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Direct Coupling Reaction of Diaryl Methanol with Ketones or Aldehydes Catalyzed by $AlCl_3$

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A novel coupling reaction of diaryl methanols with ketones or aldehydes has been developed under the catalysis of $AlCl_3$. Various ketones and aldehydes could couple with 9*H*-xanthen-9-ol smoothly, affording coupling products in 48%—88% yields. A plausible mechanism using $AlCl_3$ to activate both diaryl methanol and ketone or aldehyde is proposed.

Keywords coupling reaction, alcohol, ketone, aldehyde, $AlCl_3$, catalysis

Introduction

Carbon-carbon bond formation by direct coupling of alcohols with other partners is more environmentally benign because H_2O is usually a major byproduct.[1] Recently, alcohols, which are mainly benzylic alcohols, have been reported as useful electrophiles to couple with a range of nucleophiles, such as aldehydes,[2] ketones,[3] active methylene compounds,[4] aromatic compounds,[5] active silanes,[6] amines,[7] thiols,[8] alkynes,[9] alkenes[1b,1c,10] and alcohols.[1b,1c] Among them, the coupling reactions of alcohols, which are mainly diaryl methanols, with aldehydes or ketones are more attractive because the conventional alkylations of aldehydes or ketones are often performed through metal enolates, which not only suffer from use of strong bases and alkyl halides, but also produce a metal salt as a byproduct.[4b,11]

From 2009 to 2012, several research groups disclosed enantioselective coupling reactions of diaryl methanols with aldehydes or ketones by cooperative catalysis of amine with Brønsted acid.[2a-2c,3a-3c] Moreover, a cooperative catalysis of amine with Lewis acid was used in an enantioselective coupling reaction of diaryl methanols or benzylic alcohols with aldehydes.[2d-2e] In 2011, Chi *et al*. revealed that only benzenesulfonic acid as a Brønsted acid could also catalyze the coupling reaction of diaryl methanols with aldehydes expediently.[2f] Later, Guo's group used benzoic acid as a Brønsted acid to catalyze the coupling reaction of diaryl methanols with aldehydes.[2g]

Lewis acid catalyses have a lot of advantages and become one of the most important strategies in modern organic synthesis.[12] In the coupling reaction of alcohol with aldehyde or ketone, we thought that Lewis acid could promote not only the cleavage of hydroxyl group of alcohol but also the formation of enol of aldehyde or ketone with referring to literatures.[2e-2f,4h,13] Thus, we envision to use Lewis acid as a sole catalyst to perform a coupling reaction of alcohols with aldehydes or ketones.

Experimental

General procedure for the coupling reaction of xanthenol with ketones or aldehydes catalyzed by $AlCl_3$

To a solution of xanthenol **1** (39.6 mg, 0.2 mmol) in THF (2 mL) was added ketone or aldehyde **2** (0.6 mmol) and $AlCl_3$ (8.0 mg, 0.06 mmol). The reaction mixture was stirred at room temperature for the time indicated in Table 2. After reaction, the mixture was concentrated under vacuum, and the residue was subjected to column chromatography (silica gel, petroleum ether/ethyl acetate as eluent) to afford the corresponding products **3**.

2-(9*H*-Xanthen-9-yl)cyclohexanone (**3a**):[14] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, J=7.6 Hz, 1H), 7.25—7.18 (m, 3H), 7.08—7.00 (m, 4H), 4.93 (d, J=2.4 Hz, 1H), 2.52—2.48 (m, 1H), 2.42 (d, J=12.0 Hz, 1H), 2.28—2.20 (m, 1H), 1.94—1.91 (m, 1H), 1.78—1.68 (m, 2H), 1.52—1.37 (m, 2H), 1.15—1.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.5, 153.4, 153.7, 131.1, 129.4, 128.4, 128.3, 126.3, 124.2, 123.9, 123.5, 116.9, 116.8, 61.3, 42.8, 37.3, 28.3, 27.3, 25.4; MS (EI) *m/z*: 278 (M^+), 194, 181, 165, 152.

2-(9*H*-Xanthen-9-yl)cyclopentanone (**3b**):[14] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26—7.20 (m, 3H), 7.12—7.07 (m, 4H), 6.99 (t, J=7.4 Hz, 1H), 4.76

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(d, J=2.4 Hz, 1H), 2.44 (t, J=9.0 Hz, 1H), 2.25 (dd, J=18.4, 7.2 Hz, 1H), 1.82−1.73 (m, 2H), 1.68−1.61 (m, 1H), 1.58−1.50 (m, 1H), 1.44−1.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 219.9, 153.8, 153.1, 129.9, 128.9, 128.8, 128.4, 125.1, 124.3, 124.1, 122.5, 117.1, 117.0, 60.5, 40.0, 38.7, 24.6, 21.0; MS (EI) *m/z*: 264 (M^+), 196, 182, 165, 152.

2-(9*H*-Xanthen-9-yl)cycloheptanone (**3c**):[15] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27−7.21 (m, 3H), 7.11−7.05 (m, 4H), 7.01 (t, J=7.2 Hz, 1H), 4.65 (d, J=4.4 Hz, 1H), 2.58 (dt, J=11.6, 3.6 Hz, 1H), 2.38−2.34 (m, 1H), 2.11 (td, J=12.0, 2.4 Hz, 1H), 1.75−1.72 (m, 3H), 1.63−1.55 (m, 1H), 1.38−1.13 (m, 3H), 1.05−0.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 217.1, 153.8, 153.6, 129.7, 129.4, 128.8, 128.5, 125.1, 124.3, 123.8, 122.6, 117.2, 117.0, 63.1, 45.4, 42.7, 30.5, 29.1, 25.6, 25.4; MS (EI) *m/z*: 292 (M^+), 194, 181, 165, 152.

