锌粉促进三组分“一锅法”合成新型氨基甲酸酯

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摘要 在金属锌的促进下,以醛、溴代烃和异氰酸酯为原料,THF为溶剂,室温、非催化条件下,通过三组分“一锅法”反应合成了一系列新型的氨基甲酸酯类化合物.该方法具有反应条件温和、操作简单、产率高、原料易得、反应迅速的特点.通过 ^1H NMR, ^{13}C NMR, IR, HRMS和元素分析对产物结构进行了表征.

关键词 氨基甲酸酯; 锌粉; 一锅法; 三组分; 合成

One-Pot Three-Component Synthesis of Novel Carbamate Compounds Mediated by Zinc Powder

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Abstract A series of novel carbamate compounds were obtained from one pot three component reaction of aldehydes, bromohydrocarbons and isocyanates mediated by zinc powder under room temperature. This protocol has advantages of mild conditions, simple work-up, high yield, easily available starting materials and fast reaction rate. The structures of all products were characterized by ^1H NMR, ^{13}C NMR, IR, HRMS and elemental analysis.

Keywords carbamate compounds; zinc powder; one-pot; three-component; synthesis

氨基甲酸酯类化合物具有杀虫、抗菌、除草等生物活性,在农药方面具有广泛地应用^[1].此类化合物还具有神经保护、抗肿瘤、抗结核、抗丝虫病、对乙酰胆碱酯酶及内源性大麻素水解酶抑制的药理活性,在医药领域也有广泛地应用^[2].

由于氨基甲酸酯类化合物用途广泛,其合成方法备受关注.传统生产工艺多采用光气为原料^[3],但光气剧毒、易燃,且用量大.生产过程中产生大量强腐蚀性的盐酸,对生产装置的密封和耐腐蚀性能要求很高,致使设备投入增加,而且残余氯难以分离,影响产品质量.为了克服这些缺点,后来出现许多改进的方法,例如用氯甲酸酯^[4]、碳酸酯^[5]或异氰酸酯^[6]来代替光气.但这些方法都需要在催化剂催化,惰性气体的保护下进行,反应相对较慢,并且反应需要大量的有机溶剂.直接利用 CO_2 ^[7]或 CO ^[8]对胺的羰化反应也能合成氨基甲酸酯,但此

方法通常需在高温或高压条件下进行,近年来利用 Lossen^[9], Hofmann^[10], Curtius^[11]重排反应合成氨基甲酸酯类化合物的方法相继被报道.氰酸盐、醇、芳基卤或芳基硼酸三组分在过渡金属铜^[12]或钯^[13]催化下也能合成氨基甲酸酯.这些方法同样存在原料不易得,反应条件相对苛刻,需要有毒过渡金属或贵金属的催化.综上所述,为了克服以上这些缺点,本文报道在价格便宜且对环境友好的金属锌的作用下,利用醛、溴代物和异氰酸酯三组分“一锅法”合成一系列氨基甲酸酯衍生物(Eq. 1).此方法具有反应条件温和、不需催化剂、快速、产率高的优点.

1 结果与讨论

1.1 反应条件考察

首先我们以苯甲醛(5 mmol)、烯丙基溴(5 mmol)和

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对氯苯异氰酸酯(5 mmol)的反应为例,考察了不同金属(1.2 equiv.)对反应活性的影响,实验结果见表1。在室温条件下以四氢呋喃(THF)为溶剂,金属镁、锌、锡均能促进反应的进行。镁反应活性太高易发生副反应使产率降低,锡虽然也能高产率地得到目标产物,但需在三甲基氯硅烷的作用下反应才能引发,且锡有毒,对环境不友好。锌粉廉价易得、无毒,且反应快速、平稳、产率高。

表1 不同金属对反应活性的影响^a

Table 1 Comparison of reaction activity among different metal

Metal	Mg	Zn	Sn ^b	Al	Fe	Pb
Time/h	0.5	1.0	1.0	6.0	6.0	6.0
Yield/%	35	82	80	0	0	0

^a All reactions were carried out in THF (3 mL) at room temperature. Reaction condition: benzaldehyde (5 mmol), allyl bromide (5 mmol), 4-chlorophenyl isocyanate (5 mmol), metal (6 mmol); ^b 10% TMSiCl.

