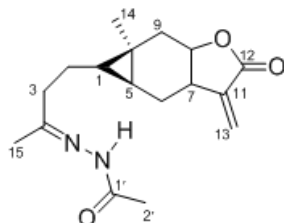


Supplementary Information

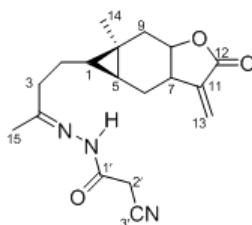
Physical Property and Spectroscopic Data of 28 Title Compounds

1. **6a**: *N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)acetohydrazide



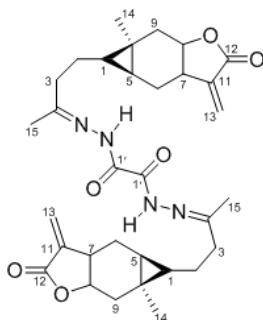
Light yellow solid, mp: 71–72 °C ; ¹H NMR (500 MHz, CDCl₃) δ: 9.16 (s, 1H, NH), 6.22 (d, *J* = 2.6 Hz, 1H, *H*-13α), 5.56 (d, *J* = 2.6 Hz, 1H, *H*-13β), 4.77–4.82 (m, 1H, *H*-8), 3.17–3.18 (m, 1H, *H*-7), 2.37 (t, *J* = 7.6 Hz, 2H, *H*-3), 2.30–2.34 (m, 2H, overlapped, H_{eq}-6, H_{eq}-9), 2.23 (s, 3H, *H*-2'), 1.88 (s, 3H, *H*-15), 1.49–1.64 (m, 2H, *H*-2), 1.09 (s, 3H, *H*-14), 0.89–1.00 (m, 2H, overlapped, H_{eq}-6, H_{eq}-9), 0.47–0.49 (m, 1H, *H*-1), 0.36–0.40 (m, 1H, *H*-5); ¹³C NMR (125 MHz, CDCl₃) δ: 173.7 (*C*-1'), 170.5 (*C*-12), 152.0 (*C*-4), 139.0 (*C*-11), 122.5 (*C*-13), 75.7 (*C*-8), 38.8 (*C*-3), 37.7 (*C*-7), 37.3 (*C*-9), 34.4 (*C*-1), 30.8 (*C*-6), 25.7 (*C*-2), 22.9 (*C*-5), 20.5 (*C*-2'), 18.3 (*C*-14), 17.1 (*C*-10), 15.5 (*C*-15); HR-MS (ESI): *m/z* calcd for C₁₇H₂₅N₂O₃([*M* + *H*]⁺), 305.1860; found, 305.1860.

2. **6b**: 2-Cyano-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)acetohydrazide



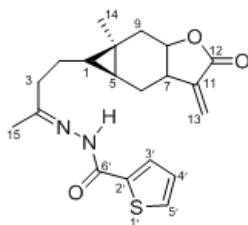
Colourless solid, mp: 79–81 °C ; ¹H NMR (500 MHz, CDCl₃) δ: 10.02 (s, 1H, NH), 6.24 (d, *J* = 2.6 Hz, 1H, *H*-13α), 5.56 (d, *J* = 2.6 Hz, 1H, *H*-13β), 4.75–4.81 (m, 1H, *H*-8), 3.81 (s, 2H, *H*-2'), 3.12–3.23 (m, 1H, *H*-7), 2.38 (t, *J* = 7.6 Hz, 2H, *H*-3), 2.25–2.31 (m, 2H, overlapped, H_{eq}-6, H_{eq}-9), 1.95 (s, 3H, *H*-15), 1.48–1.63 (m, 2H, *H*-2), 1.09 (s, 3H, *H*-14), 0.90–1.01 (m, 2H, overlapped, H_{eq}-6, H_{eq}-9), 0.40–0.46 (m, 1H, *H*-1), 0.37–0.41 (m, 1H, *H*-5); ¹³C NMR (125 MHz, CDCl₃) δ: 170.6 (*C*-12), 165.1 (*C*-1'), 156.0 (*C*-4), 139.1 (*C*-11), 129.0 (*C*-3'), 122.5 (*C*-13), 75.7 (*C*-8), 38.8 (*C*-3), 37.5 (*C*-7), 37.1 (*C*-9), 33.9 (*C*-1), 30.5 (*C*-6), 25.6 (*C*-2), 24.4 (*C*-2'), 22.8 (*C*-5), 18.1 (*C*-14), 17.0 (*C*-10), 16.2 (*C*-15); HR-MS (ESI): *m/z* calcd for C₁₈H₂₄N₃O₃([*M* + *H*]⁺), 330.1812; found, 330.1812.

3. **6c**: *N'*1,*N'*2-bis(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)oxalohydrazide



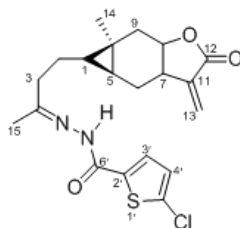
Light yellow solid, mp: 179–180 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.93 (s, 2H, NH), 6.23 (d, $J = 2.6$ Hz, 2H, H -13 α), 5.56 (d, $J = 2.6$ Hz, 2H, H -13 β), 4.85–4.98 (m, 2H, H -8), 3.11–3.19 (m, 2H, H -7), 2.49 (t, $J = 7.6$ Hz, 4H, H -3), 2.30–2.37 (m, 4H, overlapped, $H_{\text{eq}}\text{-6}$, $H_{\text{eq}}\text{-9}$), 2.01 (s, 6H, H -15), 1.48–1.75 (m, 4H, H -2), 1.09 (s, 6H, H -14), 0.89–1.01 (m, 4H, overlapped, $H_{\text{eq}}\text{-6}$, $H_{\text{eq}}\text{-9}$), 0.45–0.51 (m, 2H, H -1), 0.36–0.42 (m, 2H, H -5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (C -12), 162.4 (C -1'), 155.2 (C -4), 139.0 (C -11), 122.6 (C -13), 75.6 (C -8), 39.1 (C -3), 37.7 (C -7), 37.2 (C -9), 34.3 (C -1), 30.7 (C -6), 26.1 (C -2), 23.0 (C -5), 18.4 (C -14), 17.3 (C -10), 15.9 (C -15); HR-MS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{43}\text{N}_4\text{O}_6$ ($[\text{M} + \text{H}]^+$), 579.3177; found, 579.3183.

