Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supplementary Information

Synthesis and mesomorphism of triphenylene-based dimers with a highly ordered columnar plastic phase

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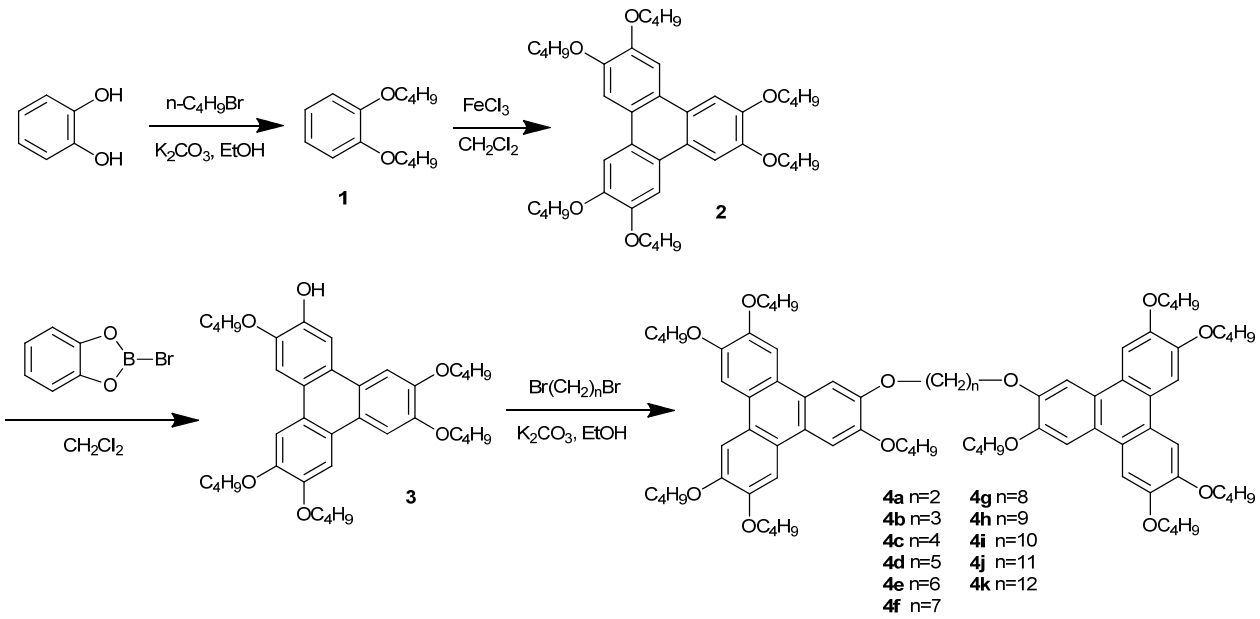
1. Synthesis and characterization



Synthesis scheme for compound 4a-k

1, 2-dibutoxybenzene (1)

1-Bromobutane (25.7g, 0.187mol) was added to a vigorously stirred solution of catechol (5.5 g, 0.05mol) and potassium carbonate (27.6g) in ethanol (500ml) under nitrogen. The reaction mixture was stirred under reflux for 24 h and filtered with copious washings of ethanol. The filtrate was concentrated in vacuo and subjected to a silica gel column chromatography on silica, eluting with 1: 2 dichloromethane: light petroleum to give the product as pale yellow oil. (10.6 g, 95 %); TLC R_f: 0.55 (dichloromethane-hexane 1:1); IR (KBr): ν_{max}/cm^{-1} 1263 (C-O-C); δ_H (300MHZ, $CDCl_3$) 6.90 (4H, s, ArH), 3.99-4.10 (4H, t, OCH_2), 1.77-1.86 (4H, m, OCH_2CH_2), 1.46-1.58 (m, 4H, $OCH_2CH_2CH_2$), 0.97-1.07 (t, 6H, CH_3).

2, 3, 6, 7, 10, 11-hexabutoxytriphenylene (2)

Compound **1** (7.5g, 0.0337mol) was added to a vigorously stirred suspension of Iron(III) chloride (16.42g, 0.0101mol) in dichloromethane (50ml). The reaction occurred with vigorous evolution of gas and was quenched with methanol (150ml) after 70 min. The reaction mixture was filtered and the filtrate concentrated in vacuo to give a black solid which was subjected to a silica gel column chromatography, eluting with 1: 1 dichloromethane: light petroleum to give **2** as pale yellow solid

which was recrystallized from ethanol. (16.95g, 76%); TLC R_f: 0.65 (dichloromethane- hexane 1:1); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.85 (6H, s, ArH), 4.22-4.26 (12H, t, OCH_2), 1.89-1.98 (12H, m, OCH_2CH_2), 1.62-1.67 (12H, m, $OCH_2CH_2CH_2$), 1.02-1.07 (18H, t, CH_3).

2-hydroxy -3, 6, 7, 10, 11-Pentabutoxytriphenylene (3)

To a cooled suspension of catechol (11g, 0.1mol) in CH_2Cl_2 (50 mL), a solution (0 °C) of BBr_3 (28.6g, 0.11mol) in CH_2Cl_2 (10 ml) was added slowly with stirring 3h under nitrogen. The mixture was brought to room temperature, the solvent removed and the product distilled under vacuum to give B-Bromocatecholboronane as white solid (16g, 80%). The solid was then used to make a 0.5 M solution by mixing with CH_2Cl_2 (160 ml) and this was used for next ether cleavage reactions.

A solution of **2** (15g, 0.0227mol) was dissolved in anhydrous CH_2Cl_2 (150 ml) and cooled to 0°C. To this was added (64ml, 0.032mol) of B-Bromocatecholboronane solution in CH_2Cl_2 under argon and the mixture was stirred at room temperature for 24h. After that it was poured over ice-water and extracted with CH_2Cl_2, the combined extract was dried with anhydrous Na_2SO_4 overnight, solvent was removed under vacuum and the crude product was purified by a silica gel column chromatography, eluting with 1: 30 ethyl acetate: light petroleum to give **3** as white solid which was recrystallized from ethanol. (6.5g, 49%); TLC R_f: 0.56 (ethyl acetate- hexane 1:8); IR (KBr): ν_{max}/cm^{-1} 3456 (O-H), 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.78-7.97 (6H, m, ArH), 5.91 (1H, s, OH) 4.20-4.38 (10H, t, OCH_2), 1.89-1.96 (10H, m, OCH_2CH_2), 1.57-1.67 (10H, m, $OCH_2CH_2CH_2$), 1.05-1.09 (18H, t, CH_3).

1, 2-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-ethane (4a)

A mixture of **3** (500mg, 0.827mmol), 1, 2-Dibromoethane (78mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4a**. (0.25g, 49%); TLC R_f: 0.15 (dichloromethane-hexane 2:1); (Found: C, 75.98; H, 8.87. $C_{78}H_{106}O_{12}$ requires: C, 75.82 ;H, 8.65%); IR (KBr): ν_{max}/cm^{-1} 1260 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.81-8.09 (12H, m, ArH), 4.74 (4H, t, OCH_2CH_2O), 4.08-4.22 (20H, m, OCH_2), 1.74-1.96 (20H, m, OCH_2CH_2), 1.43-1.69 (20H, m, $OCH_2CH_2CH_2$), 1.02-1.07 (30H, m, CH_3); HRMS (ESI) : calc. m/z 1234.7679 ($C_{78}H_{106}O_{12}$), found

m/z 1234.7652 $(M)^+$.

1, 3-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-propane (4b)

A mixture of **3** (500mg, 0.827mmol), 1, 3-Dibromopropane (83mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4b**. (0.32g, 63%); TLC R_f: 0.17 (dichloromethane-hexane 2:1); (Found: C, 75.76; H, 8.71. $C_{79}H_{108}O_{12}$ requires: C, 75.93; H, 8.71%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.81-7.96 (12H, s, ArH), 4.58 (4H, t, OCH_2), 4.13-4.27 (20H, t, OCH_2), 2.57 (2H, m, OCH_2CH_2), 1.79-1.93 (20H, m, OCH_2CH_2), 1.47-1.62 (20H, m, $OCH_2CH_2CH_2$), 0.89-1.07 (30H, m, CH_3); HRMS (ESI) : calc. m/z 1248.7835 ($C_{79}H_{108}O_{12}$), found m/z 1248.7822 $(M)^+$.

1, 4-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-butane (4c)

A mixture of **3** (500mg, 0.827mmol), 1, 4-Dibromobutane (89mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4c**. (0.30g, 59%); TLC R_f: 0.20 (dichloromethane-hexane 2:1); (Found: C, 75.90; H, 8.82. $C_{80}H_{110}O_{12}$ requires: C, 76.03; H, 8.77%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.85 (12H, s, ArH), 4.40 (4H, t, OCH_2), 4.18-4.25 (20H, t, OCH_2), 2.26 (4H, m, OCH_2CH_2), 1.82-1.95 (20H, m, OCH_2CH_2), 1.53-1.65 (20H, m, $OCH_2CH_2CH_2$), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1262.7992 ($C_{80}H_{110}O_{12}$), found m/z 1262.7968 $(M)^+$.

1, 5-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-pentane (4d)

A mixture of **3** (500mg, 0.827mmol), 1, 5-Dibromopentane (95mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4d**. (0.27g, 51%); TLC R_f:

0.28 (dichloromethane-hexane 2:1); (Found: C, 76.14; H, 8.85. $C_{81}H_{112}O_{12}$ requires: C, 76.14; H, 8.84%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.86 (12H, s, ArH), 4.24 (24H, t, OCH_2), 2.11 (4H, t, OCH_2), 1.89-2.08 (22H, m, CH_2), 1.53-1.65 (24H, m, $OCH_2CH_2CH_2$), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1276.8148 ($C_{81}H_{112}O_{12}$), found m/z 1276.8123 $(M)^+$.

1, 6-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-hexane (4e)

A mixture of **3** (500mg, 0.827mmol), 1, 6-Dibromohexane (101mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4e**. (0.26g, 49%); TLC R_f: 0.30 (dichloromethane-hexane 2:1); (Found: C, 76.17; H, 8.94. $C_{82}H_{114}O_{12}$ requires: C, 76.24; H, 8.90%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.84 (12H, s, ArH), 4.24 (24H, t, OCH_2), 1.92-2.03 (24H, m, OCH_2CH_2), 1.57-1.73 (24H, m, $OCH_2CH_2CH_2$), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1290.8305 ($C_{82}H_{114}O_{12}$), found m/z 1290.8314 $(M)^+$.

1, 7-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-heptane (4f)

A mixture of **3** (500mg, 0.827mmol), 1, 7-Dibromoheptane (107mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4f**. (0.31g, 58%); TLC R_f: 0.34 (dichloromethane-hexane 2:1); (Found: C, 76.26; H, 9.02. $C_{83}H_{116}O_{12}$ requires: C, 76.34; H, 8.95%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.84 (12H, s, ArH), 4.24 (24H, t, OCH_2), 1.89-1.98 (24H, m, OCH_2CH_2), 1.56-1.68 (26H, m, CH_2), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1304.8461 ($C_{83}H_{116}O_{12}$), found m/z 1304.8436 $(M)^+$.

1, 8-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-octane (4g)

A mixture of **3** (500mg, 0.827mmol), 1, 8-Dibromooctane (112mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting

with dichloromethane and finally recrystallized from ethanol to give pure **4g**. (0.22g, 41%); TLC R_f: 0.35 (dichloromethane-hexane 2:1); (Found: C, 76.38; H, 8.95. $C_{84}H_{118}O_{12}$ requires: C, 76.44; H, 9.01%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.84 (12H, s, ArH), 4.24 (24H, t, OCH_2), 1.89-1.96 (24H, m, OCH_2CH_2), 1.51-1.70 (28H, m, CH_2), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1318.8618 ($C_{84}H_{118}O_{12}$), found m/z 1318.8598 $(M)^+$.

1, 9-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-nonane (4h)

A mixture of **3** (500mg, 0.827mmol), 1, 9-Dibromononane (118mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4h**. (0.29g, 52%); TLC R_f: 0.40 (dichloromethane-hexane 2:1); (Found: C, 76.57; H, 9.0. $C_{85}H_{120}O_{12}$ requires: C, 76.54; H, 9.07%); IR (KBr): ν_{max}/cm^{-1} 1260 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.84 (12H, s, ArH), 4.25 (24H, t, OCH_2), 1.83-1.98 (24H, m, OCH_2CH_2), 1.46-1.68 (30H, m, CH_2), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1332.8774 ($C_{85}H_{120}O_{12}$), found m/z 1332.8784 $(M)^+$.

1, 10-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-decane (4i)

A mixture of **3** (500mg, 0.827mmol), 1, 10-Dibromodecane (124mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4i**. (0.23g, 42%); TLC R_f: 0.45 (dichloromethane-hexane 2:1); (Found: C, 76.52; H, 9.09. $C_{86}H_{122}O_{12}$ requires: C, 76.63; H, 9.12%); IR (KBr): ν_{max}/cm^{-1} 1263 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.85 (12H, s, ArH), 4.25 (24H, t, OCH_2), 1.89-1.98 (24H, m, OCH_2CH_2), 1.26-1.67 (32H, m, CH_2), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1346.8931 ($C_{86}H_{122}O_{12}$), found m/z 1346.8922 $(M)^+$.

