Supplementary Information

Effect of positional deuterium substitution on the acceptor moiety for TADF

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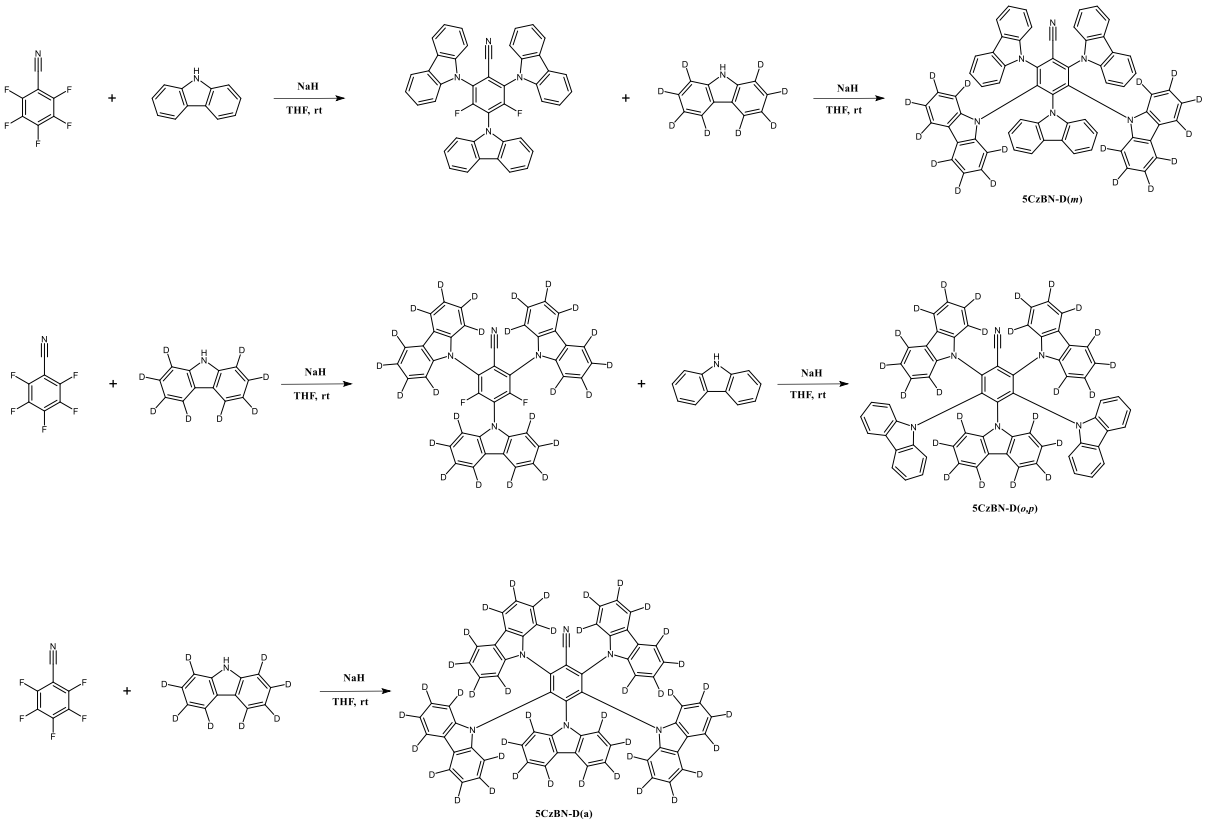
Synthesis



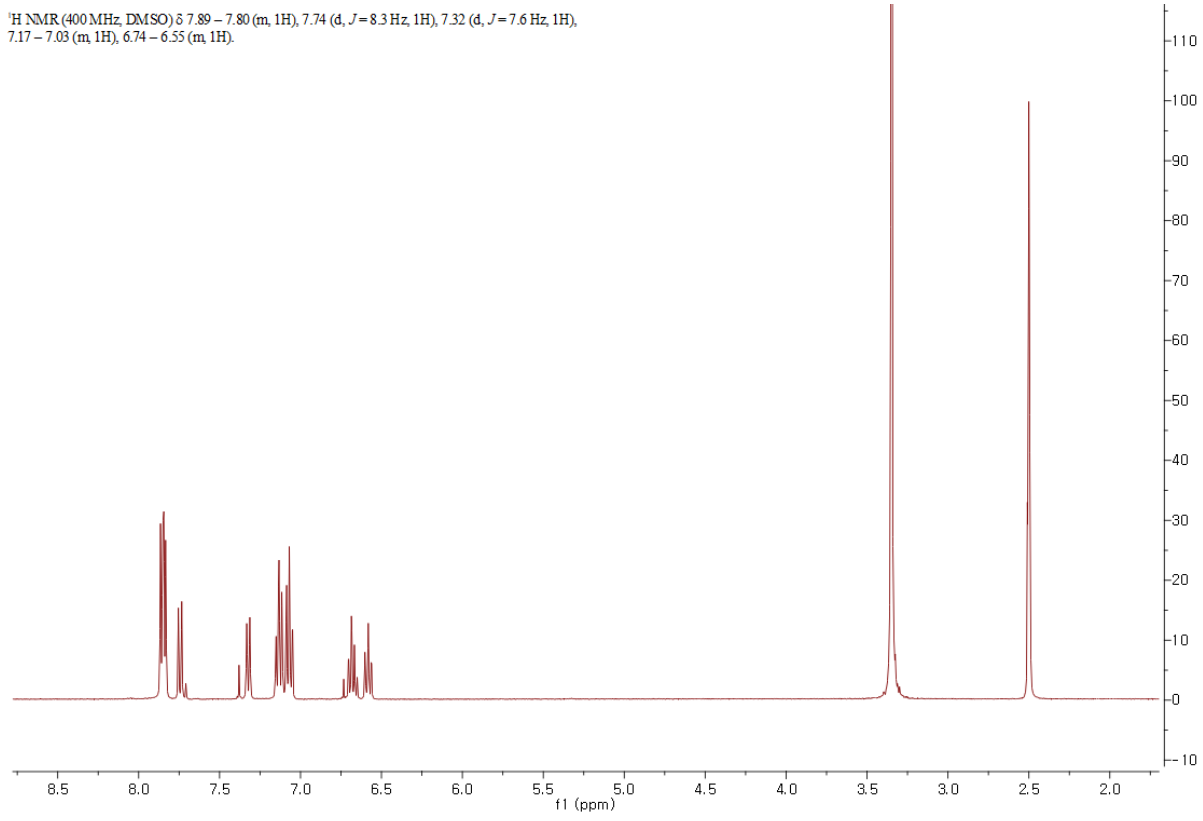
Scheme 1. Synthetic scheme for the 5CzBN-D(*m*), 5CzBN-D(*o,p*) and 5CzBN-D(a).

