Supporting Information for:
A Versatile and Efficient Synthesis of Bithiophene-BasedDicarboxaldehydes
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Table of Contents
1. Figure S1: $^1$H NMR spectra of compound 1 .................................................. S2
2. Figure S2: $^1$H NMR spectra of compound 2 ................................................. S3
3. Figure S3: $^{13}$C NMR spectra of compound 2 ............................................... S4
4. Figure S4: $^1$H NMR spectra of compound 3 ............................................... S5
5. Figure S5: $^{13}$C NMR spectra of compound 3 ............................................... S6
6. Figure S6: $^1$H NMR spectra of compound 4 ............................................... S7
7. Figure S7: $^{13}$C NMR spectra of compound 4 ............................................... S8
8. Figure S8: $^1$H NMR spectra of compound 5a ............................................. S9
9. Figure S9: $^{13}$C NMR spectra of compound 5a ............................................. S10
10. Figure S10: $^1$H NMR spectra of compound 5b.......................................... S11
11. Figure S11: $^{13}$C NMR spectra of compound 5b.......................................... S12
12. Figure S12: $^1$H NMR spectra of compound 6a.......................................... S13
13. Figure S13: $^{13}$C NMR spectra of compound 6a.......................................... S14
14. Figure S14: $^{31}$P NMR spectra of compound 6b .......................................... S15
15. Figure S15: $^1$H NMR spectra of compound 6b.......................................... S16
16. Figure S16: $^{13}$C NMR spectra of compound 6b .......................................... S17
17. Synthesis of diethyl 2,2-bis(3,7-dimethyloctyl)malonate (S1)..................... S18
18. Synthesis of 2-(3,7-dimethyloctyl)-5,9-dimethyldecanoic acid (S2)............. S18
19. Synthesis of 2-(3,7-dimethyloctyl)-5,9-dimethyldecan-1-ol (S3).................. S19
20. Synthesis of 2-(2-(3,7-dimethyloctyl)-5,9-dimethyldecyli}sindoline-1,3-dione (S4)...... S19
21. Synthesis of 2-(3,7-dimethyloctyl)-5,9-dimethyldecan-1-amine (S5).............. S19
22. Figure S17: $^1$H NMR spectra of compound 7 ............................................. S20
23. Figure S18: $^{13}$C NMR spectra of compound 7 ............................................. S21
24. Figure S19: $^1$H NMR spectra of compound 8 ............................................. S22
25. Figure S20: $^{13}$C NMR spectra of compound 8 ............................................. S23
26. Figure S21: $^{31}$P NMR spectra of compound 8 ............................................. S24
27. Figure S22: CIGARAD spectra of compound 8 ........................................... S25
28. Figure S23: HSQC spectra of compound 8 ................................................ S26
29. Figure S24: $^1$H NMR spectra of compound 9 ............................................. S27
30. Figure S25: $^{13}$C NMR spectra of compound 9 ............................................. S28
31. Figure S26: $^1$H NMR spectra of compound 10 ........................................... S29
32. Figure S27: $^{13}$C NMR spectra of compound 10 ........................................... S30
33. Figure S28: $^1$H NMR spectra of compound 11 ........................................... S31
34. Figure S29: $^{13}$C NMR spectra of compound 11 ........................................... S32
35. Figure S30: $^{31}$P NMR spectra of compound 11 ........................................... S33
36. Figure S31: COSY spectra of compound 11 .............................................. S34
37. Figure S32: HSQC spectra of compound 11 .............................................. S35
38. Figure S33: CIGARAD spectra of compound 11 ........................................... S36
39. Figure S34: $^1$H NMR spectra of compound 12 ........................................... S37
40. Figure S35: $^{13}$C NMR spectra of compound 12 ........................................... S38
41. Figure S36: $^1$H NMR spectra of compound 13 ........................................... S39
42. Figure S37: $^{13}$C NMR spectra of compound 13 ........................................... S40
43. Figure S38: $^1$H NMR spectra of compound 14 ........................................... S41
Figure S1: $^1$H NMR spectra of compound 1
Figure S2: $^1$H NMR spectra of compound 2
Figure S3: $^{13}$C NMR spectra of compound 2
Figure S4: $^1$H NMR spectra of compound 3
Figure S5: $^{13}$C NMR spectra of compound 3
Figure S6: $^1$H NMR spectra of compound 4
Figure S7: $^{13}$C NMR spectra of compound 4
Figure S8: $^1$H NMR spectra of compound 5a
Figure S9: $^{13}$C NMR spectra of compound 5a
Figure S10: $^1$H NMR spectra of compound 5b
Figure S11: $^{13}$C NMR spectra of compound 5b
Figure S12: $^1$H NMR spectra of compound 6a
Figure S13: $^1$C NMR spectra of compound 6a
Figure S14: $^1$H NMR spectra of compound 6b
Figure S15: $^1$H NMR spectra of compound 6b
Figure S16: $^1$C NMR spectra of compound 6b
diethyl 2,2-bis(3,7-dimethyloctyl)malonate (S1) A concentrated solution of sodium ethoxide (35mL) was slowly added to a mixture of diethyl malonate (31.21 mmol) and 1-bromo-3,7-dimethyl bromide (78.04 mmol) with continuous stirring and the temperature was maintained between 5 – 10°C. After the addition of NaOEt, the cold-water bath was removed and the mixture was allowed to stir overnight at rt. Excess solvent was removed and the residue was added to water and then extracted with diethyl ether. The organic phase was washed with brine and water and dried over MgSO₄ and then evaporated to give a yellow liquid. The crude material was distilled under high vacuum to yield pure product (7.9g, 57%). ¹H NMR (400 MHz, CDCl₃) δ 0.80-0.83 (br, 18H), 0.89 – 1.30 (br, 22H), 1.31 (m, 2H), 1.48 (m, 2H), 1.82 (m, 4H), 4.14 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 9.214, 11.531, 19.246, 19.265, 20.068, 20.429, 21.528, 26.568, 26.649, 27.623, 29.284, 30.738, 75.033, 95.868, 125.083, 138.437, 138.930, 146.937.

