Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

External Electric Field Control: Driving the Reactivity of Metal-Free Azide-Alkyne Click Reactions

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1. **Table S1**: Activation barrier of **1-6** at various level of theory at gas phase geometries.

Method / Molecule	B3LYP/6-31+G(d,p)			B3LYP/6-311++G(d,p)			B3LYP-D3/6-311++G(d,P)		
	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$
1	11.7	12.2	23.2 (24.9)	13.4	14.0	25.0	10.2	10.8	21.8
2	12.1	12.4	23.8 (24.8)	13.4	13.7	25.1	9.7	10.0	21.4
3	12.0	12.6	24.2	13.4	14.0	25.7	10.0	10.6	22.2
4-*syn*	9.9	10.3	22.6 (22.9)	10.8	11.2	23.4	6.44	6.9	19.1
4-*anti*	11.9	12.2	24.4 (24.2)	13.0	13.3	25.5	8.8	9.1	21.3
5	12.0	12.8	24.5 (24.8)	13.3	13.7	26.2	8.3	8.7	21.2
6-*syn*	10.2	10.7	21.8 (22.0)	11.1	11.5	24.0	6.6	7.0	19.5
6-*anti*	12.5	12.8	25.1 (23.0)	13.6	13.9	26.1	9.2	9.6	21.8

2. **Table S2**: Activation barrier of **1-6** at various DFT functional at gas phase geometries.

Method / Molecule	B3LYP/6-31+G(d,p)			BP86/6-31+G(d,p)			M06-2X/6-31+G(d,p)		
	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$
1	11.7	12.2	23.2	6.8	7.3	18.3	12.3	12.8	23.8
2	12.1	12.4	23.8	7.1	7.4	18.8	12.1	12.4	23.7
3	12.0	12.6	24.2	7.4	8.1	19.7	10.9	11.5	23.1
4-*syn*	9.9	10.3	22.6	4.9	5.4	17.5	8.1	8.6	20.7
4-*anti*	11.9	12.2	24.4	7.3	7.7	19.9	10.0	10.4	22.6
5	12.0	12.8	24.5	7.0	7.3	19.8	11.5	11.9	24.4
6-*syn*	10.2	10.7	21.8	5.6	6.0	18.6	8.7	9.1	21.6
6-*anti*	12.5	12.8	25.1	7.8	8.2	20.5	10.7	11.1	23.3

3. **Table S3**: Comparison of electronic energy barrier ($\Delta E^{\ddagger}$) (in kcal/mol) of metal –free Azide-Alkyne click reactions with higher level of theory.

Molecule	$\Delta E^{\ddagger}$ (CCSD/aug-cc-PVDZ)	$\Delta E^{\ddagger}$ (B3LYP/6-31+G(d,p)
1	14.6	11.7
2	13.1	12.1
3	13.0	12.0
4-*syn*	9.5	9.9
4-*anti*	11.3	11.9

