

Supporting information for

Vibrational Circular Dichroism of Thiolate-protected Au₂₅ Cluster: Accurate Prediction of Spectra and Chirality Transfer within the Mixed Ligand Shell

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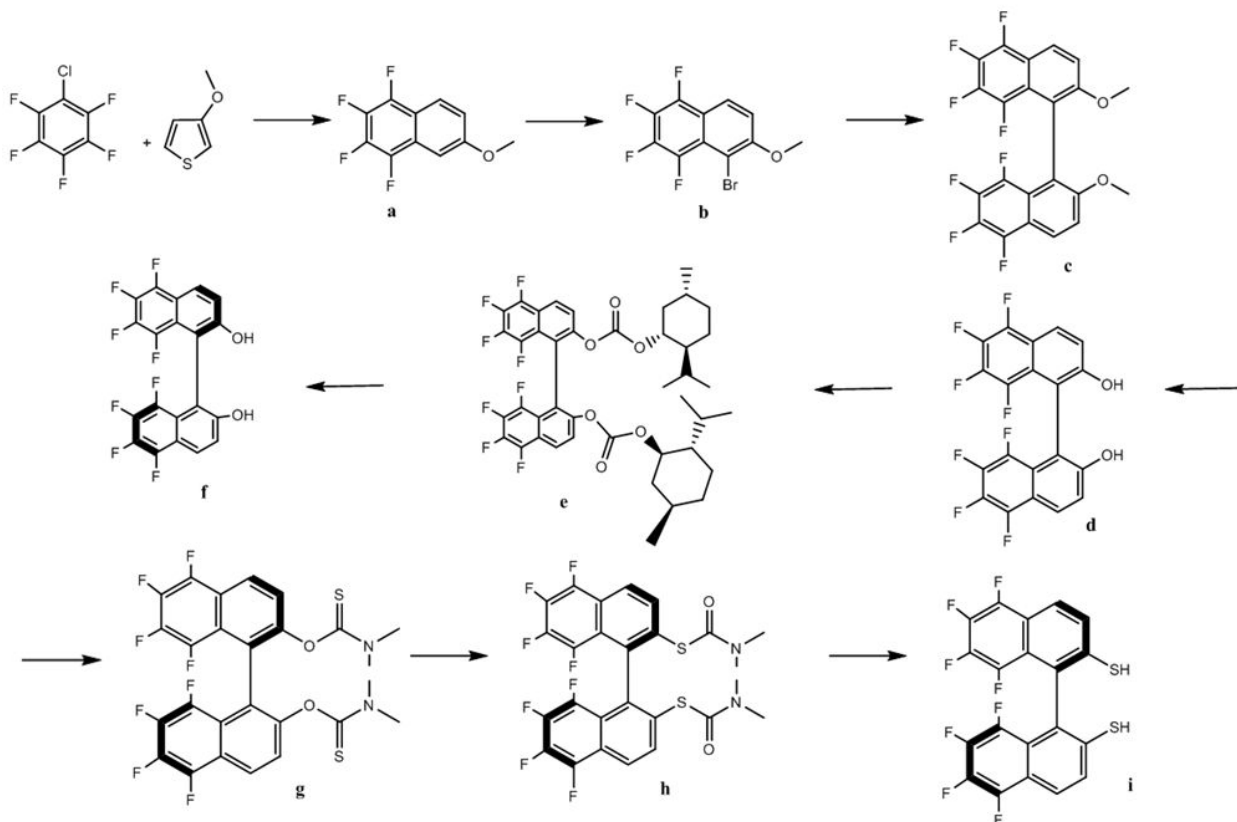
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Synthesis of (*R*)- 5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-dithiol ((*R*)-FBINAS**) (**i**)**

The synthesis was done according to Scheme S1. **a – f** were synthesized according to ¹. **h** and **i** were obtained according to ^{2,3}



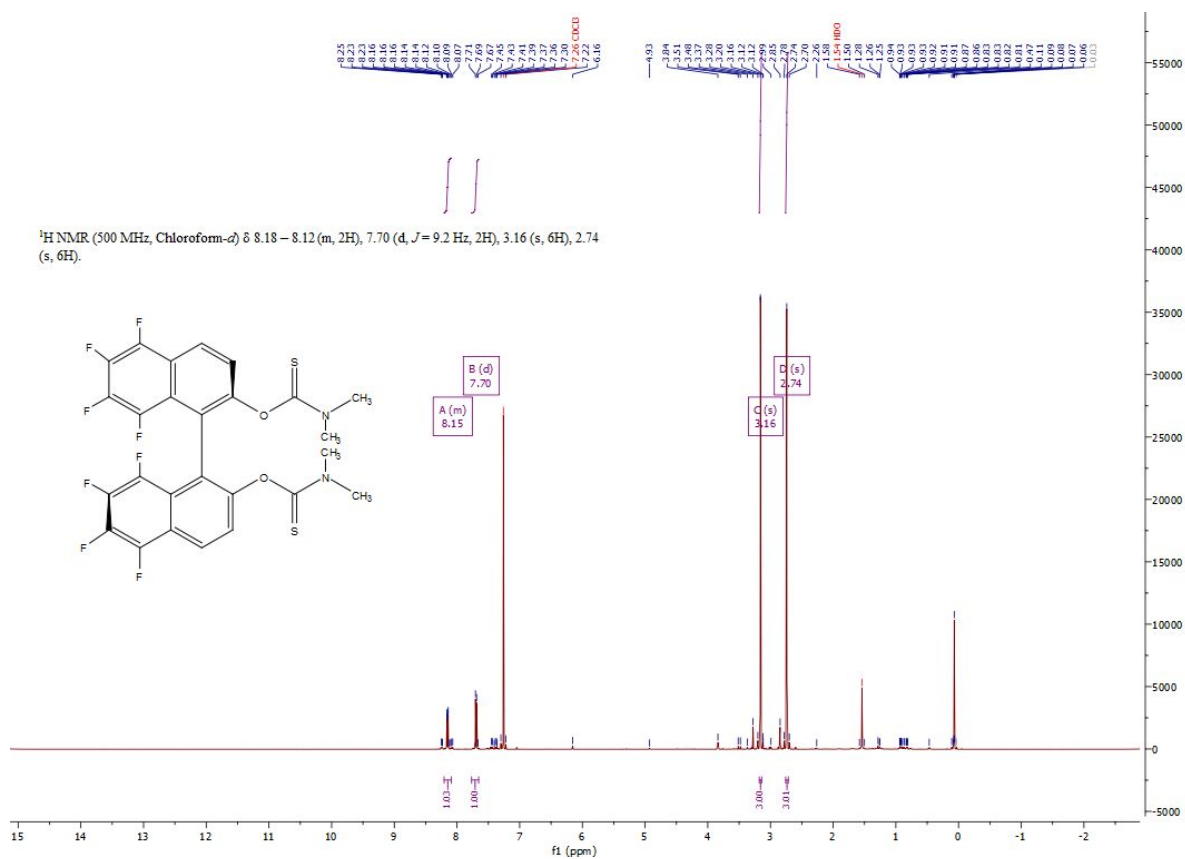
Scheme S1: General strategy for the synthesis of (*R*)-5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-dithiol

