An Efficient One-Pot Protocol for Asymmetric Bifunctionalization of 5,15-Disubstituted Porphyrins: A Simple Preparation of *meso* Acyl-, Alkoxycarbonyl-, and Carbamoyl-Substituted *meso*-Formylporphyrins

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Supporting Information

General ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-EX270, JNM-AL300, or JNM-AL400 spectrometer. The chemical shifts were reported in ppm relative to $CHCl_3$ (δ = 7.24) for ^{1}H-NMR and relative to the central resonance of $CDCl_3$ (δ = 77.0) for ^{13}C-NMR. IR spectra were recorded on a JASCO JASCO FT/IR-4100 spectrophotometer. The mass spectroscopic data were obtained on a JEOL JNM-DX302 spectrometer.

All the asymmetric difunctionalization reactions of porphyrins were carried out under an argon atmosphere in oven-dried glassware following standard Schlenk techniques. Tetrahydrofuran (THF) was distilled under argon from sodium benzophenone ketyl. Kanto Kagaku Silica Gel 60 (spherical) and Merck kiesel-gel 60 F254 were employed for silica gel column and thin layer chromatography, respectively.

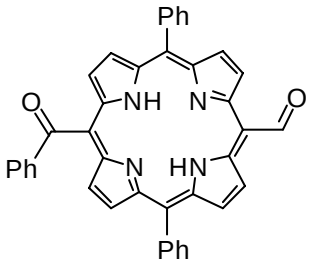
5,15-Diphenylporphyrin (**1a**),[1] 5,15-di(*p*-tolyl)porphyrin (**1b**),[2] 5,15-bis(3-methoxyphenyl)porphyrin (**1c**),[2] 5,15-bis(3-trifluoromethylphenyl)porphyrin (**1d**),[3] 5,15-di-*iso*-butylporphyrin (**1e**)[4] were prepared as described in the literature. Unless otherwise stated, all commercially available chemicals were used without further purification.

General Procedure for the One-Pot Asymmetric Difunctionalization of 5,15-Disubstituted Porphyrins. The starting 5,15-disubstituted porphyrins **1** were purified by silica gel column chromatography (CH_2Cl_2) followed by recrystallization from CH_2Cl_2/hexane, and dried over silica gel for 10 h under a reduced pressure (1 mmHg) at 110 °C just before their use.

An oven-dried 100 mL three-necked flask equipped with a magnetic stirring bar, a reflux condenser, and rubber septum was charged with a porphyrin **1** (0.1 mmol). The flask was evacuated and flushed with argon (three times), and then absolute THF (40 mL) was added. To the solution was added an ethereal solution of $PyMe_2SiCH_2Li$ (prepared by adding 0.65 mL of 1.58 M *t*BuLi in pentane to a solution of 1.2 mmol 2-pyridyltrimethylsilane in 1.5 mL of ether, followed by stirring at -78 °C for 2 h)[5] via a cannula at -78 °C. After being stirred at -78 °C for 5 min, the cooling bath was removed and the mixture was stirred at room temperature. The reaction was complete within 3 h, having been monitored by TLC. Upon completion of the reaction, the mixture was cooled to -40 °C, and then 1.0 mmol of an elctrophile (acylchlorides **2**, chloroformates **4**, or isocyanates **6**) was added. After being stirred at -40 °C for 5 min, the mixture was warmed to room temperature, stirred for 3 h, and recooled to 0 °C. To the cooled mixture was added 5 mL of 0.1 M HCl. The

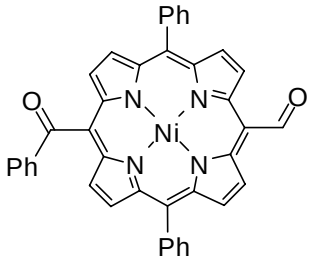
resulting solution was stirred for 10 min at 0 °C, and then DDQ (1 mmol) was added. After being stirred at 65 °C for 2–5 h, the mixture was allowed to cool to room temperature and concentrated under a reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (ca. 100 mL) and the solution was poured into brine. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined, concentrated in vacuo, and subjected to chromatography on silica gel using 5–10% hexane/CH_2Cl_2 as an eluent to give the *meso*-functionalized formylporphyrin.

^{13}C-NMR data were generally not available for the *meso*-functionalized free base porphyrins due to their poor solubility. The free bases, therefore, were further converted to their Ni^{II} complexes as follows. To a solution of a free base formylporphyrin (0.04 mmol) in DMF (3 mL) was added $Ni(OAc)_2 \cdot 4H_2O$ (50 mg, 0.2 mmol), and the mixture was stirred at 140 °C for 2 h. After completion of the reaction (monitored by TLC), the solution was poured into water (80 mL). The resulting precipitate was collected and washed with water and MeOH to give the Ni^{II} complex in a nearly quantitative yield.



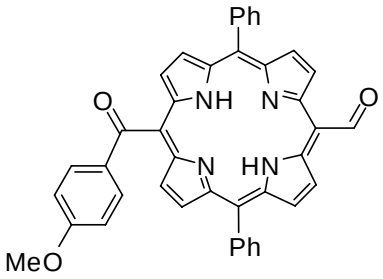
3aa

10-Benzoyl-20-formyl-5,15-diphenylporphyrin (3aa). ^{1}H-NMR ($CDCl_3$) δ: 12.55 (1H, s), 10.04 (2H, br d, J = 4.7 Hz), 9.01 (2H, d, *J* = 5.1 Hz), 8.93 (2H, d, *J* = 4.7 Hz), 8.74 (2H, d, *J* = 4.9 Hz), 8.16–8.14 (4H, m), 7.91 (2H, br d, *J* = 7.1 Hz), 7.80–7.72 (6H, m), 7.59 (1H, br t, *J* = 7.5 Hz), 7.39 (2H, br t, *J* = 7.8 Hz), -2.32 (2H, s); IR (KBr): 3322, 1674, 1548, 1348, 1251, 1153, 1114, 970, 922, 788, 702 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{40}H_{27}O_2N_4$: 595.2134. Found 595.2138.



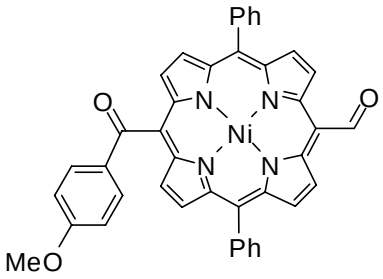
Ni-3aa

[10-Benzoyl-20-formyl-5,15-diphenylporphinato]nickel(II) (Ni-3aa). ^{1}H-NMR ($CDCl_3$) δ: 12.00 (1H, s), 9.74 (2H, d, *J* = 5.3 Hz), 8.77 (2H, d, *J* = 5.0 Hz), 8.74 (2H, d, *J* = 5.3 Hz), 8.54 (2H, d, *J* = 5.0 Hz), 7.84–7.83 (4H, m), 7.65–7.56 (8H, m), 7.45 (1H, br t, *J* = 7.4 Hz), 7.25 (2H, br t, *J* = 7.8 Hz); ^{13}C-NMR ($CDCl_3$) δ: 197.1, 192.8, 144.2, 144.0, 141.6, 140.1, 139.5, 139.4, 135.4, 133.8, 133.4, 133.1, 131.8, 131.1, 131.0, 128.4, 128.2, 127.1, 121.1, 118.6, 29.7; IR (KBr): 1675, 1658, 1595, 1576, 1550, 1441, 1356, 1314, 1245, 1179, 1157, 1082, 1007, 974, 945, 844, 792, 756, 701, 675 cm^{-1}; HRMS (EI): Calcd for $C_{40}H_{24}O_2N_4Ni$: 650.1253. Found 650.1250.



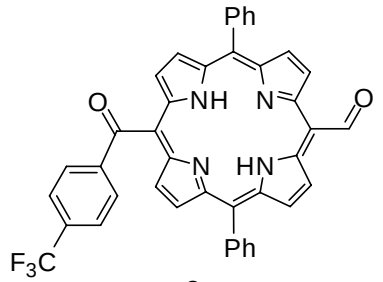
3ab

10-Formyl-20-(4-methoxybenzoyl)-5,15-diphenylporphyrin (3ab). ^{1}H-NMR ($CDCl_3$) δ: 12.53 (1H, s), 10.02 (2H, br s), 9.00 (2H, d, *J* = 5.1 Hz), 8.95 (2H, d, *J* = 4.6 Hz), 8.74 (2H, d, *J* = 4.6 Hz), 8.15 (4H, d, *J* = 6.6 Hz), 7.93–7.71 (8H, m), 6.85 (2H, d, *J* = 8.8 Hz), 3.81 (3H, s), -2.30 (2H, s); IR (KBr): 3319, 1674, 1597, 1554, 1509, 1348, 1254, 1164, 1114, 1028, 971, 946, 924, 849, 804, 731, 702, 677 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{41}H_{29}O_3N_4$: 625.2231. Found 625.2240.



