Supporting Information

ZnI₂/Zn(OTf)₂–TsOH: A Versatile Combined-Acid System for Catalytic Intramolecular Hydrofunctionalization and Polyene Cyclization

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1. General Information

The reactions were monitored by TLC (glass plates precoated with silica gel 60 F254, Merck). Column chromatography was performed on silica gel Geduran® Si 60 (Merck). $^1$H and $^{13}$C NMR spectra were recorded with Bruker AV-III 400 MHz, Bruker AV-400, Bruker AV-500, or N600 MHz spectrometers and chemical shifts were measured in $\delta$ (ppm) with residual solvent peaks as internal standards (CDCl$_3$, $\delta$ 7.26 ppm in $^1$H NMR, $\delta$ 77 ppm in $^{13}$C NMR). IR spectra were recorded with Thermo Nicolet iS-5 FT-IR spectrophotometer, max in cm$^{-1}$. Commercial grade reagents and solvents were used without further purification except as indicated below.
2. General Procedures

General Procedure A
To a 4-mL vial equipped with a stirring bar was added 1a (100 mg, 0.567 mmol), ZnI₂ (4.5 mg, 0.014 mmol), TsOH·H₂O (2.7 mg, 0.014 mmol) and CH₂Cl₂ (1.1 ml). After stirring at room temperature for the reaction time given in Table 2 or Table 3, the reaction mixture was filtered through a short pad of silica gel, washed with DCM, and then concentrated to give the product.

General Procedure B
To a 4-mL vial equipped with a stirring bar was added 1f (100 mg, 0.475 mmol), Zn(OTf)₂ (4.3 mg, 0.012 mmol), TsOH·H₂O (2.3 mg, 0.012 mmol) and CH₂Cl₂ (0.95 ml). After stirring at room temperature for the reaction time given in Table 2 or Table 3, the reaction mixture was filtered through a short pad of silica gel, washed with DCM, and then concentrated to give the product.

General Procedure C
To a 10-mL sealed tube equipped with a stirring bar was added 1h (100 mg, 0.999 mmol), Zn(OTf)₂ (9.1 mg, 0.025 mmol), TsOH·H₂O (4.8 mg, 0.025 mmol) and DCE (2 ml). After heated to reflux for the reaction time given in Table 2 or Table 3, the reaction mixture was filtered through a short pad of silica gel, washed with DCM, and then concentrated to give the product.

General Procedure D
To a 4-mL vial equipped with a stirring bar was added 3a (100 mg, 0.624 mmol), Zn(OTf)₂ (11.3 mg, 0.031 mmol), TsOH·H₂O (5.9 mg, 0.031 mmol) and CH₂Cl₂ (2.5 ml). After stirring at room temperature for the reaction time given in Table 2 or Table 3, the reaction mixture was filtered through a short pad of silica gel, washed with DCM, and then concentrated to give the product.

General Procedure E
To a 4-mL vial equipped with a stirring bar was added 3e (50 mg, 0.274 mmol), ZnI₂ (8.7 mg, 0.027 mmol), TsOH·H₂O (5.1 mg, 0.027 mmol) and CH₂Cl₂ (1.1 ml). After heated to reflux for the reaction time given in Table 2 or Table 3, the reaction mixture was filtered through a short pad of silica gel, washed with DCM, and then concentrated to give the product.

5-methyl-5-phenyldihydrofuran-2(3H)-one (2a)
Procedure A, after 16 h to afford 98% yield. Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.41-7.35 (m, 4H), 7.33-7.28 (m, 1H), 2.60-2.69 (m, 1H), 2.54-2.40 (m, 3H), 1.72 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 176.6, 144.3, 128.6, 127.6, 124.1, 87.0, 36.2, 29.4, 29.0.

5-methyl-5-(p-tolyl)dihydrofuran-2(3H)-one (2b)
Procedure A, after 16 h to afford 99% yield. Colorless solid; mp 48°C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.27 (d, \(J = 8.6\) Hz , 2H), 7.19 (d, \(J = 8.1\) Hz , 2H), 2.66-2.60 (m, 1H), 2.55-2.46 (m, 2H), 2.45-2.38 (m, 1H), 2.36 (s, 3H), 1.72 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 176.7, 141.4, 137.3, 129.3, 124.1, 87.1, 36.2, 29.4, 29.0, 21.0.