1, 11-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-undecane (4j)

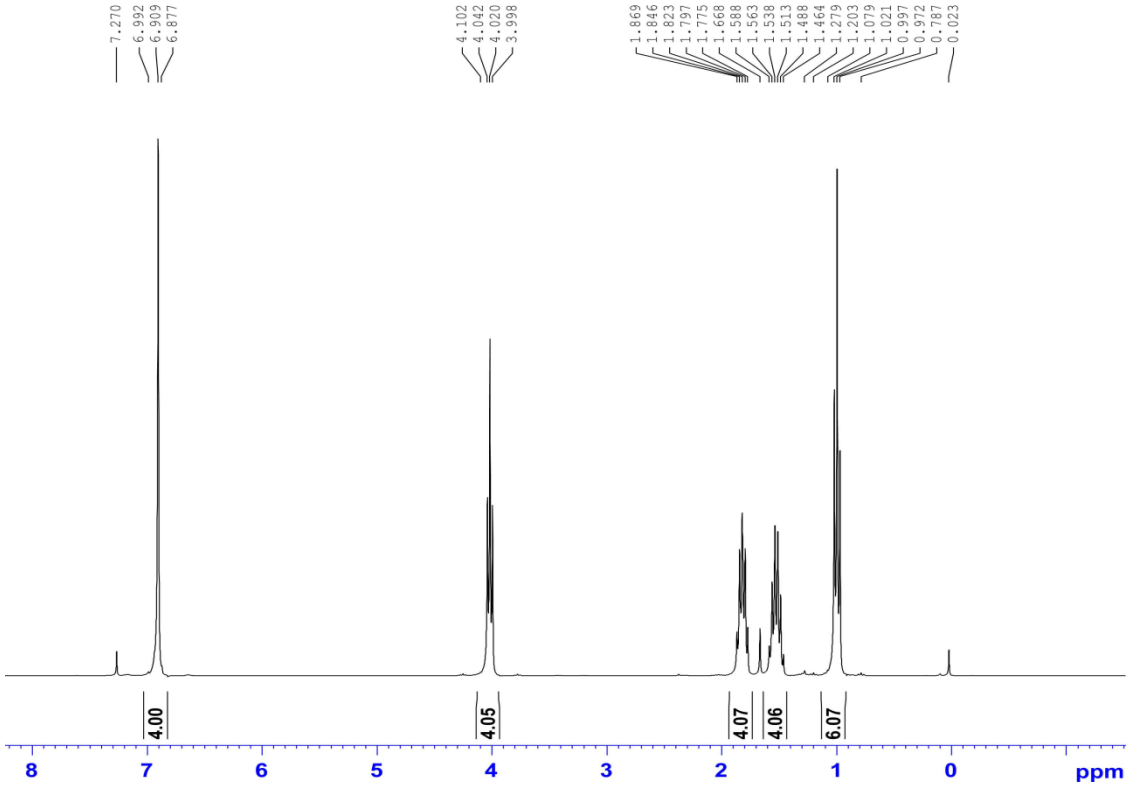
A mixture of **3** (500mg, 0.827mmol), 1, 11-Dibromoundecane (130mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml),

the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4j**. (0.26g, 47%); TLC R_f: 0.45 (dichloromethane-hexane 2:1); (Found: C, 76.55; H, 9.15. $C_{87}H_{124}O_{12}$ requires: C, 76.73; H, 9.18%); IR (KBr): ν_{max}/cm^{-1} 1263 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.84 (12H, s, ArH), 4.25 (24H, t, OCH_2), 1.89-1.96 (24H, m, OCH_2CH_2), 1.23-1.67 (34H, m, CH_2), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1360.9087 ($C_{87}H_{124}O_{12}$), found m/z 1360.9038 $(M)^+$.

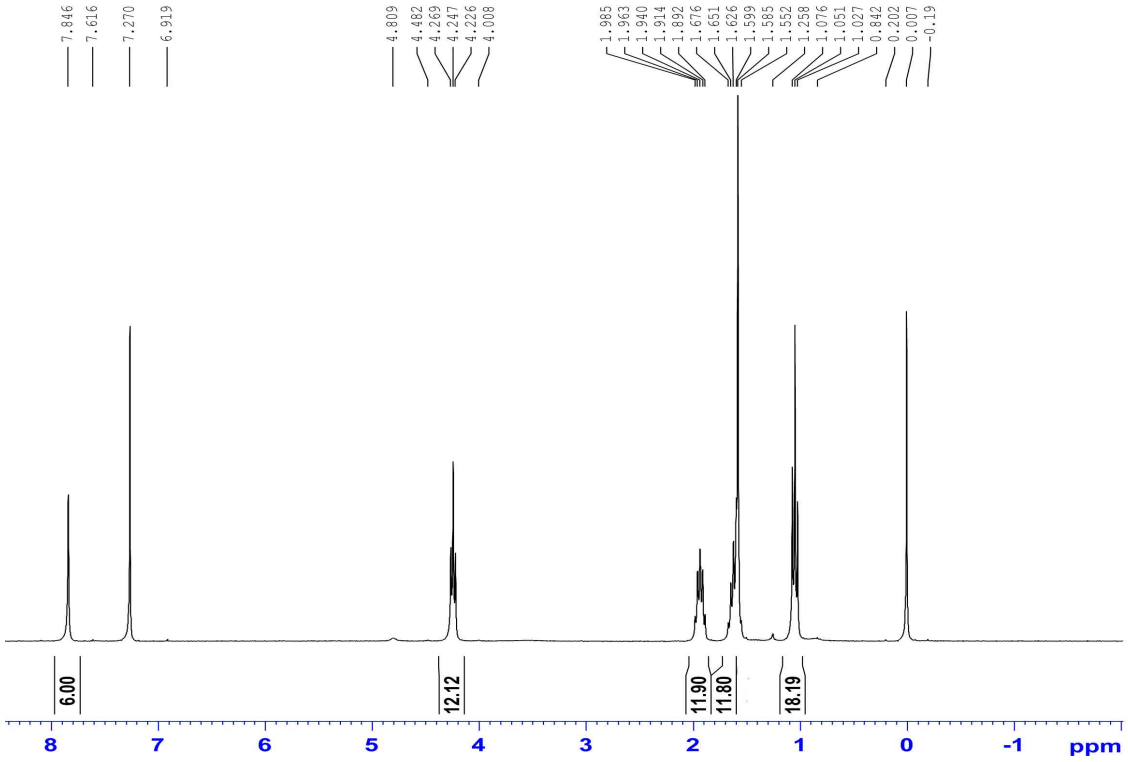
1, 12-Bis (3′, 6′, 7′, 10′, 11′-pentabutyloxytriphenylen-2′-yloxy)-dodeane (4k)

A mixture of **3** (500mg, 0.827mmol), 1, 12-Dibromododecane (135mg, 0.413mmol) and anhydrous potassium carbonate (1.0g) in ethanol (20ml) was heated under reflux for 72h. The mixture was cooled to 0 °C, filtered, washed with water(50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol to give pure **4k**. (0.21g, 37%); TLC R_f: 0.48 (dichloromethane-hexane 2:1); (Found: C, 76.54; H, 9.10. $C_{88}H_{126}O_{12}$ requires: C, 76.82; H, 9.23%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.84 (12H, s, ArH), 4.25 (24H, t, OCH_2), 1.89-1.96 (24H, m, OCH_2CH_2), 1.26-1.67 (36H, m, CH_2), 1.05 (30H, t, CH_3); HRMS (ESI) : calc. m/z 1374.9118 ($C_{88}H_{126}O_{12}$), found m/z 1374.9148 $(M)^+$.

