Supplementary information and chemical compound information 1

Convenient and efficient synthesis of disubstituted piperazine derivatives by catalyst-free, atom-economical and tricomponent domino reactions

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Experimental Section

General information:

All reactions involving air- and moisture-sensitive reagent were carried out under an argon atmosphere. All chemicals were purchased from Aldrich and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254nm). Silica gel 60 (230~400 mesh) was used for column chromatography. IR spectra were recorded with an FT-IR spectrometer as KBr plates or as thin films and peaks are reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker INOVA-400 and a Bruker AVANCE III 400 NMR spectra instrument was recorded on (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 ppm for ^{1}H or to chloroform δ = 77.0 ppm for ^{13}C as internal standard. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in Hz. Mass spectrum were recorded on a Esquire 6000 spectrometer (EI at 70eV), melting points (m.p.) were measured on an XT4-100x microscopic melting point apparatus and are uncorrected, high resolution mass spectrometry were measured with MICRO-TOF QII (ESI).

Typical procedure for the reactions

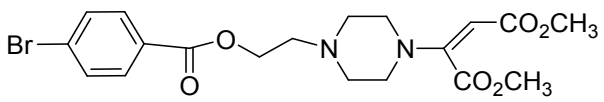
The mixture of THF (6.16 mol, 500 ml) and $LiAlH_4$ (0.08 mol, 3 g) was stirred and refluxed for two hours and steamed out as solvent of the reaction.

Place mixture of DABCO•$6H_2O$ (0.46 mol, 100 g) and benzene (120 ml) in a 250 ml flask fitted oil-water separator and a water-cooled reflux condenser was stirred and refluxed until water has not be steamed out, maintain the temperature at this level with continuous stirring for 1 hour. After solvent benzene was steamed, the residual material was cooled to room temperature. The residual material was re-crystallised by anhydrous Et_2O to obtain the reagent.

Dimethyl acetylene dicarboxylate (DMAD) was re-steamed under a small amount (20~30mg) of zinc powder and reduced pressure. The method was yet suitable for re-distillationof furfural, etc.

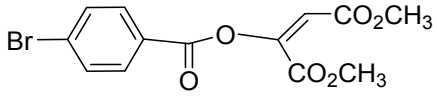
To a clear solution of the armotic acid (1 mmol, 1.00 equiv.) in anhydrous THF (2~8 ml) was added the DABCO (1 mmol, 1.00 equiv.) under stirring at room temperature. After the reaction mixture was stirred for 0.5 hours, the solution was changed from clear to paste. Then, DMAD (1.1mmol, 1.10 equiv.) was dropwise added to paste the mixture and the color of the paste mixture was gradually changed to dark and into solution. The reaction mixture was stirred for 8 hours at room temperature. The solvent was removed under reduced pressure. The given residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to afford product.

1-[2-(4-Bromobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 1a



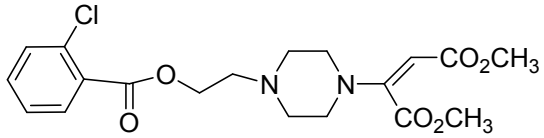
Yied: 86%; light brown sticky clumps, ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.890-7.868(d, *J* = 8.8Hz, 2H), 7.595-7.573(d, *J* = 8.8Hz, 2H), 4.775(s, 1H), 4.457-4.428(t, *J* = 5.6Hz, 2H), 3.918(s, 3H), 3.635(s, 3H), 3.190-3.166(t, *J* = 4.8Hz, 4H), 2.806-2.778(t, *J* = 5.6Hz, 2H), 2.631-2.607(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 168.0, 166.0, 165.6, 154.4, 131.7, 131.1, 128.9, 128.1, 86.4, 62.3, 56.4, 53.0, 52.2, 50.9, 47.1; IR (KBr, cm^{-1}): 3057(w, =C-H), 2947, 2850(w, C-H), 1741, 1721, 1695(s, C=O), 1587(s), 1443 (m, Ar), 1370(w, CH_3), 1273 (m, C-O), 1158, 1113 (m, C-N), 855, 752 (s, Ar); MS m/z(%): 454(2.5) ($M^{+\cdot}$), 456(2.2)(M+2), 425(4.20), 368(10.90), 282(5.74), 254(6.24), 242(12.03), 241(100), 227(17.7), 209(13.3), 185(20.03), 142(20.03), 140(7.8), 82(7), 56(6), 44(9). **HRMS** (ESI) calcd for $C_{19}H_{24}BrN_2O_6$ $[M+H]^+$ 455.0818, found 455.0821.

(*E*)-1-(4-Bromobenzencarbonyloxy)- 1,2-di(methoxycarbonyl)ethene 1b



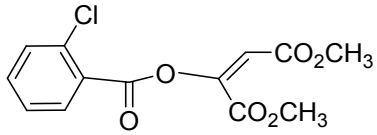
Yied: 11%; white flake, mp: 76-77°C, ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.020-7.998(d, *J* = 8.8Hz, 2H), 7.661-7.640(d, *J* = 8.4Hz, 2H), 6.795(s, 1H), 3.864(s, 1H), 3.720(s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.3, 163.2, 161.7, 146.9, 132.2, 132.1, 129.6, 127.2, 117.5, 53.5, 52.4; IR (KBr, cm^{-1}): 3093 (w, =C-H), 2955(w, C-H), 1738, 1663(s, C=O), 1590 (m, Ar), 1436(w, CH_3), 1278 (m, C-O), 1102, 1068(m, C-N), 845, 767 (s, Ar); MS m/z(%): 342(2)($M^{+\cdot}$), 186(6), 183(100), 157(21), 155(25),76(11), 44(27). **HRMS** (ESI) calcd for $C_{13}H_{12}BrO_6$ $[M+H]^+$ 342.9817, found 342.9818.

1-[2-(2-Chlorobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 2a



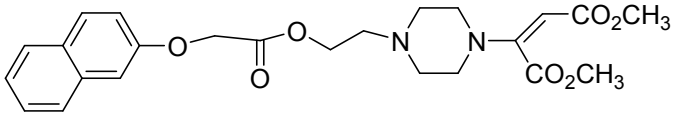
Yied: 86%; light yellow sticky clumps, ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.806-7.784(m, 1H), 7.464-7.406(m, 2H), 7.346-7.505(m, 1H), 4.774(s, 1H), 4.478-4.450(t, *J* = 5.6Hz, 2H), 3.913(s, 3H), 3.630(s, 3H), 3.189-3.164(t, *J* = 4.8Hz, 4H), 2.801-2.772(t, *J* = 5.6Hz, 2H), 2.628-2.603(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 168.0, 166.0, 165.5, 154.5, 133.4, 132.6, 131.2, 131.0, 130.1, 126.6, 86.3, 62.3, 56.3, 52.9, 52.1, 50.9, 47.0; IR (KBr, cm^{-1}): 3061(w, =C-H), 2951, 2844(w, C-H), 1741, 1697 (s, C=O), 1588(s), 1438 (m, Ar), 1370(w, CH_3), 1250 (m, C-O), 1158, 1120 (m, C-N), 869, 751 (s, Ar); MS m/z(%): 410(5) ($M^{+\cdot}$), 412(1)(M+2), 379(7), 351(4), 326(8), 324(26), 254(6), 242(12), 241(100), 238(21), 226(18), 209(15), 185(15), 183(24), 141(13), 139(37), 111(6), 82(7), 56(6), 44(9). **HRMS** (ESI) calcd for $C_{19}H_{24}ClN_2O_6$ $[M+H]^+$ 411.1323, found 411.1327.

(*E*)-1-(2-Chlorobenzencarbonyloxy)- 1,2-di(methoxycarbonyl)ethene 2b



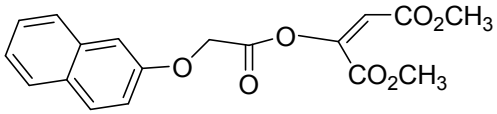
Yied: 9%; white flake, mp: 49-50°C, ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.159-8.140(d, *J* = 7.6Hz, 1H), 7.534-7.502(m, *J* = 6.8Hz, *J* = 7.6Hz, 2H), 7.412-7.371(m, *J* = 4.0Hz, *J* = 8.0Hz, 1H), 6.810(s, 1H), 3.880(s, 3H), 3.754(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.2, 161.9, 161.6, 146.6, 135.1, 133.9, 132.7, 131.5, 127.5, 126.9, 117.6, 53.5, 52.4; IR (KBr, cm^{-1}): 3088 (w, =C-H), 2955, 2925(w, C-H), 1737(s, C=O), 1663 (s), 1591 (m, Ar), 1437(w, CH_3), 1278, 1203 (m, C-O), 1105, 1032(m, C-N), 773, 745 (s, Ar); MS m/z(%): 298(0.2)($M^{+\cdot}$), 259(5), 141(33), 139(100), 113(3), 111(10), 75(6), 44(13). **HRMS** (ESI) calcd for $C_{13}H_{12}ClO_6$ $[M+H]^+$ 299.0322, found 299.0326.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-{2-[2-(naphthalen-2-yloxy)acetoyloxy]eth-1-yl}piperazine 3a



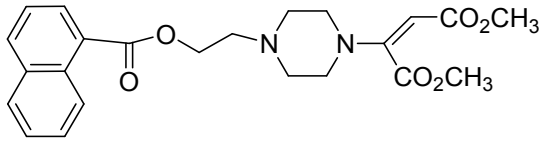
Yied: 72%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.793-7.765(dd, *J* = 8.8Hz, *J* = 2.4Hz, 2H), 7.714-7.693(d, *J* = 8.4Hz, 1H), 7.473-7.436(t, *J* = 7.6Hz, 1H), 7.389-7.352(t, *J* = 7.6Hz, 1H), 7.233-7.205(dd, *J* = 8.8Hz, *J* = 2.4Hz, 1H), 7.072-7.066(d, *J* = 2.4Hz, 1H) 4.776 (s, 2H), 4.682(s, 1H), 4.351-4.324(t, *J* = 5.6Hz, 2H), 3.906(s, 3H), 3.650(s, 3H), 3.017-2.992(t, *J* = 5.2Hz, 4H), 2.659-2.632(t, *J* = 5.2Hz, 2H), 2.458-2.433(t, *J* = 5.2Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 169.1, 168.2, 166.2, 155.8, 154.5, 134.3, 130.0, 129.6, 127.9, 127.0, 126.9, 124.4, 118.7, 107.1, 86.8, 65.5, 62.5, 56.4, 53.2, 52.3, 51.2, 47.0; IR (KBr, cm^{-1}): 3057(w, =C-H), 2924, 2853(w, C-H), 1741, 1687(s, C=O), 1590(s), 1443 (m, Ar), 1370(w, CH_3), 1268 (m, C-O), 1157, 1120 (m, C-N), 842, 795 (s, Ar); MS m/z(%): 456(6.85) ($M^{+\cdot}$), 425(2.08), 370(5.89), 284(6.46), 272(9.08), 242(13.79), 241 (100.00), 229(7.95), 209(16.64), 202(61.70), 201(40.67), 181(22.62), 157(16.28), 149(37.46), 144(76.73), 115(38.99) 100(11.44), 45(10.10), 44(42.29). **HRMS** (ESI) calcd for $C_{24}H_{29}N_2O_7$ $[M+H]^+$ 457.1975, found 457.1979.

(*E*)-1,2-Di(methoxycarbonyl)-1-(2-(naphthalen-2-yloxy)acetoyloxy)ethene 3b



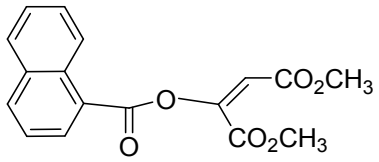
Yied: 16%; white flake, mp: 67-68°C, ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.782-7.752(m, *J* = 3.6Hz, *J* = 8.0Hz, 3H), 7.457-7.417(m, 1H), 7.368-7.328(m, *J* = 1.2Hz, *J* = 8.0Hz, 1H), 7.275-7.236(m, 2H), 6.767(s, 1H), 5.043(s, 2H), 3.813(s, 3H), 3.757(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 166.2, 163.2, 161.3, 155.6, 146.2, 134.4, 129.8, 129.6, 127.8, 127.2, 126.6, 124.3, 118.7, 117.9, 107.6, 64.9, 53.5, 52.4; IR (KBr, cm^{-1}): 3088 (w, =C-H), 2956(w, C-H), 1737(s, C=O), 1663(s), 1437(m, Ar), 1348(w, CH_3), 1277 (m, C-O), 1105, 1032(m, C-N), 871, 745 (s, Ar); MS m/z(%): 344(100)($M^{+\cdot}$), 285(1), 201(5), 185(14), 157(85), 143(9), 129(37), 127(68), 115(12), 101(7), 69(7), 45(15), 44(22). **HRMS** (ESI) calcd for $C_{18}H_{17}O_7$ $[M+H]^+$ 345.0974, found 345.0978.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(naphthalenoyloxyl)eth-1-yl]piperazine 4a



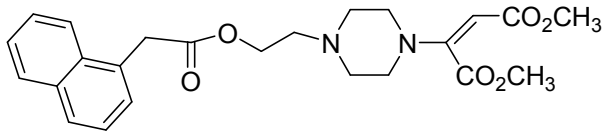
Yied: 82%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 8.913-8.892(d, *J* = 8.4Hz, 1H), 8.148-8.127(dd, *J* = 7.2Hz, *J* = 1.2Hz, 1H), 8.018-7.998(d, *J* = 8Hz, 1H), 7.881-7.861(d, *J* = 8Hz, 1H), 7.617-7.575(dt, *J* = 1.6Hz, *J* = 8.4Hz, 1H), 7.542-7.468(m, 2H), 4.770(s, 1H), 4.527-4.499(t, *J* = 5.6Hz, 2H), 3.911(s, 3H), 3.634(s, 3H), 3.181-3.156(t, *J* = 4.8Hz, 4H), 2.819-2.791(t, *J* = 5.6Hz, 2H), 2.623-2.598(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 168.0, 167.4, 166.1, 154.5, 133.8, 133.4, 131.2, 130.1, 128.6, 127.8, 127.2, 126.3, 125.7, 124.5, 86.4, 61.9, 56.5, 53.0, 52.2, 51.0, 47.1; IR (KBr, cm^{-1}): 3090(w, =C-H), 2950, 2904(w, C-H), 1743, 1700 (s, C=O), 1582(s), 1438 (m, Ar), 1370(w, CH_3), 1278, 1244 (m, C-O), 1196, 1162(m, C-N), 868, 784 (s, Ar); MS m/z(%): 426(5) ($M^{+\cdot}$), 408(7), 395(6), 341(4), 340(24), 255(6), 254(13), 242(21), 241(100), 195(15), 181(15), 155(49), 127(16), 44(15). **HRMS** (ESI) calcd for $C_{23}H_{27}N_2O_6$ $[M+H]^+$ 427.1869, found 427.1876.

