

Supporting Information

For

Exploring SiliaCat Pd-DPP as a recyclable heterogeneous catalyst for the multi-batch direct heteroarylation polymerization for P(NDI2OD-T2).

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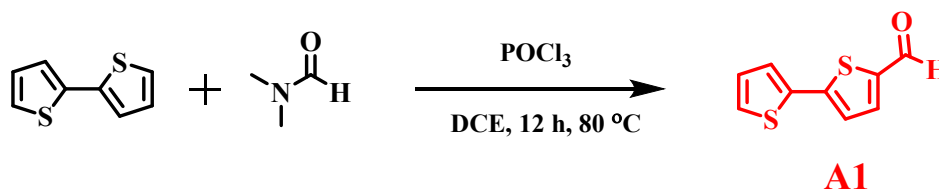
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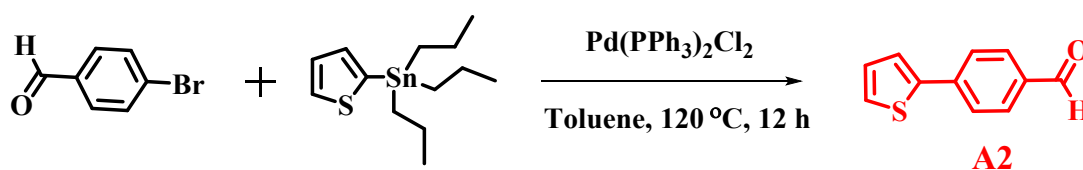
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S1. Synthesis of [2,2-bithiophene]-5-carbaldehyde (A1)



In a two necked round bottom flask equipped with a magnetic stir bar bithiophene (1 gm, 6.014 mmol) was taken in 20 ml of dry dichloroethane (DCE). Dimethyl formamide (DMF) (571.49 mg, 7.819 mmol) was added to it dropwise. The reaction mixture was cooled to -10 °C, and POCl₃ (1.2 gm, 7.819 mmol) was added to the reaction mixture. The reaction mixture was then heated at 80 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature, and 50 ml of 1M NaOAc solution was added to it and refluxed for 3 h. The reaction mixture was cooled to room temperature, and 30 ml dichloromethane (DCM) was added to it to extract the organic layer. The organic layer was dried over anhydrous Na₂SO₄ and concentrated by rotatory evaporation. The solid compound was used for the subsequent reaction without further purification. Yield = 0.915 gm (78 %). ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 9.87 (1 H, s), 7.68 (1 H, d), 7.37 (2 H, dd), 7.26 (1 H, dd), 7.08 (1 H, d). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 182.54, 147.17, 141.70, 137.29, 136.03, 128.35, 127.09, 126.14, 124.23.

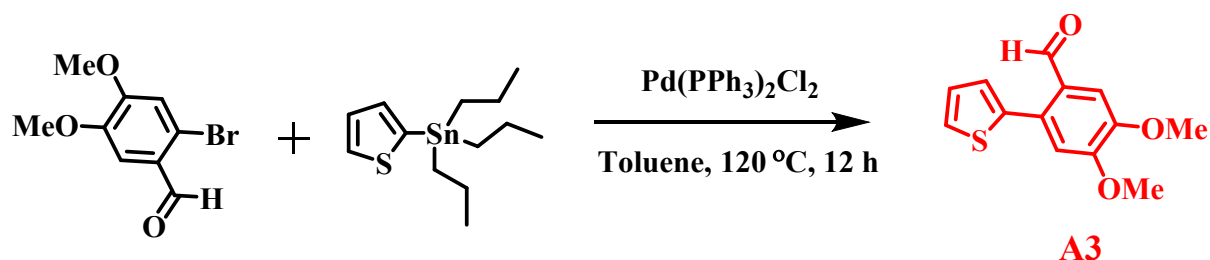
S2. Synthesis of 4-(thiophene-2-yl) benzaldehyde (A2)



An oven dry Schlenk tube (15 mL) containing magnetic stir bar was charged with 4-bromo benzaldehyde (1 gm, 5.404 mmol), 2-tri-butylstannyl thiophene (2.016 gm, 5.404 mmol) and Pd(PPh₃)₂Cl₂ (189.67 mg, 5 mol %). After adding monomers and catalyst, the flask was evacuated three times and degassed by nitrogen (N₂). Separately degassed toluene (3 mL) was added to the reaction vessel under inert condition and stirred for 15-20 min at room temperature to fully dissolve the reagents and the reaction vessel was heated in a preheated oil bath at 120 °C with stirring for 12 h. After the completion of reaction, toluene was evaporated by rotatory evaporation. The residue was dissolved in DCM and washed by water

(3 times). The crude product was extracted using DCM by separating funnel. The crude product was purified by column chromatography using hexane and ethyl acetate (98:2) as eluent. Yield = 0.825 gm (81 %). ^1H NMR spectrum (400 MHz instrument, CDCl_3) δ (ppm) 10.1 (1 H, s), 7.91-7.89 (2 H, dd), 7.79-7.77 (2 H, dd), 7.48 (1 H, d), 7.40 (1 H, dd), 7.15 (1 H, d). ^{13}C NMR spectrum (100 MHz instrument, CDCl_3) δ (ppm) 191.48, 142.75, 140.13, 135.11, 130.49, 126.07, 125.06.

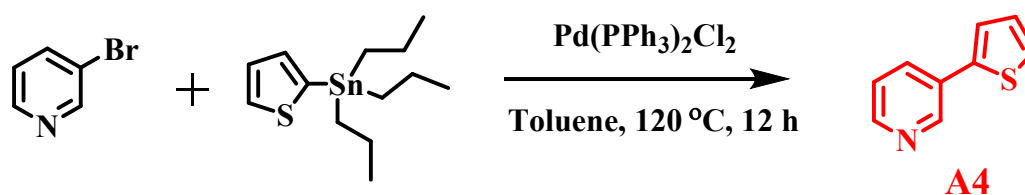
S3. Synthesis of 4,5-dimethoxy-2-(thiophen-2-yl) benzaldehyde (A3)



The experimental procedure was similar to that for the synthesis of A2 except for the reagents.

2-bromo-4,5-dimethoxybenzaldehyde (1 gm, 4.080 mmol), 2-tri-butylstannyl thiophene (1.522 gm, 4.080 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (143.20 mg, 5 mol %). The crude product was purified by column chromatography using hexane and ethyl acetate (99:1) as eluent. Yield = 0.780 gm (77 %). ^1H NMR spectrum (400 MHz instrument, CDCl_3) δ (ppm) 10.02 (1 H, s), 7.51 (2 H, s), 7.08 (2 H, m), 6.95 (1 H, d). ^{13}C NMR spectrum (100 MHz instrument, CDCl_3) δ (ppm) 190.63, 153.25, 149.12, 133.20, 129.22, 127.46, 126.89, 113.09, 108.73, 56.18.

S4. Synthesis of 3-(thiophen-2-yl) pyridine (A4)

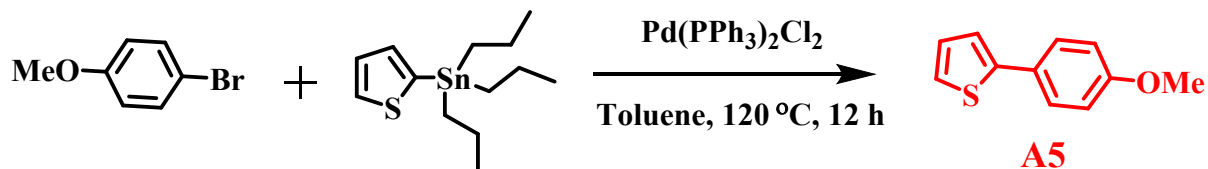


The experimental procedure was similar to that for the synthesis of A2 except for the reagents.

3-bromo pyridine (1 gm, 6.321 mmol), 2-tri-butylstannyl thiophene (2.361 gm, 6.321 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (221.90 mg, 5 mol %). The crude product was purified by column chromatography using hexane and ethyl acetate (90:10) as eluent. Yield = 0.800 gm (78 %). ^1H NMR spectrum (400 MHz instrument, CDCl_3) δ (ppm) 8.80 (1 H, d), 8.42 (1 H, dd), 7.77

(1 H, d), 7.26 (1 H, s), 7.20 (3 H, m), 7.03 (1 H, s). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 148.02, 146.56, 140.01, 132.73, 128.03, 125.80, 123.99, 123.40.

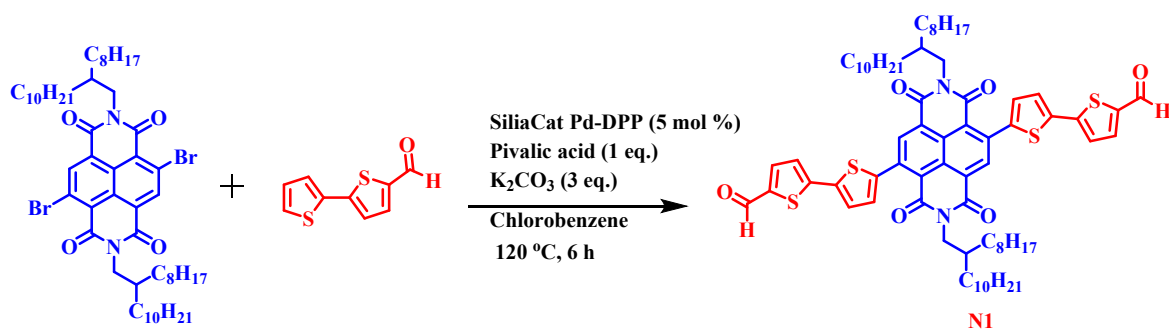
S5. Synthesis of 2-(4-methoxyphenyl) thiophene (A5)



The experimental procedure was similar to that for the synthesis of A2 except for the reagents.

2-(4-methoxyphenyl) thiophene (1 gm, 5.346 mmol), 2-tri-butylstannyl thiophene (1.995 gm, 5.346 mmol) and Pd(PPh₃)₂Cl₂ (187.64 mg, 5 mol %). The crude product was purified by column chromatography using hexane and ethyl acetate (95:5) as eluent. Yield = 0.785 gm (77 %). ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 7.55 (2 H, d), 7.22 (2 H, d), 7.07 (1 H, d), 6.93 (2 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 159.48, 144.64, 128.22, 127.53, 124.13, 114.57, 55.65.

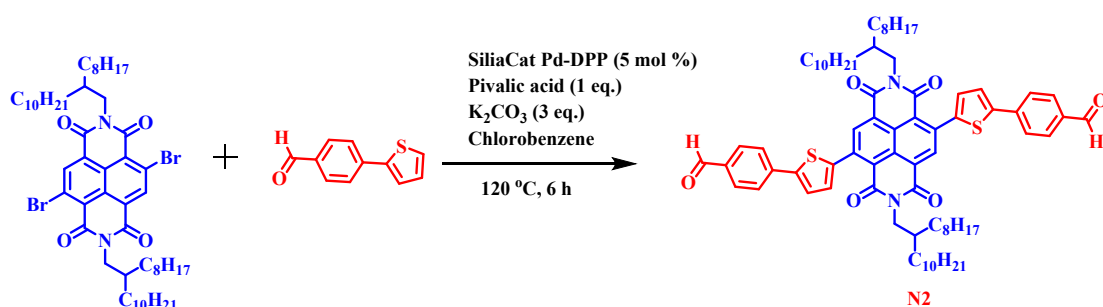
S6. Synthesis of N1



In a 10 ml oven dry Schlenk tube equipped with a stir bar were added NDIOD-Br₂ (100 mg, 0.101 mmol), 2,2-bithiophene-5-carbaldehyde (39.44 mg, 0.203 mmol), pivalic acid (10.36 mg, 0.101 mmol), K₂CO₃ (42 mg, 0.304 mmol) and SiliaCat Pd-DPP (16.92 mg, 5 mol %). The Schlenk tube was evacuated three times and purged by N₂ gas. Degassed chlorobenzene (1 mL) was added to the Schlenk tube by syringe and purged for 15 minutes. The reaction was stirred for 6 h at 120 °C and warmed to room temperature. The reaction mixture was precipitated in MeOH (50 ml) and after filtration washed with plenty of MeOH and a mixture of MeOH and acetone (50:50). The compound was dried in vacuum oven at 60 °C for 12 h.

The dried compound was used for further characterization. Yield = 89 mg (72 %). ^1H NMR spectrum (400 MHz instrument, CDCl_3) δ (ppm) 9.91 (2 H, s), 8.79 (2 H, s), 7.73 (2 H, dd), 7.46 (2 H, dd), 7.31 (4H, dd), 4.11 (4 H, dd), 1.96 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ^{13}C NMR spectrum (100 MHz instrument, CDCl_3) δ (ppm) 182.82, 162.62, 146.60, 142.62, 142.46, 139.38, 139.05, 137.49, 130.21, 126.65, 125.08, 123.61, 45.36, 36.83, 32.19, 30.37, 29.94, 22.75, 14.18. MALDI-TOF: (MW: 1211.79) m/z : 1211.64.

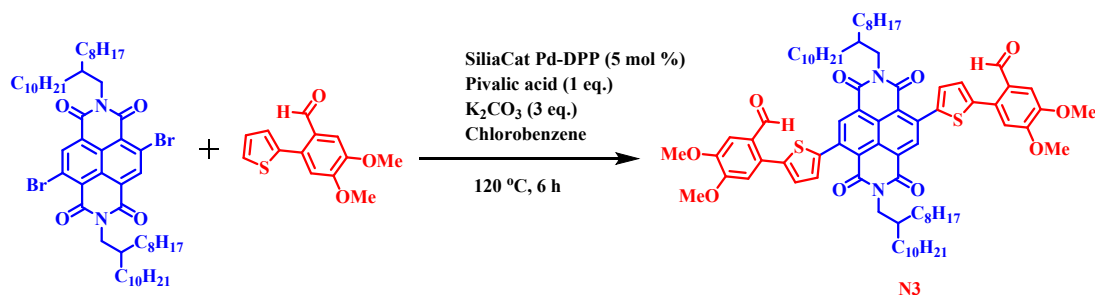
S7. Synthesis of N2



The experimental procedure was similar to that for the synthesis of N1 except for the reagents.

NDIOD- Br_2 (200 mg, 0.203 mmol), 4-(thiophene-2-yl) benzaldehyde (76.43 mg, 0.406 mmol), pivalic acid (20.73 mg, 0.203 mmol), K_2CO_3 (84.18 mg, 0.609 mmol) and SiliaCat Pd-DPP (33.85 mg, 5 mol %). Yield = 155 mg (64 %). ^1H NMR spectrum (400 MHz instrument, CDCl_3) δ (ppm) 10.04 (2 H, s), 8.82 (2 H, s), 7.96-7.92 (4 H, dd), 7.85-7.81 (4 H, dd), 7.55 (2 H, d), 7.45 (2 H, d), 4.12 (4 H, dd), 1.97 (1 H, m), 1.22 (64 H, m), 0.84 (12 H, m). ^{13}C NMR spectrum (100 MHz instrument, CDCl_3) δ (ppm) 191.04, 162.10, 145.09, 139.16, 135.16, 130.19, 125.77, 125.27, 125.04, 122.91, 44.68, 36.21, 31.56, 29.74, 29.30, 22.33, 13.17, 0.74. MALDI-TOF: (MW: 1199.75) m/z : 1201.58.

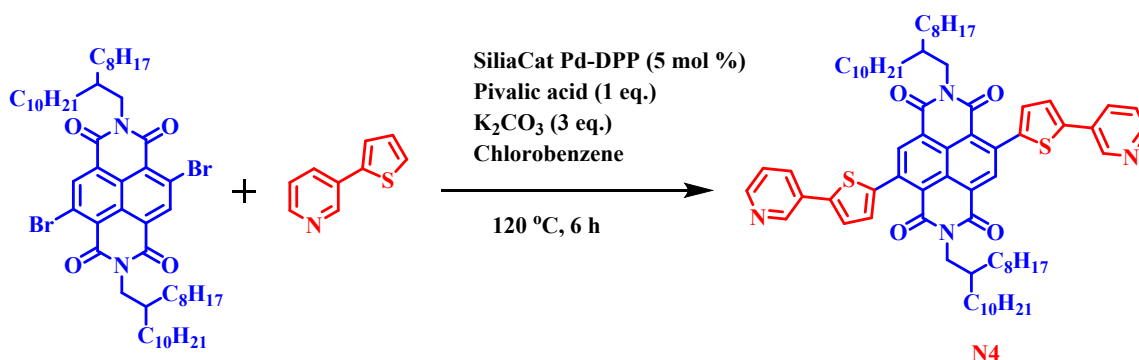
S8. Synthesis of N3



The experimental procedure was similar to that for the synthesis of N1 except for the reagents.

NDIOD-Br₂ (100 mg, 0.101 mmol), 4,5-dimethoxy-2-(thiophen-2-yl) benzaldehyde (50.41 mg, 0.203 mmol), pivalic acid (10.36 mg, 0.101 mmol), K₂CO₃ (42.091 mg, 0.304 mmol) and SiliaCat Pd-DPP (16.92 mg, 5 mol %). Yield = 88 mg (66 %). ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 10.25 (2 H, s), 8.85 (2 H, s), 7.58 (2 H, s), 7.38 (2 H, s), 7.15 (2 H, dd), 7.07 (2 H, dd), 4.13-4.02 (14 H, m), 1.98 (2 H, m), 160-1.20 (64 H, m), 0.85-0.80 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 190.57, 162.47, 153.41, 149.52, 142.29, 139.41, 132.41, 129.50, 129.15, 127.70, 127.65, 123.15, 113.12, 109.00, 56.40, 45.05, 36.56, 31.91, 29.64, 29.32, 26.43, 22.69, 14.14. MALDI-TOF: (MW: 1319.85) m/z: 1321.81.

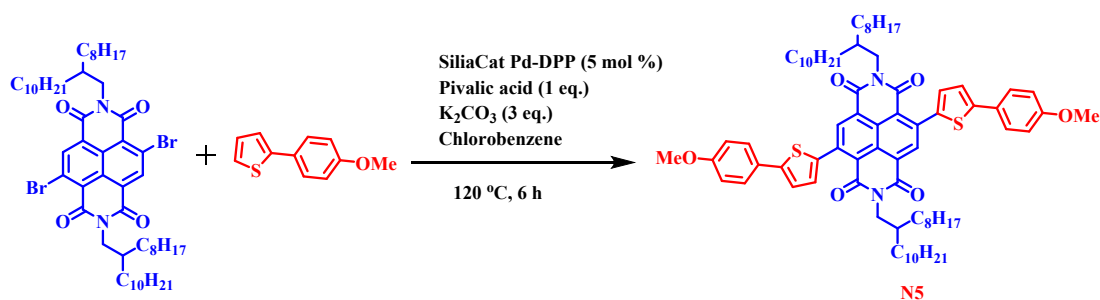
S9. Synthesis of N4



The experimental procedure was similar to that for the synthesis of N1 except for the reagents.

NDIOD-Br₂ (100 mg, 0.101 mmol), 3-(thiophen-2-yl) pyridine (32.73 mg, 0.203 mmol), pivalic acid (10.36 mg, 0.101 mmol), K₂CO₃ (42.091 mg, 0.304 mmol) and SiliaCat PdDPP (16.92 mg, 5 mol %). Yield = 85 mg (73 %). ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 8.96 (2 H, s), 8.82 (2 H, d), 8.59 (2 H, dd), 7.92 (2 H, d), 7.40 (2 H, s), 7.37 (2 H, dd), 4.12 (4 H, d), 1.97 (2 H, m), 1.21 (64 H, m), 0.86 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 162.44, 148.94, 146.94, 141.28, 136.53, 131.87, 120.05, 123.57, 127.59, 125.153, 124.58, 123.73, 125.15, 44.98, 36.48, 31.87, 30.05, 29.61, 29.55, 29.31, 22.64, 14.11. MALDI-TOF: (MW: 1145.70) m/z: 1146.06.

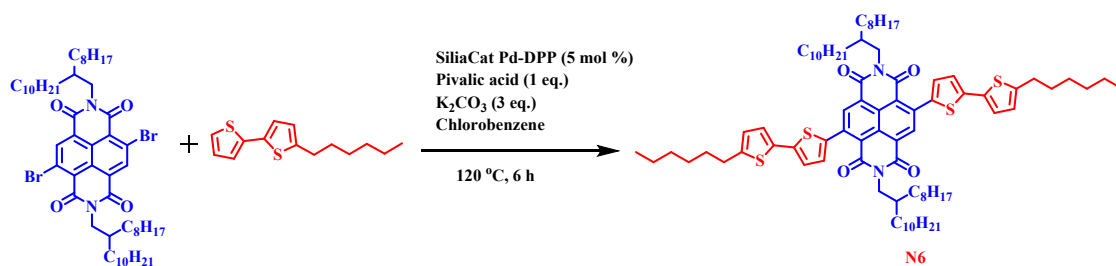
S10. Synthesis of N5



The experimental procedure was similar to that for the synthesis of N1 except for the reagents.

NDIOD-Br2 (100 mg, 0.101 mmol), 2-(4-methoxyphenyl) thiophene (38.62 mg, 0.203 mmol), pivalic acid (10.36 mg, 0.101 mmol), K₂CO₃ (42.091 mg, 0.304 mmol) and SiliaCat PdDPP (16.92 mg, 5 mol %). Yield = 38 mg (31 %). ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 8.82 (2 H, s), 7.62 (4 H, d), 7.34 (2 H, d), 7.30 (2 H, d), 6.97 (2 H, d), 4.12 (4 H, d), 3.87 (6 H, s), 1.99 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 162.65, 159.67, 147.76, 139.78, 138.98, 136.58, 130.12, 127.30, 126.76, 122.52, 114.37, 55.37, 44.93, 36.54, 31.90, 29.63, 29.57, 29.33, 22.66, 14.09. MALDI-TOF: (MW: 1203.78) m/z: 1203.66.

S11. Synthesis of N6



The experimental procedure was similar to that for the synthesis of N1 except for the reagents.

NDIOD-Br2 (100 mg, 0.101 mmol), 5-hexyl-2,2'-bithiophene (50.84 mg, 0.203 mmol), pivalic acid (10.36 mg, 0.101 mmol), K₂CO₃ (42.091 mg, 0.304 mmol) and SiliaCat Pd-DPP (16.92 mg, 5 mol %). Yield = 85 mg (63 %). ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 8.79 (2 H, s), 7.29 (2 H, d), 7.17 (2 H, d), 7.07 (2 H, d), 6.73 (2 H, d), 4.11 (4 H, d), 2.83 (4 H, t), 1.97 (2 H, m), 1.73 (4 H, m), 1.71 (4 H, m), 1.22 (80 H, m), 0.85 (18 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 162.62, 146.48, 141.50,

138.69, 134.17, 129.96, 125.35, 124.98, 124.19, 123.27, 122.42, 44.95, 36.54, 31.94, 31.60, 29.68, 29.38, 22.72, 22.62, 14.16, 14.13. MALDI-TOF: (MW: 1224.10) m/z: 1323.72.