-Synthesis of (*R*)- O,O'-(5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diyl) bis(dimethylcarbamothioate) **g**:

In a dry and degassed Schlenk 1 g of **d** and 60 ml of dry THF were placed. Some drops of pyridine were added followed by some drops of 4-dimethylaminopyridine and seven equivalents of dimethylthiocarbamoyl chloride. The mixture was heated to 65°C for 18 hours. The product was purified by column chromatography (CHCl₃) to obtain a yellow powder (650 mg).

¹H NMR (500 MHz, Chloroform-d) δ 8.18 – 8.12 (d, 2H), 7.70 (d, J = 9.2 Hz, 2H), 3.16 (s, 6H), 2.74 (s, 6H).

MS: EI⁺: m/z calculated for C₂₆H₁₆F₈N₂O₂S₂ (M⁺) 604.53, observed 605.65



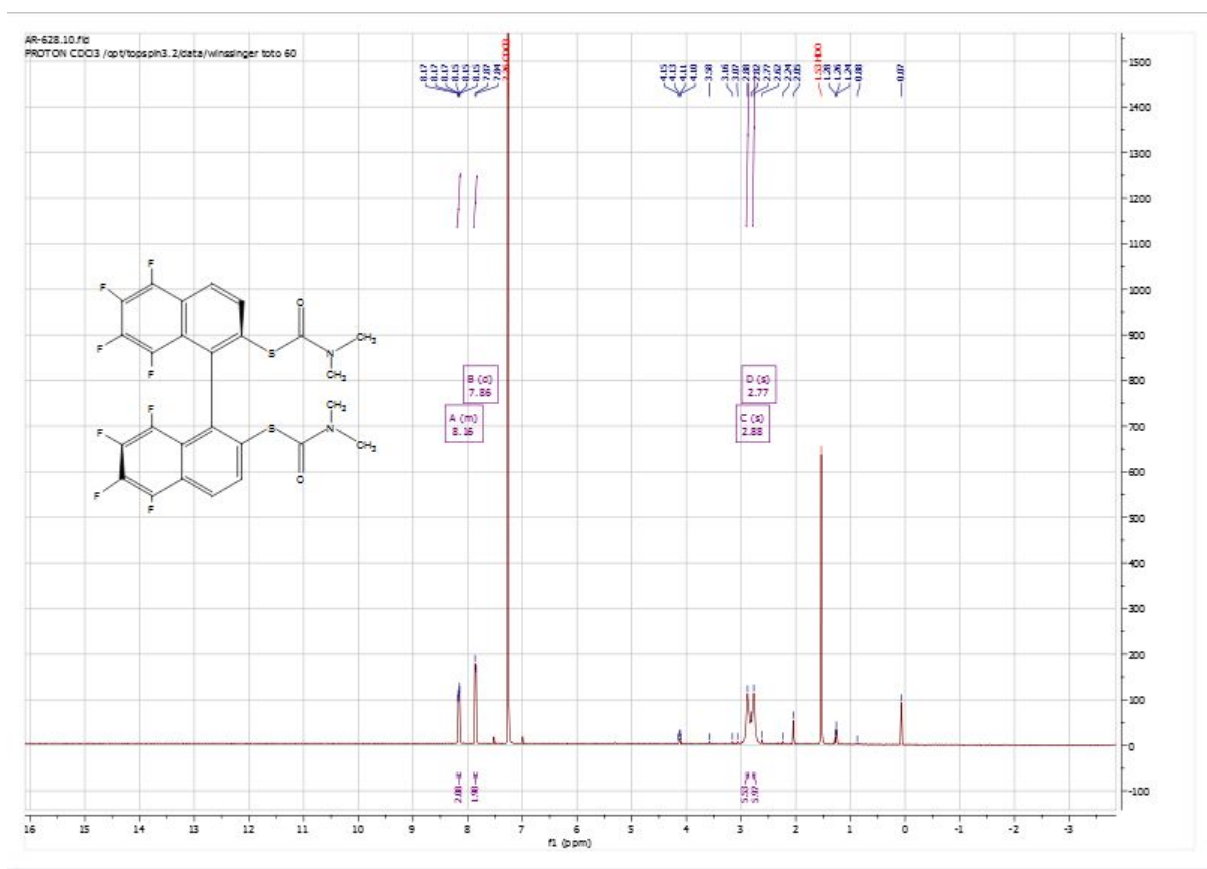
¹H NMR spectrum (*R*)-O,O'-(5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diyl) bis(dimethylcarbamothioate), **g**.

