无溶剂锌粉促进下三组分“一锅法”合成 1,2-二芳基乙酯

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摘要 在锌粉的促进下,以芳香醛、溴化苄和酸酐为原料,在无溶剂条件下三组分“一锅法”反应合成了一系列 1,2-二芳基乙酯类化合物.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,为合成 1,2-二芳基乙酯类化合物提供了一种“绿色”、方便的方法.

关键词 苄基化;“一锅法”;锌粉;无溶剂

Zinc Promoted One-Pot Three-Component Synthesis of 1,2-Diaryl Acetates under Solvent-Free Conditions

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Abstract A series of 1,2-diaryl acetates were synthesized by one-pot three-component reaction of aromatic aldehydes, benzyl bromide and anhydrides promoted by zinc powder under solvent-free conditions. This protocol has advantages of mild conditions, simple operation, high yields, easily available starting materials and fast reaction rate, which provides a convenient and “green” method for the synthesis of 1,2-diaryl acetates.

Keywords benzylation; “one-pot”; zinc powder; solvent-free

有机金属试剂对醛、酮等羰基化合物的亲核加成反应是构建碳-碳键最重要的反应之一,在天然产物和药物合成中具有广泛的应用^[1].目前报道的有机金属试剂主要包括有机锂试剂^[2]、有机镁试剂(格氏试剂)^[3]、有机铝试剂^[4]、有机锌试剂^[5]、有机锡试剂^[6]、有机硅试剂^[7]、有机铁试剂^[8]、有机钼试剂^[9]和有机硼试剂^[10]等.虽然有机金属试剂与醛的加成反应取得很大进展,然而这些方法普遍存在对水和空气敏感、金属试剂有毒、官能团相容性差、反应条件苛刻等缺点.为了克服这些缺点,化学家们一直致力于发展新的催化剂,新的反应试剂和新的反应方法.最近, Iranpoora 等^[11]报道了在锌粉和 MgCl_2 存在条件下,以 DMF 为溶剂, $\text{NiCl}_2(\text{dppf})_2$ 催化下苄基卤与醛的还原苄基化反应.目前最好的办法就是原位生成金属试剂直接与羰基化合物发生加成反应.

随着“绿色化学”概念的发展和深入,环境友好-

经济性已成为技术创新的主要推动力,同时对有机合成化学提出了严峻的挑战^[12].发展更为温和的化学合成工艺对于有机合成化学的可持续发展是非常重要的.为了降低有机合成对环境的污染,化学家们发展了许多取代传统有机溶剂的“洁净”反应介质,诸如水^[13]、离子液体^[14]、超临界流体或近临界流体^[15]、聚乙二醇^[16]等.另一种策略则是干脆不使用反应介质,即所谓的“无溶剂”有机合成^[17].无溶剂有机合成的优点显而易见:这些方法除了可取代传统有机溶剂、减少污染外,还能反应分子提供不同于反应介质中的新的反应环境,因而有可能使反应的选择性、转化率得到改善和提高,或使分离提纯等操作过程较容易进行.这些特点促使无溶剂反应的研究日益重视,使之成为绿色化学的重要组成部分.

1,2-二芳基乙酯是一类重要的化合物,在天然产物

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合成中和有机化学理论研究方面有着重要的用途^[18]. 1,2-二芳基乙酯的合成通常是分两步进行的: 第一步, 苄基有机金属试剂对羰基化合物进行加成反应制备 1,2-二芳基乙醇^[19]; 第二步, 1,2-二芳基乙醇与酰化试剂进行反应得到羧酸芳基乙酯. 此外, 多步骤有机合成反应中, 底物中的羟基往往需要保护. 如果将羟基的形成和酰化反应在一锅中进行, 则可以减少分离步骤, 简化实验操作, 从而减少浪费, 降低成本. 本文报道了环境友好无溶剂条件下锌粉促进的醛、苄基溴和酸酐三组分“一锅法”合成 1,2-二芳基乙酯的新方法(Eq. 1).

1 结果与讨论

1.1 反应条件的优化

以 2-氯苯甲醛(4 mmol)、苄基溴(5 mmol)和乙酸酐(5 mmol)的反应作为模型反应, 考察了不同金属、溶剂及反应时间对反应的影响. 实验结果见表 1. 从表 1 可以看出镁、锌铜偶都可促进该反应的进行. 用锌粉促进该反应产率明显高于用镁和锌铜偶(表 1, Entries 1, 2, 4), 而金属铜、铁、镍、铝和锰即使在加入活化试剂 TMSCl 的情况下也不能促进该反应进行. 对于金属锌, 不需向反应体系中加入 TMSCl 反应即可快速进行, 且反应后处理简单, 用 TLC 监测反应结束后, 用饱和氯化铵水溶

表 1 反应条件优化^a

Table 1 Optimization of reaction conditions

Entry	Metal	Solvent	t/h	Yield ^b /%
1	Mg	THF	12	42
2	Zn-Cu	THF	12	45
3	Cu	THF	12	0
4	Zn	THF	12	70
5	Zn	None	6	95
6 ^c	Fe	THF	12	0
7 ^c	Co	THF	12	0
8 ^c	Ni	THF	12	0
9 ^c	Mn	THF	12	0
10 ^c	Al	THF	12	0

^a All reactions were performed on the following scale: 5.0 mmol of zinc powder, 4.0 mmol of 2-chlorobenzaldehyde 5.0 mmol of benzyl bromide and 5.0 mmol of acetic anhydride at room temperature. ^b Yields of isolated products.

