Supporting Information

Semisynthesis of platensimycin derivatives with antibiotic activities in mice *via* Suzuki-Miyaura cross-coupling reactions

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Characterization Data of 3a – 3t, 6a – 6t

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-phenyl-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3a)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (s, 1H), 4.48 – 4.40 (m, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.50 (s, 1H), 2.46 (t, *J* = 6.5 Hz, 1H), 2.40 – 2.35 (m, 1H), 2.34 (dd, *J* = 5.4, 3.2 Hz, 1H), 2.13 (dd, *J* = 12.2, 3.5 Hz, 2H), 2.05 (d, *J* = 11.5 Hz, 1H), 1.94 (dd, *J* = 11.1, 3.4 Hz, 1H), 1.82 (dt, *J* = 13.3, 4.7 Hz, 2H), 1.73 – 1.68 (m, 2H), 1.48 (s, 3H), 1.35 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.56, 173.41, 150.72, 137.57, 136.67, 128.72, 127.99, 127.73, 87.08, 76.59, 60.37, 55.16, 46.56, 45.94, 45.92, 44.67, 43.49, 40.60, 31.04, 29.29, 24.17, 23.09, 14.22.
MS (ESI) *m/z* calcd for $C_{25}H_{31}O_4$, $[M+H]^+$ 395.22; Found: 395.23.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-(2-methoxyphenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 6.2 Hz, 1H), 7.06 (d, *J* = 5.9 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.86 (d, *J* = 6.6 Hz, 1H), 6.37 (s, 1H), 4.45 (s, 1H), 4.16 – 4.03 (m, 2H), 3.72 (s, 3H), 2.48 (s, 1H), 2.43 (t, *J* = 4.9 Hz, 1H), 2.37 (q, *J* = 10.0, 7.3 Hz, 2H), 2.32 – 2.23 (m, 1H), 2.12 (d, *J* = 9.4 Hz, 2H), 2.06 (d, *J* = 9.2 Hz, 1H), 1.94 (d, *J* = 8.9 Hz, 1H), 1.84 – 1.75 (m, 2H), 1.64 (d, *J* = 8.8 Hz, 1H), 1.47 (s, 3H), 1.37 (s, 3H), 1.23 (t, *J* = 5.7 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 200.98, 173.66, 164.50, 156.95, 149.84, 136.84, 130.32, 129.28, 120.60, 110.84, 87.09, 76.71, 60.27, 55.50, 55.45, 54.96, 46.52, 46.28, 45.95, 44.69, 43.59, 40.61, 31.29, 29.24, 23.97, 23.09, 14.23.
MS (ESI) *m/z* calcd for $C_{26}H_{33}O_5$, $[M+H]^+$ 425.23; Found: 425.33.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-(3,5-dichlorophenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 1.9 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 2H), 6.54 (s, 1H), 4.40 (s, 1H), 4.10 (qd, *J* = 7.2, 1.5 Hz, 2H), 2.44 (d, *J* = 6.6 Hz, 2H), 2.37 – 2.20 (m, 3H), 2.09 (dd, *J* = 11.9, 3.6 Hz, 2H), 2.01 (d, *J* = 11.6 Hz, 1H), 1.91 (dd, *J* = 11.1, 3.5 Hz, 1H), 1.82 (dd, *J* = 6.9, 5.0 Hz, 1H), 1.78 (dt, *J* = 4.1, 2.0 Hz, 1H), 1.67 (d, *J* = 11.0 Hz, 1H), 1.45 (s, 3H), 1.30 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.77, 173.20, 152.27, 139.44, 135.38, 134.38, 127.62, 127.29, 87.11, 76.41, 60.43, 55.06, 46.59, 45.99, 45.74, 44.61, 43.38, 40.54, 30.94, 29.26, 24.12, 23.02, 14.21.
MS (ESI) *m/z* calcd for $C_{25}H_{29}Cl_2O_4$, $[M+K]^+$ 463.14; Found: 463.14.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-(3,5-dimethylphenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.89 (s, 2H), 6.48 (s, 1H), 4.43 (s, 1H), 4.11 (qd, *J* = 7.1, 1.2 Hz, 2H), 2.47 (s, 1H), 2.44 (t, *J* = 6.4 Hz, 1H), 2.33 (d, *J* = 6.3 Hz, 8H), 2.11 (dd, *J* = 11.8, 3.8 Hz, 2H), 2.04 (d, *J* = 11.6 Hz, 1H), 1.92 (dd, *J* = 11.1, 3.5 Hz, 1H), 1.86 – 1.74 (m, 2H), 1.67 (d, *J* = 11.1 Hz, 1H), 1.47 (s, 3H), 1.34 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.68, 173.38, 150.40, 137.74, 137.44, 136.60, 129.40, 126.51, 87.05, 76.58, 60.32, 55.16, 46.55, 45.93, 45.91, 44.67, 43.46, 40.60, 31.02, 29.28, 24.15, 23.10, 21.30, 14.23.
MS (ESI) *m/z* calcd for $C_{27}H_{34}KO_4$, $[M+K]^+$ 461.21; Found: 461.66.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(o-tolyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3e)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.05 – 6.96 (m, 1H), 6.39 (s, 1H), 4.45 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.52 (s, 1H), 2.45 (t, *J* = 6.3 Hz, 1H), 2.32 (dt, *J* = 36.5, 12.0 Hz, 3H), 2.13 (d, *J* = 17.4 Hz, 5H), 2.06 (d, *J* = 11.5 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.87 – 1.73 (m, 2H), 1.65 (d, *J* = 11.0 Hz, 1H), 1.47 (s, 3H), 1.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.19, 173.36, 151.53, 138.71, 136.92, 136.20, 129.81, 129.71, 127.85, 125.57, 87.05, 60.35, 55.18, 46.62, 46.22, 45.84, 44.67, 43.32, 40.64, 30.91, 29.30, 24.42, 23.08, 20.04, 14.22.

MS (ESI) *m/z* calcd for $C_{26}H_{32}KO_4$, $[M+K]^+$ 447.19; Found: 447.44.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(m-tolyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.50 (s, 1H), 4.43 (s, 1H), 4.11 (qd, *J* = 7.2, 1.2 Hz, 2H), 2.48 (s, 1H), 2.44 (t, *J* = 6.5 Hz, 1H), 2.41 – 2.32 (m, 5H), 2.31 – 2.26 (m, 1H), 2.11 (dd, *J* = 12.0, 3.6 Hz, 2H), 2.04 (d, *J* = 11.6 Hz, 1H), 2.00 – 1.89 (m, 1H), 1.86 – 1.73 (m, 2H), 1.67 (d, *J* = 11.0 Hz, 1H), 1.47 (s, 3H), 1.34 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.62, 173.38, 150.57, 137.65, 137.50, 136.62, 129.40, 128.48, 127.91, 125.80, 87.06, 76.57, 60.34, 55.15, 46.55, 45.92, 44.66, 43.46, 40.60, 31.03, 29.29, 24.16, 23.10, 21.42, 14.23.
MS (ESI) *m/z* calcd for $C_{26}H_{32}KO_4$, $[M+K]^+$ 447.19; Found: 447.44.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(p-tolyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3g)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 7.5, 5.6 Hz, 4H), 6.48 (s, 1H), 4.42 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 1H), 2.43 (t, *J* = 6.6 Hz, 1H), 2.40 – 2.25 (m, 6H), 2.16 – 2.07 (m, 2H), 2.03 (d, *J* = 11.6 Hz, 1H), 1.99 – 1.88 (m, 1H), 1.85 – 1.73 (m, 2H), 1.67 (d, *J* = 10.9 Hz, 1H), 1.47 (d, *J* = 1.9 Hz, 3H), 1.33 (s, 3H), 1.27 (s, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 201.62, 173.38, 150.12, 137.47, 133.76, 128.67, 128.58, 87.04, 60.32, 55.16, 46.54, 45.94, 45.91, 44.67, 43.47, 40.60, 31.07, 29.30, 24.15, 23.09, 21.17, 14.22.
MS (ESI) *m/z* calcd for $C_{26}H_{32}KO_4$, $[M+K]^+$ 447.19; Found: 447.44.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-([1,1'-biphenyl]-2-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.23 (m, 6H), 7.19 (ddd, *J* = 8.5, 6.9, 1.8 Hz, 3H), 6.26 (s, 1H), 4.33 (t, *J* = 3.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.36 (t, *J* = 6.4 Hz, 1H), 2.29 (s, 1H), 2.21 – 2.09 (m, 2H), 2.09 – 2.00 (m, 1H), 1.99 – 1.85 (m, 3H), 1.71 (dd, *J* = 11.1, 3.5 Hz, 1H), 1.65 – 1.57 (m, 2H), 1.47 (d, *J* = 11.1 Hz, 1H), 1.42 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.01 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.83, 173.37, 152.71, 141.84, 141.79, 138.23, 135.82, 130.13, 129.59, 129.46, 127.81, 127.77, 126.96, 126.73, 86.89, 76.47, 60.25, 54.89, 46.35, 45.84, 45.62, 44.55, 42.85, 40.50, 30.93, 29.04, 24.08, 23.05, 14.24.
MS (ESI) *m/z* calcd for $C_{31}H_{34}NaO_4$, $[M+Na]^+$ 493.24; Found: 493.22.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-([1,1'-biphenyl]-3-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.57 – 7.49 (m, 2H), 7.49 – 7.40 (m, 3H), 7.40 – 7.33 (m, 1H), 7.28 (dt, *J* = 7.7, 1.4 Hz, 1H), 6.59 (s, 1H), 4.46 (s, 1H), 4.13 (qd, *J* = 7.1, 1.3 Hz, 2H), 2.53 (s, 1H), 2.46 (t, *J* = 6.4 Hz, 1H), 2.43 – 2.30 (m, 3H), 2.14 (dd, *J* = 11.9, 3.6 Hz, 2H), 2.06 (d, *J* = 11.5 Hz, 1H), 1.96 (dd, *J* = 11.0, 3.6 Hz, 1H), 1.83 (ddt, *J* = 11.0, 6.0, 2.7 Hz, 2H), 1.70 (d, *J* = 11.1 Hz, 1H), 1.49 (s, 3H), 1.37 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.56, 173.37, 151.02, 141.14, 141.12, 137.51, 137.15, 128.73, 128.41, 127.74, 127.72, 127.32, 127.30, 126.62, 87.09, 76.58, 60.39, 55.18, 46.62, 46.00, 45.94, 44.68, 43.49, 40.62, 31.06, 29.33, 24.23, 23.12, 14.26.
MS (ESI) *m/z* calcd for $C_{31}H_{34}NaO_4$, $[M+Na]^+$ 493.24; Found: 493.22.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-([1,1'-biphenyl]-4-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 7.8 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 7.9, 6.3 Hz, 3H), 6.58 (s, 1H), 4.46 (s, 1H), 4.14 (qd, *J* = 7.2, 1.3 Hz, 2H), 2.52 (s, 1H), 2.45 (t, *J* = 6.4 Hz, 1H), 2.42 – 2.31 (m, 3H), 2.13 (dd, *J* = 12.0, 3.5 Hz, 2H), 2.05 (d, *J* = 11.6 Hz, 1H), 1.96 (dd, *J* = 11.1, 3.5 Hz, 1H), 1.89 – 1.77 (m, 2H), 1.70 (d, *J* = 11.0 Hz, 1H), 1.49 (s, 3H), 1.37 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.62, 173.37, 150.73, 140.80, 140.63, 137.11, 135.66, 129.18, 128.79, 127.36, 127.10, 126.76, 87.09, 76.58, 60.38, 55.17, 46.62, 46.00, 45.94, 44.69, 43.49, 40.62, 31.09, 29.34, 24.20, 23.12, 14.26.
MS (ESI) *m/z* calcd for $C_{31}H_{34}NaO_4$, $[M+Na]^+$ 493.24; Found: 493.22.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-(3-hydroxyphenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3k)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 7.01 (s, 1H), 6.82 – 6.71 (m, 3H), 6.50 (s, 1H), 4.44 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 1H), 2.50 – 2.41 (m, 2H), 2.30 (dt, *J* = 24.6, 11.9 Hz, 3H), 2.10 (t, *J* = 11.7 Hz, 2H), 2.02 (d, *J* = 11.6 Hz, 1H), 1.93 (d, *J* = 11.1 Hz, 1H), 1.84 – 1.72 (m, 2H), 1.66 (d, *J* = 11.1 Hz, 1H), 1.48 (s, 3H), 1.30 (s, 3H), 1.25 – 1.18 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 201.87, 173.81, 155.89, 150.98, 137.94, 137.35, 129.14, 120.56, 115.89, 114.96, 87.46, 76.66, 60.61, 55.03, 46.61, 45.90, 44.66, 43.39, 40.55, 30.99, 29.68, 29.31, 24.12, 23.01, 14.17.
MS (ESI) *m/z* calcd for $C_{25}H_{30}KO_5$, $[M+K]^+$ 449.17; Found: 449.44.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(3-(trifluoromethyl)phenyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H), 7.45 (dd, *J* = 5.0, 1.9 Hz, 2H), 6.57 (s, 1H), 4.42 (s, 1H), 4.10 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.49 (s, 1H), 2.45 (t, *J* = 6.5 Hz, 1H), 2.40 – 2.23 (m, 3H), 2.12 (dd, *J* = 11.9, 3.9 Hz, 2H), 2.07 – 2.01 (m, 1H), 1.94 (dd, *J* = 10.9, 3.7 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.82 – 1.78 (m, 1H), 1.69 (d, *J* = 11.1 Hz, 1H), 1.46 (s, 3H), 1.33 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 201.14, 173.22, 151.90, 137.37, 136.42, 132.25, 128.33, 125.51, 125.48, 124.40, 124.37, 87.10, 76.47, 60.39, 55.11, 46.57, 46.00, 45.84, 44.64, 43.40, 40.55, 30.98, 29.28, 24.16, 23.01, 14.17.
MS (ESI) *m/z* calcd for $C_{26}H_{29}F_3NaO_4$, $[M+Na]^+$ 485.19; Found: 485.36.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(3-(trifluoromethoxy)phenyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.1 Hz, 2H), 6.54 (s, 1H), 4.42 (s, 1H), 4.10 (qd, *J* = 7.2, 1.3 Hz, 2H), 2.47 (d, *J* = 4.8 Hz, 1H), 2.44 (d, *J* = 6.4 Hz, 1H), 2.39 – 2.23 (m, 3H), 2.11 (dd, *J* = 12.0, 3.5 Hz, 2H), 2.06 – 2.00 (m, 1H), 1.93 (dd, *J* = 11.1, 3.6 Hz, 1H), 1.87 – 1.81 (m, 1H), 1.80 (td, *J* = 3.8, 2.2 Hz, 1H), 1.68 (d, *J* = 11.1 Hz, 1H), 1.46 (s, 3H), 1.32 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 201.07, 173.24, 151.72, 148.89, 148.87, 138.60, 136.24, 129.18, 127.24, 121.51, 120.04, 119.44, 87.09, 76.48, 60.38, 55.10, 46.58, 45.97, 45.82, 44.63, 43.40, 40.55, 30.99, 29.27, 24.12, 23.00, 14.16.
MS (ESI) *m/z* calcd for $C_{26}H_{30}F_3O_5$, $[M+H]^+$ 479.20; Found: 479.16.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(4-pentylphenyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (q, *J* = 8.1 Hz, 4H), 6.49 (s, 1H), 4.42 (t, *J* = 3.3 Hz, 1H), 4.18 – 4.04 (m, 2H), 2.65 – 2.56 (m, 2H), 2.47 (s, 1H), 2.43 (t, *J* = 6.4 Hz, 1H), 2.39 – 2.25 (m, 3H), 2.10 (dd, *J* = 11.8, 4.0 Hz, 2H), 2.03 (d, *J* = 11.6 Hz, 1H), 1.92 (dd, *J* = 11.1, 3.5 Hz, 1H), 1.80 (ddd, *J* = 13.5, 9.1, 7.0 Hz, 2H), 1.67 (d, *J* = 11.1 Hz, 1H), 1.61 (dd, *J* = 10.6, 4.5 Hz, 2H), 1.46 (s, 3H), 1.31 (d, *J* = 6.4 Hz, 8H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.68, 173.38, 150.19, 142.53, 137.37, 133.92, 128.55, 128.05, 87.04, 76.58, 60.32, 55.16, 46.54, 45.92, 44.66, 43.48, 40.60, 35.63, 31.47, 31.14, 31.05, 29.29, 24.16, 23.10, 22.55, 14.22, 14.06.
MS (ESI) *m/z* calcd for $C_{30}H_{40}NaO_4$, $[M+Na]^+$ 487.28; Found: 487.57.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-(4-formylphenyl)-4,8-dimethyl-3-oxo-

3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.59 (s, 1H), 4.40 (s, 1H), 4.19 – 3.99 (m, 2H), 2.51 – 2.41 (m, 2H), 2.38 – 2.21 (m, 3H), 2.11 (dd, *J* = 11.9, 3.6 Hz, 2H), 2.02 (d, *J* = 11.6 Hz, 1H), 1.92 (dd, *J* = 11.0, 3.4 Hz, 1H), 1.88 – 1.72 (m, 2H), 1.68 (d, *J* = 11.1 Hz, 1H), 1.44 (s, 3H), 1.31 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.07, 191.89, 173.20, 152.33, 142.89, 136.65, 135.45, 129.44, 129.31, 87.10, 76.44, 60.38, 55.09, 46.59, 46.05, 45.79, 44.61, 43.42, 40.55, 30.95, 29.26, 24.11, 23.03, 14.19.
MS (ESI) *m/z* calcd for $C_{26}H_{30}NaO_5$, $[M+Na]^+$ 445.20; Found: 445.44.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-(4-bromophenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3p)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.15 (d, *J* = 6.7 Hz, 2H), 6.52 (s, 1H), 4.44 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.47 (d, *J* = 10.8 Hz, 2H), 2.41 – 2.24 (m, 3H), 2.11 (d, *J* = 9.1 Hz, 2H), 2.04 (d, *J* = 11.6 Hz, 1H), 1.94 (d, *J* = 10.4 Hz, 1H), 1.88 – 1.78 (m, 2H), 1.68 (d, *J* = 11.0 Hz, 1H), 1.48 (s, 3H), 1.32 (s, 4H), 1.25 (dd, *J* = 7.1, 1.6 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 201.33, 173.45, 151.11, 136.58, 135.49, 131.09, 130.42, 121.91, 87.16, 76.53, 60.48, 55.12, 46.59, 45.96, 45.83, 44.66, 43.44, 40.56, 31.04, 29.31, 24.17, 23.05, 14.20.
MS (ESI) *m/z* calcd for $C_{25}H_{29}BrNaO_4$, $[M+Na]^+$ 495.11; Found: 495.16.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-2-(naphthalen-2-yl)-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 3H), 7.79 – 7.76 (m, 1H), 7.53 – 7.44 (m, 2H), 7.40 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.62 (s, 1H), 4.45 (s, 1H), 4.13 (qd, *J* = 7.1, 1.7 Hz, 2H), 2.54 (s, 1H), 2.47 – 2.41 (m, 2H), 2.40 – 2.36 (m, 2H), 2.13 (dd, *J* = 12.0, 3.4 Hz, 2H), 2.04 (d, *J* = 11.5 Hz, 1H), 1.97 (dd, *J* = 11.0, 3.6 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.69 (d, *J* = 11.0 Hz, 1H), 1.48 (s, 3H), 1.37 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.74, 173.38, 151.21, 137.53, 134.33, 133.19, 132.82, 128.06, 127.68, 127.56, 127.32, 126.87, 126.07, 126.04, 87.09, 76.59, 60.38, 55.18, 46.64, 46.06, 45.96, 44.68, 43.49, 40.61, 31.07, 29.34, 24.21, 23.11, 14.25.
MS (ESI) *m/z* calcd for $C_{29}H_{32}NaO_4$, $[M+Na]^+$ 467.22; Found: 467.45.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-2-(6-ethoxynaphthalen-2-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 3H), 7.35 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.19 – 7.07 (m, 2H), 6.58 (s, 1H), 4.44 (s, 1H), 4.13 (tdd, *J* = 7.0, 4.2, 2.5 Hz, 4H), 2.52 (s, 1H), 2.42 (dd, *J* = 12.4, 6.1 Hz, 2H), 2.37 (dd, *J* = 5.3, 3.4 Hz, 2H), 2.11 (dd, *J* = 12.0, 3.5 Hz, 2H), 2.06 – 1.98 (m, 1H), 1.95 (dd, *J* = 11.0, 3.5 Hz, 1H), 1.87 – 1.76 (m, 2H), 1.68 (d, *J* = 11.0 Hz, 1H), 1.50 – 1.43 (m, 6H), 1.36 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.86, 173.39, 157.15, 150.65, 137.48, 134.07, 131.93, 129.52, 128.58, 127.47, 127.27, 126.17, 119.14, 106.29, 87.07, 76.59, 63.41, 60.35, 55.18, 46.62, 46.03, 45.96, 44.67, 43.49, 40.61, 31.09, 29.33, 24.20, 23.11, 14.83, 14.24.
MS (ESI) *m/z* calcd for $C_{31}H_{36}NaO_5$, $[M+Na]^+$ 511.25; Found: 511.35.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(phenanthren-9-yl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 16.3, 8.2 Hz, 2H), 7.93 – 7.82 (m, 1H), 7.75 – 7.45 (m, 6H), 6.66 (s, 1H), 4.53 (s, 1H), 4.22 – 4.03 (m, 2H), 2.69 (s, 1H), 2.51 (t, *J* = 6.3 Hz, 1H), 2.44 – 2.33 (m, 2H), 2.30 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.18 (t, *J* = 5.2 Hz, 1H), 2.14 (d, *J* = 11.5 Hz, 1H), 2.10 – 2.02 (m, 1H), 1.92 (ddd, *J* = 11.3, 5.5, 3.8 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.73 (d, *J* = 11.1 Hz, 1H), 1.64 (s, 3H), 1.52 (s, 3H), 1.28 (d, *J* = 0.9 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.65, 173.35, 152.79, 134.02, 131.38, 130.38, 130.31, 128.55, 126.73, 126.67, 126.46, 126.39, 125.90, 122.97, 122.53, 87.13, 76.64, 60.39, 55.32, 46.42, 46.11, 44.76, 43.48, 40.70, 30.97, 29.70, 29.38, 24.58, 23.10, 14.21.
MS [M+K], 533.19.
MS (ESI) *m/z* calcd for $C_{33}H_{34}KO_4$, $[M+K]^+$ 533.21; Found: 533.19.

Ethyl 3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(pyren-1-yl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanoate (3t)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.7, 3.9 Hz, 3H), 8.09 – 8.02 (m, 3H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 4.53 (d, *J* = 3.2 Hz, 1H), 4.23 – 4.05 (m, 2H), 2.72 (s, 1H), 2.56 – 2.36 (m, 4H), 2.24 – 2.10 (m, 2H), 2.07 (d, *J* = 3.0 Hz, 1H), 2.03 (d, *J* = 10.9 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.82 – 1.71 (m, 1H), 1.62 (d, *J* = 11.3 Hz, 1H), 1.52 (s, 3H), 1.48 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 201.74, 173.38, 153.57, 132.31, 131.29, 131.01, 130.83, 127.53, 127.49, 127.37, 125.96, 125.26, 125.05, 124.78, 124.77, 124.52, 124.39, 87.12, 76.63, 60.42, 55.20, 46.80, 46.36, 46.12, 44.70, 43.34, 40.66, 31.07, 29.46, 24.52, 23.07, 14.27.
MS [M+K], 557.49.
MS (ESI) *m/z* calcd for $C_{35}H_{34}KO_4$, $[M+K]^+$ 557.21; Found: 557.49.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-phenyl-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 11.17 (s, 1H), 8.09 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.36 (q, *J* = 7.7, 7.0 Hz, 3H), 7.32 – 7.26 (m, 3H), 6.57 (s, 1H), 6.50 (d, *J* = 8.9 Hz, 1H), 4.70 (s, 1H), 2.74 (ddd, *J* = 15.5, 12.7, 4.8 Hz, 1H), 2.64 (s, 1H), 2.57 (dt, *J* = 12.7, 4.9 Hz, 3H), 2.30 – 2.17 (m, 2H), 2.11 (d, *J* = 11.6 Hz, 1H), 2.05 (dd, *J* = 11.4, 3.5 Hz, 1H), 1.97 – 1.84 (m, 2H), 1.76 (d, *J* = 11.3 Hz, 1H), 1.56 (s, 3H), 1.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.97, 173.55, 172.35, 154.95, 154.11, 150.53, 137.78, 136.29, 128.73, 128.18, 128.10, 127.95, 114.26, 111.03, 103.82, 88.31, 76.86, 54.93, 46.73, 46.12, 45.77, 44.77, 43.26, 40.36, 31.22, 29.80, 24.06, 22.70.
HRMS (ESI) *m/z* calcd for $C_{30}H_{32}NO_7$, $[M+H]^+$ 517.2179; Found: 518.2174.

2,4-dihydroxy-3-(3-((4S,4aR,5S,7R,8S,9aS)-2-(2-methoxyphenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)benzoic acid (6b)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.79 (s, 1H), 11.16 (s, 1H), 8.17 (s, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.48 (d, *J* = 8.9 Hz, 1H), 6.43 (s, 1H), 4.69 (s, 1H), 3.73 (s, 3H), 2.74 – 2.62 (m, 2H), 2.60 (s, 1H), 2.55 – 2.42 (m, 2H), 2.21 (dt, *J* = 11.8, 5.1 Hz, 2H), 2.13 (s, 1H), 2.09 – 2.00 (m, 1H), 1.98 – 1.81 (m, 2H), 1.72 (d, *J* = 11.2 Hz, 1H), 1.54 (s, 3H), 1.46 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 202.01, 173.91, 172.41, 156.90, 155.00, 154.23, 150.11, 136.89, 130.39, 129.60, 128.17, 126.53, 120.70, 114.29, 110.96, 110.85, 103.87, 88.15, 76.87, 55.54, 54.75, 46.76, 46.16, 44.78, 43.43, 40.44, 31.71, 31.41, 23.79, 22.76.
HRMS (ESI) *m/z* calcd for $C_{31}H_{34}NO_8$, $[M+H]^+$ 548.2284; Found: 548.2280.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-(3,5-dichlorophenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 11.12 (s, 1H), 8.08 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.31 (s, 1H), 7.19 (d, *J* = 1.9 Hz, 2H), 6.60 (s, 1H), 6.49 (d, *J* = 9.0 Hz, 1H), 4.69 (d, *J* = 3.2 Hz, 1H), 2.82 – 2.68 (m, 1H), 2.63 (s, 1H), 2.60 – 2.46 (m, 3H), 2.21 (dd, *J* = 11.9, 3.9 Hz, 2H), 2.07 (s, 2H), 1.89 (td, *J* = 10.5, 8.9, 5.9 Hz, 2H), 1.77 (d, *J* = 11.4 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.92, 173.34, 172.38, 154.98, 154.08, 151.89, 139.09, 135.65, 134.54, 128.20, 127.87, 127.31, 114.22, 111.07, 103.75, 88.41, 76.78, 60.45, 54.86, 46.79, 46.16, 45.61, 44.75, 43.18, 40.29, 31.09, 24.03, 22.62.
HRMS (ESI) *m/z* calcd for $C_{30}H_{30}Cl_2NO_7$, $[M+H]^+$ 586.1399; Found: 586.1395.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-(3,5-dimethylphenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 11.17 (s, 1H), 8.12 (s, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 6.98 (s, 1H), 6.90 (d, *J* = 1.6 Hz, 2H), 6.65 – 6.42 (m, 2H), 4.68 (s, 1H), 2.73 (ddd, *J* = 15.2, 12.5, 4.9 Hz, 1H), 2.62 (s, 1H), 2.60 – 2.47 (m, 3H), 2.33 (s, 6H), 2.20 (dd, *J* = 11.9, 3.7 Hz, 2H), 2.10 – 1.99 (m, 2H), 1.96 – 1.83 (m, 2H), 1.75 (d, *J* = 11.3 Hz, 1H), 1.55 (s, 3H), 1.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.18, 173.66, 172.59, 155.04, 154.18, 150.30, 137.97, 137.62, 136.21, 129.60, 128.19, 126.50, 114.29, 111.07, 103.80, 88.21, 76.85, 54.96, 46.75, 46.08, 45.83, 44.77, 43.28, 40.38, 31.38, 31.33, 29.71, 24.03, 22.73, 21.27.
HRMS (ESI) m/z calcd for $C_{32}H_{36}NO_7$, [M+H]+ 546.2492; Found: 546.2492.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(o-tolyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6e)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.19 (s, 1H), 7.60 – 7.51 (m, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.52 – 6.40 (m, 2H), 4.68 (s, 1H), 2.75 – 2.65 (m, 1H), 2.63 (s, 1H), 2.59 – 2.44 (m, 3H), 2.22 (dt, *J* = 12.1, 6.0 Hz, 2H), 2.12 (s, 3H), 2.09 – 2.00 (m, 2H), 1.90 (ddt, *J* = 17.9, 11.9, 7.3 Hz, 2H), 1.73 (d, *J* = 11.3 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 202.10, 173.79, 172.76, 155.14, 154.32, 151.92, 138.85, 136.43, 136.20, 129.93, 129.85, 128.30, 128.11, 125.71, 114.25, 111.06, 103.82, 88.13, 76.74, 54.98, 46.91, 46.08, 46.00, 44.77, 43.16, 40.44, 31.56, 31.46, 24.32, 22.74, 20.04.
HRMS (ESI) *m/z* calcd for $C_{31}H_{34}NO_7$, $[M+H]^+$ 532.2335; Found: 532.2331.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(m-tolyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6f)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.17 (s, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.55 (s, 1H), 6.49 (d, *J* = 8.9 Hz, 1H), 4.67 (s, 1H), 2.78 – 2.67 (m, 1H), 2.61 (s, 1H), 2.59 – 2.45 (m, 3H), 2.36 (s, 3H), 2.19 (dd, *J* = 12.0, 3.8 Hz, 2H), 2.09 – 2.06 (m, 1H), 2.04 (dd, *J* = 11.3, 3.3 Hz, 1H), 1.97 – 1.83 (m, 2H), 1.75 (d, *J* = 11.3 Hz, 1H), 1.54 (s, 3H), 1.40 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 202.16, 173.79, 172.68, 155.09, 154.27, 150.57, 137.85, 137.66, 136.28, 129.42, 128.68, 128.25, 128.02, 125.81, 114.29, 111.06, 103.83, 88.25, 76.82, 54.93, 46.77, 46.08, 45.78, 44.77, 43.26, 40.37, 31.43, 31.33, 24.02, 22.72, 21.41.
HRMS (ESI) *m/z* calcd for $C_{31}H_{34}NO_7$, $[M+H]^+$ 532.2335; Found: 532.2331.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(p-tolyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6g)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.70 (s, 1H), 8.12 (s, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.17 (s, 4H), 6.54 (s, 1H), 6.50 (d, *J* = 8.6 Hz, 1H), 4.82 – 4.60 (m, 1H), 2.78 – 2.68 (m, 1H), 2.62 (s, 1H), 2.61 – 2.49 (m, 3H), 2.37 (s, 3H), 2.20 (dd, *J* = 12.3, 3.7 Hz, 2H), 2.10 – 2.06 (m, 1H), 2.04 (dd, *J* = 11.3, 3.2 Hz, 1H), 1.87 (dd, *J* = 12.6, 5.6 Hz, 2H), 1.75 (d, *J* = 11.3 Hz, 1H), 1.55 (s, 3H), 1.40 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 202.10, 173.69, 172.55, 155.04, 154.18, 150.02, 137.75, 137.61, 133.40, 128.78, 128.60, 128.20, 114.29, 111.04, 103.80, 88.28, 76.86, 54.93, 46.74, 46.08, 45.78, 44.77, 43.26, 40.36, 31.32, 31.26, 24.05, 22.71, 21.19.
HRMS (ESI) *m/z* calcd for $C_{31}H_{34}NO_7$, $[M+H]^+$ 532.2335; Found: 532.2331.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-([1,1'-biphenyl]-2-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6h)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.88 (s, 1H), 11.13 (s, 1H), 7.96 (s, 1H), 7.60 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.36 (td, *J* = 20.8, 19.5, 7.6 Hz, 6H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 1H), 6.51 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.49 (d, *J* = 2.0 Hz, 1H), 4.56 (d, *J* = 4.1 Hz, 1H), 2.49 (t, *J* = 6.7 Hz, 1H), 2.43 (d, *J* = 10.5 Hz, 2H), 2.22 (t, *J* = 12.3 Hz, 1H), 2.12 (d, *J* = 2.0 Hz, 2H), 2.10 – 2.00 (m, 2H), 1.93 (d, *J* = 10.9 Hz, 1H), 1.78 (dd, *J* = 12.0, 7.0 Hz, 1H), 1.74 – 1.67 (m, 1H), 1.64 (d, *J* = 11.3 Hz, 1H), 1.52 (s, 3H), 1.06 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 200.92, 173.67, 172.70, 155.09, 154.24, 152.49, 141.97, 141.79, 138.85, 135.41, 129.84, 129.66, 129.61, 128.18, 128.09, 127.98, 127.24, 126.70, 114.31, 111.15, 103.78, 88.03, 77.24, 54.88, 46.45, 45.81, 45.62, 44.67, 42.73, 40.25, 31.25, 30.72, 24.26, 22.71.
HRMS (ESI) *m/z* calcd for $C_{36}H_{36}NO_7$, $[M+H]^+$ 594.2492; Found: 594.2490.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-([1,1'-biphenyl]-3-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 11.23 (s, 1H), 8.12 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.49 (s, 1H), 7.44 (t, *J* = 7.4 Hz, 3H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 6.63 (s, 1H), 6.49 (d, *J* = 8.9 Hz, 1H), 4.70 (s, 1H), 2.82 – 2.70 (m, 1H), 2.66 (s, 1H), 2.57 (dd, *J* = 15.0, 8.9 Hz, 3H), 2.27 – 2.17 (m, 2H), 2.15 – 2.09 (m, 2H), 1.90 (dd, *J* = 11.7, 6.7 Hz, 2H), 1.77 (d, *J* = 11.3 Hz, 1H), 1.56 (s, 3H), 1.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.01, 173.60, 172.44, 155.01, 154.15, 150.87, 141.26, 141.00, 137.73, 136.76, 128.73, 128.51, 128.20, 127.72, 127.70, 127.36, 127.27, 126.82, 114.27, 111.04, 103.80, 88.31, 76.85, 60.48, 54.96, 46.79, 46.16, 45.79, 44.78, 43.28, 40.37, 31.27, 24.09, 22.71.
HRMS (ESI) *m/z* calcd for $C_{36}H_{36}NO_7$, $[M+H]^+$ 594.2492; Found: 594.2490.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-([1,1'-biphenyl]-4-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 11.18 (s, 1H), 8.12 (s, 1H), 7.64 – 7.56 (m, 5H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 3H), 6.63 (s, 1H), 6.51 (d, *J* = 8.9 Hz, 1H), 4.69 (s, 1H), 2.80 – 2.69 (m, 1H), 2.66 (s, 1H), 2.57 (dt, *J* = 12.7, 4.8 Hz, 3H), 2.23 (dd, *J* = 12.0, 3.7 Hz, 2H), 2.11 – 2.01 (m, 2H), 1.98 – 1.84 (m, 2H), 1.78 (d, *J* = 11.3 Hz, 1H), 1.56 (s, 3H), 1.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.00, 173.63, 172.71, 155.11, 154.18, 150.50, 140.85, 140.71, 137.35, 135.26, 129.16, 128.78, 128.24, 127.40, 127.11, 126.85, 114.31, 111.13, 103.74, 88.25, 76.85, 54.97, 46.81, 46.16, 45.80, 44.78, 43.31, 40.38, 31.33, 24.06, 22.73, 20.67.
HRMS (ESI) *m/z* calcd for $C_{36}H_{36}NO_7$, $[M+H]^+$ 594.2492; Found: 594.2490.

