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First synthesis of ring-B C_{60}-substituted derivatives of *N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine

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ABSTRACT

A new route to ring-B C_{60}-substituted derivatives of *N*,*N*-(tetrachlorophthaloyl) dehydroabietylamine from dehydroabietylamine was reported. This advance was used to achieve the first synthesis of methanofullerene derivatives **14**–**17** and dehydroabietylamine derivatives **2**–**13**. NMR spectroscopy unambiguously proved that the methanofullerene derivatives were C_1 symmetric structures with a 6,6-junction.

1. Introduction

Since the discovery of C_{60}, various fullerene derivatives have been developed and their applications in the fields of material and biomedical sciences have been studied extensively. One of the most exciting fields of fullerene chemistry is related to their biological activity.[1–4] C_{60} derivatives exhibit a range of interesting biological activities, including inhibiting HIV-1 protease,[5–9] inducing DNA photocleavage[10–12] and scavenging free radicals.[13,14] Among these fullerene derivatives C_{60} hybrids containing bioactive groups have received considerable attention in recent years. Many bioactive molecules, such as amino acids, peptides, nucleotide, sugars and steroids have been linked to C_{60}. Hu et al.[15,16] synthesized β-alanine and cystine C_{60} derivatives and discovered their protective effect on hydrogen peroxide-induced apoptosis in rat pheochromocytoma cells. Toniolo et al.[5] obtained a C_{60}-peptide derivative, which exhibits remarkable chemotactic potency, comparable to that of the parent pentapeptide, and biological activity of inhibiting HIV-1 protease. Sofou et al.[17] synthesized proline-rich C_{60}-peptide derivative, which was found to be biologically active against sera from MCTD and SLE patients. Kato et al.[18] synthesized mannosyl [60] fullerenols and found that they decrease the activity for both aggregating erythrocytes and binding to RCA_{120} and increase the binding to an α-D-mannose specific lectin (Con A). Li et al.[19] prepared steroid-C_{60} adduct, results of a preliminary assay show that it can inhibit the reconstituted SR Ca^{2+}-ATPase in soybean phospholipid liposomes and affect the survival of human lung adenocarcinoma cancer A_{549} cells.

Dehydroabietylamine (Fig. 1), which possesses an aromatic diterpene structure with three rings and three chiral carbon atoms, is the main component of, and can be easily separated from, disproportionated rosin amine. Dehydroabietylamine and its derivatives have been utilised widely because of their biological activities, such as antimicrobial and surface activating activities and the separation of racemic mixtures.[20–22]

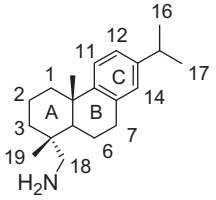

Fig. 1. Dehydroabietylamine.

These results prompted us to search for new adducts of dehydroabietylamine with C_{60} to develop new rosin amine derivatives with potential biological activity. In this paper, we report the synthesis of ring-B C_{60}-substituted derivatives of *N*,*N*-(tetrachlorophthaloyl) dehydroabietylamine from dehydroabietylamine in 10 reaction steps.

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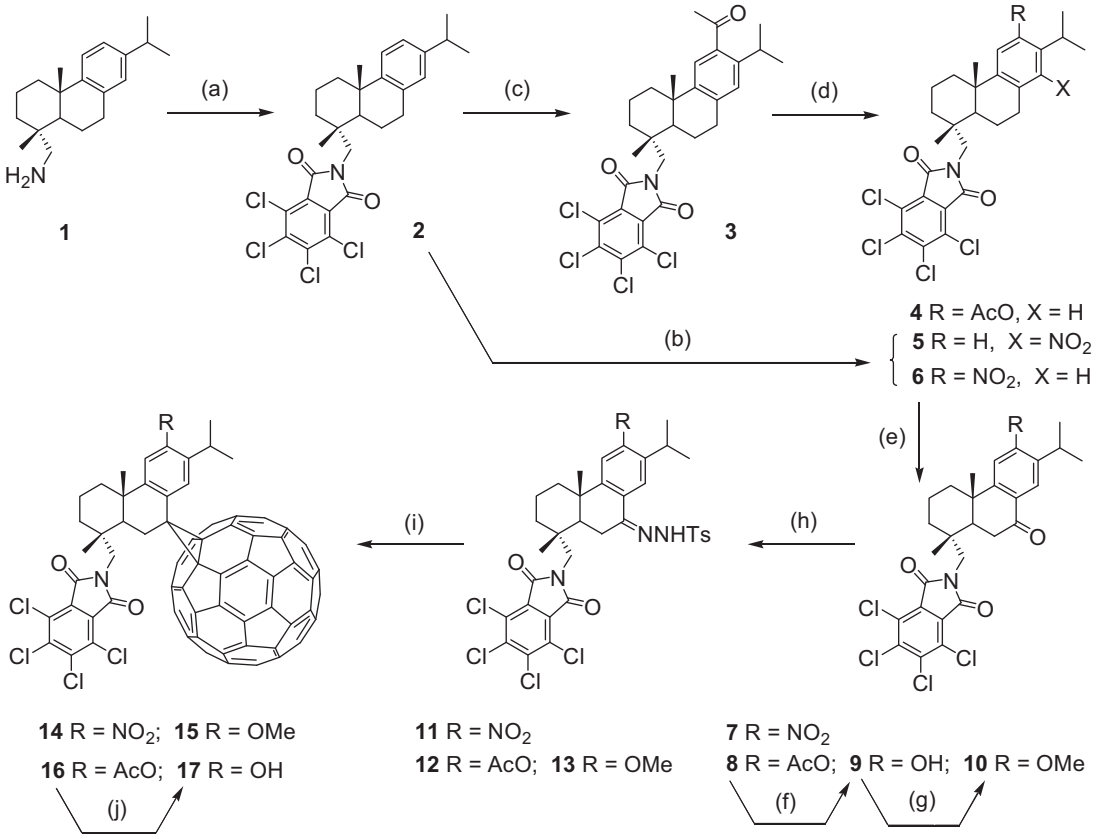
2. Results and discussion

The general procedure for the synthesis of ring-B substituted derivatives of *N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine **14**, **15**, **16** and **17** is shown in Scheme 1. Dehydroabietylamine, the starting material, was prepared as described in the literature.[23]



Scheme 1. Reagents, conditions and yields: (a) TCPA, acetic acid, N_2, 130 °C, 2.5 h, 73%; (b) claycop, Ac_2O, CH_2Cl_2, 25 °C, 2 h, 65% (**6**:**5**=3:2); (c) AcCl, $AlCl_3$, CS_2, N_2, reflux, 5 h, 77%; (d) 65% *m*-CPBA (2 equiv), PTSA (cat., 0.083 equiv), CH_2Cl_2, rt, 48 h, 71%; (e) 65% *t*-BuOOH (8 equiv), CrO_3 (0.05 equiv), pyridine (0.1 equiv), CH_2Cl_2, rt, 25 h, 38% for **7**, 66% for **8**; (f) concd HCl, $CHCl_3$/MeOH (1:2), N_2, reflux, 1.5 h, 79%; (g) CH_3I, K_2CO_3, dry acetone, N_2, reflux, 5 h, 89%; (h) $TsNHNH_2$ (1.68 equiv), PTSA (cat., 0.09 equiv), benzene/EtOH (4:1), N_2, reflux, 8 h, 82% for **11**, 77% for **12** and 85% for **13**; (i) NaOMe, pyridine, 20 min, rt; then C_{60} in chlorobenzene, N_2, 70 °C, 24 h, 37% for **14**, 40% for **15**, 33% for **16**; (j) concd HCl, CS_2/MeOH(1:1), N_2, reflux, 4 h, 91%.

Dehydroabietylamine reacted with tetrachlorophthalic anhydride (TCPA, an amino protecting group) to give imide **2** in 73% yield. Imide **2** was transformed into **3** in 77% yield by Friedel–Crafts acetylation, followed by Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) to generate **4**.

Imide **2** was mononitrated with clay-supported copper(II) nitrate (claycop)[24] in CH_2Cl_2 to give a mixture (3:2) of 12-nitro-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine **6** and 14-nitro-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine **5** in 65% yield. The product ratio of **6** to **5** was determined by ^1H NMR. As the chromatographic properties of the two nitro-compounds **6** and **5** were very similar, the mixture was C-7 benzylic oxidated without separation and then purified by column chromatography to produce **7**.

