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Recombination inhibitive molecular structure of organic dyes for cobalt complex redox electrolytes in dye-sensitised solar cells

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Supporting Information

General methods

^{1}H NMR spectra were recorded on a Bruker Avance400 (400 MHz). ^{13}C NMR spectra were recorded on a Bruker Avance400 (100 MHz). Chemical shifts are denoted in δ-unit (ppm) relative to $CDCl_3$, THF-d_8. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). Column chromatography was performed on silica gel (Kanto, Silica Gel 60N, spherical, 40-50 μm). Most of organic compound was finally purified by the preparative HPLC (YRU-880 detector from SHIMAMURA Tec.) on silica gel (pre-packed column, TSK-gel, silica-60, from TOSOH Co.Ltd). The solvents were distilled and dried, if necessary, by

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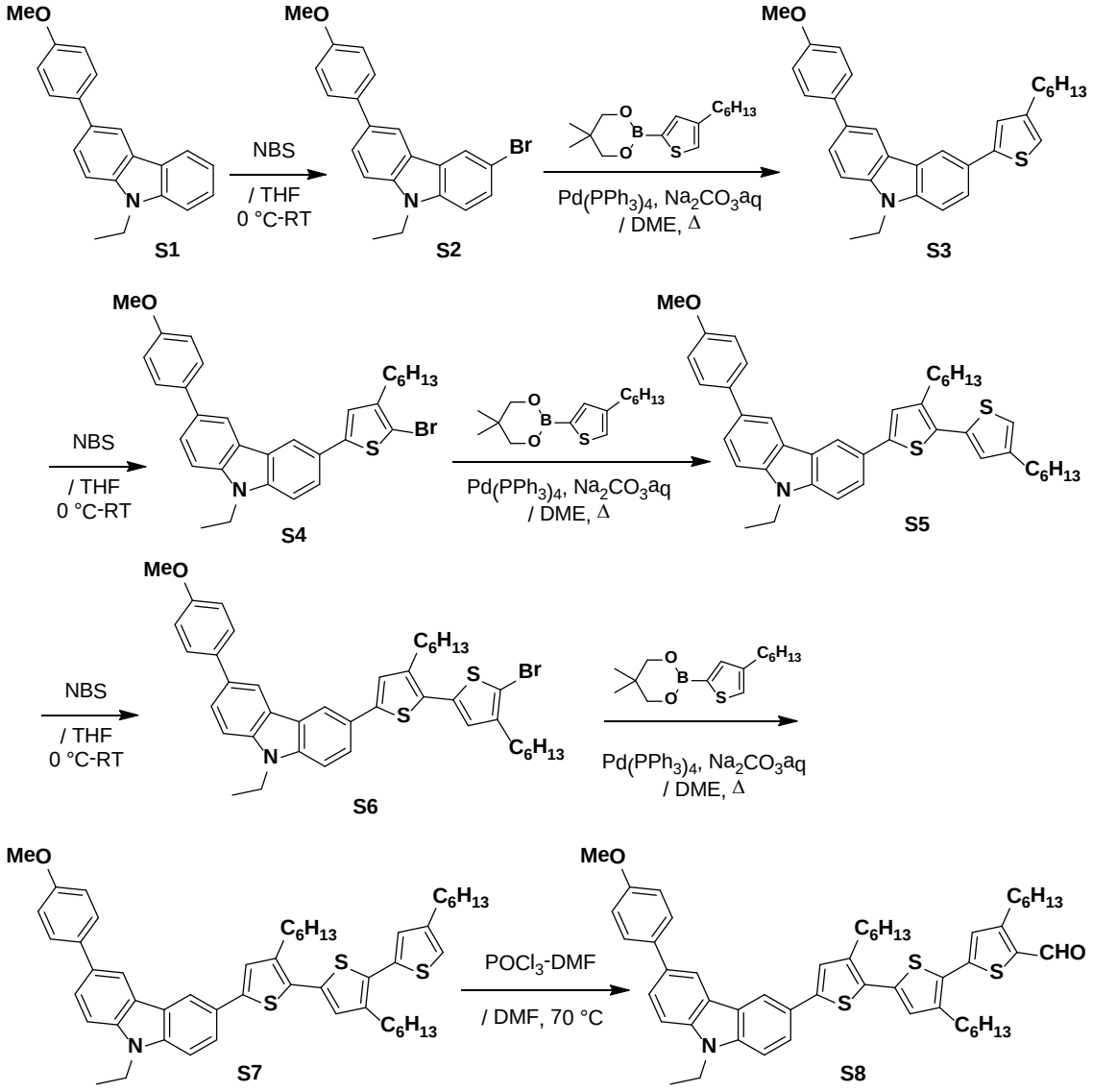
standard methods. Reagents and starting materials were used as obtained from Aldrich, Wako, Kanto Chemical, TCI, Merck. MS spectra were obtained by a Bruker autoflex speed (MALDI-TOF-MS) and a JEOL AccuTOF CS (ESI-TOF-MS). Absorption spectra were measured with a SHIMADZU UV-3101PC. Elemental analyses were measured by a CE Instruments EA1110 automatic elemental analyzer.

Synthesis



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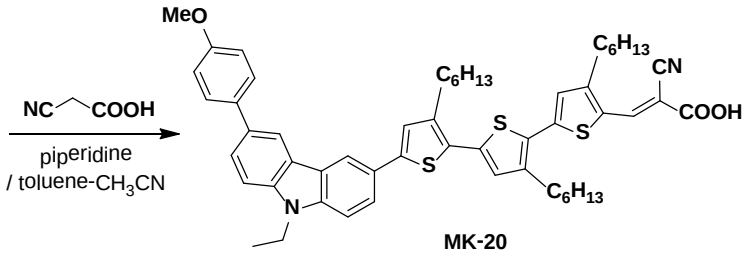

Scheme S1. Synthetic route for **MK-20**

***N*-ethyl-3-bromo-6-*p*-methoxyphenyl-9H-carbazole S2.** To the solution of *N*-ethyl-3-*p*-methoxyphenyl-9*H*-carbazole **S1** (602 mg, 2.00 mmol) in THF (15 mL) was added *N*-bromosuccinimide (392 mg, 2.20 mmol). The reaction mixture was stirred at room temperature for 1 h, and quenched with 10% aqueous solution of Na_2CO_3 and extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 10/1) to obtain bromide **S2** (638 mg, 1.68 mml, 84%) as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (1H, d, *J* = 1.9 Hz), 8.20 (1H, d, *J* = 1.7 Hz), 7.69 (1H, dd, *J* = 8.5, 1.7 Hz), 7.62 (2H, d, *J* = 8.8 Hz), 7.55 (1H, dd, *J* = 8.6, 1.9 Hz), 7.43 (1H, d, *J* = 8.5 Hz), 7.28 (1H, d, *J* = 8.6 Hz), 7.03 (2H, d, *J* = 8.8 Hz), 4.34 (2H, q, *J* = 7.2 Hz), 3.89 (3H, s), 1.43 (3H, t, *J* = 7.2 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 139.3, 138.9, 134.4, 132.5, 128.3, 128.2, 125.6, 124.8, 123.1, 122.4, 118.6, 114.2, 111.6, 110.0, 108.9, 55.4, 37.7, 13.8, Anal. Calcd for $C_{21}H_{18}BrNO$: C, 66.33; H, 4.77; N, 3.68. Found. C, 66.28; H, 4.53; N, 3.53.

***N*-Ethyl-3-*p*-methoxyphenyl-6-(4-*n*-hexylthiophen-2-yl)-9*H*-carbazole S3.** A mixture of *N*-ethyl-3-bromo-6-*p*-methoxyphenyl-9*H*-carbazole **S2** (220 mg, 0.58 mmol), 4-*n*-hexylthiophene-2-boronic acid ester (210 mg, 0.75 mmol), tetrakis(triphenylphosphine)palladium (35 mg, 0.03 mmol) and 3 mL of 10% aqueous solution of Na_2CO_3 in dimethoxyethane (5 mL) was refluxed for 12 h. After cooling, H_2O was added and the reaction mixture was extracted with EtOAc three times.

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The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain a monothiophene adduct **S3** (249 mg, 0.53 mmol, 92%) as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (1H, d, *J* = 1.8 Hz), 8.33 (1H, d, *J* = 1.8 Hz), 7.74 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.68 (2H, d, *J* = 8.7 Hz), 7.43 (1H, d, *J* = 8.5 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.24 (1H, d, *J* = 1.2 Hz), 7.05 (2H, d, *J* = 8.7 Hz), 6.88 (1H, d, *J* = 1.2 Hz), 4.35 (2H, q, *J* = 7.2 Hz), 3.90 (3H, s), 2.68 (2H, br t, *J* = 7.7 Hz), 1.77-1.69 (2H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.44-1.35 (10H, m), 0.96 (3H, t, *J* = 7.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 145.2, 144.2, 139.8, 139.5, 134.6, 132.2, 128.2, 126.0, 125.1, 124.2, 123.43, 123.42, 123.38, 118.5, 118.2, 117.6, 114.2, 108.8, 108.7, 55.3, 37.7, 31.7, 30.7, 30.4, 29.1, 29.1, 22.6, 14.1, 13.8. Anal. Calcd for $C_{31}H_{33}NOS$: C, 79.62; H, 7.11; N, 3.00; S, 6.86. Found. C, 79.13; H, 6.58; N, 2.95; S, 6.81.

***N*-Ethyl-3-*p*-methoxyphenyl-6-(5-bromo-4-*n*-hexylthiophen-2-yl)-9*H*-carbazole S4.** The bromination of 9-ethyl-3-*p*-*n*-methoxyphenyl-6-(4-*n*-hexylthiophen-2-yl)-9*H*-carbazole **S3** (239 mg, 0.51 mmol) with *N*-bromosuccinimide (100 mg, 0.56 mmol) in THF (5 mL) was carried out in a similar manner to that of **S2**. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bromide **S4** (277 mg, 0.51 mmol, 99%) as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (1H, d, *J* = 1.8 Hz), 8.26 (1H, d, *J* = 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.65 (2H, d, *J* = 8.7 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.43 (1H, d, *J* = 8.5 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.24 (1H, d, *J* = 1.2 Hz), 7.05 (2H, d, *J* = 8.7 Hz), 6.88 (1H, d, *J* = 1.2 Hz), 4.35 (2H, q, *J* = 7.2 Hz), 3.90 (3H, s), 2.68 (2H, br t, *J* = 7.7 Hz), 1.77-1.69 (2H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.44-1.35 (10H, m), 0.96 (3H, t, *J* = 7.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 145.0, 143.0, 139.9, 139.5, 134.5, 132.3, 128.2, 125.3, 125.1, 123.8, 123.4, 123.2, 122.8, 118.5, 117.4, 114.2, 108.8, 106.5, 55.3, 37.7, 31.7, 29.7, 29.0, 22.6, 14.1, 13.8. Anal. Calcd for $C_{31}H_{32}BrNOS$: C, 68.12; H, 5.90; N, 2.56; S, 5.87.

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Found. C, 66.85; H, 5.18; N, 2.47; S, 6.14, HRMS (MALDI) Calcd for $C_{31}H_{32}BrNOS$: 545.1388; found: m/z 545.1417.

***N*-Ethyl-3-*p*-methoxyphenyl-6-(3,4'-di-*n*-hexyl[2,2']bithiophen-5-yl)-9*H*-carbazole S5.** The Suzuki-coupling reaction of bromide **S4** (230 mg, 0.42 mmol) with 4-*n*-hexylthiophene-2-boronic acid ester (153 mg, 0.55 mmol) existing of $Pd(PPh_3)_4$ (24 mg, 0.02 mmol)as a catalyst in DME (10 mL) was carried out in a smilar manner to that of **S3**. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain bithiophene **S5** (190 mg, 0.30 mmol, 71%) as a slightly yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.73 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.66 (2H, d, *J* = 8.8 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.39 (1H, d, *J* = 8.5 Hz), 7.20 (1H, s), 7.03 (2H, d, *J* = 8.8 Hz), 7.02 (1H, d, *J* = 1.3 Hz), 6.90 (1H, d, *J* = 1.3 Hz), 4.38 (2H, q, *J* = 7.2 Hz), 3.89 (3H, s), 2.81 (2H, br t, *J* = 7.8 Hz), 2.64 (2H, br t, *J* = 7.8 Hz), 1.78-1.63 (4H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.44-1.32 (12H, m), 0.94-0.90 (6H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 143.6, 143.0, 140.3, 139.9, 139.5, 136.2, 134.6, 132.3, 129.3, 128.2, 126.8, 125.5, 125.2, 124.9, 123.9, 123.5, 123.4, 119.5, 118.6, 117.5, 114.2, 108.8, 108.8, 55.4, 37.8, 31.7, 31.7, 30.7, 30.5, 30.4, 29.6, 29.3, 29.0, 22.65, 22.62, 14.1, 14.1, 13.9, Anal. Calcd for $C_{41}H_{47}NOS_2$: C, 77.68; H, 7.47; N, 2.21; S, 10.12. Found. C, 77.52; H, 7.24; N, 2.21; S, 10.95.

***N*-Ethyl-3-*p*-methoxyphenyl-6-(5'-bromo-3,4'-di-*n*-hexyl[2,2']bithiophen-5-yl)-9*H*-carbazole S6.** The bromination of bithiophene **S5** (179 mg, 0.28 mmol) with *N*-bromosuccinimide (55 mg, 0.31 mmol) in THF (3 mL) was carried out in a similar manner to that of **S2**. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain bromide **S6** (199 mg, 0.28 mml, 99%) as a yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (1H, d, *J* = 1.8 Hz), 8.29 (1H, d, *J* = 1.8 Hz), 7.71 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.64

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(2H, d, *J* = 8.5 Hz), 7.45 (1H, d, *J* = 8.5 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.19 (1H, s), 7.03 (2H, d, *J* = 8.5 Hz), 6.86 (1H, s), 4.39 (2H, q, *J* = 7.2 Hz), 3.89 (3H, s), 2.75 (2H, br t, *J* = 7.8 Hz), 2.58 (2H, br t, *J* = 7.8 Hz), 1.75-1.59 (4H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.43-1.30 (12H, m), 0.93-0.89 (6H, m), ^{13}C NMR (100 MHz, acetone-*d*6) δ 159.6, 144.5, 143.4, 141.7, 140.8, 140.4, 137.0, 135.0, 132.9, 128.6, 128.4, 127.0, 125.8, 125.7, 124.4, 124.3, 124.1, 119.0, 118.1, 115.0, 110.0, 100.0, 108.1, 55.5, 38.1, 32.34, 32.31, 31.2, 30.3, 30.2, 30.04, 29.97, 29.6, 23.3, 23. 2, 14.41, 14.40, 14.1. Anal. Calcd for $C_{41}H_{46}BrNOS_2$: C, 69.08; H, 6.50; N, 1.96; S, 9.00. Found. C, 68.69; H, 6.32; N, 1.99; S, 8.36, HRMS (MALDI) Calcd for $C_{41}H_{46}BrNOS_2$: 711.2204; found: m/z 711.2229.

***N*-Ethyl-3-*p*-methoxyphenyl-6-(3,4',4''-tri-*n*-hexyl[2,2',5',2'']terthiophen-5-yl)-9*H*-carbazole S7.** The Suzuki-coupling reaction of bromide **S6** (160 mg, 0.22 mmol) with 4-*n*-hexylthiophene-2-boronic acid ester (80 mg, 0.29 mmol) existing of $Pd(PPh_3)_4$ (13 mg, 0.01 mmol)as a catalyst in DME (3 mL) was carried out in a smilar manner to that of **S3**. The crude product was purified by column chromatography (hexane/EtOAc = 10/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain terthiophene **S7** (166 mg, 0.21 mmol, 94%) as a yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 1.8 Hz), 8.31 (1H, d, *J* = 1.8 Hz), 7.73 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.65 (2H, d, *J* = 8.6 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.21 (1H, s), 7.04 (2H, *J* = 8.6 Hz), 7.01 (1H, s), 7.00 (1H, d, *J* = 1.2 Hz), 6.91 (1H, d, *J* = 1.2 Hz), 4.38 (2H, q, *J* = 7.2 Hz), 3.89 (3H, s), 2.84 (2H, br t, *J* = 7.8 Hz), 2.78 (2H, br t, *J* = 7.8 Hz), 2.63 (2H, br t, *J* = 7.8 Hz), 1.80-1.62 (6H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.43-1.33 (18H, m), 0.94-0.89 (9H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 143.6, 143.1, 140.5, 139.9, 139.5, 139.5, 135.7, 134.6, 134.2, 132.4, 130.5, 128.9, 128.2, 128.1, 127.3, 125.4, 125.3, 125.0, 123.9, 123.5, 123.4, 118.6, 117.5, 114.2, 108.8, 108.8, 55.3, 37.8, 31.72, 31.72, 30.60, 30.57, 30.5, 30.4, 29.7, 29.34, 29.32, 29.26, 29.0, 22.65, 22.64, 22.62, 14.13, 14.10, 13.9, Anal. Calcd for $C_{51}H_{61}NOS_3$: C, 76.55; H, 7.68; N, 1.75; S, 12.02. Found. C, 76.43; H, 7.36; N, 1.82; S, 11.86.

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5''-[*N*-Ethyl-3-*p*-methoxyphenyl-9*H*-carbazol-6-yl]-3',3'',4-tri-*n*-hexyl-[2,2',5',2'']terthiophene-5-carbaldehyde S8. To a cold solution of terthiophene **S7** (155 mg, 0.19 mmol) in dry DMF (2 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.05 mL of $POCl_3$ in DMF (0.2 mL). The mixture was stirred at 70 °C for 7 h, and quenched with 10% aqueous solution of NaOAc (10 mL) after cooling, and extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 10/1) and successive HPLC on silica gel (hexane/EtOAc = 10/1) to obtain aldehyde **S8** (103 mg, 0.12 mml, 65%) as an orange oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (1H, s), 8.34 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.66 (1H, d, *J* = 8.8 Hz), 7.43 (1H, d, *J* = 8.5 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.21 (1H, s), 7.05 (1H, s), 7.04 (1H, d, *J* = 8.8 Hz), 7.04 (1H, s), 4.37 (2H, q, *J* = 7.2 Hz), 3.89 (3H, s), 2.95 (2H, br t, *J* = 7.8 Hz), 2.84 (4H, br t, *J* = 7.8 Hz), 1.80-1.68 (6H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.42-1.34 (18H, m), 0.96-0.90 (9H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6, 158.6, 153.4, 149.3, 145.3, 143.9, 142.5, 141.3, 140.0, 139.5, 136.6, 136.0, 134.5, 132.4, 128.9, 128.4, 128.18, 128.15, 127.9, 125.3, 125.12, 125.07, 123.9, 123.5, 123.3, 118.5, 117.5, 114.2, 108.9, 108.9, 55.3, 37.7, 31.69, 31.66, 31.5, 31.4, 30.5, 30.2, 29.84, 29.81, 29.33, 29.26, 29.0, 28.5, 22.63, 22.60, 22.5, 14.10, 14.07, 14.0, 13.9, Anal. Calcd for $C_{52}H_{61}NO_2S_3$: C, 75.41; H, 7.42; N, 1.69; S, 11.61. Found. C, 74.90; H, 7.09; N, 1.71; S, 11.20.

2-Cyano-3-[5''-[*N*-Ethyl-3-*p*-methoxyphenyl-9*H*-carbazol-6-yl]-3',3'',4-tri-*n*-hexyl[2,2',5',2'']terthiophen-5-yl]acrylic acid, MK-20. A mixture of aldehyde **S8** (92 mg, 0.11 mmol) with cyanoacetic acid (93 mg, 1.10 mmol) in dry acetonitrile (2 mL) and dry toluene (2 mL) was refluxed in the presence of piperidine (0.5 mL) for 15 h. After cooling the mixture was diluted with chloroform, and the organic layer was washed with aqueous HCl (1N), H_2O and brine, dried over Na_2SO_4, and evaporated under reduced

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pressure. The crude product was purified by column chromatography ($CHCl_3$ → $CHCl_3$/EtOH = 10/1) to obtain a dye **MK-20** (75 mg, 0.09 mmol, 77%) as dark-red solids, ^{1}H NMR (400 MHz, THF-d_8) δ 8.47 (1H, br s), 8.41 (1H, s), 8.40 (1H, br s), 7.75-7.68 (2H, m), 7.65 (2H, d, *J* = 8.8 Hz), 7.54-7.50 (2H, m), 7.35 (1H, s), 7.23 (1H, s), 7.13 (1H, s), 6.99 (2H, d, *J* = 8.8 Hz), 4.45 (2H, q, *J* = 6.8 Hz), 3.82 (3H, s), 2.94-2.82 (6H, m), 1.81-1.66 (6H, m), 1.54-1.25 (21H, m), 0.94-0.90 (9H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 159.9, 155.2, 145.2, 144.6, 143.8, 143.3, 142.2, 141.2, 140.7, 137.9, 135.3, 133.4, 130.8, 129.8, 129.5, 128.8, 128.7, 128.1, 126.0, 125.9, 124.7, 124.4, 119.1, 118.1, 117.1, 114.9, 109.9, 109.8, 98.6, 55.4, 38.3, 32.7, 32.6, 32.2, 31.39, 31.37, 30.9, 30.7, 30.3, 30.2, 29.9, 29.5, 23.55, 23.54, 23.47, 14.5, 14.5, 14.4, 14.1. Anal. Calcd for $C_{55}H_{62}N_2O_3S_3$: C, 73.79; H, 6.98; N, 3.13; S, 10.74. Found. C, 73.18; H, 6.78; N, 3.14; S, 10.49, HRMS (ESI) Calcd for $[M–H]^-$ $C_{55}H_{61}N_2O_3S_3^-$: 893.3850; found: m/z 893.3877.

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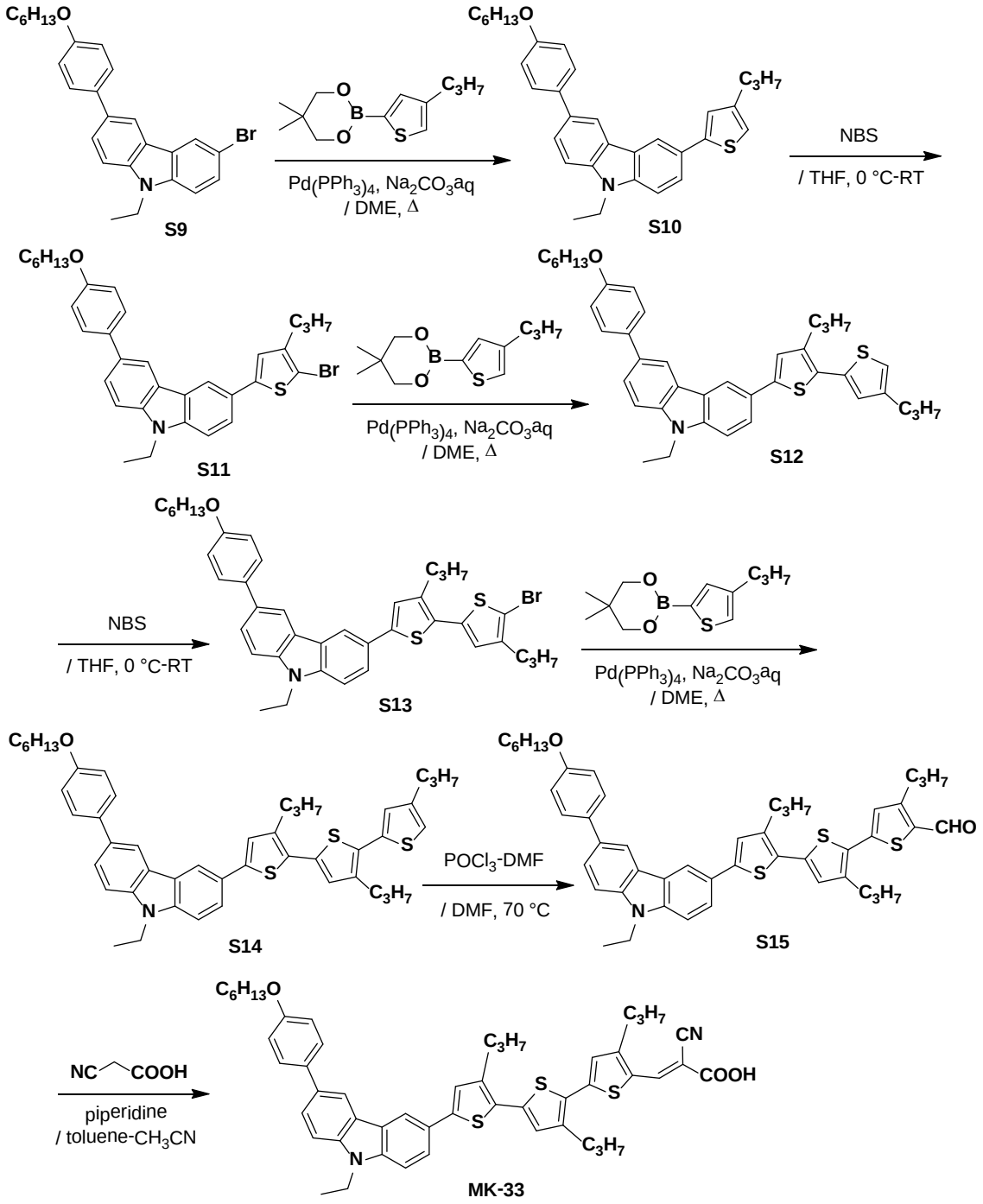

Scheme S2. Synthetic route for **MK-33**

***N*-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(4-*n*-propylthiophen-2-yl)-9*H*-carbazole S10.** A mixture of *N*-ethyl-3-bromo-6-(4-(*n*-hexyloxy)phenyl)-9*H*-carbazole **S9** (500 mg, 1.82 mmol), 2-(4-propyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboroane (917 mg, 1.82 mmol),

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tetrakis(triphenylphosphine)palladium(0) (105 mg, 0.09 mmol) and 0.5 mL of 10% aqueous solution of Na_2CO_3 in DME (30 mL) was refluxed overnight. After cooling, H_2O was added and the reaction mixture was extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/ EtOAc = 50/ 1) and HPLC on silica gel (hexane/ EtOAc = 25/ 1) to obtain a product **S10** (480 mg, 0.97 mmol, 53 %) as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.73 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.65 (2H, br d, *J* = 8.7 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.22 (1H, d, *J* = 1.3 Hz), 7.02 (2H, br d, *J* = 8.7 Hz), 6.86 (1H, d, *J* = 1.3 Hz), 4.38 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.64 (2H, t, *J* = 7.5 Hz), 1.87-1.69 (4H, m), 1.53-1.50 (2H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.41-1.35 (4H, m), 1.02 (3H, t, *J* = 7.3 Hz), 0.94 (3H, t, *J* = 7.3 Hz), 0.94 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 145.2, 143.9, 139.7, 139.4, 134.3, 132.2, 128.0, 125.9, 125.0, 124.0, 123.4, 123.3, 123.3, 118.3, 118.2, 117.5, 114.7, 108.7, 108.7, 68.0, 37.5, 32.8, 31.6, 29.3, 25.7, 23.6, 22.6, 14.0, 13.9, 13.7; HRMS (EI) Calcd for $C_{33}H_{37}NOS$: 495.2596; found: m/z 495.2597.

***N*-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(5-bromo-4-*n*-propylthiophen-2-yl)-9*H*-carbazole S11.** To a solution of *N*-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(4-*n*-propylthiophen-2-yl)-9*H*-carbazole **S10** (477 mg, 0.96 mmol) in THF (3 mL) was added *N*-bromosuccinimide (185 mg, 1.06 mmol). The reaction mixture was stirred at room temperature for 1 h, and quenched with 10 % aqueous solution of Na_2CO_3 and extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/ EtOAc = 50/ 1) and HPLC on silica gel (hexane/ EtOAc = 25/ 1) to obtain bromide **S11** (340 mg, 0.59 mmol, 62 %) as a white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (1H, dd, *J* = 1.8, 0.5 Hz), 8.27 (1H, dd, *J* = 1.8, 0.5 Hz), 7.79 (1H, dd, *J* = 8.5, 1.8 Hz), 7.65 (2H, br d, *J* = 8.9 Hz),

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7.62 (1H, dd, *J* = 8.5, 1.8 Hz), 7.42 (1H, dd, *J* = 8.5, 0.5 Hz), 7.36 (1H, dd, *J* = 8.5, 0.5 Hz), 7.06 (1H, s), 7.03 (2H, br d, *J* = 8.9 Hz), 4.35 (2H, q, *J* = 7.2 Hz), 4.04 (2H, t, *J* = 6.6 Hz), 2.61 (2H, t, *J* = 7.5 Hz), 1.88-1.81 (2H, m), 1.77-1.68 (2H, m), 1.57-1.49 (2H, m), 1.45 (3H, t, *J* = 7.2 Hz), 1.42-1.37 (4H, m), 1.04 (3H, t, *J* = 7.4 Hz), 0.96 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 145.0, 142.8, 139.9, 139.5, 134.3, 132.4, 128.1, 125.3, 125.1, 123.8, 123.5, 123.3, 122.9, 118.5, 117.4, 114.8, 108.9, 108.8, 106.7, 68.1, 37.7, 31.7, 31.6, 29.3, 25.8, 23.0, 22.6, 14.1, 13.9, 13.8; HRMS (EI) Calcd for $C_{33}H_{36}BrNOS$: 573.1701; found: m/z 573.1645.

***N*-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(3,4'-di-*n*-propyl-[2,2']bithiophen-5-yl)-9*H*-carbazole S12.** The Suzuki-coupling reaction of bromide **S11** (235 mg, 0.41 mmol) with 2-(4-propyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboroane (206 mg, 0.82 mmol) using $Pd(PPh_3)_4$ (25.4 mg, 0.02 mmol) as a catalyst in DME (30 mL) was carried out in a similar manner to that for **S10**. The crude product was purified by column chromatography (hexane/ EtOAc = 50/ 1) and HPLC on silica gel (hexane/ EtOAc = 10/ 1) to obtain product **S12** (231 mg, 0.37 mmol, 91 %) as a yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.68 (1H, dd, *J* = 8.5, 1.8 Hz), 7.64 (2H, br d, *J* = 8.7 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.39 (1H, d, *J* = 8.5 Hz), 7.20 (1H, s), 7.02 (2H, br d, *J* = 8.6 Hz), 7.01 (1H, d, *J* = 1.1 Hz), 6.90 (1H, d, *J* = 1.1 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.79 (2H, t, *J* = 7.8 Hz), 2.61 (2H, t, *J* = 7.6 Hz), 1.87-1.65 (6H, m), 1.53-1.50 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.40-1.35 (4H, m), 1.04 (3H, t, *J* = 7.4 Hz), 1.00 (3H, t, *J* = 7.4 Hz), 0.93 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 143.2, 142.9, 139.9, 139.7, 139.4, 136.2, 134.2, 132.2, 129.3, 128.0, 126.6, 125.3, 125.1, 124.7, 123.7, 123.4, 123.3, 119.5, 118.3, 117.3, 114.7, 108.7, 68.0, 37.5, 32.5, 31.6, 31.5, 29.3, 25.7, 23.8, 23.5, 22.6, 14.1, 14.0, 13.9, 13.7; HRMS (EI) Calcd for $C_{40}H_{45}NOS_2$: 619.2943; found: m/z 619.2940.

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***N*-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(5'-bromo-3,4'-di-*n*-propyl[2,2']bithiophen-5-yl)-9*H*-carbazole**

S13. The bromination of bithiophene **S12** (229 mg, 0.37 mmol) with *N*-bromosuccinimide (65.8 mg, 0.37 mmol) in cyclopentyl methyl ether (3 mL) was carried out in a similar manner to that of **S11**. The crude product was purified by column chromatography (hexane/ EtOAc = 50/ 1) and HPLC on silica gel (hexane/ EtOAc = 10/ 1) to obtain product **S13** (212 mg, 0.30 mmol, 82 %) as a yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (1H, d, *J* = 1.8 Hz), 8.29 (1H, d, *J* = 1.8 Hz), 7.71 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.64 (2H, br d, *J* = 8.7 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.39 (1H, d, *J* = 8.5 Hz), 7.19 (1H, s), 7.02 (2H, br d, *J* = 8.7 Hz), 6.86 (1H, s), 4.39 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.74 (2H, t, *J* = 7.8 Hz), 2.57 (2H, t, *J* = 7.6 Hz), 1.87-1.63 (6H, m), 1.52-1.51 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.40-1.35 (4H, m), 1.04 (3H, t, *J* = 7.4 Hz), 1.00 (3H, t, *J* = 7.4 Hz), 0.93 (3H, t, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 143.4, 142.1, 140.5, 139.8, 139.4, 136.0, 134.1, 132.2, 128.2, 128.0, 126.1, 125.1, 125.0, 124.7, 123.7, 123.4, 123.2, 118.3, 117.3, 114.7, 108.7, 108.1, 68.0, 37.5, 31.6, 31.5, 31.5, 29.3, 25.7, 23.8, 22.9, 22.6, 14.1, 14.0, 13.8, 13.8; HRMS (EI) Calcd for $C_{40}H_{44}BrNOS_2$: 697.2048; found: m/z 697.1957, HRMS (MALDI) Calcd for $C_{40}H_{44}BrNOS_2$: 697.2048; found: m/z 697.2023.

***N*-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(3,4',4''-tri-*n*-propyl[2,2',5',2'']terthiophen-5-yl)-9*H*-carbazole**

S14. The Suzuki-coupling reaction of bromide **S13** (211 mg, 0.30 mmol) with 2-(4-propyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboroane (152 mg, 0.60 mmol) using $Pd(PPh_3)_4$ (17.5 mg, 0.02 mmol) as a catalyst in DME (30 mL) was carried out in a similar manner to that for **S10**. The crude product was purified by column chromatography (hexane/ EtOAc = 50/ 1) and HPLC on silica gel (hexane/ EtOAc = 10/ 1) to obtain product **S14** (219 mg, 0.29 mmol, 98 %) as a yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.65 (2H, br d, *J* = 8.8 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.21 (1H, s), 7.02 (2H, br d, *J* = 8.6 Hz), 7.01 (1H, s), 7.00 (1H, d, *J* = 1.4 Hz), 6.91 (1H, d, *J* = 1.4

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Hz), 4.39 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.82 (2H, t, *J* = 7.8 Hz), 2.76 (2H, t, *J* = 7.8 Hz), 2.61 (2H, t, *J* = 7.6 Hz), 1.87-1.65 (8H, m), 1.52-1.50 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.40-1.35 (4H, m), 1.09-0.98 (9H, m), 0.94 (3H, t, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 143.4, 143.0, 140.2, 139.8, 139.4, 139.3, 135.6, 134.3, 134.2, 132.3, 130.5, 128.9, 128.1, 128.0, 127.0, 125.3, 125.2, 124.9, 123.8, 123.5, 123.3, 119.9, 118.4, 117.4, 114.8, 108.8, 68.0, 37.6, 32.5, 31.7, 31.6, 31.3, 29.3, 25.8, 23.8, 23.6, 22.6, 14.2, 14.1, 14.0, 13.9, 13.8. HRMS (MALDI) Calcd for $C_{47}H_{53}NOS_3$: 743.3289; found: m/z 743.3296.

