Supplementary Information

Design of Rotational Potential in Phenyltriptycene Molecular Rotor by Exploiting CH/π-Interaction between Tripticil Hydrogen and Phenyl

Hazuki Inami,[a] Yusuke Inagaki,[a] and Wataru Setaka*,[a]

[a] *Division of Applied Chemistry, Faculty of Urban Environmental Sciences, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan*

E-mail: wsetaka@tmu.ac.jp

(Total 36 pages including this cover page)

1. Experimental Procedure

All reactions were conducted under an argon atmosphere. The chemical shifts of ^{1}H and ^{13}C NMR spectra are based on the residual solvent resonances. Preparatory ger permeation chromatography (GPC) was carried out using a recycling preparative chromatograph; chloroform stabilized with ethanol was used as the eluent. Commercially available reagents were used without further purification.

Synthesis of 3,5-dinitrophenyl-9-anthracene (17)

A 2 M Na_2CO_3 aqueous solution (100 mL) was added to a solution of 9-bromoantracene (**15**, 5.25 g, 20.4 mmol), 2-(3,5-dinitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**16**, 5.00 g, 17.0 mmol), and $PdCl_2(PPh_3)_2$ (50 mg) in tetrahydrofuran (200 mL). After stirring at 60 °C for 30 h, the reaction mixture was cooled to room temperature. The volatile materials were removed in vacuo and the residue was extracted with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. The concentrated residue was purified by silica gel column chromatography (with chloroform as the eluent), and pure 9-(3,5-dinitrophenyl)anthracene (**17**, 2.06 g, 5.97 mmol, 35.2%) was obtained as yellow crystals. In this column chromatography, 9-bromoantracene (**15**) was recovered.

17: yellow crystals; mp 194-196 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.22 (s, 1H), 8.64 (s, 2H), 8.62 (s, 1H), 8.10 (d, J = 8.5 Hz, 2H), 7.51 (dd, J = 8.5, 7.0 Hz, 2H), 7.43 (t, J = 7.0 Hz, 2H), 7.42 (d, J = 7.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) δ 148.8, 143.0, 131.7, 131.2, 130.7, 129.8, 129.0, 128.9, 127.0, 125.6, 124.8, 118.1; HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{12}N_2O_2$: 345.0870, found: 345.0882.

Synthesis of 9-(3,5-dinitrophenyl)triptycene (12)

In a flask, 9-(3,5-dinitrophenyl)anthracene (**17**) (1.70 g, 4.94 mmol) was dissolved in 1,2-dichloroethane (80 mL). The flask was heated and the reaction mixture was stirred at 40 °C. A 1,2-dichloroethane (70 mL) solution of isoamyl nitrite (2.32 g, 19.8 mmol) and a 1,2-dimethoxyethane (100 mL) solution of anthranilic acid (2.03 g, 14.8 mmol) were simultaneously added dropwise to the flask over 2 h at 40 °C. After stirring at 40 °C for 48 h, the reaction mixture was cooled to room temperature. Volatile materials were removed in vacuo. Chloroform was added to the residue, and the remaining crude product was filtered. The crude product was purified using silica gel column chromatography (silica gel, dichloroethane as the eluent). Pure 9-(3,5-dinitrophenyl)triptycene (**12**, 0.463 g, 1.10 mmol, 22.3%) was obtained by recrystallization from dichloromethane as pale yellow crystals.

12: pale yellow crystals, mp > 300 °C; ^{1}H NMR ($C_2D_2Cl_4$, 500 MHz) δ 9.29 (d, J = 2.0 Hz, 2H), 9.18 (t, J = 2.0 Hz, 1H), 7.48 (d, J = 7. 0 Hz, 3H), 7.04-7.10 (m, 3H), 6.95-7.02 (m, 6H), 5.47 (s, 1H); ^{13}C{^{1}H} NMR ($C_2D_2Cl_4$, 126 MHz) δ 149.0, 146.5, 144.9, 141.5, 131.5, 126.9, 125.6, 124.9, 123.4, 118.3, 60.1, 54.9; HRMS (APCI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{26}H_{16}N_2O_4$, 421.1183; Found, 421.1167.

Synthesis of 9-(3,5-diaminophenyl)triptycene (13)

In an autoclave, hydrogen gas (3 atm) was introduced into a mixture of 9-(3,5-dinitrophenyl)anthracene (**12**) (0.10 g, 0.24 mmol), dichloroethane (20 mL), methanol (10 mL), and 10% Pd/C (0.05 g). The mixture was then allowed to stand for 72 h at 60 °C. After the excess H_2 gas was released, the mixture was filtered to remove Pd/C. Volatile materials were removed in vacuo. Pure 9-(3,5-dinitrophenyl)anthracene (**13**, 0.051 mg, 1.41 mmol, 59% yield) was obtained by column chromatography (silica gel, ethyl acetate as the eluent), followed by recrystallization from toluene.

13: colorless crystals, mp 275 °C (decomp.); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (d, J = 7.5 Hz, 3H), 7.37 (d, J = 7.5 Hz, 2H), 6.96 (t, J = 7.5 Hz, 3H), 6.91 (d, J = 7.5 Hz, 3H), 6.86 (s, 2H), 6.21 (s, 1H), 5.35 (s, 1H), 3.74 (br, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 147.4, 146.8, 146.7, 138.5, 125.0, 124.9, 124.4, 123.4, 109.6, 100.8, 60.3, 55.2; HRMS (APCI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{26}H_{20}N_2$, 361.1699; Found, 361.1691.

Synthesis of 1-Chloro-10-(3,5-dimethoxyphenyl)anthracene (20)

1-Chloroanthrone (**18**, 1.17 g, 5.15 mmol) was dissolved in dry tetrahydrofuran (THF, 12 mL) in a flask equipped with a magnetic stirrer, condenser, and dropping funnel. A 1 M THF solution of 3,5-dimethoxyphenyl bromide (200 mL) prepared from the corresponding 1-bromo-3,5-dimethoxybenzene (**19**, 5.34 g, 24.6 mmol) and magnesium (634 mg, 26.1 mmol) was introduced dropwise into the reaction flask. The reaction mixture was stirred for 2 h under reflux. The mixture was hydrolyzed using 10% H_2SO_4 (aq) and extracted with dichloromethane (DCM). The organic layer was washed with saturated $NaHCO_3$ (aq) and concentrated. The residue and acetic acid (5 mL) were placed in a flask and refluxed for 30 min. The mixture was washed with water and extracted with dichloromethane. The organic layer was then dried over anhydrous Na_2SO_4. After the removal of Na_2SO_4, the solution was concentrated, and the crude products were obtained as a yellow oil. Pure compound **20** (1.02 g, 2.93 mmol, 56.9%) was obtained after column chromatography (silica gel, chloroform:hexane = 2:1 as the eluent), followed by purification via gel permeation chromatography (GPC).

20: colorless crystals, mp 137–138 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.92 (s, 1H), 8.10 (d, J = 8.5 Hz, 3H), 7.71 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.49 (dd, J = 8.5, 7.0 Hz, 1H), 7.39 (dd, J = 8.5, 7.0 Hz, 1H), 7.23 (dd, J = 8.0, 7.0 Hz, 1H), 6.62 (t, J = 2.3 Hz, 1H), 6.56 (d, J = 2.3 Hz, 2H), 3.81 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 160.8, 140.5, 137.6, 132.0, 131.7, 130.7, 130.3, 128.8, 128.6, 126.8, 126.4, 126.2, 125.8, 125.1, 124.6, 123.7, 109.2, 99.9, 55.4; HRMS (APCI-TOF) m/z: $[M]^+$ Calcd for $C_{22}H_{17}ClO_2$, 348.0912; Found, 348.0906.

Synthesis of 1,4,5-Trichloro-9-(3,5-dimethoxyphenyl)triptycene (14)

A 1,2-dichloroethane (8 mL) solution of 1-chloro-10-(3,5-dimethoxyphenyl)anthracene (**20**, 0.15 g, 0.43 mmol) (1.70 g, 4.94 mmol) was placed in a flask. A 1,2-dichloroethane (6 mL) solution of isoamyl nitrite (0.20 g, 1.7 mmol) and a 1,2-dimethoxyethane (9 mL) solution of 3,6-dichloroanthranilic acid (0.26 g, 37 mmol) were simultaneously added dropwise to the flask over 6 h at 150 °C. After stirring for 20 h, the reaction mixture was allowed to cool to room temperature. Volatile materials were removed in vacuo. The crude products were obtained after recrystallization from the methanol solution of the residue. Pure 1,4,5-trichloro-9-(3,5-dimethoxyphenyl)triptycene (**14**, 0.095 g, 0.19 mmol, 45%) was obtained as colorless crystals by column chromatography (silica gel, chloroform as the eluent), followed by GPC purification and recrystallization from methanol.

14: colorless crystals, mp 185–186 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, 300 K) δ 7.53 (dd, J = 7.4, 1.0 Hz, 1H, H_{16}), 7.25 (dd, J = 7.5, 1.0 Hz, 1H, H_{13}), 7.10 (dd, J = 7.4, 1.0 Hz, 1H, H_6), 7.08 (td, J = 7.4, 1.0 Hz, 1H, H_{15}), 7.04 (dd, J = 7.5, 7.4 Hz, 1H, H_{14}), 7.03 (d, J = 1.8 Hz, 2H, H_{Ph2}), 6.97 (d, J = 7.7, 1.0 Hz, 1H, H_3), 6.92 (d, J = 7.7, 1.0 Hz, 1H, H_2), 6.92 (dd, J = 7.4, 1.0 Hz, 1H, H_8), 6.89 (t, J = 7.4, 1.0 Hz, 1H, H_7), 6.61 (t, J = 1.8 Hz, 1H, H_{Ph4}), 6.55 (s, 1H, H_{10}), 3.84 (s, 6H, H_{Me}); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 160.2 (C_{Ph3}), 148.9 (C_{8a}), 147.1 (C_{4a}), 145.6 (duplicated, C_{9a} and C_{12}), 144.0 (C_{11}), 141.8 (C_{10a}), 137.7 (C_{Ph1}), 129.7 (C_5), 129.6 (C_2), 129.1 (C_4), 128.5 (C_1), 126.8 (C_3), 126.4 (C_6), 126.1 (C_7), 125.9 (C_{15}), 125.7 (C_{13}), 125.6 (C_{14}), 124.4 (C_{16}), 124.2 (C_8), 110.4 (C_{Ph2}), 99.2 (C_{Ph4}), 61.7 (C_9), 55.4 (C_{Me}), 48.1 (C_{10}); HRMS (APCI-TOF) m/z: $[M]^+$ Calcd for $C_{28}H_{19}Cl_3O_2$, 493.0523; Found, 493.0541.

2. Copies of NMR and HRMS Spectra for New Compounds

a. Spectra of 3,5-Dinitrophenyl-9-anthracene (17)

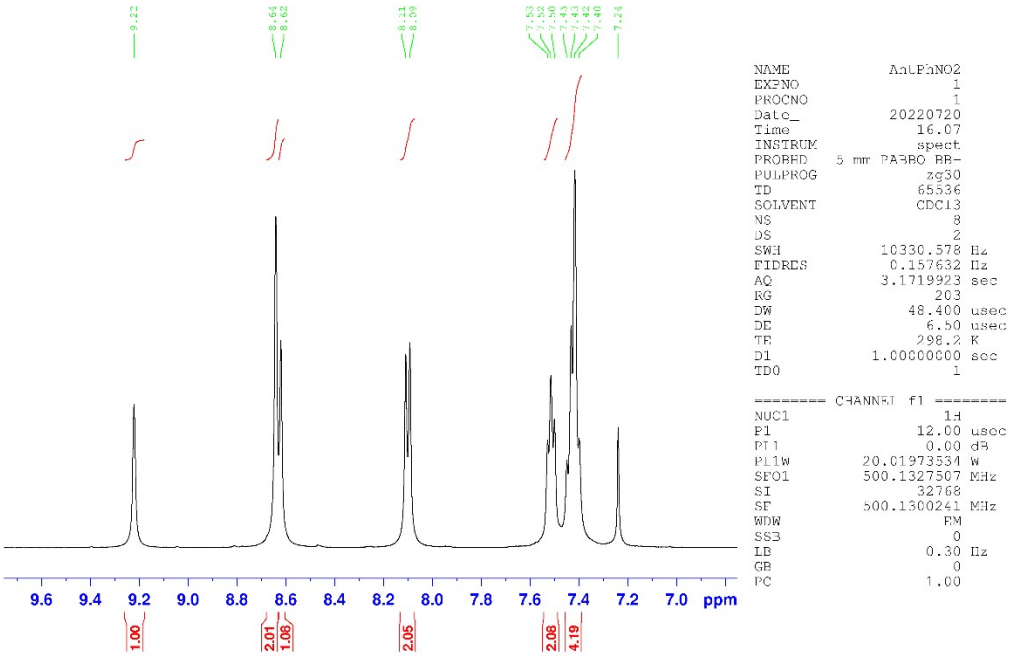

Fig. S1. ^{1}H NMR spectrum of dinitrophenylanthracene **17** in $CDCl_3$.

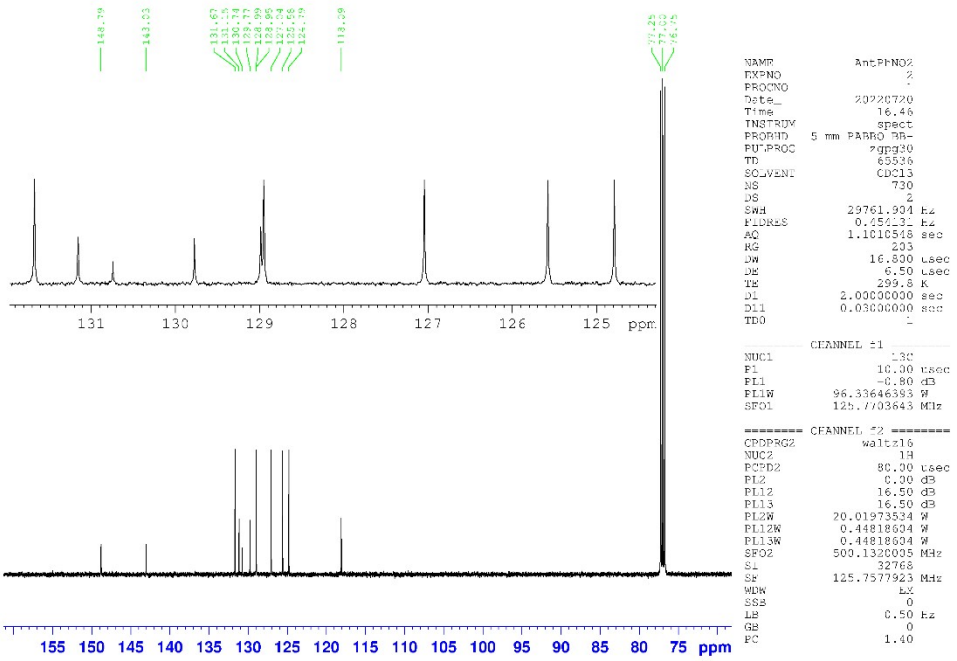

Fig. S2. ^{13}C NMR spectrum of dinitrophenylanthracene **17** in $CDCl_3$.

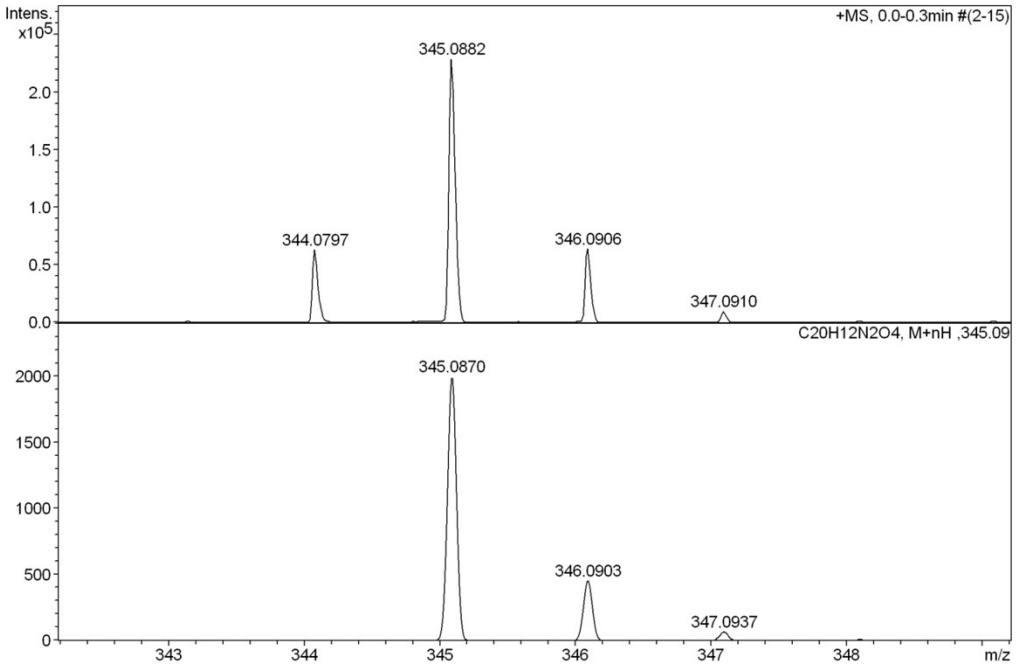

Fig. S3. HRMS spectrum of dinitrophenylanthracene **17** (APCI, positive). Top: obsd. Bottom: sim.

b. Spectra of 9-(3,5-dinitrophenyl)triptycene (12)

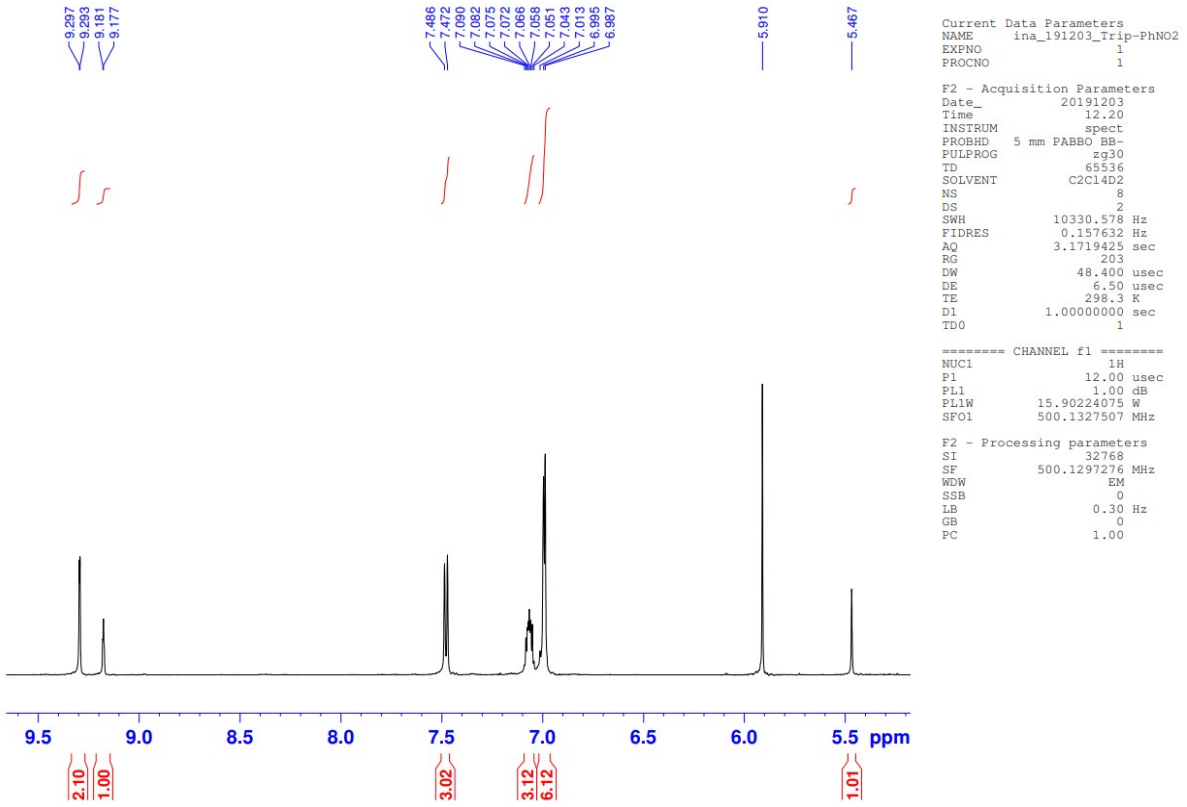

Fig. S4. ^{1}H NMR spectrum of dinitrophenyltriptycene **12** in $C_2Cl_4D_2$.

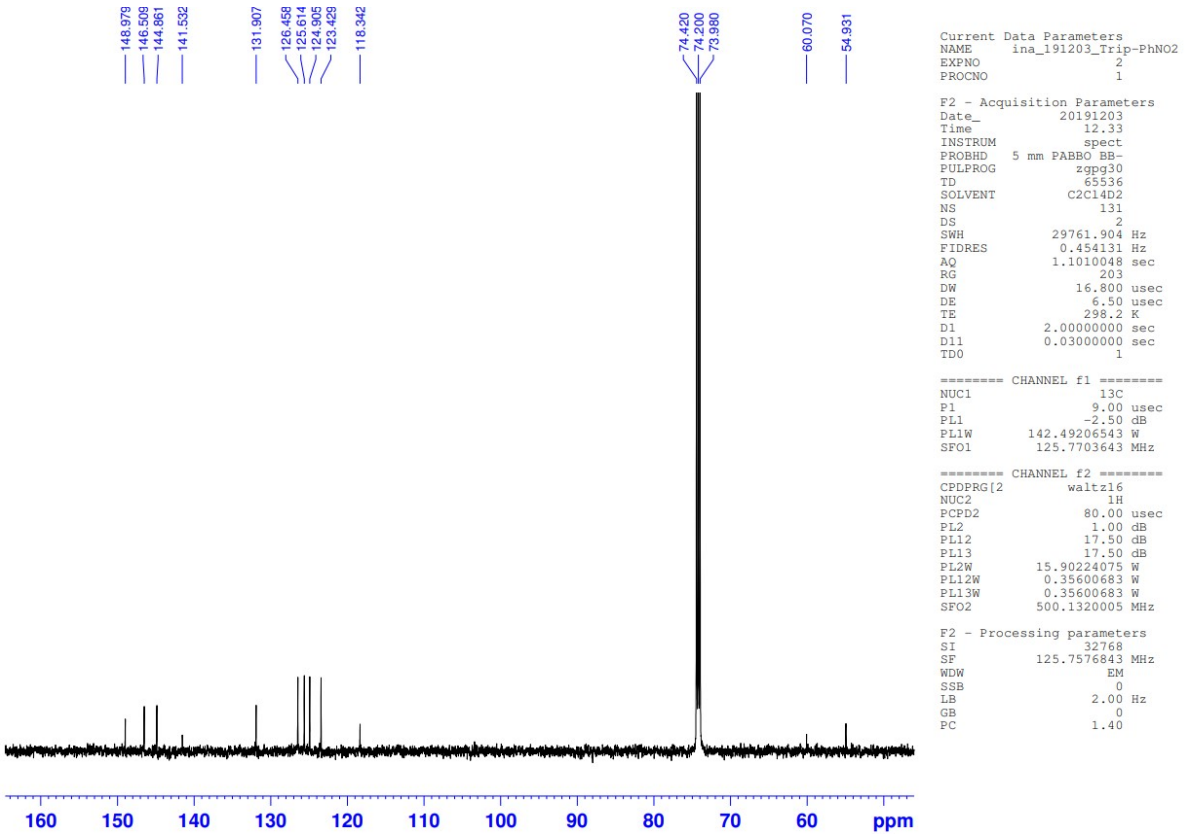

Fig. S5. ^{13}C NMR spectrum of dinitrophenyltriptycene **12** in $C_2Cl_4D_2$.

