Supplementary Information

Catalytic Regio- and Stereoselective Intermolecular [5+2] Cycloaddition via Conjugative Activation of Oxidopyrylium

Ling Zhang, Qiu Shi, Tongxiang Cao*, and Shifa Zhu*

Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, P. R. China

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1. Experimental procedures and spectroscopic data

1.1 General information

All reactions were carried out under an inert atmosphere of dry N₂ in Schlenk tube. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F). ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra (MS) were obtained using ESI, DART mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

1.2 Preparation of Maltol derived alkynes[1-2]

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\text{S1 (3.78 g, 30 mmol, 1.0 equiv), N-bromosuccinimide (5.87 g, 31 mmol, 1.1 equiv), and azobisobutyronitrile (147 mg, 9 mmol, 0.3 equiv) were added to an oven dried 500mL round bottom flask containing anhydrous carbon tetrachloride (100 mL) under an atmosphere of argon. The mixture was then heated to reflux at 95°C for 18 h. After the reaction was finished, the mixture was filtered through a short silica gel and then concentrated. The crude product was purified by flash chromatography using a gradient (PE/EA: from 5:1 to 3:1) to give pure product S2 5.3g (52% yield) as a yellow solid.}
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\text{S2 (20 mmol, 1.0 equiv) in dry DCM (40 mL) was added imidazole (40 mmol, 2.0 equiv) at room temperature under air atmosphere, and then followed by TBSCI (30 mmol, 1.5 equiv). The mixture was allowed to stir at room temperature until the starting materials were completely consumed (monitored by TLC). After the reaction was finished, the mixture was filtered through a short silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 20/1) as elute to afford the pure product S3.}
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\text{S3 (1.0 mmol, 1.0 equiv) in DMF (8 mL) was added Pd(PPh₃)₄Cl₂ (3.0 mmol%) and CuI (5.0 mmol%) under nitrogen atmosphere, and then followed by the alkynes (1.2 equiv) and Et₃N (5 mmol, 5.0 equiv). The mixture was allowed to stir at 60°C until the starting materials was completely consumed (monitored by TLC). After the reaction was finished, then the aqueous phase was extracted with EtOAc. The combined organic phases were dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 1.}
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To a magnetically stirred solution of 1 (1.0 mmol, 1.0 equiv) in THF (8 mL) was added TBAF (3.0 mmol, 3 equiv) under atmosphere. The mixture was allowed to stir at room temperature until the starting materials was completely consumed (monitored by TLC). After the reaction was finished, then the aqueous phase was extracted with EtOAc. The combined organic phases were dried over Na2SO4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 1m and 1r

3-((tert-butyldimethylsilyl)oxy)-2-methyl-5-(phenylethynyl)-4H-pyran-4-one (1a)

Yellow solid, m.p. = 138 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20/1), 170 mg, yield = 50%; 1HNMR (400 MHz, CDCl3) δ 7.94 (s, 1H), 7.56 – 7.49 (m, 2H), 7.33 – 7.27 (m, 3H), 2.31 (s, 3H), 0.96 (s, 9H), 0.29 (s, 6H); 13CNMR (100 MHz, CDCl3) δ 172.3, 155.7, 154.5, 142.2, 132.0, 128.7, 128.3, 122.7, 114.1, 95.4, 79.2, 26.0, 18.8, 15.1, -3.6; IR (KBr, cm⁻¹) 3748, 3567, 2931, 2362, 1917, 1740, 1645, 1533, 1453, 1398, 1253, 1166, 1073, 924, 899, 761; HRMS (ESI) Calcd for C20H23O3SiNa (M+Na)⁺ 363.1387, found: 363.1392.

3-((tert-butyldimethylsilyl)oxy)-2-ethyl-5-(phenylethynyl)-4H-pyran-4-one (1b)

Yellow solid, m.p. = 120-121 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20/1), 127 mg, yield = 36%; 1HNMR (500 MHz, CDCl3) δ 7.88 (s, 1H), 7.44 (d, J = 1.9 Hz, 2H), 7.21 (d, J = 2.7 Hz, 3H), 2.63-2.60 (m, 2H), 1.12 – 1.09 (m, 3H), 0.88 (s, 9H), 0.22 (s, 6H); 13CNMR (125 MHz, CDCl3) δ 172.5, 158.7, 155.8, 151.8, 141.3, 131.9, 128.6, 128.2, 122.7, 95.2, 79.2, 26.0, 21.9, 18.8, 11.0, -3.7; IR (KBr, cm⁻¹) 3286, 2975, 2358, 1602, 1530, 1450, 1352, 1294, 1186, 1156, 994, 929, 888, 761, 732, 687; HRMS (ESI) Calcd for C21H25O3SiNa(M+Na)⁺ 377.1543, found: 377.1544.

3-((tert-butyldimethylsilyl)oxy)-5-((3-fluorophenyl)ethynyl)-2-methyl-4H-pyran-4-one (1c)

Yellow solid, m.p. = 152-153 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.25 (PE/EA = 20/1), 143 mg, yield = 40%; 1HNMR (400 MHz, CDCl3) δ 7.96 (s, 1H), 7.32 (s, J = 5.7 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.03 (t, J = 8.8 Hz, 1H), 2.34 (s, 3H), 0.98 (s, 9H), 0.30 (s, 6H); 13CNMR (100 MHz, CDCl3) δ 172.3, 162.4 (d, J = 246.7 Hz), 156.0, 142.3, 130.0 (d, J = 8.5 Hz), 127.9 (d, J = 3.0 Hz), 124.6 (d, J = 9.5 Hz), 118.8 (d, J = 23.1 Hz), 116.1 (d, J = 21.2 Hz), 113.8, 94.1, 80.3, 26.1, 18.9, 15.2, -3.6; 19FNMR (376 MHz, CDCl3) δ -113.0; IR (KBr, cm⁻¹) 3743, 3649, 1835, 1740, 1645, 1515, 1465, 1337, 1252, 1009, 876, 704; HRMS (ESI) Calcd for C19H17FO3SiNa(M+Na)⁺ 381.1293, found: 381.1292.

3-((tert-butyldimethylsilyl)oxy)-5-((4-chlorophenyl)ethynyl)-2-methyl-4H-pyran-4-one (1d)

Yellow solid, m.p. = 149 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.2 (PE/EA = 20/1), 179 mg, yield = 48%; 1HNMR (400 MHz, CDCl3) δ 7.95 (s, 1H), 7.46 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 2.34 (s, 3H), 0.97 (s, 9H), 0.29 (s, 6H); 13CNMR (100 MHz, CDCl3) δ 172.4, 155.9, 154.7, 142.3, 134.9, 133.3, 128.7, 121.3, 114.0, 94.3, 80.3, 26.1, 18.88, 15.2, -3.6; IR (KBr, cm⁻¹) 3743, 3566, 2857, 1835, 1793,
3-((tert-butyldimethylsilyl)oxy)-5-((4-methoxyphenyl)ethynyl)-2-methyl-4H-pyran-4-one (1e)

Yellow solid, m.p. = 106-107 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.25 (PE/EA = 20:1), 159 mg, yield = 43%; 1HNMR (400 MHz, CDCl3) δ 7.93 (s, 1H), 7.47 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 2.33 (s, 3H), 0.97 (s, 9H), 0.29 (s, 6H); 13CNMR (100 MHz, CDCl3) δ 172.4, 159.9, 155.4, 154.4, 142.1, 133.4, 114.8, 114.3, 113.8, 95.4, 77.8, 55.3, 26.0, 18.8, 15.1, -3.7; IR (KBr, cm⁻¹) 3429, 2954, 1668, 1508, 1440, 1168, 809, 834, 786; HRMS (ESI) Calcd for C22H26O3SiH (M+H)+ 371.1673, found: 371.1675.

3-((tert-butyldimethylsilyl)oxy)-5-((4-ethylphenyl)ethynyl)-2-methyl-4H-pyran-4-one (1f)

Yellow solid, m.p. = 146 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.2 (PE/EA = 20:1), 118 mg, yield = 32%; 1HNMR (500 MHz, CDCl3) δ 7.94 (s, 1H), 7.45 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.23 (d, J = 7.7 Hz, 3H), 0.97 (s, 9H), 0.30 (s, 6H); 13CNMR (125 MHz, CDCl3) δ 172.5, 155.7, 154.5, 145.2, 142.2, 132.0, 127.9, 119.9, 114.3, 95.7, 78.5, 29.0, 26.1, 18.9, 15.4, 15.2, -3.6; IR (KBr, cm⁻¹) 3742, 3677, 3589, 2361, 1916, 1835, 1740, 1646, 1583, 1428, 1396, 902, 857, 674; HRMS (ESI) Calcd for C22H26O3SiH (M+H)+ 369.1880, found: 369.1883.

3-((tert-butyldimethylsilyl)oxy)-5-((4-butylnyl)ethynyl)-2-methyl-4H-pyran-4-one (1g)

Yellow solid, m.p. = 98-99 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20:1), 158 mg, yield = 40%; 1HNMR (400 MHz, CDCl3) δ 7.92 (s, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 2.61 – 2.56 (m, 2H), 2.31 (s, 3H), 160-1.54 (m, 2H), 1.35 – 1.30 (m, 2H), 0.97 (s, 9H), 0.91 (t, J = 7.4 Hz, 3H), 0.30 (s, 6H); 13CNMR (100 MHz, CDCl3) δ 172.4, 155.6, 154.4, 143.8, 142.1, 131.9, 128.4, 119.9, 114.3, 95.6, 78.5, 35.7, 33.4, 26.0, 22.4, 18.8, 15.1, 14.0, -3.7; IR (KBr, cm⁻¹) 3028, 2839, 1677, 1607, 1587, 1441, 1329, 1293, 1177, 1026, 923, 833, 756; HRMS (ESI) Calcd for C22H26O3SiH (M+H)+ 397.2193, found: 397.2197.

3-((tert-butyldimethylsilyl)oxy)-2-methyl-5-(naphthalen-1-ylethynyl)-4H-pyran-4-one (1h)

White solid, m.p. = 126 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20:1), 195 mg, yield = 50%; 1HNMR (500 MHz, CDCl3) δ 8.46 (d, J = 8.3 Hz, 1H), 8.05 (s, 1H), 7.84 (dd, J = 8.1, 3.6 Hz, 2H), 7.79 (d, J = 7.0 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.46 – 7.40 (m, 1H), 2.35 (s, 3H), 1.00 (s, 9H), 0.34 (s, 6H); 13CNMR (125 MHz, CDCl3) δ 172.4, 155.6, 154.6, 142.3, 133.3, 133.2, 130.9, 129.4, 128.4, 127.0, 126.6, 125.2, 120.4, 114.3, 93.8, 84.1, 26.1, 18.9, 15.2, -3.6; IR (KBr, cm⁻¹) 3456, 2968, 2934, 1678, 1605, 1496, 1365, 1297, 1026, 976, 740; HRMS (ESI) Calcd for C22H26O3SiH (M+H)+ 391.1724, found: 391.1725.
3-((tert-butyldimethylsilyl)oxy)-2-methyl-5-((thiophen-3-ylethynyl)-4H-pyran-4-one (1i)

Brown solid, m.p. = 150 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20/1), 138 mg, yield = 40%; \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (s, 1H), 7.55 (dd, \(J = 2.9, 1.0 \text{ Hz}, 1\text{H}\)), 7.26 – 7.24 (m, 1H), 7.19 (dd, \(J = 5.0, 1.0 \text{ Hz}, 1\text{H}\)), 2.33 (s, 3H), 0.96 (s, 9H), 0.29 (s, 6H); \(^1^3\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.4, 155.7, 154.6, 142.3, 130.1, 129.8, 125.3, 121.8, 114.2, 90.6, 78.8, 26.1, 18.9, 15.2, -3.6; IR (KBr, cm\(^{-1}\)) 3743, 3649, 3620, 2353, 1917, 1793, 1694, 1621, 1515, 1465, 1426, 1396, 1252, 1076, 675; HRMS (ESI) Calcd for C\(_{19}\)H\(_{20}\)O\(_3\)SSiH (M+H\(^{+}\)) 347.1132, found: 347.1122.

3-((tert-butyldimethylsilyl)oxy)-5-(3,3-dimethylbut-1-yn-1-yl)-2-methyl-4H-pyran-4-one (1j)

White solid, m.p. = 96-97 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.4 (PE/EA = 20/1), 163 mg, yield = 51%; \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (s, 1H), 2.30 (s, 3H), 1.31 (s, 9H), 0.97 (s, 9H), 0.28 (s, 6H); \(^1^3\)CNMR (100MHz, CDCl\(_3\)) \(\delta\) 172.6, 155.5, 154.2, 142.1, 114.5, 104.5, 68.9, 31.0, 28.3, 26.1, 18.8, 15.1, -3.7; IR (KBr, cm\(^{-1}\)) 3273, 296, 2870, 1693, 1613, 1519, 1454, 1312, 1216, 1185, 1029, 945, 874; HRMS (ESI) Calcd for C\(_{19}\)H\(_{20}\)O\(_3\)SNa (M+Na\(^{+}\)) 343.1700, found: 343.1700.

3-((tert-butyldimethylsilyl)oxy)-5-(cyclopropylethynyl)-2-methyl-4H-pyran-4-one (1k)

White solid, m.p. = 142 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.4 (PE/EA = 20/1), 158 mg, yield = 51%; \(^1\)HNMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.78 (s, 1H), 2.29 (s, 3H), 1.47 (tt, \(J = 8.1, 5.3 \text{ Hz}, 1\text{H}\)), 0.95 (s, 9H), 0.82 (tu, \(J = 7.6, 2.8 \text{ Hz}, 4\text{H}\)), 0.27 (s, 6H); \(^1^3\)CNMR (125 MHz, CDCl\(_3\)) 173.0, 155.5, 154.3, 142.1, 114.5, 100.0, 65.4, 26.1, 18.9, 15.2, 8.9, 0.6, -3.6; IR (KBr, cm\(^{-1}\)) 3743, 3678, 3620, 2362, 1917, 1793, 1694, 1538, 1464, 1386, 754, 679; HRMS (ESI) Calcd for C\(_{19}\)H\(_{20}\)O\(_3\)SiNa (M+Na\(^{+}\)) 327.1387, found: 327.1290.

3-((tert-butyldimethylsilyl)oxy)-5-(hept-1-yn-1-yl)-2-methyl-4H-pyran-4-one (1l)

Yellow oil, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20/1), 107 mg, yield = 32%; \(^1\)HNMR (500 MHz, CDCl\(_3\)) 7.81 (s, 1H), 2.41 (t, \(J = 7.3 \text{ Hz}, 2\text{H}\)), 2.30 (s, 3H), 1.61 – 1.55 (m, 2H), 1.38 – 1.31 (m, 4H), 0.95 (s, 9H), 0.89 (t, \(J = 7.1 \text{ Hz}, 3\text{H}\)), 0.27 (s, 6H); \(^1^3\)CNMR (100MHz, CDCl\(_3\)) \(\delta\) 173.0, 155.4, 154.4, 142.2, 114.5, 97.3, 70.1, 31.3, 28.4, 26.1, 22.3, 19.9, 18.9, 15.1, 14.1, -3.6; IR (KBr, cm\(^{-1}\)) 2956, 2930, 2361, 1686, 1528, 1437, 1370, 1292, 1183, 1073, 968, 817, 727; HRMS (ESI) Calcd for C\(_{19}\)H\(_{20}\)O\(_3\)SiH (M+H\(^{+}\)) 335.2037, found : 335.2036.