-Synthesis of (R)- S,S'-(5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diyl)

bis(dimethylcarbamothioate) h:

650 mg (1.07 mmol) of **g** were put in a Schlenk under nitrogen gas and heated to 260°C. After 15 min the exchange was complete. After purification (column, DCM/AcOEt 8/2) a yellow powder was obtained, 380mg (58.5%)

¹H NMR (400 MHz, Chloroform-d) δ 8.20 – 8.12 (m, 2H), 7.86 (d, J = 8.9 Hz, 2H), 2.88 (s, 6H), 2.77 (s, 6H).



¹H NMR spectrum of (R)-S,S'-(5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diyl)

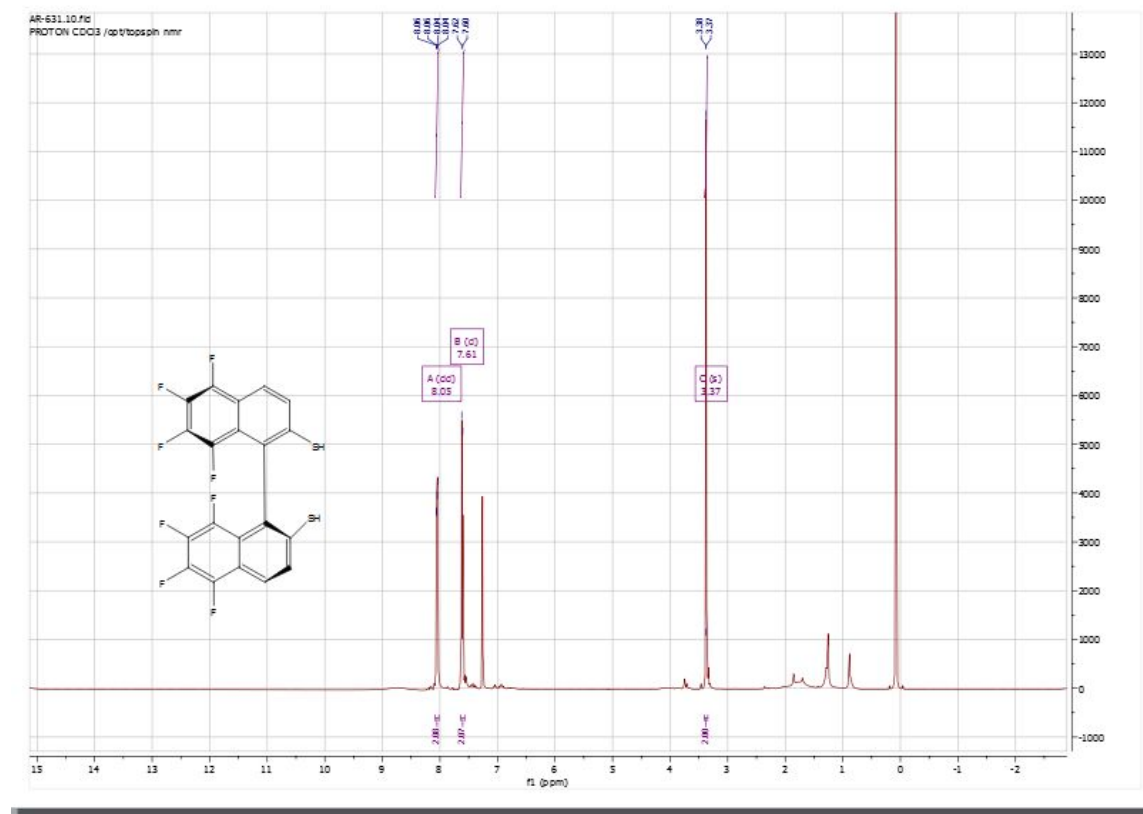
bis(dimethylcarbamothioate) h.

-Synthesis of (R)- 5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-dithiol (i):

(R)-S,S'-(5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-diyl) bis(dimethylcarbamothioate)

h: (360 mg, 0.6 mmol) was reacted with LiAlH₄ (350 mg, 3.6 mmol) in THF under reflux for three hours. The reaction mixture was then cooled to 0°C and the product was slowly hydrolysed with deionized and degassed water (10 ml) and H₂SO₄ 98 % (until pH = 1), extracted with Et₂O, dried over Na₂SO₄, filtered and concentrated to obtain as brownish powder (225 mg, 81.7%). All manipulations were done under nitrogen atmosphere.

¹H NMR (500 MHz, Chloroform-d) δ 8.05 (dd, J = 8.7, 1.8 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 3.37 (s, 2H).



¹H NMR spectrum of (R)-5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-dithiol (i)