(*E*)-1,2-Di(methoxycarbonyl)-1-(1-naphthalencarbonyloxyl)ethene 4b



Yied: 12%; white flake, mp: 63-64°C, ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.944-8.923(d, *J* = 8.4Hz, 1H), 8.478-8.457(m, 1H), 8.093-8.072(d, *J* = 8.4Hz, 1H), 7.903-7.883(d, *J* = 8.0Hz, 1H), 7.657-7.615(m, 1H), 7.570-7.531(m, 2H), 6.839(s, 1H), 3.874(s, 3H), 3.723(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 164.3, 163.5, 161.9, 147.1, 134.8, 133.9, 131.9, 131.7, 128.8, 128.5, 126.6, 125.6, 124.8, 124.7, 117.4, 53.5, 52.3; IR (KBr, cm^{-1}): 3089 (w, =C-H), 2954(w, C-H), 1734(s, C=O), 1661(s), 1437 (m, Ar), 1345(w, CH_3), 1377(m), 1246 (m, C-O), 1110, 1022(m, C-N), 807, 781 (s, Ar); MS m/z(%): 314(5)($M^{+\cdot}$), 186(4), 156(11), 155(100), 143(8), 127(31), 126(6), 101(4), 77 (3), 69(2), 44(2). **HRMS** (ESI) calcd for $C_{17}H_{15}O_6$ $[M+H]^+$ 315.0869, found 315.0862.

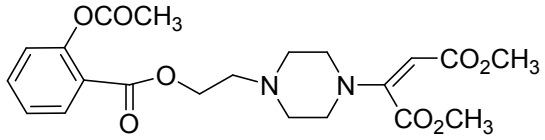
1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-((2-(naphthalen-1-yl)acetoyloxy))eth-1-yl]piperazine 5a



Yied: 62%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.985-7.966(d, *J* = 8Hz, 1H), 7.861-7.841(d, *J* = 8Hz, 1H), 7.782-7.764(d, *J* = 7.2Hz, 1H), 7.526-7.461(m, 2H), 7.430-7.380(m, 2H), 4.669(s, 1H), 4.175-4.149(t, *J* = 5.2Hz, 2H), 4.052(s, 2H), 3.906(s, 3H), 3.638(s, 3H), 2.847-2.836(m, 4H), 2.472-2.447(t, *J* = 5.2Hz, 2H), 2.192-2.170(t, *J* = 4.4Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 171.2, 168.1, 166.0, 154.4, 133.7, 132.0, 130.5, 128.7, 128.1, 128.0, 126.4, 125.9, 125.5, 123.8, 86.1, 62.2, 56.1, 53.0, 51.8, 50.9, 46.7, 39.3; IR (KBr, cm^{-1}): 3048(w, =C-H), 2950, 2842(w, C-H), 1741, 1696 (s, C=O), 1583(s), 1438 (m, Ar), 1370(w, CH_3), 1275, 1246 (m, C-O), 1214, 1160(m, C-N), 826, 732 (s, Ar); MS m/z(%):

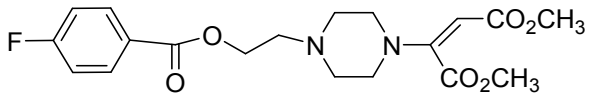
440(16) ($M^{+\cdot}$), 409(8), 381(4), 354(29), 269(4), 268(22), 256(19), 241(100), 239(5), 213(26), 209(13) ,195(8), 181(17), 168(14), 142(6), 141(48), 140(13), 115(6), 44(28). **HRMS** (ESI) calcd for $C_{24}H_{29}N_2O_6$ $[M+H]^+$ 441.2026, found 441.2032.

1-[2-(2-Acetoxybenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 6a



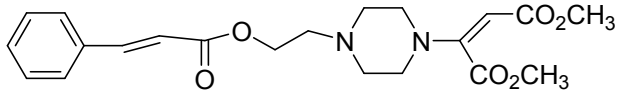
Yied: 43%; light yellow sticky clumps, ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.000-7.976(dd, *J* = 8Hz, *J* = 1.6Hz, 1H), 7.596-7.553(m, 1H), 7.340-7.302(m, 1H), 7.122-7.102(d, *J* = 8Hz, 1H), 4.769(s, 1H), 4.400-4.372(t, *J* = 5.6Hz, 2H), 3.910(s, 3H), 3.629(s, 3H), 3.176-3.152(t, *J* = 4.8Hz, 4H), 2.756-2.728(t, *J* = 5.6Hz, 2H), 2.593-2.569(t, *J* = 4.8Hz, 4H), 2.349(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 169.5, 168.0, 166.0, 164.2, 154.4, 150.7, 134.0, 131.6, 126.0, 123.8, 123.0, 86.3, 62.1, 56.3, 52.9, 52.2, 50.9, 47.0, 21.0; IR (KBr, cm^{-1}): 3083(w, =C-H), 2950, 2849(w, C-H), 1743, 1696(s, C=O), 1583(s), 1485, 1450, 1439 (m, Ar), 1369(w, CH_3), 1293, 1258, 1159 (m, C-O), 1085, 1042(m, C-N), 753, 732 (s, Ar); MS m/z(%): 434(6) ($M^{+\cdot}$), 403(6), 375(3), 348 (26), 262(8), 250(14), 254(5), 241(100), 239(7), 209 (16), 195(10), 181(21), 163(14), 140(6), 121(22), 120(3), 82(6), 56(6)，44(22); **HRMS** (ESI) calcd for $C_{21}H_{27}N_2O_8$ $[M+H]^+$ 435.1767, found 435.1768.

1-[2-(4-Fluorobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 7a



Yied: 89%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 8.061-8.025(m, 2H), 7.148-7.105(t, *J* = 8.8Hz, 2H), 4.784(s, 1H), 4.462-4.434(t, *J* = 5.6Hz, 2H), 3.921(s, 3H), 3.634(s, 3H), 3.203-3.178(t, *J* = 4.8Hz, 4H), 2.818-2.789(t, *J* = 5.6Hz, 2H), 2.646-2.621(t, *J* = 4.8Hz, 4H); ^{13}CNMR (100MHz, $CDCl_3$): δ = 167.9, 166.9, 166.0, 165.3, 164.4, 154.4, 132.1, 132.0, 126.3, 126.2, 115.6, 115.4, 86.3, 62.2, 56.4, 52.9, 52.2, 50.8, 47.0; IR(KBr, cm^{-1}): 3080(w, =C-H), 2951, 2906(w, C-H), 1742, 1720, 1693(s, C=O), 1583(s), 1439 (m, Ar), 1371(w, CH_3), 1273, 1216 (m, C-O), 1160, 1114 (m, C-N), 857, 732 (s, Ar); MS m/z(%): 394(6) ($M^{+\cdot}$), 363(11), 335(6), 308(28), 254(7), 242(11), 241(100), 222(18), 209(16), 195(9), 181(21), 167(37), 123(33), 95(9), 82(7), 56(7). **HRMS** (ESI) calcd for $C_{19}H_{24}FN_2O_6$ $[M+H]^+$ 395.1618, found 395.1626.

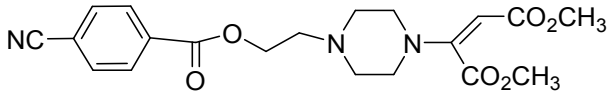
1-[2-(Cinnamoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 8a



Yied: 59%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.713-7.673(d, *J* = 16Hz, 1H), 7.542-7.520(dd, *J* = 5.6Hz, *J* = 3.2Hz, 2H), 7.399-7.383(t, *J* = 3.2Hz, 3H), 6.476-6.436(d, *J* = 16Hz, 1H), 4.781(s, 1H), 4.354-4.325(t, *J* = 5.6Hz, 2H), 3.921(s, 3H), 3.638(s, 3H), 3.208-3.183(t, *J* = 4.8Hz, 4H), 2.755-2.727(t, *J* = 5.6Hz, 2H), 2.622-2.597(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ= 168.1, 166.9, 166.1, 154.5, 145.3, 134.3, 130.5, 129.0,

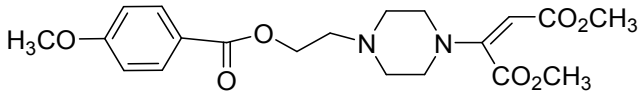
128.2, 117.8, 86.5, 61.6, 56.6, 53.1, 52.3, 51.0, 47.1; IR (KBr, cm^{-1}): 3085(w, =C-H), 2952, 2848(w, C-H), 1744, 1713, 1689 (s, C=O), 1586(s), 1450, 1435 (m, Ar), 1371(w, CH_3), 1310, 1279 (m, C-O), 1196, 1162(m, C-N), 868, 784 (s, Ar); MS m/z(%): 402(4) ($M^{+\cdot}$), 371(7), 316(22), 242(12), 241(100), 230(9), 209(14), 195(13), 181(18), 175(10), 149(11), 131(38), 103(11), 44(28). **HRMS** (ESI) calcd for $C_{21}H_{27}N_2O_6$ $[M+H]^+$ 403.1869, found 403.1876.

1-[2-(4-Cyanobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 9a



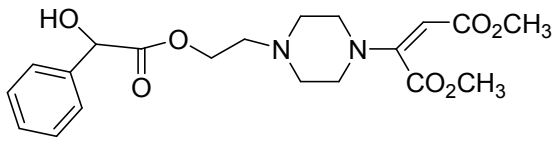
Yied: 57%; yellow solid, mp: 105-106°C, ^{1}HNMR (400MHz, $CDCl_3$): δ = 8.151-8.130(d, *J* = 8.4Hz, 2H), 7.793-7.772(d, *J* = 8.4Hz, 2H), 4.785(s, 1H), 4.515-4.487(t, *J* = 5.6Hz, 2H), 3.923(s, 3H), 3.631(s, 3H), 3.205-3.180(t, *J* = 4.8Hz, 4H), 2.841-2.813(t, *J* = 5.6Hz, 2H), 2.652-2.628(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.9, 165.9, 164.7, 154.4, 133.8, 132.2, 130.0, 117.9, 116.3, 86.3, 62.6, 56.2, 52.9, 52.1, 50.8, 47.0; IR (KBr, cm^{-1}): 3095(w, =C-H), 2951, 2921(w, C-H), 2232(m, -CN), 1740, 1717, 1695(s, C=O), 1585(s), 1439(m, Ar), 1371(w, CH_3), 1310, 1275 (m, C-O), 1161, 1109(m, C-N), 914, 733(s, Ar); MS m/z(%): 401(4) ($M^{+\cdot}$), 370(9), 320(10), 315(22), 254(8), 242(13), 241(100), 229(19), 222(7), 209(15), 195(11), 181(20), 174(29), 152(7), 140(13), 135(23), 82(10), 57(9), 44(21). **HRMS** (ESI) calcd for $C_{20}H_{24}N_3O_6$ $[M+H]^+$ 402.1665, found 402.1666.

1-[1-(4-Methoxybenzoyloxyl)eth-2-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 10a



Yied: 75%; light brown sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.985-7.962(d, *J* = 9.2Hz, 2H), 6.938-6.916(d, *J* = 8.8Hz, 2H), 4.773(s, 1H), 4.433-4.405(t, *J* = 5.6Hz, 2H), 3.918(s, 3H), 3.862(s, 3H), 3.637(s, 3H), 3.192-3.166(t, *J* = 5.2Hz, 4H), 2.802-2.774(t, *J* = 5.6Hz, 2H), 2.637-2.612(t, *J* = 5.2Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ= 168.1, 166.2, 166.1, 163.5, 154.6, 131.7, 122.5, 113.8, 86.5, 62.0, 56.6, 55.5, 53.0, 52.4, 51.0, 47.2; IR (KBr, cm^{-1}): 3058, 2951(w, =C-H), 2841(w, C-H), 1744, 1708(s, C=O), 1605, 1583(s), 1512, 1439, 1421(m, Ar), 1371(w, CH_3), 1315(m), 1276, 1258, 1215, 1167(m, C-O), 1104, 1027(m, C-N), 849, 736 (s, Ar)； MS m/z(%): 406(3.9) ($M^{+\cdot}$), 375(7.8), 347(2.5), 320(19.9), 254(15.2), 241(100), 222(11.9), 209(14), 195(16), 181(19), 179(14), 168(8), 152(8), 135(60), 107(4), 82(7), 77(4), 44(9). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_7$ $[M+H]^+$ 407.1818, found 407.1822.