接着,我们仍以苯甲醛(5 mmol)、烯丙基溴(5 mmol)和对氯苯异氰酸酯(5 mmol)的反应为例,考察了溶剂THF及Zn的用量对反应的影响。从表2可以看出,当无溶剂或溶剂的量为2 mL时反应(表2, Entries 1, 2),体系混合物快速凝固,无法搅拌,反应组分之间无法充分混合,从而反应不易进行下去,产物收率较低。当溶剂的量较大时(表2, Entries 4, 5),反应不易引发,需用热枪加热反应才能进行。当溶剂的量是3 mL时反应易发生同时又能高产率的得到目标产物(表2, Entry 3)。当Zn的量低于1.0 equiv.时(表2, Entries 6, 7),产物的量急剧降低,高于1.2 equiv.时产率没有明显增加。因此Zn的量为1.2 equiv.是最佳选择。

表2 Zn和THF的量对反应的影响^a

Table 2 Influence of Zn and THF amount on the reaction

Entry	THF/mL	Zn/equiv.	Yield/%
1	0	1.2	5
2	2	1.2	40
3	3	1.2	82
4 ^b	5	1.2	80
5 ^b	10	1.2	80
6	3	1.0	70
7	3	0.8	30
8	3	1.5	82
9	3	2.0	82

^a All reactions were carried out at room temperature, benzaldehyde (5 mmol), allyl bromide (5 mmol), 4-chlorophenyl isocyanate (5 mmol). ^b A hot air gun was used to triggered the reactions.

1.2 Zn促进的醛、溴代烃、异腈酸酯的三组分反应

在上述得到的较佳反应条件下,我们考察了底物的适用范围。醛可以是其它芳香醛和脂肪醛,溴代烃可以是烯丙基溴、炔丙基溴和溴代乙酸乙酯,异腈酸酯可以是芳基异腈酸酯和脂肪异腈酸酯。从表3可以看出,大部分反应都可高产率地获得目标产物。对于芳香醛来讲,当苯环上连接有氯吸电子基团时比连接有甲基和甲氧基供电子基团时更有利于反应的进行。由于空间因素取代基处于对位或间位时要比处于邻位时有利于反应的进行。但当苯环上连接有吸电子基团硝基时,此反应不能发生,我们推测可能由于硝基将活化好的锌粉颗粒的表面氧化,从而使溴代烃不能与金属锌发生氧化加成反应生成有机锌试剂。脂肪醛同样也适用于该反应,产率与芳香醛相当。对于溴代烃来讲烯丙基溴、炔丙基溴和溴代乙酸乙酯都能发生反应,高产率地得到目标产物,对于 ω -溴苯乙酮和溴代饱和脂肪烃不适用于该反应体系。对于异腈酸酯来讲,芳基异腈酸酯和脂肪异腈酸酯都是用于该反应体系,芳基上取代基的电子效应对反应

表3 Zn粉促进的醛、溴代烃和异腈酸酯三组分反应^a

Table 3 Three-component reaction of aldehyde, bromoalkane, and isocyanate mediated by zinc powder

Product	R ¹	R ²	R ³	Yield/%	m.p./°C
4a	Ph	Allyl	4-ClC ₆ H ₄	82	64~66
4b	2-MeOC ₆ H ₄	Allyl	4-ClC ₆ H ₄	70	66~67
4c	3-MeOC ₆ H ₄	Allyl	4-ClC ₆ H ₄	75	63~65
4d	4-MeC ₆ H ₄	Allyl	4-ClC ₆ H ₄	74	58~60
4e	1-Naphthyl	Allyl	4-ClC ₆ H ₄	80	94~96
4f	4-ClC ₆ H ₄	Allyl	4-ClC ₆ H ₄	90	61~63
4g	2-ClC ₆ H ₄	Allyl	4-ClC ₆ H ₄	82	63~64
4h	Ph	Allyl	Cyclohexyl	80	44~46
4i	4-ClC ₆ H ₄	Allyl	Ph	88	53~55
4j	4-ClC ₆ H ₄	Allyl	4-MeC ₆ H ₄	90	62~64
4k	PhCH=CH	Allyl	4-ClC ₆ H ₄	85	69~71
4l	<i>i</i> -Pr	Allyl	4-ClC ₆ H ₄	80	35~37
4m	<i>n</i> -Bu	Allyl	4-ClC ₆ H ₄	82	46~48
4n	2-MeOC ₆ H ₄	Propargyl	4-ClC ₆ H ₄	65	112~114
4o	2-ClC ₆ H ₄	Propargyl	4-ClC ₆ H ₄	80	113~115
4p	4-ClC ₆ H ₄	Propargyl	4-ClC ₆ H ₄	86	105~106
4q	4-MeOC ₆ H ₄	Propargyl	4-ClC ₆ H ₄	72	87~88
4r	Ph	Propargyl	4-ClC ₆ H ₄	76	77~79
4s	1-Naphthyl	Propargyl	4-ClC ₆ H ₄	75	109~111
4t	4-ClC ₆ H ₄	CH ₂ CO ₂ Et	4-ClC ₆ H ₄	88	99~100
4u	2-ClC ₆ H ₄	CH ₂ CO ₂ Et	4-ClC ₆ H ₄	80	111~112
4v	2-MeOC ₆ H ₄	CH ₂ CO ₂ Et	4-ClC ₆ H ₄	68	97~99
4w	3-MeOC ₆ H ₄	CH ₂ CO ₂ Et	4-ClC ₆ H ₄	79	85~86
4x	4-MeOC ₆ H ₄	CH ₂ CO ₂ Et	4-ClC ₆ H ₄	73	93~94
4y	4-MeC ₆ H ₄	CH ₂ CO ₂ Et	4-ClC ₆ H ₄	75	91~93
4z	Ph	CH ₂ CO ₂ Et	4-ClC ₆ H ₄	84	119~120