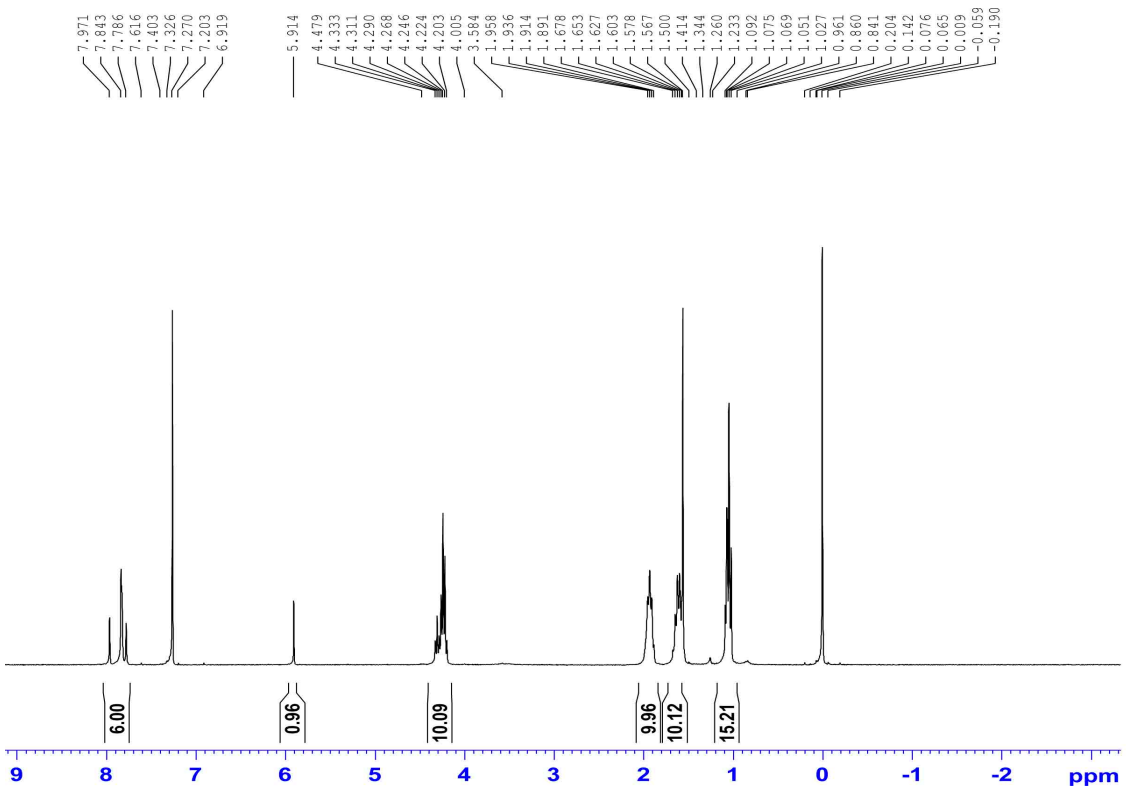
2. ^{1}H-NMR and HRMS spectra



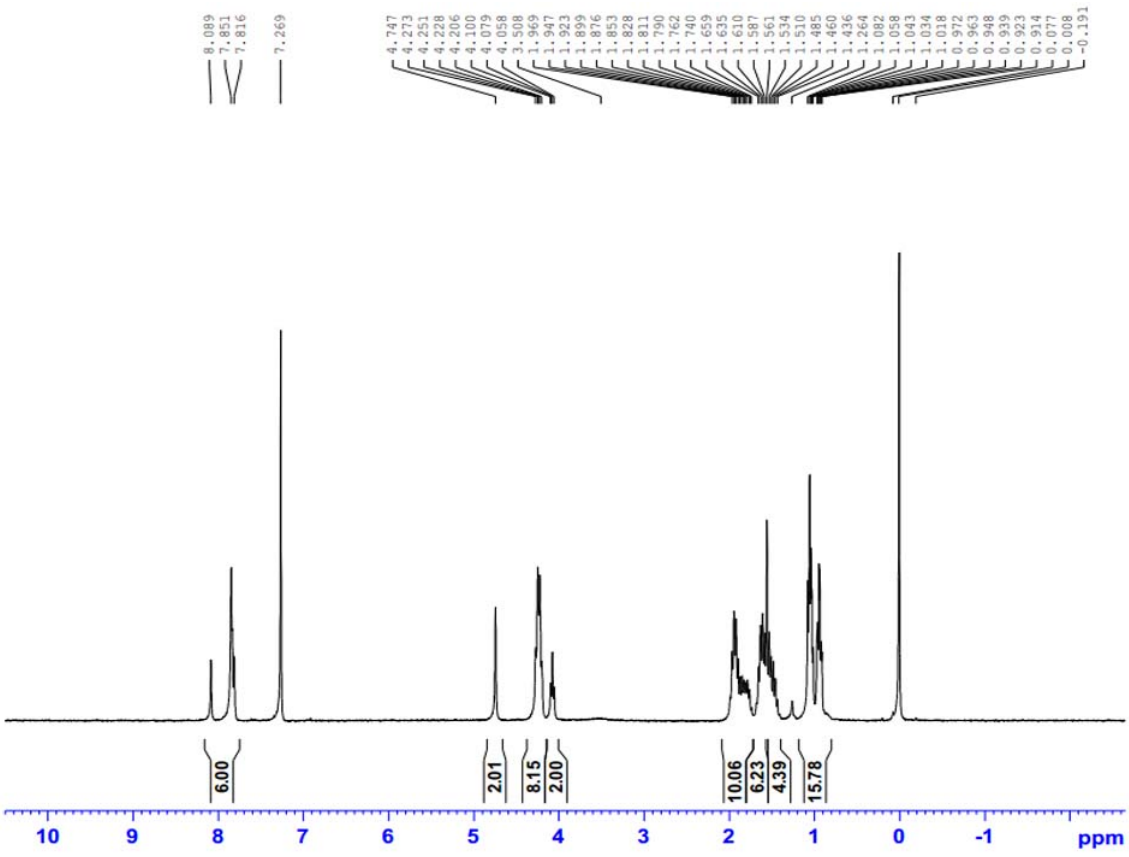
ESI Fig. 1 ^{1}H-NMR spectra of **1**



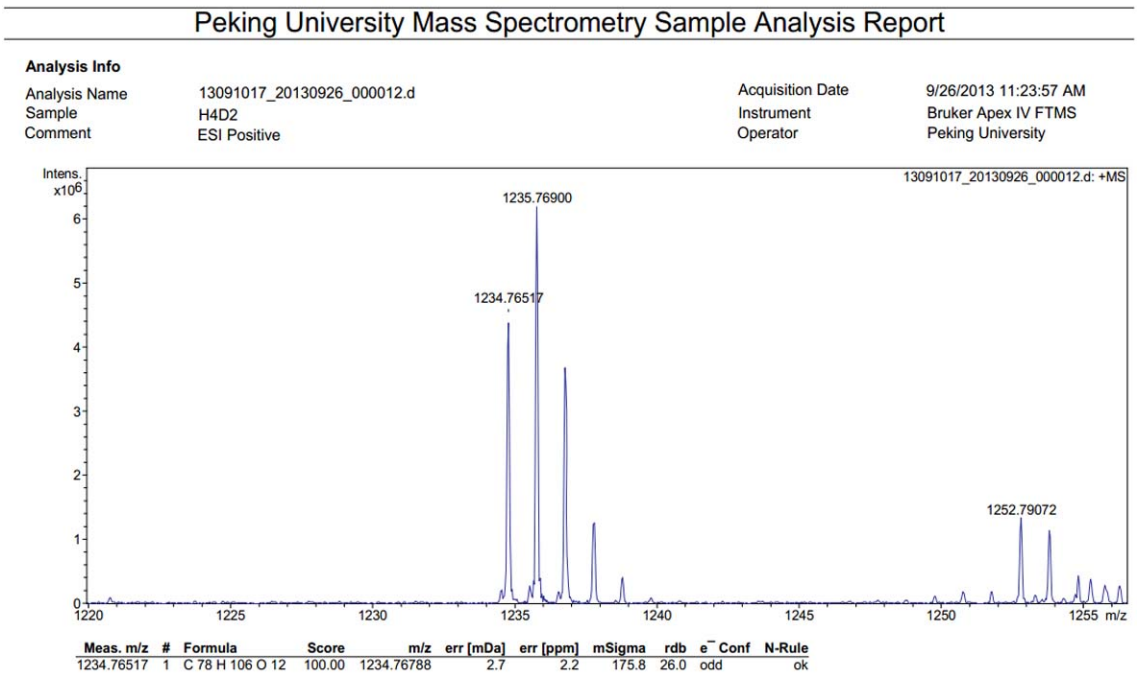
ESI Fig. 2 ^{1}H-NMR spectra of **2**



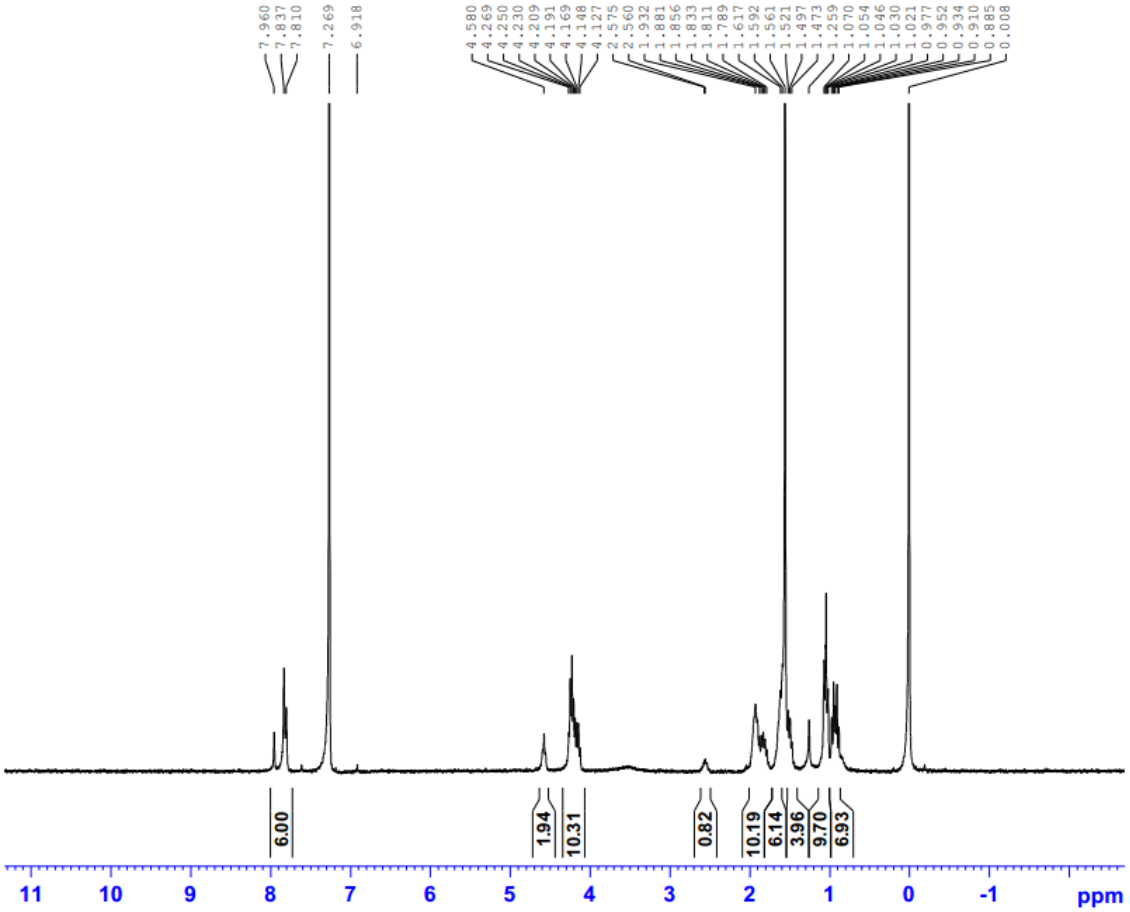
ESI Fig. 3 ^{1}H-NMR spectra of **3**



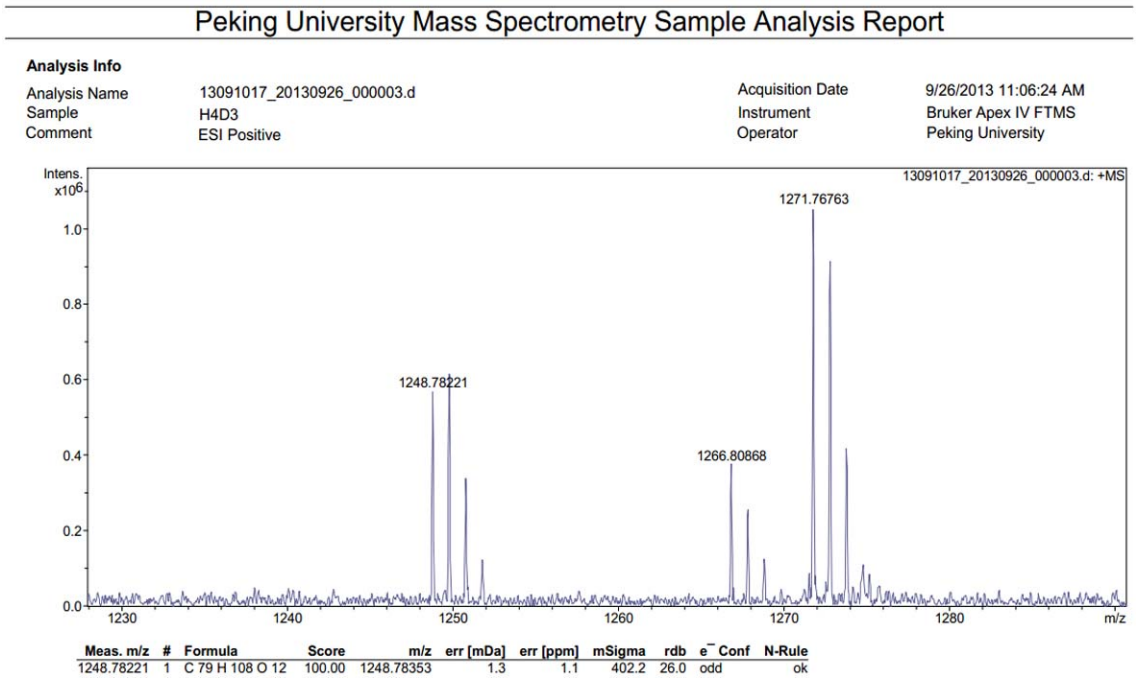
ESI Fig. 4 ^{1}H-NMR spectra of **4a**



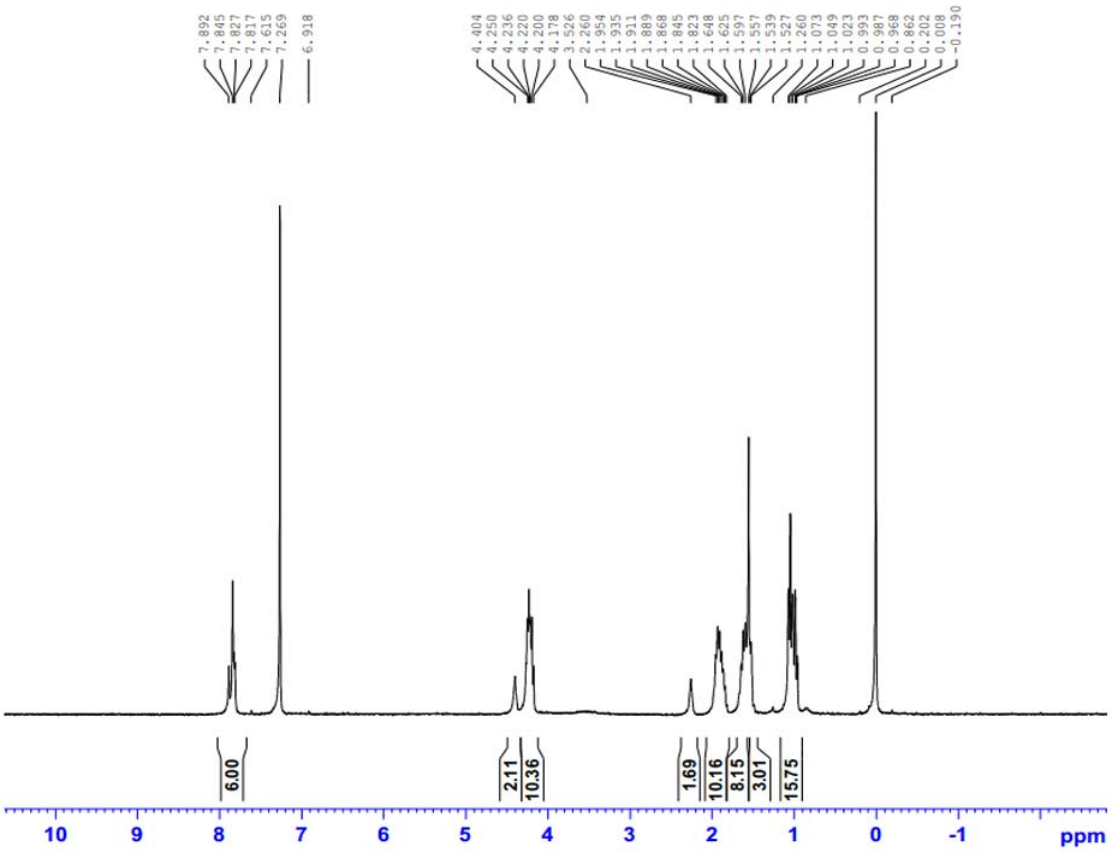
ESI Fig. 5 HRMS spectra of **4a**



