Supporting Information for

Push-Pull Derivatives Based on CF_3-Substituted Pyrimidines as Solvatofluorochromic Materials for OLEDs

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General Information.

All reagents were purchased from commercial sources and were used without further purification. 1,4-Dioxane for the microwave-assisted Suzuki cross-coupling reaction were deoxygenated by bubbling argon for 1 h. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400, AVANCE-500 and AVANCE-600 instruments using Me_4Si as an internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. High resolution mass spectrometry was performed using a Bruker maXis Impact HD spectrometer. Melting points were determined on Boetius combined heating stages and were not corrected. Flash-column chromatography was carried out using Alfa Aesar silica gel 0.040-0.063 mm (230-400 mesh), eluting with chloroform. The progress of reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia), in which the spots were visualized with UV light (λ 254 or 365 nm).

Synthesis of push-pull systems

1-(4-(Dimethylamino)phenyl)-4,4,4-trifluoro-3-hydroxy-2-buten-1-one (**3)**. In a 250 mL round bottom flask finely powdered lithium hydride (0.6 g, 75 mmol) was suspended in 100 mL of methyl *tert*-butyl ether (MTBE) and ethyl trifluoroacetate (11.00 g, 77.5 mmol) was added. 4-Acetyl-N,N-dimethylaniline **1** (8.16 g, 50 mmol) was then added in one portion with vigorous stirring and the reaction mixture was stirred at refluxing until TLC (silica, $CHCl_3$) showed complete consumption of the starting material (approx. 6-7 hours). All volatiles were removed on rotary evaporator, a residue was dissolved in glacial acetic acid (ca. 20 ml) and 85% phosphoric acid (8.50 g, 73.7 mmol) was added. The obtained solution was diluted with water (ca. 200 mL) and a precipitate was filtered off, washed with water (3×50 ml) and dried on air to yield 11.80 g (91 %) of **2** as yellow powder. m.p. 69-71 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.82 (br. s, 1H, enol-OH), 7.86 (d, *J* = 9.2 Hz, 2H), 6.68 (d, *J* = 9.2 Hz, 2H), 6.44 (s, 1H), 3.11 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 85.61 (CF_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.0 ($(CH_3)_2N$), 90.5 (q, *J* = 2.2 Hz, =CH-), 111.1, 117.7 (q, *J* = 282.6, CF_3), 119.4, 130.1, 154.3, 174.5 (q, *J* = 35.4 Hz, $CF_3\underline{C}$=O), 186.1 (C=O). Calcd. for $C_{12}H_{12}F_3NO_2$ (259.23): C, 55.60; H, 4.67; N, 5.40; F, 21.99. Found: C, 55.43; H, 4.74; N, 5.22; F, 22.09.

4-(2-(4-Bromophenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (5a). A suspension of 4-bromobenzamidine hydrochloride **4a** (0.78 g, 3.3 mmol) and Et_3N (0.91 g, 9.0 mmol) in acetonitrile (20 ml) was refluxed for 5 min. Then diketone **3** (0.77 g, 3.0 mmol) and triethylborate (2.19 g, 15 mmol) were added and the reaction mixture was stirred at refluxing until complete consumption of the starting material (ca. 5 hours). Then all volatiles were removed, a residue was washed several times with water (4×20 mL), dried on air and dissolved in CH_2Cl_2 (ca. 5 mL). The obtained solution was passed through a silica-pad (ca. 2 cm) and the silica was washed with CH_2Cl_2 (4×5 mL). Combined solutions were dissolved in methanol (ca. 50 mL), CH_2Cl_2 was distilled off on rotary evaporator at standard pressure and the obtained suspension was cooled at 0-4 °C for 1 h. A precipitate was filtered off, washed with cold methanol (3×10 mL) and dried on air to yield 1.09 g (87 %) **5a** as yellow crystalline powder. m.p. 183-184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10 (s, 6H, $2CH_3$), 6.78-6.81 (m, 2H, H-3,5 Ar), 7.63-7.65 (m, 2H, H-2,6 Ar), 7.76 (s, 1H, H-5 Pyr), 8.16-8.19 (m, 2H, Ar), 8.47-8.49 (m, 2H, Ar). ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.57 (s, CF_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.1 ($(CH_3)_2N$), 108.2 (q, *J* = 2.6 Hz, C-5 Pyr), 111.7, 121.1 (q, *J* = 275.1, CF_3), 122.6, 125.9, 128.8, 130.2, 131.7, 136.1, 152.9, 155.8 (q, *J* = 35.1 Hz, C-6 Pyr), 164.0, 166.1. Calcd. for $C_{19}H_{15}BrF_3N_3$ (422.25): C 54.05, H 3.58, N 9.95, F 13.50. Found: C 54.16, H 3.69, N 9.97, F 13.36.

4-(2-(3-Bromophenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (5b). A suspension of 3-bromobenzamidine hydrochloride **4b** (0.78 g, 3.3 mmol) and Et_3N (0.91 g, 9.0 mmol) in acetonitrile (20 mL) was refluxed for 5 min. Then diketone **3** (0.77 g, 3.0 mmol) and triethylborate (2.19 g, 15 mmol) were added and the reaction mixture was stirred at refluxing until complete consumption of the starting material (ca. 5 hours). Then all volatiles were removed, a residue was washed several times with water (4×20 mL), dried on air and dissolved in CH_2Cl_2 (ca. 5 mL). The obtained solution was passed through a silica-pad (ca. 2 cm) and the silica was washed with CH_2Cl_2 (4×5 mL). Combined solutions were dissolved in methanol (ca. 50 mL), CH_2Cl_2 was distilled off on rotary evaporator at standard pressure and the obtained suspension was cooled at 0-4 °C for 1 h. A precipitate was filtered off, washed with cold methanol (3×10 mL) and dried on air to yield 1.14 g (91 %) **5b** as yellow crystalline powder. m.p. 153-154 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10 (s, 6H, $2CH_3$), 6.79-6.83 (m, 2H, H-3,5 Ar), 7.39 (t, 1H, *J* = 7.9 Hz, Ar(Br)), 7.64 (ddd, 1H, *J* = 7.9, 2.0, 1.0 Hz, Ar(Br)), 7.77 (s, 1H, H-5 Pyr), 8.17-8.21 (m, 2H, Ar), 8.53-8.55 (m, 1H, Ar(Br)) 8.74 (m, 1H, Ar(Br)). ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.60 (s, CF_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.0 ($(CH_3)_2N$), 108.5 (q, *J* = 2.8 Hz, C-5 Pyr), 111.7, 121.0 (q, *J* = 275.2, CF_3), 122.5, 122.8, 127.2, 128.8, 130.0, 131.5, 133.9, 139.2, 153.0, 155.8 (q, *J* = 35.2 Hz, C-6 Pyr), 163.5, 166.1. Calcd. for $C_{19}H_{15}BrF_3N_3$ (422.25): C 54.05, H 3.58, N 9.95, F 13.50. Found: C 54.09, H 3.51, N 10.06, F 13.54.

