Photoinduced Nucleophilic Substitution of Iodocubanes with Arylthiolate and Diphenylphosphanide ions. Experimental and Computational Approaches

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1. Experimental Information

1.1. Experimental system description for NH$_3(l)$ reaction

- Figure SI-1: Spectrum of lamps used for photoinduced SRN1 reactions. It was obtained from the manufacturer webpage (http://www.lighting.philips.com.eg/prof/lamps/high-intensity-discharge-lamps/quartz-metal-halide/master-hpi-t-plus/928481600096_EU/product).

- Picture SI-2: Experimental device for the NH$_3(l)$ reactions
- Picture **SI-3**: Experimental device for the NH$_3$(l) reactions. Solvent drying process.

- Picture **SI-4**: Experimental device for the NH$_3$(l) reactions. Distillation of NH$_3$(l) dry.

N$_2$(l)- ethanol bath within the coldfinger’s Dewar condenser

NH$_3$(l) with Na before to distill it

N$_2$(l)- ethanol bath
-Picture SI-5: Experimental device for the NH$_3$(l) reactions. Distilled NH$_3$(l) before adding the substrates.

Picture SI-6: Experimental device for the NH$_3$(l) reactions. Dark reaction.
1.2 **Figure S1-7**: UV-visible spectra of 2, 4, 6.

In Acetonitrile

![Graph showing UV-visible spectra of 2, 4, 6 in Acetonitrile](image)

In DMSO

![Graph showing UV-visible spectra of a compound in DMSO](image)
Methyl 4-((4-methoxyphenyl)thio)cubane-1-carboxylate (7)

$^1$H-NMR (400 MHz, acetone-$d_6$)
$^{13}$C-NMR (100 MHz, acetone-$d_6$)
COSY (acetone-$d_6$)
HSQC-DEPT (acetone-$d_6$)
Methyl 4-(phenylthio)cubane-1-carboxylate (8)

$^1$H-NMR (400 MHz, acetone-$d_6$)
$^{13}$C-NMR (100 MHz, acetone-$d_6$)
COSY (acetone-$d_6$)
HMBC (acetone-$d_6$)
HSQC-DEPT (acetone-$d_6$)
Methyl 4-(4-methylphenylthio)cubane-1-carboxylate (9)

$^1$H-NMR (400 MHz, acetone-$d_6$)
$^{13}$C-NMR (100 MHz, acetone-$d_6$)
4-(diphenylphosphoryl)cubane-1-carboxylic acid (9a)

\[ ^1H-NMR \ (400 \ MHz, \ \text{dimethyl sulfoxide-}d_6) \]
$^{13}\text{C}$-NMR (100 MHz, dimethyl sulfoxide-$d_6$)
$^{13}$C-NMR (100 MHz, dimethyl sulfoxide-$d_6$)
1,4-bis((4-methoxyphenyl)thio)cubane (12a)

$^1$H-NMR (400 MHz, chloroform-$d$)
$^{13}$C-NMR (100 Hz, chloroform-$d$)
1,4-bis(phenylthio)cubane (12b)

$^1$H-NMR (400 MHz, chloroform-$d$)
$^{13}$C-NMR (100 MHz, chloroform-$d$)
(4-iodocuban-1-yl)(4-methoxyphenyl)sulfane (13a)

$^1$H-NMR (400 MHz, chloroform-$d$)
$^{13}$C-NMR (100 MHz, chloroform-$d$)
(4-iodocuban-1-yl)(phenyl)sulfane (13b)

$^1$H-NMR (400 MHz, chloroform-$d$)
$^1$H NMR (100 MHz, chloroform-d)

$^1$C-NMR (100 MHz, chloroform-d)
(4-iodocuban-1-yl)(naphthalen-2-yl)sulfane (13c)

$^1$H- NMR (400 MHz, chloroform-$d$)
$^{13}$C-NMR (100 MHz, chloroform-$d$)
Cuban-1-yl(4-methoxyphenyl)sulfane (14a)

$^1$H- NMR (400 MHz, chloroform-\textit{d})
$^{13}$C-NMR (100 MHz, chloroform-$d$)
COSY (chloroform-$d$)
HSQC-DEPT (chloroform-\textit{d})

14a

MSR SPHOMe HSQC-DEPT
HMBC (chloroform-\textit{d})
Cuban-1-yl(phenyl)sulfane (14b)

$^1$H- NMR (400 MHz, chloroform-$d$)
$^{13}$C-NMR (100 MHz, chloroform-$d$)
Cuban-1-yl diphenylphosphine oxide (14d)

$^1$H- NMR (400 MHz, chloroform-d)
$^{13}$C-NMR (100 MHz, chloroform-$d$)
$^{13}$C-NMR (100 MHz, chloroform-$d$)
3. Computational Information

3.1 Test of different solvent’s models

Since the reactions were carried out in liquid ammonia but this solvent was not available in g09, the solvent employed was methanol (as in previous works from the group). To check the differences arisen from different solvent approximations the energies of 3 molecules were computed with methanol, DMSO and liquid ammonia build using parameters available in literature. (Sieffert, N.; Thakkar, A.; Bühl, M. Chem. Commun., 2018, 54, 10431-10434; Budén, M. E; Dorn, V. B.; Gamba, M.; Pierini, A.B.; Rossi; R. A. J. Org. Chem., 2010, 75, 2206-2218).

Almost no differences were observed until the 4th decimal of the energy (~0.1 to 0.3 kcal/mol). With this small energy we considered that the results obtained in the study of the mechanism would not significantly change in either (DMSO, NH3, or methanol used instead of NH3).

| Molecule             | Solvent | SCF Energy     | ZPE Corr. | Sum of ee and thermal | \( \Delta G \) |
|----------------------|---------|----------------|-----------|-----------------------|---------------|
| iodocubanoradical    | Methanol| -605.7025463   | 0.111679  | -605.623883           |               |
|                      | DMSO    | -605.7025935   | 0.111675  | -605.623934           |               |
|                      | NH3     | -605.7024765   | 0.111684  | -605.623808           |               |
| 15-rad               | Methanol| -536.6591589   | 0.164962  | -536.530933           |               |
|                      | DMSO    | -536.6592657   | 0.164956  | -536.531041           |               |
|                      | NH3     | -536.6590012   | 0.164971  | -536.530772           |               |

3.2 Calculation of the redox potentials of phenylsulphide and dipheylphosphide anions

The overall calculated reaction is presented in the thermodynamic cycle shown in scheme 1 and eq. 1.

\[
\begin{align*}
\text{PhS}^- (\text{gas}) + \text{e}^- (\text{gas}) & \rightarrow \text{PhS}^- (\text{gas}) - \Delta G_{(solv,A^-)} \\
\text{PhS}^- (\text{sol}) + \text{e}^- (\text{gas}) & \rightarrow \text{PhS}^- (\text{sol}) - \Delta G_{(solv,A^-)} \\
\text{Ph}_2\text{P}^- (\text{gas}) + \text{e}^- (\text{gas}) & \rightarrow \text{Ph}_2\text{P}^- (\text{gas}) - \Delta G_{(solv,A^-)} \\
\text{Ph}_2\text{P}^- (\text{sol}) + \text{e}^- (\text{gas}) & \rightarrow \text{Ph}_2\text{P}^- (\text{sol}) - \Delta G_{(solv,A^-)}
\end{align*}
\]

scheme 1

In previous works, this equation has been employed for the calculation of reduction. In some cases the \( \Delta G^0_{(Solv)} \) was calculated over the gas phase geometries, in other cases different solvent models were employed to improve its quality and hence the \( \Delta G^0_{Red} \). In the present work the \( \Delta G^0_{Red} \) was directly calculated from the optimized geometries in solvent by employing the IEF-PCM continuum solvation model, including the thermal corrections and the changes in enthalpy and entropy.

\[
\Delta E = \Delta G^0_{(Red)} = -EA + \Delta G^0_{(Solv)} \quad (1)
\]
Finally, the $\Delta G^0_{\text{red}}$ is related to the redox potential, $E^0_{\text{red}}$, by the Faraday’s equation (2)

$$E^0_{\text{red}} = -\frac{\Delta G^0_{\text{red}}}{nF} \quad (2)$$

where $n$ is the number of electrons transferred (in this case is equal to 1) and $F$ is the Faraday constant (96485 C mol$^{-1}$ or 23.061 kcal mol$^{-1}$ V$^{-1}$).

