

Supplementary Material

Tuning the coverage of self-assembled monolayer by introducing bulky substituents onto rigid adamantane tripod

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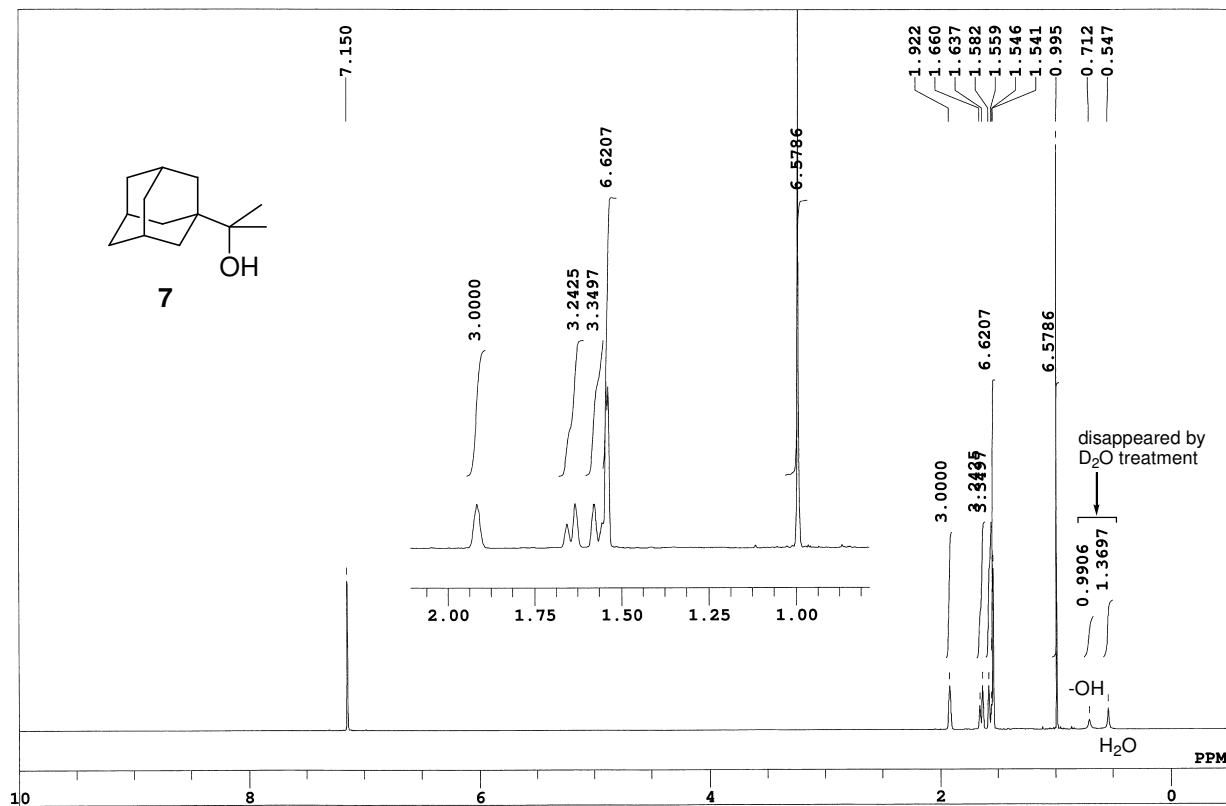


Figure S1. ¹H NMR spectrum of 7 (500 MHz, C₆D₆).

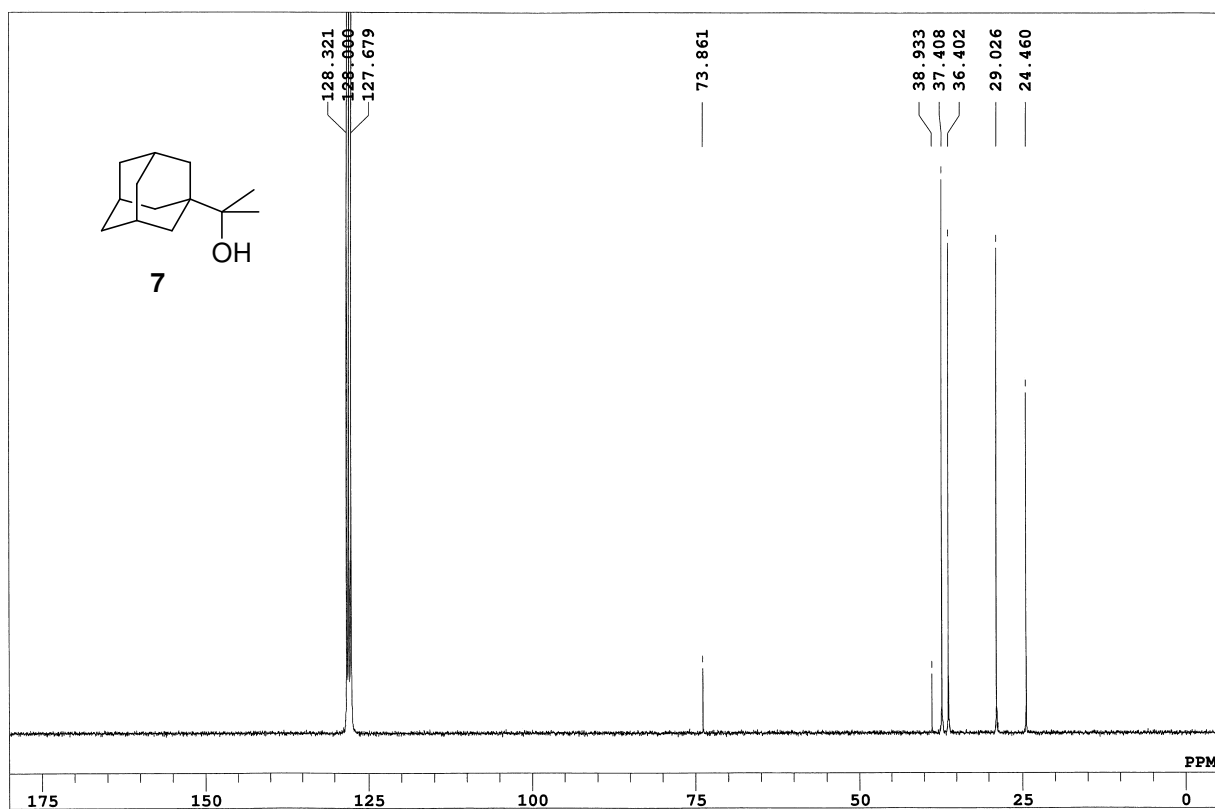


Figure S2. ¹³C NMR spectrum of 7 (75.5 MHz, C₆D₆).

