Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Effects of photo-isomerizable side groups on phase and mechanical properties of main-chain nematic elastomers

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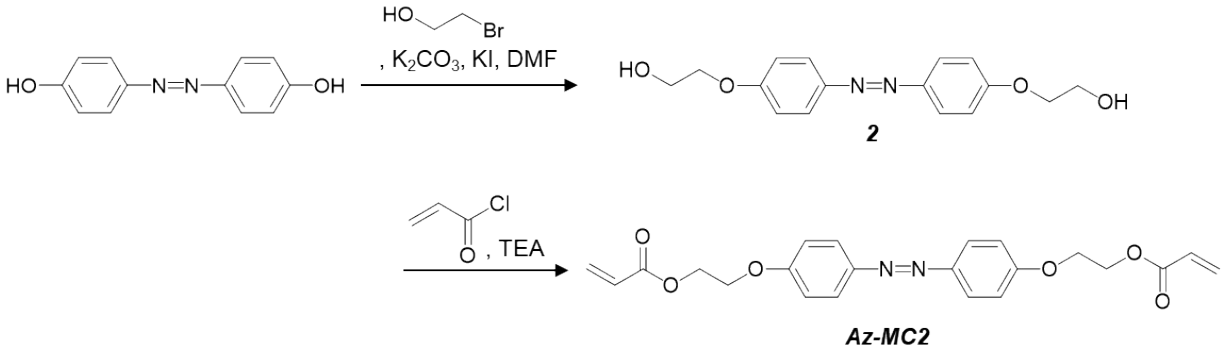
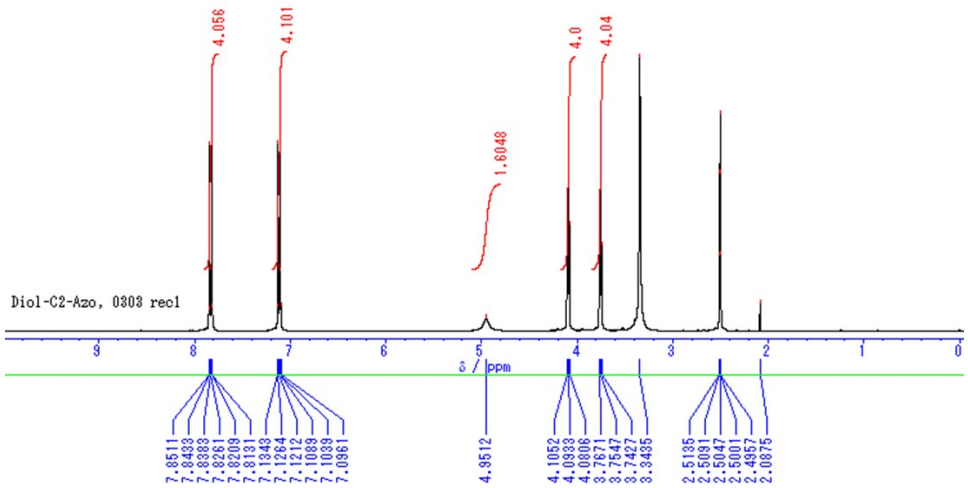
Supporting Note S1. Syntheses and NMR spectra of Intermediates of Azobenzene Monomers

General Information.

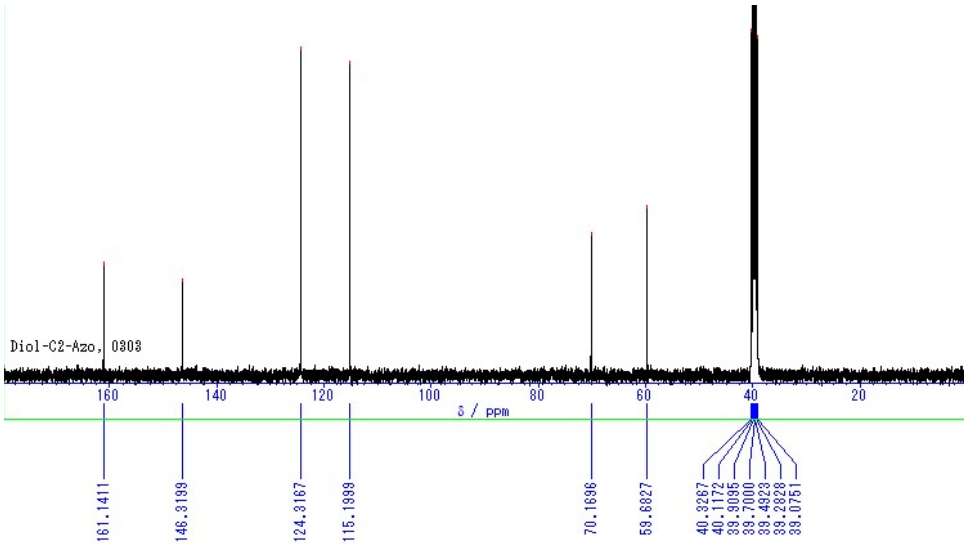
All commercially available reagents and solvents were used as received without further purification. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. Chemical shifts for NMR spectra were determined using tetramethylsilane (TMS) as internal standard in case of measurement in chloroform-*d* ($CDCl_3$) and were determined using the residual dimethylsulfoxide-d_6 (DMSO-d_6) peaks (δ_H 2.49 and δ_C 39.7) in the case of measurement in DMSO. The reaction mixture was purified by recycling gel permeation chromatography (GPC) (chloroform as eluent, Japan Analytical Industry Co., Ltd.) and silica gel column chromatography (Wakogel® 60N, 38-100 μm).



Synthesis of 4,4'-Bis(hydroxyethoxy)azobenzene (*2*). ***2*** was prepared by applying to a literature procedure.[1] To a mixture of 4,4'-dihydroxyazobenzene (6.43 g, 30.0 mmol), K_2CO_3 (16.58 g, 120.0 mmol), and KI (0.50 g, 3.0 mmol) in anhydrous dimethylformamide (DMF, 150 mL), 2-bromoethanol (15.00 g, 120.0 mmol,) was added under nitrogen. The mixture was stirred at 120 °C for 5 days. After evaporating DMF, the residue was dissolved in acetone (80 mL) then added water (300 mL). The generated solid was collected by filtration, then was purified by recrystallization from acetone/hexane to afford ***2*** as a yellow solid (8.0 g, 88% yield). ^{1}H-NMR (400 MHz, δ ppm, DMSO-d_6): 3.75 (t, J = 5.0 Hz, 4H), 4.09 (t, J = 5.1 Hz, 4H), 4.95 (s, 2 H), 7.12 (d, J = 9.0 Hz, 4 H), 7.83 (d, J = 9.0 Hz, 4 H); ^{13}C-NMR (101 MHz, δ ppm, DMSO-d_6): 59.7, 70.2, 115.2, 124.3, 146.3, 161.1. NMR spectra were shown below.

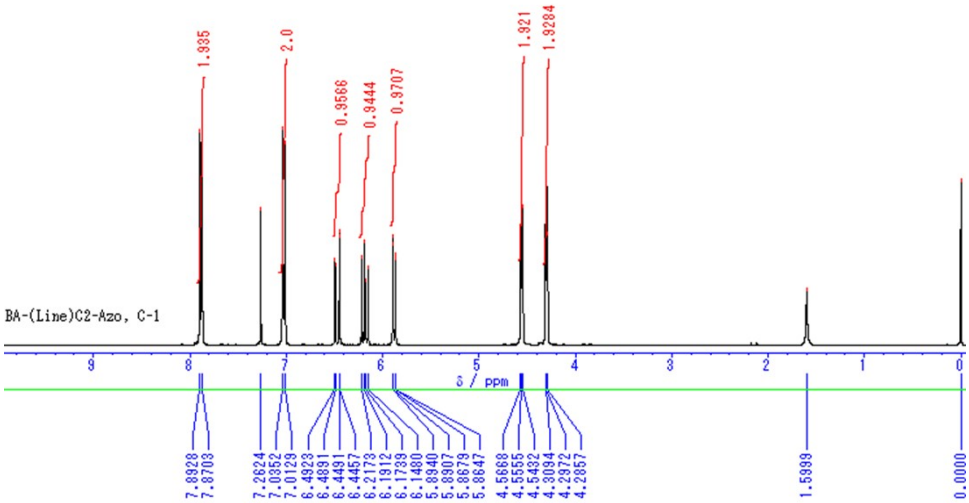


NMR charts of ^{1}H NMR spectrum of ***2***

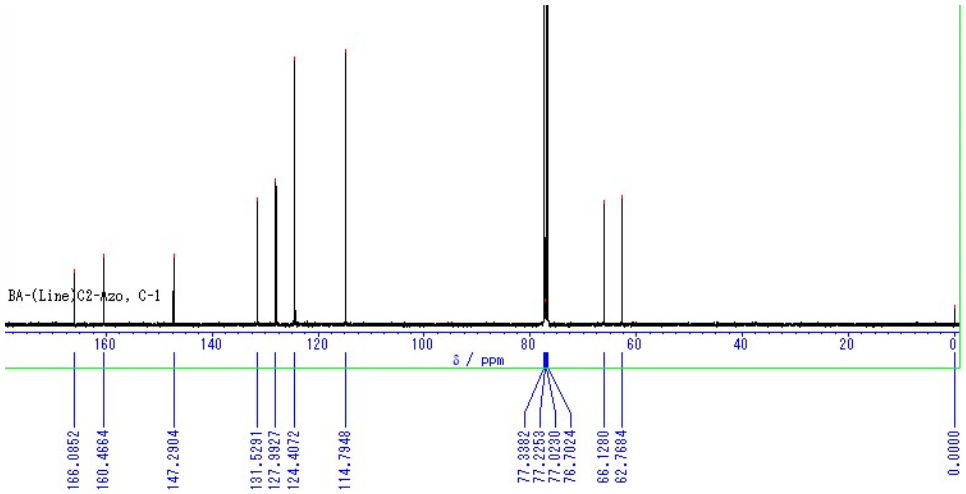


NMR charts of ^{13}C NMR spectrum of ***2***

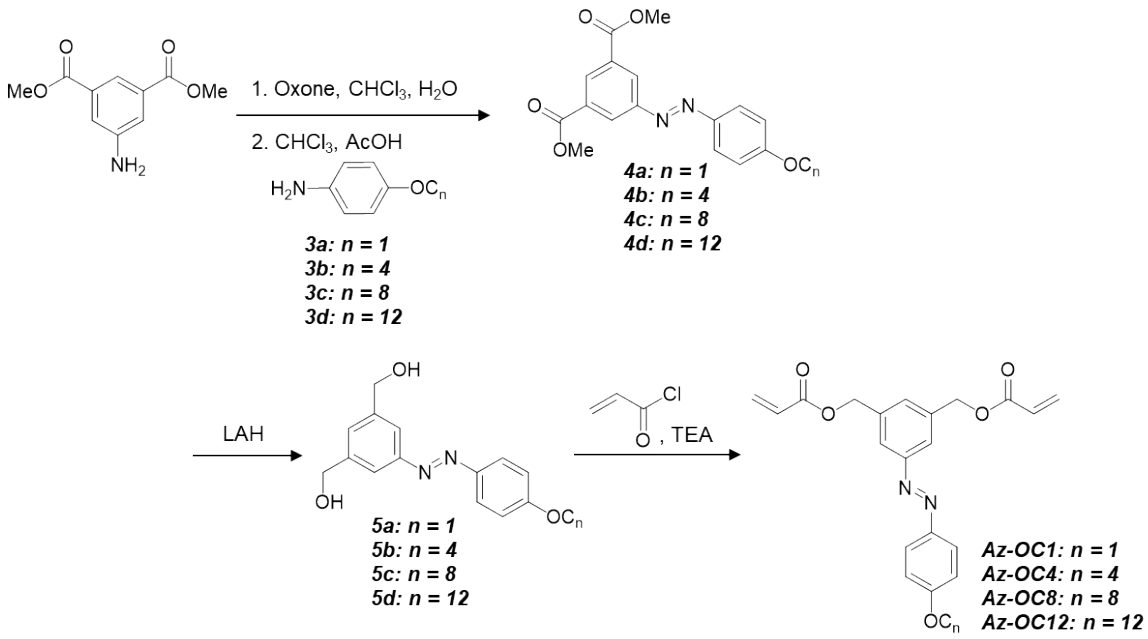
Synthesis of *Az-MC2*. NMR spectra of ***Az-MC2*** were shown below.



