

Supporting information

A Molecular Electron Density Theory (MEDT) study of the role of halogens ($X_2 = F_2, Cl_2, Br_2$ and I_2) on the aza-Michael-addition reactions

Luis R. Domingo^{a†}, Ahmad Seif^{a,b†}, Elham Mazarei^a, Ehasn Zahedi^c, Temer S. Ahmadi^d

^a Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

^b Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran

^c Department of Chemistry, Shahrood Branch, Islamic Azad University, Shahrood, Iran

^d Department of Chemistry, Villanova University, Villanova, PA, 19085, USA

Table of contents

Table S1	Optimized cartesian coordinates for all TSs at MN15-L/def2-TZVP and MN15-L /aug-cc-pVTZ levels of theory at gas phase	S2
Table S2	Optimized cartesian coordinates for all TSs at MN15-L/def2-TZVP and MN15-L /aug-cc-pVTZ levels of theory at solvent phase	S7
Table S3	The rate constant ($\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) and tunneling corrections calculated at room temperature for the uncatalyzed/dihalogen I_2 molecules-catalyzed nucleophilic attack of PYR R_1 and on the β conjugated carbon MA R_2-I_2 in the DMC at MN15-L/aug-cc-pVTZ Level of theory.	S13
Table S4	MN15-L/def2-TZVP global CDFT reactivity indices (in eV) at the GS of the reagents involved in the MAR. The values including DCM solvent effects are reported in parentheses.	S13

† Corresponding author.

E-mail address: domingo@utopia.uv.es

† Corresponding author.

E-mail address: ahmaseif@yahoo.com

Table S1. Cartesian coordinates for all TSs at MN15-L/def2-TZVP and MN15-L/aug-cc-pVTZ levels of theory at gas phase

Cartesian coordinate for TS at uncatalyzed reaction at MN15-L/ def2-TZVP level of theory

C	2.95967000	-1.05476000	-0.36350800
C	3.50617100	0.38024500	-0.33032600
C	1.53681500	-0.82064400	-0.87316500
H	2.92591500	-1.48008600	0.65692700
H	3.53993900	-1.73695000	-1.00209200
N	1.11453800	0.35976400	-0.09162100
H	1.53825700	-0.59138500	-1.95519500
H	0.81392200	-1.63402000	-0.68226100
C	2.31352300	1.18651400	0.21737400
H	2.36551600	1.30069800	1.31854400
H	2.22482900	2.19355700	-0.21998700
H	3.74498500	0.70571200	-1.35869200
H	4.41221100	0.50283600	0.28324700
C	0.20870600	-0.11865700	1.37651200
C	-0.99771300	-0.77591200	1.02704100
H	0.13174600	0.92081700	1.74069300
H	0.96839600	-0.69632300	1.92651100
C	-1.92432500	0.00692200	0.28253800
O	-1.69947800	1.15827100	-0.13830400
O	-3.10852300	-0.61643100	0.01138500
C	-4.00957300	0.13850700	-0.78784800
H	-3.56399200	0.39107200	-1.76632300
H	-4.29548000	1.08056500	-0.28919800
H	-4.89503900	-0.49890900	-0.92877700
H	-1.14066400	-1.84819100	1.15837200
H	0.33204900	0.88425400	-0.51677400

Cartesian coordinate for TS at F₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	2.91284600	-0.02310100	-1.25514700
C	3.71885800	0.06315200	0.05231000
C	1.55958600	0.53489300	-0.81422000
H	2.79582900	-1.07489800	-1.57587300
H	3.36384000	0.54042900	-2.08507700
N	1.36729800	-0.14036600	0.48036700
H	1.59635800	1.63153000	-0.67959700
H	0.70355100	0.29261400	-1.46937300
C	2.68469700	-0.30437800	1.14059500
H	2.77907200	-1.35812500	1.47082700
H	2.76619100	0.33253800	2.03703400
H	4.06367200	1.10157200	0.19972300
H	4.60355400	-0.59144800	0.07571300
C	0.49560900	-1.83836200	0.25098000
C	-0.66451000	-1.69798300	-0.52403900
H	0.38546000	-1.93214800	1.33957700
H	1.34253200	-2.40374400	-0.15973400
C	-1.73974300	-0.95469000	0.04967400
O	-1.69770400	-0.42201300	1.17744900
O	-2.82519900	-0.82639600	-0.74857600
C	-3.88612200	-0.03949600	-0.20540700
H	-3.54553000	0.98746700	0.00524400

