Efficient Synthesis of a Porphyrin-N-tripod Conjugate with Covalently Linked Proximal Ligand: Towards New Generation Active Site Models of Cytochrome *c* Oxidase

(Supplementary Material)

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Materials and methods. All reagents were used as supplied commercially unless otherwise noted. 1-Octylimidazole,[1] 1-methyl-4,5-diphenylimidazole[2] and 3-(3'-pyridyl)propionic acid[3] were prepared according to the published procedures. All melting points were determined on MEL-TEMP and are uncorrected. UV-Vis spectra were measured on a Hewlett Packard 8452A Diode Array spectrophotometer. IR and ^{1}H NMR spectra were recorded on Mattson Infinity 60AR and Varian XL-400 instruments respectively. Mass spectra were due by University of California, San Francisco, Mass Spectrometry Facility.

Synthesis and characterization

General procedure for the synthesis of bisimidazolylketones and bispyridylketones: All the bisimidazolylketones and bispyridylketones were synthesized according to the literature procedures[2,4-6] from the corresponding 1-alkylimidazoles and methyl-substituted bromopyridines. A general procedure is described as following: To a solution of 20 mmol of 1-alkylimidazole or methyl-substituted bromopyridine in 150 mL dry THF was added 20 mmol of *n*-BuLi (2.5 M in hexane) over 20 min at –78 °C under N_2 and the resulting mixture was stirred at –78 °C for 1 hour, followed by addition of 10 mmol of diethyl carbonate. The mixture was warmed to –40 °C with stirring over several hours, and then dry ice was added. Subsequently, the

mixture was warmed to rt and stirred overnight. The solvent was removed and the residue was subject to chromatography and recrystalization to give the desired ketones.

Bis(1-methyl-2-imidazolyl)ketone (8a): Yield 72%; m. p. 148-150°C (acetone) (lit.[5] m. p. 154-155°C); IR (KBr): 1632 cm^{-1}; ^1H NMR (CD_3COCD_3): δ 7.35 (s, 2H), 7.09 (s, 2H), 3.96 (s, 6H) ppm.

Bis(1-octyl-2-imidazolyl)ketone (8b): Yield 62%; oil; IR (film): 1634 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.29 (d, J= 0.8 Hz, 2H), 7.11 (d, J= 0.8Hz, 2H), 3.34 (t, J=7.3 Hz, 4H), 1.76-1.83 (m, 4H), 1.22-1.29 (m, 20H), 0.84 (t, J=6.8 Hz, 6H) ppm; MS (m/e): 69, 95, 109, 123, 179(100), 301, 357, 386(M^+); HRMS calcd. for $C_{23}H_{38}N_4O$ (M^+) 386.305, found 386.305.

Bis(1-methyl-4,5-diphenyl-2-imidazolyl)ketone (8c): Yield 82%; m. p. 254-256°C (toluene) (lit.[2] m. p. 269-272°C); IR (KBr): 1621 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.18-7.57 (m, 20H), 3.97 (s, 6H) ppm.

Bis(4-methyl-2-pyridyl)ketone (8e): Yield 69%; m. p. 104-106°C ($CHCl_3$/hexanes); IR (KBr): 1682 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.62 (d, J= 4.7 Hz, 2H), 7.89 (s, 2H), 7.30 (d, J= 4.7 Hz, 2H), 2.45 (s, 6H) ppm.

Bis(5-methyl-2-pyridyl)ketone (8f): Yield 71%; m. p. 126-128°C ($CHCl_3$/hexanes); IR (KBr): 1678 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.57 (d, J= 2.0 Hz, 2H), 7.99 (d, J= 8.0 Hz, 2H), 7.66 (dd, J= 8.0, 2.0 Hz, 2H), 2.41 (s, 6H) ppm.

Bis(3-methyl-2-pyridyl)ketone: Yield 61%; m. p. 130-132°C ($CHCl_3$/hexanes); IR (KBr): 1688 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.42 (d, J= 4.6 Hz, 2H), 7.63 (d, J= 7.8 Hz, 2H), 7.27-7.30 (m, 2H), 2.53 (s, 6H) ppm.

