

Supporting Information

Influence of Intramolecular Interactions and Transition State Energetics on the Strain-Promoted Azide-Alkyne  
Cycloaddition of 2-Aminobenzenesulfonamide-Containing Cyclononynes  
Kazuhide Nakahara\* and Kyosuke Kaneda

Hokkaido Pharmaceutical University School of Pharmacy, 7-15-4-1 Maeda Teine Sapporo, Hokkaido 006-8590, Japan

\*E-mail: nakahara-k@hus.ac.jp

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## S1. Computational Methods

### **Computational Details**

All structural optimizations and frequency analyses in this study were performed based on density functional theory (DFT). The calculations were carried out using the GAMESS (version June 30, 2023 R1) software package.

### Theoretical Level

The level of theory was a combination of the B3LYP functional and the 6-31G(d) basis set, with the DFT-D3(BJ) method used to incorporate dispersion corrections. A high-precision TIGHT GRID was used for the integration grid.

Adoption of the DFT-D3(BJ) method: This method efficiently adds a D3 correction to account for long-range van der Waals forces (dispersion forces) that are not fully captured by the standard B3LYP functional. The (BJ) stands for the Becke-Johnson damping function, which improves the accuracy of the calculation by properly handling short-range repulsions. This allows for a more accurate description of both intermolecular and intramolecular non-covalent interactions.

Convergence Criteria: The convergence criterion for geometry optimization was set to OPTTOL = 0.00045 (Hartree/Bohr). The SCF convergence criterion was set to CONV =  $1.0 \times 10^{-5}$ .

### Initial Structure Preparation

Initial structures for the DFT calculations were prepared using different methods depending on the target: For stable structures, experimental geometries determined by single-crystal X-ray analysis were used as the initial coordinates.

For the exploration of transition state (TS) structures, a preliminary search was first conducted using the semi-empirical PM7 method with MOPAC2016 via the Winmostar (V11.8.6) interface.

### Final Optimization and Solvent Effects

For this optimization, calculations were first performed under solvent-free conditions using the B3LYP-6-31G(d) method. Furthermore, optimization calculations considering the solvent effect were carried out using the structure obtained from the solvent-free conditions as the initial coordinates. The solvent effects of either dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) or acetonitrile ( $\text{CH}_3\text{CN}$ ) were incorporated using the polarizable continuum model (PCM).

### Characterization of Stationary Points

The nature of all stationary points was determined by frequency analysis:

Reactants and products were confirmed as local minima with no imaginary frequencies.

Transition states were confirmed as first-order saddle points with exactly one imaginary frequency. For instance, the imaginary frequencies for key transition states were:

Model, Major TS:  $-327 \text{ cm}^{-1}$

Model, Minor TS:  $-335 \text{ cm}^{-1}$

Unless otherwise noted, the energy values discussed in this paper include zero-point vibrational energy (ZPVE) corrections calculated at 298.15 K. No scaling factor was applied to the vibrational frequencies.

## S2. Tables of Calculated Energies

### Computational Results

The absolute energies for each computed species and the imaginary frequencies for the transition states are provided below. The atomic coordinates (in XYZ format) provided at the end of this Supporting Information.

#### Model Reactants (Table 1 & Figure 2 & Table 3)

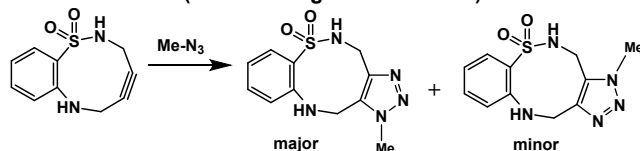


Figure S1. Formation of regioisomers in the strain-promoted cycloaddition of model molecule ABSACN with methyl azide.

Table S1. Total energies and frequency analysis results at the B3LYP-D3(BJ)/6-31G(d) level for model reactants (ABSACN and methyl azide), key transition states, and products.

| Molecule/State    | Total Energy (E) | No. of Imaginary Frequencies | Imaginary Frequency (cm <sup>-1</sup> ) |
|-------------------|------------------|------------------------------|-----------------------------------------|
| ABSACN model      | -1044.69247      | 0                            | -                                       |
| Methyl azide      | -203.98866       | 0                            | -                                       |
| TS major          | -1248.67161      | 1                            | -327                                    |
| TS minor          | -1248.67109      | 1                            | -335                                    |
| GS2 Major product | -1248.81829      | 0                            | -                                       |
| GS2 Minor product | -1248.81597      | 0                            | -                                       |

#### Model Reactants and Products

Total Reactant (E): E (ABSACN model) + E (Methyl azide) = -1044.69247 a.u. + (-203.98866 a.u.) = -1248.68113 a.u. = -1248.68113 a.u. × 627.51 kcal/mol/a.u. = -783637.38 kcal/mol

Activation Barrier for TS major: (-1248.67161 a.u.) - (-1248.68113 a.u.) = 0.00952 a.u.  
= 0.00952 a.u. × 627.51 kcal/mol/a.u. = 5.976 kcal/mol

Activation Barrier for TS minor: (-1248.67109 a.u.) - (-1248.68113 a.u.) = 0.01004 a.u.  
= 0.01004 a.u. × 627.51 kcal/mol/a.u. = 6.300 kcal/mol

Reaction Energy for GS2 Major product: (-1248.81829 a.u.) - (-1248.68113 a.u.) = -0.13716 a.u.  
= -0.13716 a.u. × 627.51 kcal/mol/a.u. = -86.06882 kcal/mol

Reaction Energy for GS2 Minor product: (-1248.81597 a.u.) - (-1248.68113 a.u.) = -0.13484 a.u.  
= -0.13484 a.u. × 627.51 kcal/mol/a.u. = -84.61510 kcal/mol

**ABSACN model: The optimized ground state structure (GS1) representing the total energy of the reactants (model molecules: optimized ABSACN Entry A and optimized MeN<sub>3</sub>).**

Table S2. Calculated thermodynamic quantities and frontier orbital energies for ABSACN model (GS1).

|                                                                  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                            | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                           | 0.889        | 1.481        | -11.07       | 2.981            | 4.968            | 42.096          |
| ROT.                                                             | 0.889        | 0.889        | -8.576       | 2.981            | 2.981            | 31.745          |
| VIB.                                                             | 127.014      | 127.014      | 116.772      | 43.919           | 43.919           | 34.35           |
| TOTAL                                                            | 128.791      | 129.384      | 97.127       | 49.881           | 51.868           | 108.191         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 6032.873 cal/mol |              |              |              |                  |                  |                 |
| Orbital Energy: HOMO: -6.1008 eV, LUMO: -0.3701 eV               |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

**Methyl azide Model: The optimized ground state structure (GS1) representing the total energy of the reactants (model molecules: optimized ABSACN Entry A and optimized MeN<sub>3</sub>).**

Table S3. Calculated thermodynamic quantities and frontier orbital energies for Methyl azide Model (GS1).

|                                                                  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                            | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                           | 0.889        | 1.481        | -9.862       | 2.981            | 4.968            | 38.044          |
| ROT.                                                             | 0.889        | 0.889        | -6.007       | 2.981            | 2.981            | 23.129          |
| VIB.                                                             | 32.807       | 32.807       | 31.022       | 7                | 7                | 5.986           |
| TOTAL                                                            | 34.584       | 35.177       | 15.153       | 12.962           | 14.949           | 67.159          |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 1007.794 cal/mol |              |              |              |                  |                  |                 |
| Orbital Energy: HOMO: -6.8545 eV, LUMO: -0.6667 eV               |              |              |              |                  |                  |                 |

**TS major Model: The transition state structure leading to the major product in the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>.**

Table S4. Calculated thermodynamic quantities and energy components for the transition state leading to the major product (TS major).

|                                                                 | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-----------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                           | 0.000        | 0.000        | 0.000        | 0.000            | 0.000            | 0.000           |
| TRANS.                                                          | 0.889        | 1.481        | -11.273      | 2.981            | 4.968            | 42.777          |
| ROT.                                                            | 0.889        | 0.889        | -9.143       | 2.981            | 2.981            | 33.645          |
| VIB.                                                            | 162.681      | 162.681      | 145.073      | 60.212           | 60.212           | 59.056          |
| TOTAL                                                           | 164.458      | 165.051      | 124.658      | 66.174           | 68.161           | 135.478         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 204.008 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -327 cm <sup>-1</sup>                      |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)

WAVEFUNCTION NORMALIZATION = .0000000000

ONE ELECTRON ENERGY = -4933.3157145563

TWO ELECTRON ENERGY = 2060.7223967211

NUCLEAR REPULSION ENERGY = 1623.9217119680

**TOTAL ENERGY = -1248.6716058672**

ELECTRON-ELECTRON POTENTIAL ENERGY = 2060.7223967211

NUCLEUS-ELECTRON POTENTIAL ENERGY = -6172.9578084715

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1623.9217119680

TOTAL POTENTIAL ENERGY = -2488.3136997824

TOTAL KINETIC ENERGY = 1239.6420939152

VIRIAL RATIO (V/T) = 2.0072839669

**TS minor Model: The transition state structure leading to the minor product in the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>.**

Table S5. Calculated thermodynamic quantities and energy components for the transition state leading to the minor product (TS minor).

|       | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC. | 0.000        | 0.000        | 0.000        | 0.000            | 0.000            | 0.000           |

|        |         |         |         |        |        |         |
|--------|---------|---------|---------|--------|--------|---------|
| TRANS. | 0.889   | 1.481   | -11.273 | 2.981  | 4.968  | 42.777  |
| ROT.   | 0.889   | 0.889   | -9.145  | 2.981  | 2.981  | 33.653  |
| VIB.   | 162.486 | 162.486 | 144.419 | 60.447 | 60.447 | 60.598  |
| TOTAL  | 164.263 | 164.856 | 124.001 | 66.408 | 68.396 | 137.027 |

VIB. THERMAL CORRECTION  $E(T)-E(0) = H(T)-H(0) = 9322.980$  cal/mol

Imaginary Frequency:  $-335\text{ cm}^{-1}$

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -4931.3068663597

TWO ELECTRON ENERGY = 2059.6945588948

NUCLEAR REPULSION ENERGY = 1622.9412199214

**TOTAL ENERGY = -1248.6710875434**

ELECTRON-ELECTRON POTENTIAL ENERGY = 2059.6945588948

NUCLEUS-ELECTRON POTENTIAL ENERGY = -6170.9519777009

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1622.9412199214

TOTAL POTENTIAL ENERGY = -2488.3161988846

TOTAL KINETIC ENERGY = 1239.6451113412

VIRIAL RATIO (V/T) = 2.0072810969

**GS2 Major product Model: The ground state structure (GS2) of the major product obtained from the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>.**

Table S6. Calculated thermodynamic quantities and energy components for the major product (GS2 major).

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.273      | 2.981            | 4.968            | 42.777          |
| ROT.   | 0.889        | 0.889        | -8.986       | 2.981            | 2.981            | 33.121          |
| VIB.   | 165.602      | 165.602      | 150.9        | 56.5             | 56.5             | 49.313          |
| TOTAL  | 167.38       | 167.972      | 130.641      | 62.461           | 64.448           | 125.211         |

VIB. THERMAL CORRECTION  $E(T)-E(0) = H(T)-H(0) = 8097.410$  cal/mol

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -5099.0309852413

TWO ELECTRON ENERGY = 2143.0121817999

NUCLEAR REPULSION ENERGY = 1707.2005164971

**TOTAL ENERGY = -1248.8182869443**

ELECTRON-ELECTRON POTENTIAL ENERGY = 2143.0121817999

NUCLEUS-ELECTRON POTENTIAL ENERGY = -6338.9295833313

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1707.2005164971

TOTAL POTENTIAL ENERGY = -2488.7168850343

TOTAL KINETIC ENERGY = 1239.8985980899

VIRIAL RATIO (V/T) = 2.0071938857

**GS2 Minor product Model: The ground state structure (GS2) of the minor product obtained from the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>.**

Table S7. Calculated thermodynamic quantities and energy components for the minor product (GS2 minor).

|  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--|--------------|--------------|--------------|------------------|------------------|-----------------|
|--|--------------|--------------|--------------|------------------|------------------|-----------------|

|                                                                  |         |         |         |        |        |         |
|------------------------------------------------------------------|---------|---------|---------|--------|--------|---------|
| ELEC.                                                            | 0       | 0       | 0       | 0      | 0      | 0       |
| TRANS.                                                           | 0.889   | 1.481   | -11.273 | 2.981  | 4.968  | 42.777  |
| ROT.                                                             | 0.889   | 0.889   | -9.007  | 2.981  | 2.981  | 33.191  |
| VIB.                                                             | 165.618 | 165.618 | 151.263 | 56.544 | 56.544 | 48.146  |
| TOTAL                                                            | 167.395 | 167.988 | 130.983 | 62.506 | 64.493 | 124.113 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 8011.266 cal/mol |         |         |         |        |        |         |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -5084.1401563981  
 TWO ELECTRON ENERGY = 2135.5547013347  
 NUCLEAR REPULSION ENERGY = 1699.7694847638  
**TOTAL ENERGY = -1248.8159702997**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2135.5547013347  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -6324.0292546924  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1699.7694847638  
 TOTAL POTENTIAL ENERGY = -2488.7050685940  
 TOTAL KINETIC ENERGY = 1239.8890982943  
 VIRIAL RATIO (V/T) = 2.0071997342

Model IRC: The vertical axis represents Total Energy (unit: kcal/mol). Calculations were performed at the B3LYP-D3(BJ)/6-31G(d) level. The figure consists of two comparative profiles: the upper profile corresponds to the pathway leading to the major product (TS major), and the lower profile corresponds to the pathway leading to the minor product (TS minor).

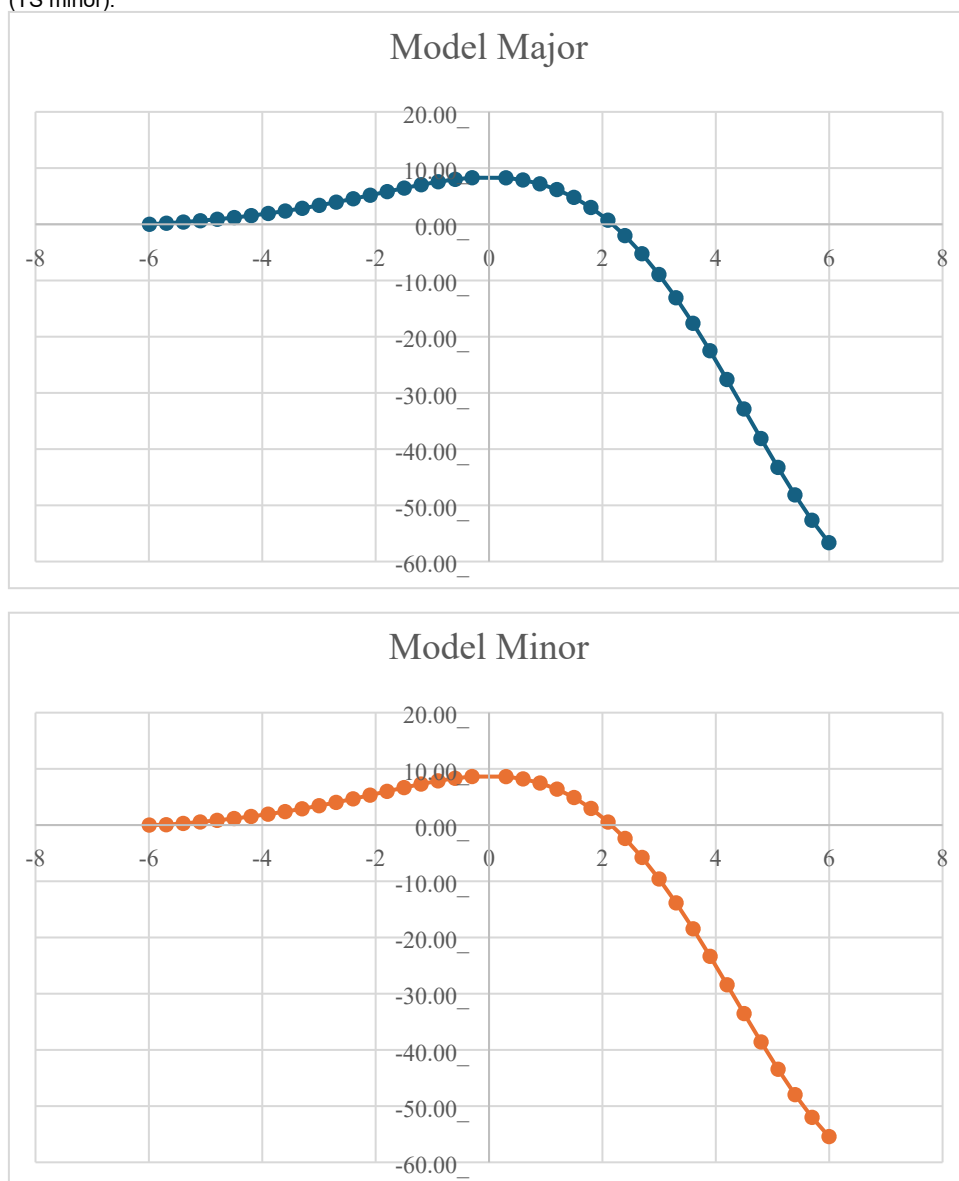
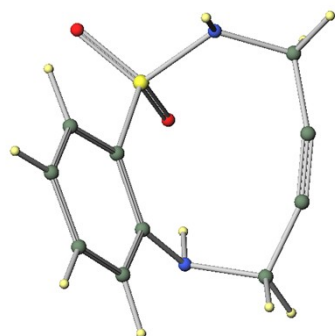
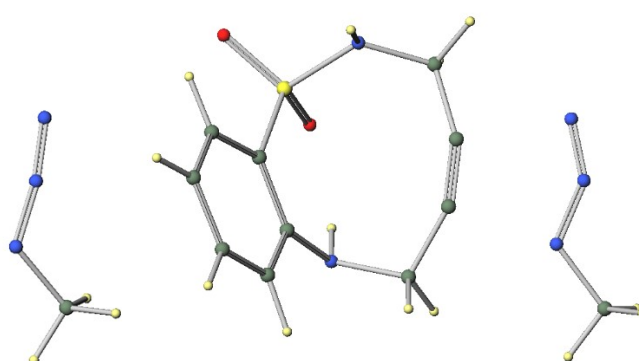


Figure S2. Comparison of potential energy profiles (IRC calculations) for the pathways leading to the major and minor products in the cycloaddition of ABSACN with methyl azide.

Model major IRC=+1

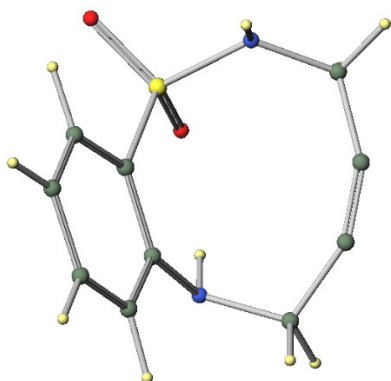


Energy -1248.68502  
Distance -5.98999

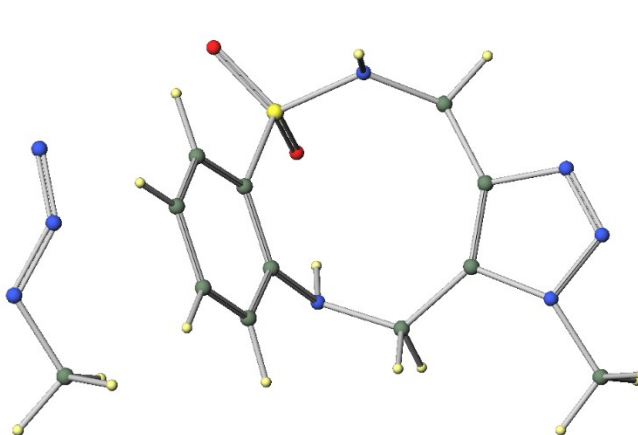


Energy -1248.67182  
Distance -0.29790

Model Major IRC=-1



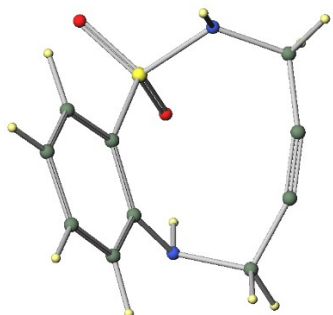
Energy -1248.67185  
Distance 0.29842



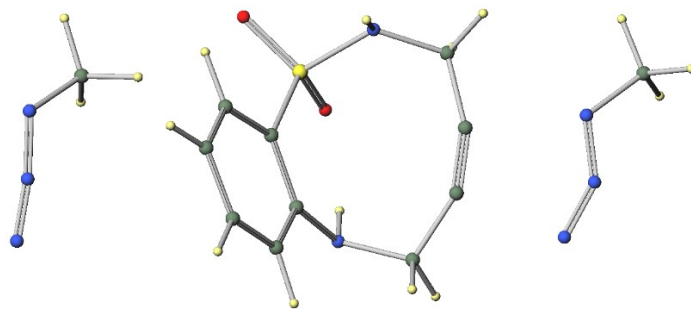
Energy -1248.77530  
Distance 5.99505

Figure S3. Results of Intrinsic Reaction Coordinate (IRC) analysis corresponding to TS major  
In the Model major IRC calculation, the IRC=+1 path proceeds from the transition state (Energy: -1248.67182, Distance: -0.29790) toward the reactant (Energy: -1248.68502, Distance: -5.98999). Conversely, the IRC=-1 path leads from the transition state (Energy: -1248.67185, Distance: -0.29842) toward the product (Energy -1248.77530, Distance 5.99505).

Model minor IRC=1

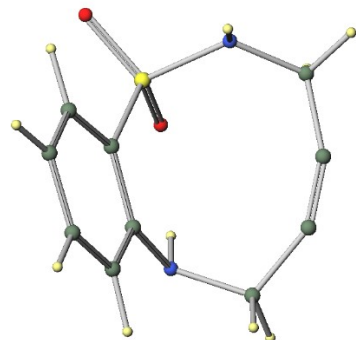


Energy -1248.68525  
Distance -5.99365

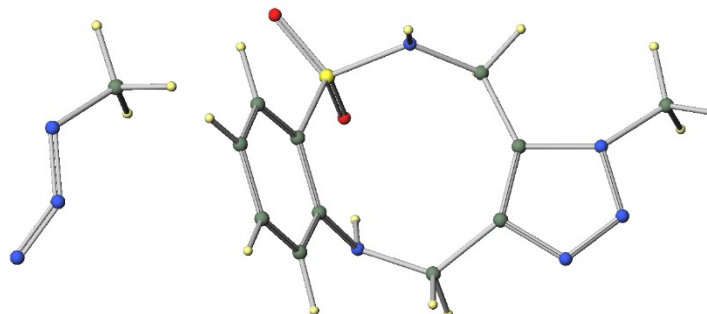


Energy -1248.67127  
Distance -0.29985

Model minor IRC=-1



Energy -1248.67129  
Distance 0.29987



Energy -1248.77334  
Distance 5.99717

Figure S4. Results of Intrinsic Reaction Coordinate (IRC) analysis corresponding to TS minor  
In the Model major IRC calculation, the IRC=+1 path proceeds from the transition state (Energy: -1248.67127, Distance: -0.29985) toward the reactant (Energy: -1248.68525, Distance: -5.99365). Conversely, the IRC=-1 path leads from the transition state (Energy: -1248.67129, Distance: -0.29987) toward the product (Energy -1248.77334, Distance 5.99717).

Reaction of the ABSACN and BnN<sub>3</sub> (Figure 3 & 4)

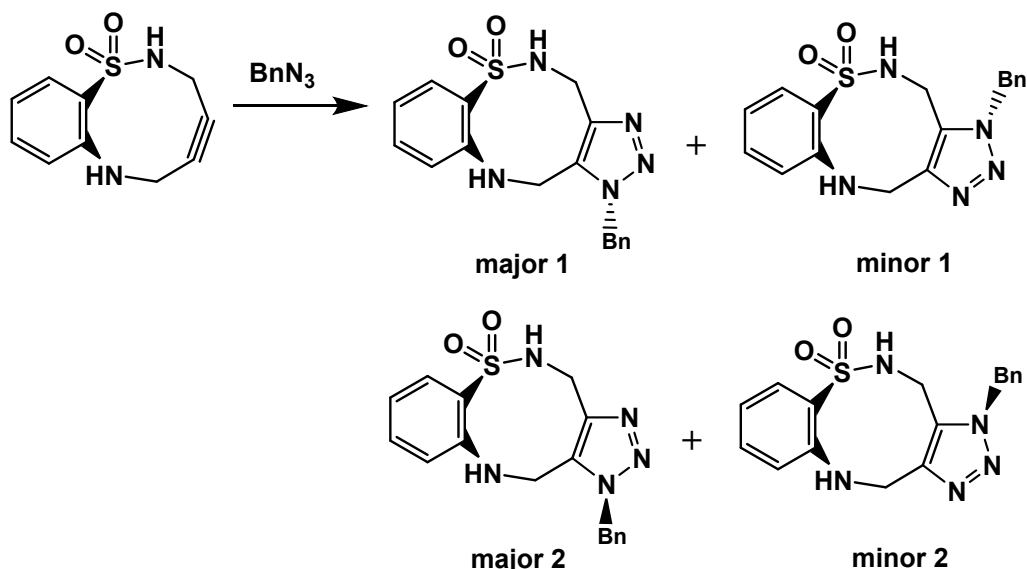


Figure S5. Formation of regioisomers in the strain-promoted cycloaddition of ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) and Benzyl azide.

Table S8. Total energies, imaginary frequencies, activation barriers, and reaction energies calculated at the B3LYP-D3(BJ)/6-31G(d) level for the ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) and Benzyl azide reaction.

| Molecule/State                            | Total Energy (E) | No. of Imaginary Frequencies | Imaginary Frequency (cm <sup>-1</sup> ) |
|-------------------------------------------|------------------|------------------------------|-----------------------------------------|
| ABSACN(R <sup>1</sup> =R <sup>2</sup> =H) | -1044.69247      | 0                            | -                                       |
| Benzyl azide (BnN <sub>3</sub> )          | -434.91764       | 0                            | -                                       |
| TS major type1                            | -1479.60254      | 1                            | -348                                    |
| TS major type2                            | -1479.60226      | 1                            | -320                                    |
| TS major type3                            | -1479.60017      | 1                            | -310                                    |
| TS minor type1                            | -1479.60270      | 1                            | -344                                    |
| TS minor type2                            | -1479.60190      | 1                            | -337                                    |
| TS minor type3                            | -1479.59935      | 1                            | -329                                    |
| GS2 major 1                               | -1479.75002      | 0                            | -                                       |
| GS2 major 2                               | -1479.75394      | 0                            | -                                       |
| GS2 minor 1                               | -1479.74798      | 0                            | -                                       |
| GS2 minor 2                               | -1479.75716      | 0                            | -                                       |

Reactions with ABSACN(R<sup>1</sup>=R<sup>2</sup>=H) and Benzyl azide

Total Reactant (E): E(ABSACN(R<sup>1</sup>=R<sup>2</sup>=H)) + E(Benzyl azide (BnN<sub>3</sub>)) = -1044.69247 a.u. + (-434.91764 a.u.) = -1479.61011 a.u. = -1479.61011 a.u. × 627.51 kcal/mol/a.u. = -928470.14 kcal/mol

Activation Barrier for TS major type1: (-1479.60254 a.u.) - (-1479.61011 a.u.) = 0.00757 a.u. = 0.00757 a.u. × 627.51 kcal/mol/a.u. = 4.750 kcal/mol

Activation Barrier for TS major type2: (-1479.60226 a.u.) - (-1479.61011 a.u.) = 0.00785 a.u. = 0.00785 a.u. × 627.51 kcal/mol/a.u. = 4.926 kcal/mol

Activation Barrier for TS major type3: (-1479.60017 a.u.) - (-1479.61011 a.u.) = 0.00994 a.u. = 0.00994 a.u. × 627.51 kcal/mol/a.u. = 6.237 kcal/mol

Activation Barrier for TS minor type1: (-1479.60270 a.u.) - (-1479.61011 a.u.) = 0.00741 a.u. = 0.00741 a.u. × 627.51 kcal/mol/a.u. = 4.649 kcal/mol

Activation Barrier for TS minor type2: (-1479.60190 a.u.) - (-1479.61011 a.u.) = 0.00821 a.u. = 0.00821 a.u. × 627.51 kcal/mol/a.u. = 5.159 kcal/mol

Activation Barrier for TS minor type3: (-1479.59935 a.u.) - (-1479.61011 a.u.) = 0.01076 a.u. = 0.01076 a.u. × 627.51 kcal/mol/a.u. = 6.752 kcal/mol

Reaction Energy for GS2 major 1: (-1479.75002 a.u.)-(-1479.61011 a.u.)=-0.13991 a.u.  
 =-0.13991 a.u.\*627.51 kcal/mol/a.u.=-87.79 kcal/mol  
 Reaction Energy for GS2 major 2: (-1479.75394 a.u.)-(-1479.61011 a.u.)=-0.14383 a.u.  
 =-0.14383 a.u.\*627.51 kcal/mol/a.u.=-90.25 kcal/mol  
 Reaction Energy for GS2 minor 1: (-1479.74798 a.u.)-(-1479.61011 a.u.)=-0.13787 a.u.  
 =-0.13787 a.u.\*627.51 kcal/mol/a.u.=-86.51 kcal/mol  
 Reaction Energy for GS2 minor 2: (-1479.75716 a.u.)-(-1479.61011 a.u.)=-0.14705 a.u.  
 =-0.14705 a.u.\*627.51 kcal/mol/a.u.=-92.28 kcal/mol

#### Entry A and Benzyl azide

**GS1 Entry A** ABSACN(R<sup>1</sup>=R<sup>2</sup>=H) : The optimized ground state structure (GS1) representing the total energy of the reactants (optimized ABSACN Entry A and optimized BnN<sub>3</sub>).