2,4-dihydroxy-3-(3-((4S,4aR,5S,7R,8S,9aS)-2-(3-hydroxyphenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)benzoic acid (6k)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.61 (s, 1H), 11.03 (s, 1H), 8.20 (s, 1H), 7.51 (d, *J* = 8.9 Hz, 1H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.77 (s, 2H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.53 (s, 1H), 6.44 (d, *J* = 8.9 Hz, 1H), 4.61 (s, 1H), 2.55 (d, *J* = 13.3 Hz, 2H), 2.49 (t, *J* = 6.5 Hz, 1H), 2.46 – 2.31 (m, 2H), 2.14 (s, 1H), 2.04 (q, *J* = 13.1, 12.1 Hz, 2H), 1.83 (d, *J* = 11.0 Hz, 2H), 1.70 (d, *J* = 11.0 Hz, 1H), 1.44 (d, *J* = 10.4 Hz, 1H), 1.31 (s, 3H), 1.28 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 202.44, 174.03, 172.36, 155.68, 154.97, 154.39, 151.05, 137.63, 137.40, 129.31, 128.34, 120.65, 116.05, 115.20, 114.18, 110.88, 103.94, 88.30, 77.24, 54.79, 46.80, 46.02, 45.59, 44.76, 43.18, 40.32, 31.44, 31.21, 23.93, 22.72.
HRMS (ESI) *m/z* calcd for $C_{30}H_{32}NO_8$, $[M+H]^+$ 534.2128; Found: 534.2123.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(3-(trifluoromethyl)phenyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 11.08 (s, 1H), 8.13 (s, 1H), 7.58 (d, *J* = 3.3 Hz, 2H), 7.54 (d, *J* = 4.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 6.63 (s, 1H), 6.48 (d, *J* = 8.9 Hz, 1H), 4.68 (s, 1H), 2.82 – 2.71 (m, 1H), 2.66 (s, 1H), 2.61 – 2.47 (m, 3H), 2.22 (dd, *J* = 11.9, 3.1 Hz, 2H), 2.13 – 2.05 (m, 2H), 1.97 – 1.83 (m, 2H), 1.79 (d, *J* = 11.4 Hz, 1H), 1.56 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.44, 173.52, 172.50, 172.42, 154.96, 154.12, 151.70, 137.04, 136.63, 132.31, 130.29, 128.46, 128.21, 125.51, 124.58, 114.24, 111.01, 103.81, 88.41, 77.26, 54.87, 47.40, 46.75, 46.17, 45.67, 44.75, 43.19, 40.30, 31.09, 24.06, 22.62.
HRMS (ESI) *m/z* calcd for $C_{31}H_{31}F_3NO_7$, $[M+H]^+$ 586.2053; Found: 586.2050.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(3-(trifluoromethoxy)phenyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 11.15 (s, 1H), 8.08 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.27 – 7.13 (m, 3H), 6.60 (s, 1H), 6.50 (d, *J* = 8.9 Hz, 1H), 4.70 (s, 1H), 2.84 – 2.69 (m, 1H), 2.65 (s, 1H), 2.57 (td, *J* = 9.5, 4.8 Hz, 3H), 2.30 – 2.17 (m, 2H), 2.15 – 1.99 (m, 2H), 1.97 – 1.83 (m, 2H), 1.78 (d, *J* = 11.4 Hz, 1H), 1.57 (s, 3H), 1.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.35, 173.40, 172.32, 154.97, 154.08, 151.42, 148.98, 138.20, 136.49, 129.88, 129.34, 128.18, 127.28, 121.54, 120.33, 114.24, 111.07, 103.77, 88.37, 76.81, 54.89, 46.77, 46.16, 45.67, 44.75, 43.21, 40.33, 31.13, 31.07, 24.06, 22.65.
HRMS (ESI) *m/z* calcd for $C_{31}H_{31}F_3NO_8$, $[M+H]^+$ 602.2002; Found: 602.1999.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(4-pentylphenyl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 11.16 (s, 1H), 8.11 (s, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.25 – 7.14 (m, 4H), 6.55 (s, 1H), 6.49 (d, *J* = 8.9 Hz, 1H), 4.70 (s, 1H), 2.74 (ddd, *J* = 15.5, 12.6, 4.8 Hz, 1H), 2.63 (d, *J* = 7.4 Hz, 3H), 2.59 (d, *J* = 5.6 Hz, 1H), 2.55 (dd, *J* = 7.8, 5.0 Hz, 2H), 2.21 (dd, *J* = 12.0, 3.6 Hz, 2H), 2.11 – 1.98 (m, 2H), 1.89 (ddd, *J* = 12.4, 9.4, 4.4 Hz, 2H), 1.76 (d, *J* = 11.4 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.38 – 1.30 (m, 4H), 0.95 – 0.87 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.19, 173.63, 172.37, 154.96, 154.14, 150.05, 142.85, 137.62, 133.54, 128.58, 128.17, 114.27, 111.00, 103.84, 88.34, 76.88, 54.94, 46.74, 46.10, 45.77, 44.78, 43.27, 40.35, 35.64, 31.49, 31.24, 31.14, 29.71, 24.05, 22.69, 22.55, 14.05.
HRMS (ESI) *m/z* calcd for $C_{35}H_{42}NO_7$, $[M+H]^+$ 588.2961; Found: 588.2961.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-(4-formylphenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 10.01 (s, 1H), 8.11 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 6.65 (s, 1H), 6.48 (d, *J* = 9.0 Hz, 1H), 4.67 (s, 1H), 2.81 – 2.68 (m, 1H), 2.64 (s, 1H), 2.54 (dt, *J* = 14.2, 5.3 Hz, 3H), 2.22 (dd, *J* = 12.0, 3.9 Hz, 2H), 2.07 (d, *J* = 6.9 Hz, 2H), 1.96 – 1.82 (m, 2H), 1.78 (d, *J* = 11.4 Hz, 1H), 1.55 (s, 3H), 1.40 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.32, 192.10, 173.53, 172.51, 155.01, 154.16, 152.08, 142.60, 136.88, 135.55, 129.49, 129.45, 128.23, 114.24, 111.06, 103.77, 88.35, 77.26, 54.88, 46.80, 46.22, 45.64, 44.75, 43.24, 40.33, 31.14, 29.70, 24.00, 22.67.
HRMS (ESI) *m/z* calcd for $C_{31}H_{32}NO_8$, $[M+H]^+$ 546.2128; Found: 546.2126.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-(4-bromophenyl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 11.16 (s, 1H), 8.10 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 3H), 7.16 (d, *J* = 8.1 Hz, 3H), 6.56 (s, 1H), 6.49 (d, *J* = 8.9 Hz, 1H), 4.66 (d, *J* = 3.2 Hz, 1H), 2.80 – 2.67 (m, 1H), 2.62 (s, 1H), 2.59 – 2.48 (m, 3H), 2.20 (dd, *J* = 11.8, 4.0 Hz, 2H), 2.09 – 2.01 (m, 2H), 1.87 (td, *J* = 11.6, 10.7, 4.0 Hz, 2H), 1.75 (d, *J* = 11.3 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.52, 173.53, 172.58, 155.05, 154.15, 150.83, 136.74, 135.20, 131.17, 130.43, 128.22, 122.11, 114.27, 111.09, 103.75, 88.27, 76.80, 54.89, 46.75, 46.12, 45.71, 44.75, 43.22, 40.33, 31.21, 29.70, 24.04, 22.68.
HRMS (ESI) *m/z* calcd for $C_{30}H_{31}BrNO_7$, $[M+H]^+$ 596.1284; Found: 596.1267.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-2-(naphthalen-2-yl)-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 11.16 (s, 1H), 8.12 (s, 1H), 7.86 – 7.79 (m, 3H), 7.78 (d, *J* = 1.7 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.38 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.68 (s, 1H), 6.47 (d, *J* = 8.9 Hz, 1H), 4.70 (t, *J* = 3.1 Hz, 1H), 2.77 (ddd, *J* = 15.5, 12.6, 4.8 Hz, 1H), 2.68 (s, 1H), 2.65 – 2.51 (m, 3H), 2.30 – 2.16 (m, 2H), 2.08 (d, *J* = 4.0 Hz, 2H), 1.90 (ddt, *J* = 16.4, 8.7, 4.0 Hz, 2H), 1.79 (d, *J* = 11.3 Hz, 1H), 1.57 (s, 3H), 1.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.13, 173.62, 172.35, 154.96, 154.13, 150.99, 137.78, 133.92, 133.16, 132.87, 128.17, 128.06, 127.82, 127.57, 127.45, 126.71, 126.17, 126.12, 114.26, 110.99, 103.80, 88.37, 76.89, 60.49, 54.96, 46.81, 46.22, 45.78, 44.79, 43.28, 40.34, 31.22, 24.09, 22.69.

HRMS (ESI) *m/z* calcd for $C_{34}H_{34}NO_7$, $[M+H]^+$ 568.2335; Found: 568.2331.

3-(3-((4S,4aR,5S,7R,8S,9aS)-2-(6-ethoxynaphthalen-2-yl)-4,8-dimethyl-3-oxo-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 11.15 (s, 1H), 8.10 (s, 1H), 7.75 – 7.67 (m, 3H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.17 – 7.11 (m, 2H), 6.65 (s, 1H), 6.48 (d, *J* = 8.9 Hz, 1H), 4.70 (s, 1H), 4.16 (d, *J* = 7.1 Hz, 2H), 2.75 (ddd, *J* = 15.5, 12.7, 4.8 Hz, 1H), 2.67 (s, 1H), 2.64 – 2.52 (m, 3H), 2.24 (dd, *J* = 11.9, 3.5 Hz, 2H), 2.17 – 2.08 (m, 2H), 1.97 – 1.84 (m, 2H), 1.79 (d, *J* = 11.3 Hz, 1H), 1.56 (s, 3H), 1.50 (t, *J* = 7.0 Hz, 3H), 1.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.26, 173.59, 172.40, 157.24, 154.99, 154.12, 150.41, 137.76, 134.15, 131.52, 129.54, 128.57, 128.16, 127.60, 127.10, 126.31, 119.23, 114.27, 111.02, 106.32, 103.77, 88.27, 77.23, 76.88, 63.46, 55.01, 46.82, 46.21, 45.83, 44.79, 43.33, 40.38, 31.30, 24.09, 22.73, 14.81.

HRMS (ESI) *m/z* calcd for $C_{36}H_{38}NO_8$, $[M+H]^+$ 612.2597; Found: 612.2595.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(phenanthren-9-yl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1H), 11.09 (s, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 8.13 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.60 – 7.51 (m, 3H), 7.32 (d, *J* = 8.9 Hz, 1H), 6.71 (s, 1H), 6.40 (s, 1H), 4.71 (s, 1H), 2.86 – 2.66 (m, 2H), 2.64 – 2.43 (m, 3H), 2.31 (dd, *J* = 11.9, 3.4 Hz, 1H), 2.21 (q, *J* = 5.7, 4.9 Hz, 1H), 2.17 – 2.11 (m, 2H), 1.92 (dt, *J* = 11.9, 6.0 Hz, 2H), 1.76 (d, *J* = 11.2 Hz, 1H), 1.56 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.60, 173.65, 172.45, 154.97, 154.15, 133.49, 131.31, 130.34, 128.55, 128.16, 126.90, 126.77, 126.53, 125.73, 123.07, 122.55, 114.15, 110.89, 103.71, 88.15, 77.27, 55.05, 47.06, 46.23, 46.16, 44.81, 43.25, 40.46, 31.40, 29.72, 24.47, 22.75.

HRMS (ESI) *m/z* calcd for $C_{38}H_{36}NO_7$, $[M+H]^+$ 618.2492; Found: 618.2489.

3-(3-((4S,4aR,5S,7R,8S,9aS)-4,8-dimethyl-3-oxo-2-(pyren-4-yl)-3,4,4a,5,6,7,8,9-octahydro-5,8-epoxy-7,9a-methanobenzo[7]annulen-4-yl)propanamido)-2,4-dihydroxybenzoic acid (6t)

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.63 (s, 1H), 11.09 (s, 1H), 8.29 – 8.16 (m, 2H), 8.16 – 8.09 (m, 2H), 8.06 (s, 2H), 8.02 (s, 1H), 7.98 (s, 1H), 7.75 (s, 2H), 7.28 (s, 1H), 6.72 (s, 1H), 6.37 (dd, *J* = 9.0, 2.2 Hz, 1H), 4.73 (s, 1H), 2.79 (d, *J* = 20.2 Hz, 2H), 2.62 (d, *J* = 10.3 Hz, 1H), 2.55 (q, *J* = 5.9 Hz, 2H), 2.31 (s, 1H), 2.21 (q, *J* = 6.3, 5.3 Hz, 2H), 2.14 (s, 1H), 1.94 (dt, *J* = 19.0, 10.7 Hz, 2H), 1.77 (d, *J* = 10.8 Hz, 1H), 1.56 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.58, 172.33, 154.93, 154.07, 131.62, 131.26, 131.16, 130.73, 128.06, 127.71, 127.63, 127.31, 126.00, 125.36, 125.14, 124.75, 124.69, 124.41, 124.22, 114.13, 110.89, 103.64, 88.19, 77.20, 55.07, 47.04, 46.32, 46.23, 44.81, 43.26, 40.45, 31.56, 31.43, 24.41, 22.74.

HRMS (ESI) *m/z* calcd for $C_{40}H_{36}NO_7$, $[M+H]^+$ 642.2492; Found: 642.2489.

Figure S1. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of iodo-PTMA ethylester **2** in $CDCl_3$.

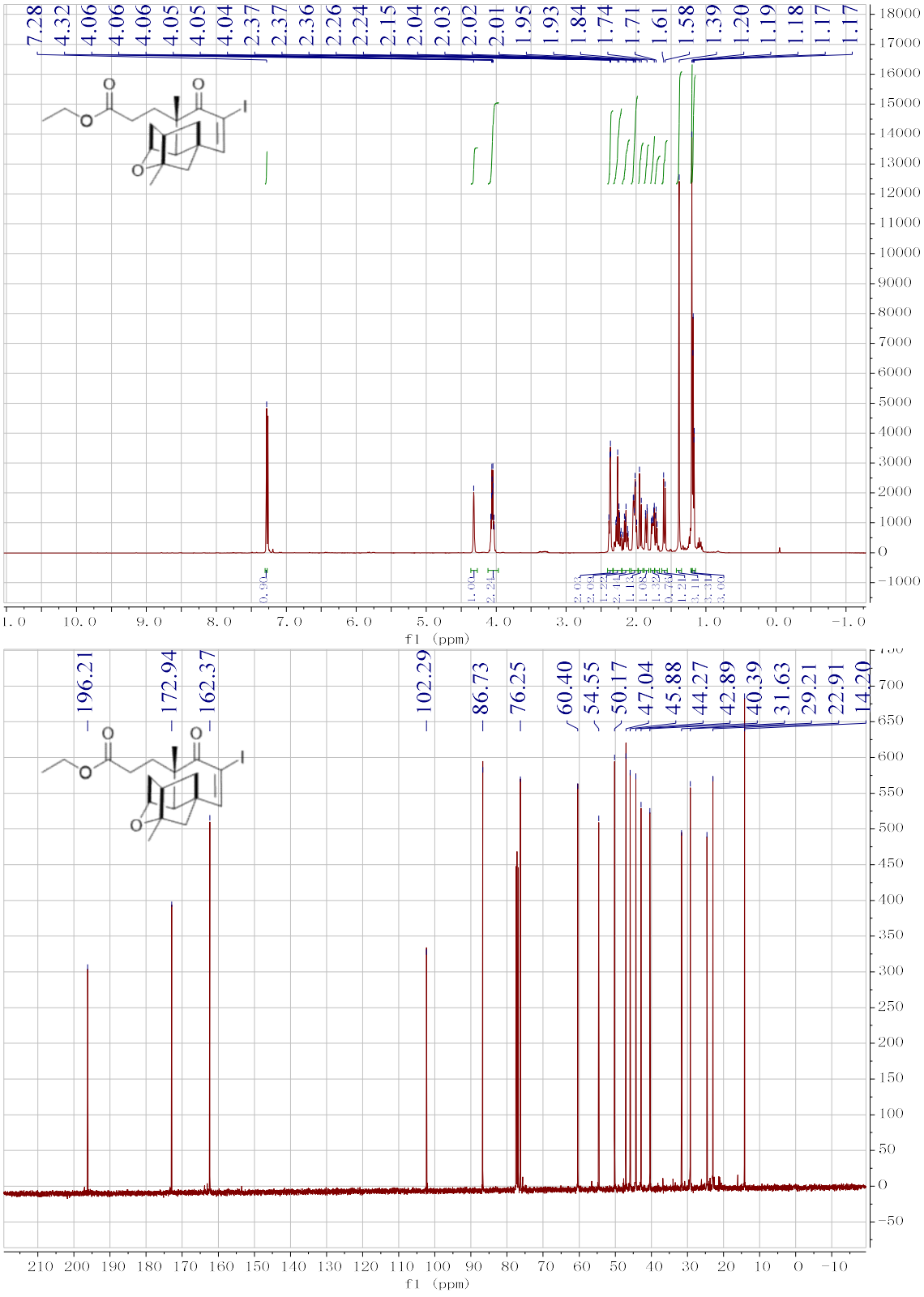


Figure S2. ^{1}H NMR (500 MHz) and ^{13}C NMR (101 MHz) spectrum of **3a** in $CDCl_3$.

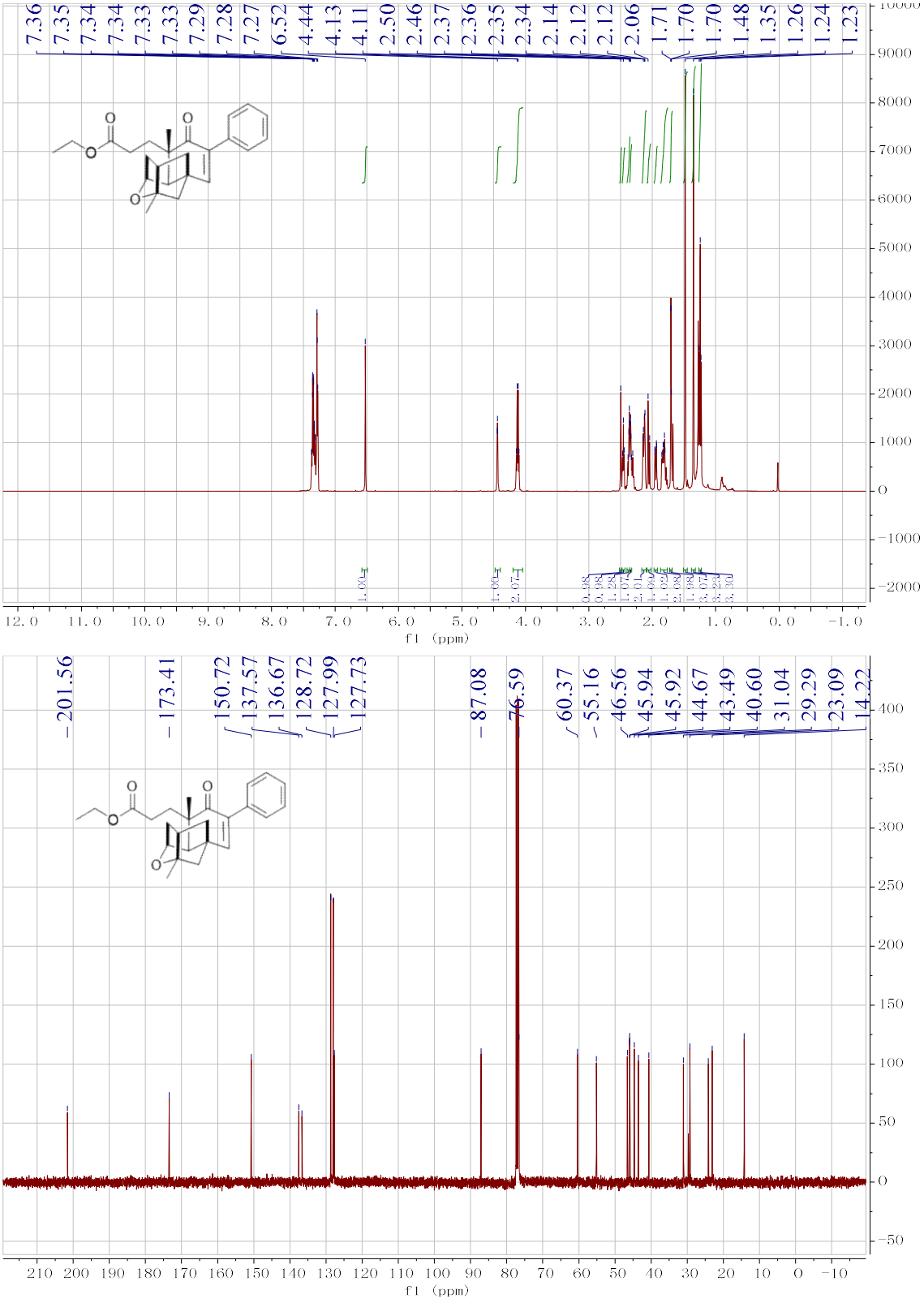


Figure S3. ^{1}H NMR (500 MHz) and ^{13}C NMR (101 MHz) spectrum of **3b** in $CDCl_3$.

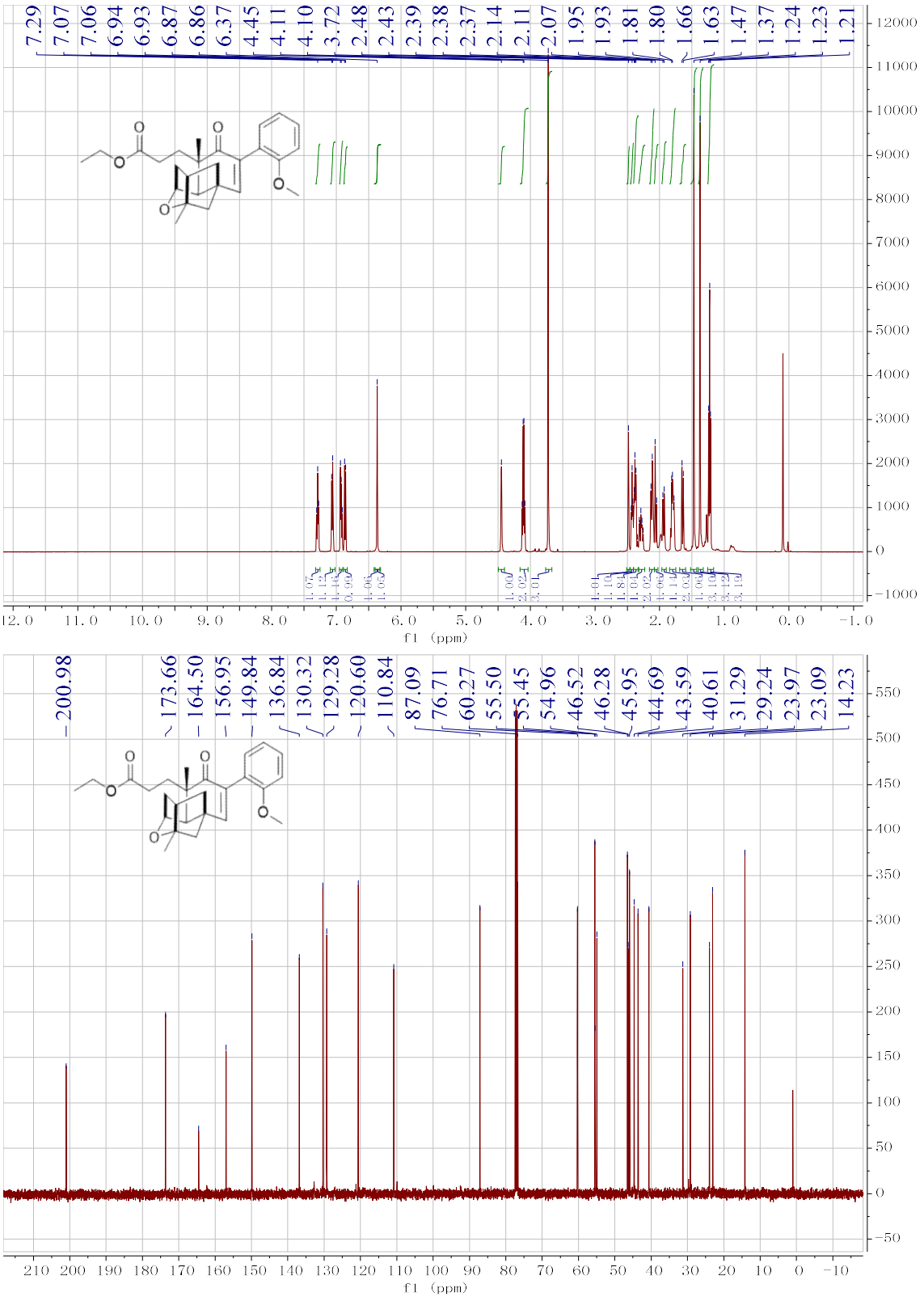


Figure S4. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3c** in $CDCl_3$.

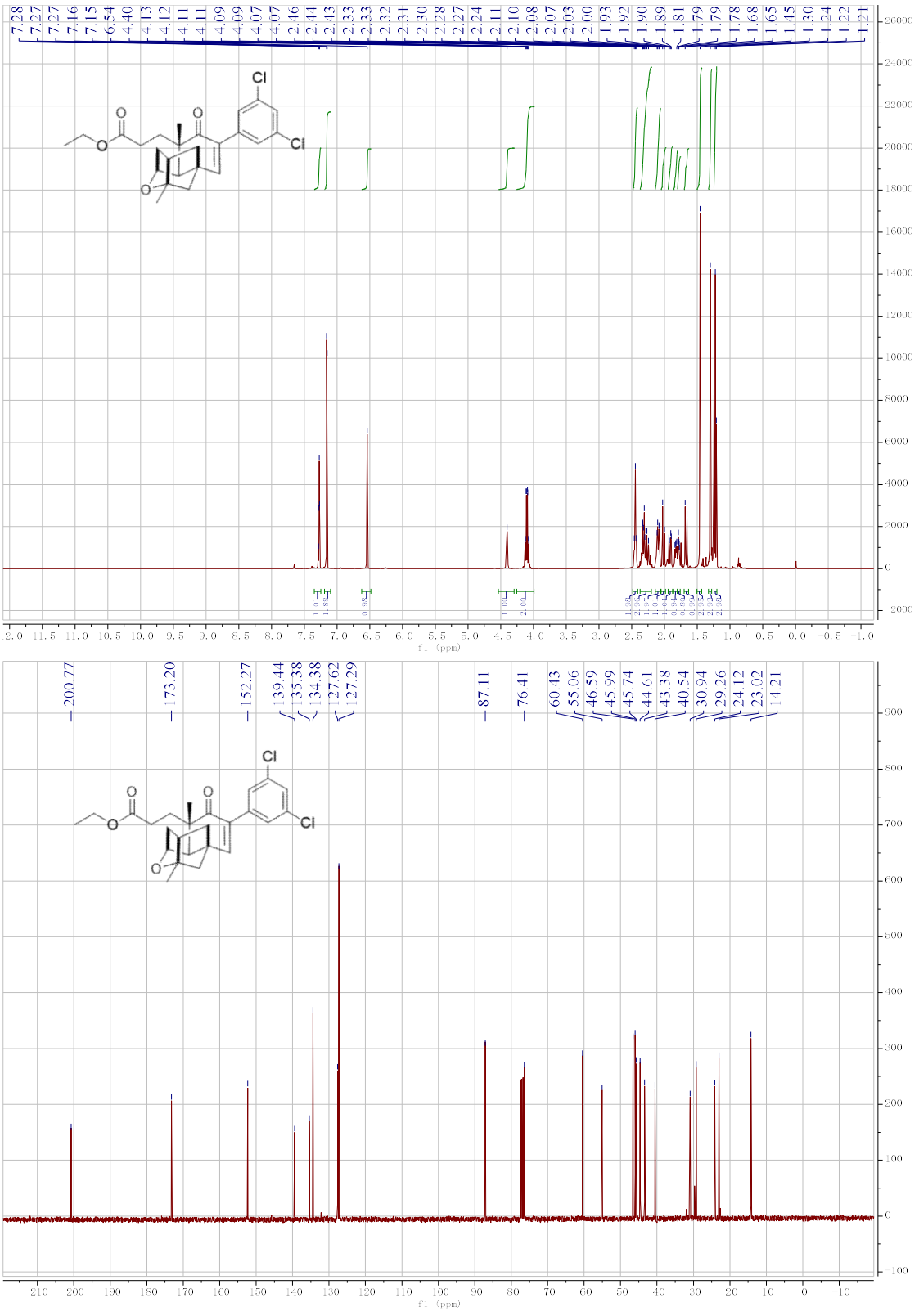


Figure S5. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3d** in $CDCl_3$.

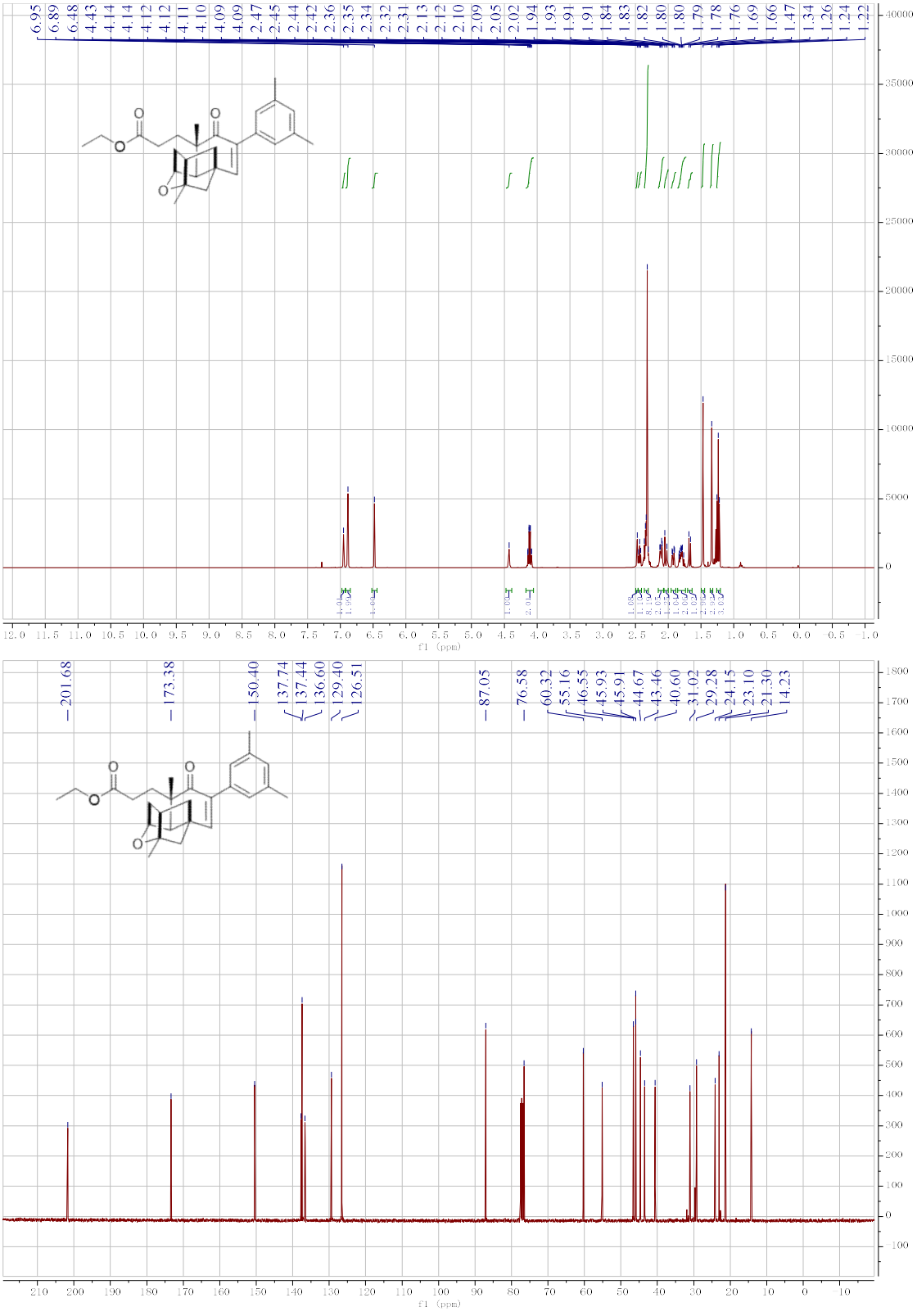


Figure S6. ^{1}H NMR (500 MHz) and ^{13}C NMR (101 MHz) spectrum of **3e** in $CDCl_3$.

