Supporting Information

Mechanistic insights on the Lewis acid-catalyzed three-components cationic Povarov reaction: Synthesis of *N*-propargyl 1,2,3,4-tetrahydroquinolines

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1. Crystallography Details

1.1. Experimental section

1.1.1. Single Crystal X-ray diffraction analysis

A suitable single crystal of compound **4** was measured by single-crystal X-ray diffraction at room temperature (296 K). The crystal was obtained by slow evaporation from a saturated MeOH/DCM solution of the compound. Data collection was performed using a Bruker D8 Venture diffractometer equipped with a PHOTON 100 detector and a sealed-tube Mo-Kα X-ray source (λ = 0.71073 Å). The measured frames were integrated using **APEX4** package and corrected for absorption effects with **SADABS**. The molecular structure was solved by Intrinsic Phasing method with **SHELXT** and refined by full- matrix least-squares against F^2 using **SHELX**. Data reduction, refinement, and visualization were carried out in the **Olex2** interface, which integrates both programs. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were positioned geometrically, fixed with isotropic parameters, and refined with riding coordinates. Table S1 summarizes crystal data, data collection parameters, and refinement.

Table S1. Crystal data and refinement details compound **4**

Crystal Data			
Empirical formula	$C_{17}H_{20}N_2O_2$	μ/mm^{-1}	0.081
Formula weight	284.35	F(000)	608.0
Temperature/K	296.15	Crystal size/mm^3	0.226 × 0.182 × 0.052
Crystal system	monoclinic	Radiation	MoKα (λ = 0.71073)
Space group	Cc	2Θ range for data collection/°	4.68 to 54.986
a [Å]	9.4298(3)	Index ranges	-12 ≤ h ≤ 11, -22 ≤ k ≤ 22, -12 ≤ l ≤ 12
b [Å]	17.4070(7)	Reflections collected	17238
c [Å]	9.4334(4)	Independent reflections	3314 [R_{int} = 0.0455, R_{sigma} = 0.0329]
α [°]	90	Data/restraints/parameters	3314/2/191
β [°]	96.2680(10)	Goodness-of-fit on F^2	1.055
γ [°]	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1138
Volume [Å^3]	1539.18(10)	Final R indexes [all data]	R_1 = 0.0546, wR_2 = 0.1212
Z	4	Largest diff. peak/hole / e	0.13/-0.20

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		Å-3	
ρ_{calc}g/cm³	1.227	CCDC number	2415596

1.1.2. Hirshfeld surfaces and fingerprints plots

Hirshfeld surfaces analysis was generated using the CrystalExplorer software. Based on Crystallographic Information File (CIF), the isosurfaces were mapped with the normalized contact distance (d_{norm}), which is defined by the terms d_e, d_i, and r^{vdW} as follows:

$$d_{norm} = \frac{(d_i - r^{vdW}_i)}{r^{vdW}_i} + \frac{(d_e - r^{vdW}_e)}{r^{vdW}_e}$$

2D fingerprint plots were generated by plotting d_e versus d_i. The isosurface was color-coded to visualize different contact distances: red indicates interactions shorter interactions, blue represents the longest contacts, and white denotes contacts approximately equal to the sum of the van der Waals radii.

The **shape index** and **curvedness** are useful for analyzing isosurface and its chemical implications on crystalline packing. The **shape index** provides a qualitative analysis of the surface, where red areas usually indicate subtle variations in curvature, such as *bumps* related to donor intermolecular interactions and *hollows* associated with acceptor groups. The **curvedness** is a function of the least squares of the surface curvature, where flat areas represent low curvature, typically associated with π–π stacking interactions.

1.2. Results

1.2.1. Molecular structure

Tetrahydroquinoline **4** crystallizes in a non-centrosymmetric monoclinic *Cc* space group, with 4 entities per unit cell (Z' = 1). The molecule contains three rings, labeled A, B, and C (Figure S1). Rings B (-C5-C4-N7-C8-C12-C13-) and C (-C5-C6-C1-C2-C3-C4-) are nearly coplanar, with a dihedral angle of 3.77(9)°. Ring A, which is bonded to atom C13, forms angles of 93.23(6)° with ring B and 93.06(16)° with ring C, indicating an almost orthogonal orientation between the rings. Furthermore, the torsion angle N14-C13-C5-C6 is -38.3(4)°, like values reported for analogs compounds. In ring B, the puckering parameters θ and φ were calculated to be 132.7(3)° and 89.3(4)°, respectively, suggesting a half-chair

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conformation for the six-membered ring. The average bonding distances for the *N*-propargyl fragment are within the expected ranges according to previous reports, with values of 1.460(4) Å for N7–C9, 1.477(5) Å C9–C10 and 1.175(5) Å for C10–C11.
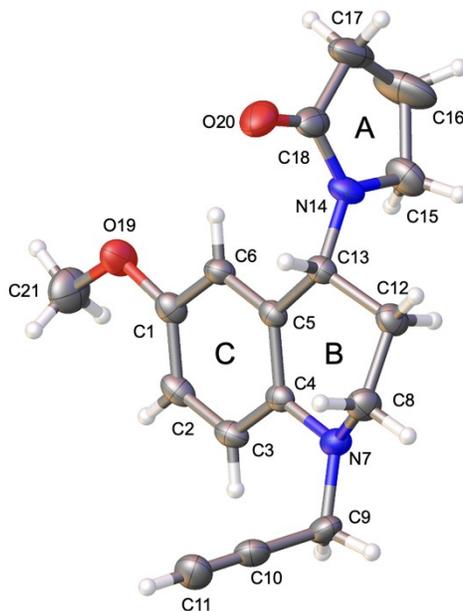
Figure S1. ORTEP plot of the THQ **4**. Thermal ellipsoids were drawn at 30% probability.

1.2.2. Crystal packing

In the crystalline arrangement, weak non-classical intermolecular interactions of the C–H⋯O type were observed (Table S1). The C8–H8A⋯O20[1], C9–H9A⋯O20[2], and C11–H11⋯O19[3] interactions present a supramolecular chain-like arrangement described by the notation $C_1^1(7, 9, 10)$ trough the [101], [110], and [100] directions, respectively (Figures S2–4). In the *ab* plane, columns extend along the *a*-axis related by a *c*-glide plane (Figure S5).
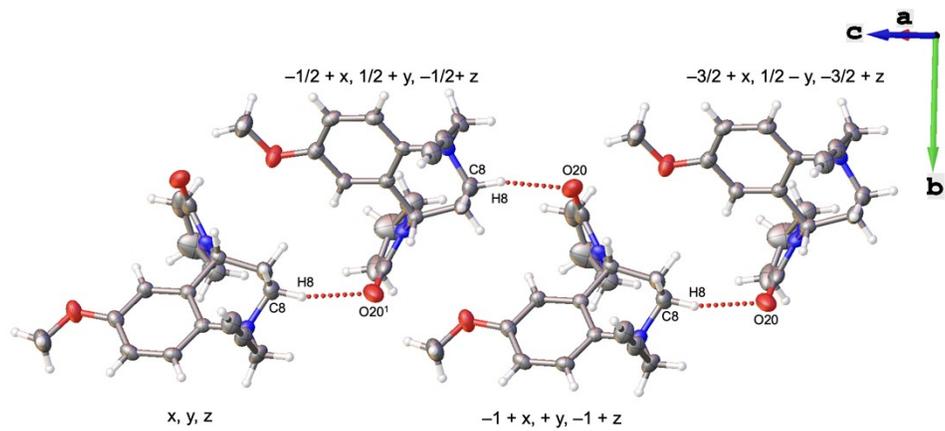
Figure S2. Intermolecular hydrogen bonds C8–H8A$\cdots$O20[1] and symmetry codes.
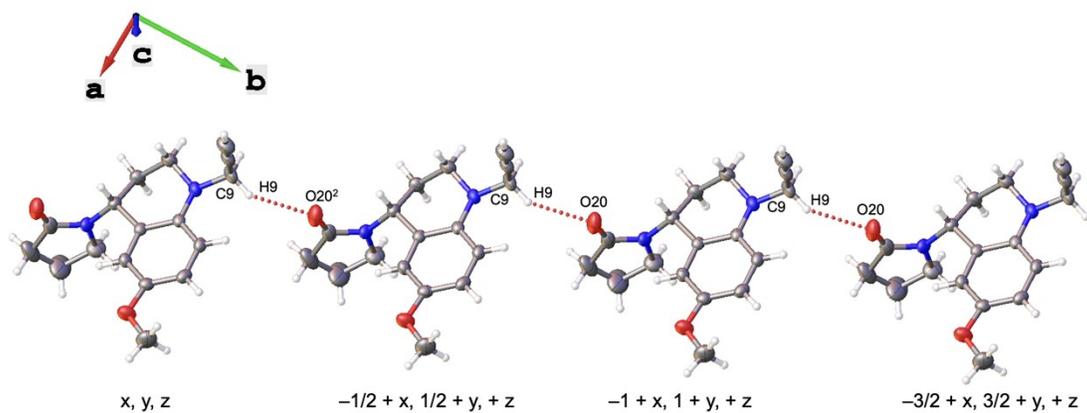
Figure S3. Intermolecular hydrogen bonds C9–H9A$\cdots$O20[2] and symmetry codes.
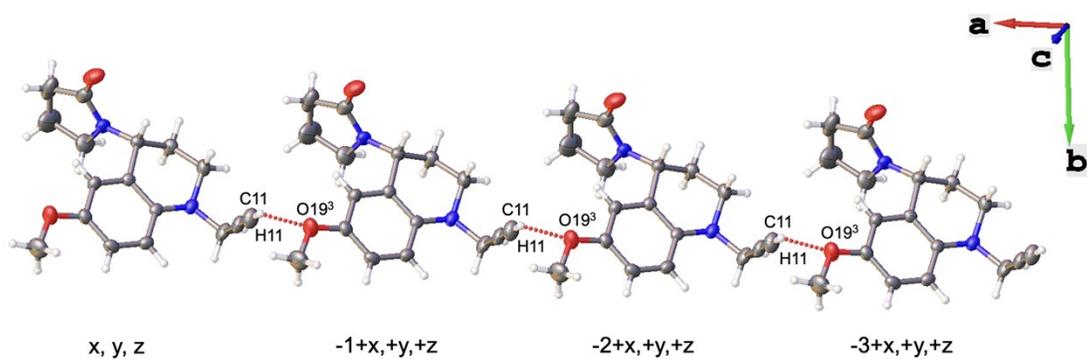
Figure S4. Intermolecular hydrogen bonds C11–H11···O19³ and symmetry codes.
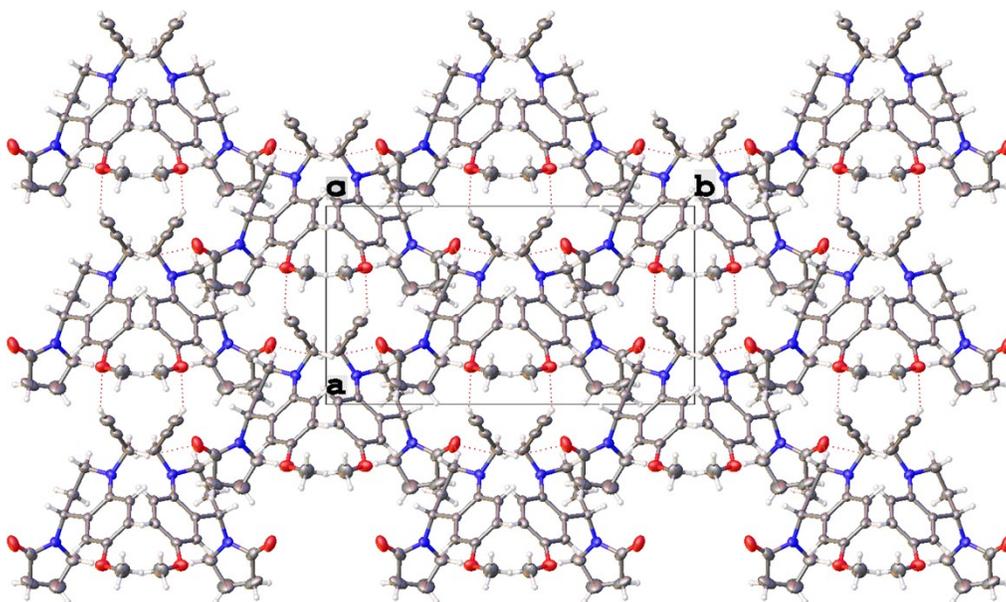
Figure S5. **Crystalline packing in the (001) view.** This view shows the **ab plane** and the arrangement of columns along *a*–**axis.**