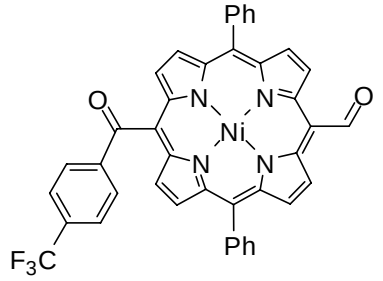
Ni-3ab

[10-Formyl-20-(4-methoxybenzoyl)-5,15-diphenylporphinato]-nickel(II) (Ni-3ab). ^{1}H-NMR ($CDCl_3$) δ: 12.07 (1H, s), 9.81 (2H, d, *J* = 4.9 Hz), 8.84 (2H, d, *J* = 4.9 Hz), 8.82 (2H, d, *J* = 4.9 Hz), 8.60 (2H, d, *J* = 4.9 Hz), 7.91 (4H, d, *J* = 5.9 Hz), 7.74–7.61 (8H, m), 6.77 (2H, d, *J* = 8.8 Hz), 3.76 (3H, s); ^{13}C-NMR (CDCl3) δ: 195.1, 192.5, 163.8, 144.1, 143.9, 141.4, 139.4, 139.2, 135.3, 133.3, 132.9, 131.7, 130.9, 128.0, 126.9, 121.0, 119.1, 113.6, 90.8, 86.1, 55.5, 30.4; IR (KBr): 1677, 1658, 1595, 1571, 1546, 1508, 1441, 1356, 1314, 1254, 1167, 1123, 1078, 1007, 972, 946, 851, 796 cm^{-1}; HRMS (EI): Calcd for $C_{41}H_{26}O_3N_4Ni$: 680.1358. Found 680.1362.



3ac

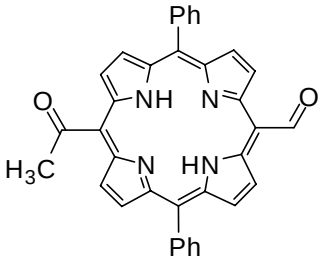
10-Formyl-20-[(4-trifluoromethyl)benzoyl]-5,15-diphenylporphyrin (3ac). ^{1}H-NMR ($CDCl_3$) δ: 12.53 (1H, s), 10.03 (2H, d, *J* = 4.2 Hz), 9.01 (2H, d, *J* = 5.1 Hz), 8.88 (2H, d, *J* = 4.8 Hz), 8.77 (2H, d, *J* = 4.8 Hz), 8.15–8.14 (4H, m), 8.01 (2H, d, *J* = 8.1 Hz), 7.83–7.73 (6H, m), 7.66 (2H, d, *J* = 8.2 Hz), -2.37 (2H, s); IR (KBr): 3316, 1554, 1510, 1440, 1411, 1325, 1250, 1169, 1128, 1064, 1017, 971, 946, 924, 879, 848, 797, 721, 679 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{41}H_{26}O_2N_4F_3$: 663.2008. Found 663.2005.



Ni-3ac

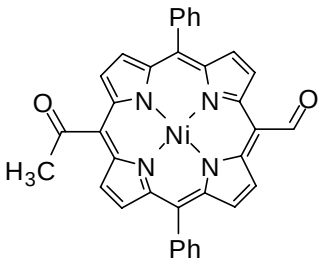
{10-Formyl-20-[(4-trifluoromethyl)benzoyl]-5,15-diphenylporphinato}nickel(II) (Ni-3ac). ^{1}H-NMR ($CDCl_3$) δ: 12.05 (1H, s), 9.79 (2H, d, *J* = 4.9 Hz), 8.83 (2H, d, *J* = 4.9 Hz), 8.76 (2H, d, *J* = 4.6 Hz), 8.61 (2H, d, *J* = 4.6 Hz), 7.89 (4H, d, *J* = 6.8 Hz), 7.78 (2H, d, *J* = 7.8 Hz), 7.74–7.61 (6H, m), 7.57 (2H, d, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$) δ: 195.8, 192.4, 168.0, 144.0, 143.9, 142.5, 141.6, 139.2, 139.0, 135.4, 133.2, 131.3, 131.2, 131.0, 128.1, 127.0, 125.4, 121.2, 117.0, 112.1, 107.0; IR (KBr): 1678, 1553,

1509, 1440, 1411, 1356, 1324, 1242, 1168, 1132, 1066, 1008, 977, 946, 851, 791, 754, 734, 703 cm^{-1}; HRMS (EI): Calcd for $C_{41}H_{23}F_3O_2N_4Ni$: 718.1127. Found 718.1132.



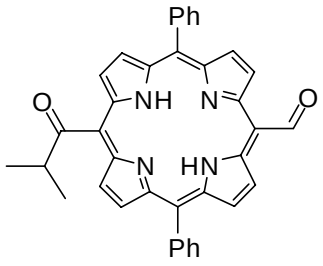
3ad

10-Acetyl-20-formyl-5,15-diphenylporphyrin (3ad). ^{1}H-NMR ($CDCl_3$) δ: 12.51 (1H, s), 10.02 (2H, br s), 9.12 (2H, d, *J* = 4.6 Hz), 8.99 (2H, d, *J* = 4.9 Hz), 8.84 (2H, d, *J* = 4.6 Hz), 8.18–8.13 (4H, m), 7.87–7.74 (6H, m), 3.47 (3H, s), -2.39 (2H, s); IR (KBr): 3332, 1701, 1674, 1550, 1358, 1274, 1223, 1160, 1106, 1068, 1024, 962, 924, 806, 730 704, 667, 635 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{35}H_{25}O_2N_4$: 533.1978. Found 533.1973.



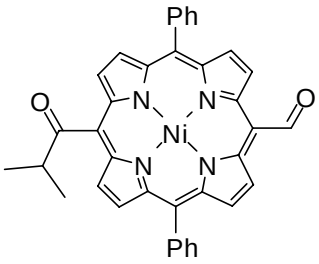
Ni-3ad

[10-Acetyl-20-formyl-5,15-diphenylporphinato]nickel(II) (Ni-3ad). ^{1}H-NMR ($CDCl_3$) δ: ^{1}H-NMR ($CDCl_3$) δ: 12.01 (1H, s), 9.76 (2H, d, *J* = 4.9 Hz), 8.99 (2H, d, *J* = 4.9 Hz), 8.81 (2H, d, *J* = 4.9 Hz), 8.67 (2H, d, *J* = 4.9 Hz), 7.90 (4H, d, *J* = 6.2 Hz), 7.76-7.53 (6H, m), 3.06 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 204.5, 192.7, 144.2, 141.9, 141.6, 139.4, 138.3, 137.6, 135.5, 133.4, 131.7, 131.2, 130.8, 128.2, 127.1, 121.1, 116.0, 36.5; IR (KBr): 1709, 1676, 1595, 1572, 1551, 1460, 1440, 1417, 1353, 1316, 1260, 1220, 1194, 1156, 1084, 1064, 1027, 1009, 945, 793, 765, 735 cm^{-1}; HRMS (EI): Calcd for $C_{35}H_{22}O_2N_4Ni$: 588.1096. Found 588.1090.



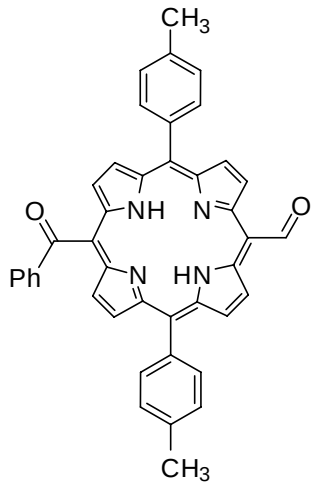
3ae

10-Formyl-20-isobutyryl-5,15-diphenylporphyrin (3ae). ^{1}H-NMR ($CDCl_3$) δ: ^{1}H-NMR ($CDCl_3$) δ: 12.48 (1H, s), 9.99 (2H, d, *J* = 4.9 Hz), 9.03 (2H, d, *J* = 4.8 Hz), 8.98 (2H, d, *J* = 4.9 Hz), 8.83 (2H, d, *J* = 4.8 Hz), 8.20–8.10 (4H, m), 7.86–7.72 (6H, m), 4.17–4.08 (1H, m), 1.52 (6H, d, *J* = 7.0 Hz), -2.41 (1.9H, s); IR (KBr): 3319, 2967, 2929, 1690, 1671, 1554, 1461, 1399, 1346, 1269, 1175, 1152, 1134, 1105, 1063, 964, 924, 799, 727, 702 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{37}H_{29}O_2N_4$: 561.2291. Found 561.2285.



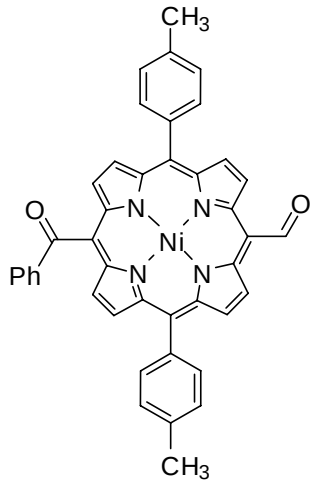
Ni-3ae

[10-Formyl-20-isobutyryl-5,15-diphenylporphinato]nickel(II) (Ni-3ae). ^{1}H-NMR ($CDCl_3$) δ: 12.03 (1H, s), 9.77 (2H, d, *J* = 5.1 Hz), 8.87 (2H, d, *J* = 4.8 Hz), 8.81 (2H, d, *J* = 5.1 Hz), 8.66 (2H, d, *J* = 4.8 Hz), 7.98–7.84 (4H, m), 7.80–7.60 (6H, m) 3.57–3.48 (1H, m), 1.22 (6H, d, *J* = 7.0 Hz); ^{13}C-NMR ($CDCl_3$) δ: 210.9, 192.7, 144.2, 144.0, 141.4, 139.5, 138.2, 135.5, 133.4, 133.3, 131.2, 131.1, 128.2, 127.1, 121.1, 120.6, 106.7, 46.0, 25.8, 18.8; IR (KBr): 1679, 1598, 1545, 1488, 1442, 1357, 1185, 1153, 1078, 1005, 946, 794, 754 cm^{-1}; HRMS (EI): Calcd for $C_{37}H_{26}O_2N_4Ni$: 616.1409. Found 616.1401.