(s)-2,4,6-tri(9H-carbazol-9-yl)-3,5-bis(9H-carbazol-9-yl-d$_8$)benzonitrile (5CzBN-D(*m*))

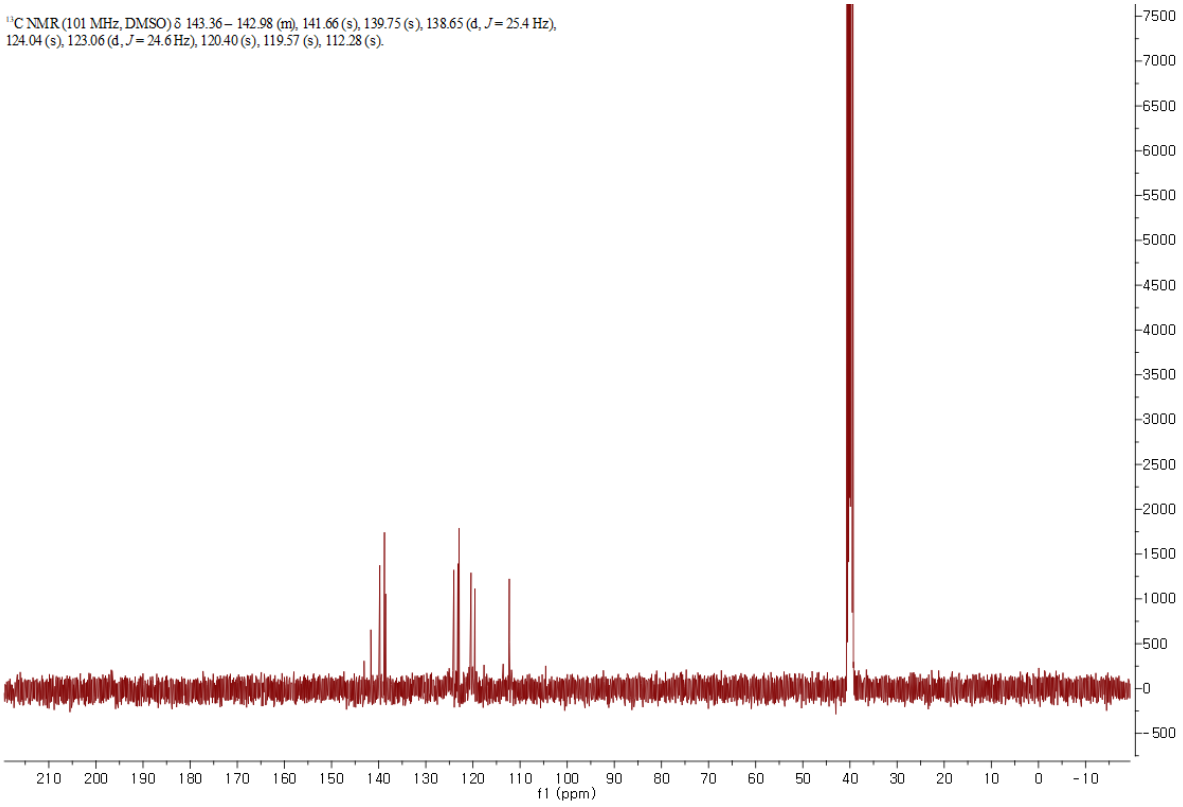
9H-carbazole (1.34 g, 8.03 mmol), NaH (0.36 g, 9.06 mmol), and THF (40 mL) were added to a 100 mL round-bottom flask, and 9H-carbazole was activated for 1 h under nitrogen atmosphere at room temperature. Then, pentafluorobenzonitrile (0.50 g, 2.59 mmol) was added to the round-bottom flask, and the mixture was stirred for 12 h under nitrogen atmosphere at room temperature. After completion of the reaction, extraction was repeated three times using methylene chloride and distilled water. The organic layers were combined and dried

