

Supporting information

**Simple Synthesis and Molecular Engineering of  
Low-cost and Star-shaped Carbazole-based Hole Transporting Materials  
For Highly Efficient Perovskite Solar Cells**

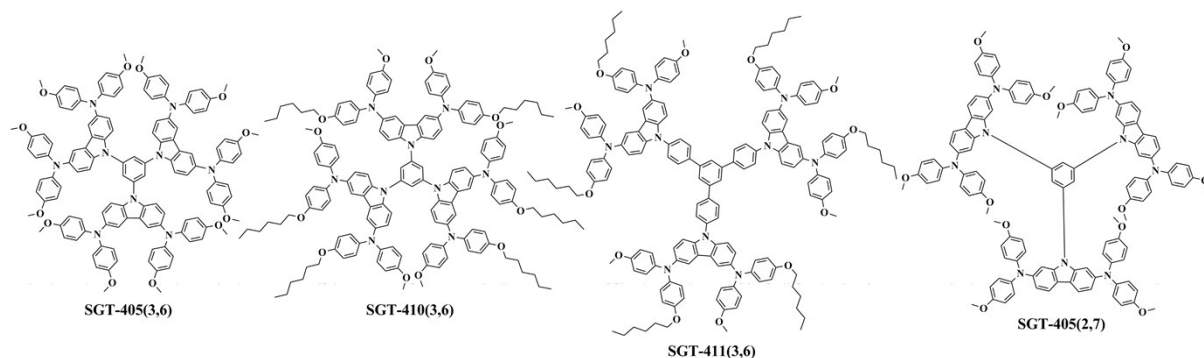
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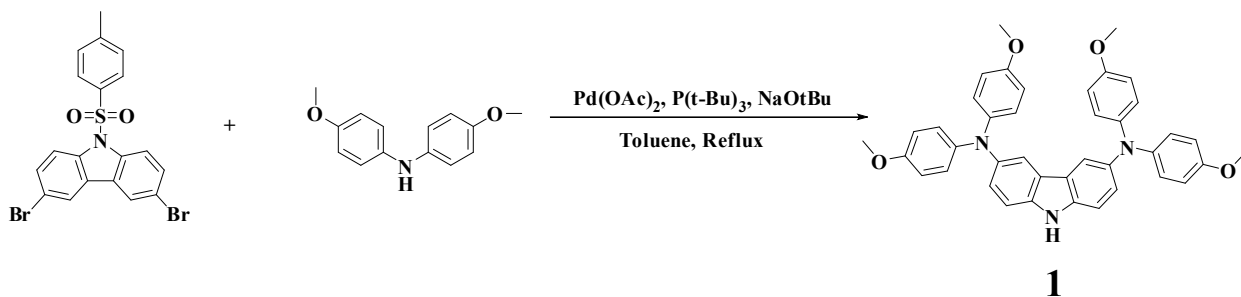
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## Chemical structures of new HTMs based on carbazole unit



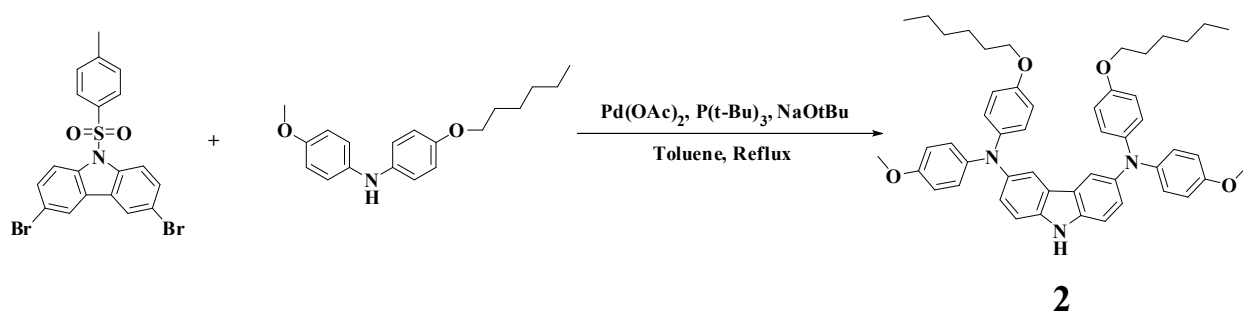
## Materials and synthesis

1,3,5-tribromobenzene, 3,6-dibromo-9H-carbazole, 4,4'-Dimethoxydiphenylamine were purchased from Tokyo Chemical Industry. 3,6-dibromo-9-tosyl-9H-carbazole was prepared by the slight modification of literature procedure.<sup>1</sup> Intermediate material compound 1 and compound 2 and new HTMs were synthesized through palladium-catalyzed Buchwald-Hartwig reaction using  $\text{Pd}(\text{OAc})_2$ ,  $(\text{tert-Bu})_3\text{P}$  and  $\text{tert-BuO-Na}^+$ .<sup>2,3</sup>

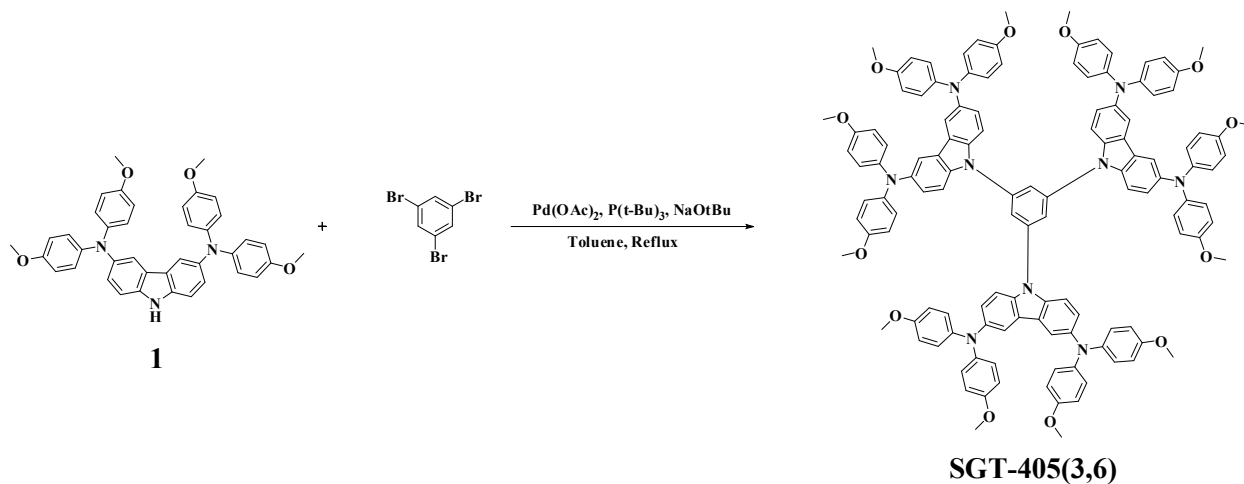


**Compound 1:** 3,6-dibromo-9-tosyl-9H-carbazole (1 g, 2.09 mmol), bis(4-methoxyphenyl)amine (1 g, 4.38 mmol), Palladium acetate (0.02 g, 0.1 mmol), tri-tert-butylphosphine(0.08 g, 0.42mmol) and sodium *tert*-butoxide(0.6 g, 6.26 mmol) dissolved in 20 ml of anhydrous toluene were refluxed over 38 hours under nitrogen atmosphere prior to being

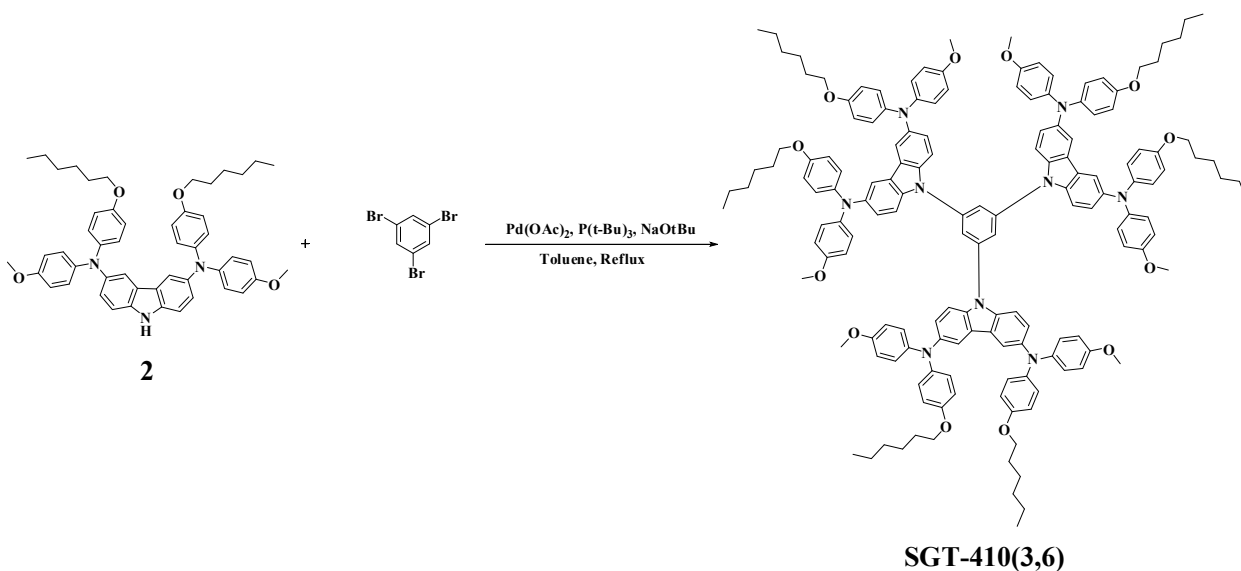
quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (EA : Hex = 1 : 5) to give **compound 1** (1.05 g, 78 %) as a yellow-green solid. <sup>1</sup>H-NMR (300 MHz; DMSO-d<sup>6</sup>; TMS) 11.14 (1H, s, Ar-NH), 7.64 (2H, s, Ar-H), 7.41 (2H, d, J=8.6Hz, Ar-H), 7.08 (2H, dd, J=2.1Hz, J=8.6Hz, Ar-H), 6.89 (8H, d, J=8.7 Hz, Ar-H), 6.81 (8H, d, J=8.7 Hz, Ar-H), 3.69 (12 H, s, Ar-OCH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz; DMSO-d<sup>6</sup>; TMS) 154.10, 142.22, 139.69, 137.09, 124.50, 123.57, 123.07, 116.97, 114.62, 112.89, 55.18.