According to these equations, the Redox potential of both molecules was calculated:

| Molecule | Electronic Energy (hartree) | ZPE Correction (hartree) | $\Delta G^0 + $ZPE (hartree) | $\Delta G^0_{\text{red}}$ (kcal/mol) | $E^0_{\text{red}}$ (V) |
|----------|-----------------------------|--------------------------|-----------------------------|-------------------------------------|---------------------|
| PhS$^-$  | -629.6816788                | 0.090641                 | -629.621524                 | -116.338                            | ~5.05               |
| PhS$^-$  | -629.8680842                | 0.09096                  | -629.806921                 | -116.338                            | ~5.05               |
| Ph$_2$P$^-$ | -804.4192103                | 0.182964                 | -804.275287                 | -82.591                             | ~3.58               |
| Ph$_2$P$^-$ | -804.5510342                | 0.182091                 | -804.406905                 | -82.591                             | ~3.58               |

Geometries. Spin densities of radicalary species:

PhS$^-$ (radical)

| C | -1.44035094526 | 1.318789519713 | -0.036036930195 |
| C | -0.051375692512 | 1.311955486295 | -0.035550753254 |
| C | 0.639497963100  | 2.522649003509 | -0.03608394537 |
| C | -0.05126423651  | 3.733405937645 | -0.037099153054 |
| C | -1.443924330165 | 3.72699608243 | -0.037571706583 |
| C | -2.14488423749  | 2.52276659088 | -0.03704008851 |
| H | -1.977359938134 | 0.379207521172 | -0.035623674105 |
| H | 0.48566682154  | 0.373744783189 | -0.034758983787 |
| H | 0.48586644717  | 4.67156678348 | -0.037527003522 |
| H | -1.977162370089 | 4.66633063185 | -0.038356357947 |
| H | -3.224486895331 | 2.522825927394 | -0.037412261598 |
| S | 2.456870727801  | 2.522566748055 | -0.035441172485 |

PhS$^-$ (anion)

| C | -1.449389385640 | 1.321980547058 | -0.036041492827 |
| C | -0.056597265234 | 1.322902023100 | -0.03552946870 |
| C | 0.674975060683  | 2.522647438050 | -0.03605525356 |
| C | -0.056486702682 | 3.722459947957 | -0.03709748311 |
| C | -1.449278846116 | 3.72350913985 | -0.03750306870 |
| C | -2.159120419136 | 2.52277322472 | -0.03704694248 |
| H | -1.980858736711 | 0.379533935875 | -0.035635673038 |
| H | 0.481350075112  | 0.384651121853 | -0.034766240143 |
| H | 0.481549806580  | 4.660660052191 | -0.037534460315 |
| H | -1.980661706514 | 4.666004276583 | -0.03834983950 |
| H | -3.239657209479 | 2.522826479787 | -0.037415637952 |
| S | 2.487779912742  | 2.522566325258 | -0.035427971771 |

Ph$_2$P$^-$

| P | 1.034921427728  | 1.059632864399 | 0.032440693934 |
| C | -0.113715728954 | 2.476810958523 | -0.260713690547 |
3.3 Hypothetical mechanism involving formation of 1,4-dehydrocubane A

We propose that 1,4-diiodocubane 2 receives an electron from the nucleophile (ArS-/Ph$_2$P–) in a photoinduced process through a dissociative-ET pathway leading directly to 4-iodocubyl radical 17. This intermediate can afford 1,4-dehydrocubane A by homolytic dissociation (with formation of iodine radicals) or by ET (with formation of iodide ions). Another possibility is its reaction with the anion, which is in excess, to afford the radical anion of the mono-iodosubstituted cubane 13 (Scheme 1-SI). Calculations indicated that the preferred reaction is the coupling with the
nucleophile to allow a typical $S_{RN1}$ pathway. Relevant energetic factors ($\Delta G^\circ$) of the three mechanistic possibilities are presented in the next Table 1-SI.6,7

![Scheme 1-SI](image)

Table 1-SI. Energetic values involved in reactions shown at Scheme 1-SI

| Reaction | $\Delta G^\circ$ (kcal/mol) (298 K) |
|----------|----------------------------------|
| ![Reactions](image) | 53.656 |

| Compounds | Electronic Energy (hartrees) | ZPE (hartrees) | $\Delta G+ZPE$ (hartrees) |
|-----------|-----------------------------|----------------|--------------------------|
| 4-Iodocubyl radical, 17 | -605.7025463 | 0.111679 | -605.623883 |
| 1-4 dehydrocubane diradical, A | -307.9851116 | 0.077481 | -307.907631 |
| Iodide radical | -297.6132423 | 0.000000 | -297.630745 |

| Reaction | $\Delta G^\circ$ (kcal/mol) (298 K) |
|----------|----------------------------------|
| ![Reactions](image) | 41.822 |

| Compounds | Electronic Energy (hartrees) | ZPE (hartrees) | $\Delta G+ZPE$ (hartrees) |
|-----------|-----------------------------|----------------|--------------------------|
| 4-Iodocubyl radical, 17 | -605.7025463 | 0.111679 | -605.623883 |
| Thiophenoxide anion, 4^- | -629.8680842 | 0.09096 | -629.806921 |
| 1-4 dehydrocubane diradical, A | -307.9851116 | 0.077481 | -307.907631 |
| Iodide anion | -297.8181529 | 0.000000 | -297.835001 |
| Thiophenyl radical, 4^- | -629.6816788 | 0.090641 | -629.621524 |

| Reaction | $\Delta G^\circ$ (kcal/mol) (298 K) |
|----------|----------------------------------|
| ![Reactions](image) | 11.0 |

| Compounds | Electronic Energy (hartrees) | ZPE (hartrees) | $\Delta G+ZPE$ (hartrees) |
|-----------|-----------------------------|----------------|--------------------------|
### Geometries:

#### 4-iodocubyl radical, \(17\)

| Atom | \(x\) | \(y\) | \(z\) |
|------|-------|-------|-------|
| C    | -0.014345381477 | -0.014648103207 | -0.014015286728 |
| C    | -0.005284423796 | -0.005322099047 | 1.556420974340 |
| C    | 1.570938211811  | -0.007604415900 | 1.522880294516 |
| C    | 1.555668188226  | -0.011751256001 | -0.053607207463 |
| C    | 1.527210130492  | 1.563919039645  | -0.098699814437 |
| C    | -0.048706777697 | 1.555034262158  | -0.053658063307 |
| C    | -0.044915416095 | 1.570394609689  | 1.5228420272205 |
| C    | 1.518914870821  | 1.555417645645  | 1.466205843640 |

| Atom | \(x\) | \(y\) | \(z\) |
|------|-------|-------|-------|
| I    | 1.232703670740 | -1.263086986913 | -1.190015814411 |
| H    | -0.620080820437 | -0.634870728982  | 2.186070440799 |
| H    | 2.129164186334  | 2.180378297153  | -0.752199292284 |
| H    | 2.207435560399  | -0.624505889030  | 2.142328411990 |
| H    | -0.676809870119 | 2.192035548328  | 2.142267295812 |
| H    | -0.69762057750  | 2.147489526206  | -0.685087489113 |
| H    | 2.163401385395  | -0.646371878440  | -0.685028744015 |

#### 1,4-dehydrocubane diradical, \(A\)

| Atom | \(x\) | \(y\) | \(z\) |
|------|-------|-------|-------|
| C    | -0.014345381477 | -0.014648103207 | -0.014015286728 |
| C    | -0.005284423796 | -0.005322099047 | 1.556420974340 |
| C    | 1.570938211811  | -0.007604415900 | 1.522880294516 |
| C    | 1.555668188226  | -0.011751256001 | -0.053607207463 |
| C    | 1.527210130492  | 1.563919039645  | -0.098699814437 |
| C    | -0.048706777697 | 1.555034262158  | -0.053658063307 |
| C    | -0.044915416095 | 1.570394609689  | 1.5228420272205 |
| C    | 1.518914870821  | 1.555417645645  | 1.466205843640 |

All the calculations were performed with the Gaussian09 program,\(^8\) the M06-2X DFT functional and the def2TZV basis set for C, H, O, S and P were employed. The def2TZVP\(^9\) basis set and pseudo-potential was used for I. Calculations were performed with full geometry optimization including in all cases the effect of the solvent (methanol as polar solvent) through the Tomasi’s polarized continuum model (IEFPCM)\(^5,10\) as implemented in the Gaussian package. After refinement the characterization of stationary points was done by Hessian matrix calculations, with all positive eigenvalues for a minimum and only one negative eigenvalue for the TSs. The energy informed for TSs and radicals includes zero-point corrections.
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3.4 Calculations involved in Schemes 4 and 5

3.4.1 Cartesian coordinates and energies (au) at PCM(methanol)-[M06-2X/def2-TZVP]. Spin densities of radicalary species. Imaginary frequencies of Transition States.