4-Methyl-2-(9*H*-xanthen-9-yl)cyclohexanone (**3d**): White solid, *dr*=2∶1. Low polar diastereomer (Major):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, J=7.6 Hz, 1H), 7.24−7.18 (m, 3H), 7.09−7.00 (m, 4H), 4.94 (d, J=2.4 Hz, 1H), 2.59−2.49 (m, 1H), 2.42−2.36 (m, 1H), 2.34−2.20 (m, 1H), 1.95−1.82 (m, 1H), 1.79−1.64 (m, 2H), 1.50−1.41 (m, 1H), 1.21−1.08 (m, 1H), 0.82 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.5, 153.9, 153.7, 131.1, 129.4, 128.4, 128.3, 126.2, 124.2, 123.9, 123.3, 117.0, 116.8, 60.5, 42.0, 37.1, 36.0, 35.2, 32.2, 22.1; High polar diastereomer (Minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J=7.6 Hz, 1H), 7.23−7.18 (m, 3H), 7.09−7.01 (m, 4H), 4.80 (d, J=4.4 Hz, 1H), 2.63−2.58 (m, 1H), 2.41−2.30 (m, 2H), 1.92−1.88 (m, 1H), 1.81−1.75 (m, 1H), 1.56−1.46 (m, 2H), 1.42−1.38 (m, 1H), 0.91 (d, J=5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.9, 153.4, 153.0, 130.0, 128.3, 127.9, 127.8, 125.1, 123.5, 123.2, 122.9, 116.4, 116.3, 55.9, 38.4, 38.1, 33.4, 32.4, 26.5, 18.9; HRMS (EI-TOF) *m/z*: calcd for $C_{20}H_{20}O_2$ 292.1463, found 292.1465.

4-*tert*-Butyl-2-(9*H*-xanthen-9-yl)cyclohexanone (**3e**): White solid, *dr* = 3 ∶ 1. Low polar diastereomer (Major):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (dd, J=7.6, 1.2 Hz, 1H), 7.25−7.17 (m, 3H), 7.08−7.00 (m, 4H), 4.91 (d, J=3.6 Hz, 1H), 2.52 (dt, J=8.0, 4.4 Hz, 1H), 2.40 (m, 1H), 2.29−2.20 (m, 1H), 1.96−1.89 (m, 1H), 1.78−1.72 (m, 1H), 1.38−1.19 (m, 2H), 0.94−0.85 (m, 1H), 0.71 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.9, 154.0, 153.7, 130.9, 129.4, 128.5, 128.3, 126.2, 124.1, 123.8, 123.5, 116.9, 116.7, 60.4, 47.0, 42.1, 37.6, 33.1, 29.1, 28.1, 28.0; High polar diastereomer (Minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25−7.01 (m, 8H), 4.66 (d, J=6.0 Hz, 1H), 2.57−2.52 (m, 1H), 2.46−2.41 (m, 1H), 2.34−2.25 (m, 1H), 1.88−1.85 (m, 1H), 1.65−1.62 (m, 1H), 1.43−1.28 (m, 2H), 0.89−0.84 (m, 1H), 0.73 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 213.7, 153.3, 153.1, 129.6, 128.1, 128.1, 128.0, 124.6, 123.5, 123.0, 122.9, 116.7, 116.5, 56.7, 41.5, 40.1, 39.8, 32.9, 27.1, 25.4, 24.9; HRMS (EI-TOF) *m/z*: calcd for $C_{23}H_{26}O_2$ 334.1933, found 334.1932.

4-Phenyl-2-(9*H*-xanthen-9-yl)cyclohexanone (**3f**): White solid, *dr*=3∶1. Mixture of two diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, J=7.6 Hz, 0.75H), 7.33 (d, J=7.6 Hz, 0.25H), 7.26−7.11 (m, 6H), 7.09−6.98 (m, 6H), 5.00 (d, J=2.4 Hz, 0.75H), 4.76 (d, J=5.2 Hz, 0.25H), 2.89−2.82 (m, 1H), 2.76−2.72 (m, 1H), 2.54−2.40 (m, 2H), 2.10−2.03 (m, 1H), 1.95−1.89 (m, 1H), 1.74−1.63 (m, 1H), 1.43−1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.7, 209.9, 153.4, 153.3, 153.0, 153.0, 144.6, 143.7, 130.4, 129.9, 128.8, 128.6, 128.5, 128.3, 128.3, 128.0, 127.9, 127.7, 126.7, 126.5, 126.5, 126.3, 125.3, 124.4, 123.7, 123.5, 123.3, 122.7, 122.5, 116.6, 116.6, 116.4, 116.3, 60.2, 56.9, 42.8, 41.6, 39.8, 39.6, 37.1, 36.6, 34.3, 34.1, 32.2, 31.1; HRMS (EI-TOF) *m/z*: calcd for $C_{25}H_{22}O_2$ 354.1620, found 354.1618.

3-(9*H*-Xanthen-9-yl)dihydro-2*H*-pyran-4(3*H*)-one (**3g**): White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, J=7.2 Hz, 1H), 7.26−7.22 (m, 3H), 7.11−7.03 (m, 4H), 4.92 (d, J=3.6 Hz, 1H), 4.07 (t, J=8.6 Hz, 1H), 3.91−3.86 (m, 1H), 3.57 (td, J=11.6, 3.6 Hz, 1H), 3.23 (t, J=10.8 Hz, 1H), 2.78−2.74 (m, 1H), 2.61−2.53 (m, 1H), 2.44 (dt, J=15.2, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.0, 153.8, 153.5, 130.8, 129.1, 128.9, 128.7, 125.0, 124.4, 124.1, 122.6, 117.2, 117.1, 69.3, 68.6, 60.9, 43.0, 35.6; HRMS (EI-TOF) *m/z*: calcd for $C_{18}H_{16}O_3$ 280.1099, found 280.1101.