5-ethynyl-3-hydroxy-2-methyl-4H-pyran-4-one (1m)

White solid, m.p. = 146-147 °C, purified by chromatography (petroleum/ethyl acetate = 2:1), Rf = 0.2 (PE/EA = 2/1), 45 mg, yield = 30%; \(^1\)HNMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.01 (s, 1H), 3.29 (s, 1H), 2.37 (s, 3H); \(^1^3\)CNMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.7, 157.8, 149.1,142.4,110.6, 84.3, 73.0, 14.5; IR (KBr, cm\(^{-1}\)) 3568, 3058, 1717, 1679, 1526, 1481, 1294, 1019, 926, 807; HRMS (ESI) Calcd for CsH\(_6\)O\(_3\)Na (M+Na\(^{+}\)) 173.0209, found: 173.0206.
3-(((tert-butyldimethylsilyl)oxy)-5-(((3-chlorophenyl)ethynyl)-2-methyl-4H-pyran-4-one (1n)

Yellow solid, m.p. = 156-157 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.25 (PE/EA = 20/1), 161 mg, yield = 43%; 1H NMR (400 MHz, CDCl3) δ 7.96 (d, J = 1.0 Hz, 1H), 7.53 (t, J = 1.6 Hz, 1H), 7.41 (s, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 2.34 (s, 3H), 0.97 (s, 9H), 0.29 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 172.2, 155.9, 154.6, 142.2, 134.1, 131.7, 130.0, 129.5, 128.9, 124.4, 113.7, 93.8, 80.4, 26.0, 18.8, 15.1, -3.7; IR (KBr, cm⁻¹) 2958, 2930, 1675, 1515, 1428, 1112, 1009, 975, 902, 867, 702; HRMS (ESI) Caled for C29H31ClO3SiNa (M+Na)+ 577.1920, found: 577.2020.

3-(((tert-butyldimethylsilyl)oxy)-2-methyl-5-((m-tolylenylyl))-4H-pyran-4-one (1o)

Yellow solid, m.p. = 150 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20/1), 141 mg, yield = 45%; 1H NMR (400 MHz, CDCl3) δ 7.94 (s, 1H), 7.37 (s, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 0.97 (s, 9H), 0.30 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 172.4, 155.7, 154.5, 142.2, 137.9, 132.6, 129.6, 129.0, 128.2, 122.5, 114.2, 95.6, 78.9, 26.1, 21.2, 18.8, 15.1, -3.6; IR (KBr, cm⁻¹) 3743, 3568, 2857, 2334, 1916, 1740, 1678, 1516, 1396, 1256, 1063, 942, 838, 782, 698; HRMS (ESI) Caled for C27H30O3SiNa (M+Na)+ 377.1543, found: 377.1544.

5-((4-((tert-butyldimethylsilyl)oxy)-2-methyl-4H-pyran-4-one (1p)

Yellow solid, m.p. = 154 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.3 (PE/EA = 20/1), 178 mg, yield = 45%; 1H NMR (400 MHz, CDCl3) δ 7.94 (s, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 2.33 (s, 3H), 1.31 (s, 9H), 0.98 (s, 9H), 0.30 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 172.5, 155.7, 154.5, 152.0, 142.3, 131.8, 125.3, 119.7, 114.4, 95.6, 78.6, 34.9, 31.3, 26.1, 18.9, 15.2, -3.6; IR (KBr, cm⁻¹) 3743, 3678, 3620, 2958, 2335, 1918, 1793, 1693, 1539, 1428, 1387, 1203, 1001, 836, 785, 674; HRMS (ESI) Caled for C27H28O2SiNa (M+Na)+ 419.1303, found: 419.1266.

3-(((tert-butyldimethylsilyl)oxy)-5-((4-ethoxyphenyl)ethynyl)-2-methyl-4H-pyran-4-one (1q)

Yellow solid, m.p. = 186 °C, purified by chromatography (petroleum/ethyl acetate = 20:1), Rf = 0.2 (PE/EA = 20/1), 161 mg, yield = 42%; 1H NMR (400 MHz, CDCl3) δ 7.93 (s, 1H), 7.46 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.03 (q, J = 6.9 Hz, 2H), 2.33 (s, 3H), 1.41 (t, J = 6.9 Hz, 3H), 0.97 (s, 9H), 0.29 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 172.5, 159.4, 155.5, 154.5, 152.8, 142.2, 133.5, 114.7, 114.5, 95.6, 77.8, 63.6, 26.1, 18.9, 15.2, 14.9, -3.6; IR (KBr, cm⁻¹) 3743, 3678, 3620, 2362, 1967, 1835, 1770, 1694, 1538, 1465, 1391, 1250, 753, 673; HRMS (ESI) Caled for C27H28O2SiNa (M+Na)+ 407.1649, found: 407.1653.

3-hydroxy-2-methyl-5-((phenylethynyl)-4H-pyran-4-one (1r)

Yellow solid, m.p. = 138 °C, purified by chromatography (petroleum/ethyl acetate = 4:1), Rf = 0.2 (PE/EA = 4/1), 172 mg, yield =76%; 1H NMR (400 MHz, CDCl3) δ 8.05 (s, 1H), 7.54 (dd, J = 6.7, 3.0 Hz, 2H), 7.33 (dd, J = 5.1, 1.9 Hz, 3H), 6.45 (s, 1H), 2.38 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 171.6, 156.8, 148.7, 142.4, 132.0, 129.0, 128.4, 122.5, 111.8, 95.9, 78.4, 14.5; IR (KBr, cm⁻¹) 3528, 2968, 2870, 1693, 1613, 1567, 1454, 1313, 1253, 1185, 1029, 945, 874; HRMS (ESI) Caled for C14H10O3Na (M+Na)+ 249.0522, found: 249.0526.
3-methoxy-2-methyl-5-(phenylethynyl)-4H-pyran-4-one (1s)

Brown solid, m.p. = 120-122 °C, Rf = 0.3 (PE/EA = 5/1), 108 mg, yield =45%; $^1$HNMR (400 MHz, CDCl$_3$) δ 7.99 (s, 1H), 7.54 (s, 2H), 7.34 (s, 3H), 3.90 (s, 3H), 2.34 (s, 3H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 172.8, 158.9, 156.2, 144.8, 131.8, 128.8, 128.3, 122.5, 115.5, 96.1, 78.8, 60.0, 14.6; IR (KBr, cm$^{-1}$) 3059, 2362, 1917, 1835, 1770, 1678, 1515, 1455, 1340, 1087, 932, 700; HRMS (ESI) Calcd for C$_{18}$H$_{12}$O$_3$Na (M+Na)$^+$ 263.0679, found: 263.0680.

1.3 General procedure for the synthesis of 3

To a 25 mL Schlenk tube with a magnetic bar under nitrogen atmosphere was PPh$_3$AuCl (5 mmol%) and AgBF$_4$ (5 mmol%) in acetonitrile (CH$_3$CN, 2 mL), then the substrates (0.1mmol) and indole derivatives (1.5 eq) were added. The resulting mixture was stirred at room temperature for 8 h. After the reaction was finished, the mixture was filtered by short silica, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the product 3.

Note: When other heteroarenes were used, the catalytic system was out of function.

9,10-dimethyl-2-phenyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3aa)

Yellow solid, m.p. = 185-186 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 29 mg, yield = 81%; $^1$HNMR (400 MHz, CDCl$_3$) δ 7.84 (d, J = 7.3 Hz, 2H), 7.50 – 7.38 (m, 3H), 7.17 (dd, J = 12.1, 7.3 Hz, 2H), 6.84 (s, 1H), 6.73 (t, J = 7.3 Hz, 1H), 6.49 (s, 1H), 5.34 (s, 1H), 4.23 (d, J = 8.5 Hz, 1H), 3.96 (d, J = 8.5 Hz, 1H), 2.98 (s, 3H), 1.66 (s, 3H); $^{13}$CNMR (100 MHz, CDCl$_3$) δ 185.6, 160.2, 153.9, 147.1, 144.3, 130.2, 129.2, 129.1, 128.9, 127.5, 125.7, 124.0, 117.9, 107.2, 102.9, 93.6, 78.9, 74.6, 56.1, 37.1, 15.1; IR (KBr, cm$^{-1}$) 3743, 3678, 3649, 3620, 2933, 1835, 1740, 1676, 1497, 1455, 1367, 1296, 1263, 1119, 1026, 972, 829, 743; HRMS (ESI) Calcd for C$_{23}$H$_{19}$NO$_3$ (M+Na)$^+$ 380.1257, found: 380.1252.

10-ethyl-9-methyl-2-phenyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ba)

Yellow solid, m.p. = 131-132 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 27 mg, yield = 72%; $^1$HNMR (500 MHz, CDCl$_3$) δ 7.84 (d, J = 7.1 Hz, 2H), 7.44 (dt, J = 12.8, 6.9 Hz, 3H), 7.19 – 7.13 (m, 2H), 6.84 (s, 1H), 6.72 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 7.8 Hz, 1H), 5.36 (s, 1H), 4.21 (d, J = 8.5 Hz, 1H), 3.96 (d, J = 8.5 Hz, 1H), 2.96 (s, 3H), 2.49 (dq, J = 14.6, 7.3 Hz, 1H), 1.89 (dq, J = 14.5, 7.3 Hz, 1H), 1.04 (t, J = 7.3 Hz, 3H); $^{13}$CNMR (125 MHz, CDCl$_3$) δ 185.4, 160.2 153.9, 147.1, 145.2, 130.2, 129.2, 129.15,
129.0, 127.6, 125.7, 124.0, 117.8, 107.1, 102.9, 97.3, 78.6, 75.1, 56.2, 37.2, 22.6, 8.9; IR (KBr, cm\(^{-1}\)) 3740, 3061, 2974, 1679, 1527, 1474, 1427, 1356, 1258, 1030, 973, 921, 880, 765, 738, 693; HRMS (ESI) Calcd for C\(_2\)H\(_7\)NO\(_3\)H (M+H)\(^{+}\) 372.1594, found: 372.1593.

5,9,10-trimethyl-2-phenyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ab)

Yellow solid, m.p. = 119-120 \(^\circ\)C, purified by chromatography (petroleum/ethyl acetate = 15:1), R\(_f\) = 0.2 (PE/EA = 15/1), 33 mg, yield = 88%; \(^1\)HNMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 7.1\) Hz, 2H), 7.45 (dt, \(J = 12.1, 6.9\) Hz, 3H), 7.09 (t, \(J = 7.7\) Hz, 1H), 6.82 (s, 1H), 6.55 (d, \(J = 7.5\) Hz, 1H), 6.35 (d, \(J = 7.9\) Hz, 1H), 5.35 (s, 1H), 4.17 (d, \(J = 8.5\) Hz, 1H), 3.96 (d, \(J = 8.5\) Hz, 1H), 2.96 (s, 3H), 2.36 (s, 3H), 1.68 (s, 3H); \(^{13}\)CNMR (125 MHz, CDCl\(_3\)) \(\delta\) 185.6, 160.4, 154.2, 147.4, 144.3, 133.5, 130.2, 129.4, 129.1, 128.9, 125.9, 125.7, 119.4, 105.1, 102.5, 93.5, 77.3, 74.8, 55.9, 37.7, 18.6, 15.3; IR (KBr, cm\(^{-1}\)) 3742, 3442, 2933, 2362, 1676, 1453, 1364, 1268, 1128, 1009, 973, 803, 765, 733; HRMS (ESI) Calcd for C\(_2\)H\(_7\)NO\(_3\)H (M+H)\(^{+}\) 372.1594, found: 372.1590.

6-fluoro-9,10-dimethyl-2-phenyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ac)

Green solid, m.p. = 189-190 \(^\circ\)C, purified by chromatography (petroleum/ethyl acetate = 12:1), R\(_f\) = 0.25 (PE/EA = 10/1), 32 mg, yield = 84%; \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 7.44 (q, \(J = 8.2, 7.3\) Hz, 3H), 6.91 (d, \(J = 7.9\) Hz, 1H), 6.87 (d, \(J = 8.9\) Hz, 1H), 6.83 (s, 1H), 6.37 (dd, \(J = 8.5, 3.9\) Hz, 1H), 5.31 (s, 1H), 4.19 (d, \(J = 8.5\) Hz, 1H), 3.95 (d, \(J = 8.5\) Hz, 1H), 2.94 (s, 3H), 1.65 (s, 3H); \(^{13}\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\) 185.4, 160.3, 156.6 (d, \(J = 234.4\) Hz), 150.3, 146.8, 144.3, 130.2, 129.2, 128.9, 128.7 (d, \(J = 8.1\) Hz), 125.7, 115.1 (d, \(J = 23.2\) Hz), 111.5 (d, \(J = 24.5\) Hz), 107.5 (d, \(J = 8.2\) Hz), 102.8, 93.6, 78.7, 75.2, 56.0, 37.9, 15.0; \(^{19}\)FNMR (376 MHz, CDCl\(_3\)) \(\delta\) -127.5; IR (KBr, cm\(^{-1}\)) 3743, 3638, 3566, 2935, 2361, 1835, 1741, 1483, 1396, 1222, 1128, 1028, 975, 874, 763; HRMS (ESI) Calcd for C\(_2\)H\(_8\)FNO\(_2\)Na (M+Na\(^{+}\)) 398.1163, found: 398.1165.

6-chloro-9,10-dimethyl-2-phenyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ad)

Green solid, m.p. = 191-192 \(^\circ\)C, purified by chromatography (petroleum/ethyl acetate = 15:1), R\(_f\) = 0.2 (PE/EA = 15/1), 29 mg, yield = 74%; \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 7.0\) Hz, 2H), 7.45 (q, \(J = 8.3, 7.3\) Hz, 3H), 7.14 (s, 1H), 7.10 (d, \(J = 8.4\) Hz, 1H), 6.82 (s, 1H), 6.36 (d, \(J = 8.4\) Hz, 1H), 5.31 (s, 1H), 4.18 (d, \(J = 8.4\) Hz, 1H), 3.98 (d, \(J = 8.5\) Hz, 1H), 2.96 (s, 3H), 1.63 (s, 3H); \(^{13}\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\) 185.3, 160.4, 152.4, 146.7, 144.3, 130.3, 129.2, 129.17, 128.9, 128.8, 125.8, 124.3, 122.3, 107.8, 102.8, 93.5, 78.7, 74.9, 55.8, 37.1, 15.1; IR (KBr, cm\(^{-1}\)) 3743, 3678, 3565, 2985, 1835, 1740, 1677, 1497, 1305, 1100, 973, 875, 802, 740; HRMS (ESI) Calcd for C\(_2\)H\(_8\)ClNO\(_2\)H (M+H\(^{+}\)) 392.1048, found: 392.1052.

