

1 / 15

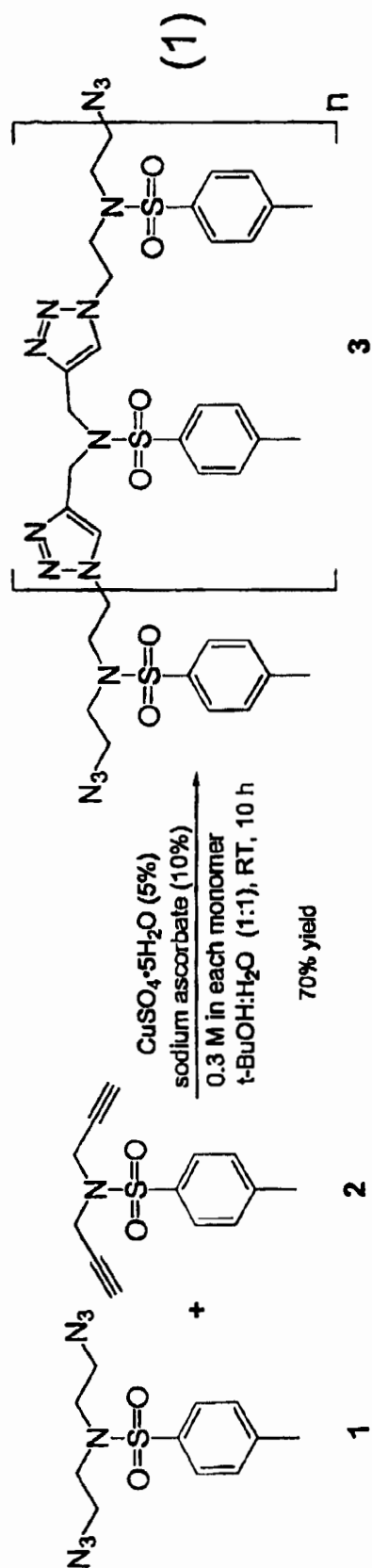


FIG. 1

2 / 15

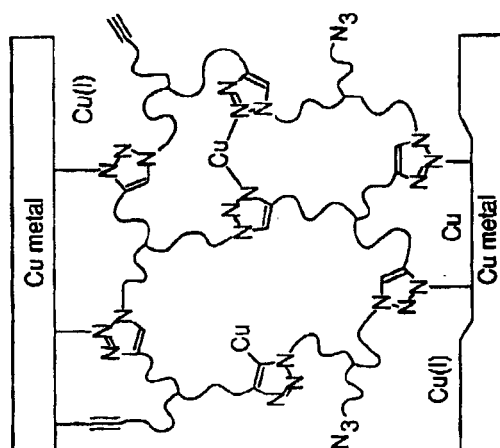


FIG. 2C