1-(9*H*-Xanthen-9-yl)propan-2-one (**3h**):[17] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27−7.20 (m, 4H), 7.11−7.03 (m, 4H), 4.62 (t, J=6.4 Hz, 1H), 2.82 (d, J=6.8 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.6, 152.2, 128.6, 127.9, 125.2, 123.5, 116.5, 54.3, 34.4, 31.1; MS (EI) *m/z*: 238 (M^+), 194, 182, 165, 152.

3-(9*H*-Xanthen-9-yl)butan-2-one (**3i**):[14] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26−7.21 (m, 2H), 7.18−7.11 (m, 4H), 7.05 (t, J=7.2 Hz, 2H), 4.34 (d, J=6.8 Hz, 1H), 2.78−2.71 (m, 1H), 1.93 (s, 3H), 0.91 (d, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 212.4, 153.8, 153.7, 130.2, 129.4, 128.7, 128.6, 125.4, 124.2, 123.7, 123.6, 117.2, 55.4, 42.5, 31.2, 13.9; MS (EI) *m/z*: 252 (M^+), 194, 182, 165, 152.

3-Methyl-3-(9*H*-xanthen-9-yl)butan-2-one (**3j**): White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (t, J=6.6 Hz, 2H), 7.13 (d, J=6.4 Hz, 4H), 7.05 (t, J=7.2 Hz, 2H), 4.38 (s, 1H), 1.96 (s, 3H), 0.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 215.7, 154.5, 130.7, 128.7, 123.6, 123.2, 117.2, 55.0, 47.2, 28.9, 22.5; HRMS (EI-TOF) *m/z*: calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1303.

3-(9*H*-Xanthen-9-yl)pentan-2-one (**3k**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27−7.21 (m, 2H), 7.16−7.02 (m, 6H), 4.08 (d, J=8.4 Hz, 1H), 2.70−2.64 (m, 1H), 1.76 (s, 3H), 1.63−1.53 (m, 1H), 1.40−1.30 (m, 1H), 0.71 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 212.5, 153.2, 129.5, 128.8, 128.0, 127.9, 124.7, 124.1, 123.4, 123.0, 116.7, 116.6, 61.1,

42.7, 33.2, 22.8, 11.9; HRMS (EI-TOF) *m/z*: calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1306.

2-(9*H*-Xanthen-9-yl)pentan-3-one (**3l**):[15] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26−7.20 (m, 2H), 7.16−7.11 (m, 4H), 7.08−7.01 (m, 2H), 4.23 (d, J=8.4 Hz, 1H), 2.76−2.69 (m, 1H), 2.26−2.16 (m, 1H), 1.96−1.86 (m, 1H), 0.92 (d, J=6.8 Hz, 3H), 0.86 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 215.0, 153.8, 153.6, 130.3, 129.4, 128.6, 128.5, 125.7, 124.2, 124.0, 123.7, 117.2, 54.0, 49.1, 37.5, 14.6, 8.0; MS (EI) *m/z*: 266 (M^+), 194, 182, 165, 152.

1-4-Tolyl-2-(9*H*-xanthen-9-yl)ethanone (**3m**):[18] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.0 Hz, 2H), 7.22−7.15 (m, 4H), 7.11 (d, J=8.4 Hz, 2H), 7.01 (t, J=7.4 Hz, 2H), 4.84 (t, J=6.6 Hz, 1H), 3.31 (d, J=6.8 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.2, 153.0, 144.6, 135.2, 129.9, 129.5, 128.9, 128.5, 126.3, 124.1, 117.2, 50.3, 35.3, 22.3; MS (EI) *m/z*: 314 (M^+), 194, 182, 165, 152.

1-(4-Methoxyphenyl)-2-(9*H*-xanthen-9-yl)ethanone (**3n**):[19] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (dd, J=7.2, 2.0 Hz, 2H), 7.31 (dd, J=7.6, 1.2 Hz, 2H), 7.20 (td, J=8.0, 1.2 Hz, 2H), 7.11 (dd, J=8.0, 0.8 Hz, 2H), 7.01 (td, J=7.6, 1.2 Hz, 2H), 6.83 (dd, J=9.2, 2.0 Hz, 2H), 4.83 (t, J=6.6 Hz, 1H), 3.82 (s, 3H), 3.29 (d, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 163.5, 152.3, 130.4, 130.2, 128.9, 127.8, 125.7, 123.4, 116.5, 113.7, 55.5, 49.4, 34.8; MS (EI) *m/z*: 330 (M^+), 194, 181, 165, 152.

1-Phenyl-2-(9*H*-xanthen-9-yl)ethanone (**3o**):[17] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=8.0 Hz, 2H), 7.49 (t, J=7.2 Hz, 1H), 7.37 (t, J=7.6 Hz, 2H), 7.32 (d, J=7.6 Hz, 2H), 7.21 (t, J=7.4 Hz, 2H), 7.11 (d, J=8.0 Hz, 2H), 7.02 (t, J=7.6 Hz, 2H), 4.85 (t, J=6.6 Hz, 1H), 3.65 (d, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.6, 153.0, 137.6, 133.8, 129.5, 129.2, 128.7, 128.5, 126.2, 124.1, 117.2, 50.4, 35.3; MS (EI) *m/z*: 300 (M^+), 194, 181, 165, 152.

1-(4-Chlorophenyl)-2-(9*H*-xanthen-9-yl)ethanone (**3p**): Yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, J=8.4 Hz, 2H), 7.33 (d, J=8.4 Hz, 2H), 7.30 (d, J=7.6 Hz, 2H), 7.21 (t, J=7.6 Hz, 2H), 7.12 (d, J=8.0 Hz, 2H), 7.02 (d, J=7.4 Hz, 2H), 4.82 (t, J=6.8 Hz, 1H), 3.30 (d, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.8, 152.3, 139.6, 135.3, 129.5, 128.8 (2C), 128.0, 125.3, 123.5, 116.6, 49.6, 34.9; HRMS *m/z*: calcd for $C_{21}H_{15}ClO_2$ 334.0761, found 334.0763.