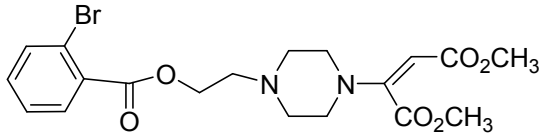
1-[2-(2-Hydroxy-2-phenylacetoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 11a



Yied: 79%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.425-7.407(d, *J* = 7.2Hz, 2H), 7.355-7.304(m, 3H), 7.321(s, 1H), 5.175(s, 1H), 4.702(s, 1H), 4.358-4.302(m, 1H), 4.181-4.127(m, 1H), 3.896(s, 3H), 3.619(s, 3H), 2.977-2.953(t, *J* = 4.8Hz, 4H), 2.526(m,

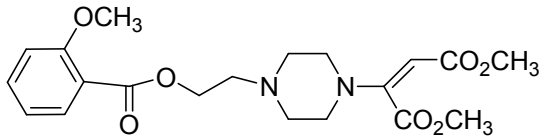
2H), 2.368-2.316(m, 2H), 2.285-2.233(m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 173.1, 168.0, 165.9, 154.3, 138.4, 128.5, 128.4, 126.7, 86.1, 72.9, 62.7, 55.9, 52.9, 51.8, 50.9, 46.7; IR (KBr, cm^{-1}): 3457(b, s, -OH), 3090, 2951, 2921 (w, =C-H), 2849(w, C-H), 1740, 1695(s, C=O), 1583(s), 1494, 1439 (m, Ar), 1370(w, CH_3), 1277(m, C-O), 1160(m, C-N), 914, 732 (s, Ar); MS m/z(%): 406(12) ($M^{+\cdot}$), 375(10), 347(3), 321(5), 320(31), 255(9), 242(11), 241(100), 234(2), 222(19), 209(17), 195(13), 181(21), 179(11), 168(7), 140(10), 107(7), 79(10), 56(7), 44(52). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_7$ $[M+H]^+$ 407.1818, found 407.1824.

1-[2-(2-Bromobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 12a



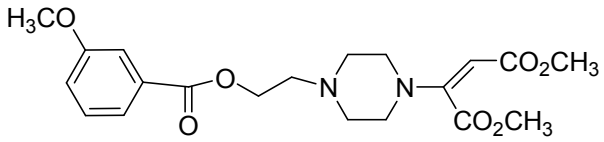
Yied: 84%; light yellow sticky clumps, ^{1}HNMR(400MHz, $CDCl_3$): δ = 7.773-7.749(dd, *J* = 7.6Hz, *J* = 2Hz, 1H), 7.669-7.647(dd, *J* = 7.6Hz, *J* = 1.2Hz, 1H), 7.339-7.321(m, 2H), 4.773(s, 1H), 4.476-4.448(t, *J* = 5.6Hz, 2H), 3.914(s, 3H), 3.630(s, 3H), 3.189-3.164(t, *J* = 4.8Hz, 4H), 2.798-2.770(t, *J* = 5.6Hz, 2H), 2.623-2.598(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.9, 165.9, 154.4, 134.2, 132.6, 132.1, 131.1, 127.2, 121.4, 86.2, 62.3, 56.2, 52.9, 52.1, 50.8, 47.0; IR (KBr, cm^{-1}): 3090, 2950(w, =C-H), 2843(w, C-H), 1740, 1696(s, C=O), 1584(s), 1436, 1370(m, Ar), 1250, 1215, 1161(m, C-O), 1110, 1025(m, C-N), 747, 733 (s, Ar); MS m/z(%): 454(4) ($M^{+\cdot}$), 456(3)(M+2), 423(6), 395(3), 368(15), 282(10), 270(8), 242(12), 241(100), 227(18), 209(13), 195(9), 185(22), 181(18), 44(11). **HRMS** (ESI) calcd for $C_{19}H_{24}BrN_2O_6$ $[M+H]^+$ 455.0818, found 455.0820.

1-[1-(2-Methoxybenzoyloxyl)eth-2-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 13a



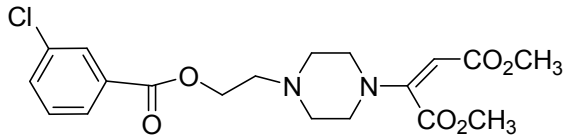
Yied: 64%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.783-7.759(dd, *J* = 8Hz, *J* = 1.6Hz, 1H), 7.503-7.460(m, 1H), 6.999-6.965(m, 2H), 4.774(s, 1H), 4.435-4.407(t, *J* = 5.6Hz, 2H), 3.913(s, 3H), 3.887(s, 3H), 3.629(s, 3H), 3.188-3.163(t, *J* = 4.8Hz, 4H), 2.789-2.761(t, *J* = 5.6Hz, 2H), 2.632-2.608(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.9, 166.0, 165.8, 159.0, 154.4, 133.6, 131.4, 120.0, 119.7, 111.9, 86.1, 61.9, 56.3, 55.8, 52.9, 52.1, 50.8, 47.0; IR(KBr, cm^{-1}): 3082(w, =C-H), 2950, 2840(w, C-H), 1743, 1696(s, C=O), 1584(s), 1492, 1437(m, Ar), 1370, 1300(w, CH_3), 11258, 1215, 1160(m, C-O), 1092, 1047, 1022(m, C-N), 757, 732(s, Ar); MS m/z(%): 406(3) ($M^{+\cdot}$), 375(7), 320(20), 254(14), 241(100), 209(14), 195(17), 181(20), 179(14), 152(10), 135(67), 85(30), 71(34), 57(35), 44(63). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_7$ $[M+H]^+$ 407.1818, found 407.1819.

1-[2-(3-Methoxybenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 14a



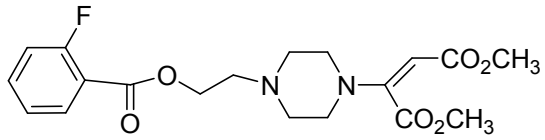
Yied: 74%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.617-7.598(d, *J* = 8Hz, 1H), 7.536(s, 1H), 7.374-7.334(t, *J* = 8Hz, 1H), 7.121-7.096(dd, *J* = 8Hz, d, *J*=2Hz, 1H), 4.775(s, 1H), 4.455-4.427(t, *J* = 5.6Hz, 2H), 3.914(s, 3H), 3.840(s, 3H), 3.629(s, 3H), 3.187-3.164(t, *J* = 4.8Hz, 4H), 2.806-2.778(t, *J* = 5.6Hz, 2H), 2.632-2.609(t, *J* = 4.8Hz, 4H); ^{13}CNMR (100MHz, $CDCl_3$): δ = 167.9, 166.1, 165.9, 159.4, 154.4, 131.2, 129.4, 121.7, 119.2, 114.1, 86.1, 62.2, 56.3, 55.3, 52.9, 52.1, 50.8, 47.0; IR (KBr, cm^{-1}): 3084(w, =C-H), 2950, 2838(w, C-H), 1743, 1720, 1697(s, C=O), 1583(s), 1489, 1451, 1437(m, Ar), 1371(w, CH_3), 1279(m), 1220, 1161 (m, C-O), 1107, 1079, 1044(m, C-N), 756, 733(s, Ar); MS m/z(%): 406(4) ($M^{+\cdot}$), 375(8), 320(30), 242(12), 241(100), 222(16), 209(13), 195(10), 181(18), 179(22), 135(38), 44(12). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_7$ $[M+H]^+$ 407.1818, found 407.1823.

1-[2-(3-Chlorobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 15a



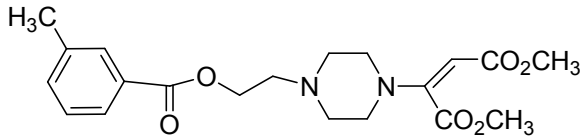
Yied: 85%; yellow flake, mp: 64-65°C, ^{1}HNMR(400MHz, $CDCl_3$): δ = 7.982(s, 1H), 7.916-7.896(d, *J* = 8Hz, 1H), 7.551-7.531(d, *J* = 8Hz, 1H), 7.422-7.382(t, *J* = 8Hz, 1H), 4.780(s, 1H), 4.470-4.441(t, *J* = 5.6Hz, 2H), 3.921(s, 3H), 3.633(s, 3H), 3.197-3.173(t, *J* = 4.8Hz, 4H), 2.813-2.785(t, *J* = 5.6Hz, 2H), 2.636-2.611(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.9, 166.0, 165.1, 154.4, 134.4, 133.0, 131.7, 129.8, 129.5, 127.6, 86.3, 62.3, 56.3, 52.9, 52.2, 50.8, 47.0; IR (KBr, cm^{-1}): 3072(w, =C-H), 2950, 2904, 2838(w, C-H), 1744, 1723, 1696(s, C=O), 1583(s), 1437, 1371(m, Ar), 1258, 1214, 1161(m, C-O), 1109, 1087(m, C-N), 751, 734 (s, Ar); MS m/z(%): 410(4) ($M^{+\cdot}$), 379(7), 351(4), 326(9), 324(26), 254(6), 242(11), 241(100), 238(19), 209(15), 195(9), 185(17), 183(26), 181(21), 140(11), 139(33), 44(7). **HRMS** (ESI) calcd for $C_{19}H_{24}ClN_2O_6$ $[M+H]^+$ 411.1323, found 411.1329.

1-[2-(2-Fluorobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 16a



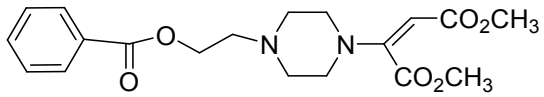
Yied: 81%; light yellow sticky clumps, ^{1}HNMR(400MHz, $CDCl_3$): δ = 7.941-7.900(m, 1H), 7.571-7.516(m, 1H), 7.243-7.125(m, 2H), 4.781(s, 1H), 4.480-4.452(t, *J* = 5.6Hz, 2H), 3.919(s, 3H), 3.630(s, 3H), 3.196-3.172(t, *J* = 4.8Hz, 4H), 2.811-2.784(t, *J* = 5.6Hz, 2H), 2.647-2.623(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ =167.9, 165.9, 164.1, 164.0, 163.0, 160.4, 154.4, 134.6, 134.5, 131.9, 124.0, 123.9, 118.5, 118.4, 117.0, 116.8, 86.1, 62.5, 56.2, 52.9, 52.1, 50.8, 47.0; IR (KBr, cm^{-1}): 3089(w, =C-H), 2951, 2914, 2845(w, C-H), 1743, 1696(s, C=O), 1612, 1586(s), 1489, 1454, 1438(m, Ar), 1371(w, CH_3), 1297, 1254, 1216, 1159(m, C-O), 1127, 1092(m, C-N), 758, 732(s, Ar); MS m/z(%): 394(6) ($M^{+\cdot}$), 363(11), 335(6), 308(33), 254(6), 242(11), 241(100), 222(29), 210(21), 195(10), 181(21), 167(42), 140(10), 123(39), 44(19). **HRMS** (ESI) calcd for $C_{19}H_{24}FN_2O_6$ $[M+H]^+$ 395.1618, found 395.1611.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(3-methylbenzoyloxyl)eth-1-yl]piperazine 17a



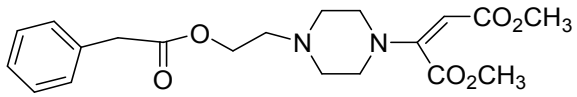
Yied: 75%; light yellow sticky clumps, ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.834-7.807(d, *J* = 10.8Hz, 2H), 7.386-7.311(m, 2H), 4.776(s, 1H), 4.453-4.425(t, *J* = 5.6Hz, 2H), 3.916(s, 3H), 3.631(s, 3H), 3.190-3.165(t, *J* = 4.8Hz, 4H), 2.808-2.780(t, *J* = 4.8Hz, 2H), 2.635-2.610(t, *J* = 5.6Hz, 4H), 2.401(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 166.5, 166.0, 154.5, 138.1, 133.8, 130.0, 129.9, 128.3, 126.6, 86.2, 62.1, 56.4, 52.9, 52.2, 50.9, 47.0, 21.3; IR (KBr, cm^{-1}): 3058(w, =C-H), 2950, 2922, 2849(w, C-H), 1743, 1696(s, C=O), 1589(s), 1439(m, Ar), 1277(m, C-O), 1158, 1109, 1084(m, C-N), 825, 744 (s, Ar); MS m/z(%): 390(4) ($M^{+\cdot}$), 304(24), 254(9), 242(12), 241(100), 218(11), 209(15), 195(12), 181(20), 163(26), 119(25), 91(14), 82(7), 44(32). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_6$ $[M+H]^+$ 391.1869, found 391.1875.

1-[2-(Benzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 18a



Yied: 89%; colorless sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.034-8.016(d, *J* = 7.2Hz, 2H), 7.590-7.553(t, *J* = 7.2Hz, 1H), 7.469-7.431(t, *J* = 7.2Hz, 2H), 4.778(s, 1H), 4.462-4.434(t, *J* = 5.6Hz, 2H), 3.915(s, 3H), 3.630(s, 3H), 3.189-3.164(t, *J* = 4.8Hz, 4H), 2.810-2.781(t, *J* = 5.6Hz, 2H), 2.635-2.610(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 166.3, 166.0, 154.4, 133.0, 130.0, 129.5, 128.4, 86.2, 62.2, 56.4, 52.9, 52.2, 50.9, 47.0; IR (KBr, cm^{-1}): 3063 (w, =C-H), 2950, 2846(w, C-H), 1744, 1719, 1696(s, C=O), 1585(s), 1491, 1449(m, Ar), 1275, 1213, 1157(m, C-O), 1111, 1070(m, C-N), 895, 714(s, Ar); MS m/z(%): 376(4) ($M^{+\cdot}$), 345(13), 290(20), 254(8), 242(12), 241(100), 209(16), 204(12), 181(21), 149(38), 105(24), 77(9), 56(6), 44(7). **HRMS** (ESI) calcd for $C_{19}H_{25}N_2O_6$ $[M+H]^+$ 377.1713, found 377.1718.