Table S9. Calculated thermodynamic quantities for the ABSACN(R<sup>1</sup>=R<sup>2</sup>=H) reactant model (GS1).

|                                                                  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                            | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                           | 0.889        | 1.481        | -11.07       | 2.981            | 4.968            | 42.096          |
| ROT.                                                             | 0.889        | 0.889        | -8.576       | 2.981            | 2.981            | 31.745          |
| VIB.                                                             | 127.014      | 127.014      | 116.772      | 43.919           | 43.919           | 34.35           |
| TOTAL                                                            | 128.791      | 129.384      | 97.127       | 49.881           | 51.868           | 108.191         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 6032.873 cal/mol |              |              |              |                  |                  |                 |

**GS1 BnN<sub>3</sub>**: The optimized ground state structure (GS1) representing the total energy of the reactants (optimized ABSACN Entry A and optimized BnN<sub>3</sub>).

Table S10. Calculated thermodynamic quantities for the Benzyl azide (BnN<sub>3</sub>) reactant model (GS1).

|                                                                  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                            | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                           | 0.889        | 1.481        | -10.615      | 2.981            | 4.968            | 40.569          |
| ROT.                                                             | 0.889        | 0.889        | -7.897       | 2.981            | 2.981            | 29.467          |
| VIB.                                                             | 86.783       | 86.783       | 79.662       | 24.894           | 24.894           | 23.884          |
| TOTAL                                                            | 88.56        | 89.153       | 61.15        | 30.855           | 32.842           | 93.92           |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 3515.684 cal/mol |              |              |              |                  |                  |                 |

**TS major type1**: The transition state structure (Type 1) leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>.

Table S11. Calculated thermodynamic quantities and energy components for the transition state structures leading to the major product (TS major type1) in the cycloaddition reaction of ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) with Benzyl azide.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.   | 0.889        | 0.889        | -9.644       | 2.981            | 2.981            | 35.325          |
| VIB.   | 216.649      | 216.649      | 192.535      | 78.224           | 78.224           | 80.88           |

|                                                                   |         |         |         |        |        |         |
|-------------------------------------------------------------------|---------|---------|---------|--------|--------|---------|
| TOTAL                                                             | 218.426 | 219.019 | 171.404 | 84.185 | 86.173 | 159.701 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11851.269 cal/mol |         |         |         |        |        |         |
| Imaginary Frequency: -348 cm <sup>-1</sup>                        |         |         |         |        |        |         |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6680.6495265446  
 TWO ELECTRON ENERGY = 2856.4314520769  
 NUCLEAR REPULSION ENERGY = 2344.6155308196  
**TOTAL ENERGY = -1479.6025436481**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2856.4314520769  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -8149.1133141787  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2344.6155308196  
 TOTAL POTENTIAL ENERGY = -2948.0663312821  
 TOTAL KINETIC ENERGY = 1468.4637876341  
 VIRIAL RATIO (V/T) = 2.0075853120

**TS major type2 : The transition state structure (Type 2) leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>.**

Table S12. Calculated thermodynamic quantities and energy components for the transition state structures leading to the major product (TS major type2) in the cycloaddition reaction of ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) with Benzyl azide.

|                                                                   | E(kcal/mol) | H(kcal/mol) | G(kcal/mol) | CV(cal/(mol·K)) | CP(cal/(mol·K)) | S(cal/(mol·K)) |
|-------------------------------------------------------------------|-------------|-------------|-------------|-----------------|-----------------|----------------|
| ELEC.                                                             | 0           | 0           | 0           | 0               | 0               | 0              |
| TRANS.                                                            | 0.889       | 1.481       | -11.487     | 2.981           | 4.968           | 43.495         |
| ROT.                                                              | 0.889       | 0.889       | -9.629      | 2.981           | 2.981           | 35.276         |
| VIB.                                                              | 216.572     | 216.572     | 192.314     | 78.377          | 78.377          | 81.362         |
| TOTAL                                                             | 218.350     | 218.942     | 171.199     | 84.339          | 86.326          | 160.133        |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11901.471 cal/mol |             |             |             |                 |                 |                |
| Imaginary Frequency: -320 cm <sup>-1</sup>                        |             |             |             |                 |                 |                |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6697.3154208224  
 TWO ELECTRON ENERGY = 2864.6994067666  
 NUCLEAR REPULSION ENERGY = 2353.0137511901  
**TOTAL ENERGY = -1479.6022628657**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2864.6994067666  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -8165.7648002675  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2353.0137511901  
 TOTAL POTENTIAL ENERGY = -2948.0516423108  
 TOTAL KINETIC ENERGY = 1468.4493794451  
 VIRIAL RATIO (V/T) = 2.0075950071

**TS major type3: The transition state structure (Type 3) leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>.** Imaginary Frequency: -310

Table S13. Calculated thermodynamic quantities and energy components for the transition state structures leading to the major product (TS major type3) in the cycloaddition reaction of ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) with Benzyl azide.

|  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--|--------------|--------------|--------------|------------------|------------------|-----------------|
|--|--------------|--------------|--------------|------------------|------------------|-----------------|

|                                                                   |         |         |         |        |        |         |
|-------------------------------------------------------------------|---------|---------|---------|--------|--------|---------|
| ELEC.                                                             | 0       | 0       | 0       | 0      | 0      | 0       |
| TRANS.                                                            | 0.889   | 1.481   | -11.487 | 2.981  | 4.968  | 43.495  |
| ROT.                                                              | 0.889   | 0.889   | -9.765  | 2.981  | 2.981  | 35.733  |
| VIB.                                                              | 216.667 | 216.667 | 193.461 | 78.174 | 78.174 | 77.831  |
| TOTAL                                                             | 218.444 | 219.037 | 172.21  | 84.136 | 86.123 | 157.059 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11804.217 cal/mol |         |         |         |        |        |         |
| Imaginary Frequency: -310 cm <sup>-1</sup>                        |         |         |         |        |        |         |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6516.1220220162  
 TWO ELECTRON ENERGY = 2774.1009476904  
 NUCLEAR REPULSION ENERGY = 2262.4209085253  
**TOTAL ENERGY = -1479.6001658005**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2774.1009476904  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -7984.5622864717  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2262.4209085253  
 TOTAL POTENTIAL ENERGY = -2948.0404302560  
 TOTAL KINETIC ENERGY = 1468.4402644555  
 VIRIAL RATIO (V/T) = 2.0075998334

**TS minor type1: The transition state structure (Type 1) leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>.**

Table S14. Calculated thermodynamic quantities and energy components for the transition state structures leading to the minor product (TS minor type1) in the cycloaddition reaction of ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) with Benzyl azide.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.65        | 2.981            | 2.981            | 35.346          |
| VIB.                                                              | 216.628      | 216.628      | 193.585      | 78.077           | 78.077           | 77.284          |
| TOTAL                                                             | 218.405      | 218.998      | 172.449      | 84.038           | 86.025           | 156.126         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11732.333 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -344 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6660.9904265150  
 TWO ELECTRON ENERGY = 2846.4934810127  
 NUCLEAR REPULSION ENERGY = 2334.8942499937  
**TOTAL ENERGY = -1479.6026955087**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2846.4934810127  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -8129.4566522879  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2334.8942499937  
 TOTAL POTENTIAL ENERGY = -2948.0689212816  
 TOTAL KINETIC ENERGY = 1468.4662257729

VIRIAL RATIO (V/T) = 2.0075837425

**TS minor type2: The transition state structure (Type 2) leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>.**

Table S15. Calculated thermodynamic quantities and energy components for the transition state structures leading to the minor product (TS minor type2) in the cycloaddition reaction of ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) with Benzyl azide.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.666       | 2.981            | 2.981            | 35.402          |
| VIB.                                                              | 216.685      | 216.685      | 192.961      | 78.148           | 78.148           | 79.573          |
| TOTAL                                                             | 218.463      | 219.055      | 171.807      | 84.109           | 86.097           | 158.469         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11815.357 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -337 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6668.7779367301  
 TWO ELECTRON ENERGY = 2850.2984654473  
 NUCLEAR REPULSION ENERGY = 2338.8775756056  
**TOTAL ENERGY = -1479.6018956772**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2850.2984654473  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -8137.2403840717  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2338.8775756056  
 TOTAL POTENTIAL ENERGY = -2948.0643430188  
 TOTAL KINETIC ENERGY = 1468.4624473416  
 VIRIAL RATIO (V/T) = 2.0075857904

**TS minor type3: The transition state structure (Type 3) leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>.**

Table S16. Calculated thermodynamic quantities and energy components for the transition state structures leading to the minor product (TS minor type3) in the cycloaddition reaction of ABSACN (R<sup>1</sup>=R<sup>2</sup>=H) with Benzyl azide.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.771       | 2.981            | 2.981            | 35.752          |
| VIB.                                                              | 216.584      | 216.584      | 192.044      | 78.272           | 78.272           | 82.307          |
| TOTAL                                                             | 218.361      | 218.954      | 170.786      | 84.234           | 86.221           | 161.554         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11926.250 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -329 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. The presence of a single imaginary frequency confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □□Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6508.6779365291  
 TWO ELECTRON ENERGY = 2770.3565400905  
 NUCLEAR REPULSION ENERGY = 2258.7220434814  
**TOTAL ENERGY = -1479.5993529572**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2770.3565400905  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -7977.1288927036  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2258.7220434814  
 TOTAL POTENTIAL ENERGY = -2948.0503091317  
 TOTAL KINETIC ENERGY = 1468.4509561745  
 VIRIAL RATIO (V/T) = 2.0075919436

**GS2 major type1: The ground state structure (GS2) of the major product (Type 1) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>**

Table S17. Calculated thermodynamic quantities and energy components for the major product (GS2 major type1).

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.574       | 2.981            | 2.981            | 35.093          |
| VIB.                                                              | 219.664      | 219.664      | 198.397      | 74.398           | 74.398           | 71.331          |
| TOTAL                                                             | 221.441      | 222.034      | 177.336      | 80.36            | 82.347           | 149.918         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 10786.781 cal/mol |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □□Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6826.3127660847  
 TWO ELECTRON ENERGY = 2928.5569070541  
 NUCLEAR REPULSION ENERGY = 2418.0058345766  
**TOTAL ENERGY = -1479.7500244540**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2928.5569070541  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -8295.0221262081  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2418.0058345766  
 TOTAL POTENTIAL ENERGY = -2948.4593845773  
 TOTAL KINETIC ENERGY = 1468.7093601234  
 VIRIAL RATIO (V/T) = 2.0075172561

**GS2 major type2: The ground state structure (GS2) of the major product (Type 2) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>**

Table S18. Calculated thermodynamic quantities and energy components for the major product (GS2 major type2).

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.482       | 2.981            | 2.981            | 34.782          |
| VIB.                                                              | 219.691      | 219.691      | 199.284      | 74.613           | 74.613           | 68.443          |
| TOTAL                                                             | 221.468      | 222.061      | 178.316      | 80.575           | 82.562           | 146.72          |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 10733.503 cal/mol |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6947.9157373566  
 TWO ELECTRON ENERGY = 2989.4236212030  
 NUCLEAR REPULSION ENERGY = 2478.7381749679  
**TOTAL ENERGY = -1479.7539411857**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2989.4236212030  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -8416.6348924536  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2478.7381749679  
 TOTAL POTENTIAL ENERGY = -2948.4730962827  
 TOTAL KINETIC ENERGY = 1468.7191550971  
 VIRIAL RATIO (V/T) = 2.0075132036

**GS2 minor type1: The ground state structure (GS2) of the minor product (Type 1) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>.**

Table S19. Calculated thermodynamic quantities and energy components for the major product (GS2 minor type1).

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.579       | 2.981            | 2.981            | 35.108          |
| VIB.                                                              | 219.72       | 219.72       | 199.073      | 74.503           | 74.503           | 69.249          |
| TOTAL                                                             | 221.497      | 222.09       | 178.007      | 80.465           | 82.452           | 147.852         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 10746.933 cal/mol |              |              |              |                  |                  |                 |

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)  
 WAVEFUNCTION NORMALIZATION = 1.0000000000  
 ONE ELECTRON ENERGY = -6828.4286924547  
 TWO ELECTRON ENERGY = 2929.6337087351  
 NUCLEAR REPULSION ENERGY = 2419.0470083866  
**TOTAL ENERGY = -1479.7479753331**  
 ELECTRON-ELECTRON POTENTIAL ENERGY = 2929.6337087351  
 NUCLEUS-ELECTRON POTENTIAL ENERGY = -8297.1318596655  
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2419.0470083866  
 TOTAL POTENTIAL ENERGY = -2948.4511425439  
 TOTAL KINETIC ENERGY = 1468.7031672108  
 VIRIAL RATIO (V/T) = 2.0075201091

**GS2 minor type2: The ground state structure (GS2) of the minor product (Type 2) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>.**

Table S20. Calculated thermodynamic quantities and energy components for the major product (GS2 minor type2).

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.   | 0.889        | 0.889        | -9.376       | 2.981            | 2.981            | 34.429          |
| VIB.   | 219.673      | 219.673      | 199.498      | 74.425           | 74.425           | 67.666          |
| TOTAL  | 221.45       | 222.042      | 178.635      | 80.387           | 82.374           | 145.591         |

VIB. THERMAL CORRECTION  $E(T)-E(0) = H(T)-H(0) = 10679.125 \text{ cal/mol}$

Note: All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

ENERGY COMPONENTS □ □ Value (Hartree)

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -7107.5010125063

TWO ELECTRON ENERGY = 3069.1902522379

NUCLEAR REPULSION ENERGY = 2558.5536019597

**TOTAL ENERGY = -1479.7571583086**

ELECTRON-ELECTRON POTENTIAL ENERGY = 3069.1902522379

NUCLEUS-ELECTRON POTENTIAL ENERGY = -8576.2442153172

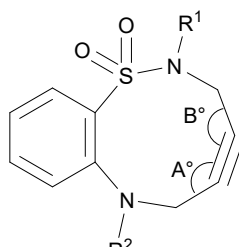
NUCLEUS-NUCLEUS POTENTIAL ENERGY = 2558.5536019597

TOTAL POTENTIAL ENERGY = -2948.5003611196

TOTAL KINETIC ENERGY = 1468.7432028110

VIRIAL RATIO (V/T) = 2.0074988980

Table S21/Table 2. **Summary of Reactivity, Frontier Orbital Energies, and Alkyne Bending Angles for N-substituted ABSACN Derivatives.**

| <div style="display: flex; align-items: center;">  <div style="margin-left: 20px;"> <p>Entry A: <math>R^1 = R^2 = H</math></p> <p>Entry B: <math>R^1 = \text{Boc}, R^2 = H</math></p> <p>Entry C: <math>R^1 = \text{Boc}, R^2 = \text{Ac}</math></p> <p>Entry D: <math>R^1 = H, R^2 = \text{Ac}</math></p> <p>Entry E: <math>R^1 = \text{Cbz}, R^2 = H</math></p> <p>Entry F: <math>R^1 = \text{Ts}, R^2 = H</math></p> </div> </div> |            |        |                    |            |            |                |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|--------|--------------------|------------|------------|----------------|
| Entry                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Reactivity | HOMO   | HOMO-LUMO gap (eV) | Angle (A°) | Angle (B°) | Alkyne bending |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 0.43       | -6.193 | 5.371              | 158.1      | 166.0      | 18.0           |
| B                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 1.50       | -6.123 | 5.301              | 155.1      | 162.0      | 21.5           |
| C                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 0.74       | -6.719 | 5.897              | 160.2      | 162.0      | 18.9           |
| D                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 0.27       | -6.797 | 5.972<br>(6.770)   | 162.9      | 164.4      | 16.4           |
| E                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 2.10       | -6.142 | 5.320              | 155.4      | 164.0      | 20.3           |
| F                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 1.30       | -6.234 | 5.412<br>(5.633)   | 157.4      | 167.0      | 17.8           |

The Reactivity values (relative rate constants) are experimentally determined. All HOMO and HOMO-LUMO gap energies are calculated in eV at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model with  $\text{CH}_2\text{Cl}_2$  as the solvent. The values in parentheses for Entry D and F are included for the purpose of electronic comparison between HOMO and LUMO. The alkyne bending angle (degree) is determined using the formula:  $180^\circ - (\text{Angle A} + \text{Angle B}) / 2$ . Benzyl azide, solvent= $\text{CH}_2\text{Cl}_2$ : orbital energy HOMO -6.6804 eV, LUMO -0.8218 eV

Entry D (solvent= $\text{CH}_2\text{Cl}_2$ : orbital energy HOMO -6.7974 eV, LUMO 0.0898 eV)

Entry F (solvent= $\text{CH}_2\text{Cl}_2$ : orbital energy HOMO -6.2341 eV, LUMO -1.0476 eV)

**Entry A** ABSACN ( $R^1 = R^2 = H$ ): The optimized structure of ABSACN Entry A under  $\text{CH}_2\text{Cl}_2$  solvent conditions.

Table S22. Calculated thermodynamic quantities and frontier orbital energy for the ABSACN Entry A ( $R^1 = R^2 = H$ ) under PCM/ $\text{CH}_2\text{Cl}_2$  solvent conditions.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.07       | 2.981            | 4.968            | 42.096          |
| ROT.   | 0.889        | 0.889        | -8.576       | 2.981            | 2.981            | 31.745          |
| VIB.   | 126.868      | 126.868      | 116.509      | 44.149           | 44.149           | 34.745          |
| TOTAL  | 128.646      | 129.238      | 96.864       | 50.111           | 52.098           | 108.586         |

VIB. THERMAL CORRECTION  $E(T)-E(0) = H(T)-H(0) = 6082.743 \text{ cal/mol}$

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= $\text{CH}_2\text{Cl}_2$ ). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The HOMO energy is -6.1933 eV.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT =  $\langle \text{PSI} | H(0) + V/2 | \text{PSI} \rangle = -1044.7054835993 \text{ a.u.}$   
INTERNAL ENERGY IN SOLVENT =  $\langle \text{PSI} | H(0) | \text{PSI} \rangle = -1044.6904587527 \text{ a.u.}$   
DELTA INTERNAL ENERGY =  $\langle D\text{-PSI} | H(0) | D\text{-PSI} \rangle = 0.0000000000 \text{ a.u.}$   
ELECTROSTATIC INTERACTION = -0.0150248466 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0150248466 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1044.7054835993 a.u.**

FREE ENERGY IN SOLVENT = -655562.66 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -655553.23 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -9.43 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -9.43 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -655562.66 kcal/mol**

**Entry B ABSACN ( $R^1 = \text{Boc}$ ,  $R^2 = \text{H}$ ): The optimized structure of ABSACN Entry B under  $\text{CH}_2\text{Cl}_2$  solvent conditions.**

Table S23. Calculated thermodynamic quantities and frontier orbital energy for the ABSACN Entry B ( $R^1 = \text{Boc}$ ,  $R^2 = \text{H}$ ) under PCM/ $\text{CH}_2\text{Cl}_2$  solvent conditions.

|                                                                             | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-----------------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                                       | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                                      | 0.889        | 1.481        | -11.4        | 2.981            | 4.968            | 43.204          |
| ROT.                                                                        | 0.889        | 0.889        | -9.241       | 2.981            | 2.981            | 33.976          |
| VIB.                                                                        | 212.214      | 212.214      | 191.385      | 74.965           | 74.965           | 69.859          |
| TOTAL                                                                       | 213.991      | 214.583      | 170.744      | 80.927           | 82.914           | 147.039         |
| VIB. THERMAL CORRECTION $E(T)-E(0) = H(T)-H(0) = 11162.631 \text{ cal/mol}$ |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= $\text{CH}_2\text{Cl}_2$ ). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The HOMO energy is -6.1226 eV.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT =  $\langle \text{PSI} | H(0) + V/2 | \text{PSI} \rangle = -1390.3665107822 \text{ a.u.}$   
INTERNAL ENERGY IN SOLVENT =  $\langle \text{PSI} | H(0) | \text{PSI} \rangle = -1390.3523902516 \text{ a.u.}$   
DELTA INTERNAL ENERGY =  $\langle D\text{-PSI} | H(0) | D\text{-PSI} \rangle = 0.0000000000 \text{ a.u.}$   
ELECTROSTATIC INTERACTION = -0.0141205306 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0141205306 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1390.3665107822 a.u.**

FREE ENERGY IN SOLVENT = -872468.25 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -872459.39 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -8.86 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol

TOTAL INTERACTION = -8.86 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -872468.25 kcal/mol**

**Entry C** ABSACN (R<sup>1</sup>= Boc, R<sup>2</sup> = Ac) : **The optimized structure of ABSACN Entry C under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.**

Table S24. Calculated thermodynamic quantities and frontier orbital energy for the ABSACN Entry C (R<sup>1</sup>=Boc, R<sup>2</sup>=Ac) under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.509      | 2.981            | 4.968            | 43.57           |
| ROT.   | 0.889        | 0.889        | -9.477       | 2.981            | 2.981            | 34.766          |
| VIB.   | 237.638      | 237.638      | 212.133      | 87.205           | 87.205           | 85.544          |
| TOTAL  | 239.415      | 240.008      | 191.147      | 93.167           | 95.154           | 163.88          |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The HOMO energy is -6.7185 eV.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1542.9563293273 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1542.9358607611 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0204685662 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0204685662 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1542.9563293273 a.u.**

FREE ENERGY IN SOLVENT = -968219.82 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -968206.97 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -12.84 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -12.84 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -968219.82 kcal/mol**

**Entry D** ABSACN (R<sup>1</sup>= H, R<sup>2</sup> = Ac) : **The optimized structure of ABSACN Entry D under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.**

Table S25. Calculated thermodynamic quantities and frontier orbital energy for the ABSACN Entry D (R<sup>1</sup>=H, R<sup>2</sup>=Ac) under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                            | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                           | 0.889        | 1.481        | -11.224      | 2.981            | 4.968            | 42.612          |
| ROT.                                                             | 0.889        | 0.889        | -8.874       | 2.981            | 2.981            | 32.744          |
| VIB.                                                             | 152.546      | 152.546      | 137.994      | 55.95            | 55.95            | 48.808          |
| TOTAL                                                            | 154.324      | 154.916      | 117.897      | 61.912           | 63.899           | 124.164         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 8146.582 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The HOMO energy is -6.7974 eV, and the

LUMO energy is 0.0898 eV.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT =  $\langle \text{PSI} | \text{H}(0) + V/2 | \text{PSI} \rangle$  = -1197.2966408345 a.u.  
INTERNAL ENERGY IN SOLVENT =  $\langle \text{PSI} | \text{H}(0) | \text{PSI} \rangle$  = -1197.2751774128 a.u.  
DELTA INTERNAL ENERGY =  $\langle \text{D-PSI} | \text{H}(0) | \text{D-PSI} \rangle$  = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0214634216 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0214634216 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1197.2966408345 a.u.**

FREE ENERGY IN SOLVENT = -751315.07 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -751301.60 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -13.47 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -13.47 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -751315.07 kcal/mol**

**Entry E** ABSACN ( $R^1 = \text{Cbz}$ ,  $R^2 = \text{H}$ ) : The optimized structure of ABSACN Entry E under  $\text{CH}_2\text{Cl}_2$  solvent conditions.

Table S26. Calculated thermodynamic quantities and frontier orbital energy for the ABSACN Entry E ( $R^1 = \text{Cbz}$ ,  $R^2 = \text{H}$ ) under PCM/ $\text{CH}_2\text{Cl}_2$  solvent conditions.

|                                                                                 | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|---------------------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                                           | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                                          | 0.889        | 1.481        | -11.489      | 2.981            | 4.968            | 43.503          |
| ROT.                                                                            | 0.889        | 0.889        | -9.573       | 2.981            | 2.981            | 35.089          |
| VIB.                                                                            | 210.727      | 210.727      | 188.697      | 76.643           | 76.643           | 73.888          |
| TOTAL                                                                           | 212.505      | 213.097      | 167.635      | 82.604           | 84.591           | 152.48          |
| VIB. THERMAL CORRECTION $E(T) - E(0) = H(T) - H(0) = 11359.987 \text{ cal/mol}$ |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= $\text{CH}_2\text{Cl}_2$ ). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The HOMO energy is -6.1416 eV.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT =  $\langle \text{PSI} | \text{H}(0) + V/2 | \text{PSI} \rangle$  = -1503.4164803067 a.u.  
INTERNAL ENERGY IN SOLVENT =  $\langle \text{PSI} | \text{H}(0) | \text{PSI} \rangle$  = -1503.4005544703 a.u.  
DELTA INTERNAL ENERGY =  $\langle \text{D-PSI} | \text{H}(0) | \text{D-PSI} \rangle$  = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0159258363 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0159258363 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1503.4164803067 a.u.**

FREE ENERGY IN SOLVENT = -943408.19 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -943398.19 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -9.99 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -9.99 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -943408.19 kcal/mol**

**Entry F** ABSACN ( $R^1 = \text{Ts}$ ,  $R^2 = \text{H}$ ) : The optimized structure of ABSACN Entry F under  $\text{CH}_2\text{Cl}_2$  solvent

**conditions.**

Table S27. Calculated thermodynamic quantities and frontier orbital energy for the ABSACN Entry E (R<sup>1</sup>=Ts, R<sup>2</sup>=H) under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.538      | 2.981            | 4.968            | 43.666          |
| ROT.                                                              | 0.889        | 0.889        | -9.583       | 2.981            | 2.981            | 35.122          |
| VIB.                                                              | 207.495      | 207.495      | 184.099      | 80.783           | 80.783           | 78.471          |
| TOTAL                                                             | 209.273      | 209.865      | 162.978      | 86.745           | 88.732           | 157.259         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 12140.795 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The HOMO energy is -6.2341 eV, and the LUMO energy is -1.04760 eV.

**RESULTS OF PCM CALCULATION**

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1863.3883458528 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1863.3715713658 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0167744870 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0167744870 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1863.3883458528 a.u.**

FREE ENERGY IN SOLVENT = -1169293.97 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -1169283.44 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -10.53 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -10.53 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1169293.97 kcal/mol**

**Benzyl azide □ solvent=CH<sub>2</sub>Cl<sub>2</sub>: The optimized structure of Benzyl azide under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.**

Table S28. Calculated thermodynamic quantities and frontier orbital energy for the Benzyl azide (BnN<sub>3</sub>) under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                            | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                           | 0.889        | 1.481        | -10.615      | 2.981            | 4.968            | 40.569          |
| ROT.                                                             | 0.889        | 0.889        | -7.896       | 2.981            | 2.981            | 29.465          |
| VIB.                                                             | 86.747       | 86.747       | 80.012       | 24.914           | 24.914           | 22.589          |
| TOTAL                                                            | 88.525       | 89.117       | 61.502       | 30.875           | 32.862           | 92.624          |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 3490.118 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The HOMO energy is -6.6804 eV, and the LUMO energy is -0.8218 eV.