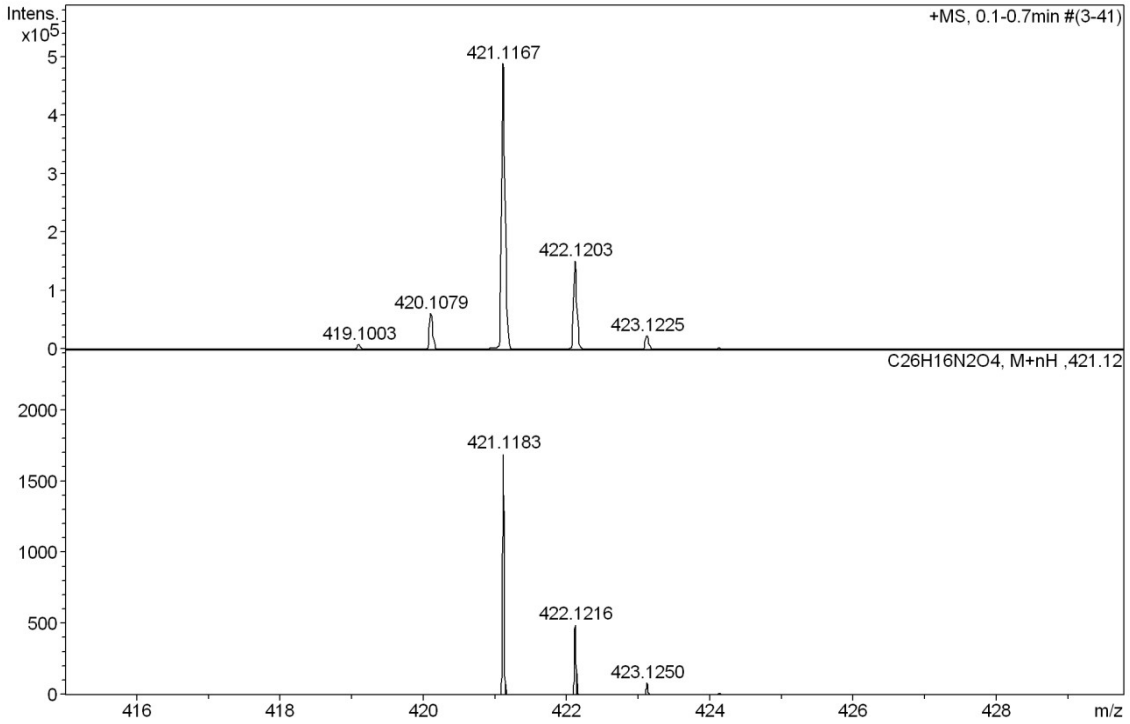

Fig. S6. HRMS spectrum of dinitrophenyltriptycene **12** (APCI, positive). Top: obsd. Bottom: sim.

c. Spectra of 9-(3,5-diaminophenyl)triptycene (13)

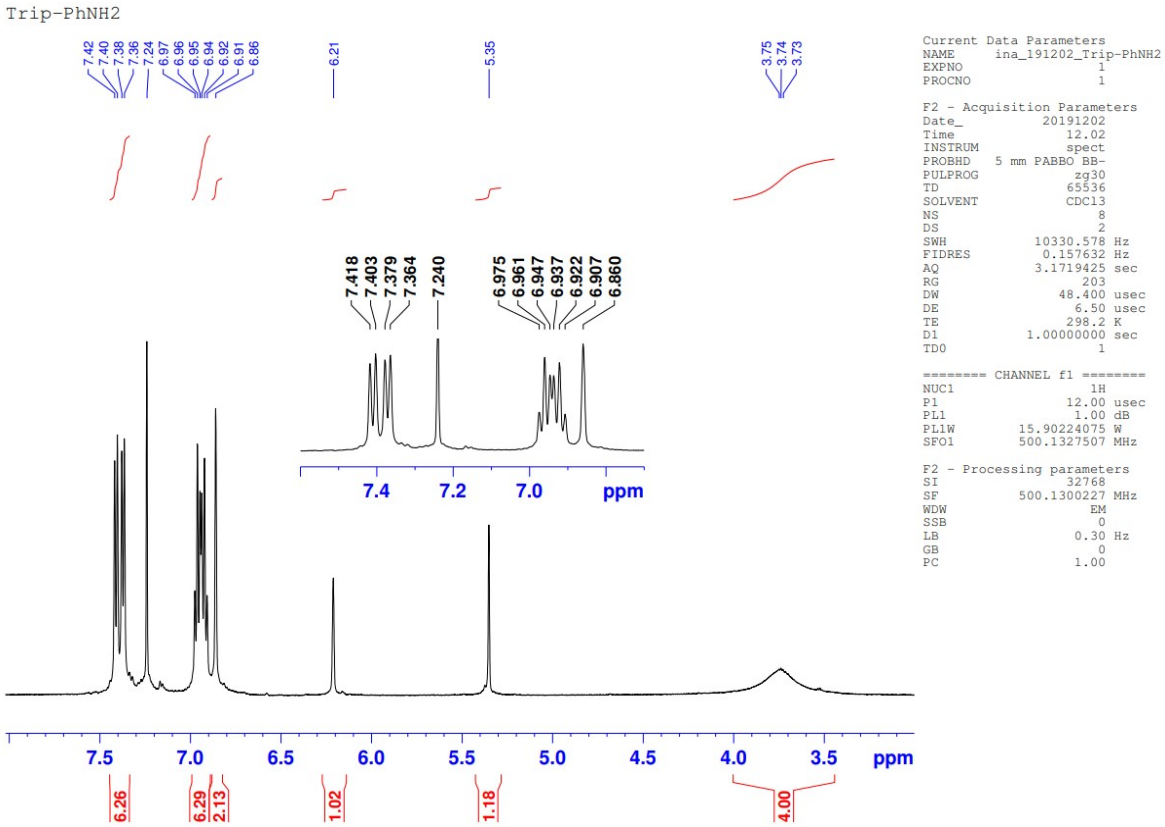

Fig. S7. ^{1}H NMR spectrum of diaminophenyltriptycene **13** in $CDCl_3$.

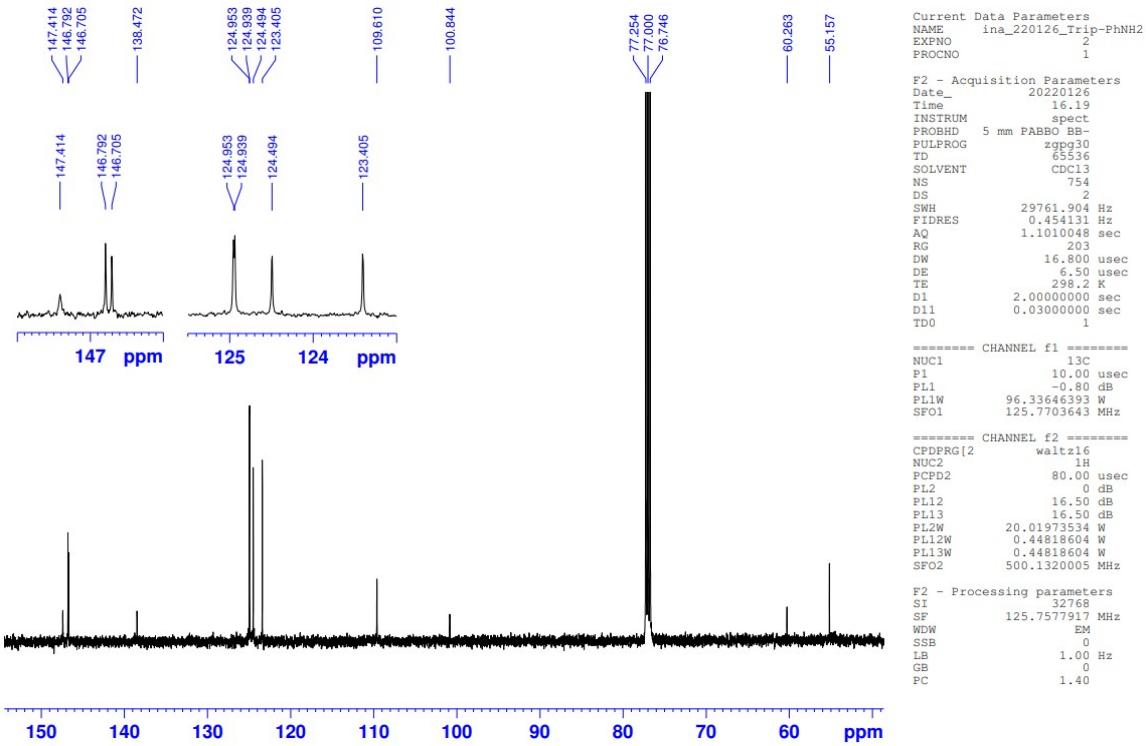

Fig. S8. ^{13}C NMR spectrum of diaminophenyltriptycene **13** in $CDCl_3$.

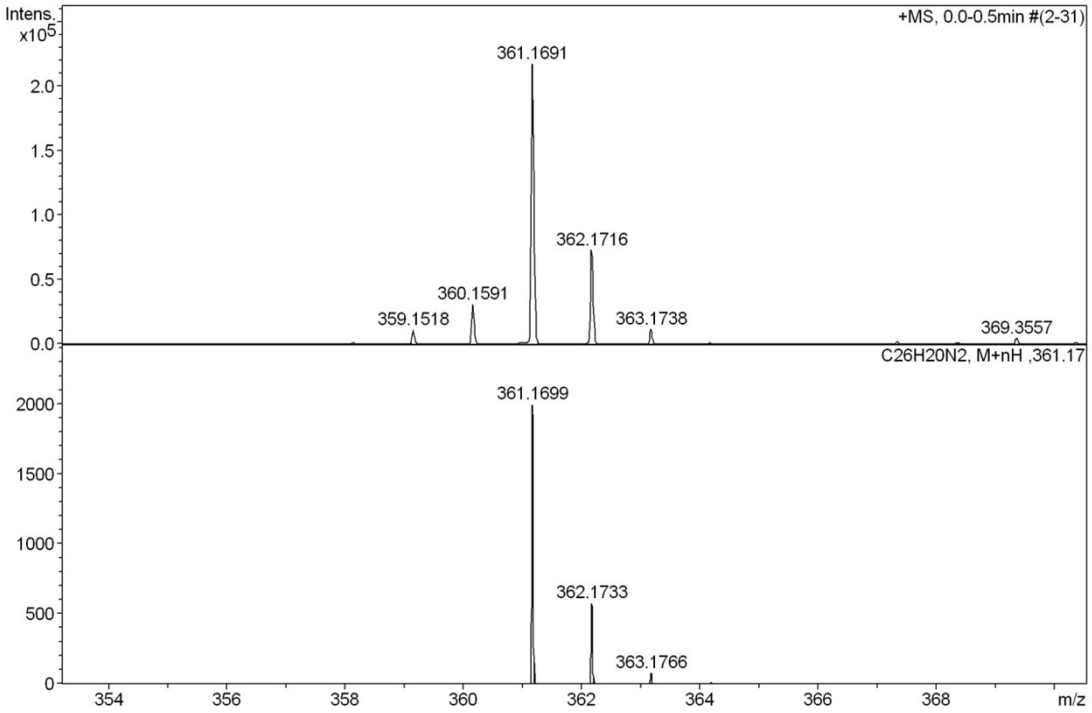

Fig. S9. HRMS spectrum of diaminophenyltriptycene **13** (APCI, positive). Top: obsd. Bottom: sim.

d. Spectra of 1-Chloro-10-(3,5-dimethoxyphenyl)anthracene (20)

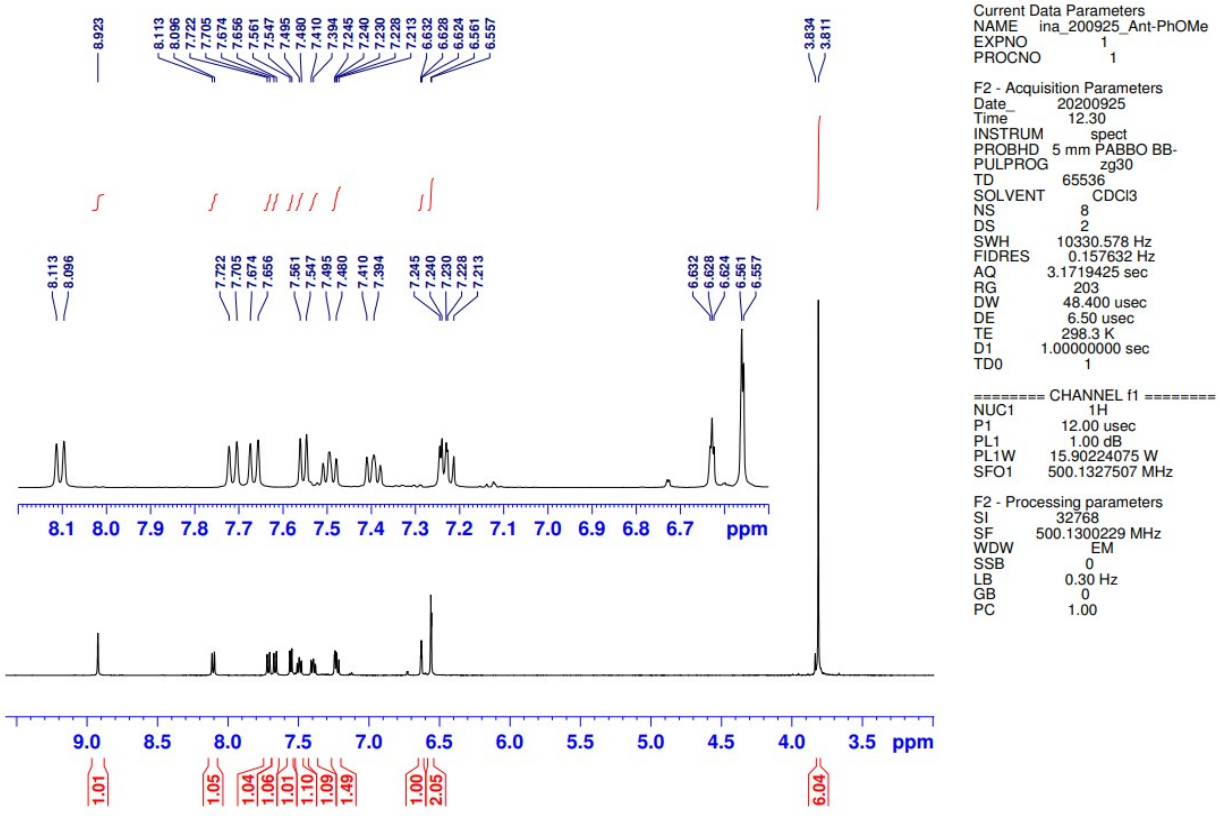

Fig. S10. ^{1}H NMR spectrum of chloro(dimethoxyphenyl)anthracene **20** in $CDCl_3$.

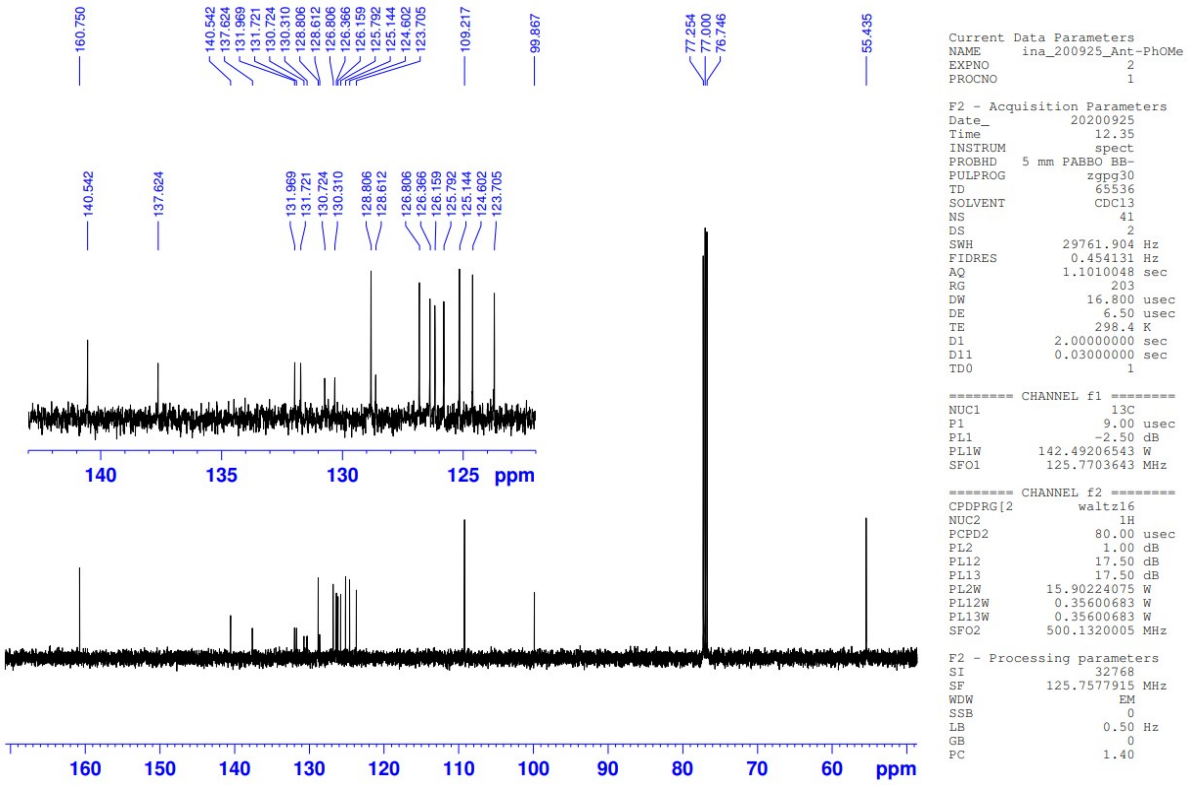

Fig. S11. ^{13}C NMR spectrum of chloro(dimethoxyphenyl)anthracene **20** in $CDCl_3$.

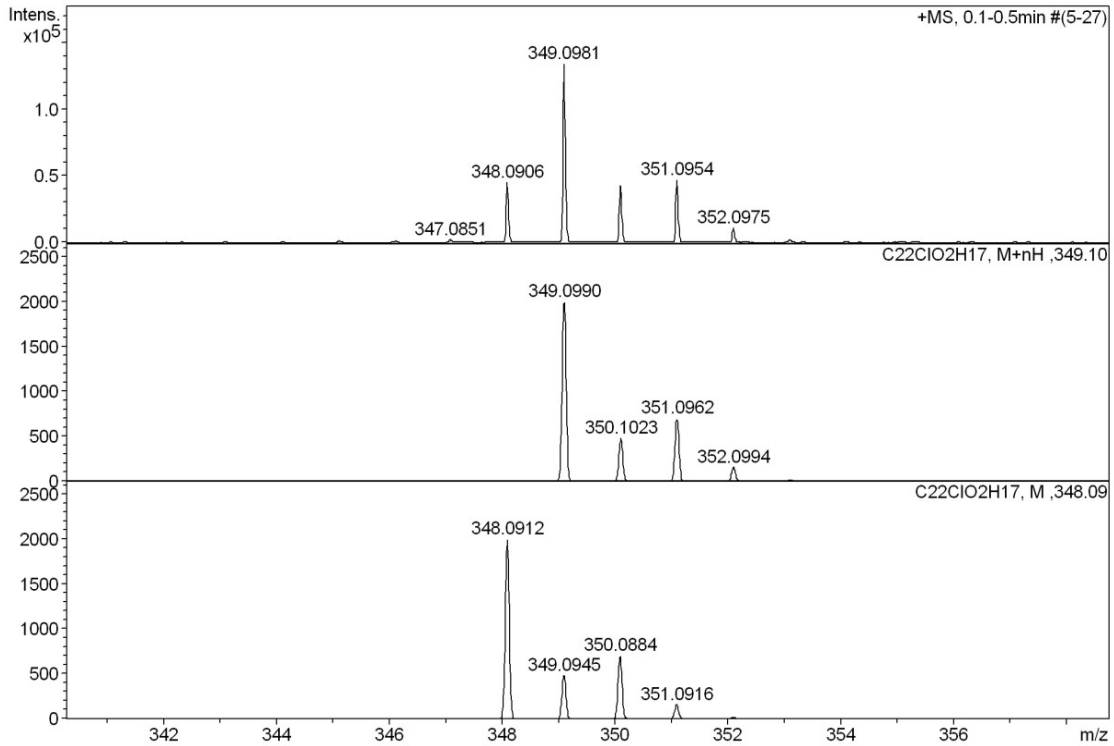

Fig. S12. HRMS spectrum of chloro(dimethoxyphenyl)anthracene **20** (APCI, positive). Top: obsd. Bottom: sim.

e. Spectra of 1,4,5-Trichloro-9-(3,5-dimethoxyphenyl)triptycene (14)

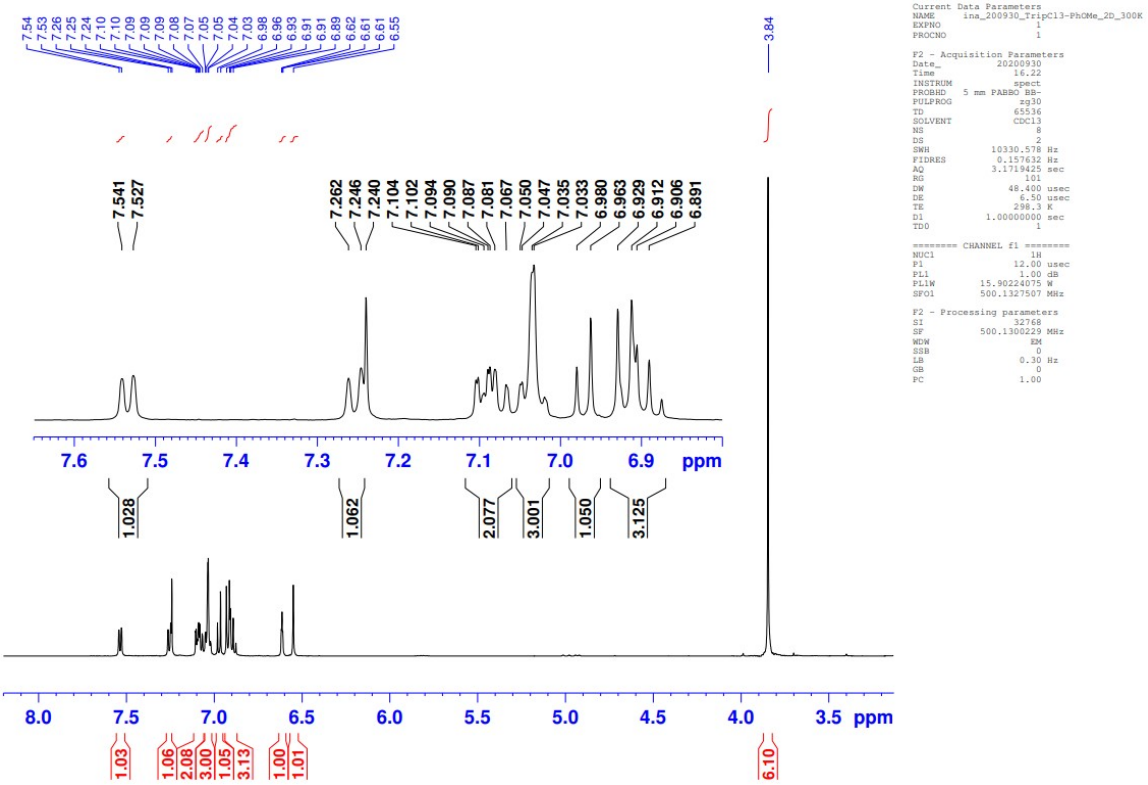

Fig. S13. ^{1}H NMR spectrum of trichloro(dimethoxyphenyl)triptycene **14** in $CDCl_3$.

