Emission Mechanism of Doubly *ortho*-Linked Quinoxaline/Diphenylfluorene or *cis*-Stilbene/Fluorene Hybrid Compounds Based on the Transient Absorption and Emission Measurements during the Pulse Radiolysis

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SUPPORTING INFORMATION

Experimental details, spectral data of compounds **1**-**4** and OLED device measurements for **1a**-**e**, **2a**, **3d**, **3f**, and **4f** (25 pages).

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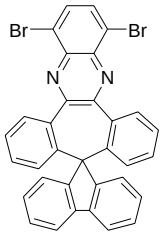
General. ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol JVM-EX400 (400 MHz ^{1}H, 100 MHz ^{13}C) spectrometers in deuterochloroform with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm (δ). Coupling constants, *J*, are reported in Hz. Mass spectra were recorded on a Finnigan TCQ-700 GC/LC/MS spectrometer with an ionization voltage of 70 or 20 eV unless otherwise stated. High-resolution mass spectra were measured on a Finnigan MAT 95S spectrometer. Combustion analyses were performed on a Perkin-Elmer 2400-CHN analyzer by the Northern Instrument Center of Taiwan. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT-95S spectrometer. Data are reported in the form m/e (intensity relative to base peak). Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light or with phosphomolybdic acid (PMA) and $KMnO_4$ staining agents. Column (flash) chromatography was performed using 32-63 μm silica gel. All reagents were purchased from ACROS, ALDRICH, and TCI with purification in advance before use. Solvents for extraction and chromatography were reagent grade. Dichloromethane and chlorobenzene were dried over CaH_2 before use. Diethyl ether, THF, 1,2-dimethoxyethane (DME) and toluene were dried over Na with benzophenone-ketyl intermediate as indicator. All reactions were run under argon.

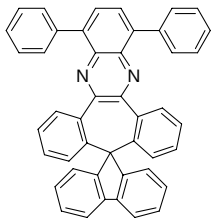
Spiro-fluorene-dibenzosuberene[d](1,4-dibromo-quinoxaline) (1)[1]



To a 50-mL, two-necked, round-bottomed flask was placed **Spiro-fluorene-dibenzosuberan-10,11-dione** (745 mg, 2 mmol), 1,2-diamino-3,6-dibromobenzene (585 mg, 2.2 mmol) and catalytic *p*-TSA in $CHCl_3$ (20 mL). The reaction mixture was stirred under reflux for 12 hours. After having been quenched with saturated aqueous $NaHCO_3$ (20 mL), the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **1**, which was further re-crystallized from CH_2Cl_2 to afford pure **1** (1084 mg, 90 %): m.p. 287 ℃ (DSC); M.W.: 602.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 7.6, 1.3, 2H), 8.03 (s, 2H), 7.75 (d, *J* = 7.6, 2H), 7.47 (td, *J* = 7.6, 1.6, 2H), 7.34 (t, *J* = 7.6, 2H), 7.25-7.19 (m, 4H), 7.07 (t, *J* = 7.6, 2H), 6.76 (d, *J* = 7.6, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.31, 149.39, 145.86, 140.02, 140.00, 136.99,

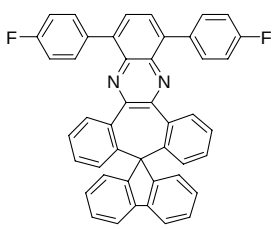
134.42, 133.36, 130.19, 128.55, 128.03, 128.01, 127.64, 127.23, 124.12, 120.48, 66.54; MS (ESI) 603.4 ($M+H^+$, 100); TLC R_f 0.30 (hexanes/CH_2Cl_2, 3/1).

Spiro-fluorene-dibenzosuberene[d](1,4-bis(4-methoxyphenyl)quinoxaline) (1a)[2]



To a 50-mL, two-necked, round-bottomed flask was placed **1** (602 mg, 1 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in DME (25 mL). A solution of phenylboronic acid (293 mg, 2.4 mmol) and Na_2CO_3 (318 mg, 3 mmol) in degassed water (12 mL) was added and the whole solution was refluxed for 24 hours. The reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **1a**, which was further re-crystallized from CH_2Cl_2/hexanes to afford pure **1a** (555 mg, 93 %): m.p. 316 ℃ (DSC); T_d 361 ℃ (TGA); T_g 122 ℃ (DSC); M.W.: 596.72; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.9, 1.3, 2H), 8.04 (s, 2H), 7.94 (d, *J* = 7.2, 4H), 7.75 (d, *J* = 7.6, 2H), 7.54 (t, *J* = 7.2, 4H), 7.45 (t, *J* = 7.2, 4H), 7.37-7.32 (m, 4H), 7.20-7.13 (m, 4H), 7.08 (t, *J* = 7.6, 2H), 6.84 (d, *J* = 7.6, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.85, 149.71, 145.50, 140.09, 139.64, 138.43, 138.43, 138.25, 133.74, 131.01, 130.30, 129.33, 128.32, 128.01, 127.92, 127.85, 127.72, 127.62, 127.16, 120.39, 66.65; MS (ESI) 597.6 ($M+H^+$, 100); TLC R_f 0.35 (EtOAc/hexanes, 1/12); HR-MS calcd for $C_{45}H_{28}N_2$: 596.2252, found: 596.2256; Anal. Calcd for $C_{45}H_{28}N_2$: C, 90.58, H, 4.73, N, 4.69. Found: C, 90.19, H, 5.01, N, 4.52.

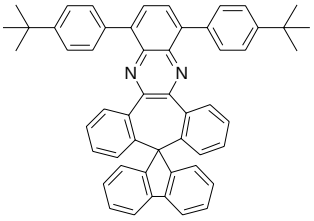
Spiro-fluorene-dibenzosuberene[d](1,4-bis(4-methoxyphenyl)quinoxaline) (1b)



To a 50-mL, two-necked, round-bottomed flask was placed **1** (602 mg, 1 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in DME (25 mL). A solution of 4-fluorophenylboronic acid (336 mg, 2.4 mmol) and Na_2CO_3 (318 mg, 3 mmol) in degassed water (12 mL) was added and the whole solution was refluxed for 24 hours. The reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **1b**, which was further re-crystallized from

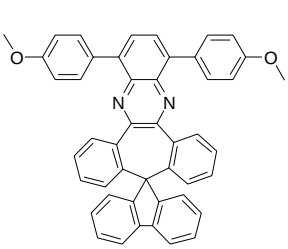
CH_2Cl_2/hexanes to afford pure **1b** (854 mg, 90 %): m.p. 298 ℃(DSC); T_d 362 ℃(TGA); T_g 161 ℃(DSC); M.W.: 632.70; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.5, 2H), 7.97 (s, 2H), 7.88 (dd, *J* = 8.7, 5.5, 4H), 7.75 (d, *J* = 7.6, 2H), 7.37-7.32 (m, 4H), 7.24-7.13 (m, 8H), 7.07 (t, *J* = 7.6, 2H), 6.80 (d, *J* = 7.3, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.86, 161.41, 151.97, 145.30, 149.60, 145.44, 140.08, 139.48, 139.06, 138.04, 134.20, 133.57, 132.51, 130.01, 129.45, 128.36, 127.94, 127.72, 127.12, 120.42, 114.93, 66.58; MS (FAB) 633.07 (M^+, 5); TLC R_f 0.32 (EtOAc/hexanes, 1/12); HR-MS calcd for $C_{45}H_{26}N_2F_2$: 632.2064, found: 632.2060; Anal. Calcd for $C_{45}H_{26}N_2F_2$: C, 85.42, H, 4.14, N, 4.43. Found: C, 85.15, H, 4.34, N, 4.53.

Spiro-fluorene-dibenzosuberene[d](1,4-bis(4-*t*-butylphenyl)Quinoxaline) (1c)



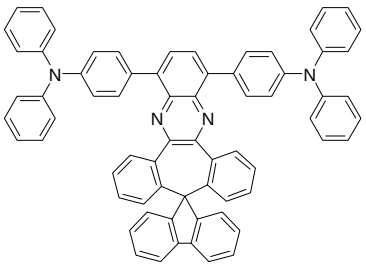
To a 50-mL, two-necked, round-bottomed flask was placed **1** (602 mg, 1 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in DME (25 mL). A solution of 4-*t*-butylphenylboronic acid (427 mg, 2.4 mmol) and Na_2CO_3 (318 mg, 3 mmol) in degassed water (12 mL) was added and the resulting mixture was refluxed for 24 hours. The reaction mixture was cooled to ambient temperature and quenched with water (20 mL). The whole mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **1c**, which was further re-crystallized from CH_2Cl_2/hexanes to afford pure **1c** (631 mg, 89 %): m.p. 402 ℃(DSC); T_d 395 ℃(TGA); T_g 181 ℃(DSC); M.W.: 708.93; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.6, 2H), 8.01 (s, 2H), 7.89 (d, *J* = 8.4, 4H), 7.71 (d, *J* = 7.6, 2H), 7.55 (d, *J* = 8.4, 4H), 7.36 (td, *J* = 7.6, 2.2, 2H), 7.30 (t, *J* = 7.6, 2H), 7.17-7.11 (m, 4H), 7.04 (bd, 2H), 6.80 (bd, 2H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.64, 150.45, 149.59, 145.35, 140.02, 139.72, 139.55, 138.31, 135.48, 133.69, 130.58, 130.24, 129.19, 128.27, 127.83, 127.69, 127.10, 124.98, 120.28, 66.56, 34.63, 31.40; MS (ESI) 709.7 ($M+H^+$, 100); TLC R_f 0.30 (EtOAc/hexanes, 1/12).

Spiro-fluorene-dibenzosuberene[d](1,4-bis(4-methoxyphenyl)quinoxaline) (1d)



To a 50-mL, two-necked, round-bottomed flask was placed **1** (602 mg, 1 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in DME (25 mL). A solution of 4-methoxyphenylboronic acid (365 mg, 2.4 mmol) and Na_2CO_3 (318 mg, 3 mmol) in degassed water (12 mL) was added and the whole solution was refluxed for 24 hours. The reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **1d**, which was further re-crystallized from CH_2Cl_2/hexanes to afford pure **1d** (624 mg, 95 %): m.p. 344 ℃ (DSC); T_d 372 ℃ (TGA); T_g 160 ℃ (DSC); M.W.: 656.77; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.6, 2H), 7.97 (s, 2H), 7.88 (d, *J* = 8.8, 4H), 7.74 (d, *J* = 7.6, 2H), 7.37-7.30 (m, 4H), 7.18-7.12 (m, 4H), 7.08 (bd, 2H), 7.06 (d, *J* = 8.8, 4H), 6.82 (bd, 2H), 3.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.27, 151.51, 149.66, 145.30, 140.05, 139.65, 139.04, 138.30, 133.66, 132.07, 130.90, 129.81, 129.21, 128.26, 127.86, 127.69, 127.11, 120.33, 113.50, 66.59, 55.33; MS (ESI) 657.7 ($M+H^+$, 100); TLC R_f 0.32 (EtOAc/hexanes, 1/10).