1-(4-Nitrophenyl)-2-(9*H*-xanthen-9-yl)ethanone (**3q**):[18] Yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (dd, J=6.8, 2.0 Hz, 2H), 7.89 (dd, J=6.8, 2.0 Hz, 2H), 7.29 (dd, J=7.6, 1.6 Hz, 2H), 7.22 (td, J=8.4, 1.6 Hz, 2H), 7.12 (dd, J=8.4, 1.2 Hz, 2H), 7.03 (td, J=7.2, 1.2 Hz, 2H), 4.82 (t, J=6.6 Hz, 1H), 3.37 (d, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.7, 152.4, 150.2, 141.3, 129.1, 128.6, 128.2, 124.9, 123.7, 123.6, 116.7, 49.9, 35.1; MS (EI) *m/z*: 345 (M^+), 194, 182, 165, 152.

1,2-Diphenyl-2-(9*H*-xanthen-9-yl)ethanone (**3r**):[20] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J=7.6 Hz, 2H), 7.41−7.35 (m, 2H), 7.25 (t, J=7.6 Hz, 2H), 7.16−7.09 (m, 7H), 7.03−6.95 (m, 3H), 6.68−6.64 (m, 1H), 6.44 (d, J=7.2 Hz, 1H), 4.85 (d, J=9.6 Hz, 1H), 4.67 (d, J=9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.1, 153.6, 153.5, 137.3, 136.3, 132.8, 130.0, 129.6, 129.1, 128.5, 128.4, 128.3, 127.8, 127.5, 127.4, 125.6, 124.0, 123.3, 122.5, 116.5, 116.0, 61.1, 43.7; MS (ESI) *m/z*: 399.1 $[M+Na]^+$.

2-(9*H*-Xanthen-9-yl)propanal (**3s**):[21] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.27−7.23 (m, 3H), 7.12−7.05 (m, 5H), 4.62 (d, J=3.6 Hz, 1H), 2.71−2.64 (m, 1H), 0.91 (d, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.4, 153.8, 153.6, 129.7, 129.2, 129.0, 128.9, 124.2, 124.1, 124.0, 122.1, 117.3, 56.5, 40.3, 10.1; MS (EI) *m/z*: 238 (M^+), 194, 181, 165, 152.

2-(9*H*-Xanthen-9-yl)butanal (**3t**):[21] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.64 (d, J=2.4 Hz, 1H), 7.27−7.20 (m, 3H), 7.12−7.04 (m, 5H), 4.46 (d, J=4.8 Hz, 1H), 2.48−2.43 (m, 1H), 1.58−1.38 (m, 2H), 0.81 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.6, 153.0, 152.9, 129.0, 128.7, 128.3, 128.3, 123.5, 123.4, 123.2, 122.2, 116.8, 116.7, 62.4, 40.0, 18.7, 12.0; MS (EI) *m/z*: 252 (M^+), 196, 181, 165, 152.

2-(9*H*-Xanthen-9-yl)pentanal (**3u**):[21] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.63 (d, J=2.8 Hz, 1H), 7.27−7.21 (m, 3H), 7.12−7.04 (m, 5H), 4.46 (d, J=4.0 Hz, 1H), 2.56−2.51 (m, 1H), 1.56−1.47 (m, 1H), 1.37−1.21 (m, 2H), 1.15−1.07 (m, 1H), 0.77 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.3, 153.6, 153.6, 129.6, 129.4, 129.0, 128.9, 124.2, 124.1, 123.7, 122.8, 117.4, 117.3, 61.2, 40.7, 28.2, 21.4, 14.6; MS (EI) *m/z*: 266 (M^+), 194, 181, 165, 152.

2-(9*H*-Xanthen-9-yl)hexanal (**3v**):[21] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.63 (d, J=2.8 Hz, 1H), 7.27−7.20 (m, 3H), 7.12−7.04 (m, 5H), 4.46 (d, J=4.8 Hz, 1H), 2.54−2.49 (m, 1H), 1.57−1.47 (m, 1H), 1.39−1.32 (m, 1H), 1.20−1.08 (m, 4H), 0.76 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.7, 152.0, 151.9, 127.9, 127.7, 127.3, 127.2, 122.5, 122.4, 122.1, 121.2, 115.8, 115.7, 59.6, 39.1, 28.6, 24.1, 21.5, 12.7; MS (EI) *m/z*: 280 (M^+), 196, 181, 165, 152.

2-(9*H*-Xanthen-9-yl)heptanal (**3w**):[21] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.63 (d, J=2.4 Hz, 1H), 7.27−7.20 (m, 3H), 7.12−7.04 (m, 5H), 4.46 (d, J=4.0 Hz, 1H), 2.54−2.49 (m, 1H), 1.56−1.47 (m, 1H), 1.39−1.31 (m, 1H), 1.23−1.11 (m, 6H), 0.79 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.4, 153.6, 153.6, 129.6, 129.4, 129.0, 128.9, 124.2, 124.1, 123.8, 122.8, 117.4, 117.3, 61.3, 40.7, 32.3, 27.8, 26.0, 23.0, 14.6; MS (EI) *m/z*: 294 (M^+), 194, 181, 165, 152.

2-(9*H*-Xanthen-9-yl)octanal (**3x**):[21] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.63 (d, J=2.8 Hz, 1H), 7.27−7.20 (m, 3H), 7.12−7.04 (m, 5H), 4.46 (d, J=4.8 Hz, 1H), 2.54−2.49 (m, 1H), 1.54−1.11 (m, 10H), 0.81 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.7, 153.0, 152.9, 128.9, 128.7, 128.3, 128.3, 123.5,

123.4, 123.1, 122.2, 116.8, 116.7, 60.6, 40.1, 31.5, 29.1, 27.4, 25.4, 22.5, 14.0; MS (EI) *m/z*: 308 (M^+), 194, 182, 165, 152.