Table S2. Intermolecular hydrogen bond interactions of molecule **4**.

D–H···A	d(D–H)/Å	d(H–A)/Å	d(D–A)/Å	D-H–A/°
C8–H8A···O20¹	0.97	2.48	3.321(4)	145.0
C9–H9B···O20²	0.97	2.46	3.335(4)	149.3
C11–H11···O19³	0.93	2.54	3.367(5)	148.9
¹-1/2+x,1/2-y,-1/2+z; ²-1/2+x,1/2+y,+z; ³-1+x,+y,+z				

The Hirshfeld surface was generated to analyze intermolecular interactions and mapped using 2D fingerprint plots. On the normalized surface (d_{norm}), the red dots primarily indicate C–H⋯O type hydrogen bonds, formed mainly by interactions between the hydrogens of the propargyl fragment and the oxygens of the methoxy group on the C ring, as well as the oxygen of the oxopyrrolidinyl ring (Figure S6–a). On the shape index surface, the red zones correspond to C–H⋯π interactions. These interactions are described as edge-to-face between the C rings, and between the hydrogens of the oxopyrrolidinyl moieties and the benzene rings (Figure S6–b). The crystal packing shows no evidence of π–π interactions. Additionally, the curvedness surface reveals no flat zones in the aromatic region (Figure S6–c).

The 2D fingerprint plots were plotted as a function of Hirshfeld surfaces and are shown in the Figure S7 with their respective atom pair and contribution to the mapped surface. The largest contribution is given by interatomic forces represented as H⋯H with 57.9% of the total surface (Figure S7–a). This is followed by H⋯π interactions with 23.9%, and non-classical hydrogen bonds of the C–H⋯O (O⋯H/O⋯H) type with 16.1% (Figures S7–c and S7–d).

| (a) | (b) | (c) |
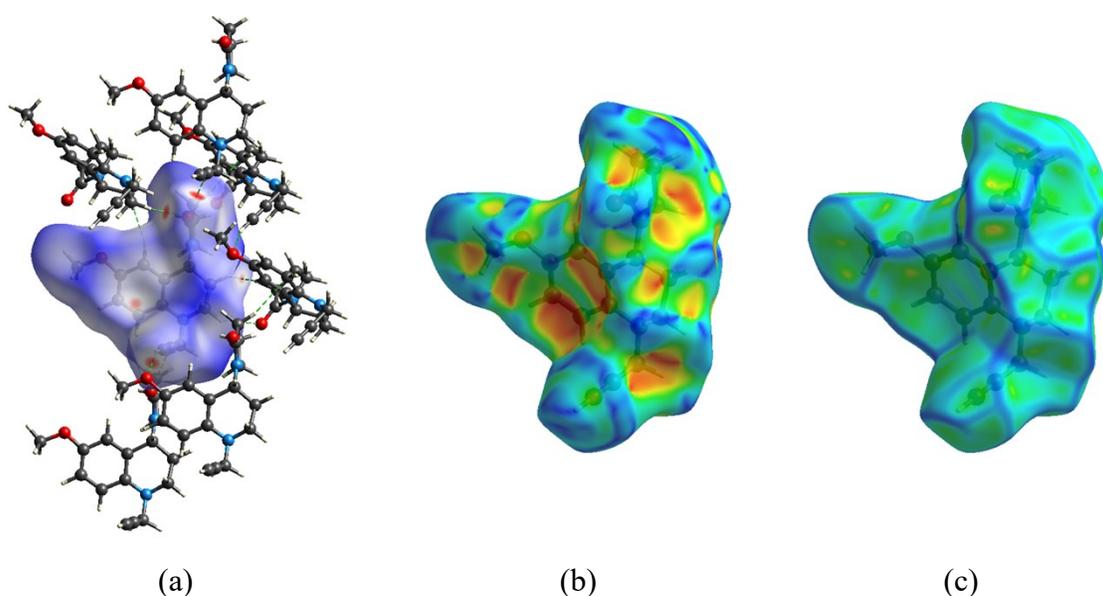
Figure S6. Hirshfeld surfaces of the molecule 4 mapped with d_{norm} surface and C–H⋯O hydrogen bonds as red spots (a), shape index (b), and curvedness shape (c).

(a) All   (b) H···H (57.9%)   (c) C···H/H···C (23.9%)

(d) O···H/H···O (16.1%)   (e) N···H/H···N (2.00%)
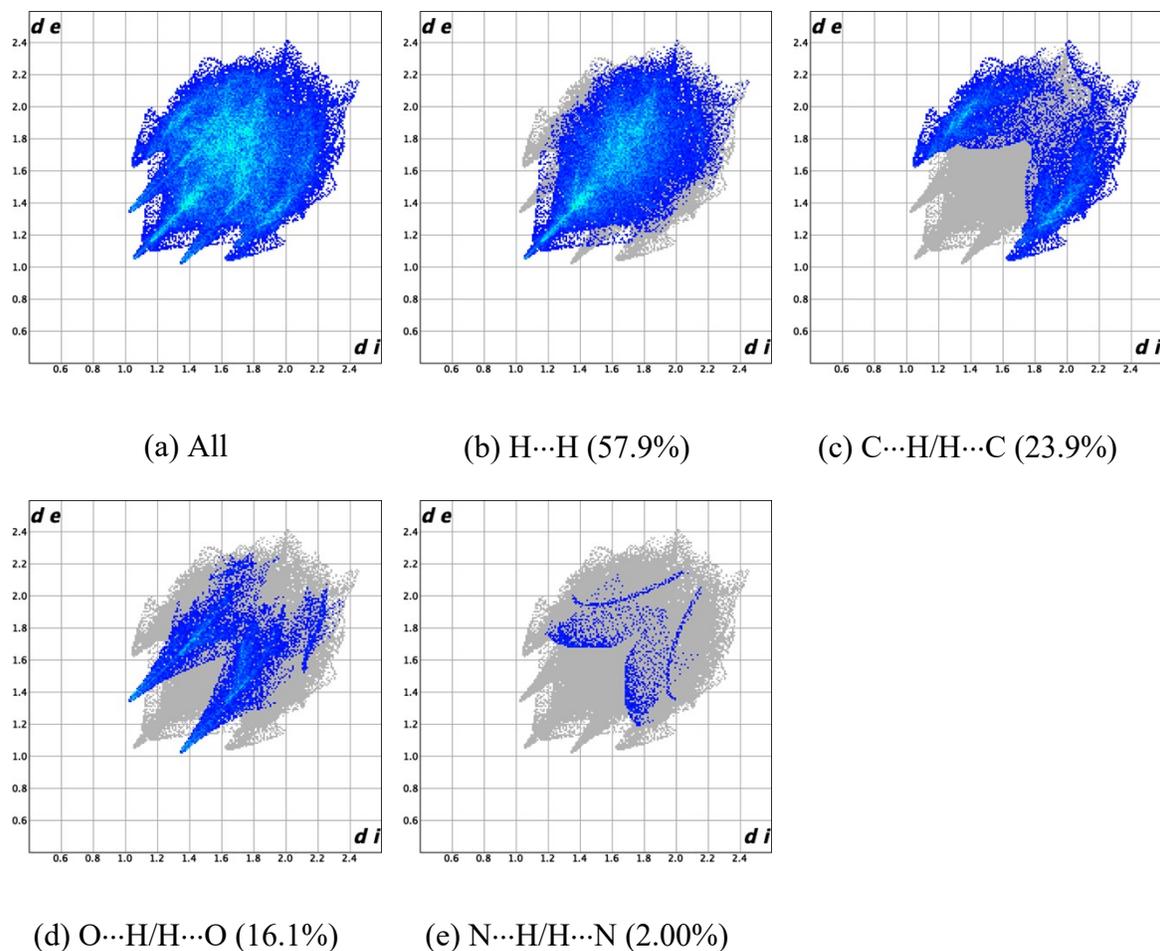
Figure S7. Fingerprint plots of molecule 4. In (a), all contacts are shown; in (b–e), the specific contacts of the compound.

