Supporting information 2

Thermal [2+2]-Cycloaddition between Silyl Alkynes and Allenyl Phenols followed by Nucleophilic Addition of Water; Metal-Free and Economical Synthesis of Arylcyclobutenals

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X-ray structure analysys

A brown block crystal of 2a ($C_{20}H_{29}O_2Si$) having approximate dimensions of 0.344 x 0.293 x 0.259 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 10.5104(3) Å
b = 11.3774(3) Å β = 93.828(7)^o
c = 32.0579(9) Å
V = 3824.95(18) Å^3

For Z = 10 and F.W. = 330.54, the calculated density is 1.435 g/cm^3. The reflection conditions of:

h0l: l = 2n
0k0: k = 2n

uniquely determine the space group to be:

$P2_1/c$

Of the 39,424 reflections were collected, where 6995 were unique (R_{int} = 0.1223); equivalent reflections were merged.

The linear absorption coefficient, μ, for Cu-Kα radiation is 14.118 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.365 to 0.694. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction[1] was applied (coefficient = -11.761000).

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F was based on 6,995 observed reflections (I > 0.00σ(I)) and 479 variable parameters and converged (largest parameter shift was 0.09 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0723$$

$$R_w = [\Sigma w (|Fo| - |Fc|)^2 / \Sigma w Fo^2]^{1/2} = 0.0919$$

The goodness of fit[4] was 1.86. The weighting scheme was based on counting statistics. Plots of $\Sigma w (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.71 and -0.60 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from International Tables for X-ray Crystallography (IT), Vol. IV, Table 2.2B [5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9,10] crystallographic software package.

References

(1) Larson, A.C. (1970), Crystallographic Computing, 291-294. F.R. Ahmed, ed. Munksgaard, Copenhagen (equation 22, with V replaced by the cell volume).

(2) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C. and Guagliardi, A. (1993). J. Appl. Cryst. 26, 343-350.

(3) Least Squares function minimized:

$\Sigma w(|F_o|-|F_c|)^2$ where w = Least Squares weights.

(4) Goodness of fit is defined as:

$[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(5) International Tables for X-ray Crystallography, Vol. IV (1974). Ed. J.A. Ibers and W.C. Hamilton, The Kynoch Press, Birmingham, England, Table 2.2B, pp. 99.

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 4.2.5: Crystal Structure Analysis Package, Rigaku Corporation (2000-2017). Tokyo 196-8666, Japan.

(10) CRYSTALS Issue 11: Carruthers, J.R., Rollett,J.S., Betteridge, P.W., Kinna, D., Pearce, L., Larsen, A., and Gabe, E. Chemical Crystallography Laboratory, Oxford, UK. (1999)