

(19)  
(12)

(KR)  
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(51) Int. Cl.<sup>7</sup>  
C08F 8/38

(11)  
(43)

2003-0081517  
2003 10 17

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(22) 2003 09 09  
2003 09 09

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(86) 2002 03 12

(87)  
(87)

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(30) JP-P-2001-00068985 2001 03 12 (JP)  
JP-P-2001-00283218 2001 09 18 (JP)

(71) 332-0012 가 4 1 8

(72) 가 , , 가 78

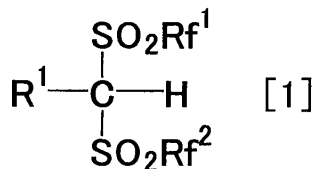
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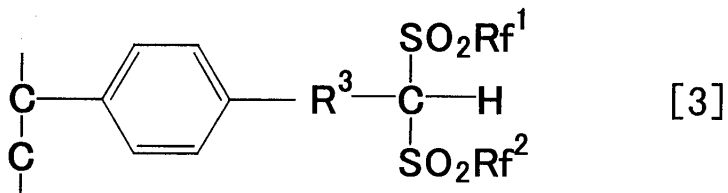
(74)

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(54) ( )

[1] ( [1] , R<sup>1</sup> , Rf<sup>1</sup> Rf<sup>2</sup> )  
( [3] ( [3] , R<sup>3</sup> ) )





( )

( Bronsted ) , ( ) , ( )

(-SO<sub>2</sub>CF<sub>3</sub>: , Tf) 가  
 (J. Am. Chem. Soc. 96, 2275, 1974, Synthesis, 691, 1997. J. Fluorine Chem. 66, 301, 1994).  
 (CH<sub>2</sub>Tf<sub>2</sub>; pKa(H<sub>2</sub>O)=-1)(J. Am. Chem. Soc. 106, 1510, 1984) (PhCHTf<sub>2</sub>; pKa(MeCN) = 7.83)(J. Org. Chem. 63, 7868, 1998)  
 Koppel Gacid( ) (J. Org. Chem. 116, 3047, 1994) : MeSO<sub>3</sub>H(315.0) < CH<sub>2</sub>Tf<sub>2</sub> (310.5) < PhCHTf<sub>2</sub> (310.3) < TfOH(299.5) < NHTf<sub>2</sub> (291.8) < CHTf<sub>3</sub> (289.0).  
 가 (J. Am. Chem. Soc. 106, 1510, 1984, J. Chem. Soc., Chem. Commun. 1675, 1987, Inorg. Chem. 27, 1593, 1988, Inorg. Chem. 27, 2473, 1988, Organometallics 9, 1290, 1990).  
 ( ) ( )

( ) , 가 (J. Org. Chem. 38, 3358, 1973, Heteroatom Chem. 5, 9, 1994, J. Fluorine Chem. 64, 47, 1993, J. Fluorine Chem. 106, 139, 2000).  
 (40% )(J. Org. Chem. 38, 3358, 1973), (61% )(Heteroatom Chem. 5, 9, 1994). 가 가 (bp= -21 )  
 ( )

, Hendrickson (J. Am. Chem. Soc. 96, 2275, 1974, Synthesis, 691, 1997, J. Fluorine Chem. 66, 301, 1994), 가 (Synthesis, 691, 1997).

, 가 , 가 가 , 가 (complex) , 가 , 가 , 가 , 가

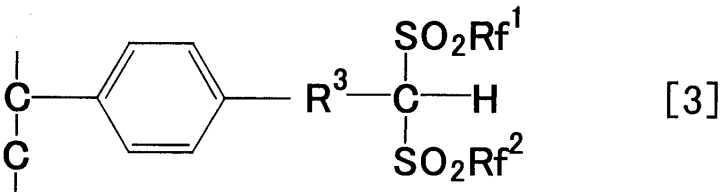




( 15) , ( ) ( 16) ,  
 ( ) ( 17) .  
 , , 1 8 ( 18) ,  
 19) , 18 19 ( 20) ,  
 , , - , , - 21 ,  
 ( 21) .

), Rf<sup>1</sup> Rf<sup>2</sup> ( ) [1]( , [1] , R<sup>1</sup> ( )  
 / ( ) , ( ) , ( )  
 , (p- 가 ), ( ) ( : : TENTAGEL)  
 , [1] ( ) ( ) {4-( )-2,3,5,6- 가  
 } ( ) , 4' [1] ( ) 가  
 ) ( 가 ) [3] ( )

( 4)



( [3] , R<sup>3</sup> , Rf<sup>1</sup> Rf<sup>2</sup> .)  
 [1] [3] Rf<sup>1</sup> Rf<sup>2</sup> ,  
 1 -SO<sub>2</sub>Rf<sup>2</sup> , C1 8 , -SO<sub>2</sub>Rf  
 , 가 .  
 [1] R<sup>1</sup> , 가 R<sup>3</sup> , C1 4 , C1  
 4 R<sup>1</sup> , , , 2,4,6- , 4-( ) , 3,5- ( )  
 , o- , p- , m- 가 , p-









