

**Supporting Information****SYNTHESIS OF AMIDE-FUNCTIONALIZED THIA[7]HELICENE-LIKE MOLECULE  
AND ITS SUPRAMOLECULAR ASSEMBLY IN THE SOLID STATE**

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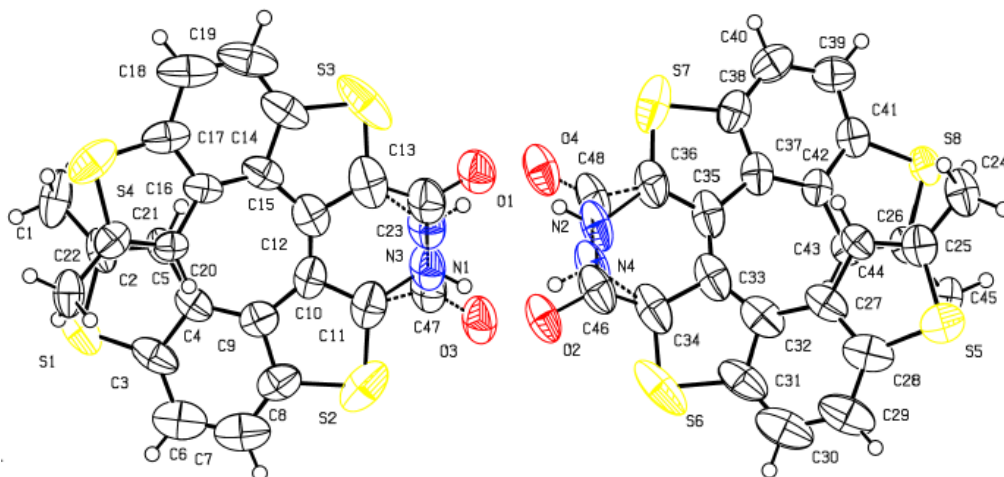
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### Crystal structure of (*P*)-**3**

(full disordered structure, 50% probability)



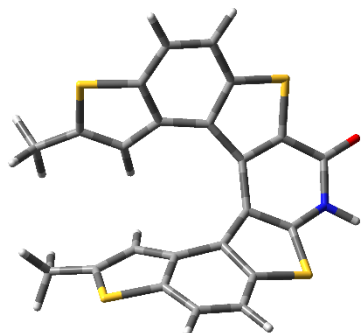
Crystallographic data for the single crystal of (*P*)-**3** obtained by recrystallization from  $\text{CHCl}_3$  and *n*-hexane:  $\text{C}_{23}\text{H}_{13}\text{NOS}_4$ ,  $M = 447.58$ , orthorhombic,  $P2_12_12_1$ ,  $a = 14.6449(3)$ ,  $b = 16.0013(3)$ ,  $c = 19.6150(4)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 4596.53(16)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.294$  g cm<sup>-3</sup>,  $T = 103$  K, 51019 reflections measured, 8530 unique. The final  $R_1$  and  $wR$  were 0.0738 and 0.1927 (all data). These data have been deposited with the Cambridge Crystallographic Data Center as CCDC 2124393.

### Computational details for an estimation of the racemization barrier of **3**

Density functional theory (DFT) calculations were performed using the Gaussian 16 software package.<sup>1)</sup> The molecular geometries for the transition states (TS) were first estimated with the *Reaction plus* software package, based on the nudged elastic band method,<sup>2)</sup> and were subsequently re-optimized using the Gaussian 16 software package. Once the stationary points were obtained at B3LYP/6-31G (d,p) level,<sup>3)</sup> the harmonic vibrational frequencies were calculated at the same level to estimate the Gibbs free energy. The nature of the stationary points was characterized via vibrational analysis. All of the Gibbs free energy values reported in this paper were calculated for a temperature of 298.15 K. All of the transition structures reported were optimized without constraints and the intrinsic reaction coordinate (IRC) routes were calculated in both directions toward the corresponding minima for the transition-state structure. For each gas-phase optimized structure (potential energy minimum or transition state computed at B3LYP/6-31G (d,p) level of theory), additional single-point energy calculations were performed at  $\omega\text{B97XD}/6\text{-}311\text{+G(d,p)}$  level of theory,<sup>4)</sup> in which solvent effects were also taken into account by estimating the solvation free energies (for chlorobenzene as solvent).