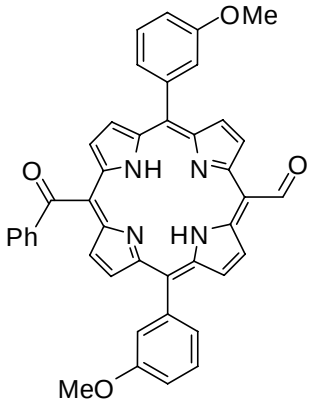
3ba

10-Benzoyl-20-formyl-5,15-di(*p*-tolyl)porphyrin (3ba). ^{1}H-NMR ($CDCl_3$) δ: 12.53 (1H, s), 10.02 (2H, br s), 9.03 (2H, d, *J* = 5.1 Hz), 8.92 (2H, d, *J* = 4.6 Hz), 8.77 (2H, d, *J* = 4.6 Hz), 8.03 (4H, d, *J* = 7.8 Hz), 7.91 (2H, d, *J* = 7.6 Hz), 7.62–7.51 (5H, m), 7.39 (2H, t, *J* = 7.8 Hz), 2.69 (6H, s), -2.30 (2H, s); IR (KBr): 3316, 1673, 1551, 1507, 1347, 1251, 1168, 1112, 971, 947, 924, 836, 796, 727, 695 cm^{-1}; HRMS-FAB^{+} ($[M+H]^{+}$): Calcd for $C_{42}H_{31}O_2N_4$: 623.2447. Found 623.2452.



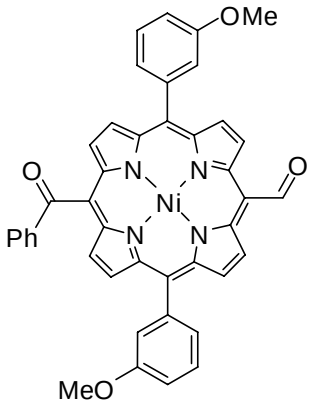
Ni-3ba

[10-Benzoyl-20-formyl-5,15-di(*p*-tolyl)porphinato]nickel(II) (Ni-3ba). ^{1}H-NMR ($CDCl_3$) δ: 12.06 (1H, s), 9.78 (2H, d, *J* = 5.1 Hz), 8.84 (2H, d, *J* = 5.1 Hz), 8.78 (2H, d, *J* = 4.9 Hz), 8.61 (2H, d, *J* = 4.9 Hz), 7.76 (4H, d, *J* = 7.9 Hz), 7.67 (2H, d, *J* = 7.5 Hz), 7.54–7.41 (5H, m), 7.30 (2H, t, *J* = 7.8 Hz), 2.62 (6H, s); ^{13}C-NMR ($CDCl_3$) δ: 197.1, 192.8, 144.2, 144.2, 141.7, 140.1, 139.3, 138.0, 136.6, 135.5, 133.7, 133.3, 133.1, 131.6, 131.0, 131.0, 128.4, 127.8, 121.3, 118.5, 106.8, 29.6, 21.4; IR (KBr): 3024, 2924, 2857, 1672, 1594, 1576, 1547, 1509, 1448, 1356, 1312, 1252, 1210, 1178, 1157, 1106, 1078, 1003, 970, 945, 906, 852, 836, 797, 714, 689 cm^{-1}; HRMS (EI): Calcd for $C_{42}H_{28}O_2N_4Ni$: 678.1566. Found 678.1571.



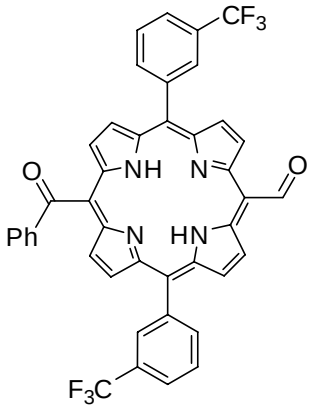
3ca

5,15-Bis(4-methoxyphenyl)-10-benzoyl-20-formylporphyrin (3ca). ^{1}H-NMR ($CDCl_3$) δ: 12.54 (1H, s), 10.04 (2H, br s), 9.06 (2H, d, *J* = 4.9 Hz), 8.92 (2H, d, *J* = 4.9 Hz), 8.79 (2H, d, *J* = 4.6 Hz), 7.91 (2H, d, *J* = 7.3 Hz), 7.79–7.69 (4H, m), 7.68–7.55 (3H, m), 7.44–7.31 (4H, m), 3.98 (6H, s), -2.33 (2H, s); IR (KBr): 3316, 1671, 1595, 1478, 1348, 1316, 1286, 1153, 1115, 1047, 976, 927, 802, 733 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{42}H_{31}O_4N_4$: 655.2345. Found 655.2352.



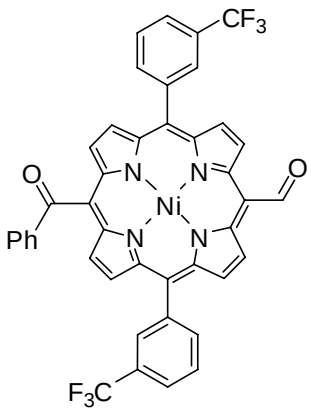
Ni-3ca

[5,15-Bis(3-methoxyphenyl)-10-benzoyl-20-formylporphinato]-nickel(II) (Ni-3ca). ^{1}H-NMR ($CDCl_3$) δ: 12.07 (1H, s), 9.80 (2H, d, *J* = 5.1 Hz), 8.89 (2H, d, *J* = 5.1 Hz), 8.80 (2H, d, *J* = 4.9 Hz), 8.65 (2H, d, *J* = 4.9 Hz), 7.68 (2H, d, *J* = 7.1 Hz), 7.59–7.42 (7H, m), 7.31 (2H, t, *J* = 7.9 Hz), 7.27–7.20 (2H, m), 3.91 (6H, s); ^{13}C-NMR ($CDCl_3$) δ: 197.0, 192.8, 158.2, 144.2, 143.9, 141.5, 140.8, 140.1, 139.4, 135.5, 133.8, 133.1, 131.7, 131.1, 131.0, 128.4, 128.0, 126.4, 125.5, 120.9, 119.5, 118.6, 113.8, 55.4; IR (KBr): 1672, 1658, 1596, 1576, 1544, 1447, 1420, 1354, 1259, 1215, 1156, 1078, 1008, 974, 950, 869, 790, 694 cm^{-1}; HRMS (EI): Calcd for $C_{42}H_{28}O_4N_4Ni$: 710.1464. Found 710.1461.



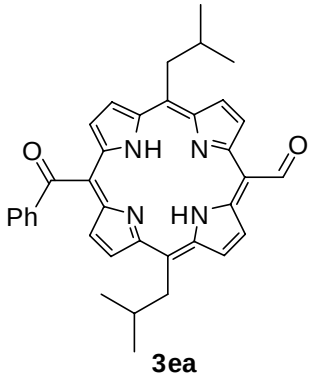
3da

5,15-Bis[3-(trifluoromethyl)phenyl]-10-benzoyl-20-formylporphyrin (3da). ^{1}H-NMR ($CDCl_3$) δ: 12.50 (1H, s), 10.04 (2H, s), 8.99 (2H, d, *J* = 4.6 Hz), 8.92 (2H, d, *J* = 5.1 Hz), 8.68 (2H, d, *J* = 4.6 Hz), 8.44 (2H, s), 8.34 (2H, d, *J* = 7.3 Hz), 8.10 (2H, d, *J* = 8.1 Hz), 7.97–7.86 (4H, m), 7.61 (1H, t, *J* = 7.4 Hz), 7.41 (2H, t, *J* = 7.8 Hz), -2.44 (2H, s); IR (KBr): 3316, 1673, 1593, 1554, 1483, 1430, 1324, 1162, 1002, 975, 928, 897, 837, 796, 707 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$) : Calcd for $C_{42}H_{25}O_2N_4F_6$: 731.1888. Found 731.1882.



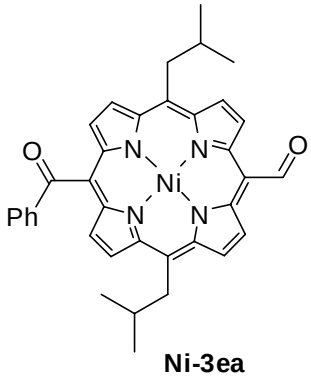
Ni-3da

{5,15-Bis[3-(trifluoromethyl)phenyl]-10-benzoyl-20-formylporphinato}nickel(II) (Ni-3da). ^{1}H-NMR ($CDCl_3$) δ: 12.10 (1H, s), 9.86 (2H, dd, *J* = 5.2, 1.6 Hz), 8.86 (2H, dd, *J* = 4.9, 1.8 Hz), 8.78 (2H, dd, *J* = 5.1, 1.6 Hz), 8.55 (2H, dd, *J* = 4.9, 1.6 Hz), 8.22 (2H, s), 8.13 (2H, d, *J* = 7.5 Hz), 8.00 (2H, d, *J* = 7.7 Hz), 7.82 (2H, t, *J* = 7.7 Hz), 7.70 (2H, d, *J* = 7.9 Hz), 7.54 (1H, t, *J* = 7.5 Hz), 7.34 (2H, t, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) δ: 196.8, 192.7, 144.4, 143.7, 141.5, 140.4, 140.0, 139.7, 136.3, 135.0, 133.9, 132.8, 132.3, 131.7, 131.0, 130.0, 129.7, 129.6, 128.5, 127.7, 125.3, 125.2, 119.3, 30.3; IR (KBr): 1674, 1594, 1548, 1448, 1430, 1371, 1327, 1260, 1163, 1129, 1093, 1075, 1009, 975, 949, 913, 843, 797, 702 cm^{-1}; HRMS (EI): Calcd for $C_{42}H_{22}O_2N_4F_6Ni$: 786.1000. Found 786.1001.



