Supporting Information

Efficient Synthesis of Camptothecin Propargylamine Derivatives in Water Catalyzed by Macroporous Adsorption Resin-Supported Gold Nanoparticles

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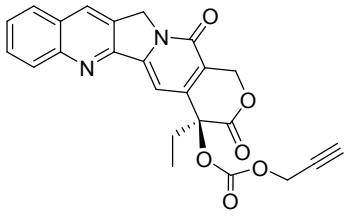
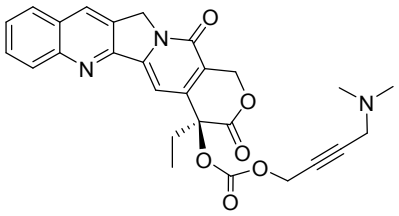
Spectroscopic data for camptothecin 20-substituted propargylamines derivatives

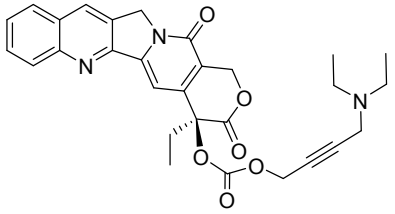


Compound 2. Yield: 76%; $[\alpha]_D^{26}$ −110 (*c* 0.1, $CHCl_3$); IR (KBr) v_{max} (cm^{-1}): 3426, 2991, 2957, 1753, 1671, 1624, 1563, 1459, 1269, 973, 762. ^1H NMR (400MHz, $CDCl_3$) *δ*: 8.41 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.85 (t, *J*=7.8Hz, 1H), 7.68 (t, *J*=7.8Hz, 1H), 7.34 (s, 1H), 5.71 (d, *J*=16Hz, 1H), 5.40 (d, *J*=16Hz, 1H), 5.30 (s, 2H), 4.71 (s, 2H), 2.52 (s, 1H), 2.14-2.32 (m, 2H), 1.02 (t, *J*=8.0Hz, 3H); ^{13}C NMR (CDCl3) δ 167.0, 157.3, 153.1, 152.3, 148.9, 146.5, 145.4, 131.1, 130.7, 129.7, 128.4, 128.2, 128.2, 128.1, 120.3, 95.9, 78.3, 76.5, 76.2, 67.1, 56.2, 50.0, 31.89, 7.6. HRESIMS *m/z* 453.1057 $[M+Na]^+$ (calcd for $C_{24}H_{18}N_2O_6Na$ 453.1046).

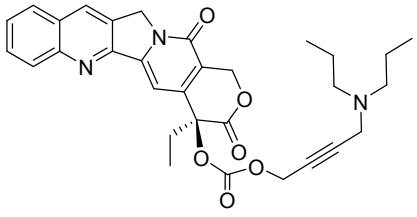


Compound 5a. Yield: 82%; $[\alpha]_D^{26}$ −130 (*c* 0.1, $CHCl_3$); IR (KBr) v_{max} (cm^{-1}): 3431, 2938, 1749, 1670, 1622, 1560, 1460, 1274. ^1H NMR (400MHz, $CDCl_3$) *δ*: 8.39 (s, 1H), 8.20 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.81-7.83 (m, 1H), 7.64-7.68 (m 1H), 7.33 (s, 1H), 5.70 (d, *J*=16Hz, 1H), 5.28 (d, *J*=16Hz, 1H), 5.27 (s, 2H), 4.74-4.78 (m, 2H), 3.21 (s, 2H), 2.19 (s, 6H), 2.13-2.32 (m, 2H), 0.99 (t, *J*=7.2Hz, 3H); ^{13}C

NMR ($CDCl_3$) δ 167.06, 157.3, 153.2, 152.3, 148.9, 146.5, 145.6, 131.2, 130.7, 129.6, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 83.5, 78.2, 77.9, 67.0, 56.7, 50.0, 47.7, 43.8, 43.8, 31.9, 7.6. HRESIMS *m*/*z* 488.1816 $[M+H]^+$ (calcd for $C_{27}H_{26}N_3O_6$ 488.1819).

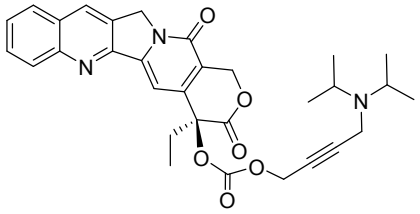


Compound 5b. Yield: 80%; $[\alpha]_D^{26}$ −110 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3429, 2963, 2930, 1754, 1671, 1624, 1562, 1459, 1269, 960. ^1H NMR (400MHz, $CDCl_3$) *δ*: 8.41 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.82-7.86 (m, 1H), 7.66-7.68 (m 1H), 7.34 (s, 1H), 5.70 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.30 (s, 2H), 4.72-4.73 (m, 2H), 3.40 (s, 2H), 2.44-2.49 (m, 4H), 2.14-2.33 (m, 2H), 0.96-1.023 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.2, 130.8, 129.6, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 83.5, 78.1, 77.9, 67.1, 56.8, 50.0, 47.2, 47.2, 40.7, 32.0, 12.5, 12.5, 7.6. HRESIMS *m*/*z* 516.2129 $[M+H]^+$ (calcd for $C_{29}H_{30}N_3O_6$ 516.2126).

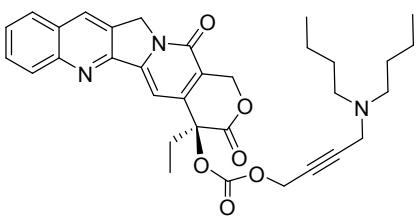


Compound 5c. Yield: 79%; $[\alpha]_D^{26}$ −130 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3434, 2958, 1751, 1663, 1618, 1564, 1457, 1271. ^1H NMR (400MHz, $CDCl_3$) *δ*: 8.40 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.93 (d, *J*=8.0Hz, 1H), 7.82-7.86 (m, 1H), 7.68-7.70 (m

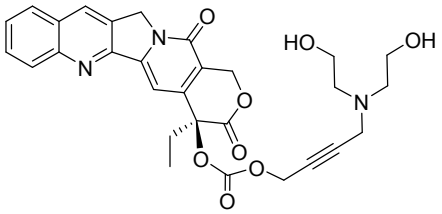
1H), 7.34 (s, 1H), 5.70 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.30 (s, 2H), 4.73 (m, 2H), 3.32-3.37 (m, 2H), 2.13-2.34 (m, 6H), 1.34-1.40 (m, 4H), 0.79-1.02 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.2, 130.8, 129.6, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 83.5, 78.1, 77.9, 67.1, 56.8, 55.6, 55.6, 50.0, 42.0, 32.0, 20.5, 20.5, 11.8, 11.8, 7.6. HRESIMS *m*/*z* 544.2442 $[M+H]^+$ (calcd for $C_{31}H_{34}N_3O_6$ 544.2438).



Compound 5d. Yield: 72%; $[\alpha]_D^{26}$ −150 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3436, 2941, 1755, 1666, 1619, 1561, 1460, 1258. ^{1}H NMR (400MHz, $CDCl_3$) *δ*: 8.45 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.96 (d, *J*=8.0Hz, 1H), 7.84-7.88 (m, 1H), 7.68-7.71 (m 1H), 7.31 (s, 1H), 5.70 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.32 (s, 2H), 4.66-4.79 (m, 2H), 3.92 (s, 2H), 3.73-3.76 (m, 2H), 2.14-2.32 (m, 2H), 1.43-1.47 (m, 12H), 1.02 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.0, 157.2, 153.2, 152.1, 148.8, 146.6, 145.3, 131.4, 130.9, 129.5, 128.4, 128.3, 128.2, 128.2, 120.2, 95.6, 82.4, 78.5, 77.9, 68.5, 67.1, 55.9, 53.1, 50.1, 34.3, 31.9, 27.8, 22.2, 18.2, 18.2, 7.6. HRESIMS *m*/*z* 544.2442 $[M+H]^+$ (calcd for $C_{31}H_{34}N_3O_6$ 544.2445).

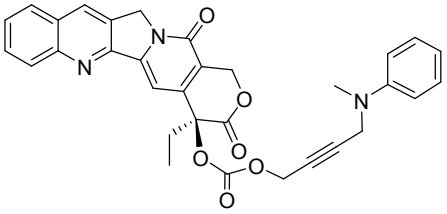


Compound 5e. Yield: 69%; $[\alpha]_D^{26}$ −130 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3432, 2961, 1751, 1663, 1617, 1561, 1458, 1260. ^1H NMR (400MHz, $CDCl_3$) δ: 8.41 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.83-7.87 (m, 1H), 7.68-7.70 (m 1H), 7.33 (s, 1H), 5.90 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.31 (s, 2H), 4.73-4.75 (m, 2H), 3.53 (s, 2H), 2.52-2.54 (m, 4H), 2.14-2.32 (m, 2H), 1.45-1.49 (m, 4H), 1.26-1.32 (m, 4H), 1.00 (t, *J*=7.2Hz, 3H), 0.85-0.90 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.2, 130.8, 129.6, 128.4, 128.2, 128.2, 128.1, 120.3, 95.9, 78.3, 77.3, 77.2, 67.1, 56.6, 53.4, 53.4, 50.0, 41.8, 31.9, 28.7, 28.7, 20.41, 20.4, 13.8, 13.8, 7.6. HRESIMS *m*/*z* 572.2755 $[M+H]^+$ (calcd for $C_{33}H_{38}N_3O_6$ 572.2753).

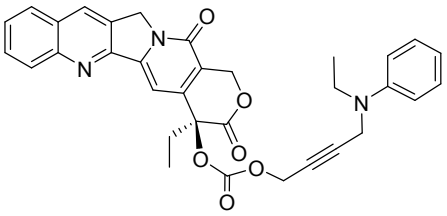


Compound 5f. Yield: 51%; $[\alpha]_D^{26}$ −140 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3642, 3436, 2941, 1755, 1670, 1629, 1563, 1469, 1255. ^1H NMR (400MHz, $CDCl_3$) δ: 8.40 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.82-7.85 (m, 1H), 7.66-7.70 (m 1H), 7.34 (s, 1H), 5.70 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.30 (s, 2H, C5-H), 4.71-4.73 (m, 2H), 3.46-3.65 (m, 6H), 1.93-2.29 (m, 6H), 0.99-1.05 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.2, 130.8, 129.6, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 83.5, 78.3, 77.2, 67.1, 59.3, 59.3, 56.6, 56.2, 56.2, 50.0, 40.7, 32.0, 7.6. HRESIMS *m*/*z* 548.2027 $[M+H]^+$ (calcd for $C_{29}H_{30}N_3O_8$

548.2019).

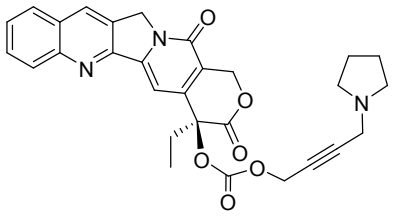


Compound 5g. Yield: 72%; $[\alpha]_D^{26}$ −150 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3436, 2929, 1752, 1663, 1603, 1567, 1454, 1255. ^1H NMR (400MHz, $CDCl_3$) δ: 8.37 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.81-7.85 (m, 1H), 7.64-7.68 (m 1H), 7.33 (s, 1H), 7.17 (t, *J*=8.0Hz, 2H), 6.73-6.76 (m, 3H), 5.69 (d, *J*=16Hz, 1H), 5.38 (d, *J*=16Hz, 1H), 5.27 (s, 2H), 4.67-4.68 (m, 2H), 4.02 (s, 2H), 2.87 (s, 3H), 2.12-2.31 (m, 2H), 1.00 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.1, 152.3, 149.0, 148.9, 146.5, 145.5, 131.2, 130.7, 129.6, 129.0, 129.0, 128.4, 128.2, 128.2, 128.1, 120.3, 118.2, 114.2, 114.2, 95.9, 84.2, 78.2, 76.6, 67.0, 56.7, 50.0, 42.6, 38.5, 31.9, 7.6. HRESIMS *m*/*z* 550.1973 $[M+H]^+$ (calcd for $C_{32}H_{28}N_3O_6$ 550.1996).

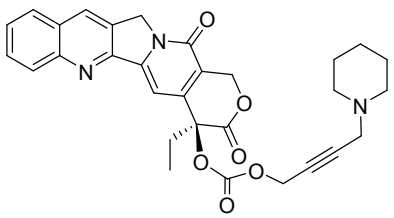


Compound 5h. Yield: 54%; $[\alpha]_D^{26}$ −130 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3429, 2971, 1752, 1664, 1615, 1566, 1454, 1253. ^1H NMR (400MHz, $CDCl_3$) *δ*: 8.39 (s, 1H), 8.21 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.81-7.85 (m, 1H), 7.65-7.69 (m 1H), 7.33 (s, 1H), 7.17-7.21 (m, 2H), 6.72-6.75 (m, 3H), 5.69 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.28 (s, 2H), 4.68-4.69 (m, 2H), 3.99 (s, 2H), 3.31-3.37 (m, 2H),

1.88-2.31 (m, 2H), 1.10 (t, *J*=8.0Hz, 3H), 1.01 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.0, 157.3, 153.1, 152.3, 148.9, 147.8, 146.5, 145.5, 131.2, 130.7, 129.6, 129.6, 129.1, 129.1, 128.4, 128.2, 128.1, 120.4, 117.7, 113.9, 113.9, 96.0, 85.1, 78.2, 76.1, 67.0, 56.8, 50.0, 45.4, 39.8, 31.9, 12.3, 7.6. HRESIMS *m*/*z* 586.1949 $[M+Na]^+$ (calcd for $C_{33}H_{29}N_3O_6Na$ 586.1940).

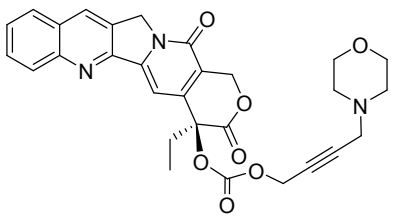


Compound 5i. Yield: 81%; $[\alpha]_D^{26}$ −150 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3430, 2957, 1750, 1667, 1612, 1563, 1443, 1265. ^{1}H NMR (400MHz, $CDCl_3$) *δ*: 8.41 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.85 (t, *J*=8.0Hz, 1H), 7.68 (t, *J*=8.0Hz, 1H), 7.34 (s, 1H), 5.69 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.30 (s, 2H), 4.73-4.74 (m, 2H), 3.40 (s, 2H), 2.52-2.55 (m, 4H), 2.14-2.30 (m, 2H), 1.70-1.74 (m, 4H), 1.01 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.1, 130.7, 129.7, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 84.4, 78.2, 77.2, 67.1, 56.8, 52.3, 52.3, 50.0, 42.9, 32.0, 23.7, 23.7, 7.6. HRESIMS *m*/*z* 514.1973 $[M+H]^+$ (calcd for $C_{29}H_{28}N_3O_6$ 514.1971).