**RESULTS OF PCM CALCULATION**

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -434.9230101714 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -434.9170131476 a.u.

DELTA INTERNAL ENERGY =  $\langle D-PSI | H(0) | D-PSI \rangle$  = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0059970238 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0059970238 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -434.9230101714 a.u.**

FREE ENERGY IN SOLVENT = -272918.34 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -272914.58 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -3.76 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -3.76 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -272918.34 kcal/mol**

#### Transition State Energetics for Substituted ABSACN Derivatives (Table 4)

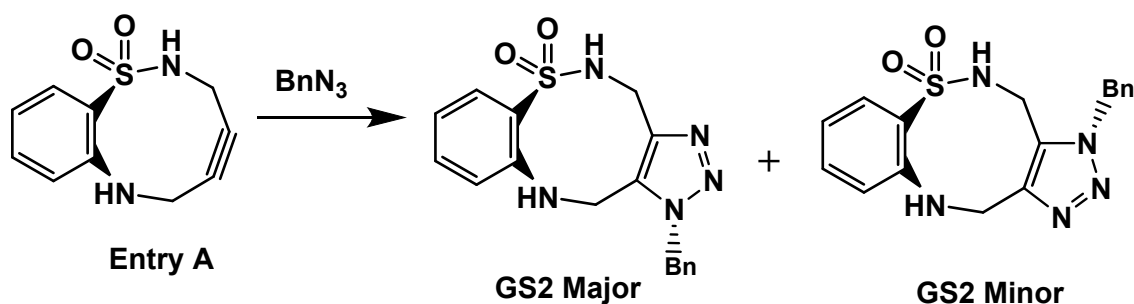


Figure S6. Formation of regioisomers in the strain-promoted cycloaddition of ABSACN Entry A ( $R^1=R^2=H$ ) and Benzyl azide with PCM calculations applied.

Table S29. Calculated Free Energies for the Cycloaddition Reaction Pathway of ABSACN Entry A with Benzyl Azide in  $\text{CH}_2\text{Cl}_2$  solvent.

| Structure | Imaginary Frequency ( $\text{cm}^{-1}$ ) | Total Free Energy in Solvent (au) | Total Free Energy in Solvent (kcal/mol) (Relative to GS1) |
|-----------|------------------------------------------|-----------------------------------|-----------------------------------------------------------|
| GS1       | N/A                                      | -1479.62849                       | 0                                                         |
| TS major1 | -360                                     | -1479.61953                       | 5.62234                                                   |
| TS major2 | -315                                     | -1479.61734                       | 6.99910                                                   |
| TS major3 | -329                                     | -1479.61717                       | 7.10755                                                   |
| TS minor1 | -360                                     | -1479.61871                       | 6.13757                                                   |
| TS minor2 | -366                                     | -1479.61803                       | 6.56823                                                   |
| TS minor3 | -350                                     | -1479.61475                       | 8.62675                                                   |
| GS2 Major | N/A                                      | -1479.76905                       | -88.19973                                                 |
| GS2 Minor | N/A                                      | -1479.76729                       | -87.09711                                                 |

Note: All free energies were calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= $\text{CH}_2\text{Cl}_2$ ) at 298.15 K and 1.0 atm. Energies are reported as Total Free Energy in Solvent (au) and relative free energies (kcal/mol) with respect to the ground state of the reactants (GS1). The single imaginary frequency ( $\text{cm}^{-1}$ ) confirms the nature of the transition states (TS). GS1 (Reactants) Total Free Energy in Solvent: -1479.62849 au.

#### GS1

Entry A solvent= $\text{CH}_2\text{Cl}_2$  + Benzyl azide  $\square$  solvent= $\text{CH}_2\text{Cl}_2$

The optimized ground state structure (GS1) representing the total energy of the reactants (each optimized ABSACN and optimized BnN<sub>3</sub>) under dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solvent conditions.

**Entry A TS major1: The transition state structure leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S30. Calculated thermodynamic quantities for TS major1 in the cycloaddition reaction of ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.647       | 2.981            | 2.981            | 35.339          |
| VIB.                                                              | 216.66       | 216.66       | 193.597      | 78.141           | 78.141           | 77.354          |
| TOTAL                                                             | 218.438      | 219.03       | 172.463      | 84.102           | 86.09            | 156.188         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11738.389 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -360 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-360 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

**RESULTS OF PCM CALCULATION**

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1479.6195340169 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1479.5997256380 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0198083789 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0198083789 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1479.6195340169 a.u.**

FREE ENERGY IN SOLVENT = -928475.37 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -928462.94 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -12.43 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -12.43 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -928475.37 kcal/mol**

**Entry A TS major2: The transition state structure leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S31. Calculated thermodynamic quantities for TS major2 in the cycloaddition reaction of ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.   | 0.889        | 0.889        | -9.751       | 2.981            | 2.981            | 35.685          |
| VIB.   | 216.751      | 216.751      | 193.594      | 78.09            | 78.09            | 77.668          |
| TOTAL  | 218.528      | 219.121      | 172.356      | 84.051           | 86.039           | 156.848         |

|                                                 |                   |
|-------------------------------------------------|-------------------|
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = | 11769.134 cal/mol |
| Imaginary Frequency: -315 cm <sup>-1</sup>      |                   |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-315 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1479.6173408154 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1479.5971028530 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0202379624 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0202379624 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1479.6173408154 a.u.</b> |

|                                       |          |                            |
|---------------------------------------|----------|----------------------------|
| FREE ENERGY IN SOLVENT                | =        | -928474.00 kcal/mol        |
| INTERNAL ENERGY IN SOLVENT            | =        | -928461.30 kcal/mol        |
| DELTA INTERNAL ENERGY                 | =        | 0.00 kcal/mol              |
| ELECTROSTATIC INTERACTION             | =        | -12.70 kcal/mol            |
| PIEROTTI CAVITATION ENERGY            | =        | 0.00 kcal/mol              |
| DISPERSION FREE ENERGY                | =        | 0.00 kcal/mol              |
| REPULSION FREE ENERGY                 | =        | 0.00 kcal/mol              |
| TOTAL INTERACTION                     | =        | -12.70 kcal/mol            |
| <b>TOTAL FREE ENERGY IN SOLVENT =</b> | <b>=</b> | <b>-928474.00 kcal/mol</b> |

**Entry A TS major3: The transition state structure leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S32. Calculated thermodynamic quantities for TS major3 in the cycloaddition reaction of ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.759       | 2.981            | 2.981            | 35.713          |
| VIB.                                                              | 216.689      | 216.689      | 193.266      | 78.178           | 78.178           | 78.561          |
| TOTAL                                                             | 218.466      | 219.059      | 172.02       | 84.14            | 86.127           | \$157.769\$     |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11803.755 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -329 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-329 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1479.6171671784 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1479.5971469542 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0200202242 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0200202242 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1479.6171671784 a.u.</b> |

|                                     |          |                            |
|-------------------------------------|----------|----------------------------|
| FREE ENERGY IN SOLVENT              | =        | -928473.89 kcal/mol        |
| INTERNAL ENERGY IN SOLVENT          | =        | -928461.33 kcal/mol        |
| DELTA INTERNAL ENERGY               | =        | 0.00 kcal/mol              |
| ELECTROSTATIC INTERACTION           | =        | -12.56 kcal/mol            |
| PIEROTTI CAVITATION ENERGY          | =        | 0.00 kcal/mol              |
| DISPERSION FREE ENERGY              | =        | 0.00 kcal/mol              |
| REPULSION FREE ENERGY               | =        | 0.00 kcal/mol              |
| TOTAL INTERACTION                   | =        | -12.56 kcal/mol            |
| <b>TOTAL FREE ENERGY IN SOLVENT</b> | <b>=</b> | <b>-928473.89 kcal/mol</b> |

**Entry A TS minor1: The transition state structure leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S33. Calculated thermodynamic quantities for TS minor1 in the cycloaddition reaction of ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.668       | 2.981            | 2.981            | 35.409          |
| VIB.                                                              | 216.508      | 216.508      | 192.881      | 78.23            | 78.23            | 79.244          |
| TOTAL                                                             | 218.285      | 218.878      | 171.726      | 84.192           | 86.179           | 158.148         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11789.874 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -360 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-360 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

**RESULTS OF PCM CALCULATION**

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1479.6187129432 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1479.5996295799 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0190833633 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0190833633 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1479.6187129432 a.u.</b> |

|                                     |          |                            |
|-------------------------------------|----------|----------------------------|
| FREE ENERGY IN SOLVENT              | =        | -928474.86 kcal/mol        |
| INTERNAL ENERGY IN SOLVENT          | =        | -928462.88 kcal/mol        |
| DELTA INTERNAL ENERGY               | =        | 0.00 kcal/mol              |
| ELECTROSTATIC INTERACTION           | =        | -11.97 kcal/mol            |
| PIEROTTI CAVITATION ENERGY          | =        | 0.00 kcal/mol              |
| DISPERSION FREE ENERGY              | =        | 0.00 kcal/mol              |
| REPULSION FREE ENERGY               | =        | 0.00 kcal/mol              |
| TOTAL INTERACTION                   | =        | -11.97 kcal/mol            |
| <b>TOTAL FREE ENERGY IN SOLVENT</b> | <b>=</b> | <b>-928474.86 kcal/mol</b> |

**Entry A TS minor2: The transition state structure leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S34. Calculated thermodynamic quantities for TS minor2 in the cycloaddition reaction of ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|       | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC. | 0            | 0            | 0            | 0                | 0                | 0               |

|                                                                   |         |         |         |        |        |         |
|-------------------------------------------------------------------|---------|---------|---------|--------|--------|---------|
| TRANS.                                                            | 0.889   | 1.481   | -11.487 | 2.981  | 4.968  | 43.495  |
| ROT.                                                              | 0.889   | 0.889   | -9.622  | 2.981  | 2.981  | 35.252  |
| VIB.                                                              | 216.301 | 216.301 | 192.254 | 78.655 | 78.655 | 80.656  |
| TOTAL                                                             | 218.079 | 218.671 | 171.145 | 84.617 | 86.604 | 159.403 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11925.534 cal/mol |         |         |         |        |        |         |
| Imaginary Frequency: -366 cm <sup>-1</sup>                        |         |         |         |        |        |         |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-366 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1479.6180266313 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1479.5988166708 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0192099604 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0192099604 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1479.6180266313 a.u.**

FREE ENERGY IN SOLVENT = -928474.43 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -928462.37 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -12.05 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -12.05 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -928474.43 kcal/mol**

#### Entry A TS minor3: The transition state structure leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.

Table S35. Calculated thermodynamic quantities for TS minor3 in the cycloaddition reaction of ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.743       | 2.981            | 2.981            | 35.659          |
| VIB.                                                              | 216.399      | 216.399      | 192.066      | 78.462           | 78.462           | 81.612          |
| TOTAL                                                             | 218.176      | 218.769      | 170.836      | 84.423           | 86.411           | 160.766         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 11925.430 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -350 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-350 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1479.6147461819 a.u.

INTERNAL ENERGY IN SOLVENT =  $\langle \text{PSI} | \text{H}(0) | \text{PSI} \rangle$  = -1479.5944736437 a.u.  
 DELTA INTERNAL ENERGY =  $\langle \text{D-PSI} | \text{H}(0) | \text{D-PSI} \rangle$  = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0202725381 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0202725381 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1479.6147461819 a.u.**

FREE ENERGY IN SOLVENT = -928472.37 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -928459.65 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -12.72 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -12.72 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -928472.37 kcal/mol**

**Entry A GS2 Major product: The ground state structure (GS2) of the major product obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent.**

Table S36. Calculated thermodynamic quantities for the Major Product (GS2 Major) in the cycloaddition reaction of ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.578       | 2.981            | 2.981            | 35.106          |
| VIB.                                                              | 219.675      | 219.675      | 198.87       | 74.461           | 74.461           | 69.779          |
| TOTAL                                                             | 221.452      | 222.045      | 177.805      | 80.423           | 82.41            | 148.38          |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 10750.711 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT =  $\langle \text{PSI} | \text{H}(0) + V/2 | \text{PSI} \rangle$  = -1479.7690488618 a.u.  
 INTERNAL ENERGY IN SOLVENT =  $\langle \text{PSI} | \text{H}(0) | \text{PSI} \rangle$  = -1479.7467680179 a.u.  
 DELTA INTERNAL ENERGY =  $\langle \text{D-PSI} | \text{H}(0) | \text{D-PSI} \rangle$  = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0222808440 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0222808440 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1479.7690488618 a.u.**

FREE ENERGY IN SOLVENT = -928569.20 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -928555.22 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -13.98 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -13.98 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -928569.20 kcal/mol**

**Entry A GS2 Minor product: The ground state structure (GS2) of the minor product obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent.**

Table S37. Calculated thermodynamic quantities for the Minor Product (GS2 Minor) in the cycloaddition reaction of

ABSACN Entry A with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.487      | 2.981            | 4.968            | 43.495          |
| ROT.                                                              | 0.889        | 0.889        | -9.583       | 2.981            | 2.981            | 35.121          |
| VIB.                                                              | 219.824      | 219.824      | 199.347      | 74.405           | 74.405           | 68.681          |
| TOTAL                                                             | 221.602      | 222.194      | 178.277      | 80.366           | 82.354           | 147.298         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 10710.472 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1479.7672917414 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1479.7449685617 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0223231797 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0223231797 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1479.7672917414 a.u.</b> |

|                                       |          |                            |
|---------------------------------------|----------|----------------------------|
| FREE ENERGY IN SOLVENT                | =        | -928568.09 kcal/mol        |
| INTERNAL ENERGY IN SOLVENT            | =        | -928554.09 kcal/mol        |
| DELTA INTERNAL ENERGY                 | =        | 0.00 kcal/mol              |
| ELECTROSTATIC INTERACTION             | =        | -14.01 kcal/mol            |
| PIEROTTI CAVITATION ENERGY            | =        | 0.00 kcal/mol              |
| DISPERSION FREE ENERGY                | =        | 0.00 kcal/mol              |
| REPULSION FREE ENERGY                 | =        | 0.00 kcal/mol              |
| TOTAL INTERACTION                     | =        | -14.01 kcal/mol            |
| <b>TOTAL FREE ENERGY IN SOLVENT =</b> | <b>=</b> | <b>-928568.09 kcal/mol</b> |

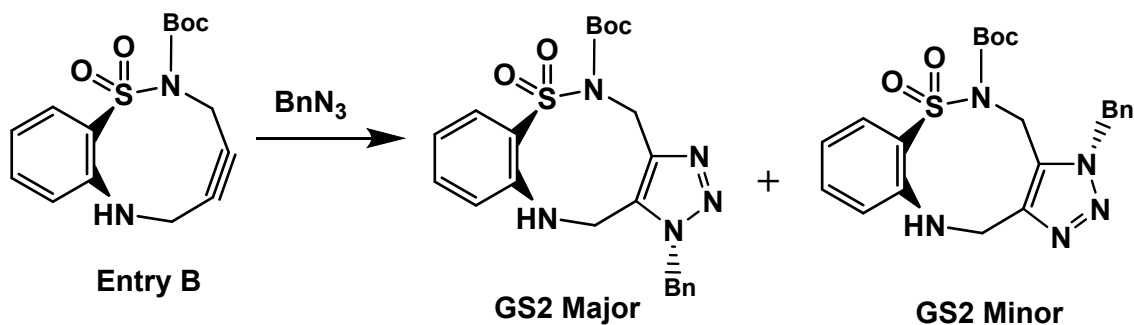


Figure S7. Formation of regioisomers in the strain-promoted cycloaddition of ABSACN Entry B (R<sup>1</sup>=Boc, R<sup>2</sup>=H) and Benzyl azide with PCM calculations applied.

Table S38. Calculated Free Energies for the Cycloaddition Reaction Pathway of ABSACN Entry B with Benzyl Azide in CH<sub>2</sub>Cl<sub>2</sub> solvent.

| Structure | Imaginary Frequency (cm <sup>-1</sup> ) | Total Free Energy in Solvent (au) | Total Free Energy in Solvent (kcal/mol) (Relative to GS1) |
|-----------|-----------------------------------------|-----------------------------------|-----------------------------------------------------------|
| GS1       | N/A                                     | -1825.28952                       | 0                                                         |
| TS major1 | -359                                    | -1825.28295                       | 4.12502                                                   |

|           |      |             |           |
|-----------|------|-------------|-----------|
| TS major2 | -334 | -1825.28107 | 5.30179   |
| TS major3 | -321 | -1825.27988 | 6.04980   |
| TS minor1 | -358 | -1825.28228 | 4.54472   |
| TS minor2 | -345 | -1825.28048 | 5.67329   |
| TS minor3 | -357 | -1825.28183 | 4.82896   |
| GS2 Major | N/A  | -1825.42984 | -88.05321 |
| GS2 Minor | N/A  | -1825.43298 | -90.02399 |

Note: All free energies were calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>) at 298.15 K and 1.0 atm. Energies are reported as Total Free Energy in Solvent (au) and relative free energies (kcal/mol) with respect to the ground state of the reactants (GS1). The single imaginary frequency (cm<sup>-1</sup>) confirms the nature of the transition states (TS). GS1 (Reactants) Total Free Energy in Solvent: -1825.28952 au.

#### GS1

##### Entry B solvent=CH<sub>2</sub>Cl<sub>2</sub> + Benzyl azide → solvent=CH<sub>2</sub>Cl<sub>2</sub>

The optimized ground state structure (GS1) representing the total energy of the reactants (each optimized ABSACN and optimized BnN<sub>3</sub>) under dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solvent conditions.

##### TS major1: The transition state structure leading to the major product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.

Table S39. Calculated thermodynamic quantities for TS major1 in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                 | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K))  | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------|--------------|--------------|--------------|-------------------|------------------|-----------------|
| ELEC.                                           | 0            | 0            | 0            | 0                 | 0                | 0               |
| TRANS.                                          | 0.889        | 1.481        | -11.707      | 2.981             | 4.968            | 44.235          |
| ROT.                                            | 0.889        | 0.889        | -10.04       | 2.981             | 2.981            | 36.656          |
| VIB.                                            | 301.746      | 301.746      | 268.26       | 109.116           | 109.116          | 112.311         |
| TOTAL                                           | 303.523      | 304.116      | 246.513      | 115.077           | 117.064          | 193.202         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = |              |              |              | 16862.806 cal/mol |                  |                 |
| Imaginary Frequency: -359 cm <sup>-1</sup>      |              |              |              |                   |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-359 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1825.2829473196 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1825.2639510386 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0189962810 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0189962810 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1825.2829473196 a.u.</b> |

|                            |   |                      |
|----------------------------|---|----------------------|
| FREE ENERGY IN SOLVENT     | = | -1145382.46 kcal/mol |
| INTERNAL ENERGY IN SOLVENT | = | -1145370.54 kcal/mol |
| DELTA INTERNAL ENERGY      | = | 0.00 kcal/mol        |
| ELECTROSTATIC INTERACTION  | = | -11.92 kcal/mol      |
| PIEROTTI CAVITATION ENERGY | = | 0.00 kcal/mol        |
| DISPERSION FREE ENERGY     | = | 0.00 kcal/mol        |

REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -11.92 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1145382.46 kcal/mol**

**TS major2: The transition state structure leading to the major product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S40. Calculated thermodynamic quantities for TS major2 in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.707      | 2.981            | 4.968            | 44.235          |
| ROT.                                                              | 0.889        | 0.889        | -10.039      | 2.981            | 2.981            | 36.653          |
| VIB.                                                              | 301.536      | 301.536      | 267.427      | 109.157          | 109.157          | 114.401         |
| TOTAL                                                             | 303.313      | 303.906      | 245.68       | 115.119          | 117.106          | 195.289         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 16917.941 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -334 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-334 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

**RESULTS OF PCM CALCULATION**

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1825.2810720248 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1825.2630797845 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0179922403 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0179922403 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1825.2810720248 a.u.**

FREE ENERGY IN SOLVENT = -1145381.29 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -1145370.00 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -11.29 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -11.29 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1145381.29 kcal/mol**

**TS major3: The transition state structure leading to the major product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S41. Calculated thermodynamic quantities for TS major3 in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.707      | 2.981            | 4.968            | 44.235          |
| ROT.   | 0.889        | 0.889        | -10.179      | 2.981            | 2.981            | 37.123          |
| VIB.   | 301.73       | 301.73       | 267.913      | 108.99           | 108.99           | 113.42          |
| TOTAL  | 303.507      | 304.1        | 246.027      | 114.952          | 116.939          | 194.778         |

|                                                 |                   |
|-------------------------------------------------|-------------------|
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = | 16880.177 cal/mol |
| Imaginary Frequency: -321 cm <sup>-1</sup>      |                   |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-321 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1825.2798799846 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1825.2616892279 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0181907567 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0181907567 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1825.2798799846 a.u.</b> |

|                                       |          |                             |
|---------------------------------------|----------|-----------------------------|
| FREE ENERGY IN SOLVENT                | =        | -1145380.54 kcal/mol        |
| INTERNAL ENERGY IN SOLVENT            | =        | -1145369.12 kcal/mol        |
| DELTA INTERNAL ENERGY                 | =        | 0.00 kcal/mol               |
| ELECTROSTATIC INTERACTION             | =        | -11.41 kcal/mol             |
| PIEROTTI CAVITATION ENERGY            | =        | 0.00 kcal/mol               |
| DISPERSION FREE ENERGY                | =        | 0.00 kcal/mol               |
| REPULSION FREE ENERGY                 | =        | 0.00 kcal/mol               |
| TOTAL INTERACTION                     | =        | -11.41 kcal/mol             |
| <b>TOTAL FREE ENERGY IN SOLVENT =</b> | <b>=</b> | <b>-1145380.54 kcal/mol</b> |

**TS minor1: The transition state structure leading to the minor product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S42. Calculated thermodynamic quantities for TS minor1 in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.707      | 2.981            | 4.968            | 44.235          |
| ROT.                                                              | 0.889        | 0.889        | -10.019      | 2.981            | 2.981            | 36.584          |
| VIB.                                                              | 301.842      | 301.842      | 268.04       | 108.963          | 108.963          | 113.371         |
| TOTAL                                                             | 303.619      | 304.212      | 246.314      | 114.925          | 116.912          | 194.19          |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 16841.166 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -358 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-358 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1825.2822784929 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1825.2654604791 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0168180138 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0168180138 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1825.2822784929 a.u.</b> |

FREE ENERGY IN SOLVENT = -1145382.04 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1145371.49 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -10.55 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -10.55 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1145382.04 kcal/mol**

**TS minor2: The transition state structure leading to the minor product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S43. Calculated thermodynamic quantities for TS minor2 in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.707      | 2.981            | 4.968            | 44.235          |
| ROT.                                                              | 0.889        | 0.889        | -9.901       | 2.981            | 2.981            | 36.189          |
| VIB.                                                              | 301.54       | 301.54       | 267.491      | 109.405          | 109.405          | 114.202         |
| TOTAL                                                             | 303.318      | 303.91       | 245.883      | 115.367          | 117.354          | 194.625         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 16911.557 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -345 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-345 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

**RESULTS OF PCM CALCULATION**

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1825.2832689007 a.u.  
 INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1825.2679526166 a.u.  
 DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0153162840 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0153162840 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1825.2832689007 a.u.**

FREE ENERGY IN SOLVENT = -1145382.67 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1145373.06 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -9.61 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -9.61 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1145382.67 kcal/mol**

**TS minor3: The transition state structure leading to the minor product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.**

Table S44. Calculated thermodynamic quantities for TS minor3 in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|       | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC. | 0            | 0            | 0            | 0                | 0                | 0               |

|                                                                   |         |         |         |         |         |         |
|-------------------------------------------------------------------|---------|---------|---------|---------|---------|---------|
| TRANS.                                                            | 0.889   | 1.481   | -11.707 | 2.981   | 4.968   | 44.235  |
| ROT.                                                              | 0.889   | 0.889   | -10.065 | 2.981   | 2.981   | 36.738  |
| VIB.                                                              | 301.796 | 301.796 | 268.523 | 108.951 | 108.951 | 111.597 |
| TOTAL                                                             | 303.574 | 304.166 | 246.751 | 114.912 | 116.899 | 192.571 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 16805.536 cal/mol |         |         |         |         |         |         |
| Imaginary Frequency: -357 cm <sup>-1</sup>                        |         |         |         |         |         |         |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-357 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1825.2818255226 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1825.2669166311 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0149088915 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0149088915 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1825.2818255226 a.u.**

FREE ENERGY IN SOLVENT = -1145381.76 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -1145372.41 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -9.36 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -9.36 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1145381.76 kcal/mol**

**GS2 Major: The ground state structure (GS2) of the major product obtained from the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent.**

Table S45. Calculated thermodynamic quantities for the Major Product (GS2 Major) in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.707      | 2.981            | 4.968            | 44.235          |
| ROT.                                                              | 0.889        | 0.889        | -10.003      | 2.981            | 2.981            | 36.53           |
| VIB.                                                              | 304.933      | 304.933      | 273.483      | 105.47           | 105.47           | 105.486         |
| TOTAL                                                             | 306.711      | 307.303      | 251.772      | 111.432          | 113.419          | 186.252         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 15900.608 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1825.4298425536 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1825.4052892048 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0245533489 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.

REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0245533489 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1825.4298425536 a.u.**

FREE ENERGY IN SOLVENT = -1145474.64 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1145459.24 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -15.41 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -15.41 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1145474.64 kcal/mol**

**GS2 Minor: The ground state structure (GS2) of the minor product obtained from the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent.**

Table S46. Calculated thermodynamic quantities for the Minor Product (GS2 Minor) in the cycloaddition reaction of ABSACN Entry B with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.707      | 2.981            | 4.968            | 44.235          |
| ROT.                                                              | 0.889        | 0.889        | -9.953       | 2.981            | 2.981            | 36.363          |
| VIB.                                                              | 304.691      | 304.691      | 272.851      | 105.967          | 105.967          | 106.792         |
| TOTAL                                                             | 306.469      | 307.061      | 251.191      | 111.929          | 113.916          | 187.391         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 16028.762 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1825.4329831971 a.u.  
 INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1825.4142996203 a.u.  
 DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0186835768 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0186835768 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1825.4329831971 a.u.**

FREE ENERGY IN SOLVENT = -1145476.61 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1145464.89 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -11.72 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -11.72 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1145476.61 kcal/mol**

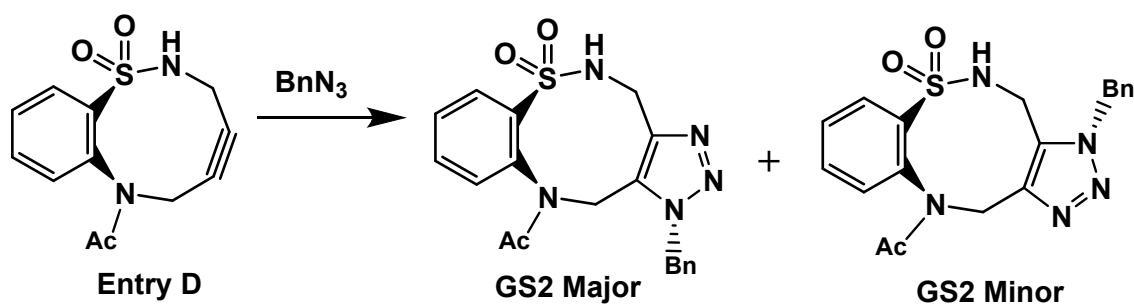


Figure S8. Formation of regioisomers in the strain-promoted cycloaddition of ABSACN Entry D ( $R^1=\text{H}$ ,  $R^2=\text{Ac}$ ) and Benzyl azide with PCM calculations applied.

Table S47. Calculated Free Energies for the Cycloaddition Reaction Pathway of ABSACN Entry D with Benzyl Azide in  $\text{CH}_2\text{Cl}_2$  solvent.

| Structure | Imaginary Frequency ( $\text{cm}^{-1}$ ) | Total Free Energy in Solvent (au) | Total Free Energy in Solvent (kcal/mol) (Relative to GS1) |
|-----------|------------------------------------------|-----------------------------------|-----------------------------------------------------------|
| GS1       | N/A                                      | -1632.21965                       | 0                                                         |
| TS major1 | -341                                     | -1632.20874                       | 6.84373                                                   |
| TS minor1 | -339                                     | -1632.20722                       | 7.80196                                                   |
| GS2 Major | N/A                                      | -1632.36004                       | -88.09790                                                 |
| GS2 Minor | N/A                                      | -1632.35784                       | -86.71641                                                 |

Note: All free energies were calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= $\text{CH}_2\text{Cl}_2$ ) at 298.15 K and 1.0 atm. Energies are reported as Total Free Energy in Solvent (au) and relative free energies (kcal/mol) with respect to the ground state of the reactants (GS1). The single imaginary frequency ( $\text{cm}^{-1}$ ) confirms the nature of the transition states (TS). GS1 (Reactants) Total Free Energy in Solvent: -1632.21965 au.