Figure S1. ^1H NMR spectrum for [2,2-bithiophene]-5-carbaldehyde (A1)

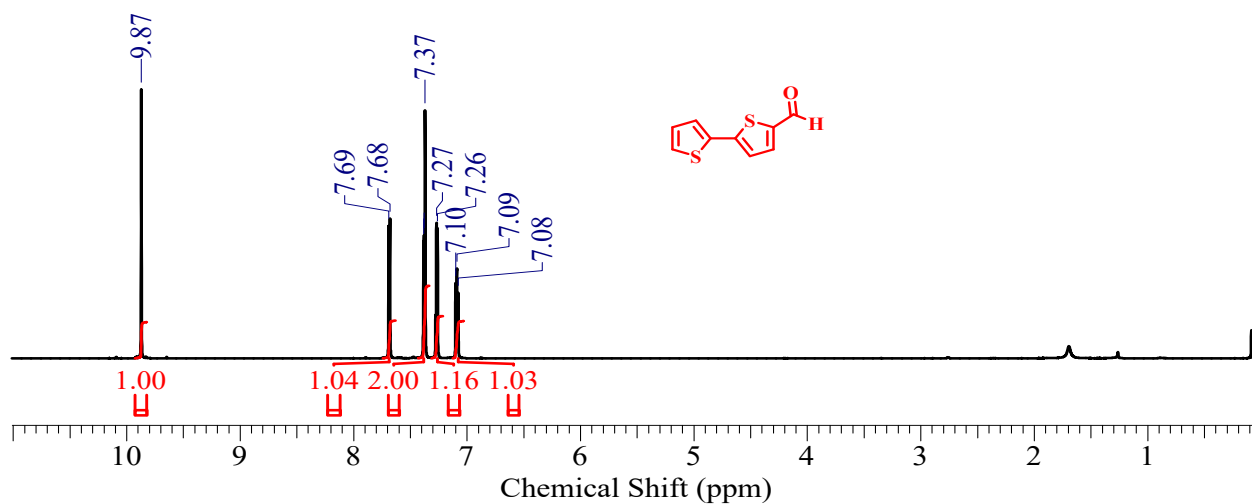


Figure S2. ^{13}C NMR spectrum for [2,2-bithiophene]-5-carbaldehyde (A1)

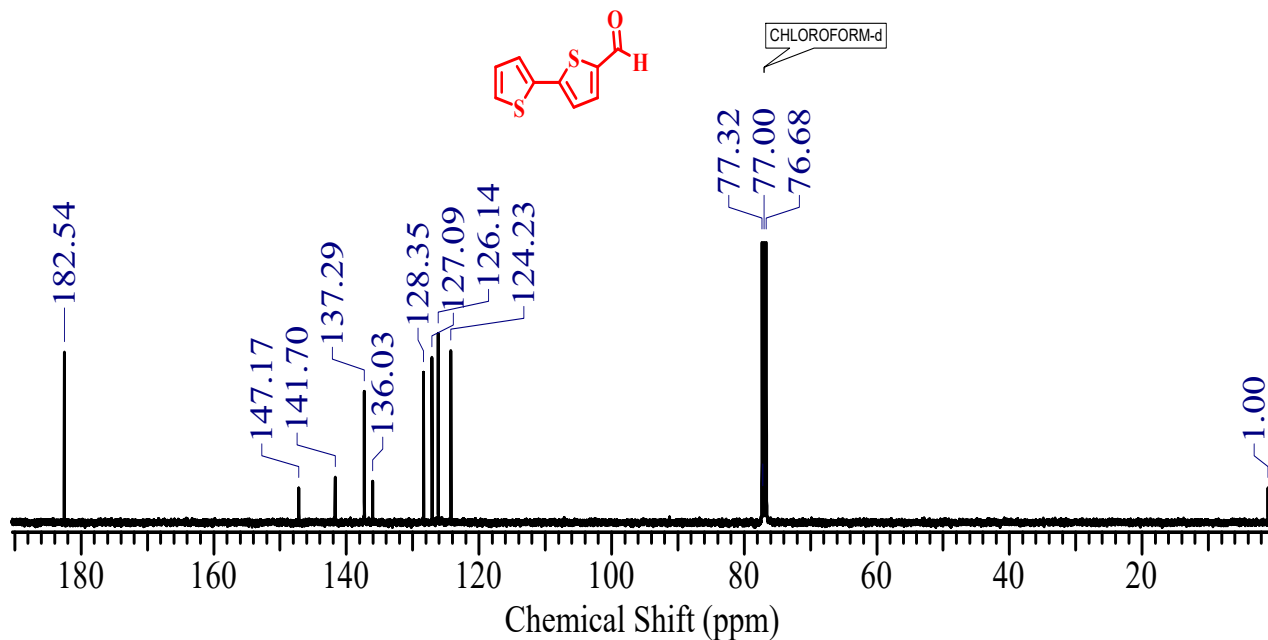


Figure S3. ^1H NMR spectrum for 4-(thiophene-2-yl) benzaldehyde (A2)

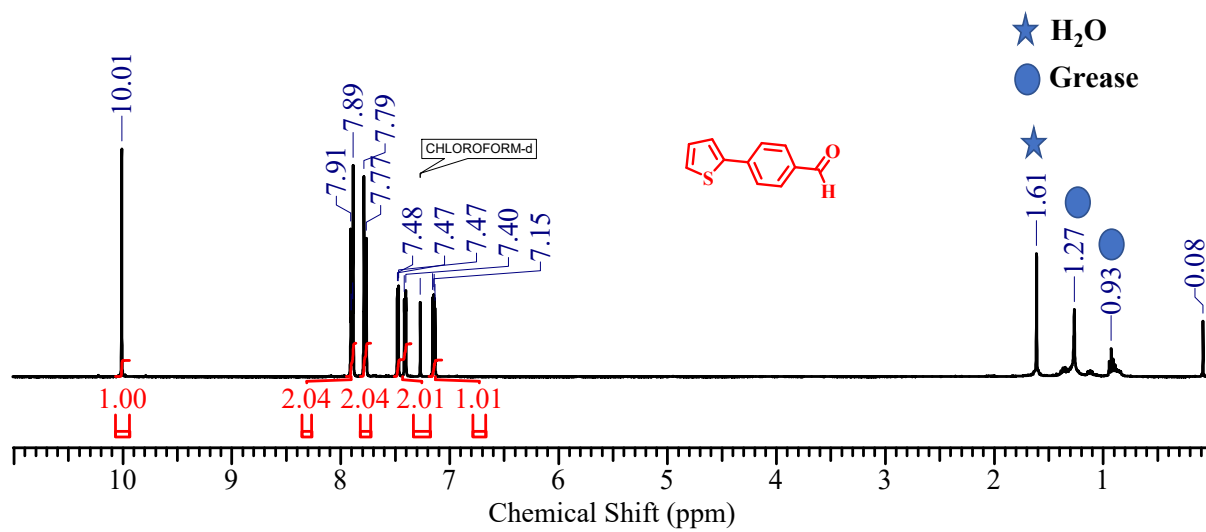


Figure S4. ^{13}C NMR spectrum for 4-(thiophene-2-yl) benzaldehyde (A2)

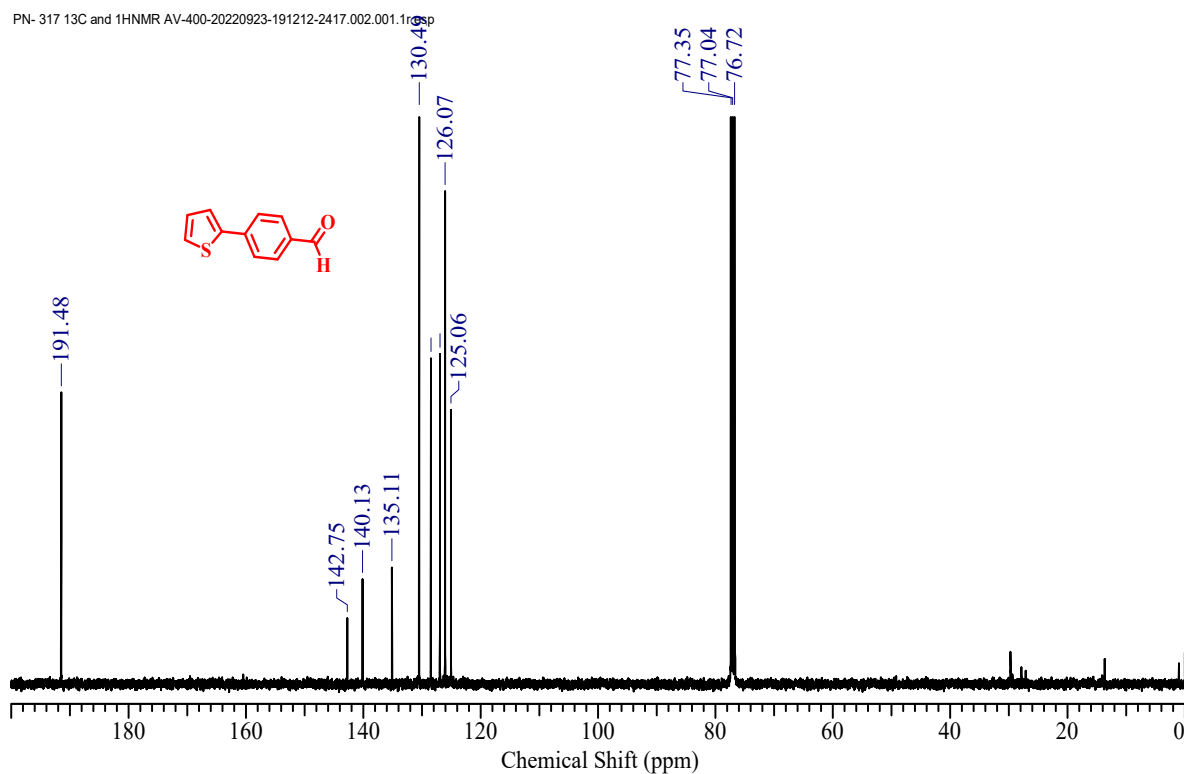


Figure S5. ^1H NMR spectrum for 4,5-dimethoxy-2-(thiophen-2-yl) benzaldehyde (A3)

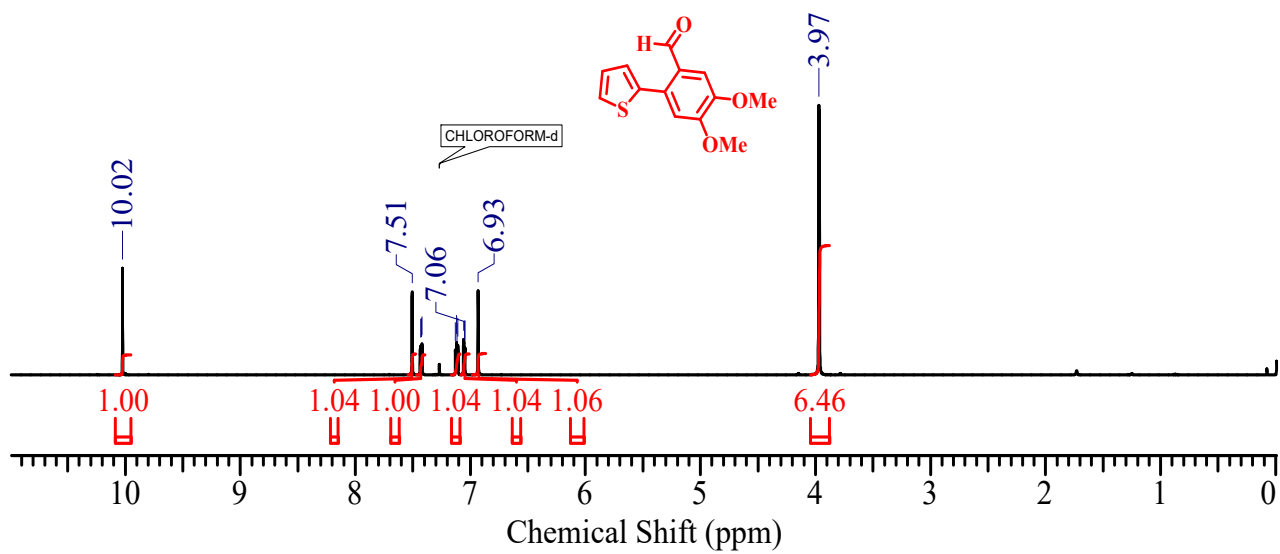


Figure S6. ^{13}C NMR spectrum for 4,5-dimethoxy-2-(thiophen-2-yl) benzaldehyde (A3)

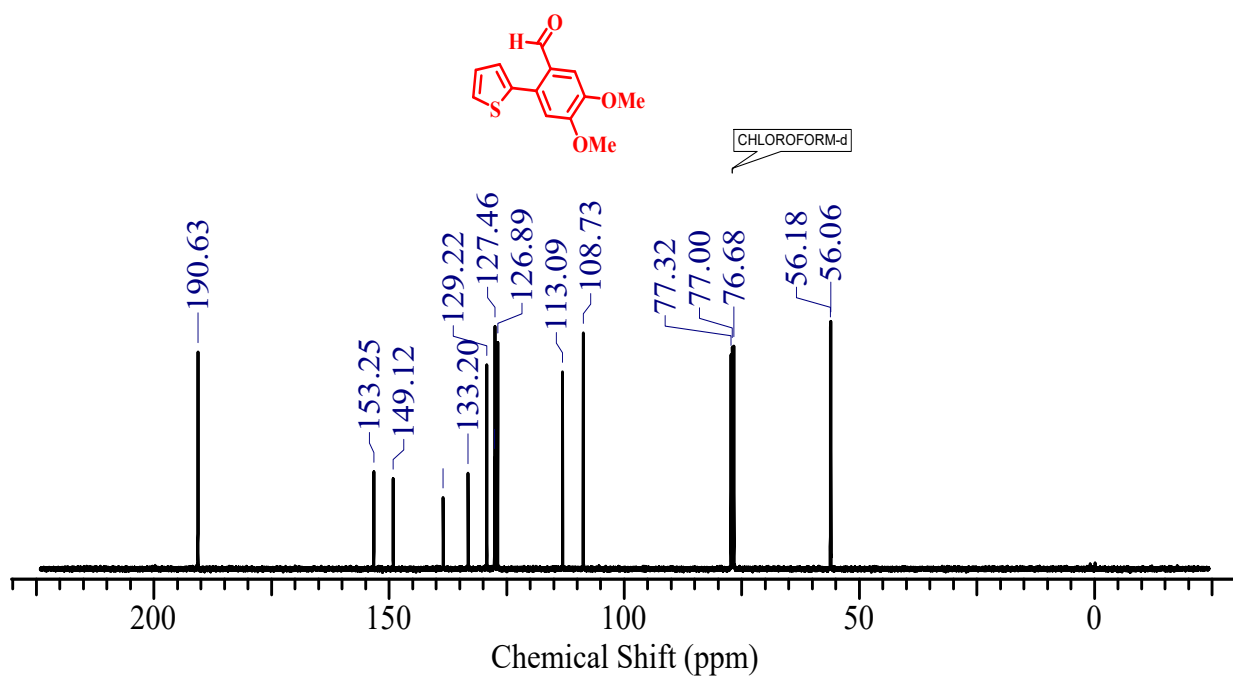


Figure S7. ^1H NMR spectrum for of 3-(thiophen-2-yl) pyridine (A4)

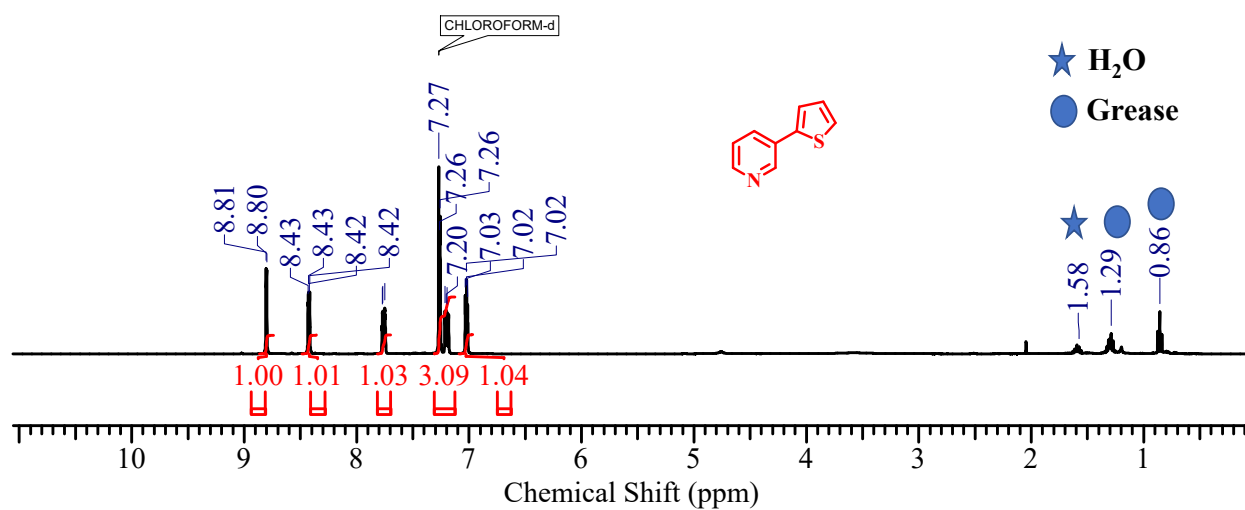


Figure S8. ^{13}C NMR spectrum for of 3-(thiophen-2-yl) pyridine (A4)

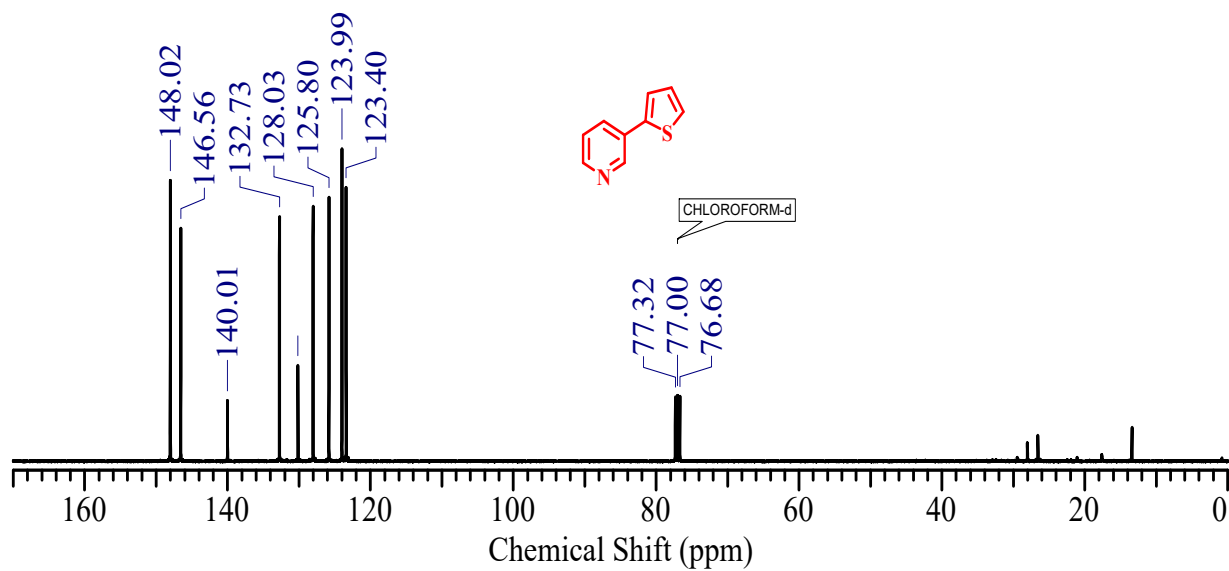


Figure S9. ^1H NMR spectrum for 2-(4-methoxyphenyl) thiophene (A5)

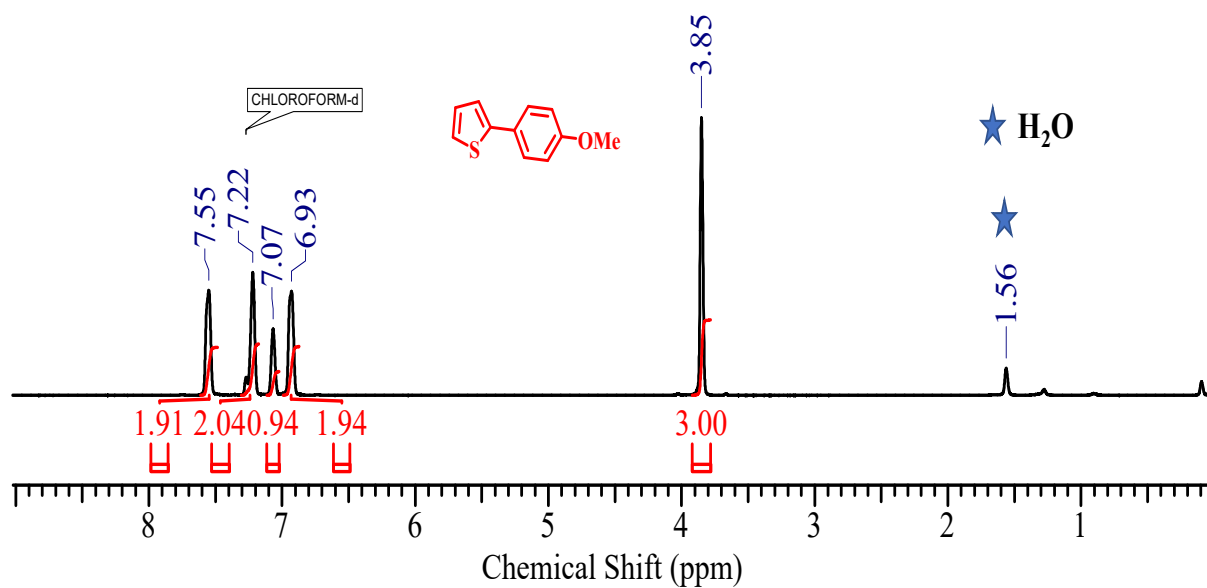


Figure S10. ^{13}C NMR spectrum for 2-(4-methoxyphenyl) thiophene (A5)