4-(2-(3,5-Dibromophenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (5c). A suspension of 3,5-dibromobenzamidine hydrochloride **4c** (1.04 g, 3.3 mmol) and Et_3N (0.91 g, 9.0 mmol) in acetonitrile (20 mL) was

refluxed for 5 min. Then diketone **3** (0.77 g, 3.0 mmol) and triethylborate (2.19 g, 15 mmol) were added and the reaction mixture was stirred at refluxing until complete consumption of the starting material (ca. 5 hours). Then all volatiles were removed, a residue was washed several times with water (4×20 ml), dried on air and dissolved in CH_2Cl_2 (ca. 5 mL). The obtained solution was passed through a silica-pad (ca. 2 cm) and the silica was washed with CH_2Cl_2 (4×5 mL). Combined solutions were dissolved in methanol (ca. 50 mL), CH_2Cl_2 was distilled off on rotary evaporator at standard pressure and the obtained suspension was cooled at 0-4 °C for 1 h. A precipitate was filtered off, washed with cold methanol (3×10 mL) and dried on air to yield 1.39 g (93 %) of **5c** as bright yellow crystalline powder. m.p. 217-218 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.11 (s, 6H, $2CH_3$), 6.81-6.82 (m, 2H, H-3,5Ar), 7.78 (s, 1H, H-5 Pyr), 7.80 (t, 1H, *J* = 1.6 Hz, H-4 Ar(Br)), 8.16-8.18 (m, 2H, H-2,6 Ar), 8.67 (d, 2H, *J* = 1.6 Hz, H-2,6 Ar(Br)). ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.63 (s, CF_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.1 ($(CH_3)_2N$), 108.9 (q, *J* = 2.8 Hz, C-5 Pyr), 111.7, 120.9 (q, *J* = 275.2, CF_3), 122.1, 123.2, 128.9, 130.3, 136.2, 140.5, 153.1, 155.8 (q, *J* = 35.3 Hz, C-6 Pyr), 162.2, 166.3. Calcd. for $C_{19}H_{14}Br_2F_3N_3$ (501.15): C 45.54, H 2.82, N 8.38, F 11.37. Found: C 45.42, H 2.98, N 8.25, F 11.50.

General procedure for the Suzuki cross-coupling reactions for the synthesis of compounds (7a-c and 8a-c): (Het)arylboronic acid pinacol ester (0.6 mmol, 1.2 equiv.) and corresponding 4-(2-(4-bromophenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (**5a**) [or 4-(2-(3-bromophenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (**5b**)] (0.5 mmol, 1.0 equiv.) were dissolved in freshly distilled 1,4-dioxane (10 mL), and argon was bubbled through the solution for 10 min. Then $Pd(PPh_3)_4$ (29 mg, 5 mol %) and K_3PO_4 (318 mg, 1.5 mmol, 2.5 equiv.) were added, and the reaction was refluxed under an argon atmosphere at 120 °C for 10-20 h (monitored by TLC). The reaction mixture was cooled to room temperature, the obtained suspension was filtered through a small plug of SiO_2 (3-4 cm), which was successively washed twice with 1,4-dioxane (2×5 mL), and the obtained filtrate was evaporated under reduced pressure to dryness. The resulting residue was purified by column chromatography (SiO_2; EtOAc/hexane 1:8) and further crystallized from a minimal amount of EtOAc.

4'-(4-(4-(Dimethylamino)phenyl)-6-(trifluoromethyl)pyrimidin-2-yl)-*N,N*-diphenyl-[1,1'-biphenyl]-4-amine (7a). Light yellow solid, 85%, m.p. 236-237 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68–8.62 (m, 2H), 8.25–8.18 (m, 2H), 7.77–7.70 (m, 3H), 7.61–7.55 (m, 2H), 7.32–7.23 (m, 4H), 7.19–7.13 (m, 6H), 7.09–7.01 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.10 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 164.8, 155.9 (q, *J* = 35.0 Hz), 152.9, 147.7, 147.6, 143.2, 135.6, 134.2, 129.3, 129.1, 128.8, 127.8, 126.6, 124.6, 123.7, 123.12, 123.10, 121.2 (q, *J* = 275.1 Hz), 111.8, 107.9 (d, *J* = 2.9 Hz), 40.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.58. Calcd. for $C_{37}H_{29}F_3N_4$ (586.66): C, 75.75; H, 4.98; N, 9.55. Found: C, 75.72; H, 4.95; N, 9.59.

4-(2-(4'-(9*H*-Carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (7b). Light yellow solid, 88%, m.p. 188-189 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77–8.72 (m, 2H), 8.28–8.22 (m, 2H), 8.20–8.14 (m, 2H), 7.95–7.90 (m, 2H), 7.88–7.83 (m, 2H), 7.79 (s, 1H), 7.72–7.67 (m, 2H), 7.54–7.48 (m, 2H), 7.48–7.38 (m, 2H), 7.35–7.28 (m, 2H), 7.26 (s, 2H), 6.89–6.84 (m, 2H), 3.12 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 164.6, 155.9 (q, *J* = 35.1 Hz), 152.9, 142.7, 140.9, 139.6, 137.3, 136.5, 129.3, 128.9, 128.6, 127.4, 127.2, 126.0, 123.5, 123.0, 121.2 (q, *J* = 275.1 Hz), 120.3, 120.0, 111.8, 109.9, 108.1 (d, *J* = 3.1 Hz), 40.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.61. Calcd. for $C_{37}H_{27}F_3N_4$ (584.65): C, 76.01; H, 4.66; N, 9.58. Found: C, 76.05; H, 4.69; N, 9.55.

4-(2-(4-(9-Ethyl-9*H*-carbazol-3-yl)phenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (7c). Light yellow solid, 89%, m.p. 192-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74–8.67 (m, 2H), 8.45–8.39 (m, 1H), 8.28–8.21 (m, 2H), 8.21–8.16 (m, 1H), 7.91–7.84 (m, 2H), 7.86–7.76 (m, 1H), 7.76 (s, 1H), 7.61–7.41 (m, 3H), 7.34–7.23 (m, 1H), 6.87–6.80 (m, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 3.11 (s, 6H), 1.48 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.0, 155.9 (q, *J* = 35.1 Hz), 152.9, 144.8, 140.5, 139.8, 135.2, 131.6, 129.1, 128.8, 127.2, 125.9, 125.2, 123.6, 123.2, 123.1, 121.2 (q, *J* = 275.1 Hz), 120.6, 119.1, 111.8, 108.8, 108.6, 107.9 (q, *J* = 2.8 Hz), 40.1, 37.7, 13.8. (One ^{13}C signal is missed due to overlapping). ^{19}F NMR (376 MHz, $CDCl_3$) δ 91.61. Calcd. for $C_{33}H_{27}F_3N_4$ (536.60): C, 73.87; H, 5.07; N, 10.44. Found: C, 73.84; H, 5.09; N, 10.40.

3'-(4-(4-(Dimethylamino)phenyl)-6-(trifluoromethyl)pyrimidin-2-yl)-*N,N*-diphenyl-[1,1'-biphenyl]-4-amine (8a). White solid, 69%, m.p. 173-174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84–8.79 (m, 1H), 8.58–8.52 (m, 1H), 8.25–8.19 (m, 2H), 7.77 (s, 1H), 7.74–7.69 (m, 1H), 7.64–7.53 (m, 3H), 7.33–7.25 (m, 4H), 7.23–7.13 (m, 6H), 7.08–7.01 (m, 2H), 6.88–6.83 (m, 2H), 3.10 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 164.9, 155.9 (q, *J* = 35.1 Hz), 152.9, 147.7, 147.4, 140.9, 137.7, 135.0, 129.4, 129.3, 128.9, 128.8, 128.0, 127.1, 126.8, 124.5, 124.0, 123.0, 122.9, 121.15 (q, *J* = 275.1 Hz), 111.8, 108.2 (d, *J* = 3.0 Hz), 40.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.65. Calcd. for $C_{37}H_{29}F_3N_4$ (586.66): C, 75.75; H, 4.98; N, 9.55. Found: C, 75.77; H, 4.94; N, 9.59.

