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Metal free highly efficient C-N bond formation through 1,6-addition: Synthesis and photophysical studies of diaryl methyl amino acid esters (DMAAEs)

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Supporting information

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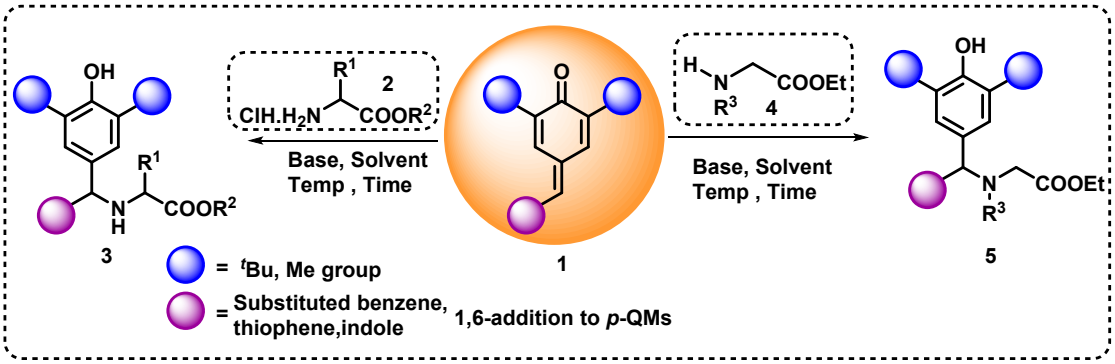
I. General Information

All reactions were performed in flame-dried glassware with a magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica gel 60- 120 Mesh basified by triethylamine. Analytical thin layer chromatography (TLC) was done using silica gel (silica gel GF254). TLC plates were analyzed by an exposure to ultraviolet light and/or by staining with dragendorff solution and/or by charring with ninhydrin solution. The starting *para*-quinone methides were prepared through literature known procedures.[1,2] Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance 400 Spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak [$CHCl_3$; δ_H = 7.26 and δ_C = 77.00]. Extra numbers of ^{13}C NMR peaks are for diastereomeric mixtures. In ^{13}C NMR spectra, they are reported as diastereomers and were not separated to report as single diastereomer. Multiplicities were given as: s (singlet); brs (broad singlet), d (doublet); t (triplet); q (quartet); dd (doublets of doublet); m (multiplets). High resolution mass spectra were taken with a 3000 mass spectrometer, using Waters Agilent 6520-Q-TofMS/MS system and JEOL-AccuTOF JMST100LC. FT-IR spectra were obtained on Perkin Elmer Spectrum Two FTIR Spectrometer. Melting points are uncorrected and were determined in capillary tubes on SMP 10 melting point apparatus. Electronic spectra were recorded on a CARY 100 BIO UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Horiba spectrofluorometer (Fluorolog) and quantum yield was calculated using the integrated sphere. Raman spectra were recorded on a Horiba LabRAM HR Evolution Raman microspectrometer. 633 nm laser source was used for sample excitation.

II. Experimental procedure

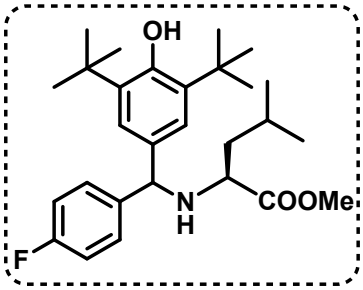


To a solution of 0.1 milimol of **1** in Chloroform (2ml) in a 10 ml round bottom flask, 0.2 milimol of **2** (amino acid ester hydrochlorides) or **4** was added. Then the reaction mixture was

then cooled to 0 ° C and K_2CO_3(6equiv) was added and the reaction mixture was stirred for 12h at RT and monitored by TLC until the starting material could not be detected. The reaction mixture was quenched with water and extracted with DCM (5 mL × 3). The organic layer was dried over Na_2SO_4 and evaporated in vacuum. The residue was purified by silica gel column chromatography to afford the desired product **3** or **5**.

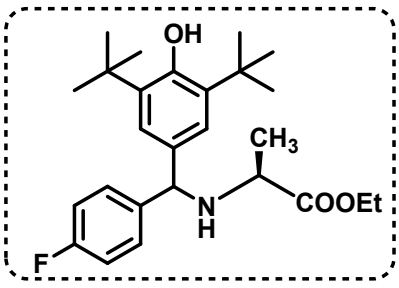
III. Spectroscopic data of synthesized compounds

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-L-leucinate (3a):



Light Yellow oil, isolated yield- 40mg (90%) ; **R_f** (10% EtOAC/Hexane) - 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3636, 3432, 2950, 1731, 1430, 1312, 1200, 1150, 1070, 814, 760; **^{1}H NMR(400MHz,$CDCl_3$):** δ 7.42-7.39 (1H,m), 7.36-7.33 (1H,m), 7.15 (1H,s), 7.10 (1H,s), 7.01-6.93 (2H,m), 5.10-5.09 (1H,m), 4.65 (1H,s), 3.74-3.71 (3H,m), 3.18-3.13 (1H,m), 1.96-1.88 (2H,m), 1.48-1.44 (1H,m), 1.41-1.40 (18H, m), 0.91-0.89 (3H,m), 0.81-0.77 (3H,m); **^{13}C NMR(100 MHz,$CDCl_3$):** δ 176.85, 176.68, 162.91, 162.76, 160.97, 160.81, 152.91, 152.85, 140.98, 138.95, 135.77, 134.95, 132.83, 129.20, 129.14, 128.78, 128.72, 124.13, 123.92, 115.16, 114.99, 65.05, 57.83, 57.42, 51.55, 43.34, 34.36, 30.32, 30.26, 24.80, 24.72, 23.21, 23.09, 22.06, 22.03; **HRMS(ESI):** m/z calcd for $C_{28}H_{41}FNO_3(M+H)^+$- 458.3065, found 458.3058.

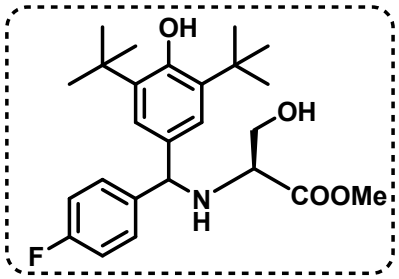
ethyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-L-alaninate(3b):



Light Yellow oil, isolated yield- 37mg (89%); **R_f** (10% EtOAC/Hexane) - 0.5; **IR (in CH_2Cl_2):** ν_{max}; 3396, 3020, 2964, 1725, 1508, 1434, 1216, 1156, 1047, 762; **^{1}H NMR(400MHz,$CDCl_3$):** δ 7.42-7.38 (1H,m), 7.34-7.30 (1H,m), 7.16 (1H,s), 7.09 (1H,s), 7.01-6.93 (2H,m), 5.09 (1H,s),

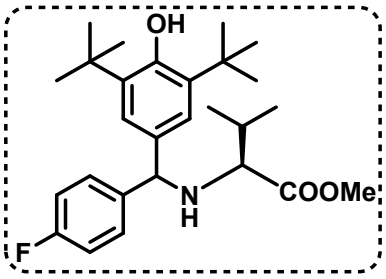
4.73-4.72 (1H,m), 4.22-4.15 (2H,m), 3.30-3.18 (1H,m), 1.41-1.39 (18H,m), 1.31-1.27 (6H,m); **^{13}C NMR(100 MHz,$CDCl_3$):** δ 176.15, 176.04, 162.87, 152.87, 139.08, 135.80, 134.77, 129.05, 128.99, 128.95, 128.88, 123.94, 115.20, 115.04, 64.91, 64.75, 60.59, 60.53, 54.61, 54.38, 34.36, 30.37, 30.27, 19.60, 14.36; **HRMS(ESI):** m/z calcd for $C_{26}H_{37}FNO_3$ $(M+H)^+$- 430.2752, found 430.2747.

methyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-L-serinate(3c):



Light Yellow oil, isolated yiel- 48mg (85%) ; **R_f** (20% EtOAC/Hexane)- 0.4; **IR(in CH_2Cl_2):** ν_{max}; 3410, 3020, 2401, 1611, 1433, 1215, 1047, 760; **1H NMR (400MHz,$CDCl_3$):** δ 7.39-7.31 (2H,m), 7.14(1H,s), 7.09 (1H,s), 7.02-6.96 (2H,m), 5.14-5.13 (1H,m), 4.81 (1H,s), 3.76-3.70 (4H,m), 3.66-3.61 (1H,m), 3.41-3.34 (1H,m), 1.40-1.39 (18H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 173.86, 173.72, 163.14, 160.77, 160.70, 153.07, 140.04, 138.48, 135.99, 133.92, 132.22, 129.19, 129.11, 128.90, 128.83, 124.04, 123.96, 115.43, 115.22, 64.99, 64.83, 63.22, 60.60, 60.35, 52.17, 34.39, 30.32, 30.25; **HRMS(ESI):** m/z calcd for $C_{25}H_{35}FNO_4(M+H)^+$ - 432.2545, found 432.2542.

