Electronic supplementary information (ESI)

Synthesis and biological evaluation of novel 1-phenanthryl-tetrahydroisoquinoline derivatives as potent p21-activated kinase 4 (PAK4) inhibitors

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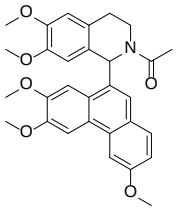
Contents: General Experimental Procedures. Chart of Analogues. Representative high-resolution mass spectrometry (HRMS) or mass spectrometry (MS), ^{1}H and ^{13}C NMR spectra of the target compounds and important intermediates.

1 General Experimental Procedures.

Unless otherwise specified, proton-1 nuclear magnetic resonance (^{1}H-NMR) spectra were recorded at 30 °C in DMSO-d_6 or $CDCl_3$ on a Bruker spectrometer at 400 MHz or 600MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was recorded at 30 °C in DMSO-d_6 or $CDCl_3$ on Bruker spectrometer at 100 MHz or 150MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. The ^{1}H and ^{13}C NMR chemical shifts were referenced to the solvent peak for DMSO-d_6 at H 2.50 and C 39.5, $CDCl_3$ at 7.26 and 77.2. ^{1}H NMR data are recorded as follows: chemical shift (d) [multiplicity, coupling constant(s) *J* (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet or combinations of the above. HPLC were recorded on a Waters 2000 HPLC system. Low-resolution Mass spectra were recorded on an Agilent 6120 MS spectrometer. High Resolution Mass spectra were taken on Agilent 6530(Q-TOF) mass spectrometer.

Silica gel (200–300 mesh) for column chromatography and silica GF254 for TLC were produced by Qingdao Marine Chemical Company (China). All air- or moisture sensitive reactions were conducted under an argon atmosphere. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated.

2 Chart of Analogues (21a-21u)



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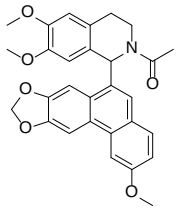

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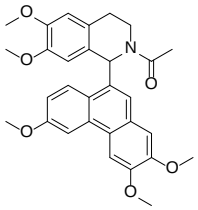

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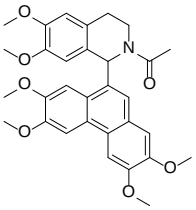

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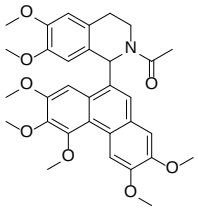

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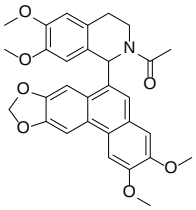

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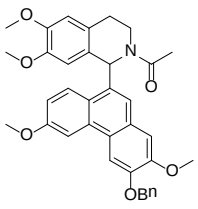

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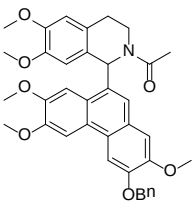

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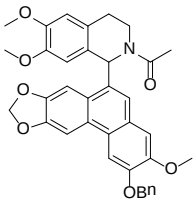

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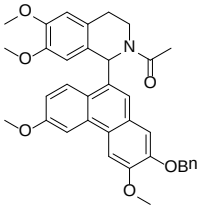

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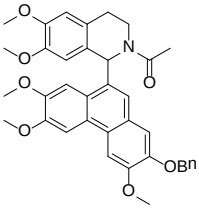

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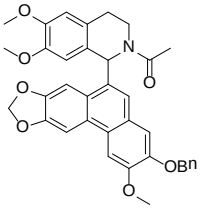

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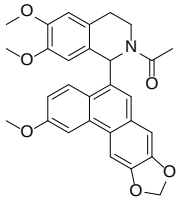

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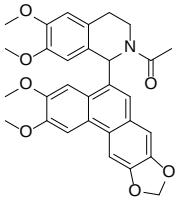

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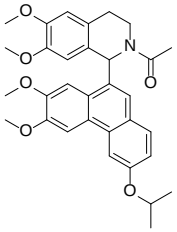

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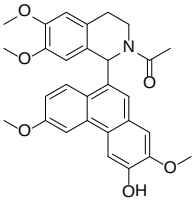

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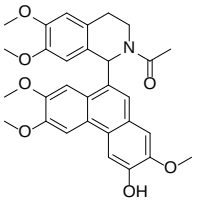

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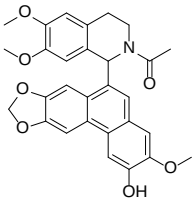

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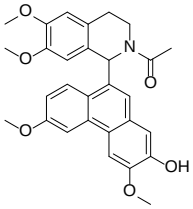

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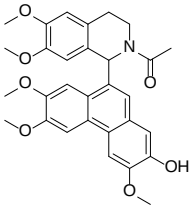

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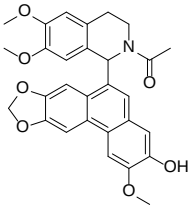
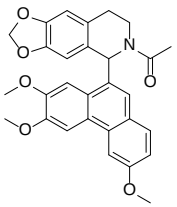


21u

Chart of Analogues (22a-22u)



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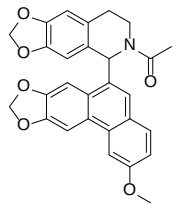

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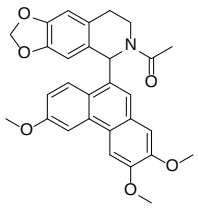

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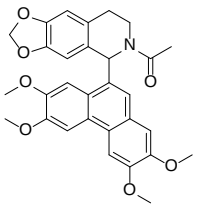

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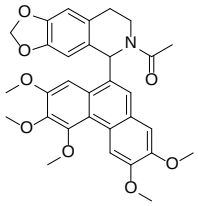

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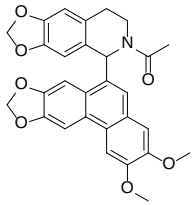

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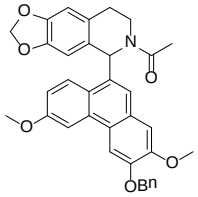

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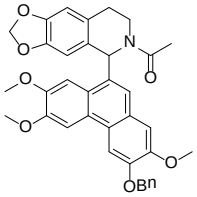

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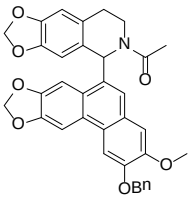

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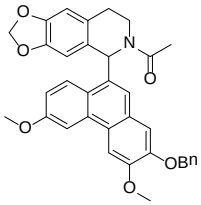

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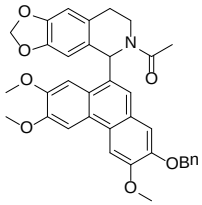

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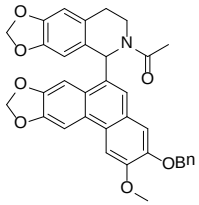

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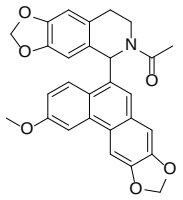

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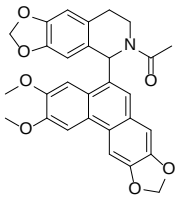

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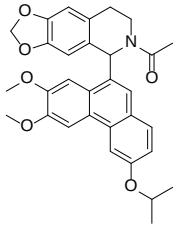

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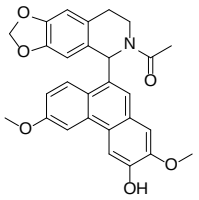

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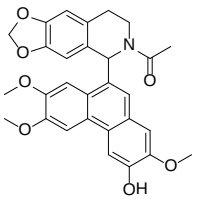

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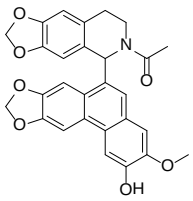

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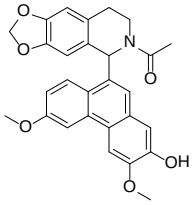

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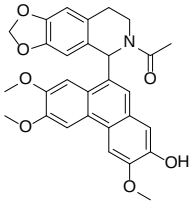

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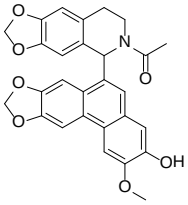
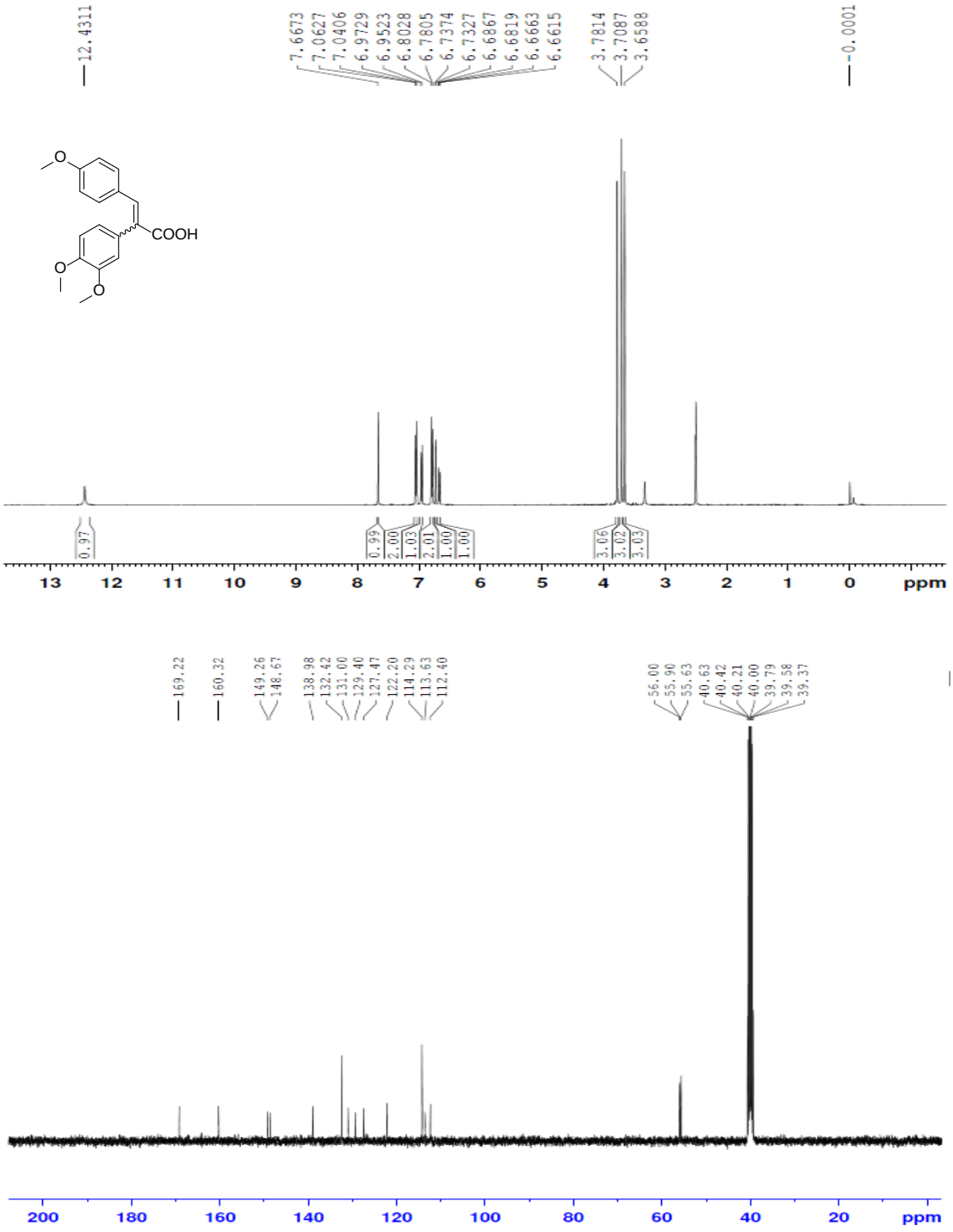


22u

3 ^{1}H and selected ^{13}C NMR spectra of important intermediates (13a-19a).

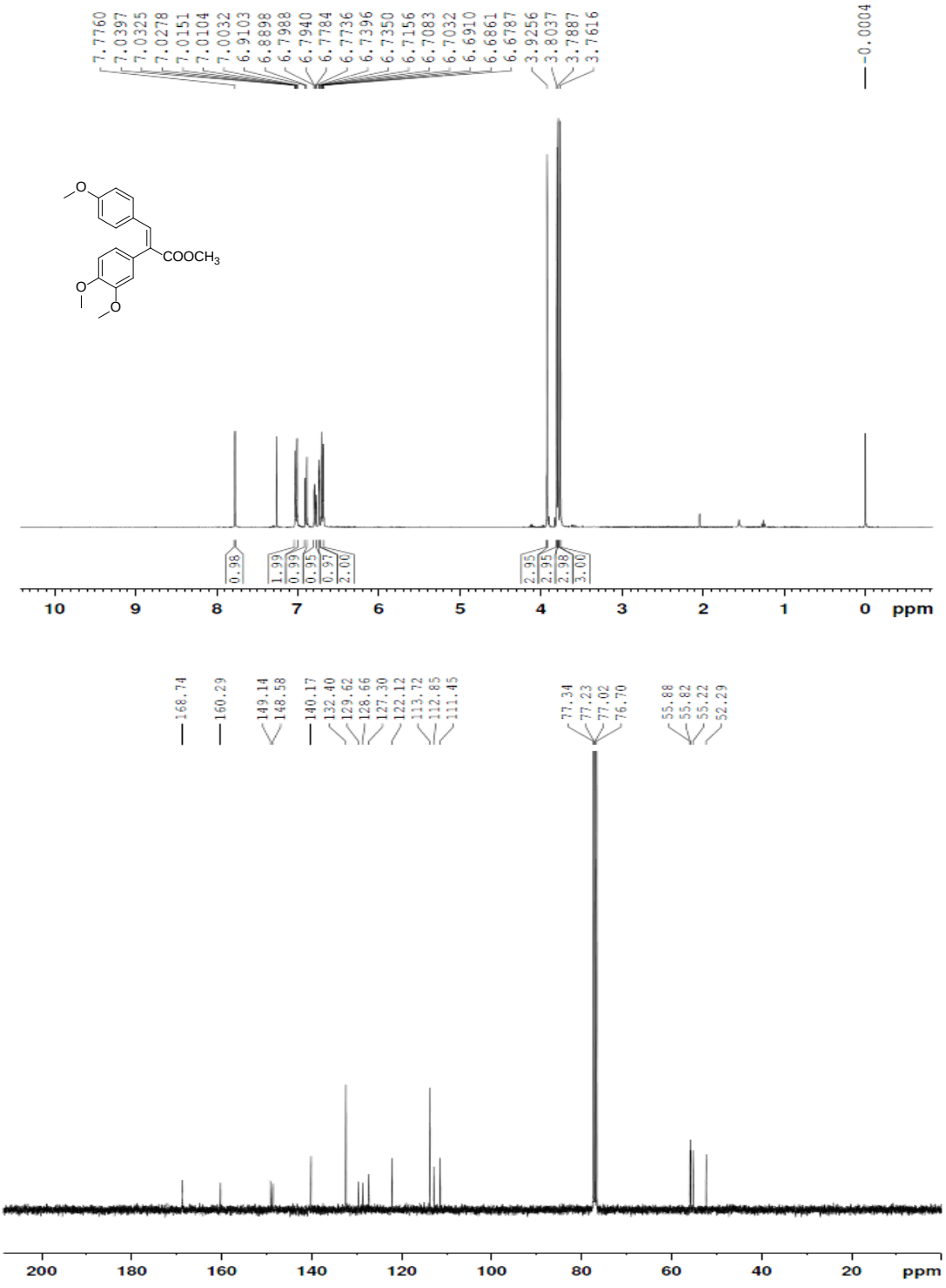
1. *(Z/E) 2-(3,4-dimethoxyphenyl)-3-(4-methoxyphenyl)acrylic acid(**13a**)*

^{1}H NMR (400MHz, DMSO-d_6) δ 12.43(s, 1H), 7.67(s, 1H), 7.04-7.06(d, J = 8.84 Hz, 2H), 6.96-6.98(d, J = 8.24 Hz, 1H), 6.78-6.80(d, J = 8.88 Hz, 2H), 6.73-6.74(d, J = 1.88 Hz, 1H), 6.66-6.68 (dd, J = 8.12, 1.88Hz, 1H), 3.78(s, 1H), 3.71(s, 1H), 3.66(s, 1H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.22, 160.32, 149.26, 148.67, 138.98, 132.42(×2), 131.00, 129.40, 127.47, 122.20, 114.29(×2), 113.63, 112.40, 56.00, 55.90, 55.63. MS (ESI) *m/z* 315.2[M+H]$^{+}$, 337.2[M+Na]$^{+}$, 353.1[M+K]$^{+}$.



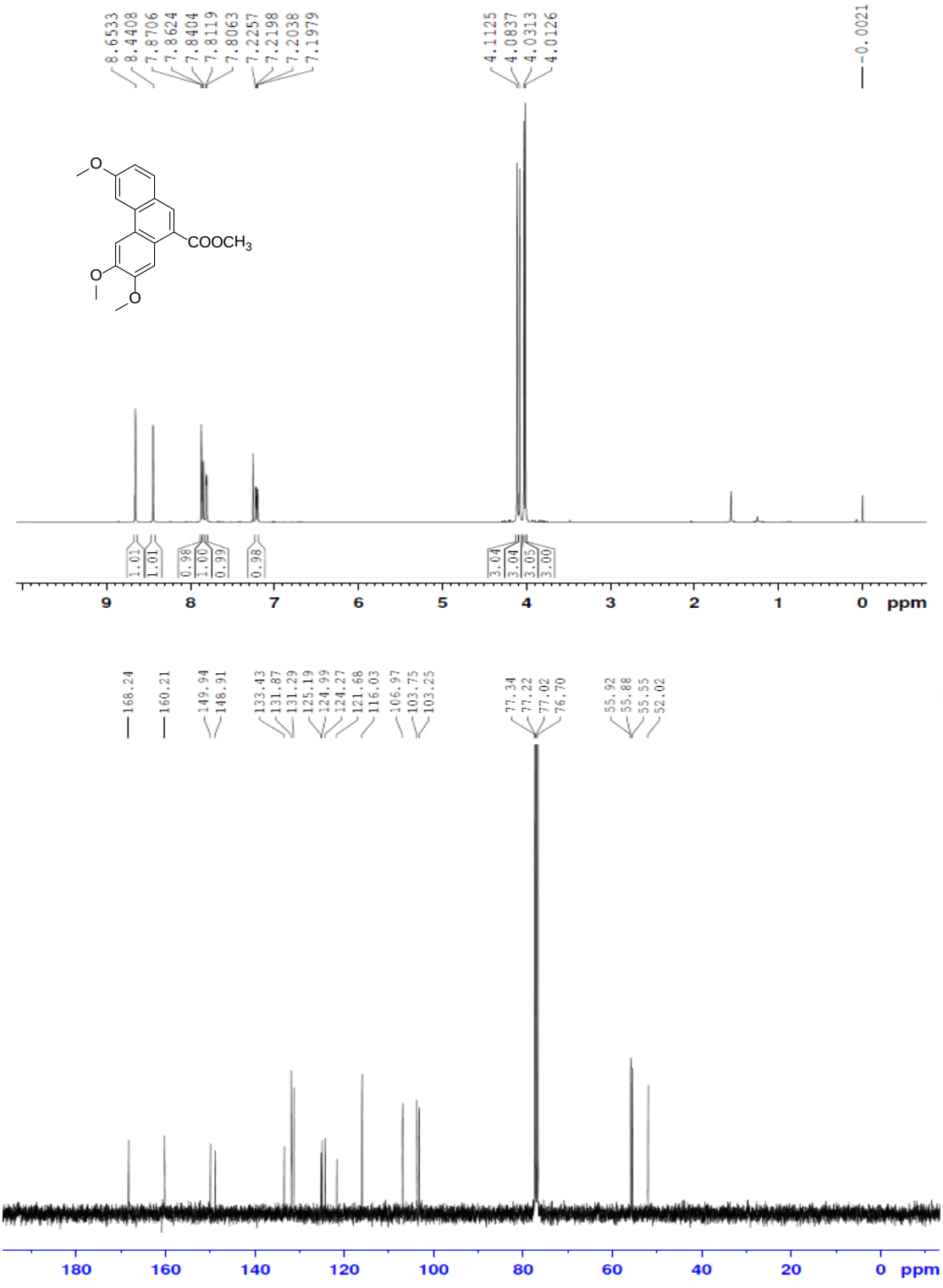
2. *Z-2-(3, 4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-acrylic acid methyl ester (**14a**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 7.78(s, 1H), 7.01-7.03(d, J = 8.88 Hz, 1H), 6.89-6.91(d, J = 8.20 Hz, 1H), 6.77-6.80(dd, J = 8.16, 1.88 Hz, 1H), 6.73-6.74(d, J = 1.88 Hz, 1H), 6.68-6.71(d, J = 8.88 Hz, 2H), 3.93(s, 1H), 3.80(s, 1H), 3.79(s, 1H), 3.76(s, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 168.74, 160.29, 149.14, 148.58, 140.17, 132.40(×2), 129.62, 128.66, 127.30, 122.12, 113.72(×2), 112.86, 111.45, 55.89, 55.82, 55.22, 52.29. MS (ESI) *m/z* 329.2[M+H]$^{+}$, 351.2[M+Na]$^{+}$, 367.1[M+K]$^{+}$.



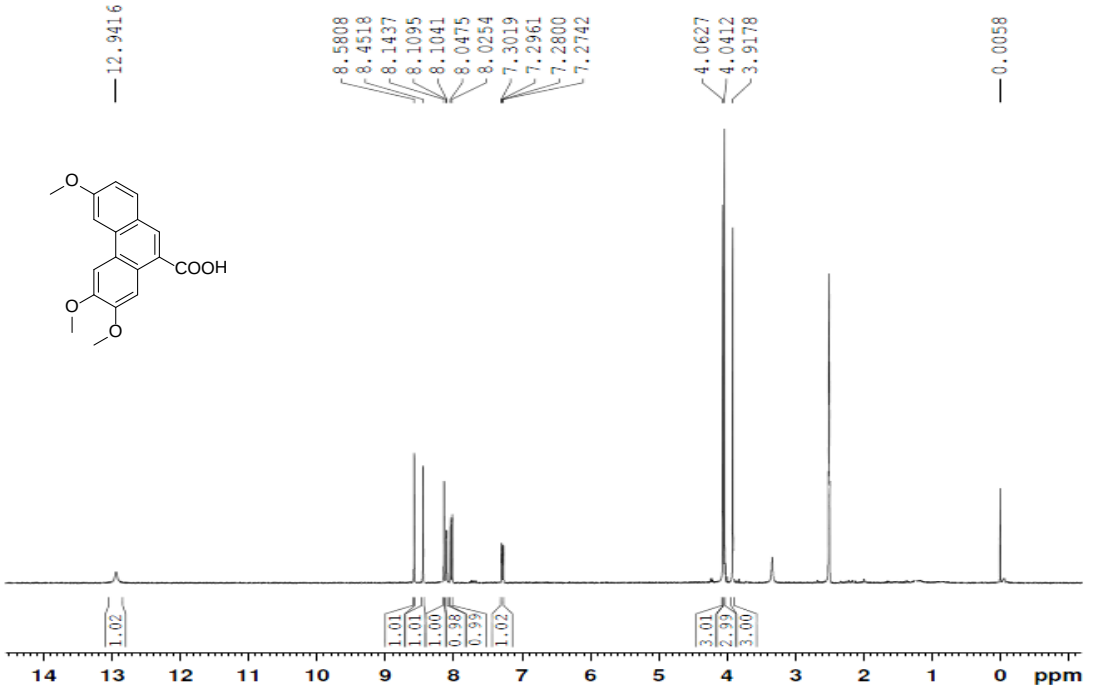
3. *3, 6, 7-trimethoxyphenanthrene-9-carboxylic acid methyl ester (**15a**)*

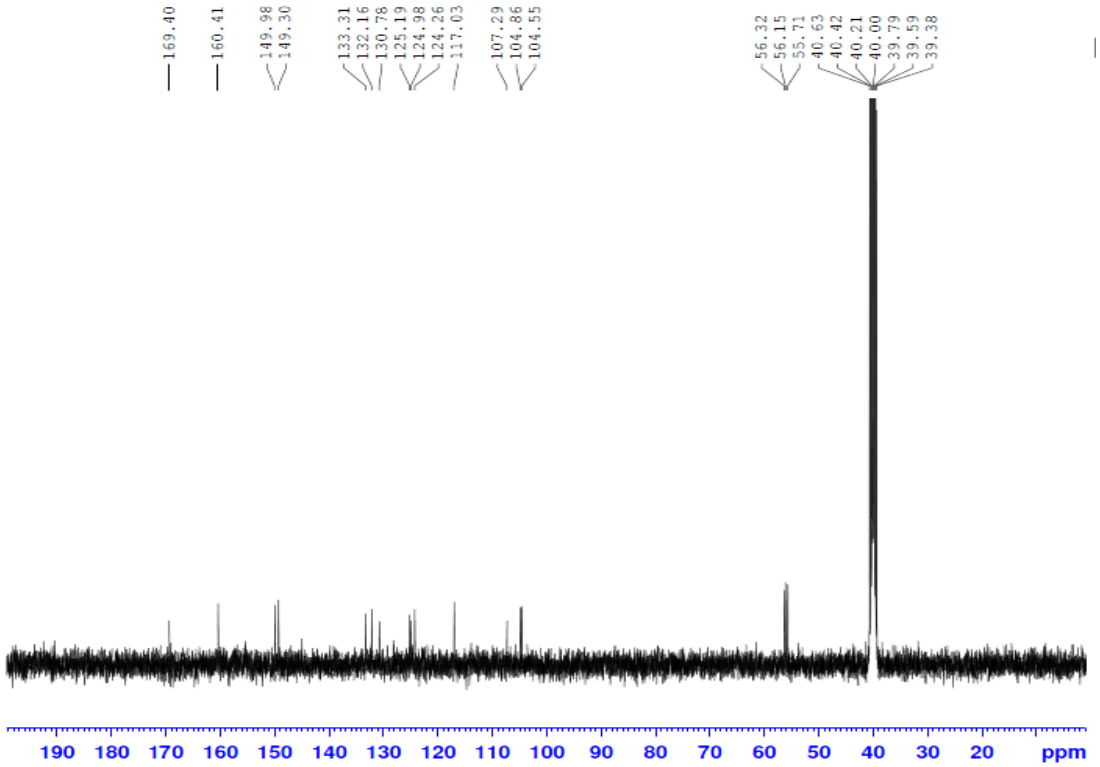
^{1}H NMR (400MHz, $CDCl_3$) δ 8.65(s, 1H), 8.44 (s, 1H), 7.87(s, 1H), 7.84-7.86(d, J = 8.80 Hz, 1H), 7.80-7.81(d, J = 2.24 Hz, 1H), 7.20-7.23(dd, J = 8.76, 2.40 Hz, 1H), 4.11(s, 1H), 4.09(s, 1H), 4.03(s, 1H), 4.01(s, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 168.24, 160.20, 149.94, 148.91, 133.43, 131.87, 131.29, 125.19, 124.99, 124.27, 121.68, 116.03, 106.97, 103.75, 103.25, 55.92, 55.88, 55.55, 52.02. MS (ESI) *m/z* 327.2$[M+H]^+$, 349.2$[M+Na]^+$, 325.1$[M-H]^-$.



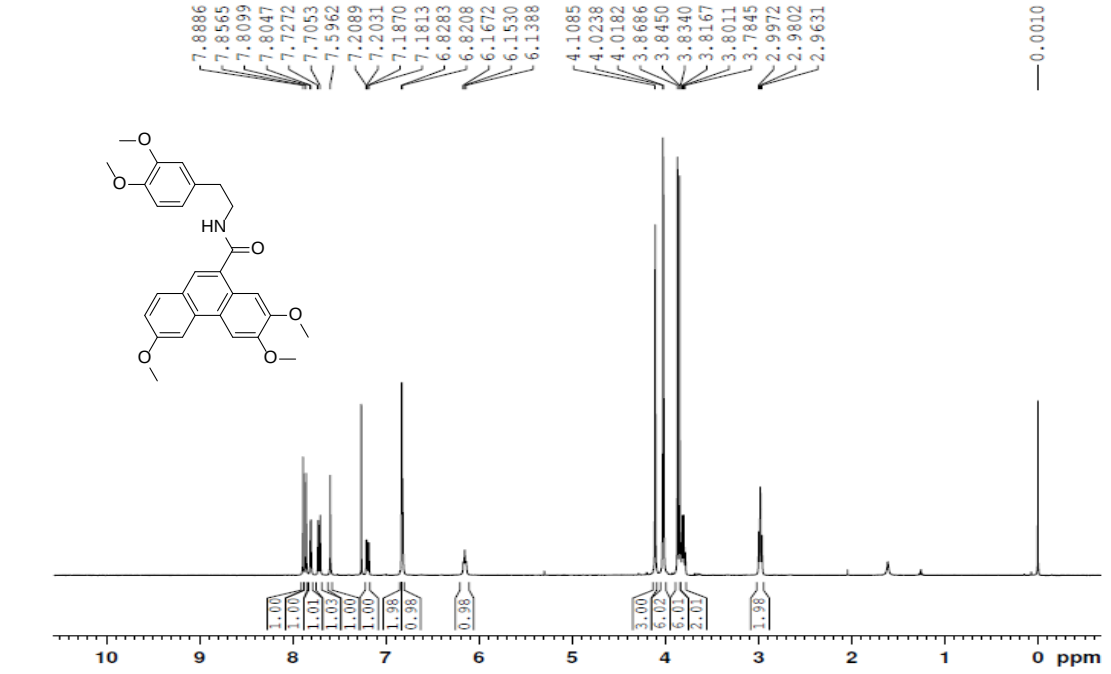
4. *3, 6, 7-trimethoxyphenanthrene-9-carboxylic acid(**16a**)*

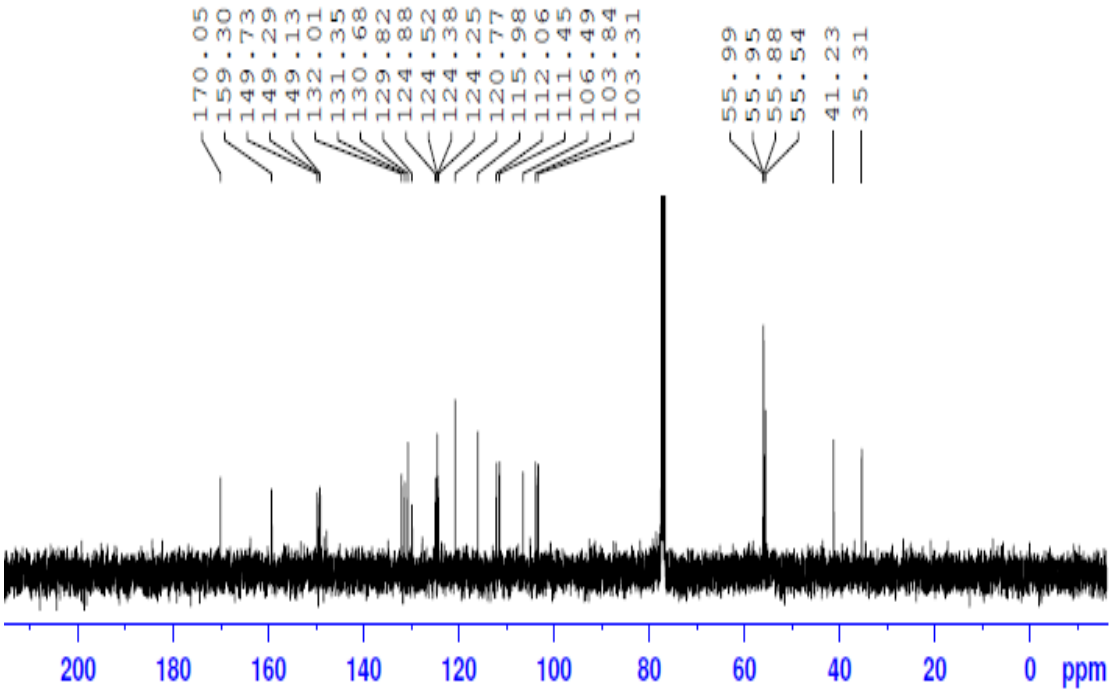
^{1}H NMR (400MHz, DMSO-d_6) δ 12.94(s, 1H), 8.58(s, 1H), 8.45 (s, 1H), 8.14 (s, 1H), 8.10-8.11(d, J = 2.16 Hz, 1H), 8.03-8.05(d, J = 8.84 Hz, 1H), 7.27-7.30(dd, J = 8.76, 2.32 Hz, 1H), 4.06(s, 3H), 4.04(s, 3H), 3.92(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.40, 160.41, 149.98, 149.30, 133.30, 132.16, 130.78, 125.19, 124.98, 124.26, 117.03, 107.29, 104.86, 104.55, 56.32, 56.15, 55.71. MS (ESI) m/z 310.9[M-H]$^-$.