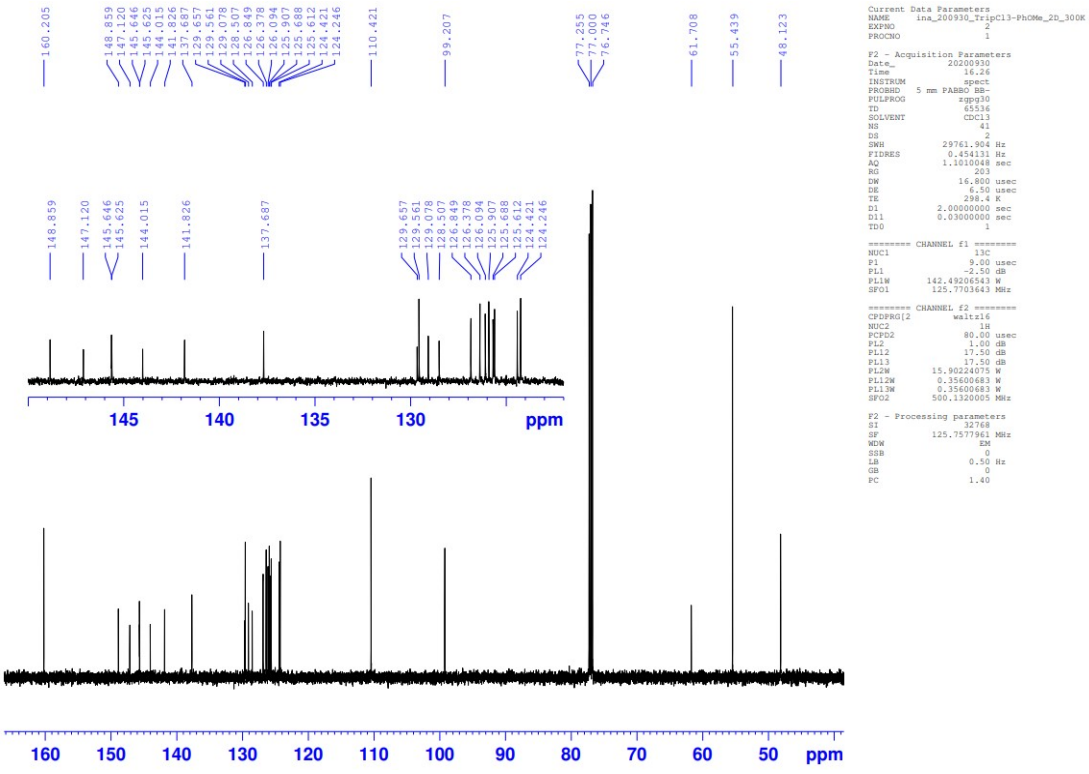

Fig. S14. ^{13}C NMR spectrum of trichloro(dimethoxyphenyl)triptycene **14** in $CDCl_3$.

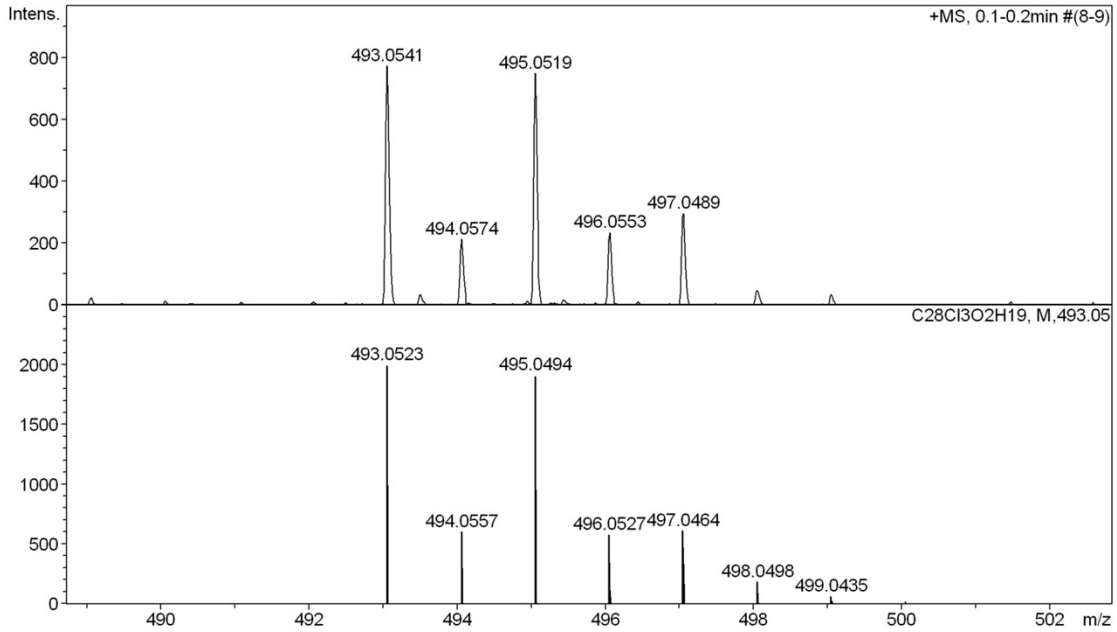

Fig. S15. HRMS spectrum of trichloro(dimethoxyphenyl)triptycene **14** (APCI, positive). Top: obsd. Bottom: sim.

3. Details of NMR Studies

3-1. Temperature dependent ^{1}H NMR of dinitrotriptycene 12 and diaminotriptycene 13

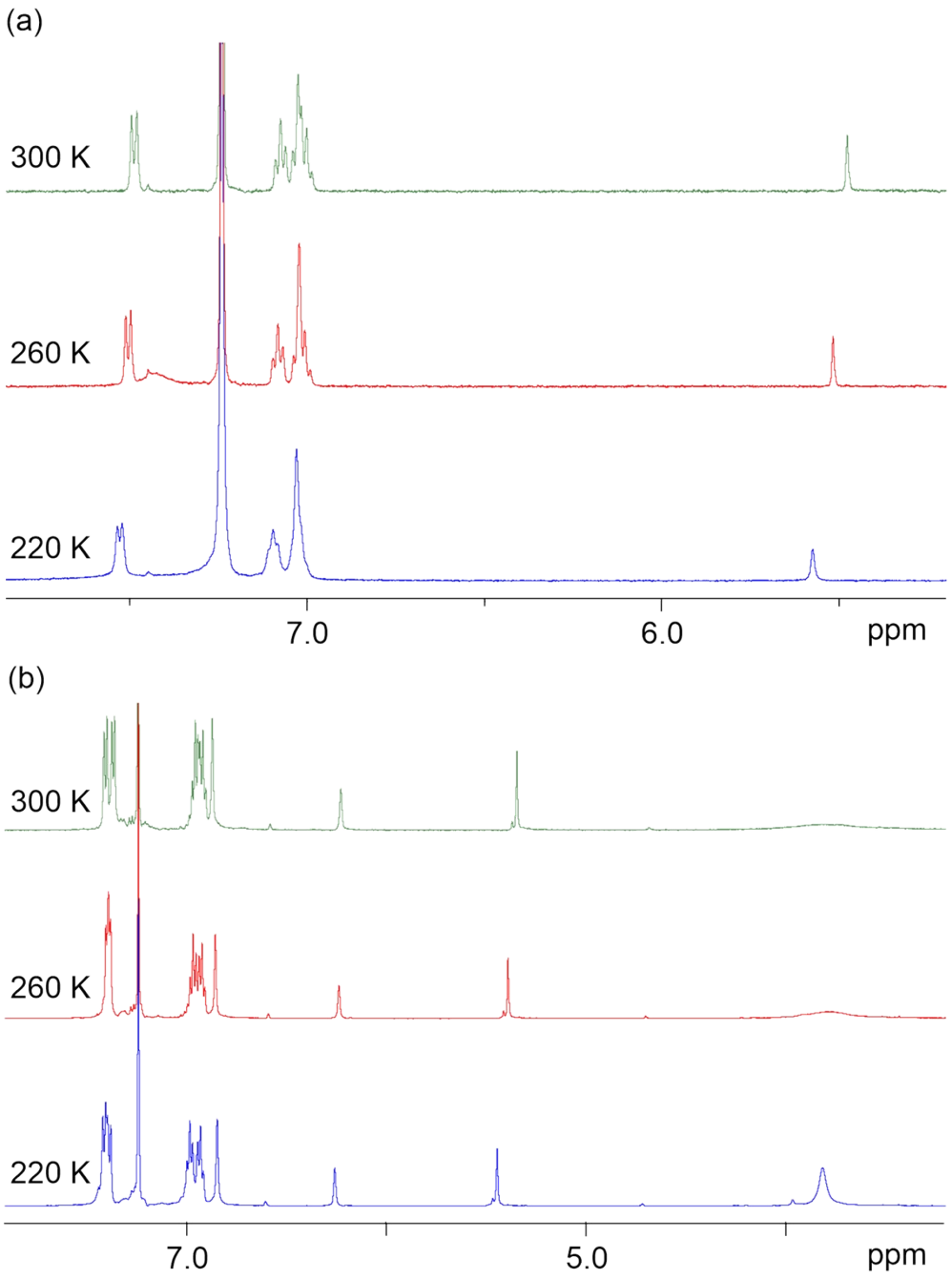

Fig. S16. Temperature dependent ^{1}H NMR of (a) dinitrotriptycene **12** and (b) diaminotriptycene **13**.

3-2. Assignments of NMR signals of trichloro(dimethoxyphenyl)triptycene 14

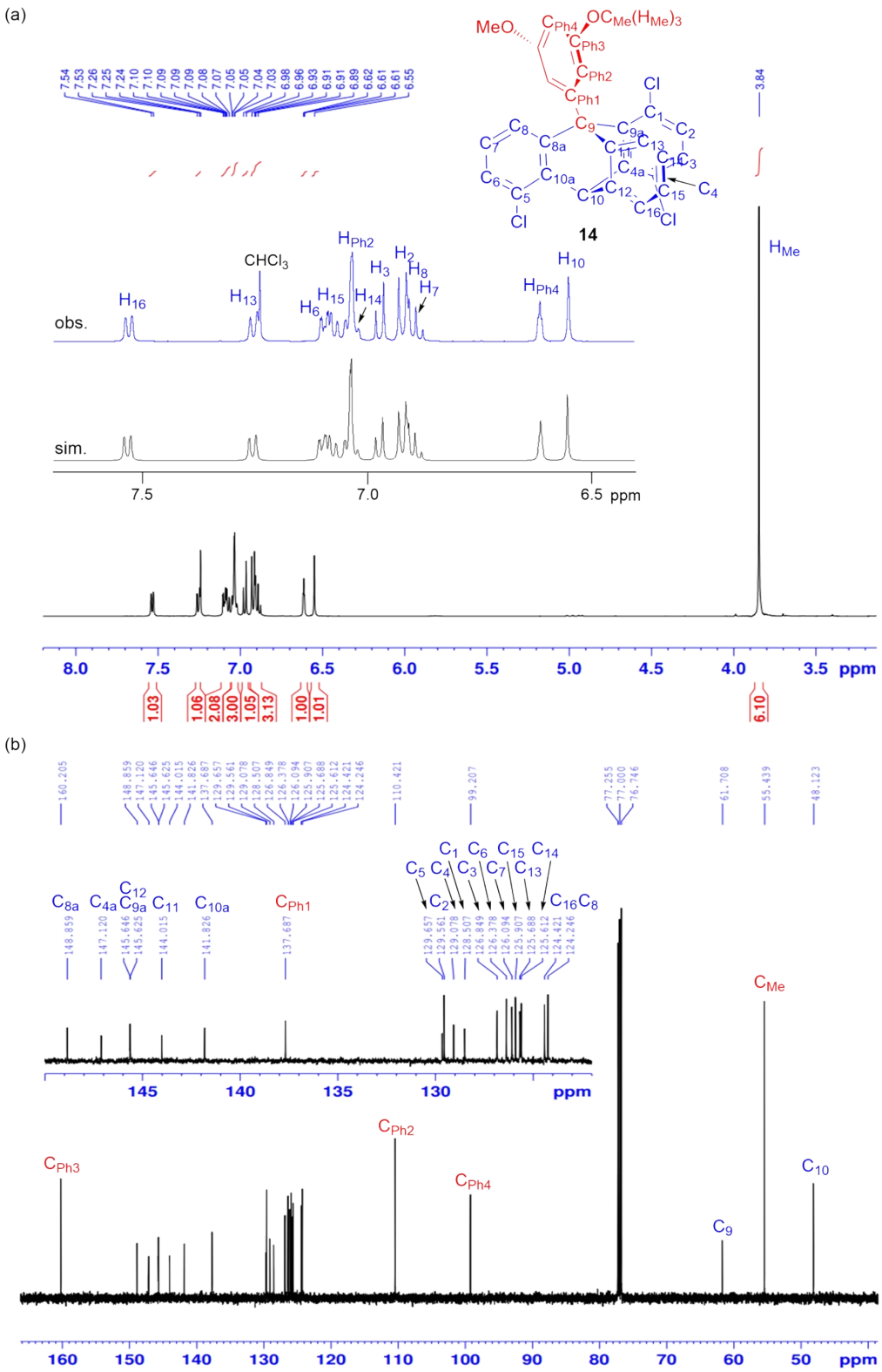

Fig. S17. NMR signals assignments for trichloro(dimethoxyphenyl)triptycene **14**: (a) ^{1}H NMR (The simulation was carried out using parameters described in the sysnthesis section.) , (b) ^{13}C NMR.

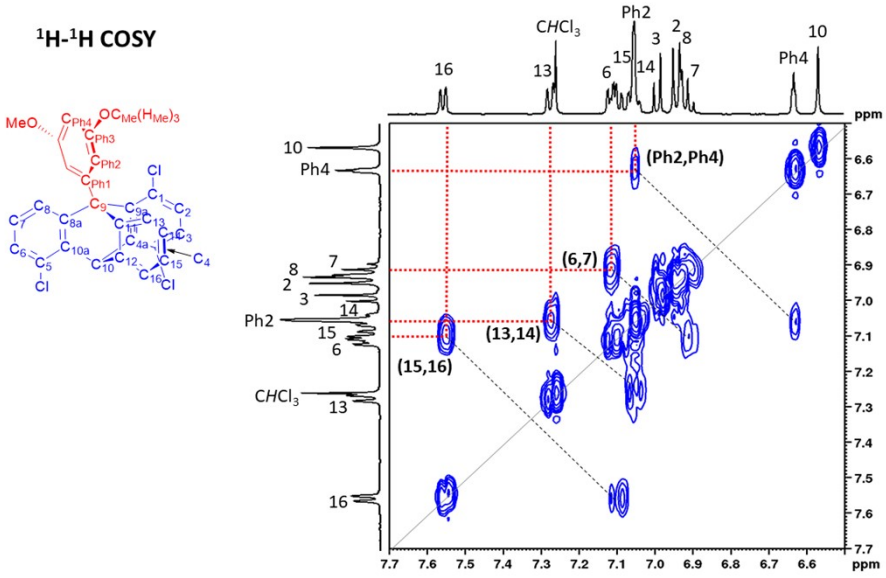

Fig. S18. ^{1}H-^{1}H COSY NMR spectum of trichloro(dimethoxyphenyl)triptycene **14** for signals assignments.

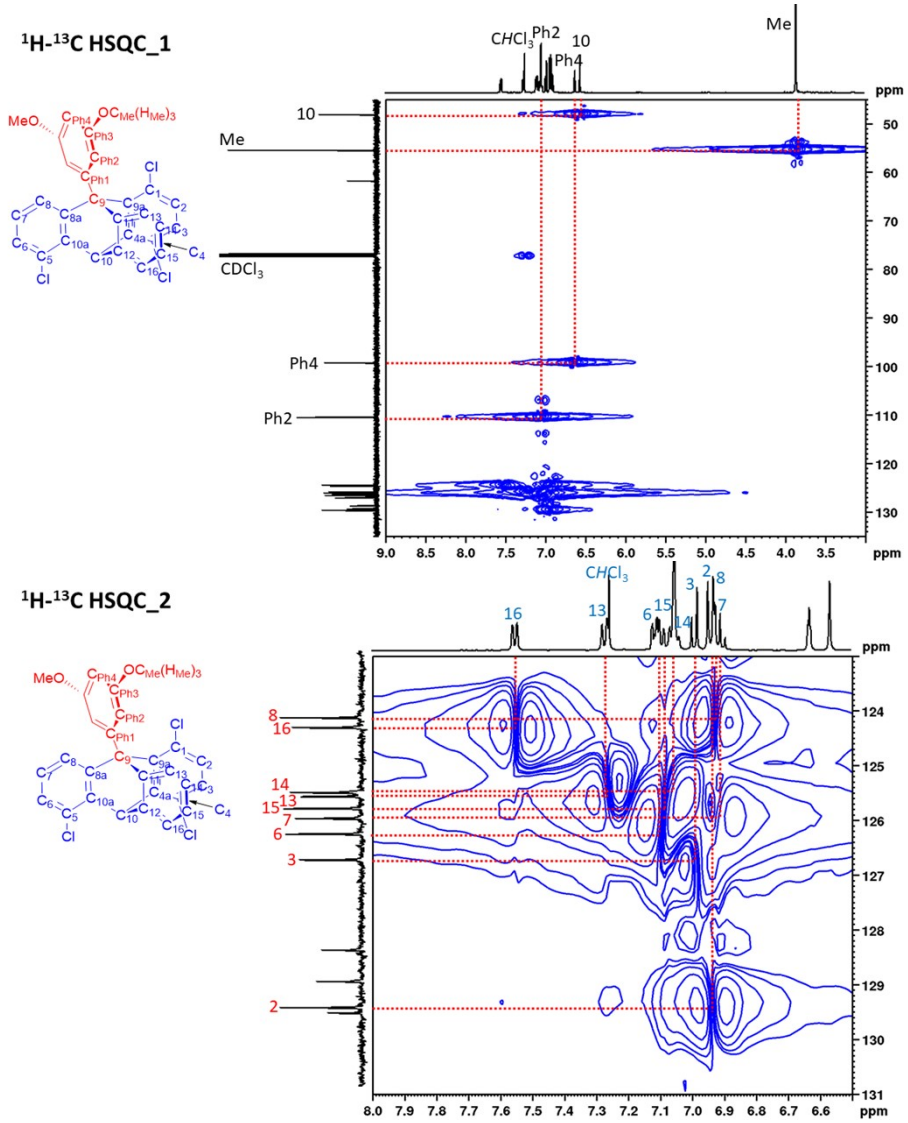

Fig. S19. ^{1}H-^{13}C HSQC NMR specta of trichloro(dimethoxyphenyl)triptycene **14** for signals assignments.

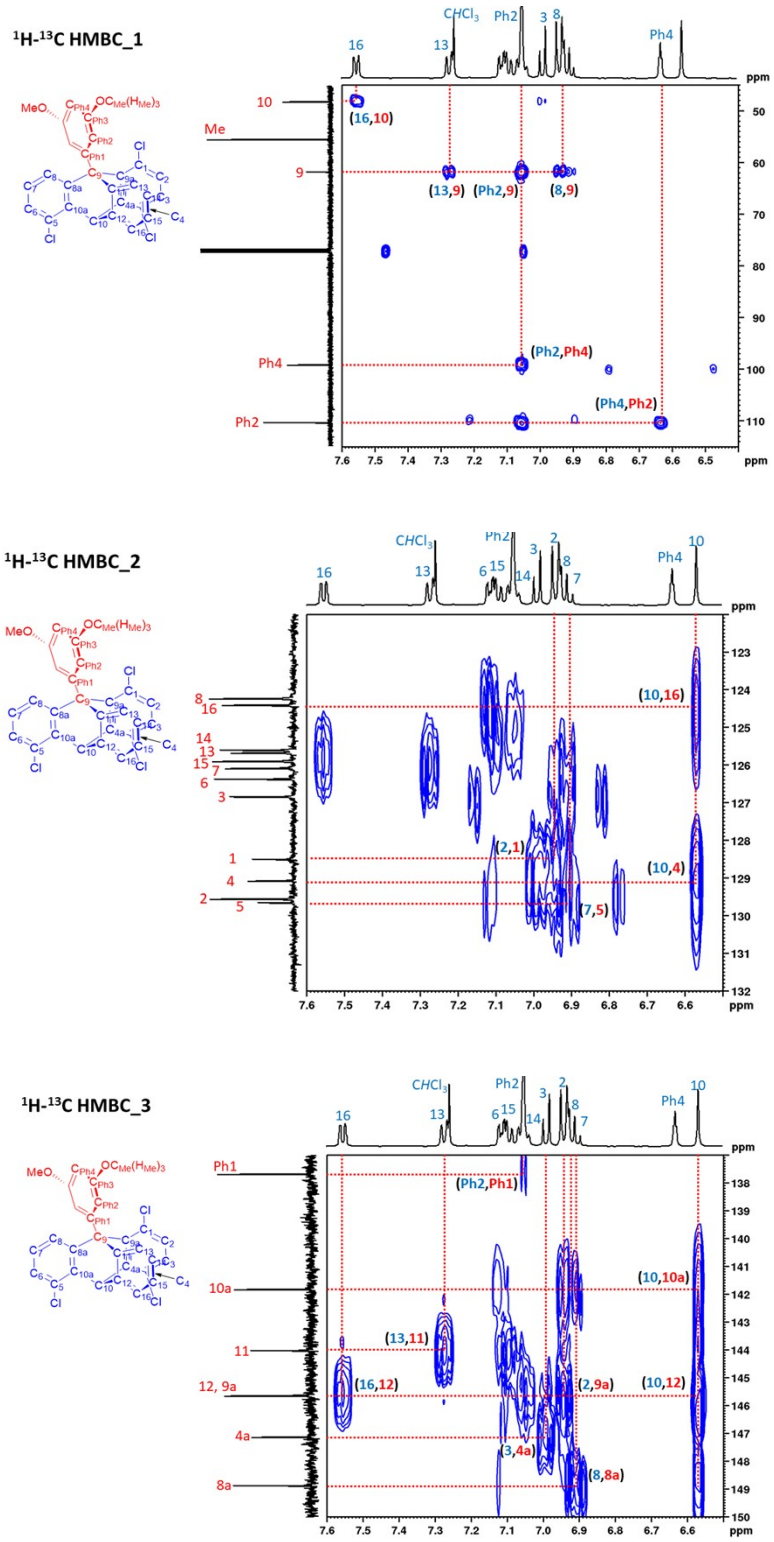

Fig. S20. ^{1}H-^{13}C HMBC NMR specta of trichloro(dimethoxyphenyl)triptycene **14** for signals assignments.

3-3. Analysis for the rotational dynamics in trichloro(dimethoxyphenyl)triptycene 14

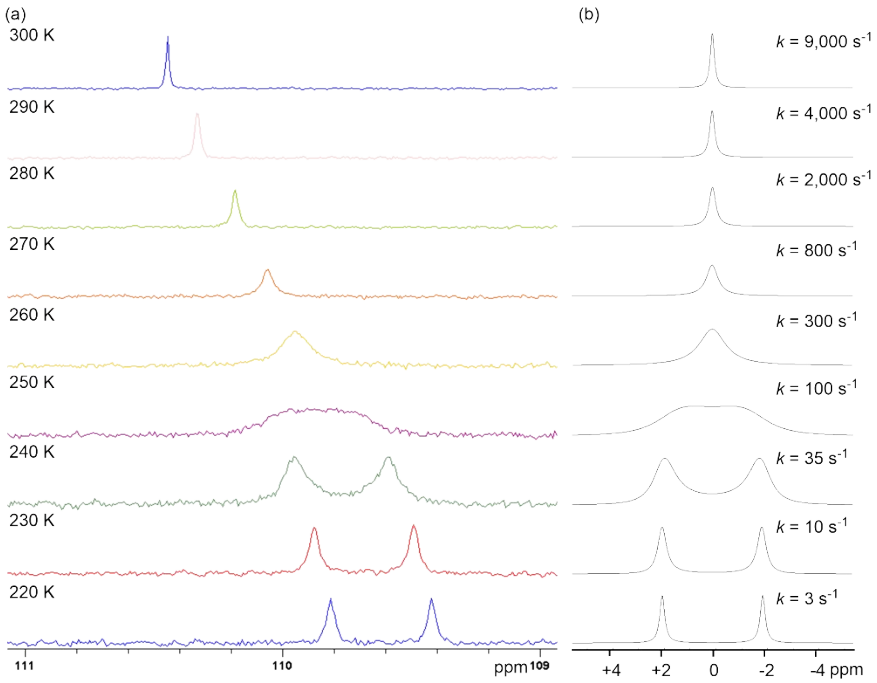

Fig. S21. Details of emperature dependent ^{13}C NMR spectra of **14** (ortho-carbons of 3,5-dimethoxy-1-phenylene) (a) observed (b) simulation with exchange rates.