Table S3. Bonds lengths (Å) of the molecule **4**

Atoms	Length/Å	Atoms	Length/Å
C1–C2	1.376(4)	C9–C10	1.477(5)
C1–C6	1.386(4)	C10–C11	1.175(5)
C1–O19	1.375(4)	C12–C13	1.514(4)
C2–C3	1.382(4)	C13–N14	1.456(3)
C3–C4	1.394(4)	N14–C15	1.453(4)
C4–C5	1.411(3)	N14–C18	1.339(4)
C4–N7	1.406(3)	C15–C16	1.468(7)
C5–C6	1.373(4)	C16–C17	1.460(8)
C5–C13	1.522(3)	C17–C18	1.508(6)
N7–C8	1.453(4)	C18–O20	1.223(4)
N7–C9	1.460(4)	O19–C21	1.408(4)
C8–C12	1.517(4)		

Table S4. Bonds angles (°) of the molecule **4**

Atoms	Angle/°	Atoms	Angle/°
C2–C1–C6	118.5(3)	N7–C9–C10	113.7(2)
O19–C1–C2	126.4(2)	C11–C10–C9	179.6(4)
O19–C1–C6	115.1(2)	C13–C12–C8	109.1(2)
C1–C2–C3	120.1(2)	C12–C13–C5	111.2(2)
C2–C3–C4	122.1(2)	N14–C13–C5	111.7(2)
C3–C4–C5	117.2(2)	N14–C13–C12	111.9(2)
C3–C4–N7	122.4(2)	C15–N14–C13	123.6(3)
N7–C4–C5	120.3(2)	C18–N14–C13	122.5(3)
C4–C5–C13	121.1(2)	C18–N14–C15	113.8(3)
C6–C5–C4	119.7(2)	N14–C15–C16	104.4(4)
C6–C5–C13	119.2(2)	C17–C16–C15	108.4(4)
C5–C6–C1	122.3(2)	C16–C17–C18	105.7(3)
C4–N7–C8	116.6(2)	N14–C18–C17	107.3(4)
C4–N7–C9	118.3(2)	O20–C18–N14	125.3(3)
C8–N7–C9	113.6(3)	O20–C18–C17	127.4(4)
N7–C8–C12	109.5(2)	C1–O19–C21	118.4(3)

2. Intrinsic Reaction Coordinate
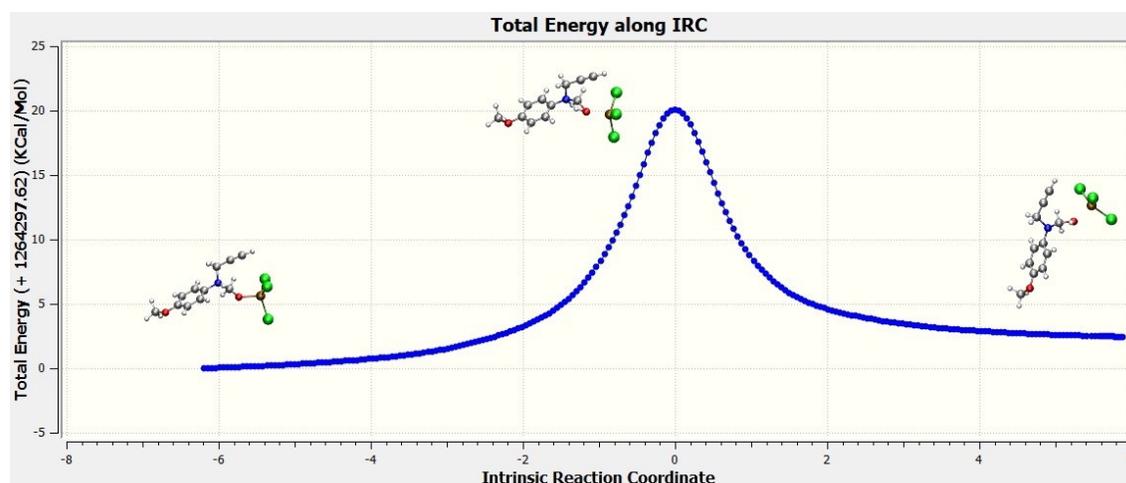
Figure S8. Intrinsic Reaction Coordinate for catalyzed formation of iminium ion intermediates using InCl$_3$ (see **Figure 2-a**).

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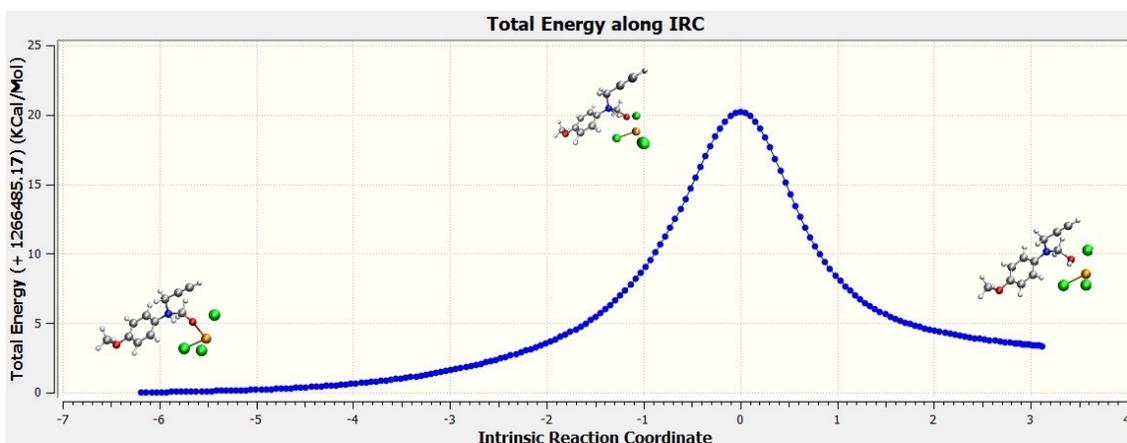
Figure S9. Intrinsic Reaction Coordinate for catalyzed formation of iminium ion intermediates using BiCl$_3$ (see **Figure 2-b**).
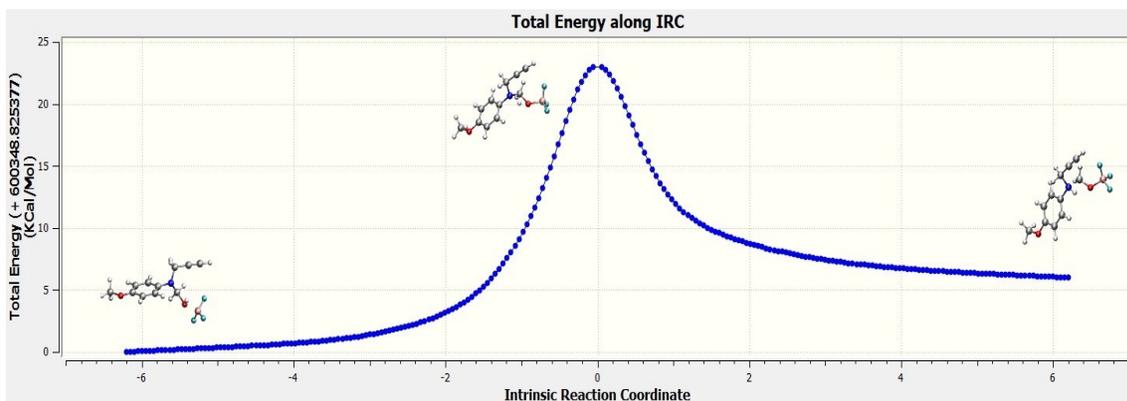
Figure S10. Intrinsic Reaction Coordinate for catalyzed formation of iminium ion intermediates using BF$_3$ (see **Figure 2-c**).
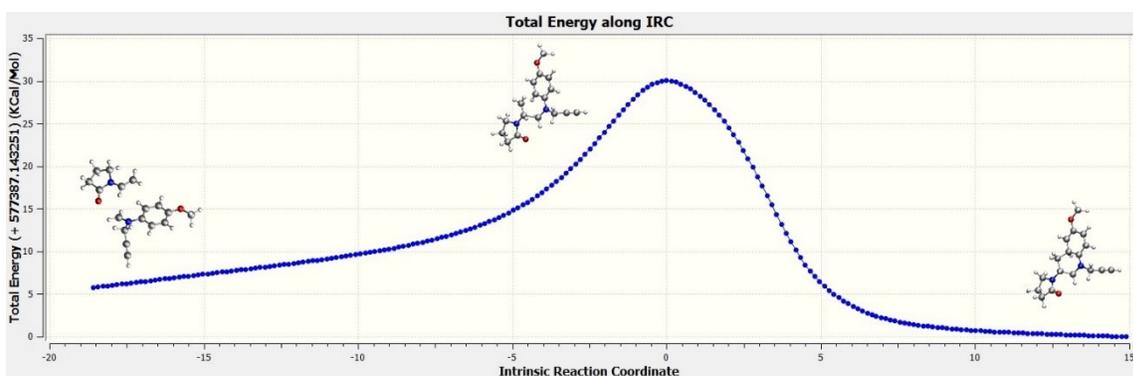
Figure S11. Intrinsic Reaction Coordinate for concerted cyclization stages of the **IMC** + **3** reaction (see **Figure 5-a**).

