Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Azacalix[2]arene[2]carbazoles: Synthesis, Structure and Properties

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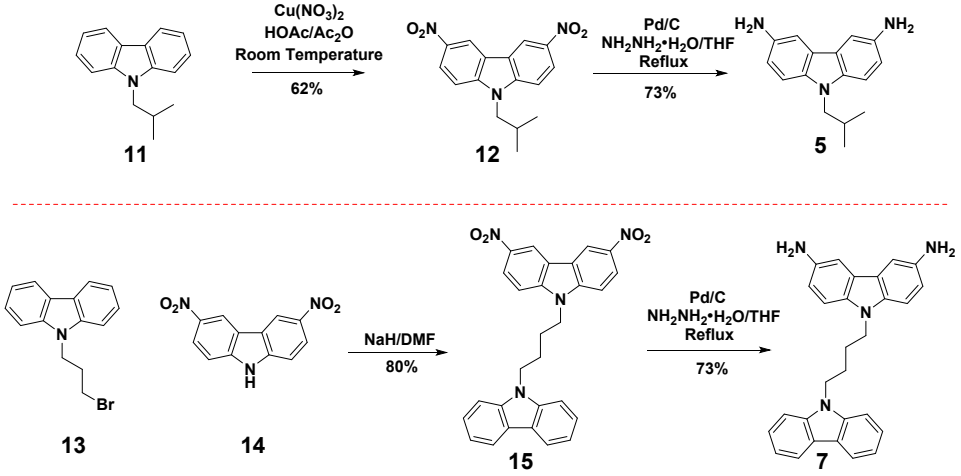
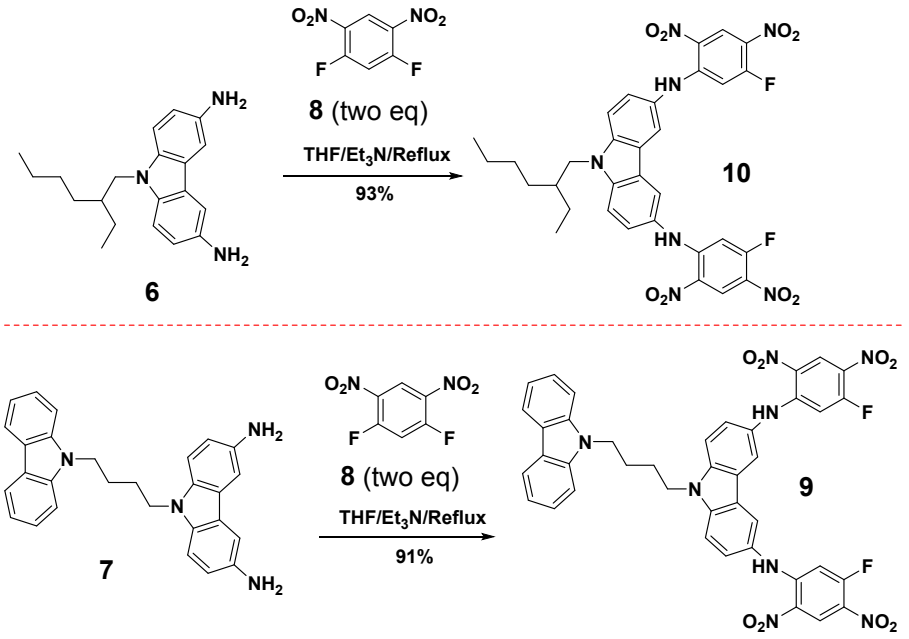
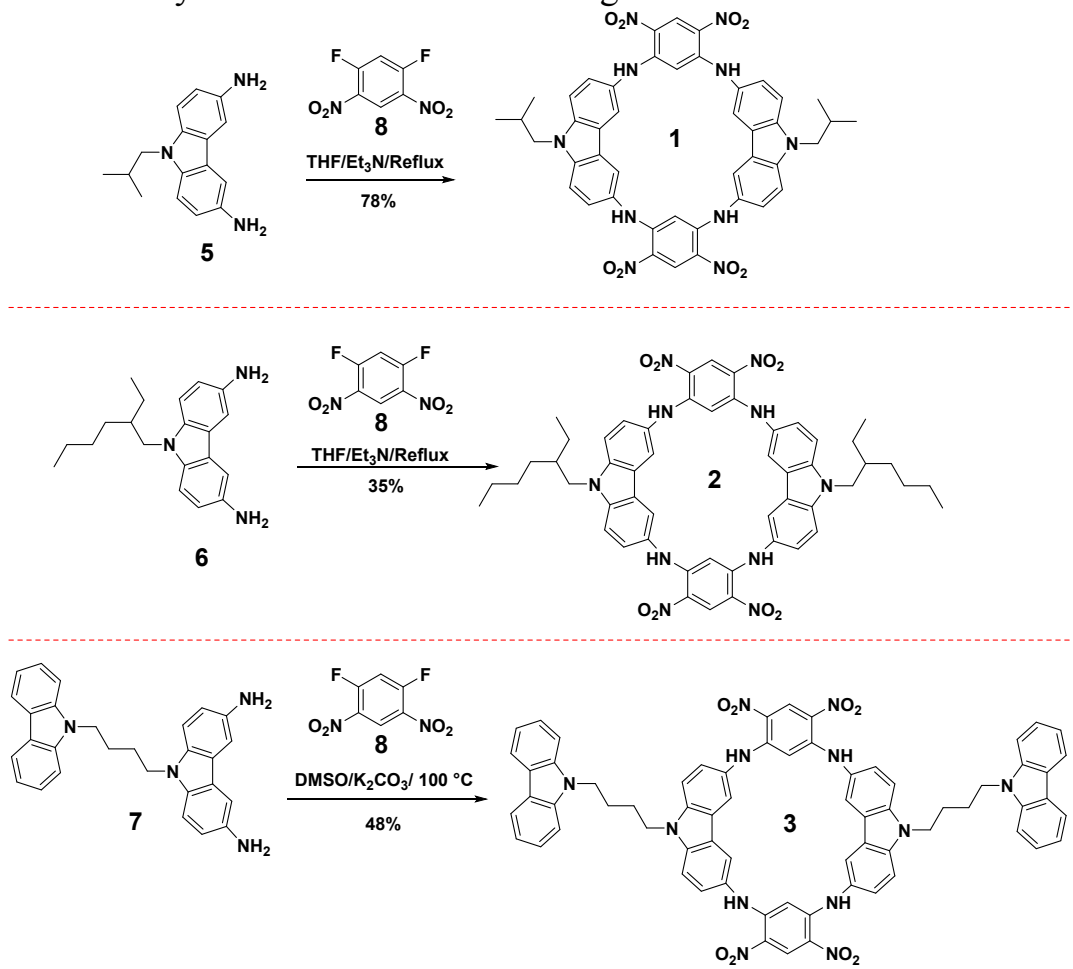


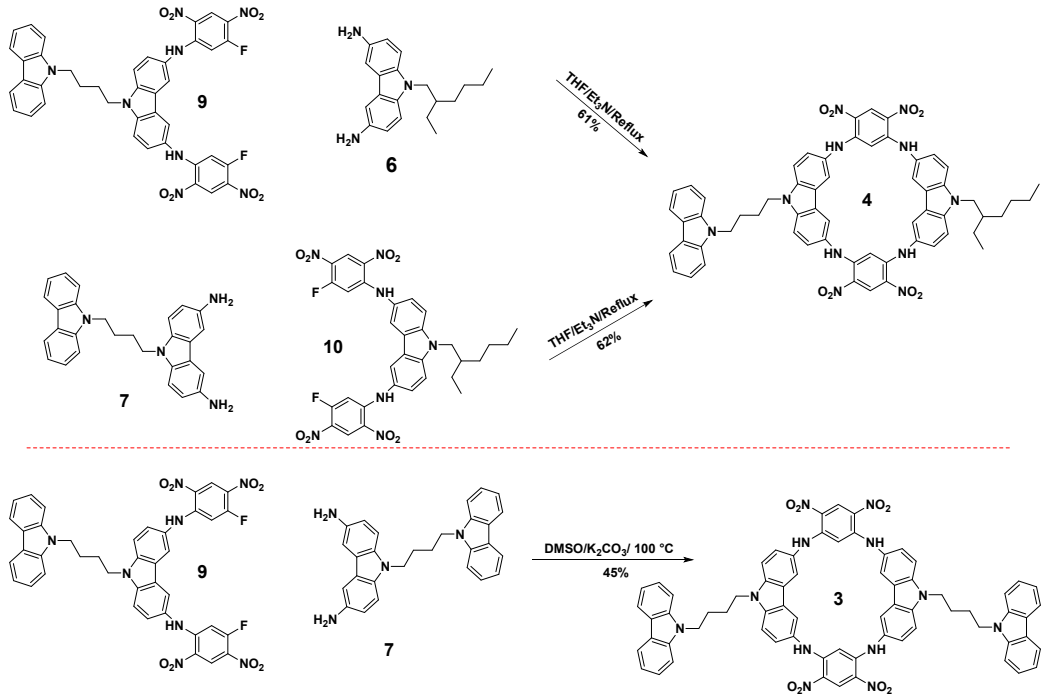
Scheme 1. Synthetic routes for 3, 6-diamino derived carbazole intermediates **5** and **7**.



Scheme 2. Synthetic routes for "2+1" fragments **9** and **10**.