NMR charts of ^{1}H NMR spectrum of ***Az-MC2***

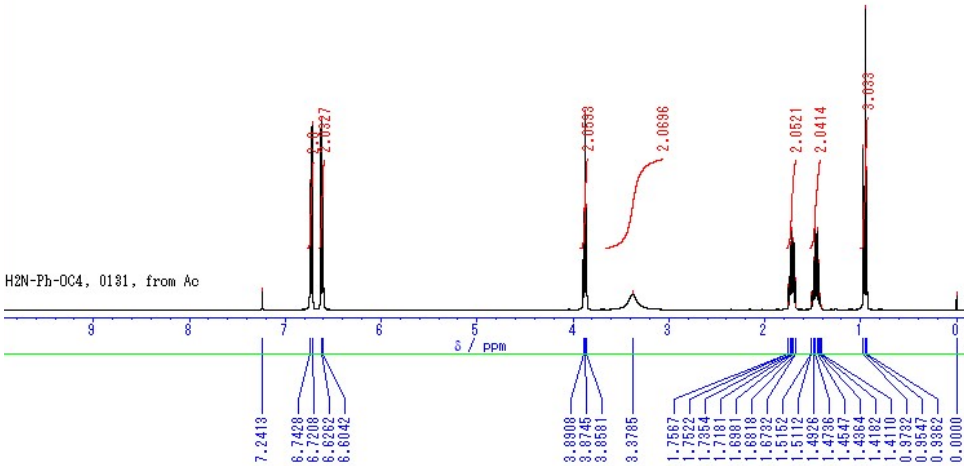


NMR charts of ^{13}C NMR spectrum of ***Az-MC2***

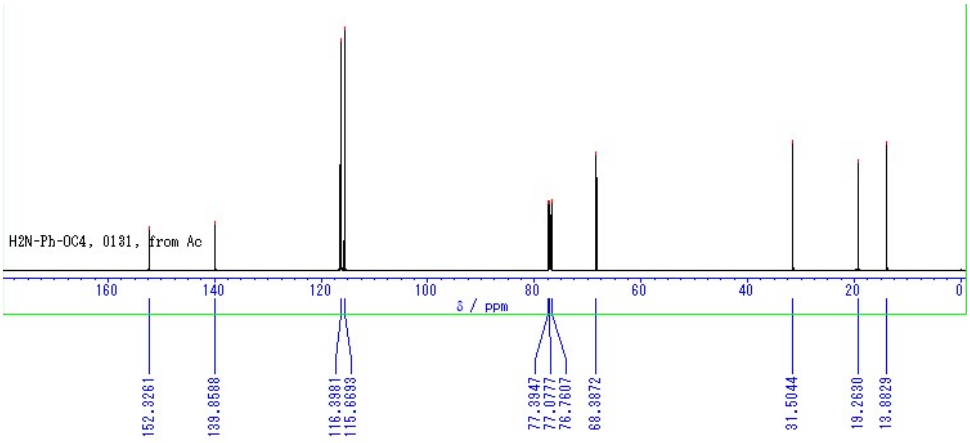


Synthesis of *3b*. ***3b*** was prepared by applying to a literature procedure.[2] To a solution of 4'-hydroxyacetanilide (1.06 g, 7.0 mmol), potassium carbonate (1.11 g, 8.0 mmol), and potassium iodide (0.17 g, 1.0 mmol,) in acetone (50 mL), 1-bromobutane (1.10 g, 8.0 mmol) was added under nitrogen, and the mixture was subsequently stirred at 85 °C for 23 h. After the reaction, acetone was evaporated to obtain crude N-(4-butoxyphenyl)acetamide, which was used without further purification. To the crude mixture in methanol was added conc. hydrochloric acid, the solution was subsequently refluxed for 18 h. After cooling, the solution was neutralized by 1N sodium hydroxide to pH = 8 at 0 °C and was added chloroform. The organic layer was washed by water,

then was dried over anhydrous $MgSO_4$ and filtered. The solvent was enough removed by evaporation. The obtained residue was sufficiently pure from NMR analysis, so it was used for the next reaction without further purification. (Pale brawn oil, 1.1 g, 92% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 0.96 (t, J = 7.4 Hz, 3 H), 1.41-1.52 (m, 2 H), 1.67-1.76 (m, 2 H), 3.38 (s, 2H), 3.88 (t, J = 6.5 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$): 31.5, 68.4, 115.7, 116.4, 139.9, 152.3.

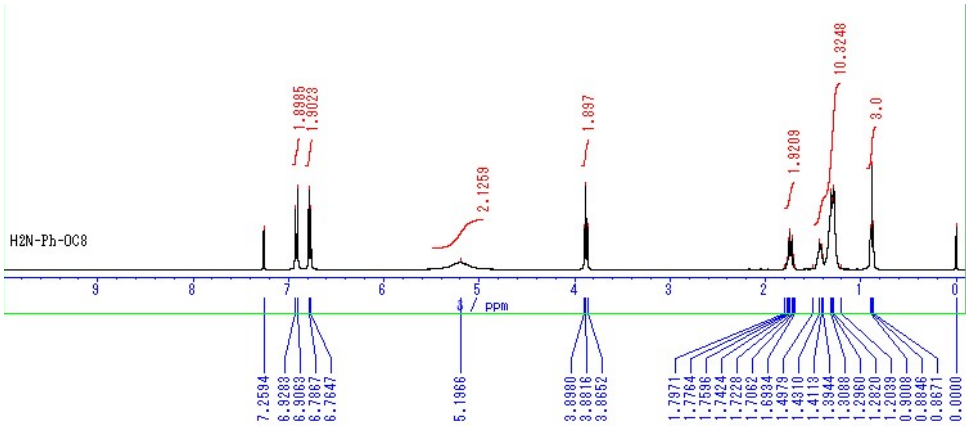


NMR charts of ^{1}H NMR spectrum of ***3b***

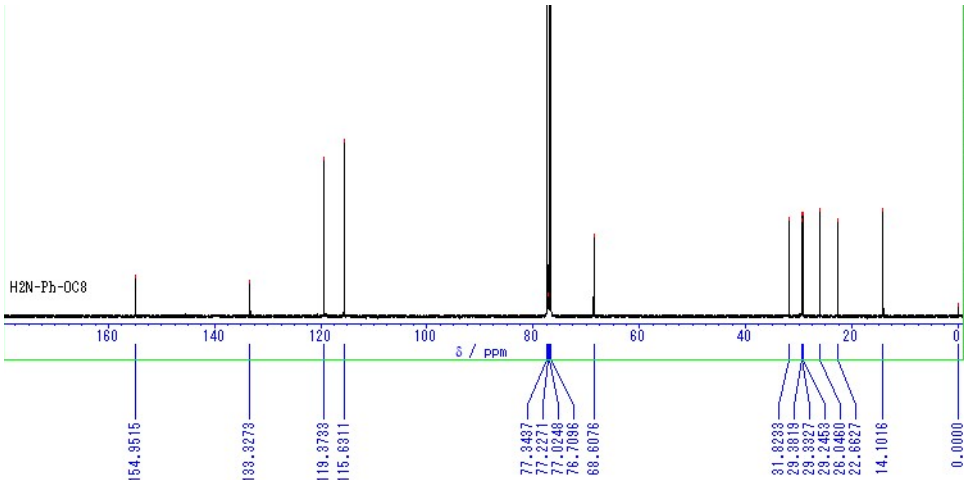


NMR charts of ^{13}C NMR spectrum of ***3b***

Synthesis of *3c*. ***3c*** was prepared in the same way as ***3b*** from 1-bromooctane (1.35 g, 7.0 mmol), and ***3b*** was purified by recrystallization from methanol/H_2O to afford ***3c*** as a pale beige solid (0.91 g, 68% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 0.89 (t, J = 6.5 Hz, 3H), 1.20-1.50 (m, 10H), 1.69-1.80 (m, 2H), 3.88 (t, J = 6.6 Hz, 2H), 2.13 (bs, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$):14.1, 22.7, 26.1, 19.3, 29.33, 29.4, 31.8, 66.6, 115.6, 119.4, 133.3, 155.0.

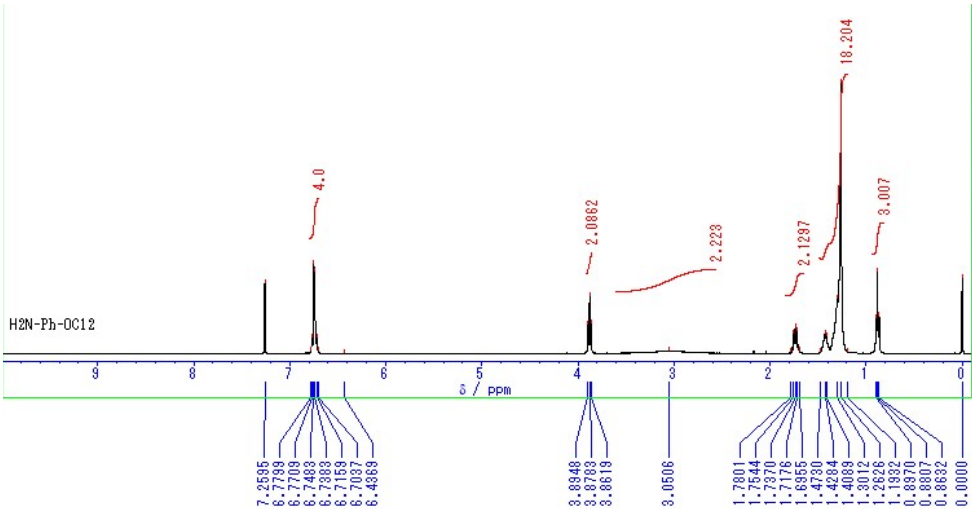


NMR charts of ^{1}H NMR spectrum of ***3c***

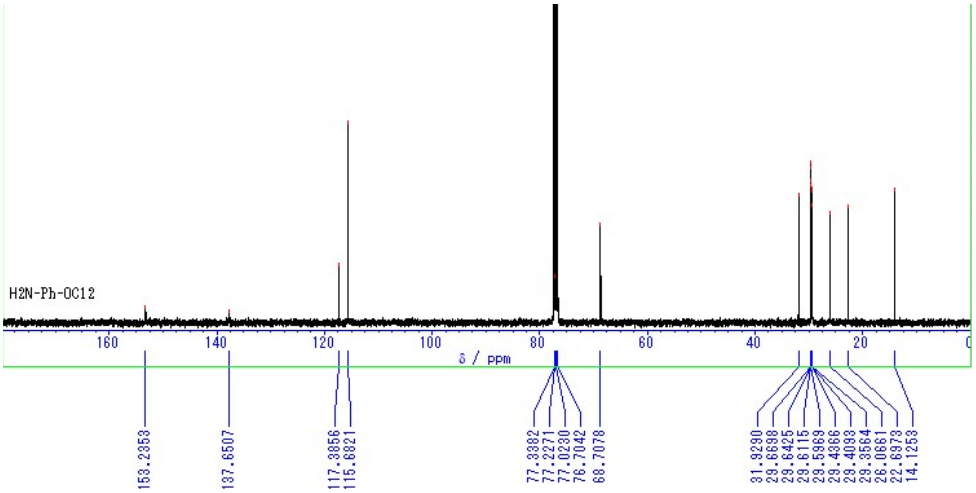


NMR charts of ^{13}C NMR spectrum of ***3c***

Synthesis of *3d*. ***3d*** was prepared in the same way as ***3b*** from 1-bromododecane (1.74 g, 7.0 mmol), and ***3d*** was purified by recrystallization from acetone/H_2O as a pale beige solid (0.75 g, 39% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 0.88 (t, J = 6.5 Hz, 3H), 1.19-1.47 (m, 18H), 1.74 (t, J = 7.0 Hz, 2H), 3.05 (bs, 2H), 3.88 (t, J = 6.6 Hz, 2H), 6.70-6.78 (m, 4H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$): 14.1, 22.7, 26.1, 29.4, 29.4, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9, 68.7, 115.7, 117.4, 137.7, 153.2.