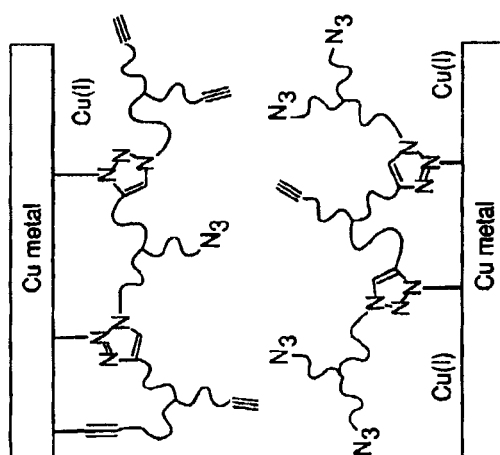


FIG. 2B

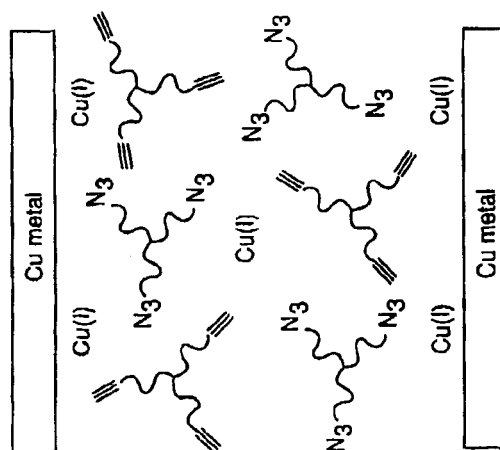


FIG. 2A

3 / 15