An activation energy for the ring flipping/rotation could be estimated the slope of an Eyring plot for temperature dependent exchange rates determined in **Fig. S21**. From the plots, the following parameters were determined (errors are shown as standard deviations):

$$\Delta H^{\ddagger} = 12.7 \pm 0.10 \text{ kcal mol}^{-1}, \Delta S^{\ddagger} = 1.98 \pm 0.36 \text{ cal mol}^{-1} \text{ K}^{-1}$$

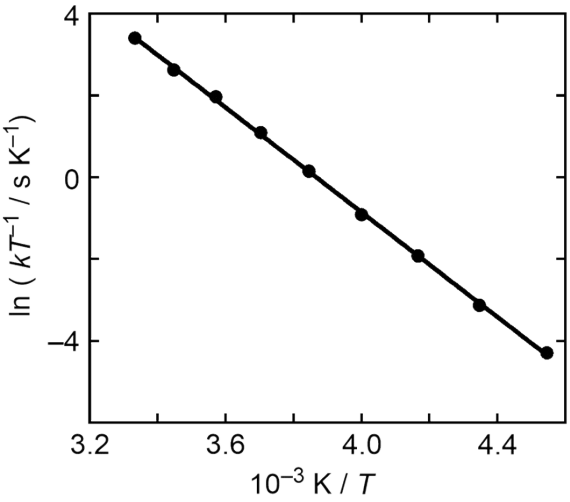

Fig. S22. Eyring plot for temperature dependent exchange rates for the rotation of the rotor in compound **11**.

4. Details of X-ray Crystallography

4-1. Crystal Data

Table S1. Crystal Data

Compound		dinitrophenyltriptycene **12**	diaminophenyltriptycene **13**	trichloro(dimethoxyphenyl)triptycene **14**
CCDC #		2182983	2182984	2182985
Empirical formula		C26 H16 N2 O4	C26 H20 N2	C28 H19 Cl3 O2
Temperature		100 K	100 K	173 K
Crystal shape & Color		Prism, colorless	Prism, colorless	Prism, colorless
Crystal size		0.250 x 0.210 x 0.080 mm^3	0.280 x 0.230 x 0.100 mm^3	0.370 x 0.220 x 0.170 mm^3
Formula weight / g mol^{-1}		420.41	360.44	493.78
Crystal system		Orthorhombic	Triclinic	Orthorhombic
Space group		*Pnma*	*P*-1	$Pca2_1$
Z		4	6	8
Calculated density		1.480 Mg/m^3	1.312 Mg/m^3	1.419 Mg/m^3
Cell parameter	*a*	17.026(3) Å	8.58090(10) Å	15.5816(4) Å
	b	13.546(2) Å	16.4594(3) Å	9.3605(2) Å
	c	8.1803(14) Å	20.4778(4) Å	31.6875(8) Å
	α	90°	105.1070(10)°	90°
	β	90°	97.6730(10)°	90°
	γ	90°	96.1400(10)°	90°
	V	1886.7(6) $Å^3$	2736.72(8) $Å^3$	4621.67(19) $Å^3$
F(000)		872	1140	2032
Absorption coefficient		0.829 mm^{-1}	0.591 mm^{-1}	3.784 mm^{-1}
θ range for collection		8.890 to 74.521° (CuKα)	2.267 to 72.424° (CuKα)	2.789 to 74.596° (CuKα)
Index ranges		-20<=h<=21, -16<=k<=16, -9<=l<=8	-10<=h<=8, -20<=k<=20, -25<=l<=25	-19<=h<=19, -11<=k<=11, -39<=l<=38
Reflections collected		15105	23640	38013
Independent reflections		1914 [R(int) = 0.0432]	10346 [R(int) = 0.0302]	8907 [R(int) = 0.0508]
Completeness		95.4 %	97.6 %	99.9 %
Goodness-of-fit on F^2		1.054	1.027	1.090
Final R indices [I>2sigma(I)]		R1 = 0.0393, wR2 = 0.0964	R1 = 0.0467, wR2 = 0.1175	R1 = 0.0600, wR2 = 0.1566
R indices (all data)		R1 = 0.0394, wR2 = 0.0965	R1 = 0.0539, wR2 = 0.1225	R1 = 0.0638, wR2 = 0.1590

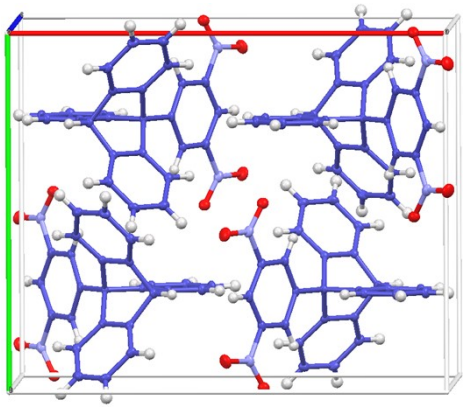

Fig. S23. Crystal packing structure of dinitrophenyltriptycene **12**.

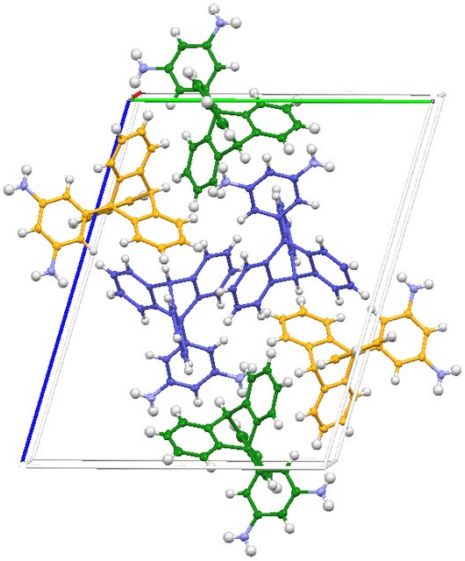

Fig. S24. Crystal packing structure of diaminophenyltriptycene **13**.

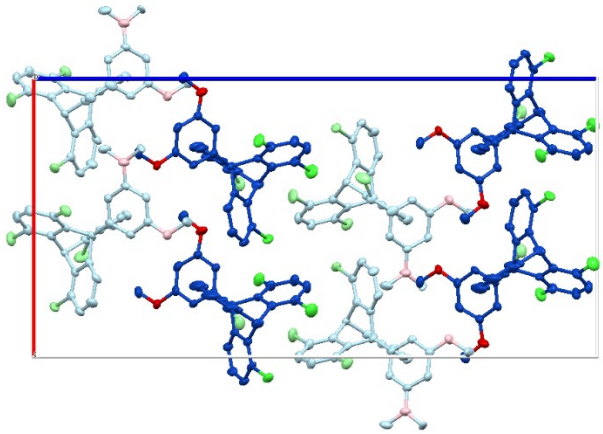

Fig. S25. Crystal packing structure of trichloro(dimethoxyphenyl)triptycene **14**.

5. Details of DFT Calculations

All calculation were carried out using Gaussian 16 (Revision C.01) program packages[S1] at the Research Center for Computational Science, Okazaki, Japan. All structural optimizations in this study were carried out using Opt=tight option that tightens the cutoffs on forces and step size.

S1: Gaussian 16, Revision C.01,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

Table S2. Calculated NPA Charges of *peri*-Hydrogens on Compounds **12** and **13**

Level of theory	**12**			**13**		
	H1 [b]	H8 [b]	H13 [b]	H1 [b]	H8 [b]	H13 [b]
ω97XD/6-311++G(d,p)	0.212	0.124	0.124	0.226	0.222	0.221
PCM[a]-ω97XD/6-311+12+G(d,p)	0.217	0.219	0.219	0.227	0.226	0.225
B3LYP-D3/6-311++G(d,p)	0.208	0.211	0.211	0.221	0.218	0.216
PCM[a]-B3LYP-D3/6-311++G(d,p)	0.213	0.215	0.215	0.222	0.221	0.220

[a] in chloroform.
[b] The atom numbring was shown below:

Compound **12** Compound **13**

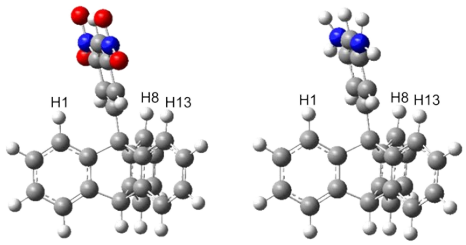

Table S2. Optimized Structural Coordinate and its Total Energy for **12** at ω97XD/6-311++G(d,p) level
total energy: HF= -1410.4956193 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.079541	0.000003	2.479178
2	6	0	-0.986332	0.000001	1.429630
3	6	0	-0.645825	0.000000	-0.081809
4	6	0	-2.353078	0.000001	1.704943
5	6	0	-3.202734	0.000000	0.459739
6	6	0	-0.544440	0.000004	3.793876
7	6	0	-1.905709	0.000004	4.059334
8	6	0	-2.818731	0.000002	3.007264
9	6	0	-1.409114	-1.197600	-0.700884
10	6	0	-2.769251	-1.201041	-0.364520
11	6	0	-3.619898	-2.175173	-0.851472
12	6	0	-0.938596	-2.133383	-1.609267
13	6	0	-1.797045	-3.115435	-2.105168
14	6	0	-3.125699	-3.152045	-1.714173
15	6	0	-1.409114	1.197598	-0.700886
16	6	0	-2.769252	1.201040	-0.364522
17	6	0	-3.619899	2.175171	-0.851476
18	6	0	-0.938597	2.133380	-1.609271
19	6	0	-1.797046	3.115431	-2.105173
20	6	0	-3.125700	3.152041	-1.714179
21	6	0	0.865050	0.000000	-0.221371
22	6	0	1.586235	-1.193020	-0.175689
23	6	0	1.586235	1.193021	-0.175689
24	6	0	2.971103	-1.170741	-0.180888
25	6	0	2.971104	1.170741	-0.180889
26	6	0	3.704427	-0.000000	-0.197523
27	7	0	3.698403	-2.458759	-0.153289
28	7	0	3.698403	2.458759	-0.153291
29	1	0	0.988517	0.000003	2.299096
30	1	0	-4.272002	0.000000	0.671843
31	1	0	0.167756	0.000005	4.610922
32	1	0	-2.259792	0.000005	5.083835
33	1	0	-3.885830	0.000002	3.203315
34	1	0	-4.670005	-2.163369	-0.578834
35	1	0	0.083019	-2.110777	-1.965881
36	1	0	-1.415766	-3.848989	-2.806034
37	1	0	-3.786185	-3.920615	-2.098712
38	1	0	-4.670006	2.163366	-0.578838
39	1	0	0.083018	2.110774	-1.965884
40	1	0	-1.415767	3.848984	-2.806041
41	1	0	-3.786187	3.920611	-2.098719
42	1	0	1.088930	-2.148857	-0.097766
43	1	0	1.088931	2.148857	-0.097767
44	1	0	4.784859	-0.000000	-0.203380
45	8	0	4.909932	-2.414016	-0.120315
46	8	0	3.035540	-3.475234	-0.167170
47	8	0	4.909932	2.414016	-0.120319
48	8	0	3.035540	3.475234	-0.167170

Table S3. Optimized Structural Coordinate and its Total Energy for **13** at ω97XD/6-311++G(d,p) level
total energy: HF= -1112.2286987 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.250090	-0.008022	1.625753
2	6	0	1.277773	-0.011010	2.557838
3	6	0	2.794403	-0.006449	2.241438
4	6	0	0.968243	-0.015867	3.916646
5	6	0	2.192512	-0.013830	4.795183
6	6	0	-1.074724	-0.011797	2.059850
7	6	0	-1.374739	-0.018420	3.415101
8	6	0	-0.345231	-0.020079	4.352940
9	6	0	3.393478	1.186420	3.030406
10	6	0	3.025129	1.188824	4.382773
11	6	0	3.495022	2.157826	5.249448
12	6	0	4.321255	2.117656	2.588479
13	6	0	4.802268	3.093041	3.462992
14	6	0	4.376691	3.130666	4.781600
15	6	0	3.402119	-1.198206	3.025938
16	6	0	3.033372	-1.208909	4.378080
17	6	0	3.510002	-2.177861	5.241166
18	6	0	4.337469	-2.120472	2.580533
19	6	0	4.824904	-3.095926	3.451444
20	6	0	4.398882	-3.142305	4.769650
21	6	0	2.959255	-0.003881	0.727681
22	6	0	2.912170	1.195758	0.021182
23	6	0	2.925058	-1.203366	0.019696
24	6	0	2.901765	1.202502	-1.376433
25	6	0	2.914727	-1.209375	-1.377222
26	6	0	2.922755	-0.002989	-2.073895
27	7	0	2.804355	2.410859	-2.064647
28	7	0	2.940690	-2.419531	-2.069515
29	1	0	0.467834	-0.000243	0.564898
30	1	0	1.956606	-0.016674	5.859882
31	1	0	-1.874943	-0.008055	1.328169
32	1	0	-2.407874	-0.021058	3.744299
33	1	0	-0.565958	-0.023825	5.415514
34	1	0	3.196195	2.142895	6.292632
35	1	0	4.694791	2.084686	1.573716
36	1	0	5.522111	3.820504	3.104520
37	1	0	4.750275	3.893957	5.454853
38	1	0	3.210724	-2.169183	6.284305
39	1	0	4.711838	-2.082135	1.566252
40	1	0	5.549883	-3.816590	3.089748
41	1	0	4.777716	-3.905693	5.439876
42	1	0	2.818541	2.137810	0.545219
43	1	0	2.853035	-2.147252	0.543731
44	1	0	2.921820	-0.003125	-3.160132
45	1	0	3.135456	2.397196	-3.016158
46	1	0	3.126409	3.221089	-1.559707
47	1	0	2.547069	-2.395459	-2.996955
48	1	0	2.623840	-3.218906	-1.543573

Table S4. Optimized Structural Coordinate and its Total Energy for phenyltriptycene at ω97XD/6-311++G(d,p) level
total energy: HF= -1001.5076009 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.188894	2.314910	-0.000008
2	6	0	-0.163736	1.380276	-0.000007
3	6	0	-0.332856	-0.159666	0.000002
4	6	0	1.159888	1.817639	-0.000013
5	6	0	2.151078	0.682496	-0.000008
6	6	0	-0.882819	3.675316	-0.000017
7	6	0	0.437530	4.102268	-0.000024
8	6	0	1.469034	3.166302	-0.000022
9	6	0	0.506910	-0.684726	-1.193016
10	6	0	1.817873	-0.189229	-1.199327
11	6	0	2.723077	-0.576682	-2.169464
12	6	0	0.152589	-1.651740	-2.121641
13	6	0	1.066441	-2.049003	-3.098700
14	6	0	2.338512	-1.500344	-3.139810
15	6	0	0.506915	-0.684711	1.193024
16	6	0	1.817877	-0.189213	1.199324
17	6	0	2.723086	-0.576653	2.169462
18	6	0	0.152598	-1.651712	2.121664
19	6	0	1.066454	-2.048962	3.098724
20	6	0	2.338525	-1.500303	3.139822
21	6	0	-1.821233	-0.475216	0.000005
22	6	0	-2.546331	-0.507950	-1.193995
23	6	0	-2.546331	-0.507946	1.194006
24	6	0	-3.927918	-0.656235	-1.196669
25	6	0	-3.927917	-0.656231	1.196681
26	6	0	-4.625904	-0.750206	0.000007
27	1	0	-4.459688	-0.682126	-2.141357
28	1	0	-4.459687	-0.682120	2.141370
29	1	0	-2.225095	1.999680	-0.000003
30	1	0	3.188309	1.019001	-0.000012
31	1	0	-1.687256	4.402243	-0.000018
32	1	0	0.667136	5.161914	-0.000031
33	1	0	2.505719	3.487187	-0.000027
34	1	0	3.733136	-0.180095	-2.157736
35	1	0	-0.820488	-2.123496	-2.089006
36	1	0	0.775451	-2.799807	-3.824774
37	1	0	3.042150	-1.809413	-3.904453
38	1	0	3.733144	-0.180066	2.157724
39	1	0	-0.820479	-2.123469	2.089039
40	1	0	0.775467	-2.799757	3.824809
41	1	0	3.042166	-1.809361	3.904466
42	1	0	-2.036547	-0.373451	-2.138763
43	1	0	-2.036546	-0.373443	2.138774
44	1	0	-5.703576	-0.868305	0.000007

Table S5. Optimized Structural Coordinate and its Total Energy for *m*-dinitrobenzene at ω97XD/6-311++G(d,p) level
total energy: HF= -641.2076232 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.102708	-1.807584	-0.345875
2	6	0	1.118534	-1.154155	-0.442703
3	6	0	1.170529	0.205998	-0.177703
4	6	0	0.053373	0.939342	0.179738
5	6	0	-1.144465	0.252736	0.265477
6	6	0	-1.246981	-1.106399	0.010153
7	7	0	-2.361864	1.002812	0.645083
8	8	0	-3.400196	0.378523	0.713567
9	8	0	-2.241526	2.189419	0.862181
10	7	0	2.470279	0.905255	-0.279978
11	8	0	2.484904	2.093989	-0.042628
12	8	0	3.435383	0.240530	-0.595044
13	1	0	-0.163031	-2.869228	-0.549019
14	1	0	2.024044	-1.678042	-0.718180
15	1	0	0.113603	1.999368	0.382565
16	1	0	-2.209882	-1.592562	0.092366

Table S6. Optimized Structural Coordinate and its Total Energy for *m*-diaminobenzene at ω97XD/6-311++G(d,p) level
total energy: HF= -342.9409943 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.642623	-0.005376	2.410542
2	6	0	0.320989	-0.005932	1.412357
3	6	0	0.051930	0.000869	-0.113374
4	6	0	1.669512	-0.010212	1.764011
5	6	0	2.585715	-0.005462	0.567677
6	6	0	-0.249956	-0.010982	3.748215
7	6	0	1.095308	-0.017015	4.090244
8	6	0	2.064729	-0.016233	3.090416
9	6	0	0.858142	1.195350	-0.685679
10	6	0	2.198391	1.198229	-0.275423
11	6	0	3.078444	2.168694	-0.716552

12	6	0	0.444507	2.127756	-1.625250
13	6	0	1.332735	3.104628	-2.077241
14	6	0	2.637430	3.142607	-1.610778
15	6	0	0.855971	-1.189261	-0.698312
16	6	0	2.195993	-1.199491	-0.287687
17	6	0	3.074314	-2.166968	-0.738797
18	6	0	0.440669	-2.110344	-1.648560
19	6	0	1.327154	-3.084300	-2.110236
20	6	0	2.631504	-3.130327	-1.643477
21	6	0	-1.455967	0.002499	-0.325246
22	6	0	-2.164607	1.201495	-0.298228
23	6	0	-2.163654	-1.197605	-0.315036
24	6	0	-3.561875	1.207105	-0.331306
25	6	0	-3.560211	-1.204746	-0.348187
26	6	0	-4.257322	0.001094	-0.375939
27	7	0	-4.253812	2.414751	-0.253403
28	7	0	-4.250333	-2.415411	-0.397638
29	1	0	-1.696196	0.001913	2.159906
30	1	0	3.642560	-0.007843	0.836594
31	1	0	-1.006185	-0.009139	4.525284
32	1	0	1.392203	-0.021088	5.133118
33	1	0	3.119923	-0.019494	3.344094
34	1	0	4.111837	2.154104	-0.385434
35	1	0	-0.558114	2.094590	-2.030235
36	1	0	0.996218	3.832987	-2.806711
37	1	0	3.321333	3.907048	-1.961997
38	1	0	4.107629	-2.157949	-0.407190
39	1	0	-0.561504	-2.072202	-2.054246
40	1	0	0.988803	-3.804061	-2.847283
41	1	0	3.313841	-3.892556	-2.002506
42	1	0	-1.644538	2.143810	-0.186814
43	1	0	-1.641313	-2.141190	-0.228269
44	1	0	-5.343061	0.000089	-0.408804
45	1	0	-5.194548	2.400872	-0.613974
46	1	0	-3.739784	3.225912	-0.558278
47	1	0	-5.189592	-2.392727	-0.033028
48	1	0	-3.733827	-3.214885	-0.065868

Table S7. Optimized Structural Coordinate and its Total Energy for benzene at ω97XD/6-311++G(d,p) level
total energy: HF= -232.2210248 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.390839	-0.000000
2	6	0	1.204502	0.695419	-0.000000
3	6	0	1.204502	-0.695419	-0.000000
4	6	0	-0.000000	-1.390839	-0.000000
5	6	0	-1.204502	-0.695419	-0.000000
6	6	0	-1.204502	0.695419	-0.000000
7	1	0	0.000000	2.475249	-0.000000
8	1	0	2.143628	1.237624	-0.000000
9	1	0	2.143628	-1.237624	-0.000000
10	1	0	-0.000000	-2.475249	-0.000000
11	1	0	-2.143628	-1.237624	-0.000000
12	1	0	-2.143628	1.237624	-0.000000

Table S8. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer A) at ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3613937 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.856142	-0.705366	2.269290
2	6	0	-0.800417	-0.706173	2.505733
3	6	0	0.152408	-0.452114	1.527336
4	6	0	-0.127963	-0.169353	0.023066
5	6	0	1.497474	-0.474945	1.875328
6	6	0	2.397554	-0.202282	0.705040
7	6	0	-0.392898	-0.966807	3.812321
8	6	0	0.954129	-0.976083	4.148899
9	6	0	1.912173	-0.728613	3.171116
10	1	0	2.969771	-0.736081	3.411767
11	6	0	0.634481	1.132972	-0.357227
12	6	0	1.959625	1.130728	0.121790
13	6	0	2.784751	2.221081	-0.069570
14	17	0	4.417061	2.232574	0.558647
15	6	0	0.272031	2.161016	-1.222594
16	6	0	1.104789	3.267625	-1.399332
17	6	0	2.343722	3.322095	-0.795586
18	6	0	0.706354	-1.198282	-0.774639
19	6	0	2.049899	-1.223153	-0.367471
20	6	0	2.939833	-2.062711	-1.010537
21	6	0	0.306653	-1.932455	-1.878780
22	6	0	1.222082	-2.766843	-2.518994
23	6	0	2.531311	-2.855126	-2.079863
24	1	0	3.450762	-0.211918	0.967274
25	1	0	-1.141330	-1.164012	4.571495
26	1	0	1.259510	-1.178552	5.169224
27	17	0	-1.129545	2.103689	-2.269377
28	1	0	0.777140	4.073795	-2.043064
29	1	0	2.988439	4.180479	-0.932953
30	1	0	-0.698937	-1.850023	-2.266135
31	1	0	0.906589	-3.350218	-3.376147
32	1	0	3.243601	-3.506124	-2.570609
33	17	0	4.618786	-2.127255	-0.515476
34	6	0	-1.642080	-0.157528	-0.124329
35	6	0	-2.333473	0.982008	0.276120
36	6	0	-2.353992	-1.316547	-0.406223
37	6	0	-3.719494	0.985141	0.320023
38	6	0	-3.746396	-1.310021	-0.361092
39	6	0	-4.448544	-0.159588	-0.010331
40	1	0	-5.527533	-0.155606	0.017927
41	1	0	-1.812186	1.883857	0.570186
42	1	0	-1.866441	-2.257786	-0.611908
43	8	0	-4.293287	2.153384	0.702877
44	8	0	-4.343318	-2.490225	-0.666334
45	6	0	-5.698703	2.220328	0.788640
46	6	0	-5.749842	-2.568903	-0.610519
47	1	0	-5.931618	3.231693	1.117388
48	1	0	-6.169555	2.042747	-0.185095
49	1	0	-6.091644	1.505129	1.520596
50	1	0	-6.004457	-3.593783	-0.875016
51	1	0	-6.124118	-2.353595	0.396999
52	1	0	-6.218943	-1.885827	-1.327996

Table S9. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer B) at ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3578748 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-2.015576	2.267837	-1.204302
2	6	0	-0.279938	2.157105	-0.981862
3	6	0	0.421007	1.111486	-0.369526
4	6	0	-0.080226	-0.230253	0.276154
5	6	0	1.819920	1.251477	-0.298113
6	6	0	2.515663	0.105012	0.379847
7	6	0	0.396069	3.267980	-1.492568
8	6	0	1.766424	3.379540	-1.412521
9	6	0	2.477620	2.356434	-0.806192
10	17	0	4.217686	2.500642	-0.698574
11	6	0	0.737902	-1.376079	-0.393036
12	6	0	2.119499	-1.148051	-0.369579
13	6	0	2.986894	-2.090940	-0.889814
14	17	0	4.715753	-1.810366	-0.879326
15	6	0	0.263579	-2.602567	-0.834510
16	6	0	1.151384	-3.547844	-1.344707
17	6	0	2.510416	-3.293342	-1.400493
18	6	0	0.510873	-0.276116	1.716668
19	6	0	1.889285	-0.047938	1.748751
20	6	0	2.606429	-0.089471	2.929856
21	6	0	-0.120760	-0.665165	2.890479
22	6	0	0.598091	-0.716046	4.084869