^c 20 mol% TMSCl were added.

液淬灭反应, 乙醚萃取, 柱色谱分离即可得到产物. 进一步优化反应条件发现, 反应在无溶剂条件下, 反应时间缩短至 6 h, 产率可以达到 95%(表 1, Entry 5).

2.2 反应的底物适用范围

无溶剂锌粉促进条件下芳香醛 **1**、苄基溴 **2**、酸酐 **3** 三组分“一锅法”合成 1,2-二芳基乙酯 **4a~4z** 的反应结果见表 2. 在实验过程中, 我们采用 $n(\text{锌粉}):n(\text{醛}):n(\text{苄基溴}):n(\text{酸酐})=5:4:5:5$ 的物料比, 以保证醛充分转化为相应的产物. 我们考察了底物的适用范围. 从表 2 可以看出, 大部分反应都可高产率地获得目标产物. 芳香醛苯环上无论连有吸电子基团还是供电子基团都适用于该反应体系. 当苯环上有吸电子基团时有利于该反应的进行, 产率较高. 例如, 4-溴苯甲醛以 86% 的反应产率得到相应的 1,2-二芳基乙酯(表 2, Entry 5); 当苯环上有供电子基团时不利于该反应的进行, 产率相对较低. 如 4-甲氧基苯甲醛则产率较低, 仅为 48%(表 2, Entry 3), 在该条件下副反应明显, 生成相应的 1,2-二苯乙烯(32%). 杂环醛、稠环醛也能得到中等产率的 1,2-二芳基乙酯, 例如呋喃甲醛和 9-蒽醛分别以 66% 和 65% 的产率得到相应的 1,2-二芳基乙酯类化合物(表 2, Entries 14, 15).

苄基溴可以是取代的苄基溴, 如 4-氯苄溴、2-氯苄溴和 α -萘甲基溴也都能参与该反应, 以中等产率(64%~75%)得到相应的 1,2-二芳基乙酯(表 2, Entries 16~20). 苯甲酸酐也能发生反应(表 2, Entries 21~26), 以较高的产率(72%~88%)得到相应的 1,2-二芳基乙酯类化合物.

2 结论

从环境友好的角度出发, 本文探索了无溶剂条件下锌粉促进芳香醛、苄基溴和酸酐三组分“一锅法”反应, 合成一系列 1,2-二芳基乙酯类化合物. 该方法不仅适用于苄基溴, 而且还适用于取代苄基溴; 乙酸酐、苯甲酸酐都能很好地参与反应. 与文献报道的方法相比, 该方法具有操作简单、底物适用范围广等特点. 更为重要的是它符合“绿色化学”的基本要求, 为力求从根本上消除溶剂污染提供了一种绿色合成方法.

3 实验部分

3.1 仪器与试剂

红外光谱仪为 FT IR 型仪器, 液体样品采用液膜法, 固体样品采用 KBr 压片法; 核磁共振氢谱 ¹H NMR (400 MHz) 和 ¹³C NMR (100 MHz) 采用 Bruker AV 400 核磁共振仪测定, 所用溶剂为 CDCl₃, TMS 为内标; 质谱用

表2 无溶剂条件下锌粉促进的芳香醛、苄基溴和酸酐三组分反应^a

Table 2 One-pot three-component synthesis of benzyl esters from aromatic aldehydes promoted by zinc powder under solvent-free conditions

Entry	R	R ¹	R ²	Product ^b	Yield ^c /%
1	H	H	Me	4a	68
2	4-Me	H	Me	4b	72
3	4-OMe	H	Me	4c	48
4	4-Cl	H	Me	4d	82
5	4-Br	H	Me	4e	88
6	2-OMe	H	Me	4f	73
7	2-Cl	H	Me	4g	95
8	2-Br	H	Me	4h	80
9	3-OMe	H	Me	4i	75
10	3-Cl	H	Me	4j	78
11	3-Br	H	Me	4k	71
12	2,4-Cl ₂	H	Me	4l	86
13	2,6-Cl ₂	H	Me	4m	91
14	(2-C ₄ H ₃ O)	H	Me	4n	66
15	(2-C ₁₄ H ₁₄)	H	Me	4o	65
16	2-Cl	4-Cl	Me	4p	70
17	4-Cl	4-Br	Me	4q	73
18	2-Cl	4-Br	Me	4r	75
19	4-Cl	(2-C ₁₀ H ₇)	Me	4s	68
20	2-Cl	(2-C ₁₀ H ₇)	Me	4t	64
21	4-Cl	H	Ph	4u	86
22	4-Br	H	Ph	4v	75
23	2-Cl	H	Ph	4w	80
24	3-Br	H	Ph	4x	72
25	2,4-Cl ₂	H	Ph	4y	88
26	2,6-Cl ₂	H	Ph	4z	84