The conventional methods for C-7 benzylic oxidations involve the use of very large excesses of chromium(VI) reagents, such as CrO_3 and Na_2CrO_4, in a mixed solvent of Ac_2O/AcOH,[25–29] which led to considerable amounts of toxic effluents and afforded low yields (approximately 10–15%) in the C-7 benzylic oxidations of compounds **4** and **6** because of their poor solubility in Ac_2O/AcOH. When **4** and **6** were treated with an excess of *t*-BuOOH (8 equiv) as an oxidant and CrO_3/pyridine mixture as a catalyst in CH_2Cl_2,[30] the yields of compounds **7** and **8** increased significantly (38% for **7**, 66% for **8**).

Ketoester **8** was hydrolysed by concd HCl in a mixed solvent of $CHCl_3$/CH_3OH (1:2) to afford ketophenol **9**, which was then converted to 12-methoxy derivative **10** in 89% yield by refluxing with CH_3I and K_2CO_3 in dry acetone. Subsequently, the reactions of **7**, **8** and **10** with *p*-tosylhydrazide yielded the corresponding *p*-tosylhydrazones **11**, **12** and **13**. We tried using EtOH as the solvent in this reaction, as described in the literature.[31] However, large amounts of the starting solid material always remained, even after extending the reaction times. To address the poor yields, the conditions were modified: a mixed benzene/ethanol (4:1) solvent was used to improve the solubility of the starting material and *p*-toluenesulphonic acid (PTSA) was added as a catalyst, giving *p*-tosylhydrazones **11**, **12** and **13** in good yields (82% for **11**, 77% for **12** and 85% for **13**).

Ring-B C_{60}-substituted derivatives **14**, **15** and **16** were prepared by the following procedure.[32] First, *p*-tosylhydrazones **11**, **12** and **13** were reacted with NaOMe in anhydrous pyridine for 20 min at room temperature. A solution of C_{60} in chlorobenzene was then added, and the mixture was stirred for 24 h at 70 °C. A mixture of the monoadduct, higher adducts and unreacted C_{60} was obtained and then purified by column chromatography to give the pure monoadducts **14**, **15** and **16**. Compound **16** was hydrolysed by concd HCl in a mixed solvent of CS_2/CH_3OH (1:1) to afford **17**.

In the reaction of C_{60} with *p*-tosylhydrazones, *p*-tosylhydrazones were first base-induced decomposed to afford diazo compounds, after which two mechanisms in the thermal reaction of C_{60} with diazo compounds are conceivable: (1) initial thermal decomposition of the diazo compounds to form carbenes followed by their concerted addition to the double 6,6 bond of fullerene and (2) initial 1,3-dipolar cycloaddition of diazo compounds to fullerene to form the cyclic pyrazoline intermediate followed by nitrogen elimination from the pyrazoline intermediate. Carbene additions produce only 6,6-closed

isomers[33] (methanofullerenes), whereas the latter pathway can afford a mixture of 5,6-open (fulleroid) and 6,6-closed isomers[34–36] (the ratio depending on the structure of the diazo compound and the reaction conditions). In most cases, 5,6-open isomers can be rearranged into the more thermodynamically stable 6,6-closed isomers by heating or photochemical isomerisation. In our experiment, no traces of the 5,6-open isomer were found and the only isolated product was the 6,6-closed isomer, even at a lower reaction temperature (40 °C) or in a shorter reaction time (3 h). Meanwhile the pyrazoline intermediate was never detected in the reaction products (Table 1). Thus, the carbene mechanism is realised in this reaction.

Table 1
Conditions[a] and yield of **16**

Run	Temp (°C)	Time (h)	Yield of **16** (%)
1	25	24	0 (0)[b]
2	40	9	5 (89)[b]
3	40	24	19 (70)[b]
4	60	3	16 (75)[b]
5	60	9	31 (71)[b]
6	60	24	38 (62)[b]
7	70	3	15 (72)[b]
8	70	9	30 (56)[b]
9	70	24	33 (49)[b]

[a] *p*-Tosylhydrazone, 2 equiv to C_{60}; NaOMe, 2.08 equiv to C_{60}; chlorobenzene.
[b] Based on converted C_{60}.

The ^{13}C NMR spectra of methanofullerenes **14**, **15**, **16** and **17**, due to the overlapping, exhibit only 44, 42, 44 and 46 resonance signals for C_{60}-sp^2 carbons, respectively (out of a maximum of 58 sp^2-carbon resonances). The two peaks at δ 77–86 ppm (83.77, 77.45 for **14**, 85.09, 78.15 for **15**, 84.62, 77.67 for **16** and 85.04, 78.05 for **17**) were assigned to the sp^3-hybridised bridgehead carbons on the cyclopropyl moiety.[37] This pattern is unambiguously diagnostic for a C_1 symmetric structure with a 6,6-junction.[37,38] The resonance signals at δ 17–56, δ 106–137 and approximately δ 164 ppm (C=O), together with the ^1H NMR results, indicated the presence of an *N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine moiety. In the IR spectra, the two sharp peaks at 1719–1776 cm^{-1} (1774, 1719 for **14**, 1775, 1719 for **15**, 1758, 1719 for **16** and 1776, 1719 for **17**) were attributed to the asymmetric and symmetric stretching vibration of the imide carbonyl (C=O) and the absorption peak at approximately 525 cm^{-1} (525 for **14**, 524 for **15**, 525 for **16** and 526 for **17**) was attributed to the fullerene skeleton. In the UV–vis spectra, the characteristic absorptions for the methanofullerenes were observed at approximately 430 and 700 nm.[32,39] Finally, the structures of **14**, **15**, **16** and **17** as monoadducts were supported by the matrix-assisted laser desorption/ionisation time-of-flight mass spectra (MALDI-TOF MS), which display the expected peaks at *m*/*z* 1316.2, 1301.5, 1329.2 and 1287.2, respectively.

3. Conclusion

In conclusion, the first synthesis of ring-B 6,6-closed-C_{60}-attached derivatives of *N*,*N*-(tetrachlorophthaloyl) dehydroabietylamine has been achieved from dehydroabietylamine, and the assigned structures of these compounds were confirmed based on the spectral data. Studies of the biological activities of these dehydroabietylamine derivatives and methanofullerene derivatives are currently underway in our laboratory.

4. Experimental

4.1. General

All chemicals and solvents were obtained from commercial sources and used as received or dried according to standard procedures. Column chromatography was performed on silica gel (ZCX II, 100–200 mesh). Chemical reactions were monitored by thin-layer chromatography using precoated silica gel GF254 plates. Melting points were determined on a XT-6 melting point apparatus and were uncorrected. NMR spectra were recorded on a Bruker AVANCE AV-500 or Bruker AVANCE AV-300 spectrometer with resonance frequencies of 300 or 500 MHz for ^1H NMR and 75 or 126 MHz for ^{13}C NMR, respectively. The chemical shifts were reported in δ (parts per million, TMS) and coupling constants in Hertz. Infrared spectra were recorded as KBr pellets on a Nicolet 360 FT-IR spectrometer, and UV–vis spectra were recorded on a Shimadzu UV-2550 UV–vis spectrometer. ESI mass spectra were obtained on an Agilent 1100 Capillary LC/Micromass Q-TOF micromass spectrometer. Matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectra were obtained using a Bruker Daltonics Autoflex III mass spectrometer with α-cyano-4-hydroxycinnamic acid (CHCA) as a matrix in negative-ion reflector mode. Microanalytical data were obtained on an Elementar Vario EL III elemental analyser.