4. Variation of electronic energy barrier ($\Delta E^{\ddagger}$) with external electric field (F_x) of **1-6**.

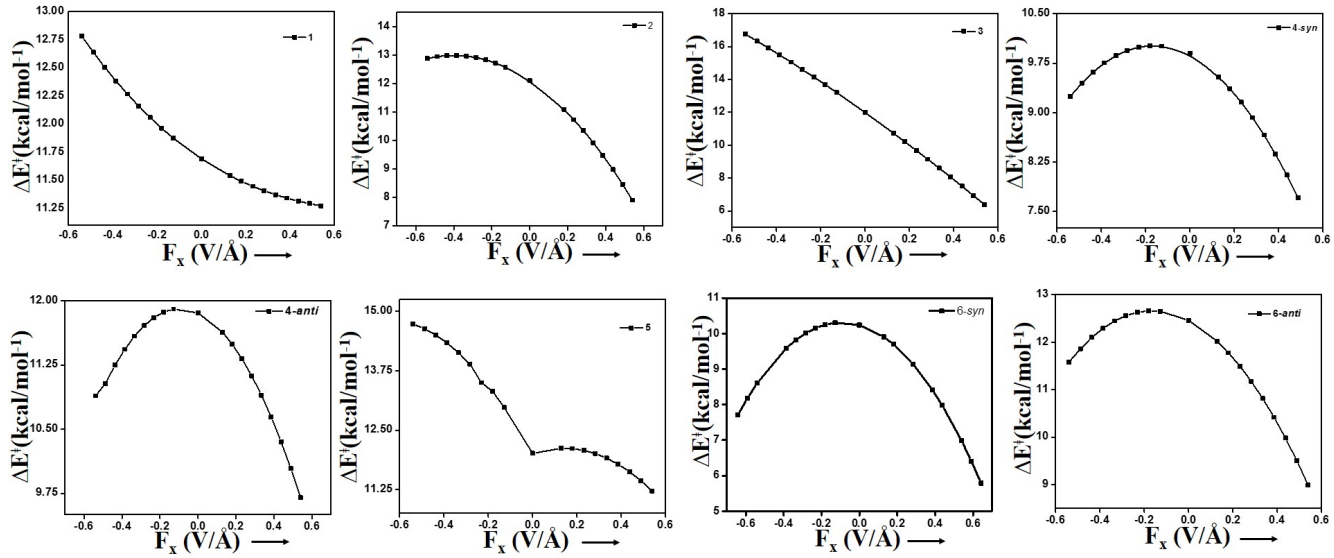

Figure S1: Effect of EEF on the electronic energy barrier ($\Delta E^{\ddagger}$) of metal-free Azide –Alkyne click reaction of the **1, 2, 3, 4-*syn*, 4-*anti*, 5, 6-*syn* and 6-*anti***.

5. Solvent corrected electronic energy barrier ($\Delta E^{\ddagger}$) of **1-6**.

Table S2. Electronic energy barrier ($\Delta E^{\ddagger}$) (in kcal/mol) of metal –free Azide-Alkyne click reactions for **1-6** in presence/absence of EEF. Activation barrier at COSMO solvation model are shown in

parentheses.

Molecule	$\Delta E^{\ddagger}_{gas}$ (F=0)	$\Delta E^{\ddagger}_{gas}$ (F=0.5V/Å)	$\Delta E^{\ddagger}_{solvn}$ (F=0)	$\Delta E^{\ddagger}_{solvn}$ (F=0.5V/Å)
1	11.7	11.3	8.2 (6.0)	5.0
2	12.1	7.9	8.7 (7.1)	2.6
3	12.0	9.7	5.3 (5.3)	0.8
4-*syn*	9.9	7.3	5.4 (3.5)	2.7
4-*anti*	11.9	9.7	5.2 (3.4)	2.6
5	12.0	11.2	8.0 (7.9)	6.2
6-*syn*	10.2	7.0	4.8 (2.1)	1.7
6-*anti*	12.5	9.0	4.7 (2.1)	1.7

6. Cartesian Coordinates, electronic energies and harmonic frequencies for all the transition state structures of **1**-**6**.

1

Atom	X	Y	Z
C	2.50449200	-0.68228300	0.26937800
C	2.47265100	0.74872800	-0.34671900
C	1.60976700	1.82880000	0.34855300
C	0.12843300	1.91864000	-0.09586600
C	1.62061200	-1.78369000	-0.36418600
C	0.18445700	-1.91797800	0.18600500
H	2.29840300	-0.62172400	1.34735900
H	2.19860500	0.68610800	-1.40918700
H	1.64280900	1.67154300	1.43434600
H	3.54020100	-1.03444700	0.19025000
H	3.50387300	1.12197200	-0.33252400
H	2.05933200	2.81340400	0.16515600
H	-0.39605900	2.65545800	0.52175000
H	0.06914100	2.27820500	-1.13196000
H	2.11366500	-2.75378600	-0.21744700

H	1.57045500	-1.62646900	-1.44957100
H	-0.35053200	-2.70804200	-0.35220400
H	0.21406400	-2.23192200	1.23858900
C	-0.54191900	-0.63565200	0.09016600
C	-0.49623100	0.59748200	0.00158900
N	-2.59154900	-1.20909200	0.08892100
N	-3.12591300	-0.17324000	-0.02060500
N	-2.81548900	1.04610300	-0.11545800
H	-3.62682300	1.65904100	-0.20848600