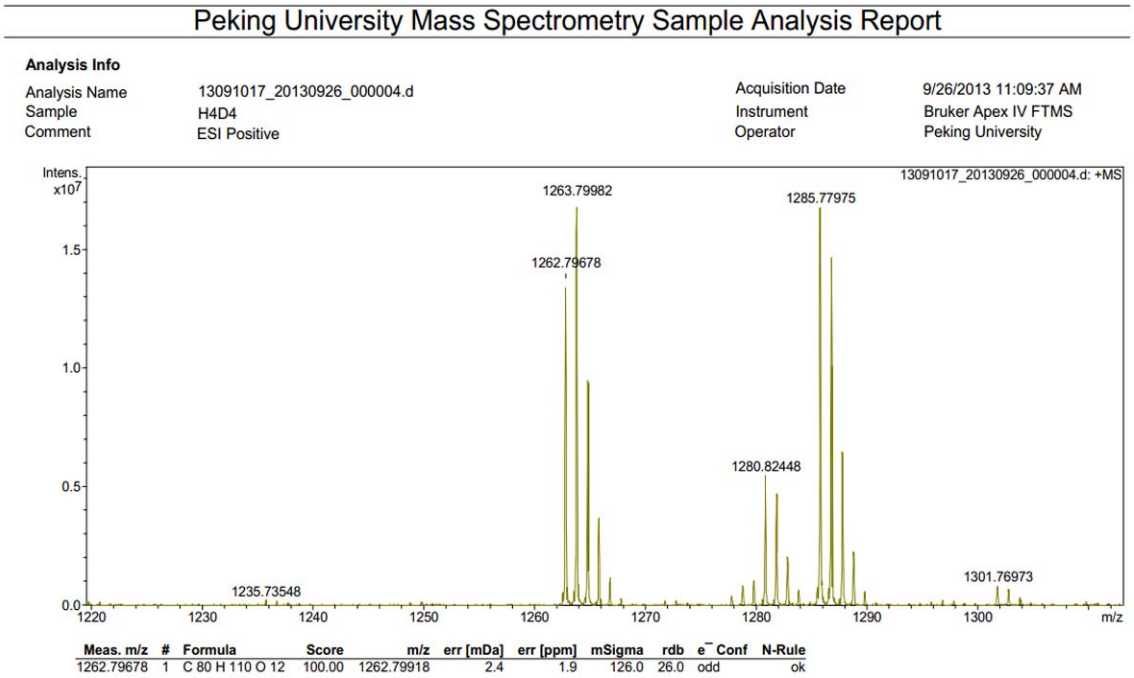
ESI Fig. 6 ^{1}H-NMR spectra of **4b**



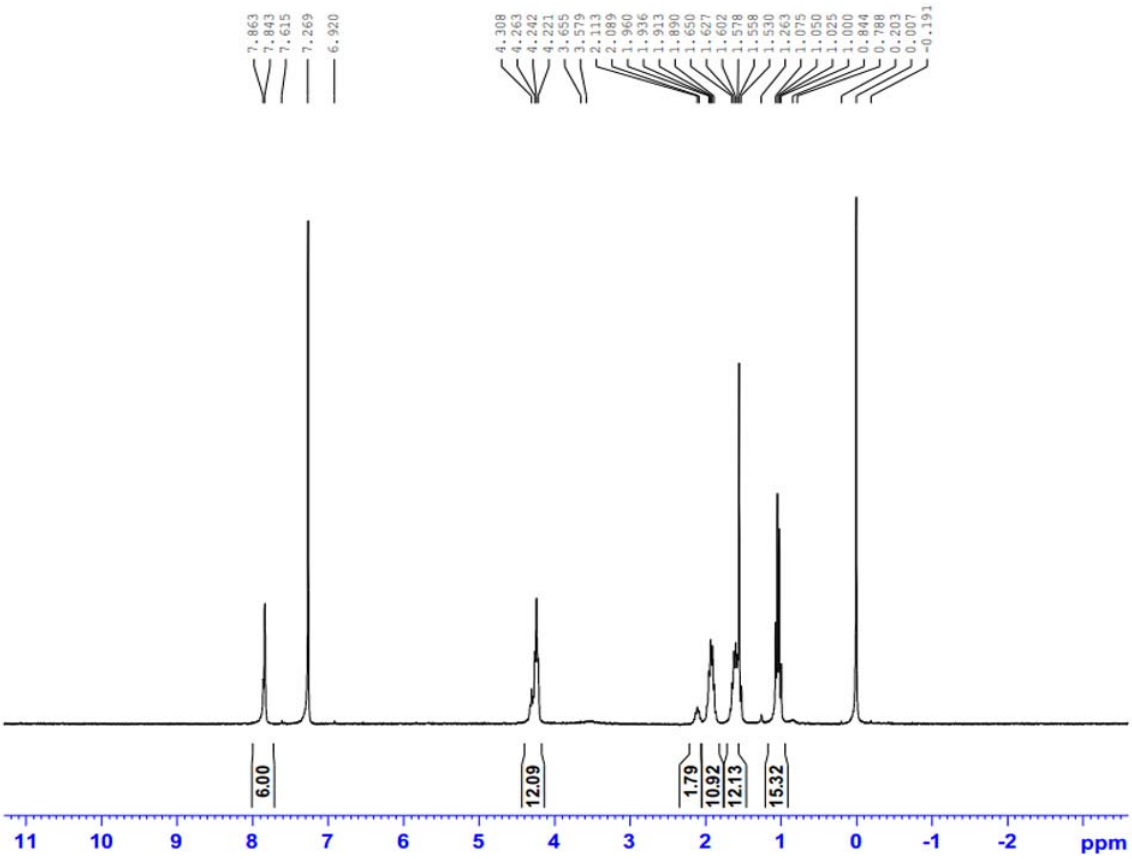
ESI Fig. 7 HRMS spectra of **4b**



ESI Fig. 8 ^{1}H-NMR spectra of **4c**



ESI Fig. 9 HRMS spectra of **4c**



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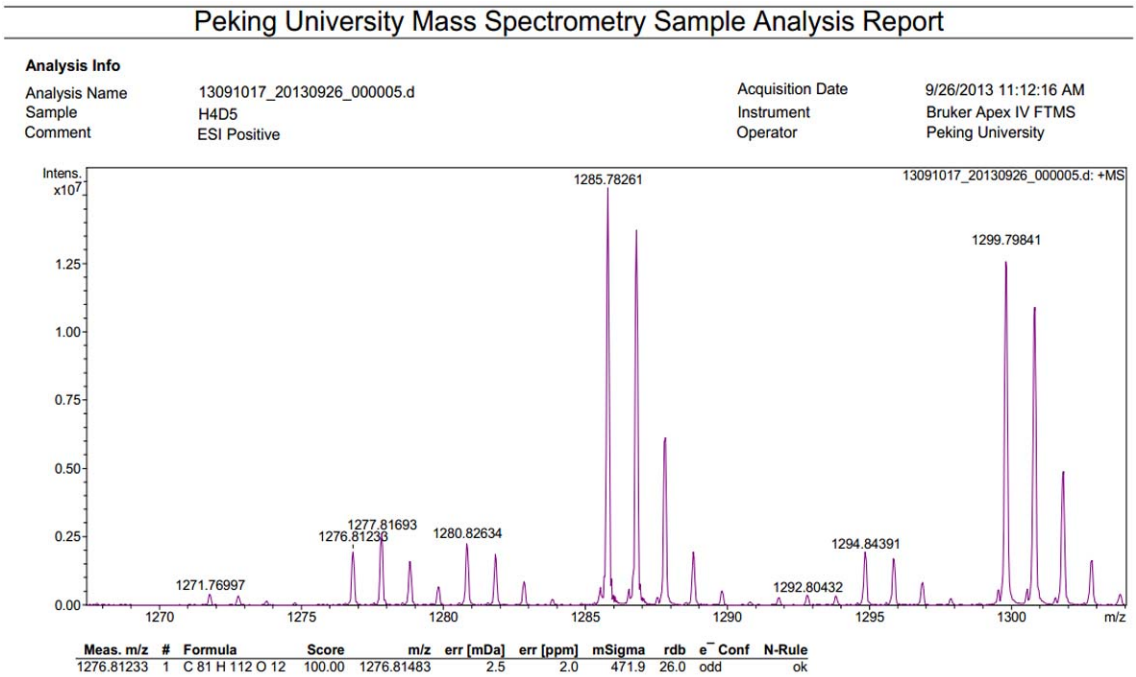

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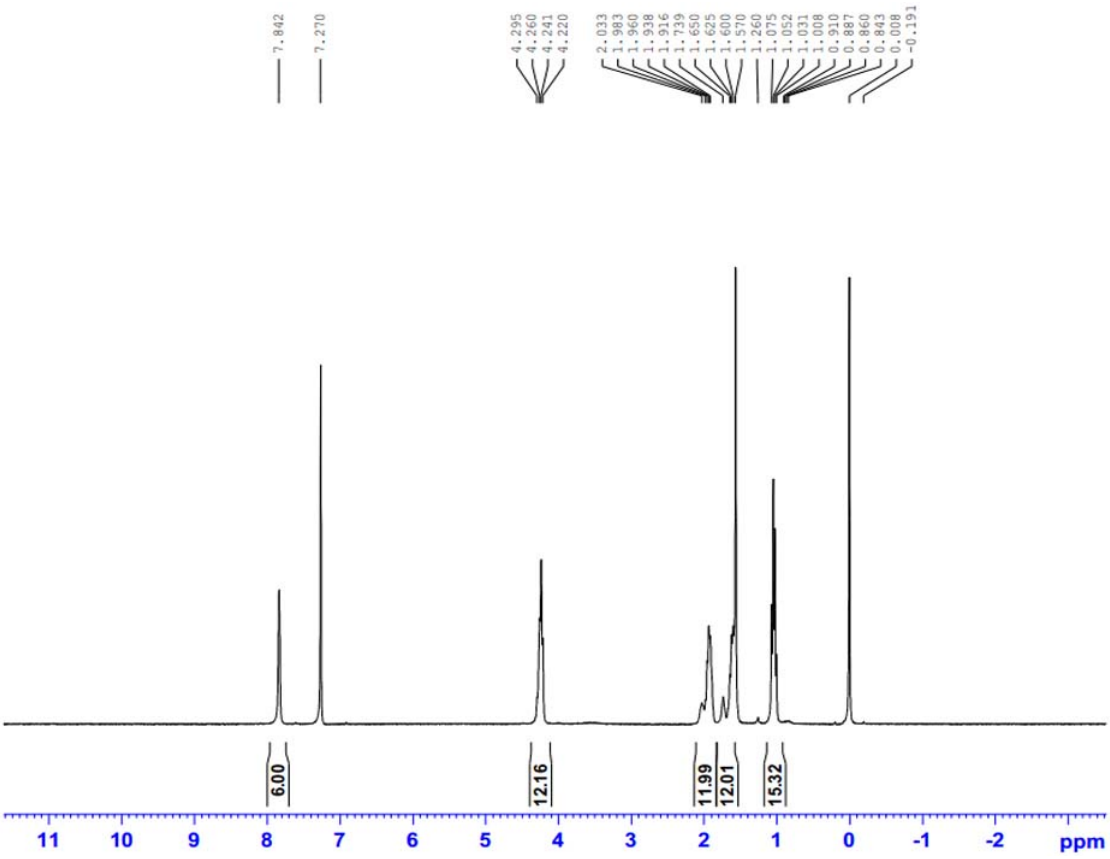
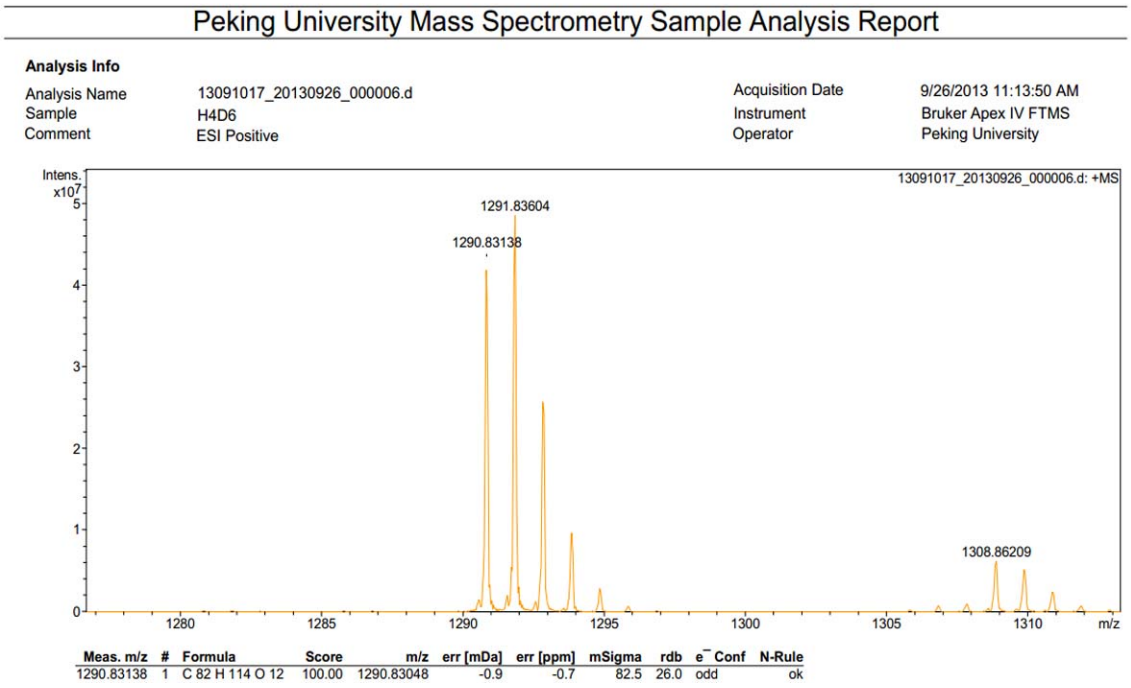
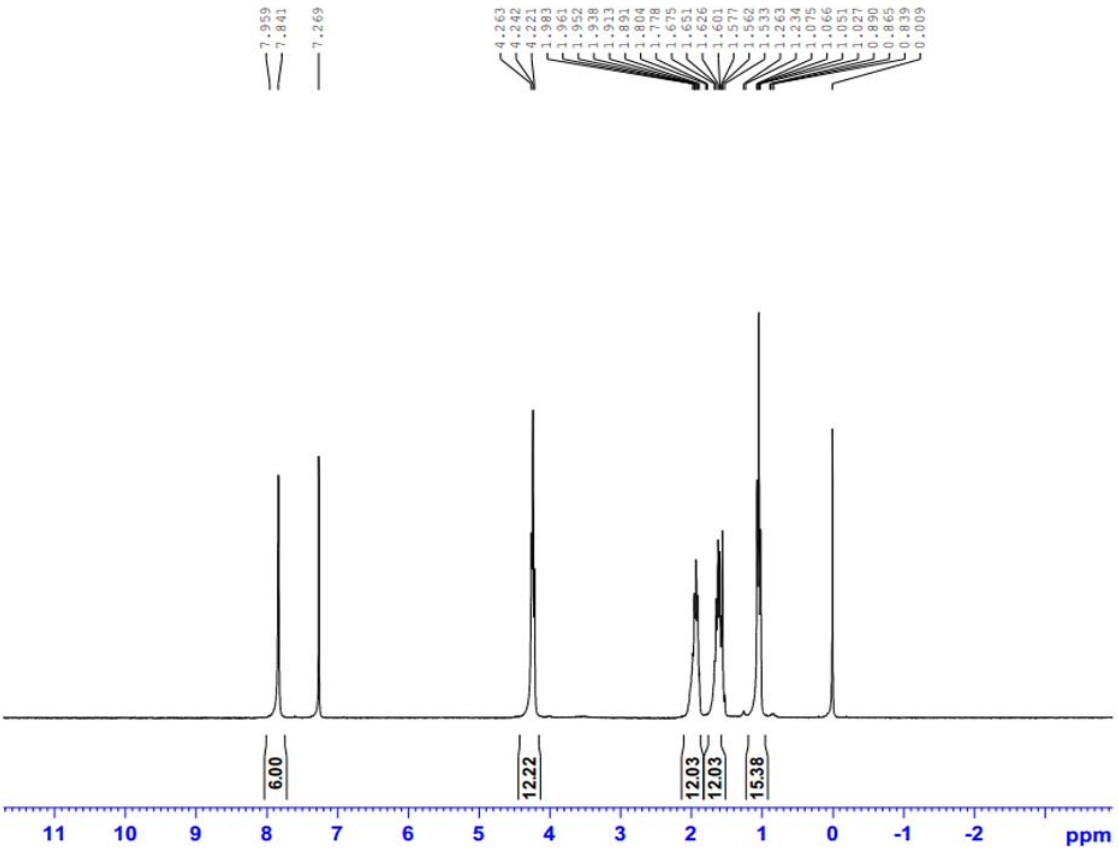