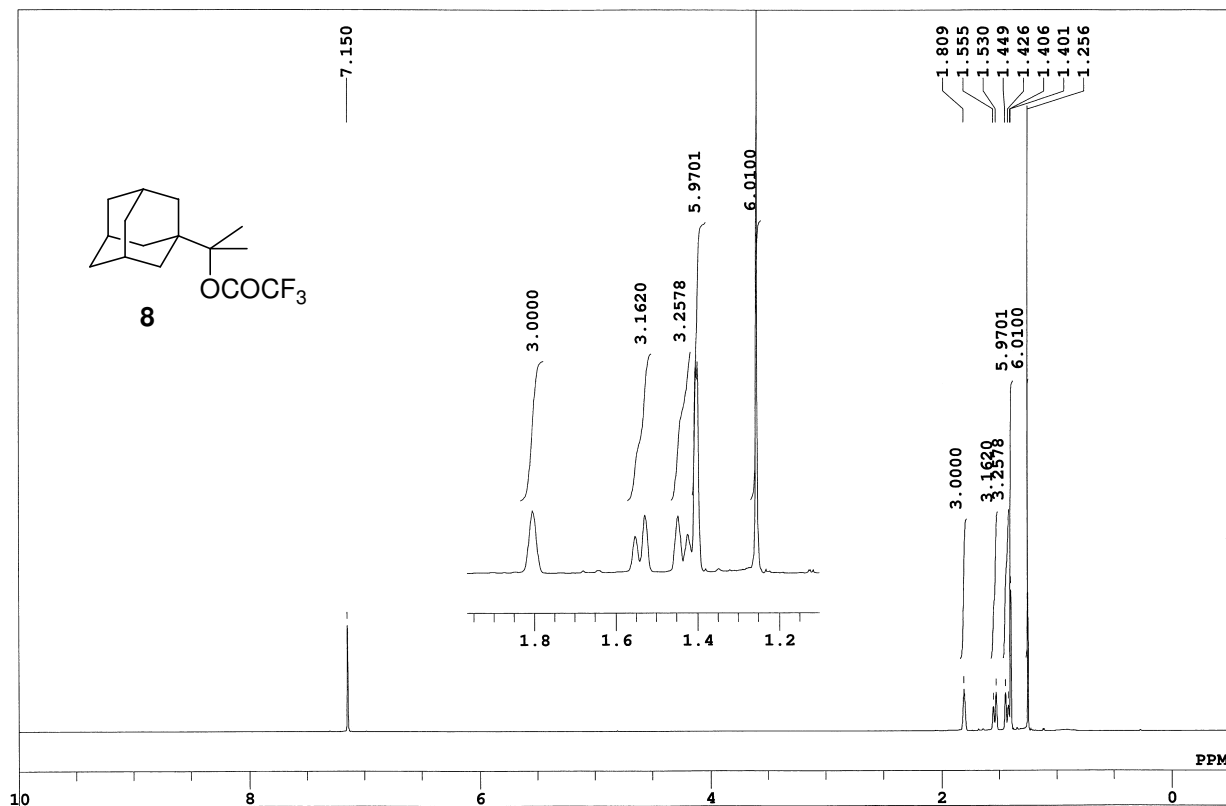


Figure S3. ¹H NMR spectrum of **8** (500 MHz, C₆D₆).

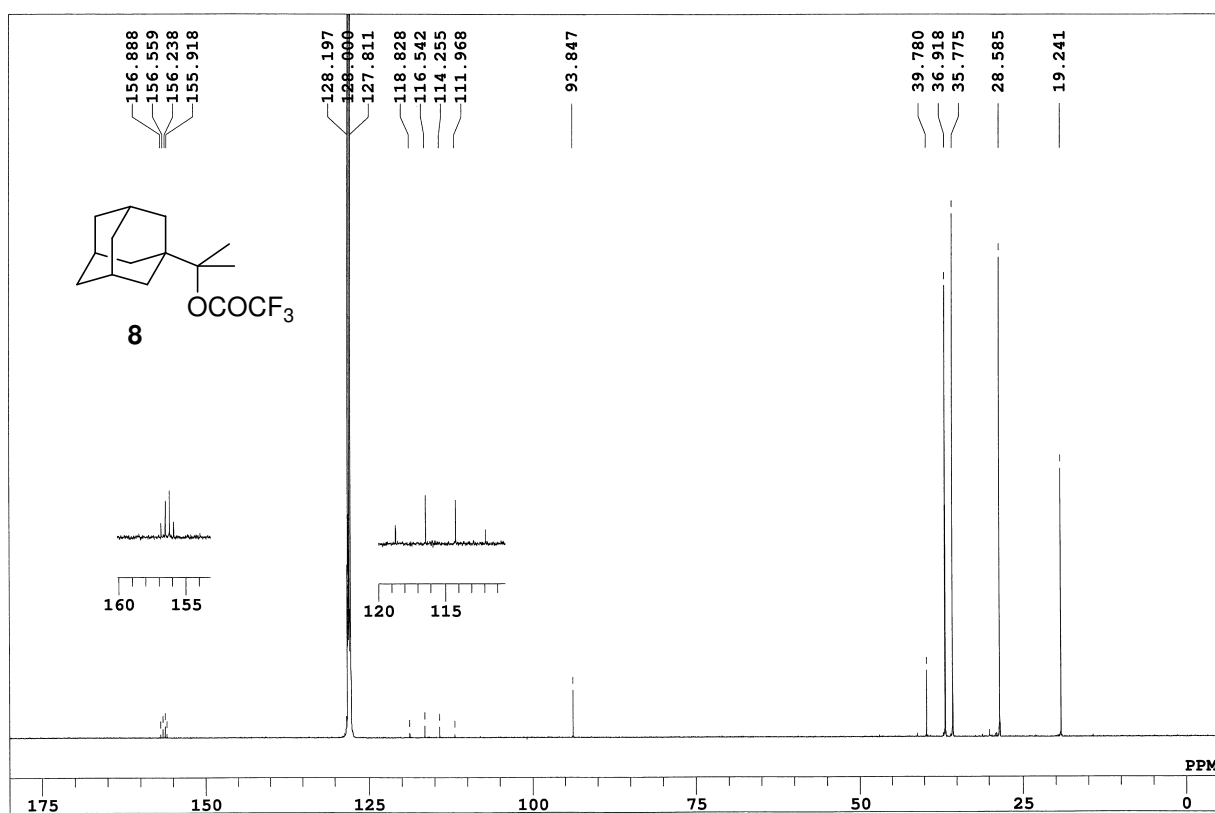


Figure S4. ¹³C NMR spectrum of **8** (125 MHz, C₆D₆).