5''-[9-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-9*H*-carbazol-6-yl]-3',3'',4-tri-*n*-propyl[2,2',5',2'']terthiophene -5-carbaldehyde S15. To a solution of terthiophene **S14** (216 mg, 0.29 mmol) in dry DMF (2 mL) at 0 °C was added 2.68 M Vilsmeier reagent (0.22 mL, 0.58 mmol), which was prepared with 0.5 mL of $POCl_3$ in 2.42 mL of DMF. The mixture was stirred at 70 °C for 4 hours, and quenched with 10% aqueous solution of NaOAc, and extracted with chloroform three times. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/ EtOAc = 10/ 1) and HPLC on silica gel (hexane/ EtOAc = 5/ 1) to obtain product **S15** (194 mg, 0.25 mmol, 87 %) as a orange solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (1H, s), 8.35 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.70 (1H, dd, *J* = 8.5, 1.8 Hz), 7.64 (2H, br d, *J* = 8.8 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.22 (1H, s), 7.06 (1H, s), 7.04 (1H, s), 7.02 (2H, br d, *J* = 8.8 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.94 (2H, t, *J* = 7.6 Hz), 2.83 (2H, t, *J* = 7.8 Hz), 2.83 (2H, t, *J* = 7.8 Hz), 1.87-1.72 (8H, m), 1.52-1.50 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.40-1.35 (4H, m), 1.09-1.01 (9H, m), 0.93 (3H, t, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.5, 158.1, 153.0, 145.2, 143.8, 142.2, 141.0, 139.9, 139.4, 136.6, 136.1, 134.2, 132.4, 129.0, 128.4, 128.2, 128.0, 127.8, 125.2, 125.0, 125.0, 123.7, 123.5, 123.3, 118.4, 117.4, 114.7, 108.8, 68.0, 37.7, 31.8, 31.6, 30.3, 29.3, 25.7, 24.6, 23.7, 23.4, 22.6,

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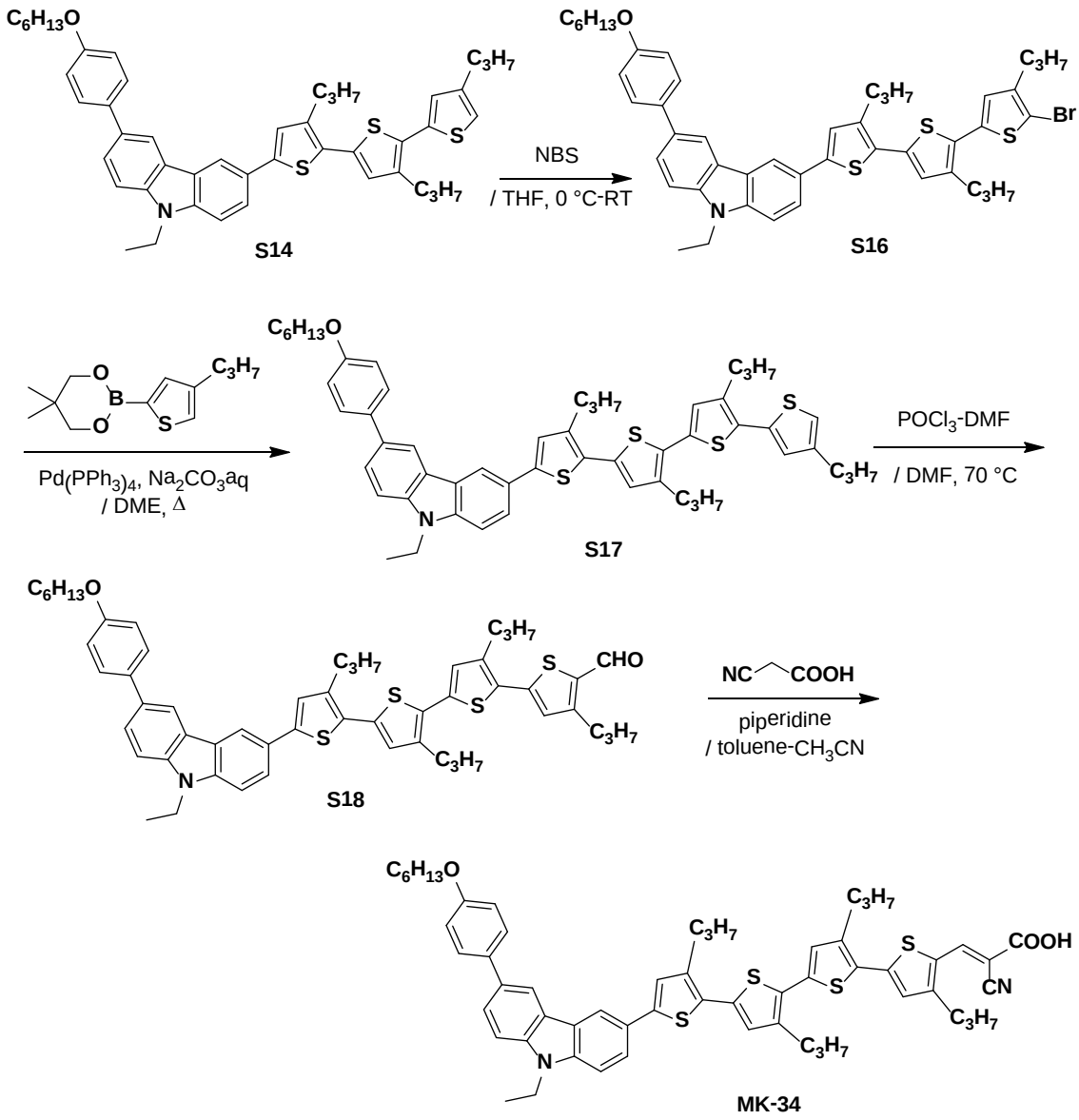
14.2, 14.1, 14.0, 13.8, 13.8. HRMS (MALDI) Calcd for $C_{48}H_{53}NO_2S_3$: 771.3238; found: m/z 771.3250.

2-Cyano-3-[5''-(9-Ethyl-6-(*p*-hexyloxyphenyl)-9*H*-carbazol-3-yl)-3',3'',4-tri-propyl[2,2',5',2'']terthiophenyl]acrylic acid MK-33. To a solution of aldehyde **S15** (178 mg, 0.23 mmol) and cyanoacetic acid (39.1 mg, 0.46 mmol) in toluene (2 mL) -acetonitrile (2 mL) was added 0.5 mL of piperidine and refluxed at 100 °C overnight. The resulting mixture was extracted with chloroform three times. The combined organic layer was washed with 1N HCl, H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography (chloroform → chloroform/ ethanol = 1/ 1) to obtain **MK-33** (149 mg, 0.18 mmol, 77 %) as a dark-red solid, ^{1}H NMR (400 MHz, THF-d_8) δ 8.48 (1H, br s), 8.42 (1H, s), 8.40 (1H, br s), 7.74 (1H, br d, *J* = 8.0 Hz), 7.70 (1H, br d, *J* = 8.0 Hz), 7.65 (2H, br d, *J* = 8.5 Hz), 7.53 (1H, br d, *J* = 8.0 Hz), 7.52 (1H, br d, *J* = 8.0 Hz), 7.37 (1H, s), 7.25 (1H, s), 7.14 (1H, s), 6.99 (2H, br d, *J* = 8.5 Hz), 4.46 (2H, q, *J* = 6.7 Hz), 4.02 (2H, t, *J* = 6.4 Hz), 2.95-2.83 (6H, m), 1.89-1.69 (8H, m), 1.56-1.29 (11H, m), 1.11-1.05 (6H, m), 1.01 (3H, t, *J* = 7.0 Hz), 0.94 (3H, t, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, THF-d_8) δ 163.7, 159.4, 145.2, 143.5, 142.0, 141.2, 140.6, 137.9, 135.2, 133.4, 130.9, 130.0, 129.7, 129.0, 128.6, 128.3, 128.2, 126.0, 125.9, 124.7, 124.4, 119.1, 118.1, 117.7, 115.5, 109.9, 109.8, 97.5, 68.6, 38.3, 32.7, 32.6, 32.6, 31.4, 30.3, 26.8, 25.2, 24.5, 23.6, 14.43, 14.39, 14.35, 14.1, Anal. Calcd for $C_{51}H_{54}N_2O_3S_3$: C, 72.99; H, 6.49; N, 3.34; S, 11.46. Found. C, 72.30; H, 6.80; N, 3.26; S, 11.30, HRMS (ESI) Calcd for $[M–H]^-$ $C_{51}H_{53}N_2O_3S_3^-$: 837.3224; found: m/z 837.3242.



Scheme S3. Synthetic route for **MK-34**

***N*-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(5'-bromo-3,4',4''-tri-*n*-propyl[2,2',5',2'']terthiophen-5-yl)-9*H*-carbazole S16.** The bromination of terthiophene **S14** (230 mg, 0.31 mmol) with *N*-bromosuccinimide (58.0 mg, 0.33 mmol) in THF (5 mL) was carried out in a similar manner to that of **S11**. The crude product was purified by column chromatography (hexane/ EtOAc = 50/ 1) and HPLC on silica gel (hexane/ EtOAc = 10/ 1) to obtain product **S16** (228 mg, 0.28 mmol, 91 %) as a yellow solid, ^{1}H NMR

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(400 MHz, $CDCl_3$) δ 8.35 (1H, br s), 8.30 (1H, d, *J* = 1.7 Hz), 7.72 (1H, dd, *J* = 8.5, 1.7 Hz), 7.69 (1H, dd, *J* = 8.5, 1.7 Hz), 7.65 (2H, br d, *J* = 8.7 Hz), 7.43 (1H, d, *J* = 8.5 Hz), 7.39 (1H, d, *J* = 8.5 Hz), 7.21 (1H, s), 7.02 (2H, br d, *J* = 8.7 Hz), 6.85 (1H, s), 4.37 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.82 (2H, t, *J* = 7.4 Hz), 2.73 (2H, t, *J* = 7.7 Hz), 2.57 (2H, t, *J* = 7.6 Hz), 1.87-1.63 (8H, m), 1.53-1.49 (2H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.40-1.36 (4H, m), 1.09-0.99 (9H, m), 0.94 (3H, t, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ158.1, 142.2, 142.1, 142.1, 140.3, 139.8, 139.4, 139.4, 134.2, 132.3, 128.0, 125.1, 125.1, 124.9, 123.7, 123.4, 123.3, 118.4, 117.4, 117.3, 114.7, 108.8, 68.0, 37.6, 31.7, 31.6, 31.5, 31.3, 29.3, 25.7, 23.8, 22.9, 22.6, 14.2, 14.1, 14.0, 13.8, HRMS (MALDI) Calcd for $C_{47}H_{52}BrNOS_3$: 821.2394; found: m/z 821.2376.

9-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-6-(3,4',4'',4'''-tetra-propyl-[2,2',5',2'',5'',2''']quaterthiophen-5-yl)- 9*H*-carbazole S17. The Suzuki-coupling reaction of bromide **S15** (220 mg, 0.27 mmol) with 2-(4-propyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboroane (103 mg, 0.41 mmol) using $Pd(PPh_3)_4$ (16.0 mg, 0.01 mmol) as a catalyst in DME (3 mL) was carried out in a similar manner to that for **S10**. The crude product was purified by column chromatography (hexane/ EtOAc = 50/ 1) and HPLC on silica gel (hexane/ EtOAc = 10/ 1) to obtain product **S17** (215 mg, 0.25 mmol, 93 %) as a orange solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 1.7 Hz), 8.31 (1H, d, *J* = 1.7 Hz), 7.73 (1H, dd, *J* = 8.5, 1.7 Hz), 7.70 (1H, dd, *J* = 8.5, 1.7 Hz), 7.65 (2H, br d, *J* = 8.7 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.22 (1H, s), 7.04-6.99 (5H, m), 6.91 (1H, d, *J* = 0.9 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.85-2.74 (6H, m), 2.61 (2H, t, *J* = 7.6 Hz), 1.87-1.65 (10H, m), 1.53-1.51 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.40-1.36 (4H, m), 1.09-0.98 (12H, m), 0.94 (3H, t, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 143.3, 143.0, 140.2, 139.8, 139.4, 139.4, 139.3, 135.5, 134.3, 134.2, 133.6, 132.2, 130.9, 130.0, 128.8, 128.3, 128.1, 128.0, 127.0, 125.2, 125.1, 124.9, 123.7, 123.4, 123.3, 120.0, 118.3, 117.3, 114.7, 108.7, 68.0, 37.5, 32.5, 31.7, 31.6, 31.4, 31.3, 29.3, 25.7, 23.8, 23.7, 23.5, 22.6, 14.2, 14.1, 14.1,

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14.0, 13.9, 13.8. HRMS (MALDI) Calcd for $C_{54}H_{61}NOS_4$: 867.3636; found: m/z 867.3625.

5''-[9-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-9*H*-carbazol-6-yl]-3,4',4'',4'''-tetra-propyl-[2,2',5',2'' ',5'',2'' ']quaterthiophen e-5-carbaldehyde S18. To a solution of quaterthiophene **S17** (202 mg, 0.24 mmol) in dry DMF (2 mL) at 0 °C was added 2.68 M Vilsmeier reagent (0.18 mL, 0.47 mmol), which was prepared with 0.5 mL of $POCl_3$ in 2.42 mL of DMF. The mixture was stirred at 70 °C for 4 hours, and quenched with 10% aqueous solution of NaOAc, and extracted with chloroform three times. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/ EtOAc = 10/ 1) and HPLC on silica gel (hexane/ EtOAc = 5/ 1) to obtain product **S18** (180 mg, 0.20 mmol, 86 %) as an orange solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (1H, s), 8.35 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.73 (1H, dd, *J* = 8.5, 1.8 Hz), 7.70 (1H, dd, *J* = 8.5, 1.8 Hz), 7.64 (2H, br d, *J* = 8.5 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.22 (1H, s), 7.06 (1H, s), 7.04-7.01 (4H, m), 4.39 (2H, q, *J* = 7.2 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 2.94 (2H, t, *J* = 7.6 Hz), 2.84-2.78 (6H, m), 1.87-1.71 (10H, m), 1.52-1.51 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.39-1.36 (4H, m), 1.09-1.01 (12H, m), 0.93 (3H, t, *J* = 7.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ181.4, 158.0, 152.9, 144.9, 143.2, 142.1, 140.3, 140.1, 139.7, 139.3, 136.0, 135.9, 135.0, 134.0, 132.1, 129.2, 129.2, 128.5, 128.4, 127.94, 127.88, 127.7, 125.0, 124.9, 124.8, 123.5, 123.3, 123.2, 118.2, 117.2, 114.6, 108.7, 67.9, 37.5, 31.7, 31.53, 31.46, 30.2, 29.2, 25.7, 24.5, 23.6, 23.5, 23.3, 22.5, 14.14, 14.06, 14.01, 13.97, 13.7, HRMS (MALDI) Calcd for $C_{55}H_{61}NO_2S_4$: 895.3585; found: m/z 895.3593.

2-Cyano-3-[5''-(9-Ethyl-6-(*p*-hexyloxyphenyl)-9*H*-carbazol-3-yl)-3,4',4'',4'''-tetra-propyl-[2,2',5',2' ' ,5'',2''']quaterthiophenyl]acrylic acid MK-34. To a solution of aldehyde **S18** (177 mg, 0.20 mmol) and cyanoacetic acid (34.0 mg, 0.40 mmol) in toluene (2 mL) -acetonitrile (2 mL) was added 0.5 mL of piperidine and refluxed at 100 °C overnight. The resulting mixture was extracted with chloroform three

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times. The combined organic layer was washed with 1N HCl, H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography (chloroform → chloroform/ ethanol = 10/ 1) to obtain **MK-34** (149 mg, 0.16 mmol, 78 %) as a dark-red solid, ^{1}H NMR (400 MHz, THF-*d*8) δ 8.46 (1H, br s), 8.41 (1H, s), 8.39 (1H, br s), 7.73 (1H, dd, *J* = 8.5, 1.4 Hz), 7.69 (1H, dd, *J* = 8.5, 1.7 Hz), 7.65 (2H, br d, *J* = 8.7 Hz), 7.53-7.48 (2H, m), 7.34 (1H, s), 7.24 (1H, s), 7.12 (1H, s), 7.10 (1H, s), 6.99 (2H, br d, *J* = 8.7 Hz), 4.43 (2H, br q, *J* = 7.0 Hz), 4.00 (2H, t, *J* = 6.4 Hz), 2.92-2.80 (8H, m), 1.83-1.74 (6H, m), 1.53-1.48 (2H, m), 1.44-1.36 (8H, m), 1.10-1.03 (8H, m), 0.99 (3H, t, *J* = 7.3 Hz), 0.93 (3H, t, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, THF-*d*8) δ 159.3, 154.8, 144.7, 144.2, 143.5, 143.2, 141.4, 141.3, 141.1, 140.6, 137.0, 136.2, 135.2, 133.4, 131.0, 130.5, 130.3, 129.3, 129.1, 128.6, 128.4, 126.1, 125.9, 125.8, 124.7, 124.43, 124.41, 119.1, 118.1, 115.5, 109.9, 109.8, 98.8, 68.6, 38.3, 32.7, 32.64, 32.55, 32.3, 31.4, 30.3, 26.8, 25.4, 24.61, 24.58, 24.5, 23.6, 14.46, 14.41, 14.38, 14.36, 14.1, 14.1, HRMS (ESI) Calcd for $[M–H]^-$ $C_{58}H_{61}N_2O_3S_4^-$: 961.3571; found: m/z 961.3588.

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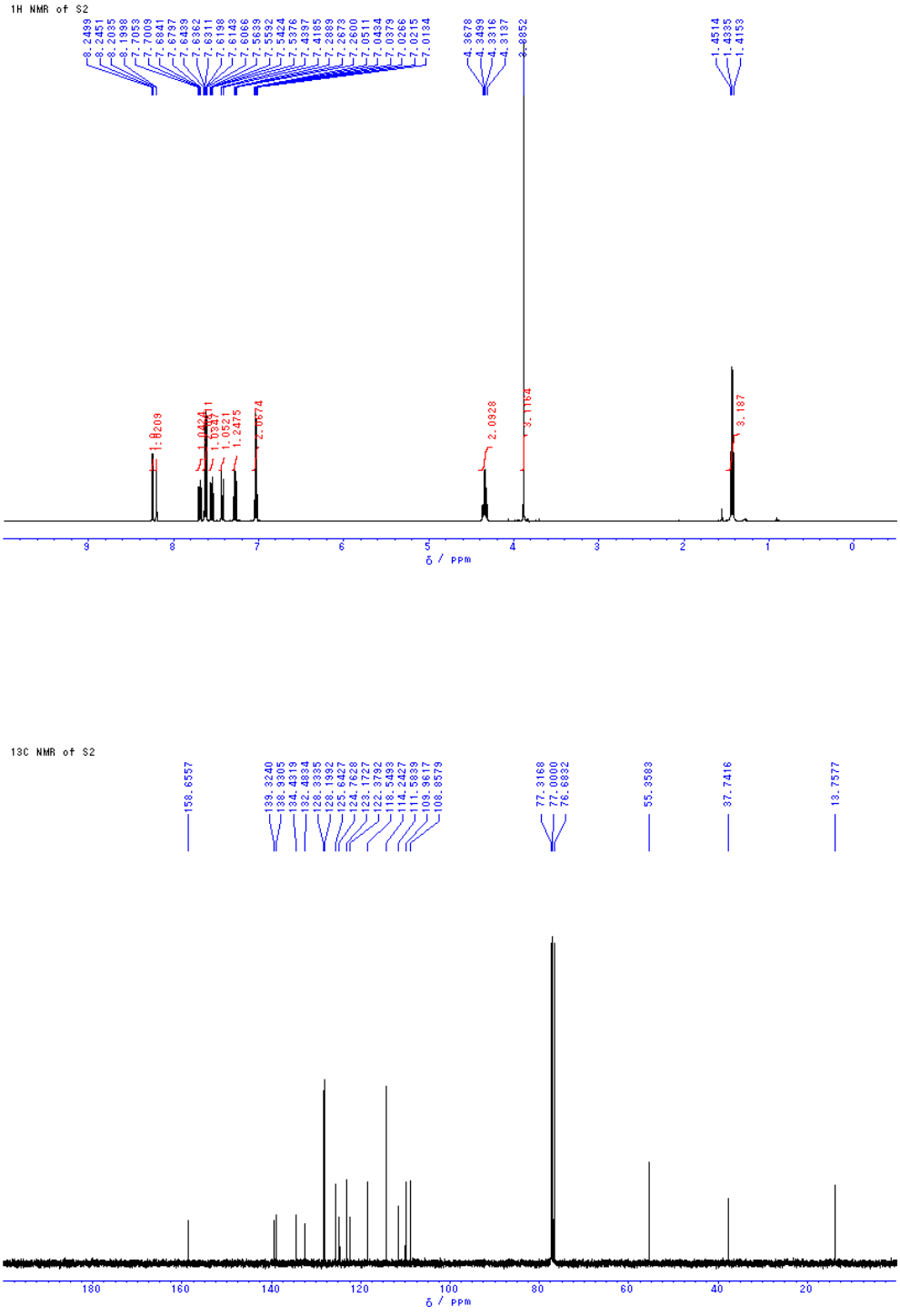

Figure S1. ^{1}H and ^{13}C NMR spectra of **S2**.

