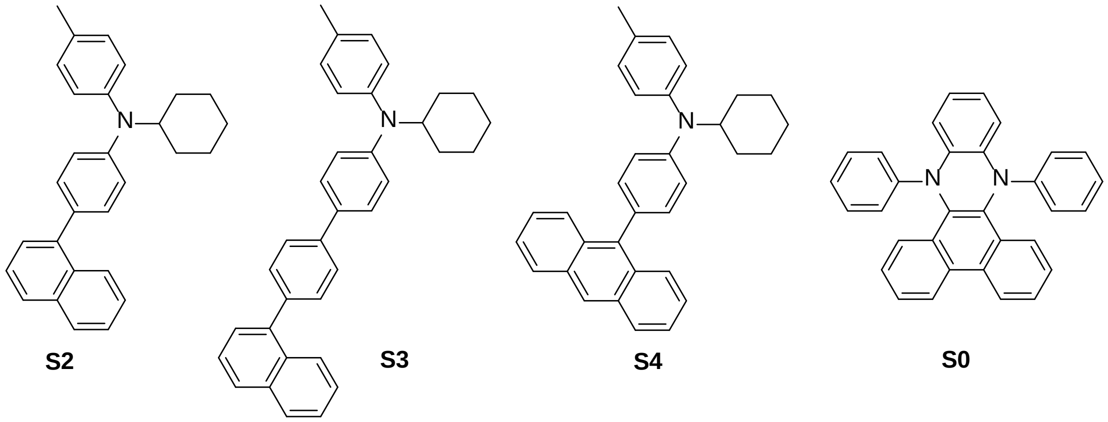
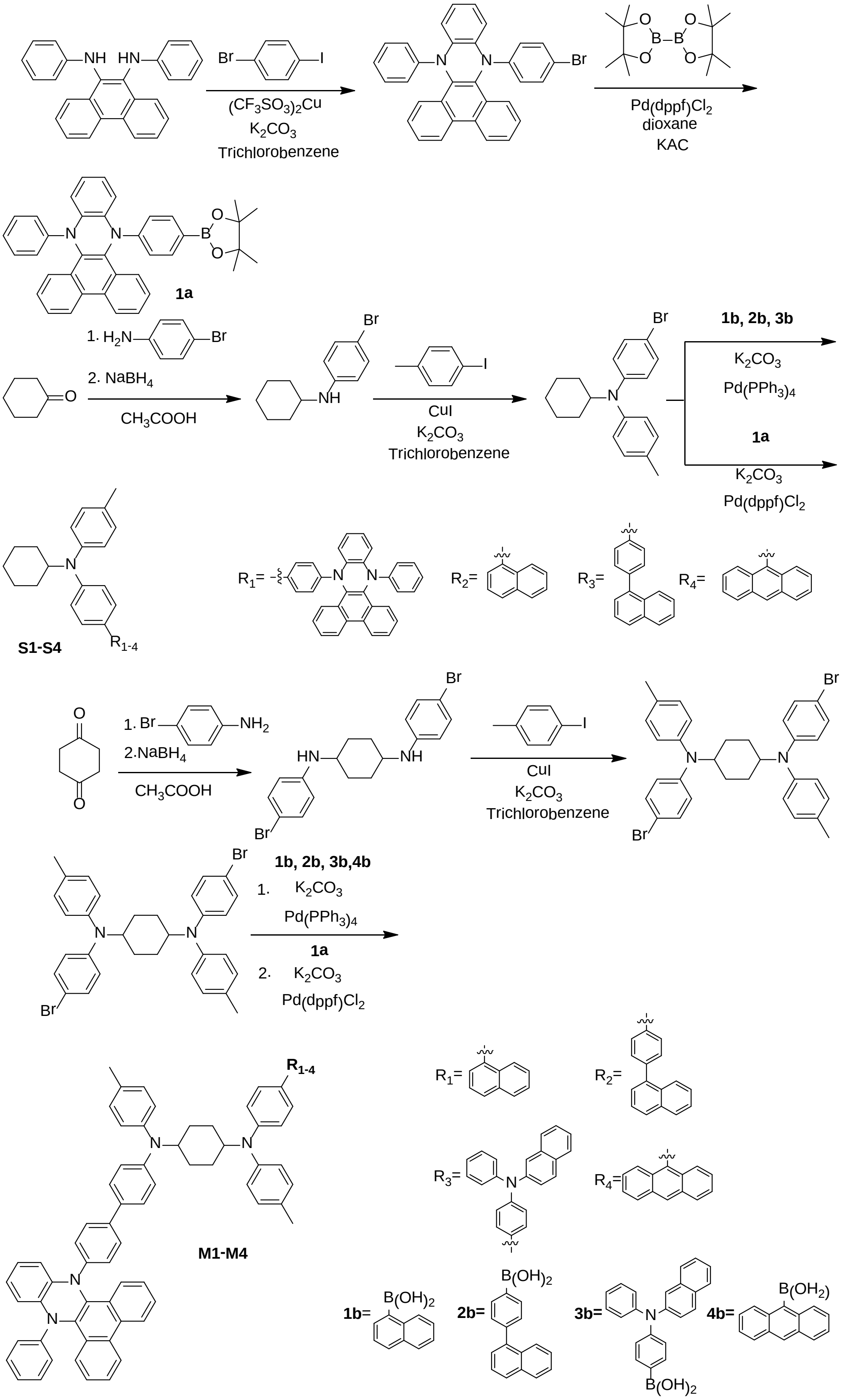
Supporting Information

General Method

^{1}H and ^{13}C NMR spectra were measured on Bruker AM-400 spectrometer using d-chloroform as solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. High resolution mass spectra measurements were carried out using a Waters LCT Premier XE spectrometer. The UV/Vis spectra were recorded on a Nicolet CARY 100 spectrophotometer. The fluorescence spectra were recorded on Horiba Fluoromax 4. The fluorescence life time measurements were performed by using the time correlated single photon counting (TCSPC) technique following excitation by nanosecond flash lamp. Calculation: *Ab initio* calculations were performed at density functional theory (DFT) level employing Gaussian09 package. Long-range corrected hybrid functions, cam-B3LYP, together with polarized double zeta basis set 6-31G* was applied throughout calculations. Each molecule was first optimized at the ground state and the absorption spectroscopy was thereafter obtained through time dependent DFT (TD-DFT) calculations. The first excitation state was subsequently optimized by taking advantage of previous results. The quantum yield for **S1, M1**-**M4** were measured by Quanta-φ F-3029 Integrating Sphere and calculated by the equation of $\Phi_F = (Ec\text{-}Ea) / (La\text{-}Lc)$, in which *Ec* is the integrated luminescence of the solution caused by direct excitation, *Ea* is the integrated luminescence of the blank solvent, *La* is the integrated excitation profile of a blank solvent and *Lc* is the integrated excitation profile of the solution. Dioxane was pre-dried over sodium for 24h and then redistilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. Starting materials were obtained from commercial sources (J&K, Aldrich), and used without further purification.



Scheme S1. The structure of the reference molecules **S2-S4** and phenazine unit **S0**.



Scheme S2. Synthetic routes for **S1, M1-M4** and the reference compounds **S2-S4**

Synthesis

9-(4-bromophenyl)-14-phenyl-9,14-dihydrodibenzo[a,c]phenazine: In a 250ml three-neck flask, 18g (0.05 mol) N^9,N^{10}-diphenylphenanthrene-9,10-diamine, 42.4g (0.15 mol) 1-bromo-4-iodobenzene, 41.46g (0.3 mol) K_2CO_3, 1.8g (5 mmol) $(CF_3SO_3)_2Cu$, 80ml trichlorobenzene was added. The mixture stirred for 8h under refluxed. The trichlorobenzene was taken out by vacuum distillation. After cooling, added 150 ml DCM and stirred for 20 min, filtered the mixture. The combined organic layer was purified by column chromatography on silica (PE: DCM = 10:1) to give a light yellow solid 10.5g. Yield: 41 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (d, *J*=38.3, 2H), 8.08 (dd, *J*=21.3, 7.7, 2H), 7.79 – 7.73 (m, 1H), 7.72 – 7.62 (m, 3H), 7.60 – 7.50 (m, 2H), 7.35 (m,, 2H), 7.06 (m, 4H), 6.96 (d, *J*=7.9, 2H), 6.86 – 6.78 (m, 3H). HRMS (ESI) (m/z): calcd for $C_{32}H_{21}BrN_2$: 513.0966 Found $[M+H]^+$ 513.0972.

9-phenyl-14-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,14-dihydrodibenzo[a,c]phenazine (1a): In a 100ml three-neck flask. 7.7g (0.015 mol) 9-(4-bromophenyl)-14- phenyl-9,14- dihydrodibenzo[a,c] phenazine, 5.84g (0.023 mol) bis(pinacolato)diboron, 4.41g (0.045 mol) KAC, 0.55g (0.75 mmol) $Pd(dppf)Cl_2$ and 50 ml anhydrous dioxane was added. The mixture refluxed for 10h under N_2 atmosphere. After cooling, the mixture was poured into 150 ml water and extracted with DCM (80ml X 3). The combined organic layer was washed with water, dried with anhydrous $MgSO_4$. The resident was purified by column chromatography on silica (PE: DCM = 2:1) to give a white solid 5.21g. Yield: 62 %.^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 (d, *J*=8.3, 2H), 8.06 (dd, *J*=26.1, 7.6, 2H), 7.81 – 7.71 (m, 2H), 7.64 (t, *J*=7.6, 2H), 7.51 (m, ,4H), 7.35 (m, 2H), 7.08 – 6.88 (m, 6H), 6.78 (t, *J*=6.7, 1H), 1.26 (s, 12H). HRMS (ESI) (m/z): calcd for $C_{38}H_{33}BN_2O_2$: 561.2713 Found $[M+H]^+$ 561.2711.

4-bromo-N-cyclohexylaniline: In a 250ml there-neck flask, 4g (0.04 mol) cyclohexanedione was dissolved in 50 ml acetic acid, and then slowly added 7g (0.04 mol) 4-bromoaniline in 30ml acetic acid. The mixture was stirred for 2h in room temperature. Then (0.46g x 5 0.06 mol) $NaBH_4$ was slowly put in at 0 ^{o}C. After 1h the mixture was poured into ice water, a white solid was precipitated. Filtered the mixture, the white residue was recrystallized by EtOH to give a white solid 7.3g. Yield: 71 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, *J*=8.7, 2H), 6.48 (d, *J*=8.7, 2H), 3.57 (s,1H), 3.36 – 3.10 (m, 1H), 2.05 (d, *J*=10.0, 2H), 1.84 – 1.73 (m, 2H), 1.68 (dd, *J*=8.8, 3.8, 1H), 1.46 – 1.32 (m, 2H), 1.31 – 1.08 (m, 3H).

4-bromo-N-cyclohexyl-N-(p-tolyl)aniline: In a 100ml flask. 5.1g (0.02 mol) 4-bromo-N-cyclohexylaniline, 12.8g (0.1 mol) K_2CO_3, 8.72g (0.04 mol) 1-iodo-4-methylbenzene, 0.91g (4.8 mmol) CuI were refluxed in trichlorobenzene (40 ml) for 48h under N_2 atmosphere. The trichlorobenzene was taken out by vacuum distillation. After cooling, added 100ml DCM and stirred for 20min, filtered the mixture. Then the solvent was distilled under reduced pressure, and the crude product was purified by column chromatography on silica (PE : DCM = 8:1) to give a white solid 2.89g. Yield: 42 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.22 (m, 2H), 7.19 (d, *J*=8.0, 2H), 6.92 (d, *J*=8.2, 2H), 6.49 (d, *J*=9.1, 2H), 3.76 (tt, *J*=11.6, 3.3, 1H), 2.39 (s, 3H), 2.00 (d, *J*=11.6, 2H), 1.81 (d, *J*=13.5, 2H), 1.46 – 1.27 (m, 3H), 1.18 – 0.99 (m, 3H).