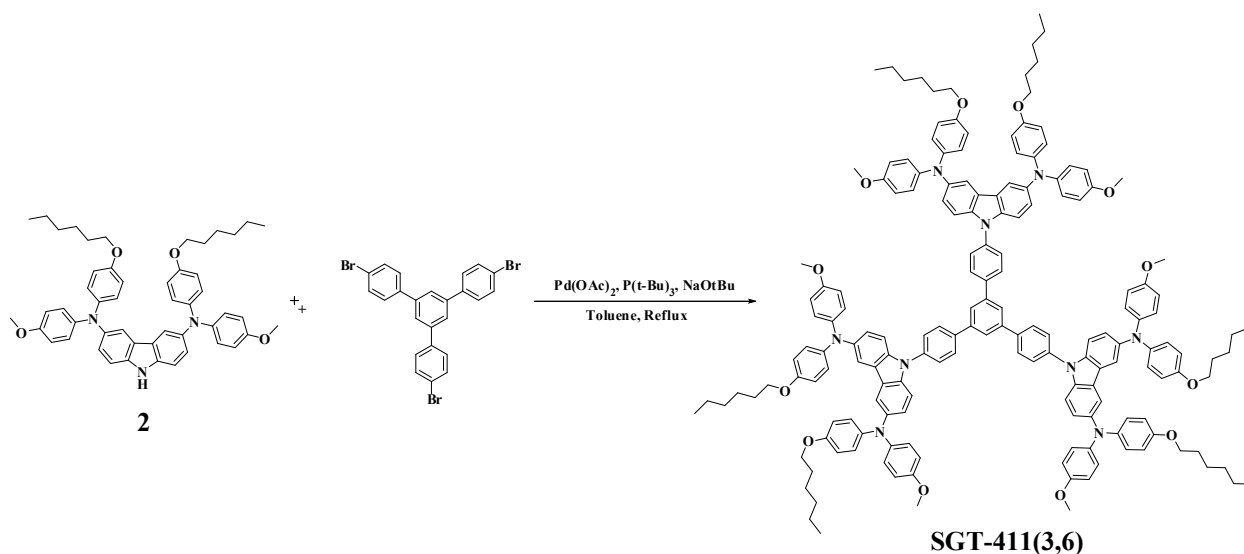
**Compound 2:** 3,6-Dibromo-9-tosyl-9H-carbazole (4.24 g, 8.85 mmol), 4-(hexyloxy)-N-(4-methoxyphenyl)aniline (5.43 g, 18.14 mmol), Palladium acetate (0.4 g, 1.77 mmol), tri-*tert*-butylphosphine (0.72 g, 3.54 mmol) and sodium *tert*-butoxide (10.2 g, 106.18 mmol) dissolved in 20 ml of anhydrous toluene were refluxed over 38 hours under nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (EA : Hex = 1 : 5) to give **compound 2** (5.5 g, 80 %) as a yellow-green solid. <sup>1</sup>H-NMR (300 MHz; DMSO-d<sup>6</sup>; TMS) 11.16 (1 H, s, Ar-NH), 7.56 (2H, s, Ar-H), 7.381 (2H, d, J=8.6Hz, Ar-H), 7.04 (2H, dd, J=2.1Hz, J=8.6Hz, Ar-H), 6.83 (8 H, d, J=8.7 Hz, Ar-H), 6.78 (8H, d, J=8.7 Hz, Ar-H), 3.81 (4 H, t, J=6.9 Hz, Ar-OCH<sub>2</sub>-), 3.64 (6H, s, Ar-OCH<sub>3</sub>), 1.62 (4H, m, -CH<sub>2</sub>-), 1.35 (12H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.84 (12H, m, -CH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz; DMSO-d<sup>6</sup>; TMS) 154.04, 153.52, 142.20, 142.05, 139.72, 137.07, 124.42, 123.56, 123.07, 116.81, 115.07, 114.52, 111.94, 67.51, 55.10, 31.02, 28.76, 25.23, 22.10, 13.89.



**SGT-405(3,6):** **1** (1.84 g, 2.95 mmol), 1,3,5-tribromobenzene (0.3 g, 0.95mmol), palladium acetate (0.06 g, 0.29 mmol), tri-*tert*-butylphosphine (0.12 g, 0.57 mmol) and sodium *tert*-butoxide (1.37 g, 14.29 mmol) dissolved in 20 ml of toluene were refluxed 38 hours under nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-405(3,6)** (1.1 g, 58 %). <sup>1</sup>H-NMR (300 MHz; THF-*d*<sup>8</sup>; TMS) 7.99 (3H, s, Ar-H), 7.68 (6H, s, Ar-H), 7.58 (6H, d, *J*=8.4 Hz, Ar-H), 7.15(6 H, d, *J*=9.3 Hz, Ar-H), 6.93(24H, d, *J*=8.4 Hz, Ar-H), 6.74(24H, d, *J*=8.4 Hz, Ar-H), 3.70 (36H, s, Ar-OCH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz; THF-*d*<sup>6</sup>; TMS) 155.86, 143.12, 139.69, 137.88, 125.35, 125.06, 121.72, 116.97, 111.16, 78.02, 55.31. MS (MALDI-TOF): *m/z* found: 1935.597, calc.: 1937.23.



**SGT-410(3,6):** **2** (2.21 g, 2.91 mmol), tris(4-bromophenyl)amine (0.3 g, 0.95 mmol), palladium acetate (0.06 g, 0.29 mmol), tri-*tert*-butylphosphine (0.12 g, 0.57 mmol) and sodium *tert*-butoxide (1.37 g, 14.29 mmol) dissolved in 20 ml of toluene were refluxed over 38 hours under nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-410(3,6)** (1.24 g, 55 %). <sup>1</sup>H-NMR (300 MHz; THF-*d*<sup>8</sup>; TMS) 7.99 (3 H, s, Ar-H), 7.69 (6 H, s, Ar-H), 7.58 (6 H, d, *J*=8.4 Hz, Ar-H), 7.15 (6 H, d, *J*=8.7 Hz, Ar-H), 6.93 (24H, dd, *J*=3Hz, *J*=3.3Hz, Ar-H), 6.90 (24H, dd, *J*=1.5Hz, *J*=2.4Hz, Ar-H), 3.90 (12 H, t, Ar-OCH<sub>2</sub>-), 3.70 (18 H, s, Ar-OCH<sub>3</sub>), 1.49 (48 H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.94 (18H, t, -CH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz; THF-*d*<sup>8</sup>; TMS) 155.80, 155.33, 143.30, 143.15, 142.99, 141.74, 137.85, 125.35, 125.03, 117.01, 115.51, 114.96, 111.16, 68.43, 55.32, 32.43, 30.17, 26.59, 23.38, 14.26. MS (MALDI-TOF): *m/z* found: 2357.08, calc.: 2358.03.



**SGT-411(3,6):** **2** (0.77 g, 1.01 mmol), tris(4-bromophenyl)amine (0.18 g, 0.33 mmol), palladium acetate (0.02 g, 0.10 mmol), tri-*tert*-butylphosphine (0.04 g, 0.20 mmol) and sodium *tert*-butoxide (0.48 g, 4.97 mmol) dissolved in 20 ml of toluene were refluxed over 38 hours under nitrogen atmosphere prior to being quenched by distilled water. The mixture was extracted with ethyl acetate and washed with brine several times. The organic layer was dried with anhydrous magnesium sulphate. The filtrate was then evaporated under vacuum and purified by column chromatography (MC : Hex = 3 : 2 containing 2% of EA) to give **SGT-411(3,6)** (0.4 g, 47%). <sup>1</sup>H-NMR (300 MHz; THF-*d*<sup>8</sup>; TMS) 8.17 (12 H, m, Ar-H), 7.79 (6 H, d, *J*=8.7, Ar-H), 7.71 (6 H, s, Ar-H), 7.39 (6 H, d, *J*=9 Hz, Ar-H), 7.14 (6 H, d, *J*=8.4 Hz, Ar-H), 6.92 (24 H, m, Ar-H), 6.76 (24 H, m, Ar-H), 5.52 (3 H, s, Ar-H), 3.91 (12 H, t, Ar-OCH<sub>2</sub>-), 3.71 (18H, s, Ar-OCH<sub>3</sub>), 1.37 (48H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.94 (18H, m, -CH<sub>3</sub>). <sup>13</sup>C-NMR (300 MHz; THF-*d*<sup>8</sup>; TMS) 176.781, 175.54, 155.80, 155.33, 143.30, 143.15, 142.99, 141.74, 138.29, 137.85, 129.52, 125.35, 125.06, 122.50, 117.01, 115.51, 115.02, 114.96, 111.16, 110.08, 68.45, 55.32, 35.33, 32.43, 30.19, 23.37, 14.24. MS (MALDI-TOF): *m/z* found: 2585.228, calc.: 2586.32.

## Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using Varian Mercury 300 spectrometer employing tetramethylsilane (TMS; *d* = 0 ppm) as the internal standard. MALDI-TOF mass spectra were

recorded by a Voyager-DETM STR biospectrometry workstation. Thermal stability of new HTMs was analyzed using DSC N-650 and TGA N-1000. UV/Vis absorption spectra were obtained in DCM on a Shimadzu UV-2401PC spectrophotometer. Photoluminescence spectra were analysed with a Fluorolog FL-3-22 fluorimeter from Horiba-Jobin-Yvon Ltd., which was equipped with a 450 W Xe lamp and two analysing monochromators. Visible emission spectra were recorded with a Hamamatsu R928 photomultiplier. All samples were measured in a 1 cm cell at room temperature.

Cyclic voltammetry was performed on a Versa STAT3 (AMETEK) instrument via conventional three-electrode system. Ag/AgCl was used as reference electrode, Pt wire was used as counter electrode. The redox potentials of each HTM were measured in distilled THF containing 0.1 M TBAPF<sub>6</sub> at a scan rate of 50 mV s<sup>-1</sup>. All redox potentials were calibrated vs. normal hydrogen electrode (NHE) by the addition of ferrocene, with the conversion  $E_{(Fc/Fc^+)} = 630 \text{ mV vs NHE}$ .

Photocurrent–voltage (I-V) measurements were performed by using a Keithley model 2400 source measurement unit. A 300W Xenon lamp (Spectra-Physics) was used as the light source and the light intensity was adjusted by using an NREL-calibrated Silicon solar cell equipped with a KG-5 filter for approximating AM1.5 G 1 sunlight intensity. The magnitude of the alternate signal was 10 mV. The incident photon-to-current efficiency (IPCE) spectra were measured as a function of wavelength from 300 to 800 nm using a specially designed IPCE system (PVMeasurements, Inc.).

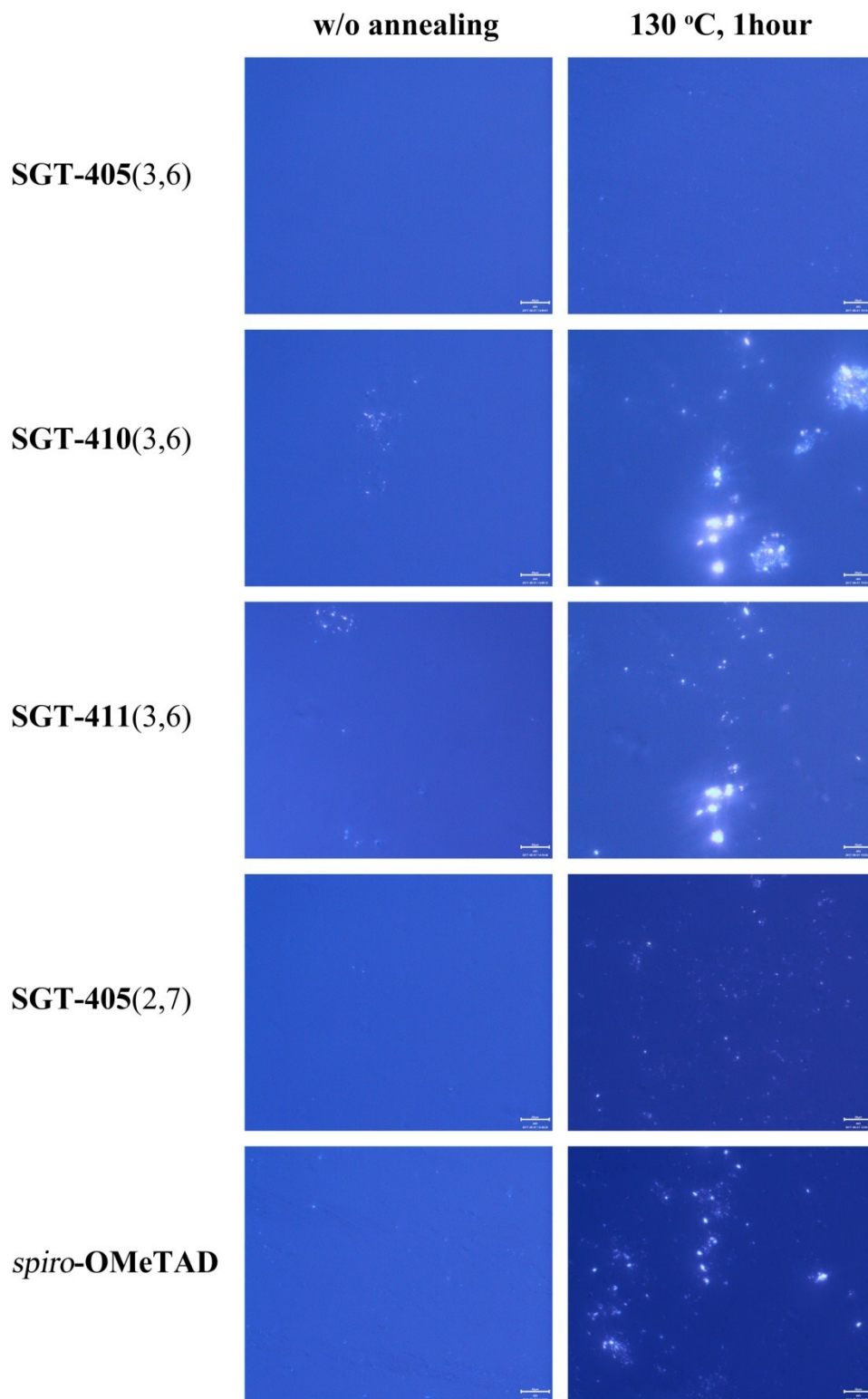
## **Surface morphology and roughness of new HTMs on top of perovskite films**

The morphologies of the perovskite films and each HTMs spin-coated on top of perovskite films were examined by field-emission scanning electron microscopy (FESEM, Hitachi S4300). The top-view morphology and surface roughness of naked perovskite films and various HTMs spin-coated on top of perovskite films were measured by AFM (Park Systems).

## **Morphology stability of HTM films upon heating**

In applying small molecular materials for electronic and optoelectronic devices, the morphology stability upon heating is often required since phase transitions during device operation (e.g., solar cells sitting in direct sunlight can get quite hot, especially in hot climatic conditions). Meanwhile, low molecular-weight organic molecules generally tend to crystallise readily, therefore it is important to design and synthesize amorphous molecular materials with relatively high glass transition temperature ( $T_g$ ). The effect of glass transition temperature  $T_g$  on the morphology stability of various HTMs films was investigated under different heating conditions (w/o heating or heating at 130 °C for 1 hour). And the changes of surface morphology of HTM films upon heating or w/o heating were characterized by polarized optical microscope (LEICA DMRXP, FP900).





**Figure S1.** Polarized optical microscope images of various HTM films spin-coated onto glass at different heating temperature (Scale bar: 20 $\mu$ m).

## Hole mobility measurement

Hole mobility of each HTMs was determined by the space-charge-limited current (SCLC) method,<sup>4, 5</sup> which can be described by the following equation:

$$J = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{d^3}$$

where  $J$  is the current density,  $\mu$  is the hole mobility,  $\epsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-12}$  F/m),  $\epsilon_r$  is the dielectric constant of the material (normally taken to approach 3 for organic semiconductors),<sup>6</sup>  $V$  is the applied bias, and  $d$  is the film thickness measured through cross-section measurement using field-emission scanning electron microscopy. The hole only device structure used in this work: FTO/pedot:pss/HTM/Au.

## Density functional calculations (DFT)

The geometry optimization and electronic structure of the molecules were calculated using by B3LYP/6-31G(d,p) level with the Gaussian 09 program<sup>7</sup>. And the reorganization energy ( $\lambda$ ) was determined by four energies (the Nelson four-point method).<sup>8</sup>

## Time-resolved photoluminescence

Time-resolved photoluminescence (TR-PL) was measured by using a time-correlated single-photon counting (TCSPC) spectrometer (FluoTime 200, PicoQuant) equipped with a picosecond diode laser (LDH-P-C-390, PicoQuant) and a hybrid photomultiplier detector (PMA Hybrid 50, PicoQuant). Samples for TR-PL measurement possessing structure of pyrex

glass/perovskite/HTMs were excited by 100 ps, 393 nm laser pulses, which were incident on the HTM side, and the emission from the sample was collected at the wavelength of 760 nm. The nominal temporal resolution of the TR-PL measurement was approximately 190 ps, but the practical time resolution was tens of picoseconds after deconvolution of the instrument response function.

**Table S1.** Summary of the parameters from fits to time-resolved PL measurement.

HTM	A1	$\tau_1$ (ns)	A2	$\tau_2$ (ns)	$R_1^a$	$R_2^a$	$\tau_{interface}$ (ns) <sup>b</sup>	$\tau_{ct}$ (ns) <sup>d</sup>	CTE(%) <sup>e</sup>
Neat perovskite	0.130	4.27	0.849	26.66	0.133	0.867	23.68 <sup>c</sup>		
<b>SGT-405(3,6)</b>	0.453	2.70	0.479	10.26	0.486	0.514	6.59	9.13	72.18
<b>SGT-410(3,6)</b>	0.359	6.32	0.581	18.67	0.382	0.618	13.95	33.95	41.09
<b>SGT-411(3,6)</b>	0.468	5.80	0.463	14.41	0.503	0.497	10.08	17.55	57.44
<b>SGT-405(2,7)</b>	0.339	3.92	0.598	10.07	0.362	0.638	7.84	11.72	66.89
<i>spiro-</i> <b>OMeTAD</b>	0.540	2.04	0.422	8.12	0.561	0.439	4.71	5.88	80.10

<sup>a</sup> $R_1$  and  $R_2$  are relative ratio factor, given by  $R_1 = \frac{A_1}{A_1 + A_2}$ ;  $R_2 = \frac{A_2}{A_1 + A_2}$ .

<sup>b</sup>The PL lifetime of each Pyrex glass/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/HTM sample corresponds to the amplitude-weighted average lifetime of a biexponential decay fit.<sup>3</sup>

<sup>c</sup>Time constant for the TR-PL decay of the neat CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> film.