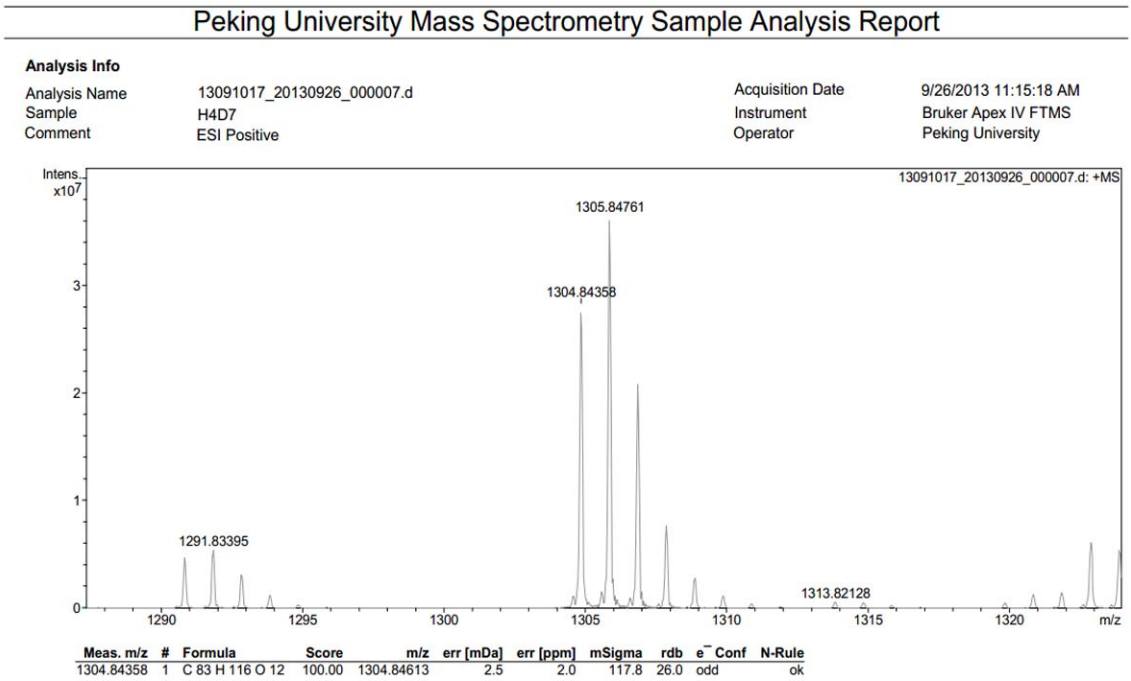
ESI Fig. 12 [1]H-NMR spectra of **4e**



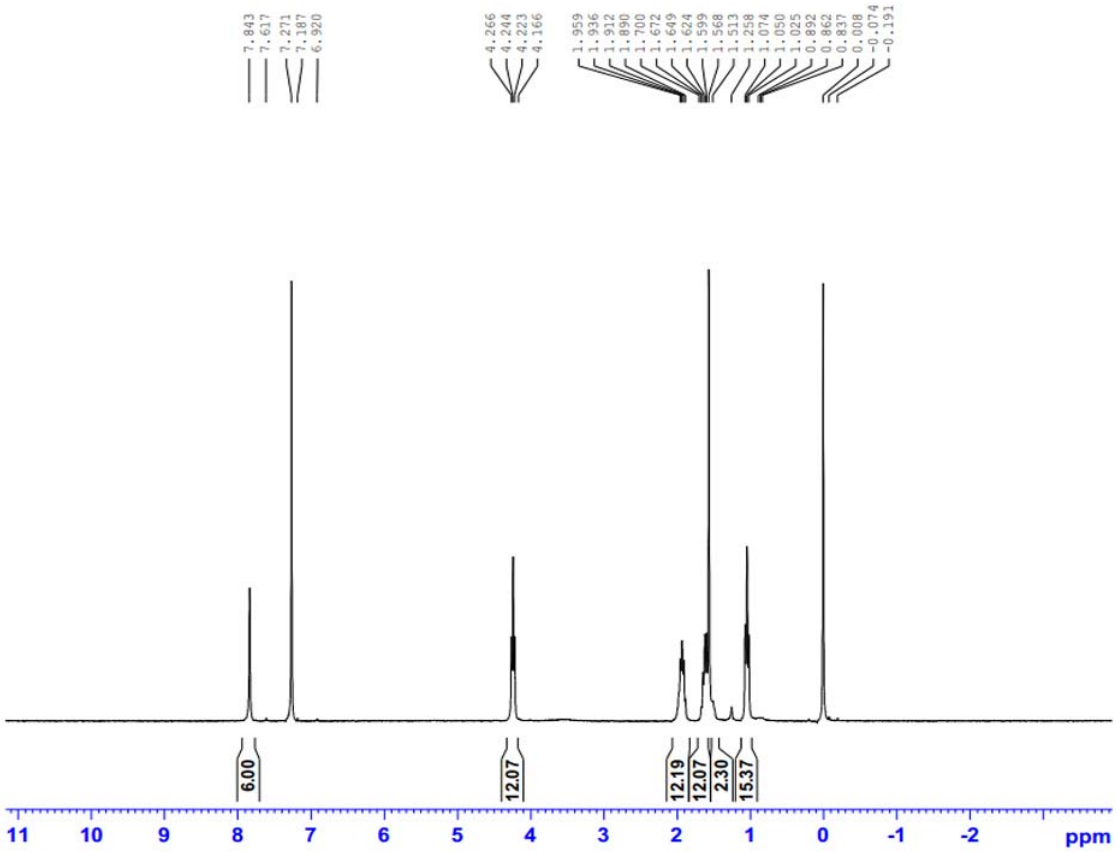
ESI Fig. 13 HRMS spectra of **4e**



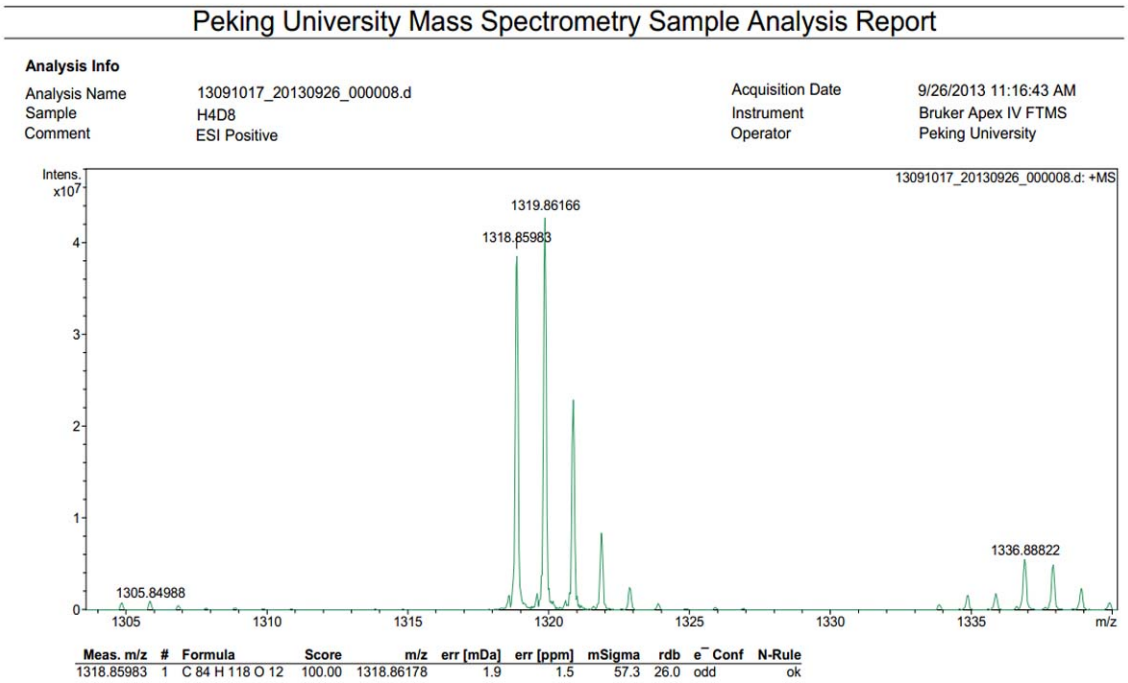
ESI Fig. 14 ^{1}H-NMR spectra of **4f**



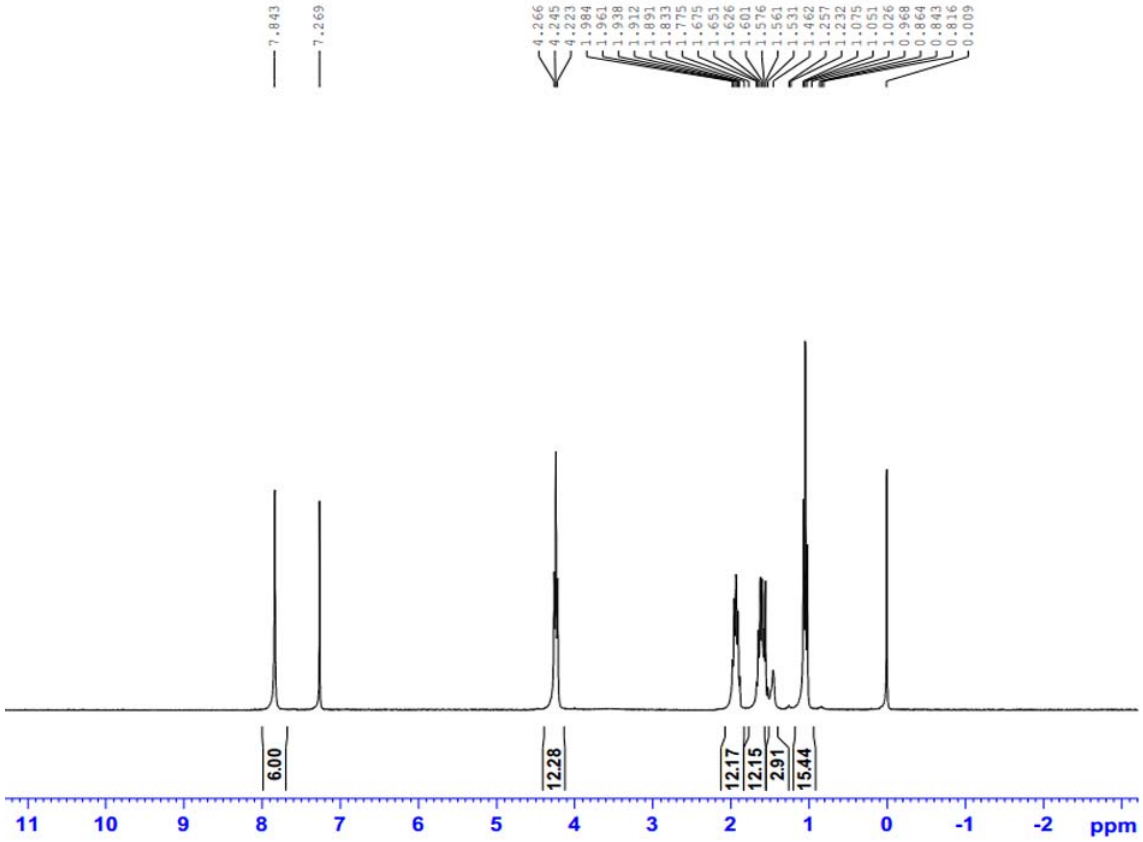
ESI Fig. 15 HRMS spectra of **4f**



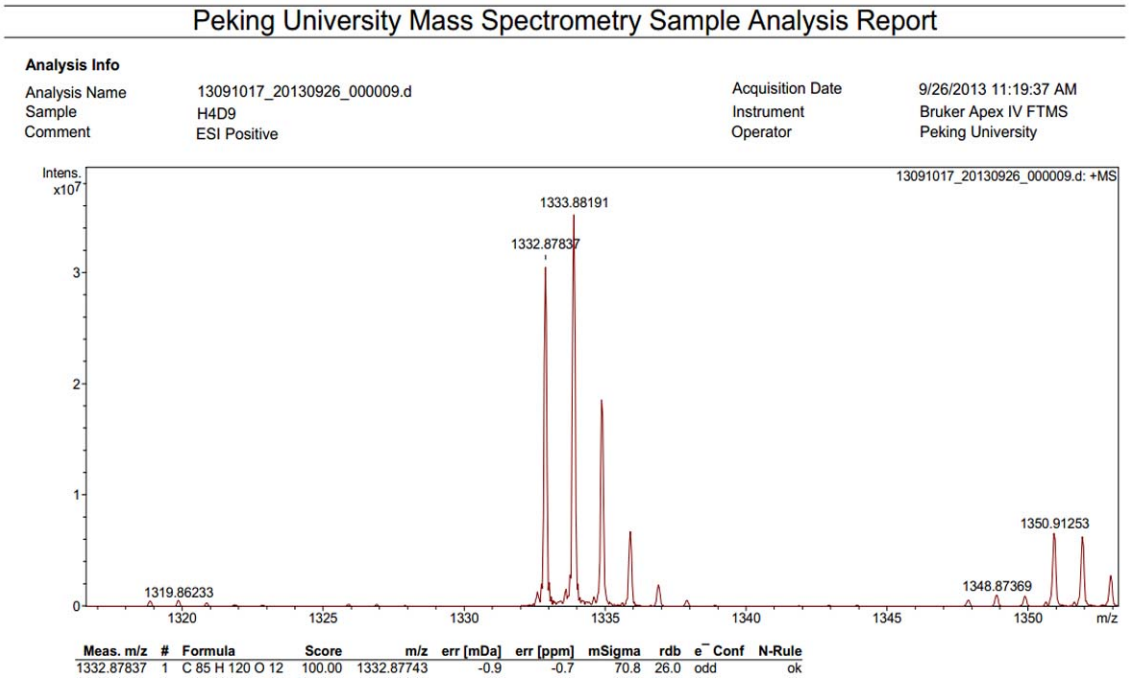
ESI Fig. 16 ^{1}H-NMR spectra of **4g**



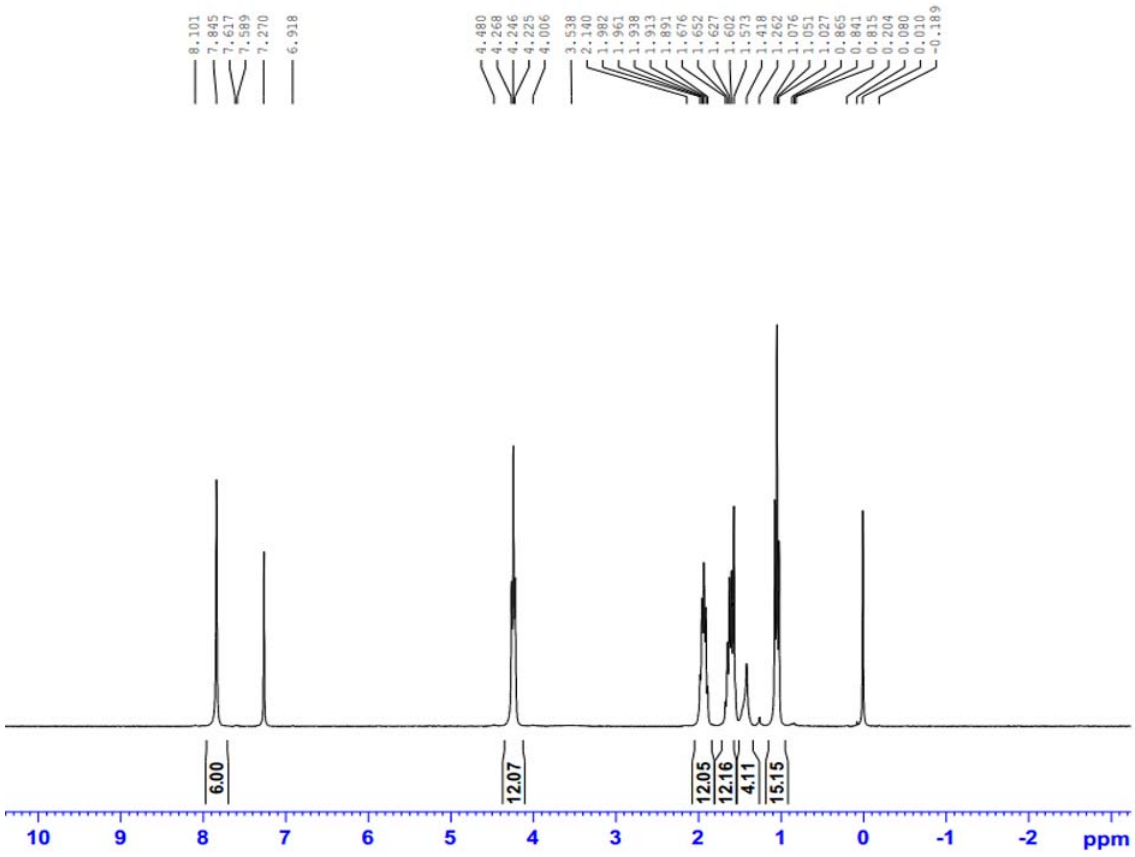
ESI Fig. 17 HRMS spectra of **4g**