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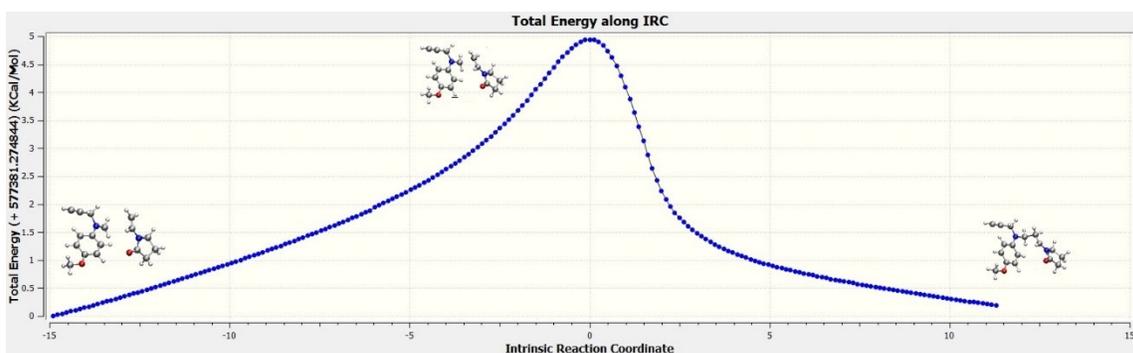
Figure S12. Intrinsic Reaction Coordinate for stepwise cyclization stages of the **IMC** + **3** reaction (see **Figure 5-b**, **TS1-Cs**).
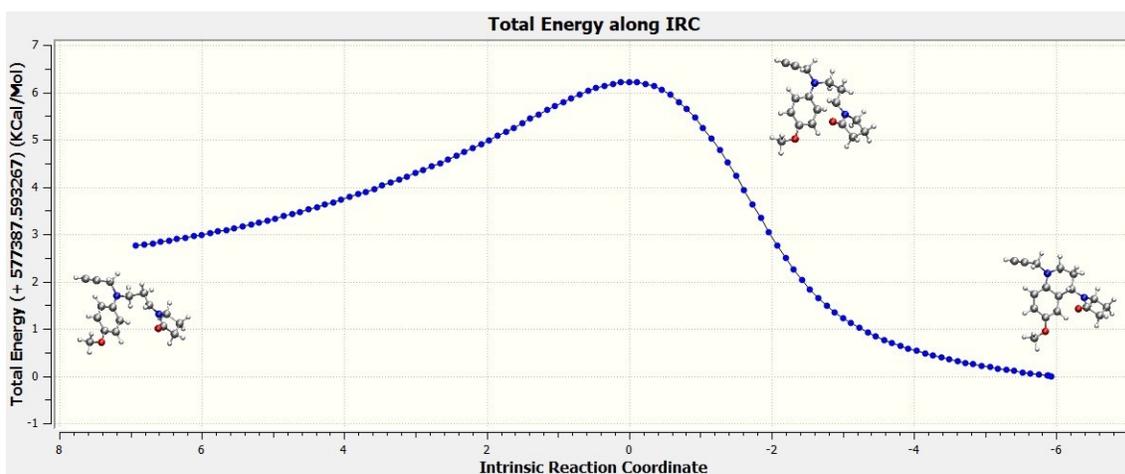
Figure S13. Intrinsic Reaction Coordinate for stepwise cyclization stages of the **IMC** + **3** reaction (see **Figure 5-b**, **TS2-Cs**).

3. Errors in the calculation of Enthalpy and Entropy.

Table S5. Error in the enthalpy calculation of the energy profile stages in Figure 2, panel a.

	H / kcal·mol^{-1}	H (scaled)/ kcal·mol^{-1}	Error/ kcal·mol^{-1}
1+2+InCl$_3$	-1264140.7	-1264145.0	-4.3
RC1	-1264191.5	-1264196.0	-4.4
TS1c	-1264189.3	-1264193.7	-4.4
PC1	-1264192.3	-1264196.7	-4.4
PRODUCTS	-1216425.7	-1216429.8	-4.2

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Table S6. Error in the enthalpy calculation of the energy profile stages in Figure 2, panel b.

	H / kcal·mol^{-1}	H (scaled)/ kcal·mol^{-1}	Error/ kcal·mol^{-1}
1+2+BiCl$_3$	-1266350.8	-1266355.0	-4.2
RC1	-1266377.8	-1266382.2	-4.4
TS1c	-1266360.6	-1266364.9	-4.3
PC1	-1266381.5	-1266385.9	-4.4
PRODUCTS	-1266365.0	-1266369.2	-4.1

Table S7. Error in the enthalpy calculation of the energy profile stages in Figure 2, panel c.

	H / kcal·mol^{-1}	H (scaled)/ kcal·mol^{-1}	Error/ kcal·mol^{-1}
1+2+BF$_3$	-600198.9	-600203.4	-4.4
RC1	-600231.6	-600236.2	-4.6
TS1c	-600205.5	-600210.0	-4.5
PC1	-600229.7	-600234.3	-4.6
PRODUCTS	-600131.4	-600136.0	-4.6

Table S8. Error in the enthalpy calculation of the energy profile stages in Figure 5, panel a.

	H / kcal·mol^{-1}	H (scaled)/ kcal·mol^{-1}	Error/ kcal·mol^{-1}
Free reactants	-577186.3	-577193.2	-6.9
PRC	-577197.0	-577203.9	-6.9
TS1	-577178.0	-577184.9	-6.9
Free products	-577205.0	-577212.0	-7.0

Table S9. Error in the enthalpy calculation of the energy profile stages in Figure 5, panel b.

	H / kcal·mol^{-1}	H (scaled)/ kcal·mol^{-1}	Error/ kcal·mol^{-1}
Free reactants	-577186.3	-577193.2	-6.9
PRC	-577197.0	-577203.9	-6.9
TS1	-577197.7	-577204.6	-6.9
Int1	-577201.0	-577207.9	-7.0
TS2	-577200.9	-577207.9	-7.0
Free products	-577207.2	-577214.2	-7.0

Table S10. Error in the entropy calculation of the energy profile stages in Figure 2, panel a.

	S / cal·K^{-1}·mol^{-1}	S (scaled) / cal·K^{-1}·mol^{-1}	Error/ cal·K^{-1}·mol^{-1}
1+2+InCl3	245.4	247.1	1.7
RC1	160.8	163.0	2.3
TS1c	165.4	167.8	2.3
PC1	160.5	162.8	2.3
PRODUCTS	195.7	196.8	1.1

Table S11. Error in the entropy calculation of the energy profile stages in Figure 2, panel b.

	S / cal·K^{-1}·mol^{-1}	S (scaled) / cal·K^{-1}·mol^{-1}	Error/ cal·K^{-1}·mol^{-1}
1+2+BiCl3	247.2	248.9	1.7
RC1	162.8	165.1	2.3
TS1c	162.8	165.1	2.3
PC1	167.4	169.7	2.3
PRODUCTS	197.5	198.6	1.1

Table S12. Error in the entropy calculation of the energy profile stages in Figure 2, panel c.

	S / cal·K^{-1}·mol^{-1}	S (scaled) / cal·K^{-1}·mol^{-1}	Error/ cal·K^{-1}·mol^{-1}
1+2+BF3	225.1	226.5	1.5
RC1	138.3	140.4	2.0
TS1c	141.4	143.4	2.0
PC1	142.7	144.8	2.1
PRODUCTS	183.2	184.4	1.1

Table S13. Error in the entropy calculation of the energy profile stages in Figure 5, panel a.

	S / cal·K^{-1}·mol^{-1}	S (scaled) / cal·K^{-1}·mol^{-1}	Error/ cal·K^{-1}·mol^{-1}
Free reactants	195.5	197.7	2.2
R-Cc	165.1	167.7	2.6
TS-Cc	148.6	151.1	2.4
P-Cc	151.4	153.8	2.4

Table S14. Error in the entropy calculation of the energy profile stages in Figure 5, panel b.