over anhydrous $MgSO_4$. After filtration, the crude mixture was evaporated using a rotary evaporator. The mixture was recrystallized from toluene and methanol to remove impurities, and the product (2,4,6-tri(9H-carbazol-9-yl)-3,5-difluorobenzonitrile) (3CzFCN) was obtained. After that, deuterated carbazole (0.83 g, 4.73 mmol), NaH (0.22 g, 5.51 mmol), THF (40 mL) were added to a 100 mL round-bottom flask, and deuterated carbazole was activated for 1 h under nitrogen atmosphere at room temperature. Then, 3CzFCN (1.00 g, 1.58 mmol) was added to the round-bottom flask, and the mixture was stirred for 24 h under nitrogen atmosphere at room temperature. After completion of the reaction, extraction was repeated three times using methylene chloride and distilled water. The organic layers were combined and dried over anhydrous $MgSO_4$. After filtration, the crude mixture was evaporated using a rotary evaporator. The mixture was recrystallized with toluene and methanol to remove impurities, and the product (D-m-5CzBN) was obtained as a yellow powder.

Yield 0.93g (62.2%), ^{1}HNMR (400 MHz, DMSO) δ 7.89 – 7.80 (m, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.03 (m, 1H), 6.74 – 6.55 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 143.15 – 142.71 (m), 141.59 (s), 139.79 (s), 138.63 (d, *J* = 17.0 Hz), 125.42 (s), 124.01 (s), 123.57 – 122.67 (m), 121.05 (s), 120.41 (s), 119.47 (s), 118.28 – 117.22 (m), 112.93 – 112.35 (m), 112.07 (s). m/z 944.43.



^{13}C NMR (101 MHz, DMSO) δ 143.36 – 142.98 (m), 141.66 (s), 139.75 (s), 138.65 (d, J = 25.4 Hz), 124.04 (s), 123.06 (d, J = 24.6 Hz), 120.40 (s), 119.57 (s), 112.28 (s).



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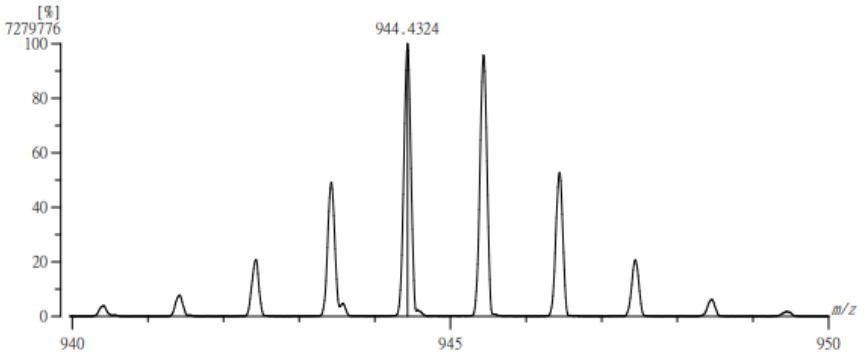
Unsaturation (U.S.) : -0.5 - 60.0



