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46

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(56)对比文件
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审查员

(54)发明名称
[60] [60]
2- [60] [60]
[60] 2

(57)摘要
[60]
[60] 2

C_{60} α ,β

[ ]

[ ]

(51) Int.Cl.

C07C 49/697 (2006.01)

C07C 49/755 (2006.01)

C07C 49/683 (2006.01)

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Marta Izquierdo .Enantioselective Cycloaddition of Mu¨nchnones onto [60] Fullerene:Organocatalysis versus Metal Catalysis. J. Am. Chem. Soc. .2014, 136 2897-2904.

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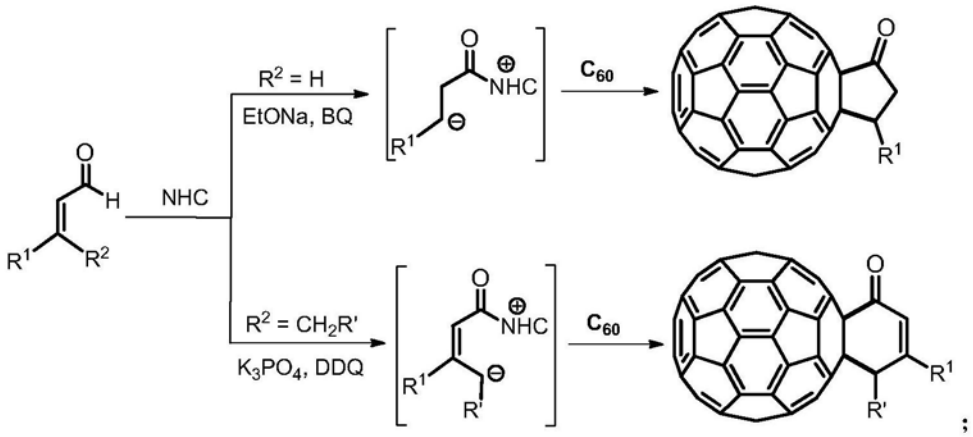
Takumi Oshima .AlCl3-Catalyzed Tandem Acetylation of Hydroarylated [60] Fullerenes. ORGANIC LETTERS .2008, 10 (15),3335-3338.

1 . [60] [60] 2
C_{60} α,β
[60] [60] [60]
2

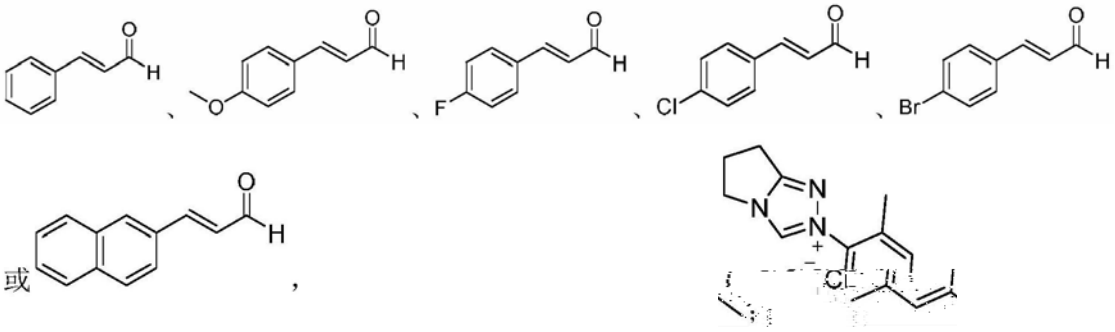


;

[60] C_{60} α,β

70 110 TLC

[60] α,β

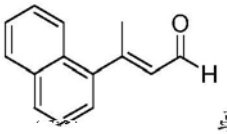
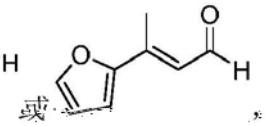


或 ,

[60] 2 C_{60} α,β
3,3',5,5' 4,4'

30 80 TLC

[60] 2 Á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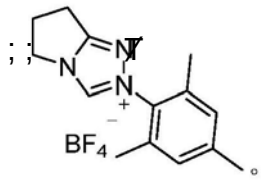
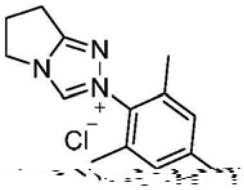