Bis(6-methyl-2-pyridyl)ketone: Yield 88%; oil; IR (film): 1683 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.87 (d, J= 7.6 Hz, 2H), 7.72 (t, J= 7.6 Hz, 2H), 7.31 (d, J= 7.6 Hz, 2H), 2.61 (s, 6H) ppm.

General procedure for the addition reaction: To a 0.25 M solution of 1-trityl-4-iodoimidazole (1.2 mmol) in dry CH_2Cl_2 was added a 3.0 M solution of EtMgBr (1.2 mmol) in diethyl ether at rt under N_2. After stirring at rt for 2 hours, the ketone (1.0 mmol) was added to the reaction system and the resulting mixture was stirred at rt for 24-48 hrs. The reaction was quenched by addition of several drops of satd. NH_4Cl aq. solution, and then the mixture was concentrated and the residue was subject to preparative TLC using silica gel plate as the solid support and $CHCl_3$/hexanes (bubbled with ammonia gas) as the eluent.

Bis(1-methyl-2-imidazolyl)(1-trityl-4-imidazolyl)carbinol (7a): Yield 67%; m. p. 194-196°C; IR (KBr): 3442 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.41 (d, J= 1.3 Hz, 1H), 7.27-7.30 (m, 9H), 7.12-7.15 (m, 6H), 6.92 (d, J=1.1 Hz, 2H), 6.88 (d, J= 1.3 Hz, 1H), 6.81 (d, J=1.1 Hz, 2H),

3.45 (s, 6H) ppm; MS (m/e): 82, 119, 165, 243(100), 416, 500(M^+); HRMS calcd. for $C_{31}H_{28}N_6O$ (M^+) 500.232, found 500.232.

Bis(1-octyl-2-imidazolyl)(1-trityl-4-imidazolyl)carbinol (**7b**): Yield 91%; oil; IR (film): 3364 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.37 (d, J= 1.4 Hz, 1H), 7.26-7.29 (m, 9H), 7.10-7.13 (m, 6H), 6.95 (d, J=1.4 Hz, 1H), 6.93 (d, J= 1.1 Hz, 2H), 6.87 (d, J=1.1 Hz, 2H), 3.73-3.92 (m, 4H), 1.32-1.40 (m, 4H), 1.10-1.26 (m, 20H), 0.84 (t, J=6.8 Hz, 6H) ppm; MS (m/e): 95, 165(100), 244, 453, 641, 696(M^+); HRMS calcd. for $C_{45}H_{56}N_6O$ (M^+) 696.452, found 696.452.

Bis(1-methyl-4,5-diphenyl-2-imidazolyl)(1-trityl-4-imidazolyl)carbinol (**7c**): Yield 99%; m. p. 146-148°C ; IR (KBr): 3384 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.10-7.47 (m, 37H), 3.36 (s, 6H) ppm; MS (m/e): 89, 116, 165(100), 243, 328, 570, 695, 804(M^+); HRMS calcd. for $C_{55}H_{44}N_6O$ (M^+) 804.358, found 804.358.

Bis(2-pyridyl)(1-trityl-4-imidazolyl)carbinol (**7d**): Yield 84%; m. p. 172-174°C; IR(KBr): 3276 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.47 (dd, J= 5.3, 1.4 Hz, 2H), 7.76 (d, J= 7.9 Hz, 2H), 7.63 (dt, J= 7.9, 1.4 Hz, 2H), 7.40 (s, 1H), 7.26-7.29(m, 9H), 7.12-7.15 (m, 2H), 7.08-7.10 (m, 6H), 6.96(s, 1H) ppm; MS (m/e): 79, 106, 145, 165, 215(100), 416, 476, 495(M^++H); HRMS calcd. for $C_{33}H_{26}N_4O$ 494.211(M^+), found 494.211.

Bis(4-methyl-2-pyridyl)(1-trityl-4-imidazolyl)carbinol (7e): Yield 55%; m. p. 56-58°C; IR (KBr): 3296 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.33 (d, J= 5.2 Hz, 2H), 7.57 (s, 2H), 7.45 (s, 1H), 7.25-7.29(m, 9H), 7.09-7.12 (m, 6H), 6.97(s, 1H), 6.96 (d, J=5.2 Hz, 2H), 2.30 (s, 6H) ppm; MS (m/e): 65, 92, 165, 243(100), 279, 430, 522(M^+); HRMS calcd. for $C_{35}H_{30}N_4O$ (M^+) 522.242, found 522.242.