^a All reactions were performed on the following scale: 5.0 mmol of zinc powder, 4.0 mmol of aromatic aldehydes, 5.0 mmol of benzyl bromide and 5.0 mmol acetic anhydride or benzoic anhydride at room temperature for 3~6 h.

^b All products were characterized by ¹H NMR, ¹³C NMR, IR, MS and elemental analysis for all new compounds. ^c Yields of isolated products.

QP-1000A GC-MS 测定, EI 源质谱仪测定; 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纯试剂, 均未进一步纯化处理.

3.2 实验方法

在干燥洁净的 50 mL 圆底烧瓶中加入 5.0 mmol 锌粉和 4.0 mmol 醛, 然后经由滴液漏斗加入 5.0 mmol 酸酐和 5.0 mmol 苄基溴的混合物, 在室温下混合物发生

反应, TLC 跟踪反应直到反应完成(约 3~6 h). 反应结束后向反应瓶中加入饱和氯化铵水溶液(10 mL)搅拌 5 min, 然后用 15 mL 乙醚萃取, 分离有机相. 水相用乙醚(15 mL×2)萃取后, 合并有机相. 将有机相用无水 MgSO₄ 干燥, 然后减压旋蒸去除溶剂, 剩余物柱色谱分离纯化, 用石油醚和乙酸乙酯作洗脱剂, 得目标产物 **4a~4z**.

乙酸[1,2-二苯基]乙酯(**4a**)^[20]: 无色油状液体; ¹H NMR (400 MHz, CDCl₃) δ: 7.36~7.09 (m, 10H), 5.96~5.92 (m, 1H), 3.21~3.17 (m, 1H), 3.08~3.02 (m, 1H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 170.1, 140.0, 137.0, 129.5, 128.3, 128.2, 127.9, 126.6, 126.5, 76.6, 42.9, 21.1; IR (KBr) ν: 3456, 3033, 2927, 1739, 1372, 1236, 1025, 758, 700 cm⁻¹; EI-MS *m/z* (%): 180 (M⁺-60, 13.6), 149 (22.4), 107 (6.5), 91 (19.2), 77 (17.3), 65 (11.8), 43 (100).

乙酸[1-(4-甲基苯基)-2-苯基]乙酯(**4b**)^[20a]: 无色油状液体; ¹H NMR (400 MHz, CDCl₃) δ: 7.37~7.11 (m, 9H), 6.34 (dd, *J*=8.0, 6.0 Hz, 1H), 3.21~3.00 (m, 2H), 2.44 (s, 3H), 1.99 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ: 170.1, 137.7, 137.1, 137.0, 129.7, 129.5, 129.0, 128.5, 128.3, 128.2, 126.6, 126.5, 76.5, 42.8, 21.2, 21.1; IR (KBr) ν: 3455, 3029, 2925, 1740, 1371, 1237, 1023, 812, 700 cm⁻¹; EI-MS *m/z* (%): 254 (M⁺, 0.1), 194 (4.2), 178 (2.5), 163 (19.6), 121 (81.8), 91 (37.2), 77 (12.8), 65 (19.2), 43 (100).

乙酸[1-(4-甲氧基苯基)-2-苯基]乙酯(**4c**): 白色固体; m.p. 84~85 °C(文献值^[20a] 82.4~83.0 °C); ¹H NMR (400 MHz, CDCl₃) δ: 7.25~6.81 (m, 9H), 5.90 (dd, *J*=7.8, 6.4 Hz, 1H), 3.78 (s, 3H), 3.19 (dd, *J*=13.6, 8.0 Hz, 1H), 3.03 (dd, *J*=13.6, 6.4 Hz, 1H), 1.99 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ: 170.1, 159.3, 137.1, 132.1, 129.5, 128.2, 128.0, 126.5, 113.7, 76.3, 55.2, 42.8, 21.2; IR (KBr) ν: 3447, 3017, 2945, 1730, 1372, 1244, 1049, 758, 698 cm⁻¹; EI-MS *m/z* (%): 270 (M⁺, 1.7), 210 (2.3), 179 (32.8), 137 (100), 107 (20.6), 91 (28.7), 77 (14.2), 65 (13.0), 43 (74.5).