5-methyl-5-(o-tolyldihydrofuran-2(3H)-one (2c)

Procedure A, after 16 h to afford 94% yield. Colorless oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 7.7\) Hz , 1H), 7.22-7.16 (m, 3H), 2.72-2.64 (m, 1H), 2.62-2.48 (m, 3H), 2.44 (s, 3H), 1.74 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 176.2, 142.0, 133.8, 132.5, 127.8, 126.1, 124.7, 87.9, 35.0, 28.8, 27.8, 21.6.

5-methyl-5-(naphthalen-2-yl)dihydrofuran-2(3H)-one (2d)

Procedure A, after 16 h to afford 98% yield. Colorless solid; mp 78°C \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.89-7.81 (m, 4H), 7.53-7.47 (m, 2H), 7.43 (dd, \(J = 8.6\) Hz , \(J = 1.9\) Hz, 1H), 2.69-2.62 (m, 1H), 2.60-2.43 (m, 3H), 1.80 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 176.7, 141.5, 133.0, 132.6, 128.7, 128.2, 127.6, 126.4, 122.7, 122.5, 87.1, 36.1, 29.3, 29.0.

5-(4-methoxyphenyl)-5-methylidihydrofuran-2(3H)-one (2e)

Procedure A, after 16 h to afford 94% yield. Colorless oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.30 (d, \(J = 8.9\) Hz , 2H), 6.90 (d, \(J = 8.6\) Hz , 2H), 3.80 (s, 3H), 2.62-2.59 (m, 1H), 2.55-2.44 (m, 2H), 2.43-2.35 (m, 1H), 1.70 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 176.6, 159.0, 136.3, 125.4, 113.9, 87.0, 55.3, 36.1, 29.5, 29.1.

5-(4-chlorophenyl)-5-methylidihydrofuran-2(3H)-one (2f)

Procedure B, after 16 h to afford 99% yield. Colorless solid; mp 50°C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.27 (m, 4H), 2.66-2.59 (m, 1H), 2.51-2.36 (m, 3H), 1.67 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 176.2, 142.9, 133.5, 128.8, 125.7, 86.5, 36.0, 29.3, 28.9.

5-cyclohexyl-5-methylidihydrofuran-2(3H)-one (2g)

Procedure A, after 16 h to afford 98% yield. Colorless solid; mp 57°C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 2.61-2.53 (m, 1H), 2.51-2.43 (m, 2H), 2.11-2.04 (m, 1H), 1.88-1.81 (m, 1H), 1.81-1.71 (m, 3H), 1.65 (t, \(J = 15.0\) Hz , 1H), 1.48 (tt, \(J = 12.1\) Hz, \(J = 2.9\) Hz, 1H), 1.25 (s, 3H), 1.23-1.13 (m, 1H), 1.09 (tt, \(J = 12.6\) Hz, \(J = 3.2\) Hz, 1H), 1.05-0.97 (m, 1H), 0.97-0.89 (m, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 176.9, 89.3, 47.6, 31.3, 29.1, 27.2, 27.1, 26.3, 26.2, 26.1, 22.6; IR (film) \(\nu_{\text{max}}\) 2922, 2850, 1756, 1385, 1207, 1164, 970, 933 cm\(^{-1}\); HRMS-El (m/z): calculated for C\(_{11}\)H\(_{18}\)O\(_2\) [M\(^+\)] 182.1307, found 182.1309.
5-methyl[2H]-pyran-2-one (2h)

Procedure C, after 16 h to afford 98% yield (GC yield). Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.67-4.60 (m, 1H), 2.60-2.49 (m, 2H), 2.39-2.32 (m, 1H), 1.87-1.79 (m, 1H), 1.41 (d, $J$ = 6.6 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 177.3, 77.2, 29.6, 29.0, 21.0

5,5-dimethyl[2H]-pyran-2-one (2i)

Procedure A, after 16 h to afford 94% yield. Colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 2.61 (t, $J$ = 8.3 Hz, 4H), 2.04 (t, $J$ = 8.2 Hz, 1H), 1.42 (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 176.7, 84.6, 34.6, 29.3, 27.7.