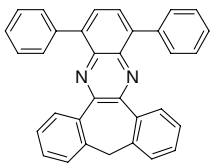
Spiro-fluorene-dibenzosuberene[d](1-(4-(*N*,*N*-diphenylamino)-phenyl)-quinoxaline) (1e)



To a 50-mL, two-necked, round-bottomed flask was placed **1** (602 mg, 1 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in DME (25 mL). A solution of 4-(N,N-diphenylamino)phenylboronic acid (694 mg, 2.4 mmol) and Na_2CO_3 (318 mg, 3 mmol) in degassed water (12 mL) was added and the whole solution was refluxed for 24 hours. The reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **1e**, which was further re-crystallized from CH_2Cl_2/hexanes to afford pure **1e** (857 mg, 92 %): m.p. 351 ℃ (DSC); T_d 412 ℃ (TGA); T_g 186 ℃ (DSC); M.W.: 931.13; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.3, 2H), 7.98 (s, 2H), 7.81 (d, *J* = 8.7, 4H), 7.72 (d, *J* = 7.4, 2H), 7.34-7.26 (m, 12H), 7.22-7.13 (m, 16H), 7.04 (t,

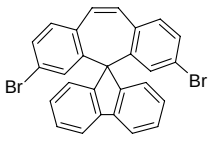
J = 7.2, 6H), 6.79 (d, J = 7.1, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 149.7, 147.8, 147.4, 145.4, 140.1, 139.7, 139.1, 138.3, 133.7, 132.3, 131.7, 129.8, 129.3, 128.3, 127.9, 127.2, 124.7, 123.0, 122.7, 120.4, 66.6; MS (FAB) 931.4 ($M+H^+$, 100); TLC R_f 0.38 (EtOAc/CH_2Cl_2, 1/3).

5H-dibenzosuberene[d](1,4-bis(4-methoxyphenyl)quinoxaline) (2a)



To a 50-mL, two-necked, round-bottomed flask was placed **5H-dibenzo[a,d]cycloheptene-10,11-dione**[3] (444 mg, 2 mmol), [1,1';4',1"]terphenyl-2',3'-diamine[4] (573 mg, 2.2 mmol) and catalytic *p*-TSA in $CHCl_3$ (20 mL). The reaction mixture was stirred under reflux for 12 hours. After having been quenched with saturated aqueous $NaHCO_3$ (20 mL), the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **2a**, which was further re-crystallized from CH_2Cl_2 to afford pure **2a** (813 mg, 91 %): m.p. 298 ℃ (DSC); T_d 377 ℃ (TGA); T_g 98 ℃ (DSC); M.W.: 446.54; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2, 2H), 7.96 (s, 2H), 7.92 (d, J = 7.4, 4H), 7.54 (t, J = 7.6, 4H), 7.45 (t, J = 7.4, 2H), 7.40-7.32 (m, 6H), 4.00 (d, J = 13.5, 1H) , 3.75 (d, J = 13.5, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.76, 142.24, 139.99, 139.42, 138.44, 136.55, 131.28, 130.94, 130.15, 129.81, 127.96, 127.54, 127.08, 126.90, 40.34; MS (ESI) 447.7 ($M+H^+$, 100); TLC R_f 0.4 (CH_2Cl_2/hexanes, 1/3); HR-MS calcd for $C_{33}H_{22}N_2$: 446.5412, found: 446.1788.

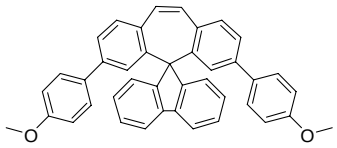
3,7-Dibromo-5,5-spirofluorenyl-5H-dibenzo[a,d]cycloheptene (3)[5]



To a 250-mL, three-necked, round-bottomed flask was placed a solution of 2-bromobiphenyl (3497 mg, 15 mmol) in THF (50 mL). The reaction flask was cooled to -78 ^{o}C and *n*-BuLi (2.5 M in hexanes, 6 mL, 15 mmol) was added dropwise. The whole solution was stirred at this temperature for 30 minutes followed by adding a solution of **3,7-Dibromo-dibenzo[a,d]cyclohepten-5-one** (3640 mg, 10 mmol) in THF (30 mL). The resulting mixture was gradually warmed to ambient temperature and then quenched with saturated, aqueous $NaHCO_3$ (30 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude residue dissolved in acetic acid

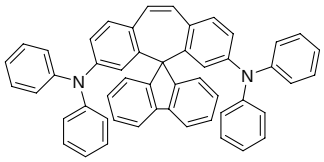
(15 mL) was placed in another 100-mL, two-necked, round-bottomed flask. Catalytic amount of aqueous HCl (12*N*, 5mol%) was then added and the whole mixture was refluxed for 30 minutes. After having been cooled to ambient temperature, the whole mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **3**, which was further re-crystallized from CH_2Cl_2/hexanes to afford 4852 mg of pure **3** (97 %): m.p. 283 ^oC (DSC); M.W.: 500.22; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7, 2H), 7.76 (d, *J* = 7.6, 2H), 7.42 (t, *J* = 7.5, 2H), 7.32 (dd, *J* = 8.2, 2.0, 2H), 7.29 (d, *J* = 7.6, 2H), 7.20 (d, *J* = 8.2, 2H), 6.98 (dd, *J* = 1.9, 2H), 6.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 143.4, 138.9, 135.2, 133.5, 132.7, 131.9, 130.5, 128.6, 127.9, 126.7, 122.8, 120.6, 65.2; MS(EI, 20eV) 500.0 (M^+, 28); TLC R_f0.35 (CH_2Cl_2/hexanes, 1/5).

3,7-Bis(*N*,*N*-diphenylamino)-5,5-spirofluorenyl-5H-dibenzo[a,d]cycloheptene (3d)



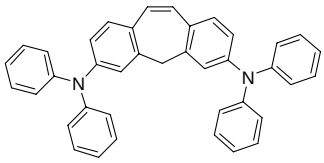
To a 25-mL, two-necked, round-bottomed flask was placed **3** (500 mg, 1 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in DME (25 mL). A solution of 4-methoxyphenylboronic acid (365 mg, 2.4 mmol) and Na_2CO_3 (318 mg, 3 mmol) in degassed water (12 mL) was added and the whole solution was refluxed for 24 hours. The reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **3d**, which was further re-crystallized from CH_2Cl_2/hexanes to afford pure **3d** (460 mg, 83 %): m.p. 242 ℃(DSC); T_d 411 ℃(TGA); T_g 118 ℃(DSC); M.W.: 554.22; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7, 2H), 7.73 (d, *J* = 7.6, 2H), 7.40-7.37 (m, 6H), 7.29 (t, *J* = 7.6, 2H), 7.19 (d, *J* = 8.7, 4H), 7.19 (d, *J* = 2.2, 2H), 6.99 (s, 2H), 6.83 (d, *J* = 8.8, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 153.0, 142.0, 140.2, 139.0, 135.0, 133.0, 132.8, 132.6, 128.0, 127.6, 127.4, 127.4, 127.0, 125.1, 120.4, 114.1, 66.3, 55.3; MS (ESI) 554.2 (M^+, 100); TLC R_f 0.35 (CH_2Cl_2/hexanes, 1/4); HR-MS calcd for $C_{69}H_{46}N_4$: 554.2246, found: 554.2248; Anal. Calcd for $C_{41}H_{30}O_2$: C, 88.78, H, 5.45. Found: C, 88.43, H, 5.46.

3,7-Bis(*N*,*N*-diphenylamino)-5,5-spirofluorenyl-5H-dibenzo[a,d]cycloheptene (3f)[6]



To a 25-mL, two-necked, round-bottomed flask was placed **3** (500 mg, 1 mmol), $Pd_2(dba)_3$ (18 mg, 0.02 mmol), sodium *tert*-butoxide (288 mg, 3 mmol), P(*t*-Bu)$_3$ (0.03 M in toluene, 2 mL, 0.06 mmol), and diphenylamine (372 mg, 2.2 mmol) in toluene (15 mL). The whole solution was refluxed for 12 hours. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (20 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel to give **3f**, which was further re-crystallized from CH_2Cl_2/hexanes to afford 643 mg of pure **3f** (95 %): m.p. 287 ^oC (DSC); T_d 443 ^oC (TGA); T_g 123 ^oC (DSC); M.W.: 676.84; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8, 2H), 7.49 (d, *J* = 7.6, 2H), 7.19-7.08 (m, 12H), 6.97 (t, *J* = 7.3, 4H), 6.89 (d, *J* = 8.2, 10H), 6.82 (s, 2H), 6.79 (t, *J* = 7.6, 2H), 6.54 (d, *J* = 2.2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 147.9, 147.1, 141.5, 138.6, 132.7, 130.7, 129.1, 128.8, 127.3, 127.0, 131.7, 124.8, 123.6, 123.1, 120.2, 119.7, 65.9; MS (ESI) 676.3 (M^+, 53); TLC R_f 0.5 (CH_2Cl_2/hexane, 1/3).

***N*,*N*,*N′*,*N′*-Tetraphenyl-5H-dibenzo[a,d]cycloheptene-3,7-diamine (4f)**



To a 25-mL, two-necked, round-bottomed flask was placed **3,7-Dibromo-5H-dibenzo[a,d]cycloheptene** (350 mg, 1 mmol), $Pd_2(dba)_3$ (18 mg, 0.02 mmol), sodium *tert*-butoxide (288 mg, 3 mmol), P(*t*-Bu)$_3$ (0.03 M in toluene, 2 mL, 0.06 mmol), and diphenylamine (372 mg, 2.2 mmol) in anhydrous toluene (15 mL). The whole solution was stirred at reflux for 12 hours. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (20 mL). The aqueous layer was separated and extracted with CH2Cl2 (3 × 20 mL). The combined organic layers were dried (MgSO4), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel (CH_2Cl_2/hexanes, 1/3) to give **4f**. The product was further re-crystallized from CH_2Cl_2/hexanes to afford 484 mg of analytically pure **4f** (485 mg, 92 %): m.p. 228 ^oC (DSC); T_d 397 ^oC (TGA); T_g 101 ^oC (DSC); M.W.: 526.67; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.7, 8H), 7.14 (d, *J* = 9.0, 2H), 7.09 (d, *J* = 7.7, 8H), 7.02 (t, *J* = 7.3, 4H), 6.92-6.90 (m, 4H), 6.86 (s,

2H), 3.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.6, 138.6, 130.3, 129.6, 129.2, 129.0, 128.5, 122.9, 122.7, 121.2, 41.8; MS (ESI) 526.2 (M+, 100); TLC R_f 0.35 (CH_2Cl_2/hexanes, 1/3).