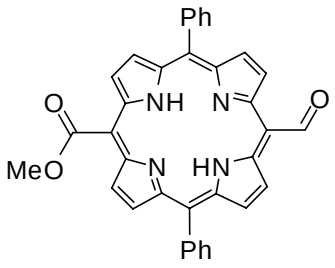
3ea

10-Benzoyl-20-formyl-5,15-diisobutylporphyrin (3ea). ^{1}H-NMR ($CDCl_3$) δ: 12.44 (1H, s), 9.96 (2H, d, *J* = 4.9 Hz), 9.47 (2H, d, *J* = 5.1 Hz), 9.27 (2H, d, *J* = 4.9 Hz), 8.96 (2H, d, *J* = 4.8 Hz), 7.91 (2H, d, *J* = 7.7 Hz), 7.59 (1H, t, *J* = 7.4 Hz), 7.39 (2H, t, *J* = 7.8 Hz), 4.69 (4H, d, *J* = 7.3 Hz), 2.70-2.61 (2H, m), 1.14 (12H, d, *J* = 6.6 Hz), -2.43 (2H, s); IR (KBr): 3317, 2953, 1673, 1660, 1554, 1466, 1241, 1173, 1127, 947, 927, 836, 784, 726, 692 cm^{-1}; HRMS-FAB^{+} ([M+H]$^{+}$): Calcd for $C_{36}H_{35}O_2N_4$: 555.2760. Found 555.2752.



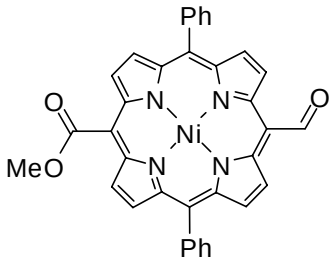
Ni-3ea

[10-Benzoyl-20-formyl-5,15-diisobutylporphinato]nickel(II) (Ni-3ea). ^{1}H-NMR ($CDCl_3$) δ: 11.93 (1H, s), 9.79 (2H, d, *J* = 5.1 Hz), 9.33 (2H, d, *J* = 5.1 Hz), 9.11 (2H, d, *J* = 5.1 Hz), 8.81 (2H, d, *J* = 4.9 Hz), 7.65 (2H, d, *J* = 7.3 Hz), 7.50 (1H, t, *J* = 7.4 Hz), 7.30 (2H, t, *J* = 7.8 Hz), 4.41 (4H, d, *J* = 7.1 Hz), 2.20–2.10 (2H, m), 0.82 (12H, d, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 196.7, 192.1, 144.1, 142.9, 141.4, 139.9, 137.9, 133.5, 133.4, 131.9, 131.4, 130.8, 130.8, 128.3, 119.6, 112.5, 105.5, 42.2, 34.4, 30.4, 29.8, 23.0; IR (KBr): 1671, 1593, 1546, 1449, 1348, 1312, 1260, 1213, 1169, 1143, 1084, 1017, 959, 908, 837, 789, 732, 700 cm^{-1}; HRMS (EI): Calcd for $C_{36}H_{32}O_2N_4Ni$: 610.1879. Found 610.1885.



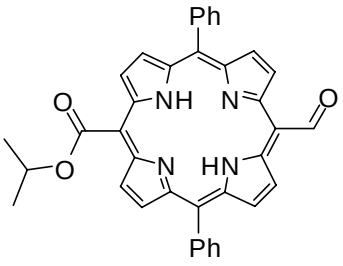
5aa

10-Formyl-20-methoxycarbonyl-5,15-diphenylporphyrin (5aa). ^{1}H-NMR ($CDCl_3$) δ: 12.54 (1H, s), 10.03 (2H, d, *J* = 4.9 Hz), 9.33 (2H, d, *J* = 4.9 Hz), 8.99 (2H, d, *J* = 4.9 Hz), 8.85 (2H, d, *J* = 4.9 Hz), 8.20–8.13 (4H, m), 7.87–7.73 (6H, m), 4.55 (3H, s), -2.54 (2H, s); IR (KBr): 3321, 1709, 1677, 1553, 1428, 1255, 1153, 1109, 1051, 972, 927, 798, 712 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{35}H_{25}O_3N_4$: 549.1927. Found 549.1924.



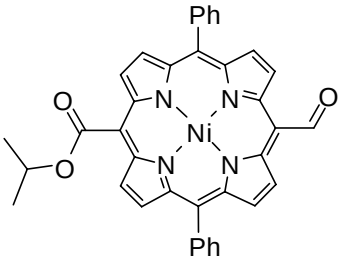
Ni-5aa

[10-Formyl-20-methoxycarbonyl-5,15-diphenylporphinato]-nickel(II) (Ni-5aa). ^{1}H-NMR ($CDCl_3$) δ: 11.92 (1H, s), 9.69 (2H, d, *J* = 5.1 Hz), 9.23 (2H, d, *J* = 4.9 Hz), 8.74 (2H, d, *J* = 5.1 Hz), 8.65 (2H, d, *J* = 4.9 Hz), 7.86 (4H, d, *J* = 6.4 Hz), 7.75–7.56 (6H, m), 4.35 (3.1H, s); ^{13}C-NMR ($CDCl_3$) δ: 192.7, 170.0, 143.8, 143.5, 141.6, 140.2, 139.4, 135.1, 133.4, 132.5, 131.3, 128.2, 127.0, 120.9, 110.4, 107.1, 77.2, 53.6; IR (KBr): 1720, 1679, 1598, 1546, 1491, 1439, 1358, 1243, 1195, 1156, 1080, 1007, 947, 902, 848, 797, 752, 725, 701, 640 cm^{-1}; HRMS (EI): Calcd for $C_{35}H_{22}O_3N_4Ni$: 604.1045. Found 604.1039.



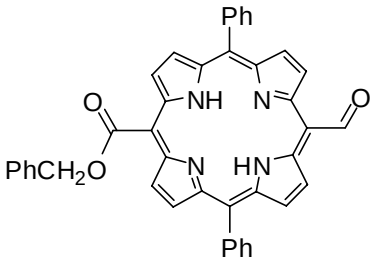
5ab

10-Formyl-20-isopropoxycarbonyl-5,15-diphenylporphyrin (5ab). ^{1}H-NMR ($CDCl_3$) δ: 12.52 (1H, s), 10.02 (2H, d, *J* = 5.1 Hz), 9.35 (2H, d, *J* = 4.9 Hz), 8.99 (2H, d, *J* = 5.1 Hz), 8.85 (2H, d, *J* = 4.9 Hz), 8.20–8.13 (4H, m), 7.86–7.73 (6H, m), 6.06–5.95 (1H, m), 1.76 (6H, d, *J* = 6.2 Hz), -2.52 (2H, s); IR (KBr): 3320, 1720, 1671, 1552, 1476, 1443, 1398, 1350, 1249, 1168, 1111, 1048, 968, 921, 902, 833, 803, 779, 728, 701 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{37}H_{29}O_3N_4$: 577.2440. Found 577.2242.



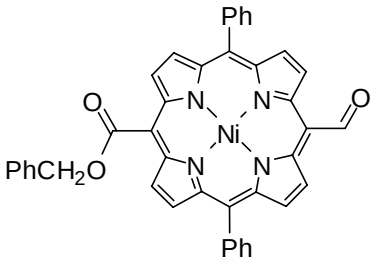
Ni-5ab

[10-Formyl-20-isopropoxycarbonyl-5,15-diphenylporphinato]-nickel(II) (Ni-5ab). ^{1}H-NMR ($CDCl_3$) δ: 11.95 (1H, s), 9.71 (2H, d, *J* = 4.9 Hz), 9.26 (2H, d, *J* = 4.9 Hz), 8.76 (2H, d, *J* = 4.9 Hz), 8.67 (2H, d, *J* = 4.9 Hz), 7.88 (4H, d, *J* = 7.3 Hz), 7.76–7.60 (6H, m), 5.84–5.78 (1H, m), 1.62 (6H, d, *J* = 6.3 Hz); ^{13}C-NMR (CDCl3) δ: 192.4, 168.7, 143.7, 143.5, 141.4, 139.8, 139.4, 135.0, 133.3, 133.2, 132.2, 131.0, 128.0, 126.9, 120.8, 111.5, 107.0, 70.9, 22.3; IR (KBr): 1715, 1679, 1547, 1442, 1358, 1245, 1194, 1156, 1079, 1007, 947, 903, 850, 832, 796, 752, 702 cm^{-1}; HRMS (EI): Calcd for $C_{37}H_{26}O_3N_4Ni$: 632.1358. Found 632.1364.



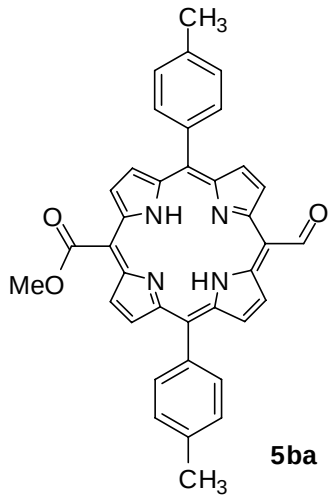
5ac

5-Benzyloxycarbonyl-15-formyl-10,20-diphenylporphyrin (5ac). ^{1}H-NMR ($CDCl_3$) δ: 12.46 (1H, s), 9.97 (2H, d, *J* = 4.9 Hz), 9.25 (2H, d, *J* = 4.9 Hz), 8.95 (2H, d, *J* = 4.9 Hz), 8.80 (2H, d, *J* = 4.9 Hz), 8.22-8.05 (4H, m), 7.86-7.66 (6H, m), 7.56-7.28 (5H, m), 6.02 (2H, s), -2.61 (2H, s); IR (KBr): 3317, 1712, 1678, 1554, 1350, 1211, 1161, 1045, 968, 922, 806, 737, 698 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{41}H_{29}N_4O_3$: 625.2240. Found: 625.2238.