4. **6d**: *N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)thiophene-2-carbohydrazide



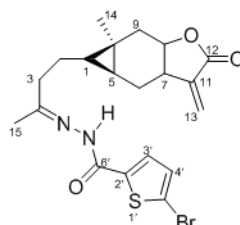
Milky-white solid, mp: 128–129 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 10.39 (s, 1H, NH), 8.14 (d, $J = 3.7$ Hz, 1H, H -3'), 7.62 (d, $J = 4.9$ Hz, 1H, H -5'), 7.10 (dd, $J = 4.9, 3.7$ Hz, 1H, H -4'), 6.16 (d, $J = 2.6$ Hz, 1H, H -13 α), 5.48 (d, $J = 2.6$ Hz, 1H, H -13 β), 4.72–4.77 (m, 1H, H -8), 3.05–3.14 (m, 1H, H -7), 2.45–2.48 (t, $J = 7.1$ Hz, 2H, H -3), 2.25–2.32 (m, 2H, overlapped, $H_{\text{eq}}\text{-6}$, $H_{\text{eq}}\text{-9}$), 2.05 (s, 3H, H -15), 1.62–1.74 (m, 2H, H -2), 1.09 (s, 3H, H -14), 0.82–0.96 (m, 2H, overlapped, $H_{\text{eq}}\text{-6}$, $H_{\text{eq}}\text{-9}$), 0.48–0.54 (m, 1H, H -1), 0.35–0.39 (m, 1H, H -5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (C -12), 163.1 (C -6'), 154.0 (C -4), 139.1 (C -11), 135.0 (C -2'), 134.5 (C -3'), 133.3 (C -5'), 126.2 (C -4'), 122.4 (C -13), 75.7 (C -8), 38.8 (C -3), 37.6 (C -7), 37.3 (C -9), 34.4 (C -1), 30.7 (C -6), 26.2 (C -2), 22.9 (C -5), 18.3 (C -14), 17.1 (C -10), 16.0 (C -15); HR-MS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ ($[\text{M} + \text{H}]^+$), 373.1580; found, 373.1581.

5. **6e**: 5-Chloro-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)thiophene-2-carbohydrazide



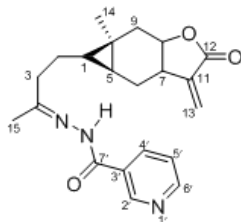
White solid, mp: 130–132 °C; ^1H NMR (500 MHz, CDCl_3) δ : 9.78 (s, 1H, NH), 7.90 (d, $J = 4.2$ Hz, 1H, $H\text{-}3'$), 6.96 (d, $J = 4.2$ Hz, 1H, $H\text{-}4'$), 6.23 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\alpha$), 5.53 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\beta$), 4.76–4.81 (m, 1H, $H\text{-}8$), 3.12–3.17 (m, 1H, $H\text{-}7$), 2.50 (t, $J = 7.1$ Hz, 2H, $H\text{-}3$), 2.28–2.39 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 2.00 (s, 3H, $H\text{-}15$), 1.49–1.81 (m, 2H, $H\text{-}2$), 1.14 (s, 3H, $H\text{-}14$), 0.89–1.00 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.51–0.56 (m, 1H, $H\text{-}1$), 0.38–0.43 (m, 1H, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (C-12), 162.0 (C-6'), 153.6 (C-4), 139.9 (C-5'), 139.0 (C-11), 134.5 (C-2'), 130.2 (C-3'), 125.5 (C-4'), 122.6 (C-13), 75.7 (C-8), 38.7 (C-3), 37.7 (C-7), 37.3 (C-9), 34.3 (C-1), 30.8 (C-6), 26.3 (C-2), 23.1 (C-5), 18.4 (C-14), 17.2 (C-10), 15.8 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{24}\text{ClN}_2\text{O}_3\text{S}([\text{M} + \text{H}]^+)$, 407.1191; found, 407.1191.

6. **6f**: 5-Bromo-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)thiophene-2-carbohydrazide



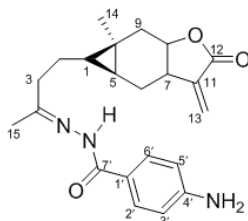
Milky-white solid, mp: 118–119 °C; ^1H NMR (500 MHz, CDCl_3) δ : 9.86 (s, 1H, NH), 7.86 (d, $J = 4.2$ Hz, 1H, $H\text{-}3'$), 7.09 (d, $J = 4.2$ Hz, 1H, $H\text{-}4'$), 6.22 (d, $J = 2.5$ Hz, 1H, $H\text{-}13\alpha$), 5.53 (d, $J = 2.5$ Hz, 1H, $H\text{-}13\beta$), 4.76–4.81 (m, 1H, $H\text{-}8$), 3.12–3.18 (m, 1H, $H\text{-}7$), 2.49 (t, $J = 7.1$ Hz, 2H, $H\text{-}3$), 2.28–2.39 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 2.01 (s, 3H, $H\text{-}15$), 1.57–1.80 (m, 2H, $H\text{-}2$), 1.15 (s, 3H, $H\text{-}14$), 0.89–1.00 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.51–0.56 (m, 1H, $H\text{-}1$), 0.38–0.44 (m, 1H, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (C-12), 162.0 (C-6'), 153.8 (C-4), 139.0 (C-11), 135.1 (C-5'), 133.2 (C-2'), 129.1 (C-3'), 123.6 (C-4'), 122.6 (C-13), 75.7 (C-8), 38.7 (C-3), 37.8 (C-7), 37.3 (C-9), 34.3 (C-1), 30.8 (C-6), 26.3 (C-2), 23.1 (C-5), 18.4 (C-14), 17.2 (C-10), 15.9 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{24}\text{BrN}_2\text{O}_3\text{S}([\text{M} + \text{H}]^+)$, 451.0686; found, 451.0684.

7. **6g**: *N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)nicotinohydrazide



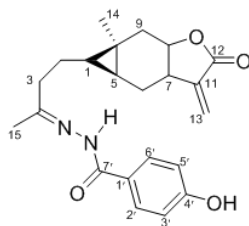
Colourless solid, mp: 46–47 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.79 (s, 1H, NH), 9.02 (s, 1H, *H*-2'), 8.65 (d, J = 6.7 Hz, 1H, *H*-6'), 8.16 (d, J = 7.5 Hz, 1H, *H*-4'), 7.34 (dd, J = 7.5, 6.7 Hz, 1H, *H*-5'), 6.16 (d, J = 2.6 Hz, 1H, *H*-13 α), 5.54 (d, J = 2.6 Hz, 1H, *H*-13 β), 4.74–4.79 (m, 1H, *H*-8), 3.10–3.17 (m, 1H, *H*-7), 2.42 (t, J = 7.6 Hz, 2H, *H*-3), 2.24–2.29 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 2.04 (s, 3H, *H*-15), 1.41–1.68 (m, 2H, *H*-2), 1.08 (s, 3H, *H*-14), 0.85–0.98 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.31–0.49 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.6 (*C*-12), 161.6 (*C*-7'), 152.0 (*C*-4), 148.4 (*C*-2'), 148.3 (*C*-6'), 139.0 (*C*-11), 135.5 (*C*-4'), 129.7 (*C*-3'), 123.3 (*C*-5'), 122.5 (*C*-13), 75.7 (*C*-8), 39.0 (*C*-3), 37.4 (*C*-7), 37.0 (*C*-9), 34.1 (*C*-1), 30.5 (*C*-6), 26.2 (*C*-2), 22.8 (*C*-5), 18.1 (*C*-14), 17.0 (*C*-10), 14.1 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{26}\text{N}_3\text{O}_3$ ($[\text{M} + \text{H}]^+$), 368.1969; found, 368.1969.