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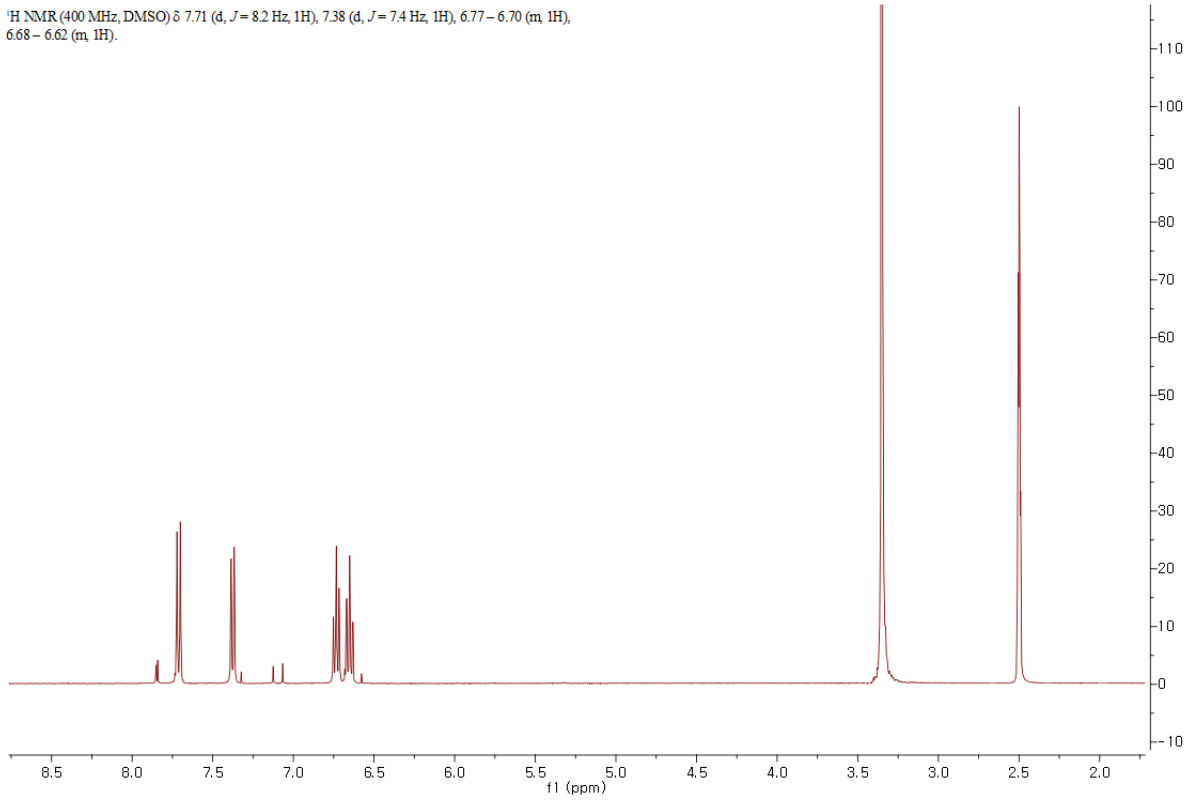
3			-6.2 / -5.9	52.5	C68 1H18 2H20 N5
4			-4.6 / -4.3	53.0	C68 1H16 2H21 N5
5			-2.9 / -2.8	53.5	C68 1H14 2H22 N5
6			-1.3 / -1.2	54.0	C68 1H12 2H23 N5
7			+0.4 / +0.3	54.5	C68 1H10 2H24 N5
8			+2.0 / +1.9	55.0	C68 1H8 2H25 N5
9			-9.3 / -8.8	48.0	C67 1H36 2H10 N6
10			-7.6 / -7.2	48.5	C67 1H34 2H11 N6
11			-6.0 / -5.7	49.0	C67 1H32 2H12 N6
12			-4.4 / -4.1	49.5	C67 1H30 2H13 N6
13			-2.7 / -2.6	50.0	C67 1H28 2H14 N6
14			-1.1 / -1.0	50.5	C67 1H26 2H15 N6
15			+0.6 / +0.5	51.0	C67 1H24 2H16 N6
16			+2.2 / +2.1	51.5	C67 1H22 2H17 N6
17			+3.8 / +3.6	52.0	C67 1H20 2H18 N6
18			+5.5 / +5.2	52.5	C67 1H18 2H19 N6
19			+7.1 / +6.7	53.0	C67 1H16 2H20 N6
20			+8.8 / +8.3	53.5	C67 1H14 2H21 N6
21			-7.4 / -7.0	45.0	C66 1H48 2H3 N7
22			-5.8 / -5.5	45.5	C66 1H46 2H4 N7
23			-4.2 / -3.9	46.0	C66 1H44 2H5 N7
24			-2.5 / -2.4	46.5	C66 1H42 2H6 N7
25			-0.9 / -0.8	47.0	C66 1H40 2H7 N7
26			+0.8 / +0.7	47.5	C66 1H38 2H8 N7
27			+2.4 / +2.3	48.0	C66 1H36 2H9 N7
28			+4.0 / +3.8	48.5	C66 1H34 2H10 N7
29			+5.7 / +5.4	49.0	C66 1H32 2H11 N7
30			+7.3 / +6.9	49.5	C66 1H30 2H12 N7
31			+9.0 / +8.5	50.0	C66 1H28 2H13 N7
32			+4.2 / +4.0	45.0	C65 1H48 2H2 N8
33			+5.9 / +5.6	45.5	C65 1H46 2H3 N8
34			+7.5 / +7.1	46.0	C65 1H44 2H4 N8
35			+9.2 / +8.6	46.5	C65 1H42 2H5 N8

3,5-di(9H-carbazol-9-yl)-2,4,6-tris(9H-carbazol-9-yl-d_8)benzonitrile (5CzBN-D(*o,p*))

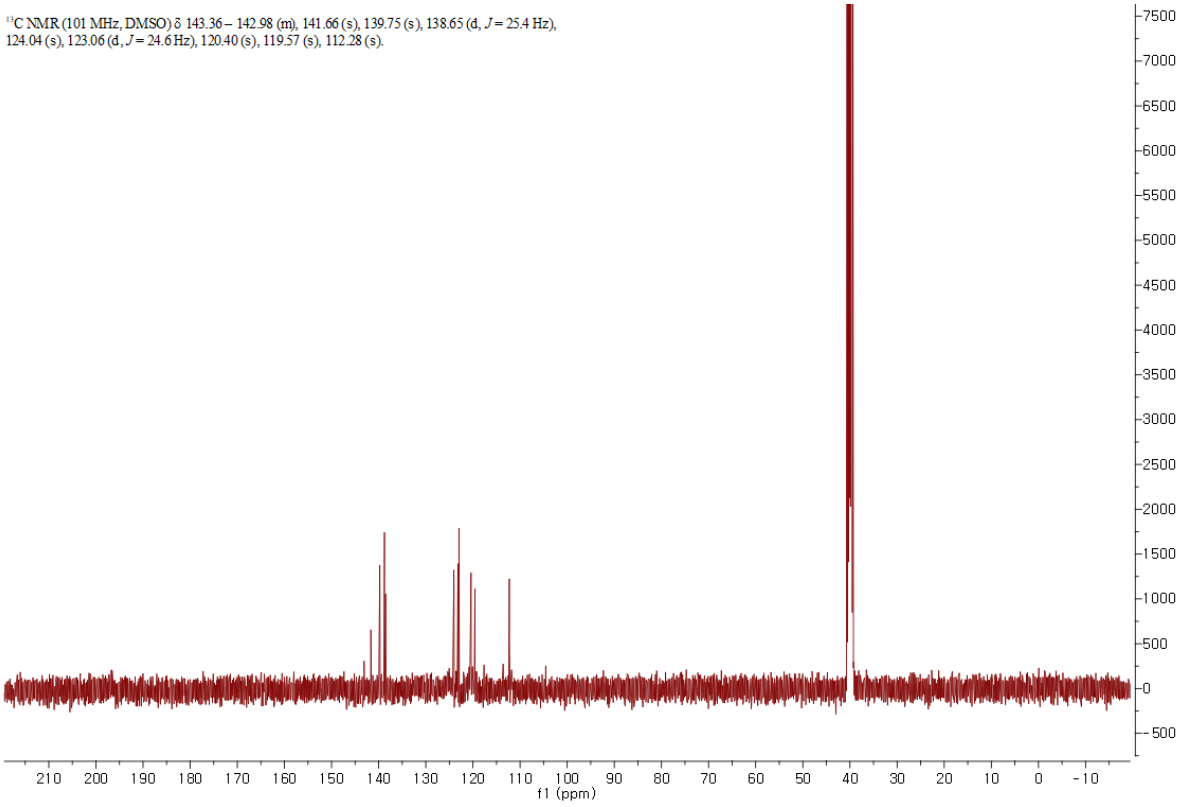
Deuterated carbazole (1.41 g, 8.03 mmol), NaH (0.36 g, 9.06 mmol), and THF (40 mL) were placed in a 100 mL round-bottom flask, and deuterated carbazole was activated for 1 h at room temperature under nitrogen atmosphere. Then, pentafluorobenzonitrile (0.50 g, 2.59 mmol) was added to the round-bottom flask, and the mixture was stirred for 12 h at room temperature under nitrogen atmosphere. After completion of the reaction, extraction was repeated three times using methylene chloride and distilled water. The organic layers were combined and dried over anhydrous $MgSO_4$. After filtration, the crude mixture was evaporated using a rotary evaporator. The mixture was recrystallized from toluene and methanol to remove impurities, and the product (2,4,6-tri(9H-carbazol-9-yl)-3,5-difluorobenzonitrile-d) (3CzFCN-d) was obtained. After that, 9H-carbazole (0.76 g, 4.55 mmol), NaH (0.21 g, 5.31 mmol), THF (40 mL) were added to a 100 mL round-bottom flask, and 9H-carbazole was activated for 1 h under nitrogen atmosphere at room temperature. Then, 3CzFCN-d (1.00 g, 1.52 mmol) was added to the round-bottom flask, and the mixture was stirred for 24 h under nitrogen atmosphere at

room temperature. After completion of the reaction, extraction was repeated three times using methylene chloride and distilled water. The organic layers were combined and dried over anhydrous $MgSO_4$. After filtration, the crude mixture was evaporated using a rotary evaporator. The mixture was recrystallized with toluene and methanol to remove impurities, and the product (5CzBN-D(o,p)) was obtained as a yellow powder.

Yield 1.00 g (69.3%), ^{1}HNMR (400 MHz, DMSO) δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 6.77 – 6.70 (m, 1H), 6.68 – 6.62 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 143.36 – 142.98 (m), 141.66 (s), 139.75 (s), 138.65 (d, *J* = 25.4 Hz), 124.04 (s), 123.06 (d, *J* = 24.6 Hz), 120.40 (s), 119.57 (s), 112.28 (s). m/z 952.48.



^{13}C NMR (101 MHz, DMSO) δ 143.36 – 142.98 (m), 141.66 (s), 139.75 (s), 138.65 (d, J = 25.4 Hz), 124.04 (s), 123.06 (d, J = 24.6 Hz), 120.40 (s), 119.57 (s), 112.28 (s).



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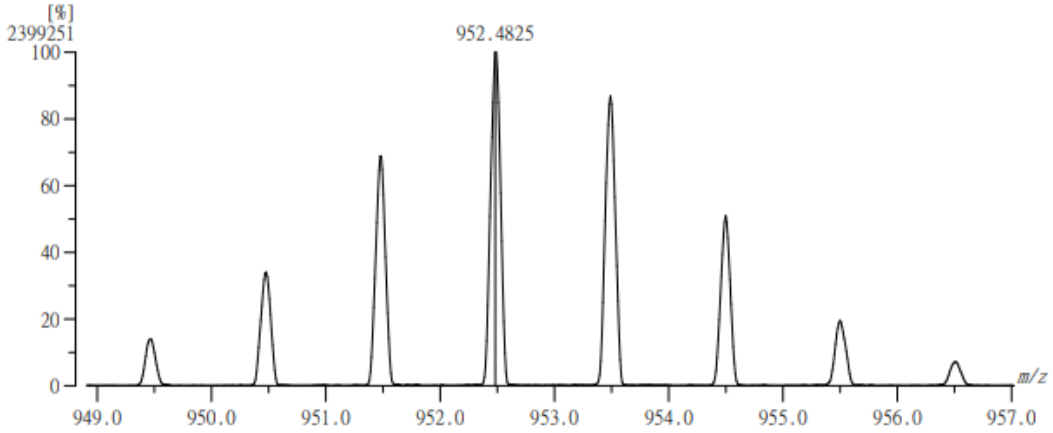

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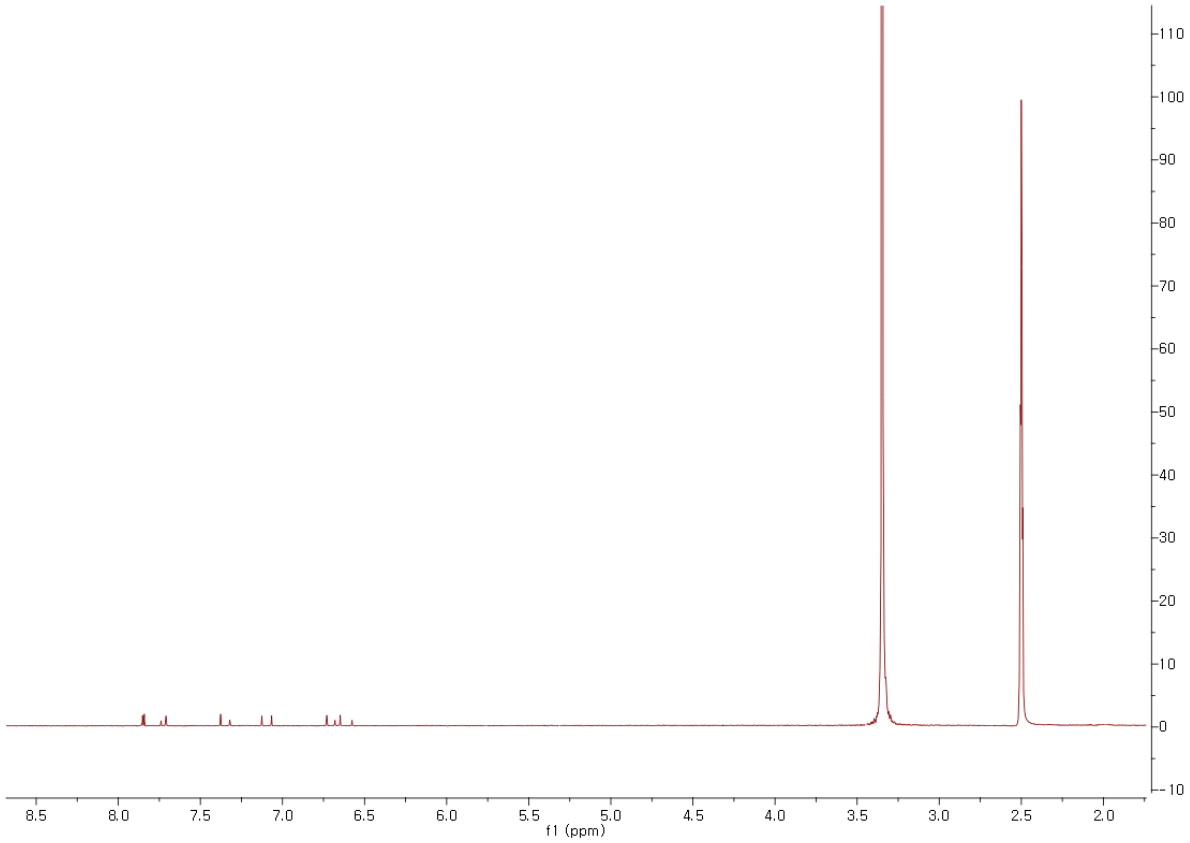
3			-7.9 / -7.5	52.0	C68 1H12 2H27 N5
4			-6.3 / -6.0	52.5	C68 1H10 2H28 N5
5			-4.6 / -4.4	53.0	C68 1H8 2H29 N5
6			-3.0 / -2.9	53.5	C68 1H6 2H30 N5
7			-1.4 / -1.3	54.0	C68 1H4 2H31 N5
8			+0.2 / +0.2	54.5	C68 1H2 2H32 N5
9			+1.9 / +1.8	55.0	C68 2H33 N5
10			-9.3 / -8.9	48.0	C67 1H28 2H18 N6
11			-7.7 / -7.3	48.5	C67 1H26 2H19 N6
12			-6.1 / -5.8	49.0	C67 1H24 2H20 N6
13			-4.4 / -4.2	49.5	C67 1H22 2H21 N6
14			-2.8 / -2.7	50.0	C67 1H20 2H22 N6
15			-1.2 / -1.1	50.5	C67 1H18 2H23 N6
16			+0.4 / +0.4	51.0	C67 1H16 2H24 N6
17			+2.1 / +2.0	51.5	C67 1H14 2H25 N6
18			+3.7 / +3.5	52.0	C67 1H12 2H26 N6
19			+5.3 / +5.1	52.5	C67 1H10 2H27 N6
20			+6.9 / +6.6	53.0	C67 1H8 2H28 N6
21			+8.6 / +8.2	53.5	C67 1H6 2H29 N6
22			-9.1 / -8.7	44.5	C66 1H42 2H10 N7
23			-7.5 / -7.1	45.0	C66 1H40 2H11 N7
24			-5.9 / -5.6	45.5	C66 1H38 2H12 N7
25			-4.2 / -4.0	46.0	C66 1H36 2H13 N7
26			-2.6 / -2.5	46.5	C66 1H34 2H14 N7
27			-1.0 / -0.9	47.0	C66 1H32 2H15 N7
28			+0.6 / +0.6	47.5	C66 1H30 2H16 N7
29			+2.3 / +2.2	48.0	C66 1H28 2H17 N7
30			+3.9 / +3.7	48.5	C66 1H26 2H18 N7
31			+5.5 / +5.2	49.0	C66 1H24 2H19 N7
32			+7.1 / +6.8	49.5	C66 1H22 2H20 N7
33			+8.8 / +8.3	50.0	C66 1H20 2H21 N7
34			-2.4 / -2.3	43.0	C65 1H48 2H6 N8
35			-0.8 / -0.8	43.5	C65 1H46 2H7 N8
36			+0.8 / +0.8	44.0	C65 1H44 2H8 N8
37			+2.5 / +2.3	44.5	C65 1H42 2H9 N8
38			+4.1 / +3.9	45.0	C65 1H40 2H10 N8
39			+5.7 / +5.4	45.5	C65 1H38 2H11 N8
40			+7.3 / +7.0	46.0	C65 1H36 2H12 N8
41			+9.0 / +8.5	46.5	C65 1H34 2H13 N8

2,3,4,5,6-pentakis(9H-carbazol-9-yl-d_8)benzonitrile (5CzBN-D(a))

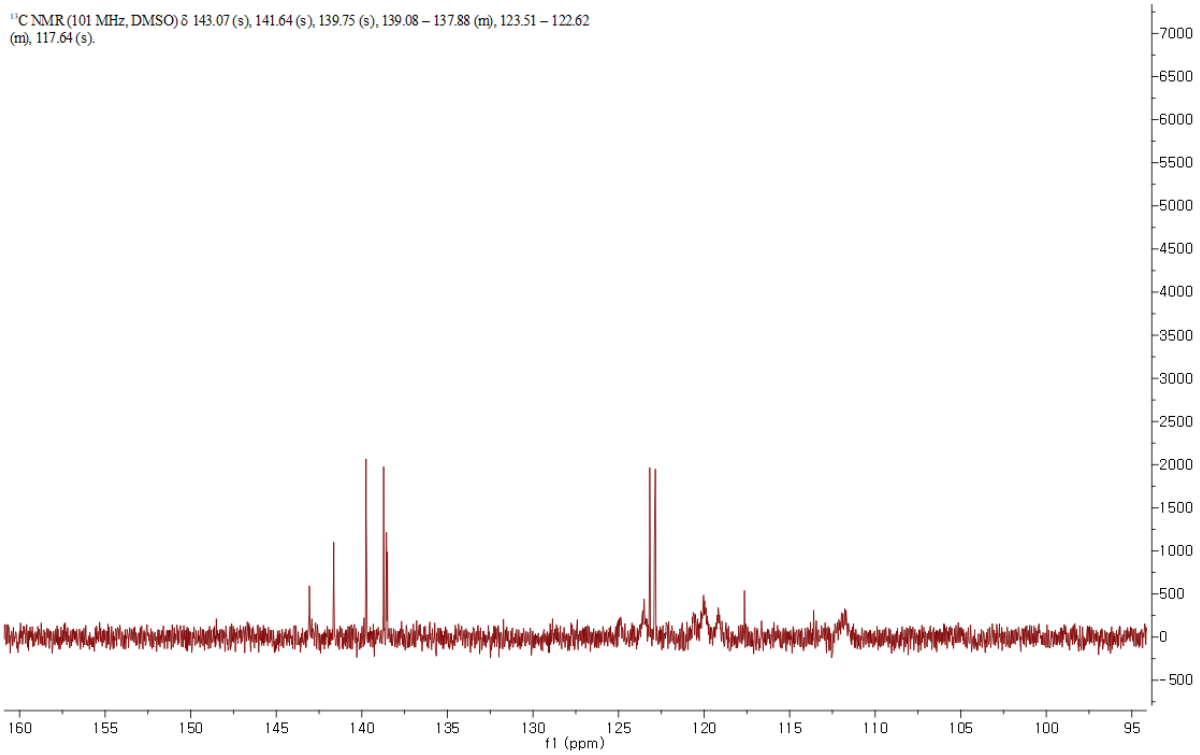
Deuterated carbazole (2.31 g, 13.21 mmol), NaH (0.62 g, 15.54 mmol), and THF (20 mL) were added to a 100 mL round-bottom flask, and deuterated carbazole was activated for 1 h at room temperature under nitrogen atmosphere. After that, pentafluorobenzonitrile (0.50 g, 2.59 mmol) was added to the round-bottom flask, and the mixture was stirred for 12 h at room temperature under nitrogen atmosphere. After completion of the