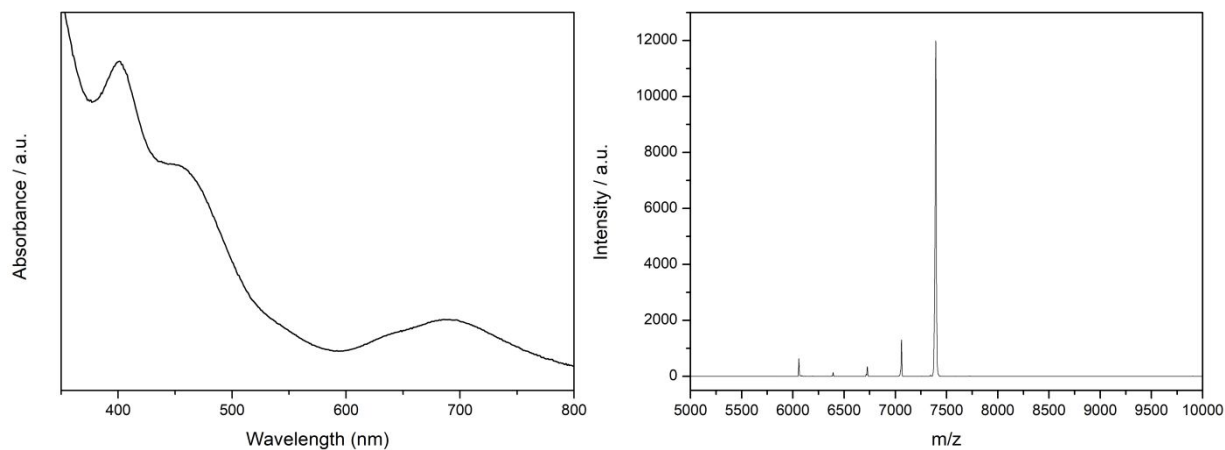


Fig. S1: UV-vis (left) and MALDI-tof (right) analysis of pure Au₂₅(PET)₁₈⁰ clusters (m/z = 7392)

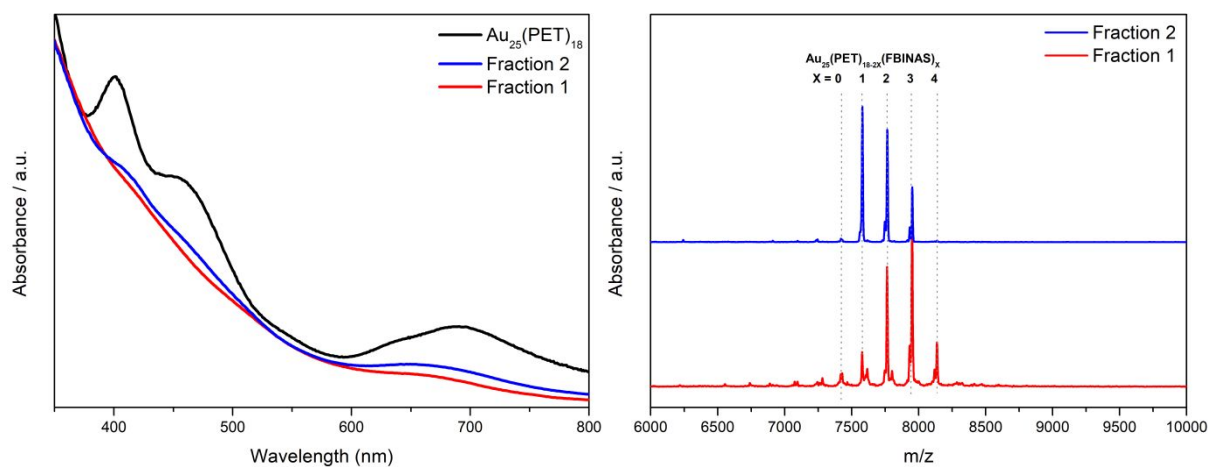


Fig. S2: UV-vis (left) and MALDI-TOF (right) analysis of Au₂₅(PET)_{18-2x}((R)-FBINAS)_x clusters after separation by SEC. Fraction 1 eluting before Fraction 2.