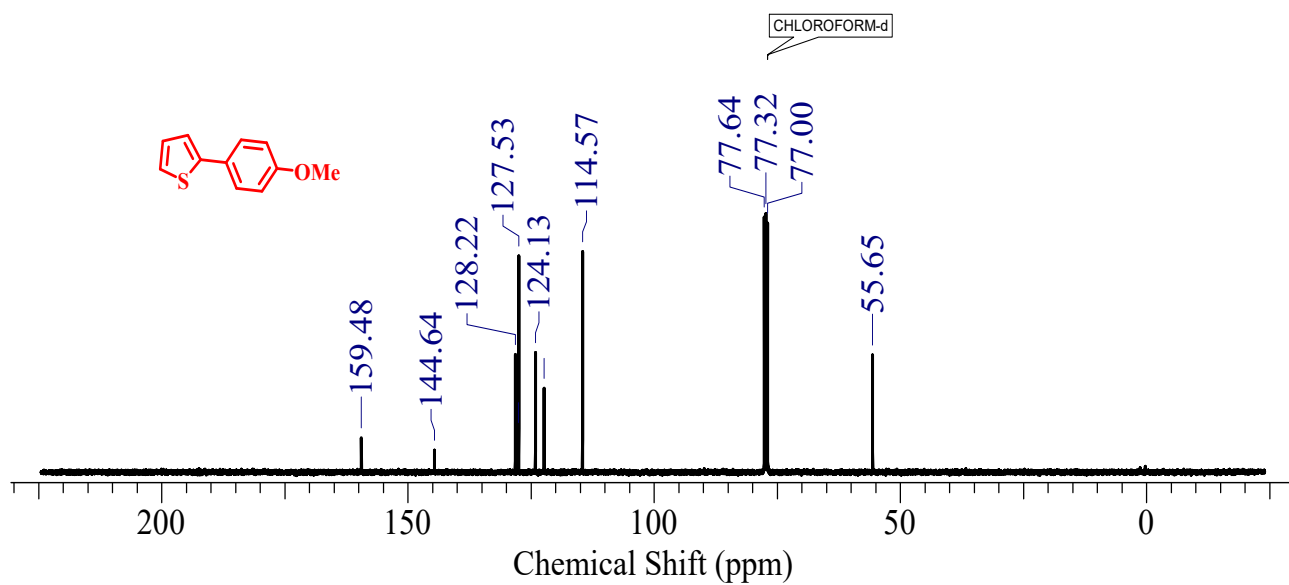


Figure S11. ^1H NMR spectrum for N1

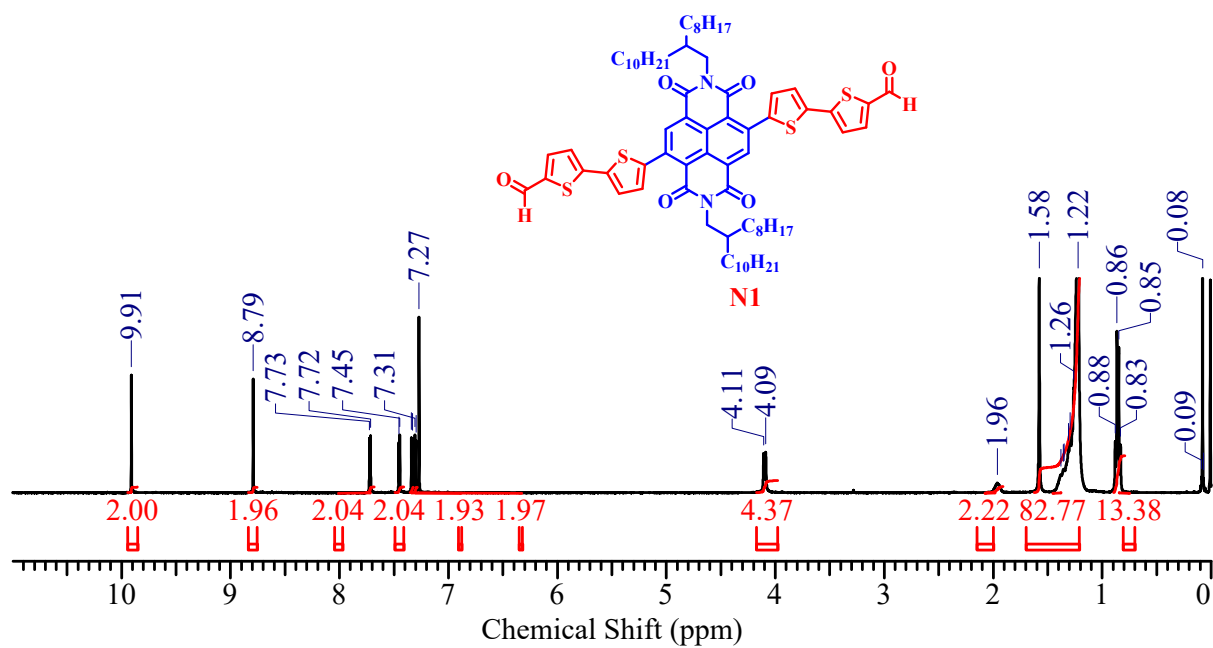


Figure S12. ^{13}C NMR spectrum for N1

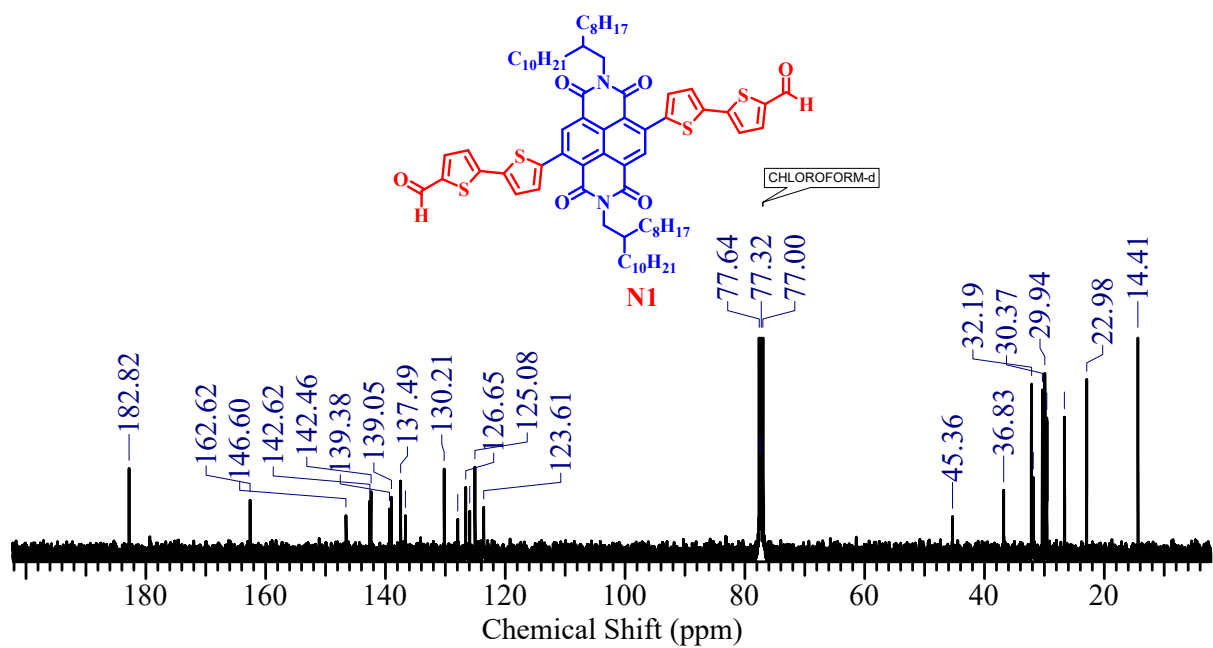


Figure S13. MALDI-TOF spectrum for N1

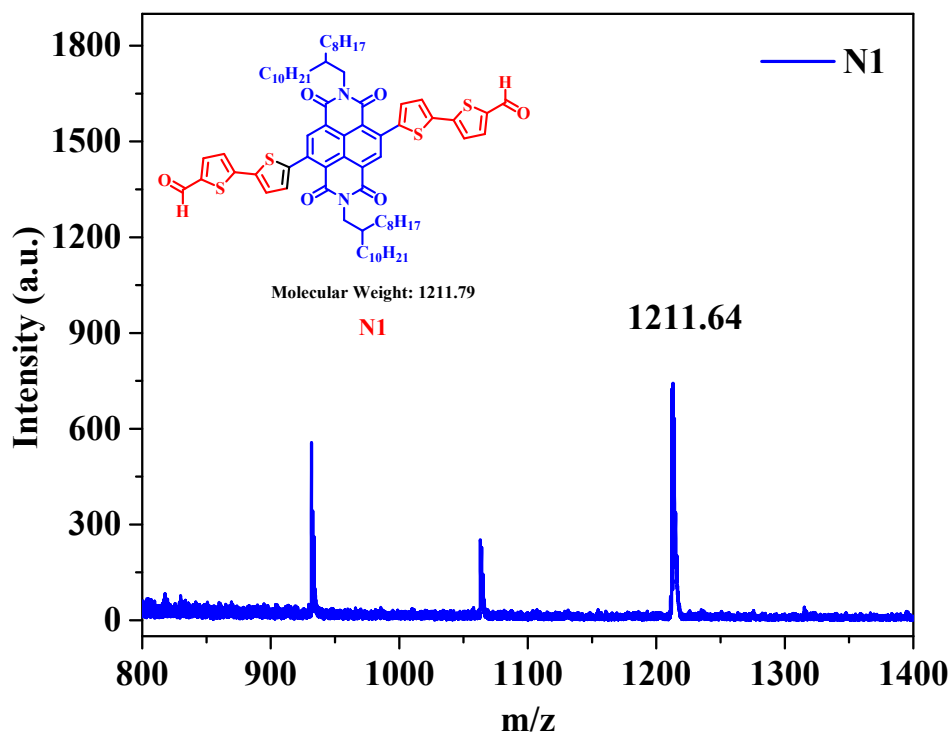


Figure S14. ¹H NMR spectrum for N2

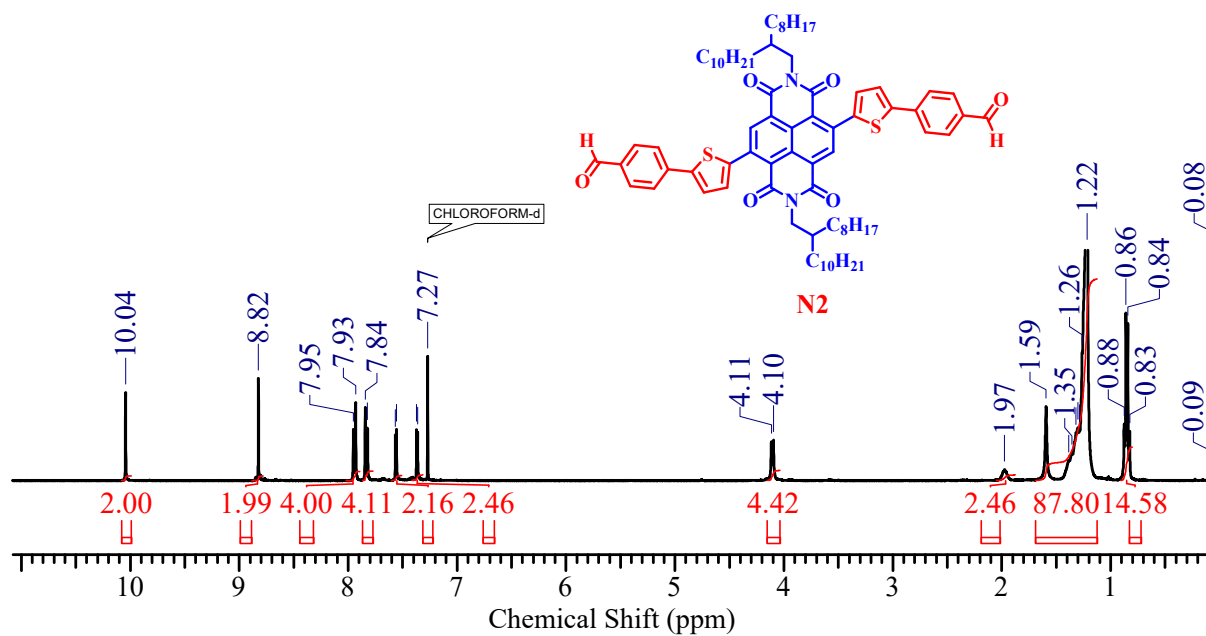


Figure S15. ^{13}C NMR spectrum for N2

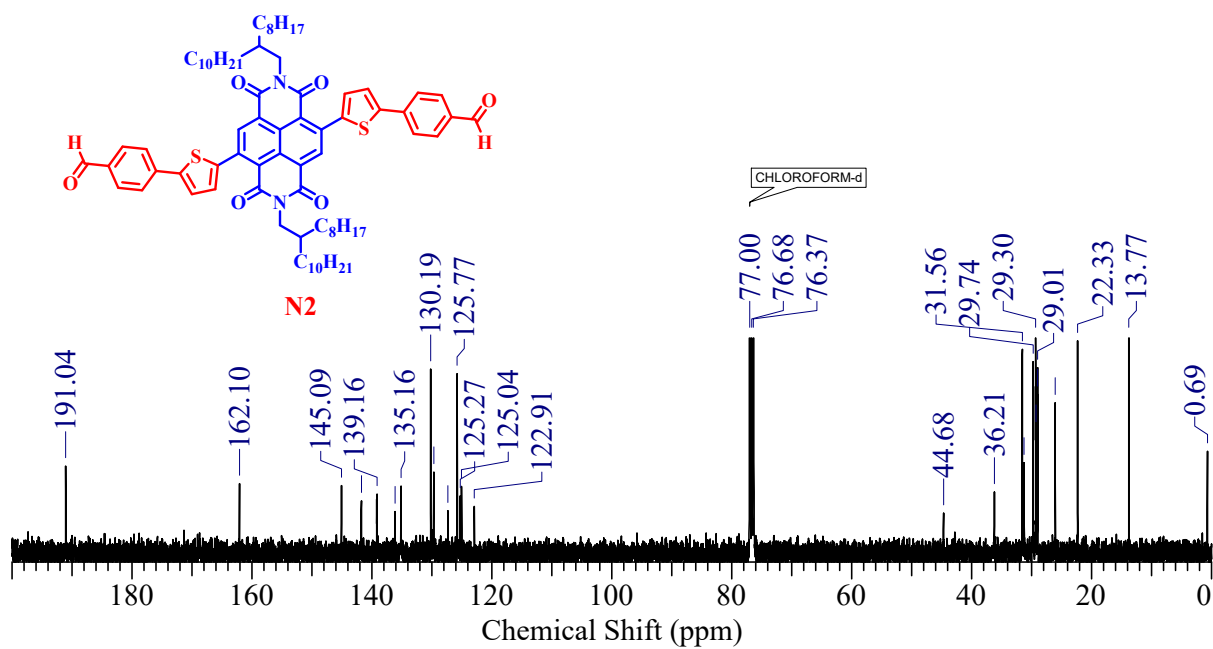


Figure S16. MALDI-TOF spectrum for N2

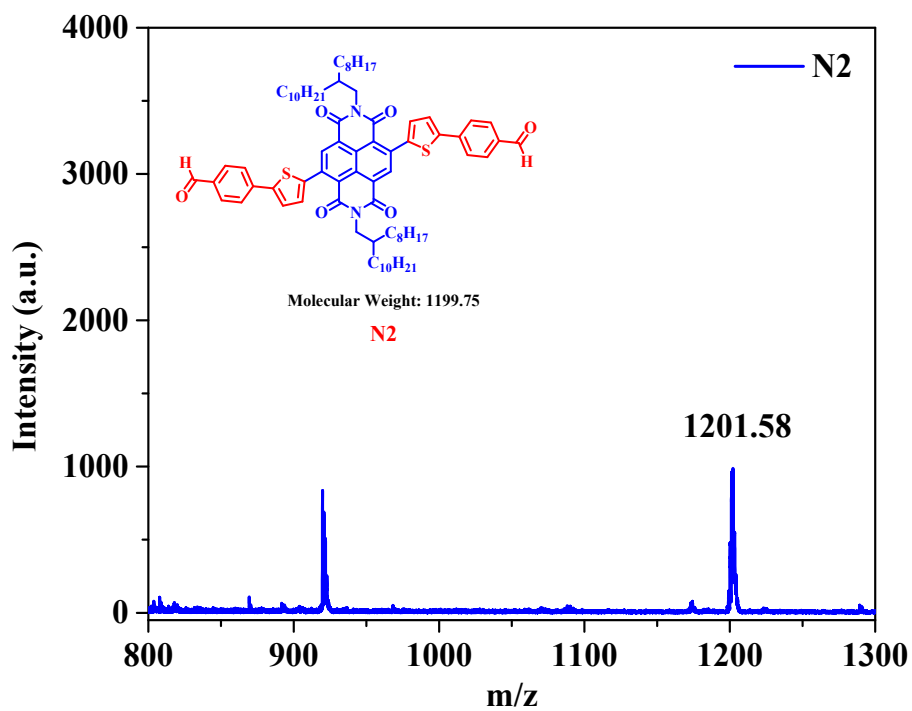


Figure S17. ^1H NMR spectrum for N3

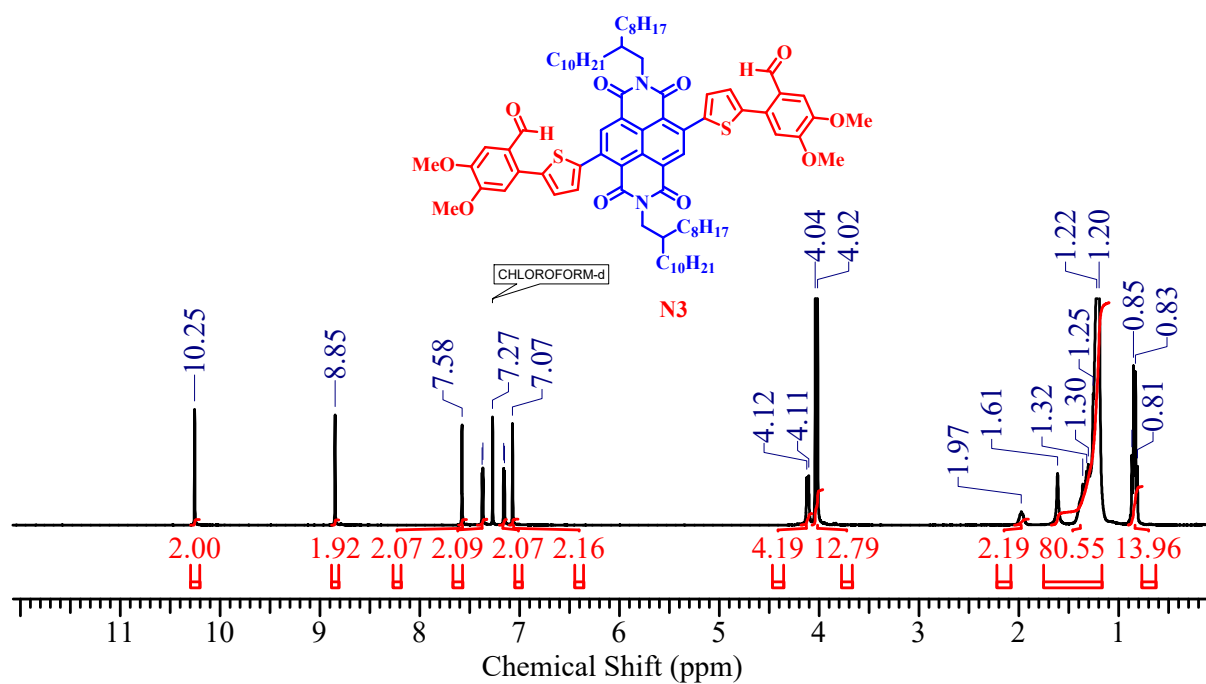


Figure S18. ^{13}C NMR spectrum for N3

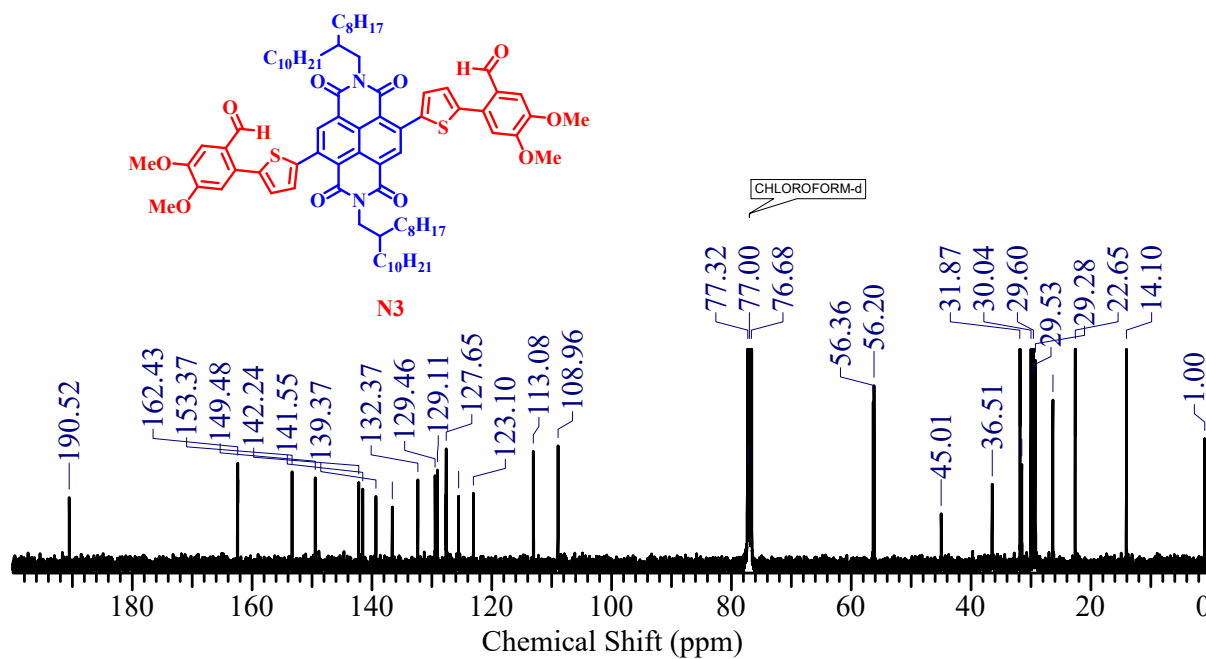


Figure S19. MALDI-TOF spectrum for N3

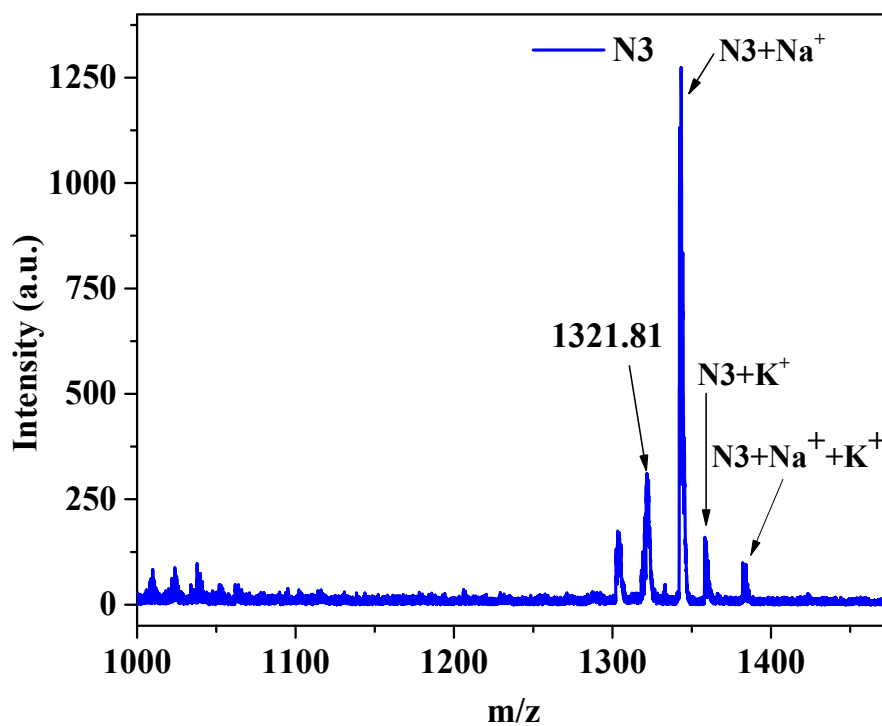


Figure S20. ¹H NMR spectrum for N4

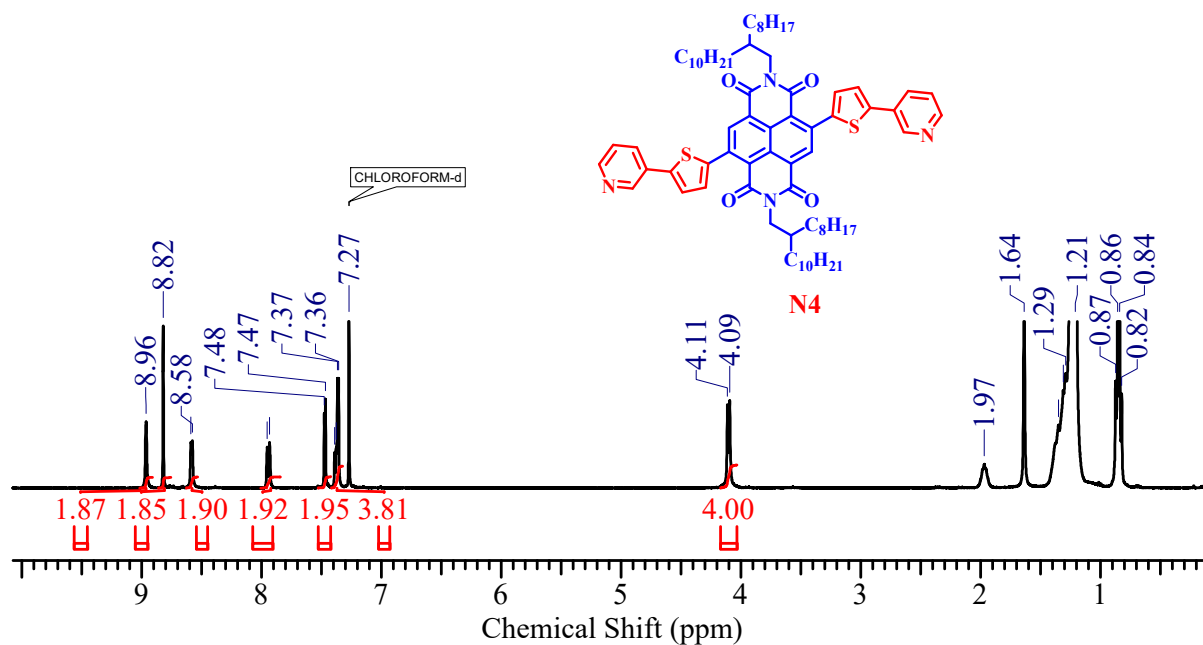


Figure S21. ^{13}C NMR spectrum for N4

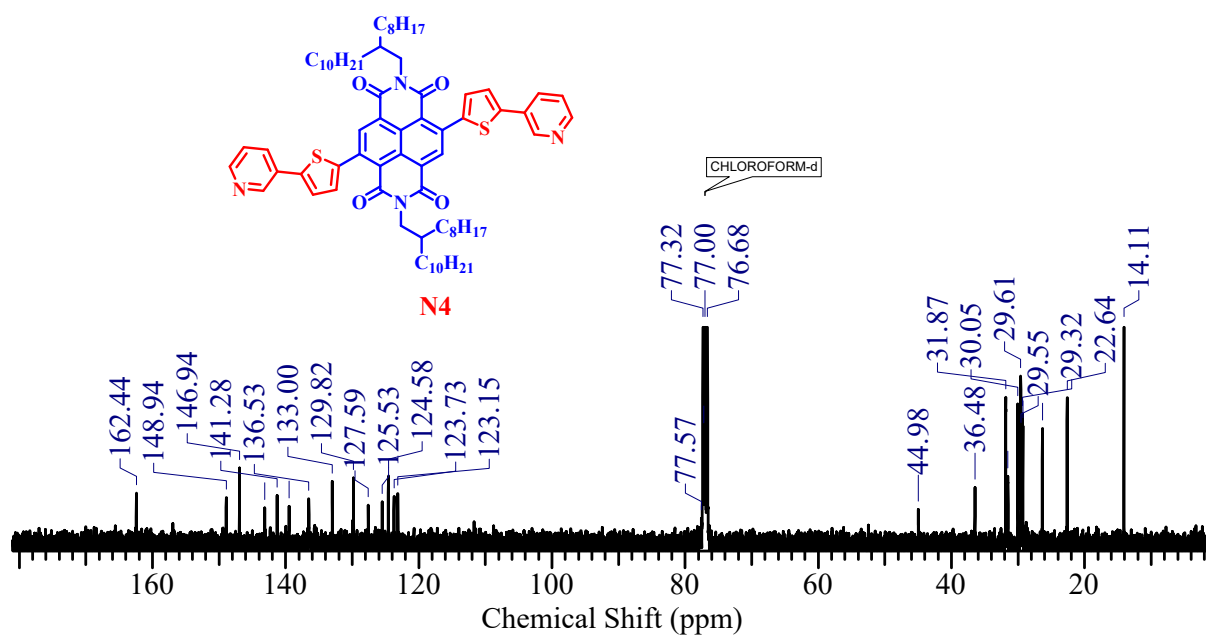


Figure S22. MALDI-TOF spectrum for N4

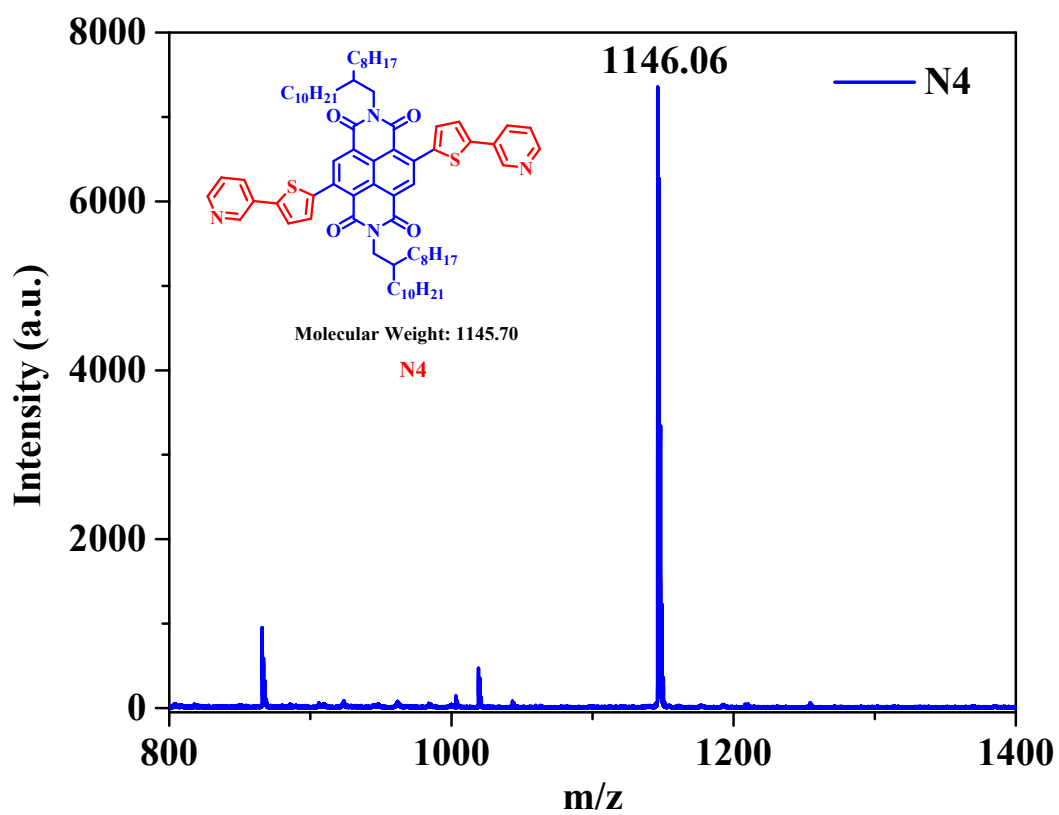


Figure S23. ^1H NMR spectrum for N5

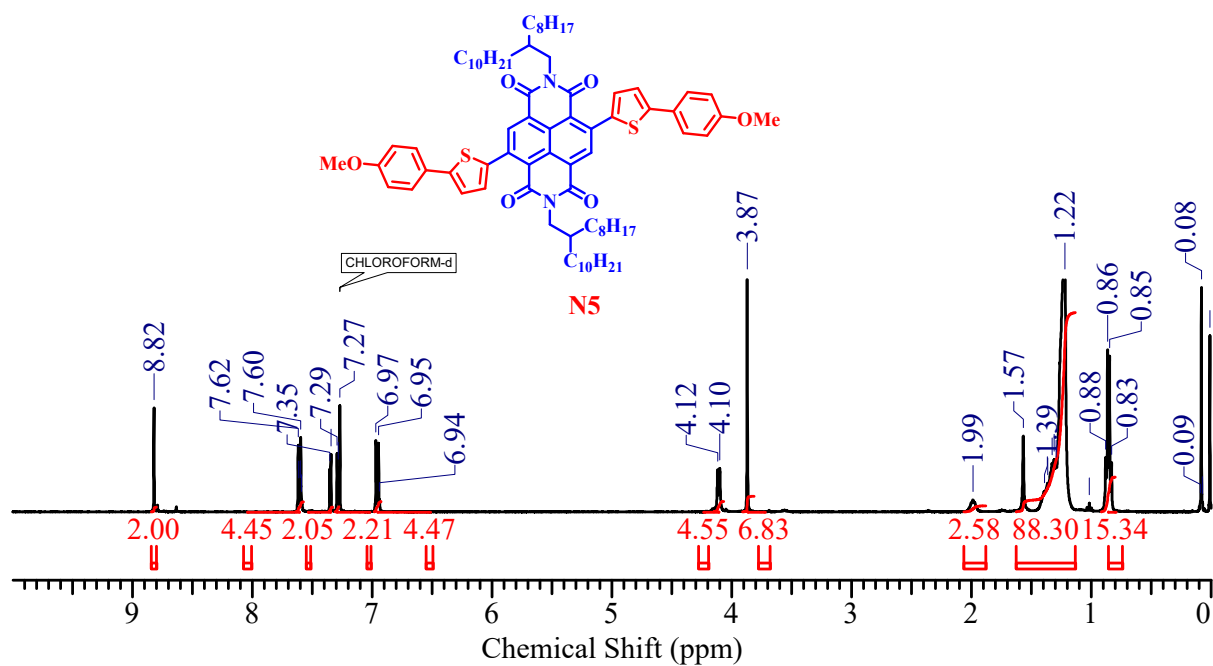


Figure S24. ^{13}C NMR spectrum for N5

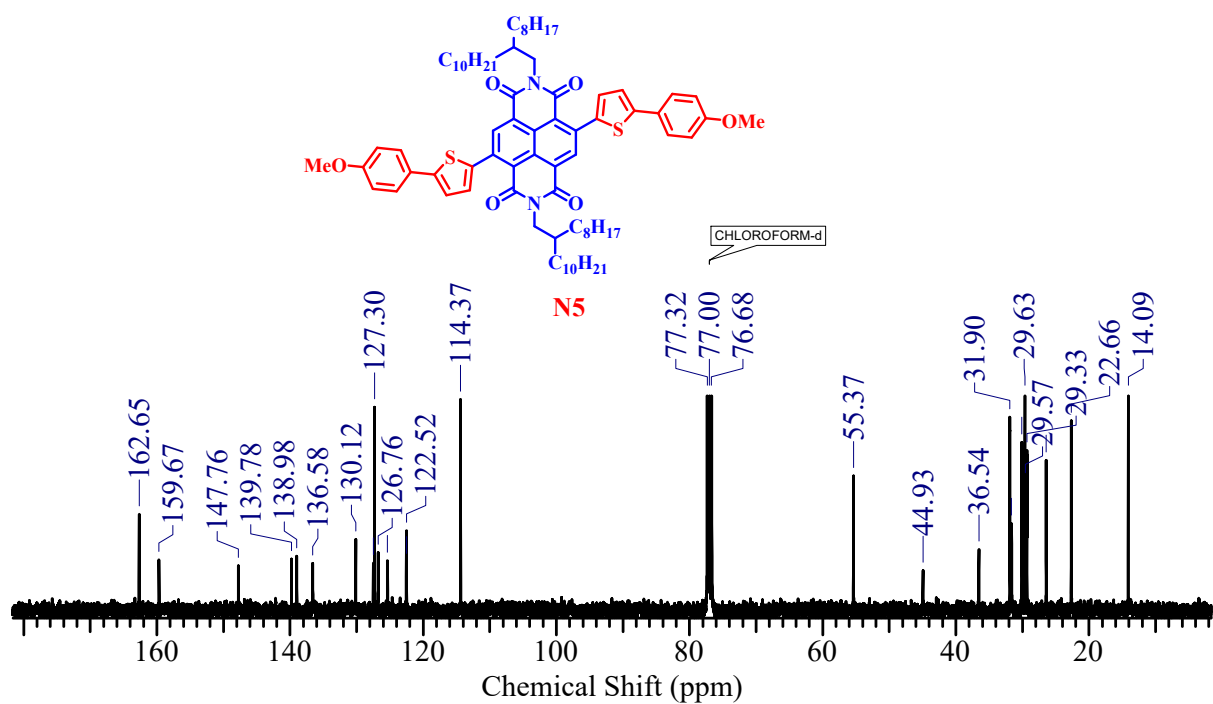


Figure S25. MALDI-TOF spectrum for N5

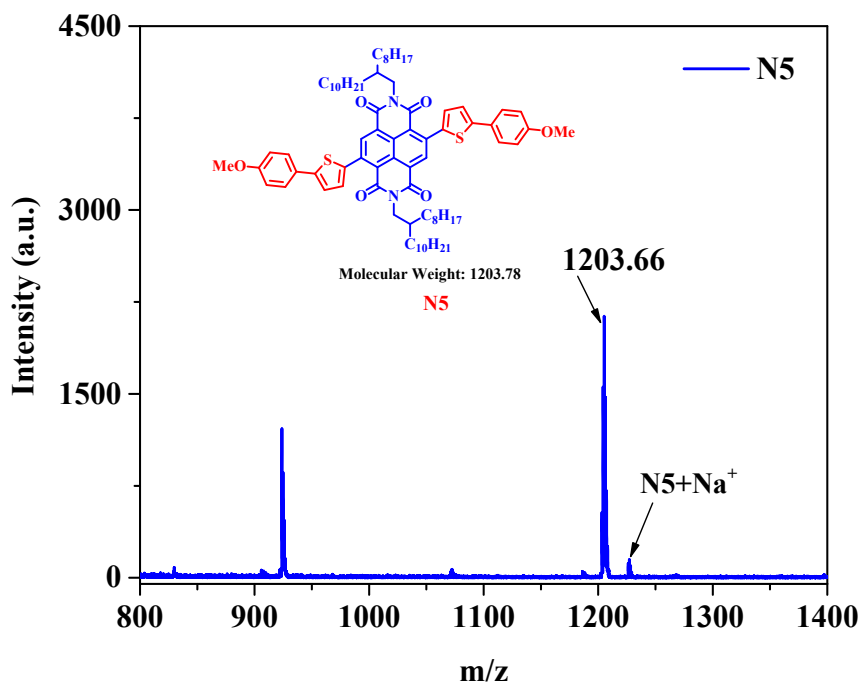


Figure S26. ¹H NMR spectrum for N6

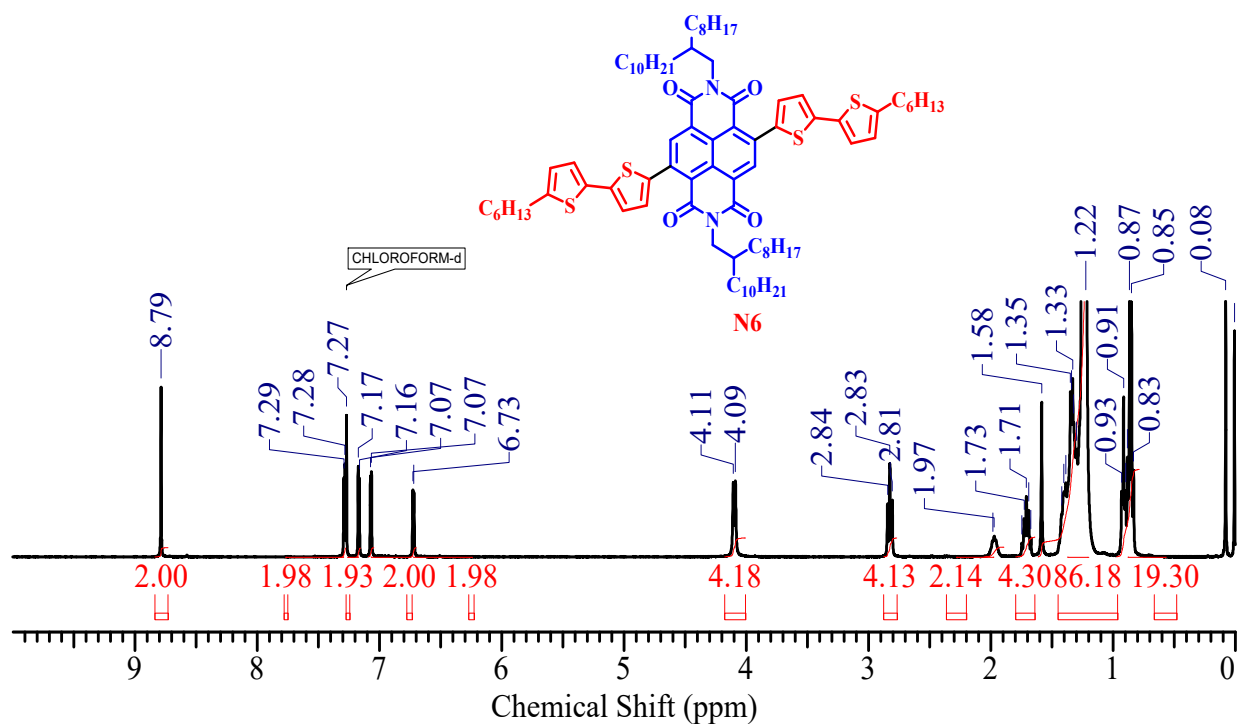


Figure S27. ^{13}C NMR spectrum for N6

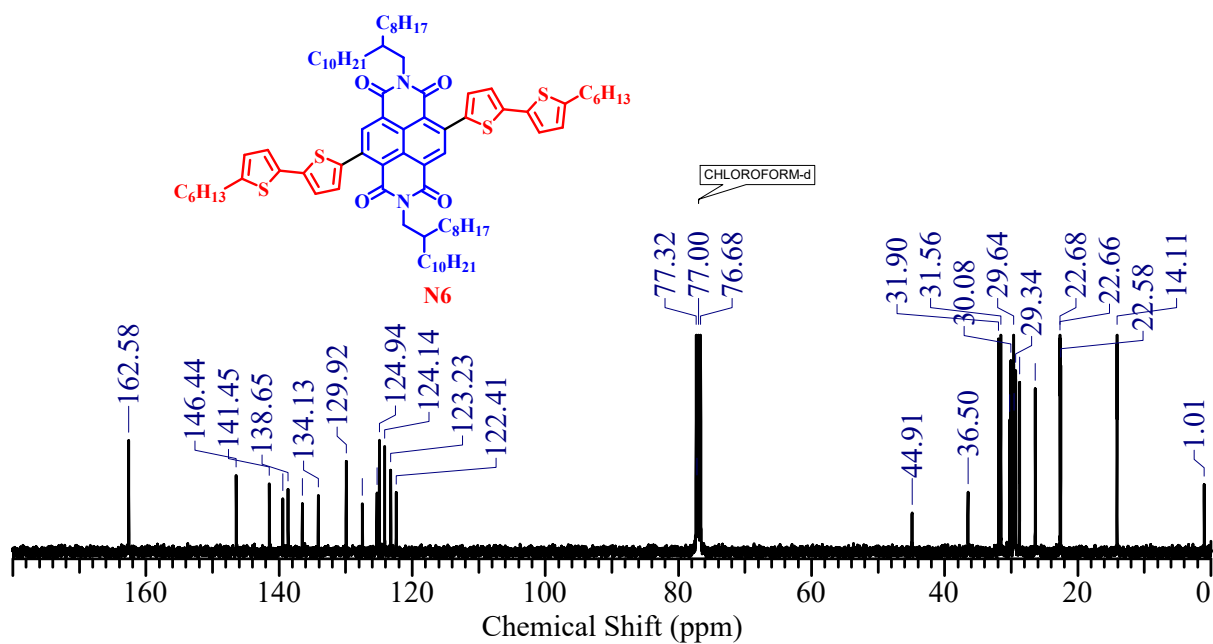


Figure S28. MALDI-TOF spectrum for N6

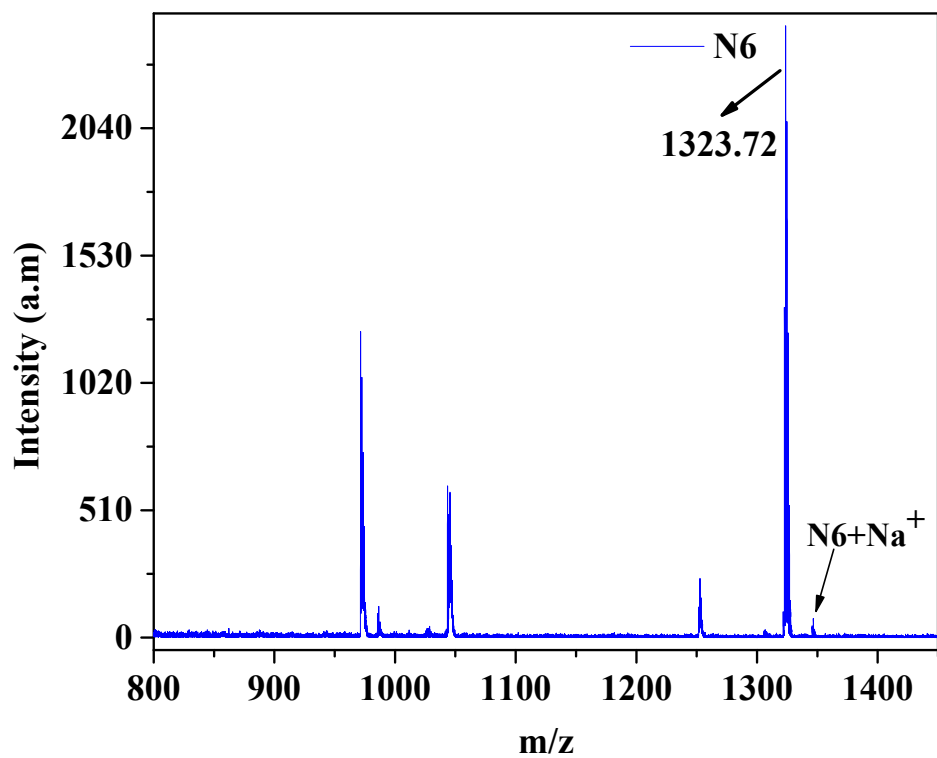


Table S1. Optimization of N1 small molecule in different solvent and base

Sr.no	Solvent	Base	Yield (%)
1	Chlorobenzene	K ₂ CO ₃	72
2	1,1,2,2-Tetrachlorobenzene	K ₂ CO ₃	45
3	Chlorobenzene	CS ₂ CO ₃	No reaction
4	1,1,2,2-Tetrachlorobenzene	CS ₂ CO ₃	No reaction

S12. Recyclability experiment for N1**Cycle-1**

In 10 ml oven dry Schlenk tube equipped with a stir bar were added NDIOD-Br₂ (150 mg, 0.152 mmol), 2,2-bithiophene-5-carbaldehyde (59.16 mg, 0.304 mmol), pivalic acid (15.55 mg, 0.152 mmol), K₂CO₃ (63.13 mg, 0.456 mmol) and SiliaCat Pd-DPP (25.39 mg, 5 mol %). The Schlenk tube was evacuated three times by vacuum and purged by N₂ gas. Degassed chlorobenzene (1.5 ml) was added to the schlenk tube by syringe and purged for 15 minutes. The reaction was stirred for 6 h at 120 °C and warmed to room temperature. The reaction mixture was precipitated in MeOH (50 ml) and after filtering the precipitate, washed with plenty of MeOH and a mixture of MeOH and acetone (50:50). The compound was dried in a vacuum oven at 60 °C for 12 h. The dried compound was used for further characterization. Yield = 168 mg (91 %). After the reaction was completed, the reaction mixture was diluted with chloroform (CHCl₃) (30 mL) and filtered using Whatman 41 filter paper to collect the SiliaCat Pd-DPP catalyst. The residue (catalyst) was further washed with ~20 mL of CHCl₃ until the disappearance of the blue colour, followed by washing with methanol and acetone. The catalyst was dried in a vacuum oven at 70 °C for 12 h and used for the next reaction cycle. The catalyst was recovered from reaction mixture; yield 23.10 mg (91 %) and used for further reaction with identical mole ratio of starting materials and solvent. ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 9.91 (2 H, s), 8.79 (2 H, s), 7.73 (2 H, dd), 7.46 (2 H, dd), 7.31 (4H, dd), 4.11 (4 H, dd), 1.96 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 182.82, 162.62, 146.60, 142.62, 142.46, 139.38, 139.05, 137.49, 130.21, 126.65, 125.08, 123.61, 45.36, 36.83, 32.19, 30.37, 29.94, 22.75, 14.18.

Cycle-2

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (136.47 mg, 0.138 mmol), 2,2-bithiophene-5-carbaldehyde (53.82 mg, 0.277 mmol), pivalic acid (14.14 mg, 0.138 mmol), K₂CO₃ (57.44 mg, 0.415 mmol) and SiliaCat