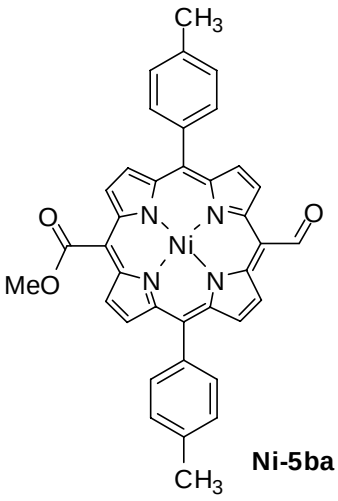
Ni-5ac

[5-Benzyloxycarbonyl-15-formyl-10,20-diphenylporphinato]-nickel(II) (Ni-5ac). ^{1}H-NMR ($CDCl_3$) δ: 11.79 (1H, s), 9.58 (2H, d, *J* = 4.8 Hz), 9.16 (2H, d, *J* = 4.8 Hz), 8.65 (2H, d, *J* = 4.8 Hz), 8.58 (2H, d, *J* = 4.8 Hz), 8.02-7.51 (10H, m), 7.48-7.28 (5H, m), 5.81 (2H, s); ^{13}C-NMR ($CDCl_3$) δ: 192.6, 169.4, 144.0, 143.8, 143.5, 141.6, 140.2, 139.5, 135.0, 133.4, 133.0, 132.4, 132.2, 131.2, 130.3, 128.8, 128.1, 127.0, 120.9, 110.5, 108.4, 68.6; IR (KBr): 1728, 1678, 1550, 1450, 1362, 1300, 1246, 1200, 1157, 1076, 1007, 949, 845, 795, 748, 698 cm^{-1}; HRMS (EI): Calcd for $C_{41}H_{26}N_4NiO_3$: 680.1358. Found 680.1366.



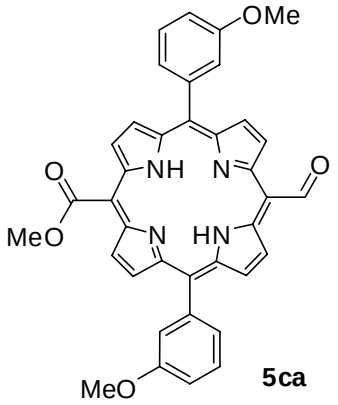
5ba

10-Formyl-20-methoxycarbonyl-5,15-di(*p*-tolyl)porphyrin (5ba). ^{1}H-NMR ($CDCl_3$) δ: 12.52 (1H, s), 10.00 (2H, d, *J* = 4.8 Hz), 9.31 (2H, d, *J* = 4.8 Hz), 9.01 (2H, d, *J* = 4.8 Hz), 8.88 (2H, d, *J* = 4.8 Hz), 8.03 (4H, d, *J* = 7.8 Hz), 7.58 (4H, d, *J* = 7.8 Hz), 4.55 (3H, s), 2.72 (6H, s), -2.54 (2H, s); IR (KBr): 3318, 1721, 1676, 1552, 1505, 1430, 1398, 1348, 1248, 1163, 1109, 1052, 970, 925, 895, 832, 798, 733 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{37}H_{29}O_3N_4$: 577.2240. Found 577.2245.



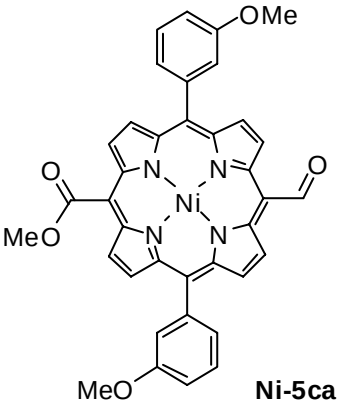
Ni-5ba

[10-Formyl-20-methoxycarbonyl-5,15-di(*p*-tolyl)porphinato]-nickel(II) (Ni-5ba). ^{1}H-NMR ($CDCl_3$) δ: 11.94 (1H, s), 9.69 (2H, d, *J* = 5.1 Hz), 9.21 (2H, d, *J* = 5.1 Hz), 8.76 (2H, d, *J* = 5.1 Hz), 8.66 (2H, d, *J* = 5.1 Hz), 7.73 (4H, d, *J* = 7.8 Hz), 7.44 (4H, d, *J* = 7.8 Hz), 4.34 (3H, s), 2.62 (6H, s); ^{13}C-NMR ($CDCl_3$) δ: 192.8 (0H, s), 170.1, 144.0, 143.5, 141.1, 140.1, 137.9, 136.5, 135.2, 133.4, 133.3, 132.4, 131.2, 127.8, 121.1, 110.3, 107.1, 53.6, 21.4; IR (KBr): 1722, 1546, 1510, 1444, 1358, 1244, 1193, 1156, 1080, 1005, 947, 849, 799, 730, 708, 673, 525 cm^{-1}; HRMS (EI): Calcd for $C_{37}H_{26}O_3N_4Ni$: 632.1358. Found 632.1354.



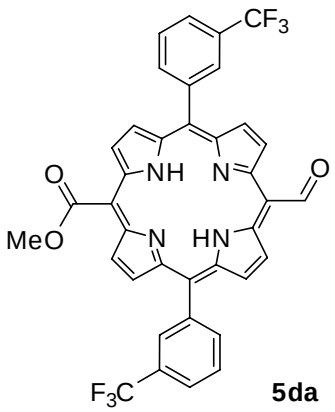
5ca

5,15-Bis(3-methoxyphenyl)-10-formyl-20-methoxycarbonyl-porphyrin (5ca). ^{1}H-NMR ($CDCl_3$) δ: 12.53 (1H, s), 10.02 (2H, d, *J* = 4.9 Hz), 9.32 (2H, d, *J* = 4.9 Hz), 9.04 (2H, d, *J* = 4.9 Hz), 8.90 (2H, d, *J* = 4.9 Hz), 7.80–7.64 (6H, m), 7.37 (2H, dd, *J* = 8.4, 2.6 Hz), 4.55 (3H, s), 3.99 (6H, s), -2.55 (2H, s); IR (KBr): 3316, 1718, 1673, 1596, 1461, 1425, 1397, 1255, 1155, 1111, 1049, 994, 911, 803, 701 cm^{-1}; HRMS-FAB^{+} ([M+H]$^{+}$): Calcd for $C_{37}H_{29}O_5N_4$: 609.2138. Found 609.2145.



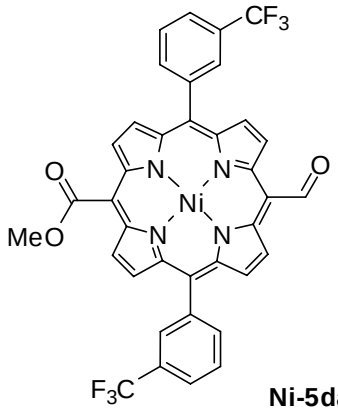
Ni-5ca

[5,15-Bis(3-methoxyphenyl)-10-formyl-20-methoxycarbonyl-porphinato]nickel(II) (Ni-5ca). ^{1}H-NMR ($CDCl_3$) δ: 12.02 (1H, s,), 9.77 (2H, d, *J* = 5.1 Hz), 9.24 (2H, d, *J* = 5.0 Hz), 8.86 (2H, d, *J* = 5.1 Hz), 8.73 (2H, d, *J* = 5.0 Hz), 7.60–7.50 (4H, m), 7.47–7.44 (2H, m), 7.29–7.26 (2H, m), 4.36 (3H, s), 3.93 (6H, s); ^{13}C-NMR ($CDCl_3$) δ: 192.5, 169.8, 158.0, 143.6, 143.5, 141.4, 140.6, 140.1, 135.1, 133.3, 132.4, 131.2, 127.9, 126.3, 120.6, 119.4, 113.7, 110.4, 107.2, 55.5, 53.7; IR (KBr): 1721, 1677, 1597, 1461, 1428, 1357, 1313, 1285, 1252, 1203, 1156, 1080, 1050, 1009, 953, 918, 792, 729, 703 cm^{-1}; HRMS (EI): Calcd for $C_{37}H_{26}O_5N_4Ni$: 664.1257. Found 664.1254.



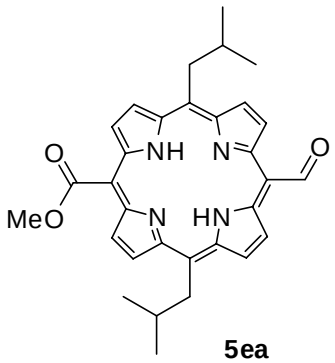
5da

5,15-Bis(3-trifluoromethylphenyl)-10-formyl-20-methoxycarbonylporphyrin (5da). ^{1}H-NMR ($CDCl_3$) δ: 12.55 (1H, s), 10.07 (2H, d, *J* = 4.9 Hz), 9.38 (2H, d, *J* = 4.9 Hz), 8.92 (2H, d, *J* = 4.9 Hz), 8.78 (2H, d, *J* = 4.9 Hz), 8.44 (2H, s), 8.37 (2H, d, *J* = 6.8 Hz), 8.12 (2H, d, *J* = 8.4 Hz), 7.94 (2H, t, *J* = 7.4 Hz), 4.56 (3H, s), -2.62 (2H, s); IR (KBr): 3313, 1674, 1554, 1439, 1404, 1331, 1267, 1245, 1177, 1124, 1073, 1003, 960, 925, 897, 863, 797, 736, 704 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{37}H_{23}F_6O_3N_4$: 685.1674. Found 685.1669.