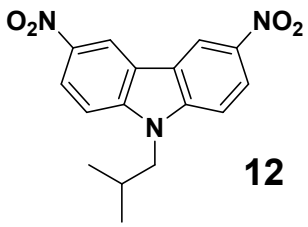
Scheme 3. One pot synthesis of symmetric macrocycles **1**~**3**.



Scheme 4. Fragment coupling strategy for the synthesis of unsymmetrical macrocycle **4** and symmetrical macrocycle **3**.

All solvents for reactions and column chromatography were used directly as received. Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 MHz or 300 MHz instruments. Chemical shifts were expressed in parts per million (δ) using residual solvent protons as internal standards. Chloroform (δ = 7.26 ppm) was used as an internal standard for chloroform-*d*. Alcohol free chloroform was used as solvent for spectroscopic measurements, which was thoroughly washed with distilled water and freshly distilled from P_2O_5. UV-vis data were recorded on UV-2501 PC SHIMADZU.

Compounds **6**[S1], **11**[S2], **13**[S3], and 14[S4] were synthesized according to similar literature procedures. All NMR experiments were performed on a Bruker AV 400 MHz instruments at 298 K if not specifically indicated.



$Cu(NO_3)_2 \cdot 3H_2O$ (362 mg, 1.5 mmol) was added into a mixture of acetic acid (1 mL) and acetic anhydride (2 mL) at room temperature and the mixture was stirred for 10

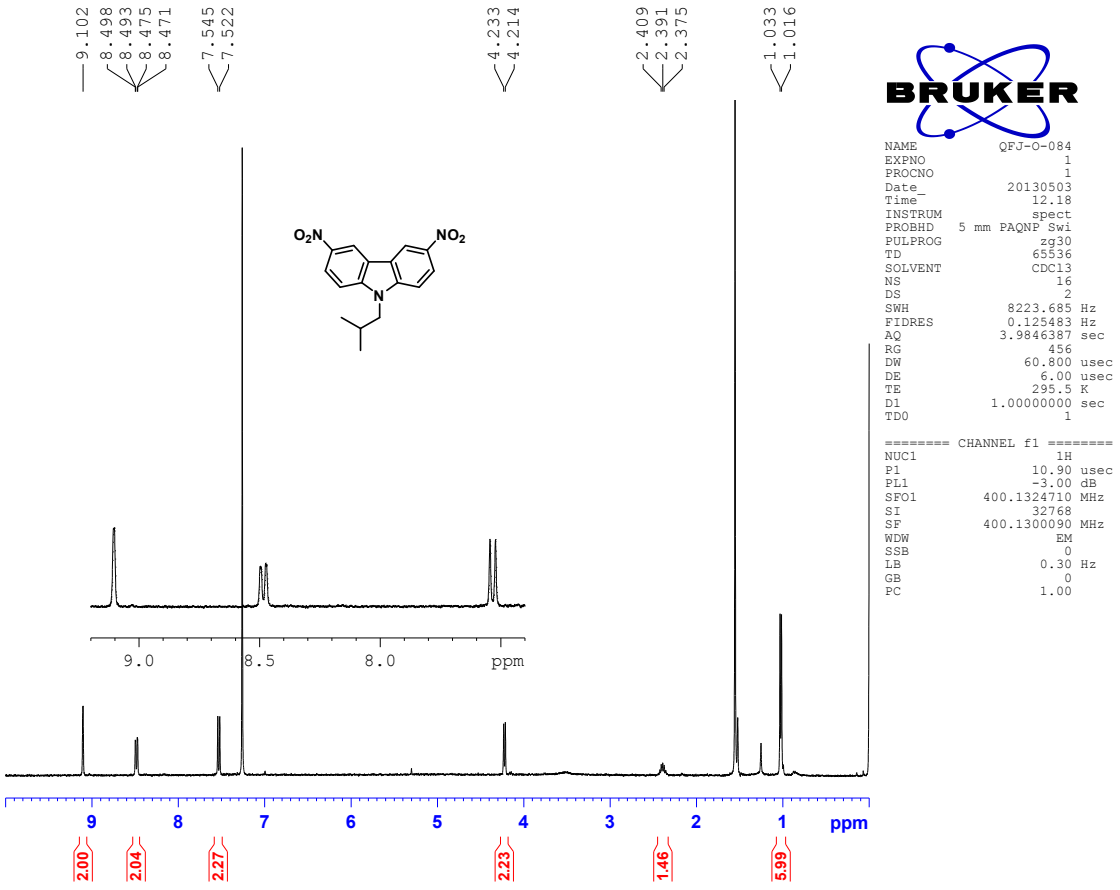
min. Then 9-(*iso*-butyl)carbazole **11** (223 mg, 1 mmol) was added slowly in portions over 5 min and heat was generated during the process. An additional 1 mL acetic acid was added. The mixture was stirred at this temperature for 15 min and then poured into distilled water (100 mL). A yellow precipitate was then collected by filtration, washed with water and dried under vacuum. The pure product as a yellow solid (194 mg, 62%) was obtained by recrystallization from ethanol.

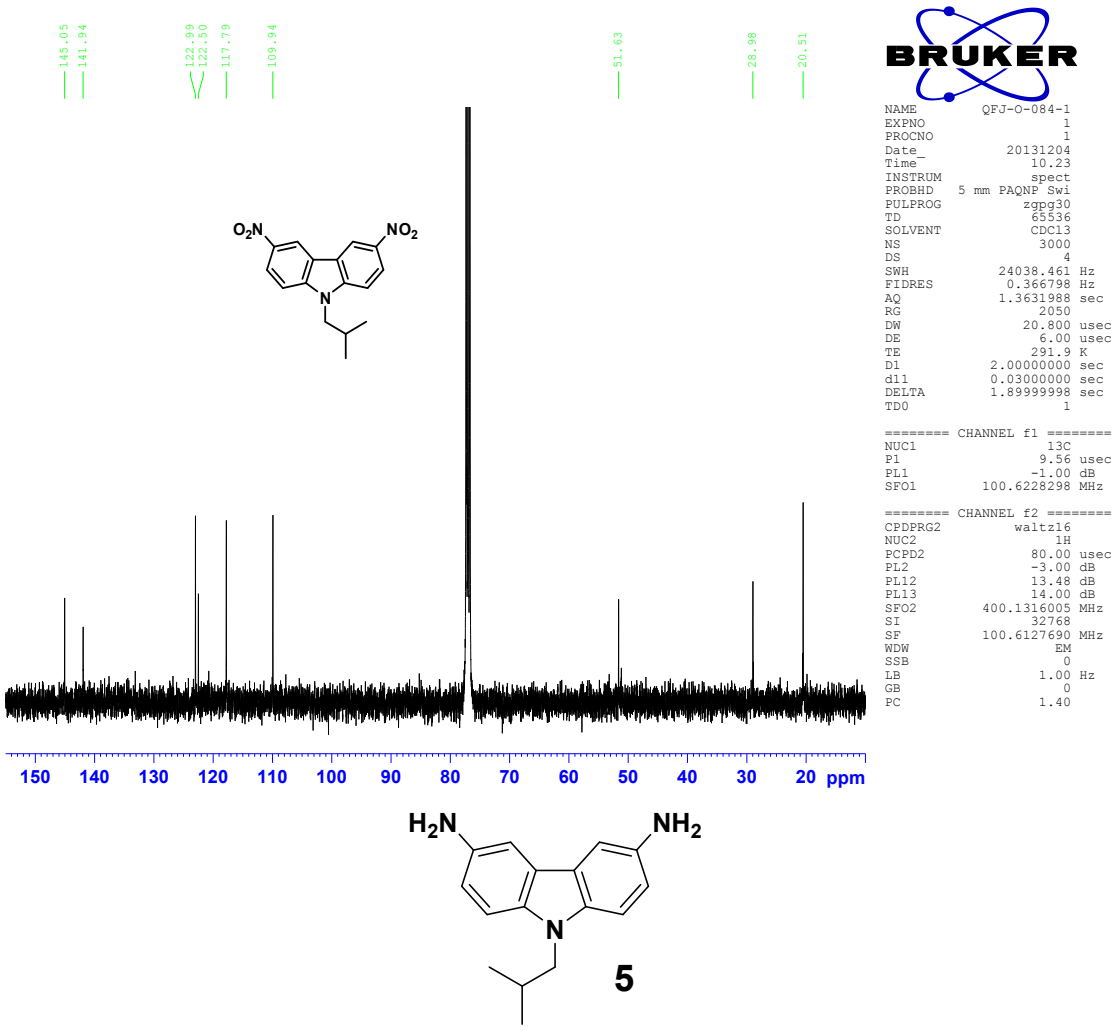
Mp: > 300 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 9.10 (s, 2H, Ar*H*), 8.48 (dd, 2H, *J* = 1.5 Hz, *J* = 9.1 Hz, Ar*H*), 7.53 (d, 2H, *J* = 9.1 Hz, Ar*H*), 4.22 (d, 2H, *J* = 7.5 Hz, CH_2), 2.39 (m, 1H, C*H*), 1.02 (d, 6H, *J* = 6.6 Hz, CH_3).

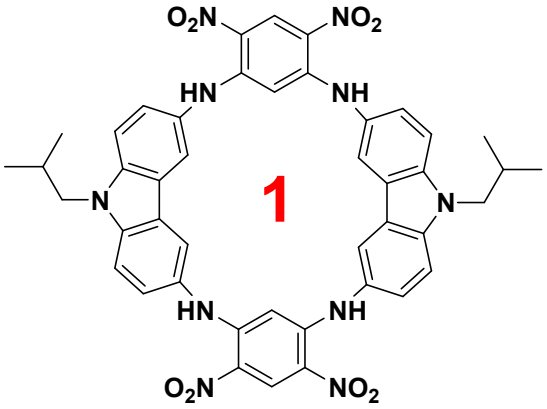
^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 145.1, 141.9, 123.0, 122.5, 117.8, 109.9, 51.6, 29.0, 20.5.

HRMS (ESI$^+$) calcd. for $[C_{16}H_{15}N_3O_4+Na]^+$ 336.0960, found: 336.0951.





Palladium on active charcoal (10%, 115 mg) was added in portions to a hot solution of 3, 6-dinitro-9-(*iso*-butyl)carbazole **12** (0.423 g, 1.35 mmol) and hydrazine hydrate (1 mL) in THF (30 mL). The mixture was heated under reflux for 5 hours. After cooling to room temperature, the solid was filtrated off and the filtrate was concentrated. The residue was triturated with petroleum ether to give the product as a yellow solid (249 mg, 73%). The product was directly for the next step without further purification and characterization.

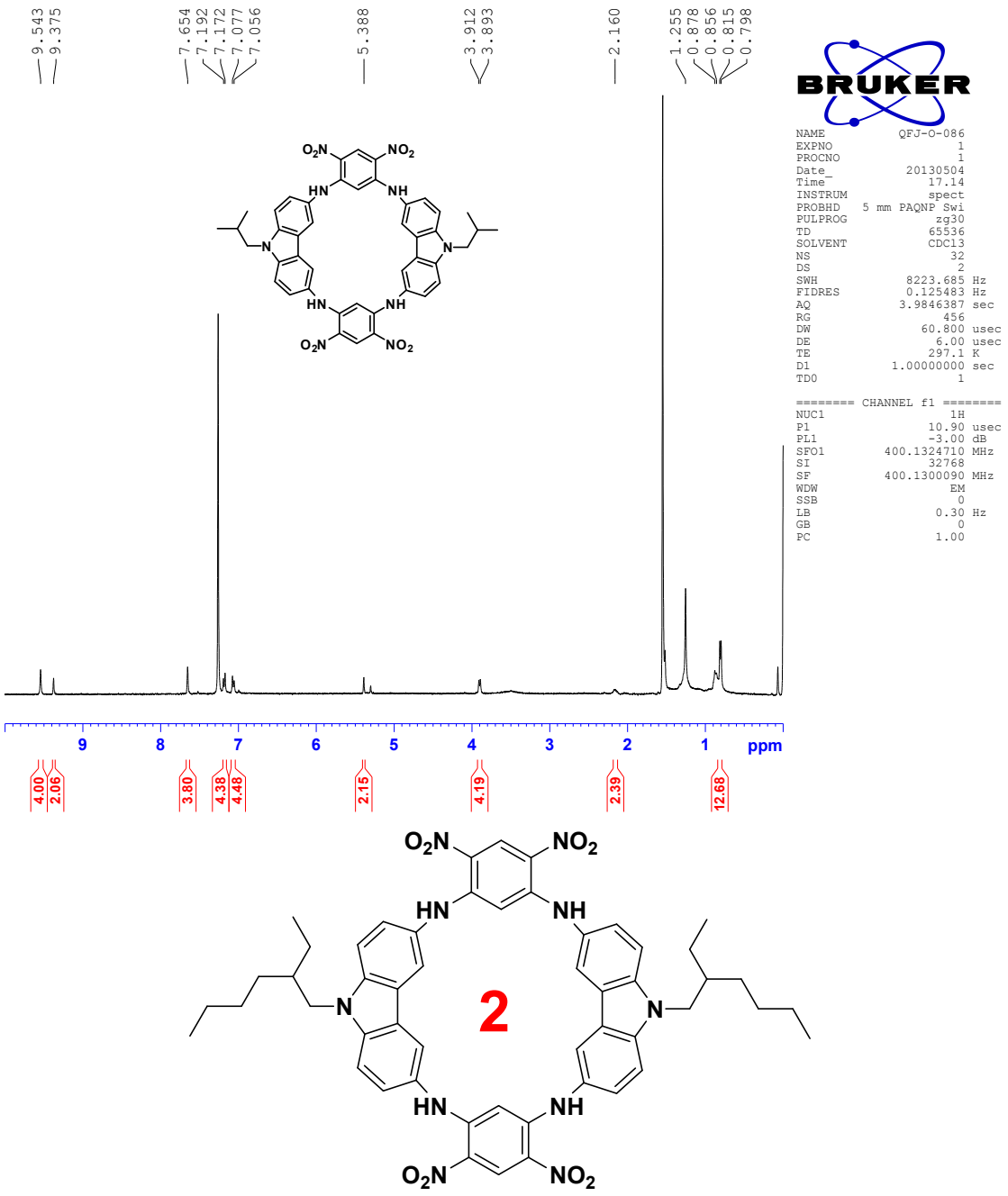


3, 6-Diamino-9-(*iso*-butyl)carbazole **5** (1.012 g, 4 mmol) was added under N_2 atmosphere into a mixture of 1, 5-difluoro-2, 4-dinitrobenzene **8** (0.816 g, 4 mmol) and triethylamine (5.8 mL) in THF (50 mL). Then the mixture was heated to reflux under nitrogen atmosphere overnight. After being cooled to room temperature, an orange solid precipitated from the solution. The solid was collected by filtration and washed with ethanol. The product was pure enough and further purification was not needed (1.3 g, 78%).

Mp: > 300 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 9.54 (s, 4H, N*H*), 9.37 (s, 2H, Ar*H*), 7.65 (s, 4H, Ar*H*-carbazole), 7.18 (d, 4H, *J* = 8.1 Hz, Ar*H*-carbazole), 7.06 (d, 4H, *J* = 8.5 Hz, Ar*H*-carbazole), 5.39 (s, 2H, Ar*H*), 3.90 (d, 4H, *J* = 7.4 Hz, CH_2), 2.16 (m, 2H, C*H*), 0.80 (d, 12H, *J* = 6.6 Hz, CH_3).

HRMS (APCI$^+$) calcd. for $[C_{44}H_{38}N_{10}O_8+H]^+$ 835.2952, found: 835.2940.



3, 6-Diamino-9-(2-ethylhexyl)carbazole **6** (309 mg, 1 mmol) was added under N_2 atmosphere into a mixture of 1, 5-difluoro-2, 4-dinitrobenzene **8** (204 mg, 1 mmol) and triethylamine (1.4 mL) in THF (30 mL) and the solution was stirred overnight under reflux. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, dichloromethane as eluent). The product was obtained as

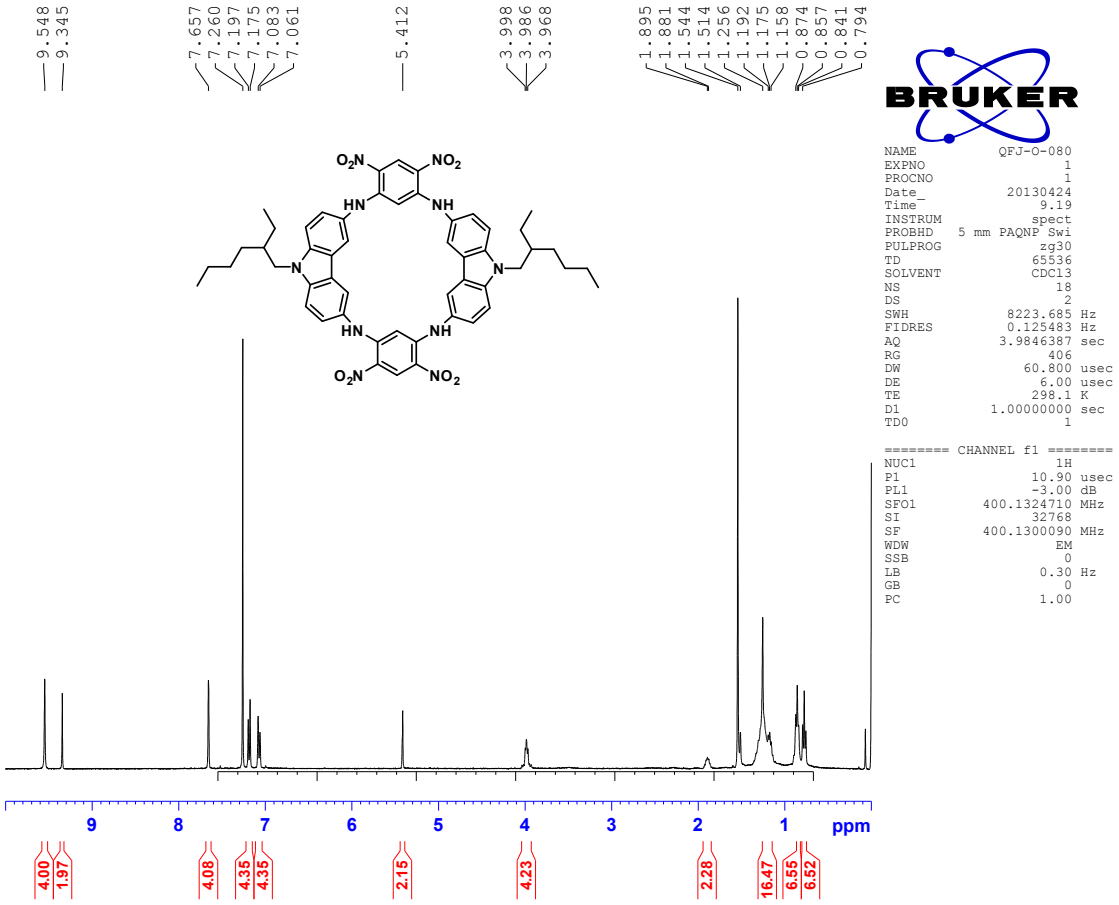
an orange solid (166 mg, 35%).