## The energies and coordinates of each structure

### (1) Transition state



Calculation Method = RB3LYP

Formula = C<sub>23</sub>H<sub>13</sub>NOS<sub>4</sub>

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2607.0213 Hartree

Imaginary Freq = 1

Temperature = 298.15 Kelvin

Pressure = 1 atm

Electronic Energy (EE) = -2607.0213 Hartree

Zero-point Energy Correction = 0.296347 Hartree

Thermal Correction to Energy = 0.319057 Hartree

Thermal Correction to Enthalpy = 0.320001 Hartree

Thermal Correction to Free Energy = 0.245764 Hartree

EE + Zero-point Energy = -2606.7249 Hartree

EE + Thermal Energy Correction = -2606.7022 Hartree

EE + Thermal Enthalpy Correction = -2606.7013 Hartree

EE + Thermal Free Energy Correction = -2606.7755 Hartree

E (Thermal) = 200.211 kcal/mol

Heat Capacity (Cv) = 91.773 cal/mol-kelvin

Entropy (S) = 156.246 cal/mol-kelvin

Calculation Type = SP

Calculation Method = Rwb97XD

Formula = C<sub>23</sub>H<sub>13</sub>NOS<sub>4</sub>

Basis Set = 6-311+G(d,p)

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

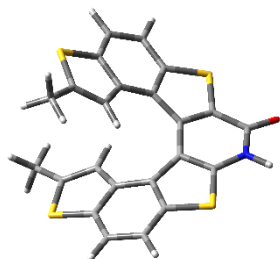
E(RwB97XD) = -2606.9421 Hartree

0 1

H	0.29257300	4.91608500	-1.80425100
C	-0.15701500	4.02633100	-1.37591700
C	-1.26090500	1.80639100	-0.03298800
C	0.61971100	3.14048400	-0.61668100
C	-1.49678900	3.74525300	-1.56740000
C	-2.03809200	2.67884800	-0.84056500
C	0.16726900	1.90928900	-0.08117400
S	2.26813800	3.50905600	-0.14302700
C	1.29632500	1.08705100	0.43950000
C	2.40634900	1.92697300	0.57758900
H	-2.12449400	4.39243300	-2.17043600
S	-3.75806800	2.44931100	-0.57166900
C	-2.10478300	1.11012300	0.89961700
H	-1.71120400	0.55631600	1.73520500
C	-3.43780300	1.34801700	0.75853100
C	-4.56879300	0.85527400	1.60740900
H	-5.24672200	0.20299700	1.04521900
H	-5.16637300	1.68487200	2.00117500
H	-4.18209700	0.28732000	2.45678300
H	2.32224600	-4.19384900	-1.92421600
C	1.54387800	-3.58893900	-1.47100200
C	-0.39218900	-2.08272800	-0.07103700
C	1.89048500	-2.49264800	-0.65941400
C	0.21152500	-3.88261900	-1.67086200
C	-0.73089600	-3.17000900	-0.91355400
C	0.95223300	-1.57741900	-0.10942000
S	3.52929600	-2.16448500	-0.17163000
C	1.63901300	-0.36766800	0.40379700

C	3.00377600	-0.66852600	0.53585400
H	-0.09000900	-4.71028100	-2.30430700
S	-2.37652600	-3.71507700	-0.63943200
C	-1.43748700	-1.85164900	0.88694300
H	-1.30587800	-1.21847600	1.74894300
C	-2.54226700	-2.63454500	0.73265300
C	-3.76128600	-2.70776100	1.59969900
H	-4.66342800	-2.39162200	1.06385700
H	-3.64245500	-2.05931600	2.47098200
H	-3.93642400	-3.72727100	1.96055200
N	3.64496800	1.53598100	1.00522200
H	4.38630000	2.21551400	1.12547600
C	4.06374100	0.20936500	0.97830000
O	5.21896800	-0.11009800	1.23891500

**(2) Ground state 1 (from X-ray structure)**



Calculation Method = RB3LYP

Formula = C<sub>23</sub>H<sub>13</sub>NOS<sub>4</sub>

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2607.0807 Hartree

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Electronic Energy (EE) = -2607.0807 Hartree

Zero-point Energy Correction = 0.297044 Hartree

Thermal Correction to Energy = 0.32068 Hartree

Thermal Correction to Enthalpy = 0.321624 Hartree  
 Thermal Correction to Free Energy = 0.244671 Hartree  
 EE + Zero-point Energy = -2606.7836 Hartree  
 EE + Thermal Energy Correction = -2606.76 Hartree  
 EE + Thermal Enthalpy Correction = -2606.7591 Hartree  
 EE + Thermal Free Energy Correction = -2606.836 Hartree  
 E (Thermal) = 201.23 kcal/mol  
 Heat Capacity (Cv) = 93.717 cal/mol-kelvin  
 Entropy (S) = 161.962 cal/mol-kelvin