乙酸[1-(4-氯苯基)-2-苯基]乙酯(**4d**): 白色固体, m.p. 90~91 °C(文献值^[20a] 89.2~89.8 °C); ¹H NMR (400 MHz, CDCl₃) δ: 7.28~7.06 (m, 9H), 5.89 (t, *J*=6.8 Hz, 1H), 3.17 (dd, *J*=13.6, 7.2 Hz, 1H), 3.01 (dd, *J*=13.6, 6.0 Hz, 1H), 2.02 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ: 170.0, 138.5, 136.5, 133.7, 129.5, 128.5, 128.3, 128.0, 126.7, 75.9, 42.8, 21.1; IR (KBr) ν: 3437, 3086, 2921, 1729, 1377, 1242, 1047, 751, 705 cm⁻¹; EI-MS *m/z*

(%): 214 ($M^+ - 60$, 9.5), 183 (18.5), 141 (39.5), 91 (26.1), 77 (13.1), 43 (100).

乙酸[1-(4-溴苯基)-2-苯基]乙酯(**4e**)^[20c]: 白色固体; m.p. 90~91 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.44~7.05 (m, 9H), 5.87 (t, $J=7.2$ Hz, 1H), 3.20 (dd, $J=13.6$, 7.6 Hz, 1H), 3.01 (dd, $J=13.6$, 6.0 Hz, 1H), 2.01 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 170.0, 139.0, 136.5, 131.5, 129.5, 128.3, 128.3, 126.7, 121.9, 76.0, 42.7, 21.1; IR (KBr) ν : 3435, 3031, 2918, 1730, 1487, 1376, 1047, 828, 706 cm⁻¹; EI-MS m/z (%): 260 ($M^+ + 2 - 60$, 3.0), 258 ($M^+ - 60$, 3.1), 229 (5.8), 227 (6.0), 187 (10.0), 185 (11.5), 91 (12.1), 77 (6.3), 43 (100).

乙酸[1-(2-甲氧基苯基)-2-苯基]乙酯(**4f**): 白色固体; m.p. 50~52 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.26~6.84 (m, 9H), 6.37 (dd, $J=8.2$, 4.8 Hz, 1H), 3.79 (s, 3H), 3.12 (dd, $J=13.6$, 4.8 Hz, 1H), 3.01 (dd, $J=13.6$, 8.4 Hz, 1H), 2.02 (s, 3H) cm⁻¹; ¹³C NMR (CDCl₃, 100 MHz) δ : 169.9, 156.0, 137.7, 129.5, 128.9, 128.6, 128.0, 126.1, 126.0, 120.4, 110.4, 71.2, 55.4, 41.8, 21.1; IR (KBr) ν : 3441, 3035, 2934, 1731, 1372, 1242, 1032, 746, 703 cm⁻¹; EI-MS m/z (%): 270 (M^+ , 1.5), 211 (2.4), 179 (28.8), 137 (100), 91 (18.6), 77 (13.3), 65 (11.3), 43 (53.7). Anal. calcd for C₁₇H₁₈O₃: C 75.53, H 6.71; found C 75.68; H 6.42.

乙酸[1-(2-氯苯基)-2-苯基]乙酯(**4g**): 无色油状液体; ¹H NMR (400 MHz, CDCl₃) δ : 7.35~7.15 (m, 9H), 6.34 (dd, $J=8.6$, 4.8 Hz, 1H), 3.17 (dd, $J=14.0$, 4.0 Hz, 1H), 3.02 (dd, $J=14.0$, 8.4 Hz, 1H), 2.02 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 169.7, 138.1, 136.9, 135.2, 132.0, 129.5, 129.5, 128.8, 128.2, 127.0, 126.6, 73.2, 41.5, 20.9; IR (KBr) ν : 3465, 3029, 2925, 1745, 1371, 1233, 1027, 757, 701 cm⁻¹; EI-MS m/z (%): 214 (6.7), 183 (42.3), 141 (17.3), 91 (13.3), 77 (8.3), 43 (100). Anal. calcd for C₁₆H₁₅ClO₂: C 69.95, H 5.50; found C 69.85, H 5.58.

乙酸[1-(2-溴苯基)-2-苯基]乙酯(**4h**): 无色油状液体; ¹H NMR (400 MHz, CDCl₃) δ : 7.55~7.12 (m, 9H), 6.34 (dd, $J=8.4$, 4.4 Hz, 1H), 3.18~2.96 (m, 2H), 2.02 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 169.7, 139.8, 136.9, 132.8, 129.5, 129.1, 128.2, 127.5, 127.1, 126.6, 122.6, 75.4, 41.6, 21.0; IR (KBr) ν : 3454, 3063, 3029, 1745, 1371, 1231, 1025, 756, 700 cm⁻¹; EI-MS m/z (%): 260 ($M^+ + 2 - 60$, 4.1), 258 ($M^+ - 60$, 4.0), 229 (2.8), 227 (2.8), 187 (8.3), 185 (9.5), 91 (12.6), 77 (6.1), 43 (100). Anal. calcd for C₁₆H₁₅BrO₂: C 60.21, H 4.74; found C 59.83, H 4.60.

