Supporting Information for

Rapid Construction of Complex Tetracyclic Frameworks via a Gold (I) -Catalyzed Tandem 1,2-Acyloxy Migration/[3+2] Cycloaddition/Friedel-Crafts Type Cyclization Reaction of Linear Enynyl Esters

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1. General information

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. Melting points were determined with a digital Koffer apparatus and were uncorrected. $^1$H and $^{13}$C NMR data were recorded on a 400 MHz spectrometer using CDCl$_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High-resolution mass spectra (HRMS) were obtained on a FT-ICR spectrometer.

2. General Procedure for Preparation of enynyl esters 1a-r and their HRMS, $^1$H NMR and $^{13}$C NMR spectra data

Enynyl esters 1a-r were readily prepared via a three or five-step routine sequence showed below.

To a solution of 4-((tert-butyldimethylsilyl)oxy)but-2-yn-1-ol S1 (10 mmol) in 100 mL THF at 0 °C was added 0.04 g (11 mmol) of 60% NaH in one portion. The mixture was stirred at 0 °C for 30 min, and then 3-bromoprop-1-ene (10 mmol) was added. The mixture was stirred at room temperature for 4 hours, and then quenched with a saturated aqueous solution of NH$_4$Cl, and the solvent was removed under reduced pressure. The residue was extracted with EtOAc (50 mL X 3 ), and the combined organic layers were washed with water and brine and dried over Na$_2$SO$_4$. After concentration under reduced pressure, the residue was dissolved in 100 mL THF and cooled to 0 °C. To this solution was added 4.8 g (15 mmol) of TBAF, and the mixture was stirred at room temperature for 2 hours. The reaction was quenched with a saturated aqueous NH$_4$Cl solution, and extracted with EtOAc (50 mL X 3). The combined organic layers were washed with water, brine and dried over Na$_2$SO$_4$. Concentration under reduced pressure followed by silica gel chromatography (PE : EtOH = 10 : 1) to give propargyl alcohol S2.

To a solution of the 2-((3,5-dimethoxybenzyl)oxy)acetic acid (5.0 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (50 mL) was added EDCI (5.0 mmol, 1.5 equiv.) at room temperature. The reaction mixture was stirred for 40 min. Subsequently, 4-(allyloxy)but-2-yn-1-ol S2 (3.3 mmol, 1.0 equiv.) and DMAP (3.3 mmol,1.0 equiv.) was added. The resulting mixture was stirred at room temperature for 12 hours. Then the crude mixture was quenched with water and extracted with CH$_2$Cl$_2$ (30 mL X 3 ). The combined organic phases were concentrated under reduced pressure to give a residue which was purified by column chromatography on silica gel (PE : EtOH = 15 : 1).

**Compound 1a:** colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.52 (d, J = 2.3 Hz, 2H), 6.40 (t, J = 2.3 Hz, 1H), 5.96 – 5.82 (m, 1H), 5.35 – 5.27 (m, 1H), 5.22 (dd, J = 10.4, 1.5 Hz, 1H), 4.82 (t, J = 1.7 Hz, 2H), 4.59 (s, 2H), 4.19 (t, J = 1.8 Hz, 2H), 4.14 (s, 2H), 4.05 (dt, J = 5.8, 1.3 Hz, 2H), 3.79 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.6, 160.9, 139.2, 133.7, 118.00, 105.7, 100.1, 83.2, 79.8, 73.3, 70.7, 66.8, 57.2, 55.3, 52.5. HRMS (ESI): m/z [M+NH$_4]^+$ calculated for [C$_{14}$H$_{26}$NO$_6$]: 352.1760, found:352.1756.
Compound 1b: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.25 (m, 1H), 6.94 (d, $J = 6.7$ Hz, 2H), 6.85 (dd, $J = 7.8$, 2.1 Hz, 1H), 5.93-5.86 (m, 1H), 5.31 (ddd, $J = 17.2$, 5.7, 1.5 Hz, 1H), 5.22 (dd, $J = 10.4$, 1.4 Hz, 1H), 4.82 (t, $J = 1.7$ Hz, 2H), 4.62 (s, 2H), 4.19 (t, $J = 1.8$ Hz, 2H), 4.14 (s, 2H), 4.05 (dt, $J = 5.7$, 1.2 Hz, 2H), 3.81 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.6, 159.8, 138.4, 133.7, 129.5, 120.2, 117.9, 113.8, 113.2, 83.2, 79.8, 73.2, 70.7, 66.9, 57.2, 55.2, 52.5. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{17}$H$_{24}$NO$_5$]+: 332.1654, found:332.1650.

Compound 1c: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (t, $J = 7.8$ Hz, 1H), 7.02 (dd, $J = 7.8$, 1.7 Hz, 1H), 6.89 (dd, $J = 7.8$, 1.7 Hz, 1H), 5.93-5.86 (m, 1H), 5.31 (dd, $J = 17.2$, 1.5 Hz, 1H), 5.22 (dd, $J = 10.4$, 1.2 Hz, 1H), 4.81 (t, $J = 1.7$ Hz, 2H), 4.70 (s, 2H), 4.19 (t, $J = 1.7$ Hz, 2H), 4.18 (s, 2H), 4.08-4.03 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.7, 152.6, 147.4, 133.8, 130.9, 124.1, 121.6, 118.00, 112.4, 83.2, 79.9, 70.7, 68.2, 67.2, 61.1, 57.3, 55.8, 52.5. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{18}$H$_{26}$NO$_6$]+: 352.1760, found:352.1757.

Compound 1d: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.34 (d, $J = 2.1$ Hz, 2H), 6.31 (t, $J = 2.1$ Hz, 1H), 5.90-5.86 (m, 1H), 5.30 (dd, $J = 17.2$, 1.5 Hz, 1H), 5.21 (dd, $J = 10.4$, 1.0 Hz, 1H), 4.72 (t, $J = 1.6$ Hz, 2H), 4.19 (t, $J = 1.7$ Hz, 2H), 4.05 (d, $J = 5.7$ Hz, 2H), 3.77 (s, 6H), 2.60 (t, $J = 7.5$ Hz, 2H), 2.37 (t, $J = 7.5$ Hz, 2H), 2.0-1.92 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.6, 160.8, 143.6, 133.8, 117.9, 106.5, 98.0, 82.7, 80.4, 70.7, 57.3, 55.2, 52.1, 35.3, 33.2, 26.1. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{19}$H$_{28}$NO$_5$]+: 350.1962, found:350.1965.

Compound 1e: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 6.38 (s, 3H), 5.93-5.86 (m, 1H), 5.32 (dd, $J = 17.2$, 1.3 Hz, 1H), 5.24 (d, $J = 10.4$ Hz, 1H), 4.64 (s, 2H), 4.43 (s, 2H), 4.20 (s, 2H), 4.06 (d, $J = 5.7$ Hz, 2H), 3.99 (s, 2H), 3.75 (s, 6H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.1, 161.1, 143.6, 137.1, 136.8, 133.8, 129.6, 127.5, 118.0, 106.3, 100.3, 83.4, 79.5, 70.8, 57.2, 55.3, 52.8, 51.4, 46.5, 21.5. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{25}$H$_{33}$N$_2$O$_7$S]+: 505.2003, found:505.2002.

Compound 1f: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.36 (d, $J = 2.2$ Hz, 2H), 6.32 (t, $J = 2.2$ Hz, 1H), 5.93-5.87 (m, 1H), 5.31 (dd, $J = 17.2$, 4.4, 1.6 Hz, 1H), 5.22 (ddd, $J = 10.4$, 2.7, 1.2 Hz, 1H), 4.74 (t, $J = 1.8$ Hz, 2H), 4.19 (t, $J = 1.8$ Hz, 2H), 4.05 (dt, $J = 4.4$, 1.3 Hz, 2H), 3.77 (s, 6H), 2.90 (t, $J = 7.8$ Hz, 2H), 2.66 (t, $J = 7.8$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.0, 161.0, 142.6, 133.8, 117.9, 106.3, 98.3, 82.8, 80.3, 70.7, 57.3, 55.2, 52.3, 35.4, 31.0. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{18}$H$_{28}$NO$_5$]+: 336.1805, found:336.1808.
Compound 1g: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.52 (d, $J$ = 2.2 Hz, 2H), 6.40 (t, $J$ = 2.2 Hz, 1H), 5.85-5.78 (m, 1H), 5.15 – 5.08 (m, 1H), 5.06 (d, $J$ = 10.3 Hz, 1H), 4.82 (t, $J$ = 1.7 Hz, 2H), 4.59 (s, 2H), 4.19 (t, $J$ = 1.8 Hz, 2H), 4.14 (s, 2H), 3.79 (s, 6H), 3.56 (t, $J$ = 6.7 Hz, 2H), 2.38-2.33 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.5, 160.9, 139.2, 134.8, 116.5, 105.7, 100.1, 83.4, 79.7, 73.3, 69.4, 66.8, 58.2, 55.3, 52.6, 33.9. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{19}$H$_{23}$NO$_3$]: 366.1911, found: 366.1912.

Compound 1h: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.52 (d, $J$ = 2.1 Hz, 2H), 6.40 (t, $J$ = 2.1 Hz, 1H), 5.84-5.77 (m, 1H), 5.03 (dd, $J$ = 17.1, 1.7 Hz, 1H), 4.97 (d, $J$ = 10.2 Hz, 1H), 4.81 (s, 2H), 4.59 (s, 2H), 4.16 (t, $J$ = 1.6 Hz, 2H), 4.13 (s, 2H), 3.79 (s, 6H), 3.50 (t, $J$ = 6.5 Hz, 2H), 2.12 (m, 2H), 1.75 – 1.64 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.6, 160.9, 139.2, 138.0, 114.9, 105.7, 100.1, 83.6, 79.5, 73.3, 69.6, 66.8, 58.2, 55.3, 52.6, 30.2, 28.6. HRMS (ESI): $m/z$ [M+Na]$^+$ calculated for [C$_{20}$H$_{23}$O$_2$Na]: 385.1622, found: 385.1624.

Compound 1i: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 8.3 Hz, 2H), 7.29 (d, $J$ = 8.3 Hz, 2H), 6.51 (d, $J$ = 2.2 Hz, 2H), 6.41 (t, $J$ = 2.2 Hz, 1H), 5.75-5.68 (m, 1H), 5.26 (dd, $J$ = 23.2, 5.8 Hz, 2H), 4.57 (s, 2H), 4.48 (s, 2H), 4.11 (s, 2H), 4.08 (s, 2H), 3.79 (s, 8H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.4, 161.0, 143.6, 139.1, 135.9, 131.8, 129.4, 127.8, 80.1, 78.9, 73.3, 66.7, 55.3, 52.0, 49.2, 36.0, 21.5. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{25}$H$_{33}$N$_2$O$_3$]: 505.2003, found: 505.2001.

Compound 1j: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 8.3 Hz, 2H), 7.28 (d, $J$ = 7.9 Hz, 2H), 6.51 (d, $J$ = 2.2 Hz, 2H), 6.41 (t, $J$ = 2.2 Hz, 1H), 5.79-5.72 (m, 1H), 5.16 – 4.99 (m, 2H), 4.57 (s, 2H), 4.50 (t, $J$ = 1.8 Hz, 2H), 4.16 (t, $J$ = 1.7 Hz, 2H), 4.08 (s, 2H), 3.79 (s, 6H), 3.22 (t, $J$ = 7.0Hz, 2H), 2.40 (s, 3H), 2.40-2.29 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.3, 160.9, 143.4, 139.1, 135.7, 134.4, 129.3, 127.6, 117.2, 105.7, 99.9, 80.1, 78.9, 73.3, 66.6, 55.3, 52.0, 45.9, 36.6, 32.2, 21.4. HRMS (ESI): $m/z$ [M+Na]$^+$ calculated for [C$_{26}$H$_{33}$N$_2$O$_3$]: 519.2159, found:519.2158.

Compound 1k: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 8.3 Hz, 2H), 7.28 (d, $J$ = 8.3 Hz, 2H), 6.51 (d, $J$ = 2.3 Hz, 2H), 6.41 (t, $J$ = 2.3 Hz, 1H), 5.84-5.74 (m, 1H), 5.07 – 4.95 (m, 2H), 4.57 (s, 2H), 4.49 (s, 2H), 4.15 (s, 2H), 4.08 (s, 2H), 3.79 (s, 6H), 3.18 – 3.14 (m, 2H), 2.40 (s, 3H), 2.09 (m, 2H), 1.65 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.3, 161.0, 143.4, 139.1, 137.4, 135.8, 129.4, 127.7, 115.3, 105.7, 100.0, 80.2, 78.9, 73.3, 66.7, 55.3, 52.1, 46.1, 36.6, 30.5, 26.7, 21.5. HRMS (ESI): $m/z$ [M+K]$^+$ calculated for [C$_{25}$H$_{33}$NO$_5$SK]: 554.1609, found:554.1611.