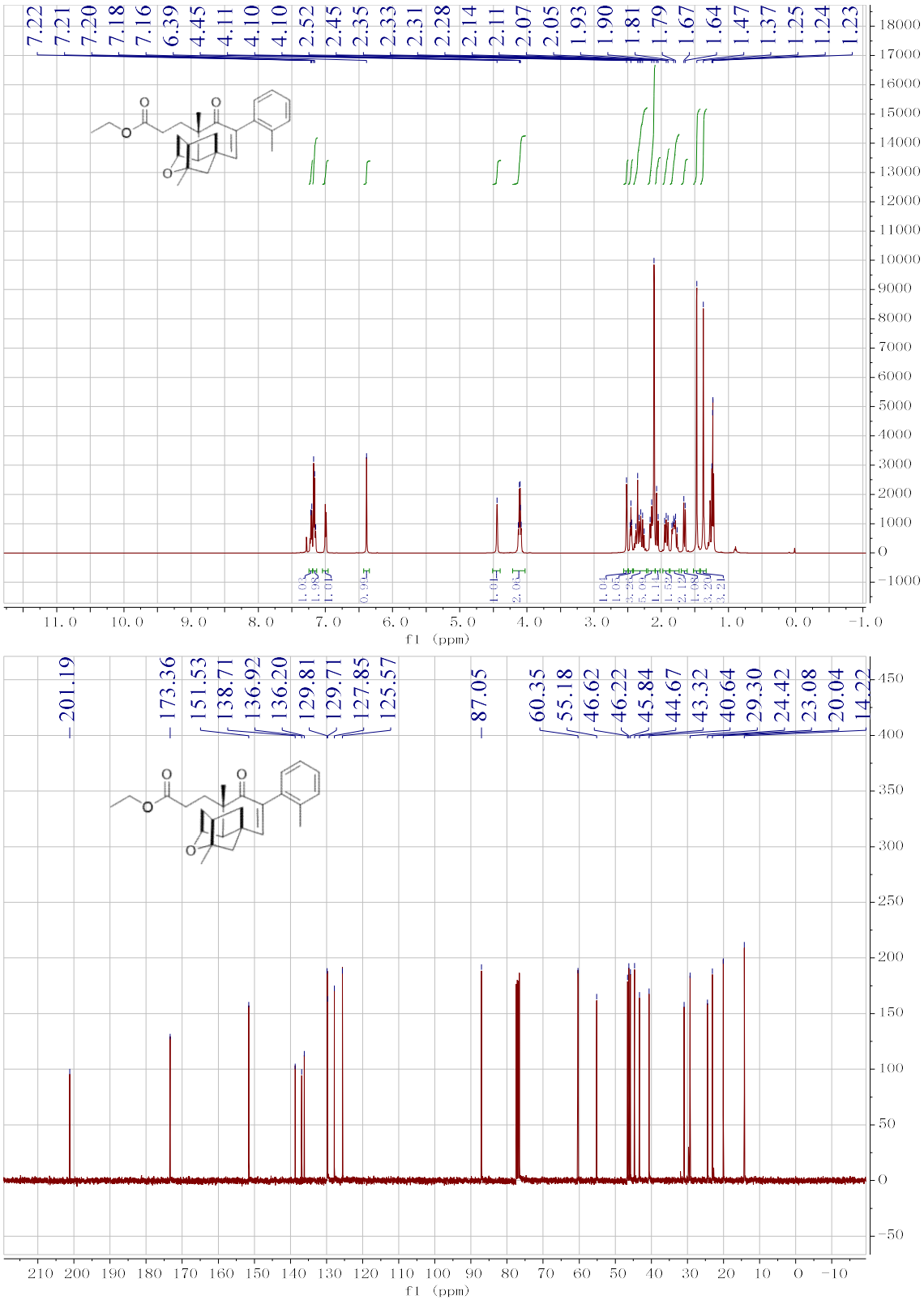


Figure S7. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3f** in $CDCl_3$.

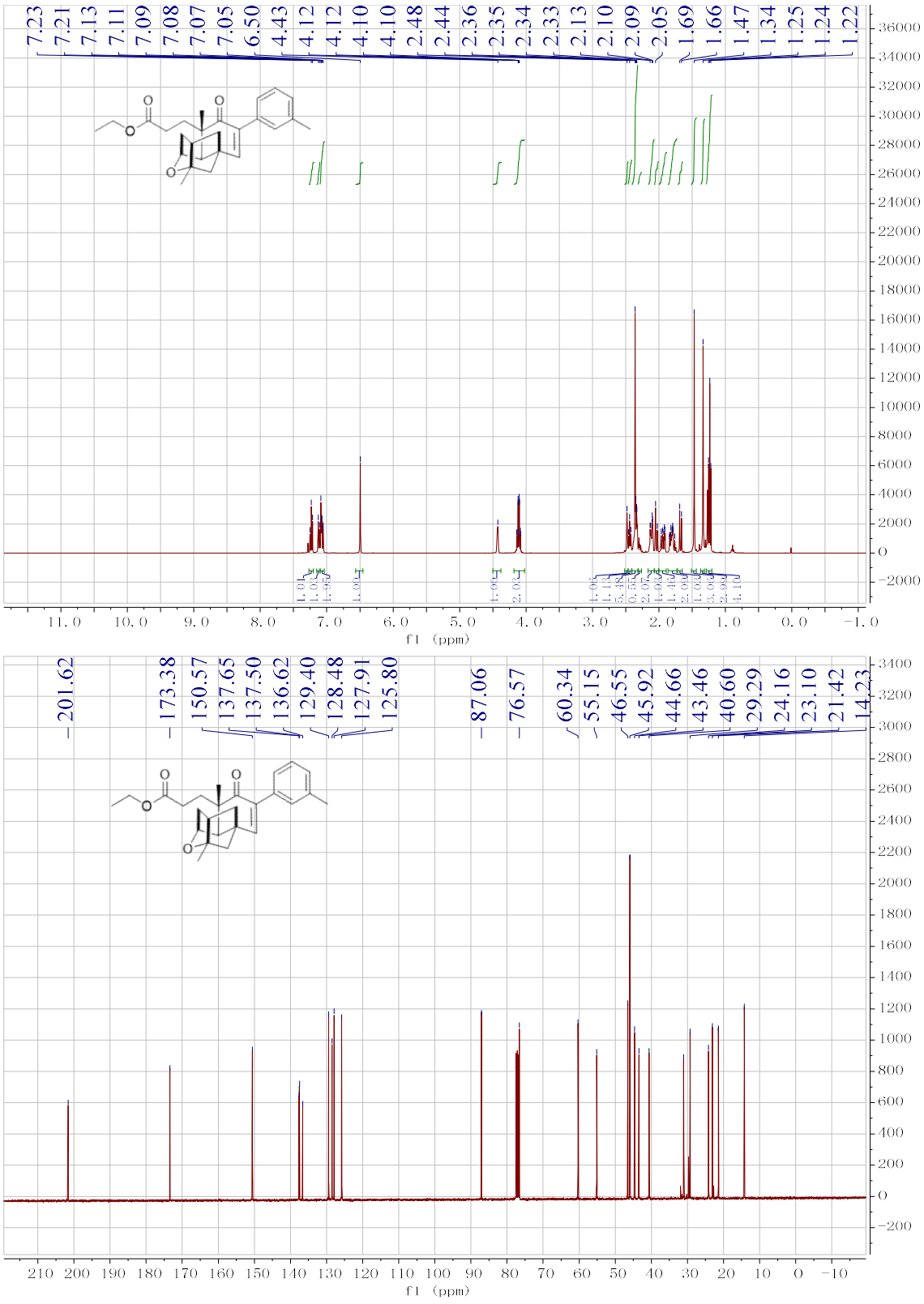
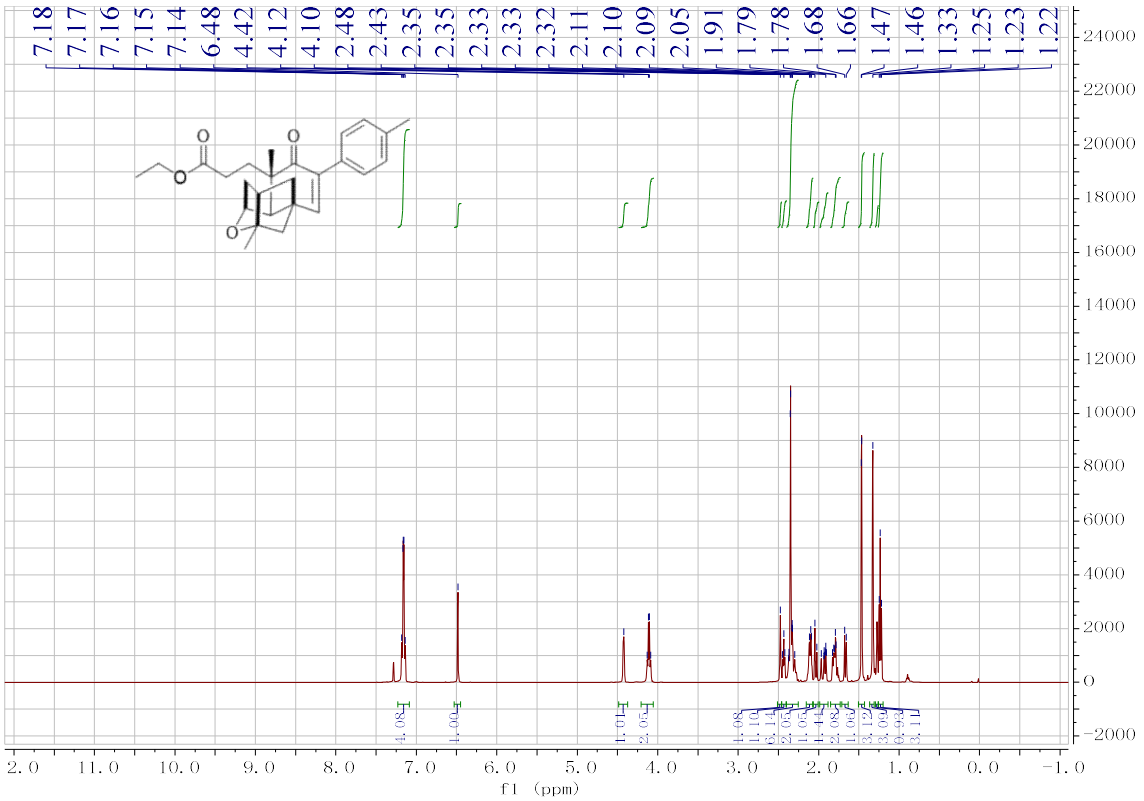


Figure S8. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **3g** in $CDCl_3$.



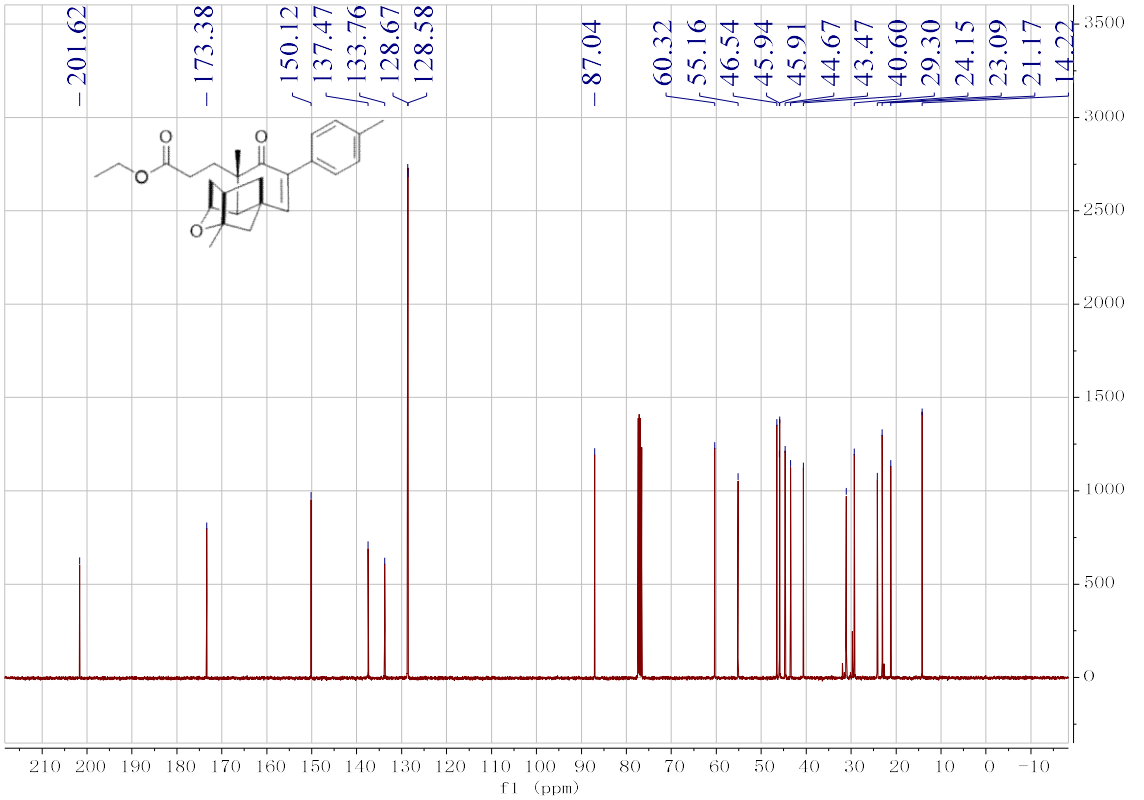


Figure S9. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3h** in $CDCl_3$.

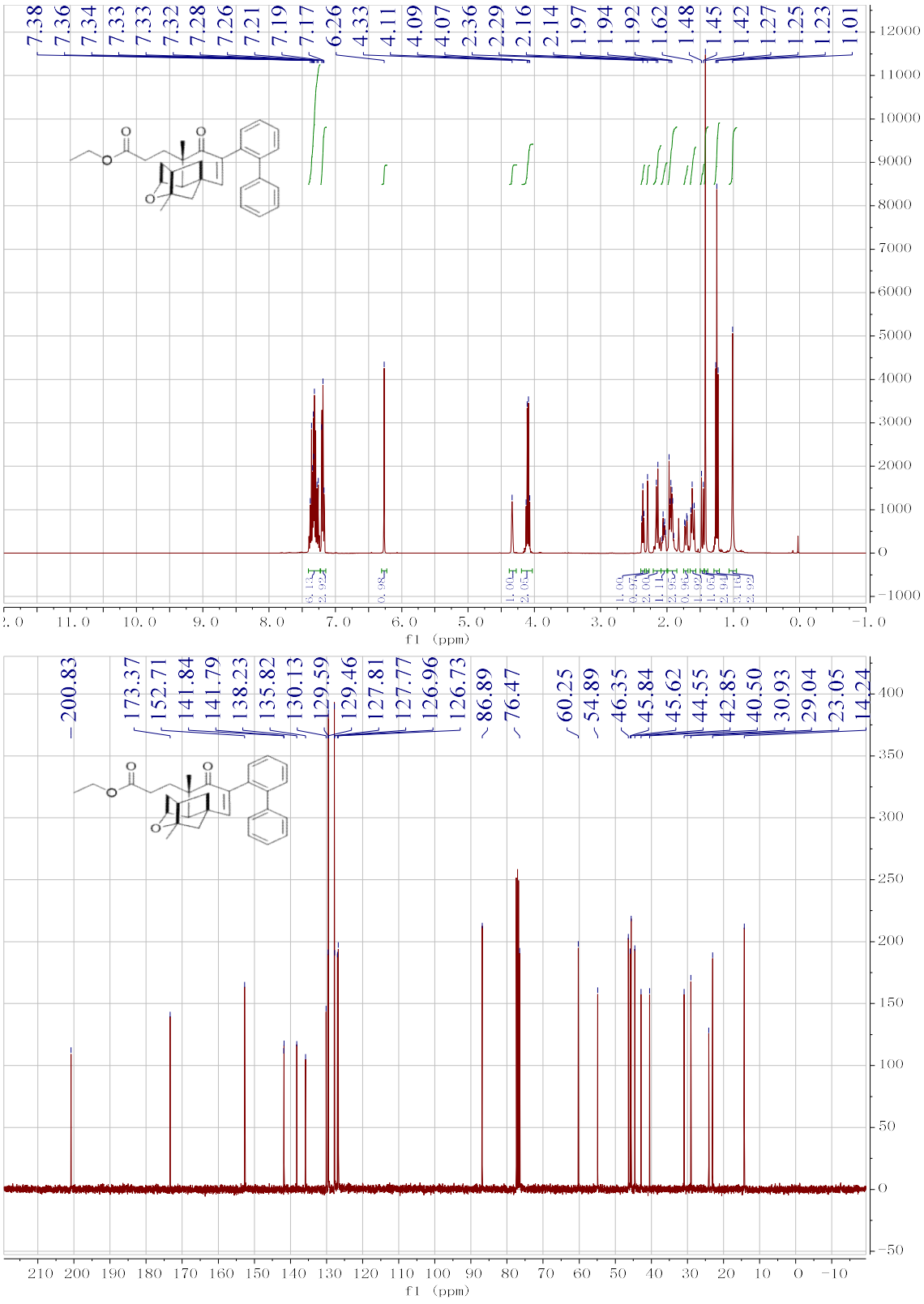


Figure S10. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3i** in $CDCl_3$.

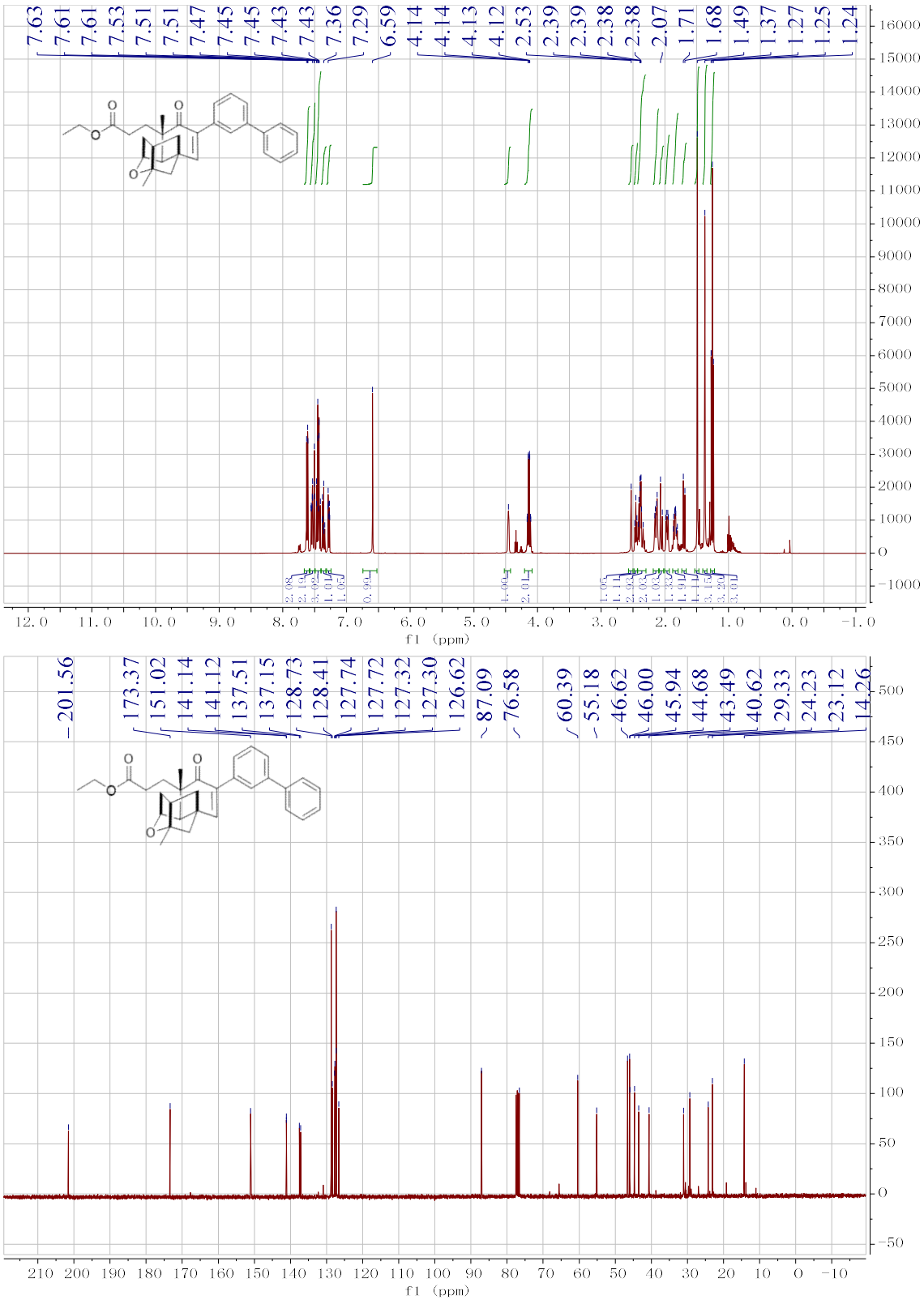


Figure S11. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3j** in $CDCl_3$.

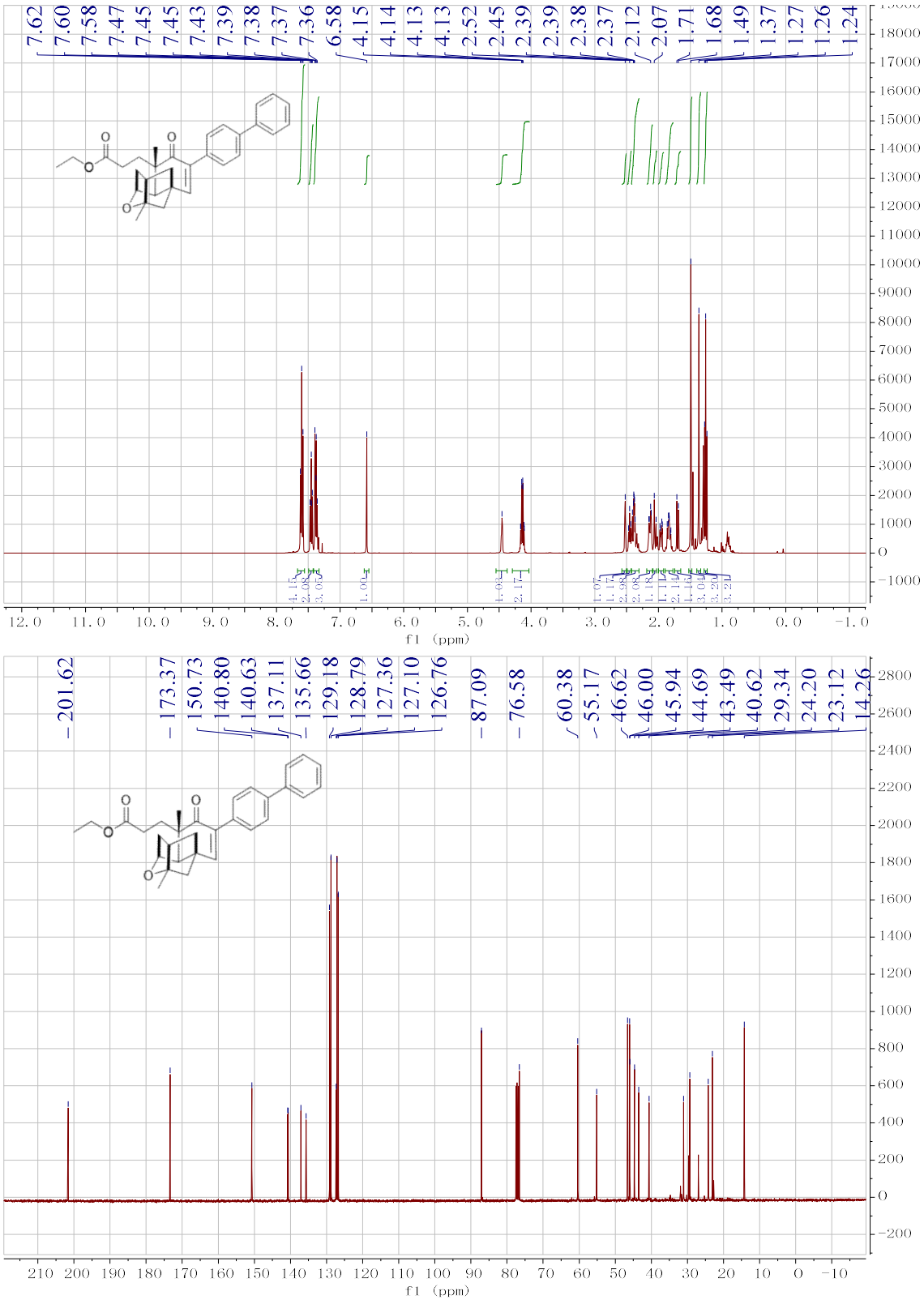


Figure S12. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **3k** in $CDCl_3$.

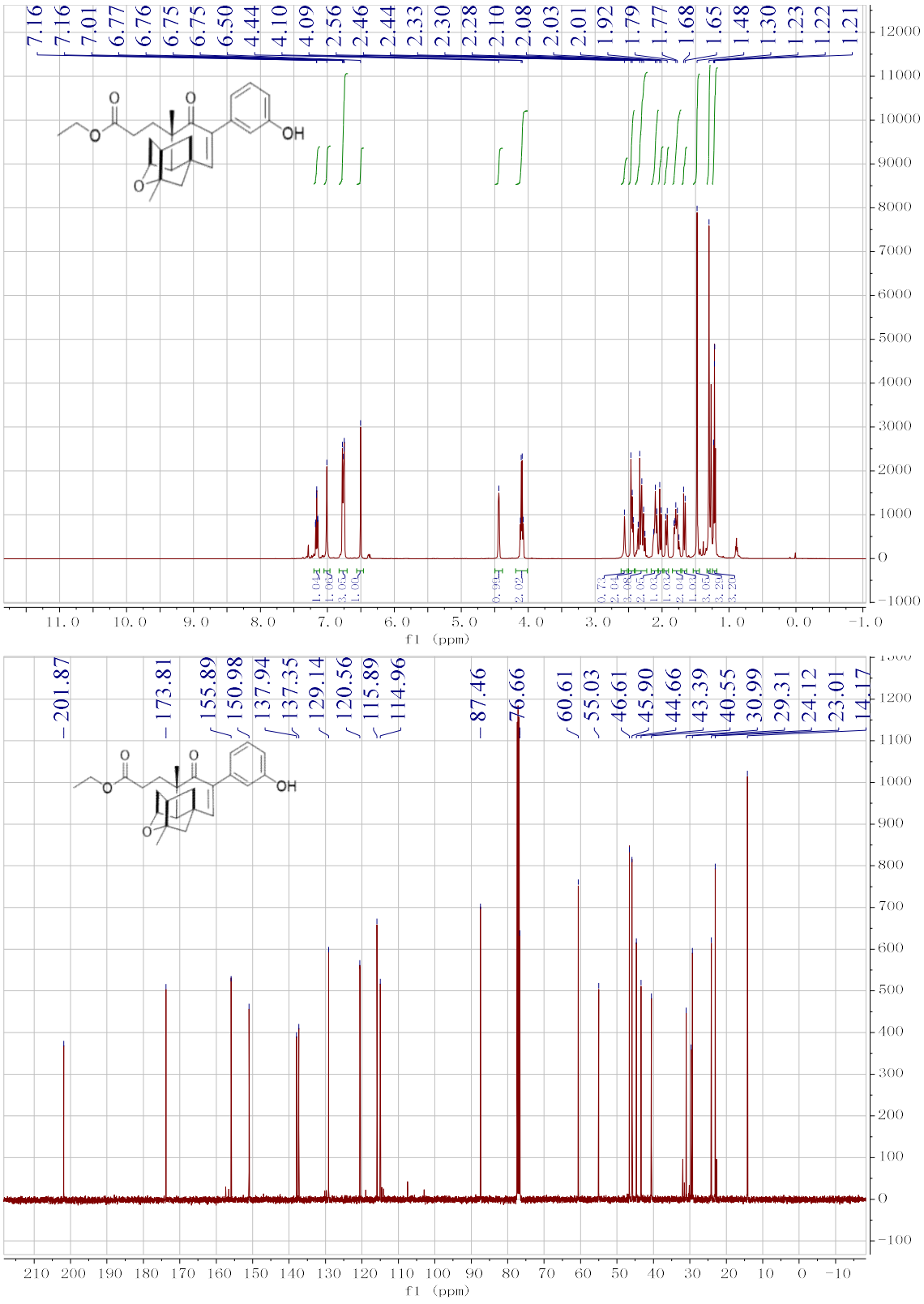


Figure S13. ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum of **3l** in $CDCl_3$.

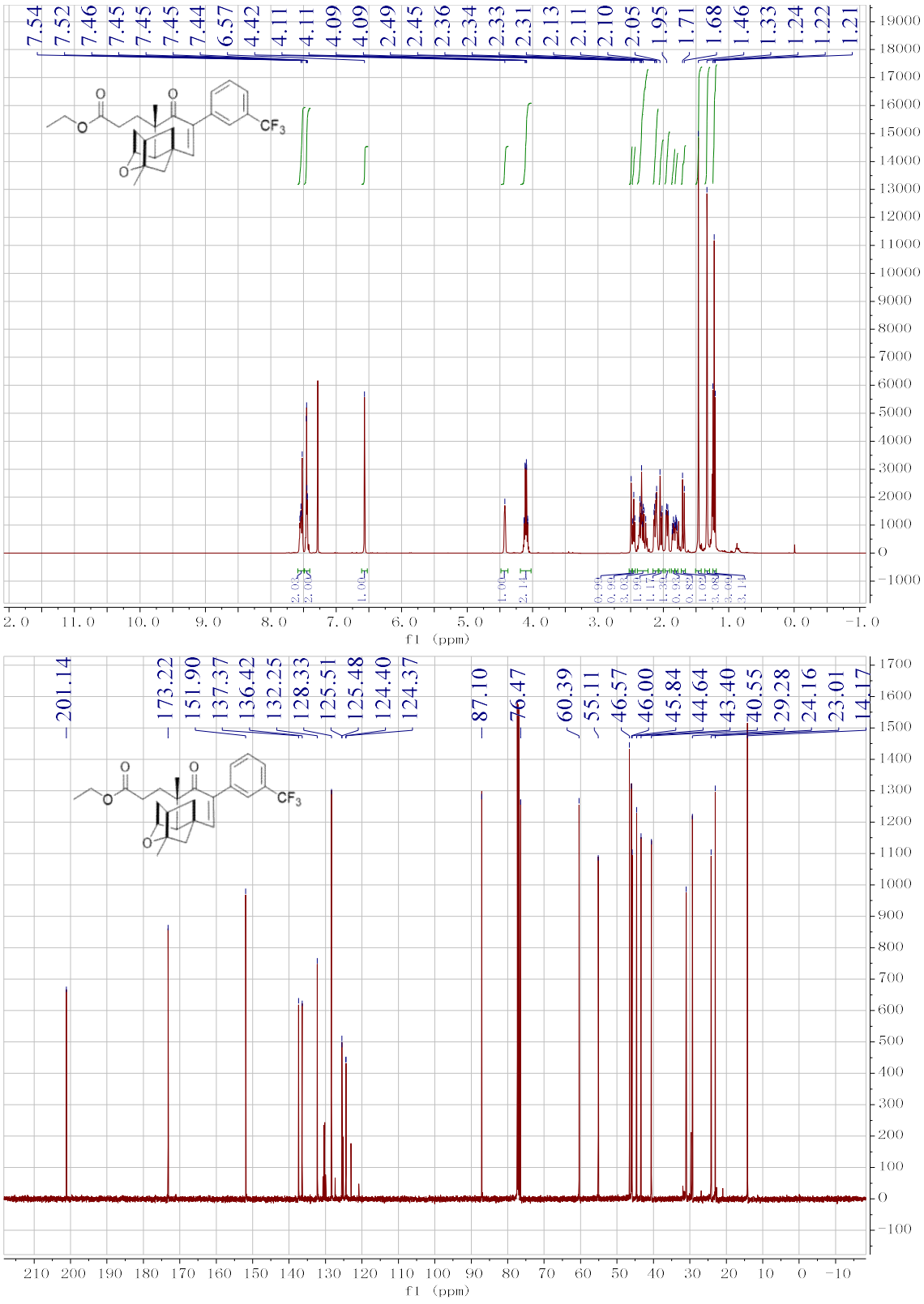


Figure S14. ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum of **3m** in $CDCl_3$.