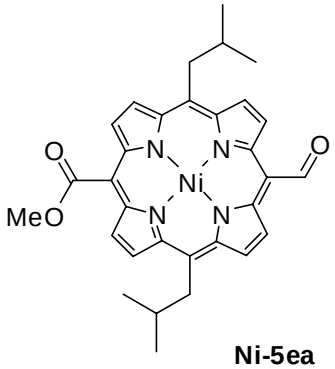
Ni-5da

[5,15-Bis(3-trifluoromethylphenyl)-10-formyl-20-methoxycarbonylporphinato]nickel(II) (Ni-5da). ^{1}H-NMR ($CDCl_3$) δ: 11.85 (1H, s), 9.69 (2H, d, *J* = 5.1 Hz), 9.28 (2H, d, *J* = 5.1 Hz), 8.66 (2H, d, *J* = 5.1 Hz), 8.59 (2H, d, *J* = 5.1 Hz), 8.20 (2H, s), 8.06 (2H, d, *J* = 7.7 Hz), 8.01 (2H, d, *J* = 7.8 Hz), 7.82 (2H, t, *J* = 7.8 Hz), 4.37 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 192.1, 169.5, 143.5, 143.3, 141.3, 140.3, 140.1, 136.2, 134.5, 133.0, 132.9, 131.7, 129.6, 129.5, 127.6, 125.3, 125.1, 125.1, 118.9, 110.8, 53.8; IR (KBr): 1725, 1681, 1548, 1433, 1362, 1326, 1259, 1236, 1166, 1128, 1078, 1009, 950, 906, 799, 703, 664 cm^{-1}; HRMS (EI): Calcd for $C_{37}H_{20}O_3N_4F_6Ni$: 740.0793. Found 740.0789.



5ea

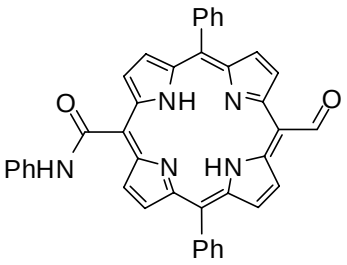
10-Formyl-20-methoxycarbonyl-5,15-diisobutylporphyrin (5ea). ^{1}H-NMR ($CDCl_3$) δ: 12.38 (1H, s), 9.90 (2H, d, *J* = 4.9 Hz), 9.41 (2H, d, *J* = 4.9 Hz), 9.37 (2H, d, *J* = 4.9 Hz), 9.30 (2H, d, *J* = 4.9 Hz), 4.68 (4H, d, *J* = 7.3 Hz), 2.68–2.59 (2H, m), 1.13 (12H, d, *J* = 6.6 Hz), -2.88 (2H, s); IR (KBr): 3313, 1726, 1672, 1556, 1469, 1435, 1381, 1363, 1343, 1278, 1237, 1189, 1124, 1050, 983, 912, 820, 789, 720 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{31}H_{33}O_3N_4$: 509.2553. Found 509.2562.



Ni-5ea

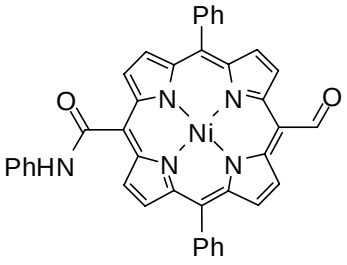
[10-Formyl-20-methoxycarbonyl-5,15-diisobutylporphinato]-nickel(II) (Ni-5ea). ^{1}H-NMR ($CDCl_3$) δ: 11.67 (1H, s), 9.59 (2H, d, *J* = 5.1 Hz), 9.21 (2H, d, *J* = 5.1 Hz), 9.17 (2H, d, *J* = 5.1 Hz), 9.12 (2H, d, *J* = 5.1 Hz), 4.38–4.32 (7H, m), 2.09-2.02 (2H, m), 0.76 (12H, d, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 191.9, 169.8, 143.9, 142.1, 141.4, 138.8, 133.0, 132.6, 131.4, 131.0, 119.2, 109.4, 105.7, 53.5, 42.1, 34.3, 22.9; IR (KBr): 1728, 1678, 1564, 1471, 1350, 1246, 1202, 1165, 1139, 1090, 1068, 1014, 957, 929,

851, 820, 789, 732 cm^{-1}; HRMS (EI): Calcd for $C_{31}H_{30}O_3N_4Ni$: 564.1671. Found 564.1671.



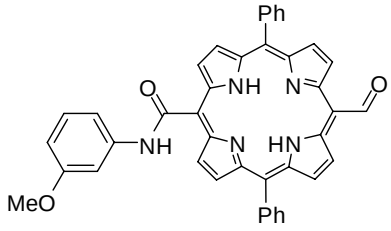
7aa

10-Formyl-20-phenylcarbamoyl-5,15-diphenylporphyrin (7aa). ^{1}H-NMR ($CDCl_3$) δ: 10.65 (1H, br s), 9.71 (1H, br s), 9.47 (2H, d, *J* = 4.6 Hz), 8.79 (2H, d, *J* = 4.6 Hz), 8.62 (2H, br s), 8.39 (2H, d, *J* = 4.9 Hz), 8.20 (2H, d, *J* = 7.8 Hz), 8.13–7.68 (10H, m), 7.60 (2H, t, *J* = 7.9 Hz), 7.35 (1H, t, *J* = 7.6 Hz), -3.81 (2H, br); IR (KBr): 3310, 3221, 1674, 1654, 1599, 1541, 1499, 1440, 1316, 1254, 1168, 970, 922, 803, 753, 703 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{40}H_{28}O_2N_5$: 610.2243. Found 610.2246.



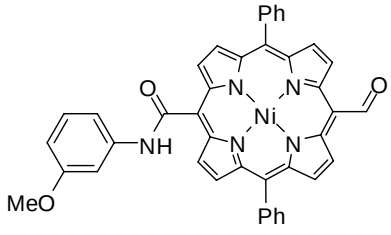
Ni-7aa

[10-Formyl-20-phenylcarbamoyl-5,15-diphenylporphinato]-nickel(II) (Ni-7aa). ^{1}H-NMR ($CDCl_3$) δ: 11.45 (1H, s), 9.35 (2H, d, *J* = 4.6 Hz), 9.30 (2H, d, *J* = 4.9 Hz), 8.67 (2H, d, *J* = 4.6 Hz), 8.64 (2H, d, *J* = 4.6 Hz), 8.27 (1H, br s), 7.94–7.83 (6H, m), 7.77–7.63 (6H, m), 7.49 (2H, t, *J* = 7.9 Hz), 7.26 (1H, t, *J* = 6.6 Hz); IR (KBr): 3291, 1675, 1656, 1597, 1537, 1498, 1439, 1357, 1314, 1248, 1195, 1160, 1077, 1007, 944, 853, 799, 752, 701 cm^{-1}; HRMS (EI): Calcd for $C_{40}H_{25}O_2N_5Ni$: 665.1362. Found 665.1362. ^{13}C-NMR data are not available owing to the poor solubility of the compound.



7ab

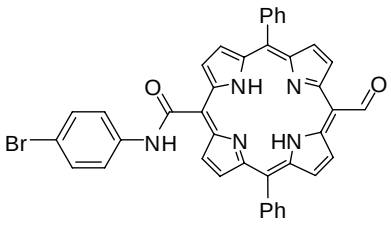
10-Formyl-20-[(3-methoxyphenyl)carbamoyl]-5,15-diphenyl-porphyrin (7ab). ^{1}H-NMR ($CDCl_3$) δ: 11.00 (1H, s), 9.49-9.43 (3H, m), 8.87 (2H, d, *J* = 4.9 Hz), 8.81 (2H, d, *J* = 4.8 Hz), 8.51 (2H, d, *J* = 4.9 Hz), 8.17–7.92 (4H, s), 7.89–7.71 (7H, s), 7.58 (1H, d, *J* = 8.8 Hz), 7.46 (1H, t, *J* = 8.2 Hz), 6.90 (1H, dd, *J* = 8.2, 1.7 Hz), 3.98 (3H, s), -3.56 (2H, br); IR (KBr): 3303, 3277, 1719, 1677, 1652, 1594, 1543, 1432, 1287, 1270, 1252, 1236, 1170, 1154, 1114, 1048, 970, 922, 876, 801, 779, 712 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{41}H_{30}N_5O_3$: 640.2349. Found 640.2344.



Ni-7ab

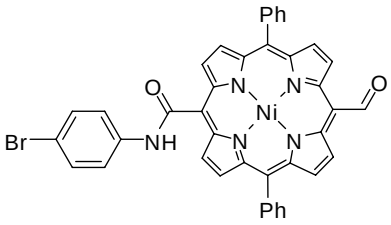
{10-Formyl-20-[(3-methoxyphenyl)carbamoyl]-5,15-diphenyl-porphinato}nickel(II) (Ni-7ab). 1H-NMR (CDCl3) δ: 11.21 (1H, s), 9.27 (2H, d, *J* = 4.4 Hz), 9.17 (2H, d, *J* = 4.2 Hz), 8.64 (2H, d, *J* = 4.4 Hz), 8.55 (2H, d, *J* = 4.2 Hz), 7.93–7.79 (4H, m), 7.77–7.61 (7H, m), 7.42–7.28 (2H, m), 6.81 (1H, d, *J* = 6.8 Hz), 3.91 (3H, s); IR (KBr): 3271, 1677, 1657, 1602, 1545, 1491, 1451, 1357, 1291,

1242, 1198, 1158, 1078, 1047, 1007, 946, 796, 754, 702 cm^{-1}; HRMS (EI): Calcd for $C_{41}H_{27}O_3N_5Ni$: 695.1467. Found 695.1467. ^{13}C-NMR data are not available owing to the poor solubility of the compound.



