Electronic Supplementary Information

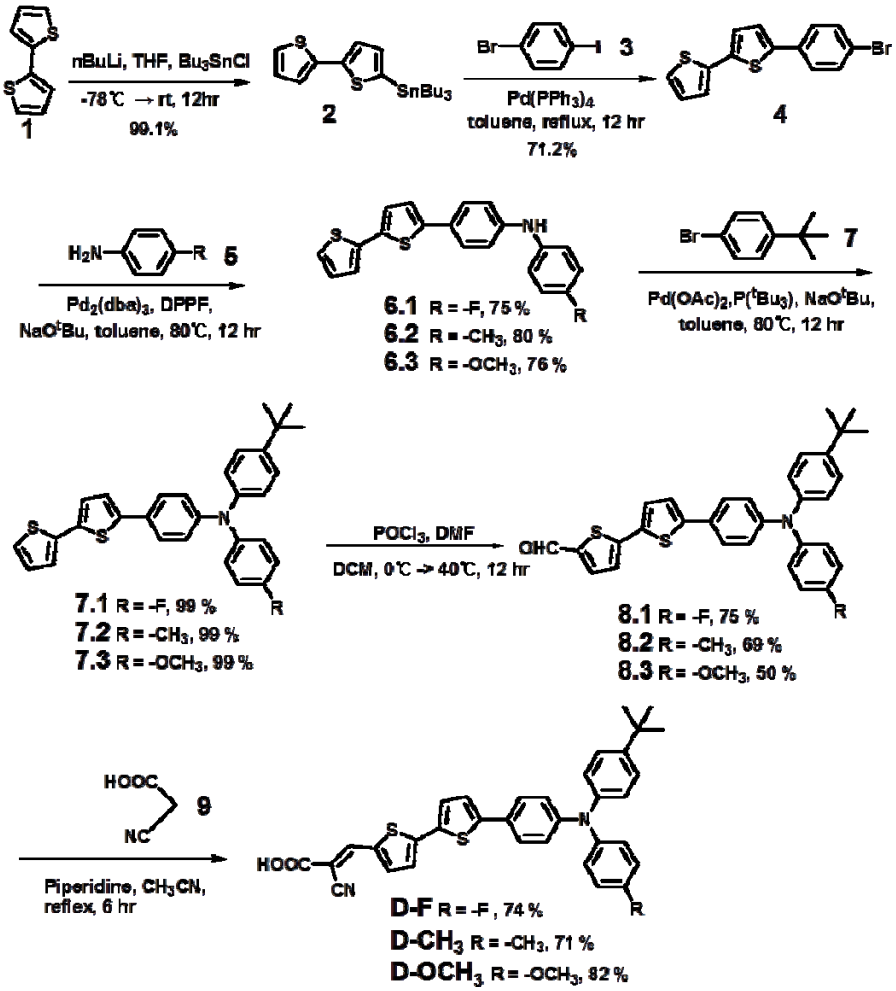
for

Chemical Compatibility Between Hole Conductors and Organic Dyes Enhancing Photovoltaic Performance in Solid-State Dye-Sensitized Solar Cells

Young Soo Kwon,†[a] Jongchul Lim,†[a] Inwoo Song,[a] In Young Song,[a] Won Suk Shin,[b] Sang-Jin Moon,[b] and Taiho Park*[a]

[a] Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea
[b] Energy Materials Research Center, Korea Research Institute of Chemical Technology 100 Jang-dong, Yuseong-gu, Daejeon, 305-600, Korea.

Contents



Scheme S1. Synthetic scheme for organic dyes **D-F**, **D-CH$_3$**, and **D-OCH$_3$**.

1. Synthesis of Organic Dyes

5-Trimethylstannyl[2,2']bithiophenyl (2). 2.2'-bithiophene (1 g, 6.02 mmol) was dissolved in dried THF (10 mL) at –78 ^{o}C under nitrogen atmosphere and stirred for 20 minutes. n-BuLi (1.6 M in hexane, 3.76 mL, 6.02 mmol) was then added to the solution dropwise while the temperature increased to room temperature slowly followed by react for 30 minutes. Cooling to –78 ^{o}C again, tributyltinchloride (1.73 mL, 6.28 mmol) was added dropwise. After reaction for 12 hours water was poured into the solution and extracted with ether for 2 times. Dried with $MgSO_4$ and evaporate solvent under vacuum gave dark brown liquid (2.7 g, 99.1 %). The crude product was used for next step without any purification. Rf = 0.74 (9:1 hexane : EA). ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.29 (d, 1H), 7.21-7.16 (m, 2H), 7.06 (d, 1H), 7.00 (dd, 1H), 1.69-1.52 (m, 6H), 1.41-1.28 (m, 6H), 1.15-1.05 (m, 6H) and 0.96-0.84 (t, 9H). 13C NMR (300 MHz; $CDCl_3$): δ 136.10, 127.76, 125.05, 124.76, 124.40,

123.82, 123.51, 29.03, 27.31, 13.70, 10.96.