[ 1 ]

		[ (%) ]
PhCH <sub>2</sub> Br	PhCH <sub>2</sub> Tf	94
2-NaphCH <sub>2</sub> Br	2-NaphCH <sub>2</sub> Tf	>99
1-NaphCH <sub>2</sub> Cl	1-NaphCH <sub>2</sub> Tf	99
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> Cl	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> Tf	90
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Tf	>99
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Br	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Tf	76
C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> Tf	89

(2-BenzylTriflone ; J. Fluorine Chem. 66, 301, 1994) : IR(KBr) 1362, 1347, 1223, 1198, 1188, 1125, 776, 698, 640, 525, 507 cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 4.48(s, 2H), 7.42-7.47(m, 5H) ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -77.6(s, 3F, CF<sub>3</sub>).

2- (2-Naphthylmethyl Triflone) : IR(KBr) 1358, 1345, 1221, 1194, 1125, 831, 756, 658, 608, 486cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 4.65(s, 2H), 7.50(dd, J=1.8, 8.4 Hz, 1H), 7.54-7.58(m, 2H), 7.86-7.94(m, 4H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 56.3, 119.8(q, J<sub>CF</sub>=326Hz, 1C), 120.3, 126.9, 127.4, 127.5, 127.8, 128.1, 129.2, 131.5, 133.1, 133.6 ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -77.6(s, 3F, CF<sub>3</sub>). Anal. Calcd for C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>F<sub>3</sub>S : C, 52.55 ; H, 3.31 ; F, 20.78 ; S, 11.69. Found C, 52.51 ; H, 3.33 ; F, 20.81 ; S, 11.65.

1- (1-Naphthylmethyl Triflone) : IR(KBr) 1510, 1358, 1223, 1200, 804, 776, 658, 486cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 4.99(s, 2H), 7.53(dd, J=7.8, 8.4Hz, 1H), 7.62(d, J=7.8Hz, 1H), 7.58(ddd, J=0.9, 6.9, 8.3Hz, 1H), 7.65(ddd, J=1.5, 6.9, 8.4Hz, 1H), 7.93(dd, J=0.9, 8.4Hz, 1H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 53.0, 119.2, 120.0(q, J<sub>CF</sub>=326Hz, 1C), 123.3, 125.3, 126.5, 127.5, 129.0, 131.1, 131.5, 132.3, 134.0 ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -78.1(s, 3F, CF<sub>3</sub>). Anal. Calcd for C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>F<sub>3</sub>S : C, 52.55 ; H, 3.31 ; F, 20.78 ; S, 11.69. Found C, 52.53 ; H, 3.29 ; F, 20.75 ; S, 11.73.

2,4,6- (2,4,6-Trimethylphenylmethyl Triflone) : IR(KBr) 1358, 1206, 1117, 864, 619, 550, 500, 469cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 2.29(s, 3H), 2.43(s, 6H) 4.62(s, 2H), 6.96(s, 2H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 20.3, 21.0(2C), 49.8, 117.0, 120.0(q, J<sub>CF</sub>=326Hz, 1C, CF<sub>3</sub>), 129.9(2C), 139.7(2C), 139.8 ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -79.7(s, 3F, CF<sub>3</sub>). Anal. Calcd for C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>F<sub>2</sub>S ; C, 49.62 ; H, 4.92 ; F, 21.40 ; S, 12.04. Found C, 49.58 ; H, 4.53 ; F, 21.35 ; S, 12.06.

4- (4-Trifluoromethyl)phenylmethyl Triflone ; Synthesis, 691, 1997) : IR(KBr) 1356, 1341, 1227, 1210, 1144, 1121, 855, 658, 513cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 4.53(s, 2H), 7.58(d, J=8.0Hz, 2H), 7.72(d, J=8.0Hz, 2H) ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -77.5(s, 3F, CF<sub>3</sub>), -64.3(s, 3F, CF<sub>3</sub>).

3,5- (3,5-Bis(trifluoromethyl)phenylmethyl Triflone) : IR(KBr) 1376, 1362, 1277, 1175, 1117, 918, 910, 669cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 4.60(s, 2H), 7.91(s, 2H), 8.01(s, 1H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 55.0, 119.6(q, J<sub>CF</sub>=326Hz, 1C, CF<sub>3</sub>), 122.6(q, J<sub>CF</sub>=272Hz, 2C, 2CF<sub>3</sub>), 124.2(septet, J<sub>CF</sub>=4Hz, 1C), 126.1, 131.3(2C), 132.9(q, J<sub>CF</sub>=34Hz, 2C) ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -77.4(s, 3F, CF<sub>3</sub>), -64.3(s, 6F, 2CF<sub>3</sub>). Anal. Calcd for C<sub>10</sub>H<sub>3</sub>O<sub>2</sub>F<sub>9</sub>S : C, 33.53 ; H, 0.84 ; F, 47.74 ; S, 8.95. Found C, 33.48 ; H, 0.91 ; F, 47.87 ; S, 8.89.