I-

\[ E (\text{PCM(methanol)}-[\text{M06-2X/def2-TZVP}]) = -297.818216336 \]

I

\[ E (\text{PCM(methanol)}-[\text{M06-2X/def2-TZVP}]) = -834.375006343 \]

| Atom | X | Y | Z |
|------|----|----|----|
| C    | -0.842921 | 0.039270 | 0.000572 |
| C    | -0.016382 | 0.777171 | -1.087925 |
| C    | 0.829035  | 1.449674 | 0.039020  |
| C    | 1.816091  | 0.255589 | 0.001191  |
| C    | 0.973797  | -0.499235 | 1.083013 |
| C    | -0.009943 | 0.709386 | 1.127832 |
| C    | 0.129349  | -1.172471 | -0.039534 |
| C    | 0.967885  | -0.431247 | -1.122906 |
| H    | 1.395088  | -1.004410 | 1.945455 |
| H    | -0.427500 | 1.278961 | -1.956812 |
| H    | -0.415349 | 1.157082 | 2.028385 |
| H    | 1.121419  | 2.493741 | 0.069660 |
| H    | 1.384742  | -0.881797 | -2.017163 |
| H    | -0.166913 | -2.215062 | -0.071068 |
| C    | 3.293718  | 0.350749 | 0.000055 |
| O    | 3.927038  | 1.377435 | -0.008040 |
| O    | 3.855037  | -0.860501 | -0.000463 |
| C    | 5.285004  | -0.891206 | 0.000228 |
| H    | 5.672579  | -0.396937 | -0.889046 |
| H    | 5.671153  | -0.394878 | 0.889020 |
| H    | 5.559512  | -1.941097 | 0.001771 |
| I    | -2.954814 | -0.108626 | 0.000012 |

I

\[ E (\text{PCM(methanol)}-[\text{M06-2X/def2-TZVP}]) = -834.419503826 \]

| Atom | X | Y | Z |
|------|----|----|----|
| C    | -0.833862 | 0.045533 | 0.014886 |
| C    | -0.031674 | 1.213529 | -0.615357 |
| C    | 0.842727  | 1.269391 | 0.677178 |
| C    | 1.835989  | 0.233211 | 0.076504 |
| C    | 0.997722  | -0.931553 | 0.677676 |
| C    | 0.016943  | 0.105182 | 1.311215 |
| C    | 0.125695  | -0.995673 | -0.616210 |
| C    | 0.934812  | 0.172257 | -1.251113 |
| H    | 1.422821  | -1.790192 | 1.189332 |
| H    | -0.468753 | 2.070291 | -1.118559 |
| H    | -0.383704 | 0.078437 | 2.319416 |
| H    | 1.143869  | 2.179517 | 1.188120 |
H  1.300582  0.198863  -2.273334
H  -0.186852 -1.903409  -1.122446
C  3.297738  0.368931   0.188075
O  3.897896  1.451065  -0.136092
O  3.892960  -0.1868   52 -1.903409 -1.122446
C  5.271480  -0.932650   0.050290
H  5.821130  -0.163694  -0.496717
H  5.472226  -0.799903  1.122116
H  5.622436  -1.917319  -0.259254
I  -2.958793  -0.111104 -0.016709

15*
E (PCM(methanol)-[M06-2X/def2-TZVP])= -536.659167544
C  2.626399  -0.320808   0.000431
C  1.915106   0.466606   1.118990
C  1.164723  1.266981   0.005177
C  0.057926   0.183732  -0.000136
C  0.807720  -0.624150  -1.111108
C  1.917484  0.475490  -1.113309
C  1.555446  -1.431185  -0.005150
C  0.805388  -0.632995  -1.105611
H  0.329827  -1.046074  -1.989877
H  2.353444   0.897826   2.012967
H  2.357804   0.913811  -2.002850
H  0.981653   2.336837   0.009150
H  0.325641  -1.062027  1.979912
H  1.712240  -2.504659  -0.09289
C  -1.399667   0.440217  -0.000270
O  -1.917271  1.529824  -0.000127
O  -2.091666  -0.702208  -0.000420
C  -3.516120  -0.573266   0.000261
H  -3.844230  -0.036985   0.889123
H  -3.845246  -0.037545  -0.888560
H  -3.906223  -1.585850   0.000818

PhS^-
E (PCM(methanol)-[M06-2X/def2-TZVP])= -629.954663140
C  -0.580831   0.000001   0.000024
C  0.160880  -1.194996   0.000003
C  0.160880   1.194996   0.000003
C  1.548483  -1.195343  -0.000002
H  -0.374823  -2.137034  -0.000005
C  1.548485   1.195342   0.000002
H  -0.374820   2.137036  -0.000005
C  2.259241   0.00000   0.000006
H  2.079707  -2.140269  -0.000004
\[
\text{Ph}_2\text{P}^- \\
E (\text{PCM(methanol)}-[\text{M06-2X/def2-TZVP}]) = -804.71295471
\]

\[
P \\ -0.000070 \\ -1.618637 \\ 0.00344
\]

\[
C \\ -1.439373 \\ -0.501883 \\ -0.016730
\]

\[
C \\ -2.661345 \\ -0.988224 \\ 0.486791
\]

\[
C \\ -1.476465 \\ 0.779453 \\ -0.596968
\]

\[
C \\ -3.835036 \\ -0.252444 \\ 0.414152
\]

\[
H \\ -2.681974 \\ -1.969664 \\ 0.950110
\]

\[
C \\ -2.644829 \\ 1.524702 \\ -0.654964
\]

\[
H \\ -0.571775 \\ 1.192961 \\ -1.026284
\]

\[
C \\ -3.839219 \\ 1.018367 \\ -0.150953
\]

\[
H \\ -4.751961 \\ -0.669598 \\ 0.814639
\]

\[
H \\ -2.624990 \\ 2.508660 \\ -1.109908
\]

\[
H \\ -4.750492 \\ 1.600553 \\ -0.196816
\]

\[
C \\ 1.439422 \\ -0.502055 \\ 0.017076
\]

\[
C \\ 1.476762 \\ 0.779116 \\ 0.597691
\]

\[
C \\ 2.661057 \\ -0.988157 \\ -0.487392
\]

\[
C \\ 2.645130 \\ 1.524360 \\ 0.655327
\]

\[
H \\ 0.572272 \\ 1.192450 \\ 1.027597
\]

\[
C \\ 3.834793 \\ -0.252369 \\ -0.415126
\]

\[
H \\ 2.681435 \\ -1.969397 \\ -0.951144
\]

\[
C \\ 3.839262 \\ 1.018197 \\ 0.150478
\]

\[
H \\ 2.625545 \\ 2.508165 \\ 1.110609
\]

\[
H \\ 4.751498 \\ -0.669347 \\ -0.816298
\]

\[
H \\ 4.750546 \\ 1.600392 \\ 0.196044
\]

\[
8^- \\
E (\text{PCM(methanol)}-[\text{M06-2X/def2-TZVP}]) = -1166.61393893
\]

\[
C \\ -4.573523 \\ 1.928233 \\ 0.387639
\]

\[
C \\ -4.096895 \\ 1.653551 \\ -0.925148
\]

\[
C \\ -3.337870 \\ 0.545083 \\ -1.197936
\]

\[
C \\ -2.999992 \\ -0.403081 \\ -0.167073
\]

\[
C \\ -3.445310 \\ -0.090344 \\ 1.167162
\]

\[
C \\ -4.203075 \\ 1.023162 \\ 1.421944
\]

\[
S \\ -1.943806 \\ -1.743388 \\ -0.478954
\]

\[
C \\ -0.293669 \\ -1.082898 \\ -0.223641
\]

\[
C \\ 0.249220 \\ -0.463727 \\ 1.103665
\]

\[
C \\ 1.538779 \\ -1.334856 \\ 0.974273
\]

\[
C \\ 2.216019 \\ -0.199134 \\ 0.166608
\]

\[
C \\ 1.669391 \\ -0.800588 \\ -1.171616
\]

\[
C \\ 1.000523 \\ -1.947661 \\ -0.356168
\]

\[
C \\ 0.381986 \\ 0.066605 \\ -1.040454
\]
8-TS$^{*}$

E (PCM(methanol)-[M06-2X/def2-TZVP]) = -1166.60040615 Neg-Freq= -270.3
| Chemical | X     | Y     | Z     |
|----------|-------|-------|-------|
| H        | -4.535849 | -0.085732 | 2.641036 |
| H        | -5.148785 | 2.173163  | 1.782273 |
| C        | 3.483840  | 0.567661  | 0.595156 |
| O        | 3.838264  | 0.610614  | 1.749278 |
| O        | 4.246243  | 1.004372  | -0.415316 |
| C        | 5.521514  | 1.538128  | -0.055723 |
| H        | 5.399556  | 2.394649  | 0.605575 |
| H        | 6.122388  | 0.779493  | 0.443433 |
| H        | 5.990649  | 1.841774  | -0.986281 |