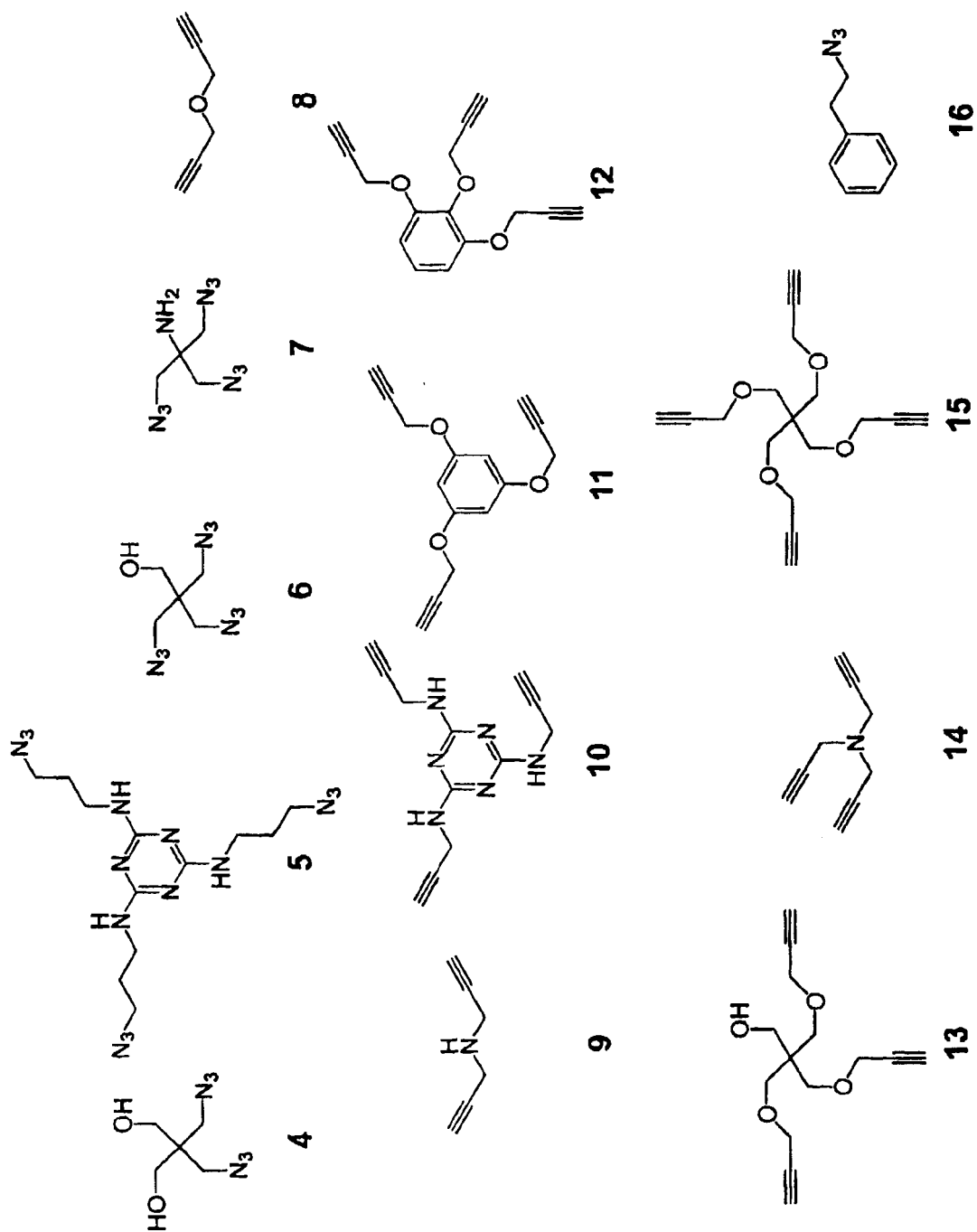
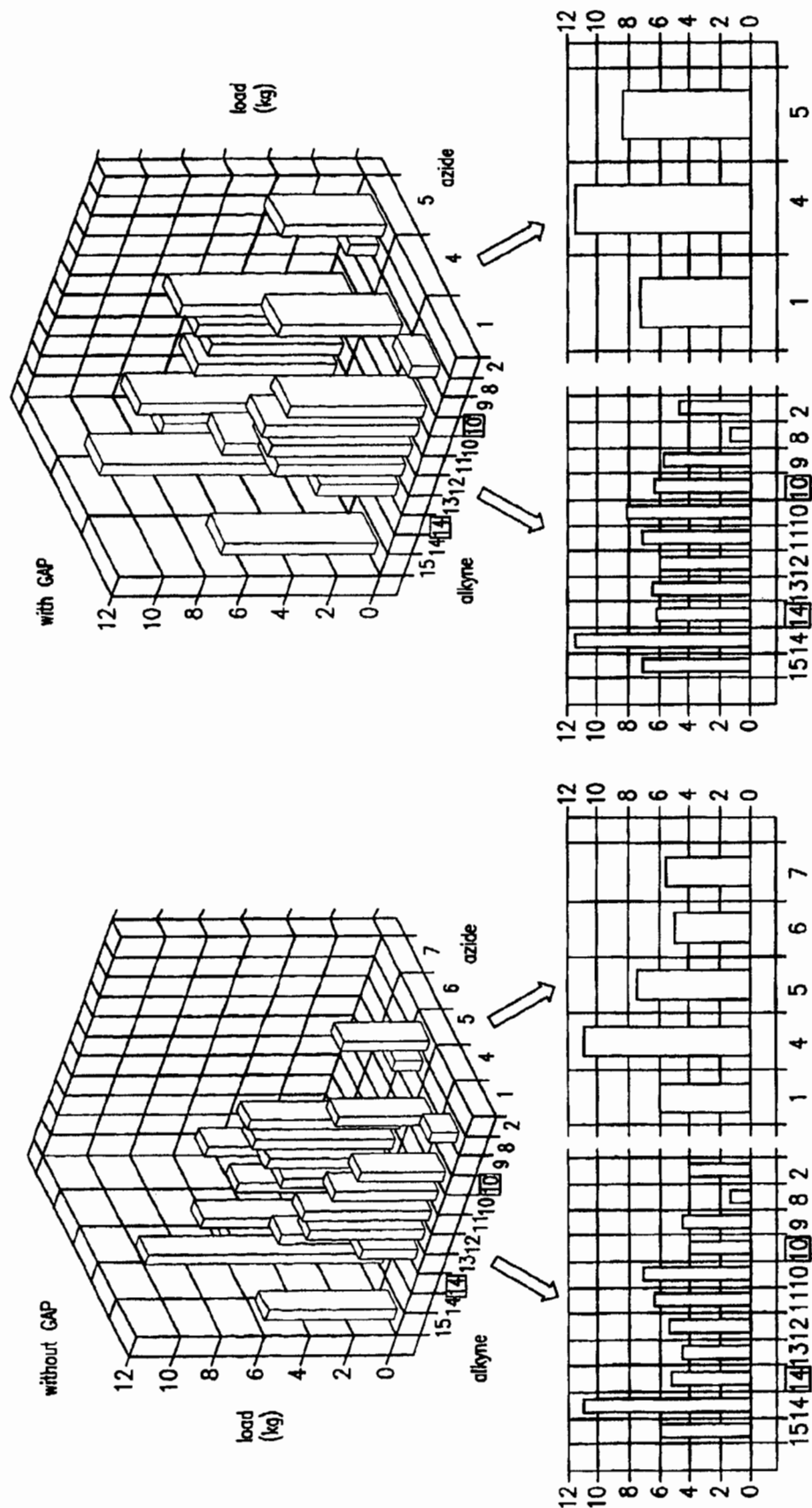
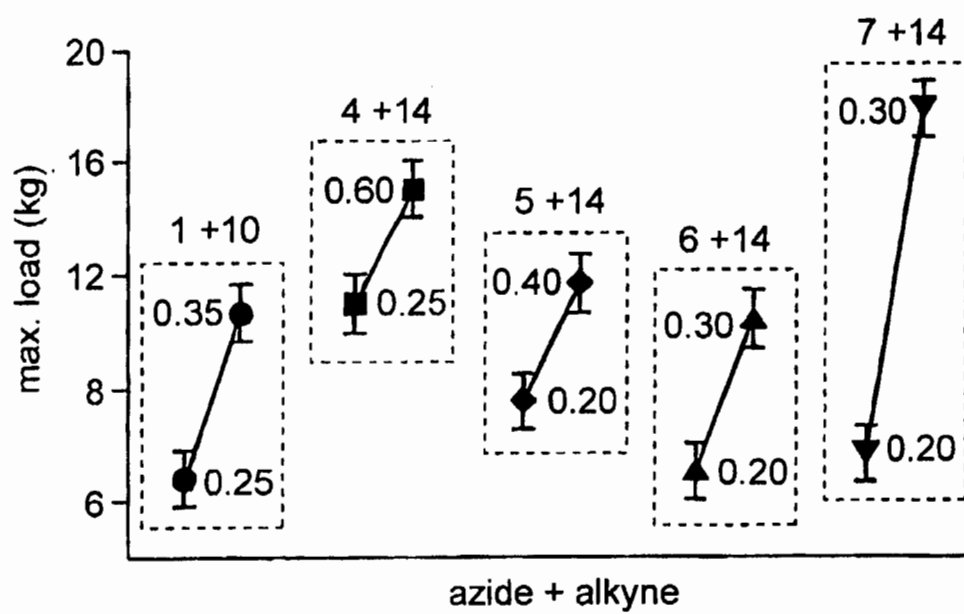