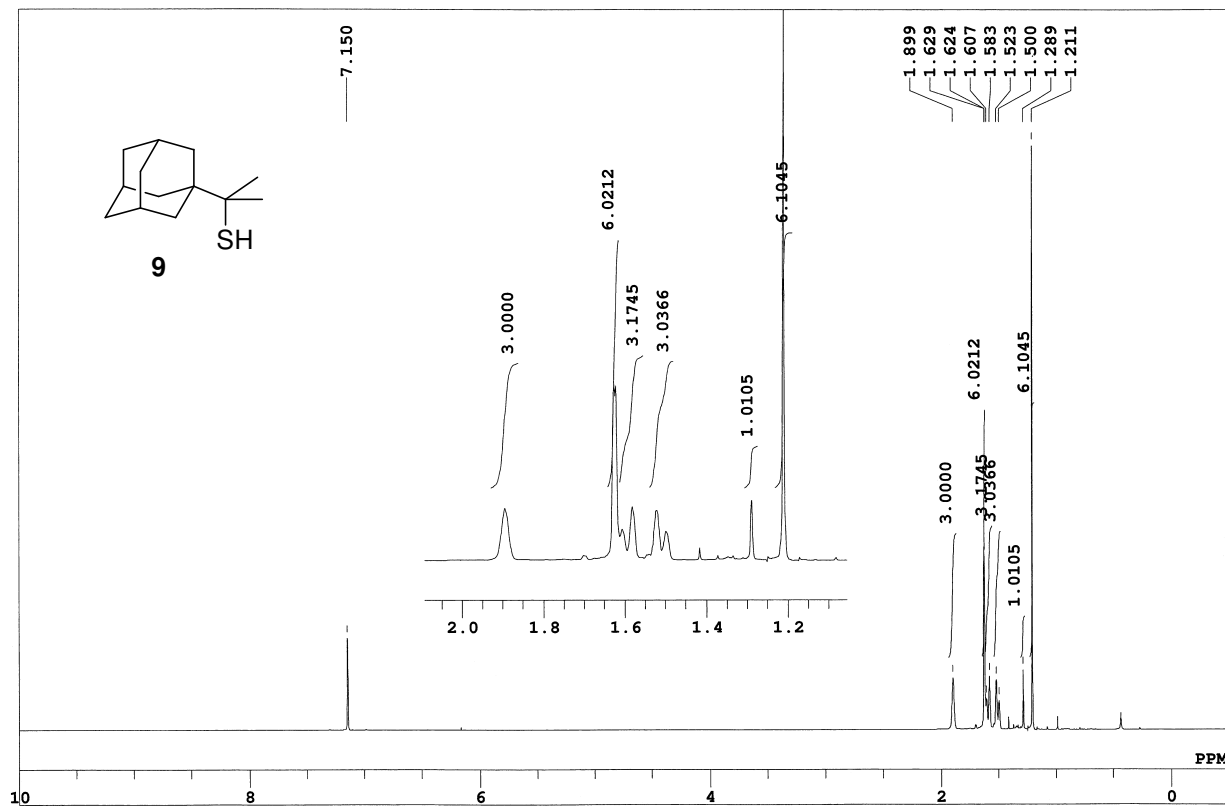


Figure S5. ^1H NMR spectrum of **9** (500 MHz, C_6D_6).

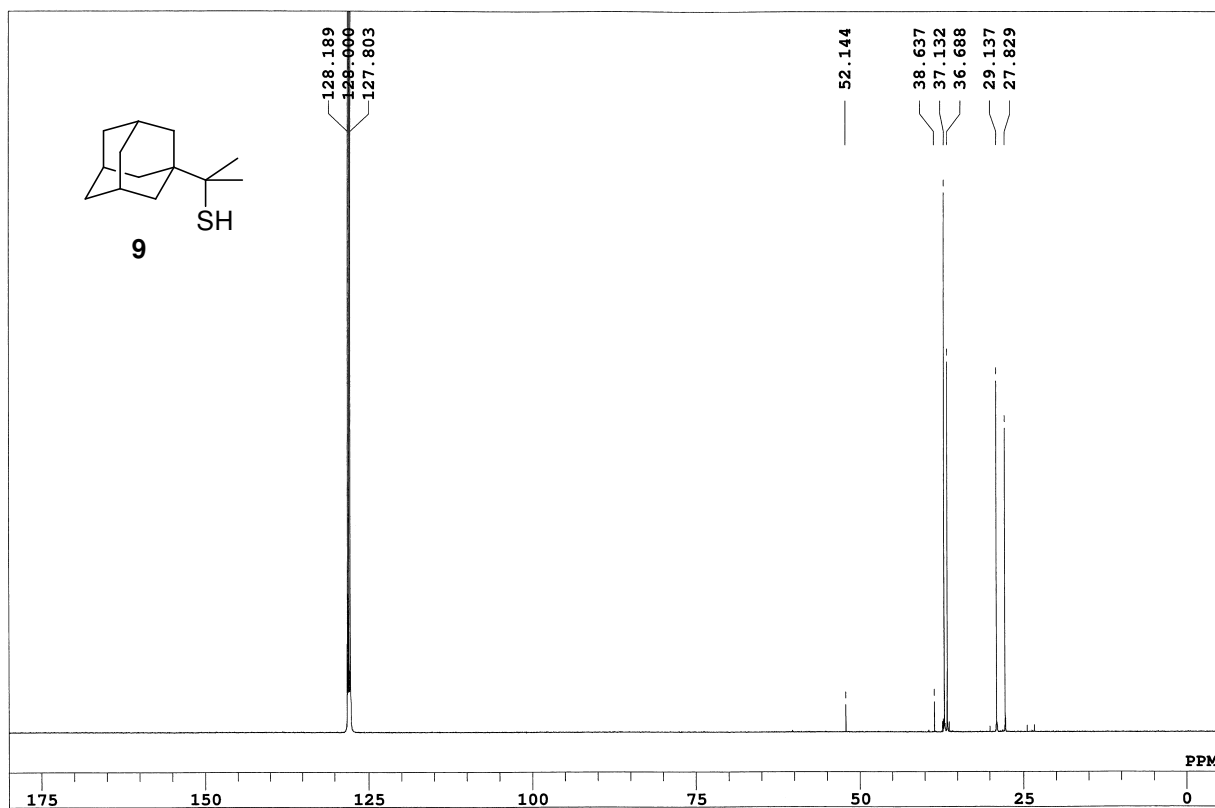


Figure S6. ^{13}C NMR spectrum of **9** (125 MHz, C_6D_6).

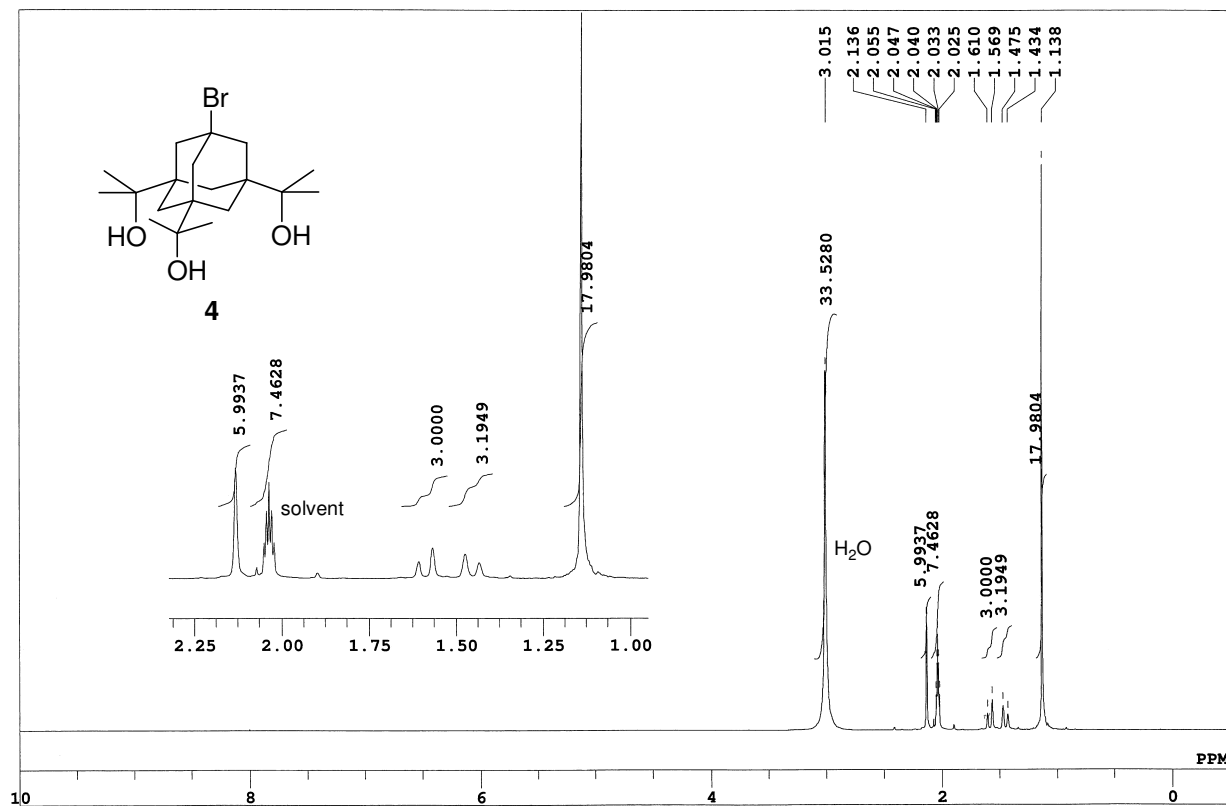


Figure S7. ^1H NMR spectrum of **4** (300 MHz, acetone- d_6).