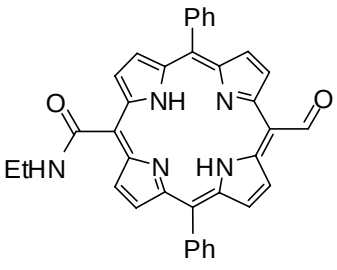
7ac

10-[(4-Bromophenyl)carbamoyl]-20-formyl-5,15-diphenyl-porphyrin (7ac). ^{1}H-NMR ($CDCl_3$) δ: 11.20 (1H, s), 9.41 (2H, d, *J* = 4.7 Hz), 9.02 (2H, d, *J* = 4.9 Hz), 8.82 (2H, d, *J* = 4.7 Hz), 8.58 (2H, d, *J* = 4.9 Hz), 8.21-8.00 (5H, m), 7.89-7.63 (10H, m), -3.42 (1H, br).; IR (KBr): 3315, 3290, 3234, 1672, 1648, 1590, 1528, 1488, 1395, 1304, 1246, 1170, 1072, 1009, 970, 922, 803, 750, 725, 703 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{40}H_{27}O_2N_5Br$: 688.1348. Found 688.1351.



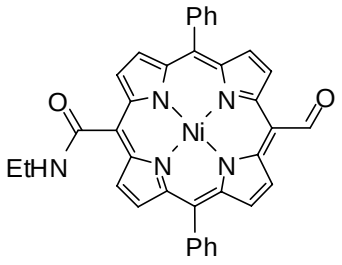
Ni-7ac

{10-[(4-Bromophenyl)carbamoyl]-20-formyl-5,15-diphenyl-porphinato}nickel(II) (Ni-7ac). ^{1}H-NMR ($CDCl_3$) δ: 11.80 (1H, s), 9.61 (2H, d, *J* = 4.9 Hz), 9.26 (2H, d, *J* = 4.9 Hz), 8.77 (2H, d, *J* = 4.9 Hz), 8.70 (2H, d, *J* = 4.9 Hz), 8.01 (1H, br s), 7.96-7.87 (4H, m), 7.80-7.65 (8H, m), 7.62-7.54 (2H, m); IR (KBr): 3290, 3262, 1678, 1654, 1529, 1487, 1459, 1440, 1392, 1357, 1307, 1246, 1164, 1073, 1009, 947, 820, 800, 702 cm^{-1}; HRMS (EI): Calcd for $C_{40}H_{24}O_2N_5BrNi$: 743.0467. Found 743.0467.
^{13}C-NMR data are not available owing to the poor solubility of the compound.



7ad

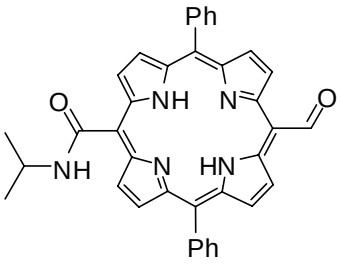
10-Ethylcarbamoyl-20-formyl-5,15-diphenylporphyrin (7ad). ^{1}H-NMR ($CDCl_3$) δ: 11.96 (1H, s), 9.60 (2H, d, *J* = 4.9 Hz), 9.33 (2H, d, *J* = 4.8 Hz), 8.81 (4H, br d, *J* = 5.1 Hz), 8.11 (4H, d, *J* = 6.4 Hz), 7.85–7.72 (6H, m), 6.98 (1H, t, *J* = 5.6 Hz), 4.16–4.03 (2H, m), 1.62 (3H, t, *J* = 7.2 Hz), -2.85 (2H, s); IR (KBr): 3845, 3734, 3618, 3313, 1655, 1539, 1088, 968, 914, 798, 671 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{36}H_{28}N_5O_2$: 562.2243. Found 562.2245.



Ni-7ad

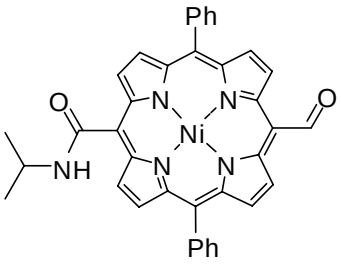
[10-Ethylcarbamoyl-20-formyl-5,15-diphenylporphinato]-nickel(II) (Ni-7ad). ^{1}H-NMR ($CDCl_3$) δ: 11.87 (1H, s), 9.65 (2H, d, *J* = 5.1 Hz), 9.19 (2H, d, *J* = 4.9 Hz), 8.77 (2H, d, *J* = 5.1 Hz), 8.66 (2H, d, *J* = 4.9 Hz), 7.94–7.85 (4H, m), 7.74–7.63 (6H, m), 3.96–3.85 (2H, m), 3.72 (1H, t, *J* = 6.2 Hz), 1.45 (3H, t, *J* = 7.2 Hz); IR (KBr): 3737, 3622, 1670, 1547, 1516, 1454, 1358, 1288, 1157, 1080, 1007, 945 cm^{-1}; HRMS (EI): Calcd for $C_{36}H_{25}N_5NiO_2$: 617.1362. Found 617.1364.

^{13}C-NMR data are not available owing to the poor solubility of the compound.



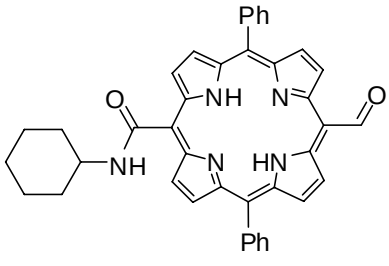
7ae

10-Formyl-20-isopropylcarbamoyl-5,15-diphenylporphyrin (7ae). ^{1}H-NMR ($CDCl_3$) δ: 11.98 (1H, s), 9.61 (2H, s), 9.34 (2H, d, *J* = 4.6 Hz), 8.81 (4H, d, *J* = 4.6 Hz), 8.11 (4H, d, *J* = 6.6 Hz), 7.87–7.72 (6H, m), 6.84 (1H, br d, *J* = 6.4 Hz), 5.05–4.92 (1H, m), 1.63 (6H, d, *J* = 6.4 Hz), -2.83 (2H, br s); IR (KBr): 3312, 3283, 1661, 1648, 1548, 1455, 1366, 1277, 1238, 1174, 1154, 1113, 1062, 971, 917, 801, 751, 726, 702 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{37}H_{30}O_2N_5$: 576.2400. Found 576.2393.



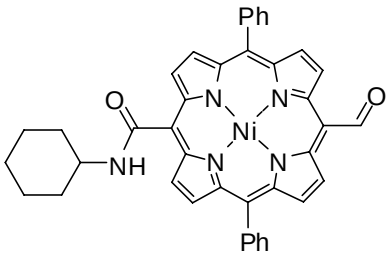
Ni-7ae

[10-Formyl-20-isopropylcarbamoyl-5,15-diphenylporphinato]-nickel(II) (Ni-7ae). ^{1}H-NMR ($CDCl_3$) δ: 11.44 (1H, s), 9.33 (2H, d, *J* = 4.8 Hz), 9.17 (2H, d, *J* = 4.8 Hz), 8.60 (2H, d, *J* = 4.8 Hz), 8.59 (2H, d, *J* = 4.8 Hz), 7.81 (4H, d, *J* = 7.0 Hz), 7.75–7.58 (6H, m), 6.38 (1H, d, *J* = 7.5 Hz), 4.86–4.71 (1H, m), 1.47 (6H, d, *J* = 6.4 Hz); ^{13}C-NMR ($CDCl_3$) δ: 192.5, 168.2, 144.1, 143.8, 141.2, 139.5, 139.2, 134.9, 133.4, 133.0, 131.7, 130.3, 128.1, 127.0, 120.8, 116.8, 106.3, 43.3, 22.8; IR (KBr): 3280, 1675, 1656, 1549, 1455, 1358, 1318, 1276, 1196, 1159, 1076, 1008, 948, 851, 797, 753, 702, 638 cm^{-1}; HRMS (EI): Calcd for $C_{37}H_{27}O_2N_5Ni$: 631.1518. Found 631.1516.



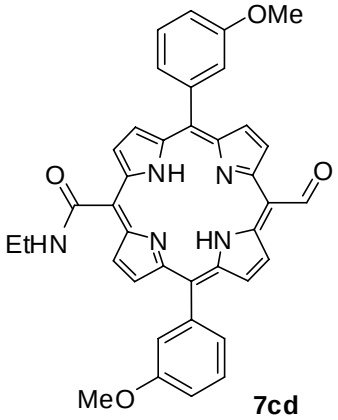
7af

10-Cyclohexylcarbamoyl-20-formyl-5,15-diphenylporphyrin (7af). ^{1}H-NMR ($CDCl_3$) δ: 12.36 (1H, s), 9.89 (2H, br d, *J* = 4.8 Hz), 9.34 (2H, d, *J* = 4.8 Hz), 8.94 (2H, d, *J* = 4.8 Hz), 8.81 (2H, d, *J* = 4.8 Hz), 8.16–8.11 (4H, m), 7.85–7.73 (6H, m), 6.64 (1H, d, *J* = 8.4 Hz), 4.77–4.63 (1H, br), 2.53–2.42 (2H, m), 1.95–1.21 (8H, m), -2.57 (2H, s); IR (KBr): 3853, 3737, 3622, 1651, 1543, 802, 671, 463 cm^{-1}; HRMS-FAB$^+$ ([M+H]$^+$): Calcd for $C_{40}H_{34}N_5O_2$: 616.2713. Found 616.2719.