Img. Frequencies (cm^{-1}) = -351.9818

Electronic Energies = -476.8021105 hartree

2

Atom	X	Y	Z
C	2.95981100	-0.23933300	0.23592600
C	2.59293900	1.17445100	-0.30956900
C	1.50007100	1.99386500	0.42369200
C	0.03949300	1.76596400	-0.03181000
C	2.34507700	-1.47941000	-0.45997400
C	0.97964100	-1.94931000	0.08291000
H	2.73548200	-0.28251800	1.31150000
H	2.33369100	1.09510400	-1.37490100
H	1.56674200	1.79057300	1.50134000
H	4.05607700	-0.33928600	0.15367300
H	3.51498200	1.77737000	-0.27124800
H	1.72471000	3.06262400	0.29476300
H	-0.62653800	2.36914300	0.59438100
H	-0.09210700	2.13683700	-1.05823000

H	3.05223400	-2.32093000	-0.36828100
H	2.24621600	-1.27310800	-1.53475500
H	0.61839500	-2.79843500	-0.50965100
H	1.09899700	-2.33289400	1.10711700
C	-0.01133100	-0.86304900	0.08433500
C	-0.31153300	0.34020400	0.03282700
N	-1.83394400	-1.92644000	0.32959500
N	-2.55740400	-1.00579100	0.30587700
N	-2.54028900	0.23897700	0.27578000
C	-3.72498500	1.02231500	-0.11735900
H	-4.55689200	0.83855000	0.56791500
H	-3.44437700	2.07371400	-0.04287600
H	-4.03740500	0.80009100	-1.14199600

Img. Frequencies (cm^{-1}) = -366.9100

Electronic Energies = -516.1130684 hartree

3

Atom	X	Y	Z
C	2.52008600	-0.38511600	0.12475700
C	2.53910000	1.07794100	-0.40131200
C	1.72520500	2.13848700	0.37541300
C	0.24867800	2.31856000	-0.04812800
C	1.56787700	-1.39769100	-0.54563600
C	0.14594400	-1.47815700	0.00685300
H	2.35615800	-0.39185800	1.20944300
H	2.25410800	1.09583700	-1.46262500
H	1.76097100	1.90765300	1.44755600
H	3.52858800	-0.78912700	-0.01907200
H	3.58399500	1.40858400	-0.37431800

H	2.20917000	3.11579300	0.25402000
H	-0.23204100	3.05528300	0.60457800
H	0.19513600	2.72363000	-1.06746400
H	1.97402200	-2.40991200	-0.43852000
H	1.48602000	-1.19647900	-1.61962000
C	-0.57740900	-0.19768600	-0.01446000
C	-0.46225100	1.03570800	-0.01374500
N	-2.72346500	-0.64797100	0.00163200
N	-3.08237700	0.45807700	-0.01126700
N	-2.63628400	1.63121500	-0.15551200
H	-3.23430100	2.33642300	0.27880500
F	-0.52889100	-2.45032000	-0.70870700
F	0.19255600	-1.95150900	1.31418600

Img. Frequencies (cm^{-1}) = -382.6977

Electronic Energies = -675.2907583 hartree

4-Syn

Atom	X	Y	Z
C	3.06961000	0.30254800	-0.39759200
C	2.58732500	-1.05293600	0.19622600
C	1.39518400	-1.76598100	-0.47865200
C	0.00312300	-1.38397700	0.02122200
C	2.61534900	1.60822600	0.29615300
C	1.26792700	2.20122500	-0.17364900
H	2.82123700	0.34849000	-1.46742000
H	2.38775700	-0.94375800	1.26934700
H	1.40852200	-1.59354600	-1.56048400
H	4.16505300	0.29261700	-0.35298000
H	3.42855100	-1.75178600	0.12623400

H	1.47233900	-2.84802300	-0.32265900
H	3.37942200	2.37874700	0.13147100
H	2.57203900	1.44524600	1.38051100
H	1.02778500	3.09758500	0.40813500
H	1.34598000	2.52824700	-1.21976500
C	0.18903700	1.20768300	-0.07827100
C	-0.25373000	0.05436400	-0.03150100
N	-1.67632200	2.44462700	0.03238500
N	-2.41920400	1.54844700	0.11039600
N	-2.47612600	0.30845700	0.26316400
F	-0.93043700	-2.09534300	-0.72884300
F	-0.15944700	-1.84860200	1.32098000
C	-3.62241300	-0.44125500	-0.25834200
H	-3.41748500	-1.49142900	-0.05516200
H	-4.54479500	-0.15352300	0.25732100
H	-3.74436300	-0.30345100	-1.33896400