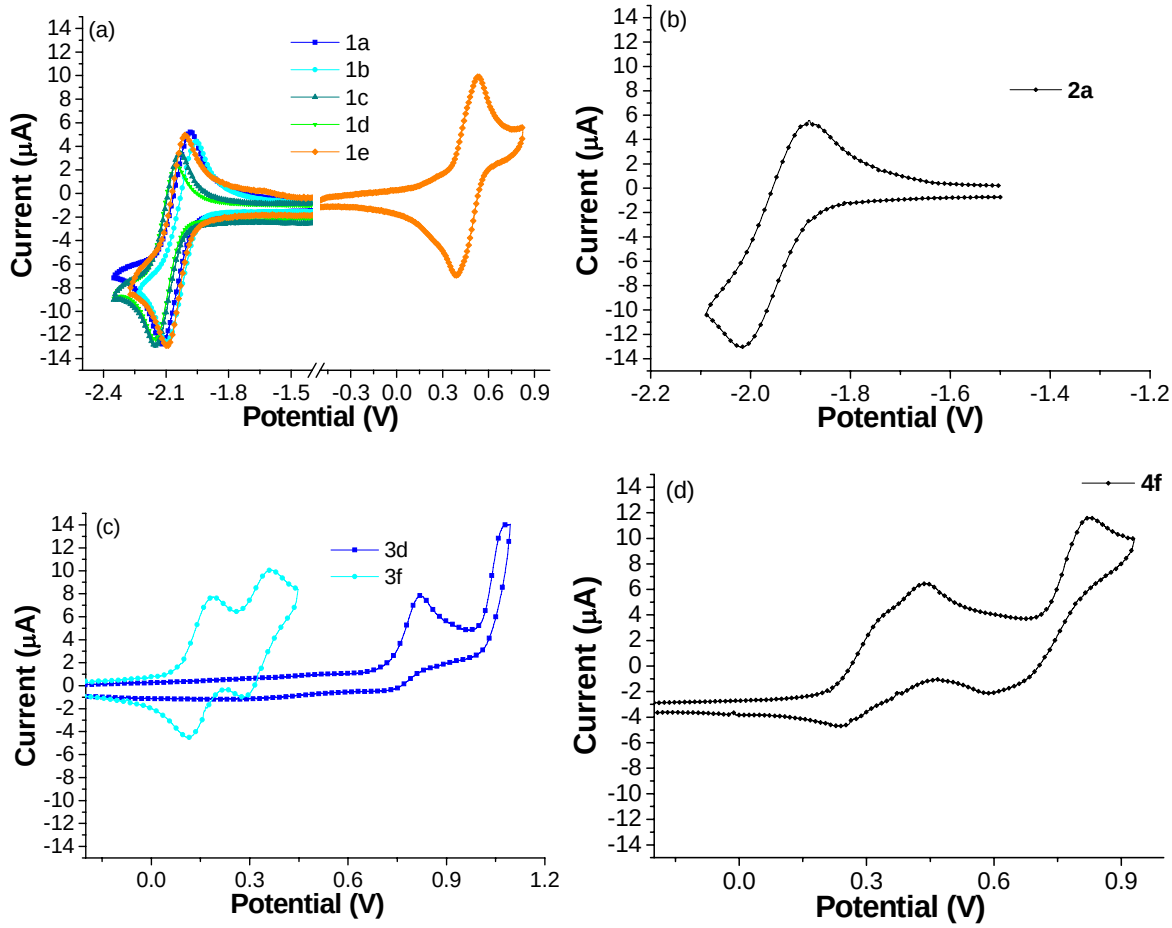


Figure S1. Stacked plots of cyclic voltammograms for (a) **1a-e**, (b) **2a**, (c) **3d** and **3f**, and (d) **4f**

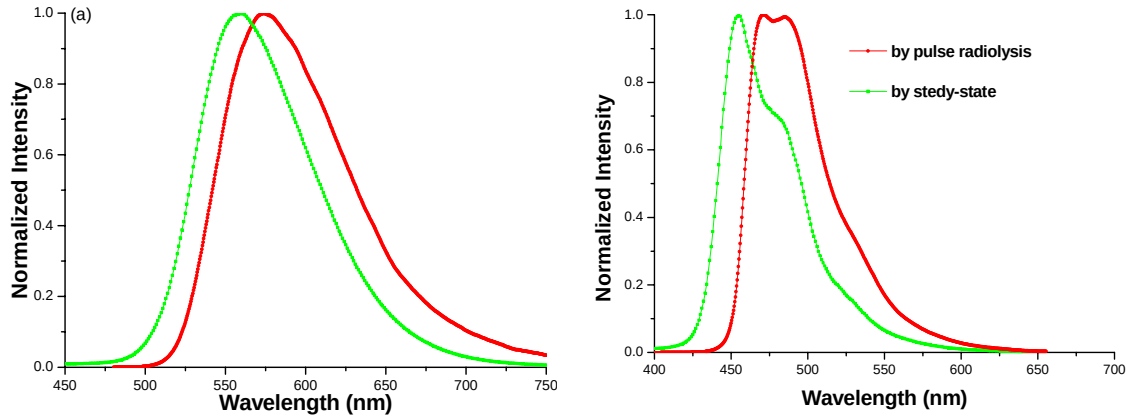
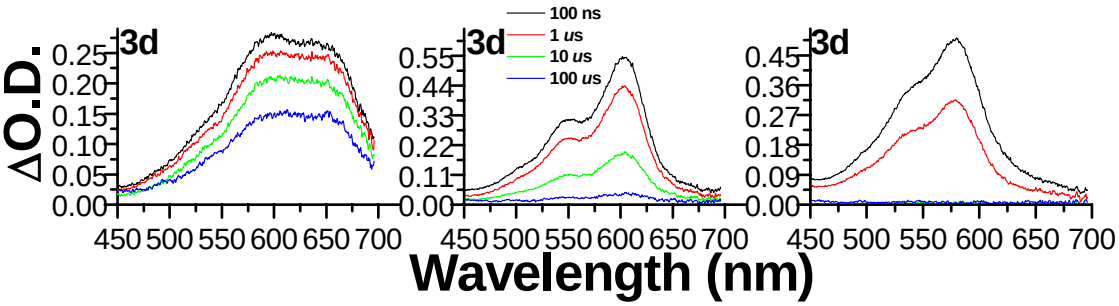


Figure S2. Stacked plots of emission spectra of **1e** (a) and **3f** (b) by steady-state at 10^{-5}M (green) and pulse radiolysis (red) measurements in Ar-saturated benzene.



(a) (b) (c)

Figure S3. Time-resolved transient absorption spectrum stacked plots of **3d** observed at t = 100 ns (black), 1 (red), 10 (green), and 100 μs (blue) after an electron pulse during pulse radiolysis measurements in Ar-saturated (a) DCE, (b) DMF, and (c) benzene solutions.

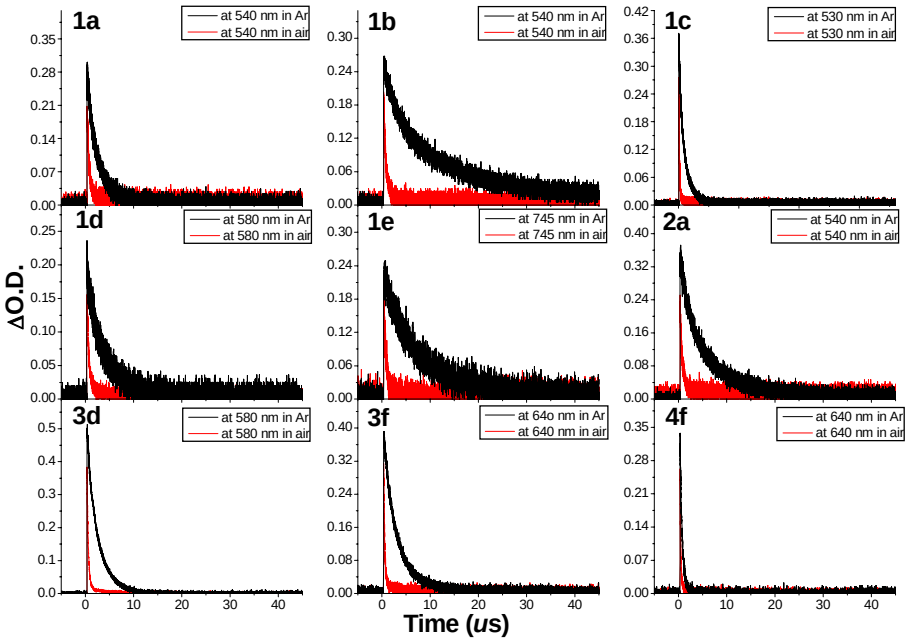


Figure S4. Decay profiles of the transient absorption of the triplet excited state observed during the pulse radiolysis for **1a**-**e**, **2a**, **3d**, **3f**, and **4f** in Ar- and air-saturated benzene solution.