Bis(5-methyl-2-pyridyl)(1-trityl-4-imidazolyl)carbinol (**7f**): Yield 46%; m. p. 52-54°C; IR (KBr): 3306 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.30 (s, 2H), 7.63 (d, J=8.1 Hz, 2H), 7.43 (s, 1H), 7.42 (d, J=8.1, 2H), 7.27-7.28 (m, 9H), 7.08-7.10 (m, 6H), 6.96(s, 1H), 2.26 (s, 6H) ppm; MS (m/e): 92, 120, 165, 243(100), 262, 427, 504, 522(M^+); HRMS calcd. for $C_{35}H_{30}N_4O$ (M^+) 522.242, found 522.242.

Bis(1-methyl-2-imidazolyl)(1-trityl-4-imidazolyl)methyl methyl ether (9): To a solution of **7a** (1.0 mmol) in dry THF was added NaH (65% in paraoil, 1.0 mmol) in one portion at rt under N_2, and the resulting mixture was stirred at rt for 30 min, followed by addition of CH_3I (1.0 mmol). Subsequently, the mixture was stirred at rt overnight and the reaction was quenched by addition of satd. NH_4Cl aq. solution. The solvent was removed and the residue was subject to preparative TLC, using silica gel plate as the solid support and $CHCl_3$/hexanes (bubbled with ammonia gas) as the eluent. Yield 93%; ^1H NMR ($CDCl_3$): δ 7.45

(s, 1H), 7.33-7.34 (m, 9H), 7.32 (s, 1H), 7.18-7.20 (m, 6H), 7.02 (s, 2H), 6.90 (s, 2H), 3.50 (s, 6H), 3.24 (s, 3H) ppm; MS (m/e): 95, 120, 165, 243(100), 482, 514 (M^+); HRMS calcd. for $C_{32}H_{30}N_6O$ (M^+) 514.248, found 514.248.

Bis(1-methyl-2-imidazolyl)(1-H-4(5)-imidazolyl)methyl methyl ether (10): A solution of **9** in 85% aq. TFA was stirred at rt overnight, and then the mixture was concentrated at reduced pressure and the residue was added into distilled water. Subsequently, the suspension was filtered and the filtrate was concentrated and dried *in vacuo* over P_2O_5. The residue was dissolved in methanol and bubbled with ammonia gas, and then the resulting mixture was concentrated and the residue was dried *in vacuo* over P_2O_5. To the residue was added chloroform and the mixture was filtered. The filtrate was concentrated and dried *in vacuo* over P_2O_5 to give the desired compound. Yield 98%; IR (KBr): 3452 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.94 (s, 1H), 7.02 (s, 1H), 6.94 (s, 2H), 6.84 (s, 2H), 3.40 (s, 6H), 3.15 (s, 3H) ppm; MS (m/e): 69, 83(100), 120, 225, 241, 257, 272(M^+); HRMS calcd. for $C_{13}H_{16}N_6O$ (M^+) 272.139, found 272.139.

***meso*-5-(4'-*tert*-Butyl-2',6'-dinitrophenyl)-10,15,20-trimesitylporphyrin (12)**: To a mixture of 630 mg (2.5 mmol) 4-*tert*-butyl-2,6-dinitrobenzaldehyde, 2.3 ml mesitaldehyde (15.0 mmol) and 5.0 g 3 Å molecular sieves in 350 ml dry CH_2Cl_2, was added 1.2 ml (17.5 mmol) freshly distilled pyrrole, followed by addition of 2.1 ml (17.5 mmol) freshly distilled $BF_3{\cdot}Et_2O$ at rt under N_2 in the dark. The resulting mixture was stirred at rt for 1 hour, and then 5.96 g (26.3 mmol) DDQ was added. After stirring at rt for 2 hours, 2.44 ml (17.5 mmol) Et_3N was added to the reaction mixture. Subsequently, the reaction mixture was filtered through a short silica gel column, and the filtration was concentrated and the residue was subject to chromatography on silica gel using CH_2Cl_2/hexanes =1/2 (v/v) as the eluent. Yield 5%. UV-Vis (λ_{max}, CH_2Cl_2): 420, 518 nm; ^1H NMR ($CDCl_3$): δ 8.66 (d, J=4.5 Hz, 2H), 8.61 (dd, J=8.6, 4.5 Hz, 4H), 8.55 (d, J=4.4 Hz, 2H), 8.43 (s, 2H), 7.26 (s, 6H), 2.61 (s, 9H), 1.85 (s, 6H), 1.84 (s, 12H), 1.67 (s, 9H), -2.52 (s, 2H) ppm; LSIMS calcd. for $C_{57}H_{55}N_6O_4$ (M^++H) 887.3, found 887.3.