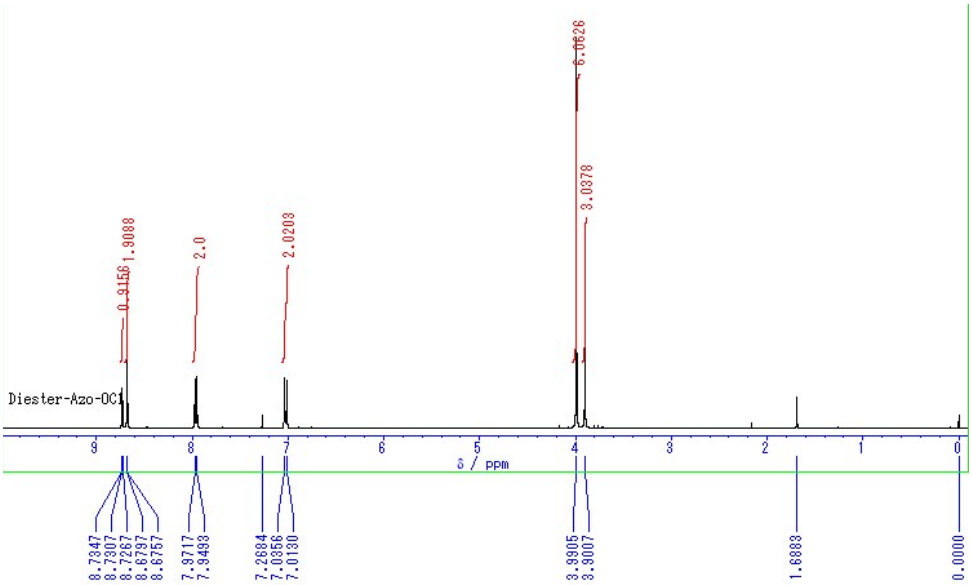
NMR charts of ^{1}H NMR spectrum of ***3d***



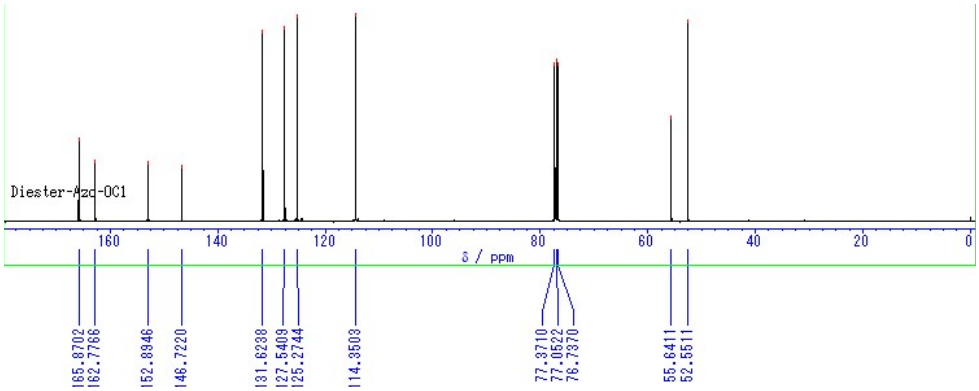
NMR charts of ^{13}C NMR spectrum of ***3d***

Synthesis of *4a*. *4a* was prepared by applying to a literature procedure.[3] A mixture of dimethyl 5-Aminoisophthalate (10.5 g, 50.0 mmol) in chloroform (200 mL) and oxone (38.48 g, 125.0 mmol) in H_2O (200 mL) was stirred vigorously at room temperature for 18 h. The organic layer was separated and washed with water and then dried over $MgSO_4$. The residue obtained after evaporation, nitroso compound, was used next reaction without further purification. The residue and 4-methoxyphenol (6.16 g, 50.0 mmol) were added to chloroform (50 mL) and acetic acid (100 mL), and the mixture was stirred for 22 h at rt. After evaporation of the solvent, the mixture was added to chloroform (150mL), and was neutralized by aq. sodium carbonate (pH≈7) at 0 °C. The organic layer was wash with water, then was dried over anhydrous $MgSO_4$ and filtered. The residue obtained after evaporation was purified by column chromatography (chloroform/hexane = 4:1) and recrystallization (acetone/water) to afford ***4a*** as an orange

solid (9.73 g, 59% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 3.90 (s, 3H), 4.00 (s, 6H), 7.02 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 8.68 (d, J = 1.6 Hz, 2H), 8.73 (s, J = 1.6 Hz, 1H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$):52.6, 55.6, 114.4, 125.3, 127.5, 131.6, 146.7, 152.9, 162.8, 165.9.

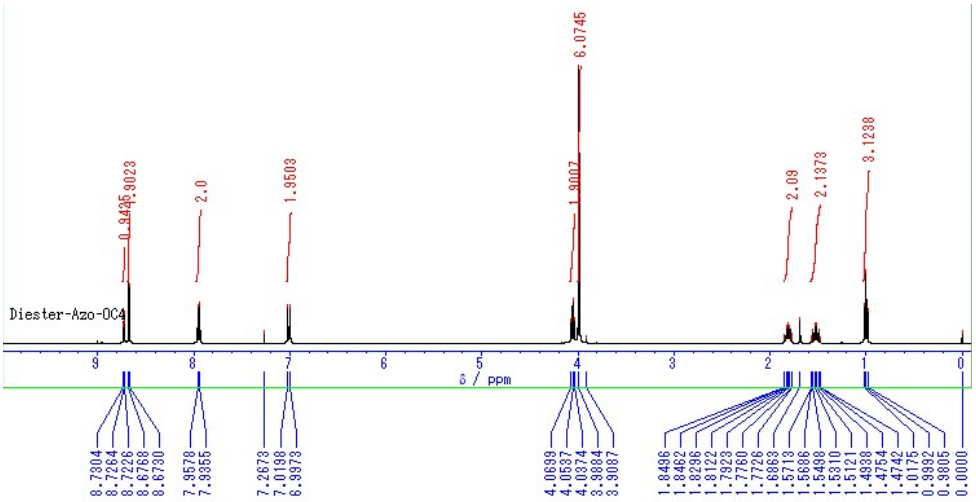


NMR charts of ^{1}H NMR spectrum of ***4a***

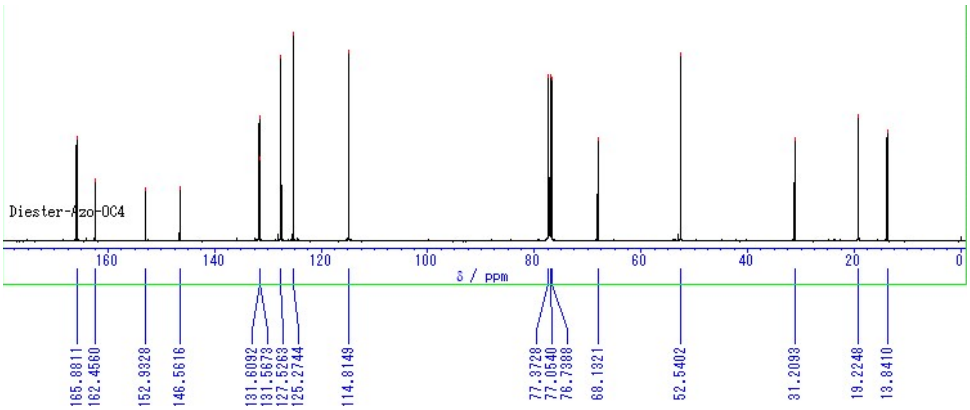


NMR charts of ^{13}C NMR spectrum of ***4a***

Synthesis of *4b* (Diester-C4). ***4b*** was prepared in the same way as ***4a*** from ***3b*** by purification using column chromatography (chloroform/hexane = 1/2) as an orange solid (5.2 g, 71% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 1.00 (t, J = 7.3, 3H), 1.47-1.57 (m, 2H), 1.77-1.85 (m, 2H), 3.99 (s, 6H), 4.06 (t, J = 6.5, 2H), 7.01 (d, J = 8.9 Hz, 2H), 7.95 (d, J = 9.0 Hz, 2H), 8.67 (t, J = 1.5 Hz, 2H), 8.73 (t, J = 1.6 Hz, 1H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$):13.8, 19.2, 31.2, 52.5, 68.1, 114.8, 125.3, 127.5, 131.6, 131.6, 146.6, 153.0, 162.5, 165.9.

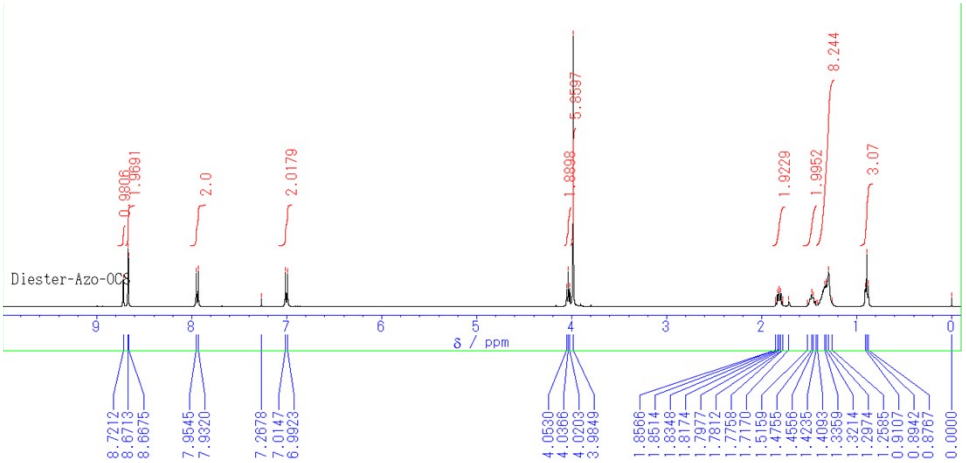


NMR charts of ^{1}H NMR spectrum of ***4b***

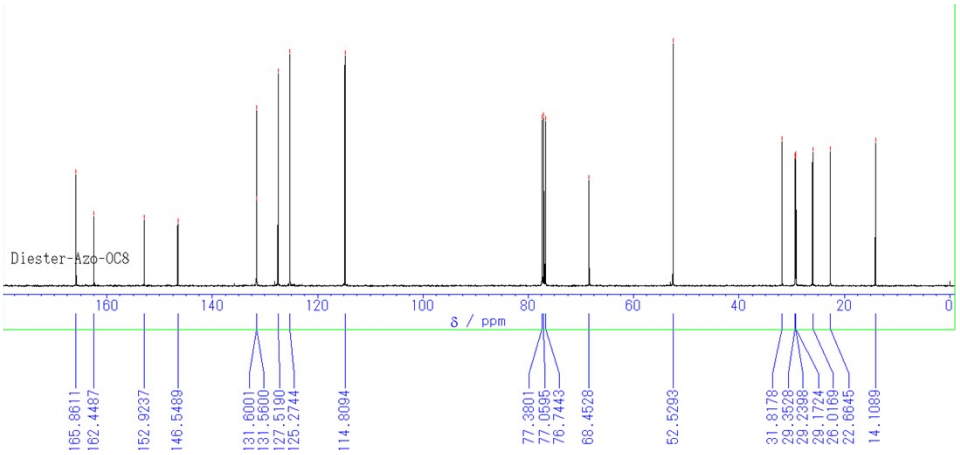


NMR charts of ^{13}C NMR spectrum of ***4b***

Synthesis of *4c*. ***4c*** was prepared in the same way as ***4a*** from ***3c*** (1.05 g, 5.0 mmol) by purification using column chromatography (chloroform/hexane = 1/1) as an orange solid (1.13 g, 53% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 0.90 (t, *J* = 6.6, 3 H), 1.26-1.41 (m, 8 H), 1.40-1.52 (m, 2H), 1.78-1.86 (m, 2H), 3.98 (s, 6 H), 4.06 (t, *J* = 6.6 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 8.67 (d, *J* = 1.5, 2H), 8.75 (s, 1H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$): 14.1, 22.7, 26.0, 29.2, 29.2, 29.4, 31.8, 52.5, 68.5, 114.8, 125.3, 127.5, 131.6, 131.6, 146.5, 152.9, 162.4, 165.9.