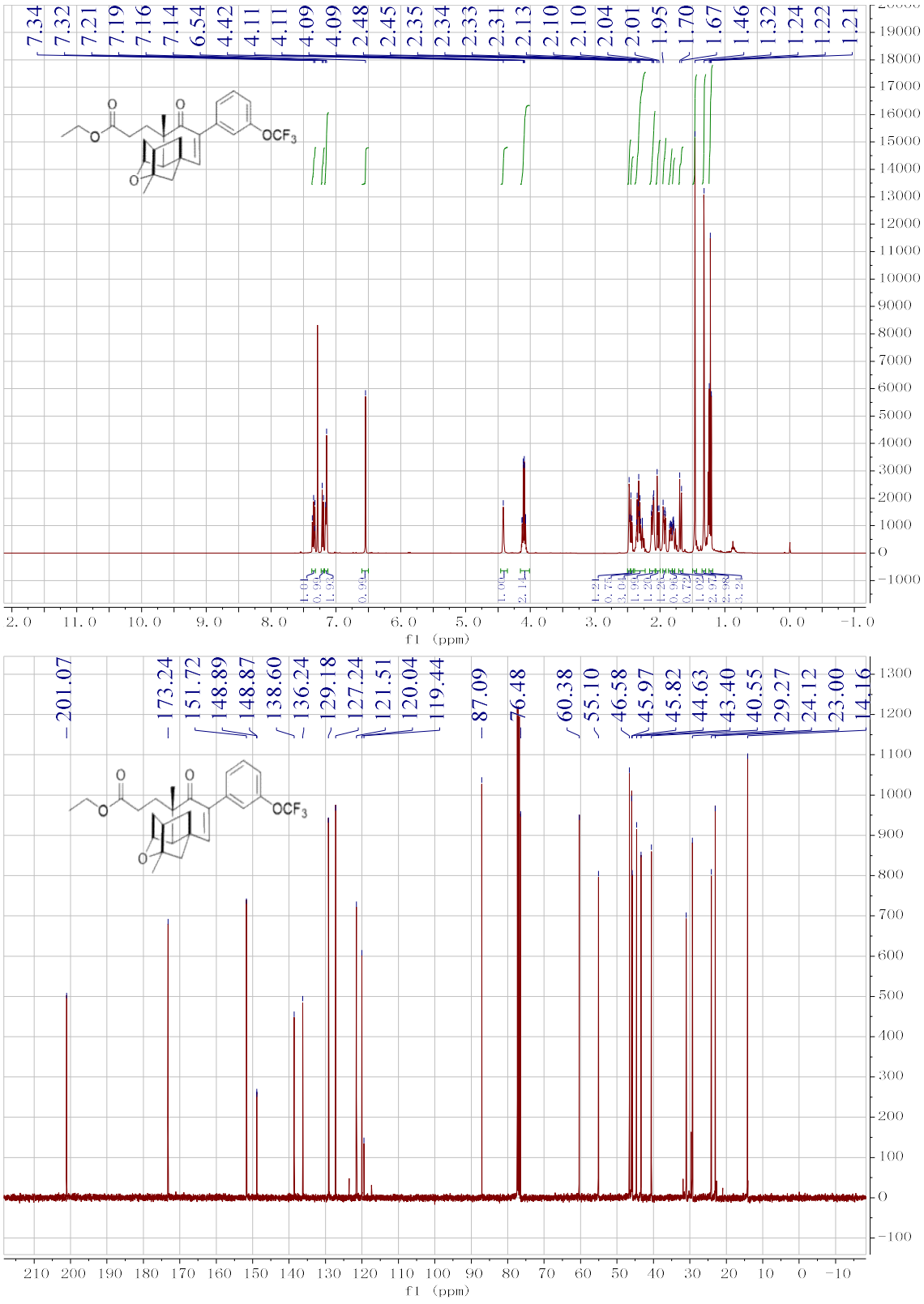


Figure S15. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3n** in $CDCl_3$.

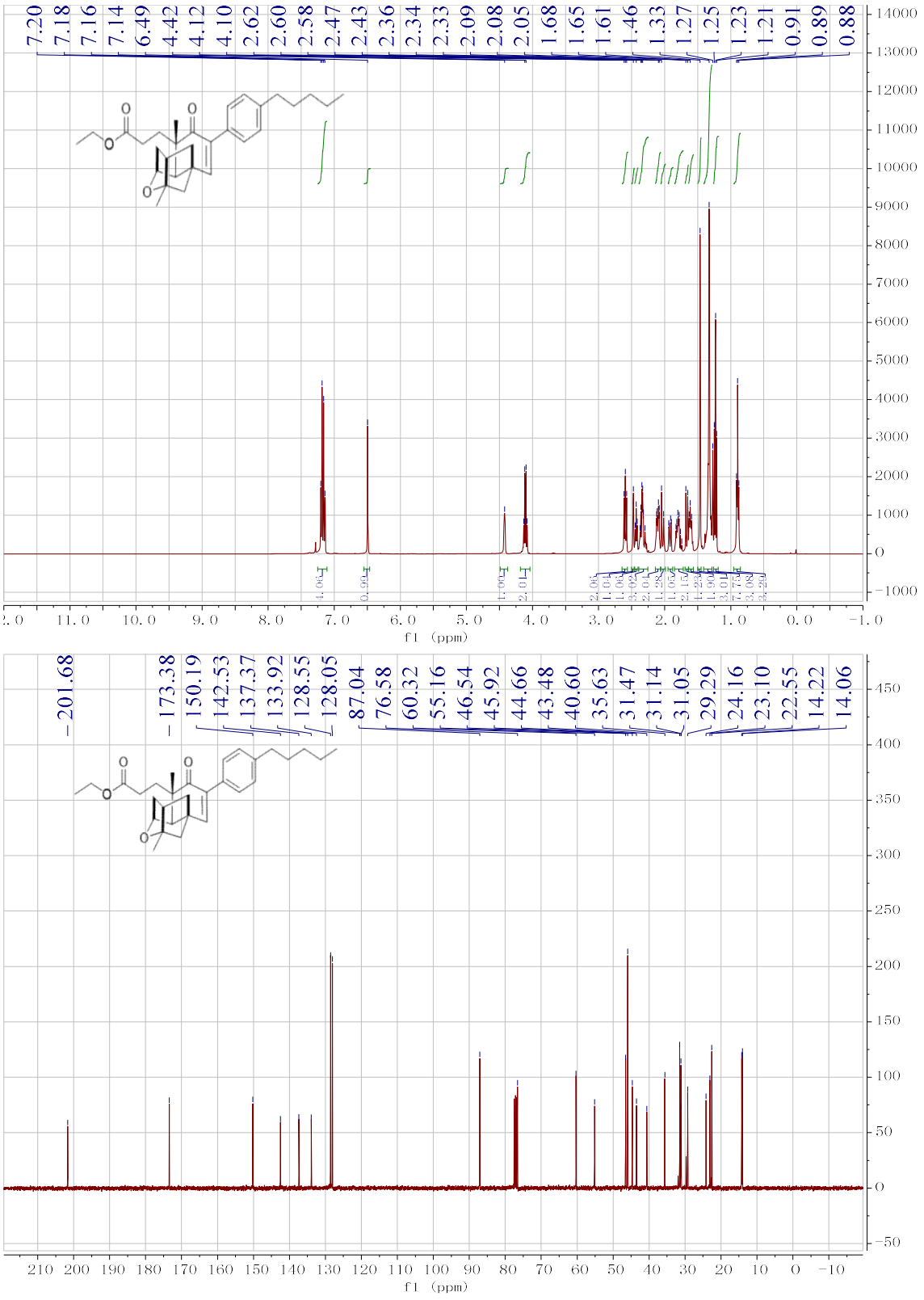
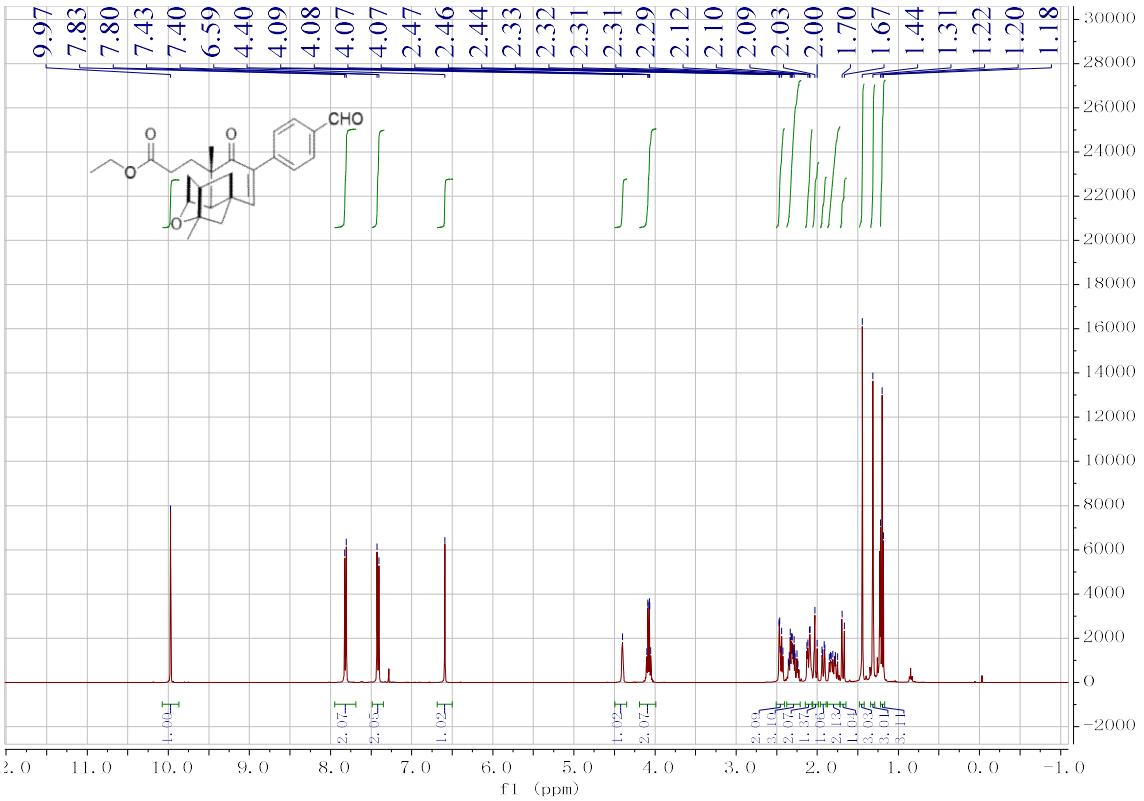


Figure S16. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3o** in $CDCl_3$.



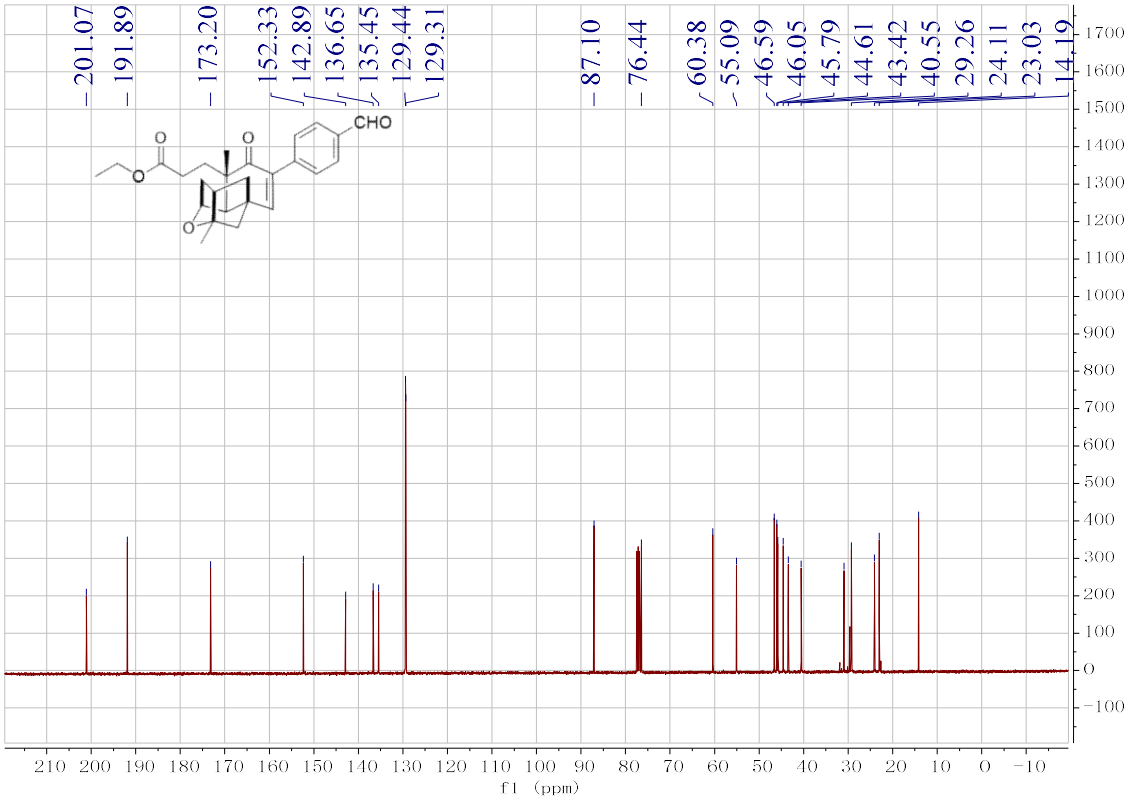


Figure S17. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **3p** in $CDCl_3$.

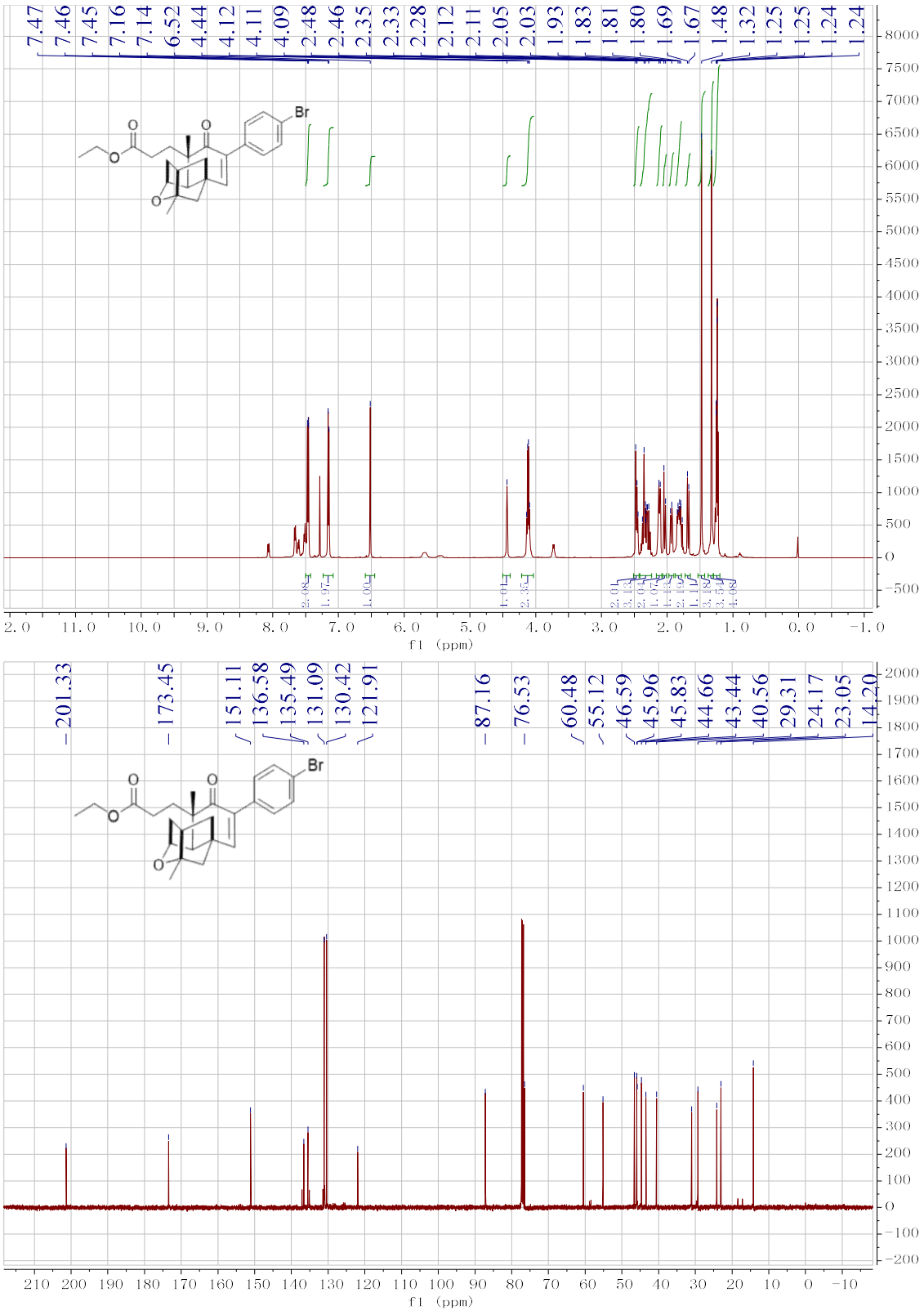


Figure S18. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3q** in $CDCl_3$.

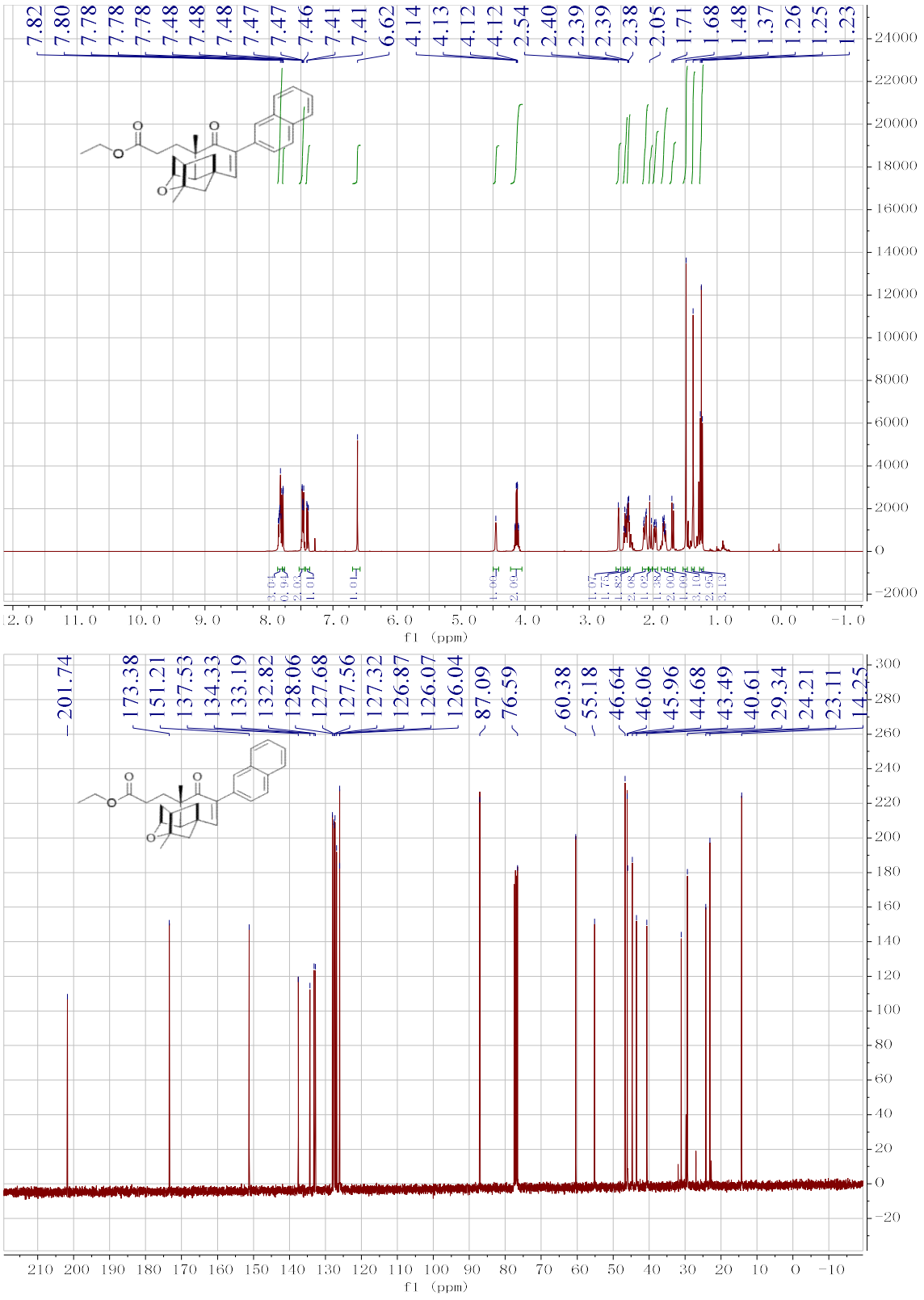


Figure S19. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **3r** in $CDCl_3$.

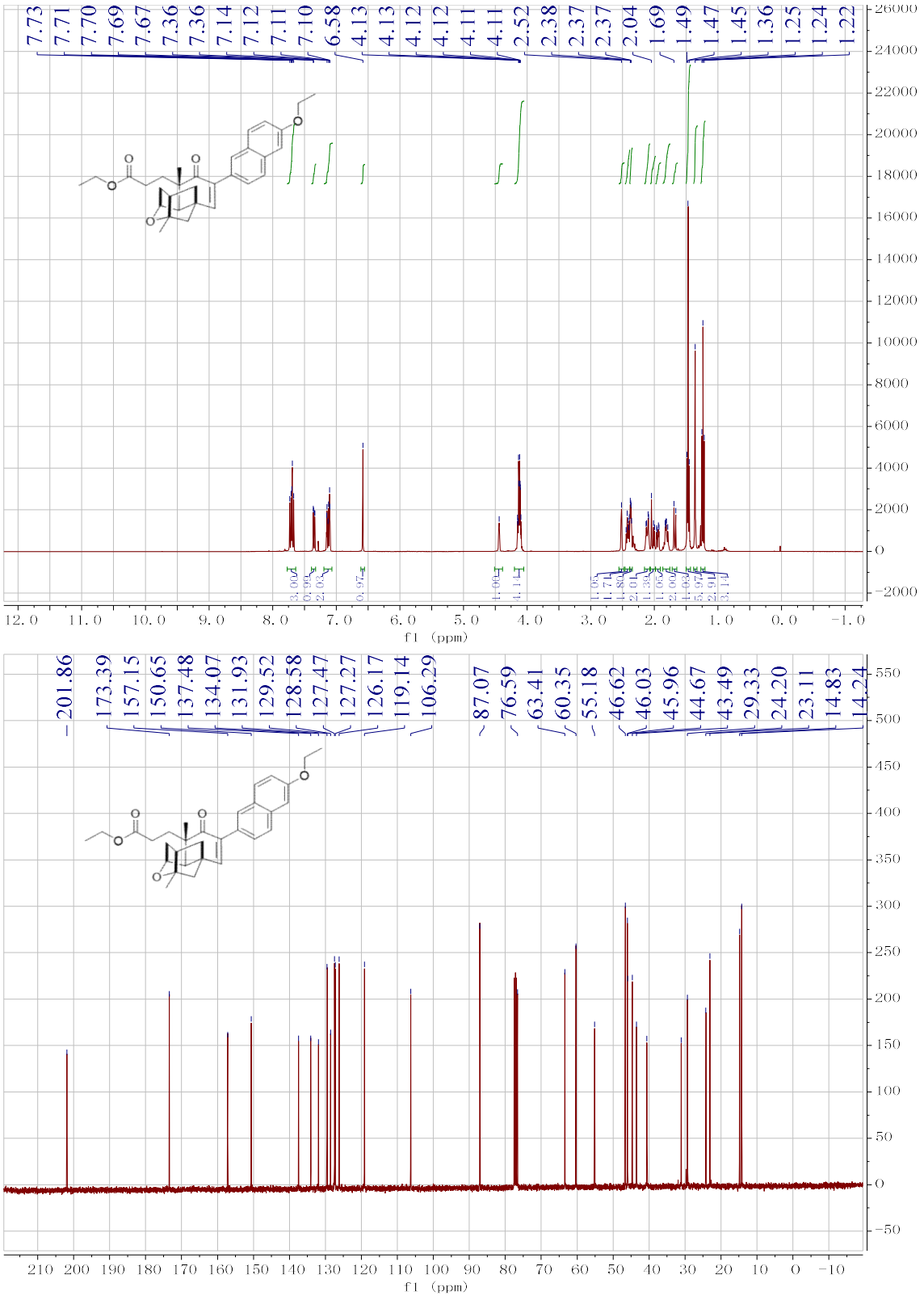


Figure S20. ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum of **3s** in $CDCl_3$.

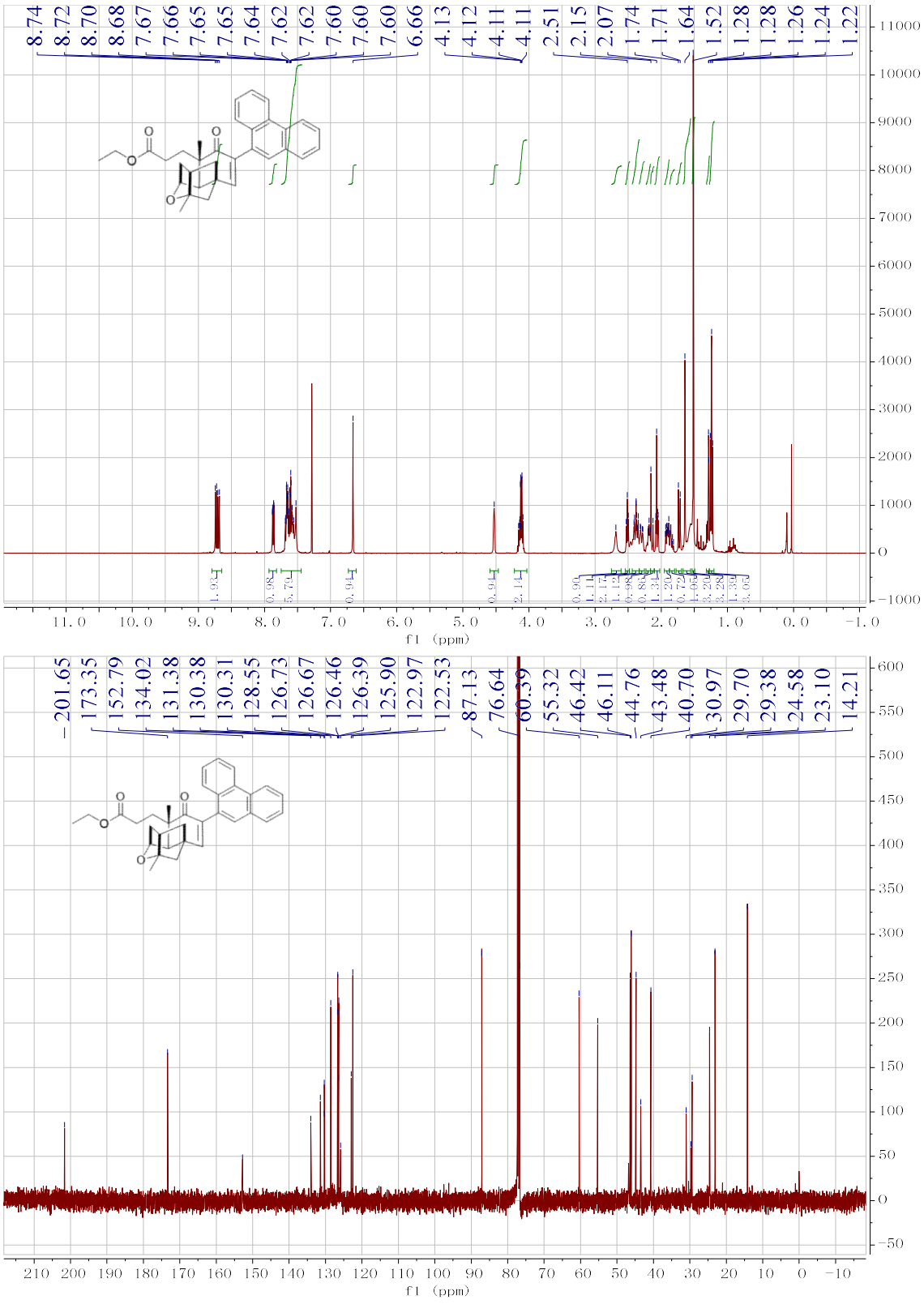


Figure S21. ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz) spectrum of **3t** in $CDCl_3$.

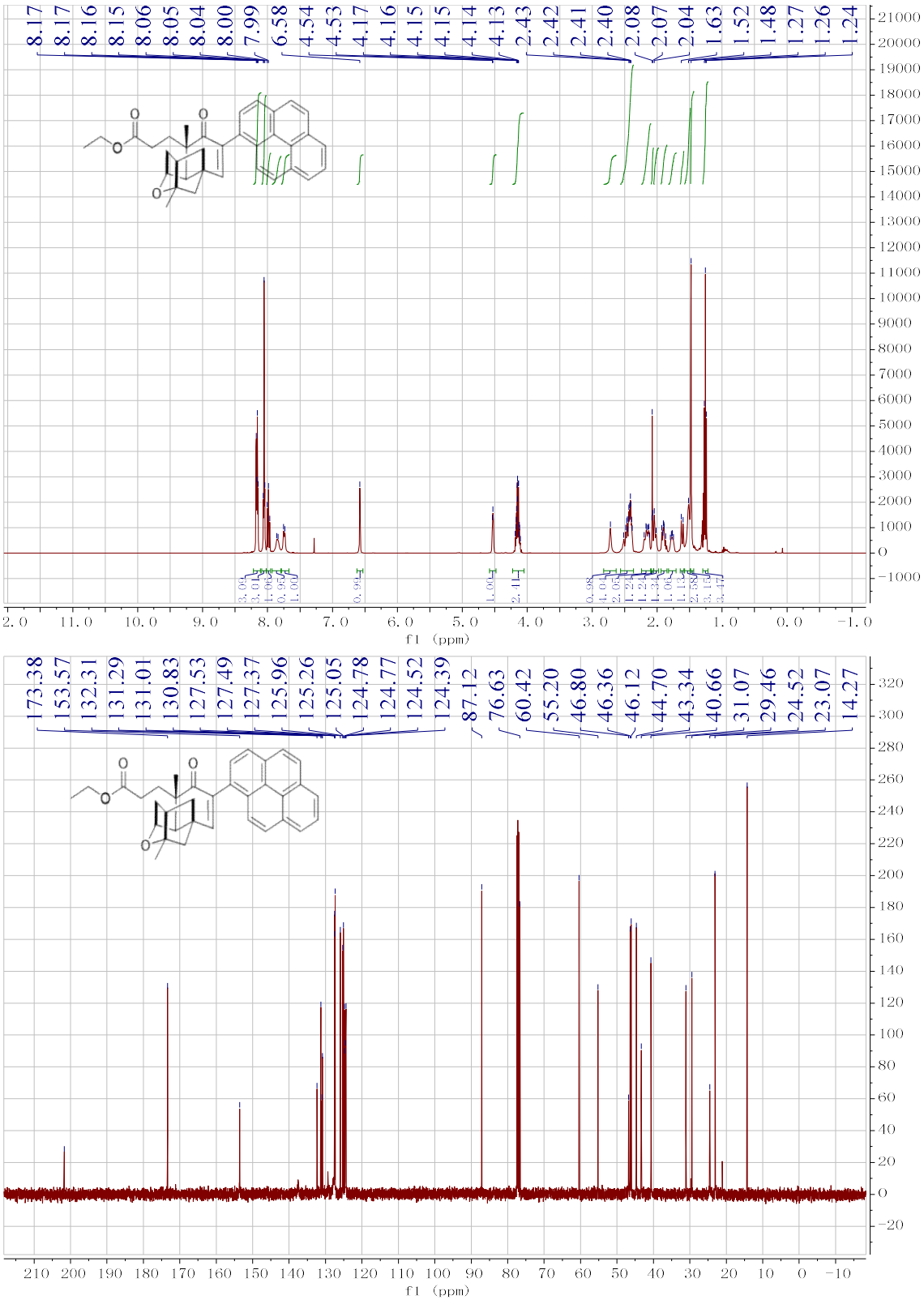


Figure S22. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6a** in $CDCl_3$.