Calculation Type = SP  
 Calculation Method = Rwb97XD  
 Formula = C<sub>23</sub>H<sub>13</sub>NOS<sub>4</sub>  
 Basis Set = 6-311+G(d,p)  
 Charge = 0  
 Spin = Singlet  
 Solvation = scrf=solvent=chlorobenzene  
 E(Rwb97XD) = -2607.0029 Hartree

0 1			
C	3.47989300	0.54934000	2.77881300
H	4.36477700	0.99436000	2.30995300
H	2.78523700	1.35768200	3.02053600
H	3.80426700	0.08614800	3.71756400
C	2.81329300	-0.43975700	1.87318700
C	1.54339300	-0.40491300	1.38604800
H	0.85402700	0.38832700	1.64001900
C	1.20317300	-1.51961800	0.54024400
C	2.27797200	-2.43683700	0.43559400
C	2.17266200	-3.67168800	-0.21822700
H	3.02034500	-4.34629900	-0.27554200
C	0.94025400	-4.04481100	-0.73218000
H	0.80347800	-5.02385500	-1.17947700
C	-0.13383200	-3.15074100	-0.63443800
C	-0.02776500	-1.84572900	-0.09986600
C	-1.29534800	-1.12380900	-0.16896900

C	-2.32709800	-1.99229700	-0.50315000
C	-1.69205000	0.24982300	0.10104100
C	-3.03160600	0.47115600	0.41978500
C	-0.96210400	1.50930600	0.05601400
C	-1.74433600	2.57476600	0.57066200
C	0.00067500	4.19117000	0.21597300
H	0.38910400	5.20190400	0.28903700
C	-1.26300200	3.89038500	0.69126700
H	-1.88754300	4.66430400	1.12498400
C	0.74204800	3.18418800	-0.42231900
C	0.28837200	1.85046800	-0.54504700
C	1.17270800	1.06895800	-1.36749800
H	0.99349000	0.03598100	-1.63083200
C	2.26190200	1.74969800	-1.82043300
S	3.68630000	-1.86446700	1.31500500
S	-1.80189300	-3.57414600	-1.03487600
S	-3.39537400	2.10066400	0.91669800
S	2.26831700	3.41640600	-1.25722800
C	3.36629000	1.24029300	-2.69448100
H	4.33927100	1.30453700	-2.19455700
H	3.18652100	0.19209400	-2.94598700
H	3.43937700	1.80806600	-3.62893100
N	-3.64900900	-1.66655500	-0.38554800
H	-4.37574300	-2.33372400	-0.61300200
C	-4.10490100	-0.48081500	0.21784700
O	-5.29683900	-0.30377100	0.44403500

**(3) Ground state 2 (enantiomer)**

Calculation Method = RB3LYP

Formula = C<sub>23</sub>H<sub>13</sub>NOS<sub>4</sub>

Basis Set = 6-31G(d,p)

Charge = 0

Spin = Singlet

Solvation = None

E(RB3LYP) = -2607.0807 Hartree

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Electronic Energy (EE) = -2607.0807 Hartree

Zero-point Energy Correction = 0.297045 Hartree

Thermal Correction to Energy = 0.32068 Hartree

Thermal Correction to Enthalpy = 0.321624 Hartree

Thermal Correction to Free Energy = 0.244673 Hartree

EE + Zero-point Energy = -2606.7836 Hartree

EE + Thermal Energy Correction = -2606.76 Hartree

EE + Thermal Enthalpy Correction = -2606.7591 Hartree

EE + Thermal Free Energy Correction = -2606.836 Hartree

E (Thermal) = 201.23 kcal/mol

Heat Capacity (Cv) = 93.716 cal/mol-kelvin

Entropy (S) = 161.958 cal/mol-kelvin

Calculation Type = SP

Calculation Method = Rwb97XD

Formula = C<sub>23</sub>H<sub>13</sub>NOS<sub>4</sub>

Basis Set = 6-311+G(d,p)