23	6	0	1.948722	-0.405769	4.115565
24	1	0	3.590902	0.241462	0.428688
25	1	0	-0.182054	4.054581	-1.959461
26	1	0	2.277256	4.245905	-1.812130
27	1	0	-0.785853	-2.849347	-0.773248
28	1	0	0.771526	-4.498930	-1.699321
29	1	0	3.202235	-4.022086	-1.803320
30	1	0	-1.161838	-0.953312	2.896628
31	1	0	0.088441	-1.010681	4.995260
32	1	0	2.497784	-0.442570	5.049477
33	1	0	3.675347	0.094849	2.920171
34	6	0	-1.594908	-0.371162	0.177135
35	6	0	-2.178404	-0.899116	-0.970897
36	6	0	-2.419489	0.170036	1.158250
37	6	0	-3.560181	-0.936971	-1.107060
38	6	0	-3.801376	0.130826	1.018880
39	6	0	-4.393600	-0.437704	-0.107403
40	1	0	-5.467443	-0.471903	-0.211933
41	1	0	-1.587840	-1.222865	-1.815271
42	1	0	-2.021951	0.700998	2.010198
43	8	0	-4.017959	-1.472174	-2.267319
44	8	0	-4.506058	0.689328	2.035406
45	6	0	-5.407934	-1.484431	-2.502631
46	6	0	-5.911249	0.740373	1.934006
47	1	0	-5.542198	-1.928191	-3.487637
48	1	0	-5.936327	-2.093719	-1.760175
49	1	0	-5.822894	-0.470005	-2.505252
50	1	0	-6.259573	1.243612	2.834340
51	1	0	-6.229083	1.313360	1.055377
52	1	0	-6.348255	-0.264131	1.893038

Table S10. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer C) at ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3614815 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.489576	-1.934551	-1.362944
2	6	0	-0.413083	-2.034902	-1.368602
3	6	0	0.387461	-1.192072	-0.610211
4	6	0	-0.119109	-0.058502	0.330903
5	6	0	1.770215	-1.355355	-0.629830
6	6	0	2.476733	-0.380551	0.265710
7	6	0	0.177099	-3.026122	-2.148029
8	6	0	1.553465	-3.186243	-2.179225
9	6	0	2.345454	-2.341895	-1.411548
10	17	0	4.083839	-2.549085	-1.440166
11	6	0	0.497598	-0.343949	1.719302
12	6	0	1.882244	-0.546812	1.655868
13	6	0	2.624467	-0.772648	2.799313
14	1	0	3.695516	-0.929522	2.728433
15	6	0	-0.117163	-0.270254	2.959589
16	6	0	0.631314	-0.493929	4.115975
17	6	0	1.988357	-0.765787	4.039654
18	6	0	0.658461	1.236211	-0.043400
19	6	0	2.041131	1.004075	-0.184036
20	6	0	2.896539	2.020245	-0.560932
21	6	0	0.229302	2.560003	-0.068903
22	6	0	1.095722	3.580273	-0.466000
23	6	0	2.418431	3.312318	-0.750321
24	1	0	3.556271	-0.495972	0.258528
25	1	0	-0.448592	-3.683681	-2.740255
26	1	0	2.014118	-3.955675	-2.785861
27	1	0	-1.164777	-0.017242	3.047556
28	1	0	0.141986	-0.444480	5.082114
29	1	0	2.560831	-0.942415	4.943057
30	17	0	-1.327032	3.090885	0.530495
31	1	0	0.722209	4.594799	-0.519681
32	1	0	3.089096	4.103989	-1.058269
33	17	0	4.607380	1.722307	-0.767501
34	6	0	-1.631878	-0.029732	0.171681
35	6	0	-2.460261	-0.797158	0.980293
36	6	0	-2.166090	0.585021	-0.957082
37	6	0	-3.822497	-0.885177	0.701704
38	6	0	-3.522540	0.495738	-1.231295
39	6	0	-4.374642	-0.232769	-0.397919
40	1	0	-5.431429	-0.297918	-0.607585
41	1	0	-2.080305	-1.383785	1.803176
42	1	0	-1.541764	1.135408	-1.649120
43	8	0	-4.543059	-1.649979	1.560674
44	8	0	-3.941998	1.148933	-2.343970
45	6	0	-5.923817	-1.810695	1.325578
46	6	0	-5.306463	1.084654	-2.692198
47	1	0	-6.289651	-2.462644	2.116970
48	1	0	-6.453925	-0.852659	1.376001
49	1	0	-6.113386	-2.282361	0.354408
50	1	0	-5.410621	1.665953	-3.606752
51	1	0	-5.624593	0.053249	-2.883811
52	1	0	-5.940841	1.524145	-1.913890

Table S11. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers A and B) at ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3559637 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.523656	3.027788	-1.027383
2	6	0	-0.497797	2.712085	-0.915030
3	6	0	-0.834475	1.481704	-0.373209
4	6	0	0.083139	0.335676	0.146637
5	6	0	-2.198277	1.175633	-0.192897
6	6	0	-2.469570	-0.143597	0.507137
7	6	0	-1.493373	3.604957	-1.311723
8	6	0	-2.830857	3.292685	-1.168272
9	6	0	-3.170592	2.071008	-0.596454
10	17	0	-4.869563	1.698805	-0.383882
11	6	0	-0.365935	0.214409	1.635712
12	6	0	-1.717643	-0.062479	1.809451
13	6	0	-2.284855	-0.164954	3.067361
14	1	0	-3.341399	-0.387955	3.169899
15	6	0	0.416804	0.463284	2.755358
16	6	0	-0.147622	0.373959	4.026168
17	6	0	-1.486654	0.045338	4.187538
18	6	0	-0.452580	-0.919608	-0.618955
19	6	0	-1.798916	-1.200103	-0.333205
20	6	0	-2.434156	-2.310954	-0.855901
21	6	0	0.171659	-1.718748	-1.578408
22	6	0	-0.472426	-2.844503	-2.093513
23	6	0	-1.761392	-3.163137	-1.719834
24	1	0	-3.529086	-0.332798	0.644199
25	1	0	-1.209624	4.560391	-1.737370
26	1	0	-3.606785	3.980818	-1.478255
27	1	0	1.461926	0.723194	2.654569
28	1	0	0.471505	0.564752	4.895435
29	1	0	-1.914314	-0.028541	5.180943
30	17	0	1.720845	-1.377003	-2.319174
31	1	0	0.050561	-3.460378	-2.813619
32	1	0	-2.253925	-4.038885	-2.122115
33	17	0	-4.101397	-2.662219	-0.460333
34	6	0	1.612199	0.389929	0.105748
35	6	0	2.391359	1.360538	-0.502717
36	6	0	2.254076	-0.684152	0.728095
37	6	0	3.782344	1.260801	-0.488335
38	6	0	3.634813	-0.782987	0.738640
39	6	0	4.425413	0.195823	0.131946
40	1	0	5.502283	0.123112	0.138387
41	1	0	1.988367	2.182742	-1.063716
42	1	0	1.687440	-1.477516	1.198885
43	8	0	4.436074	2.265212	-1.126379
44	8	0	4.143406	-1.874496	1.363997
45	6	0	5.843994	2.222884	-1.184467
46	6	0	5.541378	-2.055599	1.376125
47	1	0	6.148686	3.105580	-1.744120
48	1	0	6.288514	2.261427	-0.183239
49	1	0	6.196796	1.326067	-1.706596

50	1	0	6.048459	-1.240347	1.905258
51	1	0	5.718609	-2.989153	1.907414
52	1	0	5.944080	-2.138264	0.360117

Table S12. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers B and C) at ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3564133 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.995444	-1.585295	2.903130
2	6	0	0.057600	-1.387629	2.804256
3	6	0	0.596804	-0.799987	1.668670
4	6	0	-0.091350	-0.299787	0.364770
5	6	0	1.993432	-0.657667	1.604874
6	6	0	2.523402	-0.114284	0.290630
7	6	0	0.883997	-1.775314	3.860868
8	6	0	2.254155	-1.594277	3.796180
9	6	0	2.813917	-1.038185	2.648788
10	1	0	3.887850	-0.912243	2.562092
11	6	0	0.448742	1.160864	0.210328
12	6	0	1.846601	1.216234	0.081334
13	6	0	2.507898	2.410917	-0.133508
14	17	0	4.246528	2.455473	-0.318689
15	6	0	-0.231202	2.378923	0.266889
16	6	0	0.441742	3.579835	0.037312
17	6	0	1.802167	3.604309	-0.188356
18	6	0	0.605157	-1.179812	-0.721133
19	6	0	1.992139	-1.047664	-0.764741
20	6	0	2.734877	-1.801016	-1.656508
21	6	0	-0.017386	-2.123215	-1.525575
22	6	0	0.742584	-2.884873	-2.409213
23	6	0	2.115825	-2.720485	-2.494471
24	1	0	3.606027	-0.036400	0.282799
25	1	0	0.436174	-2.227842	4.738346
26	1	0	2.888181	-1.895883	4.621907
27	17	0	-1.910023	2.575666	0.723454
28	1	0	-0.120269	4.504500	0.059265
29	1	0	2.317026	4.539406	-0.366891
30	1	0	-1.087014	-2.272235	-1.477452
31	1	0	0.253467	-3.616985	-3.041173
32	1	0	2.708362	-3.305872	-3.186097
33	17	0	4.476324	-1.631162	-1.725720
34	6	0	-1.602727	-0.350770	0.134469
35	6	0	-2.564268	-0.687116	1.073117
36	6	0	-2.022149	0.020834	-1.145642
37	6	0	-3.917736	-0.656561	0.738460
38	6	0	-3.366373	0.052782	-1.475143
39	6	0	-4.340191	-0.292647	-0.535170
40	1	0	-5.389327	-0.269709	-0.787807
41	1	0	-2.338284	-0.913269	2.098441
42	1	0	-1.308929	0.315871	-1.904939
43	8	0	-4.765534	-0.995257	1.743075
44	8	0	-3.653811	0.437250	-2.744355
45	6	0	-6.152818	-0.959645	1.494988
46	6	0	-5.006076	0.532533	-3.131340
47	1	0	-6.632797	-1.252562	2.427187
48	1	0	-6.485136	0.048039	1.220175
49	1	0	-6.438009	-1.666081	0.706832
50	1	0	-4.999110	0.870781	-4.166111
51	1	0	-5.510348	-0.439237	-3.075486
52	1	0	-5.548328	1.261682	-2.518541

Table S13. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers C and A) at ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3427653 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.680524	3.666660	-0.670712
2	6	0	0.781095	2.750760	-0.363302
3	6	0	0.876312	1.388762	-0.074450
4	6	0	-0.156241	0.185621	0.095194
5	6	0	2.203886	0.904589	0.128764
6	6	0	2.333680	-0.576769	0.447601
7	6	0	1.913293	3.571532	-0.441083
8	6	0	3.176698	3.077953	-0.238087
9	6	0	3.309721	1.727139	0.048769
10	17	0	4.927230	1.108749	0.307516
11	6	0	0.383652	-0.832477	-0.949208
12	6	0	1.682794	-1.271563	-0.716647
13	6	0	2.271863	-2.177642	-1.582579
14	17	0	3.898940	-2.754743	-1.289776
15	6	0	-0.296291	-1.251557	-2.083661
16	6	0	0.312560	-2.149163	-2.954789
17	6	0	1.588826	-2.631213	-2.703819
18	6	0	0.191362	-0.325610	1.520958
19	6	0	1.494196	-0.777386	1.679910
20	6	0	1.953480	-1.251474	2.897208
21	6	0	-0.655504	-0.294339	2.620867
22	6	0	-0.199652	-0.758440	3.851778
23	6	0	1.092342	-1.250864	3.989738
24	1	0	3.365886	-0.876146	0.592048
25	1	0	1.773904	4.620155	-0.667704
26	1	0	4.045093	3.720394	-0.299795
27	1	0	-1.296799	-0.895100	-2.290372
28	1	0	-0.217523	-2.481792	-3.839614
29	1	0	2.060820	-3.338708	-3.373760
30	1	0	-1.667912	0.077889	2.526881
31	1	0	-0.864063	-0.735753	4.708122
32	1	0	1.434929	-1.618047	4.950489
33	1	0	2.975877	-1.600596	2.994257
34	6	0	-1.699746	0.148656	-0.017865
35	6	0	-2.588877	1.166507	-0.299936
36	6	0	-2.227533	-1.133440	0.208835
37	6	0	-3.964433	0.922133	-0.355116
38	6	0	-3.587444	-1.374472	0.152955
39	6	0	-4.487914	-0.342976	-0.131928
40	1	0	-5.550774	-0.525822	-0.175912
41	1	0	-2.275287	2.171914	-0.485546
42	1	0	-1.584716	-1.973610	0.435938
43	8	0	-4.723236	2.011294	-0.640958
44	8	0	-3.969309	-2.656481	0.390155
45	6	0	-6.121822	1.855332	-0.714199
46	6	0	-5.342834	-2.969812	0.351733
47	1	0	-6.522834	2.839552	-0.950268
48	1	0	-6.406598	1.151907	-1.505398
49	1	0	-6.538697	1.517119	0.241665
50	1	0	-5.413962	-4.034465	0.568039
51	1	0	-5.904774	-2.411803	1.109728
52	1	0	-5.773001	-2.775646	-0.637724

Table S14. Optimized Structural Coordinate and its Total Energy for **12** at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -1410.5070987 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.081538	-0.000003	2.482022
2	6	0	0.987676	-0.000002	1.431093
3	6	0	0.645355	0.000000	-0.080037
4	6	0	2.355278	-0.000002	1.704448
5	6	0	3.204928	-0.000001	0.459089
6	6	0	0.548972	-0.000005	3.796539
7	6	0	1.911496	-0.000006	4.060203
8	6	0	2.823703	-0.000004	3.006545
9	6	0	1.408498	1.197025	-0.700769
10	6	0	2.769328	1.200529	-0.365301
11	6	0	3.620550	2.174007	-0.854666
12	6	0	0.936614	2.130778	-1.611234
13	6	0	1.795418	3.111887	-2.110120
14	6	0	3.125127	3.149284	-1.719676

15	6	0	1.408497	-1.197023	-0.700772
16	6	0	2.769328	-1.200528	-0.365305
17	6	0	3.620549	-2.174006	-0.854672
18	6	0	0.936613	-2.130773	-1.611240
19	6	0	1.795416	-3.111881	-2.110128
20	6	0	3.125126	-3.149280	-1.719685
21	6	0	-0.865709	0.000000	-0.219377
22	6	0	-1.586481	1.192750	-0.173518
23	6	0	-1.586481	-1.192749	-0.173520
24	6	0	-2.971485	1.170135	-0.181742
25	6	0	-2.971485	-1.170134	-0.181744
26	6	0	-3.705133	0.000000	-0.201422
27	7	0	-3.697863	2.454205	-0.150631
28	7	0	-3.697863	-2.454204	-0.150632
29	1	0	-0.987081	-0.000003	2.305486
30	1	0	4.273700	-0.000001	0.670328
31	1	0	-0.162245	-0.000006	4.614537
32	1	0	2.267209	-0.000007	5.084213
33	1	0	3.891080	-0.000005	3.200190
34	1	0	4.670803	2.162012	-0.583100
35	1	0	-0.084802	2.107063	-1.968427
36	1	0	1.414032	3.843177	-2.813411
37	1	0	3.785667	3.916601	-2.106819
38	1	0	4.670802	-2.162012	-0.583106
39	1	0	-0.084803	-2.107058	-1.968432
40	1	0	1.414031	-3.843170	-2.813421
41	1	0	3.785665	-3.916596	-2.106829
42	1	0	-1.087557	2.147242	-0.093253
43	1	0	-1.087556	-2.147241	-0.093255
44	1	0	-4.785069	0.000000	-0.210918
45	8	0	-4.911438	2.414258	-0.137497
46	8	0	-3.040014	3.475050	-0.140940
47	8	0	-4.911437	-2.414257	-0.137498
48	8	0	-3.040013	-3.475050	-0.140942

Table S15. Optimized Structural Coordinate and its Total Energy for **13** at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -1112.240208 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.249782	-0.010162	1.626767
2	6	0	1.278519	-0.011527	2.558620
3	6	0	2.795058	-0.006307	2.240774
4	6	0	0.969163	-0.015911	3.918137
5	6	0	2.192958	-0.013540	4.797742
6	6	0	-1.075747	-0.014337	2.061016
7	6	0	-1.375243	-0.019746	3.417288
8	6	0	-0.344899	-0.020296	4.355361
9	6	0	3.393394	1.187288	3.030777
10	6	0	3.025517	1.188729	4.383892
11	6	0	3.495235	2.157328	5.252328
12	6	0	4.319031	2.121466	2.588533
13	6	0	4.800233	3.096588	3.464308
14	6	0	4.376392	3.131670	4.784389
15	6	0	3.402493	-1.198297	3.026502
16	6	0	3.034231	-1.208034	4.379423
17	6	0	3.510920	-2.176560	5.244189
18	6	0	4.335877	-2.123285	2.580885
19	6	0	4.823930	-3.098339	3.452948
20	6	0	4.399553	-3.142315	4.772608
21	6	0	2.959687	-0.003819	0.726116
22	6	0	2.913486	1.196523	0.019836
23	6	0	2.925096	-1.203859	0.018095
24	6	0	2.901995	1.203935	-1.378987
25	6	0	2.914558	-1.209913	-1.380143
26	6	0	2.922071	-0.002439	-2.076805
27	7	0	2.802122	2.412534	-2.066918
28	7	0	2.944647	-2.419850	-2.072735
29	1	0	0.466680	-0.004293	0.565652
30	1	0	1.957297	-0.016310	5.861813
31	1	0	-1.876182	-0.012399	1.329502
32	1	0	-2.408227	-0.022730	3.746998
33	1	0	-0.564964	-0.023508	5.417939
34	1	0	3.196888	2.140538	6.295513
35	1	0	4.689781	2.095044	1.572679
36	1	0	5.517326	3.826296	3.104960
37	1	0	4.749850	3.894544	5.458242
38	1	0	3.212049	-2.166232	6.287320
39	1	0	4.707309	-2.090591	1.565458
40	1	0	5.546589	-3.821002	3.090599
41	1	0	4.778404	-3.905211	5.443432
42	1	0	2.826078	2.140297	0.541537
43	1	0	2.854808	-2.149368	0.539198
44	1	0	2.919082	-0.002438	-3.162825
45	1	0	3.135621	2.394477	-3.018723
46	1	0	3.145009	3.218398	-1.566593
47	1	0	2.551551	-2.391854	-3.001424
48	1	0	2.610052	-3.215990	-1.551027

Table S16. Optimized Structural Coordinate and its Total Energy for phenyltriptycene at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -1001.5137319 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.186280	2.316420	-0.000009
2	6	0	-0.162003	1.379945	-0.000006
3	6	0	-0.334032	-0.159891	0.000001
4	6	0	1.162789	1.815774	-0.000009
5	6	0	2.153738	0.680082	-0.000004
6	6	0	-0.878689	3.677210	-0.000015
7	6	0	0.443139	4.102452	-0.000018
8	6	0	1.474145	3.164786	-0.000015
9	6	0	0.506025	-0.685375	-1.193392
10	6	0	1.818194	-0.191509	-1.198881
11	6	0	2.724486	-0.579481	-2.168865
12	6	0	0.150135	-1.650384	-2.124372
13	6	0	1.064608	-2.048539	-3.101447
14	6	0	2.338695	-1.502349	-3.140581
15	6	0	0.506026	-0.685365	1.193398
16	6	0	1.818195	-0.191498	1.198881
17	6	0	2.724489	-0.579461	2.168868
18	6	0	0.150138	-1.650366	2.124387
19	6	0	1.064613	-2.048511	3.101465
20	6	0	2.338699	-1.502321	3.140592
21	6	0	-1.823362	-0.473907	0.000003
22	6	0	-2.548656	-0.506500	-1.194290
23	6	0	-2.548657	-0.506486	1.194296
24	6	0	-3.930892	-0.653446	-1.197206
25	6	0	-3.930893	-0.653432	1.197214
26	6	0	-4.629295	-0.746373	0.000004
27	1	0	-4.462141	-0.679721	-2.142106
28	1	0	-4.462142	-0.679696	2.142114
29	1	0	-2.223073	2.002946	-0.000007
30	1	0	3.190831	1.014879	-0.000006
31	1	0	-1.682262	4.405163	-0.000018
32	1	0	0.674248	5.161798	-0.000023
33	1	0	2.511147	3.484188	-0.000017
34	1	0	3.734937	-0.184271	-2.155429
35	1	0	-0.824378	-2.119267	-2.096489
36	1	0	0.772070	-2.797157	-3.829172
37	1	0	3.042529	-1.811978	-3.904885
38	1	0	3.734940	-0.184251	2.155427
39	1	0	-0.824375	-2.119249	2.096509
40	1	0	0.772075	-2.797124	3.829196
41	1	0	3.042534	-1.811943	3.904897
42	1	0	-2.040989	-0.374927	-2.140534
43	1	0	-2.040990	-0.374902	2.140539
44	1	0	-5.707089	-0.863324	0.000005

Table S17. Optimized Structural Coordinate and its Total Energy for *m*-dinitrobenzene at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -641.2162249 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	-2.229823	0.000004
2	6	0	-1.204256	-1.539320	0.000003
3	6	0	-1.178194	-0.152228	0.000000
4	6	0	0.000000	0.572415	-0.000002
5	6	0	1.178194	-0.152228	-0.000000
6	6	0	1.204256	-1.539320	0.000002
7	7	0	2.454755	0.587019	-0.000003
8	8	0	3.481100	-0.062500	-0.000008
9	8	0	2.405174	1.800316	0.000008
10	7	0	-2.454755	0.587019	-0.000002
11	8	0	-2.405174	1.800316	0.000003
12	8	0	-3.481100	-0.062500	-0.000006
13	1	0	0.000000	-3.311885	0.000007
14	1	0	-2.151727	-2.060568	0.000004
15	1	0	0.000000	1.652734	-0.000003
16	1	0	2.151727	-2.060568	0.000003

Table S18. Optimized Structural Coordinate and its Total Energy for *m*-diaminobenzene at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -342.9489447 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000000	-0.000000	1.786954
2	6	0	0.000647	-1.211751	1.109564
3	6	0	-0.000000	-1.215264	-0.290886
4	6	0	0.000000	0.000000	-0.978971
5	6	0	0.000000	1.215264	-0.290886
6	6	0	-0.000647	1.211751	1.109564
7	7	0	-0.057216	2.417884	-0.994996
8	1	0	0.290804	3.220924	-0.493450
9	1	0	0.304958	2.381883	-1.935862
10	7	0	0.057216	-2.417884	-0.994996
11	1	0	-0.304958	-2.381883	-1.935862
12	1	0	-0.290804	-3.220924	-0.493450
13	1	0	-0.000000	-0.000000	2.871981
14	1	0	0.004946	-2.149289	1.654972
15	1	0	0.000000	0.000000	-2.065389
16	1	0	-0.004946	2.149289	1.654972

Table S19. Optimized Structural Coordinate and its Total Energy for benzene at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -232.2232422 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000000	0.000000	1.391688
2	6	0	-0.000000	1.205270	0.695855
3	6	0	0.000000	1.205270	-0.695855
4	6	0	0.000000	0.000000	-1.391688
5	6	0	-0.000000	-1.205270	-0.695855
6	6	0	-0.000000	-1.205270	0.695855
7	1	0	-0.000000	0.000000	2.476136
8	1	0	-0.000000	2.144424	1.238098
9	1	0	0.000000	2.144424	-1.238098
10	1	0	0.000000	0.000000	-2.476136
11	1	0	-0.000000	-2.144424	-1.238098
12	1	0	-0.000000	-2.144424	1.238098