8

E (PCM(methanol)-[M06-2X/def2-TZVP]) = -1166.56808560
$10^{-}$

E (PCM(methanol)-[M06-2X/def2-TZVP]) = -1341.41737877

| Atom | X | Y | Z |
|------|---|---|---|
| C    | -1.557154 | 0.992353 | -0.798798 |
| C    | -1.479392 | -0.615304 | 1.379781 |
| C    | -2.790167 | 0.338356 | -0.122856 |
| C    | -1.006475 | 1.392934 | 0.602951 |
| C    | -2.240212 | 0.737585 | 1.291674 |
| C    | -0.228295 | 0.039899 | 0.691497 |
| C    | -2.031967 | -1.025529 | -0.016977 |
| C    | -0.801626 | -0.369219 | -0.710496 |
| C    | -1.605526 | 1.639854 | -1.669320 |
| H    | -1.442303 | -1.255328 | 2.257614 |
| H    | -0.578018 | 2.358023 | 0.860313 |
| H    | -2.851109 | 1.180726 | 2.072664 |
| H    | -2.473896 | -1.985009 | -0.270391 |
| H    | -0.223221 | -0.825537 | -1.509290 |
| P    | 1.513304 | -0.043802 | 1.307739 |
| C    | 1.960955 | -1.597519 | 0.393627 |
| C    | 3.186179 | -1.713719 | -0.261898 |
| C    | 1.112350 | -2.707540 | 0.404711 |
| C    | 3.554721 | -2.899297 | -0.887166 |
| H    | 3.848593 | -0.855072 | -0.285198 |
| C    | 1.478690 | -3.897199 | -0.212172 |
| H    | 0.148263 | -2.644688 | 0.900494 |
| C    | 2.703405 | -3.997328 | -0.862482 |
| H    | 4.507363 | -2.965408 | -1.399077 |
| H    | 0.807352 | -4.747159 | -0.187894 |
| H    | 2.990141 | -4.922123 | -1.346972 |
| C    | 2.332416 | 1.260622 | 0.448001 |
| C    | 2.154050 | 1.497496 | -0.971669 |
| C    | 3.190176 | 2.163894 | 1.137484 |
| C    | 2.802667 | 2.548435 | -1.594421 |
| H    | 1.513894 | 0.841012 | -1.550726 |
| C    | 3.827166 | 3.202331 | 0.506648 |
| H    | 3.342266 | 2.018818 | 2.204308 |
| C    | 3.646714 | 3.420048 | -0.899048 |
| H    | 2.648452 | 2.699729 | -2.659578 |
| H    | 4.470569 | 3.860792 | 1.079690 |
| H    | 4.144572 | 4.236431 | -1.405241 |
| C    | -4.201534 | 0.507875 | -0.528076 |
| O    | -4.603456 | 1.268269 | -1.375782 |
| O    | -5.011563 | -0.284801 | 0.182994 |
| C    | -6.407460 | -0.175190 | -0.102509 |
| H    | -6.753429 | 0.839102 | 0.090760 |
| H    | -6.601820 | -0.431005 | -1.142899 |
| H    | -6.902782 | -0.877788 | 0.560117 |
10-TS$^{+}$

E (PCM(methanol)-[M06-2X/def2-TZVP]) = -1341.37921878. Neg-Freq= -135.27

|    |     |     |     |     |     |     |
|----|-----|-----|-----|-----|-----|-----|
| C  | 1.329391 | -0.654727 | -0.623631 |     |     |     |
| C  | 1.595702 | 0.511120  | 1.825587  |     |     |     |
| C  | 2.661243 | -0.217475 | 0.038342  |     |     |     |
| C  | 0.883578 | -1.295650 | 0.728783  |     |     |     |
| C  | 2.220780 | -0.852091 | 1.402432  |     |     |     |
| C  | 0.275198 | 0.067936  | 1.136999  |     |     |     |
| C  | 2.036968 | 1.147987  | 0.473292  |     |     |     |
| C  | 0.697356 | 0.713303  | -0.202061 |     |     |     |
| H  | 1.251402 | -1.119387 | -1.603436 |     |     |     |
| H  | 1.708687 | 0.973193  | 2.802411  |     |     |     |
| H  | 0.423047 | -2.274888 | 0.831428  |     |     |     |
| H  | 2.868616 | -1.475307 | 2.013661  |     |     |     |
| H  | 2.532394 | 2.107603  | 0.349980  |     |     |     |
| H  | 0.085132 | 1.351198  | -0.836285 |     |     |     |
| P  | -2.853239 | 0.184953  | 1.381910  |     |     |     |
| C  | -2.462687 | 1.590894  | 0.294642  |     |     |     |
| C  | -2.791569 | 1.679592  | -1.067452 |     |     |     |
| C  | -1.840268 | 2.716011  | 0.861919  |     |     |     |
| C  | -2.482168 | 2.802617  | -1.822969 |     |     |     |
| H  | -3.301290 | 0.850954  | -1.545172 |     |     |     |
| C  | -1.548568 | 3.848646  | 0.116600  |     |     |     |
| H  | -1.558381 | 2.685349  | 1.909484  |     |     |     |
| C  | -1.853990 | 3.898392  | -1.240042 |     |     |     |
| H  | -2.742412 | 2.825402  | -2.875180 |     |     |     |
| H  | -1.062131 | 4.692026  | 0.593158  |     |     |     |
| H  | -1.610972 | 4.773629  | -1.828892 |     |     |     |
| C  | -2.699659 | -1.277770 | 0.321958  |     |     |     |
| C  | -1.933016 | -1.373788 | -0.853764 |     |     |     |
| C  | -3.294353 | -2.472781 | 0.774529  |     |     |     |
| C  | -1.782573 | -2.574440 | -1.532533 |     |     |     |
| H  | -1.430407 | -0.493029 | -1.233584 |     |     |     |
| C  | -3.133329 | -3.675598 | 0.105498  |     |     |     |
| H  | -3.896288 | -2.448211 | 1.677759  |     |     |     |
| C  | -2.378393 | -3.740287 | -1.063011 |     |     |     |
| H  | -1.178753 | -2.601069 | -2.433091 |     |     |     |
| H  | -3.607324 | -4.569803 | 0.493802  |     |     |     |
| H  | -2.257928 | -4.676672 | -1.592214 |     |     |     |
| C  | 4.014925  | -0.391697 | -0.526720 |     |     |     |
| O  | 4.283559  | -0.988126 | -1.541798 |     |     |     |
| O  | 4.942268  | 0.186169  | 0.245726  |     |     |     |
| C  | 6.296832  | 0.046974  | -0.187224 |     |     |     |
| H  | 6.574609  | -1.005284 | -0.225645 |     |     |     |
| H  | 6.426210  | 0.491109  | -1.172836 |     |     |     |
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1341.36694700
H  -6.450790  -0.821713  -1.439900
H  -6.672810  -1.852462  0.002110