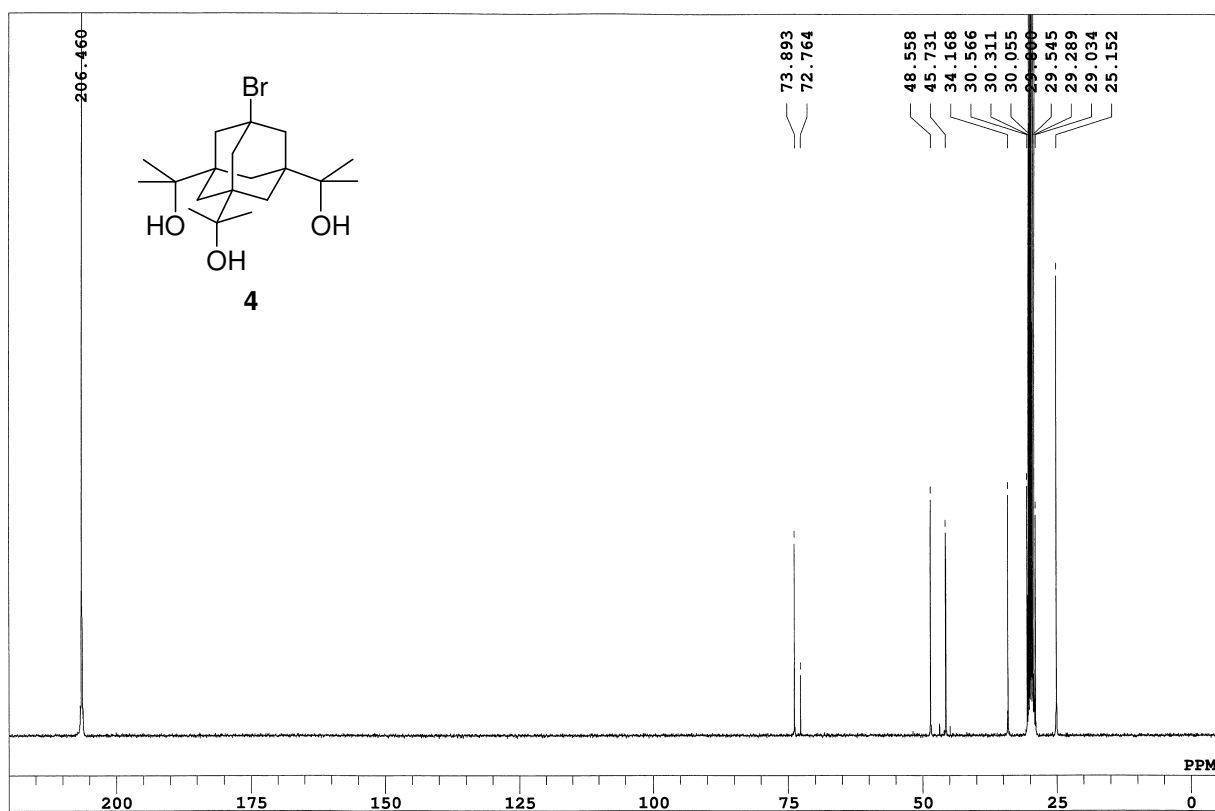


Figure S8. ^{13}C NMR spectrum of **4** (75.5 MHz, acetone- d_6).

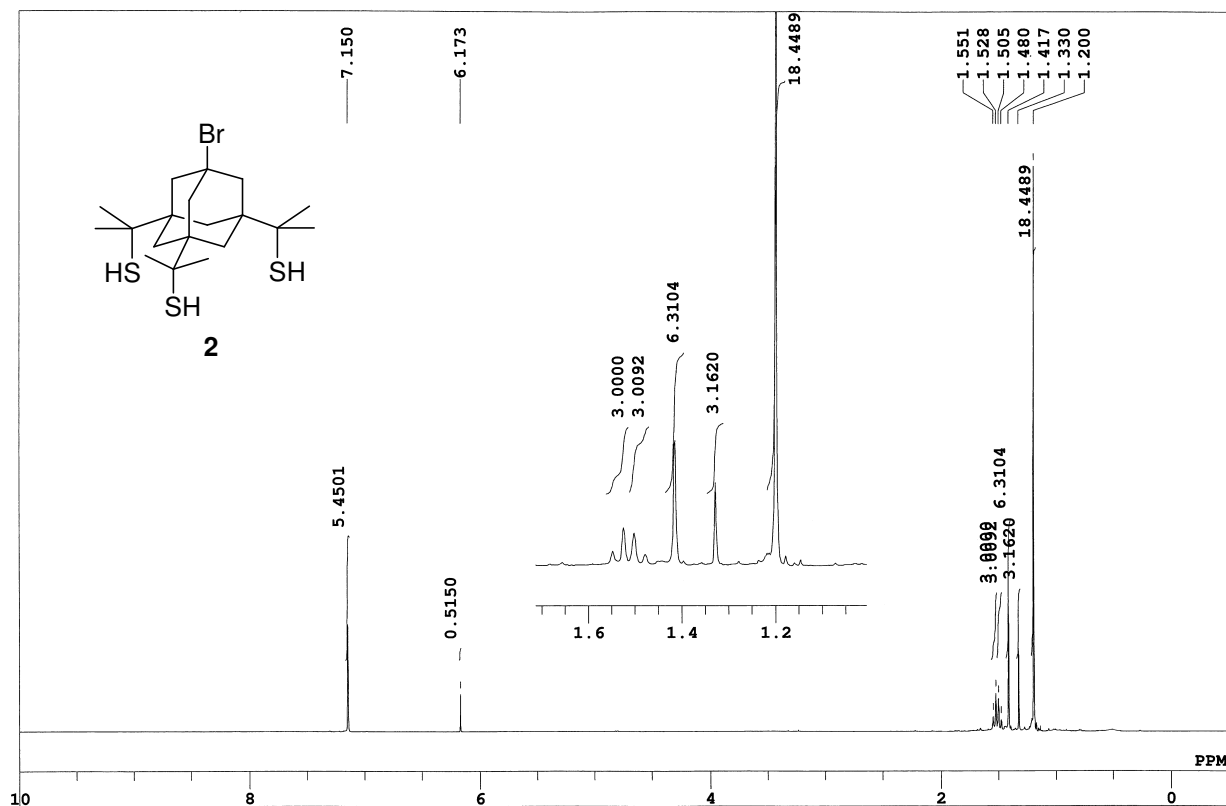


Figure S9. ^1H NMR spectrum of **2** (500 MHz, C_6D_6).

