Supplementary Information

Ni and Pd N-confused porphyrin complexes as catalysts for the synthesis of cyclic carbonates from epoxides and CO_2

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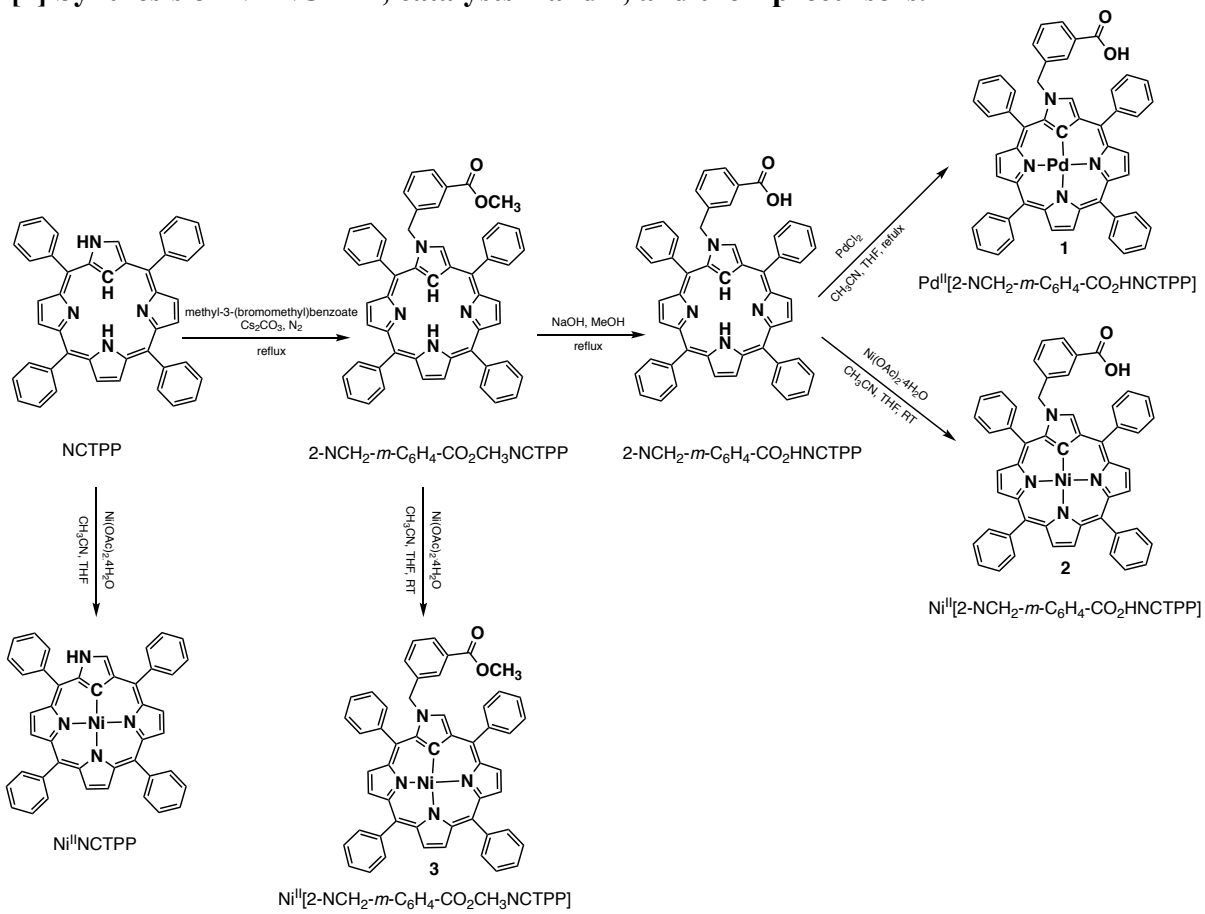
[1] Synthesis of Ni^{II}NCTPP, catalysts 1 and 2, and their precursors.



2-NCH_2-*m*-$C_6H_4CO_2CH_3$NCTPP.
A mixture of NCTPP (100.0 mg 0.163 mmol), Cs_2CO_3 (156.4 mg, 0.488 mmol), and methyl-3-(bromomethyl)benzoate (146.6 mg, 0.651 mmol) was heated at 100 ^oC in 20.0 mL dry dimethylformamide under nitrogen for two hours. After cooling down to room temperature, dimethylformamide was removed under vacuum and re-dissolved in CH_2Cl_2 to filter off excess Cs_2CO_3. The mixture was purified by silica gel column chromatography with acetone-CH_2Cl_2 [4:96 (v/v)] to obtain a green solid product (84.0 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 1H), 3.82 (s, 3H), 4.07 (br s, 1H), 4.99 (s, 2H), 6.41 (d, J = 7.7 Hz, 1H), 6.92 (t, J = 7.7 Hz, 1H), 7.29 (s, 1 H), 7.35 (d, J = 4.8 Hz, 1H), 7.40 (s, 1H), 7.43–7.47 (m, 3H), 7.53–7.58 (m, 10H), 7.63–7.71 (m, 6H), 7.78–7.82 (m, 4H), 7.88 (d, J = 4.5 Hz, 1H), 7.90-7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1, 53.6, 107.3, 115.4, 115.8, 124.4, 126.8, 127.2, 127.5, 127.8, 128.2, 128.4, 128.6, 128.7, 129.2, 129.5, 130.0, 130.2, 130.6, 130.8, 131.2, 133.2, 133.4, 133.5, 134.9, 135.9, 136.1, 137.5, 140.0, 141.1, 141.5, 143.6, 143.9, 154.0, 155.0, 163.6, 163.9 , 166.6; UV/Vis (CH_2Cl_2): λ_{max} (ε) 362 (25260), 446 (64062), 658 (6808), 716 (8738); HRMS(ESI) Calc for $C_{53}H_{39}N_4O_2$ ($[M+H]^+$) 763.3073, found 763.3082.

2-NCH_2-*m*-$C_6H_4CO_2$HNCTPP.
A mixture of 2-NCH_2-*m*-$C_6H_4CO_2CH_3$NCTPP (100.0 mg, 0.131 mmol) and 1.0 M NaOH (3.9 mL, 3.9 mmol) was refluxed at 80 ^oC in a mixture of dry THF:CH_3OH (12:8) mL under nitrogen for two hours. The reaction mixture was then dried, to which 1.0 M HCl (3.9 mL, 3.9 mmol) was added. The solid product was filtered off and washed several times with RO water. The crude product was purified by silica gel column chromatography with CH_3OH-CH_2Cl_2 [3:97 (v/v) to obtain a dark green solid product (88.3 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$):

δ 5.02 (s, 2H), 6.12 (s, 1H), 6.41 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 7.19 (s, 1H), 7.5 (d, J = 7.6 Hz, 1H), 7.57–7.65 (m, 10H), 7.70–7.87 (m, 14 H), 8.06 (d, J = 6.5 Hz, 2H), 8.21 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.3, 117.3, 118.4, 124.8, 125.6, 127.4, 127.6, 127.8, 128.1, 128.3, 129.2, 129.2, 129.5, 129.9, 130.8, 132.6, 132.8, 132.9, 133.4, 134.1, 134.3, 134.4, 134.6, 135.0, 135.2, 135.4, 136.7, 138.5, 139.6, 140.7, 169.0; UV/Vis (CH_2Cl_2): λ_{max} (ε) 307 (19592), 368 (24054), 461 (81738), 566 (3121), 720 (5374), 793 (12019); HRMS(ESI) Calc for $C_{52}H_{37}N_4O_2$ ($[M+H]^+$) 749.2917, found 749.2908.

Pd^{II}[2-NCH_2-*m*-$C_6H_4CO_2$HNCTPP] (1).

Palladium(II) chloride (94.7 mg, 0.536 mmol) was dissolved in 10 mL dry CH_3CN and added to 2-NCH_2-*m*-$C_6H_4CO_2$HNCTPP (100 mg, 0.134 mmol) that was previously dissolved in 20 mL dry THF. The mixture was refluxed to 80 °C for three hours. The crude product was dried under vacuum and purified by silica gel column chromatography with CH_3OH-CH_2Cl_2 [5:95 (v/v)] to obtain a brownish solid product (64.9 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14 (s, 2H), 6.82 (d, J = 7.8 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 7.27–7.31 (m, 2H), 7.43–7.59 (m, 14 H), 7.71 (d, J = 5.0 Hz, 1H), 7.78–7.90 (m, 10H), 8.02 (d, J = 5.0 Hz, 1H), 8.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.9, 118.6, 119.5, 122.9, 126.6, 126.9, 127.0, 127.1, 127.2, 127.5, 127.7, 128.3, 128.8, 129.2, 129.4, 129.9, 130.6, 130.8, 131.3, 131.7, 131.8, 133.1, 133.3, 133.7, 138.1, 138.9, 140.1, 141.8, 142.3, 143.7, 146.8, 148.7, 148.8, 151.4, 152.4, 170.3; UV/Vis (CH_2Cl_2): λ_{max} (ε) 376 (6923), 393 (7100), 429 (10926), 450 (15635), 533 (1327), 576 (850), 700 (987), 764 (1127); HRMS(ESI_{neg}) Calc for $C_{52}H_{33}N_4O_2Pd$ ($[M-H]^-$) 851.1638, found 851.1644; Elemental analysis calc (%) for $C_{52}H_{34}N_4PdO_2$ (MW = 853.27) +1.85 H_2O + 0.3 CH_2Cl_2 : C 68.87, H 4.23, N 6.14, found*:* C 68.47, H 4.46, N 6.57 (CH_2Cl_2 and water could not be removed from compound **1** totally despite drying it under high vacuum).

Ni^{II}[2-NCH_2-*m*-$C_6H_4CO_2$HNCTPP] (2).

Nickel(II) acetate tetrahydrate (132.9 mg, 0.536 mmol) was dissolved in 15 mL dry CH_3CN and added to 2-NCH_2-*m*-$C_6H_4CO_2$HNCTPP (100 mg, 0.134 mmol) that was previously dissolved in 20 mL dry THF. The mixture was refluxed to 80 °C for three hours. The crude product was dried under vacuum and purified by silica gel column chromatography with CH_3OH- CH_2Cl_2 [3:97 (v/v)] to obtain a greenish solid product (49.5 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 (s, 2H), 6.81 (d, J = 7.7 Hz, 1H), 7.09 (t, J = 7.7 H, 1H), 7.29–7.32 (m, 2H), 7.42–7.56 (m, 13H), 7.62–7.67 (m, 2H), 7.76–7.88 (m, 10H), 8.02 (d, J = 5.0 Hz, 1H), 8.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.8, 117.1, 118.2, 121.9, 123.8, 125.9, 126.8, 127.0, 127.1, 127.1, 127.2, 127.6, 127.7, 128.2, 128.3, 128.8, 129.2, 129.5, 130.2, 130.7, 130.9, 131.6 ,132.3 ,132.9, 133.1, 133.3, 133.5, 138.0 ,138.7, 139.8, 141.3, 144.6 ,146.3, 148.3, 149.7, 151.4, 151.6, 153.8 ,170.6; UV/Vis (CH_2Cl_2): λ_{max} (ε) 363 (23524), 429 (43297), 462 (24873), 560 (5270), 722 (2496), 792 (2634); HRMS(ESI_{neg}) Calc for $C_{52}H_{33}N_4O_2Ni$ ($[M-H]^-$) 803.1957, found 803.1967; Elemental analysis calc (%) for $C_{52}H_{34}N_4NiO_2$ (MW = 805.58) + 0.85 C_7H_8 + 1.05 H_2O : C 77.1, H 4.79, N 6.21, found*:* C 77.01, H 4.68, N 6.12 (toluene was used to freeze dry compound **2** but could not be removed totally despite drying it under high vacuum).

Ni^{II}[2-NCH_2-*m*-$C_6H_4CO_2CH_3$NCTPP] (3).

Nickel(II) acetate tetrahydrate (130.5 mg, 0.524 mmol) was dissolved in 15 mL dry CH_3CN and added to 2-NCH_2-*m*-$C_6H_4CO_2CH_3$NCTPP (100 mg, 0.131 mmol) that was previously dissolved in 20 mL dry THF. The mixture was refluxed to 80 °C for three hours. The crude product was dried under vacuum and purified by silica gel column chromatography with CH_3OH-CH_2Cl_2 [1:99 (v/v)] to obtain a greenish solid product (58.0 mg, 54%). ^{1}H NMR (400

MHz, CD_2Cl_2): δ 3.82 (s, 3 H), 5.16 (s, 2H), 6.83 (d, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.34–7.41 (m, 3H), 7.48 (d, J = 7.4 Hz, 2H), 7.53 (d, 7.5 Hz, 1H), 7.56–7.62 (m, 9H), 7.69–7.72 (m, 2H), 7.81–7.85 (m, 6H), 7.88–7.90 (m, 2H), 7.92–7.95 (m, 2H), 8.10 (d, J = 5.0 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.4, 55.5, 117.6, 118.8, 122.3, 124.7, 126.3, 127.3, 127.5, 127.6, 127.6, 127.7, 127.8, 128.0, 128.4, 128.7, 129.0, 129.1, 130.4, 130.5, 130.8, 131.7, 132.1, 132.6, 132.6, 133.2, 133.5, 133.8, 133.9, 134.1, 138.2, 139.0, 140.1, 141.7, 144.9, 146.7, 148.6, 150.0, 151.7, 152.8, 153.9, 166.8; UV/Vis (CH_2Cl_2): λ_{max} (ε) 363 (22677), 428 (40444), 462 (23687), 559 (4949), 721 (2230), 792 (2336); HRMS(ESI) Calc for $C_{53}H_{37}N_4O_2Ni$ ($[M]^+$) 819.2270, found 819.2277; Elemental analysis calc (%) for $C_{53}H_{36}N_4O_2Ni$ (MW = 819.6) + 1.05 C_7H_8 + 1.95 H_2O + 0.3 CH_2Cl_2 : C 74.56, H 5.05, N 5.73, found*:* C 73.99, H 4.46, N 5.73 (Toluene was used to freeze dry compound **3** but solvents could not be removed totally despite drying it under high vacuum).