<sup>d</sup> $\tau_{CT}$  was calculated by using the relationship of  $\frac{1}{\tau_{interface}} = \frac{1}{\tau_{perovskite}} + \frac{1}{\tau_{CT}}$ .

Charge-transfer efficiency (CTE) was calculated by using equation:

$$CTE = \frac{\kappa_{CT}}{\kappa_{interface}} = \frac{\tau_{interface}}{\tau_{CT}} \quad .3$$

Note: the fitting functions of biexponential decay equation.  $I(t) = I_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$  9

## Device fabrication

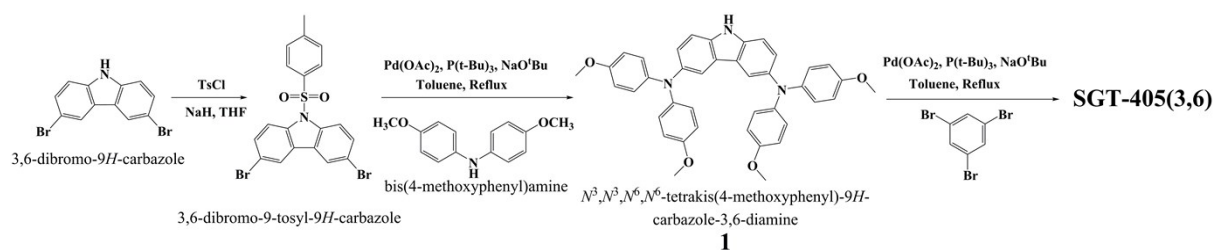
The device structure of FTO/compact TiO<sub>2</sub>/meso-porous TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/HTM/Au was applied in this research work. A 20~30 nm TiO<sub>2</sub> compact layer was deposited on the cleaned FTO glass by spray pyrolysis at 450°C from a precursor solution of 0.5 ml titanium diisopropoxide bis(acetylacetonate) solution in 19.5 ml anhydrous ethanol. A mesoporous TiO<sub>2</sub> was spin-coated on the substrate with a speed of 2500 rpm for 5 s, and then 7500rpm for 60s, from a diluted 50 nm particle paste (Dyesol) in the mixture of ethanol and terpinol, the weight ratio of TiO<sub>2</sub> (Dyesol paste): Ethanol:terpinol is 1:2:4. After that, the substrate was immediately dried on a hotplate at 100°C for 2min, and then the substrates were sintered at 500°C overnight. The perovskite film was deposited by spin-coating onto the TiO<sub>2</sub> substrate. The perovskite layer was deposited by spin coating the perovskite precursor solution in one-step, which was prepared by mixing of the chloride iodide (PbCl<sub>2</sub>), lead iodide (PbI<sub>2</sub>) and methylammonium iodide (MAI) in a mixed solvent of DMF and DMSO solution (volume ratio 9:1) with the molar concentration of 0.8M Pb<sup>2+</sup> (molar ratio (PbI<sub>2</sub>/PbCl<sub>2</sub>)4:1) and 0.8M MAI. The spin coating procedure consist of two stage: first 1000 rpm for 10 s, second 5000 rpm for 40 s with a ramp of 2500 rpm·s<sup>-1</sup>. 800µl toluene was dropped on the spinning substrate during the second spin-coating step 30 s before the end of the procedure. The substrate was then annealed at 100°C for 10 min on a hotplate. After cooling down to room temperature, the HTM was subsequently deposited on the top of the perovskite layer by spin

coating at 4000 rpm for 30 s. The HTM solutions were prepared by dissolving each HTM in chlorobenzene with concentrations of 60 mM for spiro-OMeTAD, 23.59 mM for SGT-405(3,6), SGT-405(2,7), SGT-410(3,6) and SGT-411(3,6). Tert-butylpyridine (t-BP), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) (FK209) and tris(bis(trifluoro-methyl-sulfonyl)imide) (Li-TFSI) were added as additives. Equimolar amounts of additives were added for all hole-transporters: 330 mol% t-BP, 50 mol% Li-TFSI from a 1.8M stock solution in acetonitrile and 3 mol% FK209 from a 0.3M stock solution in acetonitrile. Finally, 80 nm of gold was deposited by thermal evaporation .

## Cost evaluation

The lab synthesis costs of **SGT405(3,6)** and **SGT405(2,7)** were estimated on the base of a model proposed by Osedach et al. Required amounts of reactants, catalysts, reagents, solvents and materials for workup and purification of the 1 g of **SGT405(3,6)** and **SGT405(2,7)** are summarized in **Table S2** and **Table S3**. The price of the commercially available chemicals per kg and the cost of the intermediate products per kg were multiplied by the required quantities for the synthesis.

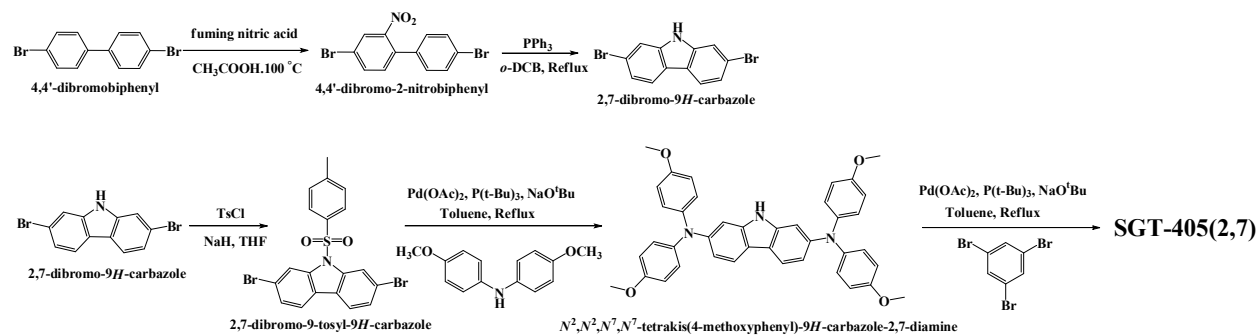
**Table S2.** Materials, quantities and cost for the synthesis of **SGT405(3,6)**



Chemical	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical (€/kg)	Chemical Cost (€/g)	Cost per step (€/g)
3,6-dibromo-9H-carbazole	1.365			195	0.266	
TsCl	0.9608			40.40	0.039	
NaH	0.1210			195.25	0.024	
THF		15.14		8.12	0.123	

Water			186	0	0	
Dichloromethane			430	1.40	0.602	
n-hexane			91.5	3.44	0.315	
MgSO <sub>4</sub>			1.852	48.04	0.089	1.458
<b>3,6-dibromo-9-tosyl-9H-carbazole</b>	1.852					
bis(4-methoxyphenyl)amine	1.8608			1100.46	2.048	
Pd(OAc) <sub>2</sub>	0.043			27360	1.176	
( <i>tert</i> -Bu) <sub>3</sub> P	0.070			53053.5	3.714	
sodium <i>tert</i> -butoxide	1.114			201.44	0.224	
toluene		22.4		3.61	0.081	
Celite			9.13	56	0.511	
Ethyl acetate			356.9	2.07	0.739	
Water			182	0	0	
MgSO <sub>4</sub>			1.826	48.04	0.088	
n-hexane			398.6	3.44	1.371	
Silicagel			430	21.19	9.112	19.064
<b>N<sup>3</sup>,N<sup>3</sup>,N<sup>6</sup>,N<sup>6</sup>-tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine(1)</b>	1.8260					
1,3,5-tribromobenzene	0.2802			271.79	0.076	
Pd(OAc) <sub>2</sub>	0.0200			27360	0.547	
( <i>tert</i> -Bu) <sub>3</sub> P	0.0360			53053.5	1.910	
sodium <i>tert</i> -butoxide	0.4277			201.44	0.086	
toluene		12.3		3.61	0.044	
Celite			5	56	0.28	
Ethyl acetate			225.5	2.07	0.467	
Water			100	0	0	
n-hexane			196.4	3.44	0.676	
MgSO <sub>4</sub>			1	48.04	0.048	
Silicagel			235.5	21.19	4.990	9.124
<b>total</b>						29.646

**Table S3.** Materials, quantities and cost for the synthesis of **SGT405(2,7)**



Chemical	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical (€/kg)	Chemical Cost (€/g)	Cost per step (€/g)
4,4'-dibromobiphenyl	<b>3.1200</b>			462.51	1.443	54.167
fuming HNO <sub>3</sub>	133.2000			350.83	46.731	
Glacial acetic acid	262.2500			22.853	5.993	
4,4'-dibromo-2-nitrobiphenyl	<b>2.792</b>					2.313
Triphenylphosphine	6.154			183.31	1.128	
1,2-Dichlorobenzene		23.4		50.62	1.185	
2,7-dibromo-9H-carbazole	<b>1.5250</b>					1.216
TsCl	1.0734			40.40	0.0434	
NaH	0.2252			195.25	0.0440	
THF		15.14		8.12	0.123	
Water			186	0	0	
Dichloromethane			430	1.40	0.602	
n-hexane			91.5	3.44	0.315	
MgSO <sub>4</sub>			1.852	48.04	0.089	
<b>2,7-dibromo-9-tosyl-9H-carbazole</b>	<b>2.069</b>					20.951
bis(4-methoxyphenyl)amine	2.0788			1100.46	2.288	
Pd(OAc) <sub>2</sub>	0.048			27360	1.313	
( <i>tert</i> -Bu) <sub>3</sub> P	0.078			53053.5	4.138	
sodium <i>tert</i> -butoxide	1.245			201.44	0.251	
toluene		22.4		3.61	0.081	
Celite			9.13	56	0.511	
Ethyl acetate			356.9	2.07	0.739	
Water			182	0	0	
MgSO <sub>4</sub>			1.826	48.04	0.088	
n-hexane			398.6	3.44	1.371	
Silicagel			480	21.19	10.171	
<b>N2,N2,N7,N7-tetrakis(4-methoxyphenyl)-9H-carbazole-2,7-diamine</b>	2.0400					
1,3,5-tribromobenze	0.3130			271.79	0.085	
Pd(OAc) <sub>2</sub>	0.0223			27360	0.610	
( <i>tert</i> -Bu) <sub>3</sub> P	0.0402			53053.5	2.133	
sodium <i>tert</i> -butoxide	0.4778			201.44	0.096	
toluene		12.3		3.61	0.044	
Celite			5	56	0.28	
Ethyl acetate			225.5	2.07	0.467	
Water			100	0	0	
n-hexane			196.4	3.44	0.676	
MgSO <sub>4</sub>			1	48.04	0.048	
Silicagel			235.5	21.19	4.990	
<b>total</b>						88.076