乙酸[1-(3-甲氧基苯基)-2-苯基]乙酯(**4i**): 无色油状液体; ¹H NMR (400 MHz, CDCl₃) δ : 7.26~6.80 (m, 9H), 5.91 (dd, $J=8.0$, 6.0 Hz), 3.76 (s, 3H), 3.17 (dd, $J=13.6$, 8.0 Hz, 1H), 3.04 (dd, $J=13.6$, 5.6 Hz, 1H), 2.00 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 170.1, 159.5, 141.6, 137.0, 129.5, 129.4, 128.2, 126.5, 118.8, 113.3, 112.2, 76.4, 55.2, 42.9, 21.1; IR (KBr) ν : 3453, 3030, 2939, 1740, 1597, 1491, 1371, 1236, 1038, 701 cm⁻¹; EI-MS m/z (%): 270 (M^+ , 3.9), 210 (5.8), 260 (3.0), 179 (18.5), 137 (52.8), 109 (15.4), 91 (19.4), 77 (10.0), 43 (100). Anal. calcd for C₁₇H₁₈O₃: C 75.53, H 6.71; found C 75.65, H 6.41.

乙酸[1-(3-氯苯基)-2-苯基]乙酯(**4j**)^[20a]: 无色油状液体; ¹H NMR (400 MHz, CDCl₃) δ : 7.28~7.08 (m, 9H), 5.89 (dd, $J=6.8$, 2.4 Hz, 1H), 3.19~2.99 (m, 2H), 2.03 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 170.0, 140.1, 136.5, 134.3, 129.6, 129.5, 128.3, 128.1, 126.7, 126.6, 124.8, 75.9, 42.9, 21.1; IR (KBr) ν : 3455, 3030, 2926, 1742, 1577, 1371, 1234, 1027, 787, 698 cm⁻¹; EI-MS m/z (%): 214 ($M^+ - 60$, 4.7), 183 (2.9), 141 (3.5), 91 (8.4), 77 (4.1), 43 (100).

乙酸[1-(3-溴苯基)-2-苯基]乙酯(**4k**)^[20c]: 无色油状液体; ¹H NMR (400 MHz, CDCl₃) δ : 7.44~7.08 (m, 9H), 5.89 (dd, $J=7.6$, 6.0 Hz, 1H), 3.17 (dd, $J=12.0$, 7.6 Hz, 1H), 3.02 (dd, $J=13.6$, 6.0 Hz, 1H), 2.03 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 169.9, 142.3, 136.4, 131.0, 129.9, 129.5, 129.4, 128.3, 126.7, 125.3, 122.5, 75.8, 42.9, 21.1; IR (KBr) ν : 3458, 3029, 2926, 1742, 1372, 1234, 1027, 784, 699 cm⁻¹; EI-MS m/z (%): 260 ($M^+ + 2 - 60$, 3.2), 258 ($M^+ - 60$, 3.2), 229 (2.4), 227 (2.5), 185 (6.7), 157 (2.6), 155 (2.6), 91 (11.2), 77 (7.4), 65 (5.7), 43 (100).

乙酸[1-(2,4-二氯苯基)-2-苯基]乙酯(**4l**): 白色固体; m.p. 38~39 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.37~7.11 (m, 8H), 6.27 (dd, $J=8.0$, 4.8 Hz, 1H), 3.13 (dd, $J=14.0$, 4.4 Hz, 1H), 3.01 (dd, $J=14.0$, 8.4 Hz, 1H), 2.03 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ : 169.6, 136.7, 136.4, 133.9, 132.8, 129.5, 129.3, 128.3, 128.0, 127.3, 126.7, 72.7, 41.3, 20.9; IR (KBr) ν : 3459, 3028, 2940, 1736, 1372, 1235, 1050, 743, 702 cm⁻¹; EI-MS m/z (%): 248 ($M^+ - 60$, 7.6), 217 (6.2), 175 (15.3), 91 (25.2), 65 (13.1), 43 (100). Anal. calcd for C₁₆H₁₄Cl₂O₂: C 62.15, H 4.56; found C 62.10, H 4.45.

