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Accessory Publication

Synthesis and properties of the bipolar triphenylamine-benzimidazole derivatives

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Experimental Section

General information: All solvents were carefully dried and freshly distilled according to common laboratory techniques. All reactants were commercially available and used without further purification. Melting points were recorded on Electrothermal digital melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 295 K on a Varian INOVA 400 MHz or a Varian NMR System 300 MHz spectrometer using $CDCl_3$ or d_6-DMSO as solvent and TMS as internal standard. UV-vis spectra were recorded on a UV-1102 spectrometer; Emission spectra were obtained on an Hitachi FL-2500 luminescence spectrometer; Mass spectroscopic (MS) measurements were carried using matrix-assisted laser desorption ionisation–time-of-flight (Voyager-DE STR MALDI TOF) technique. HRMS data were measured using TOF-MS(EI^+) and micrOTOF-Q(ESI) instrument; Thermal properties was performed on a SDT 2960 and a DSC 2010 instruments (scanning rate of 20 °C·min^{-1}).

Tris-(4-formyl-phenyl)amine (**2c**).

Tris-(4-formyl-phenyl)amine was prepared according to literature.[11d] Phosphorus oxychloride (46.6 mL, 0.5 mol) was added dropwise to a stirred 77.4 mL (1 mol) of DMF at 0 °C. The mixture was stirred at 0 °C for 1 h and additionally stirred at room temperature for 1 h. After the addition of 6 g (0.02 mol) of 2b in dichloroethane, the mixture was stirred at 80 °C for 48 h. After cooling, the solution was poured into water. The resulting mixture was neutralized to pH 7 with 5% NaOH aqueous solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column (ethyl acetate/hexane = 1/1) to produce 1.35 g of yellowish solid, 20% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.95 (s, 3H), 7.86 (d, J = 8.7 Hz, 6H), 7.28 (d, J = 8.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.8, 151.4, 132.7, 131.8, 124.8

General procedure for the synthesis of the compounds (**4**,**6**)

Compounds **4**, **6** were synthesized by **2** with **3**, **5** as following procedure: a mixture of **2** (1.00 mmol) and **3**, **5** (1.00 mmol) and CH_3COONH_4 (0.20 mL) in CH_3COOH (5.00 mL) was refluxed for 6-12 h. The resulting mixture were cooled and the precipitates were filtered to afford the crude products, which can be purified by recrystallization in EtOH.

4-(5,6-diphenyl-1*H*-benzimidazol-2-yl)-triphenylamine (**4a**): M.p. 112 °C. yield 88%, yellow. ^{1}H NMR(400 MHz, DMSO-d_6): δ 12.54 (s, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.32-7.52 (m, 14H), 7.03-7.10 (m, 8H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 148.2, 147.8, 146.4, 130.5, 129.3, 127.3, 125.3, 125.2, 124.3, 123.6;

HRMS [Found: m/z 463.2050 (M+), Calcd for $C_{33}H_{25}N_3$: M, 463.2048].

4,4'-di(5,6-diphenyl-1*H*-benzimidazol-2-yl)-triphenylamine (**4b**): M.p. 196 °C. yield 86%, yellow. ^{1}H NMR(400 MHz, DMSO-d_6): δ 12.58 (s, 2H), 8.04 (d, J = 8.4 Hz, 4H), 7.54 (d, J = 7.2 Hz, 8H), 7.36-7.41 (m, 14H), 7.14 (t, J = 8.0 Hz, 7H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 146.3, 146.0, 144.8, 129.2, 127.8, 125.9, 124.3, 124.1, 122.8;

HRMS [Found: m/z 681.2885 (M+), Calcd for $C_{48}H_{35}N_5$: M, 681.2892].

4,4',4''-tris(5,6-diphenyl-1*H*-benzimidazol-2-yl)-triphenylamine (**4c**): M.p. 228 °C. yield 84%, yellow. ^{1}H NMR(400 MHz, DMSO-d_6): δ 12.78 (s, 3H), 8.09 (d, J = 8.8 Hz, 6H), 7.54 (d, J = 7.6 Hz, 12H), 7.20-7.39 (m, 24H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 149.5, 148.1, 131.3, 130.6, 130.1, 129.6, 127.9, 126.8;

HRMS [Found: m/z 900.4 (M+H), Calcd for $C_{63}H_{45}N_7$: M, 899.4].

4-(5-(3,4-dimethoxyphenyl)-6-(2-chloro-phenyl)-1*H*-benzimidazol-2-yl)-triphenyl amine (6a): M.p. 130 °C. yield 80%, yellow. ^{1}H NMR(300 MHz, DMSO-d_6): δ 12.62 (s, 1H), 7.96 (d, J = 8.8 Hz, 2H), 7.39-7.50 (m, 4H), 7.34 (t, J = 7.6 Hz, 4H), 7.20 (d, J = 8.4 Hz, 1H), 7.04-7.08 (m, 8H), 6.87-6.95 (m, 2H), 3.72 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 148.3, 147.2, 146.8, 144.9, 132.8, 132.7, 129.8, 129.5, 126.2, 125.3, 124.4, 124.1, 123.2, 122.7, 118.1, 111.8, 109.7, 55.4, 54.9;

HRMS [Found: m/z 559.1860 (M+), Calcd for $C_{35}H_{29}N_3O_2$: M, 559.1841].

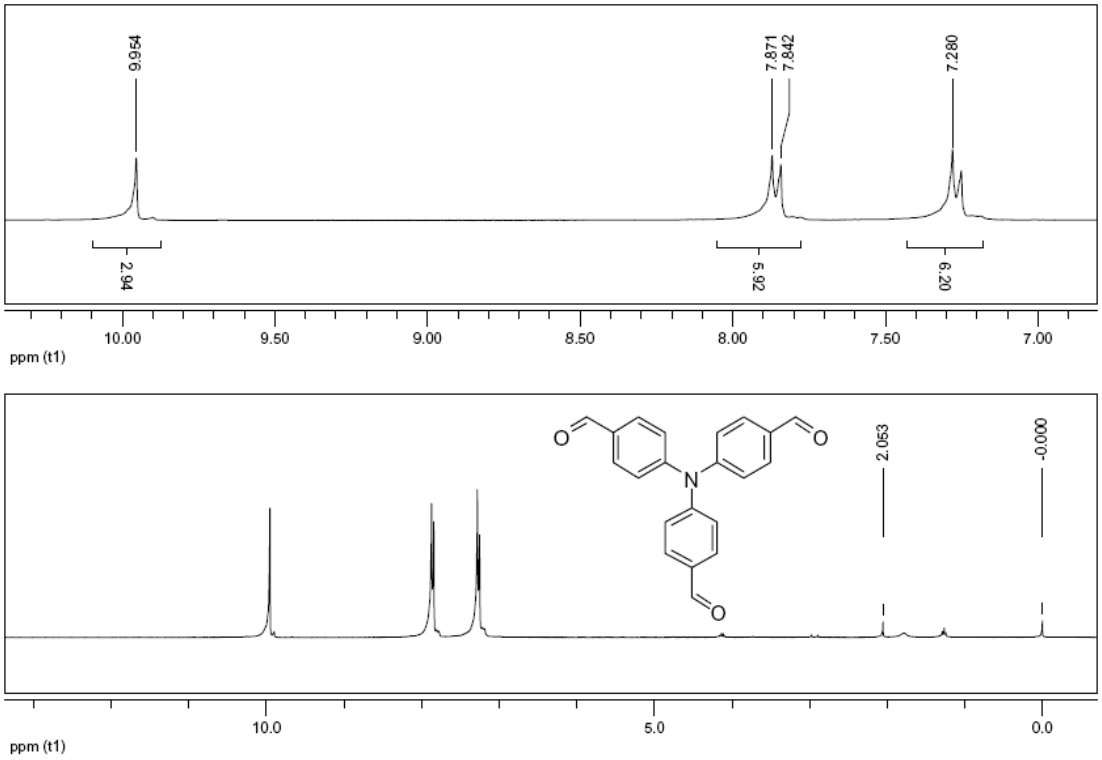
4,4'-di(5-(3,4-dimethoxyphenyl)-6-(2-chloro-phenyl)-1*H*-benzimidazol-2-yl)-triphenylamine (6b): M.p. 200 °C. yield 86%, yellow. ^{1}H NMR(400 MHz, DMSO-d_6) δ 12.67 (s, 2H), 8.01 (d, J = 8.4 Hz, 3H), 7.36-7.62 (m, 10H), 6.88-7.15 (m, 14H), 3.72 (s, 6H), 3.54 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 148.3, 147.5, 146.8, 144.8, 133.7, 132.8, 129.6, 129.5, 127.2, 126.4, 124.8, 124.5, 123.3, 118.1, 111.7, 109.6, 55.4, 54.9;

HRMS [Found: m/z 870.2616 (M+H), Calcd for $C_{52}H_{43}N_5O_4$: M, 869.2536].