FIG. 3

4 / 15



5 / 15

**FIG. 5**

6 / 15

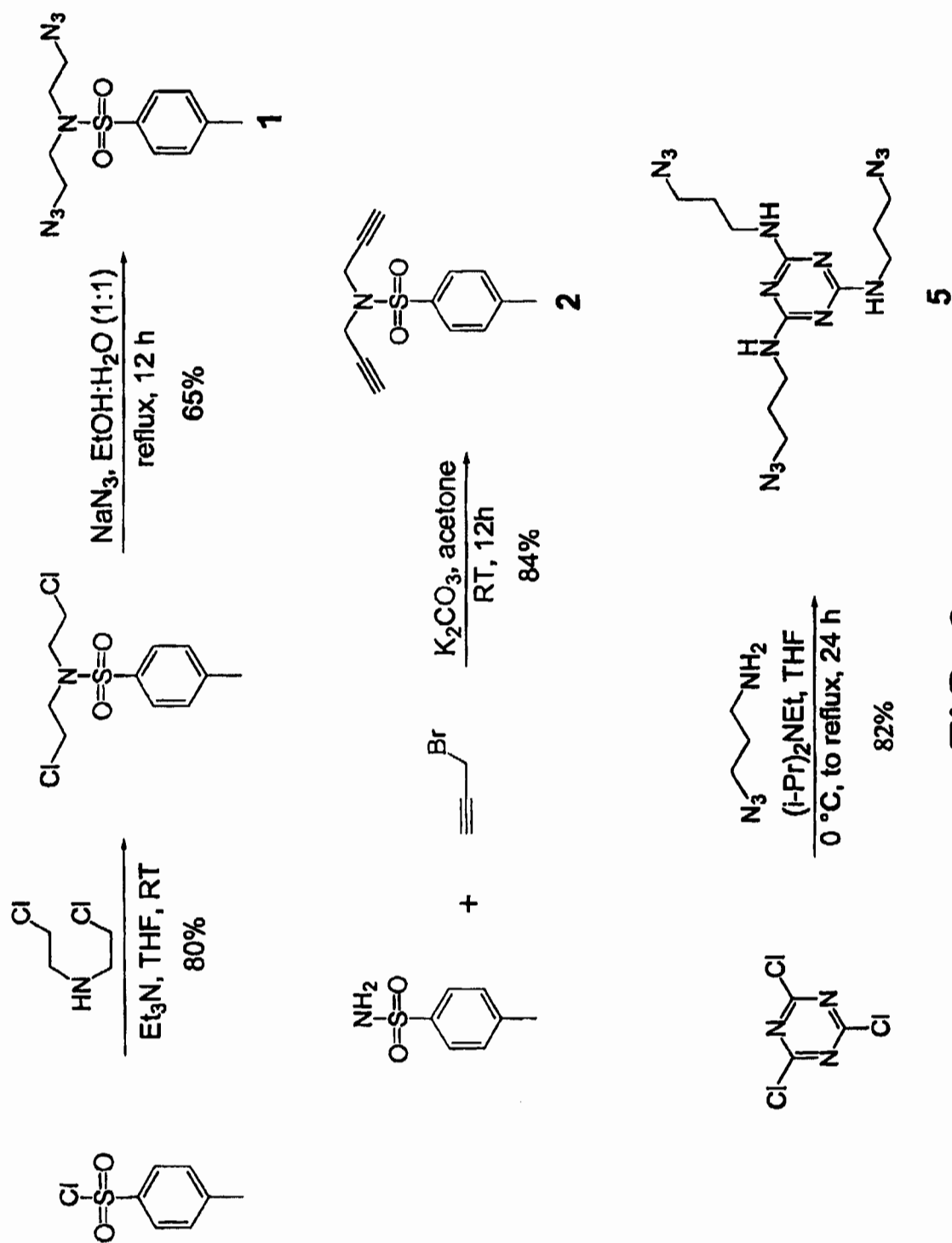


FIG. 6

7 / 15

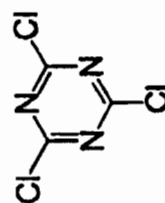
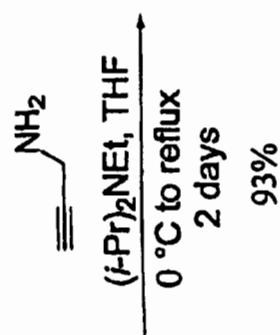
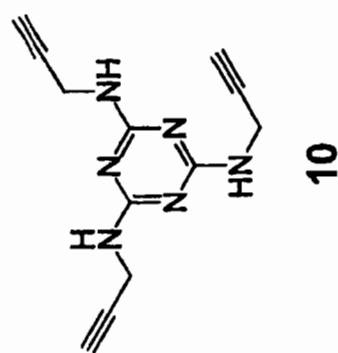
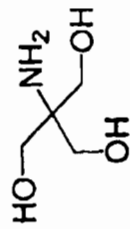
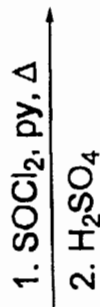
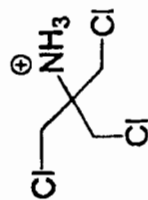
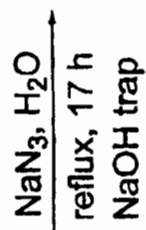
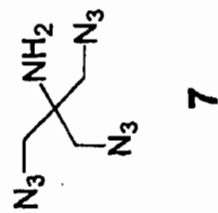
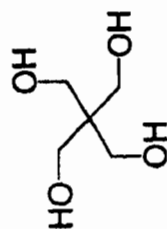
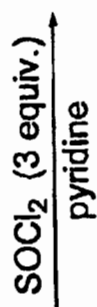
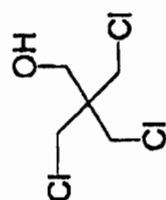
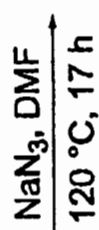
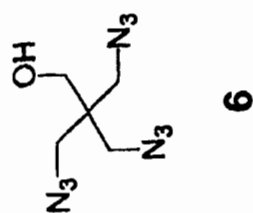