6-methyl-6-phenyltetrahydro-2H-pyran-2-one (2k)

Procedure B, after 24 h to afford 92% yield. White solid; mp 72°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 (m, 5H); 2.44 (m, 2H); 2.30 (m, 1H); 1.99 (m, 1H); 1.77 (m, 1H); 1.66 (s, 3H); 1.57 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.27, 144.40, 128.47, 127.14, 124.21, 34.13, 31.06, 28.85, 16.35

6,6-dimethyl-3-phenyltetrahydro-2H-pyran-2-one (2l)

Procedure B, after 16 h to afford 94% yield. Colorless solid; mp 116°C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35 (m, 5H); 2.80 (m, 2H); 2.32 (m, 1H), 2.16-2.08 (m, 1H), 1.95-1.84 (m, 2H), 1.51 (d, $J$ = 9.7 Hz, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 172.2, 140.0, 128.8, 128.1, 127.1, 83.0, 47.2, 33.4, 29.9, 28.4, 26.7; IR (film) $\nu$$_{max}$ 2974, 1708, 1206, 1110, 702 cm$^{-1}$; HRMS-EI ($m/z$): calculated for C$_{13}$H$_{16}$O$_2$ [M$^+$] 204.1150, found 204.1146

3-allyl-6,6-dimethyl-3-phenyltetrahydro-2H-pyran-2-one (2m)

Procedure A, after 16 h, the reaction mixture was filter through short pad of Al$_2$O$_3$ with CH$_2$Cl$_2$ and concentrated to afford 94% yield. Yellow gummy oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.34-7.28 (m, 4H), 7.25-7.21 (m, 1H), 5.80-5.71 (m, 1H), 5.13 (d, $J$ = 6.2 Hz, 1H), 5.10 (s, 1H), 2.89 (dd, $J$ = 13.8 Hz, $J$ = 5.6 Hz, 1H), 2.49 (dd, $J$ = 13.4 Hz, $J$ = 8.6 Hz, 1H), 2.28 (td, $J$ = 13.6 Hz, $J$ = 3.9 Hz, 1H), 2.06 (dt, $J$ = 14.8 Hz, $J$ = 3.5 Hz, 1H), 1.66 (td, $J$ = 14.0 Hz, $J$ = 3.3 Hz, 1H), 1.59 (dt, $J$ = 14.3 Hz, $J$ = 4.3 Hz, 1H), 1.37 (s, 3H), 1.28 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 173.6, 142.3, 134.1, 128.7, 127.0, 126.3, 119.1, 83.3, 50.9, 45.4, 31.2, 30.5, 28.2, 28.0; IR (film) $\nu$$_{max}$ 2978, 1718, 1276, 1114, 933, 761, 700 cm$^{-1}$; HRMS (EI) ($m/z$): calculated for C$_{16}$H$_{20}$O$_2$ [M$^+$] 244.1463, found 244.1470.

2-methyl-2-phenyltetrahydrofuran (2n)

Procedure B, after 14 h to afford 94% yield. Colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J$ = 8.6 Hz, 2H), 7.34 (t, $J$ = 7.6 Hz, 2H), 7.23 (d, $J$ = 7.2 Hz, 1H), 4.07-4.02 (m, 1H), 3.97-3.91 (m, 1H), 2.26-2.21 (m, 1H), 2.07-1.96 (m, 2H), 1.87-1.78 (m, 1H), 1.55 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 148.2, 128.1, 126.4, 124.7, 84.3, 67.6, 39.5, 29.8, 25.8.