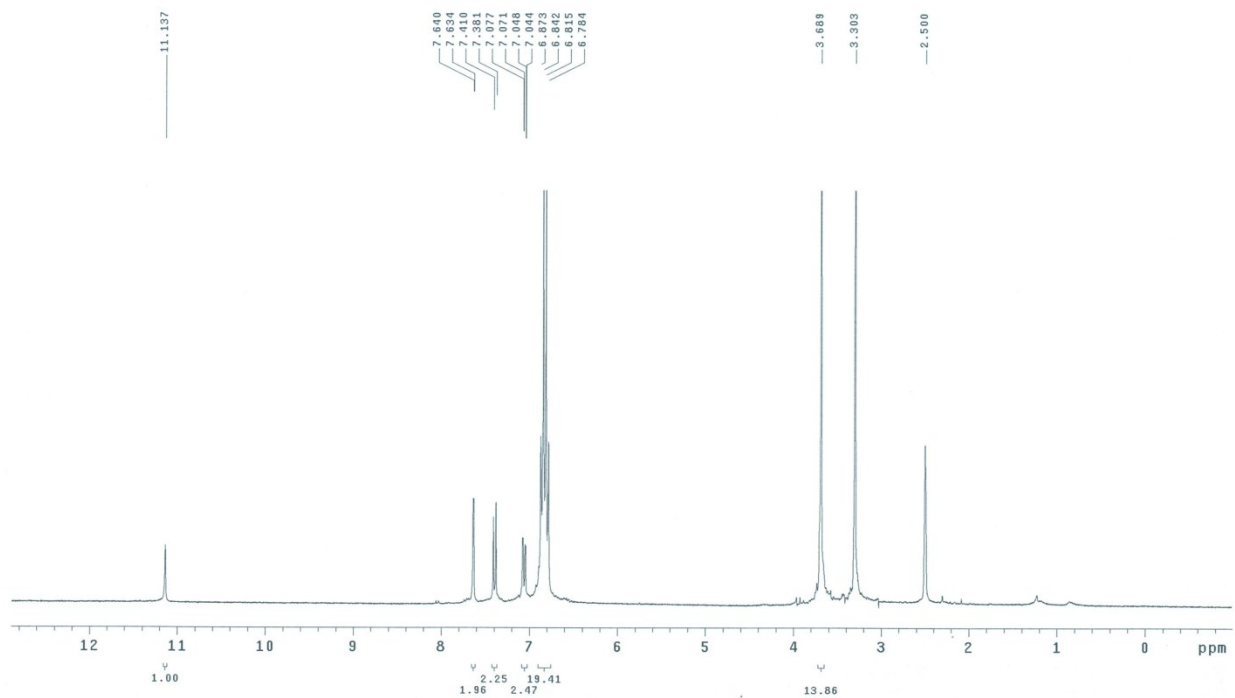


Figure S2.  $^1\text{H}$  NMR of compound **1**.

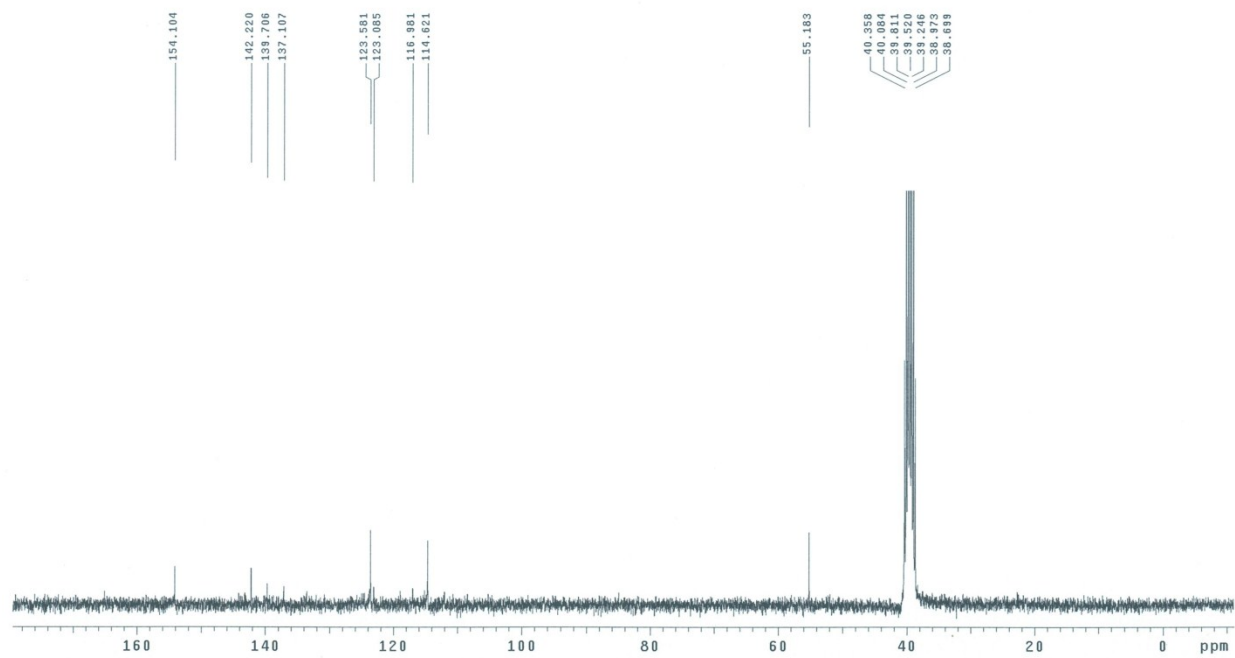


Figure S3.  $^{13}\text{C}$  NMR of compound **1**.

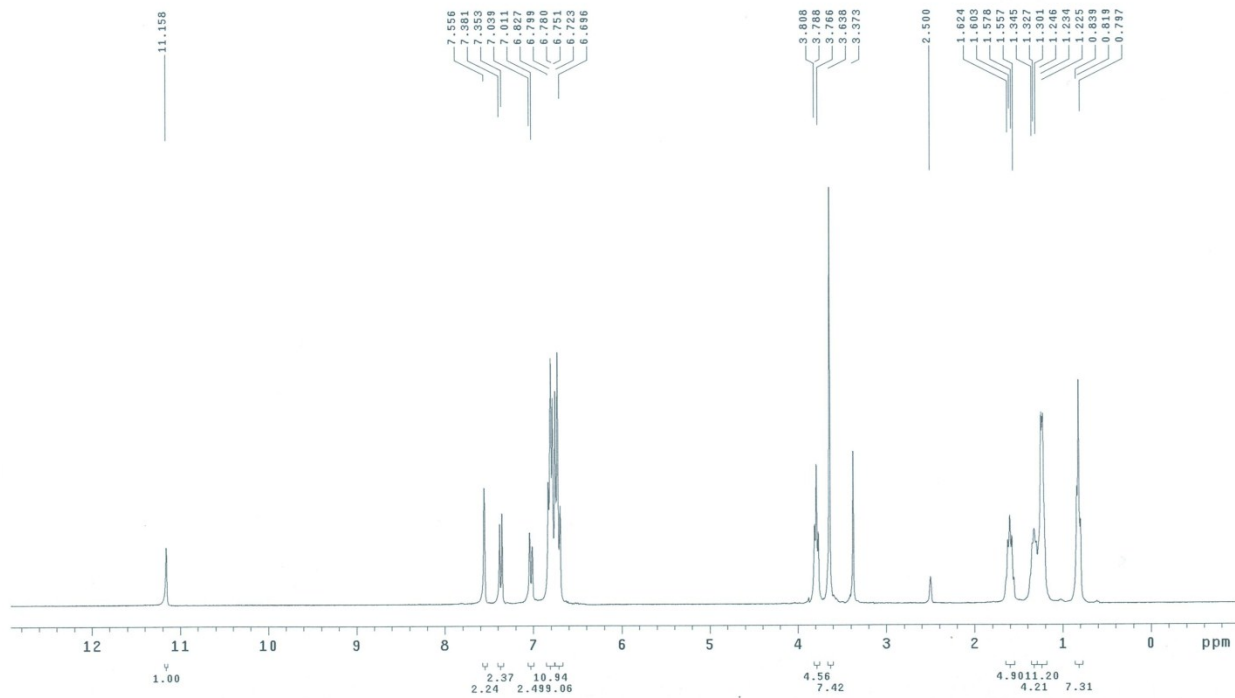


Figure S4.  $^1\text{H}$  NMR of compound 2.