FIG. 7

8 / 15

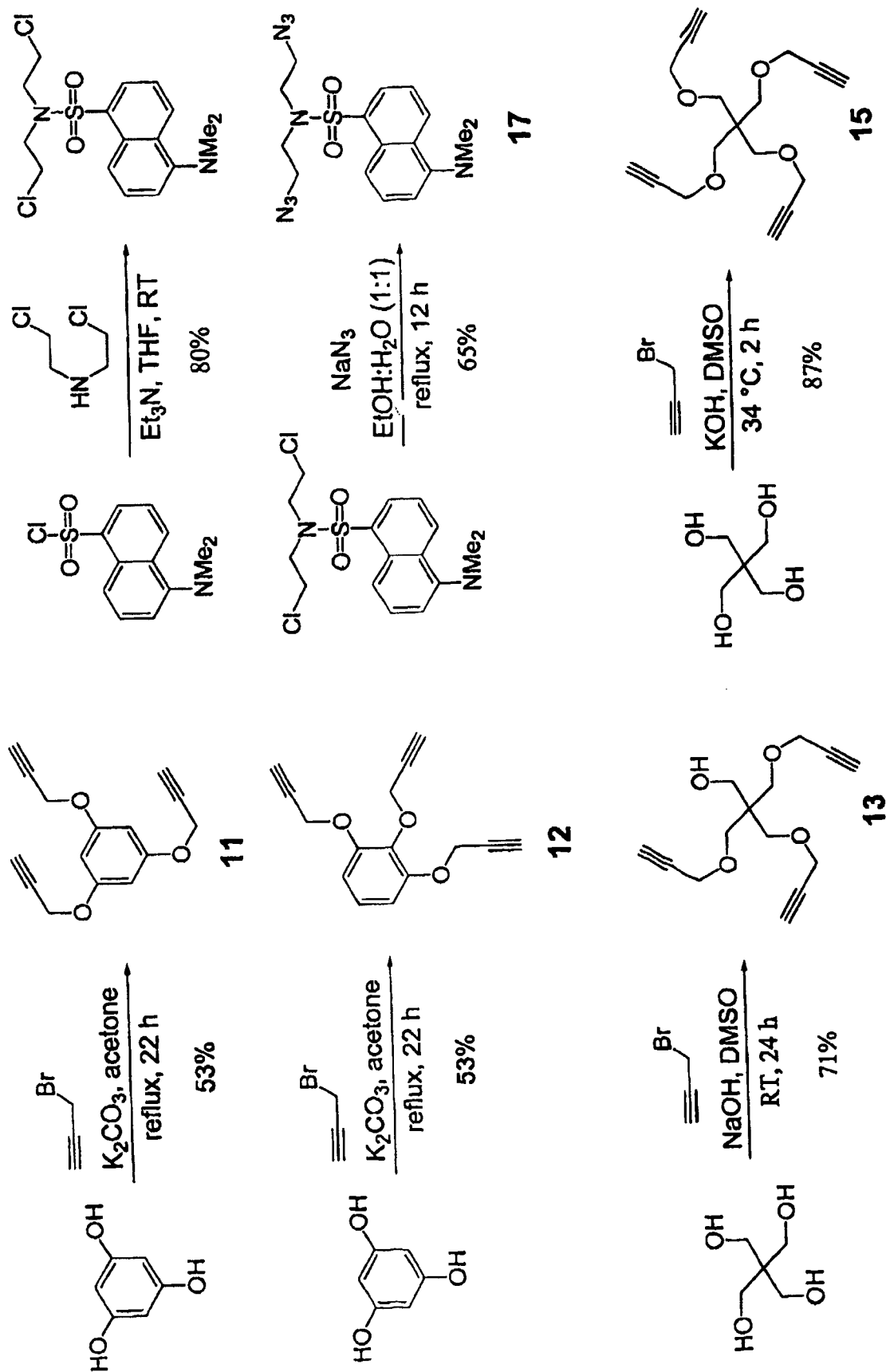


FIG. 8

9 / 15

Entry	di-azide	Tri-azide	di-alkyne	tri-alkyne	tetra-alkyne	N ₃ :CCH ^a	Load (kg) ^{b,c}	kg load per g adhesive
1a	commercial glue (27 mg) ^d						6.7	248 ± 111
1b	commercial glue (42 mg) ^d						8.9	212 ± 71
1c	commercial glue (65 mg) ^d						6.3	97 ± 46
1d	commercial glue (100 mg) ^d						7.0	70 ± 30
2	1		8			1:1	1.3 [1.3]	32 ± 25
3	17		8			1:1	1.3 [1.3]	27 ± 21
4	4		9			1:1	4.5 [5.7]	161 ± 36
5	1			10		1:1.5	4.0 [6.3]	73 ± 18
6	1			10		1:1	4.8 [7.1]	68 ± 14
7	1			11		1:1.5	5.9 [6.5]	107 ± 18
8	1			12		1:1.5	5.3 [5.9]	96 ± 18
9	1			13		1:1.5	2.5 [3.6]	45 ± 18
10	4			14		1:1.5	5.2 [6.2]	164 ± 32
11	4			14		1:1	11.0 [11.5]	268 ± 24
12	1				15	1:2	5.9 [7.0]	99 ± 17
13		5	2			1.5:1	4.0 [4.7]	64 ± 16
14		5	8			1.5:1	1.3 [1.3]	28 ± 21
15		5		10		1:1	7.0 [8.1]	114 ± 16
16		5		11		1:1	6.3 [7.0]	102 ± 16
17		5		12		1:1	5.4 [5.9]	88 ± 16
18		5		13		1:1	4.5 [6.4]	72 ± 16
19		5		14		1:1	7.5 [8.4]	148 ± 20
20		6		14		1:1	5.0	146 ± 29
21		7		14		1:1	5.6	171 ± 31
22		5			15	3:4	5.9 [7.0]	89 ± 15
more complex mixtures								
23	1 + 17		8	10		4:5	3.6 [4.7]	70 ± 19
24	1 + 17			10 + 11		1:1.5	5.9 [5.9]	100 ± 17
control experiments								
25	monoazide 16			10		1:3	1.3	
26	1						0 [0]	
27				10			0 [6.5]	
28	1			10		1:1.5	0 [0]	