Compound 1l: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.53 (s, 2H), 6.40 (s, 1H), 5.88 – 5.69 (m, 1H), 5.01 (d, $J$ = 17.2 Hz, 1H), 4.95 (d, $J$ = 10.6 Hz, 1H), 4.76 (s, 2H), 4.59 (s, 2H), 4.13 (s, 2H), 3.79 (s, 6H), 2.22 (m, 2H), 2.06 (m, 2H), 1.51 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.7, 160.9, 139.3, 138.5, 114.6, 105.7, 100.1, 88.0, 73.5, 73.3, 66.9, 55.3, 53.2, 33.2, 28.0, 27.7, 18.6. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{20}$H$_{36}$NO$_3$]: 364.2118, found:364.2121.
Compound 1m: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.53 (d, $J$ = 2.2 Hz, 2H), 6.40 (t, $J$ = 2.2 Hz, 1H), 5.83-5.76 (m, 1H), 5.00 (ddd, $J$ = 17.1, 1.8 Hz, 1H), 4.94 (ddd, $J$ = 10.2, 0.9 Hz, 1H), 4.76 (t, $J$ = 2.1 Hz, 2H), 4.59 (s, 2H), 4.13 (s, 2H), 3.79 (s, 6H), 2.21 (m, 2H), 2.05 (m, 2H), 1.51 (m, 2H), 1.45-1.31 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.7, 160.9, 139.3, 138.8, 114.4, 105.7, 100.1, 88.1, 73.4, 73.3, 66.9, 55.3, 53.2, 33.6, 28.3, 28.3, 28.2, 18.7. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{21}$H$_{32}$NO$_5$]$: 378.2275$, found: $378.2280$. 

Compound 1n: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 8.3 Hz, 2H), 7.28 (d, $J$ = 8.3 Hz, 2H), 6.51 (d, $J$ = 2.2 Hz, 2H), 6.41 (t, $J$ = 2.2 Hz, 1H), 4.79 (s, 1H), 4.73 (s, 1H), 4.57 (s, 2H), 4.50 (s, 2H), 4.07 (s, 2H), 3.79 (s, 6H), 3.28 (t, $J$ = 7.4 Hz, 2H), 2.41 (s, 3H), 2.27 (t, $J$ = 7.4 Hz, 2H), 1.75 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.3, 160.9, 143.5, 142.1, 139.1, 135.7, 129.4, 127.7, 112.5, 105.7, 100.0, 80.1, 79.0, 73.3, 66.7, 55.3, 52.0, 44.7, 36.4, 35.9, 22.1, 21.5. HRMS (ESI): $m/z$ [M+K]$^+$ calculated for [C$_{27}$H$_{33}$NO$_7$SK]$^+$: 554.1609, found: 554.1610.

Compound 1o: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.12 (s, 1H), 6.09 (s, 2H), 5.96-5.82 (m, 1H), 5.31 (dd, $J$ = 17.2, 1.4 Hz, 1H), 5.22 (d, $J$ = 10.4 Hz, 1H), 4.85 (d, $J$ = 1.4 Hz, 2H), 4.62 (d, $J$ = 0.8 Hz, 2H), 4.19 (d, $J$ = 1.4 Hz, 2H), 4.04 (dd, $J$ = 5.7, 1.4 Hz, 2H), 3.76 (d, $J$ = 1.4 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.0, 161.5, 159.4, 133.8, 118.0, 94.0, 93.6, 83.5, 79.6, 70.7, 65.1, 57.2, 55.3, 52.9. HRMS (ESI): $m/z$ [M+H]$^+$ calculated for [C$_{17}$H$_{21}$O$_6$]$: 321.1333$, found: 321.1334.

Compound 1p: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.53 (d, $J$ = 2.1 Hz, 2H), 6.40 (t, $J$ = 2.1 Hz, 1H), 5.81-5.74 (m, 1H), 5.07 - 4.95 (m, 2H), 4.76 (t, $J$ = 2.0 Hz, 2H), 4.59 (s, 2H), 4.13 (s, 2H), 3.79 (s, 6H), 2.24-2.19 (m, 2H), 2.06-2.04 (m, 2H), 1.61 (p, $J$ = 7.3 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.7, 160.9, 139.3, 137.6, 115.3, 105.7, 100.1, 87.8, 73.7, 73.3, 66.9, 55.3, 53.2, 32.7, 27.5, 18.1. HRMS (ESI): $m/z$ [M+H]$^+$ calculated for [C$_{19}$H$_{25}$O$_3$]$: 333.1697$, found: 333.1704.

Compound 1q: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 8.2 Hz, 2H), 7.29 (d, $J$ = 8.2 Hz, 2H), 6.51 (d, $J$ = 2.1 Hz, 2H), 6.41 (t, $J$ = 2.1 Hz, 1H), 4.96 (s, 1H), 4.94 (s, 1H), 4.57 (s, 2H), 4.44 (s, 2H), 4.07 (s, 2H), 3.79 (s, 6H), 3.69 (s, 2H), 2.41 (s, 3H), 1.75 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.3, 160.9, 143.5, 139.1, 139.1, 135.9, 129.3, 127.8, 115.6, 105.7, 100.0, 79.9, 79.0, 73.3, 66.6, 55.3, 52.6, 52.0, 35.7, 21.5, 19.6. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{28}$H$_{35}$N$_2$O$_7$S]$^+$: 519.2159, found: 519.2158.

3. General Procedure for the Gold (I)-Catalyzed tandem reaction and Characterization
data of the tetracyclic products 2a-q
To a solution of the 1,\n-enynyl ester (0.1 mmol, 1 equiv.) and AuClPPh$_3$ (0.05 equiv.) in dried DCM (10 mL) was added AgSbF$_6$ (0.05 eq.). The reaction mixture was stirred at room temperature until the starting material disappeared (monitored by TLC). The suspension was then directly loaded onto a silica gel column and eluted with a mixture of PE / EtOAc to yield the desired cyclization products.

Table S1. Some Examples of Gold-Catalyzed Tandem Reaction of Enynyl Esters.

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Isolated yields. Determined by analysis of the spectra data of $^1$H NMR of the crude products. 5 mol% AuP(ArO)$_3$Cl, 5 mol% AgSbF$_6$ were used as catalyst; Ar = 2,4-di-tert-butylbenzene. yield of 3f.

Compound 2a: white solid, mp: 142-144°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.34 (d, $J = 2.1$ Hz, 1H), 6.14 (d, $J = 2.1$ Hz, 1H), 4.77 (d, $J = 14.9$ Hz, 1H), 4.64 (d, $J = 14.9$ Hz, 1H), 4.12 (d, $J = 11.8$ Hz, 1H), 3.87 (t, $J = 7.2$ Hz, 1H), 2.50 (s, 3H), 2.28 (s, 3H), 1.80-1.60 (m, 8H), 1.20 (s, 9H).
4.03 (d, J = 9.5 Hz, 1H), 3.92-3.89 (m, 2H), 3.78 (s, 3H), 3.74 (d, J = 11.8 Hz, 1H), 3.66 (s, 3H), 3.48-3.44 (m, 2H), 2.78 (dd, J = 13.2, 10.9 Hz, 1H), 2.14 (s, 3H), 1.79 (dd, J = 13.3, 4.3 Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.2, 160.0, 158.5, 137.7, 118.3, 103.2, 99.5, 97.6, 82.4, 79.7, 77.4, 76.7, 69.0, 55.3, 54.2, 50.3, 43.0, 26.9. HRMS (ESI): m/z [M+NH\(_4\)]\(^+\) calculated for [C\(_{18}\)H\(_{25}\)NO\(_3\)]\(^+\): 352.1760, found: 352.1755.