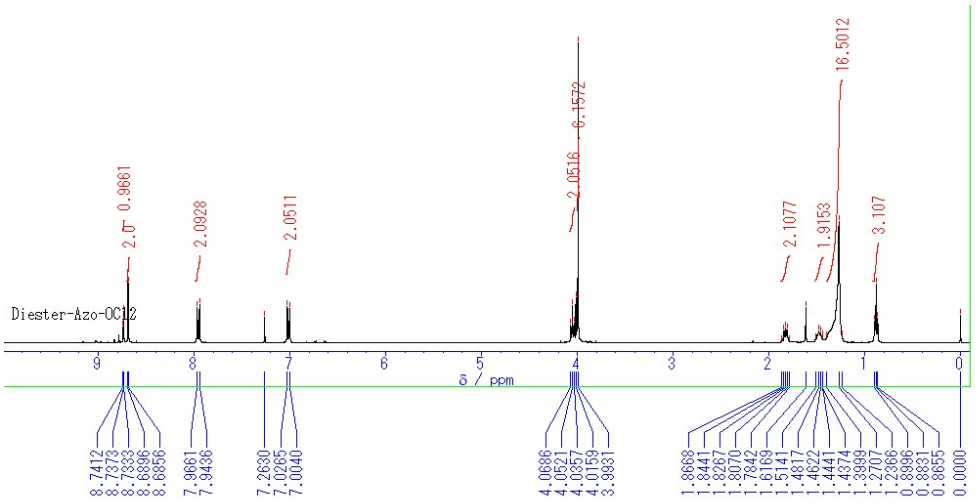


NMR charts of ^{1}H NMR spectrum of ***4c***

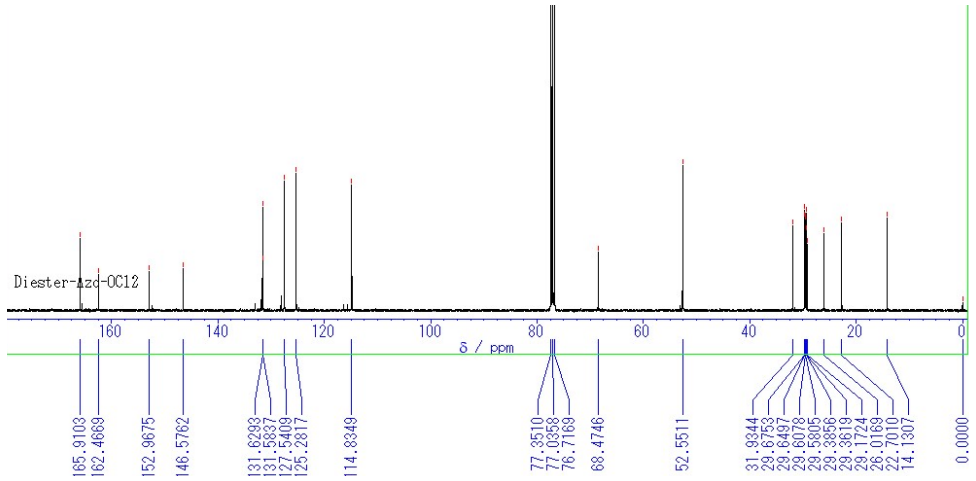


NMR charts of ^{13}C NMR spectrum of ***4c***

Synthesis of *4d*. ***4d*** was prepared in the same way as ***4a*** from ***3d*** (12.25 g, 60 mmol,) as an orange solid (15.1 g, 52% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 0.88 (t, J = 6.6, 3H), 1.24-1.40 (m, 16H), 1.44-1.51 (m, 2H),1.78-1.87 (m, 2H), 3.99 (s, 6H), 4.05 (t, J = 6.6 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 9.0 Hz, 2H), 8.69 (t, J = 1.6 Hz, 2H), 8.74 (t, J = 1.6 Hz, 1H); ^{13}C-NMR (101 MHz, ppm, δ $CDCl_3$): 14.13, 22.70, 26.02, 29.36, 29.39, 29.58, 29.65, 29.68, 31.93, 52.55, 68.47, 114.83, 125.28, 127.54, 131.59, 131.62, 146.58, 152.97, 162.47, 165.91.

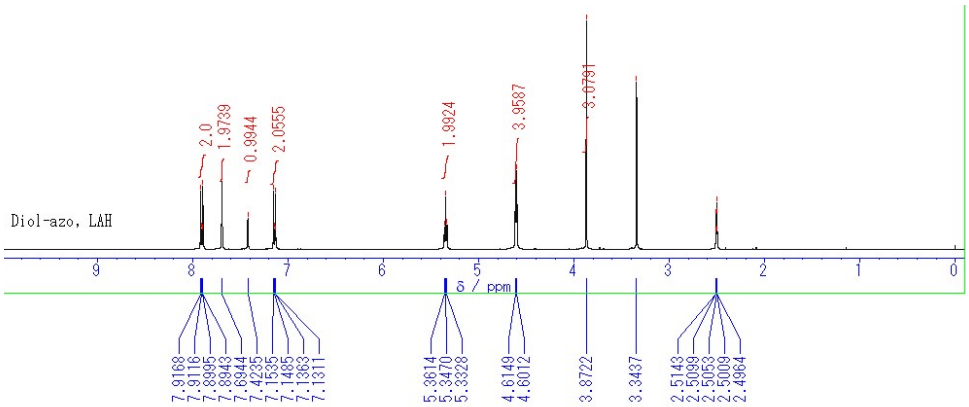


NMR charts of ^{1}H NMR spectrum of ***4d***

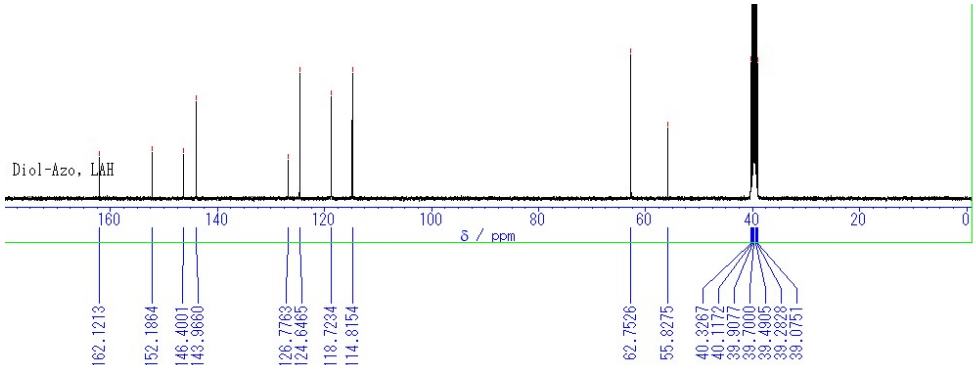


NMR charts of ^{13}C NMR spectrum of ***4d***

Synthesis of *5a*. To a lithium aluminium hydride (LAH) (0.57 g, 15mmol,) in dry THF was slowly dropped ***4a*** (1.97 g, 6 mmol,) in anhydrous THF under N_2 at 0 °C, and the mixture was subsequently stirred at rt for 4 h. After excess LAH was quenched by aqueous sodium sulfate solution, the solvent was evaporated. The obtained residue was added acetone, and insoluble part was removed by filtration, and the filtrate concentrated by evaporation. The residue was purified by using column chromatography (SiO_2, acetone / hexane = 3 / 2) to afford ***5a*** as an orange solid (1.6 g, 95% yield). ^{1}H-NMR (400 MHz, δ ppm, DMSO-d_6): 3.87 (s, 3H), 4.61 (d, J = 5.5 Hz, 4H), 6.35 (t, J = 5.8 Hz, 2H), 7.14 (dd, J = 6.9, 2.1 Hz, 2H), 7.42 (s, 1H), 7.69 (s, 2H), 7.91 (dd, J = 6.9, 2.1 Hz, 2H); ^{13}C-NMR (101 MHz, δ ppm, DMSO-d_6): 55.8, 62.8, 114.8, 118.7, 124.6, 126.8, 144.0, 146.4, 152.2, 162.1.

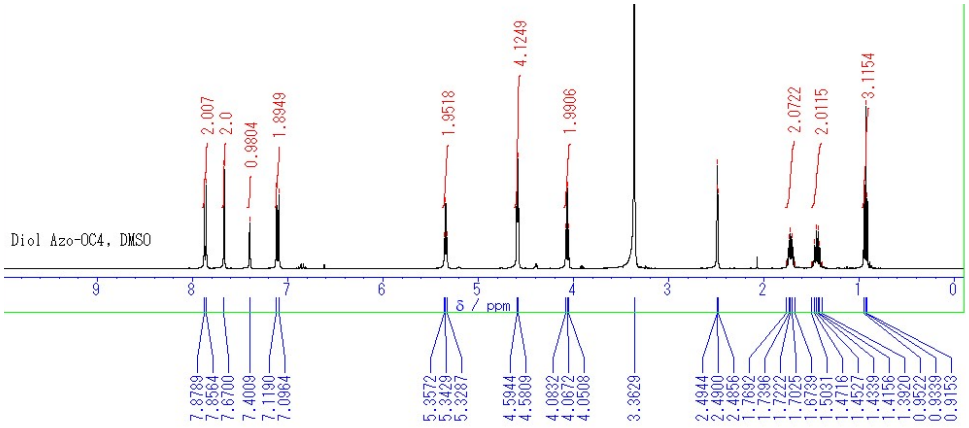


NMR charts of ^{1}H NMR spectrum of ***5a***

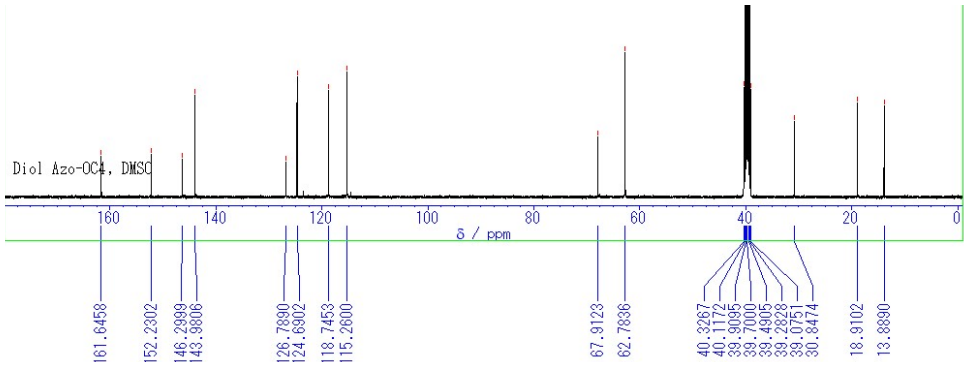


NMR charts of ^{13}C NMR spectrum of ***5a***

Synthesis of *5b*. *5b* was prepared in the same way as ***5a*** from ***4b*** (1.91 g, 5.16 mmol,) as an orange solid (0.85 g, 52% yield). ^{1}H-NMR (400 MHz, δ ppm, DMSO-d_6): 0.94 (t, J = 7.3 Hz, 3H), 1.39-1.50 (m, 2H), 1.67-1.77 (m, 2H), 4.08 (t, J = 6.4 Hz, 2H), 4.59 (d, J = 5.4 Hz, 4H), 5.35 (t, J = 5.7 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 7.40 (s, 1H), 7.67 (s, 2H), 7.86 (d, J = 9.0 Hz, 2H); ^{13}C-NMR (101 MHz, δ ppm, DMSO-d_6): 13.89, 18.91, 30.85, 62.78, 67.91, 115.26, 118.75, 124.69, 126.79, 143.98, 146.30, 152.23, 161.65.

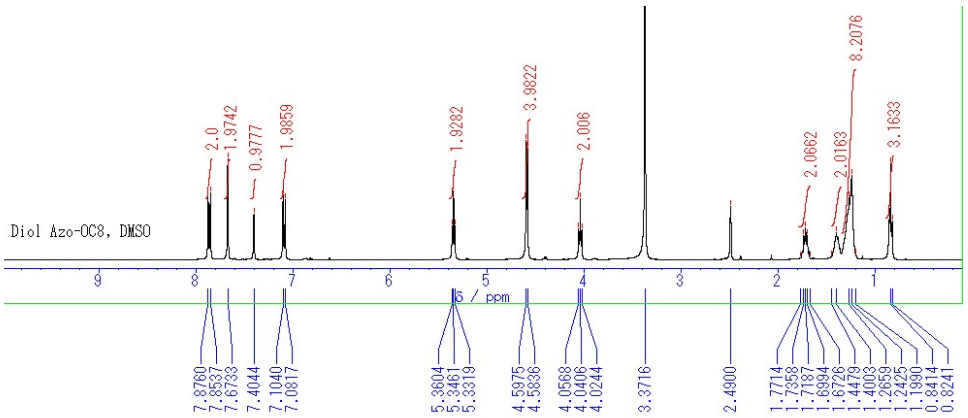


NMR charts of ^{1}H NMR spectrum of ***5b***

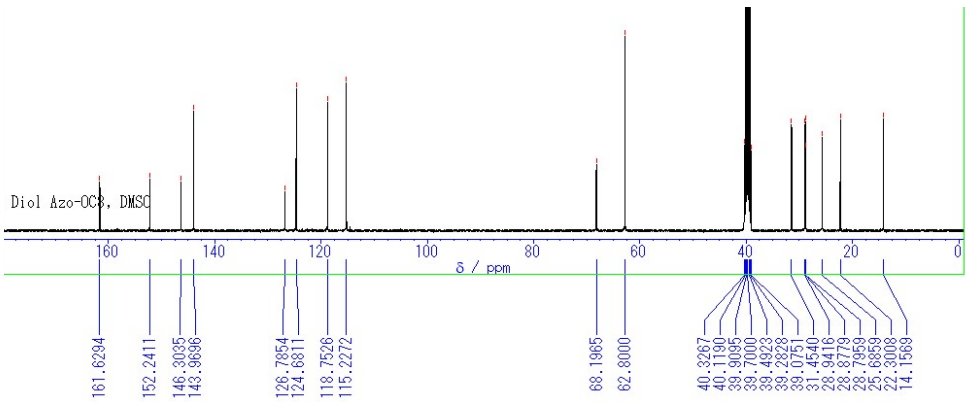


NMR charts of ^{13}C NMR spectrum of ***5b***

Synthesis of *5c*. ***5c*** was prepared in the same way as ***5a*** from ***4c*** (2.16 g, 5.1 mmol,) as an orange solid (1.37 g, 73.3% yield). ^{1}H-NMR (400 MHz, δ ppm, DMSO-d_6): 0.90 (t, J = 6.7 Hz, 3 H), 1.24-1.52 (m, 10 H), 1.78-1.88 (m, 4 H), 4.04 (t, J = 6.6 Hz, 2 H), 4.81 (d, J = 5.6 Hz, 4 H), 7.01 (d, *J* = 9.1 Hz, 2 H), 7.48 (s, 1 H), 7.80 (s, 2 H), 7.91 (d, J = 9.0 Hz, 2 H); ^{13}C-NMR (101 MHz, δ ppm, DMSO-d_6): 14.16, 2230, 25.69, 28.80, 28.88, 28.94, 31.45, 62.80, 68.20, 115.23, 118.75, 124.68, 126.79, 143.97, 146.30, 152.24, 161.63.