16-reduction
E (PCM(methanol)-[M06-2X/def2-TZVP]) = -537.333453462
C  2.650969  -0.296539  0.000799
C  1.873122  0.482026  1.107059
C  1.102641  1.278086  0.007267
C  -0.002119  0.191251  -0.000406
C  0.771000  -0.605314  -1.106095
C  1.876642  0.494566  -1.098908
C  1.541754  -1.394893  -0.007235
C  0.767542  -0.617897  1.098057
H  0.300448  -1.032759  -1.986057
H  2.309868  0.915533  2.000995
H  2.316338  0.938166  -1.986425
H  0.910334  2.346404  0.012853
H  0.294162  -1.055459  1.971503
H  1.715788  -2.465951  -0.013055
C  -1.461302  0.432916  -0.000550
O  -1.993592  1.516565  -0.000107
O  -2.145123  -0.716471  -0.000753
C  -3.569748  -0.599698  0.000523
H  -3.903066  -0.66191  0.889275
H  -3.904873  -0.066771  -0.887886
H  -3.952087  -1.615371  0.001272
H  3.719796  -0.485381  0.001334

16-reduction-TS
E (PCM(methanol)-[M06-2X/def2-TZVP]) = -593.192486780, Neg.Freq=1693.1
C  1.295859  0.599476  -1.215033
C  0.353078  -0.441733  1.103901
C  2.137167  -0.063992  -0.089051
C  0.277960  -0.577493  -1.101397
C  1.133515  -1.243346  0.018649
C  -0.503076  0.237236  -0.020664
C  1.373874  0.733442  1.000079
C  0.516061  1.399535  -0.122736
H  1.673524  1.010744  -2.145216
H  -0.059159  -0.848250  2.022031
H  -0.191056  -1.094171  -1.932753
H  1.384401  -2.297427  0.074125
H  1.815627  1.253160  1.844009
H  0.249161  2.450222  -0.175871
H  3.389337  -0.194380  -0.142174
N  4.698599  -0.385662  0.028820
| Atoms | X      | Y      | Z      |
|-------|--------|--------|--------|
| H     | 4.829624 | 0.241887 | 0.826907 |
| H     | 4.649754  | -1.314656 | 0.456055 |
| C     | -1.975884 | 0.373674  | 0.031124 |
| O     | -2.581090 | 1.415273  | 0.099466 |
| O     | -2.572039 | -0.821416 | 0.001044 |
| C     | -4.000853 | -0.814166 | 0.055584 |
| H     | -4.340810 | -0.350463 | -0.794605 |
| H     | -4.406871 | -0.268370 | -0.794605 |
| H     | -4.304909 | -1.855322 | 0.018725 |

**NH₃**

E (PCM(methanol)=[M06-2X/def2-TZVP])= -56.5551042794

| Atoms | X      | Y      | Z      |
|-------|--------|--------|--------|
| N     | 0.00000 | 0.00000 | 0.115302 |
| H     | 0.00000  | 0.938000 | -0.269038 |
| H     | -0.812332 | -0.469000 | -0.269038 |
| H     | 0.812332  | -0.469000 | -0.269038 |

**NH₂⁺**

E (PCM(methanol)=[M06-2X/def2-TZVP])= -55.8743600454

| Atoms | X      | Y      | Z      |
|-------|--------|--------|--------|
| N     | 0.00000 | 0.00000 | 0.141016 |
| H     | 0.00000  | 0.804431 | -0.493556 |
| H     | 0.00000  | -0.804431 | -0.493556 |

2

E (PCM(methanol)=[M06-2X/def2-TZVP])= -903.519254608

| Atoms | X      | Y      | Z      |
|-------|--------|--------|--------|
| C     | -0.445663 | -0.209862 | 1.263676 |
| C     | 0.445679  | 0.209956 | -1.263662 |
| C     | -1.325956 | 0.000423 | 0.000065 |
| C     | 0.444880  | -1.199292 | 0.449767 |
| C     | -0.445666 | -0.988949 | -0.813539 |
| C     | 1.325962  | -0.000386 | -0.000066 |
| C     | -0.444909 | 1.199366  | -0.449781 |
| C     | 0.445685  | 0.989018  | 0.813489 |
| H     | -0.821170 | -0.376448 | 2.267170 |
| H     | 0.821238  | 0.376565  | -2.267137 |
| H     | 0.819883  | -2.152323 | 0.806327 |
| H     | -0.821604 | -1.774916 | -1.459173 |
| H     | -0.819906 | 2.152397  | -0.806337 |
| H     | 0.821670  | 1.774992  | 1.459096 |
| I     | 3.435168  | -0.000040 | 0.000033 |
| I     | -3.435171 | 0.000004  | -0.000026 |

17

E (PCM(methanol)=[M06-2X/def2-TZVP])= -605.806842164

| Atoms | X      | Y      | Z      |
|-------|--------|--------|--------|
| C     | -2.142416 | -0.866181 | 0.955982 |
| C     | -1.257694 | 0.863326  | -0.952827 |
C  -2.988006  -0.000773  -0.000479  
C  -1.256712  -1.257180  -0.270899  
C  -2.142111  -0.395187  -1.228185  
C  -0.387569  0.000219  0.000350  
C  -2.143578  1.260937  0.271667  
C  -1.258022  0.393923  1.224108  
H  -2.492275  -1.555197  1.717194  
H  -0.878889  1.545969  1.706240  
H  -0.877414  2.250794  0.485088  
H  -2.491137  -0.709386  -2.205949  
H  -2.494371  2.264333  0.488027  
H  -0.880198  0.705375  2.192305  
I   1.727753  0.000098  0.000027  

13b^--
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1235.76278131  
C  -4.927640  -2.031408  0.000188  
C  -4.550439  -1.396082  1.216166  
C  -3.872330  -0.204677  1.225884  
C  -3.528479  0.471384  0.000081  
C  -3.871794  -0.205085  1.225650  
C  -4.549889  -1.396497  -1.215833  
S  -2.491245  1.863589  0.000075  
C  -0.836234  1.165881  0.000030  
C  -0.238415  0.238881  -1.106933  
C   1.061298  1.102068  -1.109788  
C   1.639296  0.183736  -0.000051  
C   1.061275  1.101837  1.109866  
C   0.469813  2.024561  0.000129  
C  -0.238438  0.238650  1.106809  
C   0.353281  -0.686337  -0.000154  
I   3.618784  -0.590014  -0.000121  
H   1.603022  1.433877  1.989493  
H  -0.775372  -0.099694  -1.987612  
H   0.504364  3.109747  0.000243  
H   1.603063  1.434291  -1.989334  
H   0.327882  -1.770981  -0.000269  
H  -0.775414  -0.100110  1.987405  
H  -3.595689  0.252850  2.170427  
H  -3.594739  0.252131  -2.170224  
H  -4.804536  -1.861474  2.163789  
H  -4.803559  -1.862209  -2.163414  
H  -5.452495  -2.976601  0.000231  

13b^---TS  
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1235.74940822. Neg-Freq= -246.9
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 0.604475   | -0.119185  | 1.028537   |
| C       | 0.431485   | 1.676301   | -1.002728  |
| C       | 1.714371   | 0.232261   | 0.002780   |
| C       | 0.324270   | 1.406579   | 1.199850   |
| C       | 1.449771   | 1.750217   | 0.176305   |
| C       | -0.698212  | 1.334567   | 0.020790   |
| C       | 0.711377   | 0.151323   | -1.178926  |
| C       | -0.415346  | -0.182456  | -0.151091  |
| H       | 0.704702   | -0.848639  | 1.827215   |
| H       | 0.370243   | 2.395796   | -1.816076  |
| H       | 0.177016   | 1.909214   | 2.153028   |
| H       | 2.221149   | 2.504140   | 0.306076   |
| H       | 0.895656   | -0.363361  | -2.117730  |
| H       | -1.177067  | -0.948796  | -0.279136  |
| C       | -3.682780  | 0.422658   | -0.008310  |
| C       | -3.981424  | -0.262871  | 1.204762   |
| C       | -4.003869  | -0.268592  | -1.212386  |
| C       | -4.551686  | -1.520075  | 1.205149   |
| H       | -3.747743  | 0.223961   | 2.144731   |
| C       | -4.574996  | -1.524259  | -1.197043  |
| H       | -3.786011  | 0.212833   | -2.159014  |
| C       | -4.857900  | -2.179338  | 0.008942   |
| H       | -4.761791  | -2.002826  | 2.153663   |
| H       | -4.803851  | -2.011181  | -2.138965  |
| H       | -5.302170  | -3.165512  | 0.015552   |
| S       | -2.838992  | 1.913609   | -0.016955  |
| I       | 3.656915   | -0.642003  | -0.007506  |