	S / cal·K^{-1}·mol^{-1}	S (scaled) / cal·K^{-1}·mol^{-1}	Error/ cal·K^{-1}·mol^{-1}
Free reactants	195.5	197.7	2.2

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R-Cs	165.1	167.7	2.6
TS1-Cs	150.8	153.3	2.5
Int-Cs	147.8	150.2	2.4
TS2-Cs	147.4	149.7	2.4
P-Cs	150.0	152.4	2.4

4. Optimized Cartesian coordinates

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Propargyl-structure 1

C	-0.10100	-0.85100	-0.27500
C	0.57100	0.37600	-0.20800
C	-0.19900	1.54300	-0.01700
C	-1.57900	1.48000	0.09700
C	-2.24500	0.24700	0.02100
C	-1.49900	-0.91600	-0.16700
H	0.44700	-1.77400	-0.42000
H	0.30000	2.50800	0.03300
H	-2.16500	2.38100	0.24500
H	-1.97800	-1.88600	-0.22700
O	-3.61100	0.29400	0.14300
C	-4.32300	-0.92900	0.06500
H	-5.37700	-0.67200	0.18000
H	-4.17200	-1.42000	-0.90600
H	-4.02700	-1.61800	0.86800
N	1.95900	0.48800	-0.36100
H	2.35800	1.31100	0.07000
C	2.79300	-0.69900	-0.21700
H	2.55400	-1.26200	0.70300
H	2.60200	-1.37800	-1.05800
C	4.21100	-0.34400	-0.20500
C	5.38300	-0.04800	-0.17700
H	6.41700	0.21000	-0.16100

Structure 1. Optimized Cartesian coordinates of *N*-propargyl-4-methoxyaniline structure **1**.

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Formaldehyde-structure 2

C	-0.32600	-0.04700	-0.74000
O	0.48200	-0.14100	0.15500
H	-1.17800	-0.75000	-0.83600
H	-0.25800	0.74900	-1.50900

Structure 2. Optimized Cartesian coordinates of Formaldehyde structure **2**.

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N-vinylpyrrolidone-structure 3

C	-0.01200	-0.00900	0.00700
C	-0.00800	0.00800	2.43600

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C	0.93600	-0.01300	1.22400
H	0.36800	-0.61000	-0.82500
H	-0.20600	1.00500	-0.37000
H	-0.23000	1.02900	2.77100
H	0.35300	-0.54900	3.30300
H	1.63200	0.82800	1.20100
H	1.52400	-0.93600	1.22500
C	-1.30500	-0.59900	1.91800
O	-2.25200	-1.00200	2.57500
N	-1.24400	-0.59100	0.53100
C	-2.31800	-0.97500	-0.26300
H	-3.14400	-1.36800	0.32200
C	-2.36400	-0.88200	-1.60100
H	-1.54900	-0.48200	-2.19400
H	-3.24900	-1.21400	-2.13000

Structure 3. Optimized Cartesian coordinates of *N*-vinylpyrrolidone structure **3**.

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iminium_IMC_Fig1

C	-0.07000	-0.09900	-0.16700
H	-0.07000	-0.27800	0.90200
H	0.84600	0.08100	-0.71700
C	-2.65900	0.52500	1.05900
C	-2.45700	-0.20800	-0.12300
C	-3.46800	-1.03100	-0.63000
C	-4.67600	-1.14200	0.05000
C	-4.88300	-0.41700	1.23900
C	-3.86100	0.42200	1.73200
H	-1.89500	1.20600	1.42200
H	-3.31900	-1.62200	-1.52600
H	-5.44200	-1.79900	-0.34200
H	-4.04900	0.99500	2.63300
O	-6.00800	-0.44800	1.96400
C	-7.11000	-1.26000	1.53000
H	-7.89100	-1.10700	2.27300
H	-7.46600	-0.93400	0.54700
H	-6.82500	-2.31600	1.50500
N	-1.19300	-0.10500	-0.80100
C	-1.25400	0.08400	-2.29500
H	-1.76800	-0.79200	-2.69800
H	-1.89700	0.95400	-2.45900
C	0.04300	0.24800	-2.92000
C	1.10500	0.39300	-3.47700
H	2.03900	0.52100	-3.98100

Structure 4. Optimized Cartesian coordinates of compound IMC. It can be seen in Fig 1.

31
RC1_Fig2_a_BF3

C	-0.44700	0.40000	-1.35000

O	-0.09800	-0.75200	-0.75800
H	-1.10400	0.24100	-2.21200
H	0.38900	1.06900	-1.58600
B	0.95800	-0.65200	0.29400
F	2.08700	-0.01300	-0.21500
F	1.19700	-1.90200	0.80400
F	0.40600	0.21700	1.34600
C	-3.69900	0.82700	-0.94300
C	-2.63100	0.62200	-0.07600
C	-2.75400	-0.23800	1.01900
C	-3.96500	-0.87600	1.25200
C	-5.05500	-0.66600	0.39300
C	-4.92000	0.18900	-0.71000
H	-3.60500	1.47500	-1.80800
H	-1.90200	-0.41800	1.66500
H	-4.08400	-1.55100	2.09200
H	-5.74300	0.36200	-1.39100
O	-6.19500	-1.33400	0.70900
C	-7.32800	-1.18900	-0.14000
H	-8.10700	-1.81400	0.29600
H	-7.67000	-0.14700	-0.17000
H	-7.10800	-1.53500	-1.15700
N	-1.33100	1.24900	-0.32800
H	-0.75400	1.15100	0.53400
C	-1.40900	2.70300	-0.71100
H	-1.74700	2.76000	-1.75000
H	-2.17300	3.16600	-0.08100
C	-0.12000	3.35800	-0.54700
C	0.95900	3.87400	-0.38900
H	1.92200	4.31100	-0.24400

Structure 5. Optimized Cartesian coordinates of Compound RC1_BF$_3$. It can be seen in Fig 2, panel c.

31
RC1_Fig2_b_BiCl3

C	-0.04600	1.53000	-0.60100
O	0.32000	0.63000	0.33800
H	-0.44600	1.12100	-1.53700
H	0.72300	2.28400	-0.80300
Bi	0.56700	-1.42700	-0.01700
Cl	1.82000	-0.57200	-2.20000
Cl	-1.62900	-1.66100	-1.19600
Cl	-0.31200	-1.60800	2.46100
C	-3.35000	1.39400	-0.88400
C	-2.45200	1.50000	0.17100
C	-2.60700	0.74600	1.33400
C	-3.68500	-0.11700	1.44400
C	-4.60800	-0.23000	0.39400
C	-4.44400	0.53600	-0.77000
H	-3.21000	1.94400	-1.80800

H	-1.85900	0.77100	2.12000
H	-3.79800	-0.74700	2.31800
H	-5.13300	0.45100	-1.60000
O	-5.61900	-1.11300	0.58800
C	-6.50900	-1.37800	-0.49200
H	-7.18900	-2.14900	-0.13100
H	-7.08300	-0.48300	-0.76100
H	-5.96400	-1.74800	-1.36700
N	-1.24000	2.32800	0.04000
H	-0.90100	2.51500	0.99000
C	-1.46200	3.65700	-0.64200
H	-1.51800	3.46700	-1.71700
H	-2.43200	4.03600	-0.30800
C	-0.39100	4.59000	-0.32800
C	0.49400	5.36200	-0.04600
H	1.28200	6.04100	0.19400

Structure 6. Optimized Cartesian coordinates of Compound RC1_BiCl$_3$. It can be seen in Fig 2, panel b.

31
RC1_Fig2_c_InCl3
C	-0.50700	0.40400	-1.34200
O	-0.11000	-0.75300	-0.79600
H	-1.20600	0.26900	-2.17800
H	0.29600	1.10200	-1.61500
In	1.48500	-0.81600	0.41600
Cl	3.10300	0.50100	-0.66200
Cl	2.01100	-2.97200	1.05800
Cl	0.56500	0.53700	2.19900
C	-3.68500	0.74000	-0.98700
C	-2.67800	0.62200	-0.03500
C	-2.88600	-0.10600	1.13900
C	-4.11700	-0.70700	1.36100
C	-5.14600	-0.58900	0.41200
C	-4.92700	0.14000	-0.76600
H	-3.52400	1.28900	-1.90900
H	-2.08800	-0.20600	1.86700
H	-4.30200	-1.28100	2.26100
H	-5.70200	0.24100	-1.51500
O	-6.31100	-1.21200	0.72200
C	-7.38600	-1.15400	-0.21100
H	-8.19900	-1.72300	0.23900
H	-7.71100	-0.11900	-0.37600
H	-7.10400	-1.61000	-1.16700
N	-1.36400	1.22500	-0.27300
H	-0.81200	1.13200	0.60500
C	-1.41700	2.70100	-0.59700
H	-1.82500	2.80700	-1.60600
H	-2.11900	3.16000	0.10400
C	-0.08900	3.28600	-0.49500

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C	1.04300	3.69000	-0.38700
H	2.05200	4.02300	-0.28600

Structure 7. Optimized Cartesian coordinates of RC1_ InCl$_3$. It can be seen in Fig 2, panel a.

31
TS1c_BF3_Figure_2_a

C	-0.31400	0.39700	-0.96800
O	0.48500	-0.24600	0.01500
H	-0.85500	-0.31300	-1.59400
H	0.24700	1.13300	-1.54400
B	2.06100	-0.18500	0.00700
F	2.50500	-1.47300	-0.20100
F	2.40200	0.31800	1.25300
F	2.41600	0.67500	-1.03500
C	-3.44500	0.56700	-0.96800
C	-2.58200	0.51000	0.12500
C	-3.01300	-0.05000	1.33100
C	-4.30200	-0.55500	1.44000
C	-5.17500	-0.50500	0.34000
C	-4.74200	0.05700	-0.87000
H	-3.11300	1.00000	-1.90700
H	-2.33400	-0.09700	2.17600
H	-4.65400	-1.00100	2.36400
H	-5.39400	0.10300	-1.73200
O	-6.41200	-1.02800	0.54400
C	-7.34100	-1.02100	-0.53600
H	-8.24700	-1.48700	-0.14800
H	-7.56500	0.00200	-0.85900
H	-6.96400	-1.60400	-1.38500
N	-1.23400	1.04700	0.04300
H	-0.32300	0.43200	0.72400
C	-1.21300	2.54800	0.08400
H	-1.69900	2.93600	-0.81900
H	-1.82800	2.83800	0.94000
C	0.14500	3.05300	0.21400
C	1.30200	3.38100	0.31500
H	2.33600	3.63000	0.40500

Structure 8. Optimized Cartesian coordinates of TS1c_BF$_3$. It can be seen in Fig 2, panel a.

