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Lewis acid catalyzed reactions of methylenecyclopropylcarbinols with acetals for the construction of 3-oxabicyclo[3.1.0]hexane derivatives

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ABSTRACT

Reactions of methylenecyclopropylcarbinols **1** with acetals **2** in the presence of Lewis acid $Sc(OPf)_3$ produce the ring-closure products 3-oxabicyclo[3.1.0]hexane in moderate to high total yields along with the products in trans-configuration as the sole or major one. The plausible reaction mechanism has been discussed, which is based on the Prins-type reaction mechanism.

1. Introduction

There has been a mounting interest in the application of methylenecyclopropanes (MCPs) derivatives to synthetic transformations.[1] Particular attention has been paid for the transition metals-catalyzed reactions of MCPs with various reactants in organic synthesis over the past decades and some excellent reviews have been reported.[2] Moreover, recent researches have resulted in the renaissance of Lewis or Brφnsted acids-catalyzed chemistry of MCPs, and some novel reaction patterns have been found by us and other groups.[3,4]

3-Oxabicyclo[3.1.0]hexane units are important segments for some biologically active natural molecules, such as papyracon B, Mycorrhizin A and their analogues[5,6] or precursors for some other interesting molecules.[7] Recently, we have turned our interests to the chemistry of methylenecyclopropylcarbinols (3-hydroxymethyl substituted methylenecyclopropanes) **1**,[8] and have found some highly efficient reactions of methylenecyclopropylcarbinols **1** with iodine, diphenyl diselenide, aldehyde, and aldimines to furnish the corresponding oxabicyclo[3.1.0]hexane derivatives in good to high yields under mild conditions.[9] These results promoted us to further examine the reactions of methylenecyclopropylcarbinols **1** with other reactants. Herein, we will report the Lewis acid catalyzed reactions of methylenecyclopropylcarbinols **1** with acetals **2** for the formation of oxabicyclo[3.1.0]hexane derivatives.

2. Results and discussion

Initial experiments were carried out by the reaction of methylenecyclopropylcarbinol **1a** (0.3 mmol) with acetal **2a** (0.6 mmol) in 1,2-dichloroethane (DCE) (1.0 mL) in the presence of various Lewis and Brφnsted acids. We found that the reactions proceeded smoothly for the catalysts screened to give the corresponding ring-closure product **3a** in reasonable to good yields at room temperature (Table 1, entries 2–9), but no reaction occurred in the absence of any catalyst (Table 1, entry 1). We also found that only one isomer of **3a**, with trans-configuration, was obtained in these reactions. Lewis acid $Sc(OPf)_3$ ($OPf=C_8F_{17}SO_3^-$) is the best catalyst for this reaction to give the product **3a** in 82% yield (Table 1, entry 3). Further investigation revealed that the yield of **3a** dramatically decreased to 62% when the employed amount of acetal **2a** was increased to 3.0 equiv (Table 1, entry 10). The results suggest that Lewis acid and the amount of acetal play a critical role in this ring-closure reaction. Product **3a** was also obtained but in somewhat lower yields in the other solvents as acetonitrile (CH_3CN) and toluene (Table 1, entries 11 and 12). Therefore, the optimal conditions for this reaction of MCPs **1** with acetals **2** are to carry out the reaction using Lewis acid $Sc(OPf)_3$ as the catalyst and DCE as the solvent with substrates **1** and **2** in the ratio of 1:2 at room temperature (Table 1, entry 3).

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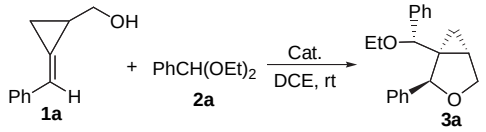
Table 1
Optimization of the reaction conditions of methylenecyclopropylcarbinol **1a** with acetal **2a**