**13b**

E (PCM(methanol)-[M06-2X/def2-TZVP]) = -1235.71640352

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -4.885132  | -1.989128  | 0.000061   |
| C       | -4.524495  | -1.395369  | 1.202779   |
| C       | -3.800559  | -0.210429  | 1.204923   |
| C       | -3.432469  | 0.382738   | 0.000038   |
| C       | -3.800323  | -0.210599  | -1.204837  |
| C       | -4.524251  | -1.395543  | -1.202670  |
| S       | -2.474991  | 1.883565   | 0.000024   |
| C       | -0.856914  | 1.150647   | -0.000007  |
| C       | -0.258373  | 0.228939   | -1.108883  |
| C       | 1.036751   | 1.098200   | -1.109505  |
| C       | 1.620943   | 0.181762   | -0.000020  |
| C       | 1.036749   | 1.098169   | 1.109492   |
| C       | 0.440568   | 2.017084   | 0.000006   |
| C       | -0.258375  | 0.228909   | 1.108841   |
| C       | 0.336075   | -0.691834  | -0.000033  |
|   |       |       |       |
|---|-------|-------|-------|
| I | 3.595972 | -0.584418 | -0.000031 |
| H | 1.572867 | 1.436205 | 1.989441 |
| H | -0.789831 | -0.111785 | 1.991757 |
| H | 0.463418 | 3.101697 | 0.000020 |
| H | 1.572870 | 1.436261 | -1.989444 |
| H | 0.310635 | -1.775974 | 0.000049 |
| H | -0.789843 | -0.111838 | 1.991701 |
| H | -3.520066 | 0.259445 | 2.139070 |
| H | -3.519655 | 0.259150 | -2.138995 |
| H | -5.451678 | -2.911274 | 0.000070 |

13d
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1410.51551002

|   |       |       |       |
|---|-------|-------|-------|
| C | 3.047426 | -3.804228 | -1.136560 |
| C | 3.073719 | -2.559377 | -1.754270 |
| C | 2.786077 | -1.413226 | -1.026488 |
| C | 2.473632 | -1.496071 | 0.331397 |
| C | 2.458943 | -2.749327 | 0.943154 |
| C | 2.737799 | -3.898604 | 0.213235 |
| C | 0.273901 | 0.092463 | 0.794659 |
| C | -0.758540 | -1.029421 | 1.156941 |
| C | -1.780929 | 0.054862 | 1.609984 |
| C | -2.324603 | 0.107007 | 0.156510 |
| C | -1.319982 | 1.232910 | -0.211371 |
| C | -0.764883 | 1.177787 | 1.245673 |
| C | -0.301200 | 0.141714 | -0.663485 |
| C | -1.314512 | -0.983314 | -0.296678 |
| I | -4.382224 | 0.127402 | -0.350154 |
| H | -1.565065 | 2.135862 | -0.761095 |
| H | -0.517732 | -1.934680 | 1.706338 |
| H | -0.537315 | 2.041729 | 1.862549 |
| H | -2.390966 | 0.017853 | 2.505949 |
| H | -1.553834 | -1.845987 | -0.909120 |
| H | 0.291036 | 0.177163 | -1.572796 |
| H | 2.814048 | -0.446852 | -1.516407 |
| H | 2.232464 | -2.826735 | 2.000826 |
| H | 3.318656 | -2.481362 | -2.806029 |
| H | 2.721628 | -4.864414 | 0.701972 |
| H | 3.274553 | -4.696849 | 1.705282 |
| P | 2.000669 | -0.038334 | 1.347357 |
| C | 2.811083 | 1.325747 | 0.434477 |
| C | 2.107015 | 2.352324 | -0.192442 |
| C | 4.207819 | 1.368956 | 0.424483 |
| C | 2.782936 | 3.393840 | -0.820096 |
| At   | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 1.024299 | 2.355089 | -0.199128 |
| C    | 4.882296  | 2.399269 | -0.211640 |
| H    | 4.771962  | 0.583466 | 0.916271 |
| C    | 4.169417  | 3.417825 | -0.835572 |
| H    | 2.220938  | 4.183566 | -1.302483 |
| H    | 5.964708  | 2.412093 | -0.216373 |
| H    | 4.693972  | 4.225960 | -1.328881 |

**E (PCM(methanol)-[M06-2X/def2-TZVP])= E=-1123.9904298**

| At   | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 0.591041780680 | 0.280063216859 | -0.346703968358 |
| C    | 0.832990251243  | 0.00503769053  | 1.00731216925  |
| C    | 2.115780280099  | -0.001147507851 | 1.54241963775  |
| C    | 3.258218410717  | 0.286669619490  | 0.693379427027 |
| C    | 2.997709641957  | 0.557914564658  | -0.678979797414 |
| C    | 1.720731077962  | 0.560416634217  | -1.197159554054 |
| C    | 4.957651308741  | -1.277180526702  | 2.429189473696 |
| C    | 4.338494722321  | -2.651859855339  | 1.979303190317 |
| C    | 5.62669777202   | -3.403372414789  | 2.481724019273 |
| C    | 4.958005794252  | -3.547141936209  | 3.893553039542 |
| C    | 5.856128693785  | -2.187897116969  | 4.363121079646 |
| C    | 6.246723296041  | -2.034212207843  | 2.944285648228 |
| C    | 4.297856478943  | -1.446472997927  | 3.852746795046 |
| C    | 3.666517926907  | -2.81062401083   | 3.390621970776 |
| I    | 4.950294641849  | -5.341074182291  | 5.054726084197 |
| H    | 6.078626056553  | -2.02270406232   | 5.313458913116 |
| H    | 3.844178838925  | -2.813340668208  | 1.028570390362 |
| H    | 7.26817373641   | -1.721598478955  | 2.759221202070 |
| H    | 6.149476320066  | -4.193607578824  | 1.957632276658 |
| H    | 2.650365658209  | -3.136295796762  | 3.574126758423 |
| H    | 3.780103751159  | -0.66207946453   | 4.392066327184 |
| H    | 2.265815412872  | -0.208617360458  | 2.594959058358 |
| H    | 3.838888016332  | 0.768592323460   | -1.333045251812 |
| H    | -0.006946993445 | -0.212180964196  | 1.659763222808 |
| H    | 1.565139088489  | 0.77165713222   | -2.47894392796 |
| H    | -0.414163510151 | 0.277476430138  | -0.744550639963 |
| P    | 4.958227774208  | 0.245101118986  | 1.316746214086 |
| C    | 4.997327747262  | 1.485158859739  | 2.750736315937 |
| C    | 5.983627417392  | 1.363078511424  | 3.735419697697 |
| C    | 4.097110564500  | 2.548247851449  | 2.825720897558 |
| C    | 6.074149937720  | 2.290655931248  | 4.771679879452 |
| H    | 6.686713969258  | 0.538933942009  | 3.694713217754 |
| C    | 4.180072956042  | 3.475283547884  | 3.866147868456 |
| H    | 3.328315497563  | 2.638912908759  | 2.068167729613 |
| C    | 5.170010119397  | 3.350347320843  | 4.840208745248 |
| H    | 6.845299603958  | 2.186822778353  | 5.523003910991 |

**13d**

E (PCM(methanol)-[M06-2X/def2-TZVP])= E=-1123.9904298
14b
E (PCM(methanol)-[M06-2X/def2-TZVP])= -938.002171856

14d
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1112.79997302
H  1.123666  -3.349935  1.585111
H  0.665618  -0.592634  1.923436
P  -0.175863  0.077618  -1.289097
C  -1.749965  -0.477880  -0.536899
C  -2.913751  0.215247  -0.880544
C  -1.853211  -1.574230  0.317096
C  -4.144336  -0.163590  0.367760
H  -2.853333  1.065402  -1.551910
C  -3.089603  -1.963251  0.822259
H  -0.972828  -2.137476  0.599801
C  -4.235558  -1.257526  0.486423
H  -5.034093  0.390799  -0.637950
H  -3.151854  -2.817484  1.484521
H  -5.196066  -1.558809  0.884170
C  0.098768  1.676417  -0.421504
C  -0.452472  1.970843  0.825934
C  0.943569  2.610433  -1.021487
C  -0.164588  3.172205  1.458471
H  -1.116344  1.259588  1.303289
C  1.240981  3.809170  -0.384181
H  1.368416  2.401237  -1.997174
C  0.684542  4.092684  0.855474
H  -0.602787  3.389467  2.424462
H  1.899565  4.524061  -0.860819
H  0.907215  5.029870  1.349275

