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Supplementary Information

Synthesis, Characterization and Photovoltaic Properties of Di-Anchoring Organic Dyes

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*Synthetic procedure of carbazole, iminodibenzy and phenothiazine-containing dyes (**S1**-**S3**)*

*N-hexylcarbazole (**2a**)*

To a 250 mL two necked flask was added with carbazole (16.72 g, 100 mmol), 100 mL DMF and potassium *tert*-butoxide (12.4 g, 110 mmol). After stirring for 30 min, the mixture was added with *N*-bromohexane (17.34 g, 105 mmol) and allowed to reflux overnight. Pouring it into a large amount of water precipitated 9-hexylcarbazole, which were collected by filtration and then recrystallized twice in methanol. The yield was 71% (mp 53 °C). ^{1}H NMR ($CDCl_3$), δ (ppm): 8.13-8.10 (d, 2H), 7.50-7.40 (m, 4H), 7.26-7.21 (m, 2H), 4.31 (t, *J* 7.0 Hz, 2H), 1.88 (quintet, *J* 5.4 Hz, 2H), 1.39 (m, 2H), 1.31 (m, 4H), 0.88 (t, *J* 3.3 Hz, 3H). Elemental analysis calculated (%) for $C_{18}H_{21}N$: C, 86.01%; H, 8.42%; N, 5.57%. Found: C, 85.96%; H, 8.40%; N, 5.55%.

*9-Hexylcarbazole-3,6-dicarbaldehyde (**4a**)*

To a 50 mL glass reactor were added with imidazole (0.718 g, 10.5 mmol) and 10 mL acetonitrile. The mixture were added under stirring with trifluoroacetic anhydride (5.775 g, 27.5 mmol) within 5 min, treated dropwise with 9-hexylcarbazole (**2a**: 1.257 g, 5 mmol) and then refluxed for 4 h. After adjusting pH > 7 with saturated aqueous solution of Na_2CO_3, the appearing precipitates were isolated by filtration and washed with water to give a precipitate. The precipitate was dissolved in CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford 3,6-bis(1,3-bistrifluoracetyl-4,5-dihydroimidazole-2-yl)-9-hexylcarbazole (**3a**: 3.55 g , 92%), which was used for the next step without further purification. To a 250 mL glass reactor were added with **3a** (6.2 g, 8 mmol), 148 mL acetonitrile and 77 mL 1.9 mol L^{-1} HCl. The mixture was refluxed for 3 h and was extracted with ethyl ether after cooling and neutralization. The crude product obtained by removing ethyl ether were purified by column chromatography (silica gel, 60-200 mm, neutrality; *n*-hexane/ethyl acetate = 4/1) to give **4a** (1.75 g, 71%, mp 143 °C). ^{1}H NMR ($CDCl_3$, ppm): δ 10.04 (s, 2H), 8.83 (s, 2H), 8.01 (d, 2H), 7.80 (d, 2H), 4.46 (t, 2H), 1.69 (m, 2H), 1.16 (m, 6H), 0.73 (t, 3H). Elemental analysis calculated (%) for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 77.98; H, 6.81; N, 4.65.

*5,5'-(9-Hexyl-carbazole-3,6-diyl)bis(methan-1-yl-1-ylidene) bis(4-oxo-2-thioxothiazolidin-3-yl-5-ylidene)diacetic acid (**S1**)*

To a stirred **4a** (0.615 g, 2 mmol) in CH_3COOH (30 mL) were added rhodanine-3-acetic acid (0.794 g, 4.15 mmol) and ammonium acetate (0.125 g, 1.625 mmol). The mixture was heated to 120 °C and the reaction was continued for 2 h at the temperature. Then the reaction mixture was allowed to cool to room temperature. The solid was collected by filtration and washed with water thoroughly. After drying in air, the crude product was purified by column chromatography on silica gel with CH_2Cl_2/methanol (10:1, v/v) as eluant to give **S1** in 93% yield, mp > 200 °C. ^{1}H NMR (DMSO-d_6), δ (ppm): 8.55 (s, 2H, -C<u>H</u>=), 8.03 (s, 2H, aromatic hydrogen), 7.84 (d, 2H, aromatic hydrogen), 7.76 (d, 2H, aromatic hydrogen), 4.76 (s, 4H, O=C-C<u>H</u>$_2$-N), 4.47 (t, 2H, N-C<u>H</u>$_2$-), 1.79 (m, 2H, N-CH$_2$-C<u>H</u>$_2$-), 1.26 (m, 6H, N-CH$_2$-CH$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-CH$_3$), 0.80 (t, 3H, N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-C<u>H</u>$_3$). Elemental analysis

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calculated (%) for $C_{30}H_{27}N_3O_6S_4$: C, 55.11%; H, 4.16%; N, 6.43%. Found: C, 54.92%; H, 4.12%; N, 6.31%.

*11-Ethyl-iminodibenzyl (**2b**)*

Iminodibenzyl (**1b**: 6.834 g, 35 mmol), iodoethane (5.93 g, 38 mmol) and 80 mL of DMF were added to a 50 mL two-necked glass reactor. The solution was warmed to 75 °C, treated portionwise with potassium *tert*-butoxide (4.264 g, 38 mmol) and then refluxed for 24 h. After 150 mL of water was added, the mixture was extracted with chloroform (75 mL). Crude oils obtained by removing the solvent were purified by column chromatography (silica gels, *n*-hexane/ethyl acetate: 20/1 as eluent) to give **2b** as a white solid (4.76 g, 61%, mp 54 °C). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.16 (t, 3H, CH_3), 3.17 (m, 4H, CH_2), 3.80 (m, 2H, CH_2), 6.92 (m, 2H, ar), 7.12 (m, 6H, ar). Elemental analysis calculated (%) for $C_{16}H_{17}N$: C, 86.05%; H, 7.67%; N, 6.27%. Found: C, 85.96%; H, 7.73%; N, 6.20%.

*11-Ethyl-3,8-diformyliminodibenzyl (**4b**)*

To a 50 mL glass reactor were added with imidazole (0.718 g, 10.5 mmol) and 10 mL acetonitrile. The mixture were added under stirring with trifluoroacetic anhydride (5.775 g, 27.5 mmol) within 5 min, treated dropwise with 11-ethyl-iminodibenzyl (**2b**: 1.117 g, 5 mmol) and then refluxed for 4 h. After adjusting pH > 7 with saturated aqueous solution of Na_2CO_3, the appearing precipitates were isolated by filtration and washed with water to give a precipitate. The precipitate was dissolved in CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford 3,8-bis(1,3-bis-trifluoracetyl-4,5-dihydroimidazole-2-yl)-11-ethyliminodibenzyl (**3b**: 3.35 g, 90%), which was used for the next step without further purification. To a 250 mL glass reactor were added with **3b** (5.95 g, 8 mmol), 148 mL acetonitrile and 77 mL 1.9 mol L^{-1} HCl. The mixture was refluxed for 3 h and was extracted with ethyl ether after cooling and neutralization. The crude products obtained by removing ethyl ether were purified by column chromatography (silica gel; *n*-hexane/ethyl acetate = 4/1) to give **4b** (1.77 g, 79%, mp 96 °C). ^{1}H NMR (acetone-d_6, ppm): δ 9.72 (s, 2H, -C<u>H</u>O), 7.54 (d, *J* 7.4 Hz, 2H), 7.48 (s, 2H), 7.09 (d, *J* 7.3 Hz, 2H), 3.73 (t, 2H), 3.05 (s, 4H), 1.07 (t, *J* 3.3 Hz, 3H). Elemental analysis calculated (%) for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.41; H, 6.16; N, 4.96.

*5,5'-(11-Ethyl-iminodibenzyl-3,8-diyl)bis(methan-1-yl-1-ylidene)bis(4-oxo-2-thioxothiazolidin-3-yl-5-ylidene)diacetic acid (**S2**)*

To a stirred **4b** (0.558 g, 2 mmol) in CH_3COOH (30 mL) were added rhodanine-3-acetic acid (0.794 g, 4.15 mmol) and ammonium acetate (0.125 g, 1.625 mmol). The mixture was heated to 120 °C and the reaction was continued for 2 h at the temperature. Then the reaction mixture was allowed to cool to room temperature. The solid was collected by filtration and washed with water thoroughly. After drying in air, the crude product was purified by column chromatography on silica gel with CH_2Cl_2/methanol (10:1, v/v) as eluent to give **S2** in 83% yield, mp > 200 °C. ^{1}H NMR (DMSO-d_6), δ (ppm): 7.79 (s, 2H, -C<u>H</u>= and aromatic hydrogen), 7.50 (m, 4H, aromatic hydrogen), 7.36 (d, 2H, aromatic hydrogen), 4.73 (s, 4H, O=C-C<u>H</u>$_2$-N), 3.94 (q, 2H, N-C<u>H</u>$_2$-), 3.18 (t, 4H, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 1.19 (t, 3H, N-CH$_2$-C<u>H</u>$_3$). Elemental analysis calculated (%) for $C_{28}H_{23}N_3O_6S_4$: C, 53.74%; H, 3.70%; N, 6.72%. Found: C, 53.51%; H, 3.62%; N, 6.58%.

*10-Ethyl-phenothiazine (**2c**)*

Phenothiazine (**1c**: 11.94 g, 60 mmol), iodoethane (10.92 g, 70 mmol) and 80 mL of DMF were added to a 50 mL two-necked glass reactor. The solution was warmed to 75 °C, treated portionwise with potassium *tert*-butoxide (7.86 g, 70 mmol) and then refluxed for 24 h. After 150 mL of water was added, the mixture was extracted with chloroform (75 mL). Crude product obtained by removing the solvent were purified by column chromatography (silica gels, *n*-hexane/ethyl acetate: 20/1 as eluent) to give **2c** as a white solid (11.32 g, yield: 83%, mp 103-104 °C). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.42 (t, 3H, CH_3), 3.92 (m, 2H, CH_2), 6.85-6.88 (m, 4H, ar), 7.11-7.16 (m, 4H, ar). Elemental analysis calculated (%) for $C_{14}H_{13}NS$: C, 73.97%; H, 5.76%; N, 6.16%; S, 14.11%. Found: C, 73.83%; H, 5.73%; N, 6.13%, S, 14.10%.

*10-Ethyl-3,7-diformylphenothiazine (**4c**)*

To a 50 mL glass reactor were added with imidazole (0.718 g, 10.5 mmol) and 10 mL acetonitrile. The mixture were added under stirring with trifluoroacetic anhydride (5.775 g, 27.5 mmol) within 5 min, treated dropwise with 10-ethyl-phenothiazine (**2c**: 1.137 g, 5 mmol) and then refluxed for 4 h. After adjusting pH > 7 with saturated aqueous solution of Na_2CO_3, the appearing precipitates were isolated by filtration and washed with water to give a precipitate. The precipitate was dissolved in CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford 3,7-bis(1,3-bistrifluoracetyl-4,5-dihydroimidazole-2-yl)-10-ethylphenothiazine (**3c**: 3.25 g , 87%), which was used for the next step without further purification. To a 250 mL glass reactor were added with **3c** (5.98 g, 8 mmol), 148 mL acetonitrile and 77 mL 1.9 mol L^{-1} HCl. The mixture was refluxed for 3 h and was

extracted with ethyl ether after cooling and neutralization. The crude product obtained by removing ethyl ether were purified by column chromatography (silica gel; *n*-hexane/ethyl acetate = 4/1) to give **4c** (1.74 g, 77%, mp 167 °C). ^{1}H NMR ($CDCl_3$, ppm): δ 9.84 (s, 2H, -C<u>H</u>O), 7.68 (dd, 2H, aromatic hydrogen), 7.59 (s, 2H, aromatic hydrogen), 6.98 (d, 2H, aromatic hydrogen), 4.05 (q, 2H, N-C<u>H</u>$_2$-), 1.50 (t, 3H, N-CH$_2$-C<u>H</u>$_3$). Elemental analysis calculated (%) for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 4.94. Found: C, 67.84; H, 4.60; N, 4.91.

*5,5'-(10-Ethyl-phenothiazine-3,7-diyl)bis(methan-1-yl-1-ylidene)bis(4-oxo-2-thioxothiazolidin-3-yl-5-ylidene) diacetic acid (**S3**)*

To a stirred **4c** (0.34 g, 1.2 mmol) in CH_3COOH (30 mL) were added rhodanine-3-acetic acid (0.476 g, 2.49 mmol) and ammonium acetate (0.075 g, 0.975 mmol). The mixture was heated to 120 °C and the reaction was continued for 2 h at the temperature. Then the reaction mixture was allowed to cool to room temperature. The solid was collected by filtration and washed with water thoroughly. After drying in air, the crude product was purified by column chromatography on silica gel with CH_2Cl_2/methanol (10:1, v/v) as eluant to give **S3** in 86% yield, mp > 200 °C. ^{1}H NMR (DMSO-d_6), δ (ppm): 7.75 (s, 2H, -C<u>H</u>=), 7.47 (d, 2H, aromatic hydrogen), 7.40 (s, 2H, aromatic hydrogen), 7.19 (d, 2H, aromatic hydrogen), 4.71 (s, 4H, O=C-C<u>H</u>$_2$-N), 4.00 (q, 2H, N-C<u>H</u>$_2$-), 1.33 (t, 3H, N-CH$_2$-C<u>H</u>$_3$). Elemental analysis calculated (%) for $C_{26}H_{19}N_3O_6S_5$: C, 49.59%; H, 3.04%; N, 6.67%. Found: C, 49.43%; H, 3.01%; N, 6.53%.

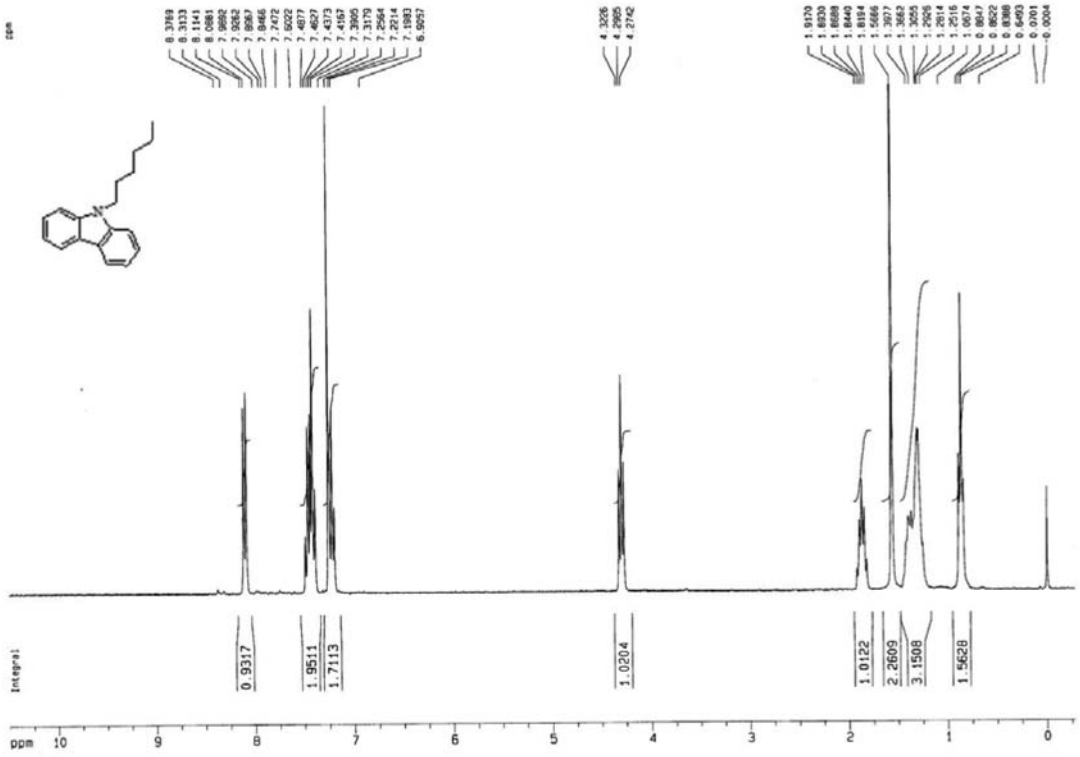

Figure S1. ^{1}H NMR (300 MHz) spectrum of *N*-hexylcarbazole (**2a**).

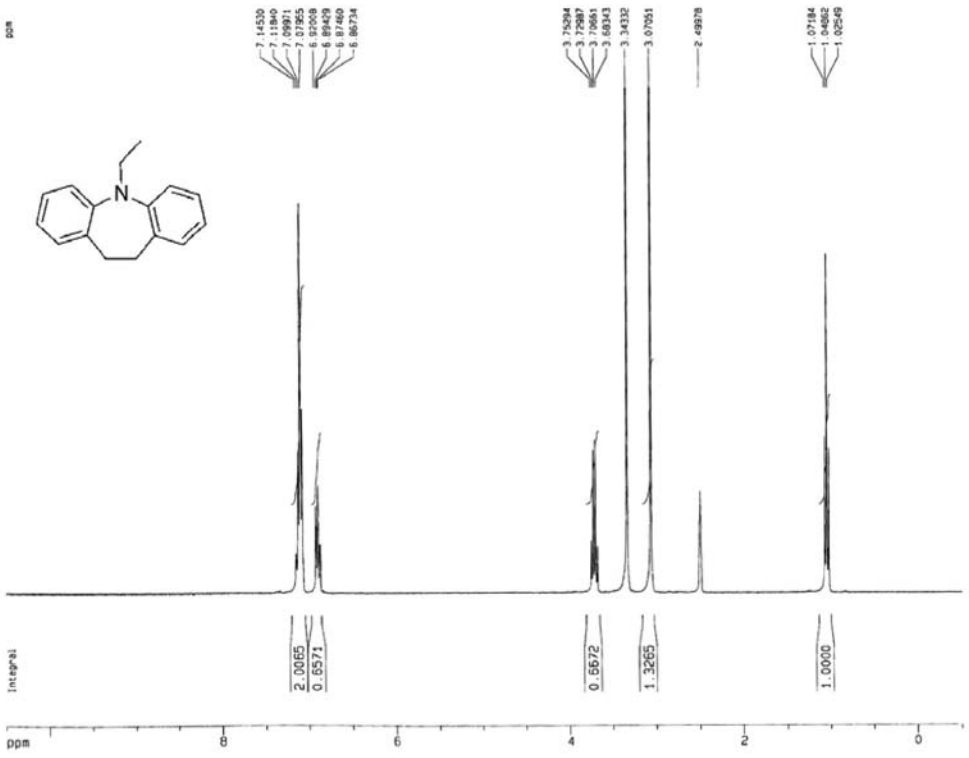

Figure S2. [1]H NMR (300 MHz) spectrum of 11-ethyl-iminodibenzyl (**2b**).

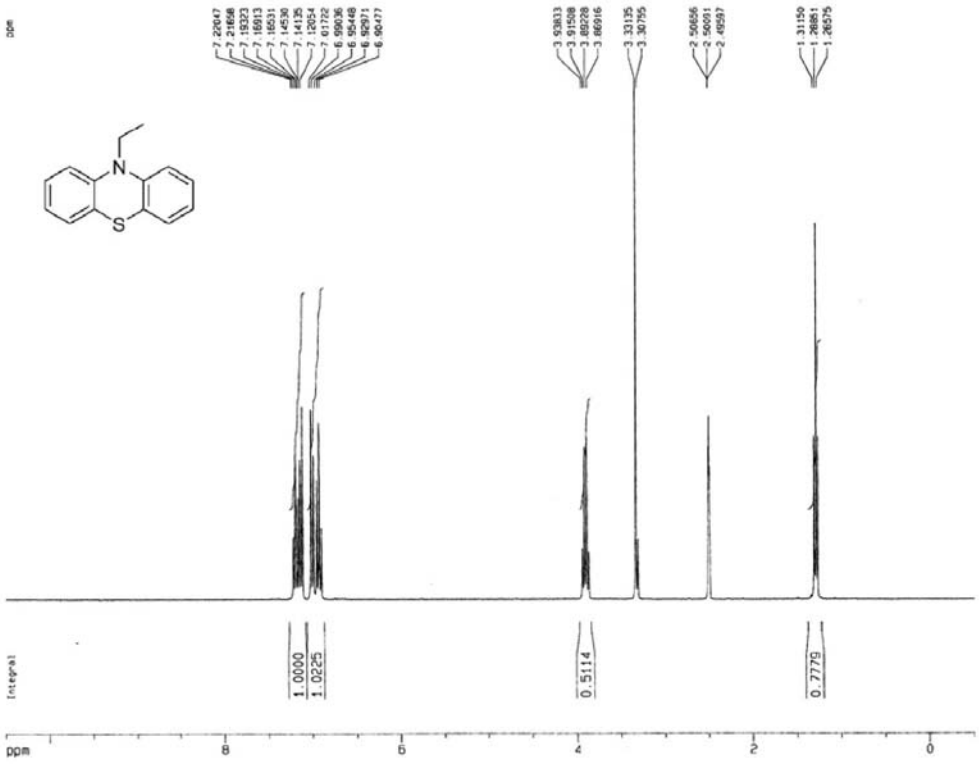

Figure S3. [1]H NMR (300 MHz) spectrum of 10-ethyl-phenothiazine (**2c**).

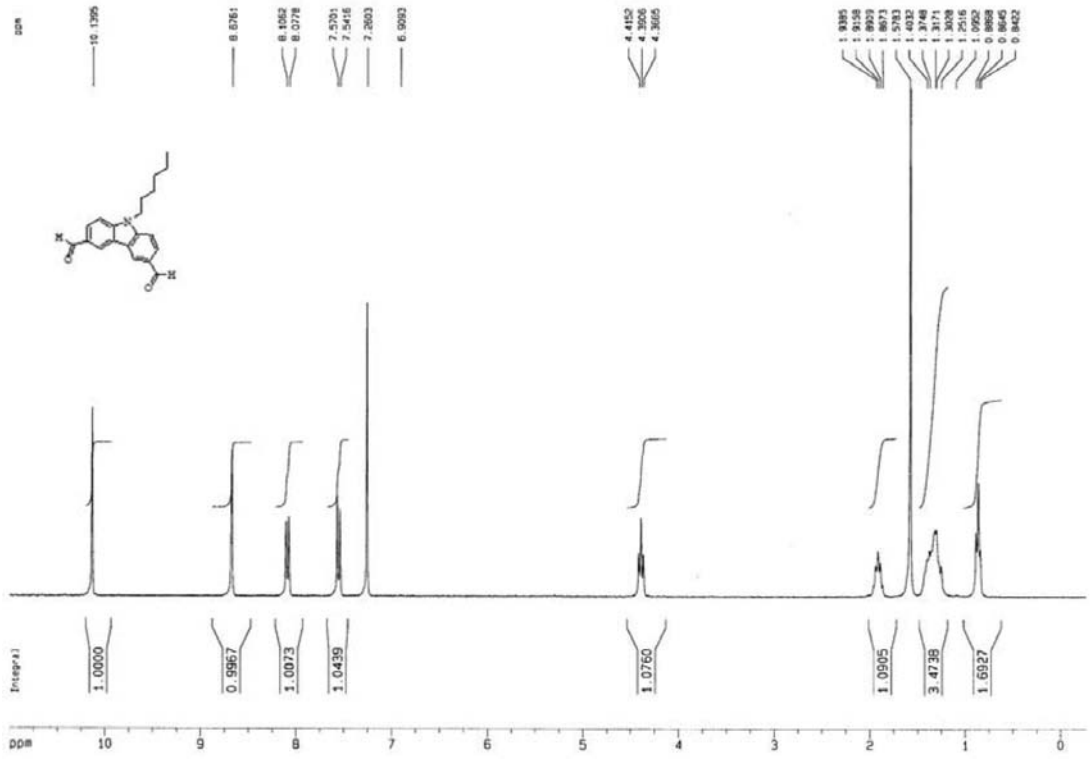

Figure S4. [1]H NMR (300 MHz) spectrum of 9-hexylcarbazole-3,6-dicarbaldehyde (**4a**).

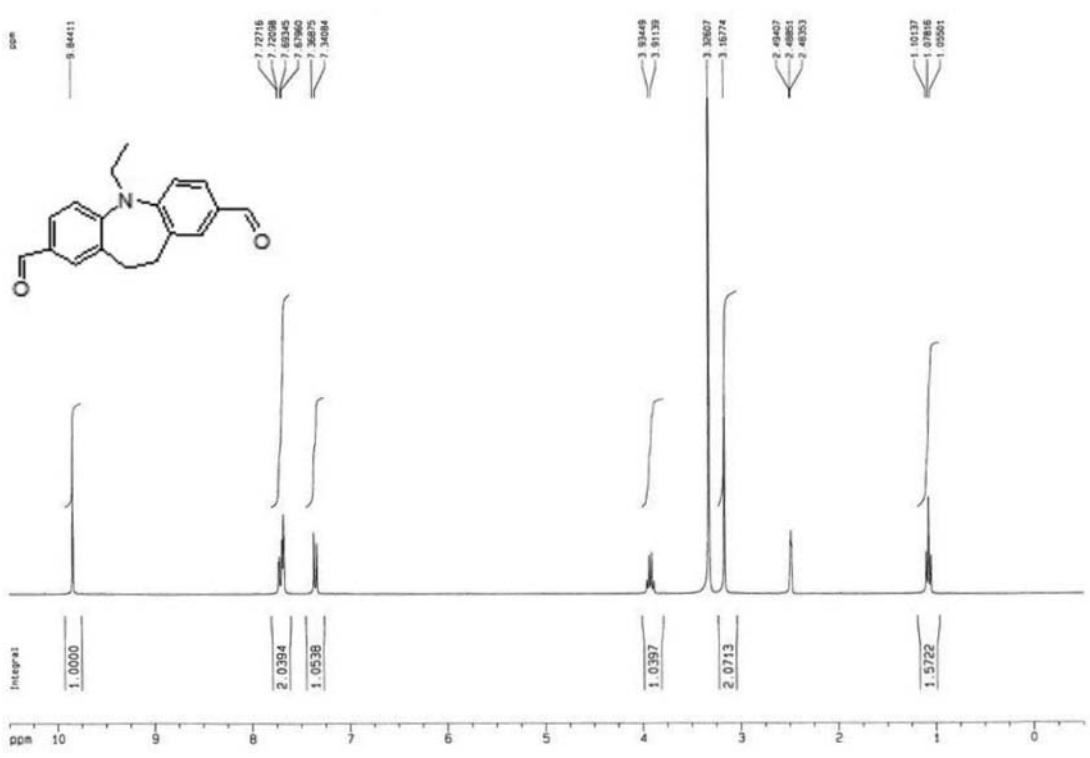

Figure S5. [1]H NMR (300 MHz) spectrum of 11-ethyl-3,8-diformyliminodibenzyl (**4b**).

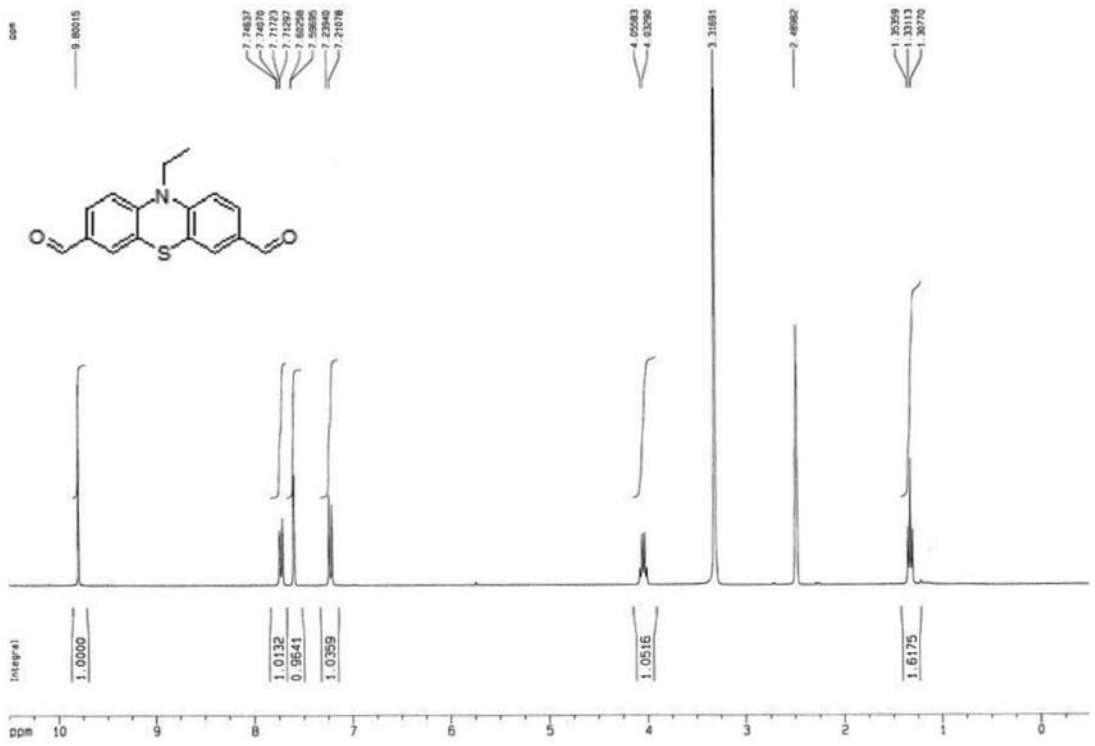

Figure S6. [1]H NMR (300 MHz) spectrum of 10-ethyl-3,7-diformylphenothiazine (**4c**).

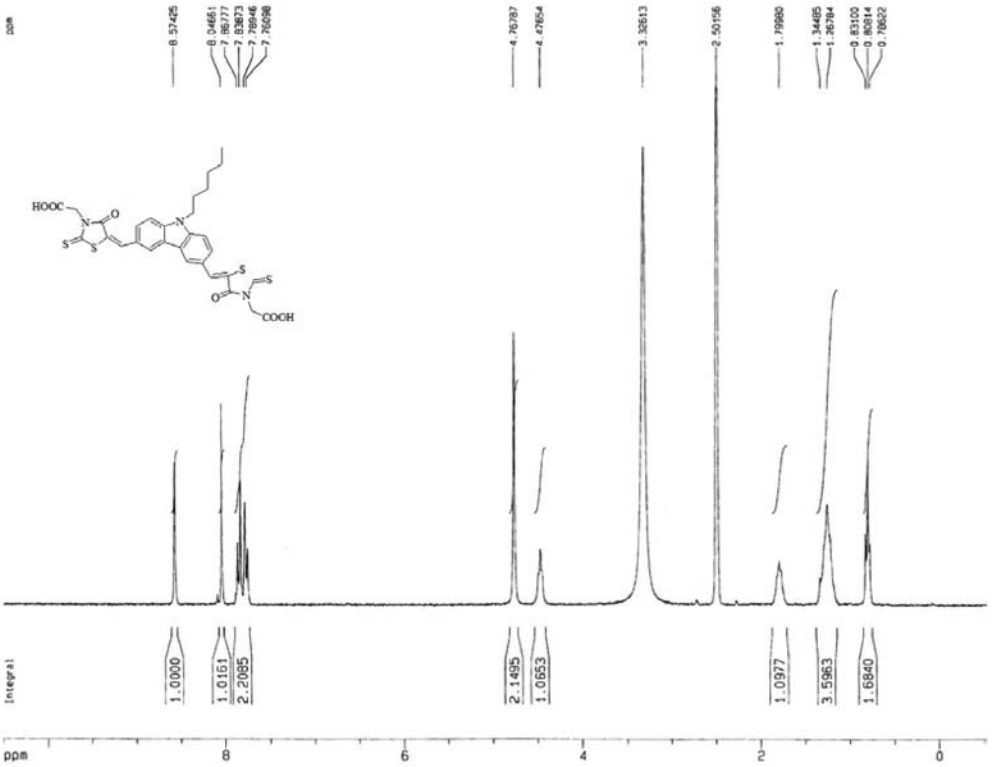

Figure S7. [1]H NMR (300 MHz) spectrum of **S1**.

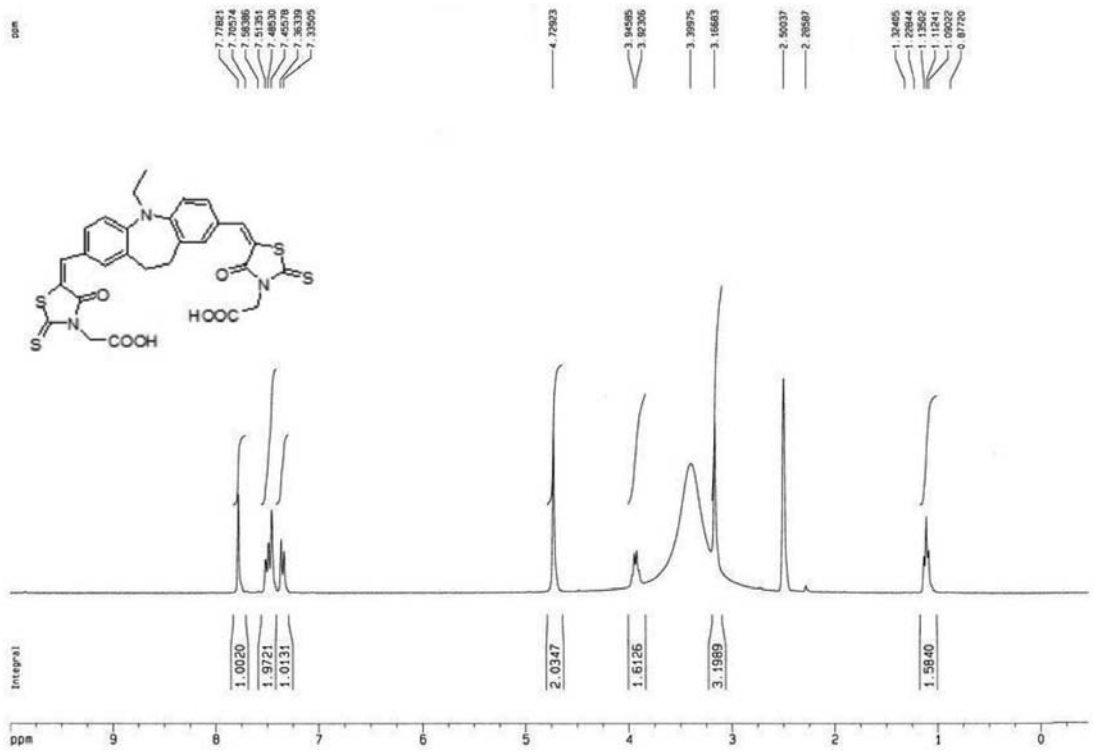

Figure S8. ^{1}H NMR (300 MHz) spectrum of **S2**.

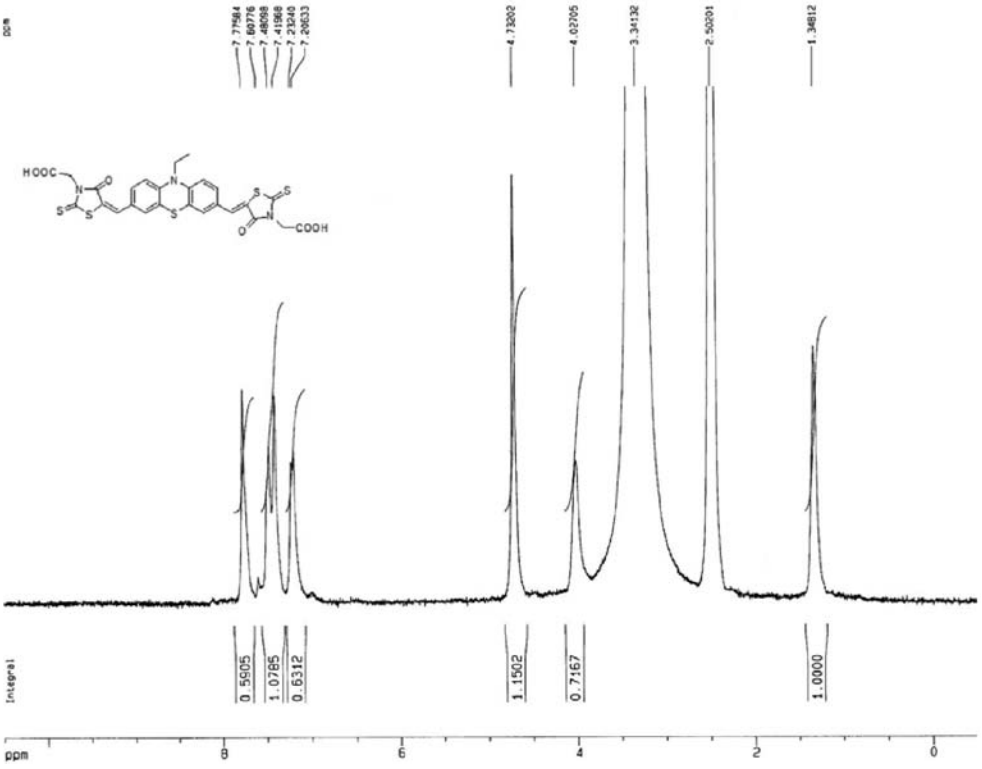

Figure S9. ^{1}H NMR (300 MHz) spectrum of **S3**.

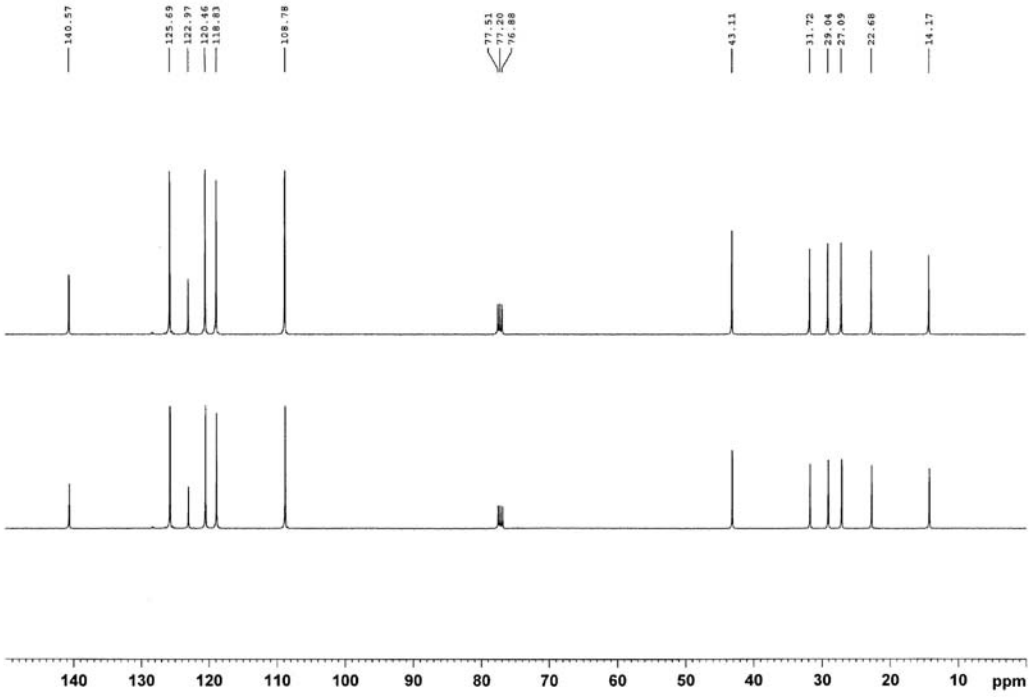

Figure S10. ^{13}C NMR (400 MHz) spectrum of *N*-hexylcarbazole (**2a**).

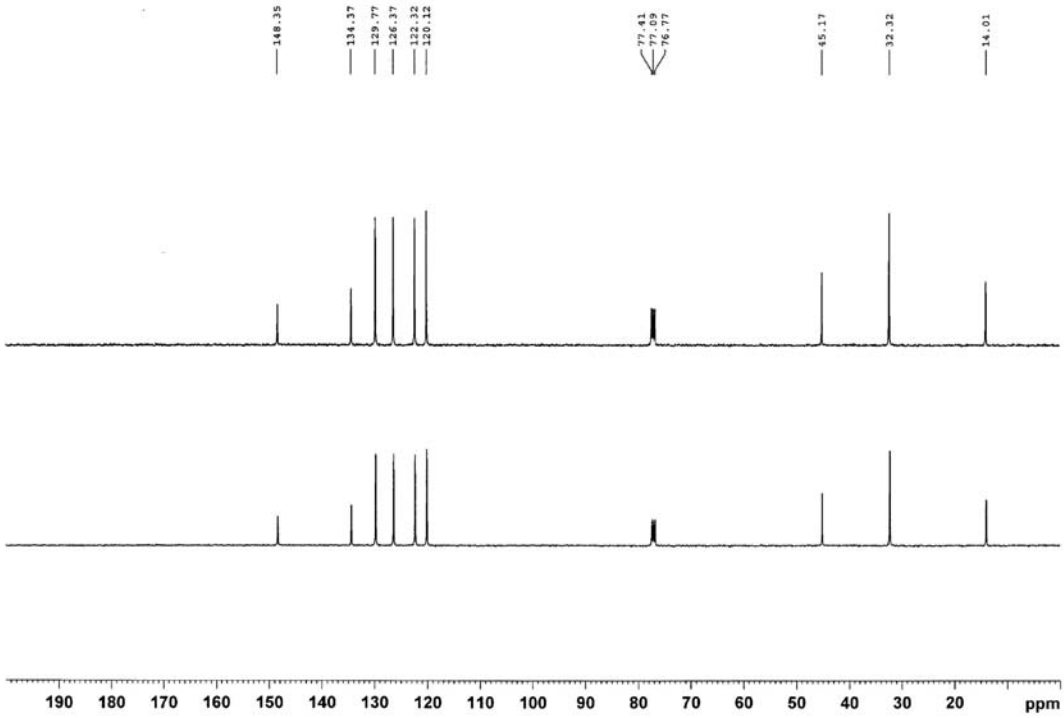

Figure S11. ^{13}C NMR (400 MHz) spectrum of 11-ethyl-iminodibenzyl (**2b**).

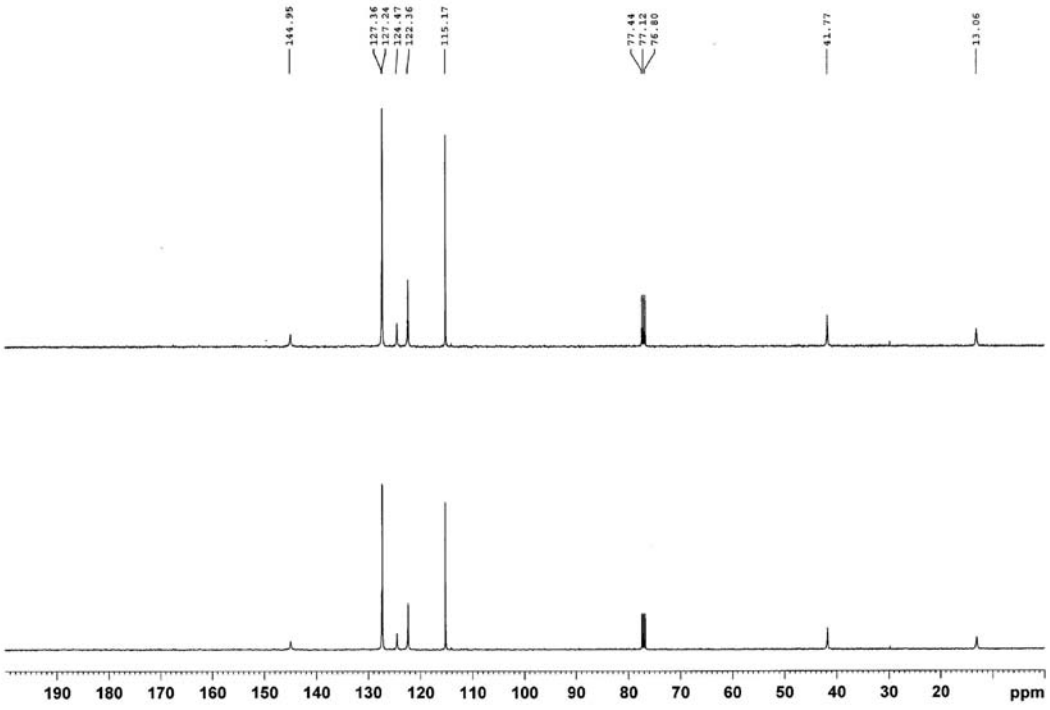

Figure S12. ^{13}C NMR (400 MHz) spectrum of 10-ethyl-phenothiazine (**2c**).

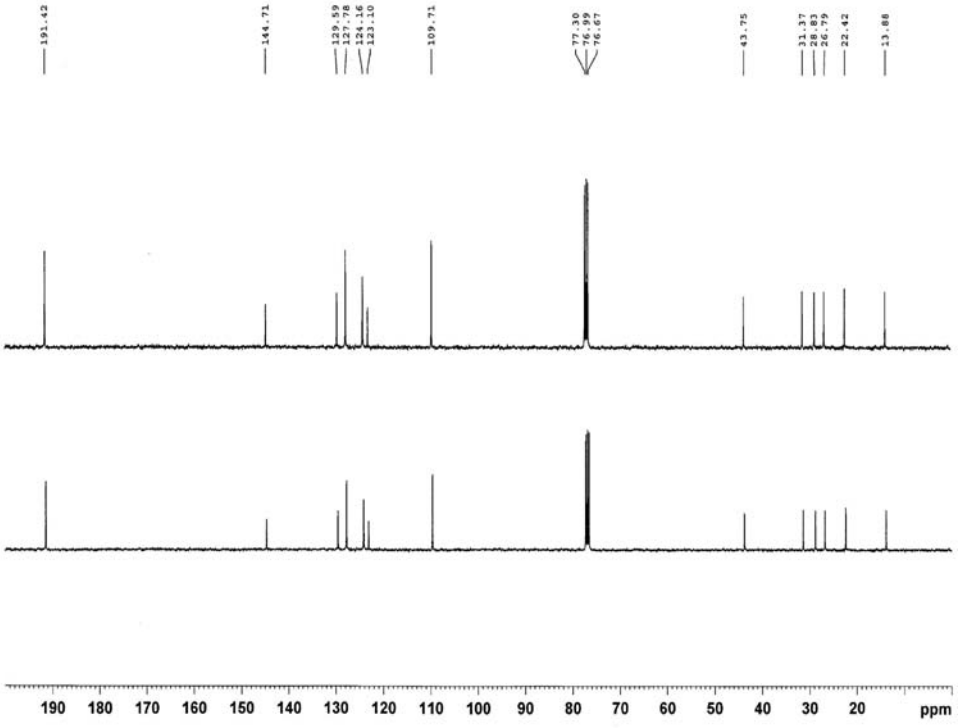

Figure S13. ^{13}C NMR (400 MHz) spectrum of 9-hexylcarbazole-3,6-dicarbaldehyde (**4a**).

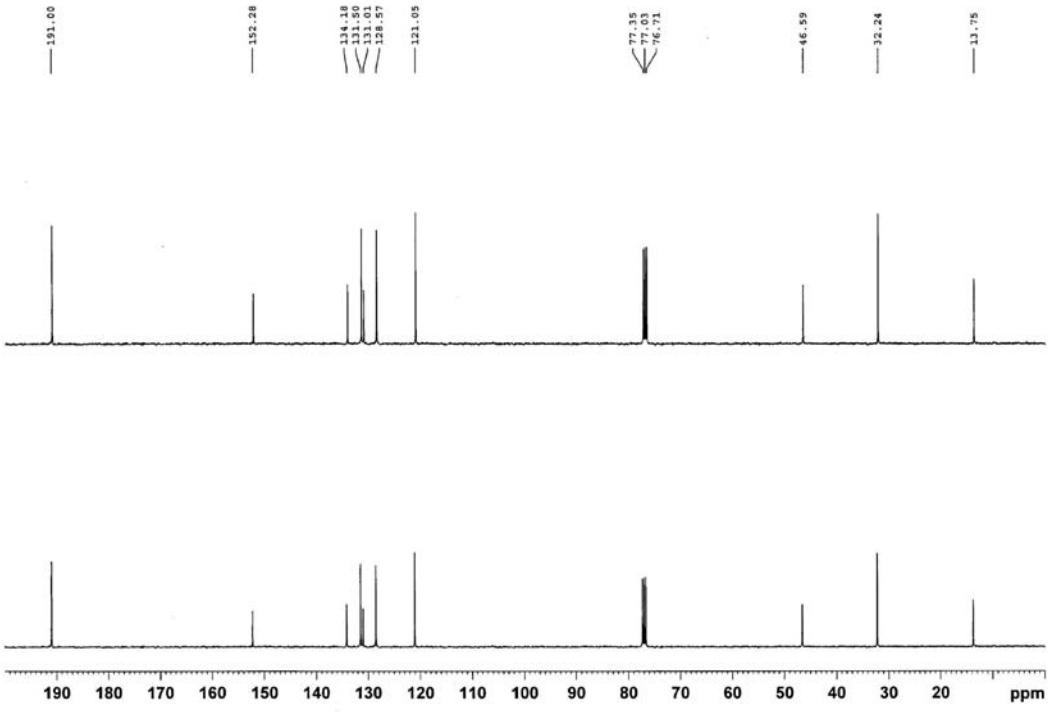

Figure S14. ^{13}C NMR (400 MHz) spectrum of 11-ethyl-3,8-diformyliminodibenzyl (**4b**).

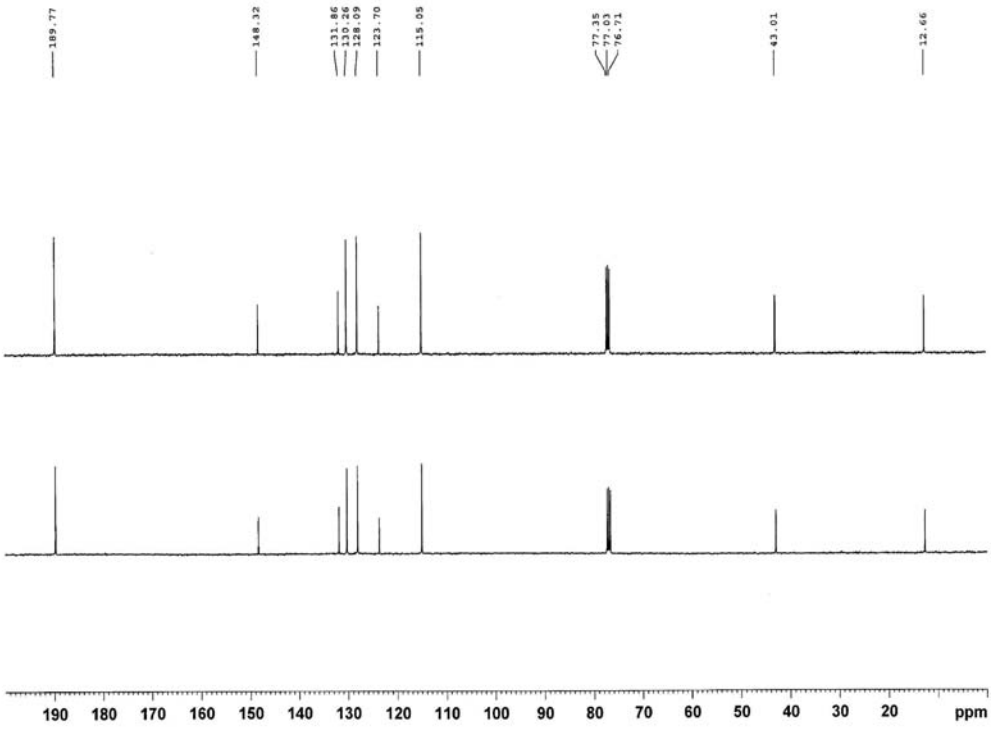

Figure S15. ^{13}C NMR (400 MHz) spectrum of 10-ethyl-3,7-diformylphenothiazine (**4c**).