2-(3,7-dimethyloctyl)-5,9-dimethyldecanoic acid (S2) In a round bottom flask S1 (7.9 g, 17.93 mmol) was dissolved in ethanol (110 mL). Then a 50% wt./wt. solution of KOH(aq) 88 g was added and the reaction heated to 80 °C overnight. The reaction was then cooled to room temperature and acidified to a pH~2.5 using concentrated HCl. The reaction mixed was then extracted with hexanes and the organic layer washed with water, then brine. Lastly, the hexanes layer was dried over sodium sulfate and the organic layer washed with water, then brine. This was used without further purification. NMR (400 MHz, CDCl₃) δ 0.86 (m, 18H), 1.00 - 1.26 (m, 21H), 1.95 (m, 4H), 11.58 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 18.06, 19.60, 22.77, 22.87, 24.83, 28.11, 31.89, 33.03, 33.41, 36.98, 39.41.
2-(3,7-dimethyloctyl)-5,9-dimethyldecan-1-ol (S3). LiAlH₄ (95%, 672 mg, 16.81 mmol) was suspended in 16 mL of anhydrous THF in a three-neck round bottom flask fitted with an addition funnel and a condenser. Then a solution of S2 (5.96 g, 16.81 mmol) in THF (16 mL) was added drop wise at 0°C. After the addition, the reaction was heated to reflux for 3 hours and then cooled back to 0°C. The reaction was diluted with 25 mL of diethyl ether and then the excess LiAlH₄ quenched by adding 1 mL of water followed by 1 mL of 15% NaOH (aq). The reaction was washed with water and the organic layer dried over MgSO₄. The solvent was removed in vacuo to afford the product (5.00 g, 91%). This was used without further purification.

NMR (400 MHz, CDCl₃) δ 0.85 (m, 17H), 1.07 - 1.29 (m, 24H), 1.53 (m, 2H), 3.53 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 19.93, 19.98, 22.86, 22.96, 25.03, 28.21, 28.30, 28.48, 28.51, 33.37, 33.41, 34.30, 34.35, 34.39, 37.43, 37.45, 37.50, 39.57, 41.35.