2 . 1 [60] [60] 2

[60] C_{60} α ,β



1 .0:3 .0:0 .3:0 .3:1 .0

3 . 1 [60] [60] 2

[60] 2 α ,β ıє A_{60} ;

一种[60]富勒烯并环戊酮和[60]富勒烯并2 环己烯酮类化合物的合成方法

技术领域

[0001] [60]

[60] 2

背景技术

[0002]

C_{60}

发明内容

[0003] [60] [60] 2

(NHCs)

[60] [60] [60]

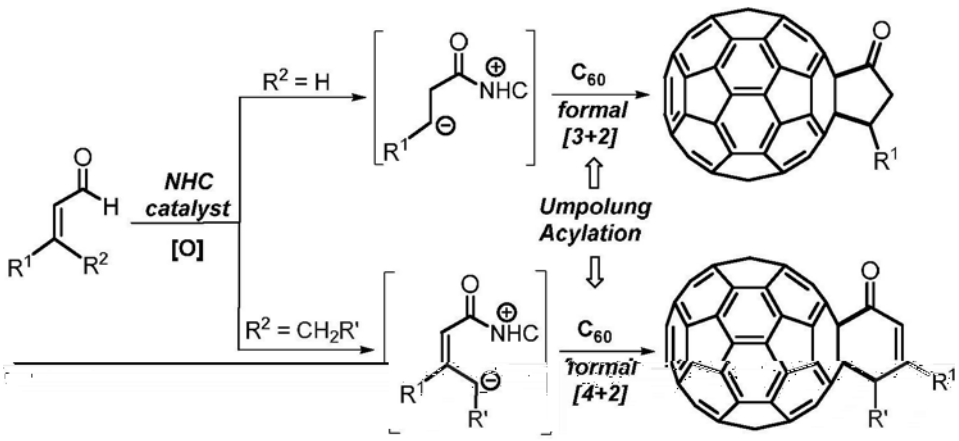
2 [60] [60] 2

[0004] [60] [60]

2 C_{60} α,β

(NHCs) [60]

[60] [60] 2

[0005] 

[0006] R^1 $C_{1\ 4}$

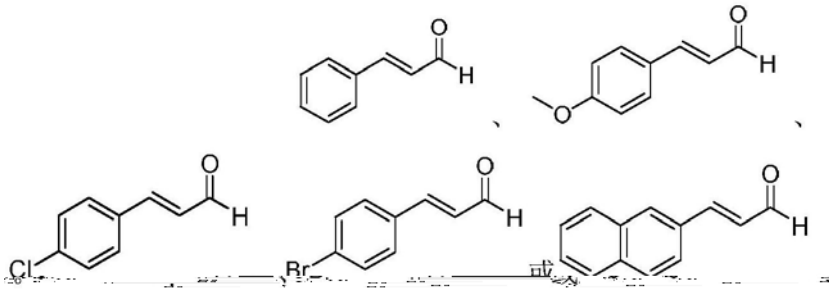
R′ $C_{1\ 4}$

[0007] [60]

C_{60} α,β

70 110 TLC

[60] α,β



[0008] C_{60} α,β

1.0:3.0:0.3:0.3:1.0

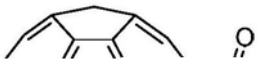
[0009] [60] 20

C_{60} α,β 3,3',5,5'

4,4'

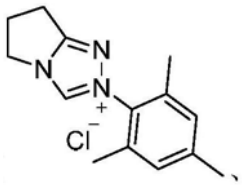
30 80

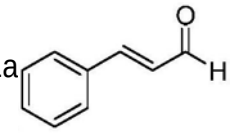
TLC



[0015]

[0016]

[0017] 0 .05mmol C_{60} 0 .015mmol  0 .015mmol 0 .05mmol

0 .15mmol 1a  25mL 4mL

1mL

90 TLC

[60] 2a 2a 56

[0018] 2a: ^{1}H NMR(400MHz ,$CDCl_3/CS_2$)δ7 .69(d ,J 7 .6Hz ,2H) ,7 .42(t ,J 7 .4Hz ,2H) , 7 .34(t ,J 7 .4Hz ,1H) ,5 .18(dd ,J 14 .0 ,6 .4Hz ,1H) ,4 .32(t ,J 15 .6Hz ,1H) ,3 .67(dd ,J 15 .6 ,6 .4Hz ,1H)