12b^-
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1567.95513041
C  0.337040  1.329061  -0.000306
C  -0.423071  -1.269607  0.000199
C  0.692781  0.292711  1.107123
C  0.692747  0.292296  1.107355
C  -0.776633  -0.234105  -1.109244
C  -0.776603  -0.233682  1.109255
H  0.616465  2.378582  -0.000507
H  -0.712307  -2.316911  0.000402
H  1.300457  0.493530  1.984552
H  1.300396  0.492789  -1.984877
H  -1.384356  -0.431008  -1.988000
H  -1.384297  -0.430253  1.988104
C  1.050284  -0.750650  0.000073
C  -1.131446  0.804619  -0.000190
S  2.470901  -1.847362  0.000245
C  3.842569  -0.785868  0.000157
C  4.398041  -0.271121  1.226219
C  4.398044  -0.271336  -1.225994
C        5.440396     0.619176     1.216756
H        3.985681 -0.612098     2.170247
C        5.440395     0.618966    -1.216684
H        3.985681 -0.612472    -2.170247
C        6.009820    1.090600    -0.000005
H        5.837366     0.970938     2.164376
H        5.837362     0.970569    -2.164365
C        6.009820    1.090600    -0.000005
H        5.837366     0.970938     2.164376
H        5.837362     0.970569    -2.164365
S        -2.517484     1.918951    -0.000407
C        -3.830352     0.716449    -0.000151
C        -4.343436     0.241261     1.204608
C        -4.342752     0.240007    -1.204703
C        -5.357593    -0.707046    -1.202551
H        -3.948104     0.619647    -2.138833
C        -5.356914    -0.708293    -1.202551
H        -3.946850     0.617378    -2.139097
C        -5.864564    -1.183045     0.000264
H        -5.752647    -1.072498     2.142113
H        -5.751417    -1.074745    -2.141635
H        -6.657256    -1.920163     0.000421

12d**
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1917.55528892
C   -0.760397   -0.635645     0.111865
C    0.546892    0.554422    -1.941231
C   -1.419616    0.285432    -0.971630
C    0.020916   -1.374357    -1.012884
C   -0.622743   -0.459524    -2.098579
C    1.212547   -0.368216    -0.862312
C   -0.232769   1.296413    -0.817759
C    0.405331    0.380458     0.267748
H   -1.292430   -1.116146     0.928897
H    1.085977    1.034353    -2.754058
H    0.144660   -2.453001    -1.085725
H   -1.052683   -0.795702    -3.038702
H   -0.359642    2.373956    -0.739828
H    0.807342    0.720436    1.217399
P    2.937813   -0.975735    -0.981361
C    3.830890    0.646420    -1.041959
C    5.150809    0.638157    -1.503521
C    3.302330    1.865148    -0.607460
C    5.916681    1.794232    -1.530809
H    5.581813   -0.297089    -1.847981
C    4.065707    3.029095    -0.632088
H    2.282662    1.917608    -0.244689
C    5.374268    2.999468    -1.092808

S65
H   6.934693  1.759517  -1.899332
H   3.634806  3.961322  -0.286464
H   5.967765  3.904754  -1.111319
C   3.326370 -1.636265   0.616376
C   3.290284 -0.851963   1.832941
C   3.855918 -2.960532   0.741992
C   3.718346 -0.301886   3.031481
H   2.937898  0.172724   1.794319
C   4.269730 -3.473595   1.944104
H   3.924182 -3.577272  -0.150371
C   4.205960 -2.692959   3.137825
H   3.677140 -0.754429   3.920395
H   4.650560  0.448336  -0.590264
H   3.913374 -4.031270  -1.095461
H   7.343741 -1.556766  -0.425328
H   6.343286 -3.809913  -0.683880
C   3.260790  1.606732   0.601357
C   3.045516  2.977562   0.743921
C   3.495112  0.840992   1.744491
C   3.050920  3.570619   2.090536
C   3.511342  1.433709   2.999419
C   3.285759  2.799135   3.130261
H   2.874470  3.586712  -0.136851
H   3.671980 -0.224243   1.652373
H   2.879917  4.635442   2.095209
H   3.698727  0.828785   3.877743
H   3.298608  3.259522   4.109960

12b--TS
E (PCM(methanol)-[M06-2X/def2-TZVP])= -1567.94122128  Neg-Freq=-265.7
C   -0.700762 -2.853041   0.144067
C   0.379469 -0.387849  -0.127337
C   0.156068 -2.379857  -1.069639
C   0.305721 -2.201127   1.140325
C   -0.482270 -0.854656   1.086754
C   -0.631280 -1.033596  -1.125618

S66
**12d--TS**

E (PCM(methanol)-[M06-2X/def2-TZVP]) = -1917.51809151  \text{Neg-Freq} = -135.1
14b
E (PCM(methanol)-[M06-2X/def2-TZVP])= -938.676890058

14b-TS
E (PCM(methanol)-[M06-2X/def2-TZVP])= -994.535682288. Neg-Freq: -1689.01
14d

E (PCM(methanol)-[M06-2X/def2-TZVP])= -1113.47198784
| Element | X   | Y    | Z    |
|---------|-----|------|------|
| C       | 0.715862 | 4.245798 | 0.678057 |
| H       | 2.792684  | 3.757660  | 0.906395  |
| H       | -1.394815 | 4.435281  | 0.323917  |
| H       | 0.814811  | 5.229552  | 1.118595  |
| P       | 0.249230  | 0.066357  | -1.271541 |
| H       | -4.483610 | -1.820889 | 1.083428  |
| C       | 1.545095  | -0.929691 | -0.441771 |
| C       | 3.732153  | -1.958865 | -0.577224 |
| C       | 2.418730  | -2.199098 | 1.421458  |
| C       | 2.489093  | 0.715949  | 0.584473  |
| C       | 1.902451  | -1.364623 | -1.054723 |
| C       | 3.444829  | -0.434691 | 0.171909  |
| H       | 0.513323  | -1.230998 | 1.426600  |
| H       | 2.824760  | -0.833477 | -2.162121 |
| H       | 2.297947  | -2.590971 | 2.423450  |
| H       | 4.635129  | -2.161578 | -1.138830 |
| H       | 4.371214  | -3.053023 | 1.154848  |

**14d-TS**

E (PCM(methanol)-[M06-2X/def2-TZVP]) = -1169.33306707. Neg-Freq=-1660.3

| Element | X   | Y    | Z    |
|---------|-----|------|------|
| C       | 0.715862 | 4.245798 | 0.678057 |
| C       | 1.902451 | -1.364623 | -1.054723 |
| C       | 3.444829 | -0.434691 | 0.171909 |
| C       | 2.047772 | 0.837021 | -0.904804 |
| C       | 3.019057 | -0.309680 | -1.317155 |
| C       | 0.917361 | -0.215722 | -0.646963 |
| C       | 2.341078 | -1.493275 | 0.437683 |
| C       | 1.372599 | -0.339804 | 0.847498 |
| C       | 2.730533 | 1.551127 | 1.234432 |
| H       | 1.654535 | -2.194804 | -1.710261 |
| H       | 1.906887 | 1.770645 | -1.442866 |
| H       | 3.681666 | -0.295084 | -2.176267 |
| H       | 2.466077 | -2.429156 | 0.974031 |
| H       | 0.708094 | -0.352926 | 1.706765 |
| C       | -1.732500 | -1.226421 | -0.467113 |
| C       | -3.125931 | -1.131535 | -0.513629 |
| C       | -1.159301 | -2.324932 | 0.171051 |
| C       | -3.923993 | -2.097467 | 0.078555 |
| H       | -3.590472 | -0.287701 | -1.012663 |
| C       | -1.959594 | -3.301290 | 0.755249 |
| H       | -0.082728 | -2.432931 | 0.220028 |
| C       | -3.341322 | -3.188656 | 0.714896 |
| H       | -5.001800 | -2.002613 | 0.040293 |
| H       | -1.497351 | -4.147853 | 1.247001 |
| H       | -3.963271 | -3.946198 | 1.174074 |
| P       | -0.746797 | 0.053595 | -1.327504 |
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| H | 4.636549  | -0.566450 | 0.540326  |
| N | 5.850427  | -0.635463 | 1.115025  |
| H | 5.949962  | 0.356480  | 1.347791  |
| H | 5.559173  | -1.063152 | 1.998449  |
| C | -1.172852 | 1.561047  | -0.365392 |
| C | -1.581009 | 1.529759  | 0.968991  |
| C | -1.017434 | 2.796810  | -0.993492 |
| C | -1.827756 | 2.709220  | 1.657682  |
| C | -1.254448 | 3.978720  | -0.302017 |
| C | -1.662904 | 3.935564  | 1.023788  |
| H | -1.713367 | 0.577636  | 1.469417  |
| H | -0.712153 | 2.833722  | -2.033440 |
| H | -2.147992 | 2.672196  | 2.691328  |
| H | -1.128956 | 4.930830  | -0.801681 |
| H | -1.857596 | 4.854588  | 1.561689  |