General procedure for the reduction reaction: To a solution of 0.5 mmol porphrin in 1000 ml CH_2Cl_2 (purged with N_2) was added 20 mmol concd. HCl at 0°C (reaction temperature was rt for mononitro porphyrin) under N_2 in the dark. This was followed by addition of 3 mmol $SnCl_2{\cdot}2H_2O$, and the reaction mixture was stirred at 0°C and monitored by TLC. After

stirring for several hours, $NH_3 \cdot H_2O$ was added to the reaction mixture, and then the mixture was washed successively with satd. $NaHCO_3$ aq. solution, brine and dried over Na_2SO_4. The solvent was removed and the residue was subject to chromatography on silica gel (eluent: CH_2Cl_2/hexanes =1/1 (v/v)) to give the corresponding amino porphyrins.

***meso*-5-(2'-Amino-4'-*tert*-butyl-6'-nitrophenyl)-10,15,20-trimesitylporphyrin (13a)**: Yield 64%; UV-Vis (λ_{max}, CH_2Cl_2): 416, 514 nm; ^{1}H NMR ($CDCl_3$): δ 8.42 (d, J=4.6 Hz, 2H), 8.66 (d, J=4.6 Hz, 2H), 8.60-8.63 (m, 4H), 7.81 (s, 1H), 7.25 (s, 3H), 7.26 (s, 3H), 6.89 (s, 1H), 3.55 (s, 2H), 2.61 (s, 9H), 2.57 (s, 6H), 1.88 (s, 6H), 1.83 (s, 9H), 1.80 (s, 6H), -2.52 (s, 2H) ppm; LSIMS calcd. for $C_{57}H_{57}N_6O_2$ (M^++H) 857.4, found 857.4.

meso-**5-(4'-*tert*-Butyl-2',6'-diaminophenyl)-10,15,20-trimesitylporphyrin (13b)**: Yield 28%; UV-Vis (λ_{max}, CH_2Cl_2) 418, 514 nm; ^{1}H NMR ($CDCl_3$): δ 8.96 (d, J=4.6 Hz, 2H), 8.68 (d, J=4.6Hz, 2H), 8.59-8.62 (m, 4H), 7.25 (s, 6H), 6.62 (s, 2H), 3.31 (s, 4H), 2.61 (s, 9H), 1.82 (s, 18H), 1.55 (s, 9H), -2.52 (s, 2H) ppm; LSIMS calcd. for $C_{57}H_{59}N_6$ (M^++H) 827.4, found 827.4.

***meso*-5-(2'-Amino-4'-*tert*-butyl-6'-(3''-(3'''-pyridyl)propionamido)phenyl)-10,15,20-trimesitylporphyrin (15)**: Yield 86%; UV-Vis (λ_{max}, CH_2Cl_2): 420, 520 nm; ^{1}H NMR ($CDCl_3$): δ 8.83 (d, J=4.6 Hz, 2H), 8.69 (d, J=4.6 Hz, 2H), 8.64 (d, J=4.4, 2H), 8.62 (d, J=4.4, 2H), 8.28 (s, 1H), 8.11 (s, 1H), 7.93 (m, 1H), 7.26 (s, 6H), 6.94 (s, 1H), 6.89-6.94 (m, 1H), 6.77 (m, 1H), 6.61 (m, 1H), 3.28 (s, 2H), 2.61 (s, 9H), 2.44 (t, J=7.5 Hz, 2H), 1.84 (s, 3H), 1.82 (s, 6H), 1.80 (s, 3H), 1.78 (s, 6H), 1.56 (s, 9H), 1.51 (t, J=7.5 Hz, 2H), -2.56 (s, 2H) ppm; LSIMS calcd. for $C_{65}H_{66}N_7O$ (M^++H) 960.5, found 960.5.