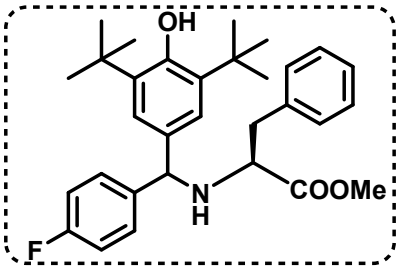
methyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-L-valinate(3d):



Light Yellow oil, isolated yield- 50.4mg (88%) ; **R_f** (10% EtOAC/Hexane) - 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3635, 3410, 2960, 1720, 1610, 1430, 1320, 1210, 1160, 1017, 761; **1H NMR (400MHz,$CDCl_3$):** δ 7.42-7.39 (1H,m), 7.34-7.31 (1H,m), 7.18 (1H,s), 7.12 (1H.s), 7.00-6.93 (2H,m), 5.10-5.08 (1H,s), 4.60 (1H,m), 3.72 (3H,s), 2.98-2.88 (1H,m),1.96-1.86 (2H,m), 1.41-1.40 (18H, m), 0.98-0.92 (6H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 176.10, 175.89, 163.13, 162.99, 160.69, 160.56, 152.84, 141.18, 139.02, 135.74, 135.11, 132.79, 129.26, 129.18, 128.83, 128.76, 124.11, 123.89, 115.23, 115.16, 115.02, 114.95, 65.24, 65.07, 64.63, 51.37, 34.36, 31.87,

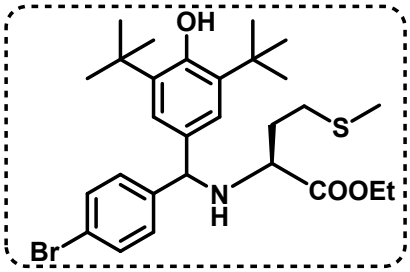
31.81, 30.39, 30.29, 30.25, 19.86, 19.63, 18.66, 18.43; **HRMS(ESI):** m/z calcd for $C_{27}H_{39}FNO_3(M+H)^+$- 444.2908, found 444.2901.

methyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-L-phenylalaninate(3e):



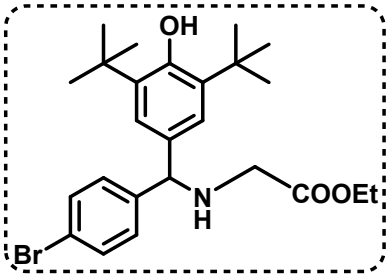
Yellow solid, isolated yield-57mg (89%); Mp-103^{o}C; **R_f** (10% EtOAC/Hexane) - 0.6; **IR(in CH_2Cl_2):** ν_{max}; 3427, 3020, 1731, 1632, 1433, 1216, 1044, 761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.31-7.24 (4H,m), 7.22-7.14 (3H,m), 7.08 (1H,s), 7.04 (1H,s), 6.96-6.92 (1H,m), 6.85-6.81 (1H,m), 5.08-5.07 (1H,m), 4.67-4.65 (1H,m), 3.67-3.63 (3H,m), 3.48-3.31 (1H,m), 2.99-2.93 (2H,m), 1.39-1.36 (18H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 175.32, 163.03, 160.56, 152.88, 140.56, 138.94, 137.83, 137.54, 135.78, 134.99, 132.81, 129.65, 129.31, 128.89, 128.81, 128.37, 128.17, 126.65, 126.59, 123.95, 123.70, 115.23, 115.15, 115.02, 114.94, 64.90, 64.84, 60.46, 60.42, 51.67, 51.57, 40.28, 40.17, 34.37, 34.33, 30.33, 30.27; **HRMS(ESI):** m/z calcd for $C_{31}H_{39}FNO_3(M+H)^+$- 492.2908, found 492.2897.

ethyl((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-L-methioninate(3f):



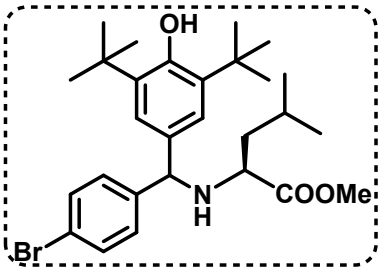
Light Yellow oil, isolated yield- 61mg (85%) ; **R_f** (10% EtOAC/Hexane) – 0.6; **IR(in CH_2Cl_2):** ν_{max}; 3635, 3332, 2962, 1725, 1435, 1350, 1210, 1120, 759; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.44-7.38 (2H,m), 7.32- 7.30 (1H,m), 7.26-7.24 (1H,m), 7.14 (1H,s), 7.09 (1H,s), 5.12- 5.11 (1H,m), 4.67 (1H,s), 4.22-4.16 (2H,m), 3.27-3.19 (1H,m), 2.76-2.67 (1H,m), 2.61-2.53 (1H,m), 2.07-2.06 (3H,m), 1.94-1.90 (1H,m), 1.85-1.79 (1H,m), 1.41-1.39 (18H,m), 1.29-1.25 (3H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 175.22, 175.08, 153.04, 153.00, 144.05, 142.32, 135.91, 134.41, 132.37, 131.51, 129.41, 128.99, 124.02, 123.87, 120.73, 65.23, 65.13, 60.78, 60.75, 58.39, 58.09, 34.39, 33.49, 33.46, 30.89, 30.74, 30.37, 30.27, 15.44, 15.38, 14.39; **HRMS(ESI):** m/z calcd for $C_{28}H_{41}BrNO_3S$ $(M+H)^+$ - 550.1985, found 550.1983.

ethyl((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)glycinate(3g):



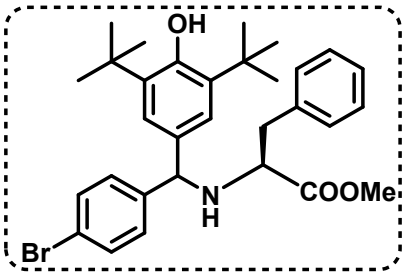
Light Yellow oil, isolated yield- 53.4mg (86%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3638, 3350, 2960, 1733, 1481, 1370, 1215, 1153, 1072, 840, 760; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.43-7.40 (2H,m), 7.32-7.29 (2H,m), 7.13 (2H,s), 5.11 (1H,s), 4.75 (1H,s), 4.20-4.15 (2H,m), 3.38-3.27 (2H,m), 1.40 (18H,s), 1.27-1.24 (3H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 172.59, 153.03, 142.93, 135.96, 133.48, 131.54, 129.16, 123.86, 120.69, 66.31, 60.72, 49.07, 34.38, 30.31, 14.25; **HRMS(ESI):** m/z calcd for $C_{25}H_{35}BrNO_3$ $(M+H)^+$- 476.1795, found 476.1708.

methyl ((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-L-leucinate(3h):



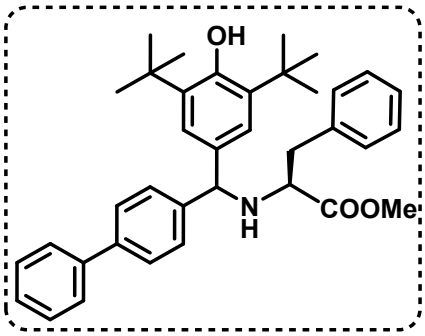
Yellow solid, isolated yield- 57.5mg (85%); Mp-109^{o}C;**R_f** (10% EtOAC/Hexane) - 0.6; **IR(in CH_2Cl_2):** ν_{max}; 3636, 3433, 2956, 1732, 1433, 1313, 1200, 1154, 1119, 1070, 814, 762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.43-7.37(2H,m), 7.33-7.31 (1H,m), 7.28-7.25 (1H,m), 7.14 (1H,s), 7.09 (1H,s), 5.10-5.09 (1H,m), 4.62-4.61 (1H,m), 3.70 (3H,s), 3.16-3.12 (1H,m), 1.94-1.89 (2H,m), 1.47-1.45 (1H,m), 1.40-1.39 (18H,m), 0.90-0.89 (3H,m), 0.82-0.76 (3H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 176.79, 176.62, 152.99, 152.95, 144.25, 142.49, 135.81, 134.60, 132.49, 131.45, 129.40, 128.96, 124.08, 123.88, 120.65, 120.61, 65.24, 65.16, 57.87, 51.59, 43.33, 34.36, 30.31, 30.26, 24.82, 24.71, 23.24, 23.11, 22.11, 22.05; **HRMS(ESI):** m/z calcd for $C_{28}H_{41}BrNO_3$ $(M+H)^+$- 520.2264, found 520.2232.

methyl((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-L-phenylalaninate(3i):



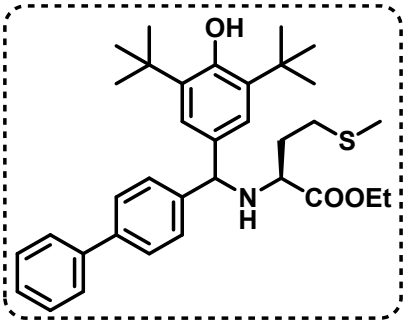
Yellow solid, isolated yield- 62.7mg (87%) ; Mp-110^{o}C; **R_f** (10% EtOAC/Hexane) - 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3409, 3020, 2401, 1432, 1216, 1047, 761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.39-7.37 (1H,m), 7.29-7.13 (7H,m), 7.08 (1H,s), 7.02 (1H,s), 6.98-6.96 (1H,m), 5.08-5.07 (1H,m), 4.65-4.62 (1H,m), 3.67-3.63 (3H,m), 3.47-3.29 (1H,m), 2.99-2.79 (2H,m), 1.38-1.36 (18H, m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 175.25, 152.98, 152.94, 143.86, 142.47, 137.79, 137.49, 135.85, 134.66, 132.47, 131.47, 131.40, 129.69, 129.31, 129.08, 128.39, 128.19, 126.68, 126.64, 123.93, 123.65, 120.67, 120.49, 65.02, 60.45, 60.31, 51.71, 51.61, 40.28, 40.15, 34.38, 34.34, 30.34, 30.27; **HRMS(ESI):** m/z calcd for $C_{31}H_{39}BrNO_3$ $(M+H)^+$- 552.2108, found 552.2102.