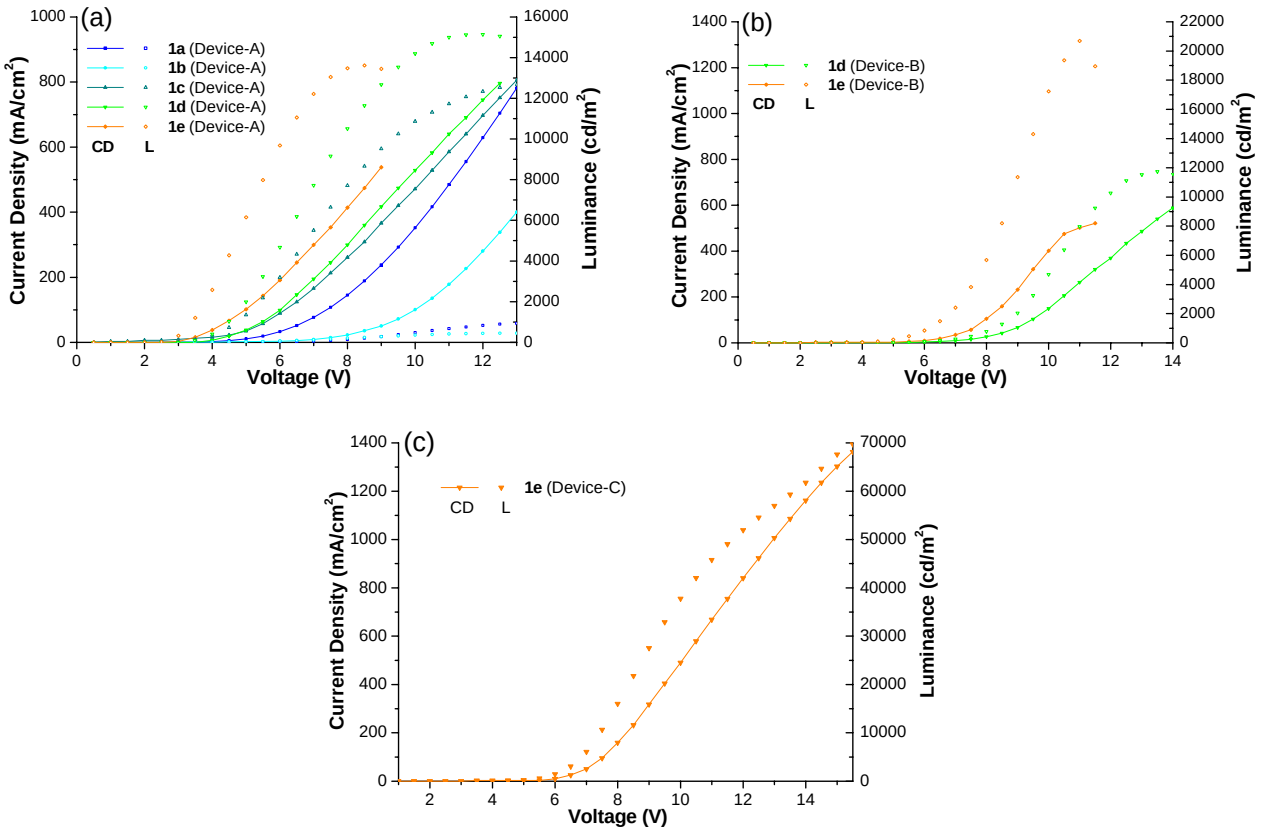


Figure S5. The stacked plots of the I-V-L characteristics [the plot of current density (mA/cm^2, I)/luminescence (cd/m^2, L) values vs. applied voltage (V, V) obtained for each device configuration] for (a) **1a-e** (Device-A), (b) **1d**-**e** (Device-B), and (c) **1e** (Device-C)

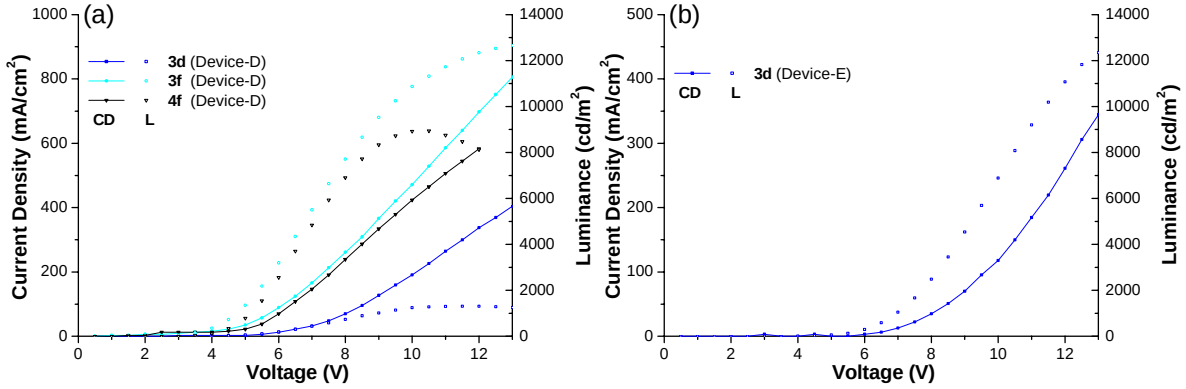


Figure S6. The stacked plots of the I-V-L characteristics for (a) **3d**, **3f**, and **4f** (Device-D) and (b) **3f** (Device-E)

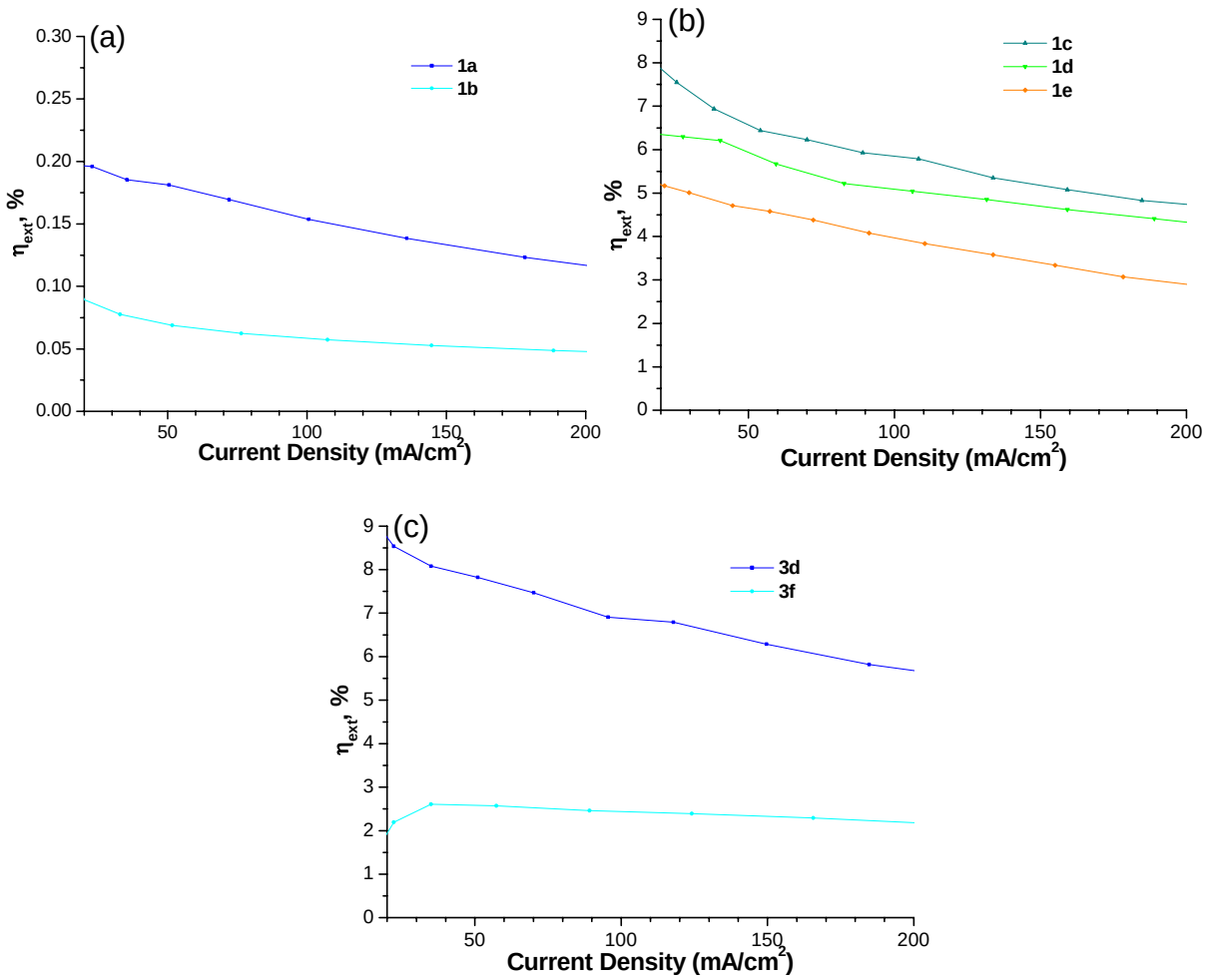


Figure S7. Current Density-External quantum efficiency stacked diagram for (a) **1a** and 1**b**, (b) **1c-e**, and (c) **3d, 3f**, and **4f**