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3.4.2 HOMO-LUMO Levels of selected compounds

HOMO-LUMO Levels of selected compounds
Represented with an isovalue of 0.05

| Compound | HOMO | LUMO | HOMO | LUMO |
|----------|------|------|------|------|
| 1        |      |      |      |      |
| 2        |      |      |      |      |
| PhS⁻     |      |      |      |      |
| Ph2P⁻    |      |      |      |      |

| Compound | HOMO | LUMO | HOMO | LUMO |
|----------|------|------|------|------|
| 1        |      |      |      |      |
| 2        |      |      |      |      |
| 8        |      |      |      |      |
| 12b      |      |      |      |      |
| 13b      |      |      |      |      |
HOMO-LUMO Levels of selected compounds

Energy (hartree)

LUMO + 1
LUMO
0.024
0.004
0.0034
0.0017
0.0005
0.0043
0.0028

-0.307
-0.303
HOMO
HOMO

-0.271
-0.276
-0.271

Compound
1
2
10
12d
13d
3.4.3 Estimation of the Activation barrier by Marcus and Savéant’s models

There can be different scenarios for dissociative electron transfer (DET) from the nucleophiles to the cubane derivatives. If ET and cleavage of the C-I bond in the iodocubane occur in different steps and involve the formation of the cubane-halide radical anion, the outer-sphere ET model is applicable and the activation barrier may be estimated from the outer-sphere Marcus-Hush model. Otherwise, when the ET and aryl halide bond cleavage are concerted (concerted dissociative ET), Savéant’s model is used.

The reorganization energy \( \lambda_0 \) according to Marcus equation can be calculated with:

\[
\lambda_0 = (332 \text{ kcal/mol}) \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \left( \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon} \right) \right) \tag{1}
\]

where \( a_1 \) and \( a_2 \) are the radii of the reactant molecules and \( R = a_1 + a_2 \). \( \varepsilon_{op} \) is the optical dielectric constant and \( \varepsilon \) is the static dielectric constant. The inner reorganization energy was estimated to be \( \lambda_i \approx 0 \).

The Marcus equation is:

\[
\Delta G_{ET}^\dagger = \Delta G_0 \left(1 + \frac{\Delta G_r}{4\Delta G_0^\dagger}\right)^2 \tag{2}
\]

where \( \Delta G_r \) is the reaction energy and \( \Delta G_0^\dagger \) is the intrinsic barrier. Within the Marcus Model the equation 3 was used, while in the Savéant Model equation 4 was used:

\[
\Delta G_0^\dagger = \frac{\lambda}{4} = \frac{\lambda + \lambda_0}{4} \tag{3}
\]

\[
\Delta G_0^\dagger = \frac{\lambda}{4} = \frac{\lambda + \lambda_0 + \text{BDFE}}{4} \tag{4}
\]

where BDFE stand for bond dissociation free energy of diiodocubane (60.0 kcal/mol).

**Single Electron Transfer from 8\(^-\) to 1 by Marcus-Hush Model**

| Solvent | \( \Delta G \) (kcal/mol) | \( \varepsilon_{op} \) | \( \varepsilon \) | \( \lambda_0 \) (kcal/mol) | \( \lambda_i \) (kcal/mol) | \( \lambda \) (kcal/mol) | \( \Delta G_{ET}^\dagger \) |
|---------|--------------------------|----------------|----------------|--------------------------|--------------------------|--------------------------|----------------|
| Methanol | +3.1 | 32.6 | 1.76 | 17.6 | 0.0 | 17.6 | +6.1 |
| a\(_0\)(7\(^-\)) | 5.38 Å | | | | | | |
| a\(_0\)(1a) | 4.79 Å | | | | | | |

**Single Electron Transfer from 10\(^-\) to 1 by Marcus-Hush Model**

| Solvent | \( \Delta G \) (kcal/mol) | \( \varepsilon_{op} \) | \( \varepsilon \) | \( \lambda_0 \) (kcal/mol) | \( \lambda_i \) (kcal/mol) | \( \lambda \) (kcal/mol) | \( \Delta G \) |
|---------|--------------------------|----------------|----------------|--------------------------|--------------------------|--------------------------|--------|
| Methanol | +6.1 | 32.6 | 1.76 | 17.6 | 0.0 | 17.6 | +8.0 |
| a\(_0\)(9\(^-\)) | 5.51 Å | | | | | | |
| a\(_0\)(1a) | 4.79 Å | | | | | | |
3.3.3 DFT functional and post-HF methods for Activation Gibb Energies ($\Delta G^\ddagger$, in kcal/mol), Activation Enthalpy ($\Delta H^\ddagger$, in kcal/mol)

Table 1. Computed Activation Gibb Energies ($\Delta G^\ddagger$, in kcal/mol), Activation Enthalpy ($\Delta H^\ddagger$, in kcal/mol) in the solvent and Kinetic parameters computed (log k) for the reaction between radical 15 and $\text{-SPh}$. The numbers in parenthesis are in the gas phase.

| Functional                        | $\Delta H^\ddagger$ | $\Delta G^\ddagger$ | Log k |
|-----------------------------------|----------------------|----------------------|-------|
| M06-2X/def2-TZVP (results presented in the manuscript) | 8.7 (-5.2)          | 17.6 (4.2)          | 1.6   |
| M06-HF/def2-TZVP                  | 6.3 (-8.3)           | 15.9 (1.6)          | 3.8   |
| M06-L/def2-TZVP                   | 9.2 (-4.7)           | 17.9 (5.0)          | 1.2   |
| M06/def2-TZVP                     | 7.2 (-5.8)           | 18.4 (5.5)          | 3.0   |
| B3LYP/def2-TZVP                   | 10.9 (-2.9)          | 19.2 (6.5)          | -0.3  |
| B3LYP+D3(BJ)/def2-TZVP            | 5.8 (-8.2)           | 14.3 (2.2)          | 4.3   |
| B3PW91+D3(BJ)/def2-TZVP           | 4.1 (-9.0)           | 12.9 (1.4)          | 5.9   |
| BH&HLYP/def2-TZVP                 | 15.6 (2.0)           | 27.1 (12.4)         | -4.6  |
| PBE0/def2-TZVP                    | 8.2 (-4.7)           | 16.3 (5.1)          | 2.1   |
| PBE0+D3(BJ)/def2-TZVP             | 4.9 (-8.0)           | 14.0 (1.8)          | 5.1   |
| TSPPh+D3(BJ)/def2-TZVP            | 3.4 (-9.5)           | 12.0 (1.4)          | 6.4   |
| wB97/def2-TZVP                    | 12.0 (-1.8)          | 22.6 (8.7)          | -1.4  |
| wB97X/def2-TZVP                   | 11.6 (-2.1)          | 22.8 (7.8)          | -1.0  |
Kinetic parameters computed (log k) were calculated from the Eyring-Polanyi equation (see below). This equation comes actually from the extension of Arrhenius equation but employing the Transition State Theory. The logarithmic expression is

\[
\log k = \log \kappa \frac{k_B T}{h} = \frac{\Delta G^+}{2.303RT}
\]

\[
\log k = \log \kappa \frac{k_B T}{h} + \frac{\Delta S^+}{2.303R} - \frac{\Delta H^+}{2.303RT}
\]

where \(\kappa\) is the transmission coefficient (normally taken as the unit), \(k_B\) is the Boltzmann’s constant, \(h\) is Planck’s constant, \(\Delta S^+\) activation entropy and \(\Delta H^+\) activation enthalpy.