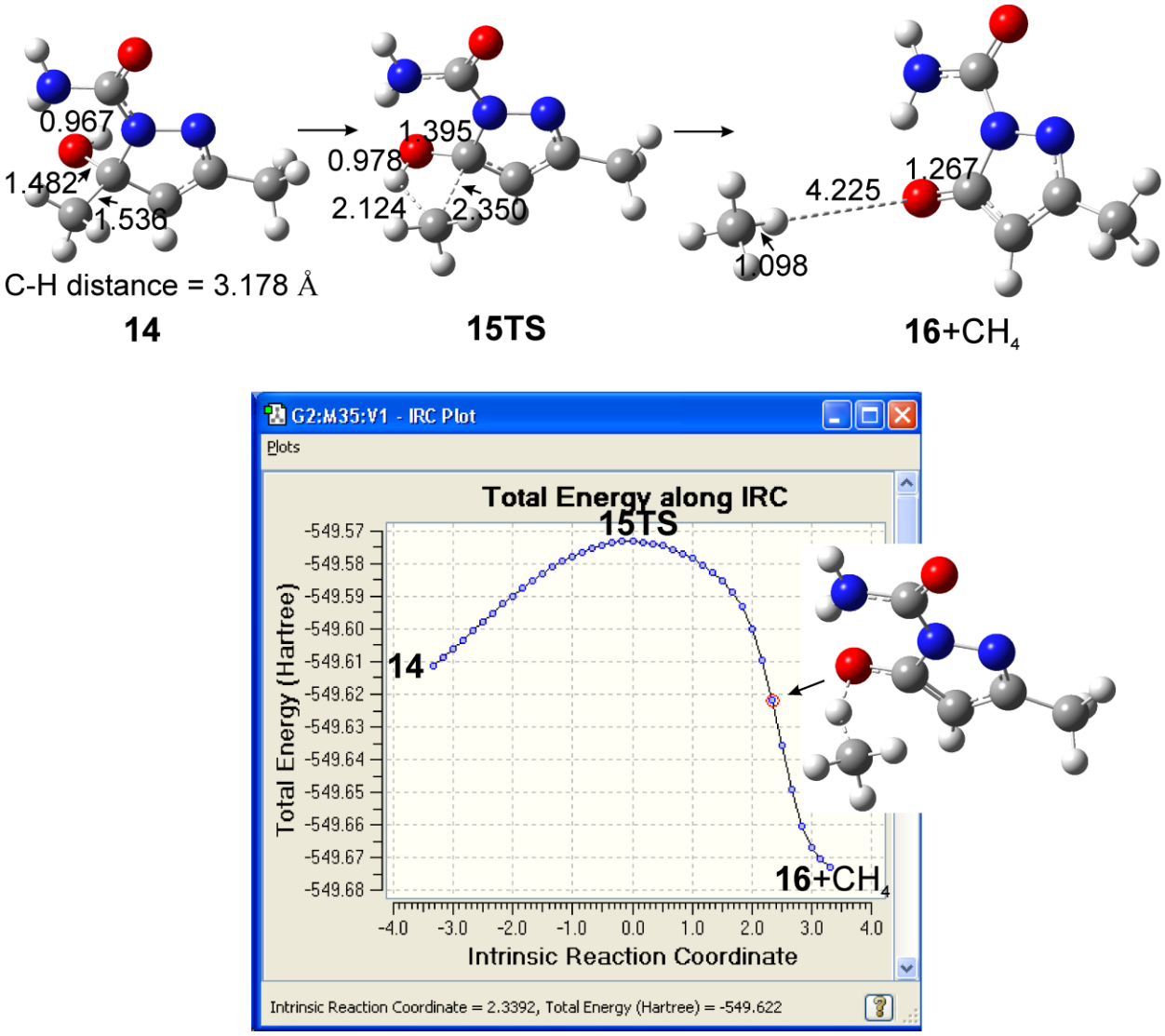



**Fig. S24.** Optimized geometries of the participants in step 5 with crucial intramolecular distances (Å), and results of the IRC calculation for related transition state.

According to mechanism **B**, step 6 for acetylacetone mono-*S*-methylisothiosemicarbazone is identical to step 6 for methyl acetoacetate *S*-methylisothiosemicarbazone.