S2: In a 50 ml flask. 0.69g (2 mmol) 4-bromo-N-cyclohexyl-N-(p-tolyl)aniline, 0.38g (2.2 mmol) 1b, 2M K_2CO_3 2ml, 19mg (0.0165 mmol) $Pd(PPh_3)_4$, 20ml THF were refluxed for 8h. After cooling the mixture were poured into water, and extracted with DCM (30ml X 3). The combined organic layer was washed with water, dried with anhydrous $MgSO_4$. The resident was purified by column chromatography on silica (PE: DCM = 6:1) to give a white solid 0.59g. Yield: 75 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J*=8.4, 1H), 7.91 (d, *J*=8.0, 1H), 7.82 (d, *J*=8.1, 1H), 7.55 – 7.41 (m, 4H), 7.34 (d, *J*=8.6, 2H), 7.25 (d, *J*=8.2, 2H), 7.05 (d, *J*=8.1, 2H), 6.75 (d, *J*=8.6, 2H), 3.92 (tt, *J*=11.5, 3.2, 1H), 2.42 (s, 3H), 2.12 (d, *J*=11.9, 2H), 1.86 (d, *J*=13.4, 2H), 1.68 (d, *J*=12.8, 1H), 1.53 – 1.39 (m, 2H), 1.21 (qd, *J*=12.6, 3.2, 2H), 1.07 (qt, *J*=13.0, 3.7, 1H). HRMS (ESI) (m/z): calcd for $C_{29}H_{29}N$: 392.2378 Found $[M+H]^+$ 392.2383.

S3: The compound was synthesized using the same procedure as described above for S2 ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, *J*=8.4, 1H), 7.94 (d, *J*=7.6, 1H), 7.89 (d, *J*=8.1, 1H), 7.68 (d, *J*=8.3, 2H), 7.61 – 7.42 (m, 8H), 7.24 (d, *J*=8.1, 2H), 7.02 (d, *J*=8.2, 2H), 6.74 (d, *J*=8.8, 2H), 3.90 (tt, *J*=11.6, 3.2, 1H), 2.42 (s, 3H), 2.09 (d, *J*=12.0, 2H), 1.85 (d, *J*=13.4, 2H), 1.68 (d, *J*=12.9, 1H), 1.53 – 1.38 (m, 2H), 1.19 (qd, *J*=12.6, 3.3, 2H), 1.13 – 0.98 (m, 1H). HRMS (ESI) (m/z): calcd for $C_{35}H_{33}N$: 468.2691 Found $[M+H]^+$ 468.2687.

S4: The compound was synthesized using the same procedure as described above for S2 ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 8.01 (d, *J*=8.4, 2H), 7.84 (d, *J*=8.7, 2H), 7.44 (t, *J*=7.4, 2H), 7.38 – 7.29 (m, 2H), 7.25 – 7.13 (m, 4H), 7.09 (d, *J*=8.1, 2H), 6.79 (d, *J*=8.5, 2H), 3.94 (t, *J*=11.4, 1H), 2.40 (s, 3H), 2.14 (d, *J*=12.5, 2H), 1.85 (d, *J*=12.9, 2H), 1.66 (d, *J*=12.4, 1H), 1.45 (dd, *J*=26.1, 12.9, 2H), 1.34 – 1.17 (m, 2H), 1.14 – 1.00 (m, 1H). HRMS (ESI) (m/z): calcd for $C_{33}H_{31}N$: 442.2535 Found $[M+H]^+$ 442.2538.

S0: The compound was synthesized using the same procedure as described above for 9-(4-bromophenyl)-14-phenyl-9,14-dihydrodibenzo[a,c]phenazine. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.74 (d, *J* = 8.3 Hz, 2H), 8.12 (d, *J* = 8.1 Hz, 2H), 7.75 (dd, *J* = 5.9, 3.5 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.34 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.09–6.93 (m, 8H), 6.78 (t, *J* = 8.1 Hz, 2H). HRMS ESI (m/z) $[M+H]^+$: calcd. for $C_{32}H_{23}N_2$ 435.1861; Found, 435.1851.

N^1, N^4-bis(4-bromophenyl)cyclohexane-1,4-diamine: In a 250ml there-neck flask, 6g (0.053 mol) 1,4-cyclohexanedione was dissolved in 100 ml acetic acid, then slowly added 18.4g (0.106 mol) 4-bromoaniline in 50 ml acetic acid. The mixture was stirred for 2h in room temperature. Then (1.2g x 5 0.159 mol) $NaBH_4$ was slowly put in at 0 ^{o}C. After 1h the mixture was poured into ice water, a white solid was precipitated. Filtered the mixture, the white residue was recrystallized by EtOH to give a white solid 15.2g. Yield: 68 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.09 (d, *J*=8.3, 4H), 6.61 (d, *J*=8.8, 4H), 4.82 (s, 2H), 3.63 (s, 2H), 1.94 (d, *J*=7.1, 4H), 1.45 (d, *J*=7.9, 4H).

N^1, N^4-bis(4-bromophenyl)-N^1,N^4-di-p-tolylcyclohexane-1,4-diamine: In a 250 ml flask. 10g (0.024 mol) N^1, N^4-bis(4-bromophenyl)cyclohexane-1,4-diamine, 16.5g (0.12 mol) K_2CO_3, 20.6g (0.094 mol) 1-iodo-4-methylbenzene, 1.82g (9.6 mmol) CuI were refluxed in trichlorobenzene (80 ml) for 48h under N_2 atmosphere. The trichlorobenzene was taken out by vacuum distillation. After cooling, added 150 ml DCM and stirred for 20min, filtered the mixture. Then the solvent was distilled under reduced pressure, and the crude product was purified by column chromatography on silica (PE: DCM = 8:1) to give a white solid 5.22g. Yield: 36 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.13 (m, 8H), 6.89 (d, *J*=8.1, 4H), 6.41 (d, *J*=9.0, 4H), 3.63 (s, 2H), 2.23 (s, 6H), 2.04 (d, *J*=7.1, 4H), 1.31 (t, *J*=9.9, 4H).

S1: In a 50 ml flask. 0.6g (0.92 mmol) 4-bromo-N-cyclohexyl-N-(p-tolyl)aniline, 0.52g (0.92 mmol) 1a, 2M K_2CO_3 2ml, 13.4mg (0.018 mmol) $Pd(dppf)Cl_2$, 20 ml THF were refluxed for 10h. After cooling the mixture were poured into water, and extracted with DCM (30ml x 3). The combined organic layer was washed with water, dried with anhydrous $MgSO_4$. The resident was purified by column chromatography on silica (PE: DCM = 6:1) to give a white solid 0.53g. Yield:

58 %^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (d, *J*=8.3, 2H), 8.22 – 8.11 (m, 2H), 7.87 – 7.47 (m, 6H), 7.42 – 7.12 (m, 8H), 7.03 (s, 6H), 6.89 (d, *J*=8.2, 2H), 6.80 (s, 1H), 6.64 (d, *J*=8.4, 2H), 3.80 (t, *J*=11.3, 1H), 2.36 (s, 3H), 2.01 (d, *J*=12.7, 2H), 1.79 (d, *J*=13.6, 2H), 1.43 – 1.35 (m, 3H), 1.12 (dd, *J*=12.0, 3.4, 2H), 1.04 – 0.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.85, 147.77, 146.54, 146.46, 144.32, 144.11, 138.62, 137.92, 134.85, 133.61, 129.87, 129.62, 129.15, 129.54, 129.48, 128.91, 128.54, 127.42, 127.37, 127.17, 127.05, 126.88, 125.74, 125.46, 125.24, 124.71, 124.19, 123.07, 122.71, 121.16, 117.00, 116.88, 58.32, 31.72, 27.3, 21.08 HRMS (ESI) (m/z): calcd for $C_{51}H_{43}N_3$: 698.3535 Found $[M+H]^+$ 698.3541

M1: In a 50 ml flask. 1g (1.65 mmol) N^1,N^4-bis(4-bromophenyl)-N^1,N^4-di-p-tolylcyclohexane -1,4-diamine, 0.34g (2 mmol) 1b, 2M K_2CO_3 2 ml, 19mg (0.0165 mmol) $Pd(PPh_3)_4$, 20 ml THF were refluxed for 8h. After cooling the mixture were poured into water, and extracted with DCM (30 ml X 3). The combined organic layer was washed with water, dried with anhydrous $MgSO_4$. The resident was recrystallized by hexane and use for next step. 0.52g (0.92 mmol) 1a, 2M K_2CO_3 2ml, 13.4mg (0.018 mmol) $Pd(dppf)Cl_2$, 20ml THF were refluxed for 10h. After cooling the mixture were poured into water, and extracted with DCM (30 ml X 3). The combined organic layer was washed with water, dried with anhydrous $MgSO_4$. The resident was purified by column chromatography on silica (PE: DCM = 6:1) to give a white solid 0.63g. Yield: 38 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 (d, *J*=8.3, 2H), 8.16 – 8.12 (m, 2H), 7.92 (s, 1H), 7.83 (t, *J*=9.5, 3H), 7.75 (dd, *J*=9.1, 6.0, 2H),7.70 – 7.61 (m, 3H), 7.59 – 7.37 (m, 6H), 7.37 – 7.31 (m, 2H), 7.24 – 7.12 (m, 8H), 7.06 – 6.93 (m, 8H), 6.87 (d, *J*=8.1, 2H), 6.84 – 6.72 (m, 1H), 6.66 (d, *J*=8.7, 2H), 6.60 (d, *J*=8.5, 2H), 3.73 (d, *J*=15.1, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 2.09 (s, 4H), 1.43 – 1.31 (m, 4H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 147.89, 147.69, 146.73, 146.29, 144.76, 141.82, 141.09, 138.36, 138.00, 137.95, 135.10, 134.11, 133.80, 133.63, 132.09, 131.18, 130.61, 130.19, 130.05, 129.86, 129.43, 128.77, 128.18, 127.95, 127.84, 127.74, 127.57, 127.35, 126.93, 126.58, 126.08, 125.29, 124.35, 122.99, 121.10, 118.01, 117.24, 116.89, 116.62, 55.86, 30.50, 21.02. HRMS (ESI) (m/z): calcd for $C_{74}H_{60}N_4$: 1005.4896 Found $[M+H]^+$ 1005.4905

M2: The compound was synthesized using the same procedure as described above for compound **M1**. Yield: 41 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (d, *J*=8.3, 2H), 8.19 – 8.14 (m, 2H), 8.01 (d, *J*=8.4, 1H), 7.94 (d, *J*=8.1, 1H), 7.88 (d, *J*=8.2, 1H), 7.78 (dd, *J*=9.0, 6.2, 2H), 7.71 – 7.63 (m, 4H), 7.62 – 7.43 (m, 10H), 7.42 – 7.34 (m, 2H), 7.29 – 7.13 (m, 7H), 7.08 – 6.95 (m, 9H), 6.90 (d, *J*=8.0, 2H), 6.85 – 6.73 (m, 1H), 6.65 (dd, *J*=20.8, 8.5, 4H), 3.76 (d, *J*=11.5, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 2.12 (s, 4H), 1.48 – 1.32 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.96, 147.73, 146.73, 146.30, 144.80, 144.70, 141.83, 141.02, 139.95, 138.51, 138.00, 135.26, 134.10, 133.83, 133.63, 131.64, 131.19, 130.37, 130.21, 130.05, 129.88, 129.45, 129.03, 128.77, 128.25, 127.57, 127.34, 127.14, 126.93, 126.58, 126.46, 126.12, 125.97, 125.74, 125.41, 124.57, 122.99, 121.10, 118.03, 117.25, 116.90, 116.34, 55.86, 30.47, 21.03. HRMS (ESI) (m/z): calcd for $C_{80}H_{64}N_4$: 1081.5209 Found $[M+H]^+$ 1081.5206

M3: The compound was synthesized using the same procedure as described above for compound **M1**. Yield: 56 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (d, *J*=8.2, 2H), 8.23 – 8.06 (m, 2H), 7.78 (s, 2H), 7.67 (t, *J*=7.1, 2H), 7.57 (t, *J*=8.7, 2H), 7.43 – 7.32 (m, 6H), 7.27 – 7.08 (m, 16H), 7.07 – 6.07 (m, 10H), 6.94 (d, *J*=7.9, 1H), 6.88 (d, *J*=7.8, 1H), 6.83 – 6.72 (m, 4H), 6.77 (dd, *J*=15.9, 7.7, 4H), 6.67 – 6.56 (m 2H), 3.85 (d, *J*=95.5, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.70 (s, 4H), 1.49 –1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.77, 145.68, 145.12, 143.77, 143.73, 142.11, 141.81, 140.79, 140.43, 136.98, 134.32, 133.60, 133.09, 132.58, 130.54, 129.08, 129.01, 128.77, 128.43, 128.16, 127.74, 127.00, 126.25, 126.11, 125.96, 125.58, 125.41, 124.33, 123.61, 123.27, 123.10, 121.96, 121.58, 120.07, 118.08, 117.24, 117.00, 116.22, 115.85, 29.44, 26.36, 19.88. HRMS (ESI) (m/z): calcd for $C_{86}H_{69}N_5$: 1172.5631 Found $[M+H]^+$ 1172.5630

