Supplementary Material

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

Toshikazu Kitagawa*[a] Shima Nakanishi,[a] Aya Mizuno,[a] Yohei Niwa,[a] Hiroki Tabata,[a] Katsuyuki Hirai,[b] and Takao Okazaki*[a]

[a] *Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu, Mie 514-8507, Japan*

[b] *Organization for the Promotion of Regional Innovation, Mie University, Tsu, Mie 514-8507, Japan*

Email: kitagawa@chem.mie-u.ac.jp

Table of Contents

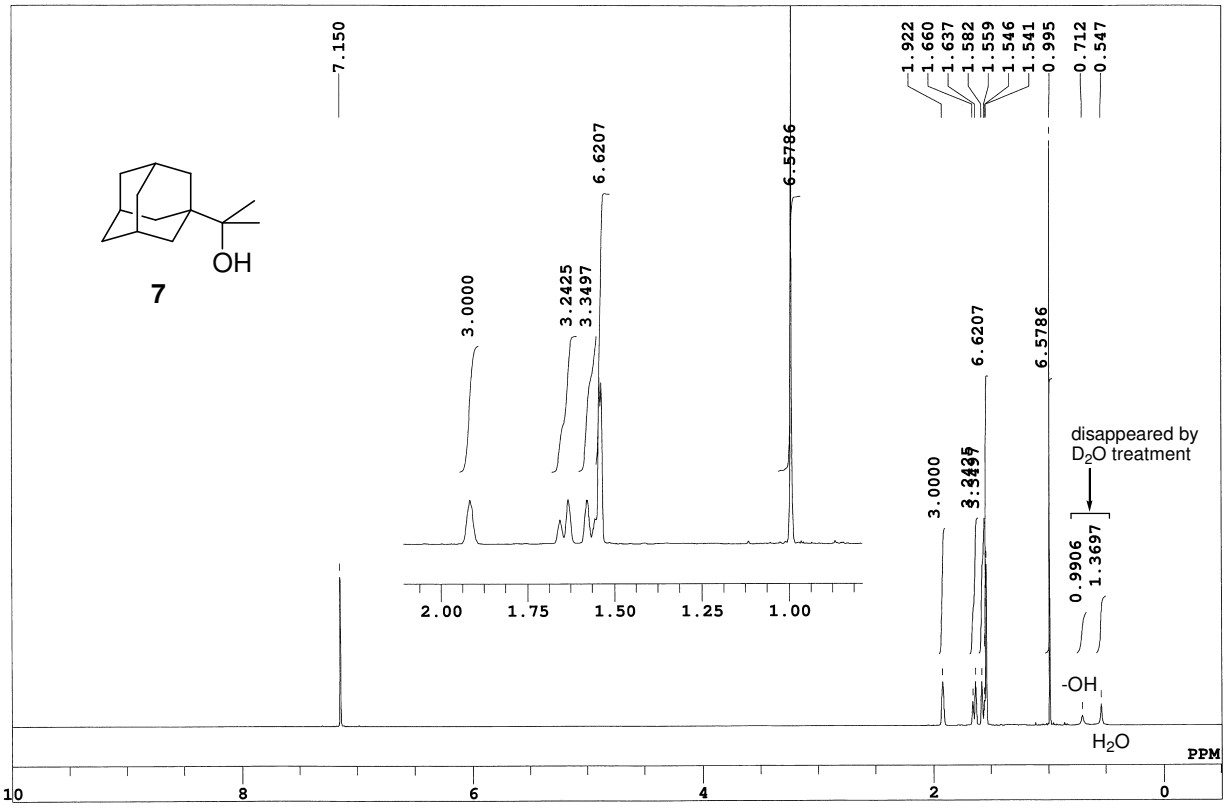


Figure S1. ^{1}H NMR spectrum of **7** (500 MHz, C_6D_6).

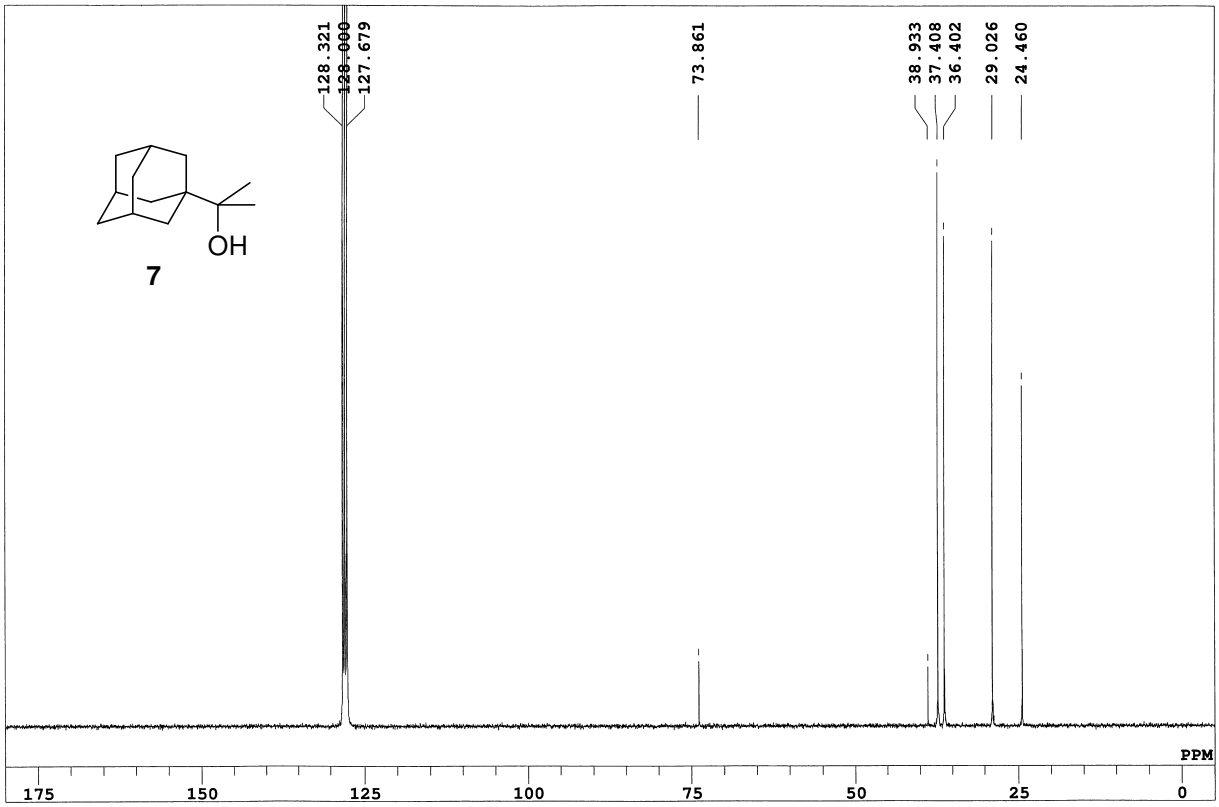


Figure S2. ^{13}C NMR spectrum of **7** (75.5 MHz, C_6D_6).