^a All reactions were carried out in THF (3 mL) at room temperature. Reaction condition: benzaldehyde (5 mmol), allyl bromide (5 mmol), 4-chlorophenyl isocyanate (5 mmol), zinc powder (6 mmol).

没有影响。

1.3 反应机理

由于金属锌能够促进 Barbier 和 Reformatsky 反应的进行, 推断该反应的历程首先是卤代烃与锌粉发生氧化加成反应生成有机锌试剂 **A**, 有机锌试剂 **A** 再与醛发生亲核加成生成中间体 **B**, 中间体 **B** 作为亲核试剂与异氰酸酯反应得到中间体 **C**, 水解得到目标产物氨基甲酸酯(**4**), 可能的反应历程如 Scheme 1 所示。

Scheme 1

2 结论

研究了不同金属促进醛、溴代烃和异氰酸酯三组分“一锅法”合成氨基甲酸酯的反应。结果表明对环境友好的锌粉能很好地促进反应进行。还研究了 THF 溶剂的量对反应的影响, 其中当底物浓度是 $1.7 \text{ mol} \cdot \text{L}^{-1}$ 时目标产物的产率最高。为合成氨基甲酸酯类化合物提供了一种新方法, 该方法具有反应条件温和、操作简单、产率高、原料易得、反应迅速的优点。

3 实验部分

3.1 仪器与试剂

核磁共振氢谱 ^1H NMR (400 MHz) 和 ^{13}C NMR (100 MHz) 采用 Bruker AV 400 核磁共振仪测定, 所用溶剂为 CDCl_3 , TMS 为内标; 熔点测定仪采用巩义予华仪器有限公司生产的 XT 5 型熔点测定仪(温度未经校正); 红外光谱用美国 VARIAN 公司 Scimitar 2000 型光谱仪测定(KBr 压片); HRMS (ESI) 采用德国 Bruker 公司 esquire-3000 高分辨质谱仪测定; 元素分析用德国 Elementar 公司 Vario EL III 元素分析仪。实验所用试剂均为市售分析化试剂。除 THF 用钠丝干燥重蒸纯化外, 其余试剂均未进一步纯化处理。

3.2 实验方法

3.2.1 锌粉的活化

将 10 g 锌粉和 100 mL 水放入带有搅拌器的 150 mL 烧瓶中。边搅拌边在 1 min 内加入 1 mL 浓盐酸。搅拌该混合物 20 min 后, 将水慢慢倒出。依次用蒸馏水(25 mL $\times$ 3)、丙酮(15 mL $\times$ 3)、(10 mL $\times$ 2)洗涤锌粉。将锌

粉放入真空干燥箱中在 100 $^\circ\text{C}$ 条件下干燥 3 h。待温度降至室温后取出锌粉。实验中所用其它金属活化方法同上。

3.2.2 氨基甲酸酯衍生物的合成

在 50 mL 反应瓶中加入 6 mmol 活化后的锌粉, 5 mmol 醛 **1**, 3 mL THF, 然后加入 5 mmol 溴代烃 **2** 和 5 mmol 异腈酸酯 **3**, 反应 1 h 后向反应瓶中加入 20 mL 乙醚和饱和 NH_4Cl 水溶液 20 mL, 搅拌 2 min, 分出有机相, 水相用乙醚(15 mL $\times$ 2)萃取后, 合并有机相, MgSO_4 干燥, 将有机相旋蒸去掉溶剂, 剩余物通过柱层析纯化, 用石油醚和乙酸乙酯作洗脱剂, 得目标产物 **4a**~**4z**。

N-(4-氯苯基)氨基甲酸[1-(苯基高烯丙)酯(**4a**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.41~7.27 (m, 9H), 6.78 (s, 1H), 5.86~5.74 (m, 2H), 5.16 (dd, $J=23.2$, 5.9 Hz, 2H), 2.80~2.62 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.7, 139.9, 136.4, 133.2, 129.0, 128.5, 128.4, 128.1, 126.5, 119.8, 118.2, 76.5, 40.7; IR (KBr) ν : 3281, 3061, 1704, 1601, 1541, 1489, 1229, 1049, 822 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 324.0762, found 324.0758. Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_2$: C 67.66, H 5.34, N 4.64; found C 67.32, H 5.28, N 4.60。