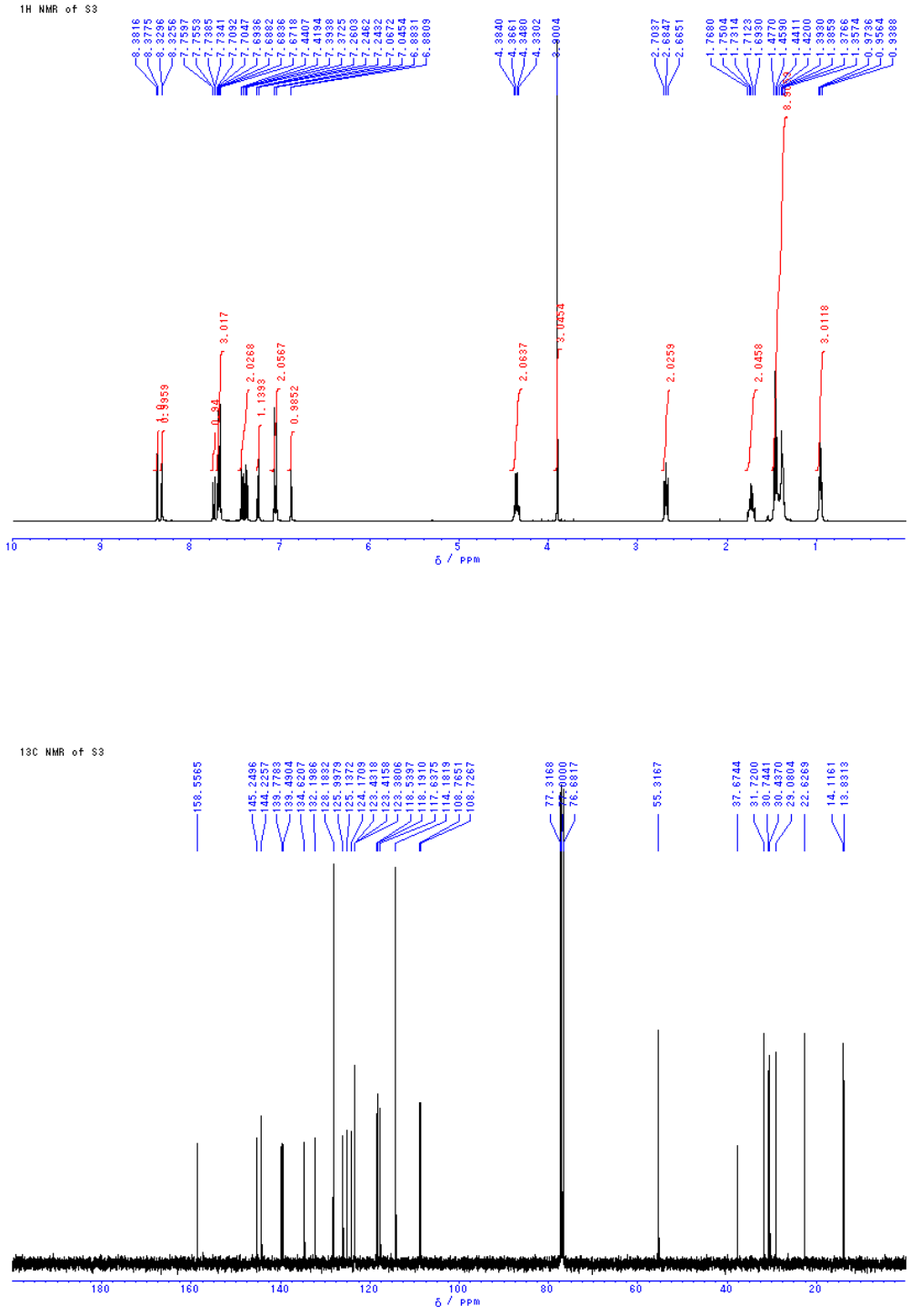

Figure S2. ^{1}H and ^{13}C NMR spectra of **S3**.

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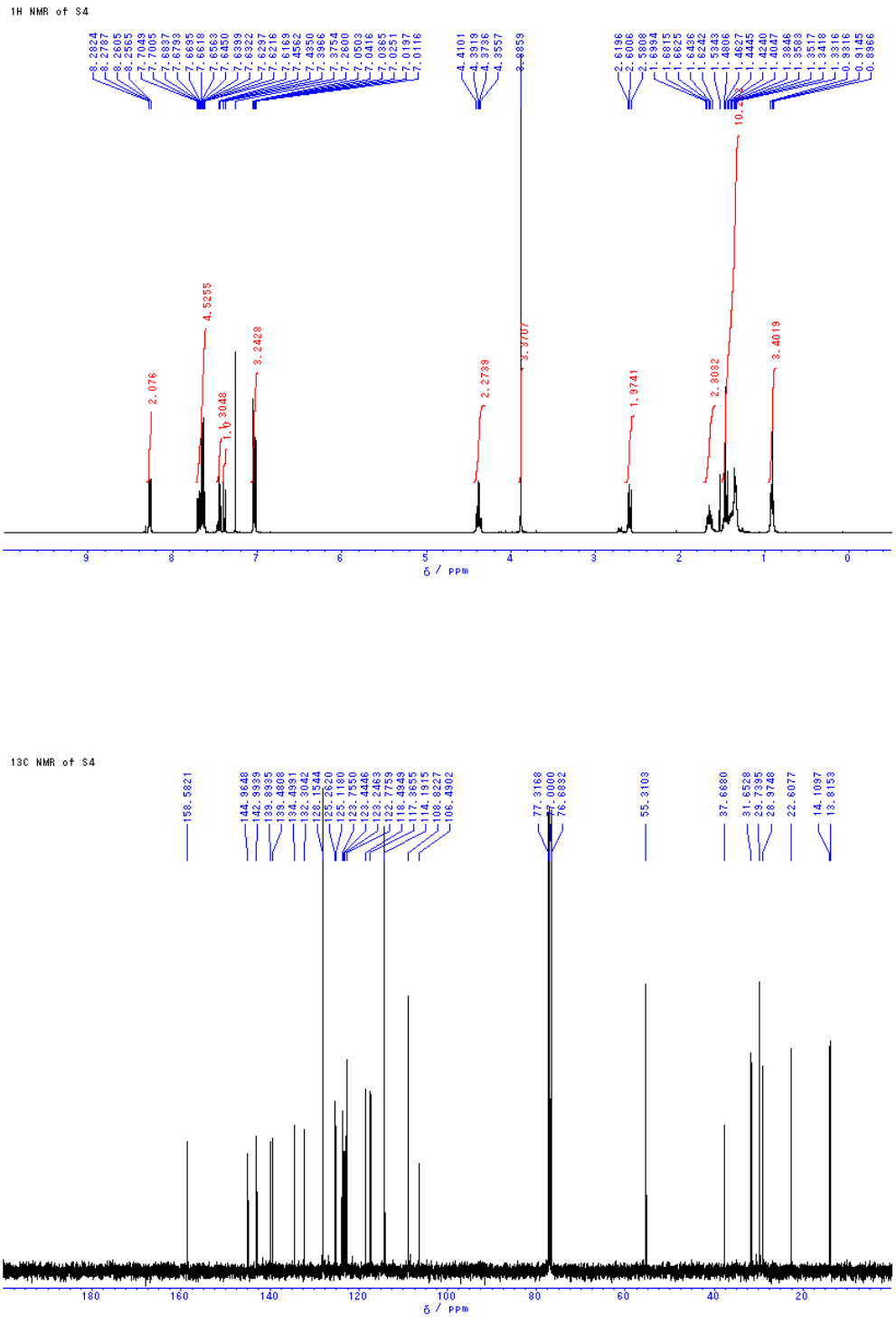
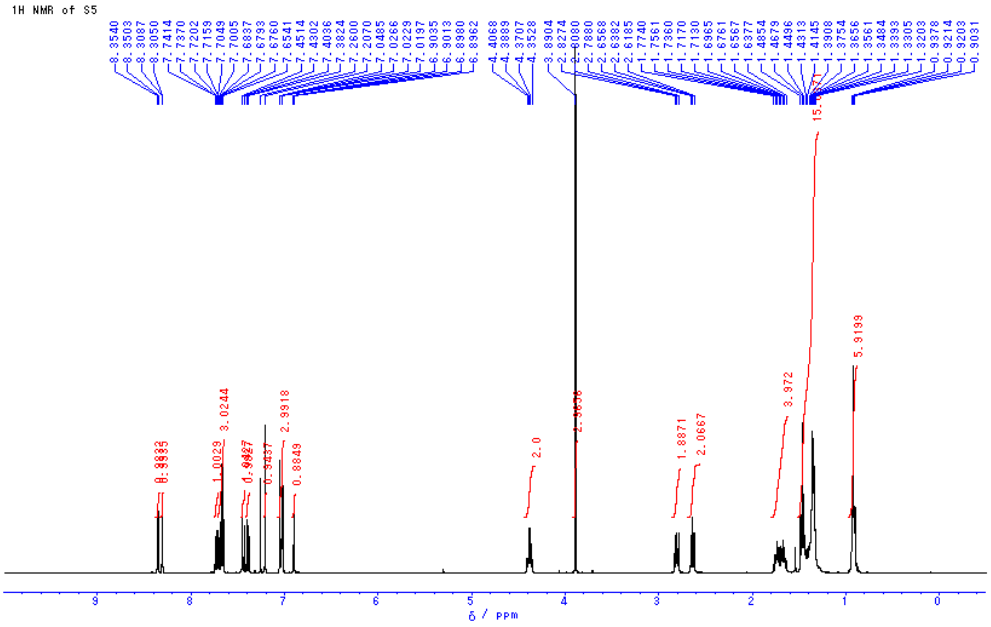


Figure S3. ^{1}H and ^{13}C NMR spectra of **S4**.



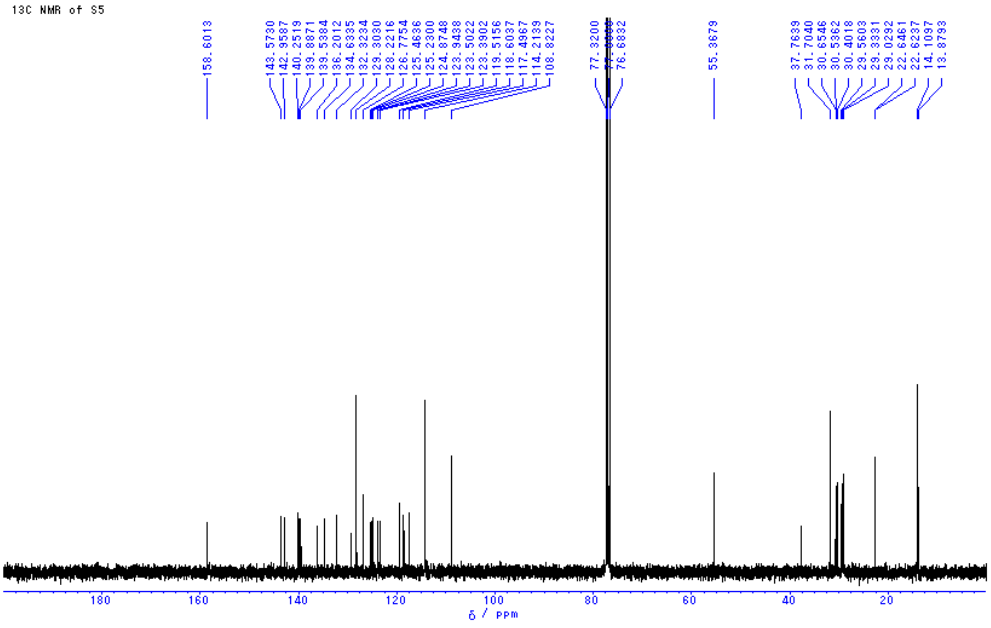


Figure S4. ^{1}H and ^{13}C NMR spectra of **S5**.

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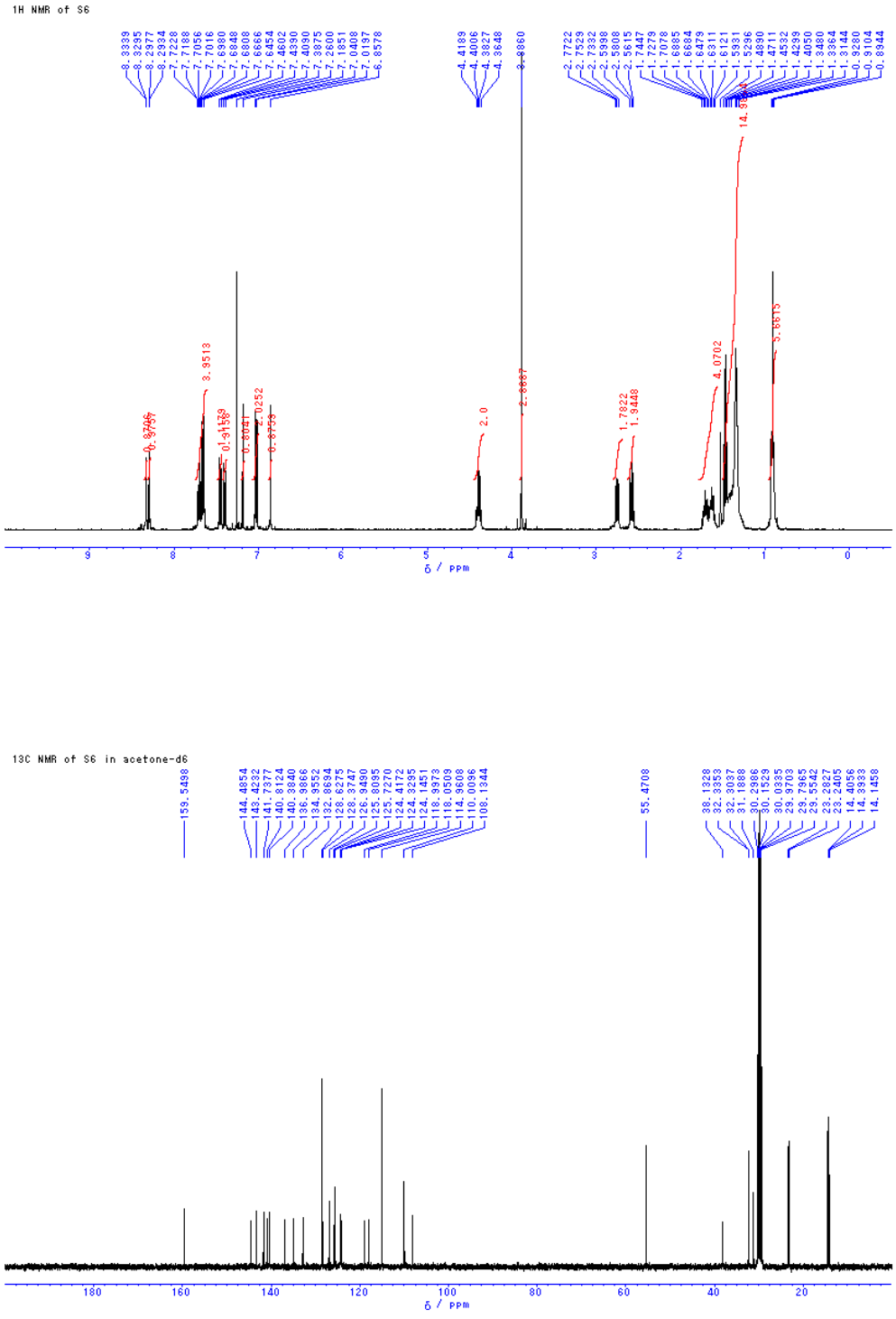

Figure S5. ^{1}H and ^{13}C NMR spectra of **S6**.

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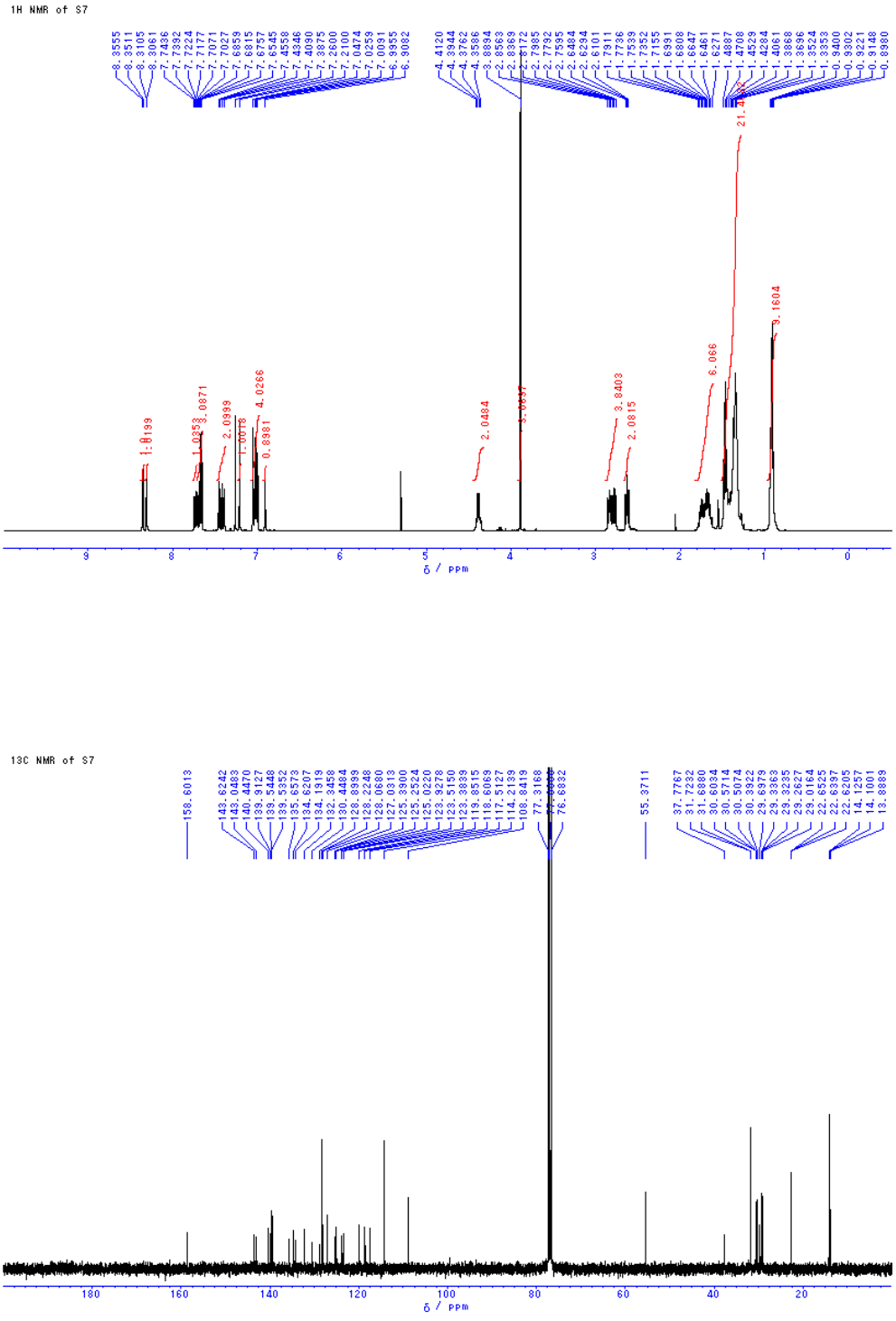

Figure S6. ^{1}H and ^{13}C NMR spectra of **S7**.

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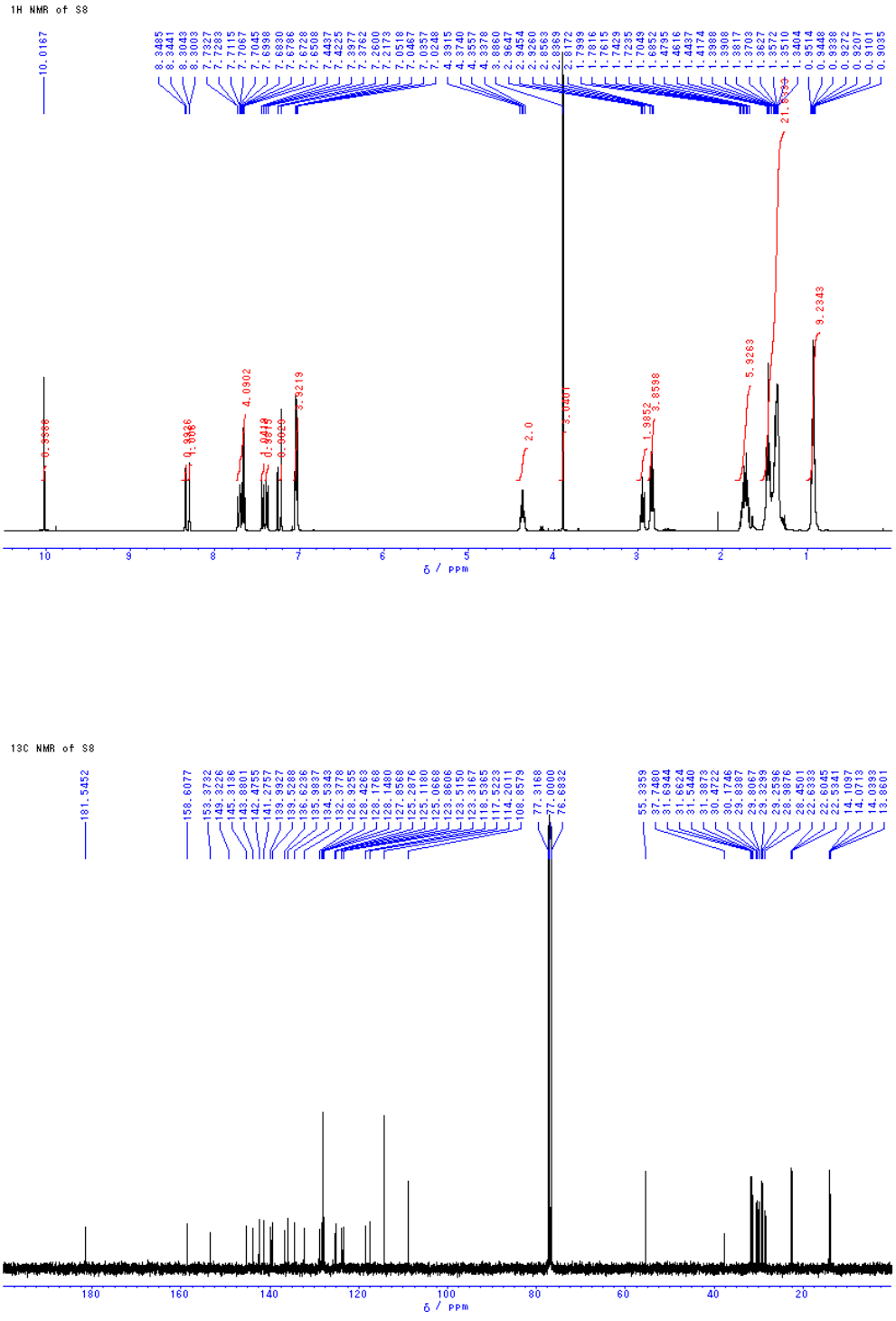


Figure S7. ^{1}H and ^{13}C NMR spectra of **S8**.

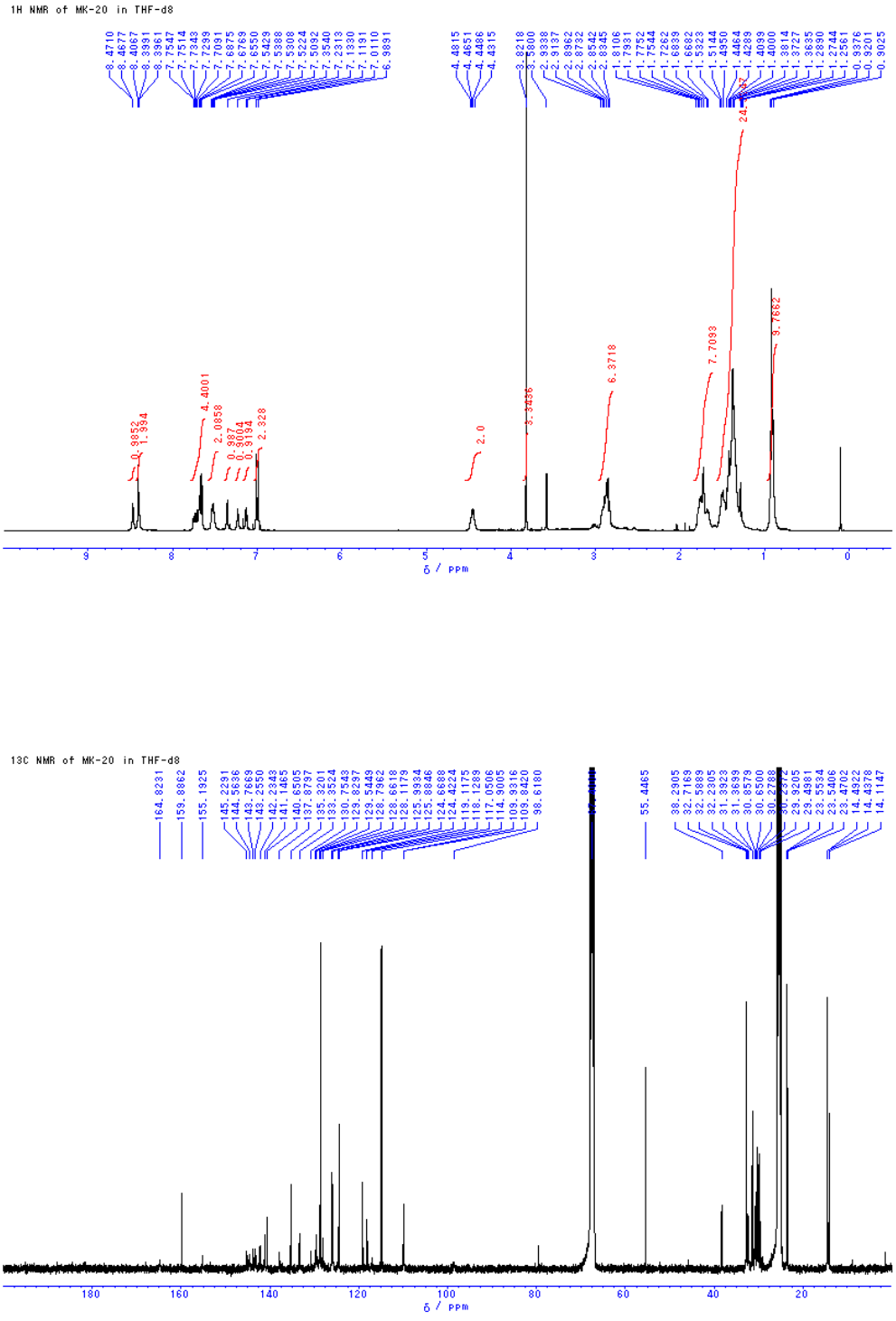
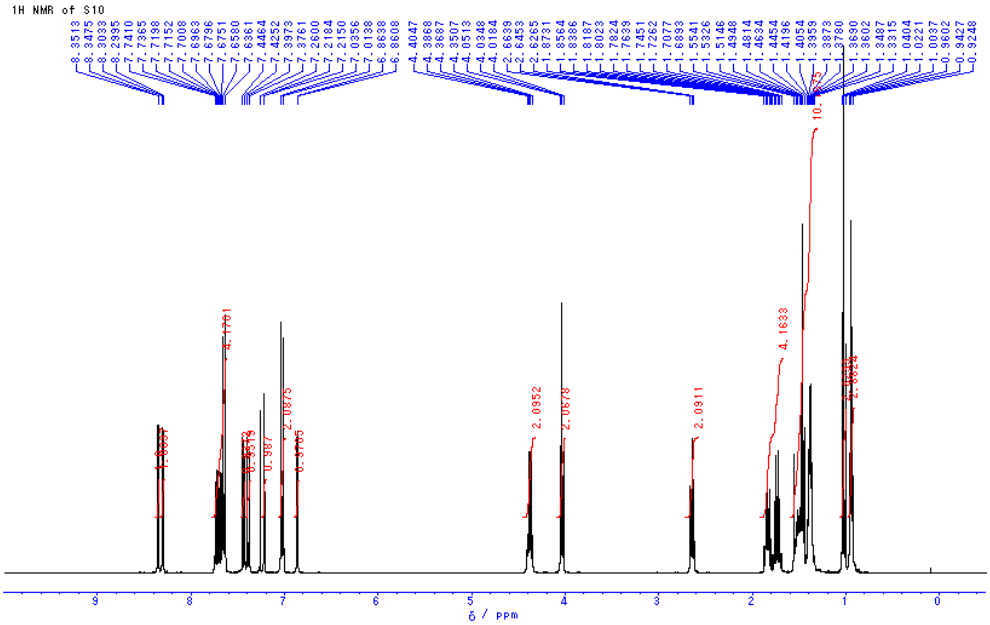


Figure S8. ^{1}H and ^{13}C NMR spectra of **MK-20**.



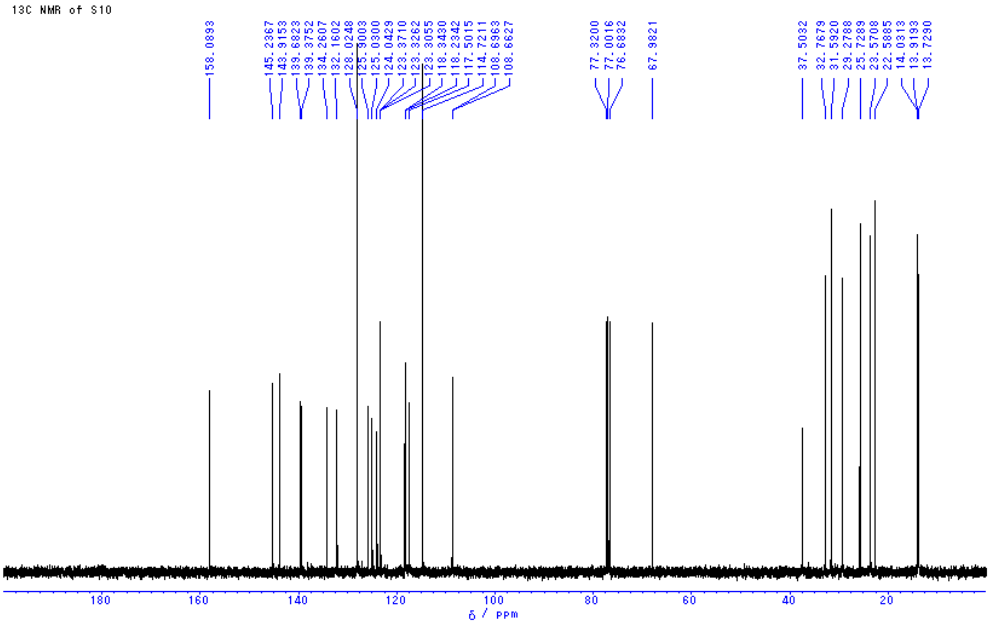


Figure S9. ^{1}H and ^{13}C NMR spectra of **S10**.

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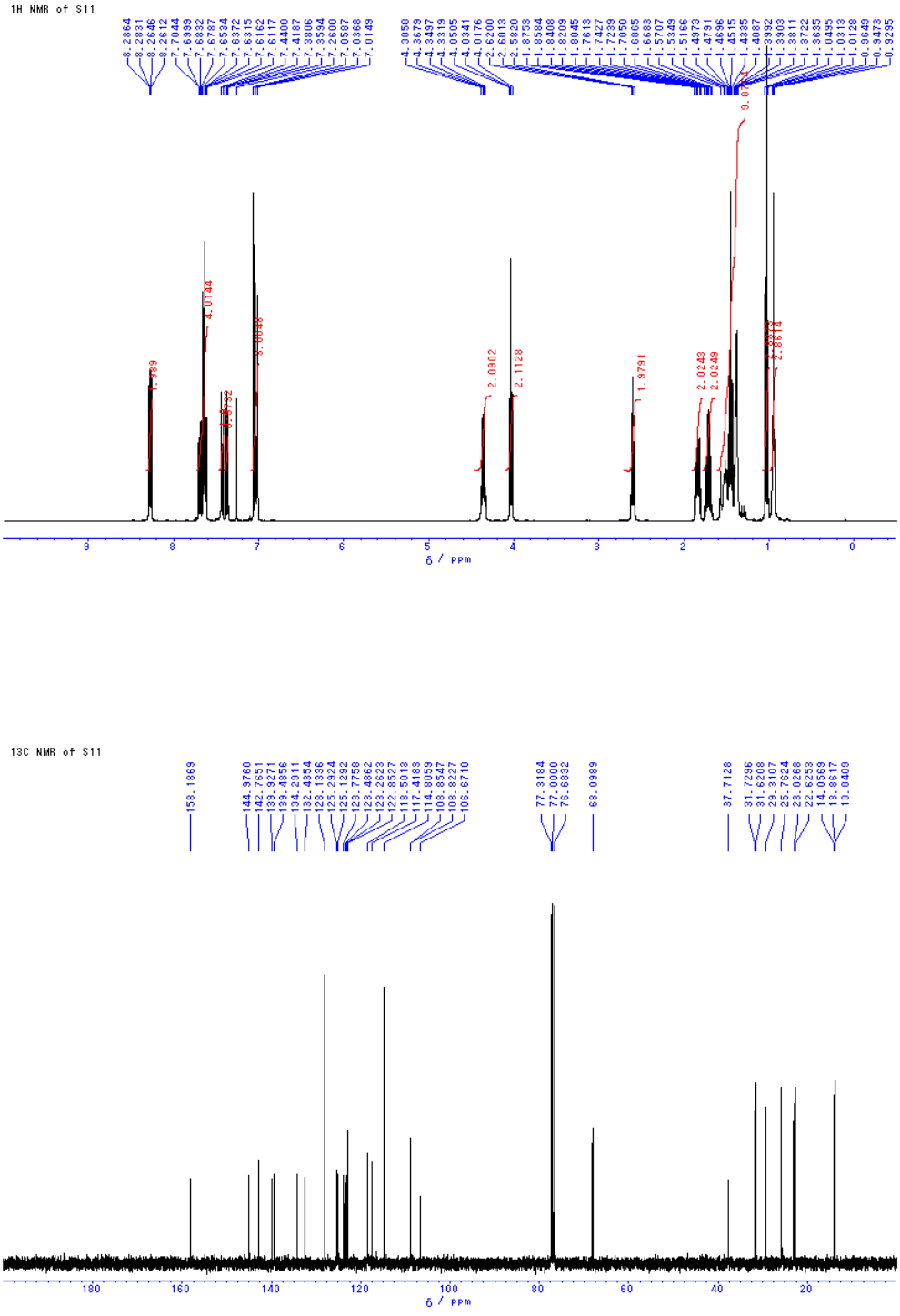

Figure S10. ^{1}H and ^{13}C NMR spectra of **S11**.

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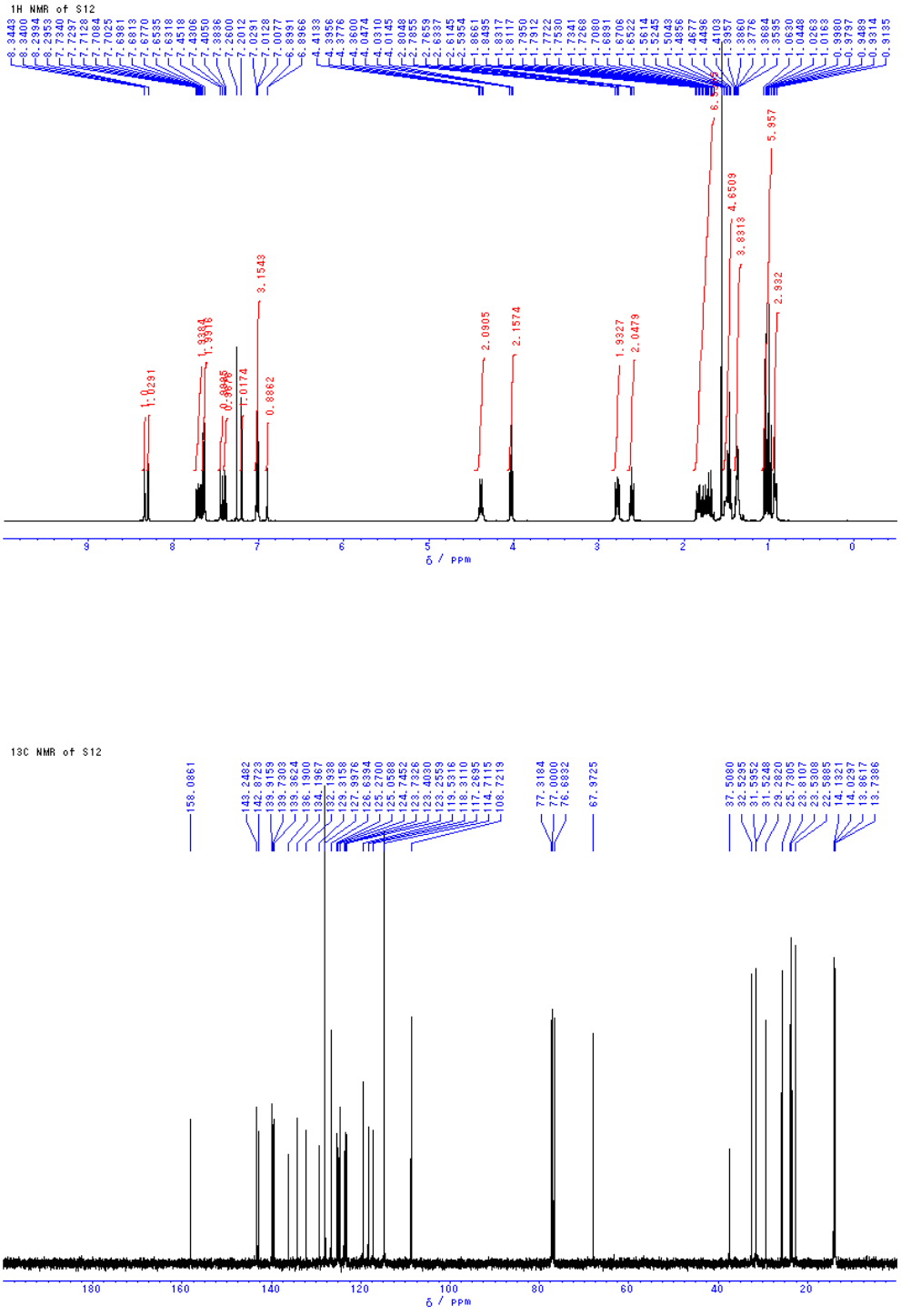

Figure S11. ^{1}H and ^{13}C NMR spectra of **S12**.

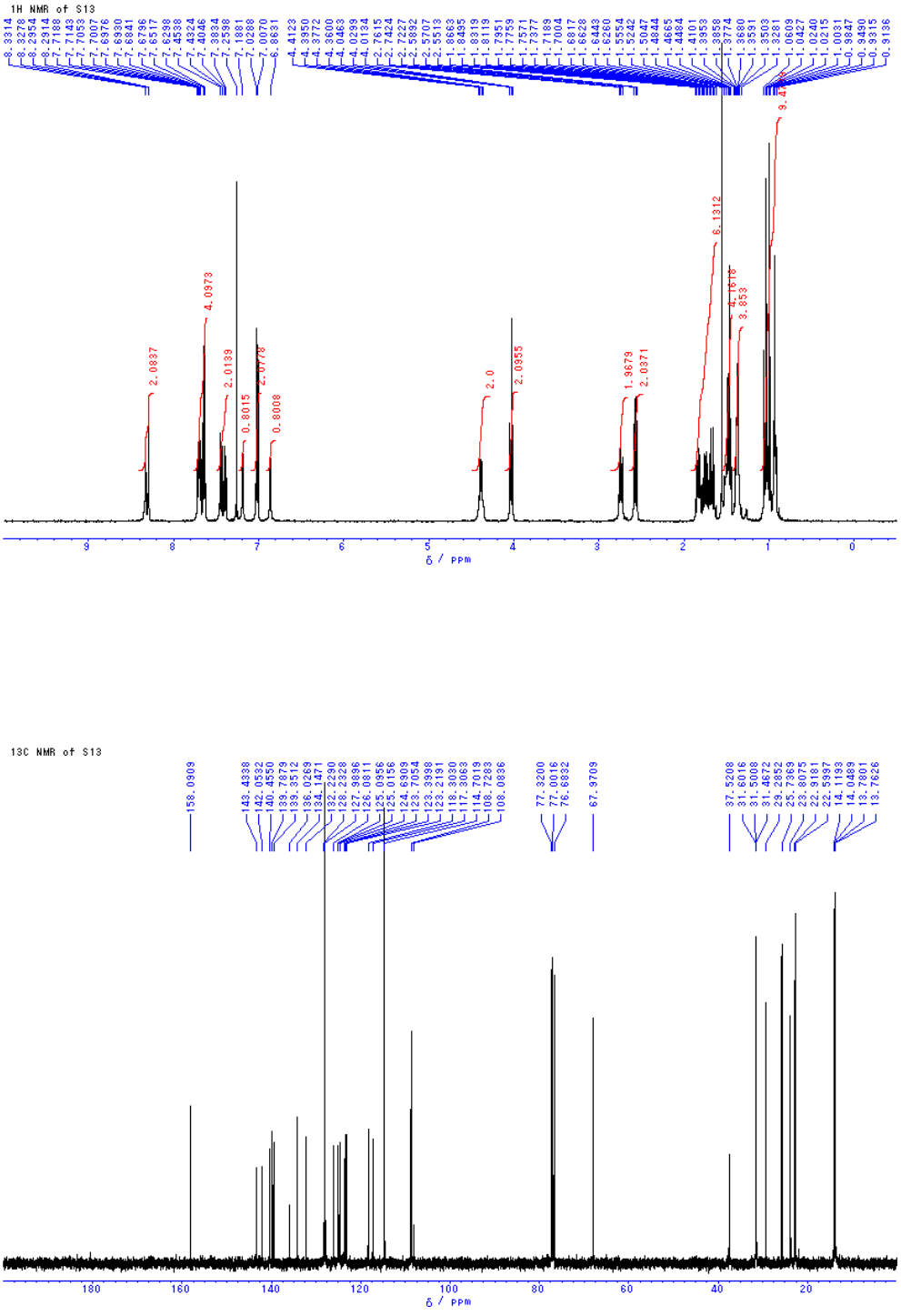

Figure S12. ^{1}H and ^{13}C NMR spectra of **S13**.

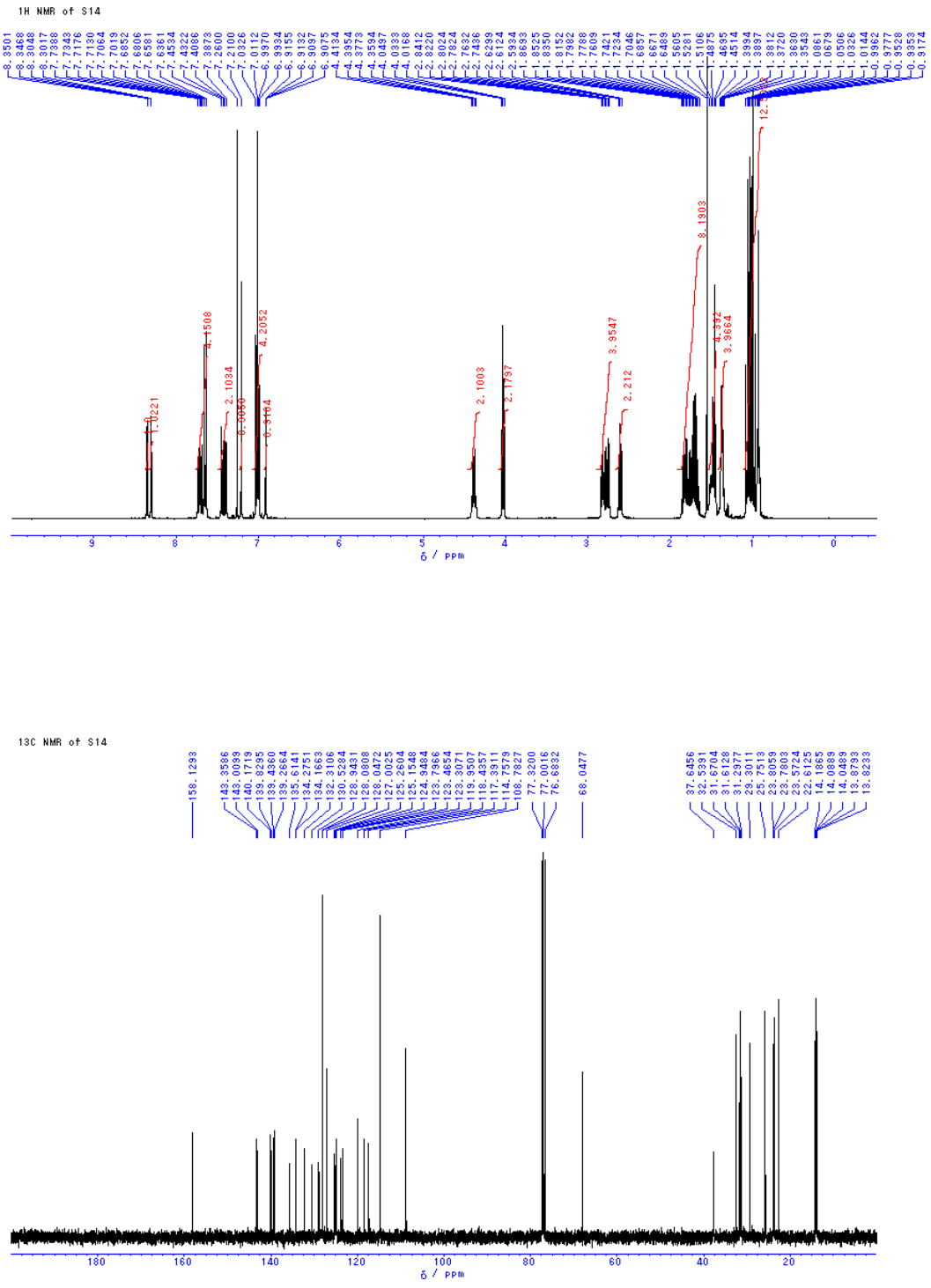

Figure S13. ^{1}H and ^{13}C NMR spectra of **S14**.

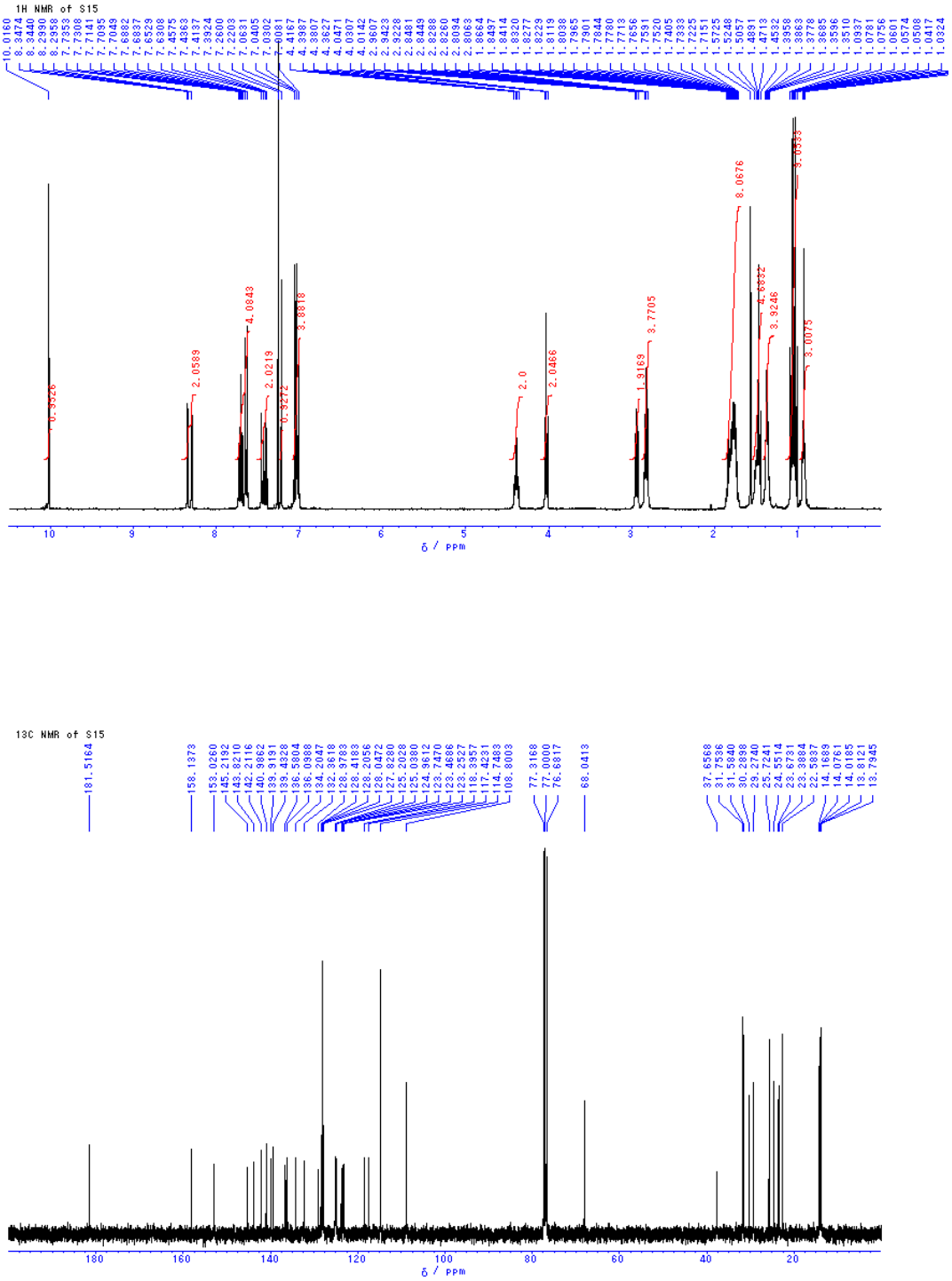

Figure S14. ^{1}H and ^{13}C NMR spectra of **S15**.

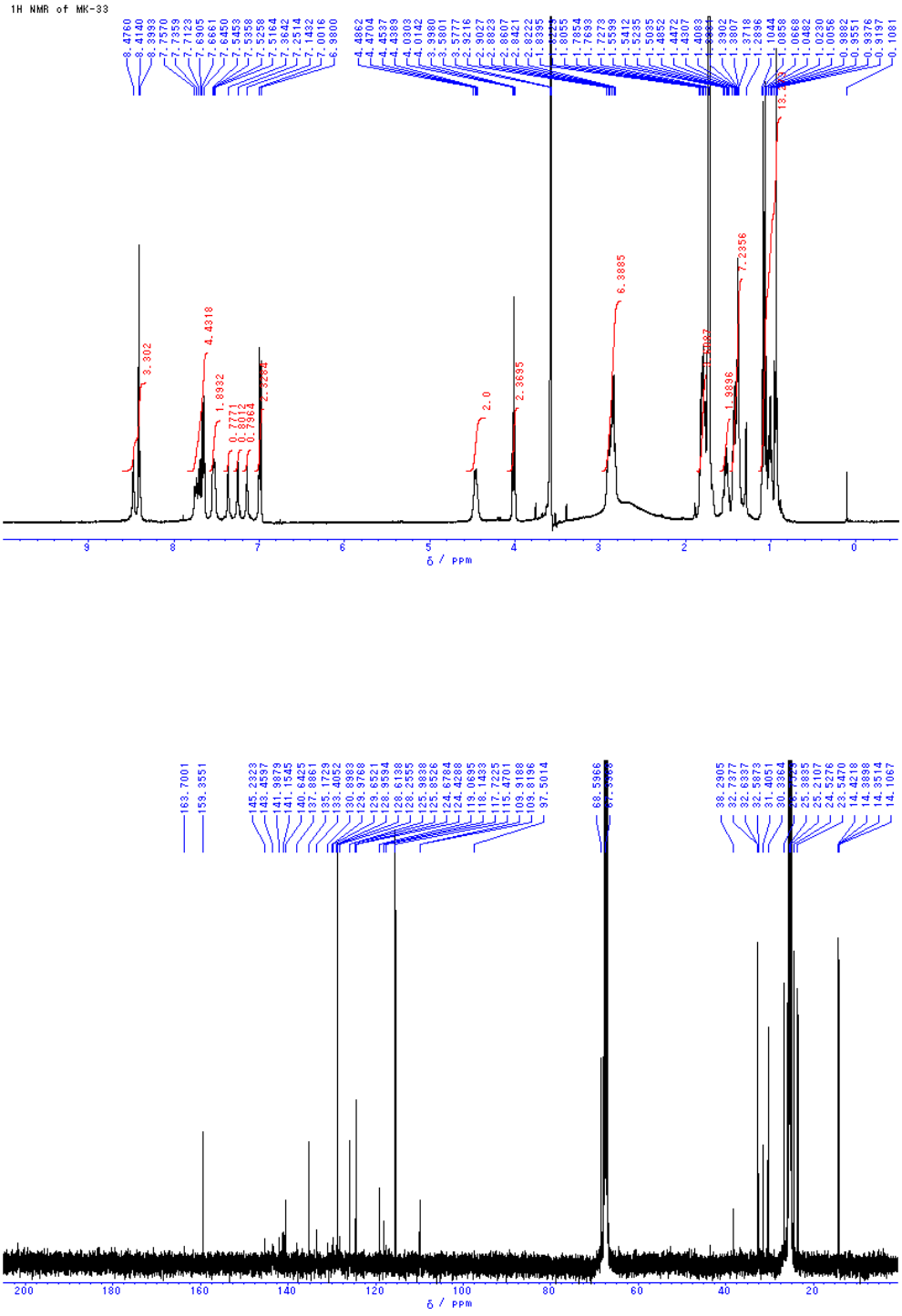

Figure S15. ^{1}H and ^{13}C NMR spectra of **MK-33**.