FIG. 9

10 / 15

entry	azide	MW azide	alkyne	MW alkyne	mmol azide	mmol alkyne	maximum load (kg)	mg	kg load per g adhesive
1a	Weld-It [®]						6.7 ± 3	27	248 ± 111
1b	Weld-It [®]						8.9 ± 3	42	212 ± 71
1c	Weld-It [®]						6.3 ± 3	65	97 ± 46
1d	Weld-It [®]						7.0 ± 3	100	70 ± 30
2	1	309.35	8	94.11	0.10	0.10	1.3 ± 1	40	32 ± 25
3	17	388.45	8	94.11	0.10	0.10	1.3 ± 1	48	27 ± 21
4	4	186.17	9	93.13	0.10	0.10	4.5 ± 1	28	161 ± 36
5	1	309.35	10	240.26	0.10	0.10	4.0 ± 1	55	73 ± 18
6	1	309.35	10	240.26	0.15	0.10	4.8 ± 1	70	68 ± 14
7	1	309.35	11	240.25	0.10	0.10	5.9 ± 1	55	107 ± 18
8	1	309.35	12	240.25	0.10	0.10	5.3 ± 1	55	96 ± 18
9	1	309.35	13	250.29	0.10	0.10	2.5 ± 1	56	45 ± 18
10	4	186.17	14	131.17	0.10	0.10	5.2 ± 1	32	164 ± 32
11	4	186.17	14	131.17	0.15	0.10	11.0 ± 1	41	268 ± 24
12	1	309.35	15	288.34	0.10	0.10	5.9 ± 1	60	99 ± 17
13	5	375.4	2	247.31	0.10	0.10	4.0 ± 1	62	64 ± 16
14	5	375.4	8	94.11	0.10	0.10	1.3 ± 1	47	28 ± 21
15	5	375.4	10	240.26	0.10	0.10	7.0 ± 1	62	114 ± 16
16	5	375.4	11	240.25	0.10	0.10	6.3 ± 1	62	102 ± 16
17	5	375.4	12	240.25	0.10	0.10	5.4 ± 1	62	88 ± 16
18	5	375.4	13	250.29	0.10	0.10	4.5 ± 1	63	72 ± 16
19	5	375.4	14	131.17	0.10	0.10	7.5 ± 1	51	148 ± 20
20	6	211.18	14	131.17	0.10	0.10	5.0 ± 1	34	146 ± 29
21	7	196.17	14	131.17	0.10	0.10	5.6 ± 1	33	171 ± 31
22	5	375.4	15	288.34	0.10	0.10	5.9 ± 1	66	89 ± 15
23	1+17	348.9	8+10	167.185	0.10	0.10	3.6 ± 1	52	70 ± 19
24	1+17	348.9	10+11	240.255	0.10	0.10	5.9 ± 1	59	100 ± 17

FIG. 10

11 / 15

Entry	monomers (mmol)	Additive (mmol) ^a	max. load (kg)	kg load per g adhesive ^c
1a		Weld-It [®] (27 mg)	7.8	289 ± 111
1b		Weld-It [®] (42 mg)	8.1	193 ± 71
1c		Weld-It [®] (65 mg)	6.1	94 ± 46
1d		Weld-It [®] (100 mg)	7.8	78 ± 30
2	1 + 10 (0.15 + 0.10)	None	0	—
3	1 + 10 (0.15 + 0.10)	CuI (0.015)	6.2	88 ± 14
4	1 + 10 (0.15 + 0.10)	CuI (0.03)	8.2	116 ± 14
5	1 + 10 (0.15 + 0.10)	CuI (0.30)	4.5	64 ± 14
6	1 + 10 (0.15 + 0.10)	CuI (0.40)	5.0	71 ± 14
7	1 + 10 (0.15 + 0.10)	CuSO ₄ • 5H ₂ O (0.30)	4.7	67 ± 14
8	5 + 10 (0.10 + 0.10)	None	0	—
9	5 + 10 (0.10 + 0.10)	CuI (0.03)	10.5	101 ± 16
10	4 + 10 (0.15 + 0.10)	CuI + sodium ascorbate (0.03 + 0.03)	6.0	119 ± 19
11	4 + 14 (0.15 + 0.10)	None	0	—
12	4 + 14 (0.15 + 0.10)	CuI (0.03)	0	—
13	4 + 14 (0.15 + 0.10)	CuI + hydroquinone (0.03 + 0.03)	0	—
14	6 + 14 (0.10 + 0.10)	CuI (0.03)	0	—
15	7 + 14 (0.10 + 0.10)	CuI (0.03)	0	—
16	6 + 10 (0.10 + 0.10)	CuI (0.03)	0	—
17	7 + 10 (0.10 + 0.10)	CuI (0.03)	0	—