(Pentafluorophenylmethyl Triflone) : IR(KBr) 1509, 1374, 1210, 1121, 995cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 4.64 ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 44.3, 100.0(dt, J<sub>CF</sub>=4.17Hz, 1C, ipso-C), 119.5(q, J<sub>CF</sub>=326Hz, 1C, CF<sub>3</sub>), 137.9(d, J<sub>CF</sub>=251Hz, 2C, 2m-C), 142.8(d, J<sub>CF</sub>=258Hz, 1C, p-c), 145.9(d, J<sub>CF</sub>=252Hz, 2C, 2o-C) ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -160.0(d, J=15.2Hz, 2F, 2m-F), 149.0(s, 1F, p-F), 139.4(d, J=15.2Hz, 2F, 2o-F), -78.3(s, 3F, CF<sub>3</sub>). Anal. Calcd for C<sub>8</sub>H<sub>2</sub>O<sub>2</sub>F<sub>8</sub>S : C, 30.59 ; H, 0.64 ; F, 48.38 ; S, 10.21. Found C, 30.49 ; H, 0.73 ; F, 48.37 ; S, 10.18.

3 [ ( ) ]

2 (0.5mmol) (3Mℓ)  
 -78 1.1 (0.55mmol) t-BuLi(0.34Mℓ, 1.6M ) 가 , 10  
 , Tf<sub>2</sub>O(46μℓ, 0.275mmol) 가 1 . -78  
 , 1.1 (0.55mmol) t-BuLi(0.34Mℓ, 1.6M ) 가 10 , Tf<sub>2</sub>O(46μℓ,  
 0.275mmol) 가 1 가  
 , 4M , 2  
 , ( )  
 , 2 ,

[ 2 ]

	( )	(%)
2-NaphCH <sub>2</sub> Tf	2-NaphCHTf <sub>2</sub>	84
1-NaphCH <sub>2</sub> Tr	1-NaphCHTf <sub>2</sub>	98
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> Tf	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CHTf <sub>2</sub>	89
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Tf	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHTf <sub>2</sub>	87
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Tf	3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHTf <sub>2</sub>	75
C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> Tf	C <sub>6</sub> F <sub>5</sub> CHf <sub>2</sub>	45

( ) (Phenylbis(triflyl)methane ; J. Org. Chem. 38, 3358, 1973, Heteroatom Chem. 5, 9, 19  
 94) : IR(KBr) 2950, 1381, 1242, 1219, 1184, 1102, 806, 695, 660, 608, 585, 507cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 3  
 00MHz) 5.97(s, 1H), 7.54-7.68(m, 5H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 80.7, 119.3, 119.3(q, J<sub>CF</sub>=329Hz,  
 2C, 2CF<sub>3</sub>), 130.0(2C), 131.8(br). 132.9(2C) ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -73.8(s, 6F, 2CF<sub>3</sub>).

2- ( ) (2-Naphthylbis(triflyl)methane) : IR(KBr) 1393, 1381, 1244, 1213, 1103, 646, 58  
 6cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 6.10(s, 1H), 7.61-7.71(m, 3H), 7.92-7.99(m, 2H), 8.03(d, J=8.4Hz, 2  
 H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 75MHz) 80.9, 116.3, 119.3(q, J<sub>CF</sub>=329Hz, 2C, 2CF<sub>3</sub>), 127.7, 128.0, 128.8, 129.  
 1, 130.1, 132.8, 133.4, 134.7 ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -73.6(s, 6F, 2CF<sub>3</sub>) ; HRMS(EI) calcd for C<sub>13</sub>  
 H<sub>8</sub>O<sub>4</sub>F<sub>6</sub>S<sub>2</sub> [M]<sup>+</sup> 405.9768, found 405.9761.

1- ( ) (1-Naphthylbis(triflyl)methane) : IR(KBr) 1389, 1383, 1215, 1111, 770, 650, 504c  
 m<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 6.87(s, 1H), 7.62-7.80(m, 4H), 8.02(d, J=8.4Hz, 1H), 8.16(d, J=8.4Hz, 1  
 H), 8.37(d, J=7.5Hz, 1H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 75MHz) 74.6, 114.1(s, 1C, ipso-C), 119.4(q, J<sub>CF</sub>=328Hz, 2  
 C, 2CF<sub>3</sub>), 119.9, 125.4, 127.0, 128.9, 130.1, 131.5, 131.7, 133.8, 134.0 ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -7  
 4.2(s, 6F, 2CF<sub>3</sub>) ; HRMS(EI) calcd for C<sub>13</sub>H<sub>8</sub>O<sub>4</sub>F<sub>6</sub>S<sub>2</sub> [M]<sup>+</sup> 405.9768, found 405.9761.