3-Phenyl-2-(9*H*-xanthen-9-yl)propanal (**3y**):[21] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.65 (s, 1H), 7.28－7.26 (m, 3H), 7.21－7.06 (m, 8H), 6.97 (d, J= 7.2 Hz, 2H), 4.60 (d, J=3.6 Hz, 1H), 3.00－2.95 (m, 1H), 2.83－2.77 (m, 1H), 2.72－2.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.3, 153.6, 153.5, 139.4, 129.7, 129.5, 129.3, 129.2, 129.1, 128.9, 127.0, 124.4, 124.2, 123.3, 122.4, 117.5, 117.5, 63.1, 40.2, 31.9; MS (EI) *m/z*: 314 (M^+), 196, 181, 168, 152.

2-(9*H*-Thioxanthen-9-yl)cyclohexanone (**5a**):[22] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, J= 7.2 Hz 1H), 7.43－7.37 (m, 2H), 7.25－7.11 (m, 5H), 4.68 (d, J=9.2 Hz, 1H), 3.15－3.08 (m, 1H), 2.35－2.32 (m, 1H), 2.23－2.15 (m, 1H), 2.00－1.97 (m, 1H), 1.75－1.72 (m, 1H), 1.67－1.45 (m, 2H), 1.38－1.35 (m, 1H), 1.26－1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 212.0, 138.5, 136.6, 133.7, 132.7, 130.9, 130.2, 127.2, 127.1, 126.6, 126.3, 126.3, 126.2, 50.4, 47.3, 43.2, 33.9, 28.9, 25.2; MS (EI) *m/z*: 294 (M^+), 221, 198, 165, 152.

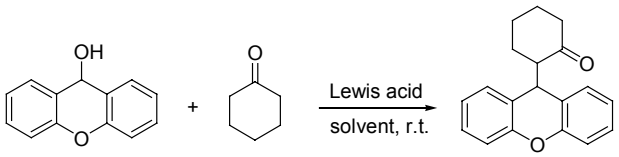
2-(9*H*-Thioxanthen-9-yl)propanal (**5s**):[2a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.54 (d, J=2.0 Hz, 1H), 7.46－7.42 (m, 2H), 7.31－7.20 (m, 6H), 4.26 (d, J=10.0 Hz, 1H), 3.22－3.14 (m, 1H), 0.88 (d, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.8, 135.9, 135.3, 133.1, 133.0, 130.0, 129.7, 127.5, 127.3, 127.0, 126.6, 126.4, 50.5, 45.7, 12.9; MS (EI) *m/z*: 254 (M^+), 197, 184, 165, 152.

Results and discussion

Initially, 9*H*-xanthen-9-ol **1** as a diaryl methanol, and cyclohexanone **2a** were chosen as model substrates to explore and optimize their coupling reaction. When $FeCl_3$ (10 mol%) was used as a Lewis acid catalyst, the coupling reaction of xanthenol **1** with cyclohexanone **2a** occurred in Et_2O at room temperature, affording the desired product **3a** in 18% yield (Table 1, Entry 1). Encouraged by this result, other Lewis acids were examined, but most of them did not work well, and gave a trace amount of desired product **3a** (Table 1, Entry 2; also see SI). $BiCl_3$ gave a slightly higher yield (Table 1, Entry 3). We were pleased to find $AlCl_3$ had the best catalytic activity to give **3a** in 39% yield (Table 1, Entry 4). No reaction took place without the Lewis catalyst (Table 1, Entry 5). Using $AlCl_3$ as a catalyst, the reaction was further optimized by screening different solvents.

When 1,2-dichloroethane was employed as a solvent, no **3a** was observed (Table 1, Entry 6). The yield of **3a** could be dramatically improved when THF was used (Table 1, Entry 7). Using DMF or dioxane as a solvent led to a slight decrease in yield (Table 1, Entries 8－9), and other solvents led to remarkable decrease in yields (Table 1, Entries 10－12). When the loading of $AlCl_3$ was increased to 30 mol%, the yield of **3a** was improved to 88% (Table 1, Entries 13－14). To elevate the reaction temperature to 40 ℃ had no effect on the yield of **3a** (Table 1, Entry 16). Thus, the optimized reaction should be performed by the catalysis of 30 mol% $AlCl_3$ in THF at room temperature.

Table 1 Optimizing of coupling reaction of xanthenol **1** with cychohexanone **2a**[a]



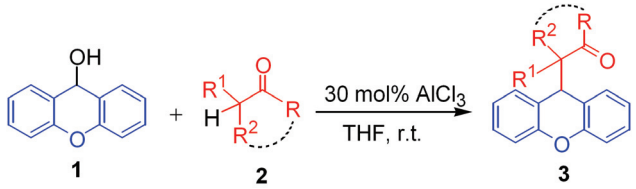
1 **2a** **3a**

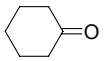
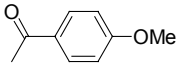
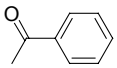
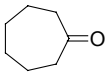
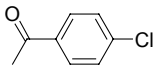
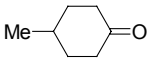
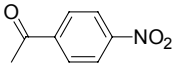
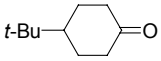
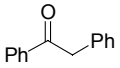
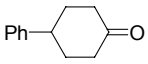
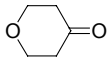
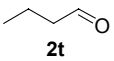
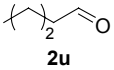
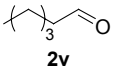
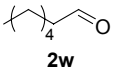
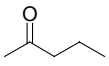
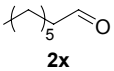
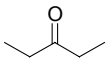
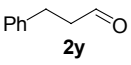
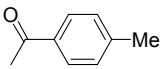
Entry	Cat.	Solvent	Time/h	Yield[b]/%
1	$FeCl_3$	Et_2O	12	18
2[c]	Lewis acids	Et_2O	12	trace
3	$BiCl_3$	Et_2O	12	20
4	$AlCl_3$	Et_2O	12	39
5	—	Et_2O	12	—
6	$AlCl_3$	DCE	12	—
7	$AlCl_3$	THF	12	68
8	$AlCl_3$	Dioxane	12	62
9	$AlCl_3$	DMF	12	66
10	$AlCl_3$	MeOH	12	15
11	$AlCl_3$	MeCN	12	13
12	$AlCl_3$	EA	12	36
13[d]	$AlCl_3$	THF	8	76
14[e]	$AlCl_3$	THF	2	88
15[f]	$AlCl_3$	THF	2	82
16[g]	$AlCl_3$	THF	2	88