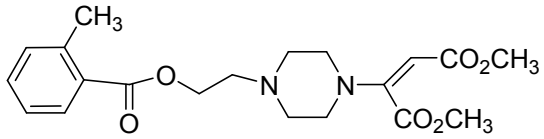
1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(2-phenylacetoyloxy)eth-1-yl]piperazine 19a



Yied: 74%; colorless sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.328-7.259(m, 5H), 4.737(s, 1H), 4.211-4.184(t, *J* = 5.6Hz, 2H), 3.903(s, 3H), 3.623(s, 2H), 3.623(s, 3H), 3.071-3.047(t, *J* = 4.8Hz, 4H), 2.602-2.575(t, *J* = 5.6Hz, 2H), 2.440-2.416(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ= 171.2, 167.9, 165.9, 154.3, 133.9, 129.2, 128.4, 127.0, 86.1, 61.8, 56.2, 52.8, 52.0, 50.8, 46.9, 41.3; MS m/z(%): 390(7) ($M^{+\cdot}$), 359(10), 331(6), 304(30), 242(12), 241(100), 218(23), 206(17), 195(8), 181(19), 163 (29), 91(24), 44(12)； IR(KBr, cm^{-1}): 3088 (w, =C-H), 2950, 2842(w, C-H), 1741, 1696(s, C=O), 1582(s), 1497, 1451, 1438 (m, Ar), 1371(w, CH_3), 1315(m), 1276, 1243, 1216, 1159(m, C-O), 1110, 1085, 1041(m, C-N), 867, 754(s, Ar). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_6$ $[M+H]^+$ 391.1869, found 391.1861.

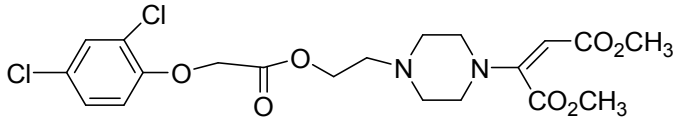
1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(2-methylbenzoyloxy)eth-1-

yl]piperazine 20a



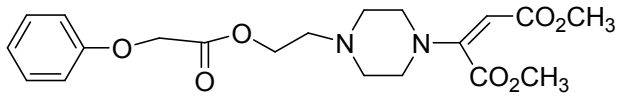
Yied: 66%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.882-7.863(d, *J* = 7.2Hz, 1H), 7.417-7.381(t, *J* = 7.2Hz, 1H), 7.261-7.234(m, 2H), 4.774(s, 1H), 4.430-4.406(t, *J* = 5.6Hz, 2H), 3.912(s, 3H), 3.628(s, 3H), 3.169-3.159(m, 4H), 2.784-2.759(t, *J* = 5.6Hz, 2H), 2.604-2.591(m, 7H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 167.9, 167.3, 166.0, 154.4, 140.0, 132.0, 131.6, 130.4, 129.5, 125.7, 86.2, 61.6, 56.4, 52.9, 52.2, 50.8, 47.0, 21.7; IR(KBr, cm^{-1}): 3058(w, =C-H), 2951, 2843(w, C-H), 1744, 1718, 1699(s, C=O), 1584(s), 1487, 1439 (m, Ar), 1370, 1332, 1294(w, CH_3), 1257, 1215, 1162(m, C-O), 1092, 1045(m, C-N), 799, 739(s, Ar); MS m/z(%): 390(4) ($M^{+\cdot}$), 359(8), 304(22), 254(8), 242(12), 241(100), 209(15), 206(11), 181(20), 163(15), 119(29), 91(10), 82(6), 44(13). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_6$ $[M+H]^+$ 391.1869, found 391.1865.

1-[2-(2-(2,4-Dichlorophenoxy)acetoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 21a



Yied: 69%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.388-7.383(d, *J* = 2Hz, 1H), 7.173-7.146(dd, *J* = 8.8Hz, *J* = 2Hz, 1H), 6.809-6.787(d, *J* = 8.8Hz, 1H), 4.763(s, 1H), 4.726(s, 2H), 4.328-4.303(t, *J* = 5.2Hz, 2H), 3.913(s, 3H), 3.631(s, 3H), 3.128(m, 4H), 2.657-2.631(t, *J* = 5.2Hz, 2H), 2.517(m, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 167.9, 165.9, 154.3, 152.1, 130.1, 127.5, 126.7, 123.8, 114.3, 86.3, 66.0, 62.2, 56.1, 52.9, 52.0, 50.8, 46.9; IR(KBr, cm^{-1}): 3091(w, =C-H), 2950, 2847(w, C-H), 1742, 1694 (s, C=O), 1585(s), 1479, 1442, 1370(m, Ar), 1159, 1107, 1086 (m, C-O), 1044(m, C-N), 802, 731(s, Ar); MS m/z(%): 474(4) ($M^{+\cdot}$), 477(1)(M+2)，446(2), 443(11), 415(6), 390(17), 388(26), 304(26), 302(40), 290(13), 254(15), 247(23), 241(100), 209(18), 195(14), 181(23), 140(17), 56(10), 44(24). **HRMS** (ESI) calcd for $C_{20}H_{25}C_{l2}N_2O_7$ $[M+H]^+$ 475.1039, found 475.1043.

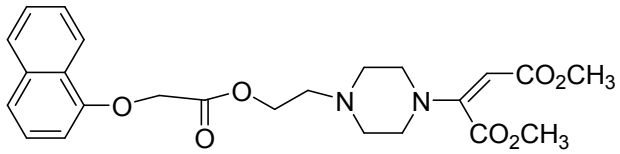
1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(2-phenoxyacetoyloxyl)eth-1-yl]piperazine 22a



Yied: 72%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.321-7.255(m, 2H), 7.007-6.970(t, *J* = 7.6Hz, 1H), 6.904-6.883(m, 2H), 4.747(s, 1H), 4.645(s, 2H), 4.321-4.294(t, *J* = 5.6Hz, 2H), 3.907(s, 3H), 3.629(s, 3H), 3.107-3.083(t, *J* = 4.8Hz, 4H), 2.641-2.614(t, *J* = 5.6Hz, 2H), 2.491-2.466(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.9, 167.9, 165.9, 157.6, 154.4, 129.5, 121.7, 114.4, 86.2, 65.1, 62.0, 56.2, 52.9, 52.0, 50.9, 46.9; IR(KBr, cm^{-1}): 3058 (w, =C-H), 2951, 2845(w, C-H), 1744, 1696(s, C=O), 1584(s), 1494, 1438(m, Ar), 1371(w, CH_3), 1277(m), 1162(b, s, C-O), 1107, 1089, 1042, 1022(m, C-N), 826, 756 (s, Ar); MS m/z(%): 406(13) ($M^{+\cdot}$), 375(15), 347(9), 321(10), 320 (54), 285(7), 254(7), 242(11),

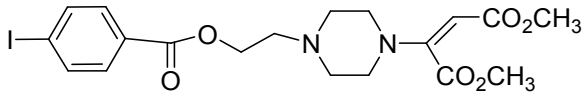
241(100), 234(56), 222(33), 209(17), 185(13), 181(22), 179(32), 140(11), 107(11), 77(9), 56(9), 44(30). **HRMS** (ESI) calcd for $C_{20}H_{27}N_2O_7$ $[M+H]^+$ 407.1818, found 407.1812.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-{2-[2-(naphthalen-1-yloxy)acetoyloxyl]eth-1-yl}piperazine 23a



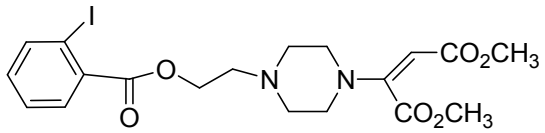
Yied: 75%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.328-8.304(m, 1H), 7.802-7.779(m, 1H), 7.514-7.437(m, 3H), 7.318-7.279(m, 1H), 6.682-6.663(d, *J* = 7.6Hz, 1H), 4.807(s, 2H), 4.668(s, 1H), 4.264-4.238(t, *J* = 5.2Hz, 2H), 3.883(s, 3H), 3.632(s, 3H), 2.931-2.907(t, *J* = 4.8Hz, 4H), 2.524-2.498(t, *J* = 5.2Hz, 2H), 2.326-2.302(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.7, 167.9, 165.9, 154.3, 153.3, 134.4, 127.4, 126.6, 125.5, 125.4, 125.3, 121.9, 121.3, 104.7, 86.1, 65.3, 62.3, 56.0, 52.8, 51.9, 50.8, 46.7; IR(KBr, cm^{-1}): 3056(w, =C-H), 2950, 2844(w, C-H), 1742, 1695(s, C=O), 1582(s), 1438, 1400, 1371(m, Ar), 1277, 1208, 1160(m, C-O), 1079, 1142, 1022(m, C-N), 794, 732(s, Ar); MS m/z(%): 456(18) ($M^{+\cdot}$), 425(10), 397(5), 370(29), 330(6), 285(7), 284(36), 271(13), 254(9), 241(100), 229(21), 209(15), 195(11), 143(11), 127(9), 105(6), 82(7), 56(8), 44(21)；**HRMS** (ESI) calcd for $C_{24}H_{29}N_2O_7$ $[M+H]^+$ 457.1975, found 457.1971.

1-[2-(4-Iodobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 24a



Yied: 74%, light yellow sticky clumps, ^{1}HNMR(400MHz, $CDCl_3$): δ = 7.824-7.803(d, *J* = 8.4Hz, 2H), 7.733-7.712(d, *J* = 8.4Hz, 2H), 4.772(s, 1H), 4.455-4.426(t, *J* = 5.6Hz, 2H), 3.920(s, 3H), 3.641(s, 3H), 3.187-3.162(t, *J* = 4.8Hz, 4H), 2.803-2.775(t, *J* = 5.6Hz, 2H), 2.629-2.604(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.2, 166.2, 166.1, 154.6, 138.0, 131.2, 129.7, 101.1, 86.7, 62.5, 56.6, 53.2, 52.4, 51.2, 47.2; IR(KBr, cm-1): 3057, 2950(w, =C-H), 2841(w, C-H), 1743, 1721, 1697(s, C=O), 1585(s), 1438, 1392(m, Ar), 1370(w, CH_3), 1271, 1215, 1160(m, C-O), 1117, 1104, 1027(m, C-N), 847, 799(s, Ar); MS m/z(%): 502(3.6) (M+.), 471(7.6), 416(31.1), 330(17.4), 318(16), 275(26.5), 242(12.1), 241(100), 231(34), 209(12), 181(17), 168(6), 140(7), 82(6), 56(5), 44(43). **HRMS** (ESI) calcd for $C_{19}H_{24}IN_2O_6$ $[M+H]^+$ 503.0679, found 503.0671.

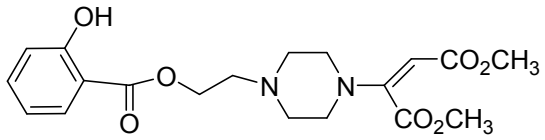
1-[2-(2-Iodobenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 25a



Yied: 65%; light brown sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.002-7.982(dt, *J* = 1.6Hz, *J* = 8Hz, 1H), 7.779-7.755(m, 1H), 7.436-7.396(dt, *J* = 0.8Hz, *J* = 7.6Hz, 1H), 7.192-7.150(dt, *J* = 1.6Hz, *J* = 7.6Hz, 1H), 4.773(s, 1H), 4.481-4.453(t, *J* = 5.6Hz, 2H), 3.920(s, 3H), 3.638(s, 3H), 3.198-3.173(t, *J* = 4.8Hz, 4H), 2.811-2.783(t, *J* = 5.6Hz, 2H), 2.633-2.608(t, *J* =

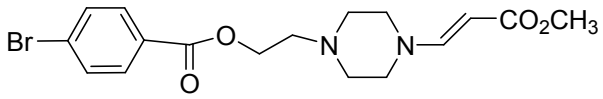
4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.1, 166.5, 166.2, 154.6, 141.4, 135.2, 132.9, 131.0, 128.1, 94.2, 86.5, 62.5, 56.4, 53.1, 52.3, 51.1, 47.2; IR(KBr, cm^{-1}): 3056(w, =C-H), 2950, 2844(w, C-H), 1742, 1695(s, C=O), 1582(s), 1438, 1400, 1371(m, Ar), 1277, 1208, 1160(m, C-O), 1079, 1142, 1022(m, C-N), 794, 732(s, Ar); MS m/z(%): 502(5)($M^{+\cdot}$), 471(9), 442(3) 416(41), 330(30), 318(29), 275(23), 254(8), 241(100), 231(49), 209(14), 195(12), 181(19), 168(8), 140(10), 126(4), 105(17), 82(7), 56(8), 44(24); **HRMS** (ESI) calcd for $C_{19}H_{24}IN_2O_6$ $[M+H]^+$ 503.0679, found 503.0672.

1-[2-(2-Hydroxybenzoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 26a



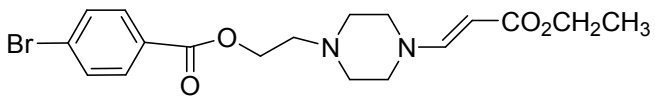
Yied: 31%; light yellow sticky clumps, ^{1}H NMR (400MHz, $CDCl_3$): δ = 10.682(s, 1H), 7.820-7.796(m, *J* = 1.6Hz, *J* = 8.0Hz, 1H), 7.485-7.442(m, *J* = 1.6Hz, *J* = 8.8Hz, 1H), 6.987-6.966(d, *J* = 8.4Hz, 1H), 6.910-6.872(t, *J* = 8.0Hz, 1H), 4.777(s, 1H), 4.482-4.454(t, *J* = 5.6Hz, 2H), 3.917(s, 3H), 3.635(s, 3H), 3.191-3.166(t, *J* = 4.8Hz, 4H), 2.814-2.785(t, *J* = 6.4Hz, 2H), 2.631-2.606(t, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 169.8, 168.0, 166.1, 161.6, 154.5, 135.9, 129.9, 119.3, 117.7, 112.4, 86.5, 62.4, 56.3, 53.0, 52.3, 50.9, 47.1; IR (KBr, cm^{-1}): 3051(w, =C-H), 2953(w, C-H), 1739(s, C=O), 1649(s), 1436(m, Ar), 1329(w, CH_3), 1259(m, C-O), 1171, 1099(m, C-N), 860, 782 (s, Ar); MS m/z(%): 392(15)($M^{+\cdot}$), 361(11), 306(24), 242(13), 241(100), 220(21), 209(22), 181(24), 165(14), 121(18), 100(11), 44(14); **HRMS** (ESI) calcd for $C_{19}H_{25}N_2O_7$ $[M+H]^+$ 393.1662, found 393.1665.