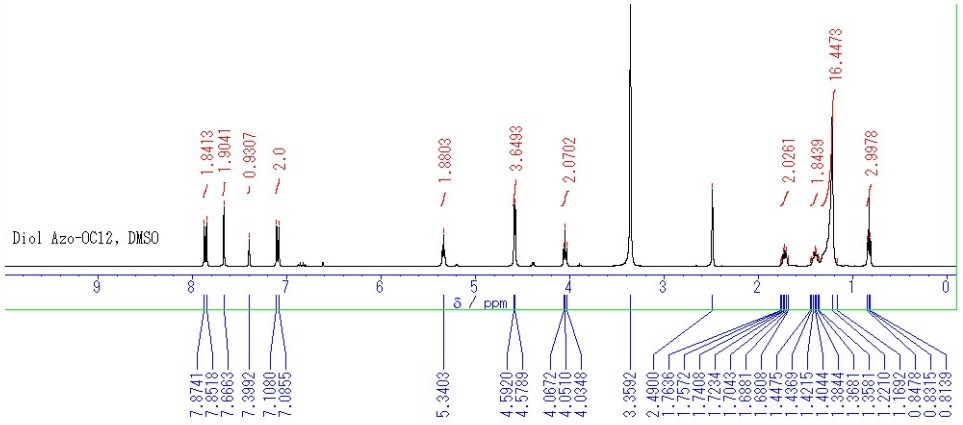


NMR charts of ^{1}H NMR spectrum of ***5c***

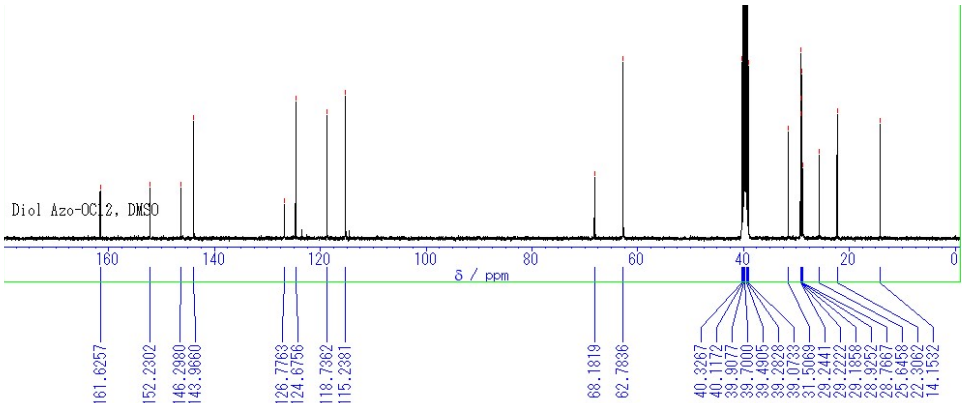


NMR charts of ^{13}C NMR spectrum of ***5c***

Synthesis of *5d*. *5d* was prepared in the same way as ***5a*** from ***4d*** (7.24 g, 15 mmol) as an orange solid (3.91 g, 61% yield). ^{1}H-NMR (400 MHz, δ ppm, DMSO-d_6) : 0.84 (t, J = 6.5 Hz, 3 H), 1.17-1.33 (m, 16 H), 1.36-1.45 (m, 2 H),1.68-1.76 (m, 4 H), 4.06 (t, J = 6.6 Hz, 2H), 4.58 (d, J = 5.2, 4H), 5.34 (t, J = 5.7 Hz, 2H), 7.10 (d, J = 9.0 Hz, 2H), 7.40 (s, 1 H), 7.67 (s, 2 H), 7.86 (d, J = 8.9 Hz, 2H); ^{13}C-NMR (101 MHz, δ ppm, DMSO-d_6): 14.2, 22.3, 25.6, 28.8, 28.9, 29.2, 29.2, 29.2, 31.5, 62.8, 68.2, 115.2, 118.7, 124.7, 126.8, 144.0, 146.3, 152.2, 161.6.

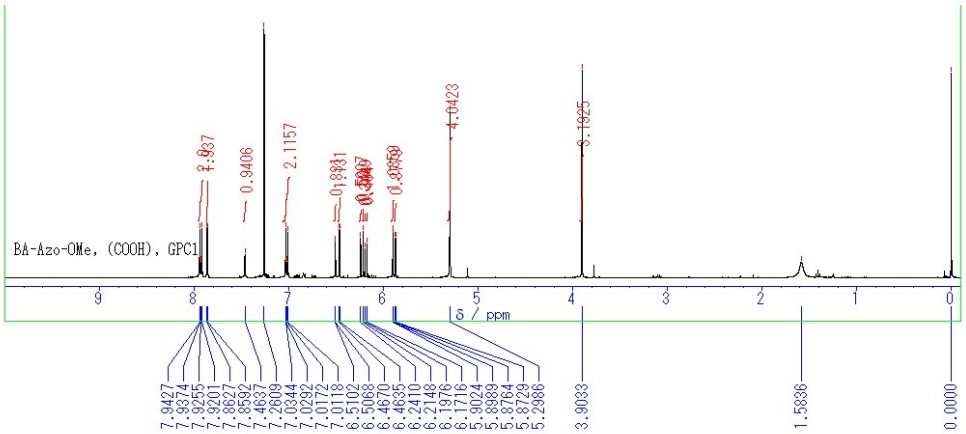


NMR charts of ^{1}H NMR spectrum of ***5d***

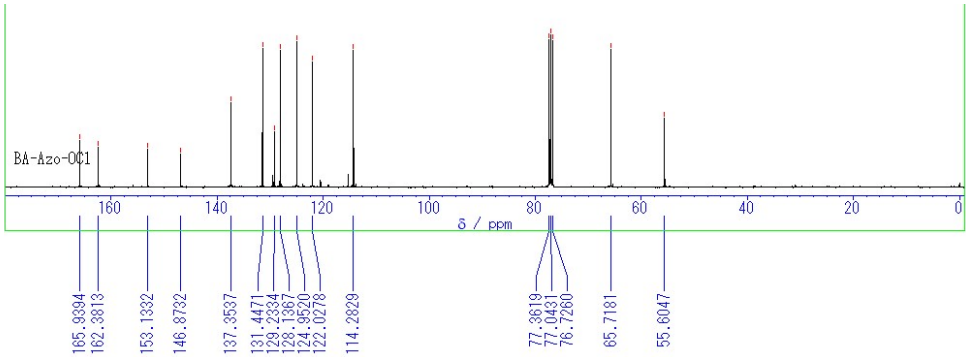


NMR charts of ^{13}C NMR spectrum of ***5d***

Synthesis of *Az-OC1*. NMR spectra of ***Az-OC1*** were shown below.

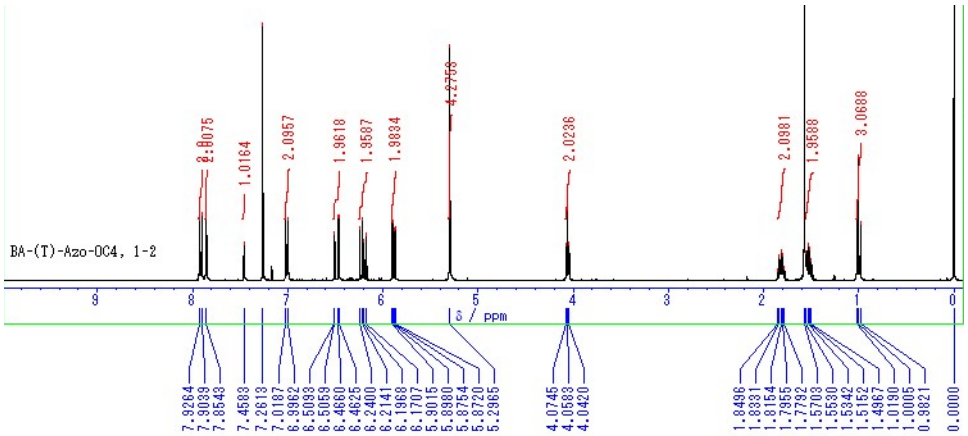


NMR charts of ^{1}H NMR spectrum of ***Az-OC1***

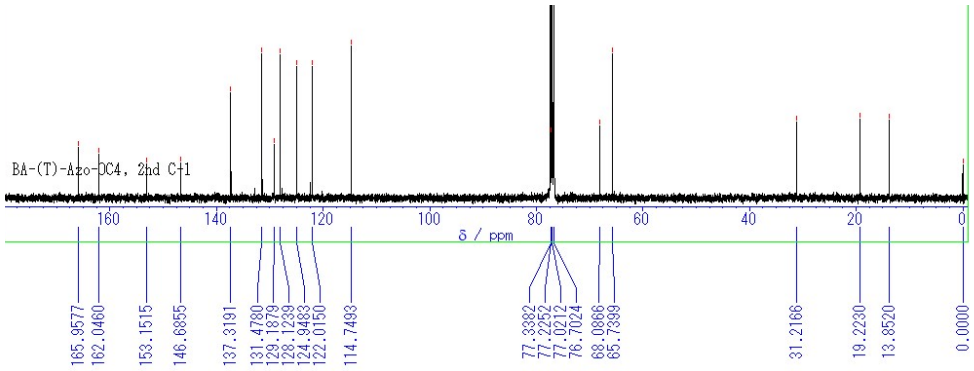


NMR charts of ^{13}C NMR spectrum of ***Az-OC1***

Synthesis of *Az-OC4*. NMR spectra of ***Az-OC4*** were shown below.

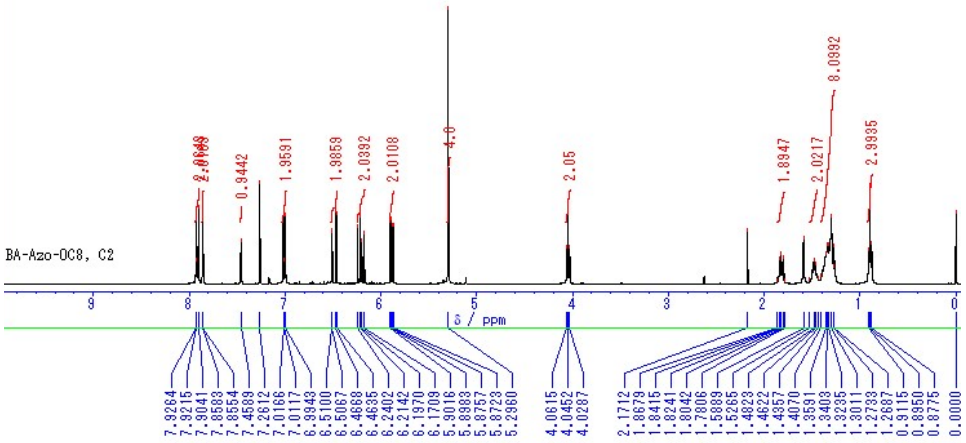


NMR charts of ^{1}H NMR spectrum of ***Az-OC4***

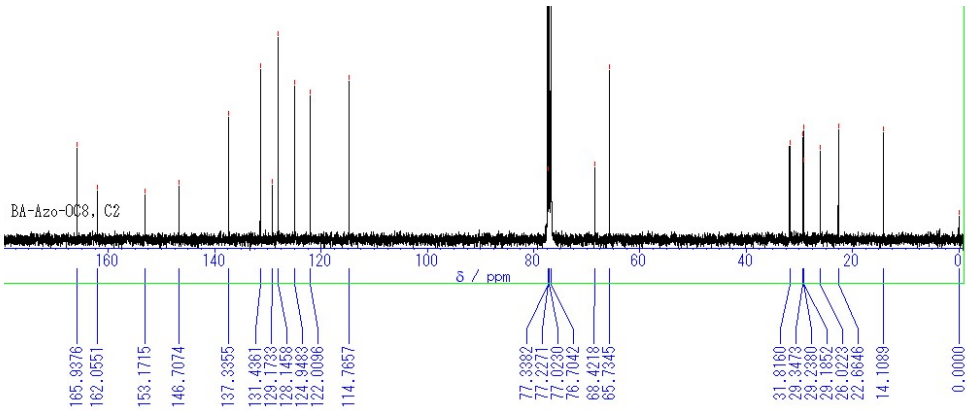


NMR charts of ^{13}C NMR spectrum of ***Az-OC4***

Synthesis of *Az-OC8*. NMR spectra of ***Az-OC8*** were shown below.