31
TS1c_BiCl3_Figure_2_b

C	-0.36700	1.02400	-1.06600
O	0.51800	0.52700	-0.04700
H	-0.77500	0.23900	-1.70000
H	0.10700	1.82200	-1.63600
Bi	1.13000	-1.53800	0.14700
Cl	1.89700	-1.10100	-2.31300
Cl	-1.11600	-2.36300	-0.52600
Cl	0.44500	-0.92400	2.61600
C	-3.46000	0.63500	-1.03700

C	-2.60000	0.78000	0.04700
C	-2.89100	0.17500	1.27200
C	-4.04900	-0.57700	1.40700
C	-4.92100	-0.73300	0.31900
C	-4.62500	-0.12400	-0.91000
H	-3.22500	1.09200	-1.99400
H	-2.18800	0.25300	2.09600
H	-4.28400	-1.07600	2.34100
H	-5.27700	-0.24100	-1.76600
O	-6.02100	-1.49800	0.54800
C	-6.91300	-1.74700	-0.53300
H	-7.69400	-2.39200	-0.13000
H	-7.36300	-0.81600	-0.90000
H	-6.40300	-2.26000	-1.35700
N	-1.36700	1.54800	-0.07400
H	-0.37200	1.04800	0.64100
C	-1.60200	3.02400	-0.07400
H	-2.17500	3.30100	-0.96800
H	-2.23200	3.23300	0.79600
C	-0.35800	3.77900	-0.00300
C	0.68100	4.39300	0.05200
H	1.60100	4.93000	0.10800

Structure 9. Optimized Cartesian coordinates of TS1c_BiCl$_3$. It can be seen in Fig 2, panel b.

31
TS1c_InCl3_Figure_2_c

C	-0.37800	0.68700	-1.32700
O	0.25600	-0.37700	-0.42100
H	-0.78700	0.10400	-2.15200
H	0.48600	1.27300	-1.63200
In	1.89700	-0.26700	0.92600
Cl	3.51300	0.77400	-0.36400
Cl	2.02200	-2.55900	1.29600
Cl	0.99000	0.90400	2.72500
C	-3.64500	0.75800	-1.24700
C	-2.57500	0.78800	-0.35500
C	-2.69800	0.14400	0.88900
C	-3.87100	-0.52200	1.22100
C	-4.94200	-0.56200	0.31300
C	-4.82700	0.08100	-0.92800
H	-3.55200	1.27000	-2.19900
H	-1.88000	0.17700	1.60400
H	-3.98100	-1.02200	2.17800
H	-5.64100	0.07000	-1.64200
O	-6.04300	-1.24600	0.72600
C	-7.18300	-1.27400	-0.12500
H	-7.94500	-1.83400	0.41800
H	-7.55000	-0.26100	-0.33100
H	-6.96000	-1.78400	-1.07100
N	-1.36200	1.46900	-0.72400
H	-0.37500	-1.09100	-0.23900

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C	-0.97400	2.57000	0.19000
H	-1.79500	3.29600	0.17500
H	-0.86600	2.21300	1.22200
C	0.27600	3.21400	-0.19500
C	1.34100	3.70400	-0.48500
H	2.29100	4.12400	-0.72600

Structure 10. Optimized Cartesian coordinates of TS1c_InCl$_3$. It can be seen in Fig 2, panel c.

31
PC1_Fig_2_a_BF3

C	-0.60900	0.83800	-1.33000
O	0.05500	0.20200	-0.13400
H	-0.90100	-0.02500	-1.92000
H	0.16100	1.42100	-1.83700
B	1.42200	-0.64400	-0.43100
F	2.25200	0.24400	-1.09000
F	0.99100	-1.68000	-1.21900
F	1.85100	-0.98000	0.82600
C	-3.56900	0.11500	-1.32800
C	-2.89300	1.00100	-0.48700
C	-3.40900	1.24300	0.79500
C	-4.57700	0.61600	1.21600
C	-5.24000	-0.28700	0.37500
C	-4.72700	-0.54100	-0.90300
H	-3.19800	-0.06400	-2.33200
H	-2.89400	1.91000	1.47800
H	-4.98100	0.80100	2.20500
H	-5.22200	-1.22500	-1.58100
O	-6.36900	-0.86100	0.88400
C	-7.06700	-1.80100	0.07800
H	-7.91200	-2.13800	0.67900
H	-7.43800	-1.33700	-0.84500
H	-6.43100	-2.65900	-0.17300
N	-1.70400	1.64600	-0.96600
H	0.21400	0.88800	0.54400
C	-1.37400	2.97400	-0.44500
H	-0.78700	3.50400	-1.20500
H	-2.30800	3.52900	-0.31600
C	-0.61200	2.97100	0.81900
C	0.05000	2.92000	1.83100
H	0.62600	2.88700	2.72900

Structure 11. Optimized Cartesian coordinates of PC1_BF$_3$. It can be seen in Fig 2, panel a.

31
PC1_Fig_2_b_BiCl3

C	-0.57600	0.97600	-1.40000
O	0.04000	0.23000	-0.23700
H	-0.86300	0.16900	-2.06600

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H	0.21500	1.58900	-1.83100
Bi	1.43300	-1.50900	-0.31900
Cl	2.71900	-0.12100	-1.96300
Cl	-0.53100	-2.44300	-1.69500
Cl	1.81100	-0.44300	2.04300
C	-3.44000	0.11700	-1.32500
C	-2.83100	1.07000	-0.50500
C	-3.38200	1.32300	0.75900
C	-4.52300	0.64800	1.18100
C	-5.12100	-0.31500	0.36000
C	-4.56900	-0.58300	-0.89900
H	-3.03500	-0.09500	-2.30900
H	-2.91400	2.03100	1.43400
H	-4.95200	0.84100	2.15900
H	-5.00500	-1.32300	-1.55800
O	-6.22700	-0.93500	0.86900
C	-6.85500	-1.93700	0.08000
H	-7.69300	-2.30200	0.67500
H	-7.23100	-1.52400	-0.86400
H	-6.16900	-2.76600	-0.13200
N	-1.66500	1.75800	-0.97800
H	0.28200	0.84900	0.48700
C	-1.32300	3.05100	-0.37700
H	-0.75700	3.62900	-1.11700
H	-2.25300	3.59600	-0.19200
C	-0.52800	2.95200	0.85900
C	0.16800	2.79700	1.83800
H	0.77900	2.64100	2.69900

Structure 12. Optimized Cartesian coordinates of PC1_BiCl$_3$. It can be in Fig 2, panel b.

31
PC1_Fig_2_c_InCl3

C	-0.57300	1.34200	-1.63900
O	0.31500	0.73400	-0.57900
H	-0.84300	0.48800	-2.25800
H	0.07000	2.04000	-2.17800
In	0.31300	-1.26100	0.18300
Cl	2.43800	-2.02700	-0.33800
Cl	-1.41200	-2.21700	-1.03700
Cl	0.01400	-0.68700	2.42500
C	-3.67100	0.57900	-1.46700
C	-2.74600	1.14000	-0.58800
C	-2.81100	0.81900	0.77600
C	-3.78100	-0.05800	1.24200
C	-4.69400	-0.63900	0.35100
C	-4.64200	-0.31300	-1.01000
H	-3.62000	0.83300	-2.52100
H	-2.09100	1.23100	1.47300
H	-3.82400	-0.33200	2.29000
H	-5.33600	-0.74800	-1.71800
O	-5.59000	-1.50600	0.90100
C	-6.48400	-2.19200	0.03300

H	-7.06900	-2.85300	0.67300
H	-7.15700	-1.49200	-0.47900
H	-5.93700	-2.78700	-0.70800
N	-1.71300	1.98900	-1.12800
H	0.48900	1.41600	0.10000
C	-1.48800	3.28900	-0.48700
H	-1.06700	3.97600	-1.23200
H	-2.46200	3.68900	-0.19300
C	-0.59300	3.25600	0.68700
C	0.16600	3.17100	1.62700
H	0.80700	3.09000	2.47700

Structure 13. Optimized Cartesian coordinates of PC1_InCl$_3$. It can be in Fig 2, panel c.