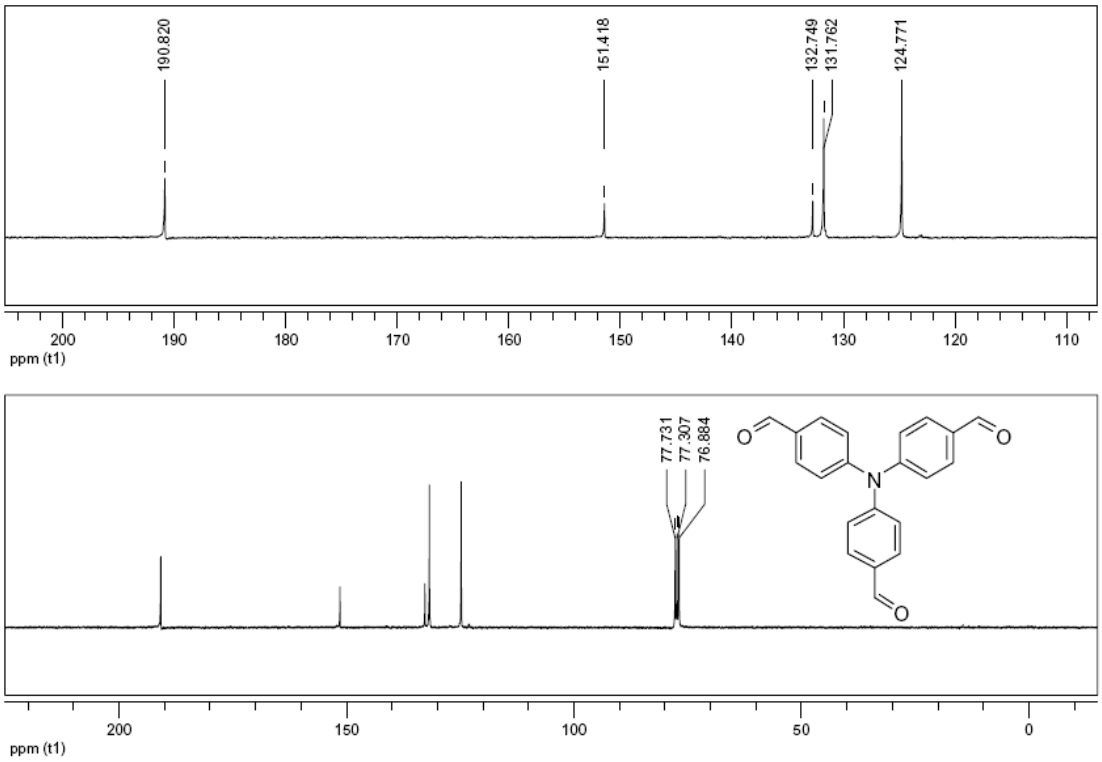
4,4',4''-tri(5-(3,4-dimethoxyphenyl)-6-(2-chloro-phenyl)-1*H*-ben-zimidazol-2-yl)-triphenylamine (6c): M.p. 219 °C. yield 85%, yellow. ^{1}H NMR(400 MHz, DMSO-d_6): δ 12.71 (s, 2H), 12.52 (s, 1H), 8.03-8.11(m, 5H), 7.52-7.66 (m, 13H), 6.89-7.21 (m, 13H), 3.72 (s, 9H), 3.54 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 148.3, 147.6, 146.5, 144.8, 133.8, 132.9, 129.6, 127.3, 126.6, 126.5, 125.2, 123.8, 118.1, 118.1, 118.0, 111.7, 109.6, 55.4, 54.9;

HRMS [Found: m/z 1183.3 (M+), Calcd for $C_{69}H_{57}N_7O_6$: M, 1181.3].

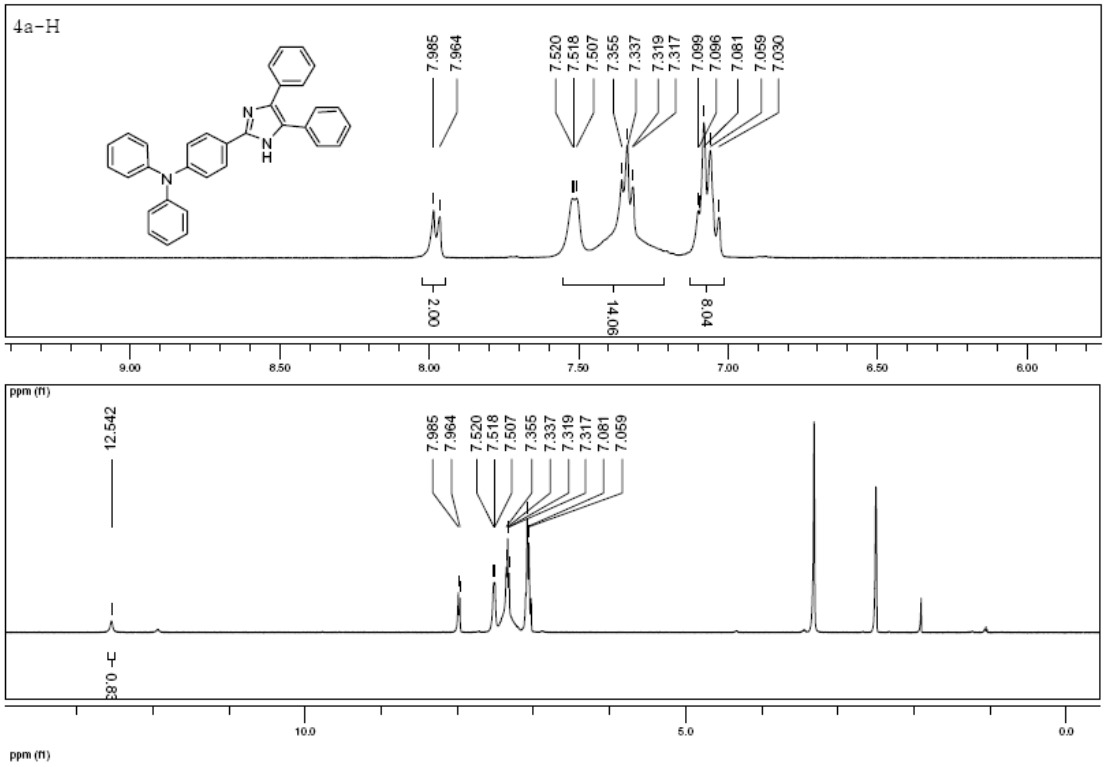
NMR spectrum and MS spectrum of all new compounds:



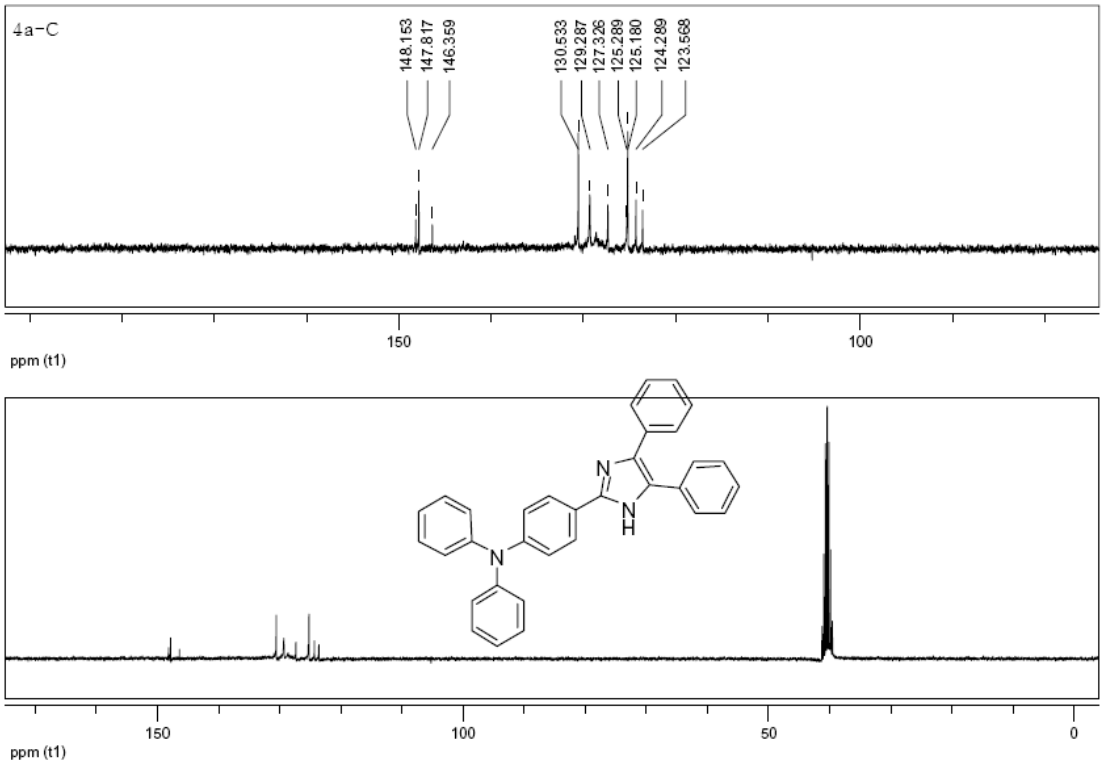
^{1}H NMR spectrum of compound **2c**



^{13}C NMR spectrum of compound **2c**



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



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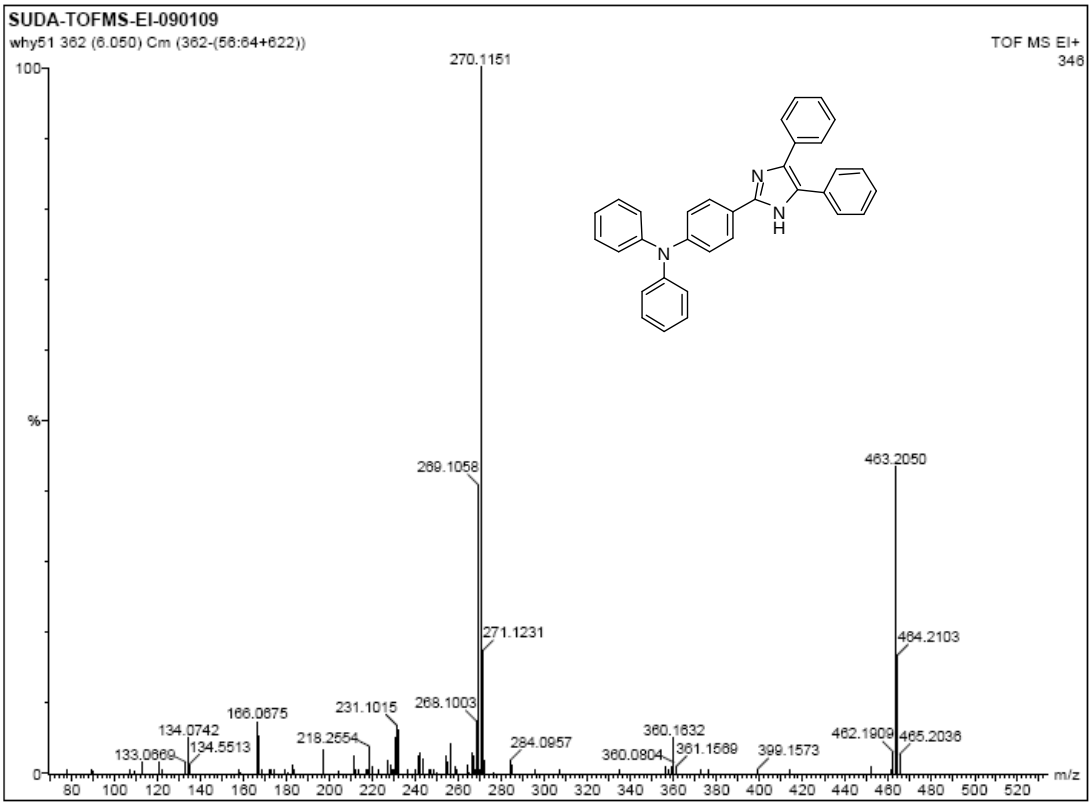
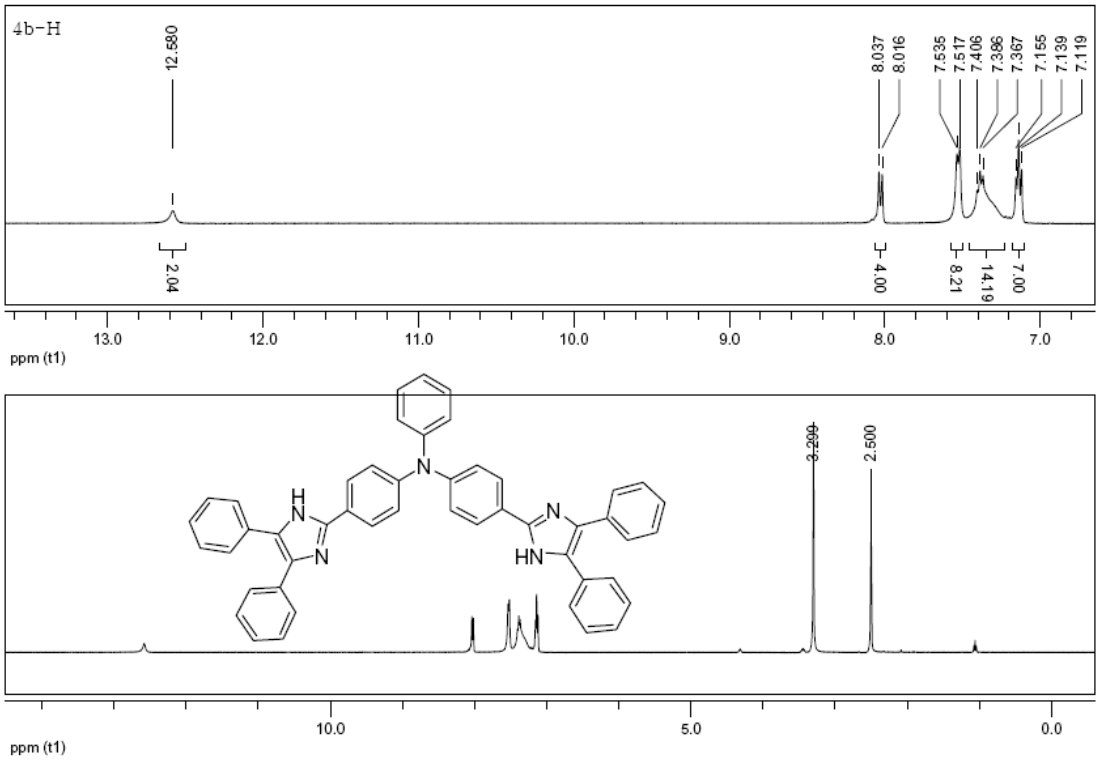
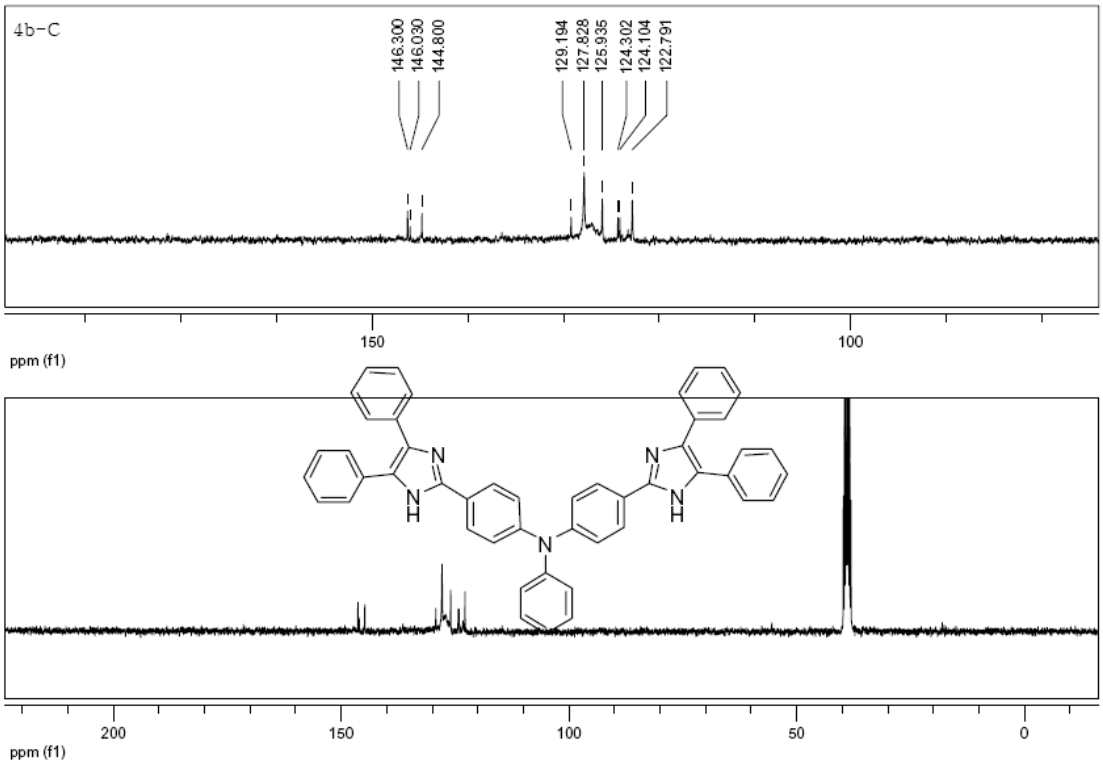


mass spectrum of compound **4a**.



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



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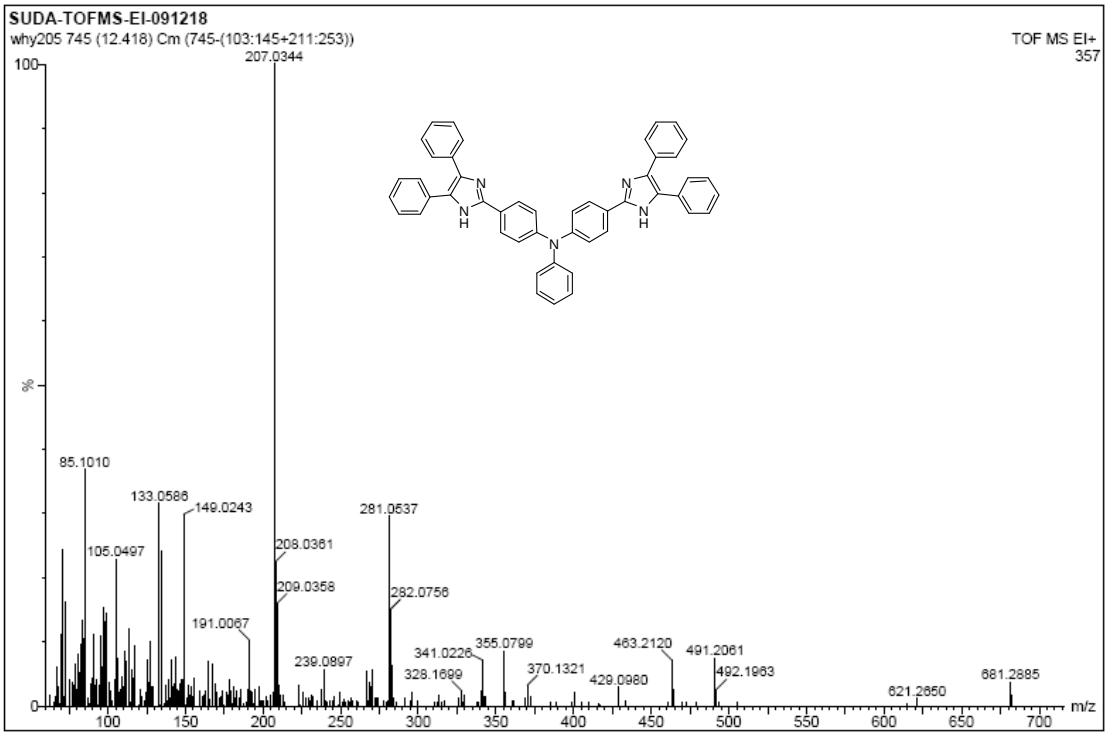

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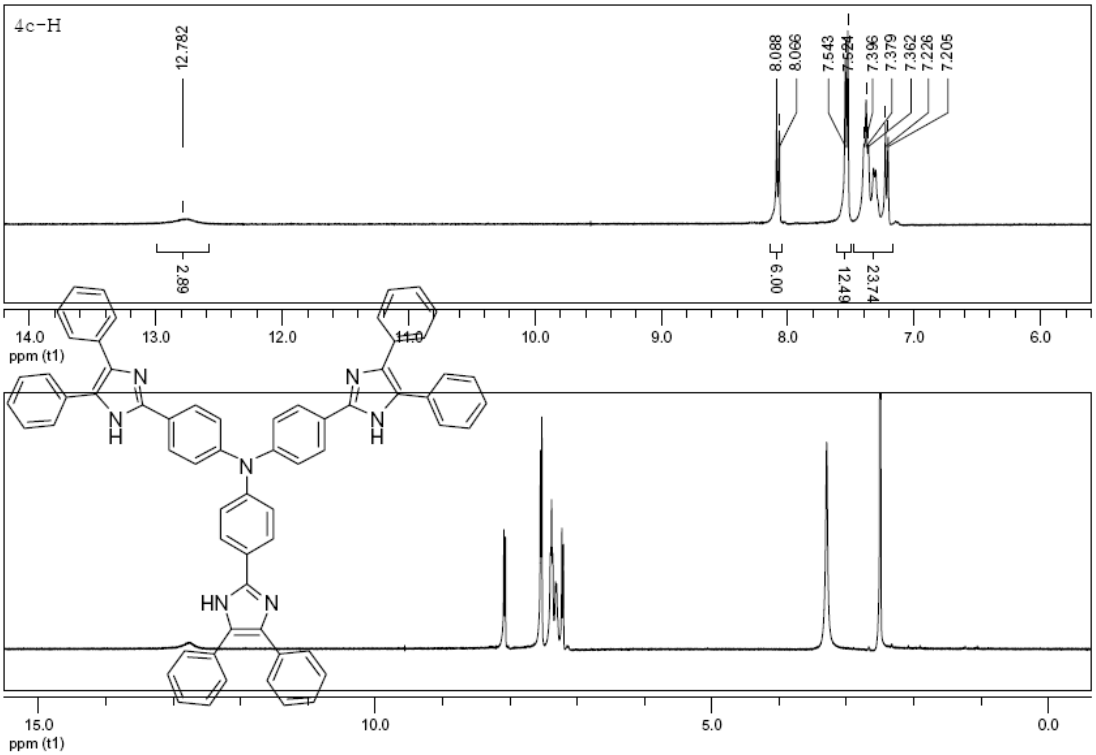

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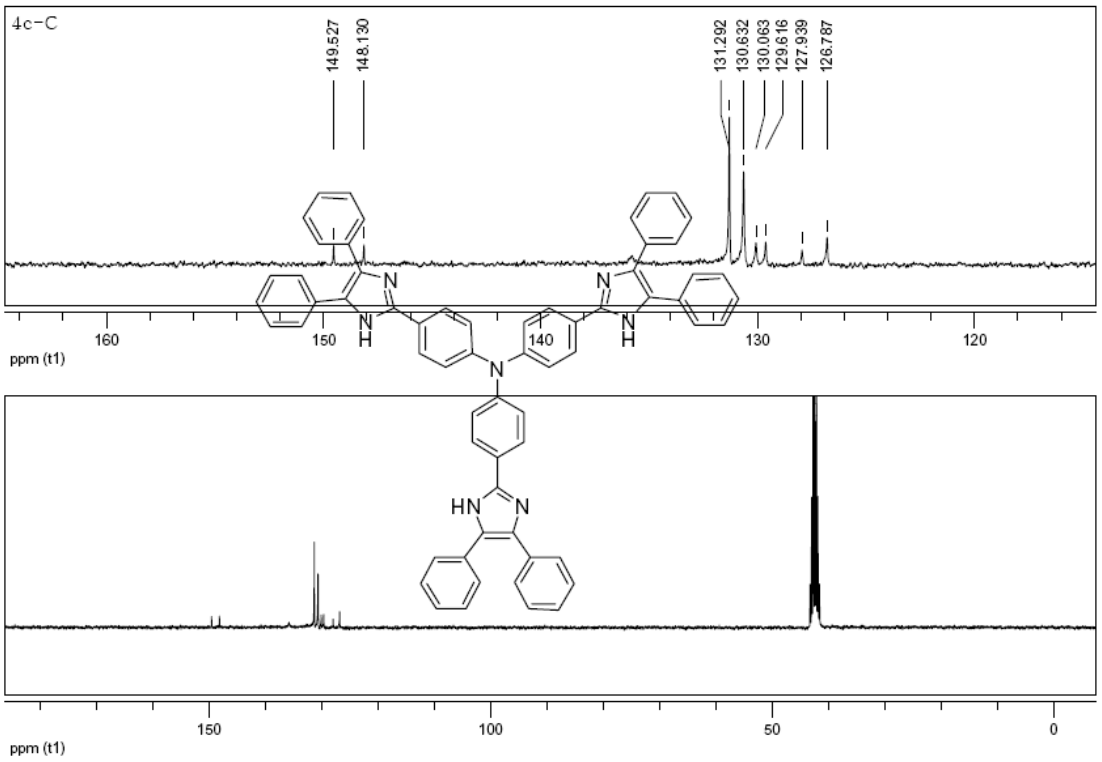

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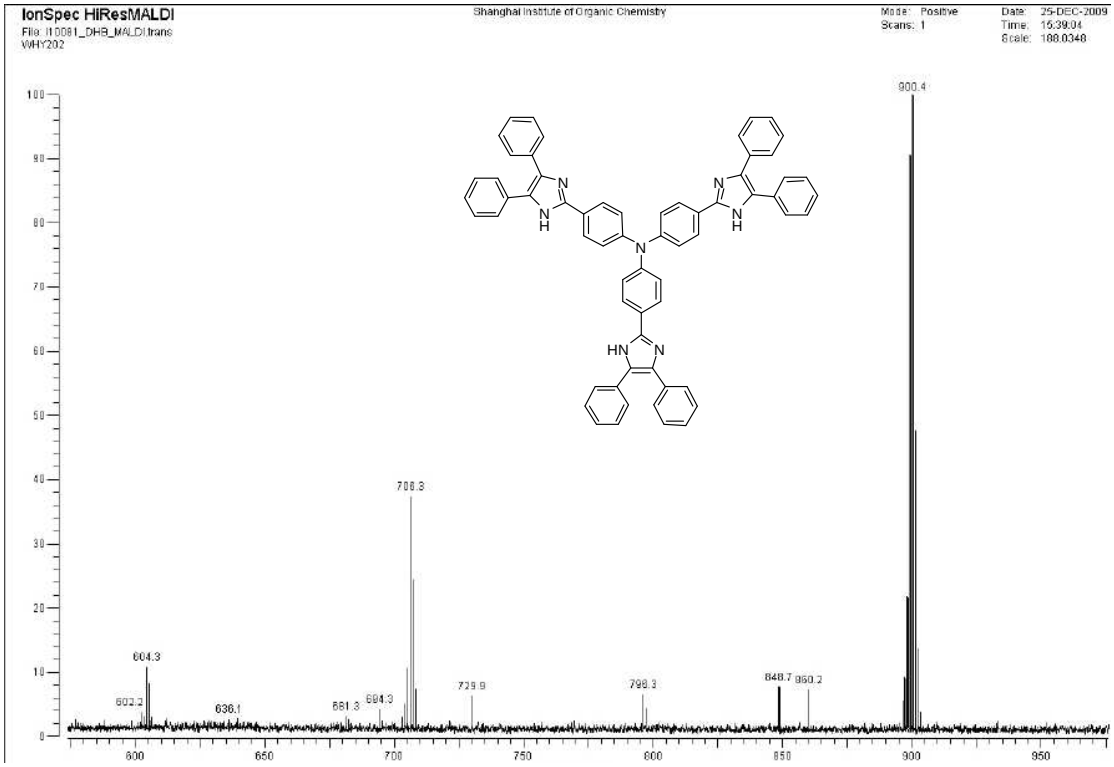

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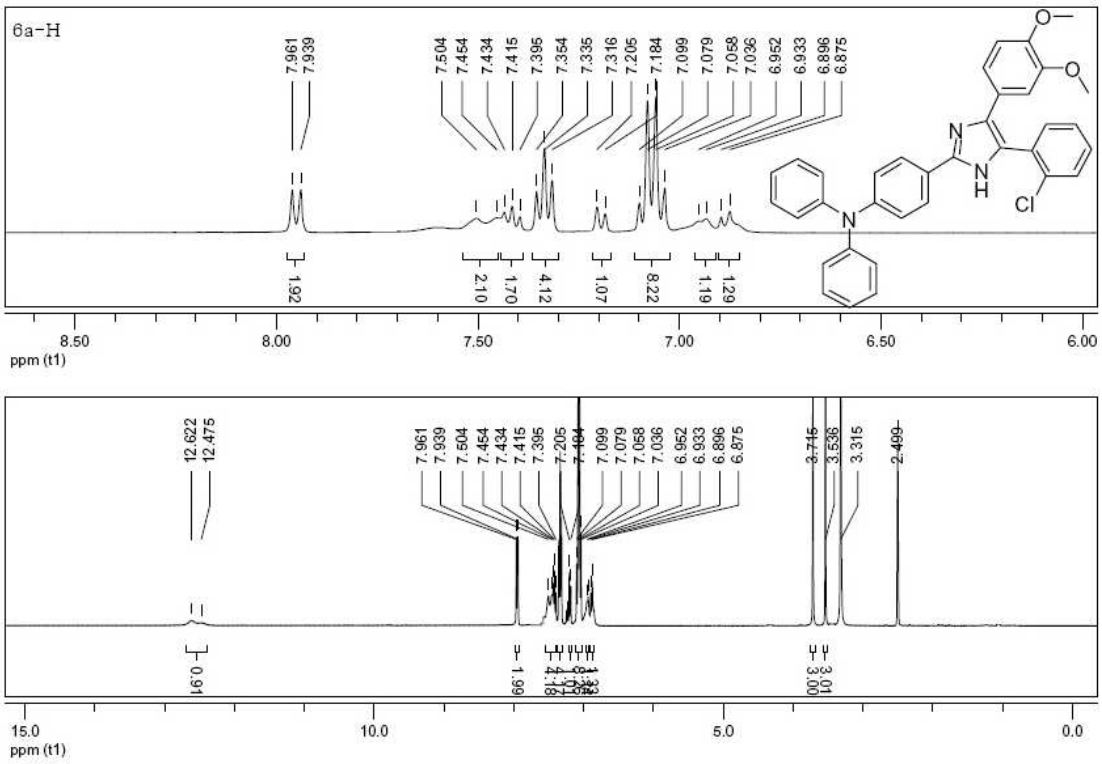
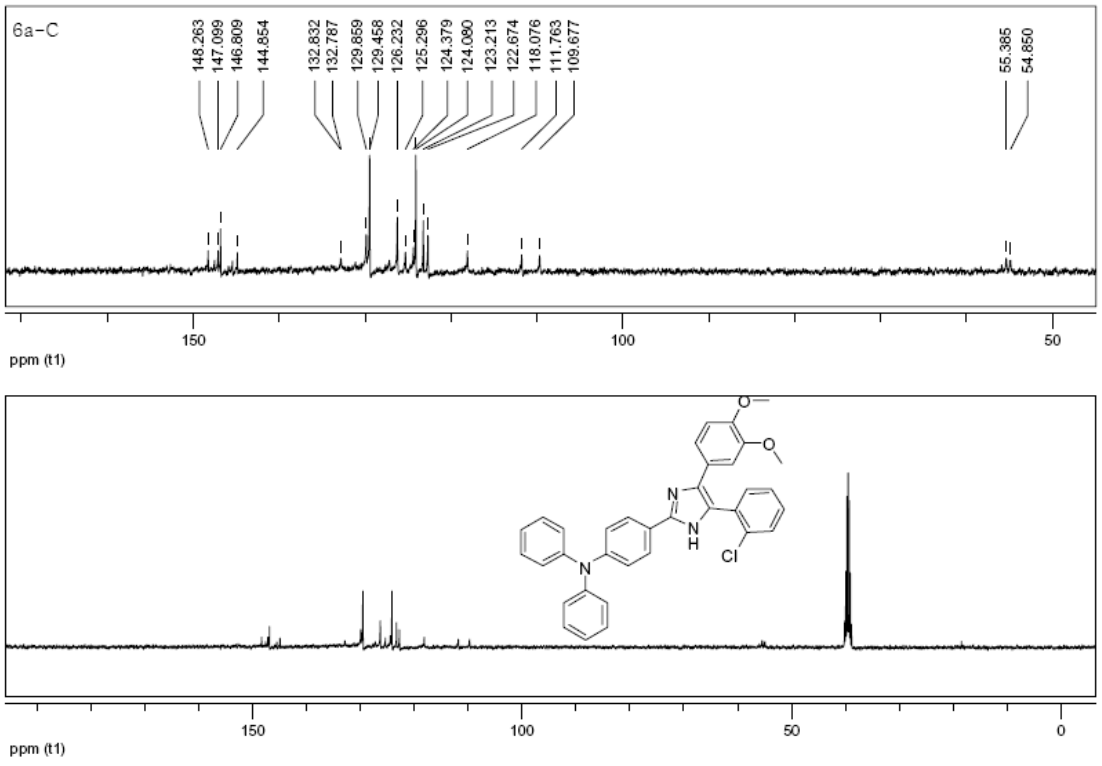
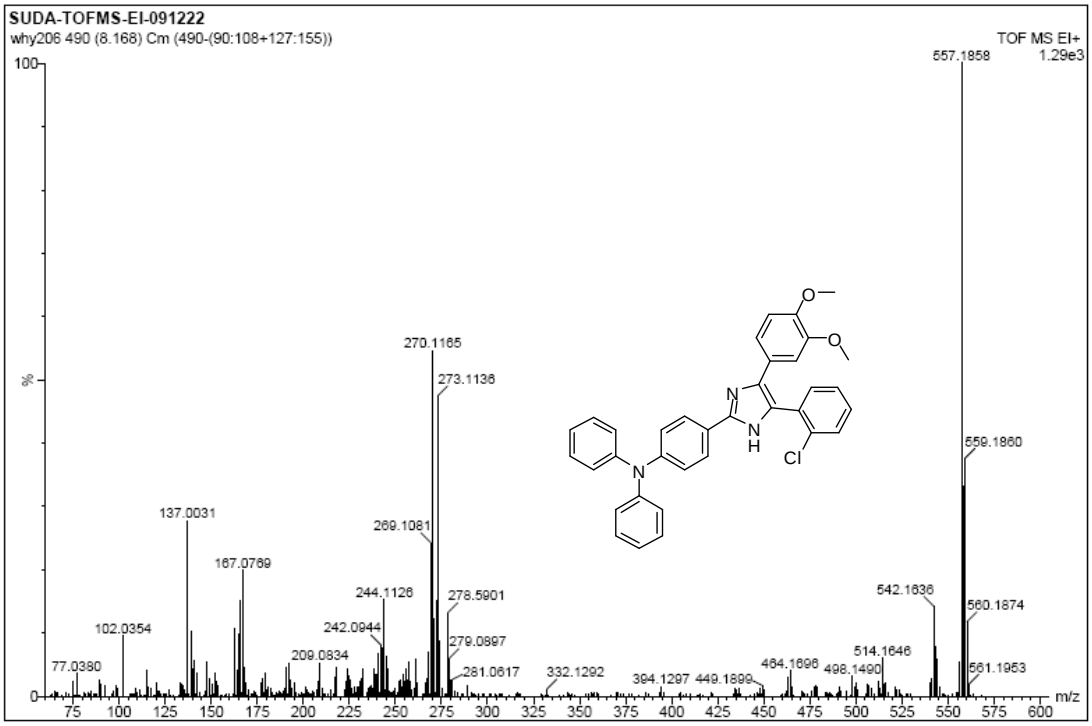


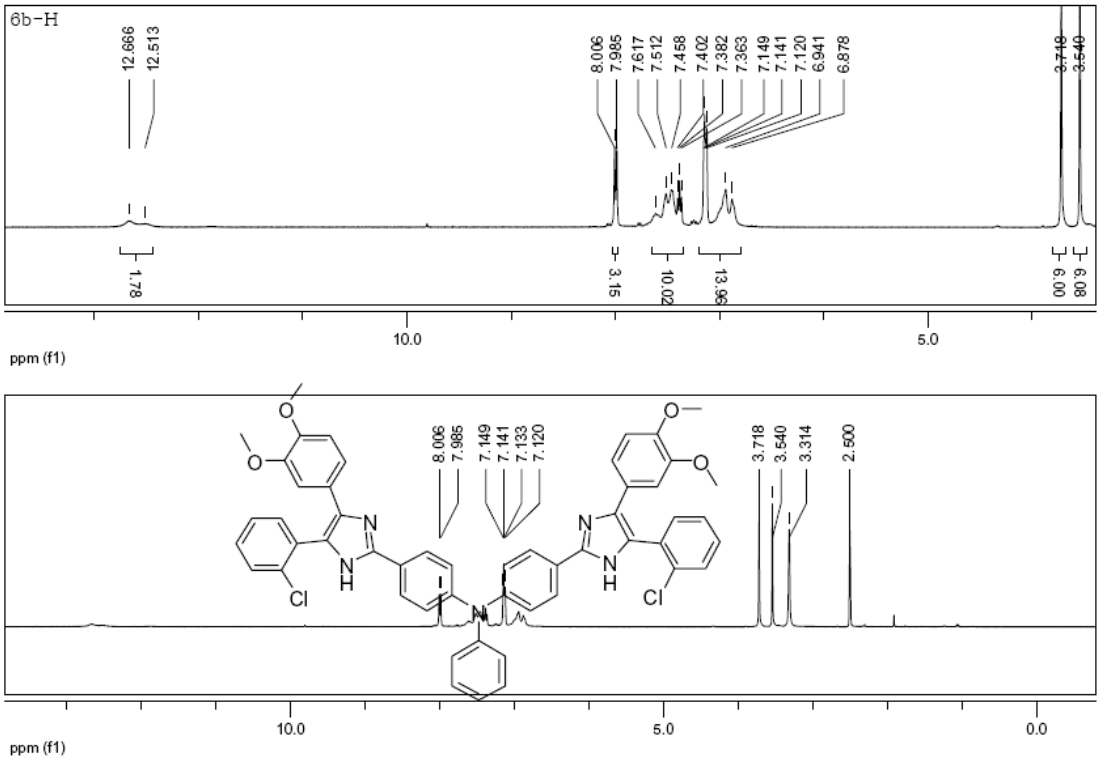
^{1}H NMR spectrum of compound **6a**



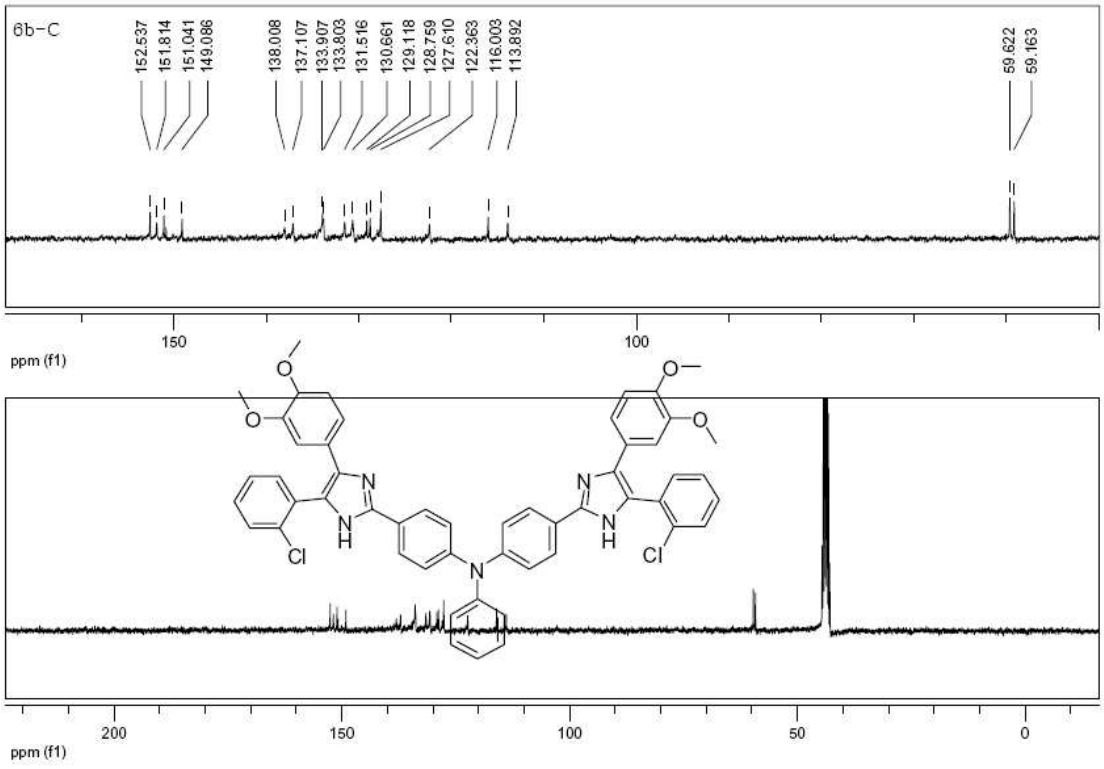
^{13}C NMR spectrum of compound **6a**



mass spectrum of compound **6a**



^{1}H NMR spectrum of compound **6b**



^{13}C NMR spectrum of compound **6b**

Display Report

Analysis Info

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Method	tune_wide.m		
Sample Name	MILKMC-2	Operator	XZNU
Comment		Instrument	micrOTOF-Q 134

Acquisition Parameter

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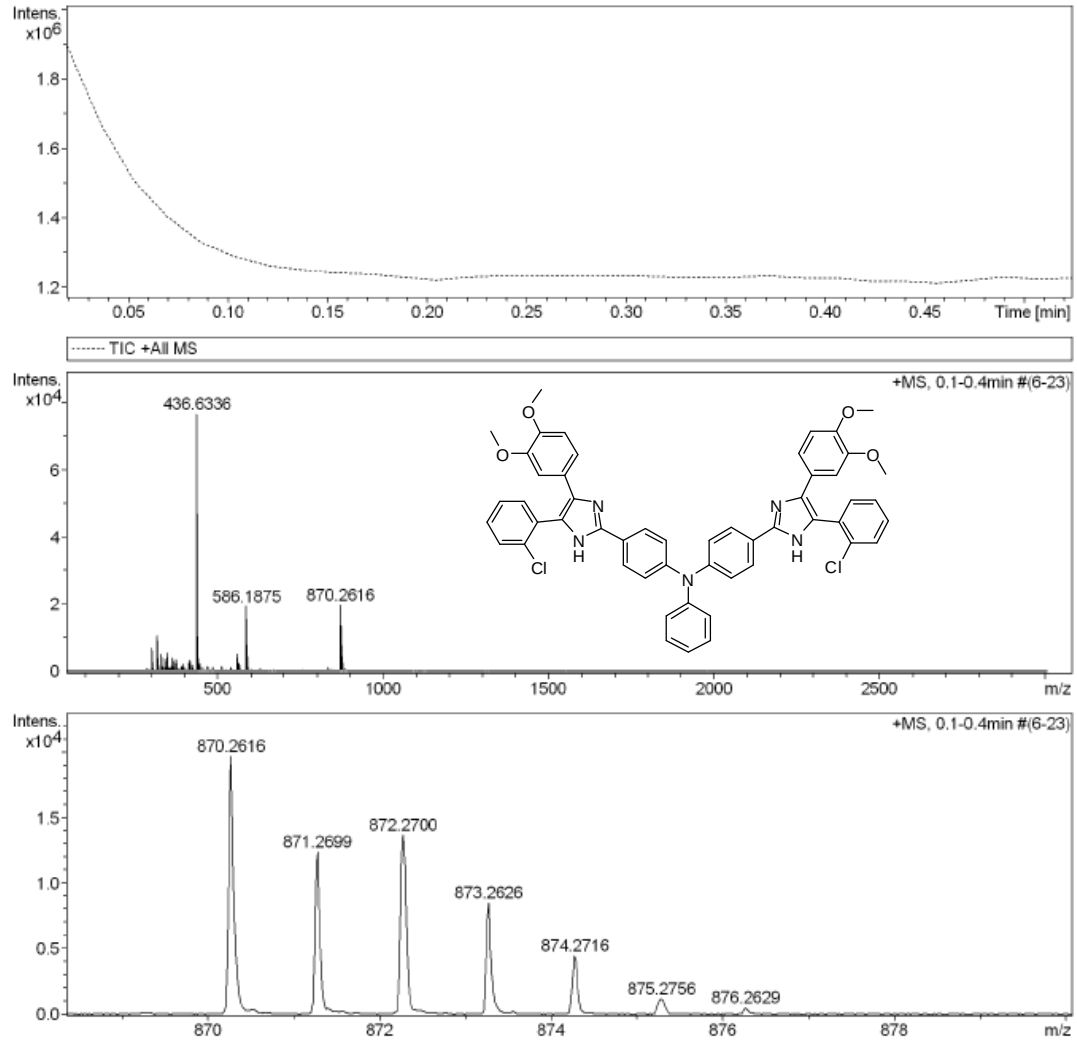
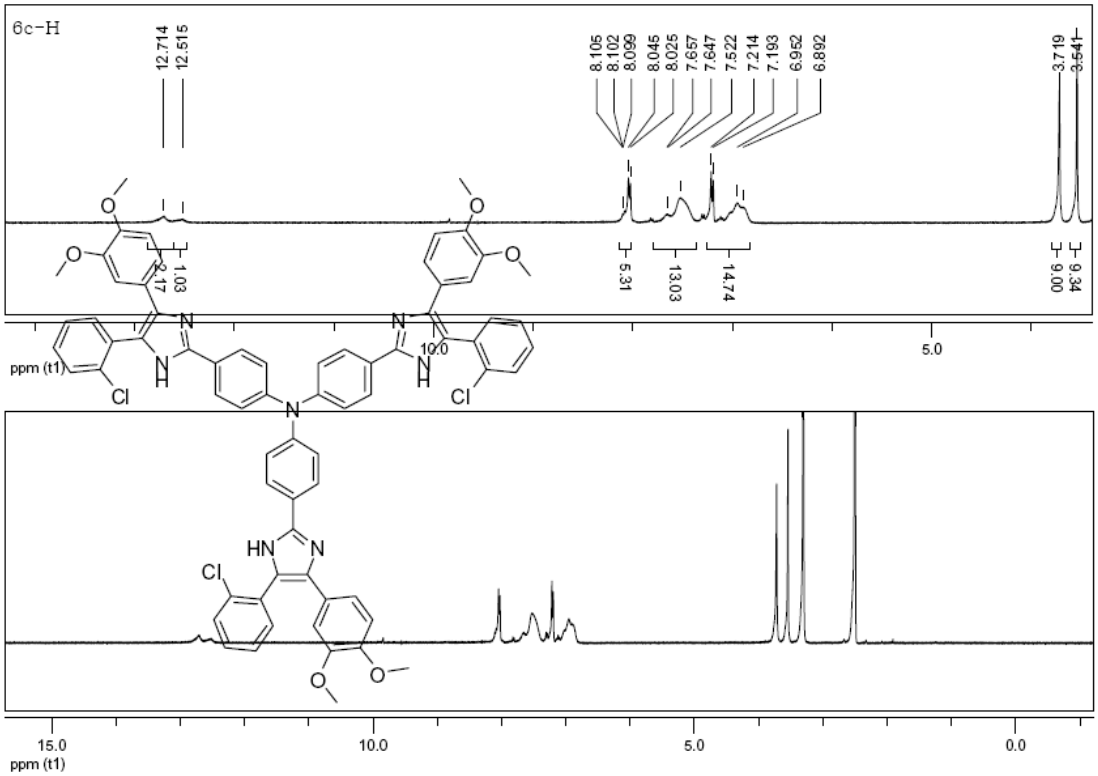
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste



mass spectrum of compound **6b**



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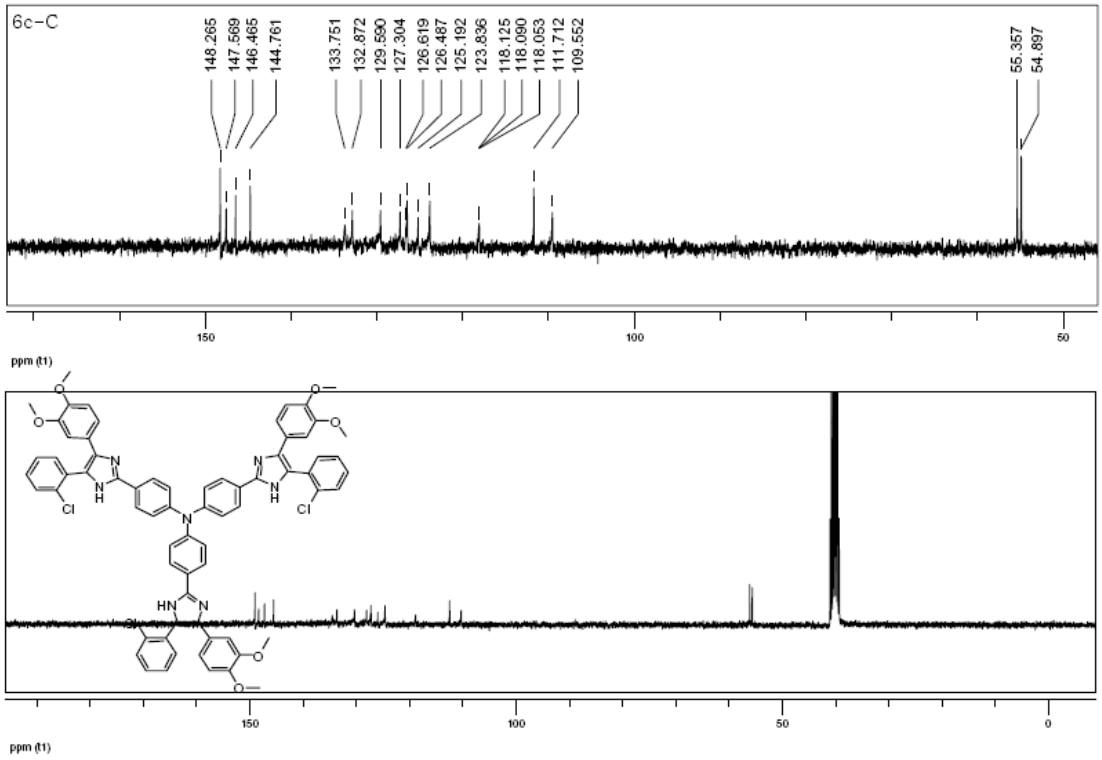
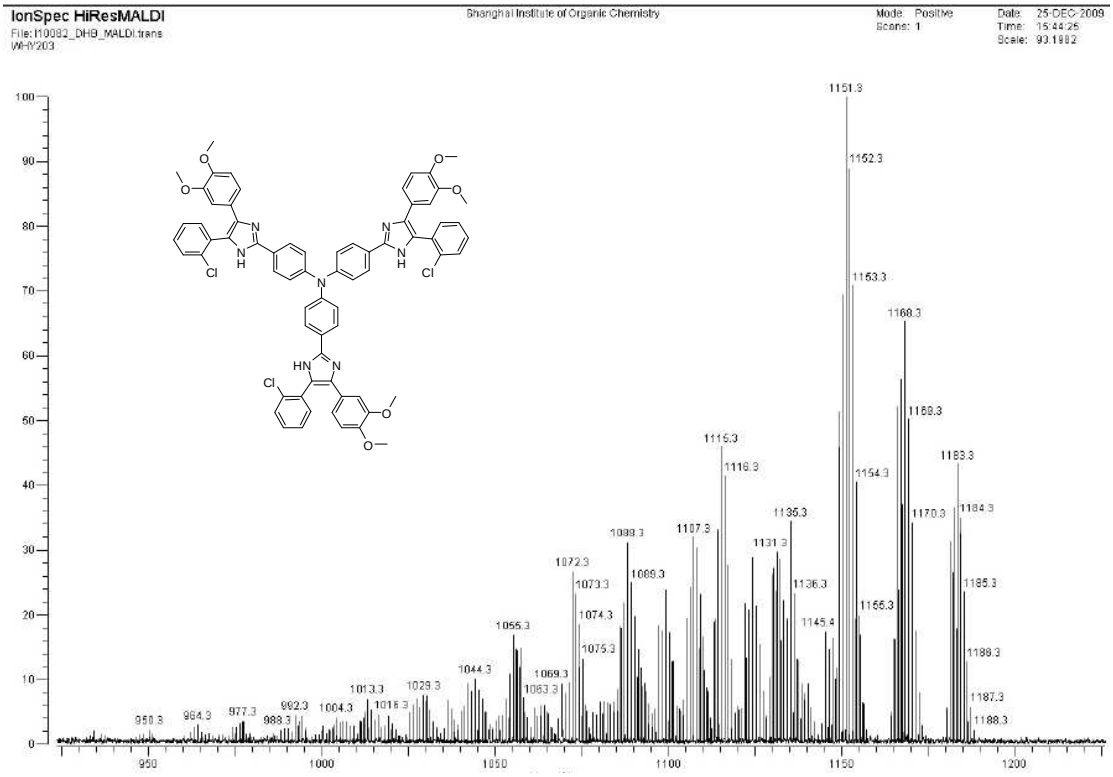


^{13}C NMR spectrum of compound **6c**



mass spectrum of compound **6c**