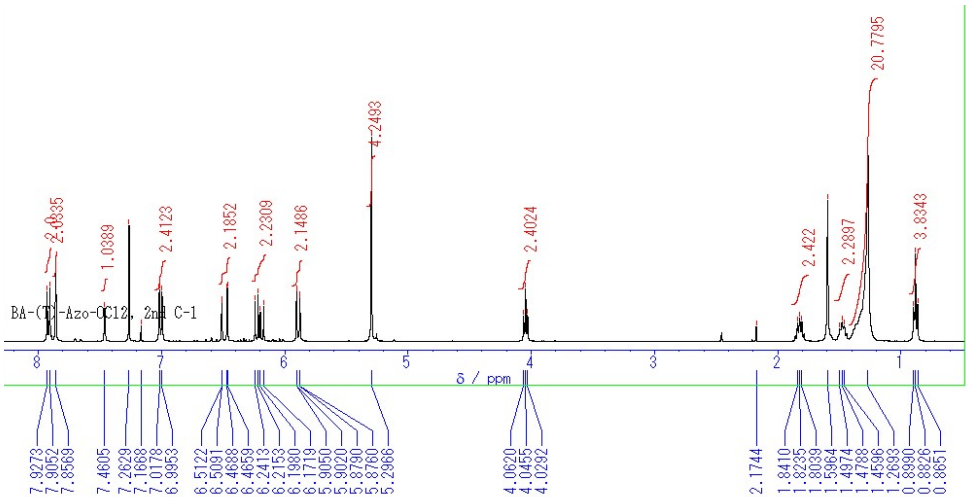


NMR charts of ^{1}H NMR spectrum of ***Az-OC8***

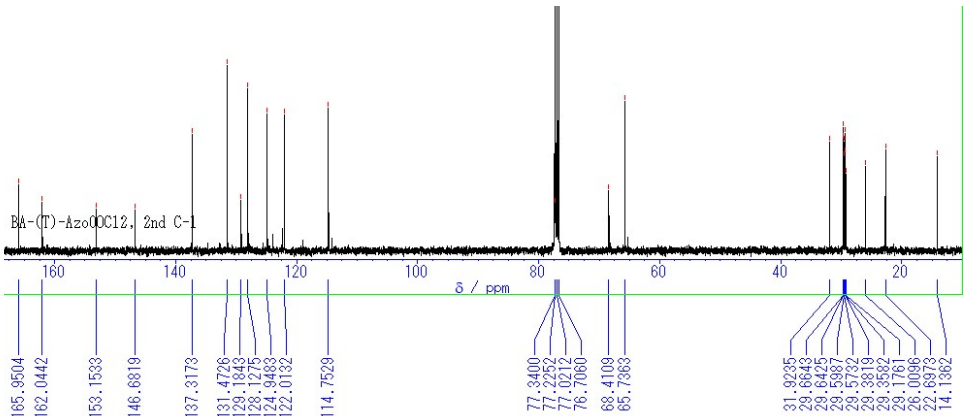


NMR charts of ^{13}C NMR spectrum of ***Az-OC8***

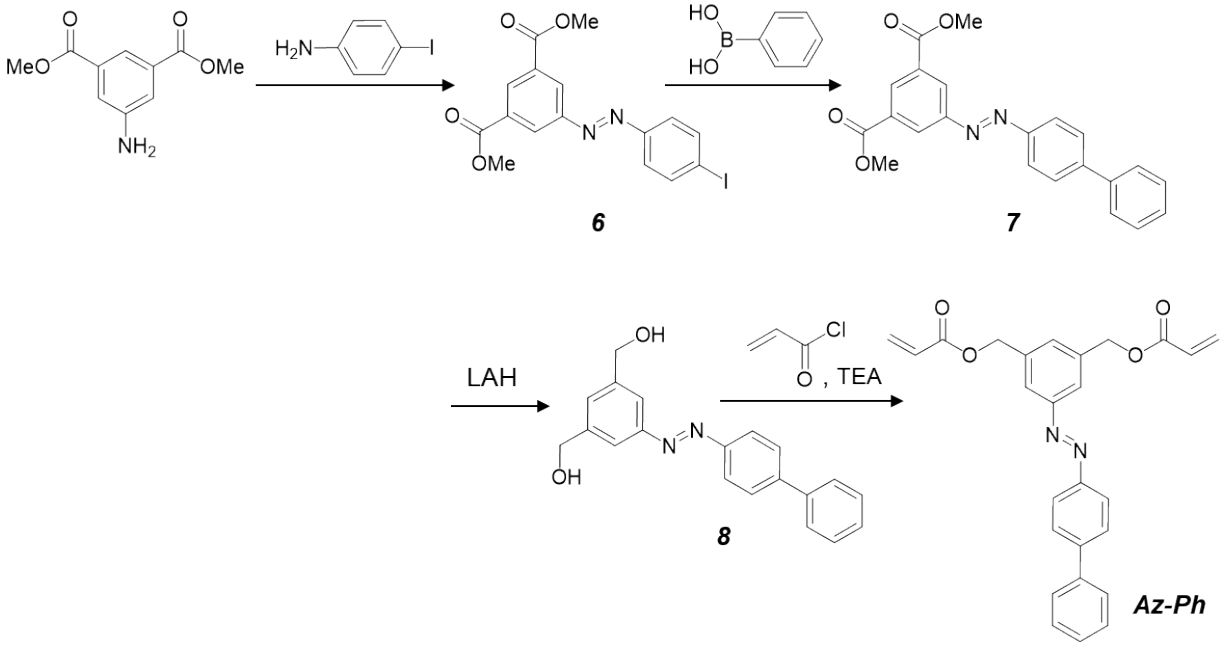
Synthesis of *Az-OC12*. NMR spectra of ***Az-OC12*** were shown below.



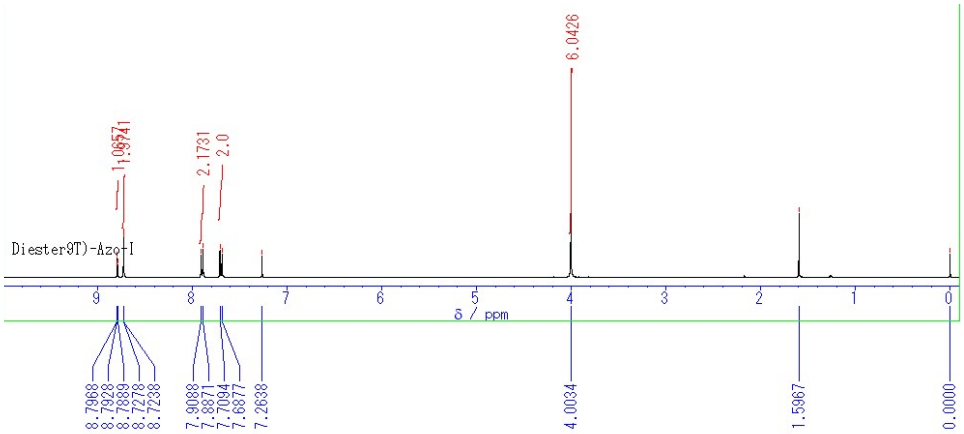
NMR charts of ^{1}H NMR spectrum of ***Az-OC12***



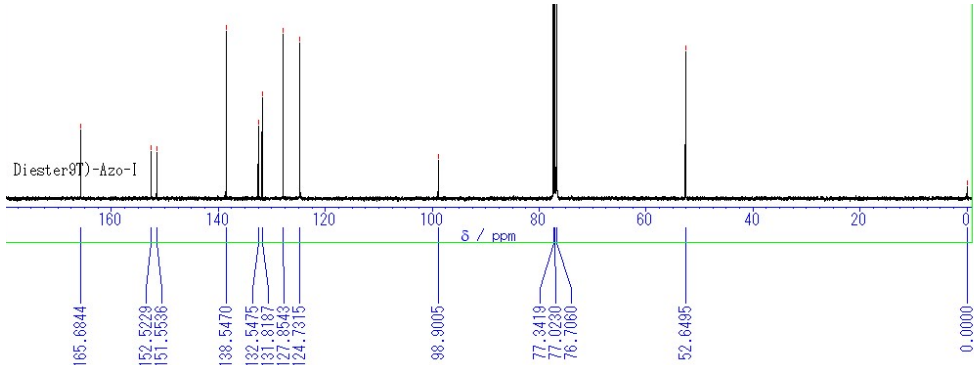
NMR charts of ^{13}C NMR spectrum of ***Az-OC12***



Synthesis of *6*. ***6*** was prepared in the same way as ***4a*** from 5-Aminoisophthalate (20.92 g, 100 mmol,) and 4-iodoaniline (21.90 g, 100 mmol,) as an orange solid (30.5 g, 72% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 4.00 (s, 6 H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 8.73 (d, *J* = 1.6 Hz, 2 H), 8.79 (t, *J* = 1.6 Hz, 1H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$):52.6, 98.9, 124.7, 127.9, 131.8, 132.5, 138.5, 151.6, 152.5, 165.7.



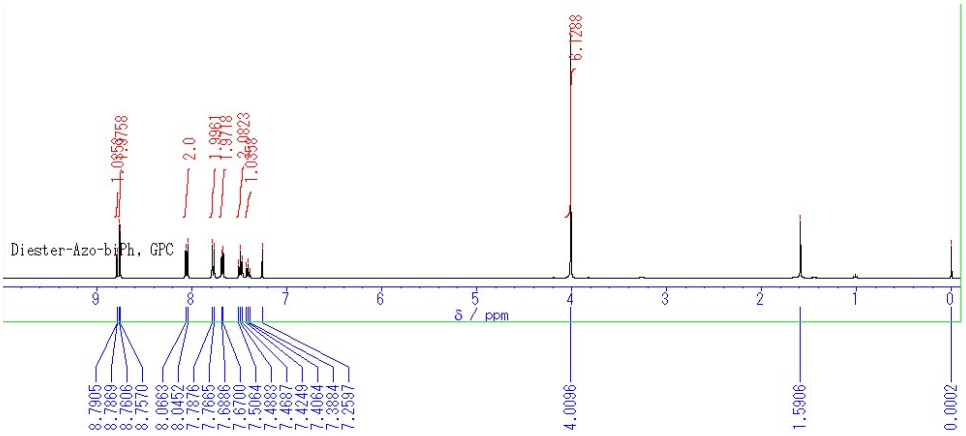
NMR charts of ^{1}H NMR spectrum of ***6***



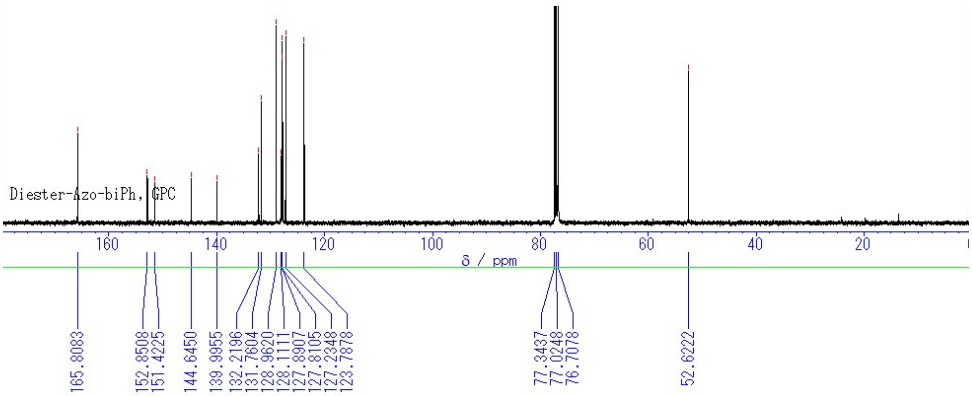
NMR charts of ^{13}C NMR spectrum of ***6***

Synthesis of *7*. ***6*** (8.48 g, 20 mmol), phenyl boronic acid (3.05 g, 25 mmol), potassium carbonate (8.29 g, 60 mmol), $Pd(PPh_3)_4$ (70.2 mg, 0.10 mmol), and tetrabutylammonium bromide (0.32 g, 1.0 mmol) were dissolved in H_2O/toluene (40 mL/40mL), the mixture was stirred under N_2 at 105 °C for 2 days. The mixture was cooled and acidified with 1N HCl until pH 6-7, after concentrated in vacuo, and the resulting residue was added chloroform. The organic layer was separated, washed with water, and dried over $MgSO_4$. The residue after evaporation, was purified by GPC to afford *7* in chloroform as an orange solid. (1.0 g, 91% yield); ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 4.00 (s, 6H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 8.4 Hz,

2H), 8.06 (d, *J* = 8.4 Hz, 2H), 8.76 (d, *J* = 1.4 Hz, 2H), 8.79 (d, *J* = 1.4 Hz, 1H). ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$): 52.62, 123.8, 127.2, 127.8, 127.9, 128.1, 129.0, 131.8, 132.2, 140.0, 144.6, 151.4, 152.9, 165.8.