2,2-dimethylchromane (2o)

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2,2-dimethyl-5,5-diphenyltetrahydro-2H-pyran (2p)\(^6\)

Procedure B, after 16 h to afford 94% yield. Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.06 (m, 2H); 6.79 (m, 2H); 2.77 (t, \(J = 6.8\) Hz, 2H); 2.83 (t, \(J = 6.8\) Hz, 2H); 1.33 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.05, 129.50, 127.30, 120.96, 119.66, 117.30, 74.13, 32.88, 26.95, 22.52

2-methyl-1-tosylpyrrolidine (2q)\(^7\)

Procedure C, after 16 h to afford 92% yield. Colorless oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.68 (d, \(J = 12.6\) Hz, 2H); 7.27 (d, \(J = 12\) Hz, 2H); 3.66 (m, 1H); 3.39 (m, 1H); 3.22 (m, 1H); 1.79 (m, 1H); 1.64 (m, 1H); 1.48 (m, 2H); 1.27 (d, \(J = 6.4\) Hz, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 142.97, 134.76, 129.38, 127.22, 55.99, 48.85, 33.28, 23.69, 22.62, 21.26

2-methyl-2-phenyl-1-tosylpyrrolidine (2r)\(^7\)

Procedure B, after 1 h to afford 92% yield. Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (d, \(J = 8.46\) Hz, 2H); 7.40 (d, \(J = 8.46\) Hz, 2H); 7.29 (m, 2H); 7.22 (m, 3H) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 129.21, 128.00, 127.06, 126.56, 125.79, 49.75, 45.77, 26.39, 22.41, 21.41

2-phenyl-1-tosylpiperidine (2s)\(^8\)

Procedure C, after 3 h to afford 93% yield. Colorless solid; mp 132ºC; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 8.3\) Hz, 2H), 7.36-7.28 (m, 6H), 7.25-7.21 (m, 1H), 5.27 (d, \(J = 4.3\) Hz, 1H), 3.84 (d, \(J = 15.0\) Hz, 1H), 3.01 (t, \(J = 14.6\) Hz, 1H), 2.42 (s, 3H), 2.21 (d, \(J = 13.3\) Hz, 1H), 1.70-1.62 (m, 1H), 1.53-1.47 (m, 1H), 1.45-1.36 (m, 2H), 1.34-1.25 (m, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 143.0, 138.9, 138.7, 129.7, 128.6, 127.02, 127.00, 126.8, 55.3, 41.9, 27.3, 24.3, 21.5, 19.0.

5,5-dimethyl-3,3-diphenyl-1-tosylpyrrolidin-2-one (2t)

Procedure B, after 1 h to afford 99% yield. Colorless solid; mp 186ºC; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 8.6\) Hz, 2H), 7.31-7.22 (m, 12H), 2.92 (s, 2H), 2.40 (m, 3H), 1.30 (s, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 175.3, 143.0, 142.4, 138.8, 128.9, 128.5, 127.8, 127.5, 127.4, 90.4, 61.9, 50.1, 28.4, 21.5; IR (film) \(n_{\text{max}}\) 2978, 1620, 1322, 1160, 1140, 1086, 780, 543 cm\(^{-1}\); HRMS-ESI (m/z): calculated for C\(_{25}\)H\(_{25}\)NO\(_3\)NaS [M + Na]\(^+\) 442.1447, found 442.1443

6-methyl-1,6-diphenylpiperidin-2-one (2u)

Procedure C, after 24 h to afford 91% yield. Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.43 ~6.97 (m, 10H), 2.68 (m, 2H), 2.08 (m, 2H), 1.71 (m, 2H), 1.52 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 172.0, 145.4, 140.1, 129.2, 128.6, 128.4, 127.3,
(9H-fluoren-9-yl)methyl 2-phenylpyrrolidine-1-carboxylate (2v)\(^7\)

To a 10-mL sealed tube equipped with a stirring bar was added 1v (50 mg, 0.135 mmol), Zn(OTf)\(_2\) (5 mg, 0.014 mmol), TsOH\(_2\)H\(_2\)O (2.5 mg, 0.014 mmol) and in DCE (0.27 ml). After heated to reflux for 36 h, the reaction mixture was filtered through a short pad of silica gel, washed with DCM, and then concentrated to give crude mixture. The crude mixture was further purified by flash chromatography (SiO\(_2\)) and concentrated to give 2v (46 mg, 92%). Yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.81~7.62 (m, 3H), 7.50~6.96 (m, 10H), 5.02 (m, 1H), 4.51~3.94 (m, 3H), 3.86~3.52 (m, 2H), 2.42~2.29 (m, 1H), 2.09~1.81 (m, 3H); \(^1\)^\(^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 155.3, 154.8, 144.4, 144.0, 143.9, 141.3, 141.1, 141.0, 128.6, 128.4, 127.6, 127.4, 127.3, 127.0, 126.9, 125.4, 125.1, 125.0, 119.9, 119.7, 119.6, 67.4, 66.9, 61.2, 61.0, 47.7, 47.5, 47.1, 35.8, 34.7, 23.5, 22.5