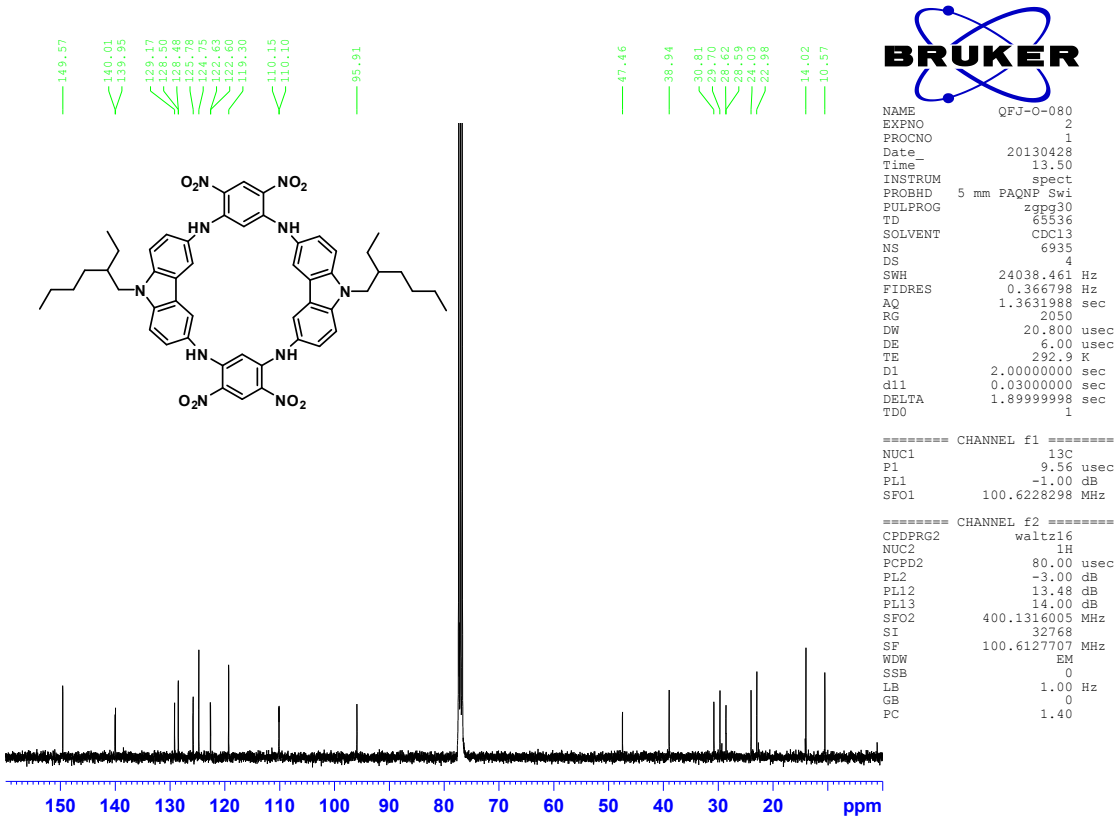
Mp: > 300 ºC.

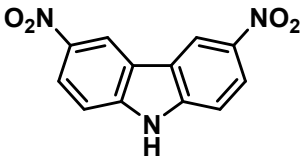
^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 9.55 (s, 4H, N*H*), 9.34 (s, 2H, Ar*H*), 7.66 (s, 4H, Ar*H*-carbazole), 7.19 (d, 4H, *J* = 8.6 Hz, Ar*H*-carbazole), 7.07 (d, 4H, *J* = 8.5 Hz, Ar*H*-carbazole), 5.41 (s, 2H, Ar*H*), 4.02-3.87 (m, 4H, NCH_2), 1.94-1.84 (m, 2H, C*H*), 1.40-1.10 (m, 16H, CH_2), 0.86 (t, 6H, *J* = 6.5 Hz, CH_3), 0.78 (t, 6H, *J* = 7.2 Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 149.6, 140.01, 139.95, 129.2, 128.50, 128.48, 125.8, 124.7, 122.64, 122.60, 119.3, 110.15, 110.10, 95.9, 47.5, 38.9, 30.8, 29.7, 28.62, 28.59, 24.0, 23.0, 14.0, 10.6.

HRMS (APCI$^+$) calcd. for $[C_{52}H_{54}N_{10}O_8+H]^+$ 947.4204, found: 947.4200.



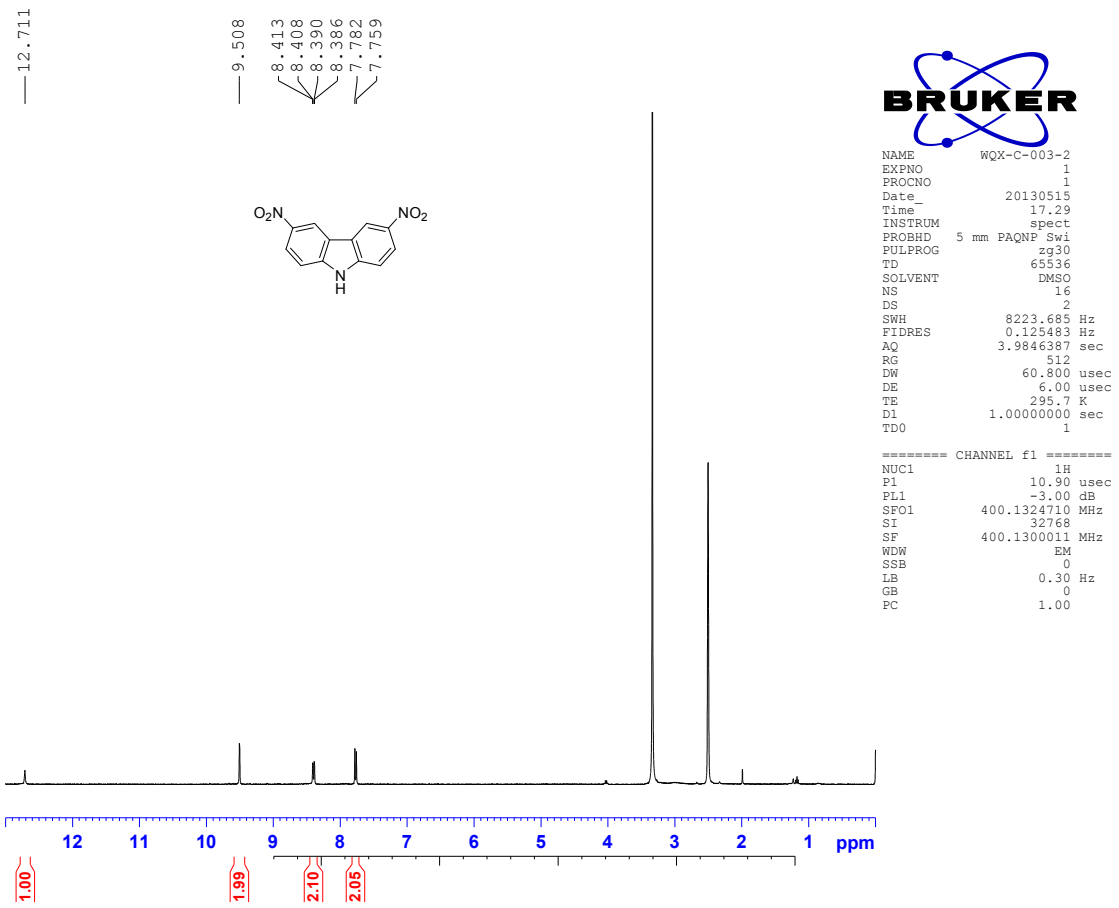


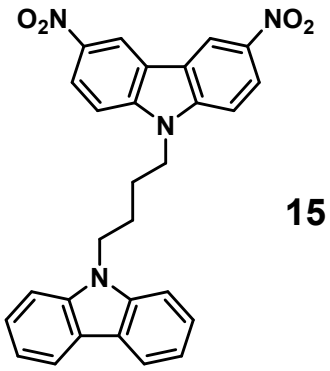


14

This compound was synthesized according to a similar literature procedure[S4].

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 12.71 (s, 1H, N*H*), 9.51 (d, 2H, J = 1.8 Hz, Ar*H*), 8.40 (dd, 2H, J = 1.8 Hz, J = 9.0 Hz, Ar*H*), 7.77 (d, 2H, J = 9.0 Hz, Ar*H*).