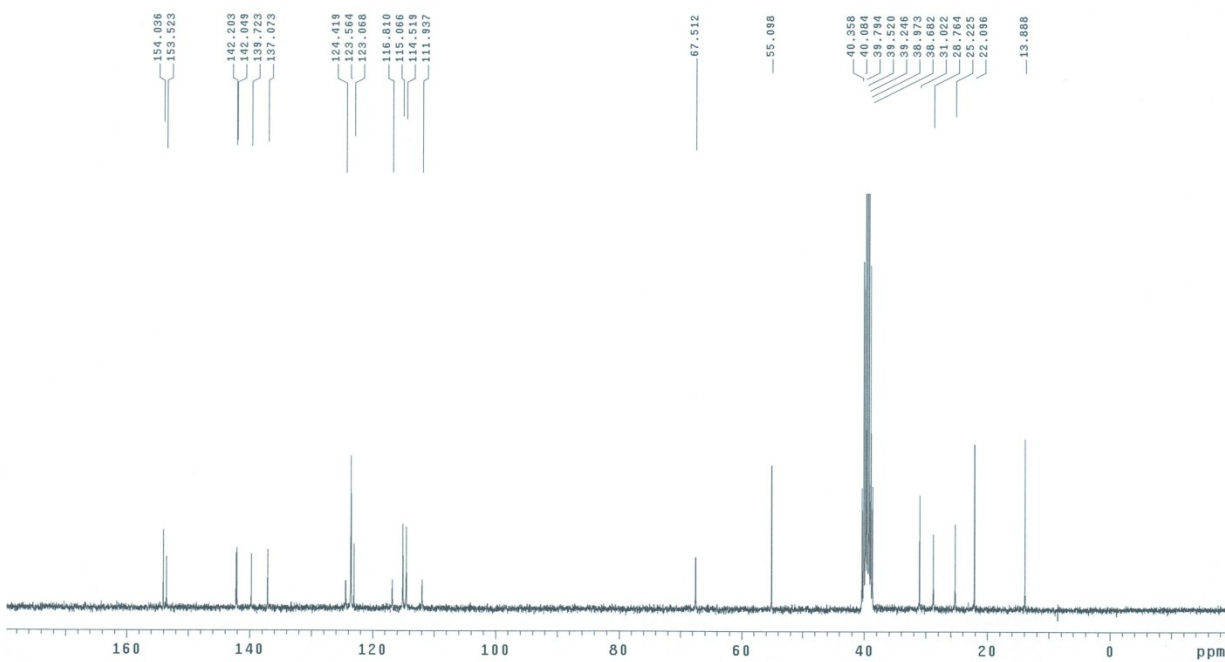


Figure S5.  $^{13}\text{C}$  NMR of compound 2.

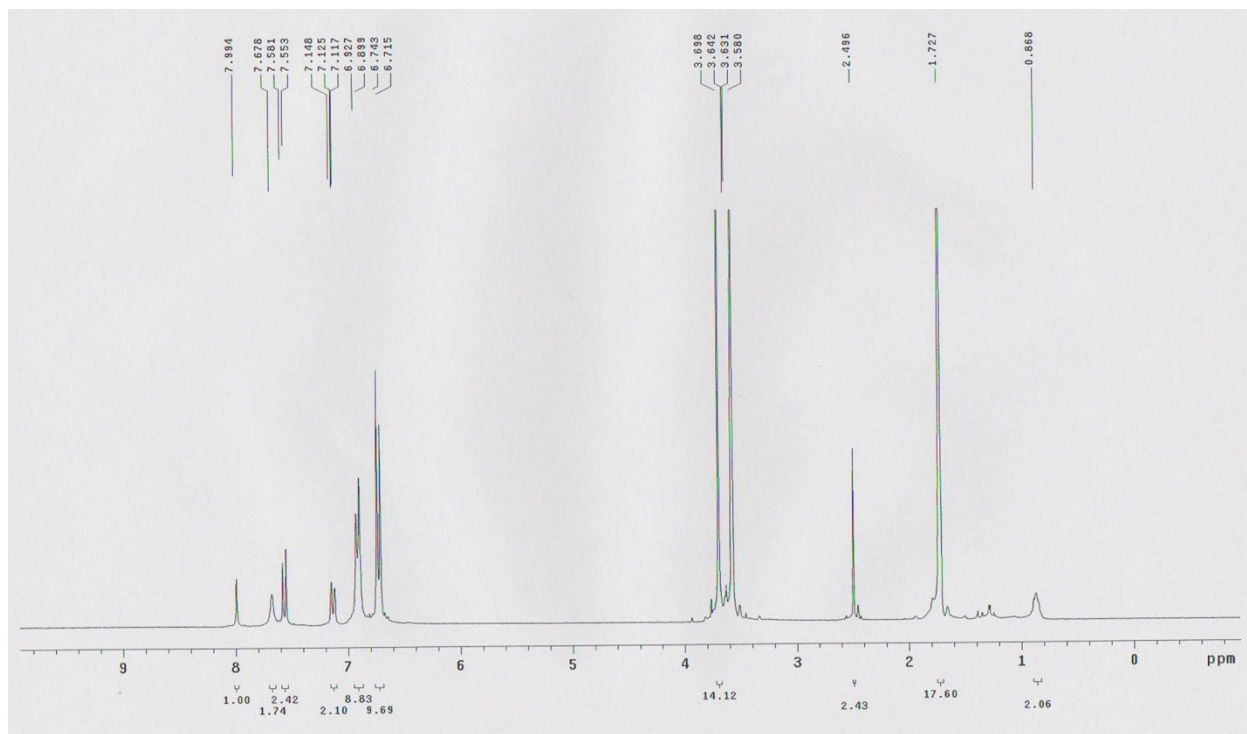


Figure S6.  $^1\text{H}$  NMR of compoundSGT-405(3,6).

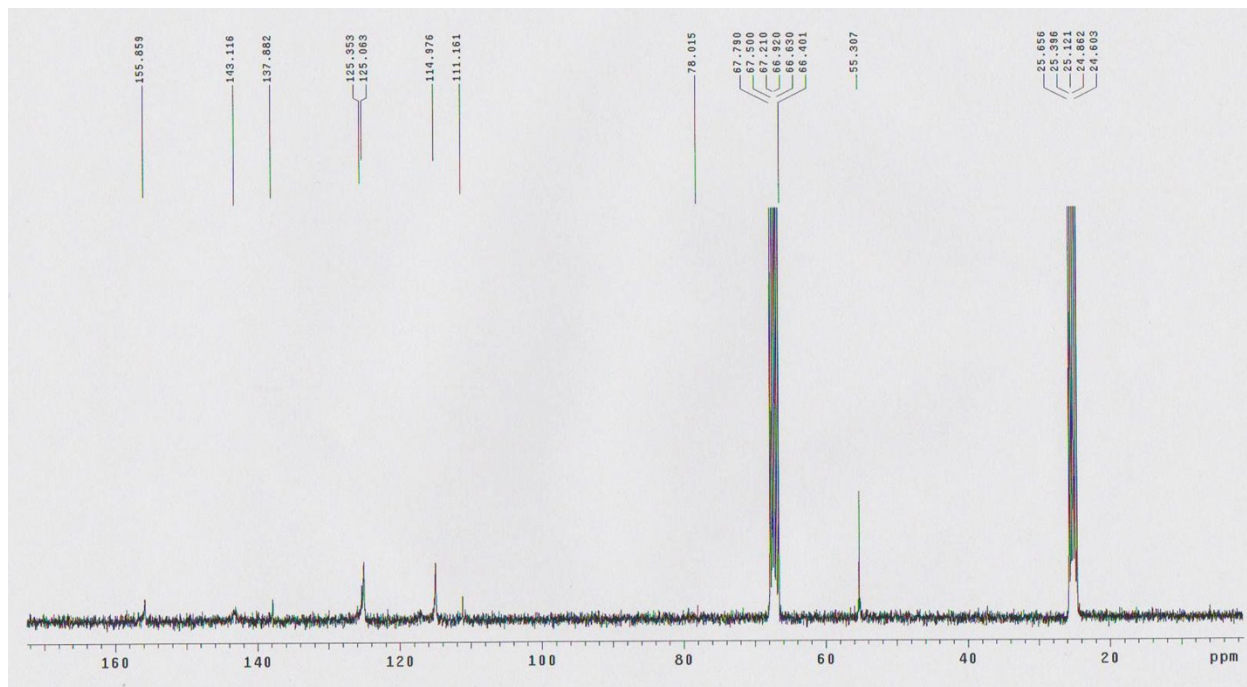
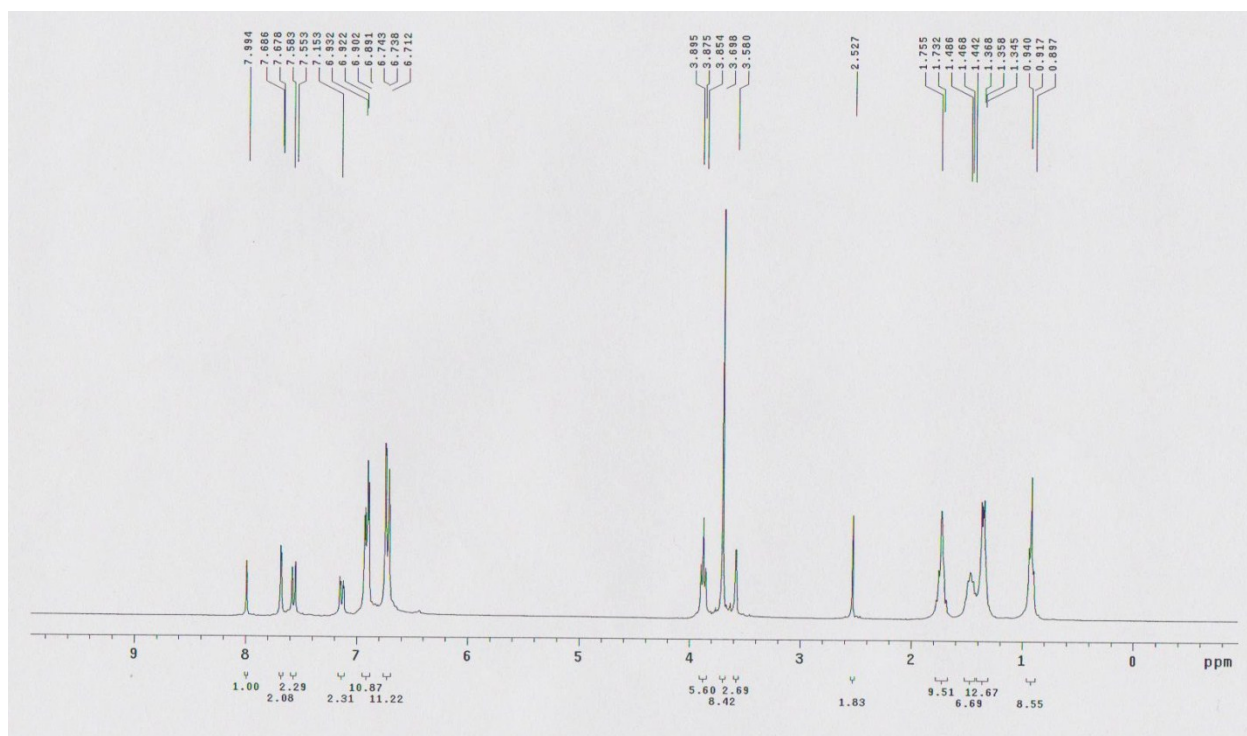
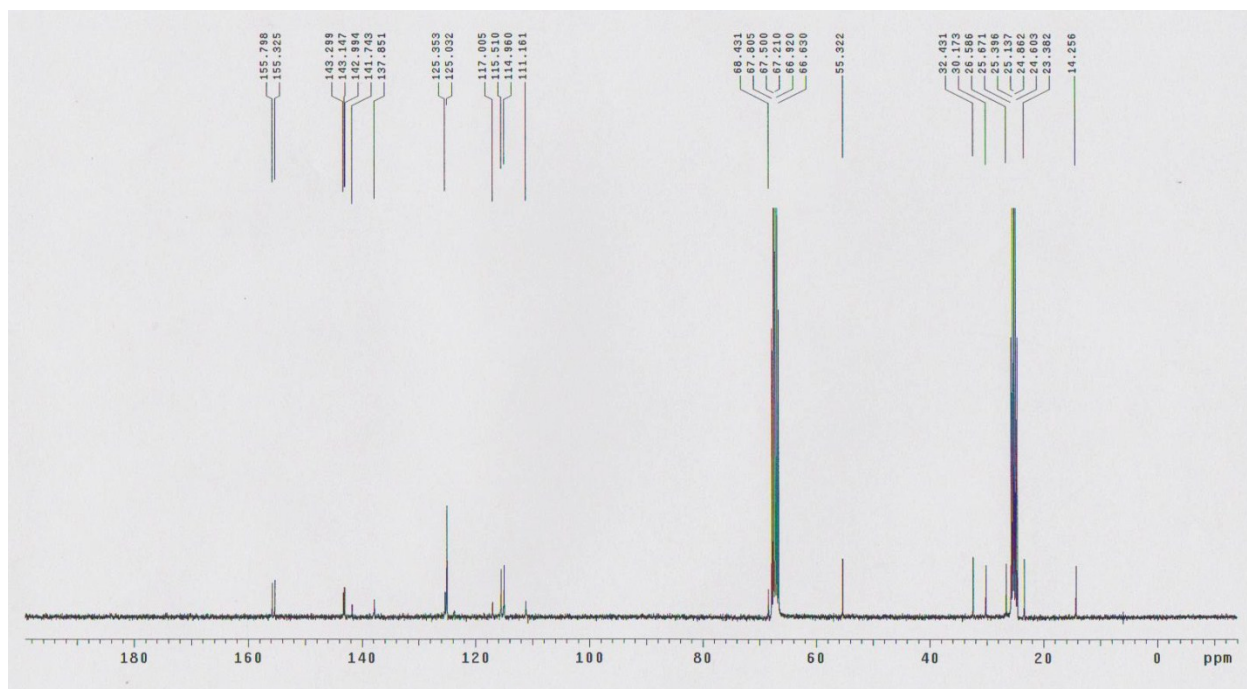