Ni^{II}NCTPP.

Ni^{II}NCTPP was first reported by Latos-Grażyński and co-workers[1] in 1994. For our study, nickel(II) acetate tetrahydrate (120.5 mg, 0.486 mmol) was dissolved in 15 mL dry CH_3CN and added to N-confused tetraphenyl porphyrin (100 mg, 0.162 mmol) that was previously dissolved in 15 mL dry THF. The mixture was refluxed to 80 ºC for six hours. The crude product was dried under vacuum and purified by silica gel column chromatography with hexane-CH_2Cl_2 [4:6 (v/v)] to obtain crystalline green product with decent yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.60–7.62 (m, 9H), 7.67–7.69 (m, 3H), 7.78–7.85 (m, 6H), 7.88–7.92 (m, 6H), 8.06 (d, J = 5.0 Hz, 1H), 8.09 (d, J = 5.0 Hz, 1H), 8.57 (d, J = 3.3 Hz, 1H), 10.23 (br s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ116.0, 117.3, 118.4, 124.1, 127.0, 127.1, 127.2, 127.4, 127.7, 128.0, 128.5, 129.0, 130.1, 131.5, 132.0, 132.3, 132.7, 133.0, 133.2, 133.4, 133.6, 137.7, 139.8, 141.6, 144.5, 144.8, 145.1, 148.5, 149.9, 151.8, 153.8; UV/Vis (CH_2Cl_2): λ_{max} (ε) 301 (15208), 360 (32414), 425 (69635), 460 (33000), 518 (6201), 556 (6280), 594 (6977), 717 (3828), 788 (4175); HRMS(ESI) Calc for $C_{44}H_{28}N_4Ni$ ($[M]^+$) 670.1667, found 670.1675.

[2] Coupling Reaction of CO_2 with Epoxide.

Procedure for a sample reaction. A 30-mL stainless autoclave was charged with epoxide (with 7.0- to 10.0- mmol range), catalyst (mole percent with respect to epoxide indicated in the text), triethylamine or 2,6-lutidine (mole percent with respect to epoxide indicated in the text), and then CO_2 (initial pressure indicated in the text). The reaction was heated with stirring at constant temperature for a reaction time. The reactor was then cooled to room temperature followed by the slow release of excess CO_2. Percent yield was determined by ^{1}H-NMR using dimethyl sulfone as an internal standard. To demonstrate obtaining isolated yield, column chromatography was done for **IB** with CH_3OH-CH_2Cl_2 [5:95 (v/v)].

4-Phenoxymethyl-1,3-dioxolan-2-one (IB). 89.6% ^{1}H NMR yield; 84.3 % isolated yield; ^{1}H NMR (CDCl3, 400 MHz) δ 4.11 (dd, *J* = 4.0, 11.0 Hz, 1H), 4.21 (dd, *J* = 4.0, 11.0 Hz, 1H), 4.50 (t, *J* = 8.0 Hz, 1H), 4.58 (t, *J* = 8.0 Hz, 1H), 4.97–5.02 (m, 1H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 66.1, 66.8, 74.1, 114.5, 121.8, 129.6, 129.5, 154.7,157.7; HRMS (EI) calcd for $C_{10}H_{10}O_4$ 194.0579, found 194.0578 ($[M]^+$)

4-(chloromethyl)-1,3-dioxolan-2-one (IIB). 98.0% ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.63–3.79 (m, 2H), 4.29 (dd, *J* = 6, 8.5 Hz, 1H), 4.51 (t, *J* = 8.5 Hz, 1H), 4.93–4.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 43.6, 66.9, 74.2, 154.1 ; HRMS (EI) calcd for $C_4H_3{}^{35}ClO_3$ 135.9927, found 135.9929 ($[M]^+$)

4-(butoxymethyl)-1,3-dioxolan-2-one (IIIB). 92.0% ^{1}H NMR ($CDCl_3$, 100 MHz) δ 0.88 (t, 7.5 Hz, 3H), 1.28–1.37 (m, 2H), 1.48–1.55 (m, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.54–3.65 (m, 2H), 4.35 (dd, *J* = 6.0, 8.3 Hz, 1H), 4.46 (t, *J* = 8.3 Hz, 1H), 4.74–4.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 19.1, 31.4, 66.2, 69.6, 71.8, 75.1, 154.9; HRMS (FAB) calcd for $C_8H_{15}O_4$ 175.0970, found 175.0969 ($[M+H]^+$)

4,4'-((ethane-1,2-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (IVB). 89.5% ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.59–3.76 (m, 8H), 4.34–4.43 (m, 2H), 4.45–4.50 (m, 2H), 4.76–4.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 66.1, 70.3, 71.3, 75.2, 155.1; HRMS (APCI) calcd for $C_{10}H_{15}O_8$ 263.0767, found 263.0759 ($[M+H]^+$)

4-methyl-1,3-dioxolan-2-one (VB). 24.8% ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.14 (d, *J* = 6.2 Hz, 3H), 3.74 (t, *J* = 7.1 Hz, 1H), 4.28 (dd, *J* = 7.1, 8.5 Hz, 1H), 4.55–4.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.9, 70.4, 73.4, 154.9; MS (EI) calcd for C4H6O3 102.0317, found 102.0316 ($[M]^+$)

[3] Sample % conversion calculation from ^{1}H NMR data.

Total crude catalytic product is weighed, from which a portion (typically 20 – 30 mg) is taken for ^{1}H NMR analysis. A known amount of dimethyl sulfone is added to the ^{1}H NMR sample as internal standard. The number of moles of catalytic product in the ^{1}H NMR sample is directly related to the ratio of the integration of the known catalytic product peak per number of proton in proportion to the standard's integration per proton:

$$\frac{n_{(p,NMR)}}{\left(\frac{I}{H}\right)_p} = \frac{n_{(s,NMR)}}{\left(\frac{I}{H}\right)_s}$$

where $n_{(p,NMR)}$ = number of moles of the product contained in the NMR tube
$n_{(s,NMR)}$ = number of moles of the standard contained in the NMR tube
$(I/H)_p$ = integration per number of protons on a selected product ^{1}H NMR peak
$(I/H)_s$ = integration per number of protons of the internal standard ^{1}H NMR peak

The total number of moles of product in the crude reaction mixture is calculated by multiplying $n_{(p,NMR)}$ by the ratio of the mass of the crude product to the mass of the crude NMR sample:

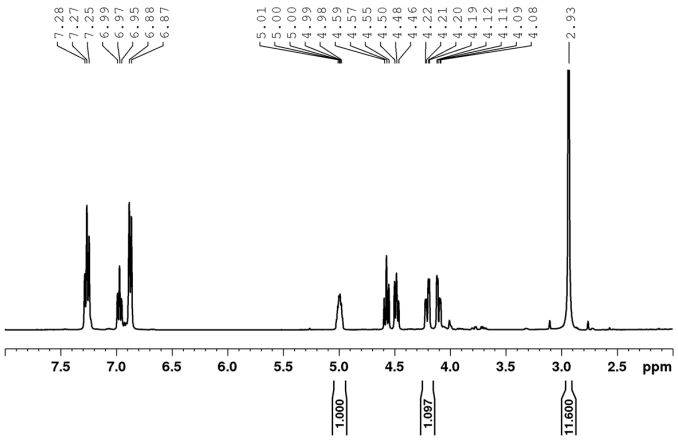
$$n_p = n_{(p,NMR)}\left(\frac{m_{crude}}{m_{NMR}}\right)$$

where n_p = total number of moles of the catalytic product
m_{crude} = mass of the total crude product
m_{NMR} = mass of the NMR sample

Percent yield, is taken as the ratio of n_p to the theoretical yield (in moles) multiplied by 100.

Sample (actual) data for the conversion of 1,2-epoxy-3-phenoxypropane, **IA** (molar mass: 150.17, density: 1.109 g/mL, purity: 99.0%) to 4-(phenoxymethyl)-1,3-dioxolan-2-one, **IB** (molar mass: 194.1) using dimethyl sulfone (molar mass: 94.13, purity: 98.0%) as standard:

initial volume of substrate **IA**:	4.08 mL
mass, crude product **IB**:	5867.3 mg
mass, NMR sample:	23.23 mg
mass, standard:	19.8 mg
Integration for the standard:	11.6 (δ 2.93, s)
Corresponding # of standard protons:	6
Integration for the product:	1 (δ 5.00, m)
Corresponding # of standard protons:	1



$$\frac{n_{(p,NMR)}}{\left(\frac{I}{H}\right)_p} = \frac{n_{(s,NMR)}}{\left(\frac{I}{H}\right)_s} \Rightarrow \frac{n_{(p,NMR)}}{\frac{1}{1}} = \frac{0.206\ mmol}{\frac{11.6}{6}}$$

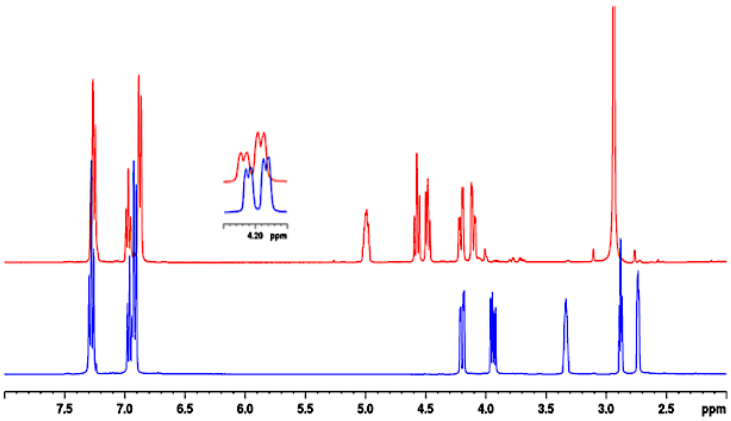
$$n_{(p,NMR)} = 0.107\ mmol$$

$$n_p = n_{(p,NMR)}\ x \left(\frac{m_{crude}}{m_{NMR}}\right) = 0.107\ mmol\ x \left(\frac{5867.3\ mg}{23.23\ mg}\right) = 26.9\ mmol$$

$$Theoretical\ yield = 4.08\ mL\ x\ \left(1109\ \frac{mg}{mL}\right)\ x\ 0.99\ x\ \left(\frac{mmol\ \boldsymbol{IA}}{150.17\ mg}\right) x \left(\frac{1\ mmol\ \boldsymbol{IB}}{1\ mmol\ \boldsymbol{IA}}\right) = 29.8\ mmol$$

$$\%\ yield = \frac{26.9\ mmol}{29.8\ mmol} = \mathbf{90.4}^{1}$$

To account for the unreacted substrate, it is noteworthy to mention that the chemical shift at *ca.* 4.20 ppm corresponds to overlapping peaks of both the substrate and the product (with an assignment of 1 proton each) as shown in the overlay of **IA** and crude **IB** ^{1}H NMR spectra below:

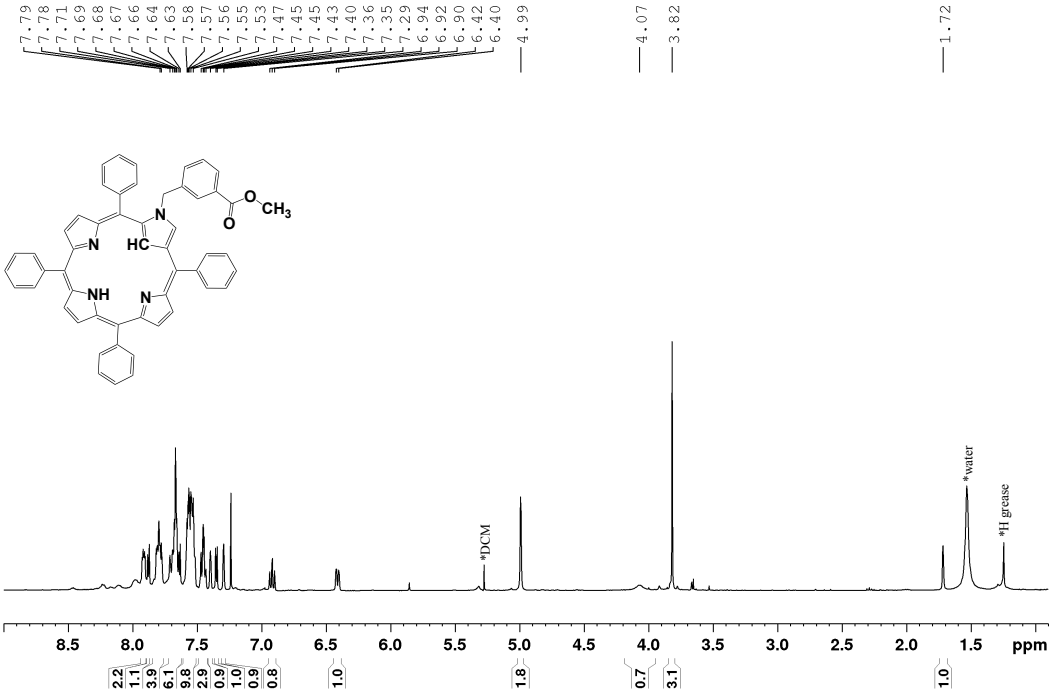


400 MHz ^{1}H NMR spectra of **IA** (—) and **IB** (—) in $CDCl_3$.

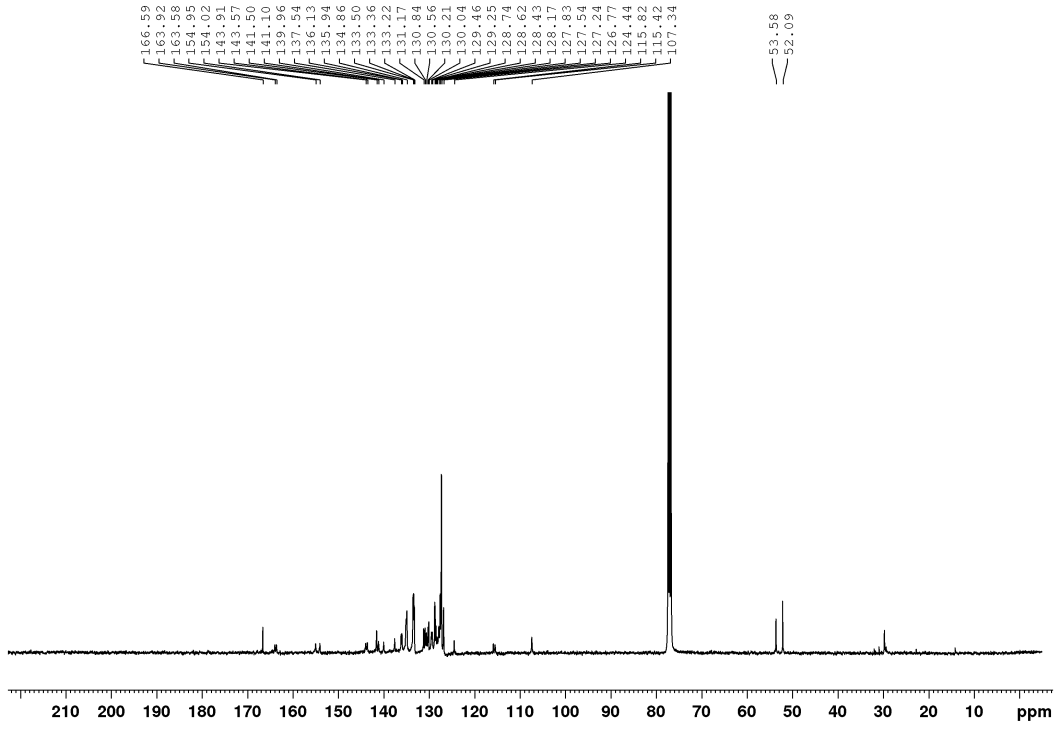
At the said chemical shift, the crude product's integration (red curve, upper panel) is 1.097, suggestive of residual unreacted substrate with an integration of 0.097. Using the same calculation, this equates to 2.61 mmol of unreacted **IA**, which, together with 26.93 mmol product yield, accounts for >99% of the initial number of moles of **IA** that initially went into the reaction.

[1] Rounding off was done in the final step of the calculation.

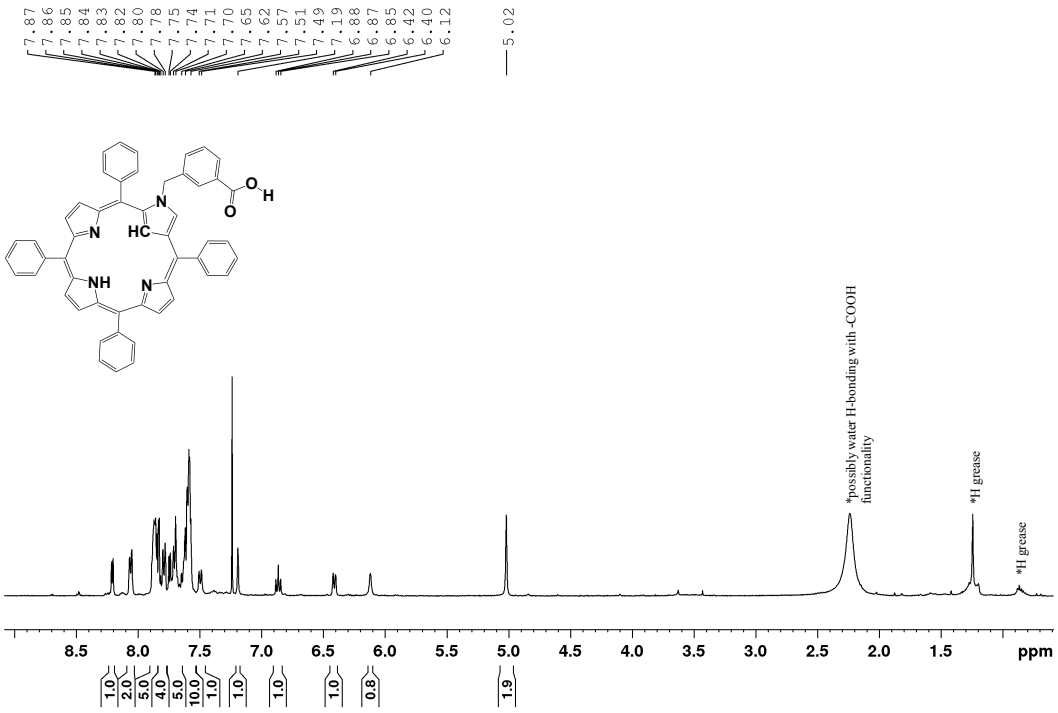
[4] ^{1}H NMR and ^{13}C NMR spectra.



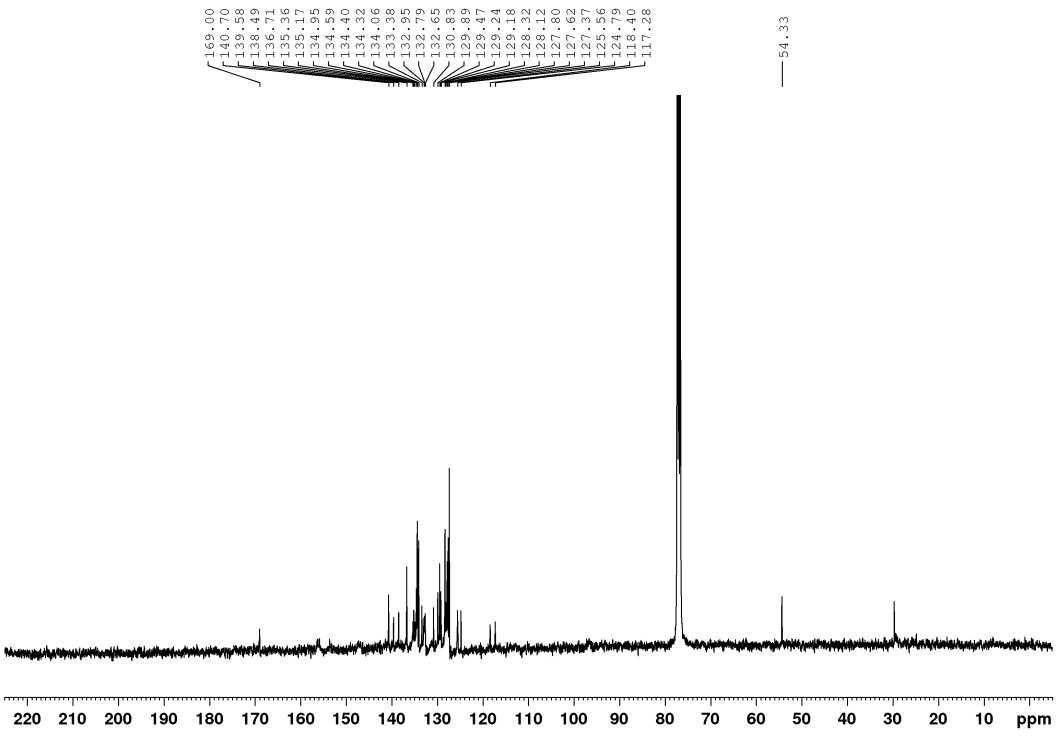
400 MHz ^{1}H NMR spectrum of 2-NCH_2-m-$C_6H_4CO_2CH_3$NCTPP in $CDCl_3$



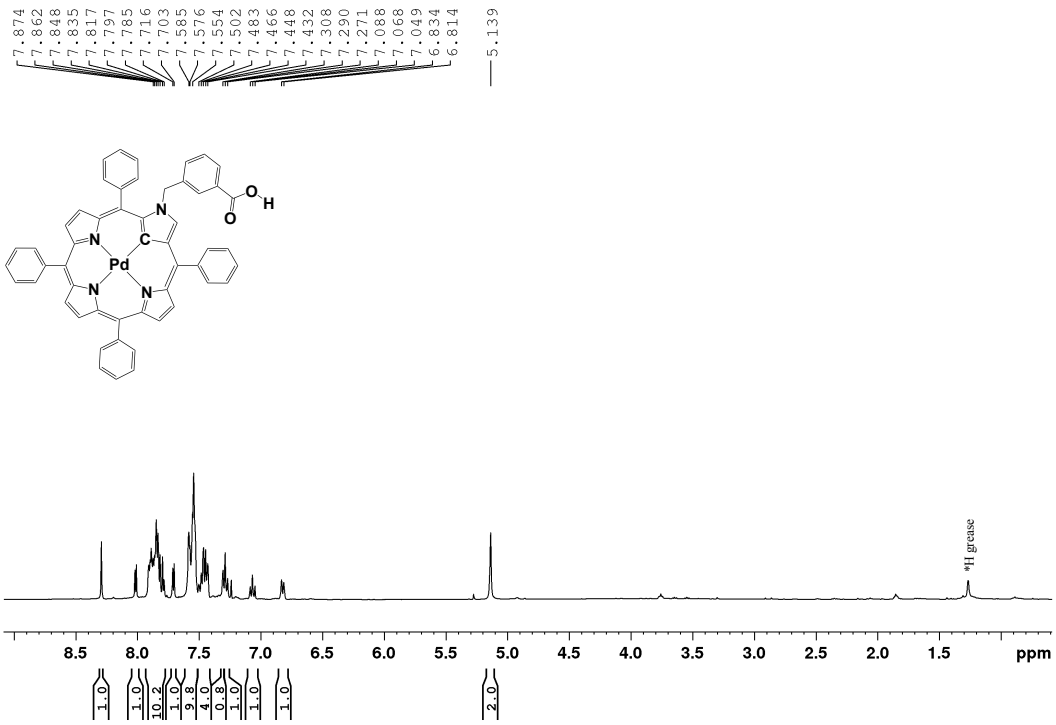
100 MHz ^{13}C NMR spectrum of 2-NCH_2-m-$C_6H_4CO_2CH_3$NCTPP in $CDCl_3$