Charge = 0

Spin = Singlet

Solvation = scrf=solvent=chlorobenzene

E(Rwb97XD) = -2607.0029 Hartree

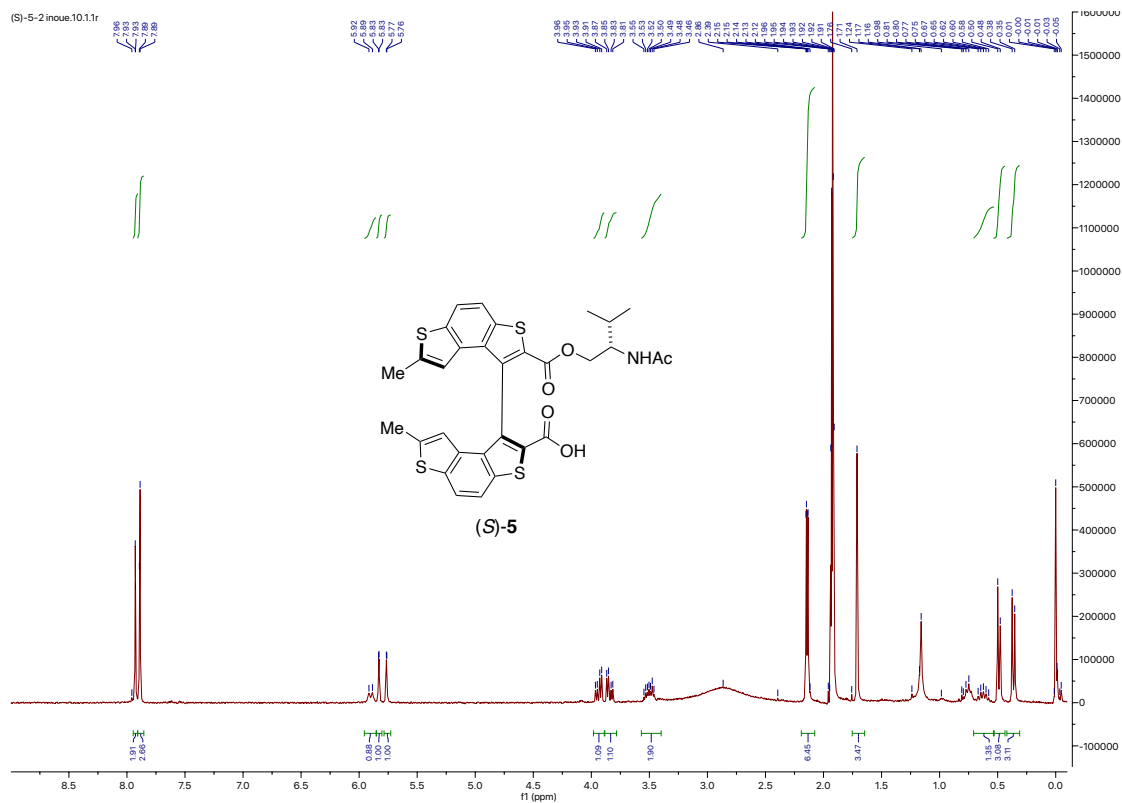
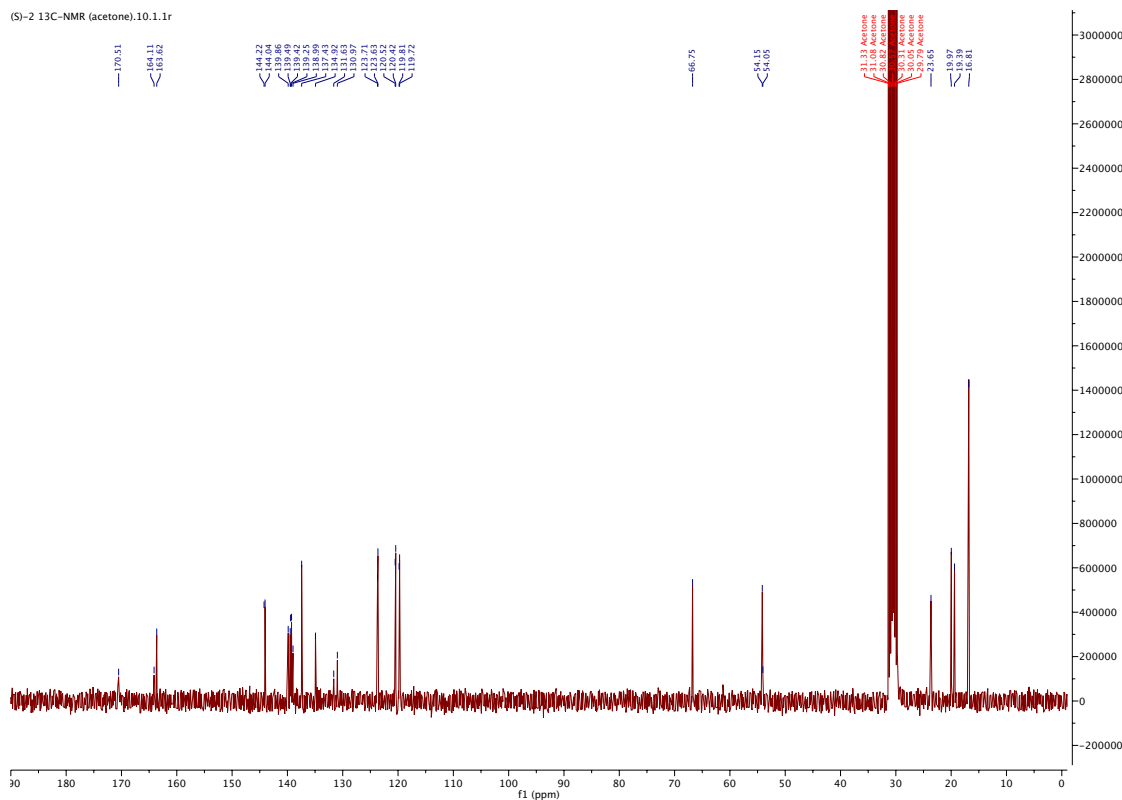
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H	0.80337000	5.02392500	-1.17938500
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C	1.20317000	1.51967600	0.54027000
C	-0.13389000	3.15080800	-0.63433100
C	2.17259400	3.67181400	-0.21808300
C	2.27795300	2.43693300	0.43565000
C	-0.02779000	1.84577300	-0.09976400
S	-1.80189500	3.57418700	-1.03489100
C	-1.29536300	1.12382300	-0.16902500
C	-2.32708300	1.99226200	-0.50334900