reaction, extraction was repeated three times using methylene chloride and distilled water. The organic layers were combined and dried over anhydrous $MgSO_4$. After filtration, the crude mixture was evaporated using a rotary evaporator. The mixture was recrystallized with toluene and methanol to remove impurities, and the product was obtained as a yellow powder.

Yield 1.54 g (61.5%), ^{1}HNMR (400 MHz, DMSO) δ. ^{13}C NMR (101 MHz, DMSO) δ 143.07 (s), 141.64 (s), 139.75 (s), 139.08 – 137.88 (m), 123.51 – 122.62 (m), 117.64 (s). m/z 968.58.



^{13}C NMR (101 MHz, DMSO) δ 143.07 (s), 141.64 (s), 139.75 (s), 139.08 – 137.88 (m), 123.51 – 122.62 (m), 117.64 (s).



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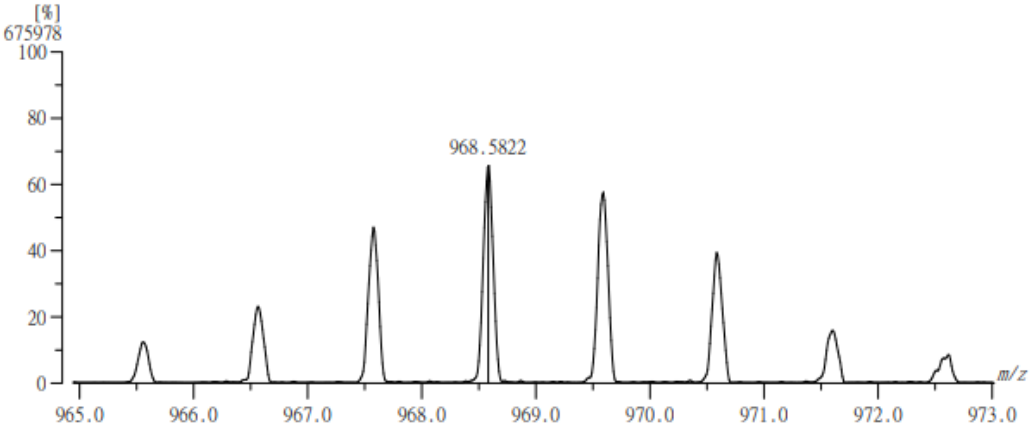

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4			-5.1 / -5.0	49.5	C67 1H6 2H37 N6
5			-3.5 / -3.4	50.0	C67 1H4 2H38 N6
6			-1.9 / -1.9	50.5	C67 1H2 2H39 N6
7			-0.3 / -0.3	51.0	C67 2H40 N6
8			-9.7 / -9.4	44.5	C66 1H26 2H26 N7
9			-8.1 / -7.9	45.0	C66 1H24 2H27 N7
10			-6.5 / -6.3	45.5	C66 1H22 2H28 N7
11			-4.9 / -4.8	46.0	C66 1H20 2H29 N7
12			-3.3 / -3.2	46.5	C66 1H18 2H30 N7
13			-1.7 / -1.7	47.0	C66 1H16 2H31 N7
14			-0.1 / -0.1	47.5	C66 1H14 2H32 N7
15			+1.5 / +1.4	48.0	C66 1H12 2H33 N7
16			+3.1 / +3.0	48.5	C66 1H10 2H34 N7
17			+4.7 / +4.5	49.0	C66 1H8 2H35 N7
18			+6.3 / +6.1	49.5	C66 1H6 2H36 N7
19			+7.9 / +7.6	50.0	C66 1H4 2H37 N7
20			+9.5 / +9.2	50.5	C66 1H2 2H38 N7
21			-9.5 / -9.2	41.0	C65 1H40 2H18 N8
22			-7.9 / -7.7	41.5	C65 1H38 2H19 N8
23			-6.3 / -6.1	42.0	C65 1H36 2H20 N8
24			-4.7 / -4.6	42.5	C65 1H34 2H21 N8
25			-3.1 / -3.0	43.0	C65 1H32 2H22 N8
26			-1.5 / -1.5	43.5	C65 1H30 2H23 N8
27			+0.1 / +0.1	44.0	C65 1H28 2H24 N8
28			+1.7 / +1.6	44.5	C65 1H26 2H25 N8
29			+3.3 / +3.2	45.0	C65 1H24 2H26 N8
30			+4.9 / +4.7	45.5	C65 1H22 2H27 N8
31			+6.5 / +6.3	46.0	C65 1H20 2H28 N8
32			+8.1 / +7.8	46.5	C65 1H18 2H29 N8
33			+9.7 / +9.4	47.0	C65 1H16 2H30 N8