<u>methyl([1,1'-biphenyl]-4-yl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-L-phenylalaninate(3j):</u>



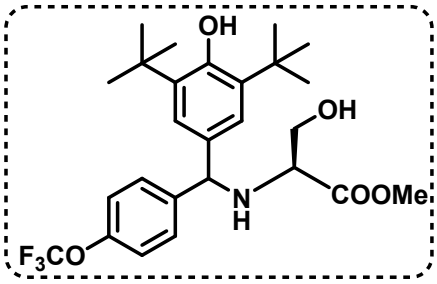
Light Yellow oil, isolated yield- 60.4mg (84%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR (in CH_2Cl_2):** ν_{max}; 3420, 3010, 2402, 1431, 1215, 1045, 762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.55-7.49 (3H,m), 7.43-7.36 (4H,m), 7.30-7.16 (8H,m), 7.12 (1H,s), 5.07 (1H,s), 4.74-4.73 (1H,m), 3.66-3.63 (3H,m), 3.52-3.42 (1H,m), 3.02-2.86 (2H,m), 1.40-1.37 (18H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 175.42, 152.94, 143.99, 142.59, 141.13, 141.07, 139.88, 139.71, 137.89, 137.68, 135.80, 135.19, 132.98, 129.75, 129.41, 128.77, 128.42, 128.23, 127.78, 127.23, 127.16, 127.09, 126.67, 124.12, 123.84, 65.46, 65.40, 60.52, 60.45, 51.67, 51.59, 40.38, 40.29, 34.44, 34.40, 30.43, 30.36; **HRMS(ESI):** m/z calcd for $C_{37}H_{44}NO_3(M+H)^+$- 550.3316, found 550.3300.

<u>ethyl ([1,1'-biphenyl]-4-yl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-L-methioninate(3k):</u>



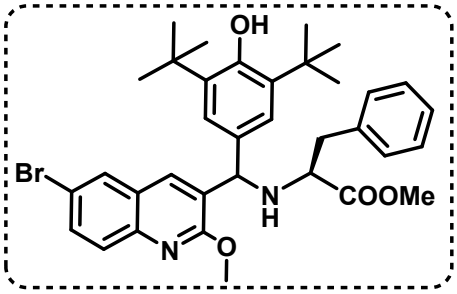
Light Yellow oil, isolated yield- 73mg (83%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3400, 3020, 1725, 1433, 1216, 1043, 762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.59-7.49 (5H,m), 7.45-7.37 (3H,m), 7.32-7.27 (1H,m), 7.23(1H,s), 7.19 (1H,s), 5.10-5.09 (1H,m), 4.77-4.76 (1H,m), 4.23-4.18 (2H,m), 3.32-3.28 (1H,m), 2.80-2.54 (2H,m), 2.07- 2.06 (3H,m), 2.00-1.78 (2H,m), 1.42-1.40 (18H, m), 1.29-1.26 (3H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 175.38, 175.27, 152.98, 152.94, 144.13, 142.35, 141.06, 141.03, 139.90, 135.81, 134.95, 132.79, 128.75, 128.09, 127.69, 127.26, 127.17, 127.07, 124.20, 124.03, 65.57, 65.52, 60.77, 60.73, 58.49, 58.26, 34.42, 33.61, 30.95, 30.82, 30.43, 30.32, 15.46, 15.43, 14.45; **HRMS(ESI):** m/z calcd for $C_{34}H_{46}NO_3S(M+H)^+$- 548.3193, found 548.3176.

<u>methyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethoxy)phenyl)methyl)-L-serinate(3l):</u>



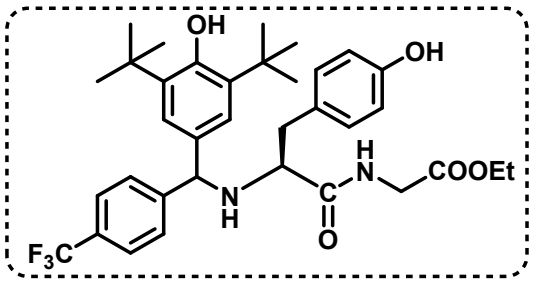
Light Yellow oil, isolated yield- 54mg (83%) ; **R_f** (20% EtOAC/Hexane)- 0.4; **IR(in CH_2Cl_2):** ν_{max}; 3638, 3436, 3019, 2959, 2401, 1731, 1483, 1362, 1215, 1071, 761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.45-7.39 (2H,m), 7.18-7.14 (3H, m), 7.09 (1H,s), 5.16-5.15 (1H,m), 4.84-4.83 (1H,m), 3.78-3.74 (4H,m), 3.68-3.63 (1H,m), 3.41-3.34 (1H,m), 1.41-1.40 (18H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 173.99, 173.66, 153.17, 148.24, 142.96, 141.55, 136.09, 133.59, 131.96, 128.92, 128.66, 124.05, 123.99, 121.03, 120.98, 65.02, 64.90, 63.27, 60.63, 60.34, 52.18, 34.39, 30.30, 30.22; **HRMS(ESI):** m/z calcd for $C_{26}H_{35}F_3NO_5(M+H)^+$- 498.2462, found 498.2466.

<u>methyl((6-bromo-2-methoxyquinolin-3-yl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-L-phenylalaninate(3m):</u>



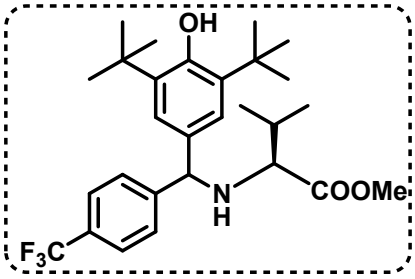
Light Yellow oil, isolated yield- 49mg (70%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3410, 3023, 2401, 1430, 1210, 1042, 760 ; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.96 (1H,s), 7.83-7.82 (1H,m), 7.65-7.56 (2H,m), 7.43-7.37 (2H,m), 7.32-7.21 (3H,m), 7.18-7.16 (2H,m), 7.11 (1H,s), 5.08-5.02 (2H,m), 4.02-3.95 (3H,m), 3.73-3.60 (3H,m), 3.48-3.32 (1H,m), 3.07-2.96 (1H,m), 2.79-2.67 (1H,m), 1.38-1.36 (18H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 175.35, 174.99, 160.87, 160.27, 152.97, 152.89, 144.11, 143.97, 138.37, 137.56, 135.62, 135.50, 133.94, 133.64, 133.21, 132.05, 131.76, 131.11, 130.20, 129.95, 129.89, 129.52, 129.28, 128.63, 128.46, 128.41, 128.21, 126.79, 126.67, 124.42, 124.14, 117.04, 116.63, 60.86, 60.31, 59.05, 58.26, 53.50, 53.38, 51.87, 51.59, 40.36, 40.18, 34.34, 34.31, 30.34, 30.27; **HRMS(ESI):** m/z calcd for $C_{35}H_{42}BrN_2O_4$ $(M+H)^+$- 633.2322, found 633.2319.

ethyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-L-tyrosylglycinate(3n):



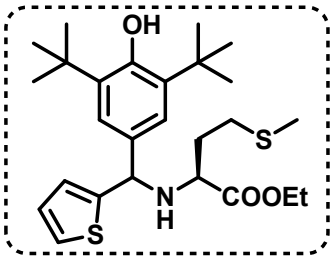
Light Yellow oil, isolated yield- 56mg (68%) ; **R_f** (40% EtOAC/Hexane)- 0.4; **IR(in CH_2Cl_2):** ν_{max}; 3398, 3020, 1741, 1662, 1516, 1436, 1325, 1216, 1124, 1067, 762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.71-7.60 (1H,m), 7.54- 7.39 (3H,m), 7.00-6.95 (3H,m), 6.86 (1H,s), 6.78-6.70 (2H,m), 5.15-5.14 (1H,m), 4.73-4.70 (1H,m), 4.26-4.19 (2H,m), 4.11-3.92 (2H, m), 3.41-3.31 (1H,m), 3.21-3.04 (1H,m), 2.88-2.82 (1H,m), 1.36- 1.35 (18H, m), 1.31-1.28 (3H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 174.46, 174.28, 169.69, 155.39, 155.12, 153.21, 153.07, 147.44, 136.15, 136.01, 132.82, 132.37, 130.47, 130.34, 128.48, 127.74, 127.49, 125.37, 124.03, 123.81, 115.68, 65.21, 64.74, 61.53, 61.31, 61.17, 41.12, 41.07, 38.02, 34.36, 34.31, 30.18, 14.14; **HRMS(ESI):** m/z calcd for $C_{35}H_{44}F_3N_2O_5(M+H)^+$- 629.3197, found 629.3195.

methyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-L-valinate (3o):



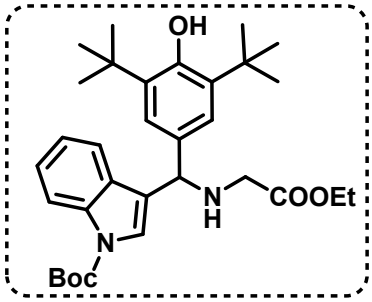
Light Yellow oil, isolated yield- 55.5mg (86%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3638, 3412, 2961, 1728, 1618, 1433, 1324, 1216, 1161, 1067, 762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.59-7.49 (4H,m), 7.18 (1H,s), 7.13 (1H,s), 5.12-5.11 (1H,m), 4.67-4.66 (1H,m), 3.72 (3H,s), 2.99-2.87 (1H,m), 1.98-1.88 (1H, m), 1.41-1.40 (18H, m), 0.99-0.94 (6H,m); **^{13}C NMR (100 MHz,$CDCl_3$):** δ 175.94, 175.73, 153.09, 153.05, 149.28, 147.72, 135.91, 135.89, 134.41, 132.12, 127.95, 127.52, 125.43, 125.39, 125.39, 125.33, 125.29, 124.13, 123.87, 65.74, 65.59, 65.17, 64.43, 51.42, 34.37, 31.89, 31.78, 30.35, 30.22, 19.88, 19.62, 18.63, 18.34; **HRMS(ESI):** m/z calcd for $C_{28}H_{39}F_3NO_3$ $(M+H)^+$- 494.2877, found 494.2875.

ethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methyl)-L-methioninate(3p):



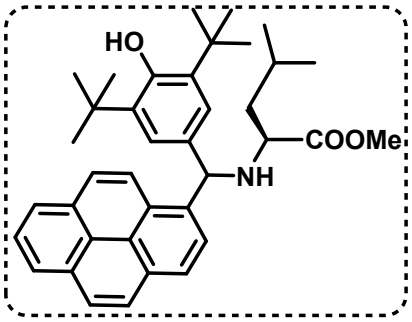
Light Yellow oil, isolated yield- 57.5mg (75%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR (in CH_2Cl_2):** ν_{max}; 3638, 3334, 2960, 1726, 1434, 1366, 1297, 1159, 1026, 889, 759 ; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.22-7.14 (3H,m), 6.91-6.87 (2H), 5.13-5.12 (1H,m), 4.99-4.98 (1H,m), 4.23- 4.16 (2H,m), 2.78-2.50 (2H,m), 2.08-2.05 (3H,m), 1.98-1.74 (2H,m), 1.42-1.41 (18H,m), 1.29-1.26 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 175.09, 175.04, 153.18, 153.10, 149.52, 148.68, 135.78, 134.37, 132.58, 126.43, 126.39, 124.74, 124.52, 124.26, 124.22, 124.03, 123.95, 61.89, 61.27, 60.78, 60.75, 58.40, 57.84, 34.39, 33.52, 33.38, 30.82, 30.74, 30.38, 30.28, 15.40, 14.40; **HRMS(ESI):** m/z calcd for $C_{26}H_{40}NO_3S_2$ $(M+H)^+$- 478.2444, found 478.2453.

tert-butyl3-((3,5-di-tert-butyl-4-hydroxyphenyl)((2-ethoxy-2-oxoethyl)amino)methyl)-1H-indole-1-carboxylate(3q):



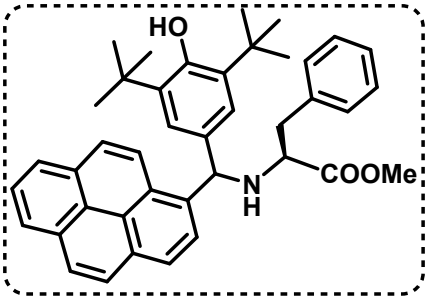
Light Yellow oil, isolated yield- 41.6mg (70%) ; **R_f** (10% EtOAC/Hexane)- 0.4; **IR(in CH_2Cl_2):** ν_{max}; 3398, 3020, 2963, 1729, 1451, 1373, 1216, 1156, 765; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.12-8.09 (1H,m), 7.76-7.74 (1H,m), 7.49 (1H,s), 7.29-7.25 (3H,m), 7.21-7.17 (1H,m), 5.11 (1H, s), 5.06 (1H,s), 4.22-4.16 (2H,m), 3.42 (2H,s), 1.65 (9H,s), 1.41 (18H,s), 1.28-1.24 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 172.84, 153.05, 149.81, 135.80, 132.54, 129.46, 124.27, 123.35, 122.39, 120.23, 115.18, 83.46, 60.67, 59.43, 48.95, 34.38, 30.35, 28.24, 14.26; **HRMS(ESI):** m/z calcd for $C_{32}H_{45}N_2O_5$ $(M+H)^+$- 537.3323, found 537.3320.

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(pyren-1-yl)methyl)-L-leucinate(3r):



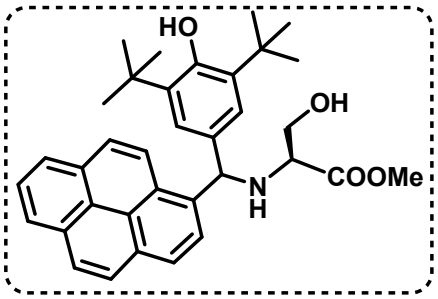
Orange oil, isolated yield- 48mg (71%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR (in CH_2Cl_2):** ν_{max}; 3400, 3019, 2924, 1729, 1611, 1435, 1212, 1038, 760; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.58-8.46 (1H,m), 8.34-8.32 (1H,m), 8.18-8.13 (1H,m), 8.07-8.02 (3H,m), 7.95-7.93 (1H,m),7.91 (1H,s), 7.89-7.84 (1H,m), 7.27 (1H,m), 7.19 (1H,s), 5.78-5.77 (1H,m), 4.98-4.97(1H,m), 3.64-3.59 (3H,m), 3.32-3.13 (1H,m), 1.97-1.87 (1H,m), 1.54-1.36 (2H,m), 1.31-1.26 (18H,m), 0.85-0.69 (6H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 177.06, 176.82, 152.81, 152.78, 138.57, 136.49, 135.71, 134.88, 132.76, 131.41, 130.77, 130.73, 130.33, 130.26, 129.07, 128.12, 127.61, 127.49, 127.13, 127.02, 126.89, 125.77, 125.74, 125.19, 125.15, 125.09, 125.03, 124.97, 124.79, 124.75, 124.73, 124.40, 123.06, 61.12, 60.89, 58.12, 57.56, 51.59, 51.55, 43.52, 43.46, 34.38, 34.35, 30.35, 30.26, 24.87, 23.19, 23.16, 22.28, 22.17; **HRMS(ESI):** m/z calcd for $C_{38}H_{46}NO_3(M+H)^+$- 564.3472, found 564.3457.

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(pyren-1-yl)methyl)-L-phenylalaninate(3s):



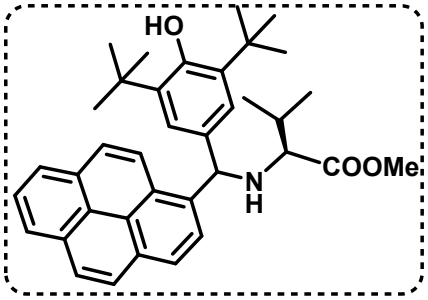
Brown oil, isolated yield- 60.2mg (72%); **R_f** (10% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** v_{max}; 3399, 3013, 2900, 1734, 1612, 1437, 1212, 1036, 760; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.56-8.37 (1H,m), 8.17-8.09 (4H,m), 8.01-7.94 (4H,m), 7.31-7.26 (4H,m), 7.23 (1H,s), 7.22-7.18 (2H,m), 5.86-5.85 (1H,m), 5.05-5.03 (1H,m), 3.69-3.62 (4H,m), 3.05-2.89 (2H,m), 1.35-1.34 (18H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 175.27, 152.76, 152.70, 138.03, 137.82, 137.70, 136.47, 135.72, 135.64, 134.77, 132.78, 131.41, 131.37, 130.76, 130.67, 130.28, 130.15, 129.69, 129.36, 128.41, 128.23, 127.50, 127.45, 127.09, 127.05, 126.86, 126.62, 125.78, 125.70, 125.34, 125.14, 125.04, 124.93, 124.80, 124.70, 124.52, 124.21, 123.07, 122.96, 60.92, 60.88, 60.76, 60.69, 51.63, 51.59, 40.34, 40.27, 34.33, 30.34, 30.25; **HRMS(ESI):** m/z calcd for $C_{41}H_{44}NO_3(M+H)^+$- 598.3316, found 598.3328.

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(pyren-1-yl)methyl)-L-serinate(3t):



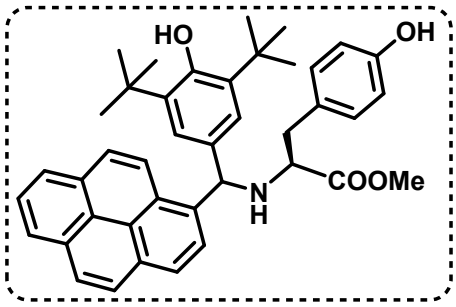
Orange oil, isolated yield- 52mg (69%); **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** v_{max}; 3600,3390, 3012, 2901, 1736, 1613, 1438, 1216, 1035, 760; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.45-8.36 (1H,m), 8.23-8.14 (4H,m), 8.08-8.03 (3H,m), 8.01-7.95(1H,m), 7.32-7.28 (2H,m), 6.03-6.00 (1H,m), 5.12-5.11 (1H,m), 3.85-3.79 (1H,m), 3.74-3.44 (1H,m), 1.38-1.36 (18H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 173.95, 173.81, 152.97, 137.35, 135.94, 135.83, 133.86, 132.48, 131.40, 130.73, 130.67, 130.49, 130.45, 129.03, 128.45, 127.81, 127.47, 127.25, 127.14, 125.91, 125.87, 125.22, 125.17, 125.11, 125.08, 124.93, 124.59, 124.39, 122.89, 122.74, 67.10, 63.52, 63.04, 61.42, 60.98, 60.52, 60.39, 52.21, 52.17, 34.40, 34.37, 30.33, 30.25; **HRMS(ESI):** m/z calcd for $C_{35}H_{40}NO_4(M+H)^+$- 538.2952, found 538.2930.