Compound 2b: white solid, mp: 136-138°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, J = 8.7 Hz, 1H), 6.87 (dd, J = 8.7, 2.4 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 4.74 (d, J = 15.0 Hz, 1H), 4.74 (d, J = 15.0 Hz, 1H), 4.22 (d, J = 9.8 Hz, 1H), 3.96 (d, J = 9.0 Hz, 1H), 3.84 – 3.80 (m, 1H), 3.79 (s, 3H), 3.66-3.58 (m, 3H), 3.28 (td, J = 9.1, 5.0 Hz, 1H), 2.66 (dd, J = 13.0, 9.1 Hz, 1H), 2.31 (s, 3H), 2.03 (dd, J = 12.8, 9.3 Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 210.9, 159.1, 136.1, 128.6, 127.5, 113.9, 107.9, 100.0, 83.4, 78.7, 75.2, 71.2, 68.5, 55.3, 48.6, 44.8, 27.5. HRMS (ESI): m/z [M+NH\(_4\)]\(^+\) calculated for [C\(_{17}\)H\(_{23}\)NO\(_3\)]\(^+\): 332.1654, found: 326.1652.

Since 2b and 2b’ were inseparable by chromatography on silica gel, the NMR spectra of purified 2b’ was not obtained. So only the NMR spectra data of the main product 2b was provided here. We provided the copies of \(^1\)H NMR spectra of crude products (for determining the dr value of 2b and 2b’), \(^1\)H NMR and \(^{13}\)C NMR spectra of purified 2b, and a mixed \(^1\)H NMR spectra of 2b’ contaminated by 2b after chromatography on silica gel (vide infra). The same phenomenon was found in the case of 2c and 2c’.

Compound 2c: colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, J = 8.6 Hz, 1H), 6.91 (d, J = 8.6 Hz, 1H), 6.48 (d, J = 15.8 Hz, 1H), 4.76 (d, J = 15.8 Hz, 1H), 4.21 (d, J = 9.8 Hz, 1H), 3.97 (d, J = 8.8 Hz, 1H), 3.87 (s, 3H), 3.84 – 3.77 (m, 4H), 3.64 – 3.50 (m, 3H), 3.28 (td, J = 9.1, 5.0 Hz, 1H), 2.66 (dd, J = 13.0, 9.1 Hz, 1H), 2.31 (s, 3H), 2.05 (dd, J = 12.8, 9.3 Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.0, 151.4, 143.4, 129.5, 129.2, 121.6, 111.7, 100.0, 83.2, 78.7, 75.2, 70.6, 65.1, 60.0, 55.8, 48.7, 44.7, 27.5. HRMS (ESI): m/z [M+NH\(_4\)]\(^+\) calculated for [C\(_{17}\)H\(_{25}\)NO\(_3\)]\(^+\): 352.1760, found: 352.1757.

Compound 2d: white solid, mp: 146-148°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.29 (d, J = 2.1 Hz, 1H), 6.22 (d, J = 2.1 Hz, 1H), 3.98-3.85 (m, 3H), 3.77 (s, 3H), 3.61 (s, 3H), 3.51 – 3.37 (m, 2H), 2.87 – 2.72 (m, 2H), 2.71 – 2.61 (m, 1H), 2.22 (dd, J = 11.3, 8.8 Hz, 1H), 2.12 (s, 3H), 2.04 – 1.96 (m, 1H), 1.94 – 1.84 (m, 2H), 1.71-1.65 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.4, 159.3, 158.9, 140.4, 122.2, 104.3, 102.7, 97.1, 86.4, 79.9, 77.6, 55.2, 54.1, 50.4, 47.4, 41.4, 31.3, 26.8, 20.6. HRMS (ESI): m/z [M+H]\(^+\) calculated for [C\(_{17}\)H\(_{25}\)O\(_3\)]\(^+\): 333.1697, found: 333.1696.

Compound 2d’: white solid, mp: 120-122°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.37 (s, 1H), 6.23 (s, 1H), 4.15 (d, J = 9.3 Hz, 1H), 3.96-3.90 (m, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 3.60 (d, J = 9.3 Hz, 1H), 3.34 (dd, J = 13.7, 8.6 Hz, 1H), 2.84 – 2.62 (m, 3H), 2.32 (s, 3H), 2.08 (dd, J = 11.8, 9.5 Hz, 1H), 1.86-1.81 (m, 2H), 1.74-1.69 (m, 1H), 1.66-1.58 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 212.5, 160.1, 159.8, 141.3, 118.4, 104.6, 99.5, 97.9, 87.7, 78.3, 75.1, 55.2, 54.8, 48.9, 42.4, 37.9, 31.5, 27.5, 20.6. HRMS (ESI): m/z [M+H]\(^+\) calculated for [C\(_{19}\)H\(_{25}\)O\(_3\)]\(^+\): 333.1697, found: 333.1696.
Compound 2e: white solid, mp: 165-167°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 8.2\) Hz, 2H), 7.36 (d, \(J = 8.2\) Hz, 2H), 6.32 (d, \(J = 2.2\) Hz, 1H), 6.16 (d, \(J = 2.2\) Hz, 1H), 4.35 (d, \(J = 14.4\) Hz, 1H), 4.03 (d, \(J = 9.2\) Hz, 1H), 3.99 – 3.85 (m, 3H), 3.80 – 3.72 (m, 4H), 3.63 (s, 3H), 3.54 – 3.46 (m, 1H), 3.42 (d, \(J = 9.6\) Hz, 1H), 2.91 (dd, \(J = 12.0\) Hz, 1H), 2.61 (dd, \(J = 12.0\) Hz, 1H), 2.44 (s, 3H), 2.21 (dd, \(J = 13.4\) Hz, 1H), 2.16 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 208.8, 159.9, 158.6, 143.7, 134.6, 133.2, 129.7, 127.8, 119.5, 102.9, 101.3, 98.1, 84.7, 78.8, 77.1, 55.3, 55.1, 54.4, 48.8, 48.1, 43.8, 26.7, 21.5. HRMS (ESI): m/z [M+NH\(_4\)]\(^+\) calculated for \([\text{C}_{25}\text{H}_{33}\text{N}_2\text{O}_7\text{S}]\): 505.2003, found: 505.2002.

