

## SUPPORT INFORMATION

# Substituent effects on intramolecular Schmidt reactions: a theoretical study on the formation of bridged lactams

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### Table of Contents

<b>1. The parent reaction .....</b>	<b>6</b>
<i>Figure S1. Optimized geometries for the formation of 1(II) from I (Figure 1) and energy profile obtained from intrinsic reaction coordinates calculations using M06-2X/6-31+G(d,p) level of theory.</i>	6
<i>Figure S2. Optimized geometries for the formation of 1(III) from I (Figure 1) and energy profile obtained from intrinsic reaction coordinates calculations using M06-2X/6-31+G(d,p) level of theory.</i>	6
1.2. NBO analysis.....	7
<i>Table S1. Total hyperconjugation energy (kcal mol<sup>-1</sup>) for species involved in the rate-determining step of system 1. ....</i>	7
1.3. Cartesian coordinates of ketoazide I (blue pathway, Figure 1).....	7
1.4 Cartesian coordinates of 1(II)-TSS1.....	8
1.5 Cartesian coordinates of 1(II)-INT.....	8
1.6 Cartesian coordinates of 1(II)-TSS2.....	9
1.7 Cartesian coordinates of lactam 1(II).....	10
1.8 Cartesian coordinates of ketoazide I (red pathway, Figure 1).....	10
1.9 Cartesian coordinates of 1(III)-TSS1.....	11
1.10 Cartesian coordinates of 1(III)-INT.....	12
1.11 Cartesian coordinates of 1(III)-TSS2.....	12
1.12 Cartesian coordinates of lactam 1(III).....	13
1.13 Cartesian coordinates of 1(III)-INT-Conformer-B.....	14
1.14 Cartesian coordinates of 1(III)-TSS2-Conformer-B.....	14
<b>2. Screening of functionals and basis sets. ....</b>	<b>15</b>
<i>Table S2. Energy barriers (in kcal mol<sup>-1</sup>)<sup>[a]</sup> and product distribution (%)<sup>[b]</sup> obtained using different levels of theory.. ....</i>	15
<b>3. Calculation data for system 1 (R<sub>1</sub>=H and R<sub>2</sub>=H) using M06-2X/6-311++G(d,p) level of theory.</b>	<b>15</b>
3.1 Cartesian coordinates of 1(II)-INT.....	15

3.2 Cartesian coordinates of 1(II)-TSS2.....	16
3.3 Cartesian coordinates of 1(III)-INT.....	17
3.4 Cartesian coordinates of 1(III)-TSS2.....	17
<b>4. Calculation data for systems 2 (R<sub>1</sub>=SCH<sub>3</sub> and R<sub>2</sub>=H) and 3 (R<sub>1</sub>=H and R<sub>2</sub>=SCH<sub>3</sub>) using M06-2X/6-311++G(d,p) level of theory.....</b>	<b>18</b>
4.1. IRCs.....	19
<i>Figure S3. Optimized geometries for the formation of 2(II) from 2(II)-INT and and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....</i>	<i>19</i>
<i>Figure S4. Optimized geometries for the formation of 2(III) from 2(III)-INT and and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....</i>	<i>19</i>
<i>Figure S5. Optimized geometries for the formation of 3(II) from 3(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.....</i>	<i>20</i>
<i>Figure S6. Optimized geometries for the formation of 3(III) from 3(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....</i>	<i>20</i>
4.2. NCI .....	21
<i>Figure S7. NCI isosurfaces for 3(II)-INT (top left), 3(II)-TSS2 (top right), 3(III)-INT (bottom left) and 3(III)-TSS2 (bottom right) obtained at M06-2X/6-311++G(d,p) level of theory using a blue-green-red color scale from <math>-0.04 &lt; \text{sign}(\lambda^2)\rho &lt; 0.04</math> a.u. Plots of the reduced density gradient and <math>\text{sign}(\lambda^2)\rho</math> are shown right under each correlated NCI isosurface obtained at the same level of theory. ....</i>	<i>22</i>
4.3 NBO analysis.....	20
<i>Table S3. Total donor-acceptor interactions of type <math>n(S) \leftrightarrow \sigma^*, \pi^*(N-N)</math> (in kcal mol<sup>-1</sup>) of system 2 (R<sub>1</sub>=SCH<sub>3</sub>, R<sub>2</sub>=H) and system 3 (R<sub>1</sub>=H, R<sub>2</sub>=SCH<sub>3</sub>) obtained by NBO calculations at M06-2X/6-311++G(d,p) level of theory.....</i>	<i>20</i>
4.4 Cartesian coordinates of 2(II)-INT.....	22
4.5 Cartesian coordinates of 2(II)-TSS2.....	23
4.6 Cartesian coordinates of 2(II) .....	23
4.7 Cartesian coordinates of 2(III)-INT.....	24
4.8 Cartesian coordinates of 2(III)-TSS2.....	25
4.9 Cartesian coordinates of 2(III) .....	26
4.10 Cartesian coordinates of 3(II)-INT.....	26
4.11 Cartesian coordinates of 3(II)-TSS2.....	27
4.12 Cartesian coordinates of 3(II) .....	28
4.13 Cartesian coordinates of 3(III)-INT.....	29
4.14 Cartesian coordinates of 3(III)-TSS2.....	29
4.15 Cartesian coordinates of 3(III) .....	30
<b>5. Calculation data for systems 4 (R<sub>1</sub>=OCH<sub>3</sub> and R<sub>2</sub>=H) and 5 (R<sub>1</sub>=H and R<sub>2</sub>=OCH<sub>3</sub>) using M06-2X/6-311++G(d,p) level of theory.....</b>	<b>31</b>
5.1. IRCs.....	31
<i>Figure S8. Optimized geometries for the formation of 3(III) from 3(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....</i>	<i>31</i>
<i>Figure S9. Optimized geometries for the formation of 3(III) from 3(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....</i>	<i>32</i>
<i>Figure S10. Optimized geometries for the formation of 3(III) from 3(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....</i>	<i>32</i>

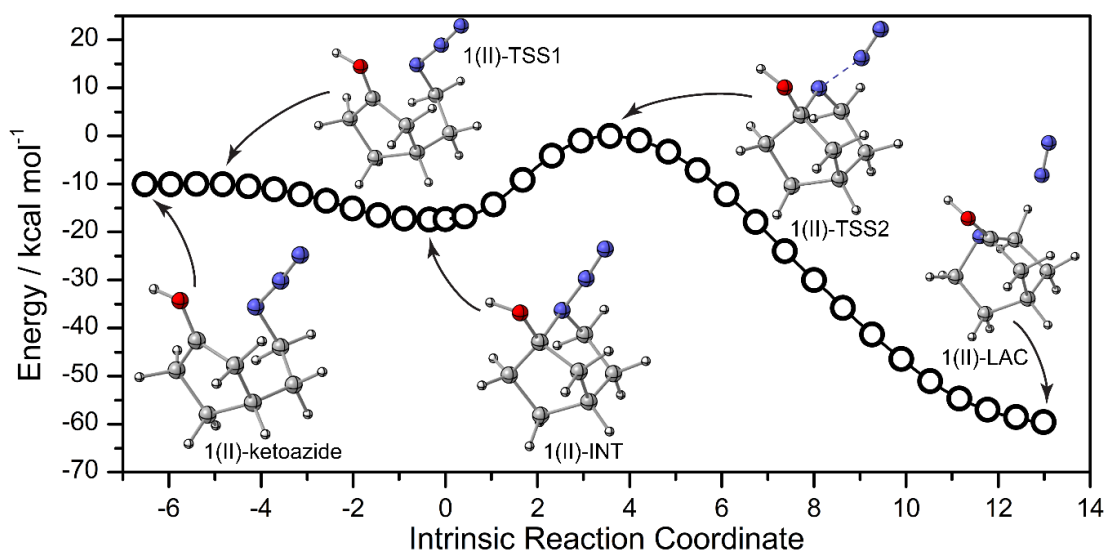
Figure S11. Optimized geometries for the formation of 3(III) from 3(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.....	33
<b>5.2. NCI .....</b>	<b>33</b>
Figure S12. NCI isosurfaces for 4(II)-INT (top left), 4(II)-TSS2 (top right), 4(III)-INT (bottom left) and 4(III)-TSS2 (bottom right) obtained at M06-2X/6-311++G(d,p) level of theory using a blue-green-red color scale from $-0.04 < \text{sign}(\lambda^2)\rho < 0.04$ a.u. Plots of the reduced density gradient and $\text{sign}(\lambda^2)\rho$ are shown right under each correlated NCI isosurface obtained at the same level of theory. ....	34
Figure S13. NCI isosurfaces for 5(II)-INT (top left), 5(II)-TSS2 (top right), 5(III)-INT (bottom left) and 5(III)-TSS2 (bottom right) obtained at M06-2X/6-311++G(d,p) level of theory using a blue-green-red color scale from $-0.04 < \text{sign}(\lambda^2)\rho < 0.04$ a.u. Plots of the reduced density gradient and $\text{sign}(\lambda^2)\rho$ are shown right under each correlated NCI isosurface obtained at the same level of theory. ....	35
5.3. Cartesian coordinates of 4(II)-TSS.....	35
5.4. Cartesian coordinates of 4(III)-TSS.....	36
5.5. Cartesian coordinates of 5(II)-TSS.....	37
5.6. Cartesian coordinates of 5(III)-TSS.....	37
<b>6. Calculation data for systems 6 (R<sub>1</sub>=phenyl and R<sub>2</sub>=H) and 7 (R<sub>1</sub>=H and R<sub>2</sub>=phenyl) using M06-2X/6-311++G(d,p) level of theory.....</b>	<b>38</b>
6.1. IRCs.....	38
Figure S14. Optimized geometries for the formation of 6(II) from 6(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....	39
Figure S15. Optimized geometries for the formation of 6(III) from 6(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....	39
Figure S16. Optimized geometries for the formation of 7(II) from 7(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....	40
Figure S17. Optimized geometries for the formation of 7(III) from 7(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory. ....	40
6.2. NBO analysis.....	41
Table S4. Total donor-acceptor interactions of type $\sigma, \pi$ (C-C(phenyl)) $\leftrightarrow \sigma^*, \pi^*$ (N-N) (in kcal mol <sup>-1</sup> ) of system 6 (R <sub>1</sub> =phenyl, R <sub>2</sub> =H) and system 7 (R <sub>1</sub> =H, R <sub>2</sub> =phenyl) obtained by NBO calculations at M06-2X/6-311++G(d,p) level of theory.....	41
6.3 Cartesian coordinates of 6(II)-INT.....	41
6.4 Cartesian coordinates of 6(II)-TSS2.....	42
6.5 Cartesian coordinates of 6(II).....	43
6.6 Cartesian coordinates of 6(III)-INT.....	44
6.7 Cartesian coordinates of 6(III)-TSS2.....	45
6.8 Cartesian coordinates of 6(III).....	46
6.9 Cartesian coordinates of 7(II)-INT.....	46
6.10 Cartesian coordinates of 7(II)-TSS2.....	47
6.11 Cartesian coordinates of 7(II).....	48
6.12 Cartesian coordinates of 7(III)-INT.....	49
6.13 Cartesian coordinates of 7(III)-TSS2.....	50
6.14 Cartesian coordinates of 7(III).....	51
<b>7. Calculation data for systems 8 (R<sub>1</sub>=t-butyl and R<sub>2</sub>=H) and 9 (R<sub>1</sub>=H and R<sub>2</sub>=t-butyl) using M06-2X/6-311++G(d,p) level of theory.....</b>	<b>52</b>

7.1. IRCs.....	52
Figure S18. Optimized geometries for the formation of 8(II) from 8(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.....	52
Figure S19. Optimized geometries for the formation of 8(III) from 8(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.....	53
Figure S20. Optimized geometries for the formation of 9(II) from 9(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.....	53
Figure S21. Optimized geometries for the formation of 9(III) from 9(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.....	54
7.2 Cartesian coordinates of 8(II)-INT.....	54
7.3 Cartesian coordinates of 8(II)-TSS2.....	55
7.4 Cartesian coordinates of 8(II).....	56
7.5 Cartesian coordinates of 8(III)-INT.....	57
7.6 Cartesian coordinates of 8(III)-TSS2.....	58
7.7 Cartesian coordinates of 8(III).....	59
7.8 Cartesian coordinates of 9(II)-INT.....	60
7.9 Cartesian coordinates of 9(II)-TSS2.....	61
7.10 Cartesian coordinates of 9(II).....	62
7.11 Cartesian coordinates of 9(III)-INT.....	63
7.12 Cartesian coordinates of 9(III)-TSS2.....	64
7.13 Cartesian coordinates of 9(III).....	65
<b>8. Additional groups data .....</b>	<b>66</b>
8.1 Calculation data for CF <sub>3</sub> -systems.....	66
Figure S22. TSSs, relative free energies (in kcal mol <sup>-1</sup> , in parentheses) and percentage of formation for the second and rate determinant step for reaction presented in Scheme 1, R <sub>1</sub> -F-System (R <sub>1</sub> =F, R <sub>2</sub> =H) and R <sub>2</sub> -F-System (R <sub>1</sub> =H, R <sub>2</sub> =F), obtained at M06-2X/6-311++G(d,p) level of theory.....	66
8.1.1 IRCs.....	67
Figure S23. IRC plot for R <sub>1</sub> -CF <sub>3</sub> (II)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.....	67
Figure S24. IRC plot for R <sub>1</sub> -CF <sub>3</sub> (III)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.....	67
Figure S25. IRC plot for R <sub>2</sub> -CF <sub>3</sub> (II)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.....	68
Figure S26. IRC plot for R <sub>2</sub> -CF <sub>3</sub> (III)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.....	68
<b>8.2 Calculation data for F-systems .....</b>	<b>69</b>
Figure S27. TSSs, relative free energies (in kcal mol <sup>-1</sup> , in parentheses) and percentage of formation for the second and rate determinant step for reaction presented in Scheme 1, R <sub>1</sub> -F-System (R <sub>1</sub> =F, R <sub>2</sub> =H) and R <sub>2</sub> -F-System (R <sub>1</sub> =H, R <sub>2</sub> =F), obtained at M06-2X/6-311++G(d,p) level of theory.....	69
Figure S28. IRC plot for R <sub>1</sub> -F(II)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.....	69
Figure S29. IRC plot for R <sub>1</sub> -F(III)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.....	70

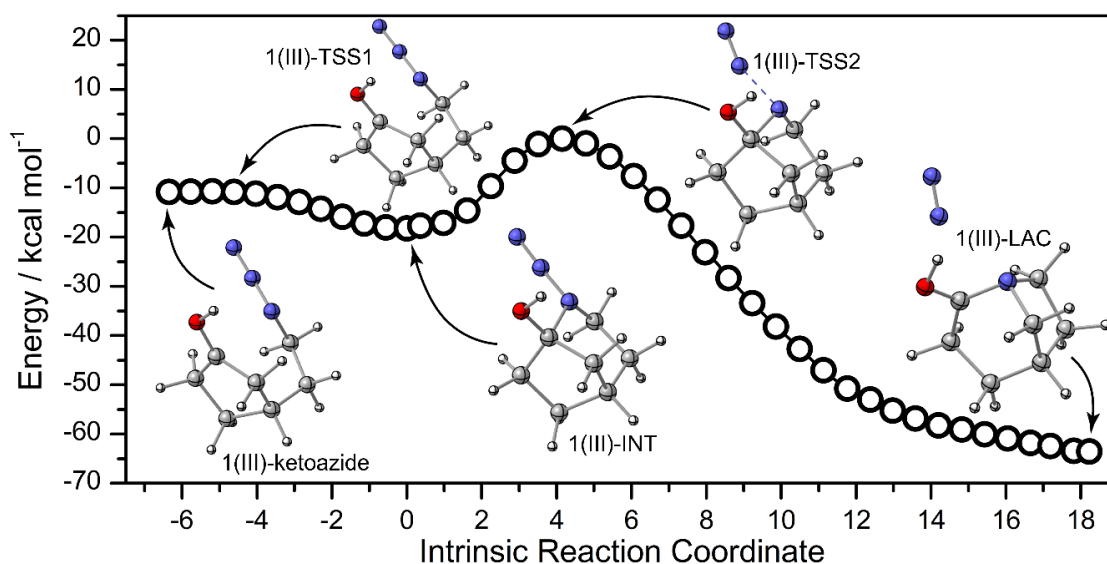
<i>Figure S30. IRC plot for R<sub>2</sub>-F(II)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.....</i>	<i>70</i>
<i>Figure S31. IRC plot for R<sub>2</sub>-F(III)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.....</i>	<i>71</i>
<b>8.3. Calculation data for CH<sub>3</sub>-systems.....</b>	<b>71</b>
<i>Figure S33. IRC plot for R<sub>1</sub>-CH<sub>3</sub>(III)-TSS2 (Figure S23) calculated at M06-2X/6-311++G(d,p) level of theory.....</i>	<i>72</i>
<i>Figure S34. IRC plot for R<sub>1</sub>-CH<sub>3</sub>(III)-TSS2 (Figure S23) calculated at M06-2X/6-311++G(d,p) level of theory.....</i>	<i>72</i>
<i>Figure S35. IRC plot for R<sub>2</sub>-CH<sub>3</sub>(II)-TSS2 (Figure S23) calculated at M06-2X/6-311++G(d,p) level of theory.....</i>	<i>73</i>
<i>Figure S36. IRC plot for R<sub>2</sub>-CH<sub>3</sub>(III)-TSS2 (Figure S23) calculated at M06-2X/6-311++G(d,p) level of theory.....</i>	<i>73</i>

## 1. The parent reaction

Calculation results for the parent system (system 1,  $R_1=H$  and  $R_2=H$ ) were obtained at M06-2X/6-31+g(d,p) level of theory. Cartesian coordinates and additional relevant data are presented as follows.



**Figure S1.** Optimized geometries for the formation of 1(II) from I (Figure 1) and energy profile obtained from intrinsic reaction coordinates calculations using M06-2X/6-31+G(d,p) level of theory.



**Figure S2.** Optimized geometries for the formation of 1(III) from I (Figure 1) and energy profile obtained from intrinsic reaction coordinates calculations using M06-2X/6-31+G(d,p) level of theory.

## 1.2. NBO analysis

NBO analysis indicated that the total hyperconjugation energy is higher in 1(II)-TSS2 than 1(III)-TSS2, as presented in Table S1, which explains a more favorable formation of 1(II). Another aspect of this is that less hyperconjugation stabilization is lost reaching 1(II)-TSS2 from 1(II)-INT than reaching 1(III)-TSS2 from 1(III)-INT, as also presented in Table S1.

**Table S1.** Total hyperconjugation energy (kcal mol<sup>-1</sup>) for species involved in the rate-determining step of system 1.

	Total hyperconjugation energy ( $\Sigma$ HE), kcal mol <sup>-1</sup>		
	INT (Eh)	TSS2 (Eh)	$\Sigma$ HE <sub>1(II)-TSS2</sub> – $\Sigma$ HE <sub>1(II)-INT</sub> (kcal mol <sup>-1</sup> )
1(II)	0.753517	0.657622	60.2
1(III)	0.752835	0.643214	68.8

## 1.3. Cartesian coordinates of ketoazide I (blue pathway, Figure 1)

M06-2X/6-31+g(d,p)

C	-2.13255900	-0.68902700	-0.25883200
C	-0.65632400	0.41204800	1.31546100
C	-0.74753500	1.22053300	0.08673900
C	-1.67765700	0.63484300	-0.91147500
H	-2.19868500	-1.49919700	-0.98849700
H	-3.12445500	-0.55280800	0.17835000
H	-1.42171400	0.84858100	1.98201400
H	0.30501200	0.49609300	1.83188600
H	-2.49486200	1.34571800	-1.09014700
H	-1.14975700	0.51037300	-1.86430200
O	-0.19262300	2.36701300	0.00518400
C	-1.10545800	-0.99558800	0.86255100
H	-1.60038400	-1.49513200	1.69739400
C	0.05986500	-1.89309500	0.41812800
H	-0.31733300	-2.91275800	0.28246500
C	0.74268800	-1.48800300	-0.88428800
H	1.59581700	-2.13944700	-1.09733200
H	0.05434300	-1.54930500	-1.72973800
N	1.18718300	-0.06709100	-0.87033500
N	2.15664400	0.15887000	-0.13422800
N	3.02106300	0.46882400	0.52025400

H	0.80207700	-1.93844400	1.22575600
H	-0.36143400	2.81573900	-0.84886500

#### 1.4 Cartesian coordinates of 1(II)-TSS1

M06-2X/6-31+g(d,p)

C	-2.18558800	-0.43015800	-0.27482700
C	-0.58863900	0.44612100	1.32120100
C	-0.51067300	1.24033200	0.07607600
C	-1.55640700	0.83472000	-0.90559400
H	-2.34209600	-1.21742400	-1.01544800
H	-3.15935800	-0.17438400	0.14854500
H	-1.29739600	1.00208400	1.95791700
H	0.35714300	0.38246400	1.86815000
H	-2.26748700	1.66652100	-0.99604800
H	-1.11503800	0.68254200	-1.89567600
O	0.17646000	2.32386000	0.03157800
C	-1.22663600	-0.88074300	0.85854400
H	-1.79343600	-1.31576100	1.68367900
C	-0.18513300	-1.91649100	0.40996400
H	-0.68251200	-2.87967100	0.25259600
C	0.53916400	-1.55980100	-0.88365800
H	1.34622300	-2.26499500	-1.10172300
H	-0.14452900	-1.55555100	-1.73503300
N	1.08394100	-0.17272400	-0.83792800
N	2.10030300	-0.03626900	-0.13699200
N	3.00777500	0.20082300	0.48528900
H	0.54554600	-2.06235200	1.21572300
H	0.08060300	2.79896700	-0.81811800

#### 1.5 Cartesian coordinates of 1(II)-INT

M06-2X/6-31+g(d,p)

C	-2.24121400	0.24759400	-0.31943000
C	-0.49968400	0.46348200	1.32628300
C	0.06752100	0.97041000	0.01108200
C	-1.14822700	1.19005300	-0.89115200
H	-2.65179800	-0.42053600	-1.08144600
H	-3.06746300	0.83894900	0.08028600
H	-0.96763000	1.31290900	1.83472000
H	0.26280200	0.03406300	1.98525500



H	-1.43124600	2.24062900	-0.77970000
H	-0.91220400	1.01844000	-1.94523400
O	0.97979900	1.97966700	0.14378400
C	-1.55286100	-0.53779000	0.82446600
H	-2.25696800	-0.81153500	1.61204700
C	-0.85503500	-1.80588700	0.30778900
H	-1.59331400	-2.54381000	-0.02131300
C	0.04675500	-1.50499300	-0.88479800
H	0.75416300	-2.30376800	-1.11159400
H	-0.51790100	-1.27761200	-1.79050800
N	0.83984500	-0.25187300	-0.62228000
N	1.98306000	-0.42486100	-0.08224600
N	3.01193000	-0.50574600	0.33226000
H	-0.26849000	-2.26088300	1.11377700
H	1.06428100	2.47596700	-0.68615100

## 1.6 Cartesian coordinates of 1(II)-TSS2

M06-2X/6-31+g(d,p)

C	-2.31067900	0.10969900	-0.16031000
C	-0.44891300	0.37716900	1.33093700
C	0.01975000	0.93250100	-0.00778400
C	-1.33653500	1.13982700	-0.78583500
H	-2.74531900	-0.55754500	-0.90996600
H	-3.13442000	0.64065600	0.32235100
H	-0.91244800	1.19672300	1.88721000
H	0.38409700	-0.02172800	1.91960000
H	-1.60379600	2.17259200	-0.54492700
H	-1.23302700	1.06905100	-1.87162100
O	0.83060400	2.03668300	0.13270500
C	-1.47761700	-0.66617600	0.88468600
H	-2.08461200	-1.02979600	1.71556000
C	-0.73233800	-1.83581800	0.22770600
H	-1.42981700	-2.61327700	-0.09644400
C	0.03615200	-1.34943100	-0.99364500
H	0.77544900	-2.04911200	-1.38987900
H	-0.63457600	-1.13079500	-1.84226300
N	0.68253600	-0.04867500	-0.85587100
N	2.16022000	-0.39260100	0.06729200
N	3.23083300	-0.46981900	0.29758400

H	-0.03446900	-2.29123900	0.94025200
H	0.99405700	2.45204500	-0.72908300

### 1.7 Cartesian coordinates of lactam 1(II)

M06-2X/6-31+g(d,p)

C	0.56480100	-0.32047200	1.55562500
C	-0.33168600	1.49501200	0.03345200
C	-1.09463300	0.29335800	-0.34676000
C	-0.05723100	-1.44096700	0.67651500
H	1.44948400	-0.70444400	2.06931400
H	-0.14920700	0.00509700	2.31977800
H	-0.92713400	2.10387000	0.71737000
H	-0.07190200	2.10201400	-0.84332800
H	-0.94659900	-1.89155200	1.11855100
H	0.64860400	-2.23668300	0.43389600
O	-2.35180800	0.22317900	-0.09804000
C	0.96049100	0.86811300	0.65457300
H	1.48450200	1.63856500	1.22163400
C	1.80202800	0.32927200	-0.50365000
H	2.61962200	-0.28298300	-0.11412900
C	0.85598900	-0.51240800	-1.39419600
H	0.58422300	0.01206600	-2.31173900
H	1.28916000	-1.47340500	-1.67338000
N	-0.41315700	-0.83058000	-0.68265300
H	2.23762100	1.14334300	-1.08834500
H	-2.71036900	-0.65870100	-0.34008600

### 1.8 Cartesian coordinates of ketoazide I (red pathway, Figure 1)

M06-2X/6-31+g(d,p)

C	1.79760100	-0.17625700	1.18121800
C	1.35749300	0.54364800	-1.09354100
C	0.51725900	1.32020500	-0.16263600
C	0.77641200	0.97882800	1.25539800
H	1.57587900	-0.96045300	1.90840100
H	2.79554000	0.20827400	1.40356100
H	2.24732500	1.18052300	-1.24604100
H	0.89076800	0.37004800	-2.06645200
H	1.14648100	1.87504300	1.76927700
H	-0.16947700	0.71994200	1.74749400

O	-0.24964500	2.29276500	-0.47098200
C	1.75309800	-0.70680100	-0.27615000
H	2.74803200	-1.03090500	-0.58778700
C	0.80119100	-1.89390500	-0.48518700
H	1.24769500	-2.77953800	-0.02072000
C	-0.58924900	-1.73302400	0.10459000
H	-1.20857500	-2.60344900	-0.13364500
H	-0.54466100	-1.62841400	1.19666600
N	-1.20769600	-0.51144600	-0.48009600
N	-2.30096400	-0.21014100	0.01523600
N	-3.29229200	0.14808300	0.41503500
H	0.71808000	-2.10159300	-1.55818800
H	-0.32609300	2.42677900	-1.43810600

### 1.9 Cartesian coordinates of 1(III)-TSS1

M06-2X/6-31+g(d,p)

C	1.82848200	0.06181400	1.15296200
C	1.23439300	0.68235700	-1.11224900
C	0.25388000	1.27482500	-0.17227900
C	0.62640200	1.02770200	1.24641100
H	1.76590400	-0.74196500	1.89011900
H	2.75149200	0.61437800	1.34332300
H	1.99503000	1.46944200	-1.25238600
H	0.80961700	0.42979100	-2.08679000
H	0.87461300	1.99812900	1.69355300
H	-0.22783500	0.64281000	1.81335000
O	-0.63369100	2.15708200	-0.45931100
C	1.83653200	-0.48430500	-0.29832700
H	2.86046200	-0.66512300	-0.63066100
C	1.05458600	-1.79523800	-0.46772700
H	1.61154800	-2.60250400	0.01885100
C	-0.34297100	-1.78477500	0.12963000
H	-0.88424600	-2.70090400	-0.12369400
H	-0.30967200	-1.68917500	1.22253200
N	-1.06298800	-0.61152800	-0.43945600
N	-2.19632300	-0.41383000	0.02667600
N	-3.22371200	-0.13936100	0.39462600
H	0.99248700	-2.04090500	-1.53388900
H	-0.73652800	2.28811400	-1.42326600

### 1.10 Cartesian coordinates of 1(III)-INT

M06-2X/6-31+g(d,p)

C	-1.82585400	-0.38824900	1.12055400
C	-1.03913400	-0.81664000	-1.11572100
C	0.16158400	-0.90080200	-0.19135800
C	-0.42360000	-1.04795200	1.21336100
H	-1.95941000	0.41108600	1.85472400
H	-2.59931500	-1.13613700	1.30649600
H	-1.47701600	-1.81974000	-1.16659000
H	-0.77904300	-0.47882500	-2.12364300
H	-0.49217800	-2.11966000	1.41497000
H	0.22640700	-0.61051700	1.97766100
O	1.16087800	-1.79155300	-0.47002200
C	-1.94558600	0.14353800	-0.33027400
H	-2.97471700	0.11461500	-0.69225100
C	-1.40453400	1.57358200	-0.47160500
H	-2.05781200	2.28392900	0.04396000
C	-0.01874600	1.72686100	0.14061100
H	0.49592400	2.62202300	-0.21155400
H	-0.04645900	1.72294200	1.23547400
N	0.80433000	0.54128900	-0.29508600
N	2.02158500	0.56626500	0.07951500
N	3.10223900	0.56208800	0.34182700
H	-1.37324400	1.85279100	-1.52941100
H	1.22797200	-1.93959700	-1.42686900

### 1.11 Cartesian coordinates of 1(III)-TSS2

M06-2X/6-31+g(d,p)

C	-1.81230900	-0.35133200	1.20782300
C	-1.17470400	-0.77480600	-1.07155900
C	0.13549100	-0.82716300	-0.20636600
C	-0.38749100	-0.96952300	1.22295900
H	-1.92371000	0.44963500	1.94428600
H	-2.55162100	-1.11960300	1.44304800
H	-1.53145000	-1.81056200	-1.07068300
H	-1.00668800	-0.44919500	-2.10211500
H	-0.40871300	-2.03562900	1.45575000
H	0.29353200	-0.48830400	1.93411300

O	1.04617200	-1.80436700	-0.54024900
C	-2.03154600	0.16613400	-0.23268900
H	-3.08161300	0.14231300	-0.53336300
C	-1.46870600	1.57044300	-0.43490400
H	-1.99769700	2.32327900	0.15624700
C	0.00692000	1.63096500	0.05328700
H	0.50010700	2.53877400	-0.29329000
H	0.01723000	1.57080800	1.14536500
N	0.68328000	0.48426500	-0.54565300
N	2.25927900	0.45964500	0.22155700
N	3.34713900	0.56919200	0.32366000
H	-1.52173300	1.85790900	-1.48838100
H	1.20916900	-1.80450600	-1.49724100

### 1.12 Cartesian coordinates of lactam 1(III)

M06-2X/6-31+g(d,p)

C	-0.11886800	1.65840600	0.28080500
C	-0.36850000	-0.62184500	1.30080100
C	1.16654500	-0.21193500	-0.32039500
C	0.80422800	1.09565700	-0.87861100
H	-0.63627000	2.52766700	-0.13223300
H	0.51824000	1.99666800	1.10451500
H	0.41963900	-0.40871100	2.02627500
H	-1.02147800	-1.40650700	1.68746900
H	1.67383700	1.72655600	-1.05501100
H	0.21588300	0.99315500	-1.79216900
O	2.34814400	-0.36588200	0.16380200
C	-1.12496000	0.60580800	0.77064600
H	-1.77593600	1.03798700	1.53410400
C	-1.90070700	0.00740000	-0.41828700
H	-2.09304800	0.75352300	-1.19382900
C	-0.97409900	-1.12743900	-0.92057700
H	-1.43120900	-2.11130200	-0.80579900
H	-0.64771900	-1.02504700	-1.95604400
N	0.21668400	-1.13628100	-0.01758200
H	-2.86010500	-0.39937200	-0.09349900
H	2.43438600	-1.23990300	0.60257500

### 1.13 Cartesian coordinates of 1(III)-INT-Conformer-B

M06-2X/6-311++g(d,p)

C	1.66199900	0.61020900	1.20315500
C	1.09688900	0.56199600	-1.15385600
C	-0.15117600	0.88749300	-0.35365800
C	0.37122400	1.43061200	0.96814200
H	1.56608800	-0.05471000	2.06197600
H	2.49606900	1.28228800	1.40294900
H	0.59141400	2.49087700	0.82277600
O	-1.11762500	1.59429800	-1.01452700
C	1.92167400	-0.19799700	-0.10464100
H	2.98169200	-0.19770000	-0.35007100
C	1.43321900	-1.66052600	-0.01071800
H	1.60203500	-2.04295200	0.99683900
C	-0.04196600	-1.80827700	-0.38861400
H	-0.18429400	-1.94633700	-1.46063700
H	-0.53744300	-2.61587400	0.14785700
N	-0.74101400	-0.53365400	-0.02398400
N	-1.94597100	-0.56397700	0.31547200
N	-3.01225600	-0.53849400	0.62086700
H	1.99774100	-2.28971300	-0.70147900
H	-1.51153400	2.25711300	-0.43178500
H	0.89452700	0.01618200	-2.07643200
H	1.55542200	1.51983100	-1.40924900
H	-0.36721000	1.33842600	1.76813300

### 1.14 Cartesian coordinates of 1(III)-TSS2-Conformer-B

M06-2X/6-311++g(d,p)

C	-1.82836700	-0.54653500	1.19916000
C	-1.25824500	-0.52808300	-1.09154900
C	0.09157100	-0.81464300	-0.33112600
C	-0.34771300	-0.96050400	1.14744700
H	-2.08047400	-0.01901700	2.11925100
H	-2.47131900	-1.42485000	1.11999800
H	-0.17942900	-1.99617000	1.43857700
O	0.82691200	-1.91439000	-0.71956500
C	-1.97538400	0.33373800	-0.04700700
H	-3.01211500	0.52350100	-0.32085300
C	-1.20008700	1.66138700	0.16684800

H	-1.00977900	1.81499100	1.23171200
C	0.11034500	1.67499000	-0.60733400
H	-0.04963900	1.88910700	-1.67261300
H	0.81435100	2.43812100	-0.27429100
N	0.81480800	0.38821600	-0.69219300
N	2.14857800	0.42998500	0.40265000
N	3.19942800	0.38599400	0.69401900
H	-1.77944900	2.51920700	-0.17825300
H	1.04076900	-1.85182200	-1.66069300
H	-1.13195300	-0.09191800	-2.08259200
H	-1.72292500	-1.51114400	-1.19735600
H	0.27425400	-0.32634500	1.78367800

## 2. Screening of functionals and basis sets.

**Table S2.** Energy barriers (in kcal mol<sup>-1</sup>)<sup>[a]</sup> and product distribution (%)<sup>[b]</sup> obtained using different levels of theory.

Level of theory	$\Delta_{\text{rel}}G^\ddagger$ (TSS2 – INT)/kcal mol <sup>-1</sup>		Product distribution	
	1(II)	1(III)	1(II)	1(III)
<b>Experimental<sup>[c]</sup></b>	-	-	<b>76%</b>	<b>24%</b>
M06-2X/6-31+G(d,p)	14.7	15.1	66%	34%
<b>M06-2X/6-311++G(d,p)</b>	<b>13.9</b>	<b>14.5</b>	<b>73%</b>	<b>27%</b>
B3LYP/6-31+G(d,p)	13.0	15.7	99%	1%
B3LYP/6-311++G(d,p)	13.1	15.7	99%	1%
$\omega$ B97X-D/6-31+G(d,p)	15.9	17.3	91%	9%
$\omega$ B97X-D/6-311++G(d,p)	15.7	17.2	93%	7%

<sup>[a]</sup> Calculated using Gibbs free energies at 298.15 K

<sup>[b]</sup> Obtained from Boltzmann distributions based on  $\Delta_{\text{rel}}G^\ddagger$ .

<sup>[c]</sup> Tani, K.; Stoltz, B. M. *Nature* **2006**, *441* (7094), 731–734.

Following data were obtained using the most representative level of theory M06-2X/6-311++G(d,p).

## 3. Calculation data for system 1 (R<sub>1</sub>=H and R<sub>2</sub>=H) using M06-2X/6-311++G(d,p) level of theory.

### 3.1 Cartesian coordinates of 1(II)-INT.

M06-2X/6-311++G(d,p)

C	-2.23932500	0.24390100	-0.31374400
C	-0.49339000	0.46078100	1.32559900
C	0.06730500	0.97109100	0.01043900

C	-1.15026700	1.18851200	-0.88729600
H	-2.64908000	-0.42341200	-1.07376800
H	-3.06350500	0.83256400	0.08846300
H	-0.96192300	1.30684100	1.83486300
H	0.27088600	0.03280900	1.98006100
H	-1.43511200	2.23656100	-0.77482600
H	-0.91643700	1.01783400	-1.93991500
O	0.97555200	1.98305600	0.14099400
C	-1.54618300	-0.54085100	0.82647300
H	-2.24572400	-0.81536400	1.61456800
C	-0.84892300	-1.80611900	0.30561500
H	-1.58687200	-2.54234800	-0.02193200
C	0.04658400	-1.50066700	-0.88915000
H	0.75145900	-2.29761900	-1.12207700
H	-0.52239300	-1.27115600	-1.78928000
N	0.84161800	-0.24855400	-0.62723800
N	1.98037200	-0.42445600	-0.08233400
N	2.99969400	-0.50692900	0.33631900
H	-0.26025100	-2.26103000	1.10747700
H	1.04793500	2.47955700	-0.68642700

### 3.2 Cartesian coordinates of 1(II)-TSS2.

M06-2X/6-311++G(d,p)

C	-2.30607300	0.10710400	-0.16041000
C	-0.44606600	0.37756900	1.32973300
C	0.01933100	0.93437900	-0.00800400
C	-1.33333300	1.13867500	-0.78471800
H	-2.73734300	-0.55989100	-0.90901700
H	-3.12876300	0.63504200	0.32250700
H	-0.91349000	1.19413600	1.88333700
H	0.38533300	-0.01815300	1.91870400
H	-1.60712000	2.16865900	-0.54818000
H	-1.22747400	1.06407800	-1.86797900
O	0.82949700	2.03877100	0.13099700
C	-1.47192200	-0.66725900	0.88375500
H	-2.07693500	-1.03068100	1.71297200
C	-0.72654300	-1.83539000	0.22684700
H	-1.42393300	-2.61026400	-0.09731600
C	0.04023300	-1.34873800	-0.99408600



H	0.77632100	-2.04861100	-1.39082700
H	-0.63124500	-1.12879400	-1.83967500
N	0.68970200	-0.04962900	-0.85288400
N	2.14895500	-0.39239400	0.06764200
N	3.21157700	-0.46978500	0.29936800
H	-0.03024000	-2.29032200	0.93821500
H	0.97351500	2.45925100	-0.72830300

### 3.3 Cartesian coordinates of 1(III)-INT.

M06-2X/6-311++G(d,p)

C	-1.82330900	-0.38503800	1.12124200
C	-1.03826900	-0.81680500	-1.11355100
C	0.16165200	-0.90129600	-0.19064500
C	-0.42240800	-1.04625000	1.21340700
H	-1.95391800	0.41491500	1.85187400
H	-2.59588000	-1.13036700	1.30874700
H	-1.47619900	-1.81803100	-1.16138200
H	-0.77855000	-0.48091900	-2.11988600
H	-0.49376200	-2.11563900	1.41565800
H	0.22702800	-0.60962200	1.97559400
O	1.15850100	-1.79318600	-0.47086800
C	-1.94363200	0.14382600	-0.32958700
H	-2.97064000	0.11411500	-0.69021700
C	-1.40252600	1.57242600	-0.47334200
H	-2.05485100	2.28214200	0.04032500
C	-0.01779600	1.72552000	0.13823100
H	0.49554900	2.61920200	-0.21447900
H	-0.04566700	1.72328500	1.23130600
N	0.80616400	0.54027900	-0.29499500
N	2.02087800	0.56617200	0.08062200
N	3.09460400	0.56297700	0.34148900
H	-1.37118400	1.84857300	-1.52991500
H	1.21627600	-1.94245800	-1.42501700

### 3.4 Cartesian coordinates of 1(III)-TSS2

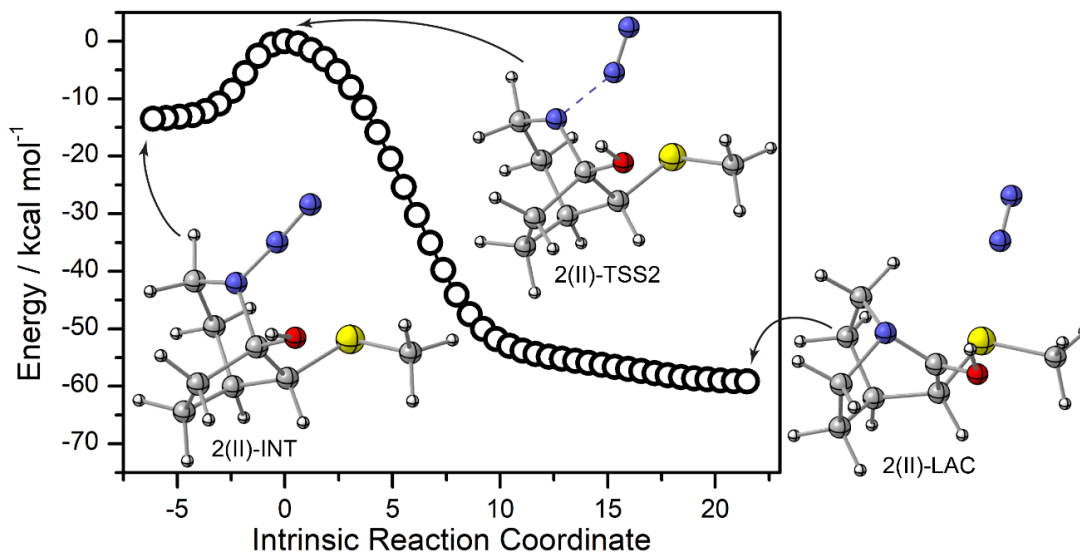
M06-2X/6-311++G(d,p)

C	-1.80528500	-0.34549600	1.21129400
C	-1.17394000	-0.78169800	-1.06578600
C	0.13530700	-0.82881500	-0.20627800

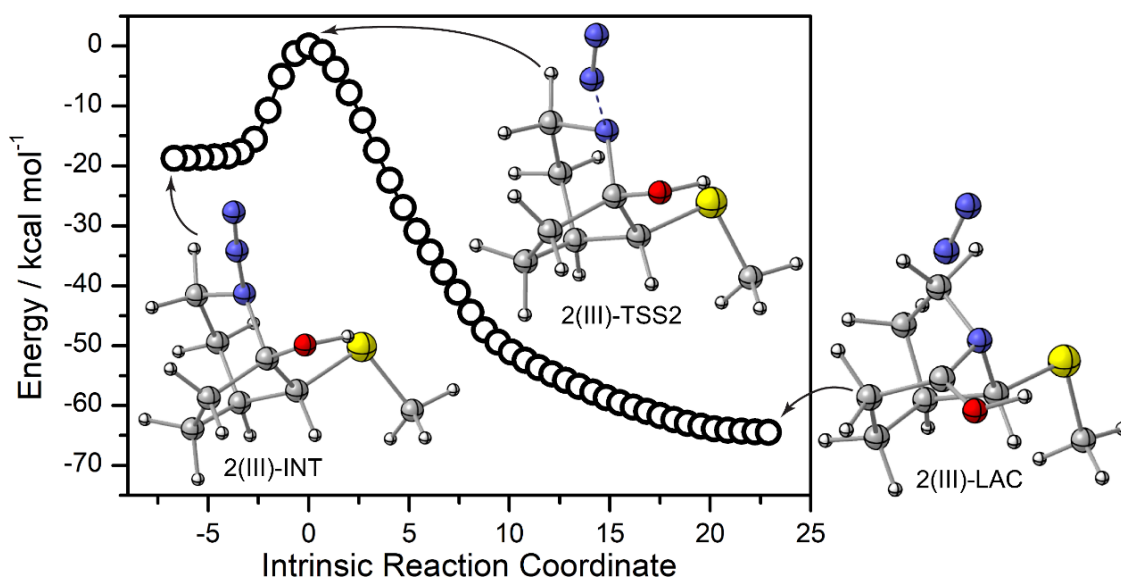
C	-0.38071200	-0.96290800	1.22519800
H	-1.91434700	0.45782800	1.94214300
H	-2.54183800	-1.11212500	1.45078900
H	-1.53460700	-1.81402100	-1.05797000
H	-1.00784200	-0.46132600	-2.09617600
H	-0.40243000	-2.02564100	1.46385700
H	0.30093600	-0.47831200	1.93001300
O	1.04669400	-1.80518500	-0.53952400
C	-2.02796000	0.16415800	-0.23060100
H	-3.07657500	0.13973000	-0.52727100
C	-1.46496300	1.56641300	-0.44044000
H	-1.99549900	2.32048000	0.14422400
C	0.00817100	1.63125700	0.04827300
H	0.49895400	2.53773700	-0.29959100
H	0.01898000	1.57386600	1.13865300
N	0.68598900	0.48428500	-0.54780800
N	2.25027100	0.46198400	0.21468300
N	3.32950400	0.56982300	0.32851900
H	-1.51682500	1.84560000	-1.49421600
H	1.19347400	-1.81245300	-1.49598300

**4. Calculation data for systems 2 ( $R_1=\text{SCH}_3$  and  $R_2=\text{H}$ ) and 3 ( $R_1=\text{H}$  and  $R_2=\text{SCH}_3$ ) using M06-2X/6-311++G(d,p) level of theory.**

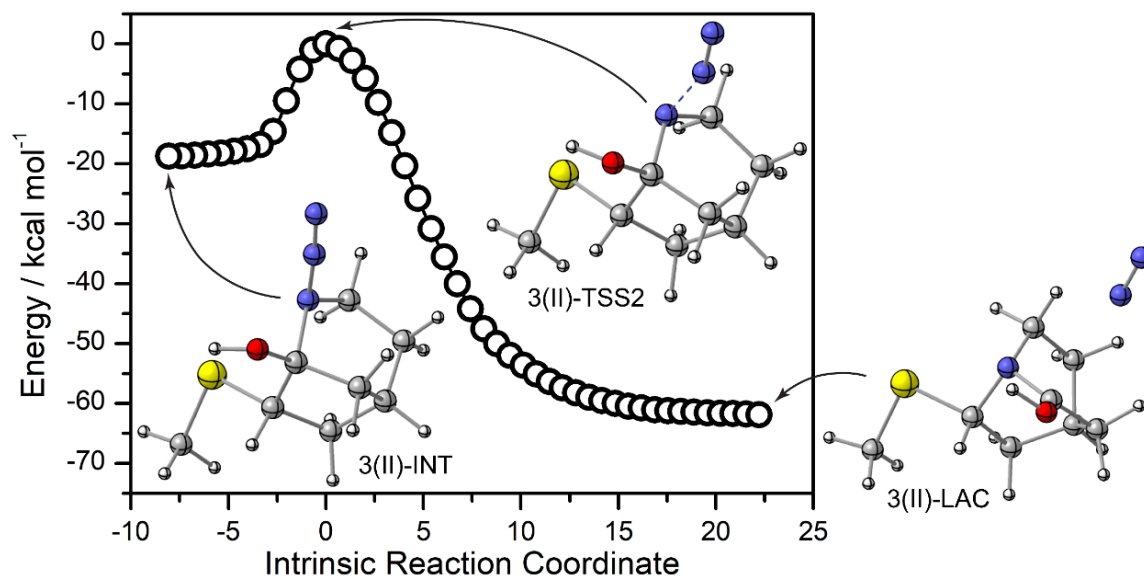
#### 4.1. IRCs.