FIG. 11

12 / 15

Entry	monomers (mmol)	Additive (mmol) ^a	max. load (kg) ^b	kg load per g adhesive ^c
1a		Weld-It [®] (27 mg)	7.8	289 ± 111
1b		Weld-It [®] (42 mg)	8.1	193 ± 71
1c		Weld-It [®] (65 mg)	6.1	94 ± 46
1d		Weld-It [®] (100 mg)	7.8	78 ± 30
2	1 + 10 (0.15 + 0.10)	None	0	—
3	1 + 10 (0.15 + 0.10)	CuI (0.015)	6.2	88 ± 14
4	1 + 10 (0.15 + 0.10)	CuI (0.03)	8.2	116 ± 14
5	1 + 10 (0.15 + 0.10)	CuI (0.30)	4.5	64 ± 14
6	1 + 10 (0.15 + 0.10)	CuI (0.40)	5.0	71 ± 14
7	1 + 10 (0.15 + 0.10)	CuSO ₄ • 5H ₂ O (0.30)	4.7	67 ± 14
8	5 + 10 (0.10 + 0.10)	None	0	—
9	5 + 10 (0.10 + 0.10)	CuI (0.03)	10.5	101 ± 16
10	4 + 10 (0.15 + 0.10)	CuI + sodium ascorbate (0.03 + 0.03)	6.0	119 ± 19
11	4 + 14 (0.15 + 0.10)	None	0	—
12	4 + 14 (0.15 + 0.10)	CuI (0.03)	0	—
13	4 + 14 (0.15 + 0.10)	CuI + hydroquinone (0.03 + 0.03)	0	—
14	6 + 14 (0.10 + 0.10)	CuI (0.03)	0	—
15	7 + 14 (0.10 + 0.10)	CuI (0.03)	0	—
16	6 + 10 (0.10 + 0.10)	CuI (0.03)	0	—
17	7 + 10 (0.10 + 0.10)	CuI (0.03)	0	—

FIG. 12

13 / 15

entry	azide	alkyne	mmol monomers ^a	ratio ^a	GAP	max. load	kg load per g adhesive ^b
1a	1	10	0.20	1:1.5	—	4.0	73 ± 18
1b	1	10	0.36	1:1.5	—	12.7	128 ± 10
2a	1	10	0.20	1:1.5	+	6.3	
2b	1	10	0.36	1:1.5	+	13.8	
3a	1	10	0.25	1:1	—	4.8	68 ± 14
3b	1	10	0.35	1:1	—	10.7	109 ± 10
4a	1	10	0.25	1:1	+	7.1	
4b	1	10	0.35	1:1	+	11.4	
5a	4	14	0.25	1:1	—	11.0	268 ± 24
5b	4	14	0.60	1:1	—	15.0	152 ± 10
6a	4	14	0.25	1:1	+	11.5	
6b	4	14	0.60	1:1	+	15.2	
7a	5	14	0.2	1:1	—	7.5	148 ± 20
7b	5	14	0.4	1:1	—	11.7	115 ± 10
8a	5	14	0.2	1:1	+	8.4	
8b	5	14	0.4	1:1	+	12.2	
9a	6	14	0.2	1:1	—	5.0	146 ± 29
9b	6	14	0.3	1:1	—	10.4	203 ± 19
10a	7	14	0.2	1:1	—	5.6	171 ± 31
10b	7	14	0.3	1:1	—	17.8	363 ± 20

FIG. 13

Entry ^a	di-azide	Tri-azide	Tri-alkyne	additive	N ₃ :CCH	Load (kg)
1*	4		14	None	1:1	11.0 (11.5)
2	4		14	CuI (0.03 mmol in MeCN)	1:1	9.3 (10.5)
3*	1		10	none	1:1.5	4.0
4	1		10	Cu ₂ O + CuSO ₄ (0.01 mmol each) ^b	1:1.5	5.2
5	1		10	Cu ₂ O (0.015 mmol)	1:1.5	5.3
6	1		10	CuSO ₄ (0.3 mmol)	1:1.5	5.2
7*	1		10	none	1:1	4.8
8	1		10	dendrimer ^c	1:1	7.1
9*		5	10	none	1:1	7.0
10		5	10	dendrimer ^c	1:1	7.9