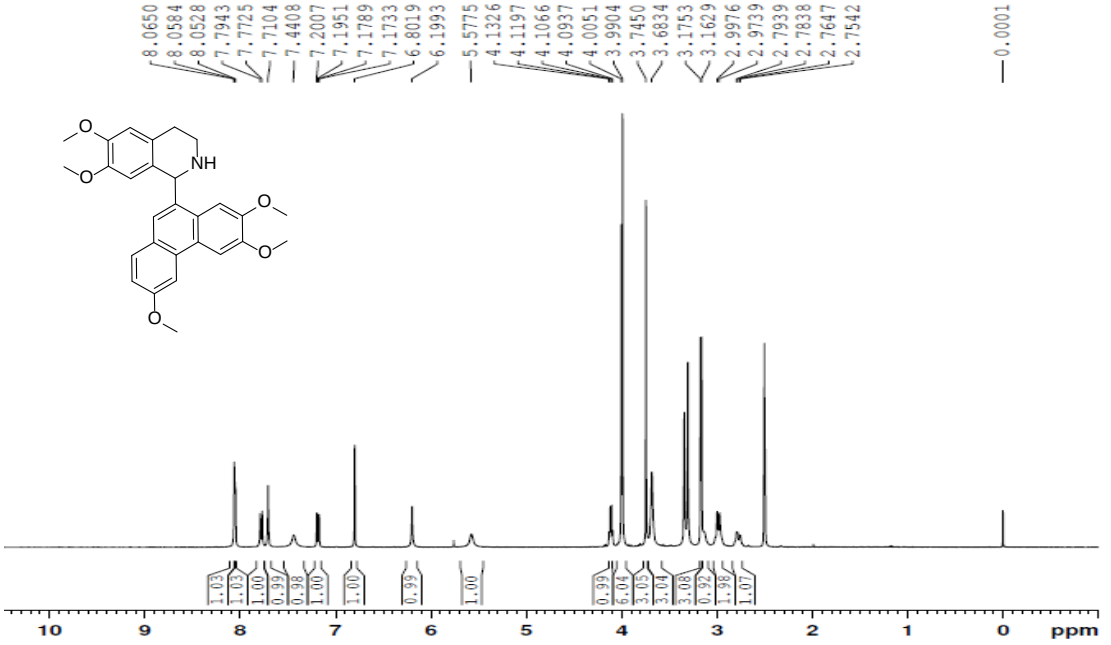
5. *N-(3,4-dimethoxyphenethyl)-2,6,7-trimethoxyphenanthrene-9-carboxamide (**17a**).* ^{1}H NMR (400MHz, $CDCl_3$) δ 7.89(s, 1H), 7.86(s, 1H), 7.80-7.81(d, J = 2.28 Hz, 1H), 7.71-7.73(d, J = 8.76 Hz, 1H), 7.18-7.21(dd, J= 8.76, 2.28 Hz, 1H), 7.60(s, 1H), 6.83(s, 2H), 6,82(s, 1H), 6.14-6.17(t, J = 5.68 Hz, 1H), 4.11(s, 3H), 4.03(s, 3H), 4.02(s, 3H), 3.87(s, 3H), 3.85(s, 3H), 3.78-3.83(q, J = 13.16, 6.90 Hz, 2H), 2.96-3.00(t, J = 6.80 Hz, 2H). ^{13}C-NMR (100MHz, $CDCl_3$) δ 170.05, 159.30, 149.73, 149.29, 149.13, 132.02, 131.35, 130.68, 129.82, 124.88, 124.52, 124.38, 124.25, 120.77, 115.98, 112.06, 111.45, 106.49, 103.84, 103.30, 55.99, 55.94(×2), 55.88, 55.54, 41.22, 35.30. MS (ESI) *m/z* 475.2[M+H]$^{+}$.

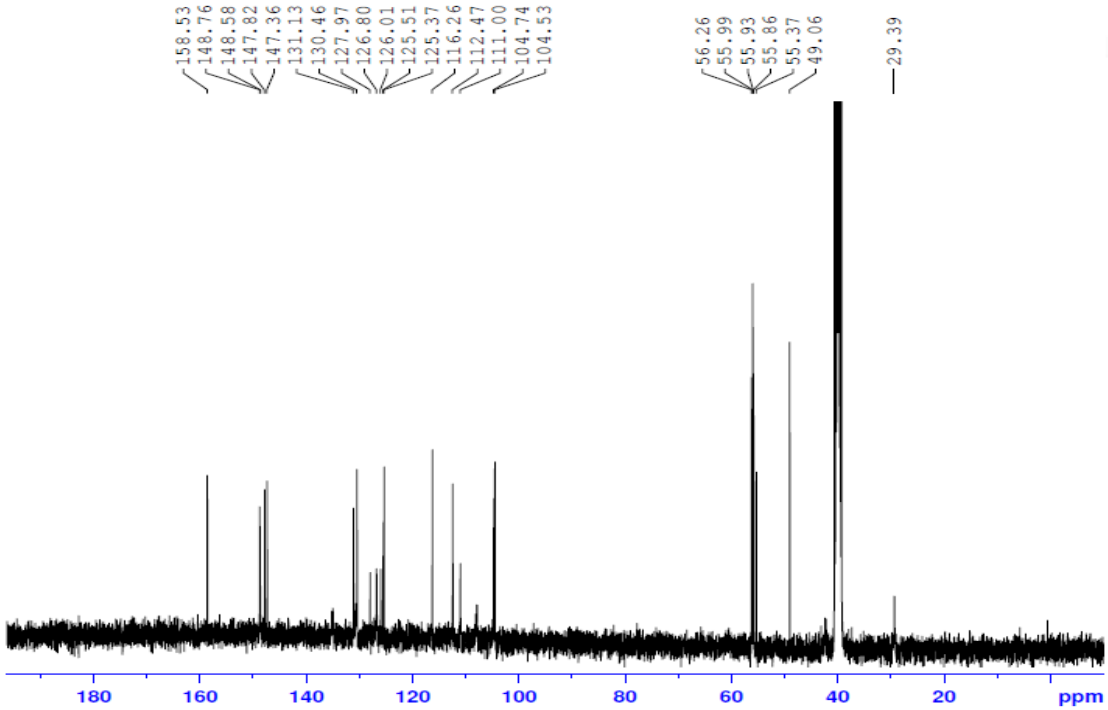




6. *6,7-dimethoxy-1-(3,6,7-trimethoxyphenanthren-9-yl)-1,2,3,4-tetrahydroisoquinoline (**19a**).*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.06(s, 1H), 8.05-8.06(d, J = 2.24 Hz, 1H), 7.77-7.79(d, J = 8.72 Hz, 1H), 7.71(s, 1H), 7.44(s, 1H), 7.17-7.20(dd, J =8.72, 2.24 Hz, 1H), 6,80(s, 1H), 6.20(s, 1H), 5.58(s, 1H), 4.13(s, 3H), 4.09-4.13(q, 1H), 4.00(s, 3H), 3.99(m, 3H), 3.74(s, 3H), 3.68(s, 3H), 3.15-3.17(m, 4H), 2.97-3.00(m, 1H), 2.75-2.79(m, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 158.53, 148.76, 148.57, 147.82, 147.36, 131.13, 130.45(×2), 127.97, 126.80, 126.00, 125.50, 125.37(×2), 116.26(×2), 112.47, 111.00, 104.74, 104.53, 56.26, 55.99(×2), 55.93, 55.86, 55.37, 49.06, 29.39. MS (ESI) *m/z* 460.3$[M+H]^+$, 482.3$[M+Na]^+$.

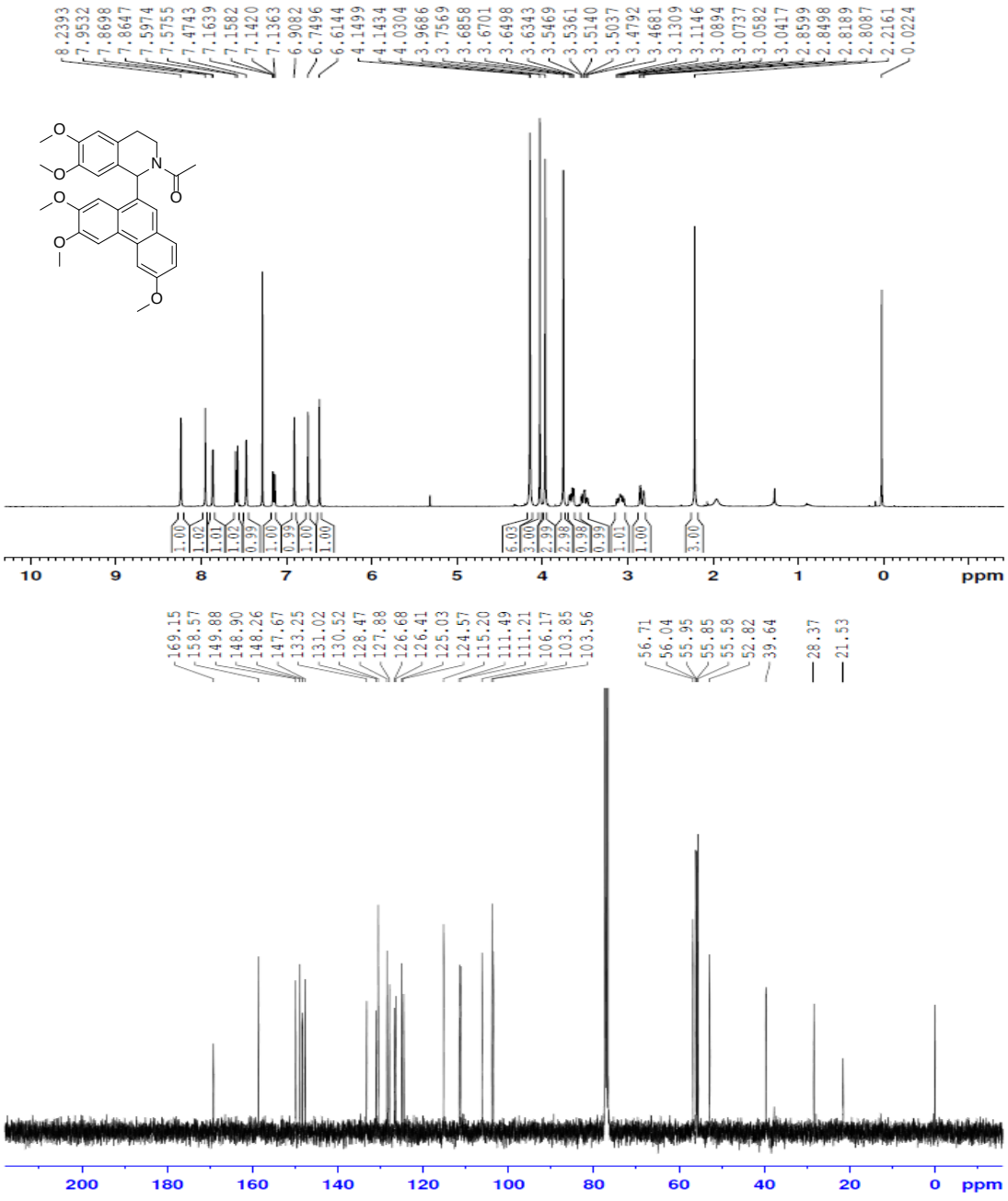




4 ^{1}H-NMR and ^{13}C-NMR Spectral of New Compounds (21a-21u, 22a-22u).

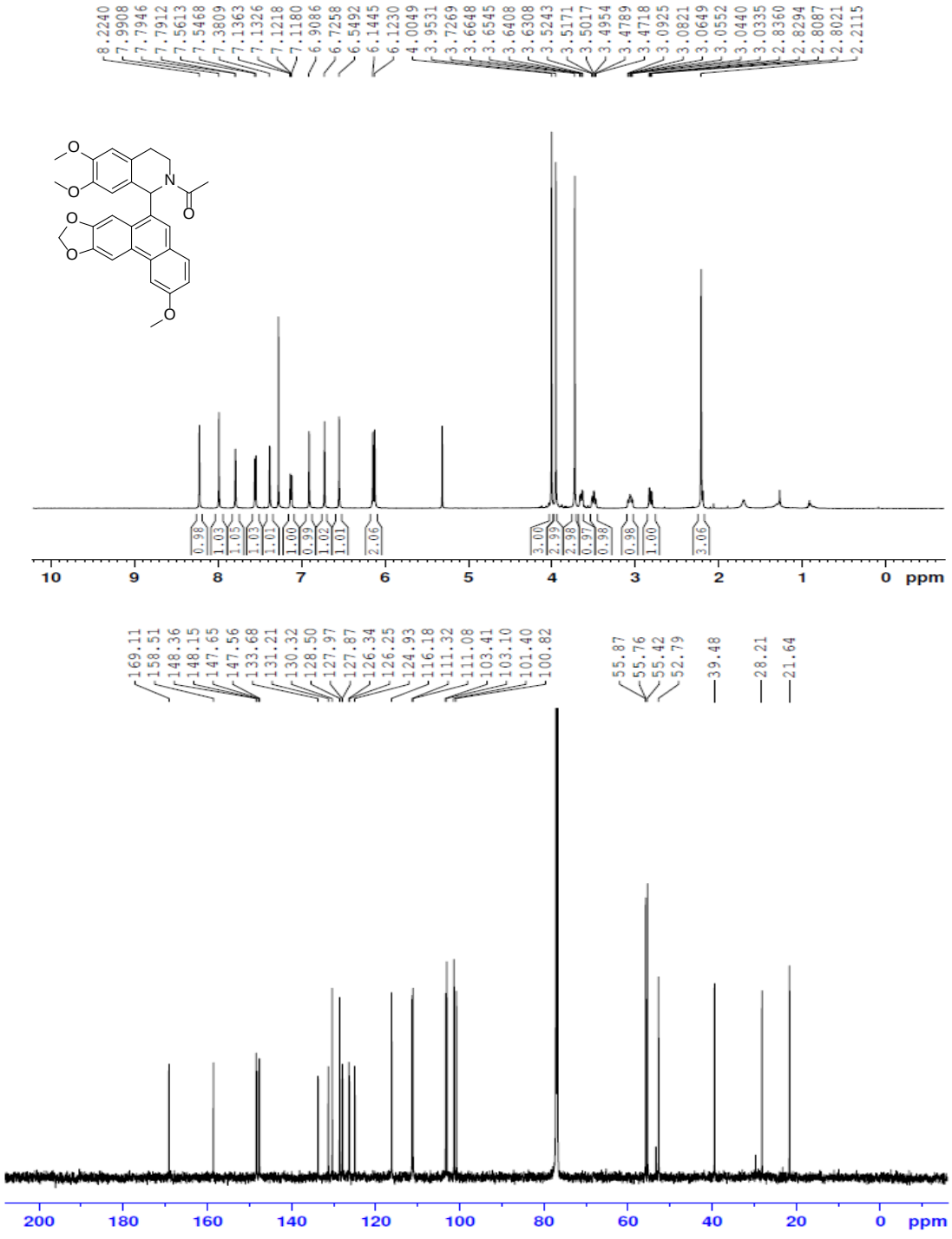
1. *1-(6,7-dimethoxy-1-(3,6,7-trimethoxyphenanthren-9-yl)-3,4-dihydroisoquino-in-2-(1H)-yl) ethanone (**21a**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.24(s, 1H), 7.95(s, 1H), 7.86-7.87(d, J = 2.28 Hz, 1H), 7.58-7.60(d, J = 8.76 Hz, 1H), 7.47(s, 1H), 7.13-7.16(dd, J = 8.76, 2.28 Hz, 1H), 6.91(s, 1H), 6.75(s, 1H), 6.61(s, 1H), 4.15(s, 3H), 4.14(s, 3H), 4.03(s, 3H), 3.97(s, 3H), 3.76(s, 3H), 3.63-3.69(m, 1H), 3.47-3.55(m, 1H), 3.04-3.13(m, 1H), 2.81-2.86(m, 1H), 2.21(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.15, 158.57, 149.88, 148.90, 147.67, 133.25, 131.02, 148.26, 130.51, 127.88, 126.68, 128.46, 126.41, 125.03, 124.56, 115.19, 111.49, 111.20, 106.17, 103.85, 103.56, 56.71, 56.03, 55.95, 55.85, 55.58, 52.81, 39.46, 28.37, 21.53. HRMS calcd for $C_{30}H_{31}NO_6Na$, $[M+Na]^+$, 524.2044; found 524.2063.



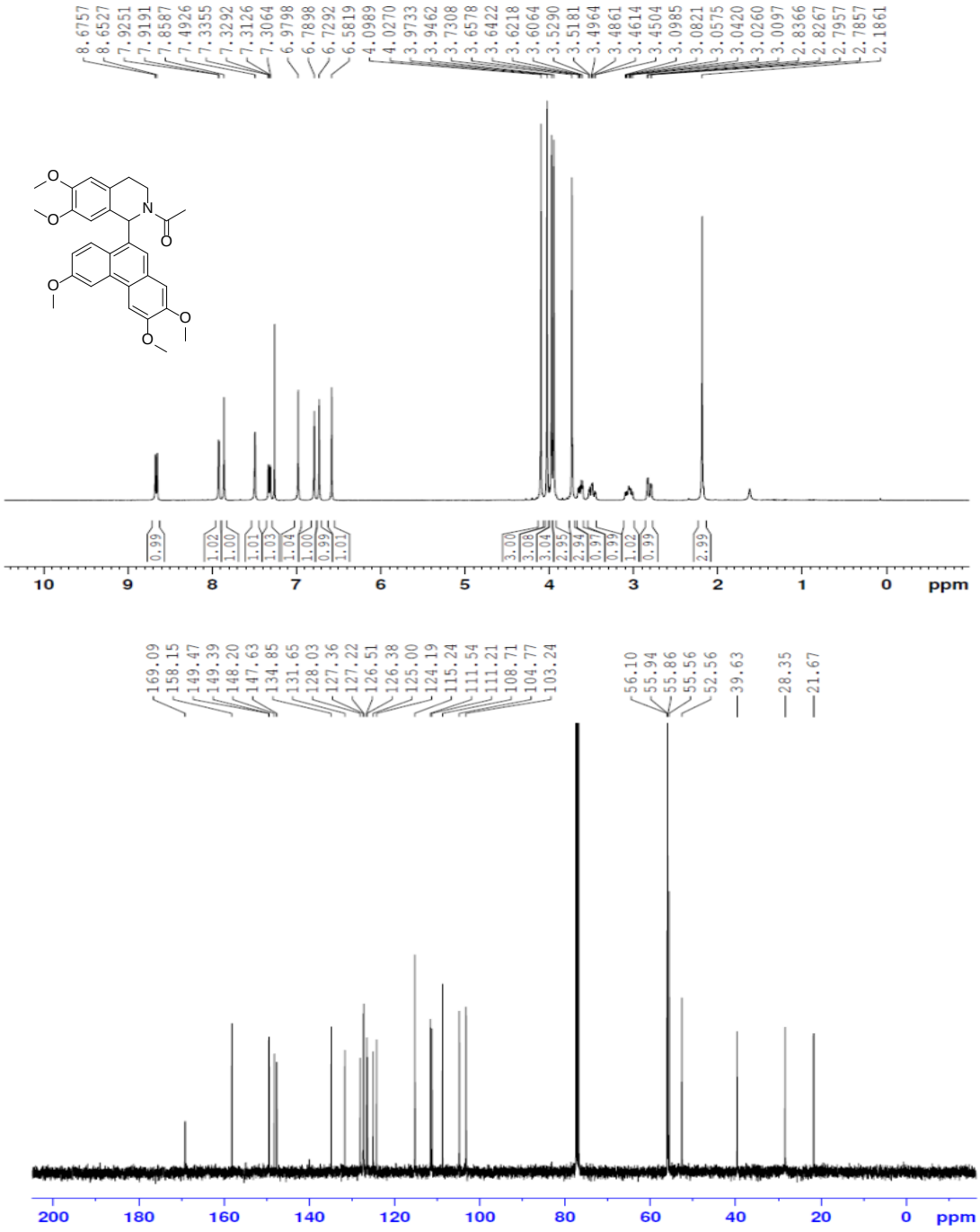
2. *1-(6,7-dimethoxy-1-(2-methoxyphenanthro[3,2-d][1,3]dioxol-6-yl)-3,4-dihydroisoquinolin-2(1H)-yl)ethanone(**21b**)*

^{1}H NMR (600MHz, $CDCl_3$) δ 8.22(s, 1H), 7.99(s, 1H), 7.79-7.80(d, J = 2.04 Hz, 1H), 7.55-7.56(d, J = 8.70 Hz, 1H), 7.38(s, 1H), 7.11-7.14(dd, J = 8.70, 2.22 Hz, 1H), 6.91(s, 1H), 6.73(s, 1H), 6.55(s, 1H), 6.12-6.14 (d, J = 12.90 Hz, 2H), 4.00(s, 3H), 3.95(s, 1H), 3.73(s, 3H), 3.63-3.66(m, 1H), 3.47-3.52(m, 1H), 3.03-3.09(m, 1H), 2.80-2.84(m, 1H), 2.21(s, 3H). ^{13}C NMR (150MHz, $CDCl_3$) δ 169.11, 158.51, 148.36, 148.14, 147.63, 147.56, 133.68, 131.21, 130.32, 128.50, 127.97, 127.87, 126.34, 126.25, 124.93, 116.18, 111.32, 111.08, 103.41, 103.10, 101.39, 100.82, 55.86, 55.75, 55.41, 52.79, 39.48, 28.21, 21.64. HRMS calcd for $C_{29}H_{27}NO_6Na$ $[M+Na]^+$, 508.1731; found 508.1732.



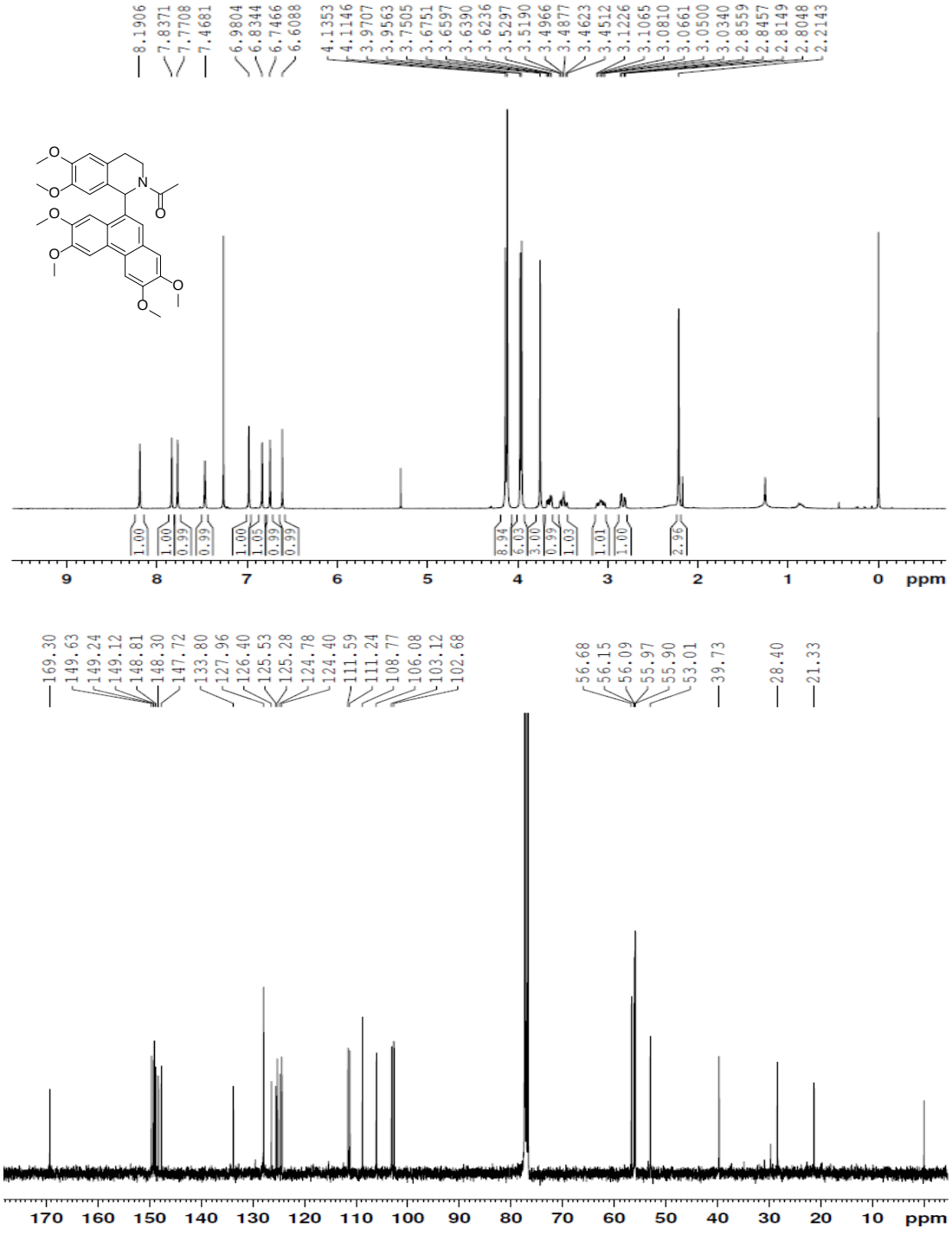
3. *1-(6,7-dimethoxy-1-(2,3,6-trimethoxyphenanthren-9-yl)-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21c**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.65-8.68(d, J = 9.20 Hz, 1H), 7.92-7.93(d, J = 2.40 Hz, 1H), 7.86(s, 1H), 7.49(s, 1H), 7.31-7.34(dd, J = 9.16, 2.52 Hz, 1H), 6.98(s, 1H), 6.79(s, 1H), 6.73(s, 1H), 6.58(s, 1H), 4.10(s, 3H), 4.03(s, 3H), 3.97 (s, 3H), 3.95(s, 3H), 3.73(s, 3H), 3.61-3.66(s, 1H), 3.45-3.53(s, 1H), 3.01-3.10(m, 1H), 2.79-2.84(m, 1H), 2.19(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ169.09, 158.15, 149.47, 149.39, 148.20, 147.63, 134.85, 131.65, 128.03, 127.35, 127.22, 126.51, 126.38, 125.00, 124.19, 115.24, 111.54, 111.21, 108.71, 104.77, 103.24, 56.10, 55.94(×2), 55.86, 55.55, 52.56, 39.63, 28.35, 21.67. HRMS calcd for $C_{30}H_{31}NO_6Na$, $[M+Na]^+$, 524.2044; found 524.2048.



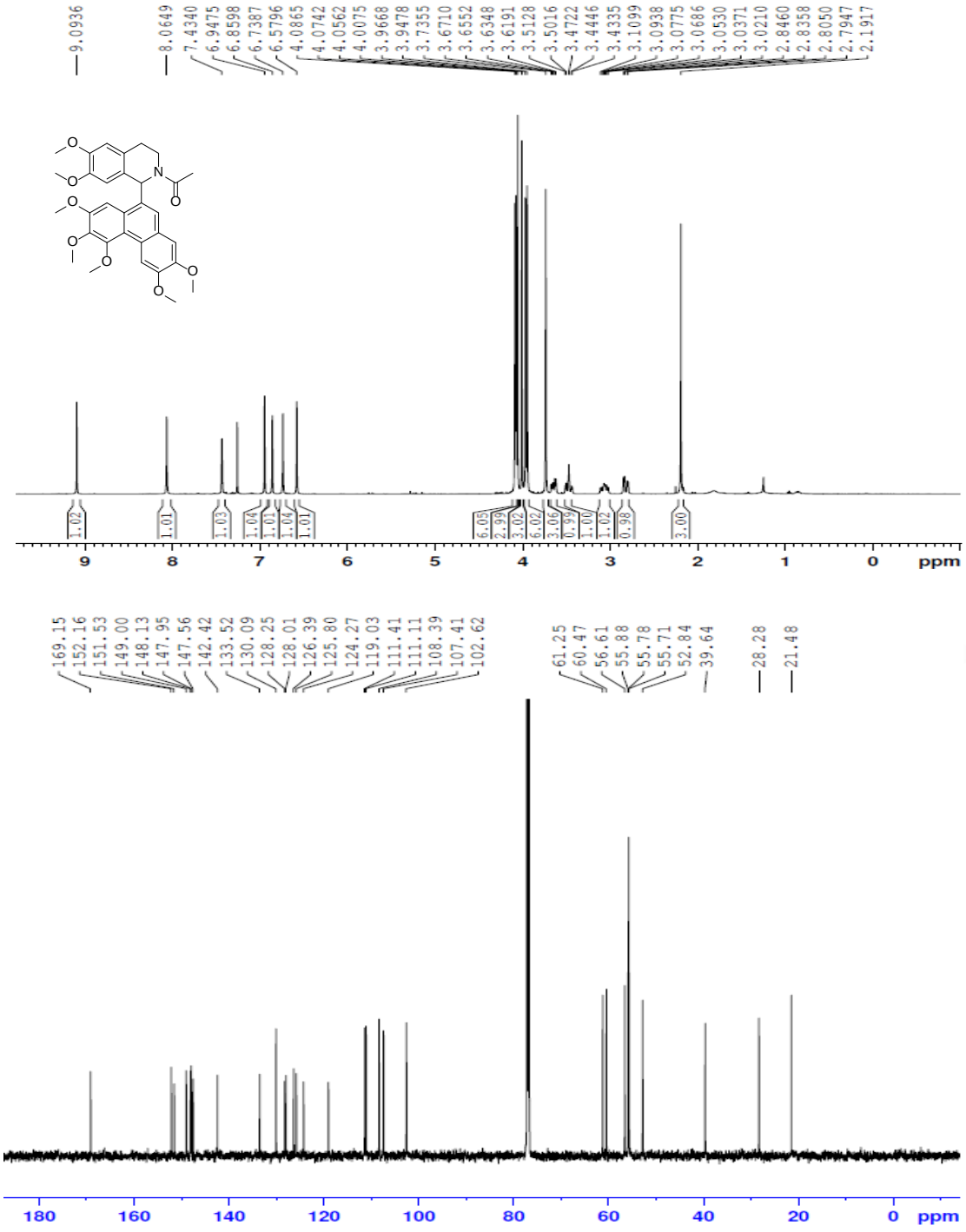
4. *1-(6,7-dimethoxy-1-(2,3,6,7-tetramethoxyphenanthren-9-yl)-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21d**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.19(s, 1H), 7.84(s, 1H), 7.77(s, 1H), 7.47(s, 1H), 6.98(s, 1H), 6.83(s, 1H), 6.75(s, 1H), 6.61(s, 1H), 4.14(s, 3H), 4.11(s, 6H), 3.97(s, 3H), 3.96(s, 3H), 3.75(s, 3H), 3.62-3.68(m, 1H), 3.45-3.53(m, 1H), 3.03-3.12(m, 1H), 2.80-2.86(m, 1H), 2.21(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.30, 149.63, 149.24, 149.12, 148.81, 148.30, 147.72, 133.80, 127.96, 126.40, 125.53, 125.28, 124.78, 124.40, 111.59, 111.24, 108.77, 106.08, 103.12, 102.68, 56.68, 56.15, 56.09, 55.97, 55.90, 53.01, 39.73, 28.40, 21.33. HRMS calcd for $C_{31}H_{33}NO_7Na$, $[M+Na]^+$, 554.2149; found 554.2164.



