Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information

Identification of chlorinated products from tyrosine and tyrosyl dipeptides during chlorination: a computational study

Zizhang Ren, Yue Qiu, Mengxue Huan, Yong Dong Liu, Rugang Zhong*

Beijing Key Laboratory of Environmental and Viral Oncology,

Faculty of Environment and Life, Beijing University of Technology,

Beijing 100124, China

*Corresponding author. Fax: +86-10-6739-2001.

E-mail: ydliu@bjut.edu.cn.

109 Pages
16 Tables
9 Figures
1 Scheme
44 Cartesian orientations of transition states

*Corresponding author. Fax: +86-10-6739-2001. E-mail: ydliu@bjut.edu.cn.

Contents

Standard orientation of TS-5-Cl-Tyr-N	48 49
Standard orientation of TS-3-Cl-Tyr-N	50 51
Standard orientation of TS-3,5-di-Cl-Tyr-N	52 53
Standard orientation of TS-*N*-Cl-Tyr-N	54 55
Standard orientation of TS-3,*N*-di-Cl-Tyr-N	56 57
Standard orientation of TS-5,*N*-di-Cl-Tyr-N	58 59
Standard orientation of TS-3,5,*N*-tri-Cl-Tyr-N	60 61
Standard orientation of TS-Tyr-Am-p-C3	62 63
Standard orientation of TS-*N*-Cl-Tyr-Am-p-C3	64 65
Standard orientation of TS-5-Cl-Tyr-Am-p-C3	66 67
Standard orientation of TS-*N*,*N*-di-Cl-Tyr-Am-p-C3	68 69
Standard orientation of TS-5,*N*-di-Cl-Tyr-Am-p-C3	70 71
Standard orientation of TS-5,*N*,*N*-tri-Cl-Tyr-Am-p-C3	72 73
Standard orientation of TS-Tyr-Am-p-C5	74 75
Standard orientation of TS-*N*-Cl-Tyr-Am-p-C5	76 77
Standard orientation of TS-3-Cl-Tyr-Am-p-C5	78 79
Standard orientation of TS-*N*,*N*-di-Cl-Tyr-Am-p-C5	80 81
Standard orientation of TS-3,*N*-di-Cl-Tyr-Am-p-C5	82 83
Standard orientation of TS-3,*N*,*N*-tri-Cl-Tyr-Am-p-C5	84 85
Standard orientation of TS-Tyr-Am-N	86 87
Standard orientation of TS-5-Cl-Tyr-Am-N	88 89

Standard orientation of TS-3-Cl-Tyr-Am-N	90 91
Standard orientation of TS-3,5-di-Cl-Tyr-Am-N	92 93
Standard orientation of TS-*N*-Cl-Tyr-Am-N	94 95
Standard orientation of TS-3,*N*-di-Cl-Tyr-Am-N	96 97
Standard orientation of TS-5,*N*-di-Cl-Tyr-Am-N	98 99
Standard orientation of TS-3,5,*N*-tri-Cl-Tyr-Am-N	100 101
Standard orientation of TS-NacTyr-p-C3	102 103
Standard orientation of TS-NacTyr-p-C5	104 105
Standard orientation of TS-3-Cl-NacTyr-p-C5	106 107
Standard orientation of TS-5-Cl-NacTyr-p-C3	108 109

Text S1

Quantum Chemical Linear Free Energy Relationship (LFER) for Estimation of pK_a Values

Based on the proton theory of acids and bases, acid is a donor of protons. The stronger the ability to provide protons, the stronger the acidity. Quantum chemical calculations were performed with the Gaussian 09 software package. The bond dissociation energies (BDEs) of X-H(X=N/O/C) in organic compounds were calculated at the M06-2X/cc-pVTZ level in conjunction with the SMD implicit solvation model. All structures were confirmed as minima by frequency calculations.

BDEs values were computed by evaluating the enthalpies difference.

$BDE = H(H_3O^+) + H(R\text{-}X^-) - H(H_2O) - H(R\text{-}X\text{-}H)$

The correlation between the BDEs and experimental pK_a values of amines was established and illustrated in Figure S1 and Table S1. The squared correlation coefficient for the above system is $R^2 = 0.982$. Based on the obtained quantum chemical LFER, the calculated pK_a and BDEs chlorinated tyrosine, Tyr-amide and *N*-Acetyl-*L*-Tyrosine were listed in Table S2.

Figure S1

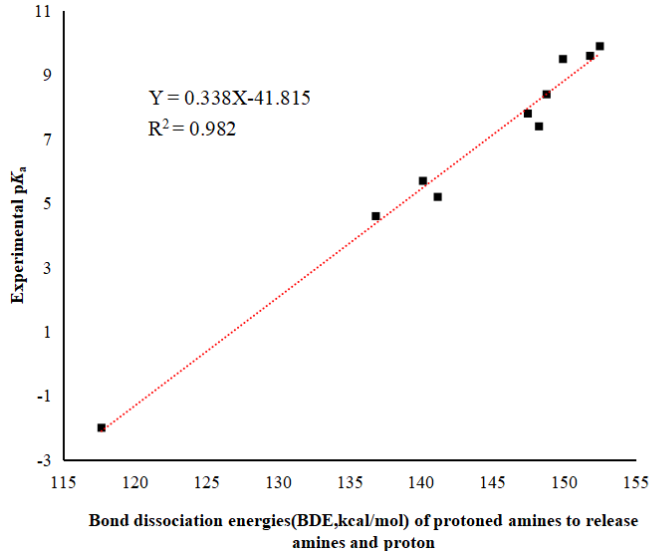


Figure S1. The correlation between the experimental pK_a values and BDEs for 10 amines.

Table S1

Table S1. The pK_a values and BDEs of 10 amines.

Amines	pK_a (exp.)	BDE (kcal/mol)	pK_a (calc.)
$CN\text{-}N(CH_2CH_3)_2$	-2.0	117.6	-2.1
$C_6H_5\text{-}NH_2$	4.6	136.8	4.4
$C_6H_5\text{-}N\text{-}(CH_3)_2$	5.2	141.2	5.9
$CF_3\text{-}CH_2\text{-}NH_2$	5.7	140.1	5.5
4-Methylmorpholine	7.4	148.3	8.3
$(C_2H_5OH)_3N$	7.8	147.5	8.0
Morpholine	8.4	148.8	8.5
$CH_2OH\text{-}CH_2\text{-}NH_2$	9.5	149.9	8.9
Glycine	9.6	151.8	9.5
Alanine	9.9	152.5	9.7

Table S2

Table S2. The pK_a values of N-H bonds in tyrosine, tyrosine-amide, their chlorinated products and *N*-Acetyl-*L*-Tyrosine calculated by using LFER.

	Phenol	
Heterolytic reaction	BDE (kcal/mol)	pK_a (calc.)
$Tyr^+ \rightarrow Tyr + H^+$	151.4	9.3
$Tyr \rightarrow Tyr^- + H^+$	202.2	26.5
$3\text{-Cl-Tyr}^+ \rightarrow 3\text{-Cl-Tyr} + H^+$	150.9	9.2
$5\text{-Cl-Tyr}^+ \rightarrow 5\text{-Cl-Tyr} + H^+$	150.7	9.1
$N\text{-Cl-Tyr}^+ \rightarrow N\text{-Cl-Tyr} + H^+$	136.8	4.4
$N\text{-Cl-Tyr} \rightarrow N\text{-Cl-Tyr}^- + H^+$	184.1	20.4
$3,5\text{-di-Cl-Tyr}^+ \rightarrow 3,5\text{-di-Cl-Tyr} + H^+$	150.4	9.0
$3,N\text{-di-Cl-Tyr}^+ \rightarrow 3,N\text{-di-Cl-Tyr} + H^+$	136.0	4.2
$3,N\text{-di-Cl-Tyr} \rightarrow 3,N\text{-di-Cl-Tyr}^- + H^+$	183.7	20.2
$5,N\text{-di-Cl-Tyr}^+ \rightarrow 5,N\text{-di-Cl-Tyr} + H^+$	136.0	4.2
$5,N\text{-di-Cl-Tyr} \rightarrow 5,N\text{-di-Cl-Tyr}^- + H^+$	183.6	20.2
$3,5,N\text{-tri-Cl-Tyr} \rightarrow 3,5,N\text{-tri-Cl-Tyr}^- + H^+$	183.0	20.0
$\text{Tyr-Amide}^+ \rightarrow \text{Tyr} + H^+$	145.6	7.4
$3\text{-Cl-Tyr-Amide}^+ \rightarrow 3\text{-Cl-Tyr-Amide} + H^+$	145.1	7.2
$5\text{-Cl-Tyr-Amide}^+ \rightarrow 5\text{-Cl-Tyr-Amide} + H^+$	144.9	7.2
$N\text{-Cl-Tyr-Amide}^+ \rightarrow N\text{-Cl-Tyr-Amide} + H^+$	127.2	1.2
$3,5\text{-di-Cl-Tyr-Amide}^+ \rightarrow 3,5\text{-di-Cl-Tyr-Amide} + H^+$	143.8	6.8
$3,N\text{-di-Cl-Tyr-Amide}^+ \rightarrow 3,N\text{-di-Cl-Tyr-Amide} + H^+$	126.8	1.1
$5,N\text{-di-Cl-Tyr-Amide}^+ \rightarrow 5,N\text{-di-Cl-Tyr-Amide} + H^+$	126.7	1.1
$3,5,N\text{-tri-Cl-Tyr-Amide}^+ \rightarrow 3,5,N\text{-tri-Cl-Tyr-Amide} + H^+$	126.1	0.8
$N\text{-Acetyl-}L\text{-Tyr}^+ \rightarrow N\text{-Acetyl-}L\text{-Tyr} + H^+$	125.4	0.6
$N\text{-Acetyl-}L\text{-Tyr} \rightarrow N\text{-Acetyl-}L\text{-Tyr}^- + H^+$	174.1	17.0

The correlation between the BDEs and experimental pK_a values of O-H bonds of substituted phenols was established and illustrated in Figure S2 and Table S3. The squared correlation coefficient for the above system is $R^2 = 0.992$. The calculated pK_a and BDEs of tyrosine, Tyr-amide, *N*-Acetyl-*L*-Tyrosine and their chlorinated products were listed in Table S4.

Figure S2

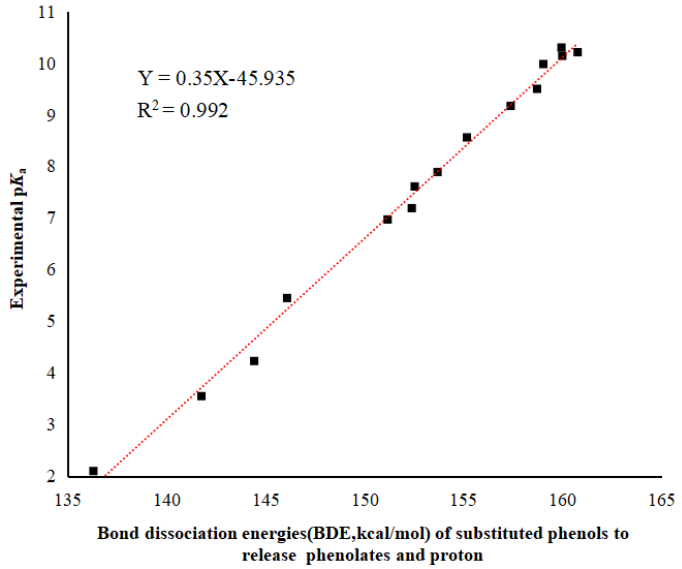


Figure S2. The correlation between the experimental pK_a values and BDE for 15 substituted phenols.

Table S3

Table S3. The pK_a values and BDEs of O-H bonds in 15 substituted phenols.

Substituted phenols	pK_a (exp.)	BDE (kcal/mol)	pK_a (calc.)
2-Cl-4,6-di-nitrophenol	2.1	136.3	1.9
2,6-di-Cl-4-nitrophenol	3.6	141.7	3.8
4-methyl-2,6-di-nitrophenol	4.2	144.4	4.7
2-Cl-4-nitrophenol	5.5	146.1	5.3
2,6-di-Cl-phenol	7.0	151.2	7.1
2,6-di-Cl-4-methylphenol	7.2	152.4	7.6
4-Formylphenol	7.6	152.5	7.6
2,4-di-Cl-phenol	7.9	153.7	8.0
2-Chlorophenol	8.6	155.2	8.5
4-Bromophenol	9.2	157.4	9.3
4-Acetaminophenol	9.5	158.7	9.8
Phenol	10.0	159.0	9.9
4-tBuphenol	10.1	160.0	10.3
4-Methoxyphenol	10.2	160.8	10.5
4-Ipropphenol	10.3	160.0	10.2

Table S4

Table S4. The pK_a values of O-H bond in tyrosine, tyrosine-amide, *N*-Acetyl-*L*-Tyrosine and their chlorinated products calculated by using LFER.

Organic Compounds	BDE(kcal/mol)	pK_a(calc.)
Tyr	160.7	10.2
2-Cl-Tyr	157.2	9.1
3-Cl-Tyr	156.7	8.9
5-Cl-Tyr	156.6	8.9
6-Cl-Tyr	157.1	9.0
N-Cl-Tyr	160.4	10.2
3, *N*-di-Cl-Tyr	156.7	8.9
5, *N*-di-Cl-Tyr	156.6	8.9
3,5-di-Cl-Tyr	152.7	7.5
N, *N*-di-Cl-Tyr	160.0	10.1
3, *N*, *N*-tri-Cl-Tyr	156.3	8.8
5, *N*, *N*-tri-Cl-Tyr	156.2	8.7
3,5, *N*-tri-Cl-Tyr	152.6	7.5
Tyr-Amide	159.6	10.0
3-Cl-Tyr-Amide	155.8	8.6
5-Cl-Tyr-Amide	155.8	8.6
N-Cl-Tyr-Amide	159.3	9.8
3, *N*-di-Cl-Tyr-Amide	155.4	8.5
5, *N*-di-Cl-Tyr-Amide	155.4	8.4
3,5-di-Cl-Tyr-Amide	152.4	7.4
N, *N*-di-Cl-Tyr-Amide	159.0	9.7
3, *N*, *N*-tri-Cl-Tyr-Amide	155.2	8.4
5, *N*, *N*-tri-Cl-Tyr-Amide	155.1	8.4
3,5, *N*-tri-Cl-Tyr-Amide	151.6	7.1
3,5, *N*,*N*-tetra-Cl-Tyr-Amide	151.1	7.0
N-Acetyl-*L*-Tyr	160.2	10.1
2-Cl-*N*-Acetyl-*L*-Tyr	157.5	9.2
3-Cl-*N*-Acetyl-*L*-Tyr	156.4	8.8
5-Cl-*N*-Acetyl-*L*-Tyr	156.4	8.8
6-Cl-*N*-Acetyl-*L*-Tyr	157.5	9.2
N-Cl-*N*-Acetyl-*L*-Tyr	160.0	10.1
3,*N*-di-Cl-*N*-Acetyl-*L*-Tyr	156.2	8.7
5,*N*-di-Cl-*N*-Acetyl-*L*-Tyr	156.0	8.7
3,5-di-Cl-*N*-Acetyl-*L*-Tyr	152.5	7.4
3,5,*N*-tri-Cl-*N*-Acetyl-*L*-Tyr	152.1	7.3

The correlation between the BDEs and experimental pK_a values of C-H bonds of organic compounds was established and illustrated in Figure S3 and Table S5. The squared correlation coefficient for the above system is $R^2 = 0.972$. The calculated pK_a and BDEs of tyrosine, *N*-Acetyl-*L*-Tyrosine and their chlorinated products were listed in Table S6.

Figure S3

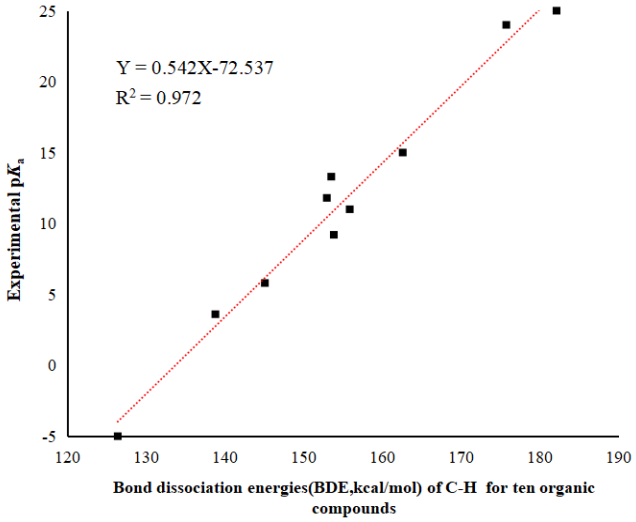


Figure S3. The correlation between the experimental pK_a values and BDEs of C-H for 10 organic compounds.

Table S5

Table S5 The pK_a values and BDEs of C-H bonds in 10 organic compounds.

Organic Compounds	pK_a (exp.)	BDE (kcal/mol)	pK_a (calc.)
$CH\text{-}(CN)_3$	-5.0	126.4	-4.0
$CH_2\text{-}(NO_2)_2$	3.6	138.8	2.7
$C_2H_5\text{-}O_2C\text{-}CH_2\text{-}NO$	5.8	145.1	6.1
HCN	9.2	153.8	10.8
$CH_3COCH2COOC_2H_5$	11.0	155.9	11.9
$CH_2\text{-}(CN)_2$	11.8	153.0	10.4
$CH_2\text{-}(COO\text{-}C_2H_5)_2$	13.3	153.5	10.7
$CH3\text{-}CO\text{-}CHCl_2$	15.0	162.6	15.6
CH3-COOH	24.0	175.7	22.7
CH3-CN	25.0	182.1	26.2

Table S6

Table S6. The pK_a values of C-H bond in tyrosine, *N*-Acetyl-*L*-Tyrosine and their chlorinated products calculated by using LFER.