H	-4.26710900	-0.48350100	0.72946900
H	-4.67340500	-0.03358800	-0.97237300
H	-0.70264900	-1.98970900	-1.57455700
H	0.64872300	0.31090700	1.05669900
F	-1.11074200	1.63517200	0.41888700
F	-0.63762400	2.94257700	-0.12552500

Cartesian coordinate for TS at Cl₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	-3.19306800	-0.06466100	1.20480000
C	-3.89340300	0.14081400	-0.14810600
C	-1.74540600	0.27426400	0.84990100
H	-3.26218200	-1.12099300	1.52465500
H	-3.59775000	0.56532700	2.01032400
N	-1.57569600	-0.42711800	-0.43898700
H	-1.60639000	1.36424100	0.71731600
H	-0.97541900	-0.09678500	1.54993900
C	-2.87654500	-0.42437600	-1.16194300
H	-3.10818700	-1.46962400	-1.44675600
H	-2.81462700	0.16889700	-2.08821600
H	-4.03883300	1.22125700	-0.32372600
H	-4.87627500	-0.34930400	-0.22343500
C	-0.93767100	-2.14164400	-0.20212900
C	0.24059300	-2.17289000	0.57258600
H	-0.83924700	-2.29912700	-1.28728300
H	-1.83966200	-2.61066300	0.21681400
C	1.42254900	-1.63933300	-0.00829200
O	1.47658500	-1.06776000	-1.12108200
O	2.53333000	-1.76672000	0.76395500
C	3.73826100	-1.26403600	0.19292700
H	3.68193100	-0.17444300	0.02888400
H	3.95342000	-1.75192500	-0.77259500
H	4.53028700	-1.49363200	0.92009600
H	0.23971700	-2.49308300	1.61485600
H	-0.79248600	-0.05150200	-0.98607500
Cl	1.30844800	1.40738100	-0.41210700
Cl	0.91298600	3.29898400	0.21661700

Cartesian coordinate for TS at Br₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	3.08142400	-1.80301300	1.23662700
C	3.43213000	-2.49317500	-0.09151900
C	1.75602300	-1.12733300	0.88666700
H	3.83549700	-1.03448100	1.48969200
H	3.00001700	-2.49729400	2.08561600
N	2.04766400	-0.55947500	-0.44567300
H	0.92954500	-1.86130900	0.81926000
H	1.44261800	-0.30599400	1.55552400
C	2.99796500	-1.46022000	-1.15322200
H	3.84784300	-0.84640200	-1.51089500
H	2.52445300	-1.92152900	-2.03460700
H	2.83081900	-3.41341700	-0.19480000
H	4.49330800	-2.77020700	-0.18606200
C	2.72788200	1.17552600	-0.31996600
C	1.95842600	2.00940600	0.51387100
H	2.64932200	1.32669300	-1.40639200
H	3.74485100	0.92032900	0.00892800

C	0.69914800	2.46186700	0.03816500
O	0.17355600	2.11192600	-1.04683100
O	0.06177200	3.31860700	0.87368400
C	-1.18574300	3.82676800	0.40481200
H	-1.93163000	3.02124400	0.29554900
H	-1.06686900	4.33023700	-0.56898900
H	-1.51868000	4.54473400	1.16759000
H	2.26792800	2.24909000	1.53187300
H	1.19023600	-0.36611500	-0.97480200
Br	-1.38665100	0.16944200	-0.41469500
Br	-2.53503600	-1.78208400	0.22426100

Cartesian coordinate for TS at I₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	3.23136300	-2.33442500	1.34366200
C	3.64990000	-3.15054500	0.08944600
C	1.91592200	-1.66067000	0.93906600
H	3.97788500	-1.55106100	1.56310100
H	3.12372300	-2.95463600	2.24508500
N	2.14196500	-1.40406700	-0.49437000
H	1.03667000	-2.32166600	1.06312100
H	1.72039700	-0.70343200	1.45122600
C	2.72670200	-2.64192800	-1.04695000
H	3.26086000	-2.40445000	-1.98406000
H	1.92672400	-3.36821300	-1.27779900
H	3.51247000	-4.23241100	0.23784200
H	4.71174200	-2.98952400	-0.15604100
C	3.31005600	0.02355300	-0.74896100
C	3.15399900	1.06040700	0.19340700
H	2.96011500	0.22380500	-1.77112700
H	4.23925600	-0.56266100	-0.71295900
C	2.12649400	2.01767600	0.00119000
O	1.30768900	2.02541000	-0.95490500
O	2.08034000	2.98151500	0.95233600
C	1.08773200	3.98972900	0.76668900
H	0.07068900	3.56486500	0.82846500
H	1.20407800	4.48561900	-0.21098500
H	1.24187400	4.71041100	1.58196300
H	3.76828300	1.11149300	1.09454500
H	1.28245600	-1.10148300	-0.97009300
I	-0.87720900	0.75337600	-0.39169300
I	-3.03502200	-0.86576000	0.22704400