4-(2-(4'-(9*H*-Carbazol-9-yl)-[1,1'-biphenyl]-3-yl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (8b). Light yellow solid, 64%, m.p. 254-255 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96–8.91 (m, 1H), 8.69–8.63 (m, 1H), 8.27–8.22 (m, 2H), 8.20–8.14 (m, 2H), 7.99–7.92 (m, 2H), 7.87–7.83 (m, 1H), 7.81 (s, 1H), 7.74–7.69 (m, 2H), 7.68–7.62 (m, 1H), 7.55–7.49 (m, 2H), 7.49–7.41 (m, 2H), 7.35–7.28 (m, 2H), 6.88–6.83 (m, 2H), 3.11 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 164.8, 155.9 (q, *J* = 34.9 Hz), 152.9, 140.9, 140.6, 140.1, 137.9, 137.0, 129.8, 129.1, 128.8, 128.7, 127.9, 127.4, 127.3, 125.9, 123.4, 122.9, 121.1 (q, *J* = 275.1 Hz), 120.3, 119.9, 111.8, 109.9, 108.3 (q, *J* = 2.9 Hz),

40.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.81. Calcd. for $C_{37}H_{27}F_3N_4$ (584.65): C, 76.01; H, 4.66; N, 9.58. Found: C, 76.05; H, 4.64; N, 9.56.

4-(2-(3-(9-Ethyl-9*H*-carbazol-3-yl)phenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (8c). Light yellow solid, 66%, m.p. 199-200 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (m, 1H), 8.61–8.55 (m, 1H), 8.45–8.40 (m, 1H), 8.26–8.21 (m, 2H), 8.21–8.19 (m, 1H), 7.89–7.82 (m, 2H), 7.79 (s, 1H), 7.66–7.59 (m, 1H), 7.56–7.51 (m, 1H), 7.50–7.48 (m, 1H), 7.48–7.42 (m, 1H), 7.30–7.23 (m, 1H), 6.85–6.79 (m, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 3.10 (s, 6H), 1.49 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 165.2, 156.1 (q, *J* = 36.3 Hz), 142.6, 140.4, 139.5, 137.4, 132.1, 130.3, 129.0, 127.46, 126.8, 125.8, 125.4, 123.5, 123.1, 121.1 (q, *J* = 275.3 Hz), 120.6, 119.2, 118.9, 113.5 (br.), 108.7, 108.6, 108.5 (br.), 41.2, 37.7, 13.8. (Three ^{13}C signals are missed due to overlapping). ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.69. Calcd. for $C_{33}H_{27}F_3N_4$ (536.60): C, 73.87; H, 5.07; N, 10.44. Found: C, 73.88; H, 5.05; N, 10.48.

General procedure for the Suzuki cross-coupling reactions for the synthesis of compounds (9a-c): (Het)arylboronic acid pinacol ester (1.2 mmol, 2.4 equiv.) and 4-(2-(3,5-dibromophenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (**5c**) (251 mg, 0.5 mmol, 1.0 equiv.) (1.0 eq.) were dissolved in freshly distilled 1,4-dioxane (10 mL), and argon was bubbled through the solution for 10 min. Then $Pd(PPh_3)_4$ (58 mg, 10 mol %) and K_3PO_4 (636 mg, 3.0 mmol, 5.0 equiv.) were added, and the reaction was refluxed under an argon atmosphere at 120 °C for 10-20 h (monitored by TLC). The reaction mixture was cooled to room temperature, the obtained suspension was filtered through a small plug of SiO_2 (3-4 cm), which was successively washed twice with 1,4-dioxane (2 × 7 ml) and $CHCl_3$ (2 × 7 ml), and the obtained filtrate was evaporated under reduced pressure to dryness. The resulting residue was crystallized twice from THF.

5'-(4-(4-(Dimethylamino)phenyl)-6-(trifluoromethyl)pyrimidin-2-yl)-*N4,N4,N4'',N4''*-tetraphenyl-[1,1':3',1''-terphenyl]-4,4''-diamine (9a). Light yellow solid, 69%, m.p. 279-280 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78–8.73 (m, 2H), 8.26–8.20 (m, 2H), 7.94–7.89 (m, 1H), 7.79 (s, 1H), 7.69–7.62 (m, 4H), 7.33–7.25 (m, 8H), 7.24–7.14 (m, 12H), 7.09–7.01 (m, 4H), 6.88–6.82 (m, 2H), 3.10 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 164.9, 155.9 (q, *J* = 35.1 Hz), 152.9, 147.7, 147.4, 141.5, 138.2, 135.0, 129.3, 128.9, 128.1, 127.9, 125.5, 124.5, 124.0, 123.0, 122.9, 121.2 (q, *J* = 275.4 Hz), 111.8, 108.3, 40.12. ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.71. Calcd. for $C_{55}H_{42}F_3N_5$ (829.97): C, 79.59; H, 5.10; N, 8.44. Found: C, 79.56; H, 5.13; N, 8.42.

4-(2-(4,4''-Di(9*H*-carbazol-9-yl)-[1,1':3',1''-terphenyl]-5'-yl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (9b). Light yellow solid, 78%, m.p. 312-313 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00–8.96 (m, 2H), 8.32–8.26 (m, 2H), 8.21–8.17 (m, 4H), 8.17–8.15 (m, 1H), 8.08–8.03 (m, 4H), 7.86 (s, 1H), 7.78–7.73 (m, 4H), 7.58–7.52 (m, 4H), 7.50–7.43 (m, 4H), 7.36–7.29 (m, 4H), 6.93–6.88 (m, 2H), 3.12 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 164.6, 156.0 (q, *J* = 35.1 Hz), 153.0, 141.4, 140.9, 140.0, 138.7, 137.3, 129.0, 128.9, 128.7, 127.5, 126.6, 126.0, 123.5, 122.8, 121.2 (q, *J* = 275.2 Hz), 120.4, 120.1, 111.8, 109.9, 108.6 (d, *J* = 3.2 Hz), 40.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ 91.96. Calcd. for $C_{55}H_{38}F_3N_5$ (825.94): C, 79.98; H, 4.64; N, 8.48. Found: C, 79.97; H, 4.62; N, 8.51.

4-(2-(3,5-*Bis*(9-ethyl-9*H*-carbazol-3-yl)phenyl)-6-(trifluoromethyl)pyrimidin-4-yl)-*N,N*-dimethylaniline (9c). Light yellow solid, 71%, m.p. 297-298 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (d, *J* = 1.8 Hz, 2H), 8.56 (d, *J* = 1.8 Hz, 2H), 8.27 (t, *J* = 8.4 Hz, 4H), 8.22 (t, *J* = 1.8 Hz, 1H), 7.98 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.84 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.57–7.51 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.28 (m, 2H), 6.86 – 6.81 (m, 2H), 4.47 (q, *J* = 7.3 Hz, 4H), 3.11 (s, 6H), 1.53 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 165.3, 155.9 (q, *J* = 34.9 Hz), 152.9, 143.1, 140.5, 139.6, 138.2, 132.4, 129.4, 128.9, 125.84, 125.80, 125.6, 123.5, 123.2, 123.0, 121.3 (q, *J* = 275.2 Hz), 120.7, 119.4, 119.0, 111.8, 108.7, 108.6, 108.2, 40.1, 37.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ 91.80. Calcd. for $C_{47}H_{38}F_3N_5$ (729.85): C, 77.35; H, 5.25; N, 9.60. Found: C, 77.38; H, 5.23; N, 9.64.