Pd-DPP (23.10 mg, 5 mol %). Yield = 158.2 mg (94 %). The catalyst was recovered from reaction mixture Yield = 21.6 mg (93 %) and used for further reaction with identical mole ratio of starting materials and solvent. ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 9.91 (2 H, s), 8.79 (2 H, s), 7.73 (2 H, dd), 7.46 (2 H, dd), 7.31 (4H, dd), 4.11 (4 H, dd), 1.96 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 182.82, 162.62, 146.60, 142.62, 142.46, 139.38, 139.05, 137.49, 130.21, 126.65, 125.08, 123.61, 45.36, 36.83, 32.19, 30.37, 29.94, 22.75, 14.18.

Cycle-3

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (127.60 mg, 0.129 mmol), 2,2-bithiophene-5-carbaldehyde (50.32 mg, 0.259 mmol), pivalic acid (13.22 mg, 0.129 mmol), K₂CO₃ (53.70 mg, 0.388 mmol) and SiliaCat Pd-DPP (21.6 mg, 5 mol %). Yield = 122 mg (78 %). The catalyst was recovered from reaction mixture Yield = 19.2 mg (88 %) and used for further reaction with identical mole ratio of starting materials and solvent. ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 9.91 (2 H, s), 8.79 (2 H, s), 7.73 (2 H, dd), 7.46 (2 H, dd), 7.31 (4H, dd), 4.11 (4 H, dd), 1.96 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 182.82, 162.62, 146.60, 142.62, 142.46, 139.38, 139.05, 137.49, 130.21, 126.65, 125.08, 123.61, 45.36, 36.83, 32.19, 30.37, 29.94, 22.75, 14.18.

Cycle-4

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (113.42 mg, 0.115 mmol), 2,2-bithiophene-5-carbaldehyde (44.73 mg, 0.230 mmol), pivalic acid (11.75 mg, 0.115 mmol), K₂CO₃ (47.74 mg, 0.345 mmol) and SiliaCat Pd-DPP (19.2 mg, 5 mol %). Yield = 85 mg (61 %). The catalyst was recovered from reaction mixture Yield = 17 mg (88 %) and used for further reaction with identical mole ratio of starting materials and solvent. ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 9.91 (2 H, s), 8.79 (2 H, s), 7.73 (2 H, dd), 7.46 (2 H, dd), 7.31 (4H, dd), 4.11 (4 H, dd), 1.96 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 182.82, 162.62, 146.60, 142.62, 142.46, 139.38, 139.05, 137.49, 130.21, 126.65, 125.08, 123.61, 45.36, 36.83, 32.19, 30.37, 29.94, 22.75, 14.18.

Cycle-5

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (100.74 mg, 0.101 mmol), 2,2-bithiophene-5-carbaldehyde (39.62 mg, 0.203 mmol), pivalic acid (10.41 mg, 0.101 mmol), K₂CO₃ (42.28 mg, 0.305 mmol) and SiliaCat Pd-DPP (17 mg, 5 mol %). Yield =75 mg (61 %). The catalyst was recovered from reaction mixture Yield = 15.2 mg (89 %) and used for further reaction with identical mole ratio of starting materials and solvent. ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 9.91 (2 H, s), 8.79 (2 H, s), 7.73 (2 H, dd), 7.46 (2 H, dd), 7.31 (4H, dd), 4.11 (4 H, dd), 1.96 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 182.82, 162.62, 146.60, 142.62, 142.46, 139.38, 139.05, 137.49, 130.21, 126.65, 125.08, 123.61, 45.36, 36.83, 32.19, 30.37, 29.94, 22.75, 14.18.

Cycle-6

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (90.06 mg, 0.091 mmol), 2,2-bithiophene-5-carbaldehyde (35.52 mg, 0.182 mmol), pivalic acid (9.33 mg, 0.091 mmol), K₂CO₃ (37.91 mg, 0.274 mmol) and SiliaCat Pd-DPP (15.24 mg, 5 mol %). The compound was dried in a vacuum oven at 60 °C for 12 h. The dried compound was used for further characterization. Yield = 35 mg (35 %) yield was calculated considering single side coupled as product. The reaction product was characterized by ¹H and ¹³C NMR spectroscopy and it was observed that a mixture of single and both side coupling products were present.

Figure S29. MALDI-TOF spectra for Cycle 1 and Cycle 6 (N1)

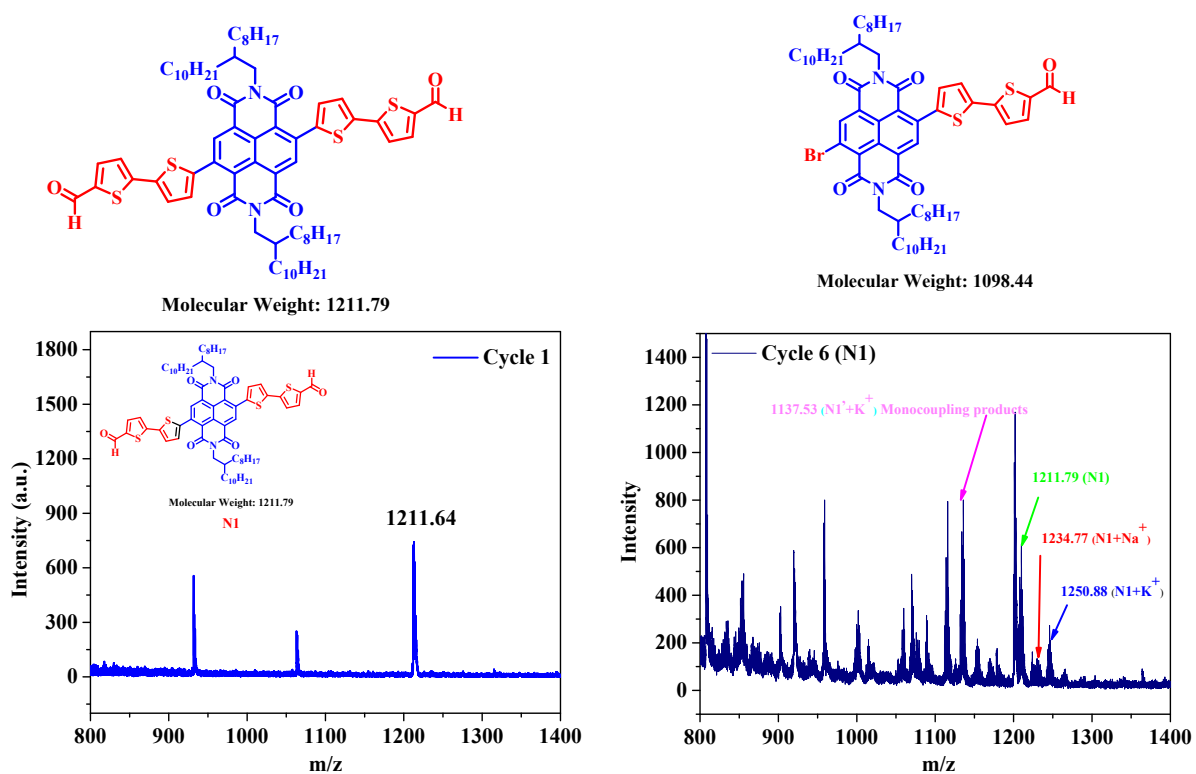


Figure S30. ¹H NMR spectrum for Cycle-1 (N1)

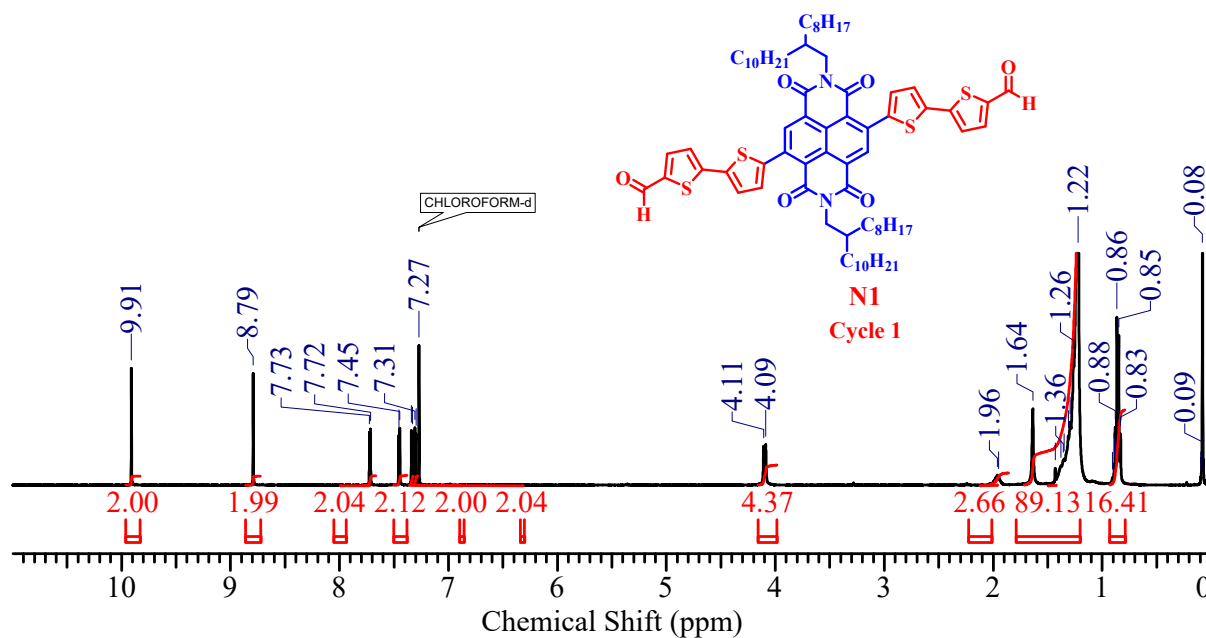


Figure S31. ^{13}C NMR spectrum for Cycle-1 (N1)