2,4,6- ( ) (2,4,6-Trimethylphenylbis(triflyl)methane) : IR(KBr) 1397, 1383, 1217,  
 1119, 1107, 642, 590cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 2.33(s, 3H), 2.35(s, 3H), 2.61(s, 3H), 6.48(s, 1H)  
 , 7.00(s, 1H), 7.08(2, 1H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 75MHz) 20.2, 21.1, 22.2, 77.7, 115.9, 119.4(q, J<sub>CF</sub>=328Hz  
 , 2C, 2CF<sub>3</sub>), 130.4, 132.2, 140.0, 142.2, 142.6 ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -76.3(s, 6F, 2CF<sub>3</sub>) ; HR  
 MS(EI) calcd for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>F<sub>6</sub>S<sub>2</sub> [M]<sup>+</sup> 398.0081, found 398.0089.

4-( ) ( ) (4-Trifluoromethyl)phenylbis(triflyl)methane) : IR(KBr) 1393, 13  
 83, 1327, 1231, 1171, 1136, 1111, 860, 671, 610cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz) 5.98(s, 1H), 7.84(s,  
 1H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 80.4, 120.0(q, J<sub>CF</sub>=329Hz, 2C, 2CF<sub>3</sub>), 123.8(q, J<sub>CF</sub>=271Hz, 1C, C  
 F<sub>3</sub>), 124.2, 127.6(q, J=4Hz, 2C), 133.0(2C), 135.6(q, J<sub>CF</sub>=33Hz, 1C) ; <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -7  
 3.5(s, 6F, 2CF<sub>3</sub>), -64.7(s, 3F, CF<sub>3</sub>) ; HRMS(EI) calce for C<sub>10</sub>H<sub>5</sub>O<sub>4</sub>F<sub>9</sub>S<sub>2</sub> [M]<sup>+</sup> 423.9846, found 42  
 3.9471.

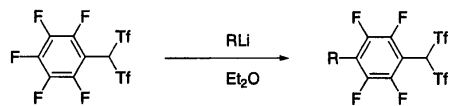
3,5- ( ) ( ) (3,5-Bis(Trifluoromethyl)phenylbis(triflyl)methane) : IR(KB  
 r) 1395, 1374, 1285, 1223, 1194, 1179, 1144, 1105, 936, 909, 629, 519cm<sup>-1</sup> ; <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300MHz)  
 6.05(s, 1H), 8.13(s, 2H), 8.18(s, 1H) ; <sup>13</sup>C NMR(CDCl<sub>3</sub>, 125MHz) 78.9, 119.2(q, J<sub>CF</sub>=329Hz, 2C, 2CF<sub>3</sub>)

$_{3}$ ), 122.2(q,  $J_{CF}=272\text{Hz}$ , 2C,  $2\text{CF}_{3}$ ), 122.9, 126.7(septet,  $J_{CF}=4\text{Hz}$ ), 131.6(s, 2C), 133.8(q,  $J=35\text{Hz}$ , 2C);  $^{19}\text{F}$  NMR( $\text{CDCl}_{3}$ , 282MHz) -73.2(s, 6F,  $2\text{CF}_{3}$ ), -64.3(s, 6F,  $2\text{CF}_{3}$ ); HRMS(EI) calce for  $\text{C}_{11}\text{H}_{4}\text{O}_{4}\text{F}_{12}\text{S}_{2}[\text{M}]^{+}$  472.9375, found 472.9372.

( ) (Pentafluorophenylbis(triflyl)methane): Mp. 86–87; IR(KBr) 1522, 1501, 1347, 1321, 1198, 1127, 1024, 988, 613 $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR( $\text{CDCl}_{3}$ , 300MHz) 6.21(hrs. 1H);  $^{12}\text{C}$  NMR( $\text{CDCl}_{3}$ , 125MHz) 70.4, 98.0(s, 1C, ipso-C), 119.2(q,  $J_{CF}=330\text{Hz}$ , 2C,  $2\text{CF}_{3}$ ), 137.8(d,  $J_{CF}=258\text{Hz}$ , 1C, m-c), 138.6(d,  $J_{CF}=257\text{Hz}$ , 1C, m-C), 144.7(d,  $J_{CF}=264\text{Hz}$ , 1C, p-c), 145.4(d,  $J_{CF}=262\text{Hz}$ , 1C, o-C), 147.2(d,  $J_{CF}=262\text{Hz}$ , 1C, o-c);  $^{13}\text{C}$  NMR( $\text{CD}_{3}\text{O}$ ( 49.0), 125MHz) 56.2, 109.1(dt,  $J=6.19\text{Hz}$ , 1C, ipso-C), 122.4(q,  $J_{CF}=324\text{Hz}$ , 2C,  $2\text{CF}_{3}$ ), 138.5(d,  $J_{CF}=250\text{Hz}$ , 2C, 2m-C), 143.0(d,  $J_{CF}=251\text{Hz}$ , 1C, p-C), 150.0(d,  $J_{CF}=245\text{Hz}$ , 1C, o-C),  $^{19}\text{F}$  NMR( $\text{CDCl}_{3}$ , 282MHz) -157.9(dt,  $J=6.2, 21.5\text{Hz}$ , 1F, m-F), -156.8(dt,  $J=6.2, 21.5\text{Hz}$ , 1F, m-F), -142.6(tt,  $J=5.9, 21.5\text{Hz}$ , 1F, p-F), -140.3(br, 1F, o-F), -127.7(ddd,  $J=5.9, 15.2, 21.5\text{Hz}$ , 1F, o-F), -75.2(s, 6F,  $2\text{CF}_{3}$ ); HRMS(EI) calcd for  $\text{C}_{9}\text{H}_{0}\text{F}_{11}\text{S}_{2}[\text{M}]^{+}$  445.9141. found 445.9137.