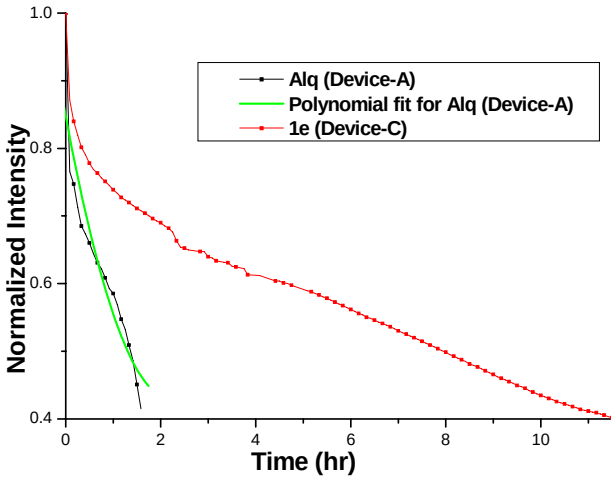
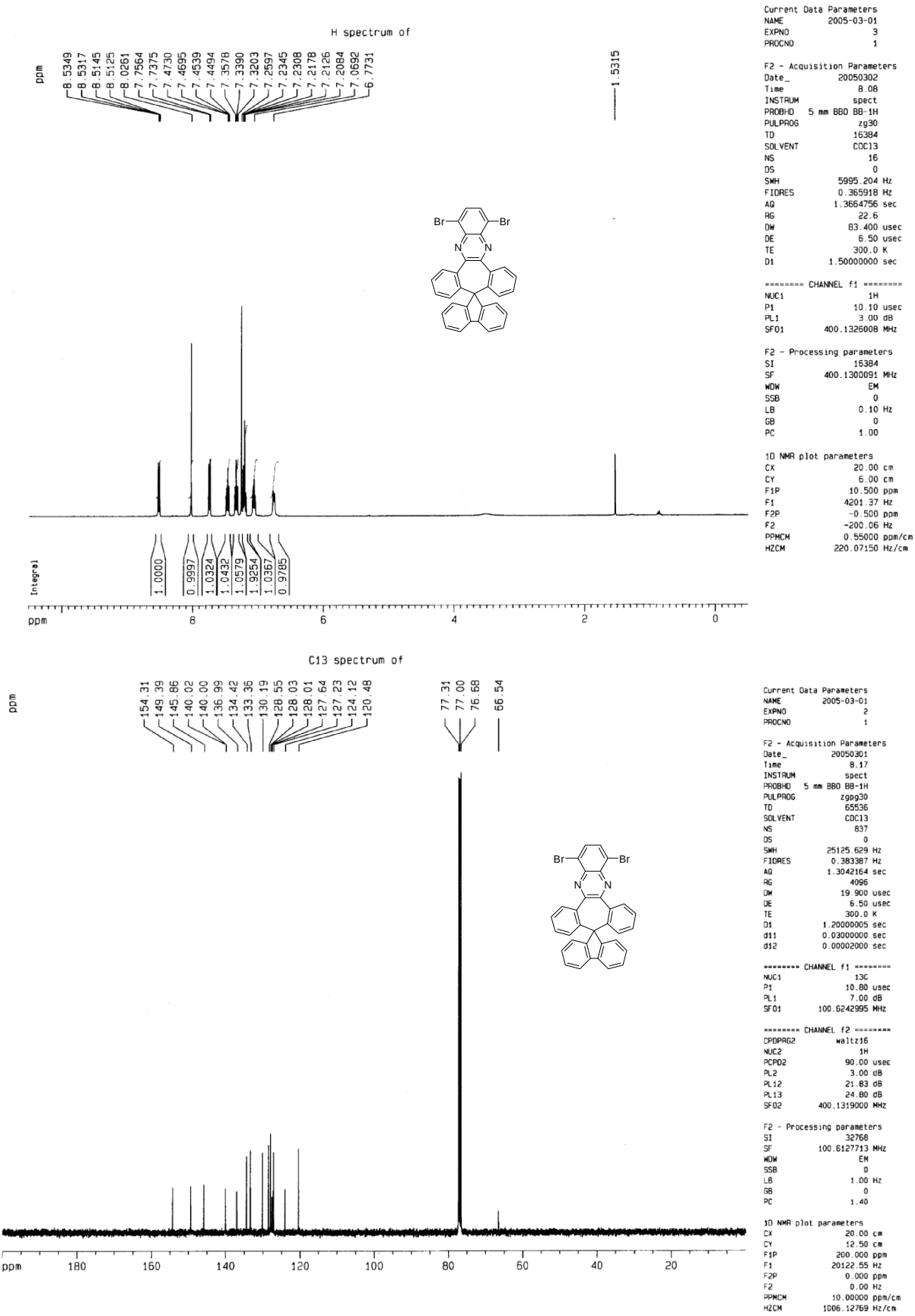
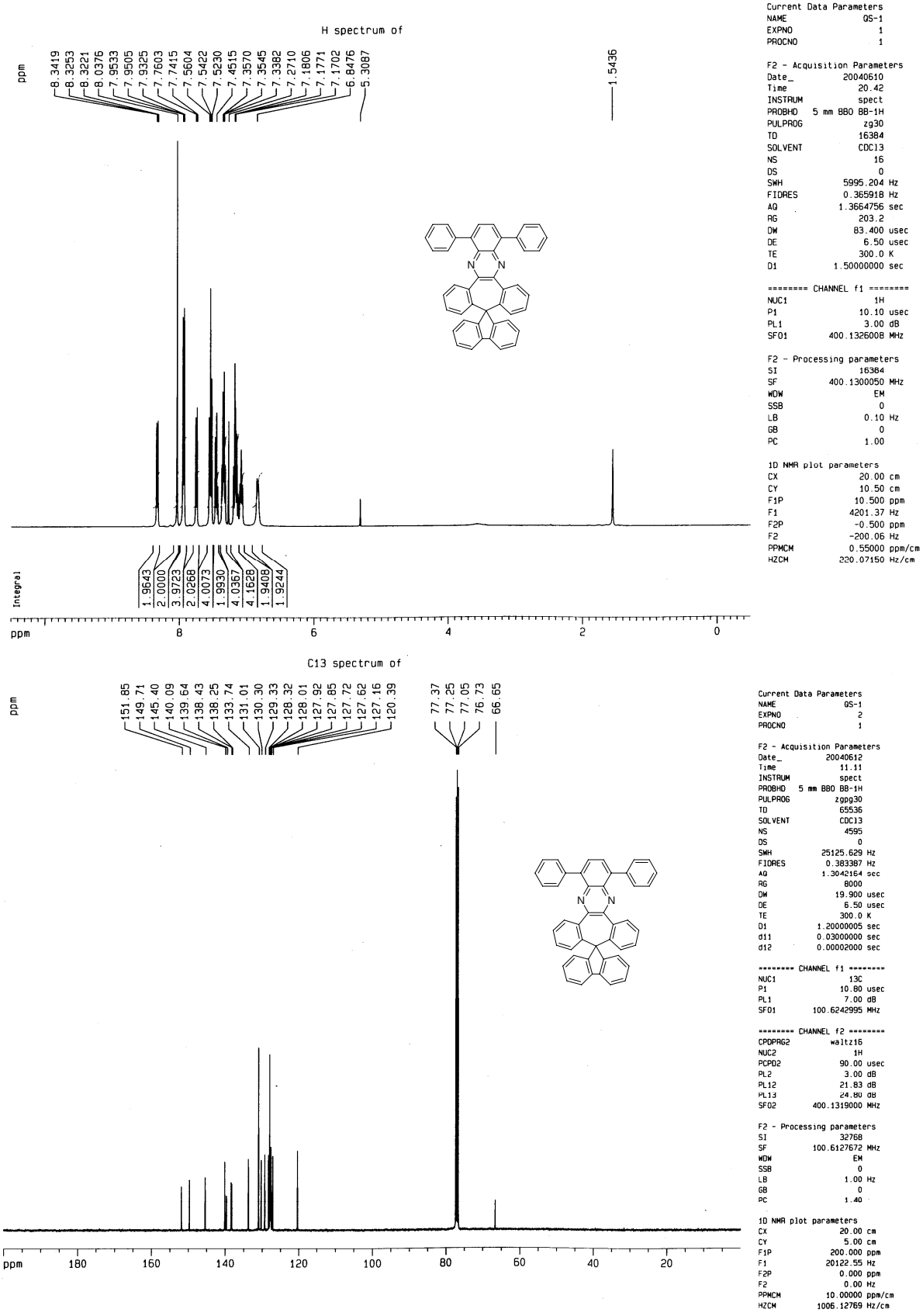


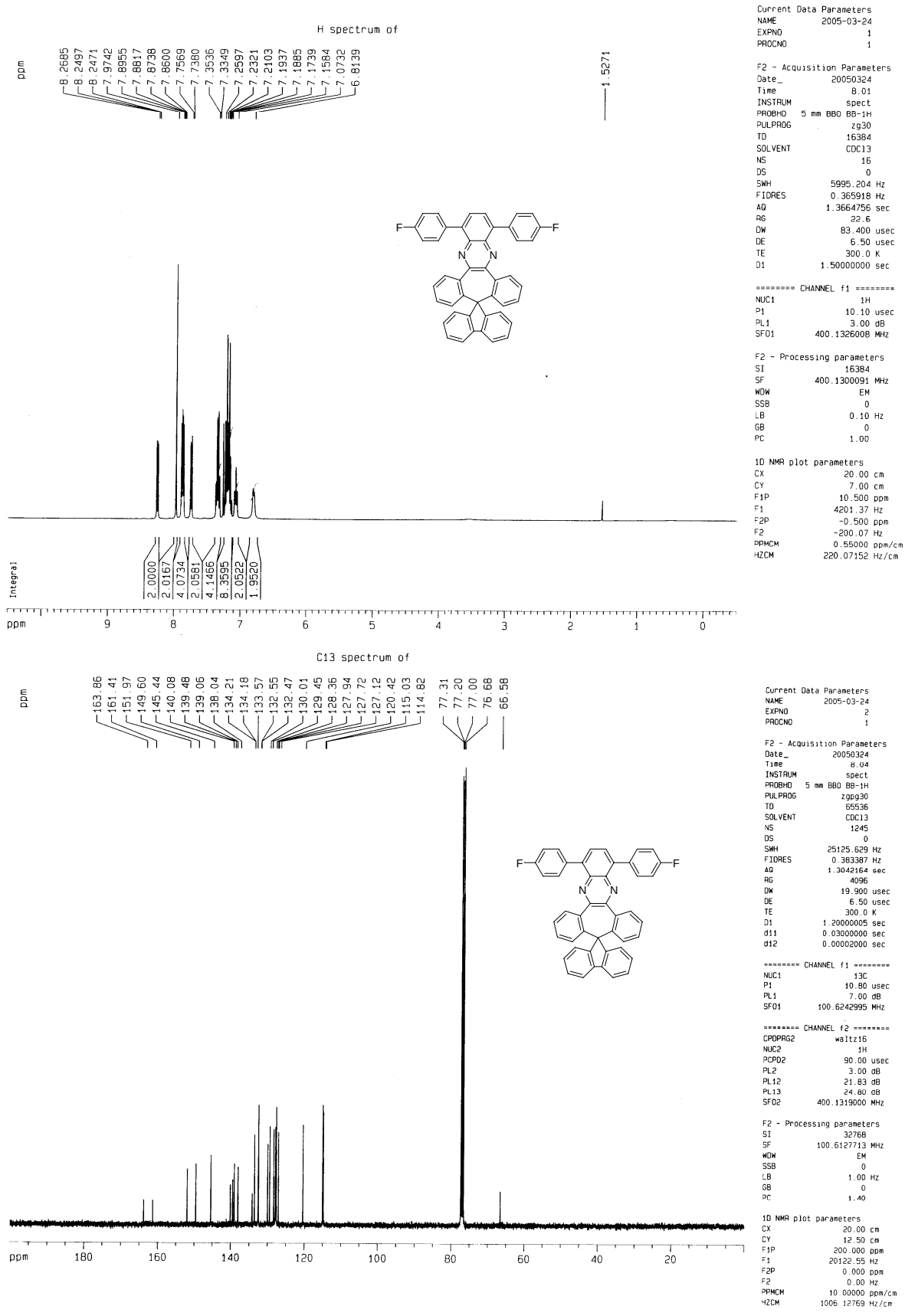
Figure S8. Stacked diagram of lifetime measurements for device-**A** of Alq and device-**C** of **1e**