Cartesian coordinate for TS at uncatalyzed reaction at MN15-L/aug-cc-pVTZ level of theory

C	2.97475800	-1.06716300	-0.32468500
C	3.52291100	0.36745200	-0.32815400
C	1.55537800	-0.84831300	-0.84983200
H	2.93415600	-1.46368400	0.70630800
H	3.55749600	-1.76596100	-0.94147900
N	1.12929900	0.35901300	-0.11214300
H	1.56258800	-0.65621500	-1.93818000
H	0.83233500	-1.65409800	-0.63402600
C	2.32734700	1.19116700	0.18470100
H	2.37007100	1.33520900	1.28199100
H	2.24461600	2.18432700	-0.28242000
H	3.77140900	0.66272400	-1.36261300

H	4.42211800	0.50542600	0.29100300
C	0.20161100	-0.06817000	1.36934400
C	-0.99955100	-0.73902900	1.03558600
H	0.12216400	0.98376400	1.69020200
H	0.95947700	-0.62512900	1.94095300
C	-1.93666600	0.01912400	0.27629100
O	-1.72358300	1.16072600	-0.17439900
O	-3.11671100	-0.62160300	0.02910600
C	-4.03575300	0.10444600	-0.77727200
H	-3.60367000	0.33507800	-1.76596300
H	-4.32276400	1.05451500	-0.29716100
H	-4.91502800	-0.54538800	-0.88956400
H	-1.13989500	-1.80655600	1.20078100
H	0.36198400	0.87283000	-0.56837100

Cartesian coordinate for TS at F₂-catalyzed reaction at MN15-L/aug-cc-pVTZ level of theory

C	-2.63663200	-0.29860700	1.38101500
C	-3.59037800	-0.43861200	0.16139400
C	-1.49949500	0.59375400	0.87062700
H	-2.22463200	-1.28139900	1.66690800
H	-3.13344600	0.12506600	2.26516300
N	-1.41202800	0.18667100	-0.53886100
H	-1.74495400	1.66919700	0.93795000
H	-0.52619800	0.42429100	1.36004000
C	-2.79114800	0.12427000	-1.04234500
H	-2.82717900	-0.52184000	-1.93719800
H	-3.14629800	1.13161400	-1.32814500
H	-4.52232400	0.12865100	0.30246800
H	-3.87221700	-1.48996800	-0.00600100
C	-0.57960200	-1.57193800	-0.69867400
C	0.51062300	-1.68079500	0.17217100
H	-0.37411900	-1.39444200	-1.75998200
H	-1.48248800	-2.16207800	-0.50079800
C	1.69393100	-0.95618500	-0.16780000
O	1.83365300	-0.29280900	-1.21517200
O	2.67215300	-1.01118200	0.76472300
C	3.83904900	-0.24210400	0.46361800
H	3.58084000	0.82147300	0.33950400
H	4.31655400	-0.60192300	-0.46174900
H	4.51196000	-0.38010900	1.32024200
H	0.42572300	-2.15388300	1.15222800
H	-0.77285300	0.77585800	-1.08132700
F	1.19291400	1.63858100	-0.38623800
F	0.57945200	2.90097800	0.19360300

Cartesian coordinate for TS at Cl₂-catalyzed reaction at MN15-L/aug-cc-pVTZ level of theory

C	-3.19490000	-0.05525300	1.20820600
C	-3.90573500	0.12934200	-0.14226200
C	-1.75104700	0.28643500	0.84162500
H	-3.25598900	-1.10706300	1.54192900
H	-3.59710400	0.58399900	2.00668700
N	-1.58582400	-0.42277300	-0.44341000
H	-1.61676200	1.37527000	0.70115100
H	-0.97773700	-0.07793600	1.54025900
C	-2.88997600	-0.43303300	-1.15861000