NMR Spectra of push-pull systems

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400, AVANCE-500 and AVANCE-600 instruments using Me_4Si as an internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. High resolution mass spectrometry was performed using a Bruker maXis Impact HD spectrometer. Melting points were determined on Boetius combined heating stages and were not corrected.

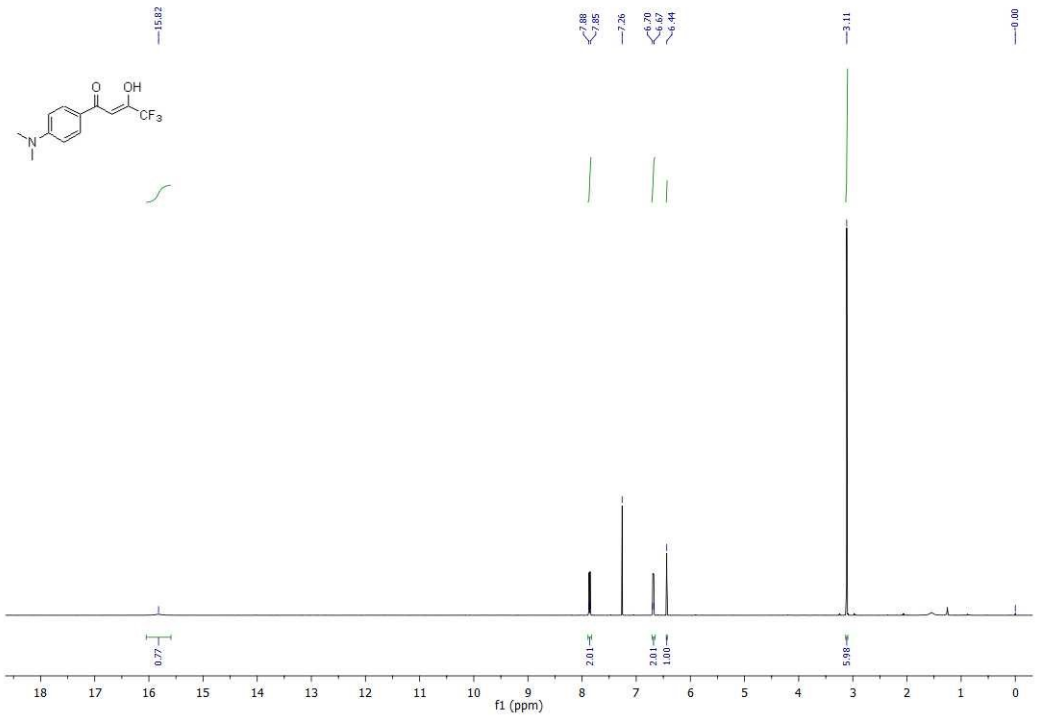


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3**

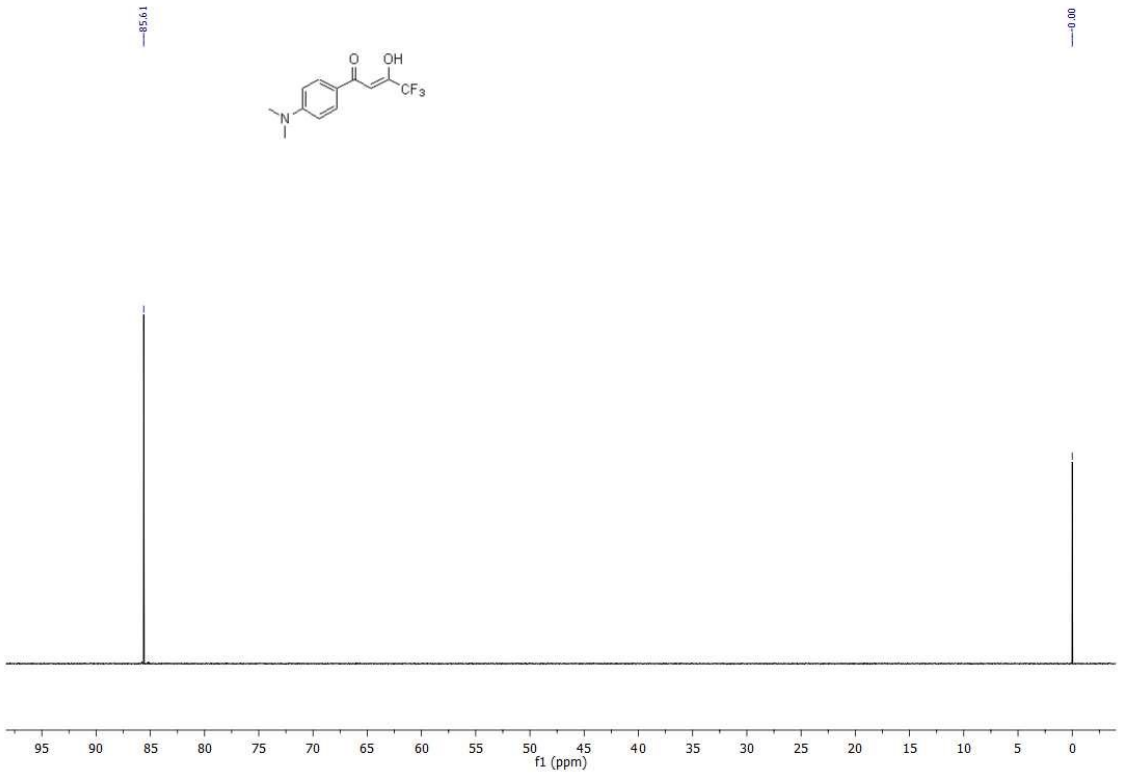


Figure S2. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3**

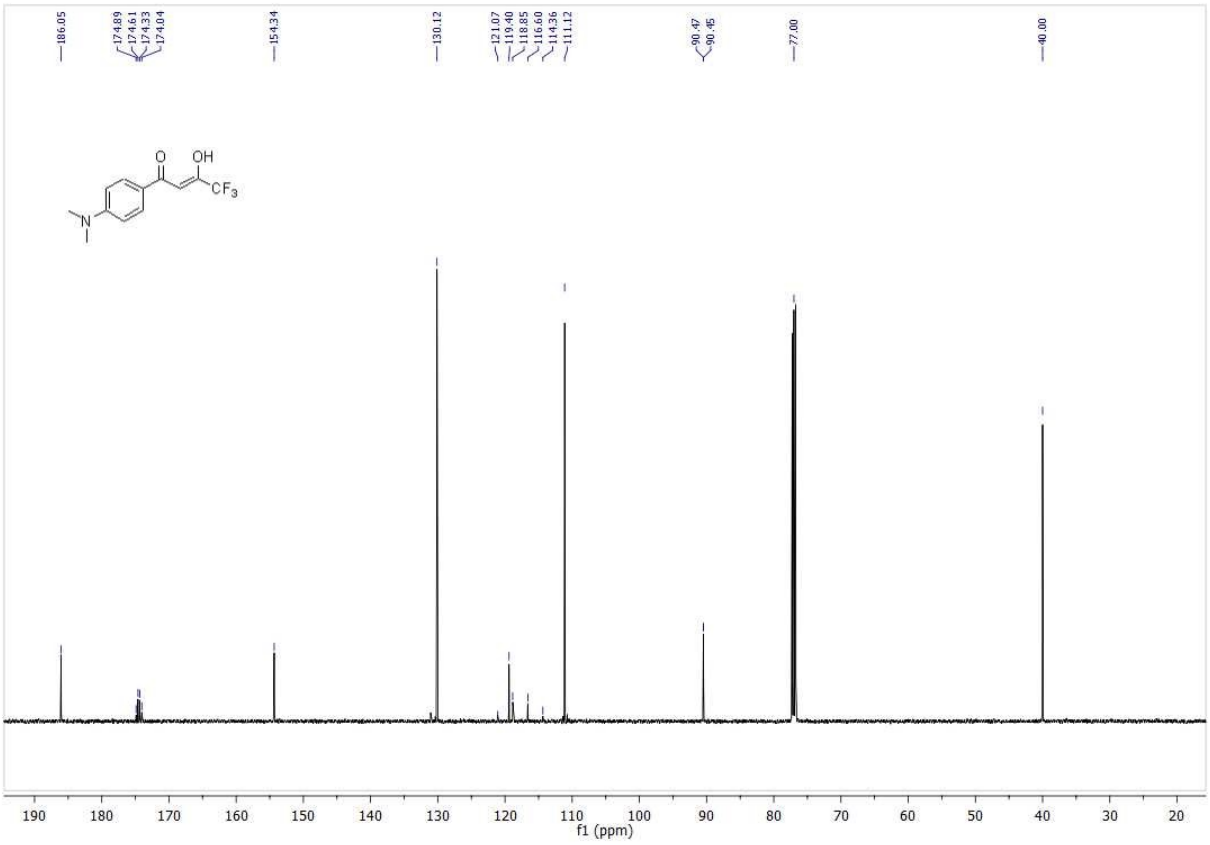