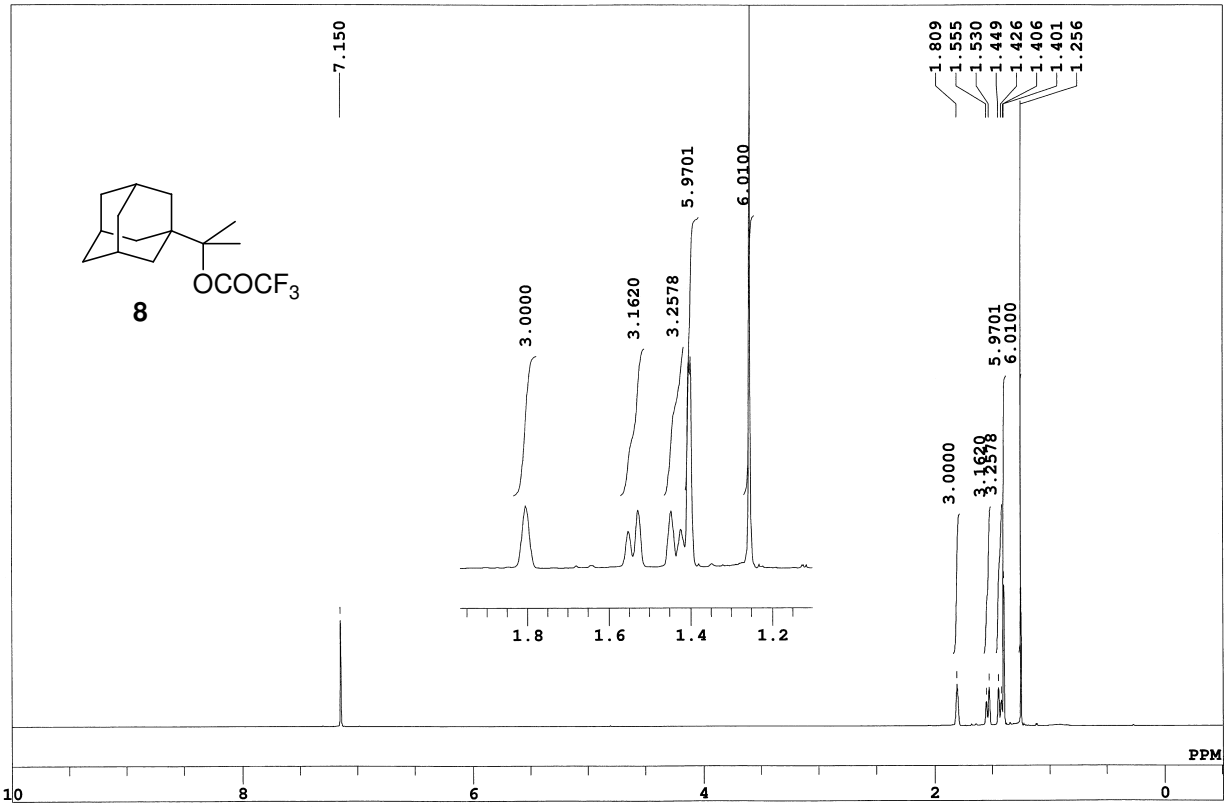


Figure S3. ^{1}H NMR spectrum of **8** (500 MHz, C_6D_6).

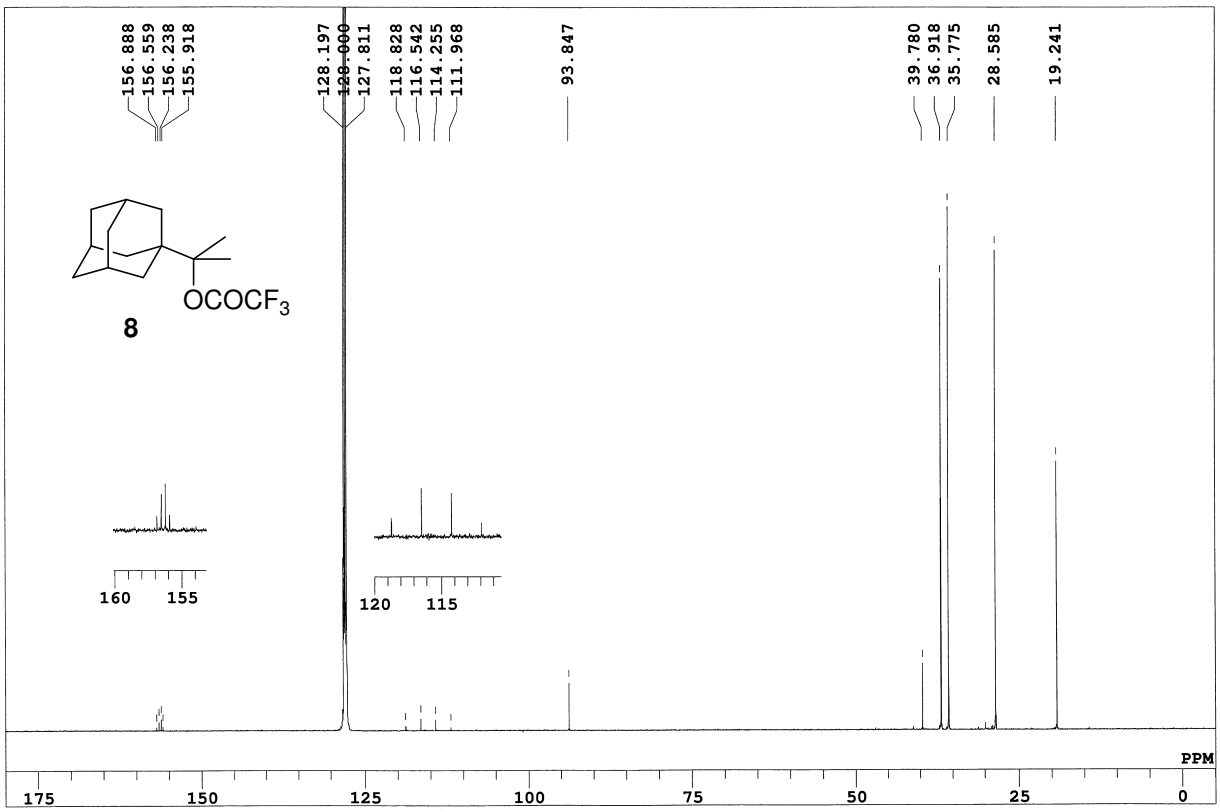


Figure S4. ^{13}C NMR spectrum of **8** (125 MHz, C_6D_6).