Heterolytic reaction	Phenol		Phenolate	
	BDE (kcal/mol)	pK_a (calc.)	BDE (kcal/mol)	pK_a (calc.)
Tyr → C_2-Tyr$^-$ + H^+	206.0	39.1	212.6	42.7
Tyr → C_3-Tyr$^-$ + H^+	200.3	36.0	215.3	44.1
Tyr → C_5-Tyr$^-$ + H^+	202.8	37.4	214.8	43.9
Tyr → C_6-Tyr$^-$ + H^+	206.4	39.3	213.3	43.1
2-Cl-Tyr$^+$ → 2-Cl-Tyr + H^+	89.95	-23.8	99.0	-18.9
3-Cl-Tyr$^+$ → 3-Cl-Tyr + H^+	100.9	-17.9	133.2	0.4
5-Cl-Tyr$^+$ → 5-Cl-Tyr + H^+	99.5	-18.6	133.6	0.1
6-Cl-Tyr$^+$ → 6-Cl-Tyr + H^+	90.1	-23.7	98.3	-19.2
C_3-3,*N*-di-Cl-Tyr$^+$ → 3,*N*-di-Cl-Tyr$^-$ + H^+	100.2	-18.2	133.1	-0.4
C_5-5,*N*-di-Cl-Tyr$^+$ → 3,*N*-di-Cl-Tyr$^-$ + H^+	99.2	-18.8	133.8	0.0
C_3-3,5-di-Cl-Tyr$^+$ → 3,5-di-Cl-Tyr$^-$ + H^+	95.3	-20.9	129.4	-2.4
C_5-3,5-di-Cl-Tyr$^+$ → 3,5-di-Cl-Tyr$^-$ + H^+	94.7	-21.2	129.9	-2.1
C_3-3,*N*,*N*-tri-Cl-Tyr$^+$ → 3,*N*,*N*-tri-Cl-Tyr + H^+	98.8	-19.0	131.8	-1.1
C_5-5,*N*,*N*-tri-Cl-Tyr$^+$ → 5,*N*,*N*-tri-Cl-Tyr + H^+	98.9	-18.9	133.4	-0.2
C_3-3,5,*N*-tri-Cl-Tyr$^+$ → 3,5,*N*-tri-Cl-Tyr + H^+	94.4	-21.4	129.2	-2.5
C_5-3,5,*N*-tri-Cl-Tyr$^+$ → 3,5,*N*-tri-Cl-Tyr + H^+	93.7	-21.8	129.9	-2.2
3-Cl-*N*-Acetyl-*L*-Tyr$^+$ → Cl-*N*-Acetyl-*L*-Tyr + H^+	99.8	-18.4	132.5	-0.7
5-Cl-*N*-Acetyl-*L*-Tyr$^+$ → Cl-*N*-Acetyl-*L*-Tyr + H^+	99.6	-18.6	133.4	0.2
C_3-3,5-di-Cl-*N*-Acetyl-*L*-Tyr$^+$ → 3,5-di-Cl- *N*-Acetyl-*L*-Tyr + H^+	94.0	-21.6	128.6	-2.8
C_5-3,5-di-Cl- *N*-Acetyl-*L*-Tyr$^+$ → 3,5-di-Cl- *N*-Acetyl-*L*-Tyr + H^+	95.5	-20.8	129.9	-2.1
C_3-3,*N*-di-Cl-*N*-Acetyl-*L*-Tyr$^+$ → 3,*N*-di-Cl-*N*-Acetyl-*L*-Tyr + H^+	98.8	-19.0	131.8	-1.1
C_5-5,*N*-di-Cl-*N*-Acetyl-*L*-Tyr$^+$ → 5,*N*-di-Cl-*N*-Acetyl-*L*-Tyr + H^+	98.8	-19.0	132.9	-0.5
C_3-3,5,*N*-tri-Cl-*N*-Acetyl-*L*-Tyr$^+$ → 3,5,*N*-tri-Cl-*N*-Acetyl-*L*-Tyr + H^+	93.6	-21.8	127.9	-3.2
C_5-3,5,*N*-tri-Cl-*N*-Acetyl-*L*-Tyr$^+$ → 3,5,*N*-tri-Cl-*N*-Acetyl-*L*-Tyr + H^+	94.7	-21.2	129.1	-2.5

Table S7

Table S7. The activation free energies $\Delta G^{\neq}$ (at 298 K and 1 atm, in kcal/mol) for the *N*-chlorination of the *α*-amino group of valine assisted by 2 water molecules calculated at the DFT/aug-cc-pVTZ//DFT/6-31+G(d) level with the SMD solvent model.

B3LYP(D3BJ)	M05-2X(D3)	M06-2X(D3)
6.3	2.7	2.3

Table S8

Table S8. The activation free energies $\Delta G^{\neq}$ (at 298 K and 1 atm, in kcal/mol) for the *N*-chlorination of the *α*-amino group of valine assisted by 2−6 water molecules calculated at the B3LYP(D3BJ)/aug-cc-pVTZ//B3LYP(D3BJ)/6-31+G(d) level with the SMD solvent model.

	2w	3w	4w	5w	6w
Val	6.3	2.9	7.7	7.2	5.2

Table S9

Table S9. The activation free energies $\Delta G^{\neq}$ (at 298 K and 1 atm, in kcal/mol) for the *N*-chlorination of the *α*-amino group in the eight amino acid model compounds assisted by 5 water molecules calculated at the B3LYP(D3BJ)/aug-cc-pVTZ//B3LYP(D3BJ)/6-31+G(d) level with the SMD solvent model.

	Gly	Ala	Val	*N*-Cl-Val	Asp	ILu	Phe	Tyr
Exp.	7.1	7.3	7.2	13.8	7.3	7.4	6.1	7.6
Calc.	6.7	6.6	7.2	11.4	7.3	6.8	6.5	5.8

Figure S4

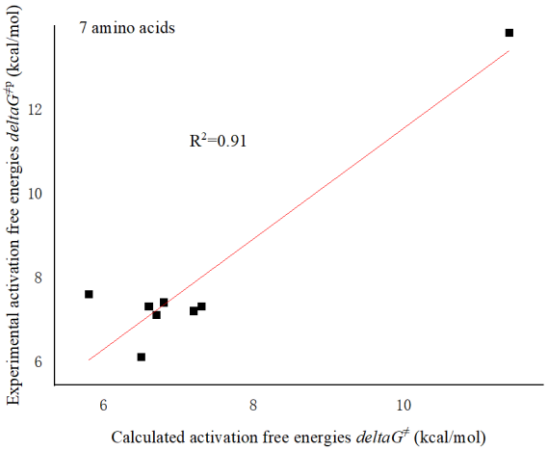
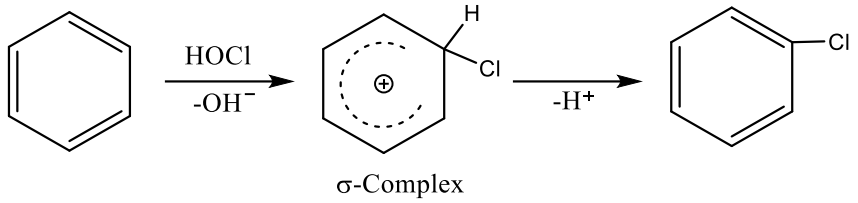


Figure S4. The estimated experimental $\Delta G^{\neq exp\text{-}est}$ for the above seven amino acids were established with the R^2 value of 0.91

Scheme S1



σ-Complex

Scheme S1 Reaction mechanism for the electrophilic substitution on the aromatic group (S_EAr)

Table S10

Table S10. The activation free energies $\Delta G^{\neq}$ (at 298 K and 1 atm, in kcal/mol) for the *C*-chlorination at the C2 site of phenolate and phenol assisted by 3 water molecules calculated at the DFT/aug-cc-pVTZ//DFT/6-31+G(d) level with the SMD solvent.

	M06-2X(D3)	M05(D3)	M05-2X(D3)	Exp.
Phenolate	8.8	5.8	7.4	11.5
Phenol	26.2	20.6	23.1	18.1

Table S11

Table S11. The activation free energies $\Delta G^{\neq}$ (at 298 K and 1 atm, in kcal/mol) calculated at the DFT/aug-cc-pVTZ//DFT/6-31+G(d) level with the SMD solvent for the *C*-chlorination at the C2 site of phenolate and phenol assisted by 2-6 water molecules.

No. of water molecules	Phenolate	Phenol
	M06-2X(D3)	M05(D3)
2w	9.4	17.2
3w	8.8	20.6
4w	9.5	20.7
5w	8.4	17.7
6w	10.1	19.5

Table S12

Table S12. The activation free energies $\Delta G^{\neq}$ (at 298 K and 1 atm, in kcal/mol) calculated at the DFT/aug-cc-pVTZ//DFT/6-31+G(d) level with the SMD solvent for the *C*-chlorination at the C2 site of the phenolate and phenol moieties in the six phenolic model compounds assisted by respective 6 and 5 water molecules.

Compounds	Phenolate		Phenol	
	Exp.	M06-2X(D3)	Exp.	M05(D3)
unsubstituted	11.5	10.1	18.1	17.7
4-methyl	11.4	9.6	18.9	18.7
4-chloro	12.9	11.5	19.8	22.0
4-cyano	14.9	12.0	19.6	20.9
3-hydroxy-4,6-dichloro	11.3	10.8	15.5	18.2
3-hydroxy-5-methyl	8.3	5.7	13.2	11.1

Figure S5

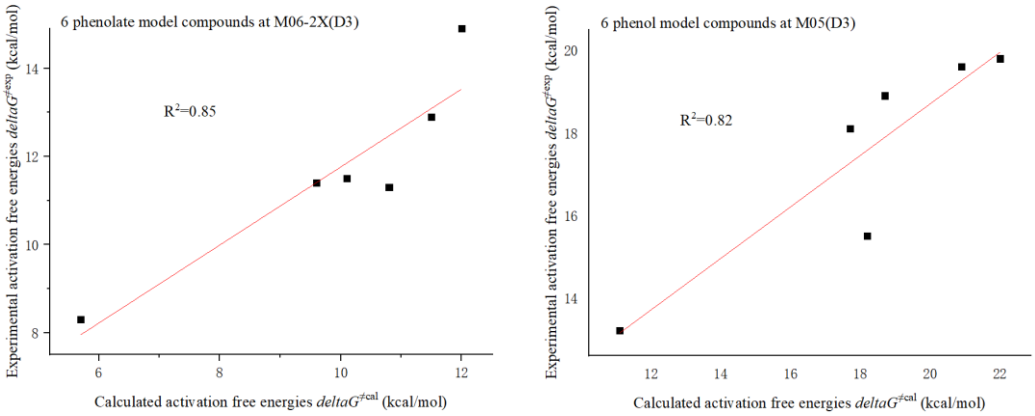


Figure S5 Linear relationship between the calculated $\Delta G^{\neq cal}$ values and the experimental $\Delta G^{\neq exp}$ values for 6 phenolic compounds

Figure S6

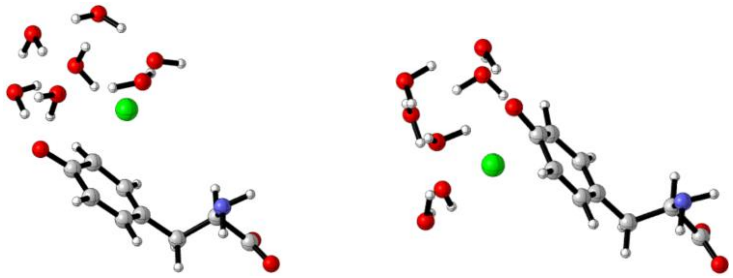


Figure S6 Two ways for HOCl attacking the phenol ring moiety in Tyr or its dipeptides

Table S13

Table S13. The $k_{obs\text{-}est}$ (M^{-1} s^{-1}) and reaction energies ΔH (at 298 K and 1 atm, in kcal/mol) for the chlorination reactions of Tyr.

Reactions	$k_{obs\text{-}est}$	ΔH
(1) Tyr → *N*-Cl-Tyr	1.7×10^{8}	-17.0
(2) Tyr → 2-Cl-Tyr	2.3×10^{-3}	-45.7
(3) Tyr → 3-Cl-Tyr	118.6	-50.4
(4) Tyr → 5-Cl-Tyr	116.9	-46.6
(5) Tyr → 6-Cl-Tyr	7.4×10^{-3}	-40.0
(6) *N*-Cl-Tyr → *N*,*N*-di-Cl-Tyr	5.9×10^{3}	-17.8
(7) *N*-Cl-Tyr → 3,*N*-di-Cl-Tyr	44.4	-52.3
(8) *N*-Cl-Tyr → 5,*N*-di-Cl-Tyr	72.4	-48.9
(9) 3-Cl-Tyr → 3,*N*-di-Cl-Tyr	8.2×10^{7}	-17.1
(10) 3-Cl-Tyr → 3,5-di-Cl-Tyr	185.2	-44.8
(11) 5-Cl-Tyr → 5,*N*-di-Cl-Tyr	5.0×10^{7}	-16.1
(12) 5-Cl-Tyr → 3,5-di-Cl-Tyr	127.3	-52.8
(13) *N*,*N*-di-Cl-Tyr → 3,*N*,*N*-tri-Cl-Tyr	89.8	-52.3
(14) *N*,*N*-di-Cl-Tyr → 5,*N*,*N*-tri-Cl-Tyr	92.9	-49.6
(15) 3,*N*-di-Cl-Tyr → 3,*N*,*N*-tri-Cl-Tyr	192.2	-17.8
(16) 3,*N*-di-Cl-Tyr → 3,5,*N*-tri-Cl-Tyr	112.0	-46.9
(17) 5,*N*-di-Cl-Tyr → 5,*N*,*N*-tri-Cl-Tyr	125.4	-20.2
(18) 5,*N*-di-Cl-Tyr → 3,5,*N*-tri-Cl-Tyr	363.1	-43.2
(19) 3,5-di-Cl-Tyr → 3,5,*N*-tri-Cl-Tyr	1.8×10^{6}	-17.0
(20) 3,5,*N*-tri-Cl-Tyr → 3,5,*N*,*N*-tetra-Cl-Tyr	238.0	-19.1
(21) 5,*N*,*N*-tri-Cl-Tyr → 3,5,*N*,*N*-tetra-Cl-Tyr	125.2	-53.1
(22) 3,*N*,*N*-tri-Cl-Tyr → 3,5,*N*,*N*-tetra-Cl-Tyr	1.3×10^{3}	-50.6

Figure S7

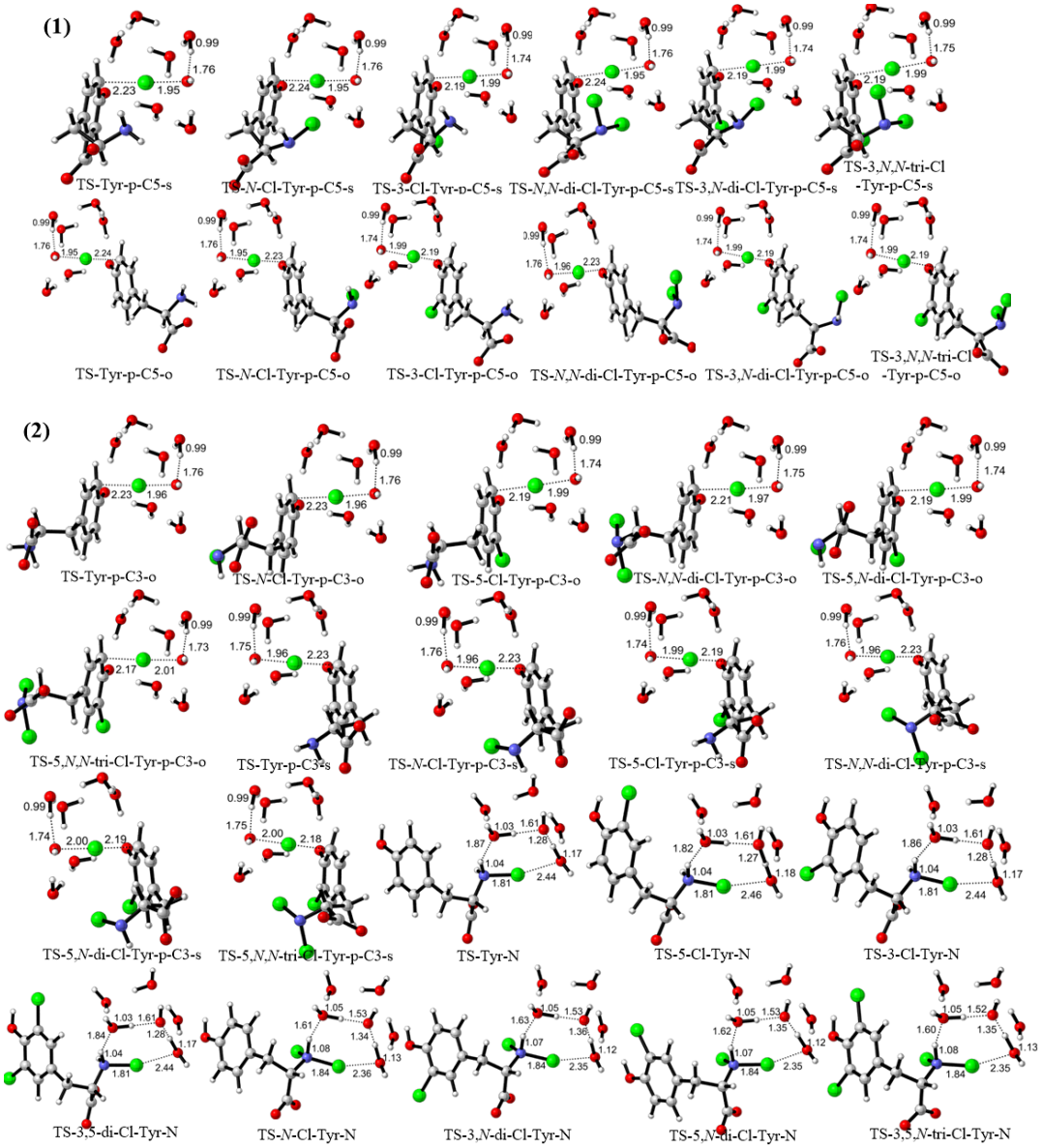


Figure S7. Structures of transition states and important geometries for the chlorination of Tyr compounds (Figure S7-(1) shows the reactions of C5 site, Figure S7-(2) shows the reactions of C3 and N sites, p represents phenolate, s represents same-side, o represents opposite-side).

Table S14

Table S14. The $k_{obs\text{-}est}$ (M^{-1} s^{-1}) and reaction energies ΔH (at 298 K and 1 atm, in kcal/mol) for the chlorination reactions of Tyr-Am and NacTyr.

Reactions	$k_{obs\text{-}est}$	ΔH
(1) Tyr-Am → *N*-Cl-Tyr-Am	5.2×10^7	-17.7
(2) Tyr-Am → 3-Cl-Tyr-Am	96.7	-46.1
(3) Tyr-Am → 5-Cl-Tyr-Am	117.0	-44.2
(4) *N*-Cl-Tyr-Am → *N*,*N*-di-Cl-Tyr-Am	1.1×10^3	-19.9
(5) *N*-Cl-Tyr-Am → 3,*N*-di-Cl-Tyr-Am	250.0	-44.4
(6) *N*-Cl-Tyr-Am → 5,*N*-di-Cl-Tyr-Am	223.3	-38.3
(7) 3-Cl-Tyr-Am → 3,*N*-di-Cl-Tyr-Am	5.0×10^7	-17.8
(8) 3-Cl-Tyr-Am → 3,5-di-Cl-Tyr-Am	185.7	-43.1
(9) 5-Cl-Tyr-Am → 5,*N*-di-Cl-Tyr-Am	2.1×10^7	-17.5
(10) 5-Cl-Tyr-Am → 3,5-di-Cl-Tyr-Am	34.3	-42.9
(11) *N*,*N*-di-Cl-Tyr-Am → 3,*N*,*N*-tri-Cl-Tyr-Am	69.8	-44.0
(12) *N*,*N*-di-Cl-Tyr-Am → 5,*N*,*N*-tri-Cl-Tyr-Am	117.1	-37.3
(13) 3,*N*-di-Cl-Tyr-Am → 3,*N*,*N*-tri-Cl-Tyr-Am	28.1	-18.4
(14) 3,*N*-di-Cl-Tyr-Am → 3,5,*N*-tri-Cl-Tyr-Am	51.6	-37.6
(15) 5,*N*-di-Cl-Tyr-Am → 5,*N*,*N*-tri-Cl-Tyr-Am	22.7	-16.1
(16) 5,*N*-di-Cl-Tyr-Am → 3,5,*N*-tri-Cl-Tyr-Am	38.3	-43.3
(17) 3,5-di-Cl-Tyr-Am → 3,5,*N*-tri-Cl-Tyr-Am	8.6×10^6	-17.6
(18) 3,5,*N*-tri-Cl-Tyr-Am → 3,5,*N*,*N*-tetra-Cl-Tyr-Am	53.3	-16.1
(19) 5,*N*,*N*-tri-Cl-Tyr-Am → 3,5,*N*,*N*-tetra-Cl-Tyr-Am	53.7	-44.8
(20) 3,*N*,*N*-tri-Cl-Tyr-Am → 3,5,*N*,*N*-tetra-Cl-Tyr-Am	1.1×10^3	-36.6
(21) NacTyr → 3-Cl-NacTyr	7.7	-55.8
(22) NacTyr → 5-Cl-NacTyr	343.3	-42.6
(23) 3-Cl-NacTyr → 3,5-di-Cl-NacTyr	134.6	-40.5
(24) 5-Cl-NacTyr → 3,5-di-Cl-NacTyr	1.4	-53.4