1-[2-(4-Bromobenzoyloxyl)eth-1-yl]-4-[(*E*)-(2-methoxycarbonyl)ethen-1-yl]piperazine 27a



Yied: 45%; white flake, mp: 152-154^{o}C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.882-7.860(dd, *J* = 2Hz, *J* = 5.8Hz, 2H), 7.593-7.521(dt, *J* = 7.2Hz, *J* = 9.2Hz, 2H), 7.385-7.352(d, *J* = 13.2Hz, 1H), 4.678-4.646 (d, *J* = 12.8Hz, 1H), 4.478-4.449(m, *J* = 5.6Hz, 2H), 3.661(s, 3H), 3.261-3.236(m, *J* = 4.8Hz, 4H), 2.838-2.810(m, *J* = 5.6Hz, 2H), 2.627-2.602(m, *J* = 4.8Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 170.3, 165.9, 151.8, 131.9, 131.2, 129.1, 128.4, 85.3, 62.3, 56.7, 53.2, 52.6, 50.8; IR(KBr, cm^{-1}): 3055(w, =C-H), 2851(w, C-H), 1721 (s, C=O), 1612, 1591(s), 1447, 1427, 1421(m, Ar), 1397(w, CH_3), 1269, 1258, 1159(m, C-O), 1104 (m, C-N), 849, 736(s, Ar); MS m/z(%): 396(1)($M^{+\cdot}$), 365(1), 343(1), 312(1), 292(3), 279(5), 264(5), 227(9), 220(21), 202(96), 200(100), 183(96), 178(3), 157(39), 127(27), 112(18), 99(55), 76(23), 75(29), 74(18), 50(27), 44(45). **HRMS** (ESI) calcd for $C_{17}H_{22}BrN_2O_4$ $[M+H]^+$ 397.0763, found 397.0762.

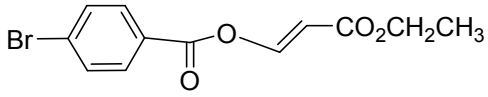
1-[2-(4-Bromobenzoyloxyl)eth-1-yl]-4-[(*E*)-(2-ethoxycarbonyl)ethen-1-yl]piperazine 28a



Yied: 39%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.893-7.872(d, *J* =

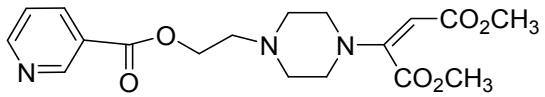
8.4Hz, 2H), 7.599-7.578(d, *J* = 8.4Hz, 2H), 7.374-7.341(d, *J* = 13.2Hz, 1H), 4.673-4.640(d, *J* = 13.2Hz, 1H), 4.463-4.435(t, *J* = 5.6Hz, 2H), 4.155-4.102(q, *J* = 7.2Hz, 2H), 3.243-3.218(t, *J* = 4.8Hz, 4H), 2.813-2.784(t, *J* = 5.6Hz, 2H), 2.596-2.571(t, *J* = 4.8Hz, 4H), 1.269-1.233(t, *J* = 7.2Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 169.9, 165.9, 151.7, 132.0, 131.3, 129.2, 128.4, 85.6, 62.5, 59.2, 56.8, 52.7, 14.8; IR(KBr, cm^{-1}): 3402(w, =C-H), 2926, 2856(w, C-H), 1721(s, C=O), 1683(s), 1512, 1449(m, Ar), 1369(w, CH_3), 1269, 1219, 1184(m, C-O), 1112, 1070(m, C-N), 851, 757(s, Ar)**;** MS m/z(%): 410(6)($M^{+\cdot}$), 383(5), 365(8), 312(11), 284(13), 270(7), 227(27), 197(81), 183(26), 151(23), 141(25), 124(14), 110(14), 82(32), 56(18), 44(100). **HRMS** (ESI) calcd for $C_{18}H_{24}BrN_2O_4$ $[M+H]^+$ 411.0919, found 411.0911.

Ethyl (*E*)-3-(4-bromobenzencarbonyloxy)-propenoate 28b



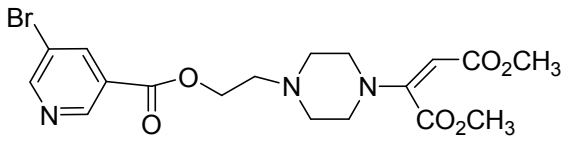
Yied: 25%; white flake, mp: 61-62^{o}C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.552-8.491(d, *J* = 12.4Hz, 1H), 7.989-7.968(d, *J* = 8.4Hz, 2H), 7.663-7.642(d, *J* = 8.4Hz, 2H), 5.922-5.890(d, *J* = 12.4Hz, 1H), 4.275-4.222(m, *J* = 6.8Hz, 2H), 1.340-1.305(t, *J* = 6.8Hz, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 166.2, 162.2, 149.8, 132.4, 131.9, 130.0, 126.9, 107.1, 60.8, 14.5; IR(KBr, cm^{-1}): 3091(w, =C-H), 2977(w, C-H), 1745, 1717(s, C=O), 1658(s), 1485(m, Ar), 1367(w, CH_3), 1313(m), 1259 (m, C-O), 1106, 1070(m, C-N), 849, 748(s, Ar); MS m/z(%): 298(5)($M^{+\cdot}$), 293(1), 279(1), 253(1), 239(1), 186(7), 183(100), 155(19), 149(3), 139(2), 119(3), 76(12), 50(6). **HRMS** (ESI) calcd for $C_{12}H_{12}BrO_4$ $[M+H]^+$ 298.9919, found 298.9911.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(nicotinoyloxyl)eth-1-yl]piperazine 29a



Yied: 68%; light brown sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 9.213-9.210(d, *J* = 1.2Hz, 1H), 8.804-8.788(dd, *J* = 4.8Hz, *J* = 1.6Hz, 1H), 8.312-8.283(dt, *J* = 1.8Hz, *J* = 8.0Hz, 1H), 7.450-7.373(m, *J* = 4.8Hz, *J* = 8.0Hz,1H), 4.784(s, 1H), 4.510-4.482(t, *J* = 5.6Hz, 2H), 3.924(s, 3H), 3.636(s, 3H), 3.200-3.176(t, *J* = 4.8Hz, 4H), 2.834-2.806(t, *J* = 5.6Hz, 2H), 2.650-2.625(t, *J* = 5.2Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 167.9, 165.9, 165.1, 154.4, 153.5, 150.7, 137.0, 125.9, 123.4, 86.3, 62.4, 56.3, 52.9, 52.2, 50.8, 47.1; IR(KBr, cm^{-1}): 3289(w, =C-H), 2996, 2953(w, C-H), 17421, 1711(s, C=O), 1583(s), 1437(m, Ar), 1366(w, CH_3), 1277(m, C-O), 1161, 1110(m, C-N), 859, 780(s, Ar); MS m/z(%): 377(9) ($M^{+\cdot}$), 349(8), 346(17), 318(17), 292(6), 291(31), 286(6), 254(7), 242(12), 241(100), 220(6), 209(18), 205(26), 193(15), 181(25), 151(7), 150(58), 140(11), 106(23), 78(12), 44(17); **HRMS** (ESI) calcd for $C_{18}H_{24}N_3O_6$ $[M+H]^+$ 378.1665, found 378.1672.

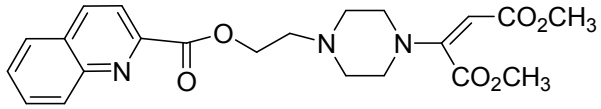
1-[2-(5-Bromonicotinoyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 30a



Yied: 89%; yellow flake, mp: 86-87^{o}C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 9.110-9.100(t, *J* = 2Hz, 1H), 8.859-8.844(m, 1H), 8.417-8.408(t, *J* = 2Hz, 1H), 4.781(s, 1H), 4.497-4.484(t, *J* =

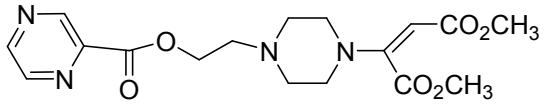
5.6Hz, 2H), 3.927(s, 3H), 3.641(s, 3H), 3.182-3.172(t, *J* = 4.8Hz, 4H), 2.809-2.796(t, *J* = 5.6Hz, 2H), 2.623-2.614(t, *J* = 5.2Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 166.1, 163.9, 154.7, 154.5, 148.9, 139.6, 127.3, 120.7, 86.6, 62.7, 56.4, 53.1, 52.3, 51.0, 47.1; IR(KBr, cm^{-1}): 3058 (w, =C-H), 2923, 2852(w, C-H), 1741, 1693, 1657(s, C=O), 1584(s), 1437, 1419(m, Ar), 1370(w, CH_3), 1306, 1268, 1213, 1159(m, C-O), 1112, 1043, 1022(m, C-N), 975, 756(s, Ar); MS m/z(%): 455(6)($M^{+\cdot}$), 457(6)(M+2), 426(8), 396(8), 369(19), 285(17), 254(7), 242(11), 241(100), 228(39), 209(18), 195(12), 185(24), 158(8), 140(15), 82(9), 56(8), 44(18); **HRMS** (ESI) calcd for $C_{18}H_{23}BrN_3O_6$ $[M+H]^+$ 456.0770, found 456.0778.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(quinoline-2-carboxyloyloxyl)eth-1-yl]piperazine 31a



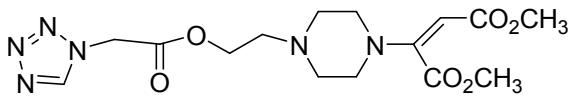
Yied: 71%; brown sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.341-8.288(m, 2H), 8.185-8.164(d, *J* = 8.4Hz, 1H), 7.906-7.885(d, *J* = 8.4Hz, 1H), 7.826-7.784(dt, *J* = 1.6Hz, *J* = 6.8Hz, 1H), 7.684-7.644(m, 1H), 4.784(s, 1H), 4.628-4.599(t, *J* = 5.6Hz, 2H), 3.922(s, 3H), 3.639(s, 3H), 3.226-3.201(t, *J* = 4.8Hz, 4H), 2.898-2.869(t, *J* = 5.6Hz, 2H), 2.681-2.656(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 166.1, 165.2, 154.5, 147.7, 147.4, 137.5, 130.5, 130.4, 129.3, 128.8, 127.6, 121.0, 86.4, 62.6, 56.3, 53.0, 52.2, 51.0, 47.0; IR(KBr, cm^{-1}): 3063(w, =C-H), 2951, 2917, 2844(w, C-H), 1741, 1697(s, C=O), 1584(s), 1531, 1498, 1439(m, Ar), 1372(w, CH_3), 1341(m), 1276, 1240, 1160(m, C-O), 1110, 1043, 1019(m, C-N), 869, 773(s, Ar); MS m/z(%): 427(83)($M^{+\cdot}$), 396(8)(M+2), 348(9), 255(9), 241(76), 229(71), 226(26), 209(15), 195(23), 181(22), 174(9), 140(12), 129(18), 128(33), 121(10), 82(14), 70(6), 55(6), 44(100). **HRMS** (ESI) calcd for $C_{22}H_{26}N_3O_6$ $[M+H]^+$ 428.1822, found 428.1829.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(pyrazine-2-carboxyloyloxyl)eth-1-yl]piperazine 32a



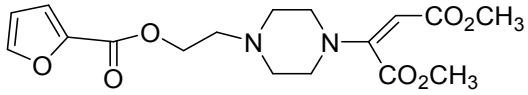
Yied: 66%; white flake, mp: 71-72^{o}C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 9.319(s, 1H), 8.832-8.826(d, *J* = 2.4Hz, 1H), 8.774-8.768(m, 1H), 4.784(s, 1H), 4.609-4.581(t, *J* = 5.6Hz, 2H), 3.924(s, 3H), 3.634(s, 3H), 3.211-3.187(t, *J* = 4.8Hz, 4H), 2.880-2.851(t, *J* = 5.6Hz, 2H), 2.671-2.647(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ= 167.8, 165.8, 163.6, 154.3, 147.7, 146.1, 144.3, 143.0, 86.1, 62.7, 56.1, 52.8, 52.0, 50.7, 46.8; IR(KBr, cm^{-1}): 3058 (w, =C-H), 2951, 2847(w, C-H), 1742, 1695(s, C=O), 1583(s), 1442 (m, Ar), 1371(w, CH_3), 1303(m), 1210, 1258, 1160(m, C-O), 1046, 1020(m, C-N), 868, 732(s, Ar)**;** MS m/z(%): 378(80)($M^{+\cdot}$), 347(25), 346(15), 319(18), 287(8), 254(20), 241(100), 225(9), 221(13), 209(23), 206(60), 195(30), 181(36), 168(9), 152(15), 151(72), 140(19), 126(16), 107(14), 82(19), 79(25), 70(10), 56(15), 44(49). **HRMS** (ESI) calcd for$C_{17}H_{23}N_4O_6$ $[M+H]^+$ 379.1618, found 379.1611.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(2-(1*H*-tetrazol-1-yl)acetoyloxyl)eth-1-yl]piperazine 33a