8. **6h**: 4-Amino-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



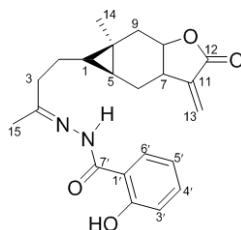
White solid, mp: 75–77 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.04 (s, 1H, NH), 7.62 (d, J = 7.9 Hz, 2H, *H*-3', *H*-5'), 6.60 (d, J = 7.9 Hz, 2H, *H*-2', *H*-6'), 6.14 (d, J = 2.6 Hz, 1H, *H*-13 α), 5.54 (d, J = 2.6 Hz, 1H, *H*-13 β), 4.66–4.77 (m, 1H, *H*-8), 4.29 (s, 2H, NH_2), 3.07–3.11 (m, 1H, *H*-7), 2.42 (t, J = 7.6 Hz, 2H, *H*-3), 2.25–2.29 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 1.95 (s, 3H, *H*-15), 1.41–1.66 (m, 2H, *H*-2), 1.03 (s, 3H, *H*-14), 0.79–0.92 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.40–0.45 (m, 1H, *H*-1), 0.29–0.35 (m, 1H, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.7 (*C*-12), 164.2 (*C*-7'), 158.0 (*C*-4), 150.8 (*C*-4'), 139.0 (*C*-11), 129.2 (*C*-2', 6'), 122.6 (*C*-13), 121.7 (*C*-1'), 113.8 (*C*-3', *C*-5'), 75.8 (*C*-8), 38.9 (*C*-3), 37.4 (*C*-7), 37.0 (*C*-9), 34.1 (*C*-1), 30.5 (*C*-6), 26.2 (*C*-2), 22.8 (*C*-5), 18.2 (*C*-14), 17.0 (*C*-10), 15.5 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{28}\text{N}_3\text{O}_3$ ($[\text{M} + \text{H}]^+$), 382.2125; found, 382.2124.

9. **6i**: 4-Hydroxy-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



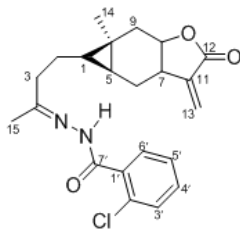
White solid, mp: 63–64 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.24 (s, 1H, NH), 7.60 (d, $J = 7.3$ Hz, 2H, $H\text{-}2'$, $H\text{-}6'$), 6.88 (d, $J = 7.3$ Hz, 2H, $H\text{-}3'$, $H\text{-}5'$), 6.23 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\alpha$), 5.57 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\beta$), 4.66–4.74 (m, 1H, $H\text{-}8$), 3.03–3.11 (m, 1H, $H\text{-}7$), 2.46 (t, $J = 7.6$ Hz, 2H, $H\text{-}3$), 2.25–2.30 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 2.16 (s, 3H, $H\text{-}15$), 1.59–1.62 (m, 2H, $H\text{-}2$), 0.99 (s, 3H, $H\text{-}14$), 0.79–0.94 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.29–0.45 (m, 2H, $H\text{-}1$, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 171.0 (C-12), 165.0 (C-7'), 161.0 (C-4'), 155.1 (C-4), 139.0 (C-11), 129.3 (C-2', 6'), 123.8 (C-1'), 122.7 (C-13), 115.8 (C-3', C-5'), 75.8 (C-8), 38.8 (C-3), 37.7 (C-7), 37.3 (C-9), 34.2 (C-1), 30.7 (C-6), 26.0 (C-2), 22.9 (C-5), 18.2 (C-14), 17.0 (C-10), 15.9 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_4$ ($[\text{M} + \text{H}]^+$), 383.1965; found, 383.1963.

10. **6j**: 2-Hydroxy-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



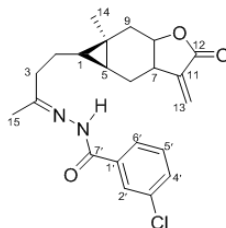
White solid, mp: 70–71 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 6.86–7.62 (m, 4H, $H\text{-}3'$, $H\text{-}4'$, $H\text{-}5'$, $H\text{-}6'$), 6.21 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\alpha$), 5.55 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\beta$), 4.74–4.78 (m, 1H, $H\text{-}8$), 3.13–3.15 (m, 1H, $H\text{-}7$), 2.46 (t, $J = 7.5$ Hz, 2H, $H\text{-}3$), 2.23–2.38 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 2.01 (s, 3H, $H\text{-}15$), 1.52–1.74 (m, 2H, $H\text{-}2$), 1.07 (s, 3H, $H\text{-}14$), 0.84–0.99 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.35–0.45 (m, 2H, $H\text{-}1$, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.7 (C-12), 166.1 (C-7'), 161.1 (C-2'), 160.3 (C-4), 139.2 (C-11), 134.4 (C-1'), 126.3 (C-4'), 122.7 (C-13), 119.0 (C-6'), 118.5 (C-5'), 114.2 (C-3'), 75.8 (C-8), 38.9 (C-3), 37.7 (C-7), 37.3 (C-9), 34.3 (C-1), 30.5 (C-6), 26.1 (C-2), 22.9 (C-5), 18.4 (C-14), 17.1 (C-10), 16.0 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_4$ ($[\text{M} + \text{H}]^+$), 383.1965; found, 383.1964.

11. 6k: 2-Chloro-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



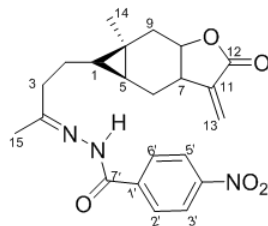
Light yellow solid, mp: 60–61 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.33 (s, 1H, NH), 7.25–7.63 (m, 4H, *H*-3', *H*-4', *H*-5', *H*-6'), 6.14 (d, $J = 2.6$ Hz, 1H, *H*-13 α), 5.53 (d, $J = 2.6$ Hz, 1H, *H*-13 β), 4.68–4.78 (m, 1H, *H*-8), 3.09–3.15 (m, 1H, *H*-7), 2.46 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.25–2.31 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 1.96 (s, 3H, *H*-15), 1.21–1.74 (m, 2H, *H*-2), 1.09 (s, 3H, *H*-14), 0.74–0.98 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.20–0.48 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.4 (C-12), 162.6 (C-7'), 159.9 (C-2'), 152.4 (C-4), 139.0 (C-11), 131.4 (C-1'), 130.8 (C-5'), 130.4 (C-6'), 130.0 (C-3'), 127.0 (C-4'), 122.4 (C-13), 75.7 (C-8), 39.0 (C-3), 37.5 (C-7), 37.1 (C-9), 34.2 (C-1), 30.6 (C-6), 26.1 (C-2), 22.9 (C-5), 18.3 (C-14), 17.1 (C-10), 16.1 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{26}\text{ClN}_2\text{O}_3$ ($[\text{M} + \text{H}]^+$), 401.1627; found, 401.1626.