42
R-Cc_Figure5_a

C	0.20800	-0.13000	0.25400
C	-0.19900	0.39100	2.59300
C	0.92100	-0.01300	1.61900
H	0.66400	-0.89200	-0.38500
H	0.22600	0.82600	-0.29200
H	-0.28300	1.47900	2.70500
H	-0.10100	-0.03100	3.59500
H	1.74600	0.70100	1.58600
H	1.32900	-0.98800	1.89800
C	-1.47400	-0.10200	1.92900
O	-2.60600	-0.13000	2.39000
N	-1.15700	-0.49600	0.63900
C	-2.23300	-0.83300	-0.26800
H	-3.02900	-1.22500	0.37000
C	-1.85600	-1.88700	-1.32900
H	-0.81200	-2.19000	-1.23400
H	-2.46200	-2.78700	-1.20200
C	-2.78800	0.45400	-0.92400
H	-1.97700	1.02200	-1.39800
H	-3.25100	1.08300	-0.16600
C	-2.07900	-1.35400	-2.78300
C	-3.44600	-0.74500	-2.89200
C	-4.29800	-1.10500	-3.97100
C	-3.89000	-2.04800	-4.87900
C	-2.60800	-2.71100	-4.80900
C	-1.74800	-2.37400	-3.81200
H	-1.36600	-0.51900	-2.91700
H	-5.26400	-0.63300	-4.09600
H	-4.56700	-2.29600	-5.68900
H	-0.77500	-2.85200	-3.75700
O	-2.22000	-3.64800	-5.70300
C	-3.10000	-4.04300	-6.76200
H	-2.55600	-4.80700	-7.31600
H	-4.02700	-4.47400	-6.36700
H	-3.32100	-3.20200	-7.42900
N	-3.78600	0.11700	-1.94300
C	-5.09600	0.81000	-1.92700

H	-5.88100	0.08300	-2.15700
H	-5.26800	1.14400	-0.90100
C	-5.12900	1.93700	-2.85500
C	-5.15500	2.86500	-3.62600
H	-5.18800	3.69400	-4.30000

Structure 14. Optimized Cartesian coordinates of R-Cc. It can be seen in Fig 5, panel a.

42
R-Cs_Fig_5_b

C	2.54100	3.29600	2.45500
C	1.99200	1.61200	4.13200
C	2.71000	2.96200	3.95400
H	3.39400	2.95200	1.85400
H	2.40400	4.36600	2.27100
H	1.46600	1.50200	5.08300
H	2.67500	0.75700	4.04300
H	2.22000	3.73100	4.55700
H	3.76200	2.93100	4.24600
C	1.00700	1.54500	2.97900
O	0.10400	0.73900	2.80300
N	1.32800	2.55900	2.08000
C	0.58000	2.78500	0.93700
H	-0.37400	2.26600	0.95900
C	0.93100	3.57500	-0.09700
H	1.86700	4.12300	-0.13300
H	0.22000	3.75400	-0.89600
C	1.33900	0.65500	-1.53100
H	1.74900	0.25600	-0.61200
H	1.83800	1.46300	-2.04900
C	-0.55600	-0.91000	0.03400
C	-0.51100	-0.87500	-1.37200
C	-1.21400	-1.82400	-2.12600
C	-1.94400	-2.82000	-1.48400
C	-1.98200	-2.86800	-0.07700
C	-1.28500	-1.89700	0.67200
H	-0.08200	-0.15400	0.65100
H	-1.17000	-1.82400	-3.21000
H	-2.46900	-3.55300	-2.08200
H	-1.35000	-1.91500	1.75400
O	-2.65900	-3.77900	0.63900
C	-3.42500	-4.78900	-0.03000
H	-3.87700	-5.38300	0.76300
H	-4.21100	-4.33800	-0.64500
H	-2.77900	-5.42500	-0.64400
N	0.26400	0.13800	-2.03500
C	-0.22000	0.65700	-3.36600
H	-1.31100	0.60200	-3.35200
H	0.06200	1.71300	-3.41400
C	0.34400	-0.08100	-4.48900
C	0.79900	-0.66400	-5.44400

| H | 1.20300 | -1.17900 | -6.28900 |

Structure 15. Optimized Cartesian coordinates of R-Cs. It can be seen in Fig 5, panel b.

42
TS-Cc_Figure5_a
C	-3.00800	-0.17400	-1.77900
H	-2.00500	0.05500	-2.11900
H	-3.43400	0.59100	-1.14000
C	-2.04100	-2.03000	-3.59800
C	-3.42700	-1.68300	-3.56300
C	-4.33300	-2.46700	-4.31700
C	-3.88700	-3.55200	-5.04500
C	-2.50900	-3.89700	-5.07200
C	-1.60000	-3.11200	-4.36800
H	-1.29300	-1.33900	-3.23300
H	-5.38600	-2.22000	-4.34500
H	-4.60900	-4.13400	-5.60400
H	-0.54300	-3.34400	-4.43600
O	-2.00600	-4.93300	-5.76400
C	-2.87500	-5.73700	-6.57400
H	-2.22900	-6.48100	-7.03900
H	-3.62800	-6.23900	-5.95800
H	-3.35600	-5.13200	-7.34900
N	-3.86300	-0.67600	-2.72300
C	-5.31900	-0.44700	-2.52700
H	-5.80800	-1.40700	-2.32000
H	-5.42700	0.17000	-1.63200
C	-5.93400	0.21400	-3.67200
C	-6.45500	0.75900	-4.61600
H	-6.91700	1.25000	-5.44400
C	-0.20100	-1.21000	0.47300
C	-0.85800	0.50800	2.07700
C	0.36700	-0.07100	1.34900
H	-0.15400	-2.18800	0.97300
H	0.32300	-1.29200	-0.48500
H	-0.81400	1.58500	2.24800
H	-1.03000	0.03000	3.05000
H	0.81800	0.69300	0.70900
H	1.14000	-0.43600	2.02700
C	-2.02900	0.15400	1.18200
O	-3.17500	0.58100	1.21000
N	-1.59800	-0.81100	0.28200
C	-2.55200	-1.48300	-0.52500
H	-3.52800	-1.51600	-0.03900
C	-2.18400	-2.64200	-1.24500
H	-1.15700	-2.97800	-1.30300
H	-2.94200	-3.35900	-1.52700

Structure 16. Optimized Cartesian coordinates of TS-Cc. It can be seen in Fig. 5, panel a

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TS1-Cs_Fig_5_b
```
C    -1.77600    1.52500    1.35300
C    -3.50700    0.34200    2.60100
C    -2.13900    1.02500    2.76700
H    -1.17900    0.79100    0.79800
H    -1.24100    2.47800    1.36600
H    -4.17200    0.45600    3.45900
H    -3.41800   -0.73200    2.39600
H    -2.22400    1.87700    3.44600
H    -1.37400    0.35600    3.16400
C    -4.12000    0.99400    1.38100
O    -5.26700    0.97400    0.99200
N    -3.07700    1.67700    0.69400
C    -3.30600    2.31100   -0.47900
H    -4.34700    2.24700   -0.78600
C    -2.37200    2.96900   -1.25000
H    -1.40000    3.22700   -0.84100
H    -2.75100    3.61700   -2.03300
C    -1.49300    1.42900   -2.63100
H    -0.85300    1.11600   -1.82100
H    -1.10400    2.14800   -3.34100
C    -2.00600   -1.11700   -1.33300
C    -2.91200   -0.41000   -2.14200
C    -4.28700   -0.60600   -1.97700
C    -4.76200   -1.44100   -0.96900
C    -3.86000   -2.08100   -0.11000
C    -2.47400   -1.94100   -0.32500
H    -0.93700   -1.04100   -1.50900
H    -5.00600   -0.09700   -2.60700
H    -5.83000   -1.54000   -0.83400
H    -1.79000   -2.49800    0.30500
O    -4.21500   -2.83600    0.95100
C    -5.61000   -3.03500    1.22200
H    -5.64600   -3.65800    2.11400
H    -6.10800   -2.07900    1.41100
H    -6.09300   -3.55700    0.38900
N    -2.42500    0.58100   -3.04700
C    -3.23900    0.94900   -4.23200
H    -4.14300    1.47000   -3.89100
H    -2.65400    1.66700   -4.81300
C    -3.58100   -0.20700   -5.04900
C    -3.87500   -1.15200   -5.73900
H    -4.13200   -1.98800   -6.35200
```

Structure 17. Optimized Cartesian coordinates of TS1-Cs. It can be seen in Fig 5, panel b.

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Int-Cs_Fig_5_b
```
C     2.21500    1.59900    2.30300
C     0.56900    1.21900    4.06000
C     1.94400    1.85700    3.79900
```

H	2.72700	0.64300	2.13600
H	2.80400	2.39300	1.83900
H	-0.03200	1.72500	4.81900
H	0.64900	0.16600	4.36200
H	1.90100	2.93400	3.98500
H	2.73500	1.44100	4.42400
C	-0.13800	1.25900	2.72500
O	-1.30300	1.11000	2.45300
N	0.86400	1.52900	1.71400
C	0.52300	1.54500	0.42000
H	-0.55300	1.49200	0.27900
C	1.36000	2.17600	-0.64400
H	2.35200	2.43700	-0.26700
H	0.85000	3.11200	-0.90500
C	1.54900	1.36500	-1.97900
H	2.41400	0.70200	-1.86300
H	1.79800	2.06600	-2.77600
C	0.70600	-0.67000	-0.32800
C	-0.06700	-0.35700	-1.48900
C	-1.30800	-1.02200	-1.64900
C	-1.77000	-1.90100	-0.68500
C	-1.01900	-2.17500	0.48700
C	0.22700	-1.58300	0.63100
H	1.76700	-0.44700	-0.31200
H	-1.90900	-0.86400	-2.53500
H	-2.72800	-2.38300	-0.84500
H	0.84200	-1.85700	1.48200
O	-1.41900	-3.00800	1.47500
C	-2.66300	-3.70500	1.35200
H	-2.74800	-4.31000	2.25300
H	-3.50400	-3.00400	1.30300
H	-2.66300	-4.35900	0.47200
N	0.37400	0.61900	-2.35200
C	-0.34800	0.94700	-3.59200
H	-1.42100	1.03200	-3.38200
H	-0.02200	1.94200	-3.90900
C	-0.11900	-0.01500	-4.67500
C	0.06200	-0.79900	-5.57700
H	0.22300	-1.48900	-6.37500

Structure 18. Optimized Cartesian coordinates of Int-Cs. It can be seen in Fig 5, panel b.