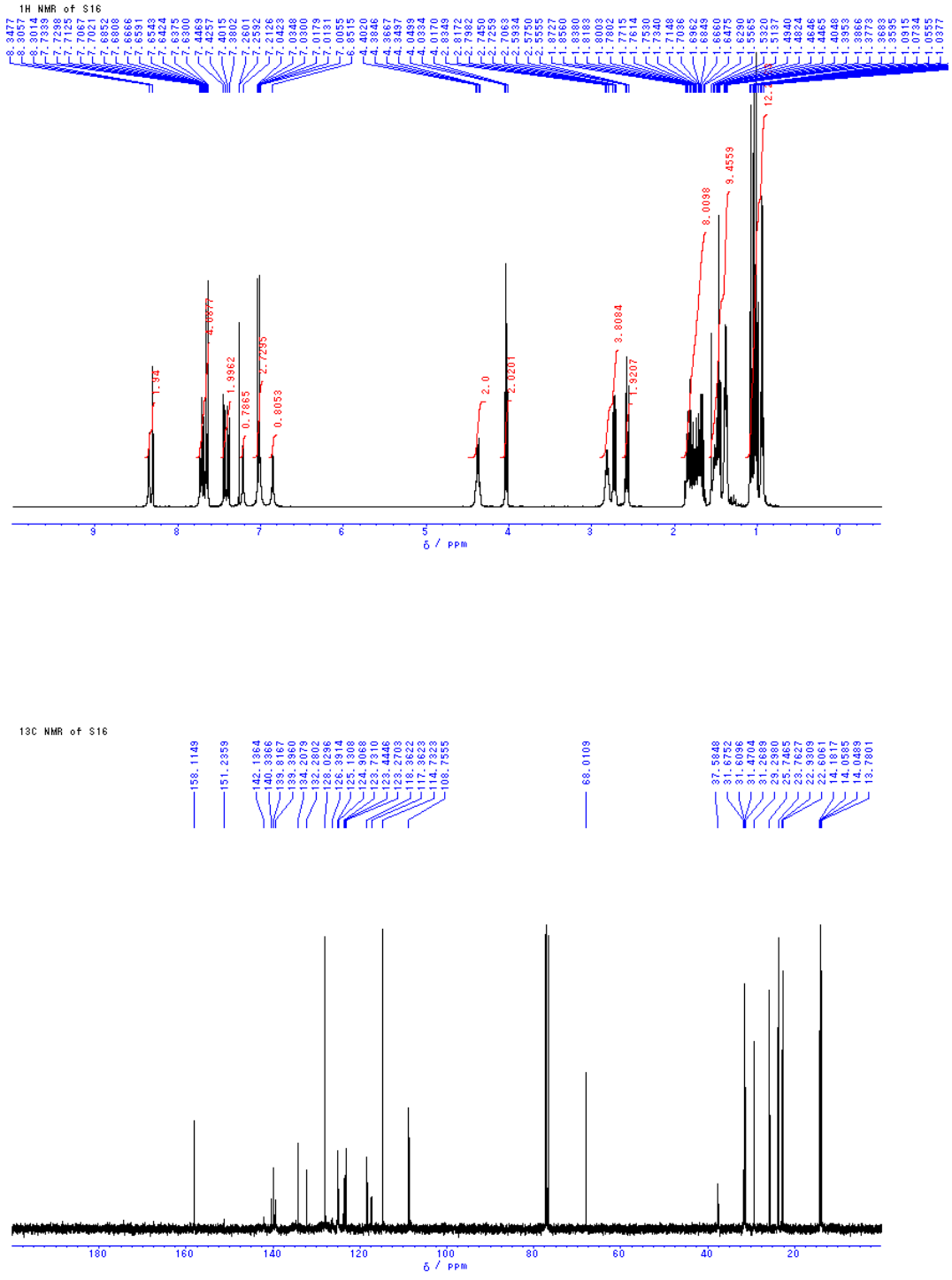

Figure S16. ^{1}H and ^{13}C NMR spectra of **S16**.

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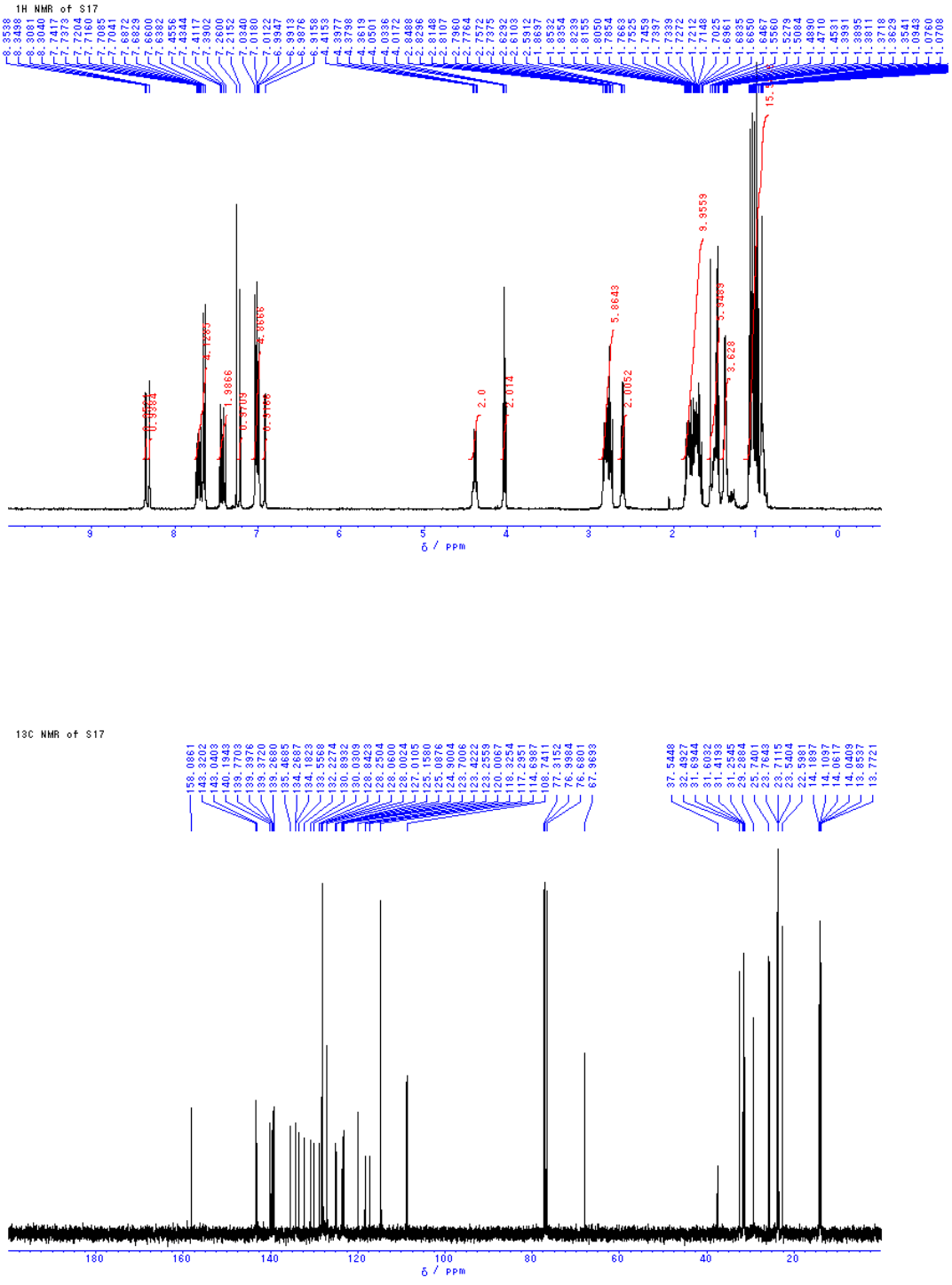

Figure S17. ^{1}H and ^{13}C NMR spectra of **S17**.

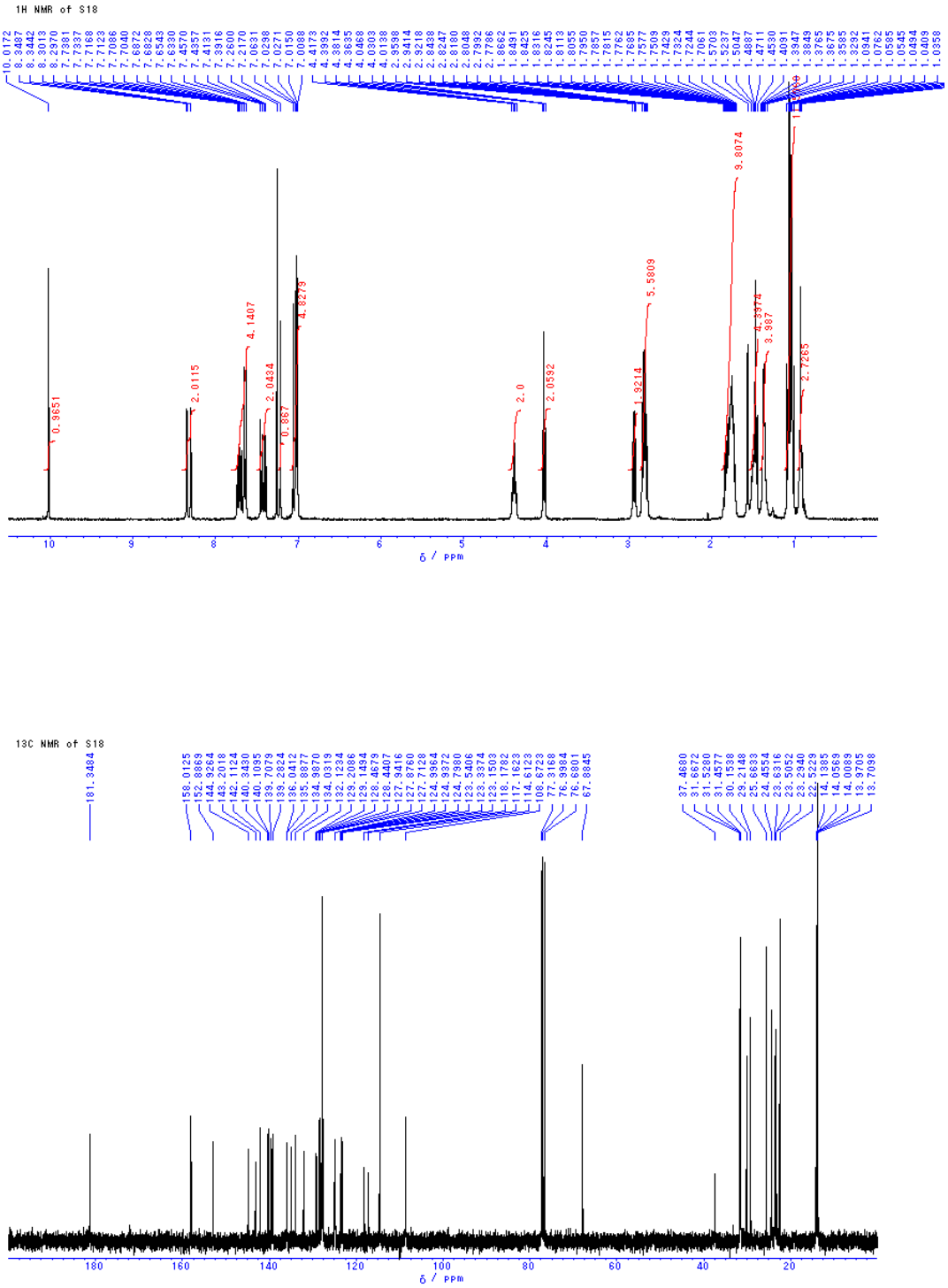

Figure S18. ^{1}H and ^{13}C NMR spectra of **S18**.

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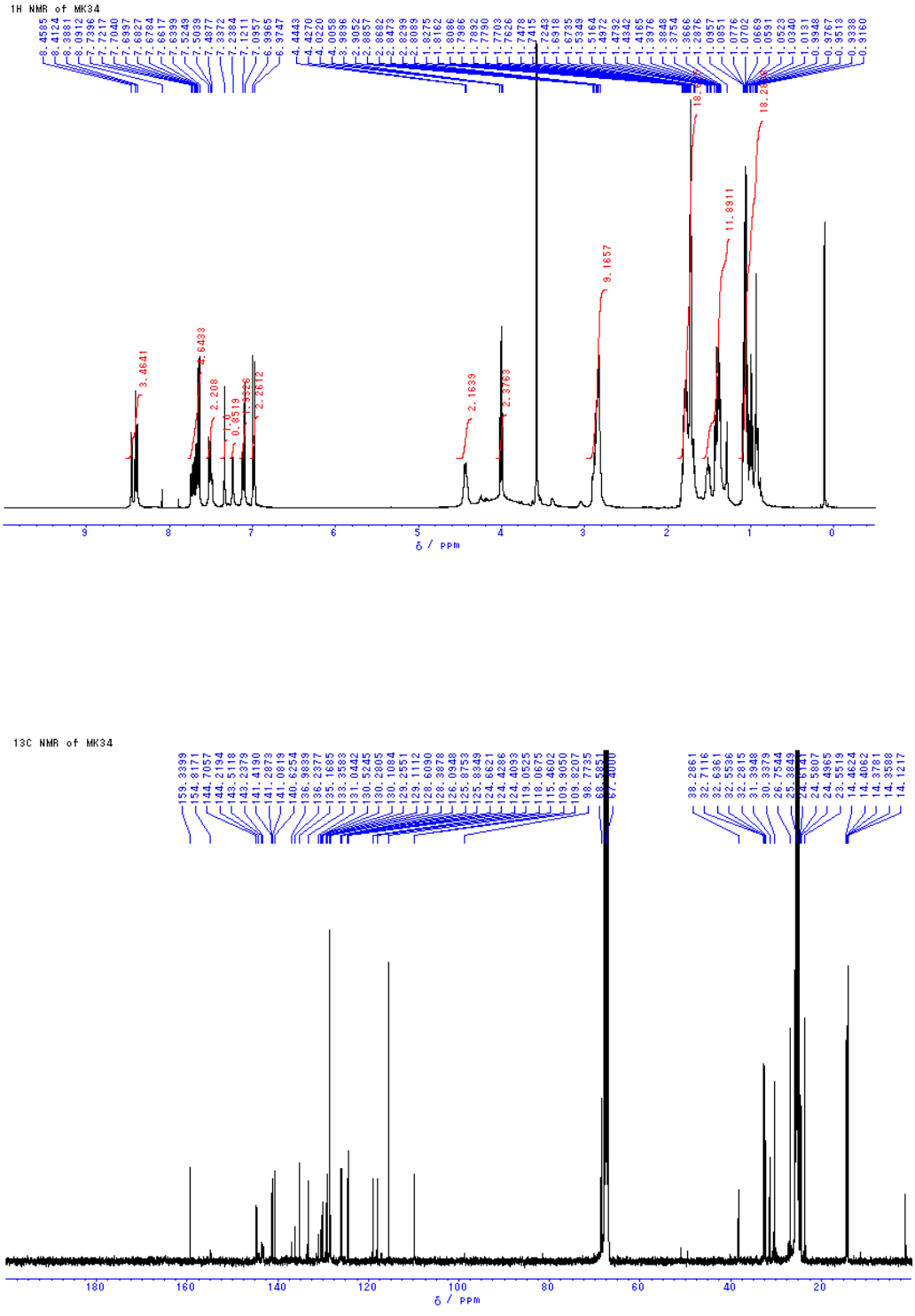

Figure S19. ^{1}H and ^{13}C NMR spectra of **MK-34.**

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
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Properties of dyes

Table S1. HOMO and LUMO levels of the dyes

Dye	HOMO / V vs. NHE	Gap / eV	LUMO / V vs. NHE
MK-75	+ 0.92	1.94	- 1.02
MK-1	+ 0.98	1.95	– 0.97
MK-2	+ 0.83	1.92	– 1.07
MK-20	+0.96	1.89	–0.93
MK-14	+0.95	1.88	–0.93
MK-33	+0.95	1.96	–1.01
MK-34	+0.90	1.89	–0.99

HOMO is oxidation potential measured by electrochemical method and the potential was calibrated by the redox potential of Ferrocene/Ferrocene^{+}. Gap was obtained from the absorption onset wavelength of the dye adsorbed TiO_2 layer. LUMO was calculated as the difference of HOMO and Gap.

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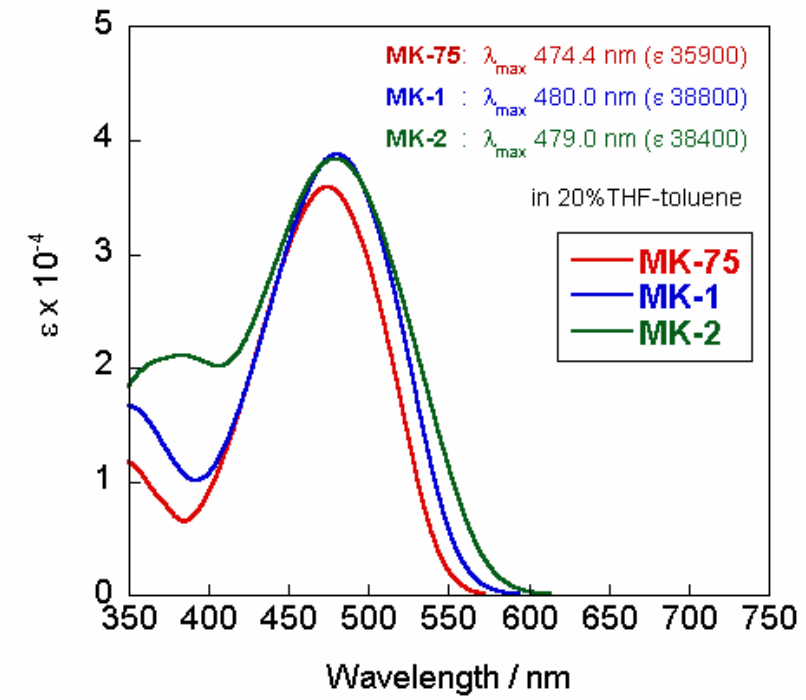

Figure S20. Absorption spectra of MK-75, MK-1, and MK-2 in 20%THF-toluene.