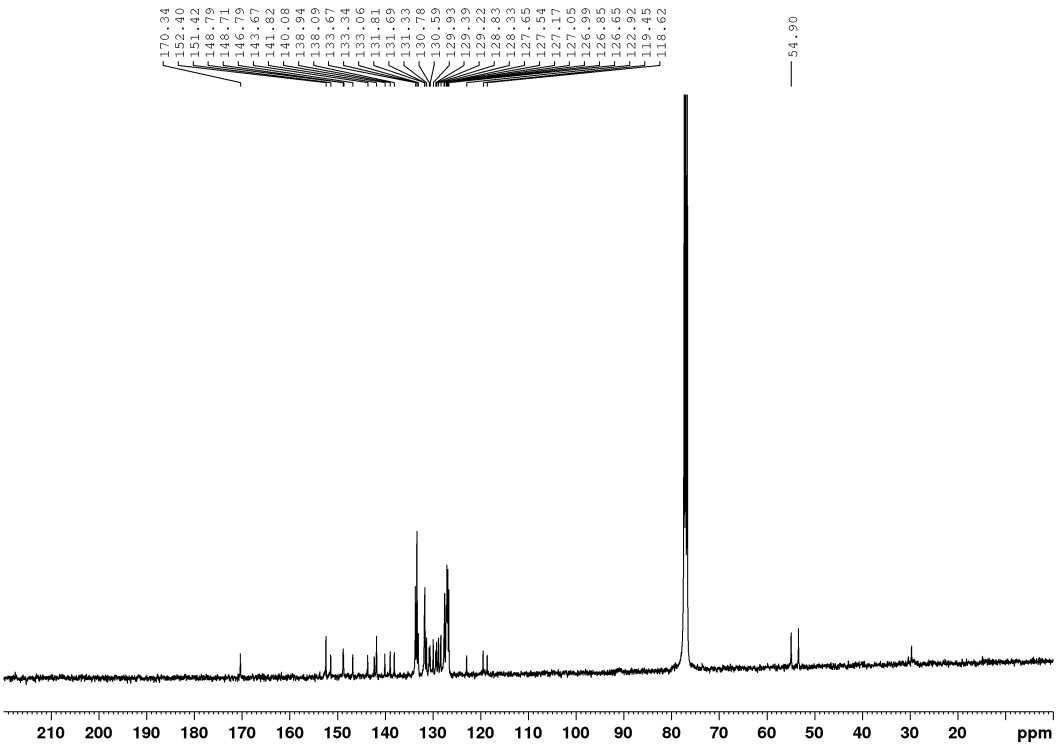
400 MHz ^{1}H NMR spectrum of 2-NCH_2-m-$C_6H_4CO_2$HNCTPP in $CDCl_3$



100 MHz ^{13}C NMR spectrum of 2-NCH_2-m-$C_6H_4CO_2$HNCTPP in $CDCl_3$

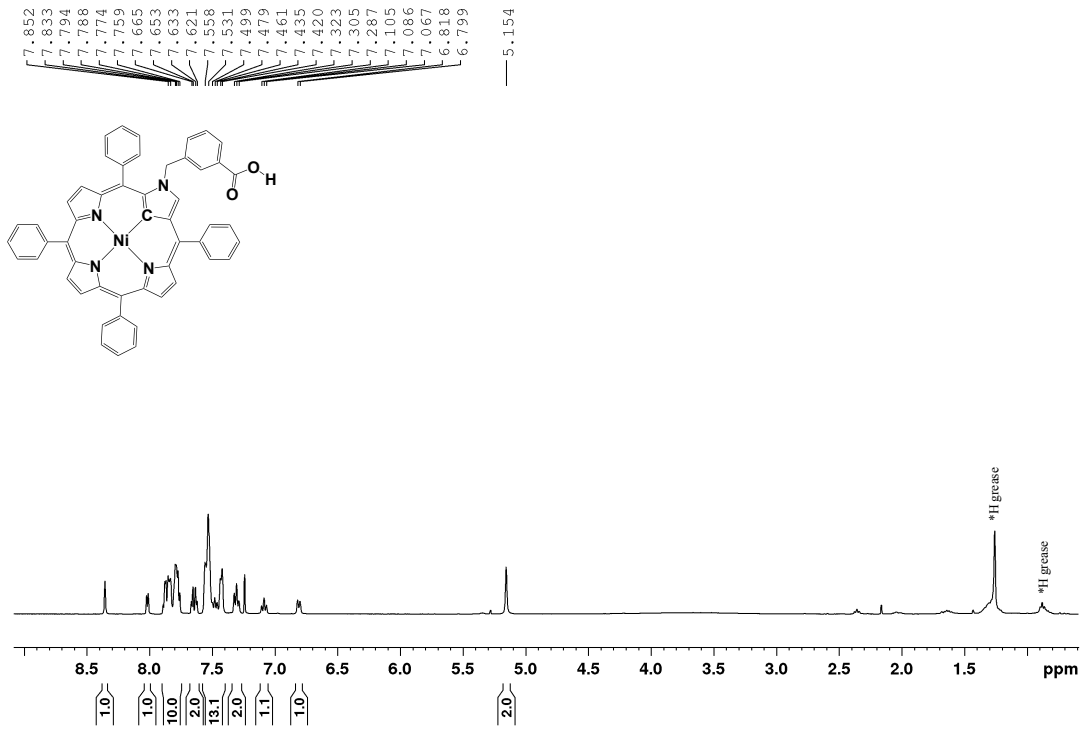


400 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$

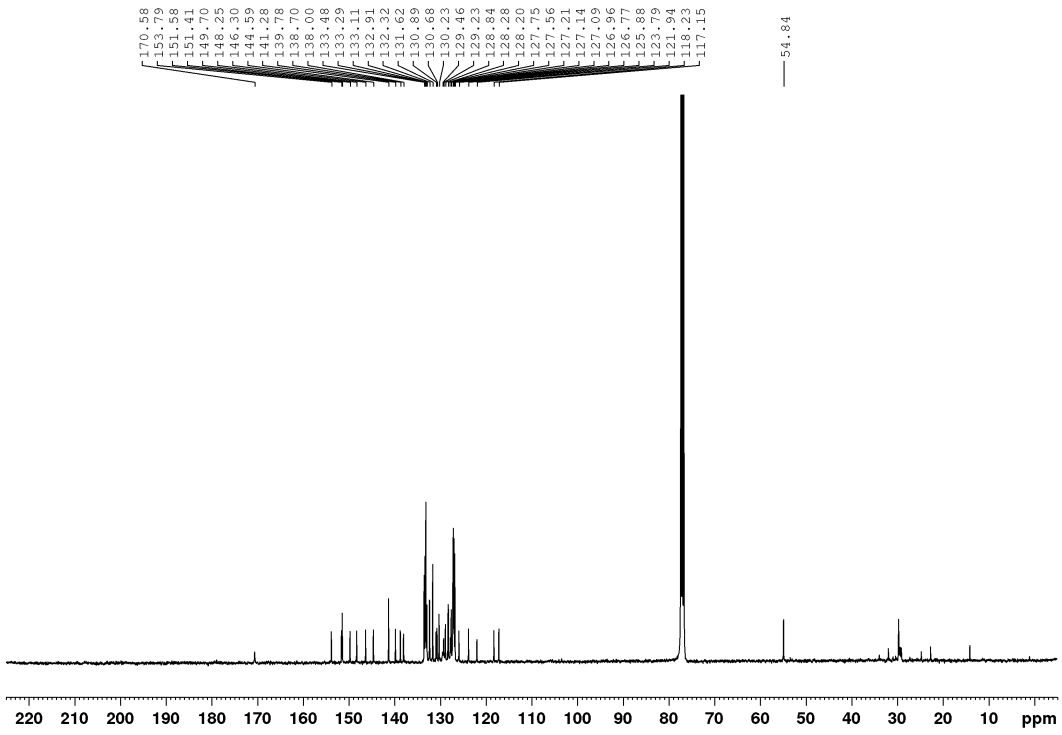


100 MHz ^{13}CNMR spectrum of **1** in $CDCl_3$

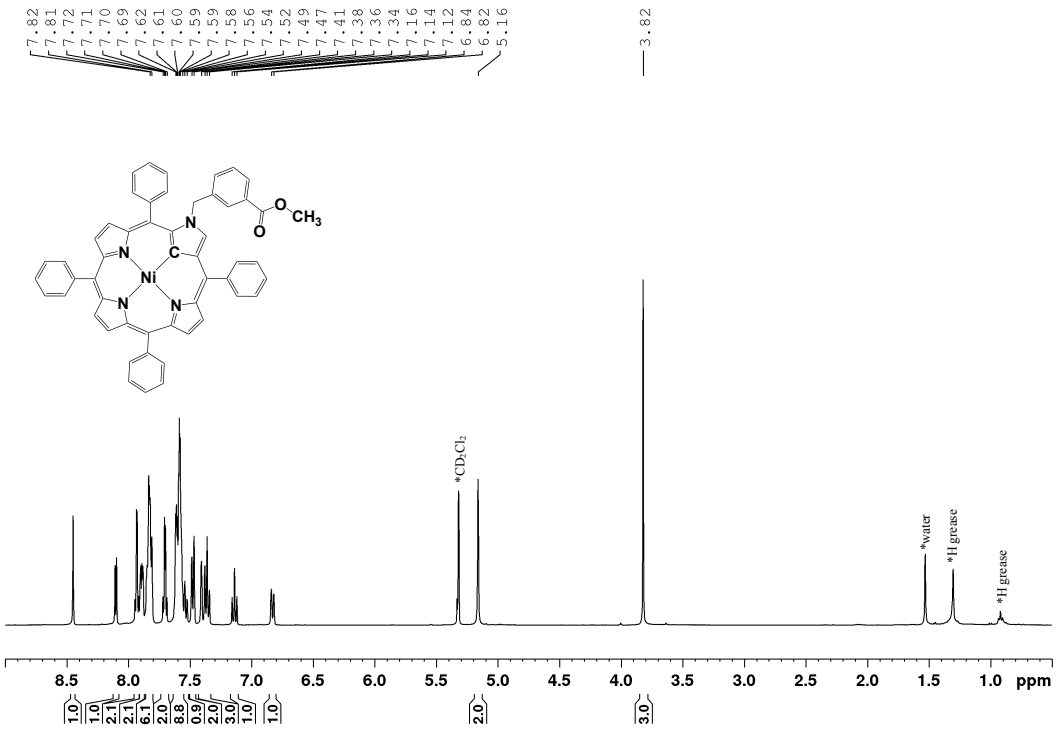
100 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$



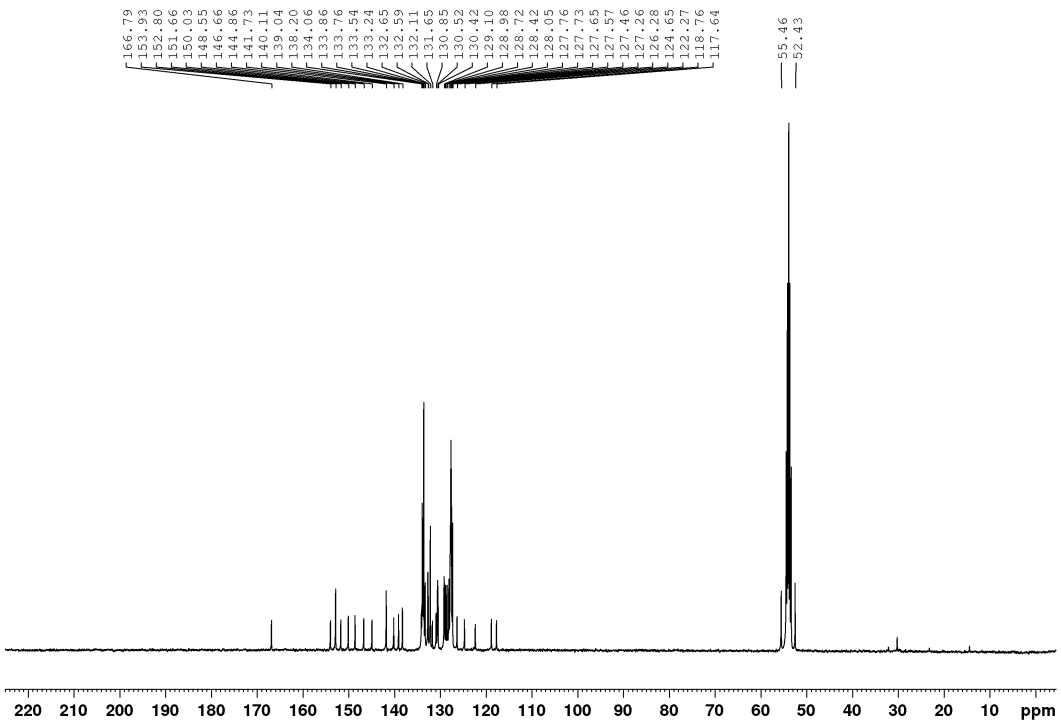
400 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$



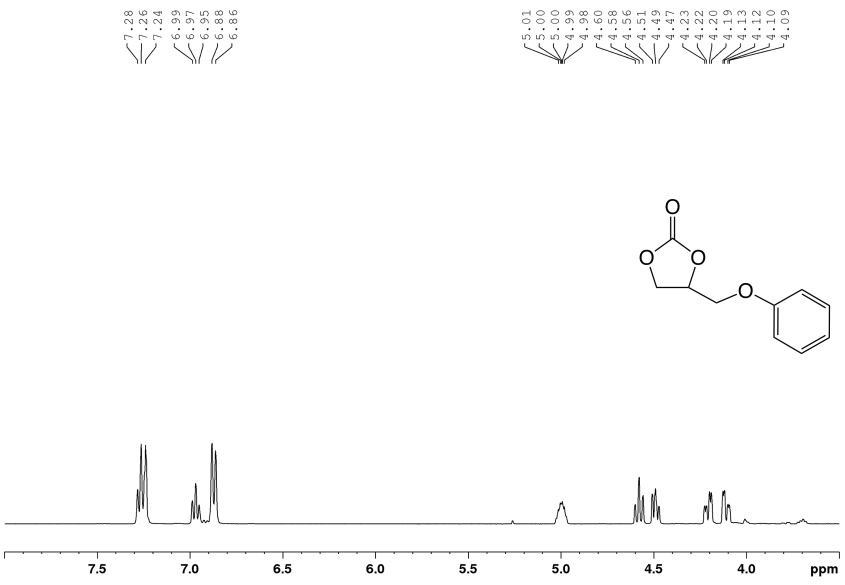
100 MHz ^{13}C NMR spectrum of **2** in $CDCl_3$