Figure S3. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3**

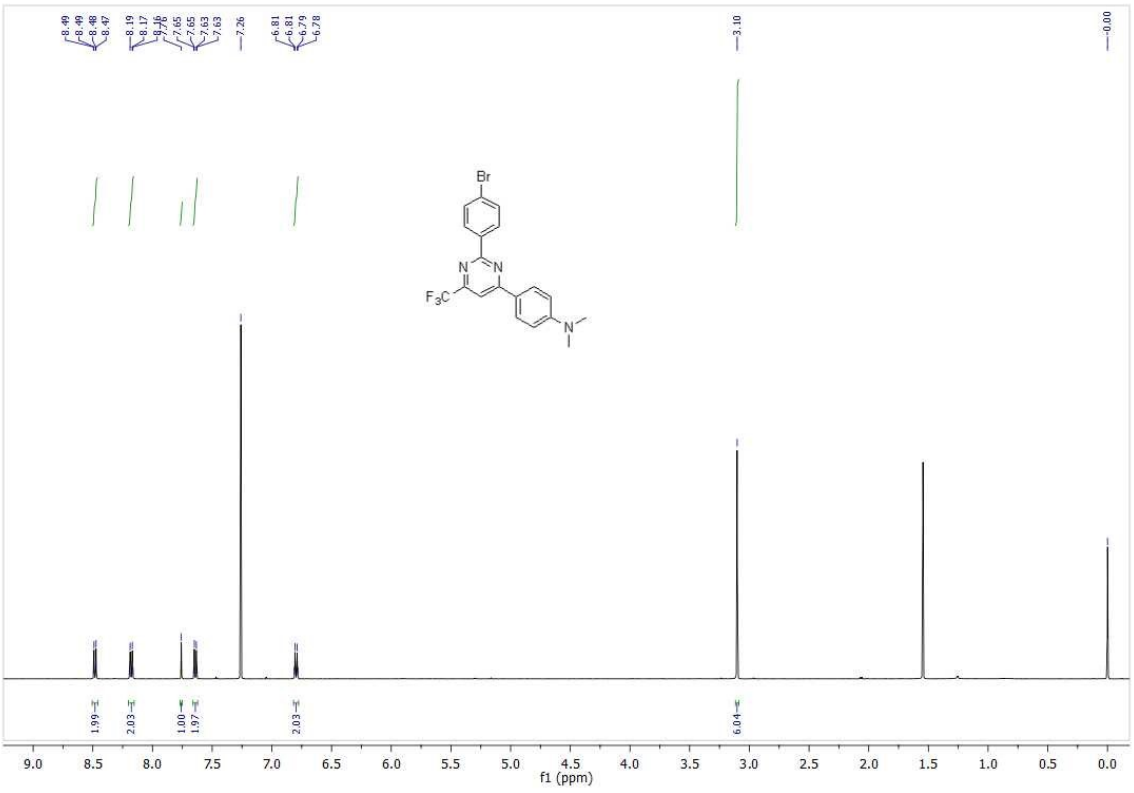


Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5a**

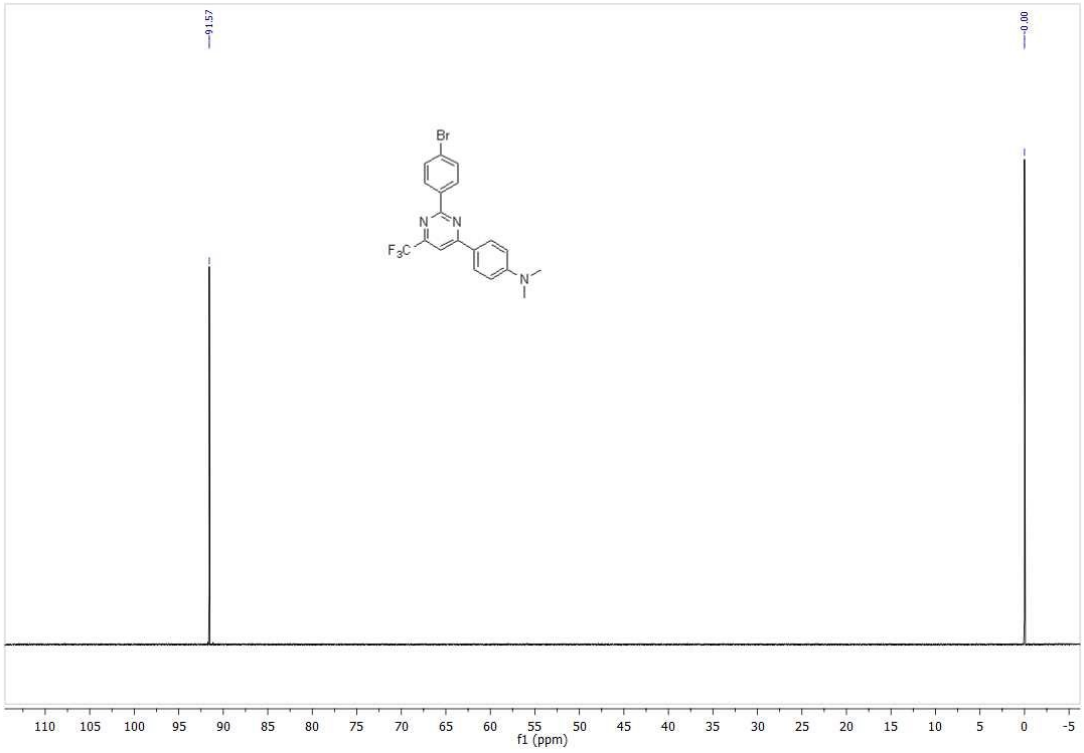


Figure S5. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **5a**

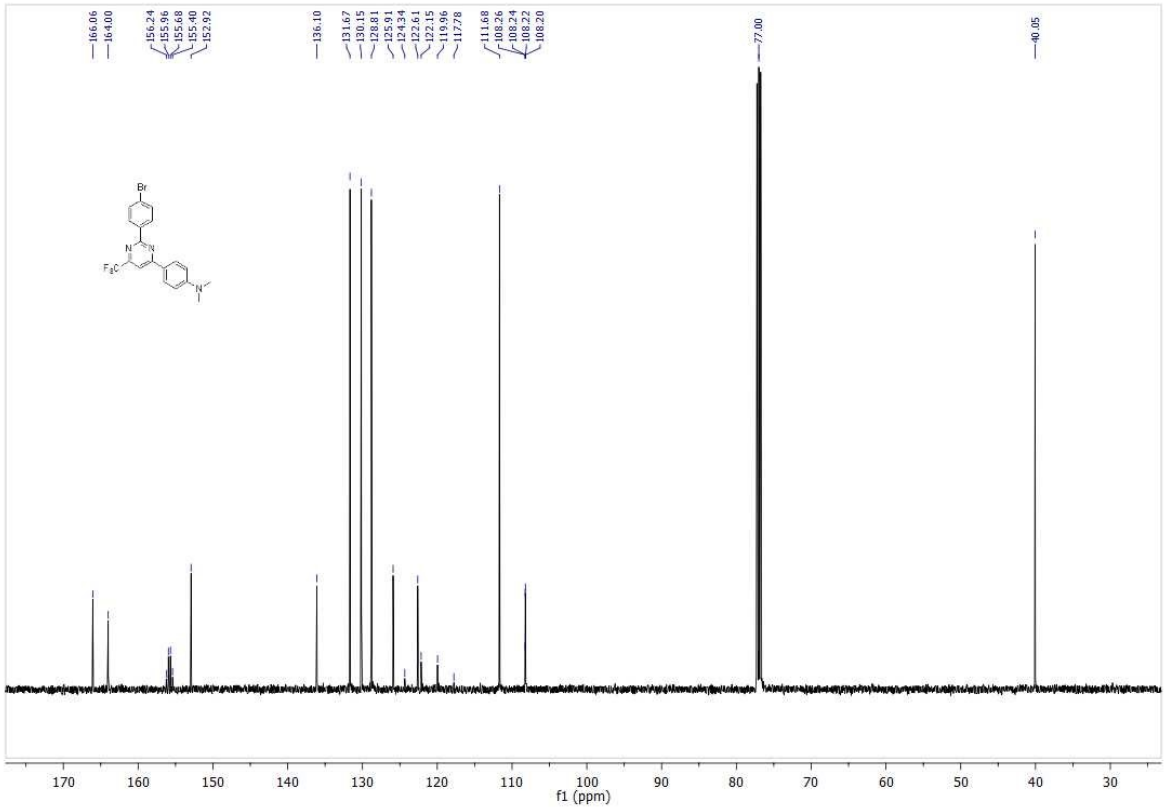