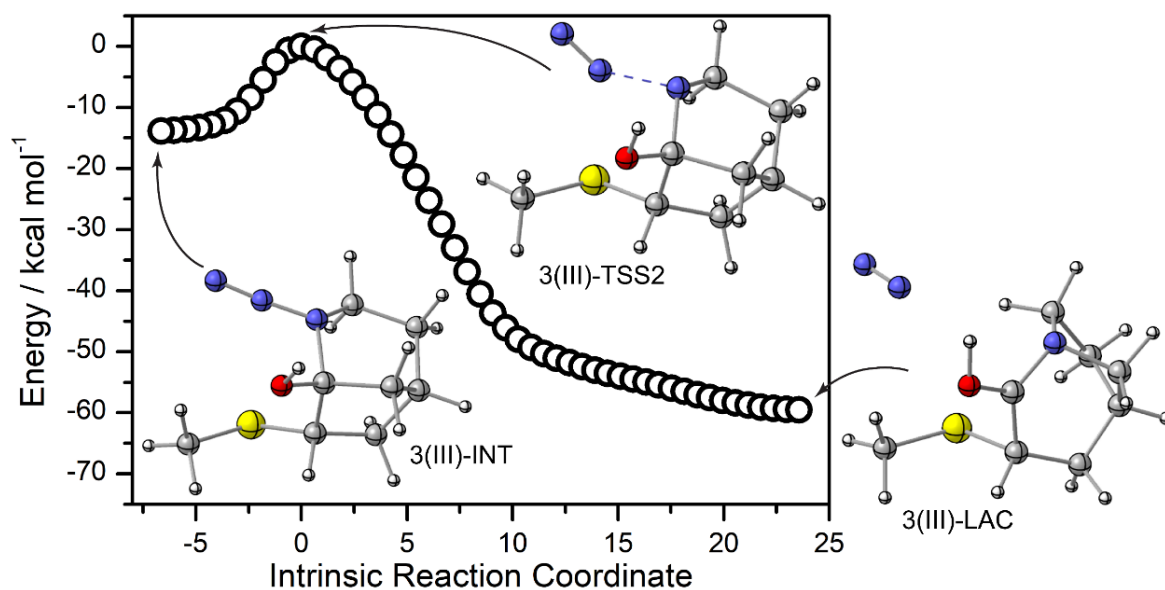
**Figure S3.** Optimized geometries for the formation of 2(II) from 2(II)-INT and and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S4.** Optimized geometries for the formation of 2(III) from 2(III)-INT and and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S5.** Optimized geometries for the formation of 3(II) from 3(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



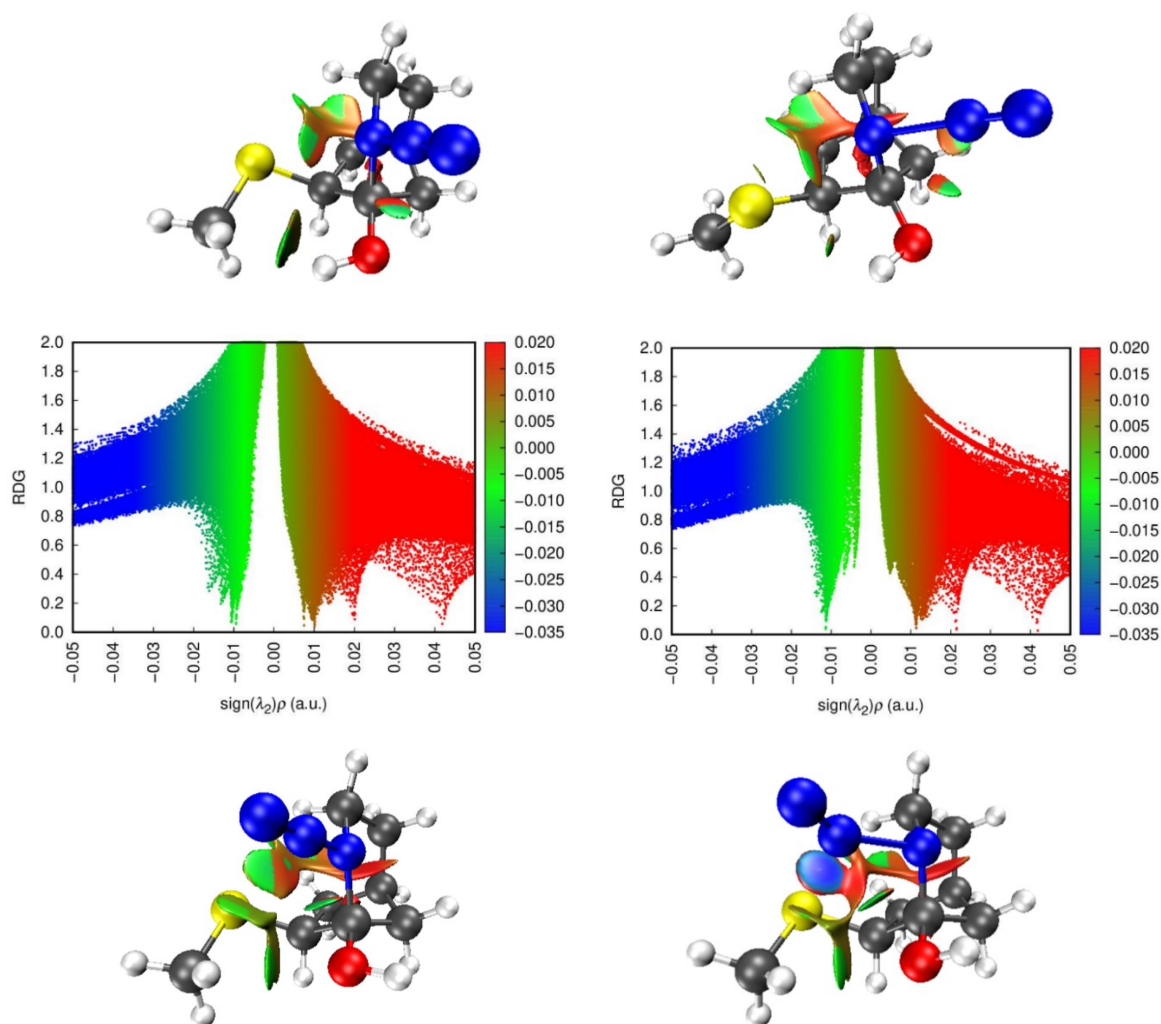
**Figure S6.** Optimized geometries for the formation of 3(III) from 3(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.

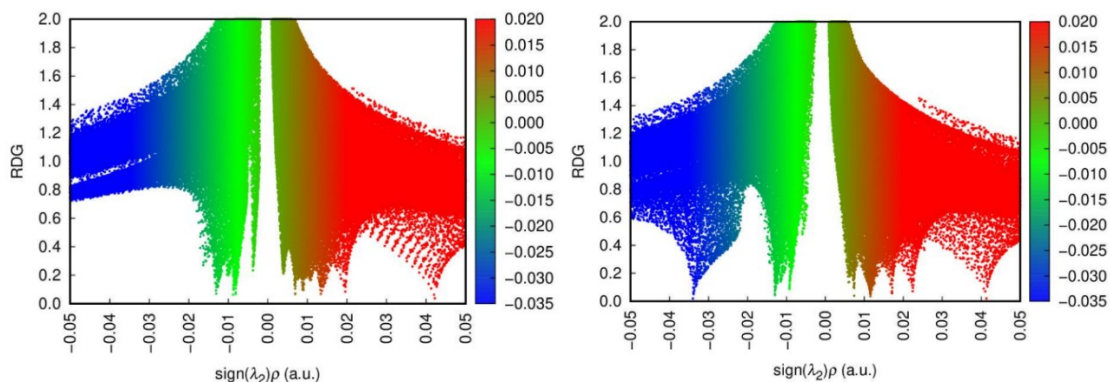
## 4.2 NBO analysis

**Table S3.** Total donor-acceptor interactions of type  $n(S) \leftrightarrow \sigma^*, \pi^*(N-N)$  (in  $\text{kcal mol}^{-1}$ ) of system 2 ( $R_1=\text{SCH}_3$ ,  $R_2=\text{H}$ ) and system 3 ( $R_1=\text{H}$ ,  $R_2=\text{SCH}_3$ ) obtained by NBO calculations at M06-2X/6-311++G(d,p) level of theory.

Structure	$\sum n(S) \leftrightarrow \sigma^*, \pi^*(N-N)$ kcal mol <sup>-1</sup>
<b>System 2</b>	
2(II)-INT	1.1
2(II)-TSS2	23.3
2(III)-INT	0.7
2(III)-TSS2	1.2
<b>System 3</b>	
3(II)-INT	0.0
3(II)-TSS2	1.8
3(III)-INT	1.3
3(III)-TSS2	26.0

### 4.3 NCI





**Figure S7.** NCI isosurfaces for 3(II)-INT (top left), 3(II)-TSS2 (top right), 3(III)-INT (bottom left) and 3(III)-TSS2 (bottom right) obtained at M06-2X/6-311++G(d,p) level of theory using a blue-green-red color scale from  $-0.04 < \text{sign}(\lambda_2)\rho < 0.04$  a.u. Plots of the reduced density gradient and  $\text{sign}(\lambda_2)\rho$  are shown right under each correlated NCI isosurface obtained at the same level of theory.

#### 4.4 Cartesian coordinates of 2(II)-INT

M06-2X/6-311++G(d,p)

C	-2.31188600	-1.17368800	0.45033700
C	0.05719100	-1.09062500	0.10597100
C	-0.29683100	0.09204800	1.01216400
C	-1.69733900	-0.24322800	1.53052500
H	-3.26789600	-0.79881100	0.08186100
H	-2.48243200	-2.16525100	0.86843200
H	0.20293400	-1.95443800	0.76265000
H	-1.56533100	-0.76954000	2.47748200
H	-2.28159600	0.65813300	1.72404500
O	0.67840300	0.40561300	1.92081500
C	-1.25880200	-1.25248000	-0.67900300
H	-1.28444000	-2.20783700	-1.20080900
C	-1.43073700	-0.11309500	-1.69445800
H	-2.36850900	-0.24524300	-2.23890500
C	-1.49351600	1.24943900	-1.01100200
H	-1.31125600	2.08051900	-1.69039700
H	-2.44519000	1.41371800	-0.50569000
N	-0.47310900	1.32773800	0.08892000
N	0.60208300	1.96091500	-0.15706100
N	1.50113600	2.59276000	-0.27845200
H	-0.62241500	-0.12960300	-2.42940600

H	0.29292300	0.85174000	2.68803200
S	1.53122800	-0.90523600	-0.93345300
C	2.84074700	-1.24977700	0.27906300
H	2.65694000	-2.20905400	0.76312600
H	3.77050300	-1.31044000	-0.28656800
H	2.91514700	-0.45647200	1.01944100

#### 4.5 Cartesian coordinates of 2(II)-TSS2

M06-2X/6-311++G(d,p)

C	-2.47523700	-1.00571400	0.11087500
C	-0.09560100	-1.07003800	-0.08546500
C	-0.38853200	0.01024600	1.00277900
C	-1.87202300	-0.35489700	1.37732000
H	-3.37031500	-0.48543000	-0.23210600
H	-2.75305100	-2.03766400	0.32443600
H	-0.05543200	-2.02627300	0.44229000
H	-1.75977300	-1.06538600	2.19783000
H	-2.42474400	0.50835900	1.74838400
O	0.53479600	-0.06383000	2.02718300
C	-1.35784000	-0.95834800	-0.95086600
H	-1.42292700	-1.77557900	-1.66755200
C	-1.35651500	0.39166700	-1.67951000
H	-2.27045100	0.49727900	-2.26675200
C	-1.30640800	1.54370300	-0.67478900
H	-1.03726300	2.50496100	-1.11233100
H	-2.28729100	1.69720200	-0.20091000
N	-0.45631200	1.33990300	0.49892800
N	1.18293300	1.62831900	-0.06569000
N	1.95622900	2.40729700	-0.05885900
H	-0.51797100	0.45989500	-2.37813700
H	0.31089100	0.57465300	2.71881200
S	1.44219900	-0.84610800	-0.97600500
C	2.64793700	-1.48696900	0.21663100
H	2.31555900	-2.45508900	0.59064100
H	3.58383300	-1.60811400	-0.32788000
H	2.78075700	-0.78697100	1.03939800

#### 4.6 Cartesian coordinates of 2(II)

M06-2X/6-311++G(d,p)

C	-1.94054300	-0.13036400	1.33195900
C	0.45498100	-0.10589200	0.74611700
C	-0.00445300	0.98514000	-0.12672800
C	-2.24332500	0.87695700	0.19024900
H	-2.81899900	-0.74389600	1.53279000
H	-1.68746800	0.40283800	2.25138600
H	0.83889000	0.27613600	1.69432100
H	-2.32798200	1.90260200	0.54722600
H	-3.15100100	0.63018500	-0.35896800
O	0.56985200	2.12530600	-0.10389300
C	-0.76686900	-1.03287700	0.90444600
H	-0.54873900	-1.78957100	1.65594800
C	-1.12097600	-1.66455000	-0.44766900
H	-2.07991600	-2.17531300	-0.35210400
C	-1.19957600	-0.53823000	-1.50162600
H	-0.38008400	-0.58931700	-2.21691000
H	-2.13639700	-0.55531400	-2.05676600
N	-1.14470400	0.81881800	-0.87233400
H	-0.38303000	-2.41094900	-0.74511200
H	0.15751100	2.72092800	-0.76584400
S	1.84273800	-0.87088400	-0.19287000
C	3.17305600	0.28510900	0.22682600
H	3.26745600	0.37748200	1.30844700
H	4.08386600	-0.15786800	-0.17786900
H	3.02243400	1.26028400	-0.23459100

#### 4.7 Cartesian coordinates of 2(III)-INT

M06-2X/6-311++G(d,p)

C	0.30243700	2.23986600	0.94377800
C	-0.96636700	0.28328300	0.42536200
C	0.41432700	-0.18988700	0.86147800
C	1.03161200	1.01425100	1.56288000
H	1.00256200	2.96753200	0.53080300
H	-0.28524100	2.74383400	1.71063700
H	-1.54323800	0.39833500	1.34901400
H	0.82027100	0.90893200	2.62734400
H	2.11557400	1.03838100	1.43696700
O	0.49704600	-1.36584400	1.53780500
C	-0.63529800	1.67314900	-0.15166400



H	-1.53569900	2.27431400	-0.27211800
C	0.07356200	1.54288400	-1.50386000
H	0.28771000	2.53450200	-1.90774500
C	1.40412700	0.81292100	-1.38462900
H	1.76468900	0.44769600	-2.34487100
H	2.17245600	1.42696900	-0.90758600
N	1.17841000	-0.38764300	-0.50691700
N	2.14376000	-1.20812100	-0.43433100
N	2.93911000	-1.97358400	-0.37901300
H	-0.57172000	1.02345300	-2.21436100
H	-0.21081600	-1.95560700	1.22431100
S	-1.81285900	-0.96054300	-0.59345500
C	-3.50419800	-0.76195000	0.03953200
H	-3.86404300	0.24869200	-0.14889700
H	-4.12661400	-1.46862700	-0.50895100
H	-3.54669100	-0.99464000	1.10285800

#### 4.8 Cartesian coordinates of 2(III)-TSS2

M06-2X/6-311++G(d,p)

C	0.10101700	2.22259100	0.98103400
C	-1.01826900	0.19621400	0.40710300
C	0.47646700	-0.18689000	0.75209800
C	0.96894200	1.04319300	1.50749300
H	0.70962900	3.03561800	0.58245700
H	-0.50072200	2.62805300	1.79379400
H	-1.49980400	0.19561700	1.39088300
H	0.80475800	0.86178400	2.56889500
H	2.04279500	1.18755400	1.35622500
O	0.62168100	-1.36196400	1.44201900
C	-0.82318900	1.62386800	-0.10626600
H	-1.77344900	2.15258900	-0.18868300
C	-0.14131000	1.56414600	-1.46588100
H	0.06623100	2.56139200	-1.85795400
C	1.25420000	0.87766900	-1.34478500
H	1.64310000	0.61837200	-2.32721400
H	1.93053700	1.55038600	-0.81454800
N	1.01422400	-0.34275700	-0.60167800
N	2.60474200	-1.01790500	-0.29820500
N	3.45713700	-1.69006300	-0.40274200

H	-0.75290000	1.02446500	-2.18886900
H	0.05445100	-2.03914400	1.03803500
S	-1.84841700	-1.05758600	-0.60562600
C	-3.50668500	-0.96113800	0.12687000
H	-3.94660700	0.02091600	-0.04047400
H	-4.11200200	-1.71397800	-0.37813100
H	-3.46454900	-1.18937600	1.19182100

#### 4.9 Cartesian coordinates of 2(III)

M06-2X/6-311++G(d,p)

C	-1.31200300	-0.93201500	1.39919200
C	0.49231600	0.33064900	0.23190500
C	-1.67762600	0.80872900	-0.15790300
C	-2.41700600	-0.29276300	0.46673000
H	-1.68771400	-1.91089600	1.69828700
H	-1.21203000	-0.31508800	2.29484800
H	0.39733000	1.08464400	1.01730100
H	-3.27793500	0.05850700	1.02993100
H	-2.72752000	-1.02502400	-0.27809600
O	-1.94097100	2.01273200	0.18763300
C	0.04263600	-1.07113400	0.68584300
H	0.76533200	-1.53016500	1.36083200
C	-0.11454800	-1.82297500	-0.64520300
H	-0.85877000	-2.61615200	-0.56627400
C	-0.54608500	-0.71832900	-1.63560800
H	0.16968600	-0.58629200	-2.44459400
H	-1.52910000	-0.86672000	-2.07924200
N	-0.53986800	0.56952300	-0.86880200
H	0.82866500	-2.26649700	-0.95981900
H	-1.31339600	2.63806800	-0.23197500
S	2.14298600	0.48529000	-0.51059100
C	3.11201800	0.20098200	0.99744900
H	3.02140400	-0.82880400	1.33986100
H	4.15112300	0.39580000	0.73218500
H	2.81377500	0.89660200	1.78232000

#### 4.10 Cartesian coordinates of 3(II)-INT

M06-2X/6-311++G(d,p)

C	-0.17153300	-2.11699700	0.25337400
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C	1.24105800	-0.58535800	1.47232300
C	0.13406200	0.23911600	0.83866400
C	-0.95595300	-0.80097100	0.51707100
H	-0.33551400	-2.50136200	-0.75628200
H	-0.51473100	-2.88075600	0.95012500
H	0.89325600	-0.89902200	2.45997100
H	2.17320900	-0.02653700	1.58613100
H	-1.52288700	-0.89366800	1.44752300
O	-0.22282100	1.34002000	1.56790200
C	1.31814900	-1.77231100	0.50091500
H	1.85793000	-2.61206700	0.93504500
C	2.02383000	-1.32593900	-0.78658300
H	2.12828100	-2.16536600	-1.47834800
C	1.23685400	-0.24295500	-1.51467300
H	1.83317800	0.30565700	-2.24275500
H	0.35086700	-0.63037700	-2.01531100
N	0.69501100	0.75555500	-0.52526100
N	1.32732700	1.84997200	-0.42055000
N	1.80922400	2.84174000	-0.33403900
H	3.02683800	-0.96360600	-0.54584400
H	-1.12831600	1.61084400	1.36476200
S	-2.13950700	-0.42045000	-0.80489700
C	-3.09511400	0.93008600	-0.05490600
H	-4.02580200	1.00141000	-0.61834500
H	-3.34196300	0.68890600	0.98108600
H	-2.58872000	1.89409200	-0.13077600

#### 4.11 Cartesian coordinates of 3(II)-TSS2

M06-2X/6-311++G(d,p)

C	1.05852400	1.60123900	0.35797000
C	-0.97627700	0.84527700	1.42519300
C	-0.39287800	-0.37439100	0.72545000
C	1.10751100	0.06455500	0.54470500
H	1.42892100	1.90533000	-0.62387900
H	1.69419300	2.07150400	1.10872000
H	-0.57693000	0.87096900	2.44034800
H	-2.06725600	0.80215100	1.47344000
H	1.51161500	-0.18437800	1.53008700
O	-0.58158200	-1.54615100	1.41525200
C	-0.42866200	1.98570800	0.55708300

H	-0.54684400	2.95614200	1.03580100
C	-1.16989000	1.96417700	-0.78453700
H	-0.81645600	2.76253000	-1.44028700
C	-0.92368000	0.63608400	-1.48368000
H	-1.55888500	0.42170100	-2.34450600
H	0.10878200	0.57280800	-1.88557200
N	-0.88152300	-0.53946200	-0.64661600
N	-2.59150700	-0.96591900	-0.34060200
N	-3.51346800	-1.54630400	-0.38365200
H	-2.24376600	2.10903200	-0.63227600
H	-0.02551200	-2.24527000	1.03879100
S	2.04119200	-0.93778700	-0.65773600
C	3.70352200	-0.43355900	-0.13555800
H	4.40890600	-0.97508700	-0.76543600
H	3.84211700	0.63707900	-0.28436900
H	3.87117000	-0.70344700	0.90723100

#### 4.12 Cartesian coordinates of 3(II)

M06-2X/6-311++G(d,p)

C	-0.41129600	-0.73146500	-1.44275800
C	-2.39274100	0.07366200	-0.07844400
C	-1.34155200	1.06419300	0.21392300
C	0.56027200	0.22368000	-0.68757000
H	0.12474200	-1.61474700	-1.79404600
H	-0.80934300	-0.21524100	-2.31972400
H	-3.06006700	0.46499200	-0.84714000
H	-2.98455600	-0.15820700	0.81414600
H	0.72949500	1.15371800	-1.22921700
O	-1.46760400	2.27225800	-0.19763900
C	-1.55206600	-1.17140400	-0.50269100
H	-2.20521600	-1.88579200	-1.00019400
C	-0.92417600	-1.74972500	0.76529900
H	-0.16251600	-2.48545600	0.50133000
C	-0.29721000	-0.56569800	1.53298500
H	-0.91875500	-0.24660400	2.36919700
H	0.69261700	-0.79997300	1.91898900
N	-0.13936700	0.62425300	0.65215900
H	-1.67330800	-2.24013600	1.38811300
H	-0.66988300	2.79833100	0.01537400
S	2.14931500	-0.54252500	-0.36802900

C	2.98532400	0.85607300	0.42313000
H	3.99928600	0.52907100	0.65262000
H	3.02870300	1.70781100	-0.25631700
H	2.47683100	1.12889500	1.34809100

#### 4.13 Cartesian coordinates of 3(III)-INT

M06-2X/6-311++G(d,p)

C	1.10403300	-1.74416400	-0.42964200
C	1.65768500	-0.28202400	1.41975600
C	0.24342400	0.04647600	0.98226200
C	-0.20242500	-1.21522600	0.22183800
H	1.06273800	-1.71512800	-1.52105000
H	1.25389700	-2.78350100	-0.14055700
H	1.58738400	-1.05191800	2.19279700
H	2.19052800	0.58518600	1.81589400
H	-0.54693200	-1.90641700	0.99466300
O	-0.66684100	0.45340200	1.92204800
C	2.24334100	-0.84462400	0.11645500
H	3.15486500	-1.41149000	0.29723300
C	2.55394400	0.32656700	-0.82363800
H	3.01940700	-0.03295800	-1.74404700
C	1.29450700	1.07686100	-1.23525000
H	1.51155100	2.08325200	-1.59051600
H	0.72399700	0.53428200	-1.99202100
N	0.41499800	1.22393700	-0.02120800
N	-0.65465700	1.88900100	-0.21584500
N	-1.53765800	2.54518200	-0.32069000
H	3.25461400	1.00861700	-0.33767900
H	-0.22075200	0.93096600	2.63560100
S	-1.55352700	-1.00801600	-0.96880100
C	-2.98074000	-0.84413000	0.14431500
H	-3.86479200	-0.83607700	-0.49348200
H	-3.03131000	-1.70519600	0.81066600
H	-2.94544000	0.07617200	0.72457000