12. 6l: 3-Chloro-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



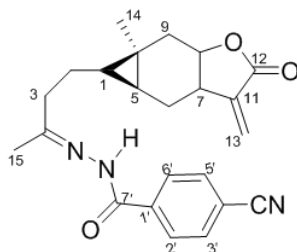
Light yellow solid, mp: 66–67 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.09 (s, 1H, NH), 7.80 (d, $J = 7.4$ Hz, 1H, *H*-4'), 7.69 (s, 1H, *H*-2'), 7.46 (d, $J = 7.7$ Hz, 1H, *H*-6'), 7.34 (dd, $J = 7.7, 7.4$ Hz, 1H, *H*-5'), 6.18 (d, $J = 2.5$ Hz, 1H, *H*-13 α), 5.54 (d, $J = 2.5$ Hz, 1H, *H*-13 β), 4.73–4.78 (m, 1H, *H*-8), 3.12–3.16 (m, 1H, *H*-7), 2.47 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.27–2.33 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 2.11 (s, 3H, *H*-15), 1.47–1.68 (m, 2H, *H*-2), 1.07 (s, 3H, *H*-14), 0.89–0.99 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.38–0.45 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (C-12), 162.9 (C-7'), 160.5 (C-4), 139.1 (C-11), 135.6 (C-3'), 134.7 (C-4'), 131.6 (C-1'), 129.9 (C-6'), 127.6 (C-5'), 125.5 (C-2'), 122.5 (C-13), 75.7 (C-8), 39.0 (C-3), 37.7 (C-7), 37.1 (C-9), 34.2 (C-1), 30.6 (C-6), 26.2 (C-2), 22.9 (C-5), 18.2 (C-14), 17.1 (C-10), 16.0 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{26}\text{ClN}_2\text{O}_3$ ($[\text{M} + \text{H}]^+$), 401.1627; found, 401.1626.

13. **6m**: *N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)-4-nitrobenzohydrazide



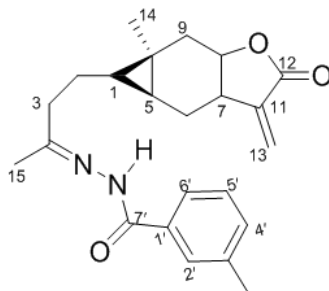
Yellow solid, mp: 69–70 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.21 (s, 1H, NH), 7.80 (d, $J = 7.7$ Hz, 1H, H -3'), 7.69 (d, $J = 7.7$ Hz, 1H, H -2'), 7.43 (d, $J = 7.4$ Hz, 1H, H -5'), 7.35 (d, $J = 7.4$ Hz, 1H, H -6'), 6.17 (d, $J = 2.4$ Hz, 1H, H -13 α), 5.54 (d, $J = 2.4$ Hz, 1H, H -13 β), 4.72–4.76 (m, 1H, H -8), 3.13–3.14 (m, 1H, H -7), 2.46 (t, $J = 7.6$ Hz, 2H, H -3), 2.24–2.31 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 2.01 (s, 3H, H -15), 1.48–1.67 (m, 2H, H -2), 1.07 (s, 3H, H -14), 0.84–0.99 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.42–0.45 (m, 1H, H -1), 0.29–0.40 (m, 1H, H -5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (C-12), 163.0 (C-7'), 160.7 (C-4), 145.6 (C-4'), 139.1 (C-11), 134.5 (C-1'), 130.5 (C-6'), 129.8 (C-2'), 125.7 (C-3'), 125.5 (C-5'), 122.5 (C-13), 75.7 (C-8), 39.0 (C-3), 37.6 (C-7), 37.1 (C-9), 34.2 (C-1), 30.5 (C-6), 26.2 (C-2), 22.9 (C-5), 18.2 (C-14), 17.1 (C-10), 16.1 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{26}\text{N}_3\text{O}_5$ ($[\text{M} + \text{H}]^+$), 412.1867; found, 412.1866.

14. **6n**: 4-Cyano-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*ff*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



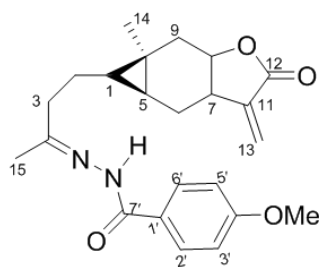
White solid, mp: 87–88 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.38 (s, 1H, NH), 7.96 (d, $J = 7.7$ Hz, 2H, H -3', H -5'), 7.76 (d, $J = 7.7$ Hz, 2H, H -2', H -6'), 6.18 (d, $J = 2.6$ Hz, 1H, H -13 α), 5.55 (d, $J = 2.6$ Hz, 1H, H -13 β), 4.74–4.79 (m, 1H, H -8), 3.15–3.16 (m, 1H, H -7), 2.46 (t, $J = 7.6$ Hz, 2H, H -3), 2.26–2.33 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 1.52–1.55 (m, 2H, H -2), 1.08 (s, 3H, H -14), 0.84–0.99 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.41–0.46 (m, 2H, H -1, H -5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.6 (C-12), 161.9 (C-7'), 154.4 (C-4), 139.0 (C-11), 137.8 (C-1'), 132.3 (C-2', C-6'), 128.2 (C-3', C-5'), 122.6 (C-13), 118.0 (C-8'), 115.0 (C-4'), 75.7 (C-8), 39.0 (C-3), 37.7 (C-7), 37.2 (C-9), 34.2 (C-1), 30.7 (C-6), 26.2 (C-2), 22.9 (C-5), 18.2 (C-14), 17.1 (C-10), 16.2 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{26}\text{N}_3\text{O}_3$ ($[\text{M} + \text{H}]^+$), 392.1969; found, 392.1965.