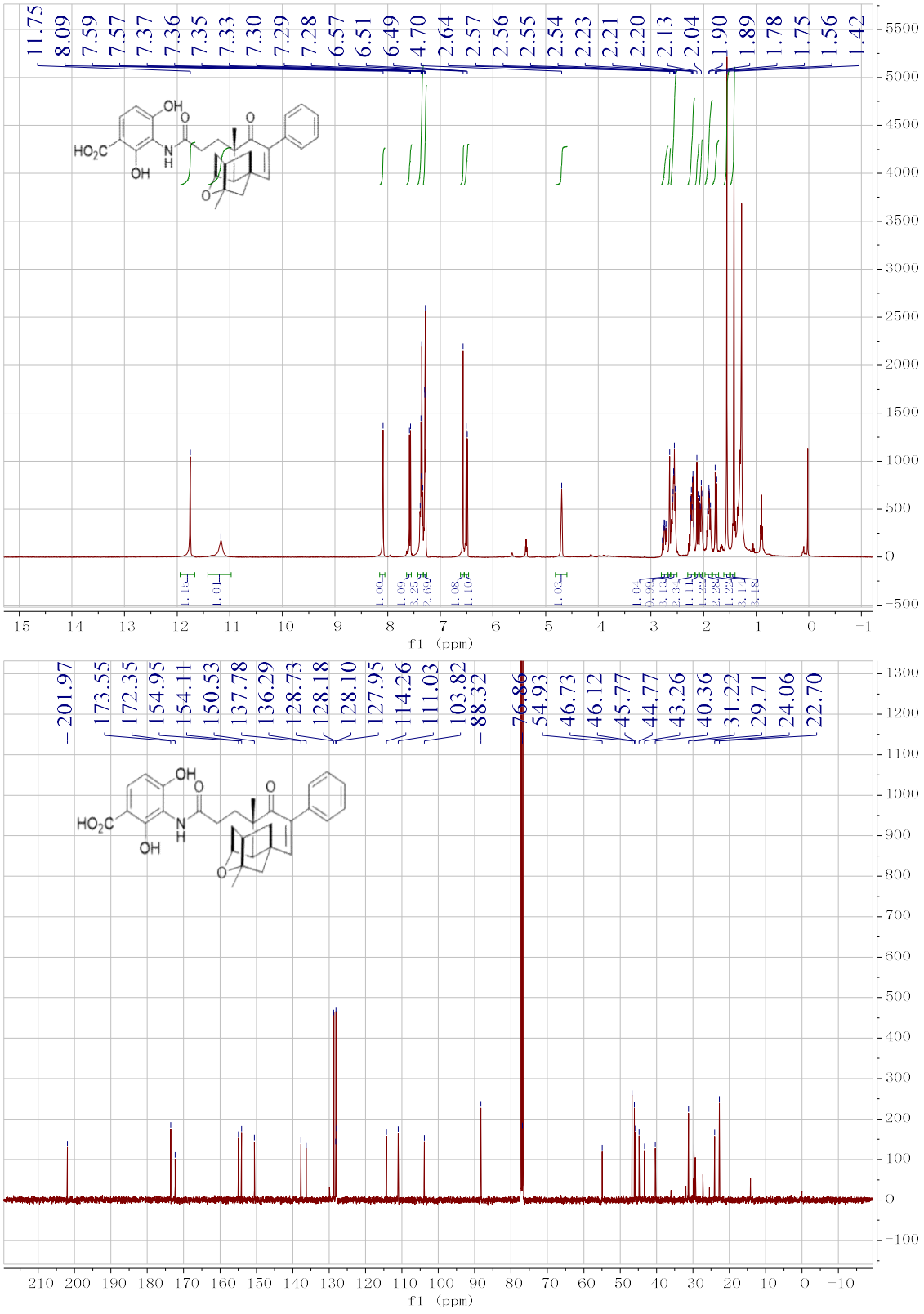


Figure S23. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **6b** in $CDCl_3$.

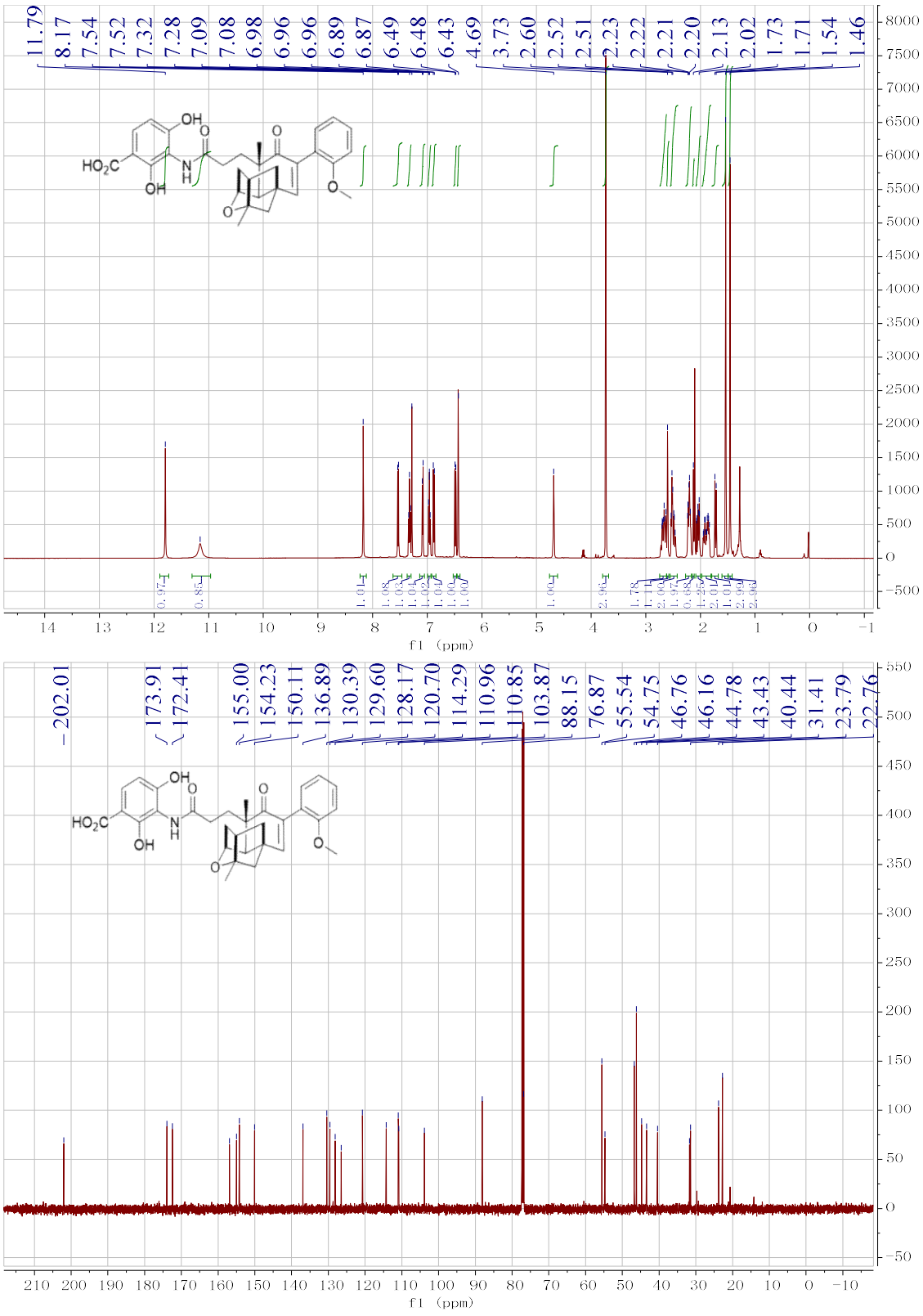


Figure S24. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6c** in $CDCl_3$.

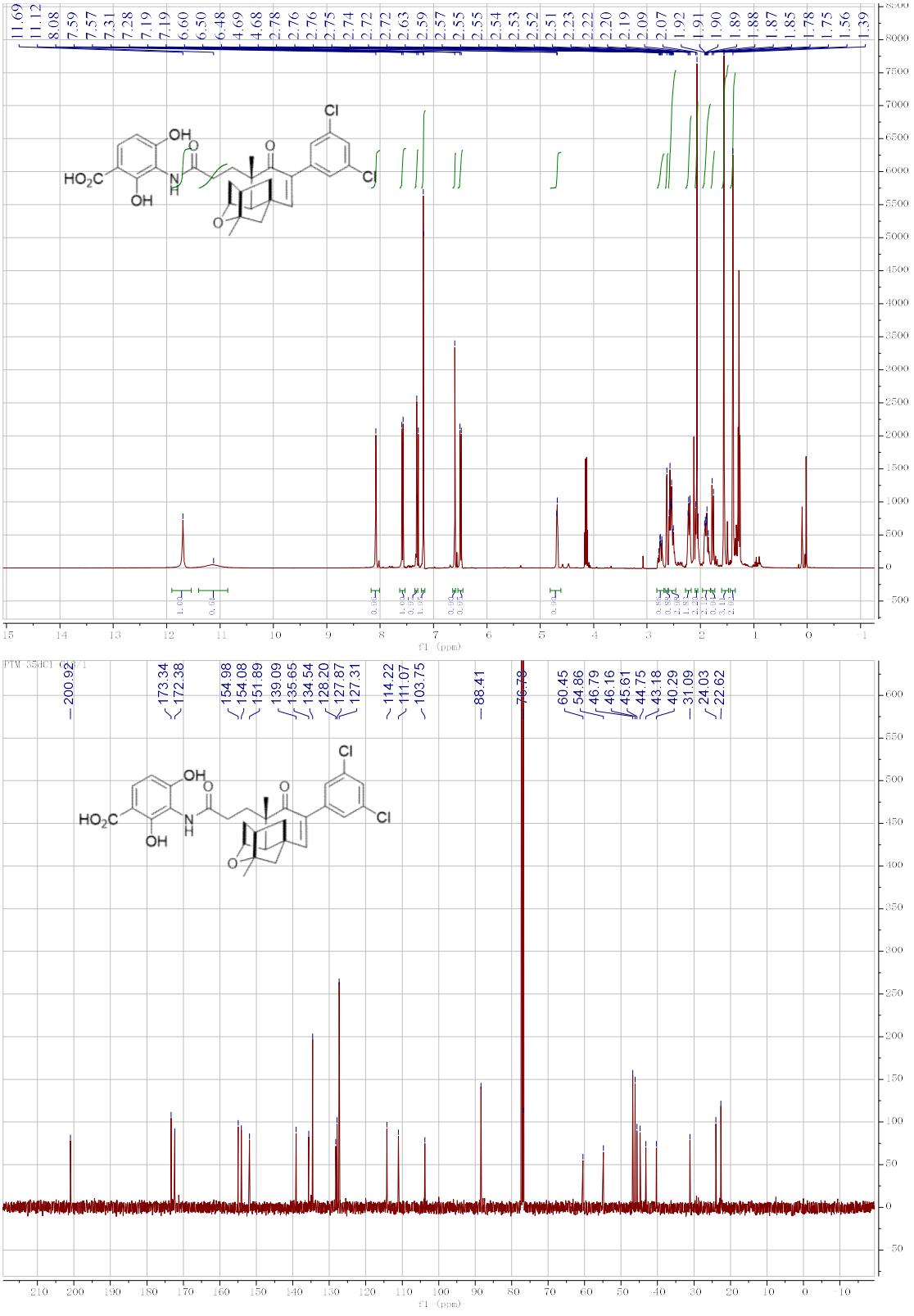


Figure S25. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6d** in $CDCl_3$.

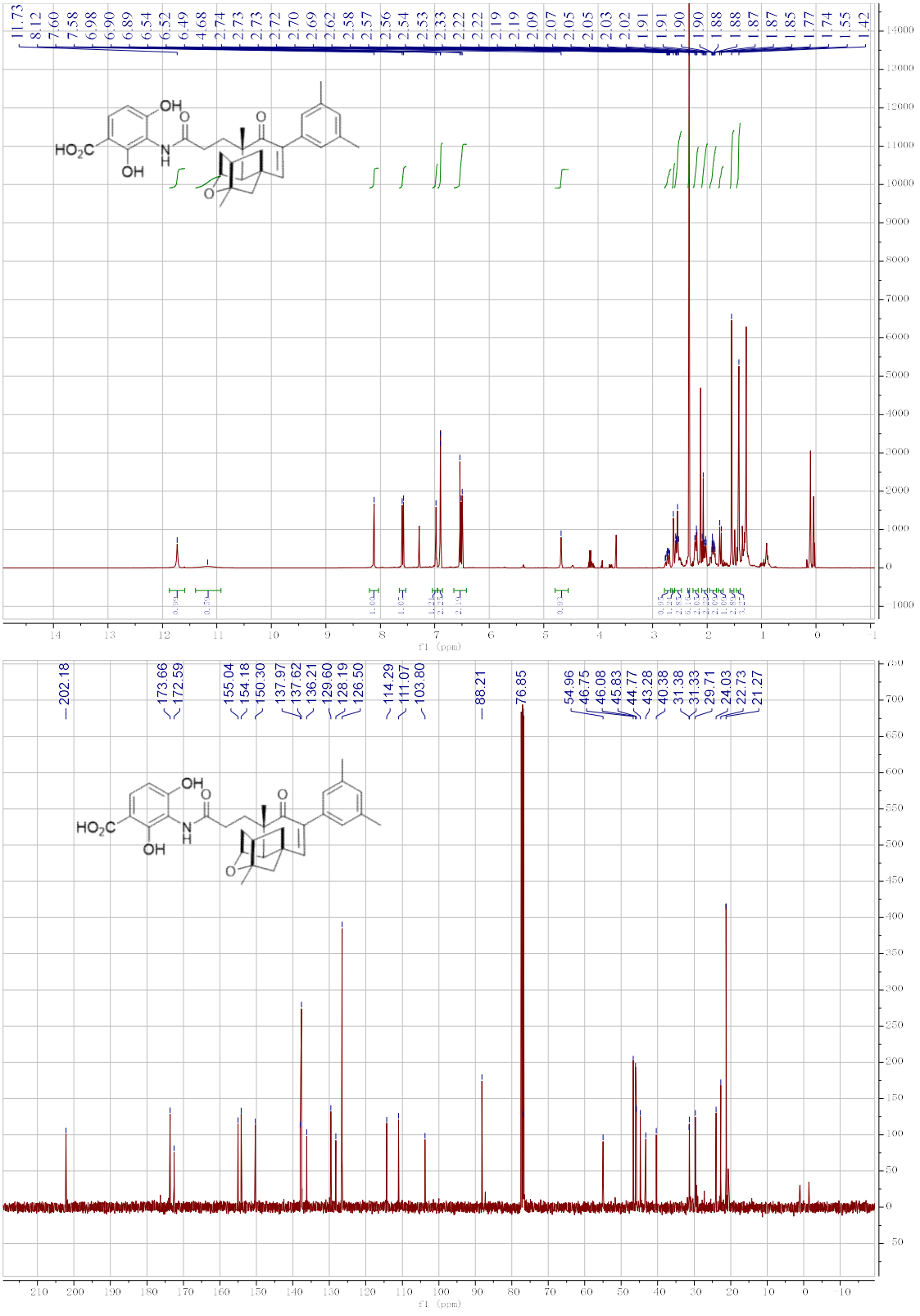


Figure S26. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **6e** in $CDCl_3$.

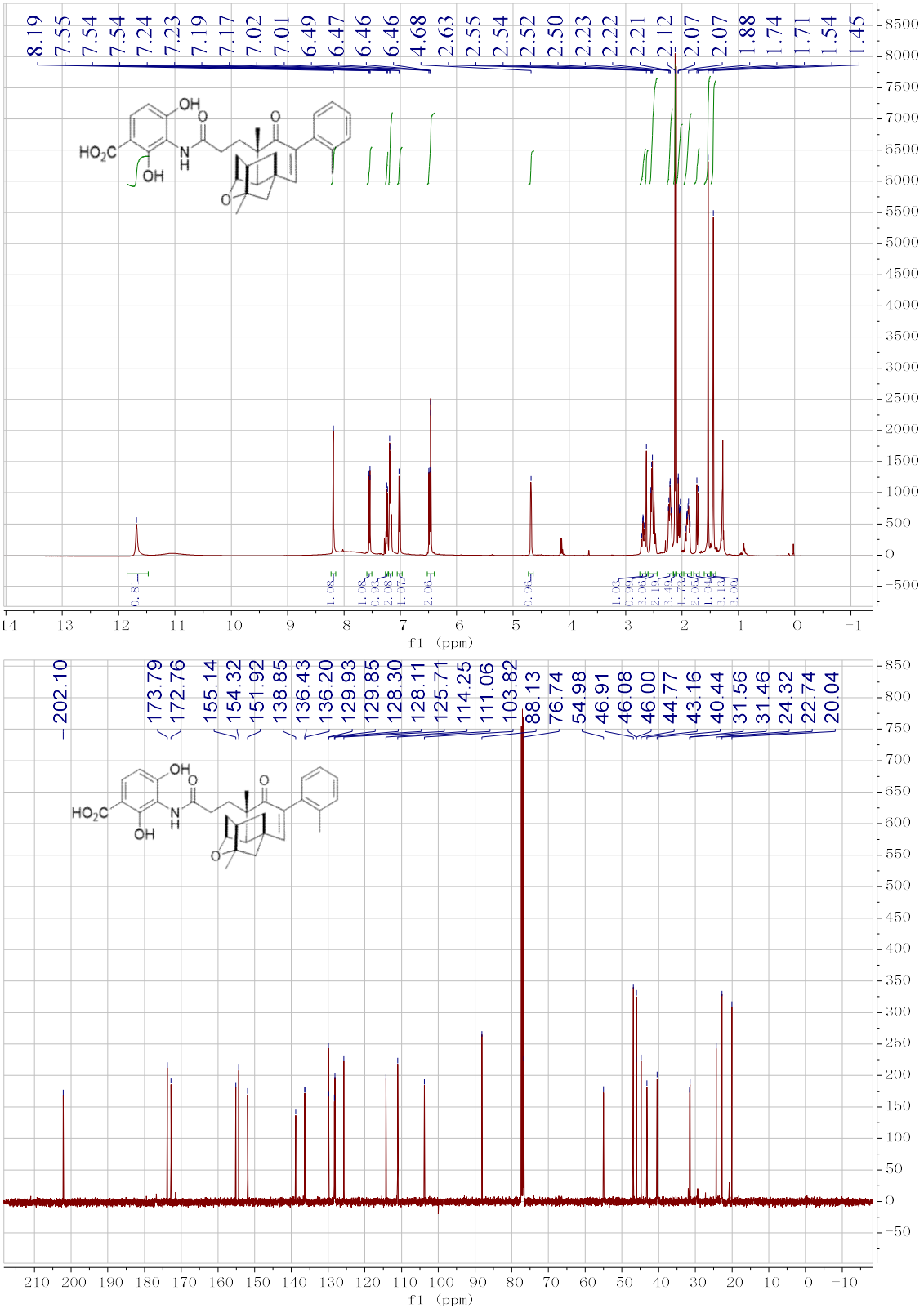


Figure S27. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **6f** in $CDCl_3$.

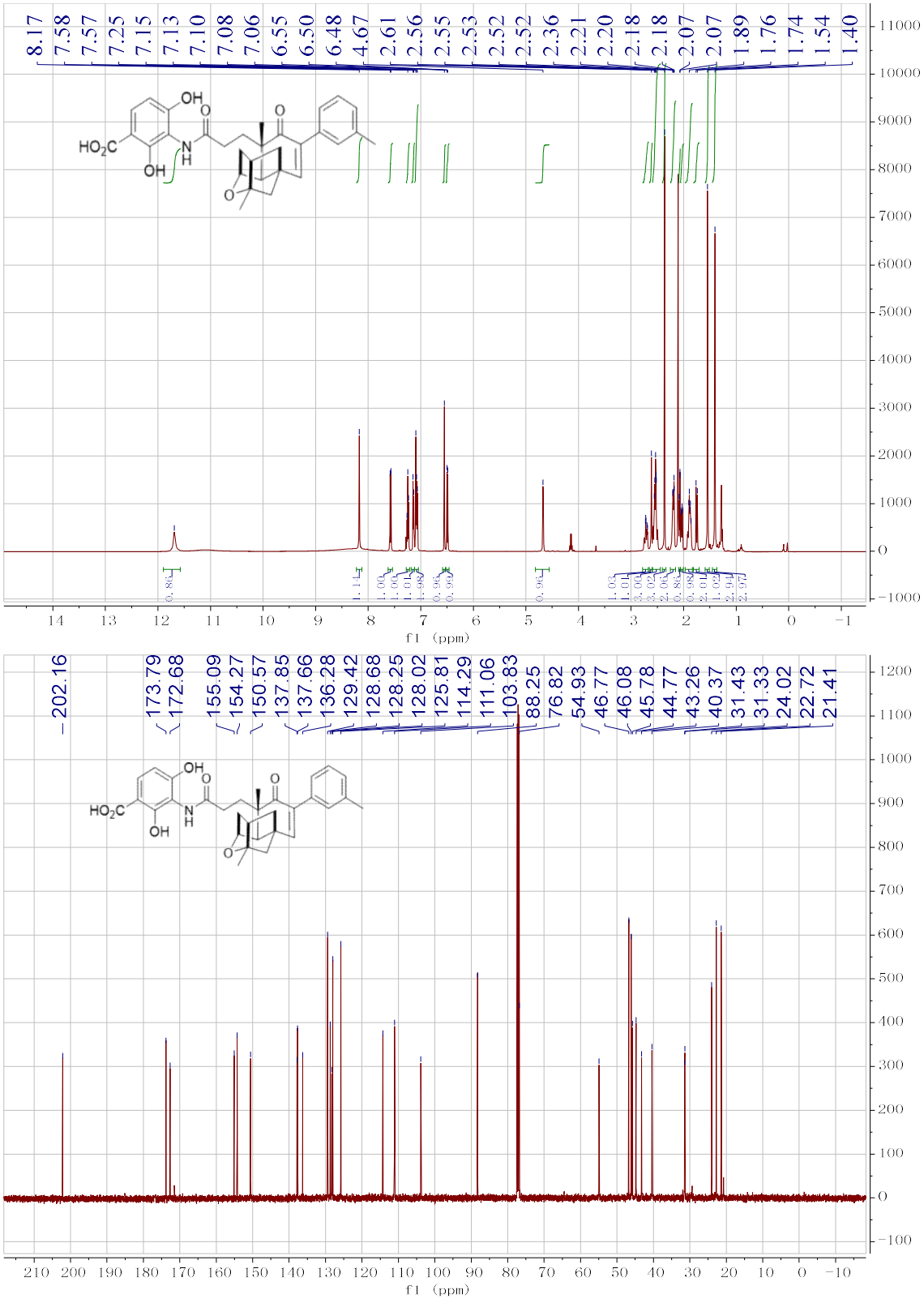


Figure S28. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **6g** in $CDCl_3$.

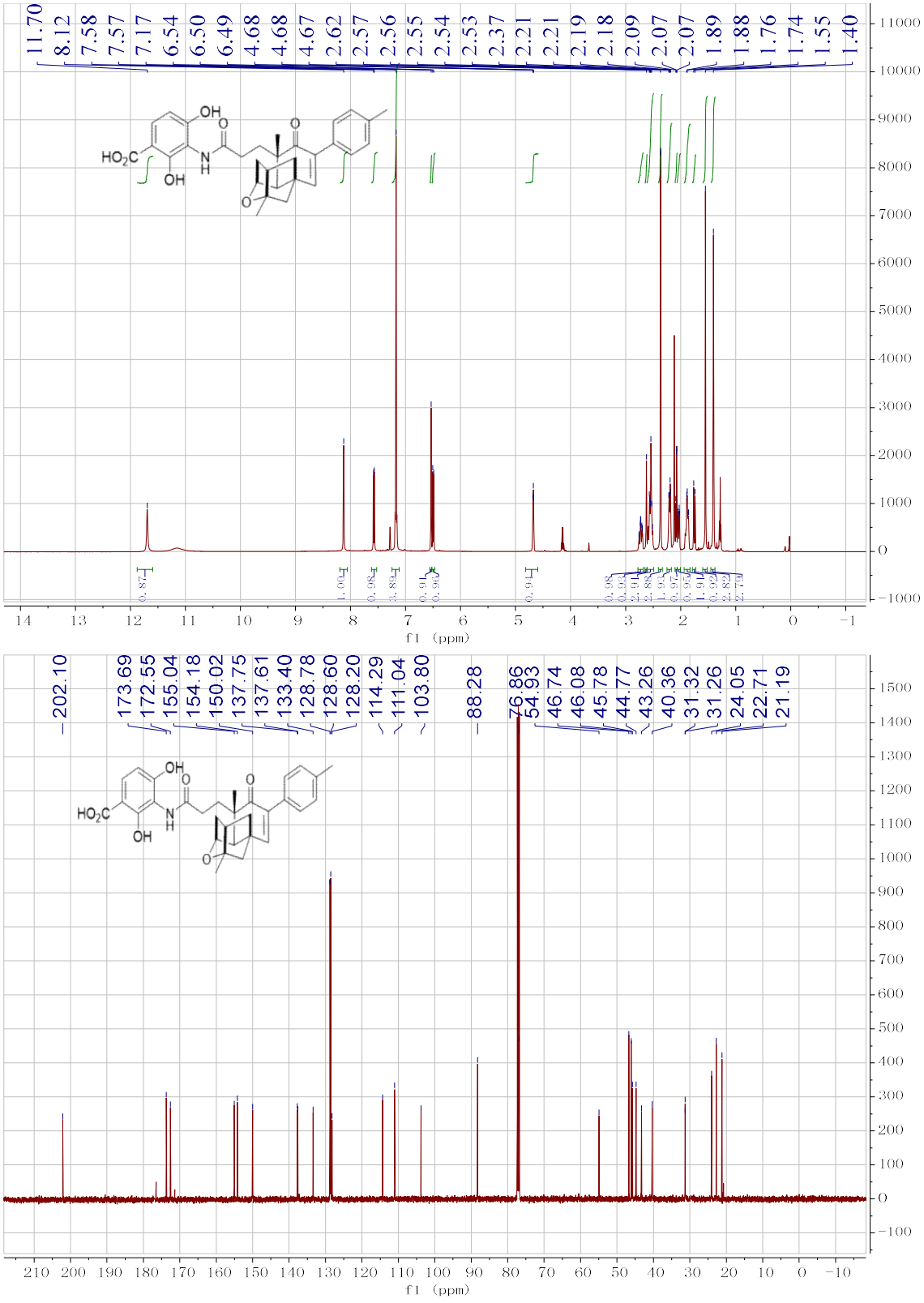


Figure S29. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **6h** in $CDCl_3$.

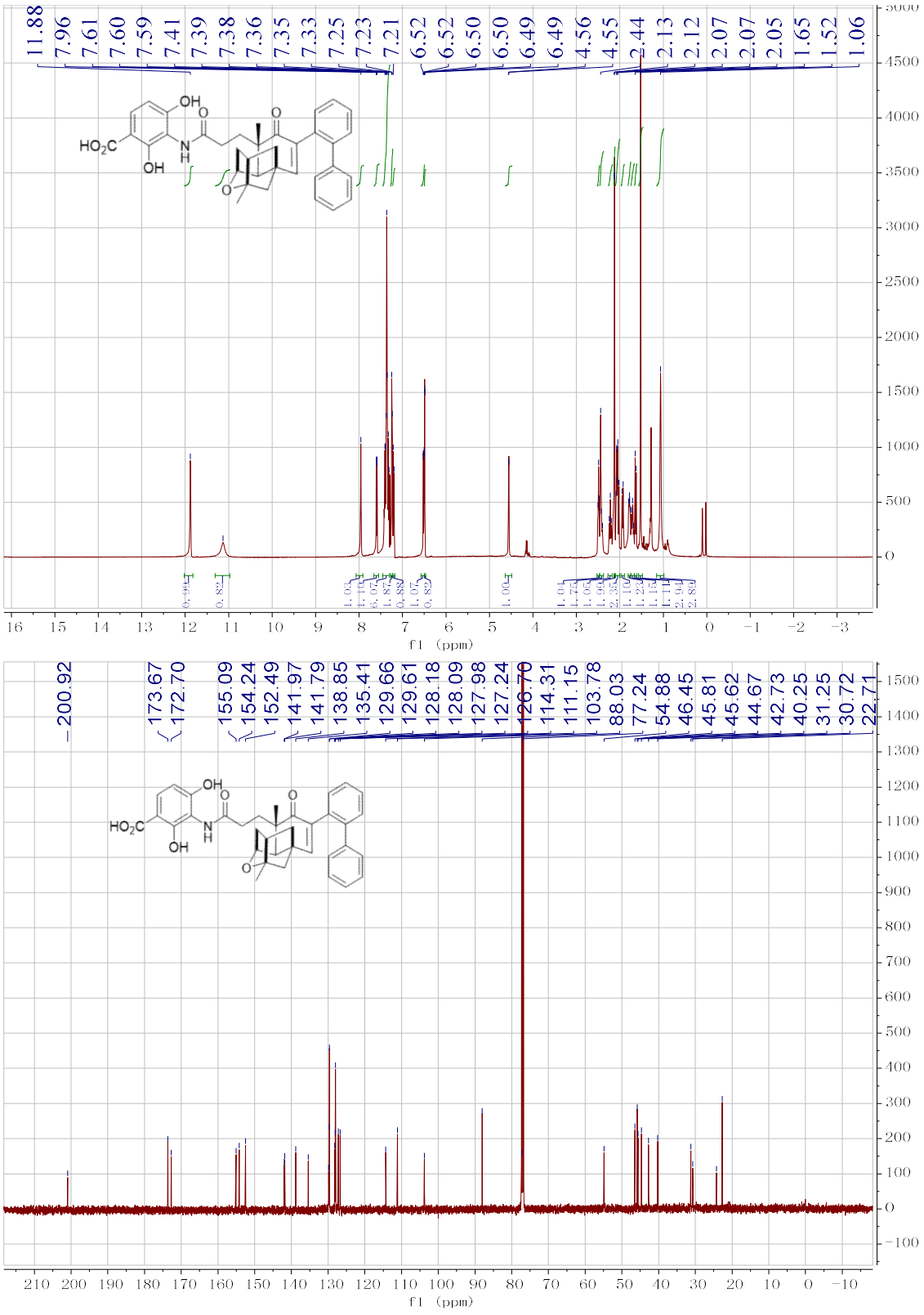


Figure S30. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6i** in $CDCl_3$.

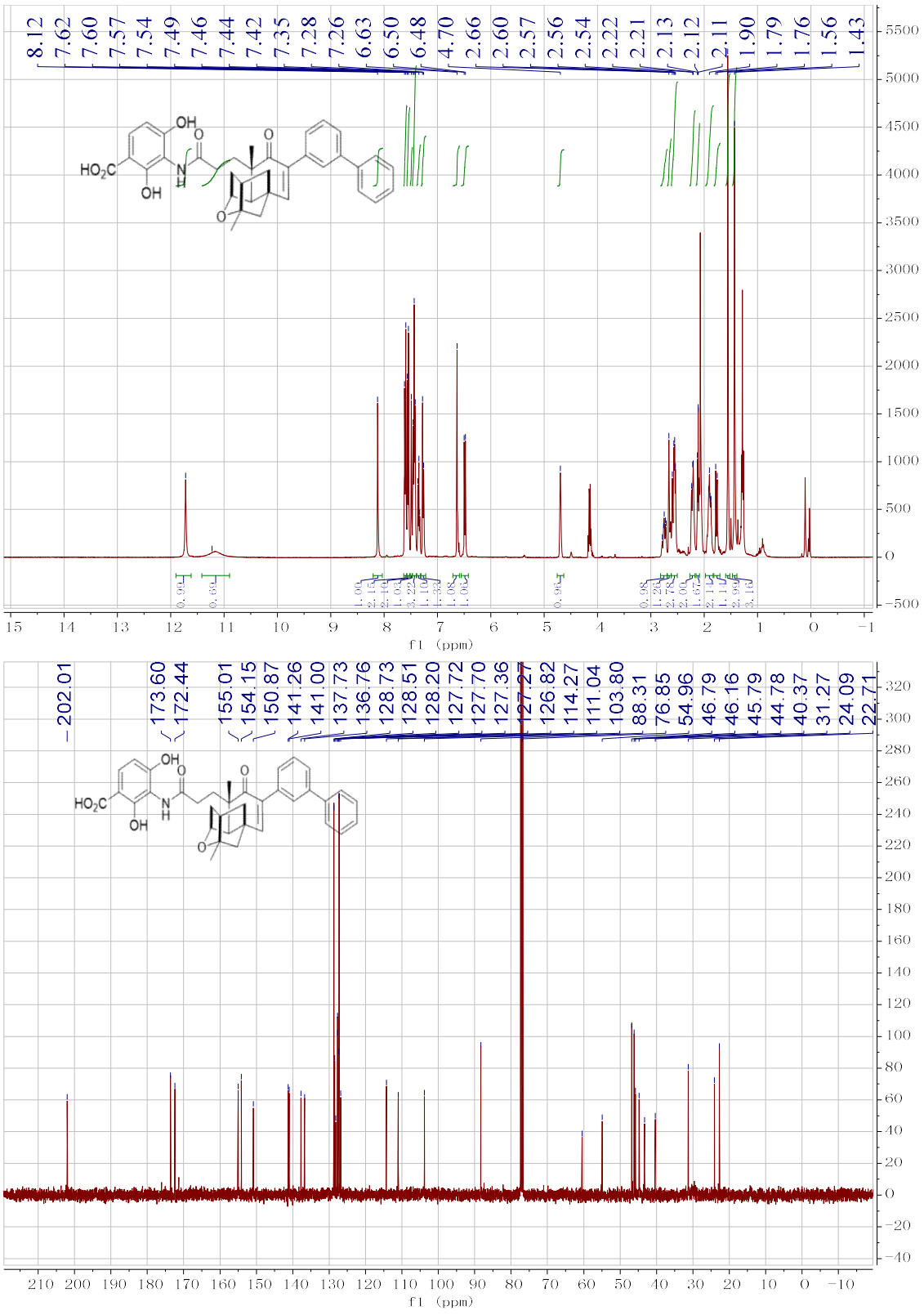


Figure S31. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6j** in $CDCl_3$.