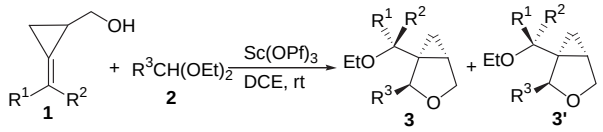


Entry[a]	Cat.	Time/h	Yield[b] %
			3a
1	—	24	—
2	CH_3SO_3H	24	50
3	$Sc(OPf)_3$[c]	4	82
4	$La(OTf)_3$	3	44
5	$Zn(OTf)_2$	3	57
6	$Sc(OTf)_3$	24	57
7	$Cu(OTf)_2$	24	48
8	$Yb(OTf)_3$	8	58
9	BF_3OTf_2	8	58
10[d]	$Sc(OPf)_3$	3	62
11[e]	$Sc(OPf)_3$	3	62
12[f]	$Sc(OPf)_3$	5	34

[a] Otherwise specified, all reactions were carried out using **1a** (0.3 mmol), **2a** (0.6 mmol) in the presence of Lewis acid (0.02 mmol) in DCE (1.0 mL).
[b] Isolated yields.
[c] $Sc(OPf)_3$=$Sc(OSO_2C_8F_{17})$.
[d] Compound **2a** (0.9 mmol) was used.
[e] CH_3CN as the solvent.
[f] Toluene as the solvent.

With the reaction conditions optimized, we then turned our attention to examine the substrate generality. A wide variety of substrates **1** and **2** were evaluated under the optimal conditions as listed in the entry 3 of Table 1. Gratifyingly, all the reactions proceeded smoothly to afford the corresponding products **3** and/or **3′** in moderate to high total yields (Table 2). It is notable that most of the reactions resulted in the *trans*-products **3** as the sole or major products except for the reaction of MCP **1b** with acetal **2a** in which the *cis*-product **3b′** was formed exclusively, presumably due to the electronic effect of the strongly electron-donating methoxyl group (Table 2, entry 1). Stereoselectivities of the reactions are not significantly affected by the substituents such as R^1, R^2, and R^3 in the cases of entries 2–14 shown in Table 2. R^1 or R^2, and R^3 could be a broad range of aromatic substituents. For example, either electron-donating groups or electron-withdrawing groups substituted aromatic groups are tolerable and the substituents had a slight influence on the yields regarding the combinations of methylenecyclopropylcarbinols **1** and acetals **2** (Table 2). To clearly determine the relative stereochemistry of the products, the structure of product **3e** was confirmed unambiguously by an X-ray diffraction (Fig. 1).[10]

Table 2
Reactions of methylenecyclopropylcarbinols **1** (0.3 mmol) with acetals **2** (0.6 mmol) in the presence of $Sc(OPf)_3$ (0.02 mmol)



Entry	**1** (R^1/R^2)	**2** (R^3)	Time/h	Yield[a] %	
				3	**3′**
1	**1b** (4-$MeOC_6H_4$/H)	**2a** (Ph)	3	—	**3b′**, 47
2	**1c** (4-MeC_6H_4/H)	**2a**	3	**3c**, 65	—
3	**1d** (3-MeC_6H_4/H)	**2a**	3	**3d**, 52	—
4	**1e** (4-ClC_6H_4/H)	**2a**	6	**3e**, 65	**3e′**, 30
5	**1f** (4-BrC_6H_4/H)	**2a**	6	**3f**, 51	**3f′**, 29
6	**1a** (Ph/H)	**2b** (4-MeC_6H_4)	4	**3g**, 64	—
7	**1e**	**2b**	4	**3h**, 82	—
8	**1a**	**2c** (4-ClC_6H_4)	4	**3i**, 60	—
9	**1c**	**2c**	4	**3j**, 74	—
10	**1e**	**2c**	10	**3k**, 63	—
11	**1g** (H/Ph)	**2a**	24	**3l**, 16	**3l′**, 60
12	**1h** (H/4-ClC_6H_4)	**2a**	24	**3m**, 20	**3m′**, 46
13	**1i** (H/4-BrC_6H_4)	**2a**	24	**3n**, 13	**3n′**, 35
14	**1j** (H/4-MeC_6H_4)	**2a**	3	—	**3o′**, 58

[a] Isolated yields.