M4: The compound was synthesized using the same procedure as described above for compound **M1**. Yield: 58 % ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 (d, *J*=8.3, 2H), 8.43 (s, 1H), 8.13 (dd, *J*=12.5, 8.0, 2H), 8.01 (d, *J*=8.4, 2H), 7.83 – 7.70 (m, 4H), 7.64 (t, *J*=7.6, 2H), 7.54 (dd, *J*=11.8, 7.6, 2H), 7.48 – 7.38 (m, 2H), 7.37 – 7.28 (m, 4H), 7.22 – 7.12 (m, 6H), 7.09 (d, *J*=8.1, 2H), 7.00 (d, *J*=6.8, 6H), 6.89 (d, *J*=8.0, 2H), 6.74 (t, *J*=9.0, 3H), 6.63 (d, *J*=8.5, 2H), 3.79 (d, *J*=30.9, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 2.15 (d, *J*=22.2, 4H), 1.47 – 1.39 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.93, 147.73, 146.75, 146.29, 144.80, 144.70, 141.83, 141.03, 138.01, 135.50, 134.08, 133.64, 131.88, 131.45, 130.55, 130.24, 130.04, 129.86, 129.60, 129.43, 128.76, 128.24, 127.45, 127.33, 127.24, 127.13, 126.95, 126.58, 126.46, 125.95, 125.35, 125.29, 124.98, 124.95, 124.64, 124.56, 122.99, 118.03, 117.25, 116.89, 115.30, 55.93, 30.58, 21.07.HRMS (ESI) (m/z): calcd for $C_{78}H_{62}N_4$: 1055.5053 Found $[M+H]^+$ 1055.5050

Absorption and fluorescence spectra

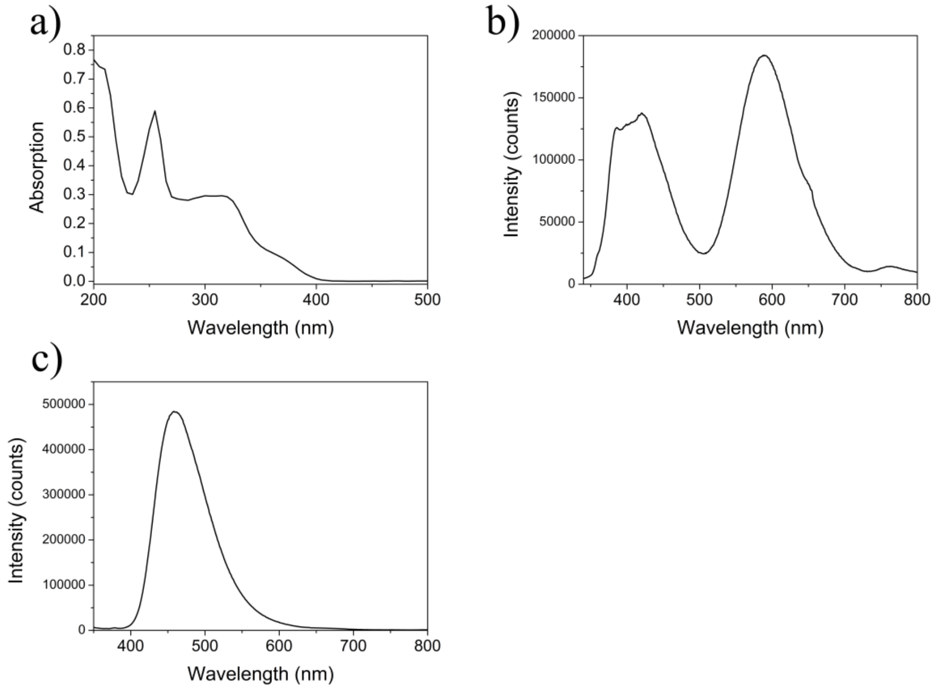


Figure S1 a) The absorption spectra of **S1** in cyclohexane at a concentration of 1x10^{-5}M. b) The emission spectra of **S1** in cyclohexane at a concentration of 1x10^{-5}M, excited at 325nm. c) The emission spectra of **S1** in solid state, excited at 325nm.

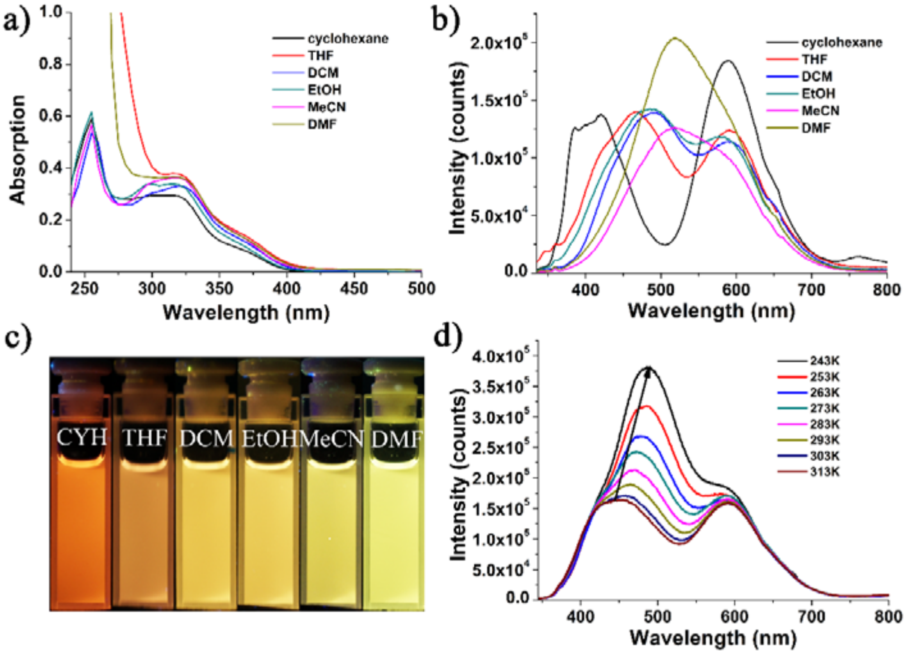


Figure S2 a) The absorption spectra of **S1** in different solvents (from cyclohexane to DMF) at a concentration of 1 x 10^{-5} M. b) The emission spectra of **S1** in different solvents (from cyclohexane to DMF) at a concentration of 1 x 10^{-5} M, excited at 325nm c) The fluorescence images of **S1** in different solvents under 365 nm UV-light irradiation. d) Temperature dependence of the emission spectra of **S1** in THF solution at a concentration of 1 x 10 $^{-5}$ M, excited at 325nm.

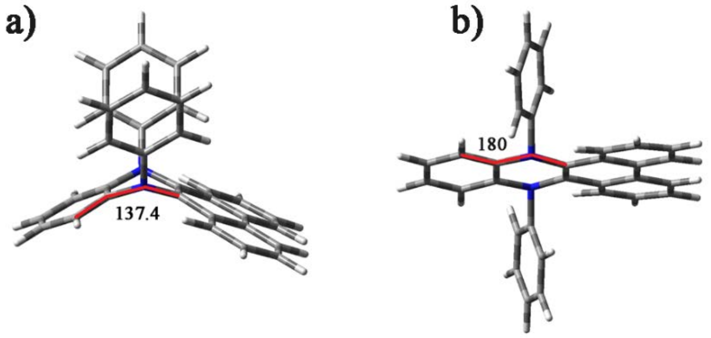


Figure S3. The calculated geometry of **S0** non-planar structure in solid (left), coplanar structure in solution (right).

Table S1. The calculated absorption and emission of **S0** in different state.

	Aborption(nm)	Fluorescence(nm)
Phenazine	311.96	390.36
Planar phenazine	353.16	589.34

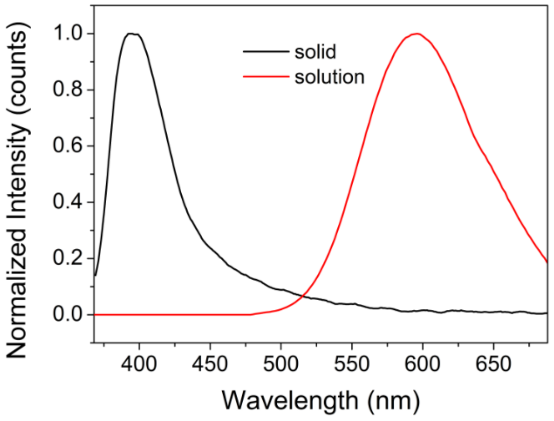


Figure S4. The emission spectra of phenazine-derivant (**S0**) in different state: solid (Black), 1 x 10^{-5}M cyclohexane solution (Red), excited at 325nm.

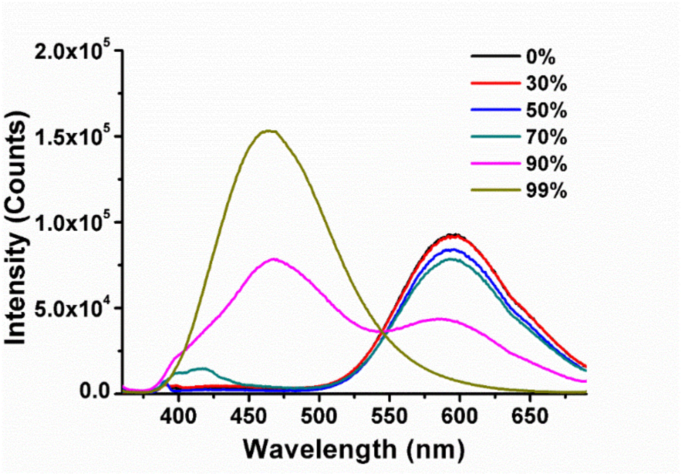


Figure S5 The fluorescence spectra of **S0** in different water fraction solution at a concentration of 1 x 10^{-5} M, excited at 325nm.

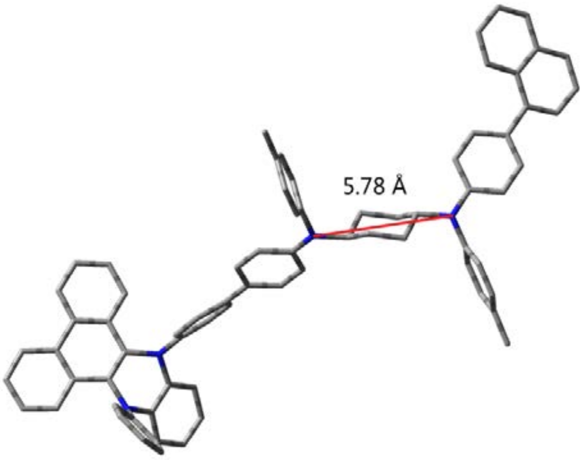


Figure S6 The calculation molecular geometry of **M1**

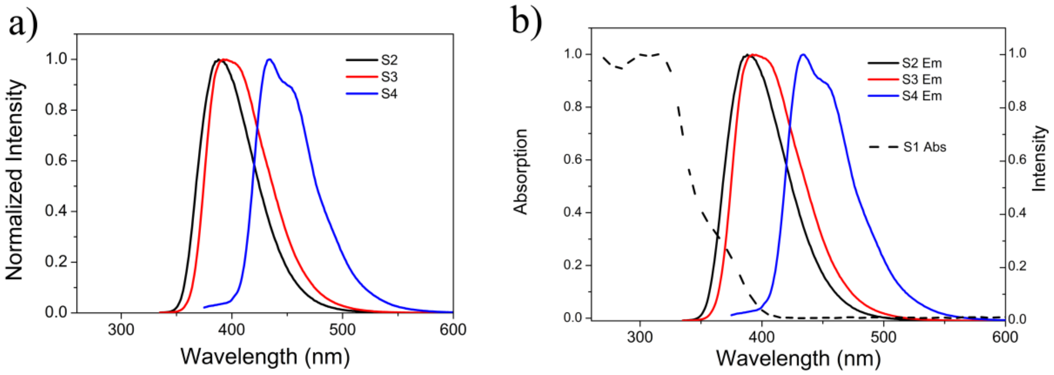


Figure S7 a) The normalized emission spectra of **S2 - S4** in cyclohexane at a concentration of 1 x 10^{-5} M. b) the absorption spectra of acceptor (**S1**) *versus* the emission spectra of donor (**S2 – S4)** in cyclohexane at concentration of 1 x 10^{-5} M.