6-bromo-9,10-dimethyl-2-phenyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ae)

Yellow solid, m.p. = 195-196 \(^\circ\)C, purified by chromatography (petroleum/ethyl acetate = 12:1), R\(_f\) = 0.2 (PE/EA = 12/1), 33 mg, yield = 76%; \(^1\)HNMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.78 – 7.73 (m, 2H), 7.40 – 7.33 (m, 3H), 7.23 – 7.19 (m, 1H), 7.15 (dt, \(J = 8.4, 2.5\) Hz, 1H), 6.74 (s, 1H), 6.25 (dd, \(J = 8.3, 3.0\) Hz, 1H), 5.24 (s, 1H), 4.11 (d, \(J = 8.5\) Hz, 1H), 3.91 (d, \(J = 8.5\) Hz, 1H), 2.88 (s, 3H), 1.56 (s, 3H); \(^{13}\)CNMR (125 MHz, CDCl\(_3\)) \(\delta\) 185.2, 160.4, 152.8,
146.7, 144.3, 131.8, 130.3, 129.7, 129.2, 128.8, 127.0, 125.7, 109.1, 108.4, 102.8, 93.5, 78.7, 74.8, 55.7, 37.0, 15.1; IR (KBr, cm⁻¹) 3059, 2935, 2364, 1675, 1525, 1453, 1367, 1271, 1099, 973, 803, 755, 692; HRMS (ESI) Calcd for C₂₃H₁₉BrNO₃H (M+H)+ 346.0543, found: 346.0542.

6,9,10-trimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-bjindol-11(4H)-one (3af)

Yellow solid, m.p. = 188-189 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rₜ = 0.2 (PE/EA = 15/1), 29 mg, yield = 77%; ¹HNMR (400 MHz, CDCl₃) δ 7.84 (d, J = 6.7 Hz, 2H), 7.45 (q, J = 9.5, 8.0 Hz, 3H), 7.02 (s, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.82 (s, 1H), 6.41 (dd, J = 7.9 Hz, 1H), 5.32 (s, 1H), 4.19 (d, J = 8.4 Hz, 1H), 3.92 (d, J = 8.5 Hz, 1H), 2.95 (s, 3H), 2.29 (s, 3H), 1.65 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 185.8, 160.2, 151.9, 147.10, 144.4, 130.2, 129.5, 129.1, 129.0, 127.7, 127.3, 125.7, 124.8, 107.3, 102.8, 93.6, 78.9, 74.9, 56.2, 37.7, 20.8, 15.0; IR (KBr, cm⁻¹) 3733, 3620, 2932, 2362, 1868, 1740, 1616, 1502, 1454, 1396, 1285, 1026, 922, 878, 763; HRMS (ESI) Calcd for C₂₃H₂₂NO₃Na (M+Na)+ 394.1414, found: 394.1416.

6-methoxy-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-bjindol-11(4H)-one (3ag)

Green solid, m.p. = 113-115 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rₜ = 0.2 (PE/EA = 10/1), 29 mg, yield = 76%; ¹HNMR (500 MHz, CDCl₃) δ 7.83 (d, J = 7.2 Hz, 2H), 7.44 (dt, J = 12.8, 6.9 Hz, 3H), 6.84 (s, 1H), 6.82 (s, 1H), 6.74 (dd, J = 8.4, 2.1 Hz, 1H), 6.43 (dd, J = 8.5 Hz, 1H), 5.32 (s, 1H), 4.20 (d, J = 8.4 Hz, 1H), 3.90 (d, J = 8.5 Hz, 1H), 3.77 (s, 3H), 2.92 (s, 3H), 1.65 (s, 3H); ¹³CNMR (125MHz, CDCl₃) δ 185.8, 160.2, 153.2, 148.5, 147.0, 144.4, 134.3, 130.2, 129.2, 128.8, 125.7, 114.1, 111.3, 108.2, 102.9, 93.6, 78.8, 75.3, 56.4, 56.3, 38.5, 15.0; IR (KBr, cm⁻¹) 3058, 2935, 2362, 1674, 1525, 1496, 1365, 1227, 1145, 1097, 1028, 924, 875, 733; HRMS (ESI) Calcd for C₂₃H₂₂NO₃Na (M+Na)+ 410.1363, found: 410.1362.

7-methoxy-9,10-dimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-bjindol-11(4H)-one (3ah)

Yellow solid, m.p. = 195-196 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rₜ = 0.2 (PE/EA = 10/1), 27 mg, yield = 70%; ¹HNMR (400 MHz, CDCl₃) δ 7.83 (dd, J = 8.1, 1.6 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.05 (d, J = 8.1 Hz, 1H), 6.82 (s, 1H), 6.25 (dd, J = 8.1, 2.2 Hz, 1H), 6.05 (d, J = 2.2 Hz, 1H), 5.28 (s, 1H), 4.15 (d, J = 8.4 Hz, 1H), 3.99 (d, J = 8.4 Hz, 1H), 3.79 (s, 3H), 2.97 (s, 3H), 1.64 (s, 3H); ¹³CNMR (100MHz, CDCl₃) δ 185.6, 161.6, 160.3, 155.2, 147.1, 144.3, 130.2, 129.2, 129.0, 125.7, 124.3, 120.1, 102.9, 102.5, 94.2, 93.5, 78.9, 75.3, 55.6, 55.5, 36.9, 15.2; IR (KBr, cm⁻¹) 3743, 3678, 3655, 2934, 2363, 1835, 1771, 1541, 1427, 1368, 1200, 1028, 972, 817, 783; HRMS (ESI) Calcd for C₂₄H₂₃NO₃Na (M+Na)+ 410.1363, found: 410.1360.

8,9,10-trimethyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-bjindol-11(4H)-one (3ai)

Yellow solid, m.p. = 165-166 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rₜ = 0.2 (PE/EA = 15/1), 28 mg, yield = 76%; ¹HNMR (500 MHz, CDCl₃) δ 7.8’ – 7.82 (m, 2H), 7.48 – 7.40 (m, 3H), 7.09 (d, J = 7.3 Hz, 1H), 6.97 (d, J = 7.4 Hz, 1H), 6.83 (s, 1H), 6.79 (t, J = 7.4 Hz, 1H), 5.26 (s, 1H), 4.27 (d, J = 8.2 Hz, 1H), 3.77 (d, J = 8.2 Hz, 1H), 3.02 (s, 3H), 2.36 (s, 3H), 1.70 (s, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 186.1, 160.1,
152.7, 146.9, 144.5, 131.8, 130.1, 129.6, 129.1, 129.0, 125.7, 121.7, 121.6, 120.5, 102.9, 93.2, 79.2, 76.2, 55.5, 42.0 19.2, 14.9; IR (KBr, cm⁻¹) 3049, 2934, 1675, 1597, 1476, 1366, 1266, 1134, 1026, 925, 822, 766, 734; HRMS (ESI) Calcd for C₂₆H₂₃NO₃H (M+H)⁺ 372.1594, found: 372.1589.

8-bromo-9,10-dimethyl-2-phenyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4 H)-one (3aj)

Yellow solid, m.p. = 185-186 °C, purified by chromatography (petroleum/ethyl acetate = 15:1); Rf = 0.2 (PE/EA = 15/1), 24 mg, yield = 56%; ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, J = 7.3 Hz, 2H), 7.45 (dt, J = 11.8, 6.8 Hz, 3H), 7.30 (d, J = 7.9 Hz, 1H), 7.14 (d, J = 7.3 Hz, 1H), 6.82 (s, 1H), 6.68 (t, J = 7.6 Hz, 1H), 5.26 (s, 1H), 4.28 (d, J = 8.3 Hz, 1H), 3.85 (d, J = 8.2 Hz, 1H), 3.21 (s, 3H), 1.69 (s, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 185.5, 160.4, 151.0, 146.4, 134.1, 132.0, 129.2, 128.9, 125.7, 123.0, 121.1, 104.4, 102.9, 93.3, 79.1, 76.3, 55.4, 41.3, 29.8, 14.9; IR (KBr, cm⁻¹) 3059, 2935, 2364, 1675, 1525, 1453, 1367, 1271, 1099, 973, 803, 755, 692; HRMS (ESI) Calcd for C₂₆H₂₁BrNO₃H (M+H)⁺ 436.0543, found: 436.0541.

2-(3-fluorophenyl)-9,10-dimethyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4 H)-one (3ca)

Yellow solid, m.p. = 148-149 °C, purified by chromatography (petroleum/ethyl acetate = 15:1); Rf = 0.2 (PE/EA = 15/1), 26 mg, yield = 70%; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 9.4 Hz, 1H), 7.42 (q, J = 8.0 Hz, 1H), 7.17 (dd, J = 11.7, 7.5 Hz, 2H), 7.11 (t, J = 8.3 Hz, 1H), 6.86 (s, 1H), 6.73 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 5.34 (s, 1H), 4.23 (d, J = 8.5 Hz, 1H), 3.96 (d, J = 8.5 Hz, 1H), 2.98 (s, 3H), 1.65 (s, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 184.5, 163.2 (d, J = 247.0 Hz), 158.2, 146.5, 146.4, 137.3, 131.2 (d, J = 8.3 Hz), 130.8 (d, J = 8.4 Hz), 128.8, 127.8, 127.5, 121.3, 121.3, 116.8 (d, J = 21.3 Hz), 112.5 (d, J = 23.8 Hz), 103.5, 91.5, 73.2, 52.9, 38.8, 19.6; ¹⁹F NMR (471 MHz, CDCl₃) δ -111.7; IR (KBr, cm⁻¹) 3654, 2928, 2362, 1678, 1525, 1464, 1298, 1204, 1157, 1025, 977, 862, 789, 731; HRMS (ESI) Calcd for C₂₆H₁₈FNO₃H (M+H)⁺ 376.1343, found: 376.1344.

2-(4-chlorophenyl)-9,10-dimethyl-4a,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4 H)-one (3da)

Yellow solid, m.p. = 145-146 °C, purified by chromatography (petroleum/ethyl acetate = 15:1); Rf = 0.2 (PE/EA = 15/1), 28 mg, yield = 72%; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 8.1 Hz, 2H), 6.82 (d, J = 3.1 Hz, 1H), 6.72 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.7 Hz, 1H), 5.33 (s, 1H), 4.22 (d, J = 8.4 Hz, 1H), 3.95 (d, J = 8.5 Hz, 1H), 2.98 (s, 3H), 1.65 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 185.7, 159.0, 153.9, 147.0, 144.5, 136.2, 129.5, 129.2, 127.4, 126.9, 124.0, 117.9, 107.3, 103.3, 93.6, 78.8, 74.5, 56.1, 37.1, 29.8, 15.1; IR (KBr, cm⁻¹) 3056, 2933, 2342, 1677, 1602, 1470, 1353, 1236, 1090, 1021, 937, 827, 738, 704; HRMS (ESI) Calcd for C₂₆H₁₈ClNO₃H (M+H)⁺ 392.1048, found: 392.1044.
2-(4-methoxyphenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ea)

Yellow solid, m.p. = 189-190 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10:1), 26 mg, yield = 68%; 1HNMR (500 MHz, CDCl3) δ 7.78 (d, J = 8.4 Hz, 2H), 7.19 – 7.13 (m, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 6.3 Hz, 2H), 6.48 (d, J = 7.8 Hz, 1H), 5.32 (s, 1H), 4.21 (d, J = 8.4 Hz, 1H), 3.96 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H), 2.98 (s, 3H), 1.65 (s, 3H); 13CNMR (125 MHz, CDCl3) δ 185.2, 161.3, 160.6, 153.9, 147.5, 143.8, 129.1, 127.5, 127.4, 124.0, 121.7, 117.8, 114.6, 107.2, 93.5, 78.9, 74.6, 56.2, 55.6, 37.1, 15.1; IR (KBr, cm−1) 3029, 2964, 2360, 1676, 1603, 1515, 1481, 1367, 1298, 1112, 1024, 973, 807; HRMS (ESI) Calcd for C23H21NO3Na (M+Na)+ 410.1363, found: 410.1356.

2-(4-ethylphenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3fa)

White solid, m.p. = 150-152 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.3 (PE/EA = 10:1), 27 mg, yield = 70%; 1HNMR (500 MHz, CDCl3) δ 7.76 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.16 (dd, J = 12.1, 7.4 Hz, 2H), 6.78 (s, 1H), 6.72 (t, J = 7.4 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 5.32 (s, 1H), 4.22 (d, J = 8.5 Hz, 1H), 3.96 (d, J = 8.5 Hz, 1H), 2.98 (s, 3H), 2.70 (q, J = 7.6 Hz, 2H), 1.65 (s, 3H), 1.27 (t, J = 7.6 Hz, 3H); 13CNMR (125 MHz, CDCl3) δ 185.6, 160.8, 154.0, 147.4, 147.0, 144.2, 129.3, 128.8, 127.7, 126.6, 125.0, 124.1, 118.0, 107.3, 102.4, 93.7, 79.0, 74.7, 56.3, 37.3, 29.1, 15.5, 15.2; IR (KBr, cm−1) 3054, 2929, 2362, 1675, 1605, 1481, 1441, 1368, 1297, 1265, 1123, 973, 927, 890, 728; HRMS (ESI) Calcd for C23H22NO3H (M+H)+ 386.1751, found: 386.1751.

2-(4-butylphenyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ga)

Yellow solid, m.p. = 122-124 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.25 (PE/EA = 15:1), 31 mg, yield = 75%; 1HNMR (500 MHz, CDCl3) δ 7.66 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 7.7 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.70 (s, 1H), 6.63 (d, J = 7.3 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 5.24 (s, 1H), 4.13 (d, J = 8.5 Hz, 1H), 3.87 (d, J = 8.5 Hz, 1H), 2.89 (s, 3H), 2.60 – 2.54 (m, 2H), 1.57 (s, 3H), 1.55 – 1.50 (m, 2H), 1.32 – 1.26 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H); 13CNMR (125 MHz, CDCl3) δ 185.4, 160.7, 153.9, 147.2, 145.6, 144.1, 129.2, 129.1, 127.5, 126.4, 125.7, 124.0, 117.9, 107.2, 102.3, 93.5, 78.9, 74.6, 56.2, 37.1, 35.7, 33.5, 29.8, 22.5, 15.1, 14.0; IR (KBr, cm−1) 3054, 2929, 2362, 1675, 1605, 1481, 1441, 1368, 1297, 1265, 1123, 973, 927, 890, 834; HRMS (ESI) Calcd for C23H22NO3H (M+H)+ 414.2064, found: 414.2061.