Figure S8

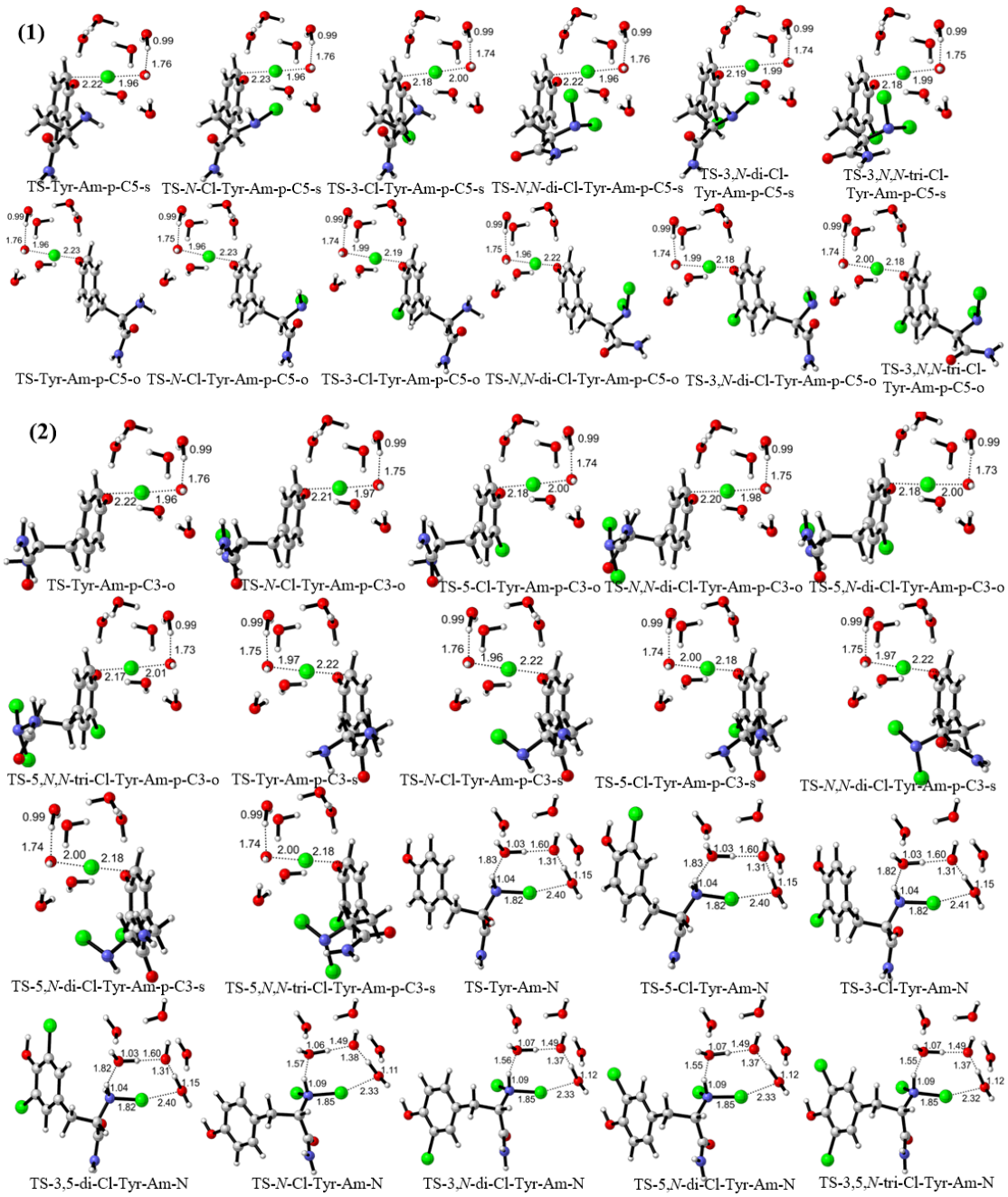


Figure S8. Structures of transition states and important geometries for the chlorination of Tyr-Am compounds (Figure S8-(1) shows the reactions of C5 site, Figure S8-(2) shows the reactions of C3 and N sites, p represents phenolate, s represents same-side, o represents opposite-side).

Figure S9

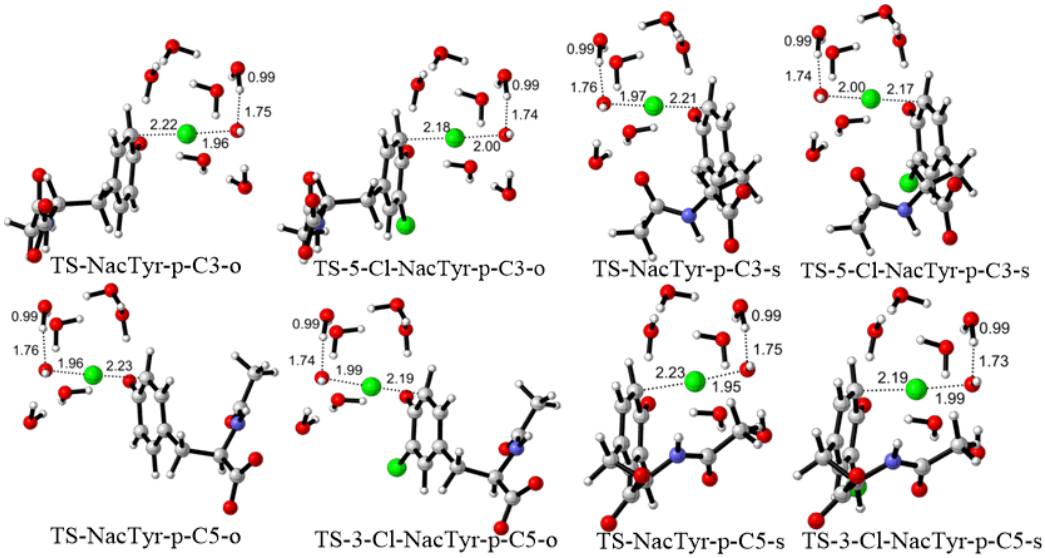


Figure S9. Structures of transition states and important geometries for the chlorination of NacTyr compounds (p represents phenolate, s represents same-side, o represents opposite-side).

Table S15

Table S15 NPA charges, FED^2 (HOMO) and BDEs of N, C3, and C5 sites in Tyr, Tyr-Am and NacTyr compounds

Compounds	NPA	FED^2	BDEs
Tyr-N	-0.940	2.000	151.4
N-Cl-Tyr-N	-0.670	5.860	136.8
3-Cl-Tyr-N	-0.940	3.360	150.9
5-Cl-Tyr-N	-0.940	7.370	150.7
3,*N*-di-Cl-Tyr-N	-0.670	7.080	136.0
5,*N*-di-Cl-Tyr-N	-0.660	5.700	136.0
3,5-di-Cl-Tyr-N	-0.940	18.100	150.4
3,5,*N*-tri-Cl-Tyr-N	-0.670	10.230	136.5
TA-N	-0.930	0.200	145.6
N-Cl-TA-N	-0.680	3.350	127.2
3-Cl-TA-N	-0.930	0.200	145.1
5-Cl-TA-N	-0.930	0.140	144.9
3,*N*-di-Cl-TA-N	-0.680	3.730	126.8
5,*N*-di-Cl-TA-N	-0.680	4.650	126.7
3,5-di-Cl-TA-N	-0.930	0.180	143.8
3,5,*N*-tri-Cl-TA-N	-0.680	5.970	126.1
Tyr-C3	-0.310	7.489	156.7
N-Cl-Tyr-C3	-0.310	9.596	156.7
5-Cl-Tyr-C3	-0.291	3.155	152.7
N,*N*-di-Cl-Tyr-C3	-0.310	8.067	156.3

5,*N*-di-Cl-Tyr-C3	-0.291	6.291	152.6
5,*N*,*N*-tri-Cl-Tyr-C3	-0.291	5.341	152.1
TA-C3	-0.310	10.686	155.8
N-Cl-TA-C3	-0.310	8.834	155.4
5-Cl-TA-C3	-0.292	7.027	152.4
N,*N*-di-Cl-TA-C3	-0.310	9.183	155.2
5,*N*-di-Cl-TA-C3	-0.293	5.819	151.6
5,*N*,*N*-tri-Cl-TA-C3	-0.293	6.261	151.1
NacTyr-C3	-0.310	7.788	156.4
5-Cl-NacTyr-C3	-0.291	4.625	152.5
Tyr-C5	-0.330	9.807	156.6
N-Cl-Tyr-C5	-0.330	7.599	156.6
3-Cl-Tyr-C5	-0.311	6.475	152.7
N,*N*-di-Cl-Tyr-C5	-0.320	8.788	156.2
3,*N*-di-Cl-Tyr-C5	-0.311	4.647	152.6
3,*N*,*N*-tri-Cl-Tyr-C5	-0.311	5.872	152.1
TA-C5	-0.320	10.846	155.8
N-Cl-TA-C5	-0.320	9.835	155.4
3-Cl-TA-C5	-0.311	6.888	152.4
N,*N*-di-Cl-TA-C5	-0.320	10.105	155.1
3,*N*-di-Cl-TA-C5	-0.302	6.646	151.6
3,*N*,*N*-tri-Cl-TA-C5	-0.312	6.897	151.1
NacTyr-C5	-0.330	9.877	156.4
3-Cl-NacTyr-C5	-0.311	6.936	152.5

Table S16

Table S16 The R^2 values of the $lgk_{obs\text{-}est}$ depending on NPA charges, FED^2 (HOMO), and BDEs for 44 reactive sites in Tyr and tyrosyl dipeptides

	NPA	FED^2	BDEs	NPA+FED^2	NPA+BDEs	FED^2+BDEs
44 sites	0.688	0.159	0.006	0.693	0.905	0.165

Standard orientation of TS-Tyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-Tyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -341.60 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.607226	1.188364	-1.464981
2	8	0	2.539894	0.690281	2.467511
3	1	0	2.031076	1.242395	3.086412
4	17	0	1.349259	0.543772	0.921336
5	8	0	3.205774	0.746369	-2.524307
6	1	0	2.993972	1.553129	-2.004489
7	1	0	2.532943	0.070659	-2.259955
8	8	0	4.496898	1.834352	0.941394
9	1	0	3.831777	1.481070	1.579370
10	1	0	4.753738	1.053275	0.397678
11	8	0	2.884201	3.038129	-0.936529
12	1	0	3.445307	2.658407	-0.214857
13	1	0	1.975648	2.998784	-0.597488
14	6	0	0.075255	0.422274	-0.904363
15	6	0	-0.449651	-1.956909	-0.642159
16	6	0	-2.067311	-0.247771	0.072822
17	6	0	-1.641334	-1.606846	-0.062189
18	1	0	-0.163769	-2.999260	-0.756374
19	1	0	-2.301088	-2.390586	0.306409
20	1	0	-1.501604	1.779460	-0.285278
21	8	0	1.513398	-1.263776	-1.779557
22	6	0	0.432006	-0.953000	-1.165435
23	6	0	-1.219060	0.731567	-0.372848
24	8	0	2.598015	-2.077946	2.674578
25	1	0	2.565917	-1.097248	2.728129
26	1	0	2.807941	-2.256776	1.734480
27	8	0	3.297154	-2.390386	-0.041236
28	1	0	3.566697	-3.269454	-0.351178
29	1	0	2.615547	-2.076363	-0.685173
30	8	0	5.057180	-0.305390	-0.746843

31	1	0	4.546367	-1.073820	-0.412481
32	1	0	4.485538	0.063843	-1.460737
33	6	0	-3.422812	0.076816	0.647149
34	1	0	-3.724937	-0.707247	1.355144
35	1	0	-3.372948	1.019313	1.202187
36	6	0	-4.522126	0.205224	-0.423274
37	1	0	-4.220294	0.985666	-1.130746
38	7	0	-4.661516	-1.049553	-1.156585
39	1	0	-4.922688	-1.777997	-0.490431
40	1	0	-5.456755	-0.968314	-1.789457
41	6	0	-5.803270	0.696528	0.278827
42	8	0	-6.683539	-0.154114	0.585046
43	8	0	-5.870550	1.934749	0.531944

Standard orientation of TS-*N*-Cl-Tyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*-Cl-Tyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -343.80 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.810774	0.192113	-1.769447
2	8	0	2.910151	1.909218	1.705753
3	1	0	2.388351	2.684027	1.978243
4	17	0	1.671719	0.929290	0.547240
5	8	0	3.364760	-0.670476	-2.586315
6	1	0	3.112466	0.279294	-2.563980
7	1	0	2.745497	-1.128633	-1.965714
8	8	0	4.708818	2.179305	-0.334043
9	1	0	4.099004	2.185608	0.442254
10	1	0	5.006381	1.241898	-0.399655
11	8	0	2.941174	2.102065	-2.449667
12	1	0	3.553808	2.196527	-1.678244
13	1	0	2.051495	2.226895	-2.082057
14	6	0	0.336798	-0.168994	-0.859016
15	6	0	-0.075181	-2.060791	0.642364
16	6	0	-1.736653	-0.259593	0.438507
17	6	0	-1.259391	-1.478554	1.013226
18	1	0	-1.876265	-1.967682	1.765475
19	1	0	-1.266546	1.287409	-0.958573
20	8	0	1.814953	-2.035822	-0.792767
21	6	0	0.744437	-1.467833	-0.375514
22	6	0	-0.947987	0.352681	-0.499268
23	8	0	3.128730	-0.319508	3.341539
24	1	0	3.043337	0.539293	2.871366
25	1	0	3.310091	-0.962352	2.624940
26	8	0	3.742017	-1.985571	1.152785
27	1	0	4.082990	-2.881100	1.305505
28	1	0	3.019937	-2.084292	0.485180
29	8	0	5.339890	-0.512641	-0.651570
30	1	0	4.892364	-0.997505	0.074608

31	1	0	4.719659	-0.608879	-1.412687
32	6	0	-3.059734	0.333835	0.869121
33	1	0	-3.511253	-0.277127	1.660594
34	1	0	-2.869457	1.322466	1.305038
35	6	0	-4.101534	0.515424	-0.259849
36	1	0	-3.598607	0.766082	-1.197412
37	7	0	-4.989929	-0.625759	-0.514349
38	6	0	-5.019211	1.690580	0.132637
39	8	0	-6.031896	1.421396	0.832866
40	8	0	-4.652394	2.837951	-0.232380
41	17	0	-4.081617	-2.103104	-0.830974
42	1	0	0.247497	-3.004104	1.075079
43	1	0	-5.482626	-0.822641	0.360564

Standard orientation of TS-5-Cl-Tyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-5-Cl-Tyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -353.55 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.614349	-1.256489	-1.590448
2	8	0	-2.569933	-1.301538	2.386525
3	1	0	-2.071107	-1.941743	2.922270
4	17	0	-1.348341	-0.964773	0.851916
5	8	0	-3.207312	-0.681866	-2.609580
6	1	0	-2.993490	-1.553342	-2.207050
7	1	0	-2.545701	-0.050519	-2.242248
8	8	0	-4.479781	-2.259739	0.699047
9	1	0	-3.823187	-1.973510	1.380960
10	1	0	-4.759034	-1.423673	0.258753
11	8	0	-2.862294	-3.152718	-1.337902
12	1	0	-3.421774	-2.885897	-0.565749
13	1	0	-1.952240	-3.156481	-1.000841
14	6	0	-0.086981	-0.600739	-0.900927
15	6	0	0.470054	1.694134	-0.289902
16	6	0	2.068469	-0.106594	0.145002
17	6	0	1.659123	1.262222	0.225684
18	1	0	2.320390	1.978071	0.709493
19	1	0	1.481122	-2.050721	-0.508604
20	8	0	-1.498269	1.209321	-1.535502
21	6	0	-0.436563	0.803959	-0.975420
22	6	0	1.210528	-0.999345	-0.435029
23	8	0	-2.520082	1.422612	2.912240
24	1	0	-2.514451	0.440993	2.852978
25	1	0	-2.789056	1.709861	2.014986
26	8	0	-3.386115	2.050977	0.300580
27	1	0	-3.648691	2.973215	0.150182
28	1	0	-2.674966	1.867261	-0.355841
29	8	0	-5.100865	0.060843	-0.714895
30	1	0	-4.605434	0.787496	-0.280014

31	1	0	-4.523255	-0.195189	-1.471264
32	6	0	3.428056	-0.515019	0.650706
33	1	0	3.730109	0.142349	1.477394
34	1	0	3.383998	-1.536813	1.039508
35	6	0	4.515590	-0.455111	-0.437104
36	1	0	4.222168	-1.131795	-1.248038
37	7	0	4.610825	0.896313	-0.979832
38	1	0	4.851991	1.529078	-0.215417
39	1	0	5.405735	0.933478	-1.617087
40	6	0	5.820499	-1.012761	0.167060
41	8	0	6.732109	-0.201102	0.485514
42	8	0	5.876460	-2.266859	0.327180
43	17	0	0.024896	3.379847	-0.196101

Standard orientation of TS-*N*,*N*-di-Cl-Tyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*,*N*-di-Cl-Tyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -353.38 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.190487	0.098388	-1.782482
2	8	0	3.451472	2.132099	1.418012
3	1	0	3.023961	2.998646	1.530456
4	17	0	2.111068	1.110397	0.392704
5	8	0	3.668568	-1.181844	-2.393417
6	1	0	3.544730	-0.217005	-2.534509
7	1	0	2.986128	-1.446783	-1.728779
8	8	0	5.302330	1.803626	-0.557086
9	1	0	4.682334	2.017765	0.181586
10	1	0	5.479369	0.839371	-0.457160
11	8	0	3.593134	1.605100	-2.704781
12	1	0	4.190819	1.747369	-1.928489
13	1	0	2.714403	1.885320	-2.402711
14	6	0	0.686020	-0.055445	-0.830589
15	6	0	0.078648	-1.629546	0.950369
16	6	0	-1.392874	0.266455	0.418716
17	6	0	-1.039697	-0.877889	1.200236
18	1	0	-1.694858	-1.165112	2.020592
19	1	0	-0.769520	1.511680	-1.199874
20	8	0	1.952559	-2.035716	-0.444376
21	6	0	0.950949	-1.300560	-0.140517
22	6	0	-0.540771	0.642994	-0.584221
23	8	0	3.382047	0.187280	3.390264
24	1	0	3.403175	0.963082	2.786549
25	1	0	3.497470	-0.580998	2.793102
26	8	0	3.830803	-1.899771	1.548380
27	1	0	4.022663	-2.779796	1.909338
28	1	0	3.114903	-2.033694	0.881227
29	8	0	5.616214	-0.961278	-0.429768
30	1	0	5.108108	-1.272858	0.349297

31	1	0	4.998780	-1.103278	-1.185628
32	6	0	-2.682179	1.007680	0.678802
33	1	0	-3.067520	0.757639	1.673218
34	1	0	-2.493250	2.084670	0.674653
35	6	0	-3.791315	0.788065	-0.366488
36	1	0	-3.426085	1.107954	-1.348458
37	7	0	-4.277259	-0.597783	-0.608620
38	6	0	-5.010557	1.690226	-0.033893
39	8	0	-6.133031	1.165886	0.156110
40	8	0	-4.745185	2.921417	0.010960
41	17	0	-3.129869	-1.508081	-1.600231
42	17	0	-4.497353	-1.473082	0.900275
43	1	0	0.308689	-2.511122	1.542818