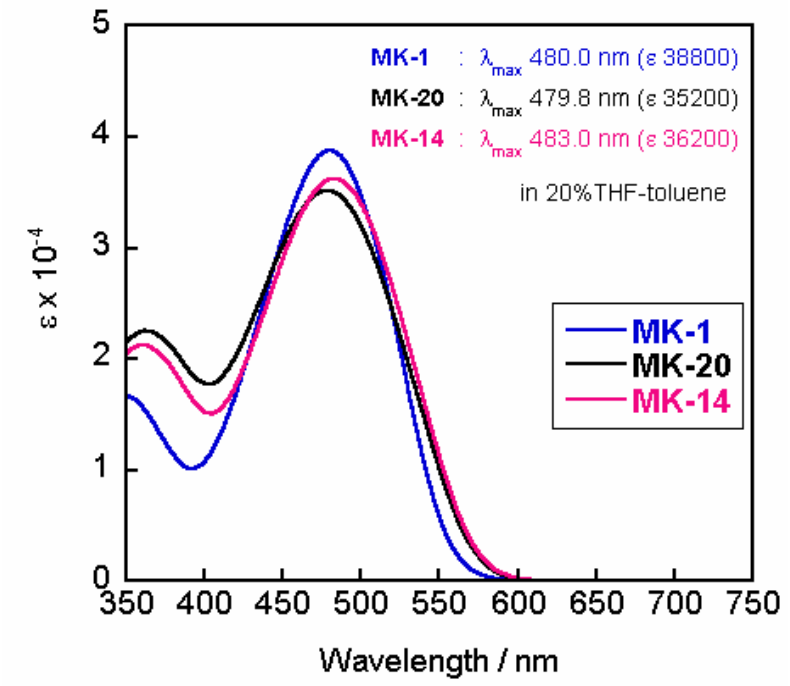

Figure S21. Absorption spectra of MK-1, MK-20, and MK-14 in 20%THF-toluene.

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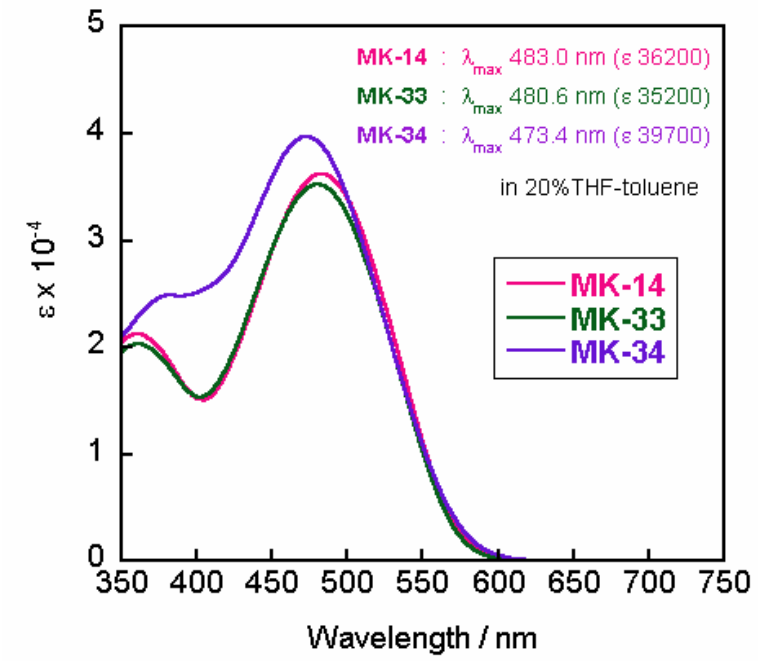

Figure S22. Absorption spectra of MK-14, MK-33, and MK-34 in 20%THF-toluene.

Measurement of the dye adsorbed amount on TiO_2

The dye adsorbed TiO_2 was added to determined amount of tetramethyl ammonium aqueous solution as the alkaline solution to desorb the dye from TiO_2. The dye in the aqueous solution was extracted by solvent extraction with determined amount of tetrahydrofuran (THF) and the solution was kept under dark condition at room temperature for 18 hours. The absorption spectrum of dye in THF solution was measured and calculated the concentration of the dye from the absorption coefficient of each dye.

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Impedance of the DSSCs

Impedance spectra were acquired using a computer-controlled potentiostat equipped with a frequency response analyser (Biologic, SP-300), and the spectra were fitted with the Randomise and Simplex method of EC-Lab 9.97 software.

The impedance spectra of the cells were acquired under one-sun conditions to evaluate the electrolyte diffusion (Fig. S23), and the data were fitted with the equivalent circuit as shown in Figure S24. The Nyquist plots of the DSSCs show a semicircle in the low frequency region, which is assigned to electrolyte diffusion resistance. The equivalent circuit consists of series resistance (R_s), the constant phase element (*CPE*), charge transfer resistance (R_{ct}), and the Warburg element for electrolyte diffusion (W_d). Because relatively thin TiO_2 films and high irradiation intensity were employed herein, the resistance of electron diffusion in TiO_2 was not included in the equivalent circuit. W_d is defined in Equation 1; R_d is the diffusion resistance, τ_d is the time constant which is equal to l_2/D, and the frequency at the peak of the semicircle in the low-frequency region corresponds to $2.54/2\pi\tau_d$. Table S2 shows the fitted W_d values. The fitted spectrum of the cell with MK-1, MK-20, MK-14, MK-33, and MK-34 is shown in Fig. S26, Fig. S27, Fig. S28, Fig. S29, and Fig. S30 and the impedance parameters except W_d are shown in Table S3. Furthermore, the impedance spectrum of the sandwich cell consisting of two platinized FTO-glass and cobalt redox electrolyte as Pt-Pt dummy cell was measured without bias potential to confirm the electrolyte diffusion resistance and the diffusion time constant of the electrolyte. The gap of the two electrodes was c.a. 30μ m. The spectrum was fitted with the equivalent circuit in Fig. S25. In the results, R_d and τ_d of the Pt-Pt cell were 19.74 ± 0.67 Ohm and 0.208 ± 0.036 s, respectively. The fitted spectrum of the Pt-Pt cell is shown in Fig. S31.

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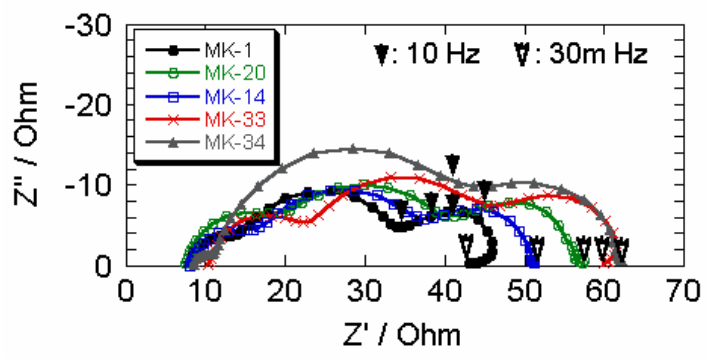

Fig. S23 Nyquist plot of the DSSCs with various dyes. The impedance spectra were measured under one-sun illumination.

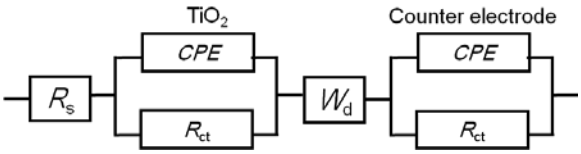

Fig. S24 Equivalent circuit for DSSCs. TiO_2 and counter electrode represent the interface between TiO_2 and electrolyte and between counter electrode and electrolyte.

$$W_d = R_d\left(\frac{\tanh\sqrt{\tau_d i2\pi f}}{\sqrt{\tau_d i2\pi f}}\right) \qquad \text{(S1)}$$

Table S2 Values of W_d in Equation S1, obtained by fitting the equivalent circuit in Fig. S24 with impedance data shown in Fig. S23.

Dye	R_d / Ohm	τ_d / s
MK-1	14.4 ± 0.2	0.208 ± 0.036
MK-20	17.8 ± 0.2	0.214 ± 0.030
MK-14	15.4 ± 0.2	0.210 ± 0.030
MK-33	19.0 ± 0.1	0.220 ± 0.028
MK-34	21.0 ± 0.1	0.225 ± 0.023

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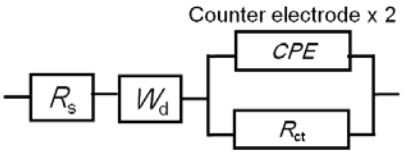

Fig. S25 Equivalent circuit for Pt-Pt dummy cell.

Spectra fitting of the Nyquist plots

Blue line with plots and Red line correspond to measured data and fitted curve, respectively.

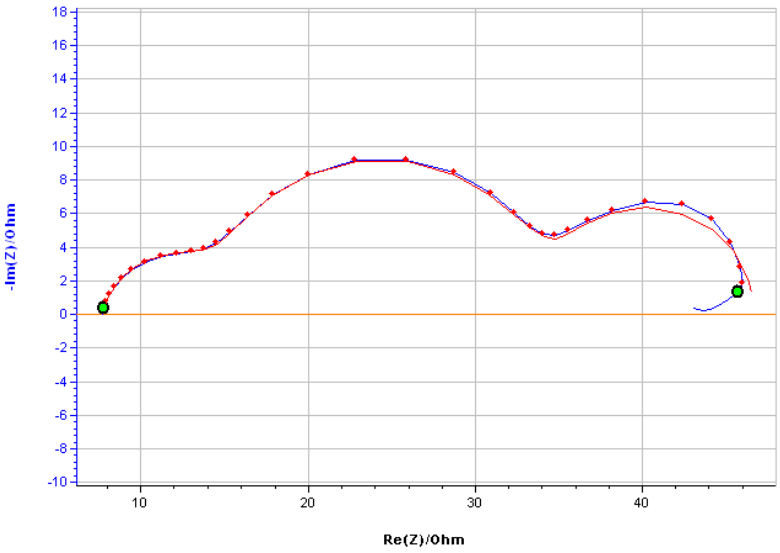

Figure S26. Measured impedance data and the fitted curve of the cell with MK-1

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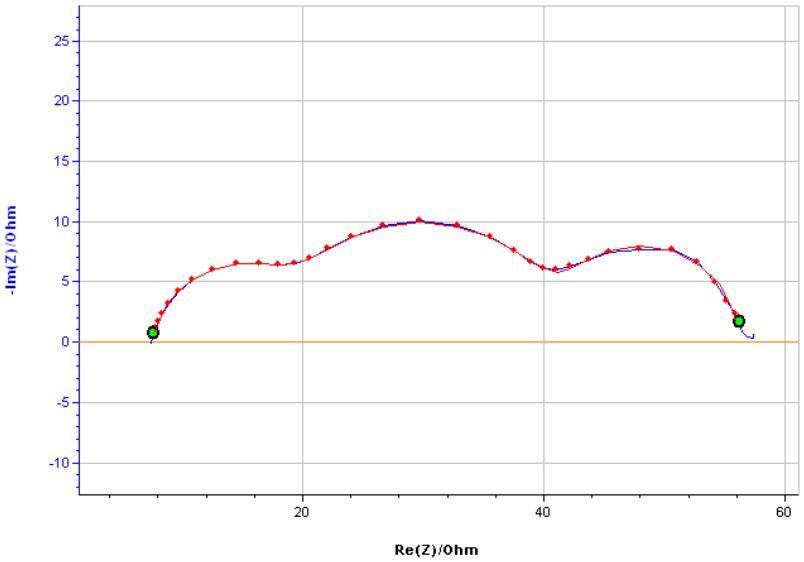

Figure S27. Measured impedance data and the fitted curve of the cell with MK-20

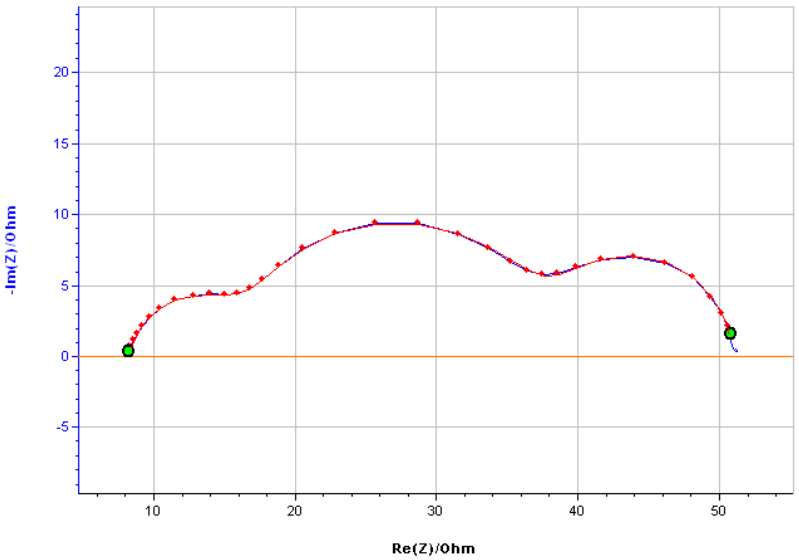

Figure S28. Measured impedance data and the fitted curve of the cell with MK-14

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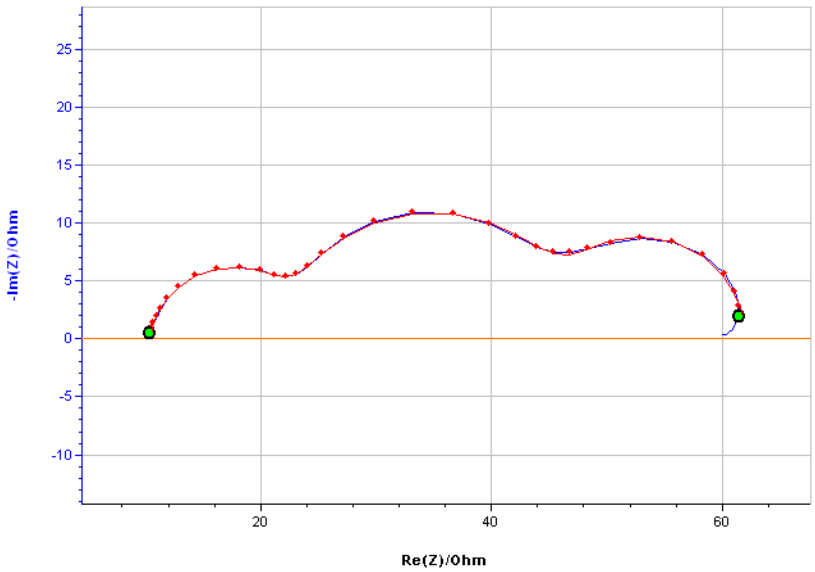

Figure S29. Measured impedance data and the fitted curve of the cell with MK-33

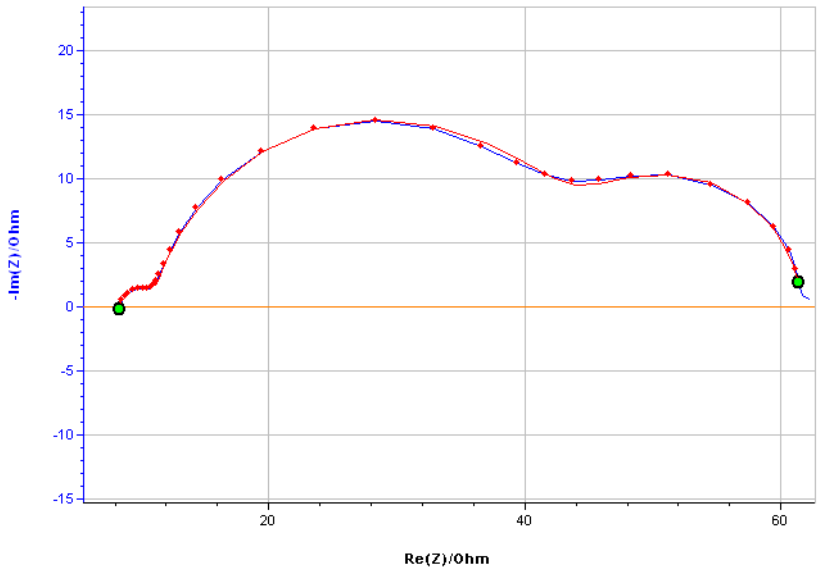

Figure S30. Measured impedance data and the fitted curve of the cell with MK-34

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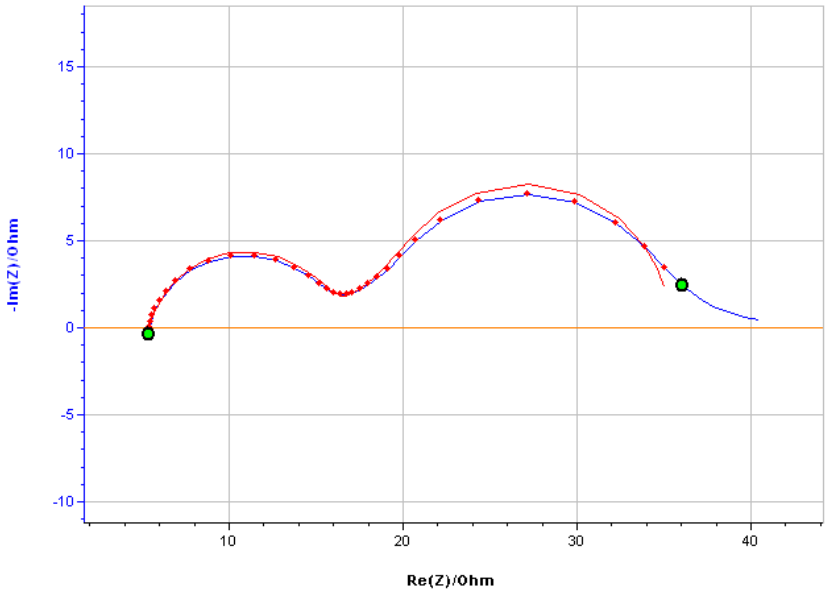

Figure S31. Measured impedance data and the fitted curve of the Pt-Pt dummy cell

Table S3 Values of impedance parameter except for W_d, obtained by fitting the equivalent circuit in Fig. S24 with impedance data shown in Fig. S23.

Dye	R_s / Ohm	R_{ct} (CE) / Ohm	*CPE*-q (CE) / 10^{-6} F.s^(α-1)	*CPE*-α (CE)	R_{ct} (TiO_2) / Ohm	*CPE*-q (TiO_2) / 10^{-3} F.s^(α-1)	*CPE*-α (TiO_2)
MK-1	7.70	6.72	18.8	0.878	17.9	0.109	0.939
MK-20	7.52	11.6	11.8	0.922	19.3	0.157	0.902
MK-14	8.31	7.71	14.6	0.910	19.5	0.196	0.885
MK-33	10.5	11.8	8.86	0.935	20.8	0.210	0.915
MK-34	8.40	2.43	6.30	1.00	29.7	0.191	0.905

CPE-q and CPE-α indicate the value of q and α in the equation (S2) for definition of the constant phase element. (TiO_2) and (CE) express the impedance parameter on TiO_2 layer and on counter electrode, respectively.

$$CPE = \frac{1}{q(i2\pi f)^{\alpha}} \qquad \text{(S2)}$$