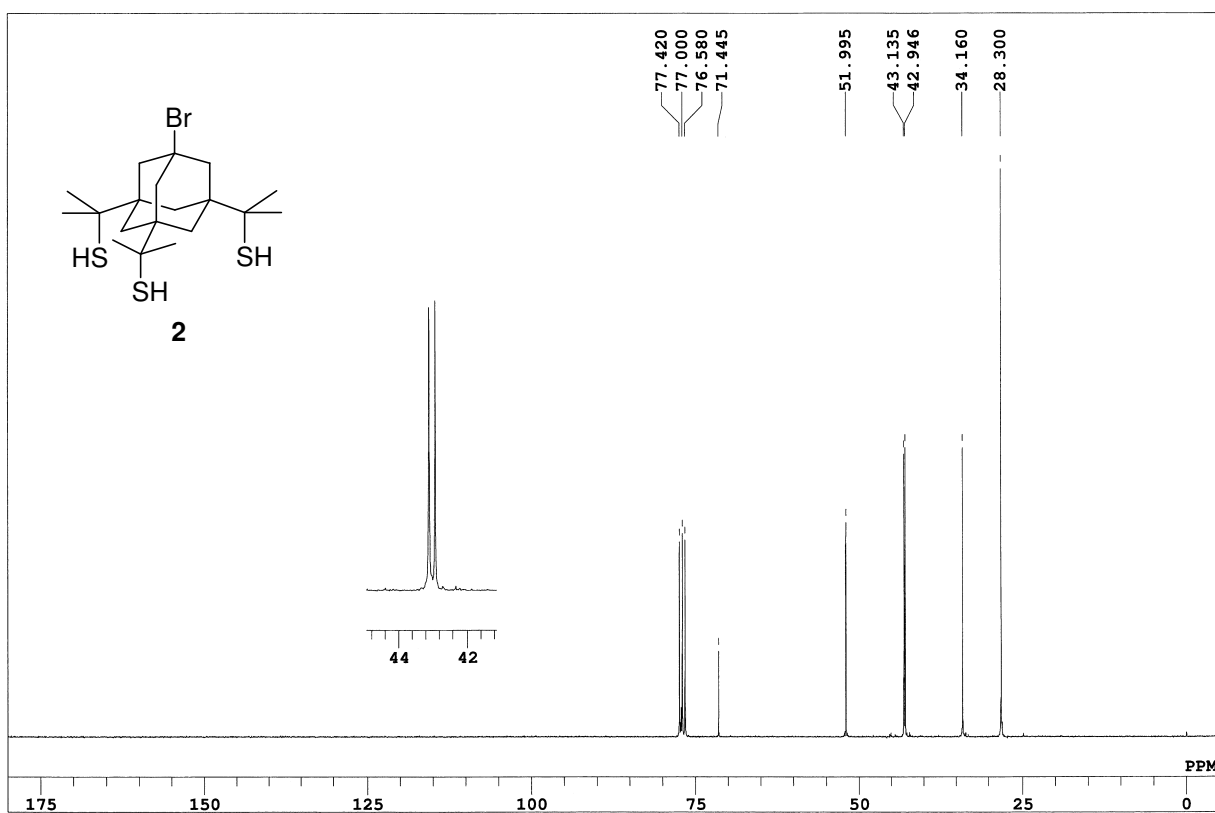


Figure S10. ^{13}C NMR spectrum of **2** (75.5 MHz, CDCl_3).

Table S1. Results of DFT calculations for Ad(CH₂S)₃ on the Au₁₉, Au₂₇, and Au₃₇ monolayers^a

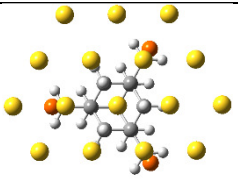
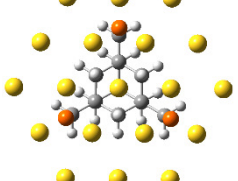
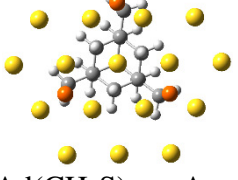
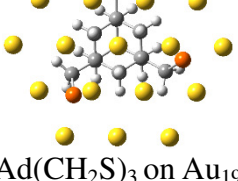
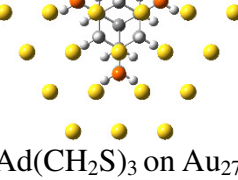
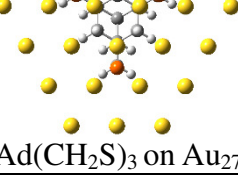
Optimized Structure	Symmetry	Nl ^b	<i>E</i> , hartree	<i>ZPE</i> , hartree	<i>G</i> , hartree	ΔE , hartree ^c	ΔE_{ads} , kcal/mol ^d
	C _{3v}	4	-4266.9980417	0.300691	-4266.750721	-1692.7326024	24.4
Ad(CH ₂ S) ₃ on Au ₁₉							
	C _{3v}	1	-4266.9973090	0.300753	-4266.757075	-1692.7318697	24.9
Ad(CH ₂ S) ₃ on Au ₁₉							
	C ₃	2	-4266.9976442	0.300762	-4266.753389	-1692.7322049	24.7
Ad(CH ₂ S) ₃ on Au ₁₉							
	C ₃	2	-4267.0014667	0.300951	-4266.756297	-1692.7360274	22.3
Ad(CH ₂ S) ₃ on Au ₁₉							
	C _{3v}	0	-5350.9763973	0.301249	-5350.734258	-1692.7485788	14.4
Ad(CH ₂ S) ₃ on Au ₂₇							
	C ₃	0	-5350.9763764	0.301151	-5350.734472	-1692.7485579	14.4
Ad(CH ₂ S) ₃ on Au ₂₇							

Table S1. Continued

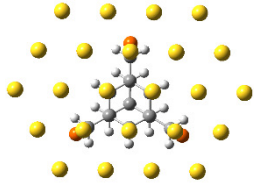
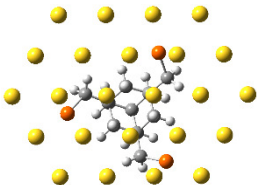
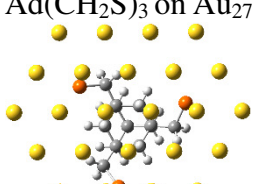
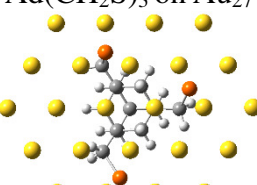
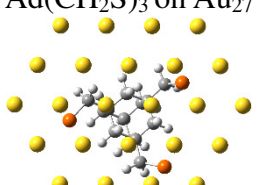
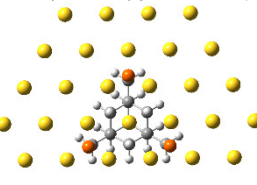
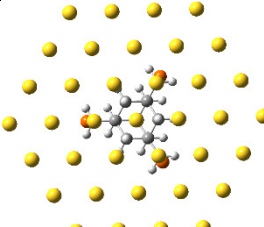
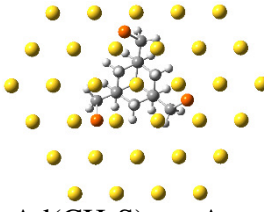
Optimized Structure	Symmetry	NI ^b	E, hartree	ZPE, hartree	G, hartree	ΔE , hartree ^c	ΔE_{ads} , kcal/mol ^d
 Ad(CH ₂ S) ₃ on Au ₂₇	C _{3v}	4	-5350.9593510	0.300178	-5350.712997	-1692.7315325	25.1
 Ad(CH ₂ S) ₃ on Au ₂₇	C ₃	0	-5350.9993497	0.301954	-5350.755071	-1692.7715312	(0)
 Ad(CH ₂ S) ₃ on Au ₂₇	C ₃	0	-5350.9909429	0.301555	-5350.747930	-1692.7631244	5.3
 Ad(CH ₂ S) ₃ on Au ₂₇	C ₁	0	-5350.9886346	0.301353	-5350.746771	-1692.7608161	6.7
 Ad(CH ₂ S) ₃ on Au ₂₇	C ₁	0	-5350.9950654	0.301565	-5350.752412	-1692.7672469	2.7
 Ad(CH ₂ S) ₃ on Au ₂₇	C _{3v}	2	-6705.9442826	0.300534	-6705.701918	-1692.7482327	14.6
 Ad(CH ₂ S) ₃ on Au ₃₇							