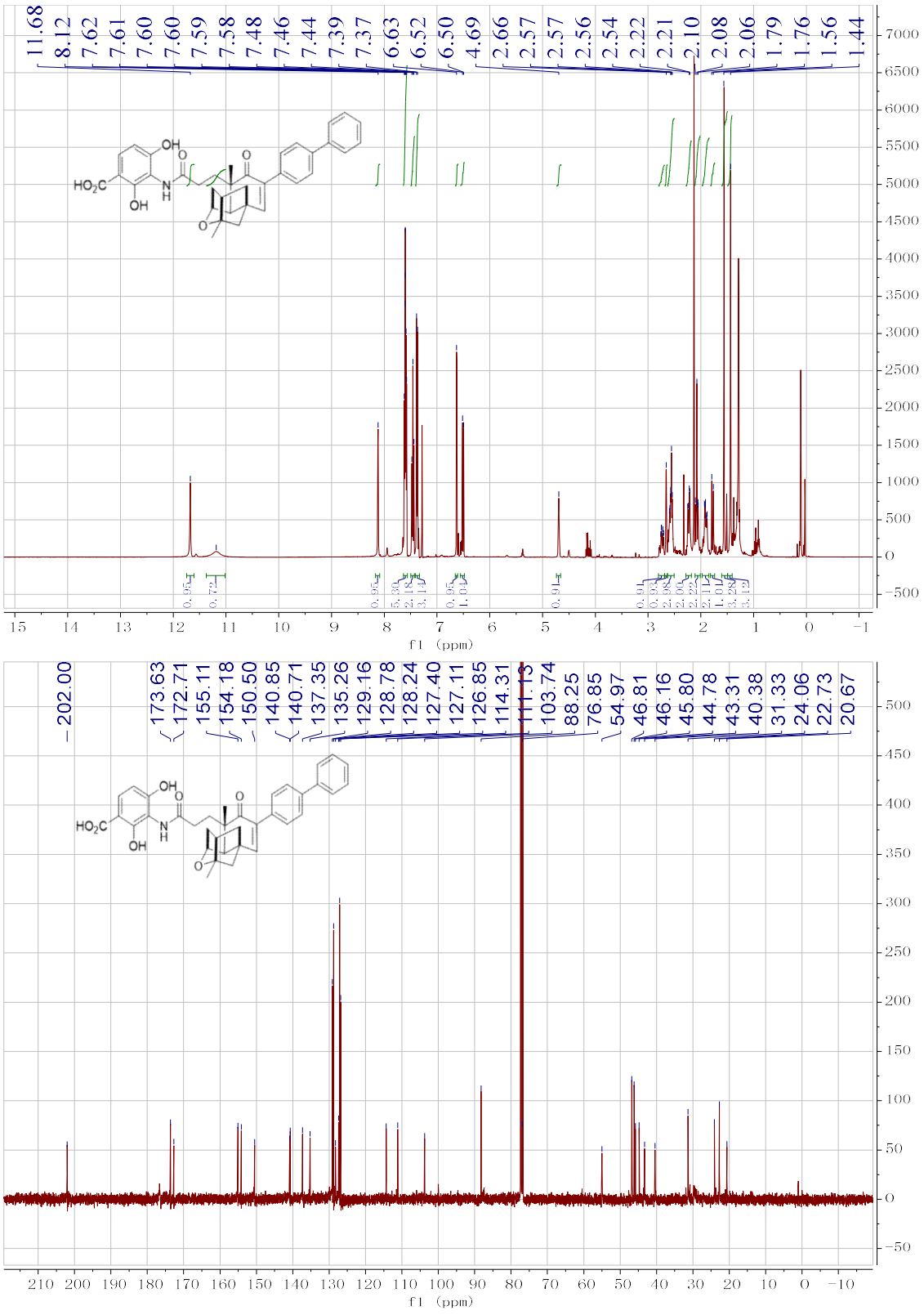


Figure S32. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **6k** in $CDCl_3$.

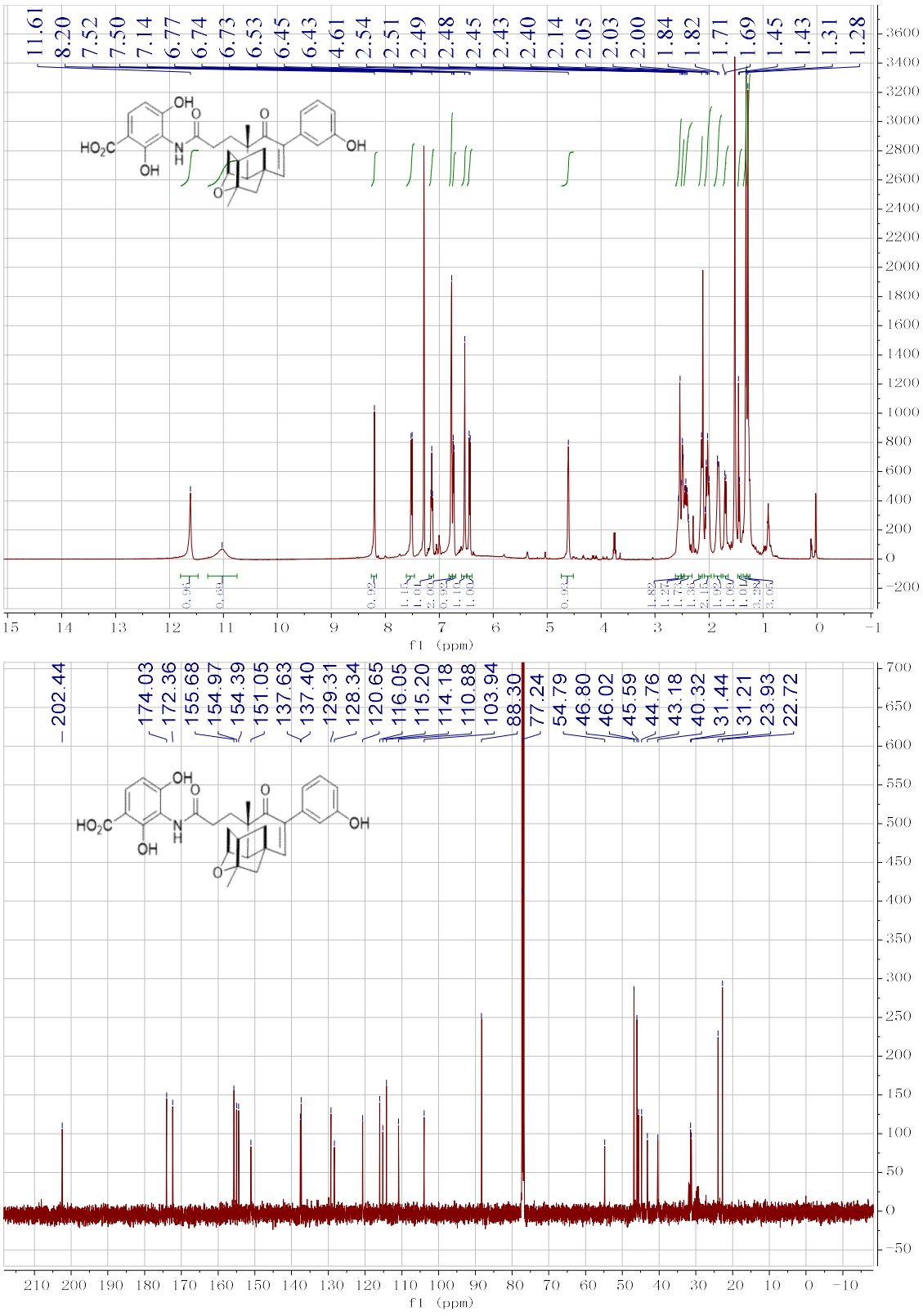


Figure S33. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6l** in $CDCl_3$.

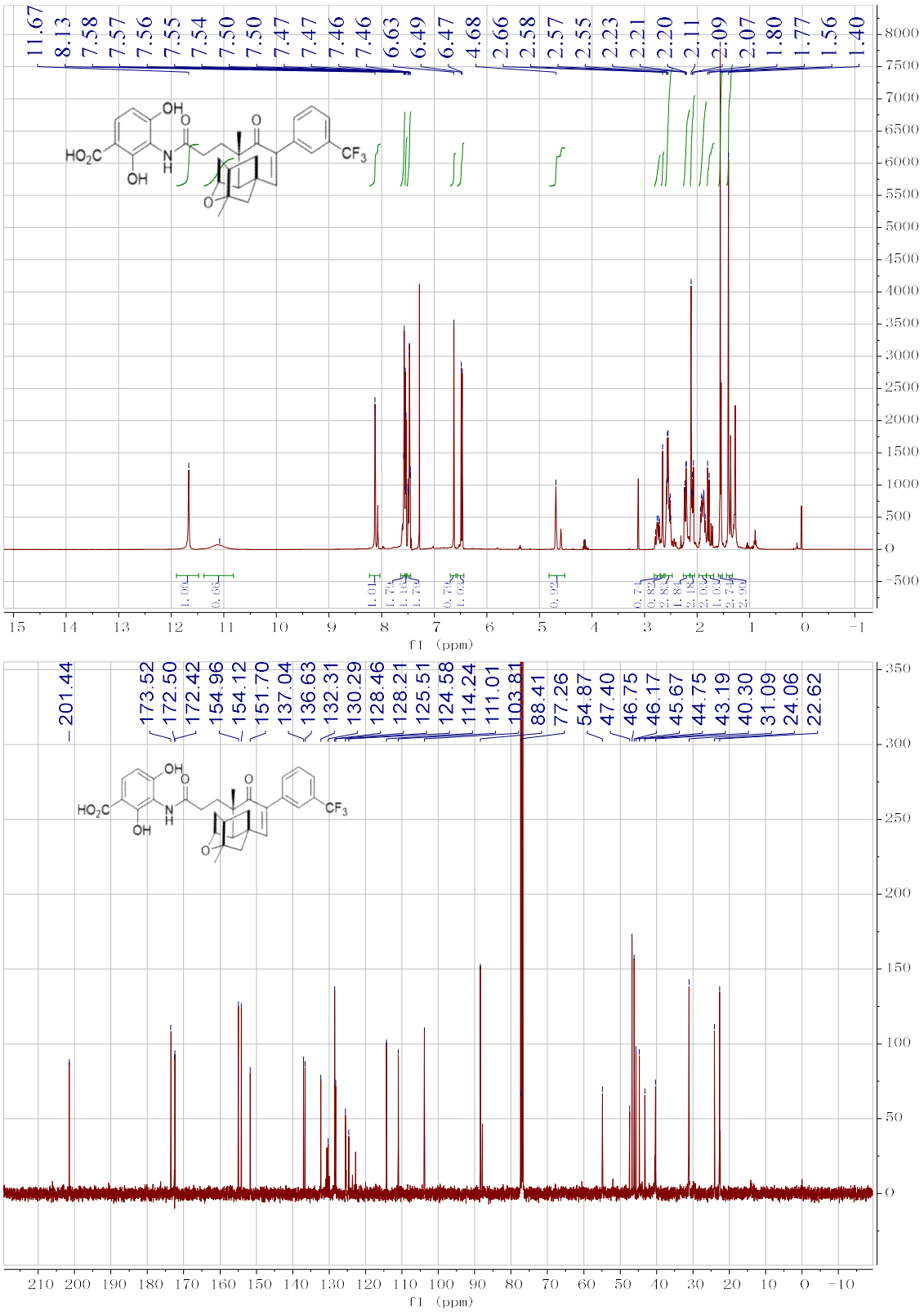


Figure S34. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6m** in $CDCl_3$.

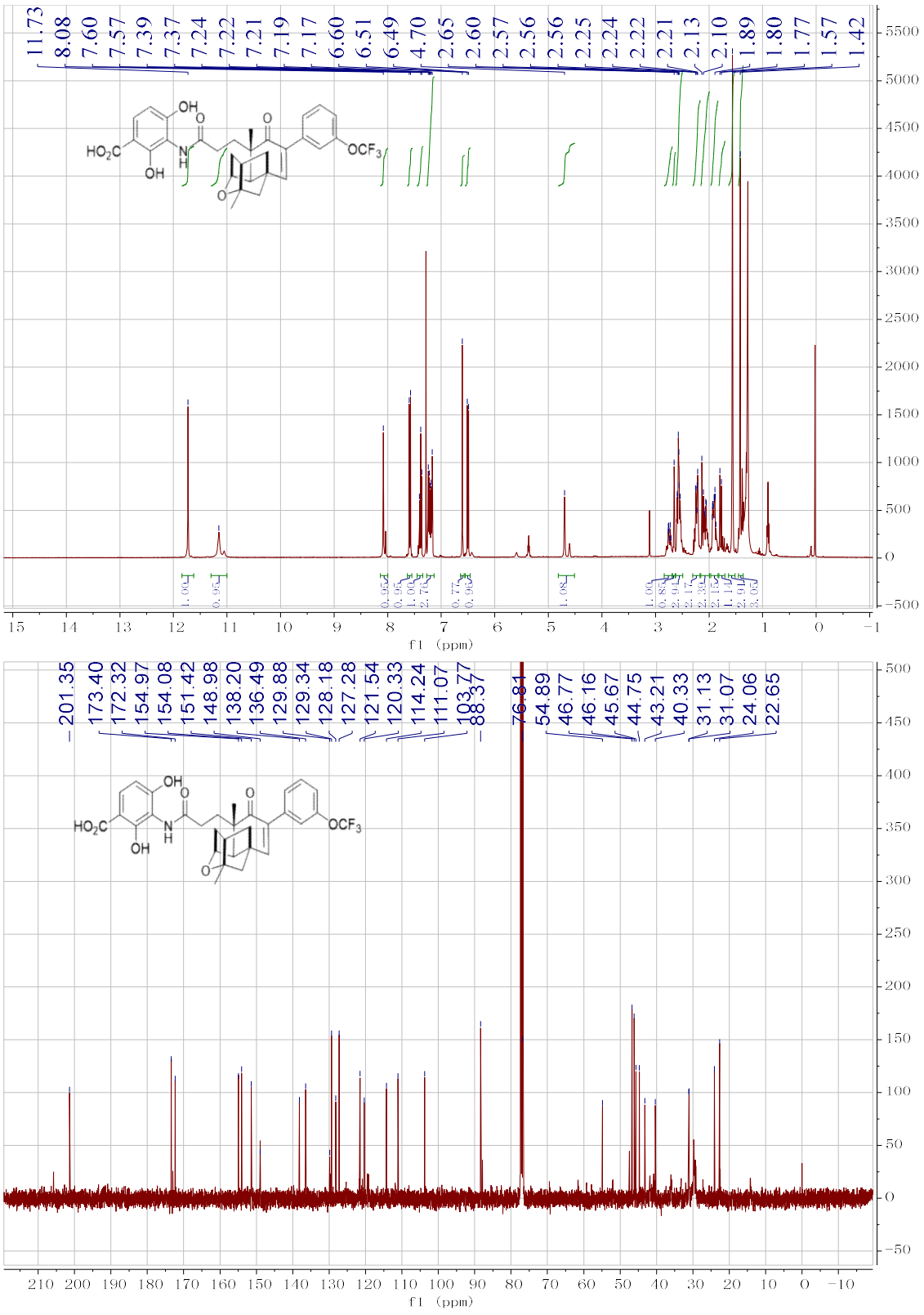


Figure S35. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6n** in $CDCl_3$.

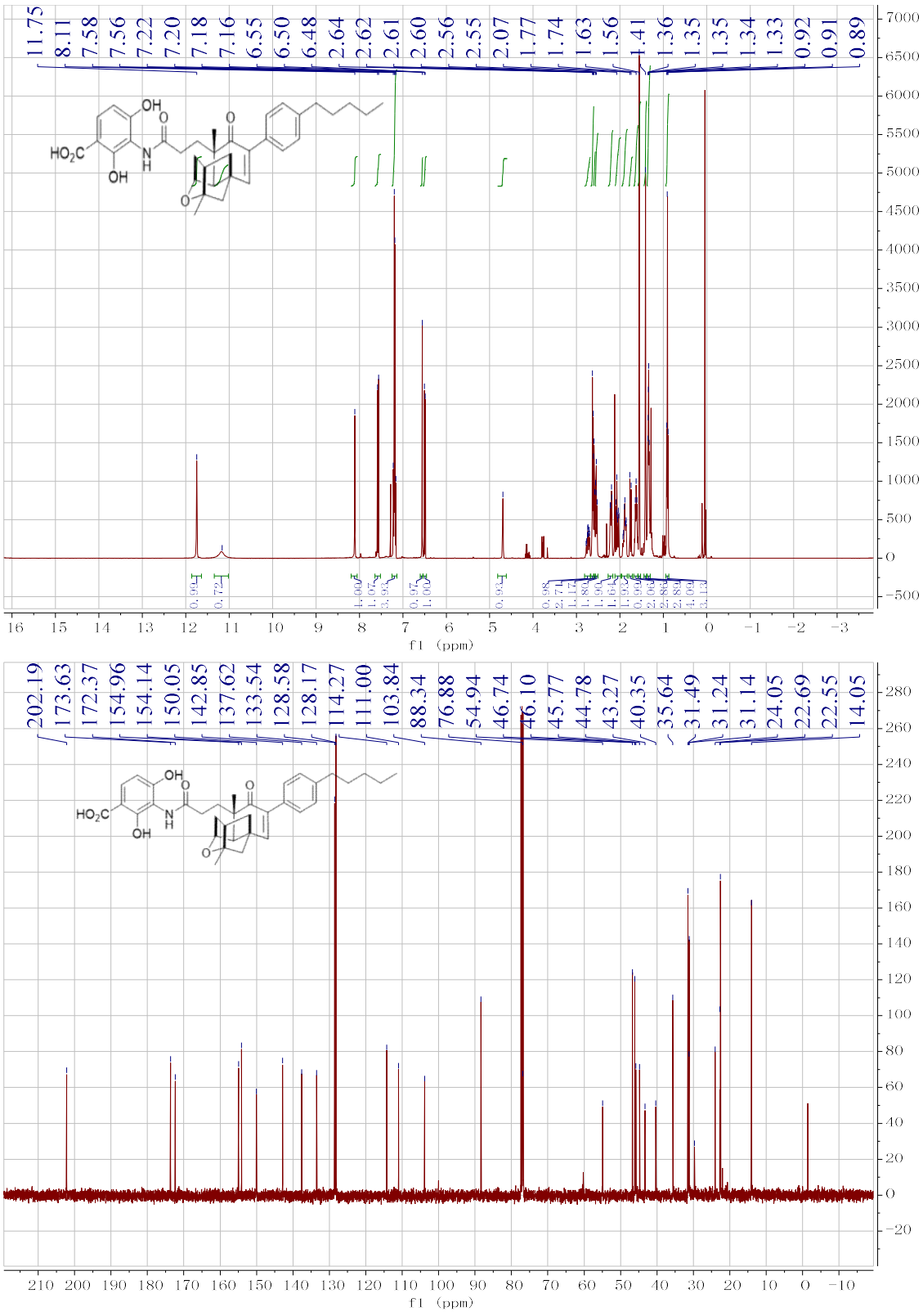


Figure S36. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6o** in $CDCl_3$.

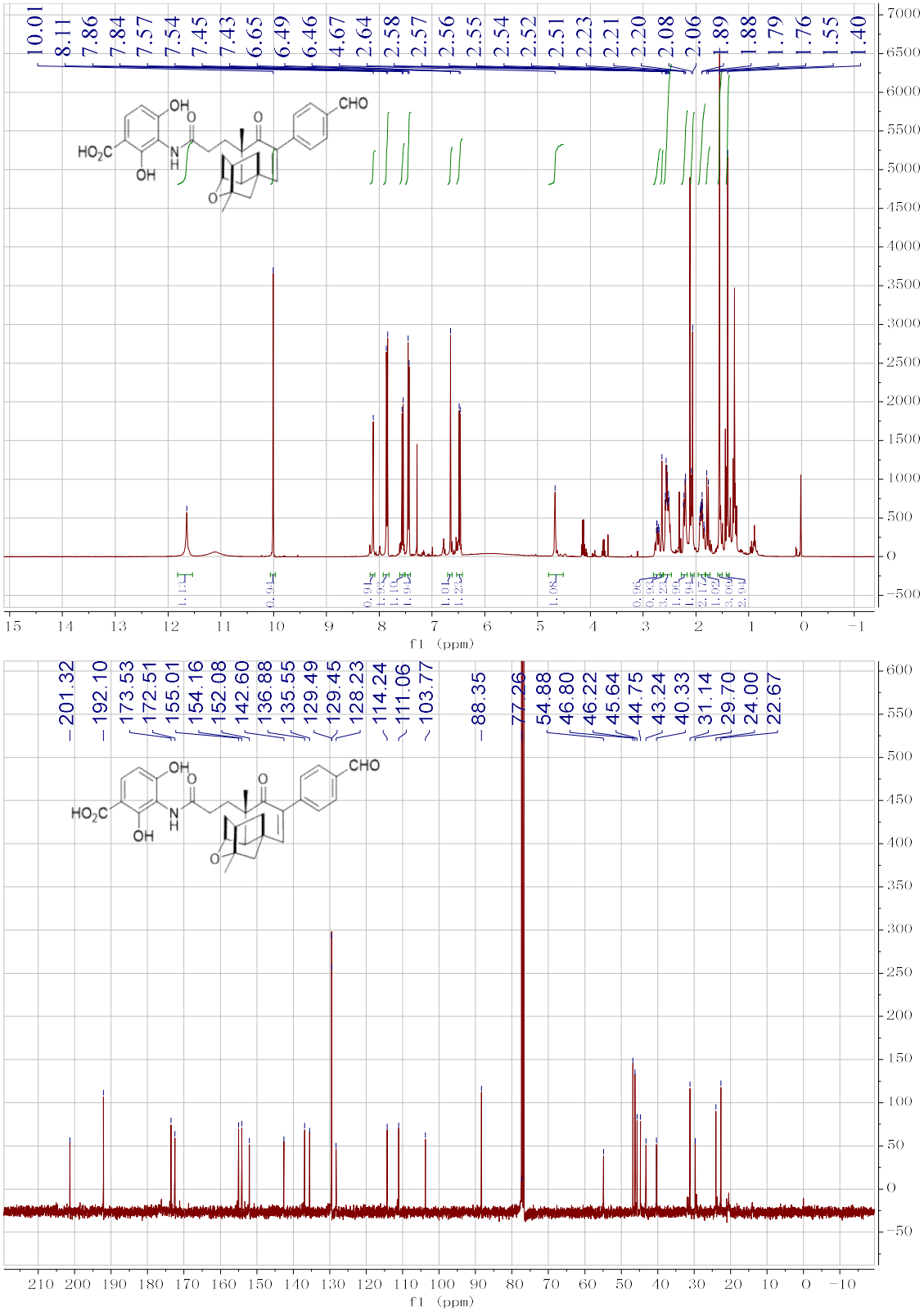


Figure S37. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6p** in $CDCl_3$.

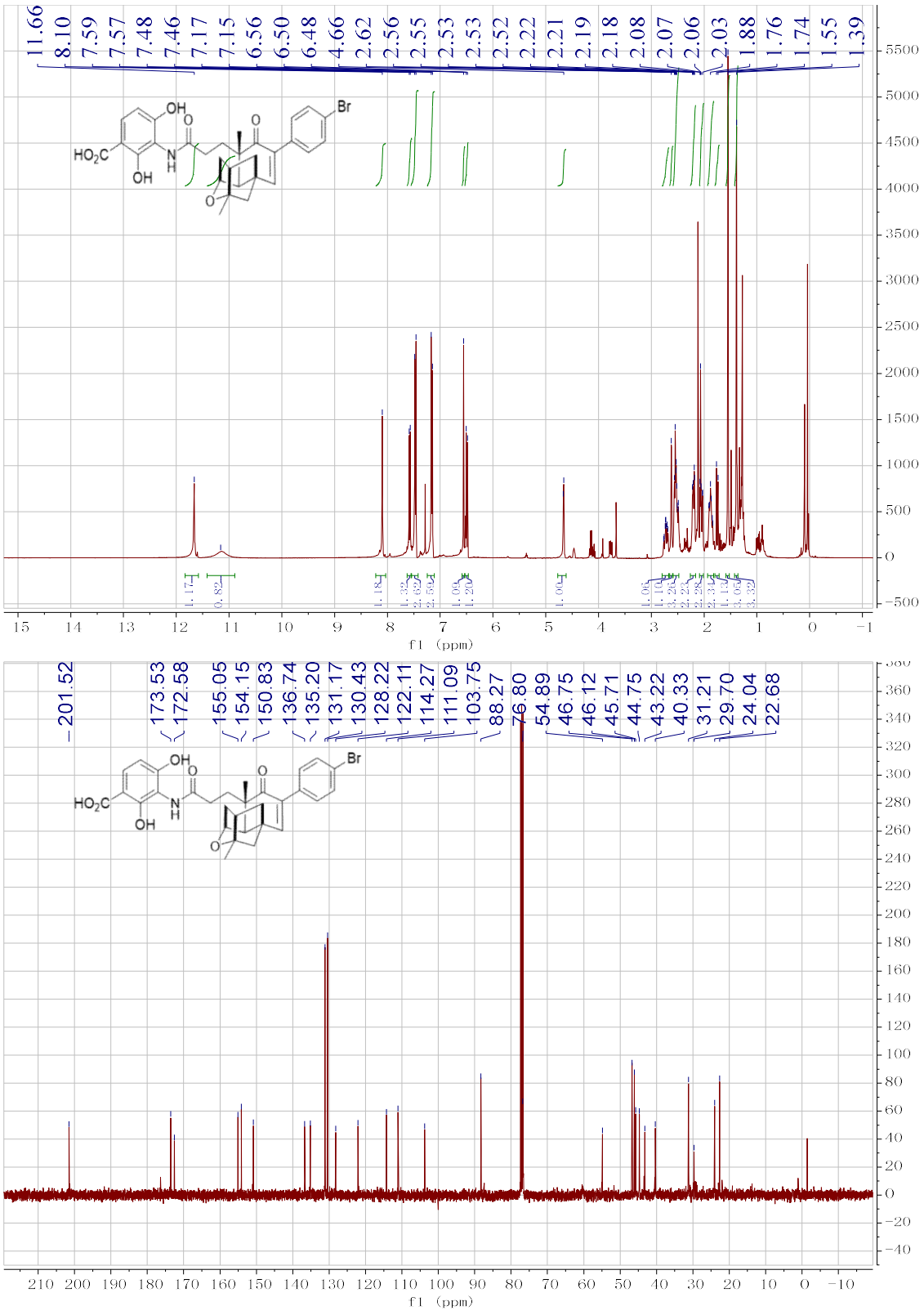


Figure S38. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6q** in $CDCl_3$.

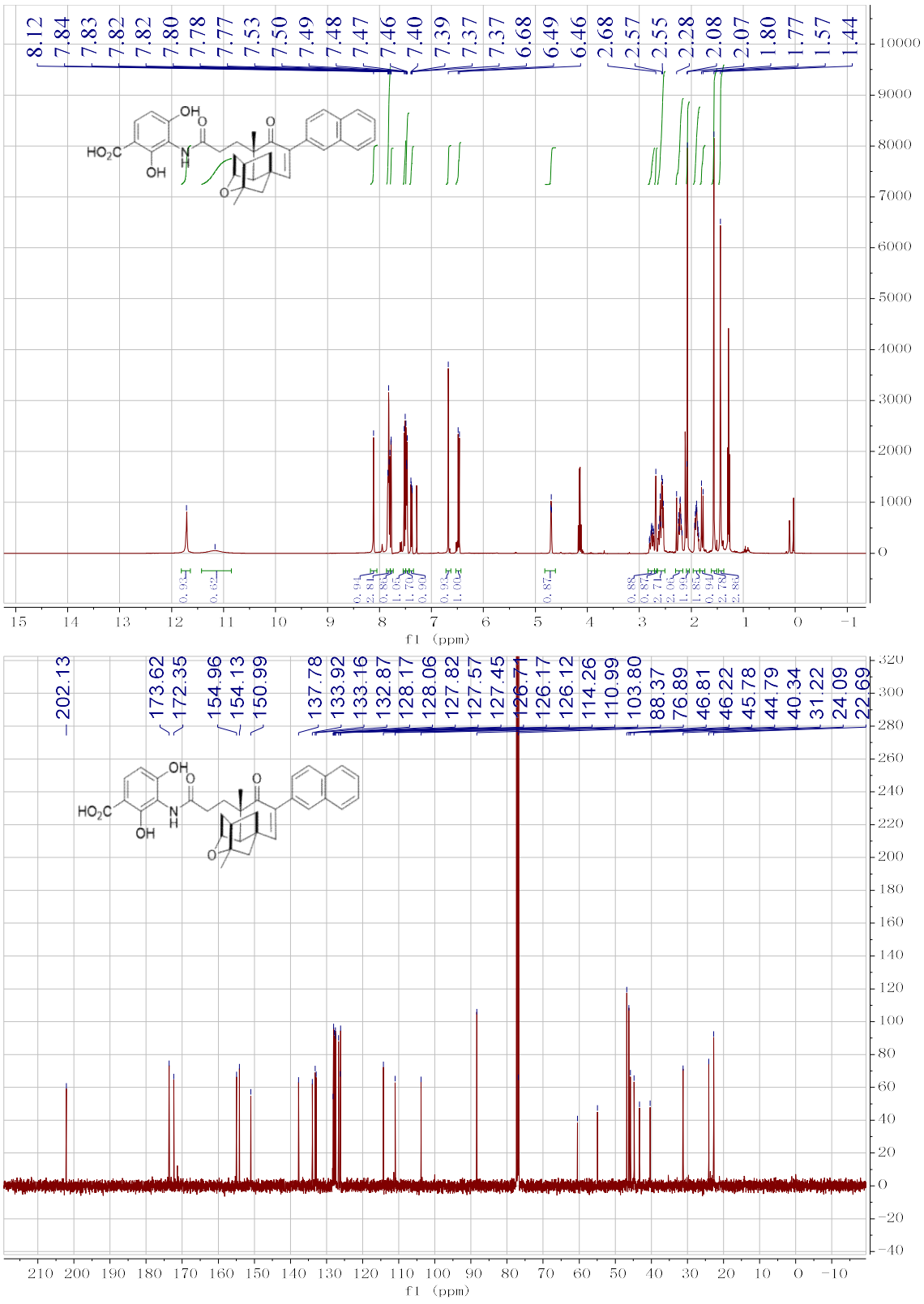


Figure S39. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6r** in $CDCl_3$.

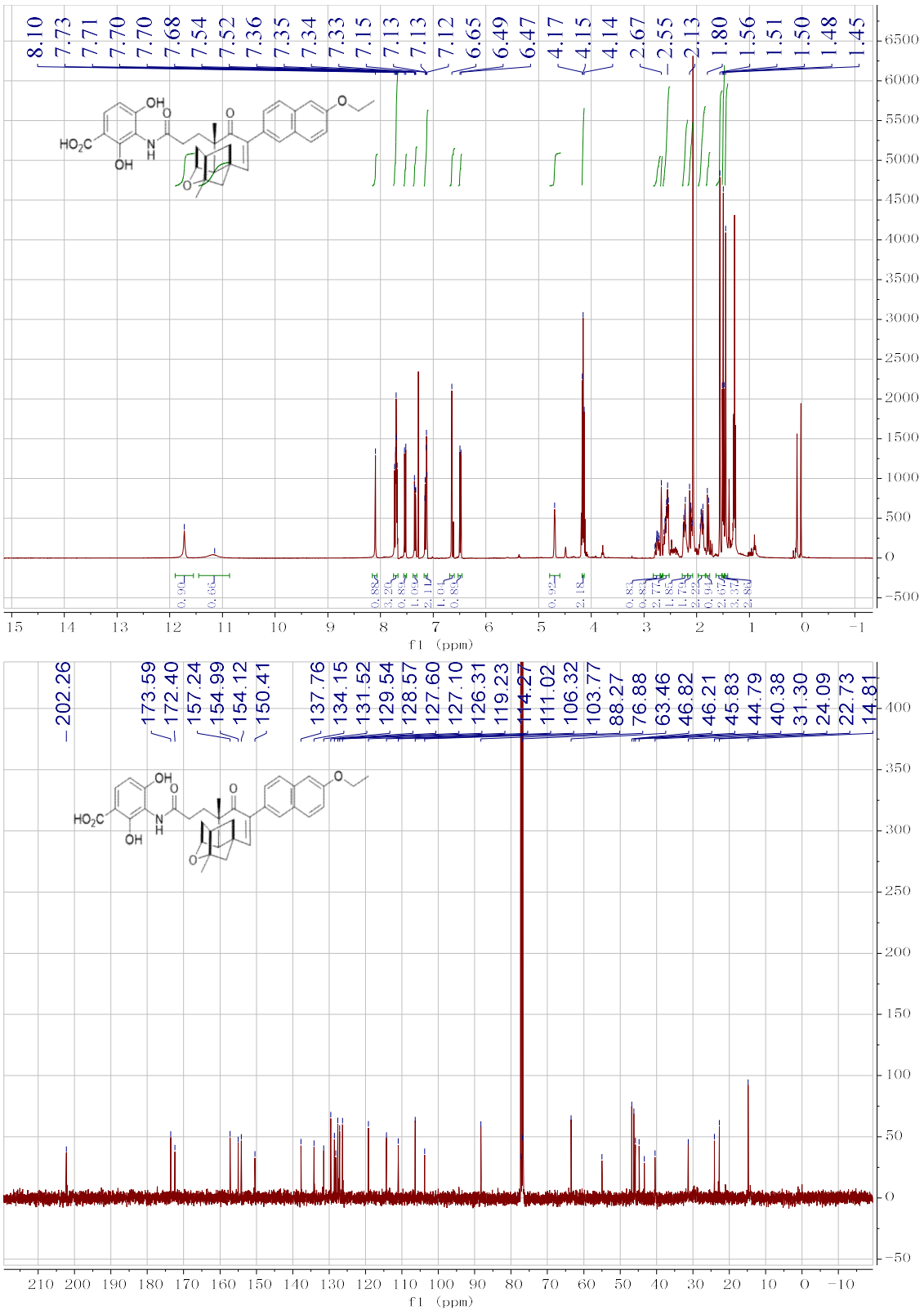


Figure S40. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectrum of **6s** in $CDCl_3$.