FIG. 14

14 / 15

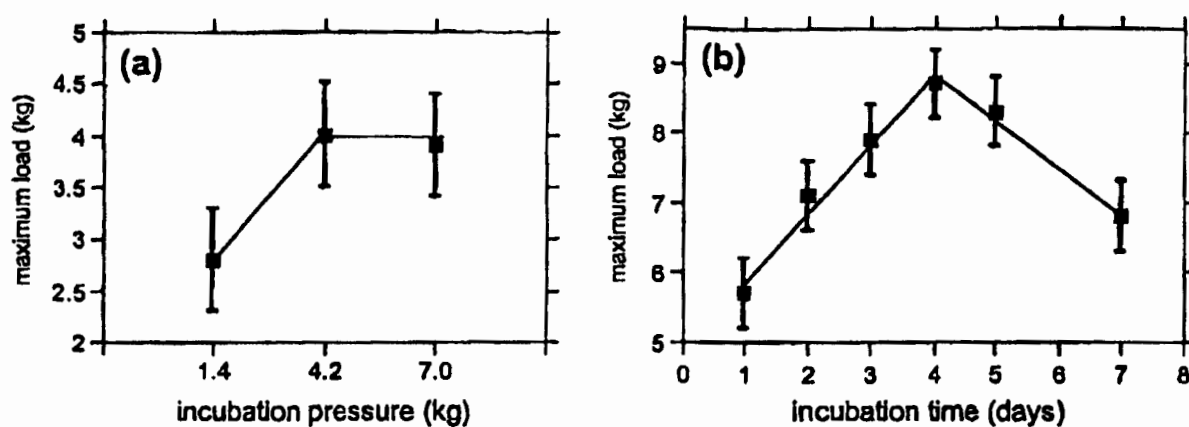


FIG. 15

sample	components	mmol Cu	Cu/triazole	max. load	kg load per g adhesive
(A) (Table S1, entry 2)	1 + 8	0.031 ± 0.005	0.16 ± 0.03	1.3 kg	32 ± 25
(B) (Table S1, entry 6)	1 + 10	0.025 ± 0.004	0.083 ± 0.02	4.8 kg	68 ± 14
(C) (Table S1, entry 11)	4 + 14	0.015 ± 0.004	0.050 ± 0.015	11.0 kg	268 ± 24

FIG. 16

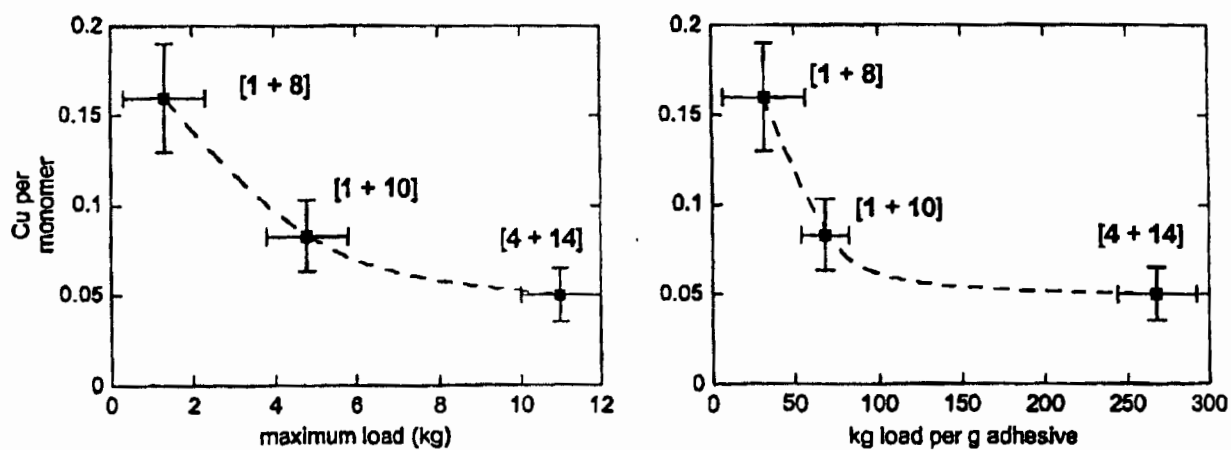


FIG. 17

15 / 15

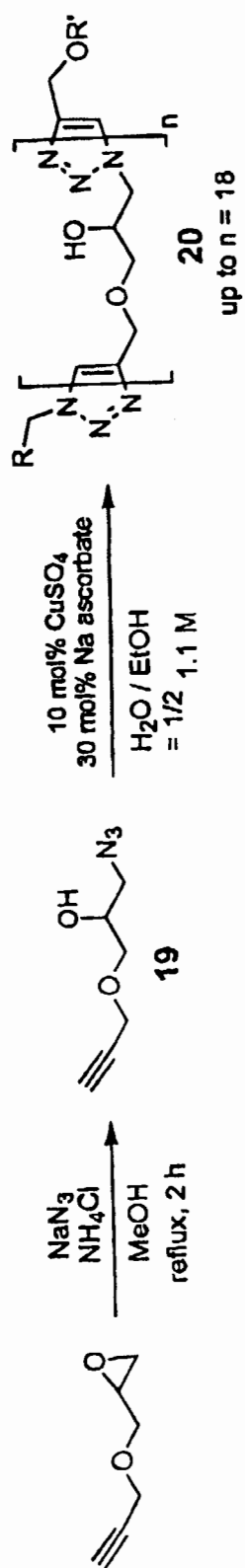


FIG. 18