N-(4-氯苯基)氨基甲酸[1-(2-甲氧苯基)高烯丙]酯(**4b**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.28~7.15 (m, 6H), 6.91~6.80 (m, 3H), 6.19 (dd, $J=7.0$, 5.7 Hz, 1H), 5.75 (ddt, $J=17.1$, 10.2, 6.9 Hz, 1H), 5.03 (dd, $J=24.4$, 6.0 Hz, 2H), 3.77 (s, 3H), 2.59~2.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 156.0, 152.8, 136.7, 133.8, 128.9, 128.8, 128.7, 128.2, 126.3, 120.5, 119.8, 117.6, 110.6, 71.1, 55.5, 39.7; IR (KBr) ν : 3279, 3066, 2932, 1702, 1599, 1531, 1494, 1233, 1045, 819 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 354.0867, found 354.0872. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3$: C 65.16, H 5.47, N 4.22; found C 65.07, H 5.51, N 4.15。

N-(4-氯苯基)氨基甲酸[1-(3-甲氧苯基)高烯丙]酯(**4c**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.38~7.27 (m, 5H), 7.00~6.81 (m, 3H), 6.81 (s, 1H), 5.82~5.70 (m, 2H), 5.19~5.11 (m, 2H), 3.85 (s, 3H), 2.77~2.62 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 159.7, 152.6, 141.6, 136.4, 133.2, 129.6, 129.0, 128.4, 119.8, 118.7, 118.2, 113.2, 112.3, 76.3, 55.2, 40.8; IR (KBr) ν : 3284, 3062, 1701, 1602, 1534, 1497, 1238, 1050, 820, 765 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 354.0867, found 354.0874. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3$: C 65.16, H 5.47, N 4.22; found C 65.04, H 5.58, N 4.01。

N-(4-氯苯基)氨基甲酸[1-(4-甲苯基)高烯丙]酯(**4d**):

白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.36~7.21 (m, 8H), 6.80 (s, 1H), 5.83~5.74 (m, 2H), 5.19~5.11 (m, 2H), 2.80~2.73 (m, 1H), 2.68~2.63 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.7, 137.9, 136.9, 136.5, 133.4, 129.2, 129.0, 128.3, 126.5, 119.8, 118.1, 76.4, 40.6, 21.2; IR (KBr) ν : 3283, 3068, 2933, 1701, 1600, 1539, 1497, 1232, 1054, 820 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 338.0918, found 338.0914. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2$: C 68.46, H 5.75, N 4.44; found C 68.65, H 5.62, N 4.56.

N-(4-氯苯基)氨基甲酸[1-(1-萘基)高烯丙]酯(**4e**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 8.21 (d, $J=8.4$ Hz, 1H), 7.92~7.85 (m, 2H), 7.61~7.52 (m, 4H), 7.35~7.26 (m, 4H), 6.85 (s, 1H), 6.65 (t, $J=6.6$ Hz, 1H), 5.94~5.83 (m, 1H), 5.17 (dd, $J=24.0, 13.6$ Hz, 2H), 2.90~2.84 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.7, 136.4, 135.8, 133.9, 133.5, 130.3, 129.0, 128.7, 128.4, 127.7, 126.5, 125.8, 125.2, 123.8, 123.1, 119.8, 118.1, 73.6, 40.4; IR (KBr) ν : 3287, 3068, 1699, 1599, 1542, 1498, 1234, 1054, 827, 782 cm^{-1} ; HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 374.0918, found 374.0922. Anal. calcd for $\text{C}_{21}\text{H}_{18}\text{ClNO}_2$: C 71.69, H 5.16, N 3.98; found C 71.93, H 5.30, N 3.65.

N-(4-氯苯基)氨基甲酸[1-(4-氯苯基)高烯丙]酯(**4f**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.38~7.27 (m, 8H), 6.75 (s, 1H), 5.81~5.70 (m, 2H), 5.17~5.125 (m, 2H), 2.76~2.58 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.5, 138.4, 136.2, 133.9, 132.7, 129.0, 128.7, 128.6, 127.9, 119.8, 118.6, 75.7, 40.6; IR (KBr) ν : 3275, 3077, 2944, 1702, 1601, 1542, 1493, 1236, 1051, 827 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 358.0372, found 358.0370. Anal. calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{NO}_2$: C 60.73, H 4.50, N 4.17; found C 60.66, H 4.34, N 4.23.