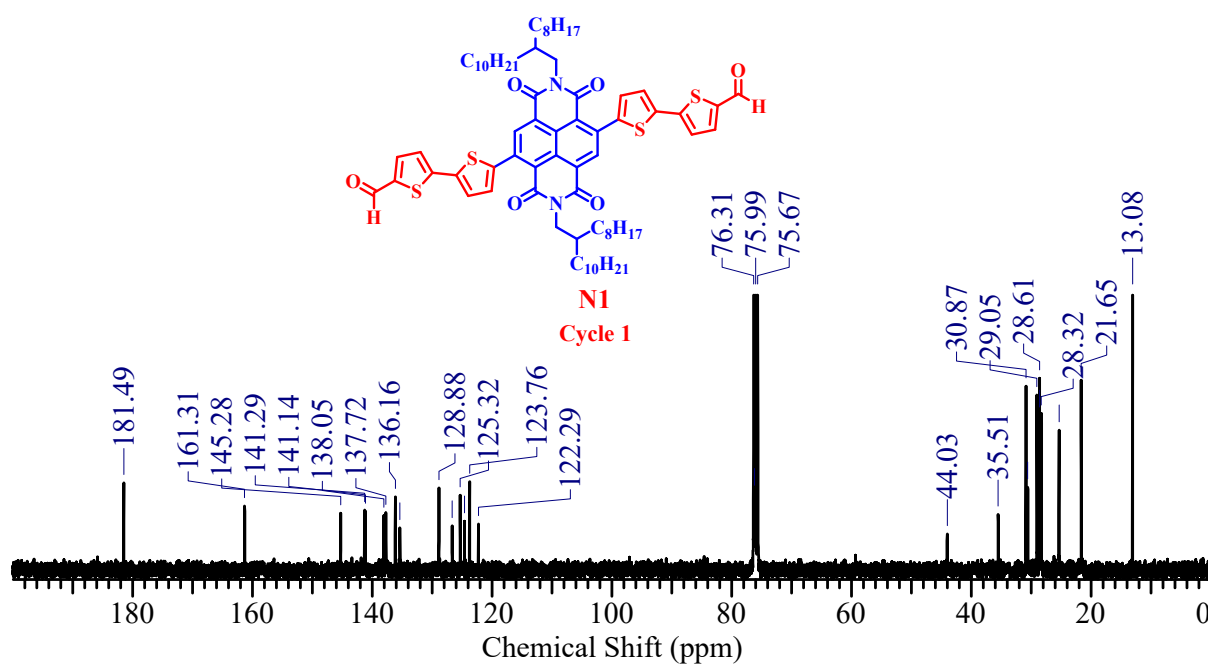


Figure S32. ^1H NMR spectrum for Cycle-2 (N1)

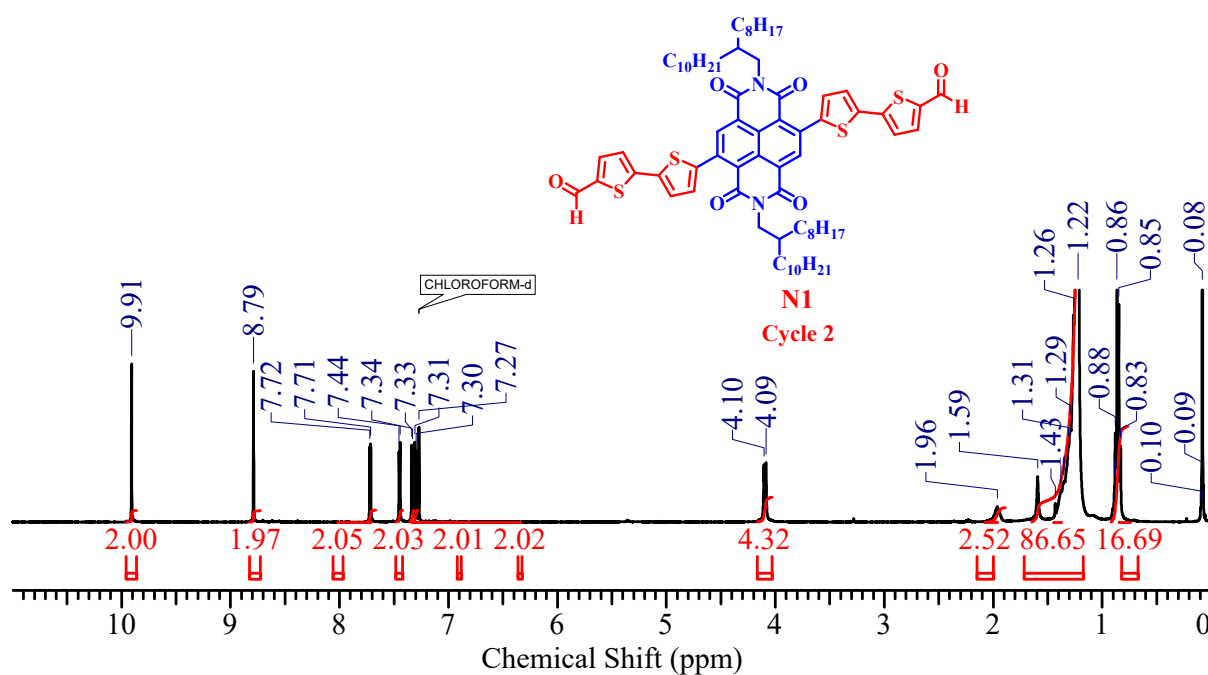


Figure S33. ^{13}C NMR spectrum for Cycle-2 (N1)

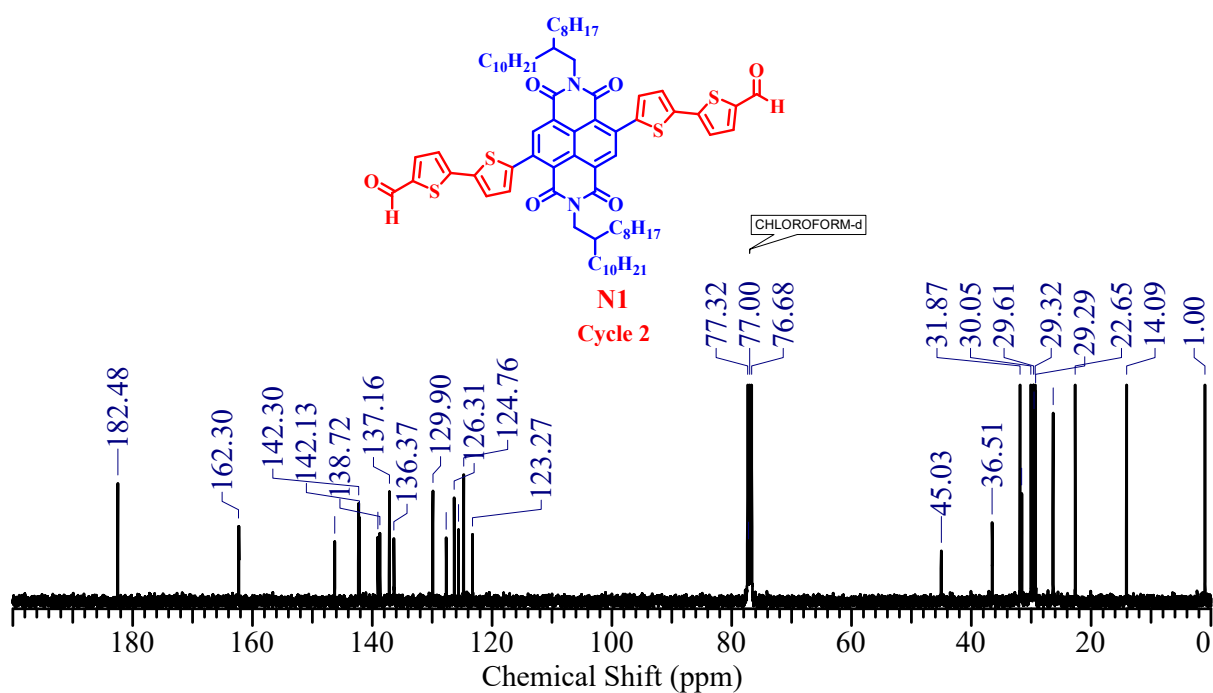


Figure S34. ^1H NMR spectrum for Cycle-3 (N1)

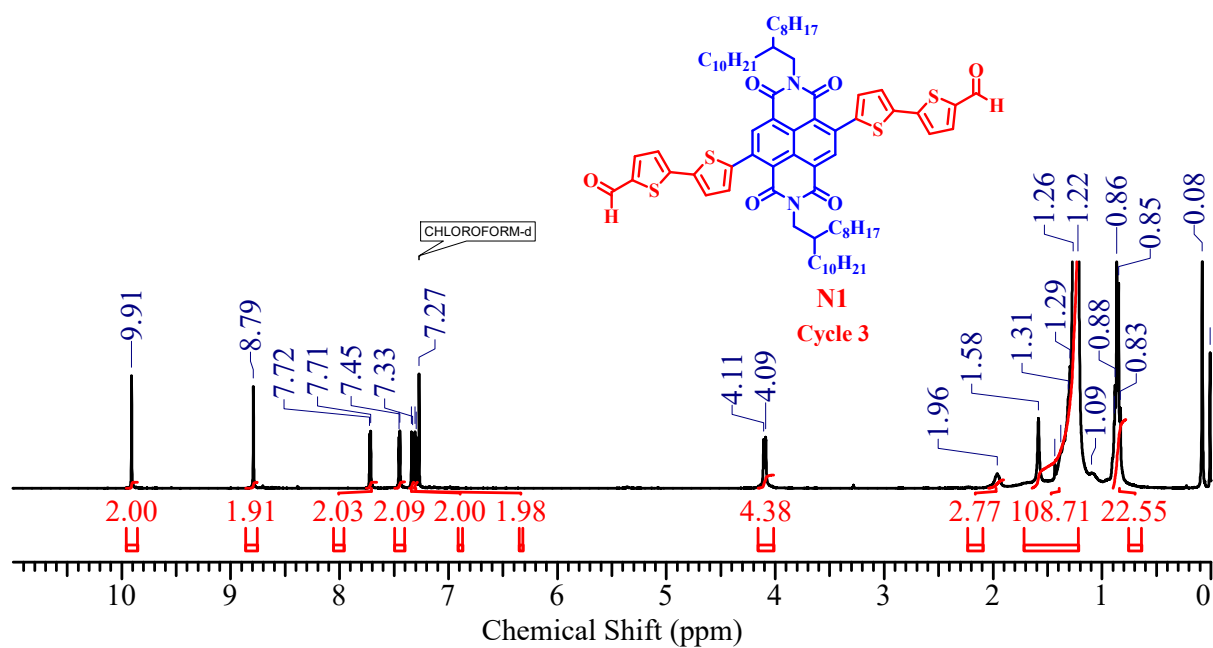


Figure S35. ^{13}C NMR spectrum for Cycle-3 (N1)

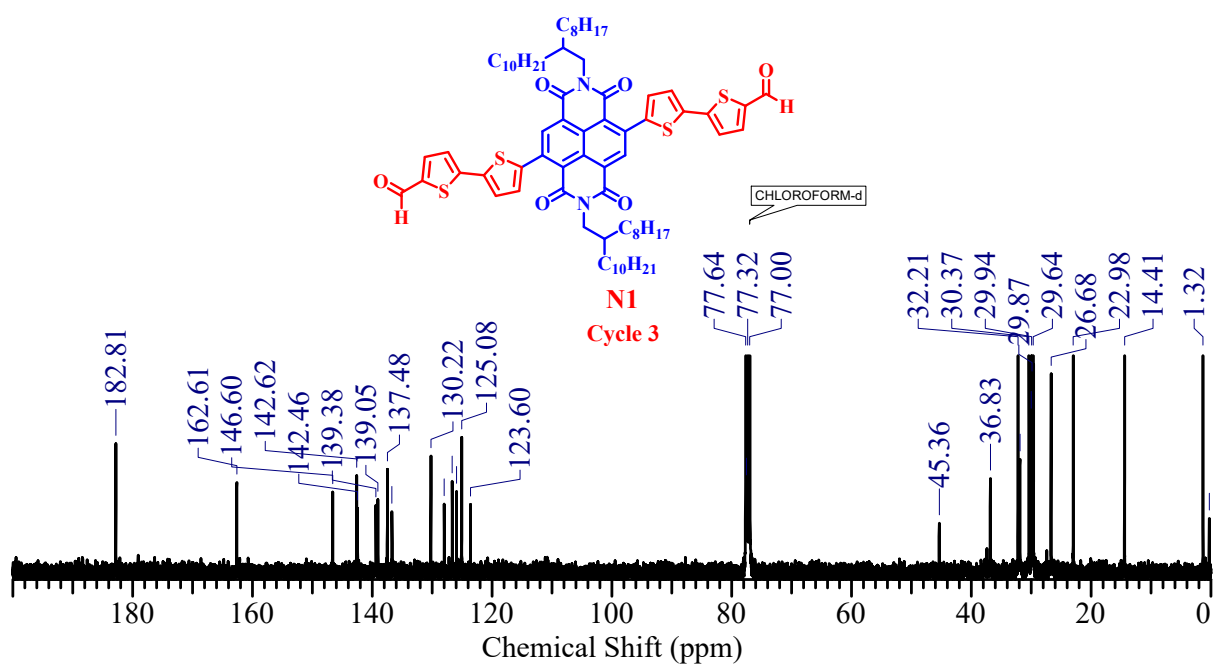


Figure S36. ^1H NMR spectrum for Cycle-4 (N1)

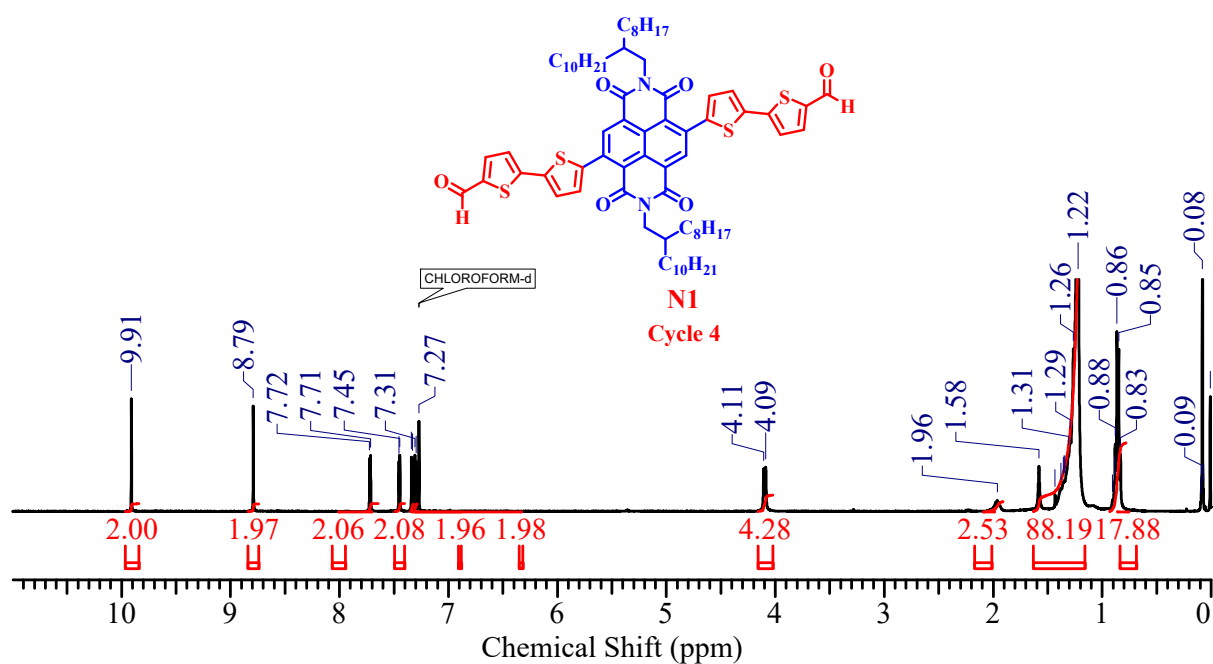


Figure S37. ¹³C NMR spectrum for Cycle-4 (N1)

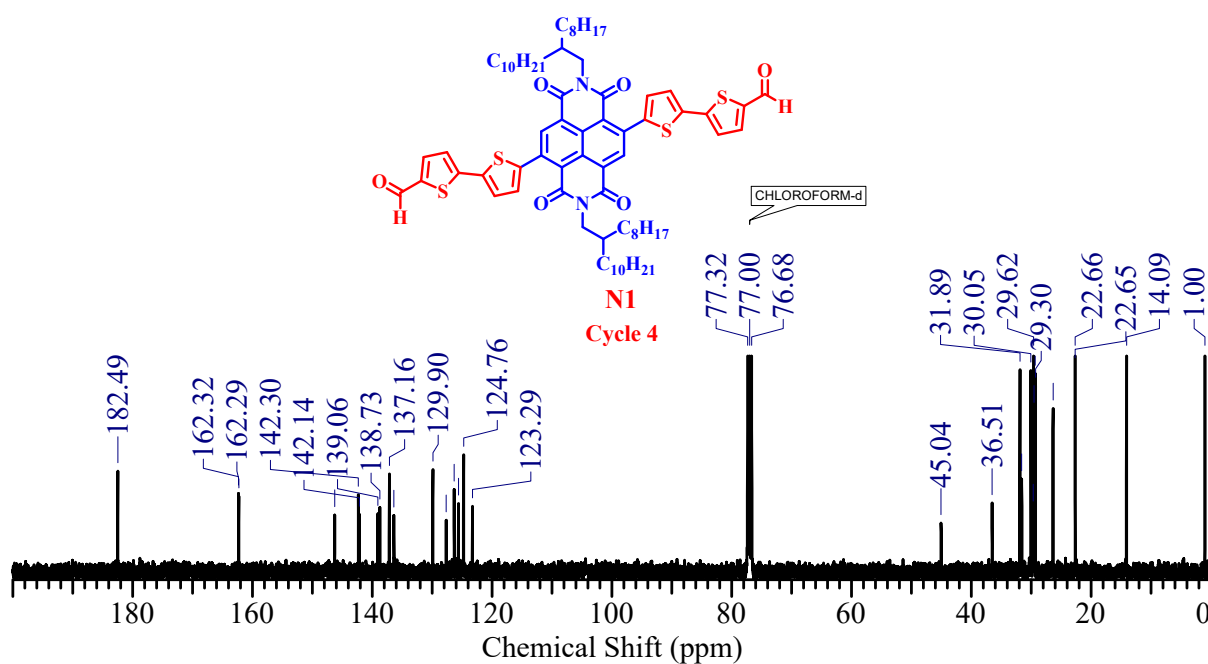


Figure S38. ¹H NMR spectrum for Cycle-5 (N1)

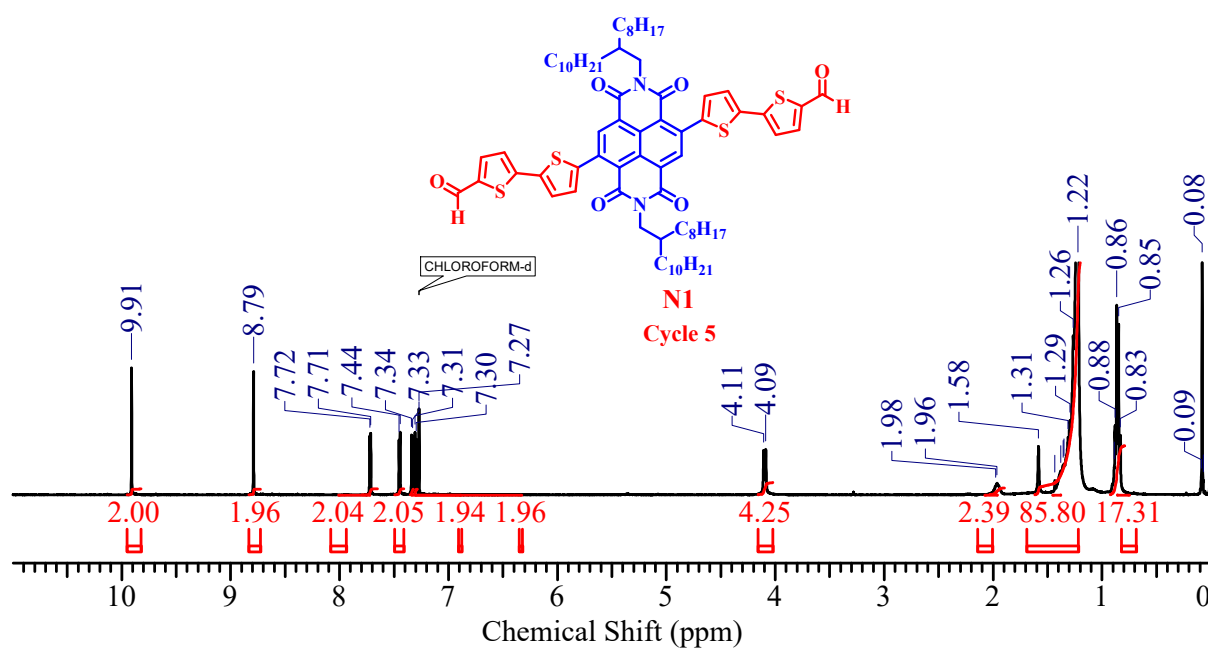


Figure S39. ^{13}C NMR spectrum for Cycle-5 (N1)

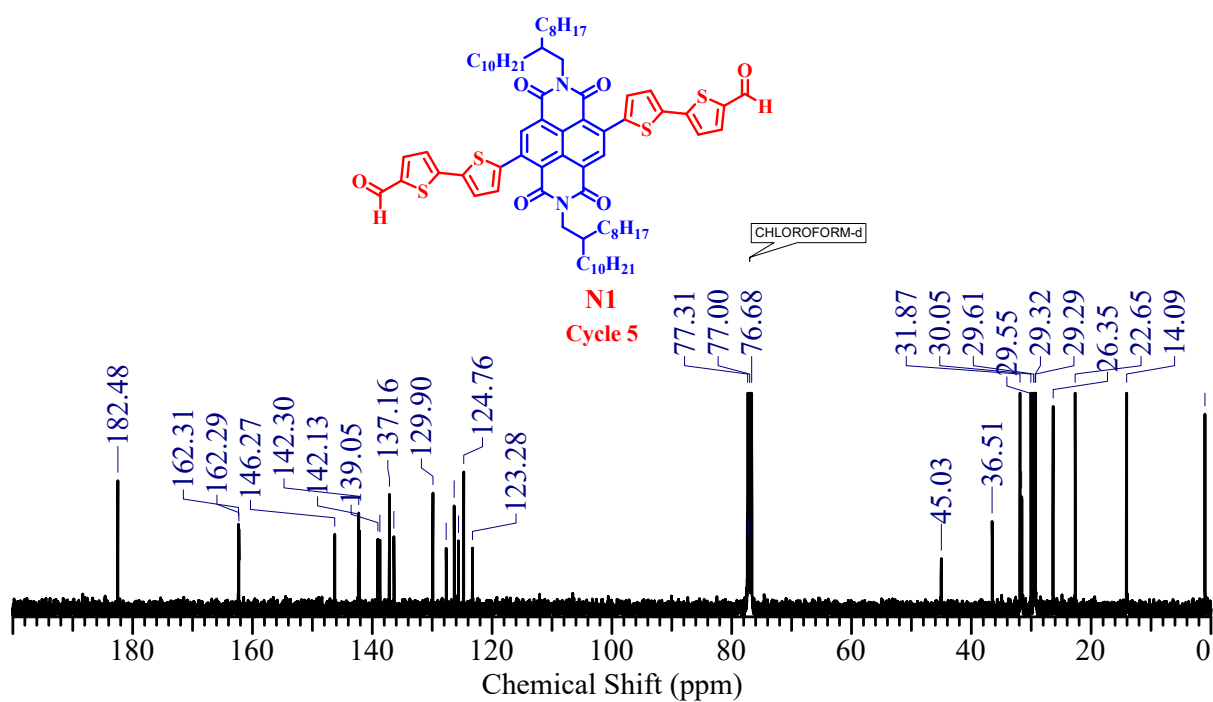


Figure S40. ^1H NMR spectrum for Cycle-6 (N1)

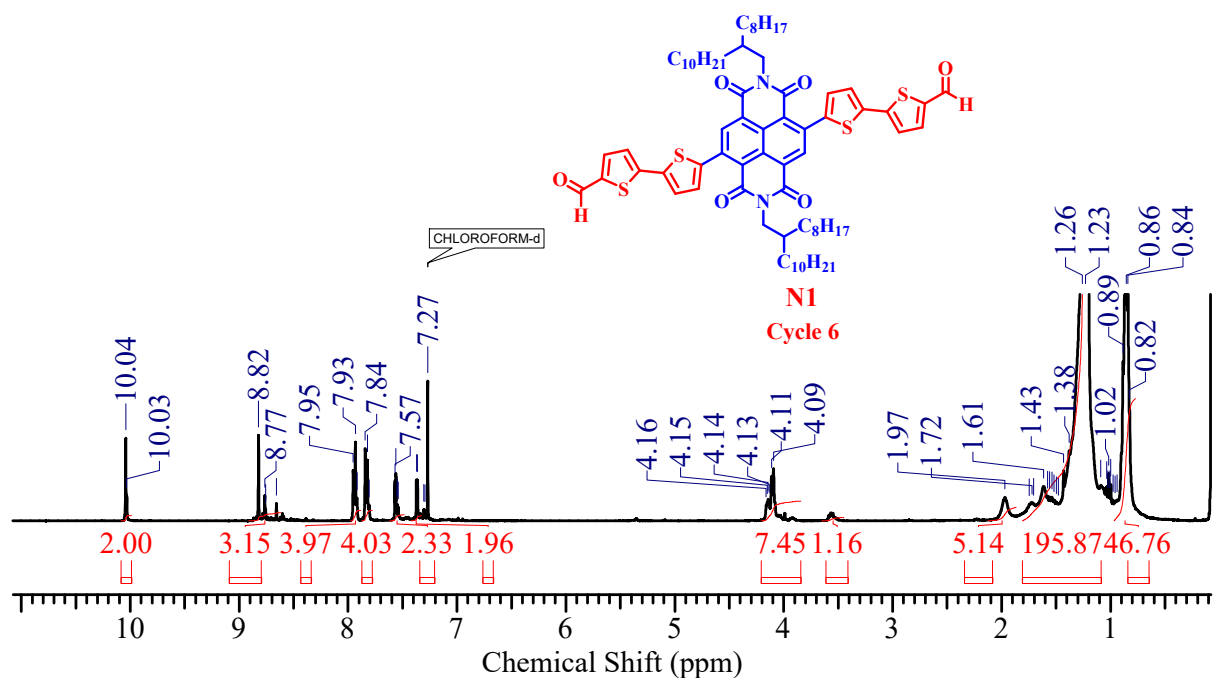
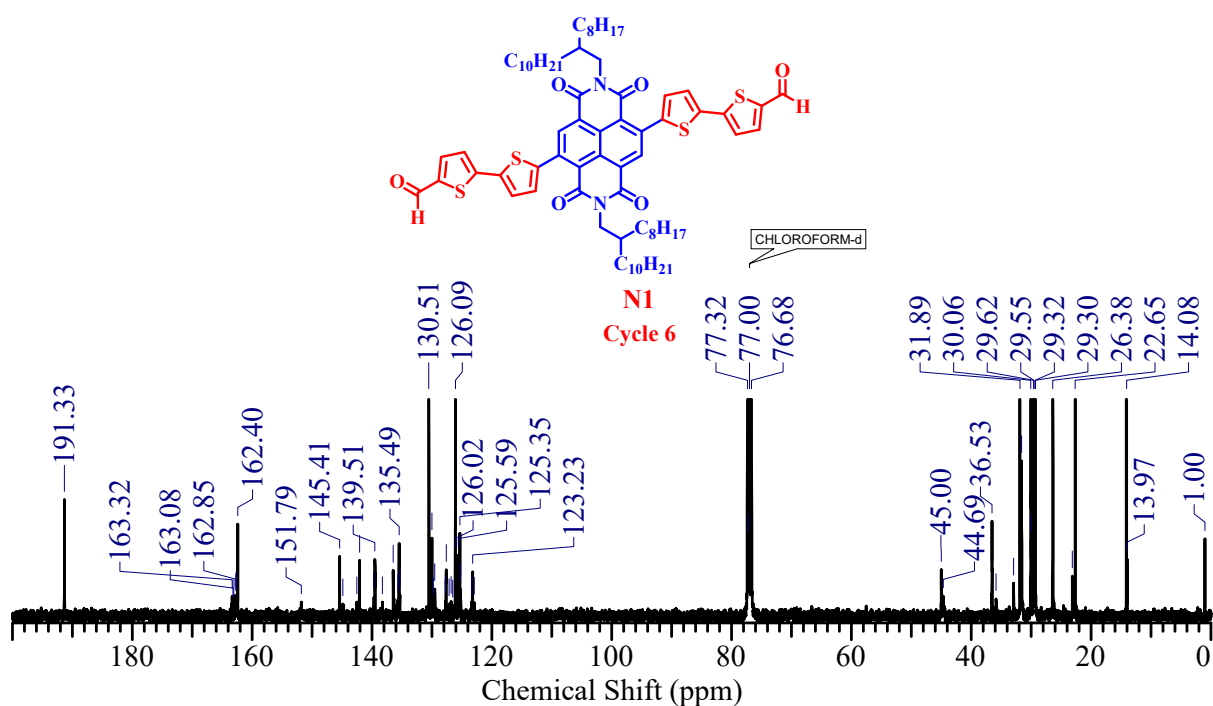


Figure S41. ^{13}C NMR spectrum for Cycle-6 (N1)



S13. Synthesis of N1 molecule using Pd_2db_3 (Homogenous) Catalyst

In 10 ml oven dry Schlenk tube equipped with a stir bar were added a NDIOD- Br_2 (100 mg, 0.101 mmol), 2,2-bithiophene-5-carbaldehyde (39.44 mg, 0.203 mmol), pivalic acid (10.36 mg, 0.101 mmol), K_2CO_3 (42.09 mg, 0.304 mmol) and Pd_2db_3 (4.64 mg, 5 mol %). The Schlenk tube was evacuated three times and purged by N_2 gas. Degassed chlorobenzene (1 ml) was added to the schlenk tube by syringe and purged for 15 minutes. The reaction was stirred for 6 h at 120 °C and warmed to room temperature. The reaction mixture was precipitated in MeOH (50 ml), filtered and washed with plenty of MeOH and a mixture of MeOH and acetone (50:50). The compound was dried in a vacuum oven at 60 °C for 12 h. The dried compound was used for further characterization. Yield = 91 mg (74 %). ^1H NMR spectrum (500 MHz instrument, CDCl_3) δ (ppm) 9.91 (2 H, s), 8.79 (2 H, s), 7.74 (2 H, dd), 7.46 (2 H, dd), 7.31 (4H, dd), 4.10 (4 H, dd), 1.96 (2 H, m), 1.22 (64 H, m), 0.86 (12 H, m). ^{13}C NMR spectrum (125 MHz instrument, CDCl_3) δ (ppm) 182.47, 162.30, 146.27, 142.30, 142.46, 139.38, 139.05, 137.49, 130.21, 126.65, 125.08, 123.61, 45.36, 36.83, 32.19, 30.37, 29.94, 22.75, 14.18.