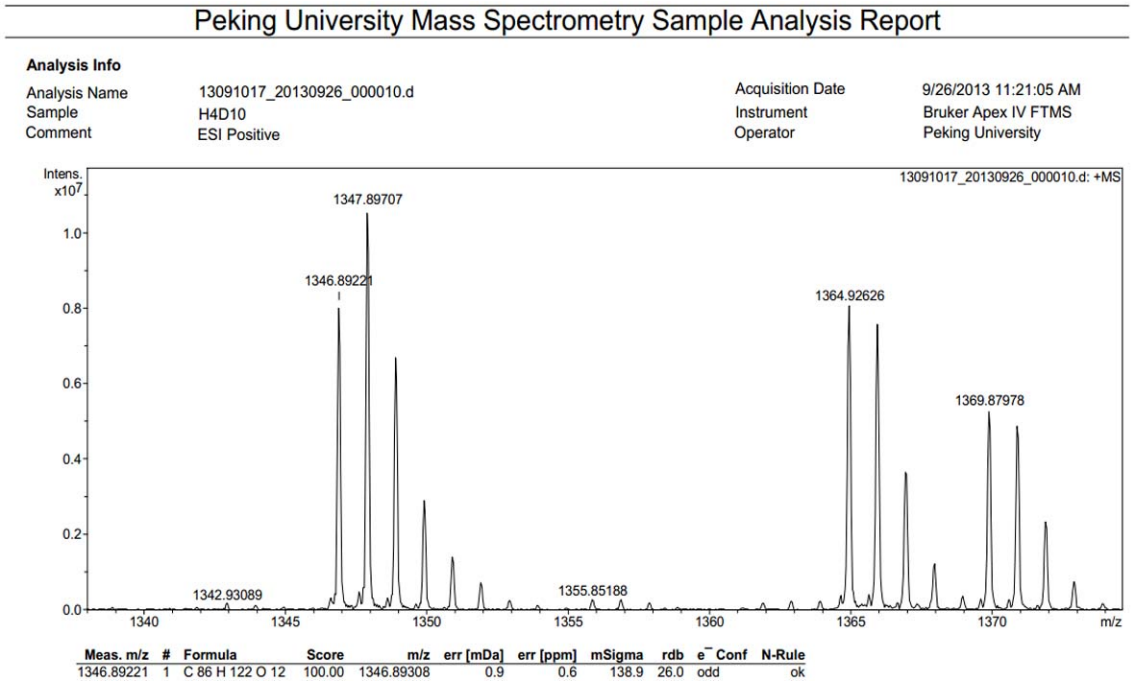
ESI Fig. 18 ^{1}H-NMR spectra of **4h**



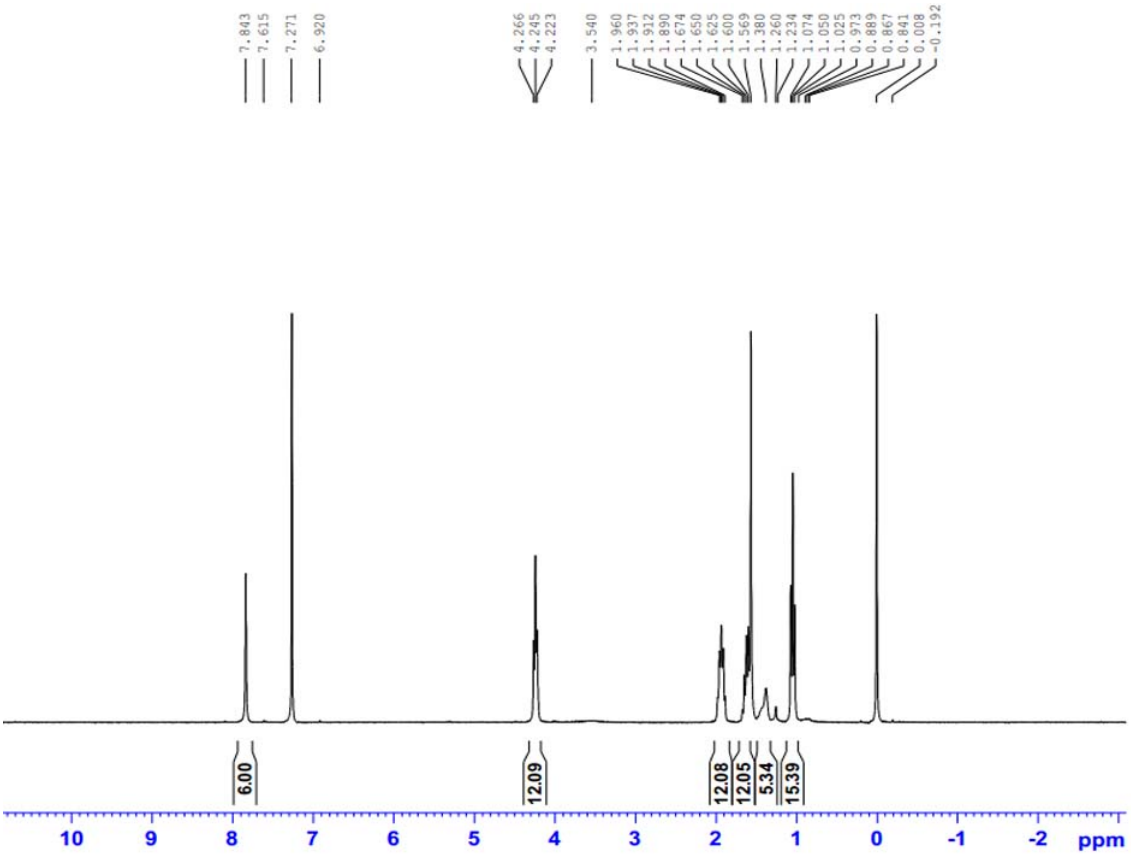
ESI Fig. 19 HRMS spectra of **4h**



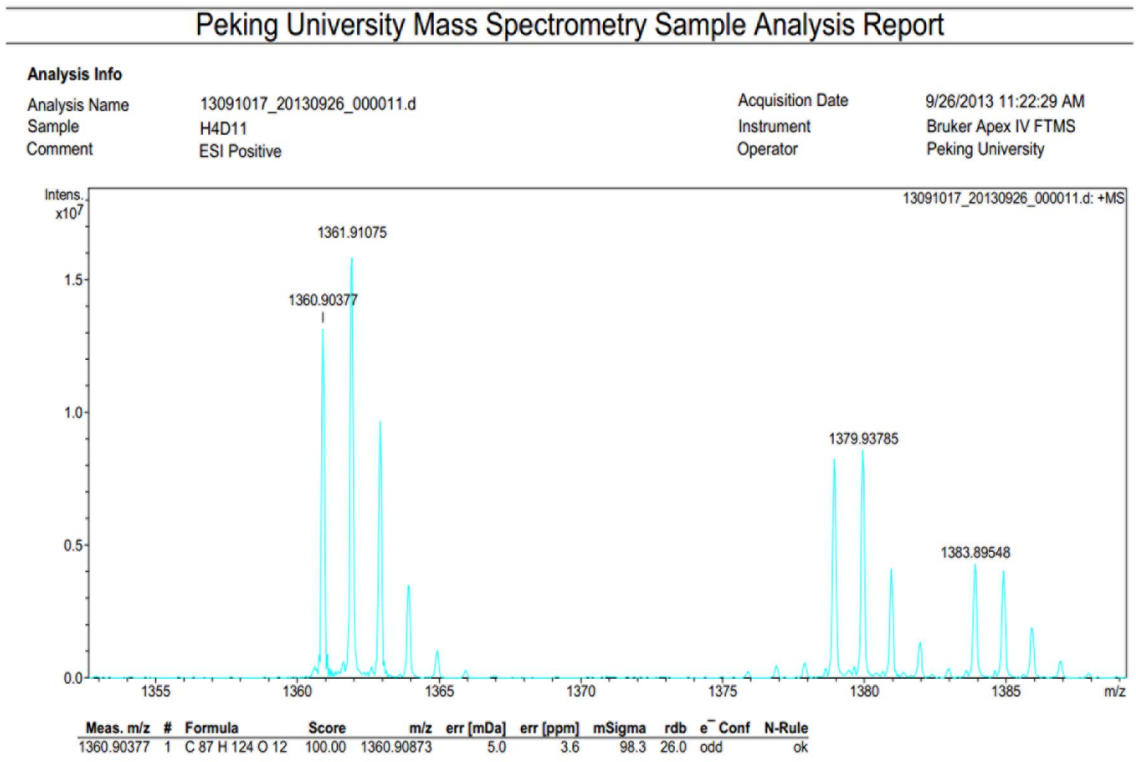
ESI Fig. 20 ^{1}H-NMR spectra of **4i**



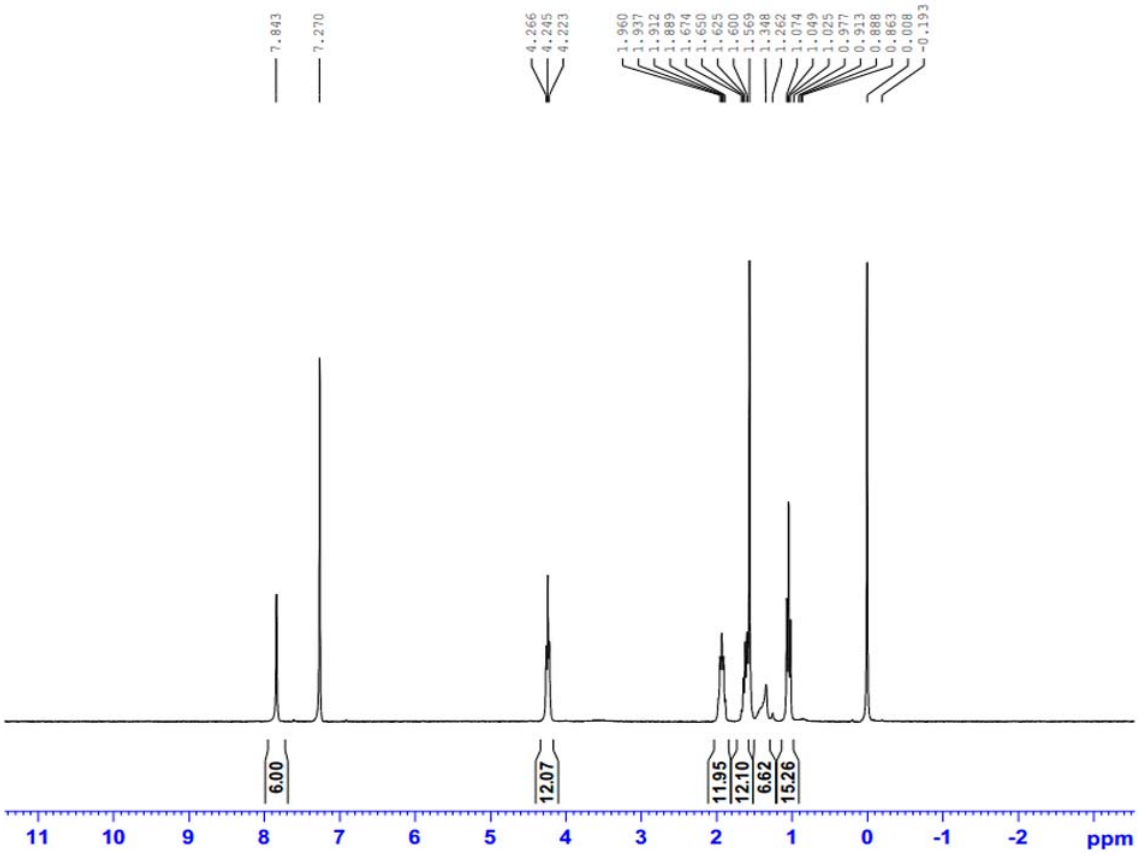
ESI Fig. 21 HRMS spectra of **4i**



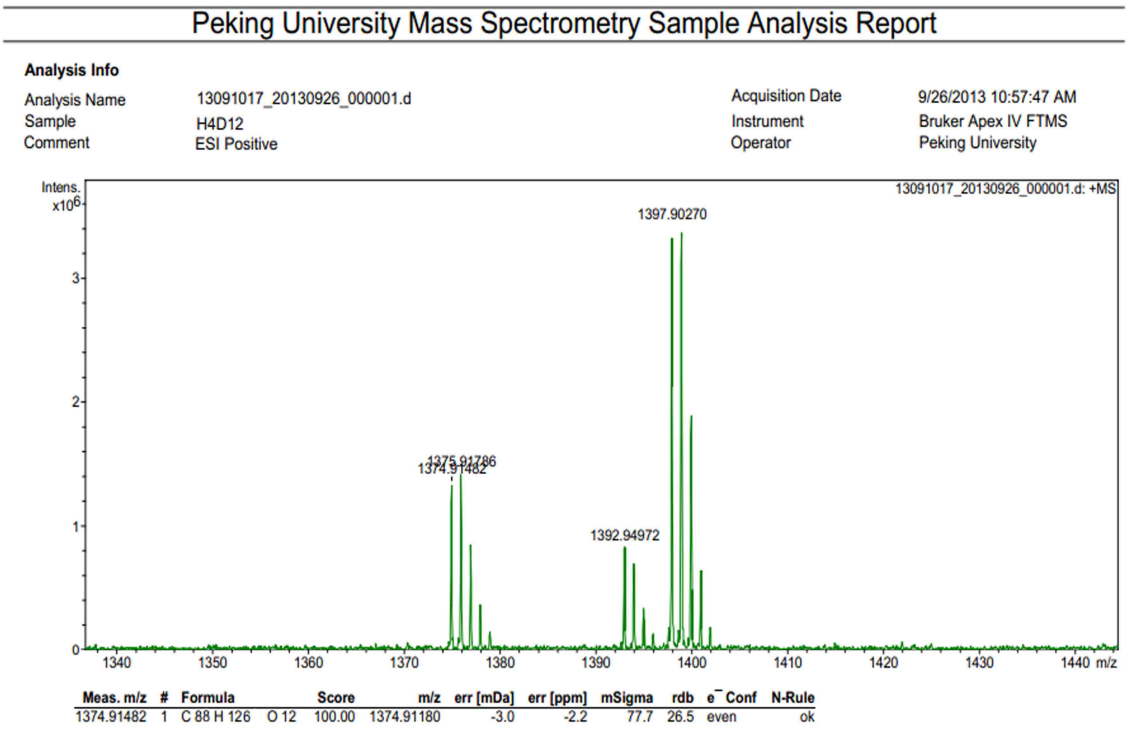
ESI Fig. 22 ^{1}H-NMR spectra of **4j**



ESI Fig. 23 HRMS spectra of **4j**