H	3.02028200	4.34641200	-0.27546700
S	3.68635000	1.86453000	1.31494400
C	1.54349200	0.40488900	1.38594500
H	0.85415200	-0.38841000	1.63980800
C	2.81339000	0.43975700	1.87306500
C	3.48006600	-0.54948900	2.77846800
H	2.78505000	-1.35728000	3.02100000
H	3.80554100	-0.08622600	3.71679500
H	4.36425600	-0.99526600	2.30900300
H	-1.88769100	-4.66432100	1.12487300
C	-1.26313800	-3.89040700	0.69115500
C	0.28833800	-1.85051000	-0.54502900
C	-1.74442300	-2.57477900	0.57061300
C	0.00052900	-4.19123500	0.21584800
C	0.74196400	-3.18426700	-0.42236100
C	-0.96214300	-1.50932300	0.05596900
S	-3.39537200	-2.10058000	0.91690900
C	-1.69205200	-0.24980300	0.10114200
C	-3.03154400	-0.47106400	0.42008200
H	0.38892400	-5.20198300	0.28892300
S	2.26828100	-3.41650300	-1.25719300
C	1.17276600	-1.06899700	-1.36740000
H	0.99357500	-0.03600300	-1.63066500
C	2.26194500	-1.74975800	-1.82031600
C	3.36636300	-1.24033900	-2.69431700
H	4.33942900	-1.30528200	-2.19465200
H	3.18697500	-0.19192200	-2.94518700
H	3.43899500	-1.80763200	-3.62909600
N	-3.64899500	1.66652700	-0.38559800
H	-4.37577400	2.33336900	-0.61387000
C	-4.10485300	0.48090000	0.21796500
O	-5.29684300	0.30369600	0.44377600