15. 6o: 3-Methyl-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



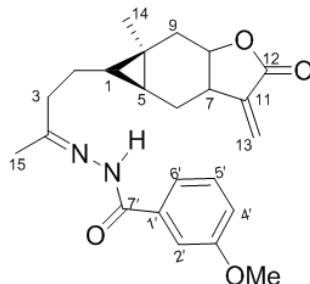
Milky-white solid, mp: 66–67 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.16 (s, 1H, NH), 7.63 (d, $J = 7.9$ Hz, 1H, *H*-6'), 7.61 (dd, $J = 8.1, 7.9$ Hz, 1H, *H*-5'), 7.38 (s, 1H, *H*-2'), 7.28 (d, $J = 8.1$ Hz, 1H, *H*-4'), 6.16 (d, $J = 2.6$ Hz, 1H, *H*-13 α), 5.53 (d, $J = 2.6$ Hz, 1H, *H*-13 β), 4.71–4.76 (m, 1H, *H*-8), 3.10–3.14 (m, 1H, *H*-7), 2.44 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.37 (s, 3H, Me), 2.26–2.31 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 2.01 (s, 3H, *H*-15), 1.46–1.61 (m, 2H, *H*-2), 1.07 (s, 3H, *H*-14), 0.89–0.95 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 0.37–0.45 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (*C*-12), 164.2 (*C*-7'), 159.3 (*C*-4), 139.1 (*C*-11), 138.3 (*C*-3'), 133.7 (*C*-1'), 132.3 (*C*-5'), 128.3 (*C*-6'), 128.0 (*C*-4'), 124.2 (*C*-2'), 122.4 (*C*-13), 75.7 (*C*-8), 39.0 (*C*-3), 37.5 (*C*-7), 37.1 (*C*-9), 34.1 (*C*-1), 30.5 (*C*-6), 26.2 (*C*-2), 22.9 (*C*-5), 21.2 (*C*-8'), 18.3 (*C*-14), 17.0 (*C*-10), 15.8 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_3$ ($[\text{M} + \text{H}]^+$), 381.2173; found, 381.2172.

16. 6p: 4-Methoxy-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



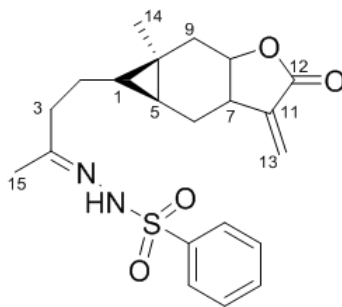
White solid, mp: 69–71 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 8.78 (s, 1H, NH), 7.81 (d, $J = 7.7$ Hz, 2H, *H*-3', *H*-5'), 6.93 (d, $J = 7.7$ Hz, 2H, *H*-2', *H*-6'), 6.22 (d, $J = 2.6$ Hz, 1H, *H*-13 α), 5.54 (d, $J = 2.6$ Hz, 1H, *H*-13 β), 4.74–4.79 (m, 1H, *H*-8), 3.85 (s, 3H, -OCH₃), 3.12–3.18 (m, 1H, *H*-7), 2.48 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.28–2.35 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 2.16 (s, 3H, *H*-15), 1.52–1.61 (m, 2H, *H*-2), 1.09 (s, 3H, *H*-14), 0.92–0.97 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 0.37–0.47 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.4 (*C*-12), 162.4 (*C*-7'), 160.2 (*C*-4'), 156.4 (*C*-4), 139.0 (*C*-11), 129.2 (*C*-2', *C*-6'), 125.8 (*C*-1'), 122.5 (*C*-13), 113.9 (*C*-3', *C*-5'), 75.6 (*C*-8), 55.4 (*C*-8'), 39.0 (*C*-3), 37.7 (*C*-7), 37.3 (*C*-9), 34.2 (*C*-1), 30.7 (*C*-6), 26.2 (*C*-2), 22.9 (*C*-5), 18.2 (*C*-14), 17.2 (*C*-10), 15.4 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_4$ ($[\text{M} + \text{H}]^+$), 397.2122; found, 397.2121.

17. **6q**: 3-Methoxy-*N'*-(4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)benzohydrazide



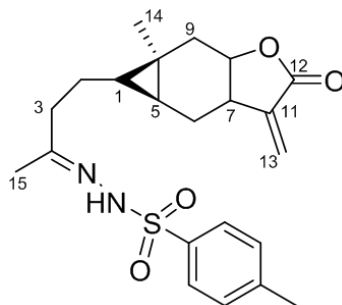
White solid, mp: 54–55 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.03 (s, 1H, NH), 7.29–7.37 (m, 3H, *H*-4', *H*-5', *H*-6'), 7.03 (s, 1H, *H*-2'), 6.18 (d, $J = 2.6$ Hz, 1H, *H*-13 α), 5.54 (d, $J = 2.6$ Hz, 1H, *H*-13 β), 4.73–4.78 (m, 1H, *H*-8), 3.82 (s, 3H, -OCH₃), 3.13–3.15 (m, 1H, *H*-7), 2.48 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.26–2.31 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 2.14 (s, 3H, *H*-15), 1.51–1.61 (m, 2H, *H*-2), 1.07 (s, 3H, *H*-14), 0.89–0.96 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 0.38–0.46 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (*C*-12), 163.8 (*C*-7'), 159.7 (*C*-3'), 153.6 (*C*-4), 139.0 (*C*-11), 135.1 (*C*-1'), 129.6 (*C*-5'), 122.5 (*C*-13), 119.0 (*C*-6'), 117.7 (*C*-2'), 112.8 (*C*-4'), 75.7 (*C*-8), 55.4 (*C*-8'), 39.0 (*C*-3), 37.6 (*C*-7), 37.1 (*C*-9), 34.2 (*C*-1), 30.6 (*C*-6), 26.2 (*C*-2), 22.9 (*C*-5), 18.2 (*C*-14), 17.1 (*C*-10), 15.8 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_4$ ($[\text{M} + \text{H}]^+$), 397.2122; found, 397.2121.

18. **7r**: *N'*-((*E*)-4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)benzenesulfonohydrazide



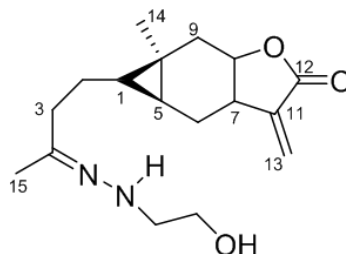
Light yellow solid, mp: 49–50 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 7.96 (d, $J = 8.7$ Hz, 2H, *H*-2', *H*-6'), 7.45–7.58 (m, 3H, *H*-3', *H*-4', *H*-5'), 6.22 (d, $J = 2.5$ Hz, 1H, *H*-13 α), 5.56 (d, $J = 2.5$ Hz, 1H, *H*-13 β), 4.70–4.75 (m, 1H, *H*-8), 3.07–3.13 (m, 1H, *H*-7), 2.48 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.26–2.31 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 1.22–1.37 (m, 2H, *H*-2), 0.99 (s, 3H, *H*-14), 0.78–0.91 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 0.21–0.39 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.8 (*C*-12), 158.8 (*C*-4), 139.0 (*C*-11), 138.4 (*C*-1'), 133.1 (*C*-4'), 128.8 (*C*-3', 5'), 128.0 (*C*-2', *C*-6'), 122.7 (*C*-13), 75.7 (*C*-8), 38.5 (*C*-3), 37.6 (*C*-7), 37.1 (*C*-9), 33.8 (*C*-1), 30.5 (*C*-6), 25.4 (*C*-2), 22.9 (*C*-5), 18.2 (*C*-14), 16.8 (*C*-10), 16.1 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ ($[\text{M} + \text{H}]^+$), 403.1686; found, 403.1689.