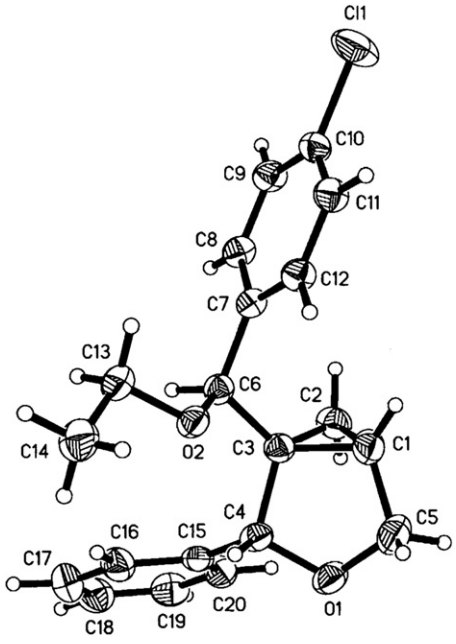
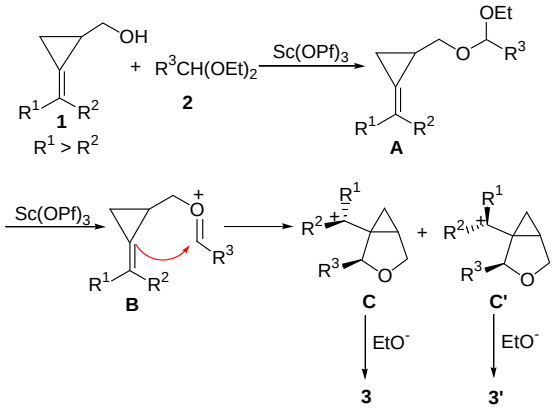


Figure 1. ORTEP drawing of **3e**.

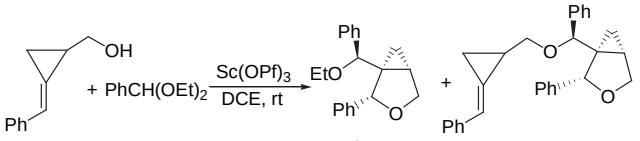
A plausible mechanism for the reactions of methylenecyclopropylcarbinols **1** with acetals **2** is proposed based on the intramolecular Prins-type reaction mechanism[11] as below: transetherification of substrates **1** with acetals **2** gives another type of acetals **A**. Lewis acid activating intermediate **A** furnishes the oxocarbenium ion **B**, which undergoes an intramolecular Prins-type reaction with the double bond of **1** to give intermediates **C** and **C′** as that previously reported.[9b] Intermediate **C** would be the major intermediate because of the steric hindrance between the bulkier groups R^1 and R^2. Attacks of the released ethoxy group (EtO^-) to intermediates **C** and **C′** afford the final products **3** and **3′**, respectively (Scheme 1).

We envisioned here that if the employed amount of methylenecyclopropylcarbinols **1** was greater than acetals **2**,



Scheme 1. Plausible mechanism for the reaction of methylenecyclopropylcarbinols **1** with acetals **2**.

intermediates **C** and **C′** shown in Scheme 1 would be attacked by substrates **1** rather than the ethoxy group to give the products as that described before.[9b] Control experiment indeed showed that our assumption was correct and the reaction of methylenecyclopropylcarbinol **1a** (3.0 equiv or 2.0 equiv) with acetal **2a** (0.3 mmol) gave the previously reported product **4**[9b] along with product **3a** in good total yields, respectively (Scheme 2).



1a	2a	3a	4
0.9 mmol	0.3 mmol	32%	37%
0.6 mmol	0.3 mmol	39%	24%

Scheme 2. Control experiments with different ratio of **1a** ans **2a**.

3. Conclusion

In conclusion, we have disclosed a novel reaction of methylenecycopropylcarbinols **1** with acetals **2** in the presence of Lewis acid $Sc(OPf)_3$ with good to high stereoselectivities to give the ring-closure products 3-oxobicyclo[3.1.0]hexane derivatives in moderate to high total yields under mild conditions. The plausible mechanism has been proposed based on the intramolecular Prins-type reaction mechanism. Efforts are underway to elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

4. Experimental section

4.1. General remarks

Melting points are uncorrected. ^1H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI and HRMS was measured by EI method. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC. Flash Column Chromatography was carried out using 300–400 mesh silica gel under increased pressure.