N-(4-氯苯基)氨基甲酸[1-(2-氯苯基)高烯丙]酯(**4g**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.46~7.25 (m, 8H), 6.80 (s, 1H), 6.26 (dd, $J=7.5, 5.3$ Hz, 1H), 5.85 (ddt, $J=17.1, 10.2, 6.9$ Hz, 1H), 5.18~5.13 (m, 2H), 2.74~2.62 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.3, 138.0, 136.3, 132.9, 132.1, 129.7, 129.0, 129.0, 128.5, 127.0, 119.8, 118.3, 73.1, 39.6; IR (KBr) ν : 3280, 3066, 2933, 1703, 1602, 1536, 1492, 1234, 1048, 821, 765 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 358.0372, found 358.0368. Anal. calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{NO}_2$: C 60.73, H 4.50, N 4.17; found C 60.63, H 4.37, N 4.21.

N-环己基氨基甲酸(1-苯基高烯丙)酯(**4h**): 白色固

体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.38~7.27 (m, 5H), 5.78~5.68 (m, 2H), 5.11~5.04 (m, 2H), 4.66 (s, 1H), 3.48~3.46 (m, 1H), 2.70~2.55 (m, 2H), 1.92 (dd, $J=36.3, 10.0$ Hz, 2H), 1.74~1.59 (m, 3H), 1.37~1.30 (m, 2H), 1.19~1.09 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 155.0, 140.7, 133.6, 128.3, 127.7, 126.4, 117.7, 75.3, 49.8, 40.9, 33.4, 25.5, 24.8; IR (KBr) ν : 3313, 3074, 2932, 1686, 1538, 1445, 1239, 1054, 694 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 296.1621, found 296.1629. Anal. calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2$: C 74.69, H 8.48, N 5.12; found C 74.81, H 8.51, N 5.01.

N-苯基氨基甲酸[1-(4-氯苯基)高烯丙]酯(**4i**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.52~7.25 (m, 8H), 7.09 (t, $J=7.3$ Hz, 1H), 6.85 (s, 1H), 5.86~5.66 (m, 2H), 5.21~5.04 (m, 2H), 2.81~2.66 (m, 1H), 2.66~2.52 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.9, 139.9, 138.9, 135.1, 134.1, 130.3, 130.0, 129.2, 124.8, 119.9, 119.8, 76.8, 41.9; IR (KBr) ν : 3280, 3060, 1702, 1600, 1539, 1484, 1227, 1043, 822 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 324.0762, found 324.0759. Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_2$: C 67.66, H 5.34, N 4.64; found C 67.41, H 5.60, N 4.41.

N-(4-甲基苯基)氨基甲酸[1-(4-氯苯基)高烯丙]酯(**4j**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.36~7.28 (m, 6H), 7.12 (d, $J=9.1$ Hz, 2H), 6.79 (s, 1H), 5.80~5.72 (m, 2H), 5.15~5.10 (m, 2H), 2.75~2.58 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.8, 138.7, 135.1, 133.7, 133.1, 132.9, 129.5, 128.6, 127.9, 118.8, 118.4, 75.4, 40.7, 20.7; IR (KBr) ν : 3282, 3061, 1703, 1601, 1540, 1487, 1228, 1047, 820 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 338.0918, found 338.0922. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_2$: C 68.46, H 5.75, N 4.44; found C 68.40, H 5.80, N 4.46.

N-(4-氯苯基)氨基甲酸[1-(2-苯乙烯基)高烯丙]酯(**4k**): 白色固体。 ^1H NMR (400 MHz, CDCl_3) δ : 7.42~7.27 (m, 9H), 6.72~6.69 (m, 2H), 6.21 (dd, $J=15.9, 7.2$ Hz, 1H), 5.86 (ddt, $J=17.2, 10.2, 7.0$ Hz, 1H), 5.51 (q, $J=6.4$ Hz, 1H), 5.22~5.14 (m, 2H), 2.61~2.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.7, 136.5, 136.2, 133.0, 132.9, 129.0, 128.6, 128.4, 128.0, 126.9, 126.6, 119.9, 118.3, 75.0, 39.2; IR (KBr) ν : 3332, 1701, 1592, 1519, 1398, 1227, 1050, 966, 822 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 350.0918, found 350.0924. Anal. calcd for $\text{C}_{19}\text{H}_{18}\text{ClNO}_2$: C 69.62, H 5.53, N 4.27; found C 69.27, H 5.40, N 4.11.