Figure S42. ^1H NMR spectrum for N1 molecule synthesized using Pd_2dba_3 (Homogenous) Catalyst

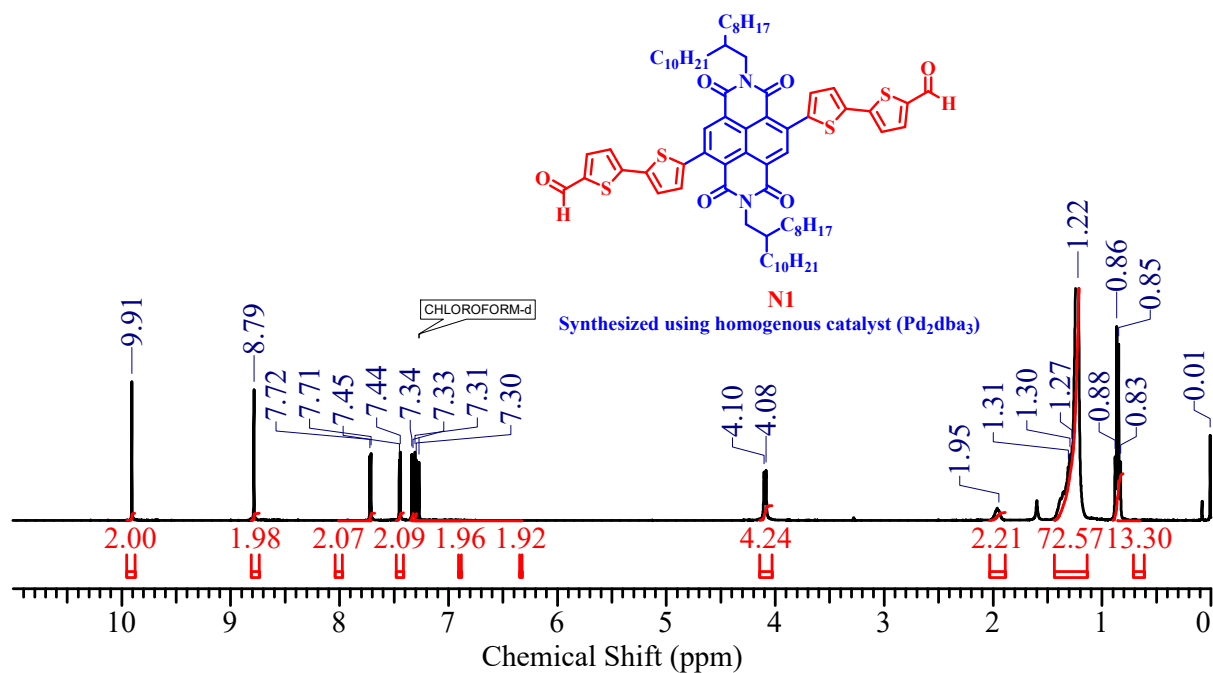
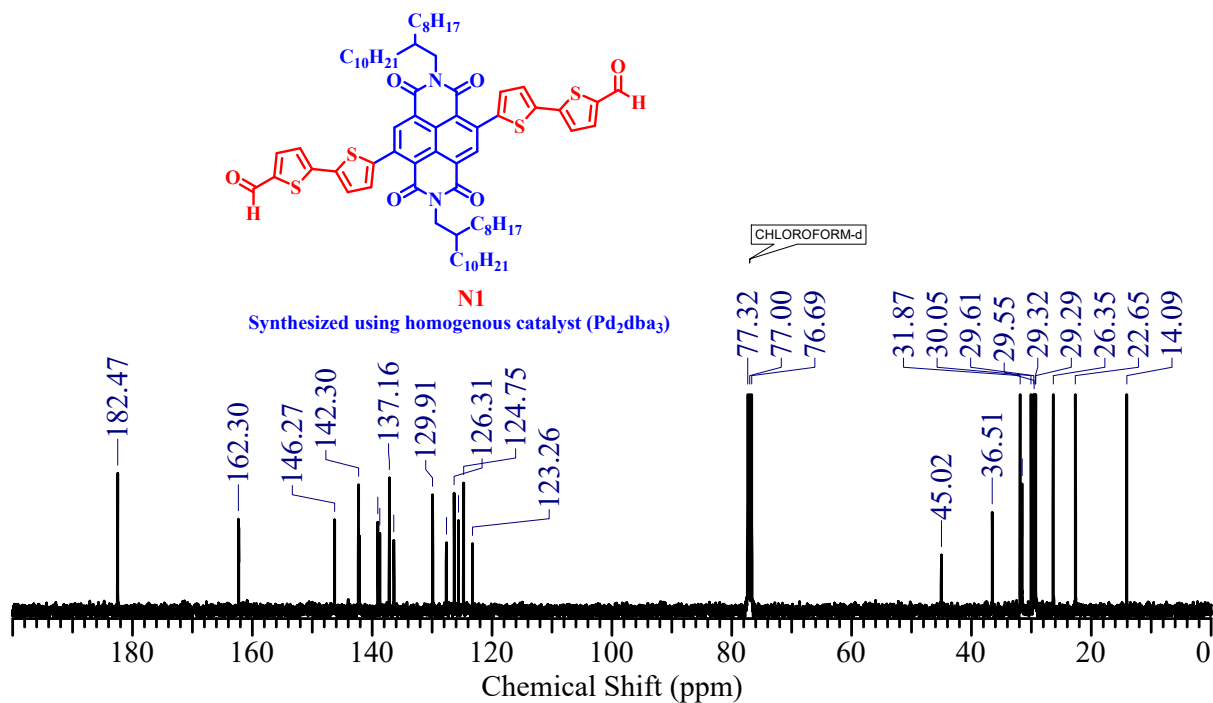


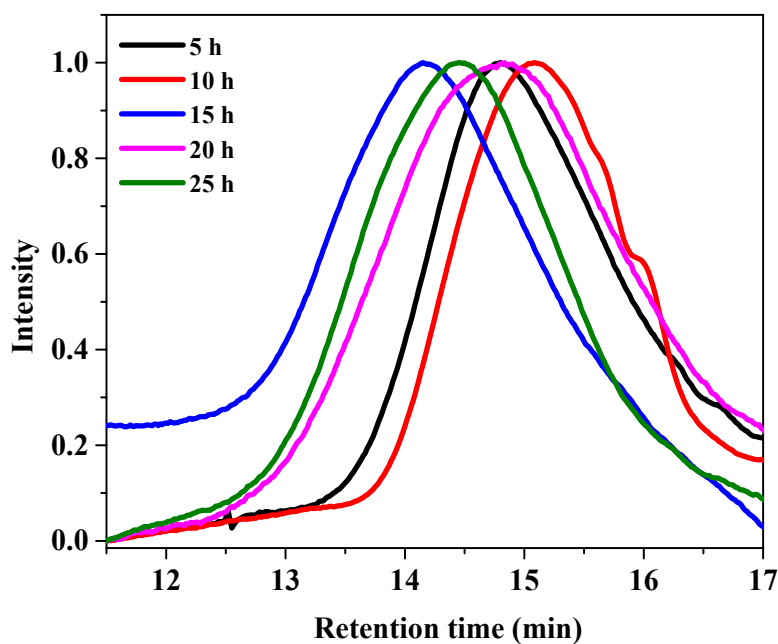
Figure S43. ^{13}C NMR spectrum for N1 molecule synthesized using Pd_2dba_3 (Homogenous) Catalyst



S14. Synthesis of P(NDIOD2-T2) using regular monomer

To an oven dry schlenk tube equipped with magnetic stir bar were added NDIOD-Br₂ (100 mg, 0.101 mmol), bithiophene (16.8 mg, 0.101 mmol), pivalic acid (10.3 mg, 0.101 mmol), K₂CO₃ (42 mg, 0.303 mmol), Silia Cat Pd-DPP (17 mg, 5 mol %). The schlenk tube was evacuated three time and purged by nitrogen gas (N₂). Degassed chlorobenzene (0.7 ml) was added in reaction mixture by syringe and purged for 15 min. The schlenk tube was kept in a pre-heated oil bath at 120 °C for 5 h. After completion of reaction, the reaction mixture was diluted with chloroform (30 mL) and filtered using Whatman 41 filter paper to remove the SiliaCat Pd-DPP catalyst. The solid was further washed with ~20 mL of CHCl₃ until the disappearance of the blue polymer colour followed by methanol and acetone. The filtrate (polymer in CHCl₃) was transferred to a separate round bottom flask for further workup. The filtrate was concentrated using rotary evaporator and precipitated in methanol. The precipitate was filtered using Buckner funnel and successively washed by methanol, acetone and hexane. The polymer was purified by soxhlet extraction in methanol, acetone and hexane. Yield – 78 mg (77 %). The catalyst was dried in vacuum oven at 70 °C and the 15.4 mg (91 %) catalyst was recovered after the polymerization.

Figure S44. GPC chromatogram for P(NDIOD2-T2) synthesized by using regular monomer for various periods of time



S15. Recyclability experiment for P(NDIOD2-T2) polymer using regular monomer

The optimized condition at 5 h was chosen for the recyclability experiment under identical conditions. The amount of all reagents, including NDIOD-Br₂ (1 eq.), bithiophene (1 eq.), pivalic acid (1 eq.), K₂CO₃ (3 eq.) siliaCat Pd-DPP (5 mol%), and solvent (chlorobenzene) were maintained constant as in previous cycle.

Cycle-1

To an oven dry schlenk tube equipped with magnetic stir bar were added NDIOD-Br₂ (100 mg, 0.101 mmol), bithiophene (16.8 mg, 0.101 mmol), pivalic acid (10.3 mg, 0.101 mmol), K₂CO₃ (42 mg, 0.303 mmol), Silia Cat Pd-DPP (17 mg, 5 mol %). The schlenk tube was evacuated three time and purged by nitrogen gas (N₂). Degassed chlorobenzene (0.7 ml) was added in reaction mixture by syringe and purged for 15 min. The schlenk tube was kept in a pre-heated oil bath at 120 °C for 5 h. After the polymerization was completed, the polymerization mixture was diluted with chloroform (CHCl₃) (30 mL) and filtered using Whatman 41 filter paper to collect the SiliaCat Pd-DPP catalyst. The residue (catalyst) was further washed with ~20 mL of CHCl₃ until the disappearance of the blue colour, followed by washing with methanol and acetone. The catalyst was dried in a vacuum oven at 70 °C for 12 h and used for the next reaction cycle. The filtrate (polymer in CHCl₃) was transferred to a separate round bottom flask for further workup. The filtrate was concentrated using rotary evaporator and precipitated in methanol. The precipitate was filtered using Buckner funnel and successively washed by methanol, acetone and hexane. The polymer was purified by soxhlet extraction in methanol, acetone and hexane. Yield - 78 mg (77 %). The recovered catalyst yield -15.4 mg (91 %)

Cycle-2

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (91 mg, 0.092 mmol), bithiophene (15.36 mg, 0.092 mmol), pivalic acid (9.43 mg, 0.092 mmol), K₂CO₃ (38.30 mg, 0.277 mmol), siliaCat Pd-DPP (15.4 mg, 5 mol %). Yield – 65 mg (71 %). The recovered catalyst yield- 14.20 mg (92 %).

Cycle-3

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (84 mg, 0.085 mmol), bithiophene (14.18 mg, 0.085 mmol), pivalic acid (8.70 mg, 0.085 mmol), K₂CO₃ (35.35 mg, 0.255 mmol), silia Cat Pd-DPP (14.21 mg, 5 mol %). Yield – 72 mg (85 %). The recovered catalyst yield- 12.80 mg (90 %).

Cycle-4

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (76 mg, 0.077 mmol), bithiophene (12.83 mg, 0.077 mmol), pivalic acid (7.87 mg, 0.077 mmol), K₂CO₃ (31.98 mg, 0.231 mmol), Silia Cat Pd-DPP (12.86 mg, 5 mol %). Yield– 61 mg (79 %). The recovered catalyst yield- 8.9 mg (69 %).

Figure S45. GPC chromatogram for P(NDIOD2-T2) synthesized by recycling SiliaCat Pd-DPP catalyst using regular monomer

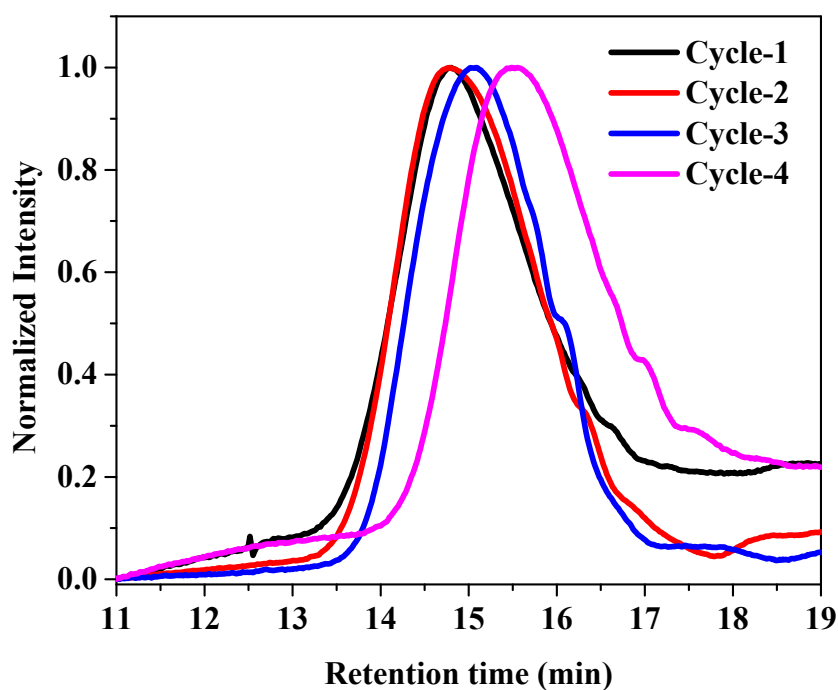


Table S2. Optimization table for synthesis of P(NDIOD-T2) using modified monomer

Sr.no	Polymer (New monomer)	Time (h)	Solvent	Mn/Mw	\bar{M}_w	Yield (%)	Catalyst recycled (%)
1	P(NDI2OD-T2)	5	CB	30.0/51.7	1.7	98	93
2	P(NDI2OD-T2)	10	CB	29.6/45.3	1.5	95	89
3	P(NDI2OD-T2)	5	TCB	29.7/48.0	1.6	93	94

S16. Recyclability experiment for P(NDIOD2-T2) polymer using modified monomer

The optimized condition at 5 h was chosen for the recyclability experiment under identical conditions. The amount of all reagents, including NDIOD-Br₂ (1 eq.), BT-NDI-BT (1 eq.), pivalic acid (1 eq.), K₂CO₃ (3 eq.) Siliacat Pd-DPP (5 mol%), and solvent (1,2,4-trichlorobenzene 0.144 M) were maintained constant to as in previous cycle.

Cycle-1

To an oven dry schlenk tube equipped with magnetic stir bar were added NDIOD-Br₂ (70 mg, 0.071 mmol), BT-NDI-BT (82.13 mg, 0.071 mmol), pivalic acid (7.25 mg, 0.071 mmol), K₂CO₃ (29.46 mg, 0.213 mmol), SiliaCat Pd-DPP (11.84 mg, 5 mol %). The Schlenk tube three time evacuated by vacuum and purged by nitrogen gas (N₂). Degassed 1,2,4-Trichlorobenzene (1 mL) was added in reaction mixture by syringe and purged for 15 min. The schlenk tube was kept in a pre-heated oil bath at 120 °C for 5 h. After the polymerization was completed, the polymerization mixture was diluted with chloroform (CHCl₃) (30 mL) and filtered using Whatman 41 filter paper to collect the SiliaCat Pd-DPP catalyst. The residue (catalyst) was further washed with ~20 mL of CHCl₃ until the disappearance of the blue colour, followed by washing with methanol and acetone. The catalyst was dried in a vacuum oven at 70 °C for 12 h and used for the next reaction cycle. The filtrate (polymer in CHCl₃) was transferred to a separate round bottom flask for further workup. The filtrate was concentrated using rotary evaporator and precipitated in methanol. The precipitate was filtered using Buckner funnel and successively washed by methanol, acetone and hexane. The polymer was purified by soxhlet extraction in methanol, acetone and hexane. Yield- 131 mg (93 %). The recovered catalyst yield-11.2 mg (94 %). ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 80 °C): δ (ppm), 8.90 (2 H), 7.42 (4 H), 4.17 (4 H), 2.08 (2 H), 1.56-1.30 (64 H), 0.90 (12 H).

Cycle-2

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (64.91 mg, 0.065 mmol), BT-NDI-BT (76.15 mg, 0.065 mmol), pivalic acid (6.72 mg, 0.065 mmol), K₂CO₃ (27.32 mg, 0.197 mmol), Silia Cat Pd-DPP (10.98 mg, 5 mol %). Yield- 119 mg (91 %). The recovered catalyst yield-9.5 mg (86 %). ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 80 °C): δ (ppm), 8.90 (2 H), 7.42 (4 H), 4.17 (4 H), 2.07 (2 H), 1.55-1.30 (64 H), 0.90 (12 H).

Cycle-3

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (56.16 mg, 0.057 mmol), BT-NDI-BT (65.89 mg, 0.057 mmol), pivalic acid (5.82 mg, 0.057 mmol), K₂CO₃ (23.63 mg, 0.171 mmol), SiliCat Pd-DPP (9.5 mg, 5 mol %). Yield- 95 mg (85 %). The recovered catalyst yield- 8.3 mg (87 %). ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 80 °C): δ (ppm), 8.92-8.90 (2 H), 7.43 (4 H), 3.93 (4 H), 2.16 (2 H), 1.56-1.33 (64 H), 0.92 (12 H).

Cycle-4

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (49.06 mg, 0.049 mmol), BT-NDI-BT (57.59 mg, 0.0490 mmol), pivalic acid (5.0 mg, 0.049 mmol), K₂CO₃ (20.66 mg, 0.149 mmol), Silia Cat Pd-DPP (8.3 mg, 5 mol %). Yield- 85 mg (84 %). The recovered catalyst yield- 6.1 mg (73 %). ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 80 °C): δ (ppm), 8.90 (2 H), 7.43 (4 H), 4.18 (4 H), 2.09 (2 H), 1.55-1.31 (64 H), 0.92-0.91(12 H).

Cycle-5

The exactly identical procedure as reported for cycle- 1 was followed.

NDIOD-Br₂ (36.05 mg, 0.036 mmol), BT-NDI-BT (42.29 mg, 0.036 mmol), pivalic acid (3.73 mg, 0.036 mmol), K₂CO₃ (15.17 mg, 0.109 mmol), Silia Cat Pd-DPP (6.1 mg, 5 mol %). Yield- 45 mg (62 %). The recovered catalyst yield- 3.2 mg (52 %). ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at 80 °C): δ (ppm), 8.86-8.90 (2 H), 7.42 (4 H), 4.17 (4 H), 2.07 (2 H), 1.55-1.30 (64 H), 0.90 (12 H).

Figure S46. GPC chromatogram for P(NDIOD2-T2) synthesized by recycling SiliaCat Pd-DPP catalyst using modified monomer.