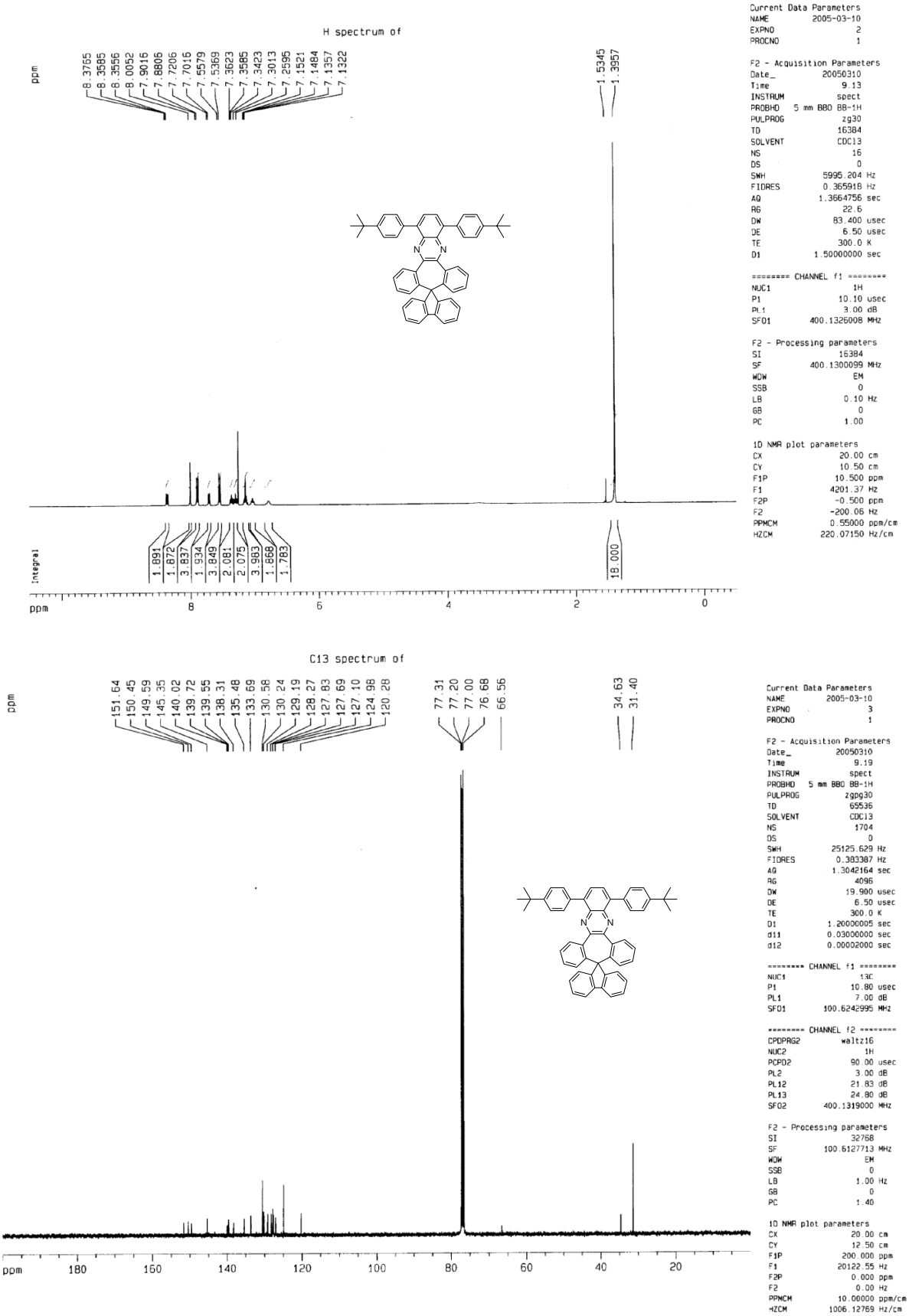
^{1}H and ^{13}C NMR spectra for **1**



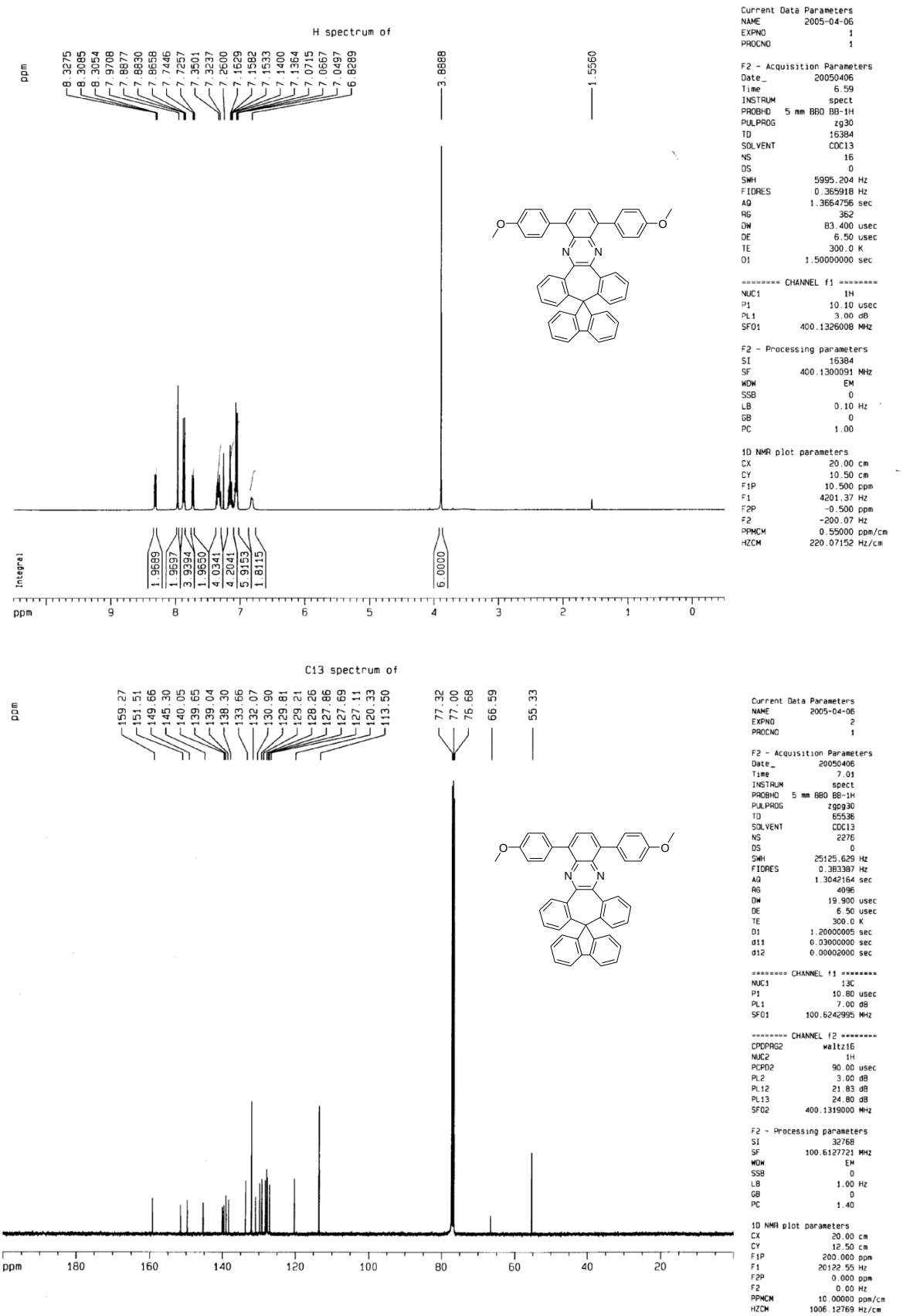
^{1}H and ^{13}C NMR spectra for **1a**



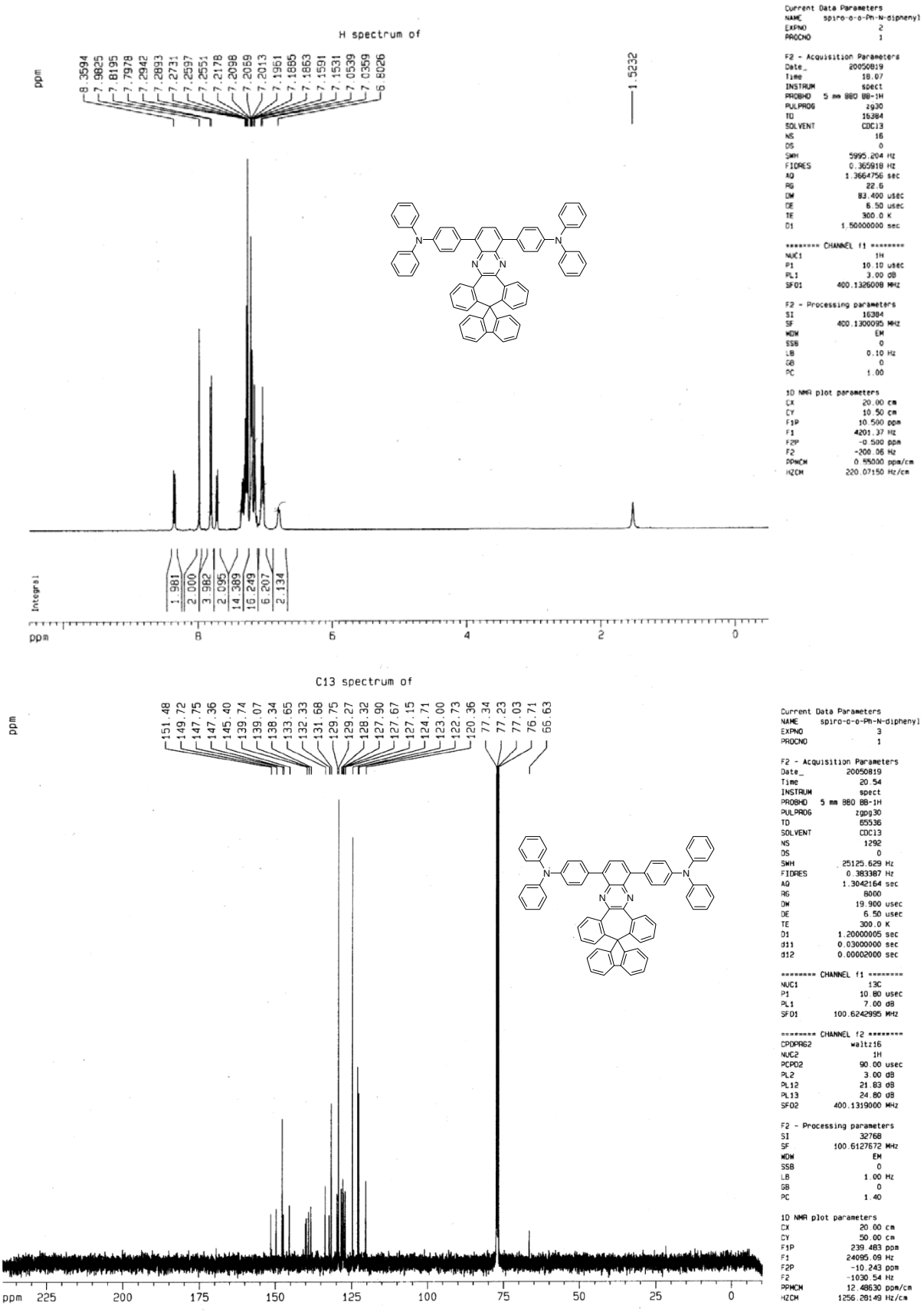
^{1}H and ^{13}C NMR spectra for **1b**



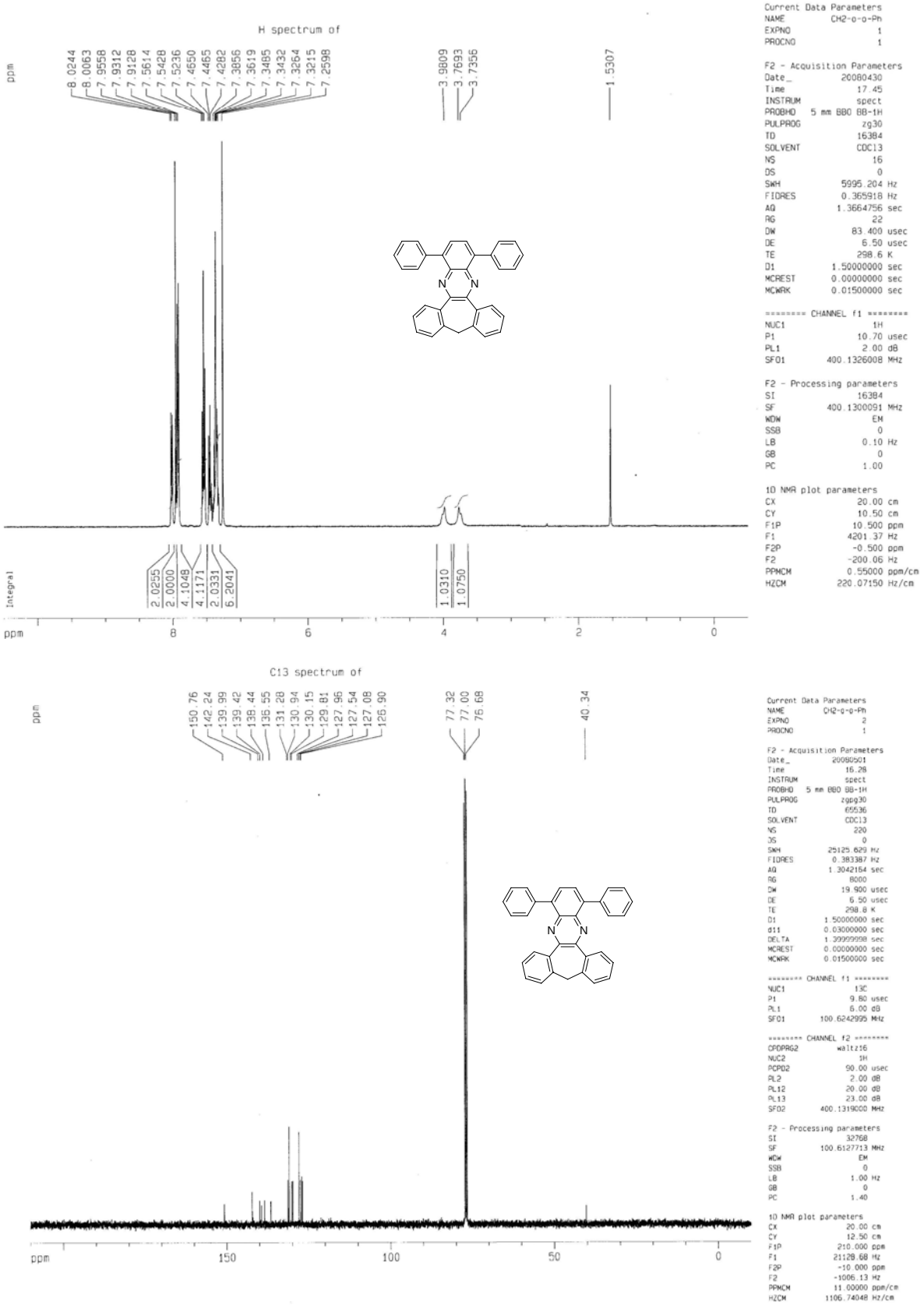