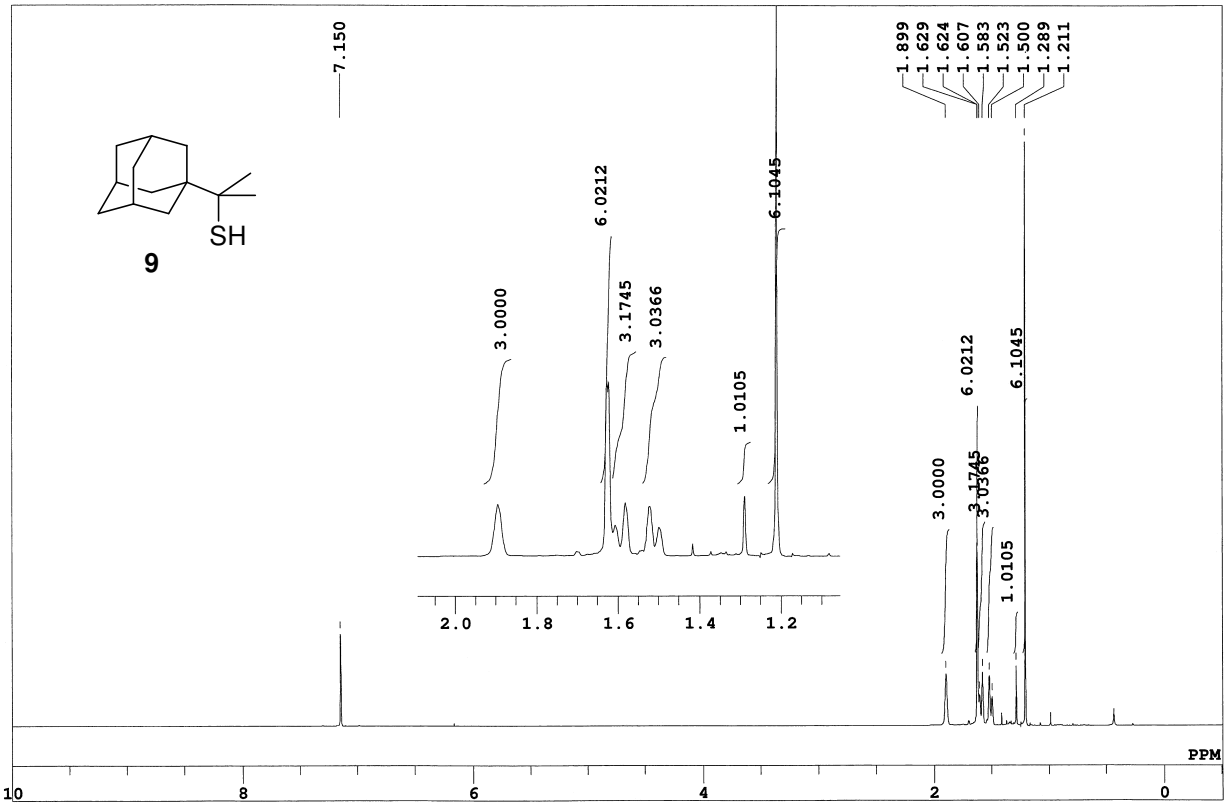


Figure S5. ^{1}H NMR spectrum of **9** (500 MHz, C_6D_6).

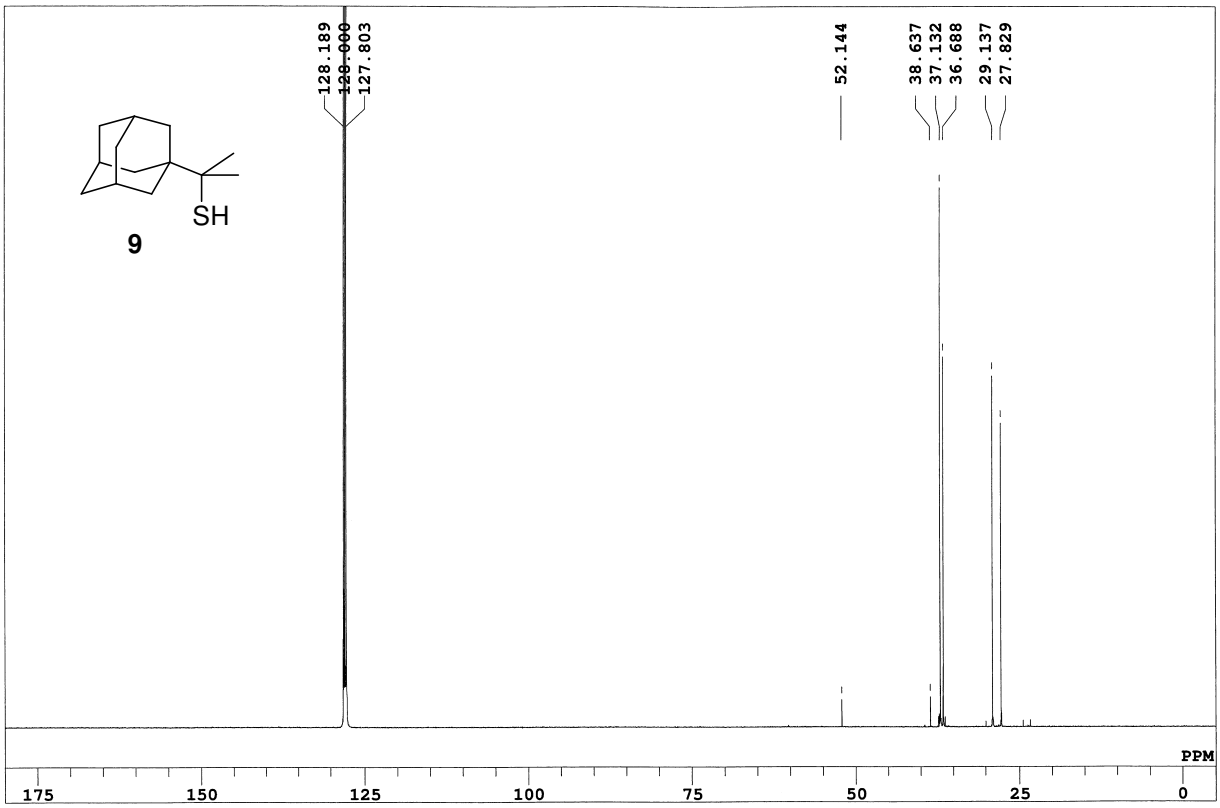


Figure S6. ^{13}C NMR spectrum of **9** (125 MHz, C_6D_6).