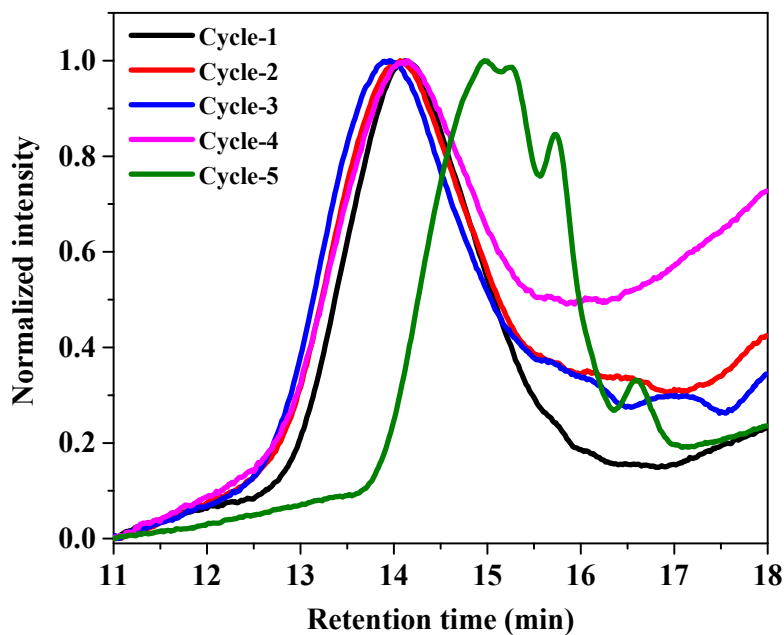


Figure S47. ^1H NMR spectrum of P(NDIOD2-T2) synthesized by recycling SiliaCat Pd-DPP catalyst using modified monomer – Cycle 1 (solvent: TCE-d2 at 90 °C, 400 MHz NMR)

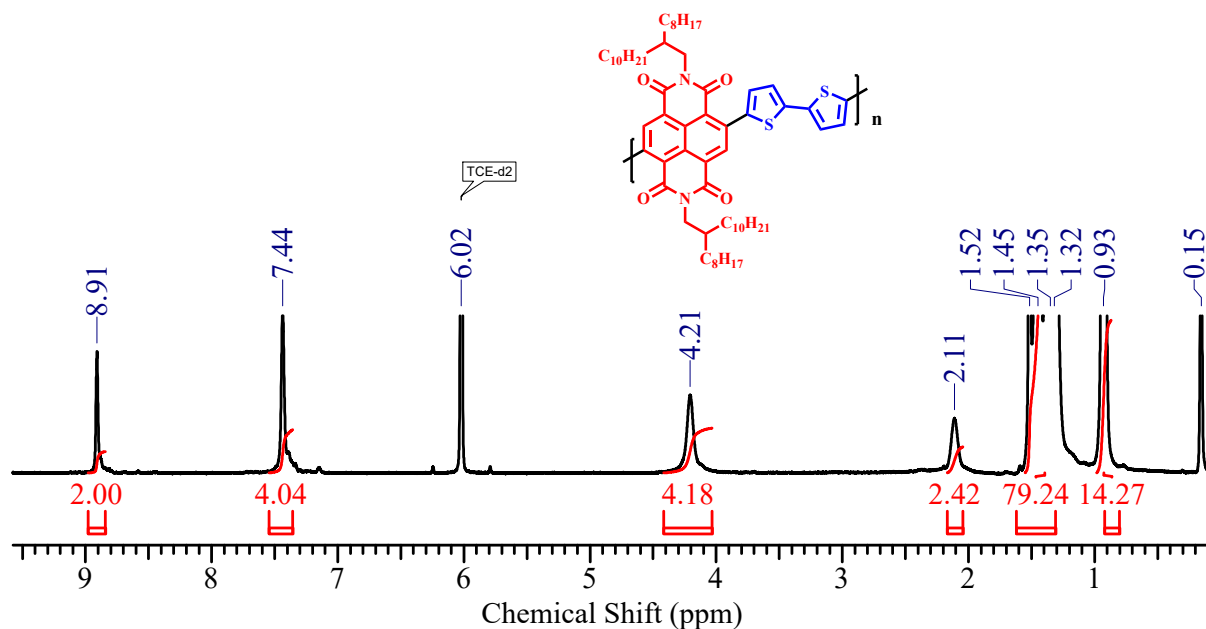


Figure S48. ^1H NMR spectrum of P(NDIOD2-T2) synthesized by recycling SiliaCat Pd-DPP catalyst using modified monomer – Cycle 2 (solvent: TCE-d2 at 90 °C, 400 MHz NMR)

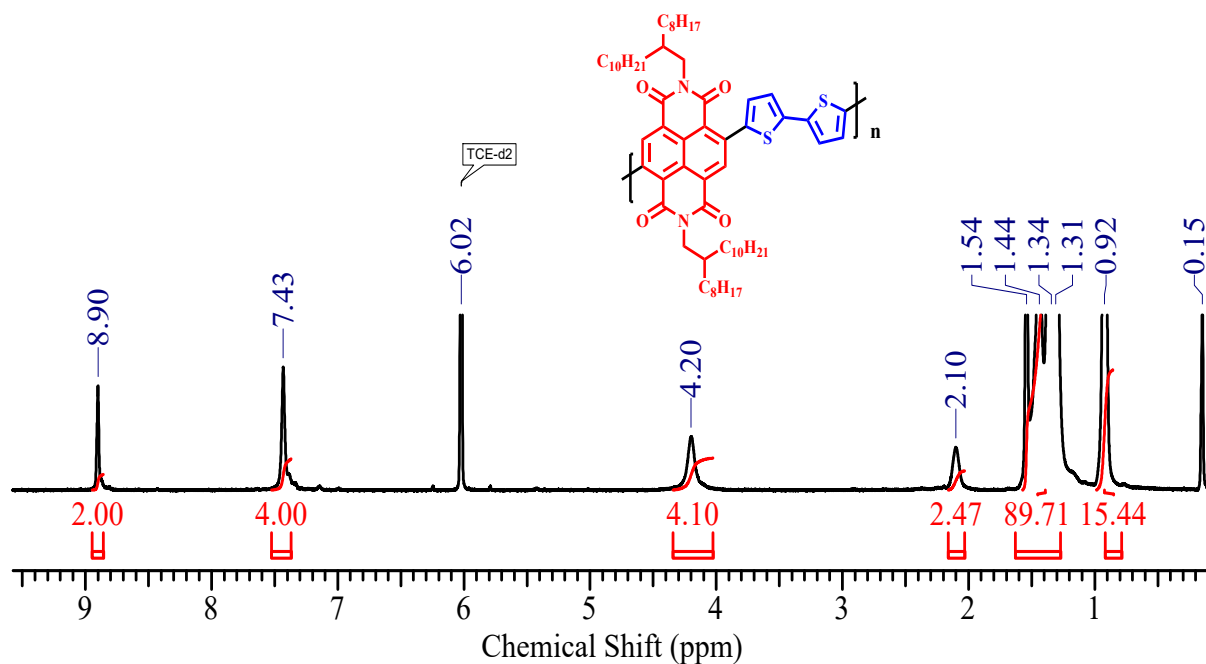


Figure S49. ^1H NMR spectrum of P(NDIOD2-T2) synthesized by recycling SiliaCat Pd-DPP catalyst using modified monomer – Cycle 3 (solvent: TCE-d2 at 90 °C, 400 MHz NMR)

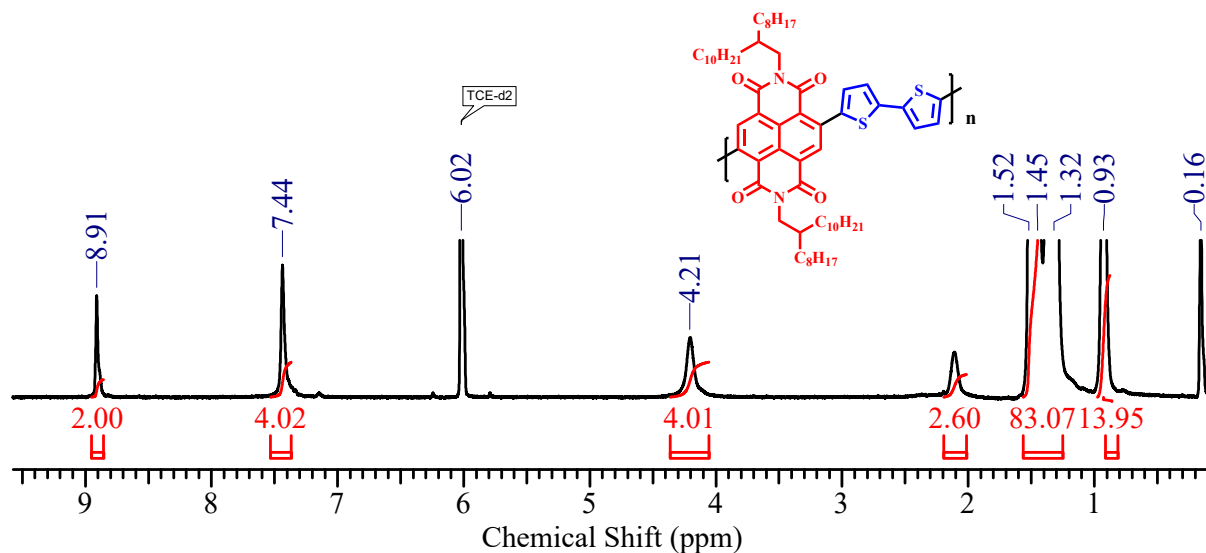


Figure S50. ^1H NMR spectrum of P(NDIOD2-T2) synthesized by recycling SiliaCat Pd-DPP catalyst using modified monomer – Cycle 4 (solvent: TCE-d2 at 90 °C, 400 MHz NMR)

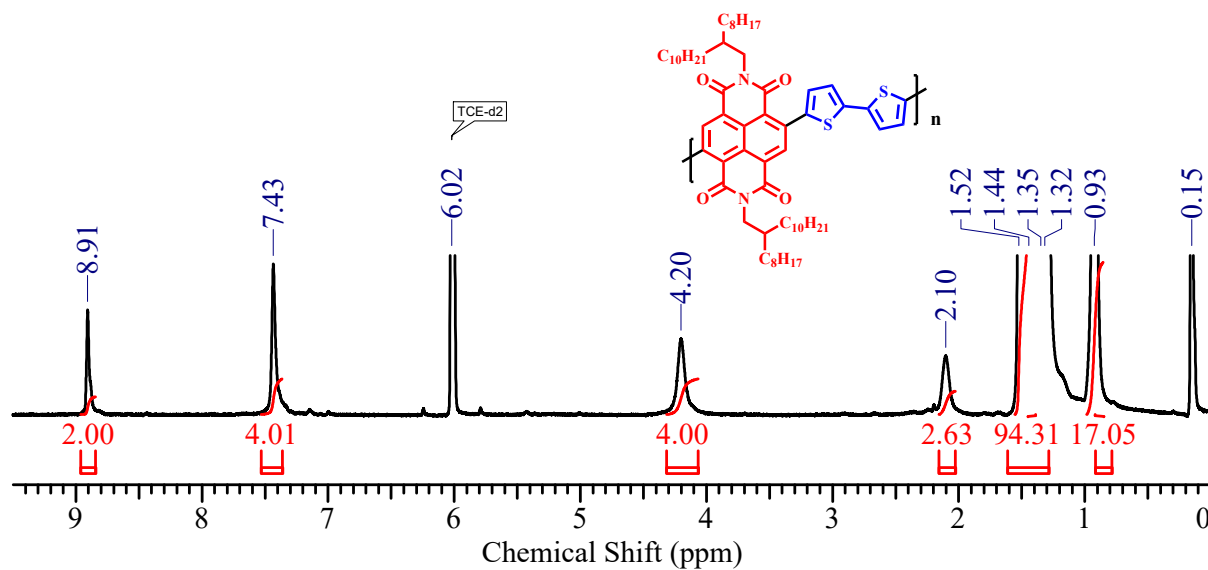


Figure S51. ^1H NMR spectrum of P(NDIOD2-T2) synthesized by recycling SiliaCat Pd-DPP catalyst using modified monomer – Cycle 5 (solvent: TCE-d2 at 90 °C, 400 MHz NMR)

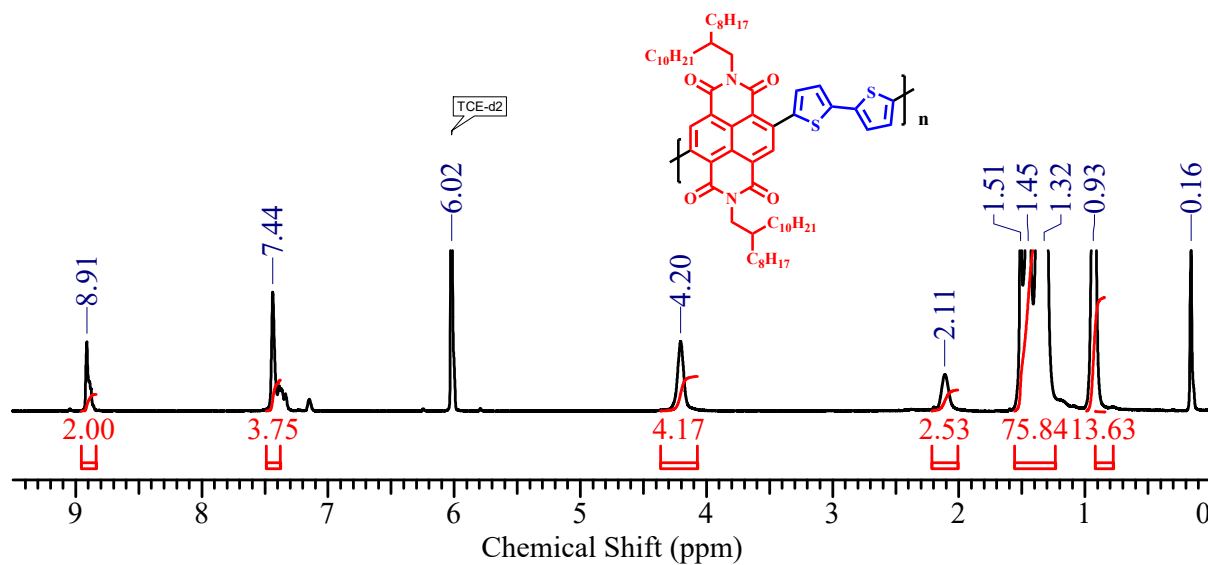
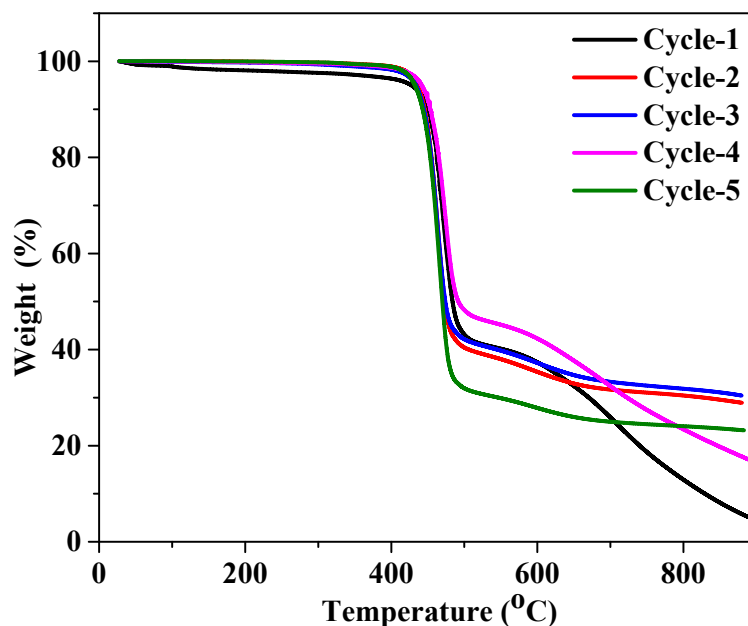
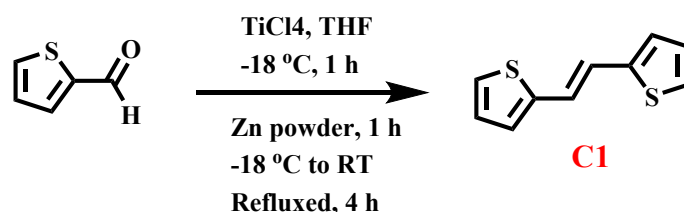


Figure S52. TGA graph for five cycles of P(NDI2OD-T2), synthesized using recycled the SiliaCat Pd-DPP as the heterogeneous catalyst.

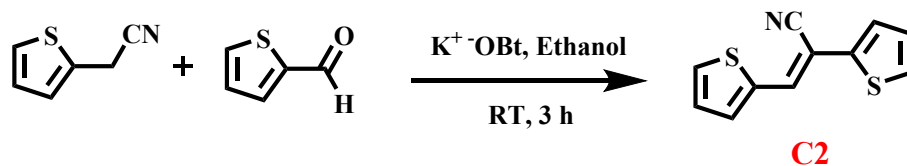


S17. Synthesis of (E)-1,2-di(thiophen-2-yl) ethene (C1)



In a two necked round bottom flask equipped with a magnetic stir bar thiophene-2-carbaldehyde (1 gm, 0.00891 mmol) in 50 ml of THF was added and stirred for 15 min. To this TiCl_4 (2.029 gm, 0.0106 mmol) was added and stirred for 1 h at -18°C . Zn powder (1.33 gm, 0.0205 mmol) was added in small portion over a period of 30 minutes. The reaction mixture was stirred for 30 minutes at -18°C , and warmed to room temperature (28°C). The reaction mixture was refluxed for 4 h and quenched by adding into ice cold water. The precipitate was filtered and washed with DCM. The DCM portion (filtrate) was concentrated using rotary evaporator to obtain a yellow solid product, which was recrystallized in hexane to obtain pure product. The crystallized product was used for further reaction without any purification. Yield = 0.982 gm (58 %). ^1H NMR spectrum (400 MHz instrument, CDCl_3) δ (ppm) 7.20(2 H, dd), 7.06 (4 H, dd), 7.1 (2 H, d). ^{13}C NMR spectrum (100 MHz instrument, CDCl_3) δ (ppm) 142.38, 127.65, 126.00, 124.29, 121.47.

S18. Synthesis of (E)-2,3-di(thiophen-2-yl) acrylonitrile (C2)



In a two necked round bottom flask equipped with a magnetic stir bar 2-(thiophene-2-yl) acetonitrile (1 gm, 0.0081mmol) and thiophene-2-carbaldehyde (0.910 gm, 0.0081 mmol) dissolved in 50 ml of ethanol were added at room temperature. After 15 minutes, ter-butoxide (0.455 gm, 0.0040 mmol) was added in the reaction mixture and the reaction was continued for 3 h. The yellow precipitate formed in the reaction mixture was filtered by using Whatman 41 filter paper. The precipitated was crystallized in hexane and used for further reaction without any purification. Yield = 0.813 gm (46 %). ¹H NMR spectrum (400 MHz instrument, CDCl₃) δ (ppm) 7.63 (1 H, s), 7.50 (1 H, d), 7.35 (1 H, d), 7.34, 7.29 (1 H, d), 7.15 (1 H, d), 7.07 (1 H, d). ¹³C NMR spectrum (100 MHz instrument, CDCl₃) δ (ppm) 138.68, 1.37.52, 132.07, 129.93, 128.17, 127.90, 126.93, 125.92, 116.94, 103.12.

Figure S53. ¹H-NMR spectrum for (E)-1,2-di(thiophen-2-yl) ethene (C1)

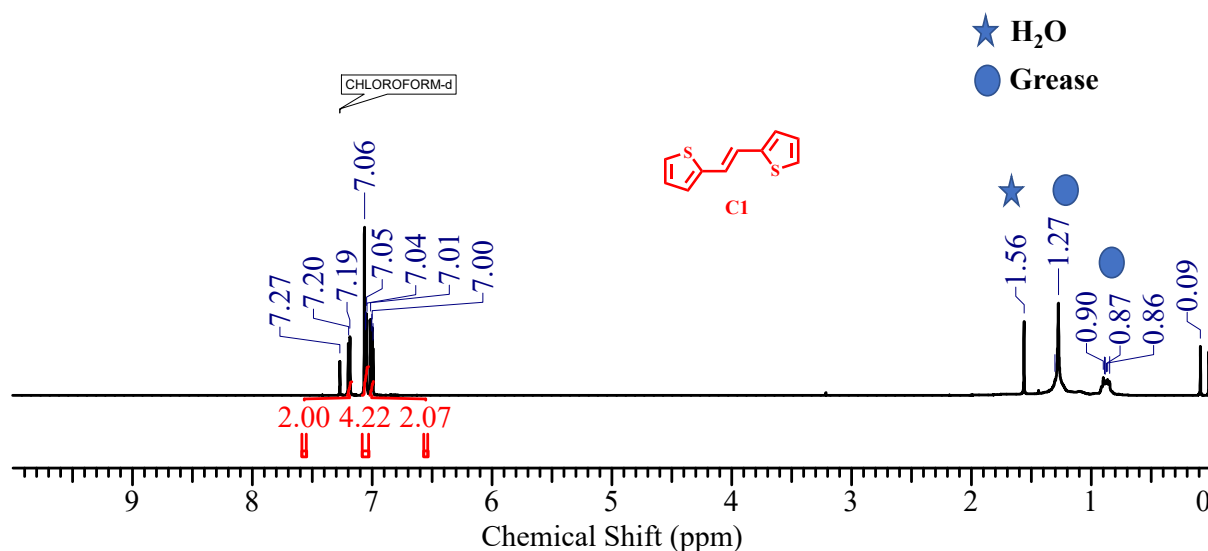


Figure S54. ^{13}C NMR spectrum for (E)-1,2-di(thiophen-2-yl) ethene (C1)

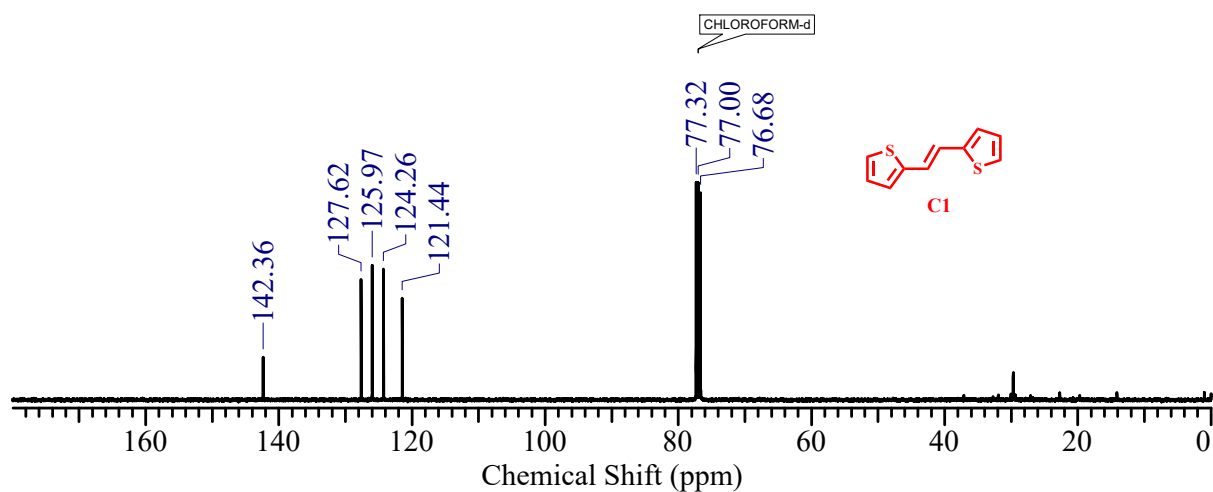


Figure S55. ^1H -NMR spectrum for (E)-2,3-di(thiophen-2-yl) acrylonitrile (C2)

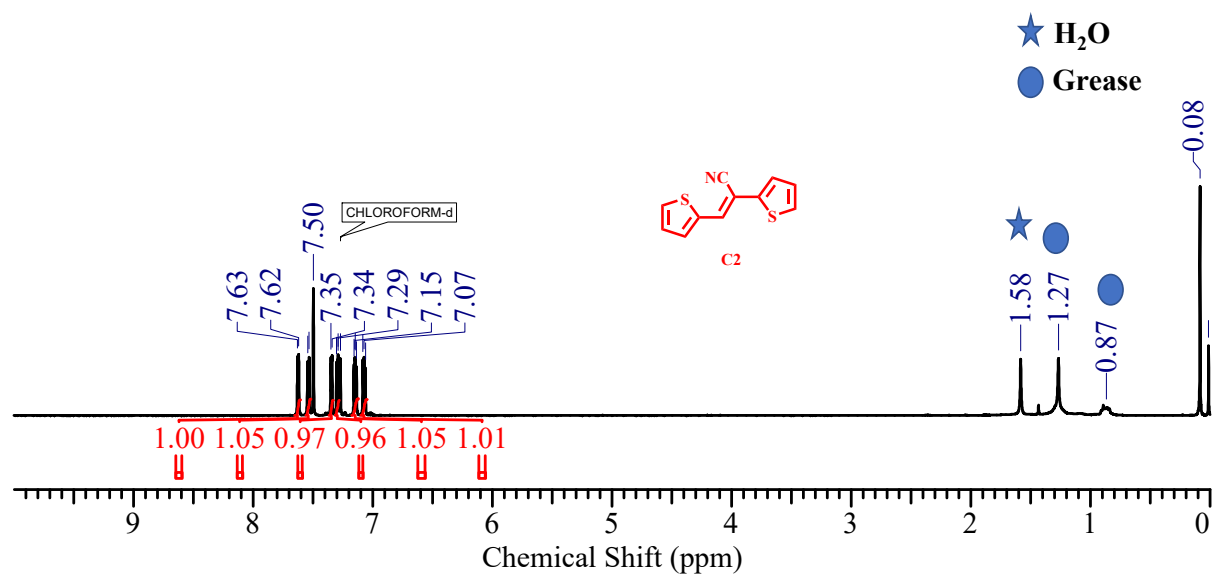
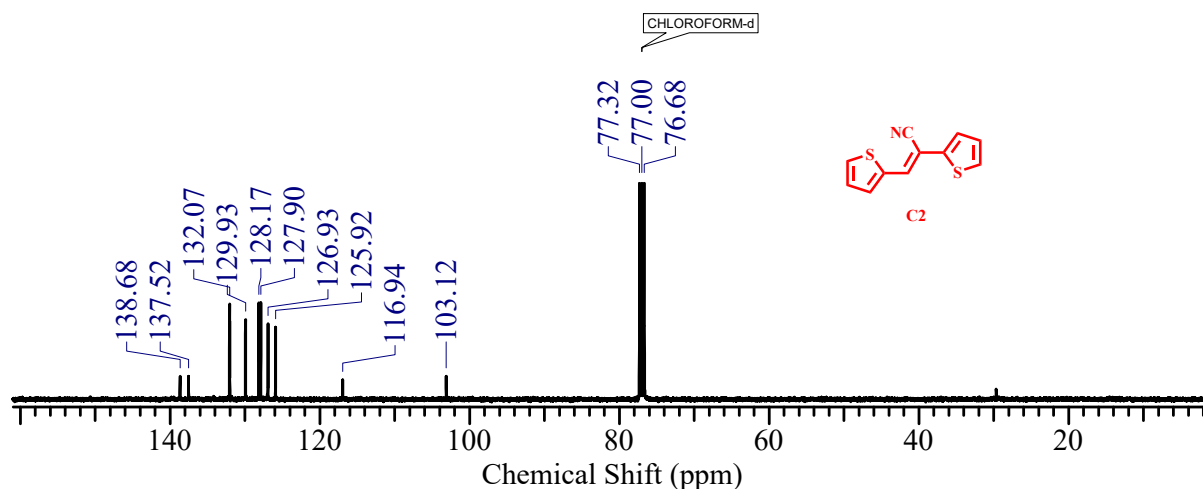
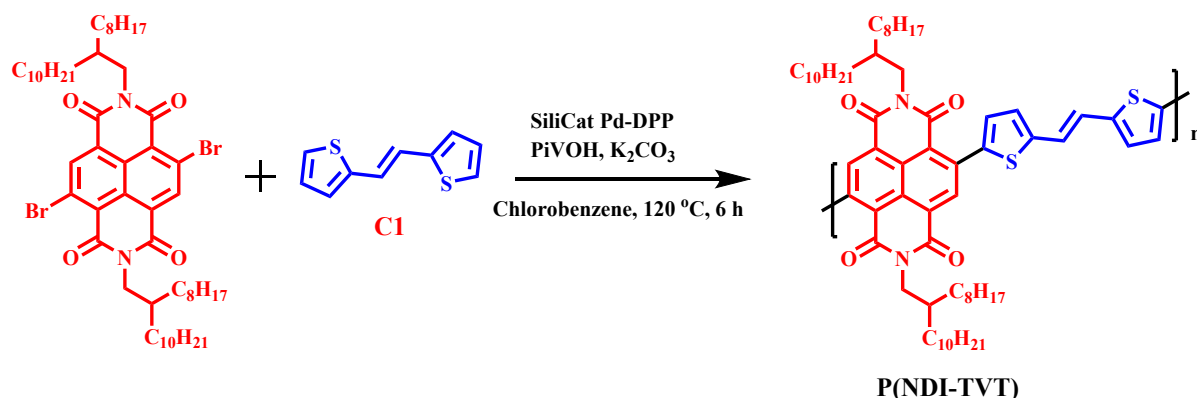


Figure S56. ^{13}C -NMR spectrum for (E)-2,3-di(thiophen-2-yl) acrylonitrile (C2)



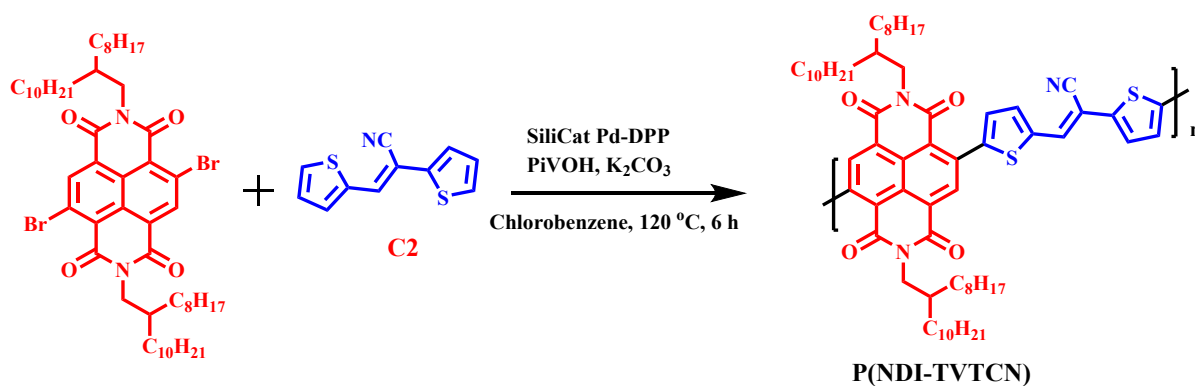
S19. Synthesis of P(NDI-TVT) Polymer



To an oven dry schlenk tube equipped with magnetic stir bar were added NDIOD- Br_2 (100 mg, 0.101 mmol), (E)-1,2-di(thiophen-2-yl) ethene (19.52 mg, 0.101 mmol), pivalic acid (10.36 mg, 0.101 mmol), K_2CO_3 (42.09 mg, 0.304 mmol) and SiliCat Pd-DPP (16.92 mg, 5 mol %). The schlenk tube was evacuated thrice and purged by nitrogen gas (N_2). Degassed 1,2,4-Trichlorobenzene (1 ml) was added to the reaction mixture by syringe and purged for 15 min. The schlenk tube was kept in a pre-heated oil bath at 120 °C for 5 h. After completion of reaction, the reaction mixture was diluted with chloroform (30 mL) and filtered using Whatman 41 filter paper to remove the SiliCat Pd-DPP catalyst. The solid was further washed with ~20 mL of CHCl_3 until the disappearance of the blue polymer colour followed by methanol and acetone. The filtrate (polymer in CHCl_3) was transferred to a separate round

bottom flask for further workup. The filtrate was concentrated using rotary evaporator and precipitated in methanol. The precipitate was filtered using Buckner funnel and successively washed by methanol, acetone and hexane. The polymer was purified by Soxhlet extraction in methanol, acetone and hexane. Yield- 75 mg (70 %). The recovered catalyst yield- 14.2 mg (84 %). ¹H NMR spectrum (400 MHz instrument, TCE-d2 at room temperature): δ (ppm), 8.81 (2 H), 7.35 (2 H), 7.21-7.13 (4H), 4.10 (4H), 2.01 (2 H), 1.67-1.26 (64 H), 0.88 (12 H).