4.2. *N*,*N*-(Tetrachlorophthaloyl)dehydroabietylamine (2)

A mixture of tetrachlorophthalic anhydride (5 g, 17.5 mmol), dehydroabietylamine (5 g, 17.5 mmol) and glacial acetic acid (60 mL) was stirred at 130 °C under nitrogen. After 2.5 h, the reaction mixture was cooled to room temperature and then poured into ice water (250 mL). The resulting precipitate was collected by filtration, washed with distilled water and ethanol and then dried in vacuo to give the crude product (8.35 g), which was purified by column chromatography on silica gel (petroleum ether/toluene, 2:1) to yield **2** as a white solid (7.11 g, 73%), mp 220–221 °C. IR (KBr) ν_{max}/cm^{-1} 2934, 2860, 1776, 1714, 1630, 1498, 1430, 1392, 1369, 1338, 1297, 1200, 1091, 1069, 879, 820, 736, 556, 476; ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J*=7.9 Hz, 1H, H-11), 6.96 (dd, *J*=8.2, 1.5 Hz, 1H, H-12), 6.91 (s, 1H, H-14), 3.68 (d, *J*=13.7 Hz, 1H, H-18), 3.55 (d, *J*=13.7 Hz, 1H, H-18), 2.98–2.96 (m, 2H, H-7), 2.81 (septet, *J*=6.9 Hz, 1H, H-15), 2.26 (br d, *J*=12.5 Hz, 1H, H-1β), 2.22–2.18 (m, 1H, H-6β), 1.86–1.79 (m, 1H, H-6α), 1.75–1.62 (m, 2H, H-2), 1.49 (dd, *J*=13.4, 1.2 Hz, 1H, H-5), 1.44–1.28 (m, 3H, H-1α, H-3), 1.23 (s, 3H, H-20), 1.21 (d, *J*=7.0 Hz, 6H, H-16, H-17), 1.05 (s, 3H, H-19); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.50 (2C=O, imide), 147.09 (C-9), 145.69 (C-13), 140.07 (2C, $-N(CO)_2C_6Cl_4$), 134.86 (C-8), 129.58 (2C, $-N(CO)_2C_6Cl_4$), 127.52 (2C, $-N(CO)_2C_6Cl_4$), 127.05 (C-14), 123.82 (C-11), 123.78 (C-12), 49.89 (C-18), 45.39 (C-5), 39.53 (C-4), 38.09 (C-1), 37.61 (C-10), 37.21 (C-3), 33.44 (C-15), 30.07(C-7), 25.81 (C-20), 23.96 (C-17), 23.94 (C-16), 19.45 (C-6), 19.06 (C-19), 18.45 (C-2); TOF MS (ES^-) *m*/*z* 524.3 ($[M(^{35}Cl_4)-27]^-$), 526.2 ($[M(^{35}Cl_3\ ^{37}Cl)-27]^-$), 528.2 ($[M(^{35}Cl_2\ ^{37}Cl_2)-27]^-$). Anal. Calcd for $C_{28}H_{29}Cl_4NO_2$ (553.3): C, 60.78; H, 5.28; N, 2.53. Found: C, 60.37; H, 5.35; N, 2.48.

4.3. 12-Acetyl-*N*,*N*(tetrachlorophthaloyl)dehydroabietylamine (3)

$AlCl_3$ (3.62 g, 27.1 mmol) and acetyl chloride (1.92 mL, 27.1 mmol) were added to a solution of compound **2** (5 g, 9.0 mmol) in CS_2 (60 mL). The mixture was stirred and heated at reflux for 5 h under nitrogen. The reaction mixture was cooled to room temperature and then poured into a mixture of crushed ice (70 g) and concd HCl (20 mL), allowed to stir for 10 min, and extracted with CH_2Cl_2 (2×30 mL). The combined organic extracts were washed with saturated solutions of $NaHCO_3$ (2×40 mL) and brine (2×40 mL), dried over anhydrous $MgSO_4$, and filtered. After the evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (cyclohexane/chloroform, 1:10) to yield **3** as a white solid (4.14 g, 77%), mp 230–231 °C. IR (KBr) ν_{max}/cm^{-1} 2926, 2858, 1778, 1716, 1681, 1552, 1431, 1394, 1369, 1344, 1262, 1198, 1092, 974, 885, 736, 560, 481; ^1H

NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1H, H-11), 7.09 (s, 1H, H-14), 3.70 (d, J=13.7 Hz, 1H, H-18), 3.57 (d, J=13.7 Hz, 1H, H-18), 3.47 (septet, J=7.0 Hz, 1H, H-15), 3.05–2.95 (m, 2H, H-7), 2.53 (s, 3H, $-COCH_3$), 2.29 (br d, J=12.8 Hz, 1H, H-1β), 2.27–2.22 (m, 1H, H-6β), 1.90–1.79 (m, 1H, H-6α), 1.79–1.66 (m, 2H, H-2), 1.54 (d, J=13.5 Hz, 1H, H-5), 1.41–1.30 (m, 3H, H-1α, H-3), 1.25 (s, 3H, H-20), 1.23 (d, J=6.7 Hz, 3H, H-17), 1.20 (d, J=6.7 Hz, 3H, H-16), 1.08 (s, 3H, H-19); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.19 ($-COCH_3$), 164.51 (2C=O, imide), 146.67 (C-9), 144.89 (C-12), 140.12 (2C, $-N(CO)_2C_6Cl_4$), 138.90 (C-13), 136.29 (C-8), 129.60 (2C, $-N(CO)_2C_6Cl_4$), 127.47 (2C, $-N(CO)_2C_6Cl_4$), 127.12 (C-14), 123.96 (C-11), 49.75 (C-18), 45.23 (C-5), 39.48 (C-4), 37.97 (C-1), 37.54 (C-10), 37.03 (C-3), 30.45 (C-15), 30.03 (C-7), 28.68 ($-COCH_3$), 25.79 (C-20), 24.18 (C-17), 24.03 (C-16), 19.21 (C-6), 19.05 (C-19), 18.31 (C-2); TOF MS (ES$^+$) m/z 594.1 ([M($^{35}Cl_4$)+H]$^+$), 596.1 ([M($^{35}Cl_3$ ^{37}Cl)+H]$^+$), 598.1 ([M($^{35}Cl_2$ $^{37}Cl_2$)+H]$^+$), 600.1 ([M($^{35}Cl^{37}Cl_3$)+H]$^+$). Anal. Calcd for $C_{30}H_{31}Cl_4NO_3$ (595.4): C, 60.52; H, 5.25; N, 2.35. Found: C, 60.15; H, 5.29; N, 2.30.

4.4. 12-Acetoxy-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine (4)

Under vigorous stirring at 0 °C, 65% *m*-chloroperbenzoic acid (4.46 g, 16.8 mmol, 2 equiv) and *p*-toluenesulphonic acid hydrate (120.1 mg, 0.697 mmol, 0.083 equiv) were carefully added to a solution of **3** (5 g, 8.4 mmol) in CH_2Cl_2 (60 mL). The mixture was stirred at room temperature for 48 h and then filtered. The filter cake was washed with CH_2Cl_2 (20 mL). The filtrate was evaporated under reduced pressure, and the solid residue was dissolved in ethyl acetate (100 mL). The resulting solution was washed successively with saturated solutions of $Na_2S_2O_3$ (2×30 mL), $NaHCO_3$ (2×30 mL) and brine (2×30 mL), dried over anhydrous $MgSO_4$ and filtered. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (chloroform) to afford **4** as a white solid (3.64 g, 71%), mp 220–221 °C. IR (KBr) ν_{max}/cm^{-1} 2933, 2866, 1757, 1712, 1496, 1433, 1395, 1369, 1343, 1206, 1163, 1091, 1040, 1014, 908, 883, 785, 735, 676, 622, 579, 502, 469; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 1H, H-14), 6.77 (s, 1H, H-11), 3.70 (d, J=13.7 Hz, 1H, H-18), 3.50 (d, J=13.7 Hz, 1H, H-18), 2.99–2.92 (m, 2H, H-7), 2.89 (septet, J=6.9 Hz, 1H, H-15), 2.28 (s, 3H, CH_3COO-), 2.25–2.17 (m, 1H, H-6β), 2.13 (br d, J=12.2 Hz, 1H, H-1β), 1.86–1.75 (m, 1H, H-6α), 1.70–1.60 (m, 2H, H-2), 1.50 (dd, J=13.4, 0.9 Hz, 1H, H-5), 1.39–1.25 (m, 3H, H-1α, H-3), 1.22 (s, 3H, H-20), 1.18 (d, J=6.7 Hz, 3H, H-17), 1.15 (d, J=6.7 Hz, 3H, H-16), 1.04 (s, 3H, H-19); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.00 (CH_3COO-), 164.52 (2C=O, imide), 148.21 (C-12), 146.00 (C-9), 140.06 (2C, $-N(CO)_2C_6Cl_4$), 136.84 (C-13), 133.03 (C-8), 129.58 (2C, $-N(CO)_2C_6Cl_4$), 127.48 (2C, $-N(CO)_2C_6Cl_4$), 127.12 (C-14), 117.47 (C-11), 49.59 (C-18), 44.54 (C-5), 39.49 (C-4), 37.93 (C-1), 37.54 (C-10), 37.10 (C-3), 29.43 (C-7), 27.11 (C-15), 25.71 (C-20), 23.01 (C-17), 22.92 (C-16), 20.93 (CH_3COO-), 19.32 (C-6), 19.08 (C-19), 18.29 (C-2); TOF MS (ES$^+$) m/z 627.2 ([M$^+$($^{35}Cl_4$)+H_2O]), 629.2 ([M$^+$($^{35}Cl_3$ ^{37}Cl)+H_2O]), 631.2 ([M$^+$($^{35}Cl_2$ $^{37}Cl_2$)+H_2O]), 633.2 ([M$^+$($^{35}Cl^{37}Cl_3$)+H_2O]). Anal. Calcd for $C_{30}H_{31}Cl_4NO_4$ (611.4): C, 58.94; H, 5.11; N, 2.29. Found: C, 58.42; H, 4.98; N, 2.20.