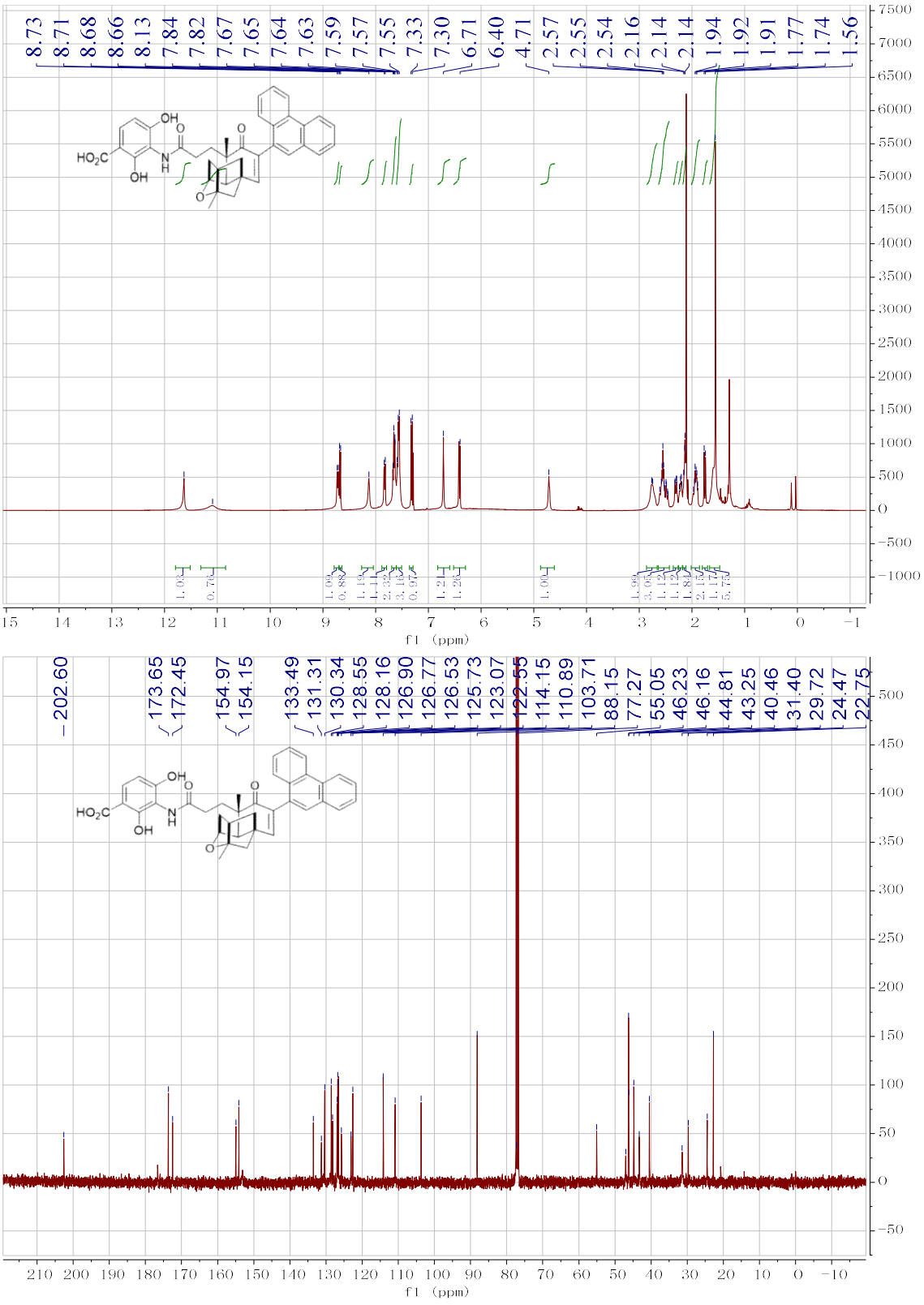


Figure S41. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectrum of **6t** in $CDCl_3$.

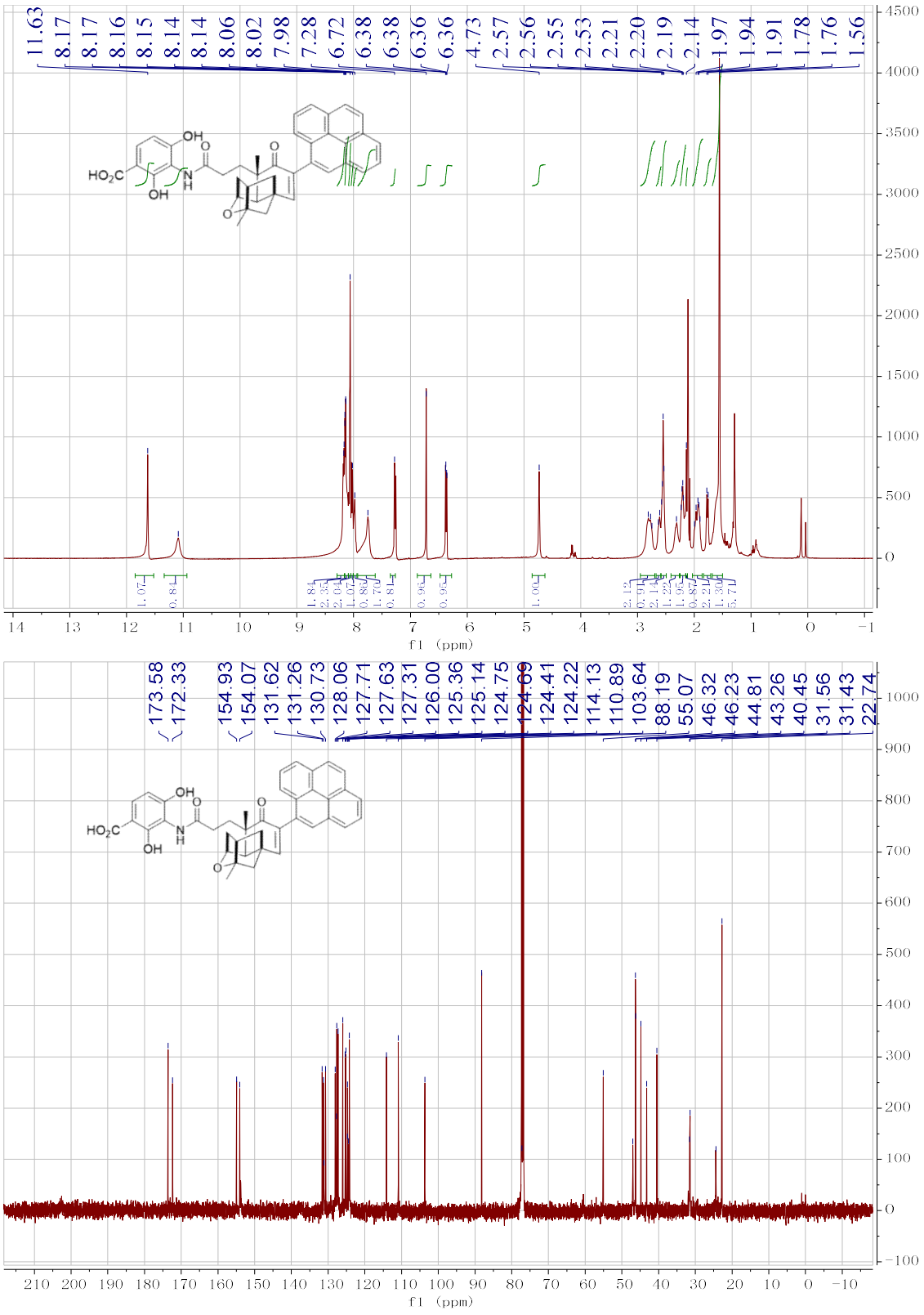


Figure S42. HRMS spectrum of **iodo-PTA ester**.

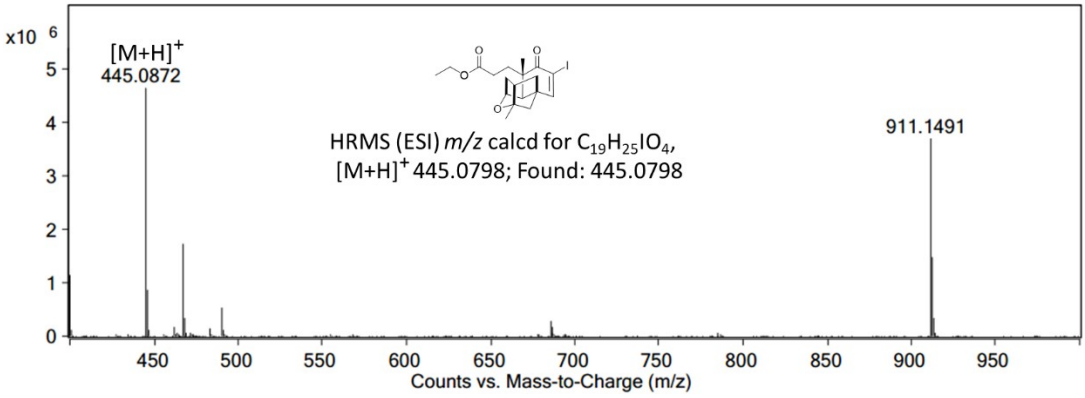
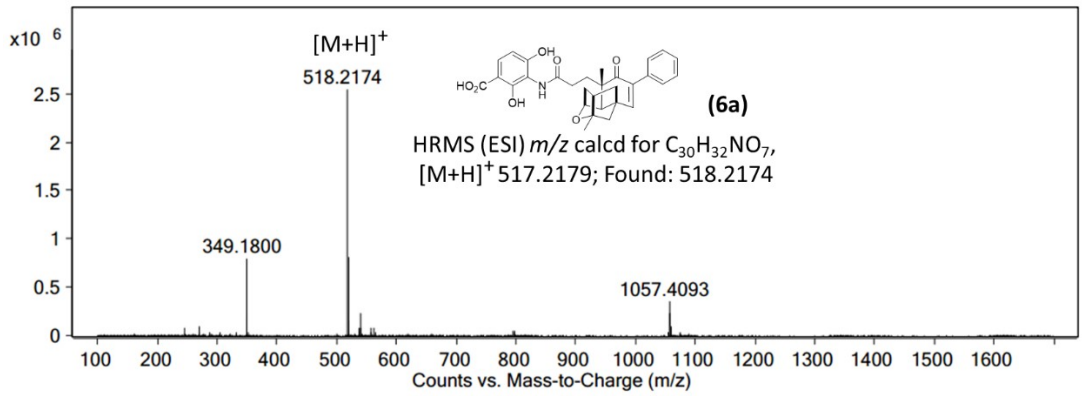
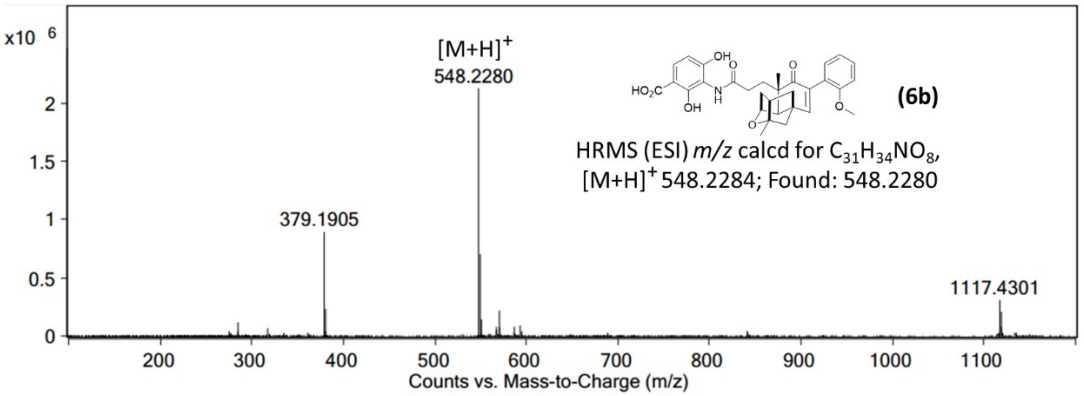
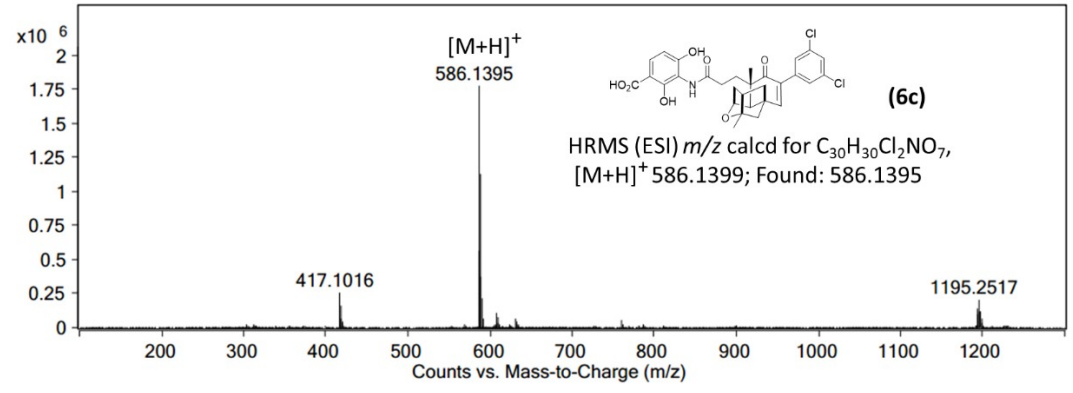
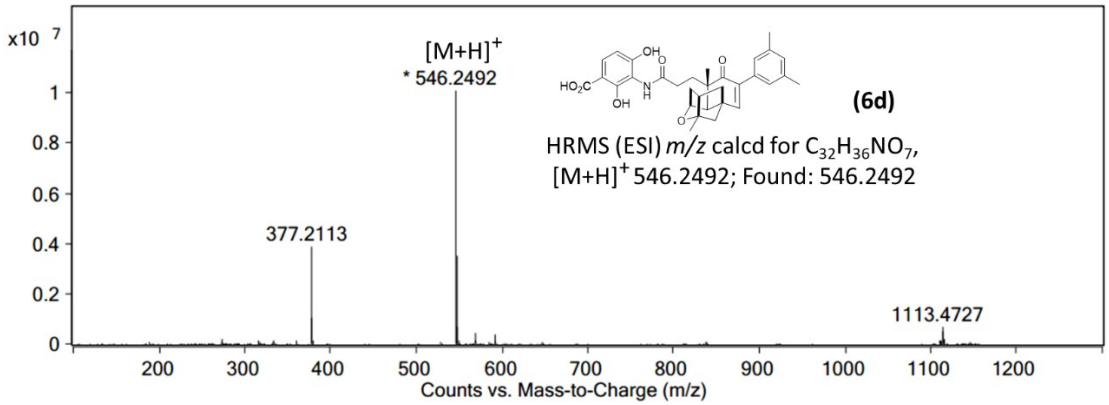


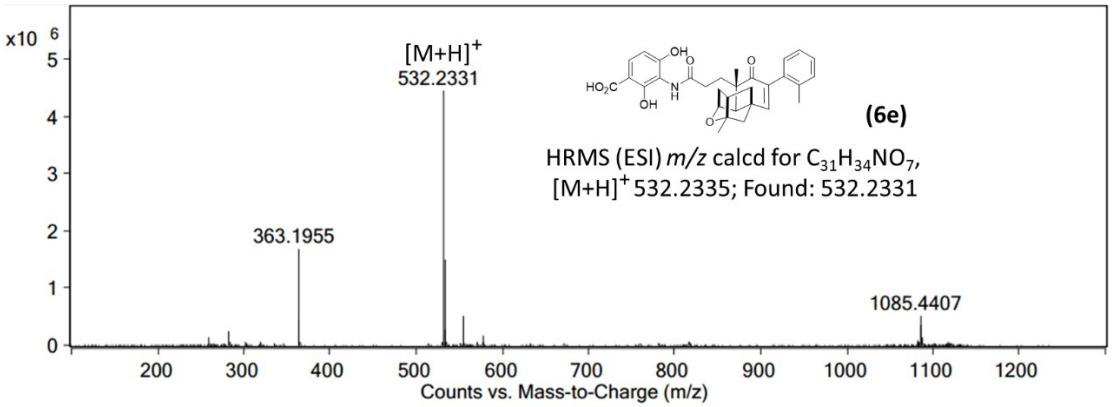
Figure S43. HRMS spectrum of **6a – 6t**.

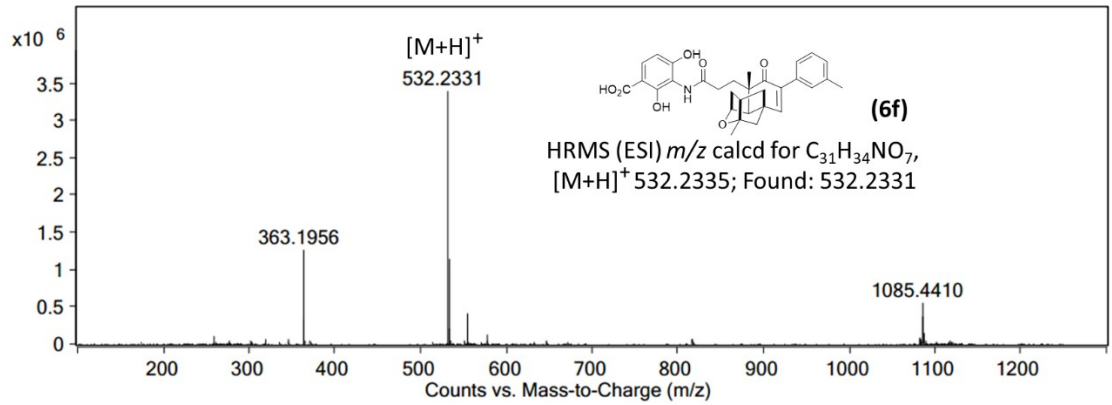


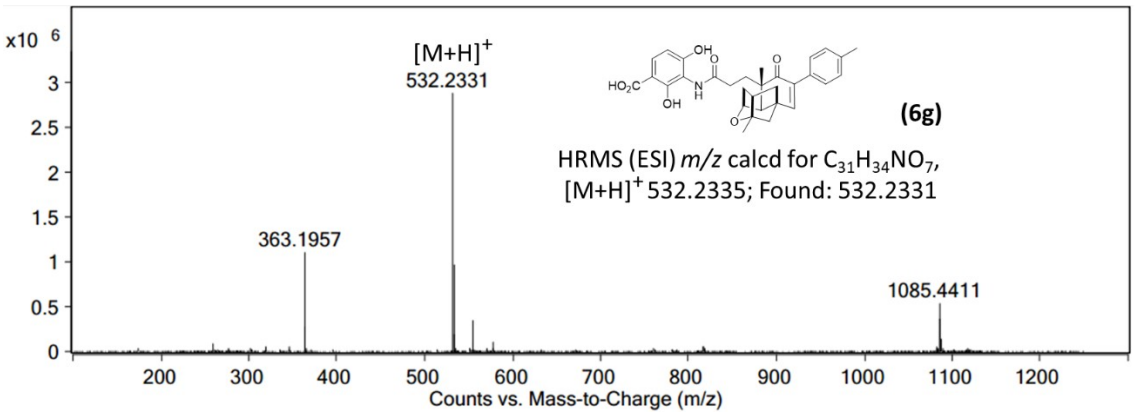


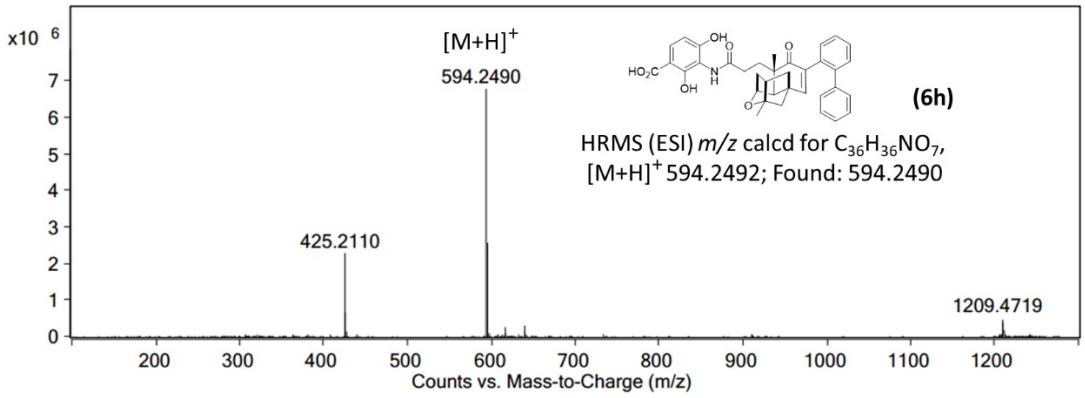



x10 7
[M+H]+
* 546.2492
377.2113
1113.4727
(6d)
HRMS (ESI) m/z calcd for C32H36NO7,
[M+H]+ 546.2492; Found: 546.2492
Counts vs. Mass-to-Charge (m/z)


x10 6
[M+H]+
532.2331
363.1955
1085.4407
(6e)
HRMS (ESI) m/z calcd for C31H34NO7,
[M+H]+ 532.2335; Found: 532.2331
Counts vs. Mass-to-Charge (m/z)

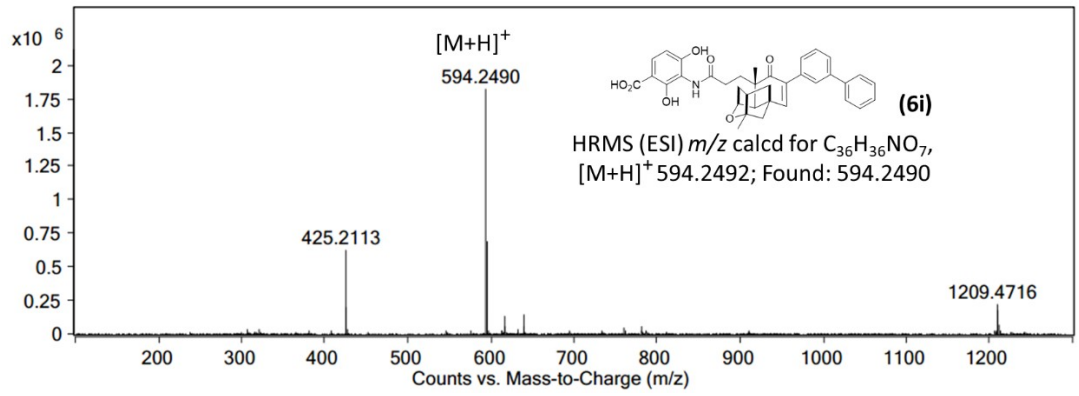

x10 6
[M+H]+
532.2331
363.1956
1085.4410
(6f)
HRMS (ESI) m/z calcd for C31H34NO7,
[M+H]+ 532.2335; Found: 532.2331
Counts vs. Mass-to-Charge (m/z)


x10 6
[M+H]+
532.2331
363.1957
1085.4411
(6g)
HRMS (ESI) m/z calcd for C31H34NO7,
[M+H]+ 532.2335; Found: 532.2331
Counts vs. Mass-to-Charge (m/z)



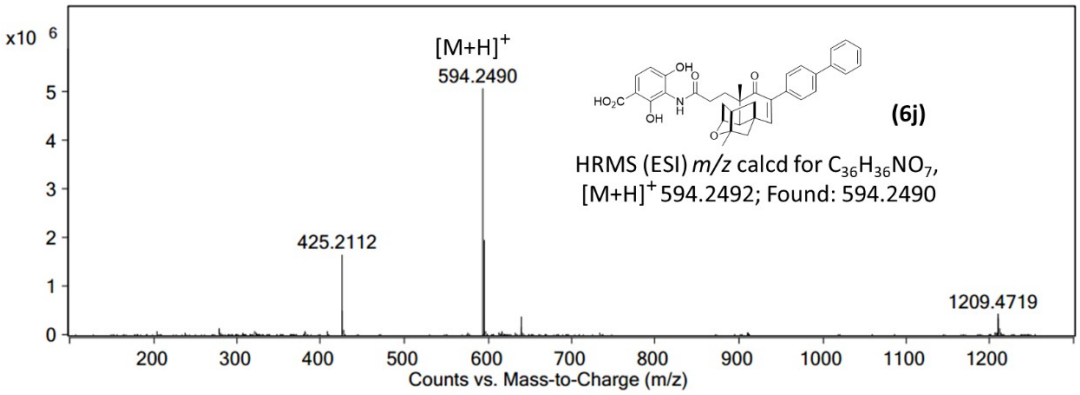
(6h)

HRMS (ESI) *m/z* calcd for $C_{36}H_{36}NO_7$, $[M+H]^+$ 594.2492; Found: 594.2490



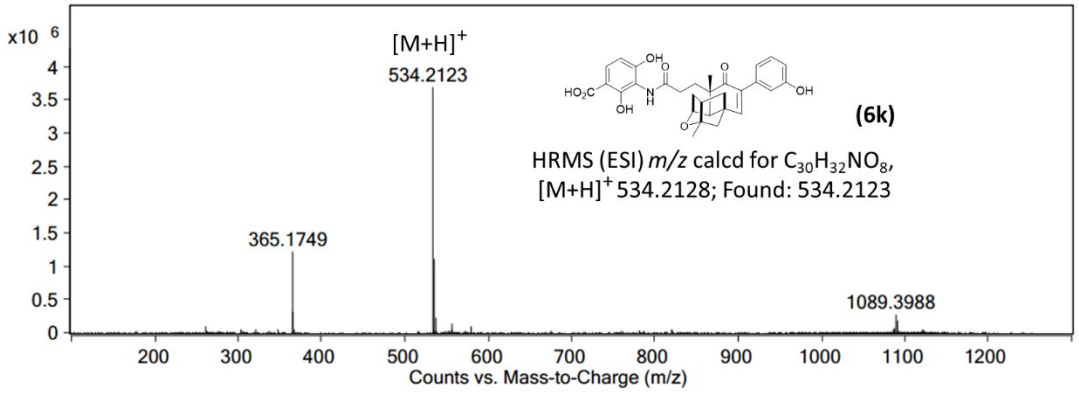
(6i)

HRMS (ESI) *m/z* calcd for $C_{36}H_{36}NO_7$, $[M+H]^+$ 594.2492; Found: 594.2490



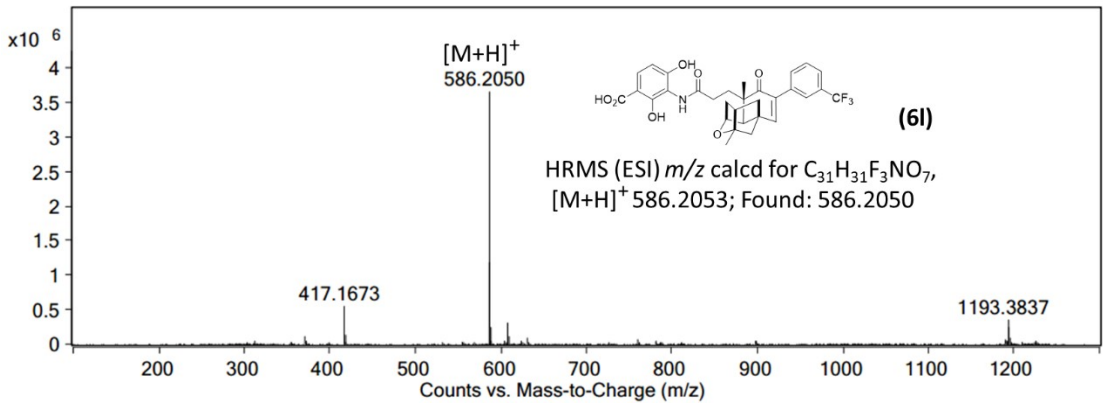
(6j)

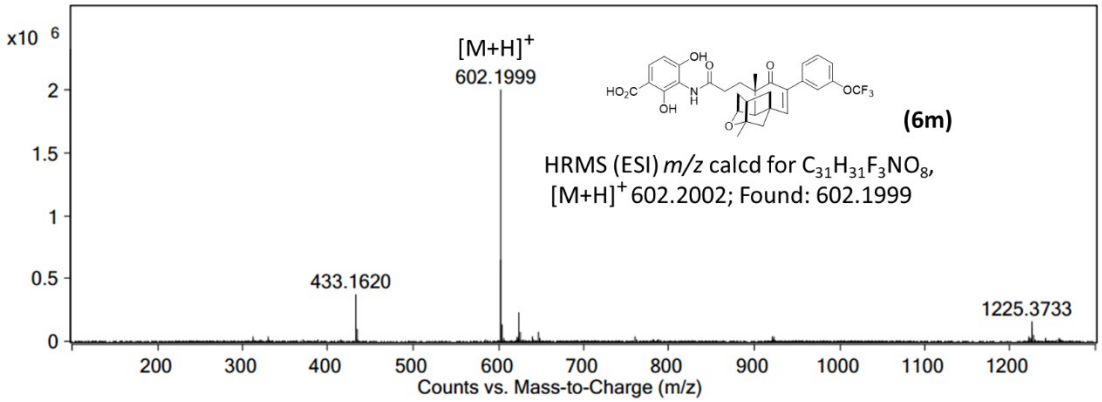
HRMS (ESI) *m/z* calcd for $C_{36}H_{36}NO_7$, $[M+H]^+$ 594.2492; Found: 594.2490

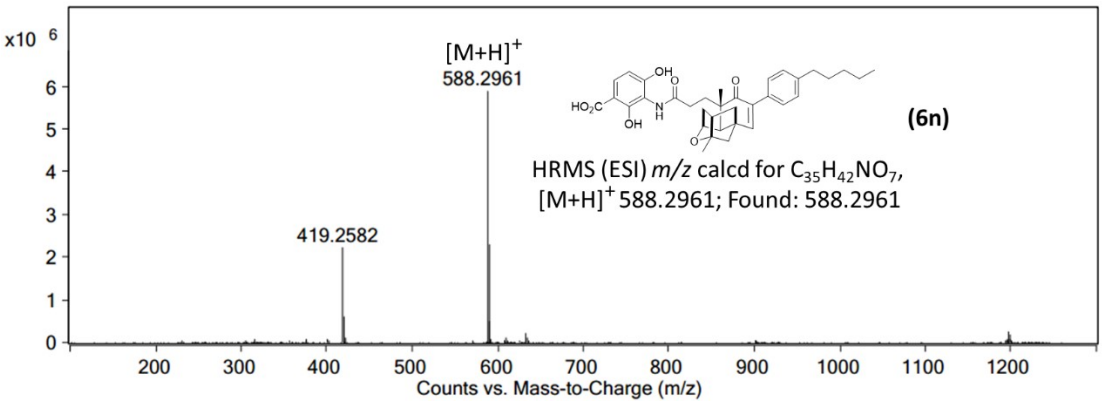


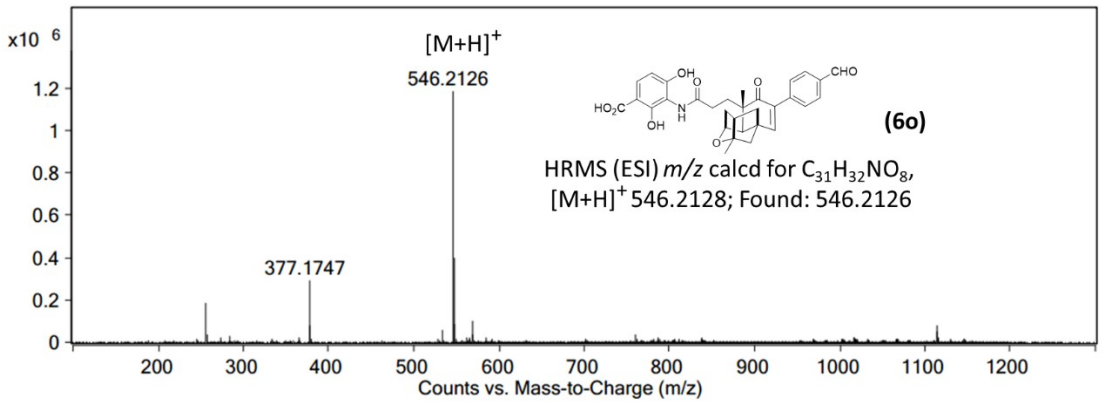
(6k)