N-(4-氯苯基)氨基甲酸(1-异丙基高烯丙)酯(**4l**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.36 (d, $J=8.3$ Hz, 2H), 7.26 (t, $J=9.1$ Hz, 2H), 6.89 (s, 1H), 5.84~5.77 (m, 1H), 5.14~5.06 (m, 2H), 4.77 (dd, $J=12.5$, 5.4 Hz, 1H), 2.36 (ddd, $J=20.9$, 10.5, 6.1 Hz, 2H), 1.91 (dd, $J=13.0$, 6.6 Hz, 1H), 0.96 (d, $J=6.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.5, 136.8, 134.0, 128.9, 128.2, 119.9, 117.5, 78.9, 36.0, 31.1, 18.5, 17.5; IR (KBr) ν : 3320, 2965, 1700, 1642, 1597, 1532, 1401, 1226, 1052, 1012, 917, 828 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 290.0918, found 290.0906. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{ClNO}_2$: C 62.80, H 6.78, N 5.23; found C 69.67, H 6.60, N 5.28.

N-(4-氯苯基)氨基甲酸(1-正丁基高烯丙)酯(**4m**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.36 (d, $J=8.3$ Hz, 2H), 7.27 (t, $J=9.1$ Hz, 2H), 6.66 (s, 1H), 5.86~5.78 (m, 1H), 5.14~5.09 (m, 2H), 4.94~4.89 (m, 1H), 2.40~2.35 (m, 2H), 1.62~1.61 (m, 2H), 1.38~1.32 (m, 4H), 0.93~0.91 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.2, 136.7, 133.6, 129.0, 128.2, 119.8, 117.7, 74.8, 38.7, 33.4, 27.4, 22.5, 13.9; IR (KBr) ν : 3316, 2955, 1697, 1644, 1593, 1532, 1401, 1235, 1058, 1012, 918, 826 cm^{-1} . HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 304.1075, found 304.1083. Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{ClNO}_2$: C 63.94, H 7.15, N 4.97; found C 63.77, H 7.32, N 4.73.

N-(4-氯苯基)氨基甲酸[1-(2-甲氧苯基)高烯丙]酯(**4n**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.42~7.25 (m, 6H), 6.98 (t, $J=7.5$ Hz, 1H), 6.91~6.89 (m, 2H), 6.31 (dd, $J=6.8$, 4.8 Hz, 1H), 3.87 (s, 3H), 2.82 (dddd, $J=17.1$, 9.6, 5.8, 2.6 Hz, 2H), 2.01 (t, $J=2.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 155.9, 152.3, 136.4, 129.2, 129.0, 128.4, 127.2, 126.4, 120.4, 119.7, 110.5, 80.1, 70.4, 69.6, 55.4, 25.1; IR (KBr) ν : 3260, 3080, 1706, 1604, 1548, 1492, 1239, 1076, 825, 748 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{ClNO}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 352.0711, found 352.0716. Anal. calcd for $\text{C}_{18}\text{H}_{16}\text{ClNO}_3$: C 65.56, H 4.89, N 4.25; found C 65.34, H 4.99, N 4.23.

N-(4-氯苯基)氨基甲酸[1-(2-氯苯基)高烯丙]酯(**4o**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.52 (d, $J=6.9$ Hz, 1H), 7.41~7.26 (m, 7H), 6.90 (s, 1H), 6.31 (dd, $J=6.4$, 5.1 Hz, 1H), 2.86 (dddd, $J=17.2$, 9.3, 5.8, 2.7 Hz, 2H), 2.04 (t, $J=2.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.0, 136.5, 136.1, 132.0, 129.7, 129.4, 129.0, 128.6, 127.3, 127.0, 119.8, 79.0, 71.2, 71.0, 25.0; IR (KBr) ν : 3278, 3069, 1703, 1600, 1537, 1496, 1235, 1066, 827, 757 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$

356.0216, found 356.0214. Anal. calcd for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{NO}_2$: C 61.10, H 3.92, N 4.19; found C 61.01, H 3.80, N 4.21.

N-(4-氯苯基)氨基甲酸[1-(4-氯苯基)高烯丙]酯(**4p**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.39~7.29 (m, 8H), 6.82 (s, 1H), 5.89 (t, $J=6.4$ Hz, 1H), 2.89~2.76 (m, 2H), 2.06 (t, $J=2.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.1, 137.3, 136.1, 134.4, 129.1, 128.8, 127.9, 119.9, 79.0, 74.0, 71.3, 26.5; IR (KBr) ν : 3287, 3071, 1704, 1602, 1541, 1490, 1229, 1078, 822 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 356.0216, found 356.0212. Anal. calcd for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{NO}_2$: C 61.10, H 3.92, N 4.19; found C 61.13, H 3.79, N 4.02.