H	-3.11642400	-1.48033300	-1.43713900
H	-2.83702100	0.15747300	-2.08635600
H	-4.06503000	1.20561400	-0.32687800
H	-4.88203000	-0.37397400	-0.20535500
C	-0.93485000	-2.14318500	-0.19759100
C	0.24117500	-2.16637100	0.57765300
H	-0.83591700	-2.29963800	-1.28144700
H	-1.83658800	-2.60743500	0.22434300
C	1.42747000	-1.64413600	-0.00809600
O	1.48861200	-1.09321400	-1.12986400
O	2.53247200	-1.75641100	0.77497700
C	3.74400100	-1.26682600	0.20553500
H	3.68849100	-0.18150700	0.02085500
H	3.96488700	-1.77456100	-0.74721300
H	4.52713200	-1.48396800	0.94461800
H	0.23782500	-2.47224500	1.62382000
H	-0.81130200	-0.04509400	-0.99753500
Cl	1.31774400	1.41029600	-0.42850400
Cl	0.91336400	3.30123200	0.22041400

Cartesian coordinate for TS at Br₂-catalyzed reaction at MN15-L/aug-cc-pVTZ level of theory

C	3.07054100	-1.81566300	1.23463800
C	3.43676900	-2.48997100	-0.09746900
C	1.75037500	-1.13303400	0.87913800
H	3.82196500	-1.05188800	1.50634900
H	2.97668900	-2.52097600	2.07226600
N	2.05345800	-0.55505300	-0.44599200
H	0.92256100	-1.86313300	0.80002200
H	1.43669000	-0.31655200	1.55253100
C	3.00894800	-1.44873200	-1.15339100
H	3.86103900	-0.83254900	-1.49947300
H	2.54142800	-1.90365100	-2.04040200
H	2.84097400	-3.41112400	-0.21622700
H	4.49983800	-2.75986100	-0.18343900
C	2.73509900	1.18788700	-0.30175500
C	1.95630400	2.01388800	0.52864200
H	2.66510000	1.34063400	-1.38736900
H	3.74602600	0.92703900	0.03776300
C	0.70080500	2.46924300	0.04127600
O	0.18899900	2.13057300	-1.05236800
O	0.05095000	3.31270600	0.88150400
C	-1.19343500	3.82480900	0.40814000
H	-1.93373700	3.01807100	0.28111600
H	-1.06454000	4.34137700	-0.55637200
H	-1.53389400	4.53027100	1.17792100
H	2.25232000	2.24296800	1.55259400
H	1.20245900	-0.35766500	-0.98032400
Br	-1.39701800	0.16426700	-0.42578200
Br	-2.52644400	-1.78410600	0.22968500

Cartesian coordinate for TS at I₂-catalyzed reaction at MN15-L/Aug.-cc-pVTZ for all atoms except I₂ and MN15-L/aug-cc-pVTZ-Lan12dZ for I₂ level of theory

C	3.23136300	-2.33442500	1.34366200
C	3.64990000	-3.15054500	0.08944600
C	1.91592200	-1.66067000	0.93906600

H	3.97788500	-1.55106100	1.56310100
H	3.12372300	-2.95463600	2.24508500
N	2.14196500	-1.40406700	-0.49437000
H	1.03667000	-2.32166600	1.06312100
H	1.72039700	-0.70343200	1.45122600
C	2.72670200	-2.64192800	-1.04695000
H	3.26086000	-2.40445000	-1.98406000
H	1.92672400	-3.36821300	-1.27779900
H	3.51247000	-4.23241100	0.23784200
H	4.71174200	-2.98952400	-0.15604100
C	3.31005600	0.02355300	-0.74896100
C	3.15399900	1.06040700	0.19340700
H	2.96011500	0.22380500	-1.77112700
H	4.23925600	-0.56266100	-0.71295900
C	2.12649400	2.01767600	0.00119000
O	1.30768900	2.02541000	-0.95490500
O	2.08034000	2.98151500	0.95233600
C	1.08773200	3.98972900	0.76668900
H	0.07068900	3.56486500	0.82846500
H	1.20407800	4.48561900	-0.21098500
H	1.24187400	4.71041100	1.58196300
H	3.76828300	1.11149300	1.09454500
H	1.28245600	-1.10148300	-0.97009300
I	-0.87720900	0.75337600	-0.39169300
I	-3.03502200	-0.86576000	0.22704400

Table S2. Cartesian coordinates for all TSs at MN15-L/def2-TZVP and MN15-L/aug-cc-pVTZ levels of theory at solvent phase