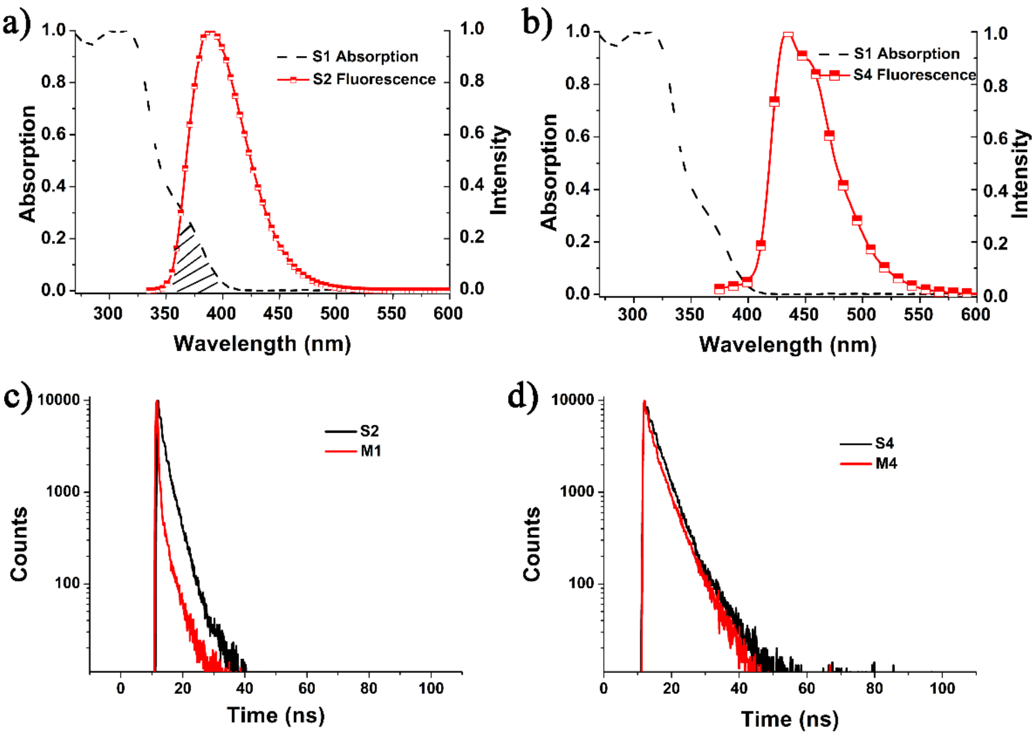


Figure S8 (a), (b) The normalized absorption spectra of acceptor **S1** (left) versus the normalized fluorescence spectra of donor **S2** and **S4** (right) for **M1** and **M4** in cyclohexane at a concentration of 1 x 10^{-5} M. (c), (d) The time-resolved fluorescence of the donor emission *versus* **M1** and **M4** in cyclohexane at concentration of 1 x 10^{-5} M.

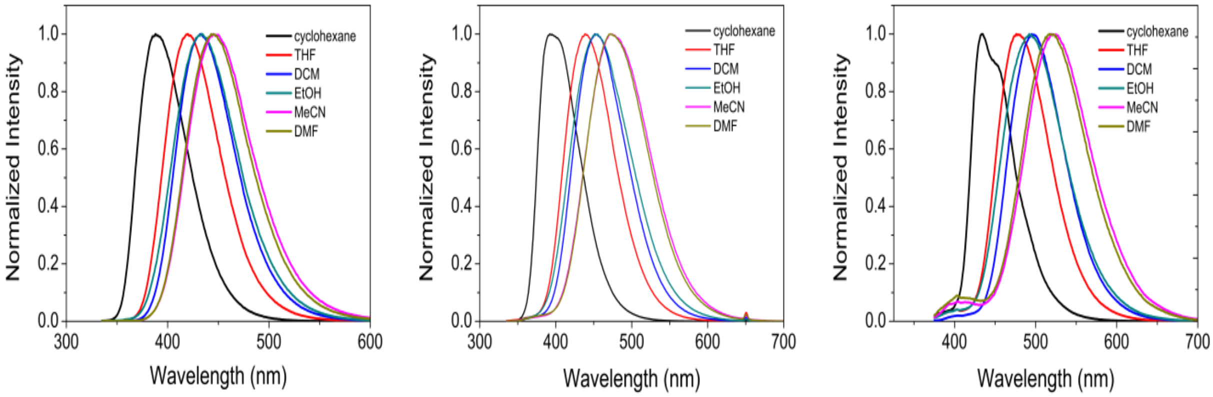


Figure S9 The normalized emission spectra of **S2** (left), **S3** (middle), **S4** (right) in different solvent at concentration of 1 x 10^{-5} M.

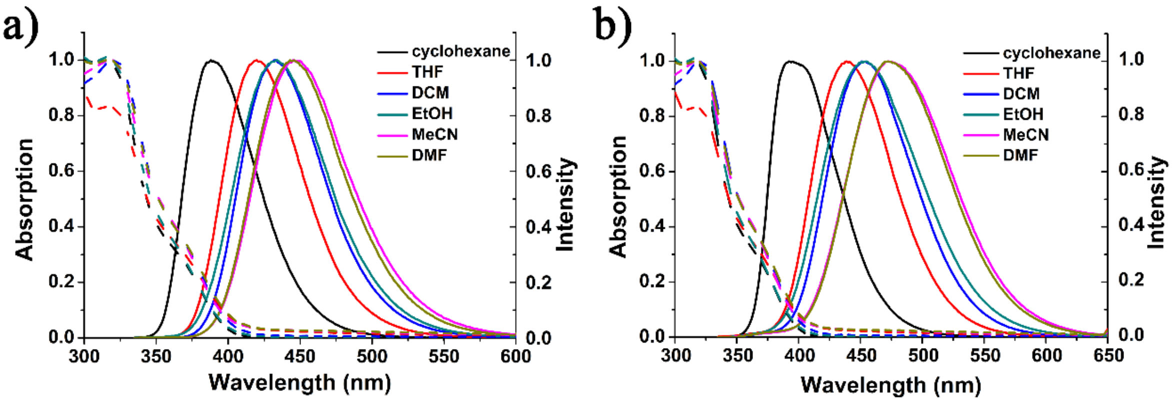


Figure S10 The absorption spectra of acceptor (**S1**) *versus* the emission spectra of donor (**S2** and **S3**) for compound **M1** (left) and **M2** (right) in different solvents at 1 x 10^{-5} M.

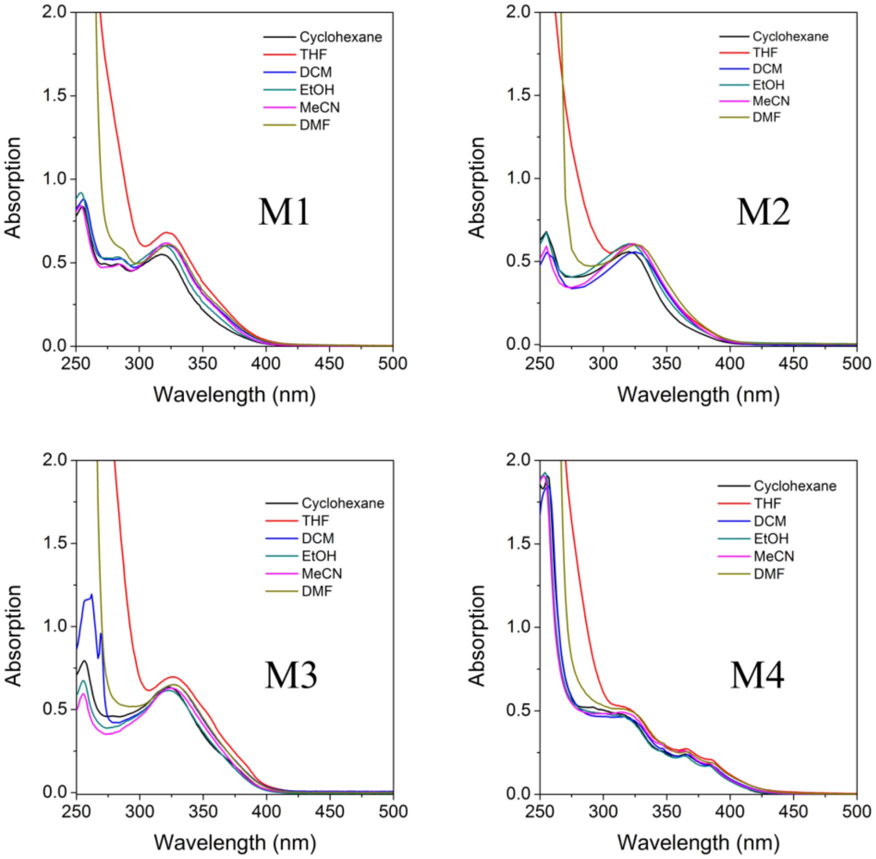


Figure S11 The absorption spectra of **M1 – M4** in different solvent at 1 x 10^{-5} M.

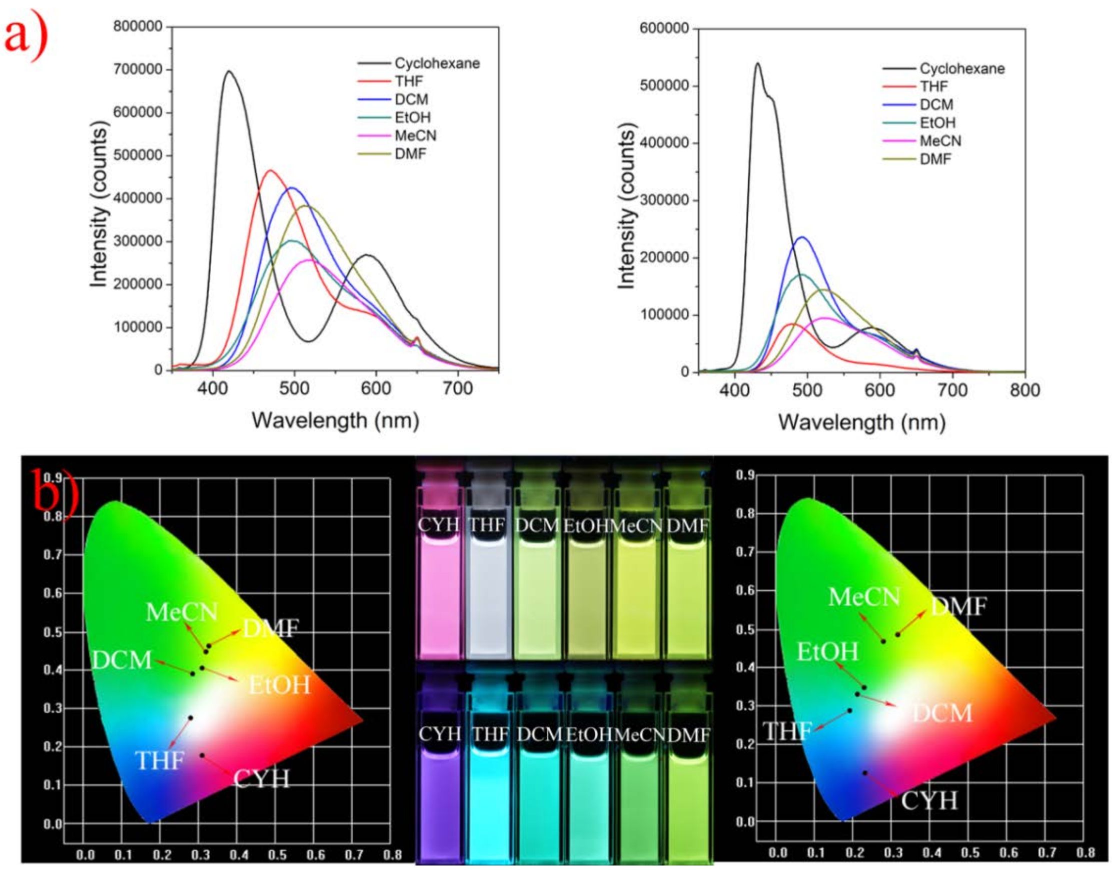


Figure S12 (a) the fluorescence spectra of **M3** (left), **M4** (right) in different solvent excited at 325nm at 1 x 10^{-5}M. (b) the chromaticity coordinates (CIE) and the fluorescence images of **M3** (top), **M4** (bottom) in different solvent at a concentration of 1 x 10^{-5} M under 365nm UV-light.