Standard orientation of TS-5,*N*-di-Cl-Tyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-5,*N*-di-Cl-Tyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -357.88 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.752450	-0.940389	-1.685273
2	8	0	-2.885346	-1.747720	2.111941
3	1	0	-2.365666	-2.425827	2.576695
4	17	0	-1.613306	-1.091896	0.725972
5	8	0	-3.314623	-0.348817	-2.736483
6	1	0	-3.066706	-1.259399	-2.459426
7	1	0	-2.708055	0.253501	-2.246897
8	8	0	-4.658215	-2.504258	0.188419
9	1	0	-4.049537	-2.305203	0.941848
10	1	0	-4.961458	-1.620705	-0.124930
11	8	0	-2.894541	-2.978291	-1.869614
12	1	0	-3.505596	-2.870417	-1.098077
13	1	0	-2.004238	-3.004701	-1.484079
14	6	0	-0.295900	-0.382807	-0.870258
15	6	0	0.101585	1.802817	0.136443
16	6	0	1.779652	0.036510	0.353916
17	6	0	1.288936	1.349729	0.636599
18	1	0	1.889869	2.010768	1.257599
19	1	0	1.328409	-1.801626	-0.634488
20	8	0	-1.773728	1.437815	-1.282489
21	6	0	-0.720698	0.996533	-0.735019
22	6	0	0.999726	-0.789350	-0.406698
23	8	0	-3.124187	0.839966	3.063335
24	1	0	-3.029022	-0.112285	2.834335
25	1	0	-3.334899	1.271155	2.209498
26	8	0	-3.804512	1.904497	0.536386
27	1	0	-4.126401	2.819871	0.513549
28	1	0	-3.053427	1.868618	-0.099813
29	8	0	-5.331516	-0.010053	-0.859462
30	1	0	-4.911379	0.665698	-0.285858

31	1	0	-4.698528	-0.107144	-1.608813
32	6	0	3.119399	-0.409351	0.895427
33	1	0	3.542609	0.361496	1.550928
34	1	0	2.960375	-1.300459	1.514998
35	6	0	4.171956	-0.772692	-0.177557
36	1	0	3.688281	-1.262576	-1.026574
37	7	0	4.988090	0.332687	-0.695311
38	1	0	5.461865	0.756717	0.106396
39	6	0	5.167576	-1.762379	0.461731
40	8	0	6.128604	-1.266896	1.109373
41	8	0	4.913631	-2.987768	0.329346
42	17	0	-0.439157	3.427221	0.477290
43	17	0	3.997251	1.638336	-1.343141

Standard orientation of TS-5,*N*,*N*-tri-Cl-Tyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-5,*N*,*N*-tri-Cl-Tyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -367.37 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.134692	-1.154999	1.562506
2	8	0	3.456442	-1.530972	-2.197495
3	1	0	3.033633	-2.240460	-2.710478
4	17	0	2.066743	-1.094333	-0.818387
5	8	0	3.594250	-0.318399	2.733499
6	1	0	3.463836	-1.237090	2.407142
7	1	0	2.935755	0.230551	2.249131
8	8	0	5.260535	-2.160696	-0.266248
9	1	0	4.648171	-1.997128	-1.026229
10	1	0	5.449365	-1.265071	0.098248
11	8	0	3.507711	-2.922080	1.710671
12	1	0	4.127788	-2.706720	0.969280
13	1	0	2.639201	-3.018716	1.288536
14	6	0	0.645831	-0.613569	0.755012
15	6	0	0.038081	1.562868	-0.169596
16	6	0	-1.442144	-0.356999	-0.490610
17	6	0	-1.082111	1.008521	-0.718963
18	1	0	-1.725859	1.625300	-1.341887
19	1	0	-0.821244	-2.180571	0.427519
20	8	0	1.894234	1.340178	1.301350
21	6	0	0.915302	0.812949	0.699466
22	6	0	-0.589446	-1.133592	0.241860
23	8	0	3.398223	1.108741	-3.019449
24	1	0	3.410569	0.142504	-2.831902
25	1	0	3.544789	1.523411	-2.144417
26	8	0	3.911590	2.115300	-0.430700
27	1	0	4.122028	3.059552	-0.352389
28	1	0	3.151230	1.961458	0.175271
29	8	0	5.611281	0.332236	0.932059
30	1	0	5.128977	0.982685	0.378133

31	1	0	4.975681	0.125235	1.655937
32	6	0	-2.753315	-0.891904	-1.012651
33	1	0	-3.128272	-0.257941	-1.823366
34	1	0	-2.597263	-1.888542	-1.432987
35	6	0	-3.851122	-1.066077	0.053014
36	1	0	-3.493644	-1.760108	0.822052
37	7	0	-4.281483	0.125144	0.832109
38	6	0	-5.108859	-1.726120	-0.579554
39	8	0	-6.225941	-1.171618	-0.454843
40	8	0	-4.878488	-2.813209	-1.172739
41	17	0	-3.089520	0.550760	2.066443
42	17	0	-4.507782	1.522532	-0.210101
43	17	0	0.418732	3.242707	-0.446871

Standard orientation of TS-Tyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-Tyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -336.26 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.044323	-0.872455	-2.029346
2	8	0	1.619151	2.413311	0.862419
3	1	0	0.962796	3.091620	0.625489
4	17	0	0.975074	0.829201	-0.083149
5	8	0	3.808889	-1.351399	-1.665785
6	1	0	3.473924	-0.538790	-2.105758
7	1	0	3.060476	-1.686648	-1.112772
8	8	0	3.991944	2.343260	-0.494905
9	1	0	3.149641	2.487285	-0.001116
10	1	0	4.380125	1.536902	-0.082075
11	8	0	3.089819	1.119648	-2.792288
12	1	0	3.381001	1.618639	-1.988774
13	1	0	2.120074	1.149201	-2.768517
14	6	0	0.325847	-0.978568	-1.219202
15	6	0	-0.383547	-2.241912	0.756731
16	6	0	-2.043186	-1.047335	-0.610131
17	6	0	-1.673157	-1.843887	0.520311
18	1	0	-0.135649	-2.872653	1.606458
19	1	0	-2.456239	-2.154944	1.210779
20	1	0	-1.287899	-0.059128	-2.343442
21	8	0	1.871366	-2.302397	0.019966
22	6	0	0.671621	-1.882597	-0.148537
23	6	0	-1.049897	-0.664144	-1.470553
24	8	0	1.417965	1.026690	3.258540
25	1	0	1.431345	1.625073	2.479277
26	1	0	1.910419	0.236640	2.953218
27	8	0	2.965742	-1.091212	2.221357
28	1	0	3.281326	-1.760249	2.849406
29	1	0	2.541995	-1.595092	1.484036
30	8	0	4.957554	-0.068345	0.508879

31	1	0	4.329666	-0.345653	1.210122
32	1	0	4.654826	-0.567704	-0.285747
33	6	0	-3.485387	-0.659552	-0.807431
34	1	0	-3.605362	-0.180902	-1.788593
35	1	0	-4.115327	-1.556574	-0.800289
36	6	0	-4.012295	0.302987	0.272041
37	1	0	-3.876506	-0.166215	1.253245
38	7	0	-3.250848	1.547770	0.252382
39	1	0	-3.381688	1.982418	-0.662238
40	1	0	-3.674345	2.195491	0.916122
41	6	0	-5.531222	0.462579	0.060403
42	8	0	-5.957655	1.527891	-0.464199
43	8	0	-6.255014	-0.515258	0.409214

Standard orientation of TS-*N*-Cl-Tyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*-Cl-Tyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -340.89 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.303640	-1.228924	-1.922106
2	8	0	1.902757	2.424353	0.488670
3	1	0	1.274916	3.072936	0.124698
4	17	0	1.248250	0.732479	-0.236313
5	8	0	4.064707	-1.694113	-1.430404
6	1	0	3.756002	-0.943322	-1.984223
7	1	0	3.296364	-1.938612	-0.856147
8	8	0	4.310517	2.107443	-0.769046
9	1	0	3.459693	2.342696	-0.327621
10	1	0	4.659255	1.356159	-0.234419
11	8	0	3.408799	0.613331	-2.900477
12	1	0	3.709399	1.204174	-2.165469
13	1	0	2.439460	0.658427	-2.876547
14	6	0	0.574621	-1.210491	-1.114404
15	6	0	-0.178213	-2.173308	1.007663
16	6	0	-1.802458	-1.160502	-0.534815
17	6	0	-1.460198	-1.799807	0.697661
18	1	0	-2.254997	-2.010628	1.412095
19	1	0	-1.009170	-0.428930	-2.375151
20	8	0	2.085035	-2.365678	0.323756
21	6	0	0.893559	-1.957767	0.078021
22	6	0	-0.792248	-0.913328	-1.424995
23	8	0	1.539505	1.368569	3.038591
24	1	0	1.609351	1.861232	2.191878
25	1	0	2.035386	0.540791	2.867962
26	8	0	3.099883	-0.893133	2.391993
27	1	0	3.403558	-1.469244	3.111291
28	1	0	2.702772	-1.495232	1.715392
29	8	0	5.158049	-0.158136	0.604332
30	1	0	4.501419	-0.327149	1.313579

31	1	0	4.873878	-0.754836	-0.127576
32	6	0	-3.246040	-0.834836	-0.836844
33	1	0	-3.326334	-0.380730	-1.832575
34	1	0	-3.808811	-1.777762	-0.870391
35	6	0	-3.969479	0.081859	0.175283
36	1	0	-3.695895	-0.185593	1.199216
37	7	0	-3.761138	1.528972	0.022389
38	6	0	-5.482804	-0.151779	-0.000226
39	8	0	-6.071233	0.532034	-0.880365
40	8	0	-6.004514	-1.048345	0.713779
41	17	0	-2.062731	1.958490	0.210315
42	1	0	0.048607	-2.683312	1.940314
43	1	0	-3.972832	1.767737	-0.949678

Standard orientation of TS-3-Cl-Tyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-3-Cl-Tyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -353.50 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.054844	-0.576402	-2.204830
2	8	0	-1.597996	-1.914174	1.996797
3	1	0	-0.928217	-2.604192	2.143117
4	17	0	-0.959510	-1.041368	0.325447
5	8	0	-3.817640	-0.033361	-2.141730
6	1	0	-3.459589	-0.948752	-2.105829
7	1	0	-3.085425	0.551560	-1.837559
8	8	0	-3.913058	-2.623781	0.750734
9	1	0	-3.080622	-2.460208	1.258576
10	1	0	-4.338531	-1.737032	0.690295
11	8	0	-3.036629	-2.707119	-1.858629
12	1	0	-3.299926	-2.736626	-0.904728
13	1	0	-2.066126	-2.714202	-1.855313
14	6	0	-0.335337	-0.093105	-1.547354
15	6	0	0.384272	1.973834	-0.470674
16	6	0	2.036456	0.275742	-1.085253
17	6	0	1.672769	1.523091	-0.483306
18	1	0	2.452384	2.133211	-0.030344
19	1	0	1.276849	-1.443320	-2.093034
20	8	0	-1.875264	1.682113	-1.161596
21	6	0	-0.692294	1.234436	-1.089621
22	6	0	1.043067	-0.486208	-1.632156
23	8	0	-1.371707	0.551512	3.250380
24	1	0	-1.387705	-0.369896	2.906551
25	1	0	-1.917327	1.049525	2.607239
26	8	0	-3.072147	1.749817	1.335785
27	1	0	-3.425226	2.631057	1.538181
28	1	0	-2.625042	1.837996	0.462678
29	8	0	-4.989258	-0.080523	0.372078
30	1	0	-4.390281	0.543312	0.835240

31	1	0	-4.685639	-0.040624	-0.565056
32	6	0	3.482297	-0.143252	-1.064155
33	1	0	3.626023	-1.004709	-1.729002
34	1	0	4.105872	0.674661	-1.442585
35	6	0	3.979242	-0.522451	0.342950
36	1	0	3.743214	0.299436	1.028411
37	7	0	3.289987	-1.720078	0.812750
38	6	0	5.516790	-0.627548	0.287575
39	8	0	6.041129	-1.773906	0.241431
40	8	0	6.152928	0.466110	0.262960
41	1	0	3.562176	-2.495521	0.207033
42	17	0	-0.004793	3.516214	0.247163
43	1	0	3.654809	-1.961838	1.733609

Standard orientation of TS-*N*,*N*-di-Cl-Tyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*,*N*-di-Cl-Tyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -338.35 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.517676	1.021975	-2.092871
2	8	0	-1.891015	-2.288412	0.812636
3	1	0	-1.163255	-2.899881	0.603005
4	17	0	-1.369877	-0.669550	-0.140226
5	8	0	-4.341351	1.292675	-1.708393
6	1	0	-3.961428	0.501309	-2.150256
7	1	0	-3.606364	1.685177	-1.174807
8	8	0	-4.274377	-2.389867	-0.522769
9	1	0	-3.417912	-2.483732	-0.042465
10	1	0	-4.699028	-1.605328	-0.103905
11	8	0	-3.477379	-1.130046	-2.841023
12	1	0	-3.728969	-1.639998	-2.031075
13	1	0	-2.507939	-1.087799	-2.820333
14	6	0	-0.820772	1.179074	-1.272298
15	6	0	-0.222846	2.504898	0.701242
16	6	0	1.528173	1.410498	-0.629079
17	6	0	1.093238	2.194529	0.485737
18	1	0	1.844993	2.565786	1.181656
19	1	0	0.867190	0.356984	-2.362449
20	8	0	-2.466551	2.403069	-0.059913
21	6	0	-1.239261	2.064560	-0.213545
22	6	0	0.576127	0.950392	-1.497862
23	8	0	-1.680639	-0.855719	3.184008
24	1	0	-1.690504	-1.462041	2.410656
25	1	0	-2.227284	-0.097539	2.890154
26	8	0	-3.402702	1.143728	2.184615
27	1	0	-3.788289	1.782732	2.804747
28	1	0	-3.048999	1.679347	1.432780
29	8	0	-5.346862	-0.036299	0.509567
30	1	0	-4.719512	0.282423	1.193499

31	1	0	-5.097039	0.475516	-0.295579
32	6	0	3.000380	1.162716	-0.840816
33	1	0	3.162107	0.698847	-1.819607
34	1	0	3.527997	2.122015	-0.854400
35	6	0	3.710150	0.330542	0.241192
36	1	0	3.597701	0.822462	1.213429
37	7	0	3.228630	-1.055716	0.493480
38	6	0	5.234898	0.293898	-0.046023
39	8	0	5.807738	-0.807490	-0.219925
40	8	0	5.781365	1.429681	-0.071605
41	17	0	1.752518	-1.027388	1.463569
42	17	0	2.868684	-1.896671	-1.010747
43	1	0	-0.525064	3.125917	1.540463

Standard orientation of TS-3,*N*-di-Cl-Tyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-3,*N*-di-Cl-Tyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -350.57 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.282315	-0.178142	-2.333714
2	8	0	-1.856869	-2.124214	1.618752
3	1	0	-1.223668	-2.862882	1.631053
4	17	0	-1.211040	-1.020179	0.096578
5	8	0	-4.054752	0.397475	-2.157754
6	1	0	-3.727792	-0.525532	-2.247357
7	1	0	-3.302706	0.913370	-1.783578
8	8	0	-4.228704	-2.556013	0.358079
9	1	0	-3.380626	-2.489065	0.862643
10	1	0	-4.622566	-1.655077	0.423484
11	8	0	-3.362992	-2.320117	-2.244175
12	1	0	-3.638493	-2.467832	-1.304723
13	1	0	-2.392868	-2.344184	-2.227800
14	6	0	-0.560231	0.195134	-1.610328
15	6	0	0.189121	2.080643	-0.259173
16	6	0	1.816093	0.456751	-1.094354
17	6	0	1.473068	1.620745	-0.337120
18	1	0	2.258675	2.163707	0.185109
19	1	0	1.030528	-1.098592	-2.322777
20	8	0	-2.076888	1.916632	-0.966170
21	6	0	-0.899096	1.447008	-0.965998
22	6	0	0.811354	-0.205790	-1.741421
23	8	0	-1.495300	0.120556	3.215763
24	1	0	-1.551181	-0.741881	2.746974
25	1	0	-2.037914	0.720140	2.662602
26	8	0	-3.206544	1.630020	1.547885
27	1	0	-3.525206	2.473861	1.906417
28	1	0	-2.785753	1.850061	0.684997
29	8	0	-5.207006	0.052498	0.345528
30	1	0	-4.575413	0.574095	0.885755

31	1	0	-4.906177	0.207290	-0.580318
32	6	0	3.263071	0.035111	-1.189788
33	1	0	3.345520	-0.859347	-1.819420
34	1	0	3.818196	0.835934	-1.696178
35	6	0	3.989640	-0.238567	0.146339
36	1	0	3.723388	0.516639	0.890588
37	7	0	3.782069	-1.559542	0.755606
38	1	0	4.013733	-2.260914	0.047887
39	6	0	5.502469	-0.132490	-0.134341
40	8	0	6.092653	-1.182014	-0.506230
41	8	0	6.020360	1.009649	-0.023151
42	17	0	-0.177887	3.521652	0.654889
43	17	0	2.082077	-1.852174	1.113709

Standard orientation of TS-3,*N*,*N*-tri-Cl-Tyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-3,*N*,*N*-tri-Cl-Tyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -350.92 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.467965	-0.187884	-2.364543
2	8	0	-1.743834	-2.077454	1.652102
3	1	0	-0.980187	-2.678735	1.700292
4	17	0	-1.275061	-0.947290	0.088678
5	8	0	-4.278225	0.070004	-2.150853
6	1	0	-3.834892	-0.803893	-2.234583
7	1	0	-3.589308	0.688213	-1.812974
8	8	0	-4.038075	-2.854954	0.402289
9	1	0	-3.200206	-2.690224	0.899305
10	1	0	-4.528294	-2.002574	0.469140
11	8	0	-3.256416	-2.538751	-2.220295
12	1	0	-3.487772	-2.709659	-1.273051
13	1	0	-2.289439	-2.456410	-2.232795
14	6	0	-0.782692	0.279581	-1.660659
15	6	0	-0.221507	2.278631	-0.378429
16	6	0	1.555701	0.804492	-1.179848
17	6	0	1.101026	1.952221	-0.456158
18	1	0	1.833955	2.583950	0.043225
19	1	0	0.929629	-0.862510	-2.352528
20	8	0	-2.464662	1.849806	-1.048812
21	6	0	-1.244094	1.508716	-1.051108
22	6	0	0.622416	0.018055	-1.792958
23	8	0	-1.618564	0.225635	3.196252
24	1	0	-1.585573	-0.642829	2.734929
25	1	0	-2.219995	0.759090	2.636554
26	8	0	-3.494668	1.497328	1.502332
27	1	0	-3.911371	2.306686	1.839229
28	1	0	-3.119849	1.738928	0.624399
29	8	0	-5.298410	-0.370019	0.392645
30	1	0	-4.723792	0.241578	0.900671

31	1	0	-5.050356	-0.198246	-0.545815
32	6	0	3.034962	0.528547	-1.271017
33	1	0	3.212858	-0.285783	-1.980957
34	1	0	3.542788	1.413551	-1.667981
35	6	0	3.746251	0.214290	0.056983
36	1	0	3.632165	1.059801	0.743185
37	7	0	3.269557	-0.950521	0.853235
38	6	0	5.269043	0.067554	-0.201946
39	8	0	5.837217	-1.024730	0.033980
40	8	0	5.816071	1.111056	-0.649374
41	17	0	-0.729381	3.702507	0.495011
42	17	0	1.806950	-0.525705	1.747858
43	17	0	2.890468	-2.325706	-0.176820