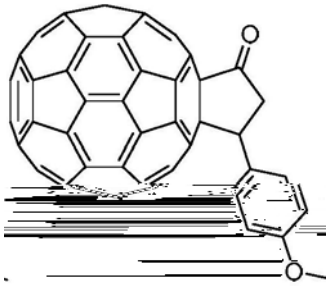
[0019] ^{13}C NMR(150MHz ,$CDCl_3/CS_2$with Cr(acac)$_3$as relaxation reagent ,all 1C unless indicated)δ206 .48 ,154 .68 ,151 .30 ,150 .87 ,150 .71 ,148 .39 ,147 .40 ,147 .14 , 146 .47 ,146 .39(2C) ,146 .33 ,146 .26 ,146 .17(2C) ,146 .15 ,146 .11 ,146 .09 ,145 .79 , 145 .59 ,145 .54(2C) ,145 .49 ,145 .47 ,145 .43(2C) ,145 .41 ,145 .36 ,145 .20 ,144 .53 , 144 .47 ,144 .40 ,144 .28 ,143 .12 ,143 .09 ,142 .79(2C) ,142 .70(2C) ,142 .41 ,142 .21 , 142 .14 ,142 .12(2C) ,142 .09 ,141 .99 ,141 .94 ,141 .90 ,141 .86(2C) ,141 .61 ,140 .85 , 140 .82 ,140 .00 ,139 .84 ,136 .68 ,136 .05 ,135 .92 ,135 .29 ,134 .41 ,129 .04(2C) ,129 .01 (2C) ,128 .45 ,79 .22(sp^3 C of C_{60}) ,74 .13(sp^3 C of C_{60}) ,54 .45 ,42 .28

[0020] FT IRν/cm ^{1}(KBr)1732 ,1449 ,1369 ,1256 ,1220 ,1151 ,1116 ,1083 ,854 ,762 ,743 , 707 ,645 ,576 ,526

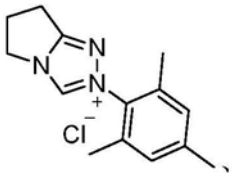
[0021] UV vis($CHCl_3$)λ_{max}/nm 210 ,257 ,431 ,696 MALDI TOF MS m/z calcd for $C_{69}H_8O$ $[M]^+$852 .0575 ,found 852 .0569

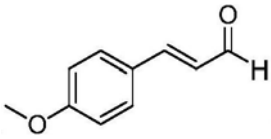
[0022] 2

[0023] [60] 2b

[0024] 

[0025]

[0026] 0.05mmol C_{60} 0.015mmol  0.015mmol 0.05mmol

0.15mmol 1b  25mL

4mL 1mL

90 TLC

[60] 2b 2b 67

[0027] 2b:^{1}H NMR(400MHz,$CDCl_3/CS_2$)δ7.60(d,J 8.4Hz,2H),6.93(d,J 8.8Hz,2H),5.14(dd,J 14.0,6.4Hz,1H),4.29(t,J 14.4Hz,1H),3.80(s,3H),3.64(dd,J 15.6,6.4Hz,1H)

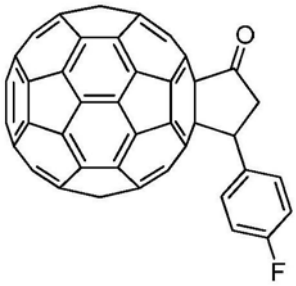
[0028] ^{13}C NMR(150MHz,$CDCl_3/CS_2$with Cr(acac)$_3$as relaxation reagent,all 1C unless indicated)δ205.87,159.24,154.63,151.18,150.84,150.55,148.22,147.15,146.91,146.38,146.23,146.15,146.10,146.02,145.94(2C),145.92,145.88,145.86,145.57,145.36(2C),145.31,145.27,145.24(2C),145.20,145.18,145.12,144.96,144.31,144.26,144.18,144.08,142.89,142.87,142.56(2C),142.48(2C),142.19,141.99,141.91(2C),141.89(2C),141.76,141.74,141.69,141.65(2C),141.41,140.60,140.56,139.86,139.67,135.82,135.70,135.04,134.15,129.80(2C),128.33,114.19(2C),79.00(sp^3 C of C_{60}),74.25(sp^3 C of C_{60}),54.98,53.66,42.31