Table S2 Photophysical property of **S1**, **M1-M4** in different solvent at a concentration of 1 x 10^{-5} M

	Solvent	**λ_{ab} (nm)**	**λ_{em} (nm)**	**QY, Φ_F**
S1	Cyclohexane	319	418, 588	0.18
	THF	320	464, 588	0.16
	DCM	323	487, 589	0.14
	EtOH	321	489, 591	0.15
	MeCN	320	521	0.13
	DMF	321	522	0.14
M1	Cyclohexane	318	426, 590	0.17
	THF	321	475, 591	0.14
	DCM	321	491, 591	0.11
	EtOH	320	492, 589	0.12
	MeCN	322	469	0.11
	DMF	323	517	0.15
M2	Cyclohexane	321	423, 589	0.19
	THF	322	453, 590	0.15
	DCM	325	455, 591	0.15
	EtOH	323	463, 589	0.12
	MeCN	324	475	0.16
	DMF	326	486	0.16
M3	Cyclohexane	322	419, 589	0.21
	THF	324	469, 590	0.16
	DCM	324	497, 593	0.14
	EtOH	325	498	0.12
	MeCN	326	518	0.12
	DMF	327	517	0.14
M4	Cyclohexane	321	430, 589	0.22
	THF	322	477, 591	0.16
	DCM	321	492,594	0.15
	EtOH	322	491	0.11
	MeCN	323	523	0.11
	DMF	325	523	0.13

Single Crystal

Crystals of phenazine (**S0**) were grown by slow evaporation from dichloromethane/ethanol mixture solutions and performed by X-ray analysis (Table S3). The three views of these compounds' single crystal structures are shown in Figure S13, together with the selected angles. The single crystal structures of phenazine exhibit non-planar conformations, in which the intersecting planes of the two aryl rings along the N1-N2 axis form a bay with bent angle (Θ_b) around 137˚ and the N,N′ -diphenyl rings located at the upside of the bay with the upward angle of ~70˚ (Θ_1 and Θ_2, Figure S13).

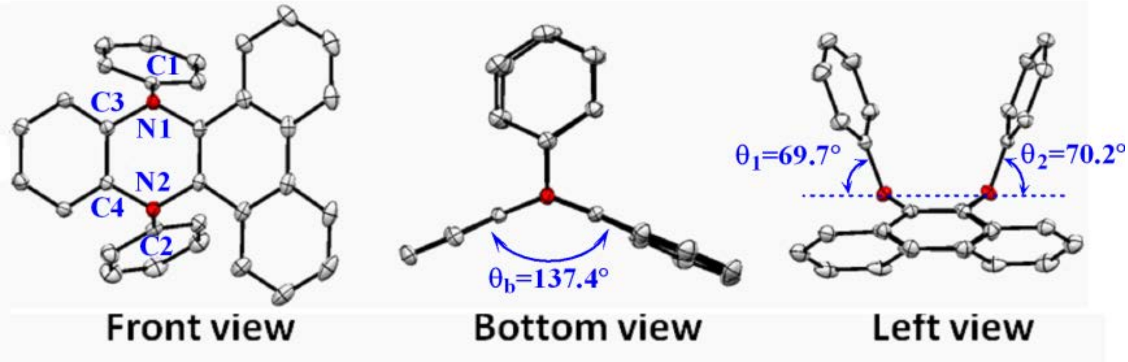


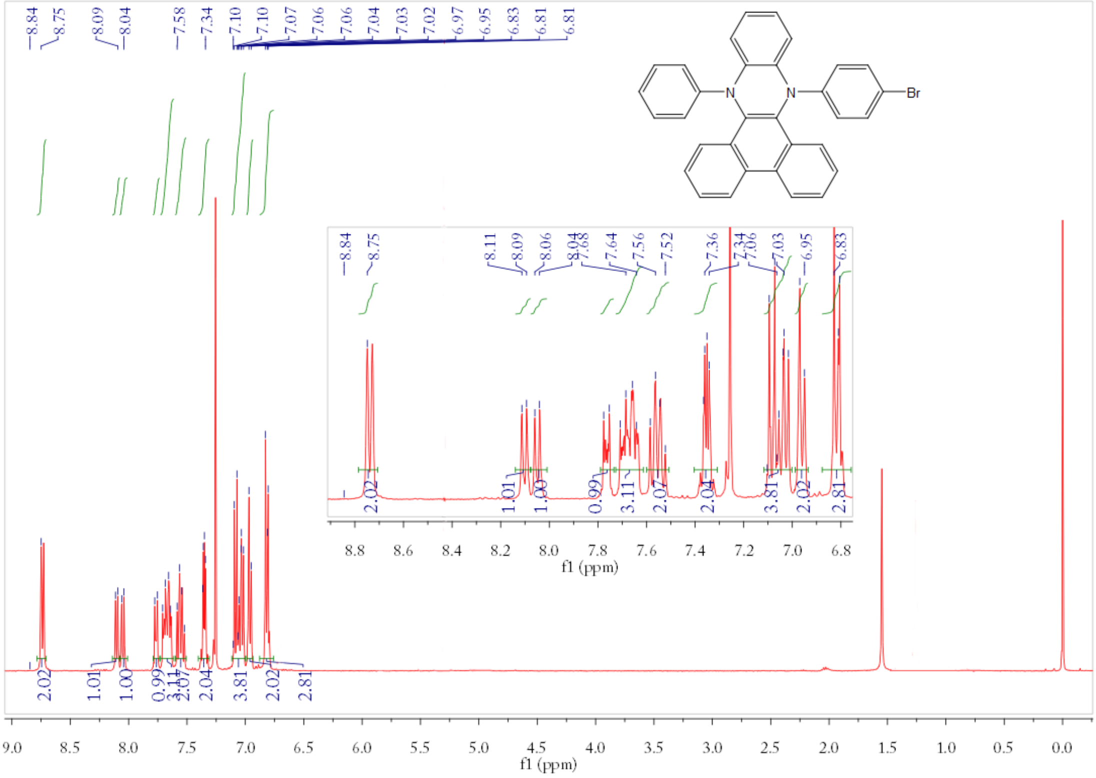
Figure S13. Single crystal structure and its three views of **S0**.

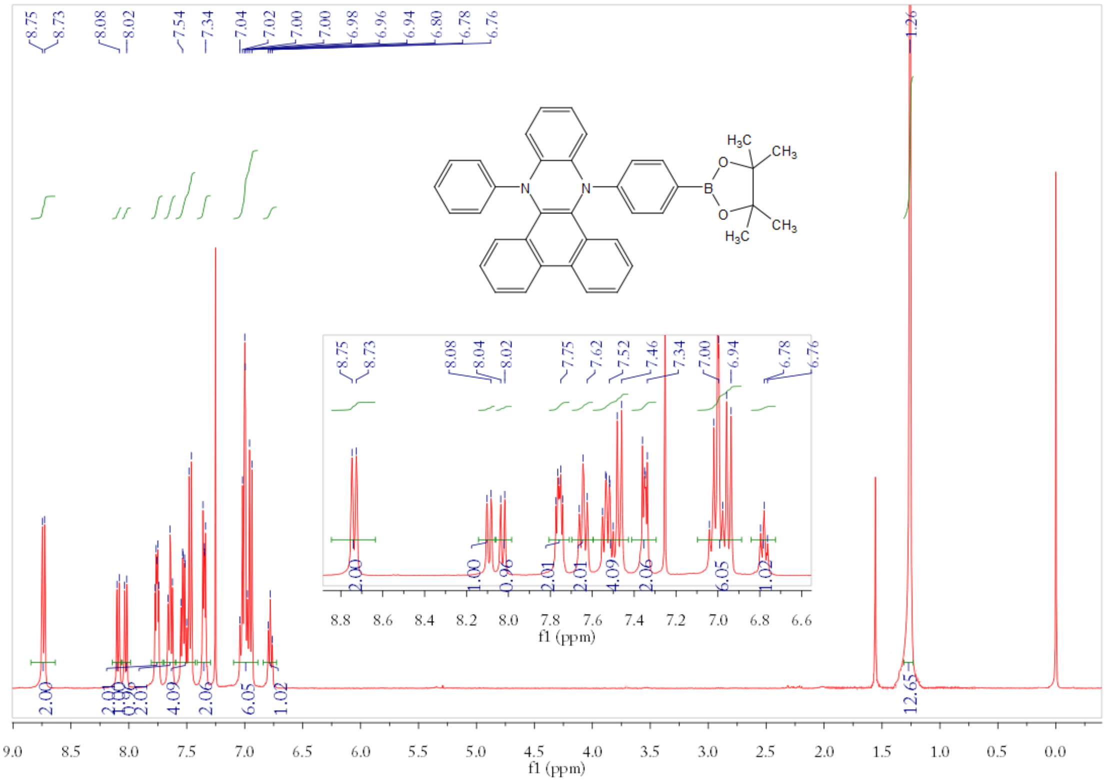
Table S3. CCDC.NO, crystal data and structure refinements of N,N′-disubstituted-dihydrophenazine and benzoannealated analogues.

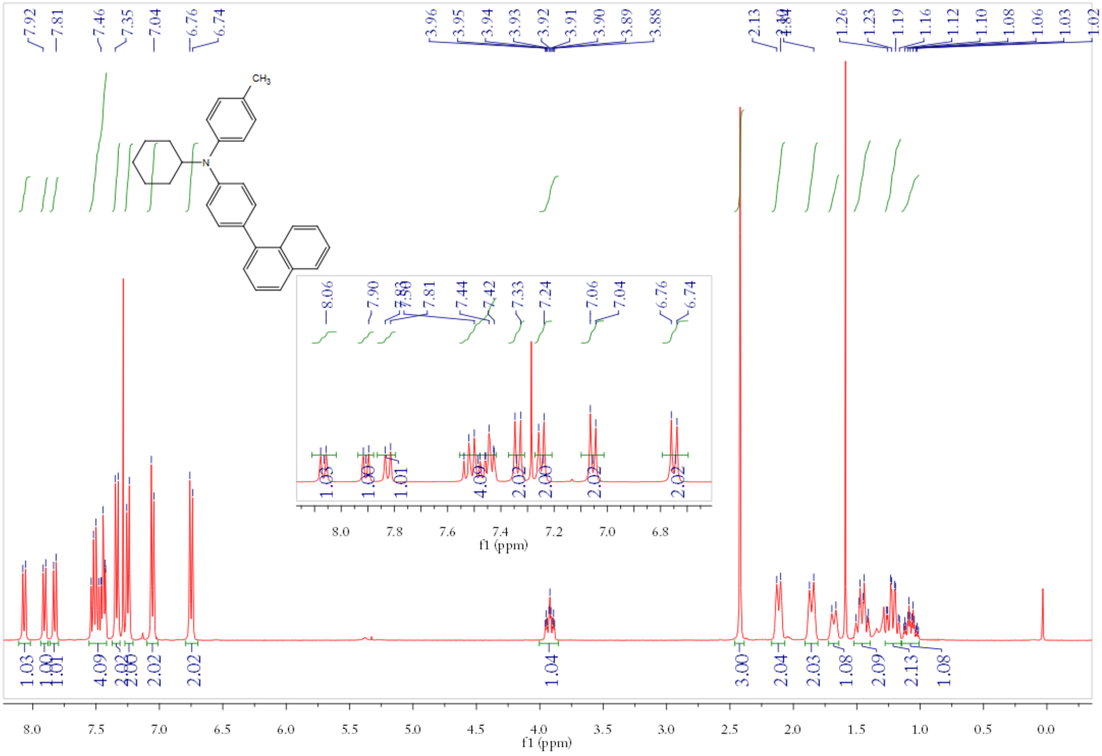
	phenazine
CCDC.NO	837117
empirical formula	$C_{32}H_{22}N_2$
formula wt	434.52
T, k	133(2)
crystal system	Monoclinic
Space group	P2(1)/n
a, Å	14.6334(15)
b, Å	8.9414(9)
c, Å	17.7375(18)