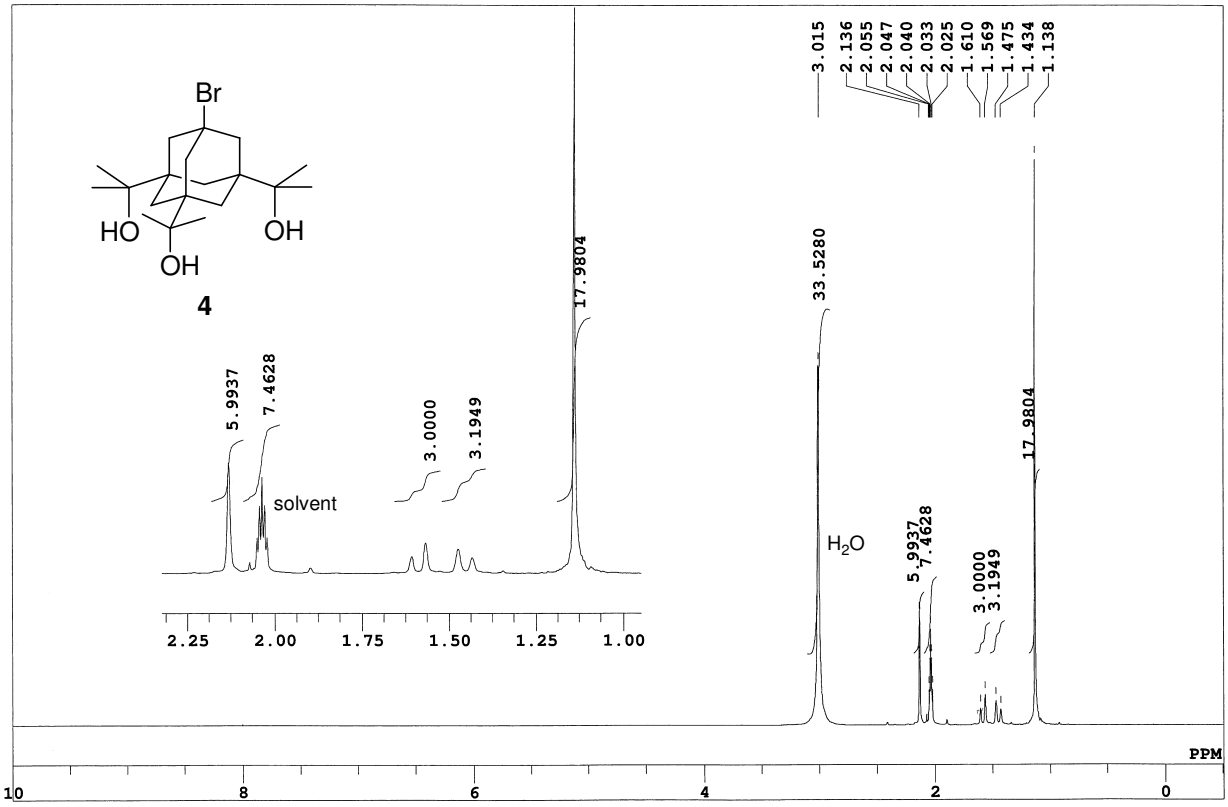


Figure S7. ^{1}H NMR spectrum of **4** (300 MHz, acetone-d_6).

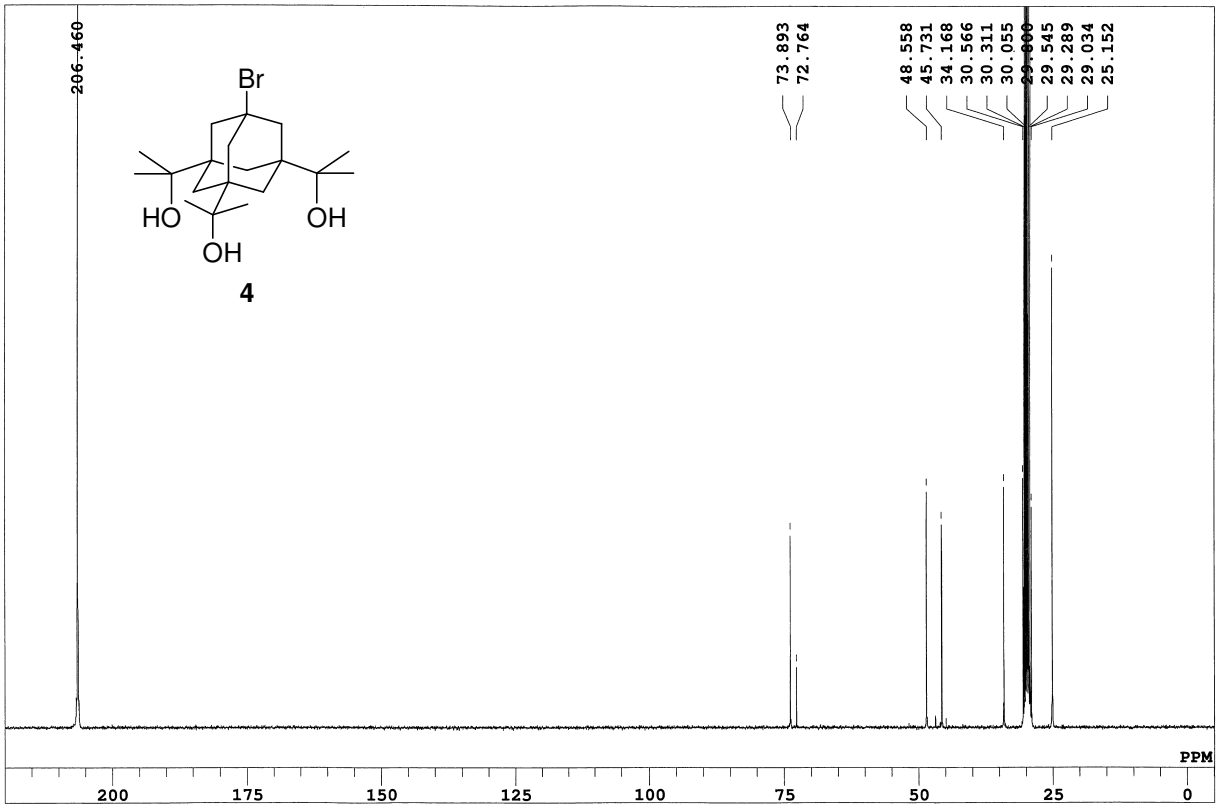


Figure S8. ^{13}C NMR spectrum of **4** (75.5 MHz, acetone-d_6).

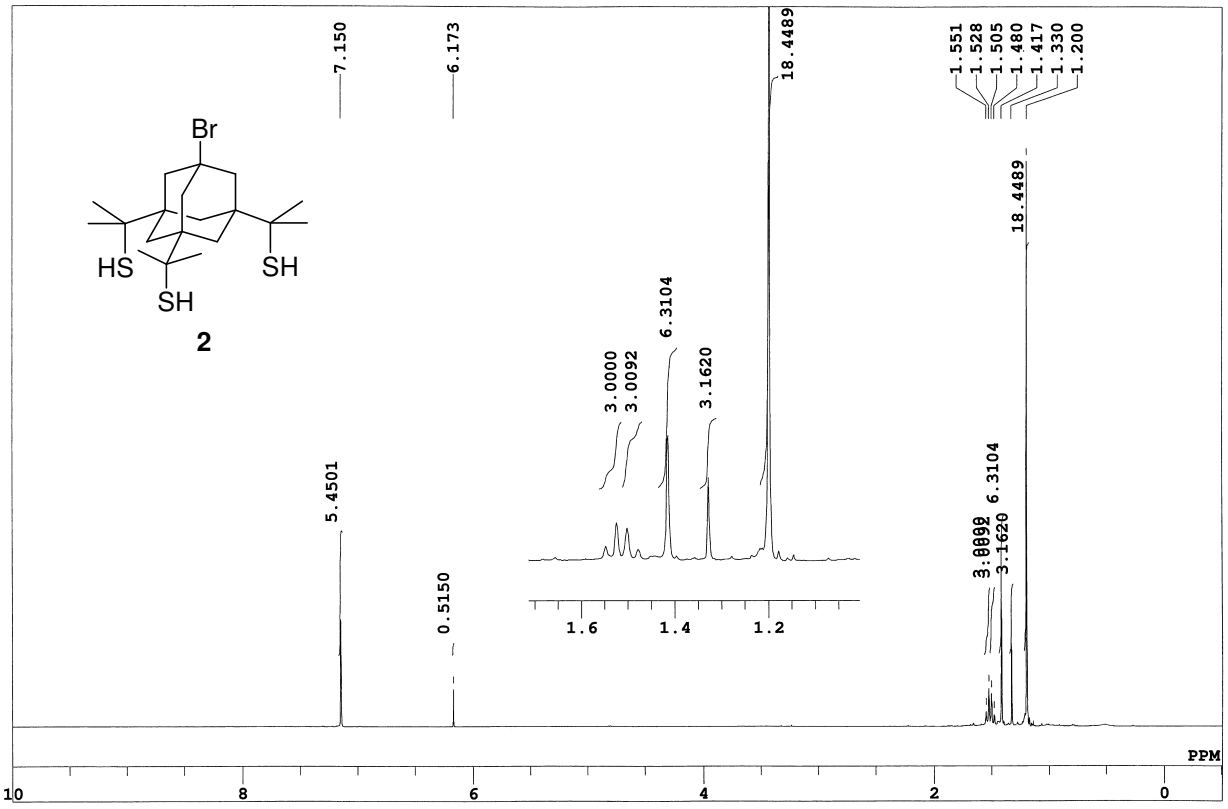


Figure S9. ^{1}H NMR spectrum of **2** (500 MHz, C_6D_6).