Table S1. Continued

Optimized Structure	Symmetry	NI ^b	E, hartree	ZPE, hartree	G, hartree	ΔE , hartree ^c	ΔE_{ads} , kcal/mol ^d
 Ad(CH ₂ S) ₃ on Au ₃₇	C _{3v}	5	-6705.9291976	0.300072	-6705.682324	-1692.7331477	24.1
 Ad(CH ₂ S) ₃ on Au ₃₇	C ₃	2	-6705.9370070	0.300870	-6705.695104	-1692.7409571	19.2

^a UB3LYP/3-21G for C, H, and S atoms and LanL2MB for Au atom. The Au-Au distance was fixed at 2.88 Å during structural optimization.

^b Number of imaginary frequencies.

^c $\Delta E = E_{\text{ads}} + E[\text{Ad}(\text{CH}_2\text{S})_3] = E[\text{Ad}(\text{CH}_2\text{S})_3/\text{Au layer}] - E(\text{Au layer})$. The values of $E(\text{Au layer})$ are summarized in Table S3.

^d Values are relative to the smallest E_{ads} .

^e In the lowest-energy structure **X1**, the center of the adamantane fragment lies above the center of three Au atoms. The Ad(CH₂S)₃ unit adopts an axially twisted conformation. Distances between the S atom and its neighboring four Au atoms were 2.70, 3.00, 3.40, and 3.61 Å. The length of CH₂-S bonds was 1.92 Å, the bond angle C(1)-CH₂-S was 118°, and the dihedral angle C(7)-C(1)-CH₂-S was 118°.

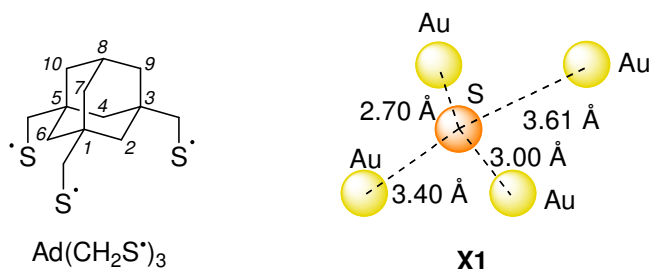
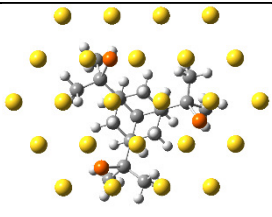
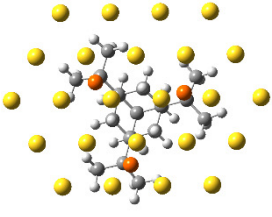



Table S2. Results of DFT calculations for Ad(CMe₂S)₃ on the Au₂₇ monolayer^a

Optimized Structure	Symmetry	NI ^b	<i>E</i> , hartree	<i>ZPE</i> , hartree	<i>G</i> , hartree	ΔE , hartree ^c	ΔE_{ads} , kcal/mol ^d
	C ₃	0	-5585.5815802	0.473559	-5585.171088	-1927.3537617	1.3
Ad(CMe ₂ S) ₃ on Au ₂₇							
	C ₃	0	-5585.5836796	0.472138	-5585.177644	-1927.3558611	(0)
 X2^e							
Ad(CMe ₂ S) ₃ on Au ₂₇							

^a UB3LYP/3-21G for C, H, and S atoms and LanL2MB for Au atom. The Au-Au distance was fixed at 2.88 Å during structural optimization.

^b Number of imaginary frequencies.

^c $\Delta E = E_{\text{ads}} + E[\text{Ad}(\text{CMe}_2\text{S})_3] = E[\text{Ad}(\text{CMe}_2\text{S})_3/\text{Au layer}] - E(\text{Au layer})$. The values of $E(\text{Au layer})$ are summarized in Table S3.

^d Values are relative to the smallest ΔE_{ads} .

^e In the lowest-energy structure **X2**, the distances between the S atom and its neighboring four Au atoms were 2.77, 2.90, 3.26, and 3.71 Å. Two of the distances were slightly longer than that in the Ad(CH₂S)₃ system (**X1**), and the other two were slightly shorter. The length of CMe₂-S bonds was 1.96 Å, the bond angle C(1)-CMe₂-S was 108°, and the dihedral angle C(7)-C(1)-CMe₂-S was 166°. The tripod Ad(CMe₂S)₃ stood almost upright in a slightly axially twisted form, due to the steric effect of the Me groups.

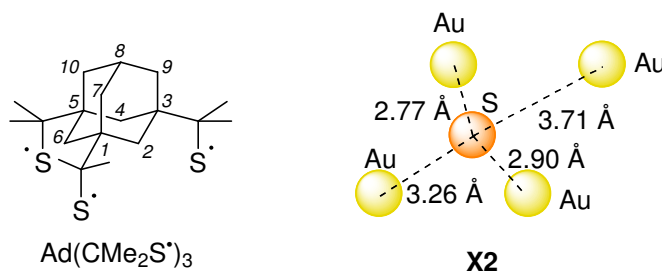
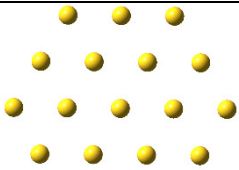
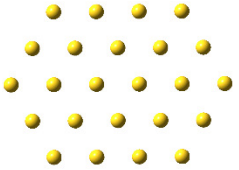
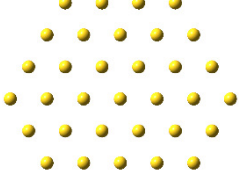


Table S3. Energies of the Au₁₉, Au₂₇, and Au₃₇ monolayers by single-point energy calculations by the DFT method^a

Structure	Symmetry	<i>E</i> , hartree
	D _{6h}	-2574.2654393
Au ₁₉		
	D _{3h}	-3658.2278185
Au ₂₇		
	D _{6h}	-5013.1960499
Au ₃₇		

^a UB3LYP/LanL2MB for Au atom. The Au-Au distance was fixed at 2.88 Å.