<u>Cartesian coordinate for TS at uncatalyzed reaction at MN15-L/ def2-TZVP level of theory</u>			
C	3.09139600	-1.11943500	0.04696800
C	3.70472900	0.25831600	-0.24066100
C	1.75925000	-1.01253800	-0.69592600
H	2.90750000	-1.23877000	1.13136000
H	3.70621700	-1.96360700	-0.29927800
N	1.30710000	0.34922200	-0.34413000
H	1.91219000	-1.10512500	-1.78748100
H	0.98821100	-1.74008500	-0.38341100
C	2.49933000	1.19898600	-0.07447200
H	2.42144200	1.57085300	0.96718400
H	2.52129900	2.07110000	-0.74625300
H	4.06898600	0.28781800	-1.28339400
H	4.53957200	0.52596300	0.42548400
C	0.14864600	0.28515500	1.19550400
C	-1.01401400	-0.46266600	0.97847300
H	0.06339300	1.38024200	1.21232200
H	0.91788100	-0.11154700	1.87184700
C	-2.08889700	0.12842000	0.23250800
O	-2.11005700	1.25884100	-0.26554800
O	-3.16077200	-0.71627800	0.10347200
C	-4.26155500	-0.19039800	-0.63156900
H	-3.96868100	0.07252700	-1.66338800
H	-4.67822800	0.70903400	-0.14525200

H	-5.02099300	-0.98653700	-0.65220900
H	-1.07072800	-1.52309000	1.23614900
H	0.67555900	0.75112600	-1.04311900

Cartesian coordinate for TS at F₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	-2.49868600	-0.65585900	1.36909100
C	-3.56032800	-0.65313000	0.23446800
C	-1.54614500	0.48809200	0.99763200
H	-1.94075400	-1.60839300	1.36979400
H	-2.93817500	-0.52319800	2.36907300
N	-1.57716800	0.44506700	-0.46393600
H	-1.91898600	1.46536400	1.36769200
H	-0.51102800	0.35164600	1.36019500
C	-2.98026800	0.28265500	-0.85498400
H	-3.04119800	-0.13579500	-1.87567100
H	-3.49914700	1.26251400	-0.85617100
H	-4.53479200	-0.27865400	0.58419200
H	-3.72179300	-1.67005900	-0.15862300
C	-0.47562400	-1.35405200	-1.12338000
C	0.52441700	-1.62247600	-0.21272600
H	-0.24066500	-0.81141100	-2.04295100
H	-1.40598200	-1.93093300	-1.11747700
C	1.76282300	-0.89447100	-0.29437800
O	2.07615100	-0.13280900	-1.22946400
O	2.57860000	-1.09142400	0.75675000
C	3.81062800	-0.35604200	0.72965700
H	3.61320000	0.72804000	0.69568000
H	4.41906600	-0.64314700	-0.14381100
H	4.33361200	-0.61998000	1.65914400
H	0.35912700	-2.27116800	0.65202800
H	-1.09860700	1.23277000	-0.91070500
F	1.24941300	1.63640500	-0.36741900
F	0.49585300	2.88831700	0.25681900

Cartesian coordinate for TS at Cl₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	-2.95717500	-0.15811100	1.39333300
C	-3.97191400	-0.15962300	0.21759400
C	-1.73433800	0.58256300	0.83906100
H	-2.66334400	-1.19144800	1.64924700
H	-3.35263800	0.31483000	2.30430900
N	-1.75712300	0.18409500	-0.57356000
H	-1.83422400	1.68258100	0.92880700
H	-0.78045900	0.27069900	1.30015300
C	-3.15741500	0.30018900	-1.01655800
H	-3.31200800	-0.32954100	-1.91071300
H	-3.38758000	1.34803000	-1.28453000
H	-4.81126100	0.52902800	0.39952300
H	-4.39766800	-1.16400900	0.06262500
C	-1.17112000	-1.69774200	-0.77209400
C	-0.16616900	-2.06194600	0.12710600
H	-0.89570600	-1.52729800	-1.81956900
H	-2.18219200	-2.09833200	-0.62815600
C	1.19704100	-1.74758900	-0.16470600
O	1.62318200	-1.18628400	-1.19271600
O	2.05410300	-2.12844500	0.82206300

C	3.43693000	-1.87328000	0.57310300
H	3.63044800	-0.79315000	0.45349700
H	3.78329000	-2.39893100	-0.33314400
H	3.97478900	-2.25247800	1.45433000
H	-0.40582000	-2.48051200	1.10850900
H	-1.10393700	0.71865900	-1.15529300
Cl	1.61914300	1.26812800	-0.41814000
Cl	1.42584900	3.17271300	0.25752300