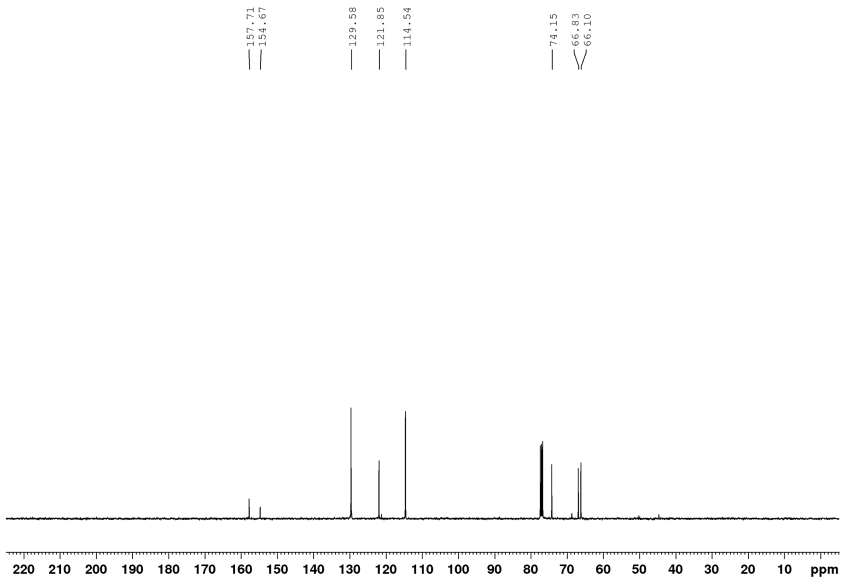
400 MHz ^{1}H NMR spectrum of **3** in CD_2Cl_2



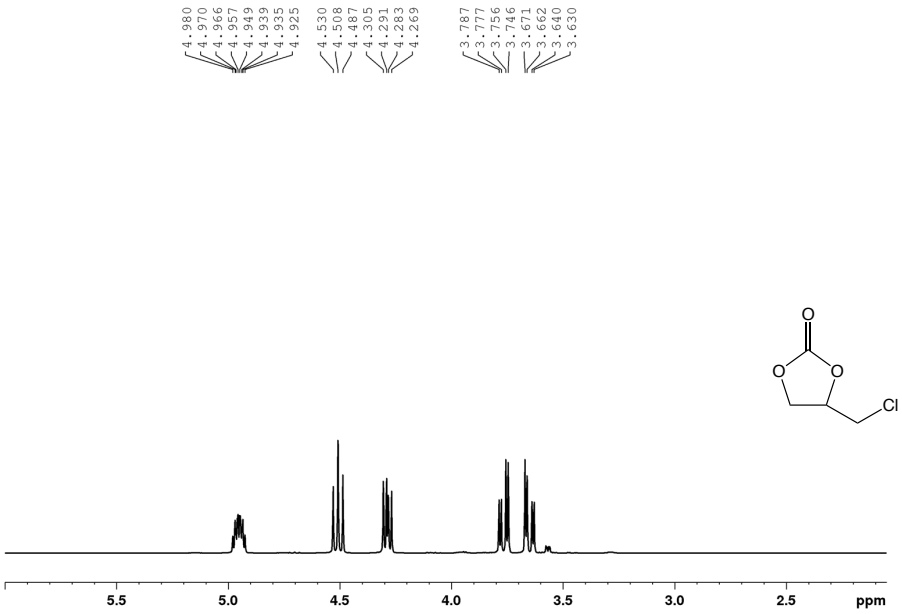
100 MHz ^{13}C NMR spectrum of **3** in CD_2Cl_2



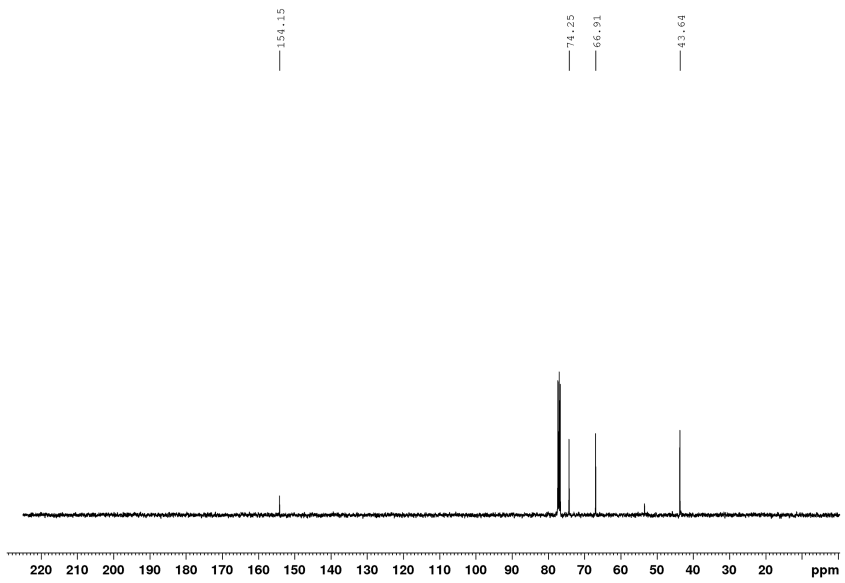
400 MHz ^{1}H NMR spectrum of **IB** in $CDCl_3$



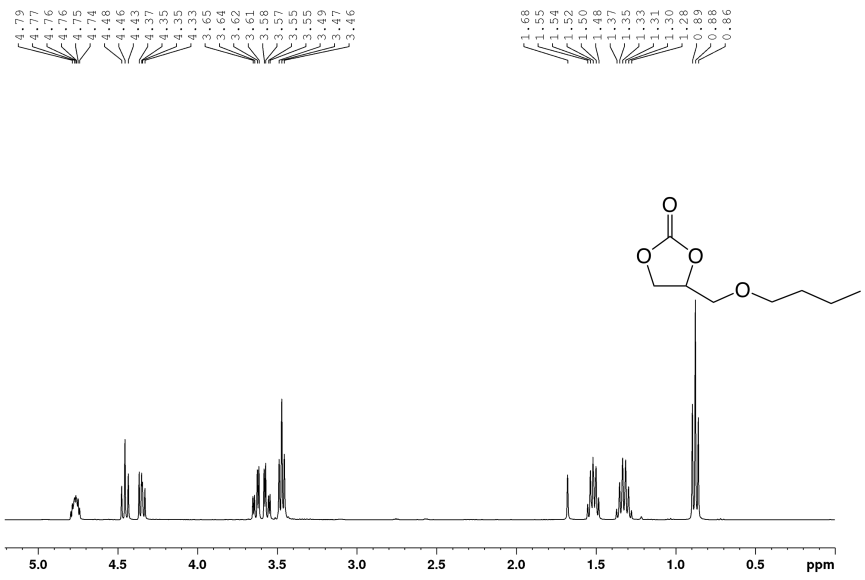
100 MHz ^{13}C NMR spectrum of **IB** in $CDCl_3$



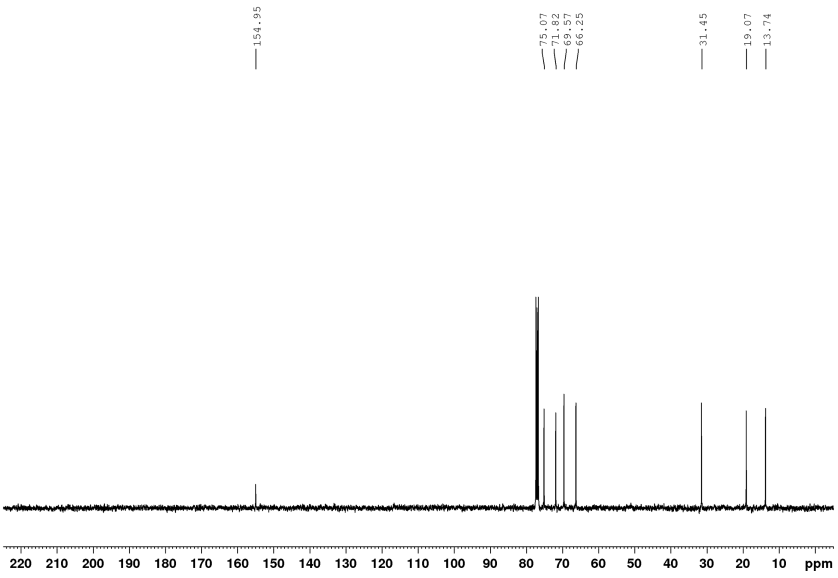
400 MHz ^{1}H NMR spectrum of **IIB** in $CDCl_3$



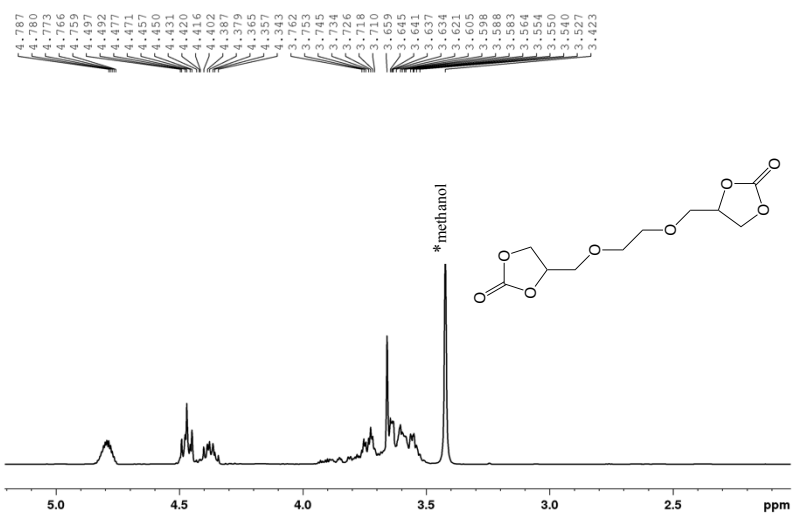
100 MHz ^{13}C NMR spectrum of **IIB** in $CDCl_3$



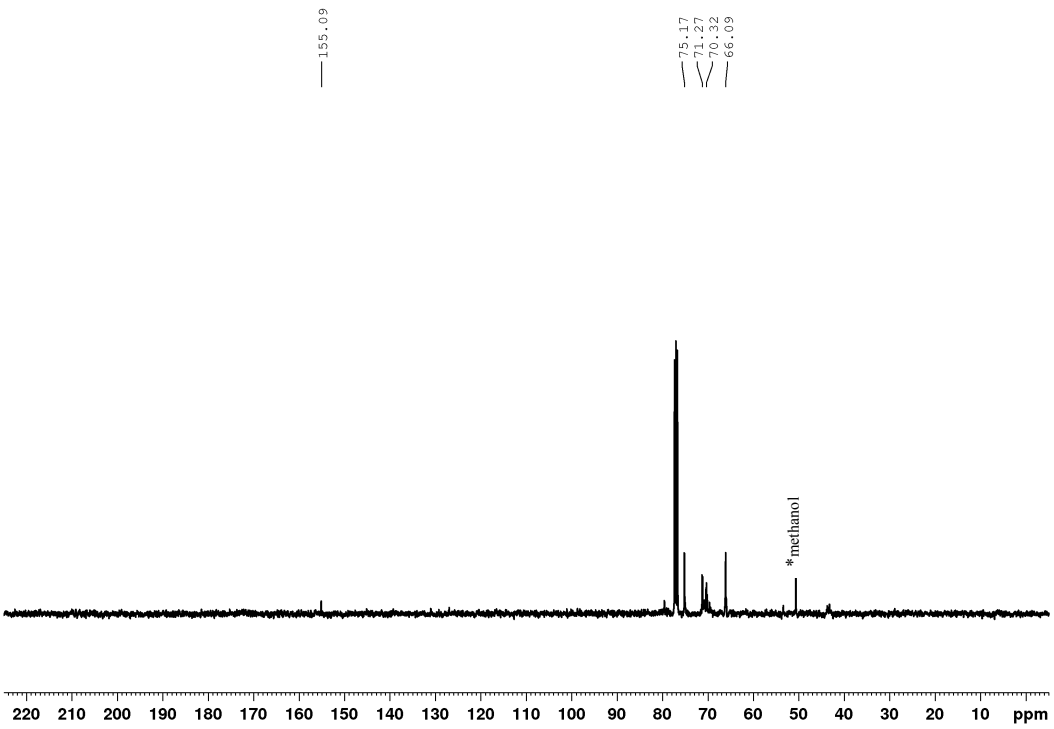
400 MHz ^{1}H NMR spectrum of **IIIB** in $CDCl_3$