15

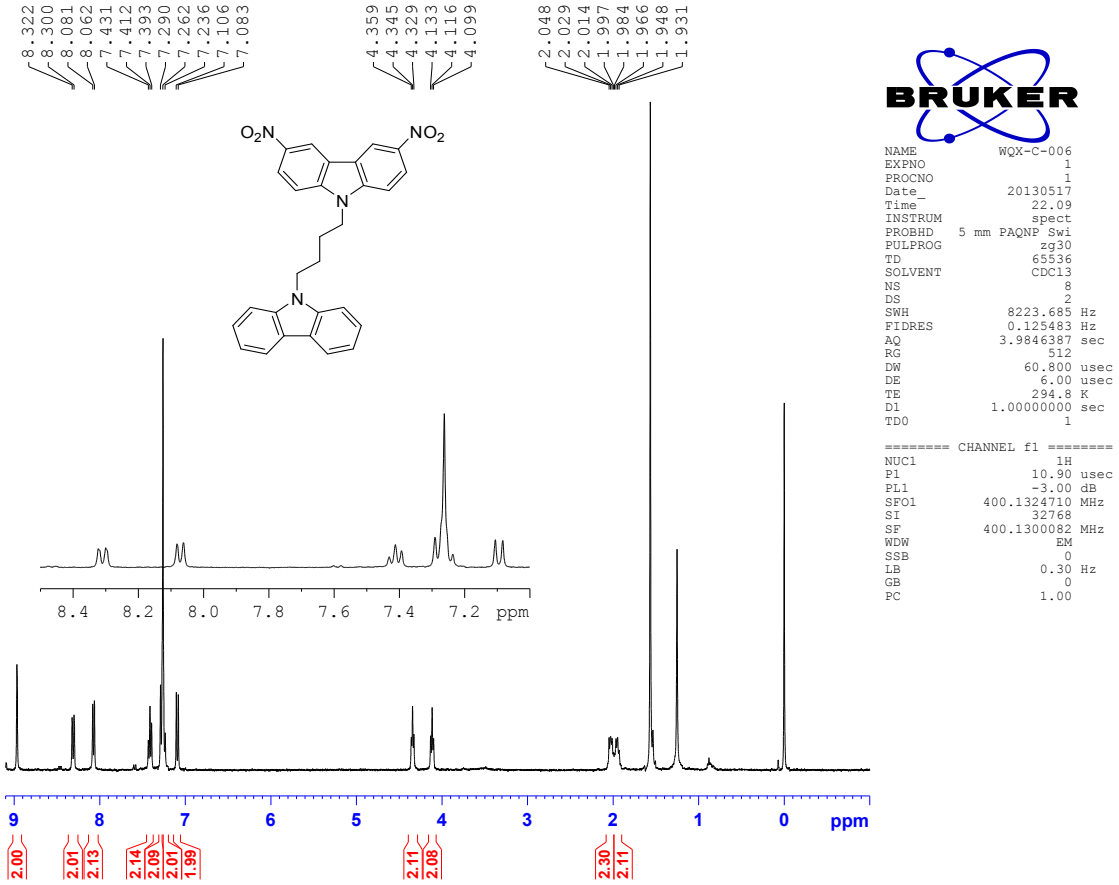
A 100 mL Schlenk flask was charged with 3, 6-dinitro-9*H*-carbazole **14** (1.23 g, 4.8 mmol), NaH (0.211 g, 5.28 mmol, 60% in mineral oil) and 40 mL DMF. The resulting mixture was stirred for 30 min. 9-(4-bromobutyl)-carbazole **13** (1.378 g, 4.8 mmol) was then added under argon and the mixture was stirred at room temperature overnight. The reaction mixture was quenched with 60 mL of water. The solid was collected by filtration and washed with methanol. The pure product as a yellow solid (1.85 g, 81%) was obtained *via* column chromatography (silica gel, petroleum ether: dichloromethane = 1:1 as eluent).

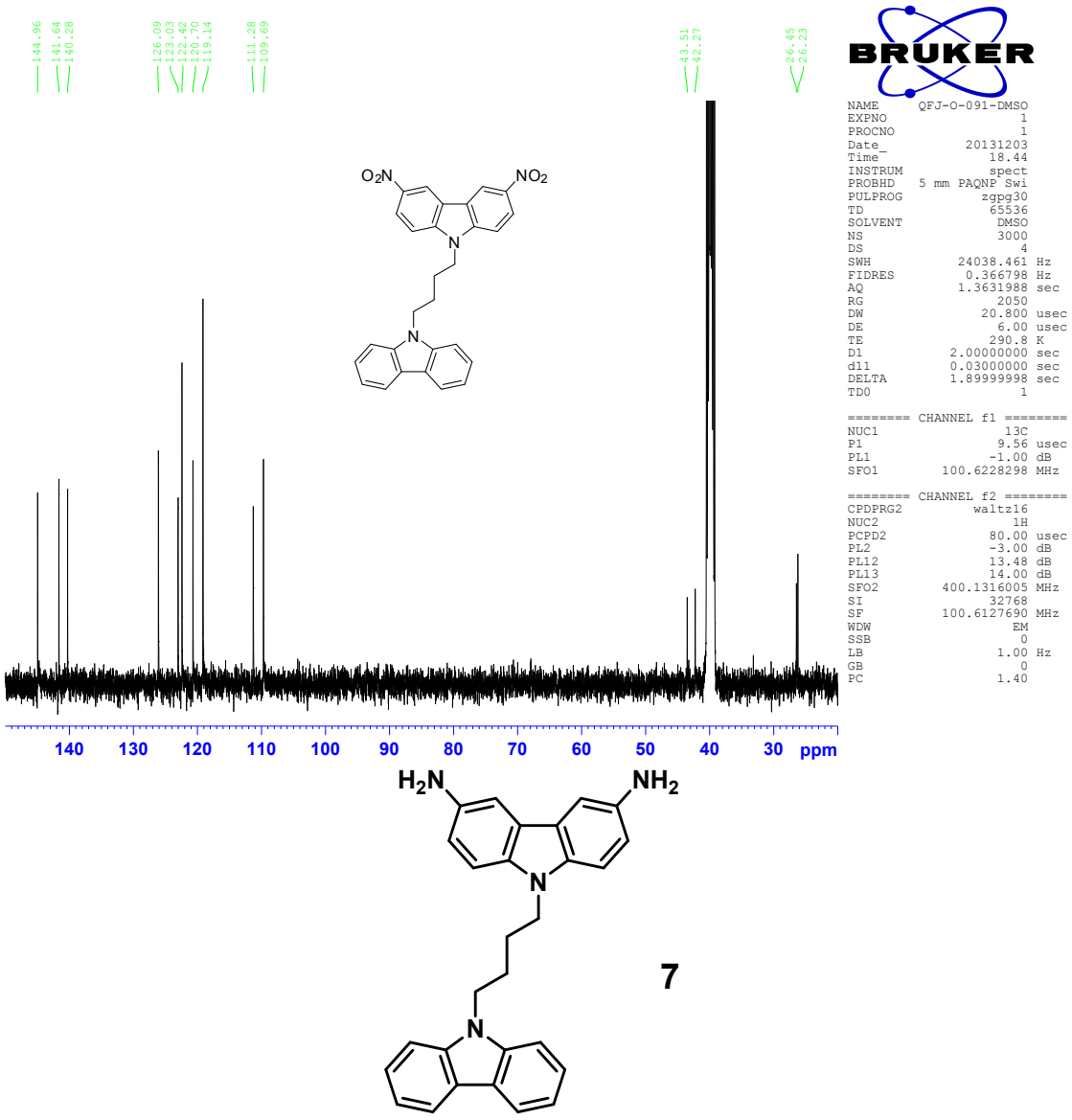
Mp: 253-254 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.97 (s, 2H, Ar*H*), 8.31 (d, 2H, *J* = 9.1 Hz, Ar*H*), 8.07 (d, 2H, *J* = 7.8 Hz, Ar*H*), 7.41 (t, 2H, *J* = 7.6 Hz, Ar*H*), 7.26 (t, 4H, *J* = 5.8 Hz, Ar*H*), 7.09 (d, 2H, *J* = 9.1 Hz, Ar*H*), 4.34 (t, 2H, *J* = 6.0 Hz, NCH_2), 4.12 (t, 2H, *J* = 6.9 Hz, NCH_2), 2.05-1.95 (m, 4H, CH_2).

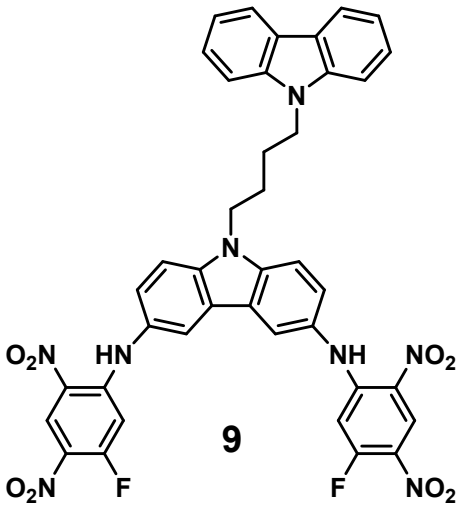
^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 145.0, 141.6, 140.3, 126.1, 123.0, 122.4, 120.7, 119.1, 111.3, 109.7, 43.5, 42.3, 26.4, 26.2.

HRMS (ESI$^+$) calcd. for $[C_{28}H_{22}N_4O_4+Na]^+$ 501.1539, found: 501.1529; calcd. for $[C_{28}H_{22}N_4O_4+K]^+$ 517.1278, found: 517.1269.





Palladium on charcoal (10%, 115 mg) was added in portions to a hot solution of 9-(4-(9H-carbazol-9-yl)butyl)-3, 6-dinitrocarbazole **15** (0.645 g, 1.35 mmol) and hydrazine monohydrate (1 mL) in THF (30 mL) and the mixture was heated under reflux for 5 hours. After being cooled to room temperature the solid was filtrated off and the filtrate was concentrated. The residue was triturated with petroleum ether to give the product as a yellow solid (412 mg, 73%). The product was directly for the next step without further purification and characterization.



9

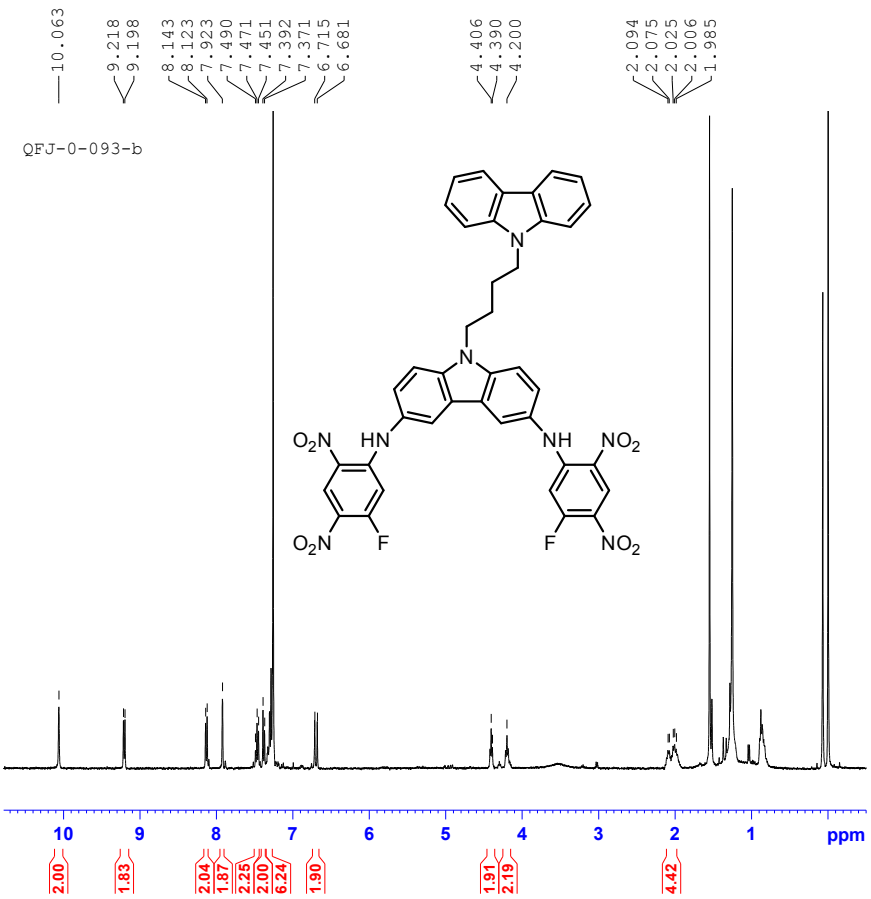
3, 6-diamino-9-(4-(9*H*-carbazol-9-yl)butyl)carbazole **7** (125 mg, 0.3 mmol) was added under N_2 atmosphere into a mixture of 1, 5-difluoro-2, 4-dinitrobenzene **8** (122 mg, 0.6 mmol) and triethylamine (0.5 mL) in THF (20 mL). The solution was stirred overnight under reflux. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL), washed with water and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, dichloromethane: petroleum ether = 5:1 as eluent). The product was obtained as an orange solid (220 mg, 93%).

Mp: 172-173 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 10.06 (s, 2H, N*H*), 9.21 (d, 2H, *J* = 7.8 Hz, Ar*H*), 8.14 (d, 2H, *J* = 7.8 Hz, Ar*H*), 7.92 (s, 2H, Ar*H*), 7.47 (t, 2H, *J* = 7.9 Hz, Ar*H*), 7.38 (d, 2H, *J* = 8.3 Hz, Ar*H*), 7.34-7.27 (m, 6H, Ar*H*), 6.70 (d, 2H, *J* = 13.6 Hz, Ar*H*), 4.41 (t, 2H, *J* = 6.3 Hz, NCH_2), 4.20 (t, 2H, *J* = 7.0 Hz, NCH_2), 2.05 (m, 4H, CH_2CH_2).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ160.6, 157.9, 148.9, 148.8, 139.8, 139.6, 127.6, 127.4, 127.0, 125.3, 124.3, 122.7, 122.5, 120.1, 118.7, 118.1, 110.3, 108.0, 102.7, 102.5, 42.9, 42.1, 31.4, 29.2, 26.2, 26.1, 22.2, 13.6.

HRMS (APCI$^+$): *m*/*z* calcd. for $[C_{40}H_{28}F_2N_8O_8+H]^+$ 787.2076, found: 787.2059.



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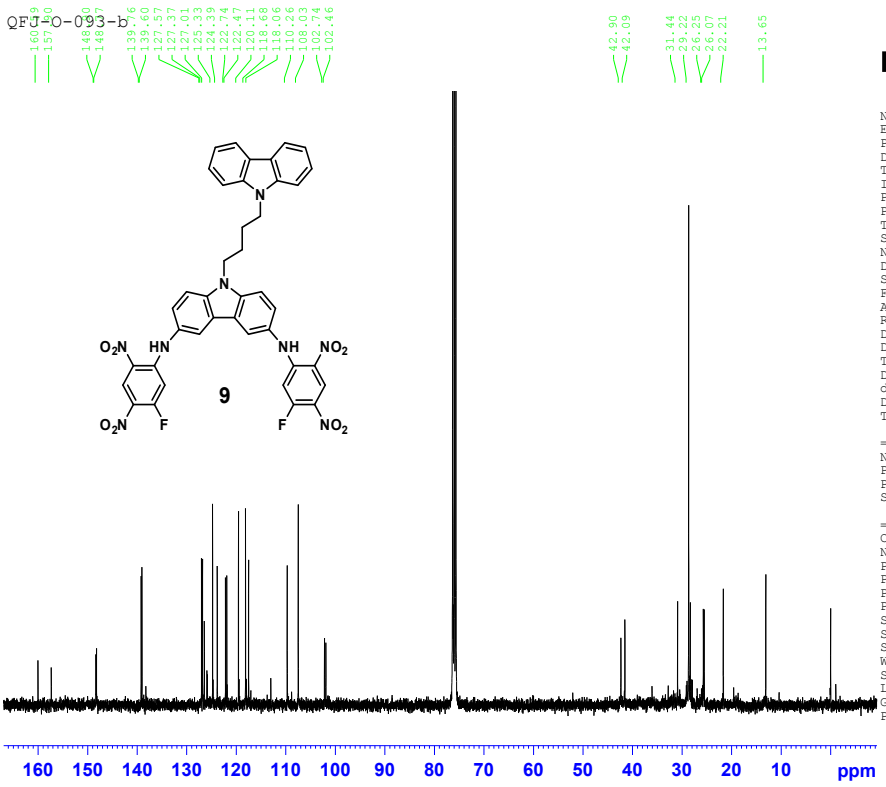

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PL13	14.00 dB
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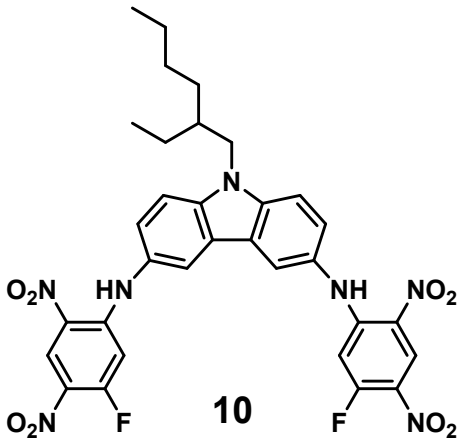


10

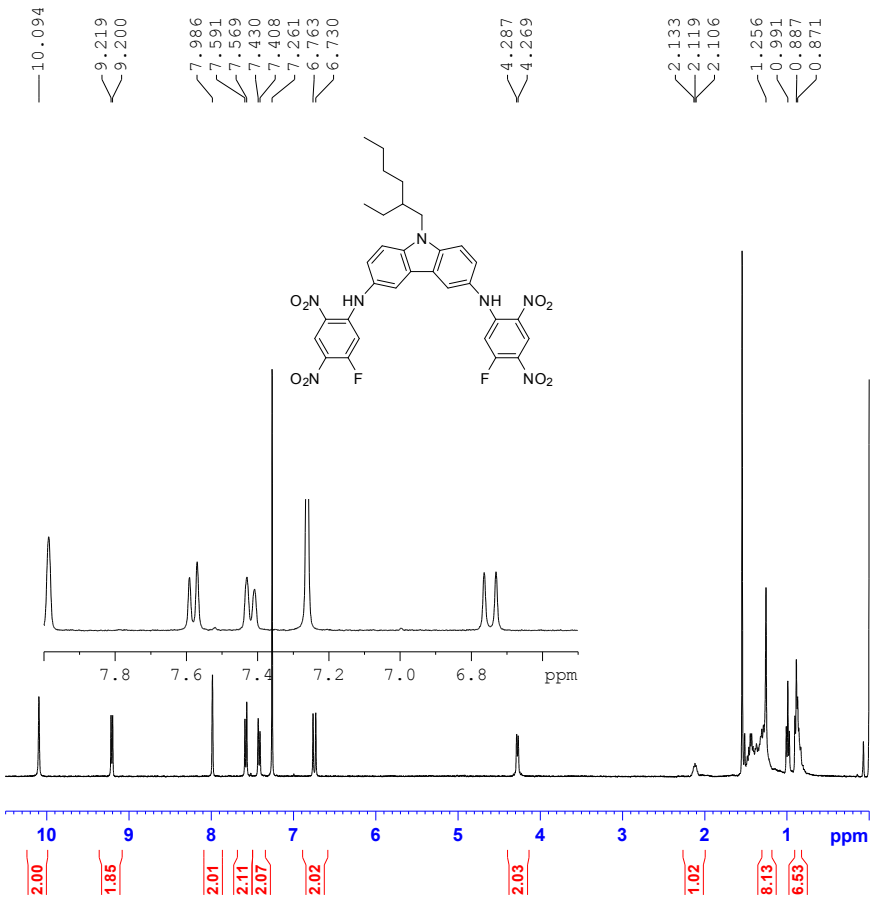
3, 6-Diamino-9-(2-ethylhexyl)carbazole **6** (93 mg, 0.3 mmol) was added under N_2 atmosphere into a mixture of 1, 5-difluoro-2, 4-dinitrobenzene **8** (122 mg, 0.6 mmol) and triethylamine (0.5 mL) in THF (20 mL) and the solution was stirred overnight under reflux. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, dichloromethane: petroleum ether = 2:1 as eluent). The product was obtained as a reddish brown solid (184 mg, 91%).

Mp: 120-121 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 10.09 (s, 2H, N*H*), 9.21 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.99 (s, 1H, Ar*H*), 7.58 (d, 2H, *J* = 8.6 Hz, Ar*H*), 7.42 (d, 2H, *J* = 8.6 Hz, Ar*H*), 6.75 (d, 2H, *J* = 13.3 Hz, Ar*H*), 4.28 (d, 2H, *J* = 7.3 Hz, CH_2), 2.16-2.08 (m, 1H, C*H*), 1.50-1.25 (m, 8H, CH_2), 0.99 (t, *J* = 7.3 Hz, CH_3), 0.89 (t, *J* = 6.6 Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 161.1, 158.4, 149.5, 149.3, 140.8, 128.01, 127.99, 127.8, 127.5, 127.0, 126.9, 124.8, 123.2, 118.5, 111.2, 103.3, 103.0, 48.1, 39.6, 31.0, 29.7, 28.8, 24.5, 23.0, 14.0, 10.9.

HRMS (APCI$^-$) calcd. for $[C_{32}H_{29}F_2N_7O_8-H]^-$ 676.1967, found: 676.1966.



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FIDRES               0.125483 Hz
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TE                    298.1 K
D1                1.00000000 sec
TD0                         1

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P1                    10.90 usec
PL1                   -3.00 dB
SFO1           400.1324710 MHz
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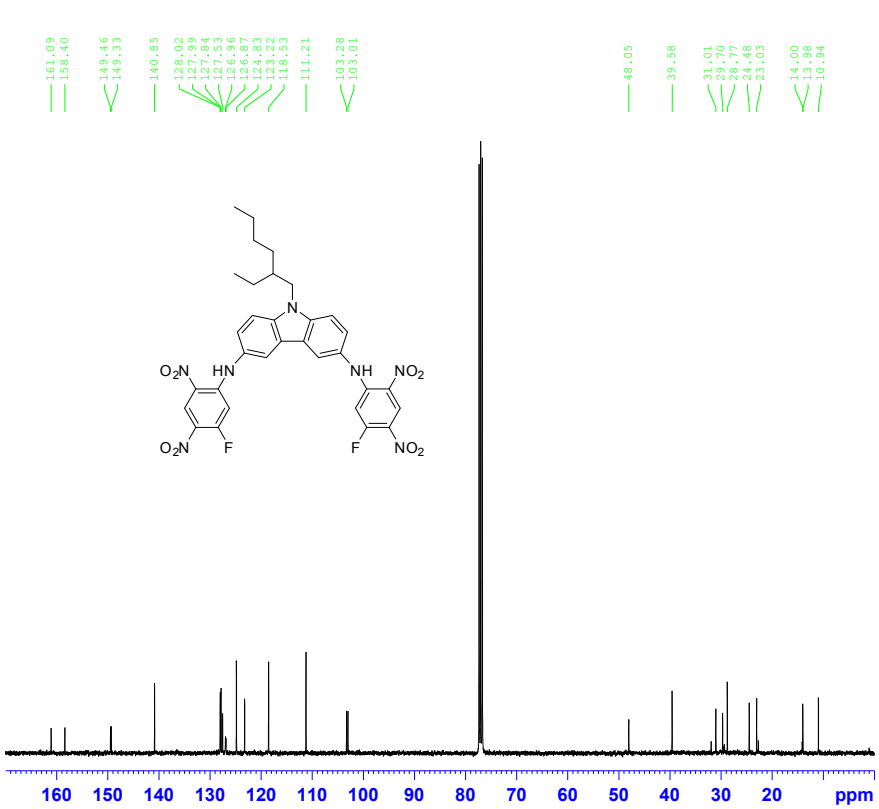

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TE                    297.7 K
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d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                    9.56 usec
PL1                  -1.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                       1H
PCPD2                80.00 usec
PL2                   -3.00 dB
PL12                  13.48 dB
PL13                  14.00 dB
SFO2           400.1316005 MHz
SI                      32768
SF             100.6127690 MHz
WDW                        EM
SSB                         0
LB                    1.00 Hz
GB                          0
PC                    1.40
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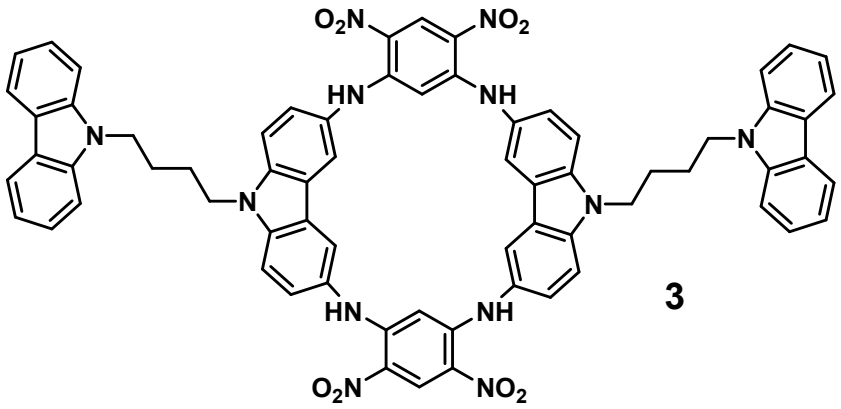


3

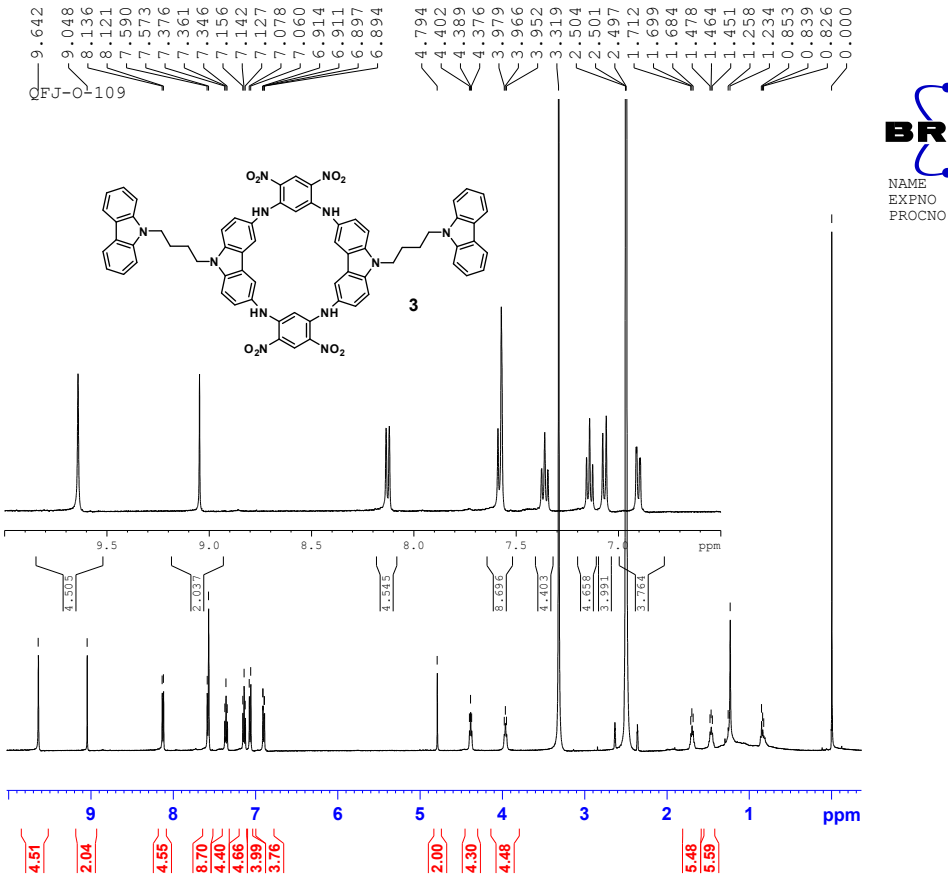
Fragment Coupling Strategy: 3, 6-diamino-9-(4-(9*H*-carbazol-9-yl)butyl)carbazole **7** (25 mg, 0.06 mmol), "2+1" fragment compound **9** (47 mg, 0.06 mmol), and anhydrous K_2CO_3 (0.15 mmol, 21 mg) were combined under ambient atmosphere. Anhydrous DMSO (5 mL) was added. The reaction mixture was heated to 100 ºC and stirred vigorously overnight. The reaction mixture was then partitioned between EtOAc (40 mL) and H_2O (30 mL) and the resulting mixture separated. The aqueous layer was extracted twice with EtOAc (10 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, dichloromethane: petroleum ether = 7:1 as eluent). The product was obtained as a yellow solid (31 mg, 45%).