#### 4.14 Cartesian coordinates of 3(III)-TSS2

M06-2X/6-311++G(d,p)

C	1.27672300	-1.63422000	-0.51651000
C	1.82742100	-0.17300300	1.32154000

C	0.33963900	0.12407100	0.95648300
C	-0.03223000	-1.18889500	0.18676800
H	1.19095900	-1.61404800	-1.60555300
H	1.50236500	-2.66021200	-0.22879500
H	1.77601400	-0.95747500	2.08126000
H	2.34381100	0.69669800	1.73041100
H	-0.32454100	-1.89430700	0.96679400
O	-0.52841300	0.30840400	2.01704900
C	2.36794500	-0.66019800	-0.01646700
H	3.33697400	-1.14790100	0.08768000
C	2.49043200	0.56691000	-0.91455100
H	2.85169000	0.31125900	-1.91262700
C	1.10469800	1.22009200	-1.10879800
H	1.18090900	2.22373600	-1.52308000
H	0.52215200	0.58867800	-1.79034000
N	0.40880300	1.31920100	0.17359600
N	-1.24881400	1.54520500	-0.28728700
N	-2.03953000	2.30704400	-0.32047900
H	3.18287400	1.28669100	-0.47476400
H	-0.25460200	1.07928600	2.53402500
S	-1.42416000	-1.00291900	-0.92914400
C	-2.83589700	-1.10993500	0.20433800
H	-3.72145900	-0.86458900	-0.38208200
H	-2.92034400	-2.12957600	0.57972400
H	-2.72852900	-0.40786100	1.02962600

#### 4.15 Cartesian coordinates of 3(III)

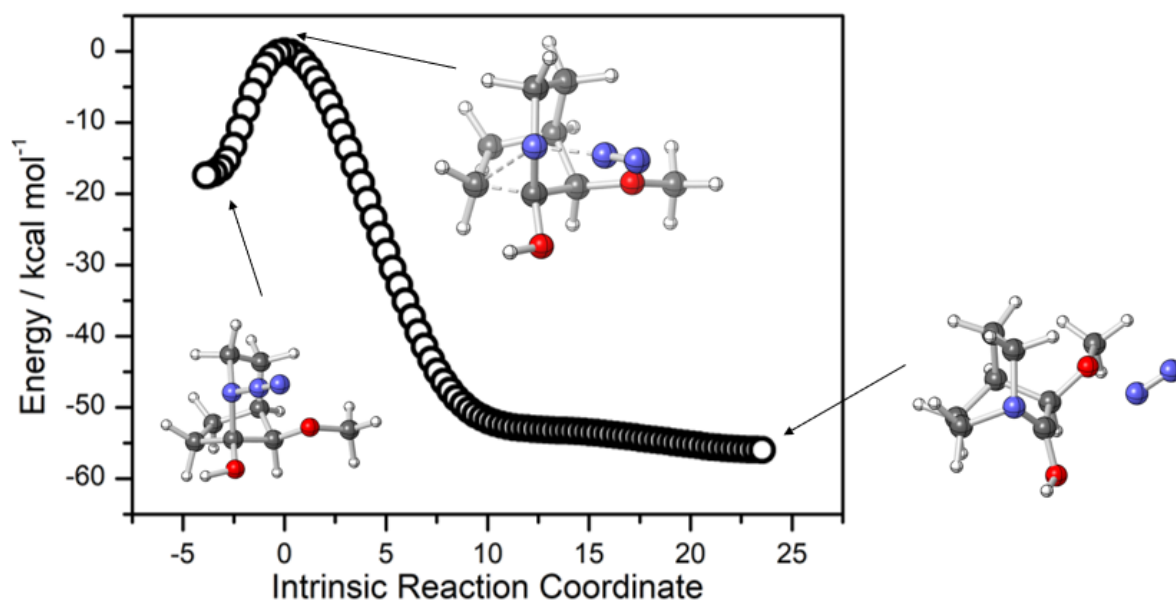
M06-2X/6-311++G(d,p)

C	-0.60944900	-1.35856300	-1.11328800
C	-2.15962600	0.48816100	-0.73389000
C	0.11671900	0.97615800	-0.44611700
C	0.54918200	-0.35066400	-0.95379600
H	-0.25980400	-2.34686800	-0.81183500
H	-0.86040800	-1.41339800	-2.17486800
H	-2.05432700	0.69963800	-1.79881500
H	-3.12674000	0.85532500	-0.38876600
H	1.18610000	-0.26810700	-1.83425800
O	0.98466800	1.92434200	-0.41490700
C	-1.87245600	-0.95140000	-0.33790600

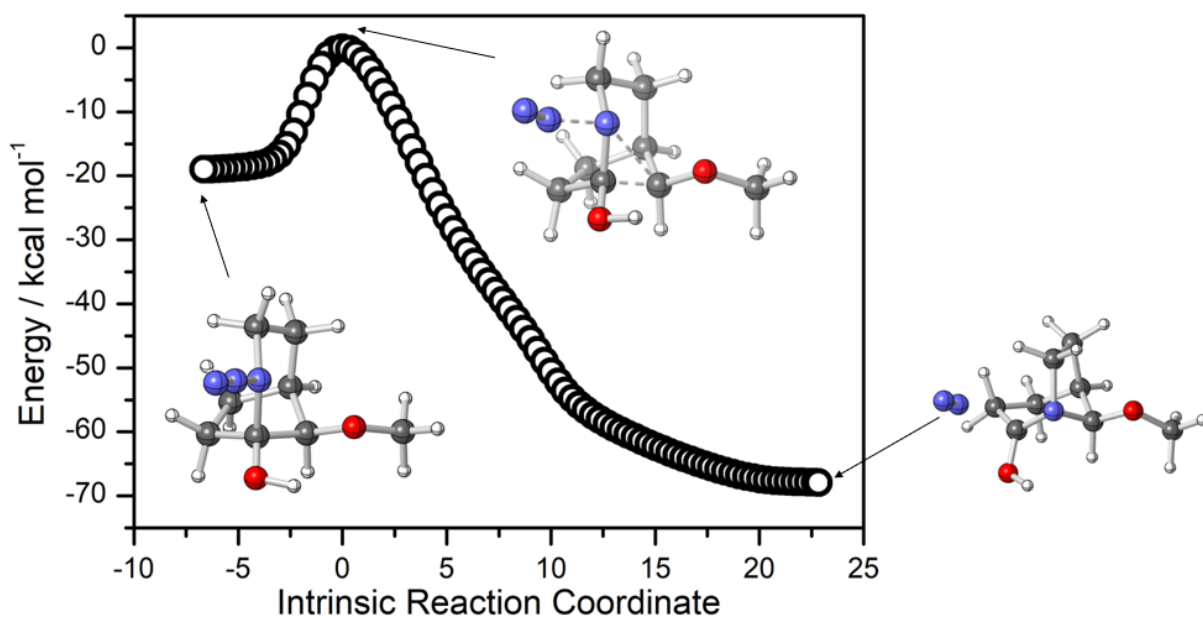
H	-2.68148600	-1.63281300	-0.59584300
C	-1.68332600	-0.82861500	1.19392000
H	-0.91718400	-1.50710400	1.57059500
C	-1.31050900	0.65870600	1.44048800
H	-2.12575800	1.22037300	1.89213100
H	-0.40400100	0.80317800	2.02579100
N	-1.12961200	1.23061900	0.04854100
H	-2.61478900	-1.06322000	1.70927900
H	0.58119700	2.72701200	-0.02606600
S	1.61085800	-0.89856700	0.46953200
C	3.15358800	0.00361200	0.19070200
H	3.89688700	-0.50953200	0.80326300
H	3.44809000	-0.06164800	-0.85651900
H	3.08370200	1.04078800	0.51220100

**5. Calculation data for systems 4 ( $R_1=OCH_3$  and  $R_2=H$ ) and 5 ( $R_1=H$  and  $R_2=OCH_3$ ) using M06-2X/6-311++G(d,p) level of theory.**

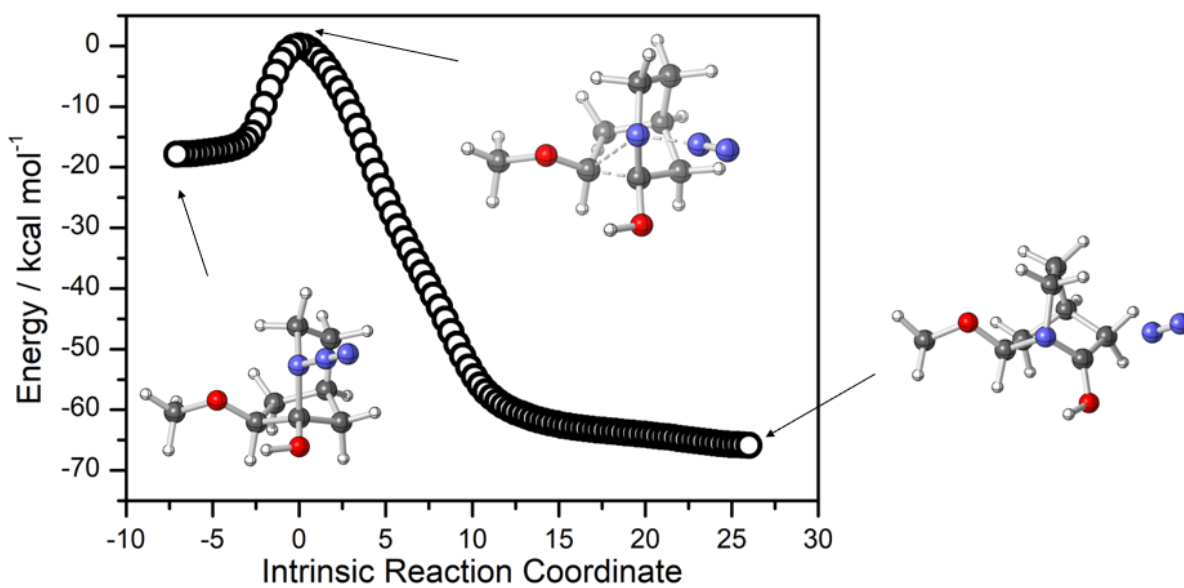
**5.1. IRCs**



**Figure S8.** Optimized geometries for the formation of 4(III) from 4(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.

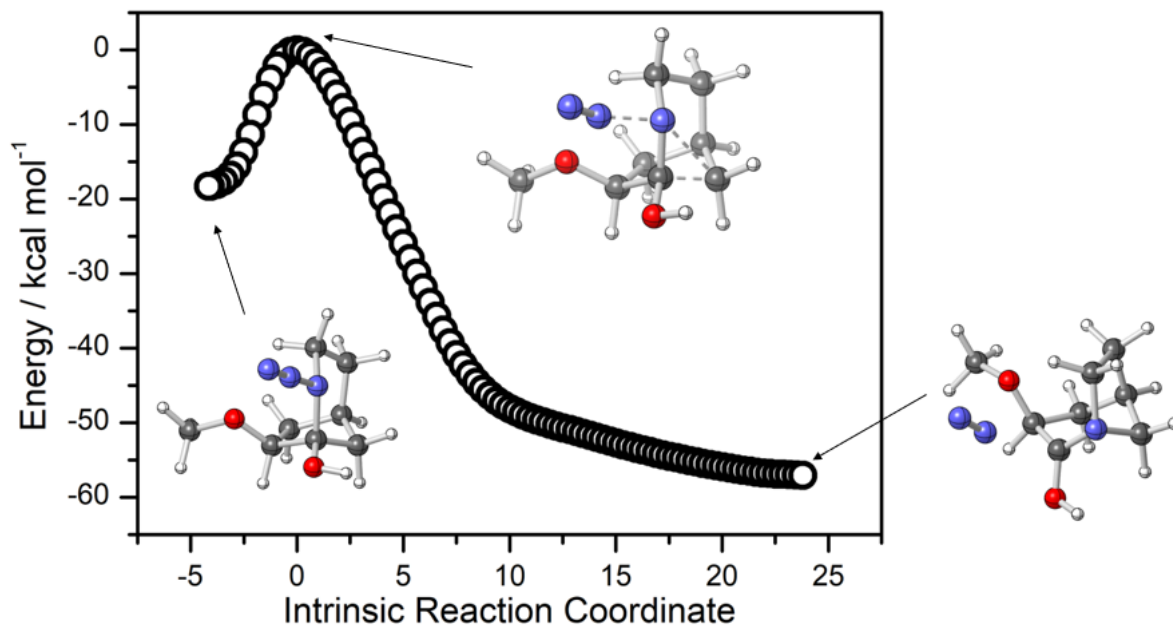


**Figure S9.** Optimized geometries for the formation of 4(III) from 4(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



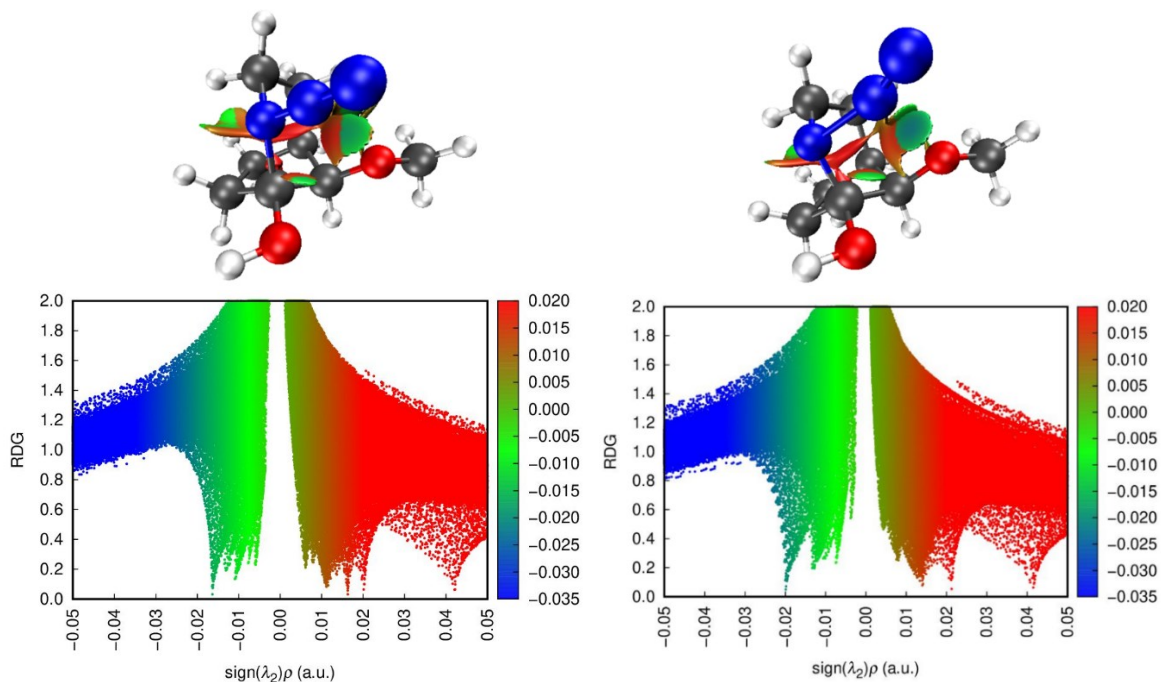
**Figure S10.** Optimized geometries for the formation of 5(III) from 5(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.

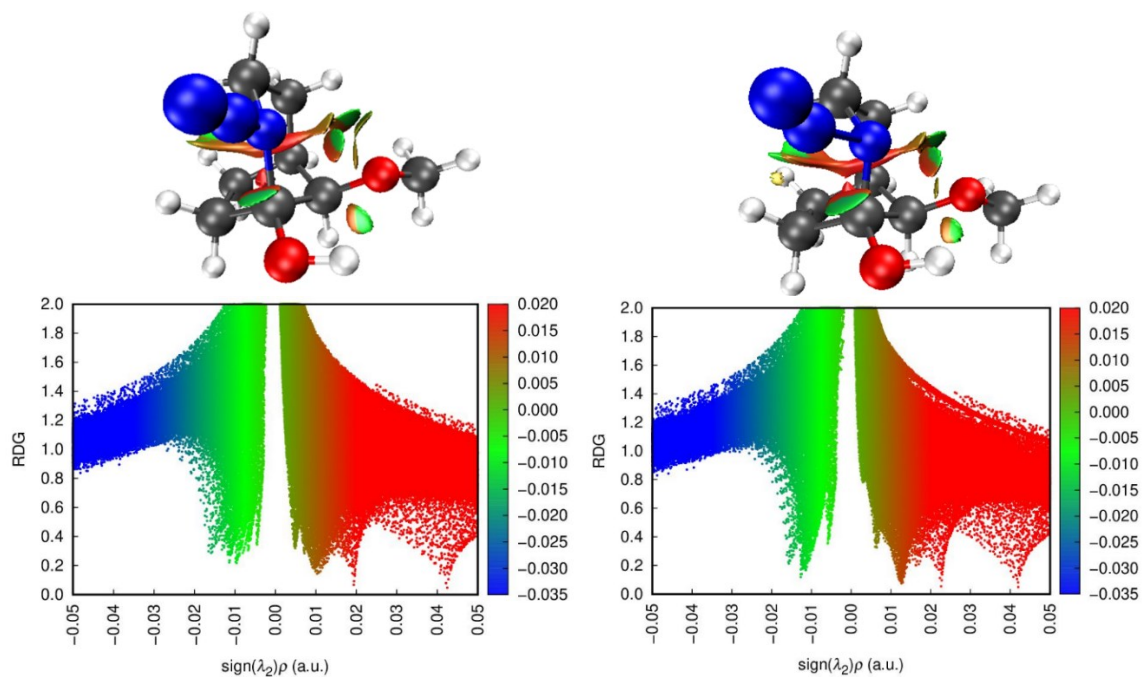




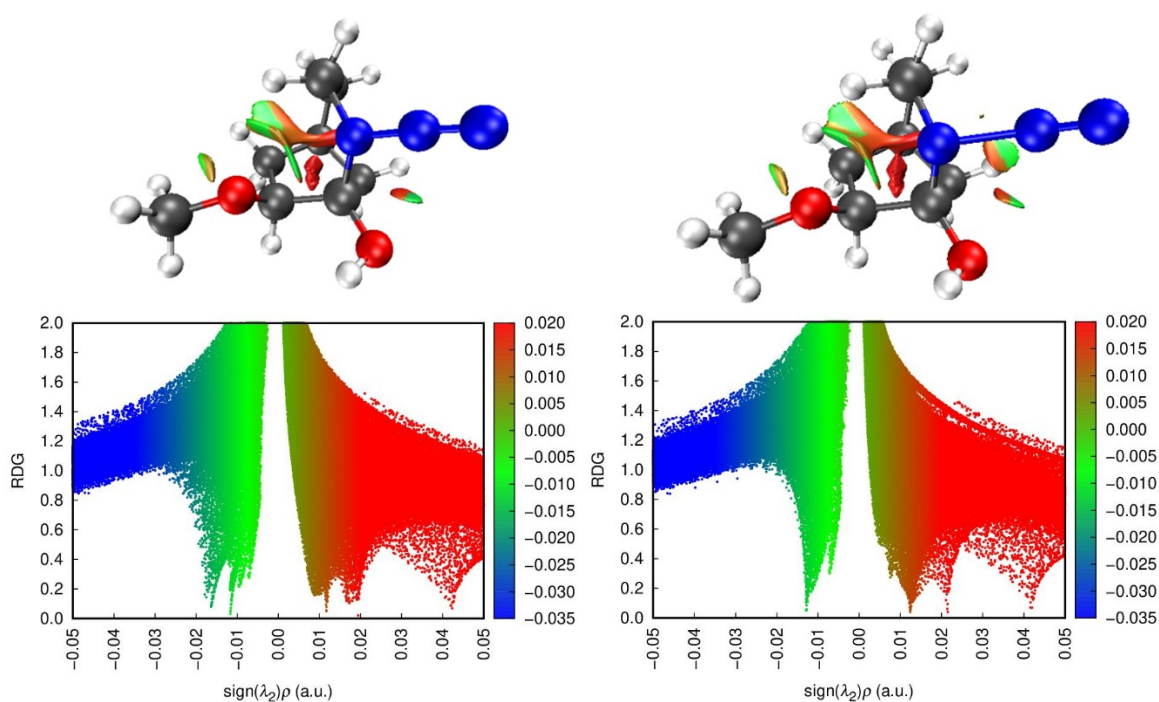
**Figure S11.** Optimized geometries for the formation of 5(III) from 5(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.

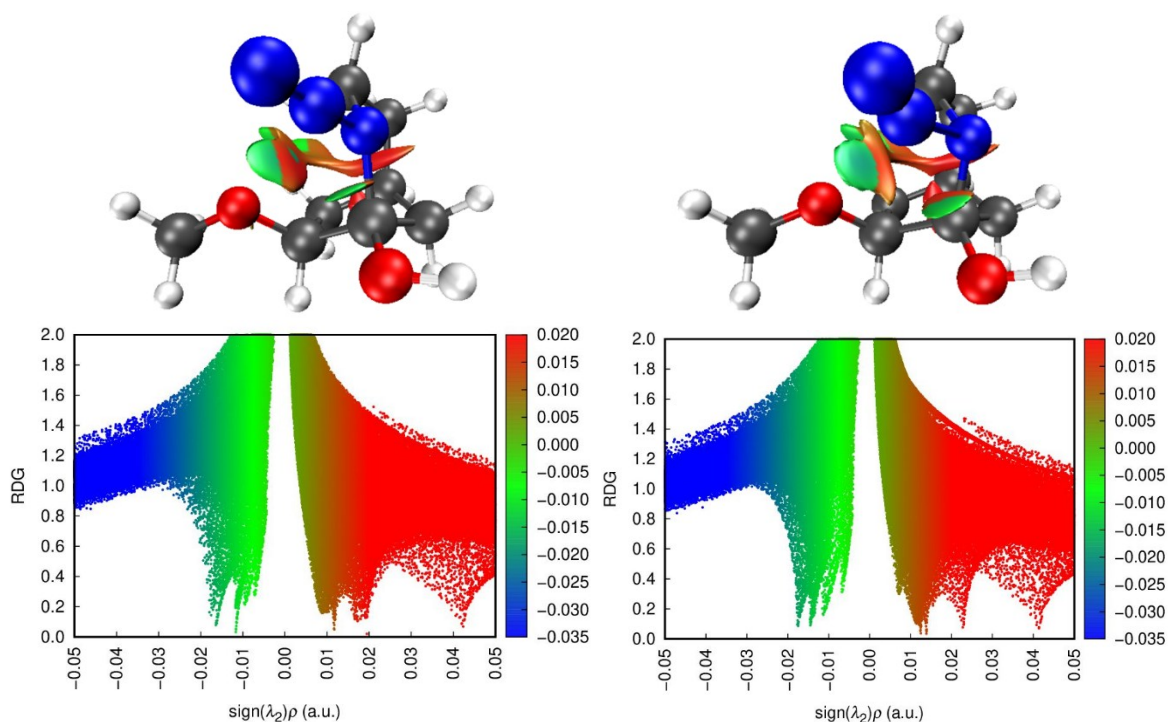
## 5.2. NCI





**Figure S12.** NCI isosurfaces for 4(II)-INT (top left), 4(II)-TSS2 (top right), 4(III)-INT (bottom left) and 4(III)-TSS2 (bottom right) obtained at M06-2X/6-311++G(d,p) level of theory using a blue-green-red color scale from  $-0.04 < \text{sign}(\lambda_2)\rho < 0.04$  a.u. Plots of the reduced density gradient and  $\text{sign}(\lambda_2)\rho$  are shown right under each correlated NCI isosurface obtained at the same level of theory.