^{1}H and ^{13}C NMR spectra for **1c**



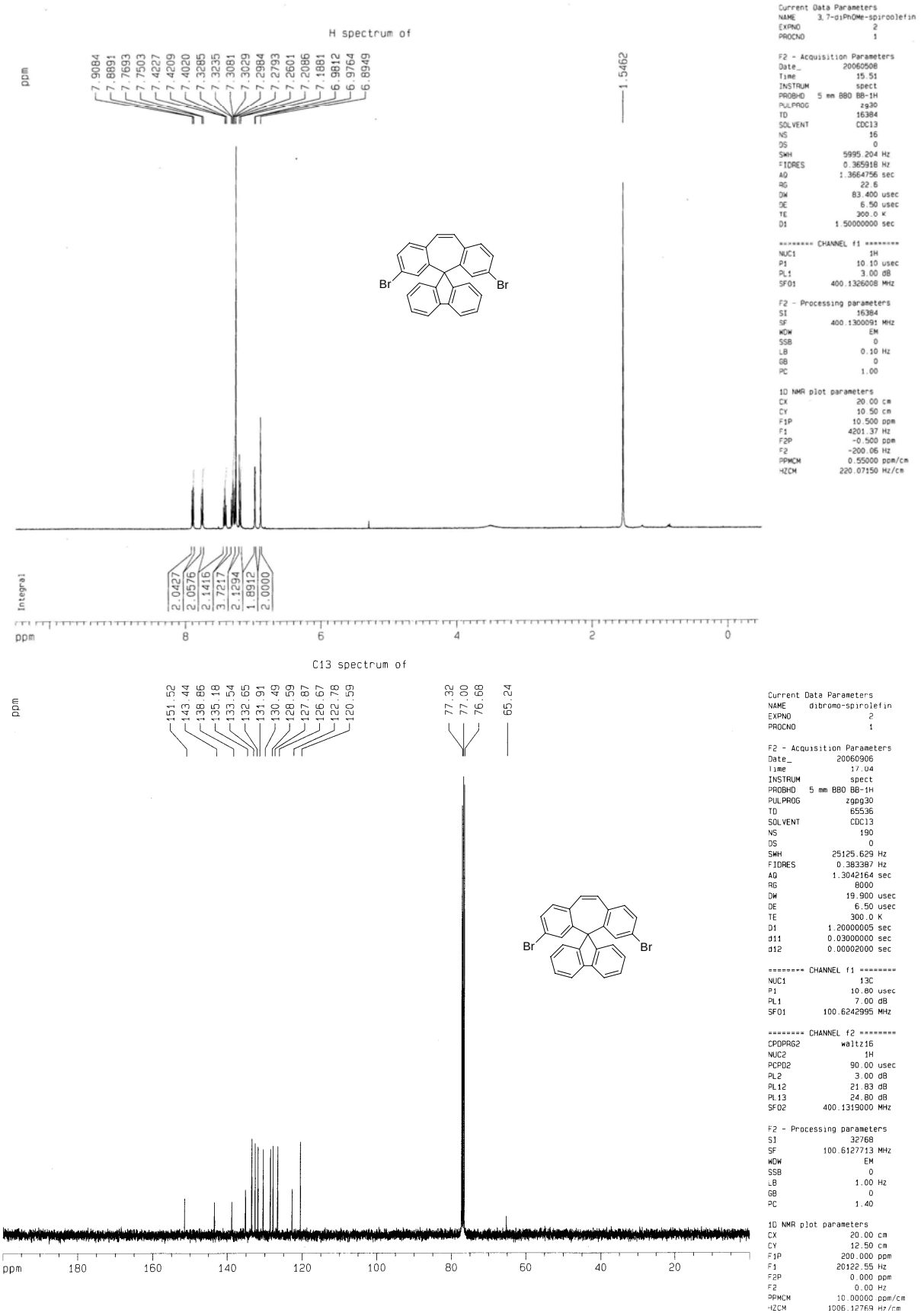
^{1}H and ^{13}C NMR spectra for **1d**



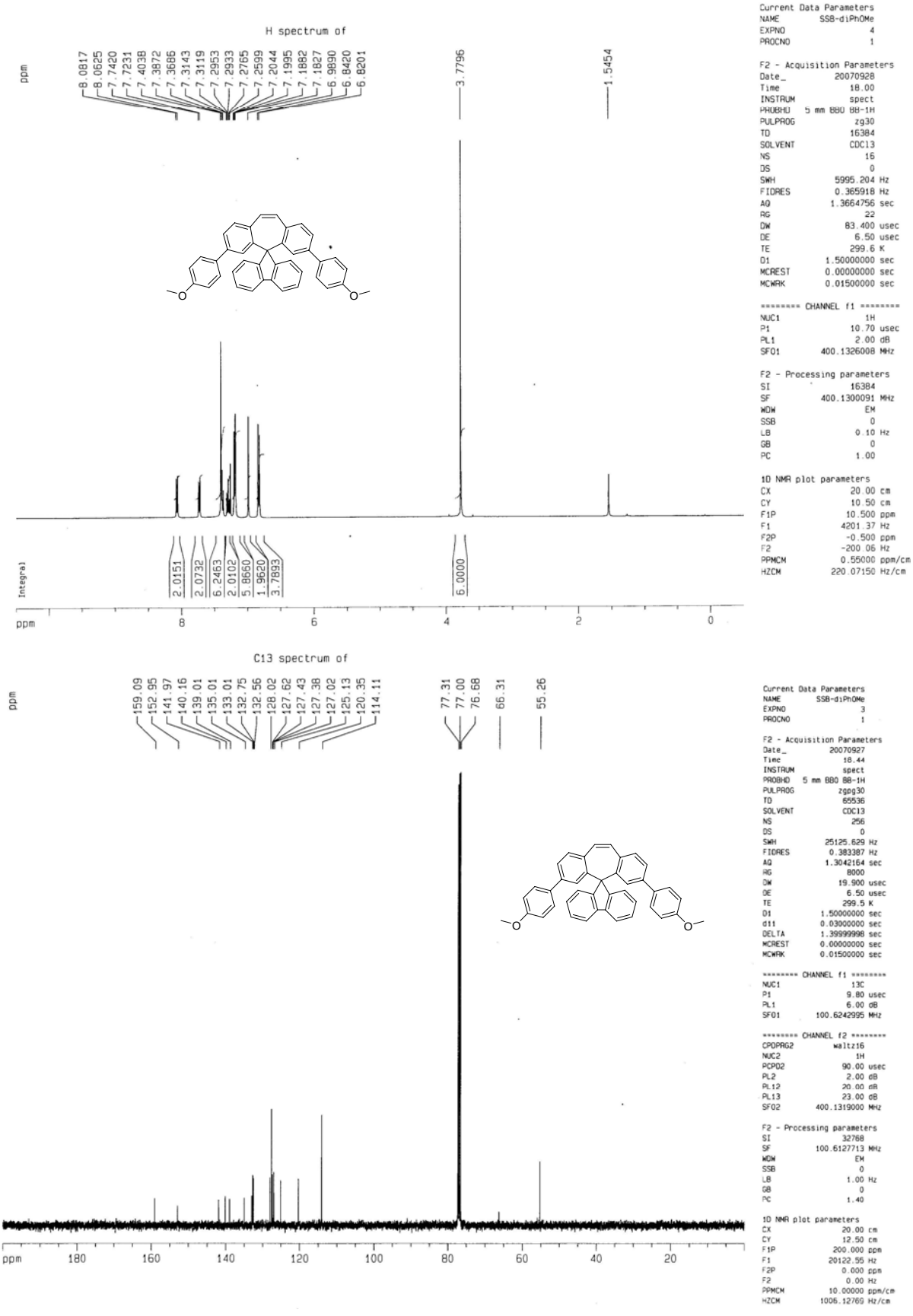
^{1}H and ^{13}C NMR spectra for **1e**



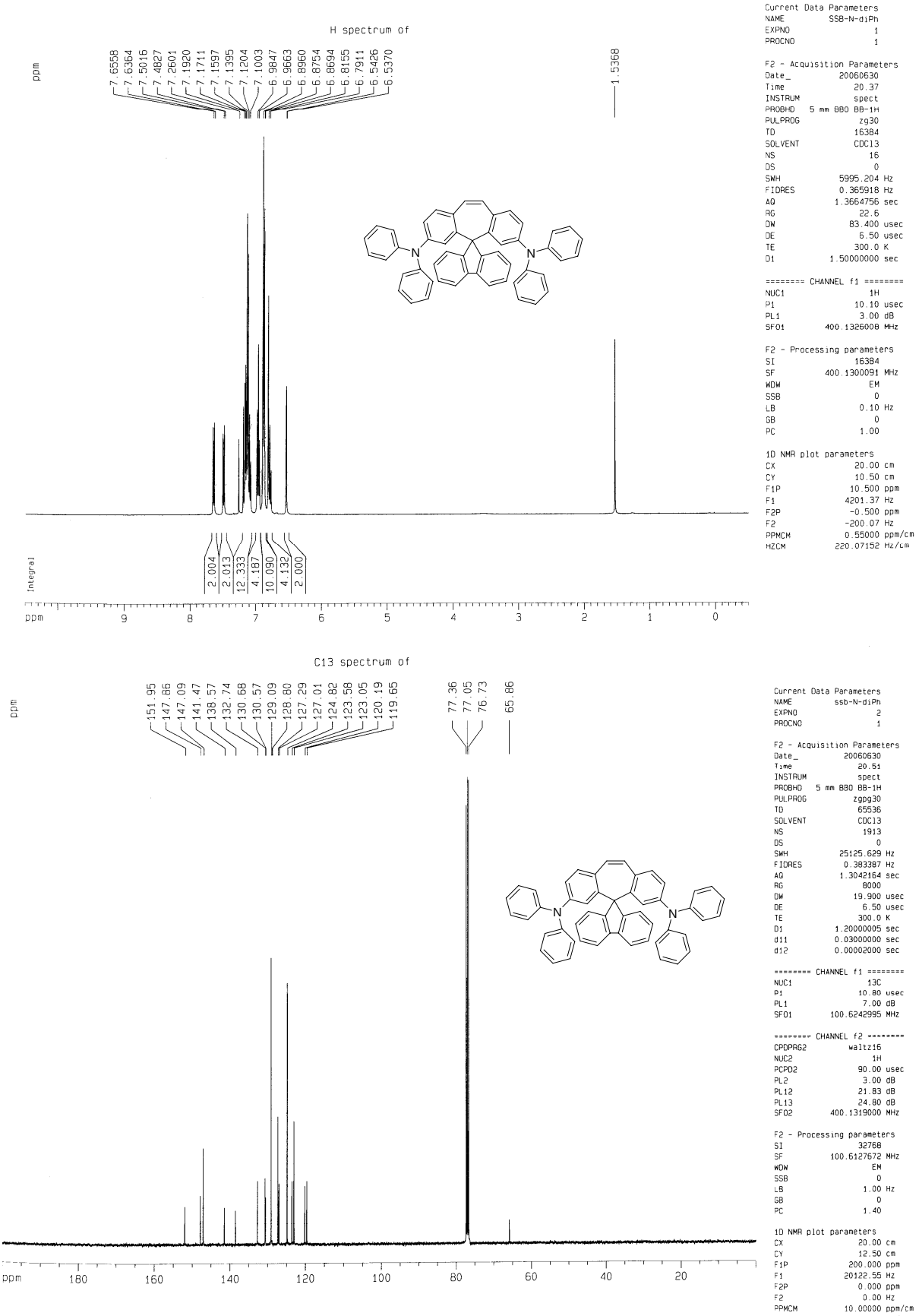
^{1}H and ^{13}C NMR spectra for **2a**