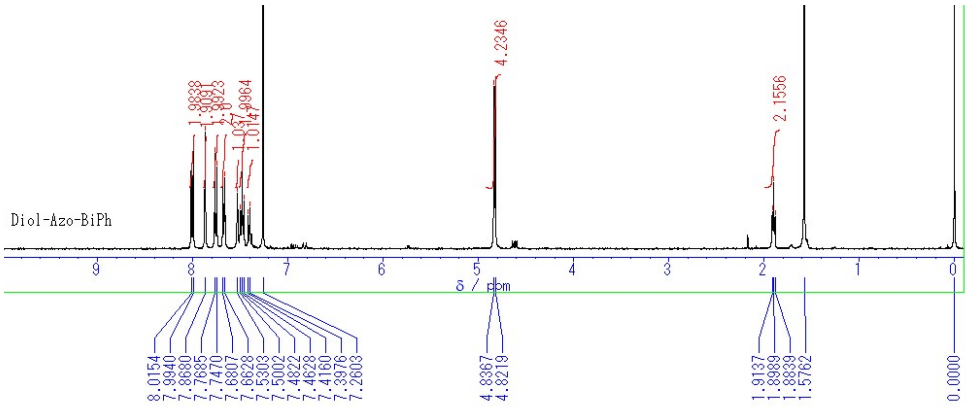


NMR charts of ^{1}H NMR spectrum of *7*

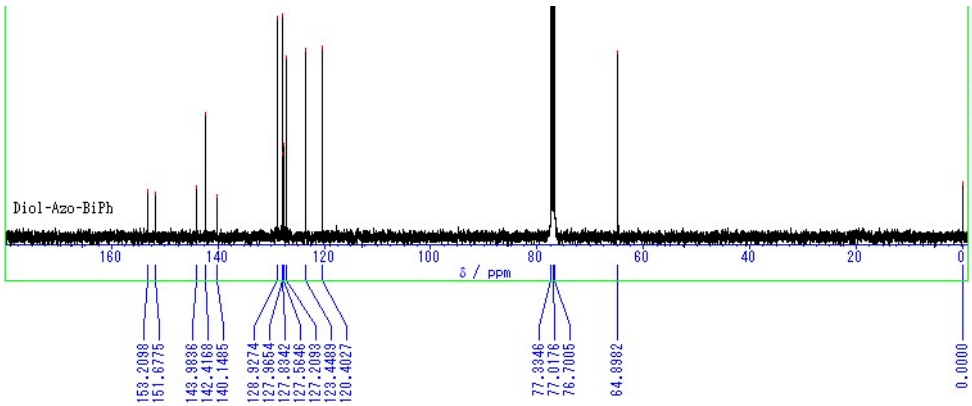


NMR charts of ^{13}C NMR spectrum of *7*

Synthesis of *8*. *8* was prepared in the same way as ***5a*** from *7* (4.49 g, 12.0 mmol) as an orange solid (2.6 g, 68% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$):1.90 (t, *J* = 5.9 Hz, 2H), 4.83 (d, *J* = 5.9 Hz, 4H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.53 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.87 (s, 2H), 8.00 (d, *J* = 8.6 Hz, 2H); ^{13}C-NMR (101 MHz, δ ppm, $CDCl_3$): 64.9, 120.4, 123.4, 127.2, 127.6, 127.8, 128.0, 128.9, 140.1, 142.4, 144.0, 151.7, 153.2.

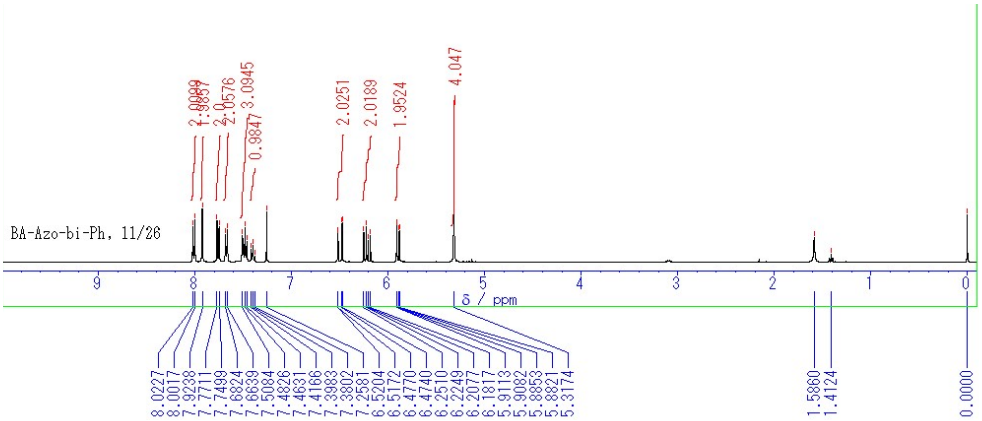


NMR charts of ^{1}H NMR spectrum of ***8***

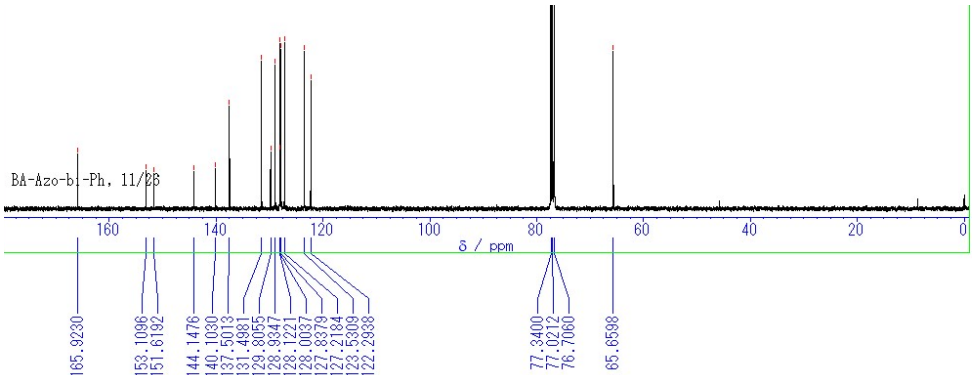


NMR charts of ^{13}C NMR spectrum of ***8***

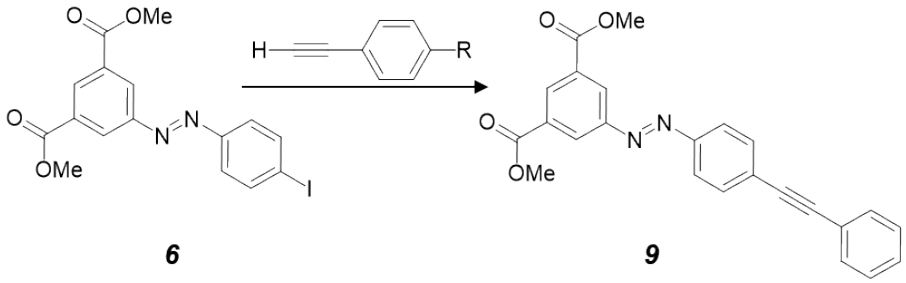
Synthesis of *Az-Ph*. NMR spectra of ***Az-Ph*** were shown below.



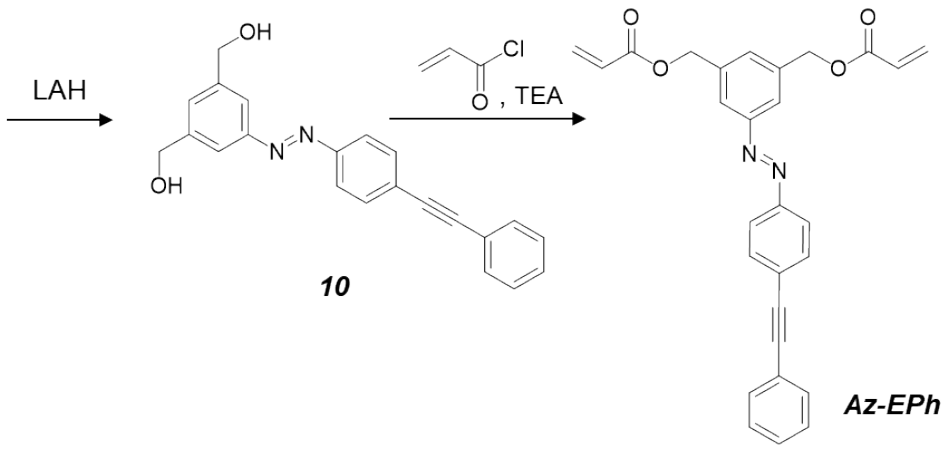
NMR charts of ^{1}H NMR spectrum of ***Az-Ph***



NMR charts of ^{13}C NMR spectrum of ***Az-Ph***



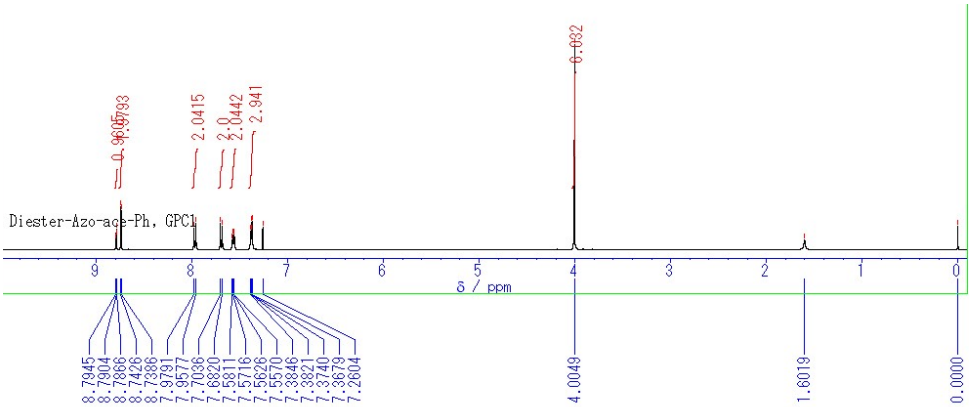
6 ***9***



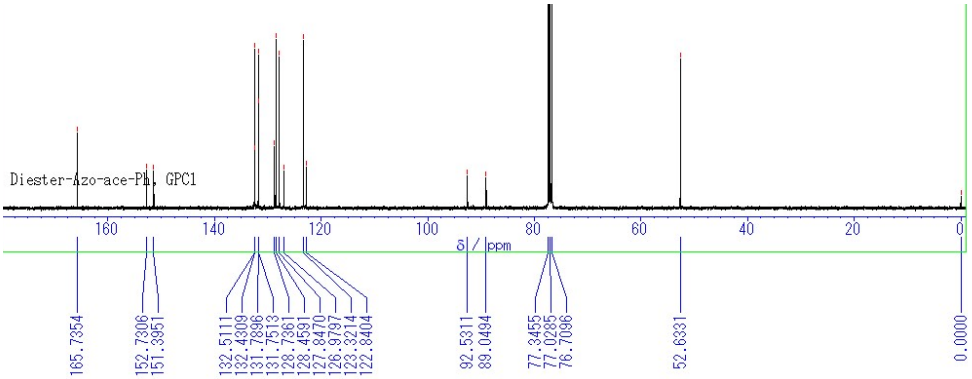
10 ***Az-EPh***

Synthesis of *9*. ***9*** was prepared by applying to a literature procedure.[4] ***6*** (12.73 g, 30.0 mmol), ethynylbenzene (4.09 g, 40.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.21 g, 0.3 mmol), CuI (57.1 mg, 0.3 mmol), and triethylamine (50 mL) were dissolved in anhydrous THF was degassed with freeze-pump-thaw. The mixture was refluxed under N2 for 24 h, and after evaporation chloroform was added. The organic layer was washed by water, then was dried over anhydrous $MgSO_4$ and filtered. After evaporation of chloroform, the residue was purified by GPC to afford ***9*** in chloroform as an orange solid (10.52 g, 63% yield). ^{1}H-NMR (400 MHz, δ ppm, $CDCl_3$): 4.00 (s, 6H), 7.36-7.40 (m, 3H), 7.69 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H), 8.74 (d, J = 1.6, Hz, 2H), 8.79 (d, J = 1.6, 1H); ^{13}C-

NMR (101 MHz, δ ppm, $CDCl_3$): 52.6, 89.0, 92.5, 122.8, 123.3, 127.0, 127.8, 128.5, 128.7, 131.8, 131.8, 132.4, 132.5, 151.4, 152.7, 165.7.