Cartesian coordinate for TS at Br₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	3.22912400	-1.31376400	1.38189400
C	4.00789300	-1.94324400	0.19495900
C	1.77731000	-1.25011400	0.89270800
H	3.58728100	-0.28724300	1.57490900
H	3.32886200	-1.88643700	2.31575000
N	1.95519400	-0.99562400	-0.54163400
H	1.24029000	-2.20709000	1.04979700
H	1.18988700	-0.43306900	1.34786800
C	3.02107600	-1.90526500	-0.99767600
H	3.46520300	-1.51224900	-1.92943600
H	2.60289200	-2.90733900	-1.20744200
H	4.31080600	-2.98009400	0.40717100
H	4.92343100	-1.37144600	-0.02621700
C	2.54212400	0.89948300	-0.84428900
C	2.02555600	1.79900000	0.08888400
H	2.11802300	0.89352200	-1.85488200
H	3.60324600	0.62883500	-0.78920200
C	0.73582900	2.37675100	-0.10752100
O	-0.01941400	2.18307500	-1.08687000
O	0.36183200	3.21033000	0.89516100
C	-0.90157600	3.85861200	0.72926300
H	-1.72401400	3.12425300	0.68058600
H	-0.91616300	4.47284800	-0.18687600
H	-1.02587000	4.49971800	1.61380600
H	2.55250700	2.01385000	1.02252900
H	1.08827100	-1.09164700	-1.07952000
Br	-1.48472900	0.21627900	-0.41380700
Br	-2.66939600	-1.70950900	0.25257700

Cartesian coordinate for TS at I₂ catalyzed reaction at MN15-L/ def2-TZVP level of theory

C	3.44004200	-2.14022800	1.36598200
C	3.95957900	-2.96664900	0.15861800
C	2.04114800	-1.68224700	0.93703300
H	4.07513200	-1.25083100	1.52408300
H	3.42217000	-2.71272500	2.30517700
N	2.21731100	-1.48924100	-0.50615300
H	1.27022800	-2.45469100	1.13159500
H	1.71994200	-0.73449700	1.40526900
C	2.97396900	-2.65437600	-0.99486000
H	3.47295100	-2.39663000	-1.94610100
H	2.29038700	-3.50366800	-1.18130500
H	3.96601400	-4.04629200	0.37396300
H	4.98961500	-2.67797300	-0.10586600
C	3.29312400	0.18509800	-0.85406800
C	3.09421000	1.18380700	0.09770500

H	2.83163000	0.30230700	-1.84121000
H	4.23549200	-0.37517500	-0.84891900
C	2.02275400	2.11611000	-0.04510100
O	1.20754200	2.16792700	-0.99480200
O	1.95099700	3.00974500	0.97125200
C	0.93983000	4.01474700	0.85262200
H	-0.06866400	3.56656000	0.83810500
H	1.08075700	4.61216600	-0.06382400
H	1.05134000	4.65473500	1.73964900
H	3.69906200	1.23038500	1.00737300
H	1.33215400	-1.34241800	-1.00264000
I	-0.92837000	0.70782200	-0.39041800
I	-3.04796200	-0.93811400	0.22605100

Cartesian coordinate for TS at uncatalyzed reaction at MN15-L/aug-cc-pVTZ level of theory

C	3.10036100	-1.12231500	0.06019800
C	3.71897500	0.25223900	-0.23072100
C	1.77249500	-1.01818900	-0.69049400
H	2.90938100	-1.23506400	1.14337800
H	3.71502400	-1.96854100	-0.27892100
N	1.32385700	0.34889200	-0.35802600
H	1.92973900	-1.12600200	-1.77931800
H	0.99916000	-1.73905900	-0.37083100
C	2.51456900	1.19669700	-0.08292500
H	2.43007200	1.57565700	0.95503400
H	2.54583800	2.06276600	-0.76095600
H	4.09281400	0.27425800	-1.26953500
H	4.54645600	0.52178500	0.44265800
C	0.13751800	0.30295400	1.19224400
C	-1.01970600	-0.44738600	0.97460300
H	0.05876300	1.39716600	1.18637800
H	0.90792000	-0.08973400	1.86737400
C	-2.10131000	0.13439900	0.22857600
O	-2.13062700	1.26292400	-0.27476300
O	-3.16673200	-0.71742600	0.10737600
C	-4.27837000	-0.20684300	-0.62397500
H	-3.99292000	0.05005700	-1.65810900
H	-4.69770800	0.69067100	-0.13915700
H	-5.02846900	-1.01049100	-0.63266000
H	-1.07503900	-1.50483600	1.24199400
H	0.70365200	0.74580500	-1.06708400