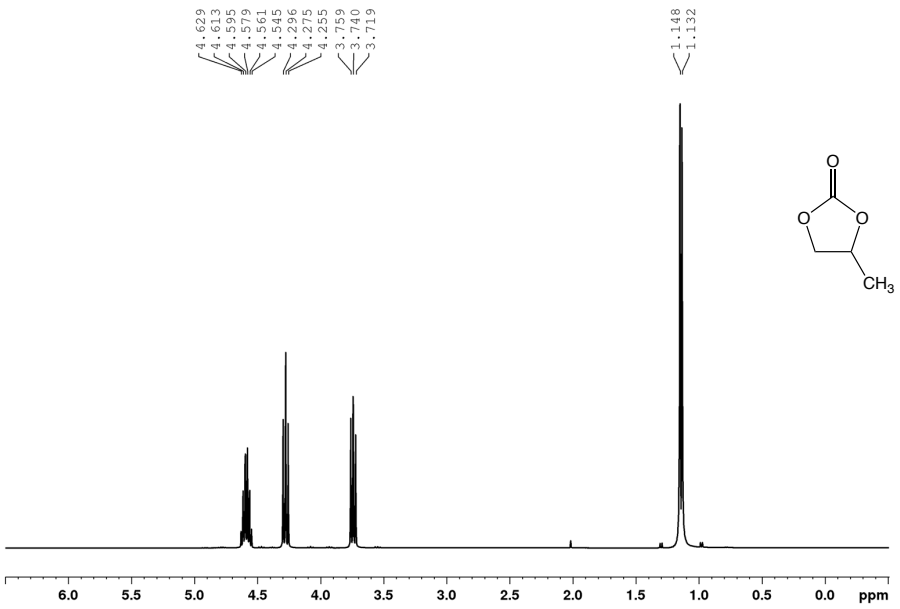
100 MHz ^{13}C NMR spectrum of **IIIB** in $CDCl_3$



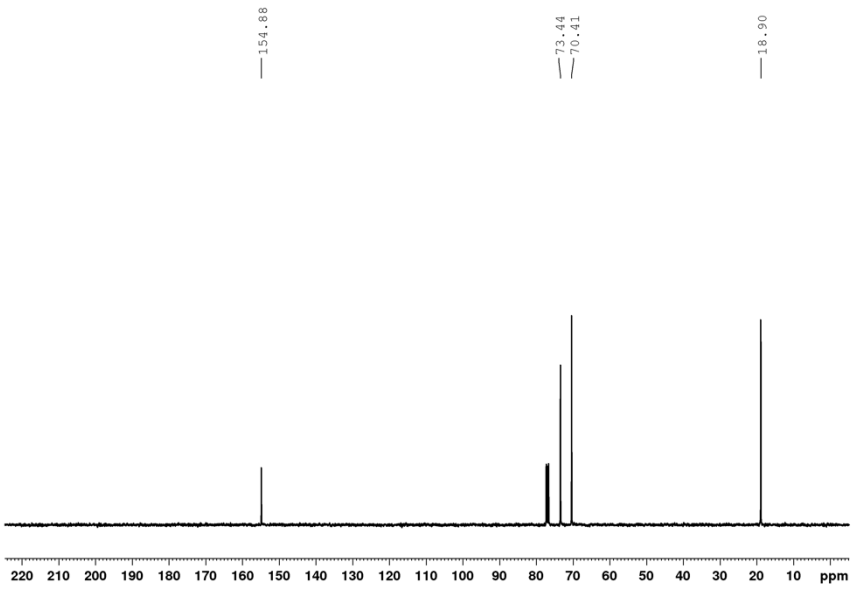
400 MHz ^{1}H NMR spectrum of **IVB** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **IVB** in $CDCl_3$

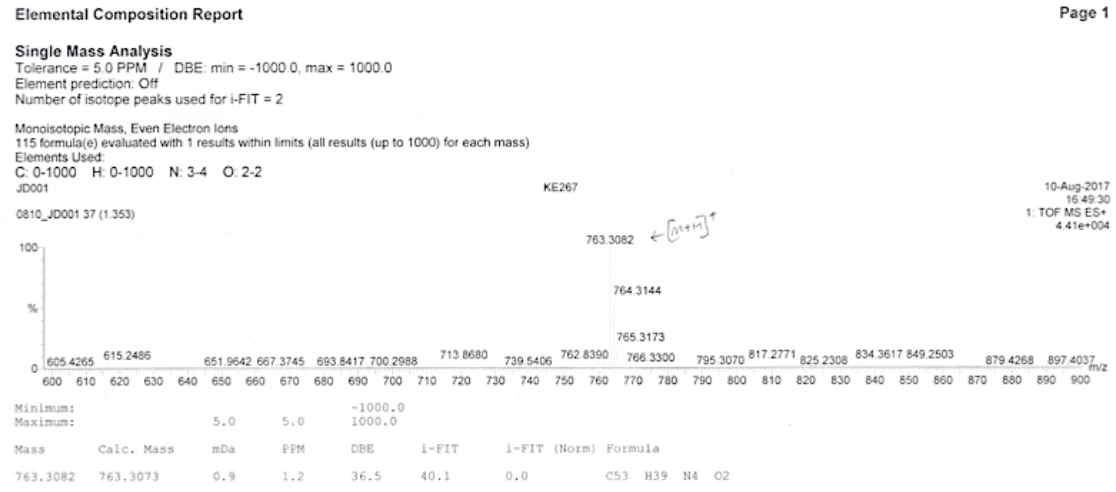


400 MHz ^{1}H NMR spectrum of **VB** in $CDCl_3$

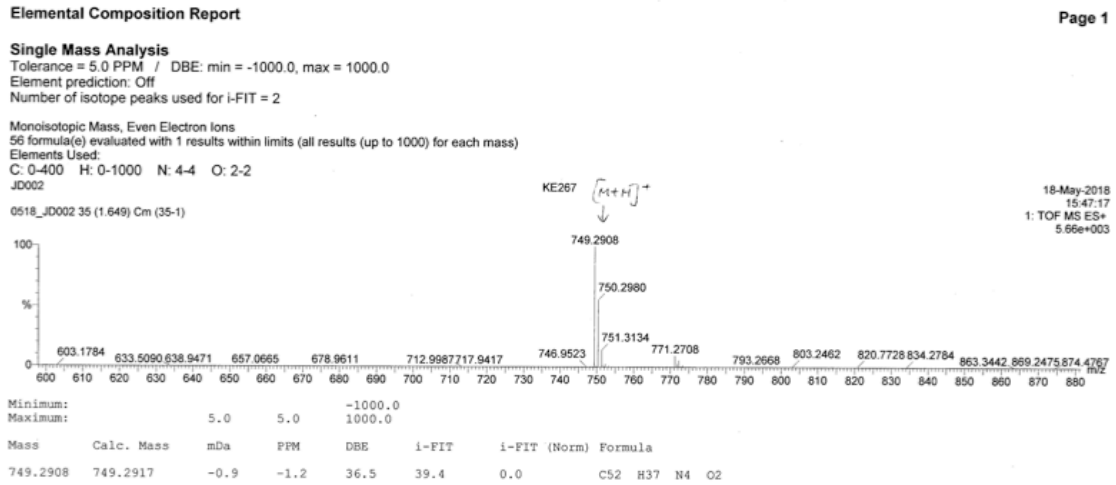


100 MHz ^{13}C NMR spectrum of **VB** in $CDCl_3$

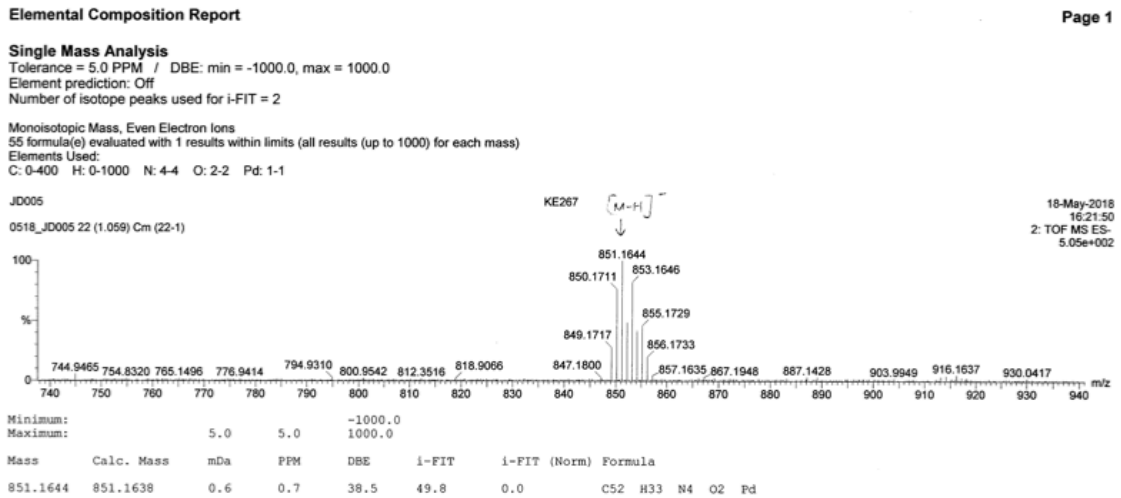
[5] High Resolution mass spectra



HRMS ESI spectrum of 2-NCH_2-*m*-$C_6H_4CO_2CH_3$NCTPP



HRMS ESI spectrum of 2-NCH_2-*m*-$C_6H_4CO_2$HNCTPP



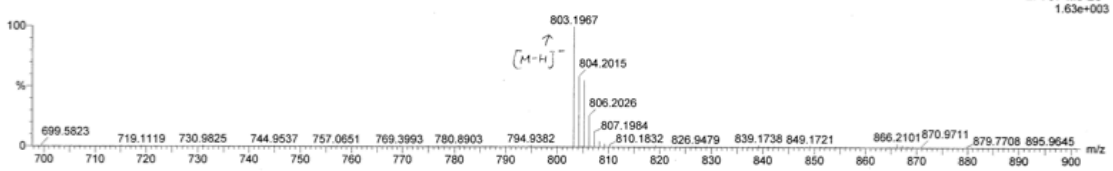
HRMS ESI spectrum of **1**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
55 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-400 H: 0-1000 N: 4-4 O: 2-2 Ni: 1-1

JD003 KE267 18-May-2018 16:45:10
0518_JD003 18 (0.869) Cm (18-1) 2: TOF MS ES- 1.63e+003



Minimum:				-1000.0			
Maximum:		5.0	5.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
803.1967	803.1957	1.0	1.2	39.0	14.1	0.0	C52 H33 N4 O2 Ni

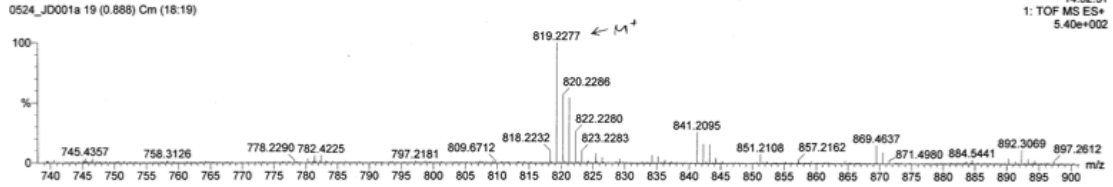
HRMS ESI spectrum of **2**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
57 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-400 H: 0-1000 N: 4-4 O: 2-2 Ni: 1-1

JD001a KE267 24-May-2018 14:32:51
0524_JD001a 19 (0.888) Cm (18:19) 1: TOF MS ES+ 5.40e+002



Minimum:				-1000.0			
Maximum:		5.0	5.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
819.2277	819.2270	0.7	0.9	38.0	27.1	0.0	C53 H37 N4 O2 Ni

HRMS ESI spectrum of **3**

[6] Elemental Analysis Report

Elemental analyses were performed by the elemental analysis service of National Chung Hsing University, Taiwan and are reported as the average of two analyses.