Standard orientation of TS-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -912.81 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.324863	-1.374401	-0.210725
2	1	0	4.650162	-2.196485	0.192449
3	8	0	4.159999	0.394071	1.480074
4	1	0	4.347745	1.191773	0.953460
5	1	0	4.264471	-0.555839	0.626231
6	8	0	1.612086	0.866329	1.971897
7	1	0	2.606332	0.663327	1.820813
8	1	0	1.554026	1.376338	2.796341
9	6	0	-1.847268	-1.333640	1.531392
10	1	0	-2.483418	-2.177786	1.813701
11	6	0	-0.726142	-1.920412	0.642075
12	6	0	-1.273156	-2.590889	-0.635713
13	8	0	-1.141083	-1.954757	-1.719887
14	8	0	-1.835428	-3.707884	-0.470277
15	1	0	-0.145645	-2.635650	1.226564
16	7	0	0.195848	-0.815398	0.243303
17	1	0	-0.189025	-0.354476	-0.592962
18	1	0	0.363415	-0.121855	1.000208
19	17	0	1.885533	-1.315064	-0.160427
20	8	0	4.047771	2.704260	-0.546842
21	1	0	3.060139	2.712597	-0.454175
22	1	0	4.264772	3.505229	-1.052799
23	8	0	1.311082	2.574672	-0.163506
24	1	0	1.356584	2.017000	0.656189
25	1	0	1.006475	3.446069	0.139624
26	8	0	4.609489	0.503818	-2.224699
27	1	0	4.567593	-0.251555	-1.592420
28	1	0	4.405013	1.289382	-1.665657
29	1	0	-1.380320	-0.951375	2.445474
30	6	0	-2.660641	-0.247362	0.864964

31	6	0	-2.295725	1.100583	0.986983
32	6	0	-3.776967	-0.561280	0.075014
33	6	0	-3.012269	2.108393	0.338621
34	1	0	-1.439516	1.373089	1.599840
35	6	0	-4.506877	0.432900	-0.575774
36	1	0	-4.081279	-1.599229	-0.032760
37	6	0	-4.119007	1.769518	-0.443357
38	1	0	-2.719564	3.150504	0.441760
39	1	0	-5.372861	0.182522	-1.181616
40	8	0	-4.870402	2.724716	-1.102969
41	1	0	-4.498782	3.606859	-0.925895

Standard orientation of TS-5-Cl-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-5-Cl-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -975.82 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.756241	0.860733	0.039071
2	1	0	5.246835	1.541327	-0.451067
3	8	0	4.122633	-0.969565	-1.464714
4	1	0	4.163029	-1.742566	-0.873137
5	1	0	4.470785	0.001236	-0.715739
6	8	0	1.519667	-0.933699	-1.843194
7	1	0	2.541886	-0.937060	-1.743934
8	1	0	1.307150	-1.446017	-2.640189
9	6	0	-1.379369	1.894659	-1.533857
10	1	0	-1.915803	2.806131	-1.813330
11	6	0	-0.155132	2.346586	-0.702112
12	6	0	-0.547934	3.176487	0.539675
13	8	0	-0.490290	2.594251	1.659876
14	8	0	-0.920427	4.359241	0.310407
15	1	0	0.516045	2.920063	-1.342642
16	7	0	0.580060	1.129525	-0.248439
17	1	0	0.156515	0.802492	0.631446
18	1	0	0.596949	0.362668	-0.953519
19	17	0	2.346027	1.335517	0.067614
20	8	0	3.580063	-3.043444	0.739094
21	1	0	2.611554	-2.837474	0.684120
22	1	0	3.641186	-3.834484	1.300600
23	8	0	0.925715	-2.314579	0.457153
24	1	0	1.054087	-1.877844	-0.424228
25	1	0	0.354726	-3.080617	0.280995
26	8	0	4.730149	-0.903125	2.174641
27	1	0	4.823329	-0.206108	1.483405
28	1	0	4.318444	-1.659639	1.695381
29	1	0	-1.006788	1.431969	-2.453192
30	6	0	-2.292985	0.936796	-0.803128

31	6	0	-2.137305	-0.444499	-0.961332
32	6	0	-3.278368	1.400071	0.082127
33	6	0	-2.936862	-1.330124	-0.242250
34	1	0	-1.391295	-0.836986	-1.645785
35	6	0	-4.079198	0.513408	0.794808
36	1	0	-3.420606	2.468710	0.215601
37	6	0	-3.915402	-0.867983	0.645489
38	8	0	-4.734297	-1.692681	1.374726
39	1	0	-4.518340	-2.627257	1.201725
40	17	0	-2.719432	-3.067235	-0.459842
41	1	0	-4.842518	0.874520	1.477426

Standard orientation of TS-3-Cl-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3-Cl-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -911.48 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.787491	-1.409618	-0.510023
2	1	0	5.126210	-2.248220	-0.154634
3	8	0	4.796408	0.312165	1.237502
4	1	0	4.954564	1.122271	0.720226
5	1	0	4.812366	-0.613820	0.351079
6	8	0	2.308278	0.809428	1.958563
7	1	0	3.282796	0.597874	1.717476
8	1	0	2.326806	1.293546	2.800221
9	6	0	-1.209859	-1.298531	1.777475
10	1	0	-1.824443	-2.133836	2.125203
11	6	0	-0.168556	-1.902409	0.807092
12	6	0	-0.822453	-2.584185	-0.413654
13	8	0	-0.771695	-1.963730	-1.513326
14	8	0	-1.381007	-3.692192	-0.186951
15	1	0	0.453275	-2.614243	1.351775
16	7	0	0.722401	-0.806006	0.325062
17	1	0	0.268193	-0.338427	-0.471395
18	1	0	0.965844	-0.119296	1.067738
19	17	0	2.362675	-1.320048	-0.233998
20	8	0	4.542263	2.695588	-0.695838
21	1	0	3.569910	2.730904	-0.502704
22	1	0	4.732394	3.502034	-1.203948
23	8	0	1.852020	2.637877	-0.045280
24	1	0	1.959579	2.016535	0.721449
25	1	0	1.638916	3.496741	0.356429
26	8	0	4.862770	0.538640	-2.482922
27	1	0	4.885372	-0.240011	-1.879763
28	1	0	4.739779	1.304912	-1.874935
29	1	0	-0.670253	-0.900285	2.643229
30	6	0	-2.069872	-0.219267	1.160070

31	6	0	-1.698389	1.130409	1.232772
32	6	0	-3.236227	-0.551828	0.460566
33	6	0	-2.461239	2.121546	0.618466
34	1	0	-0.800307	1.413610	1.775943
35	6	0	-3.999848	0.439267	-0.149787
36	1	0	-3.552215	-1.587876	0.387552
37	6	0	-3.623185	1.786941	-0.083146
38	1	0	-2.166723	3.166246	0.679187
39	8	0	-4.407969	2.726797	-0.700839
40	1	0	-4.022297	3.609895	-0.560450
41	17	0	-5.463102	-0.008648	-1.017257

Standard orientation of TS-3,5-di-Cl-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3,5-di-Cl-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -914.09 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.080544	-1.266407	0.360065
2	1	0	-5.530849	-2.008555	-0.076632
3	8	0	-4.838687	0.612031	-1.199974
4	1	0	-4.906372	1.380656	-0.605268
5	1	0	-4.987685	-0.390694	-0.415017
6	8	0	-2.300115	0.872011	-1.856394
7	1	0	-3.297449	0.758064	-1.640101
8	1	0	-2.246896	1.415466	-2.659455
9	6	0	0.960450	-1.641581	-1.816053
10	1	0	1.533135	-2.501227	-2.174904
11	6	0	-0.144785	-2.207237	-0.893004
12	6	0	0.432020	-2.981235	0.312749
13	8	0	0.409863	-2.396202	1.432467
14	8	0	0.906579	-4.120278	0.053510
15	1	0	-0.800825	-2.851182	-1.480014
16	7	0	-0.963863	-1.068210	-0.385164
17	1	0	-0.498788	-0.674543	0.444427
18	1	0	-1.131479	-0.325318	-1.095726
19	17	0	-2.657884	-1.456891	0.111230
20	8	0	-4.308377	2.752489	0.941836
21	1	0	-3.334362	2.656691	0.781048
22	1	0	-4.396147	3.529328	1.519477
23	8	0	-1.634198	2.329620	0.377216
24	1	0	-1.803385	1.871093	-0.486131
25	1	0	-1.197417	3.164458	0.140069
26	8	0	-4.987219	0.497706	2.499874
27	1	0	-5.084186	-0.208692	1.819574
28	1	0	-4.741290	1.296967	1.978179
29	1	0	0.474677	-1.178571	-2.680875
30	6	0	1.868471	-0.644398	-1.133619

31	6	0	1.569742	0.721850	-1.158465
32	6	0	2.992241	-1.075432	-0.418781
33	6	0	2.373170	1.625082	-0.470472
34	1	0	0.711589	1.088754	-1.712690
35	6	0	3.789737	-0.158755	0.256189
36	1	0	3.246080	-2.129949	-0.385777
37	6	0	3.501295	1.214056	0.252916
38	8	0	4.319651	2.062402	0.934698
39	1	0	4.011111	2.982106	0.833771
40	17	0	1.976781	3.340087	-0.506091
41	17	0	5.197451	-0.721928	1.139394

Standard orientation of TS-*N*-Cl-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*-Cl-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -487.89 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.240406	-1.630481	-0.248434
2	1	0	4.440925	-2.511191	0.112484
3	8	0	4.088381	0.021245	1.584648
4	1	0	4.546421	0.796077	1.212352
5	1	0	4.200541	-0.905010	0.617936
6	8	0	1.685854	0.954785	1.702786
7	1	0	2.652352	0.546102	1.694424
8	1	0	1.431197	1.084454	2.631368
9	6	0	-1.702274	-0.879160	1.647840
10	1	0	-2.177097	-1.679734	2.223859
11	6	0	-0.655620	-1.605843	0.774071
12	6	0	-1.212088	-2.695160	-0.176579
13	8	0	-0.954233	-2.627271	-1.403999
14	8	0	-1.874510	-3.591823	0.418641
15	1	0	0.026416	-2.112642	1.465020
16	7	0	0.265949	-0.614398	0.115823
17	1	0	0.626360	0.091751	0.842418
18	17	0	1.903201	-1.320636	-0.334674
19	8	0	4.872513	2.469147	-0.073292
20	1	0	3.914859	2.727336	-0.081652
21	1	0	5.346927	3.233633	-0.441085
22	8	0	2.166885	3.055132	0.002512
23	1	0	1.926537	2.360640	0.667216
24	1	0	2.096778	3.897379	0.482352
25	8	0	5.099915	0.406698	-1.974341
26	1	0	4.859259	-0.396546	-1.461890
27	1	0	5.014991	1.139576	-1.319656
28	17	0	-0.413909	0.355504	-1.198387
29	1	0	-1.157401	-0.253166	2.362089
30	6	0	-2.745584	-0.047843	0.937871

31	6	0	-2.725302	1.347825	1.046849
32	6	0	-3.747694	-0.635761	0.151374
33	6	0	-3.658713	2.143922	0.380624
34	1	0	-1.956921	1.824761	1.650359
35	6	0	-4.684368	0.143644	-0.526302
36	1	0	-3.799513	-1.716757	0.060826
37	6	0	-4.634275	1.536390	-0.413925
38	1	0	-3.629020	3.227137	0.470738
39	1	0	-5.455013	-0.317817	-1.136987
40	8	0	-5.581898	2.268295	-1.106370
41	1	0	-5.439189	3.218138	-0.949028

Standard orientation of TS-3,*N*-di-Cl-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3,*N*-di-Cl-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -415.73 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.594751	-1.852638	-0.393607
2	1	0	4.741847	-2.739771	-0.022563
3	8	0	4.769125	-0.142362	1.391162
4	1	0	5.246951	0.579093	0.944128
5	1	0	4.706902	-1.111927	0.441009
6	8	0	2.468526	0.984506	1.698548
7	1	0	3.394655	0.497290	1.613296
8	1	0	2.332291	1.189714	2.638254
9	6	0	-1.178777	-0.588062	1.862116
10	1	0	-1.617032	-1.337896	2.528534
11	6	0	-0.184858	-1.387796	0.991723
12	6	0	-0.827764	-2.470104	0.089492
13	8	0	-0.708432	-2.380806	-1.157203
14	8	0	-1.427148	-3.372423	0.740472
15	1	0	0.487459	-1.903767	1.684900
16	7	0	0.773419	-0.472849	0.279023
17	1	0	1.246077	0.194847	0.974531
18	17	0	2.306420	-1.327608	-0.279624
19	8	0	5.599125	2.157924	-0.459663
20	1	0	4.683164	2.524459	-0.353734
21	1	0	6.108292	2.861310	-0.896300
22	8	0	3.004272	3.026599	-0.062625
23	1	0	2.760060	2.352329	0.621776
24	1	0	3.075190	3.864682	0.424321
25	8	0	5.338326	0.058510	-2.312042
26	1	0	5.116455	-0.708316	-1.739944
27	1	0	5.425012	0.809319	-1.678062
28	17	0	0.100388	0.565368	-0.984383
29	1	0	-0.599071	0.094776	2.491724
30	6	0	-2.273309	0.179972	1.156279

31	6	0	-2.277213	1.580131	1.165220
32	6	0	-3.312818	-0.482804	0.492145
33	6	0	-3.274459	2.304913	0.516595
34	1	0	-1.481111	2.114210	1.676435
35	6	0	-4.306194	0.241527	-0.160856
36	1	0	-3.358032	-1.566495	0.481888
37	6	0	-4.301504	1.642155	-0.162335
38	1	0	-3.265648	3.391960	0.526680
39	8	0	-5.305858	2.305819	-0.819728
40	1	0	-5.177955	3.266216	-0.723142
41	17	0	-5.599724	-0.617919	-0.988446

Standard orientation of TS-5,*N*-di-Cl-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-5,*N*-di-Cl-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -440.23 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.779787	1.260845	-0.215915
2	1	0	-5.096661	2.091140	0.179703
3	8	0	-4.443195	-0.443513	1.547969
4	1	0	-4.774510	-1.256792	1.126970
5	1	0	-4.664391	0.509986	0.612859
6	8	0	-1.933467	-1.014168	1.719876
7	1	0	-2.949983	-0.752357	1.688878
8	1	0	-1.692953	-1.139260	2.652824
9	6	0	1.257147	1.299631	1.655778
10	1	0	1.601383	2.143602	2.261932
11	6	0	0.074039	1.869835	0.842673
12	6	0	0.425609	3.052786	-0.094166
13	8	0	0.203206	2.947950	-1.325492
14	8	0	0.908553	4.048371	0.516103
15	1	0	-0.649083	2.247140	1.573221
16	7	0	-0.713994	0.768086	0.188026
17	1	0	-0.980461	0.016542	0.908689
18	17	0	-2.431191	1.264767	-0.256471
19	8	0	-4.810561	-2.889864	-0.274027
20	1	0	-3.828944	-3.022643	-0.217846
21	1	0	-5.151093	-3.685381	-0.716688
22	8	0	-2.068788	-3.145088	-0.005262
23	1	0	-1.949441	-2.429870	0.670654
24	1	0	-1.944709	-3.976005	0.483387
25	8	0	-5.207424	-0.784651	-2.094409
26	1	0	-5.127539	0.019387	-1.536314
27	1	0	-5.055505	-1.528000	-1.463746
28	17	0	0.075018	-0.104926	-1.133316
29	1	0	0.857898	0.551984	2.348914
30	6	0	2.413316	0.710703	0.880771

31	6	0	2.654157	-0.664691	0.935587
32	6	0	3.260650	1.505765	0.094138
33	6	0	3.697619	-1.226547	0.204460
34	1	0	2.016111	-1.306664	1.535245
35	6	0	4.299132	0.941096	-0.639949
36	1	0	3.109446	2.579499	0.050342
37	6	0	4.528234	-0.437950	-0.600271
38	8	0	5.564512	-0.940011	-1.347490
39	1	0	5.616459	-1.908489	-1.248262
40	17	0	3.978996	-2.966408	0.282710
41	1	0	4.950134	1.558478	-1.251589

Standard orientation of TS-3,5,*N*-tri-Cl-Tyr-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3,5,*N*-tri-Cl-Tyr-N

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -473.59 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	5.066336	-1.253517	-0.036355
2	1	0	5.435194	-1.987285	0.484995
3	8	0	4.556107	0.676728	1.425182
4	1	0	4.804786	1.432954	0.863450
5	1	0	4.871332	-0.394388	0.666491
6	8	0	2.011762	1.044074	1.509614
7	1	0	3.049735	0.868457	1.521991
8	1	0	1.727853	1.217085	2.422647
9	6	0	-0.841157	-1.329366	1.892411
10	1	0	-1.328803	-2.134718	2.447455
11	6	0	0.198014	-2.029740	0.991796
12	6	0	-0.305887	-3.227776	0.139208
13	8	0	0.182471	-3.384366	-1.007968
14	8	0	-1.125989	-3.981495	0.732083
15	1	0	0.962077	-2.443470	1.659053
16	7	0	0.973941	-1.001889	0.209230
17	1	0	1.183990	-0.136294	0.818239
18	17	0	2.726346	-1.449001	-0.121724
19	8	0	4.659914	2.834647	-0.734754
20	1	0	3.675910	2.936058	-0.660972
21	1	0	4.953572	3.582506	-1.281856
22	8	0	1.916659	3.017367	-0.386520
23	1	0	1.871535	2.351331	0.346432
24	1	0	1.780034	3.875935	0.047905
25	8	0	5.231780	0.513894	-2.224918
26	1	0	5.254570	-0.191409	-1.542625
27	1	0	5.008228	1.329304	-1.717262
28	17	0	0.176650	-0.367203	-1.241576
29	1	0	-0.295523	-0.716966	2.616321
30	6	0	-1.864529	-0.472636	1.186220

31	6	0	-1.759451	0.919546	1.240542
32	6	0	-2.897204	-1.043917	0.433592
33	6	0	-2.655290	1.715981	0.535134
34	1	0	-0.964519	1.386017	1.813491
35	6	0	-3.781077	-0.234175	-0.268495
36	1	0	-3.004096	-2.121523	0.379886
37	6	0	-3.681196	1.165550	-0.245260
38	8	0	-4.575403	1.902526	-0.961016
39	1	0	-4.378673	2.853411	-0.871922
40	17	0	-5.063180	-0.972110	-1.213545
41	17	0	-2.503770	3.468700	0.610257

Standard orientation of TS-Tyr-Am-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-Tyr-Am-p-C3

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -346.72 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.627106	1.220552	-1.407940
2	8	0	2.571359	0.601011	2.496185
3	1	0	2.052211	1.118320	3.136115
4	17	0	1.376776	0.491618	0.943502
5	8	0	3.216855	0.875676	-2.492163
6	1	0	2.985559	1.655529	-1.940717
7	1	0	2.559945	0.174449	-2.256793
8	8	0	4.488219	1.862697	1.011418
9	1	0	3.835291	1.467613	1.637488
10	1	0	4.761728	1.109356	0.437628
11	8	0	2.843514	3.100066	-0.817056
12	1	0	3.414501	2.706524	-0.110720
13	1	0	1.937383	3.034532	-0.475670
14	6	0	0.108854	0.422963	-0.879467
15	6	0	-0.387298	-1.974292	-0.734730
16	6	0	-2.024894	-0.321573	0.059737
17	6	0	-1.584096	-1.667679	-0.141893
18	1	0	-2.236572	-2.475603	0.184970
19	1	0	-1.485947	1.728386	-0.198191
20	8	0	1.569302	-1.200960	-1.829634
21	6	0	0.483392	-0.934691	-1.205540
22	6	0	-1.190299	0.689621	-0.336187
23	8	0	2.657792	-2.169692	2.601410
24	1	0	2.616702	-1.191748	2.691055
25	1	0	2.874658	-2.310667	1.656639
26	8	0	3.374015	-2.358103	-0.122511
27	1	0	3.676319	-3.210396	-0.474329
28	1	0	2.689506	-2.034549	-0.757401
29	8	0	5.086835	-0.206625	-0.751689
30	1	0	4.591554	-0.996389	-0.444868

31	1	0	4.508132	0.176901	-1.452090
32	6	0	-3.383036	-0.043366	0.651306
33	1	0	-3.698466	-0.885080	1.281356
34	1	0	-3.337019	0.846199	1.289178
35	6	0	-4.463646	0.181999	-0.422306
36	1	0	-4.152806	1.015713	-1.060973
37	7	0	-4.614363	-1.004923	-1.252724
38	6	0	-5.753346	0.569743	0.297921
39	8	0	-6.498465	-0.292465	0.789549
40	7	0	-6.008919	1.881323	0.392776
41	1	0	-6.815024	2.206434	0.915380
42	1	0	-5.388584	2.568779	-0.017400
43	1	0	-4.901755	-1.782266	-0.656756
44	1	0	-0.088706	-3.006073	-0.899935
45	1	0	-5.377145	-0.858018	-1.913069