Cartesian coordinate for TS at F₂ catalyzed reaction at MN15-L/ aug-cc-pVTZ level of theory

C	-2.47788600	-0.63933300	1.38074000
C	-3.54271600	-0.63250300	0.24829700
C	-1.51671100	0.49683400	1.00520200
H	-1.92835900	-1.59566300	1.38461900
H	-2.91540800	-0.49688000	2.37947700
N	-1.57037100	0.47267300	-0.45386300
H	-1.87496700	1.47310000	1.39182600
H	-0.47860900	0.34771800	1.35158500
C	-2.97400700	0.31885600	-0.83227300
H	-3.04886800	-0.08212300	-1.85804100
H	-3.49099700	1.29994800	-0.81057600
H	-4.51922600	-0.27177400	0.60439800

H	-3.69270500	-1.64552600	-0.15741700
C	-0.46069800	-1.42117300	-1.15754700
C	0.52132100	-1.66986200	-0.23117400
H	-0.23283500	-0.84912000	-2.05950200
H	-1.40191000	-1.97738400	-1.14265600
C	1.75401100	-0.91911000	-0.29385700
O	2.08320600	-0.19420800	-1.25000000
O	2.52189800	-1.05078000	0.79698400
C	3.74914000	-0.30257800	0.79194400
H	3.54036000	0.77472800	0.70457200
H	4.39257800	-0.62250600	-0.04264000
H	4.23167900	-0.52458400	1.75228200
H	0.35277700	-2.31937000	0.63155600
H	-1.07425000	1.24309100	-0.90746200
F	1.27429900	1.60242600	-0.41218000
F	0.50100900	2.89876800	0.20230900

Cartesian coordinate for TS at Cl₂ catalyzed reaction at MN15-L/ aug-cc-pVTZ level of theory

C	-2.96016200	-0.09468000	1.39617100
C	-3.97491400	-0.13377600	0.22114000
C	-1.72583900	0.60322900	0.81218300
H	-2.68200200	-1.11902300	1.69834700
H	-3.34945800	0.42554600	2.28290800
N	-1.75931500	0.15716100	-0.58533200
H	-1.80527600	1.70675000	0.86535400
H	-0.77772700	0.28871800	1.28163300
C	-3.15853100	0.27526300	-1.02892700
H	-3.32307100	-0.38318200	-1.89936300
H	-3.37746100	1.31566800	-1.33077600
H	-4.81014000	0.56493700	0.37770900
H	-4.40326000	-1.14129200	0.10258600
C	-1.18431400	-1.74912100	-0.72844700
C	-0.16708100	-2.07865600	0.16738400
H	-0.92864400	-1.60720900	-1.78404800
H	-2.19422200	-2.13525900	-0.55120700
C	1.19208900	-1.76507800	-0.15164800
O	1.60208900	-1.23687700	-1.20242500
O	2.06067300	-2.10228600	0.84107300
C	3.44212300	-1.85962200	0.57012500
H	3.63402200	-0.78652700	0.40411900
H	3.77701400	-2.42433600	-0.31547000
H	3.98525600	-2.20265800	1.46161500
H	-0.39248900	-2.46092400	1.16613400
H	-1.10177700	0.66095400	-1.18615100
Cl	1.62946600	1.27632200	-0.43822000
Cl	1.42830600	3.17813000	0.25391800

Cartesian coordinate for TS at Br₂ catalyzed reaction at MN15-L/ aug-cc-pVTZ level of theory

C	3.19557700	-1.37646300	1.38592400
C	3.98073500	-1.99130300	0.19571900
C	1.75535800	-1.25942100	0.87282700
H	3.57585200	-0.36643900	1.61632900
H	3.26140100	-1.98032000	2.30216300
N	1.96517500	-0.97791400	-0.55167300
H	1.18819500	-2.20269700	1.00043300