4 [ ( ) ]  
 , 2 ( ) 45%  
 ( ) , 1 : 1 ( )  
 ) 4-tert- -2,3,5,6- ( ) ( )  
 45%). , 1.0 t-BuLi 0.5 Tf<sub>2</sub>O ( ) 4-tert- -2,3,5,6- ( )  
 95% ( ) , ( ) Tf<sub>2</sub>O  
 ( ) ( )  
 3 , 3 ( )  
 ( ) , 3  
 「Bn」 .

( 3)



RLi (당량)	조건	수율(%)
<i>t</i> -BuLi (3)	-78°C, 1시간	87
BuLi (3)	-78°C, 1시간	>95
BnLi (5)	-78°C, 6시간	83
PhLi (3)	-78°C로부터 실온, 1일	>95
3,4,5-F <sub>3</sub> C <sub>6</sub> H <sub>2</sub> Li (5)	-20°C로부터 실온 3시간	75
3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Li (5)	-20°C로부터 실온 3시간	70

5 [{4- ( ) } -2,3,5,6- ( ) ]  
 4- ;  
 (10g, 30mmol) THF(50Mℓ) , -78 (1  
 3Mℓ, 15mmol) 0.5 , 2 , 2 .  
 가 , ,  
 , 4- , 4,4'- ,  
 ( , 30 : 3 : 67) .  
 4-( ) ;

4- (100Mℓ) , N- (NBS)(26.7g, 150mmol), AIBN(0.99g, 6mmol), 4 가 1 가 TLC  
 NBS AIBN 가 285mmol NBS, 15mmol AIBN 가  
 100 : 1) , 4-( ) (7.36g, 18mmol, 60%) =

$^1\text{H NMR}(\text{CDCl}_3, 30\text{MHz})$  4.58(s, 2H,  $\text{CH}_2\text{Br}$ );  $^{19}\text{F NMR}(\text{CDCl}_3, 282\text{MHz})$  -138.02(dd,  $J=10.6, 19.8\text{Hz}$ , 2F), -138.56(dt,  $J=9.1, 20.3\text{Hz}$ , 2F), -142.36(dd,  $J=10.6, 19.8\text{Hz}$ , 2F), -150.59(t,  $J=20.3\text{Hz}$ , 1F), -161.08(dt,  $J=7.1, 20.3\text{Hz}$ , 2F).

{4-( )-2,3,5,6-( )}

4-( ) (3.68g, 9mmol) (1.69g, 10.8mmol)  
 (30Mℓ) , 12 가 가  
 ( - ) = 20 : 1 8 : 1 1 : 1) {4-( )-2,3,5,6-( )}  
 6-( ) (3.91g, 8.46mmol, 94%)

$^1\text{H NMR}(\text{CDCl}_3, 300\text{MHz})$  4.75(s, 2H,  $\text{CH}_2\text{Tf}$ );  $^{19}\text{F NMR}(\text{CDCl}_3, 282\text{MHz})$  -78.24(s, 3F,  $\text{CF}_3$ ), -136.82 -136.62(m, 1F), -137.72(dd,  $J=10.7, 18.3\text{Hz}$ , 2F), -138.84(dd,  $J=10.7, 18.3\text{Hz}$ , 2F), -149.69(t,  $J=21.3\text{Hz}$ , 1F), -160.63(dt,  $J=6.1, 21.3\text{Hz}$ , 2F).