[0029] FT IRν/cm^{-1}(KBr)1731,1449,1369,1256,1220,1151,1116,1083,854,762,743,707,645,576,526

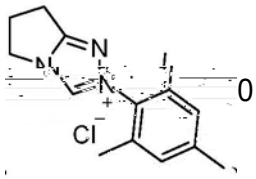
[0030] UV vis($CHCl_3$)λ_{max}/nm 255,314,431,697 MALDI TOF MS m/z calcd for $C_{70}H_{10}O_2$ $[M]^+$882.0681,found 882.0679

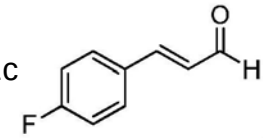
[0031] 3

[0032] [60] 2c

[0033] 

[0034]

[0035] 0.05mmol C_{60} 0.015mmol  0.015mmol 0.05mmol

0.15mmol 1c  25mL

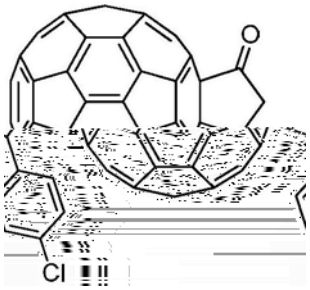
4mL 1mL

110 TLC

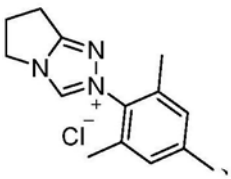
[60] 2c 2c 45

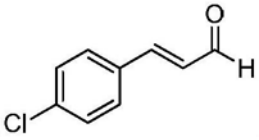
[0036] 2c: ^{1}H NMR (400MHz, $CDCl_3/CS_2$) δ 7.69 (dd, J 8.8, 5.2Hz, 2H), 7.12 (t, J 8.4Hz, 2H), 5.18 (dd, J 13.6, 6.4Hz, 1H), 4.28 (dd, J 15.6, 13.6Hz, 1H), 3.67 (dd, J 15.6, 6.4Hz, 1H)

[0037] ^{13}C NMR (150MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent) δ 136 H

[0042] 

[0043]

[0044] 0.05mmol C_{60} 0.015mmol  0.015mmol 0.05mmol

0.15mmol 1d  25mL

4mL 1mL

110 TLC

[60] 2d 2d 50

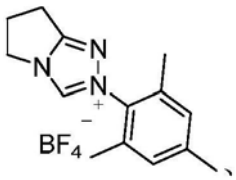
[0045] 2d: ^{1}H NMR(400MHz,$CDCl_3/CS_2$)δ7.65(d,J 8.4Hz,2H),7.41(d,J 8.4Hz,2H),5.16(dd,J 14.0,6.4Hz,1H),4.28(t,J 15.6Hz,1H),3.66(dd,J 15.6,6.4Hz,1H)

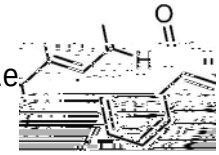
[0046] ^{13}C NMR(150MHz,$CDCl_3/CS_2$with $Cr(acac)_3$as relaxation reagent,all 1C unless indicated)δ205.12,153.96,150.81,150.25,149.95,148.03,147.11,146.84,146.17,146.09,146.07,145.98,145.92,145.89,145.87,145.83,145.80(2C),145.51,145.33,145.24,145.20(2C),145.13(2C),145.11(2C),144.99,144.93,144.24,144.15,144.11,143.97,142.84,142.82,142.52(2C),142.43(2C),142.12,141.93,141.83(3C),141.74,141.69,141.64,141.60(2C),141.56,141.32,140.57(2C),139.84,139.65,135.78,135.65,134.94,134.83,134.30,134.21,129.96(2C),129.00(2C),78.79(sp^3 C of C_{60}),73.56(sp^3 C of C_{60}),53.60,41.90

[0047] FT IRν/cm^{-1}(KBr)1752,1511,1414,1170,1151,1118,1092,1013,822,681,643,573,542,526

[0048] UV vis($CHCl_3$)λ_{max}/nm 257,316,431,696 MALDI TOF MS m/z calcd for $C_{69}H_7ClO$[M]C> "Co