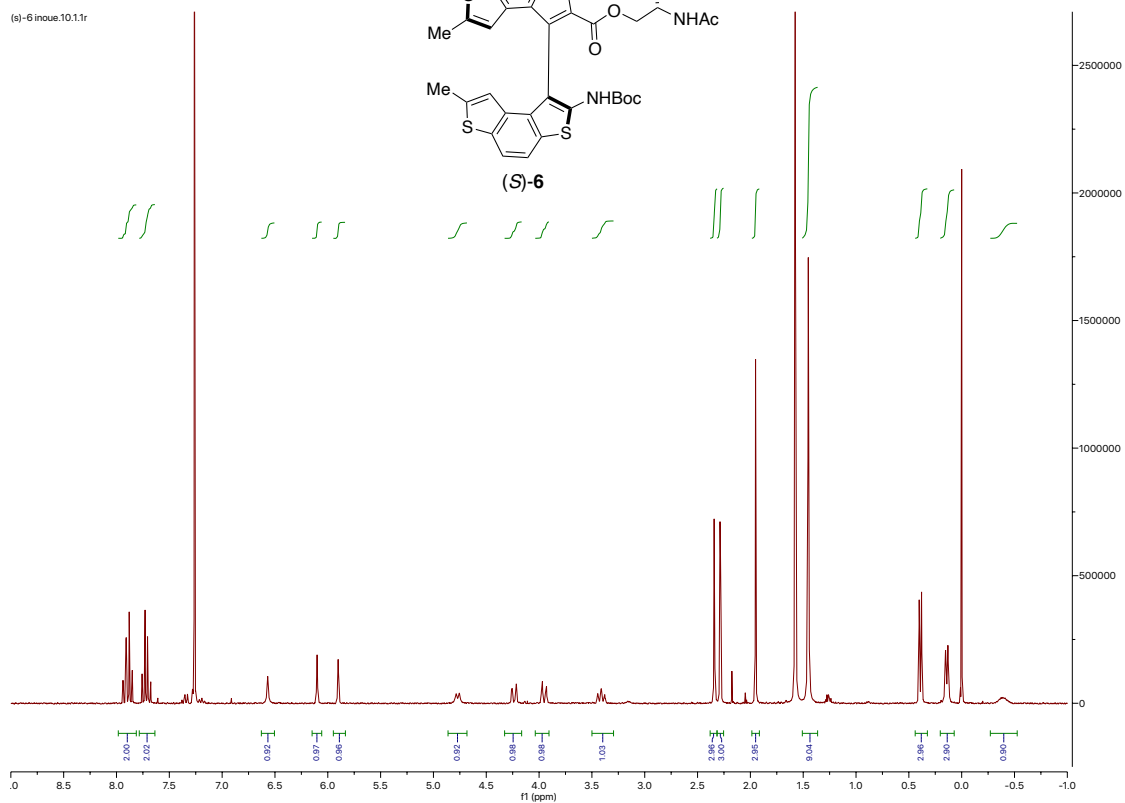
**References**

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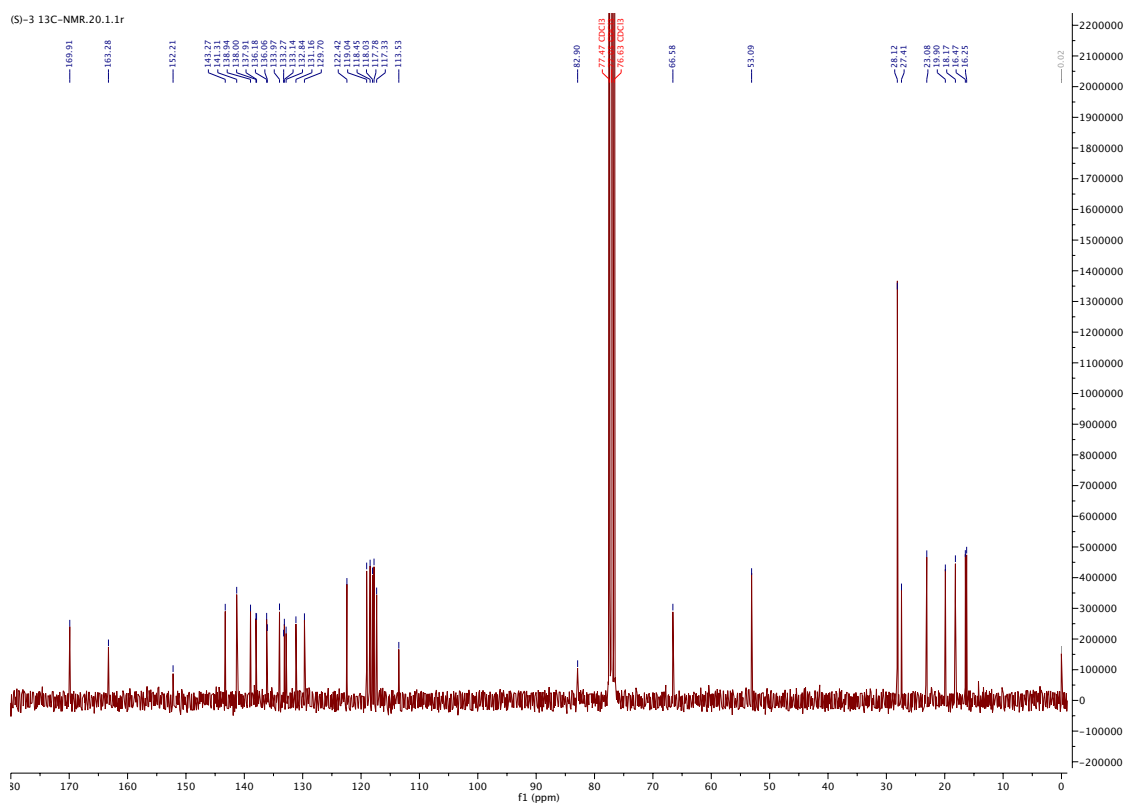
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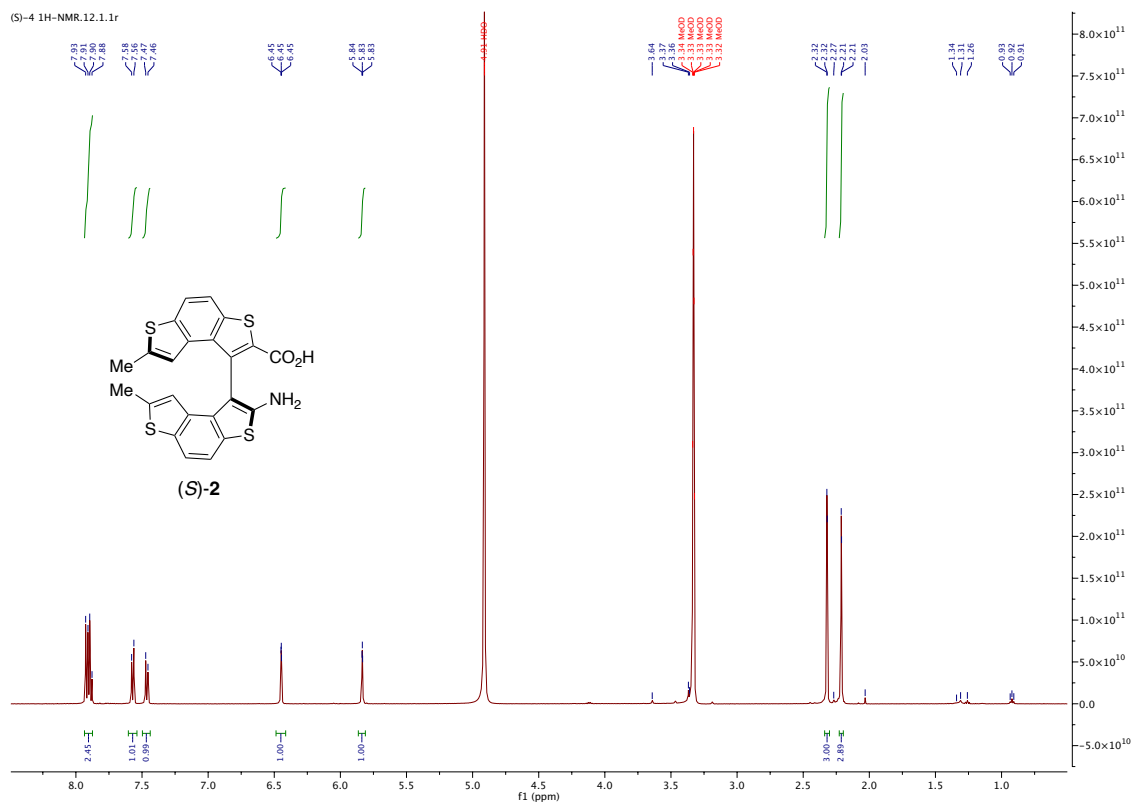