{4-( )-2,3,5,6-( )} ( ) ;

{4-( )-2,3,5,6-( )} ( ) (4.6g, 10mmol) (120 Mℓ)  
 가 , -78 tert- (5Mℓ, 10mmol, 2.0M )  
 가 -78 0.5 tert- 0 0.5 -78  
 , (0.84Mℓ, 5mmol) 가 , 2 , -78 te  
 rt- (3.75Mℓ, 7.5mmol, 2.0M) ) 가 -78 0.  
 5 , 0 0.5 -78 (0.84Mℓ, 5mmol) 가 , 1M ,  
 5mmol) 가 2 , 가 4M ,  
 {4-( )-2,3,5,6-( )} ( ) (2.79g, 4.7mmol, 47%)

$^1\text{H NMR}(\text{CDCl}_3, 300\text{MHz})$  6.32(s, 1H, CH);  $^{19}\text{F NMR}(\text{CDCl}_3, 282\text{MHz})$  -75.1(s, 6F,  $2\text{CF}_3$ ), -127.72 -127.58(m, 1F), -133.43(dd,  $J=10.2, 21.3\text{Hz}$ , 1F), -134.60(dd,  $J=9.4, 21.3\text{Hz}$ , 1F), -137.08 -137.35(m, 2F), -140.07(br, 1F), -148.38(t,  $J=21.3\text{Hz}$ , 1F), -160.01(dt,  $J=6.2, 21.3\text{Hz}$ , 2F).

6 [ ( ) ]

3 ( ) (1mmol) ,  $\text{LiOH} \cdot \text{H}_2\text{O}$ (1mmol) (10Mℓ)  
 ) 12 , ( )  
 (100% ). ( )

( ) (LithiumPentafluorophenylbis(triflyl)methaide) :  $^{13}\text{C NMR}(\text{CD}_2\text{O D}, 125\text{MHz})$  56.1, 109.0(dt,  $J=4, 19\text{Hz}$ , 1C, ipso-C), 122.3(q,  $J_{\text{CF}}=324\text{Hz}$ , 2C,  $2\text{CF}_3$ ), 138.5(d,  $J_{\text{CF}}=247\text{Hz}$ , 2C, 2m-C), 143.0(d,  $J_{\text{CF}}=251\text{Hz}$ , 1C, p-C), 149.5(d,  $J_{\text{CF}}=245\text{Hz}$ , 2C, 2o-C).

7 [ {4-( )-2,3,5,6-( )} ( ) ]

5 {4-( )-2,3,5,6-( )} ( ) (1mmol) ,  $\text{LiOH} \cdot \text{H}_2\text{O}$ (1mmol)  
 $2\text{O}$ (1mmol) )-2,3,5,6- (10Mℓ) 12 , {4-( )-2,3,5,6-( )} ( ) (100% ).

8 [ ( ) ( ) ]

(3Mℓ) Ag<sub>2</sub>CO<sub>3</sub> (66mg, 0.24mmol) 가 ( ) (0.20g, 0.40mmol)  
 , ( ) ( ) 가  
 ( ) ( ) ( ) (99%) ( )

( ) ( ) (Silver( )Pentafluorophenylbis(triflyl)methide) : <sup>19</sup>F NMR(CDCl<sub>3</sub>, 282MHz) -162.6(dt, J=7.6, 21.4Hz, 2F, 2m-F), -150.6(t, J=21.4Hz, 1F, p-F), -134.7-134.6(m, 2F, 2o-F), -79.5(s, 6F, 2CF<sub>3</sub>).

9 [ ( ) ( ) (No.1)]

Sc<sub>2</sub>O<sub>3</sub> (21mg, 0.155mmol) ( ) (0.277g, 0.62mmol) (0.5Mℓ) 12  
 가 , Sc<sub>2</sub>O<sub>3</sub> ( ) ,  
 ( ) ( ) , 100  
 (50%) ( ) .

10 [ ( ) ( ) (No. 2)]

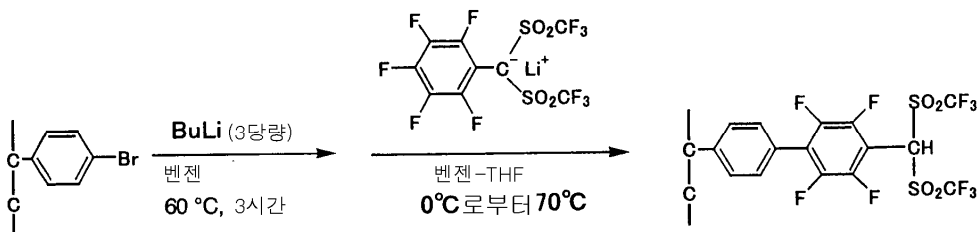
8 ( ) ( ) (0.19g, 0.34mmol) Sc( )Cl<sub>3</sub> · (H<sub>2</sub>O)  
 6 (29mg, 0.11mmol) (3Mℓ) , 12  
 ( ) ( ) , 100  
 9 ( ) ( ) (50%) ( ) .

( ) ( ) (Scandiyum( )Pentafluorophenylbis(triflyl)methide) : Mp. >250 (decomposed) ; <sup>13</sup>C NMR(CD<sub>3</sub>OD( 49.0), 125MHz) 56.2, 109.0(dt, J<sub>CF</sub> =2, 20Hz, 1C, ipso-C), 122.3(q, J<sub>CF</sub> =324Hz, 2C, 2CF<sub>3</sub>), 137.8(d, J<sub>CF</sub> =247Hz, 2C, 2m-C), 142.3(d, J<sub>CF</sub> =251Hz, 1C, p-C), 148.9(d, J<sub>CF</sub> =245Hz, 2C, 2o-C) ; <sup>19</sup>F NMR(CD<sub>3</sub>OD, 282MHz) -166.4(dt, J=6.1, 21.3Hz, 2F, 2m-F), -155.9(t, J=21.3Hz, 1F, p-F), -134.9 -134.9(m, 2F, 2o-F), -80.9(s, 6F, 2CF<sub>3</sub>).