1.本實驗數據為檢測結果，不得用於商業廣告、認證及法律証據使用。(This result is for academic use only, not to be used for any judicial or commercial advertising purpose.)
2.儀器負責人: 鄭政峯 教授　檢測技術員: 陳宜絹。
(Instrument Director : Prof. Jen-Fon Jen　Operator : I-Chuan Chen)

樣品資訊：

Web NO	SEA0001002019020036		
Department :	中央研究院化研所		DATE
Supervisor :	洪政雄	收件日：	2019.03.05
User name :	洪政雄	分析日：	2019.03.06

分析結果：

Sample code	*Weight(mg)*	*N %*	*C %*	*H %*	*O %*	*S %*	*Repeat*	*Charge*
J0005	1.646	6.53	68.69	4.48			1	$ 1,500
	1.937	6.61	68.24	4.43				
推測值		6.57	73.20	4.02				
J0003	2.002	6.05	77.15	4.98			1	$ 1,500
	2.036	6.19	76.86	4.37				
推測值		6.96	77.53	4.25				
J0001a	2.385	5.17	73.99	4.53			1	$ 1,500
	1.758	5.14	73.99	4.39				
推測值		6.84	77.67	4.43				

備註:

使用儀器: Elementar vario EL CUBE(CHN-OS Rapid, German), Accuracy: 0.1%, Precision: 0.2%

	標準品	*N %*	*C %*	*H %*	*O %*	*S %*
★	*Acetanilide*	*10.36*	*71.09*	*6.71*		
	Benzoic acid				*26.20*	
	Sulfanilic acid	*8.09*	*41.60*	*4.07*		*18.50*
	Daily standard	*10.30*	*71.02*	*6.69*		

Labels:
JD005 = complex **1**
JD003 = complex **2**
JD001a = complex **3**

[7] Theoretical calculations coordinates and relative energies

The optimized structures shown in Fig. 3 are the results of computations performed at M06/6-31g(d) level. Following are their respective coordinates. The energies of the ring-opening intermediates (namely, **IntIA** and **IntVA**) are relative to the energies of the corresponding initial states of the catalyst and epoxides (namely, **2**COO$^-$-**IA** and **2**COO$^-$-**VA**).

2COO$^-$-**IA**

Atom	Coordinates (Angstroms) X	Y	Z
C	1.61138000	-2.77965200	-2.15559200
C	2.64202700	-1.91914200	-2.32534800
C	2.19916300	-0.64661100	-1.83583800
N	0.88349000	-0.69525800	-1.45154000
C	0.52471000	-2.02363900	-1.61105400
C	-3.91624700	-1.08667600	-0.93727400
N	-3.14147900	-2.17590800	-0.92415800
C	-1.79531400	-1.71518400	-1.06645500
C	-1.75637000	-0.31236200	-1.09424900
C	-3.13120100	0.06392700	-1.04508500
C	3.51947800	2.61750700	-0.52849300
C	2.74082200	3.56377800	0.03419100
C	1.37304300	3.15861300	-0.19471700
N	1.32192700	1.93978800	-0.81769200
C	2.62824500	1.61057200	-1.05628000
C	-3.21982900	3.78255300	-0.65672700
C	-2.13682300	4.47032400	-0.23684200
C	-1.02355400	3.55517100	-0.26800700
N	-1.40549900	2.32574300	-0.71299300
C	-2.78164900	2.43724000	-0.91098000
C	-0.72780500	-2.56921700	-1.36890900
C	-3.64552800	1.38080100	-1.07126200
C	3.06263800	0.44318700	-1.65740400
C	0.27451400	3.94783900	0.08643400
C	-0.88819700	-4.02854900	-1.57824400
C	-5.10345300	1.61794300	-1.17023400
C	4.48863400	0.33241500	-2.04776900
C	-1.66143500	-4.50592000	-2.64087400
C	-1.81375300	-5.87247000	-2.84575400
C	-1.19310800	-6.77776000	-1.98922100
C	-0.41198700	-6.30954100	-0.93667900
C	-0.24873500	-4.94350500	-0.73262200
C	-5.64488800	2.30587100	-2.26127000
C	-7.01386400	2.52983400	-2.35420900
C	-7.86814500	2.06705600	-1.35833000
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C	-5.97274900	1.16487300	-0.17026200
C	5.32554100	-0.64231400	-1.49472700
C	6.66329900	-0.71920500	-1.86429700
C	7.19169300	0.17787900	-2.78759500
C	6.37188200	1.15860900	-3.33766700
C	5.03325800	1.23348100	-2.97017500
C	0.46115900	5.27902300	0.71638600
C	1.13115400	6.31306900	0.05532600
C	1.28086000	7.56131100	0.65004000
C	0.75767900	7.79775300	1.91740200
C	0.08869300	6.77702700	2.58654600

C	-0.05791100	5.52956900	1.99135100
Ni	-0.24502700	0.81061100	-1.02848200
C	-1.65126400	-3.07279500	3.05593400
C	-0.16256200	-3.14009500	3.42082000
O	0.13365100	-2.75629800	4.56909000
O	0.59595900	-3.50386700	2.48362100
C	-0.78234000	-0.08130600	2.34027300
C	0.62074900	-0.32944200	2.03892300
C	1.61468500	-0.38264800	3.15758200
O	0.03044400	0.95008000	1.80560100
C	-2.62306000	-2.61412400	3.94375900
C	-3.93651700	-2.43246000	3.51611100
C	-4.29002600	-2.69201000	2.19194600
C	-3.32808900	-3.16922700	1.30088800
C	-2.02955700	-3.36333500	1.75435800
C	-3.60786200	-3.35714000	-0.16426300
O	2.91000500	0.04957300	2.74398300
C	3.79667600	-0.86518200	2.29020300
C	5.10273600	-0.38956900	2.11393900
C	6.10943300	-1.24514700	1.69494800
C	5.82699600	-2.58269900	1.41995000
C	4.52146000	-3.03992400	1.57421300
C	3.49595000	-2.20338200	2.01070000
H	1.57408800	-3.83554200	-2.39464600
H	3.62699000	-2.12388700	-2.72536600
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H	4.60140800	2.55241400	-0.54675700
H	3.04405000	4.45622100	0.56867900
H	-4.24384600	4.12810000	-0.74119700
H	-2.07517100	5.50862700	0.06763000
H	-2.14764600	-3.78930400	-3.30293700
H	-2.41798700	-6.23135300	-3.67824100
H	-1.31820300	-7.84902200	-2.14269500
H	0.07137800	-7.01159300	-0.25929200
H	0.34233100	-4.57401400	0.10986800
H	-4.97194300	2.66177300	-3.04118300
H	-7.41593300	3.06541900	-3.21336800
H	-8.94082600	2.24044200	-1.43184300
H	-8.00091000	1.03183200	0.52691100
H	-5.55718000	0.65466900	0.69946600
H	4.92723200	-1.33004400	-0.74894100
H	7.29844100	-1.48116300	-1.41279700
H	8.24119800	0.11703800	-3.07381300
H	6.77482900	1.86781100	-4.06017700
H	4.38588700	1.99701100	-3.40169200
H	1.53168100	6.12657700	-0.94119200
H	1.80325300	8.35534300	0.11741400
H	0.87292800	8.77551200	2.38378700
H	-0.31791100	6.95087700	3.58208600
H	-0.57297200	4.72237000	2.51190000
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H	1.30185500	0.33866300	3.92443200
H	-2.31035400	-2.37971200	4.96095100
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H	6.61531300	-3.25837800	1.08808300
H	4.28093800	-4.08157300	1.36217100
H	2.49385600	-2.62001400	2.16096900
H	-4.68480300	-3.44291600	-0.36648000
H	-3.12171600	-4.25580400	-0.55444800

2COO^--**VA**

Atom	Coordinates (Angstroms) X	Y	Z
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C	-0.21735300	-2.58752100	-1.18776700
N	-0.32604900	-1.22578700	-1.09805300
C	-1.58998500	-0.95016000	-1.59928700
C	-1.19566300	3.45974400	-0.37805900
N	-2.18193500	2.60517700	-0.63919600
C	-1.57019600	1.34329700	-0.91011400
C	-0.17889900	1.42695400	-0.73643000
C	0.04217400	2.80863000	-0.47939400
C	3.07791900	-3.53454700	0.38064400
C	4.08720800	-2.65982300	0.57062400
C	3.60010400	-1.36994100	0.14233900
N	2.29321800	-1.44594400	-0.26032700
C	1.98052800	-2.78414400	-0.17697900
C	3.76178500	3.25819100	-0.38766300
C	4.62132500	2.22397300	-0.26026800
C	3.82283800	1.03004400	-0.16883700
N	2.49024300	1.30985100	-0.31333700
C	2.43896600	2.70288800	-0.38044700
C	1.28950000	3.45956200	-0.38757700
C	0.82592000	-3.36079000	-0.65959000
C	4.37646100	-0.22279200	0.11582300
C	1.35273200	4.93473100	-0.31877900
C	0.68180300	-4.83891800	-0.64374800
C	1.99989000	5.58304600	0.74099400
C	2.04800700	6.97018700	0.80603900
C	1.44707800	7.73987900	-0.18519700
C	0.79484100	7.11057700	-1.24103800
C	0.74586400	5.72321600	-1.30518000
C	-0.28964100	-5.44471000	0.16118500
C	-0.42343400	-6.82898500	0.16759800
C	0.40129800	-7.62266900	-0.62474700
C	1.37022100	-7.02672700	-1.42584800
C	1.50851000	-5.64306500	-1.43409400
C	5.82465300	-0.32472400	0.42461700
C	6.67416600	-1.09697100	-0.37539200
C	8.02967700	-1.20440500	-0.08498500
C	8.56458100	-0.53730600	1.01249800
C	7.73256900	0.23435900	1.81802000
C	6.37725400	0.33682600	1.52752000
Ni	1.06901300	0.02251400	-0.62194000
C	-4.67846500	0.41279900	2.53759900
C	-5.43273200	-0.93196900	2.54852300
O	-5.49381200	-1.50417500	3.65202600

O	-5.83455700	-1.31590400	1.41971800
C	-2.99199600	-2.53177500	1.48583700
C	-2.15199100	-2.04637800	2.57155200
C	-1.11857800	-0.98249300	2.36290100
O	-1.89492000	-3.31052700	1.96016600
C	-4.00536500	0.89230800	3.65800300
C	-3.21024100	2.03512000	3.57204100
C	-3.05583000	2.69395800	2.35570700
C	-3.74287400	2.23454100	1.22845800
C	-4.56885300	1.12467500	1.34824100
C	-3.54415100	2.86280000	-0.12421200
H	-3.16838500	-2.17790200	-2.59737800
H	-1.47987300	-4.21522600	-2.05289800
H	-1.41075200	4.48284800	-0.08098900
H	5.07307200	-2.84608600	0.98028900
H	3.98861600	4.31306800	-0.49056000
H	5.70405000	2.24862600	-0.23277700
H	2.45483500	4.98044700	1.52614300
H	2.55138600	7.45345300	1.64239200
H	1.48440900	8.82696800	-0.13311400
H	0.32495000	7.70323700	-2.02482500
H	0.24970000	5.23040900	-2.14087800
H	-0.91968700	-4.81561100	0.79396200
H	-1.17846300	-7.28967900	0.80308800
H	0.28968700	-8.70648700	-0.61691900
H	2.01787500	-7.64049500	-2.05129600
H	2.26129800	-5.16731800	-2.06318600
H	6.25338800	-1.61402500	-1.23760200
H	8.67211900	-1.80999700	-0.72320800
H	9.62644700	-0.61962100	1.24060200
H	8.13978400	0.75365700	2.68475400
H	5.72324000	0.93315300	2.16340100
H	-0.26555100	-1.11712500	3.04270500
H	-1.54988300	0.01239500	2.54884300
H	-4.10785300	0.32752600	4.58458700
H	-2.68251000	2.40223400	4.45309200
H	-2.39676200	3.56252400	2.28336700
H	-5.14389000	0.76171100	0.50160200
H	-0.73502000	-1.00473100	1.33368300
H	-3.99228000	-2.91214200	1.69888000
H	-2.85334500	-2.10261600	0.48762800
H	-2.57455400	-2.12574500	3.57834600
H	-3.63476500	3.95808500	-0.09088600
H	-4.28331700	2.49023400	-0.84020200
C	-2.25567500	0.26209400	-1.47525500
H	3.05263400	-4.59684100	0.59349600
C	-3.62515800	0.37981500	-2.03065000
C	-3.85883100	1.24977000	-3.10206800
C	-4.69325500	-0.35568800	-1.50632300
C	-5.13641300	1.39146700	-3.63069300
H	-3.02438300	1.81840500	-3.51361500
C	-5.97443200	-0.19585400	-2.02421500
H	-4.56645100	-0.99545900	-0.63009000
C	-6.19920800	0.67271000	-3.08701100
H	-5.30432800	2.07030400	-4.46620900
H	-6.79245600	-0.73937400	-1.55427300
H	-7.20370200	0.79777000	-3.48996000

IntIA (Energy: 18.8 kcal/mol)