Compound 2e': colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68 (d, \(J = 8.2\) Hz, 2H), 7.37 (d, \(J = 8.2\) Hz, 2H), 6.37 (d, \(J = 2.2\) Hz, 1H), 6.15 (d, \(J = 2.2\) Hz, 1H), 4.33 (d, \(J = 14.6\) Hz, 1H), 4.18 (d, \(J = 8.8\) Hz, 1H), 3.98 (d, \(J = 14.6\) Hz, 1H), 3.94 – 3.85 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.66 (d, \(J = 9.5\) Hz, 1H), 3.42 – 3.25 (m, 2H), 2.65 (dd, \(J = 11.2\) Hz, 1H), 2.59 – 2.46 (m, 2H), 2.45 (s, 3H), 2.29 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 210.7, 160.3, 159.7, 144.1, 135.1, 132.7, 129.9, 127.7, 116.4, 101.5, 100.2, 98.6, 85.9, 77.9, 74.8, 55.3, 55.0, 53.3, 49.0, 48.4, 40.5, 27.4, 21.6. HRMS (ESI): m/z [M+H]\(^+\) calculated for \([\text{C}_{25}\text{H}_{30}\text{NO}_7\text{S}]\): 488.1737, found: 488.1734.

Compound 2f: white solid, mp: 109-111°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.37 (d, \(J = 1.9\) Hz, 1H), 6.25 (d, \(J = 1.9\) Hz, 1H), 3.96 (d, \(J = 9.4\) Hz, 1H), 3.94 – 3.85 (m, 2H), 3.79 (s, 3H), 3.75 (d, \(J = 9.4\) Hz, 1H), 3.46 – 3.37 (m, 1H), 3.06 (dt, \(J = 16.0, 8.0\) Hz, 1H), 2.86 (dd, \(J = 12.8, 9.7\) Hz, 1H), 2.75 (dd, \(J = 12.8, 9.7\) Hz, 1H), 2.52 (dd, \(J = 13.6, 8.1\) Hz, 1H), 2.37 – 2.24 (m, 1H), 2.07 – 1.98 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 212.9, 161.9, 156.4, 147.6, 125.1, 101.4, 100.7, 96.7, 96.4, 79.5, 76.3, 55.4, 51.8, 43.9, 41.7, 30.4, 27.0. HRMS (ESI): m/z [M+H]\(^+\) calculated for \([\text{C}_{18}\text{H}_{23}\text{O}_5\text{S}]\): 319.1540, found: 319.1543.

Compound 2f': colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.36 (s, 1H), 6.33 (s, 1H), 4.12 (d, \(J = 9.4\) Hz, 1H), 3.93 (d, \(J = 9.4\) Hz, 1H), 3.86 (dd, \(J = 8.4, 4.7\) Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.70 (d, \(J = 9.4\) Hz, 1H), 3.27-3.21 (m, 1H), 3.00-2.92 (m, 1H), 2.78-2.70 (m, 2H), 2.33 (s, 3H), 2.18 – 1.98 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.7, 162.2, 157.8, 146.8, 122.3, 100.7, 98.8, 97.8, 97.2, 74.0, 55.4, 55.2, 49.2, 40.7, 39.5, 30.2, 27.1. HRMS (ESI): m/z [M+H]\(^+\) calculated for \([\text{C}_{18}\text{H}_{23}\text{O}_5\text{S}]\): 319.1540, found: 319.1541.

Compound 2g: white solid, mp: 144-146°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.33 (d, \(J = 2.1\) Hz, 1H), 6.12 (d, \(J = 2.1\) Hz, 1H), 4.78 (d, \(J = 15.0\) Hz, 1H), 4.66 (d, \(J = 15.0\) Hz, 1H), 4.16 (d, \(J = 11.6\) Hz,
1H), 3.86-3.81 (m, 2H), 3.78 (s, 3H), 3.72 (d, J = 11.6 Hz, 1H), 3.70 – 3.56 (m, 5H), 3.30 – 3.17 (m, 1H), 2.59 (dd, J = 13.0, 10.3 Hz, 1H), 2.18 – 2.01 (m, 4H), 1.91 (dd, J = 13.1, 8.4 Hz, 1H), 1.75 – 1.62 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 211.8, 159.8, 158.6, 137.6, 119.0, 99.4, 97.6, 90.5, 79.4, 77.5, 70.0, 69.0, 62.6, 55.3, 54.1, 40.6, 37.1, 25.4, 25.0. HRMS (ESI): m/z [M+H]$^+$ calculated for [C$_{11}$H$_{20}$O$_3$]: 349.1646, found: 349.1651.

Compound 2g': colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.39 (d, J = 2.3 Hz, 1H), 6.13 (d, J = 2.3 Hz, 1H), 4.75 (d, J = 14.9 Hz, 1H), 4.64 (d, J = 15.0 Hz, 1H), 4.01 (d, J = 12.1 Hz, 1H), 3.92 – 3.85 (m, 5H), 3.78 (s, 3H), 3.69 – 3.56 (m, 3H), 3.03 – 2.83 (m, 2H), 2.30 (s, 3H), 2.22 (ddt, J = 14.2, 11.9, 5.9 Hz, 1H), 2.27-2.20 (m, 1H), 1.70 (dt, J = 15.0, 7.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.9, 160.2, 159.4, 139.3, 115.4, 99.9, 98.3, 84.0, 80.0, 74.2, 69.4, 68.5, 63.8, 55.3, 54.9, 36.3, 35.1, 25.5, 25.4. HRMS (ESI): m/z [M+Na]$^+$ calculated for [C$_{10}$H$_{20}$NaO$_3$]: 371.1465, found: 371.1464.

Compound 2h: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.32 (d, J = 2.3 Hz, 1H), 6.10 (d, J = 2.2 Hz, 1H), 4.76 (d, J = 14.9 Hz, 1H), 4.63 (d, J = 14.8 Hz, 1H), 4.02 (d, J = 11.6 Hz, 1H), 3.86 (d, J = 12.9 Hz, 1H), 3.80 – 3.74 (m, 4H), 3.73 – 3.58 (m, 6H), 3.45 – 3.32 (m, 1H), 2.68 (dd, J = 13.1, 11.2 Hz, 1H), 2.12 (s, 3H), 2.07 – 1.95 (m, 1H), 1.89 – 1.67 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 211.3, 159.9, 158.7, 137.6, 118.5, 99.3, 97.5, 96.4, 79.6, 77.8, 75.1, 74.6, 69.0, 55.3, 54.1, 43.0, 42.2, 31.7, 29.3, 24.6. HRMS (ESI): m/z [M+Na]$^+$ calculated for [C$_{10}$H$_{20}$NaO$_3$]: 380.2068, found: 380.2067.