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TS2-Cs_Fig5_b

C	-1.23000	1.43800	1.38900
C	-2.90000	0.97000	3.09400
C	-1.51900	1.61500	2.89300
H	-0.72000	0.48900	1.17700
H	-0.62900	2.25200	0.97800
H	-3.51200	1.43600	3.86800
H	-2.82700	-0.09800	3.33700

H	-1.56200	2.68000	3.13400
H	-0.73900	1.16200	3.50600
C	-3.57600	1.07900	1.74700
O	-4.73600	0.90800	1.44700
N	-2.57100	1.41400	0.78800
C	-2.87100	1.37400	-0.53700
H	-3.94700	1.36900	-0.68700
C	-2.03700	2.11800	-1.54600
H	-1.07600	2.41100	-1.11800
H	-2.58400	3.03500	-1.79200
C	-1.75800	1.35000	-2.87800
H	-0.87000	0.72100	-2.75000
H	-1.52900	2.06200	-3.66900
C	-2.58100	-0.61300	-1.18700
C	-3.32300	-0.40600	-2.40300
C	-4.54900	-1.10100	-2.56600
C	-5.01700	-1.93400	-1.57100
C	-4.29200	-2.14400	-0.36100
C	-3.06900	-1.52500	-0.20900
H	-1.50600	-0.46200	-1.20600
H	-5.12300	-0.99800	-3.47700
H	-5.96300	-2.43800	-1.72800
H	-2.48000	-1.73500	0.67600
O	-4.71500	-2.94000	0.64400
C	-5.97400	-3.61100	0.52900
H	-6.08900	-4.17100	1.45600
H	-6.79400	-2.89200	0.43300
H	-5.97400	-4.30600	-0.31800
N	-2.88800	0.53900	-3.27900
C	-3.65100	0.87300	-4.49400
H	-4.70000	1.05400	-4.23000
H	-3.25800	1.81800	-4.87800
C	-3.55900	-0.16100	-5.52500
C	-3.49300	-1.01700	-6.37400
H	-3.43100	-1.76800	-7.13000

Structure 19. Optimized Cartesian coordinates of TS2-Cs. It can be seen in Fig 5, panel b.

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P-Cc_Fig5_a_4

C	0.20800	-0.13000	0.25400
C	-0.19900	0.39100	2.59300
C	0.92100	-0.01300	1.61900
H	0.66400	-0.89200	-0.38500
H	0.22600	0.82600	-0.29200
H	-0.28300	1.47900	2.70500
H	-0.10100	-0.03100	3.59500
H	1.74600	0.70100	1.58600
H	1.32900	-0.98800	1.89800
C	-1.47400	-0.10200	1.92900
O	-2.60600	-0.13000	2.39000
N	-1.15700	-0.49600	0.63900
C	-2.23300	-0.83300	-0.26800

H	-3.02900	-1.22500	0.37000
C	-1.85600	-1.88700	-1.32900
H	-0.81200	-2.19000	-1.23400
H	-2.46200	-2.78700	-1.20200
C	-2.78800	0.45400	-0.92400
H	-1.97700	1.02200	-1.39800
H	-3.25100	1.08300	-0.16600
C	-2.07900	-1.35400	-2.78300
C	-3.44600	-0.74500	-2.89200
C	-4.29800	-1.10500	-3.97100
C	-3.89000	-2.04800	-4.87900
C	-2.60800	-2.71100	-4.80900
C	-1.74800	-2.37400	-3.81200
H	-1.36600	-0.51900	-2.91700
H	-5.26400	-0.63300	-4.09600
H	-4.56700	-2.29600	-5.68900
H	-0.77500	-2.85200	-3.75700
O	-2.22000	-3.64800	-5.70300
C	-3.10000	-4.04300	-6.76200
H	-2.55600	-4.80700	-7.31600
H	-4.02700	-4.47400	-6.36700
H	-3.32100	-3.20200	-7.42900
N	-3.78600	0.11700	-1.94300
C	-5.09600	0.81000	-1.92700
H	-5.88100	0.08300	-2.15700
H	-5.26800	1.14400	-0.90100
C	-5.12900	1.93700	-2.85500
C	-5.15500	2.86500	-3.62600
H	-5.18800	3.69400	-4.30000

Structure 20. Optimized Cartesian coordinates of P-Cc. It can be seen in Fig 5, panel a.

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P-Cs_Fig5_b_4

C	0.09200	-0.05300	0.47900
C	-0.54800	-0.10800	2.82400
C	0.67600	0.04500	1.90500
H	0.10300	-1.09000	0.10800
H	0.63900	0.56500	-0.23900
H	-0.50000	0.48200	3.74200
H	-0.72100	-1.15100	3.11800
H	1.12900	1.03100	2.04300
H	1.44700	-0.70700	2.08000
C	-1.72400	0.33300	1.96900
O	-2.87400	0.54600	2.31600
N	-1.27900	0.42300	0.65700
C	-2.20500	0.69100	-0.40600
H	-3.11200	1.04600	0.08700
C	-1.69500	1.73700	-1.42400
H	-0.70000	2.08600	-1.13900
H	-2.35600	2.60700	-1.40700
C	-1.63200	1.19100	-2.85400
H	-0.83700	0.43900	-2.95400

H	-1.42200	1.98500	-3.57100
C	-2.60900	-0.66000	-1.16000
C	-3.40800	-0.35200	-2.38400
C	-4.62700	-1.03900	-2.61800
C	-5.09200	-1.94900	-1.70100
C	-4.38900	-2.26700	-0.48400
C	-3.20300	-1.64900	-0.23300
H	-1.64600	-1.07100	-1.51900
H	-5.19400	-0.86800	-3.52400
H	-6.03000	-2.44900	-1.91400
H	-2.66900	-1.87800	0.68100
O	-4.84500	-3.16400	0.41800
C	-6.14000	-3.75200	0.24900
H	-6.28600	-4.38000	1.12700
H	-6.92200	-2.98500	0.21900
H	-6.17900	-4.37500	-0.65100
N	-2.91400	0.57100	-3.20700
C	-3.56300	0.91400	-4.49100
H	-4.63600	1.04700	-4.32100
H	-3.17400	1.88700	-4.80000
C	-3.31400	-0.09200	-5.52000
C	-3.11000	-0.92800	-6.36800
H	-2.93100	-1.65800	-7.12700

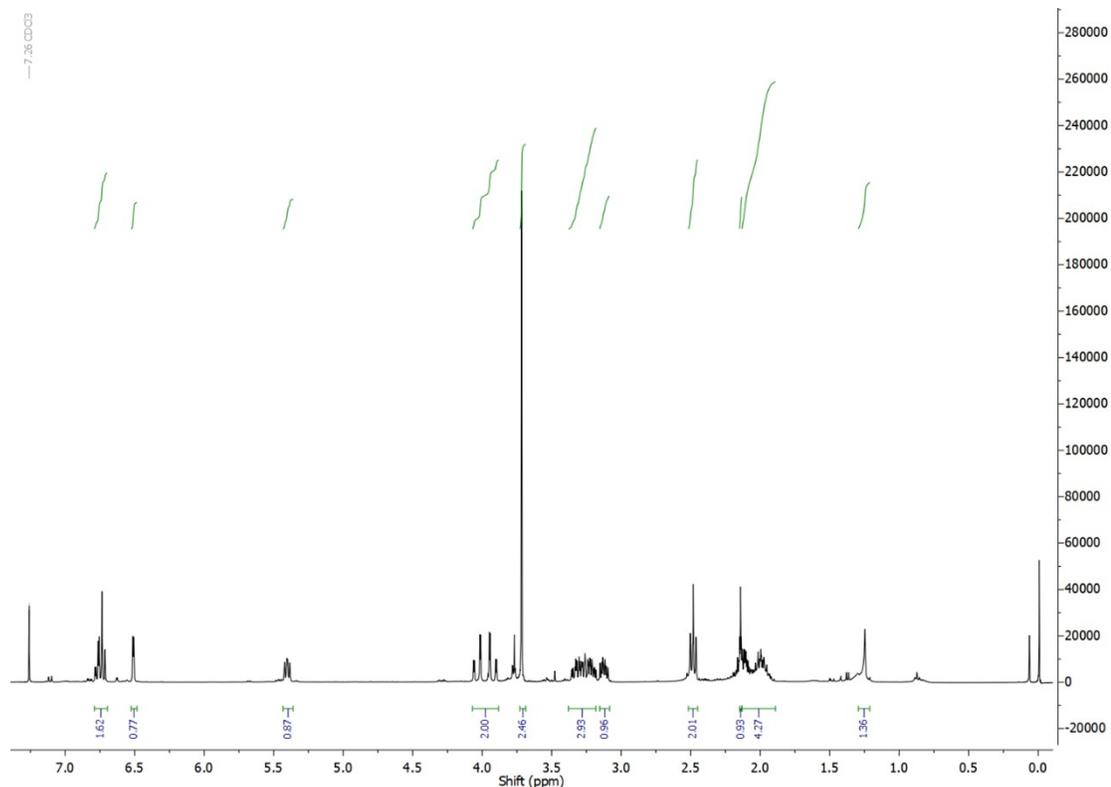**Structure 21.** Optimized Cartesian coordinates of P-Cs. It can be seen in Fig 5, panel b.

Figure S14. ¹H NMR spectra of compound **4**