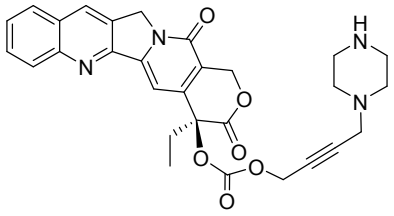


Compound 5j. Yield: 83%; $[\alpha]_D^{26}$ −80 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3433,

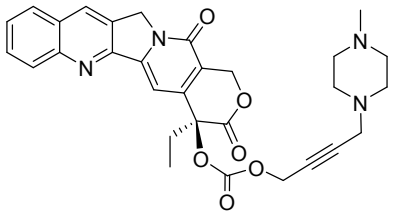
2932, 1753, 1664, 1618, 1562, 1453, 1261. ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.41 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.85 (t, *J*=8.0Hz, 1H), 7.68 (t, *J*=8.0Hz, 1H), 7.34 (s, 1H), 5.70 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.29 (s, 2H), 4.74 (m, 2H), 3.23 (s, 2H), 2.39-2.41 (m, 4H), 2.14-2.30 (m, 2H), 1.50-1.56 (m, 4H), 1.34-1.39 (m, 2H), 1.01 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.2, 130.7, 129.7, 128.4, 128.2, 128.2, 128.1, 120.3, 95.9, 84.2, 78.2, 77.5, 67.1, 56.8, 53.1, 53.2, 50.0, 47.7, 31.9, 25.8, 25.8, 23.7, 7.6. HRESIMS *m*/*z* 528.2129 $[M+H]^+$ (calcd for $C_{30}H_{30}N_3O_6$ 528.2141).



Compound 5k. Yield: 76%; $[\alpha]_D^{26}$ −100 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3435, 2925, 1751, 1664, 1611, 1564, 1445, 1265. ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.41 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.85 (t, *J*=8.0Hz, 1H), 7.68 (t, *J*=8.0Hz, 1H), 7.34 (s, 1H), 5.70 (d, *J*=16Hz, 1H), 5.39 (d, *J*=16Hz, 1H), 5.30 (s, 2H), 4.73-4.74 (m, 2H), 3.64-3.67 (m, 4H), 3.26 (s, 2H), 2.47-2.49 (m, 4H), 2.14-2.32 (m, 2H), 1.01 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.2, 130.8, 129.6, 128.5, 128.2, 128.2, 128.1, 120.4, 95.9, 83.2, 78.2, 77.2, 67.1, 66.7, 66.7, 56.6, 52.2, 52.2, 50.0, 47.3, 32.0, 7.6. HRESIMS *m*/*z* 530.1922 $[M+H]^+$ (calcd for $C_{29}H_{28}N_3O_7$ 530.1931).

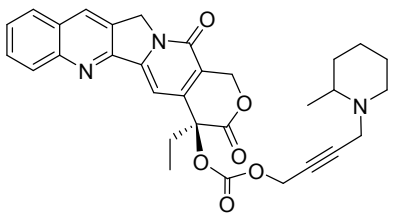


Compound 5l. Yield: 62%; $[\alpha]_D^{26}$ −160 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3429, 2930, 1752, 1664, 1616, 1564, 1454, 1256. ^1H NMR (400MHz, $CDCl_3$) δ: 8.43 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.96 (d, *J*=8.0Hz, 1H), 7.86 (t, *J*=8.0Hz, 1H), 7.69 (t, *J*=8.0Hz, 1H), 7.32 (s, 1H), 5.72 (d, *J*=16.0 Hz, 1H), 5.40 (d, *J*=16Hz, 1H), 5.32 (s, 2H), 4.64-4.78 (m, 2H), 3.19-3.33 (m, 6H), 2.62-2.89 (m, 4H), 2.14-2.33 (m, 2H), 1.01 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ168.0, 157.2, 153.2, 152.2, 148.9, 146.6, 145.2, 131.3, 130.8, 129.6, 128.5, 128.3, 128.2, 128.2, 120.1, 95.8, 83.6, 78.2, 77.8, 67.1, 56.7, 56.2, 56.2, 51.6, 51.6, 50.0, 46.8, 31.9, 7.6. HRESIMS *m*/*z* 529.2082 $[M+H]^+$ (calcd for $C_{29}H_{29}N_4O_6$: 529.2074).

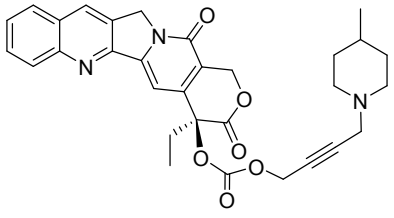


Compound 5m. Yield: 72%; $[\alpha]_D^{26}$ −130 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3438, 2957, 1750, 1672, 1619, 1562, 1460, 1280. ^1H NMR (400MHz, CDCl3) δ: 8.41 (s, 1H), 8.23 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.85 (t, *J*=8.0Hz ,1H), 7.68 (t, *J*=8.0Hz ,1H), 7.34 (s, 1H), 5.70 (d, *J*=16.0 Hz, 1H), 5.39 (d, *J*=16.0 Hz, 1H), 5.31 (s, 2H), 4.72-4.73 (m, 2H), 3.26 (s, 2H), 2.43-2.54 (m, 4H), 2.13-2.32 (m, 2H), 2.26 (s, 3H), 1.73 (m, 4H), 1.01 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2,

152.3, 148.9, 146.5, 145.5, 131.2, 130.7, 129.7, 128.4, 128.2, 128.1, 128.0, 120.4, 96.0, 83.7, 78.2, 77.8, 67.1, 56.7, 54.7, 54.7, 51.7, 51.7, 50.0, 46.9, 45.7, 32.0, 7.6. HRESIMS *m/z* 543.2238 $[M+H]^+$ (calcd for $C_{30}H_{31}N_4O_6$ 543.2224).

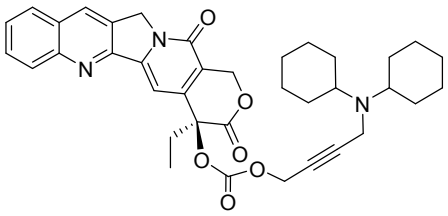


Compound 5n. Yield: 71%; $[\alpha]_D^{26}$ −120 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3430, 2930, 1753, 1669, 1622, 1561, 1458, 1262. ^1H NMR (400MHz, $CDCl_3$) *δ*: 8.41 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.95 (d, *J*=8.0Hz, 1H), 7.84 (t, *J*=8.0Hz, 1H), 7.68 (t, *J*=8.0Hz, 1H), 7.35 (s, 1H), 5.70 (d, *J*=16.0 Hz, 1H), 5.39 (d, *J*=16.0 Hz, 1H), 5.29 (s, 2H), 4.74 (m, 2H), 3.61-3.67 (m, 1H), 3.29-3.34 (m, 1H), 2.14-2.76 (m, 7H), 1.51-1.63 (m, 4H), 0.98-1.04 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.5, 131.2, 130.7, 129.6, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 82.8, 78.2, 77.2, 67.1, 56.7, 54.8, 53.2, 50.0, 43.3, 34.3, 32.0, 25.9, 24.2, 19.6, 7.6. HRESIMS *m/z* 542.2286 $[M+H]^+$ (calcd for $C_{31}H_{32}N_3O_6$ 542.2286).

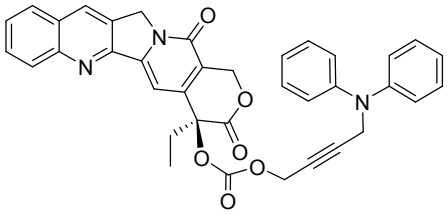


Compound 5o. Yield: 82%; $[\alpha]_D^{26}$ −100 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3434, 2927, 1753, 1668, 1621, 1562, 1458, 1263. ^1H NMR (400MHz, $CDCl_3$) *δ*: 8.40 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.84 (t, *J*=8.0Hz, 1H), 7.68 (t,

J=8.0Hz, 1H), 7.34 (s, 1H), 5.70 (d, *J*=16.0 Hz, 1H), 5.39 (d, *J*=16.0 Hz, 1H), 5.30 (s, 2H), 4.74 (m, 2H), 3.24 (s, 2H), 2.72-2.78 (m, 2H), 2.14-2.30 (m, 2H), 2.04-2.11 (m, 2H), 1.53-1.59 (m, 2H), 1.15-1.26 (m, 3H), 1.01 (t, *J*=7.2Hz, 3H), 0.86 (d, *J*=4.0Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.5, 145.6, 131.1, 130.7, 129.7, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 84.2, 78.2, 77.5, 67.0, 56.8, 52.6, 52.6, 50.0, 47.3, 34.1, 34.1, 32.0, 30.1, 21.7, 7.6. HRESIMS *m*/*z* 542.2286 $[M+H]^+$ (calcd for $C_{31}H_{32}N_3O_6$ 542.2273).



Compound 5p. Yield: 51%; $[\alpha]_D^{26}$ −120 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3430, 2927, 1757, 1670, 1617, 1569, 1451, 1252. ^{1}H NMR (400MHz, $CDCl_3$) *δ*: 8.40 (s, 1H), 8.22 (d, *J*=8.0Hz, 1H), 7.94 (d, *J*=8.0Hz, 1H), 7.84 (t, *J*=8.0Hz, 1H), 7.68 (t, *J*=8.0Hz, 1H), 7.34 (s, 1H), 5.69 (d, *J*=16.0 Hz, 1H), 5.39 (d, *J*=16.0 Hz, 1H), 5.29 (s, 2H), 4.71 (s, 2H), 3.42-3.44 (m, 2H), 2.64-2.69 (m, 2H), 2.14-2.32 (m, 2H), 1.69-1.76 (m, 8H), 1.52-1.57 (m, 2H), 1.16-1.25 (m, 8H), 0.99-1.06 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.3, 153.2, 152.3, 148.9, 146.4, 145.6, 131.1, 130.7, 129.7, 128.4, 128.2, 128.2, 128.1, 120.4, 96.0, 88.7, 78.0, 75.2, 67.0, 57.4, 57.4, 57.2, 50.0, 35.1, 32.0, 31.2, 31.2, 31.2, 31.2, 26.2, 26.2, 26.1, 26.1, 26.1, 26.1, 7.6. HRESIMS *m*/*z* 624.3068 $[M+H]^+$ (calcd for $C_{37}H_{42}N_3O_6$ 624.3064).



Compound 5q. Yield: 39%; $[\alpha]_D^{26}$ −140 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3428, 2958, 1754, 1663, 1596, 1564, 1456, 1257. ^1H NMR (400MHz, $CDCl_3$) δ: 8.38 (s, 1H), 8.17 (d, *J*=8.0Hz, 1H), 7.92 (d, *J*=8.0Hz, 1H), 7.82 (t, *J*=8.0Hz, 1H), 7.66 (t, *J*=8.0Hz, 1H), 7.33 (s, 1H), 7.21-7.24 (m, 5H), 6.94-7.00 (m, 5H), 5.70 (d, *J*=16.0 Hz, 1H), 5.39 (d, *J*=16.0 Hz, 1H), 5.24-5.27 (m, 2H), 4.68 (s, 2H), 4.37-4.41 (m, 2H), 2.12-2.31 (m, 2H), 1.01 (t, *J*=7.2Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 157.30, 153.2, 152.3, 148.9, 146.5, 145.6, 131.2, 130.7, 129.7, 129.32, 129.23, 129.2, 129.2, 129.2, 129.2 128.4, 128.2, 128.2, 128.1, 122.1, 122.1, 121.0, 121.0, 121.0, 121.0, 120.4, 96.0, 83.5, 78.2, 77.2, 67.0, 56.7, 50.0, 42.2, 31.9, 7.6. HRESIMS *m*/*z* 612.2048 $[M+H]^+$ (calcd for $C_{37}H_{30}N_3O_6$ 612.2056).

The recyclability of MAR-AuNPs catalyst

Compound **2** (1 mmol) was suspended in 4 mL water under N_2 atmosphere, MAR-AuNPs (1.12 g, contains 0.06 mmol of Au) was then added. The mixture was heated at 80 ℃ until the suspended solids disappeared. After that, diethylamine (1.2 mmol), formaldehyde (1.5 mmol) and a dropwise of HCl were added into this reaction mixture at room temperature. The reaction mixture ware heated at 80 ℃ again for 24 h. The completion of the reaction was confirmed by thin layer chromatography (TLC) using ethyl acetate/chloroform as the eluent. After filtration, the catalyst was washed with acetone (4×5 mL). After being air-dried, it can be reused directly without further

purification. The results were shown in Fig. S3

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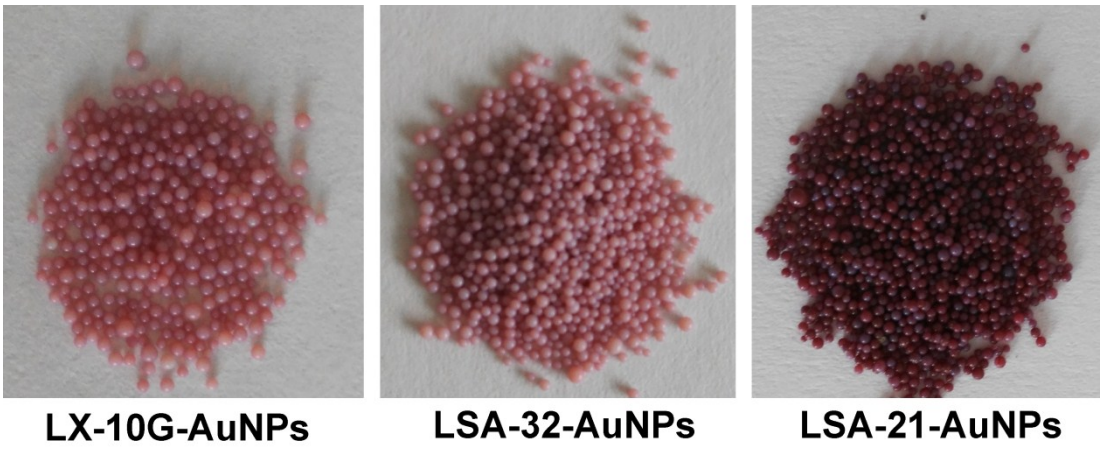


Fig. S1 Optical photos of MAR-supported AuNPs prepared from different types of MAR.