Compound 2h': white solid, mp: 153-155 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.38 (d, J = 2.2 Hz, 1H), 6.10 (d, J = 2.2 Hz, 1H), 4.67 (d, J = 14.9 Hz, 1H), 4.59 (d, J = 14.9 Hz, 1H), 4.03 (d, J = 12.7 Hz, 1H), 3.94 (d, J = 11.9 Hz, 1H), 3.88 (d, J = 13.4 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 3.58 (d, J = 11.4 Hz, 1H), 3.48 – 3.34 (m, 3H), 2.38 (t, J = 11.7 Hz, 1H), 2.32 (s, 3H), 2.25 (dd, J = 12.5, 8.5 Hz, 1H), 2.20 – 2.11 (m, 1H), 1.87 – 1.73 (m, 1H), 1.71 – 1.55 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.2, 160.1, 159.3, 138.6, 116.4, 99.6, 98.5, 91.6, 80.6, 74.4, 73.6, 71.6, 69.2, 55.3, 54.9, 42.1, 38.4, 31.1, 28.8, 25.3. HRMS (ESI): m/z [M+NH$_4$]$^+$ calculated for [C$_3$H$_{10}$NO$_2$]: 380.2068, found: 380.2067.

Compound 2i: white solid, mp: 179-181°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 6.30 (d, J = 2.1 Hz, 1H), 6.13 (d, J = 2.1 Hz, 1H), 4.76 (d, J = 15.0 Hz, 1H), 4.63 (d, J = 15.0 Hz, 1H), 4.18 (d, J = 11.9 Hz, 1H), 3.82 – 3.70 (m, 4H), 3.60 (m, 4H), 3.44 (d, J = 9.4 Hz, 1H), 3.33 (ddt, J = 11.0, 5.7 Hz, 1H), 2.87 (dd, J = 9.3, 7.0 Hz, 1H), 2.74 (dd, J = 13.2, 10.9 Hz, 1H), 2.60 (d, J = 10.0 Hz, 1H), 2.44 (s, 3H), 2.07 (s, 3H), 1.86 (dd, J = 13.3, 4.9 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.5, 160.0, 158.3, 144.0, 137.8, 131.3, 129.7, 128.0, 118.0, 100.0, 99.5, 97.5, 82.3, 76.9, 68.9, 59.7, 56.3, 55.3, 54.1, 47.7, 42.8, 26.2, 21.5. HRMS (ESI): m/z [M+H]$^+$ calculated for [C$_{23}$H$_{30}$NO$_5$S]: 488.1737, found:488.1735.
**Compound 2j** : white solid, mp: 85-87°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 8.2\) Hz, 2H), 7.32 (d, \(J = 8.0\) Hz, 2H), 6.31 (s, 1H), 6.12 (s, 1H), 4.77 (d, \(J = 15.0\) Hz, 1H), 4.64 (d, \(J = 15.0\) Hz, 1H), 4.12 (d, \(J = 11.6\) Hz, 1H), 3.77 (s, 3H), 3.72 (d, \(J = 11.8\) Hz, 1H), 3.61 (s, 3H), 3.36 (dt, \(J = 10.1, 5.6\) Hz, 1H), 3.28 – 3.06 (m, 4H), 2.51 (dd, \(J = 13.1, 10.7\) Hz, 1H), 2.44 (s, 3H), 2.12 (s, 3H), 1.99 – 1.87 (m, 1H), 1.84 (dd, \(J = 13.2, 8.1\) Hz, 1H), 1.79 – 1.68 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.2, 159.9, 158.4, 143.5, 137.8, 134.0, 129.7, 127.5, 118.9, 99.4, 97.5, 91.6, 79.8, 77.6, 69.0, 55.3, 54.0, 49.3, 40.5, 40.3, 38.2, 25.0, 24.7, 21.5. HRMS (ESI): \(m/z\) [M+H\(^+\)] calculated for [C\(_{26}\)H\(_{36}\)N\(_2\)O\(_3\)S\(^+\)]: 519.2159, found: 519.2166.

**Compound 2j’** : white solid, mp: 220-222°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.70 (d, \(J = 8.2\) Hz, 2H), 7.36 (d, \(J = 8.2\) Hz, 2H), 6.28 (d, \(J = 2.3\) Hz, 1H), 6.10 (d, \(J = 2.3\) Hz, 1H), 4.70 (d, \(J = 15.0\) Hz, 1H), 4.58 (d, \(J = 15.0\) Hz, 1H), 3.84 (d, \(J = 12.4\) Hz, 1H), 3.75 (s, 3H), 3.60 – 3.50 (m, 3H), 3.34 (s, 3H), 3.07 (d, \(J = 12.4\) Hz, 1H), 3.04 – 2.94 (m, 1H), 2.76 (td, \(J = 11.0, 3.5\) Hz, 1H), 2.64 (t, \(J = 12.4\) Hz, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.22 – 2.09 (m, 1H), 1.95 (dd, \(J = 12.5, 8.0\) Hz, 1H), 1.78 – 1.68 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 208.4, 160.2, 159.1, 143.6, 139.2, 134.1, 129.7, 127.7, 115.0, 99.9, 98.2, 85.4, 80.1, 74.1, 69.3, 55.3, 54.2, 47.7, 42.4, 36.7, 34.8, 25.6, 25.0, 21.5. HRMS (ESI): \(m/z\) [M+H\(^+\)] calculated for [C\(_{26}\)H\(_{36}\)NO\(_3\)S\(^+\)]: 502.1894, found: 502.1892.

**Compound 2k** : white solid, mp: 79-80°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.66 (d, \(J = 8.2\) Hz, 2H), 7.33 (d, \(J = 8.2\) Hz, 2H), 6.36 (d, \(J = 2.1\) Hz, 1H), 6.11 (d, \(J = 2.0\) Hz, 1H), 4.69 (d, \(J = 14.9\) Hz, 1H), 4.59 (d, \(J = 14.9\) Hz, 1H), 4.12 (dd, \(J = 13.9, 1.5\) Hz, 1H), 3.84 – 3.73 (m, 4H), 3.69 (s, 3H), 3.49 (q, \(J = 11.5\) Hz, 2H), 3.34 – 3.21 (m, 1H), 2.92 (d, \(J = 13.9\) Hz, 1H), 2.49 (s, 3H), 2.45 (s, 3H), 2.33 – 2.13 (m, 3H), 2.12 – 2.00 (m, 1H), 1.87-1.88 (m, 1H), 1.75-1.72 (m, 1H), 1.42-1.40 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 210.7, 160.1, 159.2, 143.6, 138.6, 134.0, 129.6, 127.7, 116.1, 99.6, 98.5, 91.6, 80.3, 73.4, 69.2, 55.3, 54.7, 52.5, 51.1, 41.9, 39.9, 30.9, 25.9, 25.8, 21.5. HRMS (ESI): \(m/z\) [M+NH\(_4\)+] calculated for [C\(_{26}\)H\(_{37}\)N\(_2\)O\(_3\)S\(^+\)]: 533.2316, found: 533.2315.