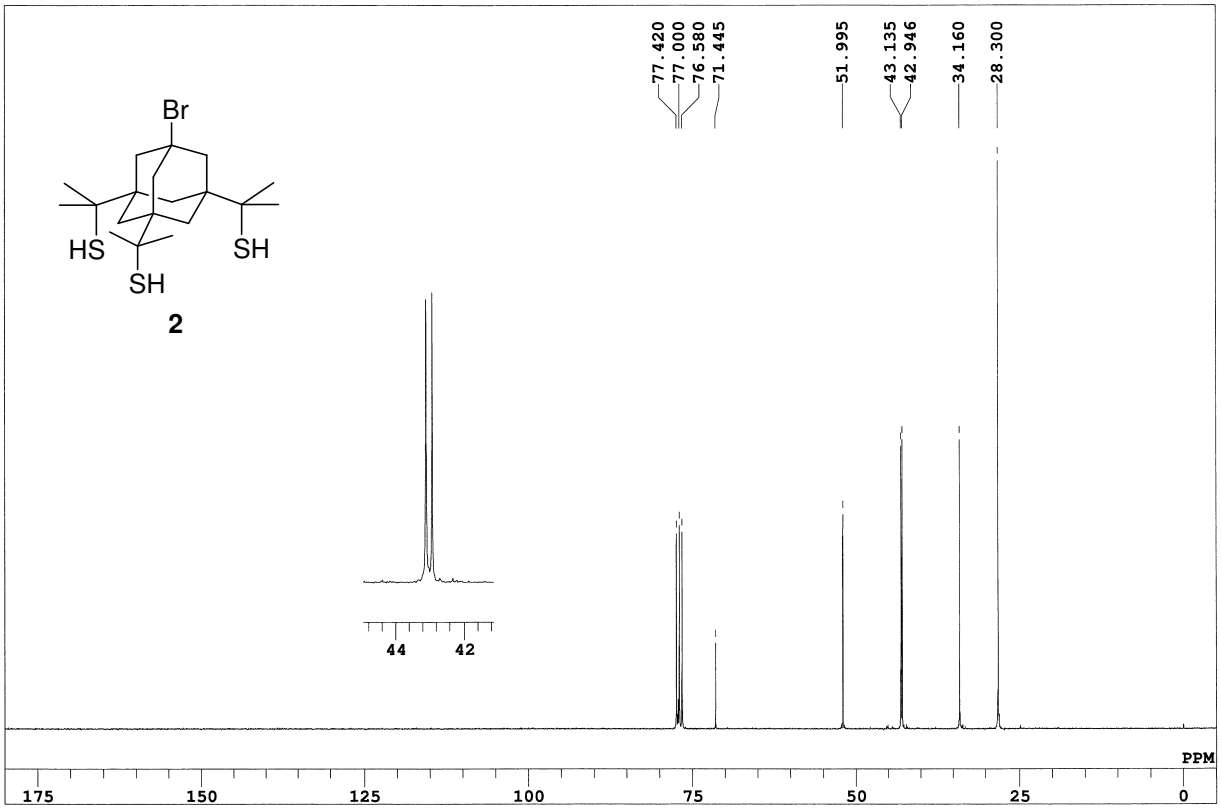


Figure S10. ^{13}C NMR spectrum of **2** (75.5 MHz, $CDCl_3$).

Table S1. Results of DFT calculations for $Ad(CH_2S)_3$ on the Au_{19}, Au_{27}, and Au_{37} monolayers[a]

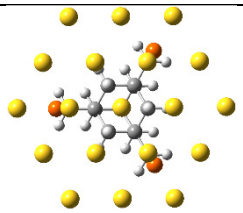
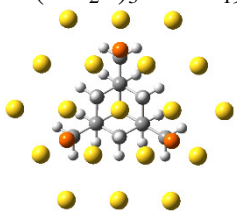
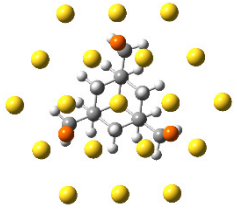
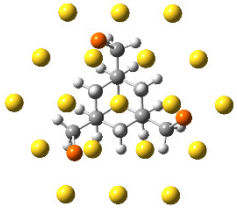
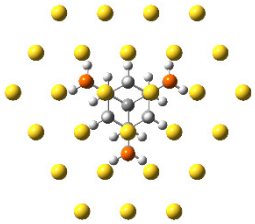
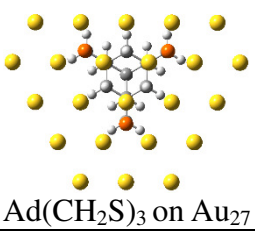
Optimized Structure	Sym-metry	NI[b]	*E*, hartree	*ZPE*, hartree	*G*, hartree	Δ*E*, hartree[c]	ΔE_{ads}, kcal/mol[d]
 $Ad(CH_2S)_3$ on Au_{19}	C_{3v}	4	-4266.9980417	0.300691	-4266.750721	-1692.7326024	24.4
 $Ad(CH_2S)_3$ on Au_{19}	C_{3v}	1	-4266.9973090	0.300753	-4266.757075	-1692.7318697	24.9
 $Ad(CH_2S)_3$ on Au_{19}	C_3	2	-4266.9976442	0.300762	-4266.753389	-1692.7322049	24.7
 $Ad(CH_2S)_3$ on Au_{19}	C_3	2	-4267.0014667	0.300951	-4266.756297	-1692.7360274	22.3
 $Ad(CH_2S)_3$ on Au_{27}	C_{3v}	0	-5350.9763973	0.301249	-5350.734258	-1692.7485788	14.4
 $Ad(CH_2S)_3$ on Au_{27}	C_3	0	-5350.9763764	0.301151	-5350.734472	-1692.7485579	14.4

Table S1. Continued

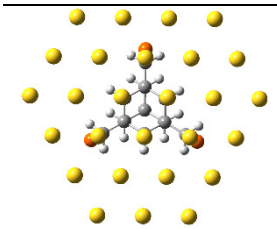
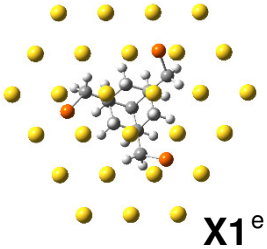
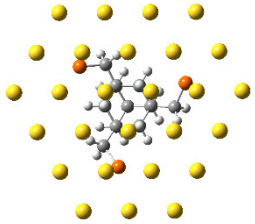
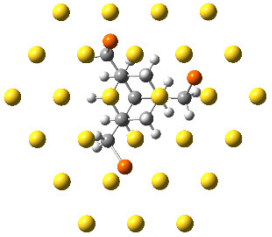
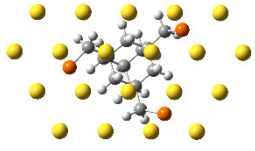
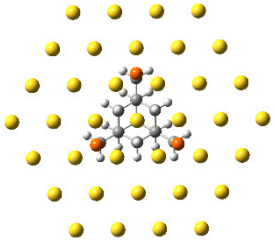
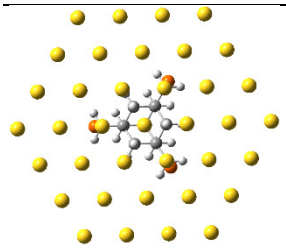
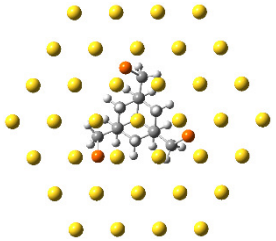
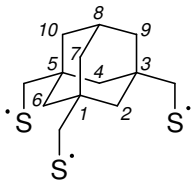
Optimized Structure	Sym-metry	NI[b]	E, hartree	ZPE, hartree	G, hartree	ΔE, hartree[c]	ΔE_{ads}, kcal/mol[d]
 $Ad(CH_2S)_3$ on Au_{27}	C_{3v}	4	-5350.9593510	0.300178	-5350.712997	-1692.7315325	25.1
 **X1**[e] $Ad(CH_2S)_3$ on Au_{27}	C_3	0	-5350.9993497	0.301954	-5350.755071	-1692.7715312	(0)
 $Ad(CH_2S)_3$ on Au_{27}	C_3	0	-5350.9909429	0.301555	-5350.747930	-1692.7631244	5.3
 $Ad(CH_2S)_3$ on Au_{27}	C_1	0	-5350.9886346	0.301353	-5350.746771	-1692.7608161	6.7
 $Ad(CH_2S)_3$ on Au_{27}	C_1	0	-5350.9950654	0.301565	-5350.752412	-1692.7672469	2.7
 $Ad(CH_2S)_3$ on Au_{37}	C_{3v}	2	-6705.9442826	0.300534	-6705.701918	-1692.7482327	14.6

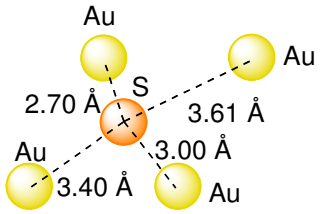
Table S1. Continued

Optimized Structure	Sym-metry	NI[b]	E, hartree	ZPE, hartree	G, hartree	ΔE, hartree[c]	ΔE_{ads}, kcal/mol[d]
 $Ad(CH_2S)_3$ on Au_{37}	C_{3v}	5	-6705.9291976	0.300072	-6705.682324	-1692.7331477	24.1
 $Ad(CH_2S)_3$ 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] $\Delta E = E_{ads} + E[Ad(CH_2S)_3] = E[Ad(CH_2S)_3/Au\ layer] - E(Au\ layer)$. The values of E(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 $Ad(CH_2S)_3$ 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 CH_2-S bonds was 1.92 Å, the bond angle C(1)-CH_2-S was 118°, and the dihedral angle C(7)-C(1)-CH_2-S was 118°.

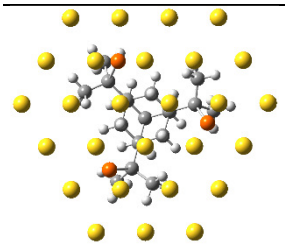
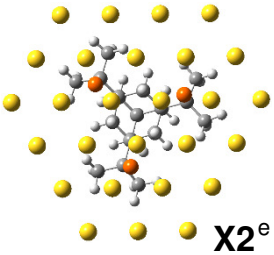


$Ad(CH_2S^{\bullet})_3$

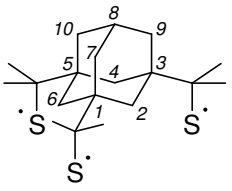


X1

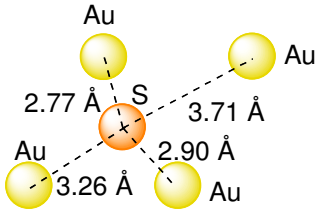
Table S2. Results of DFT calculations for $Ad(CMe_2S)_3$ on the Au_{27} monolayer[a]

Optimized Structure	Sym-metry	NI[b]	*E*, hartree	*ZPE*, hartree	*G*, hartree	ΔE, hartree[c]	ΔE_{ads}, kcal/mol[d]
 $Ad(CMe_2S)_3$ on Au_{27}	C_3	0	-5585.5815802	0.473559	-5585.171088	-1927.3537617	1.3
 **X2**[e] $Ad(CMe_2S)_3$ on Au_{27}	C_3	0	-5585.5836796	0.472138	-5585.177644	-1927.3558611	(0)

[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] $\Delta E = E_{ads} + E[Ad(CMe_2S)_3] = E[Ad(CMe_2S)_3/Au\ layer] - E(Au\ layer)$. The values of E(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 $Ad(CH_2S)_3$ system (**X1**), and the other two were slightly shorter. The length of CMe_2-S bonds was 1.96 Å, the bond angle C(1)-CMe_2-S was 108°, and the dihedral angle C(7)-C(1)-CMe_2-S was 166°. The tripod $Ad(CMe_2S)_3$ stood almost upright in a slightly axially twisted form, due to the steric effect of the Me groups.

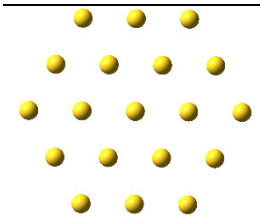
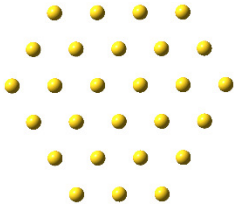
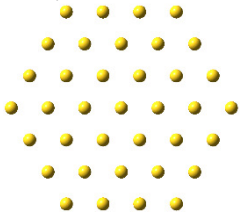


$Ad(CMe_2S^{\bullet})_3$



X2

Table S3. Energies of the Au_{19}, Au_{27}, and Au_{37} monolayers by single-point energy calculations by the DFT method[a]

Structure	Symmetry	*E*, hartree
 Au_{19}	D_{6h}	-2574.2654393
 Au_{27}	D_{3h}	-3658.2278185
 Au_{37}	D_{6h}	-5013.1960499

[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 $Ad(CH_2S)_3$ by single-point energy calculations by the DFT method under periodic boundary conditions (PBC)[a]

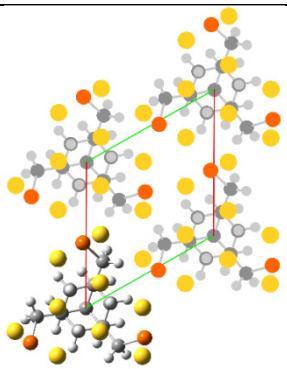
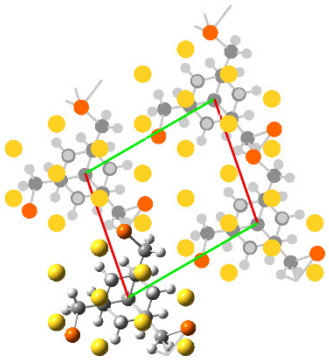
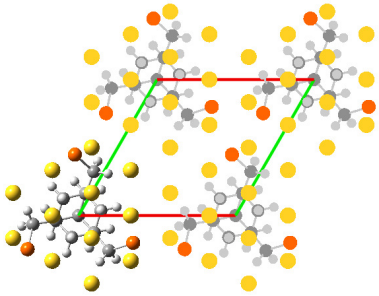
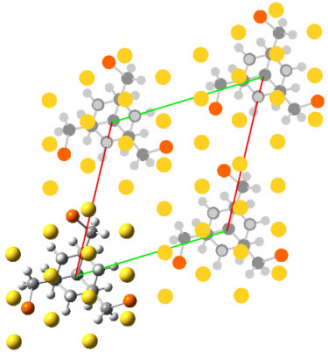
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	*E*, hartree	E_{ads}, kcal/mol[b]	
				per unit cell	per Au atom
 $Ad(CH_2S)_3$ $(3 \times 3)R60°$	8.64	9	-2911.0949984	-38.5	-4.28
 $Ad(CH_2S)_3$ with a $(3 \times \sqrt{7})$ unit cell	7.62, 8.64, and 10.38	9	-2910.5063241	330.9	36.76
 $Ad(CH_2S)_3$ $(2\sqrt{3} \times 2\sqrt{3})R30°$	9.98	12	-3317.3476154	-39.4	-3.28
 $Ad(CH_2S)_3$ $(\sqrt{13} \times \sqrt{13})R46.1°$	10.38	13	-3452.7653224	-44.8	-3.45

Table S4. Continued

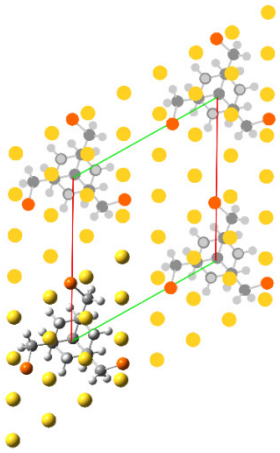
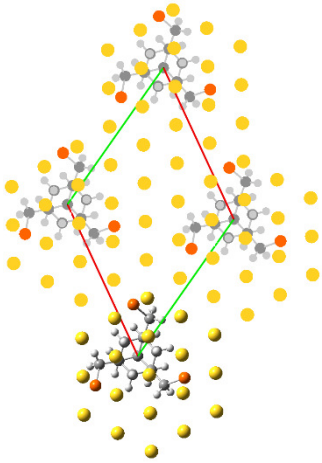
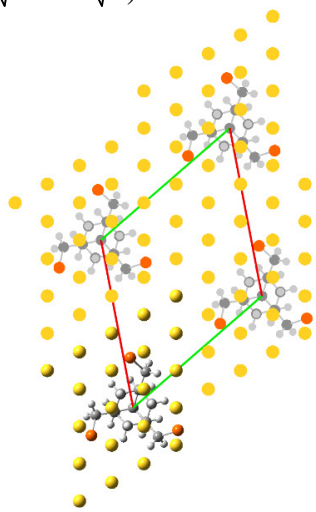
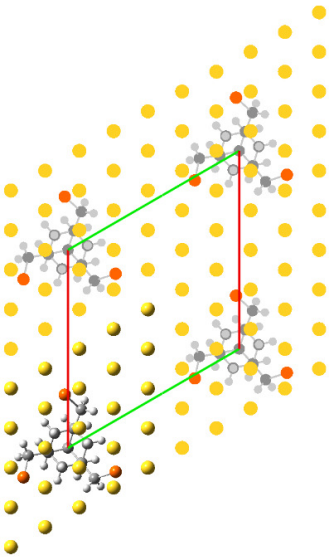
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	*E*, hartree	E_{ads}, kcal/mol[b] per unit cell	E_{ads}, kcal/mol[b] per Au atom
 $Ad(CH_2S)_3$ $(4 \times 4)R60°$	11.52	16	-3859.0056044	-39.5	-2.47
 $Ad(CH_2S)_3$ $(2\sqrt{7} \times 2\sqrt{7})R19.1°$	12.55	19	-4265.2532868	-44.6	-2.35
 $Ad(CH_2S)_3$ $(\sqrt{21} \times \sqrt{21})R10.9°$	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	E_{ads}, kcal/mol[b] per Au atom
 $Ad(CH_2S)_3$ (5 × 5)R60°	14.40	25	-5077.7354420	-41.2	-1.65

[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 $Ad(CH_2S)_3$ in **X1** (Table S1) was used.

[b] E_{ads} = *E*[$Ad(CH_2S)_3$/Au layer] – *E*[$Ad(CH_2S)_3$] – *E*(Au layer). The values of *E*(Au layer) and *E*[$Ad(CH_2S)_3$] are summarized in Tables S6 and S7, respectively.

Table S5. Energies of infinite Au monolayers adsorbed with $Ad(CMe_2S)_3$ by single-point energy calculations by the DFT method under periodic boundary conditions (PBC)[a]

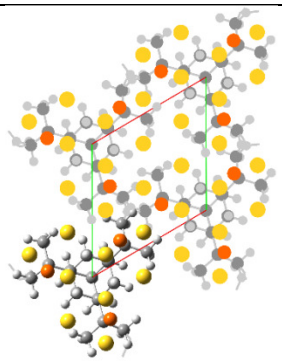
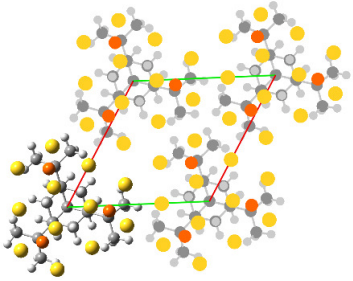
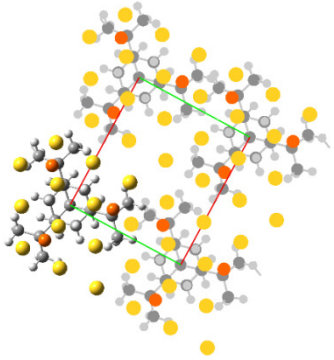
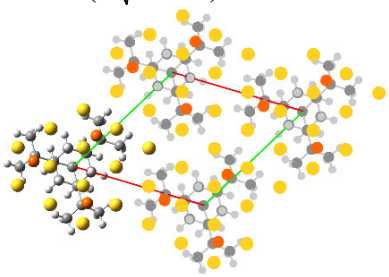
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	*E*, hartree	E_{ads}, kcal/mol[b]	
				per unit cell	per Au atom
 $Ad(CMe_2S)_3$ $(3 \times 3)R60°$	8.64	9	-3142.6967958	1747.8	194.20
 $Ad(CMe_2S)_3$ $(2\sqrt{3} \times 2\sqrt{3})R30°$	9.98	12	-3551.6618885	44.9	3.74
 $Ad(CMe_2S)_3$ with a $(2\sqrt{3} \times 3)$ unit cell	8.64, 9.98, and 13.20	12	-3550.7546656	614.2	51.18
 $Ad(CMe_2S)_3$ $(\sqrt{13} \times \sqrt{13})R46.1°$	10.38	13	-3687.1847163	-26.5	-2.04