#### GS1

**Entry D solvent= $\text{CH}_2\text{Cl}_2$  + Benzyl azide  $\rightarrow$  solvent= $\text{CH}_2\text{Cl}_2$**

The optimized ground state structure (GS1) representing the total energy of the reactants (each optimized ABSACN and optimized  $\text{BnN}_3$ ) under dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) solvent conditions.

**TS major1: The transition state structure leading to the major product in the click reaction between ABSACN Entry D and  $\text{BnN}_3$  with  $\text{CH}_2\text{Cl}_2$  solvent.**

Table S48. Calculated thermodynamic quantities for TS major1 in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/ $\text{CH}_2\text{Cl}_2$  solvent conditions.

|                                                                     | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|---------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                               | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                              | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.                                                                | 0.889        | 0.889        | -9.838       | 2.981            | 2.981            | 35.978          |
| VIB.                                                                | 242.035      | 242.035      | 214.223      | 90.372           | 90.372           | 93.281          |
| TOTAL                                                               | 243.812      | 244.405      | 192.799      | 96.333           | 98.32            | 173.088         |
| VIB. THERMAL CORRECTION $E(T)-E(0) = H(T)-H(0) =$ 13976.849 cal/mol |              |              |              |                  |                  |                 |

Imaginary Frequency: -341 cm<sup>-1</sup>

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-341 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1632.2087448394 a.u.  
 INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1632.1823538408 a.u.  
 DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0263909986 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0263909986 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1632.2087448394 a.u.**

FREE ENERGY IN SOLVENT = -1024226.56 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1024210.00 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -16.56 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -16.56 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1024226.56 kcal/mol**

#### TS minor1: The transition state structure leading to the minor product in the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent.

Table S49. Calculated thermodynamic quantities for TS minor1 in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.                                                              | 0.889        | 0.889        | -9.883       | 2.981            | 2.981            | 36.128          |
| VIB.                                                              | 242.24       | 242.24       | 214.407      | 90.039           | 90.039           | 93.355          |
| TOTAL                                                             | 244.018      | 244.61       | 192.937      | 96.001           | 97.988           | 173.311         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 13893.656 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -339 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= CH<sub>2</sub>Cl<sub>2</sub>). The presence of a single imaginary frequency (-339 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1632.2072177979 a.u.  
 INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1632.1797771080 a.u.  
 DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0274406899 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0274406899 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1632.2072177979 a.u.**

FREE ENERGY IN SOLVENT = -1024225.60 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1024208.38 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol

ELECTROSTATIC INTERACTION = -17.22 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -17.22 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1024225.60 kcal/mol**

**GS2 Major: The ground state structure (GS2) of the major product obtained from the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent.**

Table S50. Calculated thermodynamic quantities for the Major Product (GS2 Major) in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.                                                              | 0.889        | 0.889        | -9.715       | 2.981            | 2.981            | 35.565          |
| VIB.                                                              | 245.116      | 245.116      | 219.794      | 86.519           | 86.519           | 84.932          |
| TOTAL                                                             | 246.894      | 247.486      | 198.492      | 92.481           | 94.468           | 164.326         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 12982.833 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1632.3600438287 a.u.  
 INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1632.3330054969 a.u.  
 DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0270383319 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0270383319 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1632.3600438287 a.u.**

FREE ENERGY IN SOLVENT = -1024321.50 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1024304.54 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -16.97 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -16.97 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1024321.50 kcal/mol**

**GS2 Minor: The ground state structure (GS2) of the minor product obtained from the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent.**

Table S51. Calculated thermodynamic quantities for the Minor Product (GS2 Minor) in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.   | 0.889        | 0.889        | -9.745       | 2.981            | 2.981            | 35.667          |
| VIB.   | 245.147      | 245.147      | 219.453      | 86.532           | 86.532           | 86.177          |

|                                                                   |         |         |         |        |        |         |
|-------------------------------------------------------------------|---------|---------|---------|--------|--------|---------|
| TOTAL                                                             | 246.924 | 247.517 | 198.121 | 92.494 | 94.481 | 165.673 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 12965.200 cal/mol |         |         |         |        |        |         |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>2</sub>Cl<sub>2</sub>). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1632.3578422848 a.u.  
INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1632.3308264346 a.u.  
DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
ELECTROSTATIC INTERACTION = -0.0270158502 a.u.  
PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
DISPERSION FREE ENERGY = 0.0000000000 a.u.  
REPULSION FREE ENERGY = 0.0000000000 a.u.  
TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0270158502 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1632.3578422848 a.u.**

FREE ENERGY IN SOLVENT = -1024320.12 kcal/mol  
INTERNAL ENERGY IN SOLVENT = -1024303.17 kcal/mol  
DELTA INTERNAL ENERGY = 0.00 kcal/mol  
ELECTROSTATIC INTERACTION = -16.95 kcal/mol  
PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
DISPERSION FREE ENERGY = 0.00 kcal/mol  
REPULSION FREE ENERGY = 0.00 kcal/mol  
TOTAL INTERACTION = -16.95 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1024320.12 kcal/mol**

Table S52. Calculated Free Energies for the Cycloaddition Reaction Pathway of ABSACN Entry D with Benzyl Azide in CH<sub>3</sub>CN solvent.

| Structure | Imaginary Frequency (cm <sup>-1</sup> ) | Total Free Energy in Solvent (au) | Total Free Energy in Solvent (kcal/mol) (Relative to GS1) |
|-----------|-----------------------------------------|-----------------------------------|-----------------------------------------------------------|
| GS1       | N/A                                     | -1632.22227                       | 0                                                         |
| TS major1 | -364                                    | -1632.21239                       | 6.19486                                                   |
| TS minor1 | -339                                    | -1632.20983                       | 7.80423                                                   |
| GS2 Major | N/A                                     | -1632.36265                       | -88.09464                                                 |
| GS2 Minor | N/A                                     | -1632.36042                       | -86.69445                                                 |

Note: All free energies were calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent=CH<sub>3</sub>CN) at 298.15 K and 1.0 atm. Energies are reported as Total Free Energy in Solvent (au) and relative free energies (kcal/mol) with respect to the ground state of the reactants (GS1). The single imaginary frequency (cm<sup>-1</sup>) confirms the nature of the transition states (TS). GS1 (Reactants) Total Free Energy in Solvent: -1632.22227 au.

#### GS1

Entry D solvent= CH<sub>3</sub>CN + Benzyl azide  $\rightarrow$  solvent= CH<sub>3</sub>CN

#### Entry D $\square$ solvent=CH<sub>3</sub>CN: The optimized structure of ABSACN Entry D under CH<sub>3</sub>CN solvent conditions.

Table S53. Calculated thermodynamic quantities for the ABSACN Entry D (R<sup>1</sup>=H, R<sup>2</sup>=Ac) under PCM/ CH<sub>3</sub>CN solvent conditions.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.224      | 2.981            | 4.968            | 42.612          |
| ROT.   | 0.889        | 0.889        | -8.873       | 2.981            | 2.981            | 32.743          |
| VIB.   | 152.534      | 152.534      | 137.986      | 55.952           | 55.952           | 48.793          |

|                                                                  |         |         |         |        |        |         |
|------------------------------------------------------------------|---------|---------|---------|--------|--------|---------|
| TOTAL                                                            | 154.312 | 154.904 | 117.889 | 61.913 | 63.901 | 124.148 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 8146.012 cal/mol |         |         |         |        |        |         |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= CH<sub>3</sub>CN). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1197.2987138534 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1197.2742025973 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0245112562 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0245112562 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1197.2987138534 a.u.</b> |

|                                       |          |                            |
|---------------------------------------|----------|----------------------------|
| FREE ENERGY IN SOLVENT                | =        | -751316.37 kcal/mol        |
| INTERNAL ENERGY IN SOLVENT            | =        | -751300.99 kcal/mol        |
| DELTA INTERNAL ENERGY                 | =        | 0.00 kcal/mol              |
| ELECTROSTATIC INTERACTION             | =        | -15.38 kcal/mol            |
| PIEROTTI CAVITATION ENERGY            | =        | 0.00 kcal/mol              |
| DISPERSION FREE ENERGY                | =        | 0.00 kcal/mol              |
| REPULSION FREE ENERGY                 | =        | 0.00 kcal/mol              |
| TOTAL INTERACTION                     | =        | -15.38 kcal/mol            |
| <b>TOTAL FREE ENERGY IN SOLVENT =</b> | <b>=</b> | <b>-751316.37 kcal/mol</b> |

#### BnN<sub>3</sub> solvent=CH<sub>3</sub>CN: The optimized structure of Benzyl azide under CH<sub>3</sub>CN solvent conditions.

Table S54. Calculated thermodynamic quantities for the Benzyl azide (BnN<sub>3</sub>) reactant model (GS1) under PCM/CH<sub>3</sub>CN solvent conditions.

|                                                                  | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                            | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                           | 0.889        | 1.481        | -10.615      | 2.981            | 4.968            | 40.569          |
| ROT.                                                             | 0.889        | 0.889        | -7.896       | 2.981            | 2.981            | 29.464          |
| VIB.                                                             | 86.729       | 86.729       | 79.935       | 24.943           | 24.943           | 22.788          |
| TOTAL                                                            | 88.506       | 89.099       | 61.424       | 30.905           | 32.892           | 92.821          |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 3502.124 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= CH<sub>3</sub>CN). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                             |
|---------------------------------------------------|----------|-----------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -434.9235514934 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -434.9168626027 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.           |
| ELECTROSTATIC INTERACTION                         | =        | -0.0066888907 a.u.          |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.           |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.           |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.           |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0066888907 a.u.          |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-434.9235514934 a.u.</b> |

|                            |   |                     |
|----------------------------|---|---------------------|
| FREE ENERGY IN SOLVENT     | = | -272918.68 kcal/mol |
| INTERNAL ENERGY IN SOLVENT | = | -272914.48 kcal/mol |
| DELTA INTERNAL ENERGY      | = | 0.00 kcal/mol       |
| ELECTROSTATIC INTERACTION  | = | -4.20 kcal/mol      |

PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -4.20 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -272918.68 kcal/mol**

**TS major1: The transition state structure leading to the major product in the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>3</sub>CN solvent.**

Table S55. Calculated thermodynamic quantities for TS major1 in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/CH<sub>3</sub>CN solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.                                                              | 0.889        | 0.889        | -9.79        | 2.981            | 2.981            | 35.815          |
| VIB.                                                              | 242.376      | 242.376      | 215.466      | 90.016           | 90.016           | 90.257          |
| TOTAL                                                             | 244.154      | 244.746      | 194.09       | 95.978           | 97.965           | 169.901         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 13799.590 cal/mol |              |              |              |                  |                  |                 |
| Imaginary Frequency: -364 cm <sup>-1</sup>                        |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= CH<sub>3</sub>CN). The presence of a single imaginary frequency (-364 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT = <PSI| H(0)+V/2 |PSI> = -1632.2123932095 a.u.  
 INTERNAL ENERGY IN SOLVENT = <PSI| H(0) |PSI> = -1632.1828581917 a.u.  
 DELTA INTERNAL ENERGY = <D-PSI| H(0) |D-PSI> = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0295350178 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0295350178 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1632.2123932095 a.u.**

FREE ENERGY IN SOLVENT = -1024228.85 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1024210.32 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -18.53 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -18.53 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1024228.85 kcal/mol**

**TS minor1: The transition state structure leading to the minor product in the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>3</sub>CN solvent.**

Table S56. Calculated thermodynamic quantities for TS minor1 in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/CH<sub>3</sub>CN solvent conditions.

|        | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|--------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.  | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS. | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.   | 0.889        | 0.889        | -9.885       | 2.981            | 2.981            | 36.134          |

|                                                                   |         |         |         |        |        |         |
|-------------------------------------------------------------------|---------|---------|---------|--------|--------|---------|
| VIB.                                                              | 242.288 | 242.288 | 214.569 | 89.981 | 89.981 | 92.969  |
| TOTAL                                                             | 244.065 | 244.658 | 193.098 | 95.943 | 97.93  | 172.932 |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 13871.165 cal/mol |         |         |         |        |        |         |
| Imaginary Frequency: -339 cm <sup>-1</sup>                        |         |         |         |        |        |         |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= CH<sub>3</sub>CN). The presence of a single imaginary frequency (-339 cm<sup>-1</sup>) confirms the nature of the transition state. ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1632.2098285285 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1632.1783482807 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0314802478 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0314802478 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1632.2098285285 a.u.</b> |

|                                     |          |                             |
|-------------------------------------|----------|-----------------------------|
| FREE ENERGY IN SOLVENT              | =        | -1024227.24 kcal/mol        |
| INTERNAL ENERGY IN SOLVENT          | =        | -1024207.49 kcal/mol        |
| DELTA INTERNAL ENERGY               | =        | 0.00 kcal/mol               |
| ELECTROSTATIC INTERACTION           | =        | -19.75 kcal/mol             |
| PIEROTTI CAVITATION ENERGY          | =        | 0.00 kcal/mol               |
| DISPERSION FREE ENERGY              | =        | 0.00 kcal/mol               |
| REPULSION FREE ENERGY               | =        | 0.00 kcal/mol               |
| TOTAL INTERACTION                   | =        | -19.75 kcal/mol             |
| <b>TOTAL FREE ENERGY IN SOLVENT</b> | <b>=</b> | <b>-1024227.24 kcal/mol</b> |

**GS2 Major: The ground state structure (GS2) of the major product obtained from the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>3</sub>CN as the solvent.**

Table S57. Calculated thermodynamic quantities for the Major Product (GS2 Major) in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/CH<sub>3</sub>CN solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.                                                              | 0.889        | 0.889        | -9.765       | 2.981            | 2.981            | 35.733          |
| VIB.                                                              | 244.968      | 244.968      | 220.139      | 86.489           | 86.489           | 83.277          |
| TOTAL                                                             | 246.746      | 247.338      | 198.788      | 92.451           | 94.438           | 162.838         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 12853.083 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= CH<sub>3</sub>CN). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

|                                                   |          |                              |
|---------------------------------------------------|----------|------------------------------|
| FREE ENERGY IN SOLVENT = <PSI  H(0)+V/2  PSI>     | =        | -1632.2389625104 a.u.        |
| INTERNAL ENERGY IN SOLVENT = <PSI  H(0)  PSI>     | =        | -1632.2082621908 a.u.        |
| DELTA INTERNAL ENERGY = <D-PSI  H(0)  D-PSI>      | =        | 0.0000000000 a.u.            |
| ELECTROSTATIC INTERACTION                         | =        | -0.0307003196 a.u.           |
| PIEROTTI CAVITATION ENERGY                        | =        | 0.0000000000 a.u.            |
| DISPERSION FREE ENERGY                            | =        | 0.0000000000 a.u.            |
| REPULSION FREE ENERGY                             | =        | 0.0000000000 a.u.            |
| TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) | =        | -0.0307003196 a.u.           |
| <b>TOTAL FREE ENERGY IN SOLVENT</b>               | <b>=</b> | <b>-1632.2389625104 a.u.</b> |

|                            |   |                      |
|----------------------------|---|----------------------|
| FREE ENERGY IN SOLVENT     | = | -1024245.52 kcal/mol |
| INTERNAL ENERGY IN SOLVENT | = | -1024226.26 kcal/mol |

DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -19.26 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -19.26 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1024245.52 kcal/mol**

**GS2 Minor: The ground state structure (GS2) of the minor product obtained from the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>3</sub>CN as the solvent.**

Table S58. Calculated thermodynamic quantities for the Minor Product (GS2 Minor) in the cycloaddition reaction of ABSACN Entry D with Benzyl azide under PCM/CH<sub>3</sub>CN solvent conditions.

|                                                                   | E (kcal/mol) | H (kcal/mol) | G (kcal/mol) | CV (cal/(mol·K)) | CP (cal/(mol·K)) | S (cal/(mol·K)) |
|-------------------------------------------------------------------|--------------|--------------|--------------|------------------|------------------|-----------------|
| ELEC.                                                             | 0            | 0            | 0            | 0                | 0                | 0               |
| TRANS.                                                            | 0.889        | 1.481        | -11.586      | 2.981            | 4.968            | 43.828          |
| ROT.                                                              | 0.889        | 0.889        | -9.744       | 2.981            | 2.981            | 35.664          |
| VIB.                                                              | 245.233      | 245.233      | 219.824      | 86.413           | 86.413           | 85.220          |
| TOTAL                                                             | 247.01       | 247.603      | 198.494      | 92.374           | 94.361           | 164.713         |
| VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) = 12931.039 cal/mol |              |              |              |                  |                  |                 |

Note: All thermodynamic properties were calculated at 298.15 K and 1.0 atm. All values are calculated at the B3LYP-D3(BJ)/6-31G(d) level using the PCM solvation model (solvent= CH<sub>3</sub>CN). ELEC., TRANS., ROT., and VIB. denote electronic, translational, rotational, and vibrational contributions, respectively. The structure corresponds to a ground state (GS), confirmed by the absence of imaginary frequencies.

#### RESULTS OF PCM CALCULATION

FREE ENERGY IN SOLVENT =  $\langle \text{PSI} | H(0) + V/2 | \text{PSI} \rangle$  = -1632.3604216385 a.u.  
 INTERNAL ENERGY IN SOLVENT =  $\langle \text{PSI} | H(0) | \text{PSI} \rangle$  = -1632.3297882423 a.u.  
 DELTA INTERNAL ENERGY =  $\langle \text{D-PSI} | H(0) | \text{D-PSI} \rangle$  = 0.0000000000 a.u.  
 ELECTROSTATIC INTERACTION = -0.0306333963 a.u.  
 PIEROTTI CAVITATION ENERGY = 0.0000000000 a.u.  
 DISPERSION FREE ENERGY = 0.0000000000 a.u.  
 REPULSION FREE ENERGY = 0.0000000000 a.u.  
 TOTAL INTERACTION (DELTA + ES + CAV + DISP + REP) = -0.0306333963 a.u.  
**TOTAL FREE ENERGY IN SOLVENT = -1632.3604216385 a.u.**

FREE ENERGY IN SOLVENT = -1024321.74 kcal/mol  
 INTERNAL ENERGY IN SOLVENT = -1024302.52 kcal/mol  
 DELTA INTERNAL ENERGY = 0.00 kcal/mol  
 ELECTROSTATIC INTERACTION = -19.22 kcal/mol  
 PIEROTTI CAVITATION ENERGY = 0.00 kcal/mol  
 DISPERSION FREE ENERGY = 0.00 kcal/mol  
 REPULSION FREE ENERGY = 0.00 kcal/mol  
 TOTAL INTERACTION = -19.22 kcal/mol  
**TOTAL FREE ENERGY IN SOLVENT = -1024321.74 kcal/mol**

**Boltzmann Distribution for Product Ratio**

The ratio of products can be predicted using the Boltzmann distribution (or Eyring equation at constant temperature), which relates the relative populations to the energy difference:

$$\frac{\text{Major Product}}{\text{Minor Product}} = e^{-\frac{\Delta\Delta G^\ddagger}{RT}}$$

R is the ideal gas constant (1.987 cal/(mol·K) or 0.001987 kcal/(mol·K))

T is the temperature in Kelvin. Since no temperature is specified, we'll assume room temperature (298.15 K), which is standard for these types of predictions unless otherwise stated.

Table S59. Comparison of Boltzmann Distribution Predictions and Observed Product Ratios for the Cycloaddition Reactions of ABSACN Derivatives (Entry A and B).

| Entry   | Transition State Energy Difference ( $\Delta\Delta G^\ddagger$ , kcal/mol) | Product Ratio (Major : Minor) | Observed product ratio (Major : Minor) |
|---------|----------------------------------------------------------------------------|-------------------------------|----------------------------------------|
| Entry A | 0.52                                                                       | 71:29                         | 5:2(= 71.4:28.6)                       |
| Entry B | 0.41                                                                       | 67:33                         | 5:3(= 62.5:37.5)                       |

Note: The predicted product ratio was calculated using the Boltzmann distribution: Major/Minor =  $e^{-(\Delta\Delta G^\ddagger)/RT}$ .

$\Delta\Delta G^\ddagger$  is the difference in Gibbs free energy between the major and minor transition states (TS) in kcal/mol. The predicted ratio calculation assumes a temperature (T) of 298.15 K and the ideal gas constant (R) of 0.001987 kcal/(mol·K). The  $\Delta\Delta G^\ddagger$  values were obtained from B3LYP-D3(BJ)/6-31G(d) PCM/CH<sub>2</sub>Cl<sub>2</sub> calculations (relative to GS1).  $\Delta\Delta G^\ddagger$  is the free energy difference between TS minor1 and TS major1 ( $\Delta G^\ddagger_{\text{minor1}} - \Delta G^\ddagger_{\text{major1}}$ ).

### 3. Cartesian Coordinates of Optimized Structures

**ABSACN model:** The optimized ground state structure (GS1) representing the total energy of the reactants (model molecules: optimized ABSACN Entry A and optimized MeN<sub>3</sub>). (Table 1 & Table S2)

|   |          |          |          |
|---|----------|----------|----------|
| C | 8.032096 | 5.011177 | 7.411510 |
| C | 8.717739 | 5.998100 | 7.547344 |
| O | 6.623756 | 9.586610 | 5.970628 |
| N | 5.983673 | 5.081813 | 6.195087 |
| C | 5.651087 | 7.403630 | 7.101762 |
| C | 5.331854 | 6.030424 | 7.019998 |
| C | 4.273956 | 5.566767 | 7.821239 |
| H | 4.008258 | 4.516607 | 7.743073 |
| C | 4.909488 | 8.267717 | 7.919352 |
| C | 9.307206 | 7.329687 | 7.479805 |
| O | 7.441772 | 7.328940 | 5.118990 |
| S | 7.008640 | 8.194659 | 6.228219 |
| C | 6.910852 | 4.188620 | 6.929865 |
| H | 6.369892 | 3.699916 | 7.745871 |
| H | 7.251657 | 3.404591 | 6.245381 |
| H | 6.518491 | 5.566217 | 5.475026 |
| N | 8.228087 | 8.343526 | 7.411421 |
| C | 3.869470 | 7.780881 | 8.698872 |
| H | 5.162741 | 9.321820 | 7.932009 |
| C | 3.560482 | 6.417705 | 8.653962 |
| H | 3.300128 | 8.457148 | 9.328916 |
| H | 2.743624 | 6.023787 | 9.252424 |
| H | 8.582308 | 9.296210 | 7.331772 |
| H | 9.976515 | 7.386403 | 6.609215 |
| H | 9.894296 | 7.572547 | 8.373413 |

**MeN<sub>3</sub> model:** The optimized ground state structure (GS1) representing the total energy of the reactants (model molecules: optimized ABSACN Entry A and optimized MeN<sub>3</sub>). (Table 1 & Table S3)

|   |          |           |           |
|---|----------|-----------|-----------|
| N | 0.560202 | -3.042146 | 3.563729  |
| N | 0.320273 | -3.338847 | 1.221031  |
| N | 0.472297 | -3.250982 | 2.443277  |
| C | 0.739840 | -4.618377 | 0.620991  |
| H | 0.171374 | -5.464009 | 1.028462  |
| H | 0.537642 | -4.538358 | -0.447469 |
| H | 1.811649 | -4.803144 | 0.767421  |

**ABSACN Entry A solvent=CH<sub>2</sub>Cl<sub>2</sub>:** The optimized structure of ABSACN Entry A under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions. (Table 2 & Table S22)

|   |          |          |          |
|---|----------|----------|----------|
| C | 8.021798 | 5.013852 | 7.418190 |
| C | 8.702182 | 6.004057 | 7.563127 |
| O | 6.612059 | 9.575197 | 5.944341 |
| N | 5.980274 | 5.070543 | 6.191319 |
| C | 5.655254 | 7.397056 | 7.096016 |
| C | 5.329840 | 6.024673 | 7.013338 |
| C | 4.270584 | 5.565796 | 7.815898 |
| H | 4.002750 | 4.515778 | 7.744877 |
| C | 4.920154 | 8.264213 | 7.918549 |
| C | 9.299904 | 7.333006 | 7.496124 |
| O | 7.443108 | 7.329245 | 5.104749 |
| S | 7.012926 | 8.187158 | 6.225821 |
| C | 6.908818 | 4.180172 | 6.935669 |
| H | 6.367259 | 3.690889 | 7.750177 |
| H | 7.258007 | 3.397904 | 6.254545 |
| H | 6.521605 | 5.551877 | 5.474822 |
| N | 8.224471 | 8.352869 | 7.399235 |
| C | 3.876905 | 7.781840 | 8.696749 |
| H | 5.178465 | 9.316961 | 7.940096 |
| C | 3.560678 | 6.419770 | 8.649605 |
| H | 3.313348 | 8.460390 | 9.329328 |
| H | 2.742909 | 6.028910 | 9.248107 |
| H | 8.589045 | 9.302836 | 7.322889 |
| H | 9.982390 | 7.385890 | 6.637636 |
| H | 9.871655 | 7.585395 | 8.395566 |

**ABSACN Entry B solvent=CH<sub>2</sub>Cl<sub>2</sub>: The optimized structure of ABSACN Entry B under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.  
(Table 2 & Table S23)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 6.603153  | 7.750081  | 5.239264  |
| O | 6.854118  | 6.428885  | 4.644504  |
| O | 5.953886  | 8.784618  | 4.435494  |
| N | 6.298254  | 5.157650  | 7.212815  |
| C | 5.695775  | 7.557543  | 6.771865  |
| C | 5.742121  | 6.397065  | 7.586207  |
| C | 5.111508  | 6.476415  | 8.841301  |
| H | 5.126858  | 5.592200  | 9.471625  |
| C | 4.950181  | 8.681221  | 7.158106  |
| C | 9.312054  | 7.355338  | 5.592062  |
| C | 9.134065  | 6.339261  | 6.626534  |
| C | 8.622947  | 5.558075  | 7.398491  |
| C | 7.523584  | 4.743779  | 7.941699  |
| H | 7.377961  | 4.886645  | 9.015513  |
| H | 7.689770  | 3.675708  | 7.770145  |
| H | 6.506424  | 5.151068  | 6.216521  |
| N | 8.193466  | 8.333087  | 5.646167  |
| C | 4.320034  | 8.717736  | 8.393331  |
| H | 4.888299  | 9.518467  | 6.477813  |
| C | 4.432167  | 7.616110  | 9.249785  |
| H | 3.745388  | 9.590308  | 8.687240  |
| H | 3.950412  | 7.631918  | 10.222967 |
| C | 8.432195  | 9.500145  | 6.395265  |
| H | 9.314059  | 6.892527  | 4.603181  |
| H | 10.223640 | 7.941438  | 5.701446  |
| O | 7.356763  | 10.279387 | 6.452294  |
| O | 9.523748  | 9.721526  | 6.888193  |
| C | 7.374782  | 11.533006 | 7.260406  |
| C | 7.581365  | 11.173154 | 8.730584  |
| C | 8.443062  | 12.483352 | 6.718828  |
| C | 5.981850  | 12.113005 | 7.025765  |
| H | 6.830551  | 10.442662 | 9.049649  |
| H | 8.577369  | 10.761436 | 8.902712  |
| H | 7.466778  | 12.075201 | 9.341186  |
| H | 9.447893  | 12.099049 | 6.893289  |
| H | 8.300917  | 12.641782 | 5.644414  |
| H | 8.343768  | 13.450689 | 7.222562  |
| H | 5.783220  | 12.220735 | 5.955020  |
| H | 5.207771  | 11.481266 | 7.468221  |
| H | 5.918154  | 13.101087 | 7.491715  |