4.2. General procedure

Under an argon atmosphere, methylenecyclopropylcarbinols **1** (0.3 mmol) and acetals **2** (0.6 mmol), $Sc(OPf)_3$ (0.02 mmol), and DCE (1.0 mL) were successively added into a Schlenk tube. The mixture was stirred at room temperature until the disappearance of substrates **1** monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography under increased pressure to give the pure products.

*4.2.1. Product **3a**.* A colorless liquid; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.03–0.07 (m, 1H), 0.76 (t, 1H, J=4.8 Hz), 1.25 (t, 3H, J=6.9 Hz), 1.52–1.57 (m, 1H), 3.35–3.47 (m, 2H), 3.93–3.98 (m, 2H), 4.59 (s, 1H), 5.29 (s, 1H), 7.18–7.47 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.0, 15.4, 19.8, 37.9, 64.5, 69.5, 79.9, 80.2, 126.7, 127.3, 127.48, 127.49, 128.0, 128.1, 139.45, 139.55. IR (neat) ν 3085, 3062, 3029, 3002, 2972, 2927, 2858, 2246, 1954, 1884, 1814, 1604, 1585, 1494, 1453, 1399, 1102, 1022, 910, 809, 781, 767, 720, 700 cm^{-1}. MS (%) m/z 294 (M^+, 1), 248 (36), 105 (100). HRMS calcd for $C_{20}H_{22}O_2$: 294.1620, found: 294.1620.

*4.2.2. Product **3a′**.* A colorless liquid; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.87 (t, 1H, J=4.8 Hz), 0.96–1.04 (m, 4H), 1.66–1.71 (m, 1H), 3.19–3.32 (m, 2H), 3.80–3.84 (m, 1H), 3.94 (d, 1H, J=8.7 Hz), 4.53 (s, 1H), 4.60 (s, 1H), 7.21–7.49 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 7.1, 15.1, 21.6, 38.0, 64.2, 69.5, 79.6, 82.2, 127.2, 127.61, 127.63, 127.8, 128.0, 128.3, 128.7, 140.7. IR (neat) ν 3085, 3062, 3029, 2973, 2927, 2864, 1946, 1722, 1602, 1493, 1453, 1097, 1073, 1026, 955, 766, 757, 724, 699 cm^{-1}. MS (%) m/z 294 (M^+, 10), 248 (71), 247 (28), 170 (28), 105 (100). HRMS calcd for $C_{20}H_{22}O_2$: 294.1620, found: 294.1588.

*4.2.3. Product **3b′**.* A colorless liquid; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.84 (t, 1H, J=4.8 Hz), 0.92–1.03 (m, 4H), 1.66–1.73 (m, 1H), 3.16–3.30 (m, 2H), 3.78–3.84 (m, 4H), 3.94 (d, 1H, J=8.4 Hz), 4.47 (s, 1H), 4.59 (s, 1H), 6.88 (d, 2H, J=8.4 Hz, Ar), 7.23 (d, 2H, J=8.4 Hz, Ar), 7.29–7.34 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 6.9, 15.1, 21.5, 38.1, 55.2, 64.0, 69.5, 78.9, 82.1, 113.6, 127.1, 127.6, 128.0, 128.7, 132.7, 139.5, 159.1. IR (neat) ν 3067, 3062, 3030, 3000, 2971, 2928, 2853, 1610, 1585, 1511, 1495, 1454, 1303, 1248, 1171, 1089, 1034, 955, 834, 755, 726, 699 cm^{-1}. MS (%) m/z 324 (M^+, 6), 216 (29), 170 (100), 105 (64). HRMS calcd for $C_{21}H_{24}O_3$: 324.1725, found: 324.1720.

*4.2.4. Product **3c**.* A colorless liquid; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ −0.09 to −0.05 (m, 1H), 0.63 (t, 1H, J=4.8 Hz), 1.14 (t, 3H, J=7.2 Hz), 1.41–1.45 (m, 1H), 3.21–3.38 (m, 2H), 3.82–3.90 (m, 2H), 4.45 (s, 1H), 5.19 (s, 1H), 6.96–7.02 (m, 4H, Ar), 7.16–7.36 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.0, 15.4, 19.9, 21.1, 38.0, 64.5, 69.5, 79.8, 80.2, 126.7, 127.3, 127.4, 128.1, 128.7, 136.3, 137.1, 139.6. IR (neat) ν 3080, 3060, 3030, 3002, 2971, 2925, 2853, 1602, 1512, 1493, 1453, 1100, 1084, 1018, 959, 910, 813, 722, 698 cm^{-1}. MS (%) m/z 308 (M^+, 1), 262 (18), 247 (100), 105 (83). HRMS calcd for $C_{21}H_{24}O_3$: 308.1776, found: 308.1785.