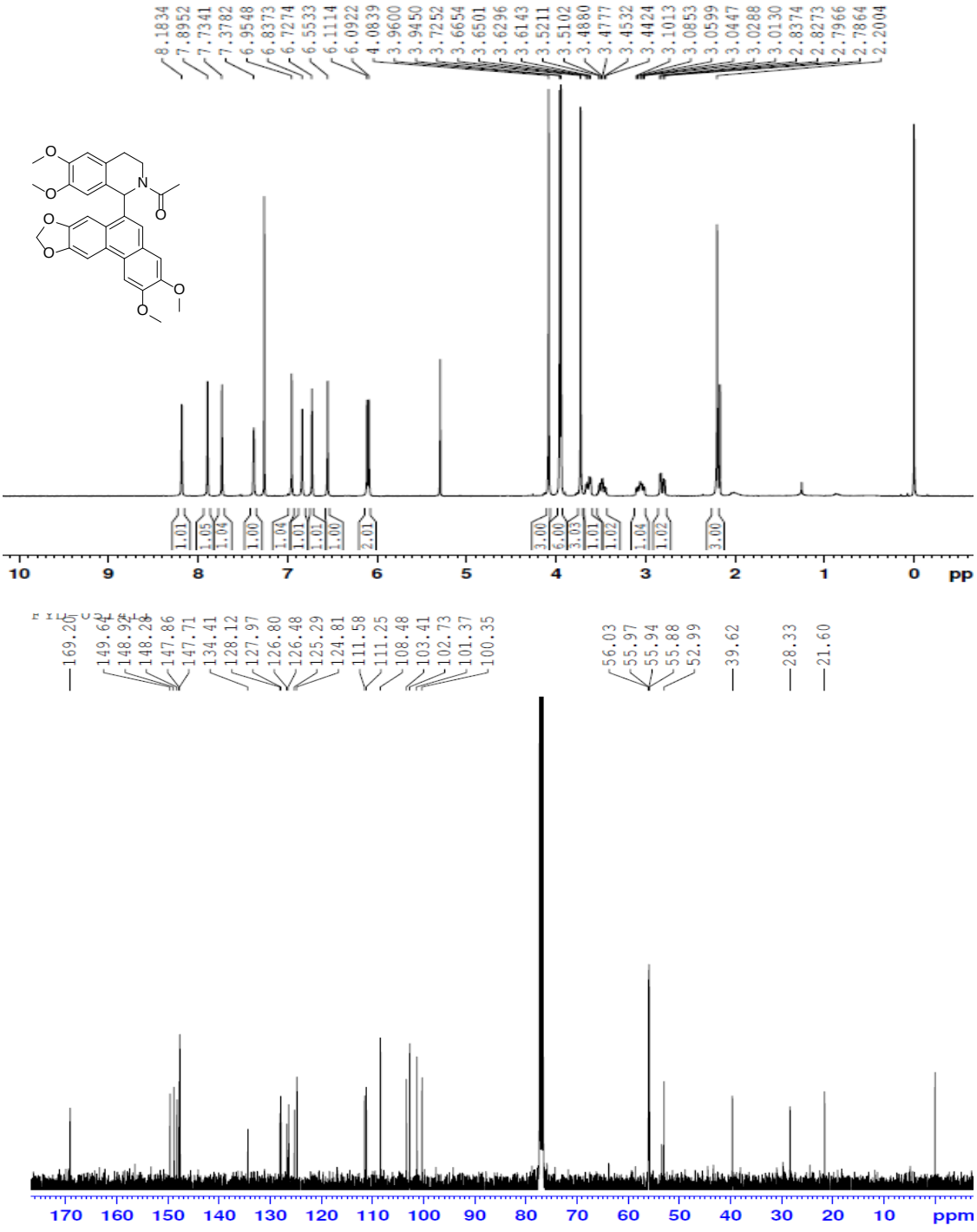
5. *1-(6,7-dimethoxy-1-(2,3,5,6,7-pentamethoxyphenanthren-9-yl)-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21e**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 9.09(s, 1H), 8.02(s, 1H), 7.39(s, 1H), 6.99(s, 1H), 6.90(s, 1H), 6.71(s, 1H), 6.55(s, 1H), 5.99-6.00(d, J = 0.90 Hz, 1H), 5.92-5.93(d, J = 0.96 Hz, 1H), 4.08(s, 6H), 4.05(s, 3H), 4.00(s, 3H), 3.97(s, 3H), 3.90(s, 3H), 3.60-3.61(s, 1H), 3.42-3.48(m, 1H), 3.00-3.06(m, 1H), 2.78-2.81(m, 1H), 2.17(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.08, 152.14, 151.52, 148.99, 147.94, 146.96, 146.26, 142.42, 133.40, 130.01, 129.10, 128.22, 127.58, 125.74, 124.32, 119.07, 108.84, 108.34(×2), 107.42, 102.59, 100.95, 61.26, 60.49, 56.60, 55.77, 55.71, 53.05, 39.45, 28.77, 21.47. HRMS calcd for $C_{32}H_{35}NO_8Na$, $[M+Na]^+$, 584.2225; found 584.2229.



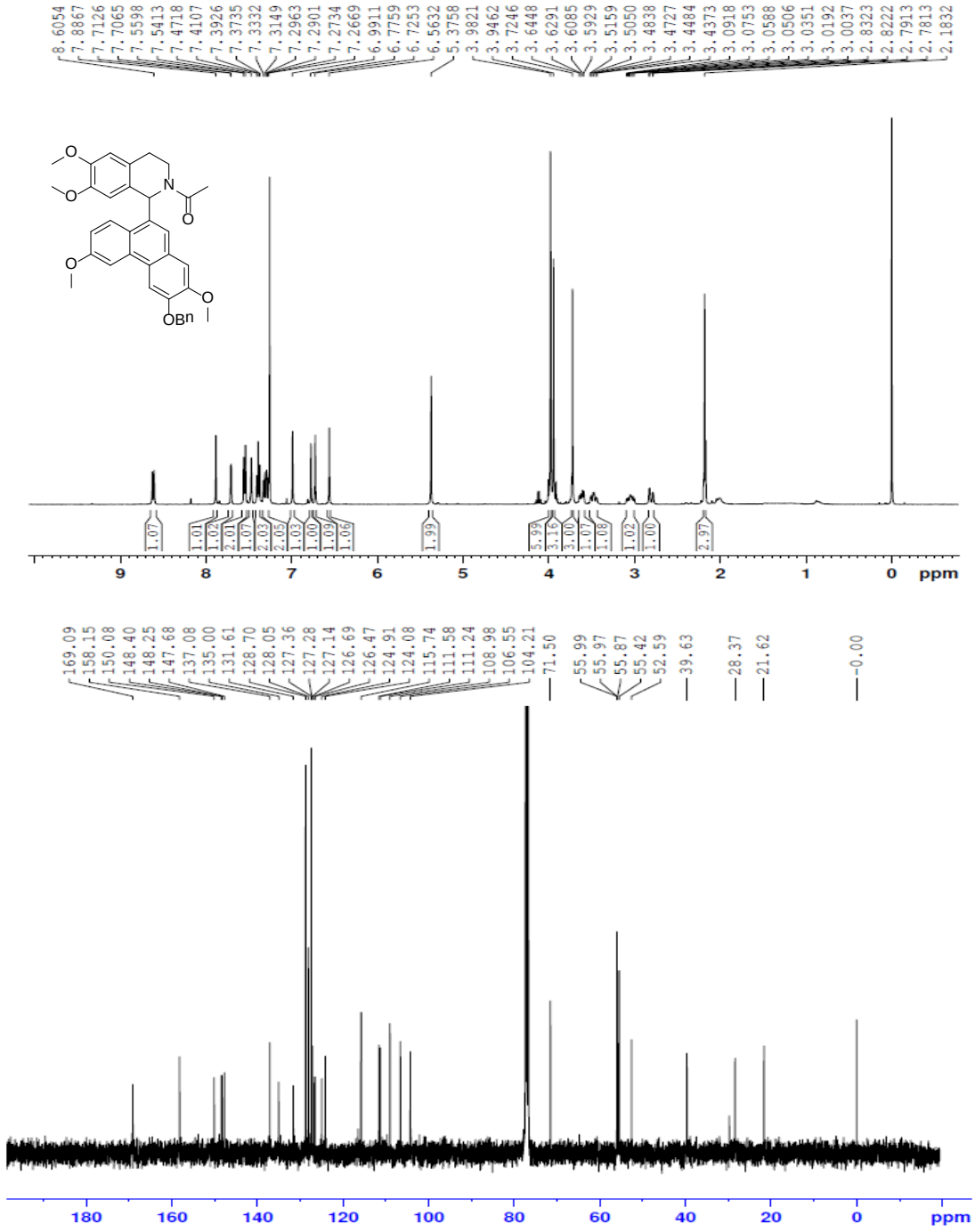
6. *1-(1-(2,3-dimethoxyphenanthro[3,2-d][1,3]dioxol-6-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21f**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.18(s, 1H), 7.90(s, 1H), 7.73(s, 1H), 7.38(s, 1H), 6.95(s, 1H), 6.84(s, 1H), 6.73(s, 1H), 6.55(s, 1H), 6.09-6.11(d, J = 7.69 Hz, 2H), 4.08(s, 3H), 3.96(s, 3H), 3.95(s, 3H), 3.73(s, 3H), 3.61-3.67(m, 1H), 3.44-3.52(m, 1H), 3.01-3.10(m, 1H), 2.79-2.84(m, 1H), 2.20(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.20, 149.64, 148.92, 148.28, 147.86, 147.71, 134.41, 128.12, 127.97, 126.80, 126.48, 125.29, 124.81, 111.58, 111.25, 108.48, 103.41, 102.73, 101.37, 100.35, 56.03, 55.97, 55.94, 55.88, 52.99, 39.62, 28.33, 21.60. HRMS calcd for $C_{30}H_{29}NO_7Na$, $[M+Na]^+$, 538.1836; found 538.1829.



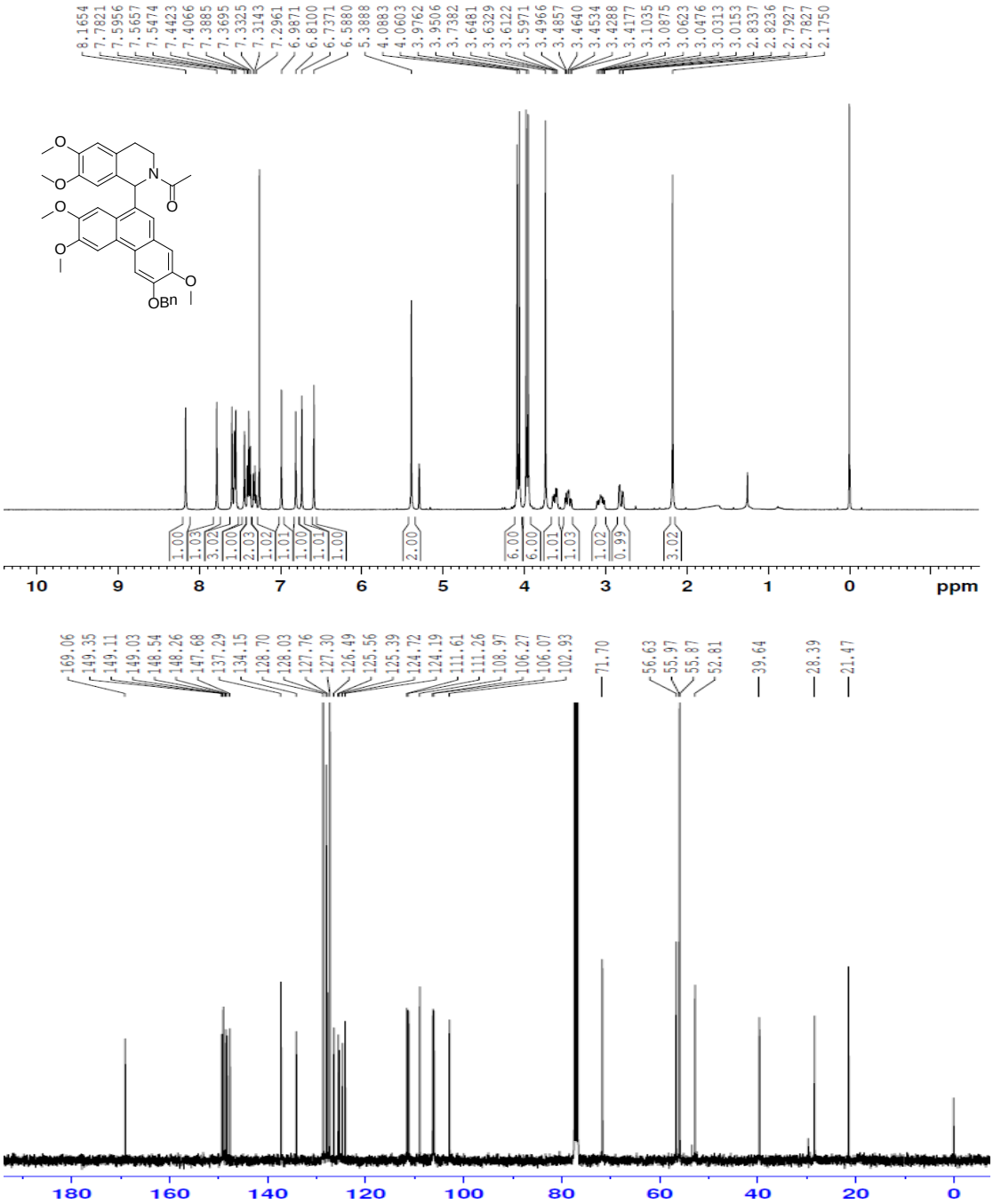
7. *1-(1-(3-(benzyloxy)-2,6-dimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone* (***21g***)

^{1}H NMR (400MHz, $CDCl_3$) δ 8.61-8.63(d, J = 9.20 Hz, 1H), 7.89(s, 1H), 7.70-7.71(d, J = 2.44 Hz, 1H), 7.54-7.56(d, J = 7.40 Hz, 2H), 7.47(s, 1H), 7.37-7.41(m, 2H), 7.27-7.33(m, 2H), 6.99(s, 1H), 6.78(s, 1H), 6.73(s, 1H), 6.56(s, 1H), 5.38(s, 2H), 3.98(s, 6H), 3.95(s, 3H), 3.73(s, 3H), 3.59-3.65(m, 1H), 3.44-3.52 (m, 1H), 3.00-3.09(m, 1H), 2.78-2.83(m, 1H), 2.18(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.09, 150.08, 148.40, 148.25, 147.68, 137.08, 135.00, 131.61, 128.70(×2), 128.05(×2), 127.36(×2), 127.28, 127.14, 126.69, 126.47, 124.91, 124.08, 115.74, 111.58, 111.24, 108.98, 106.55, 104.21, 71.50, 55.99, 55.97, 55.87, 55.42, 52.59, 39.63, 28.37, 21.62. HRMS calcd for $C_{36}H_{35}NO_6Na$, $[M+Na]^+$, 600.2357; found 600.2349.



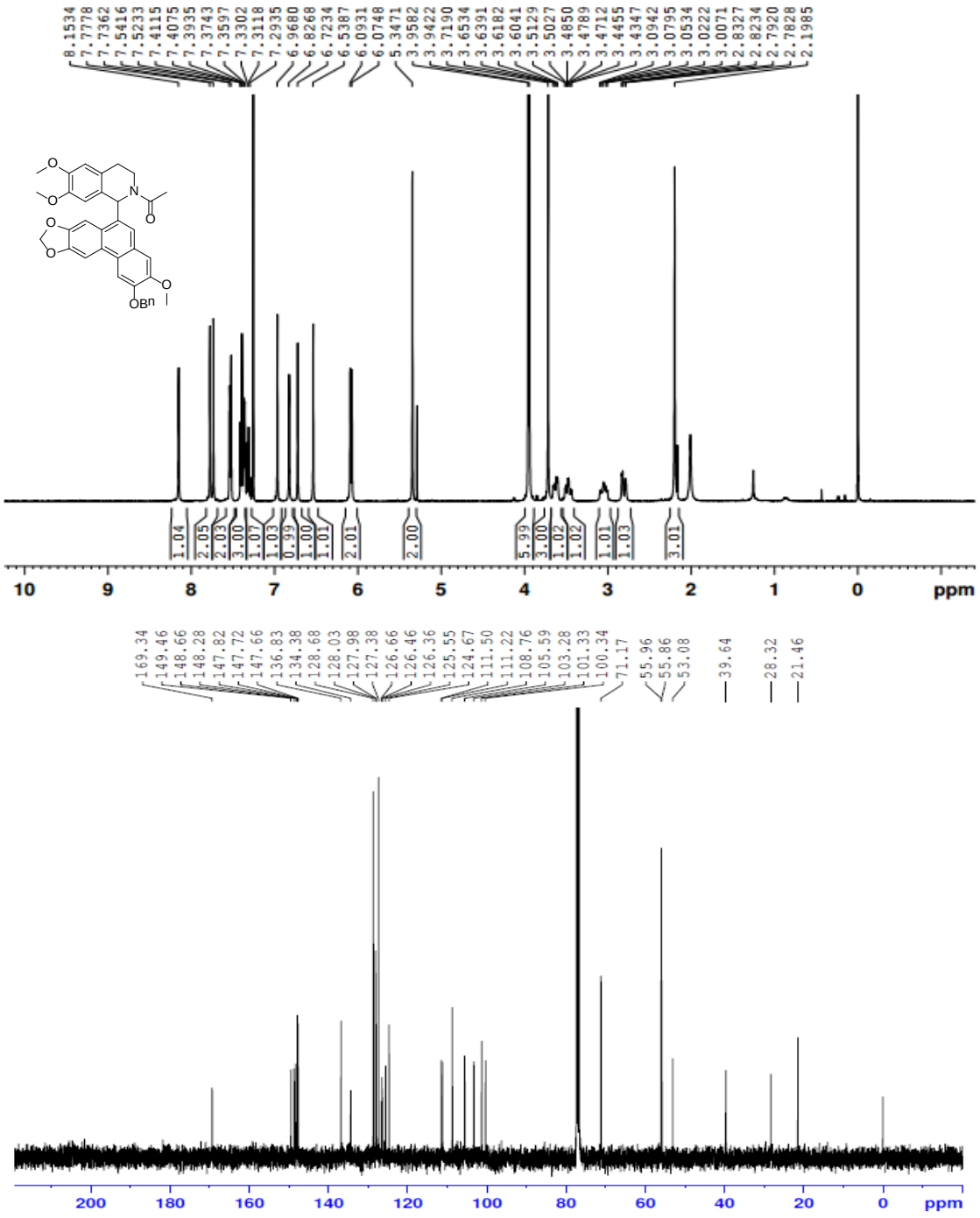
8. *1-(1-(3-(benzyloxy)-2,6,7-trimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydro isoquinolin-2(1H)-yl)ethanone* ***(21h)***

^{1}H NMR (400MHz, $CDCl_3$) δ 8.17(s, 1H)，7.78(s, 1H), 7.60(s, 1H), 7.57(s, 1H), 7.55(s, 1H), 7.44(s, 1H), 7.37-7.41(m, 2H), 7.30-7.33(m, 1H), 6.99(s, 1H), 6.81(s, 1H), 6.74(s, 1H), 6.59(s, 1H), 5.39(s, 2H), 4.09(s, 3H), 4.06(s, 3H), 3.98(s, 3H), 3.95(s, 3H), 3.74(s, 3H), 3.61-3.65(m, 1H), 3.42-3.50(m, 1H), 3.01-3.10(m, 1H), 2.78-2.83(m, 1H), 2.18(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.06, 149.35, 149.11, 149.03, 148.54, 148.26, 147.68, 137.29, 134.15, 128.70(×2), 128.03(×2), 127.76, 127.30(×2), 126.49, 125.56, 125.39, 124.72, 124.19, 111.61, 111.26, 108.97, 106.27, 106.07, 102.93, 71.70, 56.63, 55.97(×2), 55.87(×2), 52.81, 39.64, 28.39, 21.47. HRMS calcd for $C_{37}H_{37}NO_7Na$, $[M+Na]^+$, 630.2462; found 630.2461.



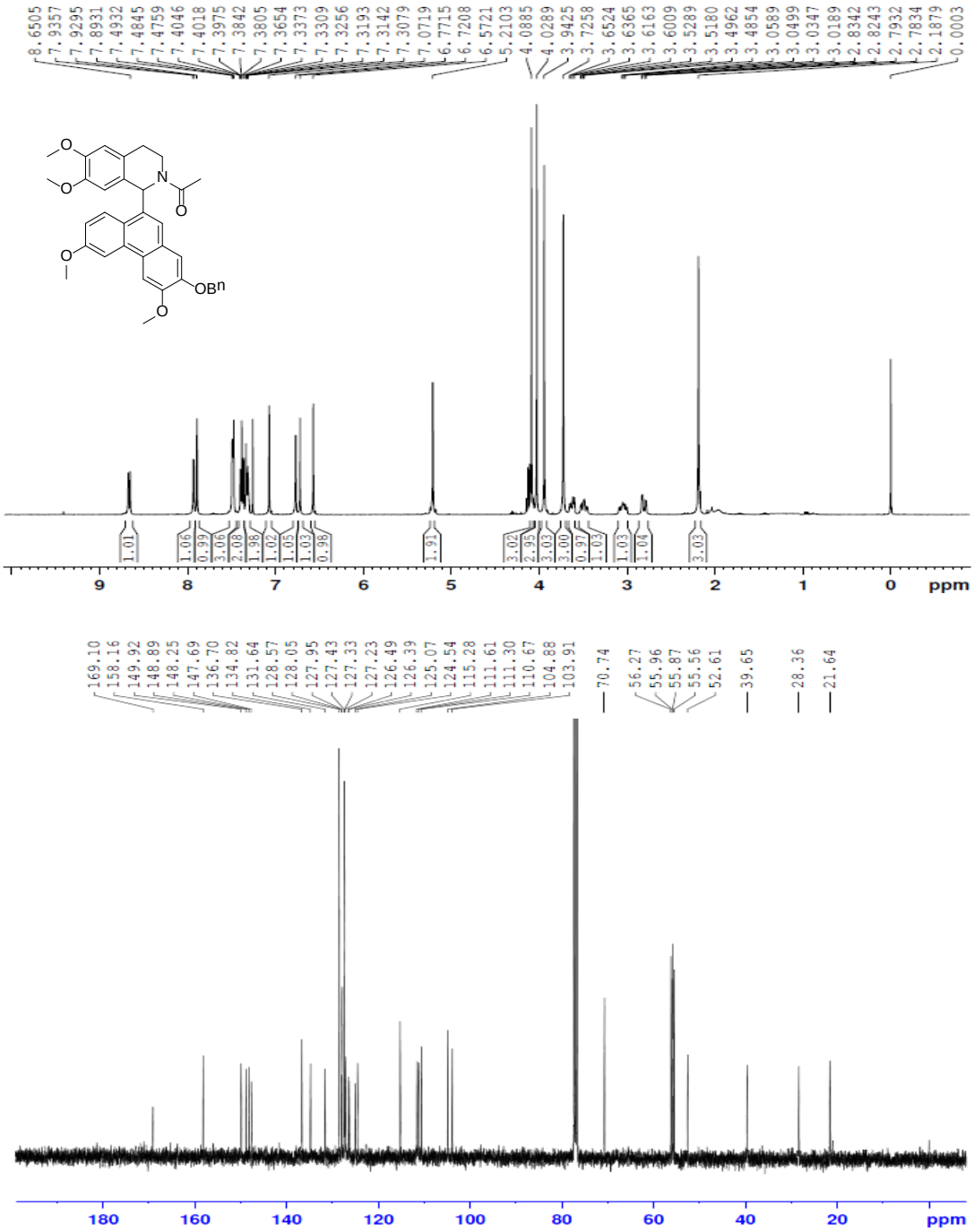
9. *1-(1-(2-(benzyloxy)-3-methoxyphenanthro[3,2-d][1,3]dioxol-6-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21i**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.15(s, 1H), 7.78(s, 1H), 7.74(s, 1H), 7.54(s, 1H), 7.52(s, 1H), 7.36-7.41(m, 3H), 7.29-7.33(m, 1H), 6.97(s, 1H), 6.83(s, 1H), 6.72(s, 1H), 6.54(s, 1H), 6.09(s, 1H), 6.07(s, 1H), 5.35(s, 2H), 3.96(s, 3H), 3.94(s, 3H), 3.72(s, 3H), 3.60-3.65(m, 1H), 3.43-3.51(m, 1H), 3.01-3.09(m, 1H), 2.78-2.83(m, 1H), 2.20(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.35, 149.47, 148.66, 148.29, 147.82, 147.72, 147.66, 136.83, 134.38, 128.68(×2), 128.04, 127.98, 127.38(×2), 126.66, 126.47, 126.36, 125.55, 124.67, 111.51, 111.22, 108.76, 105.59, 103.29, 101.34, 100.34, 77.24, 71.17, 55.97(×2), 55.86, 53.08, 39.64, 28.32, 21.46. HRMS calcd for $C_{36}H_{33}NO_7Na$, $[M+Na]^+$, 614.2150; found 614.2148.



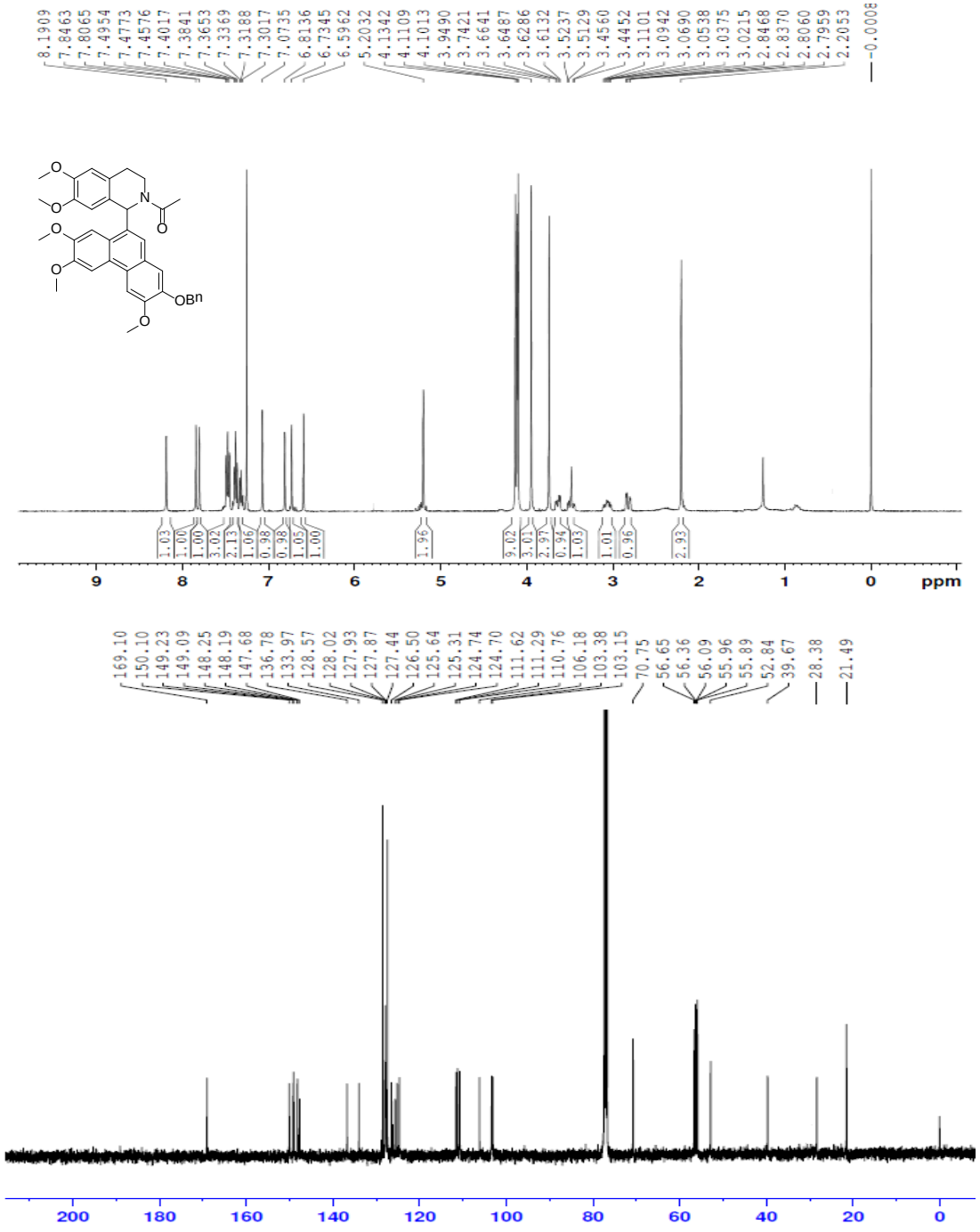
10. *1-(1-(2-(benzyloxy)-3,6-dimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21j**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.65-8.67(d, J = 9.20 Hz, 1H), 7.93-7.94(d, J = 2.44 Hz, 1H), 7.89(s, 1H), 7.47-7.49(m, 3H), 7.36-7.40(m, 2H), 7.30-7.34(m, 2H), 7.07(s, 1H), 6.77(s, 1H), 6.72(s, 1H), 6.57(s, 1H), 5.21(s, 2H), 4.03(s, 3H), 3.94(s, 3H), 3.73(s, 3H), 3.60-3.65(m, 1H), 3.45-3.53(m, 1H), 3.00-3.09(m, 1H), 2.78-2.83(m, 1H), 2.19(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.10, 158.16, 149.92, 148.89, 148.25, 147.69, 136.70, 134.82, 131.64, 128.57(×2), 128.05, 127.95, 127.43(×2), 127.33, 127.23, 126.49, 126.39, 125.07, 124.54, 115.28, 111.61, 111.30, 110.67, 104.88, 103.91, 70.74, 56.27, 55.96, 55.87, 55.56, 52.61, 39.65, 28.36, 21.64. HRMS calcd for $C_{36}H_{35}NO_6Na$, $[M+Na]^+$, 600.2357; found 600.2359.