**ABSACN Entry C solvent=CH<sub>2</sub>Cl<sub>2</sub>: The optimized structure of ABSACN Entry C under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.  
(Table 2 & Table S24)**

|   |           |          |          |
|---|-----------|----------|----------|
| S | 6.886781  | 7.976958 | 5.370642 |
| O | 7.221078  | 6.772699 | 4.610121 |
| O | 6.303557  | 9.124748 | 4.675785 |
| N | 6.267062  | 5.085676 | 6.926455 |
| C | 5.784352  | 7.566138 | 6.745871 |
| C | 5.619733  | 6.290697 | 7.336681 |
| C | 4.734802  | 6.177430 | 8.415765 |
| H | 4.606597  | 5.194440 | 8.858509 |
| C | 5.014254  | 8.646457 | 7.192466 |
| C | 9.532563  | 7.545960 | 5.982336 |
| C | 9.190632  | 6.372629 | 6.778756 |
| C | 8.558657  | 5.506547 | 7.335593 |
| C | 7.438008  | 4.642552 | 7.706801 |
| H | 7.203158  | 4.706336 | 8.774310 |
| H | 7.618486  | 3.597322 | 7.449367 |
| C | 5.898750  | 4.359419 | 5.809191 |
| N | 8.396864  | 8.502625 | 6.033802 |
| C | 4.136710  | 8.504714 | 8.262738 |
| H | 5.108090  | 9.594586 | 6.685083 |
| C | 4.008500  | 7.266718 | 8.889886 |
| H | 3.551096  | 9.356333 | 8.594528 |
| H | 3.326449  | 7.139495 | 9.724695 |
| C | 8.591844  | 9.692711 | 6.756883 |
| H | 9.718493  | 7.267544 | 4.942506 |
| H | 10.397997 | 8.096963 | 6.350955 |

|   |          |           |          |
|---|----------|-----------|----------|
| O | 7.452355 | 10.347422 | 6.945340 |
| O | 9.699289 | 10.023484 | 7.141562 |
| C | 7.441890 | 11.694081 | 7.582543 |
| C | 7.945908 | 11.585345 | 9.021320 |
| C | 8.261244 | 12.661703 | 6.730714 |
| C | 5.961538 | 12.067019 | 7.554698 |
| H | 7.383679 | 10.816055 | 9.561399 |
| H | 9.008408 | 11.341870 | 9.057085 |
| H | 7.785310 | 12.543595 | 9.526556 |
| H | 9.319218 | 12.396256 | 6.732720 |
| H | 7.893787 | 12.664702 | 5.699177 |
| H | 8.154568 | 13.673399 | 7.135906 |
| H | 5.572817 | 12.036530 | 6.531975 |
| H | 5.376201 | 11.387234 | 8.180970 |
| H | 5.835033 | 13.081580 | 7.944273 |
| O | 6.521549 | 3.355662  | 5.475055 |
| C | 4.684705 | 4.847426  | 5.046652 |
| H | 4.292309 | 4.010599  | 4.466399 |
| H | 3.904224 | 5.243040  | 5.701002 |
| H | 4.988570 | 5.640267  | 4.356308 |

**ABSACN Entry D solvent=CH<sub>2</sub>Cl<sub>2</sub>: The optimized structure of ABSACN Entry D under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.  
(Table 2 & Table S25)**

|   |           |          |          |
|---|-----------|----------|----------|
| S | 7.153461  | 8.379644 | 6.418987 |
| O | 7.713281  | 7.630027 | 5.288091 |
| O | 6.670967  | 9.752933 | 6.197027 |
| N | 6.208782  | 5.206264 | 6.146131 |
| C | 5.771381  | 7.473431 | 7.154109 |
| C | 5.438796  | 6.122558 | 6.926294 |
| C | 4.302557  | 5.603291 | 7.559577 |
| H | 4.053508  | 4.562114 | 7.377483 |
| C | 4.965040  | 8.262185 | 7.984819 |
| C | 9.386460  | 7.586366 | 7.800511 |
| C | 8.854898  | 6.230852 | 7.708747 |
| C | 8.198591  | 5.254846 | 7.434624 |
| C | 7.171905  | 4.368793 | 6.885461 |
| H | 6.645557  | 3.813837 | 7.669881 |
| H | 7.582969  | 3.656013 | 6.167749 |
| C | 6.158761  | 5.123826 | 4.769645 |
| N | 8.256997  | 8.543197 | 7.693319 |
| C | 3.841857  | 7.724215 | 8.604996 |
| H | 5.221972  | 9.304223 | 8.135177 |
| C | 3.507542  | 6.386903 | 8.390564 |
| H | 3.229435  | 8.350092 | 9.246238 |
| H | 2.630838  | 5.954852 | 8.863116 |
| H | 8.560371  | 9.517285 | 7.701769 |
| H | 10.131076 | 7.747340 | 7.009997 |
| H | 9.868520  | 7.787014 | 8.762877 |
| O | 6.873831  | 4.337958 | 4.152848 |
| C | 5.169496  | 6.032771 | 4.072135 |
| H | 4.989266  | 5.634007 | 3.072642 |
| H | 4.223525  | 6.118309 | 4.612684 |
| H | 5.603641  | 7.033202 | 3.979263 |

**ABSACN Entry E solvent=CH<sub>2</sub>Cl<sub>2</sub>: The optimized structure of ABSACN Entry E under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.  
(Table 2 & Table S26)**

|   |          |          |          |
|---|----------|----------|----------|
| S | 6.552976 | 7.431366 | 5.422248 |
| O | 7.029491 | 6.194631 | 4.786286 |
| O | 5.924105 | 8.458031 | 4.593560 |
| N | 6.168972 | 4.637538 | 7.092725 |
| C | 5.447263 | 7.031419 | 6.775702 |
| C | 5.442094 | 5.790192 | 7.462908 |
| C | 4.585971 | 5.682495 | 8.573618 |
| H | 4.557436 | 4.731818 | 9.098211 |
| C | 4.565318 | 8.062410 | 7.138281 |
| C | 9.200744 | 7.279613 | 6.216515 |
| C | 8.920272 | 6.150979 | 7.098136 |
| C | 8.377547 | 5.252828 | 7.702491 |

|   |          |           |          |
|---|----------|-----------|----------|
| C | 7.305606 | 4.282452  | 7.980523 |
| H | 6.974084 | 4.302450  | 9.022101 |
| H | 7.620266 | 3.259197  | 7.753715 |
| H | 6.529375 | 4.740655  | 6.146474 |
| N | 7.991110 | 8.136424  | 6.100853 |
| C | 3.718391 | 7.912665  | 8.226813 |
| H | 4.559455 | 8.973885  | 6.556139 |
| C | 3.750677 | 6.721751  | 8.960699 |
| H | 3.035391 | 8.711954  | 8.496164 |
| H | 3.092196 | 6.590130  | 9.814501 |
| C | 8.039287 | 9.396153  | 6.705326 |
| H | 9.481517 | 6.927128  | 5.220926 |
| H | 9.990170 | 7.937760  | 6.581183 |
| O | 6.837450 | 9.972780  | 6.758918 |
| O | 9.072605 | 9.877150  | 7.135348 |
| C | 6.790237 | 11.336322 | 7.288389 |
| C | 7.047819 | 12.351963 | 6.209491 |
| H | 5.775760 | 11.413408 | 7.681527 |
| H | 7.509401 | 11.411595 | 8.104271 |
| C | 6.012032 | 12.733254 | 5.347194 |
| C | 8.318754 | 12.916448 | 6.044653 |
| C | 8.548596 | 13.851711 | 5.033797 |
| C | 6.240996 | 13.663617 | 4.333707 |
| C | 7.511132 | 14.225007 | 4.176444 |
| H | 9.125334 | 12.616408 | 6.706888 |
| H | 9.536111 | 14.289735 | 4.916203 |
| H | 5.022274 | 12.301263 | 5.473909 |
| H | 5.430095 | 13.954448 | 3.671583 |
| H | 7.689813 | 14.953499 | 3.390031 |

**ABSACN Entry F solvent=CH<sub>2</sub>Cl<sub>2</sub>: The optimized structure of ABSACN Entry F under CH<sub>2</sub>Cl<sub>2</sub> solvent conditions.  
(Table 2 & Table S27)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 6.624632  | 8.037714  | 5.987020  |
| O | 7.274664  | 7.019222  | 5.152520  |
| O | 5.818050  | 9.080611  | 5.352700  |
| N | 6.555936  | 4.925492  | 7.035533  |
| C | 5.623478  | 7.259734  | 7.252209  |
| C | 5.714612  | 5.898606  | 7.627734  |
| C | 4.888202  | 5.472397  | 8.681967  |
| H | 4.933259  | 4.424787  | 8.964564  |
| C | 4.717653  | 8.128998  | 7.880082  |
| C | 9.214930  | 8.190349  | 6.975280  |
| C | 9.020163  | 6.860168  | 7.535171  |
| C | 8.626240  | 5.761657  | 7.854525  |
| C | 7.744231  | 4.584080  | 7.860582  |
| H | 7.417829  | 4.310792  | 8.867777  |
| H | 8.234285  | 3.708016  | 7.425309  |
| H | 6.891605  | 5.257822  | 6.133450  |
| N | 7.887490  | 8.862011  | 6.829214  |
| C | 3.917122  | 7.673851  | 8.918510  |
| H | 4.668635  | 9.161428  | 7.557846  |
| C | 4.013545  | 6.338625  | 9.324350  |
| H | 3.221246  | 8.351601  | 9.402349  |
| H | 3.386705  | 5.967540  | 10.130061 |
| S | 7.770286  | 10.547689 | 7.185098  |
| H | 9.709762  | 8.128494  | 6.000097  |
| H | 9.808662  | 8.833289  | 7.626691  |
| O | 6.410014  | 10.800354 | 7.657754  |
| O | 8.915158  | 10.796476 | 8.067785  |
| C | 8.049563  | 11.405743 | 5.657235  |
| C | 6.965245  | 11.868580 | 4.913166  |
| C | 9.367764  | 11.606935 | 5.237483  |
| C | 9.593151  | 12.279030 | 4.041248  |
| C | 7.215730  | 12.543578 | 3.720712  |
| C | 8.524369  | 12.752682 | 3.263666  |
| H | 10.198413 | 11.264438 | 5.844988  |
| H | 10.614176 | 12.446087 | 3.709164  |
| H | 5.954426  | 11.701364 | 5.262648  |
| H | 6.378869  | 12.914584 | 3.135570  |
| C | 8.786026  | 13.456527 | 1.956565  |

|   |          |           |          |
|---|----------|-----------|----------|
| H | 9.636262 | 14.141840 | 2.037961 |
| H | 9.029159 | 12.729649 | 1.170658 |
| H | 7.911919 | 14.024294 | 1.625029 |

**Model Major TS: The transition state structure leading to the major product in the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>. (Figure 2 & Table S4)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | -1.791233 | -1.389487 | 0.346033  |
| O | -1.200476 | -1.615766 | 1.674400  |
| O | -3.098025 | -1.945283 | -0.000887 |
| N | -0.167329 | 1.092285  | 1.653761  |
| C | -1.897807 | 0.376443  | 0.001895  |
| C | -1.072117 | 1.349639  | 0.604824  |
| C | -1.189861 | 2.672495  | 0.142146  |
| H | -0.582629 | 3.434749  | 0.621312  |
| C | -2.828933 | 0.733351  | -0.984651 |
| C | 0.720215  | -2.221003 | -0.430890 |
| C | 1.471321  | -0.979029 | -0.151391 |
| C | 1.644257  | 0.104661  | 0.412817  |
| C | 1.255021  | 1.224896  | 1.289103  |
| H | 1.416555  | 2.190676  | 0.802548  |
| H | 1.851844  | 1.222529  | 2.208544  |
| H | -0.331714 | 0.165648  | 2.044348  |
| N | -0.700697 | -2.041119 | -0.765685 |
| C | -2.919660 | 2.046928  | -1.426336 |
| H | -3.478738 | -0.034393 | -1.390037 |
| C | -2.083007 | 3.015966  | -0.863218 |
| H | -3.641759 | 2.315628  | -2.190937 |
| H | -2.149171 | 4.049938  | -1.190465 |
| H | -0.875918 | -1.680974 | -1.700110 |
| H | 0.765229  | -2.864198 | 0.452694  |
| H | 1.151967  | -2.783124 | -1.263089 |
| N | 3.356894  | -1.292554 | -1.297918 |
| N | 3.697166  | 0.760749  | -0.343110 |
| N | 3.893606  | -0.315118 | -0.959817 |
| C | 4.834440  | 1.467272  | 0.242907  |
| H | 5.527432  | 1.826714  | -0.527134 |
| H | 4.421739  | 2.334369  | 0.762881  |
| H | 5.384387  | 0.850698  | 0.965346  |

**Model Minor TS: The transition state structure leading to the minor product in the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>. (Figure 2 & Table S5)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 1.339768  | 1.621492  | 0.372286  |
| O | 0.711244  | 1.612154  | 1.702597  |
| O | 2.388754  | 2.586606  | 0.048607  |
| N | 0.613282  | -1.278219 | 1.595580  |
| C | 2.001510  | -0.002224 | -0.033103 |
| C | 1.519333  | -1.207100 | 0.523964  |
| C | 2.017008  | -2.408860 | -0.012981 |
| H | 1.674951  | -3.341683 | 0.425257  |
| C | 2.979638  | -0.010924 | -1.039091 |
| C | -1.316989 | 1.646480  | -0.367960 |
| C | -1.648801 | 0.249574  | -0.031511 |
| C | -1.492532 | -0.870272 | 0.466018  |
| C | -0.711688 | -1.833991 | 1.272342  |
| H | -0.594366 | -2.787964 | 0.750903  |
| H | -1.238107 | -2.049127 | 2.208272  |
| H | 0.496959  | -0.362121 | 2.024695  |
| N | 0.086132  | 1.897658  | -0.734934 |
| C | 3.453664  | -1.212667 | -1.548254 |
| H | 3.357408  | 0.936564  | -1.407853 |
| C | 2.953273  | -2.415371 | -1.037304 |
| H | 4.210569  | -1.213756 | -2.326327 |
| H | 3.318986  | -3.363782 | -1.421240 |
| H | 0.344600  | 1.552003  | -1.656017 |
| H | -1.546025 | 2.285370  | 0.490344  |
| H | -1.905081 | 2.015783  | -1.212443 |
| N | -3.771223 | 0.064153  | -0.873208 |
| N | -3.374441 | -1.954308 | 0.135777  |
| N | -3.944439 | -1.080299 | -0.385342 |

|   |           |          |           |
|---|-----------|----------|-----------|
| C | -4.888424 | 1.008009 | -0.858547 |
| H | -4.486369 | 1.966611 | -1.193816 |
| H | -5.679554 | 0.707838 | -1.555981 |
| H | -5.316402 | 1.135036 | 0.143622  |

**GS2 model major: The ground state structure (GS2) of the major product obtained from the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>. (Table 3 & Table S6)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | -0.075068 | -0.115533 | 0.067389  |
| O | 1.315523  | 0.155998  | -0.334291 |
| O | -1.048862 | 0.957222  | 0.253329  |
| N | 1.383999  | -2.416604 | -1.526980 |
| C | -0.774135 | -1.267332 | -1.123030 |
| C | -0.000673 | -2.289935 | -1.714656 |
| C | -0.670270 | -3.220815 | -2.526539 |
| H | -0.087088 | -3.997108 | -3.013678 |
| C | -2.145867 | -1.159596 | -1.375567 |
| C | 1.077037  | -1.883058 | 1.835763  |
| C | 0.727503  | -3.286551 | 1.446757  |
| C | 1.064991  | -4.023810 | 0.323834  |
| C | 1.852341  | -3.659527 | -0.906434 |
| H | 1.811783  | -4.480633 | -1.630431 |
| H | 2.911118  | -3.518367 | -0.664541 |
| H | 1.788001  | -1.584899 | -1.106848 |
| N | 0.034153  | -0.881273 | 1.552436  |
| C | -2.784391 | -2.091263 | -2.186997 |
| H | -2.693878 | -0.341547 | -0.921152 |
| C | -2.039100 | -3.130237 | -2.751240 |
| H | -3.849317 | -2.007122 | -2.378911 |
| H | -2.524286 | -3.862741 | -3.390646 |
| H | -0.884712 | -1.112111 | 1.923845  |
| H | 1.992033  | -1.535761 | 1.352205  |
| H | 1.245759  | -1.847046 | 2.916382  |
| N | -0.106510 | -4.035942 | 2.225673  |
| N | 0.393025  | -5.195095 | 0.495118  |
| N | -0.310440 | -5.190649 | 1.654631  |
| C | 0.315301  | -6.349330 | -0.380830 |
| H | -0.332581 | -7.074984 | 0.111391  |
| H | -0.120006 | -6.065308 | -1.343617 |
| H | 1.304906  | -6.788436 | -0.537340 |

**GS2 model minor: The ground state structure (GS2) of the minor product obtained from the click reaction between the model molecules, ABSACN Entry A and MeN<sub>3</sub>. (Table 3 & Table S7)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | -0.051240 | -0.103901 | -0.065623 |
| O | 1.363592  | 0.056144  | -0.440408 |
| O | -0.935896 | 1.046117  | 0.104131  |
| N | 1.193918  | -2.593967 | -1.497690 |
| C | -0.841141 | -1.234580 | -1.203430 |
| C | -0.172055 | -2.384726 | -1.681337 |
| C | -0.944451 | -3.336674 | -2.371050 |
| H | -0.459968 | -4.236340 | -2.735834 |
| C | -2.196072 | -1.009600 | -1.476764 |
| C | 0.976480  | -1.880736 | 1.782654  |
| C | 0.608439  | -3.301730 | 1.475152  |
| C | 0.892700  | -4.140923 | 0.409153  |
| C | 1.632186  | -3.841748 | -0.865737 |
| H | 1.496788  | -4.693413 | -1.539563 |
| H | 2.710276  | -3.746422 | -0.695379 |
| H | 1.676805  | -1.768894 | -1.159839 |
| N | -0.017969 | -0.852113 | 1.446483  |
| C | -2.927070 | -1.951453 | -2.189396 |
| H | -2.655784 | -0.097890 | -1.111754 |
| C | -2.295152 | -3.125662 | -2.614405 |
| H | -3.976882 | -1.778929 | -2.404183 |
| H | -2.859232 | -3.878797 | -3.157602 |
| H | -0.959732 | -1.004288 | 1.796958  |
| H | 1.892753  | -1.606206 | 1.257336  |
| H | 1.191239  | -1.773448 | 2.852520  |
| N | -0.152869 | -4.077200 | 2.300097  |
| N | 0.297542  | -5.346640 | 0.634583  |
| N | -0.331341 | -5.312823 | 1.779584  |

C -0.746002 -3.747535 3.582407  
H 0.024927 -3.461652 4.304476  
H -1.468178 -2.930823 3.481047  
H -1.260530 -4.642371 3.933318

**GS1 Entry A: The optimized ground state structure (GS1) representing the total energy of the reactants (optimized ABSACN Entry A and optimized BnN<sub>3</sub>). (Figure 3&4, Table S9))**

C 8.032096 5.011177 7.411510  
C 8.717739 5.998100 7.547344  
O 6.623756 9.586610 5.970628  
N 5.983673 5.081813 6.195087  
C 5.651087 7.403630 7.101762  
C 5.331854 6.030424 7.019998  
C 4.273956 5.566767 7.821239  
H 4.008258 4.516607 7.743073  
C 4.909488 8.267717 7.919352  
C 9.307206 7.329687 7.479805  
O 7.441772 7.328940 5.118990  
S 7.008640 8.194659 6.228219  
C 6.910852 4.188620 6.929865  
H 6.369892 3.699916 7.745871  
H 7.251657 3.404591 6.245381  
H 6.518491 5.566217 5.475026  
N 8.228087 8.343526 7.411421  
C 3.869470 7.780881 8.698872  
H 5.162741 9.321820 7.932009  
C 3.560482 6.417705 8.653962  
H 3.300128 8.457148 9.328916  
H 2.743624 6.023787 9.252424  
H 8.582308 9.296210 7.331772  
H 9.976515 7.386403 6.609215  
H 9.894296 7.572547 8.373413

**GS1 BnN<sub>3</sub>: The optimized ground state structure (GS1) representing the total energy of the reactants (optimized ABSACN Entry A and optimized BnN<sub>3</sub>). (Figure 3&4, Table S10))**

N 0.777908 -2.955269 3.757762  
N 0.446852 -3.431246 1.454845  
N 0.643369 -3.241350 2.660057  
C 0.931114 -4.748539 0.944790  
H 0.306402 -5.551159 1.358018  
H 0.746731 -4.701178 -0.130492  
C 2.388483 -5.002511 1.243746  
C 2.761751 -5.878351 2.267696  
C 3.384346 -4.318913 0.534178  
C 4.729199 -4.515125 0.839056  
C 4.109182 -6.078375 2.574132  
C 5.094385 -5.397114 1.859912  
H 3.097842 -3.627794 -0.254710  
H 5.494087 -3.982560 0.280473  
H 1.993499 -6.408520 2.825993  
H 4.386978 -6.763789 3.370040  
H 6.143580 -5.551354 2.096503

**GS2 major1: The ground state structure (GS2) of the major product (Type 1) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 3, Table S17))**

S -0.110866 -0.083870 0.074439  
O 1.260906 0.218299 -0.367902  
O -1.094095 0.968994 0.317830  
N 1.326724 -2.334843 -1.603375  
C -0.832853 -1.226174 -1.109992  
C -0.065088 -2.231982 -1.737775  
C -0.750990 -3.170027 -2.527841  
H -0.175262 -3.937488 -3.037319  
C -2.214579 -1.137904 -1.310459  
C 1.128102 -1.863791 1.773089  
C 0.796944 -3.268788 1.372932  
C 1.109783 -3.978772 0.225816  
C 1.843797 -3.579586 -1.025717  
H 1.797990 -4.389267 -1.759788  
H 2.907638 -3.424676 -0.817786

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 1.731427  | -1.502445 | -1.185464 |
| N | 0.060175  | -0.876381 | 1.539973  |
| C | -2.868299 | -2.073571 | -2.104614 |
| H | -2.757395 | -0.332208 | -0.828525 |
| C | -2.128336 | -3.098603 | -2.701131 |
| H | -3.940715 | -2.004737 | -2.256934 |
| H | -2.626050 | -3.836117 | -3.324861 |
| H | -0.842362 | -1.128201 | 1.936700  |
| H | 2.021764  | -1.491697 | 1.268416  |
| H | 1.329558  | -1.843263 | 2.848607  |
| N | 0.024342  | -4.057144 | 2.177460  |
| N | 0.478240  | -5.170839 | 0.405218  |
| N | -0.164376 | -5.211373 | 1.598873  |
| C | 0.498765  | -6.355309 | -0.443230 |
| H | -0.215192 | -7.043430 | 0.018848  |
| H | 0.114082  | -6.089058 | -1.433406 |
| C | 1.881886  | -6.963127 | -0.542492 |
| C | 2.652359  | -7.139022 | 0.612998  |
| C | 2.400835  | -7.353040 | -1.779591 |
| C | 3.673977  | -7.920672 | -1.864353 |
| C | 3.924412  | -7.700996 | 0.528399  |
| C | 4.438116  | -8.093686 | -0.710594 |
| H | 1.808718  | -7.212555 | -2.681385 |
| H | 4.069072  | -8.218871 | -2.831484 |
| H | 2.251058  | -6.830099 | 1.574695  |
| H | 4.516080  | -7.832123 | 1.430045  |
| H | 5.430723  | -8.530327 | -0.775263 |

**GS2 major2: The ground state structure (GS2) of the major product (Type 2) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 3, Table S18))**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | -0.124276 | -0.188275 | -0.226529 |
| O | 1.221279  | -0.036177 | -0.808599 |
| O | -1.006097 | 0.959317  | -0.026716 |
| N | 0.972466  | -2.758485 | -1.625827 |
| C | -1.032877 | -1.391503 | -1.195827 |
| C | -0.412241 | -2.561078 | -1.689037 |
| C | -1.237337 | -3.527228 | -2.288226 |
| H | -0.794088 | -4.439241 | -2.672590 |
| C | -2.405506 | -1.173912 | -1.352328 |
| C | 1.221587  | -1.783596 | 1.576783  |
| C | 0.886760  | -3.242189 | 1.470695  |
| C | 1.026390  | -4.144747 | 0.426621  |
| C | 1.482449  | -3.972052 | -1.000990 |
| H | 1.182840  | -4.845367 | -1.588704 |
| H | 2.576467  | -3.925456 | -1.051305 |
| H | 1.476348  | -1.916755 | -1.365218 |
| N | 0.128472  | -0.841572 | 1.292745  |
| C | -3.197220 | -2.135613 | -1.969855 |
| H | -2.830612 | -0.250130 | -0.976237 |
| C | -2.604874 | -3.318135 | -2.421259 |
| H | -4.262431 | -1.967236 | -2.093762 |
| H | -3.208746 | -4.085842 | -2.894138 |
| H | -0.742415 | -1.019320 | 1.786055  |
| H | 2.053648  | -1.504296 | 0.928182  |
| H | 1.536050  | -1.589954 | 2.607054  |
| N | 0.380512  | -3.906361 | 2.552417  |
| N | 0.601264  | -5.321712 | 0.960619  |
| N | 0.205968  | -5.162132 | 2.249025  |
| C | 0.471384  | -6.633465 | 0.335702  |
| H | 1.394616  | -6.863339 | -0.204303 |
| H | 0.389132  | -7.335362 | 1.170534  |
| C | -0.730177 | -6.726858 | -0.580274 |
| C | -1.991108 | -6.332957 | -0.118224 |
| C | -0.596935 | -7.218787 | -1.881163 |
| C | -1.713775 | -7.324492 | -2.714013 |
| C | -3.105083 | -6.441217 | -0.946449 |
| C | -2.969770 | -6.938242 | -2.245903 |
| H | 0.381787  | -7.524140 | -2.245362 |
| H | -1.600292 | -7.707751 | -3.724226 |
| H | -2.090698 | -5.938210 | 0.889257  |

H -4.080022 -6.131911 -0.580631  
H -3.840812 -7.022071 -2.890006

**GS2 minor1: The ground state structure (GS2) of the minor product (Type 1) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 4, Table S19))**

S -0.158934 -0.045508 -0.132252  
O 1.227010 0.185729 -0.571339  
O -1.105901 1.053796 0.039893  
N 1.190338 -2.487651 -1.567482  
C -0.918412 -1.256418 -1.208370  
C -0.193574 -2.368146 -1.696231  
C -0.928812 -3.383435 -2.334484  
H -0.399597 -4.255616 -2.703809  
C -2.296596 -1.130726 -1.423238  
C 1.030482 -1.719255 1.713423  
C 0.715827 -3.158808 1.431106  
C 1.030595 -4.004135 0.378903  
C 1.725783 -3.688444 -0.916420  
H 1.635131 -4.563297 -1.567795  
H 2.797778 -3.515737 -0.770494  
H 1.631481 -1.626840 -1.263140  
N -0.020518 -0.740428 1.398144  
C -2.992165 -2.134192 -2.085538  
H -2.801469 -0.245164 -1.053384  
C -2.300269 -3.270444 -2.519737  
H -4.060032 -2.038167 -2.254490  
H -2.834278 -4.070977 -3.024249  
H -0.937465 -0.924882 1.795862  
H 1.916746 -1.412809 1.155552  
H 1.270089 -1.594872 2.774472  
N -0.009019 -3.951113 2.272493  
N 0.495949 -5.233146 0.631677  
N -0.125806 -5.206427 1.781099  
C -0.559104 -3.642688 3.586899  
C 0.515831 -3.416796 4.629076  
H -1.214280 -2.767889 3.508028  
H -1.186352 -4.503293 3.836384  
C 1.571353 -4.328609 4.750636  
C 0.460882 -2.309511 5.479442  
C 1.445625 -2.116685 6.450760  
C 2.555669 -4.133972 5.717024  
C 2.494179 -3.028497 6.570051  
H -0.353758 -1.595315 5.381703  
H 1.395870 -1.252239 7.106614  
H 1.615601 -5.184549 4.082564  
H 3.371961 -4.845227 5.805703  
H 3.263350 -2.877752 7.322134

**GS2 minor2: The ground state structure (GS2) of the minor product (Type 2) obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 4, Table S20))**