*4.2.5. Product **3d**.* A colorless liquid; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ −0.05 (dd, 1H, J=4.8, 8.1 Hz), 0.64 (t, 1H, J=4.8 Hz), 1.14 (t, 3H, J=6.9 Hz), 1.42–1.47 (m, 1H), 2.22 (s, 3H), 3.24–3.37 (m, 2H), 3.83–3.91 (m, 2H), 4.45 (s, 1H), 5.19 (s, 1H), 6.88–7.35 (m, 9H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.1, 15.4, 19.9, 21.4, 38.0, 64.5, 69.5, 80.0, 80.3, 124.4, 126.8, 127.5, 127.9, 128.0, 128.1, 128.2, 137.6, 139.4, 139.6. IR (neat) ν 3050, 3028, 3003, 2971, 2924, 2857, 1736, 1606, 1491, 1453, 1101, 1083, 1017, 769, 721, 699 cm^{-1}. MS (%) m/z 308 (M^+, 1), 262 (85), 247 (35), 105 (100). HRMS calcd for $C_{21}H_{24}O_2$: 308.1776, found: 308.1777.

*4.2.6. Product **3e**.* A white solid, mp: 117–120 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.02 (dd, 1H, J=4.8, 8.4 Hz), 0.75 (t, 1H, J=4.8 Hz), 1.19 (t, 3H, J=6.9 Hz), 1.45–1.47 (m, 1H), 3.30–3.39 (m, 2H), 3.92 (s, 2H), 4.51 (s, 1H), 5.19 (s, 1H), 7.09 (d, 2H, J=8.4 Hz, Ar), 7.23 (d, 2H, J=8.4 Hz, Ar), 7.28–7.38 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.0, 15.4, 19.8, 37.9, 64.6, 69.4, 79.3, 80.2, 126.7, 127.6, 128.1, 128.2, 128.7, 133.2, 138.1, 139.3. IR (CH_2Cl_2) ν 3095, 3062, 3030, 2973, 2926, 2858, 1595, 1490, 1453, 1397, 1104, 1088, 1014, 959, 836, 724, 699 cm^{-1}. MS (%) m/z 328 (M^+, 1), 247 (29), 105 (100). HRMS calcd for $C_{20}H_{21}ClO_2$: 328.1230, found: 328.1232.

*4.2.7. Product **3e′**.* A colorless liquid; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.90–0.96 (m, 2H), 1.02 (t, 3H, J=6.6 Hz), 1.61–1.66 (m, 1H), 3.20–3.30 (m, 2H), 3.79–3.83 (m, 1H), 3.94 (d, 1H, J=8.4 Hz), 4.49 (s, 1H), 4.58 (s, 1H), 7.19–7.36 (m, 9H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 7.2, 15.1, 21.5, 37.8, 64.4, 69.4, 79.0, 82.0, 127.2, 127.7, 128.0, 128.5, 128.7, 128.8, 133.4, 139.3. IR (neat) ν 3086, 3062, 3030, 2973, 2926, 2852, 1893, 1724, 1595, 1489, 1451, 1399, 1087, 1014, 833, 728, 699 cm^{-1}. MS (%) m/z 328 (M^+, 8), 282 (16), 247 (97), 170 (100), 105 (84). HRMS calcd for $C_{20}H_{21}ClO_2$: 328.1230, found: 328.1201.