H	1.18661300	-0.43493400	1.33634400
C	3.01630100	-1.90144900	-1.01177400
H	3.48650700	-1.49556400	-1.92414400
H	2.57931900	-2.88763100	-1.25280000
H	4.25783800	-3.03883700	0.38611800
H	4.90992400	-1.43223400	0.00416500
C	2.59756900	0.92064700	-0.80563800
C	2.05617600	1.80688800	0.12393300
H	2.20729300	0.92711200	-1.82867700
H	3.65070600	0.63354000	-0.71537200
C	0.76703600	2.38179600	-0.09755400
O	0.03841600	2.19918700	-1.09675200
O	0.36327800	3.19354700	0.91268800
C	-0.89369000	3.84928400	0.72708200
H	-1.71495300	3.11847100	0.64281400
H	-0.88002700	4.48035300	-0.17639500
H	-1.03780400	4.47249700	1.62018400
H	2.55377600	2.00262600	1.07697200
H	1.10717200	-1.03712000	-1.10569700
Br	-1.49699200	0.21726700	-0.42470800
Br	-2.67877900	-1.69255700	0.25352700

Cartesian coordinate for TS at I₂ catalyzed reaction at MN15-L/Aug.-cc-pVTZ for all atoms except I₂ and MN15-L/aug-cc-pVTZ-LanI2dZ for I₂ level of theory

C	3.23136400	-2.33442500	1.34366200
C	3.64990100	-3.15054400	0.08944600
C	1.91592200	-1.66067000	0.93906600
H	3.97788500	-1.55106000	1.56310100
H	3.12372400	-2.95463600	2.24508500
N	2.14196500	-1.40406700	-0.49437000
H	1.03667100	-2.32166600	1.06312100
H	1.72039700	-0.70343200	1.45122600
C	2.72670300	-2.64192800	-1.04695000
H	3.26086100	-2.40445000	-1.98406000
H	1.92672500	-3.36821300	-1.27779900
H	3.51247100	-4.23241100	0.23784200
H	4.71174300	-2.98952300	-0.15604100
C	3.31005600	0.02355300	-0.74896100
C	3.15399900	1.06040700	0.19340700
H	2.96011500	0.22380500	-1.77112700
H	4.23925600	-0.56266000	-0.71295900
C	2.12649400	2.01767600	0.00119000
O	1.30768900	2.02541000	-0.95490500
O	2.08034000	2.98151500	0.95233600
C	1.08773100	3.98972900	0.76668900
H	0.07068900	3.56486500	0.82846500
H	1.20407700	4.48561900	-0.21098500
H	1.24187300	4.71041100	1.58196300
H	3.76828300	1.11149400	1.09454500
H	1.28245600	-1.10148300	-0.97009300
I	-0.87720900	0.75337600	-0.39169300
I	-3.03502200	-0.86576100	0.22704400

Table S3. The rate constant ($\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) and tunneling corrections calculated at room temperature for the uncatalyzed/dihalogen I_2 molecules-catalyzed nucleophilic attack of PYR \mathbf{R}_1 and on the β conjugated carbon MA \mathbf{R}_2 - I_2 in the DMC at MN15-L/aug-cc-pVTZ Level of theory.

bimolecular reactions	No correction		Wigner tunneling		Eckart tunneling	
	k	κ (T)	k	κ (T)	k	κ (T)
$\mathbf{R}_1 + \mathbf{R}_2 \rightarrow \text{IN1}$	6.74×10^{-23}	1.0	7.31×10^{-23}	1.08	7.39×10^{-23}	1.10
$\mathbf{R}_1 + \mathbf{R}_2 - \text{I}_2 \rightarrow \text{IN} - \text{I}_2$	5.16×10^{-20}	1.0	5.52×10^{-20}	1.07	5.52×10^{-20}	1.07

Table S4. MN15-L/def2-TZVP global CDFT reactivity indices (in eV) at the GS of the reagents involved in the MAR. The values including DCM solvent effects are reported in parentheses.

Species	μ	η	ω	N
\mathbf{R}_1	-2.51	6.39	0.49	3.41
	(-2.39)	(6.58)	(0.43)	(3.45)
\mathbf{R}_2	-4.47	5.03	1.98	2.14
	(-4.41)	(5.14)	(1.89)	(2.14)
$\mathbf{R}_2 - \text{F}_2$	-5.33	3.62	3.92	1.99
	(-5.42)	(3.32)	(4.41)	(2.04)
$\mathbf{R}_2 - \text{Cl}_2$	-5.06	4.38	2.92	1.87
	(-5.15)	(4.13)	(3.21)	(1.91)
$\mathbf{R}_2 - \text{Br}_2$	-4.98	3.53	3.51	2.38
	(-5.13)	(3.55)	(3.70)	(2.22)
$\mathbf{R}_2 - \text{I}_2$	-4.62	2.60	4.10	3.20
	(-4.54)	(2.73)	(3.77)	(3.22)