Img. Frequencies (cm^{-1}) = -339.8197

Electronic Energies = -714.6057276 hartree

4-anti

Atom	X	Y	Z
C	2.69095500	0.06955000	0.24512600
C	2.41543000	1.47029400	-0.37120600
C	1.34613800	2.36366800	0.29948300
C	-0.10597500	2.19341400	-0.20455900
C	2.01730700	-1.16464300	-0.39046800
C	0.61729600	-1.51878900	0.10852400
H	2.48073700	0.08556800	1.32170200

H	2.19361000	1.36872600	-1.44293000
H	1.36621400	2.19986900	1.38430400
H	3.76925300	-0.10817300	0.16199000
H	3.35901700	2.02615700	-0.31982900
H	1.61462400	3.41604300	0.14178800
H	-0.76910700	2.84619000	0.37474000
H	-0.18225000	2.52264700	-1.24971700
H	2.62572200	-2.05511300	-0.19541400
H	1.95372600	-1.05112300	-1.47849600
C	-0.36135400	-0.43368600	-0.04116300
C	-0.52751500	0.79045000	-0.11923400
N	-2.38503000	-1.34954600	-0.10802200
N	-2.95305700	-0.33857400	-0.21132600
N	-2.78170500	0.89230400	-0.40773700
F	0.21254200	-2.66433600	-0.55342400
F	0.69327100	-1.88009800	1.45092600
C	-3.74746500	1.83265700	0.16579000
H	-3.36739000	2.83380900	-0.04400400
H	-4.72918400	1.73640500	-0.31099000
H	-3.85589900	1.71009500	1.25045000

Img. Frequencies (cm^{-1}) = -343.2092

Electronic Energies = -714.6025655 hartree

5

Atom	X	Y	Z
C	4.58567000	-0.11087800	0.60757800
C	3.92620100	-1.52193700	0.65621500
C	3.14871200	-2.01643200	-0.58721600

C	1.64912600	-1.63944100	-0.65772500
C	3.85505700	1.07500100	1.28261500
C	2.85280600	1.85590300	0.40419300
H	4.81883500	0.14842400	-0.43479400
H	3.28461700	-1.59762300	1.54545900
H	3.64659600	-1.64697500	-1.49294500
H	5.55659800	-0.20166600	1.10979200
H	4.73658100	-2.24299100	0.81843200
H	3.20762400	-3.11210700	-0.62717800
H	1.23285000	-1.98135100	-1.61187100
H	1.09567900	-2.16777300	0.13125000
H	4.60686600	1.79410900	1.63390400
H	3.33342600	0.71399800	2.17886400
C	1.84362400	0.95091200	-0.17635000
C	1.48812800	-0.19030700	-0.49263100
N	0.21116700	2.28593200	-0.74068900
N	-0.55195200	1.49967600	-1.14913400
N	-0.63309100	0.26817300	-1.39929500
C	-1.94525300	-0.34149400	-1.62478500
H	-1.71967200	-1.38859200	-1.85760800
H	-2.41415500	0.08117000	-2.52314800
C	-2.91437200	-0.27179900	-0.45427000
C	-4.29265000	-0.21074100	-0.69817900
C	-2.46249000	-0.30514500	0.87186700
C	-5.20523700	-0.19399500	0.35995500
H	-4.65609000	-0.17142700	-1.72266800
C	-3.37316000	-0.28457500	1.93102300
H	-1.39546000	-0.33700100	1.07186100
C	-4.74715700	-0.23116400	1.67934800
H	-6.27054900	-0.14314700	0.15322500

H	-3.00831700	-0.30641400	2.95410500
H	-5.45379100	-0.21227500	2.50399000
H	2.37505600	2.64657100	0.99365100
H	3.38641500	2.36515700	-0.41032400