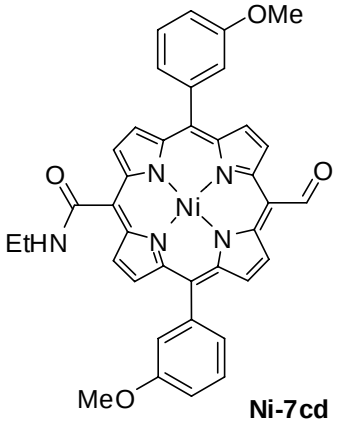
Ni-7af

[10-Cyclohexylcarbamoyl-20-formyl-5,15-diphenylporphinato]nickel(II) (Ni-7af). ^{1}H-NMR ($CDCl_3$) δ: 11.76 (1H, s), 9.57 (2H, d, *J* = 5.1 Hz), 9.19 (2H, d, *J* = 4.9 Hz), 8.72 (2H, d, *J* = 5.1 Hz), 8.65 (2H, d, *J* = 4.9 Hz), 7.91–7.83 (4H, m), 7.76–7.61 (6H, m), 6.23 (1H, br d, *J* = 7.9 Hz), 4.58–4.41 (1H, m), 2.37–2.27 (2H, m), 1.87–1.16 (8H, m); ^{13}C-NMR ($CDCl_3$) δ: 192.8, 168.2, 144.3, 144.2, 141.5, 139.6, 139.3, 135.3, 133.5, 133.2, 131.9, 130.9, 128.2, 127.1, 121.0, 116.8, 50.2, 33.2, 29.7, 25.5, 24.9; IR (KBr): 3892, 3853, 3737, 3622, 1678, 1651, 1543, 1516, 1080, 795, 671 cm^{-1}; HRMS (EI): Calcd for $C_{40}H_{31}N_5NiO_2$: 671.1831. Found 671.1833.



7cd

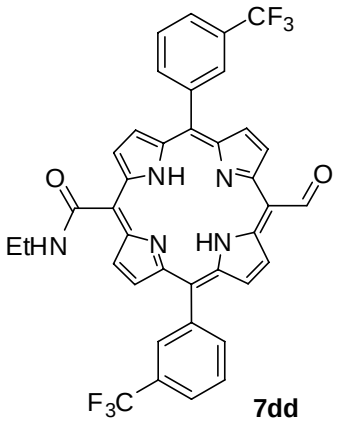
5,15-Bis(3-methoxyphenyl)-10-ethylcarbamoyl-20-formylporphyrin (7cd). ^{1}H-NMR ($CDCl_3$) δ: 12.37 (1H, s), 9.90 (2H, d, *J* = 4.8 Hz), 9.32 (2H, d, *J* = 4.8 Hz), 8.99 (2H, d, *J* = 4.8 Hz), 8.86 (2H, d, *J* = 4.8 Hz), 7.81–7.59 (6H, m), 7.36 (2H, br d, *J* = 5.9 Hz), 6.73 (1H, t, *J* = 5.5 Hz), 4.15–4.03 (2H, m), 3.99 (6H, s), 1.60 (3H, t, *J* = 7.2 Hz), -2.57 (2H, s); IR (KBr): 3737, 3622, 1651, 1547, 1520, 1153, 1099, 1053, 798, 671 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{38}H_{32}N_5O_4$: 622.2454. Found 622.2462.



Ni-7cd

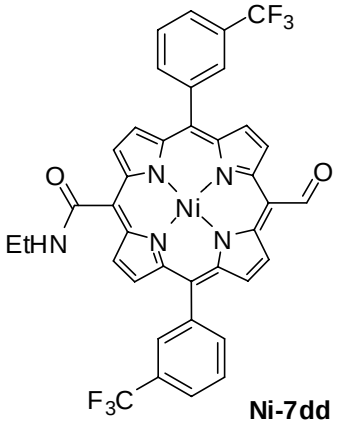
[5,15-Bis(3-methoxyphenyl)-10-ethylcarbamoyl-20-formylporphinato]nickel(II) (Ni-7cd). ^{1}H-NMR ($CDCl_3$) δ: 11.91 (1H, s), 9.67 (2H, d, *J* = 4.9 Hz), 9.18 (2H, d, *J* = 4.9 Hz), 8.82 (2H, d, *J* = 4.9 Hz), 8.71 (2H, d, *J* = 4.9 Hz), 7.63–7.41 (8H, m), 6.24 (1H, br), 3.94–3.86 (8H, m), 1.45 (3H, t, *J* = 7.2 Hz); IR (KBr): 3737, 3622, 1678, 1547, 1516, 1076, 1014, 791, 675 cm^{-1}; HRMS (EI): Calcd for C38H29N5NiO4: 677.1573. Found 677.1570.

^{13}C-NMR data are not available owing to the poor solubility of the compound.



7dd

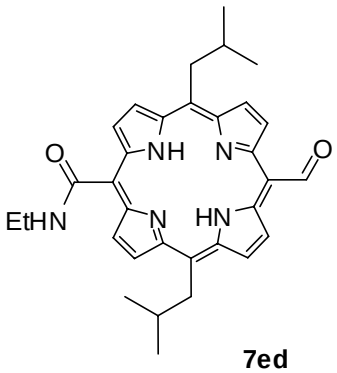
5,15-Bis(3-trifluoromethylphenyl)-10-ethylcarbamoyl-20-formylporphyrin (7dd). ^{1}H-NMR ($CDCl_3$) δ: 12.38 (1H, s), 9.94 (2H, br d, *J* = 5.1 Hz), 9.38 (2H, d, *J* = 4.8 Hz), 8.87 (2H, d, *J* = 5.1 Hz), 8.75 (2H, d, *J* = 4.8 Hz), 8.42 (2H, s), 8.34 (2H, d, *J* = 7.1 Hz), 8.11 (2H, d, *J* = 7.5 Hz), 7.93 (2H, t, *J* = 7.7 Hz), 6.76 (1H, t, *J* = 5.5 Hz), 4.16–4.04 (2H, m), 1.62 (3H, t, *J* = 7.3 Hz); IR (KBr): 3737, 3622, 1736, 1651, 1547, 1327, 1130, 1076, 798, 675 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{38}H_{26}F_6N_5O_2$: 698.1991. Found 698.2000.



Ni-7dd

[5,15-Bis(3-trifluoromethylphenyl)-10-ethylcarbamoyl-20-formylporphinato]nickel(II) (Ni-7dd). ^{1}H-NMR ($CDCl_3$) δ: 11.87 (1H, s), 9.68 (2H, d, *J* = 4.9 Hz), 9.24 (2H, d, *J* = 4.9 Hz), 8.68 (2H, d, *J* = 4.9 Hz), 8.59 (2H, d, *J* = 4.9 Hz), 8.20 (2H, s), 8.07 (2H, d, *J* = 7.0 Hz), 8.01 (2H, d, *J* = 7.3 Hz), 7.82 (2H, t, *J* = 7.8 Hz), 6.30 (1H, br s), 4.01-3.84 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz); IR (KBr): 3737, 1678, 1655, 1550, 1516, 1323, 1165, 1126, 1076, 1011, 795, 675 cm^{-1}; HRMS (EI): Calcd for $C_{38}H_{23}F_6N_5NiO_2$: 753.1109. Found 753.1106.

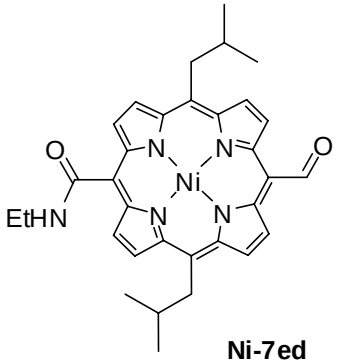
^{13}C-NMR data are not available owing to the poor solubility of the compound.



7ed

10-Ethylcarbamoyl-20-formyl-5,15-diisobutylporphyrin (7ed). 08-01-39-3 ethyl-NHCO-isobutyl-Por-CHO

^{1}H-NMR ($CDCl_3$) δ: 12.26 (1H, s), 9.80 (2H, d, *J* = 4.9 Hz), 9.37 (2H, d, *J* = 4.9 Hz), 9.32 (4H, s), 6.84 (1H, br), 4.66 (4H, d, *J* = 7.1 Hz), 4.19-4.03 (2H, m), 2.72-2.53 (2H, m), 1.65 (3H, t, *J* = 7.2 Hz), 1.12 (12H, d, *J* = 6.6 Hz), -2.78 (2H, br); IR (KBr): 3737, 1693, 1651, 1547, 1520, 1462, 1076, 914, 791, 671 cm^{-1}; HRMS-FAB$^+$ ($[M+H]^+$): Calcd for $C_{32}H_{36}N_5O_2$: 522.2869. Found 522.2870.



Ni-7ed

[10-Ethylcarbamoyl-20-formyl-5,15-diisobutylporphinato]-nickel(II) (Ni-7ed). ^{1}H-NMR ($CDCl_3$) δ: 11.91 (1H, s), 9.75 (2H, d, *J* = 5.1 Hz), 9.31 (2H, d, *J* = 5.2 Hz), 9.16 (4H, br s), 6.06–5.99 (1H, br), 4.41 (4H, d, *J* = 7.3 Hz), 3.94–3.82 (2H, m), 2.19–2.08 (2H, m), 1.44 (3H, t, *J* = 7.2 Hz), 0.82 (12H, d, *J* = 6.6 Hz); ^{13}C-NMR (CDCl3) δ: 192.4, 162.2, 144.5, 142.9, 141.4, 137.9, 133.4, 132.0, 131.6, 131.2, 131.0, 130.8, 119.4, 42.1, 36.0, 34.3, 22.9, 15.0; IR (KBr): 3737, 3622, 1651, 1547, 1516, 1462, 1084, 787, 671 cm^{-1}; HRMS (EI): Calcd for $C_{32}H_{33}N_5NiO_2$: 577.1988. Found 577.1987.

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