2-(4-nitropheny1)-1-tosylpyrrolidine (2w)

To a 10-mL sealed tube equipped with a stirring bar was added 1w (50 mg, 0.144 mmol), Zn(OTf)\(_2\) (10.5 mg, 0.029 mmol), TsOH\(_2\)H\(_2\)O (32.9 mg, 0.173 mmol) and in DCE (0.36 ml). After heated to reflux for 36 h, the reaction mixture was filtered through a short pad of silica gel, washed with DCM, and then concentrated to give crude mixture. The crude mixture was further purified by flash chromatography (SiO\(_2\)) and concentrated to give 2w (49mg, 91%). White solid; mp 179 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 (d, \(J = 8.51\) Hz, 2H), 7.69 (d, \(J = 7.66\) Hz, 2H), 7.50 (d, \(J = 8.08\) Hz, 2H), 7.32 (d, \(J = 7.66\) Hz, 2H), 4.84~4.78 (m, 1H), 3.70~3.62 (m, 1H), 3.48~3.39 (m, 1H), 2.44 (s, 3H), 2.15~2.04 (m, 1H), 1.91~1.75 (m, 2H), 1.75~1.63 (m, 1H); \(^1\)^\(^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 150.8, 147.1, 143.9, 134.3, 129.8, 127.5, 127.1, 123.7, 62.8, 49.6, 35.8, 24.1, 21.6 IR (film) \(\nu_{\text{max}}\) 3650, 1654, 1637, 1341, 1156, 1085 cm\(^\text{-1}\); HRMS-ESI (m/z): calculated for C\(_{17}\)H\(_{14}\)N\(_2\)O\(_2\)Na\([\text{M+Na}]^+\) 369.0879, found 369.0870.

1,1-dimethyl-1,2,3,4-tetrahydronaphthalene (4a)\(^9\)

Procedure D, after 1 h to afford 99% yield. Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (m, 1H); 7.21 (m, 1H); 7.13 (m, 2H) 2.84 (m, 2H); 1.88 (m, 2H); 1.75 (m, 2H); \(^1\)^\(^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 128.94, 126.51, 125.70, 125.14, 39.26, 31.78, 30.66, 19.65

7-methoxy-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene (4b)\(^9\)

Procedure D, after 1 h to afford 99% yield. Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.02 (d, \(J = 8.28\) Hz, 1H); 6.94 (m, 1H); 6.72 (dd, \(J = 8.31\) Hz, 1H) 3.84 (s, 3H); 2.76 (t, \(J = 12.2\) Hz, 2H); 1.85 (m, 2H); 1.71 (m, 2H); 1.35 (s, 6H); \(^1\)^\(^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.70, 147.00, 129.77, 128.33, 112.13, 110.91, 55.15, 39.23, 34.05, 31.83, 29.87, 19.85
1,1,7-trimethyl-1,2,3,4-tetrahydronaphthalene (4c)

Procedure D, after 1 h to afford 95% yield. Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.99 (m, 3H); 2.72 (t, \(J = 12.9\) Hz, 2H); 2.31 (s, 3H) 1.79 (m, 2H); 1.65 (m, 2H); 1.28 (s, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)); \(\delta\) 145.58, 135.01, 133.00, 128.93, 127.12, 126.17, 39.45, 33.75, 31.86, 30.35, 21.21, 19.8; IR (film) \(v\)\(_{\text{max}}\) 3446, 2957, 2927, 1505, 1456 cm\(^{-1}\); HRMS-ESI (m/z): calculated for C\(_{13}\)H\(_{18}\) [M\(^+\)] 174.1409, found 174.1413