Figure S6. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5a**

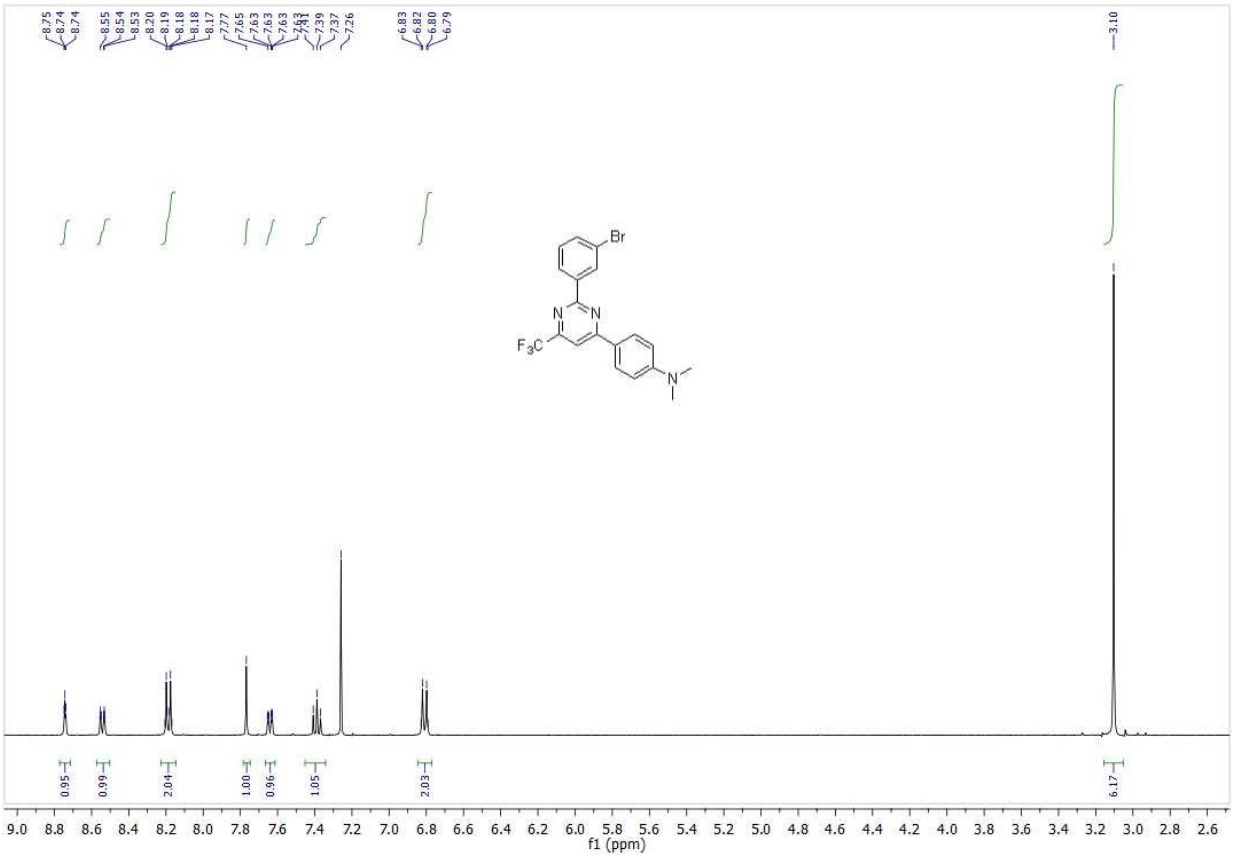


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5b**

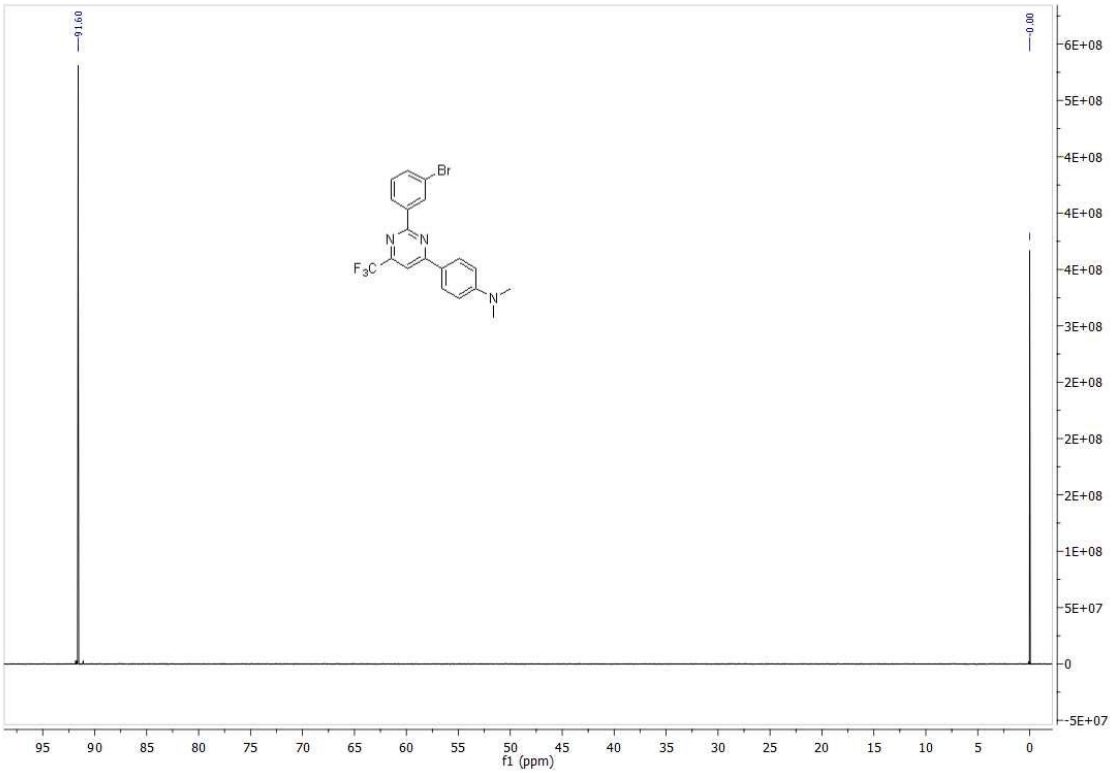


Figure S8. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **5b**

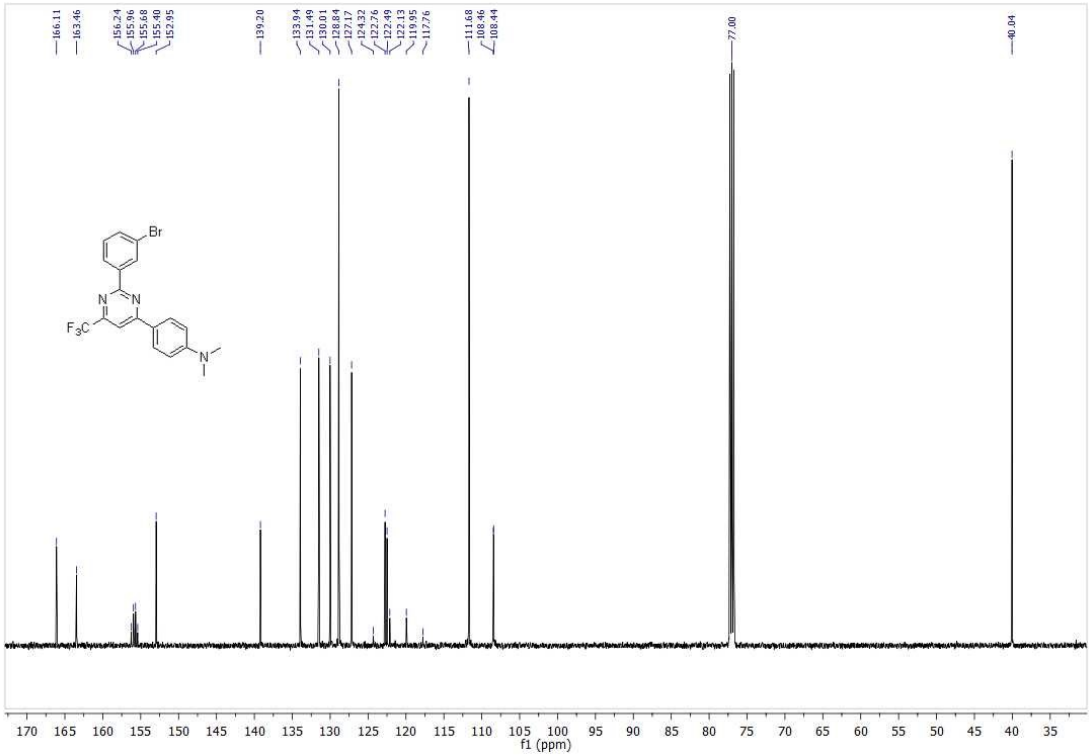


Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5b**