19. **7s**: 4-Methyl-*N'*-((*E*)-4-((4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)benzenesulfonohydrazide



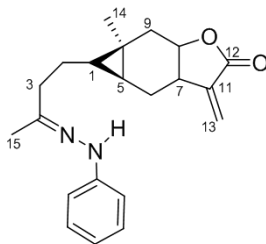
Colourless solid, mp: 55–56 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 7.74 (d, $J = 7.9$ Hz, 2H, *H*-2', *H*-6'), 7.29 (d, $J = 7.9$ Hz, 2H, *H*-3', *H*-5'), 6.24 (d, $J = 2.6$ Hz, 1H, *H*-13 α), 5.56 (d, $J = 2.6$ Hz, 1H, *H*-13 β), 4.71–4.75 (m, 1H, *H*-8), 3.09–3.18 (m, 1H, *H*-7), 2.40 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.24–2.30 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 1.79 (s, 3H, *H*-15), 1.51–1.65 (m, 2H, *H*-2), 1.26 (s, 3H, *H*-7'), 1.02 (s, 3H, *H*-14), 0.81–0.97 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 0.28–0.47 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (*C*-12), 158.1 (*C*-4), 144.0 (*C*-4'), 139.1 (*C*-11), 135.5 (*C*-1'), 129.4 (*C*-3', 5'), 128.1 (*C*-2', *C*-6'), 122.5 (*C*-13), 75.6 (*C*-8), 38.5 (*C*-3), 37.7 (*C*-7), 37.2 (*C*-9), 34.0 (*C*-1), 30.6 (*C*-6), 25.5 (*C*-2), 23.0 (*C*-5), 21.5 (*C*-7'), 18.2 (*C*-14), 17.0 (*C*-10), 16.0 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_4\text{S}([\text{M} + \text{H}]^+)$, 417.1843; found, 417.1845.

20. **8a**: (4*aS*,5*S*,5*aR*)-5-(3-(2-(2-hydroxyethyl)hydrazono)butyl)-5*a*-methyl-3-methyleneoctahydro-2*H*-cyclopropa[*f*]benzofuran-2-one



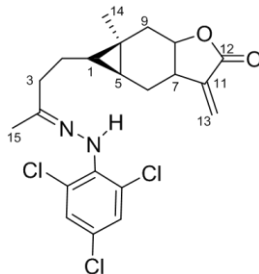
Milky-white ropy liquid; ^1H NMR (500 MHz, CDCl_3) δ : 6.24 (d, $J = 2.6$ Hz, 1H, *H*-13 α), 5.5(d, $J = 2.6$ Hz, 1H, *H*-13 β), 4.74–4.81 (m, 1H, *H*-8), 3.82 (t, $J = 4.6$ Hz, 2H, *H*-2'), 3.72 (s, 1H, -OH), 3.27 (t, $J = 4.6$ Hz, 2H, *H*-1'), 3.13–3.19 (m, 1H, *H*-7), 2.40 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.24–2.30 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 2.17 (s, 3H, *H*-15), 1.48–1.63 (m, 2H, *H*-2), 1.09 (s, 3H, *H*-14), 0.86–0.98 (m, 2H, overlapped, *H*_{eq}-6, *H*_{eq}-9), 0.28–0.46 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.4 (*C*-12), 150.0 (*C*-4), 139.1 (*C*-11), 122.5 (*C*-13), 75.6 (*C*-8), 63.7 (*C*-2'), 51.9 (*C*-1'), 38.8 (*C*-3), 37.7 (*C*-7), 37.3 (*C*-9), 34.3 (*C*-1), 30.7 (*C*-6), 23.4 (*C*-2), 23.0 (*C*-5), 18.2 (*C*-14), 17.2 (*C*-10), 14.5 (*C*-15); HR-MS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{O}_3([\text{M} + \text{H}]^+)$, 307.1940; found, 307.1938.

21. **8b**: (4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-5-(3-(2-phenylhydrazono)butyl)octahydro-2*H*-cyclopropa[*ff*]benzofuran-2-one



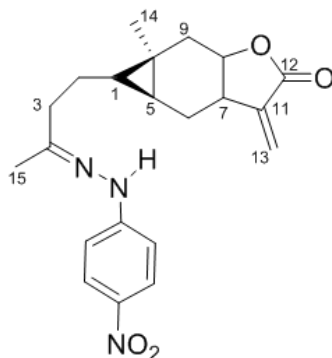
Yellow solid, mp: 41–42 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 7.35–7.47 (m, 6H, Ar-H, –NH), 6.22 (d, $J = 2.5$ Hz, 1H, *H*-13 α), 5.54 (d, $J = 2.5$ Hz, 1H, *H*-13 β), 4.75–4.77 (m, 1H, *H*-8), 3.09–3.17 (m, 1H, *H*-7), 2.44 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.25–2.31 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 1.55 (s, 3H, *H*-15), 1.22–1.45 (m, 2H, *H*-2), 1.06 (s, 3H, *H*-14), 0.88–0.96 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 0.33–0.47 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.7 (C-12), 151.0 (C-4), 139.1 (C-11), 131.4 (C-1'), 129.2 (C-3', C-5'), 122.6 (C-13), 122.5 (C-2', C-6'), 104.9 (C-4'), 75.8 (C-8), 38.5 (C-3), 37.7 (C-7), 37.3 (C-9), 34.2 (C-1), 30.8 (C-6), 26.3 (C-2), 22.9 (C-5), 18.2 (C-14), 17.2 (C-10), 15.7 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_2$ ($[\text{M} + \text{H}]^+$), 339.2067; found, 339.2068.