\(N\)-((4,4-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)-4-methylbenzenesulfonamide (4d)

Procedure D, after 16 h to afford 95% yield. White solid; mp 132°C; \(^1\)H NMR (600 MHz, CDCl\(_3\)); \(\delta\) 7.78 (d, \(J = 7.49\) Hz, 2H); 7.31 (m, 3H); 7.17 (t, \(J = 7.3\) Hz, 1H); 7.05 (m, 2H); 5.03 (t, \(J = 6.6\) Hz, 1H); 3.16 (m, 2H); 2.93 (m, 1H); 2.43 (s, 3H); 1.87 (m, 2H); 1.67 (m, 1H); 1.53 (m, 1H); 1.27 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)); \(\delta\) 146.45, 143.27, 138.93, 129.64, 128.46, 127.00, 126.85, 126.69, 125.55, 47.85, 38.39, 34.52, 33.71, 31.86, 31.41, 21.43; IR (film) \(v\)\(_{\text{max}}\) 3285, 2957, 2930, 1756, 1323, 1158, 1093, 662, 550 cm\(^{-1}\); HRMS-ESI (m/z): Calcd. for C\(_{20}\)H\(_{25}\)NO\(_2\)S [M\(^+\)] 343.16, found [M + Na\(^+\)] 366.1496

\(3aR,7aS\)-4,4,7a-trimethylhexahydrobenzofuran-2(3\(H\))-one (4e)

Procedure E, after 70 h, the crude mixture was further purified by flash chromatography (SiO\(_2\)) to afford 94% yield. Colorless oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)); \(\delta\) 2.49 (dd, \(J = 17.2\) Hz, \(J = 12.6\) Hz, 1H), 2.41 (dd, \(J = 17.5\) Hz, \(J = 8.4\) Hz, 1H), 2.05 (dd, \(J = 12.7\) Hz, \(J = 8.1\) Hz, 1H), 1.85 (d, \(J = 13.4\) Hz, 1H), 1.63-1.57 (m, 1H), 1.51 (s, 3H), 1.50-1.23 (m, 4H), 1.04 (s, 3H), 0.90 (s, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)); \(\delta\) 175.8, 86.1, 51.9, 34.7, 33.6, 33.3, 32.2, 30.1, 28.4, 26.9, 18.9.

\((4aS,10aS)-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a\)-octahydrophenanthrene (4f)

Procedure D, after 44 h to afford 92% yield. Colorless oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)); \(\delta\) 7.29 (d, \(J = 7.7\) Hz, 1H), 7.16 (t, \(J = 7.3\) Hz, 1H), 7.10 (t, \(J = 7.6\) Hz, 1H), 7.07 (d, \(J = 7.5\) Hz, 1H), 2.98 (dd, \(J = 17.0\) Hz, \(J = 6.9\) Hz, 1H), 2.94-2.86 (m, 1H), 2.33 (d, \(J = 12.9\) Hz, 1H), 1.95-1.89 (m, 1H), 1.84-1.71 (m, 2H), 1.68-1.61 (m, 1H), 1.52 (d, \(J = 13.3\) Hz, 1H), 1.44 (td, \(J = 13.4\) Hz, \(J = 3.4\) Hz, 1H), 1.38 (dd, \(J = 12.3\) Hz, \(J = 2.4\) Hz, 1H), 1.31-1.25 (m, 1H), 1.23 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)); \(\delta\) 150.2, 135.3, 129.1, 125.6, 125.2, 124.4, 50.3, 41.7, 38.9, 37.9, 33.5, 33.4, 30.5, 24.9, 21.7, 19.4, 19.1.