11 [ ( ) ( ) ]

4- ( ) ( ) ,  
 ( ) ( ) (7). 4- (2%  
 , 200-400 , 3.03mmol/g ; (0.33g, 1mmol) (5Mℓ) ,  
 1.6M (1.88Mℓ, 3mmol) 가 60 ( )  
 ) 가 , 3 , 5 ( )  
 (1Mℓ) THF(1Mℓ) 가 , 0 ( )  
 (1.36g, 3mmol) 가 , 2 ( )  
 12 , 0 , 4M (10Mℓ) 가 70 ( )  
 (10Mℓ) , 10Mℓ), (5Mℓ) - THF(5Mℓ) , THF(10Mℓ),  
 1torr , 80 5 ,  
 ( ) (0.413g) .

( 5)

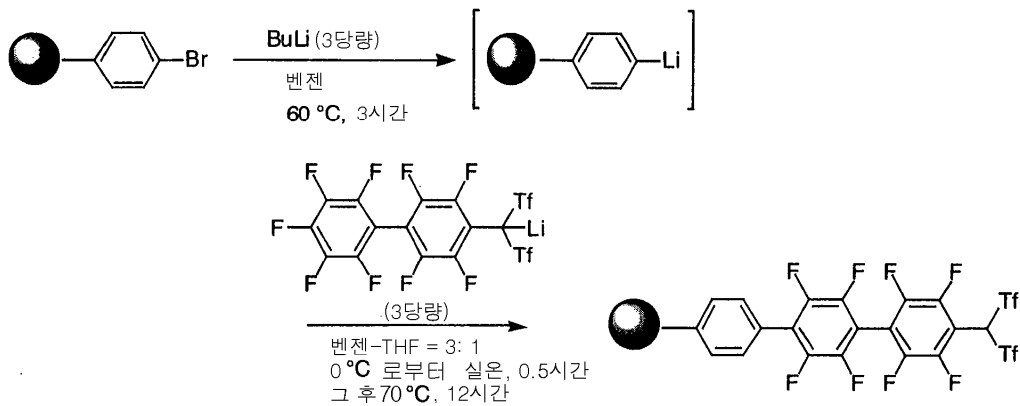


1.06mmol/g

( ) (Polysthylene resin, cross-linked with 2% divinylbenzene with the Pentafluorophenylbis(triflyl)methane) : IR(KBr) 1475, 1352, 1194, 1119, 1022, 976, 700, 612cm<sup>-1</sup>

12 [ {4- ( ) -2,3,5,6- } ( ) ]  
 4- {4-( ) -2,3,5,6- } ( )  
 , {4- ( ) -2,3,5,6- } ( )  
 ( 8). 4- ( ) , 200-400 ,  
 3.03mmol/g : (0.33g, 1mmol) (5Mℓ)  
 1.6M (1.8Mℓ, 3mmol) 가 60 ( ) 가 , 3 ,  
 , 7 {4-( ) -2,3,5,6- } ( )  
 (1.78g, 3mmol) 가 , 0.5 , 70 ( )  
 12 , 4M (10Mℓ) 가 , THF(10Mℓ),  
 (10Mℓ) (10Mℓ), (5Mℓ) - THF(5Mℓ) , THF(10Mℓ),  
 {4-( ) -2,3,5,6- } ( ) (0.440g) .

( 6)

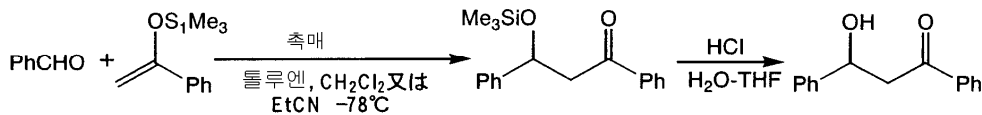


{4-( ) -2,3,5,6- } ( )  
 0.9mmol/g .

13 [ ]

11 ( ) ( , 9).  
 (16mg, 1.06mmol/g) 1Mℓ 가 , -78 ,  
 (0.12Mℓ, 0.6mmol) (0.05Mℓ, 0.5mmol) 가 , -78 , 7  
 , -78 2,3 가 ,  
 , 1M (1Mℓ) THF(1Mℓ) 가 15 ,  
 ( : = 8 :  
 1 4 :1) (109.7mg, 0.49mmol) 97% 4M  
 (1Mℓ), (1Mℓ), (0.5Mℓ) - THF(0.5Mℓ) , THF(1Mℓ), (1Mℓ)  
 , 100% .