**Compound 2k’** : white solid, mp: 82-84°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 (d, \(J = 8.0\) Hz, 2H), 7.30 (d, \(J = 8.0\) Hz, 2H), 6.32 (s, 1H), 6.10 (s, 1H), 4.76 (d, \(J = 14.9\) Hz, 1H), 4.61 (d, \(J = 14.9\) Hz, 1H), 3.93 (t, \(J = 13.2\) Hz, 2H), 3.77 (s, 3H), 3.71 – 3.56 (m, 5H), 3.42 (dt, \(J = 15.5, 4.1\) Hz, 1H), 2.89 – 2.72 (m, 2H), 2.50 – 2.37 (m, 4H), 2.24 (s, 3H), 1.98 – 1.88 (m, 1H), 1.88 – 1.73 (m, 2H), 1.69 – 1.55 (m, 1H), 1.51 (dd, \(J = 13.4, 4.8\) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 209.6, 160.0, 158.7, 143.4, 137.7, 134.8, 129.7, 127.5, 117.7, 99.4, 97.4, 95.0, 80.0, 78.2, 69.0, 55.3, 53.9, 53.5, 52.0, 43.1, 42.8, 32.6, 28.0, 24.5, 21.5. HRMS (ESI): \(m/z\) [M+NH\(_4\)+] calculated for [C\(_{26}\)H\(_{37}\)N\(_2\)O\(_3\)S\(^+\)]: 533.2316, found: 533.2314.
Compound 2l: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.31 (d, $J = 2.3$ Hz, 1H), 6.10 (d, $J = 2.3$ Hz, 1H), 4.79 (d, $J = 15.0$ Hz, 1H), 4.67 (d, $J = 15.0$ Hz, 1H), 4.04 (d, $J = 11.4$ Hz, 1H), 3.77 (s, 3H), 3.71 (d, $J = 11.4$ Hz, 1H), 3.64 (s, 3H), 3.11 (ddd, $J = 14.9, 9.1, 5.9$ Hz, 1H), 2.58 (ddd, $J = 13.0, 9.7$ Hz, 1H), 2.10 (s, 3H), 1.88 – 1.71 (m, 3H), 1.67 – 1.53 (m, 3H), 1.53 – 1.44 (m, 2H), 1.44 – 1.32 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 213.0, 159.7, 158.6, 137.6, 119.3, 99.3, 97.4, 90.9, 78.4, 78.0, 68.9, 55.2, 54.0, 41.4, 38.5, 32.5, 26.9, 24.4, 19.7, 19.6. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{20}$H$_{30}$NO$_5$]: 364.2118, found: 364.2117.

Compound 2l': colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.38 (d, $J = 2.2$ Hz, 1H), 6.12 (d, $J = 2.2$ Hz, 1H), 4.75 (d, $J = 14.9$ Hz, 1H), 4.63 (d, $J = 14.9$ Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.69 – 3.59 (m, 2H), 2.90 (t, $J = 12.3$ Hz, 1H), 2.78 – 2.63 (m, 1H), 2.29 (s, 3H), 2.22 – 2.09 (m, 1H), 1.94 – 1.77 (m, 3H), 1.76 – 1.62 (m, 2H), 1.62 – 1.52 (m, 1H), 1.52 – 1.41 (m, 1H), 1.40 – 1.18 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 213.9, 160.0, 159.4, 139.1, 116.1, 99.8, 98.3, 88.0, 78.8, 74.3, 69.4, 55.3, 54.8, 37.3, 37.1, 30.7, 26.0, 25.4, 20.9, 20.2. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{20}$H$_{30}$NO$_5$]: 364.2118, found: 364.2122.

Compound 2m: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.30 (d, $J = 2.3$ Hz, 1H), 6.09 (d, $J = 2.3$ Hz, 1H), 4.77 (d, $J = 14.8$ Hz, 1H), 4.62 (d, $J = 14.8$ Hz, 1H), 3.97 (d, $J = 11.5$ Hz, 1H), 3.77 (s, 3H), 3.67 (d, $J = 11.5$ Hz, 1H), 3.63 (s, 3H), 3.28 (t, $J = 11.3, 3.6$ Hz, 1H), 2.85 (ddd, $J = 13.3, 10.9$ Hz, 1H), 2.06 (s, 3H), 1.97 (dd, $J = 14.5, 8.4$ Hz, 1H), 1.87 – 1.74 (m, 3H), 1.71 – 1.60 (m, 2H), 1.60 – 1.49 (m, 2H), 1.49 – 1.36 (m, 1H), 1.34 – 1.22 (m, 1H), 1.15 – 0.99 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 212.42, 159.78, 158.71, 137.80, 118.33, 99.29, 97.42, 97.25, 78.88, 78.09, 68.99, 55.26, 53.80, 43.50, 43.20, 36.67, 34.42, 31.00, 28.37, 23.90, 22.75. HRMS (ESI): $m/z$ [M+NH$_4$]$^+$ calculated for [C$_{21}$H$_{32}$NO$_5$]: 378.2275, found: 378.2273.
 Compound 2n: white solid, mp: 238-239 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 8.0$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 6.27 (d, $J = 1.8$ Hz, 1H), 6.12 (d, $J = 1.8$ Hz, 1H), 4.79 (d, $J = 15.0$ Hz, 1H), 4.64 (d, $J = 13.3$ Hz, 1H), 4.17 (d, $J = 11.8$ Hz, 1H), 3.76 (s, 3H), 3.68 – 3.54 (m, 3H), 3.30 (s, 3H), 3.28 - 3.17 (m, 2H), 3.13 – 3.01 (m, 1H), 2.44 (s, 3H), 2.33 (s, 3H), 2.00 – 1.90 (m, 1H), 1.90 – 1.78 (m, 1H), 1.67 (d, $J = 13.3$ Hz, 1H), 1.21 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 209.2, 160.2, 158.8, 143.3, 139.4, 134.9, 129.6, 127.6, 115.8, 100.0, 98.2, 89.4, 79.3, 75.7, 69.1, 55.3, 54.0, 48.4, 45.7, 42.7, 41.1, 36.9, 28.4, 27.8, 21.5. HRMS (ESI): $m/z$ [M+H]$^+$ calculated for [C$_{27}$H$_{37}$N$_2$O$_5$S]$^+ $: 533.2316, found: 533.2321.