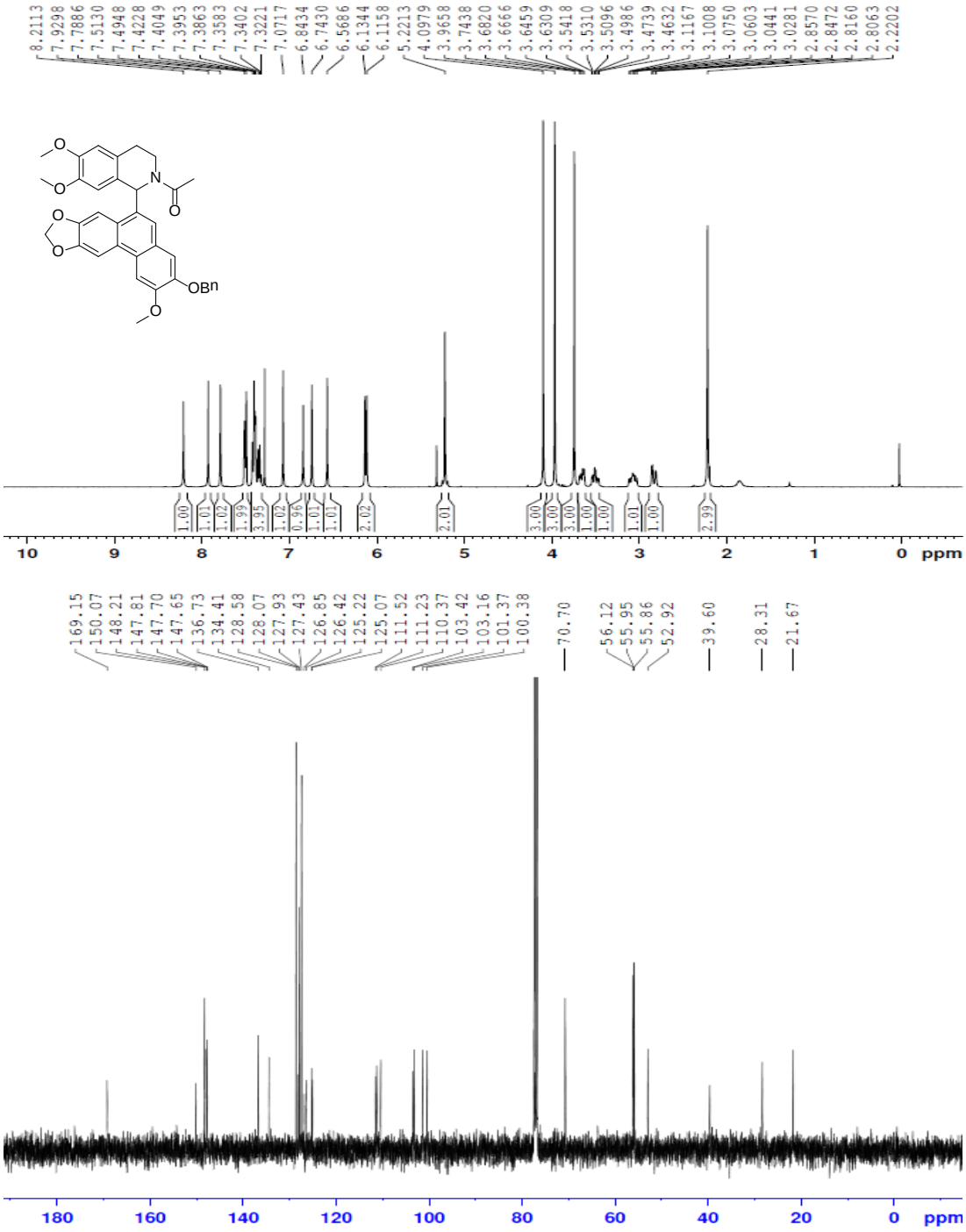
11. *1-(1-(2-(benzyloxy)-3,6,7-trimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydro isoquinolin-2(1H)-yl)ethanone (**21k**)*

^{1}H NMR(400MHz, $CDCl_3$) δ 8.19(s, 1H), 7.85(s, 1H), 7.81(s, 1H), 7.37-7.40(m, 2H), 7.30-7.34(m, 1H), 7.07(s, 1H), 6.81(s, 1H), 6.73(s, 1H), 6.60(s, 1H), 5.20(s, 2H), 4.13(s, 3H), 4.11(s, 3H), 4.10(s, 3H), 3.95(s, 3H), 3.74(s, 3H), 3.61-3.66(m, 1H), 3.45-3.52(m, 1H), 3.02-3.11(m, 1H), 2.80-2.85(m, 1H), 2.21(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.10, 150.10, 149.23, 149.09, 148.25, 148.19, 147.68, 136.78, 133.97, 128.57(×2), 128.02, 127.93, 127.87, 127.44(×2), 126.50, 125.64, 125.31, 124.74, 124.70, 111.62, 111.29, 110.76, 106.18, 103.38, 103.15, 70.75, 56.65, 56.36, 56.09, 55.96, 55.89, 52.84, 39.67, 28.38, 21.49. HRMS calcd for $C_{37}H_{37}NO_7Na$, $[M+Na]^+$, 630.2462; found 630.2463.



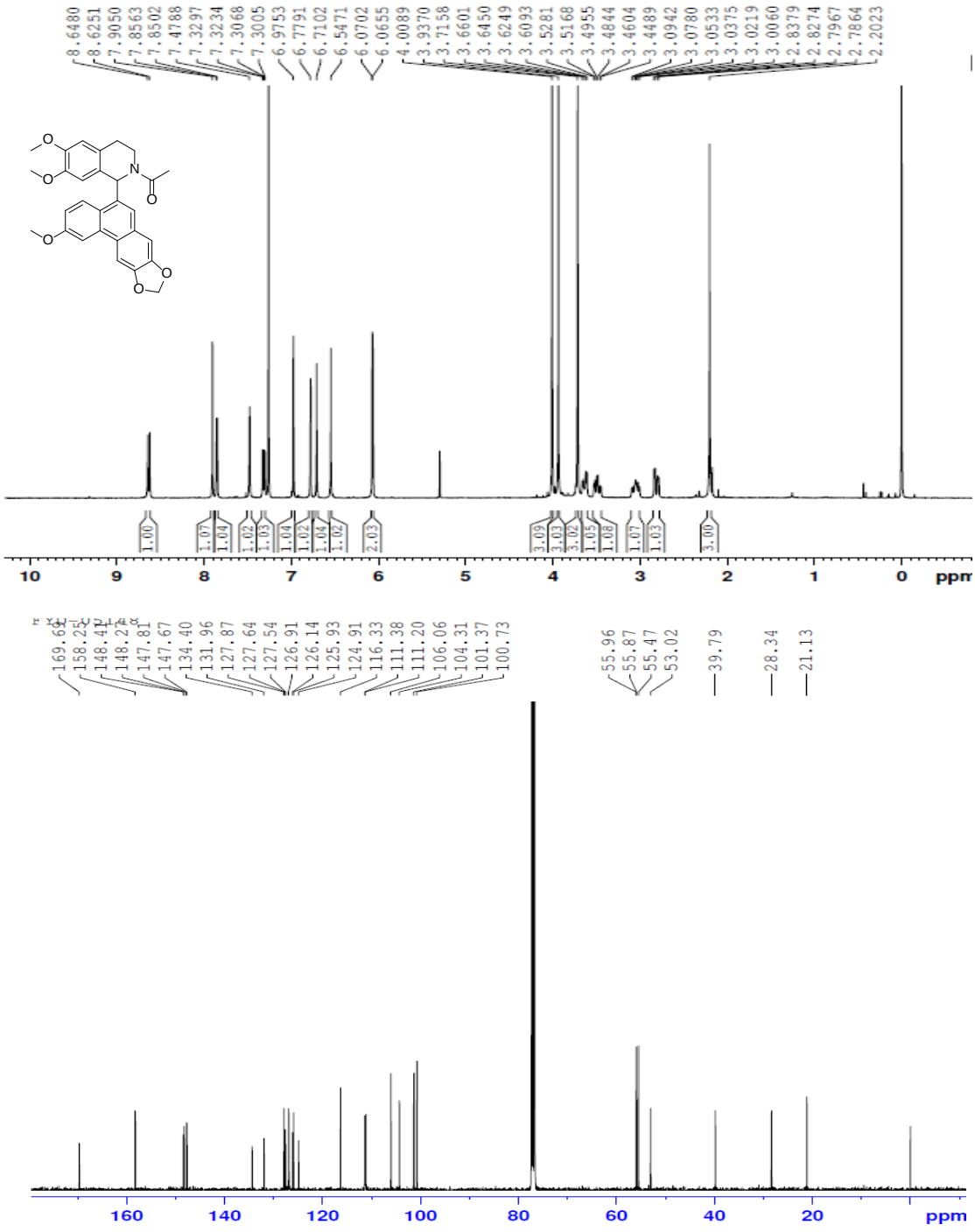
12. *1-(1-(3-(benzyloxy)-2-methoxyphenanthro[3,2-d][1,3]dioxol-6-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21l**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.21(s, 1H), 7.93(s, 1H), 7.79(s, 1H), 7.49-7.51(m, 2H), 7.32-7.42(m, 4H), 7.07(s, 1H), 6.84(s, 1H), 6.74(s, 1H), 6.57(s, 1H), 6.11-6.14(d, J = 7.44 Hz, 2H), 5.22(s, 2H), 4.10(s, 3H), 3.97(s, 3H), 3.74(s, 3H), 3.63-3.68(m, 1H), 3.46-3.54(s, 1H), 3.03-3.12(s, 1H), 2.80-2.86(m, 1H), 2.22(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.15, 150.07, 148.21(×2), 147.81, 147.70, 147.65, 136.73, 134.41, 128.58(×2), 128.07, 127.93(×2), 127.42(×2), 126.85, 126.42(×2), 125.22, 125.07, 111.52, 111.23, 110.37, 103.42, 103.16, 101.37, 100.37, 70.70, 56.12, 55.95, 55.86, 52.92, 39.60, 28.31, 21.67. HRMS calcd for $C_{36}H_{33}NO_7Na$, $[M+Na]^+$, 614.2149; found 614.2141.



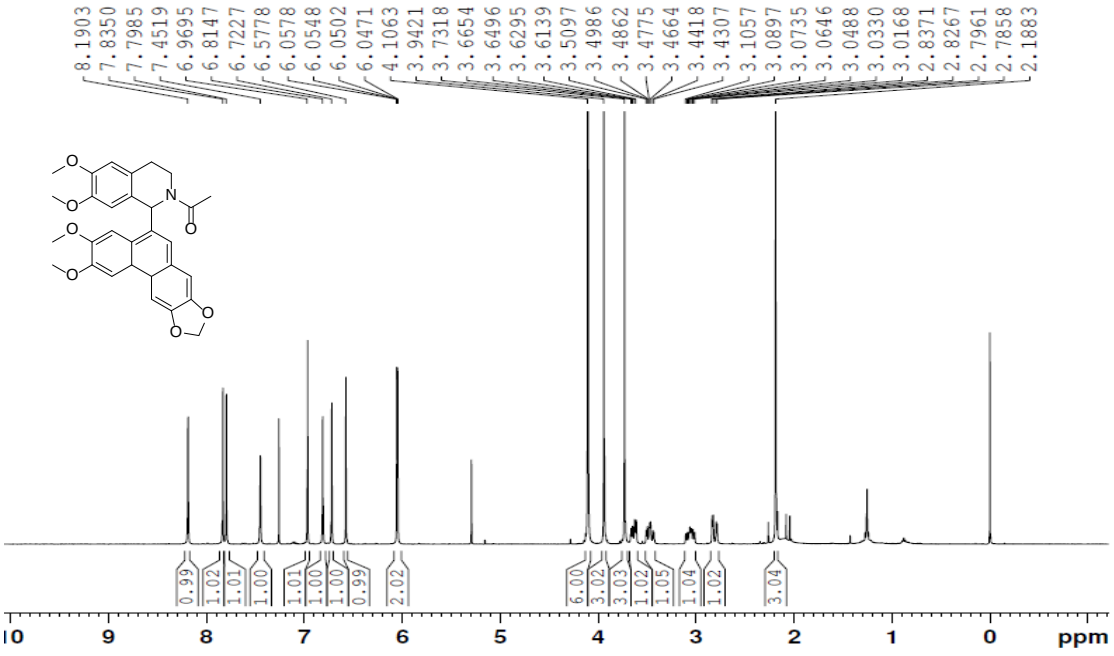
13. *1-(6,7-dimethoxy-1-(2-methoxyphenanthro[2,3-d][1,3]dioxol-5-yl)-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21m**)*

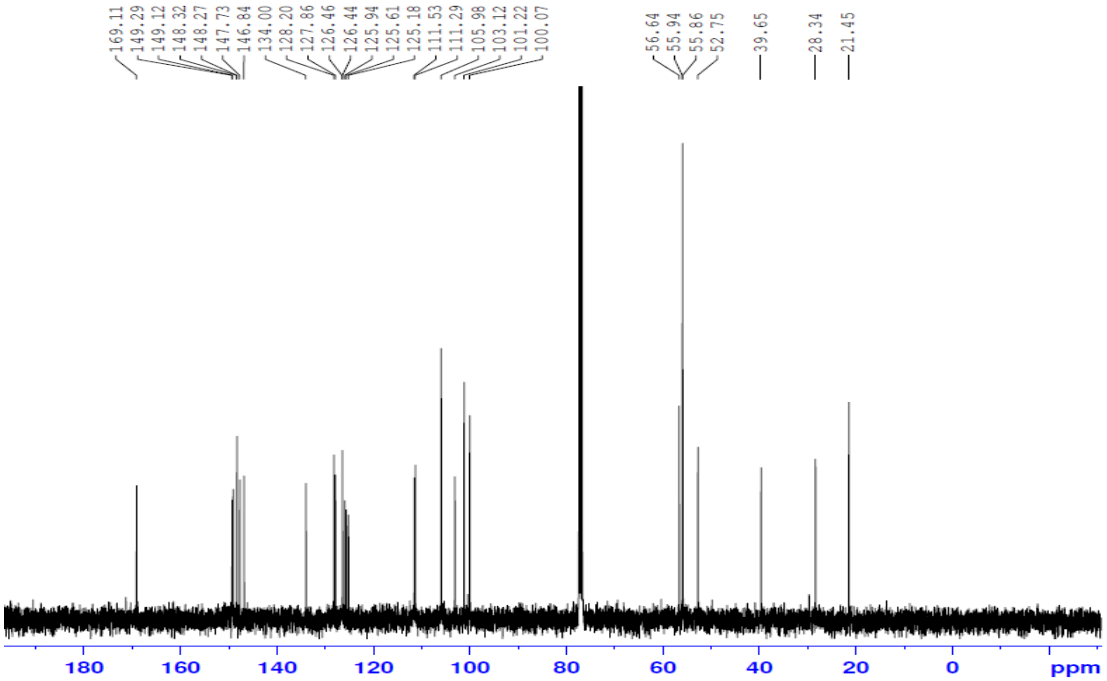
^{1}H NMR (400MHz, $CDCl_3$) δ 8.63-8.65(d, J = 9.16 Hz, 1H), 7.91(s, 1H), 7.85-7.86 (d, J = 2.44 Hz, 1H), 7.48(s, 1H), 7.30-7.33(m, 1H), 6.98(s, 1H), 6.78(s, 1H), 6.71(s, 1H), 6.55(s, 1H), 6.06-6.07(s, 2H), 4.01(s, 3H), 3.94(s, 3H), 3.72(s, 3H), 3.61-3.66(m, 1H), 3.45-3.53(m, 1H), 3.01-3.09(m, 1H), 2.79-2.84(m, 1H), 2.20(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.69, 158.25, 148.41, 148.27, 147.81, 147.67, 134.40, 131.96, 127.87, 127.64, 127.54, 126.91, 126.14, 125.93, 124.91, 116.33, 111.38, 111.20, 106.06, 104.31, 101.37, 100.73, 55.96, 55.87, 55.47, 53.02, 39.79, 28.34, 21.13. HRMS calcd for $C_{29}H_{27}NO_6Na$, $[M+Na]^+$, 508.1731; found 508.1724.



14. *1-(1-(2,3-dimethoxyphenanthro[2,3-d][1,3]dioxol-5-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21n**)*

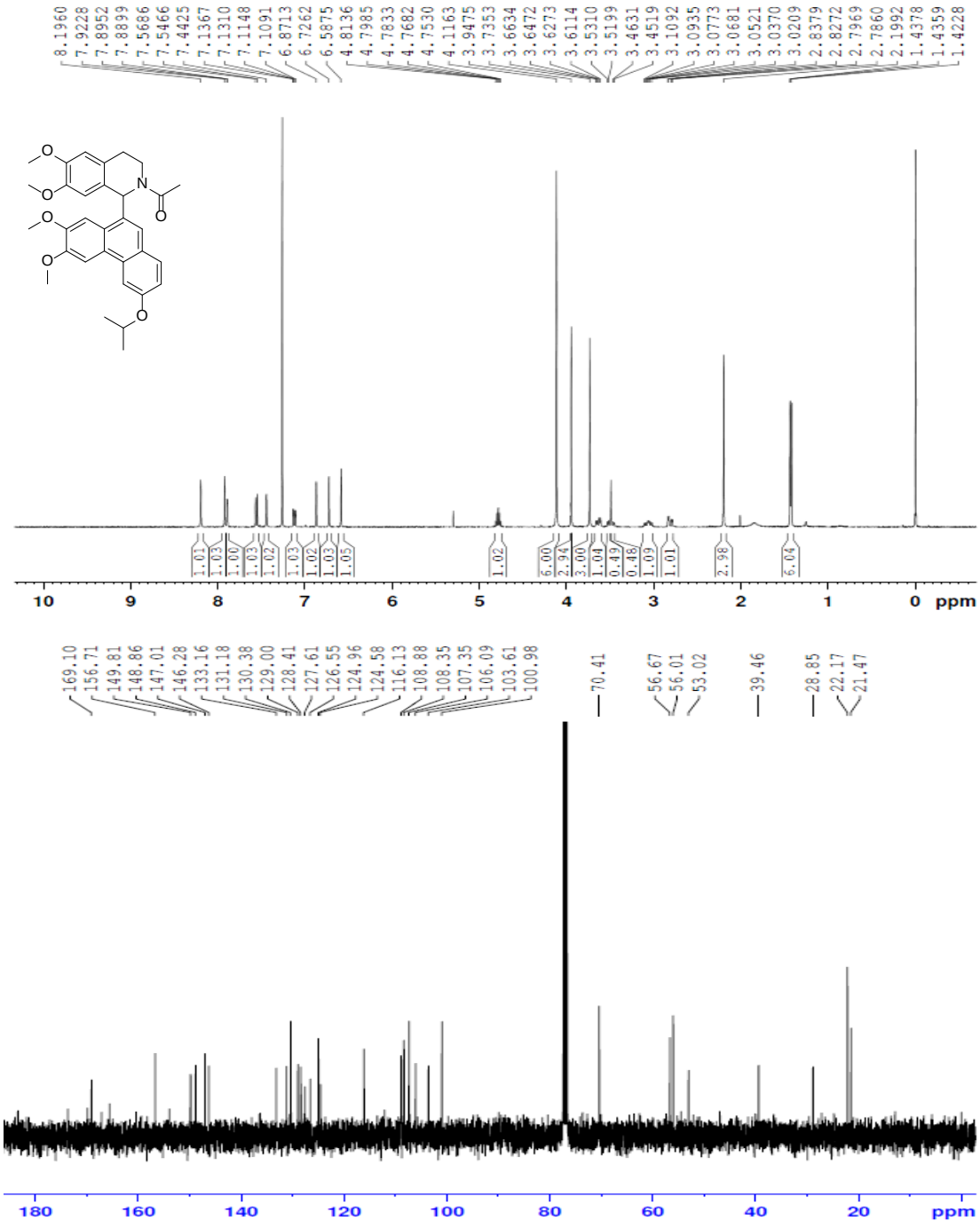
^{1}H NMR (400MHz, $CDCl_3$) δ 8.19(s, 1H), 7.84(s, 1H), 7.80(s, 1H), 7.45(s, 1H), 6.97(s, 1H), 6.81(s, 1H), 6.72(s, 1H), 6.58(s, 1H), 6.05-6.06(m, 2H), 4.11(s, 6H), 3.94(s, 3H), 3.73(s, 3H), 3.61-3.67(m, 1H), 3.43-3.51(m, 1H), 3.02-3.11(m, 1H), 2.79-2.84(m, 1H), 2.19(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.11, 149.29, 149.12, 148.32, 148.27, 147.73, 146.84, 134.00, 128.20, 127.86, 126.46, 126.44, 125.94, 125.61, 125.18, 111.53, 111.29, 105.98(×2), 103.12, 101.22, 100.07, 56.64, 55.94(×2), 55.86, 52.75, 39.65, 28.34, 21.45 HRMS calcd for $C_{30}H_{29}NO_7Na$, $[M+Na]^+$, 538.1836; found 538.1829.





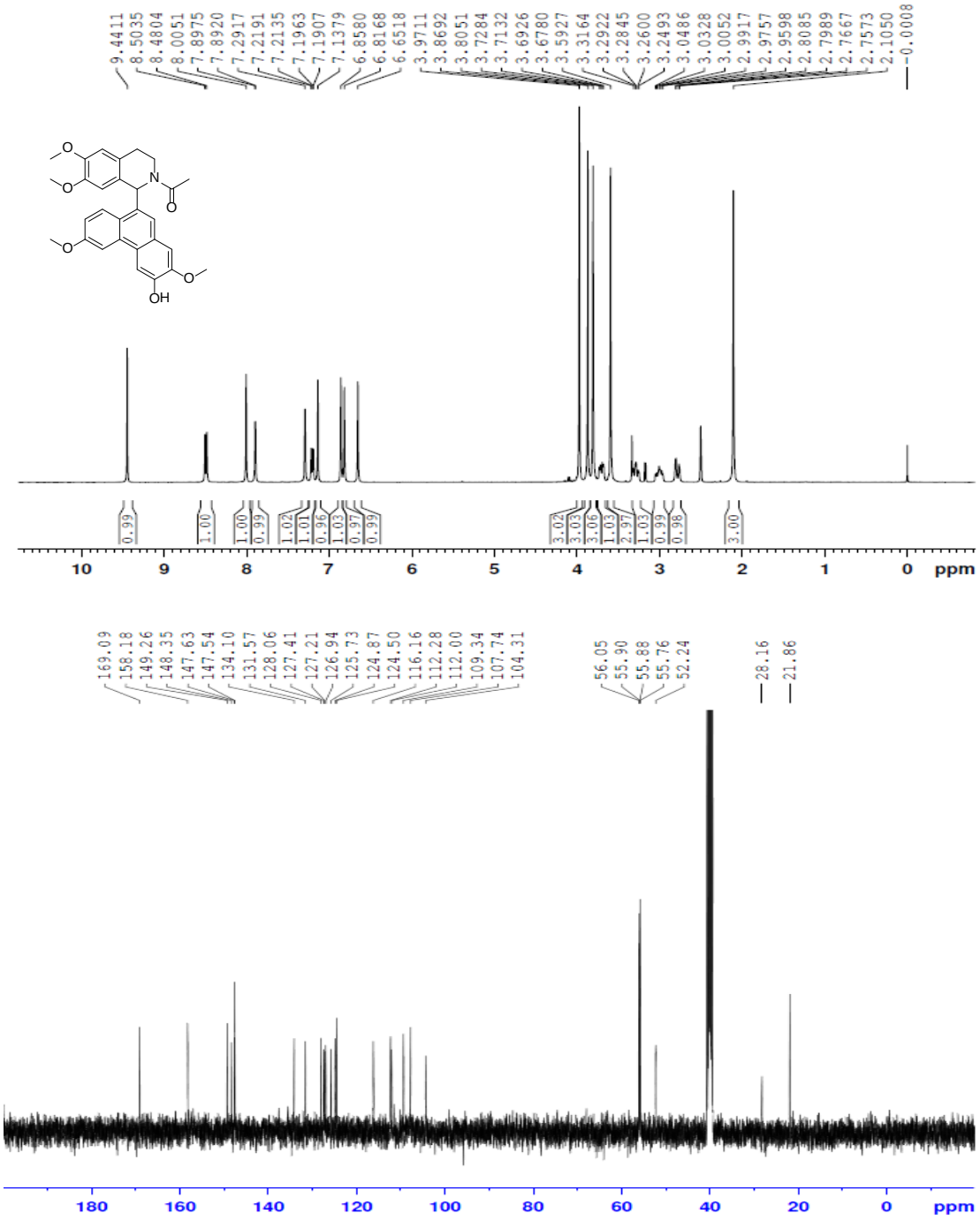
15. *1-(1-(3-isopropoxy-6,7-dimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21o**)*

^{1}H-NMR (400MHz, $CDCl_3$) δ 8.20(s, 1H), 7.92(s, 1H), 7.89-7.90(d, J = 2.12 Hz, 1H), 7.55-7.57(d, J = 8.80 Hz, 1H), 7.44(s, 1H), 7.11-7.14(dd, J = 8.76, 2.28 Hz, 1H), 6.87(s, 1H), 6.73(s, 1H), 6.59(s, 1H), 4.75-4.81(m, 1H), 4.11(s, 6H), 3.95 (s, 3H), 3.74(s, 3H), 3.61-3.66(m, 1H), 3.45-3.53(m, 1H), 2.92-3.11(m, 1H), 2.79-2.84(m, 1H), 2.20(s, 3H), 1.42-1.44(dd, J = 6.00, 0.76 Hz, 6H). ^{13}C-NMR (100MHz, $CDCl_3$) δ 169.10, 156.71, 149.80, 148.86, 147.01, 146.28, 133.16, 131.17, 130.38(×2), 129.00, 128.41, 127.61, 126.55, 124.96, 124.58, 116.12, 108.88, 108.35, 107.35, 106.09, 103.60, 100.98, 70.41, 56.67, 56.01, 53.02, 39.46, 28.85, 22.17(×2), 21.46. HRMS calcd for $C_{32}H_{35}NO_6Na$, $[M+Na]^+$, 552.2357; found 552.2369.



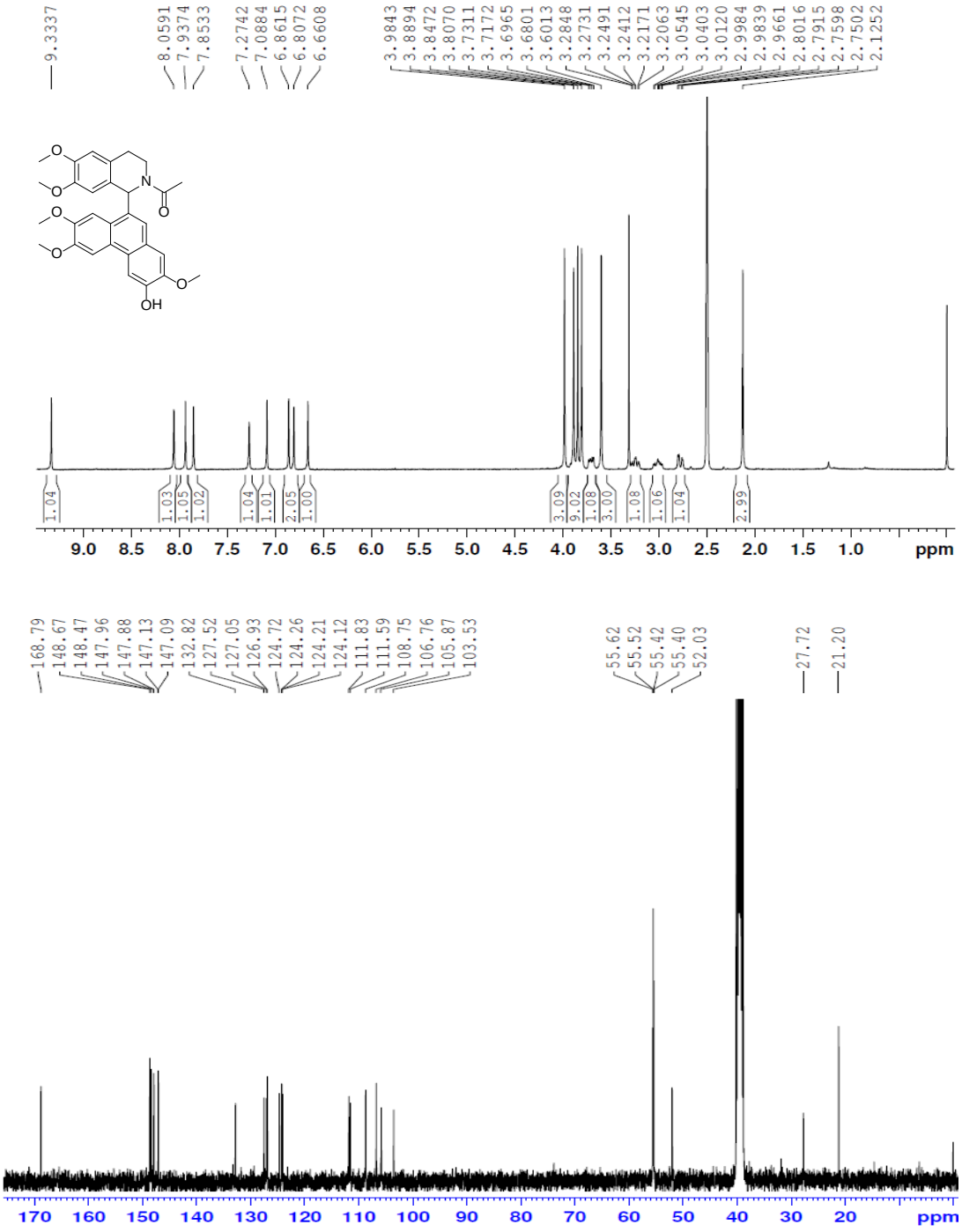
16. *1-(1-(3-hydroxy-2,6-dimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21p**).*

^{1}H NMR (400MHz, DMSO-d_6) δ 9.44(s, 1H), 8.48-8.50(d, J = 9.24 Hz, 1H), 8.01(s, 1H), 7.88-7.90(d, J = 2.20 Hz, 1H), 7.29(s, 1H), 7.19-7.22(dd, J = 9.12, 2.24 Hz, 1H), 7.14(s, 1H), 6.86(s, 1H), 6.82(s, 1H), 6.65(s, 1H), 3.97(s, 3H), 3.87(s, 3H), 3.80(s, 1H), 3.68-3.73(m, 1H), 3.59(s, 1H), 3.24-3.32(m, 1H), 2.96-3.05(s, 1H), 2.76-2.81(m, 1H), 2.11(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.09, 158.18, 149.26, 148.35, 147.63, 147.54, 134.10, 131.57, 128.06, 127.41, 127.21, 126.94, 125.73, 124.87, 124.49, 116.16, 112.28, 112.00, 109.33, 107.74, 104.31, 56.05, 55.89(×2), 55.88, 55.76, 52.24, 28.16, 21.85. HRMS calcd for $C_{29}H_{30}NO_6$, $[M+H]^+$, 488.2068; found 488.2066.