9,10-dimethyl-2-(napthalen-1-yl)-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ha)

White solid, m.p. = 166-168 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1) (exo:endo=1:1) 40 mg, yield = 98%; 1HNMR (500 MHz, CDCl3) δ 8.31 (d, J = 8.4 Hz, 1H), 7.82 (dd, J = 11.0, 8.1 Hz, 2H), 7.77 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.2 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.44 (dd, J = 8.7, 4.3 Hz, 3H), 7.39 –
7.29 (m, 3H), 7.12 (d, J = 7.3 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 7.3 Hz, 1H), 6.86 (t, J = 7.7 Hz, 1H), 6.81 (s, 1H), 6.65 (d, J = 7.4 Hz, 1H), 6.55 (t, J = 7.4 Hz, 1H), 6.39 (d, J = 7.9 Hz, 1H), 6.19 (s, 1H), 6.07 (d, J = 8.0 Hz, 1H), 5.48 (d, J = 7.0 Hz, 1H), 5.31 (s, 1H), 4.45 (dd, J = 10.4, 7.0 Hz, 1H), 4.20 (d, J = 8.5 Hz, 1H), 4.10 (d, J = 10.4 Hz, 1H), 3.91 (d, J = 8.5 Hz, 1H), 2.89 (s, 3H), 2.62 (s, 3H), 1.71 (s, 3H), 1.59 (s, 3H); 1H NMR (125 MHz, CDCl3) δ 185.7, 184.5, 160.0, 157.3, 153.8, 153.2, 146.6, 146.3, 144.6, 141.6, 134.0, 133.7, 130.9, 130.5, 130.3, 129.2, 128.9, 128.5, 128.0, 127.6, 127.5, 127.4, 127.0, 126.5, 126.48, 126.2, 125.3, 125.2, 125.1, 124.3, 124.0, 117.9, 117.2, 109.0, 107.6, 107.2, 93.6, 91.0, 79.6, 78.9, 77.9, 74.5, 56.1, 53.6, 37.1, 35.6, 19.5, 15.1; IR (KBr, cm–1) 3428, 2980, 2364, 1683, 1521, 1494, 1285, 1163, 1065, 982, 896, 736; HRMS (ESI) Calcd for C27H21O3NNa (M+Na)+ 430.1414, found: 430.1411.

9,10-dimethyl-2-(thiophen-3-yl)-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ia)

Green solid, m.p. = 138-139 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 26 mg, yield = 72%; 1HNMR (500 MHz, CDCl3) δ 7.85 – 7.80 (m, 1H), 7.44 (d, J = 4.5 Hz, 1H), 7.40 (dd, J = 5.1, 3.0 Hz, 1H), 7.16 (t, J = 8.1 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 6.67 (s, 1H), 6.48 (d, J = 7.8 Hz, 1H), 5.32 (s, 1H), 4.21 (d, J = 8.4 Hz, 1H), 3.95 (d, J = 8.5 Hz, 1H), 2.98 (s, 3H), 1.65 (s, 3H); 13CNMR (125MHz, CDCl3) δ 185.5, 156.7, 153.8, 147.1, 143.7, 130.7, 129.2, 127.44, 127.3, 125.2, 124.2, 124.0, 117.9, 107.2, 102.7, 93.5, 78.8, 74.5, 56.1, 37.1, 15.1; IR (KBr, cm–1) 3108, 2935, 1673, 1603, 1552, 1495, 1364, 1297, 1020, 975, 858, 789, 739, 702; HRMS (ESI) Calcd for C27H17NO3SH (M+H)+ 364.1002, found: 364.1001.

2-(tert-butyl)-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ja)

White solid, m.p. = 156-157 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 24 mg, yield = 72%; 1HNMR (500 MHz, CDCl3) δ 7.14 (dt, J = 7.4, 4.0 Hz, 2H), 6.70 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 8.2 Hz, 1H), 6.24 (s, 1H), 5.24 (s, 1H), 4.17 (d, J = 8.5 Hz, 1H), 3.93 (d, J = 8.5 Hz, 1H), 2.97 (s, 3H), 1.62 (s, 3H), 1.35 (s, 9H); 13CNMR (125 MHz, CDCl3) δ 185.4, 172.4, 153.9, 146.6, 143.8, 129.1, 127.6, 124.0, 117.8, 107.2, 101.6, 93.4, 78.9, 74.5, 56.0, 37.1, 33.7, 28.9, 15.1; IR (KBr, cm–1) 3054, 2930, 2364, 1677, 1570, 1461, 1382, 1264, 1160, 975, 882, 782, 704; HRMS (ESI) Calcd for C23H22NO3H (M+H)+ 338.1751, found: 338.1748.

2-cyclopropyl-9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ka)

White solid, m.p. = 153-155 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 20 mg, yield = 61%; 1HNMR (500 MHz, CDCl3) δ 7.18 – 7.10 (m, 2H), 6.69 (t, J = 7.4 Hz, 1H), 6.46 (d, J = 8.1 Hz, 1H), 6.20 (s, 1H), 5.21 (s, 1H), 4.14 (d, J = 8.5 Hz, 1H), 3.89 (d, J = 8.5 Hz, 1H), 2.95 (s, 3H), 2.06 – 1.97 (m, 1H), 1.60 (s, 3H), 1.13 – 1.00 (m, 4H); 13CNMR (125 MHz, CDCl3) δ 184.7, 166.3, 153.9, 147.2, 143.1, 129.1, 127.6, 124.0, 117.8, 107.1, 102.5, 93.3, 78.8, 74.6, 56.1, 37.1, 31.5, 15.0, 10.0, 9.0; IR (KBr, cm–1) 2983, 2935, 1674, 1529, 1495, 1368, 1298, 1158, 978, 958, 832, 742; HRMS (ESI) Calcd for C20H16NO3H (M+H)+ 322.1438, found: 322.1425.
9,10-dimethyl-2-pentyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3la)

White solid, m.p. = 100-101 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 27 mg, yield = 78%; 1H NMR (500 MHz, CDCl3) δ 7.14 (dt, J = 7.3, 3.7 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 8.1 Hz, 1H), 6.23 (s, 1H), 5.24 (s, 1H), 4.15 (d, J = 8.5 Hz, 1H), 3.91 (d, J = 8.5 Hz, 1H), 2.96 (s, 3H), 2.72 (t, J = 7.7 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.62 (s, 3H), 1.35 (dt, J = 7.0, 3.6 Hz, 4H), 0.93 – 0.88 (m, 3H); 13CNMR (125 MHz, CDCl3) δ 185.2, 165.1, 153.8, 146.6, 143.8, 129.0, 127.4, 123.9, 117.7, 107.0, 104.0, 93.2, 78.7, 74.4, 56.0, 37.0, 31.3, 28.5, 27.3, 22.3, 14.9, 13.9; IR (KBr, cm⁻¹) 3054, 2931, 2866, 1677, 1606, 1520, 1495, 1336,1265, 1120, 1026, 981, 739, 704; HRMS (ESI) Caled for C22H28NO3H (M+H)⁺ 352.1907, found: 352.1902.

9,10-dimethyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ma)

White solid, m.p. = 174-175 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 19 mg, yield = 67%; 1H NMR (500 MHz, CDCl3) δ 7.64 (s, 1H), 7.16 (t, J = 8.2 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 6.61 (s, 1H), 6.48 (d, J = 7.8 Hz, 1H), 5.32 (s, 1H), 4.18 (d, J = 8.5 Hz, 1H), 3.92 (d, J = 8.5 Hz, 1H), 2.97 (s, 3H), 1.63 (s, 3H); 13CNMR (125 MHz, CDCl3) δ 186.3, 153.8, 148.8, 145.3, 145.0, 129.2, 127.4, 124.0, 117.9, 108.2, 107.2, 93.5, 78.9, 74.3, 56.1, 37.1, 15.0; IR (KBr, cm⁻¹) 3056, 2993, 2890, 2362, 1717, 1625, 1525, 1442, 1335, 1220, 1119, 1050, 970, 792; HRMS (ESI) Caled for C17H13NO3Na(M+Na)⁺ 304.0944, found: 304.0950.

9-benzyl-10-methyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3ak)

Yellow solid, m.p. = 190-191 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 39 mg, yield = 91%; 1H NMR (400 MHz, CDCl3) δ 8.37 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 11.3, 8.1 Hz, 2H), 7.84 (d, J = 7.2 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.25 – 7.19 (m, 5H), 7.14 (dd, J = 23.3, 7.3 Hz, 3H), 6.90 (s, 1H), 6.75 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 7.9 Hz, 1H), 5.43 (s, 1H), 4.80 (d, J = 16.4 Hz, 1H), 4.38 – 4.29 (m, 2H), 4.19 (d, J = 8.5 Hz, 1H), 1.70 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 185.7, 160.0, 153.1, 146.2, 144.7, 137.5, 134.0, 130.9, 130.3, 129.2, 129.0, 128.8, 128.0, 127.7, 127.6, 127.4, 126.6, 126.55, 125.3, 125.1, 124.2, 118.3, 108.3, 107.2, 93.6, 78.7, 71.2, 56.0, 52.6, 15.3; IR (KBr, cm⁻¹) 3649, 3054, 2829, 1677, 1515, 1454, 1365, 1228, 1110, 1034, 970, 825, 704; HRMS(ESI)Caled for C28H30NO3 (M+Na)⁺ 456.1570,found: 456.1573.

9-benzyl-2-(4-chlorophenyl)-10-methyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3',2':4,5]cyclohepta[1,2-b]indol-11(4H)-one (3dk)

Yellow solid, m.p. = 117-118 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 34 mg, yield = 72%; 1H NMR (500 MHz, CDCl3) δ 7.65 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.19 – 7.11 (m, 4H), 7.07 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 7.7 Hz, 1H), 6.72 (s, 1H), 6.66 (t, J = 7.4 Hz, 1H), 6.49 (d, J = 7.9 Hz, 1H), 5.27 (s, 1H), 4.70 (d, J = 16.3 Hz, 1H), 4.24 (d, J = 16.4 Hz, 1H), 4.13 (d, J = 8.5 Hz, 1H), 4.03 (d, J = 8.5 Hz, 1H), 1.58 (s, 3H); 13CNMR (125 MHz, CDCl3) δ 185.7, 158.9, 153.1, 146.6, 144.5, 137.4, 136.2, 129.5, 129.2, 128.8, 127.7, 127.6, 127.4, 127.4, 126.8, 124.2, 118.3, 108.3, 103.3, 93.5, 78.6, 71.2, 55.9, 52.7, 15.2; IR (KBr, cm⁻¹) 3656, 2980, 2362, 1675,1515, 1442, 1368, 1217, 1112, 1098, 927, 856, 742, 702; HRMS (ESI) Caled for C29H22ClNO3H (M+Na)⁺ 468.1361, found: 468.1363.
9-allyl-10-methyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3al)

White solid, m.p. = 148-150 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 23 mg, yield = 60%; 1HNMR (400 MHz, CDCl3) δ 7.84 (d, J = 1.7 Hz, 1H), 7.82 (d, J = 1.3 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.19 (d, J = 7.3 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H), 6.84 (s, 1H), 6.79 – 6.72 (m, 1H), 6.57 (d, J = 7.9 Hz, 1H), 5.83-5.7 (m, 1H), 5.35 (s, 1H), 5.18 (dd, J = 7.9, 1.4 Hz, 1H), 5.15 (t, J = 1.4 Hz, 1H), 4.23 (d, J = 8.5 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.74 (dd, J = 16.4, 6.6 Hz, 1H), 1.65 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 185.8, 160.2, 152.9, 146.9, 144.4, 132.9, 130.2, 129.2, 129.0, 128.96, 128.1, 125.7, 124.1, 118.5, 118.2, 108.7, 102.9, 93.4, 78.8, 71.6, 56.1, 52.3, 15.3; IR (KBr, cm⁻¹) 3768, 3649, 1886, 1770, 1676, 1516, 1425, 1396, 1236, 1115, 1025, 971, 827; HRMS (ESI) Caled for C25H21NO3Na (M+Na)⁺ 406.1414, found: 406.1409.

9-allyl-2-(4-ethylphenyl)-10-methyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3f)

Yellow solid, m.p. = 151-152 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.2 (PE/EA = 15/1), 28 mg, yield = 68%; 1HNMR (400 MHz, CDCl3) 7.67 (d, J = 7.9 Hz, 2H), 7.26 – 7.16 (m, 2H), 7.10 (d, J = 7.3 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.70 (s, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.49 (d, J = 7.9 Hz, 1H), 5.69 (d, J = 10.7, 5.3 Hz, 1H), 5.25 (s, 1H), 5.15 – 5.02 (m, 2H), 4.14 (d, J = 8.5 Hz, 1H), 4.02 (dd, J = 19.2, 6.7 Hz, 2H), 3.66 (dd, J = 16.4, 6.6 Hz, 1H), 2.61 (q, J = 7.7 Hz, 2H), 1.57 (s, 3H), 1.19 (t, J = 7.6 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ 185.6, 160.6, 152.9, 147.1, 146.8, 144.1, 132.9, 129.0, 128.7, 128.2, 126.4, 125.8, 124.1, 118.4, 118.2, 108.6, 102.3, 93.3, 78.8, 71.6, 56.1, 52.3, 28.9, 15.4, 15.3; IR (KBr, cm⁻¹) 3542, 2980, 2832, 1617, 1549, 1444, 1328, 1259, 1198, 1009, 928, 843, 765; HRMS (ESI) Caled for C25H21NO3H (M+H)⁺ 412.1907, found: 412.1901.

10-methyl-2-phenyl-4a,9,9a,10-tetrahydro-4,10-epoxyfuro[3′,2′:4,5]cyclohepta[1,2-b]indol-11(4H)-one (3am)

Green solid, m.p. = 178-179 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 24 mg, yield =70%; 1HNMR (400 MHz, CDCl3) δ 7.86 (d, J = 7.1 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.25 (d, J = 7.3 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.87 (s, 1H), 6.79 (t, J = 7.4 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 5.36 (s, 1H), 4.31 (d, J = 8.2 Hz, 1H), 4.24 (d, J = 8.2 Hz, 1H), 1.64 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 185.8, 160.3, 151.5, 146.7, 144.5, 130.2, 129.1, 129.0, 128.9, 127.2, 125.7, 124.2, 119.0, 109.0, 103.0, 92.6, 79.1, 66.2, 56.6, 15.1; IR (KBr, cm⁻¹) 3687, 3421, 2927, 1670, 1528, 1466, 1368, 1257, 1106, 1022, 973, 828, 754; HRMS (ESI) Caled for C25H21NO3Na (M+Na)⁺ 366.1101, found: 366.1103.
### 1.4 Optimization of reaction conditions

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<th>Cat. (mol %)</th>
<th>Solv. (mL)</th>
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<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
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<td>PPh₃AuCl/AgBF₄ (5)</td>
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<tr>
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*a* Reaction conditions: 1a (0.1 mmol), 4a (0.15 mmol) and catalyst in 2 mL DCE were stirred for 12 h. *b* isolated yield.

### 1.5 General procedure for the synthesis of 5

To a 25 mL Schlenk tube with a magnetic bar under nitrogen atmosphere were added substrates 1 (0.1 mmol) and olefin (1.5eq) in 1,2-dichloroethane (DCE, 2 mL), then ZnI₂ (20 mol%) was added. The resulting mixture was stirred at room temperature for 12 h. After the reaction was finished, the mixture was filtered by short silica. the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the product 5.