\((4aS,10aS)-1,1,4a,6-tetramethyl-1,2,3,4,4a,9,10,10a\)-octahydrophenanthrene (4g)

Procedure D, after 14 h to afford 98% yield. Colorless oil; \(^1\)H NMR (600 MHz, CDCl\(_3\)); \(\delta\) 7.11 (s, 1H), 6.98 (d, \(J = 7.8\) Hz, 1H), 6.94 (t, \(J = 7.8\) Hz, 1H), 2.95 (dd, \(J = 16.7\) Hz, \(J = 6.7\) Hz, 1H), 2.91-2.83 (m, 1H), 2.39-2.31 (m, 1H), 2.34 (s, 3H), 1.94-1.89 (m, 1H), 1.83-1.70 (m, 2H), 1.68-1.63 (m, 1H), 1.53 (d, \(J = 13.1\) Hz, 1H), 1.44 (td, \(J = 13.3\) Hz, \(J = 3.3\) Hz, 1H), 1.38 (dd, \(J = 12.7\) Hz, \(J = 2.2\) Hz, 1H), 1.31-1.25 (m, 1H), 1.23 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)); \(\delta\) 150.0, 134.8, 132.1, 129.0, 126.1, 125.0, 50.5, 41.8, 38.9, 37.8, 33.5, 33.4, 30.1, 24.9, 21.7, 21.4, 19.4, 19.2.
(4aS,10aS)-8-methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (4h)\textsuperscript{13}

Procedure D, after 23 h to afford 98% yield. Colorless solid; mp 109ºC; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.15 (t, \(J = 7.8\) Hz, 1H), 6.94 (d, \(J = 8.0\) Hz, 1H), 6.67 (d, \(J = 7.8\) Hz, 1H), 3.83 (s, 3H), 2.92 (dd, \(J = 17.8\) Hz, \(J = 6.7\) Hz, 1H), 2.67-2.59 (m, 1H), 2.31 (d, \(J = 12.6\) Hz, 1H), 1.98-1.92 (m, 1H), 1.80-1.73 (m, 1H), 1.70-1.61 (m, 2H), 1.51 (d, \(J = 13.8\) Hz, 1H), 1.41 (td, \(J = 13.2\) Hz, \(J = 3.5\) Hz, 1H), 1.35 (dd, \(J = 12.5\) Hz, \(J = 1.8\) Hz, 1H), 1.28-1.21 (m, 1H), 1.23 (s, 3H), 0.98 (s, 3H), 0.96 (s, 3H); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 157.1, 151.6, 126.0, 124.3, 116.6, 106.3, 55.2, 49.9, 41.7, 39.1, 37.8, 33.5, 33.4, 24.8, 24.6, 21.7, 19.4, 18.5.

(4aS,10aS)-6-methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (4i)\textsuperscript{11}

Procedure D, after 14 h to afford 99% yield. Colorless oil; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 6.98 (d, \(J = 8.6\) Hz, 1H), 6.84 (d, \(J = 2.4\) Hz, 1H), 6.68 (dd, \(J = 8.6\) Hz, \(J = 2.9\) Hz, 1H), 3.79 (s, 3H), 2.91 (dd, \(J = 16.7\) Hz, \(J = 6.8\) Hz, 1H), 2.85-2.78 (m, 1H), 2.27 (d, \(J = 13.0\) Hz, 1H), 1.92-1.86 (m, 1H), 1.80-1.67 (m, 2H), 1.66-1.61 (m, 1H), 1.50 (d, \(J = 13.3\) Hz, 1H), 1.43 (td, \(J = 13.0\) Hz, \(J = 3.2\) Hz, 1H), 1.35 (dd, \(J = 12.3\) Hz, \(J = 2.0\) Hz, 1H), 1.29-1.23 (m, 1H), 1.21 (s, 3H), 0.97 (s, 3H), 0.95 (s, 3H); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 157.7, 151.5, 129.8, 127.5, 110.7, 110.2, 55.3, 50.3, 41.7, 38.9, 38.0, 33.5, 33.4, 29.6, 24.8, 21.7, 19.4, 19.2.
3. $^1$H & $^{13}$C NMR Spectra
4. Mass Information

\[ \text{ZnI}_2 + \text{TsOH-H}_2\text{O} \rightarrow \text{DCM/THF} \]

Exact Mass: 444.6431

\[ \text{TsO}_{\text{OTs}} - \text{ZnI} \]

Exact Mass: 532.8573

\[ \text{TsO}_{\text{OTs}} - \text{ZnI} \]

Exact Mass: 576.9645
5. References