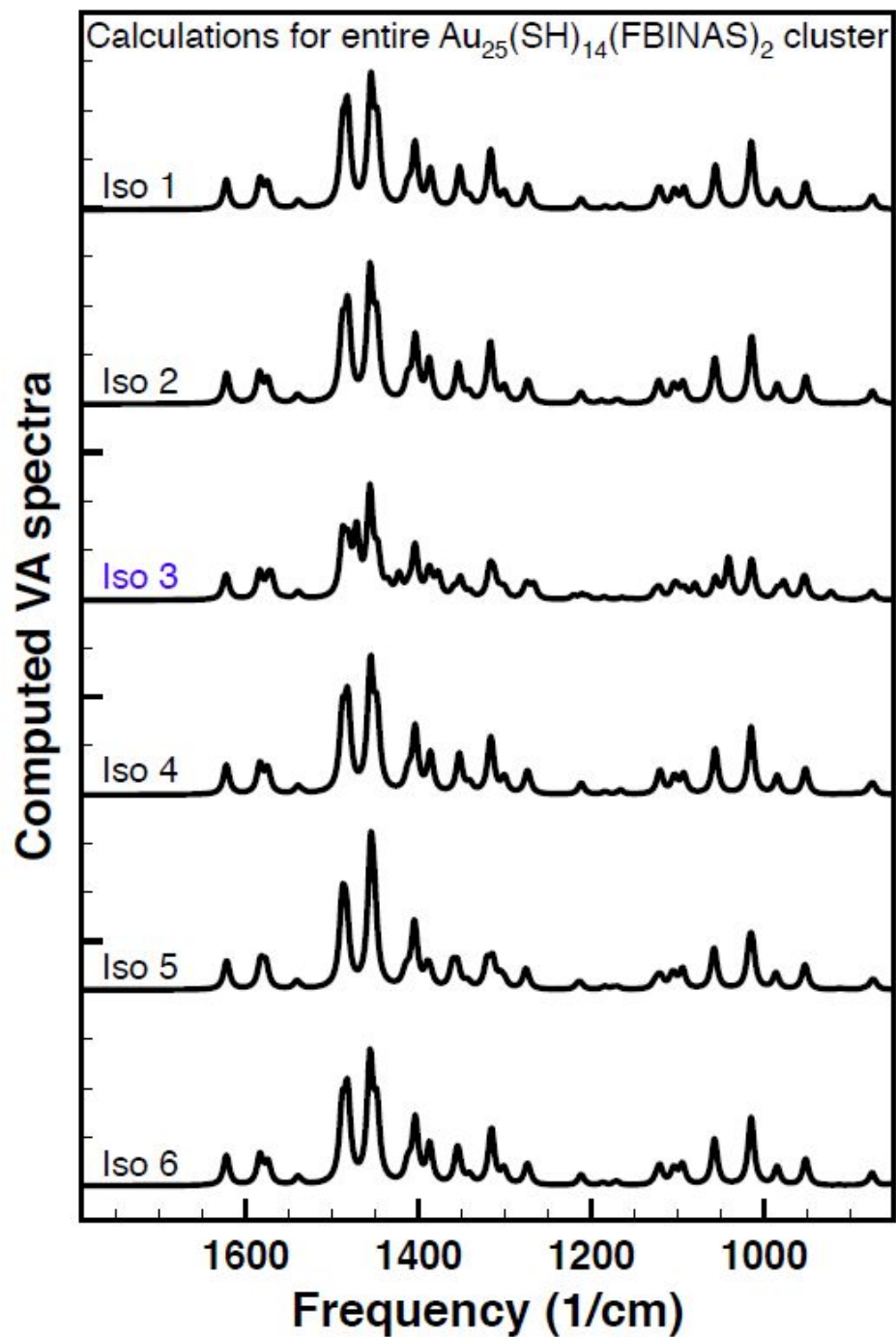


Fig. S3: Calculated IR spectra of different isomers of $\text{Au}_{25}(\text{SH})_{14}(\text{FBINAS})_2$.

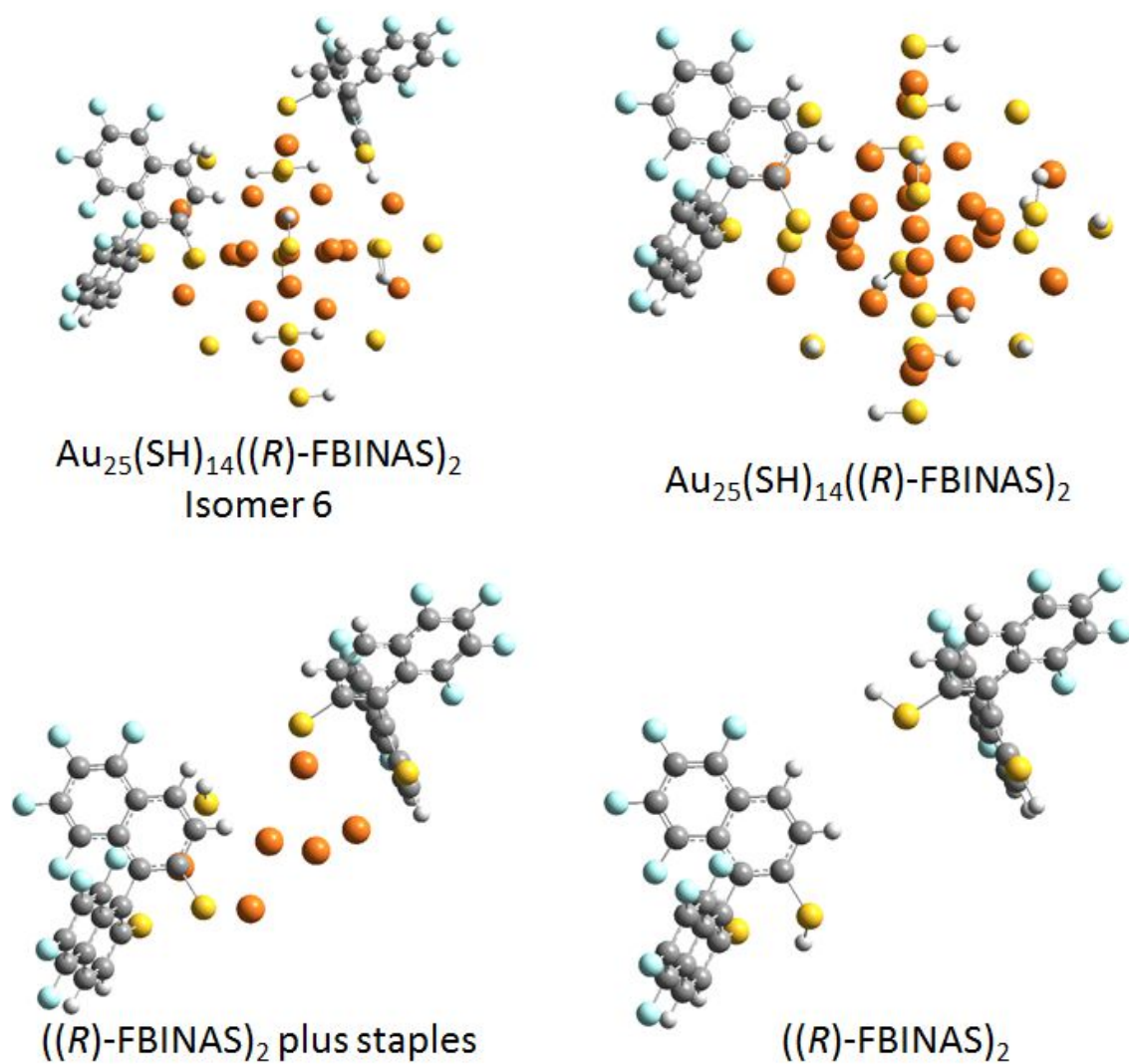
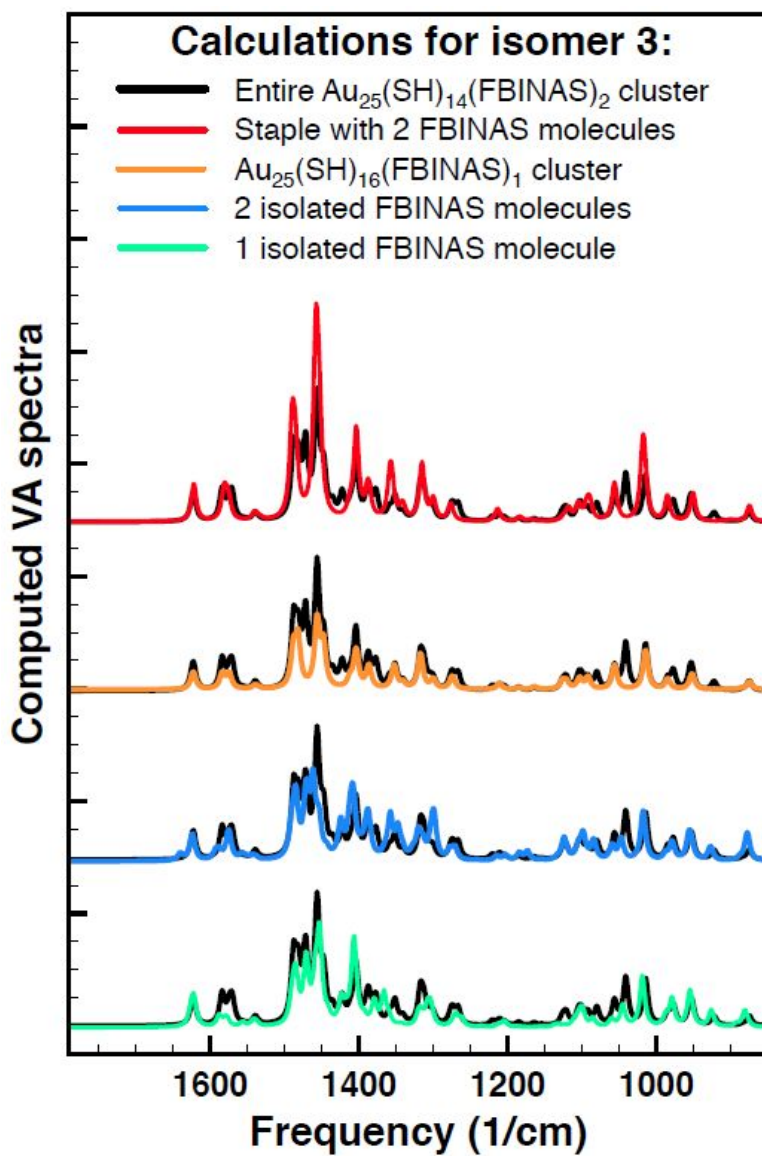