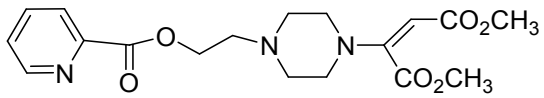
Yied: 55%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.964(s, 1H), 5.376(s, 2H), 4.768(s, 1H), 4.359-4.332(t, *J* = 5.6Hz, 2H), 3.903(s, 3H), 3.627(s, 3H), 3.166-3.141(t, *J* = 4.8Hz, 4H), 2.694-2.666(t, *J* = 5.6Hz, 2H), 2.547-2.522(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.1, 166.1, 165.4, 154.4, 144.0, 86.4, 63.2, 56.0, 53.1, 52.1, 51.0, 48.7, 46.9; IR(KBr, cm^{-1}): 3137(w, =C-H), 2997, 2953, 2847(w, C-H), 1743, 1690(s, C=O), 1584(s), 1439(m, Ar), 1373(w, CH_3), 1278, 1216(m, C-O), 1161, 1102, 1043(m, C-N), 798, 732(s, Ar); MS m/z(%): 382(4)($M^{+\cdot}$), 384(1)(M+2), 351(25), 323(17), 322(24), 320(8), 296(13), 242(11), 241(100), 239(13), 210(64), 209(26), 185(22), 181(34), 168(12), 140(36), 127(39), 126(12), 97(6), 84(9), 82(19), 70(12), 55(20), 44(61). **HRMS** (ESI) calcd for $C_{15}H_{23}N_6O_6$ $[M+H]^+$ 383.1679, found 383.1670.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(furan-2-carboyloxyl)eth-1-yl]piperazine 34a



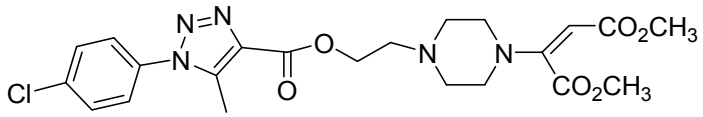
Yied: 79%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.622(d, 1H), 7.197-7.188(d, *J* = 3.6Hz, 1H), 6.544-6.535(t, *J* = 3.6Hz, 1H), 4.780(s, 1H), 4.444-4.418(t, *J* = 5.2Hz, 2H), 3.916(s, 3H), 3.630(s, 3H), 3.183-3.172(t, *J* = 4.8Hz, 4H), 2.787-2.761(t, *J* = 5.2Hz, 2H), 2.619-2.609(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 167.8, 165.8, 158.2, 154.3, 146.4, 144.2, 118.0, 111.8, 86.0, 61.8, 56.2, 52.8, 52.1, 50.7, 46.9; IR(KBr, cm^{-1}): 3141(w, C-H), 3057(w, =C-H), 2951, 2908, 2842(w, C-H), 1740, 1697(s, C=O), 1582(s), 1475, 1438, 1396(m, Ar), 1371(w, CH_3), 1297(b, s, C-O), 1215, 1163, 1120(m), 1078, 1043, 1017(m, C-N), 916, 733(s, Ar); MS m/z(%): 366(8) ($M^{+\cdot}$), 335(16), 307(5), 278(27), 254(8), 242(11), 241(100), 226(4), 209 (18), 194(21), 181(28), 168(8), 140(12), 139(54), 82(8), 56(8), 44(31); **HRMS** (ESI) calcd for $C_{17}H_{23}N_2O_7$ $[M+H]^+$ 367.1505, found 367.1509.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(picolinoyloxyl)eth-1-yl]piperazine 35a



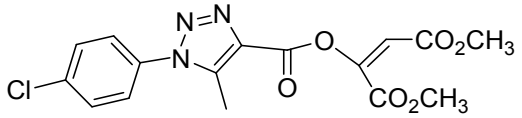
Yied: 77%; light brown sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.779-8.765(dd, *J* = 0.8Hz, *J* = 4.8Hz, 1H), 8.144-8.124(d, *J* = 8Hz, 1H), 7.900-7.857(dt, *J* = 1.6Hz, *J* = 3.6Hz, 1H), 7.533-7.499(m, 1H), 4.772(s, 1H), 4.566-4.537(t, *J* = 5.6Hz, 2H), 3.920(s, 3H), 3.638(s, 3H), 3.196-3.171(t, *J* = 4.8Hz, 4H), 2.858-3.829(t, *J* = 5.6Hz, 2H), 2.651-2.626(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.1, 166.2, 165.2, 154.6, 150.0, 147.9, 137.3, 127.2, 125.3, 86.5, 62.6, 56.4, 53.1, 52.3, 51.1, 47.1; IR(KBr, cm^{-1}): 3057(w, =C-H), 2951, 2844(w, C-H), 1742, 1722, 1697(s, C=O), 1585(s, C=N), 1438(m, Ar), 1370(w, CH_3), 1273, 1246(m, C-O), 1160, 1117 (m, C-N), 895, 753(s, Ar); MS m/z(%): 377(53) ($M^{+\cdot}$), 346(34), 328(21), 318(80), 300(56), 286(10), 271(5), 242(8), 241(77), 226(30), 205(57), 195(61), 179(93), 150(100), 149(54), 140(38), 124(20), 106(22), 82(28), 78(46), 69(46), 56(23). **HRMS** (ESI) calcd for $C_{18}H_{24}N_3O_6$ $[M+H]^+$ 378.1665, found 378.1669.

1-[2-(1-(4-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 36a



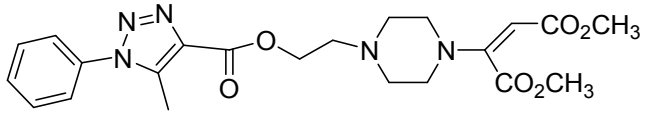
Yied: 68%; white needle, mp: 161-163°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.583-7.561(d, *J* = 8.8Hz, 2H), 7.438-7.416(d, *J* = 8.8Hz, 2H), 4.770(s, 1H), 4.545-4.516(t, *J* = 5.6Hz, 2H), 3.917(s, 3H), 3.637(s, 3H), 3.201-3.177(t, *J* = 4.8Hz, 4H), 2.876-2.849(t, *J* = 5.6Hz, 2H), 2.678(t, *J* = 4.8Hz, 4H), 2.598(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.2, 166.2, 161.6, 154.6, 139.3, 136.7, 136.5, 134.0, 130.2, 126.7, 86.7, 62.0, 56.5, 53.2, 52.4, 51.1, 47.2, 10.2; IR(KBr, cm^{-1}): 3093, 2951(w, =C-H), 2848(w, C-H), 1726(s, C=O), 1575(s), 1442, 1413, 1410(m, Ar), 1373(w, CH_3), 1273, 1253, 1223, 1159(m, C-O), 1106(m, C-N), 858, 786(s, Ar); MS m/z(%): 491(3)($M^{+\cdot}$), 460(5), 432(43), 400(7), 321(9), 319(28), 293(17), 266(11), 264(32), 241(74), 194(23), 192(69), 191(28), 166(18), 164(60), 152(53), 128(21), 111(36), 101(17), 75(20), 69(15), 44(100). **HRMS** (ESI) calcd for $C_{22}H_{27}ClN_5O_6$ $[M+H]^+$ 492.1650, found 492.1658.

1-(1-(4-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazole-4-carbonyloxy)-(*E*)-1,2-di(methoxycarbonyl)ethene 36b



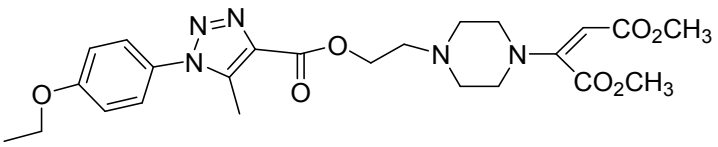
Yied: 38%; white flake, mp: 90-91°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.596-7.575(d, *J* = 8.4Hz, 2H), 7.460-7.439(d, *J* = 8.4Hz, 2H), 6.850(s, 1H), 3.886(s, 3H), 3.754(s, 3H), 2.635(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 163.2, 161.6, 158.3, 146.3, 140.7, 136.6, 135.3, 133.9, 130.2, 126.8, 117.9, 53.5, 52.4, 10.3; IR(KBr, cm^{-1}): 3098, 3070(w, =C-H), 2955, 2928(w, C-H), 1736(s, C=O), 1589(s), 1502, 1436(m, Ar), 1342(w, CH_3), 1279(m), 1201, 1179(m, C-O), 1104, 1063(m, C-N), 836, 737(s, Ar); MS m/z(%): 379(4)($M^{+\cdot}$), 348(3), 322(7), 320(20), 292(2), 264(2), 236(3), 222(22), 220(67), 194(23), 192(69), 191(28), 166(18), 164(60), 152(53), 128(21), 111(36), 101(17), 75(20), 69(15), 44(100). **HRMS** (ESI) calcd for $C_{16}H_{15}ClN_3O_6$ $[M+H]^+$ 380.0649, found 380.0649.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-yl]piperazine 37a



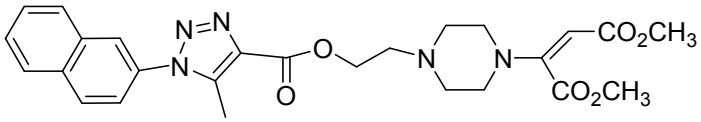
Yied: 71%; white flake, mp: 90-91°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.612-7.569(m, 3H), 7.477-7.453(m, 2H), 4.773(s, 1H), 4.546-4.517(t, *J* = 5.6Hz, 2H), 3.924(s, 3H), 3.639(s, 3H), 3.200-3.176(t, *J* = 4.8Hz, 4H), 2.861-2.832(t, *J* = 5.6Hz, 2H), 2.670-2.646(t, *J* = 4.8Hz, 4H), 2.603(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 168.2, 166.2, 161.7, 154.6, 139.3, 136.5, 135.5, 130.3, 129.9, 125.5, 86.5, 61.9, 56.5, 53.2, 52.4, 51.1, 47.2, 10.2; IR(KBr, cm^{-1}): 3067(w, =C-H), 2951, 2844(w, C-H), 1741, 1712 (s, C=O), 1581(s), 1437(m, Ar), 1278(w, CH_3), 1242(m, C-O), 1161, 1111(m, C-N), 768(s, Ar); MS m/z(%): 457 (2)($M^{+\cdot}$), 398(13), 366(3), 285(6), 259(6), 241(12), 230(9), 195(7), 181(8), 158(9), 130(6), 77(9), 69(10), 45(14), 44(100). **HRMS** (ESI) calcd for $C_{22}H_{28}N_5O_6$ $[M+H]^+$ 458.2040, found 458.2045.

1-[2-(1-(4-Ethoxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 38a



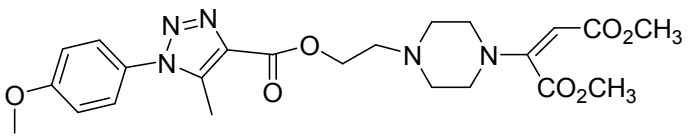
Yied: 64%; white flake, mp: 105-106°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.354-7.332(d, *J* = 8.8Hz, 2H), 7.054-7.032(d, *J* = 8.8Hz, 2H), 4.766(s, 1H), 4.518(m, 2H), 4.135-4.084(q, *J* = 6.8Hz, 2H), 3.913(s, 3H), 3.632(s, 3H), 3.186(m, 4H), 2.849(m, 2H), 2.666(m, 4H), 2.551(s, 3H), 1.480-1.446(t, *J* = 6.8Hz, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.1, 166.1, 161.7, 160.3, 154.6, 139.4, 136.3, 128.1, 126.8, 115.4, 86.6, 64.1, 61.9, 56.5, 53.1, 52.4, 51.0, 47.2, 14.8, 10.1; IR(KBr, cm^{-1}): 2974(w, =C-H), 2927, 2891(w, C-H), 1731(s, C=O), 1580(s), 1452(m, Ar), 1382(w, CH_3), 1218(m, C-O), 1090(m, C-N), 881, 630(s, Ar); MS m/z(%): 501(2)($M^{+\cdot}$), 470(3), 442(18), 398(19), 384(7), 329(8), 303(13), 255(14), 241(100), 211(21), 181(18), 140(11), 99(11), 70(7), 56(13), 44(39). **HRMS** (ESI) calcd for $C_{24}H_{32}N_5O_7$ $[M+H]^+$ 502.2302, found 502.2309.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(5-methyl-1-(naphthalen-2-yl)-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-yl]piperazine 39a



Yied: 82%; white flake, mp: 111-112°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.056-8.034(d, *J* = 8.8Hz, 1H), 7.974-7.934(m, 3H), 7.654-7.604(m, 2H), 7.551-7.525(dd, *J* = 8.8Hz, *J* = 2Hz, 1H), 4.776(s, 1H), 4.561-4.533(t, *J* = 5.6Hz, 2H), 3.920(s, 3H), 3.636(s, 3H), 3.208-3.183(t, *J* = 5.2Hz, 4H), 2.889-2.862(t, *J* = 5.2Hz, 2H), 2.686(t, *J* = 5.2Hz, 4H), 2.650(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.1, 166.2, 161.7, 154.6, 139.5, 136.6, 133.5, 133.1, 132.8, 130.1, 128.5, 128.1, 128.0, 127.8, 124.6, 122.7, 86.7, 61.9, 56.5, 53.1, 52.4, 51.1, 47.2, 10.3; IR(KBr, cm^{-1}): 2974(w, =C-H), 2927, 2890(w, C-H), 1730, 1703(s, C=O), 1581(s), 1452(m, Ar), 1381(w, CH_3), 1275(m, C-O), 1192, 1090(m, C-N), 881(s, Ar); MS m/z(%): 507(1)($M^{+\cdot}$), 469(2), 436(7), 377(7), 370(14), 349(11), 324(23), 293(19), 272(16), 241(100), 226(5), 209(7), 185(45), 183(34), 167(4), 112(32), 99(72), 97(13), 70(21), 44(29). **HRMS** (ESI) calcd for $C_{26}H_{30}N_5O_6$ $[M+H]^+$ 508.2196, found 508.2190.