Img. Frequencies (cm^{-1}) = -313.1936

Electronic Energies = -747.1788235 hartree

6-Syn

Atom	X	Y	Z
C	5.13334200	-0.03343400	0.05853100
C	4.73378200	-1.50225800	0.38372300
C	3.79174500	-2.23832900	-0.59426100
C	2.29380600	-2.08533200	-0.33829900
C	4.39254300	1.10677800	0.79543800
C	3.08296700	1.60699000	0.14523300
H	5.08036800	0.13386800	-1.02662200
H	4.32619000	-1.56490100	1.40018000
H	3.97817300	-1.91305700	-1.62369500
H	6.19386900	0.06800100	0.31744400
H	5.65834800	-2.09014200	0.40380300
H	3.98425200	-3.31655000	-0.55619300
H	5.06374700	1.97192900	0.87005100
H	4.18002900	0.79322400	1.82544200
H	2.62697200	2.38390700	0.76801100
H	3.30158000	2.07976000	-0.82227900
C	2.14523800	0.49839600	-0.08350600
C	1.85999900	-0.69135900	-0.26323500

N	0.14080300	1.48658700	-0.14511800
N	-0.48034400	0.51367800	-0.31306800
N	-0.38378000	-0.73400900	-0.34228900
F	1.61599600	-2.77675500	-1.33994500
F	1.96012400	-2.75012800	0.83664500
C	-1.36173100	-1.53326500	-1.10993100
H	-0.90961000	-2.52552000	-1.15645700
H	-1.44054400	-1.15374700	-2.13586400
C	-2.72884300	-1.59687900	-0.45834200
C	-3.82802900	-0.95859200	-1.04451100
C	-2.90987800	-2.29431400	0.74513700
C	-5.08961500	-1.01682800	-0.44346700
H	-3.69934700	-0.41399900	-1.97689400
C	-4.16665800	-2.35180200	1.34818200
H	-2.06028800	-2.78798200	1.20969600
C	-5.26104100	-1.71299000	0.75450800
H	-5.93391000	-0.51826600	-0.91100100
H	-4.29409300	-2.89691400	2.27911600
H	-6.23975300	-1.75980700	1.22322200

Img. Frequencies (cm^{-1}) = -323.1060

Electronic Energies = -945.6716279 hartee

6-Anti

Atom	X	Y	Z
C	4.72207500	-0.65682300	-0.60640600
C	4.64430700	0.88029600	-0.82621200
C	3.94902700	1.73679800	0.25744500
C	2.42715300	1.95239600	0.08786100

C	3.68059300	-1.55824600	-1.30151500
C	2.36052900	-1.78262900	-0.56545100
H	4.73996600	-0.88212500	0.46712600
H	4.19878800	1.09353800	-1.80815900
H	4.13671800	1.29587400	1.24451500
H	5.69570800	-0.98427800	-0.98864600
H	5.67781700	1.24051200	-0.89015400
H	4.41011500	2.73258000	0.27198700
H	2.04772200	2.53655000	0.93426800
H	2.23127300	2.54853400	-0.81372400
H	4.10240800	-2.55952300	-1.44551900
H	3.43478000	-1.16745800	-2.29531100
C	1.63068200	-0.54585300	-0.25527400
C	1.72685800	0.66840500	-0.03221600
N	-0.51852000	-1.05043800	-0.06152200
N	-0.86219000	0.03502800	0.17973600
N	-0.45554000	1.22661900	0.21539700
F	1.59623500	-2.64704500	-1.32863300
F	2.61426500	-2.46899000	0.61929800
C	-1.08698300	2.15717400	1.17203300
H	-0.42983700	3.03173900	1.16679800
H	-1.07332200	1.73695000	2.18569300
C	-2.49713900	2.56532900	0.79110000
C	-3.58679100	2.16441800	1.57261300
C	-2.73048700	3.34354200	-0.35210000
C	-4.88912600	2.53543900	1.22260600
H	-3.41862000	1.55833000	2.45952800
C	-4.02857500	3.71324900	-0.70488800
H	-1.89151900	3.65276700	-0.97023800
C	-5.11247800	3.31014200	0.08303700

H	-5.72481000	2.21682300	1.83892500
H	-4.19588500	4.31654100	-1.59258200
H	-6.12287200	3.59895200	-0.19128600

Img. Frequencies (cm^{-1}) = -329.4842

Electronic Energies = -945.6681091 hartree

7. References :

Complete reference for G09.

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