乙酸[1-(2,6-二氯苯基)-2-苯基]乙酯(**4m**): 白色固体; m.p. 68~69 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.39~7.09 (m, 8H), 6.52 (dd, $J=9.2$, 6.0 Hz, 1H), 3.47 (dd, $J=15.6$, 8.8 Hz, 1H), 3.23 (dd, $J=13.6$, 6.0 Hz, 1H),

2.02 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 170.2, 136.7, 134.3, 129.7, 129.5, 129.2, 128.3, 126.7, 73.6, 38.2, 20.7; IR (KBr) ν : 3448, 3032, 2933, 1734, 1363, 1232, 1018, 756, 702 cm^{-1} ; EI-MS (m/z) %: 248 ($\text{M}^+ - 60$, 10.6), 217 (2.7), 175 (16.6), 91 (25.9), 65 (12.1), 43 (100). Anal. calcd for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_2$: C 62.15, H 4.56; found C 62.36, H 4.58.

乙酸[1-(2-呋喃基)-2-苯基]乙酯(**4n**): 无色油状液体; ^1H NMR (400 MHz, CDCl_3) δ : 7.41 (t, $J=0.8$ Hz, 1H), 7.27~7.13 (m, 5H), 6.31~6.25 (m, 2H), 6.02 (t, $J=7.2$ Hz, 1H), 3.25 (d, $J=7.2$ Hz, 2H), 2.00 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 170.0, 151.7, 142.5, 136.6, 129.3, 128.3, 126.7, 110.3, 109.1, 69.3, 39.0, 21.0; IR (KBr) ν : 3462, 3030, 2932, 1742, 1271, 1232, 1015, 743 cm^{-1} ; EI-MS (m/z) %: 230 (M^+ , 2.4), 188 (1.2), 170 (2.6), 171 (2.4), 150 (1.5), 139 (27.3), 97 (100), 91 (18.7), 65 (11.3), 43 (41.4), 39 (9.0). Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3$: C 73.03, H 6.13; found C 73.03, H 5.82.

乙酸[1-(10-蒎基)-2-苯基]乙酯(**4o**): 浅黄色固体; m.p. 147~148 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.89~6.69 (m, 14H), 4.16 (dd, $J=8.8$, 7.2 Hz, 1H), 2.91 (dd, $J=6.8$, 2.8 Hz, 1H), 2.88 (dd, $J=7.2$, 3.6 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 167.6, 139.5, 138.7, 138.3, 134.2, 131.9, 131.4, 129.7, 128.2, 128.0, 127.8, 127.7, 127.1, 126.8, 126.6, 126.0, 123.7, 119.3, 49.9, 46.4, 21.1; IR (KBr) ν : 3460, 3026, 2915, 1756, 1369, 1211, 1088, 772, 699 cm^{-1} ; EI-MS (m/z) %: 340 (M^+ , 4.5), 249 (16.9), 207 (64.4), 178 (26.3), 91 (48.1), 65 (15.1), 43 (100). Anal. calcd for $\text{C}_{24}\text{H}_{20}\text{O}_2$: C 84.68, H 5.92; found C 84.36, H 5.33.

乙酸[1-(2-氯苯基)-2-(4-氯苯基)]乙酯(**4p**): 白色固体; m.p. 55~56 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.36~7.06 (m, 8H), 6.30 (dd, $J=8.4$, 4.0 Hz, 1H), 3.13 (dd, $J=14.0$, 4.0 Hz, 1H), 3.00 (dd, $J=14.0$, 8.0 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 169.6, 137.7, 135.3, 132.5, 132.0, 130.9, 129.6, 128.9, 128.3, 127.0, 126.9, 72.9, 40.7, 21.0; IR (KBr) ν : 3457, 2965, 2929, 1735, 1371, 1238, 1045, 813, 761 cm^{-1} ; EI-MS (m/z) %: 252 ($\text{M}^+ - 60$, 0.4), 250 (2.4), 248 (3.7), 183 (4.1), 141 (15.8), 125 (5.8), 89 (6.4), 77 (5.3), 43 (100). Anal. calcd for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_2$: C 62.15, H 4.56; found C 61.96, H 4.41.

乙酸[1-(2-氯苯基)-2-(4-溴苯基)]乙酯(**4q**): 白色固体; m.p. 79~80 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.39~7.01 (m, 8H), 6.30 (dd, $J=8.2$, 4.4 Hz, 1H), 3.12 (dd, $J=14.0$, 4.0 Hz, 1H), 2.99 (dd, $J=14.4$, 8.4 Hz, 1H),

2.04 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 169.6, 137.7, 135.8, 132.0, 131.3, 131.3, 129.6, 129.0, 127.0, 126.9, 120.6, 72.8, 40.8, 21.0; IR (KBr) ν : 3450, 3032, 2965, 2927, 1730, 1237, 1043, 809, 760 cm^{-1} ; EI-MS (m/z) %: 294 ($\text{M}^+ + 2 - 60$, 4.3), 292 ($\text{M}^+ - 60$, 3.2), 183 (5.7), 141 (14.8), 89 (5.9), 77 (3.9), 43 (100). Anal. calcd for $\text{C}_{16}\text{H}_{14}\text{BrClO}_2$: C 54.34, H 3.99; found C 54.47, H 3.84.