N-(4-氯苯基)氨基甲酸[1-(4-甲氧苯基)高烯丙]酯(**4q**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.40~7.27 (m, 6H), 6.94 (d, $J=8.6$ Hz, 2H), 6.81 (s, 1H), 5.89 (t, $J=6.6$ Hz, 1H), 3.85 (s, 3H), 2.84 (qdd, $J=16.9$, 6.5, 2.5 Hz, 2H), 2.05 (t, $J=2.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 159.7, 152.4, 136.3, 130.9, 129.0, 128.5, 127.9, 119.8, 113.9, 79.6, 74.4, 70.8, 55.3, 26.4; IR (KBr) ν : 3348, 3267, 3013, 1703, 1600, 1522, 1222, 1031, 824 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{ClNO}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 352.0711, found 352.0716. Anal. calcd for $\text{C}_{18}\text{H}_{16}\text{ClNO}_3$: C 65.56, H 4.89, N 4.25; found C 65.34, H 4.73, N 4.40.

N-(4-氯苯基)氨基甲酸(1-苯基高烯丙)酯(**4r**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.34~7.15 (m, 9H), 6.71 (s, 1H), 5.82 (t, $J=6.5$ Hz, 1H), 2.80~2.66 (m, 2H), 1.93 (t, $J=2.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.3, 138.8, 136.3, 129.0, 128.6, 128.5, 126.4, 119.9, 79.4, 74.7, 70.9, 26.6; IR (KBr) ν : 3285, 3072, 1703, 1601, 1541, 1487, 1228, 1077, 820 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 322.0605, found 322.0610. Anal. calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_2$: C 68.12, H 4.71, N 4.67; found C 68.34, H 4.89, N 4.39.

N-(4-氯苯基)氨基甲酸[1-(1-萘基)高烯丙]酯(**4s**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 8.18 (d, $J=8.4$ Hz, 1H), 7.91 (dd, $J=19.2$, 8.0 Hz, 2H), 7.76~7.51 (m, 4H), 7.39~7.28 (m, 4H), 6.90 (s, 1H), 6.75 (t, $J=6.3$ Hz, 1H), 3.04~3.02 (m, 2H), 2.09 (t, $J=2.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.4, 136.2, 134.5, 133.8, 130.2, 129.1, 129.0, 128.6, 126.7, 125.9, 125.2, 124.0, 122.7, 119.8, 79.6, 71.8, 71.1, 26.1; IR (KBr) ν : 3291, 3067, 1703, 1601, 1541, 1503, 1231, 1060, 782 cm^{-1} ; HRMS calcd for $\text{C}_{21}\text{H}_{16}\text{ClNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 372.0762, found 372.0766. Anal. calcd for $\text{C}_{21}\text{H}_{16}\text{ClNO}_2$: C 72.10, H 4.61, N 4.00; found C 72.45, H 4.88, N 3.85.

3-(4-氯苯基)-3-(4-氯苯基甲酰氧基)丙酸乙酯(**4t**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.38~7.26 (m, 8H), 6.78 (s, 1H), 6.17 (dd, $J=8.9, 5.3$ Hz, 1H), 4.18 (qd, $J=7.1, 1.4$ Hz, 2H), 2.92 (ddd, $J=21.1, 15.7, 7.1$ Hz, 2H), 1.26 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.4, 152.0, 137.6, 136.1, 134.4, 129.0, 128.9, 128.6, 127.9, 119.8, 72.7, 61.0, 41.4, 14.1; IR (KBr) ν : 3319, 3055, 2982, 1728, 1706, 1596, 1536, 1494, 1227, 1042, 822 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 404.0427, found 404.0432. Anal. calcd for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}_4$: C 56.56, H 4.48, N 3.66; found C 56.45, H 4.65, N 3.57.

3-(3-氯苯基)-3-(4-氯苯基甲酰氧基)丙酸乙酯(**4u**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.48~7.26 (m, 8H), 6.91 (s, 1H), 6.56 (dd, $J=9.1, 4.4$ Hz, 1H), 4.26~4.17 (m, 2H), 2.93 (qd, $J=15.8, 6.7$ Hz, 2H), 1.28 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.6, 151.8, 137.1, 136.2, 131.9, 129.9, 129.4, 129.0, 128.6, 127.2, 126.8, 119.8, 70.5, 61.0, 40.2, 14.1; IR (KBr) ν : 3333, 3067, 2981, 1735, 1707, 1602, 1538, 1493, 1231, 1185, 1092, 1035, 824 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 404.0427, found 404.0430. Anal. calcd for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}_4$: C 56.56, H 4.48, N 3.66; found C 56.46, H 4.57, N 3.76.