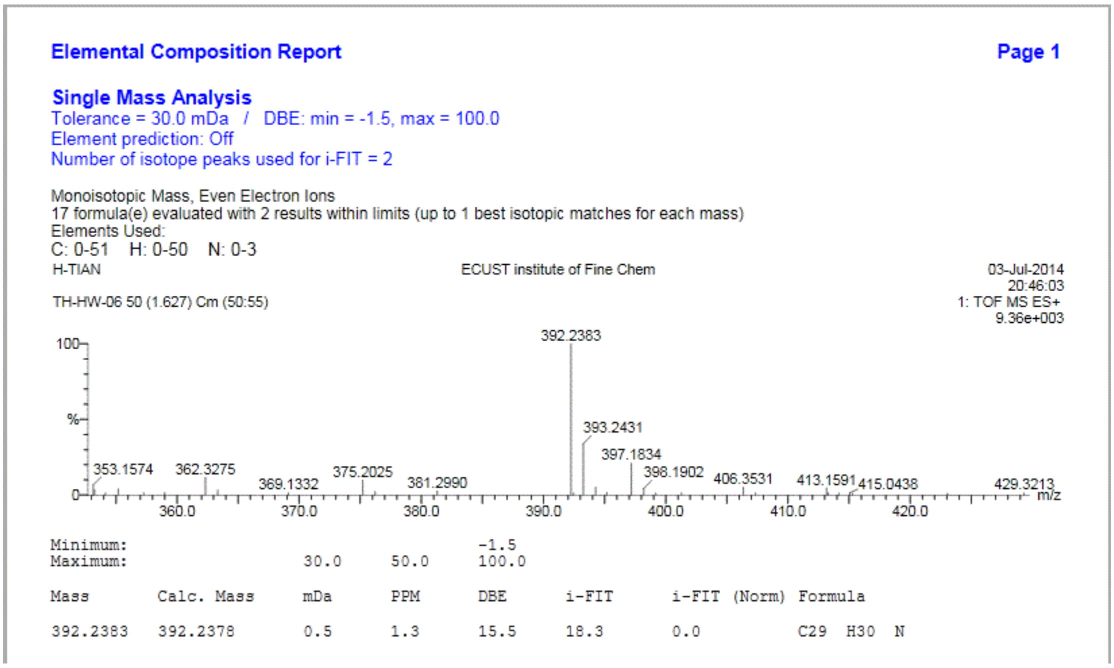
α, deg	90.00
β, deg	105.381(2)
γ, deg	90.00
V, Å^3	2237.7(4)
Z	4
density, g/cm^3	1.290
μ(Mo Kα), mm^{-1}	0.075
θ range, deg	2.10-29.00
No. of reflns collected	18255
No. of independent reflns	5947
R(int)	0.0253
GOF	1.019
$R_1[I > 2\sigma(I)]$	0.0424
$wR_2[I > 2\sigma(I)]$	0.1174
R_1 (all data)	0.0560
wR_2 (all data)	0.1280

^{1}H NMR and HRMS Spectra of synthesized compounds









Elemental Composition Report **Page 1**

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Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
17 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-51 H: 0-50 N: 0-3

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20:46:03
TH-HW-06 50 (1.627) Cm (50:55) 1: TOF MS ES+
9.36e+003

```
Minimum:                                    -1.5
Maximum:                   30.0      50.0   100.0

Mass       Calc. Mass      mDa       PPM    DBE      i-FIT    i-FIT (Norm) Formula

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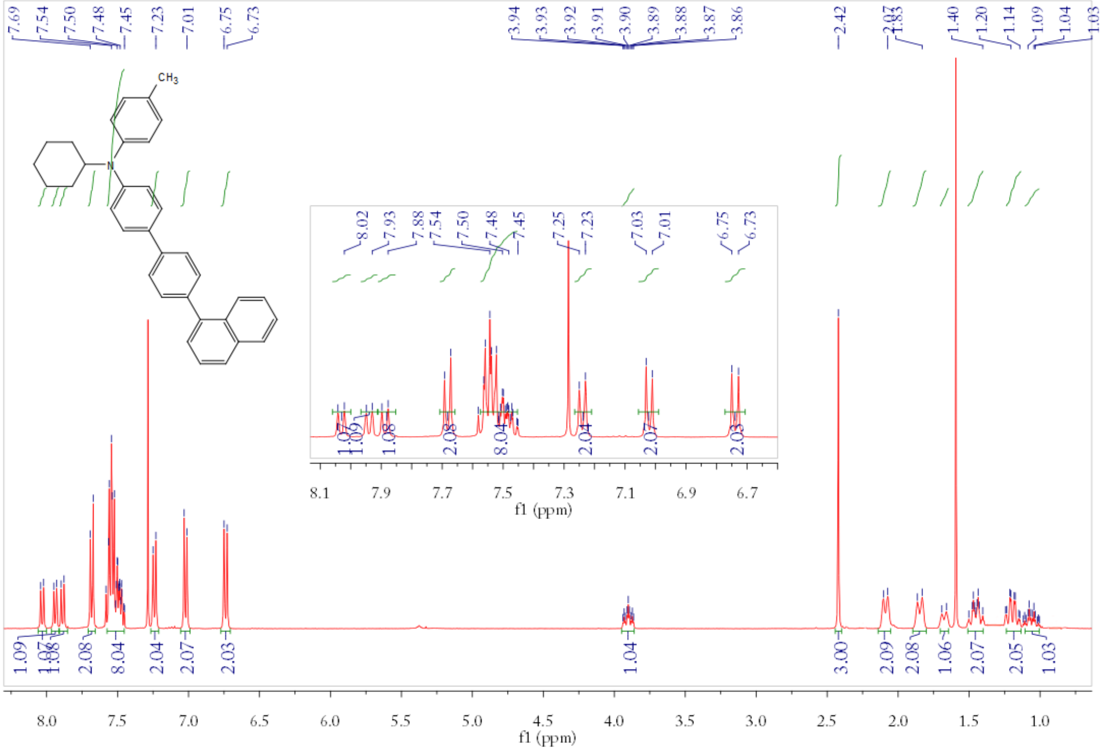

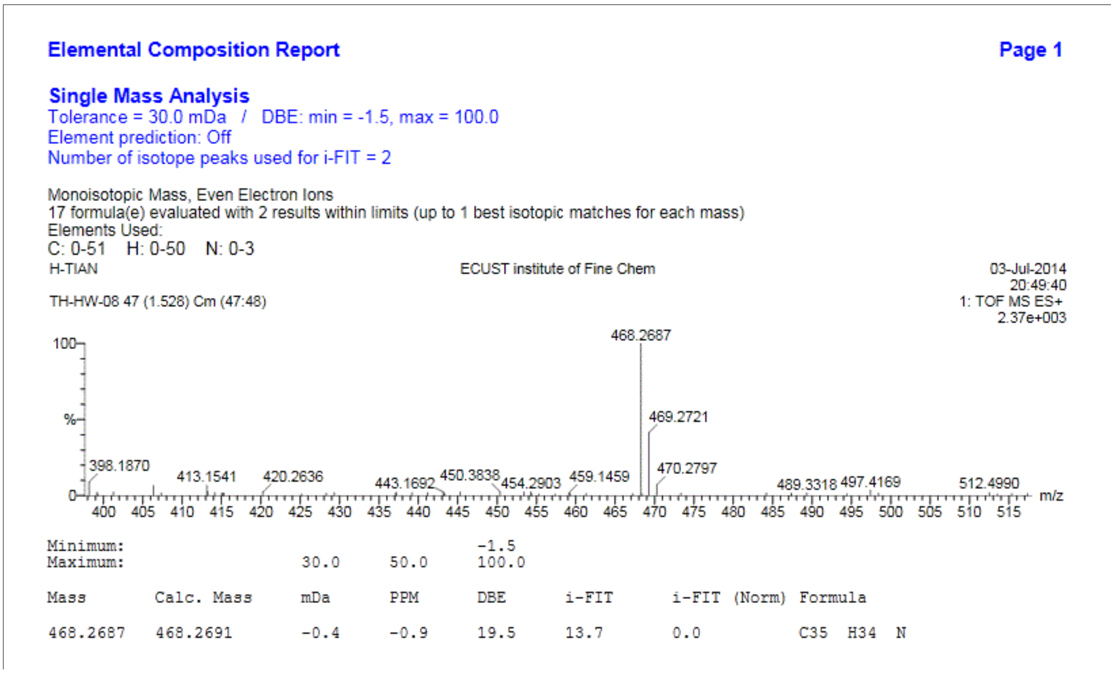

Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
17 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
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2.37e+003

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Maximum:                  30.0      50.0    100.0

Mass       Calc. Mass     mDa       PPM     DBE       i-FIT      i-FIT (Norm) Formula

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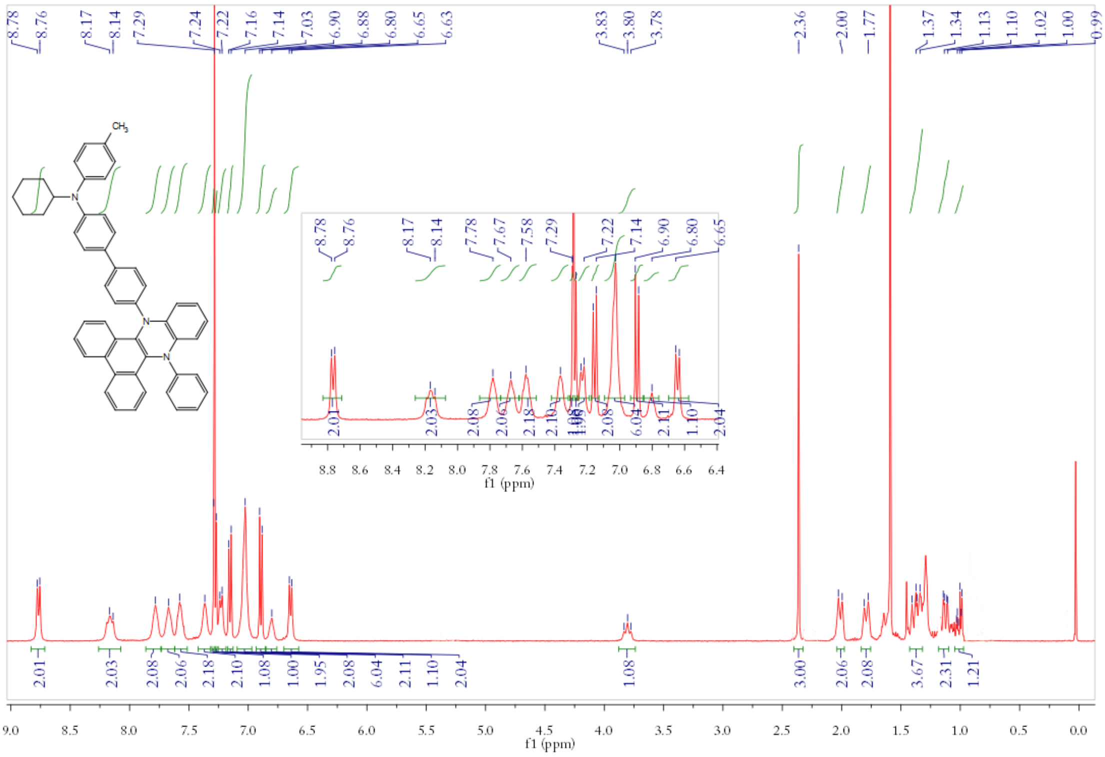

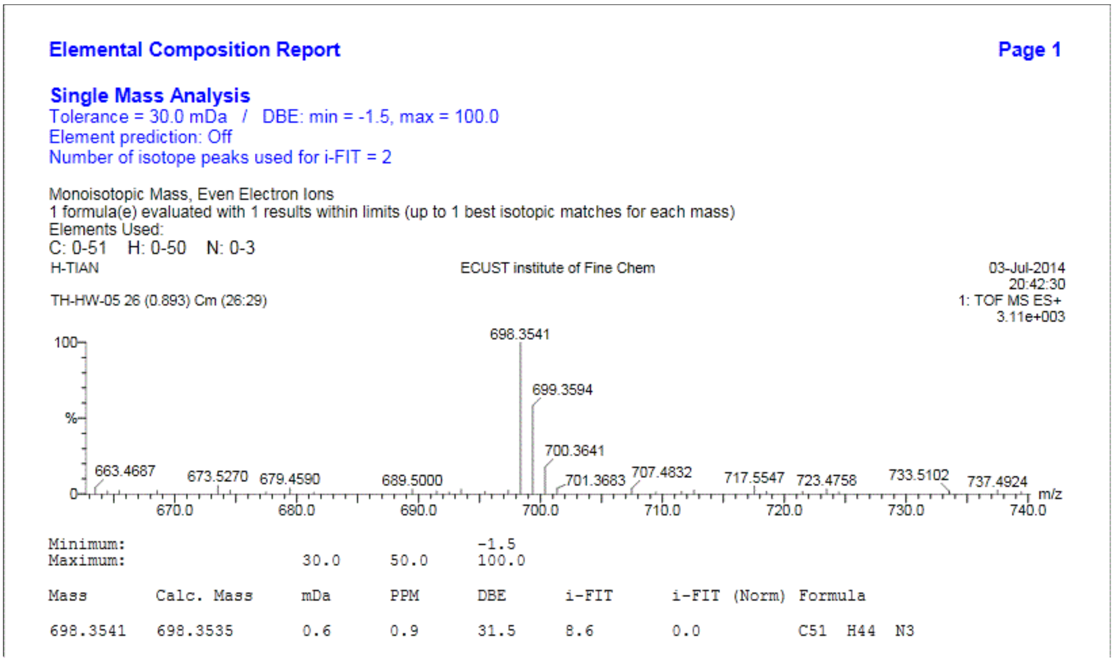

Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

1 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-51 H: 0-50 N: 0-3

H-TIAN ECUST institute of Fine Chem 03-Jul-2014 20:42:30

TH-HW-05 26 (0.893) Cm (26:29) 1: TOF MS ES+ 3.11e+003

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Minimum:                                    -1.5
Maximum:                 30.0       50.0    100.0

Mass      Calc. Mass     mDa        PPM     DBE      i-FIT     i-FIT (Norm) Formula

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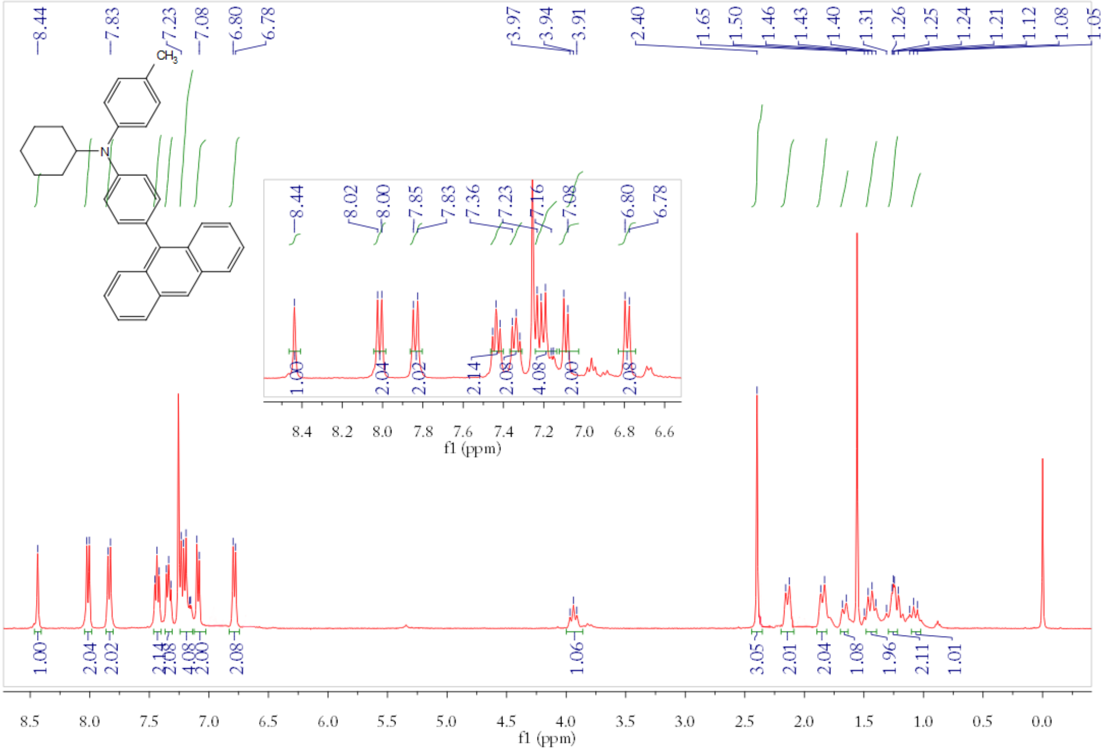

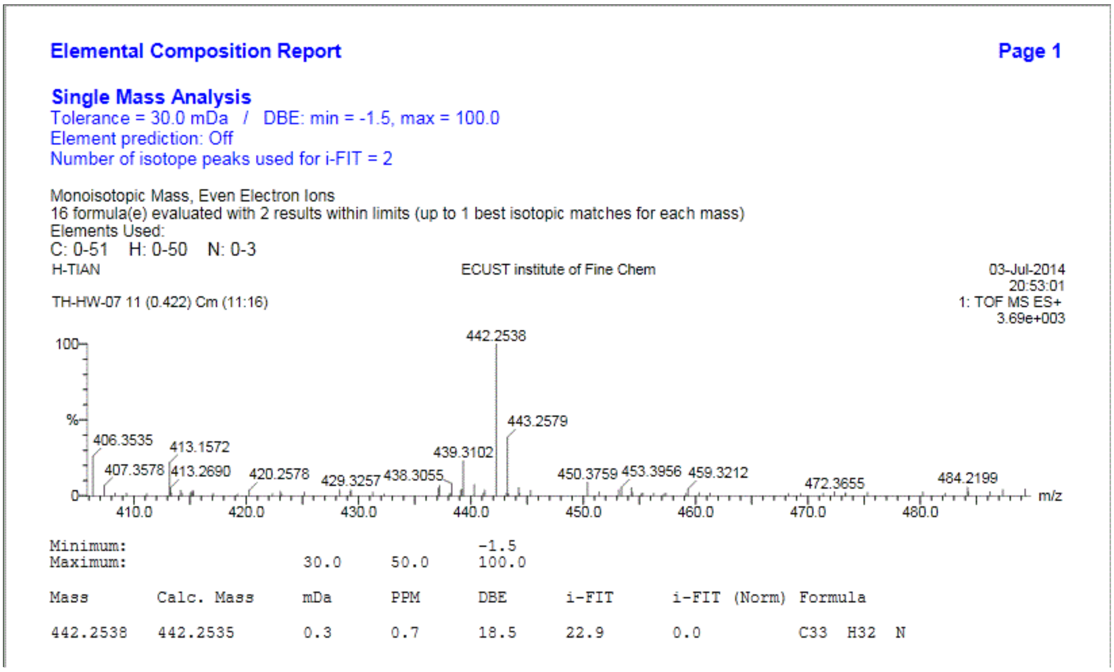

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
16 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
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H-TIAN ECUST institute of Fine Chem 03-Jul-2014 20:53:01
TH-HW-07 11 (0.422) Cm (11:16) 1: TOF MS ES+ 3.69e+003