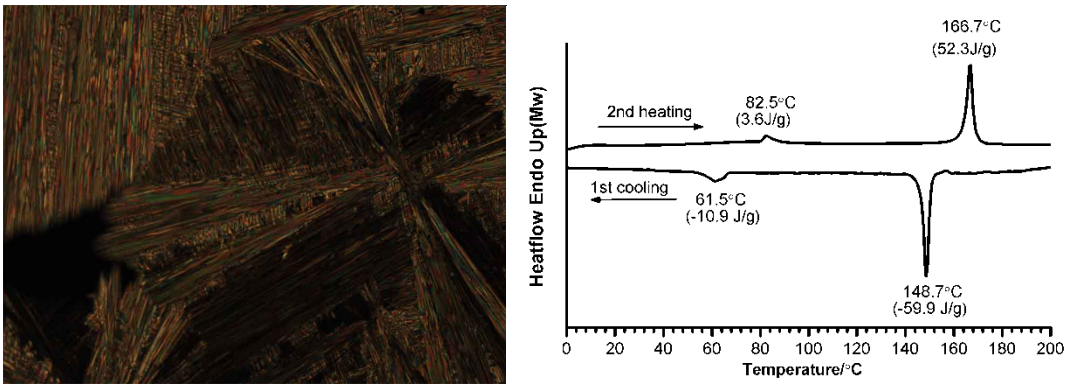
ESI Fig. 24 ^{1}H-NMR spectra of **4k**



ESI Fig. 25 HRMS spectra of **4k**

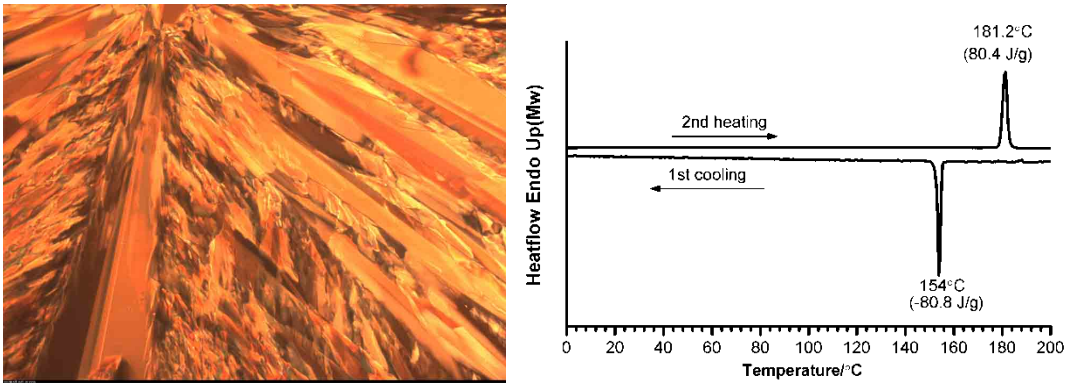
3. Mesomorphism

Mesomorphism of 4a



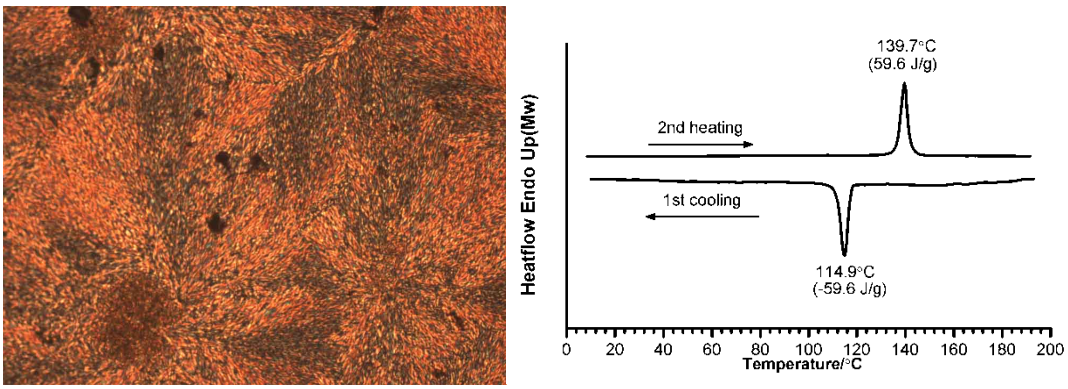
ESI Fig. 26 Crystalline texture observed by POM with 90° angle of compound **4a** sandwiched between clean glass slides on cooling from isotropic phase at 140 ºC (left); DSC trace of compound **4a** run at 10 ºC/min under N^2 (right).