***meso*-5-(2'-Amino-4'-*tert*-butyl-6'-chloroacetamidophenyl)-10,15,20-trimesityl porphyrin (17)**: Yield 94%; UV-Vis (λ_{max}, CH_2Cl_2): 418, 514 nm; ^{1}H NMR ($CDCl_3$): δ 8.82 (d, J=4.8 Hz, 2H), 8.68 (d, J=4.8 Hz, 2H), 8.63 (d, J=4.4, 2H), 8.61 (d, J=4.4, 2H), 8.25 (s, 1H), 8.02 (s, 1H), 7.23-7.28 (m, 6H), 6.95 (d, J=1.6 Hz, 1H), 3.35 (s, 2H), 3.32 (s, 2H), 2.92 (s, 9H), 1.97 (s, 3H), 1.85 (s, 6H), 1.79 (s, 6H), 1.72 (s, 3H), 1.55 (s, 9H), -2.52 (s, 2H) ppm; LSIMS calcd. for $C_{59}H_{60}ClN_6O$ (M^++H) 903.4, found 903.4.

General procedure for the acylation reaction: To a solution of 0.1 mmol monoamino porphyrin in 100 ml dry THF was added 3 mmol dry Et_3N, followed by addition of 0.6 mmol freshly distilled chloroacetyl chloride at 0°C under N_2. The resulting mixture was stirred at 0°C for 1 hour, and then was warmed to rt and stirred overnight. Subsequently, the reaction was quenched by addition of methanol. After removal of the solvent, the residue was dissolved in CH_2Cl_2, washed with satd. $NaHCO_3$ aq. solution and brine and dried over Na_2SO_4. The solvent

was evaporated and the residue was subject to preparative TLC using silica gel plate as the solid support and CH_2Cl_2/hexanes =1/1 (v/v) as the eluent.

***meso*-5-(4'-*tert*-Butyl-2'-chloroacetamido-6'-nitrophenyl)-10,15,20-trimesityl porphyrin (16)**: Yield 92%; UV-Vis (λ_{max}, CH_2Cl_2): 420, 518 nm; ^{1}H NMR ($CDCl_3$): δ 9.08 (d, J=1.8 Hz, 1H), 8.67 (d, J=4.6 Hz, 2H), 8.63 (d, J=4.6 Hz, 2H), 8.62 (d, J=4.6 Hz, 2H), 8.59 (d, J=4.6 Hz, 2H), 8.17 (d, J=1.8 Hz, 1H), 8.15 (s, 1H), 7.67 (s, 2H), 7.25 (s, 4H), 3.30 (s, 2H), 2.61 (s, 9H), 1.94 (s, 3H), 1.84 (s, 6H), 1.81 (s, 6H), 1.78 (s, 3H), 1.64 (s, 9H), -2.49 (s, 2H) ppm; LSIMS calcd. for $C_{59}H_{58}ClN_6O_3$ (M^++H) 933.4, found 933.4.

***meso*-5-(4'-*tert*-Butyl-2'-chloroacetamido-6'-(3''-(3'''-pyridyl)propionamidophenyl)-10,15,20-trimesitylporphyrin (11)**: Yield 84%; UV-Vis (λ_{max}, CH_2Cl_2): 420, 514 nm; ^{1}H NMR ($CDCl_3$): δ 8.64-8.70 (m, 8H), 8.60 (s, 1H), 8.48 (s, 1H), 8.11 (s, 1H), 8.03 (s, 1H), 7.91 (s, 1H), 7.29 (s, 1H), 7.28 (s, 4H), 7.26 (s, 1H), 6.84 (d, J=7.8 Hz, 1H), 6.73 (m, 1H), 6.51 (s, 1H), 3.37 (s, 2H), 2.62 (s, 9H), 2.43 (t, J=7.7 Hz, 2H), 1.96 (s, 3H), 1.81 (s, 6H), 1.79 (s, 6H), 1.76 (s, 3H), 1.63 (s, 9H), 1.47 (t, J=7.7 Hz, 2H), -2.51 (s, 2H) ppm; LSIMS calcd. for $C_{67}H_{67}ClN_7O_2$ (M^++H) 1036.5, found 1036.5.