**Figure S13.** NCI isosurfaces for 5(II)-INT (top left), 5(II)-TSS2 (top right), 5(III)-INT (bottom left) and 5(III)-TSS2 (bottom right) obtained at M06-2X/6-311++G(d,p) level of theory using a blue-green-red color scale from  $-0.04 < \text{sign}(\lambda_2)\rho < 0.04$  a.u. Plots of the reduced density gradient and  $\text{sign}(\lambda_2)\rho$  are shown right under each correlated NCI isosurface obtained at the same level of theory.

### 5.3. Cartesian coordinates of 4(II)-TSS

M06-2X/6-311++G(d,p)

C	-2.47743700	0.10509600	-0.07725100
C	-0.27727400	0.84232200	-0.65967100
C	-0.24746300	-0.68820200	-0.81111600
C	-1.77852500	-1.03919700	-0.85245800
H	-3.08493300	-0.27139700	0.74649700
H	-3.13896100	0.64808400	-0.75233400
H	-0.61790600	1.24863400	-1.62147400
H	-2.00817300	-1.02954000	-1.91959800
H	-1.99279500	-2.03916100	-0.47357800
O	0.50325800	-1.08594100	-1.89112500
C	-1.34616100	1.01964100	0.42844300
H	-1.66430000	2.05736200	0.52423700
C	-0.76275700	0.51909100	1.75414600
H	-1.49680500	0.61881400	2.55591000
C	-0.37961500	-0.95210300	1.64449200

H	0.26782200	-1.32207700	2.44090700
H	-1.26570100	-1.60962400	1.67720800
N	0.19068900	-1.38386000	0.37669200
N	1.92609300	-0.91671900	0.46264400
N	3.00609100	-1.04965800	0.52745900
H	0.11635100	1.10597000	2.03150400
H	0.41088000	-2.03905300	-2.02888100
O	0.99998800	1.29938400	-0.34557400
C	1.11846400	2.71675600	-0.37688500
H	0.50429500	3.18118800	0.40064600
H	2.16612200	2.95046200	-0.19630900
H	0.82262600	3.10402600	-1.35691500

#### 5.4. Cartesian coordinates of 4(III)-TSS

M06-2X/6-311++G(d,p)

C	-0.59262100	1.95444500	1.06319600
C	-1.18937000	-0.26449800	0.45264400
C	0.36313900	-0.27436300	0.71969200
C	0.55449900	1.00586800	1.52489100
H	-0.21309200	2.89818700	0.66932600
H	-1.24036300	2.18856400	1.90736400
H	-1.63055300	-0.42407600	1.44762400
H	0.46391900	0.74722500	2.57924100
H	1.55509300	1.41843500	1.36855600
O	0.81821100	-1.41031700	1.34372400
C	-1.38786500	1.17669300	-0.01036700
H	-2.44190400	1.45636900	-0.03315300
C	-0.78202100	1.30244800	-1.40167600
H	-0.87069000	2.31755500	-1.79297900
C	0.75028900	1.02044200	-1.35421200
H	1.15354200	0.90148900	-2.35766500
H	1.24024400	1.83972100	-0.82416700
N	0.87827200	-0.23821100	-0.64895300
N	2.60050500	-0.46484000	-0.40444000
N	3.59131900	-0.89538600	-0.55447400
H	-1.25974800	0.61376100	-2.09870100
H	0.44547300	-2.18492100	0.89512200
O	-1.52350600	-1.29972500	-0.41173500
C	-2.92044700	-1.57559500	-0.43195800
H	-3.48218900	-0.72764500	-0.83509000

H	-3.06165800	-2.44152900	-1.07583700
H	-3.28001300	-1.80638600	0.57625900

### 5.5. Cartesian coordinates of 5(II)-TSS

M06-2X/6-311++G(d,p)

C	1.49147000	1.29660300	0.45341700
C	-0.60296100	0.68968600	1.48043800
C	-0.19633900	-0.51504100	0.64088100
C	1.34550700	-0.24581100	0.45183800
H	1.89884000	1.65303600	-0.49643000
H	2.17834000	1.60015100	1.24358000
H	-0.17875500	0.56497000	2.47858200
H	-1.68930400	0.77604700	1.56610300
H	1.76952400	-0.67600800	1.36896000
O	-0.51338700	-1.72322300	1.21834000
C	0.06735800	1.83626100	0.70977800
H	0.06770200	2.76413600	1.27901700
C	-0.67431000	2.03419500	-0.61687500
H	-0.22047100	2.83752200	-1.20069800
C	-0.62289400	0.75697500	-1.44297100
H	-1.29388600	0.72609800	-2.30216800
H	0.38699100	0.56838200	-1.86019600
N	-0.75028600	-0.48196200	-0.71473700
N	-2.47892600	-0.66160800	-0.37691800
N	-3.48243500	-1.08281900	-0.44538500
H	-1.71912500	2.30495200	-0.43353500
H	-0.09485200	-2.44062500	0.72019200
O	1.83837900	-0.92418100	-0.66593200
C	3.26007200	-0.99459000	-0.67158400
H	3.54723700	-1.53030900	-1.57440700
H	3.70324800	0.00584600	-0.68606600
H	3.61867400	-1.53991400	0.20755900

### 5.6. Cartesian coordinates of 5(III)-TSS

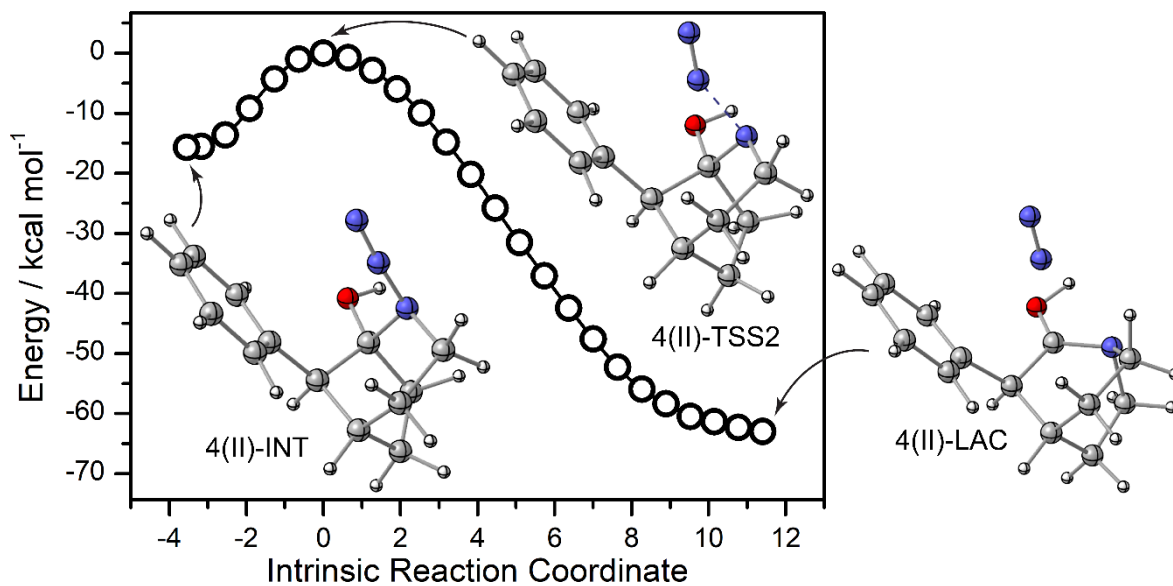
M06-2X/6-311++G(d,p)

C	-1.35035100	1.48468600	-0.12730200
C	-1.68094000	-0.53349000	1.14594700
C	-0.13729300	-0.38141500	0.92560000
C	-0.00064100	1.10722400	0.54266700
H	-1.19070600	1.82332700	-1.15423700

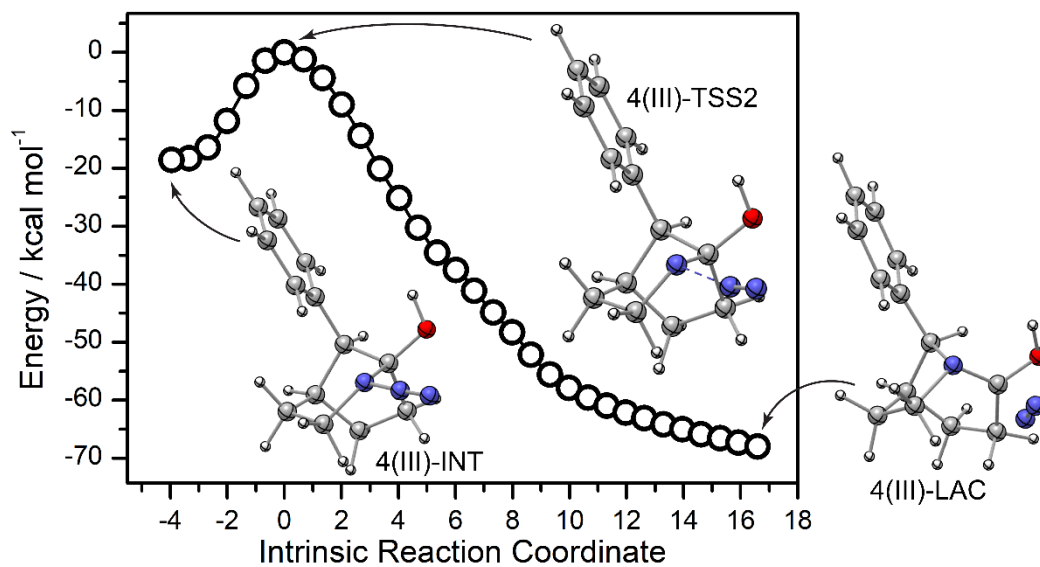
H	-1.82451500	2.29801800	0.42159900
H	-1.86129800	-0.02218900	2.09574600
H	-2.00739400	-1.57170200	1.22573900
H	0.13782300	1.65183200	1.48326500
O	0.66744800	-0.70568200	1.99280500
C	-2.22363900	0.21241700	-0.06688900
H	-3.28532700	0.43772200	0.03807900
C	-2.00361700	-0.69753400	-1.26851600
H	-2.33202000	-0.24144700	-2.20433200
C	-0.48397000	-0.96749400	-1.45624900
H	-0.31243100	-1.80161300	-2.13313900
H	-0.01405100	-0.05582400	-1.82609100
N	0.06063900	-1.32446300	-0.15098400
N	1.82184200	-1.26024600	-0.39529700
N	2.84270200	-1.61585400	-0.53713600
H	-2.53568500	-1.64056400	-1.13620300
H	0.46981900	-1.60233400	2.29871400
O	1.13627500	1.25119400	-0.26361100
C	1.57359700	2.59949500	-0.37982600
H	2.45311800	2.59482400	-1.02133500
H	0.79847300	3.22547300	-0.83306300
H	1.83925600	3.00099000	0.60303200

**6. Calculation data for systems 6 ( $R_1$ =phenyl and  $R_2$ =H) and 7 ( $R_1$ =H and  $R_2$ =phenyl) using M06-2X/6-311++G(d,p) level of theory**

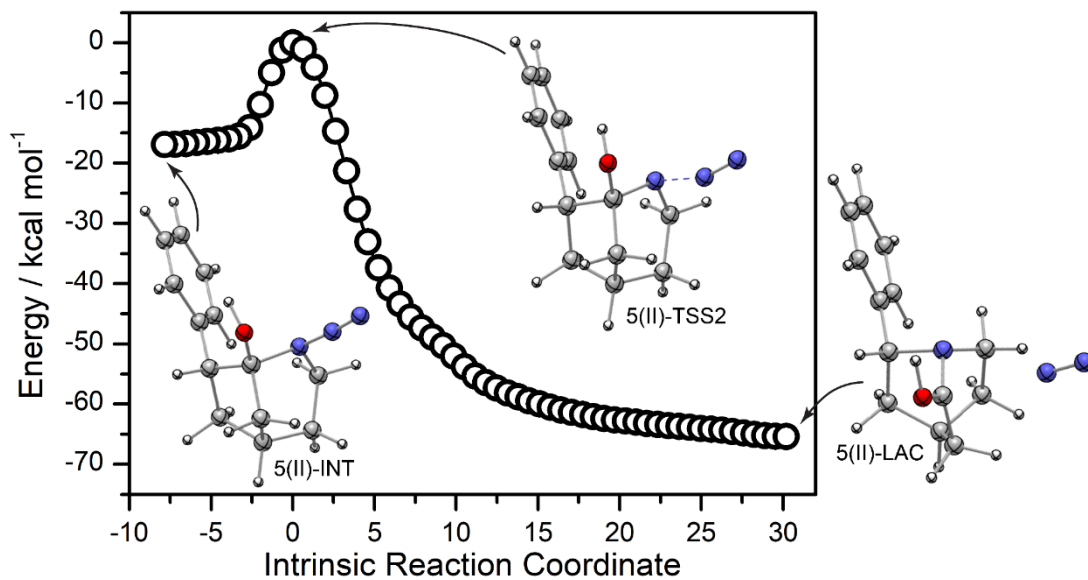
### **6.1. IRCs**



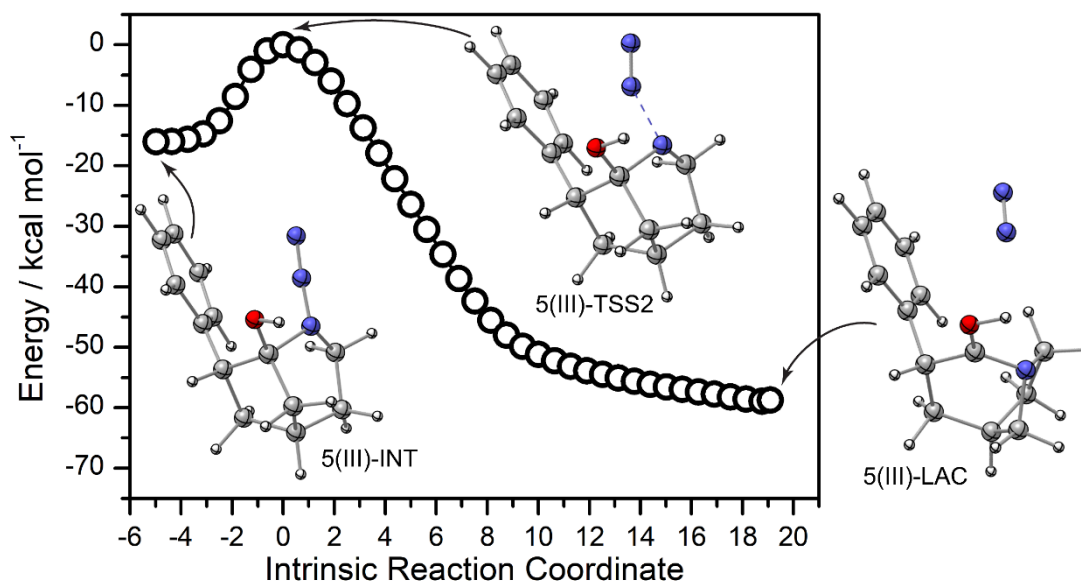
**Figure S14.** Optimized geometries for the formation of 6(II) from 6(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S15.** Optimized geometries for the formation of 6(III) from 6(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S16.** Optimized geometries for the formation of 7(II) from 7(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S17.** Optimized geometries for the formation of 7(III) from 7(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



## 6.2. NBO analysis

**Table S4.** Total donor-acceptor interactions of type  $\sigma, \pi$  (C–C(phenyl))  $\leftrightarrow$   $\sigma^*, \pi^*$ (N–N) (in kcal mol<sup>-1</sup>) of system 6 (R<sub>1</sub>=phenyl, R<sub>2</sub>=H) and system 7 (R<sub>1</sub>=H, R<sub>2</sub>= phenyl) obtained by NBO calculations at M06-2X/6-311++G(d,p) level of theory.

Structure	$\Sigma \sigma, \pi$ (C–C(phenyl)) $\leftrightarrow$ $\sigma^*, \pi^*$ (N–N) kcal mol <sup>-1</sup>
<b>System 6</b>	
4(II)-INT	0.9
4(II)-TSS2	7.1
4(III)-INT	0.0
4(III)-TSS2	1.0
<b>System 7</b>	
5(II)-INT	0.0
5(II)-TSS2	0.0
5(III)-INT	1.3
5(III)-TSS2	8.1

## 6.3 Cartesian coordinates of 6(II)-INT

M06-2X/6-311++G(d,p)

C	2.63297000	-1.41768200	-0.72208200
C	0.37427800	-0.60501500	-0.90737000
C	1.28425600	0.62065700	-0.73461900
C	2.68788300	0.09685600	-1.03950100
H	3.41235500	-1.72251400	-0.02235800
H	2.76717200	-1.99322000	-1.63765700
H	0.44236900	-0.84063700	-1.97738900
H	2.85613300	0.27308500	-2.10350900
H	3.44964400	0.64671300	-0.48426100
O	0.89084100	1.75361100	-1.39760300
C	1.21980200	-1.66046800	-0.14834400
H	0.87315800	-2.67072100	-0.36162700
C	1.19372800	-1.42655800	1.37243700
H	1.79300600	-2.19306900	1.86987200
C	1.78017800	-0.07240100	1.75141100
H	1.50830400	0.24861600	2.75609700
H	2.86563400	-0.04052600	1.66167300

N	1.29129300	0.97249800	0.78885000
N	0.31945100	1.69591200	1.17138500
N	-0.46569300	2.40456500	1.49422100
H	0.17776100	-1.49855600	1.76180700
H	1.65692300	2.31914900	-1.56977800
C	-1.09452100	-0.46786900	-0.54407900
C	-1.82822500	0.66910100	-0.90399000
C	-1.77423500	-1.52059100	0.07786400
C	-3.18386400	0.76780300	-0.60592200
H	-1.34608900	1.48289700	-1.43028800
C	-3.13231600	-1.42680100	0.36589300
H	-1.25152700	-2.43516200	0.33168600
C	-3.84078300	-0.27668100	0.03572200
H	-3.72861200	1.66111200	-0.88914100
H	-3.63553500	-2.25768900	0.84675300
H	-4.89768000	-0.20127800	0.26322200

#### 6.4 Cartesian coordinates of 6(II)-TSS2

M06-2X/6-311++G(d,p)

C	2.79900000	-0.99396100	-0.98120800
C	0.49188900	-0.36368500	-1.00091700
C	1.25675400	0.87024700	-0.44344600
C	2.72904100	0.54944100	-0.88747300
H	3.60659800	-1.40660900	-0.37551600
H	2.97701700	-1.28810700	-2.01566400
H	0.61594500	-0.27691200	-2.08616900
H	2.80336200	1.02907900	-1.86464600
H	3.47877300	1.00347500	-0.23824500
O	0.75208000	2.07033400	-0.90122400
C	1.41894600	-1.49192600	-0.50351200
H	1.15130800	-2.45282900	-0.94268300
C	1.42930600	-1.60447000	1.03084600
H	2.15929200	-2.35884200	1.33145700
C	1.82360100	-0.28180200	1.67413900
H	1.56711300	-0.19685200	2.73044900
H	2.90930200	-0.10184100	1.62959100
N	1.33743300	0.91695600	1.00022400
N	-0.33941300	1.04582700	1.50161300
N	-1.12894700	1.46344700	2.13099500

H	0.46636700	-1.91361300	1.43387200
H	1.33075200	2.79476000	-0.62537700
C	-0.98904200	-0.39525500	-0.70147200
C	-1.79296800	0.67214800	-1.13300500
C	-1.60806800	-1.46649400	-0.04748900
C	-3.14929200	0.70531800	-0.84108600
H	-1.34673600	1.48670200	-1.68827300
C	-2.96972500	-1.43763500	0.23619700
H	-1.04099700	-2.34630800	0.22664200
C	-3.73988800	-0.34084400	-0.13598100
H	-3.74870400	1.54593400	-1.17076800
H	-3.42882000	-2.27733400	0.74485800
H	-4.79804400	-0.31348500	0.09689000

## 6.5 Cartesian coordinates of 6(II)

M06-2X/6-311++G(d,p)

C	2.57838500	-1.00614700	-0.82183500
C	0.27489900	0.03333200	-0.88753000
C	1.14430100	1.05704700	-0.24682900
C	3.10252200	0.02934200	0.21056600
H	3.14200700	-1.93495100	-0.72975000
H	2.71700200	-0.63094100	-1.83976500
H	0.31551600	0.23723000	-1.96319000
H	3.76299800	0.77470800	-0.22798600
H	3.60793400	-0.43002900	1.05849100
O	1.41186300	2.13835500	-0.88024300
C	1.08258600	-1.27405200	-0.55289000
H	0.71693700	-2.08173800	-1.18546500
C	0.92274300	-1.58757700	0.93525500
H	1.64260500	-2.35657100	1.22037200
C	1.18965600	-0.27332200	1.70177600
H	0.26599100	0.18955000	2.04691900
H	1.83957400	-0.41610800	2.56339200
N	1.88130900	0.71746500	0.83238700
H	-0.07531800	-1.95695500	1.16943900
H	2.06026800	2.68201000	-0.38626500
C	-1.18132600	0.04266700	-0.44040200
C	-1.74107500	1.15822300	0.18119800
C	-1.98368600	-1.06783300	-0.70461500

C	-3.08374800	1.15953500	0.54945200
H	-1.14015100	2.04166700	0.37856400
C	-3.32498000	-1.06293100	-0.33999900
H	-1.56704300	-1.93772800	-1.20016500
C	-3.87764900	0.04846200	0.29118900
H	-3.50542000	2.03176600	1.03489400
H	-3.93968500	-1.92986700	-0.55218600
H	-4.92305400	0.04838300	0.57591600

## 6.6 Cartesian coordinates of 6(III)-INT

M06-2X/6-311++G(d,p)

C	1.98621900	-2.16849900	-0.02601600
C	-0.07576400	-1.00362800	-0.40916100
C	1.04996200	-0.10372300	-0.90853800
C	2.24259800	-1.04272000	-1.06652100
H	2.81381300	-2.27790800	0.67648500
H	1.86225100	-3.12224100	-0.53817400
H	-0.21221100	-1.70603500	-1.23947100
H	2.21884200	-1.42243500	-2.08853000
H	3.18992300	-0.51819200	-0.92825000
O	0.80513100	0.69597400	-1.98586200
C	0.66958000	-1.78783000	0.69788800
H	0.09903000	-2.66598300	0.99797400
C	0.92282800	-0.90919200	1.92581200
H	1.42188200	-1.49302100	2.70249600
C	1.83642400	0.26730700	1.60715800
H	1.77622700	1.05839200	2.35454200
H	2.87617200	-0.04447700	1.48153400
N	1.38363600	0.85427100	0.29845700
N	1.95021600	1.93155000	-0.05177700
N	2.38027500	2.89844300	-0.37363800
H	-0.02359900	-0.55595800	2.33837800
H	-0.13038300	0.95354800	-1.99645400
C	-1.42636100	-0.37512600	-0.14371400
C	-1.63573800	0.77319200	0.63211700
C	-2.54204900	-0.98539300	-0.72995000
C	-2.91873400	1.28376900	0.81260700
H	-0.81011900	1.28495700	1.10946000
C	-3.82354400	-0.48069800	-0.54338000

H	-2.40103600	-1.87161300	-1.34038000
C	-4.01567600	0.65990000	0.22910800
H	-3.05824100	2.17381800	1.41517800
H	-4.66893400	-0.97567200	-1.00689300
H	-5.01202600	1.06103500	0.37323400

## 6.7 Cartesian coordinates of 6(III)-TSS2

M06-2X/6-311++G(d,p)