Fig. S4: Structure elements used for the calculations of IR and VCD spectra. The structures are derived from $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$, Isomer 6 (shown on top left).



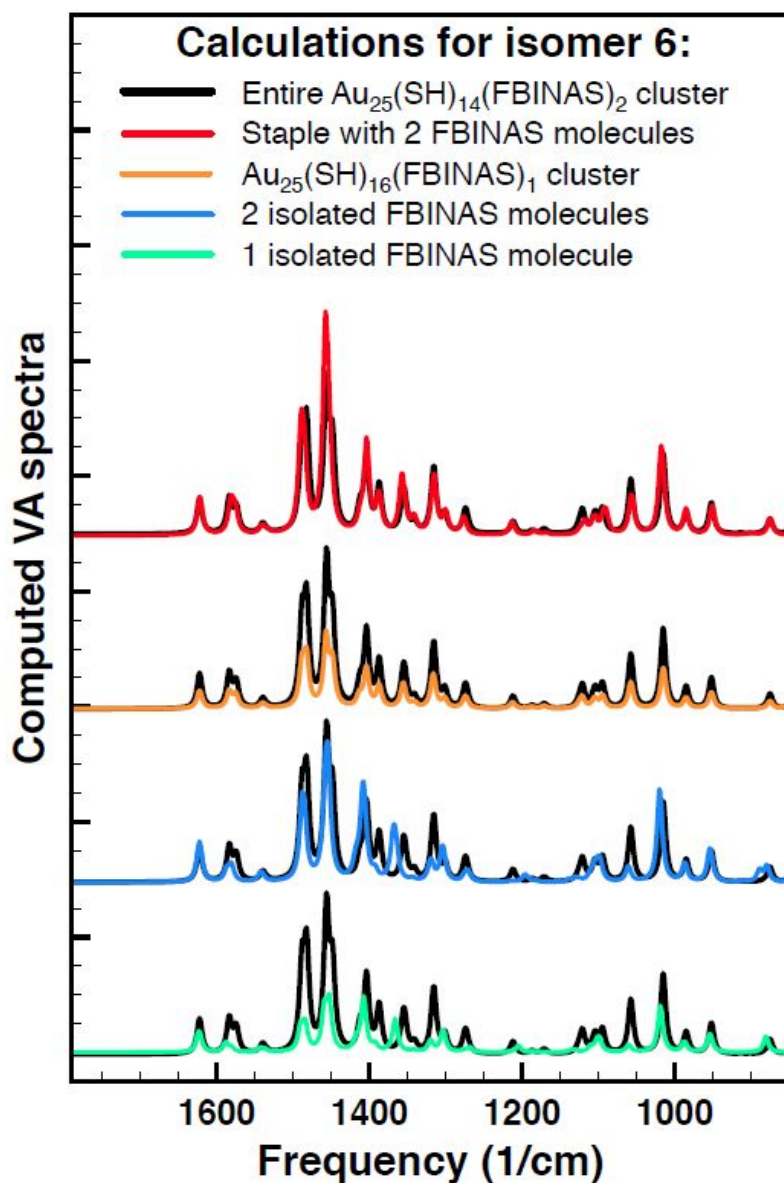


Fig. S5: Calculated IR spectra of different structural elements for isomers 3 and 6 of $\text{Au}_{25}(\text{SH})_{14}(\text{FBINAS})_2$. Black: entire $\text{Au}_{25}(\text{SH})_{14}(\text{FBINAS})_2$ cluster, red: staple plus two FBINAS molecules, orange: $\text{Au}_{25}(\text{SH})_{16}(\text{FBINAS})_1$ cluster, blue: two isolated FBINAS molecules, green: one single FBINAS molecule.