S -0.772169 -0.374085 0.501510  
O 0.494664 0.257835 0.095673  
O -1.950874 0.414105 0.854392  
N 1.058639 -2.110271 -1.370700  
C -1.265260 -1.539080 -0.767203  
C -0.317298 -2.330665 -1.454486  
C -0.810170 -3.389668 -2.238776  
H -0.100710 -4.027397 -2.755310  
C -2.640505 -1.741831 -0.932193  
C 0.807891 -2.053866 2.015764  
C 0.798863 -3.441777 1.436189  
C 1.302273 -3.952822 0.250396  
C 1.903796 -3.224395 -0.916551  
H 2.063462 -3.952235 -1.718748  
H 2.883914 -2.798586 -0.675960  
H 1.281938 -1.227042 -0.924221  
N -0.413566 -1.250445 1.885836  
C -3.101404 -2.773454 -1.740718  
H -3.327737 -1.090325 -0.404884  
C -2.174493 -3.610545 -2.372914

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | -4.167700 | -2.929021 | -1.874008 |
| H | -2.520316 | -4.432966 | -2.993012 |
| H | -1.252543 | -1.657006 | 2.290117  |
| H | 1.614223  | -1.475598 | 1.560092  |
| H | 1.029806  | -2.101676 | 3.088161  |
| N | 0.257824  | -4.535937 | 2.049294  |
| N | 1.029501  | -5.288049 | 0.196925  |
| N | 0.398955  | -5.643548 | 1.283684  |
| C | -0.498518 | -4.627527 | 3.290627  |
| C | -1.786936 | -3.834160 | 3.227242  |
| H | -0.681736 | -5.696924 | 3.428451  |
| H | 0.124197  | -4.281981 | 4.122810  |
| C | -2.606045 | -3.902296 | 2.092029  |
| C | -2.139709 | -2.982996 | 4.279078  |
| C | -3.293442 | -2.200089 | 4.199600  |
| C | -3.757777 | -3.121286 | 2.014424  |
| C | -4.101194 | -2.264126 | 3.063803  |
| H | -1.497326 | -2.915520 | 5.154062  |
| H | -3.547176 | -1.528217 | 5.014181  |
| H | -2.322900 | -4.539352 | 1.258662  |
| H | -4.376014 | -3.168616 | 1.123771  |
| H | -4.986714 | -1.640048 | 2.990818  |

**TS major1: The transition state structure (Type 1) leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 3, Table S11)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 2.757814  | -1.411999 | -0.673720 |
| O | 1.744605  | -1.592374 | -1.724772 |
| O | 4.085842  | -2.011333 | -0.795558 |
| N | 0.880991  | 1.137367  | -1.356224 |
| C | 3.029377  | 0.342424  | -0.364782 |
| C | 2.083783  | 1.349674  | -0.655269 |
| C | 2.385217  | 2.657646  | -0.234860 |
| H | 1.679054  | 3.445877  | -0.478508 |
| C | 4.238860  | 0.652257  | 0.274634  |
| C | 0.630080  | -2.169081 | 0.907609  |
| C | -0.117212 | -0.894484 | 0.899137  |
| C | -0.445392 | 0.196469  | 0.423619  |
| C | -0.341228 | 1.301367  | -0.548603 |
| H | -0.321789 | 2.274967  | -0.050915 |
| H | -1.206634 | 1.296102  | -1.220187 |
| H | 0.879227  | 0.211489  | -1.781386 |
| N | 2.087640  | -2.059142 | 0.733906  |
| C | 4.506934  | 1.951755  | 0.684377  |
| H | 4.960604  | -0.140737 | 0.437648  |
| C | 3.563715  | 2.954283  | 0.435426  |
| H | 5.443803  | 2.184180  | 1.180954  |
| H | 3.762525  | 3.977711  | 0.741574  |
| H | 2.590141  | -1.733275 | 1.555405  |
| H | 0.255051  | -2.798558 | 0.095324  |
| H | 0.486144  | -2.723381 | 1.838719  |
| N | -1.546464 | -1.170496 | 2.602547  |
| N | -2.114038 | 0.905546  | 1.799911  |
| N | -2.133982 | -0.180438 | 2.431761  |
| C | -3.407581 | 1.467866  | 1.354690  |
| H | -4.095304 | 1.507577  | 2.207770  |
| H | -3.189545 | 2.497076  | 1.060513  |
| C | -4.010102 | 0.703066  | 0.196552  |
| C | -4.539098 | -0.579045 | 0.391470  |
| C | -4.015759 | 1.250606  | -1.090130 |
| C | -4.536315 | 0.531086  | -2.167650 |
| C | -5.056451 | -1.300770 | -0.682335 |
| C | -5.055276 | -0.747465 | -1.965202 |
| H | -3.613353 | 2.248852  | -1.247529 |
| H | -4.535763 | 0.969065  | -3.161904 |
| H | -4.542658 | -1.015382 | 1.387106  |
| H | -5.463306 | -2.294799 | -0.519069 |
| H | -5.458845 | -1.311043 | -2.801768 |

**TS major2: The transition state structure (Type 2) leading to the major product in the click reaction between**

**ABSACN Entry A and BnN<sub>3</sub>. (Figure 3, Table S12)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 3.382793  | 0.472138  | -0.038757 |
| O | 3.200052  | 1.236388  | 1.204218  |
| O | 4.721284  | 0.168726  | -0.543240 |
| N | 0.972267  | -0.470698 | 1.909561  |
| C | 2.511325  | -1.101050 | 0.051453  |
| C | 1.402449  | -1.343385 | 0.891376  |
| C | 0.718786  | -2.560703 | 0.720330  |
| H | -0.124050 | -2.769232 | 1.372898  |
| C | 2.947613  | -2.068614 | -0.865294 |
| C | 1.567461  | 2.346814  | -0.938905 |
| C | 0.375952  | 1.833010  | -0.234915 |
| C | -0.219720 | 1.163380  | 0.612384  |
| C | -0.338307 | 0.165756  | 1.690728  |
| H | -1.084041 | -0.598405 | 1.450697  |
| H | -0.654580 | 0.644250  | 2.623606  |
| H | 1.670633  | 0.252089  | 2.075891  |
| N | 2.612096  | 1.358281  | -1.255052 |
| C | 2.257784  | -3.265024 | -1.008238 |
| H | 3.834236  | -1.863233 | -1.455915 |
| C | 1.126485  | -3.498521 | -0.219229 |
| H | 2.601858  | -4.009789 | -1.719172 |
| H | 0.577925  | -4.431536 | -0.316559 |
| H | 2.403269  | 0.764301  | -2.052988 |
| H | 2.028614  | 3.121754  | -0.319430 |
| H | 1.305873  | 2.814492  | -1.892155 |
| N | -1.215302 | 3.173427  | -1.059573 |
| N | -2.296678 | 2.107575  | 0.652947  |
| N | -2.075421 | 2.817164  | -0.357132 |
| C | -3.649460 | 1.590549  | 0.909067  |
| H | -3.740872 | 1.503069  | 1.995187  |
| H | -4.389961 | 2.328980  | 0.579428  |
| C | -3.903291 | 0.244627  | 0.262270  |
| C | -4.177282 | -0.877404 | 1.049897  |
| C | -3.873039 | 0.106370  | -1.131370 |
| C | -4.125876 | -1.128807 | -1.723434 |
| C | -4.432898 | -2.116963 | 0.458716  |
| C | -4.409372 | -2.243624 | -0.929613 |
| H | -3.651422 | 0.969829  | -1.753597 |
| H | -4.106769 | -1.222427 | -2.805883 |
| H | -4.201001 | -0.777975 | 2.133025  |
| H | -4.652167 | -2.978992 | 1.083068  |
| H | -4.612767 | -3.204963 | -1.392953 |

**TS major3: The transition state structure (Type 3) leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 3, Table S13)**

|   |           |          |          |
|---|-----------|----------|----------|
| S | 9.559718  | 6.967166 | 7.012666 |
| O | 9.970348  | 5.672542 | 7.576628 |
| O | 10.551703 | 7.921414 | 6.520412 |
| N | 7.734506  | 4.400385 | 6.295408 |
| C | 8.380246  | 6.725706 | 5.672025 |
| C | 7.575602  | 5.573706 | 5.533569 |
| C | 6.580289  | 5.597802 | 4.539957 |
| H | 5.973136  | 4.707382 | 4.404583 |
| C | 8.226732  | 7.821416 | 4.809599 |
| C | 8.113320  | 7.010939 | 9.360383 |
| C | 7.111651  | 5.985051 | 9.006212 |
| C | 6.638793  | 5.058756 | 8.339921 |
| C | 6.633242  | 4.093502 | 7.223301 |
| H | 5.684315  | 4.107441 | 6.677987 |
| H | 6.770793  | 3.075256 | 7.602851 |
| H | 8.607651  | 4.432960 | 6.818715 |
| N | 8.709520  | 7.757770 | 8.239582 |
| C | 7.234822  | 7.818237 | 3.837121 |
| H | 8.898093  | 8.666929 | 4.915824 |
| C | 6.400179  | 6.701942 | 3.717416 |
| H | 7.119713  | 8.669681 | 3.173193 |
| H | 5.623264  | 6.681636 | 2.957859 |
| H | 8.119747  | 8.490822 | 7.855356 |
| H | 8.929780  | 6.523662 | 9.901778 |

|   |          |          |           |
|---|----------|----------|-----------|
| H | 7.696229 | 7.769769 | 10.028181 |
| N | 5.819076 | 6.040669 | 10.812995 |
| N | 5.002736 | 4.244606 | 9.656214  |
| N | 5.120151 | 5.158207 | 10.513022 |
| C | 3.660714 | 3.709759 | 9.372885  |
| H | 3.822545 | 2.985152 | 8.568834  |
| C | 3.018869 | 3.044108 | 10.571090 |
| H | 3.006872 | 4.500037 | 8.979455  |
| C | 3.596783 | 1.904263 | 11.143226 |
| C | 1.856603 | 3.576764 | 11.134139 |
| C | 1.273061 | 2.977801 | 12.252916 |
| C | 3.018089 | 1.306748 | 12.260445 |
| C | 1.853309 | 1.842355 | 12.817626 |
| H | 1.408632 | 4.465571 | 10.696437 |
| H | 0.369521 | 3.400898 | 12.682795 |
| H | 4.510387 | 1.498126 | 10.716464 |
| H | 3.473640 | 0.422999 | 12.697754 |
| H | 1.402526 | 1.375792 | 13.689218 |

**TS minor1: The transition state structure (Type 1) leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 4, Table S14)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | -2.100344 | 1.724054  | -0.144225 |
| O | -1.109456 | 1.697682  | -1.231602 |
| O | -2.954549 | 2.892458  | 0.058259  |
| N | -1.709195 | -1.098899 | -1.661272 |
| C | -3.196091 | 0.299347  | -0.233423 |
| C | -2.846902 | -0.918629 | -0.856936 |
| C | -3.727665 | -2.003012 | -0.689509 |
| H | -3.483324 | -2.937471 | -1.185736 |
| C | -4.404352 | 0.433168  | 0.467750  |
| C | 0.145524  | 0.973870  | 1.264211  |
| C | 0.284627  | -0.385770 | 0.711272  |
| C | 0.052255  | -1.359970 | -0.013908 |
| C | -0.679893 | -2.005880 | -1.124810 |
| H | -1.145515 | -2.942582 | -0.804893 |
| H | 0.016568  | -2.259627 | -1.930542 |
| H | -1.280847 | -0.201181 | -1.879244 |
| N | -1.219944 | 1.520412  | 1.291594  |
| C | -5.256231 | -0.653733 | 0.612491  |
| H | -4.658091 | 1.399048  | 0.891090  |
| C | -4.901092 | -1.880946 | 0.041493  |
| H | -6.190231 | -0.545927 | 1.155163  |
| H | -5.559699 | -2.739154 | 0.142735  |
| H | -1.811979 | 1.125198  | 2.017718  |
| H | 0.763880  | 1.662595  | 0.679997  |
| H | 0.498713  | 1.024141  | 2.298322  |
| N | 2.211536  | -1.007193 | 1.715157  |
| N | 1.709852  | -2.760349 | 0.328926  |
| N | 2.312794  | -2.073174 | 1.051373  |
| C | 3.409045  | -0.177371 | 1.887228  |
| H | 3.033926  | 0.733312  | 2.369186  |
| H | 4.087817  | -0.648583 | 2.610030  |
| C | 4.155391  | 0.164103  | 0.611594  |
| C | 3.484965  | 0.331731  | -0.606253 |
| C | 5.541503  | 0.346553  | 0.657018  |
| C | 6.249353  | 0.701916  | -0.491168 |
| C | 4.193979  | 0.681384  | -1.755681 |
| C | 5.575962  | 0.870038  | -1.701935 |
| H | 6.070761  | 0.206481  | 1.597259  |
| H | 7.326237  | 0.838239  | -0.441054 |
| H | 2.412000  | 0.176476  | -0.659226 |
| H | 3.663314  | 0.806337  | -2.695647 |
| H | 6.125331  | 1.140859  | -2.599404 |

**TS minor2 : The transition state structure (Type 2) leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 4, Table S15)**

|   |           |          |           |
|---|-----------|----------|-----------|
| S | 0.227100  | 2.054480 | -1.176631 |
| O | 1.695855  | 1.984961 | -1.189507 |
| O | -0.464582 | 3.341460 | -1.139397 |

N 1.544980 -0.260297 -3.010563  
 C -0.464593 1.148408 -2.570168  
 C 0.202602 0.093188 -3.228836  
 C -0.524149 -0.622060 -4.199276  
 H -0.012352 -1.416802 -4.732800  
 C -1.777882 1.501279 -2.916150  
 C 0.626500 0.254494 0.875076  
 C 1.014552 -0.914977 0.063409  
 C 1.388796 -1.522429 -0.945896  
 C 1.760415 -1.571565 -2.376170  
 H 1.186863 -2.336218 -2.908006  
 H 2.816434 -1.842018 -2.479028  
 H 2.019584 0.457632 -2.466540  
 N -0.264089 1.219361 0.212470  
 C -2.469675 0.778324 -3.878850  
 H -2.237536 2.349840 -2.422188  
 C -1.837035 -0.298320 -4.509941  
 H -3.484672 1.057451 -4.144035  
 H -2.363090 -0.867671 -5.271085  
 H -1.231367 0.917560 0.128576  
 H 1.530476 0.792558 1.173808  
 H 0.106279 -0.029643 1.794319  
 N 1.407139 -2.455914 1.687390  
 N 1.967745 -3.524628 -0.260171  
 N 1.720466 -3.356588 0.865690  
 C 0.558245 -2.819731 2.829637  
 H 1.149756 -3.368986 3.573138  
 H 0.300888 -1.858357 3.287694  
 C -0.688898 -3.596660 2.464882  
 C -0.982310 -4.800070 3.111673  
 C -1.558259 -3.125660 1.472511  
 C -2.708045 -3.841440 1.146052  
 C -2.134080 -5.519238 2.785601  
 C -3.000687 -5.039043 1.804121  
 H -1.318198 -2.209057 0.940186  
 H -3.377107 -3.466303 0.376293  
 H -0.303030 -5.178692 3.872521  
 H -2.347319 -6.455691 3.293668  
 H -3.896694 -5.597208 1.547400

**TS minor3 :The transition state structure (Type 2) leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub>. (Figure 4, Table S16)**

S -0.173852 -0.166817 0.268915  
 O 1.289687 -0.026518 0.217026  
 O -1.027156 1.005088 0.456759  
 N 1.360470 -2.127739 -1.786555  
 C -0.789969 -1.023142 -1.187952  
 C -0.023055 -1.942646 -1.938636  
 C -0.694932 -2.677466 -2.933309  
 H -0.113133 -3.368752 -3.536177  
 C -2.146610 -0.808706 -1.473465  
 C 0.558737 -2.048900 2.146572  
 C 1.145322 -3.052859 1.240382  
 C 1.527768 -3.544659 0.173031  
 C 1.791248 -3.442117 -1.278368  
 H 1.281888 -4.234608 -1.834342  
 H 2.862439 -3.558947 -1.472486  
 H 1.757611 -1.395202 -1.200669  
 N -0.501864 -1.210057 1.566564  
 C -2.780847 -1.544000 -2.465780  
 H -2.686545 -0.059829 -0.905199  
 C -2.047822 -2.495213 -3.184122  
 H -3.830398 -1.373522 -2.683767  
 H -2.529532 -3.075067 -3.966488  
 H -1.381046 -1.698027 1.415281  
 H 1.345335 -1.377199 2.502743  
 H 0.108005 -2.514461 3.027495  
 N 1.848531 -4.589242 2.745806  
 N 2.562056 -5.412762 0.729207  
 N 2.445524 -5.282397 1.880893  
 C 2.552606 -4.313022 4.011435

|   |          |           |          |
|---|----------|-----------|----------|
| H | 3.520346 | -3.834067 | 3.815435 |
| H | 1.916949 | -3.578680 | 4.516546 |
| C | 2.735792 | -5.539318 | 4.879203 |
| C | 4.017022 | -5.967176 | 5.235314 |
| C | 1.623944 | -6.262246 | 5.328600 |
| C | 1.793610 | -7.391456 | 6.126363 |
| C | 4.189176 | -7.096938 | 6.037534 |
| C | 3.077817 | -7.810337 | 6.484602 |
| H | 0.626337 | -5.940728 | 5.039491 |
| H | 0.924554 | -7.945510 | 6.470570 |
| H | 4.884531 | -5.413427 | 4.884080 |
| H | 5.190778 | -7.418606 | 6.308810 |
| H | 3.209188 | -8.690132 | 7.108648 |

**TS Entry A major1 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S30)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 2.787510  | -1.405342 | -0.652081 |
| O | 1.789154  | -1.615801 | -1.715795 |
| O | 4.124748  | -1.996075 | -0.790137 |
| N | 0.885328  | 1.113783  | -1.371469 |
| C | 3.040066  | 0.348724  | -0.360771 |
| C | 2.082681  | 1.341871  | -0.662588 |
| C | 2.364443  | 2.655344  | -0.245621 |
| H | 1.648852  | 3.433595  | -0.493132 |
| C | 4.239799  | 0.675279  | 0.291455  |
| C | 0.677229  | -2.187240 | 0.935509  |
| C | -0.080299 | -0.919108 | 0.905183  |
| C | -0.428503 | 0.160125  | 0.413828  |
| C | -0.341653 | 1.264007  | -0.562825 |
| H | -0.334564 | 2.238860  | -0.068636 |
| H | -1.206022 | 1.244765  | -1.234539 |
| H | 0.891634  | 0.184878  | -1.788354 |
| N | 2.136902  | -2.074148 | 0.745629  |
| C | 4.488313  | 1.980270  | 0.695088  |
| H | 4.969314  | -0.105181 | 0.476914  |
| C | 3.534771  | 2.970188  | 0.432022  |
| H | 5.416538  | 2.224448  | 1.201430  |
| H | 3.717324  | 3.996905  | 0.736021  |
| H | 2.641103  | -1.752396 | 1.569549  |
| H | 0.294199  | -2.843961 | 0.148831  |
| H | 0.555594  | -2.716864 | 1.883101  |
| N | -1.528867 | -1.211807 | 2.586587  |
| N | -2.093798 | 0.854646  | 1.768663  |
| N | -2.120137 | -0.223410 | 2.407989  |
| C | -3.377295 | 1.456442  | 1.340020  |
| H | -4.049828 | 1.507089  | 2.203125  |
| H | -3.134246 | 2.480192  | 1.049179  |
| C | -4.010475 | 0.710746  | 0.186022  |
| C | -4.567487 | -0.560151 | 0.381998  |
| C | -4.020720 | 1.267049  | -1.097455 |
| C | -4.577630 | 0.567694  | -2.171123 |
| C | -5.121736 | -1.261391 | -0.688066 |
| C | -5.125081 | -0.700034 | -1.968545 |
| H | -3.598369 | 2.256793  | -1.255254 |
| H | -4.581356 | 1.012698  | -3.162230 |
| H | -4.571796 | -1.000897 | 1.375787  |
| H | -5.552501 | -2.245200 | -0.523469 |
| H | -5.557824 | -1.246884 | -2.801557 |

**TS Entry A major2 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S31)**

|   |          |           |           |
|---|----------|-----------|-----------|
| S | 3.656197 | -0.793222 | 0.232588  |
| O | 3.465004 | -1.500792 | -1.046662 |
| O | 4.987993 | -0.777042 | 0.851082  |
| N | 1.671490 | 0.611921  | -1.907780 |
| C | 3.134676 | 0.919768  | 0.096515  |
| C | 2.180128 | 1.377653  | -0.838450 |
| C | 1.740520 | 2.707559  | -0.710351 |
| H | 1.023230 | 3.080229  | -1.435393 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 3.659818  | 1.781024  | 1.073330  |
| C | 1.449717  | -2.296157 | 0.896341  |
| C | 0.436448  | -1.519313 | 0.152702  |
| C | 0.064536  | -0.727710 | -0.719394 |
| C | 0.241004  | 0.261408  | -1.798874 |
| H | -0.344140 | 1.166624  | -1.617423 |
| H | -0.089259 | -0.151357 | -2.757725 |
| H | 2.213543  | -0.242173 | -2.025589 |
| N | 2.639049  | -1.544717 | 1.340541  |
| C | 3.208070  | 3.089991  | 1.173901  |
| H | 4.420262  | 1.408242  | 1.750144  |
| C | 2.229090  | 3.545046  | 0.283553  |
| H | 3.615621  | 3.749077  | 1.933616  |
| H | 1.866585  | 4.566803  | 0.348359  |
| H | 2.481622  | -0.952909 | 2.154035  |
| H | 1.796853  | -3.115482 | 0.260224  |
| H | 1.038669  | -2.745428 | 1.803157  |
| N | -1.444071 | -2.412976 | 0.910427  |
| N | -2.187021 | -0.934890 | -0.660692 |
| N | -2.179942 | -1.828521 | 0.214861  |
| C | -3.415572 | -0.640341 | -1.421700 |
| H | -3.102362 | 0.092985  | -2.169254 |
| H | -3.750975 | -1.537038 | -1.955788 |
| C | -4.519109 | -0.079988 | -0.552259 |
| C | -4.534761 | 1.277690  | -0.211430 |
| C | -5.509593 | -0.924648 | -0.038813 |
| C | -6.502965 | -0.420525 | 0.803103  |
| C | -5.526253 | 1.784206  | 0.628934  |
| C | -6.512686 | 0.934992  | 1.138637  |
| H | -5.502557 | -1.980205 | -0.300700 |
| H | -7.269441 | -1.084624 | 1.193338  |
| H | -3.765856 | 1.938667  | -0.604216 |
| H | -5.531789 | 2.840310  | 0.884901  |
| H | -7.285964 | 1.329677  | 1.792004  |

**TS Entry A major3 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the major product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S32)**

|   |           |          |           |
|---|-----------|----------|-----------|
| S | 9.540343  | 6.998999 | 6.993027  |
| O | 10.008428 | 5.728825 | 7.574745  |
| O | 10.520798 | 7.945103 | 6.446565  |
| N | 7.785838  | 4.360703 | 6.355939  |
| C | 8.336438  | 6.705474 | 5.692928  |
| C | 7.572535  | 5.523051 | 5.586684  |
| C | 6.549030  | 5.501198 | 4.622375  |
| H | 5.971288  | 4.588280 | 4.512201  |
| C | 8.106106  | 7.795454 | 4.837800  |
| C | 8.166589  | 7.058015 | 9.373000  |
| C | 7.183102  | 6.004878 | 9.049193  |
| C | 6.722558  | 5.051027 | 8.411948  |
| C | 6.713123  | 4.053716 | 7.322548  |
| H | 5.752243  | 4.031370 | 6.800781  |
| H | 6.885743  | 3.050538 | 7.725420  |
| H | 8.667659  | 4.426914 | 6.860153  |
| N | 8.728715  | 7.808015 | 8.228691  |
| C | 7.085383  | 7.746237 | 3.897276  |
| H | 8.732761  | 8.676647 | 4.921512  |
| C | 6.297009  | 6.593826 | 3.803436  |
| H | 6.909265  | 8.592524 | 3.241050  |
| H | 5.496683  | 6.539260 | 3.070864  |
| H | 8.093592  | 8.505057 | 7.842491  |
| H | 9.004725  | 6.604396 | 9.909431  |
| H | 7.742145  | 7.821490 | 10.029635 |
| N | 5.841657  | 6.114440 | 10.838926 |
| N | 5.069092  | 4.285419 | 9.702919  |
| N | 5.156818  | 5.220930 | 10.534451 |
| C | 3.733028  | 3.766404 | 9.345489  |
| H | 3.924879  | 3.060961 | 8.532673  |
| C | 3.046482  | 3.077949 | 10.503979 |
| H | 3.108191  | 4.575152 | 8.947843  |
| C | 3.531558  | 1.858528 | 10.993220 |

|   |          |          |           |
|---|----------|----------|-----------|
| C | 1.943019 | 3.672141 | 11.122316 |
| C | 1.326475 | 3.056073 | 12.214352 |
| C | 2.919791 | 1.243365 | 12.084502 |
| C | 1.816561 | 1.843205 | 12.699731 |
| H | 1.564593 | 4.619174 | 10.746381 |
| H | 0.468207 | 3.526108 | 12.685804 |
| H | 4.392113 | 1.395128 | 10.517524 |
| H | 3.301891 | 0.296906 | 12.456162 |
| H | 1.340452 | 1.362849 | 13.550078 |

**TS Entry A minor1 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S33)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | -2.340006 | 1.795062  | -0.120188 |
| O | -1.517891 | 1.910145  | -1.338153 |
| O | -3.285309 | 2.867898  | 0.212178  |
| N | -1.852704 | -0.943163 | -1.775200 |
| C | -3.286181 | 0.270282  | -0.125782 |
| C | -2.906986 | -0.885995 | -0.842501 |
| C | -3.661647 | -2.053055 | -0.623985 |
| H | -3.396547 | -2.944027 | -1.185554 |
| C | -4.401072 | 0.260554  | 0.728475  |
| C | 0.124602  | 1.249703  | 0.977529  |
| C | 0.274637  | -0.125386 | 0.463468  |
| C | 0.038284  | -1.100691 | -0.259749 |
| C | -0.700238 | -1.764774 | -1.355366 |
| H | -1.049088 | -2.757661 | -1.059970 |
| H | -0.039100 | -1.904149 | -2.216897 |
| H | -1.524917 | -0.006597 | -2.001526 |
| N | -1.262095 | 1.715440  | 1.171974  |
| C | -5.125433 | -0.907415 | 0.924461  |
| H | -4.687960 | 1.177049  | 1.231614  |
| C | -4.739573 | -2.071913 | 0.250636  |
| H | -5.985612 | -0.908664 | 1.586070  |
| H | -5.298985 | -2.992553 | 0.389314  |
| H | -1.718507 | 1.333268  | 1.998869  |
| H | 0.606260  | 1.944601  | 0.282961  |
| H | 0.605704  | 1.383582  | 1.948981  |
| N | 2.078464  | -0.849927 | 1.624267  |
| N | 1.587600  | -2.587407 | 0.215139  |
| N | 2.165188  | -1.926643 | 0.983319  |
| C | 3.312147  | -0.101586 | 1.910984  |
| H | 2.958024  | 0.862335  | 2.293931  |
| H | 3.849897  | -0.582462 | 2.736544  |
| C | 4.227210  | 0.092899  | 0.719427  |
| C | 3.709985  | 0.388463  | -0.548688 |
| C | 5.612924  | -0.003512 | 0.884353  |
| C | 6.472432  | 0.202646  | -0.196798 |
| C | 4.567377  | 0.591330  | -1.630030 |
| C | 5.951152  | 0.502858  | -1.456757 |
| H | 6.020716  | -0.243422 | 1.863612  |
| H | 7.546930  | 0.122999  | -0.055281 |
| H | 2.635054  | 0.442379  | -0.692950 |
| H | 4.154549  | 0.818108  | -2.609335 |
| H | 6.617995  | 0.659683  | -2.300176 |