Table S20. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer A) at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3700401 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.858797	-0.715042	2.265964
2	6	0	-0.803182	-0.712739	2.503310
3	6	0	0.150842	-0.454450	1.526417
4	6	0	-0.127927	-0.172270	0.021541
5	6	0	1.495526	-0.474199	1.876993
6	6	0	2.397287	-0.200090	0.708173
7	6	0	-0.397258	-0.974079	3.810945
8	6	0	0.950011	-0.979520	4.149955
9	6	0	1.909472	-0.728005	3.173654
10	1	0	2.966596	-0.733004	3.416373
11	6	0	0.634016	1.130712	-0.358789
12	6	0	1.958341	1.131477	0.122536
13	6	0	2.781407	2.223266	-0.070683
14	17	0	4.415275	2.235583	0.559089
15	6	0	0.272983	2.158174	-1.225611
16	6	0	1.102876	3.266604	-1.403270
17	6	0	2.341452	3.323757	-0.797943
18	6	0	0.709582	-1.201584	-0.773420
19	6	0	2.053210	-1.222282	-0.364430
20	6	0	2.945027	-2.060298	-1.006966
21	6	0	0.313159	-1.940699	-1.875852
22	6	0	1.231200	-2.774495	-2.514058
23	6	0	2.541313	-2.857154	-2.074927
24	1	0	3.449228	-0.208237	0.974731
25	1	0	-1.146479	-1.174646	4.568432
26	1	0	1.254313	-1.182184	5.170535
27	17	0	-1.127485	2.096576	-2.277024
28	1	0	0.776899	4.073289	-2.047126
29	1	0	2.983014	4.184208	-0.936677
30	1	0	-0.692201	-1.865637	-2.264919
31	1	0	0.917408	-3.361697	-3.368989
32	1	0	3.254262	-3.507751	-2.565302
33	17	0	4.626663	-2.116633	-0.510784
34	6	0	-1.642343	-0.159164	-0.126980
35	6	0	-2.331749	0.980352	0.278176
36	6	0	-2.356550	-1.315650	-0.413311
37	6	0	-3.718687	0.985624	0.323374
38	6	0	-3.750246	-1.307060	-0.365553
39	6	0	-4.450032	-0.156713	-0.009979
40	1	0	-5.528807	-0.151599	0.021279
41	1	0	-1.806777	1.879542	0.575046
42	1	0	-1.869771	-2.256023	-0.625350
43	8	0	-4.291265	2.153036	0.709566
44	8	0	-4.350330	-2.484095	-0.673207
45	6	0	-5.702425	2.218508	0.802037
46	6	0	-5.763296	-2.557266	-0.621961
47	1	0	-5.933931	3.228000	1.135938
48	1	0	-6.173795	2.043933	-0.170635
49	1	0	-6.087792	1.499338	1.532269
50	1	0	-6.020263	-3.580172	-0.889776
51	1	0	-6.136707	-2.342378	0.384646
52	1	0	-6.223404	-1.869950	-1.339364

Table S21. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer B) at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3664629 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.858797	-0.715042	2.265964
2	6	0	-0.803182	-0.712739	2.503310
3	6	0	0.150842	-0.454450	1.526417
4	6	0	-0.127927	-0.172270	0.021541
5	6	0	1.495526	-0.474199	1.876993
6	6	0	2.397287	-0.200090	0.708173
7	6	0	-0.397258	-0.974079	3.810945
8	6	0	0.950011	-0.979520	4.149955
9	6	0	1.909472	-0.728005	3.173654
10	1	0	2.966596	-0.733004	3.416373
11	6	0	0.634016	1.130712	-0.358789
12	6	0	1.958341	1.131477	0.122536
13	6	0	2.781407	2.223266	-0.070683
14	17	0	4.415275	2.235583	0.559089
15	6	0	0.272983	2.158174	-1.225611

16	6	0	1.102876	3.266604	-1.403270
17	6	0	2.341452	3.323757	-0.797943
18	6	0	0.709582	-1.201584	-0.773420
19	6	0	2.053210	-1.222282	-0.364430
20	6	0	2.945027	-2.060298	-1.006966
21	6	0	0.313159	-1.940699	-1.875852
22	6	0	1.231200	-2.774495	-2.514058
23	6	0	2.541313	-2.857154	-2.074927
24	1	0	3.449228	-0.208237	0.974731
25	1	0	-1.146479	-1.174646	4.568432
26	1	0	1.254313	-1.182184	5.170535
27	17	0	-1.127485	2.096576	-2.277024
28	1	0	0.776899	4.073289	-2.047126
29	1	0	2.983014	4.184208	-0.936677
30	1	0	-0.692201	-1.865637	-2.264919
31	1	0	0.917408	-3.361697	-3.368989
32	1	0	3.254262	-3.507751	-2.565302
33	17	0	4.626663	-2.116633	-0.510784
34	6	0	-1.642343	-0.159164	-0.126980
35	6	0	-2.331749	0.980352	0.278176
36	6	0	-2.356550	-1.315650	-0.413311
37	6	0	-3.718687	0.985624	0.323374
38	6	0	-3.750246	-1.307060	-0.365553
39	6	0	-4.450032	-0.156713	-0.009979
40	1	0	-5.528807	-0.151599	0.021279
41	1	0	-1.806777	1.879542	0.575046
42	1	0	-1.869771	-2.256023	-0.625350
43	8	0	-4.291265	2.153036	0.709566
44	8	0	-4.350330	-2.484095	-0.673207
45	6	0	-5.702425	2.218508	0.802037
46	6	0	-5.763296	-2.557266	-0.621961
47	1	0	-5.933931	3.228000	1.135938
48	1	0	-6.173795	2.043933	-0.170635
49	1	0	-6.087792	1.499338	1.532269
50	1	0	-6.020263	-3.580172	-0.889776
51	1	0	-6.136707	-2.342378	0.384646
52	1	0	-6.223404	-1.869950	-1.339364

Table S22. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer C) at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -2609.37016 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.493166	-1.941950	-1.346216
2	6	0	-0.416484	-2.040602	-1.354288
3	6	0	0.385812	-1.194443	-0.600714
4	6	0	-0.119188	-0.057716	0.337965
5	6	0	1.768907	-1.357264	-0.623658
6	6	0	2.477323	-0.380755	0.268718
7	6	0	0.171051	-3.034191	-2.133565
8	6	0	1.548069	-3.192801	-2.170264
9	6	0	2.340541	-2.344818	-1.406883
10	17	0	4.081864	-2.548065	-1.443371
11	6	0	0.499780	-0.341199	1.726163
12	6	0	1.884827	-0.543507	1.660377
13	6	0	2.630662	-0.767042	2.802577
14	1	0	3.701729	-0.922650	2.729999
15	6	0	-0.112766	-0.268727	2.968140
16	6	0	0.638752	-0.490355	4.123711
17	6	0	1.996893	-0.759463	4.044850
18	6	0	0.659227	1.235534	-0.040915
19	6	0	2.041296	1.002349	-0.184940
20	6	0	2.894680	2.017243	-0.570193
21	6	0	0.232508	2.560112	-0.071059
22	6	0	1.096794	3.579341	-0.474968
23	6	0	2.418709	3.309372	-0.763674
24	1	0	3.556643	-0.496706	0.262899
25	1	0	-0.456157	-3.693938	-2.721451
26	1	0	2.005206	-3.963480	-2.778002
27	1	0	-1.160965	-0.020109	3.060464
28	1	0	0.150809	-0.441888	5.090561
29	1	0	2.571685	-0.934192	4.947122
30	17	0	-1.323336	3.094610	0.532522
31	1	0	0.726105	4.594614	-0.533095
32	1	0	3.086452	4.100815	-1.078248
33	17	0	4.605843	1.714484	-0.784226
34	6	0	-1.632162	-0.026257	0.177503
35	6	0	-2.464601	-0.786277	0.988901
36	6	0	-2.162122	0.582733	-0.956823
37	6	0	-3.827269	-0.874442	0.705689
38	6	0	-3.518704	0.493417	-1.235166
39	6	0	-4.374644	-0.228128	-0.399781
40	1	0	-5.430576	-0.293539	-0.612766
41	1	0	-2.087501	-1.366842	1.817502
42	1	0	-1.532795	1.126876	-1.649755
43	8	0	-4.552512	-1.632147	1.565693
44	8	0	-3.935044	1.139906	-2.352579
45	6	0	-5.938308	-1.792271	1.324002
46	6	0	-5.301252	1.057674	-2.714689
47	1	0	-6.308096	-2.438461	2.117598
48	1	0	-6.463230	-0.832357	1.366527
49	1	0	-6.120751	-2.268796	0.355185
50	1	0	-5.401971	1.629958	-3.634733
51	1	0	-5.602563	0.021228	-2.899008
52	1	0	-5.944709	1.496734	-1.945344

Table S23. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers A and B) at PCM-ω97XD/6-311++G(d,p) level
total energy: HF= -2609.3647092 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.526991	3.032821	-1.012232
2	6	0	-0.494286	2.714368	-0.906076
3	6	0	-0.833139	1.481016	-0.371377
4	6	0	0.083462	0.333154	0.147519
5	6	0	-2.197731	1.175482	-0.193920
6	6	0	-2.470943	-0.142499	0.507738
7	6	0	-1.488274	3.609483	-1.303440
8	6	0	-2.826989	3.296526	-1.167308
9	6	0	-3.167265	2.072877	-0.599743
10	17	0	-4.869248	1.698598	-0.393749
11	6	0	-0.366330	0.214379	1.636845
12	6	0	-1.718823	-0.060603	1.810301
13	6	0	-2.288046	-0.159739	3.068201
14	1	0	-3.344885	-0.381116	3.170763
15	6	0	0.415551	0.465631	2.757152
16	6	0	-0.150239	0.379937	4.028288
17	6	0	-1.490392	0.052584	4.189237
18	6	0	-0.454435	-0.922750	-0.616391
19	6	0	-1.801722	-1.200573	-0.331506
20	6	0	-2.438036	-2.310836	-0.854575
21	6	0	0.167475	-1.727259	-1.573119
22	6	0	-0.477148	-2.852908	-2.087692
23	6	0	-1.768032	-3.167718	-1.715805
24	1	0	-3.530256	-0.330149	0.647366
25	1	0	-1.202607	4.566490	-1.723757
26	1	0	-3.600083	3.986998	-1.479267
27	1	0	1.461059	0.724770	2.658273
28	1	0	0.468270	0.572656	4.897555
29	1	0	-1.919197	-0.018510	5.182323
30	17	0	1.720558	-1.391700	-2.313452
31	1	0	0.043382	-3.473788	-2.805223
32	1	0	-2.259919	-4.043614	-2.118362
33	17	0	-4.109233	-2.655239	-0.460935
34	6	0	1.612765	0.387538	0.103796
35	6	0	2.389650	1.352891	-0.516703
36	6	0	2.257021	-0.680983	0.733305
37	6	0	3.782068	1.254616	-0.503534
38	6	0	3.638980	-0.778172	0.742347
39	6	0	4.427412	0.196225	0.126060
40	1	0	5.504279	0.125053	0.132275
41	1	0	1.982644	2.168068	-1.085723
42	1	0	1.690622	-1.469895	1.212229

43	8	0	4.434834	2.252207	-1.151554
44	8	0	4.151032	-1.863230	1.375469
45	6	0	5.848979	2.213293	-1.203323
46	6	0	5.556274	-2.033565	1.398402
47	1	0	6.152508	3.091572	-1.769576
48	1	0	6.285325	2.262035	-0.200264
49	1	0	6.203356	1.312714	-1.715368
50	1	0	6.050012	-1.206695	1.919438
51	1	0	5.736804	-2.958475	1.942575
52	1	0	5.962610	-2.125329	0.385885

Table S24. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers B and C) at PCM-ω97XD/6-311++G(d,p) level

total energy: HF= -2609.3651828 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.000448	-1.596822	2.897088
2	6	0	0.052040	-1.394149	2.801580
3	6	0	0.593985	-0.799373	1.670308
4	6	0	-0.091658	-0.296908	0.365645
5	6	0	1.990986	-0.656440	1.610206
6	6	0	2.524287	-0.113860	0.296726
7	6	0	0.876521	-1.784491	3.859574
8	6	0	2.247173	-1.599792	3.799867
9	6	0	2.809914	-1.039127	2.655307
10	1	0	3.884003	-0.912397	2.572542
11	6	0	0.451006	1.163011	0.210228
12	6	0	1.849227	1.216705	0.083274
13	6	0	2.510903	2.410373	-0.136896
14	17	0	4.251488	2.449714	-0.324184
15	6	0	-0.225668	2.383411	0.260129
16	6	0	0.447706	3.583365	0.027137
17	6	0	1.808819	3.605476	-0.197698
18	6	0	0.606378	-1.178894	-0.718206
19	6	0	1.993880	-1.047142	-0.759593
20	6	0	2.735823	-1.801590	-1.651130
21	6	0	-0.014750	-2.124405	-1.521874
22	6	0	0.745740	-2.887966	-2.404144
23	6	0	2.119489	-2.722923	-2.489259
24	1	0	3.606907	-0.037660	0.293371
25	1	0	0.426778	-2.242105	4.733366
26	1	0	2.879370	-1.903026	4.626377
27	17	0	-1.907295	2.584711	0.712600
28	1	0	-0.110779	4.510234	0.043449
29	1	0	2.322548	4.540345	-0.380261
30	1	0	-1.084264	-2.274830	-1.475623
31	1	0	0.257454	-3.621259	-3.035097
32	1	0	2.710851	-3.309633	-3.180801
33	17	0	4.479733	-1.629251	-1.719921
34	6	0	-1.603324	-0.346092	0.135454
35	6	0	-2.564747	-0.671315	1.078647
36	6	0	-2.023230	0.016538	-1.147019
37	6	0	-3.919571	-0.642237	0.744235
38	6	0	-3.368769	0.046472	-1.476069
39	6	0	-4.342363	-0.290384	-0.532855
40	1	0	-5.391519	-0.269802	-0.785448
41	1	0	-2.336071	-0.886606	2.106090
42	1	0	-1.308753	0.303215	-1.908650
43	8	0	-4.768037	-0.969259	1.751195
44	8	0	-3.658027	0.420796	-2.747566
45	6	0	-6.160540	-0.940360	1.498256
46	6	0	-5.016293	0.490662	-3.140679
47	1	0	-6.641040	-1.222338	2.432994
48	1	0	-6.491407	0.062711	1.209795
49	1	0	-6.438350	-1.657604	0.718938
50	1	0	-5.011092	0.816136	-4.179046
51	1	0	-5.501623	-0.488458	-3.072276
52	1	0	-5.568593	1.218257	-2.537154

Table S25. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers C and A) at PCM-ω97XD/6-311++G(d,p) level

total energy: HF= -2609.3511523 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.677544	3.666954	-0.670247
2	6	0	0.785566	2.750722	-0.364183
3	6	0	0.878136	1.388595	-0.074246
4	6	0	-0.156095	0.186564	0.095376
5	6	0	2.205303	0.903368	0.129617
6	6	0	2.333501	-0.577706	0.451407
7	6	0	1.917682	3.571353	-0.444236
8	6	0	3.181327	3.076499	-0.242426
9	6	0	3.311202	1.725752	0.046076
10	17	0	4.929701	1.103473	0.302633
11	6	0	0.384767	-0.832431	-0.948044
12	6	0	1.683360	-1.272829	-0.713209
13	6	0	2.271572	-2.178737	-1.580000
14	17	0	3.900745	-2.756728	-1.284624
15	6	0	-0.293119	-1.250252	-2.084636
16	6	0	0.315697	-2.148374	-2.955945
17	6	0	1.591509	-2.632361	-2.703099
18	6	0	0.189924	-0.323064	1.522247
19	6	0	1.492300	-0.776039	1.683134
20	6	0	1.950896	-1.249044	2.901805
21	6	0	-0.657882	-0.288951	2.621941
22	6	0	-0.203442	-0.751533	3.854619
23	6	0	1.088587	-1.245654	3.994237
24	1	0	3.364665	-0.878254	0.599728
25	1	0	1.781899	4.620259	-0.671531
26	1	0	4.048778	3.719838	-0.306789
27	1	0	-1.292419	-0.892711	-2.295206
28	1	0	-0.213066	-2.479749	-3.841843
29	1	0	2.062091	-3.340061	-3.373850
30	1	0	-1.669979	0.084276	2.528019
31	1	0	-0.868442	-0.726474	4.710435
32	1	0	1.430163	-1.611736	4.955755
33	1	0	2.972751	-1.599193	3.000598
34	6	0	-1.699860	0.149849	-0.018985
35	6	0	-2.589932	1.167404	-0.300467
36	6	0	-2.227762	-1.132133	0.206991
37	6	0	-3.966496	0.922383	-0.355466
38	6	0	-3.588561	-1.373914	0.151332
39	6	0	-4.489643	-0.342893	-0.132666
40	1	0	-5.552422	-0.525757	-0.175851
41	1	0	-2.275071	2.172614	-0.485763
42	1	0	-1.583099	-1.971357	0.433260
43	8	0	-4.726731	2.010359	-0.640390
44	8	0	-3.970603	-2.655548	0.387799
45	6	0	-6.130575	1.849506	-0.717829
46	6	0	-5.350331	-2.968733	0.348307
47	1	0	-6.533187	2.832787	-0.952898
48	1	0	-6.407297	1.146684	-1.510760
49	1	0	-6.545310	1.508063	0.236426
50	1	0	-5.421980	-4.032797	0.564960
51	1	0	-5.908567	-2.408585	1.105650
52	1	0	-5.775960	-2.773309	-0.641480

Table S26. Optimized Structural Coordinate and its Total Energy for **12** at B3LYP-D3/6-311++G(d,p) level

total energy: HF= -1411.0233882 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.080230	0.000002	2.488961
2	6	0	0.988764	0.000002	1.435364
3	6	0	0.646172	-0.000001	-0.083464
4	6	0	2.360501	0.000003	1.711146
5	6	0	3.213098	0.000002	0.463124
6	6	0	0.546749	0.000004	3.807696

7	6	0	1.912329	0.000005	4.073517
8	6	0	2.827278	0.000005	3.017481
9	6	0	1.415523	1.202572	-0.704213
10	6	0	2.779978	1.205022	-0.364173
11	6	0	3.635006	2.180629	-0.852110
12	6	0	0.947310	2.142406	-1.616162
13	6	0	1.810443	3.125771	-2.113269
14	6	0	3.142891	3.160452	-1.719380
15	6	0	1.415524	-1.202575	-0.704210
16	6	0	2.779979	-1.205022	-0.364169
17	6	0	3.635008	-2.180629	-0.852104
18	6	0	0.947313	-2.142411	-1.616156
19	6	0	1.810447	-3.125777	-2.113259
20	6	0	3.142895	-3.160456	-1.719370
21	6	0	-0.869155	-0.000001	-0.223539
22	6	0	-1.593839	1.196065	-0.177244
23	6	0	-1.593839	-1.196067	-0.177244
24	6	0	-2.983859	1.175363	-0.182340
25	6	0	-2.983860	-1.175364	-0.182340
26	6	0	-3.718162	-0.000000	-0.198878
27	7	0	-3.715074	2.468647	-0.154174
28	7	0	-3.715075	-2.468648	-0.154175
29	1	0	-0.986816	0.000001	2.309054
30	1	0	4.281866	0.000003	0.676601
31	1	0	-0.165483	0.000004	4.624722
32	1	0	2.267241	0.000007	5.097721
33	1	0	3.894429	0.000006	3.212439
34	1	0	4.684392	2.166976	-0.577462
35	1	0	-0.073871	2.121430	-1.972049
36	1	0	1.430880	3.859763	-2.814615
37	1	0	3.805425	3.927576	-2.103280
38	1	0	4.684395	-2.166973	-0.577456
39	1	0	-0.073869	-2.121438	-1.972044
40	1	0	1.430885	-3.859771	-2.814603
41	1	0	3.805430	-3.927579	-2.103268
42	1	0	-1.096582	2.150463	-0.100953
43	1	0	-1.096584	-2.150465	-0.100953
44	1	0	-4.797819	-0.000000	-0.205372
45	8	0	-4.936345	2.424265	-0.127818
46	8	0	-3.048106	3.494165	-0.161059
47	8	0	-4.936346	-2.424265	-0.127818
48	8	0	-3.048107	-3.494165	-0.161060

Table S27. Optimized Structural Coordinate and its Total Energy for **13** at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -1112.6519459 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.639652	-0.001466	2.423628
2	6	0	0.323556	-0.003102	1.419555
3	6	0	0.048580	0.000205	-0.112603
4	6	0	1.677763	-0.005656	1.769135
5	6	0	2.594374	-0.003081	0.567983
6	6	0	-0.242709	-0.004006	3.764534
7	6	0	1.107633	-0.008099	4.104318
8	6	0	2.077050	-0.008592	3.098634
9	6	0	0.859713	1.198225	-0.691428
10	6	0	2.204956	1.202335	-0.280056
11	6	0	3.087845	2.173802	-0.726188
12	6	0	0.446436	2.131259	-1.636835
13	6	0	1.337797	3.108806	-2.094245
14	6	0	2.646816	3.147751	-1.626877
15	6	0	0.858745	-1.195389	-0.698388
16	6	0	2.203850	-1.203258	-0.286744
17	6	0	3.086091	-2.172781	-0.738389
18	6	0	0.444668	-2.122403	-1.649625
19	6	0	1.335404	-3.098139	-2.112195
20	6	0	2.644275	-3.141091	-1.644744
21	6	0	-1.464377	0.001166	-0.323941
22	6	0	-2.176880	1.203108	-0.299484
23	6	0	-2.176351	-1.201546	-0.310423
24	6	0	-3.578648	1.209796	-0.333059
25	6	0	-3.577400	-1.209409	-0.345247
26	6	0	-4.276217	0.000189	-0.376097
27	7	0	-4.271918	2.422083	-0.253444
28	7	0	-4.269348	-2.424278	-0.398516
29	1	0	-1.692579	0.004062	2.174743
30	1	0	3.651258	-0.004264	0.835899
31	1	0	-0.997169	-0.001392	4.543358
32	1	0	1.407498	-0.009792	5.146350
33	1	0	3.132899	-0.010524	3.348984
34	1	0	4.121055	2.159068	-0.395023
35	1	0	-0.556086	2.097922	-2.039976
36	1	0	1.001113	3.834927	-2.825906
37	1	0	3.331414	3.910417	-1.980601
38	1	0	4.119288	-2.160734	-0.407027
39	1	0	-0.557564	-2.087305	-2.053319
40	1	0	0.997657	-3.819737	-2.847760
41	1	0	3.328230	-3.902337	-2.002786
42	1	0	-1.657711	2.145212	-0.191071
43	1	0	-1.655457	-2.144717	-0.222333
44	1	0	-5.361760	-0.000695	-0.411224
45	1	0	-5.216456	2.410951	-0.609062
46	1	0	-3.759918	3.235659	-0.561025
47	1	0	-5.212004	-2.405355	-0.037541
48	1	0	-3.754755	-3.227743	-0.068274

Table S28. Optimized Structural Coordinate and its Total Energy for phenyltriptycene at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -1001.8936544 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.190774	2.326939	-0.000003
2	6	0	-0.164973	1.386991	-0.000002
3	6	0	-0.337782	-0.160140	0.000000
4	6	0	1.164129	1.823706	-0.000003
5	6	0	2.157020	0.684764	-0.000002
6	6	0	-0.881649	3.691076	-0.000005
7	6	0	0.443530	4.117135	-0.000006
8	6	0	1.476021	3.176006	-0.000005
9	6	0	0.507896	-0.687567	-1.197741
10	6	0	1.823400	-0.189633	-1.203230
11	6	0	2.732681	-0.579153	-2.174551
12	6	0	0.155349	-1.658048	-2.129776
13	6	0	1.073576	-2.057552	-3.107872
14	6	0	2.349727	-1.507133	-3.147435
15	6	0	0.507896	-0.687563	1.197743
16	6	0	1.823401	-0.189629	1.203229
17	6	0	2.732682	-0.579146	2.174552
18	6	0	0.155350	-1.658042	2.129782
19	6	0	1.073578	-2.057543	3.107878
20	6	0	2.349729	-1.507123	3.147439
21	6	0	-1.830817	-0.475990	0.000001
22	6	0	-2.559871	-0.509329	-1.196935
23	6	0	-2.559871	-0.509327	1.196937
24	6	0	-3.945389	-0.658627	-1.199809
25	6	0	-3.945389	-0.658625	1.199811
26	6	0	-4.646001	-0.752763	0.000001
27	1	0	-4.476722	-0.685330	-2.144759
28	1	0	-4.476722	-0.685326	2.144762
29	1	0	-2.226538	2.014121	-0.000002
30	1	0	3.194022	1.021256	-0.000002
31	1	0	-1.685041	4.419187	-0.000005
32	1	0	0.675441	5.176279	-0.000008
33	1	0	2.513346	3.494322	-0.000006
34	1	0	3.742332	-0.182009	-2.160994
35	1	0	-0.817709	-2.128204	-2.098779
36	1	0	0.783487	-2.808823	-3.833855
37	1	0	3.055004	-1.816452	-3.910469
38	1	0	3.742334	-0.182002	2.160992
39	1	0	-0.817707	-2.128198	2.098787
40	1	0	0.783490	-2.808811	3.833863
41	1	0	3.055006	-1.816439	3.910473
42	1	0	-2.050573	-0.376973	-2.141273