4.5. 12-Nitro-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine (6) and 14-nitro-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine (5)

Montmorillonite clay (K10, 30 g) was added to a solution of copper(II) nitrate trihydrate (28 g) in acetone (375 mL) with vigorous stirring. The resulting suspension was placed on a rotary evaporator, and the solvent was removed under reduced pressure on a water bath at 50 °C. After 30 min, the dry solid crust adhering to the walls of the flask was flaked off and coarsely crushed with a spatula. Evaporation continued for another 30 min to produce clay-supported copper(II) nitrate (claycop) as a light-blue powder (58 g).[24]

Compound **2** (5.54 g, 10.0 mmol) was added to a suspension of claycop (4.80 g) in a mixture of CH_2Cl_2 (30 mL) and acetic anhydride (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 2 h and then filtered. The filter cake was washed with CH_2Cl_2 (100 mL). The combined organic portions were washed with water, dried over anhydrous Na_2SO_4, and filtered. After the removal of the solvent under reduced pressure, the residue was separated by column chromatography on silica gel (petroleum ether/toluene, 1:1) to give a mixture of **6** and **5** (3:2, 3.87 g, 65%).

4.6. Preparation of compounds 7 and 8

To a suspension of CrO_3 (45 mg, 0.45 mmol, 0.05 equiv) in CH_2Cl_2 (90 mL) were added 65% *t*-BuOOH (11.6 mL, 72.3 mmol, 8 equiv) and pyridine (0.073 mL, 0.904 mmol, 0.1 equiv). The mixture was stirred for 3 min at room temperature. Next, compound **4** or a mixture of compounds **6** and **5** (9.035 mmol) was added. After 25 h of stirring at room temperature, the reaction mixture was concentrated to approximately 15 mL in vacuo at 30 °C and then poured into methanol (60 mL). The precipitate formed was collected by filtration and washed with methanol to give the crude product, which was purified by column chromatography on silica gel to afford compound **8** or **7**.

*4.6.1. 12-Nitro-7-oxo-N,N-(tetrachlorophthaloyl)dehydroabietylamine (**7**).* The crude product was purified by column chromatography on silica gel (toluene) to afford **7** as a white solid (2.11 g, 38%), mp 168–170 °C. IR (KBr) ν_{max}/cm^{-1} 2966, 2932, 2870, 1780, 1722, 1691, 1611, 1526, 1461, 1434, 1368, 1340, 1294, 1251, 1196, 1093, 888, 815, 738, 628, 580, 499; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H, H-11), 7.55 (s, 1H, H-14), 3.59 (d, J=14.0 Hz, 1H, H-18), 3.55 (d, J=14.0 Hz, 1H, H-18), 3.30–3.22 (m, 1H, H-15), 3.19 (dd, J=18.3, 3.7 Hz, 1H, H-6β), 2.79 (dd, J=18.3, 14.0 Hz, 1H, H-6α), 2.28 (br d, J=12.5 Hz, 1H, H-1β), 1.96 (dd, J=14.0, 3.7 Hz, 1H, H-5), 1.79–1.69 (m, 2H, H-2), 1.59–1.50 (m, 2H, H-1α, H-3), 1.43–1.34 (m, 1H, H-3), 1.32 (d, J=7.0 Hz, 3H, H-17), 1.31 (s, 3H, H-20), 1.28 (d, J=7.0 Hz, 3H, H-16), 1.14 (s, 3H, H-19); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.85 (C=O, C-7), 164.44 (2C=O, imide), 153.94 (C-12), 152.94 (C-9), 140.32 (C-8), 140.02 (2C, $-N(CO)_2C_6Cl_4$), 133.13 (C-13), 129.79 (2C, $-N(CO)_2C_6Cl_4$), 127.43 (C-14), 127.38 (2C, $-N(CO)_2C_6Cl_4$), 118.87 (C-11), 49.24 (C-18), 44.76 (C-5), 39.21 (C-4), 38.11 (C-10), 37.12 (C-1), 36.61 (C-3), 36.25 (C-6), 28.47 (C-15), 24.10 (C-20), 23.49 (C-17), 23.34 (C-16), 18.86 (C-19), 17.75 (C-2); TOF MS (ES$^+$) m/z 611.1 ([M($^{35}Cl_4$)+H]$^+$), 613.1 ([M($^{35}Cl_3$ ^{37}Cl)+H]$^+$), 615.1 ([M($^{35}Cl_2$ $^{37}Cl_2$)+H]$^+$), 617.1 ([M($^{35}Cl^{37}Cl_3$)+H]$^+$), 619.1 ([M($^{37}Cl_4$)+H]$^+$). Anal. Calcd for $C_{28}H_{26}Cl_4N_2O_5$ (612.3): C, 54.92; H, 4.28; N, 4.57. Found: C, 54.28; H, 4.24; N, 4.44.

*4.6.2. 12-Acetoxy-7-oxo-N,N-(tetrachlorophthaloyl)dehydroabietylamine (**8**).* The crude product was purified by column chromatography on silica gel (chloroform/acetone, 20:0.3) to afford **8** as a white solid (3.70 g, 66%), mp 160–162 °C. IR (KBr) ν_{max}/cm^{-1} 2962, 2927, 2871, 1756, 1716, 1680, 1608, 1562, 1433, 1404, 1374, 1335, 1299, 1267, 1201, 1165, 1120, 1093, 1039, 1016, 932, 909, 865, 786, 759, 630, 587, 502; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H, H-14), 6.95 (s, 1H, H-11), 3.58 (s, 2H, H-18), 3.15 (dd, J=18.2, 3.5 Hz, 1H, H-6β), 3.00 (septet, J=6.7 Hz, 1H, H-15), 2.75 (dd, J=18.2, 13.9 Hz, 1H, H-6α), 2.34 (s, 3H, CH_3COO-), 2.21 (br d, J=12.8 Hz, 1H, H-1β), 1.99 (dd, J=13.9, 3.5 Hz, 1H, H-5), 1.75–1.68 (m, 2H, H-2), 1.58–1.50 (m, 2H, H-1α, H-3), 1.43–1.35 (m, 1H, H-3), 1.29 (s, 3H, H-20), 1.25 (d, J=7.0 Hz, 3H, H-17), 1.21 (d, J=6.7 Hz, 3H, H-16), 1.14 (s, 3H, H-19); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.52 (C=O, C-7), 169.19 (CH_3COO-), 164.42 (2C=O, imide), 154.47 (C-12), 152.51 (C-9), 140.15 (2C, $-N(CO)_2C_6Cl_4$), 138.59 (C-8), 129.69 (2C, $-N(CO)_2C_6Cl_4$),

129.02 (C-13), 127.44 (2C, $-N(CO)_2C_6Cl_4$), 126.72 (C-14), 117.43 (C-11), 49.26 (C-18), 44.60 (C-5), 39.19 (C-4), 37.87 (C-10), 37.10 (C-1), 36.78 (C-3), 36.20 (C-6), 27.30 (C-15), 24.12 (C-20), 22.77 (C-17), 22.69 (C-16), 20.94 (CH_3COO-), 18.85 (C-19), 17.85 (C-2); TOF MS (ES^+) *m*/*z* 624.1 ($[M(^{35}Cl_4)+H]^+$), 626.1 ($[M(^{35}Cl_3\,^{37}Cl)+H]^+$), 628.1 ($[M(^{35}Cl_2\,^{37}Cl_2)+H]^+$), 630.1 ($[M(^{35}Cl^{37}Cl_3)+H]^+$), 632.1 ($[M(^{37}Cl_4)+H]^+$). Anal. Calcd for $C_{30}H_{29}Cl_4NO_5$ (625.4): C, 57.62; H, 4.67; N, 2.24. Found: C, 57.34; H, 4.66; N, 2.06.

4.7. 12-Hydroxy-7-oxo-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine (9)

Concd HCl (10 mL) was added to a solution of compound **8** (5 g, 8.0 mmol) in a mixture of $CHCl_3$ (30 mL) and MeOH (60 mL). The reaction mixture was stirred and heated at reflux for 1.5 h under nitrogen, concentrated to approximately 40 mL in vacuo at 35 °C and cooled. The resulting precipitate was collected by filtration, washed with absolute methanol (10 mL), and dried in vacuo. The crude product was purified by column chromatography on silica gel (chloroform/ethyl acetate, 20:1) to give **9** as a white solid (3.70 g, 79%), mp 292–294 °C. IR (KBr) ν_{max}/cm^{-1} 3414, 2936, 2867, 1778, 1718, 1652, 1596, 1571, 1501, 1459, 1434, 1371, 1342, 1302, 1269, 1199, 1175, 1094, 1041, 977, 915, 890, 869, 739, 662, 632, 574, 534, 497, 428; ^1H NMR (500 MHz, $CDCl_3$/DMSO-d_6) δ 7.66 (s, 1H, H-14), 6.75 (s, 1H, H-11), 3.52 (d, *J*=14.1 Hz, 1H, H-18), 3.30 (d, *J*=14.1 Hz, 1H, H-18), 3.13 (septet, *J*=7.0 Hz, 1H, H-15), 2.95 (dd, *J*=17.8, 3.4 Hz, 1H, H-6β), 2.57 (dd, *J*=17.8, 13.8 Hz, 1H, H-6α), 2.05 (br d, *J*=12.0 Hz, 1H, H-1β), 1.92 (dd, *J*=13.7, 3.4 Hz, 1H, H-5), 1.71–1.57 (m, 2H, H-2), 1.50–1.30 (m, 3H, H-1α, H-3), 1.17 (s, 3H, H-20), 1.16 (d, *J*=6.9 Hz, 3H, H-17), 1.13 (d, *J*=6.9 Hz, 3H, H-16), 1.05 (s, 3H, H-19); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6) δ 196.06 (C=O, C-7), 163.48 (2C=O, imide), 159.66 (C-12), 154.76 (C-9), 138.94 (2C, $-N(CO)_2C_6Cl_4$), 132.54 (C-8), 128.50 (2C, $-N(CO)_2C_6Cl_4$), 126.81 (2C, $-N(CO)_2C_6Cl_4$), 125.23 (C-14), 122.17 (C-13), 108.49 (C-11), 48.77 (C-18), 44.52 (C-5), 38.24 (C-4), 36.93 (C-10), 36.28 (C-1), 35.93 (C-3), 35.22 (C-6), 25.72 (C-15), 23.15 (C-20), 21.65 (C-17), 21.49 (C-16), 17.93 (C-19), 17.15 (C-2); TOF MS (ES^+) *m*/*z* 582.1 ($[M(^{35}Cl_4)+H]^+$), 584.1 ($[M(^{35}Cl_3\,^{37}Cl)+H]^+$), 586.1 ($[M(^{35}Cl_2\,^{37}Cl_2)+H]^+$), 588.1 ($[M(^{35}Cl^{37}Cl_3)+H]^+$), 590.1 ($[M(^{37}Cl_4)+H]^+$). Anal. Calcd for $C_{28}H_{27}Cl_4NO_4$ (583.3): C, 57.65; H, 4.67; N, 2.40. Found: C, 57.35; H, 4.62; N, 2.18.

4.8. 12-Methoxy-7-oxo-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine (10)

A mixture of compound **9** (2 g, 3.43 mmol), CH_3I (2.44 g, 17.15 mmol), K_2CO_3 (0.95 g, 6.86 mmol) and dry acetone (40 mL) was stirred and heated at reflux for 5 h under nitrogen. After evaporation of the solvent under reduced pressure, water (50 mL) was added and extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were washed with water (40 mL) and brine (40 mL), dried over anhydrous $MgSO_4$ and filtered. After the removal of the solvent under reduced pressure, the residue was column chromatographed on silica gel (chloroform/acetone, 20:0.3) to afford **10** as a white solid (1.82 g, 89%), mp 156–158 °C. IR (KBr) ν_{max}/cm^{-1} 2932, 2866, 1779, 1722, 1671, 1599, 1561, 1494, 1460, 1436, 1370, 1338, 1274, 1255, 1196, 1172, 1124, 1093, 1068, 1043, 961, 917, 889, 850, 803, 738, 658, 629, 562, 496, 449; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H, H-14), 6.74 (s, 1H, H-11), 3.90 (s, 3H, CH_3O-), 3.68 (d, *J*=13.7 Hz, 1H, H-18), 3.51 (d, *J*=13.5 Hz, 1H, H-18), 3.26 (septet, *J*=7.0 Hz, 1H, H-15), 3.01 (dd, *J*=17.9, 3.5 Hz, 1H, H-6β), 2.74 (dd, *J*=17.9, 13.9 Hz, 1H, H-6α), 2.31 (br d, *J*=12.2 Hz, 1H, H-1β), 2.02 (dd, *J*=13.9, 3.5 Hz, 1H, H-5), 1.78–1.71 (m, 2H, H-2), 1.62–1.50 (m, 2H, H-1α, H-3), 1.48–1.38 (m, 1H, H-3), 1.31 (s, 3H, H-20), 1.24 (d, *J*=7.0 Hz, 3H, H-17), 1.21 (d, *J*=7.0 Hz, 3H, H-16), 1.13 (s, 3H, H-19); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.22 (C=O, C-7), 164.38 (2C=O, imide), 161.68 (C-12), 155.74 (C-9), 140.16 (2C, $-N(CO)_2C_6Cl_4$), 135.48 (C-8), 129.67 (2C, $-N(CO)_2C_6Cl_4$), 127.44 (2C, $-N(CO)_2C_6Cl_4$), 125.90 (C-14), 123.99 (C-13), 104.11(C-11), 55.41 (CH_3O-), 49.85 (C-18), 45.84 (C-5), 39.20 (C-4), 38.27 (C-10), 37.32 (C-1), 36.84 (C-3), 36.14 (C-6), 26.56 (C-15), 23.99 (C-20), 22.50 (C-17), 22.33 (C-16), 18.70 (C-19), 17.99 (C-2); TOF MS (ES^+) *m*/*z* 596.1 ($[M(^{35}Cl_4)+H]^+$), 598.1 ($[M(^{35}Cl_3\,^{37}Cl)+H]^+$), 600.1 ($[M(^{35}Cl_2\,^{37}Cl_2)+H]^+$), 602.1 ($[M(^{35}Cl^{37}Cl_3)+H]^+$), 604.1 ($[M(^{37}Cl_4)+H]^+$). Anal. Calcd for $C_{29}H_{29}Cl_4NO_4$ (597.4): C, 58.31; H, 4.89; N, 2.34. Found: C, 57.26; H, 4.95; N, 2.28.

4.9. Preparation of compounds 11–13

Compound **7**, **8** or **10** (5.29 mmol) was dissolved in a mixture of benzene (120 mL) and ethanol (30 mL). Next, *p*-toluenesulphonyl hydrazide (1.65 g, 8.86 mmol, 1.68 equiv) and *p*-toluenesulphonic acid (82 mg, 0.48 mmol, 0.09 equiv) were added successively. The reaction mixture was stirred and refluxed for 8 h under nitrogen, concentrated to approximately 60 mL under reduced pressure and cooled in an ice bath. The resulting precipitate was collected by filtration and washed with ethanol to give the crude product, which was purified by column chromatography on silica gel to afford **11**, **12** or **13**.

*4.9.1. 12-Nitro-N,N(tetrachlorophthaloyl)dehydroabietylamine p-tosylhydrazone (**11**).* The crude product was purified by column chromatography on silica gel (toluene/ethyl acetate, 20:0.4) to afford **11** as a white solid (3.40 g, 82%), mp 220–221 °C. IR (KBr) ν_{max}/cm^{-1} 3258, 2931, 2859, 1779, 1719, 1627, 1597, 1559, 1519, 1454, 1434, 1393, 1367, 1341, 1298, 1201, 1165, 1091, 1039, 930, 814, 738, 711, 673, 578, 548, 500, 468; ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H, NH), 8.01 (d, *J*=8.4 Hz, 2H, *o*-$HArSO_2-$), 7.97 (s, 1H, H-14), 7.48 (s, 1H, H-11), 7.36 (d, *J*=8.2 Hz, 2H, *m*-$HArSO_2-$), 3.63 (d, *J*=14.1 Hz, 1H, H-18), 3.49 (d, *J*=14.1 Hz, 1H, H-18), 3.34 (septet, *J*=6.8 Hz, 1H, H-15), 3.22 (dd, *J*=17.5, 4.1 Hz, 1H, H-6β), 2.45 (s, 3H, CH_3ArSO_2-), 2.41 (dd, *J*=17.1, 13.4 Hz, 1H, H-6α), 2.19 (br d, *J*=12.5 Hz, 1H, H-1β), 1.73–1.64 (m, 2H, H-2), 1.60–1.54 (m, 2H, H-1α, H-3), 1.45 (dd, *J*=13.4, 4.1 Hz, 1H, H-5), 1.44–1.36 (m, 1H, H-3), 1.31 (d, *J*=6.8 Hz, 3H, H-17), 1.23 (d, *J*=7.0 Hz, 3H, H-16), 1.16 (s, 3H, H-20), 1.11 (s, 3H, H-19); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.50 (2C=O, imide), 150.80 (C-12), 150.23 (C=N), 149.52 (C-9), 144.34 (*p*-$ArSO_2-$), 140.32 (2C, $-N(CO)_2C_6Cl_4$), 139.82 (C-8), 135.34 (*p*-$ArCH_3$), 133.88 (C-13), 129.74 (2C, $-N(CO)_2C_6Cl_4$), 129.57 (2C, *m*-$ArSO_2-$), 128.47 (2C, *o*-$ArSO_2-$), 127.27 (2C, $-N(CO)_2C_6Cl_4$), 124.64 (C-14), 118.79 (C-11), 48.99 (C-18), 42.38 (C-5), 39.43 (C-4), 37.27 (C-10), 37.07 (C-1), 37.01 (C-3), 28.28 (C-15), 23.52 (C-20), 23.47 (C-6), 23.42 (C-16, C-17), 21.63 (CH_3ArSO_2-), 19.12 (C-19), 17.78 (C-2); TOF MS (ES^+) *m*/*z* 779.2 ($[M(^{35}Cl_4)+H]^+$), 781.1 ($[M(^{35}Cl_3\,^{37}Cl)+H]^+$), 783.1($[M(^{35}Cl_2\,^{37}Cl_2)+H]^+$), 785.2 ($[M(^{35}Cl^{37}Cl_3)+H]^+$). Anal. Calcd for $C_{35}H_{34}Cl_4N_4O_6S$ (780.5): C, 53.86; H, 4.39; N, 7.18. Found: C, 53.52; H, 4.29; N, 7.02.

*4.9.2. 12-Acetoxy-N,N-(tetrachlorophthaloyl)dehydroabietylamine p-tosylhydrazone (**12**).* The crude product was purified by column chromatography on silica gel (toluene/ethyl acetate, 20:1.2) to afford **12** as a white solid (3.22 g, 77%), mp 180–181 °C. IR (KBr) ν_{max}/cm^{-1} 3235, 2927, 2868, 1759, 1719, 1622, 1599, 1490, 1433, 1371, 1333, 1297, 1201, 1163, 1122, 1085, 1034, 910, 809, 737, 665, 574, 549, 500, 470; ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J*=8.2 Hz, 2H, *o*-$HArSO_2-$), 7.96 (s, 1H, NH), 7.85 (s, 1H, H-14), 7.35 (d, *J*=7.9 Hz, 2H, *m*-$HArSO_2-$), 6.76 (s, 1H, H-11), 3.67 (d, *J*=14.0 Hz, 1H, H-18), 3.45 (d, *J*=14.0 Hz, 1H, H-18), 3.23 (dd, *J*=17.2, 4.1 Hz, 1H, H-6β), 2.92 (septet, 6.9 Hz, 1H, H-15), 2.45 (s, 3H, CH_3ArSO_2-), 2.38 (dd, *J*=17.4, 13.5 Hz, 1H, H-6α), 2.30 (s, 3H, CH_3COO-), 2.10 (br d, *J*=13.1 Hz, 1H, H-1β), 1.72–1.61 (m, 3H, H-2, H-1α), 1.57 (br d, *J*=13.7 Hz, 1H, H-3), 1.49 (dd, *J*=13.4, 4.0 Hz, 1H, H-5), 1.43–1.36 (m, 1H, H-3), 1.24 (d, *J*=7.0 Hz, 3H, H-17), 1.17 (d, *J*=7.0 Hz, 3H, H-16), 1.15 (s, 3H, H-20), 1.11 (s, 3H, H-19); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.61 (CH_3COO-),

164.51 (2C=O, imide), 152.95 (C-12), 150.11 (C=N), 149.63 (C-9), 143.95 (*p*-ArSO$_2$–), 140.13 (2C, –N(CO)$_2$C$_6$Cl$_4$), 137.68 (C-8), 135.53 (*p*-ArCH$_3$), 129.66 (2C, –N(CO)$_2$C$_6$Cl$_4$), 129.42 (2C, *m*-ArSO$_2$–), 128.45 (2C, *o*-ArSO$_2$–), 128.05 (C-13), 127.36 (2C, –N(CO)$_2$C$_6$Cl$_4$), 124.08 (C-14), 116.71 (C-11), 48.94 (C-18), 41.92 (C-5), 39.46 (C-4), 37.20 (C-10), 37.07 (C-1, C-3), 27.29 (C-15), 23.64 (C-20), 23.56 (C-6), 22.83 (C-17), 22.63 (C-16), 21.58 (*C*H$_3$ArSO$_2$–), 20.92 (*C*H$_3$COO–), 19.17 (C-19), 17.92 (C-2); TOF MS (ES$^+$) *m*/*z* 792.2 ([M(^{35}Cl$_4$)+H]$^+$), 794.2 ([M(^{35}Cl$_3$ ^{37}Cl)+H]$^+$), 796.2 ([M(^{35}Cl$_2$ ^{37}Cl$_2$)+H]$^+$), 798.2 ([M(^{35}Cl^{37}Cl$_3$)+H]$^+$), 780.2 ([M(^{37}Cl$_4$)+H]$^+$). Anal. Calcd for C$_{37}$H$_{37}$Cl$_4$N$_3$O$_6$S (793.6): C, 56.00; H, 4.70; N, 5.29. Found: C, 55.60; H, 4.76; N, 5.07.

*4.9.3. 12-Methoxy-N,N-(tetrachlorophthaloyl)dehydroabietylamine p-tosylhydrazone (**13**).* The crude product was purified by column chromatography on silica gel (chloroform/ethyl acetate, 20:0.4) to afford **13** as a white solid (3.45 g, 85%), mp 182–184 °C. IR (KBr) ν_{max}/cm^{-1} 3227, 2927, 2864, 1779, 1720, 1654, 1594, 1496, 1458, 1436, 1379, 1330, 1276, 1240, 1194, 1164, 1087, 1042, 954, 913, 848, 809, 738, 698, 662, 623, 548, 501, 475; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.02 (d, *J*=8.3 Hz, 2H, *o*-HArSO$_2$–), 7.91 (s, 1H, NH), 7.80 (s, 1H, H-14), 7.32 (d, *J*=8.1 Hz, 2H, *m*-HArSO$_2$–), 6.60 (s, 1H, H-11), 3.79 (s, 3H, CH$_3$O–), 3.62 (d, *J*=14.0 Hz, 1H, H-18), 3.50 (d, *J*=14.0 Hz, 1H, H-18), 3.27–3.11 (m, 2H, H-6β, H-15), 2.42 (s, 3H, C*H*$_3$ArSO$_2$–), 2.40 (dd, *J*=16.7, 13.1 Hz, 1H, H-6α), 2.20 (br d, *J*=12.3 Hz, 1H, H-1β), 1.78–1.64 (m, 2H, H-2), 1.62–1.35 (m, 4H, H-1α, H-5, H-3), 1.22 (d, *J*=6.9 Hz, 3H, H-17), 1.18 (d, *J*=6.8 Hz, 3H, H-16), 1.14 (s, 3H, H-20), 1.12 (s, 3H, H-19); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.44 (2C=O, imide), 158.89 (C-12), 154.26 (C-9), 150.64 (C=N), 143.80 (*p*-ArSO$_2$–), 140.13 (2C, –N(CO)$_2$C$_6$Cl$_4$), 135.53 (*p*-ArCH$_3$), 134.91 (C-8), 129.61 (2C, –N(CO)$_2$C$_6$Cl$_4$), 129.32 (2C, *m*-ArSO$_2$–), 128.55 (2C, *o*-ArSO$_2$–), 127.29 (2C, –N(CO)$_2$C$_6$Cl$_4$), 123.46 (C-13), 122.18 (C-8), 103.98 (C-11), 55.25 (CH$_3$O–), 49.37 (C-18), 43.09 (C-5), 39.45 (C-4), 37.43 (C-10), 37.24 (C-1), 37.16 (C-3), 26.52 (C-15), 23.62 (C-20, C-6), 22.44 (C-17), 22.40 (C-16), 21.56 (*C*H$_3$ArSO$_2$–), 19.03 (C-19), 18.02 (C-2); TOF MS (ES$^+$) *m*/*z* 764.2 ([M(^{35}Cl$_4$)+H]$^+$), 766.2 ([M(^{35}Cl$_3$ ^{37}Cl)+H]$^+$), 768.2 ([M(^{35}Cl$_2$ ^{37}Cl$_2$)+H]$^+$), 770.2 ([M(^{35}Cl^{37}Cl$_3$)+H]$^+$), 772.2 ([M(^{37}Cl$_4$)+H]$^+$). Anal. Calcd for C$_{36}$H$_{37}$Cl$_4$N$_3$O$_5$S (765.6): C, 56.48; H, 4.87; N, 5.49. Found: C, 55.69; H, 4.92; N, 5.23.

4.10. Preparation of compounds 14 and 15

Compound **11** or **13** (0.834 mmol) was dissolved in dry pyridine (10 mL) in a dried three-necked flask under nitrogen flow. Next, NaOMe (46.9 mg, 0.867 mmol) was added and the mixture was stirred for 20 min at room temperature. A solution of C$_{60}$ (300 mg, 0.417 mmol) in dry chlorobenzene (80 mL) was added, and the mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel to give the product **14** or **15**.

*4.10.1. Ring-B [6,6]-closed-C$_{60}$-adduct of 12-nitro-N,N-(tetrachlorophthaloyl)dehydroabietylamine (**14**).* The residue was purified by column chromatography on silica gel, pre-eluted with CS$_2$ to remove unreacted C$_{60}$ (91.4 mg) and then with CS$_2$/CHCl$_3$ (3:1) to give **14** as a dark-brown solid (200.9 mg, 37%; or 53% based on converted C$_{60}$). IR (KBr) ν_{max}/cm^{-1} 3445, 2922, 2856, 1774, 1719, 1647, 1558, 1514, 1459, 1427, 1365, 1336, 1286, 1189, 1069, 895, 738, 555, 525, 471; UV–vis (CHCl$_3$) λ_{max} (nm): 693.00, 494.00, 433.50; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.65 (s, 1H, H-14), 7.84 (s, 1H, H-11), 3.82 (d, *J*=13.9 Hz, 1H, H-18), 3.68–3.63 (m, 2H, H-18, H-6β), 3.57–3.51 (m, 2H, H-6α, H-15), 2.39 (br d, *J*=12.4 Hz, 1H, H-1β), 1.92 (dd, *J*=10.5, 9.0 Hz, 1H, H-5), 1.89–1.78 (m, 5H, H-20, H-2), 1.78–1.70 (m, 1H, H-1α), 1.64 (br d, *J*=13.1 Hz, 1H, H-3), 1.50–1.42 (m, 1H, H-3), 1.36 (d, *J*=6.7 Hz, 3H, H-17), 1.34 (s, 3H, H-19), 1.33 (d, *J*=6.7 Hz, 3H, H-16); ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.59 (2C=O, imide), 151.89 (C-12), 149.44, 149.20 (C-9), 148.50, 147.04, 146.61, 145.66, 145.63, 145.40, 145.36, 144.97, 144.92, 144.90, 144.85, 144.82, 144.78, 144.75, 144.48, 144.45, 144.03, 143.97, 143.92, 143.75, 143.39, 143.30, 143.24, 143.17, 143.14, 143.06, 143.00, 142.90, 142.28, 142.17, 142.14, 142.11, 141.79, 141.41, 141.24, 141.21, 140.99, 140.48 (2C, –N(CO)$_2$C$_6$Cl$_4$), 140.45, 139.50 (C-13), 138.61, 138.40, 138.22, 137.92, 137.75, 129.84 (2C, –N(CO)$_2$C$_6$Cl$_4$ and C-8), 127.46 (2C, –N(CO)$_2$C$_6$Cl$_4$ and C-14), 119.22 (C-11), 83.77 (C$_{60}$-sp^3), 77.45 (C$_{60}$-sp^3), 49.98 (C-18), 47.97 (C-5), 43.42 (C-7), 40.87 (C-4), 39.23 (C-1), 39.08 (C-10), 37.28 (C-3), 28.83 (C-15), 27.99 (C-6), 23.88 (C-17), 23.61 (C-16), 22.13 (C-20), 19.20 (C-19), 17.94 (C-2); MALDI-TOF MS (matrix: CHCA, reflectron negative) *m*/*z* 1314.2 ([M(^{35}Cl$_4$)]$^-$), 1316.2 ([M(^{35}Cl$_3$ ^{37}Cl)]$^-$), 1318.2 ([M(^{35}Cl$_2$ ^{37}Cl$_2$)]$^-$), 1320.2 ([M(^{35}Cl^{37}Cl$_3$)]$^-$). Anal. Calcd for C$_{88}$H$_{26}$Cl$_4$N$_2$O$_4$ (1316.97): C, 80.26; H, 1.99; N, 2.13. Found: C, 79.88; H, 2.05; N, 1.98.

*4.10.2. Ring-B [6,6]-closed-C$_{60}$-adduct of 12-methoxy-N,N-(tetrachlorophthaloyl)dehydroabietylamine (**15**).* The residue was purified by column chromatography on silica gel, pre-eluted with CS$_2$ to remove unreacted C$_{60}$ (85.9 mg) and then with CS$_2$/CHCl$_3$ (10:0.5) to give **15** as a dark-brown solid (217.3 mg, 40%; or 57% based on converted C$_{60}$). IR (KBr) ν_{max}/cm^{-1} 3426, 2922, 2853, 1775, 1719, 1623, 1563, 1545, 1494, 1460, 1425, 1367, 1325, 1263, 1047, 893, 737, 672, 553, 524, 474; UV–vis (CHCl$_3$) λ_{max} (nm): 697.00, 492.50, 436.50; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.38 (s, 1H, H-14), 7.01 (s, 1H, H-11), 3.93 (s, 3H, CH$_3$O–), 3.89 (d, *J*=13.5 Hz, 1H, H-18), 3.63 (dd, *J*=14.1, 10.5 Hz, 1H, H-6β), 3.59 (d, *J*=13.7 Hz, 1H, H-18), 3.43–3.35 (m, 2H, H-6α, H-15), 2.38 (br d, *J*=10.1 Hz, 1H, H-1β), 2.01 (t, *J*=9.5 Hz, 1H, H-5), 1.92–1.78 (m, 6H, H-20, H-2, H-1α), 1.62–1.49 (m, 2H, H-3), 1.31 (s, 3H, H-19), 1.25 (d, *J*=6.7 Hz, 3H, H-17), 1.24 (d, *J*=6.7 Hz, 3H, H-16); ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.52 (2C=O, imide), 156.08 (C-12), 151.44 (C-9), 150.77, 150.00, 148.21, 147.79, 146.03, 145.98, 145.28, 145.26, 145.21, 145.04, 145.01, 144.96, 144.89, 144.80, 144.78, 144.68, 144.65, 144.19, 144.17, 143.98, 143.88, 143.68, 143.26, 143.19, 143.16, 143.04, 142.84, 142.78, 142.23, 142.21, 142.15, 142.06, 141.90, 141.41, 141.12, 141.04, 140.84, 140.34 (2C, –N(CO)$_2$C$_6$Cl$_4$), 140.22, 138.64, 138.51, 137.82, 137.78, 132.88 (C-13), 129.74 (2C, –N(CO)$_2$C$_6$Cl$_4$), 127.52 (2C, –N(CO)$_2$C$_6$Cl$_4$), 126.28 (C-14), 124.00 (C-8), 106.31 (C-11), 85.09 (C$_{60}$-sp^3), 78.15 (C$_{60}$-sp^3), 55.42 (CH$_3$O–), 50.53 (C-18), 48.70 (C-5), 44.56 (C-7), 40.90 (C-4), 39.31 (C-10), 39.15 (C-1), 37.54 (C-3), 28.42 (C-6), 26.61 (C-15), 23.08 (C-17), 22.91 (C-16), 22.43 (C-20), 18.91 (C-19), 18.20 (C-2); MALDI-TOF MS (matrix: CHCA, reflectron negative) *m*/*z* 1299.5 ([M(^{35}Cl$_4$)]$^-$), 1301.5 ([M(^{35}Cl$_3$ ^{37}Cl)]$^-$), 1303.6 ([M(^{35}Cl$_2$ ^{37}Cl$_2$)]$^-$), 1305.5 ([M(^{35}Cl^{37}Cl$_3$)]$^-$). Anal. Calcd for C$_{89}$H$_{29}$Cl$_4$NO$_3$ (1302.00): C, 82.10; H, 2.25; N, 1.08. Found: C, 81.56; H, 2.22; N, 1.08.

4.11. Ring-B [6,6]-closed-C$_{60}$-adduct of 12-acetoxy-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine (16)

Compound **12** (2.205 g, 2.778 mmol) was dissolved in dry pyridine (33 mL) in a dried three-necked flask under nitrogen flow. Next, NaOMe (156.2 mg, 2.888 mmol) was added and the mixture was stirred for 20 min at room temperature. A solution of C$_{60}$ (1 g, 1.389 mmol) in dry chlorobenzene (260 mL) was added, and the mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel, pre-eluted with CS$_2$ to remove unreacted C$_{60}$ (329.3 mg) and then with CS$_2$/CHCl$_3$ (10:1) to give **16** as a dark-brown solid (602.8 mg, 33%; or 49% based on converted C$_{60}$). IR (KBr) ν_{max}/cm^{-1} 3426, 2921, 2853, 1758, 1719, 1632, 1460, 1425, 1365, 1324, 1196, 1163, 1080, 906, 737, 557, 525, 478; UV–vis (CHCl$_3$) λ_{max} (nm): 697.00, 494.50, 437.00; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.47 (s, 1H, H-14), 7.11 (s, 1H, H-

11), 3.80 (d, J=13.6 Hz, 1H, H-18), 3.66 (d, J=13.6 Hz, 1H, H-18), 3.62 (dd, J=14.0, 10.4 Hz, 1H, H-6β), 3.50 (dd, J=14.0, 8.7 Hz, 1H, H-6α), 3.09 (septet, J=6.7 Hz, 1H, H-15), 2.37 (s, 3H, CH_3COO–), 2.28 (br d, J=11.9 Hz, 1H, H-1β), 1.99 (t, J=9.6 Hz, 1H, H-5), 1.88–1.79 (m, 5H, H-20, H-2), 1.78–1.70 (m, 1H, H-1α), 1.60 (br d, J=13.4 Hz, 1H, H-3),1.52–1.45 (m, 1H, H-3), 1.31 (s, 3H, H-19), 1.25 (d, J=7.0 Hz, 3H, H-17), 1.24 (d, J=7.0 Hz, 3H, H-16); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.68 (CH_3COO–), 164.59 (2C=O, imide), 151.66 (C-12), 150.39, 149.83 (C-9), 147.89, 147.43, 145.91, 145.33, 145.30, 145.26, 145.24, 145.15, 145.01, 144.94, 144.92, 144.89, 144.80, 144.69, 144.28, 144.25, 144.00, 143.95, 143.90, 143.70, 143.28, 143.21, 143.19, 143.10, 143.07, 143.05, 143.01, 142.87, 142.80, 142.25, 142.20, 142.14, 142.08, 141.84, 141.33, 141.21, 141.06, 140.86, 140.33 (2C, $-N(CO)_2C_6Cl_4$), 140.24, 138.63, 138.47, 137.97, 137.83, 136.36 (C-13), 130.13 (C-8), 129.77 (2C, $-N(CO)_2C_6Cl_4$), 127.58 (2C, $-N(CO)_2C_6Cl_4$), 126.70 (C-14), 117.77 (C-11), 84.62 (C_{60}-sp^3), 77.67 (C_{60}-sp^3), 50.13 (C-18), 47.75 (C-5), 44.20 (C-7), 40.89 (C-4), 39.21 (C-10), 38.88 (C-1), 37.48 (C-3), 28.16 (C-6), 27.49 (C-15), 23.37 (C-17), 23.05 (C-16), 22.39 (C-20), 21.07 (CH_3COO–), 19.09 (C-19), 18.09 (C-2); MALDI-TOF MS (matrix: CHCA, reflectron negative) m/z 1327.2 ([M($^{35}Cl_4$)]$^-$), 1329.2 ([M($^{35}Cl_3^{37}Cl$)]$^-$), 1331.2 ([M($^{35}Cl_2$ $^{37}Cl_2$)]$^-$), 1333.2 ([M($^{35}Cl^{37}Cl_3$)]$^-$). Anal. Calcd for $C_{90}H_{29}Cl_4NO_4$ (1330.01): C, 81.27; H, 2.20; N, 1.05. Found: C, 81.35; H, 2.27; N, 1.02.

4.12. Ring-B [6,6]-closed-C_{60}-adduct of 12-hydroxy-*N*,*N*-(tetrachlorophthaloyl)dehydroabietylamine (17)

Methanol (50 mL) and concd HCl (20 mL) were added to a solution of compound **16** (300 mg, 0.226 mmol) in CS_2 (50 mL). The mixture was stirred and refluxed for 4 h under nitrogen. After the removal of the solvent under reduced pressure, the residue was transferred to a centrifuge tube as a suspension in methanol (40 mL). The suspension was centrifuged, and the resulting supernatant was decanted. The dark-brown powder was washed with methanol (2×40 mL) using the centrifuge method and dried in vacuo at 60 °C to give **17** (265.7 mg, 91%). IR (KBr) ν_{max}/cm^{-1} 3437, 2921, 2853, 1776, 1719, 1632, 1450, 1425, 1369, 1338, 1284, 1165, 1043, 738, 554, 526, 473; UV–vis ($CHCl_3$) λ_{max} (nm): 696.00, 504.50, 431.00; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H, H-14), 6.92 (s, 1H, H-11), 3.88 (d, J=13.7 Hz, 1H, H-18), 3.62 (dd, J=14.2, 10.4 Hz, 1H, H-6β), 3.59 (d, J=13.7 Hz, 1H, H-18), 3.40 (dd, J=14.0, 8.8 Hz, 1H, H-6α), 3.26 (septet, J=6.8 Hz, 1H, H-15), 2.30 (br d, J=12.4 Hz, 1H, H-1β), 1.99 (dd, J=10.2, 9.1 Hz, 1H, H-5), 1.86–1.71 (m, 6H, H-20, H-2, H-1α), 1.60–1.49 (m, 2H, H-3), 1.30 (s, 3H, H-19), 1.29 (d, J=6.9 Hz, 3H, H-17), 1.28 (d, J=6.9 Hz, 3H, H-16); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.53 (2C=O, imide), 152.15 (C-12), 151.79 (C-9), 150.71, 149.94, 148.15, 147.71, 145.99, 145.95, 145.31, 145.27, 145.22, 145.19, 145.02, 144.98, 144.94, 144.89, 144.81, 144.79, 144.68, 144.66, 144.22, 144.18, 144.00, 143.96, 143.89, 143.68, 143.27, 143.20, 143.16, 143.05, 143.02, 142.84, 142.79, 142.23, 142.21, 142.15, 142.13, 142.07, 141.90, 141.39, 141.15, 141.06, 140.84, 140.34 (2C, $-N(CO)_2C_6Cl_4$), 140.21, 138.58, 138.45, 137.82, 137.78, 130.12 (C-13), 129.75 (2C, $-N(CO)_2C_6Cl_4$), 127.51 (2C, $-N(CO)_2C_6Cl_4$), 126.58 (C-14), 124.49 (C-8), 111.36 (C-11), 85.04 (C_{60}-sp^3), 78.05 (C_{60}-sp^3), 50.46 (C-18), 48.54 (C-5), 44.42 (C-7), 40.88 (C-4), 39.28 (C-10), 38.75 (C-1), 37.53 (C-3), 28.37 (C-6), 26.98 (C-15), 22.98 (C-17), 22.81 (C-16), 22.36 (C-20), 18.93 (C-19), 18.16 (C-2); MALDI-TOF MS (matrix: CHCA, reflectron negative) m/z 1285.2 ([M($^{35}Cl_4$)]$^-$), 1287.2 ([M($^{35}Cl_3^{37}Cl$)]$^-$), 1289.2 ([M($^{35}Cl_2^{37}Cl_2$)]$^-$), 1291.2 ([M($^{35}Cl^{37}Cl_3$)]$^-$). Anal. Calcd for $C_{88}H_{27}Cl_4NO_3$ (1287.97): C, 82.06; H, 2.11; N, 1.09. Found: C, 81.88; H, 2.16; N, 1.10.

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