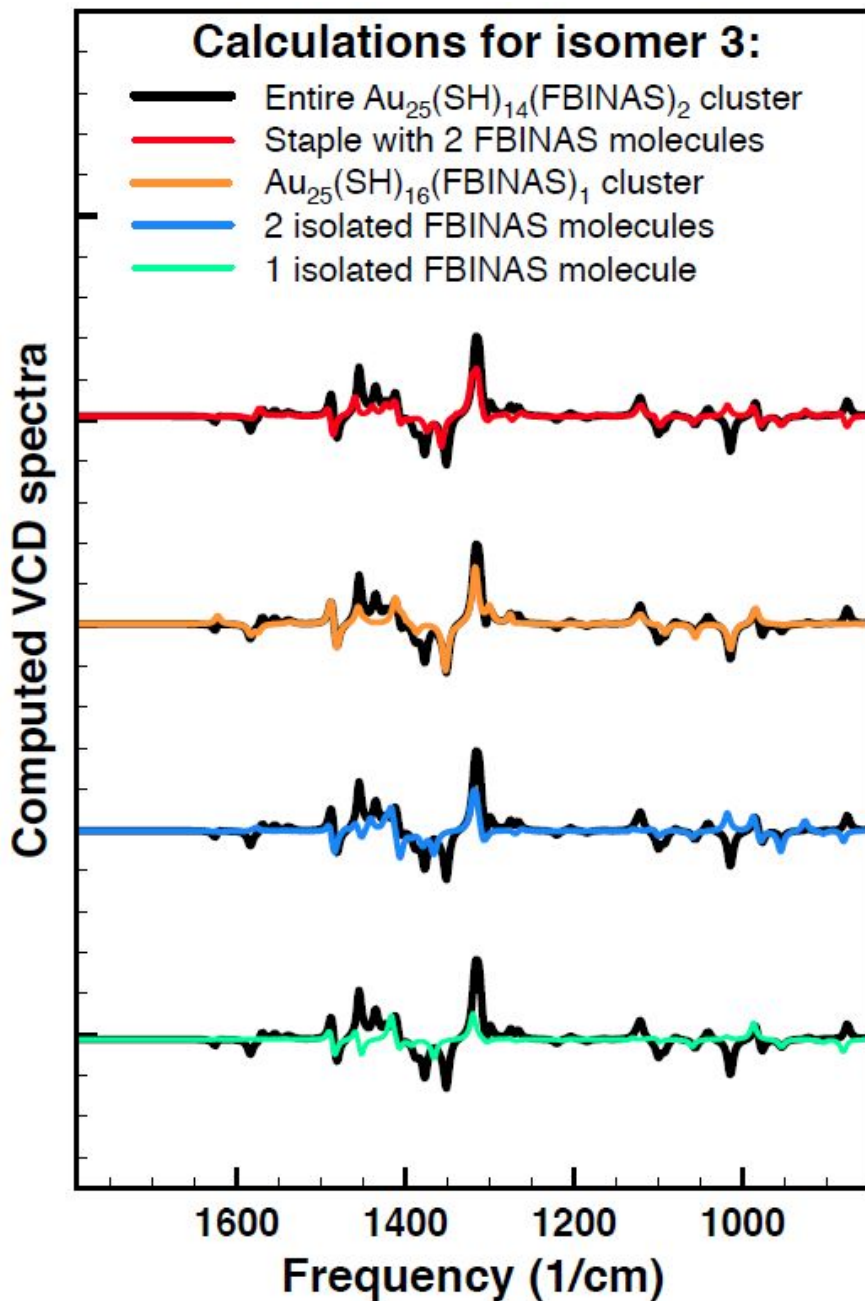


Fig. S6: Calculated VCD spectra of different structural elements for isomer 3 of $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$. Black: entire $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$ cluster, red: staple plus two FBINAS molecules, orange: $\text{Au}_{25}(\text{SH})_{16}((R)\text{-FBINAS})_1$ cluster, blue: two isolated FBINAS molecules, green: one single FBINAS molecule.