3-(2-甲氧苯基)-3-(4-氯苯基甲酰氧基)丙酸乙酯(**4v**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.38~7.25 (m, 6H), 6.98~6.91 (m, 3H), 6.55 (dd, $J=8.9, 4.5$ Hz, 1H), 4.24~4.15 (m, 2H), 3.90 (s, 3H), 2.97~2.86 (m, 2H), 1.27 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.7, 159.8, 152.1, 140.7, 136.3, 129.8, 129.0, 128.5, 119.8, 118.5, 113.7, 112.1, 73.2, 60.9, 55.2, 41.7, 14.1; IR (KBr) ν : 3311, 3066, 2988, 1734, 1702, 1598, 1538, 1493, 1229, 1026, 832 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 400.0922, found 400.0924. Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_5$: C 60.40, H 5.34, N 3.71; found C 60.26, H 5.23, N 3.78.

3-(3-甲氧苯基)-3-(4-氯苯基甲酰氧基)丙酸乙酯(**4w**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.36~7.26 (m, 5H), 7.03~6.97 (m, 2H), 6.89 (dd, $J=8.2, 2.1$ Hz, 1H), 6.81 (s, 1H), 6.19 (dd, $J=9.3, 4.8$ Hz, 1H), 4.19 (qd, $J=7.1, 2.7$ Hz, 2H), 3.84 (s, 3H), 2.93 (ddd, $J=20.5, 15.7, 7.1$ Hz, 2H), 1.27 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.7, 159.8, 152.1, 140.7, 136.3, 129.8, 129.0, 128.5, 119.8, 118.5, 113.8, 112.1, 73.2, 60.9, 55.2, 41.7, 14.1; IR (KBr) ν : 3311, 3061, 2989, 1727, 1700, 1599, 1538, 1494, 1286, 1224, 1041, 825 cm^{-1} ; HRMS

calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 400.0922, found 400.0926. Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_5$: C 60.40, H 5.34, N 3.71; found C 60.49, H 5.45, N 3.63.

3-(4-甲氧苯基)-3-(4-氯苯基甲酰氧基)丙酸乙酯(**4x**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.36~7.22 (m, 6H), 6.91~6.88 (m, 2H), 6.15 (dd, $J=9.0, 5.3$ Hz, 1H), 4.15 (qd, $J=7.1, 1.8$ Hz, 2H), 3.80 (s, 3H), 2.91 (ddd, $J=20.9, 15.6, 7.2$ Hz, 2H), 1.23 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.7, 159.7, 152.1, 136.3, 131.1, 128.9, 128.4, 128.0, 119.7, 114.0, 73.1, 60.8, 55.2, 41.4, 14.1; IR (KBr) ν : 3368, 3060, 2982, 1739, 1702, 1596, 1530, 1218, 1161, 1087, 829 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 400.0922, found 400.0926. Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_5$: C 60.40, H 5.34, N 3.71; found C 60.65, H 5.43, N 3.62.

3-(4-甲氧苯基)-3-(4-氯苯基甲酰氧基)丙酸乙酯(**4y**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.32~7.17 (m, 8H), 6.70 (s, 1H), 6.16 (dd, $J=9.1, 5.1$ Hz, 1H), 4.16 (qd, $J=7.1, 1.8$ Hz, 2H), 2.91 (ddd, $J=20.7, 15.6, 7.1$ Hz, 2H), 2.35 (s, 3H), 1.24 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.7, 152.1, 138.4, 136.3, 136.1, 129.3, 128.9, 128.4, 126.4, 119.7, 73.3, 60.8, 41.5, 21.1, 14.1; IR (KBr) ν : 3309, 3062, 2980, 1739, 1704, 1601, 1539, 1218, 1171, 1093, 820 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 384.0973, found 384.0976. Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{ClNO}_4$: C 63.07, H 5.57, N 3.87; found C 63.23, H 5.43, N 3.67.

3-苯基-3-(4-氯苯基甲酰氧基)丙酸乙酯(**4z**): 白色固体. ^1H NMR (400 MHz, CDCl_3) δ : 7.43~7.23 (m, 9H), 6.73 (s, 1H), 6.19 (dd, $J=9.1, 5.1$ Hz, 1H), 4.16 (qd, $J=7.1, 2.3$ Hz, 2H), 2.92 (ddd, $J=20.7, 15.6, 7.1$ Hz, 2H), 1.23 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.7, 152.1, 139.1, 136.2, 129.0, 128.7, 128.5, 126.4, 119.8, 73.3, 60.9, 41.6, 14.1; IR (KBr) ν : 3363, 2985, 1732, 1714, 1597, 1533, 1497, 1317, 1218, 1046, 841, 703 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 370.0817, found 370.0821. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_4$: C 62.16, H 5.22, N 4.03; found C 62.38, H 5.28, N 3.85.

辅助材料(Supporting Information) 合成产物的 ^1H NMR 及 ^{13}C NMR 谱图. 这些材料可以免费从本刊网站 (<http://sioc-journal.cn/>) 上下载.

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