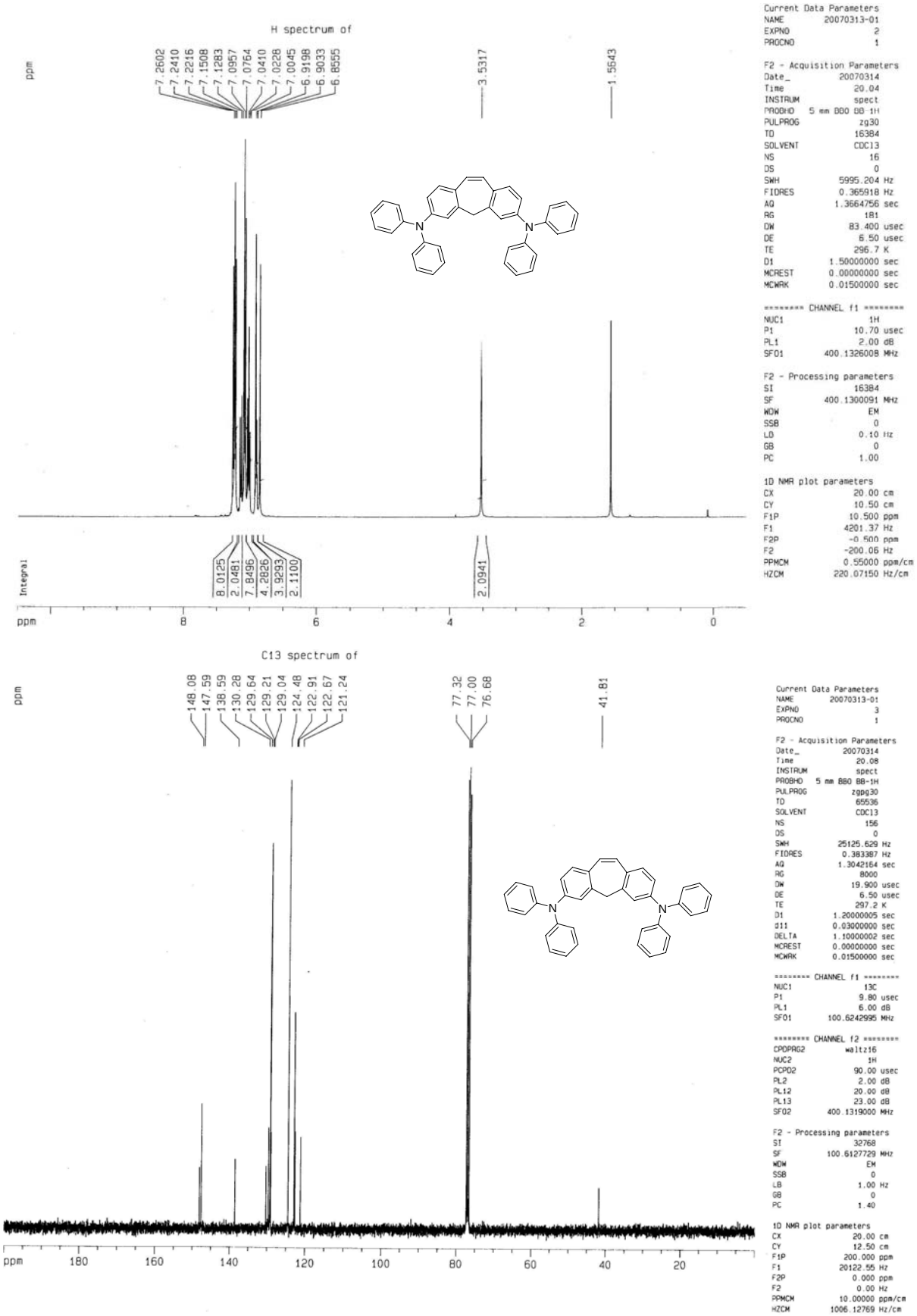
^{1}H and ^{13}C NMR spectra of **3**



^{1}H and ^{13}C NMR spectra of **3d**



^{1}H and ^{13}C NMR spectra of **3f**



^{1}H and ^{13}C NMR spectra of **4f**

References and Notes

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