S20. Synthesis of P(NDI-TVTCN) Polymer



The exactly identical synthesis procedure as reported for P(NDI-TVT) polymer was followed except for the reagents.

NDIOD-Br₂ (100 mg, 0.101 mmol), (E)-2,3-di(thiophen-2-yl) acrylonitrile (22.05 mg, 0.101 mmol), pivalic acid (10.36 mg, 0.101 mmol), K₂CO₃ (42.09 mg, 0.304 mmol), SiliaCat Pd-DPP (16.92 mg, 5 mol %). Yield- 65 mg (68 %). The catalyst recovered yield- 13.8 mg (82 %). ¹H NMR spectrum (400 MHz instrument, TCE-d2 at room temperature): δ (ppm), 8.81 (2 H), 7.74 (1 H), 7.64-7.51 (2 H), 7.38 (2 H), 4.11 (4H), 2.01 (2 H), 1.67-1.26 (64 H), 0.88 (12 H).

Figure S57. ^1H NMR spectrum of P(NDI-TVTCN) synthesized using SiliaCat Pd-DPP catalyst (solvent: TCE-d2 at 28 °C, 400 MHz NMR)

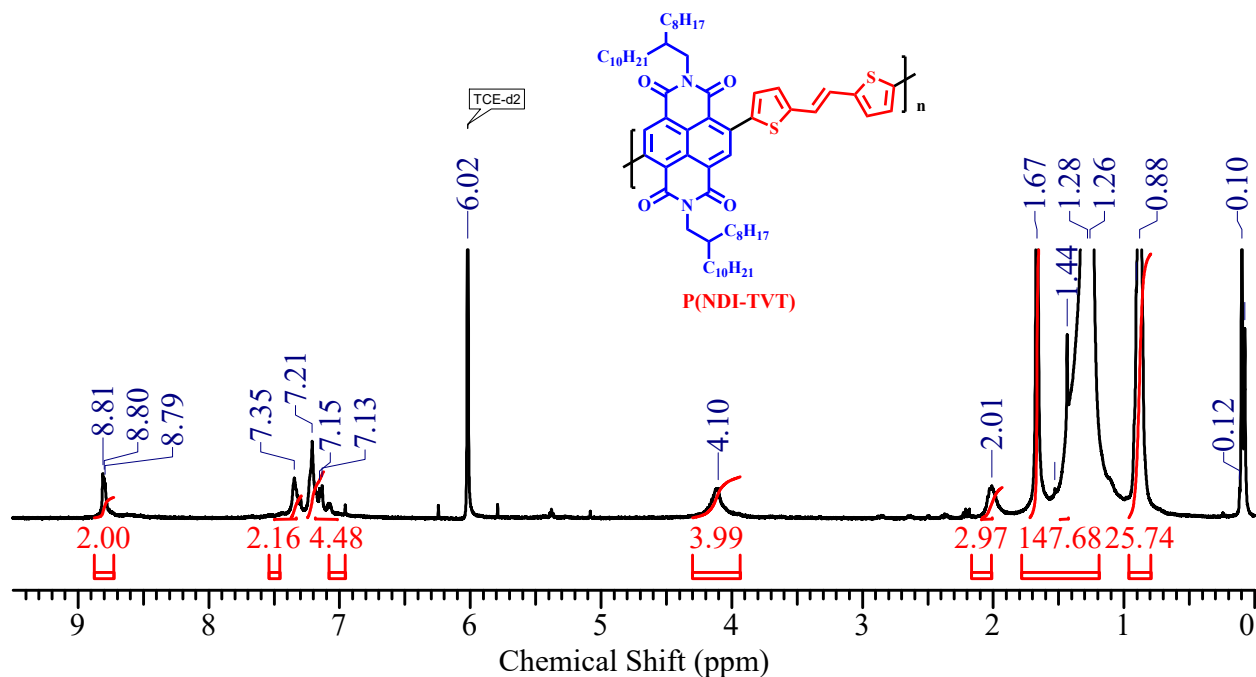


Figure S58. ^1H NMR spectrum of P(NDI-TVTCN) synthesized using SiliaCat Pd-DPP catalyst (solvent: TCE-d2 at 28 °C, 400 MHz NMR)

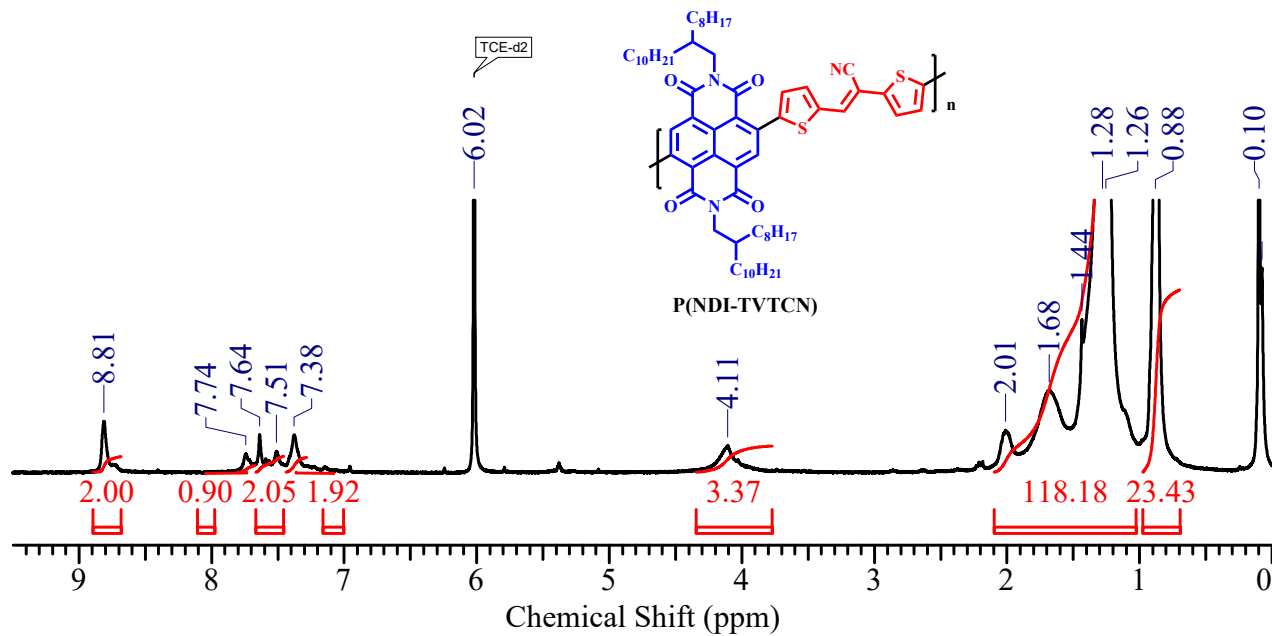
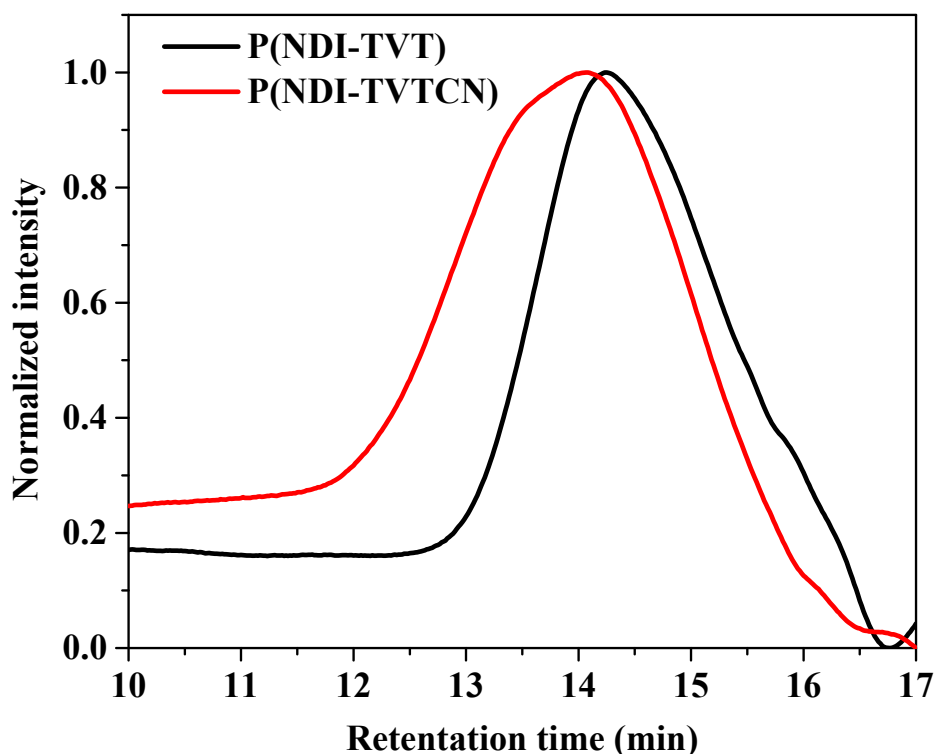


Figure S59. GPC chromatogram for P(NDI-TVT) and P(NDI-TVTCN) synthesized by SiliaCat Pd-DPP catalyst.



S21. Recyclability experiment for P(NDI-TVTCN) polymer

The exactly identical synthesis procedure as reported for P(NDI-TVT) polymer was followed except for the reagents.

Cycle-1

NDIOD-Br₂ (200 mg, 0.203 mmol), (E)-2,3-di(thiophen-2-yl) acrylonitrile (44.11 mg, 0.203 mmol), pivalic acid (20.73 mg, 0.203 mmol), K₂CO₃ (84.18 mg, 0.609 mmol), SiliaCat Pd-DPP (33.85 mg, 5 mol %). Yield- 148 mg (87 %). The catalyst recovered yield- 29.4 mg (87 %). ¹H NMR spectrum (400 MHz instrument, TCE-d₂ at room temperature): δ (ppm), 8.81 (2 H), 7.74 (1 H), 7.64-7.51 (2 H), 7.38 (2 H), 4.12 (4H), 2.00 (2 H), 1.67-1.26 (64 H), 0.88 (12 H).

Cycle-2

NDIOD-Br₂ (173.70 mg, 0.176 mmol), (E)-2,3-di(thiophen-2-yl) acrylonitrile (38.31 mg, 0.176 mmol), pivalic acid (18.00 mg, 0.176 mmol), K₂CO₃ (73.11 mg, 0.529 mmol), SiliaCat Pd-DPP (29.40 mg, 5 mol %). Yield- 112 mg (68 %). The catalyst recovered yield- 25.3 mg

(86 %). ¹H NMR spectrum (400 MHz instrument, TCE-d2 at room temperature): δ (ppm), 8.81 (2 H), 7.75 (1 H), 7.64-7.51 (2 H), 7.38 (2 H), 4.12 (4H), 2.00 (2 H), 1.67-1.26 (64 H), 0.88 (12 H).

Cycle-3

NDIOD-Br₂ (149.47 mg, 0.151 mmol), (E)-2,3-di(thiophen-2-yl) acrylonitrile (32.97 mg, 0.151 mmol), pivalic acid (15.49 mg, 0.176 mmol), K₂CO₃ (62.91 mg, 0.455 mmol), SiliaCat Pd-DPP (25.30 mg, 5 mol %). Yield- 82 mg (57 %). The catalyst recovered yield- 21.9 mg (87 %). ¹H NMR spectrum (400 MHz instrument, TCE-d2 at room temperature): δ (ppm), 8.81 (2 H), 7.74 (1 H), 7.64-7.51 (2 H), 7.38 (2 H), 4.11 (4H), 2.01 (2 H), 1.67-1.26 (64 H), 0.88 (12 H).

Cycle-4

NDIOD-Br₂ (129.38 mg, 0.131 mmol), (E)-2,3-di(thiophen-2-yl) acrylonitrile (28.54 mg, 0.131 mmol), pivalic acid (13.41 mg, 0.131 mmol), K₂CO₃ (54.42 mg, 0.394 mmol), SiliaCat Pd-DPP (21.90 mg, 5 mol %). Yield- 71 mg (57 %). The catalyst recovered yield- 17.3 mg (79 %). ¹H NMR spectrum (400 MHz instrument, TCE-d2 at room temperature): δ (ppm), 8.81 (2 H), 7.74 (1 H), 7.64-7.51 (2 H), 7.38 (2 H), 4.11 (4H), 2.01 (2 H), 1.67-1.26 (64 H), 0.88 (12 H).

Cycle-5

The exactly identical synthesis procedure as reported for P(NDI-TVT) polymer was followed except for the reagents and time. The cycle 5 was continue for 12 h.

NDIOD-Br₂ (102.2 mg, 0.103 mmol), (E)-2,3-di(thiophen-2-yl) acrylonitrile (22.54 mg, 0.103 mmol), pivalic acid (10.59 mg, 0.103 mmol), K₂CO₃ (43.01 mg, 0.311 mmol), SiliaCat Pd-DPP (17.30 mg, 5 mol %). Yield- 43 mg (44 %). The catalyst recovered yield- 14.1 mg (81 %). ¹H NMR spectrum (400 MHz instrument, TCE-d2 at room temperature): δ (ppm), 8.81 (2 H), 7.74 (1 H), 7.64-7.51 (2 H), 7.38 (2 H), 4.11 (4H), 2.01 (2 H), 1.67-1.26 (64 H), 0.88 (12 H).

Figure S60. GPC chromatogram for P(NDI-TVTCN) synthesized by recycling SiliaCat Pd-DPP catalyst.

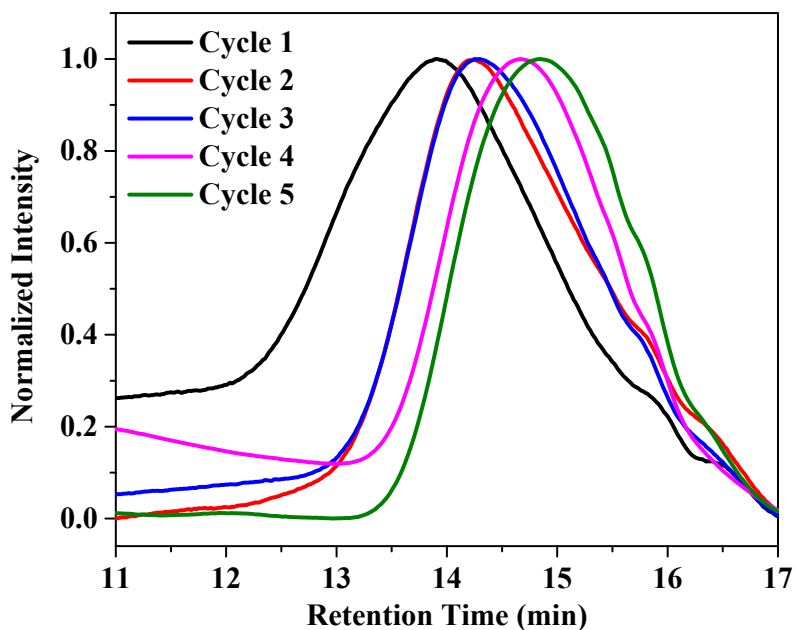


Figure S61. ^1H NMR spectrum of P(NDI-TVTCN) synthesized by recycling SiliaCat Pd-DPP catalyst Cycle-1 (solvent: TCE-d₂ at room temperature, 400 MHz NMR)

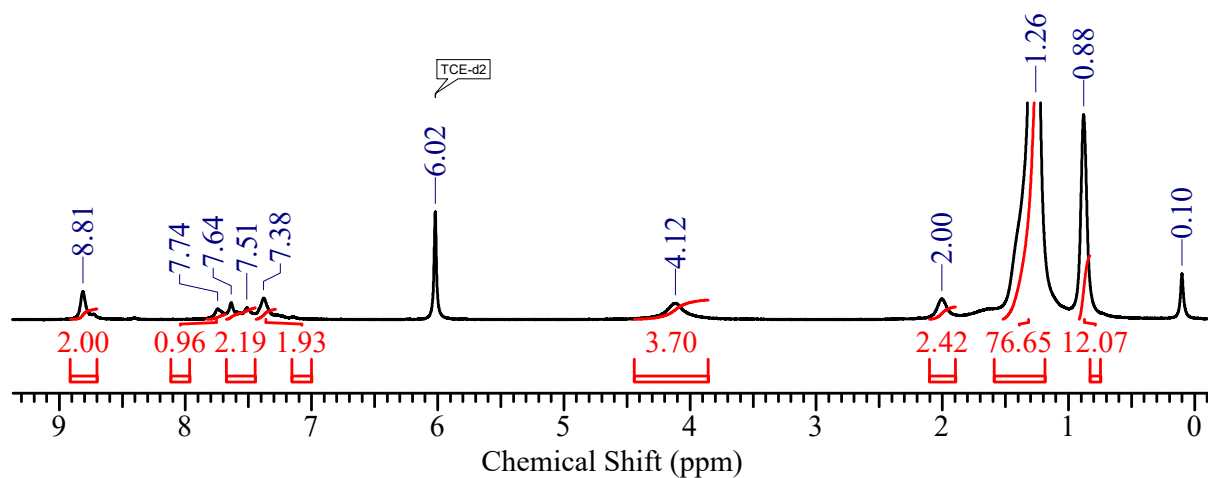


Figure S62. ^1H NMR spectrum of P(NDI-TVTCN) synthesized by recycling SiliaCat Pd-DPP catalyst Cycle-2 (solvent: TCE-d₂ at room temperature, 400 MHz NMR)

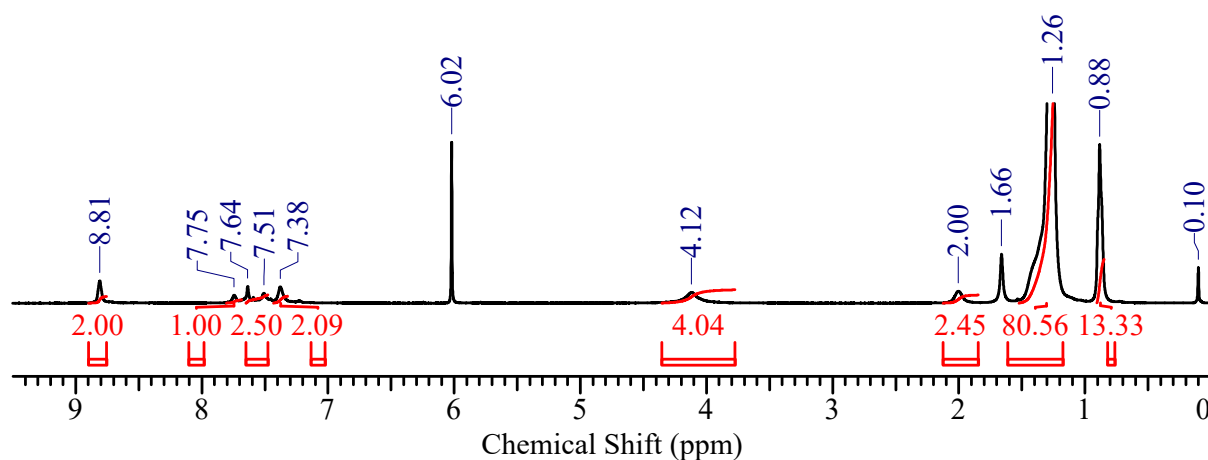


Figure S63. ^1H NMR spectrum of P(NDI-TVTCN) synthesized by recycling SiliaCat Pd-DPP catalyst Cycle-3 (solvent: TCE-d₂ at room temperature, 400 MHz NMR)

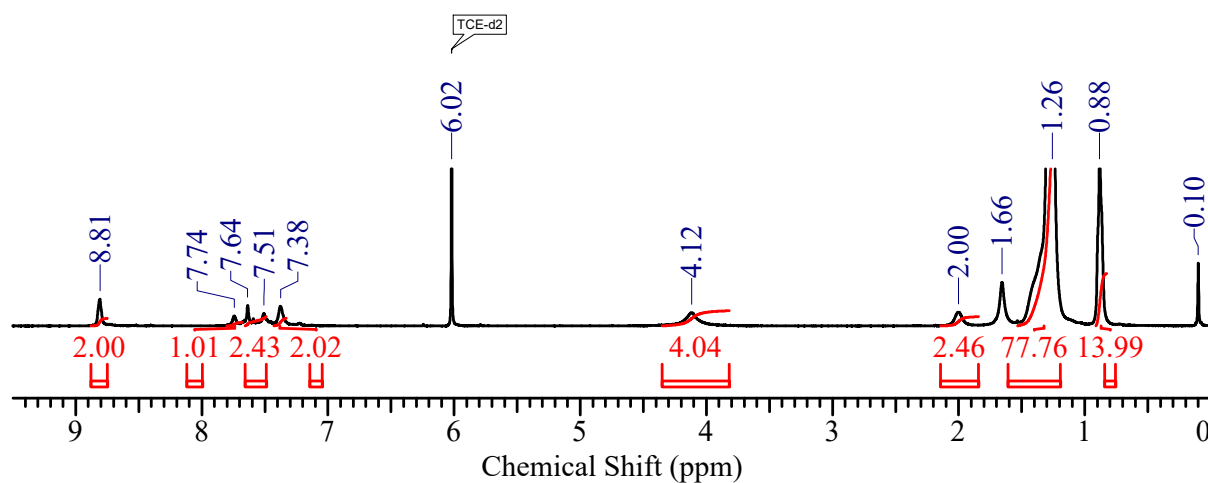


Figure S64. ^1H NMR spectrum of P(NDI-TVTCN) synthesized by recycling SiliaCat Pd-DPP catalyst Cycle-4 (solvent: TCE-d2 at room temperature, 400 MHz NMR)

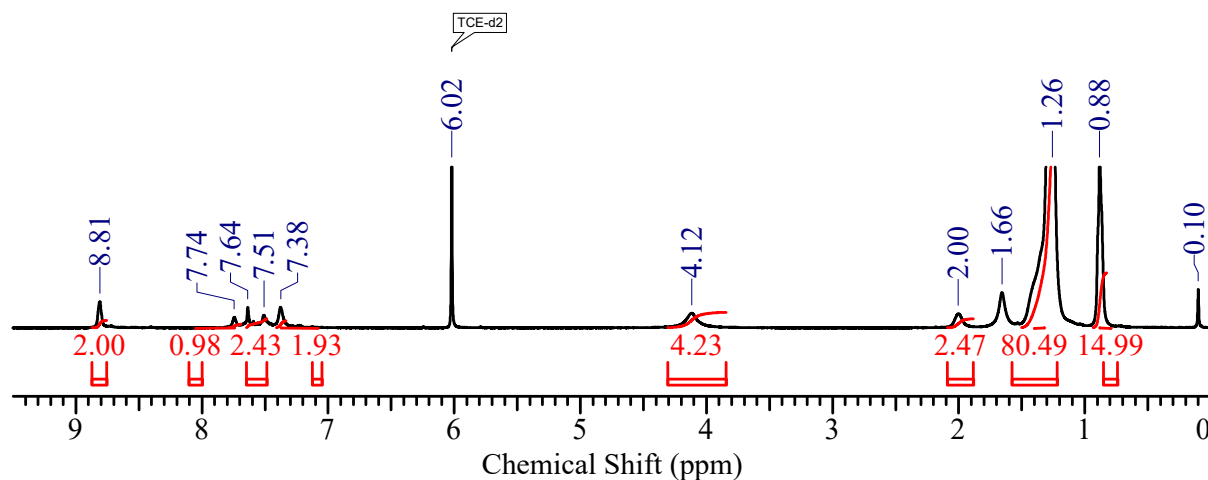


Figure S65. ^1H NMR spectrum of P(NDITVTCN) synthesized by recycling SiliaCat Pd-DPP catalyst Cycle-5 (solvent: TCE-d2 at room temperature, 400 MHz NMR)