2-(2-(3,7-dimethyloctyl)-5,9-dimethyldecyl)isoindoline-1,3-dione (S4). A three-neck round bottom flask fitted with an addition funnel and a condenser was charged with triphenyl phosphine (5.16 g, 19.69 mmol), S3 (6.34 g, 19.69 mmol) and phthalimide (4.19 g, 19.69 mmol). Then 20 mL of anhydrous ether was added and the reaction cooled to 0°C and purged with Ar. Then a solution of DIAD (2.90 g, 19.69 mmol) was added and the reaction allowed to warm up to room temperature. After stirred overnight the reaction was filtered and washed with water. The solvent was removed in vacuo and the crude solid purified by column chromatography (1:1 hexanes/ethyl ether) to afford the product (4.76 g, 53%).

NMR (400 MHz, CDCl₃) δ 0.84 (m, 19H), 1.07 - 1.29 (m, 25H), 1.51 (m, 3H), 1.96 (m, 1H), 3.66 (d, J = 4.0 Hz, 2H), 7.69 (d, J = 2 Hz, 2H), 7.84 (d, J = 2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 19.83, 19.84, 19.90, 19.91, 21.78, 22.80, 22.90, 24.88, 22.90, 24.93, 28.13, 28.83, 28.89, 29.01, 33.20, 33.23, 33.49, 33.51, 33.59, 37.25, 37.28, 37.42, 37.45, 37.52, 39.48, 39.50, 42.52, 123.30, 132.28, 133.98, 168.83.

2-(3,7-dimethyloctyl)-5,9-dimethyldecan-1-amine (S5). A three-neck round bottom flask fitted with an addition funnel and a condenser was charged with S4 (2.13 g, 4.67 mmol) and 10 mL of absolute ethanol. Then a solution of hydrazine hydrate (55%, 821 mg, 14.02 mmol) in 2 mL of ethanol is added and the reaction is heated at reflux for 48 hours. After that time 15 mL of 6M HCl and 5 mL of ethanol was added and the reaction refluxed for another hour. The reaction was filtered, washed with water and then concentrated in vacuo. The crude solid was taken up into 25 mL of NaOH and extracted with ether (2 x 150 mL). The organic layer was dried over MgSO₄ and concentrated to afford the product in near quantitative yield (1.50 g, 99%). The product can be distilled. NMR (400 MHz, CDCl₃) δ 0.86 (m, 18H), 1.06 - 1.28 (m, 25H), 2.51 (m, 2H), 2.56 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 19.95, 19.99, 22.84, 22.93, 25.01, 28.19, 28.86, 29.04, 29.92, 33.36, 33.40, 34.17, 34.20, 34.24, 34.27, 34.44, 37.47, 37.49, 39.56, 41.73, 45.33, 45.50, 45.67.
Figure S17: $^1$H NMR spectra of compound 7
Figure S18: $^{13}$C NMR spectra of compound 7
Figure S19: $^1$H spectra of compound 8
Figure S20: $^{13}$C NMR spectra of compound 8
Figure S21: $^{31}$P NMR spectra of compound 8
Figure S22: CIGARAD spectra of compound 8
Figure S23: HSQC spectra of compound 8
Figure S24: $^1$H NMR spectra of compound 9
Figure S25: $^{13}$C NMR spectra of compound 9
Figure S26: $^1$H NMR spectra of compound 10
Figure S27: $^{13}$C NMR spectra of compound 10
Figure S28: $^1$H NMR spectra of compound 11
Figure S29: $^{13}$C NMR spectra of compound 11
Figure S30: $^1$H spectra of compound 12
Figure S27: $^{13}$C spectra of compound 12
Figure S28: $^{31}$P spectra of compound 12
Figure S29: COSY spectra of compound 12
Figure S29: HSQC spectra of compound 11
Figure S30: CIGARAD spectra of compound 11
Figure S31: $^1$H NMR spectra of compound 12
Figure S32: $^{13}$C NMR spectra of compound 12
Figure S33: $^1$H NMR spectra of compound 13
Figure S34: $^{13}$C NMR spectra of compound 13
Figure S35: $^1$H NMR spectra of compound 14