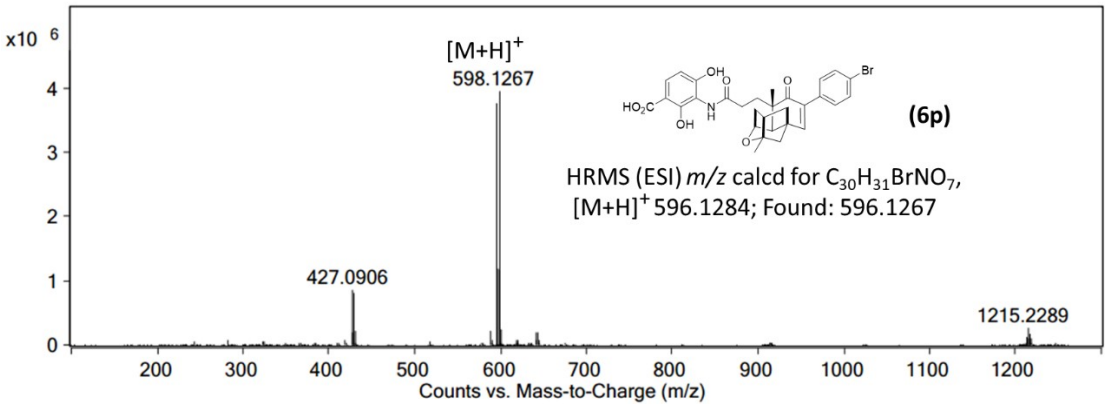
HRMS (ESI) *m/z* calcd for $C_{30}H_{32}NO_8$, $[M+H]^+$ 534.2128; Found: 534.2123

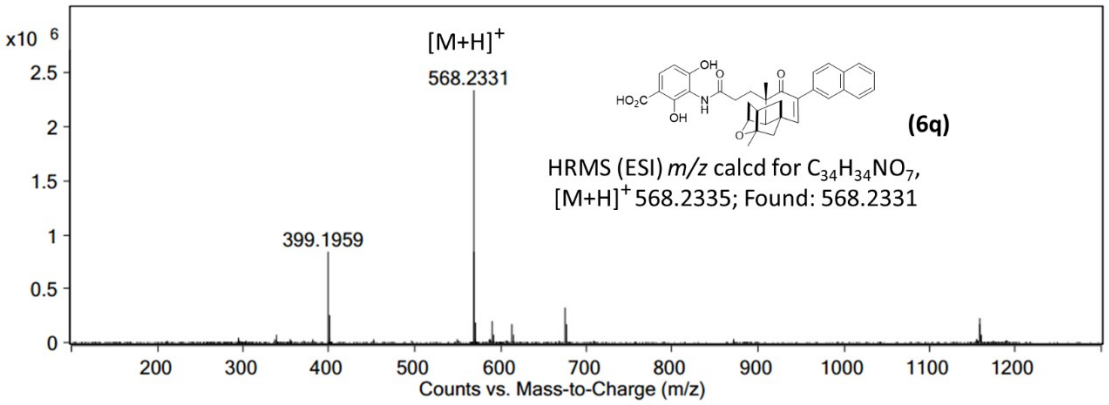

x10 6
[M+H]+
586.2050
417.1673
1193.3837
(6l)
HRMS (ESI) m/z calcd for C31H31F3NO7,
[M+H]+ 586.2053; Found: 586.2050
Counts vs. Mass-to-Charge (m/z)

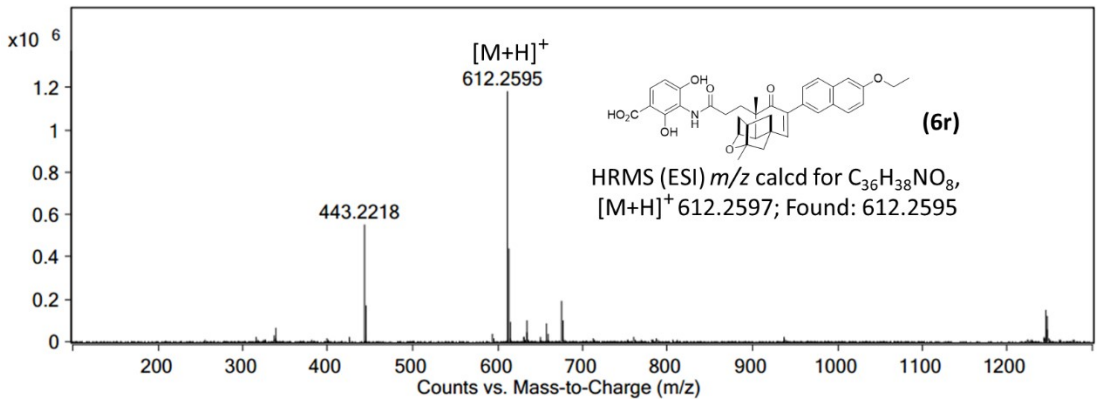

x10 6
[M+H]+
602.1999
433.1620
1225.3733
(6m)
HRMS (ESI) m/z calcd for C31H31F3NO8,
[M+H]+ 602.2002; Found: 602.1999
Counts vs. Mass-to-Charge (m/z)

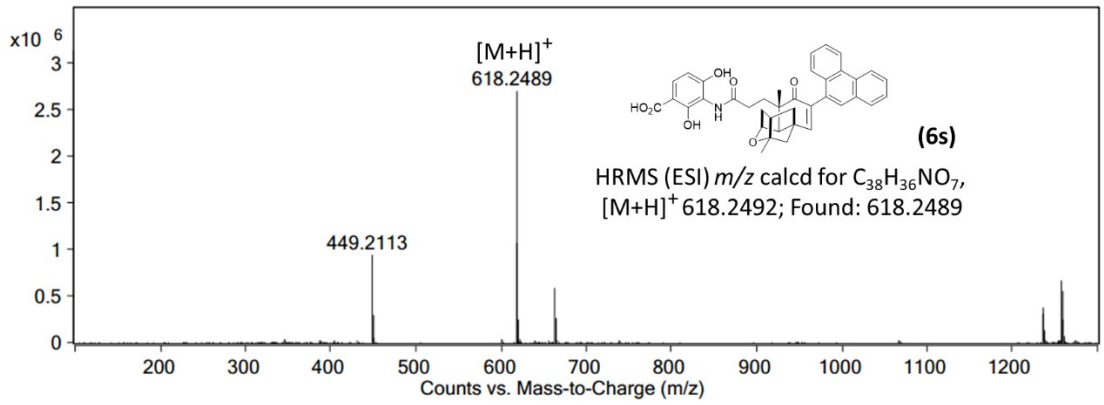

x10 6
[M+H]+
588.2961
419.2582
(6n)
HRMS (ESI) m/z calcd for C35H42NO7,
[M+H]+ 588.2961; Found: 588.2961
Counts vs. Mass-to-Charge (m/z)

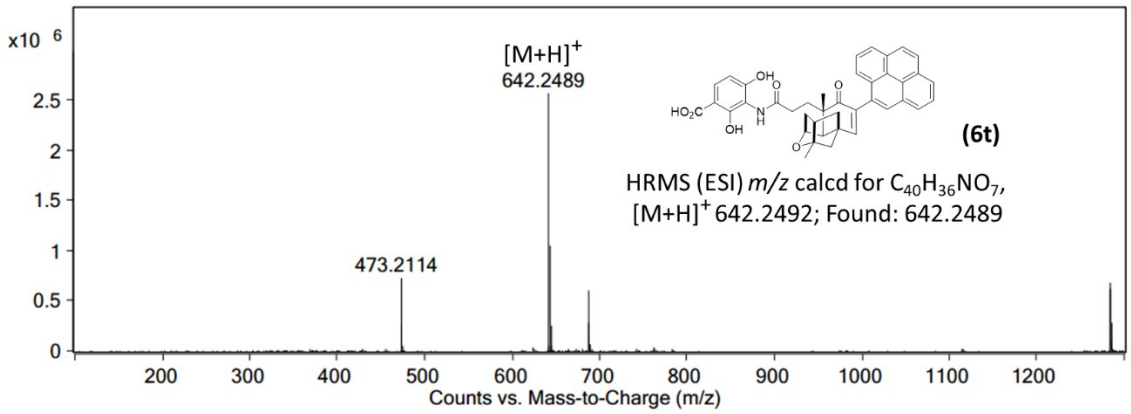

x10 6
[M+H]+
546.2126
377.1747
(6o)
HRMS (ESI) m/z calcd for C31H32NO8,
[M+H]+ 546.2128; Found: 546.2126
Counts vs. Mass-to-Charge (m/z)


x10 6
[M+H]+
598.1267
427.0906
1215.2289
(6p)
HRMS (ESI) m/z calcd for C30H31BrNO7,
[M+H]+ 596.1284; Found: 596.1267
Counts vs. Mass-to-Charge (m/z)


x10 6
[M+H]+
568.2331
399.1959
(6q)
HRMS (ESI) m/z calcd for C34H34NO7,
[M+H]+ 568.2335; Found: 568.2331
Counts vs. Mass-to-Charge (m/z)


x10 6
[M+H]+
612.2595
443.2218
(6r)
HRMS (ESI) m/z calcd for C36H38NO8,
[M+H]+ 612.2597; Found: 612.2595
Counts vs. Mass-to-Charge (m/z)

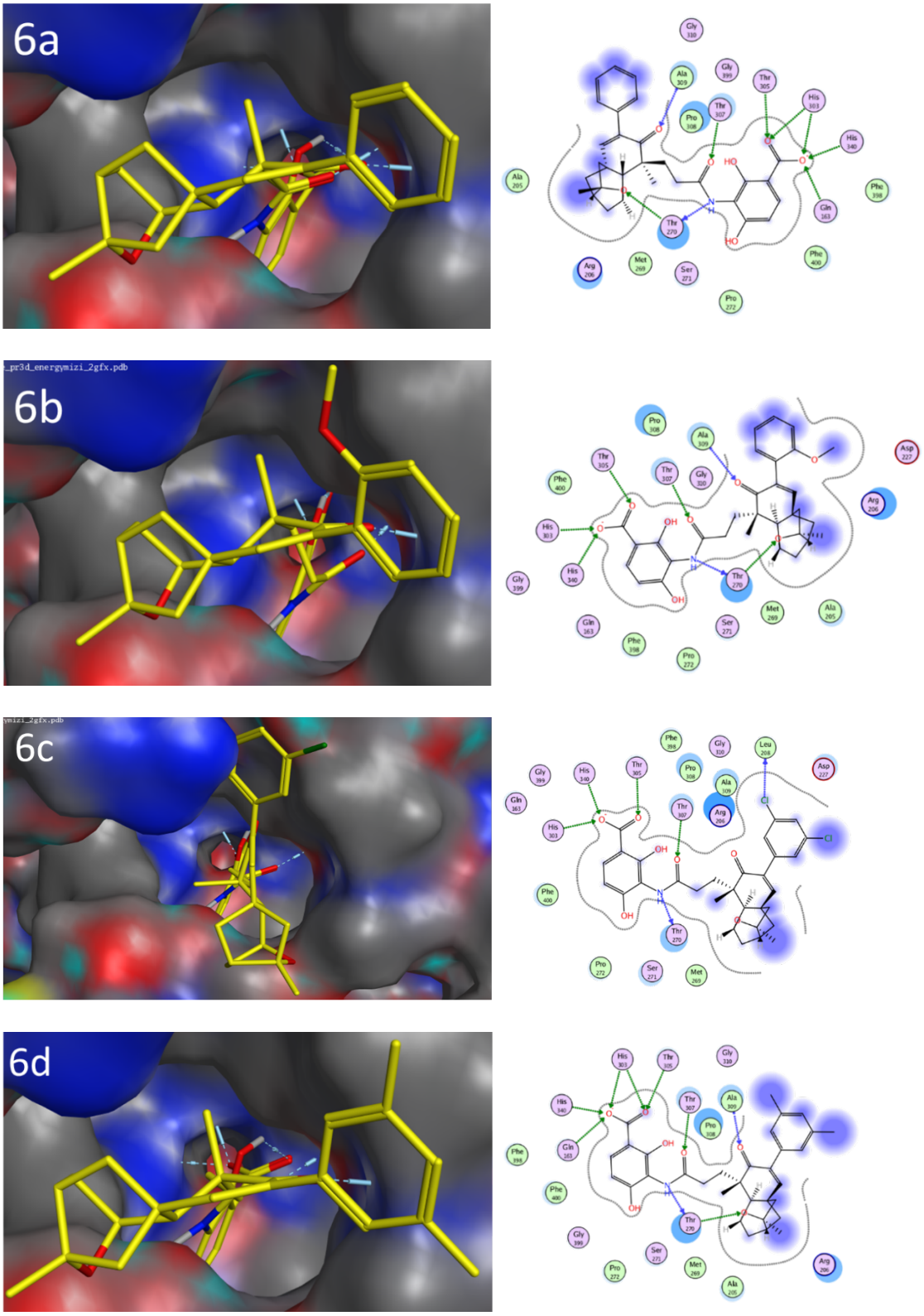

x10 6
[M+H]+
618.2489
449.2113
(6s)
HRMS (ESI) m/z calcd for C38H36NO7,
[M+H]+ 618.2492; Found: 618.2489
Counts vs. Mass-to-Charge (m/z)

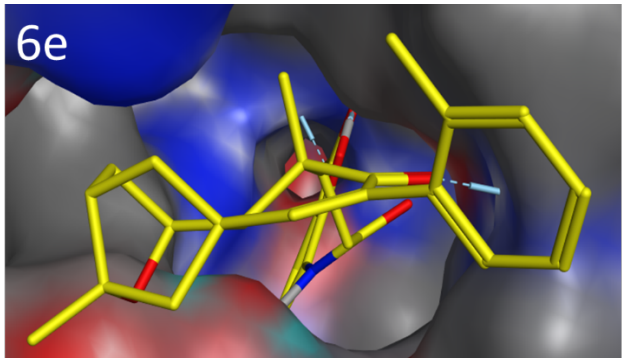


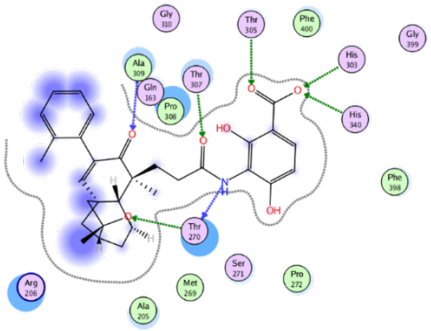
(6t)

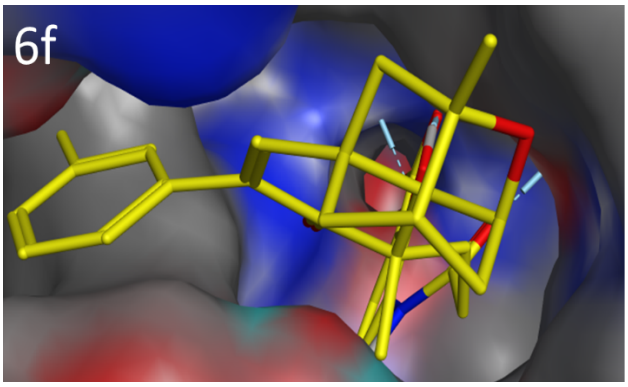
HRMS (ESI) *m/z* calcd for $C_{40}H_{36}NO_7$, $[M+H]^+$ 642.2492; Found: 642.2489

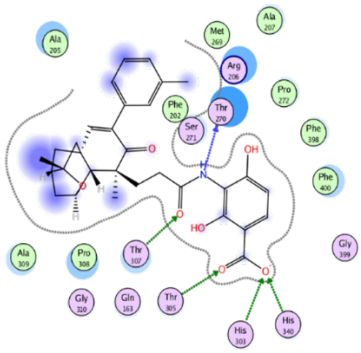
Figure S44. Predicted binding modes of compounds 6a – 6t with ecFabF(CQ163)

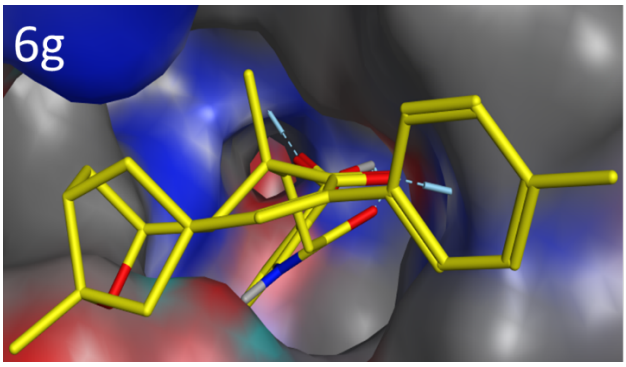


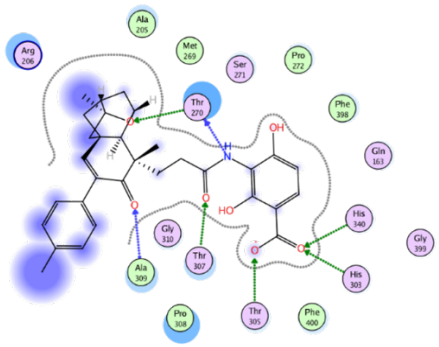

6e

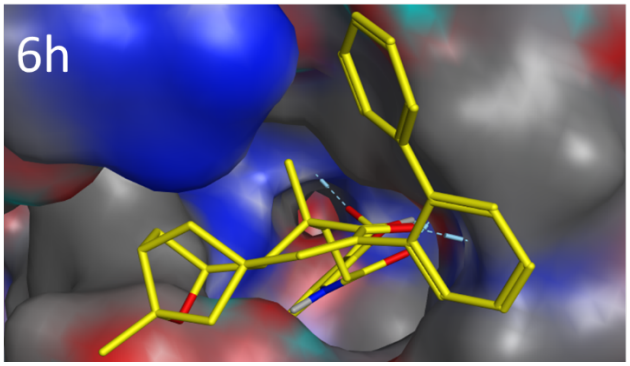


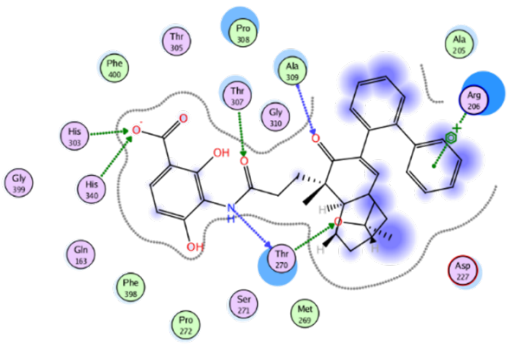

6f

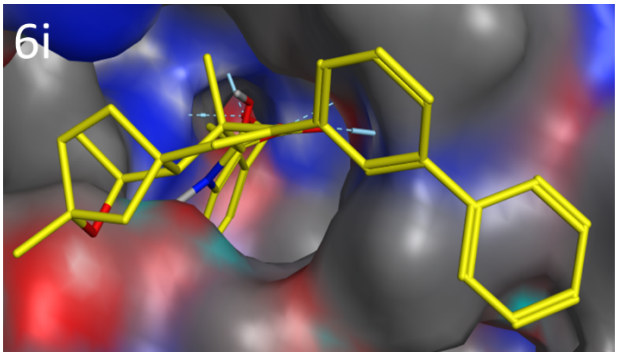


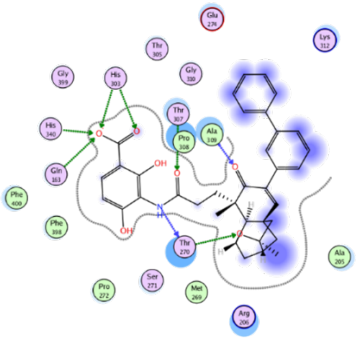

6g

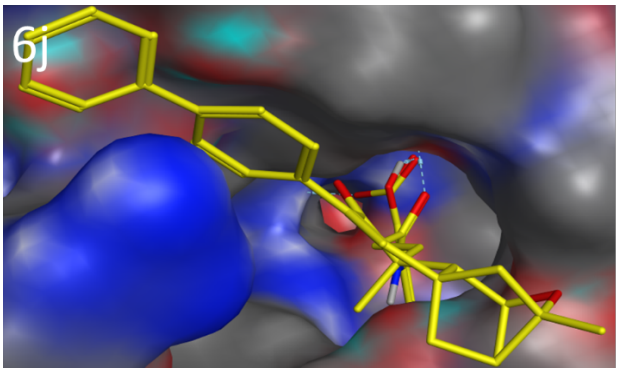



6h




6i

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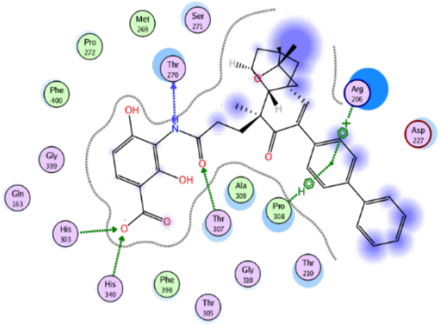

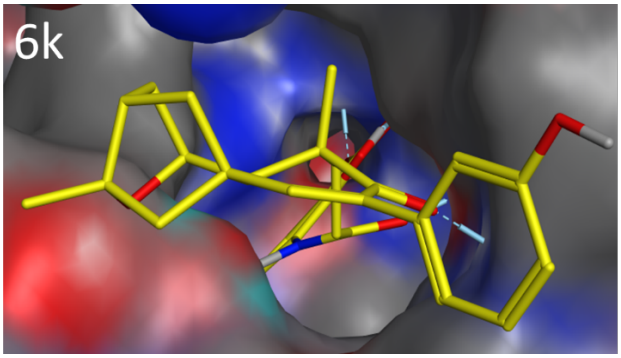
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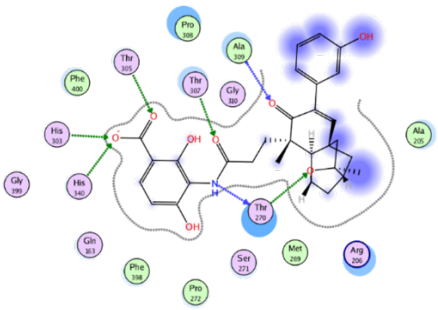

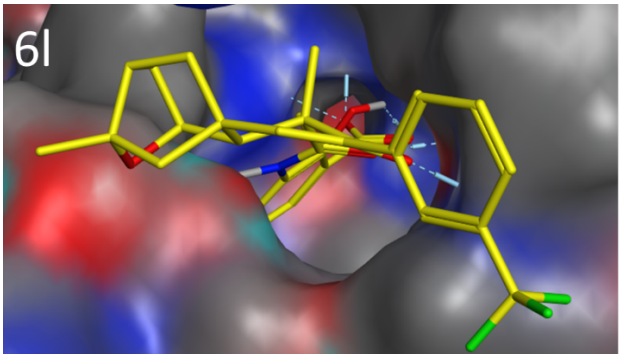
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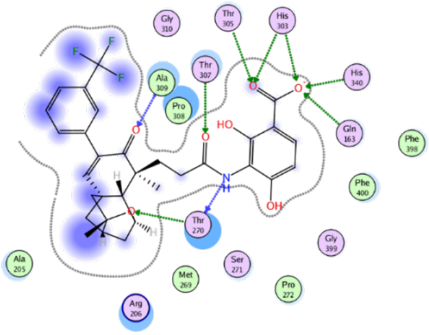
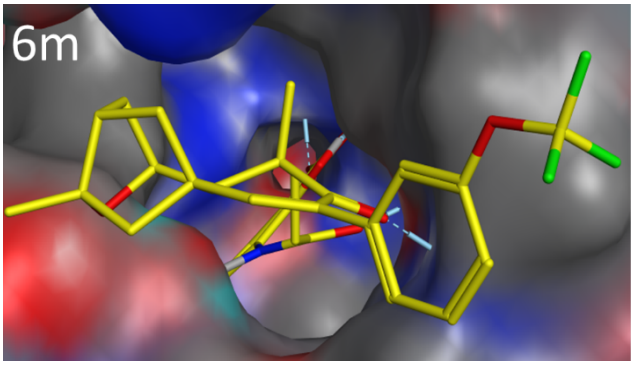
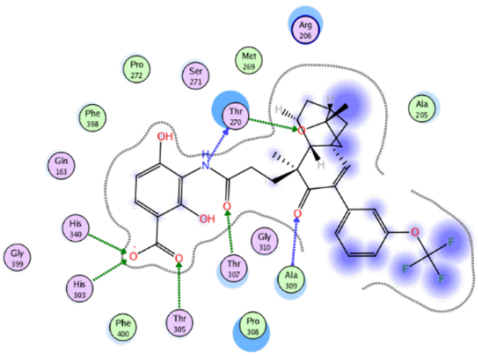
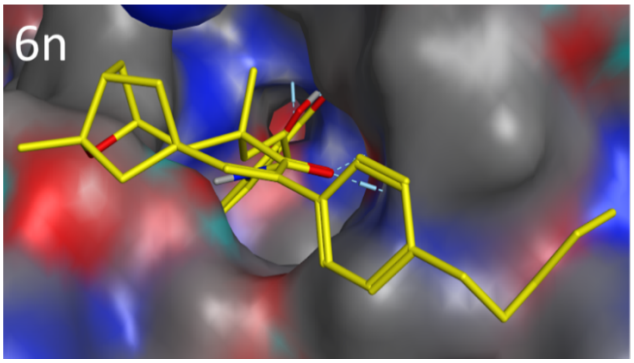



6m

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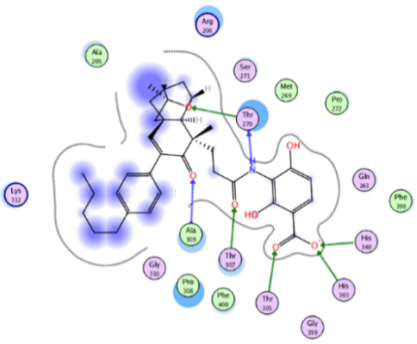

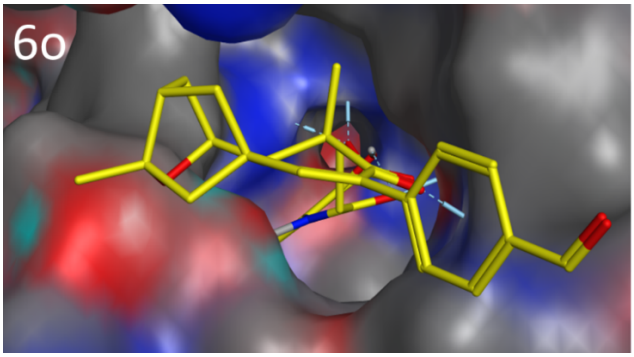
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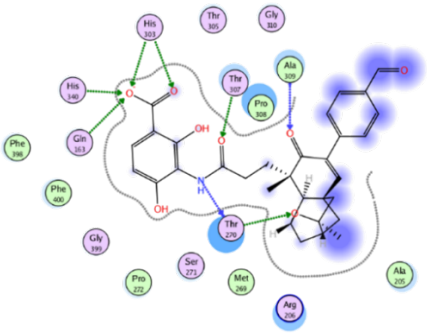
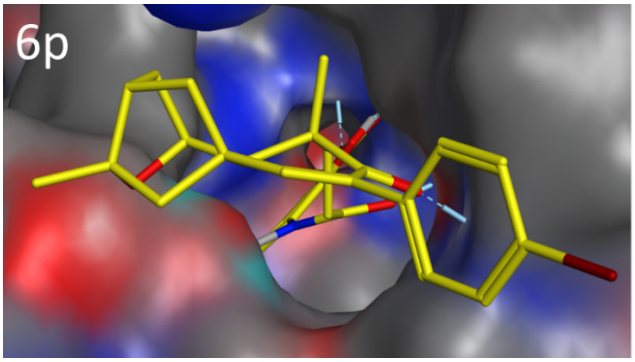
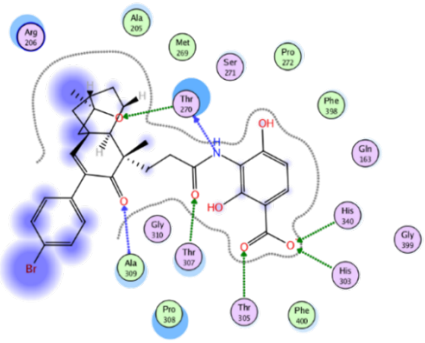
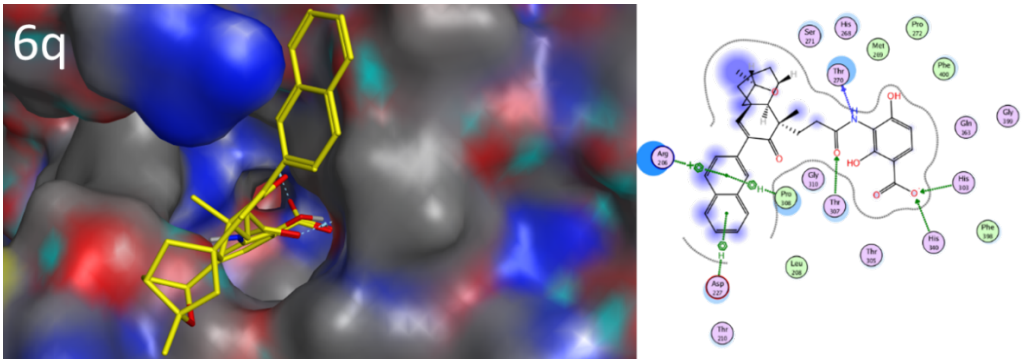
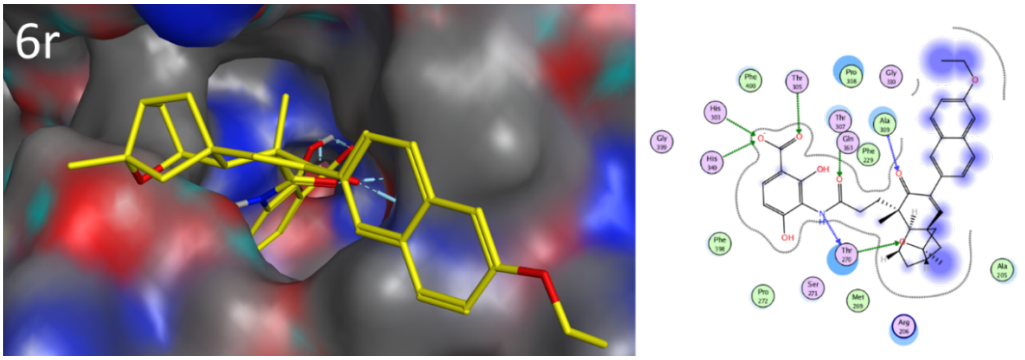



6p




6q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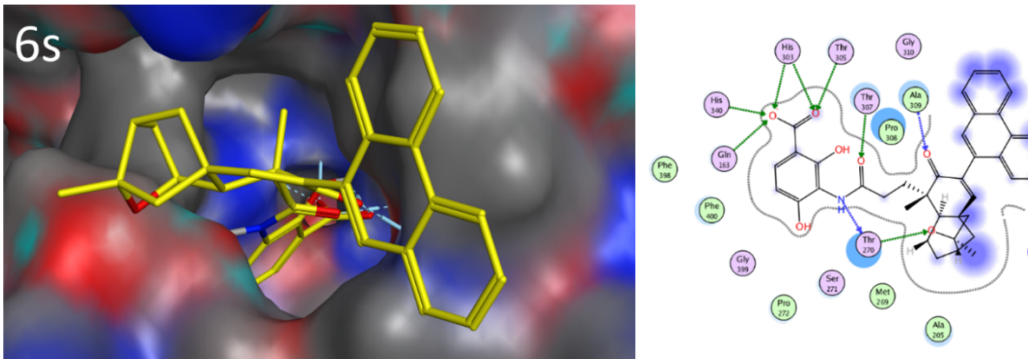
6s

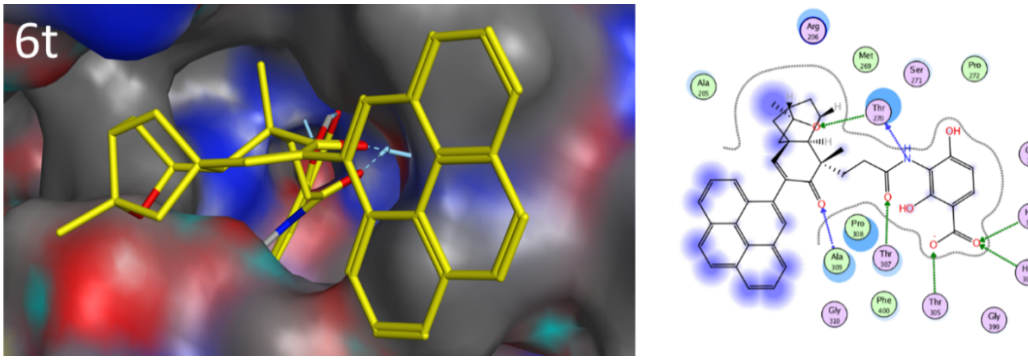
6t

Figure S45. 96 well plate assay of **6s**, **6t** and **PTM**. One representative clinical MRSA strain was grown to exponential phase (OD_{600} = 0.5) and diluted to 10^6 CFU/ml in Mueller-Hinton broth. Then 100 µl of different concentrations of **6s**, **6t** and **PTM** (0.5, 1, 2, 4 and 8 µg/ml) and 100 µl of bacterial solution were added per well, with or without 10% human serum. The 96 well plates were incubated at 37 ℃. After 18 h, 50 µl resazurin were added into each well.