17. *1-(1-(3-hydroxy-2,6,7-trimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21q**)*

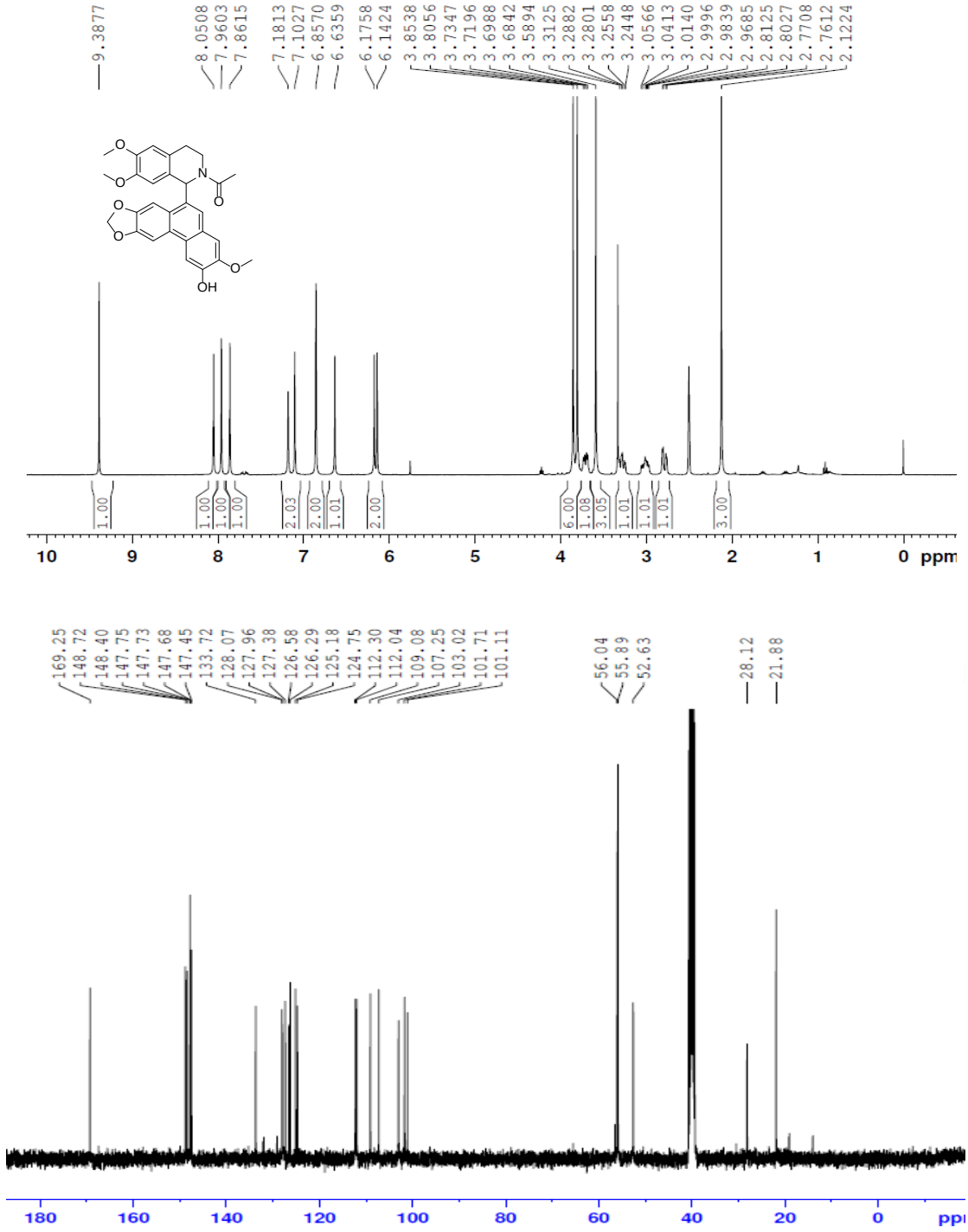
^{1}H NMR (400MHz, DMSO-d_6) δ 9.33(s, 1H), 8.06(s, 1H), 7.94(s, 1H), 7.85(s, 1H), 7.27(s, 1H), 7.09(s, 1H), 6.86(s, 1H), 6.81(s, 1H), 6.66(s, 1H), 3.98(s, 3H), 3.89(s, 3H), 3.85(s, 3H), 3.81(s, 3H), 3.68-3.73(m, 1H), 3.60(s, 3H), 3.21-3.28(m, 1H), 2.97-3.05(m, 1H), 2.75-2.80(m, 1H), 2.13(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 168.79, 148.67, 148.47, 147.96, 147.88, 147.13, 147.09, 127.52, 132.82, 127.05, 126.93, 124.72, 124.26, 124.21, 124.12, 111.83, 111.59, 108.75, 106.76, 105.87, 103.53, 55.62, 55.52, 55.42, 55.40, 52.03, 27.72, 21.20. HRMS calcd for $C_{30}H_{32}NO_7$, $[M+H]^+$, 518.2173; found 518.2184.



18. *1-(1-(2-hydroxy-3-methoxyphenanthro[3,2-d][1,3]dioxol-6-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21r**)*

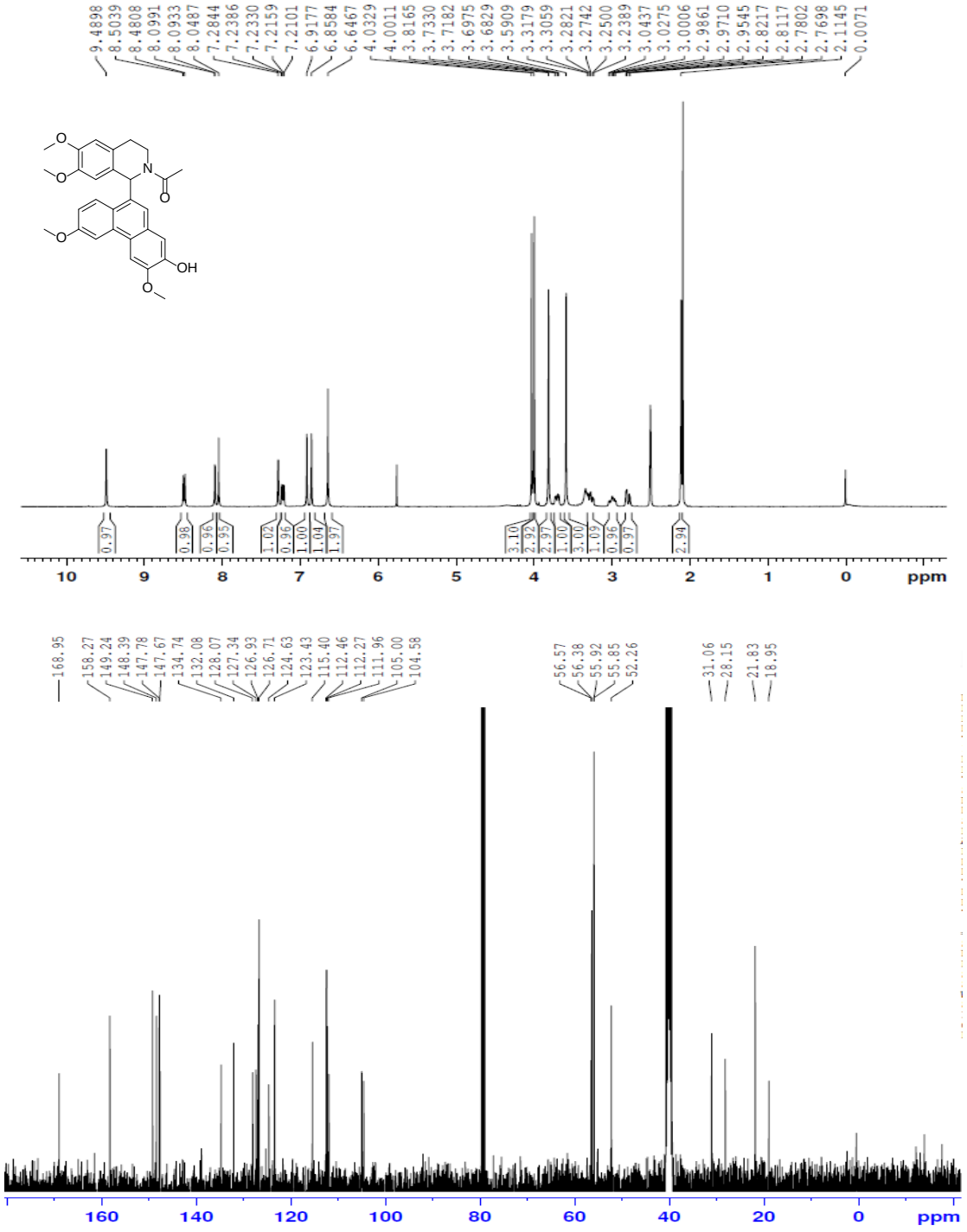
^{1}H NMR (400MHz, DMSO-d_6) δ 9.39(s, 1H), 8.05(s, 1H), 7.96(s, 1H), 7.86(s, 1H), 7.18(s, 1H), 7.10(s, 1H), 6.86(s, 2H), 6.64(s, 1H), 6.18(s, 1H), 6.14(s, 1H), 3.85(s, 3H), 3.81(s, 3H), 3.68-3.73(m, 1H), 3.59(s, 3H), 3.24-3.31(m, 1H), 2.97-3.06(m, 1H), 2.76-2.81(m, 1H), 2.12(s, 3H).

^{13}C NMR (100MHz, DMSO-d_6) δ 169.25, 148.72, 148.40, 147.75, 147.73, 147.68, 147.45, 133.72, 128.07, 127.96, 127.38, 126.58, 126.29, 125.18, 124.75, 112.30, 112.04, 109.08, 107.25, 103.02, 101.71, 101.11, 56.04(×2), 55.89(×2), 52.63, 28.12, 21.88. HRMS calcd for $C_{29}H_{28}NO_7$, $[M+H]^+$, 502.1860; found 502.1847.



19. *1-(1-(2-hydroxy-3,6-dimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21s**)*

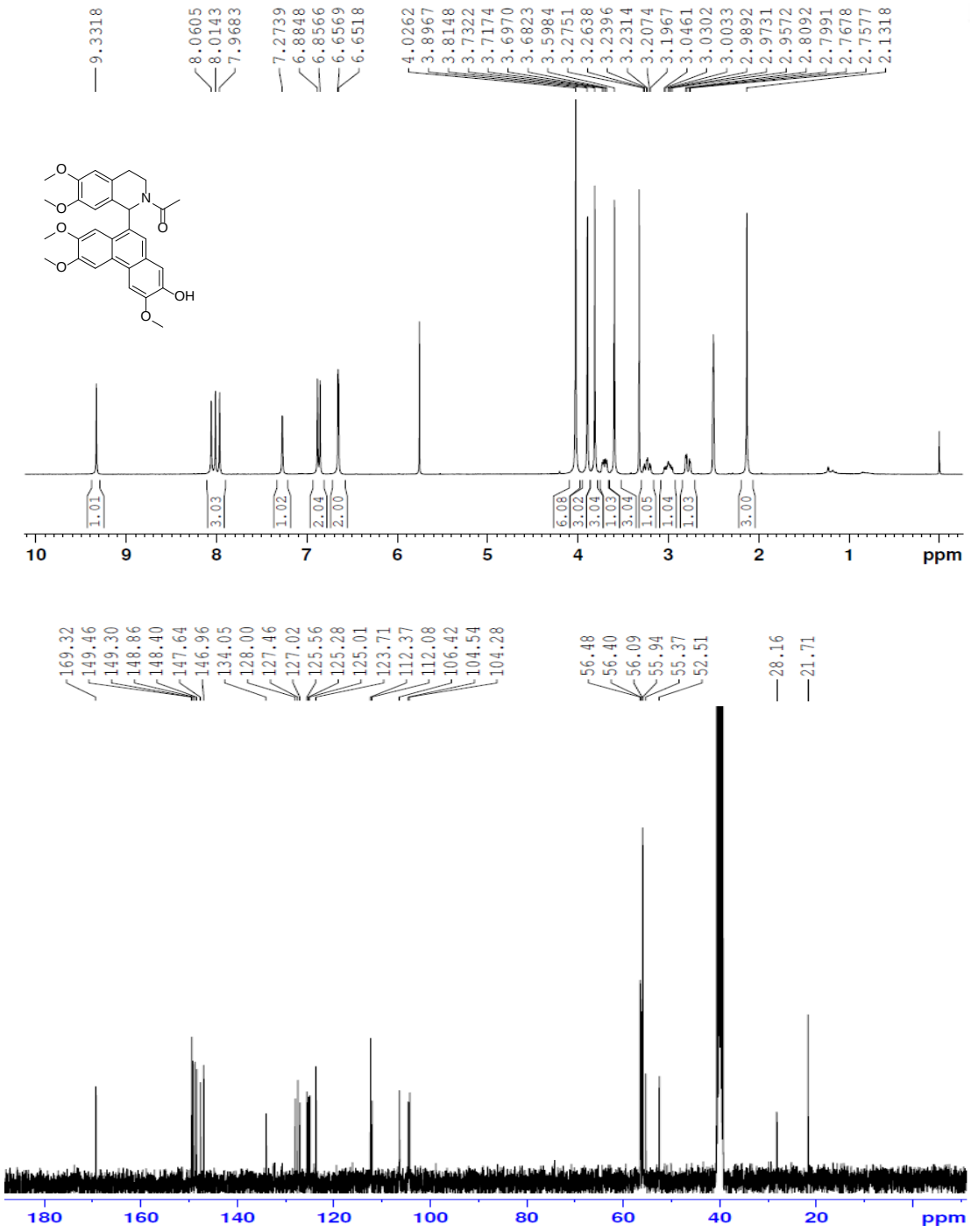
^{1}H NMR (400MHz, DMSO-d_6) δ 9.48(s, 1H), 8.48-8.50(d, J = 9.24 Hz, 1H), 8.08-8.09(d, J = 2.36 Hz, 1H), 8.04(s, 1H), 7.28(s, 1H), 7.20-7.23(m, 1H), 6.91 (s, 1H), 6.85(s, 1H), 6.64(s, 2H), 3.99-4.02(d, J = 12.72 Hz, 6H), 3.81(s, 3H), 3.68-3.73(s, 1H), 3.59(s, 3H), 3.23-3.28(m, 1H), 2.95-3.04(m, 1H), 2.76-2.82(m, 1H), 2.11(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 168.95, 158.27, 149.24, 148.39, 147.78, 147.67, 134.74, 132.08, 128.07, 127.34, 126.93, 126.71, 124.63, 123.43, 115.40, 112.46, 112.27, 111.96, 105.00, 104.58, 56.57, 56.38, 55.92, 55.85, 52.26, 31.06, 28.15, 21.83, 18.95. HRMS calcd for $C_{29}H_{30}NO_6$, $[M+H]^+$, 488.2068; found 488.2075.



20. *1-(1-(2-hydroxy-3,6,7-trimethoxyphenanthren-9-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanone (**21t**)*

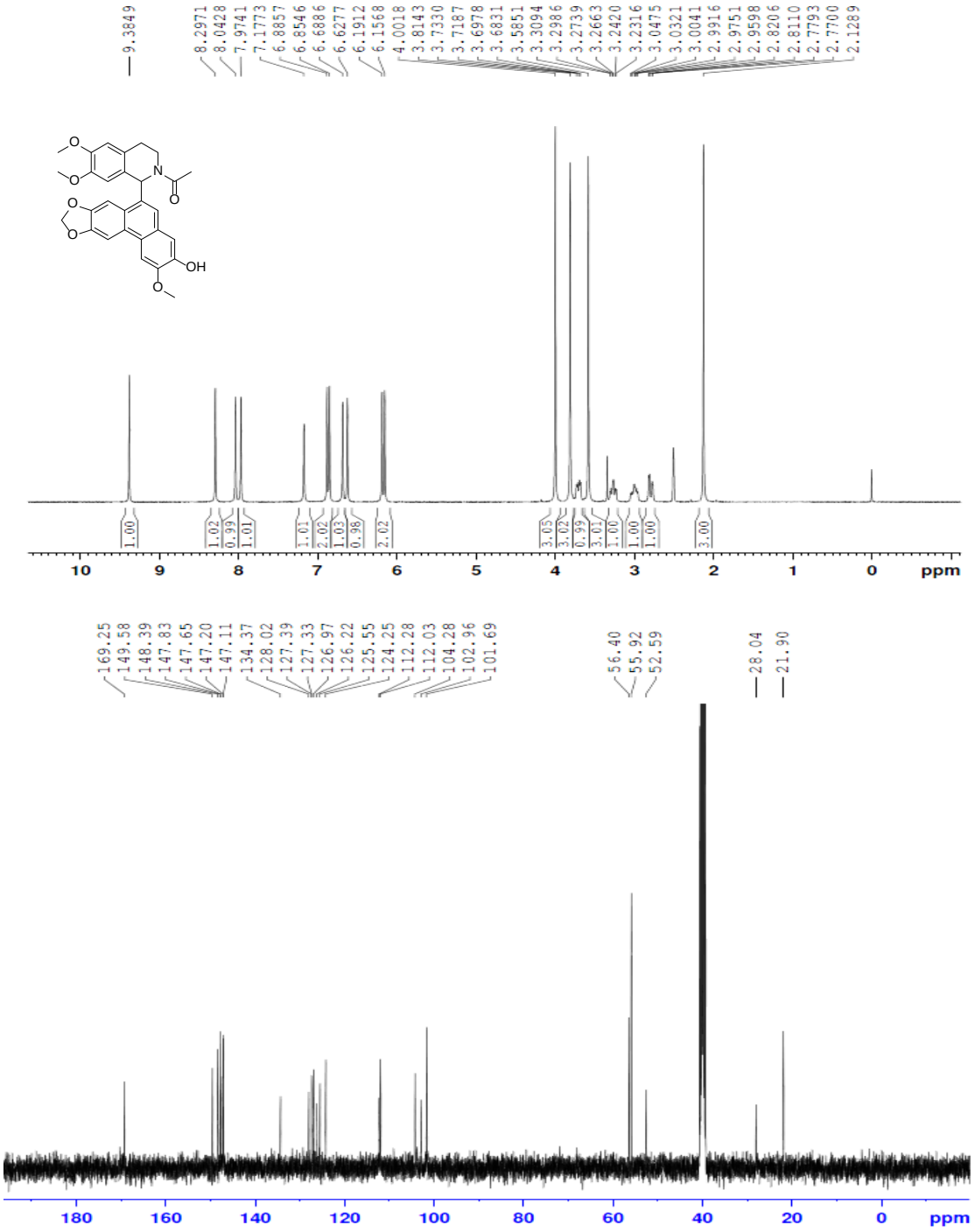
^{1}H NMR (400MHz, DMSO-d_6) δ 9.33(s, 1H), 8.06(s, 1H), 8.01(s, 1H), 7.97(s, 1H), 7.27(s, 1H), 6.88(s, 1H), 6.86(s, 1H), 6.66(s, 1H), 6.65(s, 1H), 4.03(s, 6H), 3.90(s, 3H), 3.81(s, 3H), 3.68-3.73(m, 1H), 3.60(s, 1H), 3.20-3.28(m, 1H), 2.96-3.05(m, 1H), 2.76-2.81(m, 1H), 2.13(s, 3H).

^{13}C NMR (100MHz, DMSO-d_6) δ 169.32, 149.46, 149.30, 148.86, 148.40, 147.64, 146.96, 134.05, 128.00, 127.46, 127.02, 125.56, 125.28, 125.01, 123.71, 112.37(×2), 112.08, 106.42, 104.54, 104.28, 56.48, 56.40, 56.09, 55.94(×2), 55.37, 52.51, 28.16, 21.71. HRMS calcd for $C_{30}H_{32}NO_7$, $[M+H]^+$, 518.2173; found 518.2177.



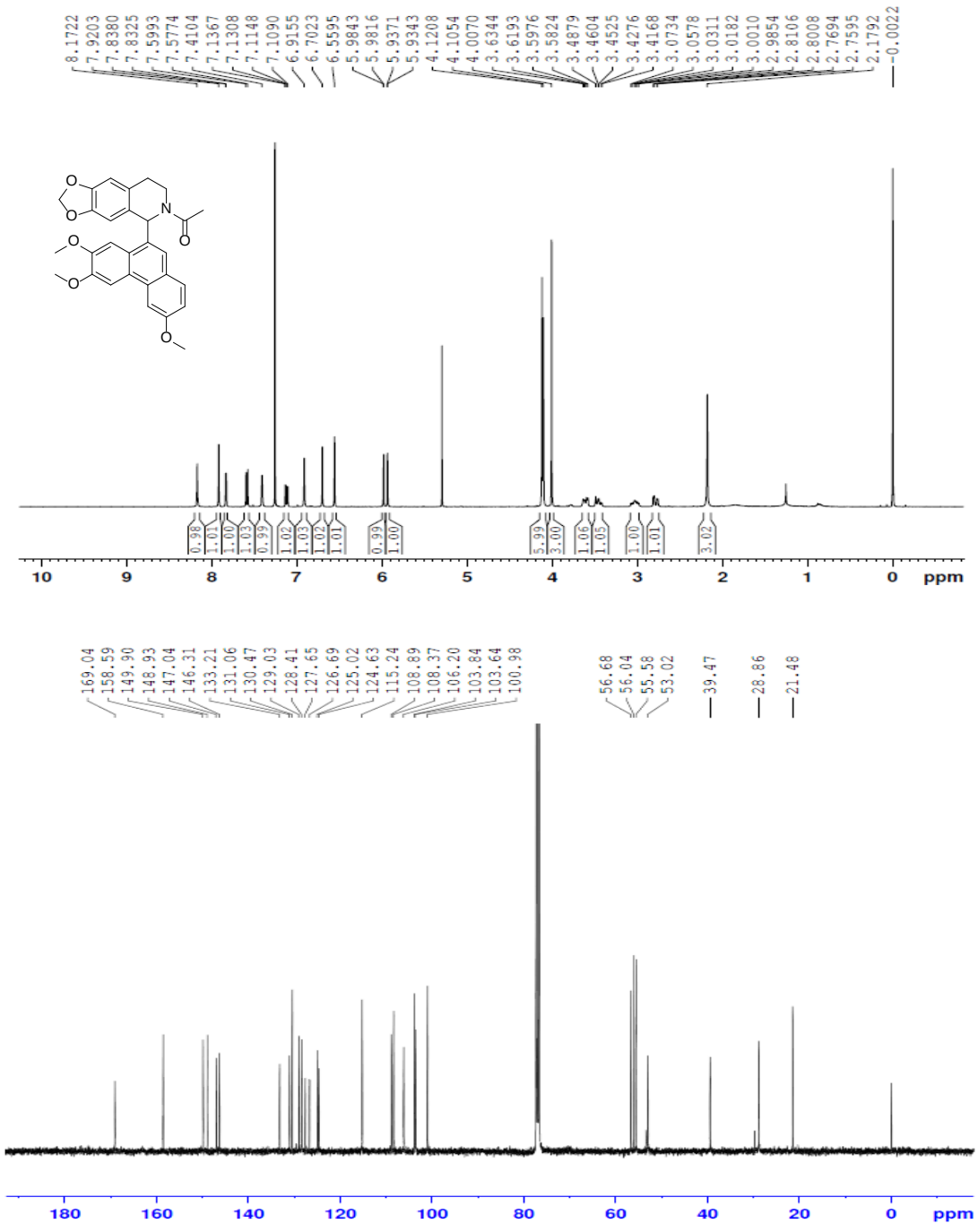
21. *1-(1-(3-hydroxy-2-methoxyphenanthro[3,2-d][1,3]dioxol-6-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)ethanon (**21u**)*

^{1}H NMR (400MHz, DMSO-d_6) δ 9.38(s, 1H), 8.30(s, 1H), 8.04(s, 1H), 7.97(s, 1H), 7.18(s, 1H), 6.89(s, 1H), 6.85(s, 1H), 6.69 (s, 1H), 6.63(s, 1H), 6.16-6.19(d, J = 13.76 Hz, 2H), 4.00(s, 3H), 3.81(s, 3H), 3.68-3.73(m, 1H), 3.59(s, 3H), 3.23-3.31(s, 1H), 2.96-3.05(s, 1H), 2.77-2.82(m, 1H), 2.13(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.25, 149.57, 148.39, 147.83, 147.65, 147.20, 147.11, 134.37, 128.02, 127.39, 127.33, 126.22, 125.55, 126.97, 124.25, 112.28, 112.03(×2), 104.28, 102.96, 101.69(×2), 56.40(×2), 55.92(×2), 52.58, 39.60, 28.04, 21.90. HRMS calcd for $C_{29}H_{28}NO_7$, $[M+H]^+$, 524.1680; found 524.1676.



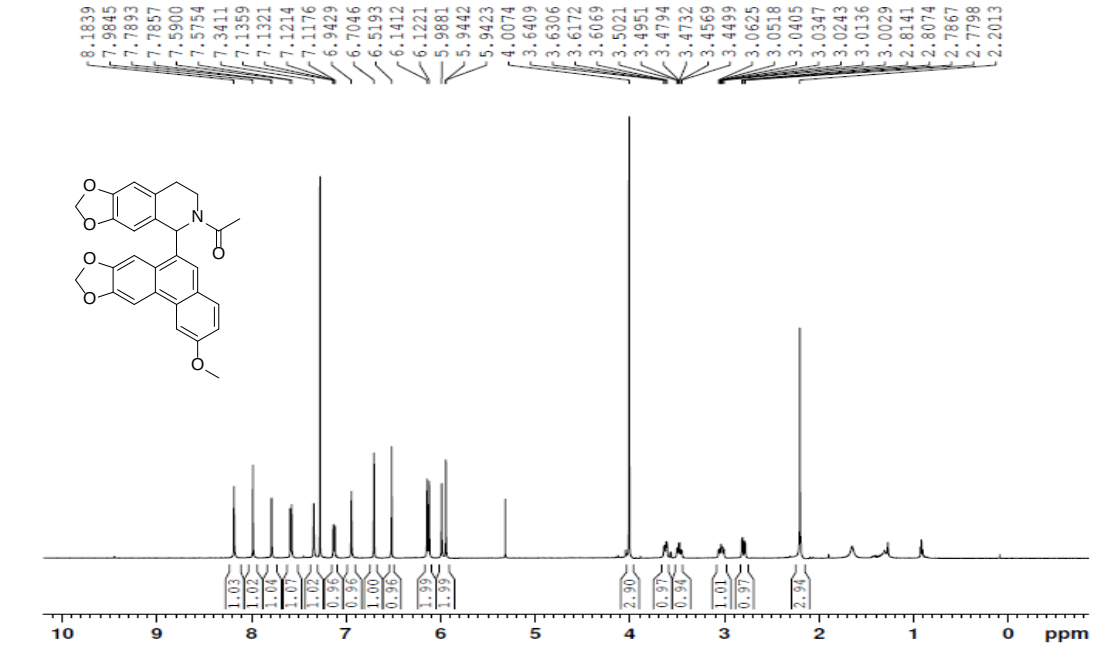
22. *1-(5-(3,6,7-trimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinoli n-6(5H)-yl)ethanone (22a)*

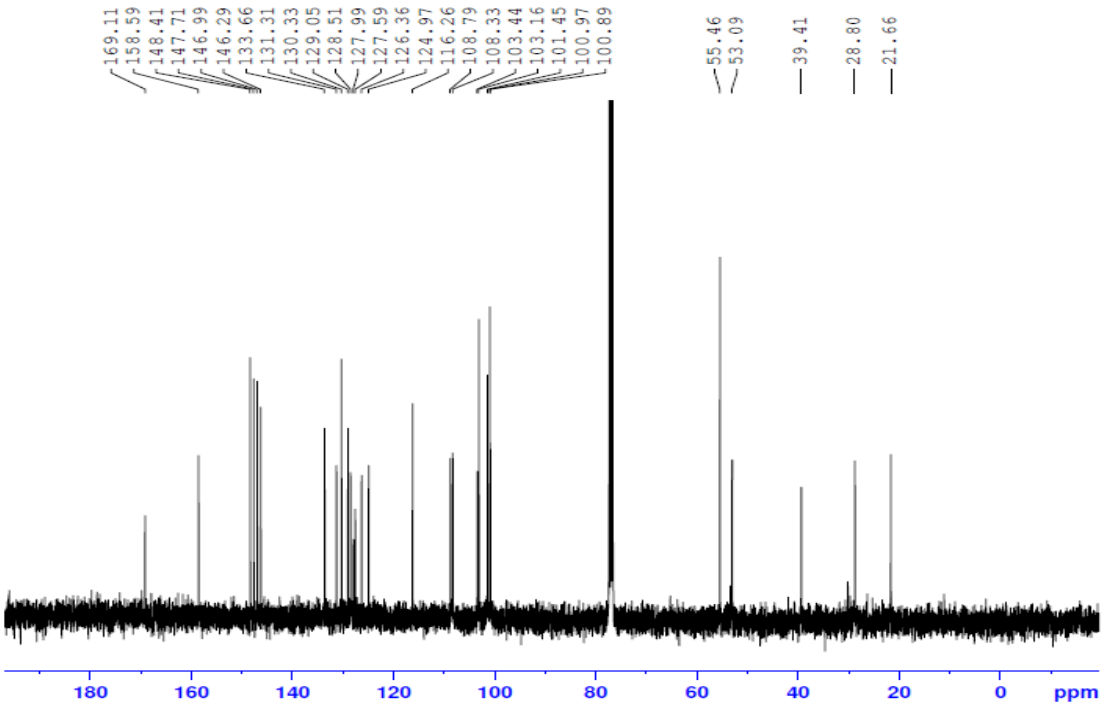
^{1}H NMR (400MHz, $CDCl_3$) δ 8.17(s, 1H), 7.92(s, 1H), 7.83-7.84(d, J = 2.20 Hz, 1H), 7.62(s, 1H), 7.58-7.60(d, J = 8.76 Hz, 1H), 7.41(s, 1H), 7.11-7.14 (dd, J = 8.72, 2.36 Hz, 1H), 6.92(s, 1H), 6.70(s, 1H), 6.56(s, 1H), 5.98-5.99(d, J = 1.08 Hz, 1H), 5.93-5.94(d, J = 1.12 Hz, 1H), 4.12(s, 1H), 4.11(s, 1H), 4.01(s, 1H), 3.60-3.63(m, 1H), 3.42-3.49(m, 1H), 2.98-3.07(m, 1H), 2.76-2.81(m, 1H), 2.18(s, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.04, 158.59, 149.90, 148.93, 147.04, 146.31, 133.21, 131.06, 130.47, 129.03, 128.41, 127.65, 126.69, 125.02, 124.63, 115.24, 108.89, 108.37, 106.20, 103.84, 103.64, 100.98, 56.68, 56.04, 55.58, 53.02, 39.47, 28.86, 21.48. HRMS calcd for $C_{29}H_{27}NO_6Na$, $[M+Na]^+$, 508.1731; found 508.1736.



23. *1-(5-(2-methoxyphenanthro[3,2-d][1,3]dioxol-6-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22b**)*

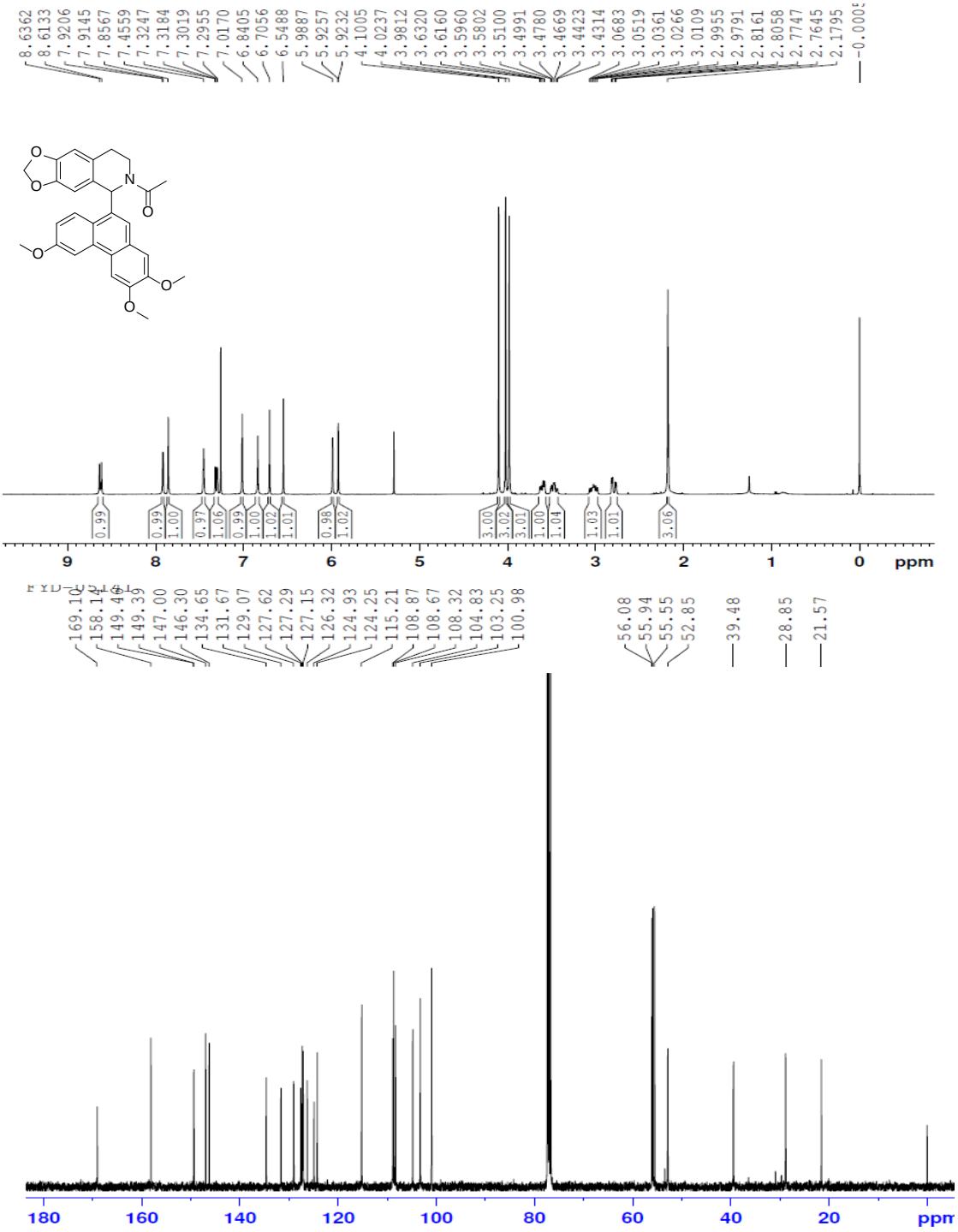
^{1}H NMR (600MHz, $CDCl_3$) δ 8.18(s, 1H), 7.89(s, 1H), 7.78-7.79(d, J = 2.16 Hz, 1H), 7.57-7.59(d, J = 8.76 Hz, 1H), 7.34(s, 1H), 7.11-7.14(dd, J = 8.70, 2.28 Hz, 1H), 6.94(s, 1H), 6.70(s, 1H), 6.52(s, 1H), 6.12-6.14 (d, J = 11.46 Hz, 2H), 5.99(s, 1H), 5.94-5.95(d, J = 1.14 Hz, 1H), 4.01(s, 3H), 3.61-3.64(m, 1H), 3.45-3.50 (m, 1H), 3.00-3.06(m, 1H), 2.78-2.81(m, 1H), 2.20(s, 3H). ^{13}C NMR (150MHz, $CDCl_3$) δ 160.11, 158.59, 148.41, 147.71, 146.99, 146.29, 133.66, 131.31, 130.33, 129.05, 128.51, 127.99, 127.59, 126.36, 124.98, 116.26, 108.79, 108.33, 103.44, 103.16, 101.45, 100.97, 100.89, 55.46, 53.09, 39.41, 21.66, 28.80. HRMS calcd for $C_{28}H_{24}NO_6$ $[M+H]^+$, 470.1598; found 470.1615.





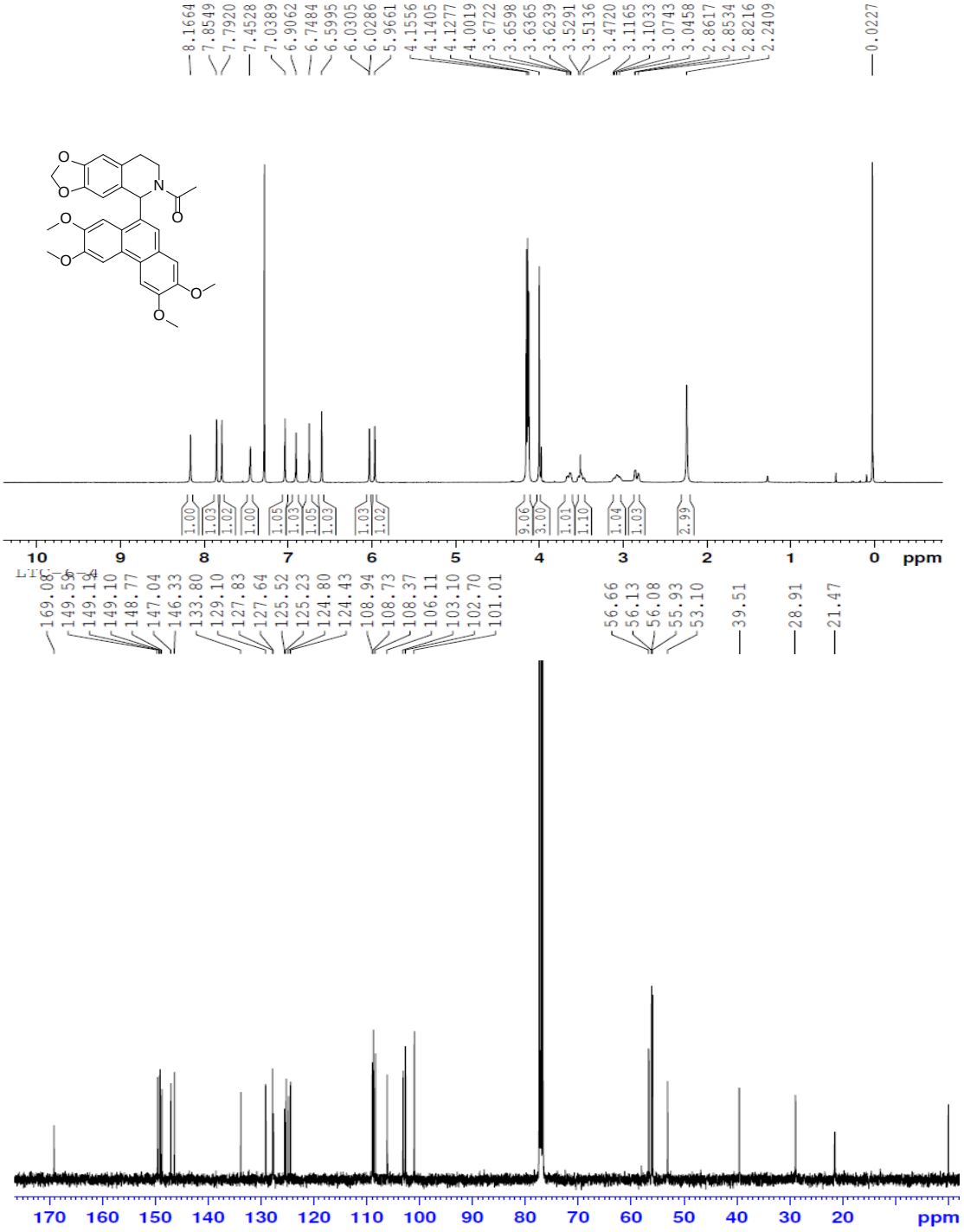
24. *1-(5-(2,3,6-trimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinoli n-6(5H)-yl)ethanone (**22c**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.61-8.64(d, J = 9.16 Hz, 1H), 7.91-7.92(d, J = 2.44 Hz, 1H), 7.86(s, 1H), 7.46(s, 1H), 7.29-7.32(m, 1H), 7.02(s, 1H), 6.84(s, 1H), 6.71 (s, 1H), 6.55(s, 1H), 5.99(s, 1H), 5.92(s, 1H), 4.10(s, 3H), 4.02(s, 3H), 3.98(s, 3H), 3.58-3.63(m, 1H), 3.43-3.51(m, 1H), 2.98-3.07(m, 1H), 2.76-2.82(m, 1H), 2.18(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.10, 158.14, 149.40, 149.39, 147.00, 146.30, 134.65, 131.67, 129.07, 127.62, 127.29, 127.15, 126.32, 124.93, 124.25, 115.21, 108.87, 108.67, 108.32, 104.83, 103.25, 100.98, 56.08, 55.94, 55.55, 52.85, 39.48, 28.85, 21.57. HRMS calcd for $C_{29}H_{27}NO_6Na$, $[M+Na]^+$, 508.1731; found 508.1726.



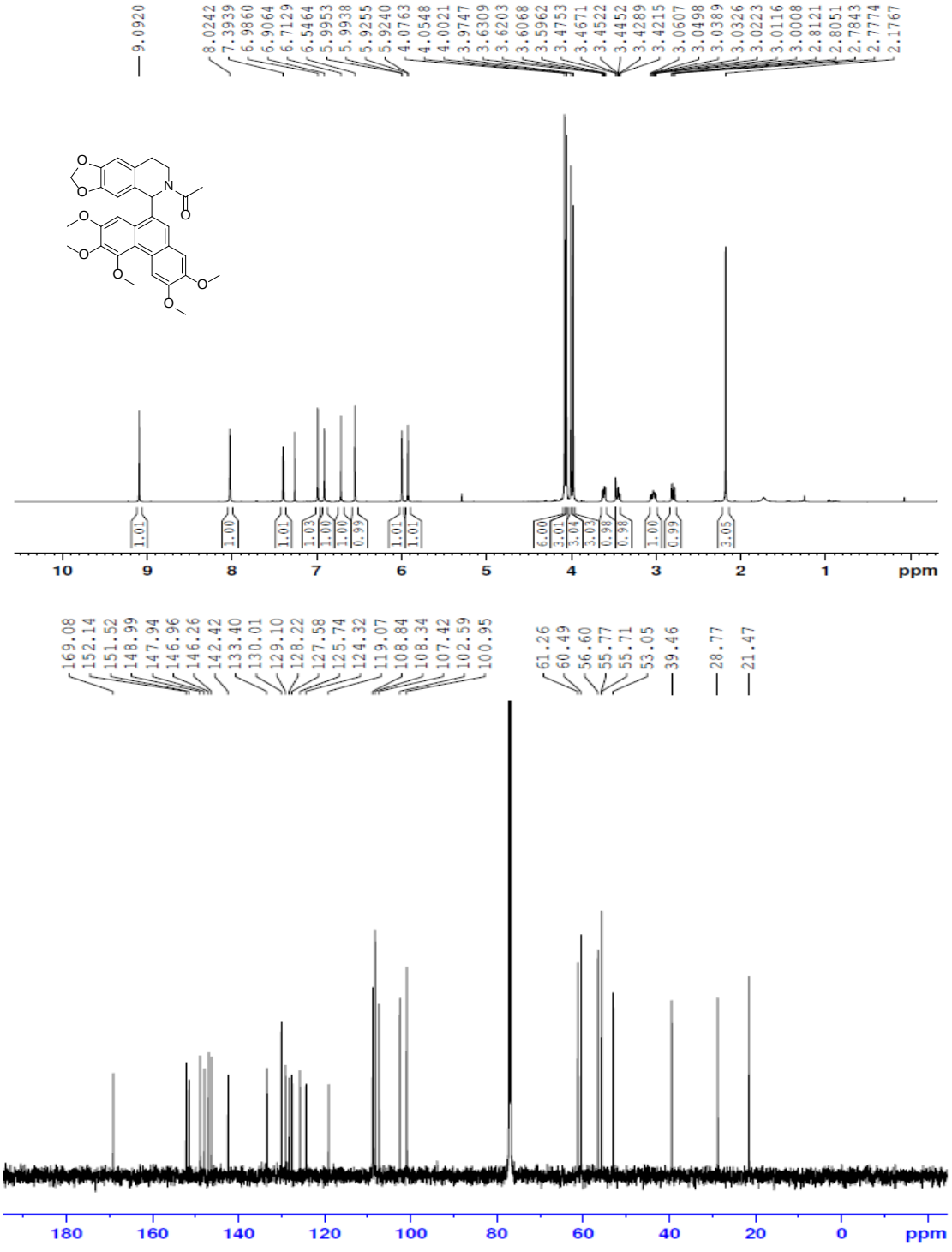
25. *1-(5-(2,3,6,7-tetramethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22d**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.17(s, 1H). 7.85(s, 1H), 7.79(s, 1H), 7.45(s, 1H), 7.04(s, 1H), 6.91(s, 1H), 6.75(s, 1H), 6.60(s, 1H), 6.02-6.03(d, J = 0.76 Hz, 1H), 5.97(s, 1H), 4.16(s, 3H), 4.14(s, 3H), 4.13(s, 3H), 4.00(s, 3H), 3.62-3.67(m, 1H), 3.47-3.53(m, 1H), 3.05-3.12(m, H), 2.82-2.86(m, 1H), 2.24(s, 3H), ^{13}C NMR (100MHz, $CDCl_3$) δ 169.08, 149.59, 149.19, 149.10, 148.77, 147.04, 146.33, 133.80, 129.10, 127.83, 127.64, 125.52, 125.23, 124.80, 124.43, 108.94, 108.73, 108.37, 106.11, 103.10, 102.70, 101.01, 56.66, 56.13, 56.08, 55.93, 53.10, 39.51, 28.91, 21.47. HRMS calcd for $C_{30}H_{29}NO_7Na$, $[M+Na]^+$, 538.1836; found 538.1835.



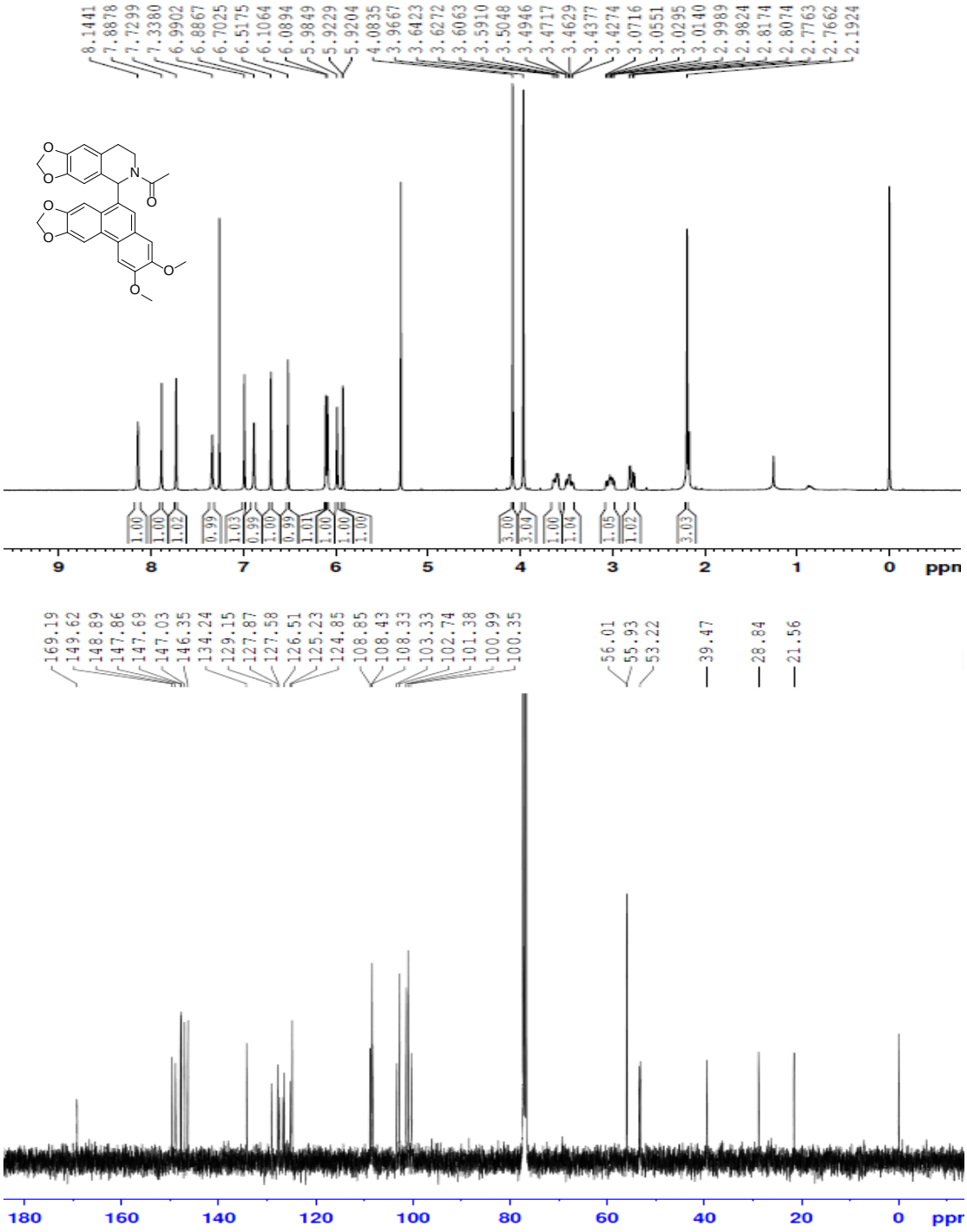
26. *1-(5-(2,3,5,6,7-pentamethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22e**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 9.09(s, 1H), 8.02(s, 1H), 7.39(s, 1H), 6.99(s, 1H), 6.90(s, 1H), 6.71(s, 1H), 6.55(s, 1H), 5.99-6.00(d, J = 0.90 Hz, 1H), 5.92-5.93(d, J = 0.96 Hz, 1H), 4.08(s, 6H), 4.05(s, 3H), 4.00(s, 3H), 3.97(s, 3H), 3.90(s, 3H), 3.60-3.61(m, 1H), 3.42-3.48(m, 1H), 3.00-3.06(m, 1H), 2.78-2.81(m, 1H), 2.19(s, 3H). ^{13}C-NMR (400MHz, $CDCl_3$) δ 169.08, 152.14, 151.52, 148.99, 147.94, 146.96, 146.26, 142.42, 133.40, 130.01, 129.10, 128.22, 127.58, 125.74, 124.32, 119.07, 108.84, 108.34(×2), 107.42, 102.59, 100.95, 61.26, 60.49, 56.60, 55.77, 55.71, 53.05, 39.45, 28.77, 21.47. HRMS calcd for $C_{39}H_{41}NO_9Na$, $[M+Na]^+$, 568.2111; found 568.2109.



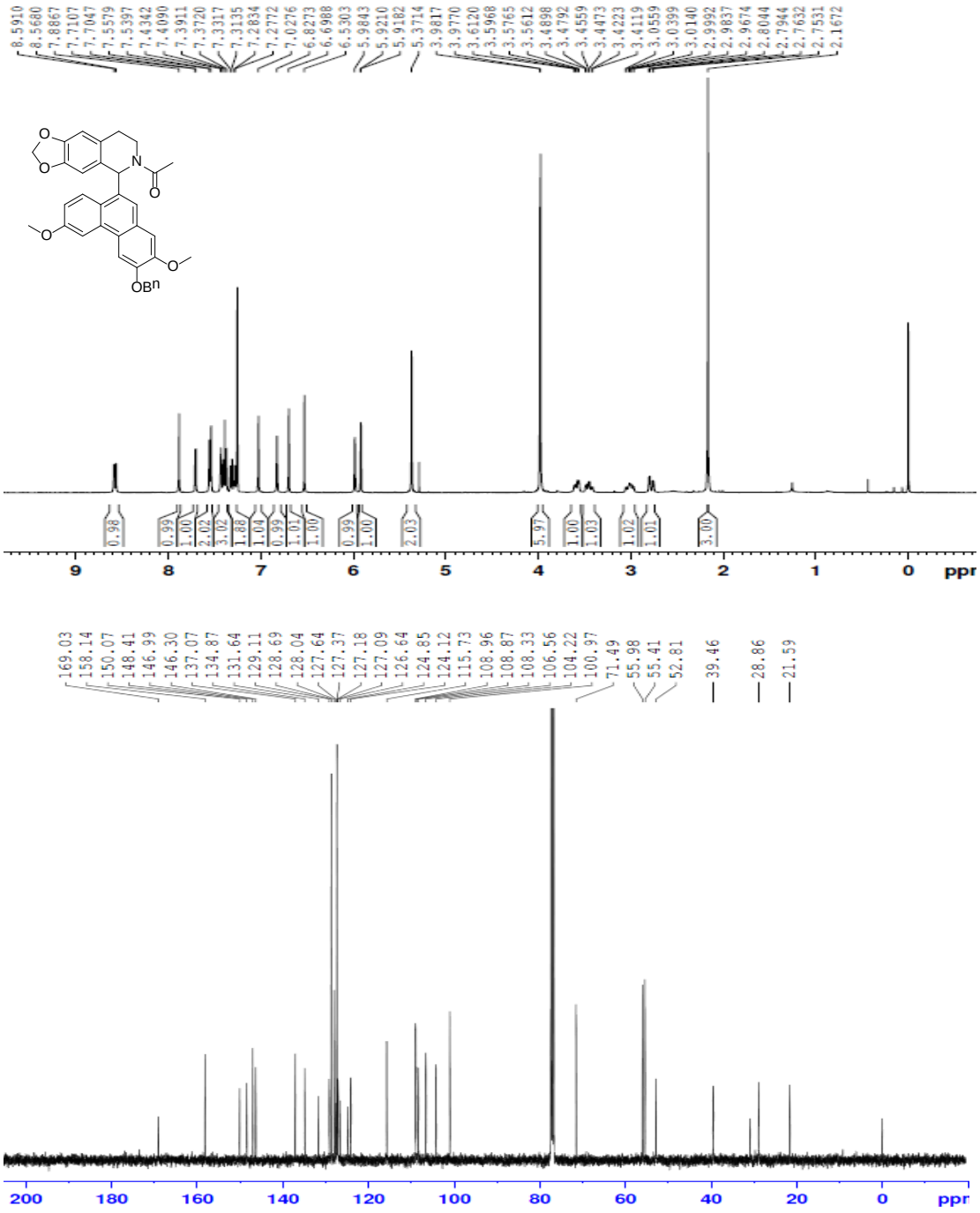
27. *1-(5-(2,3-dimethoxyphenanthro[2,3-d][1,3]dioxol-6-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22f**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.14(s, 1H), 7.89(s, 1H), 7.73(s, 1H), 7.34(s, 1H), 6.99(s, 1H), 6.89(s, 1H), 6.70(s, 1H), 6.52(s, 1H), 6.09-6.11(d, J = 6.80 Hz, 1H), 5.98(s, 1H), 5.92-5.93(d, J = 1.00 Hz, 1H), 4.08(s, 3H), 3.97(s, 3H), 3.59-3.64(m, 1H), 3.43-3.50(m, 1H), 2.98-3.07(m, 1H), 2.77-2.82(m, 1H), 2.19(s, 3H). ^{13}C NMR(100MHz, $CDCl_3$) δ 169.19, 149.61, 148.89, 147.85, 147.68, 147.02, 146.34, 134.23, 129.14, 127.86, 127.57, 126.51, 125.23, 124.84, 108.84, 108.43, 108.32, 103.32, 102.74, 101.38, 100.99, 100.35, 56.00, 55.92, 53.22, 39.46, 28.83, 21.55. HRMS calcd for $C_{29}H_{26}NO_7$, $[M+H]^+$, 500.1704; found 500.1703.



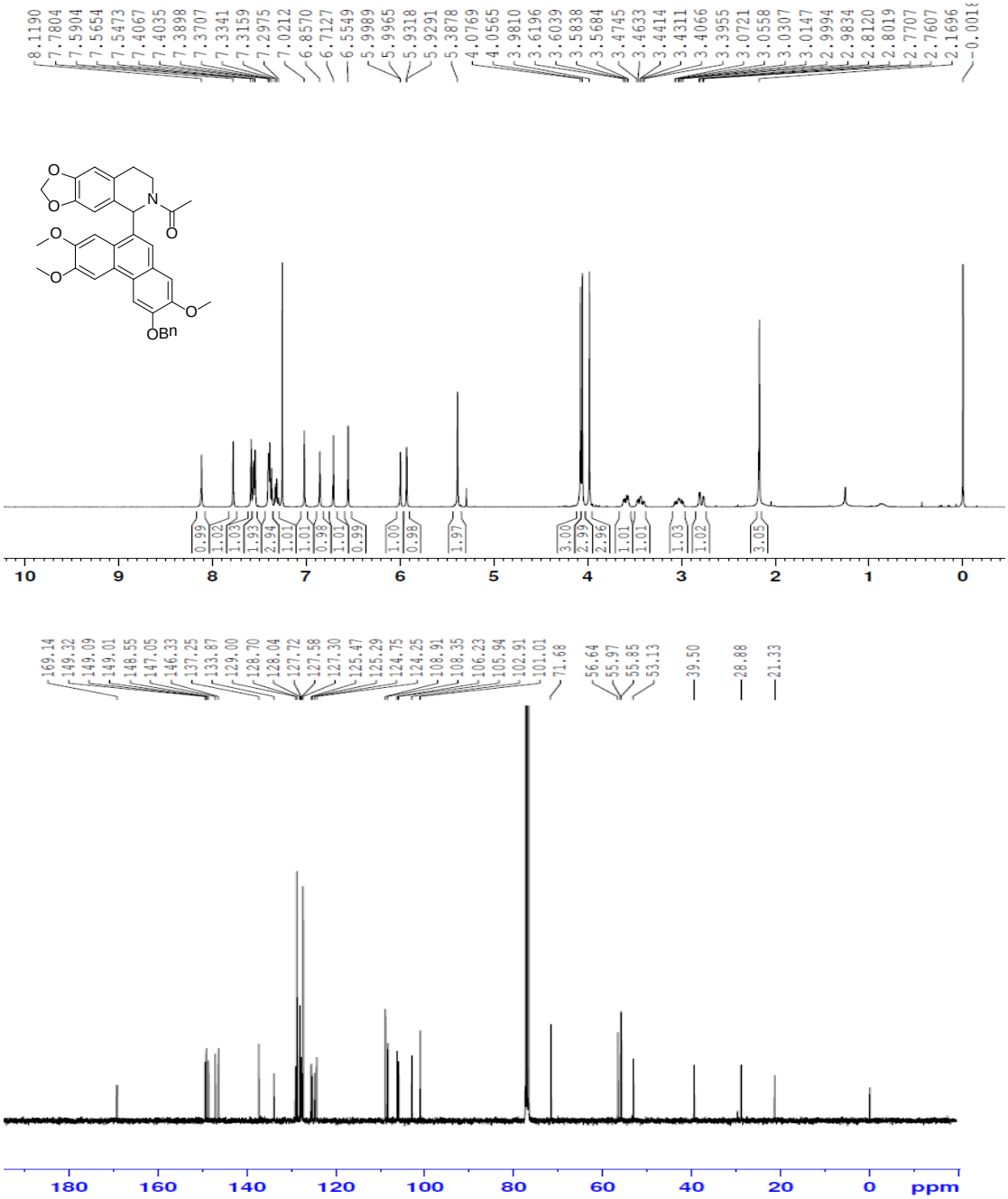
28. *1-(5-(3-(benzyloxy)-2,6-dimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22g**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.57-8.59 (d, J = 9.20 Hz, 1H), 7.89(s, 1H), 7.70-7.71(d, J = 2.40 Hz, 1H), 7.37-7.43(m, 3H), 7.28-7.33(m, 2H), 7.03(s, 1H), 6.83(s, 1H), 6.70(s, 1H), 6.53(s, 1H), 5.98 (s, 1H), 5.91-5.92(d, J = 1.12Hz, 1H), 5.37(s, 2H), 3.98(s, 3H), 3.97(s, 3H), 3.56 -3.61(m, 1H), 3.41-3.49 (m, 1H), 2.97-3.06(m, 1H), 2.75-2.80(m, 1H), 2.17(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.03, 158.14, 150.07, 148.48, 147.00, 146.31, 137.07, 134.87, 131.64, 129.11, 128.69(×2), 128.04, 127.64, 127.38(×2), 127.18, 127.09, 126.64, 124.85, 124.13, 115.73, 108.96, 108.87, 108.33, 106.56, 104.22, 100.97, 71.49, 55.98, 55.41, 52.81, 39.46, 28.86, 21.59. HRMS calcd for $C_{35}H_{31}NO_6Na$, $[M+Na]^+$, 584.2044; found 584.2022.



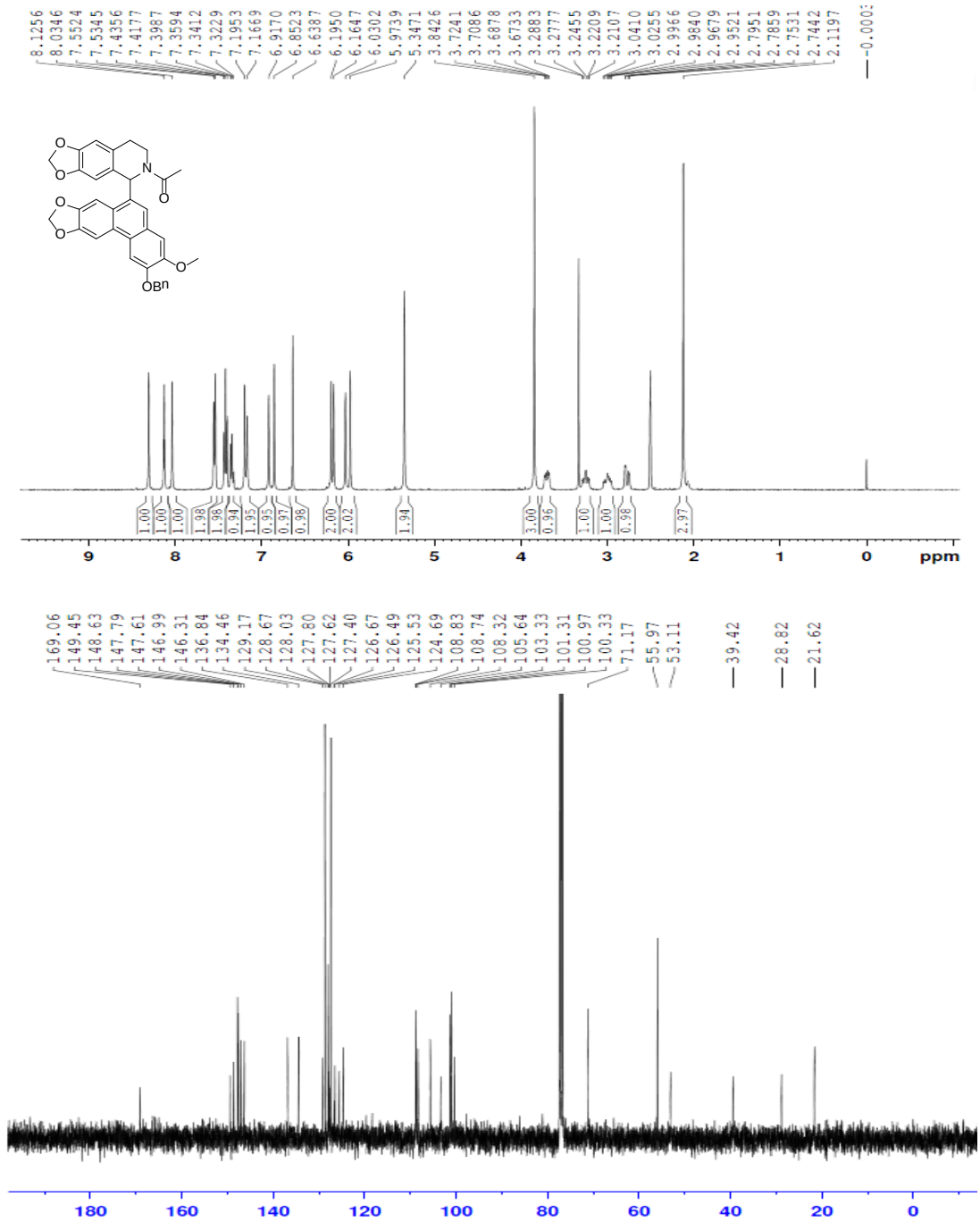
29. *1-(5-(3-(benzyloxy)-2,6,7-trimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22h**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.12(s, 1H), 7.78(s, 1H), 7.59(s, 1H), 7.57(s, 1H), 7.55(s, 1H), 7.40-7.41(d, J = 1.28 Hz, 1H), 7.39(s, 1H), 7.37(s, 1H), 7.30-7.33(m, 1H), 7.02(s, 1H), 6.86(s, 1H), 6.71(s, 1H), 6.55(s, 1H), 5.99-6.00 (d, J = 0.96 Hz, 1H), 5.92-5.93 (d, J = 1.08 Hz, 1H), 5.39(s, 2H), 4.08(s, 3H), 4.06(s, 3H), 3.98(s, 3H), 3.57-3.62(m, 1H), 3.40-3.47(m, 1H), 2.98-3.07(m, 1H), 2.76-2.81(m, 1H), 2.17(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.14, 149.32, 149.09, 149.01, 148.55, 147.05, 146.33, 137.25, 133.87, 129.00, 128.70(×2), 128.04, 127.72, 127.58, 127.30(×2), 125.47, 125.29, 124.75, 124.25, 108.91, 108.35, 106.23, 105.94, 102.91, 101.01, 71.68, 56.64, 55.97, 55.85, 53.13, 39.50, 28.88, 21.33. HRMS calcd for $C_{36}H_{33}NO_7Na$, $[M+Na]^+$, 614.2149; found 614.2160.



30. *1-(5-(2-(benzyloxy)-3-methoxyphenanthro[2,3-d][1,3]dioxol-6-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22i**)*

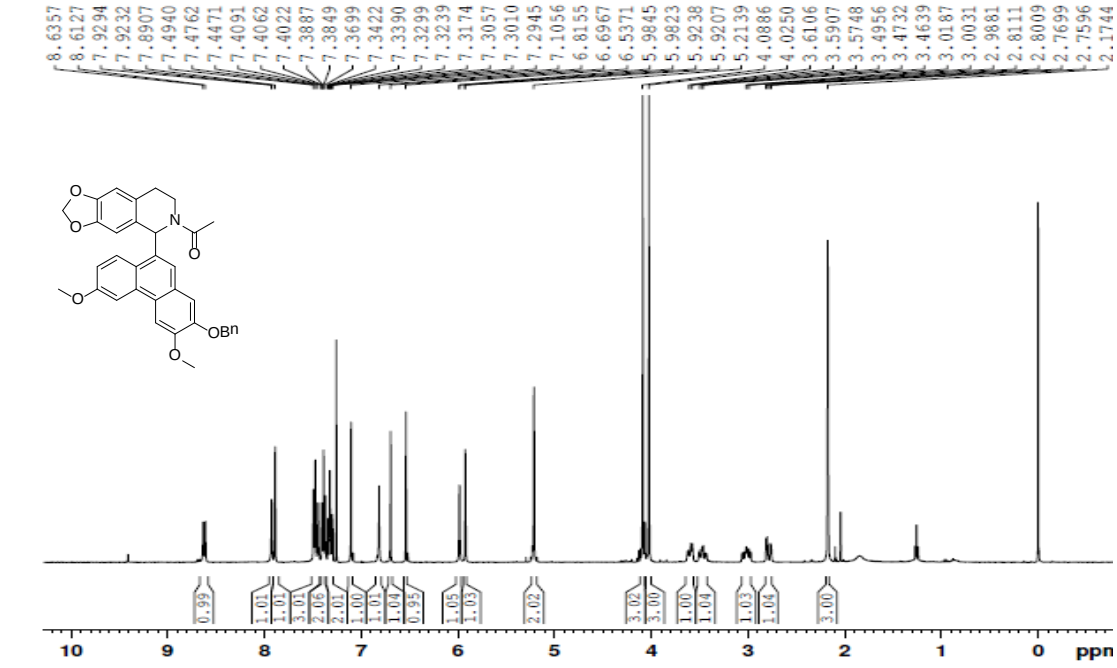
^{1}H NMR (400MHz, $CDCl_3$) δ 8.30(s, 1H), 8.12(s, 1H), 8.03(s, 1H), 7.55(s, 1H), 7.53(s, 1H), 7.40-7.43(m, 2H), 7.32-7.36(m, 1H), 7.19(s, 1H), 7.17(s, 1H), 6.92(s, 1H), 6.85(s, 1H), 6.64(s, 1H), 6.19(s, 1H), 6.16(s, 1H), 6.03(s, 1H), 5.97(s, 1H), 5.35(s, 2H), 3.84(s, 3H), 3.67-3.72(m, 1H), 3.21-3.29(m, 1H), 2.95-3.04(m, 1H), 2.74-2.79(m, 1H), 2.12(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ169.06, 149.45, 148.63, 147.79, 147.61, 146.99, 146.31, 136.84, 134.46, 129.17, 128.67(×2), 128.03, 127.80, 127.62, 127.40(×2), 126.67, 126.49, 125.53, 124.69, 108.83, 108.74, 108.32, 105.64, 103.33, 101.31, 100.97, 100.33, 71.17, 55.97, 53.10, 39.42, 28.82, 21.62. HRMS calcd for $C_{36}H_{33}NO_7Na$, $[M+Na]^+$, 598.1836; found 598.1854.

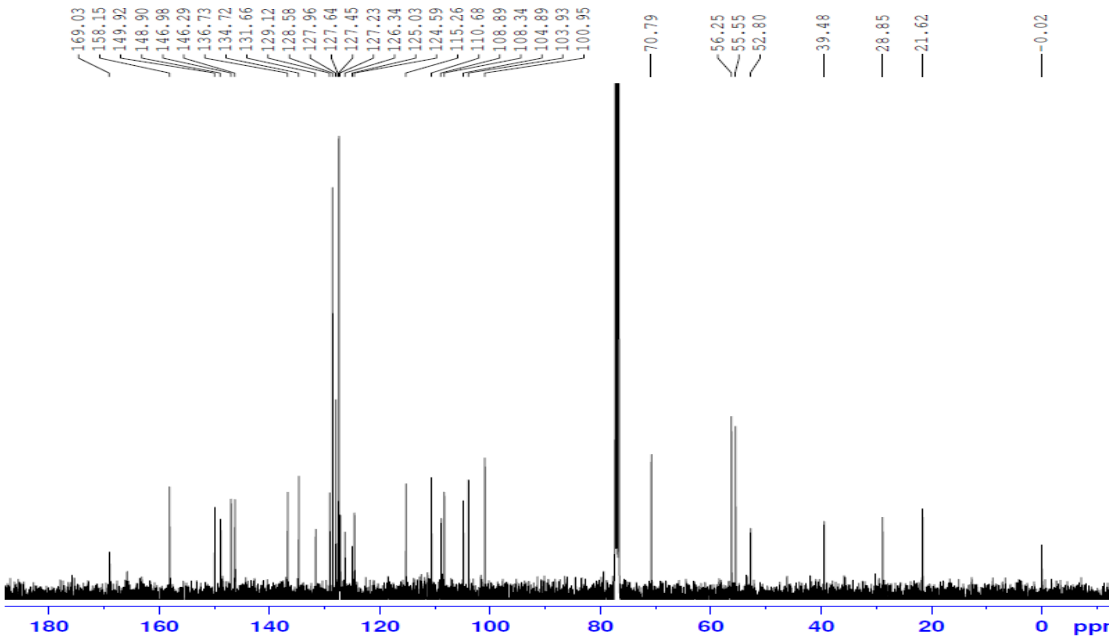


31. *1-(5-(2-(benzyloxy)-3,6-dimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22j**)*

^{1}H-NMR(400MHz, $CDCl_3$) δ 8.61-8.64(d, J = 9.20 Hz, 1H), 7.92-7.93(d, J = 2.48 Hz, 1H), 7.89(s, 1H), 7.45-7.49(m, 3H), 7.37-7.41(m, 2H), 7.29-7.34(m, 2H), 7.11(s, 1H), 6.82(s, 1H), 6.70(s, 1H), 6.54(s, 1H), 5.98-5.99(d, J = 0.88 Hz, 2H), 5.92-5.93(d, J = 1.24 Hz, 2H), 5.21(s, 2H), 4.09(s, 3H), 4.03(s, 3H), 3.57-3.63(m, 1H), 3.43-3.51(m, 1H), 2.97-3.06(m, 1H), 2.76-2.81(m, 1H), 2.17(s, 3H).

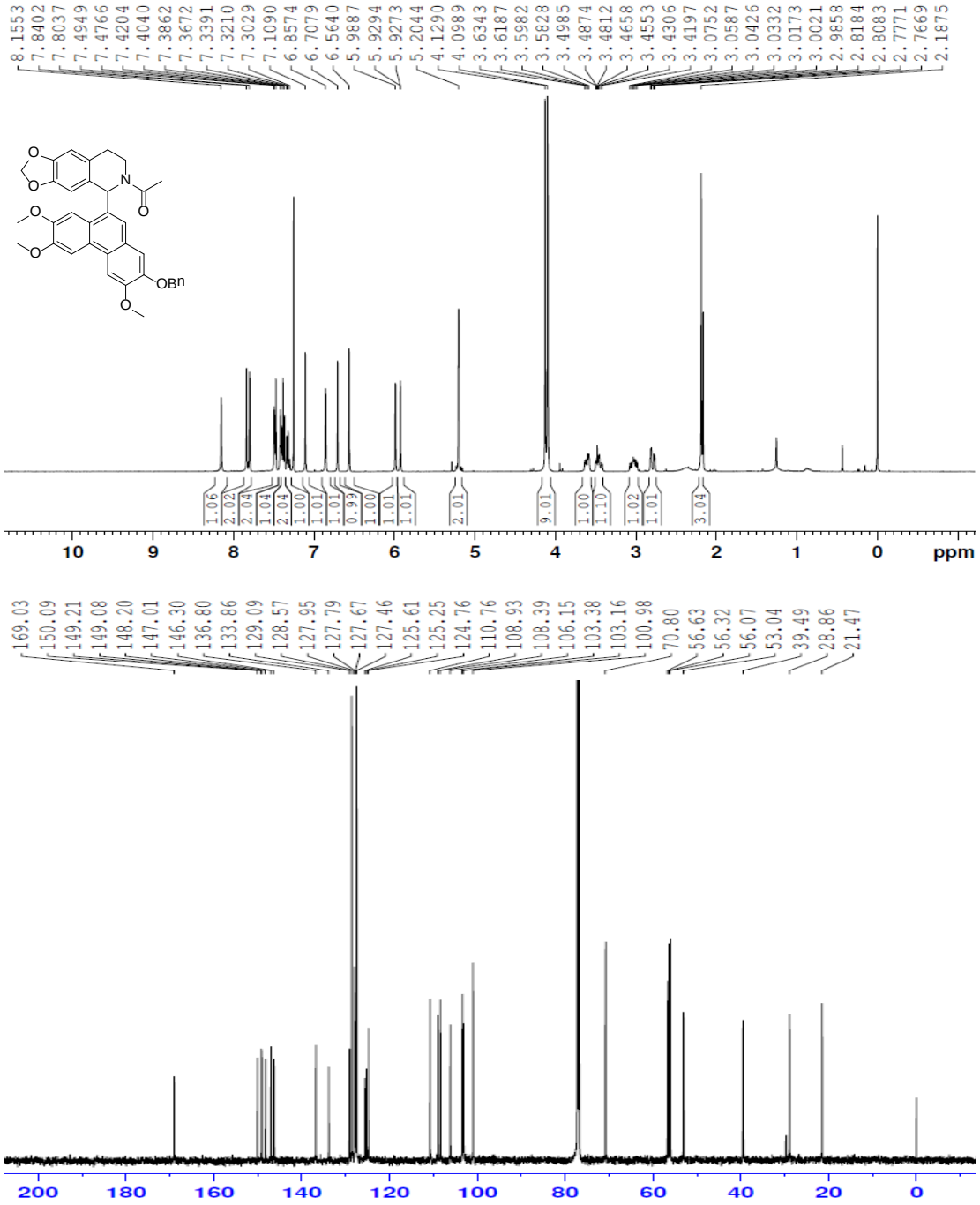
^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.03, 158.15, 149.92, 148.90, 146.98, 146.29, 136.73, 134.72, 131.66, 129.12, 128.58(×2), 127.96, 127.64, 127.45(×2), 127.23(×2), 126.34, 125.03, 124.59, 115.26, 110.68, 108.89, 108.34, 104.89, 103.93, 100.95, 70.79, 56.25, 55.55, 52.80, 39.48, 28.85, 21.62. HRMS calcd for $C_{36}H_{35}NO_6Na$, $[M+Na]^+$, 584.2225; found 584.2229.





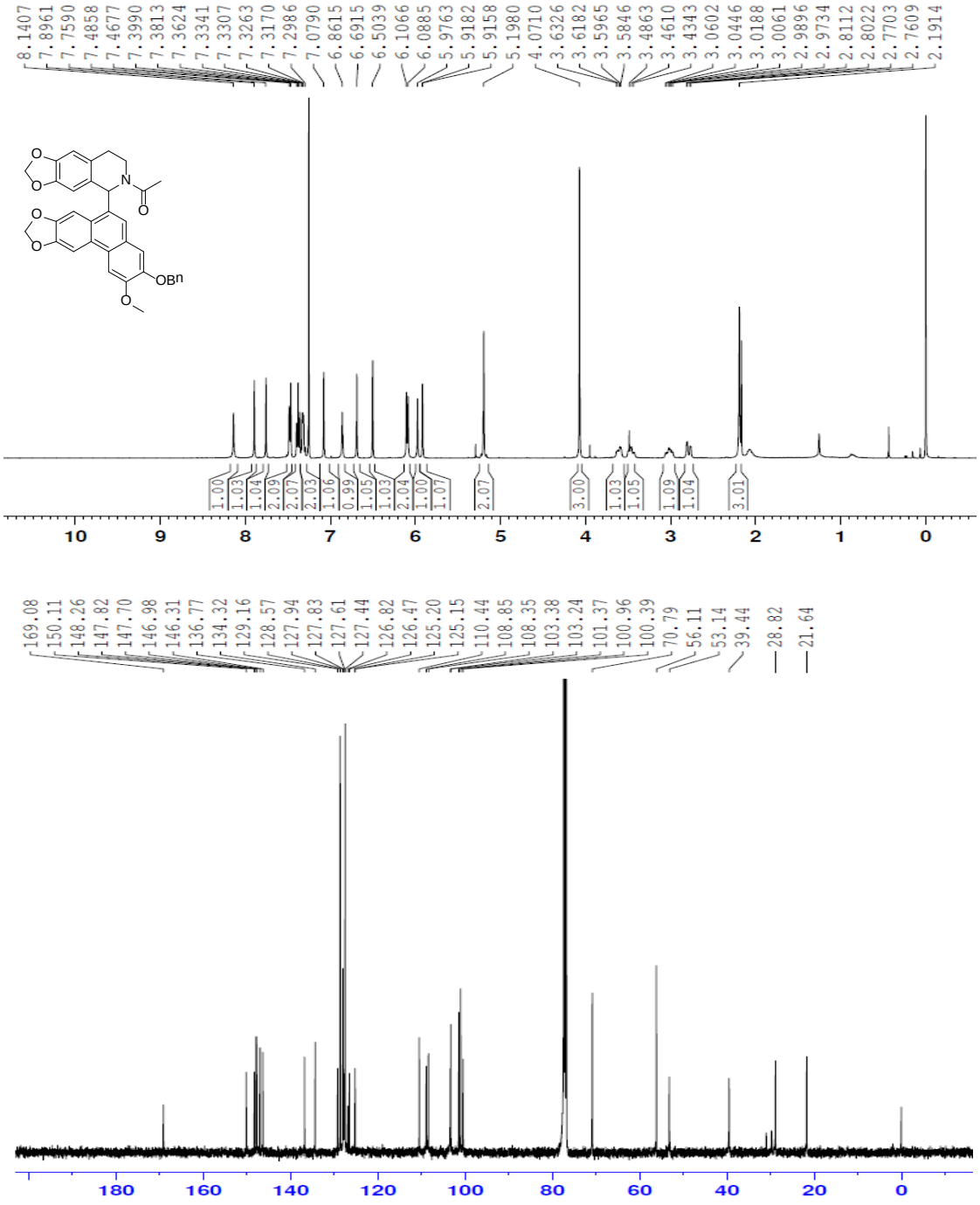
32. *1-(5-(2-(benzyloxy)-3,6,7-trimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22k**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.16(s, 1H), 7.84(s, 1H), 7.80(s, 1H), 7.42(s, 1H), 7.37-7.39(m, 2H), 7.30-7.34(m, 1H), 7.11(s, 1H), 6.86(s, 1H), 6.71(s, 1H), 6.56(s, 1H), 5.99(s, 1H), 5.92-5.93(d, J = 0.84 Hz, 1H), 5.20(s, 2H), 4.13(s, 3H), 4.10(s, 6H), 3.58-3.63(m, 1H), 3.42-3.50(m, 1H), 2.99-3.08(m, 1H), 2.77-2.82(m, 1H), 2.19(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.03, 150.09, 149.21, 149.08, 148.20, 147.01, 146.30, 136.80, 133.86, 129.09, 128.57(×2), 127.95, 127.79, 127.67, 127.46(×2), 125.61, 125.25, 124.76, 110.76, 108.93, 108.39, 106.15, 103.38, 103.16, 100.98, 70.80, 56.63, 56.32, 56.07, 53.04, 39.49, 28.86, 21.47. HRMS calcd for $C_{36}H_{33}NO_7Na$, $[M+Na]^+$, 614.2149; found 614.2149.



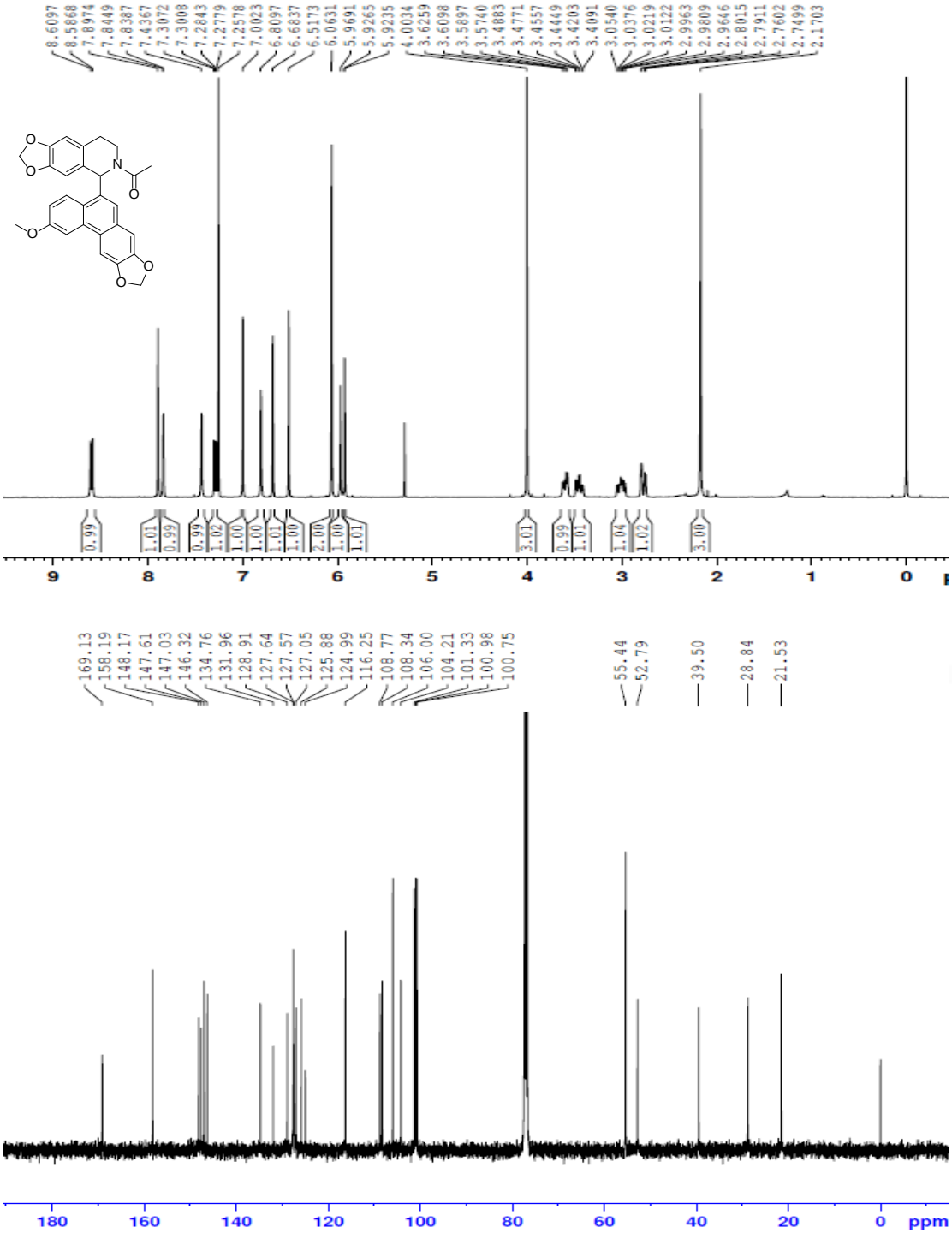
33. *1-(5-(3-(benzyloxy)-2-methoxyphenanthro[2,3-d][1,3]dioxol-6-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22l**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.14(s, 1H), 7.90(s, 1H), 7.76(s, 1H), 7.49(s, 1H), 7.47(s, 1H), 7.36-7.40(m, 2H), 7.30-7.33(m, 2H), 7.08(s, 1H), 6.86(s, 1H), 6.69(s, 1H), 6.50(s, 1H), 6.11(s, 1H), 6.09(s, 1H), 5.98(s, 1H), 5.91-5.92(d, J = 0.96 Hz, 1H), 5.20(s, 2H), 4.07(s, 3H), 3.58-3.63(m, 1H), 3.43-3.49(m, 1H), 2.97-3.06(m, 1H), 2.76-2.81(m, 1H), 2.19(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.08, 150.11, 148.26, 147.82, 147.70, 146.98, 146.31, 136.77, 134.32, 129.16, 128.57(×2), 127.94, 127.83, 127.61, 127.44(×2), 126.82, 126.47, 125.20, 125.15, 110.44, 108.85, 108.35, 103.38, 103.24, 101.37, 100.96, 100.39, 70.79, 56.11, 53.14, 39.44, 28.82, 21.64. HRMS calcd for $C_{35}H_{29}NO_7Na$, $[M+Na]^+$, 598.1836; found 598.1854.



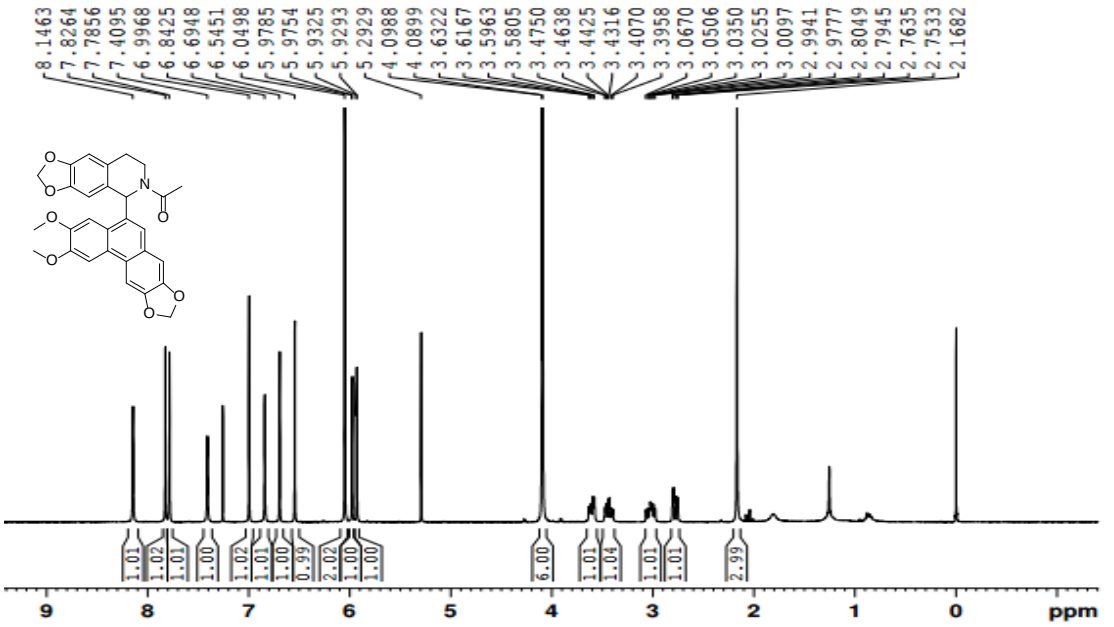
34. *1-(5-(2-methoxyphenanthro[2,3-d][1,3]dioxol-5-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g] isoquinolin-6(5H)-yl)ethanone (**22m**)*

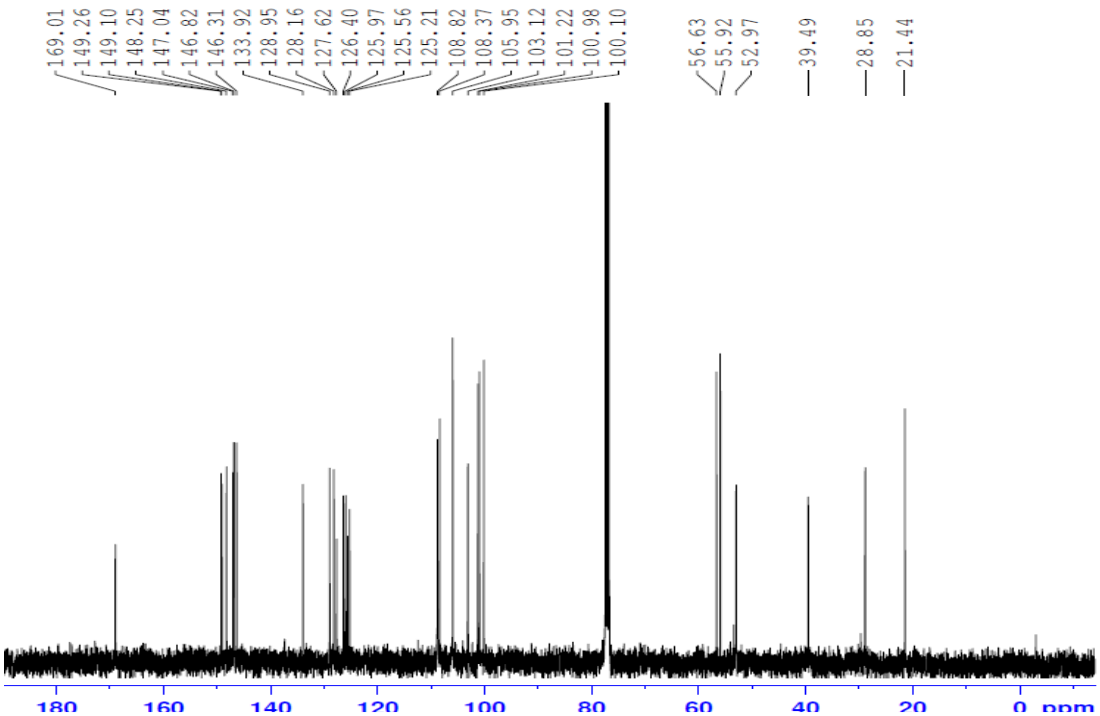
^{1}H NMR (400MHz, $CDCl_3$) δ 8.59-8.61(d, J = 9.16 Hz, 1H), 7.90(s, 1H), 7.84-7.85(d, J = 2.48 Hz, 1H), 7.44(s, 1H), 7.26-7.31(m, 1H), 7.28-7.30(m, 1H), 7.00(s, 1H), 6.81(s, 1H), 6.68 (s, 1H), 6.52(s, 1H), 6.06(s, 2H), 5.97(s, 1H), 5.92-5.93(d, J = 1.20 Hz, 1H), 4.00(s, 3H), 3.57-3.63(m, 1H), 3.41-3.49(m, 1H), 3.00-3.05(m, 1H), 2.75-2.80(m, 1H), 2.17(s, 3H). ^{13}C-NMR (100MHz, $CDCl_3$) δ 169.13, 158.19, 148.17, 147.61, 147.03, 146.32, 134.76, 131.96, 128.91, 127.64(×2), 127.57, 127.05, 125.88, 124.99, 116.25, 108.77, 108.34, 106.00, 104.21, 101.33, 100.98, 100.75, 55.44, 52.79, 39.50, 28.84, 21.53. HRMS calcd for $C_{28}H_{23}NO_6Na$, $[M+Na]^+$, 492.1418; found 492.1389.



35. *1-(5-(2,3-dimethoxyphenanthro[2,3-d][1,3]dioxol-5-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22n**)*

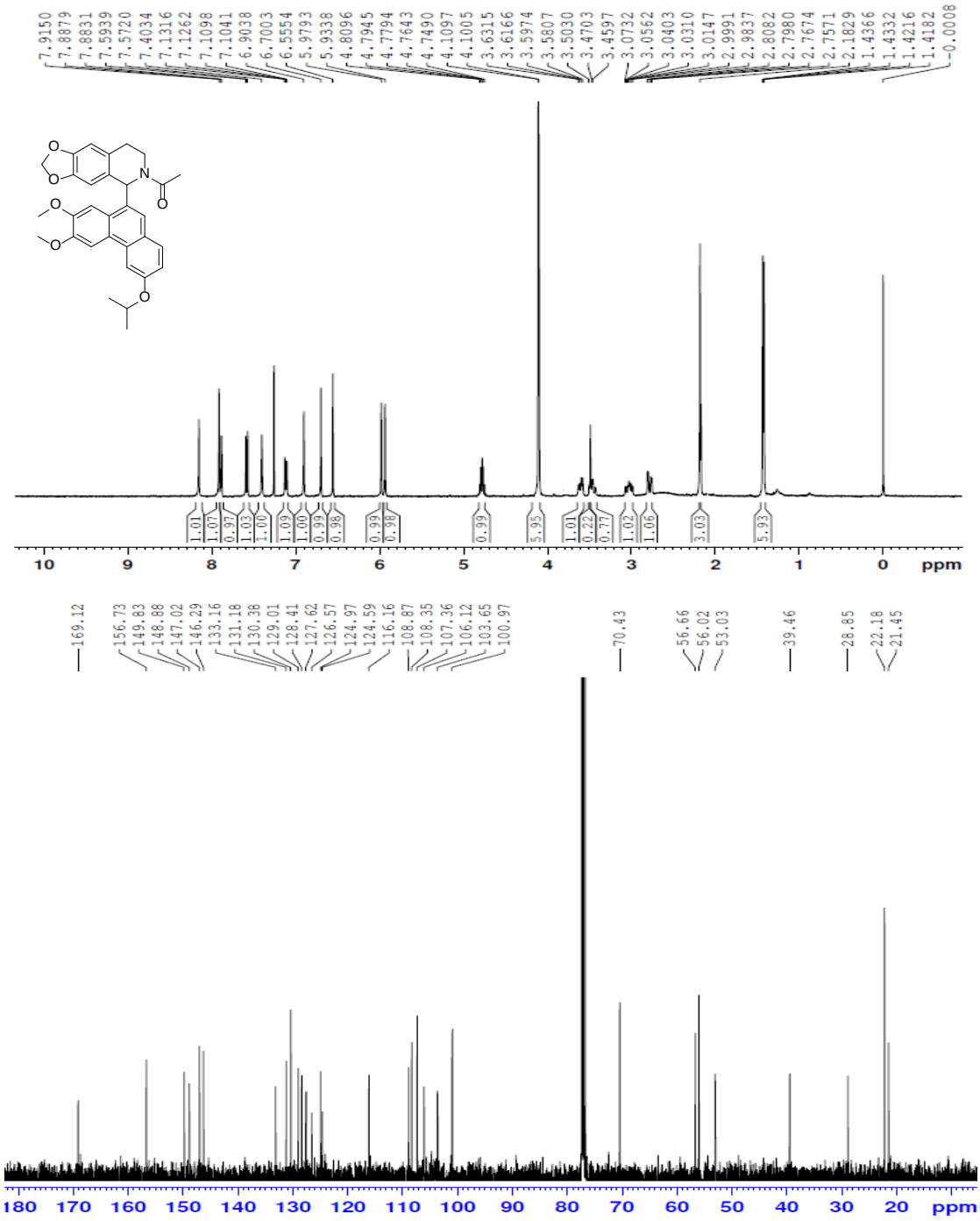
^{1}H NMR (400MHz, $CDCl_3$) δ 8.15(s, 1H), 7.83(s, 1H), 7.79(s, 1H), 7.41(s, 1H), 7.00(s, 1H), 6.84(s, 1H), 6.69(s, 1H), 6.55(s, 1H), 6.05(s, 2H), 5.97-5.98(d, J = 1.24 Hz, 1H), 5.92-5.93(d, J = 1.28 Hz, 1H), 4.10(s, 3H), 4.09(s, 3H), 3.58-3.63(m, 1H), 3.40-3.48(m, 1H), 2.98-3.07(m, 1H), 2.75-2.80(m, 1H), 2.17(s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.01, 149.26, 149.10, 148.25, 147.04, 146.82, 146.31, 133.92, 128.95, 128.16, 127.62, 126.40, 125.97, 125.56, 125.21, 108.37, 105.95(×2), 103.12, 108.82, 101.22, 100.98, 100.10, 56.63, 55.92, 52.97, 39.49, 28.85, 21.44. HRMS calcd for $C_{29}H_{26}NO_7$, $[M+H]^+$, 500.1704; found 500.1703.





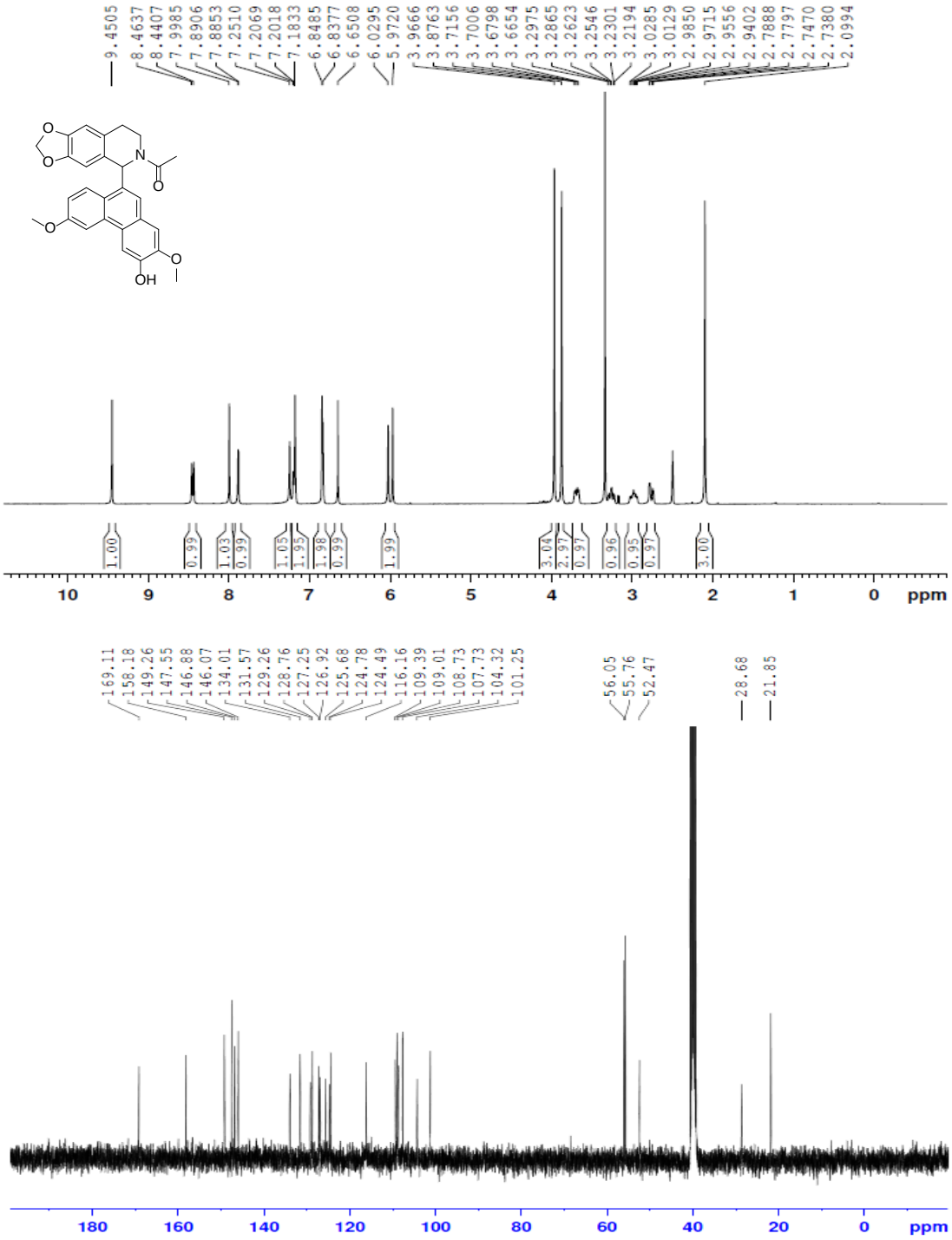
36. *1-(5-(3-isopropoxy-6,7-dimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22o**)*

^{1}H NMR (400MHz, $CDCl_3$) δ 8.16(s, 1H), 7.92(s, 1H), 7.88-7.89 (d, J = 1.88 Hz, 1H), 7.57-7.59(d, J = 8.76 Hz, 1H), 7.40(s, 1H), 7.10-7.13 (dd, J = 8.72, 2.28 Hz, 1H), 6.90(s, 1H), 6.70(s, 1H), 6.56(s, 1H), 5.93-5.98(m, 2H), 4.75-4.81(m, 1H), 4.11(s, 3H), 4.10(s, 3H), 3.58-3.63(m, 1H), 3.43-3.50(m, 1H), 2.98-3.07(m, 1H), 2.76-2.81(m, 1H), 2.18(s, 3H), 1.42-1.44(dd, J = 6.00, 1.36 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.12, 156.73, 149.83, 148.88, 147.02, 146.29, 133.16, 131.18, 130.38, 129.01, 128.41, 127.62, 126.57, 124.97, 124.59, 116.16, 108.87, 108.35, 107.36, 106.12, 103.65, 100.97, 70.43, 56.66, 56.02, 53.03, 39.46, 28.85, 22.18(×2), 21.45. HRMS calcd for $C_{31}H_{31}NO_6Na$, $[M+Na]^+$, 536.2044; found 536.2048.



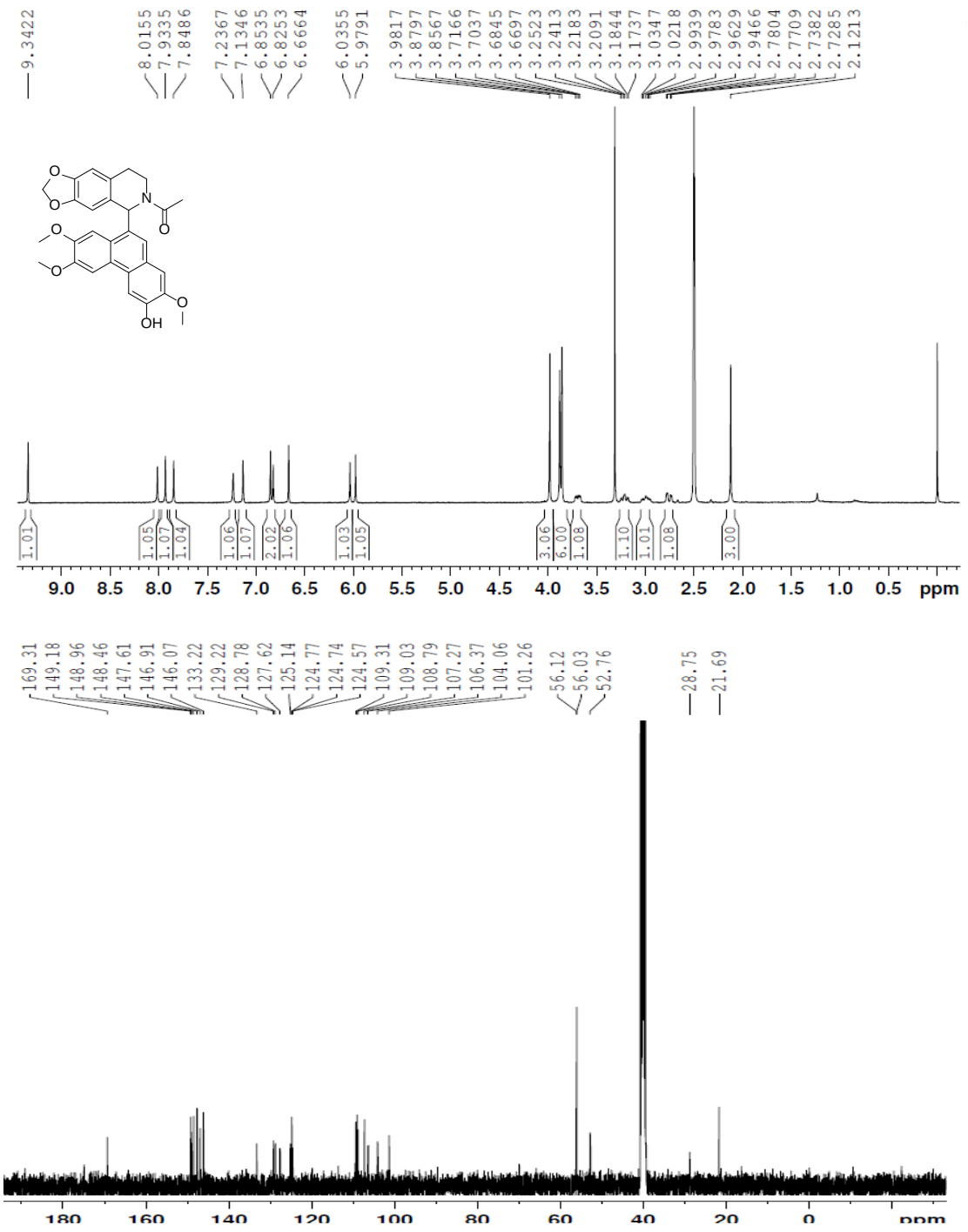
37. *1-(5-(3-hydroxy-2,6-dimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22p**)*

^{1}H NMR (400MHz, DMSO-*d*) δ 9.45(s, 1H), 8.44-8.46(d, J = 8.12 Hz, 1H), 8.00(s, 1H), 7.88-7.89(d, J = 2.12 Hz, 1H), 7.25(s, 1H), 7.20-7.21(d, J = 2.04 Hz, 1H), 7.18(s, 1H), 6.85(s, 1H), 6.84(s, 1H), 6.65(s, 1H), 6.03(s, 1H), 5.97(s, 1H), 3.88(s, 3H), 3.67-3.72(m, 1H), 3.22-3.30(m, 1H), 3.97(s, 3H), 2.94-3.03(s, 1H), 2.74-2.79(m, 1H), 2.09(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.11, 158.18, 149.26, 147.55, 146.88, 146.07, 134.01, 131.57, 129.26, 128.76, 127.25, 126.92, 125.68, 124.78, 124.49, 116.16, 109.39, 109.01, 108.73, 107.73, 104.32, 101.25, 56.05, 55.76(×2), 52.47, 28.67, 21.85. HRMS calcd for $C_{28}H_{26}NO_6$, $[M+H]^+$, 472.1755; found 472.1753.



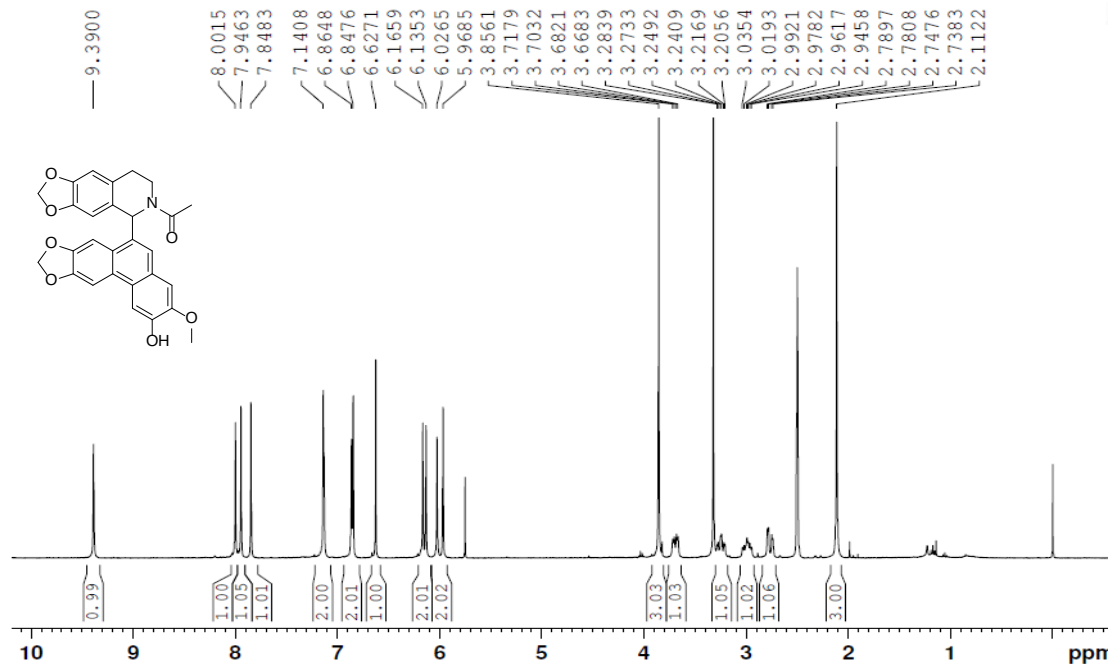
38. *1-(5-(3-hydroxy-2,6,7-trimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22q**)*

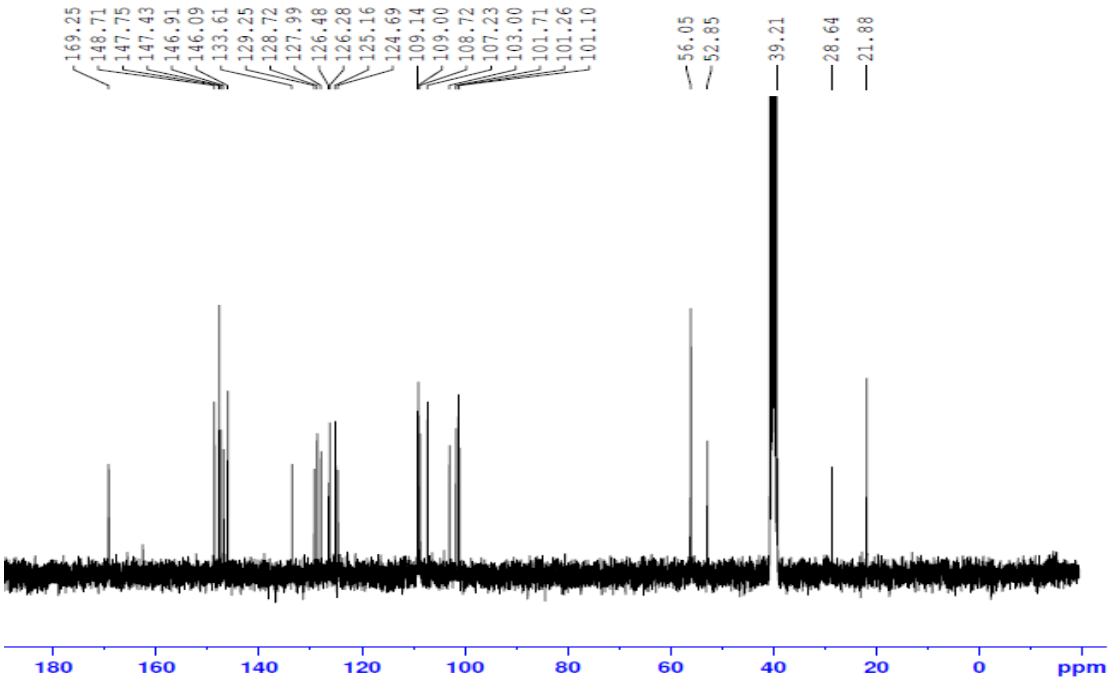
^{1}H NMR (400MHz, DMSO-d_6) δ 9.35(s, 1H), 8.03(s, 1H), 7.94(s, 1H), 7.86(s, 1H), 7.25(s, 1H), 7.14(s, 1H), 6.86(s, 1H), 6.84(s, 1H), 6.68(s, 1H), 6.05(s ,1H), 5.99(s, 1H), 3.99(s, 3H), 3.89(s, 3H), 3.87(s, 3H), 3.68-3.73(m, 1H), 3.18-3.26(m ,1H), 2.96-3.04(m, 1H), 2.74-2.79(m, 1H), 2.13(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.31, 149.18, 148.96, 148.46, 147.61, 146.91, 146.07, 133.22, 129.22, 128.78, 127.62, 125.14, 124.77, 124.74, 124.57, 109.31, 109.03, 108.79, 107.27, 106.37, 104.06, 101.26, 56.12, 56.03(×2), 52.76, 39.26, 28.75, 21.69. HRMS calcd for $C_{29}H_{28}NO_7$, $[M+H]^+$, 502.1860; found 502.1862.



39. *1-(5-(2-hydroxy-3-methoxyphenanthro[2,3-d][1,3]dioxol-6-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22r**)*

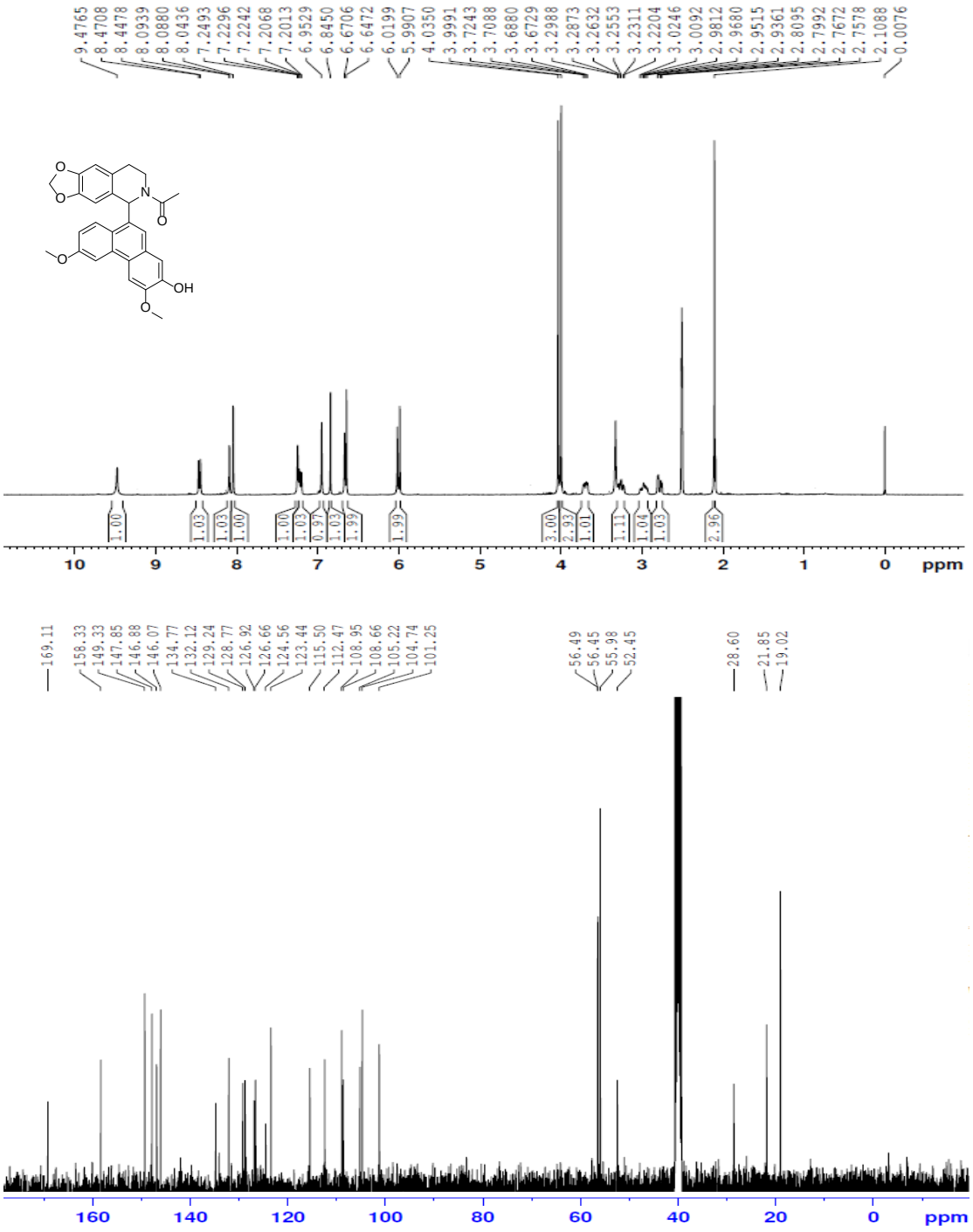
^{1}H NMR (400MHz, DMSO-d_6) δ 9.39(s, 1H), 8.00(s, 1H), 7.95(s, 1H), 7.85(s, 1H), 7.14(s, 2H), 6.86(s, 1H), 6.85(s, 1H), 6.63(s, 1H), 6.17(s, 1H), 6.14(s, 1H), 6.03(s, 1H), 5.97(s, 1H), 3.86(s, 3H), 3.67-3.72(m, 1H), 3.21-3.28(m, 1H), 2.95-3.04(m, 1H), 2.74-2.79(m, 1H), 2.11(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.25, 148.71, 147.75, 147.43, 146.91, 146.09, 133.61, 129.25, 128.72, 127.99, 126.48, 126.28, 125.16, 124.69, 109.14, 109.00, 108.72, 107.23, 103.00, 101.71, 101.26, 101.10, 56.05, 52.85, 39.21, 28.64, 21.88. HRMS calcd for $C_{28}H_{23}NO_7Na$, $[M+Na]^+$, 508.1367; found 508.1353.





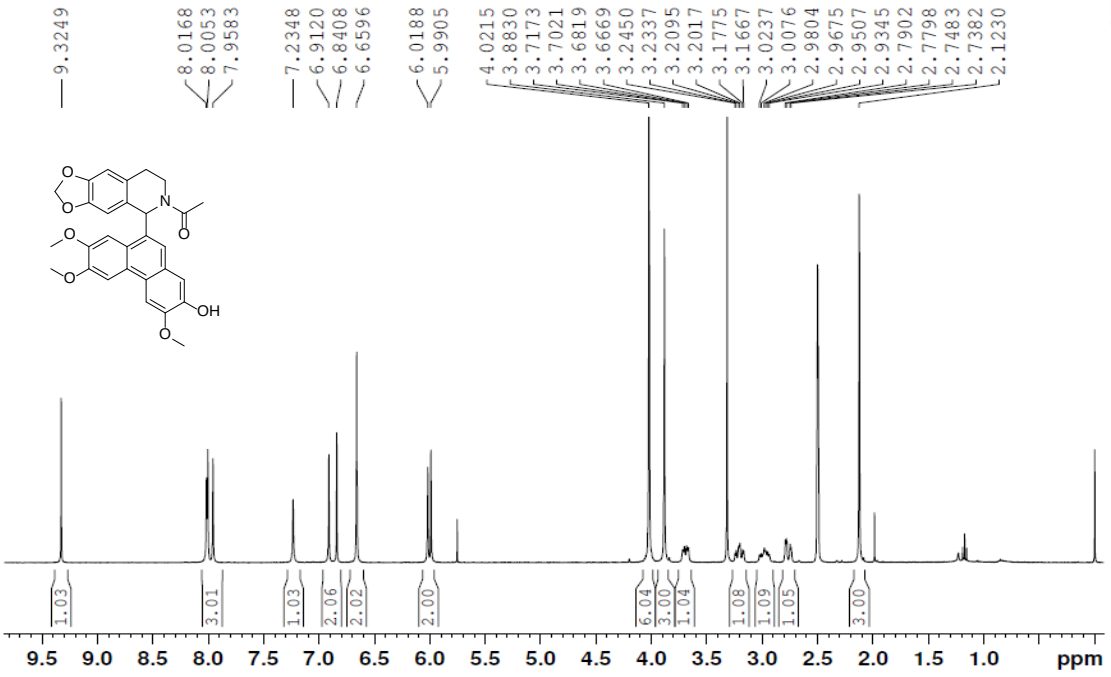
40. *1-(5-(2-hydroxy-3,6-dimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22s**)*

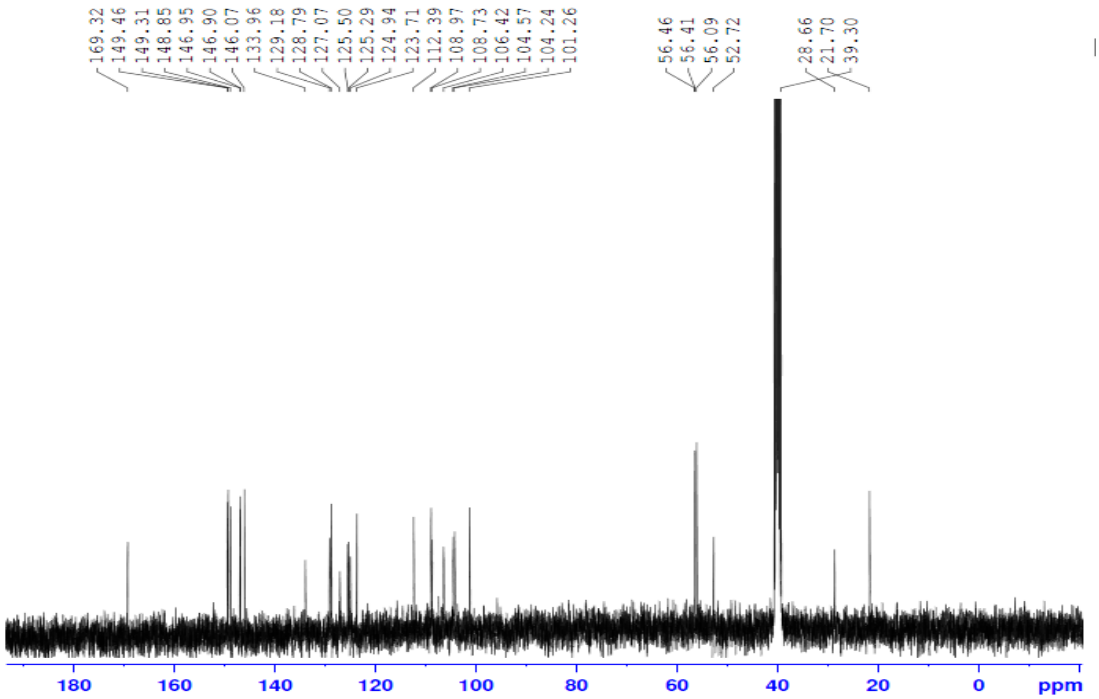
^{1}H NMR (400MHz, DMSO-d_6) δ 9.47(s, 1H), 8.44-8.46(d, J = 9.24 Hz, 1H), 8.08-8.09(d, J = 2.36 Hz, 1H), 8.04(s, 1H), 7.19-7.24(m, 1H), 6.94(s, 1H), 6.84 (s, 1H), 6.66(s, 1H), 6.64(s, 1H), 5.98-6.01(d, J = 11.68 Hz, 2H), 4.03(s, 3H), 4.00(s, 3H), 3.66-3.72(m, 1H), 3.21-3.29(m, 1H), 2.93-3.02(m, 1H), 2.75-2.80(m, 1H), 2.10(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.11, 158.33, 149.33, 147.85, 146.88, 146.07, 134.77, 132.12, 129.24, 128.77, 126.92, 126.66, 124.56, 123.44, 115.50, 112.47, 108.95, 108.66, 105.22, 104.74, 101.25, 56.49, 55.98, 56.45, 52.45, 28.60, 21.85, 19.02. HRMS calcd for $C_{28}H_{26}NO_6$, $[M+H]^+$, 472.1755; found 472.1754.



41. *1-(5-(2-hydroxy-3,6,7-trimethoxyphenanthren-9-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22t**)*

^{1}H NMR (400MHz, DMSO-d_6) δ 9.32(s, 1H), 8.02(s, 1H), 8.01(s, 1H), 7.96(s, 1H), 7.23(s, 1H), 6.91(s, 1H), 6.84(s, 1H), 6.66(s, 2H), 6.02(s, 1H), 5.99(s, 1H), 4.02(s, 3H), 3.88(s, 3H), 3.67-3.72(m, 1H), 3.17-3.25(m, 1H), 2.93-3.02(m, 1H), 2.74-2.79(m, 1H), 2.12(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.32, 149.46, 149.31, 148.85, 146.95, 146.90, 146.07, 133.96, 129.18, 128.79, 127.07, 125.50, 125.29, 124.94, 123.71, 112.39, 108.97, 108.73, 106.42, 104.57, 104.24, 101.26, 56.46, 56.41, 56.09, 52.72, 39.28, 28.66, 21.70. HRMS calcd for $C_{29}H_{28}NO_7$, $[M+H]^+$, 502.1680; found 502.1682.





42. *1-(5-(3-hydroxy-2-methoxyphenanthro[2,3-d][1,3]dioxol-6-yl)-7,8-dihydro-[1,3]dioxolo[4,5-g]isoquinolin-6(5H)-yl)ethanone (**22u**)*

^{1}H NMR (400MHz, DMSO-d_6) δ 9.37(s, 1H), 8.28(s, 1H), 8.00(s, 1H), 7.96(s, 1H), 7.13(s, 1H), 6.91(s, 1H), 6.84(s, 1H), 6.70(s, 1H), 6.62(s, 1H), 6.18(s, 1H), 6.15(s, 1H), 6.01(s, 1H), 5.98(s, 1H), 4.00(s, 3H), 3.68-3.70(m, 1H), 3.21-3.27(m, 1H), 2.98-3.01(m, 1H), 2.76-2.80(m, 1H), 2.24-2.27(m, 1H), 2.12(s, 3H). ^{13}C NMR (100MHz, DMSO-d_6) δ 169.23, 149.58, 147.84, 147.18, 147.10, 146.89, 146.08, 134.30, 129.21, 128.72, 127.35, 126.97, 126.14, 125.49, 124.25, 112.06, 108.93, 108.64, 104.24, 102.94, 101.69(×2), 101.25, 56.38, 52.79, 39.22, 28.56, 21.88. HRMS calcd for $C_{28}H_{23}NO_7Na$, $[M+Na]^+$, 508.1367; found 508.1377.