[a] A mixture of xanthydrol **1** (0.2 mmol), **2a** (0.6 mmol), catalyst (0.02 mmol) in solvent (2 mL) was stirred for the time indicated at room temperature. [b] Isolated yields. [c] $CuCl_2$, $ZnCl_2$, $InCl_3$, $Cu(OTf)_2$, $Yb(OTf)_3$, $Zn(OAc)_2$ were used as catalysts. [d] 20 mol% $AlCl_3$. [e] 30 mol% $AlCl_3$. [f] 2 equiv. **2a**. [g] Reaction temperature was 40 ℃.

Under the optimized conditions, we examined the scope of the coupling reaction of xanthenol **1**. It was found that various aliphatic cyclic ketones **2a**－**2g** completed the coupling reaction with xanthenol **1** in only 2 h, affording the desired products **3a**－**3g** in good yields (Table 2, Entries 1－7). Using acetone **2h** also resulted in the expected product **3h** in a good yield (Table 2, Entry 8). Interestingly, the reaction was highly regioselective for the nonsymmetric ketones **2i**, **2j** and **2k**, and the C－C bonds formed only at more substituted α-carbon of ketones **2i**, **2j** and **2k** to give the corresponding products **3i**, **2j** and **3k** (Table 2, Entries 9－11). This result is consistent with the formation of a stable enol under Lewis acid catalysis. Various aromatic ketones **2m**－**2r** were also suitable to the transformation (Table 2, Entries 13－18). Even 1,2-di-phenylethanone

Table 2 Coupling reaction of xanthenol **1** with ketones **2a**—**2r** or aldehydes **2s**—**2y**[a]



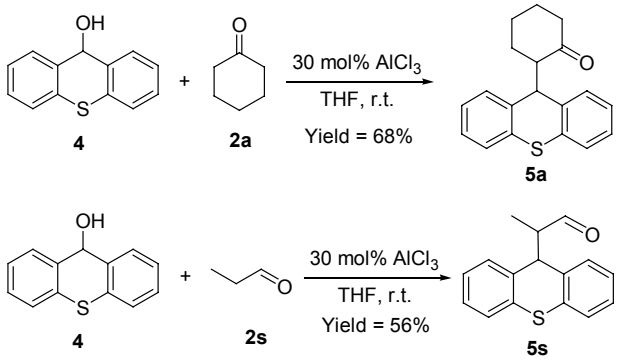
Entry	2	Time/h	Product	Yield[b]/%	Entry	2	Time/h	Product	Yield[b]/%
1	 **2a**	2	**3a**	88	14	 **2n**	5	**3n**	74
2	 **2b**	2	**3b**	86	15	 **2o**	6	**3o**	70
3	 **2c**	2	**3c**	82	16	 **2p**	20	**3p**	68
4	 **2d**	2	**3d**	84[c,d]	17	 **2q**	20	**3q**	61
5	 **2e**	2	**3e**	85[c,e]	18	 **2r**	20	**3r**	61
6	 **2f**	2	**3f**	80[c,e]	19	 **2s**	12	**3s**	85
7	 **2g**	2	**3g**	87	20	 **2t**	12	**3t**	62
8	 **2h**	12	**3h**	80	21	 **2u**	12	**3u**	78
9	 **2i**	12	**3i**	74	22	 **2v**	12	**3v**	71
10	 **2j**	12	**3j**	60	23	 **2w**	12	**3w**	65
11	 **2k**	12	**3k**	69	24	 **2x**	12	**3x**	75
12	 **2l**	12	**3l**	48	25	 **2y**	12	**3y**	74
13	 **2m**	5	**3m**	73					

[a] A mixture of xanthydrol **1** (0.2 mmol), aldehydes or ketones **2** (0.6 mmol), catalyst (0.02 mmol) in THF (2 mL) was stirred at room temperature. [b] Isolated yields. [c] Diastereoselectivity was determined by ^{1}H NMR spectroscopic analysis. [d] *dr*=2∶1. [e] *dr*=3∶1.

2r, which has a bulky phenyl group at α-position, also led to coupling product **3r** in a 61% yield (Table 2, Entry 18). The aromatic methyl ketones bearing electron-rich groups on benzene rings **2m**—**2n** led to better yields than those bearing electron-deficient groups **2p**—**2q** (Table 2, Entries 13—14 vs. 16—17). Furthemore, we also found that various aldehydes **2s**—**2y** could perform the coupling reaction expediently with xanthenol **1** to give the desired products **3s**—**3y** in satisfactory yields (Table 2, Entries 19—25).

Further investigation indicated that diphenyl methanol did not undergo the coupling reaction with ketone or aldehyde **2**. The reason may be that the less stablility of diphenyl methyl carbocation made carbon-oxygen bond in diaryl methanol more difficult to be broken as compared to that of xanthenol **1**. However, 9*H*-thioxanthen-9-ol **4** was suitable to this transformation as expected. Our experiment demonstrated that under the above optimized conditions, both ketone **2a** and aldehyde **2s** performed the coupling reaction expediently with 9*H*-thioxanthen-9-ol **4** to give the desired products **5a** and **5s** in 68% and 56% yields, respectively.