Atom	Coordinates (Angstroms) X	Y	Z
C	-2.01285500	-2.96313000	-1.98430800
C	-0.86124700	-3.60325000	-1.66621100
C	0.11829200	-2.58299700	-1.42724700
N	-0.42393600	-1.33563400	-1.53472800
C	-1.75445500	-1.56197300	-1.83499600
C	-2.83513200	2.65174800	-0.42953200
N	-3.47373100	1.59260400	-0.93972900
C	-2.46494400	0.68079000	-1.38324100
C	-1.19218200	1.21824400	-1.14907800
C	-1.45930700	2.49757300	-0.58346700
C	3.85183500	-2.17490100	-1.34206200
C	4.46803000	-0.98388500	-1.50028100
C	3.43863400	0.02718200	-1.39420000
N	2.20396700	-0.54314900	-1.26482400
C	2.44080700	-1.89281500	-1.21857700
C	1.83966600	4.24771100	-0.29002700
C	2.99642500	3.68265100	-0.69601300
C	2.69555400	2.30907700	-1.01760600
N	1.37155200	2.03755700	-0.84766000
C	0.82414200	3.23630300	-0.39620800
C	-2.76192300	-0.60658100	-1.83297400
C	-0.51366400	3.48000000	-0.20770200
C	1.47572300	-2.87441200	-1.20856000
C	3.69954500	1.38605600	-1.33963500
C	-4.11693400	-0.98640800	-2.30336600
C	-0.96394500	4.77924100	0.33475400
C	1.89538100	-4.26869100	-0.92823000
C	-4.94491300	-1.85973200	-1.59219600
C	-6.22510700	-2.15186400	-2.05091300
C	-6.69480500	-1.58351300	-3.23072800
C	-5.87299100	-0.72447100	-3.95641600
C	-4.59615300	-0.42856300	-3.49444900
C	-1.83023600	5.60668500	-0.39115100
C	-2.25153100	6.82712700	0.12399600
C	-1.81685300	7.24427000	1.37824000
C	-0.95844900	6.43091800	2.11192700
C	-0.53659000	5.21116000	1.59643000
C	2.36347800	-4.57634200	0.35426500
C	2.78293200	-5.86513200	0.66438800
C	2.74072500	-6.86577900	-0.30195500
C	2.27941500	-6.56969600	-1.58153800
C	1.86142500	-5.27996600	-1.89215700
C	5.09777900	1.86914700	-1.46516400
C	6.04400300	1.59108900	-0.47248500
C	7.34930800	2.05811300	-0.58198300
C	7.73048700	2.81918400	-1.68317700
C	6.79727200	3.10999500	-2.67361700
C	5.49378800	2.63802000	-2.56389900
Ni	0.46953100	0.34755400	-1.17166700
C	-4.42625000	-0.67865800	2.61741500
C	-3.46609500	-1.01800300	3.72091600
O	-3.78650900	-0.81123800	4.87320600
O	-2.28267700	-1.55872800	3.46020900
C	-1.86760000	-2.12130100	2.19990900
C	-0.64167000	-1.37945100	1.65358800

C	0.44668500	-1.39701600	2.74041200
O	-0.91248500	-0.16166300	1.19224900
C	-5.75463200	-1.03240400	2.85593200
C	-6.74577700	-0.68171500	1.94992400
C	-6.41055400	0.07160500	0.83467500
C	-5.09068000	0.46472300	0.60487400
C	-4.07892600	0.06943600	1.48391500
C	-4.86075600	1.34270200	-0.60352000
O	1.70850800	-1.22813500	2.10084700
C	2.81388600	-1.15479900	2.85989800
C	4.03428200	-1.10019900	2.16887200
C	5.22917900	-1.03913700	2.86547100
C	5.24378000	-1.02682900	4.26123100
C	4.03508000	-1.08016400	4.94252600
C	2.82227800	-1.14660600	4.25911700
H	-2.96904000	-3.39936000	-2.24790100
H	-0.67761900	-4.66976500	-1.61677900
H	-3.39143500	3.45121500	0.05246800
H	4.28456700	-3.16926400	-1.34943400
H	5.52200200	-0.78162600	-1.65572600
H	1.66565500	5.26995200	0.02608500
H	3.98087500	4.13195800	-0.75853400
H	-4.58916500	-2.27848100	-0.65033100
H	-6.86437700	-2.81400900	-1.46805600
H	-7.69937800	-1.81044200	-3.58574100
H	-6.22984000	-0.28180200	-4.88573600
H	-3.94976800	0.25198200	-4.04863800
H	-2.15543100	5.28753300	-1.38127900
H	-2.91649100	7.46001100	-0.46298800
H	-2.14863500	8.19925700	1.78383300
H	-0.61940700	6.74454900	3.09843600
H	0.12239000	4.56448200	2.17430800
H	2.38429600	-3.78055000	1.10087600
H	3.14256100	-6.08803600	1.66809500
H	3.06831200	-7.87614500	-0.05917900
H	2.25078500	-7.34633500	-2.34540600
H	1.50880800	-5.04027500	-2.89555900
H	5.73265400	1.01097000	0.39767800
H	8.07067400	1.83542000	0.20359900
H	8.75195100	3.18871700	-1.76729300
H	7.08627300	3.70581200	-3.53905000
H	4.75722300	2.86279000	-3.33559500
H	0.46929300	-2.34656100	3.31105700
H	0.25660200	-0.56532300	3.43580200
H	-5.99553800	-1.57944900	3.76544100
H	-7.77925200	-0.98024300	2.12183300
H	-7.18097400	0.35808000	0.11494900
H	-3.01339300	0.29716700	1.30875700
H	4.01206700	-1.12123600	1.07956300
H	6.16598500	-1.00734800	2.30740200
H	6.18573000	-0.97819100	4.80579500
H	4.02386200	-1.07154200	6.03263000
H	1.88893900	-1.18670600	4.81423500
H	-5.30774000	2.33185000	-0.41919900
H	-5.39172200	0.92991800	-1.46992000
H	-2.67478200	-2.06918900	1.45685700
H	-1.64884400	-3.17925200	2.41763600
H	-0.25115100	-2.11576900	0.88533500

IntVA (Energy: 25.1 kcal/mol)

Atom	Coordinates (Angstroms) X	Y	Z
C	-1.96118000	-2.77077100	-1.73950900
C	-1.04595900	-3.58708400	-1.15529000
C	-0.00602700	-2.74268000	-0.64374000
N	-0.28524200	-1.43164700	-0.87414600
C	-1.52293200	-1.42792600	-1.49747400
C	-1.96964400	2.99832500	-0.35145600
N	-2.72993800	2.04804700	-0.94135800
C	-1.86630500	0.92835300	-1.16084600
C	-0.56791600	1.22322100	-0.71843300
C	-0.65035700	2.57380700	-0.25889500
C	3.68062600	-3.00093300	0.17281900
C	4.53736200	-1.98454600	-0.06775400
C	3.72740900	-0.83408500	-0.41457300
N	2.41636100	-1.15942800	-0.43186400
C	2.35641700	-2.49155900	-0.09851500
C	2.90613800	3.73337500	-0.04390700
C	3.94298600	2.93674400	-0.37368600
C	3.42440700	1.58564000	-0.44846200
N	2.07568800	1.58001700	-0.26813000
C	1.73140000	2.89450100	-0.00132400
C	-2.30668200	-0.29404100	-1.68896100
C	0.45479200	3.39408400	0.11450100
C	1.21013700	-3.25673700	-0.14107600
C	4.24613700	0.45753900	-0.56548500
C	-3.57218900	-0.40093800	-2.44962700
C	0.24858600	4.79361800	0.53515000
C	1.24747800	-4.68991300	0.23735300
C	-3.72556200	0.35056100	-3.62169700
C	-4.90227100	0.29093800	-4.35821200
C	-5.95103100	-0.52146500	-3.93316500
C	-5.80844500	-1.27664500	-2.77350200
C	-4.62995500	-1.21723900	-2.03762200
C	0.78143400	5.24894400	1.74915700
C	0.59738300	6.56169300	2.16602700
C	-0.13103500	7.45200400	1.38259500
C	-0.66516300	7.01734200	0.17319700
C	-0.47620100	5.70576300	-0.24564600
C	0.46344700	-5.14539700	1.30403600
C	0.47535000	-6.48460800	1.67444700
C	1.26457200	-7.39753000	0.98026400
C	2.03892400	-6.96031900	-0.08945200
C	2.02732200	-5.61925100	-0.45885600
C	5.71193600	0.60445500	-0.71560000
C	6.36719700	-0.00685500	-1.79338200
C	7.74461500	0.09020500	-1.94977200
C	8.50478100	0.80614000	-1.02998800
C	7.87248500	1.41370900	0.05099900
C	6.49541800	1.30841300	0.20909200
Ni	0.87271400	0.05349400	-0.45497600
C	-4.38745000	-0.33436000	2.14187700
C	-3.60880100	-1.01152100	3.24780500
O	-4.22256300	-1.56757500	4.13788200
O	-2.28271100	-1.06540000	3.26018300
C	-1.35756900	-0.42967800	2.34167300
C	0.08172700	-0.92792000	2.49907200

C	0.50533700	-0.92484700	3.97059200
O	0.86806800	-0.13040400	1.75465000
C	-5.72336600	-0.74185400	2.03446100
C	-6.55069400	-0.22306900	1.04919300
C	-6.04886200	0.69543800	0.13408900
C	-4.72847900	1.12391300	0.22806500
C	-3.91892900	0.63473800	1.25082900
C	-4.17865900	2.07231300	-0.81113900
H	-2.87205500	-3.05310700	-2.25394000
H	-1.04275100	-4.67047300	-1.11416500
H	-2.42520400	3.92700300	-0.01830700
H	3.90842400	-4.00935500	0.49888900
H	5.61780100	-1.98042300	0.02407300
H	2.90441400	4.80916700	0.09184900
H	4.97417400	3.21924300	-0.55040100
H	-2.90190000	0.98818500	-3.94272700
H	-5.00087400	0.88014900	-5.26917800
H	-6.87636500	-0.56595200	-4.50630300
H	-6.62777000	-1.90415300	-2.42372000
H	-4.52946700	-1.78451100	-1.11238000
H	1.33345000	4.54398100	2.36941700
H	1.01733400	6.88883100	3.11661500
H	-0.28028200	8.47965800	1.71169200
H	-1.22455200	7.70861100	-0.45684100
H	-0.86879300	5.37884200	-1.20809000
H	-0.14660500	-4.42358000	1.84778800
H	-0.13305600	-6.81521900	2.51542800
H	1.27354400	-8.44751600	1.27099500
H	2.65156700	-7.66829600	-0.64705700
H	2.62086600	-5.27818700	-1.30690500
H	5.76963500	-0.56136600	-2.51690100
H	8.22712000	-0.39231900	-2.79955800
H	9.58447700	0.88641800	-1.15157200
H	8.45825400	1.96312800	0.78764200
H	6.00672200	1.76101200	1.07136500
H	-1.67277200	-0.60503600	1.30566200
H	-1.34168700	0.65171200	2.55094100
H	0.07508700	-2.01219000	2.17009500
H	-0.11376400	-1.58003200	4.60024600
H	0.44547300	0.10309600	4.36013200
H	-6.08649300	-1.47748400	2.74759500
H	-7.58465600	-0.55815300	0.97531800
H	-6.67471000	1.05797300	-0.68397500
H	-2.90552700	1.01092400	1.31711300
H	-4.43966400	3.11185000	-0.56121300
H	-4.65400200	1.85967500	-1.77856300
H	1.55332700	-1.24385300	4.03357900

1. P. J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz, T. Glowiak, *Angewandte Chemie International Edition in English,* 1994**, 33**, 779.

[8] Crystal structure report of 2-NH_2-*m*-C_6H_4-CO_2CH_3NCTPP (i14918; CCDC1889366)

General Information

The crystals of **2-NH_2-*m*-C_6H_4-CO_2CH_3NCTPP** suitable for X-ray diffraction structural analysis were obtained from diffusion of hexane into a solution of the compound in CH_2Cl_2. Diffraction measurements were carried out at 173.0 (2) K on a Bruker SMART Apex CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined using full-matrix least-squares methods against F^2 values using the SHELXTL program packages (Version 6.14). The positions of the hydrogen atoms were geometrically generated with a fixed distance and were assigned isotropic thermal parameters by the SHELXTL idealization methods. Refinement was carried out using anisotropic thermal parameters for all the non-hydrogen atoms. The absorption correction program SADABS was used for these three structures. Summary and experimental details for X-ray data collections are provided in Table S1.

Table S1. Crystal data and structure refinement for i14918.

Identification code	i14918	
Empirical formula	C54 H40 Cl2 N4 O2	
Formula weight	847.80	
Temperature	173.0 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2504(6) Å	α= 106.468(3)°.
	b = 13.7475(7) Å	β= 95.196(3)°.
	c = 16.1283(10) Å	γ = 105.201(3)°.
Volume	2069.6(2) $Å^3$	
Z	2	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.207 mm^{-1}	
F(000)	884	
Crystal size	0.120 x 0.100 x 0.060 mm^3	
Theta range for data collection	1.740 to 26.373°.	
Index ranges	-12<=h<=12, -17<=k<=17, -20<=l<=20	
Reflections collected	44185	
Independent reflections	8453 [R(int) = 0.0678]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9588 and 0.8323	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8453 / 168 / 560	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.1678	
R indices (all data)	R1 = 0.0942, wR2 = 0.1866	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.813 and -0.832 $e.Å^{-3}$	

Figure S1. Molecular structure of 2-NH_2-*m*-C_6H_4-CO_2CH_3NCTPP from X-ray single structure determination with atoms presented in 30% thermal ellipsoids