43	1	0	-2.050573	-0.376968	2.141275
44	1	0	-5.723568	-0.871745	0.000002

Table S29. Optimized Structural Coordinate and its Total Energy for *m*-dinitrobenzene at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -641.4442762 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.103086	-1.814253	-0.347146
2	6	0	1.121889	-1.159480	-0.444402
3	6	0	1.175386	0.205638	-0.178685
4	6	0	0.053382	0.939501	0.179768
5	6	0	-1.149350	0.252573	0.266361
6	6	0	-1.250930	-1.111575	0.009850
7	7	0	-2.371568	1.007161	0.647777
8	8	0	-3.419134	0.379747	0.717325
9	8	0	-2.250108	2.203026	0.866565
10	7	0	2.480455	0.909203	-0.281092
11	8	0	2.495014	2.107226	-0.041837
12	8	0	3.454405	0.240977	-0.598545
13	1	0	-0.163413	-2.875979	-0.550300
14	1	0	2.026398	-1.684068	-0.719833
15	1	0	0.113570	1.998784	0.382454
16	1	0	-2.212912	-1.598480	0.091739

Table S30. Optimized Structural Coordinate and its Total Energy for *m*-diaminobenzene at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -343.0736928 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.100819	-1.774191	-0.339516
2	6	0	1.138779	-1.144239	-0.379664
3	6	0	1.220832	0.232155	-0.118342
4	6	0	0.053650	0.944129	0.180672
5	6	0	-1.190351	0.304236	0.220988
6	6	0	-1.264707	-1.071816	-0.044408
7	7	0	-2.353217	1.043328	0.465777
8	1	0	-3.139206	0.509053	0.805911
9	1	0	-2.224673	1.897945	0.987535
10	7	0	2.462374	0.877601	-0.098182
11	1	0	2.438948	1.872805	-0.265951
12	1	0	3.192202	0.423560	-0.627443
13	1	0	-0.161267	-2.837929	-0.543076
14	1	0	2.037095	-1.708681	-0.604619
15	1	0	0.114200	2.009659	0.384575
16	1	0	-2.223840	-1.577612	-0.024257

Table S31. Optimized Structural Coordinate and its Total Energy for benzene at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -232.3163902 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000000	1.394918	0.000000
2	6	0	1.208035	0.697459	0.000000
3	6	0	1.208035	-0.697459	0.000000
4	6	0	-0.000000	-1.394918	0.000000
5	6	0	-1.208035	-0.697459	0.000000
6	6	0	-1.208035	0.697459	0.000000
7	1	0	-0.000000	2.479334	0.000000
8	1	0	2.147166	1.239667	0.000000
9	1	0	2.147166	-1.239667	0.000000
10	1	0	-0.000000	-2.479334	0.000000
11	1	0	-2.147166	-1.239667	0.000000
12	1	0	-2.147166	1.239667	0.000000

Table S32. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer A) at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.8806517 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.845940	-0.717694	2.289389
2	6	0	-0.790434	-0.716821	2.521972
3	6	0	0.159446	-0.457850	1.536485
4	6	0	-0.130723	-0.171999	0.026907
5	6	0	1.511003	-0.478465	1.878955
6	6	0	2.408031	-0.201869	0.702085
7	6	0	-0.375143	-0.980081	3.830274
8	6	0	0.977657	-0.986950	4.161494
9	6	0	1.933085	-0.734448	3.176340
10	1	0	2.991690	-0.739859	3.411612
11	6	0	0.634005	1.137935	-0.356289
12	6	0	1.965669	1.136883	0.121081
13	6	0	2.789779	2.233410	-0.071168
14	17	0	4.435069	2.252996	0.557280
15	6	0	0.267392	2.170749	-1.221719
16	6	0	1.100048	3.282387	-1.400085
17	6	0	2.344265	3.337611	-0.797563
18	6	0	0.707444	-1.202921	-0.778439
19	6	0	2.057501	-1.226273	-0.373737
20	6	0	2.948194	-2.068053	-1.022023
21	6	0	0.304712	-1.940854	-1.884262
22	6	0	1.222005	-2.775583	-2.530295
23	6	0	2.536958	-2.862324	-2.094304
24	1	0	3.461235	-0.210626	0.960080
25	1	0	-1.119672	-1.180685	4.592437
26	1	0	1.288734	-1.190734	5.179838
27	17	0	-1.145271	2.112161	-2.273136
28	1	0	0.769546	4.089139	-2.041175
29	1	0	2.987499	4.196898	-0.933853
30	1	0	-0.702598	-1.861450	-2.265390
31	1	0	0.904349	-3.359810	-3.386157
32	1	0	3.249153	-3.511859	-2.586328
33	17	0	4.640878	-2.137263	-0.529609
34	6	0	-1.649500	-0.160705	-0.117351
35	6	0	-2.345173	0.982105	0.281457
36	6	0	-2.365945	-1.322726	-0.397979
37	6	0	-3.735218	0.986291	0.323103
38	6	0	-3.762042	-1.315961	-0.354636
39	6	0	-4.466946	-0.161427	-0.006356
40	1	0	-5.544810	-0.156922	0.019483
41	1	0	-1.825991	1.885806	0.568919
42	1	0	-1.879901	-2.263421	-0.604500
43	8	0	-4.308321	2.166270	0.703266
44	8	0	-4.359209	-2.506256	-0.661243
45	6	0	-5.724126	2.246720	0.787789
46	6	0	-5.776252	-2.595551	-0.609771
47	1	0	-5.945349	3.262805	1.110790
48	1	0	-6.195600	2.067876	-0.185524
49	1	0	-6.124374	1.539165	1.523349
50	1	0	-6.019558	-3.623144	-0.875427
51	1	0	-6.155787	-2.383053	0.396473
52	1	0	-6.248054	-1.916112	-1.329084

Table S33. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer B) at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.8774532 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-2.052777	2.255240	-1.183578
2	6	0	-0.302389	2.154866	-0.977460
3	6	0	0.411670	1.110141	-0.368163
4	6	0	-0.080745	-0.241582	0.285643
5	6	0	1.815785	1.259253	-0.304811
6	6	0	2.523687	0.114689	0.375167
7	6	0	0.364567	3.272732	-1.496449

8	6	0	1.738817	3.392462	-1.425667
9	6	0	2.463269	2.372258	-0.820549
10	17	0	4.214907	2.537100	-0.725591
11	6	0	0.748096	-1.387648	-0.387777
12	6	0	2.133089	-1.147863	-0.371431
13	6	0	3.006889	-2.090309	-0.893328
14	17	0	4.746888	-1.799695	-0.893151
15	6	0	0.279819	-2.622571	-0.825327
16	6	0	1.174896	-3.566811	-1.336195
17	6	0	2.536148	-3.302371	-1.397837
18	6	0	0.522132	-0.278557	1.729189
19	6	0	1.903893	-0.038977	1.752269
20	6	0	2.630011	-0.071862	2.932983
21	6	0	-0.100973	-0.668173	2.912341
22	6	0	0.627443	-0.710815	4.106244
23	6	0	1.980412	-0.390637	4.127502
24	1	0	3.597224	0.257615	0.419125
25	1	0	-0.220120	4.056121	-1.960060
26	1	0	2.242234	4.260905	-1.829413
27	1	0	-0.767492	-2.874437	-0.760842
28	1	0	0.800471	-4.521739	-1.686497
29	1	0	3.232383	-4.026841	-1.799812
30	1	0	-1.139825	-0.961396	2.924778
31	1	0	0.125061	-1.005330	5.020740
32	1	0	2.535797	-0.420413	5.057929
33	1	0	3.697259	0.120134	2.916216
34	6	0	-1.598152	-0.392635	0.188873
35	6	0	-2.182001	-0.915117	-0.967124
36	6	0	-2.430154	0.144382	1.172321
37	6	0	-3.566713	-0.946032	-1.111349
38	6	0	-3.815074	0.112052	1.025073
39	6	0	-4.405932	-0.446609	-0.111407
40	1	0	-5.478112	-0.474340	-0.222306
41	1	0	-1.590464	-1.234963	-1.811099
42	1	0	-2.037645	0.670811	2.027992
43	8	0	-4.019612	-1.474971	-2.286926
44	8	0	-4.523525	0.673128	2.049690
45	6	0	-5.416990	-1.478915	-2.543875
46	6	0	-5.939086	0.740709	1.948543
47	1	0	-5.536270	-1.916407	-3.533869
48	1	0	-5.958917	-2.090319	-1.812873
49	1	0	-5.827116	-0.462443	-2.546168
50	1	0	-6.278547	1.241087	2.854132
51	1	0	-6.251413	1.324049	1.074676
52	1	0	-6.387210	-0.258652	1.900272

Table S34. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer C) at B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.8807348 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.476497	-1.943461	-1.390636
2	6	0	-0.400639	-2.038958	-1.396285
3	6	0	0.396093	-1.195540	-0.627533
4	6	0	-0.122011	-0.068540	0.327971
5	6	0	1.785043	-1.351200	-0.645407
6	6	0	2.486511	-0.378027	0.263301
7	6	0	0.197777	-3.024017	-2.184972
8	6	0	1.579170	-3.177458	-2.214629
9	6	0	2.367422	-2.332399	-1.436225
10	17	0	4.118613	-2.536834	-1.464700
11	6	0	0.498686	-0.366696	1.720007
12	6	0	1.889569	-0.561776	1.655359
13	6	0	2.634582	-0.795272	2.800387
14	1	0	3.706400	-0.944508	2.728010
15	6	0	-0.118133	-0.311966	2.965017
16	6	0	0.633306	-0.543165	4.123086
17	6	0	1.996724	-0.804951	4.044544
18	6	0	0.655463	1.239909	-0.033348
19	6	0	2.044916	1.014362	-0.175034
20	6	0	2.898372	2.042649	-0.539282
21	6	0	0.220009	2.566693	-0.046286
22	6	0	1.084918	3.598561	-0.431121
23	6	0	2.413768	3.338711	-0.714846
24	1	0	3.565463	-0.488712	0.256412
25	1	0	-0.423248	-3.680325	-2.783625
26	1	0	2.046026	-3.939335	-2.825396
27	1	0	-1.167378	-0.069809	3.053878
28	1	0	0.142614	-0.508246	5.089188
29	1	0	2.570393	-0.987005	4.946108
30	17	0	-1.349728	3.088698	0.560022
31	1	0	0.707141	4.611678	-0.475352
32	1	0	3.082253	4.135778	-1.012355
33	17	0	4.624134	1.758741	-0.746398
34	6	0	-1.638910	-0.041912	0.166663
35	6	0	-2.471854	-0.820155	0.968033
36	6	0	-2.177421	0.588173	-0.956969
37	6	0	-3.838249	-0.903075	0.689757
38	6	0	-3.538226	0.504831	-1.231064
39	6	0	-4.393132	-0.234489	-0.404002
40	1	0	-5.449274	-0.294537	-0.612420
41	1	0	-2.093608	-1.413895	1.785312
42	1	0	-1.555587	1.151780	-1.638662
43	8	0	-4.560293	-1.682847	1.548579
44	8	0	-3.956857	1.180852	-2.341496
45	6	0	-5.953668	-1.843759	1.322191
46	6	0	-5.331263	1.132876	-2.697769
47	1	0	-6.309262	-2.503317	2.112281
48	1	0	-6.484207	-0.886636	1.385861
49	1	0	-6.151671	-2.307104	0.348597
50	1	0	-5.424695	1.730789	-3.603009
51	1	0	-5.657213	0.107372	-2.907558
52	1	0	-5.964730	1.564678	-1.914296

Table S35. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers A and B) at B3LYP-D3/6-311++G(d,p) level
total energy: HF= hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.523001	3.037228	-1.012485
2	6	0	-0.499134	2.724986	-0.901810
3	6	0	-0.837738	1.489639	-0.361818
4	6	0	0.084610	0.338704	0.158938
5	6	0	-2.207209	1.179440	-0.188165
6	6	0	-2.479140	-0.150399	0.503509
7	6	0	-1.496440	3.621998	-1.299119
8	6	0	-2.838437	3.308443	-1.158837
9	6	0	-3.180486	2.080371	-0.592058
10	17	0	-4.893845	1.709765	-0.387061
11	6	0	-0.375922	0.204925	1.651172
12	6	0	-1.732839	-0.077525	1.814477
13	6	0	-2.309058	-0.191280	3.071827
14	1	0	-3.365429	-0.417817	3.165581
15	6	0	0.400997	0.447027	2.781477
16	6	0	-0.173160	0.346852	4.051994
17	6	0	-1.516646	0.013239	4.202537
18	6	0	-0.448775	-0.917757	-0.623381
19	6	0	-1.801111	-1.203833	-0.344399
20	6	0	-2.431559	-2.316159	-0.881119
21	6	0	0.183155	-1.709345	-1.590414
22	6	0	-0.457515	-2.835285	-2.120669
23	6	0	-1.751108	-3.160721	-1.753433
24	1	0	-3.537746	-0.343242	0.634115
25	1	0	-1.212025	4.578651	-1.721785
26	1	0	-3.614187	3.996857	-1.467434
27	1	0	1.445630	0.708924	2.689275
28	1	0	0.440114	0.532127	4.926620
29	1	0	-1.950977	-0.069159	5.192375
30	17	0	1.746193	-1.353582	-2.323254
31	1	0	0.069097	-3.444029	-2.843838
32	1	0	-2.240480	-4.033980	-2.164131
33	17	0	-4.110268	-2.684488	-0.494742
34	6	0	1.617051	0.396290	0.123866

35	6	0	2.398647	1.374243	-0.479461
36	6	0	2.263442	-0.685986	0.737046
37	6	0	3.792955	1.272504	-0.472571
38	6	0	3.647944	-0.787539	0.739582
39	6	0	4.439491	0.197335	0.135935
40	1	0	5.515063	0.122665	0.135545
41	1	0	1.993016	2.202424	-1.028218
42	1	0	1.698579	-1.484045	1.199394
43	8	0	4.446712	2.289964	-1.109459
44	8	0	4.156752	-1.895185	1.356083
45	6	0	5.865136	2.253713	-1.181411
46	6	0	5.563779	-2.091800	1.362332
47	1	0	6.158093	3.144721	-1.734595
48	1	0	6.318943	2.283351	-0.183942
49	1	0	6.217090	1.364191	-1.716636
50	1	0	6.080732	-1.286540	1.897362
51	1	0	5.730091	-3.032347	1.885241
52	1	0	5.962748	-2.169488	0.344378

Table S36. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers B and C) at B3LYP-D3/6-311++G(d,p) level

total energy: HF= -2609.876139 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.996911	-1.605363	2.899152
2	6	0	0.056478	-1.411139	2.802895
3	6	0	0.597882	-0.819732	1.665093
4	6	0	-0.093085	-0.313628	0.357112
5	6	0	1.999138	-0.671365	1.604821
6	6	0	2.531112	-0.113624	0.291697
7	6	0	0.884047	-1.802122	3.862876
8	6	0	2.258511	-1.618848	3.800065
9	6	0	2.820464	-1.054956	2.652423
10	1	0	3.893932	-0.924810	2.569091
11	6	0	0.444271	1.158412	0.217348
12	6	0	1.847653	1.221081	0.091639
13	6	0	2.504407	2.425863	-0.108144
14	17	0	4.255283	2.487449	-0.289894
15	6	0	-0.243233	2.376557	0.288061
16	6	0	0.425979	3.587287	0.073996
17	6	0	1.790865	3.620189	-0.149131
18	6	0	0.615497	-1.185053	-0.738734
19	6	0	2.007059	-1.043795	-0.776645
20	6	0	2.758286	-1.788989	-1.674801
21	6	0	-0.000650	-2.127863	-1.555813
22	6	0	0.768860	-2.880941	-2.445475
23	6	0	2.145659	-2.708321	-2.524676
24	1	0	3.612377	-0.030775	0.286874
25	1	0	0.435412	-2.256677	4.738935
26	1	0	2.892112	-1.921852	4.625638
27	17	0	-1.935380	2.558179	0.747206
28	1	0	-0.139392	4.509345	0.105841
29	1	0	2.302585	4.558917	-0.315443
30	1	0	-1.068813	-2.282884	-1.512855
31	1	0	0.285957	-3.610506	-3.085245
32	1	0	2.744655	-3.284306	-3.218068
33	17	0	4.511583	-1.611533	-1.740061
34	6	0	-1.607013	-0.368455	0.122643
35	6	0	-2.571965	-0.718152	1.059228
36	6	0	-2.029919	0.022093	-1.155436
37	6	0	-3.929392	-0.677530	0.727459
38	6	0	-3.378489	0.064659	-1.482335
39	6	0	-4.354544	-0.290781	-0.543185
40	1	0	-5.402953	-0.258812	-0.792730
41	1	0	-2.343219	-0.963524	2.078672
42	1	0	-1.318138	0.328556	-1.909992
43	8	0	-4.779399	-1.030935	1.737525
44	8	0	-3.664513	0.473659	-2.753919
45	6	0	-6.179731	-0.985401	1.502117
46	6	0	-5.024547	0.586742	-3.149016
47	1	0	-6.648716	-1.291618	2.435926
48	1	0	-6.510825	0.027901	1.246806
49	1	0	-6.476088	-1.678194	0.705880
50	1	0	-5.006451	0.940600	-4.178664
51	1	0	-5.537075	-0.381639	-3.110430
52	1	0	-5.564026	1.311103	-2.528003

Table S37. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers C and A) at B3LYP-D3/6-311++G(d,p) level

total energy: HF= -2609.8616669 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.699373	3.678045	-0.671552
2	6	0	0.775276	2.759883	-0.363130
3	6	0	0.875095	1.393333	-0.073893
4	6	0	-0.160038	0.180188	0.097660
5	6	0	2.209667	0.910580	0.128500
6	6	0	2.342462	-0.576790	0.447374
7	6	0	1.908251	3.586769	-0.441808
8	6	0	3.176932	3.094723	-0.239381
9	6	0	3.315387	1.740477	0.047430
10	17	0	4.949218	1.129015	0.305743
11	6	0	0.386023	-0.838122	-0.953829
12	6	0	1.691193	-1.275722	-0.720082
13	6	0	2.283385	-2.182734	-1.589581
14	17	0	3.921456	-2.765871	-1.296080
15	6	0	-0.293134	-1.257185	-2.093699
16	6	0	0.320592	-2.154331	-2.969005
17	6	0	1.600846	-2.636840	-2.716286
18	6	0	0.194654	-0.330870	1.529134
19	6	0	1.503815	-0.781230	1.684600
20	6	0	1.969255	-1.255818	2.903929
21	6	0	-0.649690	-0.299983	2.636209
22	6	0	-0.187047	-0.764257	3.869666
23	6	0	1.109844	-1.256787	4.003397
24	1	0	3.374339	-0.874603	0.590228
25	1	0	1.768292	4.635270	-0.667684
26	1	0	4.043514	3.739164	-0.301365
27	1	0	-1.293348	-0.902374	-2.300282
28	1	0	-0.207537	-2.486015	-3.855447
29	1	0	2.075501	-3.342680	-3.385522
30	1	0	-1.661947	0.071258	2.547262
31	1	0	-0.848405	-0.741640	4.728414
32	1	0	1.456742	-1.623565	4.962758
33	1	0	2.992591	-1.602582	2.996947
34	6	0	-1.707471	0.141257	-0.014842
35	6	0	-2.598364	1.163078	-0.296667
36	6	0	-2.239771	-1.143799	0.210734
37	6	0	-3.977677	0.921533	-0.353237
38	6	0	-3.604723	-1.382650	0.153412
39	6	0	-4.505573	-0.347066	-0.131445
40	1	0	-5.567543	-0.528038	-0.176395
41	1	0	-2.281324	2.166706	-0.480389
42	1	0	-1.600019	-1.985233	0.436846
43	8	0	-4.736558	2.021765	-0.640030
44	8	0	-3.987144	-2.674128	0.390959
45	6	0	-6.147139	1.877272	-0.718071
46	6	0	-5.369451	-2.998144	0.352295
47	1	0	-6.535742	2.867025	-0.952925
48	1	0	-6.436292	1.178463	-1.511903
49	1	0	-6.570045	1.540633	0.235817
50	1	0	-5.431059	-4.063631	0.568606
51	1	0	-5.934830	-2.443764	1.110546
52	1	0	-5.800969	-2.806304	-0.637140

Table S38. Optimized Structural Coordinate and its Total Energy for **12** at PCM- B3LYP-D3/6-311++G(d,p) level

total energy: HF= -1411.0347546 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.082984	-0.000000	2.492111
2	6	0	0.990588	0.000000	1.436967
3	6	0	0.645820	-0.000000	-0.081416
4	6	0	2.363192	0.000000	1.710332
5	6	0	3.215295	0.000000	0.461848
6	6	0	0.552367	-0.000000	3.810495
7	6	0	1.919228	0.000000	4.074118
8	6	0	2.833033	0.000000	3.016262
9	6	0	1.414639	1.201961	-0.704182
10	6	0	2.779793	1.204564	-0.365365
11	6	0	3.635043	2.179711	-0.855760
12	6	0	0.944760	2.139485	-1.618257
13	6	0	1.807917	3.122116	-2.118384
14	6	0	3.141411	3.157888	-1.725154
15	6	0	1.414640	-1.201961	-0.704182
16	6	0	2.779794	-1.204563	-0.365364
17	6	0	3.635044	-2.179710	-0.855760
18	6	0	0.944761	-2.139485	-1.618256
19	6	0	1.807918	-3.122117	-2.118383
20	6	0	3.141412	-3.157888	-1.725153
21	6	0	-0.869644	-0.000000	-0.220566
22	6	0	-1.593795	1.195757	-0.174003
23	6	0	-1.593795	-1.195757	-0.174003
24	6	0	-2.984182	1.174895	-0.182633
25	6	0	-2.984182	-1.174896	-0.182634
26	6	0	-3.718674	-0.000000	-0.202628
27	7	0	-3.714057	2.463175	-0.151418
28	7	0	-3.714058	-2.463175	-0.151418
29	1	0	-0.984623	-0.000000	2.315850
30	1	0	4.283631	0.000001	0.674004
31	1	0	-0.158649	-0.000000	4.628644
32	1	0	2.276050	0.000000	5.097708
33	1	0	3.900480	0.000001	3.208537
34	1	0	4.684601	2.166007	-0.582398
35	1	0	-0.076170	2.116888	-1.974845
36	1	0	1.428048	3.853690	-2.822171
37	1	0	3.803768	3.923903	-2.111696
38	1	0	4.684602	-2.166006	-0.582397
39	1	0	-0.076169	-2.116889	-1.974844
40	1	0	1.428050	-3.853690	-2.822170
41	1	0	3.803769	-3.923902	-2.111695
42	1	0	-1.094664	2.148620	-0.094989
43	1	0	-1.094665	-2.148621	-0.094989
44	1	0	-4.797774	0.000000	-0.213067
45	8	0	-4.937643	2.424122	-0.143836
46	8	0	-3.052712	3.493602	-0.136159
47	8	0	-4.937643	-2.424122	-0.143835
48	8	0	-3.052712	-3.493602	-0.136161