C	1.71788400	-2.32205300	-0.07147100
C	-0.19099600	-0.92708000	-0.44156000
C	1.08978900	-0.07113800	-0.81361800
C	2.14791800	-1.15640900	-1.00705200
H	2.49241200	-2.57154200	0.65565300
H	1.51952300	-3.21635200	-0.66142600
H	-0.30812600	-1.50552700	-1.36429100
H	2.12993800	-1.45044100	-2.05578400
H	3.14448400	-0.76249600	-0.78749200
O	0.94230400	0.75130900	-1.90541500
C	0.41690800	-1.85363700	0.62112000
H	-0.25678800	-2.67875500	0.85472000
C	0.70199500	-1.04467300	1.87848400
H	1.14895400	-1.65945300	2.66235400
C	1.75374500	0.05889200	1.57577100
H	1.81123500	0.78213600	2.38713100
H	2.72189600	-0.41781100	1.40636800
N	1.28256500	0.74573200	0.38056400
N	2.59105300	1.79040300	-0.07202900
N	3.14684400	2.72088800	-0.19579400
H	-0.20961900	-0.59567900	2.27428500
H	0.11537700	1.25174700	-1.83006200
C	-1.50867100	-0.23466200	-0.19165000
C	-1.68404300	0.91494800	0.58671700
C	-2.63998700	-0.81819900	-0.77631700
C	-2.95346000	1.45536700	0.77737800
H	-0.83704300	1.40844800	1.04717200
C	-3.90742900	-0.28569300	-0.57723600
H	-2.52279700	-1.70420400	-1.39221500
C	-4.06758800	0.85713300	0.20050900
H	-3.06685200	2.35010200	1.37833700

H	-4.76733800	-0.75846900	-1.03713600
H	-5.05331700	1.28187500	0.35007000

### 6.8 Cartesian coordinates of 6(III)

M06-2X/6-311++G(d,p)

C	2.39865400	1.33218900	0.65516300
C	0.24361800	0.04261100	0.56864100
C	2.24197500	-0.95144000	0.14331400
C	3.20478000	0.14364200	-0.01140000
H	2.91455900	2.24985300	0.37064000
H	2.45568400	1.22718300	1.74102100
H	0.46821600	-0.26397500	1.59473800
H	4.14249800	-0.05328700	0.50213900
H	3.38540800	0.37608700	-1.06004300
O	2.45980500	-1.83821600	1.04584600
C	0.93417000	1.37352400	0.19586300
H	0.43727900	2.22975300	0.65003800
C	0.84354100	1.36895400	-1.33920000
H	1.64529600	1.95675100	-1.78826900
C	0.94617700	-0.13013400	-1.70204500
H	0.05474700	-0.48900000	-2.21294100
H	1.81128900	-0.39233700	-2.30914000
N	1.00597100	-0.87351200	-0.40639300
H	-0.11056400	1.77527700	-1.67367500
H	1.69527700	-2.44399600	1.12792100
C	-1.24728100	-0.03630500	0.32938400
C	-1.83020300	-1.15311300	-0.26700000
C	-2.06185400	1.01132100	0.76378200
C	-3.21034200	-1.21986100	-0.43337300
H	-1.20333000	-1.97039600	-0.60603400
C	-3.44102600	0.94087500	0.59857300
H	-1.62794700	1.88318700	1.24011500
C	-4.01874600	-0.17342000	-0.00240100
H	-3.65246100	-2.09179200	-0.90132600
H	-4.06380000	1.75937200	0.94035600
H	-5.09316000	-0.22541900	-0.13336400

### 6.9 Cartesian coordinates of 7(II)-INT

M06-2X/6-311++G(d,p)

C	-0.68469800	-2.03722000	-0.63717800
C	-2.23945200	-0.27424300	-1.25532000
C	-0.92747100	0.37706400	-0.86574000
C	0.10582300	-0.75794900	-1.02045400
H	-0.30382200	-2.51693900	0.26507800
H	-0.60109200	-2.76466700	-1.44378000
H	-2.21594700	-0.45365200	-2.33251700
H	-3.10790400	0.34506100	-1.01821500
H	0.24405900	-0.76973800	-2.10693800
O	-0.66512100	1.56079100	-1.49237500
C	-2.15953800	-1.58516700	-0.45393900
H	-2.86012400	-2.32732200	-0.83275400
C	-2.48538600	-1.29114400	1.01748700
H	-2.48869900	-2.21472000	1.60154000
C	-1.45055400	-0.36561700	1.64588200
H	-1.80312800	0.12896900	2.55067900
H	-0.52088600	-0.87672200	1.88124000
N	-1.05633300	0.71349700	0.67053200
N	-1.60666500	1.84288900	0.86217900
N	-2.01736700	2.85798600	1.01398700
H	-3.48158000	-0.84684700	1.09004700
H	0.27839000	1.77326800	-1.41681900
C	1.46165500	-0.46788100	-0.41502200
C	2.30768900	0.41449700	-1.09927600
C	1.91210200	-1.01485300	0.78798700
C	3.54260000	0.78097900	-0.57446100
H	2.02212500	0.78141100	-2.08205700
C	3.15257200	-0.65821100	1.30973900
H	1.31771100	-1.74848500	1.31925900
C	3.96542500	0.24974500	0.63932800
H	4.18097900	1.46197500	-1.12520700
H	3.48785000	-1.10158300	2.24024100
H	4.93099200	0.52305600	1.04810400

## 6.10 Cartesian coordinates of 7(II)-TSS2

M06-2X/6-311++G(d,p)

C	-0.43057500	-2.04235400	-0.73792300
C	-2.16112300	-0.43286800	-1.24857200
C	-0.96725100	0.37901000	-0.77197600

C	0.22236000	-0.66414600	-1.00311900
H	-0.00108200	-2.56048300	0.12039900
H	-0.26887500	-2.67961500	-1.60754100
H	-2.08527000	-0.54208300	-2.33172500
H	-3.10635300	0.06204700	-1.00866900
H	0.32235700	-0.53158500	-2.08491000
O	-0.83491400	1.58055900	-1.43002400
C	-1.93582500	-1.75999600	-0.51578600
H	-2.56891200	-2.55607100	-0.90385500
C	-2.22284500	-1.53969600	0.97472900
H	-2.08304100	-2.46328900	1.54023300
C	-1.27274100	-0.49188700	1.53553000
H	-1.53429000	-0.10021000	2.51901000
H	-0.24781300	-0.88402900	1.65550400
N	-0.98199800	0.63319300	0.66392700
N	-2.33828100	1.70020600	0.82790600
N	-2.89393400	2.59459700	1.11275100
H	-3.25730300	-1.21352300	1.12039800
H	-0.01256800	2.01497700	-1.15751600
C	1.56372900	-0.31636900	-0.39863000
C	2.30627500	0.71073900	-0.99579000
C	2.10296100	-0.96295400	0.71582900
C	3.52982700	1.10870400	-0.47070800
H	1.93970400	1.18143800	-1.90399900
C	3.33223100	-0.56967000	1.23873100
H	1.58675700	-1.79665100	1.17756600
C	4.04413200	0.47187300	0.65500000
H	4.08909300	1.90245000	-0.95204000
H	3.73697100	-1.08872500	2.09982800
H	5.00249500	0.77260100	1.06151800

### 6.11 Cartesian coordinates of 7(II)

M06-2X/6-311++G(d,p)

C	-1.03096500	-0.75645400	-1.39248900
C	-3.08595700	-0.27419400	0.01936100
C	-2.22955300	0.90859900	0.20667000
C	-0.21975900	0.39831400	-0.73017600
H	-0.37016100	-1.53897500	-1.76126700
H	-1.56506100	-0.35601000	-2.25783800



H	-3.84689800	-0.05950800	-0.73154500
H	-3.58245000	-0.56270700	0.95267100
H	-0.30020500	1.30165900	-1.33481800
O	-2.59128500	2.04398700	-0.26968900
C	-2.03655400	-1.35924000	-0.38816600
H	-2.56197900	-2.20576500	-0.82668100
C	-1.27816800	-1.74398900	0.87965800
H	-0.41902000	-2.36709100	0.62827500
C	-0.82759400	-0.42268500	1.54637100
H	-1.43543400	-0.18115100	2.41754000
H	0.21346800	-0.44789800	1.86277400
N	-0.95301600	0.72747300	0.61028800
H	-1.91554900	-2.30567700	1.56389700
H	-1.89571900	2.71792700	-0.12831700
C	1.24599200	0.20083900	-0.41283600
C	1.96837800	1.33058600	-0.01502400
C	1.89790000	-1.02754700	-0.48900000
C	3.31570200	1.23599700	0.30047000
H	1.46404800	2.28965900	0.05049500
C	3.25329900	-1.12248000	-0.17478100
H	1.37066100	-1.92287700	-0.79333700
C	3.96302400	0.00380300	0.22029600
H	3.86333500	2.12090200	0.60292400
H	3.75107000	-2.08255200	-0.24270900
H	5.01680000	-0.07343000	0.46131400

## 6.12 Cartesian coordinates of 7(III)-INT

M06-2X/6-311++G(d,p)

C	1.38965000	1.40705000	-1.20177100
C	2.56327900	-0.68167000	-0.81946600
C	1.09655900	-0.90189500	-0.51690400
C	0.37696100	0.23117500	-1.27867000
H	1.01720200	2.25228500	-0.62127300
H	1.58622600	1.77672500	-2.20748500
H	2.71216700	-0.93400300	-1.87271800
H	3.22212000	-1.29452800	-0.20067600
H	0.34985400	-0.14000500	-2.30749300
O	0.55228600	-2.13804100	-0.73992700
C	2.68728500	0.82739000	-0.57287000

H	3.58048400	1.23948400	-1.03933200
C	2.76328300	1.05570800	0.94168100
H	2.90558800	2.11518300	1.16634800
C	1.48642000	0.62904600	1.65493200
H	1.65442900	0.40628800	2.70809000
H	0.70465500	1.38322400	1.55895600
N	0.96887100	-0.63866700	1.02039600
N	-0.12946600	-1.06006800	1.51361000
N	-1.03744200	-1.48713600	1.97665600
H	3.61903300	0.51158200	1.34605000
H	1.21626800	-2.82517400	-0.58839200
C	-1.05430200	0.42154900	-0.81963000
C	-1.98935500	-0.56113100	-1.17110700
C	-1.47084100	1.47058400	0.00303100
C	-3.28664200	-0.52124900	-0.67724200
H	-1.68865400	-1.36976300	-1.82816100
C	-2.77418600	1.51404500	0.49564400
H	-0.79082000	2.27353900	0.26147000
C	-3.68084000	0.51291500	0.16913200
H	-3.99212700	-1.29529800	-0.95622900
H	-3.07901500	2.33823900	1.13027500
H	-4.69307400	0.54653400	0.55479500

### 6.13 Cartesian coordinates of 7(III)-TSS2

M06-2X/6-311++G(d,p)

C	-1.46559000	-1.58078800	-0.92882000
C	-2.64818300	0.53077700	-0.81572000
C	-1.13678600	0.82822400	-0.55216100
C	-0.45544000	-0.42875600	-1.17778500
H	-1.08991700	-2.34070400	-0.24235500
H	-1.67721500	-2.08111600	-1.87313500
H	-2.75794500	0.66419500	-1.89487900
H	-3.32092800	1.21572100	-0.29577300
H	-0.45686800	-0.18809900	-2.24359800
O	-0.64448000	1.99081500	-1.10869500
C	-2.74416600	-0.91818500	-0.35856100
H	-3.65591600	-1.39889100	-0.71351400
C	-2.73456500	-0.88298700	1.16559500
H	-2.77567300	-1.88204700	1.60422800

C	-1.41218200	-0.25721000	1.67078200
H	-1.47801400	0.03926100	2.71574500
H	-0.61910100	-0.99406900	1.54059200
N	-1.11123600	0.94428100	0.88583300
N	0.56000800	1.24481100	1.24029100
N	1.34526600	1.75463800	1.80569600
H	-3.58541000	-0.30983200	1.53678500
H	-1.15625300	2.74818900	-0.79161500
C	0.98345400	-0.55989600	-0.74481800
C	1.91037300	0.35353400	-1.27530300
C	1.43572300	-1.49306000	0.19781700
C	3.22311900	0.37536700	-0.83087800
H	1.58298800	1.06159200	-2.02801500
C	2.75486300	-1.47175100	0.64229600
H	0.77314600	-2.26070200	0.57902100
C	3.64551500	-0.52709000	0.14561700
H	3.92095500	1.09403400	-1.24439300
H	3.08642500	-2.20070700	1.37225100
H	4.67048200	-0.50853100	0.49710100

### 6.14 Cartesian coordinates of 7(III)

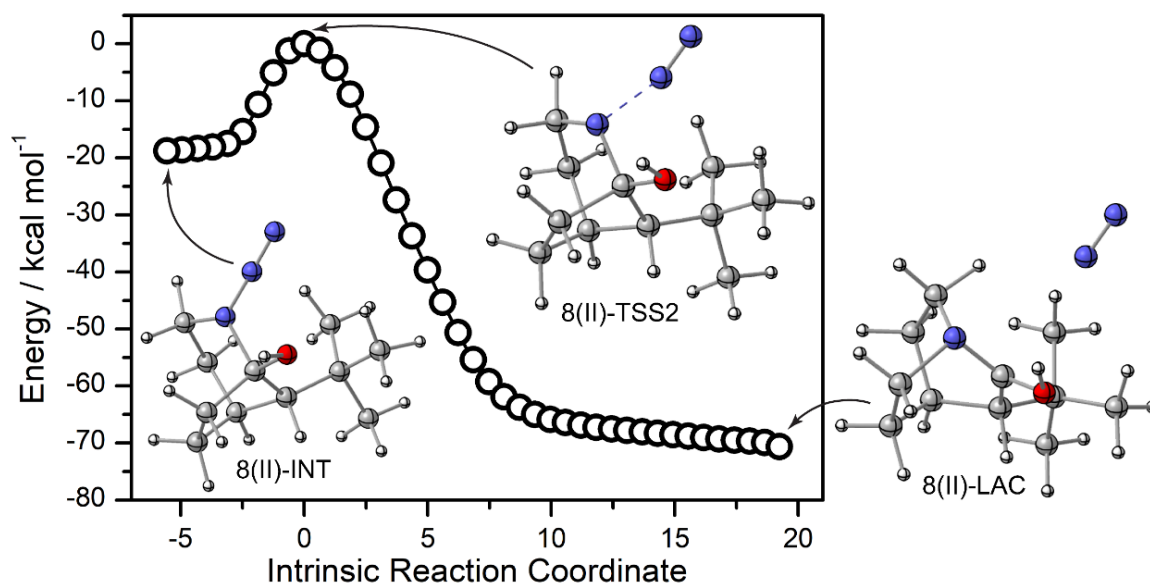
M06-2X/6-311++G(d,p)

C	0.77741800	1.06247400	1.04521500
C	2.62322000	1.13095100	-0.58574200
C	0.86056000	-0.40646400	-0.88587600
C	0.02160800	0.67084600	-0.28617900
H	0.43861700	0.40174400	1.84452800
H	0.45145600	2.07390800	1.28971500
H	2.10432200	1.92088700	-1.12240700
H	3.68902600	1.18758400	-0.80321000
H	0.08066300	1.52662100	-0.96420100
O	0.32803200	-1.56345300	-1.11479000
C	2.31769400	1.01377200	0.90781600
H	2.77696000	1.80052500	1.50225200
C	2.94310800	-0.37846500	1.22458200
H	2.33780200	-0.93325400	1.94275400
C	3.00596400	-1.12339300	-0.13970500
H	4.00408900	-1.15169100	-0.56895200
H	2.60231300	-2.13331300	-0.10925500

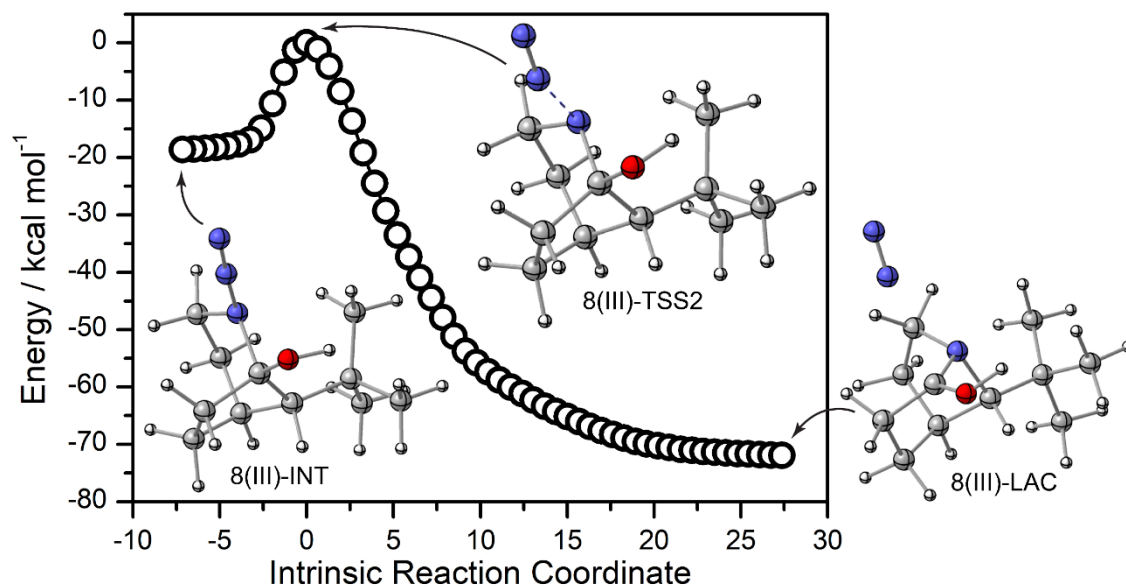
N	2.16574900	-0.21526300	-0.99906700
H	3.94494900	-0.26565800	1.63792300
H	0.96893400	-2.19942700	-1.48243500
C	-1.43146300	0.31445200	-0.08399600
C	-2.41779500	1.01006400	-0.78037900
C	-1.80582500	-0.68689900	0.81444700
C	-3.76315700	0.71117000	-0.58293000
H	-2.13459600	1.79280300	-1.47662400
C	-3.14767800	-0.98829200	1.00919000
H	-1.04642300	-1.23635300	1.36230900
C	-4.12943900	-0.28756100	0.31180200
H	-4.52247600	1.26165500	-1.12594800
H	-3.42900600	-1.76813200	1.70700600
H	-5.17641200	-0.51935300	0.46884800

## 7. Calculation data for systems 8 ( $R_1$ =t-butyl and $R_2$ =H) and 9 ( $R_1$ =H and $R_2$ =t-butyl) using M06-2X/6-311++G(d,p) level of theory

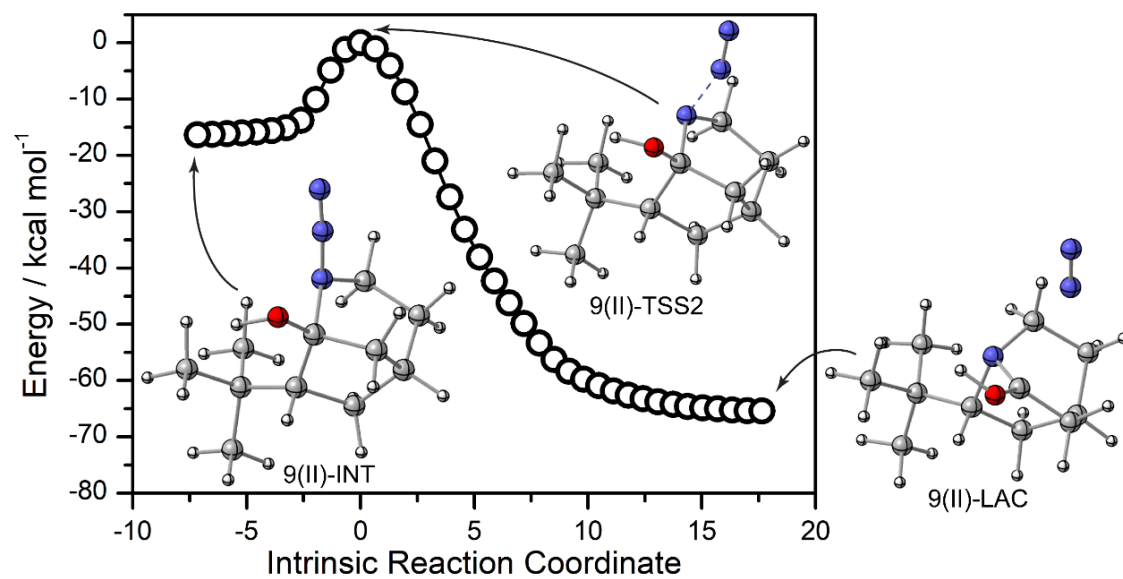
### 7.1. IRCs



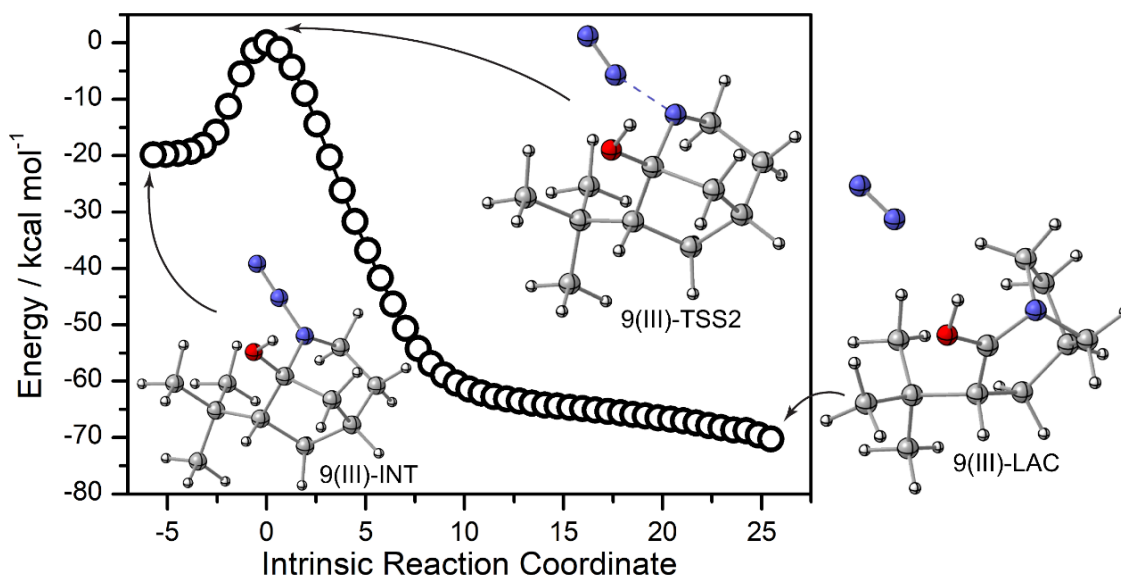
**Figure S18.** Optimized geometries for the formation of 8(II) from 8(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S19.** Optimized geometries for the formation of 8(III) from 8(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S20.** Optimized geometries for the formation of 9(II) from 9(II)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.



**Figure S21.** Optimized geometries for the formation of 9(III) from 9(III)-INT and IRC plot obtained using M06-2X/6-311++G(d,p) level of theory.