Scheme 1 Coupling reaction of 9*H*-thioxanthen-9-ol **4** with ketone **2a** or aldehyde **2s**

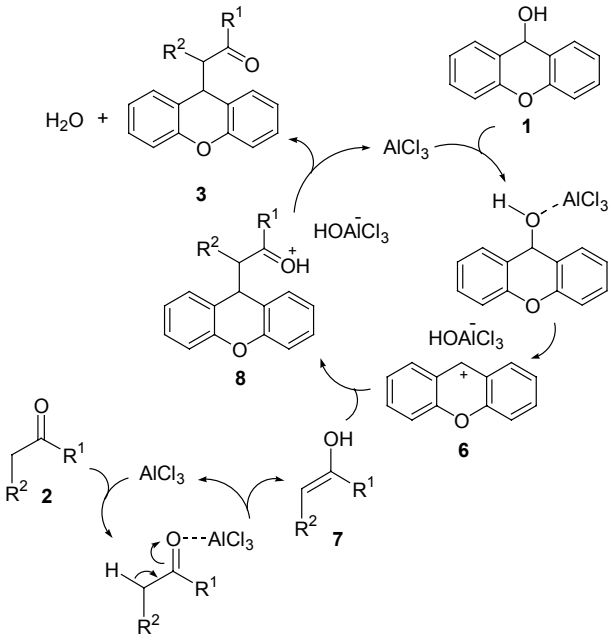


Based on the literature,[4h,13] a possible mechanism of the coupling reaction is proposed (Scheme 2). First, $AlCl_3$ coordinates the oxygen atom of hydroxy group in xanthenol **1** to activate the carbon-oxygen bond. Then, cleavage of the carbon-oxygen bond leads to the formation of carbocation **6** and trichlorohydroxoaluminate anion. The cabocation **6** is easily attacked by enol **7** resulting from **2** under the catalysis of $AlCl_3$, giving coupling product **8**. Finally, **8** and trichlorohydroxoaluminate anion lose water to form desired product **3** and regenerate $AlCl_3$.

Conclusions

In conclusion, we have developed a novel coupling reaction of diaryl methanols with either ketones or aldehydes only using $AlCl_3$ as a catalyst. Various ketones and aldehydes coupled with 9*H*-xanthen-9-ol smoothly, affording the corresponding products in moderate to good yields. A plausible mechanism using $AlCl_3$

Scheme 2 Plausible mechanism



as a Lewis acid to activate both diaryl methanol and ketone or aldehyde is proposed. Further studies on direct coupling reactions of other alcohols with ketones or aldehydes by the catalysis of Lewis acids, the mechanisms and asymmetric versions are currently under way.

Acknowledgement

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References

[1] (a) Emer, E.; Sinisi, R.; Capdevila, M. G.; Petruzziello, D.; De Vincentiis, F.; Cozzi, P. G. *Eur. J. Org. Chem.* **2011**, 647; (b) Liu, Z.; Zhang, Y.; Zhao, L.; Li, Z.; Wang, J.; Li, H.; Wu, L. *Org. Lett.* **2011**, *13*, 2208; (c) Aoyama, T.; Koda, S.; Takeyoshi, Y.; Ito, T.; Takido, T.; Kodomari, M. *Chem. Commun.* **2013**, *49*, 6605.

[2] (a) Cozzi, P. G.; Benfatti, F.; Zoli, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 1313; (b) Xiao, J.; Zhao, K.; Loh, T.-P. *Chem. Asian J.* **2011**, *6*, 2890; (c) Xiao, J.; Zhao, K.; Loh, T.-P. *Chem. Commun.* **2012**, 3548; (d) Xiao, J. *Org. Lett.* **2012**, *14*, 1716; (e) Capdevila, M. G.; Emer, E.; Benfatti, F.; Gualandi, A.; Wilson, C. M.; Cozzi, P. G. *Asian J. Org. Chem.* **2012**, *1*, 38; (f) Xing, C.; Sun, H.; Zhang, J.; Li, G.; Chi, Y. R. *Chem. Eur. J.* **2011**, *17*, 12272; (g) Zhu, X.; Wang, T.; Guo, Q. *Chin. J. Chem.* **2012**, *30*, 15.

[3] (a) Zhang, L.; Cui, L.; Li, X.; Li, J.; Luo, S.; Cheng, J. *Chem. Eur. J.* **2010**, *16*, 2045; (b) Zhang, L.; Cui, L.; Li, X.; Li, J.; Luo, S.; Cheng, J. *Eur. J. Org. Chem.* **2010**, 4876; (c) Trifonidou, M.; Kokotos, C. G. *Eur. J. Org. Chem.* **2012**, 1563; (d) Song, L.; Guo, Q.-X.; Li, X.-C.; Tian, J.; Peng, Y.-G. *Angew. Chem., Int. Ed.* **2012**, *51*, 1899; (e) Pan, X.; Li, M.; Gu, Y. *Chem. Eur. J.* **2014**, *9*, 268.

[4] (a) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem.* **2006**, *118*, 2667; *Angew. Chem., Int. Ed.* **2006**, *45*, 2605; (b) Yasuda, M.; Somyo, T.; Baba, A. *Angew. Chem.* **2006**, *118*, 807; *Angew. Chem., Int. Ed.* **2006**, *45*, 793; (c) Yuan, Y.;

Shi, Z.; Feng, X.; Liu, X. *Appl*. *Organometal*. *Chem*. **2007**, *21*, 958; (d) Kischel, J.; Mertins, K.; Michalik, D.; Zapf, A.; Beller, M. *Adv*. *Synth*. *Catal*. **2007**, *345*, 865; (e) Rueping, M.; Nachtsheim, B. J.; Kuenkel, A. *Org*. *Lett*. **2007**, *9*, 825; (f) Sanz, R.; Miguel, D.; Martínez, A.; Álvarez-Gutérrez, J. M.; Rodríguez, F. *Org*. *Lett*. **2007**, *9*, 2027; (g) Liu, P.; Zhou, Z.; Lau, C. P. *Chem*. *Eur*. *J*. **2007**, *13*, 8610; (h) Noji, M.; Konno, Y.; Ishii, K. *J*. *Org*. *Chem*. **2007**, *72*, 5161; (i) Biswas, U.; Jana, S.; Maiti, S. *Tetrahedron Lett*. **2007**, *48*, 4065; (j) Wang, G.-W.; Shen, Y.-B.; Wu, X.-L. *Eur*. *J*. *Org*. *Chem*. **2008**, 4999; (k) Liu, P.; Xia, F.; Wang, Q.; Ren, Y.; Chen, J. *Green Chem*. **2010**, *12*, 1049.