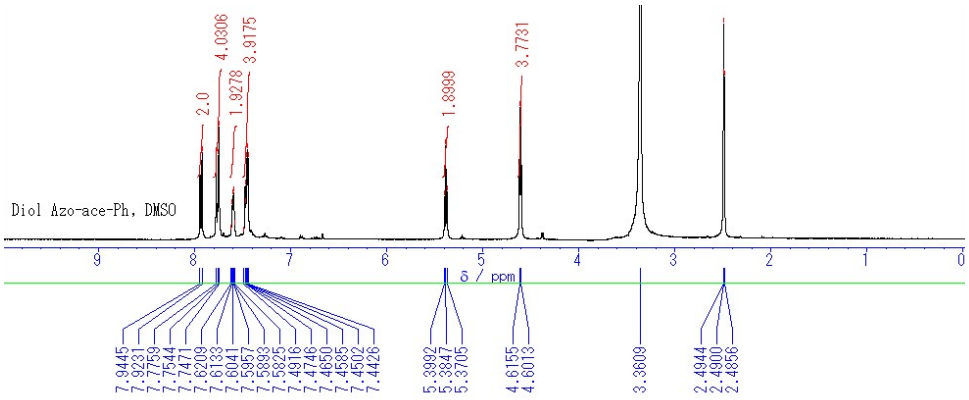


NMR charts of ^{1}H NMR spectrum of ***9***

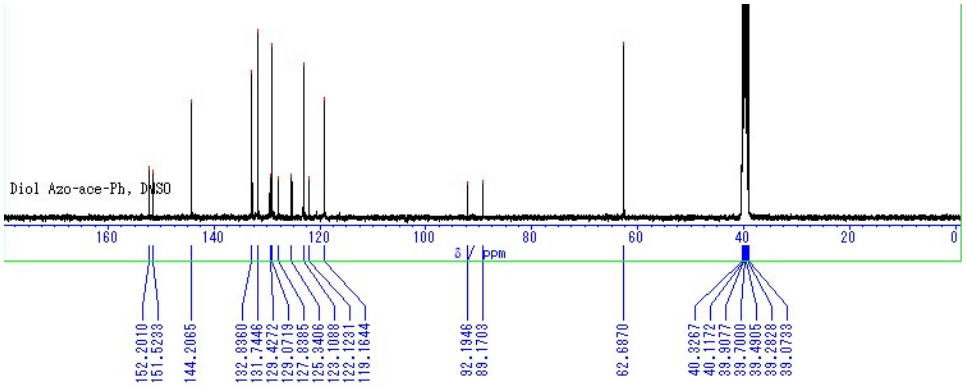


NMR charts of ^{13}C NMR spectrum of ***9***

Synthesis of *10*. *10* was prepared in the same way as ***5a*** from ***9*** (1.72 g, 4.52 mmol) as an orange solid (0.95 g, 61% yield). ^{1}H-NMR (400 MHz, δ ppm, DMSO-d_6): 4.61 (d, J = 5.7 Hz, 4H), 5.37 (t, J = 5.8 Hz, 2H), 7.42-7.49 (m, 4H), 7.58-7.62 (m, 2H), 7.74 (s, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H); ^{13}C-NMR (101 MHz, δ ppm, DMSO-d_6): 62.7, 89.2, 92.2, 119.2, 122.1, 123.1, 125.3, 127.8, 129.1, 129.4, 131.7, 132.8, 144.2, 151.5, 152.2.

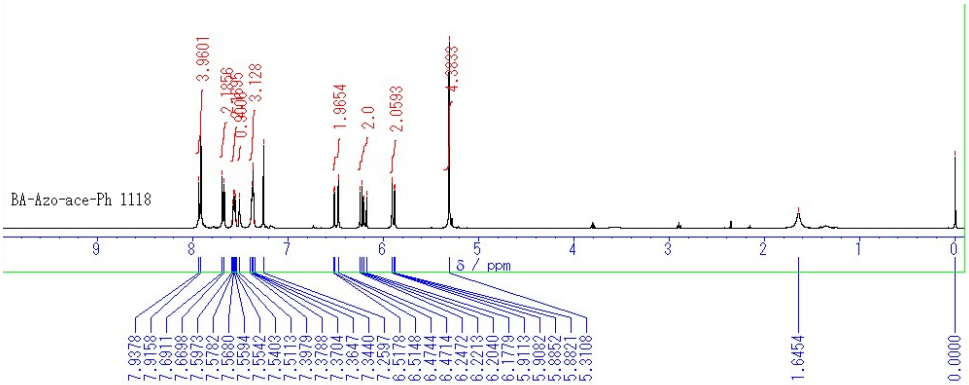


NMR charts of ^{1}H NMR spectrum of ***10***

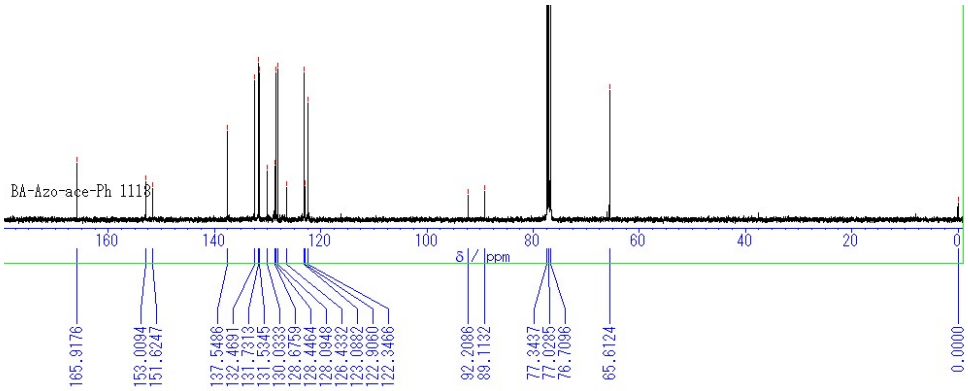


NMR charts of ^{13}C NMR spectrum of ***10***

Synthesis of *Az-EPh*. NMR spectra of ***Az-EPh*** were shown below.



NMR charts of ^{1}H NMR spectrum of ***Az-EPh***



NMR charts of ^{13}C NMR spectrum of ***Az-EPh***

References of Supporting Note S1.

1. J. Poym. Sci. A, 2010, **48**, 18, 4055-4066, https://doi.org/10.1002/pola.24191.

2. Angew. Chem., Int. Ed., 2015, 54, 1532-1536, https://doi.org/10.1002/anie.201410184.

3. ChemBioChem, 2014, **15**, 14, 2053-2057, https://doi.org/10.1002/cbic.201402237.

4. Organic & Biomolecular Chemistry, 2010, 8, 3655-3664, https://doi.org/10.1039/C002657C.

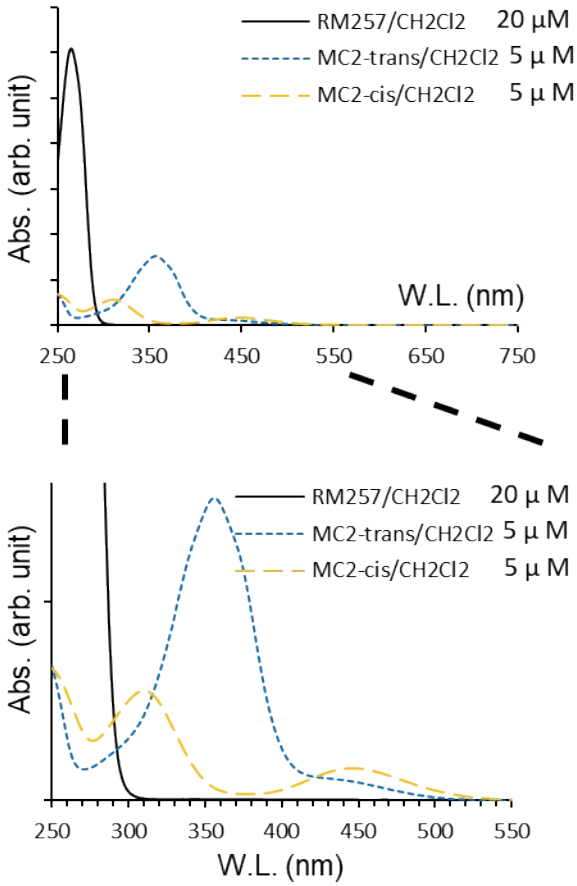


Fig. S1. UV/vis absorption spectrum of RM257 in dichloromethane. For comparison, spectra of the dichloromethane solution of Az-MC2 in the *trans* and *cis* states are also shown. The molar ratio of RM257 and Az-MC2 is 4:1, which is the same as that in the LCE. RM257 shows only one strong absorption band at around 267 nm ranging up to ~310 nm. Thus, the wavelength range higher than ~310 nm of the UV/vis spectra of LCEs is regarded as information originating from the azobenzene moieties.

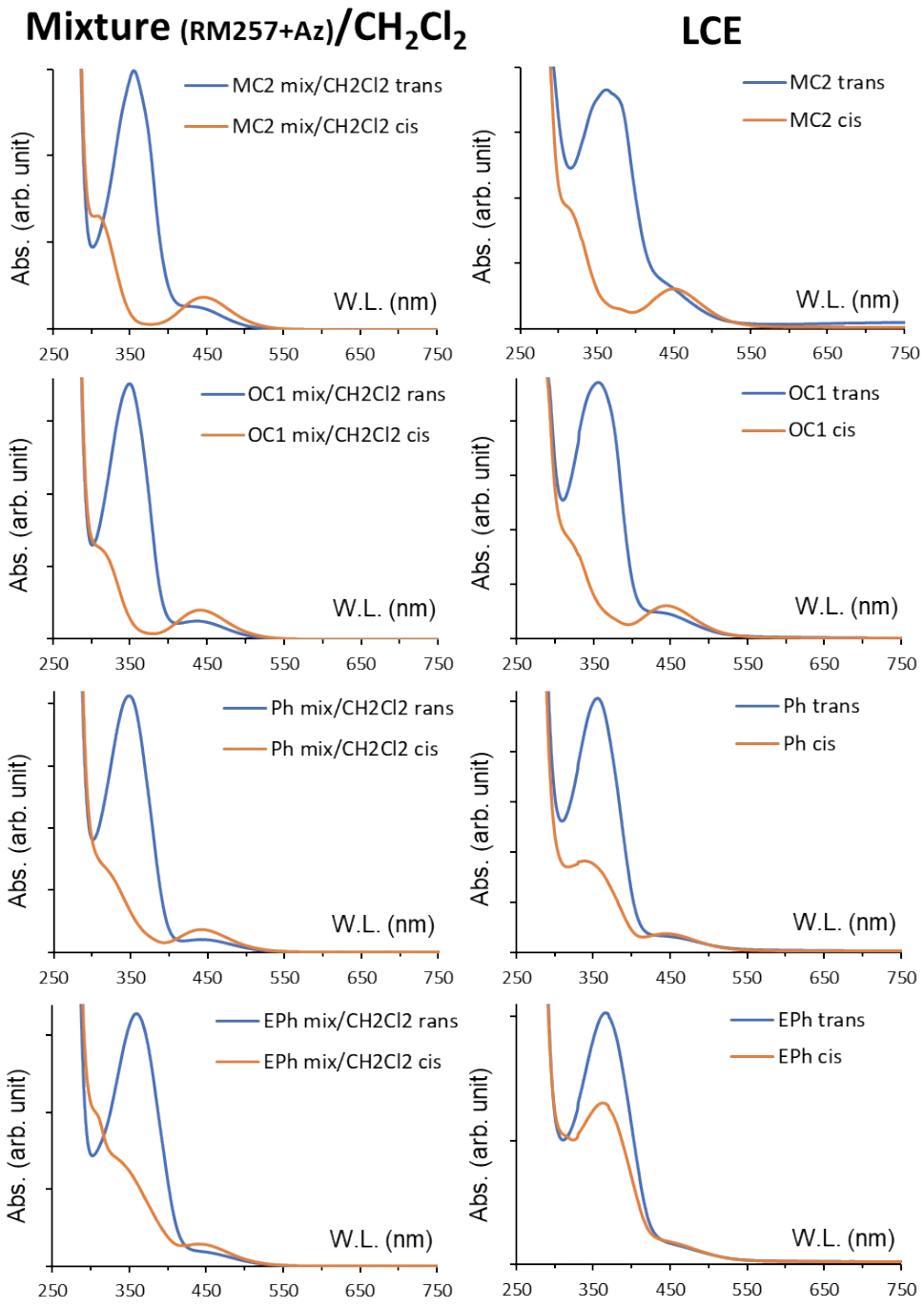


Fig. S2. UV/vis absorption spectra of some monomer mixtures in dichloromethane and corresponding LCEs on quartz substrates. The comparison between the solution and solid (LCE) spectra suggests that a certain portion of azobenzenes after UV irradiation remained as the *trans* state. Thus, the *trans*-to-*cis* isomerization in the LCE states is suppressed probably due to the lower molecular mobility. The data of OC1 is shown as the representative one of OC1, OC4, OC8 and OC12, which are qualitatively similar to each other.