## 7.2 Cartesian coordinates of 8(II)-INT

M06-2X/6-311++G(d,p)

C	-0.79695100	2.39291100	-0.74530900
C	0.74646100	0.56154900	-0.51075500
C	-0.59279900	-0.02543000	-0.95504000
C	-1.37180300	1.17004400	-1.50686900
H	-1.57602300	2.96142500	-0.23519500
H	-0.30277500	3.06600500	-1.44535900
H	1.16536500	0.95256000	-1.44793500
H	-1.15459500	1.22997100	-2.57561400
H	-2.44832000	1.03545600	-1.38684100
O	-0.53531700	-1.15654500	-1.72262400
C	0.23855200	1.81374600	0.24990700
H	1.05339400	2.51439600	0.42592700
C	-0.41326300	1.47209000	1.59593500
H	-0.74689700	2.39051900	2.08515100
C	-1.64127800	0.58315900	1.43266800
H	-1.89273000	0.04328400	2.34469500
H	-2.51495700	1.14156600	1.08991000
N	-1.33235400	-0.42814900	0.37689200
N	-1.76869000	-1.59252600	0.47840900
N	-2.11574700	-2.64522300	0.54801500
H	0.30662900	0.99210500	2.25870500

H	-1.24813900	-1.15735700	-2.37641900
C	1.84349600	-0.36231500	0.08551300
C	1.34091800	-1.46880100	1.02592400
C	2.56983100	-1.05022500	-1.08317700
C	2.86731900	0.50695400	0.82827000
H	0.77596600	-1.09665900	1.88364600
H	0.73895900	-2.20865100	0.48948600
H	2.20790700	-2.00434000	1.42217000
H	3.04084300	-0.31044200	-1.73685500
H	3.35418400	-1.70822500	-0.69960000
H	1.88372400	-1.65095100	-1.68319500
H	3.72708100	-0.10479500	1.11402100
H	3.23161600	1.31685700	0.18927000
H	2.45593200	0.94882900	1.73940500

### 7.3 Cartesian coordinates of 8(II)-TSS2

M06-2X/6-311++G(d,p)

C	-1.73163400	-2.02207500	0.29352300
C	0.33860500	-0.81869900	0.37806900
C	-0.72175600	0.15787900	0.93623300
C	-1.90484100	-0.84089600	1.27478900
H	-2.63739100	-2.21066200	-0.28476600
H	-1.49962200	-2.92867800	0.85294900
H	0.49721300	-1.47231400	1.24476400
H	-1.69706700	-1.11564100	2.31060800
H	-2.88745700	-0.36694600	1.25058600
O	-0.28664500	0.91440500	2.00260400
C	-0.54229600	-1.62287300	-0.60589100
H	-0.01677100	-2.49246400	-0.99887400
C	-1.05292500	-0.76013200	-1.77151600
H	-1.71354100	-1.36218600	-2.40016000
C	-1.86598200	0.42121900	-1.26180700
H	-2.00016300	1.23088700	-1.97983600
H	-2.88574300	0.12093300	-0.97935100
N	-1.41716200	1.02027700	-0.00086100
N	-0.28024700	2.24616100	-0.41313500
N	0.05589100	3.28175000	-0.49497800
H	-0.24312000	-0.40918600	-2.40553500
H	-1.04558600	1.30954400	2.45440400

C	1.78336100	-0.39644500	-0.02816900
C	1.96738400	0.15293600	-1.45046000
C	2.37420900	0.60056100	0.97956500
C	2.62610100	-1.68302700	0.05604000
H	1.78755700	-0.61776800	-2.20344000
H	1.33714800	1.01183800	-1.68726400
H	3.00549000	0.47739900	-1.56198600
H	2.23940000	0.25558800	2.00698200
H	3.44672800	0.69851800	0.79087800
H	1.93241800	1.59545400	0.90296100
H	3.65361300	-1.47154000	-0.25106600
H	2.65239800	-2.07023400	1.07829500
H	2.23690800	-2.46578000	-0.60042300

#### 7.4 Cartesian coordinates of 8(II)

M06-2X/6-311++G(d,p)

C	1.89737900	-0.58883800	-1.39986600
C	-0.36217700	0.09775400	-0.61533000
C	0.47532300	1.09352100	0.09117400
C	2.56956900	0.40665400	-0.41671000
H	2.57230900	-1.42066000	-1.60411700
H	1.68193700	-0.09334700	-2.34938000
H	-0.51210900	0.53646300	-1.61146300
H	2.84563400	1.34807700	-0.88950000
H	3.45229200	-0.00520200	0.07051800
O	0.26986400	2.34557800	-0.06501700
C	0.59089300	-1.11731300	-0.77148300
H	0.12571100	-1.85219300	-1.42636800
C	0.94515100	-1.72173400	0.58880700
H	1.74474800	-2.45216900	0.45410600
C	1.41483300	-0.56872000	1.50191200
H	0.70842000	-0.35367100	2.30083700
H	2.38100500	-0.77359500	1.96190300
N	1.61206800	0.69966000	0.73885700
H	0.09724300	-2.24405100	1.03066100
H	0.93741300	2.86009900	0.43658500
C	-1.82093600	-0.09922700	-0.04521100
C	-1.88376300	-0.17099300	1.48481800
C	-2.66350500	1.09665300	-0.50608800



C	-2.39312700	-1.38290700	-0.64767100
H	-1.38401200	-1.05155600	1.88887100
H	-1.46222800	0.72527900	1.95332500
H	-2.93243100	-0.22605200	1.78731000
H	-2.67660400	1.17355100	-1.59644700
H	-3.69207900	0.96982000	-0.16016600
H	-2.29264700	2.04080500	-0.09907000
H	-3.44158600	-1.47713000	-0.35372200
H	-2.34985000	-1.36555800	-1.74032800
H	-1.86440200	-2.27025100	-0.29152000

## 7.5 Cartesian coordinates of 8(III)-INT

M06-2X/6-311++G(d,p)

C	0.64568700	2.27301000	1.00413900
C	-0.81418500	0.41081000	0.57092300
C	0.57044900	-0.15508700	0.89034200
C	1.31089200	0.99293200	1.57422700
H	1.37094900	2.95034500	0.55068700
H	0.14376100	2.81677000	1.80423000
H	-1.21871900	0.64973000	1.56432700
H	1.13894700	0.88743100	2.64592300
H	2.38758600	0.93583300	1.40191500
O	0.69410500	-1.34695200	1.54787900
C	-0.39791700	1.77906500	-0.02740800
H	-1.25193500	2.45222700	-0.08239800
C	0.21976400	1.64641100	-1.42467500
H	0.47775200	2.63723000	-1.80646000
C	1.50679400	0.83528500	-1.40108500
H	1.78569300	0.45761400	-2.38422800
H	2.33705100	1.40008000	-0.97170900
N	1.26993000	-0.35176900	-0.51666900
N	2.15492700	-1.25057600	-0.53394600
N	2.87602800	-2.09073600	-0.55287300
H	-0.48927200	1.20216900	-2.12308300
H	-0.04619000	-1.93002100	1.33387100
C	-1.88673700	-0.47818200	-0.12326300
C	-2.95570600	0.43544600	-0.73940800
C	-1.35734800	-1.42857000	-1.20885900
C	-2.59148600	-1.32744100	0.95098800

H	-3.35257200	1.13224700	0.00439800
H	-2.56919100	1.01518500	-1.58031900
H	-3.78723600	-0.17141600	-1.10662900
H	-0.66240300	-2.17739200	-0.81406100
H	-2.20325200	-1.97819700	-1.63039100
H	-0.86223900	-0.90956400	-2.03144300
H	-3.37885000	-1.92872500	0.48963200
H	-1.92773600	-2.02592500	1.47141900
H	-3.05242400	-0.69051400	1.71016600

## 7.6 Cartesian coordinates of 8(III)-TSS2

M06-2X/6-311++G(d,p)

C	0.47285000	-2.23183400	-1.08380600
C	-0.87103500	-0.31880100	-0.54849800
C	0.62159400	0.19103400	-0.75358900
C	1.25552000	-0.96635500	-1.52409300
H	1.12798200	-2.99523000	-0.66112700
H	-0.03530500	-2.67112800	-1.94185200
H	-1.17888100	-0.41274100	-1.59792900
H	1.13064400	-0.75869700	-2.58615000
H	2.32887300	-1.01725800	-1.31926800
O	0.78197900	1.39527800	-1.40536900
C	-0.57012400	-1.74187500	-0.05328500
H	-1.46509500	-2.36303600	-0.05805900
C	0.01692800	-1.69895200	1.35197300
H	0.27736100	-2.69949400	1.70475200
C	1.35161400	-0.90851300	1.35391300
H	1.65928600	-0.64904500	2.36521400
H	2.11367500	-1.51589900	0.86107100
N	1.10828100	0.32933100	0.61781700
N	2.67833700	1.01222000	0.39591400
N	3.52343900	1.67894200	0.57401200
H	-0.68021300	-1.26333500	2.06607900
H	0.27217100	2.08596100	-0.95968200
C	-1.94913300	0.57962300	0.12390500
C	-3.11551200	-0.32463500	0.55356600
C	-1.48611600	1.40512200	1.33304700
C	-2.49587600	1.55811400	-0.93182100
H	-3.46805900	-0.93888600	-0.27986400

H	-2.84034400	-0.98738500	1.37779200
H	-3.95019400	0.29588200	0.88898300
H	-0.74450500	2.16105100	1.05808200
H	-2.34978600	1.93692300	1.74138400
H	-1.06621000	0.79831500	2.13661000
H	-3.28984500	2.16795900	-0.49368500
H	-1.73612400	2.24422500	-1.31676500
H	-2.91591100	1.01857000	-1.78471100

### 7.7 Cartesian coordinates of 8(III)

M06-2X/6-311++G(d,p)

C	-1.78424900	-0.73331300	1.36095000
C	0.33255900	0.12156800	0.37852300
C	-1.64077300	0.95375200	-0.30744900
C	-2.64140800	0.05962700	0.29460300
H	-2.37347700	-1.60479000	1.64783800
H	-1.65325100	-0.09975400	2.24094300
H	0.14438000	0.89968900	1.12588000
H	-3.45640500	0.61203700	0.75572700
H	-3.03661100	-0.64039800	-0.44202300
O	-1.69730400	2.20951400	-0.04227000
C	-0.41556000	-1.16177800	0.80158500
H	0.12949100	-1.71690400	1.56470600
C	-0.62212200	-1.95102400	-0.50097300
H	-1.53210100	-2.55169900	-0.45126400
C	-0.72744400	-0.84965400	-1.57622100
H	0.04878700	-0.93087100	-2.33077600
H	-1.68444500	-0.82381800	-2.09525100
N	-0.51661500	0.45968700	-0.88269400
H	0.20793800	-2.62362100	-0.70834900
H	-0.92166200	2.67127800	-0.42181300
C	1.85021900	0.17450900	0.12791900
C	2.52310900	-0.32774600	1.41337600
C	2.35532800	-0.64127000	-1.06466800
C	2.22231800	1.64543900	-0.09649500
H	2.13325400	0.18433000	2.29866900
H	2.38340100	-1.40328200	1.54641300
H	3.59691000	-0.13347600	1.35971700
H	2.00540700	-0.22601900	-2.01225500

H	3.44752000	-0.59722800	-1.07640700
H	2.07343800	-1.69361400	-1.00498300
H	3.29775000	1.73836500	-0.26484300
H	1.70960800	2.04812400	-0.97493800
H	1.96294900	2.25707400	0.77312600

## 7.8 Cartesian coordinates of 9(II)-INT

M06-2X/6-311++G(d,p)

C	-0.55698300	1.85831600	-0.33276700
C	1.26856100	0.78440500	-1.50784700
C	0.43666400	-0.30076800	-0.84661400
C	-0.92764000	0.37499200	-0.62761900
H	-0.80154200	2.15050100	0.69089800
H	-1.12318200	2.51403800	-0.99378000
H	0.87892700	0.92301900	-2.51862700
H	2.32736700	0.52157700	-1.57204200
H	-1.31520400	0.35064700	-1.65465100
O	0.48814400	-1.49145600	-1.51593500
C	0.96656100	1.98776800	-0.60525400
H	1.21361900	2.92891800	-1.09355500
C	1.79296900	1.85323000	0.68028900
H	1.64276300	2.71943000	1.32965400
C	1.37667100	0.62400400	1.47674000
H	2.11824500	0.30610900	2.20829800
H	0.43098100	0.77620400	1.98816800
N	1.12470300	-0.54711500	0.55948000
N	2.07746100	-1.38372000	0.48082200
N	2.85128800	-2.17058300	0.41075400
H	2.85602800	1.80345500	0.43003200
H	-0.29958600	-2.01978700	-1.33256000
C	-2.05114400	-0.27494300	0.22282200
C	-1.80965300	-0.30473700	1.73652900
C	-3.31710900	0.55326200	-0.04449800
C	-2.30898500	-1.71635900	-0.24151800
H	-0.95498400	-0.92926500	2.00782100
H	-1.67668700	0.69491000	2.15763900
H	-2.68967100	-0.73754500	2.22013900
H	-3.56048900	0.56826200	-1.11110100
H	-4.16602800	0.12158600	0.49156900

H	-3.19660800	1.58567700	0.29400100
H	-3.23460600	-2.08791100	0.20499100
H	-2.42843100	-1.78065200	-1.32909900
H	-1.51969300	-2.40261000	0.09072200

## 7.9 Cartesian coordinates of 9(II)-TSS2

M06-2X/6-311++G(d,p)

C	-0.69737000	1.80943800	-0.41773900
C	1.22943500	0.78878900	-1.46231300
C	0.50072300	-0.33216000	-0.73121700
C	-0.95942800	0.29194000	-0.60633200
H	-1.00761800	2.16930600	0.56630800
H	-1.27792100	2.36450600	-1.15535600
H	0.84498300	0.82423400	-2.48268200
H	2.30832900	0.61309900	-1.49595200
H	-1.25179800	0.14094400	-1.65242000
O	0.60187500	-1.52542200	-1.41421100
C	0.82281400	2.01204300	-0.63776100
H	1.04706200	2.94670600	-1.14926300
C	1.58519600	1.94251600	0.68989100
H	1.34951900	2.79936700	1.32512200
C	1.18517800	0.68312600	1.44413200
H	1.83750200	0.41316800	2.27529600
H	0.18734200	0.79491700	1.88783100
N	0.97421500	-0.52069600	0.63804000
N	2.55878500	-1.15804400	0.37782800
N	3.38903200	-1.86399000	0.42526100
H	2.66401600	1.94772300	0.50812400
H	-0.03112700	-2.16931300	-1.07145600
C	-2.09502500	-0.37365200	0.20887400
C	-2.20545000	-1.86195600	-0.14973200
C	-1.99176600	-0.26746500	1.73394600
C	-3.38592100	0.33226100	-0.23848400
H	-2.24673900	-2.01999000	-1.23214900
H	-1.38160300	-2.44355600	0.28169100
H	-3.12287600	-2.27618200	0.27561500
H	-1.90909700	0.76553100	2.08388100
H	-2.90457900	-0.67838900	2.17290300
H	-1.15777500	-0.85273500	2.12971600

H	-4.24645400	-0.12315300	0.25760800
H	-3.37079700	1.39412700	0.02036900
H	-3.52991100	0.24290400	-1.31901400

## 7.10 Cartesian coordinates of 9(II)

M06-2X/6-311++G(d,p)

C	-0.19373000	-1.18012000	-1.05570900
C	-2.27590700	0.24264000	-0.90441600
C	-1.46206700	1.11050400	-0.02438700
C	0.44328300	0.07581800	-0.43081900
H	0.24627400	-2.09174600	-0.64345300
H	-0.00310800	-1.17746900	-2.12994500
H	-2.21951400	0.65094700	-1.92038000
H	-3.32774000	0.30111000	-0.60023000
H	0.39096600	0.87657300	-1.18088300
O	-1.59726900	2.37667600	-0.05945500
C	-1.70665100	-1.17693400	-0.75028600
H	-2.24387100	-1.86188900	-1.40337400
C	-1.88046700	-1.55302600	0.72213300
H	-1.56166400	-2.58219800	0.89051500
C	-1.00041000	-0.58906500	1.54781800
H	-1.54143500	-0.14318900	2.38092900
H	-0.13032800	-1.09373600	1.95286700
N	-0.46332800	0.55731400	0.73163100
H	-2.92943800	-1.47364700	1.01460600
H	-0.96497500	2.79411300	0.56413100
C	1.93291600	0.03738400	-0.02962900
C	2.38774700	1.45938700	0.31076600
C	2.23699600	-0.88645700	1.15234300
C	2.69551000	-0.45456200	-1.26898600
H	2.24579500	2.13460000	-0.53921700
H	1.83810000	1.85421200	1.16810900
H	3.45094700	1.45936900	0.56341700
H	1.82166200	-1.88860700	1.01513000
H	3.32099600	-0.99058200	1.24755300
H	1.86739700	-0.47103400	2.09250700
H	3.76976700	-0.36905000	-1.08880200
H	2.47516600	-1.50153900	-1.49083600

H 2.45314000 0.14572200 -2.15139400

### 7.11 Cartesian coordinates of 9(III)-INT

M06-2X/6-311++G(d,p)

C	-0.12774600	1.96307300	-0.13276600
C	-1.59064400	0.81572700	1.42288100
C	-0.49148700	-0.14333400	1.00076400
C	0.63983500	0.78812100	0.53807700
H	0.01865900	1.98294100	-1.21508600
H	0.23971400	2.91274200	0.25485700
H	-1.25008300	1.32218000	2.32949200
H	-2.53726200	0.30702800	1.62311800
H	1.00857700	1.15178200	1.50514600
O	-0.11641200	-1.11431500	1.88939900
C	-1.62828800	1.76893800	0.22120700
H	-2.11244600	2.71103400	0.47271200
C	-2.41575700	1.09317700	-0.90917000
H	-2.50635400	1.76358000	-1.76667600
C	-1.72990200	-0.17203200	-1.41154300
H	-2.42696800	-0.86418800	-1.88319300
H	-0.91728900	0.05703800	-2.09981800
N	-1.12897100	-0.88770100	-0.23364500
N	-0.78381100	-2.08606400	-0.38861100
N	-0.50554900	-3.15557400	-0.47617100
H	-3.42307600	0.85928500	-0.55812400
H	-0.84536100	-1.30549600	2.49594000
C	1.90233500	0.25909600	-0.18846100
C	2.54534200	-0.87849000	0.61545000
C	1.68429900	-0.22024100	-1.62992600
C	2.88704300	1.43841200	-0.23588100
H	2.69887100	-0.59064400	1.65879600
H	1.93777200	-1.78655800	0.60654300
H	3.51871800	-1.12535700	0.18309200
H	1.24853300	0.55299800	-2.26692700
H	2.65675400	-0.47483500	-2.06000100
H	1.07515900	-1.12542100	-1.70195200
H	3.82983000	1.12005400	-0.68773900
H	2.49333000	2.26729800	-0.83044500

H 3.10235500 1.80975100 0.77027500

## 7.12 Cartesian coordinates of 9(III)-TSS2

M06-2X/6-311++G(d,p)

C	0.29697000	-1.97963800	-0.18191900
C	1.76330500	-0.77119000	1.30948200
C	0.57472000	0.18988400	0.92892100
C	-0.50458400	-0.83796400	0.50696400
H	0.10372200	-2.03137700	-1.25560600
H	0.00124100	-2.93967200	0.24035600
H	1.42327600	-1.25535100	2.22851400
H	2.70080900	-0.24590500	1.50391600
H	-0.80102300	-1.21515500	1.49200000
O	0.15225300	1.02036900	1.94610800
C	1.79193000	-1.69506600	0.09936000
H	2.36280300	-2.60324400	0.29341100
C	2.44494200	-0.90501700	-1.02963100
H	2.48087900	-1.46830300	-1.96431900
C	1.60305500	0.36003900	-1.34397800
H	2.17299500	1.07194300	-1.93757800
H	0.69944800	0.05267100	-1.86598600
N	1.28997100	0.98660800	-0.06232000
N	0.27376300	2.31918100	-0.42122400
N	0.03288800	3.38176600	-0.49285600
H	3.46147000	-0.61622300	-0.75824900
H	0.91744000	1.41743600	2.38564600
C	-1.84920300	-0.42752700	-0.15045800
C	-2.55052800	0.64039600	0.69855200
C	-1.76981600	0.05705300	-1.60476000
C	-2.72024300	-1.69535400	-0.14173100
H	-2.63529200	0.31997600	1.74018700
H	-2.02298300	1.59615500	0.69047600
H	-3.55853400	0.81155700	0.31135000
H	-1.30327100	-0.67889100	-2.26503400
H	-2.78648800	0.21693700	-1.97423000
H	-1.25141600	1.01203800	-1.71875500
H	-3.71576400	-1.46368700	-0.52894200
H	-2.29230800	-2.48223400	-0.76868800
H	-2.83466700	-2.08820900	0.87266100



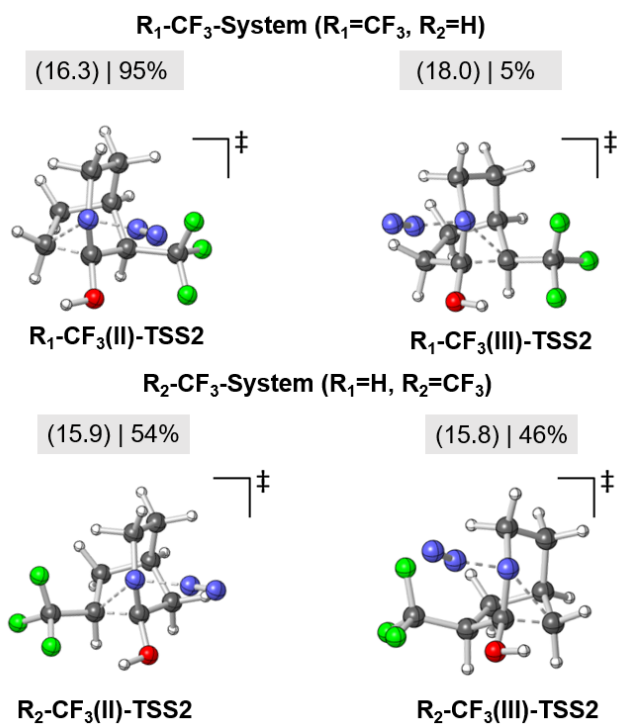
### 7.13 Cartesian coordinates of 9(III)

M06-2X/6-311++G(d,p)

C	-0.23677800	-1.45011400	0.28701100
C	-1.95423100	-0.60272300	-1.25641600
C	-0.34791900	0.88287300	-0.36869400
C	0.56391900	-0.29378800	-0.43170700
H	-0.02132500	-1.42637200	1.35604800
H	0.15325100	-2.38606000	-0.11219600
H	-1.31650700	-0.88741700	-2.08889900
H	-2.98970600	-0.56679900	-1.59177500
H	0.61301100	-0.57177200	-1.49114500
O	0.04323800	1.98093700	0.19992700
C	-1.76193800	-1.38987700	0.04047300
H	-2.17739300	-2.39446400	-0.00074400
C	-2.53974400	-0.49441200	1.05127500
H	-2.02812700	-0.44513300	2.01387500
C	-2.60503900	0.91018600	0.38790600
H	-3.57134500	1.13254300	-0.05714900
H	-2.32541900	1.72403400	1.05327100
N	-1.61505800	0.73939200	-0.73533300
H	-3.54493200	-0.88065900	1.21762700
H	-0.65115500	2.66501300	0.19466900
C	2.03045700	-0.10094400	0.03255400
C	2.72248600	0.91134900	-0.89007100
C	2.16645000	0.34365800	1.49466500
C	2.73493300	-1.45670900	-0.12786200
H	2.67680900	0.58400400	-1.93306100
H	2.28136900	1.90719600	-0.81855100
H	3.77634600	0.99698100	-0.61399400
H	1.63896900	-0.32649200	2.17799200
H	3.22406400	0.31724200	1.76985900
H	1.81012800	1.36033500	1.65883300
H	3.80627800	-1.33008500	0.04445600
H	2.36853800	-2.19331500	0.59082500
H	2.60106900	-1.85901100	-1.13683500

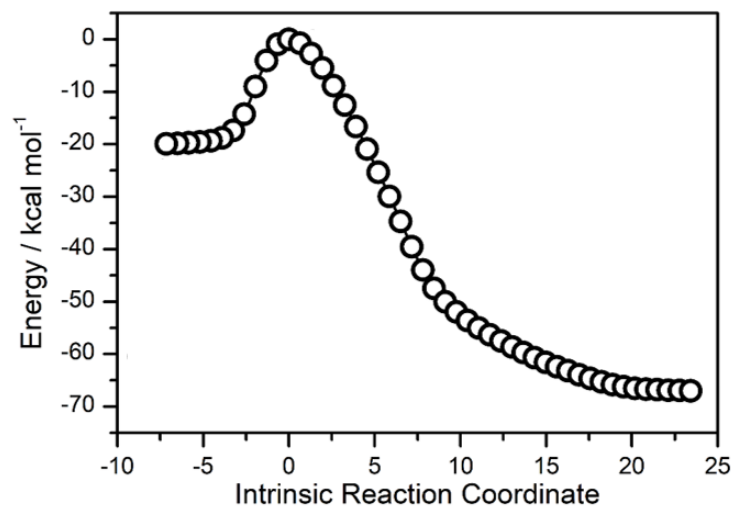
## 8. Additional groups data

### 8.1 Calculation data for CF<sub>3</sub>-systems

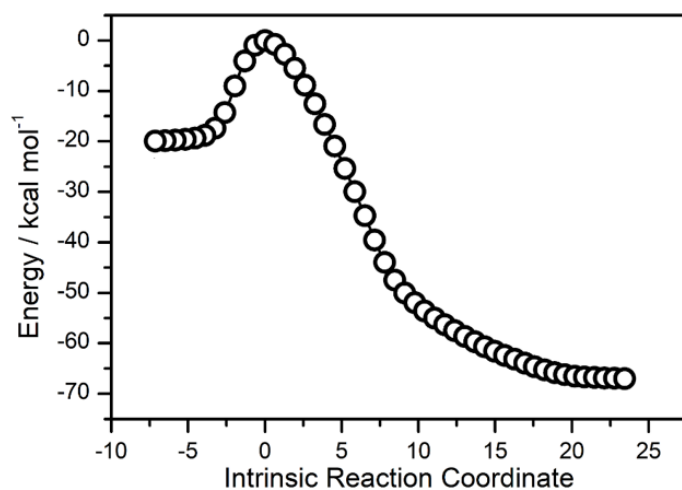


**Figure S22.** TSSs, relative free energies (in kcal mol<sup>-1</sup>, in parentheses) and percentage of formation for the second and rate determinant step for reaction presented in Scheme 1, R<sub>1</sub>-F-System (R<sub>1</sub>=F, R<sub>2</sub>=H) and R<sub>2</sub>-F-System (R<sub>1</sub>=H, R<sub>2</sub>=F), obtained at M06-2X/6-311++G(d,p) level of theory.