5-(4-bromophenyl)-[2,2']bithiophenyl (4) To a solution of **2** (8.05 g, 17.67 mmol) and 1-bromo-4-iodobenzene (5 g, 17.67 mmol) in toluene was added a solution of $Pd(PPh_3)_4$ (204 mg, 0.18 mmol) in THF (15mL). After reflux for 13 hours, water was poured into the solution and organic layer was extracted with dichloromethane (DCM) 2 times. Washing with NaOH and dried with $MgSO_4$ followed by evaporation of solvent under vacuum. Soxhlet extraction with hexane for purification and dried in vacuum gave light green solid product. (4.04 g, 71.2 %). R_f = 0.34 (9:1 hexane : EA). ^{1}H NMR (300 MHz; DMSO-d_6): δ 7.65-7.57 (m, 4H), 7.55-7.53 (m, 2H), 7.36 (dd, 1H), 7.32 (d, 1H), and 7.10 (dd, 1H).

[(4-[2,2']Bithiophenyl-5-yl-phenyl)-(4-fluoro-phenyl)] amine (6.1) To a solution of 4-fluoroaniline (1.94 g, 17.43 mmol) and **4** (4g, 12.45mmol), NaO^{t}Bu (1.44g, 14.94 mmol) in toluene was added a solution of $Pd_2(dba)_3$ (74.7 mg, 0.12 mmol) and DPPF (138.1 mg, 0.25 mmol) in toluene(15 mL) at 80 ^{o}C. After reflux for 12 hours, water was poured into the solution and organic layer was extracted with dichloromethane 2 times followed by treatment of brine and evaporation of solvent under vacuum. Recrystallization with methanol / dichloromethane and dried in vacuum gave green solid product. (3.30 g, 75.4 %). R_f = 0.23 (9:1 hexane : EA). ^{1}H NMR (300 MHz; DMSO-d_6): δ 8.35 (s, 1H), 7.52-7.46 (m, 3H), 7.29-7.27 (m, 2H), 7.24 (d, 1H), 7.13-7.06 (m, 5H), 7.02 (d, 2H).

[(4-[2,2']Bithiophenyl-5-yl-phenyl)-p-tolyl]amine (6.2) To a solution of toluidine (1.87g, 17.43 mmol) and **4** (4 g, 12.45 mmol), NaO^{t}Bu (1.44 g, 14.94 mmol) in toluene was added a solution of $Pd_2(dba)_3$ (74.7 mg, 0.12 mmol) and DPPF (138.1 mg, 0.25 mmol) in toluene (15 mL) at 80 ^{o}C. After reflux for 12 hours, water was poured into the solution and organic layer was extracted with dichloromethane 2 times followed by treatment of brine and evaporation of solvent under vacuum. Recrystallization with methanol / dichloromethane and dried in vacuum gave brown solid product. (3.45 g, 79.7 %). R_f = 0.27 (9:1 hexane : EA). ^{1}H NMR (300 MHz; DMSO-d_6): δ 8.26 (s, 1H), 7.50-7.47 (m, 3H), 7.29-7.26 (m, 2H), 7.24 (d, 1H), 7.10-7.06 (m, 3H), 7.01 (d, 4H), 2.23 (s, 3H).

[(4-[2,2']Bithiophenyl-5-yl-phenyl)-(4-methoxy-phenyl)]amine (6.3) To a solution of anisidine (2.15 g, 17.43 mmol) and **4** (4 g, 12.45 mmol), NaO^{t}Bu (1.44 g, 14.94 mmol) in toluene was added a solution of $Pd_2(dba)_3$ (74.7 mg, 0.12 mmol) and DPPF (138.1 mg, 0.25 mmol) in toluene (15 mL) at 80 ^{o}C. After reflux for 12 hours, water was poured into the solution and organic layer was extracted with dichloromethane 2 times followed by treatment of brine and evaporation of solvent under vacuum. Recrystallization with methanol /

dichloromethane and dried in vacuum gave brown solid product. (3.45 g, 76.4 %). R_f = 0.19 (9:1 Hexane : EA). ^{1}H NMR (300 MHz; DMSO-d_6): δ 8.12 (s, 1H), 7.48-7.44 (m, 3H), 7.27-7.23 (m, 3H), 7.09-7.05 (m, 3H), 6.91 (dd, 4H), 3.72 (s, 3H).

[(4-[2,2']Bithiophenyl-5-yl-phenyl)-(4-tert-butyl-phenyl)-(4-fluoro-phen-yl)]amine (7.1) To a solution of 1-bromo-4-tert-butyl-benzene (0.50 g, 2.35 mmol), **6.1** (0.81 g, 2.30 mmol) and NaO^{t}Bu (0.287 g, 2.99 mmol) was added to a solution of $Pd(OAc)_2$ (10.33 mg, 0.046 mmol) and P(^{t}Bu)$_3$ (18.61 mg, 0.092 mmol) in toluene (7 mL). After reaction for 12 hours water was poured into the solution and organic layer was extracted with toluene 2 times. Dried with $MgSO_4$ and evaporated under vacuum. Column chromatography (95:5 hexane : EA) yielded light yellow solid (1.1 g, 99.6 %). R_f = 0.68 (9:1 hexane : EA). ^{1}H NMR (300 MHz; DMSO-d_6): δ 7.53 (dd, 2H), 7.49 (dd, 1H), 7.36-7.32 (m, 3H), 7.30 (dd, 1H), 7.26 (d, 1H), 7.18-7.13 (m, 2H), 7.10(d, 1H), 7.09-7.05 (m, 2H), 6.98 (dd, 2H), 6.90 (dd, 2H), 1.27 (s, 9H).

[(4-[2,2']Bithiophenyl-5-yl-phenyl)-(4-tert-butyl-phenyl)-p-tolyl]amine (7.2) To a solution of 1-bromo-4-tert-butyl-benzene (0.50 g, 2.35 mmol), **6.2** (0.80 g, 2.30 mmol) and NaO^{t}Bu (0.287 g, 2.99 mmol) was added to a solution of $Pd(OAc)_2$ (10.33 mg, 0.046 mmol) and P(^{t}Bu)$_3$ (18.61 mg, 0.092 mmol) in toluene (7 mL). After reaction for 12 hours water was poured into the solution and organic layer was extracted with toluene 2 times. Dried with $MgSO_4$ and evaporated under vacuum. Column chromatography (95:5 hexane : EA) yielded light yellow solid (1.1 g, 99.7 %). R_f = 0.66 (9:1 hexane : EA). ^{1}H NMR (300 MHz; DMSO-d_6): δ 7.53-7.48 (m, 3H), 7.35-7.29 (m, 4H), 7.26 (d, 1H), 7.13 (d, 2H), 7.08 (dd, 1H), 6.98-6.93 (m, 4H), 6.89 (dd, 2H), 2.27 (s, 3H), 1.27 (s, 9H).

[(4-[2,2']Bithiophenyl-5-yl-phenyl)-(4-tert-butyl-phenyl)-(4-methoxy-phen-yl)]amine (7.3) To a solution of 1-bromo-4-tert-butyl-benzene (0.50 g, 2.35 mmol), **6.3** (0.84 g, 2.30 mmol) and NaO^{t}Bu (0.287 g, 2.99 mmol) was added to a solution of $Pd(OAc)_2$ (10.33 mg, 0.046 mmol) and P(^{t}Bu)$_3$ (18.61 mg, 0.092 mmol) in toluene (7 mL). After reaction for 12 hr water was poured into the solution and organic layer was extracted with toluene 2 times. Dried with $MgSO_4$ and evaporated under vacuum. Column chromatography (95:5 hexane : EA) yielded light yellow solid (1.13 g, 99.6 %). R_f = 0.56 (9:1 hexane : EA). ^{1}H NMR (300 MHz; DMSO-d_6): δ 7.50-7.47 (m, 3H), 7.33-7.24 (m, 5H), 7.10-7.02 (m, 3H), 6.97-6.91 (m, 4H), 6.84 (dd, 2H), 3.74 (s, 3H), 1.26 (s, 9H).

5'-{4-[(4-tert-Butyl-phenyl)-(4-fluoro-phenyl)-amino]-phenyl}-[2,2']bithio-phenyl-5-carbaldehyde (8.1) $POCl_3$ (0.95 g, 6.20 mmol) was slowly dissolved in DMF (0.61 g, 8.27

mmol) at 0 ^{o}C under nitrogen atmosphere. (colorless liquid became orange colored viscous liquid). After 1 hour reaction, temperature increased to room temperature followed by adding **7.1** (1 g, 2.07 mmol) in dichloromethane (12 mL) under N_2. Temperature increased to 40 ^{o}C and reacted for 12 hours. The reaction was quenched by adding aqueous sodium acetate (0.84 g) and extracted with dichloromethane for 2 times. Crude product was purified with column chromatography (9:1 hexane : EA) and dried under vacuum gave red solid pure product. (0.79 g, 74.5 %). R_f = 0.24 (9:1 hexane : EA). ^{1}H NMR (500 MHz; DMSO-d_6): δ 9.88 (s, 1H), 7.98 (d, 1H), 7.59-7.56 (m, 3H), 7.52 (d, 1H), 7.43 (d, 1H), 7.36 (dd, 2H) 7.20-7.16 (m, 2H), 7.13-7.07 (m, 2H), 7.00 (dd, 2H), 6.91 (dd, 2H), 1.27 (s, 9H). ^{13}C NMR (500 MHz; DMSO-d_6): δ 184.15, 160.06, 158.14, 148.23, 146.74, 146.10, 145.75, 144.43, 143.51, 141.42, 139.70, 133.61, 128.75, 127.48, 127.42, 127.12, 126.95, 126.37, 125.28, 124.67, 124.50, 121.91, 117.03, 116.85, 34.58, 31.65.

5'-{4-[(4-tert-Butyl-phenyl)-p-tolyl-amino]-phenyl}-[2,2']bith-iophenyl-5-carbaldehyde (8.2) $POCl_3$ (0.58 g, 3.75 mmol) was slowly dissolved in DMF (0.37 g, 5.00 mmol) at 0 ^{o}C under N_2. (colorless liquid became orange colored viscous liquid). After 1 hour reaction, temperature increased to room temperature followed by adding **7.2** (0.6 g, 1.25 mmol) in dichloromethane (12 mL) under N_2. Temperature increased to 40 ^{o}C and reacted for 12 hours. The reaction was quenched by adding aqueous sodium acetate (0.84 g) and extracted with dichloromethane for 2 times. Crude product was purified with column chromatography (9:1 hexane : EA) and dried under vacuum gave red solid pure product. (0.44 g, 68.5 %). R_f = 0.24 (9:1 hexane : EA). ^{1}H NMR (500 MHz; DMSO-d_6): δ 9.89 (s, 1H), 8.00 (d, 1H), 7.60-7.56 (m, 3H), 7.53 (d, 1H), 7.43 (d, 1H), 7.36 (dd, 2H) 7.17 (d, 2H), 7.02-6.98 (m, 4H), 6.92 (dd, 2H), 2.30 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (500 MHz; DMSO-d_6): δ 184.14, 148.36, 146.46, 146.14, 145.88, 144.60, 144.59, 141.38, 139.72, 133.70, 133.48, 130.72, 128.76, 127.03, 126.82, 126.05, 125.60, 125.25, 124.63, 124.37, 121.81, 34.56, 31.67, 20.92.

5'-{4-[(4-tert-Butyl-phenyl)-(4-methoxy-phenyl)-amino]-phenyl}-[2,2']bithio-phenyl-5-carbaldehyde (8.3) $POCl_3$ (0.93 g, 6.05 mmol) was slowly dissolved in DMF (0.59 g, 8.07 mmol) at 0 ^{o}C under N_2. (colorless liquid became orange colored viscous liquid). After 1 hour reaction, temperature increased to room temperature followed by adding **7.3** (1 g, 2.02 mmol) in dichloromethane (12 mL) under N_2. Temperature increased to 40 ^{o}C and reacted for 12 hours. The reaction was quenched by adding aqueous sodium acetate (0.82 g) and extracted with dichloromethane for 2 times. Crude product was purified with column chromatography (9:1 hexane : EA) and dried under vacuum gave red solid pure product. (0.53 g, 50.1 %). R_f =

0.12 (9:1 hexane : EA). ^{1}H NMR (500 MHz; DMSO-d_6): δ 9.88 (s, 1H), 7.99 (d, 1H), 7.58 (d, 1H), 7.55 (dd, 2H), 7.52 (d, 1H), 7.41 (d, 1H) 7.35 (dd, 2H), 7.08 (dd, 2H), 7.00 (dd, 2H), 6.96 (dd, 2H), 6.86 (dd, 2H), 3.77 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (500 MHz; DMSO-d_6): δ 184.11, 156.86, 148.65, 146.19, 146.01, 144.64, 141.33, 139.81, 139.71, 133.31, 128.74, 128.10, 126.98, 126.76, 125.45, 125.18, 124.20, 120.74, 115.65, 55.76, 34.53, 31.67.

3-(5'-{4-[(4-tert-Butyl-phenyl)-(4-fluoro-phenyl)-amino]-phenyl}-[2,2']bithio-phenyl-5-yl)-2-cyano-acrylic acid (D-F) Reflux the mixture of **8.1** (0.5 g, 0.98 mmol), cyanoacetic acid (124.7 mg, 1.47 mmol), piperidine (83.2 mg, 0.98 mmol) in acetonitrile (8 mL) for 6 hours. Solvent was removed under vacuum and extracted with dichloromethane for 2 times followed by dried with $MgSO_4$. Crude product was purified by column chromatography (hexane → DCM → methanol) gave red solid product. (0.42 g, 74.2 %). R_f = 0.15 (9:1 DCM : methanol). ^{1}H NMR (500 MHz; DMSO-d_6): δ 8.05 (s, 1H), 7.64 (d, 1H), 7.56 (dd, 2H), 7.44 (d, 1H), 7.41 (d, 1H), 7.39 (d, 1H) 7.35 (dd, 2H), 7.18-7.14 (m, 2H), 7.12-7.07 (m, 2H), 6.99 (dd, 2H), 6.89 (dd, 2H), 1.27 (s, 9H). ^{13}C NMR (500 MHz; DMSO-d_6): δ 148.01, 146.66, 144.49, 143.56, 141.76, 140.54, 136.68, 136.05, 134.15, 127.42, 127.35, 126.94, 126.64, 124.61, 124.39, 122.01, 119.72, 117.02, 116.84, 34.58, 31.66. FAB Mass m/z: 579.1573 [M+].

3-(5'-{4-[(4-tert-Butyl-phenyl)-p-tolyl-amino]-phenyl}-[2,2'] bithiophenyl-5-yl)-2-cyano-acrylic acid (D-CH_3) Reflux the mixture of **8.2** (0.39 g, 0.77 mmol), cyanoacetic acid (98 mg, 1.15 mmol), piperidine (65.4 mg, 0.77 mmol) in acetonitrile (6 mL) for 6 hours. Solvent was removed under vacuum and extracted with dichloromethane for 2 times followed by dried with $MgSO_4$. Crude product was purified by column chromatography (hexane → DCM → methanol) gave red solid product. (0.35 g, 79.4 %). R_f = 0.27 (9:1 DCM : methanol). ^{1}H NMR (500 MHz; DMSO-d_6): δ 8.08 (s, 1H), 7.65 (d, 1H), 7.54 (dd, 2H), 7.45 (d, 1H), 7.41 (d, 1H), 7.38 (d, 1H) 7.33 (dd, 2H), 7.14 (d, 2H), 7.00-6.94 (m, 4H), 6.88 (dd, 2H), 2.27(s, 3H), 1.27 (s, 9H). ^{13}C NMR (500 MHz; DMSO-d_6): δ 148.16, 146.38, 144.71, 144.65, 144.59, 135.90, 133.99, 133.57, 130.70, 127.42, 126.89, 126.81, 126.29, 125.57, 124.61, 124.56, 124.27, 121.90, 119.60, 34.56, 31.67, 20.91. FAB Mass m/z: 575.1823 [M+].

3-(5'-{4-[(4-tert-Butyl-phenyl)-(4-methoxy-phenyl)-amino]-phenyl}-[2,2']bithiophenyl-5-yl)-2-cyano-acrylic acid (D-OCH_3) Reflux the mixture of **8.3** (0.49 g, 0.93 mmol), cyanoacetic acid (118.2 mg, 1.34 mmol), piperidine (79 mg, 0.93 mmol) in acetonitrile (8 mL) for 6 hours. Solvent was removed under vacuum and extracted with dichloromethane for 2 times followed by dried with $MgSO_4$. Crude product was purified by column

chromatography (hexane → DCM → methanol) gave red solid product. (0.45 g, 82.3 %). R_f = 0.27 (9:1 DCM : methanol). ^{1}H NMR (500 MHz; DMSO-d_6): δ 7.97 (s, 1H), 7.60 (d, 1H), 7.54 (dd, 2H), 7.42 (d, 1H), 7.38 (d, 1H), 7.36 (d, 1H) 7.34 (dd, 2H), 7.07 (dd, 2H), 6.99 (dd, 2H), 6.95 (dd, 2H), 6.85(dd, 2H), 3.76 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (500 MHz; DMSO-d_6): δ 162.30, 156.81, 148.39, 146.07, 144.72, 144.52, 139.89, 139.50, 135.99, 128.08, 127.09, 126.83, 126.75, 125.79, 124.42, 124.11, 120.88, 120.12, 115.64, 55.76, 34.53, 31.68. FAB Mass m/z: 591.1772 [M+].

2. ^{1}H NMR spectrum of organic dyes

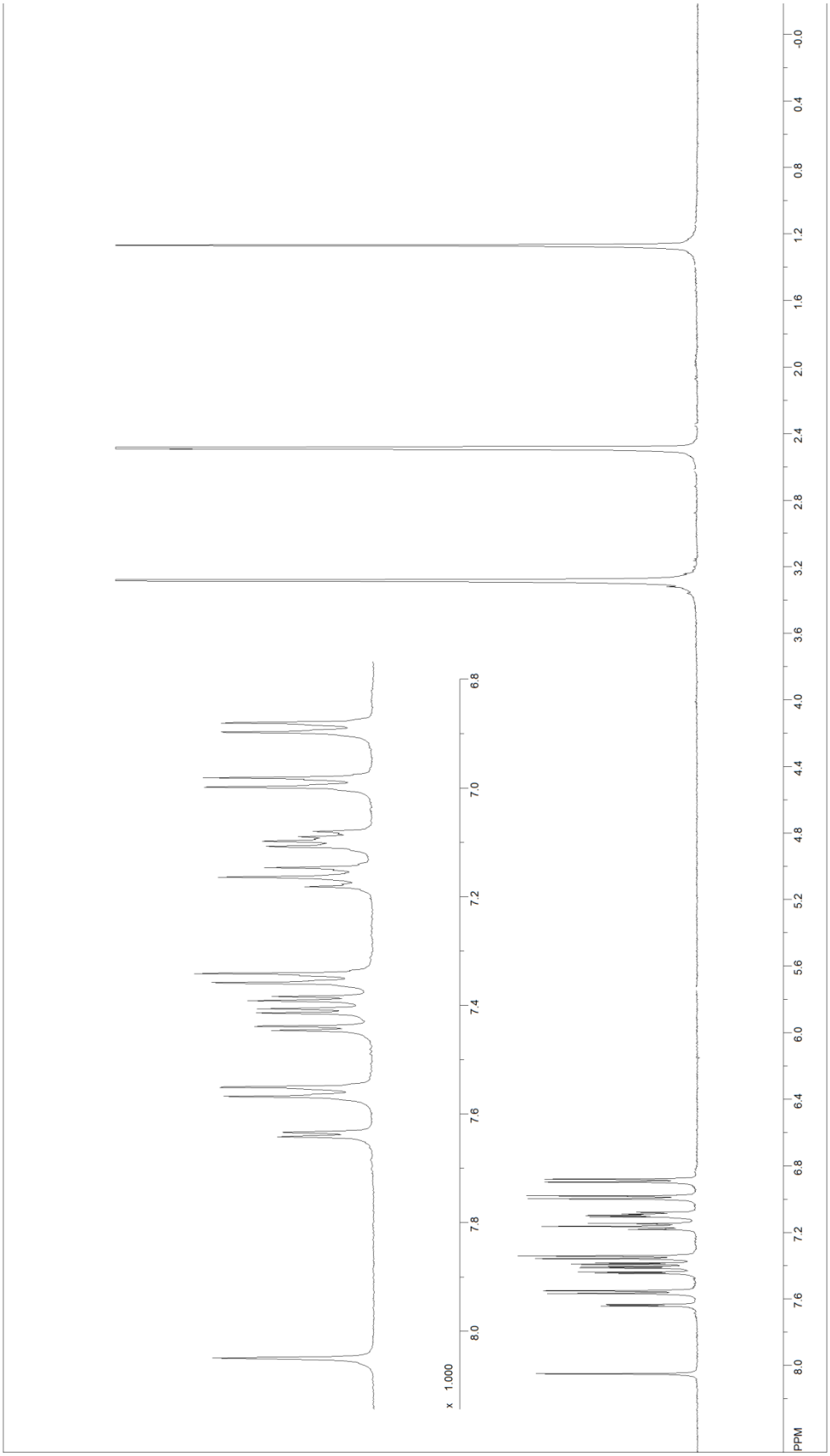


Figure S1. ^{1}H NMR spectrum of **D-F**

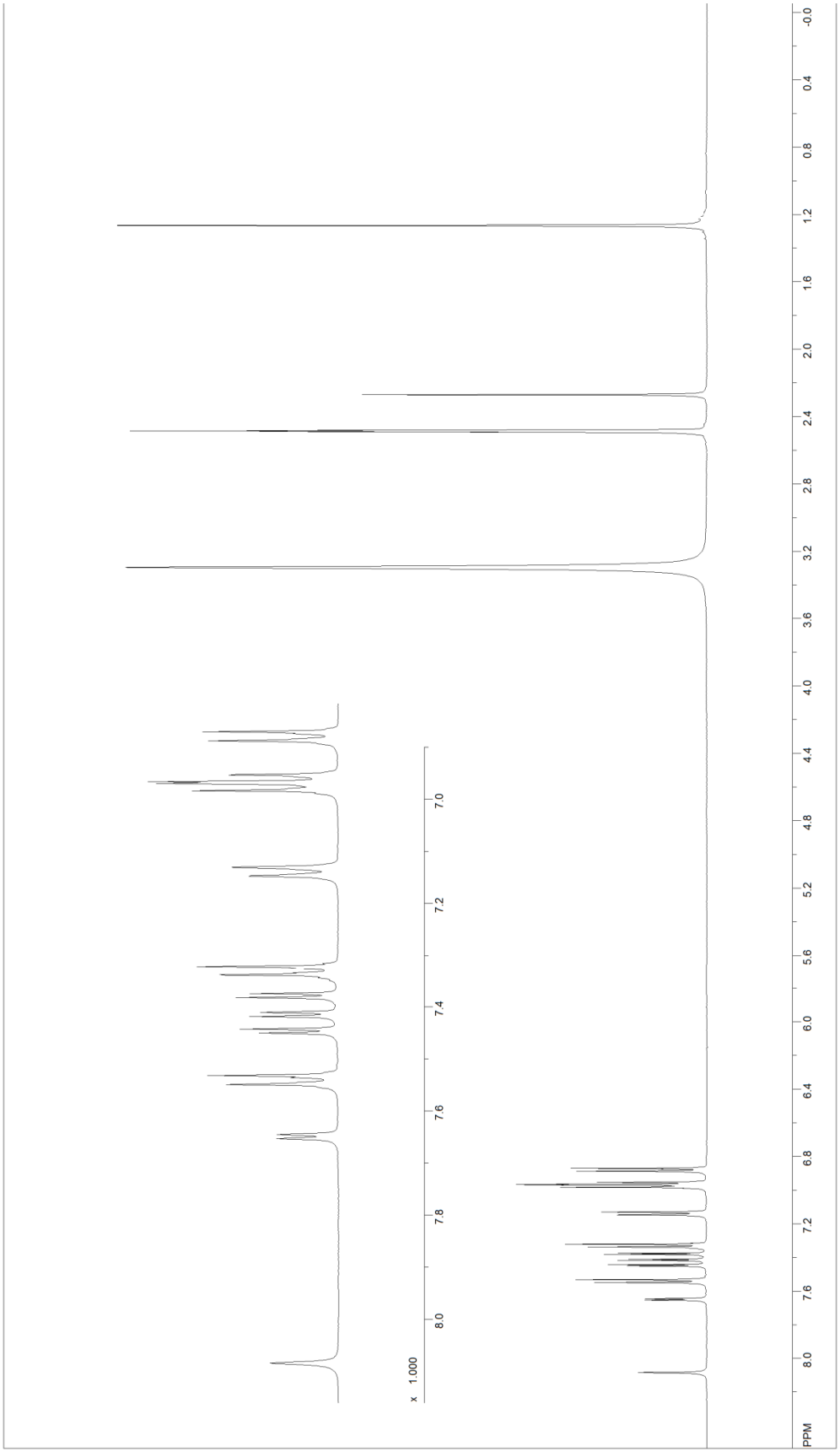