#### 7-methyl-2,6-diphenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5aa)

Yellow solid, m.p. = 179-181 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rₚ = 0.3 (PE/EA = 1/1), 32 mg, yield = 99%; *HNMR* (400 MHz, CDCl₃) δ 7.85 (d, J = 7.5 Hz, 2H), 7.50 – 7.37 (m, 3H), 7.19 (d, J = 5.2 Hz, 3H), 6.82 (d, J = 5.3 Hz, 3H), 5.44 (d, J = 7.1 Hz, 1H), 3.57 (dd, J = 11.0, 4.5 Hz, 1H), 3.04 (td, J = 11.9, 7.4 Hz, 1H), 2.22 (dd, J = 12.7, 4.6 Hz, 1H), 1.68 (s, 3H); *CNMR* (100 MHz, CDCl₃) δ 184.3, 159.7, 146.6, 146.2, 137.4, 129.9, 129.1, 129.08, 128.7, 127.9, 127.4, 125.6, 102.6, 91.4, 73.2, 55.0, 38.9, 19.6; *IR* (KBr, cm⁻¹) 3743, 3678, 3788, 2981, 1832, 1741, 1690, 1530, 1453, 1389, 1258, 1112, 979, 766, 695; *HRMS* (ESI) Caled for C₂₂H₁₈O₃Na (M+Na)⁺ 353.1148, found: 353.1147.
7-ethyl-2,6-diphenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5ba)

Yellow solid, m.p. = 155-156 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.25 (PE/EA = 10/1), 30 mg, yield = 86%; 1HNMR (400 MHz, CDCl3) δ 7.17 (dd, J = 5.0, 2.1 Hz, 3H), 6.74 (dd, J = 6.4, 2.5 Hz, 2H), 6.20 (s, 1H), 5.34 (d, J = 7.0 Hz, 1H), 3.52 (dd, J = 11.0, 4.6 Hz, 1H), 2.98 (td, J = 11.9, 11.3, 7.1 Hz, 1H), 2.74 (t, J = 7.6 Hz, 2H), 2.14 (dd, J = 12.7, 4.6 Hz, 1H), 1.73 (d, J = 7.0 Hz, 2H), 1.63 (s, 3H), 1.35 (dt, J = 7.2, 3.9 Hz, 4H), 0.92 (t, J = 6.8 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ 183.8, 159.5, 146.8, 146.4, 137.5, 129.9, 129.1, 129.1, 128.6, 128.0, 127.3, 125.6, 102.6, 94.4, 73.0, 51.0, 38.7, 26.3, 8.5; IR (KBr, cm⁻¹) 3657, 2972, 1672, 1605, 1525, 1494, 1297, 1032, 886, 738, 690; HRMS (ESI) Calcd for C25H28O3Na (M+Na⁺) 367.1305, found: 367.1299.

2-(3-fluorophenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5ca)

Yellow solid, m.p. = 188 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 27 mg, yield = 78%; 1HNMR (400 MHz, CDCl3) δ 7.62 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 9.5 Hz, 1H), 7.42 (q, J = 7.9 Hz, 1H), 7.18 (s, 3H), 7.11 (t, J = 8.2 Hz, 1H), 6.81 (d, J = 9.0 Hz, 3H), 5.44 (d, J = 7.0 Hz, 1H), 3.57 (dd, J = 11.0, 4.6 Hz, 1H), 3.05 (td, J = 12.0, 7.3 Hz, 1H), 2.22 (dd, J = 12.7, 4.5 Hz, 1H), 1.67 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 184.5, 163.2 (d, J = 247.0 Hz), 158.2, 146.5, 146.4, 137.3, 131.2 (d, J = 8.3 Hz), 130.8 (d, J = 8.4 Hz), 128.8, 127.8, 127.5, 121.3 (d, J = 3.0 Hz), 116.8 (d, J = 21.3 Hz), 112.5 (d, J = 23.8 Hz), 103.5, 91.5, 73.2, 52.9, 38.8, 19.6; 19FNMRI (376 MHz, CDCl3) δ -111.8; IR (KBr, cm⁻¹) 3743, 3649, 3620, 2981, 2362, 1917, 1679, 1516, 1397, 1202, 1113, 980, 821, 787; HRMS (ESI) Calcd for C22H12FO3Na (M+Na⁺) 371.1054, found: 371.1056.

2-(3-chlorophenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5na)

Yellow solid, m.p. = 154-155 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.3 (PE/EA = 10/1), 26 mg, yield = 72%; 1HNMR (500 MHz, CDCl3) δ 7.83 (s, 1H), 7.71 (d, J = 6.3 Hz, 1H), 7.38 (d, J = 5.7 Hz, 2H), 7.18 (d, J = 6.1 Hz, 3H), 6.83 (s, 1H), 6.80 (d, J = 5.6 Hz, 2H), 5.44 (d, J = 7.0 Hz, 1H), 3.57 (dd, J = 11.0, 4.6 Hz, 1H), 3.05 (td, J = 12.0, 7.2 Hz, 1H), 2.22 (dd, J = 12.8, 4.7 Hz, 1H), 1.67 (s, 3H); 13CNMR (125 MHz, CDCl3) δ 184.5, 158.0, 146.6, 146.3, 137.2, 135.3, 130.8, 130.4, 129.8, 128.8, 127.8, 127.5, 126.0, 123.6, 103.5, 91.4, 73.2, 52.9, 38.8, 19.6; IR (KBr, cm⁻¹) 3768, 3649, 1886, 1770, 1676, 1516, 1425, 1396, 1236, 1115, 1025, 971, 827; HRMS (ESI) Calcd for C22H12ClO3Na (M+Na⁺) 387.0758, found: 387.0750.

2-(4-ethoxyphenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5qa)

White solid, m.p. = 185-186 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.15 (PE/EA = 10/1), 33 mg, yield = 87%; 1HNMR (400 MHz, CDCl3) δ 7.77 (d, J = 8.8 Hz, 2H), 7.21 – 7.15 (m, 3H), 6.96 (d, J = 8.9 Hz, 2H), 6.82 (dd, J = 7.3, 2.0 Hz, 2H), 6.66 (s, 1H), 5.41 (d, J = 7.0 Hz, 1H), 4.09 (q, J = 7.0 Hz, 2H), 3.55 (dd, J = 11.1, 4.8 Hz, 1H), 3.03 (ddd, J = 12.6, 11.2, 7.2 Hz, 1H), 2.20 (dd, J = 12.7, 4.8 Hz, 1H), 1.66 (s, 3H), 1.45 (t, J = 7.0 Hz, 3H); 13CNMR (100 MHz, CDCl3) δ 183.9, 160.6, 160.2, 147.0, 145.7, 137.5, 128.7, 127.9, 127.4, 127.3, 121.8, 115.1, 101.0, 91.3, 73.3, 63.8, 53.1, 39.0, 19.7, 14.9; IR (KBr, cm⁻¹) 3649, 3566, 2980, 1868, 1793, 1618, 1539, 1478, 1368, 1253, 1112, 1036, 978, 830, 746; HRMS (ESI) Calcd for C24H22O4Na (M+Na⁺) 397.1410, found: 397.1414.
2-(4-methoxyphenyl)-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ea)

Yellow solid, m.p. = 110-112°C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 31 mg, yield = 86%; \(^1\)HNMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.79 (d, \(J = 8.4\ Hz, 2H\)), 7.18 (d, \(J = 6.6\ Hz, 3H\)), 6.97 (d, \(J = 8.4\ Hz, 2H\)), 6.83 (d, \(J = 7.6\ Hz, 2H\)), 6.68 (s, 1H), 5.42 (d, \(J = 7.1\ Hz, 1H\)), 3.86 (s, 3H), 3.55 (dd, \(J = 11.1, 4.8\ Hz, 1H\)), 3.03 (td, \(J = 11.9, 7.1\ Hz, 1H\)), 2.20 (dd, \(J = 12.7, 4.7\ Hz, 1H\)), 1.67 (s, 3H); \(^13\)CNMR (125 MHz, CDCl\(_3\)) \(\delta\) 183.9, 161.1, 160.0, 147.0, 145.6, 137.4, 128.7, 127.9, 127.4, 127.3, 121.9, 114.5, 101.1, 91.3, 73.2, 55.5, 53.0, 38.9, 19.6; IR (KBr, cm\(^{-1}\)) 3028, 2980, 1683, 1521, 1474, 1352, 1245, 1163, 1024, 982, 859, 736; HRMS (ESI) Calcd for C\(_{25}\)H\(_{29}\)O\(_3\)Na (M+Na\(^+\)) 383.1254, found: 383.1247.

7-methyl-2-(naphthalen-1-yl)-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ha)

Yellow solid, m.p. = 150-152 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 33 mg, yield = 86%; \(^1\)HNMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.43 (d, \(J = 8.4\ Hz, 1H\)), 7.94 (t, \(J = 9.0\ Hz, 2H\)), 7.89 (d, \(J = 6.9\ Hz, 1H\)), 7.63 – 7.52 (m, 3H), 7.22 (q, \(J = 6.2\ Hz, 3H\)), 6.89 (s, 1H), 6.87 (d, \(J = 6.7\ Hz, 2H\)), 5.52 (d, \(J = 7.0\ Hz, 1H\)), 3.62 (dd, \(J = 11.0, 4.5\ Hz, 1H\)), 3.12 – 3.05 (m, 1H), 2.31 (dd, \(J = 12.8, 4.5\ Hz, 1H\)), 1.73 (s, 3H); \(^13\)CNMR (125 MHz, CDCl\(_3\)) \(\delta\) 184.4, 159.7, 146.6, 146.0, 137.5, 134.0, 130.7, 130.3, 128.9, 128.7, 127.9, 127.8, 127.6, 127.5, 126.8, 126.5, 125.3, 125.1, 106.8, 91.4, 73.4, 52.9, 38.9, 19.6; IR (KBr, cm\(^{-1}\)) 2963, 2930, 2361, 1686, 1528, 1437, 1370, 1292, 1183, 1073, 968, 817, 727; HRMS (ESI) Calcd for C\(_{27}\)H\(_{32}\)O\(_3\)Na (M+Na\(^+\)) 403.1305, found: 403.1303.

7-methyl-6-phenyl-2-(thiophen-3-yl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ia)

Yellow solid, m.p. = 195 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.3 (PE/EA = 10/1), 26 mg, yield = 78%; \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (dd, \(J = 2.9, 1.2\ Hz, 1H\)), 7.46 (dd, \(J = 5.1, 1.1\ Hz, 1H\)), 7.41 (dd, \(J = 5.1, 2.9\ Hz, 1H\)), 7.22 – 7.15 (m, 3H), 6.82 (d, \(J = 2.4\ Hz, 1H\)), 6.81 (d, \(J = 1.6\ Hz, 1H\)), 6.63 (s, 1H), 5.42 (d, \(J = 7.0\ Hz, 1H\)), 3.56 (dd, \(J = 11.0, 4.8\ Hz, 1H\)), 3.03 (m, 1H), 2.21 (dd, \(J = 12.7, 4.8\ Hz, 1H\)), 1.66 (s, 3H); \(^13\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\) 184.2, 156.3, 146.7, 145.6, 137.4, 131.0, 128.7, 127.9, 127.5, 127.2, 125.3, 124.0, 102.4, 91.4, 73.2, 53.0, 38.9, 19.6; IR (KBr, cm\(^{-1}\)) 3768, 3620, 2979, 1740, 1679, 1531, 1429, 1369, 1264, 1110, 955, 887, 746, 699; HRMS (ESI) Calcd for C\(_{23}\)H\(_{29}\)O\(_3\)Na (M+Na\(^+\)) 359.0712, found: 359.0713.

7-methyl-2-(m-toly)-6-(p-toly)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ob)

Yellow solid, m.p. = 152-154 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 31 mg, yield = 87%; \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (s, 1H), 7.53 (d, \(J = 7.7\ Hz, 1H\)), 7.23 (t, \(J = 7.7\ Hz, 1H\)), 7.12 (d, \(J = 7.5\ Hz, 1H\)), 6.89 (d, \(J = 7.9\ Hz, 2H\)), 6.68 (s, 1H), 6.60 (d, \(J = 7.9\ Hz, 2H\)), 5.31 (d, \(J = 7.1\ Hz, 1H\)), 3.43 (dd, \(J = 11.1, 4.6\ Hz, 1H\)), 2.91 (td, \(J = 11.9, 7.3\ Hz, 1H\)), 2.31 (s, 3H), 2.14 (s, 3H), 2.08 (dd, \(J = 12.7, 4.6\ Hz, 1H\)), 1.57 (s, 3H); \(^13\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\) 184.4, 159.8, 146.6, 146.1, 138.9, 137.0, 134.3, 130.7, 129.4, 129.0, 128.9, 127.6, 126.2, 122.8, 102.5, 91.3, 73.2, 52.6, 38.8, 21.4, 21.0, 19.6; IR (KBr, cm\(^{-1}\)) 3756, 2983, 1681, 1566, 1482, 1387, 1253, 1162, 925, 892,784; HRMS (ESI) Calcd for C\(_{23}\)H\(_{29}\)O\(_3\)Na (M+Na\(^+\)) 381.1461, found: 381.1463.
7-methyl-2,6-di-p-toly-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5eb)

White solid, m.p. = 146-148 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.3 (PE/EA = 10/1), 33 mg, yield = 88%; ¹HNMR (500 MHz, CDCl₃) δ 7.73 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 5.6 Hz, 2H), 6.74 (s, 1H), 6.71 (d, J = 2.5 Hz, 4H), 5.39 (d, J = 7.0 Hz, 1H), 3.70 (s, 3H), 3.50 (dd, J = 11.1, 4.7 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.39 (s, 3H), 2.14 (dd, J = 12.7, 4.7 Hz, 1H), 1.64 (s, 3H); ¹³CNMR (125 MHz, CDCl₃) δ 184.4, 160.0, 158.8, 146.8, 145.9, 140.3, 129.8, 129.3, 128.8, 126.4, 125.6, 114.1, 101.9, 91.1, 73.1, 55.2, 52.2, 39.0, 21.6, 19.6; IR (KBr, cm⁻¹) 3078, 2394, 1625, 1559, 1452, 1375, 1254, 1182, 1059, 970,835; HRMS (ESI) Calcd for C₂₅H₂₀O₂ (M+H)⁺ 397.1610, found: 397.1613.

2-(4-ethylphenyl)-7-methyl-6-(p-tolyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5fb)

White solid, m.p. = 167 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.3 (PE/EA = 10/1), 33 mg, yield = 89%; ¹HNMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 7.8 Hz, 2H), 6.76 (s, 1H), 6.71 (d, J = 7.9 Hz, 2H), 5.42 (d, J = 7.0 Hz, 1H), 3.53 (dd, J = 11.0, 4.6 Hz, 1H), 3.02 (td, J = 11.9, 7.3 Hz, 1H), 2.71 (q, J = 7.6 Hz, 2H), 2.25 (s, 3H), 2.19 (dd, J = 12.7, 4.7 Hz, 1H), 1.67 (s, 3H), 1.29 (d, J = 7.6 Hz, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 184.3, 160.0, 146.7, 146.6, 145.9, 137.0, 134.3, 129.4, 128.6, 127.7, 126.6, 125.7, 102.0, 91.3, 73.2, 52.6, 38.9, 28.9, 21.1, 19.6, 15.5; IR (KBr, cm⁻¹) 3743, 3620, 2930, 2362, 1741, 1680, 1515, 1480, 1368, 1290, 1186, 1114, 1024, 979, 871, 675; HRMS (ESI) Calcd for C₂₅H₂₀O₂Na (M+Na)⁺ 395.1618, found: 395.1620.