```
Minimum:                                 -1.5
Maximum:             30.0      50.0     100.0

Mass     Calc. Mass  mDa       PPM       DBE      i-FIT      i-FIT (Norm) Formula

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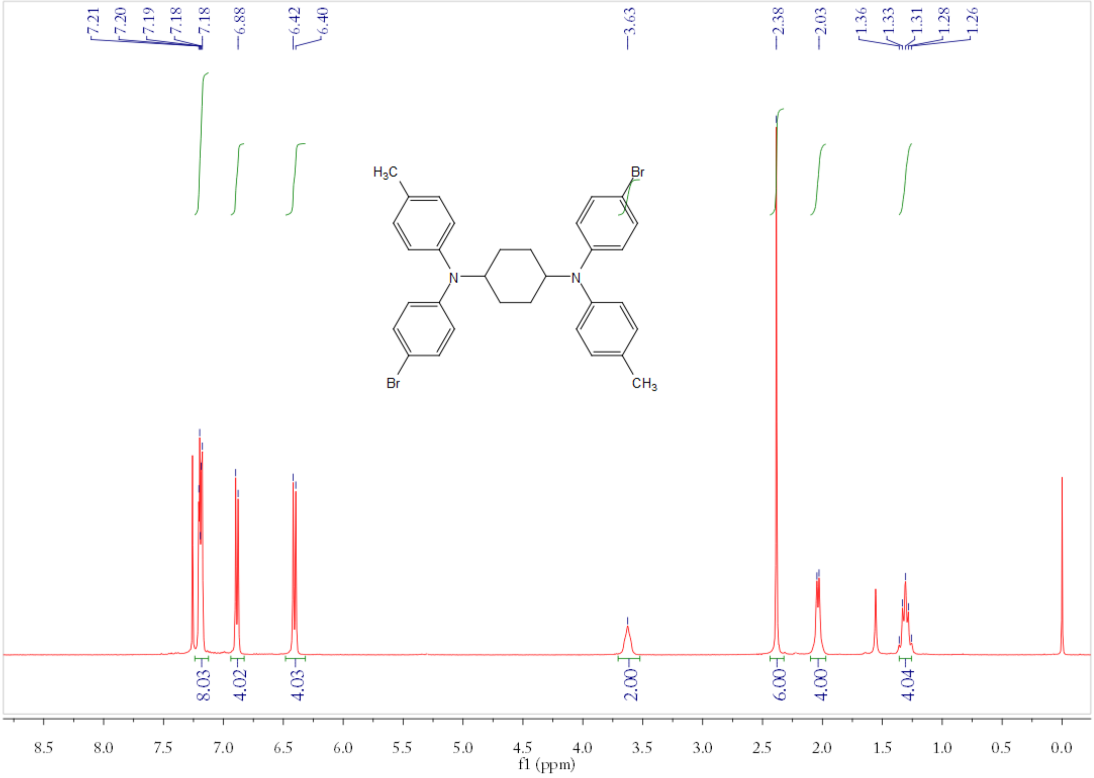
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7.20
7.19
7.18
7.18
6.88
6.42
6.40
3.63
2.38
2.03
1.36
1.33
1.31
1.28
1.26
H_3C
Br
N
N
Br
CH_3
8.03
4.02
4.03
2.00
6.00
4.00
4.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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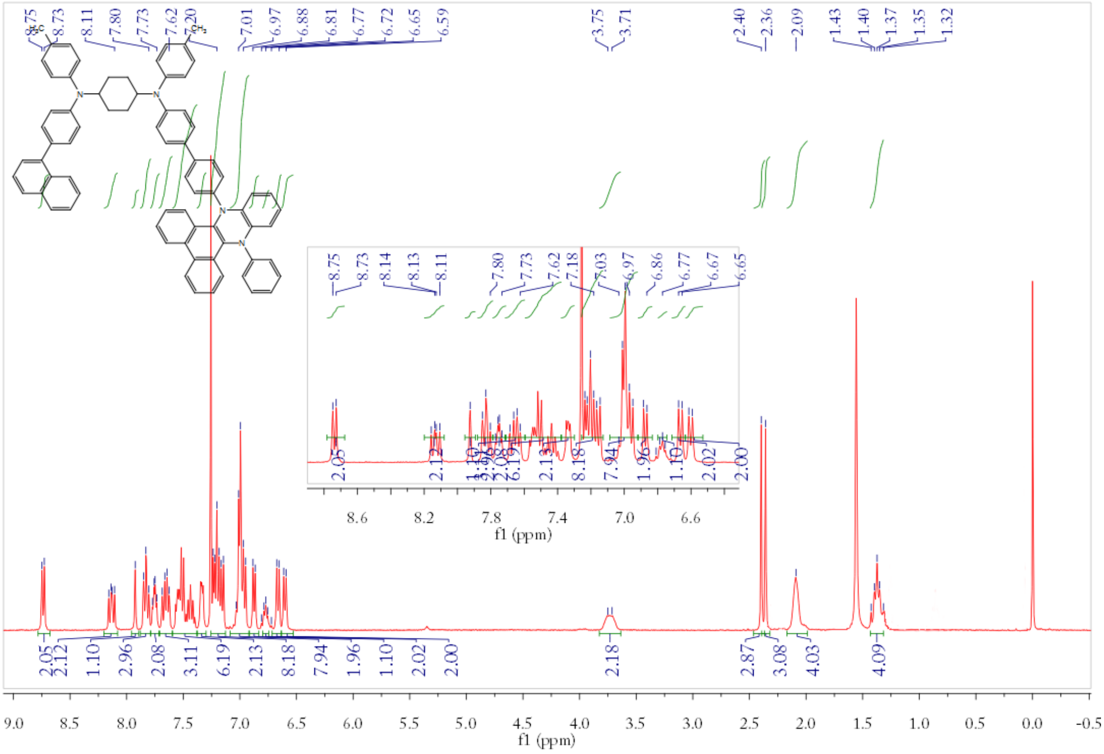
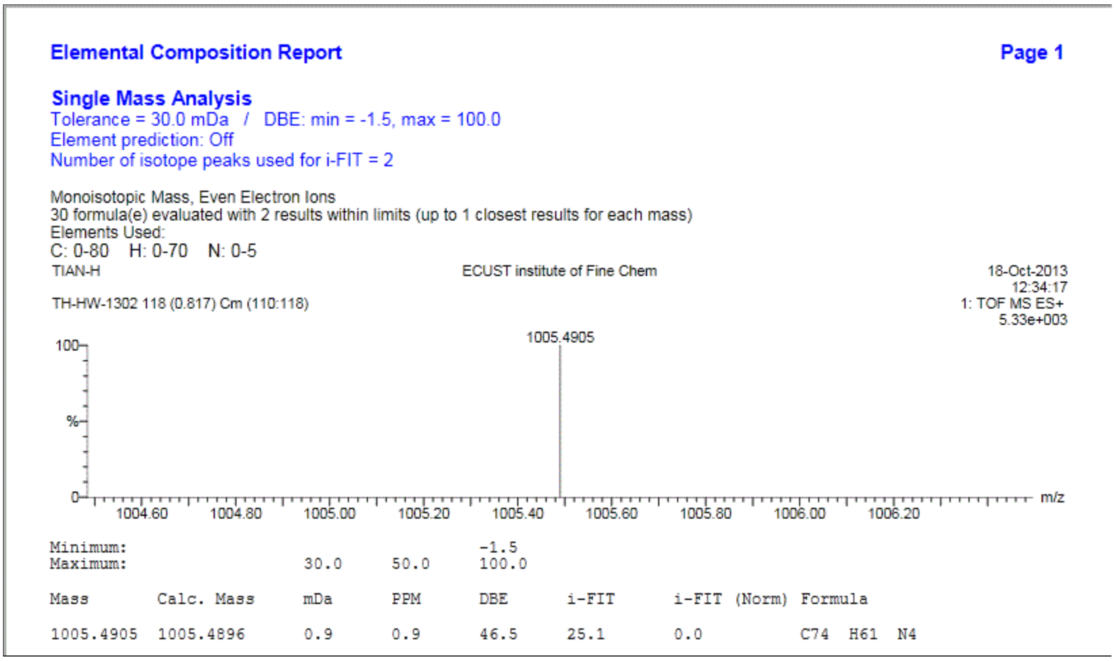
1.0
0.5
0.0
f1 (ppm)





Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
30 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
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TIAN-H ECUST institute of Fine Chem 18-Oct-2013
12:34:17
TH-HW-1302 118 (0.817) Cm (110:118) 1: TOF MS ES+
5.33e+003

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Minimum:                                   -1.5
Maximum:                 30.0      50.0    100.0

Mass      Calc. Mass     mDa       PPM     DBE      i-FIT     i-FIT (Norm)  Formula

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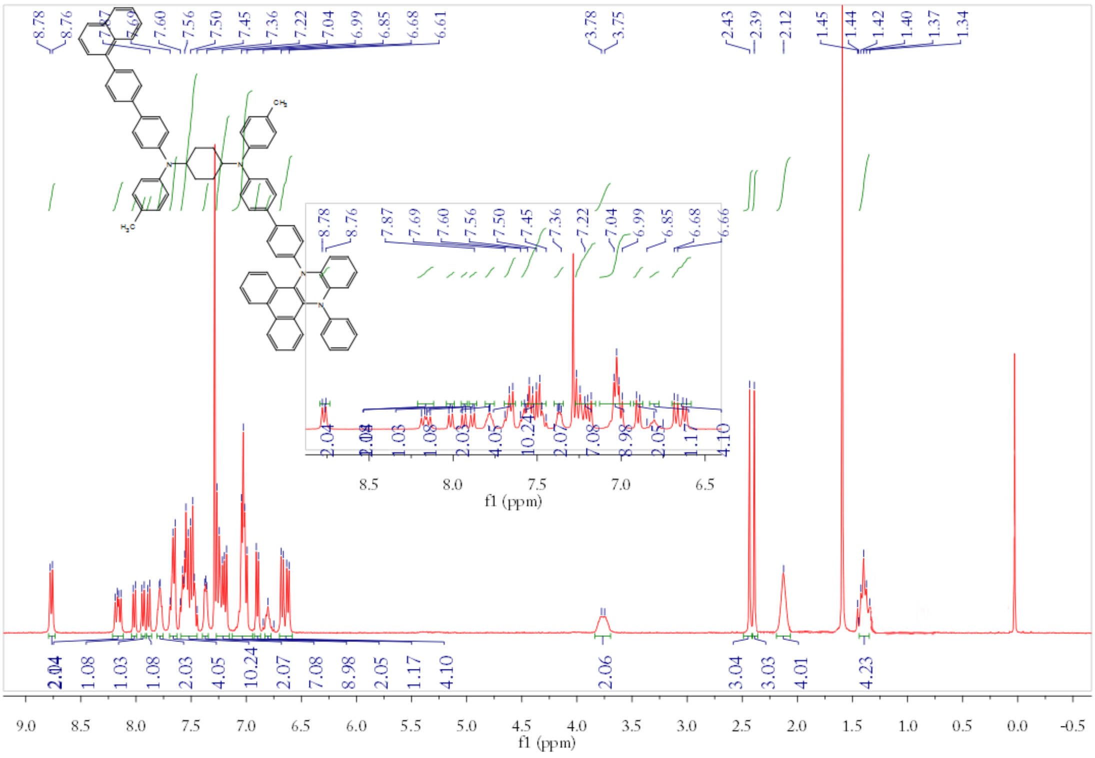

Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
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Elements Used:
C: 0-100 H: 0-70 N: 0-4

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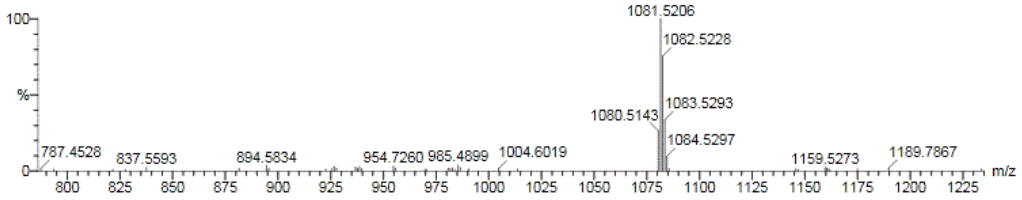

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Maximum:          30.0    50.0   100.0

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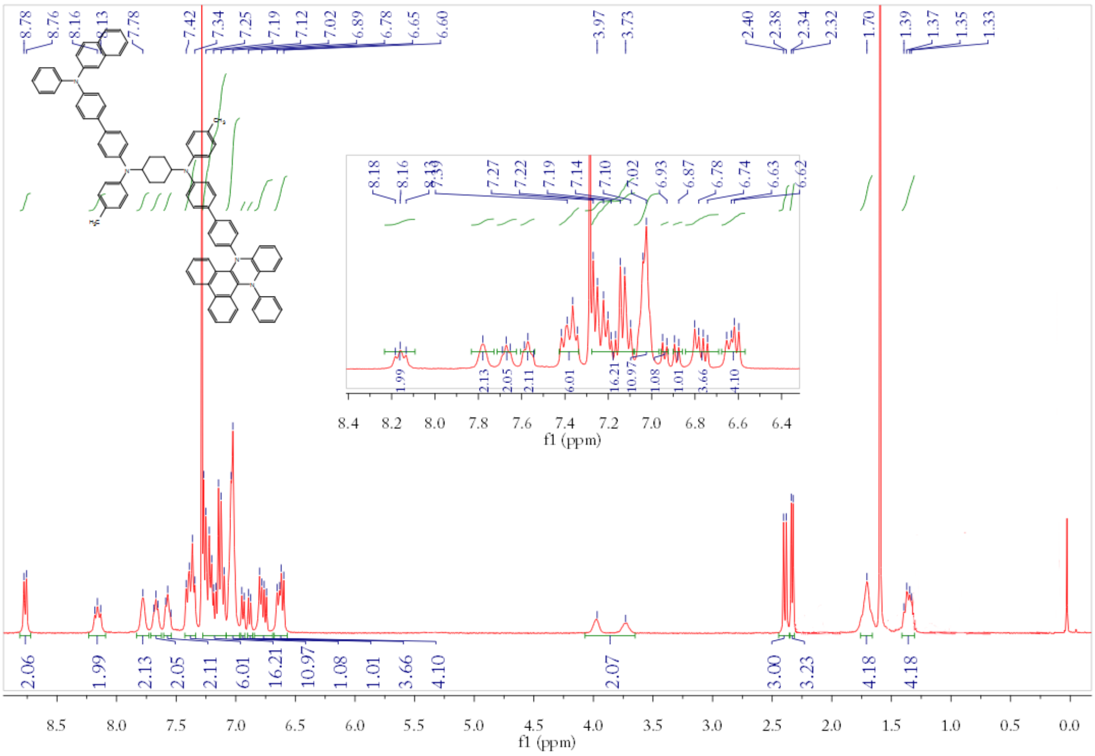

Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
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Elements Used:
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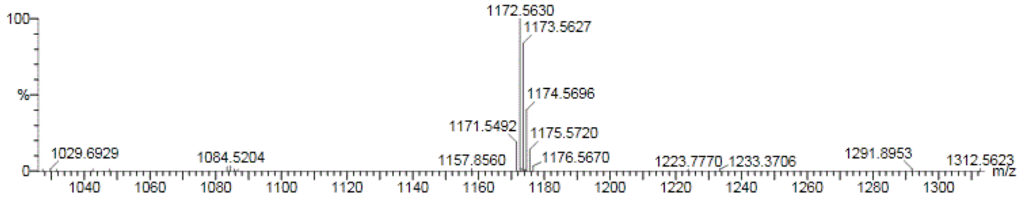

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Minimum:                                    -1.5
Maximum:                30.0      50.0      100.0

Mass      Calc. Mass    mDa       PPM       DBE       i-FIT      i-FIT (Norm)  Formula

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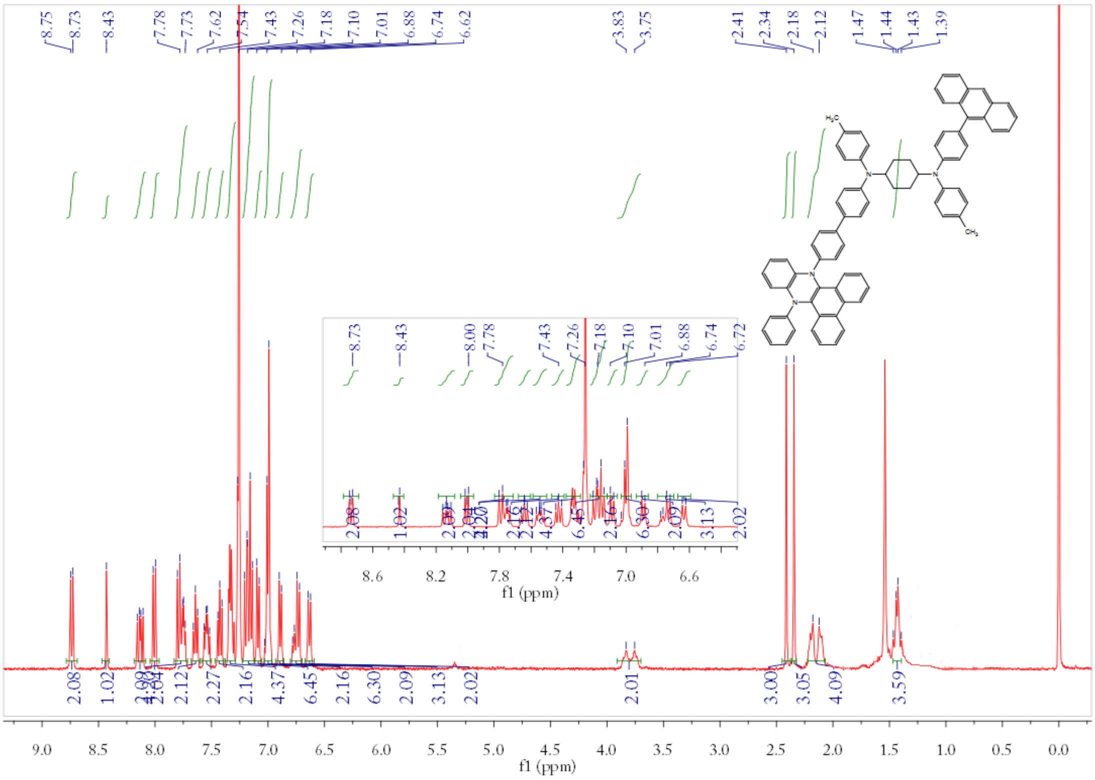

Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-80 H: 0-70 N: 0-5

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12:43:44
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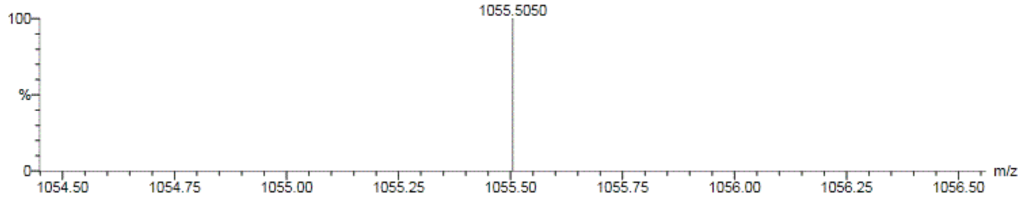
2.57e+003



```
Minimum:                              -1.5
Maximum:              30.0     50.0   100.0

Mass       Calc. Mass    mDa      PPM      DBE      i-FIT      i-FIT (Norm) Formula

1055.5050  1055.5053     -0.3     -0.3     49.5     23.8       0.0          C78  H63  N4
```