22. **8c**: (4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-5-(3-(2-(2,4,6-trichlorophenyl)hydrazono)butyl)octahydro-2*H*-cyclopropa[*ff*]benzofuran-2-one



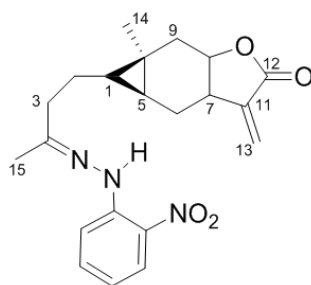
Light yellow solid, mp: 72–73 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 9.21 (s, 1H, NH), 7.42 (s, 2H, *H*-3', *H*-5'), 6.23 (d, $J = 2.6$ Hz, 1H, *H*-13 α), 5.55 (d, $J = 2.6$ Hz, 1H, *H*-13 β), 4.76–4.81 (m, 1H, *H*-8), 3.13–3.19 (m, 1H, *H*-7), 2.46 (t, $J = 7.6$ Hz, 2H, *H*-3), 2.25–2.31 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 1.62 (s, 3H, *H*-15), 1.41–1.68 (m, 2H, *H*-2), 1.10 (s, 3H, *H*-14), 0.87–1.00 (m, 2H, overlapped, $\text{H}_{\text{eq}}\text{-6}$, $\text{H}_{\text{eq}}\text{-9}$), 0.36–0.52 (m, 2H, *H*-1, *H*-5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.6 (C-12), 153.3 (C-4), 145.5 (C-1'), 139.1 (C-11), 128.7 (C-2', C-3', C-5', C-6'), 127.0 (C-4'), 122.5 (C-13), 75.7 (C-8), 38.6 (C-3), 37.8 (C-7), 37.4 (C-9), 34.5 (C-1), 30.8 (C-6), 26.1 (C-2), 23.0 (C-5), 18.3 (C-14), 17.2 (C-10), 15.1 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{Cl}_3\text{N}_2\text{O}_2$ ($[\text{M} + \text{H}]^+$), 441.0898; found, 441.0896.

23. **8d**: (4a*S*,5*S*,5a*R*)-5a-methyl-3-methylene-5-(3-(2-(4-nitrophenyl)hydrazono)butyl)octahydro-2H-cyclopropa[*ff*]benzofuran-2-one



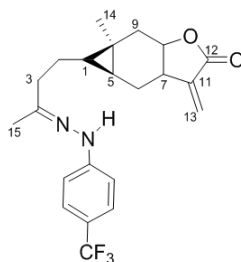
Yellow solid, mp: 93–94 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 8.12 (d, $J = 8.4$ Hz, 2H, $H\text{-}3'$, $H\text{-}5'$), 7.74 (s, 1H, NH), 7.06 (d, $J = 8.4$ Hz, 2H, $H\text{-}2'$, $H\text{-}6'$), 6.21 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\alpha$), 5.54 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\beta$), 4.78–4.80 (m, 1H, $H\text{-}8$), 3.16–3.18 (m, 1H, $H\text{-}7$), 2.42 (t, $J = 7.6$ Hz, 2H, $H\text{-}3$), 2.26–2.35 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 1.93 (s, 3H, $H\text{-}15$), 1.56–1.69 (m, 2H, $H\text{-}2$), 1.11 (s, 3H, $H\text{-}14$), 0.92–1.03 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.48–0.52 (m, 1H, $H\text{-}1$), 0.39–0.43 (m, 1H, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.7 (C-12), 150.7 (C-4), 150.5 (C-4'), 139.6 (C-1'), 139.1 (C-11), 126.1 (C-2', C-6'), 122.7 (C-13), 111.6 (C-3', C-5'), 75.8 (C-8), 38.9 (C-3), 37.6 (C-7), 37.3 (C-9), 34.3 (C-1), 30.7 (C-6), 26.0 (C-2), 23.0 (C-5), 18.4 (C-14), 17.2 (C-10), 15.0 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{26}\text{N}_3\text{O}_4$ ($[\text{M} + \text{H}]^+$), 384.1918; found, 384.1917.

24. **8e**: (4a*S*,5*S*,5a*R*)-5a-methyl-3-methylene-5-(3-(2-(2-nitrophenyl)hydrazono)butyl)octahydro-2H-cyclopropa[*ff*]benzofuran-2-one



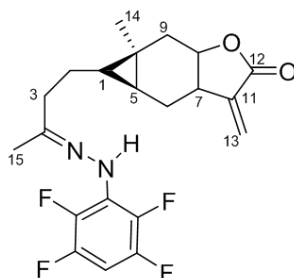
Red solid, mp: 89–90 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 10.67 (s, 1H, NH), 8.15 (d, $J = 8.7$ Hz, 1H, $H\text{-}3'$), 7.51–7.75 (m, 2H, $H\text{-}4'$, $H\text{-}5'$), 7.49 (t, $J = 7.8$, 7.8 Hz, 1H, $H\text{-}4'$), 6.77 (d, $J = 8.0$ Hz, 1H, $H\text{-}6'$), 6.22 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\alpha$), 5.52 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\beta$), 4.76–4.79 (m, 1H, $H\text{-}8$), 3.15–3.17 (m, 1H, $H\text{-}7$), 2.48 (t, $J = 7.7$, 7.7 Hz, 2H, $H\text{-}3$), 2.28–2.38 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 2.01 (s, 3H, $H\text{-}15$), 1.52–1.78 (m, 2H, $H\text{-}2$), 1.12 (s, 3H, $H\text{-}14$), 0.92–1.01 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.50–0.55 (m, 1H, $H\text{-}1$), 0.37–0.42 (m, 1H, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.5 (C-12), 152.8 (C-4), 142.6 (C-2'), 139.1 (C-11), 136.2 (C-1'), 130.7 (C-5'), 125.9 (C-3'), 122.5 (C-13), 117.5 (C-4'), 115.8 (C-6'), 75.6 (C-8), 39.0 (C-3), 37.7 (C-7), 37.4 (C-9), 34.6 (C-1), 30.8 (C-6), 26.1 (C-2), 23.0 (C-5), 18.4 (C-14), 17.2 (C-10), 15.8 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{26}\text{N}_3\text{O}_4$ ($[\text{M} + \text{H}]^+$), 384.1918; found, 384.1917.

25. **8f**: (4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-5-(3-(2-(4-(trifluoromethyl)phenyl)hydrazono)butyl)octahydro-2*H*-cyclopropa[*ff*]benzofuran-2-one



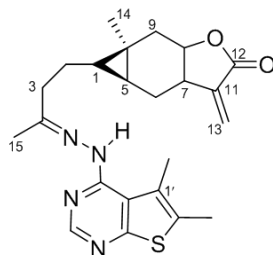
Brown solid, mp: 67–68 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 7.42 (d, $J = 8.3$ Hz, 2H, $H\text{-}2'$, $H\text{-}6'$), 7.09 (d, $J = 8.3$ Hz, 2H, $H\text{-}3'$, $H\text{-}5'$), 6.18 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\alpha$), 5.49 (d, $J = 2.6$ Hz, 1H, $H\text{-}13\beta$), 4.74–4.76 (m, 1H, $H\text{-}8$), 3.11–3.13 (m, 1H, $H\text{-}7$), 2.39 (t, $J = 7.6$ Hz, 2H, $H\text{-}3$), 2.23–2.31 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 1.86 (s, 3H, $H\text{-}15$), 1.51–1.67 (m, 2H, $H\text{-}2$), 1.08 (s, 3H, $H\text{-}14$), 0.86–0.98 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.45–0.50 (m, 1H, $H\text{-}1$), 0.34–0.39 (m, 1H, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.7 (C-12), 153.0 (C-4), 148.6 (C-1'), 148.1 (C-7'), 139.2 (C-11), 126.4 (C-3', C-5'), 122.8 (C-4'), 122.5 (C-13), 112.2 (C-2', C-6'), 75.9 (C-8), 38.8 (C-3), 37.6 (C-7), 37.3 (C-9), 34.5 (C-1), 30.8 (C-6), 26.1 (C-2), 22.9 (C-5), 18.2 (C-14), 17.1 (C-10), 14.8 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_2$ ($[\text{M} + \text{H}]^+$), 407.1941; found, 407.1932.