[5] (a) Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukuzawa, S. *Synlett* **1996**, 557; (b) Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukuzawa, S. *J*. *Org*. *Chem*. **1997**, *62*, 6991; (c) Noji, M.; Ohno, T.; Fuji, K.; Futaba, N.; Tajima, H.; Ishii, K. *J*. *Org*. *Chem*. **2003**, *68*, 9340; (d) Sarca, V. D.; Laali, K. K. *Green Chem*. **2006**, *8*, 615; (e) Zhan, Z.-P.; Yang, W.-Z.; Yang, R.-F.; Yu, J.-L.; Li, J.-P.; Liu, H.-J. *Chem*. *Commun*. **2006**, 3352; (f) Niggemann, M.; Meel, M. J. *Angew*. *Chem*., *Int*. *Ed*. **2010**, *49*, 3684; (g) Sato, Y.; Aoyama, T.; Takido, T.; Kodomari, M. *Tetrahedron* **2012**, *68*, 7077; (h) Sarkar, S.; Maiti, S.; Bera, K.; Jalal, S.; Jana, U. *Tetrahedron Lett*. **2012**, *53*, 5544; (i) Han, X.; Wu, J. *Angew*. *Chem*., *Int*. *Ed*. **2013**, *52*, 1.

[6] (a) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew*. *Chem*., *Int*. *Ed*. **2004**, *43*, 1414; (b) Saito, T.; Yasuda, M.; Baba, A. *Synlett* **2005**, 1737; (c) Saito, T.; Nishimoto, Y.; Yasuda, M.; Baba, A. *J*. *Org*. *Chem*. **2006**, *71*, 8516; (d) Nishimoto, Y.; Kajioka, M.; Saito, T.; Yasuda, M.; Baba, A. *Chem*. *Commun*. **2008**, 6396.

[7] (a) Terrasson, V.; Marque, S.; Georgy, M.; Campagne, J.-M.; Prim, D. *Adv*. *Synth*. *Catal*. **2006**, *348*, 2063; (b) Qin, H.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew*. *Chem*., *Int*. *Ed*. **2007**, *119*, 413; (c) Ohshima, T.; Ipposhi, J.; Nakahara, Y.; Shibuya, R.; Mashima, K. *Adv*. *Synth*. *Catal*. **2012**, *354*, 2447.

[8] Han, X.; Wu, J. *Org*. *Lett*. **2010**, *12*, 5780.

[9] (a) Xiang, S.-K.; Zhang, L.-H.; Jiao, N. *Chem*. *Commun*. **2009**, 6487; (b) Liu, Z.-Q.; Wang, J.-G.; Han, J.; Zhao, Y.-K.; Zhou, B. *Tetrahedron Lett*. **2009**, *50*, 1240; (c) Bu, X.; Hong, J.; Zhou, X. *Adv*. *Synth*. *Catal*. **2011**, *353*, 2111.

[10] Wawzonek, S.; Dufek, E. *J*. *Am*. *Chem*. *Soc*. **1956**, *78*, 3530.

[11] (a) Caine, D. In *Comprehensive Organic Synthesis*, Eds.: Trost, B. M.; Fleming, I., Pergamon, Oxford **1991**, Vol. 3, p. 1; (b) Ibrahem, I.; Cordova, A. *Angew*. *Chem*., *Int*. *Ed*. **2006**, *45*, 1952.

[12] *Lewis Acids in Organic Synthesis*, Ed.: Yamamoto, H., Wiley-VCH, Weinheim, **2002**, Vol. 1 and 2.

[13] (a) Yamamoto, H.; Futatsugi, K. *Angew*. *Chem*., *Int*. *Ed*. **2005**, *44*, 1924; (b) Kelleher, R. G.; McKervey, M. A.; Vibulijan, P. J. *J*. *Chem*. *Soc*., *Chem*. *Commun*. **1980**, 486.

[14] Jones, G. W.; Chang, K.; Shechter, H. *J*. *Am*. *Chem*. *Soc*. **1979**, *101*, 3906.

[15] Pintér, Á.; Sud, A.; Sureshkumar, D.; Klussmann, M. *Angew*. *Chem*. **2010**, *122*, 5124; *Angew*. *Chem*., *Int*. *Ed*. **2010**, *49*, 5004.

[16] There is no literature on *anti*- and *syn*-configurations of diastereomers **3d**—**3f**.

[17] Huang, X.; Zhang, T. *J*. *Org*. *Chem*. **2010**, *75*, 506.

[18] Pintér, Á.; Klussmann, M. *Adv*. *Synth*. *Catal*. **2012**, *354*, 701.

[19] Lu, C.; Dubrovskiy, A.; Larock, R. C. *Tetrahedron Lett*. **2012**, *53*, 2202.

[20] Krhőnke, F.; Dickoré, K. *Chemische Berichte* **1959**, *92*, 46.

[21] Zhang, B.; Xiang, S.; Zhang, L.; Cui, Y.; Jiao, N. *Org*. *Lett*. **2011**, *13*, 5212.

[22] Weng, Z.-T.; Li, Y.; Tian, S.-K. *J*. *Org*. *Chem*. **2011**, *76*, 8095.

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