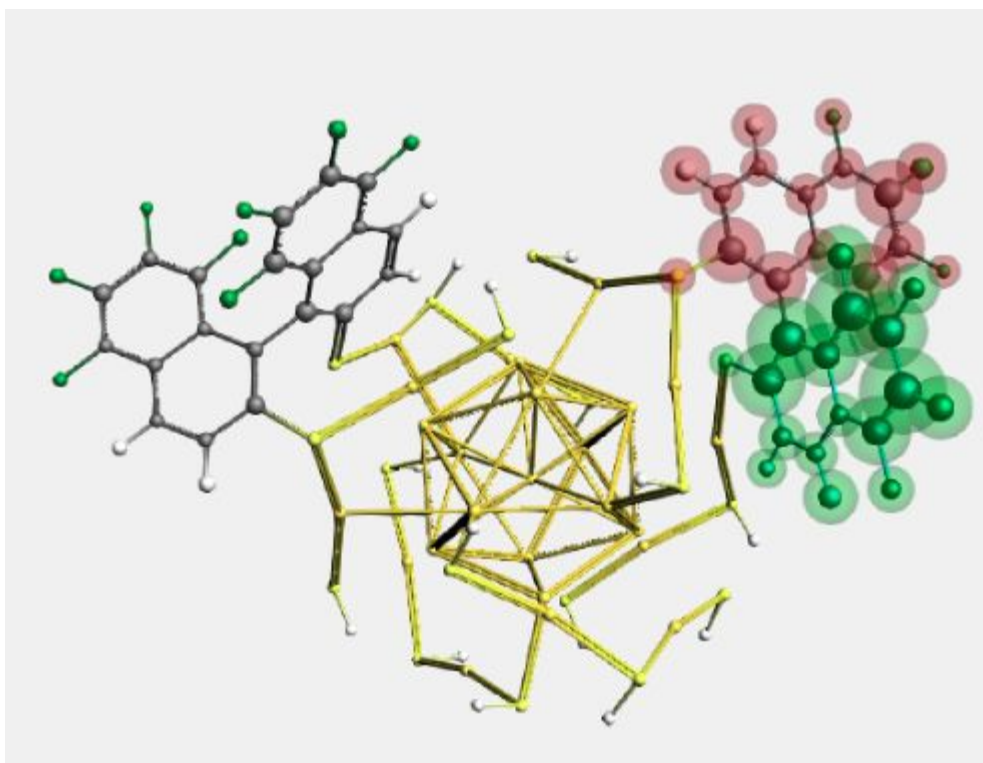


Fig. S7: Visualization of generalised coupled oscillator analysis for one mode (Nr. 303, see text below for more details)-

A generalised coupled oscillator analysis (GCO)⁴ has been performed for all normal modes in the fingerprint region. In this type of analysis, the atoms of a molecule are grouped into three fragments: two important fragments (A and B) and an unimportant fragment labeled as "rest". Then, the rotational strengths is decomposed into three terms. The first term is labeled R_{if} and represents the contribution from the individual isolated fragments A and B. The second term is labeled R_{gco} and is associated with the interaction of the electric dipole transition moments of fragments A and B. When the fragments A and B are chosen correctly, the R_{gco} term is expected to be the dominant term. Finally, we have the R_{rest} term, which is associated with the unimportant fragments. This term is expected to be significantly smaller than the other two.

Figure S8 summarises the GCO analysis performed for mode 303. The two symmetric halves of the FBINAS ligand has been chosen as the important fragments (A and B) and as such are highlighted in red and green. The rest of the atoms belong to region "rest". As can be seen in the right side table, R_{gco} is larger than R_{if} which in turn is much larger than R_{rest} (-387.95 vs. -181.65 vs. +68.22). This shows clearly that: (1) the intensity of this mode is determined mostly by the FBINAS ligand (via R_{if} and R_{gco}), and (2) the high intensity observed for this mode is a consequence of exciton-coupling interactions (R_{gco}). We note that the situation is similar for all modes that exhibit intense VCD signals.

Mode	Freq.	D.S.	R.S.	
303	1316.3	460.45	-501.38	
=====				
EDTM				
Frag.	X	Y	Z	Length
A:	-7.7	-1.1	1.2	7.8
B:	-10.6	-11.6	-2.2	15.9
REST:	2.3	-1.6	-0.4	2.8

TOTAL:	-16.0	-14.3	-1.3	21.5
MDTM				
Frag.	X	Y	Z	Length
A:	9.2	5.4	31.6	33.3
B:	11.7	10.5	-47.4	50.0
REST:	-3.4	1.0	0.6	3.6

TOTAL:	17.5	16.9	-15.3	28.8
Frag.	NM localization (%)			

A:	31.8			
B:	56.6			
REST:	11.6			

TOTAL:	100.0			
R_gco -->	Subtotal:	-387.95		

EDTM_A*MDTM_B(0_dft):	-159.34			
EDTM_B*MDTM_A(0_dft):	-228.61			
R_if -->	Subtotal:	-181.65		

EDTM_A*MDTM_A(0_dft):	-37.56			
EDTM_B*MDTM_B(0_dft):	-144.09			
R_rest -->	Subtotal:	68.22		

EDTM_rest*MDTM_rest(0_dft):	-9.69			
EDTM_A*MDTM_rest(0_dft):	25.60			
EDTM_B*MDTM_rest(0_dft):	23.02			
EDTM_rest*MDTM_A(0_dft):	0.25			
EDTM_rest*MDTM_B(0_dft):	29.04			
=====				
R = R_gco + R_if + R_rest:	-501.38			
R_CO:				-155.14757

sin[EDTM_A vs EDTM_B]* EDTM_A * EDTM_B :	84.72755			
Y_AB*cos[Y_AB vs. (EDTM_A x EDTM_B)]:	-4.42793			
pi*Freq/c:	0.41354			

R_CCO:				-232.79836

sin[EDTM_A vs EDTM_B]* EDTM_A * EDTM_B :	84.72755			
-Y_CCO*cos[Y_AB vs. (EDTM_A x EDTM_B)]:	-6.64410			
pi*NM_frequency/c:	0.41354			

Fig. S8: Generalised coupled oscillator analysis (see text for more details).

References:

- (1) Yudin, A. K.; Martyn, L. J. P.; Pandiaraju, S.; Zheng, J.; Lough, A. *Org. Lett.* **2000**, *2*, 41.
- (2) He, H.; Chen, L. Y.; Wong, W. Y.; Chan, W. H.; Lee, A. W. M. *Eur. J. Org. Chem.* **2010**, 4181.
- (3) Cossu, S.; DeLucchi, O.; Fabbri, D.; Valle, G.; Painter, G. F.; Smith, R. A. J. *Tetrahedron* **1997**, *53*, 6073.
- (4) Nicu, V. P. *Phys. Chem. Chem. Phys.* **2016**, *18*, 21202.