Standard orientation of TS-*N*-Cl-Tyr-Am-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*-Cl-Tyr-Am-p-C3

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -352.97 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.883635	-0.239900	-1.762543
2	8	0	3.080234	2.360488	1.038602
3	1	0	2.614026	3.214314	1.029480
4	17	0	1.773528	1.138850	0.210926
5	8	0	3.377327	-1.504722	-2.194034
6	1	0	3.198632	-0.584030	-2.488096
7	1	0	2.719277	-1.693454	-1.481124
8	8	0	4.889849	1.839146	-0.933680
9	1	0	4.277459	2.135875	-0.217662
10	1	0	5.119021	0.913394	-0.685130
11	8	0	3.163888	1.180433	-2.977100
12	1	0	3.755013	1.492516	-2.247062
13	1	0	2.273636	1.473889	-2.725892
14	6	0	0.383583	-0.254526	-0.796354
15	6	0	-0.178924	-1.544781	1.214990
16	6	0	-1.699584	0.205152	0.399220
17	6	0	-1.318480	-0.796613	1.347395
18	1	0	-1.974631	-0.974911	2.198588
19	1	0	-1.117433	1.192889	-1.401721
20	8	0	1.713159	-2.103432	-0.100298
21	6	0	0.687574	-1.362555	0.084240
22	6	0	-0.863981	0.437689	-0.659618
23	8	0	3.092619	0.777565	3.310068
24	1	0	3.084380	1.438255	2.581626
25	1	0	3.235081	-0.075794	2.850990
26	8	0	3.615571	-1.546735	1.796212
27	1	0	3.899517	-2.357189	2.248102
28	1	0	2.898458	-1.822605	1.175605
29	8	0	5.327509	-0.845741	-0.336929
30	1	0	4.835199	-1.035490	0.490412

31	1	0	4.714542	-1.147617	-1.048073
32	6	0	-3.007505	0.938274	0.555675
33	1	0	-3.314068	0.936259	1.608781
34	1	0	-2.889954	1.984762	0.250100
35	6	0	-4.161698	0.344535	-0.272403
36	1	0	-3.912720	0.361404	-1.336299
37	7	0	-4.558599	-1.034919	0.076011
38	6	0	-5.401702	1.194718	-0.018705
39	8	0	-5.978132	1.152345	1.077316
40	17	0	-3.570520	-2.223503	-0.752205
41	7	0	-5.791375	1.990532	-1.019591
42	1	0	-6.585403	2.609171	-0.891981
43	1	0	-5.312692	1.992484	-1.912224
44	1	0	-4.367439	-1.190528	1.069475
45	1	0	0.073260	-2.320019	1.933558

Standard orientation of TS-5-Cl-Tyr-Am-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-5-Cl-Tyr-Am-p-C3

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -354.66 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.644547	-1.258676	-1.579281
2	8	0	-2.571229	-1.257045	2.416381
3	1	0	-2.043578	-1.856755	2.970946
4	17	0	-1.366102	-0.927943	0.859996
5	8	0	-3.228914	-0.776106	-2.579886
6	1	0	-2.971483	-1.626973	-2.159284
7	1	0	-2.586535	-0.109098	-2.244121
8	8	0	-4.429031	-2.353855	0.758126
9	1	0	-3.786124	-2.026476	1.434663
10	1	0	-4.740644	-1.536127	0.305230
11	8	0	-2.785941	-3.216728	-1.273459
12	1	0	-3.346733	-2.957607	-0.499685
13	1	0	-1.874466	-3.206323	-0.940474
14	6	0	-0.125448	-0.582583	-0.903358
15	6	0	0.403347	1.732399	-0.338295
16	6	0	2.024243	-0.039246	0.127441
17	6	0	1.598127	1.326105	0.183585
18	1	0	2.249719	2.058437	0.655412
19	1	0	1.462023	-2.004102	-0.484910
20	8	0	-1.557432	1.196571	-1.575187
21	6	0	-0.492009	0.816863	-1.007242
22	6	0	1.178875	-0.954772	-0.433813
23	8	0	-2.555127	1.474551	2.886078
24	1	0	-2.538190	0.491743	2.843392
25	1	0	-2.838276	1.741339	1.987061
26	8	0	-3.463032	2.010513	0.266229
27	1	0	-3.786013	2.907489	0.083919
28	1	0	-2.755914	1.842519	-0.397725
29	8	0	-5.121820	-0.065101	-0.673942
30	1	0	-4.642510	0.682332	-0.256437

31	1	0	-4.545606	-0.315304	-1.433260
32	6	0	3.382929	-0.424617	0.652191
33	1	0	3.678921	0.251540	1.464431
34	1	0	3.343078	-1.438723	1.063581
35	6	0	4.473744	-0.377480	-0.433931
36	1	0	4.184670	-1.049850	-1.249127
37	7	0	4.602792	0.969871	-0.970035
38	6	0	5.767274	-0.893250	0.196319
39	8	0	6.509153	-0.139538	0.845150
40	7	0	6.028309	-2.197210	0.035203
41	1	0	6.834325	-2.614591	0.487939
42	1	0	5.405621	-2.797010	-0.492528
43	1	0	4.880476	1.594477	-0.211813
44	1	0	5.365582	0.989886	-1.646126
45	17	0	-0.066899	3.411626	-0.270070

Standard orientation of TS-*N*,*N*-di-Cl-Tyr-Am-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*,*N*-di-Cl-Tyr-Am-p-C3

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -355.84 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.210754	0.352514	-1.705730
2	8	0	3.481168	1.858574	1.761496
3	1	0	3.035012	2.673924	2.048263
4	17	0	2.130233	1.004697	0.595310
5	8	0	3.642333	-0.748608	-2.555802
6	1	0	3.477583	0.220232	-2.530310
7	1	0	2.994472	-1.149832	-1.926982
8	8	0	5.247160	1.967847	-0.309945
9	1	0	4.653276	2.023718	0.477928
10	1	0	5.463616	1.009302	-0.383208
11	8	0	3.485591	2.052049	-2.422529
12	1	0	4.093029	2.091017	-1.641713
13	1	0	2.608099	2.274147	-2.072663
14	6	0	0.710782	0.046839	-0.789107
15	6	0	0.105409	-1.802367	0.708440
16	6	0	-1.371133	0.148902	0.489197
17	6	0	-1.016523	-1.107182	1.075017
18	1	0	-1.672739	-1.526703	1.835125
19	1	0	-0.752204	1.645684	-0.902576
20	8	0	1.980867	-1.965342	-0.734497
21	6	0	0.978958	-1.295148	-0.312875
22	6	0	-0.520381	0.689314	-0.436118
23	8	0	3.513357	-0.402428	3.356938
24	1	0	3.499492	0.463892	2.891370
25	1	0	3.634164	-1.055416	2.636992
26	8	0	3.967380	-2.113804	1.158212
27	1	0	4.210383	-3.039445	1.318857
28	1	0	3.216661	-2.142788	0.517958
29	8	0	5.658353	-0.766981	-0.655207
30	1	0	5.183668	-1.224993	0.071144

31	1	0	5.023017	-0.806425	-1.408548
32	6	0	-2.665163	0.835002	0.855842
33	1	0	-3.071617	0.427210	1.786932
34	1	0	-2.477167	1.899737	1.031403
35	6	0	-3.743777	0.774361	-0.243401
36	1	0	-3.342096	1.209853	-1.163493
37	7	0	-4.260466	-0.555365	-0.669900
38	6	0	-4.958312	1.604921	0.183394
39	8	0	-5.971165	1.096559	0.671209
40	17	0	-3.140407	-1.316495	-1.793967
41	17	0	-4.488644	-1.642880	0.687173
42	1	0	0.337758	-2.768186	1.148881
43	7	0	-4.810169	2.924809	0.011629
44	1	0	-5.537365	3.554592	0.332879
45	1	0	-3.972948	3.320586	-0.400725

Standard orientation of TS-5,*N*-di-Cl-Tyr-Am-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-5,*N*-di-Cl-Tyr-Am-p-C3

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -362.61 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.866117	-1.095866	-1.645458
2	8	0	-3.074491	-1.640205	2.165934
3	1	0	-2.627744	-2.366937	2.632518
4	17	0	-1.739020	-1.130044	0.762667
5	8	0	-3.371950	-0.306015	-2.715553
6	1	0	-3.208146	-1.226121	-2.409220
7	1	0	-2.717831	0.253190	-2.237564
8	8	0	-4.919654	-2.254522	0.269402
9	1	0	-4.290426	-2.095153	1.016499
10	1	0	-5.137664	-1.354831	-0.067780
11	8	0	-3.192633	-2.934598	-1.759667
12	1	0	-3.804595	-2.750123	-1.003307
13	1	0	-2.315366	-3.022028	-1.353821
14	6	0	-0.371220	-0.568183	-0.832613
15	6	0	0.205185	1.594166	0.147609
16	6	0	1.727547	-0.304138	0.390623
17	6	0	1.345814	1.048956	0.660437
18	1	0	1.995516	1.662199	1.282681
19	1	0	1.136996	-2.111105	-0.578492
20	8	0	-1.679680	1.368996	-1.285958
21	6	0	-0.674540	0.848041	-0.724099
22	6	0	0.886575	-1.074992	-0.360750
23	8	0	-3.004563	0.970980	3.076707
24	1	0	-3.016785	0.009893	2.865185
25	1	0	-3.193718	1.404582	2.219056
26	8	0	-3.659417	2.031233	0.538927
27	1	0	-3.899146	2.971324	0.510037
28	1	0	-2.916504	1.926198	-0.098134
29	8	0	-5.355258	0.261226	-0.849086
30	1	0	-4.871343	0.902788	-0.286291

31	1	0	-4.734874	0.087876	-1.594518
32	6	0	3.049239	-0.817016	0.901568
33	1	0	3.326665	-0.285763	1.820090
34	1	0	2.964164	-1.881735	1.147679
35	6	0	4.207329	-0.664534	-0.101968
36	1	0	3.988515	-1.219154	-1.017879
37	7	0	4.550930	0.719715	-0.485351
38	6	0	5.465938	-1.223951	0.553283
39	8	0	6.006433	-0.619410	1.489831
40	17	0	3.551036	1.293883	-1.805789
41	7	0	5.911414	-2.392695	0.081567
42	1	0	6.722281	-2.831678	0.505286
43	1	0	5.461733	-2.853827	-0.700183
44	17	0	-0.200584	3.259156	0.471108
45	1	0	4.332158	1.344646	0.295500

Standard orientation of TS-5,*N*,*N*-tri-Cl-Tyr-Am-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-5,*N*,*N*-tri-Cl-Tyr-Am-p-C3

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -368.69 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.126050	-1.126415	1.567817
2	8	0	3.432729	-1.566809	-2.199482
3	1	0	2.997135	-2.277837	-2.699345
4	17	0	2.054284	-1.095529	-0.812074
5	8	0	3.622367	-0.337275	2.724805
6	1	0	3.474804	-1.253797	2.399540
7	1	0	2.969579	0.221909	2.245419
8	8	0	5.235039	-2.215724	-0.278056
9	1	0	4.619620	-2.043646	-1.034337
10	1	0	5.442018	-1.322296	0.081904
11	8	0	3.478914	-2.939662	1.706870
12	1	0	4.101455	-2.737452	0.963539
13	1	0	2.607218	-3.015119	1.287062
14	6	0	0.653148	-0.577960	0.755571
15	6	0	0.085083	1.614152	-0.165154
16	6	0	-1.424637	-0.279512	-0.495896
17	6	0	-1.043413	1.081635	-0.718115
18	1	0	-1.673884	1.709568	-1.343233
19	1	0	-0.842305	-2.116604	0.421285
20	8	0	1.938035	1.351105	1.301068
21	6	0	0.949172	0.844544	0.701579
22	6	0	-0.591685	-1.073231	0.239705
23	8	0	3.393682	1.064003	-3.042624
24	1	0	3.397908	0.098613	-2.849189
25	1	0	3.556122	1.481688	-2.171909
26	8	0	3.956147	2.077197	-0.463686
27	1	0	4.190118	3.016997	-0.399335
28	1	0	3.201097	1.948824	0.153787
29	8	0	5.635075	0.277282	0.904222
30	1	0	5.159029	0.930805	0.348568

31	1	0	5.001945	0.084932	1.634117
32	6	0	-2.735878	-0.794556	-1.038802
33	1	0	-3.121753	-0.126170	-1.815149
34	1	0	-2.578400	-1.771570	-1.507995
35	6	0	-3.818704	-1.012630	0.035600
36	1	0	-3.453745	-1.735559	0.771793
37	7	0	-4.261638	0.147749	0.857151
38	6	0	-5.075213	-1.590764	-0.624526
39	8	0	-6.034671	-0.885840	-0.948311
40	17	0	-3.120340	0.446930	2.163385
41	17	0	-4.397548	1.617424	-0.088926
42	7	0	-5.024028	-2.909291	-0.850111
43	1	0	-5.786380	-3.361124	-1.343706
44	1	0	-4.230653	-3.471070	-0.563918
45	17	0	0.498717	3.285989	-0.437338

Standard orientation of TS-Tyr-Am-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-Tyr-Am-p-C5

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -341.10 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.086103	-0.412669	-2.163255
2	8	0	1.611928	2.163345	1.393270
3	1	0	0.941545	2.864486	1.316669
4	17	0	0.988812	0.817761	0.109907
5	8	0	3.840325	-0.928080	-1.925759
6	1	0	3.491829	-0.042348	-2.171139
7	1	0	3.100881	-1.388428	-1.458253
8	8	0	3.976283	2.417058	0.048000
9	1	0	3.137586	2.436583	0.568246
10	1	0	4.377214	1.543374	0.265008
11	8	0	3.085246	1.723555	-2.465109
12	1	0	3.368197	2.036198	-1.569780
13	1	0	2.115033	1.732999	-2.439693
14	6	0	0.368878	-0.697109	-1.396262
15	6	0	-0.329705	-2.364193	0.261042
16	6	0	-1.998659	-0.922485	-0.826364
17	6	0	-1.621996	-1.935366	0.113084
18	1	0	-0.075840	-3.159751	0.956531
19	1	0	-2.403240	-2.390473	0.720861
20	1	0	-1.255526	0.418073	-2.310176
21	8	0	1.922120	-2.251568	-0.477659
22	6	0	0.721614	-1.812131	-0.547810
23	6	0	-1.010574	-0.353897	-1.583277
24	8	0	1.480120	0.265965	3.410531
25	1	0	1.472452	1.020456	2.780494
26	1	0	1.981114	-0.430568	2.937656
27	8	0	3.031904	-1.570456	1.934699
28	1	0	3.393561	-2.352415	2.381228
29	1	0	2.605146	-1.906381	1.109367
30	8	0	4.983272	-0.144843	0.477869

31	1	0	4.364278	-0.586936	1.097908
32	1	0	4.687689	-0.457699	-0.409269
33	6	0	-3.443474	-0.514431	-0.938130
34	1	0	-3.599873	0.069530	-1.853564
35	1	0	-4.076900	-1.407601	-1.004473
36	6	0	-3.916577	0.331750	0.259404
37	1	0	-3.678795	-0.199636	1.187253
38	7	0	-3.231452	1.617138	0.276870
39	1	0	-3.498290	2.134899	-0.561391
40	1	0	-3.569611	2.165756	1.066864
41	6	0	-5.433002	0.473254	0.150011
42	8	0	-5.944504	1.316019	-0.604131
43	7	0	-6.165705	-0.376725	0.881395
44	1	0	-7.176621	-0.376010	0.799946
45	1	0	-5.730202	-1.056592	1.492808

Standard orientation of TS-*N*-Cl-Tyr-Am-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*-Cl-Tyr-Am-p-C5

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -342.44 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.346722	-1.361235	-1.853245
2	8	0	1.904680	2.440430	0.338101
3	1	0	1.281199	3.061924	-0.077160
4	17	0	1.270477	0.700862	-0.292213
5	8	0	4.110461	-1.772573	-1.301836
6	1	0	3.807659	-1.055191	-1.901421
7	1	0	3.336355	-1.984954	-0.723204
8	8	0	4.327507	2.074768	-0.873928
9	1	0	3.469107	2.323375	-0.454774
10	1	0	4.678755	1.358391	-0.294838
11	8	0	3.477774	0.437017	-2.920141
12	1	0	3.756034	1.079727	-2.220766
13	1	0	2.508032	0.477187	-2.924184
14	6	0	0.611782	-1.291624	-1.053602
15	6	0	-0.155667	-2.120901	1.121278
16	6	0	-1.769433	-1.219857	-0.497479
17	6	0	-1.435652	-1.775634	0.777692
18	1	0	-2.236102	-1.943048	1.497477
19	1	0	-0.967283	-0.604508	-2.376170
20	8	0	2.112517	-2.345801	0.469384
21	6	0	0.923153	-1.960703	0.186868
22	6	0	-0.754706	-1.022810	-1.394235
23	8	0	1.481507	1.552052	2.941978
24	1	0	1.568764	1.990657	2.067372
25	1	0	1.989312	0.720869	2.834840
26	8	0	3.090967	-0.715056	2.444700
27	1	0	3.400927	-1.242361	3.198114
28	1	0	2.708850	-1.363445	1.804124
29	8	0	5.175001	-0.100823	0.638298
30	1	0	4.504585	-0.221113	1.344599

31	1	0	4.904036	-0.745905	-0.056528
32	6	0	-3.211948	-0.922889	-0.827525
33	1	0	-3.298106	-0.565287	-1.860627
34	1	0	-3.784582	-1.858577	-0.763923
35	6	0	-3.910036	0.096606	0.096461
36	1	0	-3.667573	-0.100538	1.144122
37	7	0	-3.639760	1.520795	-0.160389
38	6	0	-5.413324	-0.042988	-0.112916
39	8	0	-5.940455	0.369076	-1.155823
40	17	0	-1.978170	1.928115	0.227487
41	1	0	0.066617	-2.568329	2.086478
42	1	0	-3.708809	1.675251	-1.170002
43	7	0	-6.093699	-0.652657	0.862200
44	1	0	-7.088201	-0.822249	0.753449
45	1	0	-5.635987	-0.968128	1.708825

Standard orientation of TS-3-Cl-Tyr-Am-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-3-Cl-Tyr-Am-p-C5

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -354.83 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.092736	-0.641809	-2.178275
2	8	0	-1.616719	-1.835796	2.069356
3	1	0	-0.934505	-2.505704	2.247540
4	17	0	-0.984550	-1.017510	0.362432
5	8	0	-3.846581	-0.122428	-2.135391
6	1	0	-3.476613	-1.031354	-2.068688
7	1	0	-3.122355	0.481690	-1.851976
8	8	0	-3.915323	-2.619886	0.841471
9	1	0	-3.085842	-2.429310	1.344929
10	1	0	-4.350946	-1.740701	0.751107
11	8	0	-3.047165	-2.781144	-1.765970
12	1	0	-3.303465	-2.781703	-0.809712
13	1	0	-2.076905	-2.800900	-1.770934
14	6	0	-0.373707	-0.134279	-1.538814
15	6	0	0.343750	1.974493	-0.540403
16	6	0	1.997673	0.261141	-1.102178
17	6	0	1.633564	1.528228	-0.543067
18	1	0	2.413345	2.156446	-0.115972
19	1	0	1.242054	-1.496348	-2.044130
20	8	0	-1.916629	1.649110	-1.212784
21	6	0	-0.732966	1.209250	-1.128900
22	6	0	1.006004	-0.524475	-1.616702
23	8	0	-1.402871	0.666496	3.236077
24	1	0	-1.417633	-0.266038	2.922101
25	1	0	-1.953971	1.140581	2.579731
26	8	0	-3.116501	1.785723	1.284472
27	1	0	-3.479747	2.669200	1.456980
28	1	0	-2.670021	1.849824	0.409446
29	8	0	-5.014493	-0.098865	0.380195
30	1	0	-4.421792	0.545505	0.822648