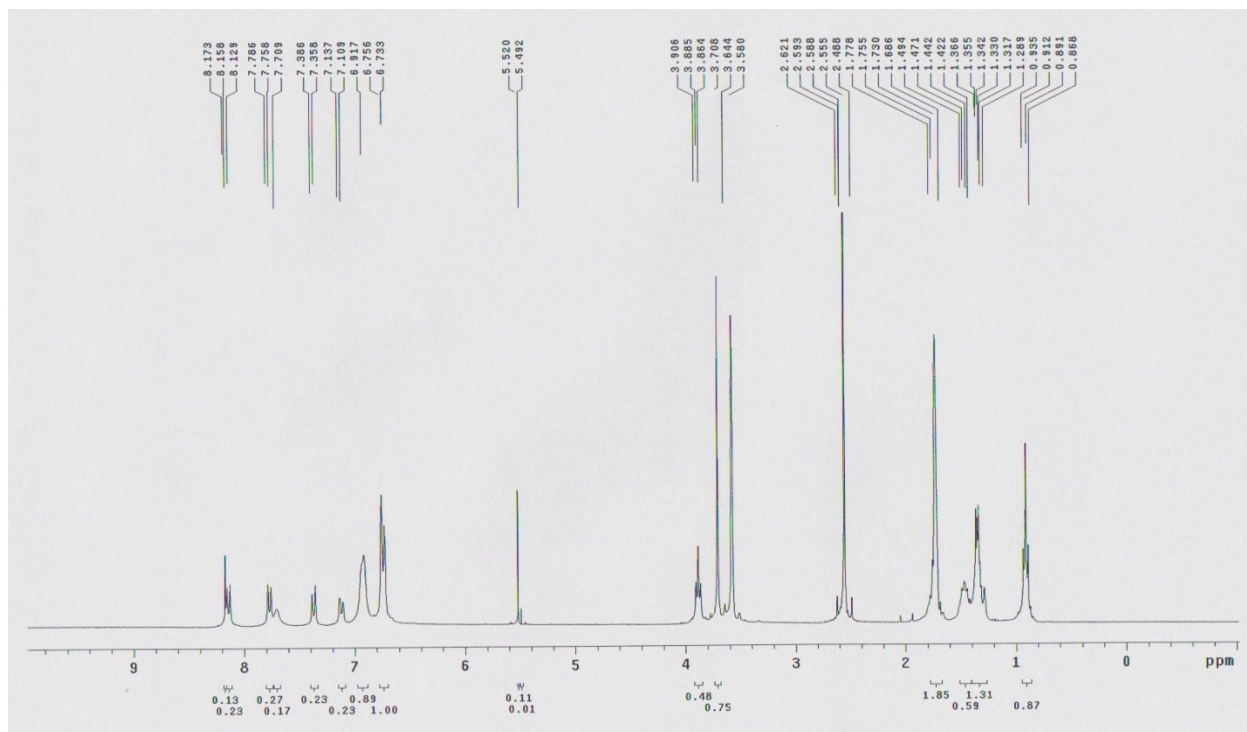
Figure S7.  $^{13}\text{C}$  NMR of compoundSGT-405(3,6).



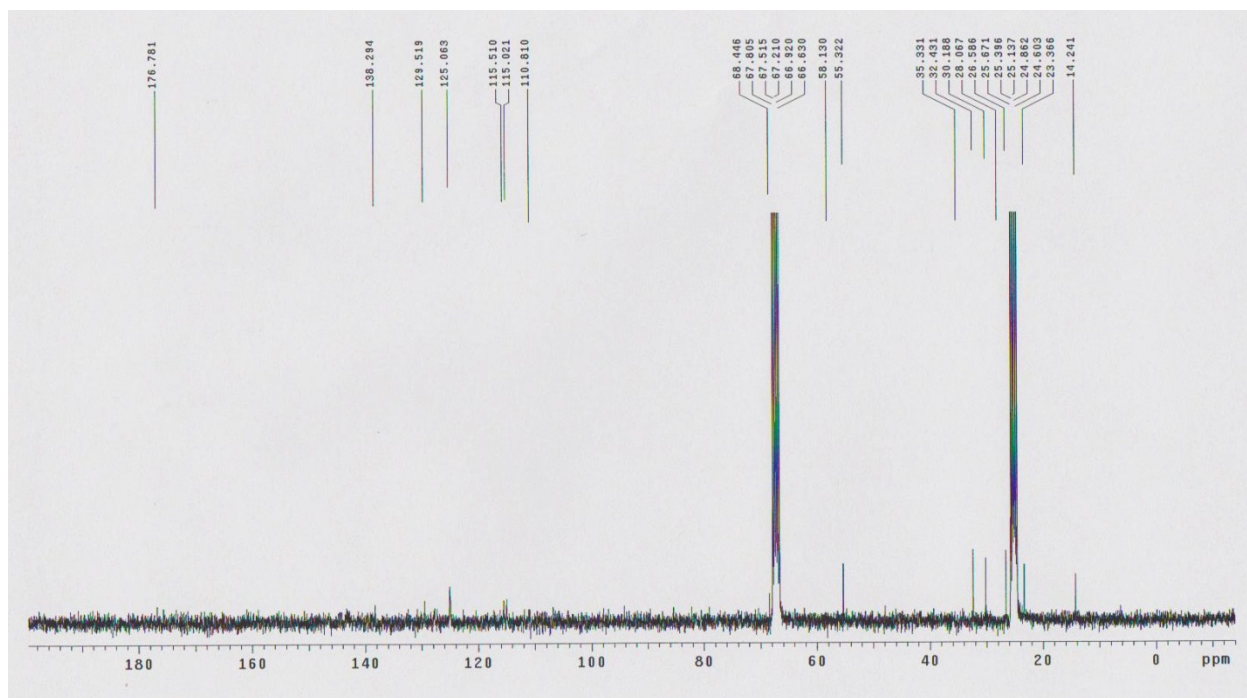
**Figure S8. <sup>1</sup>H NMR of compound SGT-410(3,6).**