2-(4-(tert-butyl)phenyl)-7-methyl-6-(p-tolyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5pb)

White solid, m.p. = 150 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 32 mg, yield = 80%; ¹HNMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 7.6 Hz, 2H), 6.78 (s, 1H), 6.70 (d, J = 7.7 Hz, 2H), 5.42 (d, J = 7.0 Hz, 1H), 3.53 (dd, J = 11.0, 4.4 Hz, 1H), 3.02 (td, J = 11.8, 7.3 Hz, 1H), 2.25 (s, 3H), 2.19 (dd, J = 12.7, 4.5 Hz, 1H), 1.67 (s, 3H), 1.37 (s, 9H); ¹³CNMR (100 MHz, CDCl₃) δ 184.3, 159.9, 153.4, 146.7, 146.0, 137.0, 134.3, 129.4, 127.7, 126.4, 126.0, 125.4, 102.1, 91.3, 73.2, 52.6, 38.9, 35.0, 31.3, 21.1, 19.6; IR (KBr, cm⁻¹) 3754, 2938, 1606, 1496, 1368, 1296, 1119, 922, 836, 701; HRMS (ESI) Calcd for C₂₅H₂₀O₂Na (M+Na)⁺ 423.1931, found: 423.1935.

2-cyclopropyl-7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5ka)

Yellow oil, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.3 (PE/EA = 15/1), 22 mg, yield =75%; ¹HNMR (400 MHz, CDCl₃) δ 7.24 – 7.09 (m, 3H), 6.82 – 6.71 (m, 2H), 6.15 (s, 1H), 5.31 (d, J = 7.0 Hz, 1H), 3.50 (dd, J = 11.0, 4.8 Hz, 1H), 2.97 (td, J = 11.9, 11.2, 7.1 Hz, 1H), 2.12 (dd, J = 12.6, 4.8 Hz, 1H), 2.08 – 1.98 (m, 1H), 1.62 (s, 3H), 1.10 – 0.99 (m, 4H); ¹³CNMR (100MHz, CDCl₃) δ 183.5, 165.7, 146.6, 145.1, 137.6, 128.6, 127.9, 127.4, 102.0, 91.1, 73.2, 53.0, 38.9, 19.6, 10.0, 9.0, 8.8; IR (KBr, cm⁻¹) 3678, 3620, 1835, 1770, 1740, 1646, 1515, 1465, 1396, 1284, 1019, 787; HRMS (ESI) Calcd for C₁₉H₁₈O₂H (M+H)⁺ 295.1329, found: 295.13232.

7-methyl-2-pentyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycycloheptafuran-8-one (5la)

Yellow oil, purified by chromatography (petroleum/ethyl acetate = 15:1), Rf = 0.3 (PE/EA = 15/1), 26 mg, yield = 85%; ¹HNMR (500 MHz, CDCl₃) δ 7.17 (dd, J = 5.0, 2.1 Hz, 3H), 6.74 (dd, J = 6.4, 2.5 Hz, 2H), 6.20 (s, 1H), 5.34 (d, J = 7.0 Hz, 1H), 3.52
7-methyl-6-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ma)

White solid, m.p. = 190-191°C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.25 (PE/EA = 10/1), 19 mg, yield = 75%; 1HNMR (400 MHz, CDCl3) δ 7.65 (d, J = 1.8 Hz, 1H), 7.18 (dd, J = 5.1, 1.9 Hz, 3H), 6.72 (dd, J = 6.7, 2.9 Hz, 2H), 6.58 (d, J = 1.8 Hz, 1H), 5.42 (d, J = 7.0 Hz, 1H), 3.55 (dd, J = 11.1, 4.7 Hz, 1H), 3.01 (td, J = 11.9, 11.3, 7.1 Hz, 1H), 2.17 (dd, J = 12.7, 4.6 Hz, 1H), 1.65 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 184.8, 148.3, 147.2, 144.4, 137.3, 128.7, 127.8, 127.5, 107.9, 91.3, 73.3, 52.8, 38.8, 19.5; IR (KBr, cm⁻¹) 3725, 3286, 2986, 1606, 1445, 1386, 1297, 1132, 1025, 973, 824; HRMS (ESI) Caled for C12H13O2Na (M+Na)+ 325.1798, found: 325.1797.

6-(4-methoxyphenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ac)

Brown solid, m.p. = 156-157 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.3 (PE/EA = 1/1), 35 mg, yield = 98%; 1HNMR (400 MHz, CDCl3) δ 7.85 (d, J = 7.6 Hz, 2H), 7.51 – 7.37 (m, 3H), 6.81 (s, 1H), 6.72 (s, 4H), 5.41 (d, J = 7.4 Hz, 1H), 3.71 (s, 3H), 3.52 (dd, J = 11.1, 4.5 Hz, 1H), 3.02 (td, J = 11.9, 7.3 Hz, 1H), 2.16 (dd, J = 12.7, 4.6 Hz, 1H), 1.66 (s, 3H); 13CNMR (100MHz, CDCl3) δ 184.6, 159.6, 158.8, 146.6, 146.2, 129.9, 129.3, 129.1, 129.0, 128.8, 125.6, 114.1, 102.6, 91.2, 73.1, 55.2, 52.1, 39.0, 19.6; IR (KBr, cm⁻¹) 3743, 3678, 3620, 2990, 2883, 1740, 1691, 1515, 1454, 1369, 1266, 1114, 929, 825, 766. 690; HRMS (ESI) Caled for C21H18O4Na (M+Na)+ 383.1254, found: 383.1254.

7-methyl-2-phenyl-6-(p-tolyl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ad)

Yellow solid, m.p. = 150-151 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 32 mg, yield = 92%; 1HNMR (400 MHz, CDCl3) δ 7.85 (d, J = 7.5 Hz, 2H), 7.44 (dt, J = 11.6, 7.0 Hz, 3H), 6.99 (d, J = 7.6 Hz, 2H), 6.81 (s, 1H), 6.70 (d, J = 7.7 Hz, 2H), 5.43 (d, J = 7.1 Hz, 1H), 3.53 (dd, J = 11.0, 4.5 Hz, 1H), 3.02 (td, J = 11.9, 7.4 Hz, 1H), 2.24 (s, 3H), 2.19 (dd, J = 12.7, 4.5 Hz, 1H), 1.66 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 184.5, 159.6, 146.6, 146.2, 137.0, 134.3, 129.9, 129.5, 129.2, 129.1, 127.1, 127.5, 102.6, 91.3, 73.2, 52.6, 38.9, 21.1, 19.6; IR (KBr, cm⁻¹) 3743, 3620, 3565, 2979, 1835, 1740, 1690, 1517, 1426, 1388, 1259, 1112, 923, 870, 811, 765, 699,540; HRMS (ESI) Caled for C22H19O4Na (M+Na)+ 367.1305, found: 367.1303.

6-(4-(tert-butyl)phenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5ae)

Yellow solid, m.p. = 158 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 10/1), 34 mg, yield = 89%; 1HNMR (400 MHz, CDCl3) δ 7.87 (d, J = 7.3 Hz, 2H), 7.45 (dt, J = 12.2, 6.9 Hz, 3H), 7.20 (d, J = 7.9 Hz, 2H), 6.81 (s, 1H), 6.75 (d, J = 8.0 Hz, 2H), 5.42 (d, J = 7.0 Hz, 1H), 3.53 (dd, J = 11.0, 4.6 Hz, 1H), 3.04 (td, J = 11.9, 7.2 Hz, 1H), 2.18 (dd, J = 12.6, 4.7 Hz, 1H), 1.66 (s, 3H), 1.24 (s, 9H); 13CNMR (100 MHz, CDCl3) δ 184.5, 159.7, 150.1, 146.8, 146.2, 134.3, 129.9, 129.2, 129.1, 127.7, 125.7, 102.6, 91.3, 73.2, 52.6, 39.4, 34.5, 31.4, 19.7; IR(KBr, cm⁻¹) 3743, 3649, 3566, 3961, 2365, 1867, 1679, 1515, 1456, 1397, 1261, 1024, 979, 823, 763; HRMS (ESI) Caled for C28H28O3Na (M+Na)+ 409.1774, found: 409.1775.
6-(4-chlorophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxy-cyclohepta[b]/furan-8-one (5a)

Yellow solid, m.p. = 210-211 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rf = 0.2 (PE/EA = 1/1), 35 mg, yield = 96 %; 1HNMR (400 MHz, CDCl3) δ 7.84 (d, J = 7.5 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.14 (d, J = 8.2 Hz, 2H), 6.81 (s, 1H), 6.74 (d, J = 8.2 Hz, 2H), 5.43 (d, J = 7.1 Hz, 1H), 3.53 (dd, J = 11.0, 4.6 Hz, 1H), 3.04 (td, J = 11.9, 7.2 Hz, 1H), 2.15 (dd, J = 12.8, 4.7 Hz, 1H), 1.66 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 184.0, 159.9, 146.7, 146.0, 136.0, 133.3, 130.1, 129.1, 129.0, 129.0, 128.9, 125.6, 102.6, 91.3, 73.1, 52.4, 38.9, 19.6; IR (KBr, cm⁻¹) 3743, 3678, 3560, 2982, 2854, 1835, 1742, 1679, 1530, 1497, 1426, 1369, 1288, 1257, 1094, 1027, 980, 924, 818, 764, 687; HRMS (ESI) Calcd for C29H17ClO3Na (M+Na)+ 387.0758, found: 387.0757.

6-(4-bromophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxy-cyclohepta[b]/furan-8-one (5ag)

Brown solid, m.p. = 195 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), Rf = 0.2 (PE/EA = 1/1), 35 mg, yield = 85%; 1HNMR (400 MHz, CDCl3) δ 7.85 (d, J = 8.5 Hz, 2H), 7.44 (p, J = 6.4 Hz, 3H), 7.30 (d, J = 8.1 Hz, 2H), 6.81 (s, 1H), 6.68 (d, J = 8.1 Hz, 2H), 5.43 (d, J = 7.1 Hz, 1H), 3.51 (dd, J = 11.1, 4.7 Hz, 1H), 3.04 (td, J = 11.9, 7.1 Hz, 1H), 2.15 (dd, J = 12.8, 4.7 Hz, 1H), 1.65 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 184.0, 160.0, 146.7, 146.0, 136.5, 131.9, 130.1, 129.5, 129.1, 129.0, 125.7, 121.5, 102.6, 91.3, 73.2, 52.5, 38.9, 19.6; IR (KBr, cm⁻¹) 3743, 3678, 3649, 3521, 2980, 2352, 1680, 1529, 1454, 1368, 1258, 1111, 1009, 1027, 980, 924, 818, 764, 687; HRMS (ESI) Calcd for C29H17BrO3Na (M+Na)+ 431.0253, found: 431.0255.

6-(4-fluorophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxy-cyclohepta[b]/furan-8-one (5ah)

Brown solid, m.p. = 198 °C, purified by chromatography (petroleum/ethyl acetate = 9:1), Rf = 0.2 (PE/EA = 9/1), 30 mg, yield = 87%; 1HNMR (400 MHz, CDCl3) δ 7.84 (d, J = 7.1 Hz, 2H), 7.44 (q, J = 9.9, 8.2 Hz, 3H), 6.87 (t, J = 8.5 Hz, 2H), 6.81 (s, 1H), 6.80 – 6.74 (m, 2H), 5.43 (d, J = 7.0 Hz, 1H), 3.54 (dd, J = 11.1, 4.6 Hz, 1H), 3.04 (td, J = 12.0, 7.2 Hz, 1H), 2.15 (dd, J = 12.8, 4.6 Hz, 1H), 1.66 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 184.2, 162.1 (d, J = 245.9 Hz), 159.9, 146.7, 146.1, 133.2 (d, J = 3.3 Hz), 130.0, 129.3 (d, J = 8.1 Hz), 129.1, 129.0, 125.6, 115.6 (d, J = 21.4 Hz), 102.6, 91.2, 73.1, 52.2, 39.1, 19.5; 19FNMR (376 MHz, CDCl3) δ -115.3; IR (KBr, cm⁻¹) 3743, 3650, 2980, 2362, 1741, 1680, 1515, 1426, 1287, 1162, 980, 821, 765; HRMS (ESI) Calcd for C29H17F2O3Na (M+Na)+ 371.0545, found: 371.0555.

7-methyl-2-phenyl-6-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydro-8H-4,7-epoxy-cyclohepta[b]/furan-8-one (5ai)

Yellow solid, m.p. = 184-185 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), Rf = 0.2 (PE/EA = 8/1), 26 mg, yield = 66%; 1HNMR (400 MHz, CDCl3) δ 7.85 (d, J = 7.3 Hz, 2H), 7.48 – 7.41 (m, 5H), 6.93 (d, J = 7.9 Hz, 2H), 6.83 (s, 1H), 5.46 (d, J = 7.0 Hz, 1H), 3.61 (dd, J = 10.9, 4.4 Hz, 1H), 3.07 (td, J = 11.9, 7.5 Hz, 1H), 2.20 (dd, J = 12.8, 4.4 Hz, 1H), 1.68 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 183.7, 160.1, 146.8, 146.0, 141.7, 130.1, 129.6 (q, J = 32.5 Hz), 129.1, 128.9, 128.3, 125.7 (q, J = 3.4 Hz), 124.1 (q, J = 272.0 Hz), 102.6, 102.6, 91.4, 73.2, 52.8, 39.0, 19.6; 19FNMR (376 MHz, CDCl3) δ -62.6; IR (KBr, cm⁻¹) 3743, 3620, 2993, 1741, 1624, 1529, 1424, 1369, 1325, 1257, 1164, 1068, 929, 765, 625; HRMS (ESI) Calcd for C32H17F3O3Na (M+Na)+ 421.1022, found: 421.1019.
7-methyl-6-(4-nitrophenyl)-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5aj)

Brown solid, m. p. = 160-161 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), Rf = 0.2 (PE/EA = 1/1), 29 mg, yield = 76%; ¹HNMR (400 MHz, CDCl₃) δ 8.03 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 6.6 Hz, 2H), 7.45 (q, J = 7.5, 6.8 Hz, 3H), 6.96 (d, J = 8.6 Hz, 2H), 6.84 (s, 1H), 5.48 (d, J = 7.0 Hz, 1H), 3.66 (dd, J = 10.9, 4.5 Hz, 1H), 3.09 (td, J = 12.0, 11.2, 7.2 Hz, 1H), 2.23 (dd, J = 12.9, 4.5 Hz, 1H), 1.69 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 183.4, 160.4, 147.3, 146.8, 145.9, 145.2, 130.3, 129.2, 128.8, 128.7, 125.7, 123.9, 102.6, 91.6, 73.3, 52.8, 38.8, 19.6; IR (KBr, cm⁻¹) 3742, 3678, 3566, 2983, 2335, 1917, 1740, 1618, 1517, 1426, 1345, 1275, 1111, 1025, 980, 882, 765; HRMS (ESI) Calcd for C₂₂H₁₁NO₃ (M+H)⁺ 376.1179, found: 376.1178.