31	1	0	-4.711211	-0.087336	-0.557788
32	6	0	3.443126	-0.157606	-1.075603
33	1	0	3.590280	-1.028766	-1.725266
34	1	0	4.071157	0.654138	-1.462621
35	6	0	3.927292	-0.520637	0.340822
36	1	0	3.701516	0.309182	1.019126
37	7	0	3.238651	-1.709605	0.825116
38	1	0	3.499509	-2.497061	0.230316
39	1	0	3.579682	-1.935572	1.758977
40	6	0	5.441950	-0.703143	0.271713
41	8	0	5.938614	-1.755489	-0.159679
42	7	0	6.187380	0.337360	0.665605
43	1	0	7.197823	0.297060	0.587895
44	1	0	5.762335	1.182756	1.026965
45	17	0	-0.048446	3.538824	0.125177

Standard orientation of TS-*N*,*N*-di-Cl-Tyr-Am-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*,*N*-di-Cl-Tyr-Am-p-C5

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -338.84 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.575853	1.292271	-2.001814
2	8	0	-1.741097	-2.353018	0.536721
3	1	0	-1.006659	-2.903676	0.212974
4	17	0	-1.332802	-0.612089	-0.257650
5	8	0	-4.413832	1.363437	-1.525181
6	1	0	-4.014538	0.633856	-2.049018
7	1	0	-3.681699	1.734980	-0.974434
8	8	0	-4.169073	-2.425910	-0.712989
9	1	0	-3.291232	-2.529011	-0.273739
10	1	0	-4.607328	-1.704281	-0.204317
11	8	0	-3.474114	-0.900902	-2.900525
12	1	0	-3.699234	-1.501728	-2.146924
13	1	0	-2.507824	-0.813891	-2.868161
14	6	0	-0.877488	1.364924	-1.170645
15	6	0	-0.294112	2.466501	0.942762
16	6	0	1.468487	1.560324	-0.506855
17	6	0	1.025874	2.207181	0.690315
18	1	0	1.773867	2.508531	1.423143
19	1	0	0.821050	0.708585	-2.352399
20	8	0	-2.541373	2.387392	0.192570
21	6	0	-1.308141	2.109330	-0.010883
22	6	0	0.522901	1.193513	-1.425107
23	8	0	-1.420388	-1.142070	3.032278
24	1	0	-1.437393	-1.668666	2.203119
25	1	0	-2.022718	-0.393520	2.840307
26	8	0	-3.319073	0.834801	2.322227
27	1	0	-3.704724	1.373803	3.031034
28	1	0	-3.032657	1.474379	1.626207
29	8	0	-5.277484	-0.226397	0.580390
30	1	0	-4.637713	0.042316	1.274066

31	1	0	-5.075874	0.375764	-0.173954
32	6	0	2.940126	1.336770	-0.744738
33	1	0	3.104368	0.992539	-1.770795
34	1	0	3.478649	2.283643	-0.638038
35	6	0	3.619786	0.367928	0.234619
36	1	0	3.578000	0.780197	1.250584
37	7	0	3.070352	-1.004545	0.379015
38	6	0	5.118041	0.247234	-0.093308
39	8	0	5.729601	1.233959	-0.518251
40	17	0	1.678058	-1.039687	1.437530
41	7	0	5.704129	-0.928341	0.146570
42	1	0	6.699209	-1.028818	-0.021604
43	1	0	5.177845	-1.712863	0.511188
44	17	0	2.629253	-1.682789	-1.178713
45	1	0	-0.603738	2.980822	1.848760

Standard orientation of TS-3,*N*-di-Cl-Tyr-Am-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-3,*N*-di-Cl-Tyr-Am-p-C5

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -352.89 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.333601	-0.236448	-2.316359
2	8	0	-1.878888	-2.070797	1.692424
3	1	0	-1.267190	-2.827175	1.706859
4	17	0	-1.235662	-1.012252	0.130244
5	8	0	-4.116809	0.370768	-2.126814
6	1	0	-3.800724	-0.557617	-2.198938
7	1	0	-3.353528	0.886444	-1.776711
8	8	0	-4.261245	-2.513968	0.459810
9	1	0	-3.408369	-2.437859	0.955709
10	1	0	-4.651196	-1.610358	0.507557
11	8	0	-3.432757	-2.347650	-2.159056
12	1	0	-3.690881	-2.471189	-1.211098
13	1	0	-2.462336	-2.365388	-2.160519
14	6	0	-0.602924	0.152191	-1.609845
15	6	0	0.166736	2.079622	-0.325709
16	6	0	1.779124	0.429558	-1.136793
17	6	0	1.448101	1.615656	-0.408202
18	1	0	2.243119	2.172219	0.085023
19	1	0	0.979285	-1.160522	-2.310354
20	8	0	-2.106869	1.895792	-0.997879
21	6	0	-0.931361	1.425159	-0.999280
22	6	0	0.767301	-0.252592	-1.750326
23	8	0	-1.450008	0.214108	3.215948
24	1	0	-1.526456	-0.661168	2.774811
25	1	0	-2.002367	0.802048	2.659984
26	8	0	-3.194718	1.685695	1.546489
27	1	0	-3.509015	2.537519	1.889742
28	1	0	-2.791508	1.884813	0.670749
29	8	0	-5.228452	0.100279	0.405007
30	1	0	-4.583337	0.628186	0.922422

31	1	0	-4.943421	0.231153	-0.529409
32	6	0	3.225795	0.009985	-1.231977
33	1	0	3.322503	-0.864997	-1.885182
34	1	0	3.790590	0.825159	-1.703323
35	6	0	3.910730	-0.309009	0.116530
36	1	0	3.572133	0.380782	0.894982
37	7	0	3.747357	-1.675868	0.634770
38	6	0	5.414709	-0.158742	-0.080281
39	8	0	6.053531	-1.023460	-0.695693
40	17	0	2.064990	-2.008764	1.002670
41	1	0	3.971510	-2.323368	-0.125765
42	7	0	5.967041	0.955677	0.407439
43	1	0	6.953369	1.138175	0.254149
44	1	0	5.419535	1.638032	0.918328
45	17	0	-0.186296	3.550181	0.544457

Standard orientation of TS-3,*N*,*N*-tri-Cl-Tyr-Am-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-3,*N*,*N*-tri-Cl-Tyr-Am-p-C5

State=1-A
Charge = -1 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -352.00 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.534167	-0.126377	-2.386592
2	8	0	-1.652856	-2.136760	1.588425
3	1	0	-0.890854	-2.741609	1.574497
4	17	0	-1.259717	-0.958458	0.030996
5	8	0	-4.360556	0.069095	-2.061314
6	1	0	-3.905856	-0.793550	-2.188440
7	1	0	-3.667696	0.691504	-1.740597
8	8	0	-3.970444	-2.922632	0.391594
9	1	0	-3.118086	-2.755555	0.863668
10	1	0	-4.470581	-2.080556	0.500971
11	8	0	-3.290070	-2.516713	-2.248283
12	1	0	-3.486583	-2.718635	-1.299304
13	1	0	-2.325968	-2.412875	-2.289241
14	6	0	-0.842685	0.330121	-1.681475
15	6	0	-0.285313	2.310968	-0.363960
16	6	0	1.495742	0.879969	-1.229776
17	6	0	1.039728	2.007624	-0.475482
18	1	0	1.772954	2.640000	0.022654
19	1	0	0.873907	-0.768087	-2.431094
20	8	0	-2.534898	1.853635	-0.986280
21	6	0	-1.310248	1.536929	-1.029836
22	6	0	0.564129	0.095357	-1.846995
23	8	0	-1.382442	0.155899	3.154842
24	1	0	-1.377908	-0.706586	2.682349
25	1	0	-2.032525	0.686111	2.649013
26	8	0	-3.412060	1.404081	1.616908
27	1	0	-3.835368	2.184820	2.008697
28	1	0	-3.101869	1.690849	0.728447
29	8	0	-5.246421	-0.448835	0.520869
30	1	0	-4.648010	0.145641	1.021444

31	1	0	-5.044067	-0.246955	-0.422373
32	6	0	2.974454	0.610704	-1.340403
33	1	0	3.151543	-0.188370	-2.066796
34	1	0	3.483881	1.502632	-1.718169
35	6	0	3.672123	0.266628	-0.016421
36	1	0	3.616468	1.124236	0.665746
37	7	0	3.156052	-0.868459	0.789803
38	6	0	5.174967	0.035216	-0.253162
39	8	0	5.759871	0.676189	-1.133256
40	17	0	1.749010	-0.415778	1.726132
41	7	0	5.792496	-0.829575	0.555237
42	1	0	6.791114	-0.974811	0.454110
43	1	0	5.286244	-1.328099	1.276892
44	17	0	-0.796868	3.707154	0.549663
45	17	0	2.757294	-2.241756	-0.227035

Standard orientation of TS-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -663.45 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.245004	1.426729	0.378918
2	1	0	4.543857	2.284570	0.032866
3	8	0	4.207517	-0.246364	-1.425422
4	1	0	4.425370	-1.064355	-0.943404
5	1	0	4.253621	0.672221	-0.491639
6	8	0	1.697774	-0.799051	-1.986244
7	1	0	2.683078	-0.561630	-1.806902
8	1	0	1.666174	-1.238222	-2.851737
9	6	0	-1.865386	1.236640	-1.563310
10	1	0	-2.502297	2.073813	-1.865190
11	6	0	-0.729495	1.840949	-0.698572
12	6	0	-1.247273	2.525044	0.566464
13	8	0	-1.236989	1.923034	1.653086
14	1	0	-0.151905	2.536056	-1.310731
15	7	0	0.186431	0.753966	-0.267771
16	1	0	0.409106	0.089509	-1.041180
17	17	0	1.851472	1.284491	0.224295
18	8	0	4.164498	-2.680655	0.443582
19	1	0	3.180908	-2.736303	0.327309
20	1	0	4.414217	-3.497080	0.908189
21	8	0	1.432060	-2.680833	0.000744
22	1	0	1.467780	-2.043884	-0.759790
23	1	0	1.216179	-3.538921	-0.401174
24	8	0	4.562858	-0.580769	2.277695
25	1	0	4.507459	0.219279	1.706851
26	1	0	4.416343	-1.327951	1.650960
27	1	0	-1.395640	0.837994	-2.468361
28	6	0	-2.671707	0.164079	-0.869804
29	6	0	-2.290186	-1.182325	-0.951817
30	6	0	-3.796032	0.489535	-0.096626

31	6	0	-2.999856	-2.178349	-0.278877
32	1	0	-1.426543	-1.461519	-1.551116
33	6	0	-4.519038	-0.493413	0.577860
34	1	0	-4.112684	1.526714	-0.021534
35	6	0	-4.115098	-1.828914	0.486745
36	8	0	-4.859319	-2.771660	1.169839
37	1	0	-4.478890	-3.655184	1.020215
38	7	0	-1.719206	3.764062	0.397302
39	1	0	-2.144803	4.253251	1.177528
40	1	0	-1.711517	4.213433	-0.511524
41	1	0	-0.221332	0.247929	0.529574
42	1	0	-2.695298	-3.219622	-0.349819
43	1	0	-5.391590	-0.235581	1.170900

Standard orientation of TS-5-Cl-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-5-Cl-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -675.59 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.726357	0.822277	0.209437
2	1	0	5.220289	1.531877	-0.234904
3	8	0	4.248807	-0.998020	-1.376045
4	1	0	4.226796	-1.774433	-0.788075
5	1	0	4.533195	-0.010975	-0.562739
6	8	0	1.693141	-0.930196	-1.989181
7	1	0	2.703482	-0.943185	-1.791056
8	1	0	1.559949	-1.425782	-2.813517
9	6	0	-1.399610	1.885397	-1.546389
10	1	0	-1.919832	2.816458	-1.790632
11	6	0	-0.117430	2.283271	-0.769643
12	6	0	-0.418946	3.045856	0.521267
13	8	0	-0.457620	2.445701	1.608007
14	1	0	0.527420	2.865808	-1.430080
15	7	0	0.614829	1.049335	-0.391208
16	1	0	0.681841	0.357124	-1.169221
17	17	0	2.364998	1.247770	0.050786
18	8	0	3.509588	-3.080500	0.774212
19	1	0	2.550192	-2.884899	0.617283
20	1	0	3.519888	-3.871255	1.339412
21	8	0	0.895767	-2.369390	0.216962
22	1	0	1.105200	-1.920557	-0.642263
23	1	0	0.341341	-3.130604	-0.021923
24	8	0	4.467148	-0.947672	2.349966
25	1	0	4.640129	-0.247394	1.680845
26	1	0	4.119789	-1.701980	1.818465
27	1	0	-1.073741	1.432552	-2.487973
28	6	0	-2.310805	0.941226	-0.796803
29	6	0	-2.166993	-0.442587	-0.946962
30	6	0	-3.287833	1.420934	0.087952

31	6	0	-2.973160	-1.315026	-0.219714
32	1	0	-1.425922	-0.847009	-1.630049
33	6	0	-4.096763	0.547050	0.806977
34	1	0	-3.417896	2.492008	0.214637
35	6	0	-3.947208	-0.836674	0.665216
36	8	0	-4.773845	-1.648172	1.398693
37	1	0	-4.572503	-2.586221	1.226250
38	7	0	-0.657330	4.352593	0.374193
39	1	0	-0.937556	4.908193	1.175406
40	1	0	-0.620463	4.797938	-0.535962
41	17	0	-2.772601	-3.055214	-0.421832
42	1	0	-4.855863	0.920029	1.487786
43	1	0	0.158753	0.606471	0.417396

Standard orientation of TS-3-Cl-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3-Cl-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -688.93 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.732205	-1.405790	0.621068
2	1	0	-5.055273	-2.264595	0.300160
3	8	0	-4.816602	0.257858	-1.188999
4	1	0	-4.976576	1.081726	-0.694462
5	1	0	-4.799542	-0.654104	-0.251714
6	8	0	-2.364568	0.764119	-1.981034
7	1	0	-3.334559	0.544902	-1.712289
8	1	0	-2.395717	1.149778	-2.871592
9	6	0	1.215572	-1.251282	-1.794874
10	1	0	1.829651	-2.087971	-2.141137
11	6	0	0.147689	-1.851360	-0.845489
12	6	0	0.759035	-2.527552	0.381839
13	8	0	0.826716	-1.920144	1.463135
14	1	0	-0.471518	-2.551021	-1.409575
15	7	0	-0.734124	-0.761400	-0.358252
16	1	0	-1.023146	-0.111279	-1.122894
17	17	0	-2.352562	-1.284982	0.276934
18	8	0	-4.554519	2.709119	0.648333
19	1	0	-3.589230	2.760624	0.425665
20	1	0	-4.751985	3.531979	1.126494
21	8	0	-1.882928	2.682920	-0.074266
22	1	0	-2.003034	2.038043	-0.819148
23	1	0	-1.693729	3.532927	-0.505649
24	8	0	-4.765777	0.627814	2.531595
25	1	0	-4.800037	-0.177787	1.968357
26	1	0	-4.681296	1.366083	1.883131
27	1	0	0.682349	-0.851602	-2.663370
28	6	0	2.068758	-0.176599	-1.162978
29	6	0	1.687255	1.171143	-1.219901
30	6	0	3.236898	-0.511160	-0.468072

31	6	0	2.443746	2.159082	-0.593492
32	1	0	0.787657	1.454820	-1.760069
33	6	0	3.994198	0.477253	0.154150
34	1	0	3.560270	-1.545805	-0.408824
35	6	0	3.608115	1.823194	0.103843
36	8	0	4.386366	2.759732	0.732375
37	1	0	3.996691	3.642516	0.600856
38	7	0	1.222228	-3.765254	0.182822
39	1	0	1.706303	-4.249491	0.931495
40	1	0	1.150885	-4.217693	-0.721735
41	1	0	-0.265903	-0.240175	0.394825
42	17	0	5.460146	0.029153	1.015606
43	1	0	2.142640	3.202460	-0.641515

Standard orientation of TS-3,5-di-Cl-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3,5-di-Cl-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -667.11 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.002915	-1.292777	0.473588
2	1	0	-5.417914	-2.082535	0.087513
3	8	0	-4.884502	0.503897	-1.203381
4	1	0	-4.988629	1.301451	-0.654846
5	1	0	-4.977739	-0.474892	-0.336363
6	8	0	-2.371277	0.827237	-1.904268
7	1	0	-3.363908	0.689713	-1.668416
8	1	0	-2.344649	1.340340	-2.728276
9	6	0	0.982997	-1.599001	-1.824309
10	1	0	1.550802	-2.464315	-2.178127
11	6	0	-0.148986	-2.147438	-0.917857
12	6	0	0.379294	-2.913810	0.296610
13	8	0	0.474530	-2.347182	1.397797
14	1	0	-0.809096	-2.773047	-1.521279
15	7	0	-0.948956	-1.007853	-0.403139
16	1	0	-1.153811	-0.295006	-1.137724
17	17	0	-2.628581	-1.403644	0.166621
18	8	0	-4.394037	2.786063	0.885169
19	1	0	-3.425258	2.697925	0.691806
20	1	0	-4.468391	3.570647	1.454172
21	8	0	-1.727198	2.396072	0.258816
22	1	0	-1.896174	1.902337	-0.584881
23	1	0	-1.319520	3.234617	-0.014213
24	8	0	-4.942015	0.570105	2.543403
25	1	0	-5.024065	-0.170132	1.899971
26	1	0	-4.744670	1.354409	1.979437
27	1	0	0.503922	-1.137186	-2.692962
28	6	0	1.888654	-0.606452	-1.134768
29	6	0	1.582017	0.758217	-1.148575
30	6	0	3.015438	-1.039180	-0.426577

31	6	0	2.382132	1.659445	-0.454509
32	1	0	0.721068	1.124635	-1.698848
33	6	0	3.809718	-0.124370	0.254580
34	1	0	3.274484	-2.092717	-0.403863
35	6	0	3.513585	1.246944	0.263638
36	8	0	4.327993	2.092413	0.951835
37	1	0	4.014837	3.011697	0.861211
38	7	0	0.740251	-4.179793	0.067920
39	1	0	1.163727	-4.725132	0.811295
40	1	0	0.651970	-4.598983	-0.851033
41	17	0	1.977698	3.371958	-0.474704
42	1	0	-0.461073	-0.565605	0.387065
43	17	0	5.221548	-0.687575	1.129955

Standard orientation of TS-*N*-Cl-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-*N*-Cl-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -383.17 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.162684	1.744889	-0.481950
2	1	0	-4.308808	2.659530	-0.183598
3	8	0	-4.256836	0.177770	1.446078
4	1	0	-4.735273	-0.583254	1.070504
5	1	0	-4.245165	1.082820	0.406974
6	8	0	-1.954309	-0.868479	1.800481
7	1	0	-2.904268	-0.402423	1.686857
8	1	0	-1.769811	-0.936065	2.752006
9	6	0	1.726009	0.692206	1.660287
10	1	0	2.141187	1.484247	2.293932
11	6	0	0.614034	1.398809	0.844330
12	6	0	1.102615	2.448843	-0.160134
13	8	0	1.138017	2.234636	-1.378166
14	1	0	-0.030131	1.895422	1.577220
15	7	0	-0.337902	0.433080	0.215100
16	1	0	-0.810969	-0.179259	0.979643
17	17	0	-1.889225	1.245324	-0.381736
18	8	0	-5.076178	-2.278303	-0.171865
19	1	0	-4.160982	-2.634076	-0.029986
20	1	0	-5.586371	-3.020514	-0.537385
21	8	0	-2.486688	-3.116911	0.318708
22	1	0	-2.239017	-2.366214	0.916723
23	1	0	-2.571419	-3.887957	0.904221
24	8	0	-4.881659	-0.360720	-2.215866
25	1	0	-4.681584	0.465316	-1.725838
26	1	0	-4.937441	-1.047207	-1.509328
27	1	0	1.223446	-0.011375	2.331614
28	6	0	2.833698	-0.008347	0.908328
29	6	0	2.937220	-1.404405	0.946591
30	6	0	3.794308	0.706210	0.177452