Table S5. Continued

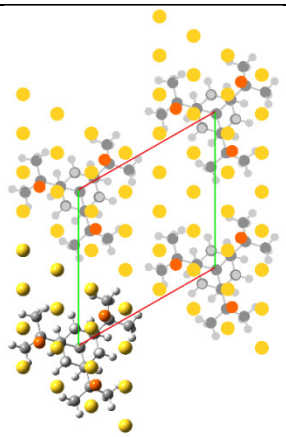
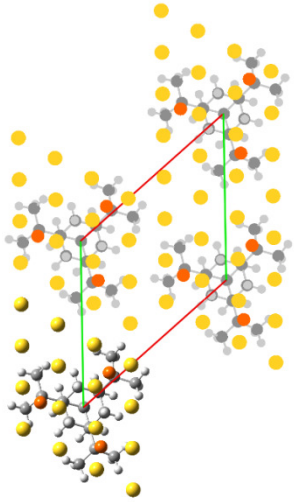
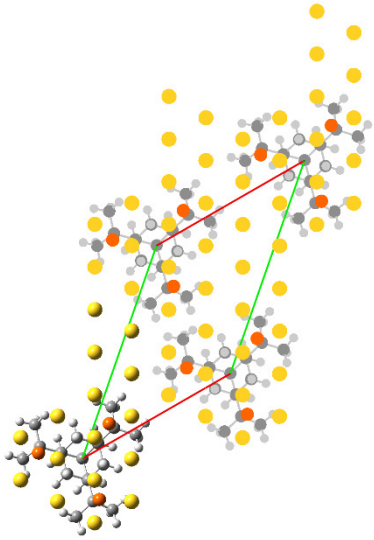
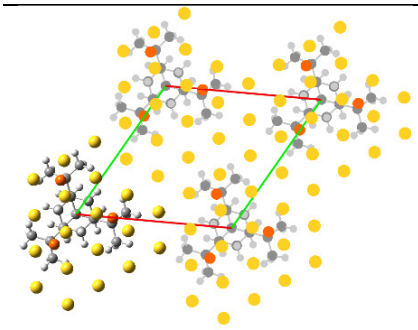
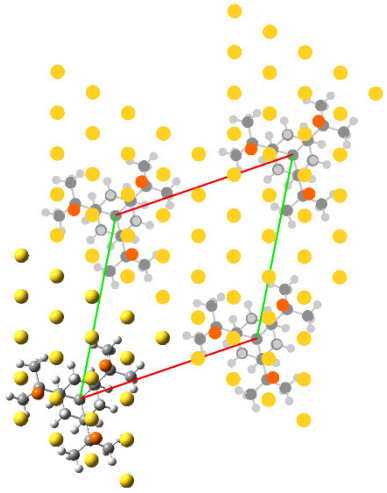
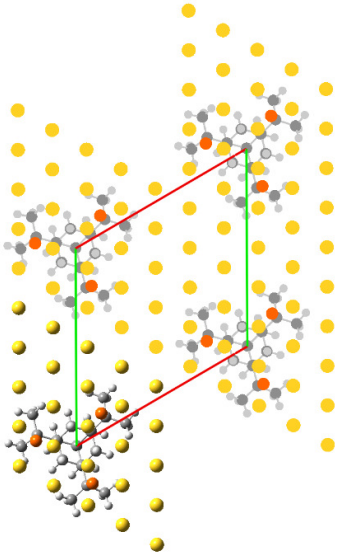
Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	*E*, hartree	E_{ads}, kcal/mol[b] per unit cell	E_{ads}, kcal/mol[b] per Au atom
 $Ad(CMe_2S)_3$ $(4 \times 4)R60°$	11.52	16	-4093.4320290	-25.6	-1.60
 $Ad(CMe_2S)_3$ with a $(4 \times \sqrt{13})$ unit cell	10.38, 11.52, and 13.20	16	-4093.4311871	-25.1	-1.57
 $Ad(CMe_2S)_3$ with a $(4 \times 2\sqrt{3})$ unit cell	9.98, 11.52, and 15.24	16	-4093.4027449	-7.3	-0.45

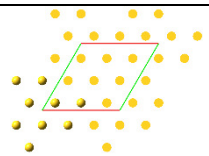
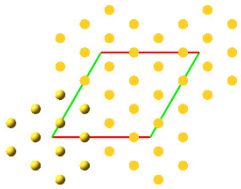
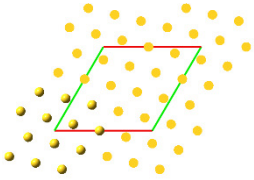
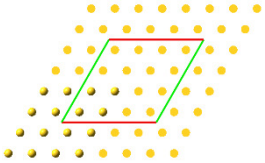
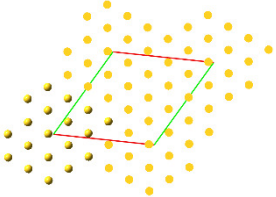
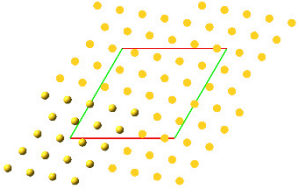
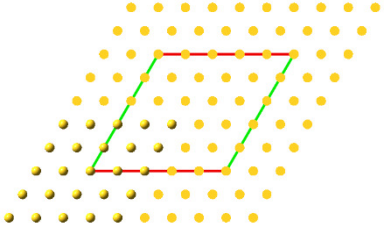
Table S5. Continued

Structure	Nearest molecular distance, Å	Number of Au atoms per unit cell	*E*, hartree	E_{ads}, kcal/mol[b] per unit cell	E_{ads}, kcal/mol[b] per Au atom
 $Ad(CMe_2S)_3$ $(2\sqrt{7} \times 2\sqrt{7})R19.1°$	12.55	19	-4499.6755203	-28.1	-1.48
 $Ad(CMe_2S)_3$ $(\sqrt{21} \times \sqrt{21})R10.9°$	13.20	25	-4770.5044626	-28.0	-1.33
 $Ad(CMe_2S)_3$ $(5 \times 5)R60°$	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 $Ad(CMe_2S)_3$ in **X2** (Table S2) was used.

[b] $E_{ads} = E[Ad(CMe_2S)_3/Au\ layer] - E[Ad(CMe_2S)_3] - E(Au\ layer)$. Values of E(Au layer) and $E[Ad(CMe_2S)_3]$ 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 $(3 \times 3)R60°$	-1218.7219777
 Au_{12} $(2\sqrt{3} \times 2\sqrt{3})R30°$	-1624.9732912
 Au_{13} $(\sqrt{13} \times \sqrt{13})R46.1°$	-1760.3823117
 Au_{16} $(4 \times 4)R60°$	-2166.6309828
 Au_{19} $(2\sqrt{7} \times 2\sqrt{7})R19.1°$	-2572.8705455
 Au_{21} $(\sqrt{21} \times \sqrt{21})R10.9°$	-2843.6996318
 Au_{25} $(5 \times 5)R60°$	-3385.3581436

[a] UBLYP/LanL2MB was used. The Au-Au distance was fixed at 2.88 Å.

Table S7. Energy of $Ad(CX_2S)_3$ (X = H or Me) by single-point energy calculations by the DFT method[a]

Compound	Spin multiplicity	*E*, hartree	Δ*E*, kcal/mol[b]
$Ad(CH_2S^{\cdot})_3$	2	-1692.3115693	0.02
	4	-1692.3116050[c]	(0)
$Ad(CMe_2S^{\cdot})_3$	2	-1926.7597718	0.3
	4	-1926.7601828[c]	(0)

[a] UBLYP/3-21G level. Geometry of $Ad(CX_2S)_3$ (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 $E_{ads.}$.