7-methyl-8-oxo-5,6,7,8-tetrahydro-4H-4,7-epoxycyclohepta[b]furan-6-yl)benzoic acid (5ak)

Brown solid, m. p. = 196 °C, purified by chromatography (petroleum/ethyl acetate = 7:1), Rf = 0.2 (PE/EA = 7/1), 28 mg, yield = 75%; ¹HNMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 7.6 Hz, 2H), 7.49 – 7.41 (m, 3H), 6.90 (d, J = 8.2 Hz, 2H), 6.82 (s, 1H), 5.47 (d, J = 7.0 Hz, 1H), 3.62 (dd, J = 11.0, 4.6 Hz, 1H), 3.06 (td, J = 12.0, 11.4, 7.2 Hz, 1H), 2.24 (dd, J = 12.8, 4.6 Hz, 1H), 1.68 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 183.7, 172.2, 160.1, 146.7, 146.0, 143.7, 130.7, 130.6, 130.1, 129.2, 129.0, 128.0, 125.7, 102.6, 91.6, 70.2, 53.1, 38.8, 19.7; IR (KBr, cm⁻¹) 3743, 3678, 3590, 2362, 1868, 1740, 1675, 1517, 1454, 1387, 1262, 1101, 1071, 971, 829, 760, 689; HRMS (ESI) Calcd for C₂₂H₁₃O₃Na (M+Na)⁺ 397.1046, found: 397.1044.

4-(7-methyl-8-oxo-5,6,7,8-tetrahydro-4H-4,7-epoxycyclohepta[b]furan-6-yl)phenyl acetate (5al)

Yellow solid, m. p. = 185 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), Rf = 0.1 (PE/EA = 8/1), 35 mg, yield = 86%; ¹HNMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.0 Hz, 2H), 7.50 – 7.38 (m, 3H), 6.91 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 6.7 Hz, 3H), 5.42 (d, J = 7.0 Hz, 1H), 3.55 (dd, J = 11.1, 4.7 Hz, 1H), 3.03 (td, J = 12.0, 11.4, 7.2 Hz, 1H), 2.23 (s, 3H), 2.16 (dd, J = 12.8, 4.7 Hz, 1H), 1.66 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 184.1, 169.4, 159.8, 149.9, 146.7, 146.1, 135.0, 130.0, 129.1, 129.0, 128.9, 125.6, 121.8, 102.6, 91.3, 73.1, 52.4, 39.2, 21.2, 19.6; IR (KBr, cm⁻¹) 3743, 3620, 2981, 2362, 1835, 1680, 1514, 1454, 1368, 1257, 1114, 979, 873, 690; HRMS (ESI) Calcd for C₂₃H₂₀O₃Na (M+Na)⁺ 411.1203, found: 411.1205.

6-(3-bromophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5am)

Yellow solid, m. p. = 207-211 °C, purified by chromatography (petroleum/ethyl acetate = 9:1), Rf = 0.25 (PE/EA = 9/1), 38 mg, yield = 93%; ¹HNMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.6 Hz, 2H), 7.31 (q, J = 9.9, 8.5 Hz, 3H), 7.17 – 7.11 (m, 1H), 6.90 (t, J = 7.9 Hz, 1H), 6.84 (s, 1H), 6.67 (s, 1H), 6.54 (d, J = 7.7 Hz, 1H), 5.30 (d, J = 7.0 Hz, 1H), 3.37 (dd, J = 11.0, 4.4 Hz, 1H), 2.89 (td, J = 11.9, 7.1 Hz, 1H), 2.03 (dd, J = 12.8, 4.5 Hz, 1H), 1.54 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 183.9, 160.1, 146.5, 146.2, 140.0, 131.5, 130.6, 130.3, 130.1, 129.2, 129.1, 126.3, 125.8, 122.8, 102.7, 91.4, 73.4, 52.7, 39.0, 19.7; IR(KBr, cm⁻¹) 3743, 3678, 3620, 3566, 2982, 2854, 1835, 1741, 1679, 1530, 1497, 1426, 1369, 1288, 1257, 1094, 1027, 980, 924, 818, 764, 687; HRMS (ESI) Calcd for C₂₆H₂₁BrO₂Na(M+Na)⁺ 431.0253, found: 431.0252.
6-(2-chlorophenyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5an)

Yellow solid, m.p.=158-159 °C, purified by chromatography (petroleum/ethyl acetate = 9:1); Rf = 0.2 (PE/EA = 9/1), 33 mg, yield = 92%; 1H NMR (400 MHz, CDCl3) δ 7.86 (d, J = 6.8 Hz, 2H), 7.45 (q, J = 9.9, 8.3 Hz, 3H), 7.34 (d, J = 8.8 Hz, 1H), 7.07 (t, J = 6.9 Hz, 1H), 6.99 (t, J = 7.1 Hz, 1H), 6.83 (s, 1H), 6.37 (dd, J = 7.9, 1.7 Hz, 1H), 5.45 (d, J = 7.1 Hz, 1H), 4.36 (dd, J = 11.2, 4.9 Hz, 1H), 3.19 – 3.05 (m, 1H), 2.07 (dd, J = 12.8, 5.0 Hz, 1H), 1.74 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 184.1, 159.9, 146.8, 146.3, 135.3, 135.1, 130.0, 129.96, 129.1, 129.0, 128.4, 127.2, 125.6, 102.7, 92.1, 73.0, 47.3, 40.4, 20.1; IR (KBr, cm⁻¹) 3742, 3649, 3064, 2982, 2361, 1681, 1527, 1473, 1370, 1260, 1110, 1049, 980, 825; HRMS (ESI) Calcd for C22H17ClO2Na (M+Na)+ 387.0758, found: 387.0759.

10-methyl-2-phenyl-4a,5,9b,10-tetrahydro-4,10-epoxybenzo[1,2]azulen-6,5-bifuran-11(4H)-one (5ao)

White solid, m.p. = 165-167 °C, purified by chromatography (petroleum/ethyl acetate = 10:1); Rf = 0.2 (PE/EA = 10/1), 16 mg, yield = 46%; 1H NMR (400 MHz, CDCl3) δ 7.67 (d, J = 7.1 Hz, 2H), 7.36 (d, J = 7.9 Hz, 3H), 7.08 (d, J = 5.4 Hz, 2H), 6.97 (t, J = 7.1 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 5.40 (d, J = 7.2 Hz, 1H), 4.07 (d, J = 9.7 Hz, 1H), 3.72 (q, J = 9.1 Hz, 1H), 3.02 (dd, J = 17.4, 9.9 Hz, 1H), 2.58 (d, J = 17.2 Hz, 1H), 1.85 (s, 3H); 13CNMR (100 MHz, CDCl3) δ 185.2, 158.5, 146.2, 143.2, 141.7, 139.4, 129.7, 129.0, 128.9, 127.7, 126.7, 125.5, 125.0, 124.5, 90.2, 60.0, 46.0, 32.4, 29.8, 21.0; IR (KBr, cm⁻¹) 3704, 3066, 2655, 1681, 1574, 1464, 1256, 1106, 1016, 920, 869, 814, 754, 683; HRMS (ESI) Calcd for C23H16O2Na (M+Na)+ 365.1148, found: 365.1150.

9-methyl-2-phenyl-4a,5,6,8a,9-hexahydro-10H-4,9-epoxybenzo[4,5]cyclohepta[1,2-b]furan-10-one (5ap)

Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1); Rf = 0.4 (PE/EA = 10/1), 13 mg, yield = 43%; 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 7.2 Hz, 2H), 7.42 (q, J = 5.9, 5.0 Hz, 3H), 6.72 (s, 1H), 5.73 (d, J = 12.0 Hz, 1H), 5.60 (d, J = 10.3 Hz, 1H), 5.23 (d, J = 6.8 Hz, 1H), 3.08 (dt, J = 12.5, 6.3 Hz, 1H), 2.76 (d, J = 10.3 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.67 (s, 3H), 1.39 – 1.18 (m, 3H); 13CNMR (100 MHz,CDCl3) δ 186.1, 159.1, 145.6, 144.5, 130.0, 129.8, 129.1, 129.5, 124.3, 104.1, 90.5, 66.4, 44.2, 39.9, 21.7, 21.4, 20.0; IR (KBr, cm⁻¹) 3743, 2935, 2362, 1917, 1793, 1741, 1493, 1367, 1222, 1023, 975, 874, 802; HRMS (ESI) Calcd for C20H16O2Na (M+Na)+ 329.1148, found: 329.1152.

9-methyl-2-phenyl-4a,5,6,8a,9-hexahydro-10H-4,9-epoxybenzo[4,5]cyclohepta[1,2-b]furan-10-one (5ap')

Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1); Rf = 0.4 (PE/EA = 10/1), 13 mg, yield = 43%; 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 7.3 Hz, 2H), 7.41 (dt, J = 12.5, 6.9 Hz, 3H), 6.71 (s, 1H), 6.03 (d, J = 8.5 Hz, 1H), 5.66 (d, J = 10.0 Hz, 1H), 4.92 (s, 1H), 2.67 – 2.57 (m, 1H), 2.37 (ddd, J = 12.8, 7.7, 4.8 Hz, 1H), 2.20 – 2.08 (m, 1H), 2.04 – 1.99 (m, 1H), 1.94 (d, J = 15.5 Hz, 1H), 1.56 (dd, J = 12.2, 4.6 Hz, 1H), 1.48 (s, 3H); 13CNMR (100 MHz,CDCl3) δ 187.6, 159.4, 144.5, 143.9, 130.3, 129.8, 129.2, 129.1, 125.5, 124.1, 103.0, 88.8, 78.2, 42.2, 40.7, 27.0, 23.7, 16.2; IR (KBr, cm⁻¹) 3607, 3568, 2936, 1792, 1745, 1525, 1427, 1319, 1219, 1109, 1011, 970, 875, 842; HRMS (ESI) Calcd for C20H16O2Na (M+Na)+ 329.1148, found: 329.1155.

6-butyl-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5aq)

Brown oil, purified by chromatography (petroleum/ethyl acetate = 10:1); Rf = 0.3 (PE/EA = 10/1), 17 mg, yield = 56%; 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 7.1 Hz, 2H), 7.45-7.35 (m, 3H), 6.68 (s, 1H), 5.24 (d, J = 7.1 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.17 (dt, J = 10.5, 6.1 Hz, 1H), 1.60 (s, 3H), 1.53 (dd, J = 12.3, 4.3 Hz, 1H), 1.30 – 1.21 (m, 4H), 0.91 (s,
2H), 0.84 (d, J = 6.8 Hz, 3H); \(^1\)H NMR (100 MHz, CDCl₃) δ 185.8, 159.5, 147.8, 145.2, 129.8, 129.2, 129.0, 125.5, 102.6, 89.9, 72.7, 46.4, 37.2, 31.8, 31.7, 22.7, 19.7, 14.1; IR (KBr, cm⁻¹) 2678, 3649, 2928, 2859, 1835, 1741, 1679, 1529, 1454, 1370, 1258, 1122, 1021, 981, 838, 765; HRMS (ESI) Calcd for C₆H₃O₂Na (M+Na)⁺ 333.1461, found: 333.1367.

6-(2-bromoethyl)-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5a)

Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1), Rᵣ = 0.3 (PE/EA = 10/1), 32 mg, yield = 88%; \(^1\)H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 6.8 Hz, 2H), 7.47 – 7.39 (m, 3H), 6.69 (s, 1H), 5.28 (d, J = 7.2 Hz, 1H), 3.43 (dt, J = 12.3, 6.4 Hz, 1H), 3.38 – 3.27 (m, 1H), 2.87 – 2.68 (m, 1H), 2.51 (dt, J = 9.8, 5.2 Hz, 1H), 1.94 (dq, J = 13.4, 6.5 Hz, 1H), 1.63 (s, 3H), 1.55 (dd, J = 12.3, 4.1 Hz, 2H); \(^1\)C NMR (100 MHz, CDCl₃) δ 185.2, 160.0, 147.9, 145.0, 130.1, 129.1, 129.0, 125.6, 102.6, 89.6, 72.7, 44.2, 37.0, 34.9, 32.2, 19.7; IR (KBr, cm⁻¹) 3742, 3620, 2974, 2361, 1867, 1740, 1518, 1454, 1258, 1023, 923, 819, 702; HRMS (ESI) Calcd for C₁₈H₂₁BrO₂Na (M+Na)⁺ 383.0253, found: 383.0250.

6-butoxy-2-(4-( tert-butyl)phenyl)-7-methyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5p)

Yellow oil, purified by chromatography (petroleum/ethyl acetate = 10:1), Rᵣ = 0.3 (PE/EA = 10/1), 33 mg, yield = 87%; \(^1\)H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 6.64 (s, 1H), 5.20 (d, J = 6.9 Hz, 1H), 4.03 (d, J = 7.9 Hz, 1H), 3.50 (q, J = 6.6 Hz, 1H), 3.31 (q, J = 6.6 Hz, 1H), 2.73 (dt, J = 12.8, 8.3 Hz, 1H), 1.89 (d, J = 12.7 Hz, 1H), 1.67 (s, 3H), 1.40 (d, J = 6.9 Hz, 1H), 1.33 (s, 9H), 1.21 (dt, J = 13.9, 7.2 Hz, 3H), 0.81 (t, J = 7.3 Hz, 3H); \(^1\)C NMR (100 MHz, CDCl₃) δ 184.1, 159.3, 153.1, 145.9, 145.7, 126.6, 126.0, 125.3, 102.2, 88.8, 85.4, 72.9, 71.5, 39.3, 35.0, 31.8, 31.3, 19.4, 19.3, 13.9; IR (KBr, cm⁻¹) 3743, 3678, 2959, 2362, 1917, 1687, 1538, 1480, 1437, 1095, 981, 928, 833, 669; HRMS (ESI) Calcd for C₂₃H₂₆O₂Na (M+Na)⁺ 405.2036, found: 405.2041.