[0052]

[0053] 0.05mmol C_{60} 0.015mmol  0.05mmol K_3PO_4 0.06mmol3,

3',5,5' 4,4' 0.15mmol 1e 

30 TLC

[60] 2 2e 2e

67

[0054] 2e:^{1}H NMR(400MHz,$CDCl_3/CS_2$)δ7.88 7.86(m,2H),7.56 7.53(m,3H),7.29(s,1H),4.73(s,2H)

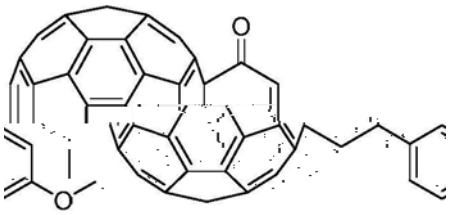
[0055] ^{13}C NMR(150MHz,DMSO $d_6/CS_2$with Cr(acac)$_3$as relaxation reagent,all 2C unless indicated)δ188.51(1C),154.92,152.90(1C),151.81,146.93,146.74(1C),146.54(1C),145.57(4C),145.30,145.27,144.84,144.70,144.62,144.46(4C),144.17,143.75,143.66,142.10,141.75,141.68,141.37,141.13,140.88,140.82,140.73,140.65,139.45,139.14,136.75(1C),134.41,134.27,129.92(1C),128.48,126.13,124.35(1C),74.86(sp^3 C of C_{60},1C),61.42(sp^3 C of C_{60},1C),40.40(1C)

[0056] FT IRν/cm^{-1}(KBr)1673,1649,1613,1572,1512,1462,1445,1426,1213,1187,1032,940,920,903,868,775,761,746,693,580,526

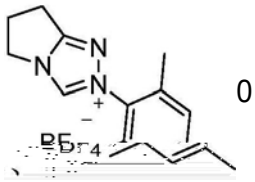
[0057] UV vis($CHCl_3$)λ_{max}/nm 256,433,632,698 MALDI TOF MS m/z calcd for $C_{70}H_8O$ $[M]^+$864.0575,found 864.0559

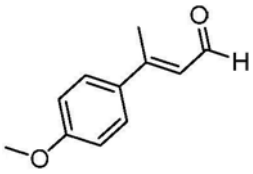
[0058] 6

[0059] [60] 2 2f

[0060] 

[0061]

[0062] 0.05mmol C_{60} 0.015mmol  0.05mmol K_3PO_4 0.06mmol3,

3',5,5' 4,4' 0.15mmol 1f 

40 TLC

[60] 2 2f 2f

65

[0063] 2f:^{1}H NMR(400MHz,DMSO d_6/CS_2)δ7.90(d,J 8.4Hz,2H),7.24(s,1H),7.05(d,J 8.8Hz,2H),4.78(s,2H),3.89(s,3H)

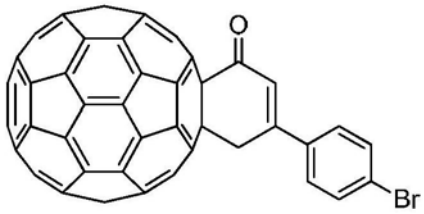
[0064] ^{13}C NMR(150MHz,DMSO d_6/$CS_2$with Cr(acac)$_3$as relaxation reagent,all 2C unless indicated)δ188.13(1C),155.11,152.12,147.05,146.73(1C),146.51(1C),145.54(3C),145.28,145.24,144.85,144.65,144.59,144.43(4C),144.22,143.76,143.65,142.09,141.73,141.66,141.36,141.11,140.87,140.79,140.74,140.62,139.40,139.10,134.27(4C),128.58(1C),127.83,122.18(1C),113.94,74.69(sp^3 C of C_{60},1C),61.30(sp^3 C of C_{60},1C),54.49(1C),40.11(1C)

[0065] FT IRν/cm^{-1}(KBr)1750,1510,1425,1120,794,759,728,576,553,526,470

[0066] UV vis($CHCl_3$)λ_{max}/nm 256,326,433,699 MALDI TOF MS m/z calcd for $C_{71}H_{10}O_2$ $[M]^+$894.0681,found 894.0674