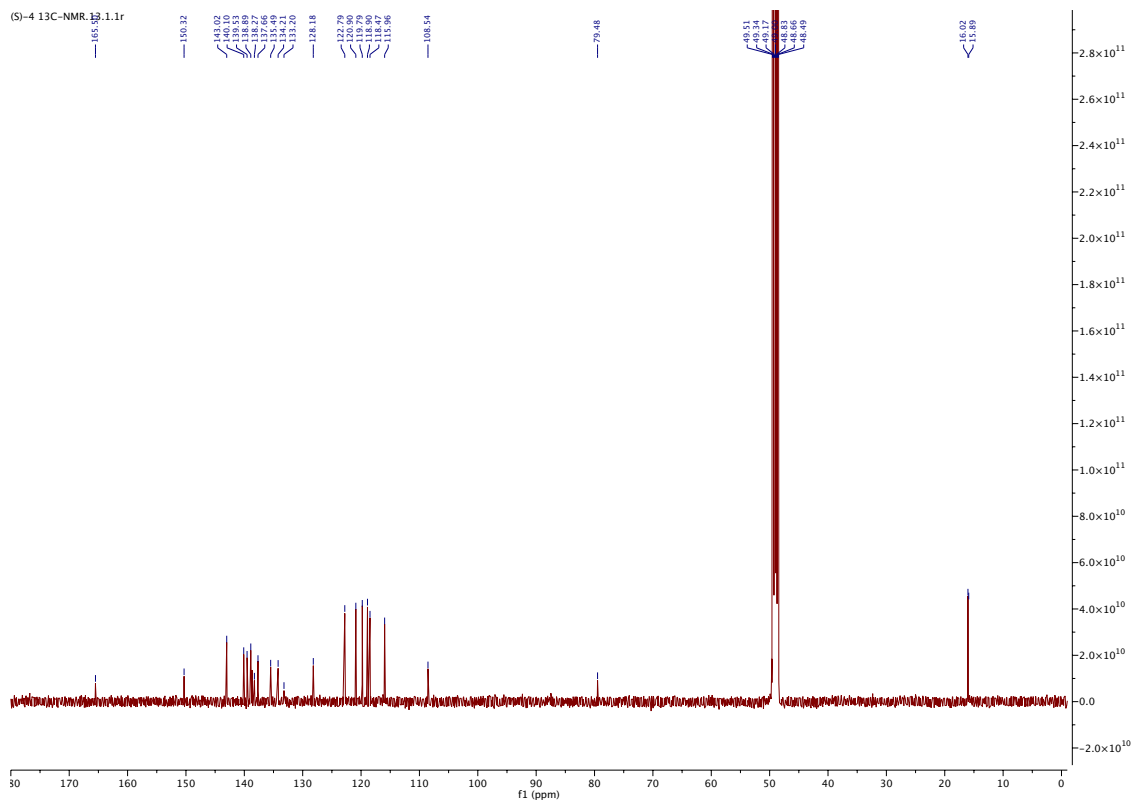
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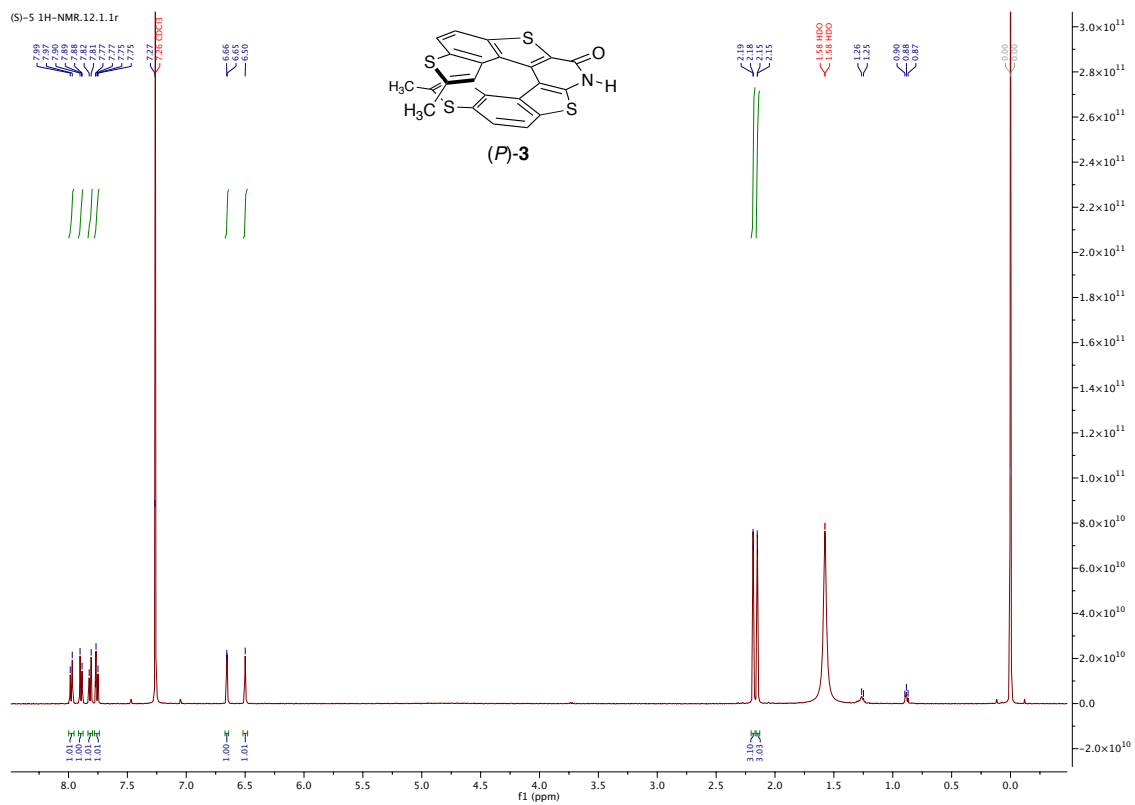
(s)-6 inoue.10.1.1r

 $^{13}\text{C}$  NMR of (*S*)-**6** in  $\text{CDCl}_3$ 

(S)-3 13C-NMR.20.1.1r



$^1\text{H}$  NMR of (*S*)-**2** in  $\text{CD}_3\text{OD}$  $^{13}\text{C}$  NMR of (*S*)-**2** in  $\text{CD}_3\text{OD}$ 

<sup>1</sup>H NMR of (*P*)-**3** in CDCl<sub>3</sub><sup>13</sup>C NMR of (*P*)-**3** in CDCl<sub>3</sub>