*4.2.8. Product **3f**.* A white solid, mp: 96–99 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.03 (dd, 1H, J=5.1, 8.4 Hz), 0.76 (t, 1H, J=5.1 Hz),

1.20 (t, 3H, J=6.9 Hz), 1.46–1.49 (m, 1H), 3.31–3.40 (m, 2H), 3.93 (s, 2H), 4.51 (s, 1H), 5.20 (s, 1H), 7.05 (d, 2H, J=8.1 Hz, Ar), 7.24–7.41 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.0, 15.4, 19.8, 37.8, 64.6, 69.4, 79.4, 80.2, 121.3, 126.7, 127.6, 128.1, 129.0, 131.2, 138.6, 139.3. IR (CH_2Cl_2) ν 3063, 3029, 2972, 2926, 2858, 1591, 1486, 1453, 1396, 1103, 1084, 1073, 1011, 960, 834, 724, 699 cm^{-1}. MS (%) m/z 372 (M^+, 1), 247 (60), 105 (100). HRMS calcd for $C_{20}H_{21}BrO_2$: 372.0725, found: 372.0725.

4.2.9. Product ***3f***. A white solid, mp: 68–71 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.89–0.98 (m, 2H), 1.02 (t, 3H, J=6.9 Hz), 1.64–1.69 (m, 1H), 3.23–3.30 (m, 2H), 3.81 (dd, 1H, J=2.7, 8.1 Hz), 3.94 (d, 1H, J=8.1 Hz), 4.47 (s, 1H), 4.58 (s, 1H), 7.17 (d, 2H, J=8.1 Hz, Ar), 7.28–7.36 (m, 5H, Ar), 7.41 (d, 2H, J=8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 7.2, 15.1, 21.5, 37.7, 64.4, 69.4, 79.1, 82.0, 126.7, 127.2, 127.8, 128.1, 129.0, 129.2, 131.4, 139.8. IR (neat) ν 3086, 3061, 3028, 2971, 2926, 2854, 1726, 1589, 1485, 1453, 1398, 1103, 1087, 1072, 1009, 955, 829, 726, 699 cm^{-1}. MS (%) m/z 372 (M^+, 10), 247 (81), 170 (66), 105 (68). HRMS calcd for $C_{20}H_{21}BrO_2$: 372.0725, found: 372.0687.

4.2.10. Product ***3g***. A colorless liquid; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.03 (dd, 1H, J=5.1, 8.1 Hz), 0.76 (t, 1H, J=5.1 Hz), 1.25 (t, 3H, J=6.6 Hz), 1.50–1.55 (m, 1H), 2.40 (s, 3H), 3.35–3.48 (m, 2H), 3.92–4.00 (m, 2H), 4.59 (s, 1H), 5.27 (s, 1H), 7.19–7.36 (m, 9H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.0, 15.4, 19.8, 21.2, 37.9, 64.6, 69.4, 80.0, 80.2, 126.7, 127.3, 127.4, 128.0, 128.8, 136.5, 137.0, 139.5. IR (neat) ν 3062, 3026, 3001, 2970, 2921, 2849, 1513, 1492, 1452, 1099, 1074, 1018, 929, 813, 719, 701 cm^{-1}. MS (%) m/z 308 (M^+, 1), 262 (48), 119 (100). HRMS calcd for $C_{21}H_{24}O_2$: 308.1776, found: 308.1777.

4.2.11. Product ***3h***. A white solid, mp: 175–178 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.01 (dd, 1H, J=5.1, 8.1 Hz), 0.75 (t, 1H, J=5.1 Hz), 1.21 (t, 3H, J=6.6 Hz), 1.43–1.48 (m, 1H), 2.37 (s, 3H), 3.32–3.40 (m, 2H), 3.92–3.95 (m, 2H), 4.53 (s, 1H), 5.18 (s, 1H), 7.11 (d, 2H, J=8.1 Hz, Ar), 7.16 (d, 2H, J=7.8 Hz, Ar), 7.25 (d, 2H, J=8.1 Hz, Ar), 7.27 (d, 2H, J=7.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.0, 15.4, 19.7, 21.2, 37.8, 64.7, 69.4, 79.4, 80.2, 126.7, 128.2, 128.7, 128.9, 133.2, 136.3, 137.2, 138.2. IR (CH_2Cl_2) ν 3050, 3020, 2972, 2924, 2857, 1595, 1514, 1489, 1103, 1088, 1014, 814 cm^{-1}. MS (%) m/z 342 (M^+, 1), 296 (16), 261 (29), 119 (100). HRMS calcd for $C_{20}H_{23}ClO_2$: 342.1387, found: 342.1389.