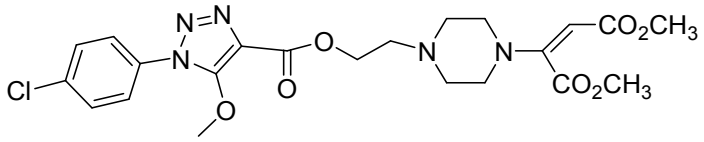
1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(1-(4-methoxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-yl]piperazine 40a



Yied: 60%; white block, mp: 118-119°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.378-7.356(d, *J* = 8.8Hz, 2H), 7.077-7.055(d, *J* = 8.8Hz, 2H), 4.769(s, 1H), 4.534-4.505(t, *J* = 5.6Hz, 2H), 3.916(s, 3H), 3.891(s, 3H), 3.632(s, 3H), 3.205-3.180(t, *J* = 4.8Hz, 4H), 2.866-2.838(t, *J* = 5.6Hz, 2H), 2.680-2.656(t, *J* = 4.8Hz, 4H), 2.556(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 166.1, 161.6, 160.8, 154.5, 139.3, 136.2, 128.2, 126.8, 114.8, 86.4, 61.7, 56.4, 55.7, 53.0, 52.3, 50.9, 47.0, 10.0; IR(KBr, cm^{-1}): 2975(w, =C-H), 2928, 2892(w, C-H), 1736, 1656(s, C=O), 1452(m, Ar), 1382(w, CH_3), 1308(m, C-O), 1160(m, C-N), 881(s, Ar); MS

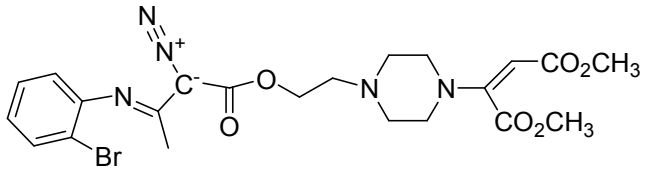
m/z(%): 487(3)($M^{+\cdot}$), 443(12), 442(48), 428(51), 398(10), 329(21), 315(30), 303(54), 289(35), 266(16), 260(23), 241(100), 234(21), 211(17), 209(34), 195(45), 188(50), 181(35), 160(25), 146(50), 140(31), 112(26), 99(31), 70(32), 56(26), 44(67). **HRMS** (ESI) calcd for $C_{23}H_{30}N_5O_7$ $[M+H]^+$ 488.2145, found 488.2141.

1-[2-(1-(4-Chlorophenyl)-5-methoxy-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-y]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 41a



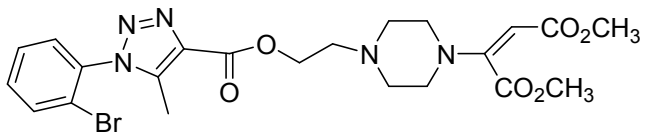
Yied: 63%; white flake, mp: 145-147°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.974-7.952(d, *J* = 8.8Hz, 2H), 7.475-7.453(d, *J* = 8.8Hz, 2H); 4.763(s, 1H), 4.482-4.455(t, *J* = 5.6Hz, 2H), 4.326(s, 3H), 3.913(s, 3H), 3.631(s, 3H), 3.189-3.167(t, *J* = 4.4Hz, 4H), 2.827-2.800(t, *J* = 5.6Hz, 2H), 2.678-2.667(t, *J* = 4.4Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.1, 166.1, 159.2, 155.5, 154.6, 134.0, 133.7, 129.5, 122.2, 109.9, 86.3, 62.3, 56.3, 53.1, 52.4, 51.0, 47.1, 42.0; IR(KBr, cm^{-1}): 3056 (w, =C-H), 2952, 2845(w, C-H), 1742, 1697(s, C=O), 1582(s), 1422(m, Ar), 1371(w, CH_3), 1273, 1219, 1161(m, C-O), 1110, 1092(m, C-N), 839, 736(s, Ar); MS m/z(%): 507(2)($M^{+\cdot}$), 476(5), 448(12), 335(7), 309(19), 280(7), 254(11), 241(33), 236(17), 209(11), 195(24), 181(17), 168(10), 140(10), 111(15), 82(23), 70(13), 56(19), 44(100). **HRMS** (ESI) calcd for $C_{22}H_{27}ClN_5O_7$ $[M+H]^+$ 508.1599, found 508.1592.

1-{2-[2-Diazo-3-(*E*)-(2-bromophenylimino)-butyroyloxyl]ethan-1-yl}-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperaine 42a



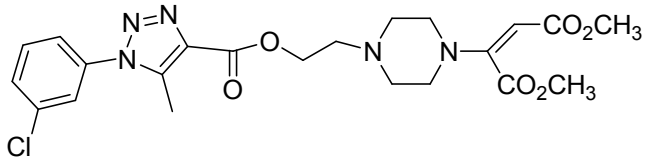
Yied: 35%; white flake, mp: 83-84°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.792-7.769(dd, *J* = 8.0; 5.2Hz, 1H), 7.535-7.408(m, 3H), 4.717(s, 1H), 4.717-4.695(t, *J* = 5.2Hz, 2H), 3.909(s, 3H), 3.641(s, 3H), 3.037-3.012(t, *J* = 5.2Hz, 4H), 2.754(s, 3H), 2.684-2.658(t, *J* = 5.2Hz, 2H), 2.421-2.396(t, *J* = 5.2Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 192.8, 168.1, 166.1, 154.5, 152.5, 133.8, 133.8, 132.3, 130.6, 129.5, 128.6, 121.6, 86.8, 73.6, 57.1, 53.1, 52.2, 51.1, 47.1, 28.3; IR(KBr, cm^{-1}): 3065, 2998(w, =C-H), 2843(w, C-H), 2134(s, diazo-), 1741, 1712(s, C=O), 1493, 1438(m, Ar), 1365(w, CH_3), 1279, 1222, 1162(m, C-O), 1043, 1023(m, C-N), 869, 768(s, Ar); MS m/z(%): 535(1)($M^{+\cdot}$), 403(6), 402(22), 370(4), 331(4), 281(9), 255(37), 254(25), 241(43), 239(7), 209(31), 202(26), 195(81), 181(43), 168(39), 140(27), 135(15), 91(21), 82(56), 70(21), 56(35), 44(100). **HRMS** (ESI) calcd for $C_{22}H_{27}BrN_5O_6$ $[M+H]^+$ 536.1145, found 536.1149.

1-[2-(1-(2-Bromophenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 43a



Yied: 49%; white block, mp: 95-96°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.820-7.801(d, *J* = 8.4Hz, 1H), 7.580-7.485(m, 2H), 7.442-7.423(d, *J* = 7.6Hz, 1H), 4.772(s, 1H), 4.543-4.516(t, *J* = 5.6Hz, 2H), 3.914(s, 3H), 3.632(s, 3H), 3.204-3.194(t, *J* = 4.4Hz, 4H), 2.868-2.841(t, *J* = 5.6Hz, 2H), 2.678-2.667(t, *J* = 4.4Hz, 4H), 2.460(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 166.0, 161.5, 154.5, 140.7, 136.0, 134.6, 133.9, 132.5, 129.3, 128.8, 121.5, 86.5, 61.9, 56.4, 53.0, 52.3, 50.9, 47.1, 9.6; IR(KBr, cm^{-1}): 3065, 2998(w, =C-H), 2843(w, C-H), 1741, 1712(s, C=O), 1493, 1438(m, Ar), 1365(w, CH_3), 1279, 1222, 1162(m, C-O), 1043, 1023(m, C-N), 869, 768(s, Ar)**;** MS m/z(%): 535(2)($M^{+\cdot}$), 476(14), 447(5), 363(6), 337(9), 310(7), 282(6), 262(26), 241(100), 230(9), 209(21), 195(40), 181(37), 168(19), 140(15), 112(3), 82(18), 56(17); **HRMS** (ESI) calcd for $C_{22}H_{27}BrN_5O_6$ $[M+H]^+$ 536.1145, found 536.1141.

1-[2-(1-(3-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazole-4-carboyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 44a

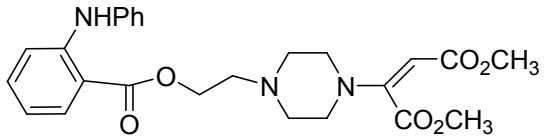


Yied: 67%; white flake, mp: 88-89°C, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.576-7.513(m, 3H), 7.393-7.366(m, 1H), 4.768(s, 1H), 4.540-4.512(t, *J* = 5.6Hz, 2H), 3.916(s, 3H), 3.635(s, 3H), 3.195-3.132(t, *J* = 4.8Hz, 4H), 2.860-2.831(t, *J* = 5.6Hz, 2H), 2.670-2.645(t, *J* = 4.8Hz, 4H), 2.619(s, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 166.0, 161.4, 154.5, 139.2, 136.6, 136.4, 135.5, 130.8, 130.4, 125.6, 123.5, 86.5, 61.9, 56.4, 53.0, 52.3, 50.9, 47.1, 10.1; IR(KBr, cm^{-1}): 3062(w, =C-H), 2951(w, C-H), 1742(s, C=O), 1491, 1438(m, Ar), 1371(w, CH_3), 1272, 1242, 1213, 1162(m, C-O), 1116, 1022(m, C-N), 843, 736(s, Ar); MS m/z(%): 491(3)($M^{+\cdot}$), 460(5), 432(43), 400(7), 321(9), 319(28), 293(17), 266(11), 264(32), 241(74), 209(23), 195(30), 192(34), 181(41), 152(24), 140(22), 111(5), 99(16), 82(22), 70(19), 56(28), 44(100). **HRMS** (ESI) calcd for $C_{22}H_{27}ClN_5O_6$ $[M+H]^+$ 492.1650, found 492.1646.

Typical procedure for the reactions

To a clear solution of the armotic acid (1 mmol, 1.00 equiv.) in anhydrous THF (2~8 ml) was added the DABCO (1 mmol, 1.00 equiv.) under stirring at room temperature. After the reaction mixture was stirred for 0.5 hours, the solution was changed from clear to paste. Then, DMAD (2.2mmol, 2.20 equiv.) was dropwise added to paste the mixture and the color of the paste mixture was gradually changed to dark and into solution. The reaction mixture was stirred for 8 hours at room temperature. The solvent was removed under reduced pressure. The given residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to afford product.

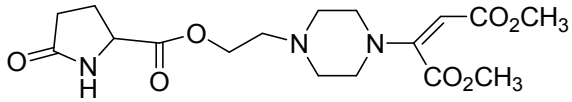
1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(2-(phenylamino)benzoyloxyl)eth-1-yl]piperazine 45a



Yied: 89%; light brown sticky clumps, ^{1}HNMR(400MHz, $CDCl_3$): δ = 9.434(s, 1H), 7.932-

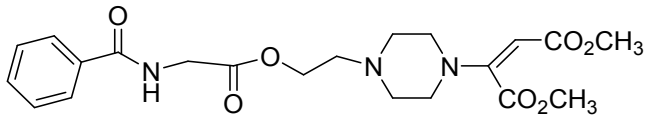
7.914(d, *J* = 7.2Hz, 1H), 7.341-7.274(m, 3H), 7.246-7.213(m, 3H), 7.089-7.052(t, *J* = 7.2Hz, 1H), 6.732-6.696(t, *J* = 7.2Hz, 1H), 4.758(s, 1H), 4.414-4.386(t, *J* = 5.6Hz, 2H), 3.901(s, 3H), 3.621(s, 3H), 3.156-3.133(t, *J* = 4.4Hz, 4H), 2.783-2.755(t, *J* = 5.6Hz, 2H), 2.604-2.582(t, *J* = 4.4Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.0, 167.9, 165.9, 154.4, 147.8, 140.5, 134.2, 131.5, 129.3, 123.6, 122.4, 117.1, 113.9, 111.7, 86.3, 61.7, 56.3, 52.9, 52.1, 50.8, 46.9; IR(KBr, cm^{-1}): 3322(m, -NH), 3088 (w, =C-H), 2950, 2904, 2837(w, C-H), 1744, 1686(s, C=O), 1578(s), 1517, 1453, 1438(m, Ar), 1371(w, CH_3), 1319(m), 1258, 1231, 1161(m, C-O), 1109, 1088(m, C-N), 752, 733(s, Ar); MS m/z(%): 467(27) ($M^{+\cdot}$), 436(8), 408(31), 330(25), 282(9), 255(18), 241(86), 240(11), 213(33), 196(57), 195(61), 181(16), 167(32), 155(35), 149(16), 139(11), 115(8), 97(12), 91(43), 83(20), 69(20), 44(100). **HRMS** (ESI) calcd for $C_{25}H_{30}N_3O_6$ $[M+H]^+$ 468.2135, found 468.2132.