Table S4. Energies of infinite Au monolayers adsorbed with Ad(CH₂S)₃ by single-point energy calculations by the DFT method under periodic boundary conditions (PBC)^a

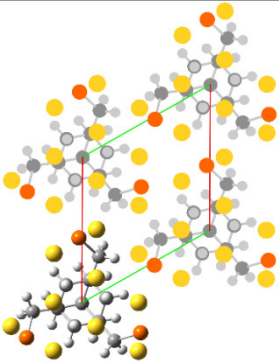
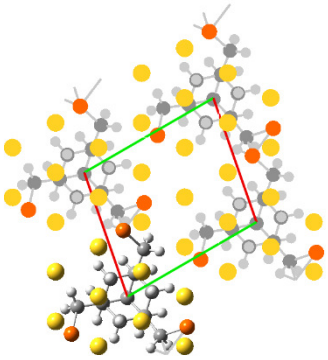
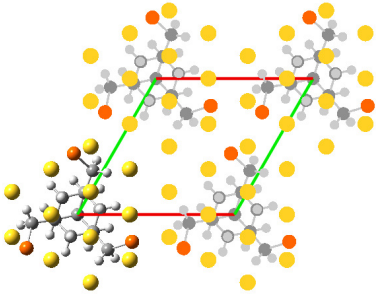
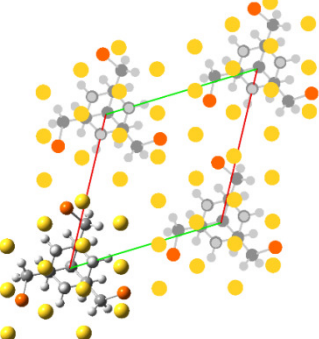
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	<i>E</i> , hartree	<i>E</i> _{ads} , kcal/mol ^b	
				per unit cell	per Au atom
 Ad(CH ₂ S) ₃ (3 × 3)R60°	8.64	9	-2911.0949984	-38.5	-4.28
 Ad(CH ₂ S) ₃ with a (3 × √7) unit cell	7.62, 8.64, and 10.38	9	-2910.5063241	330.9	36.76
 Ad(CH ₂ S) ₃ (2√3 × 2√3)R30°	9.98	12	-3317.3476154	-39.4	-3.28
 Ad(CH ₂ S) ₃ (√13 × √13)R46.1°	10.38	13	-3452.7653224	-44.8	-3.45

Table S4. Continued

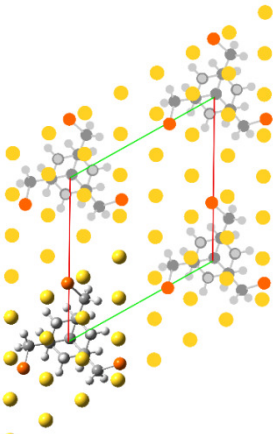
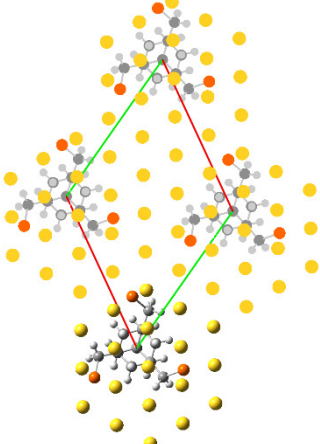
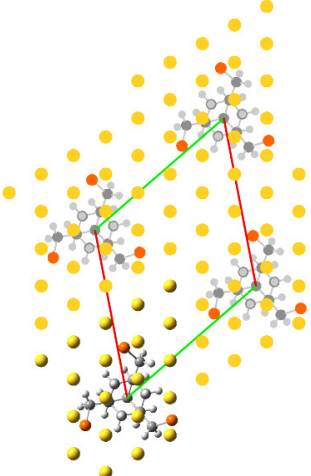
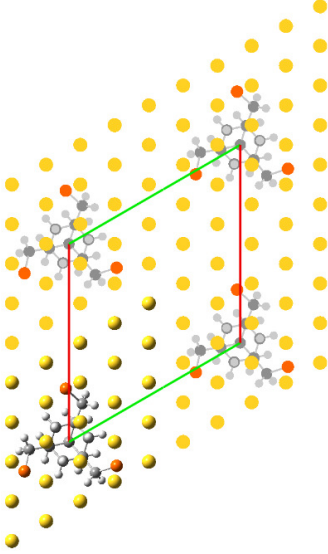
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	E , hartree	E_{ads} , kcal/mol ^b	
				per unit cell	per Au atom
 Ad(CH ₂ S) ₃ (4 × 4)R60°	11.52	16	-3859.0056044	-39.5	-2.47
 Ad(CH ₂ S) ₃ (2√7 × 2√7)R19.1°	12.55	19	-4265.2532868	-44.6	-2.35
 Ad(CH ₂ S) ₃ (√21 × √21)R10.9°	13.20	21	-4536.0793139	-42.7	-2.03

Table S4. Continued

Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	E , hartree	E_{ads} , kcal/mol ^b	
				per unit cell	per Au atom
	14.40	25	-5077.7354420	-41.2	-1.65
Ad(CH ₂ S) ₃ (5 × 5)R60°					

^a UBLYP/3-21G for C, H, and S atoms and LanL2MB for Au atom. The Au-Au distance was fixed at 2.88 Å. The geometry of Ad(CH₂S)₃ in **X1** (Table S1) was used.

^b $E_{\text{ads}} = E[\text{Ad}(\text{CH}_2\text{S})_3/\text{Au layer}] - E[\text{Ad}(\text{CH}_2\text{S})_3] - E(\text{Au layer})$. The values of $E(\text{Au layer})$ and $E[\text{Ad}(\text{CH}_2\text{S})_3]$ are summarized in Tables S6 and S7, respectively.

Table S5. Energies of infinite Au monolayers adsorbed with Ad(CMe₂S)₃ by single-point energy calculations by the DFT method under periodic boundary conditions (PBC)^a

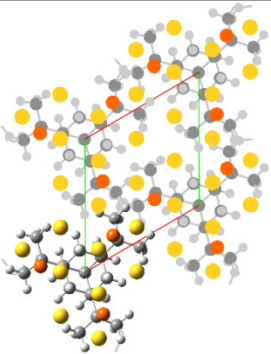
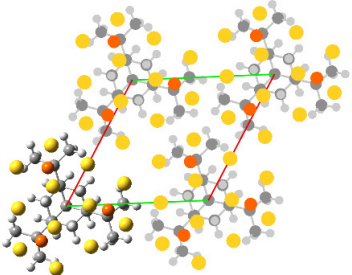
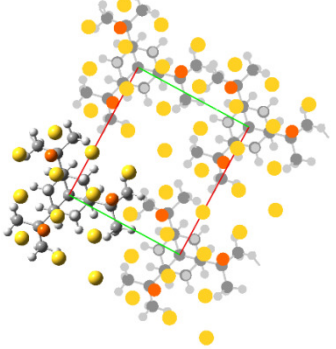
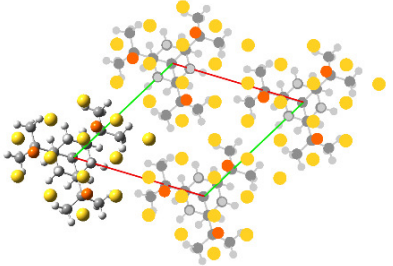
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	<i>E</i> , hartree	<i>E</i> _{ads} , kcal/mol ^b	
				per unit cell	per Au atom
 Ad(CMe ₂ S) ₃ (3 × 3)R60°	8.64	9	-3142.6967958	1747.8	194.20
 Ad(CMe ₂ S) ₃ (2√3 × 2√3)R30°	9.98	12	-3551.6618885	44.9	3.74
 Ad(CMe ₂ S) ₃ with a (2√3 × 3) unit cell	8.64, 9.98, and 13.20	12	-3550.7546656	614.2	51.18
 Ad(CMe ₂ S) ₃ (√13 × √13)R46.1°	10.38	13	-3687.1847163	-26.5	-2.04

Table S5. Continued

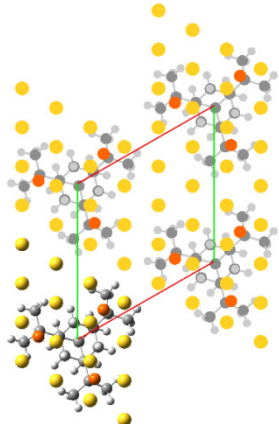
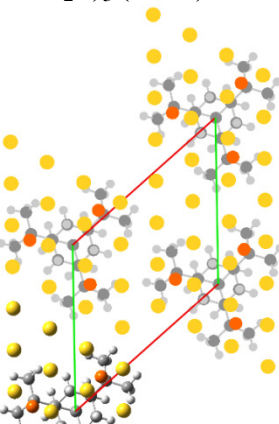
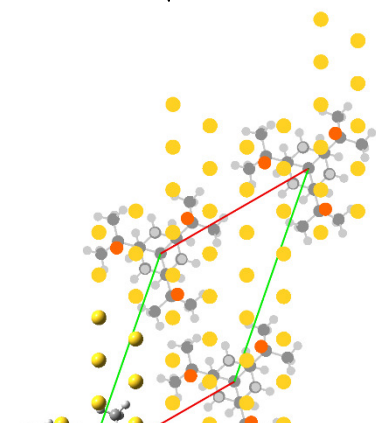
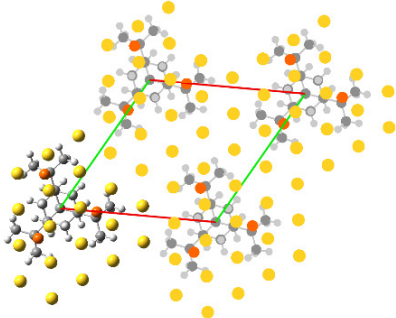
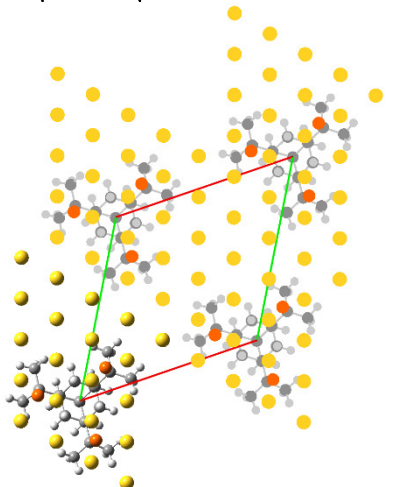
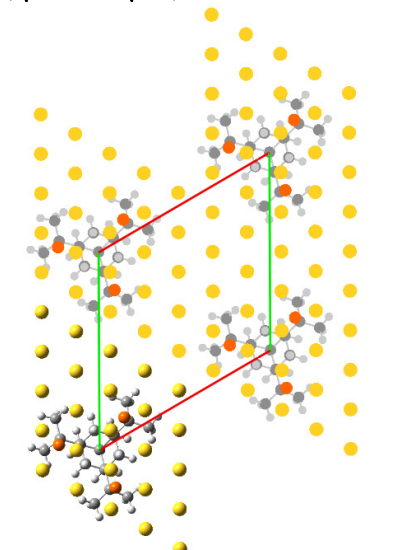
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	E , hartree	E_{ads} , kcal/mol ^b	
				per unit cell	per Au atom
 Ad(CMe ₂ S) ₃ (4 × 4)R60°	11.52	16	-4093.4320290	-25.6	-1.60
 Ad(CMe ₂ S) ₃ with a (4 × √13) unit cell	10.38, 11.52, and 13.20	16	-4093.4311871	-25.1	-1.57
 Ad(CMe ₂ S) ₃ with a (4 × 2√3) unit cell	9.98, 11.52, and 15.24	16	-4093.4027449	-7.3	-0.45

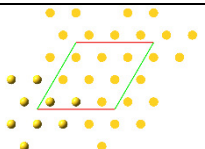
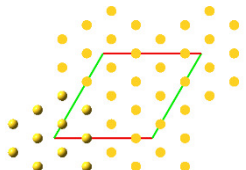
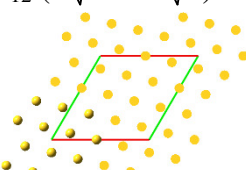
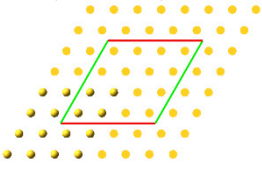
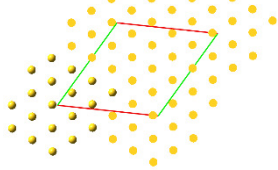
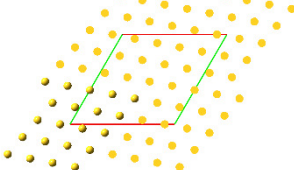
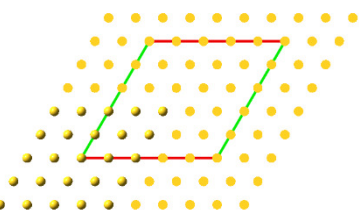
Table S5. Continued

Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	E , hartree	E_{ads} , kcal/mol ^b	
				per unit cell	per Au atom
 Ad(CMe ₂ S) ₃ (2√7 × 2√7)R19.1°	12.55	19	-4499.6755203	-28.1	-1.48
 Ad(CMe ₂ S) ₃ (√21 × √21)R10.9°	13.20	25	-4770.5044626	-28.0	-1.33
 Ad(CMe ₂ S) ₃ (5 × 5)R60°	14.40	25	-5312.1623492	-27.6	-1.10

^a UBLYP/3-21G for C, H, and S atoms and LanL2MB for Au atom. The Au-Au distance was fixed at 2.88 Å. The geometry of Ad(CMe₂S)₃ in **X2** (Table S2) was used.

^b $E_{\text{ads}} = E[\text{Ad}(\text{CMe}_2\text{S})_3/\text{Au layer}] - E[\text{Ad}(\text{CMe}_2\text{S})_3] - E(\text{Au layer})$. Values of $E(\text{Au layer})$ and $E[\text{Ad}(\text{CMe}_2\text{S})_3]$ are summarized in Tables S6 and S7, respectively.

Table S6. Energies of unit cells of infinite Au monolayer by single-point energy calculations by the DFT method under periodic boundary conditions (PBC)^a

Structure	E , hartree
 Au ₉ (3 × 3)R60°	-1218.7219777
 Au ₁₂ (2√3 × 2√3)R30°	-1624.9732912
 Au ₁₃ (√13 × √13)R46.1°	-1760.3823117
 Au ₁₆ (4 × 4)R60°	-2166.6309828
 Au ₁₉ (2√7 × 2√7)R19.1°	-2572.8705455
 Au ₂₁ (√21 × √21)R10.9°	-2843.6996318
 Au ₂₅ (5 × 5)R60°	-3385.3581436

^a UBYLP/LanL2MB was used. The Au-Au distance was fixed at 2.88 Å.

Table S7. Energy of Ad(CX₂S)₃ (X = H or Me) by single-point energy calculations by the DFT method^a

Compound	Spin multiplicity	<i>E</i> , hartree	ΔE , kcal/mol ^b
Ad(CH ₂ S [·]) ₃	2	-1692.3115693	0.02
	4	-1692.3116050 ^c	(0)
Ad(CMe ₂ S [·]) ₃	2	-1926.7597718	0.3
	4	-1926.7601828 ^c	(0)

^a UBLYP/3-21G level. Geometry of Ad(CX₂S)₃ (X = H or Me) in **X1** or **X2** from Table S1 or S2 was used.

^b Values relative to that of the most stable spin state.

^c Values used for the evaluation of E_{ads} .