乙酸[1-(4-氯苯基)-2-(4-溴苯基)]乙酯(**4r**): 白色固体; m.p. 72~73 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.37~6.92 (m, 8H), 5.85 (t, $J=7.2$ Hz, 1H), 3.12 (dd, $J=13.8$, 7.4 Hz, 1H), 2.96 (dd, $J=13.6$, 6.4 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 170.0, 138.1, 135.4, 133.9, 131.4, 131.2, 128.6, 128.0, 120.7, 75.6, 42.1, 21.1; IR (KBr) ν : 3437, 3085, 2908, 1732, 1487, 1367, 1236, 1007, 789 cm^{-1} ; EI-MS (m/z) %: 294 ($\text{M}^+ + 2 - 60$, 2.5), 292 ($\text{M}^+ - 60$, 1.8), 260 (3.0), 183 (10.3), 141 (16.5), 89 (6.3), 77 (4.5), 43 (100). Anal. calcd For $\text{C}_{16}\text{H}_{14}\text{BrClO}_2$: C 54.34, H 3.99; found: C 54.28, H 3.80.

乙酸[1-(2-氯苯基)-2-(2-萘基)]乙酯(**4s**): 白色固体; m.p. 105~106 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.83~7.20 (m, 11H), 6.44 (dd, $J=8.6$, 4.2 Hz, 1H), 3.34 (dd, $J=14.4$, 4.0 Hz, 1H), 3.18 (dd, $J=14.4$, 8.8 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 169.7, 138.1, 134.5, 133.4, 132.3, 132.1, 129.6, 128.7, 128.1, 127.8, 127.8, 127.6, 127.6, 127.0, 125.9, 125.5, 73.2, 41.6, 21.0; IR (KBr) ν : 3456, 3050, 2921, 2845, 1737, 1367, 1231, 1028, 822, 747 cm^{-1} ; EI-MS (m/z) %: 324 (M^+ , 0.8), 264 (12.2), 229 (4.8), 184 (3.1), 141 (63.9), 115 (22.4), 77 (11.4), 43 (100). Anal. calcd for $\text{C}_{20}\text{H}_{17}\text{ClO}_2$: C 73.96, H 5.28; found C 73.56, H 5.37.

乙酸[1-(4-氯苯基)-2-(2-萘基)]乙酯(**4t**): 白色固体; m.p. 79~78 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.81~7.72 (m, 3H), 7.45~7.42 (m, 3H), 7.28~7.20 (m, 5H), 6.00 (t, $J=7.2$ Hz, 1H), 3.35 (dd, $J=13.6$, 7.2 Hz, 1H), 3.17 (dd, $J=13.6$, 6.0 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 170.0, 138.4, 134.0, 133.7, 133.3, 132.3, 128.6, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 126.0, 125.6, 75.9, 42.9, 21.1; IR (KBr) ν : 3458, 3055, 2926, 2857, 1739, 1371, 1234, 1020, 821. 750 cm^{-1} ; EI-MS (m/z) %: 324 (M^+ , 0.5), 264 (9.5), 229 (1.4), 184 (3.6), 141 (56.7), 115 (21.0), 77 (10.3), 43 (100). Anal. calcd for $\text{C}_{20}\text{H}_{17}\text{ClO}_2$: C 73.96, H 5.28; found C 73.41, H 5.12.

苯甲酸[1-(4-氯苯基)-2-苯基]乙酯(**4u**): 白色固体; m.p. 74~76 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.05~

7.11 (m, 14H), 6.13 (t, $J=6.8$ Hz, 1H), 3.33 (dd, $J=13.6$, 7.2 Hz, 1H), 3.16 (dd, $J=14.4$, 6.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 165.5, 138.5, 136.4, 133.7, 133.1, 130.1, 129.6, 128.6, 128.4, 128.3, 127.9, 126.7, 76.6, 43.0; IR (KBr) ν : 3449, 3027, 2953, 1708, 1498, 1270, 1109, 750, 707 cm^{-1} ; EI-MS m/z (%): 245 (M^+-91 , 4.3), 214 (3.8), 178 (2.6), 139 (2.1), 105 (100), 91 (10.6), 77 (31.5), 65 (5.6), 51 (12.4). Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{ClO}_2$: C 74.89, H 5.09; found C 74.89, H 4.98.

苯甲酸[1-(4-溴苯基)-2-苯基]乙酯(4v): 白色固体 m.p. 86~87 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.04~7.11 (m, 14H), 6.11 (t, $J=6.4$ Hz, 1H), 3.33 (dd, $J=13.6$, 7.2 Hz, 1H), 3.12 (dd, $J=13.6$, 6.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 165.5, 139.1, 136.4, 133.1, 131.5, 130.1, 129.6, 128.4, 128.3, 126.7, 121.9, 76.6, 42.9; IR (KBr) ν : 3402, 3027, 2951, 1707, 1488, 1270, 1108, 997, 819, 709 cm^{-1} ; EI-MS m/z (%): 291 (M^++2-91 , 2.3), 289 (M^+-91 , 2.0), 260 (2.3), 258 (2.4), 178 (3.5), 105 (100), 91 (12.6), 77 (38.1), 51 (19.4). Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{BrO}_2$: C 66.16, H 4.49; found C 66.28, H 4.38.