(±)-1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(5-oxopyrrolidine-2-carboyloxyl)eth-1-yl]piperazine 46a



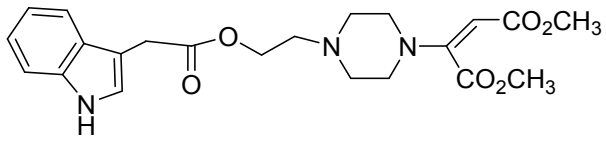
Yied: 68%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.540(s, 1H), 4.780(s, 1H), 4.304-4.264(m, 3H), 3.915(s, 3H), 3.634(s, 3H), 3.182-3.159(t, *J* = 4.8Hz, 4H), 2.693-2.666(t, *J* = 5.6Hz, 2H), 2.582-2.558(t, *J* = 4.8Hz, 4H), 2.504-2.421(m, 1H), 2.401-2.315(m, 2H), 2.249-2.183(m, 1H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 178.6, 172.1, 168.0, 166.0, 154.4, 86.3, 61.9, 56.2, 55.6, 53.0, 52.1, 50.9, 46.9, 29.3, 24.8; IR(KBr, cm^{-1}): 3095, 3059(w, =C-H), 2953, 2847(w, C-H), 1743, 1696(s, C=O), 1584(s), 1439(b, Ar), 1372(w, CH_3), 1278, 1212, 1160, 1112(m, C-O), 1042, 1019(m, C-N), 868, 734(s, Ar); MS m/z(%): 383(16)($M^{+\cdot}$), 352(12), 324(18), 292(9), 272(3), 255(5), 242(11), 241(98), 239(7), 209(20), 199(9), 186(14), 181(27), 149(15), 140(17), 100(9), 84(44), 73(11), 56(13), 44(100). **HRMS** (ESI) calcd for $C_{17}H_{26}N_3O_7$ $[M+H]^+$ 384.1771, found 384.1768.

1-[2-(2-(Benzamido)acetoyloxy)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 47a



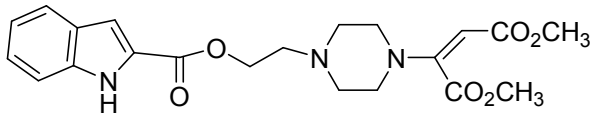
Yied: 90%; light yellow sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 7.851-7.832(d, *J* = 7.6Hz, 2H), 7.524-7.487(t, *J* = 7.6Hz, 1H), 7.434-7.397(m, *J* = 7.6Hz, 3H), 4.731(s, 1H), 4.271-4.244(t, *J* = 5.6Hz, 2H), 4.198-4.184(d, *J* = 5.6Hz, 2H), 3.892(s, 3H), 3.616(s, 3H), 3.118-3.094(t, *J* = 4.8Hz, 4H), 2.651-2.624(t, *J* = 5.6Hz, 2H), 2.523-2.499(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 169.8, 168.0, 167.6, 166.0, 154.3, 133.4, 131.8, 128.5, 127.1, 86.1, 62.2, 56.1, 52.9, 52.0, 50.9, 46.8, 41.7; IR(KBr, cm^{-1}): 3359(m, -NH), 3063, 2951, 2843(w, =C-H), 1744, 1695(s, C=O), 1581(s), 1537, 1489, 1439(m, Ar), 1373(w, CH_3), 1278, 1163(m, C-O), 1110, 1081, 1043(m, C-N), 801, 732(s, Ar); MS m/z(%): 433(9)($M^{+\cdot}$), 402(9), 374(26), 347(22), 268(9), 261(35), 241(100), 235(25), 209(20), 195(15), 181(24), 168(8), 140(11), 105(31), 77(12), 44(29); **HRMS** (ESI) calcd for $C_{21}H_{28}N_3O_7$ $[M+H]^+$ 434.1927, found 434.1922.

1-[2-(2-(1*H*-Indol-3-yl)acetoyloxy)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 48a



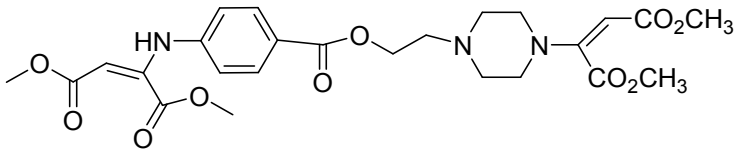
Yied: 61%; light brown sticky clumps, ^{1}HNMR(400MHz, $CDCl_3$): δ = 8.604(s, 1H), 7.603-7.583(d, *J* = 8Hz, 1H), 7.334-7.314(d, *J* = 8Hz, 1H), 7.194-7.156(m, 1H), 7.122-7.063(m, 2H), 4.703(s, 1H), 4.214-4.188(t, *J* = 5.2Hz, 2H), 3.898(s, 3H), 3.764(s, 2H), 3.649(s, 3H), 2.959-2.934(t, *J* = 4.8Hz, 4H), 2.581-2.554(t, *J* = 5.2Hz, 2H), 2.333-2.308(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 172.1, 168.3, 166.2, 154.5, 136.2, 128.9, 123.4, 122.1, 119.6, 118.9, 111.5, 108.1, 86.3, 62.0, 56.3, 53.1, 52.0, 51.1, 46.9, 31.6; IR(KBr, cm^{-1}): 3396(m, N-H), 3084(w, =C-H), 2953, 2875, 2849(w, C-H), 1732, 1695(s, C=O), 1582(s), 1457, 1438(m, Ar), 1372(w, CH_3), 1279(m, C-O), 1216, 1162(m, C-N), 911, 733(s,Ar); MS m/z(%): 429(69)($M^{+\cdot}$), 398(6), 370(4), 343(7), 273(11), 255(6), 242(12), 241(100), 239(7), 209(14), 202(10), 181(19), 170(8), 157(31), 149(16), 130(41), 129(10), 103(3), 82(7), 56(6), 44(37). **HRMS** (ESI) calcd for $C_{22}H_{28}N_3O_6$ $[M+H]^+$ 430.1978, found 430.1971.

1-[2-(1*H*-Indole-2-carboyloxyl)eth-1-yl]-4-[(*E*)-1,2-(dimethoxycarbonyl)ethen-1-yl]piperazine 49a



Yied: 77%; light brown sticky clumps, ^{1}H NMR(400MHz, $CDCl_3$): δ = 9.877(s, 1H), 7.673-7.653(d, *J* = 8.4Hz, 1H), 7.418-7.397(d, *J* = 8.4Hz, 1H), 7.318-7.272(m, 1H), 7.174-7.114(m, 2H), 4.763(s, 1H), 4.466-4.439(t, *J* = 5.6Hz, 2H), 3.893(s, 3H), 3.630(s, 3H), 3.161-3.136(d, *J* = 4.8Hz, 4H), 2.786-2.758(d, *J* = 5.6Hz, 2H), 2.607-2.582(d, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 168.1, 166.1, 162.0, 154.5, 137.2, 127.3, 127.0, 125.4, 122.6, 120.8, 112.1, 109.0, 86.4, 61.9, 56.5, 53.1, 52.2, 51.0, 47.0; IR(KBr, cm^{-1}): 3059(w, =C-H), 2951, 2841(w, C-H), 1743, 1702(s, C=O), 1582(s), 1531, 1498, 1438(m, Ar), 1373(w, CH_3), 1341(m), 1307, 1272, 1243(m, C-O), 1194, 1163(m, C-N), 826, 751(s, Ar); MS m/z(%): 415(16)($M^{+\cdot}$), 384(7), 329(26), 286(32), 254(15), 241(100), 231(11), 209(15), 181(20), 144(41), 143(32), 115(11), 89(7), 82(9), 69(5), 56(7), 44(61); **HRMS**(ESI) calcd for $C_{21}H_{26}N_3O_6$ $[M+H]^+$ 416.1822, found 416.1818.

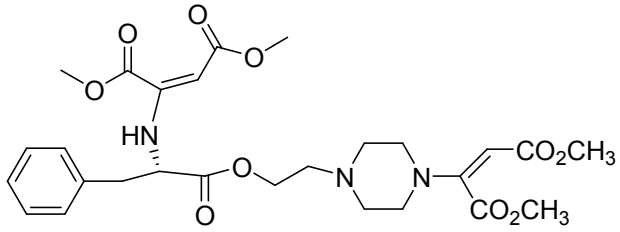
1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-[2-(4-((*E*)-1,2-di(methoxycarbonyl)vinylamino)benzoyloxyl)eth-1-yl]piperazine 50a



Yied: 69%; light yellow sticky clumps, ^{1}HNMR(400MHz, $CDCl_3$): δ = 9.746(s, 1H), 7.950-7.928(d, *J* = 8.8Hz, 2H), 6.888-6.866(d, *J* = 8.8Hz, 2H), 5.559(s, 1H), 4.780(s, 1H), 4.442-4.414(t, *J* = 5.6Hz, 2H), 3.916(s, 3H), 3.759(s, 6H), 3.635(s, 3H), 3.203-3.178(t, *J* = 4.8Hz, 4H), 2.812-2.784(t, *J* = 5.6Hz, 2H), 2.650-2.625(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 169.5, 168.1, 166.1, 165.9, 164.4, 154.5, 146.2, 144.6, 131.0, 124.9, 119.2, 97.1, 86.6, 62.0, 56.5, 53.1, 53.0, 52.3, 51.5, 51.0, 47.0; IR(KBr, cm^{-1}): 3058(w, =C-H), 2950, 2924, 2851(w, C-H), 1741, 1695(s, C=O), 1582(s, C=N), 1511, 1437, 1370(m, Ar), 1275(w, CH_3),

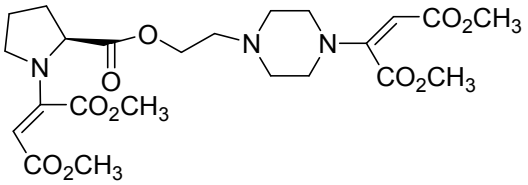
1213, 1160, 1115(m, C-O), 1042, 1022(m, C-N), 794, 743(s, Ar); MS m/z(%): 533(1) ($M^{+\cdot}$), 485(2), 377(9), 349(8), 346(17), 318(17), 292(6), 291(31), 286(6), 254(7), 242(12), 241(100), 220(6), 209(18), 205(26), 193(15), 181(25), 151(7), 150(58), 140(11), 106(23), 78(12), 44(17). **HRMS** (ESI) calcd for $C_{25}H_{32}N_3O_{10}$ $[M+H]^+$ 534.2088, found 534.2082.

1-[(*E*)-1,2-(Dimethoxycarbonyl)ethen-1-yl]-4-{2-[(2-(*S*)-(*E*)-1,2-(dimethoxycarbonyl)ethen-1-amino)-3-phenyl-propionoyloxyl]ethan-1-yl}piperaine 51a



Yied: 55%; light brown sticky clumps, $[\alpha]^{25}_D$= -22.0º(C = 0.1, $CHCl_3$), ^{1}H NMR(400MHz, $CDCl_3$): δ = 8.433-8.415(d, *J* = 7.8Hz, 1H), 7.319-7.207(m, 5H), 5.283 (s, 1H), 4.915-4.860(m, 1H), 4.76(s, 1H), 4.239-4.213(t, *J* = 5.2Hz, 2H), 3.917(s, 3H), 3.721(s, 3H), 3.686(s, 3H), 3.673(s, 3H), 3.149-3.114(m, 5H), 3.051-2.997(m, 1H), 2.610-2.583(t, *J* = 4.8Hz, 2H), 2.507-2.483(t, *J* = 4.8Hz, 4H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 171.8, 170.1, 168.1, 166.1, 163.9, 154.5, 148.7, 136.0, 129.6, 128.7, 127.2, 90.5, 86.5, 62.4, 58.3, 56.2, 53.1, 52.8, 52.1, 51.1, 51.0, 47.0, 40.2; IR(KBr, cm^{-1}): 3058, 3029(w, =C-H), 2952(w, C-H), 1739(s, C=O), 1696(s), 1584(m, Ar), 1496(w, CH_3), 1272, 1217, 1163(m, C-O), 1114, 1041(m, C-N), 979, 736(s, Ar); MS m/z(%): 561(11)($M^{+\cdot}$), 420(9), 419(38), 402(9), 377(3), 262(8), 260(22), 241(31), 239(9), 209(8), 181(13), 170(17), 169(11), 115(11), 113(24), 99(61), 91(20), 70(28), 56(31), 44(100); **HRMS** (ESI) calcd for $C_{27}H_{36}N_3O_{10}$ $[M+H]^+$ 562.2401, found 562.2407.

1-[(*E*)-1,2(Dimethoxycarbonyl)ethen-1-yl]-4-{2-[*N*-[(*E*)-1,2-di(methoxycarbonyl)ethen-1-yl]-(*S*)-pyrrolidine-2-carboyloxyl]eth-1-yl}piperazine 52a



Yied: 78%; light yellow sticky clumps, $[\alpha]^{25}_D$= -68.0º(C = 0.1, $CHCl_3$), ^{1}H NMR(400MHz, $CDCl_3$): δ = 4.767 (s, 1H), 4.568(s, 1H), 4.282(t, *J* = 5.6Hz, 2H), 4.138-4.103(m, 1H), 3.908-3.889(2s, 6H), 3.625-3.619(2s, 6H), 3.457-3.352(m, 2H), 3.173-3.149(t, *J* = 4.8Hz, 4H), 2.736-2.724(t, *J* = 5.6Hz, 2H), 2.588-2.581(t, *J* = 4.8Hz, 4H), 2.333-2.232(m, 1H), 2.129-2.064(m, 3H); ^{13}C NMR(100MHz, $CDCl_3$): δ = 171.3, 167.8, 167.5, 165.8, 165.4, 154.3, 151.2, 86.2, 86.0, 61.9, 60.9, 56.1, 52.7, 52.0, 50.7, 50.6, 48.5, 46.7, 30.3, 23,0, 20.8; IR(KBr, cm^{-1}): 3058(w, =C-H), 2952, 2883, 2850(w, C-H), 1743, 1694(s, C=O), 1582(s), 1439, 1420(m, Ar), 1375(w, CH_3), 1345(m), 1272, 1222, 1158 (m, C-O), 1109, 1093, 1043, 1024(m, C-N), 796, 735(s, Ar)**;** MS m/z(%): 511(100)($M^{+\cdot}$), 480(16), 478(4), 420(6), 334(8), 281(10), 255(11), 252(16), 241(35), 239(27), 214(16), 212(32), 181(14), 154(18), 140(11), 85(12), 70(8), 44(37); **HRMS** (ESI) calcd for $C_{23}H_{34}N_3O_{10}$ $[M+H]^+$ 512.2244, found 512.2248.