4.2.12. Product ***3i***. A colorless liquid; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.10 (dd, 1H, J=5.1, 7.8 Hz), 0.69 (t, 1H, J=5.1 Hz), 1.22 (t, 3H, J=6.9 Hz), 1.52–1.57 (m, 1H), 3.31–3.45 (m, 2H), 3.90–3.96 (m, 2H), 4.51 (s, 1H), 5.21 (s, 1H), 7.17–7.20 (m, 2H, Ar), 7.24–7.33 (m, 3H, Ar), 7.34 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.1, 15.4, 20.2, 38.0, 64.5, 69.5, 79.6, 80.1, 127.3, 127.6, 128.08, 128.09, 128.2, 133.1, 138.2, 139.3. IR (CH_2Cl_2) ν 3062, 3030, 2971, 2927, 2857, 1893, 1599, 1492, 1453, 1090, 1013, 822, 779, 703 cm^{-1}. MS (%) m/z 328 (M^+, 1), 282 (46), 138 (100). HRMS calcd for $C_{20}H_{21}ClO_2$: 328.1230, found: 328.1211.

4.2.13. Product ***3j***. A white solid, mp: 88–90 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.10 (dd, 1H, J=4.8, 7.8 Hz), 0.68 (t, 1H, J=4.8 Hz), 1.22 (t, 3H, J=6.9 Hz), 1.52–1.55 (m, 1H), 2.33 (s, 3H), 3.30–3.45 (m, 2H), 3.91–3.97 (m, 2H), 4.48 (s, 1H), 5.22 (s, 1H), 7.07 (d, 2H, J=8.1 Hz, Ar), 7.11 (d, 2H, J=8.1 Hz, Ar), 7.35 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.1, 15.4, 20.2, 21.0, 38.0, 64.4, 69.5, 79.6, 79.8, 127.2, 128.1, 128.2, 128.7, 133.1, 136.2, 137.2, 138.2. IR (CH_2Cl_2) ν 3051, 3025, 2972, 2925, 2859, 1904, 1597, 1512, 1492, 1090, 1013, 961, 816 cm^{-1}. MS (%) m/z 342 (M^+, 2), 283 (27), 281 (100), 138 (86). HRMS calcd for $C_{21}H_{23}ClO_2$: 342.1387, found: 342.1367.

4.2.14. Product ***3k***. A white solid, mp: 103–105 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.08 (dd, 1H, J=5.1, 7.5 Hz), 0.71 (t, 1H, J=5.1 Hz), 1.21 (t, 3H, J=6.9 Hz), 1.49–1.52 (m, 1H), 3.30–3.41 (m, 2H), 3.93 (s, 2H), 4.48 (s, 1H), 5.16 (s, 1H), 7.12 (d, 2H, J=7.8 Hz, Ar), 7.27 (d, 2H, J=7.8 Hz, Ar), 7.32 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.0, 15.3, 20.1, 37.9, 64.6, 69.4, 79.4, 79.6, 128.0, 128.26, 128.30, 128.6, 133.2, 133.3, 137.9, 138.0. IR (CH_2Cl_2) ν 3052, 2972, 2927, 2859, 1597, 1491, 1409, 1104, 1089, 1013, 819 cm^{-1}. MS (%) m/z 362 (M^+, 2), 316 (23), 283 (25), 281 (87), 141 (84), 138 (100). HRMS calcd for $C_{20}H_{20}Cl_2O_2$: 362.0840, found: 362.0836.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.04.072.

References and notes

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10. The crystal data of **3e** have been deposited in CCDC with number 609203. Empirical Formula: $C_{20}H_{21}ClO_2$; formula weight: 328.82; crystal color, habit: colorless, prismatic; crystal system: orthorhombic; lattice type: primitive; lattice parameters: a=10.6244(8) Å, b=18.1687(14) Å, c=18.1917(14) Å, α=90°, β=90°, γ=90°, V=3511.6(5) Å^3; space group: Pbca; Z=8; D_{calcd}=1.244 g/cm^3; F_{000}=1392; diffractometer: Rigaku AFC7R; residuals: R; Rw: 0.0485, 0.1136.
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