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(pyren-1-yl)methyl)-L-valinate(3u):



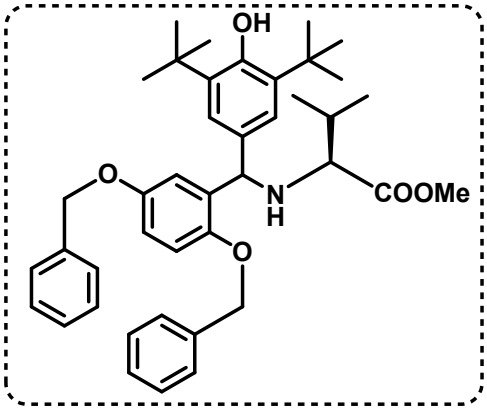
Light brown oil, isolated yield- 46.5mg (70%) ; **R_f** (10% EtOAC/Hexane)- 0.6; **IR(in CH_2Cl_2):** ν_{max}; 3392, 3015, 2904, 1737, 1614, 1439, 1217, 1036, 760; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.57-8.43 (1H,m), 8.22-8.20 (1H,m), 8.15-8.09 (3H,m), 8.04-8.00 (2H,m), 7.98-7.90 (2H,m), 7.39-7.31 (2H,m), 5.82-5.81 (1H,m), 5.06-5.05 (1H,m), 3.72-3.69 (3H,m),2.56-2.51 (1H,m), 2.01-1.92 (1H,m), 1.39-1.35 (18H,m),1.05-0.94 (6H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 176.25, 176.08, 152.78, 138.81, 136.58, 135.71, 135.00, 132.90, 131.42, 130.79, 130.74, 130.26, 129.14, 128.16, 127.60, 127.51, 127.11, 127.06, 126.92, 125.79, 125.74, 125.48, 125.36, 125.22, 125.17, 125.07, 125.02, 124.98, 124.74, 124.39, 123.18, 123.09, 65.42, 64.93, 61.31, 61.06, 51.42, 51.37, 34.43, 34.37, 32.02, 30.44, 30.28, 19.89, 19.74, 18.86, 18.79; **HRMS(ESI):** m/z calcd for $C_{37}H_{44}NO_3$ $(M+H)^+$- 550.3316, found 550.3320.

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(pyren-1-yl)methyl)-L-tyrosinate(3v):



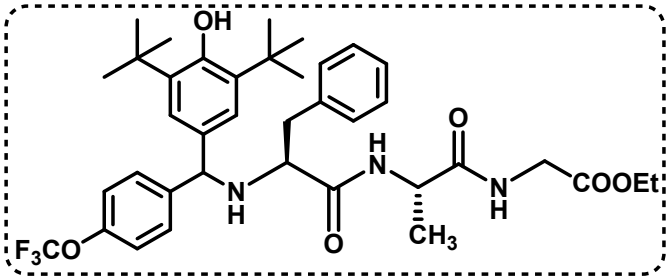
Orange oil, isolated yield- 44.5mg (60%) ; **R_f** (20% EtOAC/Hexane)- 0.4; **IR(in CH_2Cl_2):** ν_{max}; 3401, 3020, 2926, 1730, 1610, 1436, 1215, 1037, 760; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.57-8.55 (1H,m), 8.16-8.09 (4H,m), 8.06-7.94 (4H,m), 7.27-7.26 (2H,m), 7.06-7.03 (2H,m), 6.76-6.72 (2H,m), 5.86-5.85 (1H,m), 5.06-5.04 (1H,m), 3.64-3.62 (3H,m), 3.40-3.27 (1H,m), 2.96-2.83 (2H,m), 1.35-1.34 (18H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 171.19, 154.68, 135.71, 130.72, 130.45, 128.89, 127.49, 127.43, 127.02, 125.69, 125.38, 125.13, 124.98, 124.79, 124.48, 124.21, 115.28, 115.08, 67.97, 60.41, 51.55, 34.31, 31.93, 30.30, 30.22; **HRMS(ESI):** m/z calcd for $C_{41}H_{44}NO_4(M+H)^+$- 614.3265, found 614.3259.

methyl((2,5-bis(benzyloxy)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-L-valinate(3w):



Light Yellow oil, isolated yield- 58mg (83%) ; **R_f** (10% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3398, 2955, 1731, 1492, 1200, 1028, 739; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.51-7.50 (1H,m), 7.43-7.41 (3H,m), 7.39-7.25 (13H,m), 7.21-7.18 (3H,m), 6.76-6.71 (3H,m), 5.16-5.11 (2H,m), 5.04-5.03 (3H,m), 5.01-4.99 (2H,m), 4.93-4.92 (2H,m), 3.63-3.59 (4H,m), 2.99-2.87 (1H,m), 1.92-1.83 (2H,m), 1.35-1.34 (27H,m),1.01-0.90 (9H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 176.20, 153.43, 153.27, 152.65, 152.55, 150.97, 149.86, 137.69, 137.57, 137.46, 135.47, 135.40, 135.24, 134.80, 133.38, 133.07, 128.89, 128.56, 128.45, 128.41, 127.89, 127.83, 127.61, 127.56, 127.41, 127.09, 126.92, 124.52, 124.26, 114.55, 114.07, 113.92, 113.52, 113.08, 112.99, 70.67, 70.62, 65.49, 64.68, 58.17, 58.04, 51.25, 51.12, 34.31, 31.92, 31.84, 30.38, 30.29, 19.75, 19.62, 19.04, 18.76; **HRMS(ESI):** m/z calcd for $C_{41}H_{52}NO_5(M+H)^+$- 638.3840, found 638.3832.

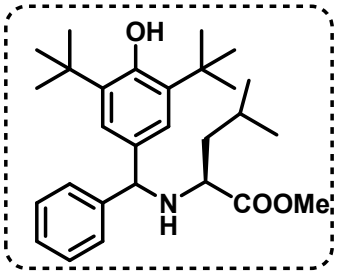
ethyl((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethoxy)phenyl)methyl)-L-phenylalanyl-L-alanylglycinate(3x):



Light Yellow oil, isolated yield- 68mg (75%) ; **R_f** (40% EtOAC/Hexane)- 0.4; **IR (in CH_2Cl_2):** ν_{max}; 3638, 3348, 3018, 2962, 2402, 1743, 1658, 1507, 1437, 1378, 1260, 1166, 1021, 926, 850, 761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.55-7.44 (1H,m), 7.37-7.33 (1H,m), 7.31-7.29 (2H,m), 7.24-7.20 (1H,m), 7.17-7.11 (3H,m), 7.00-6.96 (1H,m), 6.91-6.78 (2H,m), 5.27(1H,s), 5.16-5.15 (1H,m), 4.73-4.67 (1H,m), 4.60-4.49 (1H,m), 4.22-4.16 (2H,m), 4.07-3.91 (2H,m), 3.38-3.22 (1H,m), 3.18-3.09 (1H,m), 3.00-2.73 (1H,m),2.03 (2H,s), 1.37-1.23 (24H,m);**^{13}C NMR (100MHz,$CDCl_3$):** δ 174.15, 174.06, 173.78, 172.19, 169.70, 169.61, 153.14, 148.16, 148.00, 141.95, 141.39, 137.42, 137.21, 136.09, 135.97, 132.58, 129.49, 129.39, 129.24, 128.91, 128.72, 128.59, 127.06, 126.93, 124.09, 120.88, 64.95, 64.11, 61.46, 61.01, 53.42, 48.33, 41.28, 39.32,

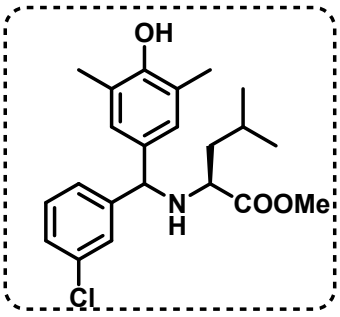
38.79, 34.34, 30.23, 18.12, 14.12; **HRMS(ESI):** m/z calcd for $C_{38}H_{49}F_3N_3O_6(M+Na)^+$- 722.3387, found 722.3363.

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-L-leucinate (3y):



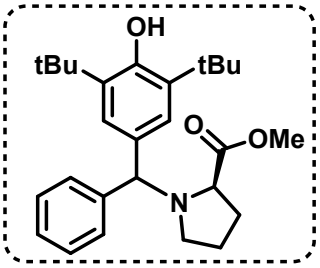
Light Yellow oil, isolated yield- 40mg (90%) ; **R_f** (10% EtOAC/Hexane) - 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3400, 2954, 1732, 1660, 1434, 1219, 1153, 1115, 768; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.45-7.42 (1H,m), 7.39-7.37 (1H,m), 7.31-7.24 (2H,m), 7.19-7.17 (2H,m), 7.14 (1H,s), 5.07-5.05 (1H,m), 4.67-4.66 (1H,m), 3.70-3.69 (3H,m), 3.20-3.15 (1H,m), 1.99-1.86 (2H,m), 1.51-1.44 (1H,m), 1.40-1.39 (18H,m), 0.90-0.88 (3H,m), 0.81-0.77 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 176.91, 176.82, 152.83, 152.78, 145.21, 143.29, 135.64, 135.19, 132.99, 128.38, 128.29, 127.74, 127.25, 126.95, 126.84, 124.24, 124.04, 65.83, 57.86, 57.48, 51.51, 43.39, 34.35, 30.34, 30.28, 24.82, 24.71, 23.24, 23.12, 22.10; **HRMS(ESI):** m/z calcd for $C_{28}H_{42}NO_3(M+H)^+$- 440.3159, found 440.3152.