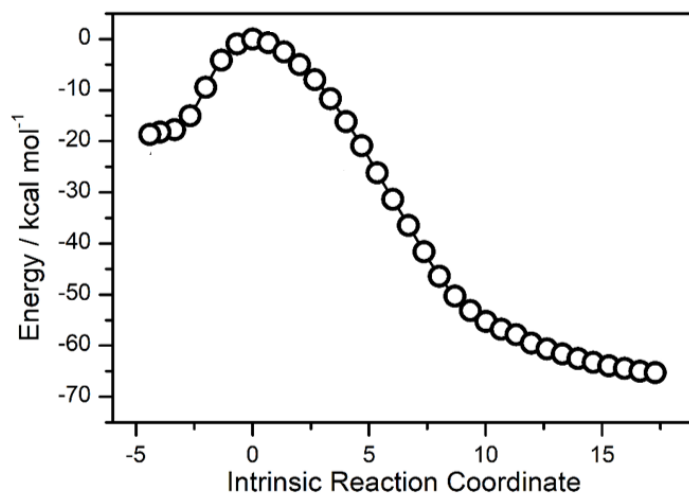
### 8.1.1 IRCs



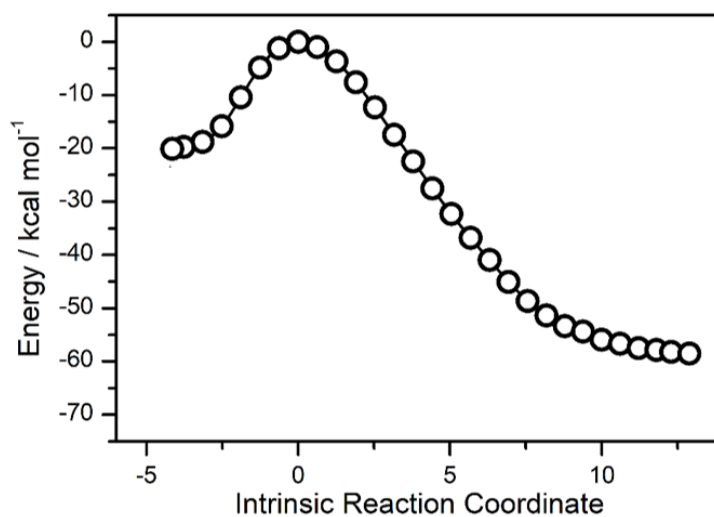
**Figure S23.** IRC plot for R<sub>1</sub>-CF<sub>3</sub>(II)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.



**Figure S24.** IRC plot for R<sub>1</sub>-CF<sub>3</sub>(III)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.

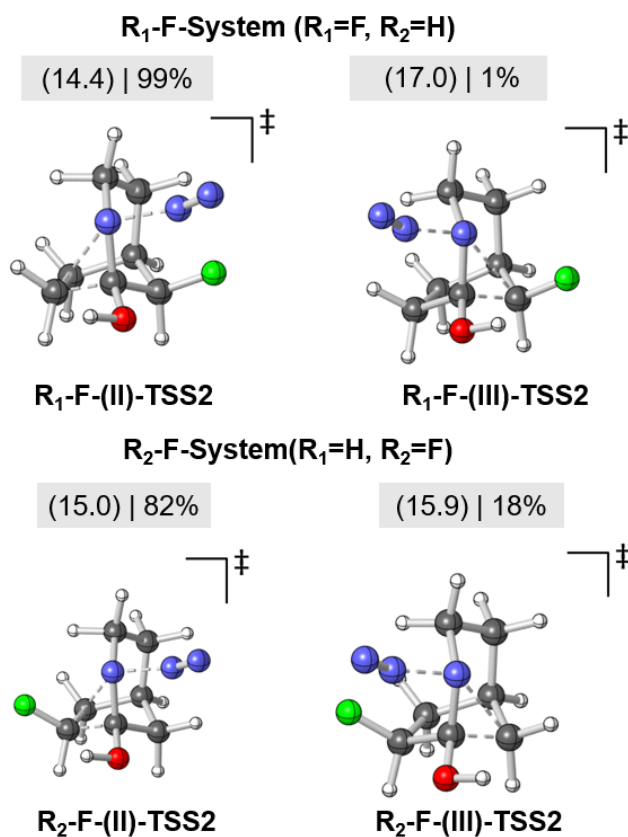


**Figure S25.** IRC plot for R<sub>2</sub>-CF<sub>3</sub>(II)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.

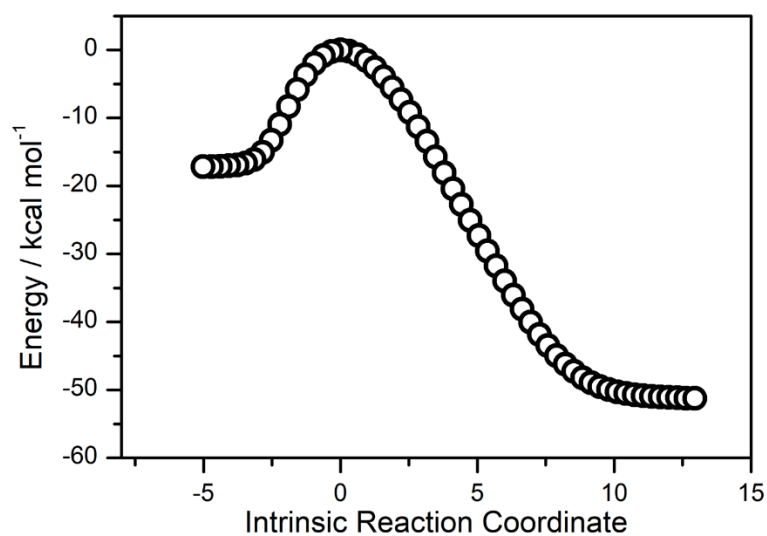


**Figure S26.** IRC plot for R<sub>2</sub>-CF<sub>3</sub>(III)-TSS2 (Figure S22) calculated at M06-2X/6-311++G(d,p) level of theory.

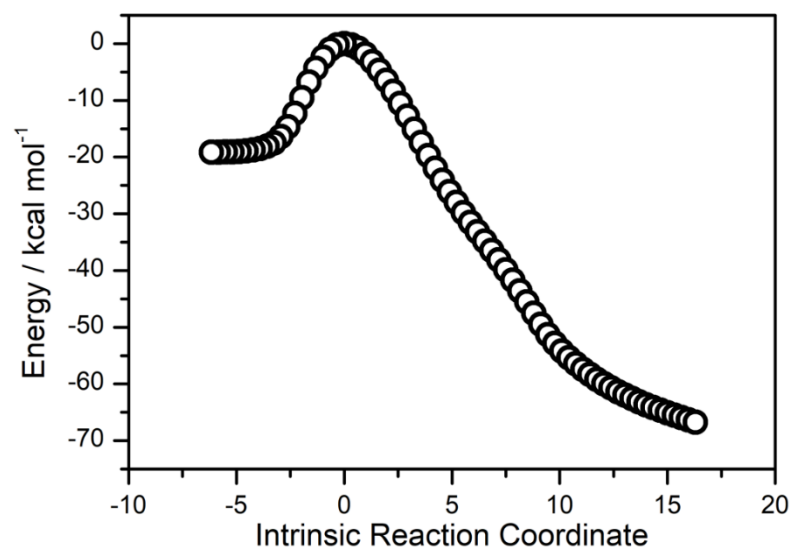
## 8.2 Calculation data for F-systems



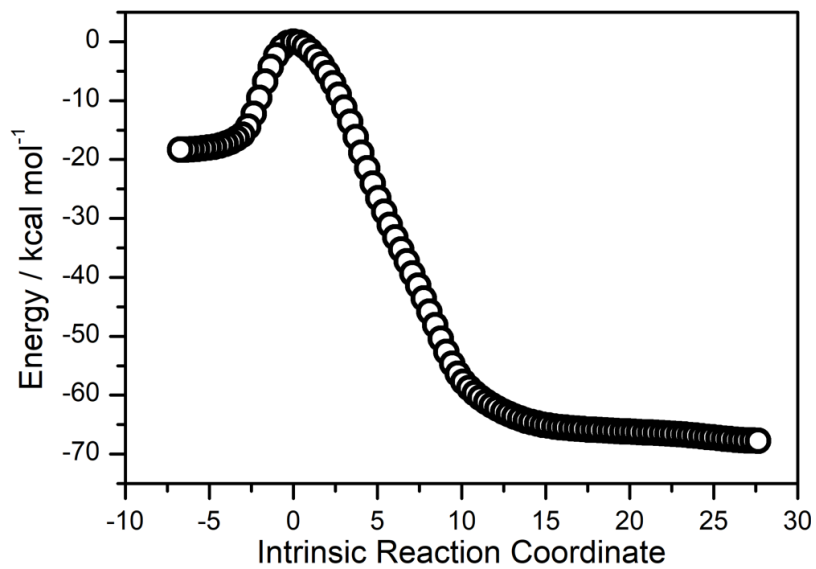
**Figure S27.** TSSs, relative free energies (in kcal mol<sup>-1</sup>, in parentheses) and percentage of formation for the second and rate determinant step for reaction presented in Scheme 1, R<sub>1</sub>-F-System (R<sub>1</sub>=F, R<sub>2</sub>=H) and R<sub>2</sub>-F-System (R<sub>1</sub>=H, R<sub>2</sub>=F), obtained at M06-2X/6-311++G(d,p) level of theory.



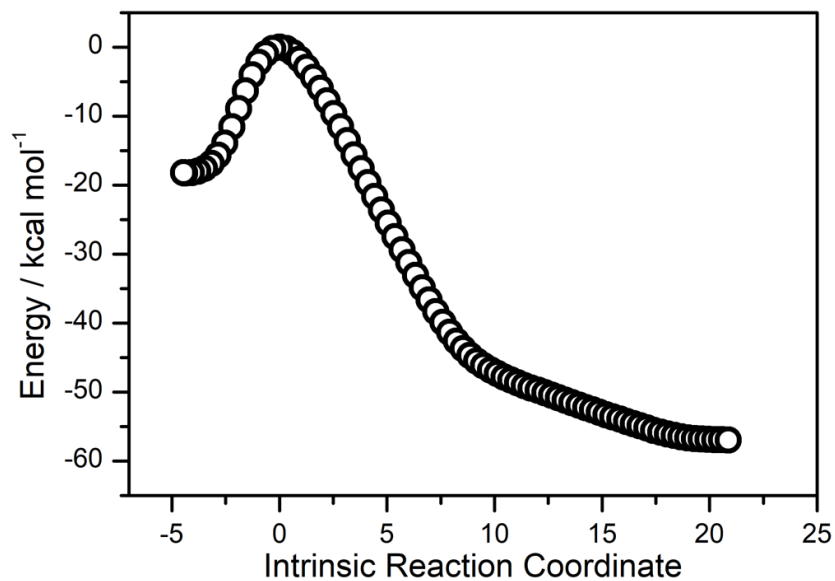
**Figure S28.** IRC plot for R<sub>1</sub>-F-(II)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.



**Figure S29.** IRC plot for R<sub>1</sub>-F(III)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.

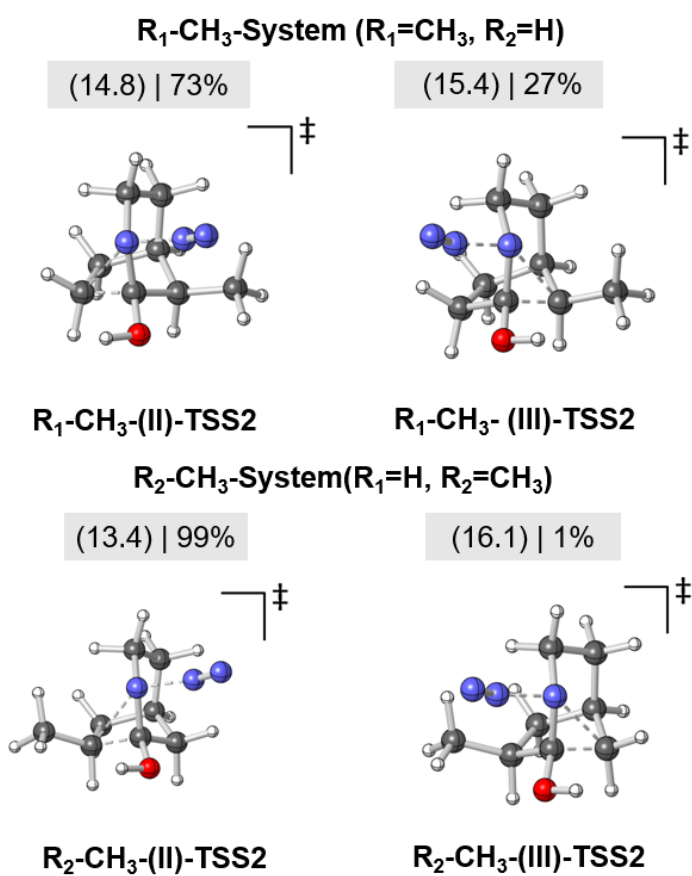


**Figure S30.** IRC plot for R<sub>2</sub>-F(II)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.

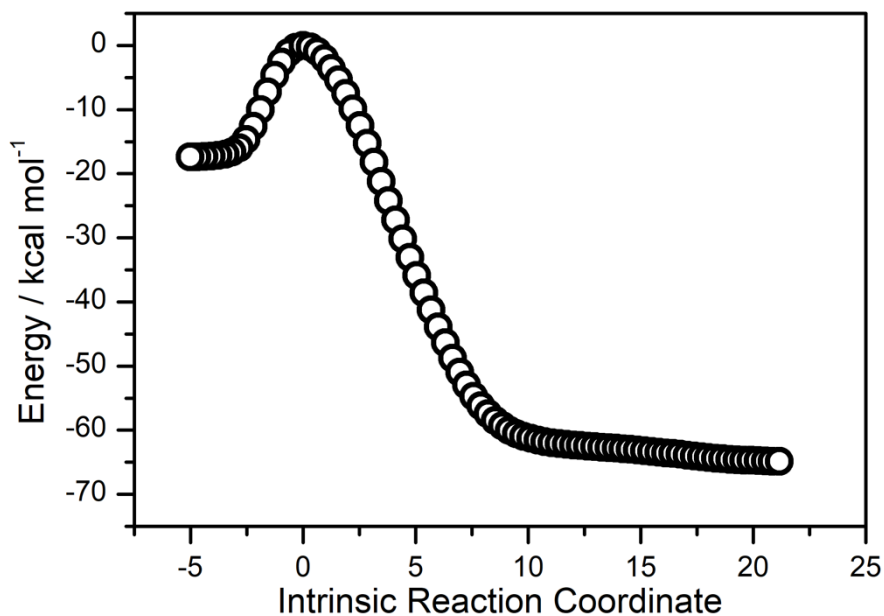


**Figure S31.** IRC plot for R<sub>2</sub>-F(III)-TSS2 (Figure S27) calculated at M06-2X/6-311++G(d,p) level of theory.

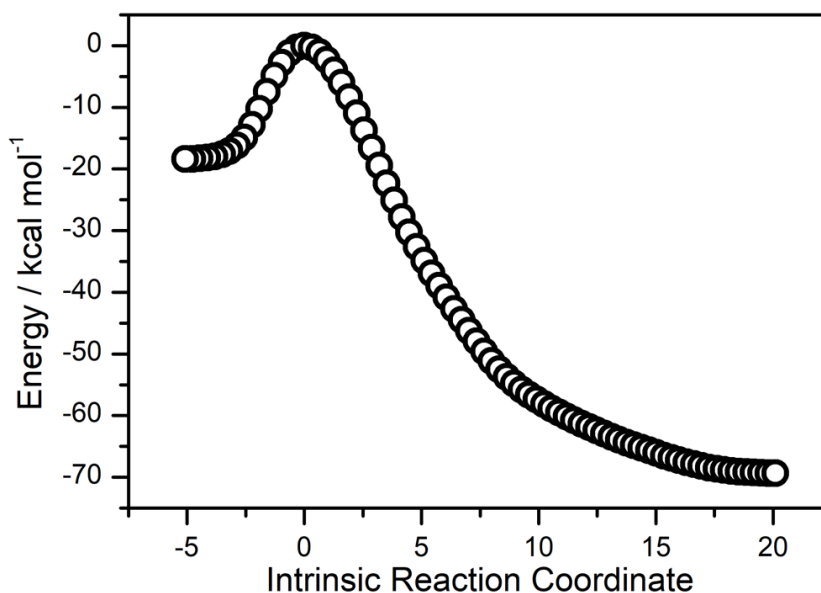
### 8.3. Calculation data for CH<sub>3</sub>-systems



**Figure S32.** TSSs, relative free energies (in kcal mol<sup>-1</sup>, in parentheses) and percentage of formation for the second and rate determinant step for reaction presented in Scheme 1, R<sub>1</sub>-CH<sub>3</sub>-System (R<sub>1</sub>= CH<sub>3</sub>, R<sub>2</sub>=H) and R<sub>2</sub>- CH<sub>3</sub>-System (R<sub>1</sub>=H, R<sub>2</sub>= CH<sub>3</sub>), obtained at M06-2X/6-311++G(d,p) level of theory.

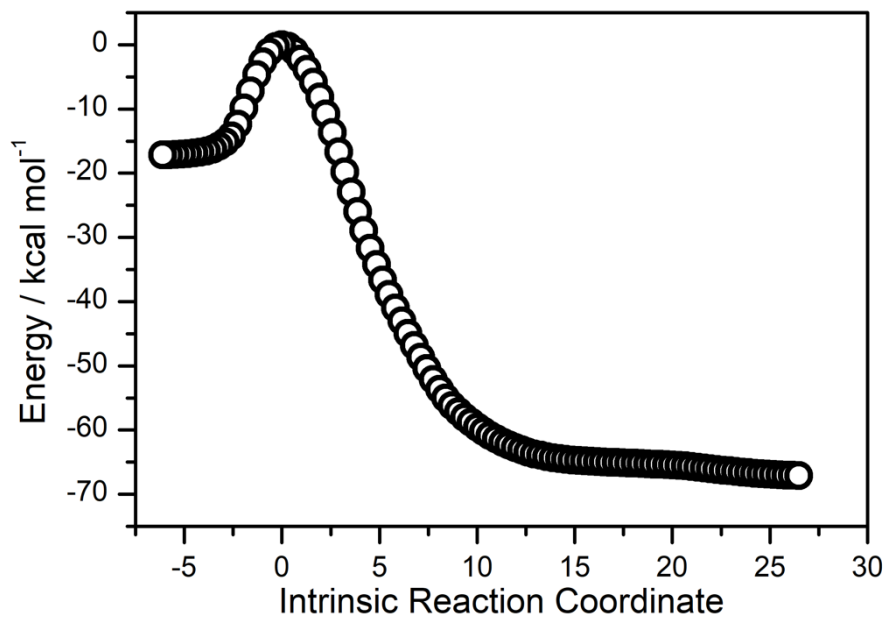


**Figure S33.** IRC plot for R<sub>1</sub>-CH<sub>3</sub>(III)-TSS2 (Figure S32) calculated at M06-2X/6-311++G(d,p) level of theory.

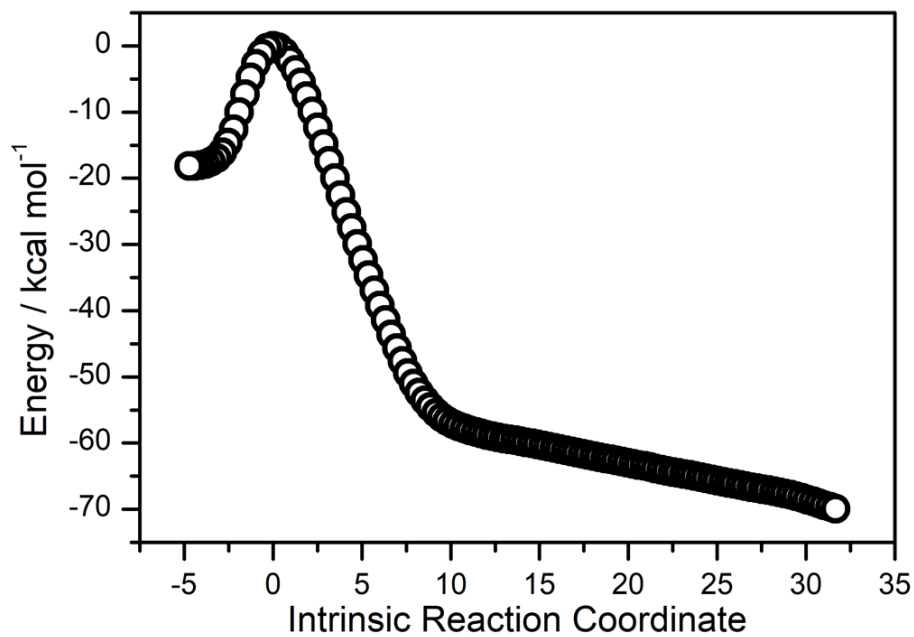


**Figure S34.** IRC plot for R<sub>1</sub>-CH<sub>3</sub>(III)-TSS2 (Figure S32) calculated at M06-2X/6-311++G(d,p) level of theory.





**Figure S35.** IRC plot for R<sub>2</sub>-CH<sub>3</sub>(II)-TSS2 (Figure S32) calculated at M06-2X/6-311++G(d,p) level of theory.



**Figure S36.** IRC plot for R<sub>2</sub>-CH<sub>3</sub>(III)-TSS2 (Figure S32) calculated at M06-2X/6-311++G(d,p) level of theory.