**TS Entry A minor2 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S34)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 0.280587  | 2.121946  | -1.310314 |
| O | 1.751456  | 2.078656  | -1.389701 |
| O | -0.413611 | 3.414186  | -1.362539 |
| N | 1.565765  | -0.324615 | -2.994211 |
| C | -0.444884 | 1.108056  | -2.602743 |
| C | 0.216319  | 0.016489  | -3.208453 |
| C | -0.524587 | -0.761229 | -4.116707 |
| H | -0.018381 | -1.587912 | -4.607219 |
| C | -1.771123 | 1.425641  | -2.937275 |
| C | 0.761202  | 0.496267  | 0.868660  |
| C | 1.050472  | -0.752795 | 0.134917  |
| C | 1.400219  | -1.432201 | -0.838016 |
| C | 1.776336  | -1.588383 | -2.259463 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 1.202816  | -2.387751 | -2.736729 |
| H | 2.832973  | -1.864025 | -2.339932 |
| H | 2.051017  | 0.425224  | -2.506320 |
| N | -0.119477 | 1.452802  | 0.174621  |
| C | -2.476003 | 0.640191  | -3.839252 |
| H | -2.237098 | 2.293480  | -2.484094 |
| C | -1.847287 | -0.467342 | -4.419399 |
| H | -3.500381 | 0.891986  | -4.094211 |
| H | -2.383022 | -1.087085 | -5.132967 |
| H | -1.116787 | 1.263639  | 0.247196  |
| H | 1.704027  | 1.009211  | 1.079439  |
| H | 0.276673  | 0.319620  | 1.831981  |
| N | 1.189869  | -2.258291 | 1.819021  |
| N | 1.747459  | -3.455609 | -0.054509 |
| N | 1.453599  | -3.213861 | 1.047567  |
| C | 0.164751  | -2.475214 | 2.860500  |
| H | 0.580500  | -3.110865 | 3.650628  |
| H | 0.011420  | -1.484520 | 3.298904  |
| C | -1.127032 | -3.051314 | 2.327259  |
| C | -1.552398 | -4.324093 | 2.719624  |
| C | -1.896725 | -2.330100 | 1.405273  |
| C | -3.074614 | -2.867452 | 0.890769  |
| C | -2.733875 | -4.866173 | 2.207277  |
| C | -3.495776 | -4.139215 | 1.291894  |
| H | -1.564978 | -1.347863 | 1.081032  |
| H | -3.663540 | -2.296718 | 0.178690  |
| H | -0.956509 | -4.893300 | 3.429456  |
| H | -3.053938 | -5.856125 | 2.520523  |
| H | -4.413597 | -4.559487 | 0.890364  |

**TS Entry A minor3 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the minor product in the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S35)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 0.323411  | 2.148906  | -1.339830 |
| O | 1.795916  | 2.105230  | -1.376444 |
| O | -0.362177 | 3.445397  | -1.398498 |
| N | 1.647002  | -0.271166 | -3.039766 |
| C | -0.377123 | 1.145202  | -2.653517 |
| C | 0.295305  | 0.060315  | -3.258931 |
| C | -0.438185 | -0.723077 | -4.168731 |
| H | 0.073750  | -1.544641 | -4.660840 |
| C | -1.707214 | 1.449597  | -2.986149 |
| C | 0.753373  | 0.502310  | 0.821610  |
| C | 1.077844  | -0.725797 | 0.068951  |
| C | 1.451157  | -1.399264 | -0.897664 |
| C | 1.862696  | -1.538410 | -2.310930 |
| H | 1.313261  | -2.342327 | -2.808788 |
| H | 2.925678  | -1.795913 | -2.371050 |
| H | 2.121916  | 0.478629  | -2.541771 |
| N | -0.133999 | 1.452968  | 0.124413  |
| C | -2.405046 | 0.657149  | -3.887095 |
| H | -2.181184 | 2.311474  | -2.530260 |
| C | -1.764577 | -0.443320 | -4.468535 |
| H | -3.433459 | 0.896581  | -4.137840 |
| H | -2.295554 | -1.069809 | -5.179335 |
| H | -1.109351 | 1.159554  | 0.093499  |
| H | 1.680788  | 1.030407  | 1.058531  |
| H | 0.253684  | 0.296116  | 1.770557  |
| N | 1.062413  | -2.265029 | 1.720807  |
| N | 1.697860  | -3.466759 | -0.119643 |
| N | 1.345779  | -3.221498 | 0.966806  |
| C | 0.108842  | -2.451609 | 2.835129  |
| H | -0.692751 | -1.722026 | 2.676593  |
| H | -0.340673 | -3.447289 | 2.776506  |
| C | 0.761096  | -2.223318 | 4.180140  |
| C | 0.474742  | -1.075624 | 4.924792  |
| C | 1.666942  | -3.161545 | 4.692077  |
| C | 2.268785  | -2.958111 | 5.933063  |
| C | 1.077529  | -0.867562 | 6.168124  |
| C | 1.973505  | -1.809819 | 6.675316  |
| H | 1.899604  | -4.053841 | 4.115302  |

H 2.966141 -3.694226 6.324090  
H -0.230204 -0.344469 4.535272  
H 0.844504 0.027711 6.738155  
H 2.441741 -1.651314 7.642721

**TS Entry B major1 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the major product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S39)**

S 1.554519 -0.666161 1.722199  
O 0.275662 -1.042876 2.346806  
O 2.745504 -0.558215 2.564065  
O 1.815204 2.552819 -0.426261  
O 3.368439 1.043188 0.291198  
N 1.235012 0.883905 1.026504  
N -0.476835 -2.383487 -0.074969  
N -3.007300 0.603681 -1.976608  
N -2.892307 1.758141 -1.496565  
N -2.237644 2.430656 -0.810101  
C 1.897549 -1.750677 0.346931  
C 0.874386 -2.330041 -0.444150  
C 1.273496 -2.958339 -1.638812  
H 0.508157 -3.418273 -2.256685  
C 2.611040 -3.052425 -1.998755  
H 2.878078 -3.554293 -2.924567  
C 3.613543 -2.553241 -1.158143  
H 4.661335 -2.669787 -1.415764  
C 3.250551 -1.900889 0.011921  
H 3.995501 -1.478735 0.672176  
C -0.160243 1.387812 1.016295  
H -0.077000 2.462372 0.864612  
H -0.589256 1.213170 2.005294  
C -0.992633 0.734873 -0.006493  
C -1.415251 -0.244019 -0.629965  
C -1.455117 -1.687223 -0.931676  
H -2.447360 -2.098851 -0.721835  
H -1.237030 -1.889340 -1.983775  
C 2.152855 1.577691 0.220507  
C 4.508214 1.648110 -0.449711  
C 5.686042 0.763178 -0.045882  
H 5.561069 -0.256517 -0.419972  
H 5.789232 0.731530 1.043137  
H 6.607972 1.170644 -0.471981  
C 4.725113 3.082112 0.033330  
H 3.888479 3.725657 -0.239932  
H 5.637445 3.477583 -0.425404  
H 4.852650 3.100155 1.120914  
C 4.240850 1.553185 -1.950948  
H 3.405607 2.189715 -2.247394  
H 4.020374 0.517437 -2.230066  
H 5.136054 1.871613 -2.495854  
H -0.605923 -2.087895 0.889251  
C -4.380470 0.043439 -2.067868  
H -4.238356 -0.976484 -2.430816  
C -5.109305 0.059090 -0.744801  
H -4.934097 0.592510 -2.838219  
C -5.717435 1.237340 -0.292298  
C -5.138973 -1.076810 0.071933  
C -5.757189 -1.036993 1.322909  
C -6.334429 1.281334 0.957907  
C -6.353171 0.144110 1.769876  
H -4.684502 -2.001603 -0.275179  
H -5.774144 -1.927391 1.945399  
H -5.709957 2.123847 -0.922127  
H -6.803735 2.201094 1.296107  
H -6.834923 0.178141 2.743181

**TS Entry B major2 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the major product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S40)**

S 9.462307 7.120171 6.939981  
O 9.908674 5.832298 7.496167  
O 10.463644 8.109436 6.543281

|   |          |           |           |
|---|----------|-----------|-----------|
| N | 7.647140 | 4.540270  | 6.306718  |
| C | 8.365140 | 6.818474  | 5.561400  |
| C | 7.547051 | 5.664078  | 5.470385  |
| C | 6.623748 | 5.620561  | 4.409613  |
| H | 6.002958 | 4.734607  | 4.311484  |
| C | 8.316335 | 7.824037  | 4.584340  |
| C | 8.195543 | 6.946108  | 9.390021  |
| C | 7.156551 | 5.943651  | 9.099804  |
| C | 6.595237 | 5.104769  | 8.387966  |
| C | 6.506141 | 4.240358  | 7.195168  |
| H | 5.568732 | 4.388544  | 6.651194  |
| H | 6.551910 | 3.185047  | 7.482892  |
| H | 8.501693 | 4.570500  | 6.856883  |
| N | 8.508997 | 7.796105  | 8.212863  |
| C | 7.410425 | 7.737152  | 3.535745  |
| H | 8.991529 | 8.665312  | 4.666987  |
| C | 6.545060 | 6.638404  | 3.468980  |
| H | 7.379887 | 8.511490  | 2.775698  |
| H | 5.829616 | 6.557470  | 2.655277  |
| C | 7.988582 | 9.101376  | 8.209045  |
| H | 9.111208 | 6.442792  | 9.706521  |
| H | 7.899992 | 7.641327  | 10.173432 |
| O | 8.173914 | 9.703094  | 7.038178  |
| O | 7.435443 | 9.565864  | 9.190343  |
| C | 7.849306 | 11.147355 | 6.868967  |
| C | 6.351828 | 11.375834 | 7.081862  |
| C | 8.713889 | 11.974097 | 7.820683  |
| C | 8.234578 | 11.409560 | 5.415961  |
| H | 5.768528 | 10.707409 | 6.439813  |
| H | 6.067138 | 11.209990 | 8.120905  |
| H | 6.107514 | 12.408669 | 6.810622  |
| H | 8.467090 | 11.769964 | 8.863898  |
| H | 9.775054 | 11.761580 | 7.654340  |
| H | 8.543123 | 13.038656 | 7.626768  |
| H | 9.292558 | 11.186139 | 5.246494  |
| H | 7.628530 | 10.800776 | 4.738172  |
| H | 8.060094 | 12.464377 | 5.181101  |
| N | 6.021663 | 5.859895  | 11.022872 |
| N | 5.027894 | 4.208712  | 9.781806  |
| N | 5.268342 | 5.032414  | 10.693371 |
| C | 3.642282 | 3.737918  | 9.573880  |
| H | 3.240719 | 3.389177  | 10.532481 |
| C | 2.731888 | 4.772529  | 8.946350  |
| H | 3.730371 | 2.865729  | 8.922402  |
| C | 2.340901 | 5.909845  | 9.666465  |
| C | 2.259484 | 4.601344  | 7.640802  |
| C | 1.408488 | 5.546738  | 7.061805  |
| C | 1.497665 | 6.858653  | 9.088925  |
| C | 1.027687 | 6.678212  | 7.784325  |
| H | 2.547757 | 3.716778  | 7.077367  |
| H | 1.043447 | 5.396732  | 6.049357  |
| H | 2.691467 | 6.052047  | 10.685916 |
| H | 1.201293 | 7.735479  | 9.658379  |
| H | 0.365947 | 7.415023  | 7.336991  |

**TS Entry B major3 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the major product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S41)**

|   |           |          |          |
|---|-----------|----------|----------|
| S | 9.453203  | 7.131410 | 6.984703 |
| O | 9.907316  | 5.850442 | 7.550216 |
| O | 10.447004 | 8.132184 | 6.598713 |
| N | 7.696312  | 4.519417 | 6.323992 |
| C | 8.373203  | 6.815474 | 5.596521 |
| C | 7.575980  | 5.647689 | 5.496075 |
| C | 6.652826  | 5.597456 | 4.435404 |
| H | 6.047018  | 4.702141 | 4.329693 |
| C | 8.306184  | 7.828458 | 4.628238 |
| C | 8.144474  | 6.945158 | 9.412100 |
| C | 7.121081  | 5.931901 | 9.102846 |
| C | 6.600958  | 5.067769 | 8.388994 |

|   |          |           |           |
|---|----------|-----------|-----------|
| C | 6.555891 | 4.191361  | 7.202495  |
| H | 5.622112 | 4.302746  | 6.643924  |
| H | 6.631878 | 3.140492  | 7.500103  |
| H | 8.545968 | 4.565284  | 6.880707  |
| N | 8.474090 | 7.797899  | 8.242253  |
| C | 7.400881 | 7.735624  | 3.579984  |
| H | 8.964849 | 8.681415  | 4.719829  |
| C | 6.555061 | 6.622346  | 3.504201  |
| H | 7.355158 | 8.516740  | 2.827653  |
| H | 5.839921 | 6.536268  | 2.690841  |
| C | 7.937457 | 9.095515  | 8.222954  |
| H | 9.058112 | 6.448942  | 9.745148  |
| H | 7.828033 | 7.637251  | 10.190007 |
| O | 8.135025 | 9.690970  | 7.050986  |
| O | 7.362877 | 9.559493  | 9.192019  |
| C | 7.813351 | 11.133404 | 6.870905  |
| C | 6.313694 | 11.361739 | 7.063858  |
| C | 8.666961 | 11.961234 | 7.831088  |
| C | 8.217812 | 11.389473 | 5.422103  |
| H | 5.739886 | 10.687881 | 6.418940  |
| H | 6.017352 | 11.200902 | 8.100359  |
| H | 6.070899 | 12.392438 | 6.783602  |
| H | 8.408631 | 11.756842 | 8.871486  |
| H | 9.729690 | 11.747808 | 7.676267  |
| H | 8.498242 | 13.025613 | 7.635204  |
| H | 9.277482 | 11.163179 | 5.267677  |
| H | 7.619233 | 10.779217 | 4.739087  |
| H | 8.048458 | 12.443609 | 5.181045  |
| N | 5.886723 | 5.899317  | 10.960782 |
| N | 4.998868 | 4.186013  | 9.727847  |
| N | 5.166093 | 5.046771  | 10.623884 |
| C | 3.635729 | 3.689596  | 9.450454  |
| H | 3.767285 | 2.982336  | 8.627242  |
| C | 2.992120 | 3.012418  | 10.641891 |
| H | 3.003206 | 4.509149  | 9.088080  |
| C | 3.508727 | 1.811595  | 11.146631 |
| C | 1.882521 | 3.592940  | 11.263633 |
| C | 1.289371 | 2.981237  | 12.371199 |
| C | 2.920248 | 1.200975  | 12.253452 |
| C | 1.808834 | 1.785732  | 12.869435 |
| H | 1.479560 | 4.525970  | 10.877460 |
| H | 0.425306 | 3.440539  | 12.843470 |
| H | 4.374817 | 1.358629  | 10.670668 |
| H | 3.325659 | 0.268281  | 12.636246 |
| H | 1.350000 | 1.307978  | 13.730795 |

**TS Entry B minor1** solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the minor product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S42)

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 0.349068  | 2.097670  | -1.042362 |
| O | 1.820319  | 2.047252  | -1.082305 |
| O | -0.318089 | 3.397842  | -1.007766 |
| N | 1.674271  | -0.347359 | -2.681249 |
| C | -0.318259 | 1.137051  | -2.390268 |
| C | 0.344020  | 0.014706  | -2.947025 |
| C | -0.380274 | -0.747894 | -3.883242 |
| H | 0.113035  | -1.603379 | -4.334451 |
| C | -1.594855 | 1.520734  | -2.827179 |
| C | 1.012677  | 0.477340  | 1.090511  |
| C | 1.257134  | -0.807126 | 0.412014  |
| C | 1.524031  | -1.505679 | -0.570870 |
| C | 1.881623  | -1.642046 | -1.997043 |
| H | 1.289630  | -2.413752 | -2.495086 |
| H | 2.933579  | -1.927738 | -2.101668 |
| H | 2.153489  | 0.384783  | -2.162879 |
| N | -0.048711 | 1.262434  | 0.419006  |
| C | -2.272922 | 0.757891  | -3.766162 |
| H | -2.039292 | 2.412927  | -2.408662 |
| C | -1.665484 | -0.397471 | -4.273180 |
| H | -3.259103 | 1.060153  | -4.104015 |
| H | -2.184915 | -1.008373 | -5.005858 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -1.361100 | 1.034385  | 0.866807  |
| H | 1.925032  | 1.075451  | 1.085483  |
| H | 0.676246  | 0.368330  | 2.118650  |
| O | -2.255157 | 1.653963  | 0.103313  |
| O | -1.580200 | 0.348915  | 1.849818  |
| C | -3.707688 | 1.583250  | 0.421069  |
| C | -4.178086 | 0.133109  | 0.327665  |
| C | -3.956248 | 2.207978  | 1.793840  |
| C | -4.335055 | 2.434000  | -0.680712 |
| H | -3.911546 | -0.289606 | -0.646677 |
| H | -3.737055 | -0.478350 | 1.115909  |
| H | -5.268721 | 0.104290  | 0.426682  |
| H | -3.498041 | 1.618453  | 2.588947  |
| H | -3.554045 | 3.225728  | 1.825687  |
| H | -5.034698 | 2.260950  | 1.974386  |
| H | -3.909599 | 3.442463  | -0.679103 |
| H | -4.174390 | 1.981053  | -1.662610 |
| H | -5.413361 | 2.510778  | -0.511526 |
| N | 0.671369  | -2.362886 | 1.950521  |
| N | 1.424696  | -3.637497 | 0.193180  |
| N | 1.083832  | -3.320540 | 1.260251  |
| C | 1.063647  | -2.284347 | 3.374792  |
| H | 0.532878  | -1.409849 | 3.757033  |
| H | 0.672089  | -3.161916 | 3.900715  |
| C | 2.556560  | -2.146148 | 3.561055  |
| C | 3.373385  | -3.283483 | 3.579033  |
| C | 3.148322  | -0.881782 | 3.664917  |
| C | 4.533386  | -0.753621 | 3.782141  |
| C | 4.758670  | -3.158990 | 3.695489  |
| C | 5.341459  | -1.892715 | 3.796154  |
| H | 2.522067  | 0.006771  | 3.663529  |
| H | 4.979233  | 0.233928  | 3.863841  |
| H | 2.922801  | -4.271256 | 3.508523  |
| H | 5.381706  | -4.049025 | 3.713979  |
| H | 6.419702  | -1.795626 | 3.889426  |

**TS Entry B minor2 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the minor product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S43)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 0.316488  | 1.901986  | -1.418746 |
| O | 1.755912  | 1.698747  | -1.653293 |
| O | -0.231962 | 3.254970  | -1.508215 |
| N | 1.163249  | -0.885279 | -2.775657 |
| C | -0.630111 | 0.822719  | -2.478597 |
| C | -0.162927 | -0.447680 | -2.896197 |
| C | -1.091940 | -1.285206 | -3.543077 |
| H | -0.753181 | -2.260314 | -3.879145 |
| C | -1.919628 | 1.267344  | -2.803563 |
| C | 1.199113  | 0.619624  | 0.867018  |
| C | 1.349867  | -0.757455 | 0.366409  |
| C | 1.431159  | -1.633493 | -0.500154 |
| C | 1.416714  | -2.056873 | -1.914388 |
| H | 0.650758  | -2.816008 | -2.095192 |
| H | 2.376642  | -2.502388 | -2.192333 |
| H | 1.774798  | -0.123552 | -2.492256 |
| N | 0.085223  | 1.333418  | 0.195602  |
| C | -2.799822 | 0.430906  | -3.474654 |
| H | -2.212918 | 2.265518  | -2.508879 |
| C | -2.386017 | -0.863285 | -3.814322 |
| H | -3.795596 | 0.778755  | -3.730442 |
| H | -3.067492 | -1.534667 | -4.329194 |
| C | -1.163112 | 1.271576  | 0.843731  |
| H | 2.117960  | 1.181881  | 0.690570  |
| H | 0.965445  | 0.661648  | 1.928341  |
| O | -2.126893 | 1.847846  | 0.128307  |
| O | -1.275034 | 0.751412  | 1.935704  |
| C | -3.541032 | 1.762351  | 0.590634  |
| C | -3.977840 | 0.299329  | 0.543657  |
| C | -3.688705 | 2.378069  | 1.982727  |
| C | -4.288375 | 2.599040  | -0.444639 |
| H | -3.827389 | -0.110001 | -0.461176 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | -3.422861 | -0.301809 | 1.266283  |
| H | -5.044489 | 0.235501  | 0.785405  |
| H | -3.204233 | 1.765945  | 2.742853  |
| H | -3.260312 | 3.385992  | 2.003144  |
| H | -4.755658 | 2.458446  | 2.218073  |
| H | -3.898057 | 3.620736  | -0.472049 |
| H | -4.202302 | 2.160231  | -1.441069 |
| H | -5.349479 | 2.639267  | -0.180616 |
| N | 1.862377  | -1.943812 | 2.251420  |
| N | 1.983532  | -3.507742 | 0.577429  |
| N | 1.945088  | -3.033008 | 1.642644  |
| C | 1.241801  | -1.894621 | 3.584477  |
| H | 1.617236  | -2.735668 | 4.180970  |
| H | 1.621432  | -0.983664 | 4.054143  |
| C | -0.276246 | -1.873946 | 3.574266  |
| C | -0.946453 | -1.194744 | 4.597521  |
| C | -1.024476 | -2.531135 | 2.593186  |
| C | -2.419269 | -2.517576 | 2.642890  |
| C | -2.339899 | -1.180320 | 4.648597  |
| C | -3.082027 | -1.843264 | 3.669996  |
| H | -0.528913 | -3.046406 | 1.777549  |
| H | -2.988221 | -3.031358 | 1.872631  |
| H | -0.373287 | -0.666711 | 5.356556  |
| H | -2.844774 | -0.643184 | 5.447023  |
| H | -4.168134 | -1.829212 | 3.702996  |

**TS Entry B minor3 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the minor product in the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S44)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 0.204564  | 2.069086  | -1.255349 |
| O | 1.673183  | 2.067273  | -1.357884 |
| O | -0.501181 | 3.345357  | -1.159612 |
| N | 1.548639  | -0.292129 | -2.997931 |
| C | -0.479597 | 1.127389  | -2.610533 |
| C | 0.207442  | 0.053564  | -3.231209 |
| C | -0.500561 | -0.672028 | -4.208434 |
| H | 0.016166  | -1.485033 | -4.709687 |
| C | -1.769487 | 1.500195  | -3.018706 |
| C | 1.026157  | 0.441002  | 0.817866  |
| C | 1.290716  | -0.822522 | 0.105093  |
| C | 1.538698  | -1.494864 | -0.901539 |
| C | 1.799738  | -1.598276 | -2.351430 |
| H | 1.175408  | -2.362698 | -2.821490 |
| H | 2.842047  | -1.882053 | -2.531671 |
| H | 2.028720  | 0.437563  | -2.477384 |
| N | -0.098816 | 1.183429  | 0.202244  |
| C | -2.427839 | 0.778619  | -4.004034 |
| H | -2.238495 | 2.355447  | -2.551039 |
| C | -1.792782 | -0.328344 | -4.580733 |
| H | -3.420272 | 1.077080  | -4.326514 |
| H | -2.295387 | -0.901818 | -5.354305 |
| C | -1.370260 | 0.987170  | 0.760276  |
| H | 1.911123  | 1.078153  | 0.778349  |
| H | 0.753109  | 0.304743  | 1.861926  |
| O | -2.324350 | 1.546047  | 0.024964  |
| O | -1.517856 | 0.367095  | 1.801274  |
| C | -3.719068 | 1.658069  | 0.535870  |
| C | -4.319691 | 0.265763  | 0.724932  |
| C | -3.716902 | 2.480698  | 1.823965  |
| C | -4.425462 | 2.410586  | -0.589033 |
| H | -4.220916 | -0.322115 | -0.193790 |
| H | -3.836143 | -0.268082 | 1.543627  |
| H | -5.386388 | 0.367534  | 0.952504  |
| H | -3.190112 | 1.963189  | 2.627774  |
| H | -3.244819 | 3.453892  | 1.654439  |
| H | -4.750800 | 2.653234  | 2.141198  |
| H | -3.940592 | 3.374540  | -0.771836 |
| H | -4.417756 | 1.825634  | -1.513689 |
| H | -5.467032 | 2.593256  | -0.306358 |
| N | 1.240221  | -2.377836 | 1.733007  |
| N | 1.687975  | -3.616433 | -0.147338 |

|   |           |           |          |
|---|-----------|-----------|----------|
| N | 1.404528  | -3.335926 | 0.948251 |
| C | 0.210984  | -2.470300 | 2.795853 |
| H | -0.552450 | -1.723875 | 2.553803 |
| H | -0.260321 | -3.457368 | 2.761500 |
| C | 0.794901  | -2.199219 | 4.163451 |
| C | 0.416481  | -1.061473 | 4.882958 |
| C | 1.713438  | -3.092495 | 4.731442 |
| C | 2.235094  | -2.858188 | 6.002784 |
| C | 0.937592  | -0.824324 | 6.158641 |
| C | 1.845556  | -1.722789 | 6.721186 |
| H | 2.016463  | -3.976167 | 4.174420 |
| H | 2.943571  | -3.559573 | 6.435686 |
| H | -0.293076 | -0.364452 | 4.443118 |
| H | 0.634866  | 0.061524  | 6.710665 |
| H | 2.250277  | -1.541135 | 7.713277 |

**TS Entry D major1 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the major product in the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S48)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 2.891665  | -0.987748 | -1.180600 |
| O | 1.993035  | -0.334767 | -2.137058 |
| O | 4.253303  | -1.354919 | -1.592366 |
| N | 1.037290  | 1.426098  | 0.079645  |
| C | 3.119233  | 0.035918  | 0.298497  |
| C | 2.253678  | 1.059644  | 0.732338  |
| C | 2.581654  | 1.757257  | 1.902029  |
| H | 1.917963  | 2.554795  | 2.222273  |
| C | 4.282072  | -0.252454 | 1.026908  |
| C | 0.693310  | -2.585828 | -0.833811 |
| C | -0.109296 | -1.636670 | -0.035289 |
| C | -0.367392 | -0.512375 | 0.404515  |
| C | -0.212748 | 0.923359  | 0.670088  |
| H | -0.212469 | 1.122048  | 1.747158  |
| H | -1.022852 | 1.494030  | 0.211228  |
| C | 0.967858  | 2.283883  | -1.002291 |
| N | 2.151822  | -2.419658 | -0.722722 |
| C | 4.582836  | 0.447132  | 2.192066  |
| H | 4.960397  | -1.014771 | 0.662313  |
| C | 3.728243  | 1.457303  | 2.632540  |
| H | 5.487434  | 0.210278  | 2.743348  |
| H | 3.958181  | 2.017341  | 3.533893  |
| H | 2.566231  | -2.810256 | 0.121023  |
| H | 0.427395  | -2.475782 | -1.888806 |
| H | 0.494241  | -3.623648 | -0.557347 |
| N | -1.777307 | -2.886463 | 0.559192  |
| N | -2.310339 | -0.894806 | 1.533348  |
| N | -2.398008 | -2.080318 | 1.138625  |
| C | -3.526853 | -0.161257 | 1.942172  |
| H | -4.055633 | -0.747655 | 2.702420  |
| H | -3.157636 | 0.745372  | 2.426796  |
| C | -4.442445 | 0.189989  | 0.789375  |
| C | -5.360166 | -0.747982 | 0.297657  |
| C | -4.368799 | 1.450014  | 0.185592  |
| C | -5.194131 | 1.770453  | -0.894065 |
| C | -6.184963 | -0.431801 | -0.782643 |
| C | -6.101763 | 0.827856  | -1.382291 |
| H | -3.668942 | 2.188433  | 0.570064  |
| H | -5.130093 | 2.754424  | -1.350429 |
| H | -5.433709 | -1.727393 | 0.765278  |
| H | -6.896794 | -1.164968 | -1.152642 |
| H | -6.745866 | 1.076052  | -2.221547 |
| O | -0.112479 | 2.580906  | -1.505965 |
| C | 2.275208  | 2.844939  | -1.520750 |
| H | 2.959078  | 3.128595  | -0.716800 |
| H | 2.771377  | 2.094163  | -2.143788 |
| H | 2.046205  | 3.717392  | -2.135159 |