Figure S2. ^{1}H NMR spectrum of **D-CH$_3$**

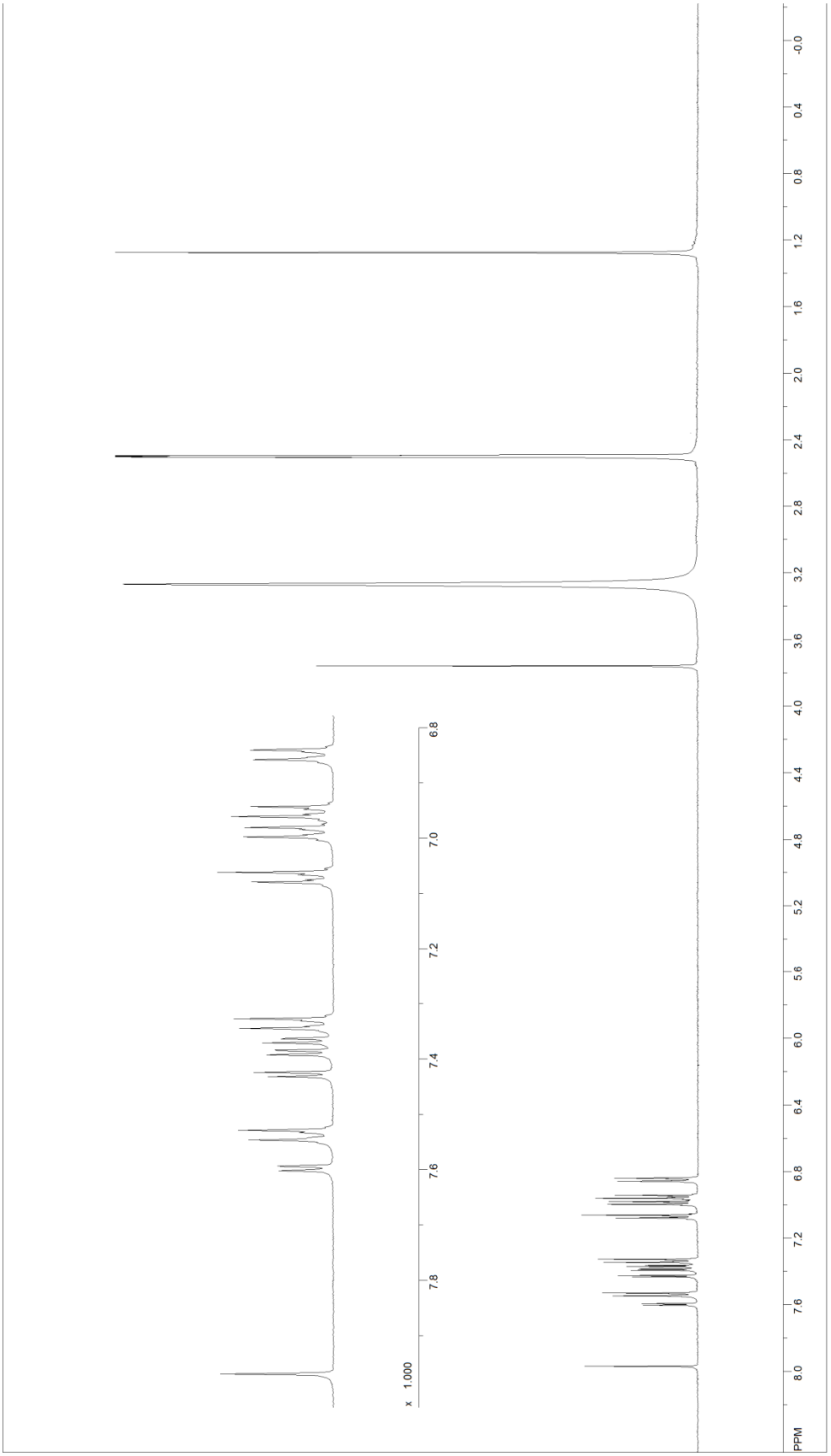


Figure S3. ^{1}H NMR spectrum of **D-OCH$_3$**