Table S39. Optimized Structural Coordinate and its Total Energy for **13** at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -1112.6624914 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.638872	-0.009844	2.423415
2	6	0	0.324208	-0.007459	1.418444
3	6	0	0.047778	0.000581	-0.113602
4	6	0	1.679045	-0.010644	1.767885
5	6	0	2.596652	-0.004547	0.567219
6	6	0	-0.241884	-0.016381	3.765010
7	6	0	1.109446	-0.020457	4.104386
8	6	0	2.079145	-0.017356	3.097960
9	6	0	0.859946	1.200799	-0.688406
10	6	0	2.205862	1.202851	-0.277453
11	6	0	3.090328	2.175313	-0.720495
12	6	0	0.446229	2.139267	-1.629078
13	6	0	1.338674	3.117989	-2.083758
14	6	0	2.649149	3.153263	-1.617868
15	6	0	0.859045	-1.193655	-0.702272
16	6	0	2.204857	-1.201830	-0.291126
17	6	0	3.088524	-2.169910	-0.745284
18	6	0	0.444536	-2.120656	-1.654057
19	6	0	1.336185	-3.094947	-2.119736
20	6	0	2.646507	-3.137005	-1.653951
21	6	0	-1.466062	0.002037	-0.324605
22	6	0	-2.178236	1.204630	-0.297716
23	6	0	-2.177976	-1.201274	-0.313499
24	6	0	-3.581217	1.212056	-0.329716
25	6	0	-3.580325	-1.209088	-0.347391
26	6	0	-4.279133	0.001648	-0.374336
27	7	0	-4.274448	2.424404	-0.244847
28	7	0	-4.272502	-2.423724	-0.406723
29	1	0	-1.691997	-0.005295	2.175068
30	1	0	3.652908	-0.006452	0.834835
31	1	0	-0.996215	-0.017404	4.543986
32	1	0	1.409737	-0.025300	5.146276
33	1	0	3.134978	-0.019593	3.347677
34	1	0	4.123504	2.157914	-0.389794
35	1	0	-0.557467	2.113101	-2.029440
36	1	0	1.001024	3.848348	-2.810674
37	1	0	3.334231	3.916622	-1.969191
38	1	0	4.121684	-2.157280	-0.414280
39	1	0	-0.558940	-2.089611	-2.054628
40	1	0	0.997631	-3.816476	-2.854965
41	1	0	3.330892	-3.896936	-2.013979
42	1	0	-1.660755	2.147923	-0.193338
43	1	0	-1.659601	-2.146065	-0.229693
44	1	0	-5.364508	0.000955	-0.406447
45	1	0	-5.218690	2.409717	-0.604172
46	1	0	-3.765985	3.234468	-0.570406
47	1	0	-5.215982	-2.401324	-0.045337
48	1	0	-3.762269	-3.224346	-0.060327

Table S40. Optimized Structural Coordinate and its Total Energy for phenyltriptycene at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -1001.8990148 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.187638	2.328685	-0.000007
2	6	0	-0.162929	1.386764	-0.000002
3	6	0	-0.338919	-0.160176	-0.000001
4	6	0	1.167365	1.821642	-0.000000
5	6	0	2.159736	0.681934	0.000002
6	6	0	-0.876703	3.693093	-0.000008
7	6	0	0.449998	4.117189	-0.000005
8	6	0	1.481738	3.174163	-0.000002
9	6	0	0.506896	-0.688230	-1.198070
10	6	0	1.823625	-0.192210	-1.202809
11	6	0	2.733743	-0.582376	-2.174083
12	6	0	0.152527	-1.656701	-2.132278
13	6	0	1.071121	-2.057234	-3.110500
14	6	0	2.349333	-1.509462	-3.148271
15	6	0	0.506893	-0.688228	1.198071
16	6	0	1.823623	-0.192208	1.202813
17	6	0	2.733737	-0.582372	2.174090
18	6	0	0.152520	-1.656695	2.132283
19	6	0	1.071111	-2.057225	3.110508
20	6	0	2.349323	-1.509455	3.148280
21	6	0	-1.832905	-0.474267	-0.000001
22	6	0	-2.562088	-0.507360	-1.197217
23	6	0	-2.562090	-0.507347	1.197214
24	6	0	-3.948221	-0.655368	-1.200322
25	6	0	-3.948222	-0.655356	1.200319
26	6	0	-4.649226	-0.748539	-0.000001
27	1	0	-4.479037	-0.682392	-2.145458
28	1	0	-4.479039	-0.682370	2.145455
29	1	0	-2.224028	2.017807	-0.000009
30	1	0	3.196648	1.016498	0.000003
31	1	0	-1.679071	4.422363	-0.000012
32	1	0	0.683596	5.175966	-0.000006
33	1	0	2.519436	3.490709	-0.000000
34	1	0	3.743819	-0.186783	-2.158901
35	1	0	-0.822011	-2.123790	-2.105556

36	1	0	0.779328	-2.806324	-3.838036
37	1	0	3.054630	-1.819456	-3.911044
38	1	0	3.743813	-0.186780	2.158910
39	1	0	-0.822019	-2.123781	2.105560
40	1	0	0.779315	-2.806313	3.838046
41	1	0	3.054619	-1.819448	3.911056
42	1	0	-2.054591	-0.377748	-2.142814
43	1	0	-2.054593	-0.377726	2.142810
44	1	0	-5.726893	-0.866393	-0.000001

Table S41. Optimized Structural Coordinate and its Total Energy for *m*-dinitrobenzene at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -641.4531891 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000000	-2.238214	0.000003
2	6	0	-1.207855	-1.546268	0.000001
3	6	0	-1.183201	-0.153892	0.000000
4	6	0	-0.000000	0.571151	0.000000
5	6	0	1.183201	-0.153892	0.000001
6	6	0	1.207855	-1.546268	0.000002
7	7	0	2.464073	0.588868	0.000001
8	8	0	3.499863	-0.064191	-0.000008
9	8	0	2.414934	1.812005	0.000004
10	7	0	-2.464073	0.588868	-0.000001
11	8	0	-2.414934	1.812005	0.000002
12	8	0	-3.499863	-0.064191	-0.000005
13	1	0	-0.000000	-3.320325	0.000004
14	1	0	-2.154687	-2.067607	0.000001
15	1	0	0.000000	1.650663	-0.000000
16	1	0	2.154686	-2.067607	0.000003

Table S42. Optimized Structural Coordinate and its Total Energy for *m*-diaminobenzene at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -343.0812178 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	1.792450
2	6	0	0.000188	-1.215179	1.113169
3	6	0	-0.000000	-1.219414	-0.291918
4	6	0	-0.000000	-0.000000	-0.981300
5	6	0	0.000000	1.219414	-0.291918
6	6	0	-0.000188	1.215179	1.113169
7	7	0	-0.061566	2.425913	-0.997740
8	1	0	0.284102	3.233162	-0.497993
9	1	0	0.296181	2.393901	-1.942246
10	7	0	0.061566	-2.425913	-0.997740
11	1	0	-0.296181	-2.393901	-1.942246
12	1	0	-0.284102	-3.233162	-0.497993
13	1	0	0.000000	0.000000	2.877384
14	1	0	0.004424	-2.152570	1.658542
15	1	0	-0.000000	-0.000000	-2.067548
16	1	0	-0.004424	2.152570	1.658542

Table S43. Optimized Structural Coordinate and its Total Energy for benzene at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -232.3183712 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	-0.000000	1.395788
2	6	0	0.000000	1.208752	0.697888
3	6	0	0.000000	1.208752	-0.697888
4	6	0	0.000000	-0.000000	-1.395788
5	6	0	-0.000000	-1.208752	-0.697888
6	6	0	-0.000000	-1.208752	0.697888
7	1	0	0.000000	-0.000000	2.480188
8	1	0	0.000000	2.147890	1.240056
9	1	0	0.000000	2.147890	-1.240056
10	1	0	0.000000	-0.000000	-2.480188
11	1	0	-0.000000	-2.147890	-1.240056
12	1	0	-0.000000	-2.147890	1.240056

Table S44. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer A) at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.8888448 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.848688	-0.727179	2.285480
2	6	0	-0.793334	-0.723846	2.519055
3	6	0	0.157863	-0.460787	1.535238
4	6	0	-0.130637	-0.174633	0.025262
5	6	0	1.508984	-0.479092	1.880221
6	6	0	2.407787	-0.200636	0.704986
7	6	0	-0.379718	-0.988540	3.828244
8	6	0	0.973303	-0.992448	4.161868
9	6	0	1.930210	-0.735962	3.178309
10	1	0	2.988350	-0.739462	3.415489
11	6	0	0.633888	1.136009	-0.357112
12	6	0	1.964770	1.137211	0.122632
13	6	0	2.786816	2.235177	-0.070419
14	17	0	4.434016	2.254996	0.559824
15	6	0	0.269048	2.169080	-1.222962
16	6	0	1.098991	3.282489	-1.401266
17	6	0	2.342820	3.339584	-0.797062
18	6	0	0.710417	-1.205579	-0.778022
19	6	0	2.060551	-1.225418	-0.371650
20	6	0	2.952544	-2.065423	-1.020250
21	6	0	0.310498	-1.947481	-1.882530
22	6	0	1.229947	-2.781434	-2.527306
23	6	0	2.545857	-2.863201	-2.091618
24	1	0	3.459767	-0.208332	0.967085
25	1	0	-1.125105	-1.192405	4.588639
26	1	0	1.283208	-1.197028	5.180357
27	17	0	-1.143007	2.107855	-2.278903
28	1	0	0.770125	4.090332	-2.041693
29	1	0	2.983212	4.200817	-0.933743
30	1	0	-0.696728	-1.874486	-2.264770
31	1	0	0.913748	-3.368763	-3.381332
32	1	0	3.258563	-3.512071	-2.583756
33	17	0	4.648543	-2.127387	-0.527127
34	6	0	-1.649659	-0.162026	-0.120342
35	6	0	-2.343564	0.980836	0.282463
36	6	0	-2.368145	-1.321889	-0.404648
37	6	0	-3.734511	0.986923	0.325144
38	6	0	-3.765430	-1.313357	-0.358671
39	6	0	-4.468205	-0.158779	-0.006460
40	1	0	-5.545814	-0.153324	0.022221
41	1	0	-1.820865	1.882131	0.572177
42	1	0	-1.882526	-2.261732	-0.616522
43	8	0	-4.306880	2.166370	0.707616
44	8	0	-4.365748	-2.500953	-0.666662
45	6	0	-5.728779	2.244737	0.798935
46	6	0	-5.789523	-2.584927	-0.618722
47	1	0	-5.949062	3.259406	1.125393
48	1	0	-6.200516	2.066921	-0.173008
49	1	0	-6.120725	1.534090	1.534034
50	1	0	-6.035072	-3.610949	-0.886324
51	1	0	-6.167219	-2.371654	0.386662
52	1	0	-6.252739	-1.902052	-1.338418

Table S45. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer B) at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.8855398 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	17	0	-2.050225	2.290040	-1.124129
2	6	0	-0.296482	2.176000	-0.937011
3	6	0	0.414200	1.118346	-0.346302
4	6	0	-0.081574	-0.241340	0.288772
5	6	0	1.819215	1.261549	-0.286369
6	6	0	2.524759	0.107862	0.380423
7	6	0	0.371487	3.297006	-1.447558
8	6	0	1.747360	3.408510	-1.385259
9	6	0	2.467921	2.377171	-0.794938
10	17	0	4.223534	2.530204	-0.709285
11	6	0	0.745389	-1.380468	-0.400046
12	6	0	2.131084	-1.143972	-0.382130
13	6	0	3.000329	-2.081791	-0.919476
14	17	0	4.743737	-1.792124	-0.920864
15	6	0	0.273868	-2.608626	-0.853715
16	6	0	1.165648	-3.548789	-1.378610
17	6	0	2.528045	-3.286672	-1.439386
18	6	0	0.522252	-0.298516	1.731322
19	6	0	1.904892	-0.061678	1.755930
20	6	0	2.633385	-0.111271	2.935180
21	6	0	-0.099848	-0.702425	2.910677
22	6	0	0.630418	-0.762163	4.103369
23	6	0	1.984680	-0.444765	4.126902
24	1	0	3.598309	0.248014	0.428304
25	1	0	-0.209688	4.090634	-1.897856
26	1	0	2.250734	4.279319	-1.783659
27	1	0	-0.773948	-2.859302	-0.793394
28	1	0	0.788456	-4.497784	-1.741279
29	1	0	3.220311	-4.008177	-1.853346
30	1	0	-1.138925	-0.994326	2.922596
31	1	0	0.128584	-1.067828	5.014438
32	1	0	2.541443	-0.487794	5.055933
33	1	0	3.700950	0.078760	2.919711
34	6	0	-1.599075	-0.390415	0.184602
35	6	0	-2.176560	-0.886483	-0.986494
36	6	0	-2.437048	0.121014	1.176625
37	6	0	-3.561370	-0.916301	-1.138551
38	6	0	-3.822305	0.089802	1.021214
39	6	0	-4.406539	-0.442592	-0.131092
40	1	0	-5.477926	-0.468641	-0.248470
41	1	0	-1.578365	-1.188921	-1.832477
42	1	0	-2.048821	0.626189	2.046999
43	8	0	-4.008997	-1.416675	-2.328206
44	8	0	-4.538177	0.625503	2.053876
45	6	0	-5.413171	-1.435883	-2.581488
46	6	0	-5.960429	0.678010	1.950867
47	1	0	-5.528690	-1.853913	-3.579763
48	1	0	-5.939364	-2.070180	-1.860458
49	1	0	-5.835005	-0.425746	-2.559891
50	1	0	-6.306737	1.152332	2.867240
51	1	0	-6.274899	1.277680	1.090454
52	1	0	-6.391984	-0.325706	1.877534

Table S46. Optimized Structural Coordinate and its Total Energy for **14** (Rotamer C) at PCM- B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.8889592 hartree (NImag = 0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.480905	-1.949636	-1.374060
2	6	0	-0.404954	-2.044256	-1.382021
3	6	0	0.393942	-1.197758	-0.618284
4	6	0	-0.122057	-0.067034	0.334378
5	6	0	1.783135	-1.353708	-0.639219
6	6	0	2.486980	-0.378881	0.266008
7	6	0	0.190289	-3.032402	-2.170008
8	6	0	1.572239	-3.185238	-2.204803
9	6	0	2.361192	-2.336637	-1.430973
10	17	0	4.115689	-2.538509	-1.467053
11	6	0	0.500775	-0.362824	1.726344
12	6	0	1.891833	-0.558285	1.659620
13	6	0	2.640053	-0.789378	2.803650
14	1	0	3.711753	-0.938126	2.729744
15	6	0	-0.113954	-0.307885	2.972844
16	6	0	0.640094	-0.536963	4.130324
17	6	0	2.004362	-0.797213	4.049603
18	6	0	0.656905	1.239489	-0.031903
19	6	0	2.045771	1.012145	-0.176600
20	6	0	2.897633	2.038848	-0.548879
21	6	0	0.224675	2.567236	-0.049883
22	6	0	1.087975	3.597673	-0.441392
23	6	0	2.416033	3.335203	-0.728879
24	1	0	3.565621	-0.490805	0.260225
25	1	0	-0.432547	-3.690792	-2.764154
26	1	0	2.035378	-3.948906	-2.816127
27	1	0	-1.163523	-0.068967	3.065324
28	1	0	0.150745	-0.501917	5.097039
29	1	0	2.580025	-0.977295	4.950239
30	17	0	-1.344832	3.093885	0.559873
31	1	0	0.713313	4.611655	-0.490323
32	1	0	3.082295	4.131600	-1.032742
33	17	0	4.624286	1.749867	-0.762532
34	6	0	-1.639200	-0.037493	0.172313
35	6	0	-2.475554	-0.808854	0.976759
36	6	0	-2.174168	0.586895	-0.956594
37	6	0	-3.842358	-0.892386	0.694470
38	6	0	-3.535197	0.503086	-1.234157
39	6	0	-4.393181	-0.229933	-0.404915
40	1	0	-5.448423	-0.290803	-0.616478
41	1	0	-2.099351	-1.396765	1.799266
42	1	0	-1.547834	1.144352	-1.639645
43	8	0	-4.568603	-1.665642	1.554564
44	8	0	-3.951816	1.172478	-2.349219
45	6	0	-5.967415	-1.826017	1.321916
46	6	0	-5.328549	1.105553	-2.718805
47	1	0	-6.326487	-2.480332	2.114097
48	1	0	-6.492654	-0.866958	1.378355
49	1	0	-6.158218	-2.293622	0.350356
50	1	0	-5.419597	1.694286	-3.629707
51	1	0	-5.636872	0.074424	-2.920748
52	1	0	-5.970586	1.536875	-1.943814

Table S47. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers A and B) at PCM-B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.8839779 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.525271	3.041256	-1.001120
2	6	0	-0.496633	2.726652	-0.895414
3	6	0	-0.836877	1.488937	-0.361033
4	6	0	0.084859	0.336712	0.159176
5	6	0	-2.206983	1.179194	-0.189291
6	6	0	-2.480330	-0.149046	0.504818
7	6	0	-1.492591	3.625476	-1.293509
8	6	0	-2.835691	3.311292	-1.159302
9	6	0	-3.177587	2.081730	-0.595680
10	17	0	-4.894357	1.709069	-0.396332
11	6	0	-0.375804	0.206056	1.651858
12	6	0	-1.733281	-0.074692	1.815663
13	6	0	-2.310771	-0.184808	3.073330
14	1	0	-3.367320	-0.409891	3.167660
15	6	0	0.400893	0.451003	2.782230
16	6	0	-0.173889	0.354734	4.053390
17	6	0	-1.518339	0.022224	4.204353
18	6	0	-0.450784	-0.920770	-0.620688
19	6	0	-1.803939	-1.204293	-0.341833
20	6	0	-2.435226	-2.316308	-0.878283
21	6	0	0.178537	-1.717939	-1.584915
22	6	0	-0.462577	-2.844021	-2.114044
23	6	0	-1.757869	-3.165740	-1.747937
24	1	0	-3.538652	-0.340501	0.638355
25	1	0	-1.206672	4.583299	-1.711961
26	1	0	-3.609006	4.001551	-1.469857
27	1	0	1.445779	0.712226	2.690956

28	1	0	0.439213	0.542253	4.927611
29	1	0	-1.953228	-0.057183	5.194140
30	17	0	1.745606	-1.368469	-2.317808
31	1	0	0.061590	-3.457813	-2.834623
32	1	0	-2.246764	-4.039285	-2.158329
33	17	0	-4.118095	-2.678301	-0.493088
34	6	0	1.617520	0.394256	0.121117
35	6	0	2.397175	1.367373	-0.493263
36	6	0	2.265895	-0.683096	0.740945
37	6	0	3.792818	1.266778	-0.487283
38	6	0	3.651523	-0.783329	0.742181
39	6	0	4.441198	0.197519	0.129934
40	1	0	5.516681	0.124102	0.129528
41	1	0	1.987864	2.189351	-1.049157
42	1	0	1.700930	-1.477030	1.210618
43	8	0	4.446209	2.277840	-1.133372
44	8	0	4.163736	-1.885328	1.365682
45	6	0	5.871323	2.245150	-1.196814
46	6	0	5.578455	-2.071605	1.382108
47	1	0	6.163714	3.131915	-1.756107
48	1	0	6.315054	2.284816	-0.196550
49	1	0	6.225616	1.351823	-1.721531
50	1	0	6.082214	-1.255483	1.910505
51	1	0	5.748054	-3.004706	1.916172
52	1	0	5.980346	-2.156516	0.367193

Table S48. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers B and C) at PCM-B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.884448 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.000068	-1.621522	2.891503
2	6	0	0.052667	-1.422019	2.798586
3	6	0	0.596104	-0.822078	1.665605
4	6	0	-0.093130	-0.312248	0.357889
5	6	0	1.997566	-0.672461	1.608650
6	6	0	2.532118	-0.113347	0.296914
7	6	0	0.878830	-1.816648	3.859097
8	6	0	2.253675	-1.629272	3.800883
9	6	0	2.817858	-1.059222	2.656595
10	1	0	3.891347	-0.927807	2.576794
11	6	0	0.446002	1.159533	0.219358
12	6	0	1.849698	1.221428	0.095215
13	6	0	2.505863	2.426006	-0.107740
14	17	0	4.259099	2.484188	-0.291615
15	6	0	-0.238793	2.379516	0.285951
16	6	0	0.429937	3.590104	0.070390
17	6	0	1.795426	3.621807	-0.152256
18	6	0	0.616971	-1.183599	-0.737450
19	6	0	2.008944	-1.042000	-0.773546
20	6	0	2.759083	-1.786618	-1.672920
21	6	0	0.002255	-2.127466	-1.554879
22	6	0	0.772182	-2.880798	-2.444592
23	6	0	2.149385	-2.706831	-2.523965
24	1	0	3.613303	-0.031650	0.296010
25	1	0	0.428829	-2.277378	4.731135
26	1	0	2.885885	-1.934674	4.626585
27	17	0	-1.933964	2.563841	0.742101
28	1	0	-0.132619	4.513922	0.098509
29	1	0	2.305633	4.560824	-0.320966
30	1	0	-1.065681	-2.284315	-1.513356
31	1	0	0.290157	-3.610813	-3.084200
32	1	0	2.747314	-3.282780	-3.218284
33	17	0	4.515255	-1.605887	-1.738546
34	6	0	-1.607337	-0.365284	0.123458
35	6	0	-2.572303	-0.706229	1.063726
36	6	0	-2.030467	0.019456	-1.156291
37	6	0	-3.930937	-0.665759	0.732023
38	6	0	-3.380243	0.061469	-1.482827
39	6	0	-4.356143	-0.287359	-0.541225
40	1	0	-5.404518	-0.256437	-0.790525
41	1	0	-2.341088	-0.943554	2.084835
42	1	0	-1.317136	0.319187	-1.912374
43	8	0	-4.782194	-1.009927	1.743471
44	8	0	-3.668117	0.463847	-2.755934
45	6	0	-6.187895	-0.970606	1.501861
46	6	0	-5.034653	0.553772	-3.157153
47	1	0	-6.658066	-1.268802	2.437092
48	1	0	-6.517369	0.039072	1.235576
49	1	0	-6.475621	-1.672038	0.711764
50	1	0	-5.018179	0.898981	-4.189245
51	1	0	-5.528807	-0.422207	-3.109749
52	1	0	-5.583438	1.274742	-2.542536

Table S49. Optimized Structural Coordinate and its Total Energy for **14 14** (TS1: a transition state between Rotamers C and A) at PCM-B3LYP-D3/6-311++G(d,p) level
total energy: HF= -2609.869642 hartree (NImag = 1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.696130	3.678646	-0.671515
2	6	0	0.779960	2.759762	-0.363524
3	6	0	0.876923	1.393135	-0.073324
4	6	0	-0.159820	0.181099	0.098204
5	6	0	2.211141	0.909260	0.129537
6	6	0	2.342378	-0.577912	0.450712
7	6	0	1.912707	3.586627	-0.443988
8	6	0	3.181583	3.093310	-0.242583
9	6	0	3.316722	1.739084	0.045309
10	17	0	4.952032	1.123786	0.301243
11	6	0	0.386891	-0.837859	-0.952638
12	6	0	1.691593	-1.276778	-0.717130
13	6	0	2.282347	-2.183432	-1.587852
14	17	0	3.923151	-2.767739	-1.292631
15	6	0	-0.290786	-1.255607	-2.094229
16	6	0	0.322481	-2.153166	-2.970036
17	6	0	1.602451	-2.637527	-2.716100
18	6	0	0.193625	-0.328765	1.530527
19	6	0	1.502269	-0.780505	1.687456
20	6	0	1.967199	-1.254567	2.907813
21	6	0	-0.651456	-0.295431	2.637495
22	6	0	-0.190031	-0.758795	3.872375
23	6	0	1.106858	-1.253162	4.007319
24	1	0	3.373262	-0.876912	0.596871
25	1	0	1.776159	4.635405	-0.670329
26	1	0	4.047307	3.738517	-0.306767
27	1	0	-1.290018	-0.899702	-2.303568
28	1	0	-0.204760	-2.483664	-3.857238
29	1	0	2.075548	-3.343498	-3.386276
30	1	0	-1.663339	0.076948	2.548799
31	1	0	-0.851819	-0.734159	4.730697
32	1	0	1.452874	-1.619290	4.967208
33	1	0	2.989991	-1.602424	3.002093
34	6	0	-1.707489	0.142516	-0.015348
35	6	0	-2.599153	1.164172	-0.296511
36	6	0	-2.240025	-1.142396	0.209426
37	6	0	-3.979411	0.922136	-0.353091
38	6	0	-3.605850	-1.381788	0.152133
39	6	0	-4.507096	-0.346564	-0.131937
40	1	0	-5.568956	-0.527432	-0.176242
41	1	0	-2.280688	2.167534	-0.479739
42	1	0	-1.598500	-1.982903	0.434760
43	8	0	-4.739860	2.021342	-0.638910
44	8	0	-3.988972	-2.672919	0.388822
45	6	0	-6.155908	1.871406	-0.721817
46	6	0	-5.377938	-2.996116	0.348807
47	1	0	-6.546390	2.860210	-0.955289
48	1	0	-6.436083	1.173372	-1.517799
49	1	0	-6.576617	1.530785	0.230152
50	1	0	-5.440574	-4.060972	0.565476
51	1	0	-5.939253	-2.439160	1.106297
52	1	0	-5.804402	-2.802652	-0.641053