**TS Entry D minor1 solvent=CH<sub>2</sub>Cl<sub>2</sub>: The transition state structure leading to the minor product in the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent. (Table 4, Table S49)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 13.141031 | -0.830613 | 15.276523 |
|---|-----------|-----------|-----------|

|   |           |           |           |
|---|-----------|-----------|-----------|
| O | 14.281663 | -0.669095 | 16.180976 |
| O | 11.771081 | -0.681497 | 15.783475 |
| N | 13.234252 | -2.387866 | 14.659673 |
| N | 15.666972 | 0.886117  | 14.090174 |
| N | 17.721647 | -2.172641 | 12.034815 |
| N | 17.378842 | -3.291541 | 12.067831 |
| N | 16.475555 | -4.005651 | 12.557985 |
| C | 13.237844 | 0.316954  | 13.878082 |
| C | 14.391234 | 1.009933  | 13.465141 |
| C | 14.301793 | 1.847586  | 12.346475 |
| H | 15.192663 | 2.388296  | 12.041541 |
| C | 13.107300 | 2.000651  | 11.648075 |
| H | 13.067179 | 2.659481  | 10.786194 |
| C | 11.966471 | 1.317599  | 12.070042 |
| H | 11.024525 | 1.435464  | 11.543738 |
| C | 12.031505 | 0.486972  | 13.184732 |
| H | 11.139896 | -0.021964 | 13.532048 |
| C | 14.533873 | -3.075720 | 14.548442 |
| H | 14.301521 | -4.049294 | 14.112487 |
| H | 14.904059 | -3.250733 | 15.562971 |
| C | 15.559321 | -2.345923 | 13.779707 |
| C | 16.244165 | -1.380227 | 13.428078 |
| C | 16.647620 | 0.035965  | 13.403427 |
| H | 17.598702 | 0.174369  | 13.921032 |
| H | 16.770521 | 0.383960  | 12.372414 |
| H | 12.628901 | -2.504694 | 13.849255 |
| C | 16.597774 | -5.474759 | 12.565225 |
| H | 16.512200 | -5.849046 | 11.538248 |
| H | 15.713742 | -5.818843 | 13.109164 |
| C | 17.862911 | -5.981287 | 13.218789 |
| C | 18.978507 | -6.297874 | 12.435271 |
| H | 18.919128 | -6.202705 | 11.353394 |
| C | 20.159387 | -6.743345 | 13.032496 |
| H | 21.017611 | -6.992119 | 12.414182 |
| C | 20.234708 | -6.871050 | 14.421119 |
| H | 21.151703 | -7.222265 | 14.886497 |
| C | 19.125081 | -6.554578 | 15.210023 |
| H | 19.177377 | -6.657382 | 16.290473 |
| C | 17.946835 | -6.108494 | 14.610298 |
| H | 17.083295 | -5.864869 | 15.224947 |
| C | 16.024858 | 1.537838  | 15.252727 |
| O | 17.138807 | 1.391114  | 15.750122 |
| C | 14.984983 | 2.450476  | 15.868405 |
| H | 15.498989 | 3.158366  | 16.520914 |
| H | 14.405374 | 2.992969  | 15.117609 |
| H | 14.293175 | 1.855435  | 16.472457 |

**TS Entry D major1 solvent=CH<sub>3</sub>CN: The transition state structure leading to the major product in the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>3</sub>CN solvent. (Table 4, Table S55)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 2.700035  | -0.924760 | -1.263567 |
| O | 1.773083  | -0.248167 | -2.177013 |
| O | 4.051033  | -1.266955 | -1.730094 |
| N | 0.889253  | 1.452353  | 0.098520  |
| C | 2.961085  | 0.044190  | 0.244243  |
| C | 2.108426  | 1.056868  | 0.724611  |
| C | 2.448411  | 1.705651  | 1.917583  |
| H | 1.791565  | 2.493551  | 2.273543  |
| C | 4.128809  | -0.280255 | 0.949018  |
| C | 0.511233  | -2.523281 | -0.902500 |
| C | -0.239347 | -1.604282 | -0.025018 |
| C | -0.489601 | -0.496302 | 0.457195  |
| C | -0.349713 | 0.944686  | 0.703047  |
| H | -0.344466 | 1.159388  | 1.776809  |
| H | -1.170381 | 1.496940  | 0.240616  |
| C | 0.815635  | 2.314734  | -0.975660 |
| N | 1.977160  | -2.378123 | -0.839063 |
| C | 4.442638  | 0.371704  | 2.138165  |
| H | 4.799135  | -1.031282 | 0.548350  |
| C | 3.598028  | 1.368768  | 2.626303  |
| H | 5.349794  | 0.107965  | 2.672570  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 3.839168  | 1.892201  | 3.546193  |
| H | 2.401811  | -2.780426 | -0.005593 |
| H | 0.210168  | -2.354151 | -1.939826 |
| H | 0.311857  | -3.572364 | -0.673484 |
| N | -1.812183 | -2.923283 | 0.805479  |
| N | -2.206482 | -0.927270 | 1.853360  |
| N | -2.341739 | -2.105982 | 1.448126  |
| C | -3.415863 | -0.112831 | 2.108906  |
| H | -4.039991 | -0.627972 | 2.847727  |
| H | -3.044387 | 0.802688  | 2.573691  |
| C | -4.192415 | 0.198785  | 0.850367  |
| C | -5.049797 | -0.759045 | 0.293242  |
| C | -4.042363 | 1.433359  | 0.209646  |
| C | -4.734930 | 1.709537  | -0.971153 |
| C | -5.742819 | -0.486212 | -0.886372 |
| C | -5.585374 | 0.748807  | -1.521752 |
| H | -3.391548 | 2.188584  | 0.643697  |
| H | -4.612560 | 2.674010  | -1.455917 |
| H | -5.180879 | -1.718822 | 0.787794  |
| H | -6.409302 | -1.234458 | -1.306607 |
| H | -6.126911 | 0.961879  | -2.439179 |
| O | -0.267020 | 2.623771  | -1.468618 |
| C | 2.124870  | 2.869397  | -1.495997 |
| H | 2.817769  | 3.128127  | -0.691274 |
| H | 2.606087  | 2.123983  | -2.136152 |
| H | 1.903485  | 3.756014  | -2.092311 |

**TS Entry D minor1 solvent=CH<sub>3</sub>CN: The transition state structure leading to the minor product in the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>3</sub>CN solvent. (Table 4, Table S56)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 13.139461 | -0.825110 | 15.274333 |
| O | 14.280336 | -0.662257 | 16.179112 |
| O | 11.770785 | -0.675863 | 15.786208 |
| N | 13.231869 | -2.382581 | 14.661007 |
| N | 15.662073 | 0.893522  | 14.087768 |
| N | 17.732638 | -2.167889 | 12.053387 |
| N | 17.393992 | -3.288344 | 12.090274 |
| N | 16.493330 | -4.003067 | 12.582373 |
| C | 13.233293 | 0.322627  | 13.876857 |
| C | 14.385675 | 1.016882  | 13.463081 |
| C | 14.295360 | 1.854293  | 12.344662 |
| H | 15.185404 | 2.395770  | 12.038769 |
| C | 13.100184 | 2.005879  | 11.646902 |
| H | 13.059197 | 2.664334  | 10.784882 |
| C | 11.960384 | 1.321519  | 12.069292 |
| H | 11.018226 | 1.437762  | 11.543167 |
| C | 12.026537 | 0.490772  | 13.183892 |
| H | 11.135468 | -0.019719 | 13.530064 |
| C | 14.530863 | -3.071855 | 14.547932 |
| H | 14.296898 | -4.042774 | 14.107373 |
| H | 14.900785 | -3.252504 | 15.561552 |
| C | 15.557303 | -2.340040 | 13.782317 |
| C | 16.241601 | -1.374092 | 13.430139 |
| C | 16.642132 | 0.042908  | 13.400496 |
| H | 17.594970 | 0.184532  | 13.913946 |
| H | 16.760593 | 0.388765  | 12.368183 |
| H | 12.624270 | -2.502913 | 13.852582 |
| C | 16.606141 | -5.473254 | 12.574201 |
| H | 16.517850 | -5.835749 | 11.543424 |
| H | 15.721097 | -5.817978 | 13.115861 |
| C | 17.870132 | -5.990604 | 13.221797 |
| C | 18.984242 | -6.302780 | 12.434223 |
| H | 18.923898 | -6.198257 | 11.353093 |
| C | 20.165076 | -6.755492 | 13.026679 |
| H | 21.022032 | -7.000905 | 12.405209 |
| C | 20.241726 | -6.895474 | 14.414378 |
| H | 21.158685 | -7.252551 | 14.875699 |
| C | 19.133416 | -6.583728 | 15.207237 |
| H | 19.186640 | -6.695936 | 16.286927 |
| C | 17.955182 | -6.130370 | 14.612327 |
| H | 17.092803 | -5.890255 | 15.230011 |

|   |           |          |           |
|---|-----------|----------|-----------|
| C | 16.018932 | 1.544905 | 15.249065 |
| O | 17.132486 | 1.396595 | 15.749141 |
| C | 14.980049 | 2.459418 | 15.863323 |
| H | 15.494020 | 3.167129 | 16.516112 |
| H | 14.402156 | 3.002320 | 15.111656 |
| H | 14.286394 | 1.865877 | 16.466779 |

**BnN<sub>3</sub> solvent=CH<sub>2</sub>Cl<sub>2</sub>:** The optimized ground state structure (GS1) representing the total energy of the reactants (each optimized ABSACN and optimized BnN<sub>3</sub>) under dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solvent conditions. (Table 4, Table S28)

|   |          |           |           |
|---|----------|-----------|-----------|
| N | 0.844744 | -2.849386 | 3.688997  |
| N | 0.437581 | -3.435167 | 1.425997  |
| N | 0.671319 | -3.188466 | 2.611162  |
| C | 0.925931 | -4.768592 | 0.946937  |
| H | 0.299864 | -5.555244 | 1.383813  |
| H | 0.739893 | -4.747757 | -0.128309 |
| C | 2.383883 | -5.008874 | 1.252528  |
| C | 2.759762 | -5.895775 | 2.266707  |
| C | 3.376983 | -4.310899 | 0.551370  |
| C | 4.723623 | -4.506195 | 0.852980  |
| C | 4.109369 | -6.096566 | 2.567781  |
| C | 5.092481 | -5.400896 | 1.862752  |
| H | 3.088922 | -3.613905 | -0.231729 |
| H | 5.486185 | -3.963347 | 0.301265  |
| H | 1.993893 | -6.437726 | 2.816404  |
| H | 4.390114 | -6.792821 | 3.353138  |
| H | 6.142306 | -5.555171 | 2.096566  |

**BnN<sub>3</sub> solvent=CH<sub>3</sub>CN:** The optimized ground state structure (GS1) representing the total energy of the reactants (optimized ABSACN Entry D and optimized BnN<sub>3</sub>) under dichloromethane (CH<sub>3</sub>CN) solvent conditions. (Table 4, Table S54)

|   |          |           |           |
|---|----------|-----------|-----------|
| N | 0.785047 | -2.857460 | 3.664170  |
| N | 0.413212 | -3.435427 | 1.393477  |
| N | 0.627857 | -3.192008 | 2.582374  |
| C | 0.919432 | -4.764274 | 0.917761  |
| H | 0.291240 | -5.556252 | 1.341550  |
| H | 0.751168 | -4.741237 | -0.160378 |
| C | 2.373289 | -4.994983 | 1.248230  |
| C | 2.737979 | -5.886623 | 2.262382  |
| C | 3.373030 | -4.285496 | 0.568391  |
| C | 4.715942 | -4.475867 | 0.889405  |
| C | 4.084019 | -6.082771 | 2.582623  |
| C | 5.074024 | -5.376812 | 1.897721  |
| H | 3.093308 | -3.584938 | -0.214625 |
| H | 5.483788 | -3.925136 | 0.353149  |
| H | 1.966783 | -6.437245 | 2.795604  |
| H | 4.356491 | -6.783963 | 3.366540  |
| H | 6.121084 | -5.528282 | 2.145488  |

**GS2 Entry A major solvent=CH<sub>2</sub>Cl<sub>2</sub>:** The ground state structure (GS2) of the major product obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. (Table 4, Table S36)

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | -0.134804 | -0.082424 | 0.084163  |
| O | 1.220628  | 0.271356  | -0.380447 |
| O | -1.121074 | 0.968585  | 0.354284  |
| N | 1.315555  | -2.300293 | -1.621435 |
| C | -0.854617 | -1.214513 | -1.100402 |
| C | -0.079019 | -2.204459 | -1.745216 |
| C | -0.761557 | -3.138528 | -2.543084 |
| H | -0.184267 | -3.894139 | -3.067576 |
| C | -2.241616 | -1.144053 | -1.280478 |
| C | 1.161107  | -1.854779 | 1.746338  |
| C | 0.824323  | -3.258076 | 1.344854  |
| C | 1.123159  | -3.963850 | 0.189700  |
| C | 1.841006  | -3.556158 | -1.068125 |
| H | 1.778382  | -4.354106 | -1.812453 |
| H | 2.906987  | -3.405503 | -0.873168 |
| H | 1.721042  | -1.480578 | -1.182052 |
| N | 0.081279  | -0.865820 | 1.544264  |
| C | -2.890546 | -2.078847 | -2.078621 |

H -2.795827 -0.358154 -0.779785  
 C -2.141850 -3.083721 -2.700020  
 H -3.965832 -2.025497 -2.214400  
 H -2.635243 -3.820437 -3.327643  
 H -0.811723 -1.132208 1.956609  
 H 2.044552 -1.478940 1.228154  
 H 1.382899 -1.835578 2.817202  
 N 0.071127 -4.054970 2.157100  
 N 0.502457 -5.159579 0.372011  
 N -0.121159 -5.209212 1.571614  
 C 0.524292 -6.343328 -0.484781  
 H -0.216384 -7.021162 -0.052366  
 H 0.172312 -6.062131 -1.481471  
 C 1.898463 -6.975516 -0.545659  
 C 2.607658 -7.226397 0.635622  
 C 2.465231 -7.322009 -1.775004  
 C 3.725030 -7.924222 -1.825862  
 C 3.866286 -7.822900 0.585226  
 C 4.426419 -8.176601 -0.646301  
 H 1.920796 -7.124873 -2.695561  
 H 4.157620 -8.189437 -2.786584  
 H 2.171484 -6.950527 1.592405  
 H 4.410144 -8.013183 1.506262  
 H 5.407161 -8.642491 -0.684068

**GS2 Entry A minor solvent=CH<sub>2</sub>Cl<sub>2</sub>: The ground state structure (GS2) of the minor product obtained from the click reaction between ABSACN Entry A and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. (Table 4, Table S37)**

S -0.169201 -0.058874 -0.131854  
 O 1.217886 0.189509 -0.568926  
 O -1.104538 1.058545 0.026116  
 N 1.194361 -2.493091 -1.563547  
 C -0.919842 -1.255735 -1.222558  
 C -0.188462 -2.362195 -1.713511  
 C -0.914781 -3.363408 -2.383510  
 H -0.380020 -4.226371 -2.766755  
 C -2.297010 -1.128176 -1.448624  
 C 1.010924 -1.723519 1.720334  
 C 0.691805 -3.162555 1.439886  
 C 1.000198 -4.009333 0.385051  
 C 1.704312 -3.705430 -0.908671  
 H 1.599743 -4.574947 -1.564242  
 H 2.777677 -3.553807 -0.755886  
 H 1.637628 -1.644213 -1.230747  
 N -0.038136 -0.738681 1.397393  
 C -2.983745 -2.121326 -2.135283  
 H -2.813091 -0.254259 -1.067373  
 C -2.284745 -3.248299 -2.583623  
 H -4.050331 -2.024844 -2.310795  
 H -2.810783 -4.038511 -3.111835  
 H -0.959166 -0.924997 1.788348  
 H 1.905002 -1.422739 1.173094  
 H 1.239076 -1.597074 2.782880  
 N -0.018267 -3.953756 2.293397  
 N 0.472830 -5.237561 0.649026  
 N -0.137314 -5.206606 1.809453  
 C -0.551512 -3.636259 3.616866  
 C 0.538890 -3.412078 4.643911  
 H -1.204262 -2.761327 3.538428  
 H -1.180545 -4.490019 3.882634  
 C 1.614222 -4.304542 4.736065  
 C 0.465870 -2.327583 5.523010  
 C 1.451342 -2.141354 6.495411  
 C 2.599777 -4.116113 5.703664  
 C 2.519358 -3.034972 6.586756  
 H -0.365680 -1.630934 5.450180  
 H 1.386391 -1.296326 7.174900  
 H 1.674633 -5.143988 4.048687  
 H 3.431115 -4.812239 5.769501  
 H 3.288389 -2.888534 7.339877

**GS2 Entry B major solvent=CH<sub>2</sub>Cl<sub>2</sub>: The ground state structure (GS2) of the major product obtained from the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. (Table 4, Table S45)**

S 13.898820 -1.252057 15.228777  
O 15.209606 -1.177817 15.903621  
O 12.697024 -1.362341 16.052467  
O 12.972526 -4.280546 13.027105  
O 11.886652 -2.344836 13.561411  
N 14.024193 -2.641248 14.224007  
N 16.109970 -0.089915 13.451286  
N 16.708939 -2.484066 10.676659  
N 16.295122 -3.765225 10.537497  
N 15.770537 -4.127538 11.676325  
C 13.744214 0.088865 14.080833  
C 14.829528 0.403361 13.228329  
C 14.567262 1.291906 12.169412  
H 15.372388 1.562981 11.494572  
C 13.309798 1.861404 12.008229  
H 13.145631 2.552117 11.186224  
C 12.267787 1.583924 12.901930  
H 11.296459 2.052277 12.782585  
C 12.487844 0.683245 13.935898  
H 11.696452 0.407358 14.621845  
C 15.340456 -3.278176 13.968677  
H 15.220592 -4.348023 14.144648  
H 16.030007 -2.889838 14.715381  
C 15.849530 -3.094097 12.567769  
C 16.465603 -2.021634 11.930901  
C 16.913612 -0.653429 12.382156  
H 17.949462 -0.708699 12.734819  
H 16.926233 0.031927 11.531293  
C 12.916831 -3.184931 13.550687  
C 10.561614 -2.743924 13.021910  
C 9.700341 -1.523165 13.336008  
H 10.089283 -0.636964 12.826120  
H 9.686395 -1.332197 14.413572  
H 8.674550 -1.699497 12.997770  
C 10.056480 -3.979026 13.765218  
H 10.666038 -4.855249 13.539443  
H 9.023779 -4.182787 13.462299  
H 10.068817 -3.801849 14.845676  
C 10.681319 -2.961997 11.514615  
H 11.313711 -3.822471 11.289611  
H 11.103951 -2.072160 11.035705  
H 9.684350 -3.136531 11.095074  
H 16.235801 -0.537304 14.351681  
C 17.433243 -1.829601 9.589449  
H 17.295531 -2.479808 8.721597  
H 16.953615 -0.871582 9.369549  
C 18.898598 -1.641890 9.921723  
C 19.646499 -2.714969 10.423587  
C 19.516567 -0.403699 9.728306  
C 20.872875 -0.239942 10.020480  
C 20.998274 -2.550759 10.720316  
C 21.615588 -1.312682 10.516311  
H 18.936960 0.434338 9.347927  
H 21.344364 0.726664 9.866923  
H 19.165582 -3.676750 10.583143  
H 21.572191 -3.387842 11.109063  
H 22.669864 -1.186665 10.747164

**GS2 Entry B minor solvent=CH<sub>2</sub>Cl<sub>2</sub>: The ground state structure (GS2) of the minor product obtained from the click reaction between ABSACN Entry B and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. (Table 4, Table S46)**

S 13.308185 -1.049401 15.418815  
O 14.415149 -0.679739 16.322716  
O 12.030582 -1.437563 16.011440  
O 13.624569 -4.037309 12.975965  
O 11.967478 -2.533832 13.415748  
N 13.943610 -2.369772 14.498709  
N 15.486706 0.451471 13.924839  
N 17.340231 -1.794274 11.607909

|   |           |           |           |
|---|-----------|-----------|-----------|
| N | 17.342247 | -3.104817 | 11.549058 |
| N | 16.631941 | -3.556822 | 12.595551 |
| C | 13.071145 | 0.205964  | 14.196984 |
| C | 14.196897 | 0.691213  | 13.486970 |
| C | 13.935314 | 1.473974  | 12.345516 |
| H | 14.767157 | 1.862390  | 11.767738 |
| C | 12.632661 | 1.799185  | 11.988340 |
| H | 12.467936 | 2.420545  | 11.112505 |
| C | 11.537710 | 1.368564  | 12.750114 |
| H | 10.527202 | 1.650782  | 12.473660 |
| C | 11.762228 | 0.553221  | 13.851340 |
| H | 10.942151 | 0.148452  | 14.431931 |
| C | 15.368037 | -2.752113 | 14.617779 |
| H | 15.413727 | -3.803059 | 14.906468 |
| H | 15.777535 | -2.179056 | 15.448018 |
| C | 16.170029 | -2.526233 | 13.364771 |
| C | 16.642120 | -1.395030 | 12.707710 |
| C | 16.580830 | 0.074292  | 13.047681 |
| H | 17.516075 | 0.371154  | 13.537373 |
| H | 16.530396 | 0.643249  | 12.116403 |
| C | 13.171706 | -3.069746 | 13.562388 |
| C | 11.006018 | -3.058523 | 12.408040 |
| C | 9.784019  | -2.170074 | 12.624369 |
| H | 10.020187 | -1.126174 | 12.402558 |
| H | 9.436744  | -2.241997 | 13.659698 |
| H | 8.975897  | -2.492785 | 11.960549 |
| C | 10.675187 | -4.518506 | 12.714089 |
| H | 11.542298 | -5.164978 | 12.574925 |
| H | 9.877305  | -4.849912 | 12.041031 |
| H | 10.315355 | -4.618468 | 13.743525 |
| C | 11.597681 | -2.854467 | 11.014750 |
| H | 12.473363 | -3.486938 | 10.858144 |
| H | 11.883268 | -1.806021 | 10.877441 |
| H | 10.843609 | -3.106522 | 10.261694 |
| C | 16.557589 | -4.995755 | 12.842493 |
| H | 16.931850 | -5.461288 | 11.926617 |
| H | 15.507454 | -5.261744 | 12.962679 |
| C | 17.375764 | -5.409707 | 14.048894 |
| C | 18.633638 | -4.843740 | 14.289793 |
| H | 19.025096 | -4.093660 | 13.607883 |
| C | 19.379926 | -5.235383 | 15.400726 |
| H | 20.352994 | -4.786868 | 15.581132 |
| C | 18.877522 | -6.198548 | 16.280427 |
| H | 19.458006 | -6.500089 | 17.147838 |
| C | 17.626193 | -6.769299 | 16.041841 |
| H | 17.227141 | -7.515341 | 16.723431 |
| C | 16.876310 | -6.371824 | 14.932458 |
| H | 15.896862 | -6.809187 | 14.753756 |
| H | 15.561022 | 0.114914  | 14.876646 |

**GS2 Entry D major solvent=CH<sub>2</sub>Cl<sub>2</sub>: The ground state structure (GS2) of the major product obtained from the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. (Table 4, Table S50)**

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 13.835873 | -1.342590 | 15.116622 |
| O | 14.840086 | -0.991268 | 16.126319 |
| O | 12.409168 | -1.346944 | 15.460906 |
| N | 14.167880 | -2.911068 | 14.653494 |
| N | 16.468556 | 0.018929  | 13.857163 |
| N | 16.527180 | -2.045612 | 11.033272 |
| N | 15.772396 | -3.117525 | 10.704846 |
| N | 15.385054 | -3.681421 | 11.821616 |
| C | 13.992839 | -0.217432 | 13.704099 |
| C | 15.209086 | 0.336633  | 13.261403 |
| C | 15.191923 | 1.198431  | 12.160258 |
| H | 16.128887 | 1.642791  | 11.837277 |
| C | 14.002179 | 1.500475  | 11.499057 |
| H | 14.015464 | 2.172466  | 10.646535 |
| C | 12.802933 | 0.943810  | 11.941667 |
| H | 11.869483 | 1.173511  | 11.437785 |
| C | 12.798556 | 0.093121  | 13.045273 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 11.870570 | -0.331220 | 13.408951 |
| C | 15.543378 | -3.307670 | 14.289615 |
| H | 15.605947 | -4.386175 | 14.458811 |
| H | 16.220348 | -2.820622 | 14.993854 |
| C | 15.896348 | -2.981579 | 12.874403 |
| C | 16.643902 | -1.927623 | 12.383304 |
| C | 17.386503 | -0.844116 | 13.090081 |
| H | 18.095219 | -1.263552 | 13.806804 |
| H | 17.974924 | -0.252959 | 12.379208 |
| H | 13.452289 | -3.262787 | 14.018379 |
| C | 17.006443 | 0.736474  | 14.912691 |
| C | 17.123261 | -1.228048 | 9.979025  |
| H | 16.663326 | -1.581979 | 9.052754  |
| H | 16.812841 | -0.189748 | 10.126594 |
| C | 18.631752 | -1.344839 | 9.936354  |
| C | 19.249728 | -2.595911 | 10.052534 |
| C | 19.418392 | -0.202781 | 9.759189  |
| C | 20.809280 | -0.308397 | 9.689005  |
| C | 20.638243 | -2.700803 | 9.988831  |
| C | 21.421384 | -1.557514 | 9.804825  |
| H | 18.944519 | 0.772728  | 9.677199  |
| H | 21.411316 | 0.585493  | 9.552501  |
| H | 18.642110 | -3.485610 | 10.195236 |
| H | 21.109579 | -3.675285 | 10.081453 |
| H | 22.503513 | -1.640004 | 9.756927  |
| O | 18.149220 | 0.508451  | 15.299473 |
| C | 16.130352 | 1.801563  | 15.534185 |
| H | 15.773594 | 2.512858  | 14.782641 |
| H | 15.260096 | 1.343206  | 16.009038 |
| H | 16.719974 | 2.328917  | 16.285159 |

**GS2 Entry D minor solvent=CH<sub>2</sub>Cl<sub>2</sub>:** The ground state structure (GS2) of the minor product obtained from the click reaction between ABSACN Entry D and BnN<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. (Table 4, Table S51)

|   |           |           |           |
|---|-----------|-----------|-----------|
| S | 13.513267 | -1.118551 | 15.516949 |
| O | 14.186215 | -0.328380 | 16.552485 |
| O | 12.150425 | -1.618246 | 15.732519 |
| N | 14.431241 | -2.500003 | 15.314211 |
| N | 15.723319 | 0.834717  | 14.258631 |
| N | 17.054935 | -1.378552 | 11.803561 |
| N | 16.816694 | -2.653089 | 11.613375 |
| N | 16.383089 | -3.163376 | 12.785266 |
| C | 13.466262 | -0.178426 | 13.973081 |
| C | 14.509287 | 0.655727  | 13.525665 |
| C | 14.366453 | 1.299775  | 12.293727 |
| H | 15.171208 | 1.941293  | 11.947912 |
| C | 13.217368 | 1.133686  | 11.522294 |
| H | 13.131824 | 1.647154  | 10.569556 |
| C | 12.183243 | 0.318618  | 11.981005 |
| H | 11.279963 | 0.189572  | 11.393267 |
| C | 12.307217 | -0.334061 | 13.205771 |
| H | 11.509127 | -0.965280 | 13.577056 |
| C | 15.893257 | -2.428704 | 15.157195 |
| H | 16.302144 | -3.360858 | 15.556720 |
| H | 16.246205 | -1.617927 | 15.796344 |
| C | 16.355491 | -2.205354 | 13.752978 |
| C | 16.788050 | -1.063898 | 13.103385 |
| C | 16.962008 | 0.316048  | 13.643582 |
| H | 17.723979 | 0.351515  | 14.424117 |
| H | 17.294766 | 0.968711  | 12.827545 |
| H | 13.948299 | -3.173937 | 14.723992 |
| C | 16.074506 | -4.589609 | 12.891224 |
| H | 16.141119 | -4.974100 | 11.870195 |
| H | 15.036101 | -4.706583 | 13.216939 |
| C | 17.019113 | -5.311877 | 13.827450 |
| C | 18.404158 | -5.177153 | 13.670544 |
| H | 18.796128 | -4.546094 | 12.877033 |
| C | 19.274728 | -5.843492 | 14.531111 |
| H | 20.348088 | -5.734217 | 14.403491 |
| C | 18.768829 | -6.650142 | 15.555340 |
| H | 19.449035 | -7.165452 | 16.227435 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 17.389587 | -6.787406 | 15.714875 |
| H | 16.990121 | -7.408823 | 16.511198 |
| C | 16.516981 | -6.116850 | 14.853960 |
| H | 15.442029 | -6.220965 | 14.982673 |
| C | 15.857685 | 1.810454  | 15.237597 |
| O | 16.949395 | 2.033223  | 15.753152 |
| C | 14.616741 | 2.598015  | 15.598747 |
| H | 14.883440 | 3.305145  | 16.385431 |
| H | 14.245950 | 3.148817  | 14.727241 |
| H | 13.819777 | 1.942044  | 15.951574 |