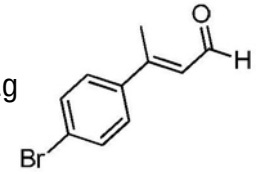
[0067] 7

[0068] [60] 2 2g

[0069] 

[0070]

[0071] 0.05mmol C_{60} 0.015mmol  0.05mmol K_3PO_4 0.06mmol3,

3',5,5' 4,4' 0.15mmol 1g 

35 TLC

[60] 2 2g 2g

62

[0072] 2g:^{1}H NMR(400MHz,DMSO d_6/CS_2)δ7.88(d,J 8.4Hz,2H),7.68(d,J 8.4Hz,2H),7.36(s,1H),4.80(s,2H)

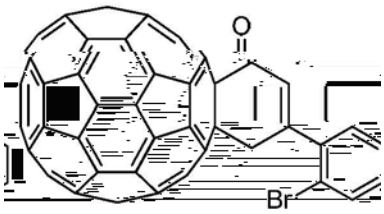
[0073] ^{13}C NMR(150MHz,DMSO d_6/$CS_2$with Cr(acac)$_3$as relaxation reagent,all 2C unless indicated)δ188.55(1C),154.78,151.66(3C),146.86,146.74(1C),146.54(1C),145.57(4C),145.31,145.27,144.82,144.71,144.63,144.47(4C),144.18,143.74,143.66,142.11,141.76,141.69,141.37,141.12,140.85,140.81,140.70,140.65,139.42,139.14,135.61(1C),134.42,134.26,131.62,127.88,124.75(1C),124.71(1C),74.79(sp^3 C of C_{60},1C),61.40(sp^3 C of C_{60},1C),43.36(1C)

[0074] FT IRν/cm^{-1}(KBr)1668,1615,1583,1505,1262,1212,1185,1073,1008,873,815,765,580,526

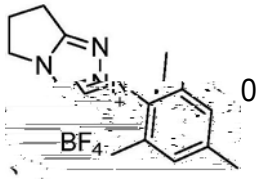
[0075] UV vis($CHCl_3$)λ_{max}/nm 260,314,433,632,697 MALDI TOF MS m/z calcd for $C_{70}H_7BrO$[M] 941.9686,found 941.9675

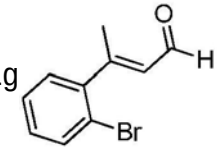
[0076] 8

[0077] [60] 2 2h

[0078] 

[0079]

[0080] 0.05mmol C_{60} 0.015mmol 

0.05mmol K_3PO_4 0.06mmol3,3',5,5' 4,4' 0.15mmol 1g 

45 TLC

[60] 2 2g 2g

40

[0081] 2g:^{1}H NMR(400MHz,DMSO d_6/CS_2)δ7.74(d,J 8.0Hz,1H),7.70(d,J 7.6Hz,1H),7.52(t,J 7.6Hz,1H),7.38(t,J 7.6Hz,1H),7.03(s,1H),4.74(s,2H)

[0082] ^{13}C NMR(150MHz,DMSO d_6/$CS_2$with Cr(acac)$_3$as relaxation reagent,all 2C unless indicated)δ188.37(1C),154.99,151.58,146.96,146.85(1C),146.68(1C),145.70,145.66,145.43,145.40,144.92,144.87,144.72,144.60,144.58,144.15,143.85,

143 .81 ,142 .24 ,141 .88 ,141 .80 ,141 .49 ,141 .26 ,141 .00 ,140 .94 ,140 .84 ,140 .77 ,139 .59 , 139 .55(1C) ,139 .27 ,134 .66 ,134 .28 ,132 .92 ,130 .19(1C) ,129 .68(1C) ,128 .73(1C) , 127 .44(1C) ,120 .88(1C) ,75 .17(sp^3 C of C_{60} ,1C) ,61 .81(sp^3 C of C_{60} ,1C) ,42 .57(1C)

[0083] FT IRν/cm ^{1}(KBr)1676 ,1512 ,1463 ,1429 ,1096 ,855 ,793 ,766 ,660 ,580 ,527

[0084] UV vis($CHCl_3$)λ_{max}/nm 257 ,329 ,433 ,698 MALDI TOF MS m/z calcd for $C_{70}H_7BrO$[M] 941 .9686 ,found 941 .9671

[0085]