methyl ((3-chlorophenyl)(4-hydroxy-3,5-dimethylphenyl)methyl)-L-leucinate(3z):



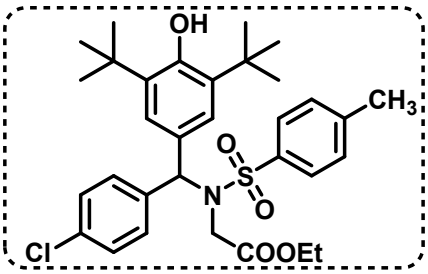
White solid, isolated yield- 39mg (84%); Mp- 120^{o}C; **R_f** (10% EtOAC/Hexane)- 0.5; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.36 (1H, s), 7.25-7.23 (1H,m), 7.21-7.13 (2H,m), 6.98 (2H,s), 4.65-4.61 (2H,m), 3.71-3.70 (3H,m), 3.23-3.15 (1H,m), 2.20 (6H,s), 2.02-1.92 (2H, m), 1.53-1.37 (2H,m), 0.91 (3H, d, *J*= 6.72 Hz), 0.81 (3H, d, *J*= 6.50 Hz); **^{13}C NMR (100MHz,$CDCl_3$):** δ 176.73, 151.50, 147.05, 134.22, 133.48, 129.72, 127.62, 127.31, 127.18, 127.13, 125.39, 123.12, 64.47, 57.30, 51.65, 43.25, 24.69, 23.20, 21.67, 16.01; **HRMS(ESI):** m/z calcd for $C_{22}H_{29}ClNO_3$ $(M+H)^+$- 390.1830, found 390.1824.

methyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-D-prolinate (3z'):



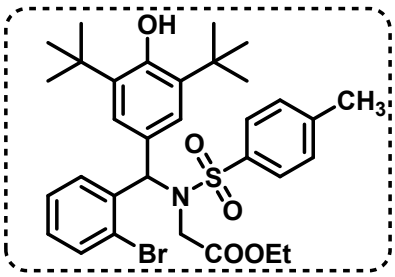
Light yellow oil. isolated yield- 49mg (75%); $\mathbf{R_f}$ (10% EtOAC/Hexane)- 0.5; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.48-7.46 (3H,m), 7.25-7.24 (1H,m), 7.20-7.15 (3H,m), 5.03 (1H,s), 4.55 (1H,s), 3.39 (3H,s), 3.03-2.98 (1H,m), 2.53-2.47 (1H,m), 2.16-2.06 (1H,m), 1.95-1.75 (4H,m), 1.39 (18H,s); **^{13}C NMR (100MHz,$CDCl_3$):** δ 175.42, 152.66, 144.05, 135.22, 130.36, 128.25, 127.83, 126.69, 125.08, 73.97, 63.65, 52.99, 51.09, 34.30, 30.35, 29.56, 23.69; **HRMS(ESI):** m/z calcd for $C_{22}H_{29}ClNO_3$ $(M+H)^+$- 424.2846, found 424.2835.

ethyl N-((4-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-N-tosylglycinate(5a):



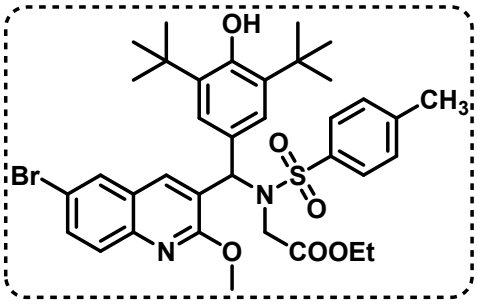
Light Yellow oil, isolated yield- 66mg (75%) ; $\mathbf{R_f}$ (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3400, 2950, 2401, 1725, 1435, 1057,761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.78-7.76 (2H,m), 7.24-7.21 (4H,m), 7.17-7.15 (2H,m), 6.69 (2H,s),6.11 (1H,s), 5.17 (1H,s), 4.09-3.96 (2H,m), 3.90-3.82 (2H,m), 2.40 (3H,s), 1.28 (18H,s), 1.08-1.04 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 169.05, 153.45, 143.42, 137.61, 137.24, 135.72, 133.32, 130.18, 129.32, 128.22, 128.13, 127.64, 126.01, 64.77, 60.95, 46.61, 34.21, 30.09, 21.49, 13.96; **HRMS(ESI):** m/z calcd for $C_{32}H_{44}ClN_2O_5S$ $(M+NH_4)^+$- 603.2654, found 603.2655.

ethyl N-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-N-tosylglycinate(5b):



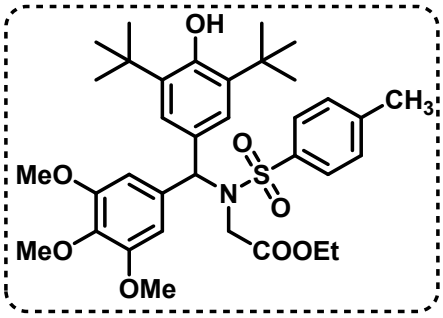
Light Yellow oil, isolated yield-75%; **R_f** (20% EtOAC/Hexane)- 0.5; **IR (in CH_2Cl_2):** ν_{max}; 3406, 2954, 2410, 1722, 1430, 1053,761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.80-7.78 (2H,m), 7.59-7.57 (1H,m), 7.49-7.47 (1H,m),7.25-7.21 (3H,m), 7.12-7.07 (1H,m),6.61(2H,s), 6.35(1H,s), 5.14(1H,s), 4.15-4.09 (1H,m), 3.99-3.93 (3H,m), 2.39 (3H,s), 1.26 (18H,s), 1.14-1.11 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 169.29, 153.41, 143.38, 139.47, 136.49, 135.65, 132.99, 129.54, 129.23, 128.69, 128.25, 127.11, 126.81, 126.52, 123.92, 65.33, 60.92, 47.74, 34.18, 30.08, 21.48, 14.03; **HRMS(ESI):** m/z calcd for $C_{32}H_{44}BrN_2O_5S(M+NH_4)^+$- 647.2149, found 647.2144.

Ethyl N-((6-bromo-2-methoxyquinolin-3-yl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-N-tosylglycinate(5c):



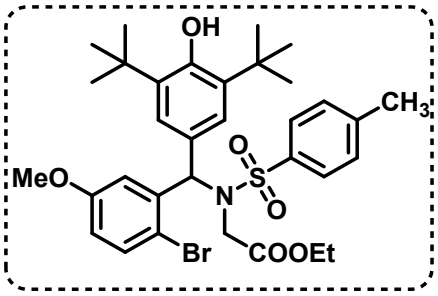
Light Yellow oil, isolated yield- 70%; **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3415, 2952, 2414, 1725, 1431, 1055,761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.85 (1H,s), 7.76-7.75 (1H,m), 7.72-7.69 (2H,m), 7.66-7.65 (2H,m), 7.15- 7.13 (2H,m), 6.77 (2H,s), 6.42 (1H,s), 5.18 (1H,s), 4.10-3.94 (2H,m), 3.89 (3H,s), 3.87-3.79 (2H,m), 2.32 (3H,s), 1.29 (18H,s), 1.04-1.00 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 169.39, 153.44, 144.56, 143.49, 136.86, 135.79, 132.58, 129.67, 129.21, 128.47, 127.98, 126.71, 126.07, 125.49, 125.21, 117.12, 60.99, 60.87, 53.56, 47.16, 34.27, 30.15, 21.41, 13.90; **HRMS(ESI):** m/z calcd for $C_{36}H_{47}BrN_3O_6S$ $(M+NH_4)^+$- 728.2363; found 728.2356.

EthylN-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4,5-trimethoxyphenyl)methyl)-N-tosylglycinate(5d):



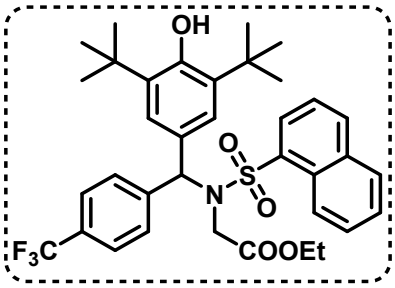
Light Yellow oil, isolated yield- 78%; **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** v_{max}; 3420, 2957, 2418, 1729, 1438, 1053,761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.75-7.73 (2H,m), 7.21-7.19 (2H,m), 6.83 (2H,s), 6.41(2H,s), 6.10 (1H,s), 5.18 (1H,s), 4.01-3.99 (2H,m), 3.95-3.88 (2H,m), 3.82 (3H,s), 3.70 (6H,s), 2.38 (3H,s), 1.32 (18H,s), 1.10-1.06 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 153.88, 152.80, 135.58, 134.24, 129.19, 128.16, 127.76, 126.05, 106.19, 65.49, 60.98, 60.79, 56.00, 53.42, 46.73, 34.25, 30.18, 21.47, 13.99; **HRMS(ESI):** m/z calcd for $C_{35}H_{51}N_2O_8S$ $(M+NH_4)^+$- 659.3361, found 659.3320.

ethylN-((2-bromo-5-methoxyphenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-N-tosylglycinate(5e):



Light Yellow oil, isolated yield- 69%; **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** v_{max}; 3426, 2951, 2419, 1723, 1431, 1051,761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.76-7.74 (2H,m), 7.35-7.31 (2H,m), 7.23-7.21 (2H,m), 6.67-6.64 (3H,m), 6.28 (1H,s), 5.15 (1H,s), 4.05-3.96 (4H,m), 3.76 (3H,m), 2.39 (3H,s), 1.26 (18H,s), 1.17-1.14 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 169.54, 158.91, 153.51, 143.38, 140.42, 136.47, 135.74, 133.39, 129.22, 128.14, 126.61, 115.27, 114.76, 114.02, 65.63, 60.99, 55.55, 47.81, 34.19, 30.10, 21.46, 14.05; **HRMS(ESI):** m/z calcd for $C_{33}H_{46}BrN_2O_6S$ $(M+NH_4)^+$- 677.2254, found 677.2249.