 Compound 2p: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.53 (s, 2H), 6.41 (s, 1H), 5.47 (s, 1H), 4.81 (d, $J = 11.4$ Hz, 2H), 4.59 (s, 2H), 4.14 (s, 2H), 3.79 (s, 6H), 3.05 (s, 2H), 2.36 – 2.19 (m, 4H), 1.95 – 1.76 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.3, 160.9, 153.7, 139.3, 139.2, 127.6, 105.6, 102.6, 100.1, 73.2, 66.8, 55.3, 35.4, 34.5, 32.5, 23.5. HRMS (ESI): $m/z$ [M+H]$^+$ calculated for [C$_{19}$H$_{30}$O$_5$]$: 333.1697, found: 333.1699.

 Compound 2q: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 6.50 (d, $J = 2.1$ Hz, 2H), 6.40 (t, $J = 2.1$ Hz, 1H), 6.35 (d, $J = 8.0$ Hz, 1H), 5.30 (d, $J = 8.0$ Hz, 1H), 4.55 (s, 2H), 4.33 (d, $J = 11.9$ Hz, 1H), 4.07 (s, 2H), 3.95 (s, 2H), 3.90 (d, $J = 11.8$ Hz, 1H), 3.80 (d, $J = 15.7$ Hz, 7H), 2.71 (d, $J = 11.5$ Hz, 1H), 2.42 (s, 3H), 1.18 (s, 3H), 0.86 (d, $J = 4.9$ Hz, 1H), 0.65 (d, $J = 4.8$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.4, 160.9, 143.8, 139.3, 134.9, 129.8, 127.0, 121.8, 113.5, 105.7, 100.0, 73.2, 67.4, 66.9, 55.3, 46.3, 31.0, 24.2, 21.9, 21.5, 17.4. HRMS (ESI): $m/z$ [M+H]$^+$ calculated for [C$_{26}$H$_{39}$O$_5$S]$^+ $: 519.2159, found: 519.2147.

 Compound 3f: white solid, mp:89-90 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.35 (s, 1H), 6.32 (s, 1H), 4.18 (d, $J = 9.8$ Hz, 1H), 4.06 (t, $J = 7.6$ Hz, 1H), 3.85 (s, 3H), 3.84 – 3.74 (m, 6H), 2.95 – 2.84 (m, 3H), 2.61 (s, 1H), 2.36 – 2.25 (m, 1H), 2.11 – 1.99 (m, 2H), 1.92-1.86 (m, 1H), 1.50 (dd, $J = 13.3$, 2.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 207.8, 161.1, 157.1, 145.3, 126.8, 100.7, 97.4, 82.7, 72.6, 69.4, 55.4, 55.2, 53.8, 47.5, 46.7, 37.6, 30.9, 30.2. HRMS (ESI): $m/z$ [M+H]$^+$ calculated for [C$_{19}$H$_{32}$O$_5$]$: 319.1540, found: 319.1542.

 Compound 2aa: yellow solid, mp: 91-93 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 16.1$ Hz, 1H), 7.54 (d, $J = 8.8$ Hz, 2H), 7.40 (d, $J = 16.1$ Hz, 1H), 6.20 (d, $J = 2.3$ Hz, 1H),
6.17 (d, $J = 2.3$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.68 (d, $J = 15.0$ Hz, 1H), 4.19 (d, $J = 11.8$ Hz, 1H), 4.09 (d, $J = 9.4$ Hz, 1H), 4.01 – 3.91 (m, 2H), 3.80 (d, $J = 6.4$ Hz, 1H), 3.76 (s, 3H), 3.60 (d, $J = 9.5$ Hz, 1H), 3.57 – 3.50 (m, 1H), 3.48 (s, 3H), 2.86 (dd, $J = 13.2, 10.8$ Hz, 1H), 1.84 (dd, $J = 13.2, 4.2$ Hz, 1H).  
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.8, 160.1, 158.6, 148.3, 141.0, 139.1, 137.7, 128.9, 125.4, 124.0, 117.9, 102.6, 99.4, 97.3, 82.9, 80.0, 77.3, 76.7, 69.0, 55.3, 53.9, 52.2, 42.8.  
HRMS (ESI): $m/z$ [M+H]$^+$ calculated for [C$_{25}$H$_{26}$NO$_8$]$^+$: 468.1653, found: 468.1656.

**Figure S1.** X-ray structure of 2d (CCDC 1547619)  
**Figure S2.** X-ray structure of 2g (CCDC 1547616)  
**Figure S3.** X-ray structure of 2h (CCDC 1547593)  
**Figure S4.** X-ray structure of 2i (CCDC 1547620)  
**Figure S5.** X-ray structure of 2n (CCDC 1539474)  
**Figure S6.** X-ray structure of 2n’ (CCDC 1539475)
$^{1}$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}$H NMR (400M, CDCl$_3$)
\(^{13}\text{C NMR (101 M, CDCl}_3\))

1b
$^{1}H$ NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)

![NMR spectrum](image)
$\text{1d}$

$\text{H NMR (400M, CDCl}_3)$
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}H$ NMR (400M, CDCl$_3$)
\[ \text{13 C NMR (101 M, CDCl}_3) \]
$\text{H NMR (400M, CDCl}_3\text{)}$
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400M, CDCl$_3$)
$^1\text{H}$ NMR (101 M, CDCl$_3$)

$^1\text{C}$ NMR (101 M, CDCl$_3$)

1p
$^1$H NMR (400M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}\text{H NMR (400 M, CDCl}_3\text{)}$
\[ ^{13}\text{C NMR (101 M, CDCl}_3\text{)} \]
$^1$H NMR (300M CD$_3$Cl)

2.9: 1 dr
$^1$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)


\[ \text{H NMR (400 M, CDCl}_3) \]
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^{1}$H NMR (400 M, CDCl$_3$)
\[ ^{13}\text{C} \text{ NMR (101 M, CDCl}_3 \]
$^1$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^{1}$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)

2f'
$\text{H NMR (400 M, CDCl}_3\text{)}$
$^1$H NMR (400 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^\text{13}C$ NMR (101 M, CDCl$_3$)
\(^1\)H NMR (400 MHz, CDCl\(_3\) )
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}$H NMR (400 M, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{1}$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)
$^{13}$C NMR (101 M, CDCl$_3$)
$^1$H NMR (400 M, CDCl$_3$)

2p
$^{13}$C NMR (101 M, CDCl$_3$)

![NMR Spectrum Image]
$^{1}$H NMR (400 M, CDCl$_3$)

![NMR spectrum](image-url)
\[ ^{13}\text{C NMR (101 M, CDCl}_3 \text{)} \]
$^1\text{H NMR (400 M, CDCl}_3$)
$^{13}$C NMR (101 M, CDCl$_3$)