6-(4-fluorophenyl)-6,7-dimethyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5q)

Brown solid, m.p. = 165-166 °C, purified by chromatography (petroleum/ethyl acetate = 8:1), Rᵣ = 0.25 (PE/EA = 8/1), 30 mg, yield = 82%; \(^1\)H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 6.9 Hz, 2H), 7.41 (q, J = 8.3, 7.3 Hz, 3H), 6.98 (dd, J = 8.7, 5.2 Hz, 2H), 6.84 (t, J = 8.6 Hz, 2H), 6.74 (s, 1H), 5.37 (d, J = 7.2 Hz, 1H), 2.82 (d, J = 13.1 Hz, 1H), 2.52 (dd, J = 13.1, 7.3 Hz, 1H), 1.63 (s, 3H), 1.60 (s, 3H); \(^1\)C NMR (100 MHz, CDCl₃) δ 185.4, 161.5 (d, J = 246.5 Hz), 159.6, 145.8, 145.5, 138.1 (d, J = 3.3 Hz), 129.9, 129.1, 129.0, 128.2 (d, J = 8.0 Hz), 125.6, 115.1 (d, J = 21.2 Hz), 102.4, 92.5, 71.9, 49.6, 46.0, 28.7, 16.3; \(^1\)F NMR (376 MHz, CDCl₃) δ -116.2; IR (KBr, cm⁻¹) 3742, 3568, 2931, 2362, 1917, 1740, 1645, 1533, 1454, 1398, 1253, 1166, 1073, 924, 839, 761; HRMS (ESI) Calcd for C₂₃H₁₉F₂O₃Na (M+Na)⁺ 385.1210, found: 385.1211.

7-methyl-2,6,6-triphenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5u)

Yellow solid, m.p. = 154-155 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), Rᵣ = 0.2 (PE/EA = 10/1), 33 mg, yield = 82%; \(^1\)H NMR (400 MHz, CDCl₃ ) δ 7.65 (d, J = 7.1 Hz, 2H), 7.29 (d, J = 7.4 Hz, 3H), 7.21 (d, J = 8.2 Hz, 3H), 7.15 (dd, J = 15.7, 8.9 Hz, 5H), 6.99 (d, J = 7.5 Hz, 2H), 6.63 (s, 1H), 5.46 (d, J = 7.5 Hz, 1H), 3.36 (dd, J = 12.9, 7.8 Hz, 1H), 3.12 (d, J = 13.1 Hz, 1H), 1.35 (s, 3H); \(^1\)C NMR (100 MHz, CDCl₃) δ 185.5, 159.4, 148.2, 147.7, 144.7, 141.3, 129.8, 129.0, 128.99, 128.9, 128.1, 127.9, 127.0, 126.5, 125.6, 102.3, 94.1, 71.7, 59.9, 50.3, 19.6; IR (KBr, cm⁻¹) 3743, 3678, 3565, 2986, 2336, 1835, 1770, 1676, 1516, 1454, 1368, 1023, 935, 815, 758; HRMS
(ESI) Caled for C_{26}H_{23}O_{3}Na (M+Na)^+ 429.1461, found: 429.1462.

6,7-dimethyl-2-phenyl-6-(prop-1-en-2-yl)-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5av)

White solid, m.p. = 156 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.4 (PE/EA = 10/1), 17 mg, yield = 56%; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 6.9 Hz, 2H), 7.39 (dd, J = 12.8, 7.3 Hz, 3H), 6.68 (s, 1H), 5.24 (d, J = 7.2 Hz, 1H), 4.69 (s, 1H), 4.39 (s, 1H), 2.55 (d, J = 12.9 Hz, 1H), 2.22 (dd, J = 12.9, 7.3 Hz, 1H), 1.72 (s, 3H), 1.59 (s, 3H), 1.36 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 185.8, 159.3, 146.9, 145.8, 145.4, 129.8, 129.2, 129.0, 125.5, 113.0, 102.4, 91.6, 71.8, 51.1, 44.5, 25.8, 21.6, 17.1; IR (KBr, cm⁻¹) 3768, 3649, 2987, 1741, 1646, 1531, 1455, 1365, 1263, 1098, 974, 898, 812, 764, 690; HRMS (ESI) Caled for C_{26}H_{23}O_{3}Na (M+Na)^+ 331.1305, found: 331.1310.

6,6-diethyl-7-methyl-2-phenyl-4,5,6,7-tetrahydro-8H-4,7-epoxycyclohepta[b]furan-8-one (5aw)

White solid, m.p. = 140 °C, purified by chromatography (petroleum/ethyl acetate = 10:1), R_f = 0.3 (PE/EA = 10/1), 27 mg, yield = 86%; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 7.5 Hz, 2H), 7.41 (dt, J = 12.1, 6.8 Hz, 3H), 6.67 (s, 1H), 5.14 (d, J = 7.6 Hz, 1H), 2.42 (dd, J = 12.4, 7.7 Hz, 1H), 1.82 (dd, J = 13.8, 7.2 Hz, 1H), 1.62 – 1.56 (m, 2H), 1.52 (s, 3H), 1.41 (dt, J = 13.8, 7.3 Hz, 1H), 1.26 – 1.16 (m, 1H), 0.95 – 0.90 (m, 3H), 0.82 (t, J = 7.4 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ 187.0, 159.4, 147.9, 144.8, 129.8, 129.2, 129.1, 125.5, 102.5, 92.4, 71.5, 48.0, 44.7, 29.0, 26.4, 17.4, 9.3, 9.1; IR (KBr, cm⁻¹) 3768, 3619, 3591, 2867, 2362, 1917, 1792, 1619, 1516, 1428, 1395, 1264, 1109, 1021, 976, 822, 762; HRMS (ESI) Caled for C_{26}H_{22}O_{3}Na (M+Na)^+ 333.1461, found: 333.1464.

1.6 Product further transformation

To a solution of CH_3PPhBr (71 mg, 0.2 mmol) in THF (2 mL), was added t-BuOK (22 mg, 0.2 mmol). The resulting solution was stirred at rt for 30 min, and then compound 3a (36 mg, 0.1 mmol) in THF (2.5 mL) was added. The mixture was stirred at room temperature. After the reaction was finished, the reaction mixture was quenched with NH_4Cl. The solution was extracted with Ethyl Acetate. The combined organic layers were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE:EA=15:1) afforded the compound 6.

9,10-Dimethyl-11-methylene-2-phenyl-4,4a,9a,10,11-hexahydro-4,10-epoxycyclohepta[1,2-b]indole (6)

Yellow solid, m.p. = 120-121 °C, purified by chromatography (petroleum/ethyl acetate = 15:1), R_f = 0.3 (PE/EA = 15/1), 27 mg, yield = 75%; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 7.7 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.4 Hz, 1H), 7.13 (dd, J = 12.9, 7.1 Hz, 2H), 6.71 – 6.65 (m, 2H), 6.42 (d, J = 7.8 Hz, 1H), 5.45 (s, 1H), 5.14 (s, 1H), 5.04 (s, 1H), 4.23 (d, J = 8.5 Hz, 1H), 3.88 (d, J = 8.5 Hz, 1H), 2.98 (s, 3H), 1.67 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 154.1, 153.4, 147.4, 140.6, 130.6, 129.4, 129.1, 128.9, 128.8, 127.9, 127.9, 124.1, 124.0, 117.4, 106.6, 102.9, 101.5, 88.0, 78.8, 78.7, 59.1, 37.3, 18.2; IR (KBr, cm⁻¹) 3052, 2963, 2837, 2364, 1672, 1581,
Cycloadduct 3a (33.0 mg, 0.1 mmol) was dissolved in MeOH (2 mL) in a round-bottom flask. To the resultant solution was added NaBH₄ (7.6 mg, 0.2 mmol, 2.0 equiv). The reaction was stirred at room temperature for 30 min. The reaction was the quenched with NH₄Cl (5 mL). The aqueous phase was separated and extracted with EtOAc (5 x 5 mL). The combined organic fractions were washed with brine (5 mL). All combined organic layers were dried over Na₂SO₄, filtered, concentrated and purified by column chromatography (silica gel, PE:EA=10:1) to afford diastereomERICally pure 7.

7-methyl-2,6-diphenyl-5,6,7,8-tetrahydro-4H-4,7-epoxycyclohepta[b]furan-8-ol (7)

White solid, m.p. = 173-174 ºC, purified by chromatography (petroleum/ethyl acetate = 10:1), Rᵣ = 0.25 (PE/EA = 10/1), 33 mg, yield = 99%: ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 7.7 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.4 Hz, 1H), 7.27 (d, J = 7.3 Hz, 3H), 6.96 (d, J = 6.9 Hz, 2H), 6.64 (s, 1H), 5.18 (d, J = 6.2 Hz, 1H), 4.92 (d, J = 12.3 Hz, 1H), 3.59 (dd, J = 11.9, 3.4 Hz, 1H), 2.93 (dd, J = 12.1, 6.3 Hz, 1H), 2.40 (dd, J = 12.5, 3.4 Hz, 1H), 1.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.3, 149.3, 139.8, 130.8, 129.2, 128.8, 128.5, 127.6, 127.5, 126.9, 123.8, 101.8, 86.4, 74.7, 73.9, 53.6, 42.8, 24.8; IR (KBr, cm⁻¹) 3563, 2935, 2862, 1677, 1580, 1481, 1369, 1255, 1157, 1026, 980, 833, 736; HRMS (ESI) Calcd for C₂₂H₂₃O₃Na (M+Na)+ 355.1305, found: 355.1303.

1.7 Control experiments

From following experiments, it’s easy to find that the TBS group should preserve during the cycloaddition course to ensure the stereoselectivity and the leaving of protecting group might be synchronous with the cycloaddition, or at least not later than the latter, because once a post-cycloaddition oxonium species was formed, it would convert into 3a inevitably. The inefficient results of other dipolaraphiles indicated that reaction was influence by the electronic nature and steric property of these heterocycles.

Reaction conditions: *1a* (0.1 mmol), 2 (0.15 mmol), 5 mmol% PPh₃AuCl and 5 mmol% AgBF₄ in 2 mL acetonitrile were stirred at 25 ºC for 8 h. *1a* (0.1 mmol), 4 (0.15 mmol) and 5 mmol% ZnI₂ in 2 mL DCE was stirred at 25 ºC for 12 h.

2 References
3 Crystal data

3.1 X-ray diffraction analysis data of 3aa

Table 1 Crystal data and structure refinement for 3aa.

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3.2 X-ray diffraction analysis data of 5ad

![Chemical structure](image)

Table 1 Crystal data and structure refinement for 5ad

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### 3.3 X-ray diffraction analysis data of 5ap'

![Diagram of 5ap']

#### Table 1 Crystal data and structure refinement for 5ap'

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4. Copies of NMR spectrum

$^1$H and $^{13}$C NMR spectra of 1a
$^1$H and $^{13}$C NMR spectra of 1b
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 1c
$^1$H and $^{13}$C NMR spectra of 1d
$^{1}H$ and $^{13}C$ NMR spectra of 1e

![NMR spectra](image)

![NMR spectra](image)
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 1f
$^1$H and $^{13}$C NMR spectra of 1g
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 1h
$^1$H and $^{13}$C NMR spectra of 1i
$^1$H and $^{13}$C NMR spectra of 1j
$^1$H and $^{13}$C NMR spectra of 1k

\[ \text{1H NMR spectrum} \]

\[ \text{13C NMR spectrum} \]
$^1$H and $^{13}$C NMR spectra of 11
$^1$H and $^{13}$C NMR spectra of 1m
$^{1}$H and $^{13}$C NMR spectra of 1n
$^1$H and $^{13}$C NMR spectra of 10
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 1p
$^1$H and $^{13}$C NMR spectra of 1q
$^1$H and $^{13}$C NMR spectra of 1r
$^1$H and $^{13}$C NMR spectra of 1s
$^1$H and $^{13}$C NMR spectra of 3aa
$^1$H and $^{13}$C NMR spectra of 3ba
$^1$H and $^{13}$C NMR spectra of 3ab
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 3ac
$^1$H and $^{13}$C NMR spectra of 3ad
$^1$H and $^{13}$C NMR spectra of 3ae
\(^1\)H and \(^{13}\)C NMR spectra of 3af
$^1$H and $^{13}$C NMR spectra of 3ag
$^1$H and $^{13}$C NMR spectra of 3ah
$^1$H and $^{13}$C NMR spectra of 3ai
\(^1\)H and \(^{13}\)C NMR spectra of 3aj
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 3ca
$^1$H and $^{13}$C NMR spectra of 3da

![NMR spectra image]
$^1$H and $^{13}$C NMR spectra of 3ea
$^{1}H$ and $^{13}C$ NMR spectra of 3fa
$^1$H and $^{13}$C NMR spectra of 3ga
$^1$H and $^13$C NMR spectra of 3ha
$^1$H and $^{13}$C NMR spectra of 3ia
$^1$H and $^{13}$C NMR spectra of 3ja
$^1$H and $^{13}$C NMR spectra of 3ka
$^1$H and $^{13}$C NMR spectra of 3la
$^1$H and $^{13}$C NMR spectra of 3ma
$^1$H and $^{13}$C NMR spectra of 3ak
$^1$H and $^{13}$C NMR spectra of 3dk

![NMR spectra image]
$^1$H and $^{13}$C NMR spectra of 3al
$^1$H and $^{13}$C NMR spectra of 3f1
$^1$H and $^{13}$C NMR spectra of 3am
$^1$H and $^{13}$C NMR spectra of 5aa
$^1$H and $^{13}$C NMR spectra of 5ba

![NMR spectra of 5ba](image)
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 5ca
$^1$H and $^{13}$C NMR spectra of 5na
$^1$H and $^{13}$C NMR spectra of 5qa
$^1$H and $^{13}$C NMR spectra of 5ea
$^1$H and $^{13}$C NMR spectra of 5ha
$^1$H and $^{13}$C NMR spectra of 5ia
$^1$H and $^{13}$C NMR spectra of 5ob
$^{1}H$ and $^{13}C$ NMR spectra of 5eb
$^1$H and $^{13}$C NMR spectra of 5fb
$^1$H and $^{13}$C NMR spectra of 5pb
$^1$H and $^{13}$C NMR spectra of 5ka
$^1$H and $^{13}$C NMR spectra of 5la
H and $^{13}$C NMR spectra of 5ma
$^{1}H$ and $^{13}C$ NMR spectra of 5ac
$^1$H and $^{13}$C NMR spectra of 5ad
$^1$H and $^{13}$C NMR spectra of 5ae
$^1$H and $^{13}$C NMR spectra of 5af
$^1$H and $^{13}$C NMR spectra of 5ag
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 5ah
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 5ai
$\text{H and }^{13}\text{C NMR spectra of 5aj}$
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 5ak
$^1$H and $^{13}$C NMR spectra of 5aI
$^{1}H$ and $^{13}C$ NMR spectra of 5am
$^1$H and $^{13}$C NMR spectra of 5an
$^1$H and $^{13}$C NMR spectra of 5ao

![NMR spectra图像](image-url)
$^1$H and $^{13}$C NMR spectra of 5ap
$^1$H and $^{13}$C NMR spectra of 5ap'
$^1$H and $^{13}$C NMR spectra of 5aq
$^{1}H$ and $^{13}C$ NMR spectra of 5ar
$^1$H and $^{13}$C NMR spectra of 5ps
$^1$H and $^{13}$C NMR and $^{19}$FNMR spectra of 5at
$^1$H and $^{13}$C NMR spectra of 5au
$^1$H and $^{13}$C NMR spectra of 5av
$^{1}H$ and $^{13}C$ NMR spectra of 5aw
$^{1}$H and $^{13}$C NMR spectra of 6
$^1$H and $^{13}$C NMR spectra of 7