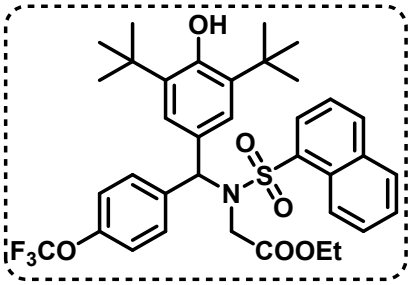
ethylN-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-N-(naphthalen-1-ylsulfonyl)glycinate(5f):



Light Yellow solid, isolated yield- 70%; Mp-125^{o}C; **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** v_{max}; 3411, 3020, 2401,1326, 1216,1066,762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.79-8.76 (1H,m), 8.22-8.19 (1H,m), 7.94-7.92 (1H,m), 7.86-7.84 (1H,m), 7.64-7.60 (1H,m), 7.58-7.54 (1H,m), 7.39-7.33 (3H,m), 7.26-7.24 (2H,m), 6.74 (2H,s), 6.40 (1H,s), 5.15 (1H,s), 4.24-4.11 (2H,m), 3.79-3.65 (2H,m), 1.23 (18H,s), 0.93-0.89 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ

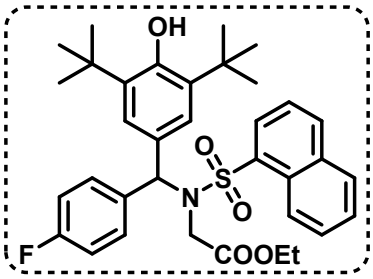
168.71, 157.55, 143.26, 135.77, 135.46, 134.34, 134.21, 130.66, 128.96, 128.75, 128.16, 127.36, 126.74, 126.26, 125.03, 124.74, 124.04, 65.29, 60.95, 47.25, 34.16, 30,03, 13.75; **HRMS(ESI):** m/z calcd for $C_{36}H_{44}F_3N_2O_5S$ $(M+NH_4)^+$- 673.2918, found 673.2914.

ethylN-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethoxy)phenyl)methyl)-N-(naphthalen-1-ylsulfonyl)glycinate(5g):



Yellow oil, isolated yield- 68%; **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** v_{max}; 3416, 3025, 2400,1325, 1213,1069,762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.79-8.77 (1H,m), 8.22-8.19 (1H,m), 7.94-7.84 (2H,m), 7.64-7.53 (2H,m), 7.39-7.35 (1H,m), 7.16-7.14 (2H,m), 6.95-6.93 (2H,m), 6.73 (2H,s), 6.38 (1H,s), 5.13 (1H,s), 4.18-4.17 (2H,m), 3.77-3.68 (2H,m), 1.23 (18H,s), 0.93-0.89 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 168.78, 153.40, 140.24, 137.81, 135.67, 135.56, 134.25, 134.19, 130.64, 129.98, 128.92, 128.11, 127.73, 126.69, 126.03, 125.06, 124.01, 120.25, 64.91, 60.93, 47.20, 34.15, 30.03, 13.73; **HRMS(ESI):** m/z calcd for $C_{36}H_{44}F_3N_2O_6S$ $(M+NH_4)^+$- 689.2867, found 689.2860.

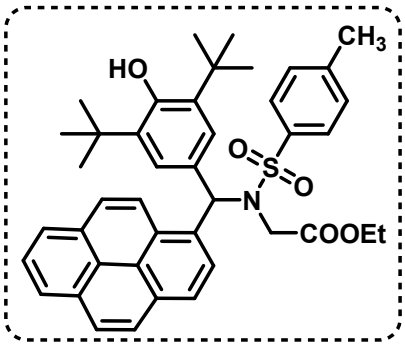
ethylN-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-N-(naphthalen-1-ylsulfonyl)glycinate(5h):



Yellow oil, isolated yield- 65%; **R_f** (20% EtOAC/Hexane)- 0.4; **IR(in CH_2Cl_2):** v_{max}; 3418, 3020, 2961, 2401, 1729, 1605, 1509, 1435, 1330, 1216, 1158, 1057, 927, 761; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.80-8.78 (1H,m), 8.24-8.21 (1H,m), 7.96-7.94 (1H,m), 7.87-7.85 (1H,m), 7.64-7.53 (2H,m), 7.41-7.37 (1H,m), 7.13-7.09 (2H,m), 6.84-6.79 (2H,m), 6.74 (2H,s), 6.37 (1H,s), 5.10 (1H,s), 4.17 (2H,s), 3.76-3.67 (2H,m), 1.23 (18H,s), 0.92-0.89 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 168.80, 163.17, 160.72, 153.25, 135.70, 135.56, 134.80, 134.77, 134.19, 130.59, 130.48, 130.40, 128.88, 128.08, 126.67, 125.83, 125.15, 124.03, 114.86, 114.64, 64.89,

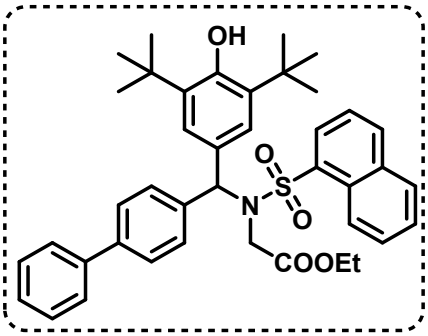
60.89, 53.43, 47.09, 34.13, 30.04, 13.74; **HRMS(ESI):** m/z calcd for $C_{35}H_{44}FN_2O_5S$ $(M+NH_4)^+$- 623.2949, found 623.2360.

ethyl N-((3,5-di-tert-butyl-4-hydroxyphenyl)(pyren-1-yl)methyl)-N-tosylglycinate(5i):



Yellow oil, isolated yield-60%; **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 3429, 2956, 2420, 1728, 1430, 1050,762; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.49-8.47 (1H,m), 8.21-8.18 (2H,m), 8.14-8.11 (1H,m), 8.07-8.03 (1H,m), 8.02-7.99 (2H,m), 7.74-7.72 (1H,m), 7.59-7.58 (2H,m), 7.32 (1H,s), 6.98-6.96 (2H,m), 6.85 (2H,s), 5.14 (1H,s), 4.31-4.09 (2H,m), 3.67-3.59 (1H,m), 3.52-3.44 (1H,m), 2.21 (3H,s), 1.26 (18H,s), 0.73-0.69 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 169.11, 153.14, 142.99, 136.92, 135.78, 132..40, 131.26, 131.01, 130.69, 129.59, 128.98, 128.93, 125.95, 127.91, 127.63, 127.33, 126.94, 125.98, 125.67, 125.25, 124.83, 124.57, 124.32, 123.66, 62.71, 60.72, 47.72, 34.21, 30.12, 21.32, 13.53; **HRMS(ESI):** m/z calcd for $C_{42}H_{49}N_2O_5S(M+NH_4)^+$- 693.3357; 693.3334.

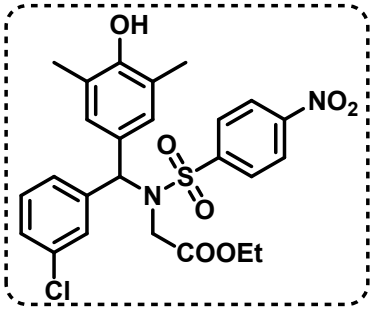
ethylN-([1,1'-biphenyl]-4-yl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-N-(naphthalen-1-ylsulfonyl)glycinate(5j):



Yellow oil, isolated yield- 72%; **R_f** (20% EtOAC/Hexane)- 0.5; **IR(in CH_2Cl_2):** ν_{max}; 2858, 1729, 1600, 1437, 1332, 1210, 1158, 1061, 974, 888, 799, 761, 696; **^{1}H NMR (400MHz,$CDCl_3$):** δ 8.83-8.81 (1H,m), 8.25-8.23 (1H,m), 7.94-7.92 (1H,m), 7.85-7.83 (1H,m), 7.65-7.61 (1H,m), 7.56-7.51 (3H,m), 7.44-7.39 (3H,m), 7.37-7.33 (3H,m),7.19-7.17 (2H,m),6.82 (2H,s), 6.42 (1H,s), 5.10 (1H,s),4.31-4.18 (2H,m), 3.74-3.65 (2H,m), 1.24 (18H,s), 0.89-0.86 (3H,m); **^{13}C NMR (100MHz,$CDCl_3$):** δ 168.94, 153.22, 140.61, 140.05, 137.94, 135.88, 134.18,

134.07, 130.61, 129.15, 128.82, 128.76, 128.25, 128.03, 127.31, 126.97, 126.61, 126.56, 126.02, 125.26, 124.04, 65.41, 60.85, 47.29, 34.16, 30.09, 14.12; **HRMS(ESI):** m/z calcd for $C_{41}H_{49}N_2O_5S$ $(M+NH_4)^+$- 681.3357, found 681.3362.