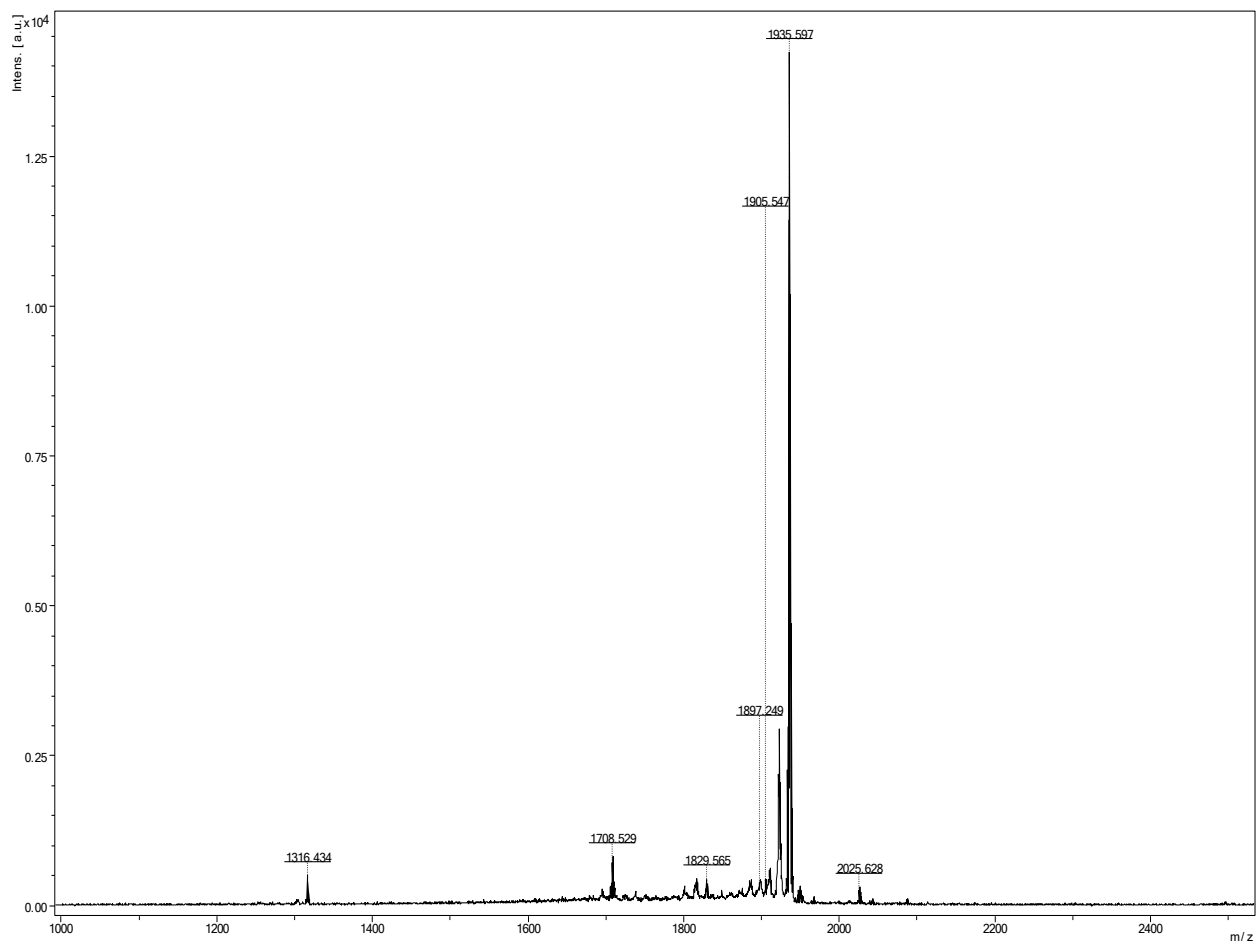
**Figure S9. <sup>13</sup>C NMR of compound SGT-410(3,6).**



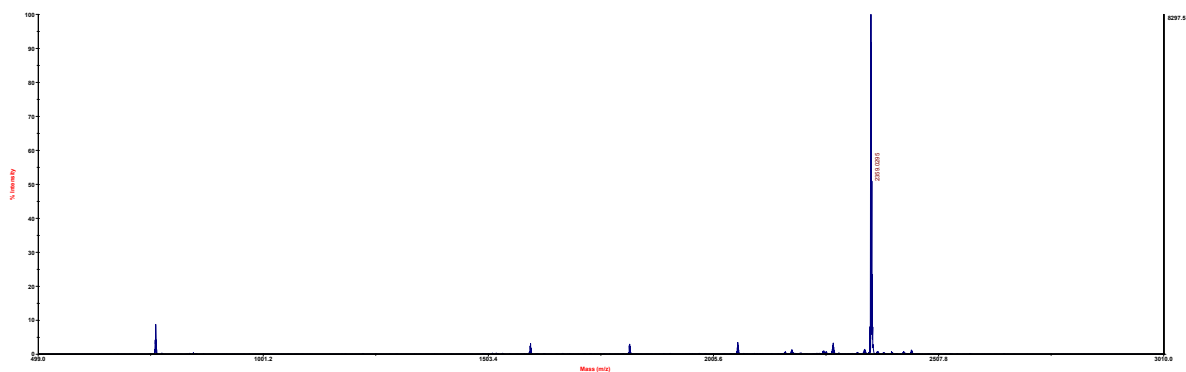
**Figure S10.**  $^1\text{H}$  NMR of compoundSGT-411(3,6).



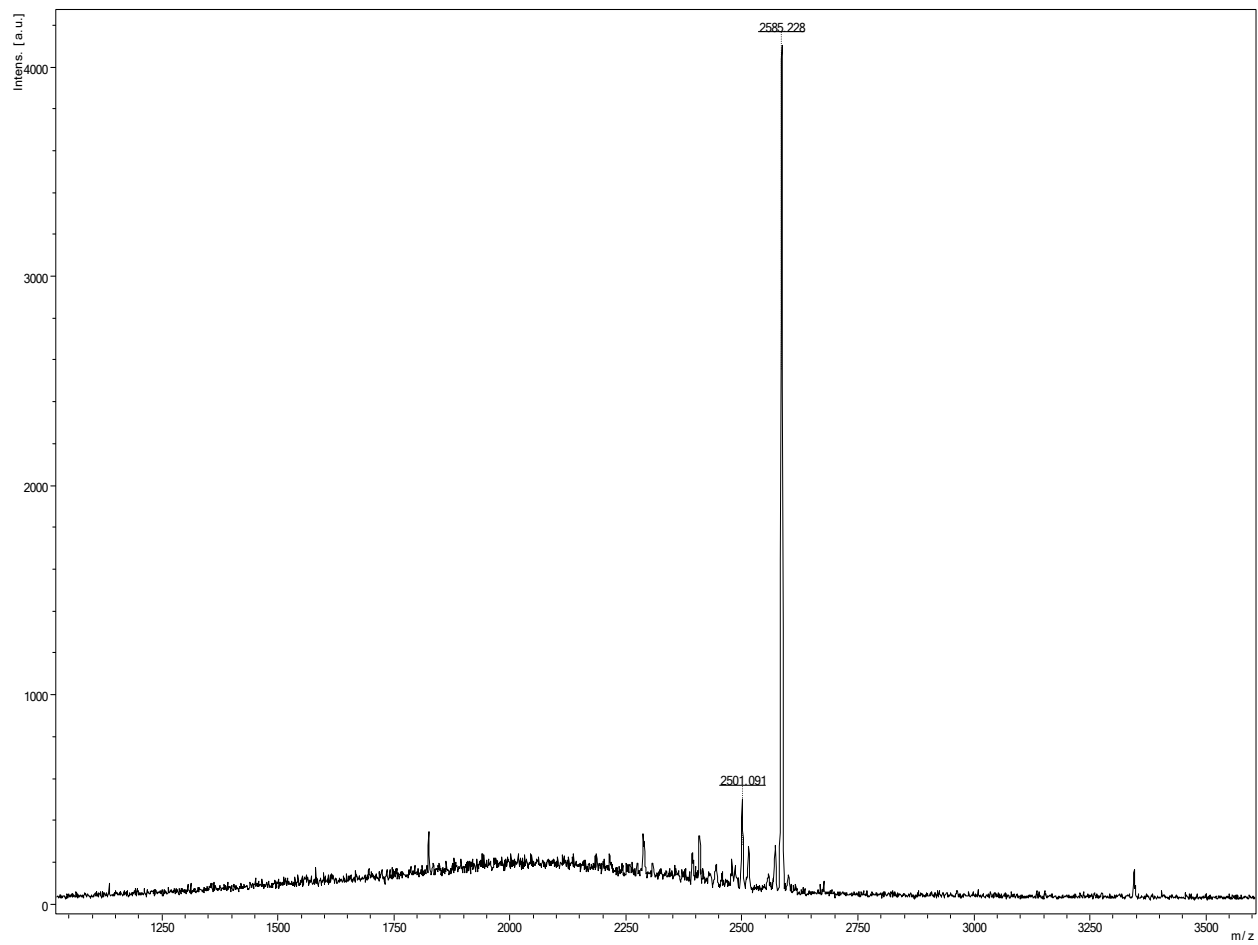
**Figure S11.**  $^{13}\text{C}$  NMR of compoundSGT-411(3,6).



**Figure S12.** MALDI-TOF spectrum of SGT-405(3,6).



**Figure S13.** MALDI-TOF spectrum of SGT-410(3,6).



**Figure S14.** MALDI-TOF spectrum of **SGT-411(3,6)**.

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