26. **8g**: (4*aS*,5*S*,5*aR*)-5*a*-methyl-3-methylene-5-(3-(2-(2,3,5,6-tetrafluorophenyl)hydrazono)butyl)octahydro-2*H*-cyclopropa[*ff*]benzofuran-2-one



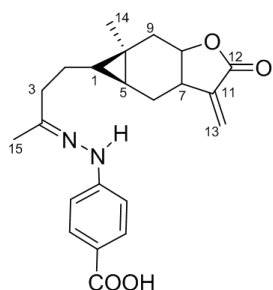
Brown ropy liquid; ^1H NMR (500 MHz, CDCl_3) δ : 6.78 (s, 1H, Ar-H), 6.20 (d, $J = 2.5$ Hz, 1H, $H\text{-}13\alpha$), 5.55 (d, $J = 2.5$ Hz, 1H, $H\text{-}13\beta$), 4.76–4.81 (m, 1H, $H\text{-}8$), 3.16–3.20 (m, 1H, $H\text{-}7$), 2.46 (t, $J = 7.6$ Hz, 2H, $H\text{-}3$), 2.26–2.33 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 1.94 (s, 3H, $H\text{-}15$), 1.49–1.69 (m, 2H, $H\text{-}2$), 1.10 (s, 3H, $H\text{-}14$), 0.88–1.00 (m, 2H, overlapped, $H_{\text{eq}}\text{-}6$, $H_{\text{eq}}\text{-}9$), 0.45–0.54 (m, 1H, $H\text{-}1$), 0.36–0.42 (m, 1H, $H\text{-}5$); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.6 (C-12), 153.9 (C-4), 147.4 (C-3', C-5'), 145.4 (C-2', C-6'), 139.2 (C-11), 126.7 (C-1'), 122.3 (C-13), 96.3 (C-4'), 75.7 (C-8), 38.5 (C-3), 37.6 (C-7), 37.2 (C-9), 34.4 (C-1), 30.7 (C-6), 25.9 (C-2), 22.9 (C-5), 18.0 (C-14), 17.1 (C-10), 14.7 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{F}_4\text{N}_2\text{O}_2$ ($[\text{M} + \text{H}]^+$), 411.1690; found, 411.1689.

27. **8h**: (4a*S*,5*S*,5a*R*)-5-(3-(2-(5,6-dimethylthieno[2,3-*d*]pyrimidin-4-yl)hydrazono)butyl)-5a-methyl-3-methyleneoctahydro-2*H*-cyclopropa[*f*]benzofuran-2-one



Light yellow solid, mp: 82–83 °C ; ^1H NMR (500 MHz, CDCl_3) δ : 8.42 (s, 1H, Ar-H), 6.21 (d, $J = 2.5$ Hz, 1H, H -13 α), 5.53 (d, $J = 2.5$ Hz, 1H, H -13 β), 4.76–4.81 (m, 1H, H -8), 3.12–3.18 (m, 1H, H -7), 2.51 (s, 3H, H -10'), 2.44 (t, $J = 7.6$ Hz, 2H, H -3), 2.40 (s, 3H, H -11'), 2.28–2.32 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 2.07 (s, 3H, H -15), 1.52–1.72 (m, 2H, H -2), 1.09 (s, 3H, H -14), 0.93–1.03 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.46–0.51 (m, 1H, H -1), 0.36–0.41 (m, 1H, H -5); ^{13}C NMR (125 MHz, CDCl_3) δ : 170.4 (C-12), 165.0 (C-1'), 157.4 (C-3'), 152.3 (C-4), 139.1 (C-11), 130.9 (C-8'), 130.8 (C-5'), 123.4 (C-7'), 122.5 (C-13), 116.8 (C-9'), 75.6 (C-8), 39.0 (C-3), 37.6 (C-7), 37.2 (C-9), 34.4 (C-1), 30.7 (C-6), 26.6 (C-2), 23.0 (C-5), 18.4 (C-14), 17.2 (C-10), 15.5 (C-15), 14.2 (C-11'), 13.2 (C-10'); HR-MS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{29}\text{N}_4\text{O}_2\text{S}([\text{M} + \text{H}]^+)$, 425.2006; found, 425.2004.

28. **8i**: 4-(2-(4-((4a*S*,5*S*,5a*R*)-5a-methyl-3-methylene-2-oxooctahydro-2*H*-cyclopropa[*f*]benzofuran-5-yl)butan-2-ylidene)hydrazinyl)benzoic acid



Brown solid, mp: 70–71 °C ; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$) δ : 10.86 (s, 1H, $-\text{COOH}$), 8.20 (d, $J = 8.1$ Hz, 2H, H -2', H -6'), 7.85 (d, $J = 8.1$ Hz, 2H, H -3', H -5'), 6.07 (d, $J = 2.6$ Hz, 1H, H -13 α), 5.61 (d, $J = 2.6$ Hz, 1H, H -13 β), 4.80–4.86 (m, 1H, H -8), 3.20–3.27 (m, 1H, H -7), 2.40 (t, $J = 7.6$ Hz, 2H, H -3), 2.24–2.33 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 1.51–1.59 (m, 2H, H -2), 1.46 (s, 3H, H -15), 1.10 (s, 3H, H -14), 0.89–1.03 (m, 2H, overlapped, H_{eq} -6, H_{eq} -9), 0.52–0.58 (m, 1H, H -1), 0.40–0.45 (m, 1H, H -5); ^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{CO}$) δ : 170.7 (C-12), 150.7 (C-1'), 150.5 (C-4), 139.6 (C-4'), 139.1 (C-11), 126.1 (C-3', C-5'), 122.7 (C-13), 111.6 (C-2', C-6'), 75.8 (C-8), 38.9 (C-3), 37.6 (C-7), 37.3 (C-9), 34.3 (C-1), 30.7 (C-6), 26.0 (C-2), 23.0 (C-5), 18.4 (C-14), 17.2 (C-10), 15.0 (C-15); HR-MS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_4([\text{M} + \text{H}]^+)$, 383.1965; found, 383.1966.