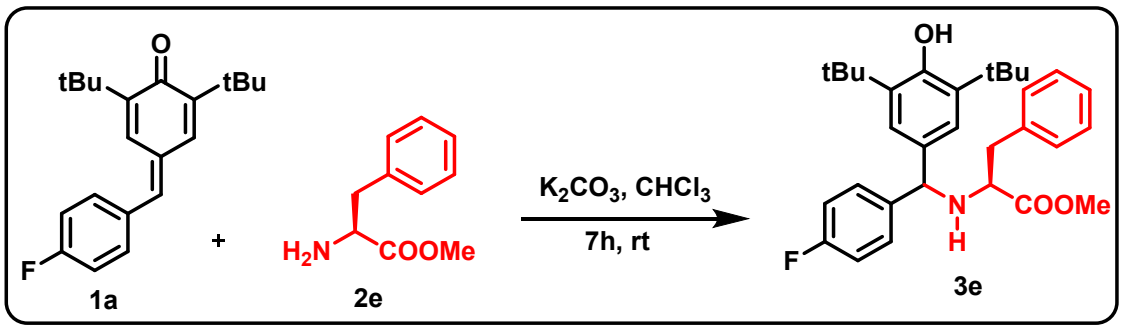
ethylN-((3-chlorophenyl)(4-hydroxy-3,5-dimethylphenyl)methyl)-N-((4-nitrophenyl)sulfonyl)glycinate (5k):



Yellow solid, isolated yield- 71%; $\mathbf{R_f}$ (20% EtOAC/Hexane)- 0.5; **^{1}H NMR (400MHz,DMSO-d_6):** δ 8.33-8.26 (3H,m), 8.05-8.03 (2H,m), 7.27-7.26 (2H,m), 7.14 (1H,s), 7.09-7.07 (3H,m), 6.45 (1H,s), 6.12 (1H,s), 4.14 (2H,s), 3.83-3.77 (2H, m),1.97 (6H,s), 0.99-0.96 (3H,m); **^{13}C NMR (100MHz,DMSO-d_6):** δ 173.76, 158.27, 154.85, 150.41, 146.51, 138.04, 135.16, 134.34, 134.29, 133.30, 132.56, 132.24, 131.97, 129.20, 129.13, 69.30, 65.86, 52.48, 21.72, 18.91; **HRMS(ESI):** m/z calcd for $C_{25}H_{29}ClN_3O_7S$ $(M+NH_4)^+$- 550.1409, found 550.1400.

IV. Gram Scale Experiment

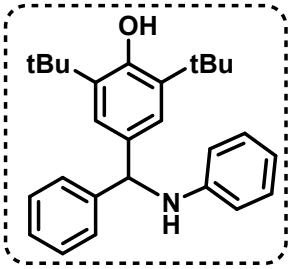
To a solution of *p*-QM **1a** (1g, 3.20 mmol) in $CHCl_3$ (7ml) in a 50 ml round bottom flask, 3.52 milimol of **2e** was added. Then the reaction mixture was then cooled to 0 ° C and K_2CO_3 (19.2 mmol, 6eq) was added and the reaction mixture was stirred for 7 h at rt and monitored by TLC until the starting material could not be detected. The reaction mixture was quenched with water and extracted with DCM (5 mL × 3). The organic layer was dried over Na_2SO_4 and evaporated in vacuum. The residue was purified by silica gel column chromatography to afford the desired product **3e** (89% yield, 1.4 gm).



V. Some more Examples

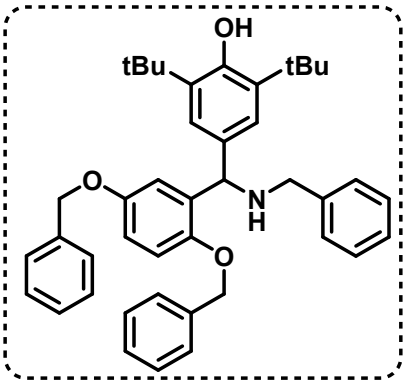
Our methodology worked with primary amine aswellas secondary amine also.

2,6-di-tert-butyl-4-(phenyl(phenylamino)methyl)phenol (6):



Light yellow solid, isolated yield- 72%; $\mathbf{R_f}$ (10% EtOAC/Hexane)- 0.5; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.41-7.39 (2H,m), 7.33-7.29 (2H,m), 7.24-7.20 (1H,m), 7.12-7.08 (2H,m), 7.07 (2H,s), 6.68-6.64 (1H,m), 6.55-6.53 (2H,m), 5.40 (1H,s), 5.15 (1H,s), 4.23 (1H, brs), 1.38 (18H,s); **^{13}C NMR (100MHz,$CDCl_3$):** δ 153.05, 147.68, 143.16, 136.01, 134.12, 129.07, 128.56, 127.14, 126.92, 124.60, 117.35, 113.46, 63.22, 34.41, 30.28; **HRMS(ESI):** m/z calcd for $C_{27}H_{34}NO$ $(M+H)^+$- 388.2635, found 388.2625.

4-((benzylamino)(2,5-bis(benzyloxy)phenyl)methyl)-2,6-di-tert-butylphenol (7):

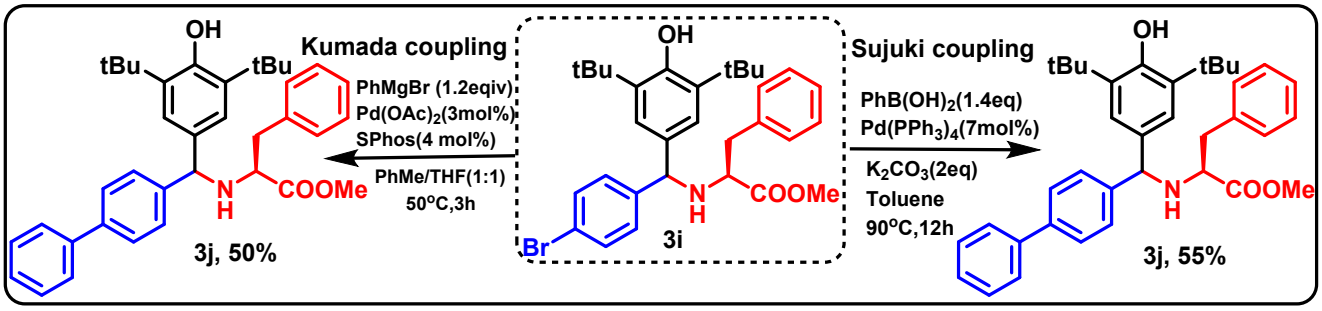


Light yellow solid, isolated yield- 78%; $\mathbf{R_f}$ (10% EtOAC/Hexane)- 0.4; **^{1}H NMR (400MHz,$CDCl_3$):** δ 7.42-7.41 (2H.m), 7.37-7.28 (13H, m), 7.24-7.22 (3H,m), 6.81-6.74 (2H,m), 5.21 (1H,s), 5.03-5.01 (3H,m), 4.95 (2H,s), 3.73-3.65 (2H,m), 1.35 (18H,s); **^{13}C NMR (100MHz,$CDCl_3$):** δ 153.36, 152.56, 150.59, 140.91, 137.47, 135.41, 134.29, 133.96, 128.56, 128.48, 128.35, 128.26, 127.86, 127.70, 127.54, 127.21, 126.74, 124.37, 114.85, 113.40, 113.08, 70.67, 70.62, 60.10, 52.23, 34.34, 30.37; **HRMS(ESI):** m/z calcd for $C_{42}H_{48}NO_3$ $(M+H)^+$- 614.3629, found 614.3605.

VI. Synthetic Application

Sujuki-Miyaura coupling: A mixture of **3i** (1equiv), phenylboronic acid (1.4 equiv), K_2CO_3 (2 equiv) and $Pd(PPh_3)_4$ (7 mol%) in toluene (2 mL) was stirred at 90°C for 12h in N_2 to afford the corresponding product **3j** with 55% yield.

Kumada coupling: $Pd(OAc)_2$ (3 mol%), SPhos (4 mol%) and **3i** (1equiv) were added to an 25ml screw-capped reaction vial equipped with a magnetic stir bar and Teflon septum. The vial was purged by an argon balloon and toluene (1 mL) was added. Another 4 mL screwcapped glass vial equipped with a Teflon septum was purged by an argon balloon, then a slight excess of Grignard reagent in THF (1.3 equiv) was added and diluted in toluene to a final concentration of 0.32 M. PhMgBr solution was added over 1h at 50 °C.The reaction mixture was monitored by TLC until the starting material was consumed. After quenching with aqueous NH_4Cl, the reaction mixture was extracted with EtOAc and the combined organic layers were filtered through a short plug of silica gel and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford the product **3j** with 50% yield.



VII. Photo-physical studies

Table. Data related to Absorption and Fluorescence emission for compounds **3a,3d,3e, 3f,3j and 5g**.

Compound	Absorption λ_{max} (nm)					Fluorescence peak positions (nm)				
	ACN	EtOH	MeOH	THF	Dioxane	ACN	EtOH	MeOH	THF	Dioxane
3a	355	354	354	355	355	400; 424	426	424	354	348; 361; 372; 400; 422
3d	354	354	360	354	350	389;424	480	NF	375; 384; 398; 425	373;381;395;423
3e	354	361	258	354	354	356	421	NF	417	349; 372; 492

3f	354	354	354	354	354	356; 400; 425	NF	NF	356; 389; 401; 425	356; 389; 401; 425
3j	375	375	376	375	374	354; 422	NF	452	354	377; 397
5g	357	351	356	351; 427	351	324; 375	NF	392	NF	377; 397
NF : Nonfluorescent										

VIII. References

1) Chu, W. D.; Zhang, L.F.; X. H.; Zeng, C.; Du, J.Y.; Zhang, G. B.; Wang, F. X.; Ma, X. Y.; Fan, C. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 9229.

2) Muthusamy, S.; Sivaguru, M. *Org. Lett.* **2014**, *16*, 4248-4251.