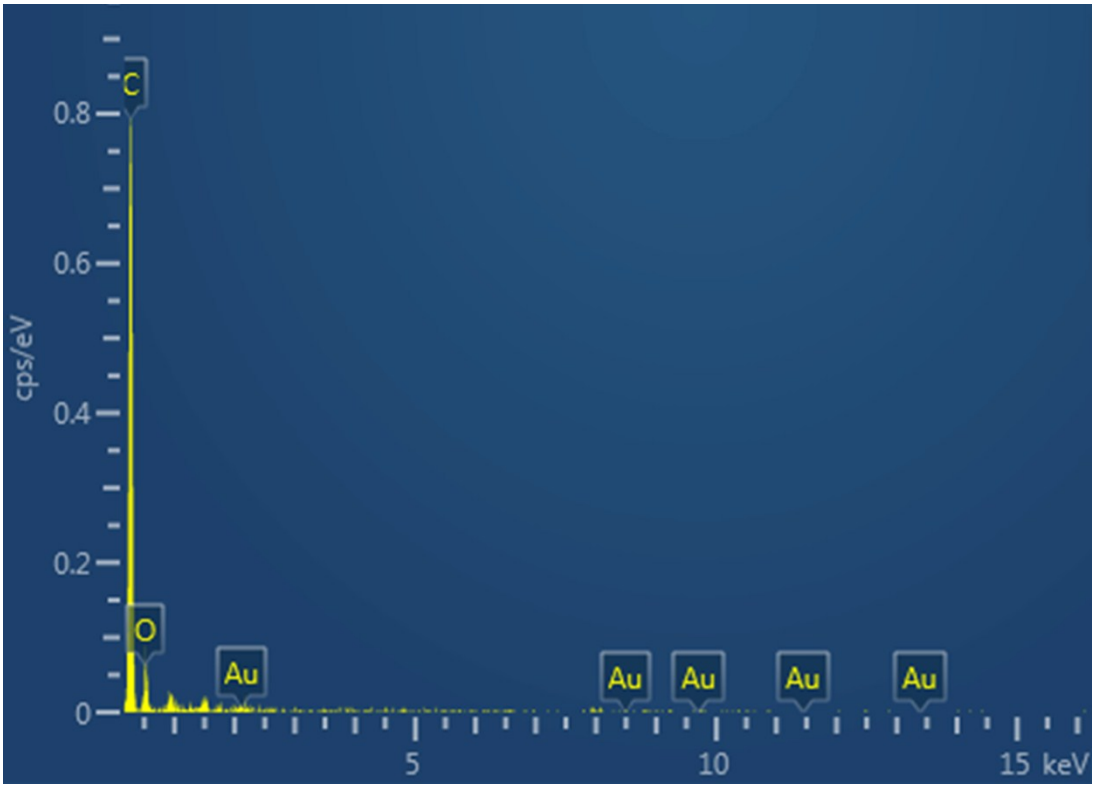


Fig. S2 EDS mapping analysis of MAR-AuNPs.

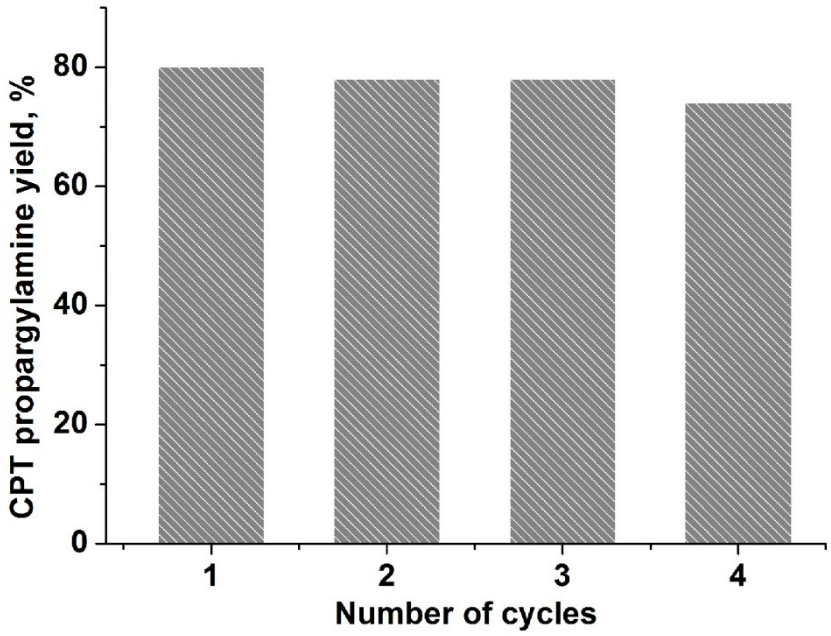
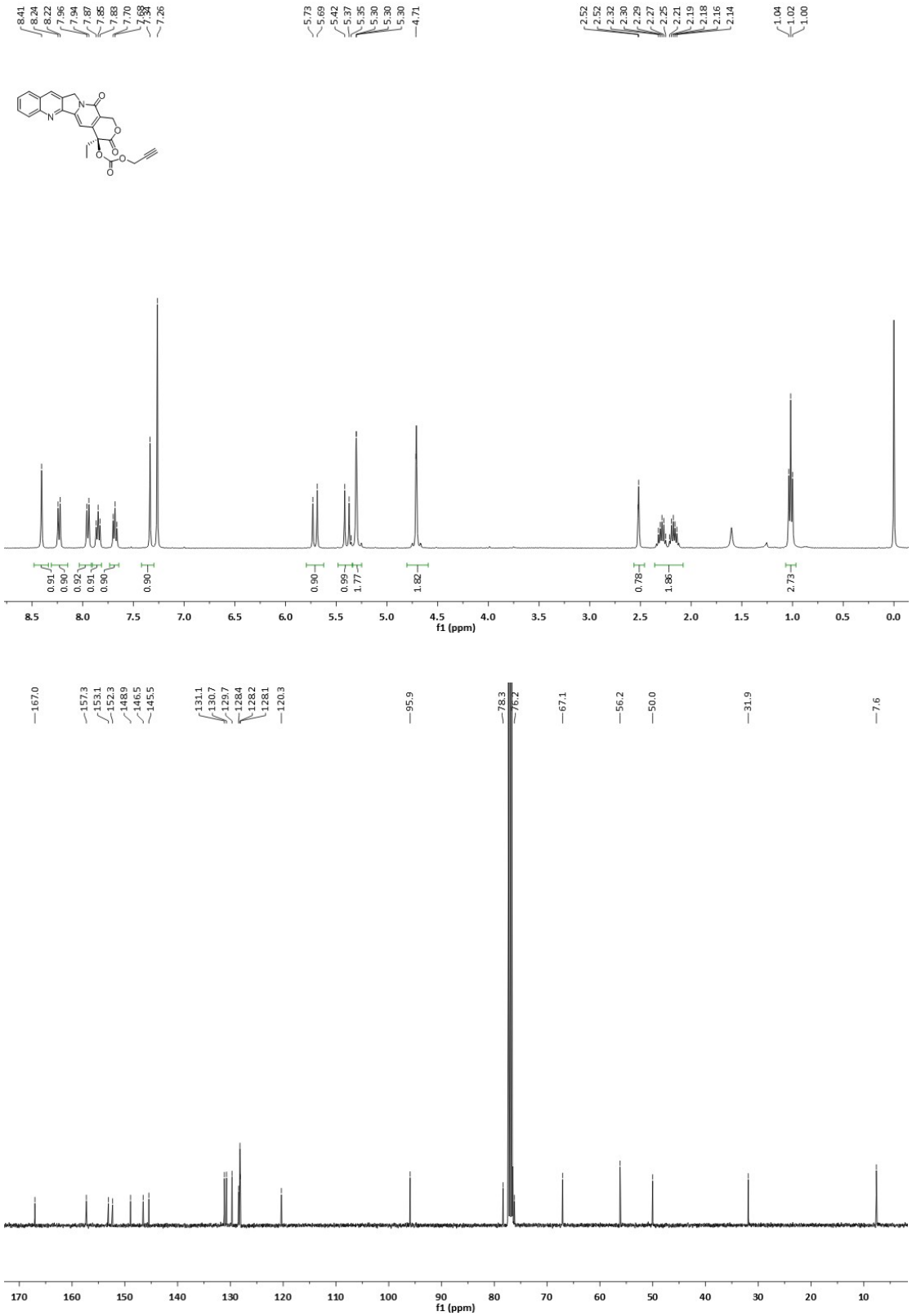


Fig.S3 Catalyst recycling studies in the Mannich reaction of CPT-propargyl, diethylamine and formaldehyde.

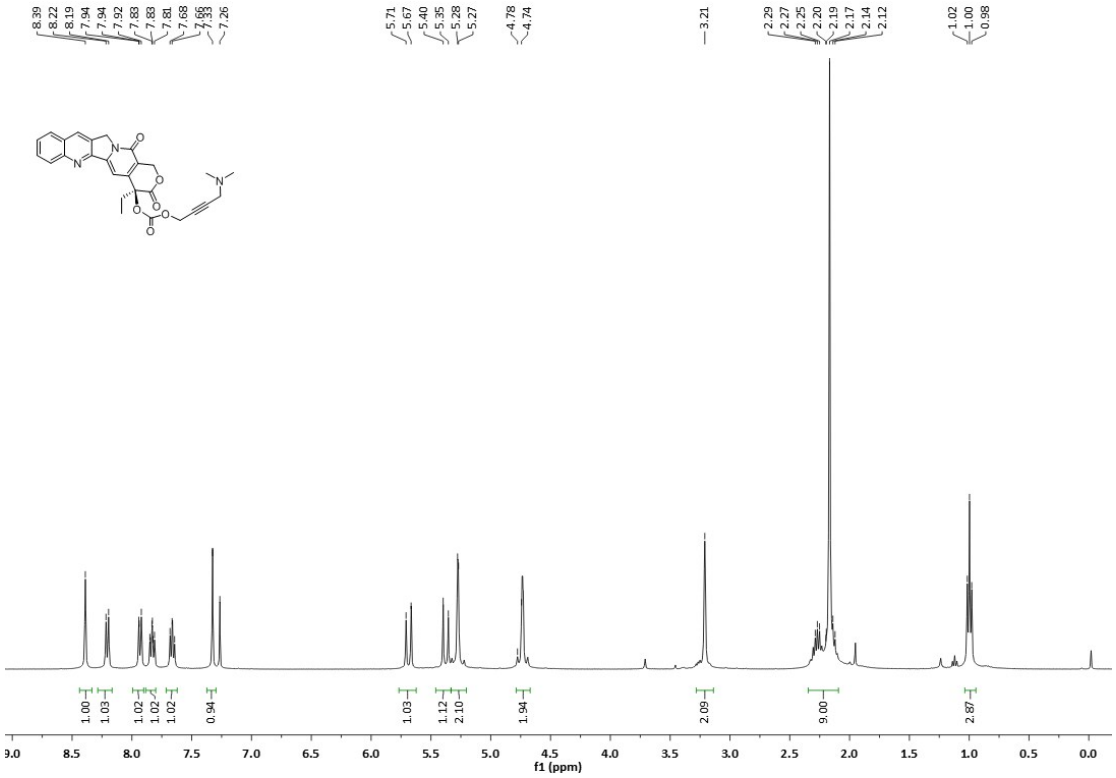
Table S1. *In vitro* biological activity of compounds 5**a-q** and **2** against HL-60 and HCT-116 cell lines.

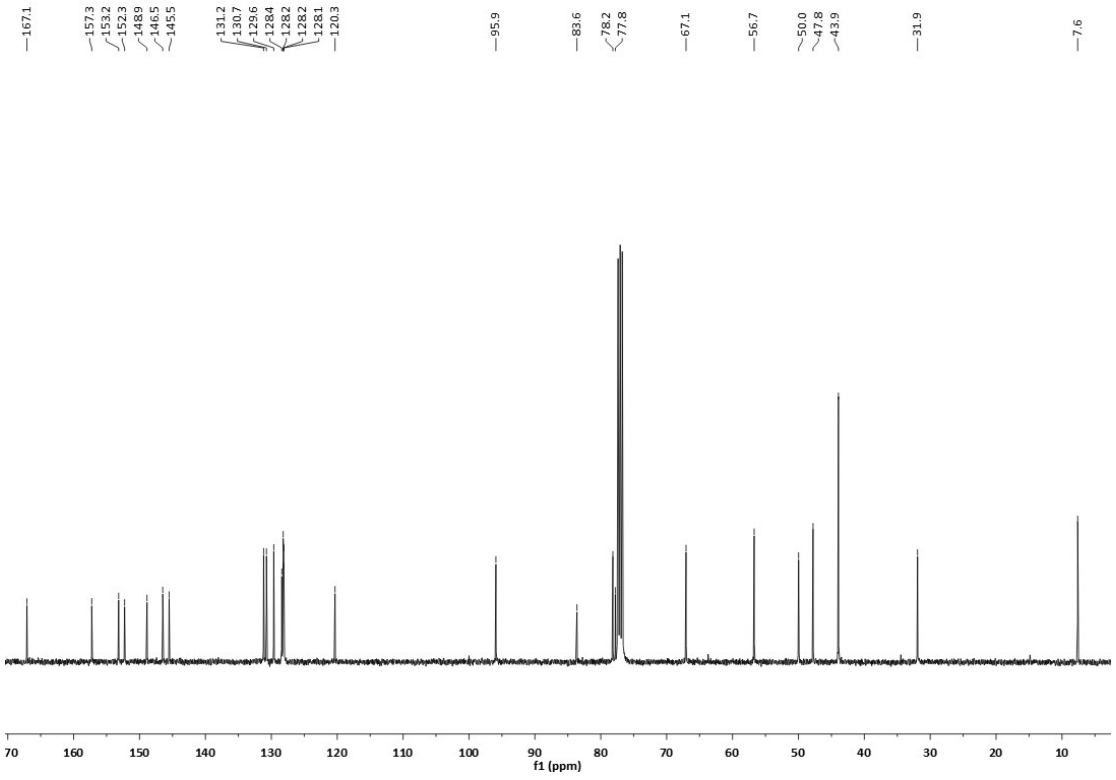
Compd	IC_{50}(μmol L^{-1})	
	HL-60	HCT-116
5a	0.06	0.60
5b	0.14	0.94
5c	1.92	0.21
5d	0.22	1.29
5e	0.33	2.58
5f	0.31	2.26
5g	0.42	1.01
5h	0.08	0.62
5i	0.06	0.62
5j	0.15	0.59
5k	0.61	1.88
5l	0.10	0.83
5m	0.04	0.25
5n	2.61	1.11
5o	0.54	1.09
5p	0.62	2.99
5q	0.09	0.34
2	0.24	0.96
CPT	0.01	0.07

^{1}H and ^{13}C NMR spectra of compound **2**:

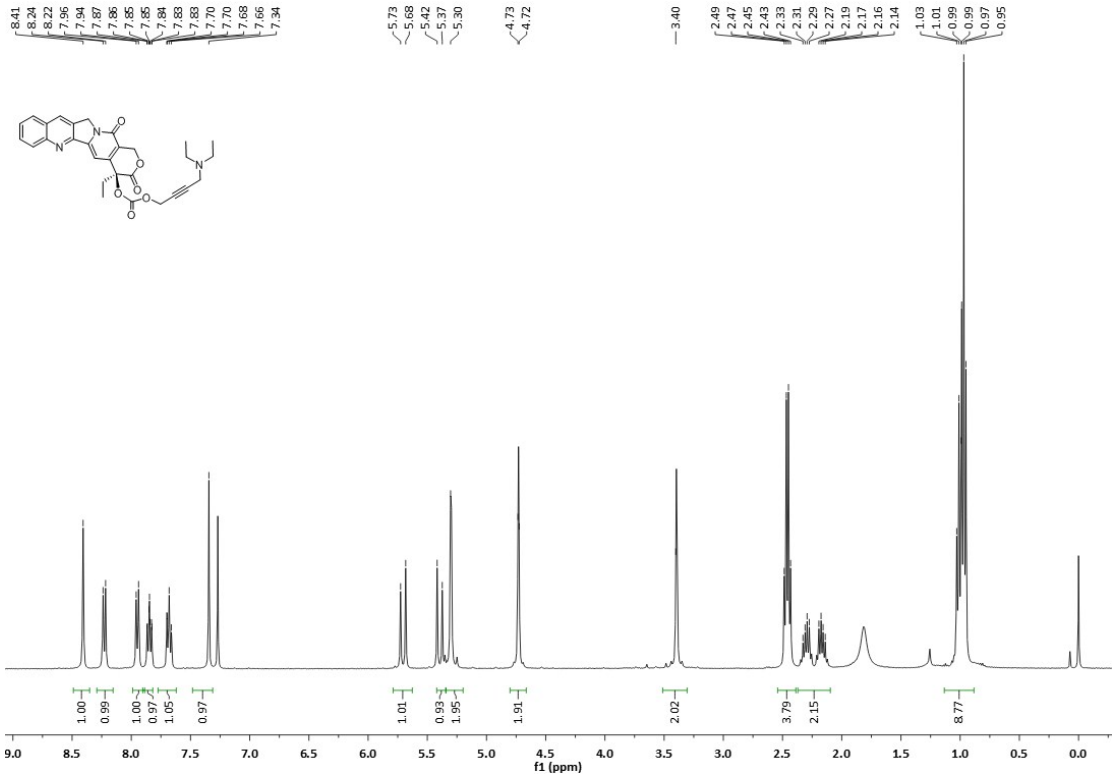


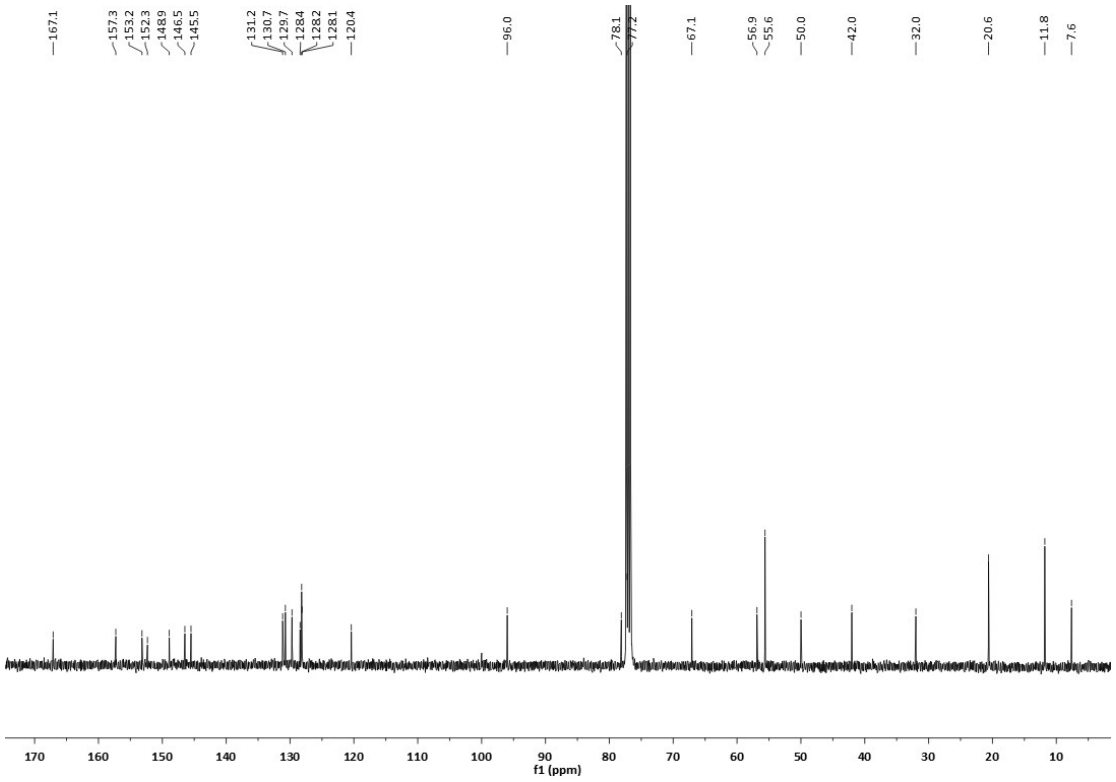
^{1}H and ^{13}C NMR spectra of compound **5a**:



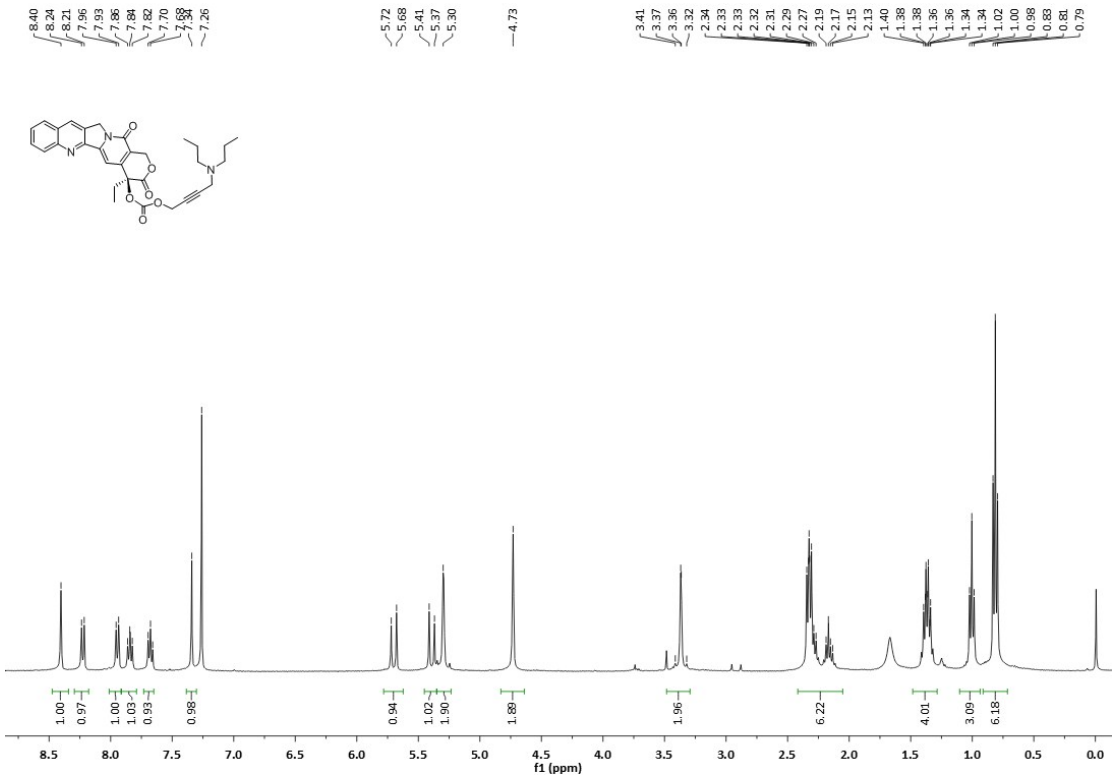


^{1}H and ^{13}C NMR spectra of compound **5b**:

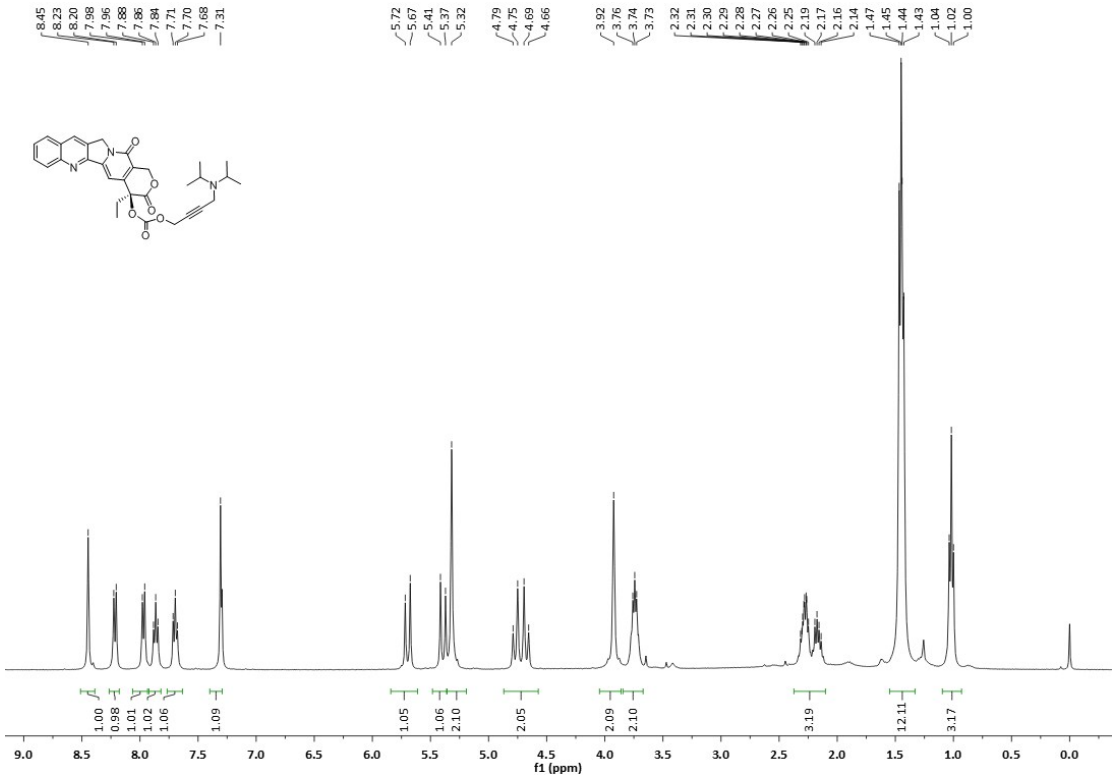


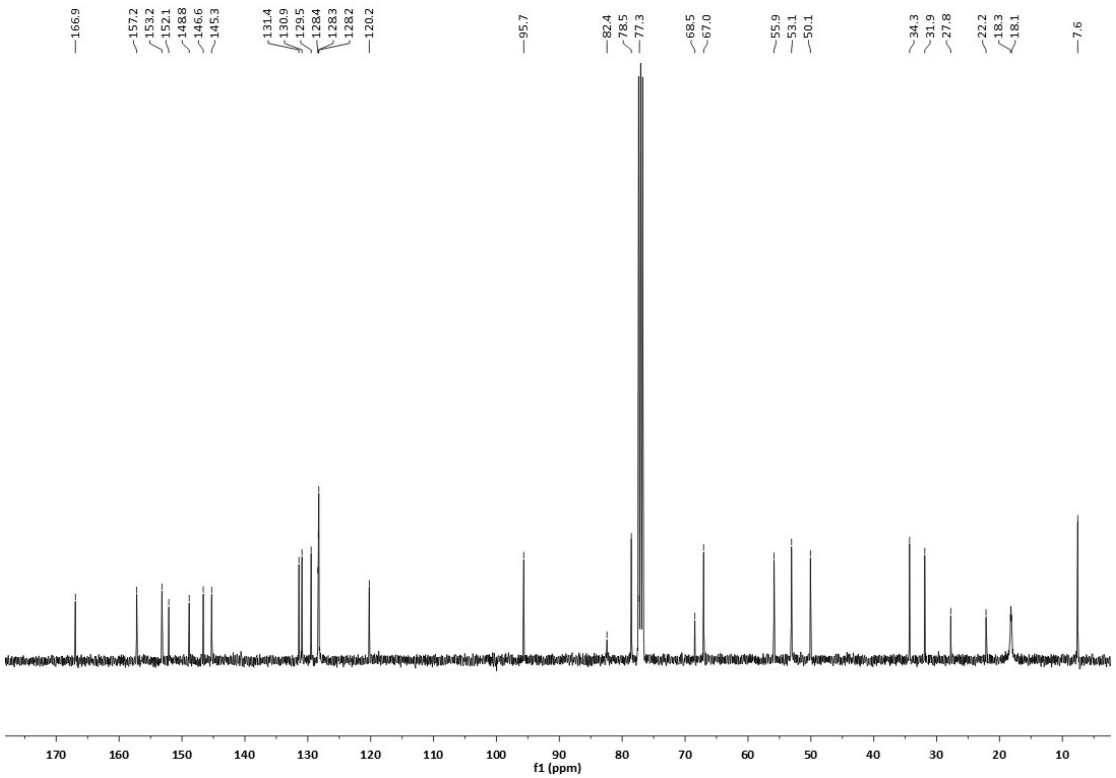


^{1}H and ^{13}C NMR spectra of compound **5c**:

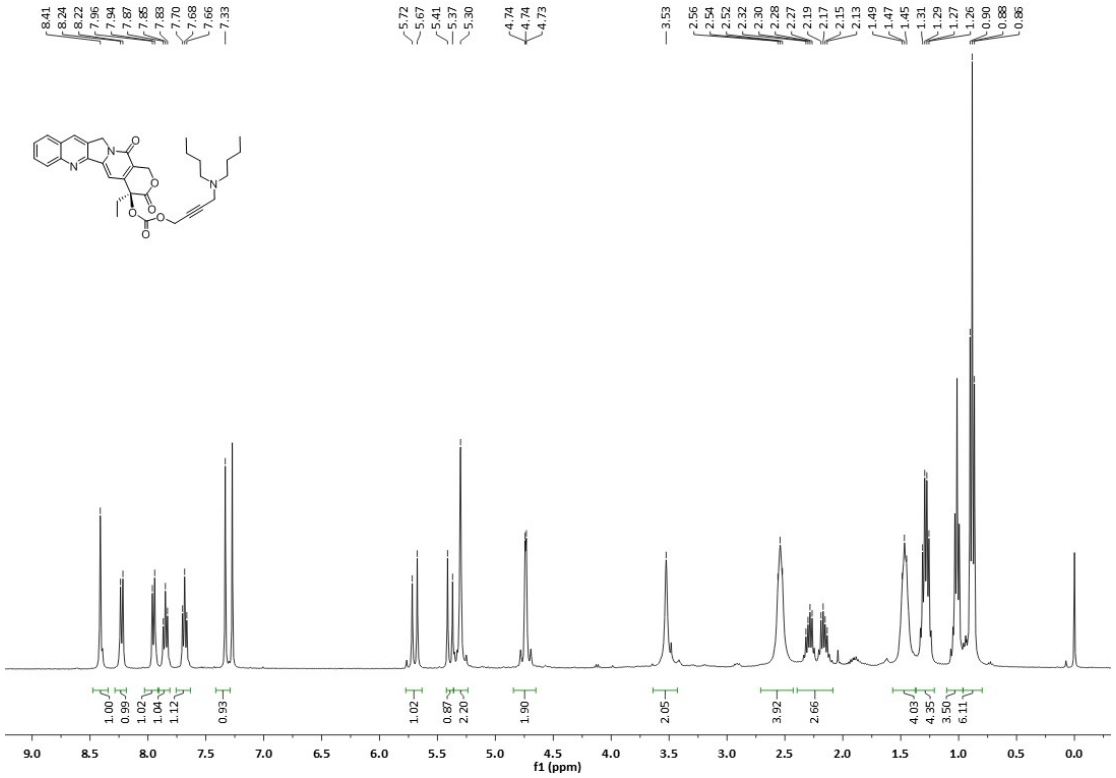


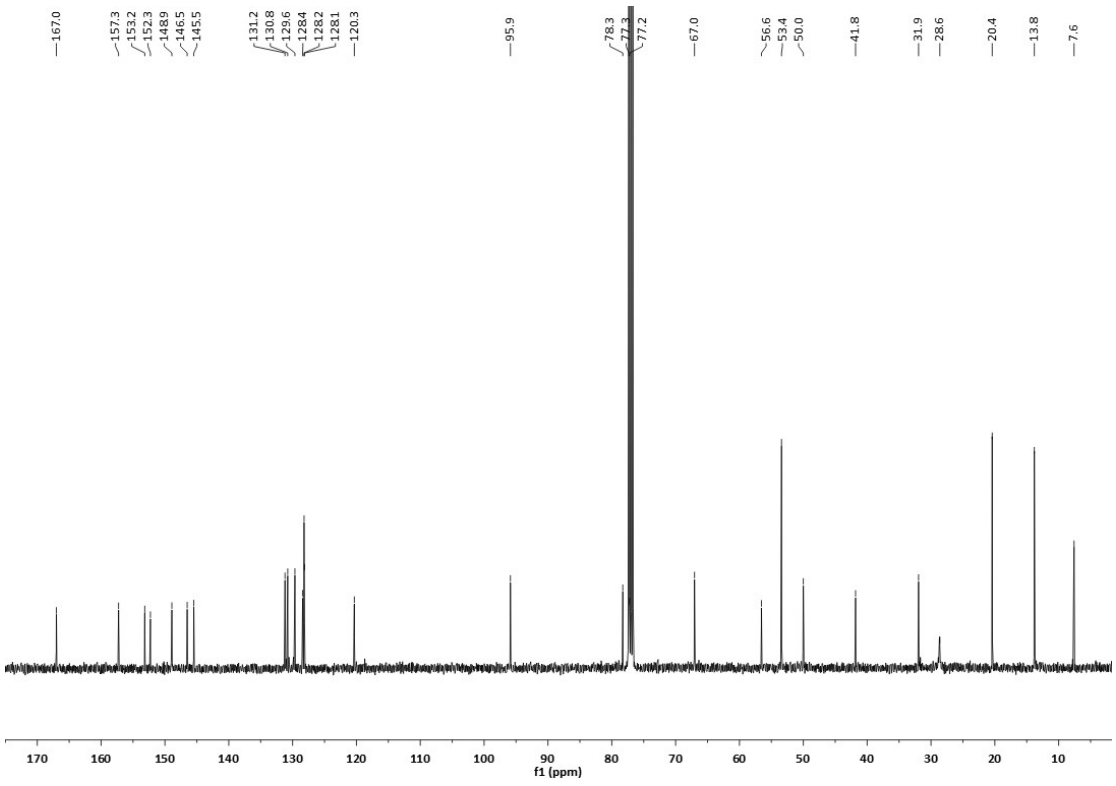
^{1}H and ^{13}C NMR spectra of compound **5d**:



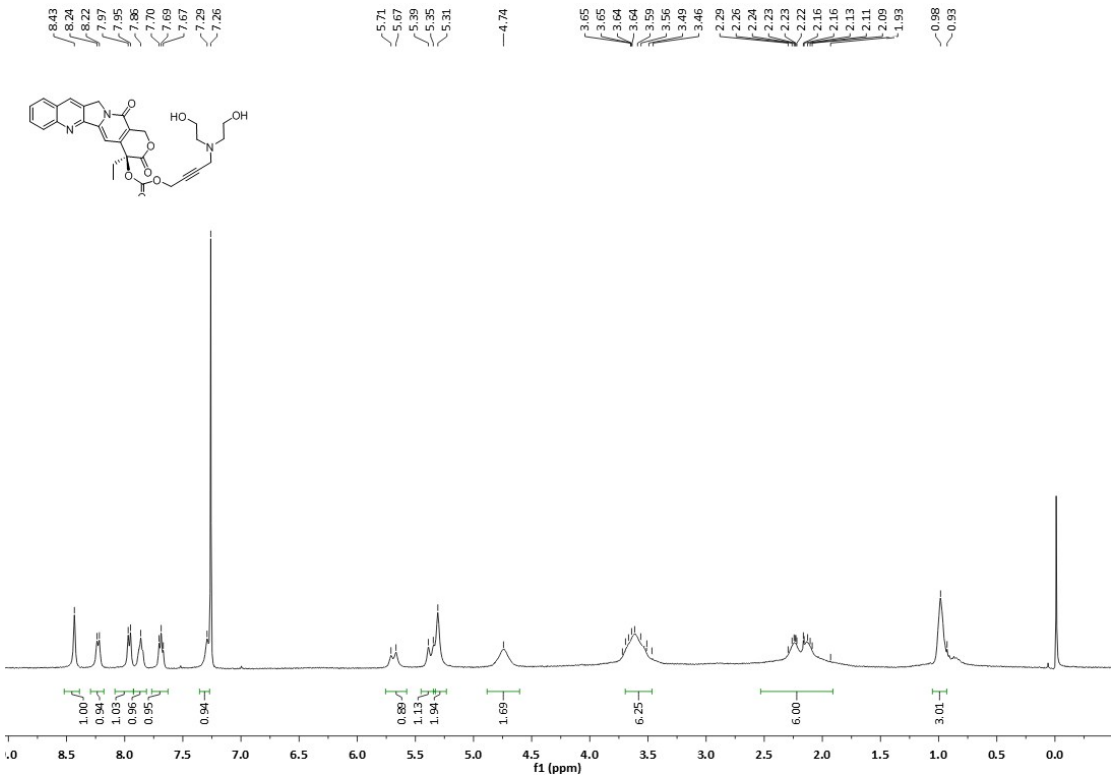


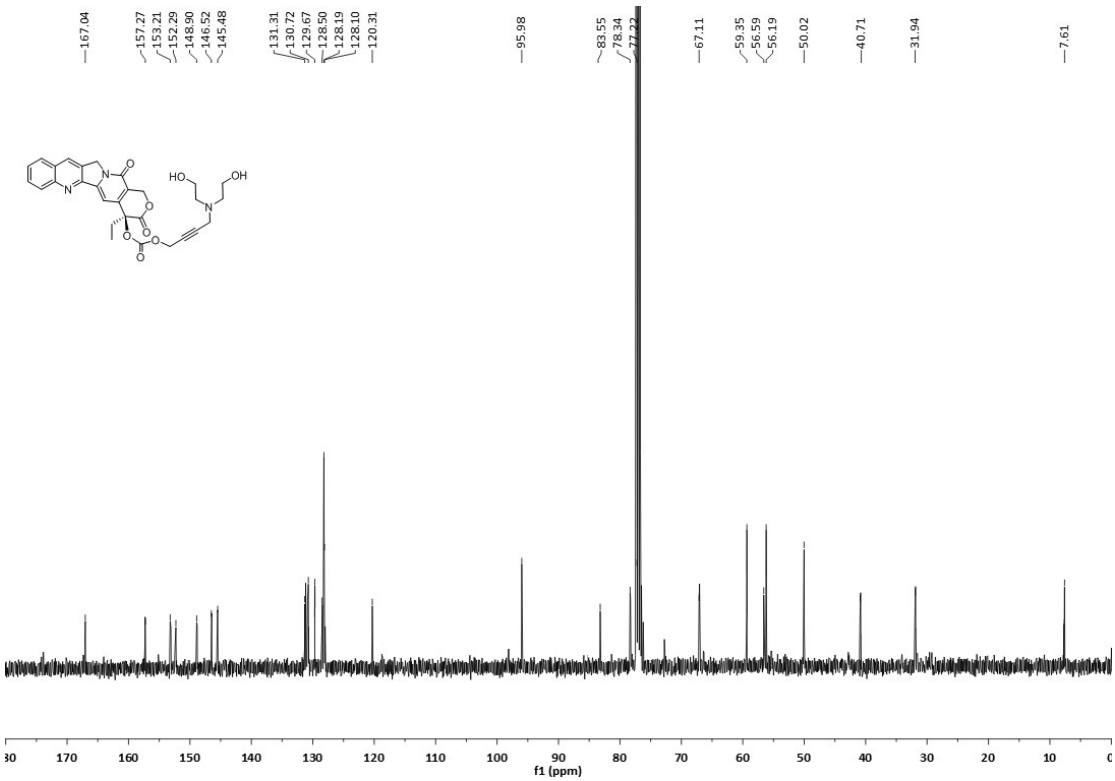
^{1}H and ^{13}C NMR spectra of compound **5e**:



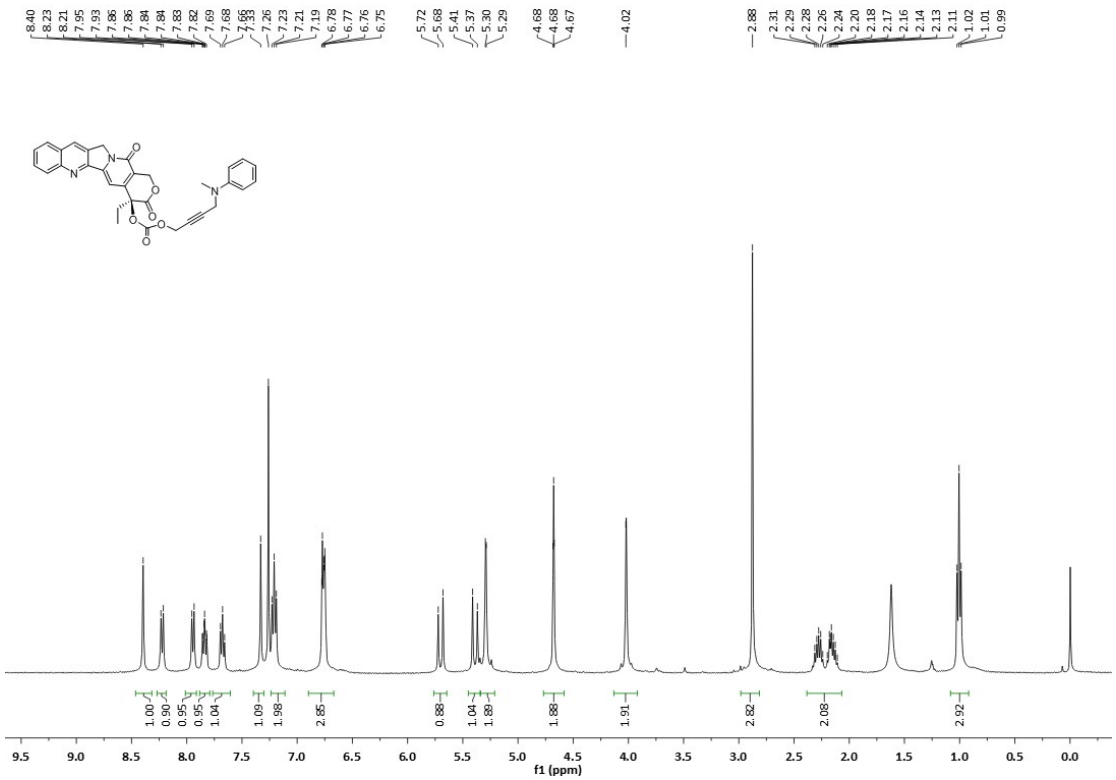


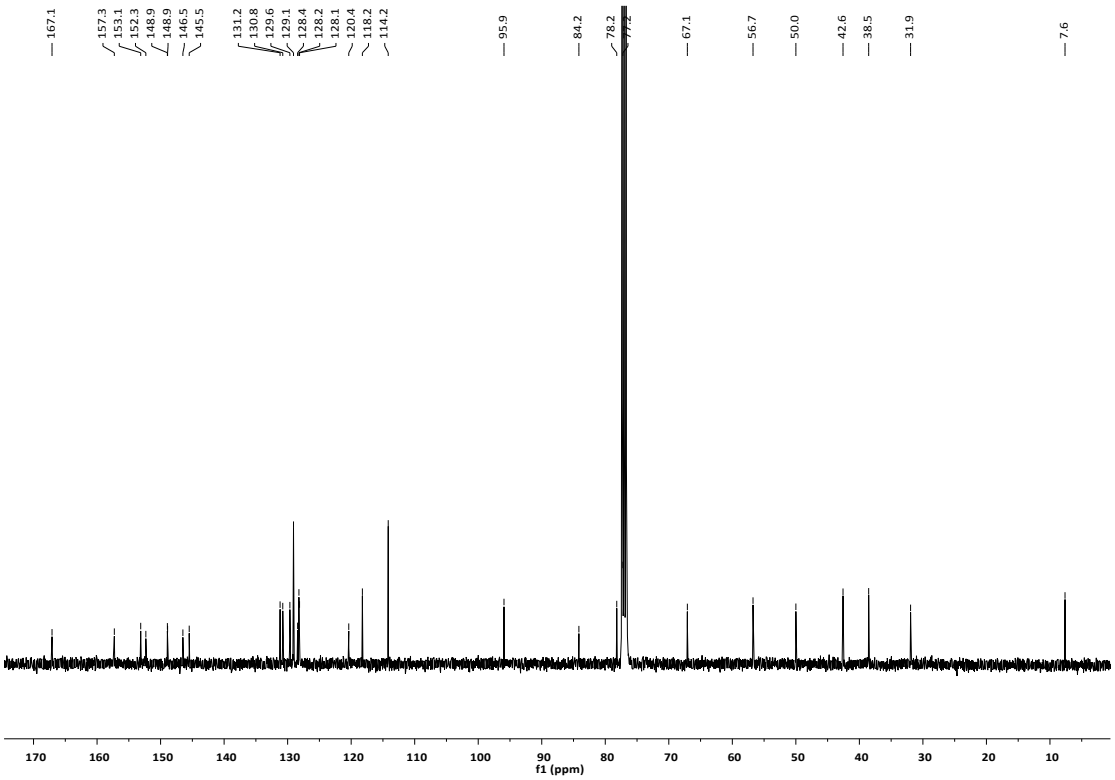
^{1}H and ^{13}C NMR spectra of compound **5f**:



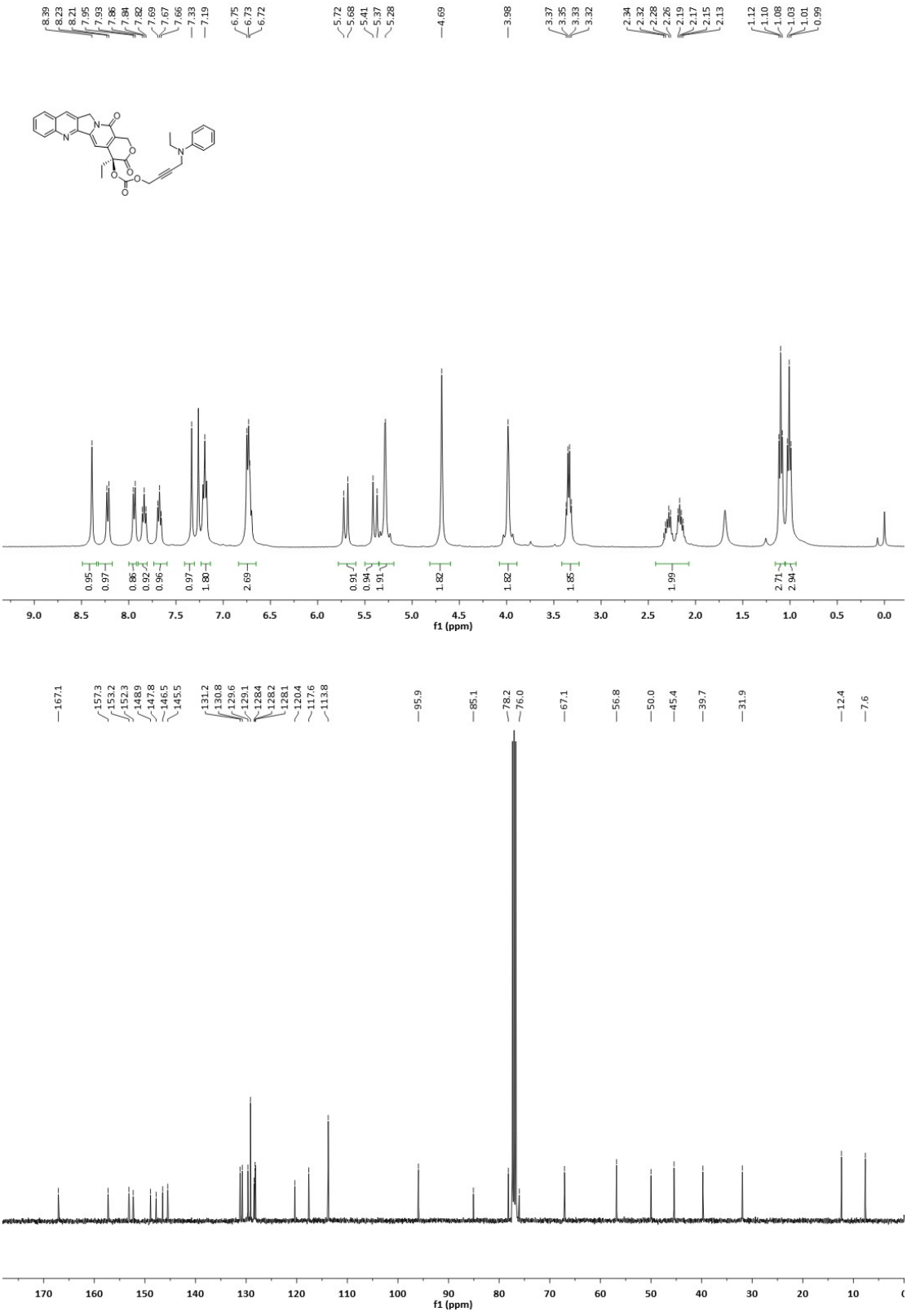


^{1}H and ^{13}C NMR spectra of compound **5g**:

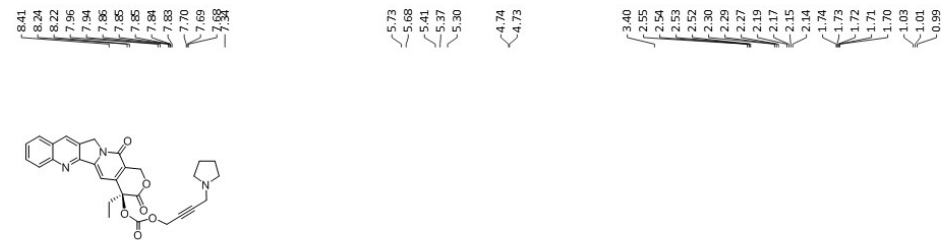


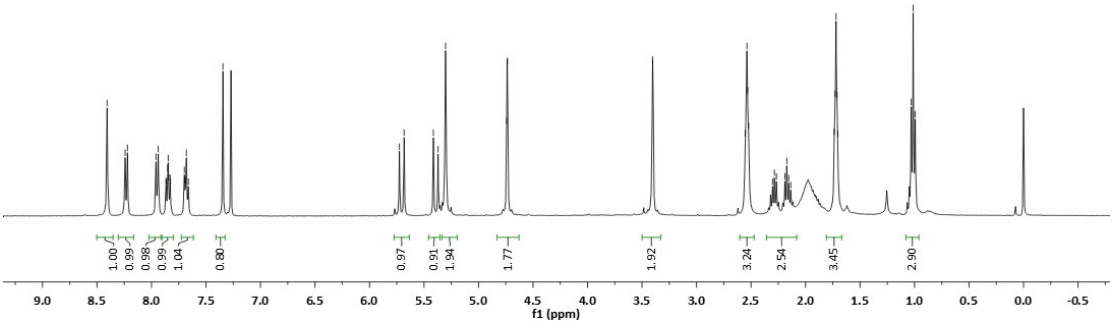


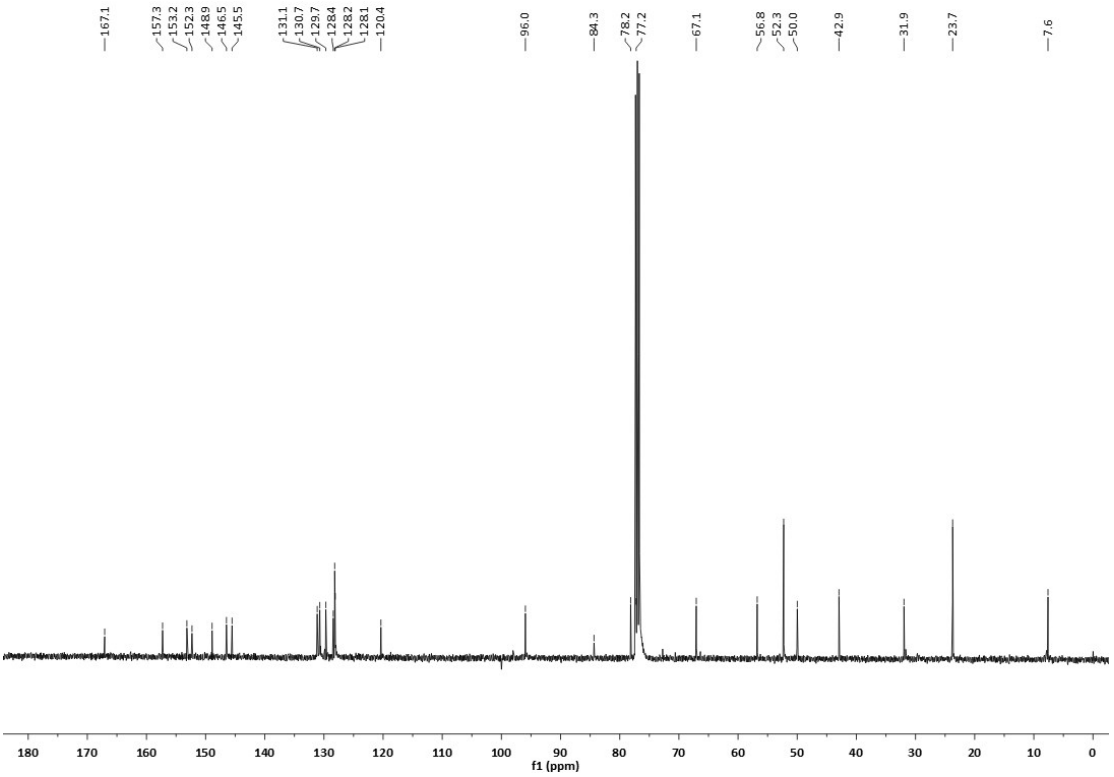
^{1}H and ^{13}C NMR spectra of compound **5h**:



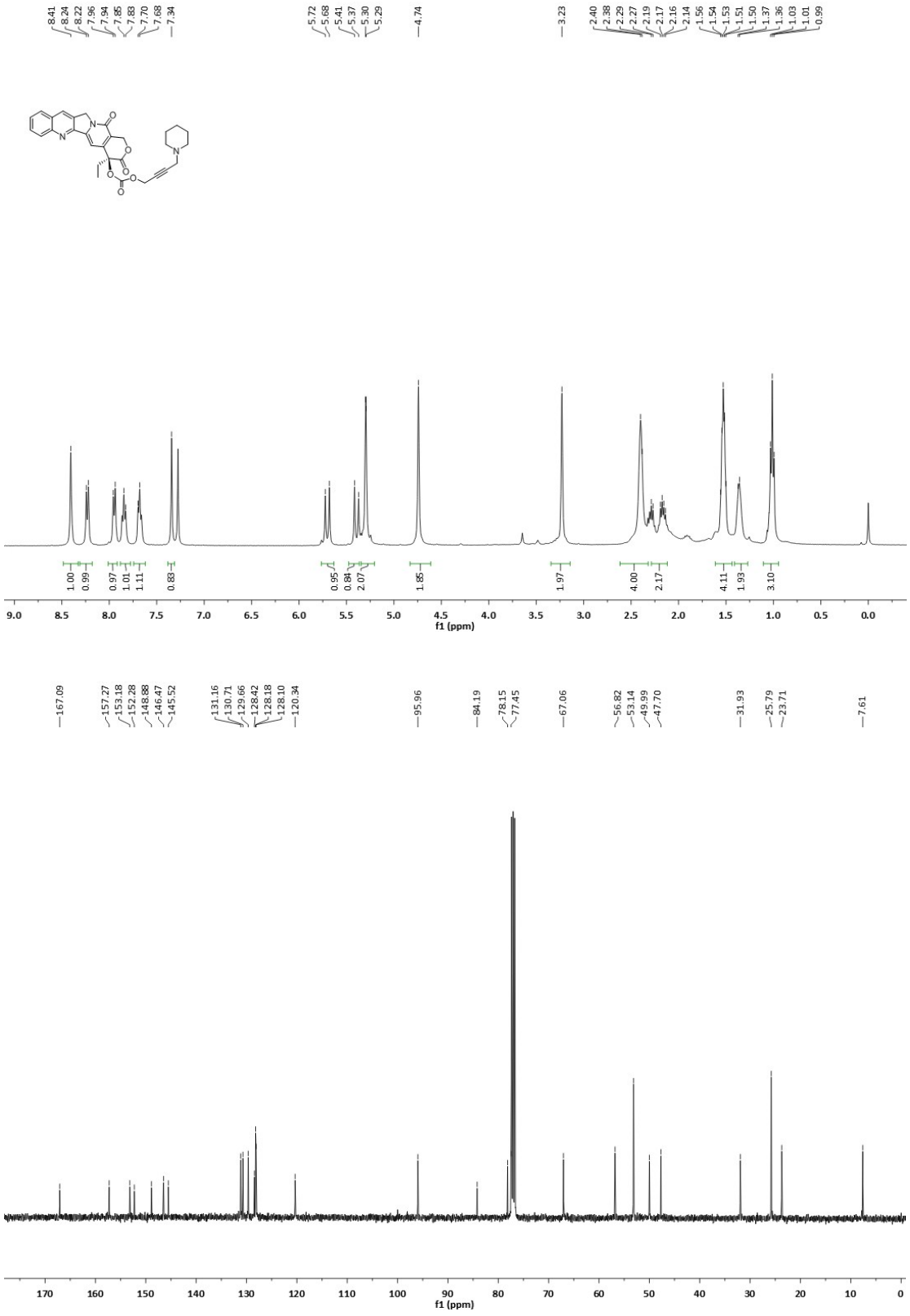
^{1}H and ^{13}C NMR spectra of compound **5i**:



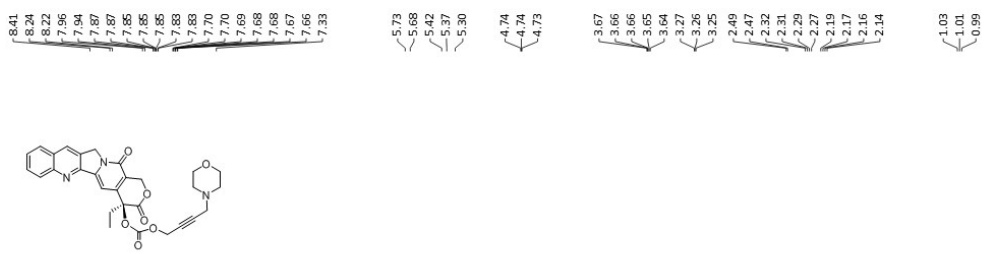


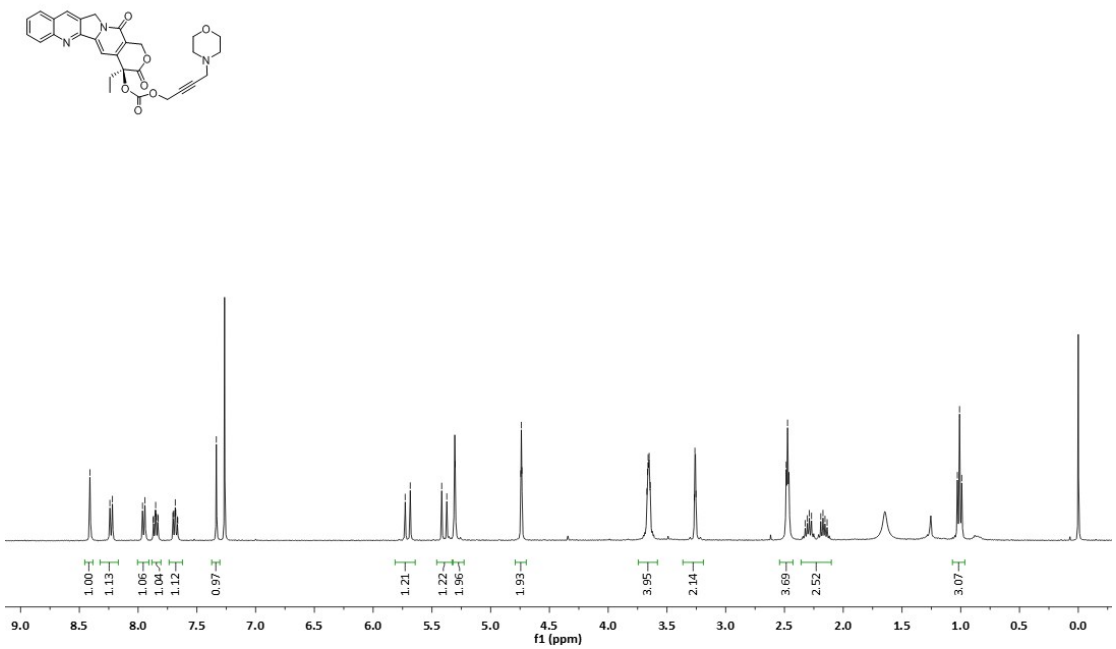


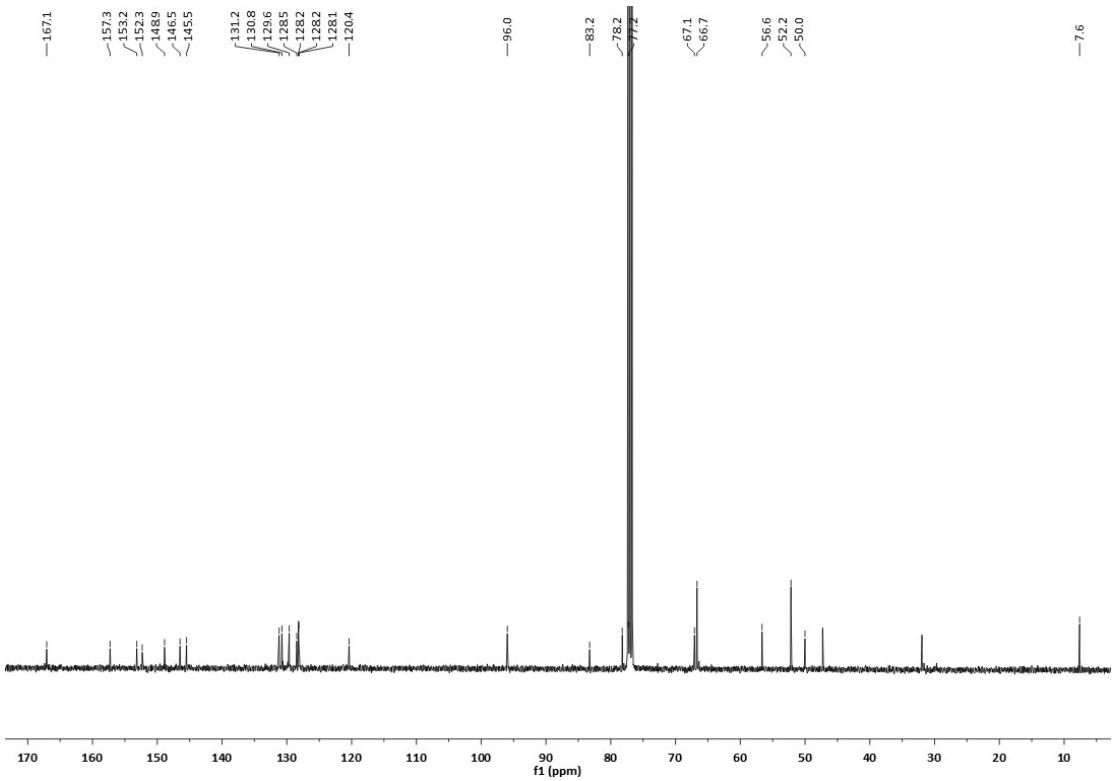
^{1}H and ^{13}C NMR spectra of compound **5j**:



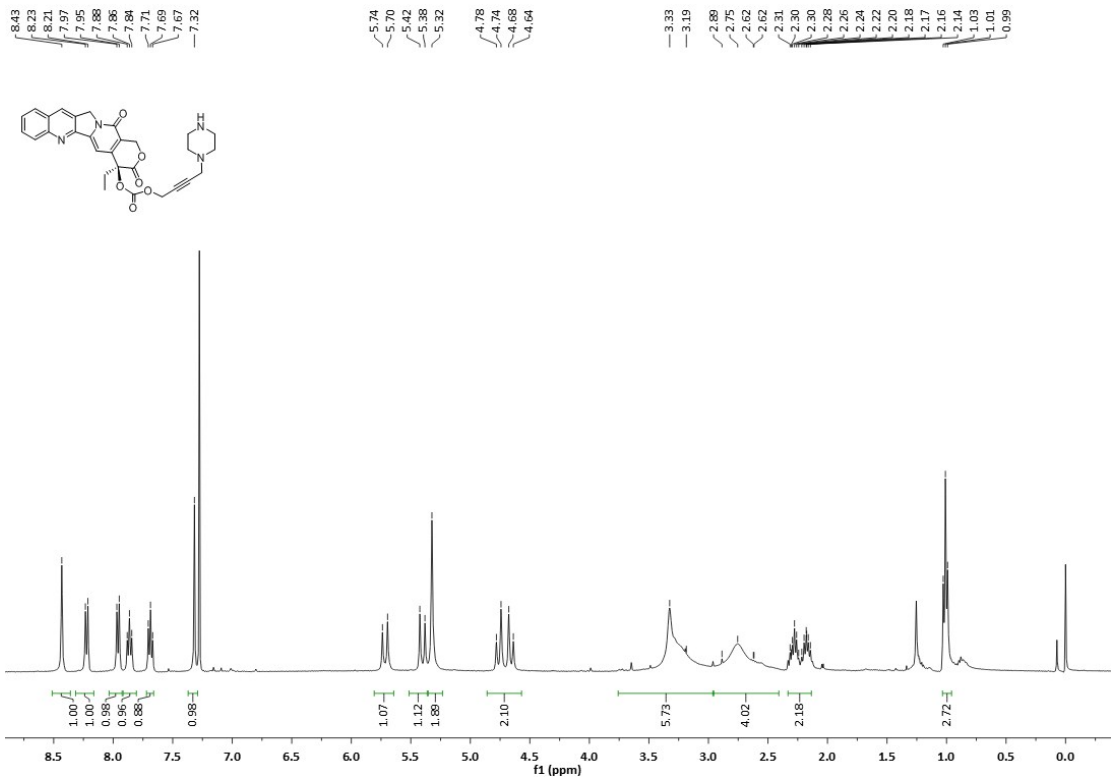
^{1}H and ^{13}C NMR spectra of compound **5k**:

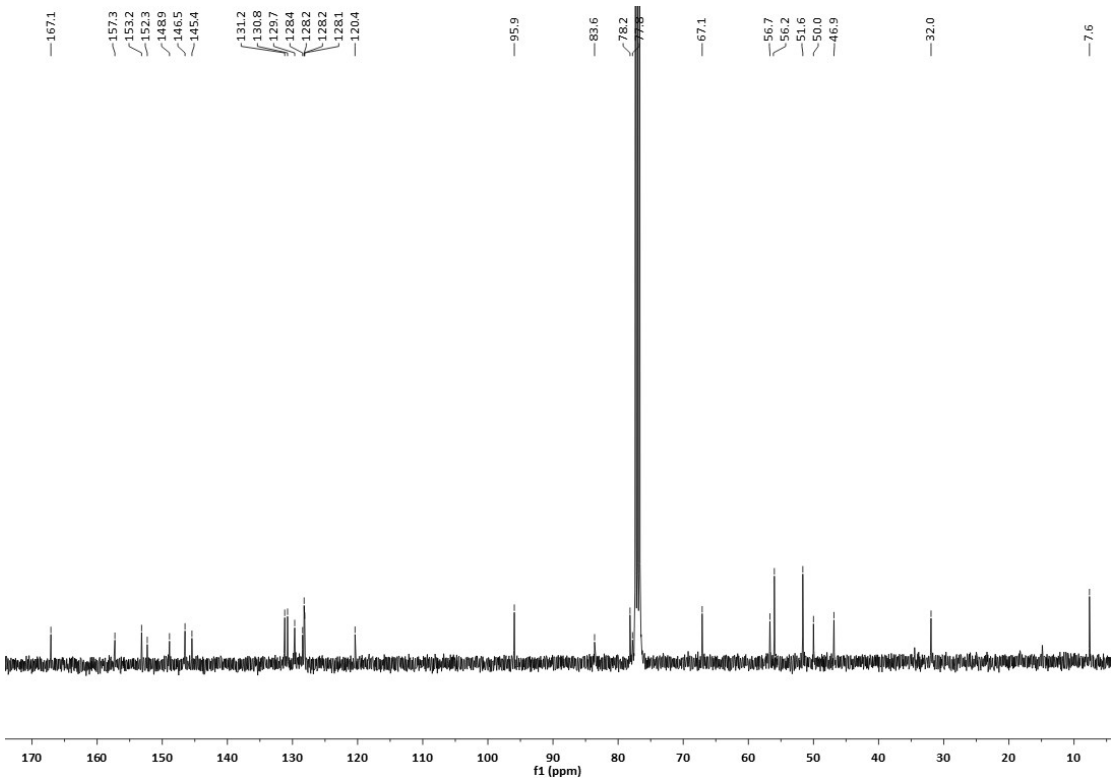




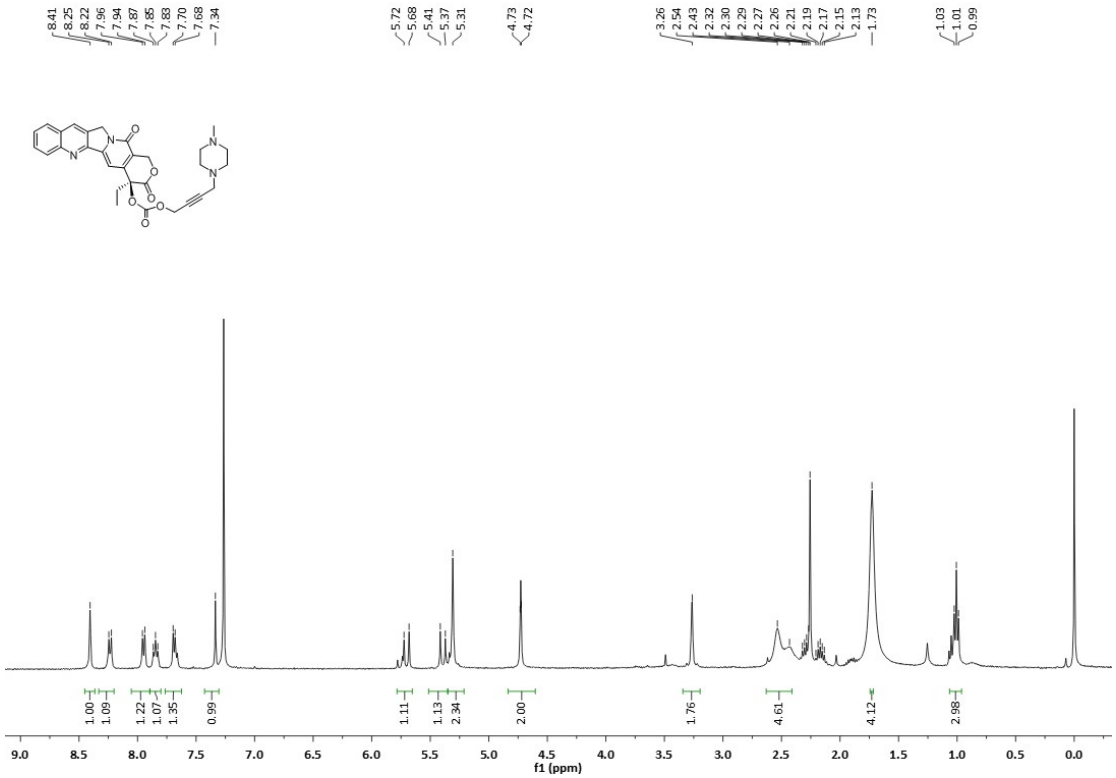


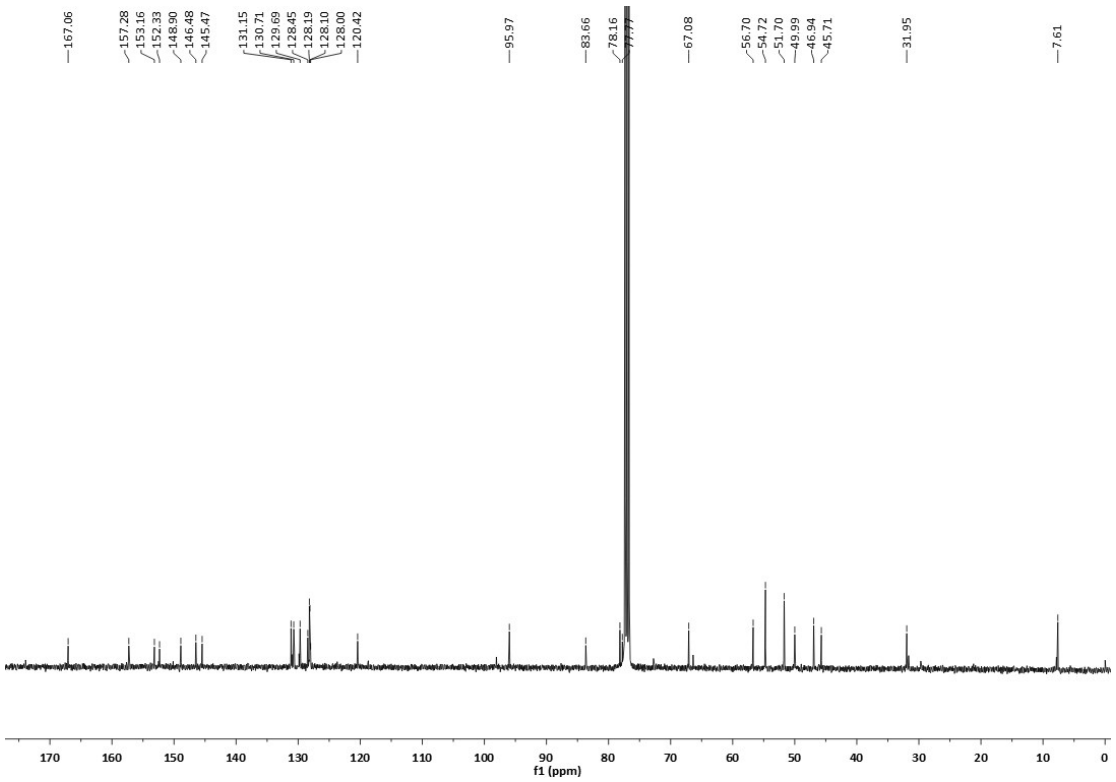
^{1}H and ^{13}C NMR spectra of compound **5l**:



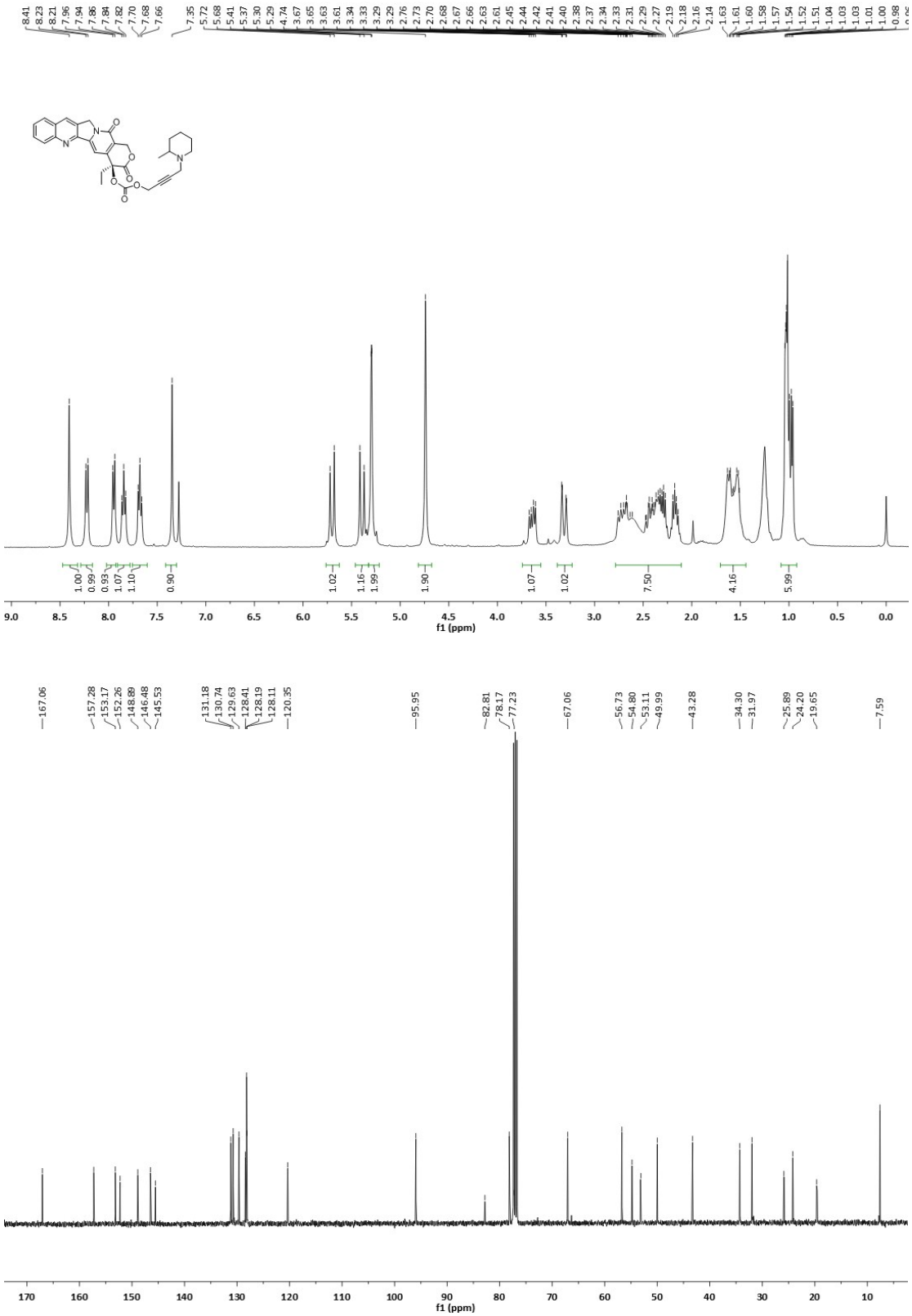


^{1}H and ^{13}C NMR spectra of compound **5m**:

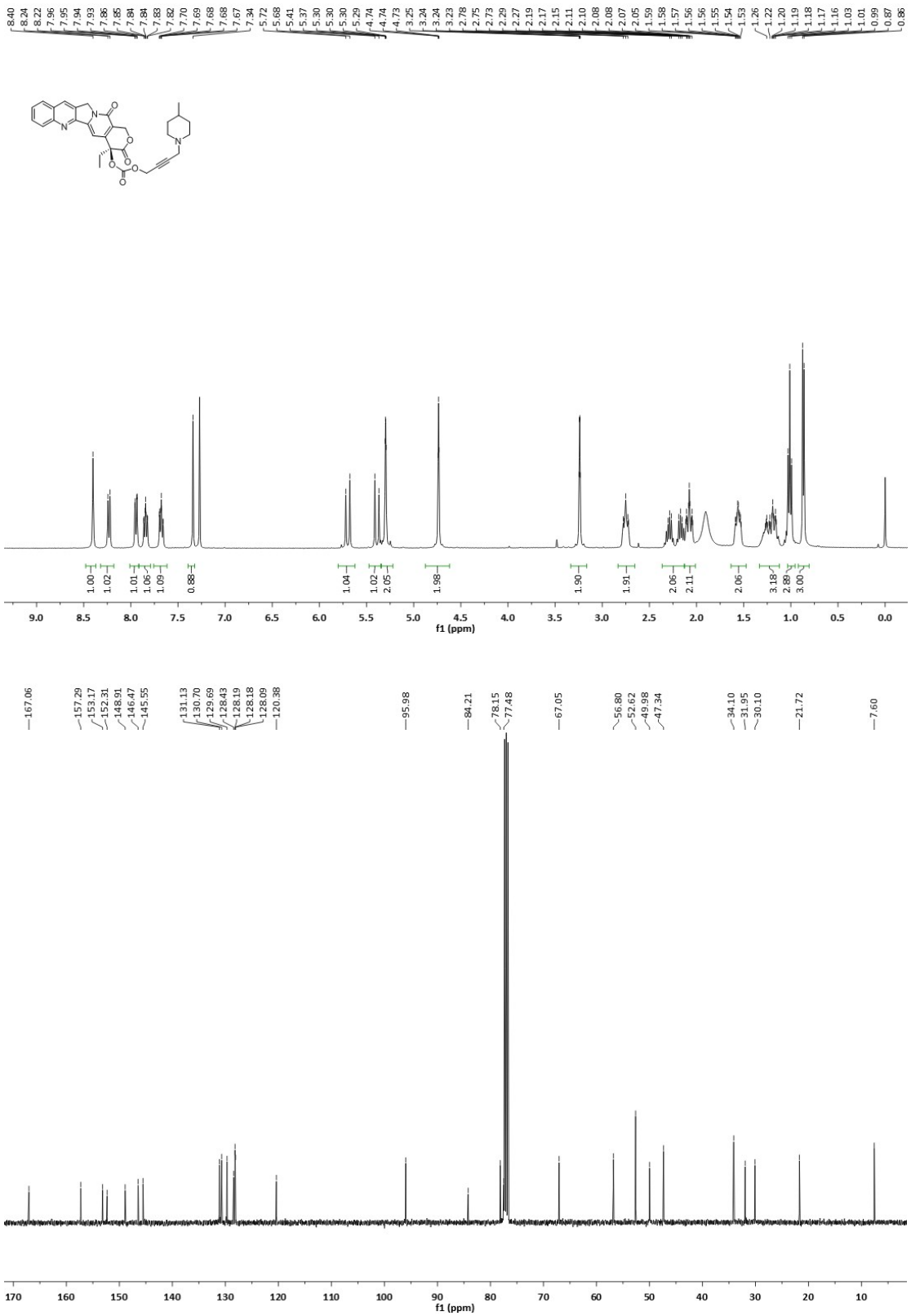




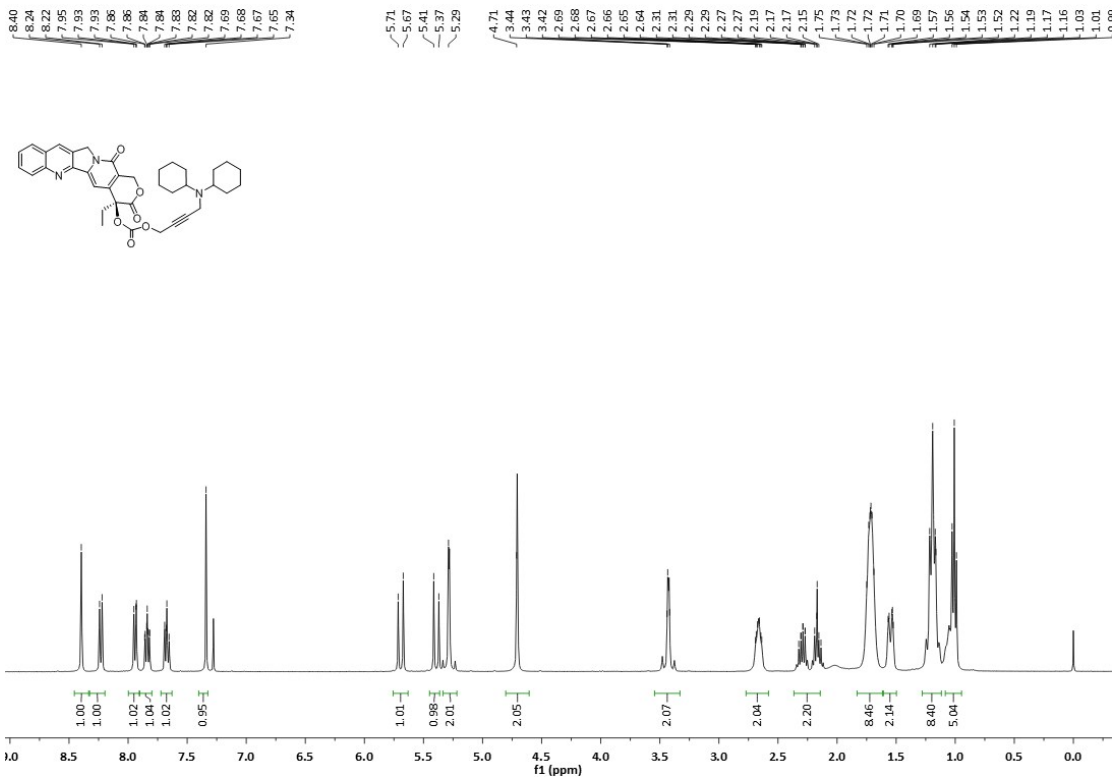
^{1}H and ^{13}C NMR spectra of compound **5n**:

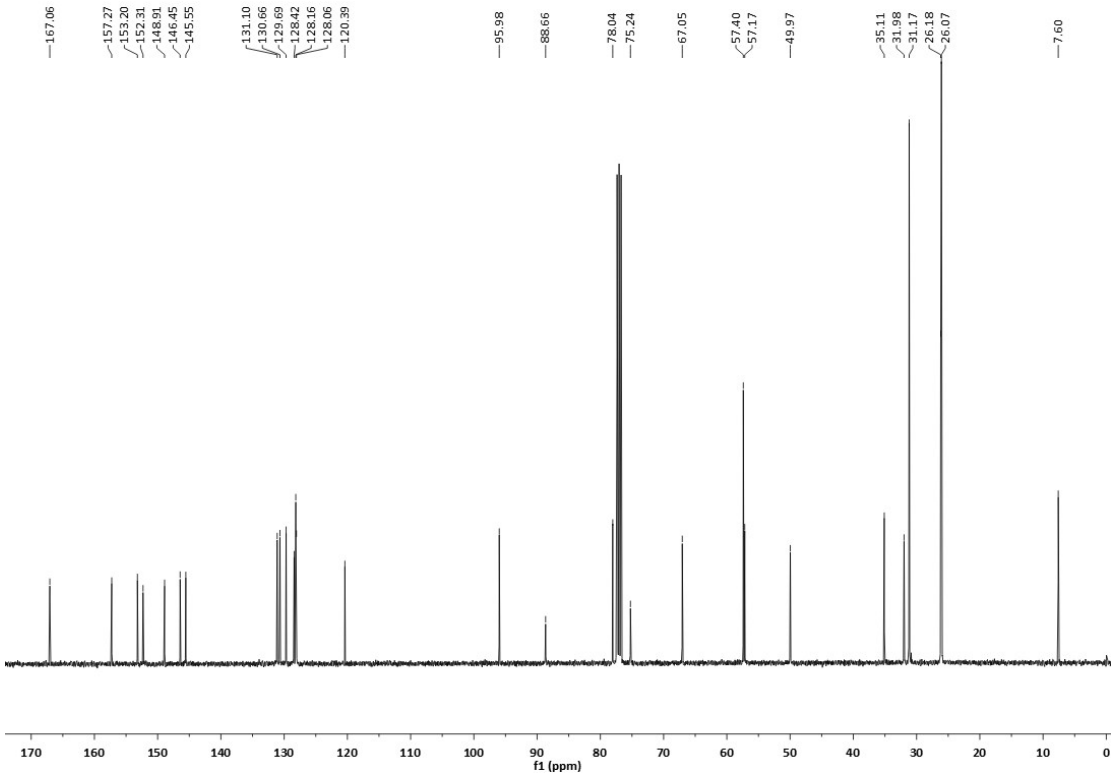


^{1}H and ^{13}C NMR spectra of compound **5o**:



^{1}H and ^{13}C NMR spectra of compound **5p**:





^{1}H and ^{13}C NMR spectra of compound **5q**: