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Synthesis and properties of new luminescent hole transporting materials of triarylamine with dehydroabietic acid methyl ester moieties

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ABSTRACT

A series of triarylamines based on dehydroabietic acid methyl ester moieties (6a-h) were synthesized for possible application as hole transporting materials for organic electroluminescent devices. The target compounds were characterized by elemental analysis, FT-IR, NMR, and mass spectrometry. Their optical, electrochemical, and thermal properties were investigated using UV–vis, PL spectroscopy, cyclic voltammetry (CV), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC), respectively. CV measurements show that the compounds present suitable HOMO values (in a range of -4.63 to -5.11 eV) for hole injection, which is confirmed by theoretical calculations. All compounds were thermally stable. Organic light-emitting diode devices having **6f**, **6g**, and **6h** as a hole transporting layer showed better performance of maximum brightness, turn-on voltage, and maximum luminous efficiency than a comparable device NPB. These compounds could be excellent candidates for applications in OLED devices.

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1. Introduction

Molecular organic semiconductors have been of great interest due to their applications in organic light-emitting diodes (OLEDs), especially for next generation flat-panel displays.¹ Layered device consisting of charge-transporting and light-emitting layers can achieve higher charge injection efficiency and better charge balance than those of single-layer devices using emitting materials alone.²

In general, the hole transporting layer in layered OLEDs facilitates hole injection from the anode into the organic layer and transports the injected holes to the emitting layer. The hole transporting layer (HTL) can also prevent electrons from escaping the emitting layer to the anode.³ They could improve the luminance efficiency and working life of the device by increasing the efficiency of injection and formation of exciton. The ideal hole transporting material (HTM) should display excellent solubility, high thermal stability, good film-forming ability, and proper HOMO energy value for efficient hole injection and high mobility.⁴

So far, triarylamine derivatives, such as *N*,*N*'-bis-(naphthyl)-N,N'-bis-phenyl-1,1'-biphenyl-4,4'-diamine(NPB)⁵ and N,N'-bis(3methylphenyl)-N,N'-bis-phenyl-benzidine (TPD),⁶ have been the most widely used hole transporting materials because of their high hole mobilities.^{7–10} However, TPD films prepared by sublimation tend to crystallize over time, even at ambient temperature. Numerous efforts have been devoted to synthesizing new HTM with better thermal and morphological stability. There is strong interest in the development of amorphous molecular materials for these applications.¹¹⁻¹⁵ How to improve the thermal stability and keep the hole transporting is the aim of this study. Previous studies showed that the introduction of the backbone of dehydroabietic acid could improve the thermal stability.¹⁶ In this paper, a new group of eight hole transporting materials were synthesized by combining methyl 13-aminodehydrodeisopropylabietate with aryl halides through the cross-coupling reaction (Scheme 2). Theoretical calculations were carried out to provide more insights into the







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Scheme 1. The structures of the intermediates 1-4.



Scheme 2. The synthetic routes of triarylamines 6a-h.

electronic structure of compounds obtained. Optical, electrochemical, thermal, and hole transporting properties of synthesized compounds were studied as well.

2. Results and discussion

2.1. Synthesis

The starting material, dehydroabietic acid, was obtained from commercial product of disproportionated rosin and purified by repeated crystallization by the ethanolamine salt.¹⁷ The intermediates, i.e., methyl dehydroabietate **1**,¹⁸ methyl 12-bromodehydroabietate **2**,¹⁹ methyl 12-bromo-13-nitro-deisopropyldehydroabietate **3**,^{20,21} and methyl 13-aminodeisopropyldehydroabietate **4**^{22–24} were prepared according to procedures described in references, and their structures were described in Scheme 1.

The intermediates, diarylamines (**5a** and **5b**) were synthesized by palladium catalyzed cross-coupling reactions of aryl halides with compound $\mathbf{4}$,²⁵ and triarylamines compounds $\mathbf{6a}$ – \mathbf{h} were synthesized by the same conditions with diarylamine **5a** or **5b**. The synthetic routes were described in Scheme 2.

2.2. Quantum-chemical calculations

To understand the electronic properties of 6a-f, quantumchemical calculations were performed at the B3LYP/6-31G^{*} level using the Gaussian 09 program.²⁶ Since electronic excitation from the highest occupied molecular orbitals (HOMO) to lowest unoccupied molecular orbitals (LUMO) produces the excited state, the orbital features might provide important clues toward understanding the distinct photophysical properties of the synthesized compounds.²⁷

Calculated HOMO, LUMO energies, and HOMO-LUMO energy gaps ($E_{g cal}$) are listed in Table 1. It can be seen from Table 1 that the electron-donating power of the substituent increases to strengthen the nitrogen electron density, the HOMO value gradually increases from -4.87 eV for 6d to -4.72 eV for 6a and -4.53 eV for 6e, same tendency occurs among **6d**, **6c**, and **6g**. In addition, lower E_{σ} of **6f** (3.84 eV), 6b (4.01 eV), and 6h (4.13 eV) than other compounds is ascribed to the extended conjugation system could decrease the energy gap between the HOMO and LUMO.²⁸ It also indicates that the conjugated length in the compounds could be increased by the introduction of naphthalene and biphenyl units. Sample maps of HOMO and LUMO of 6a and 6f are listed in Fig. 1, while other compounds can be seen in Supplemental data. It shows that HOMOs have π -electrons delocalized over the three benzene/aryl rings and N atom, while in LUMOs, π -electrons are localized on the benzene/naphthene/bipenyl rings.

2.3. Physical properties

2.3.1. Optical properties. UV—vis absorption and photolumin escence spectra of compounds **6a**—**h** in methanol are shown in Fig. 2 and related data are summarized in Table 1. As shown in the UV—vis spectra, the absorption spectra of compounds **6a**, **6c**, **6e**, and **6g** are similar and their absorption maxima show slight red-shifts with changing the substituents on the benzene rings, compared to **6d**. Large differences exist among the absorption spectra of

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Physical and	photophysical	data	of 6a-	-h

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Compd	$\lambda_{abs} (nm)^a$	$\lambda_{em} (nm)^{b}$	$\Phi_{\rm f}{}^{\rm a}$	$\tau_{F1/}\tau_{F2} (ns)^a$	$T_{\rm m}/T_{\rm 5d}~(^{\circ}{\rm C})^{\rm c}$	$E_{\rm g\ cal}\ ({\rm eV})^{\rm d}$	HOMO/LUMO (eV) ^d	$E_{\rm g\ exp}\ ({\rm eV})^{\rm e}$	$E_{\text{onset}}^{\text{ox}}(V)^{\text{f}}$	HOMO/LUMO (eV) ^g
6a	240, 298	376	15.81	2.27/7.54	122.8/311.1	4.44	-4.72/-0.28	3.33	0.29	-4.73/-1.40
6b	240, 318	419	74.13	0.71/2.70	—/461.4	4.01	-4.95/-0.94	3.20	0.82	-5.26/-2.06
6c	240, 292	369	87.96	2.03/8.06	173.7/350.6	4.54	-4.80/-0.26	3.38	0.45	-4.89/-1.51
6d	240, 291	366	80.90	1.88/8.87	147.5/307.8	4.59	-4.87/-0.28	3.40	0.52	-4.96/-1.56
6e	240, 298	389	36.01	4.41/5.80	—/360.4	4.28	-4.53/-0.25	3.23	0.19	-4.63/-1.40
6f	219, 286	452	33.90	2.97/16.86	117.3/378.1	3.84	-4.91/-1.07	3.07	0.67	-5.11/-2.04
6g	240, 294	372	34.55	4.91/6.84	151.1/289.6	4.50	-4.73/-0.23	3.35	0.36	-4.80/-1.45
6h	240, 318	418	52.95	2.66/2.66	—/426.6	4.13	-4.85/-0.72	3.22	0.47	-4.91/-1.69

^a Measured in a dilute methanol solution $(1.0 \times 10^{-5} \text{ mol/l})$ at room temperature.

^b Measured in methanol solutions $(1.0 \times 10^{-6} \text{ mol/l})$ at room temperature.

^c Obtained from DSC on the first heating cycle and TGA measurements under N₂ at a heating rate of 10 °C/min.

^d Obtained from quantum-chemical calculation using B3LYP/6-31G (d,p).

^e Estimated from the onset of the absorption spectra ($E_{g exp}=1240/\lambda_{onset}$).

^f Measured using a three electrode system fitted with a glassy carbon working electrode, a platinum rod counter electrode, and Ag/Ag⁺ reference electrode in degassed CH₂Cl₂ containing 0.1 M Bu₄NClO₄ as a supporting electrolyte at a scan rate of 100 mV/s.

^g Calculated using the empirical equation: HOMO= $-(E_{onset}^{ox}+4.44)$ and LUMO=HOMO+ $E_{g exp}$.

HOMO of 61 LUMO of 61

Fig. 1. HOMO and LUMO orbitals of 6a and 6f.



Fig. 2. UV-vis absorption and PL spectra of **6a**-**h** in methanol.

compounds **6f**, **6b**, and **6h**, which may be due to the presence of the naphthalene and biphenyl moieties attached to N atom. As a result, compound **6f** with naphthalene moiety shows a broad $\pi - \pi^*$ transition band with maximum at 286 nm. Compounds **6b** and **6h** with biphenyl moieties show broad $\pi - \pi^*$ transition bands with a maximum at 318 nm.

As shown in Table 1, emission peaks of **6a–h** in methanol are at 366–452 nm, corresponding to blue light emission. Similar to the UV–vis absorption, compounds with electron-donating substituents on aromatic rings, such as OCH₃ (**6a**, **6e**), and CH₃ (**6c**, **6g**) show slight red-shift fluorescence emission and increased fluorescence intensity over **6d** (without substituent on aromatic rings, which is due to electron-donating substituents on aromatic rings producing $p-\pi$ conjugations. However, the introduction of nathaphene (**6f**) and biphenyl (**6b** and **6h**) moieties causes a large red-shift of fluorescence emission spectra, which is rising from the extension of the conjugated length. Their maximum emission

peaks even shift to a longer wavelength of the blue light region, which are 452 nm, 419 nm, and 418 nm for **6f**, **6b**, and **6h**, respectively. Therefore, substituents of electron-donating and extended conjugation system have a great influence on the fluorescence properties of molecules.

In additional, the fluorescence quantum yields ranges from 15.81% to 87.96%. Larger values are found for **6d** (80.9%), and **6c** (87.96%). The fluorescence lifetime is found in the range between 2.66 ns and 16.86 ns. The compound **6f** has the highest value (16.86 ns). The fluorescence quantum yields and lifetimes are not directly affected by the substituents and conjugated system.

2.3.2. Electrochemical properties. Cyclic voltammetry (CV) was employed to investigate electrochemical properties of the compounds. Additionally, the HOMO and LUMO energy levels were estimated from CV measurement results.²⁹ CV was carried out on a Chi660D electrochemistry workstation with a three-electrode cell in chloroform in the presence of tetrabutylammonium perchlorate (Bu₄NCIO₄, 0.10 M) as the supporting electrolyte with a scanning rate of 100 mV/s at room temperature (Fig. 3) and the results are listed in Table 1. Glassy carbon and platinum wire are used as working and counter electrodes, respectively, and an Ag/Ag⁺ electrode is used as the reference electrode. All solutions have been deaerated with N₂ gas prior to the experiments.



Fig. 3. CV curves of 6a-h measured in CH₂Cl₂/n-Bu₄NPF₆ at a scanning rate of 100 mV/s.

The onset oxidation potentials (E_{onset}^{Ox}) are obtained by the tangent method from the thresholds of oxidation potentials. The HOMO and LUMO energy levels of **6a**–**h** are calculated from the oxidation onset potentials (E_{onset}^{Ox}) and energy gaps ($E_{g exp}$). These results are summarized in Table 1. HOMO levels of eight compounds ranging from –5.26 to –4.63 eV are higher than the widely used HTM NPB (–5.40 eV). The higher HOMO energy means that a smaller energy barrier exists between the interface of ITO and the synthesized materials and results in higher hole injection efficiency and lower joule heat.³⁰

HOMO energies from experimental and theoretical studies are in good agreement but LUMO energies are quite different. Neither experimental (using empirical method) nor theoretical studies could give the exact values of HOMO or LUMO energies. Instead the relative value of their differences, $E_{g cal}$ and $E_{g exp}$ are more important. Though there are some differences in their absolute values, the perfect linear relationship is observed between them (R^2 =0.956), as shown in Fig. 4. It implies that both $E_{g cal}$ and $E_{g exp}$ could demonstrate the trend of HOMO–LUMO gaps and, as a result, is used to evaluate π – π * transitions and luminous properties in this work.





2.3.3. Thermal properties. For OLED applications, thermal stability of organic materials is crucial for device stability and lifetime. Thermal instability of the amorphous organic layer may result in degradation of organic devices due to morphological changes. The thermal properties of 6a-h were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Table 1 (also see Supplementary data). TGA shows that all compounds are stable in nitrogen with temperature at 5% weight loss (T_{5d}) well over 300 °C, except compound **6g** (*T*_{5d}=289.6 °C); moreover, compounds **6b** and **6h** have *T*_{5d} greater than 400 °C. It is important to keep thermal degradation temperatures above 300 °C in order to be well above operating temperatures of relevant devices and so that compounds can be applied using vacuum deposition techniques. A higher thermal degradation temperature means there is a wider temperature range in which the compounds could be used. During the first heating DSC scan of samples 6a-h, compounds 6a, 6c, 6d, 6f, and **6g** exhibited endothermic melting peaks (T_m) at 122.8, 173.7, 147.5, 117.3, and 115.1 °C, respectively, while compounds 6b, 6e, and 6h had no observed melting peaks.

2.4. Hole transporting properties

To investigate the hole transporting properties of **6a**–**h**, OLEDs (devices **6a**–**h**) were fabricated using these compounds as hole transporting layers (HTL) with the device configuration of ITO/triarylamine (50 nm)/Alq3 (50 nm)/LiF (0.8 nm)/Al (80 nm). Tris(8-hydroxyquinolinato) aluminum (Alq3) served as the emitting layer (EML) as well as the electron-transporting layer while LiF/Al was used as a bilayer cathode. A control device was fabricated using NPB as the HTL in the same device architecture. The luminance–voltage (*L*–*V*), current density–voltage (*J*–*V*), and luminance efficiency–current density (η –*J*) characteristics of the devices are shown in Figs. 5–7, and their electrical parameters are summarized in Table 2.

The turn-on voltage at 1 cd/m² for devices **6a** and **6d**—**h** is in the range of 2.6–3.9 V and the operating voltage at 100 cd/m² is in the range of 3.5–5.6 V. This indicates good performance for these devices. Devices having **6a**, **6d**—**h** as HTL show good performance with a high maximum brightness of 8914, 7063, 6518, 14,602, 16,141, and 12,554 cd/m² at 9.0 V, respectively, a low turn-on voltage of 3.0, 3.9, 3.0, 3.2, 2.7, and 2.6 V and a maximum luminance efficiency of 2.4, 3.2, 2.1, 2.7, 2.1, and 2.1 cd/A. However, the device **6b** shows lower performance in terms of maximum brightness (1422 cd/m²), turn-on voltage (3.7 V), and maximum luminance efficiency (1.8 cd/A). The device **6c** shows higher luminance efficiency (2.7 cd/A), but lower brightness (236 cd/m²) and higher turn-on voltage (4.8 V). A comparable device performance is observed from device NPB,



Fig. 5. *L*–*V* characteristics of OLED devices.



Fig. 6. J-V characteristics of OLED devices.



Fig. 7. η –*J* characteristics of OLED devices.

which with a maximum brightness of 9467 cd/m^2 , a turn-on voltage of 3.5 V, and a maximum luminance efficiency of 2.0 cd/A. OLED devices having **6f**, **6g**, and **6h** as HTL demonstrate better performance of maximum brightness, lower turn-on voltage, and higher maximum luminance efficiency than a control device NPB. Among them, device **6f**, having compound **6f** as HTL, exhibits the best

Table 2
Device characteristics of OLEDs with 6a-h and NPB as HTI

Device	Structure	$V_{\rm on}{}^{\rm a}$	<i>V</i> ₁₀₀ ^b	L _{max} ^c	J^{d}	$\eta^{\rm e}/V$
6a	ITO/6a/Alq3/LiF/Al	3.0	4.8	8914	601	2.4/5.2
6b	ITO/ 6b /Alq3/LiF/Al	3.7	6.0	1422	132	1.8/6.2
6c	ITO/ 6c /Alq3/LiF/Al	4.8	7.8	236	8.4	2.7/8.2
6d	ITO/ 6d /Alq3/LiF/Al	3.9	5.6	7063	316	3.2/6.7
6e	ITO/ 6e /Alq3/LiF/Al	3.0	4.8	6518	450	2.1/5.7
6f	ITO/ 6f /Alq3/LiF/Al	3.2	4.7	14,602	638	2.7/6.7
6g	ITO/ 6g /Alq3/LiF/Al	2.7	3.8	16,141	1095	2.1/6.2
6h	ITO/ 6h /Alq3/LiF/Al	2.6	3.5	12,554	1226	2.1/4.7
NPB	ITO/NPB/Alq3/LiF/Al	3.5	4.8	9467	572	2.0/6.9

^a Turn-on voltage (V) at luminance of 1 cd/m².

^b Voltage (V) at luminance of 100 cd/m².

^c Maximum luminance (cd/m²).

^d Current density (mA/cm²) at maximum luminance.

^e Luminance efficiency (cd/A).

performance with a high maximum brightness of 14,602 cd/m², a lower turn-on voltage of 3.2 V, and a maximum luminance efficiency of 2.7 cd/A.

In order to explain the different efficiencies of the OLED devices, analysis of band energy diagrams of all devices revealed that the HOMO levels of all HTM materials (-4.63 to 5.26 eV) lay between those of ITO (-4.80 eV) and Alq3 (-5.7 eV). The injection barrier for holes to migrate from the HTL to EML (Alq3) is 0.97 eV (6a), 0.44 eV (6b), 0.81 eV (6c), 0.74 eV (6d), 1.07 eV (6e), 0.59 eV (6f), 0.90 eV (6g), and 0.79 eV (6h), respectively. Energy barriers of 6f, 6d, and 6c are narrower. It suggests that a migration of holes from the HTL to EML layer are more effective in devices 6f, 6d, and 6c compared to devices **6a**, **6e**, **6g**, and **6h**, which is due to the charges efficiently recombining in the emitting layer and higher luminance efficiency. As to the device **6b**, it shows lower performance in spite of its narrowest energy barrier. This may be the effect of electronwithdrawing bromine on biphenyl and the fluoro group with electron withdrawing ability reducing the electron density of nitrogen. Therefore, 6b becomes more difficult to be oxidized and thus shows the lowest-lying HOMO energy level of -5.26 eV.

3. Conclusion

In summary, eight luminescent hole transporting materials $(\mathbf{6a}-\mathbf{h})$ containing triarylamine and dehydroabietic acid methyl ester moieties have been synthesized and characterized. The photoluminescence spectra of these compounds exhibit a maximum between 366 and 452 nm in methanol, corresponding to blue light region. The HOMO values of molecules are -4.63 to -5.11 eV, which are in favor of the hole-injection. The synthesized materials **6a–h** show stable thermal properties. OLED devices having **6f**, **6g**, and **6h** as HTL demonstrate better performance of maximum brightness, lower turn-on voltage, and higher maximum luminous efficiency than a control device NPB. Among them, **6f** gives the most promising and balanced performance. These results imply that the hole transporting materials containing triarylamine with dehydroabietic acid methyl ester moieties could be a great candidate for the application in OLEDs.

4. Experimental

4.1. General procedure

Reagents and solvents were commercially available and used as received. UV–vis absorption spectra were recorded with a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were collected with a PE LS50-B spectrophotometer at room temperature. The fluorescence absolute quantum yields (Φ_f) and the

fluorescence lifetime (τ_F) were measured by Fluoromax-4 fluorescence spectrometer (Horiba Jobin Yvon Inc., France). TGA and DSC of the synthesized compounds were determined by 409PC thermogravimetric analyzer and a Diamond DSC thermal analyzer. Cyclic voltammetry (CV) were carried out on a Chi660D electrochemistry workstation.

4.2. Fabrication of OLEDs



The devices have the structure of ITO/triarylamine (50 nm)/Alq3 (50 nm)/LiF (0.8 nm)/Al (80 nm). In the devices, triarylamine was used as the hole transport layer, and tris(8-hydroxyquinolinato) aluminum (Alq3) served as the emitting layer (EML) as well as the electron-transport layer while LiF/Al was used as a bilayer cathode. The device was fabricated using an indium tin oxide coated glass substrate with a sheet resistance of 10 Ω per square. The substrate was cleaned in ultrasonic baths of detergent, alcohol, and acetone, de-ionized water in turn, and then dried at 120 °C in a vacuum oven for more than 1 h.

The respective organic layers and the cathode layer were deposited at 5×10^{-4} Pa. The deposition rates of organic layer, LiF, and Al were 0.1–0.2 nm/s, 0.02–0.04 nm/s, and 0.3–0.5 nm/s, respectively. The film thickness was monitored by a quartz oscillator thickness meter. The emission area of the device was 12 mm², and only the luminance in the forward direction was measured. The Electroluminescence characteristics of the devices were measured using a Keithley 2602 source-measure unit. All of the devices were characterized without encapsulation and all of the measurements were carried out at room temperature under ambient conditions.

4.3. General procedure for synthesis 6a-h

A mixture of 0.4 mmol diarylamine (**5a** or **5b**), 0.44 mmol aryl bromide, and 0.48 mmol sodium *tert*-butoxide was transferred to dry 1 mL *o*-xylene in a flask under nitrogen atmosphere and 0.04 mmol tri-*tert*-butylphosphine and 0.01 mmol palladium acetate were then added. The solution was stirred at 130 °C until the complete consumption of diarylamine as determined by TLC. The reaction mixture was then cooled to room temperature, dissolved in diethyl ether (5 mL), and then washed with brine. The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica column chromatography using mixtures of petroleum ether/ ethyl acetate (9/1 to 12/1) as eluent.

4.4. Characterization of 6a-h

4.4.1. Methyl 13-[N,N-(4-methoxyphenyl)-phenyl]aminodeisopropyl dehydroabietate **6a**. White crystal, mp=122.8 °C; Anal. Calcd for C₃₁H₃₅NO₃: C, 79.28%; H, 7.51%; N, 2.98%. Found: C, 79.74%; H, 8.01%; N, 3.00%. IR (Smart iTR) ν_{max}/cm^{-1} : 2936, 1722, 1593, 1597, 1242; ¹H NMR (DMSO-*d*₆, 500 MHz) δ : 1.14 (3H, s, CH₃), 1.19 (3H, s, CH₃), 1.23–1.34 (2H, m, 2× CH), 1.56–1.77 (5H, m, 2× CH₂ and CH), 2.01–2.04 (1H, dd, *J*=2.15 and 12.5, CH), 2.25–2.28 (1H, d, *J*=13.3, CH), 2.63–2.71 (2H, m, CH₂), 3.60 (3H, s, COOCH₃), 3.73 (3H, s, OCH₃), 6.61 (1H, s, Ar–H), 6.71–6.73 (1H, dd, *J*=2.45 and 8.5, CH),

6.84–6.86 (2H, d, *J*=1.1, Ar–H), 6.87–6.91 (3H, m, Ar–H), 6.97–6.99 (2H, m, Ar–H), 7.14–7.15 (1H, d, *J*=8.65, Ar–H), 7.18–7.21 (2H, m, Ar–H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ : 16.2, 17.94, 20.92, 24.63, 29.23, 36.13, 36.33, 37.59, 44.77, 46.85, 51.76, 55.15, 114.90 (2C), 120.76, 121.12, 121.43 (2C), 122.61, 125.08, 127.05 (2C), 129.07 (2C), 135.31, 139.96, 143.48, 144.73, 147.85, 155.72, 177.92 (C=O); *m*/*z* (ESI) 470.3 [M+H]⁺.

4.4.2. Methyl 13-[N,N-(p-bromobiphenyl)-phenyl]aminodeisopropyld ehydroabietate 6b. Yellow solid, mp=150.2 °C; Anal. Calcd for C31H35NO3: C, 72.72%; H, 6.10%; N, 2.36%. Found: C, 73.04%; H, 5.99%; N 2.16%. IR (Smart iTR) ν_{max}/cm^{-1} : 2934, 1724, 1594, 1486, 1257; ¹H NMR (DMSO-*d*₆, 500 MHz) δ: 1.16 (3H, s, CH₃), 1.20 (3H, s, CH₃), 1.25–1.39 (2H, m, 2× CH), 1.59–1.75 (5H, m, 2× CH₂ and CH), 2.04-2.06 (1H, d, J=11.0, CH), 2.27-2.29 (1H, d, J=13.5, CH), 2.62-2.75 (2H, m, CH₂), 3.60 (3H, s, COOCH₃), 6.73 (1H, s, Ar-H), 6.82-6.83 (1H, d, J=7.0, Ar-H), 6.97-7.04 (4H, d, J=7.5, Ar-H), 7.20-7.22 (1H, d, J=8.5, Ar-H), 7.27-7.31 (2H, d, J=7.85, Ar-H), 7.35–7.38 (1H, t, J=7.0, Ar–H), 7.40–7.48 (2H, t, J=7.8, Ar–H), 7.53–7.57 (2H, d, *J*=2.9, Ar–H), 7.58–7.66 (4H, d, *J*=7.5, Ar–H); ¹³C NMR (DMSO-d₆, 125 MHz) δ: 16.25, 17.97, 20.92, 24.67, 29.21, 36.16, 36.48, 37.59, 44.74, 46.90, 51.83, 122.35, 122.85, 123.74, 123.96, 124.37, 125.44, 126.06, 126.54, 126.81, 127.47, 127.79, 128.07, 128.67, 128.75, 128.82, 128.99, 129.48, 131.75, 131.86, 133.60, 135.71, 139.61, 144.73, 147.11, 177.97 (C=O); *m*/*z* (ESI) 513.3 [M+H-Br]⁺.

4.4.3. Methyl 13-[N,N-(4-methylphenyl)-phenyl]aminodeisopropylde hvdroabietate 6c. White crystal, mp=173.7 °C: Anal. Calcd for C31H33NO2: C, 82.08%; H, 7.78%; N, 3.09%. Found: C, 82.11%; H, 7.53%; N, 3.02%. IR (Smart iTR) ν_{max}/cm^{-1} : 2938, 1723, 1593, 1496, 1250; ¹H NMR (DMSO-*d*₆, 500 MHz) δ: 1.15 (3H, s, CH₃), 1.20 (3H, s, CH₃), 1.24–1.35 (2H, m, 2× CH), 1.56–1.76 (5H, m, 2× CH₂ and CH), 2.01–2.04 (1H, d, J=12.15, CH), 2.25 (3H, s, Ar–CH₃), 2.29–2.33 (1H, d, J=20.5, 2H), 2.64-2.70 (2H, m, CH₂), 3.60 (3H, s, COOCH₃), 6.62 (1H, s, Ar–H), 6.73–6.74 (1H, d, J=8.05, Ar–H), 6.87–6.90 (4H, d, J=7.5, Ar-H), 6.92-6.95 (1H, t, J=7.6, Ar-H), 7.08-7.10 (2H, d, J=11.0, Ar-H), 7.15-7.17 (1H, d, J=8.6, Ar-H), 7.21-7.24 (2H, t, J=7.65, Ar–H); ¹³C NMR (DMSO- d_6 , 125 MHz) δ : 16.22, 17.95, 20.32, 20.92, 24.66, 29.21, 36.14, 36.38, 37.59, 44.76, 46.87, 51.87, 121.42, 121.81, 122.51 (2C), 123.32, 124.30 (2C), 125.20, 129.20 (2C), 129.95 (2C), 132.07, 135.43, 143.91, 144.54, 144.73, 47.58, 177.96 (C=O); m/z (ESI) 454.5 [M+H]⁺.

4.4.4. Methyl 13-(N,N-bis-phenyl) aminodeisopropyldehydroabietate **6d**. Brown powder, mp=147.5 °C; Anal. Calcd for $C_{30}H_{33}NO_2$: C, 81.97%; H, 7.57%; N, 3.19%. Found: C, 82.11%; H, 7.43%; N, 3.07%. IR (Smart iTR) ν_{max}/cm^{-1} : 2940, 1724, 1590, 1491, 1255; ¹H NMR (DMSO- d_6 , 500 MHz) δ : 1.15 (3H, s, CH₃), 1.20 (3H, s, CH₃), 1.24–1.36 (2H, m, 2× CH), 1.57–1.77 (5H, m, 2× CH₂ and CH), 2.02–2.05 (1H, dd, *J*=2.05 and 12.45, CH), 2.27–2.29 (1H, d, *J*=13.1, CH), 2.65–2.71 (2H, m, CH₂), 3.60 (3H, s, COOCH₃), 6.67 (1H, s, Ar–H), 6.76–6.78 (1H, dd, *J*=2.3 and 8.5, Ar–H), 6.94–6.95 (4H, d, *J*=7.6, Ar–H), 7.00–7.02 (2H, t, *J*=9.65, Ar–H), 7.18–7.20 (1H, d, *J*=8.6, Ar–H), 7.24–7.29 (4H, t, *J*=7.5, Ar–H); ¹³C NMR (DMSO- d_6 , 125 MHz) δ : 16.20, 17.94, 20.89, 24.62, 29.18, 36.12, 36.41, 37.57, 44.72, 46.86, 51.77, 121.96, 122.35 (2C), 123.23 (4C), 123.95, 125.28, 129.29 (4C), 135.54, 143.70, 144.33, 144.36, 147.33, 177.91 (C=O); *m/z* (ESI) 440.2 [M+H]⁺.

4.4.5. *Methyl* 13-[*N*,*N*-*bis*(4-*methoxyphenyl*)]*aminodeisopropyldehy droabietate* **6***e*. White crystal, mp=160.2 °C; Anal. Calcd for C₃₂H₃₇NO₄: C, 76.92%; H, 7.46%; N, 2.80%. Found: C, 76.39%; H, 7.69%; N, 2.50%. IR (Smart iTR) ν_{max}/cm^{-1} : 2940, 1724, 1606, 1502, 1241; ¹H NMR (CDCl₃, 500 MHz) δ : 1.19 (3H, s, CH₃), 1.26 (3H, s, CH₃), 1.33–1.50 (1H, m, 2× CH), 1.62–1.81 (5H, m, 2× CH₂ and CH), 2.18–2.25 (2H, d, *J*=13.1, 2× CH), 2.71–2.75 (2H, m, CH₂), 3.65 (3H,

s, COOCH₃), 3.77 (6H, s, $2 \times$ OCH₃), 6.59 (1H, s, Ar–H), 6.69–6.71 (1H, d, *J*=7.4, Ar–H), 6.78–6.80 (4H, d, *J*=8.85, Ar–H), 7.00–7.01 (4H, d, *J*=7.6, Ar–H), 7.01–7.03 (1H, d, *J*=8.5, Ar–H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ : 16.19, 17.95, 20.98, 24.65, 29.32, 36.15, 36.21, 37.63, 44.85, 46.85, 51.75, 55.13 (2C), 114.72 (4C), 118.59, 120.16, 124.82, 125.83 (4C), 134.98, 140.61 (2C), 141.94, 145.59, 155.14 (2C), 177.94 (C=O); *m*/*z* (ESI) 500.8 [M+H]⁺.

4.4.6. Methyl 13- $[N,N-(\alpha-naphthalene)-phenyl]aminodeisopropyldeh$ ydroabietate 6f. Light yellow crystal, mp=117.3 °C; Anal. Calcd for C34H35NO2: C, 83.40%; H, 7.20%; N, 2.86%. Found: C, 82.93%; H, 7.27%; N, 2.71%. IR (Smart iTR) ν_{max}/cm^{-1} : 2939, 1723, 1592, 1495, 1383, 1250; ¹H NMR (DMSO-*d*₆, 500 MHz) δ: 1.11 (3H, s, CH₃), 1.17 (3H, s, CH₃), 1.18–1.29 (2H, m, 2× CH), 1.56–1.71 (5H, m, 2× CH₂ and CH), 1.99–2.02 (1H, d, J=12.5, CH), 2.21–2.23 (1H, d, J=13.0, CH), 2.58–2.63 (2H, m, CH₂), 3.58 (3H, s, COOCH₃), 6.63 (1H, s, Ar–H), 6.72-6.73 (1H, d, J=8.5, Ar-H), 6.80-6.81 (2H, d, J=8.0, Ar-H), 6.83-6.86 (1H, t, J=7.5, Ar-H), 7.10-7.11 (1H, d, J=8.5, Naphthalene–H), 7.13–7.16 (2H, t, J=8.15, Ar–H), 7.29–7.31 (1H, d, J=7.0, Ar-H), 7.38-7.41 (1H, t, J=7.4, Naphthalene-H), 7.48-7.52 (2H, d, *J*=7.5, Naphthalene–H), 7.85–7.91 (2H, t, *J*=5.05, Naphthalene–H), 7.96–8.00 (1H, d, J=11.0, Naphthalene–H); ¹³C NMR (DMSO-d₆, 125 MHz) δ: 16.17, 17.91, 20.90, 24.59, 29.23, 36.10, 36.30, 37.55, 44.72, 46.82, 51.72, 119.89, 120.24 (2C), 120.81, 121.62, 123.46, 125.07, 125.82, 126.13, 126.44, 126.52, 127.11, 127.62, 128.41, 129.05 (2C), 130.70, 135.27, 142.79, 143.33, 144.95, 148.06, 177.88 (C=O); *m*/*z* (ESI) 490.1 [M+H]⁺.

4.4.7. Methyl 13-[N,N-bis(4-methylphenyl)-phenyl]aminodeisopropyl dehydroabietate **6g**. Colorless crystal, mp=151.1 °C; Anal. Calcd for C₃₂H₃₇NO₂: C, 82.19%; H, 7.97%; N, 3.00%. Found: C, 81.93%; H, 8.27%; N, 2.37%. IR (KBr) ν_{max}/cm^{-1} : 2936, 1720, 1605, 1503, 1262; ¹H NMR (DMSO-*d*₆, 500 MHz) δ : 1.14 (3H, s, CH₃), 1.19 (3H, s, CH₃), 1.32–1.39 (2H, m, CH₂), 1.58–1.74 (5H, m, 2× CH₂ and CH), 2.00–2.03 (1H, dd, *J*=2.05 and 12.45, CH), 2.24 (6H, s, 2× Ar–CH₃), 2.28–2.30 (1H, d, *J*=10.0, CH), 2.62–2.68 (2H, m, CH₂), 3.60 (3H, s, CO2CH₃), 6.58 (1H, s, Ar–H), 6.68–6.70 (1H, dd *J*=2.4 and 8.5, Ar–H), 6.83–6.85 (4H, d, *J*=8.4, Ar–H), 7.05–7.07 (4H, d, *J*=8.15, Ar–H), 7.12–7.14 (1H, d, *J*=8.65, Ar–H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ : 16.19, 18.01, 20.16, 21.11, 24.77, 29.50, 36.14, 36.19, 37.74, 45.05, 46.88, 51.74, 120.72, 122.52, 123.63 (4C), 125.02, 129.79 (4C), 131.45 (2C), 135.24, 143.32, 144.80 (2C), 144.99, 177.93; *m*/z (ESI) 468.0 [M+H]⁺.

4.4.8. Methyl 13-[N,N-biphenyl-phenyl]aminodeisopropyldehydroab ietate **6h**. Yellow crystal, mp=157.0 °C; Anal. Calcd for C₃₆H₃₇NO₃₂: C, 83.85%; H, 7.23%; N, 2.72%. Found: C, 83.45%; H, 7.66%; N, 2.76%. IR (Smart iTR) ν_{max}/cm^{-1} : 2932, 1722, 1593, 1479, 1248; ¹H NMR (DMSO-d₆, 500 MHz) δ : 1.16 (3H, s, CH₃), 1.20 (3H, s, CH₃), 1.25–1.37 (2H, m, 2× CH), 1.57–1.78 (5H, m, 2× CH₂ and CH), 2.03–2.05 (1H, d, *J*=10.2, CH), 2.28–2.30 (1H, d, *J*=11.55, CH), 2.67–2.73 (2H, m, CH₂), 3.60 (3H, s, COOCH₃), 6.73 (1H, s, Ar–H), 6.82–6.84 (1H, dd, *J*=8.35, and 1.75, Ar–H), 6.98–7.02 (3H, t, *J*=8.85, Ar–H), 7.02–7.04 (1H, d, *J*=8.7, Ar–H), 7.21–7.23 (1H, d, *J*=8.6, Ar–H), 7.27–7.29 (1H, d, *J*=7.4, Ar–H), 7.30–7.31 (1H, d, *J*=7.05, Ar–H), 7.40–7.48 (3H, t, *J*=7.75, Ar–H), 7.55–7.56 (2H, d, Ar–H), 7.60–7.61 (2H, d, *J*=7.55, Ar–H), 7.65–7.66 (1H, d, *J*=7.6, Ar–H); ¹³C NMR (DMSO-d₆, 125 MHz) δ : 16.22, 17.95, 20.89, 24.63, 29.18, 36.13, 36.46, 37.57, 44.72, 46.87, 51.79, 122.32, 122.77, 122.82 (2C), 123.71, 124.34, 125.40, 126.03, 126.61, 126.77, 127.33, 127.44, 128.79 (2C), 128.84, 129.41 (2C), 133.58, 135.68, 139.59, 144.12, 144.71, 146.81, 147.09, 177.93 (C=O); m/z (ESI) 516.4 [M+H]⁺.

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Supplementary data

More results on quantum-chemical calculation, and DSC/TGA thermograms. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.071.

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