Mesomorphism of 4b



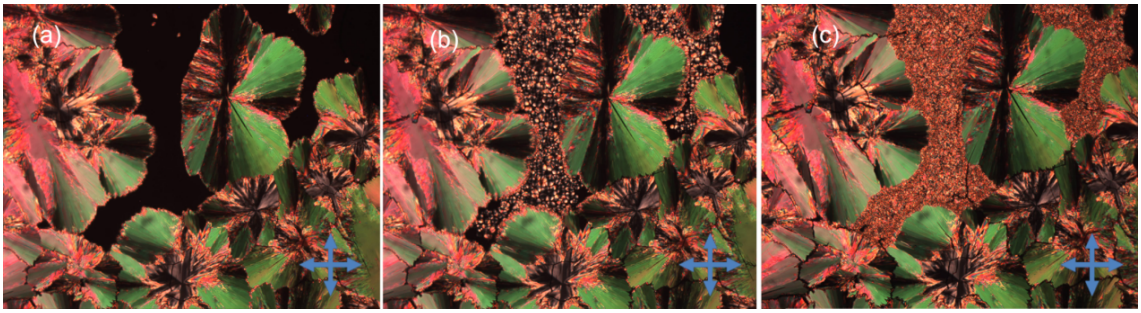
ESI Fig. 27 Crystalline texture observed by POM with 90° angle of compound **4b** sandwiched between clean glass slides on cooling from isotropic phase at 145 ºC (left); DSC trace of compound **4b** run at 10 ºC/min under N^2 (right).

Mesomorphism of 4c

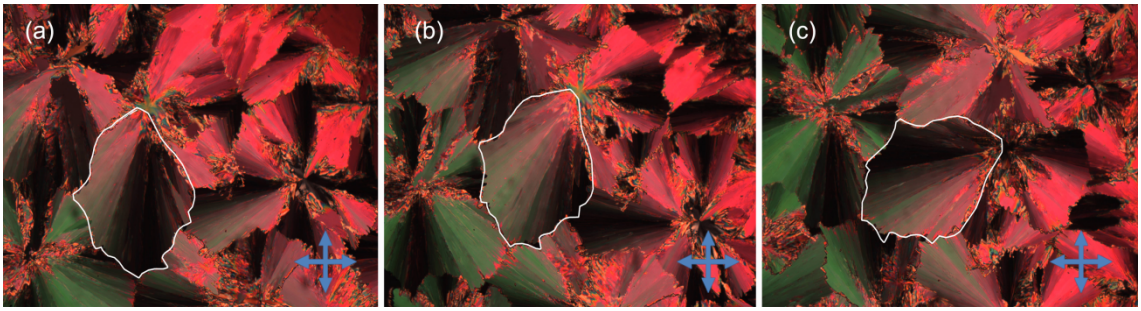


ESI Fig. 28 Crystalline texture observed by POM with 90° angle of compound **4c** sandwiched between clean glass slides on cooling from isotropic phase at 127 ºC (left); DSC trace of compound **4c** run at 10 ºC/min under N^2 (right).

Mesomorphism of 4d

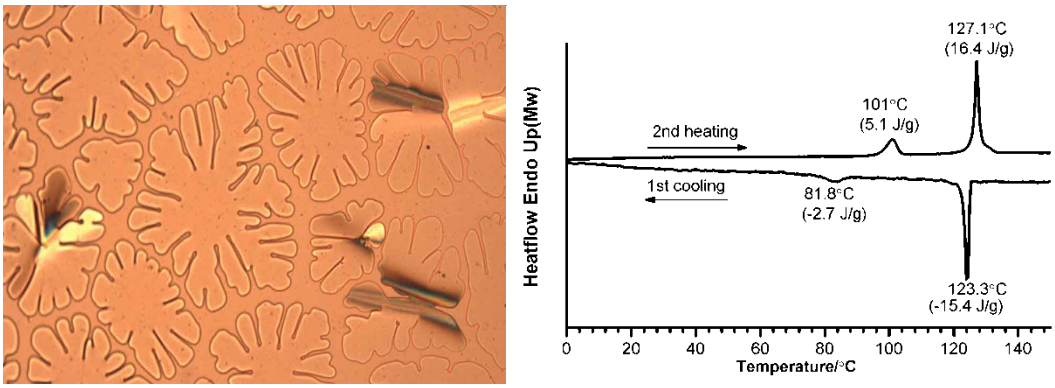


ESI Fig. 29 texture of compound 4d observed by POM when cooling from isotropic phase at (a) 85°C, (b)75°C and (c)70°C



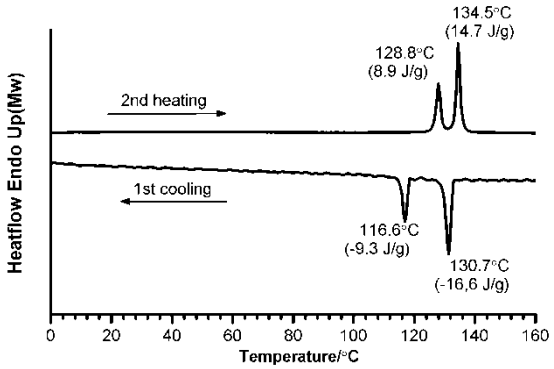
ESI Fig. 30 Focal conic texture of compound **4d** sandwiched between clean glass slides on cooling from isotropic phase at 110 ºC (a); sample in (a) is rotated by 30° (b) and 60° (c) around the optical axis between the crossed polarizers. This highly birefringent texture with extinction branches is characteristic of an edge-on alignment, when sample is rotated between the crossed polarizers, the extinction branches rotate respect to the sample as well. (White solid curves indicate the same grain)

Mesomorphism of 4e



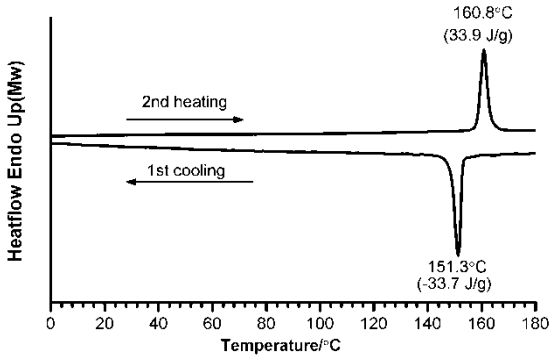
ESI Fig. 31 Dendritic texture of compound **4e** sandwiched between clean glass slides on cooling from isotropic phase at 120 ºC (left), this texture which indicated a Col_h phase was observed by POM with 45° angle and did not show any changes when cooled to room temperature; DSC trace of compound **4e** run at 10 ºC/min under N^2 (right).

Mesomorphism of 4f



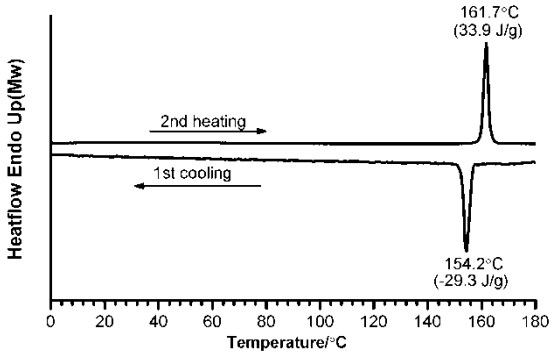
ESI Fig. 32 DSC trace of compound **4f** run at 10 ºC/min under N^2.

Mesomorphism of 4g



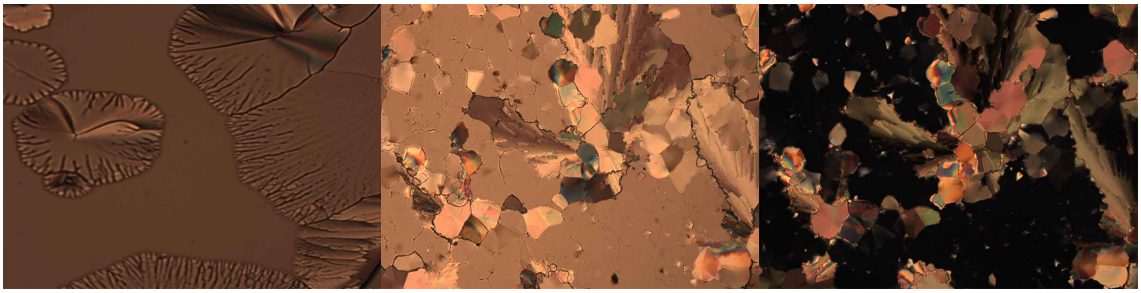
ESI Fig. 33 DSC trace of compound **4g** run at 10 ºC/min under N^2.

Mesomorphism of 4h

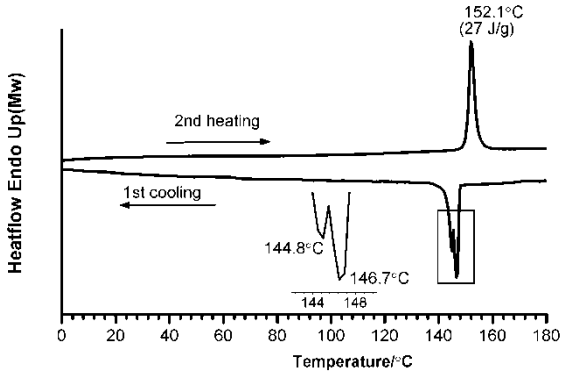


ESI Fig. 34 DSC trace of compound **4h** run at 10 ºC/min under N^2.

Mesomorphism of 4i



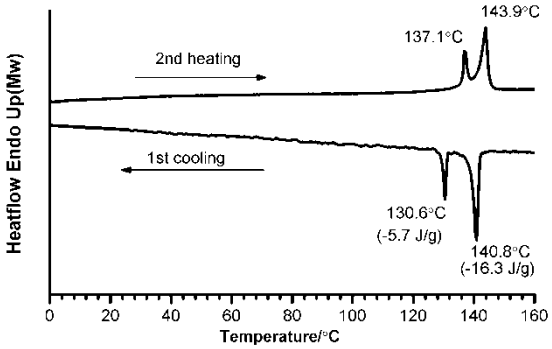
ESI Fig. 35 Optical textures of compound **4i** sandwiched between clean glass slides on cooling from isotropic phase: (left) dendritic texture which indicated a Col_h phase observed by POM with 45° angle at 148 ºC; (middle) mosaic texture which indicated a Col_{hp} phase observed by POM with 45° angle at 140 ºC; (right) mosaic texture which indicated a Col_{hp} phase observed by POM with 90° angle at 140 ºC. Phase transition between Col_h and Col_{hp} was clearly observed for the colours and areas of domain were changed while the birefringence increases.



ESI Fig. 36 DSC trace of compound **4i** run at 10 ºC/min under N^2.

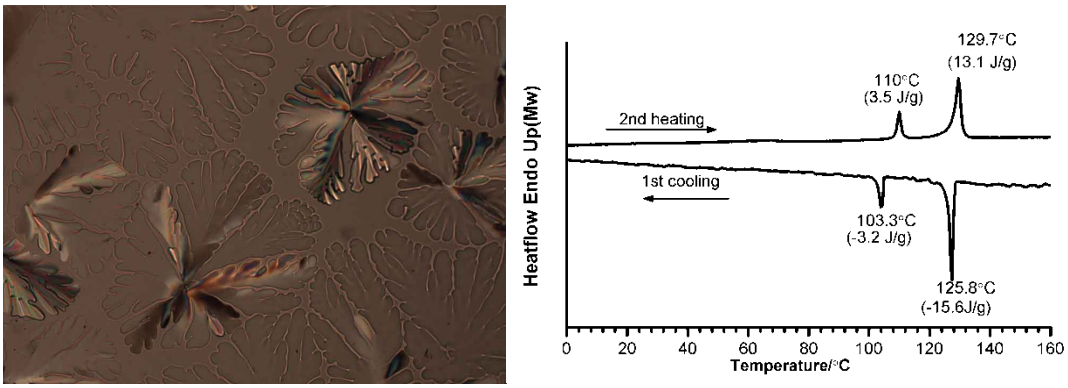
Mesomorphism of 4j

ESI Fig. 37 Optical textures of compound **4j** sandwiched between clean glass slides on cooling from isotropic phase: (left) dendritic texture which indicated a Col_h phase observed by POM with 45° angle at 140 ºC; (right) mosaic texture which indicated a Col_{hp} phase observed by POM with 90° angle at 100 ºC. Phase transition between Col_h and Col_{hp} was clearly observed for the colours and areas of domain were changed while the birefringence increases.



ESI Fig. 38 DSC trace of compound **4j** run at 10 ºC/min under N^2.

Mesomorphism of 4k



ESI Fig. 39 Dendritic texture of compound **4k** sandwiched between clean glass slides on cooling from isotropic phase at 125 ºC (left), this texture which indicated a Col_h phase was observed by POM with 45° angle and did not show any changes when cooled to room temperature; DSC trace of compound **4k** run at 10 ºC/min under N^2 (right).