31	6	0	3.948822	-2.077817	0.260924
32	1	0	2.207569	-1.978717	1.511670
33	6	0	4.807365	0.050073	-0.520521
34	1	0	3.762018	1.791451	0.150581
35	6	0	4.878193	-1.345420	-0.482784
36	8	0	5.896407	-1.953694	-1.192014
37	1	0	5.827562	-2.919653	-1.095027
38	7	0	1.484643	3.602734	0.405946
39	1	0	1.892636	4.330176	-0.171413
40	1	0	1.448984	3.745261	1.409155
41	1	0	4.015908	-3.162396	0.297378
42	1	0	5.544770	0.610161	-1.087996
43	17	0	0.319098	-0.691229	-0.977400

Standard orientation of TS-3,*N*-di-Cl-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3,*N*-di-Cl-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -416.52 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.524351	1.913963	-0.514871
2	1	0	-4.632466	2.821624	-0.181145
3	8	0	-4.777939	0.281624	1.339684
4	1	0	-5.296387	-0.432254	0.926347
5	1	0	-4.676451	1.218294	0.343279
6	8	0	-2.564648	-0.930595	1.713097
7	1	0	-3.478774	-0.396274	1.595305
8	1	0	-2.418417	-1.060038	2.664934
9	6	0	1.181106	0.443651	1.837114
10	1	0	1.592150	1.179494	2.537190
11	6	0	0.153120	1.244326	1.000673
12	6	0	0.754937	2.308084	0.075694
13	8	0	0.893115	2.126439	-1.140409
14	1	0	-0.501730	1.741927	1.723195
15	7	0	-0.813308	0.361875	0.277858
16	1	0	-1.358171	-0.261010	0.987510
17	17	0	-2.288184	1.286889	-0.350043
18	8	0	-5.729675	-2.041857	-0.384001
19	1	0	-4.837915	-2.458591	-0.259199
20	1	0	-6.287288	-2.737894	-0.770344
21	8	0	-3.189247	-3.036684	0.060815
22	1	0	-2.916588	-2.348711	0.719639
23	1	0	-3.292953	-3.853755	0.576639
24	8	0	-5.361268	-0.065303	-2.344746
25	1	0	-5.107207	0.721863	-1.817139
26	1	0	-5.485623	-0.773409	-1.668927
27	17	0	-0.155113	-0.738342	-0.935135
28	1	0	0.613603	-0.275248	2.436372
29	6	0	2.303555	-0.263108	1.113051
30	6	0	2.341347	-1.661776	1.056111

31	6	0	3.344609	0.455109	0.513146
32	6	0	3.374738	-2.329708	0.404313
33	1	0	1.546531	-2.238340	1.520607
34	6	0	4.373823	-0.212191	-0.145171
35	1	0	3.368933	1.538623	0.560983
36	6	0	4.404206	-1.610826	-0.211272
37	1	0	3.394095	-3.415822	0.364093
38	8	0	5.442597	-2.221138	-0.864926
39	1	0	5.334208	-3.187177	-0.807679
40	17	0	5.665795	0.716866	-0.894353
41	7	0	1.122027	3.430343	0.710121
42	1	0	1.603607	4.160417	0.195885
43	1	0	0.996027	3.545778	1.709548

Standard orientation of TS-5,*N*-di-Cl-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-5,*N*-di-Cl-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -440.15 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.762023	1.349426	-0.380088
2	1	0	-5.050532	2.214165	-0.039619
3	8	0	-4.533761	-0.272678	1.483577
4	1	0	-4.900792	-1.091302	1.103816
5	1	0	-4.702361	0.646231	0.486682
6	8	0	-2.088587	-0.946236	1.746840
7	1	0	-3.105047	-0.635202	1.671574
8	1	0	-1.861007	-0.990446	2.690504
9	6	0	1.237254	1.148115	1.638903
10	1	0	1.541746	1.963336	2.304412
11	6	0	0.044430	1.724806	0.836679
12	6	0	0.393482	2.864292	-0.128012
13	8	0	0.442874	2.702145	-1.353544
14	1	0	-0.662451	2.105631	1.581457
15	7	0	-0.762276	0.655509	0.173902
16	1	0	-1.117292	-0.056962	0.920060
17	17	0	-2.437188	1.238251	-0.358640
18	8	0	-5.005066	-2.799154	-0.150958
19	1	0	-4.035785	-2.994754	-0.071590
20	1	0	-5.401315	-3.606627	-0.519199
21	8	0	-2.283396	-3.187022	0.172043
22	1	0	-2.142885	-2.442449	0.810381
23	1	0	-2.195400	-3.996431	0.702679
24	8	0	-5.228403	-0.816832	-2.134155
25	1	0	-5.134302	0.019154	-1.629482
26	1	0	-5.140174	-1.520332	-1.448200
27	17	0	0.033548	-0.300020	-1.079522
28	1	0	0.835409	0.356400	2.279271
29	6	0	2.434232	0.636520	0.872616
30	6	0	2.709380	-0.733506	0.854369

31	6	0	3.305784	1.502244	0.195332
32	6	0	3.814348	-1.219798	0.161602
33	1	0	2.055101	-1.428551	1.371396
34	6	0	4.408592	1.013500	-0.498608
35	1	0	3.133164	2.573732	0.213905
36	6	0	4.677844	-0.358389	-0.526391
37	8	0	5.782274	-0.783761	-1.219615
38	1	0	5.877976	-1.751316	-1.146487
39	7	0	0.642999	4.032150	0.481239
40	1	0	0.952873	4.825588	-0.069620
41	1	0	0.596969	4.131761	1.489268
42	17	0	4.136889	-2.953250	0.142946
43	1	0	5.082467	1.686276	-1.020261

Standard orientation of TS-3,5,*N*-tri-Cl-Tyr-Am-N

Cartesian coordinates of the transition states optimized at the B3LYP(D3BJ)/6-31+G(d) level:
Standard orientation of transition state of TS-3,5,*N*-tri-Cl-Tyr-Am-N

State=1-A
Charge = 0 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -422.26 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.945916	-1.763867	-0.497749
2	1	0	5.124684	-2.657878	-0.157373
3	8	0	5.043783	-0.106541	1.349862
4	1	0	5.513149	0.642704	0.940612
5	1	0	5.032154	-1.054101	0.357980
6	8	0	2.738058	0.929217	1.684461
7	1	0	3.694076	0.468658	1.580718
8	1	0	2.563615	1.039675	2.633983
9	6	0	-0.844150	-0.735012	1.835805
10	1	0	-1.166490	-1.475100	2.576240
11	6	0	0.241105	-1.463780	1.005441
12	6	0	-0.278730	-2.598056	0.113208
13	8	0	-0.436840	-2.458372	-1.105844
14	1	0	0.947298	-1.882779	1.730116
15	7	0	1.116883	-0.517542	0.249600
16	1	0	1.606635	0.167098	0.945237
17	17	0	2.667467	-1.322687	-0.359589
18	8	0	5.825091	2.296353	-0.354208
19	1	0	4.896105	2.629862	-0.253746
20	1	0	6.321046	3.032399	-0.750484
21	8	0	3.196074	3.066438	0.021353
22	1	0	2.972952	2.364294	0.683637
23	1	0	3.227491	3.893337	0.531013
24	8	0	5.668598	0.280812	-2.307509
25	1	0	5.467515	-0.525030	-1.785392
26	1	0	5.715203	0.997362	-1.630835
27	17	0	0.354512	0.487393	-0.985000
28	1	0	-0.344958	0.066372	2.388811
29	6	0	-2.045931	-0.189249	1.099819
30	6	0	-2.217787	1.190877	0.966213

31	6	0	-3.012005	-1.043799	0.555616
32	6	0	-3.314676	1.696225	0.277379
33	1	0	-1.489387	1.875669	1.387689
34	6	0	-4.098448	-0.523595	-0.137510
35	1	0	-2.928728	-2.118823	0.669986
36	6	0	-4.276753	0.857347	-0.303753
37	8	0	-5.360378	1.301736	-0.997282
38	1	0	-5.346239	2.274635	-1.062770
39	17	0	-5.288758	-1.615532	-0.822043
40	7	0	-0.557283	-3.727986	0.778048
41	1	0	-0.976958	-4.507800	0.282901
42	1	0	-0.409868	-3.812838	1.777624
43	17	0	-3.510553	3.438416	0.116194

Standard orientation of TS-NacTyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-NacTyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -349.11 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.983700	-0.054765	1.812773
2	8	0	3.306739	-2.213636	-1.255971
3	1	0	2.917924	-3.104379	-1.301086
4	17	0	1.935999	-1.185246	-0.298536
5	8	0	3.390254	1.400940	2.277245
6	1	0	3.309329	0.447288	2.501286
7	1	0	2.687011	1.581684	1.605836
8	8	0	5.154897	-1.660258	0.674715
9	1	0	4.541842	-1.963325	-0.037454
10	1	0	5.278992	-0.699408	0.494367
11	8	0	3.455843	-1.350971	2.820803
12	1	0	4.047766	-1.535092	2.049317
13	1	0	2.585863	-1.694143	2.561488
14	6	0	0.455676	-0.004509	0.862667
15	6	0	-0.260095	1.379470	-1.031348
16	6	0	-1.608827	-0.552699	-0.329717
17	6	0	-1.330263	0.541813	-1.209012
18	1	0	-0.088797	2.223200	-1.694820
19	1	0	-2.008563	0.719584	-2.042081
20	1	0	-0.910083	-1.607939	1.389306
21	8	0	1.600237	2.007377	0.299157
22	6	0	0.640631	1.191177	0.070731
23	6	0	-0.731330	-0.789048	0.694580
24	8	0	3.152018	-0.433231	-3.372800
25	1	0	3.214970	-1.153889	-2.707169
26	1	0	3.219503	0.386862	-2.841295
27	8	0	3.463709	1.813845	-1.698821
28	1	0	3.633425	2.681278	-2.099149
29	1	0	2.750378	1.960824	-1.030882
30	8	0	5.317265	1.096211	0.308403

31	1	0	4.781645	1.317964	-0.483128
32	1	0	4.706166	1.275043	1.061741
33	6	0	-2.889066	-1.331670	-0.474242
34	1	0	-3.177934	-1.392062	-1.531271
35	1	0	-2.760313	-2.352221	-0.100947
36	6	0	-4.056300	-0.684342	0.311192
37	1	0	-3.826593	-0.710528	1.379594
38	7	0	-4.256698	0.699178	-0.076942
39	1	0	-4.846611	0.857662	-0.887357
40	6	0	-5.330479	-1.505977	0.050577
41	8	0	-6.189299	-1.027896	-0.737157
42	8	0	-5.387962	-2.630563	0.617050
43	6	0	-3.690699	1.752312	0.533293
44	8	0	-2.989457	1.643711	1.556740
45	6	0	-3.936384	3.099806	-0.093338
46	1	0	-4.277388	3.795262	0.677760
47	1	0	-2.983084	3.470627	-0.485015
48	1	0	-4.665382	3.063165	-0.905326

Standard orientation of TS-NacTyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-NacTyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -339.72 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.359435	-1.841179	-1.468583
2	8	0	1.714079	2.381306	-0.380096
3	1	0	1.070020	2.845147	-0.943588
4	17	0	1.137207	0.522090	-0.490249
5	8	0	4.119181	-1.981077	-0.932916
6	1	0	3.754144	-1.472301	-1.690455
7	1	0	3.374748	-2.074003	-0.287167
8	8	0	4.118288	1.822823	-1.540861
9	1	0	3.259059	2.128061	-1.161648
10	1	0	4.534811	1.310333	-0.809241
11	8	0	3.294182	-0.326142	-3.048915
12	1	0	3.556295	0.488920	-2.552148
13	1	0	2.323852	-0.333412	-3.030177
14	6	0	0.621477	-1.642551	-0.694375
15	6	0	-0.080839	-2.034930	1.621998
16	6	0	-1.759935	-1.646322	-0.129965
17	6	0	-1.385117	-1.884277	1.230339
18	1	0	-2.174034	-1.950224	1.978789
19	1	0	-1.004679	-1.388263	-2.108545
20	8	0	2.203257	-2.186293	1.000234
21	6	0	0.983497	-1.983787	0.660281
22	6	0	-0.760374	-1.563693	-1.062485
23	8	0	1.421212	2.241174	2.385913
24	1	0	1.425453	2.427481	1.421968
25	1	0	1.959626	1.426262	2.464542
26	8	0	3.118925	-0.018549	2.416339
27	1	0	3.451704	-0.309440	3.280221
28	1	0	2.756144	-0.829637	1.984474
29	8	0	5.144469	0.185083	0.460985
30	1	0	4.497194	0.230076	1.197391

31	1	0	4.885593	-0.629922	-0.030644
32	6	0	-3.209242	-1.471157	-0.496389
33	1	0	-3.310331	-1.468554	-1.588681
34	1	0	-3.807142	-2.303578	-0.108287
35	6	0	-3.822047	-0.163854	0.056954
36	1	0	-3.836308	-0.204991	1.149080
37	7	0	-3.059961	1.005914	-0.335741
38	1	0	-3.291552	1.419379	-1.233441
39	6	0	-5.271068	-0.063347	-0.453547
40	8	0	-5.512112	0.743863	-1.390474
41	8	0	-6.102401	-0.844465	0.083014
42	6	0	-2.206506	1.657253	0.473086
43	8	0	-1.944469	1.269930	1.625862
44	6	0	-1.615024	2.928708	-0.080748
45	1	0	-2.344741	3.737489	0.037392
46	1	0	-0.717843	3.183416	0.485486
47	1	0	-1.375954	2.836229	-1.144240
48	1	0	0.175882	-2.237692	2.658342

Standard orientation of TS-3-Cl-NacTyr-p-C5

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-3-Cl-NacTyr-p-C5

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -350.71 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.317352	0.219476	-2.378134
2	8	0	-1.677844	-2.386266	1.141471
3	1	0	-1.022212	-3.092008	1.005718
4	17	0	-1.088771	-0.990720	-0.142851
5	8	0	-4.091525	0.606561	-2.109974
6	1	0	-3.703345	-0.260276	-2.364954
7	1	0	-3.369347	1.096405	-1.652048
8	8	0	-4.034534	-2.725650	-0.161197
9	1	0	-3.184084	-2.690005	0.343935
10	1	0	-4.486954	-1.880509	0.066131
11	8	0	-3.206462	-1.993294	-2.677492
12	1	0	-3.467095	-2.320560	-1.779843
13	1	0	-2.236298	-1.967515	-2.664714
14	6	0	-0.587477	0.533819	-1.635323
15	6	0	0.098999	2.282064	-0.075989
16	6	0	1.788681	0.931842	-1.215170
17	6	0	1.406734	1.953561	-0.288595
18	1	0	2.183382	2.478513	0.264703
19	1	0	1.052318	-0.516997	-2.594878
20	8	0	-2.187497	2.010144	-0.673737
21	6	0	-0.978894	1.652140	-0.802307
22	6	0	0.800191	0.268942	-1.886381
23	8	0	-1.416384	-0.504135	3.160690
24	1	0	-1.411235	-1.257332	2.528534
25	1	0	-1.984164	0.161263	2.720036
26	8	0	-3.210573	1.193344	1.769522
27	1	0	-3.573753	1.945880	2.263511
28	1	0	-2.820099	1.578202	0.951702
29	8	0	-5.171368	-0.224193	0.310668
30	1	0	-4.549942	0.220013	0.926460

31	1	0	-4.898560	0.105616	-0.577177
32	6	0	3.244411	0.592377	-1.386820
33	1	0	3.355926	-0.093380	-2.235107
34	1	0	3.827581	1.493972	-1.604999
35	6	0	3.857915	-0.069176	-0.131231
36	1	0	3.870584	0.652377	0.689512
37	7	0	3.098788	-1.226101	0.302159
38	1	0	3.339111	-2.113663	-0.128398
39	6	0	5.307226	-0.467144	-0.463613
40	8	0	5.542928	-1.681744	-0.700170
41	8	0	6.143313	0.474635	-0.518437
42	6	0	2.236201	-1.216770	1.333852
43	8	0	1.966783	-0.184936	1.973757
44	6	0	1.644899	-2.551225	1.712053
45	1	0	0.741594	-2.387372	2.301455
46	1	0	1.415601	-3.158066	0.831117
47	1	0	2.370387	-3.096970	2.325541
48	17	0	-0.322497	3.539386	1.058327

Standard orientation of TS-5-Cl-NacTyr-p-C3

Cartesian coordinates of the transition states optimized at the M06-2X(D3)/6-31+G(d) level:
Standard orientation of transition state of TS-5-Cl-NacTyr-p-C3

State=1-A
Charge = -2 Multiplicity = 1
Lowest Harmonic Vibrational Frequency (LHVF) = -355.37 cm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.979061	-1.047496	1.679885
2	8	0	3.325663	-1.701875	-2.025234
3	1	0	2.954750	-2.496996	-2.444506
4	17	0	1.918113	-1.202496	-0.701914
5	8	0	3.360239	0.041819	2.724294
6	1	0	3.278333	-0.913913	2.507007
7	1	0	2.674254	0.496962	2.183839
8	8	0	5.142059	-2.020879	-0.023557
9	1	0	4.534897	-1.976029	-0.802963
10	1	0	5.277554	-1.080637	0.237656
11	8	0	3.418615	-2.670205	2.022533
12	1	0	4.021679	-2.501491	1.255779
13	1	0	2.555436	-2.870153	1.626271
14	6	0	0.455928	-0.638534	0.818143
15	6	0	-0.285804	1.366790	-0.358789
16	6	0	-1.626134	-0.677138	-0.460615
17	6	0	-1.354486	0.673644	-0.851224
18	1	0	-2.030542	1.165705	-1.547591
19	1	0	-0.910244	-2.322824	0.693022
20	8	0	1.572753	1.441529	1.125911
21	6	0	0.632324	0.783701	0.592323
22	6	0	-0.738325	-1.297436	0.372586
23	8	0	3.044309	0.812630	-3.154067
24	1	0	3.134462	-0.124077	-2.866843
25	1	0	3.176619	1.325413	-2.329804
26	8	0	3.547948	2.105985	-0.695361
27	1	0	3.699550	3.063770	-0.736290
28	1	0	2.799208	1.981556	-0.067944
29	8	0	5.351386	0.612024	0.870387
30	1	0	4.833450	1.158098	0.241157

31	1	0	4.721981	0.450451	1.611285
32	6	0	-2.924412	-1.317867	-0.872278
33	1	0	-3.214459	-0.976113	-1.873713
34	1	0	-2.819022	-2.406426	-0.902012
35	6	0	-4.071050	-0.974303	0.112075
36	1	0	-3.851076	-1.416706	1.086586
37	7	0	-4.211447	0.459716	0.284168
38	1	0	-4.765736	0.944190	-0.414440
39	6	0	-5.374081	-1.582239	-0.434839
40	8	0	-6.183764	-0.811717	-1.015657
41	8	0	-5.502966	-2.828661	-0.298465
42	6	0	-3.595574	1.175381	1.239575
43	8	0	-2.914307	0.652716	2.141189
44	6	0	-3.755440	2.671138	1.165397
45	1	0	-4.095526	3.042270	2.135736
46	1	0	-2.770602	3.107264	0.964884
47	1	0	-4.451164	2.987174	0.385610
48	17	0	-0.019636	3.027569	-0.822892