General procedure for the attachment of proximal pyridine ligand: To a solution of 0.05 mmol monoamino porphyrin in 5 ml dry DMF was added 1 mmol dry N,N-diethylaniline, followed by addition of a solution of 3-(3'-pyridyl)propionyl chloride hydrochloride in dry DMF (0.1 mmol 3-(3'-pyridyl)propionic acid was dissolved in 2 ml freshly distilled $SOCl_2$, stirred at rt for 4 hours, and then the excess $SOCl_2$ was removed and the residue was dried *in vacuo*. The residue was dissolved in dry DMF and used for the acylation reaction without further purification.) under N_2. The resulting mixture was stirred at rt for 3 hours and the reaction was quenched by addition of methanol. The solvent was removed and the residue was redissolved in CH_2Cl_2, washed with satd. $NaHCO_3$ aq. solution and brine, and dried over Na_2SO_4. After evaporation of the solvent, the residue was subject to preparative TLC using silica gel plate as the solid support and CH_2Cl_2/methanol =100/1 (v/v) as the eluent.

***meso*-5-(4'-*tert*-Butyl-2'-nitro-6'-(3''-(3'''-pyridyl)propionamidophenyl)-10,15,20-trimesitylporphyrin (14)**: Yield 68%; UV-Vis (λ_{max}, CH_2Cl_2): 420, 514 nm; ^{1}H NMR ($CDCl_3$): δ 9.10 (s, 1H), 8.58-8.67 (m, 8H), 8.15 (d, J=1.7 Hz, 1H), 8.11 (d, J=4.3 Hz, 1H), 7.93 (s, 1H), 7.25-7.26 (m, 6H), 6.80-6.81 (m, 1H), 6.73-6.76 (m, 1H), 6.68 (s, 1H), 2.61 (s, 9H), 2.40 (t, J=7.5 Hz, 2H), 1.85 (s, 3H), 1.83 (s, 3H), 1.82 (s, 6H), 1.77 (s, 6H), 1.65 (s, 9H), 1.46 (t, J=7.5 Hz, 2H), -2.53 (s, 2H) ppm; LSIMS calcd. for $C_{65}H_{63}N_7O_3$ (M^+) 989.5, found 989.5.

***meso*-5-(4'-*tert*-Butyl-2'-chloroacetamido-6'-(3'''-(3''''-pyridyl)propionamidophenyl)-10,15,20-trimesitylporphyrin (11)**: Yield 63%.

4: To a solution of 0.05 mmol **11** in 50 ml CH_3CN were added 0.1 mmol **10** and 0.30 mmol Cs_2CO_3, and then the resulting mixture was stirred at rt for 48 hours. The solvent was removed and the residue was dissolved in $CHCl_3$, washed with satd. $NaHCO_3$ aq. solution and brine, and dried over Na_2SO_4. After removal of the solvent, the residue was subject to preparative TLC using $CHCl_3$/methanol =100/1 (v/v) (bubbled with ammonia gas) as the eluent. Yield 32%; UV-Vis (λ_{max}, CH_2Cl_2): 420, 518 nm; ^{1}H NMR ($CDCl_3$): δ 8.68-8.74 (m, 8H), 8.64 (s, 1H), 8.41 (s, 1H), 8.11 (s, 1H), 7.90 (s, 1H), 7.26-7.28 (s, 6H), 7.14 (s, 1H), 7.01 (s, 1H), 6.95 (s, 2H), 6.82-6.84 (m, 1H), 6.77 (s, 2H), 6.73 (s, 2H), 6.44 (s, 1H), 3.62 (s, 2H), 3.30 (s, 6H), 2.95 (s, 3H), 2.64 (s, 9H), 2.41 (t, J=6.2 Hz, 2H), 1.86 (s, 6H), 1.85 (s, 6H), 1.77 (s, 6H), 1.62 (s, 9H), 1.46 (t, J=6.2 Hz, 2H), -2.51 (s, 2H) ppm; LSIMS calcd. for $C_{80}H_{82}N_{13}O_3$ (M^++H) 1272.6, found 1272.6.

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