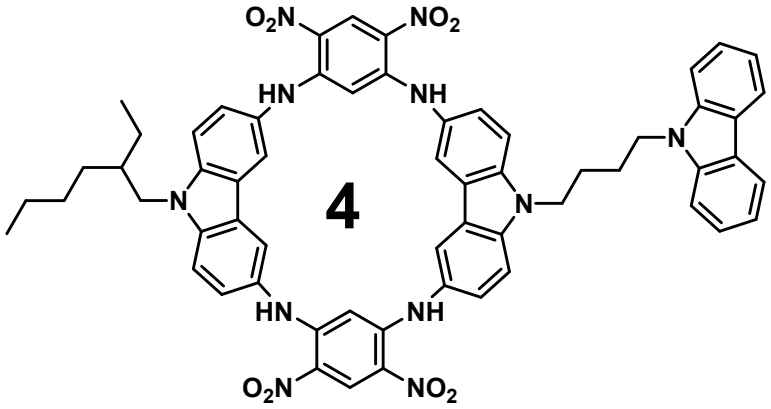
One Pot Strategy: 9-(4-(9*H*-carbazol-9-yl)butyl)-9*H*-carbazole-3, 6-diamine **7** (125 mg, 0.3 mmol), 1, 5-difluoro-2, 4-dinitrobenzene **8** (61 mg, 0.3 mmol), and anhydrous K_2CO_3 (0.75 mmol, 104 mg) were combined under ambient atmosphere. Anhydrous DMSO (10 mL) was added. The reaction mixture was heated to 100 ºC and stirred vigorously overnight. The reaction mixture was then partitioned between EtOAc (80 mL) and H_2O (60 mL), the resulting mixture separated. The aqueous layer was extracted twice with EtOAc (30 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, dichloromethane: petroleum ether = 7:1 as eluent). The product was obtained as a yellow solid (83 mg, 48%).

Mp: > 300 ºC.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.64 (s, 4H, N*H*), 9.05 (s, 2H, Ar*H*), 8.12 (d, 4H, *J* = 7.7 Hz, Ar*H*), 7.56 (d+s, 8H, *J* = 7.3 Hz, Ar*H*), 7.36 (t, 4H, *J* = 7.6 Hz, Ar*H*), 7.14 (t, 4H, *J* = 7.3 Hz, Ar*H*), 7.06 (d, 4H, *J* = 8.7 Hz, Ar*H*), 6.90 (dd, 4H, *J* = 8.6 Hz, *J* = 1.7 Hz, Ar*H*), 4.79 (s, 2H, Ar*H*), 4.39 (t, 4H, *J* = 6.6 Hz, NCH_2), 3.97 (t, 4H, *J* = 6.8 Hz, NCH_2), 1.74-1.66 (m, 4H, CH_2CH_2), 1.52-1.42 (m, 4H, CH_2CH_2).

HRMS (APCI$^+$) calcd. for $[C_{68}H_{52}N_{12}O_8+H]^+$ 1165.4109, found: 1165.4108.





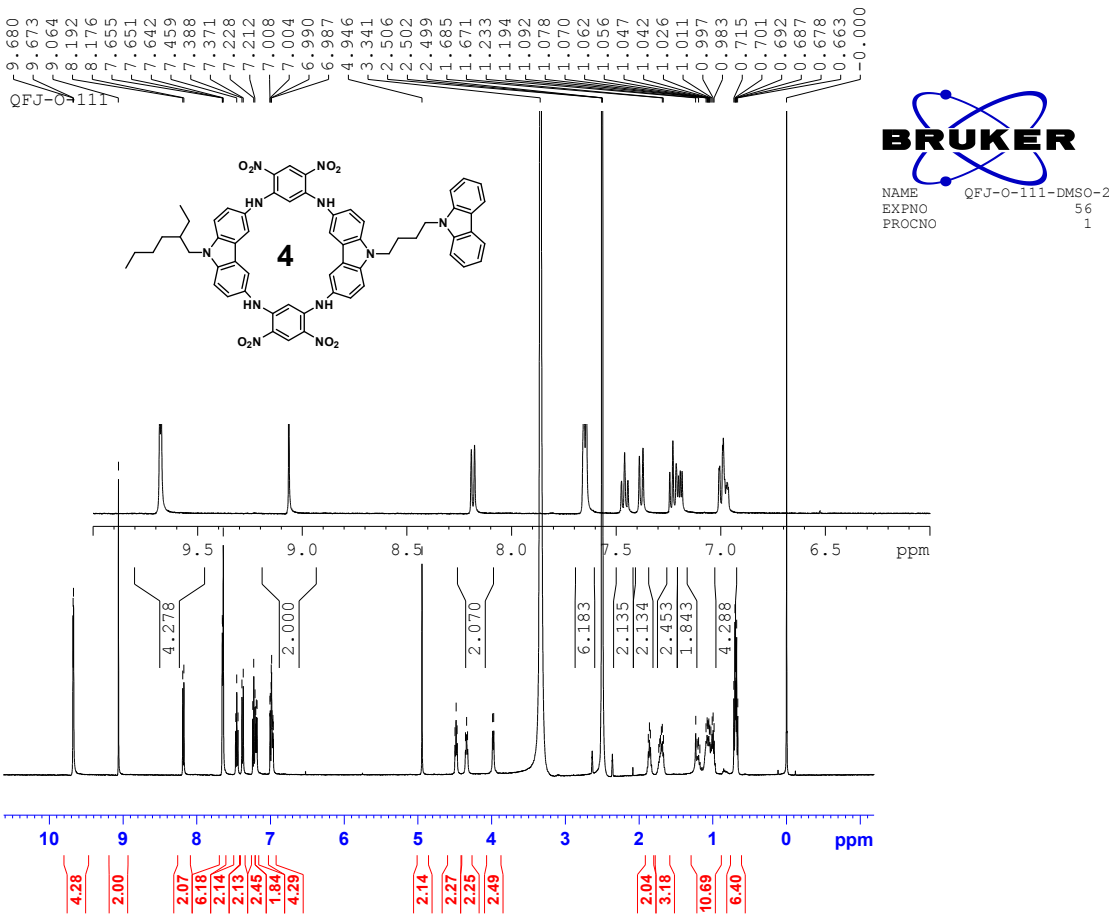
Strategy one: 3, 6-Diamino-9-(2-ethylhexyl)carbazole **6** (31 mg, 0.1 mmol) was added under N_2 atmosphere into a mixture of "2+1" fragment compound **9** (79 mg, 0.1

mmol) and triethylamine (0.2 mL) in THF (20 mL) and the solution was stirred overnight under reflux. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, dichloromethane: petroleum ether = 10:1 as eluent). The product was obtained as an orange solid (64 mg, 61%).

Strategy two: 9-(4-(9*H*-carbazol-9-yl)butyl)-9*H*-carbazole-3,6-diamine **7** (125 mg, 0.3 mmol) was added under N_2 atmosphere into a mixture of "2+1" fragment compound **10** (203 mg, 0.3 mmol) and triethylamine (0.5 mL) in THF (20 mL) and the solution was stirred overnight under reflux. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with water and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, dichloromethane: petroleum ether = 10:1 as eluent). The product was obtained as an orange solid (197 mg, 62%).

Mp: > 300 ℃. ^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 9.680 (s, 2H, N*H*), 9.673 (s, 2H, N*H*), 9.06 (s, 2H, Ar*H*), 8.18 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.66-7.58 (m, 6H, Ar*H*), 7.46 (t, 2H, *J* = 7.7 Hz, Ar*H*), 7.38 (d, 2H, *J* = 8.6 Hz, Ar*H*), 7.23 (t, 2H, *J* = 7.6 Hz, Ar*H*), 7.17(t, 2H, *J* = 4.4 Hz, Ar*H*), 7.03-6.95 (m, 4H, Ar*H*), 4.95 (s, 2H, Ar*H*), 4.48 (t, 2H, *J* = 7.1 Hz, NCH_2), 4.34 (t, 2H, *J* = 7.2 Hz, NCH_2), 3.98 (d, 2H, *J* = 7.4 Hz, NCH_2), 1.90-1.80 (m, 2H, CH_2CH_2), 1.75-1.62 (m, 3H, CH_2CH_2&C*H*), 1.06-0.96 (m, 8H, CH_2), 0.72-0.64 (m, 6H, CH_3).

HRMS (APCI$^+$) calcd. for $[C_{60}H_{53}N_{11}O_8+H]^+$ 1056.4157, found: 1056.4153.



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