( 7)



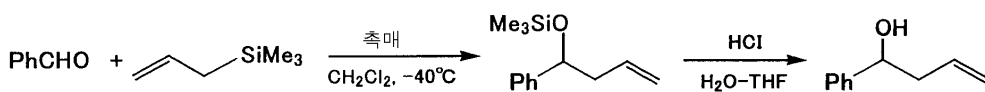
SAC-13( ) 16mg  
 (16mg, 1.06mmol/g)

14 [ - ]

11 ( )

10). 가 (0.48Mℓ, 3mmol) (57mg, 1.06mmol/g) 0.41Mℓ (0.2 Mℓ, 2mmol) 30 가 30 -40 1, -40 2 3  
 가 1M (2.5Mℓ) THF(2.5Mℓ) 가 30  
 M (1Mℓ), (1Mℓ), (267mg, 1.8mmol) 90% 4  
 (0.5Mℓ) - THF(0.5Mℓ), THF(1Mℓ), (1Mℓ)

( 8)



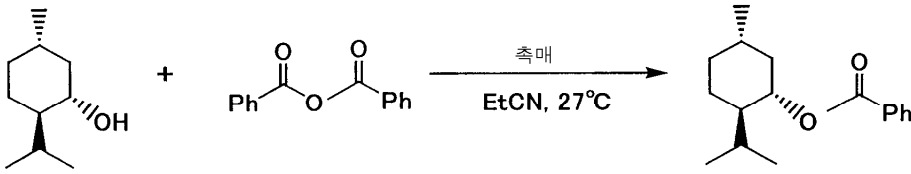
SAC-13( ) 57mg  
 2% ( ) 100%

15 [ ]

11 ( )

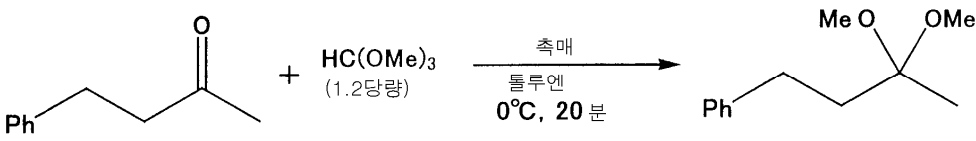
가 27 (340mg, 1.5mmol), (65mg, 1.06mmol/g) 4.8Mℓ (10Mℓ)  
 = 10 : 1 (1Mℓ), (1Mℓ), (260mg, 1mmol) >99%  
 4M (0.5Mℓ) - THF(0.5Mℓ), THF(1Mℓ), (1Mℓ)

( 9)



촉매  
EtCN, 27°C

SAC-13( ) 57mg  
0% , 100%  
( )  
16 [ ]  
11 ( )  
(10.6mg, 0.5mol%, 1.06mmol/g) (2Mℓ) 가 30 ( ) , 0  
(0.30Mℓ, 2.0mmol) (0.26Mℓ, 0.24mmol) 가 . 0 20  
(5Mℓ) (10Mℓ)  
( : =10 : 1) (388mg, 2mmol)  
ol) , THF(1Mℓ), >99% (1Mℓ) 4M (1Mℓ), (1Mℓ), (0.5Mℓ) - THF(0.5Mℓ)  
100%  
( 10)



촉매  
톨루엔  
0°C, 20 분

SAC-13( ) 10.6mg  
16% , 100%  
( )

가

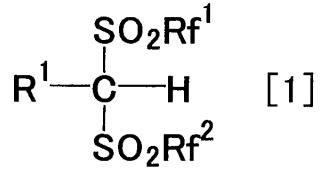
( ) , ( ) ) ( ) , ( )  
( ) , 가 ( ) , ( ) , ( )  
( ) , 가 ( ) , 가 ( ) , 가 ( ) , 가

(57)

1.  
[1] ( )



( ) .



( [1] , R<sup>1</sup> , Rf<sup>1</sup> Rf<sup>2</sup> .)

2.

1 , ( ) .

3.

2 , ( 가 ) .

4.

3 , 가 ( ) .

5.

1 4 , [1] ( ) ( ) .

6.

1 5 ( , [1] ) Rf<sup>1</sup> Rf<sup>2</sup> .

7.

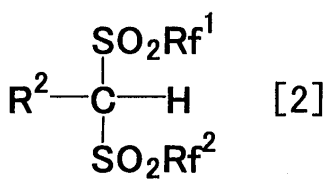
1 6 ( , [1] ) R<sup>1</sup> , , 2,4,6-  
4-( ) , 3,5- ( ) , ( ) .

8.

1 7 ( ) , 1- ( ) , 2,4,6- ( ) , 2-  
( ) , 3,5- ( ) ( ) , 4-( )  
, {4-( )-2,3,5,6- } ( ) .

9.

1 8 ( [2] ) ( ) .



( [2] , R<sup>2</sup> , Rf<sup>1</sup> Rf<sup>2</sup> .)