苯甲酸[1-(2-氯苯基)-2-苯基]乙酯(4w): 白色固体; m.p. 63~65 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.06~7.18 (m, 14H), 6.57 (dd, $J=8.4$, 4.4 Hz, 1H), 3.31 (dd, $J=14.0$, 4.4 Hz, 1H), 3.16 (dd, $J=14.4$, 7.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 165.3, 138.1, 136.8, 133.1, 132.0, 130.0, 129.6, 128.9, 128.4, 127.0, 126.9, 126.7, 77.6, 74.0, 41.5; IR (KBr) ν : 3419, 3067, 3028, 1718, 1437, 1276, 1105, 768, 708 cm^{-1} ; EI-MS m/z (%): 245 (M^+-91 , 2.3), 214 (9.3), 178 (3.2), 139 (1.8), 105 (100), 91 (9.2), 77 (31.4), 65 (5.1), 51 (11.0). Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{ClO}_2$: C 74.89, H 5.09; found C 75.00, H 4.55.

苯甲酸[1-(3-溴苯基)-2-苯基]乙酯(4x): 无色油状液体; ^1H NMR (400 MHz, CDCl_3) δ : 8.07~7.98 (m, 2H), 7.62~7.36 (m, 4H), 7.34~7.13 (m, 8H), 6.11 (dd, $J=7.6$, 6.4 Hz, 1H), 3.31 (dd, $J=13.6$, 7.6 Hz, 1H), 3.17 (dd, $J=13.6$, 5.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 165.5, 142.4, 136.4, 133.1, 131.1, 130.0, 129.6, 129.5, 129.4, 128.4, 128.4, 126.8, 125.2, 122.5, 76.5, 43.1; IR (KBr) ν : 3446, 3064, 3030, 1720, 1452, 1267, 1107, 783, 710 cm^{-1} ; EI-MS m/z (%): 291 (M^++2-91 , 1.4), 289 (M^+-91 , 1.6), 260 (6.2), 258 (6.5), 178 (4.3), 105 (100), 91 (14.6), 77 (34.9), 65 (6.5), 51 (15.5). Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{BrO}_2$: C 66.16, H 4.49; found C 66.18, H 4.41.

苯甲酸[1-(2,4-二氯苯基)-2-苯基]乙酯(4y): 白色固体; m.p. 91~92 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ :

8.04~7.98 (m, 2H), 7.62~7.52 (m, 1H), 7.46~7.30 (m, 6H), 7.28~7.16 (m, 4H), 6.50 (dd, $J=7.2$, 4.8 Hz, 1H), 3.28 (dd, $J=14.0$, 4.8 Hz, 1H), 3.16 (dd, $J=14.0$, 8.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 165.2, 136.7, 136.3, 134.0, 133.2, 132.7, 129.8, 129.6, 129.5, 129.4, 128.5, 128.3, 128.0, 127.3, 126.8, 73.5, 41.3; IR (KBr) ν : 3446, 3077, 3023, 1715, 1471, 1269, 1105, 742, 703 cm^{-1} ; EI-MS m/z (%): 279 (M^+-91 , 1.3), 248 (4.9), 178 (2.2), 105 (100), 91 (13.6), 77 (34.5), 65 (7.2), 51 (14.1). Anal. calcd for $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{O}_2$: C 67.94, H 4.34; found C 68.26, H 3.93.

苯甲酸[1-(2,6-二氯苯基)-2-苯基]乙酯(4z): 白色固体; m.p. 91~92 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.09~7.98 (m, 2H), 7.62~7.50 (m, 1H), 7.50~7.38 (m, 2H), 7.38~7.10 (m, 8H), 6.82 (dd, $J=8.8$, 6.8 Hz, 1H), 3.66 (dd, $J=13.6$, 8.8 Hz, 1H), 3.39 (dd, $J=13.6$, 6.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 165.6, 136.6, 134.2, 133.0, 129.8, 129.5, 129.4, 128.3, 126.7, 74.0, 38.4; IR (KBr) ν : 3445, 3062, 3032, 1713, 1450, 1270, 1105, 758, 697 cm^{-1} ; EI-MS m/z (%): 279 (M^+-91 , 0.8), 248 (8.9), 178 (3.4), 105 (100), 91 (12.4), 77 (35.5), 65 (6.2), 51 (13.3). Anal. calcd for $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{O}_2$: C 67.94, H 4.34; found C 68.00, H 3.99.

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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