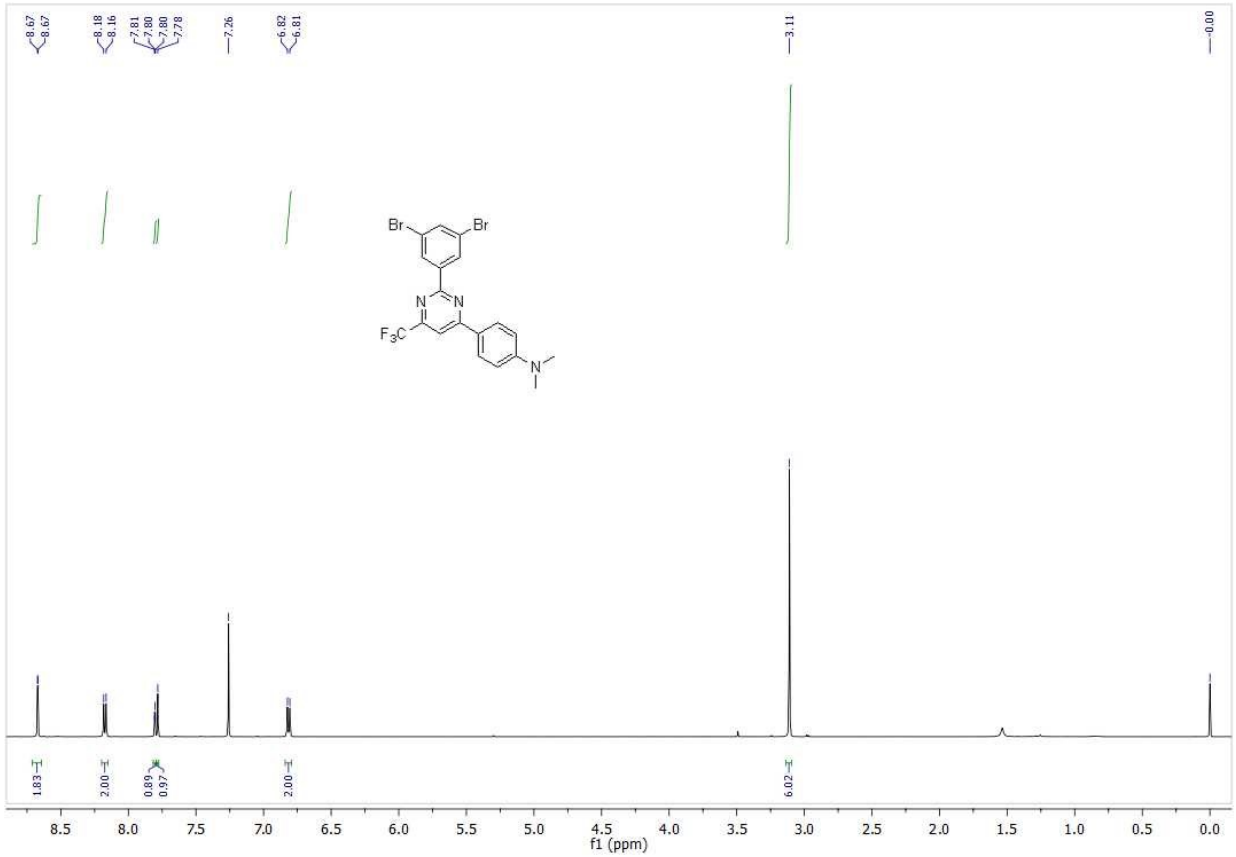


Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5c**

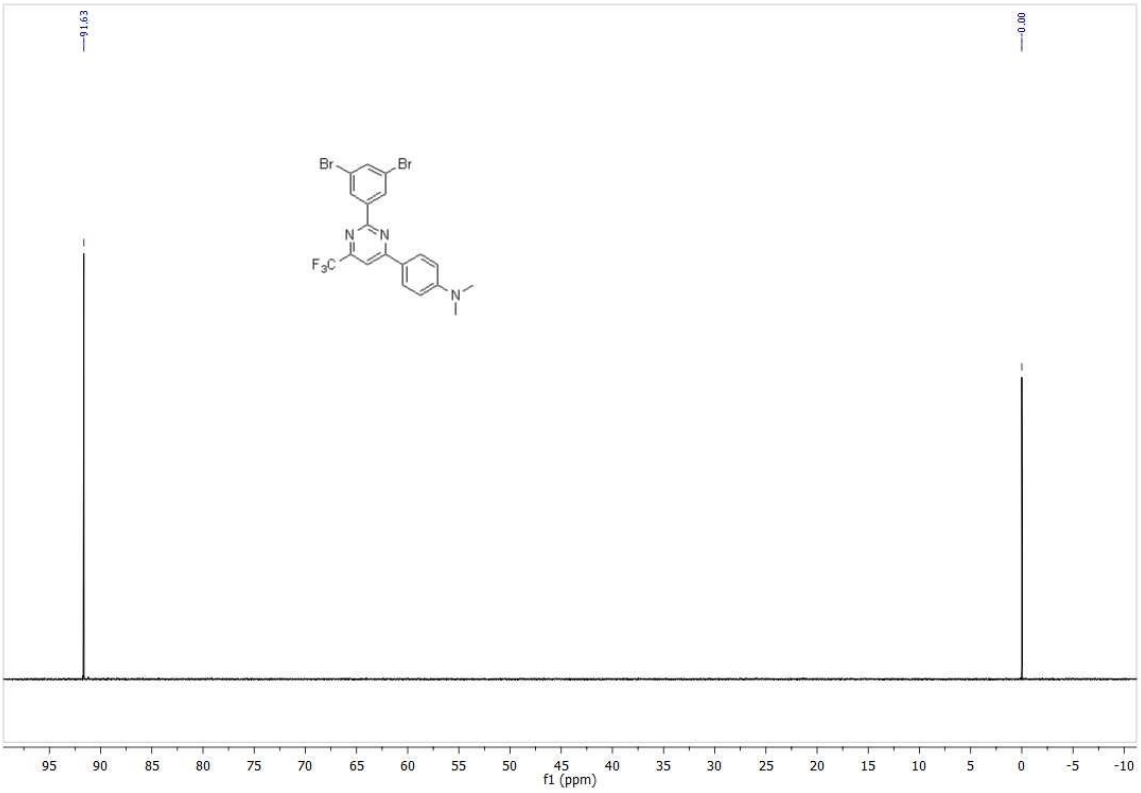


Figure S11. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **5c**

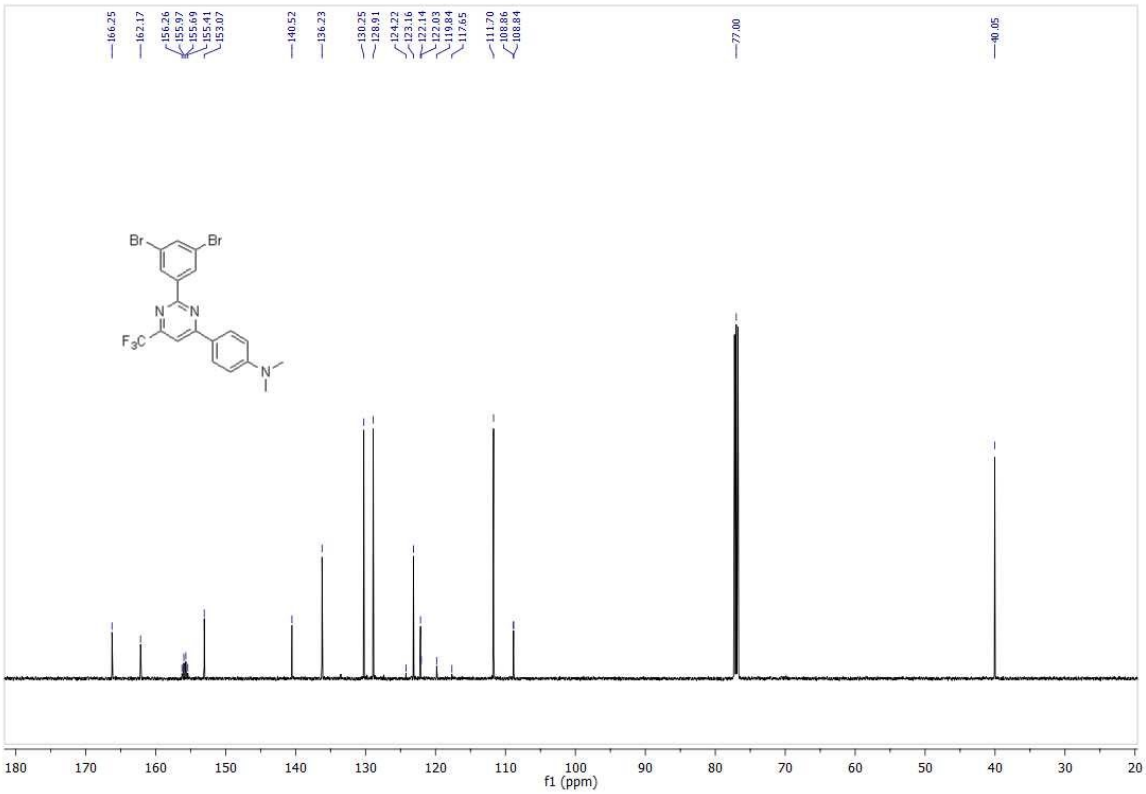


Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5c**

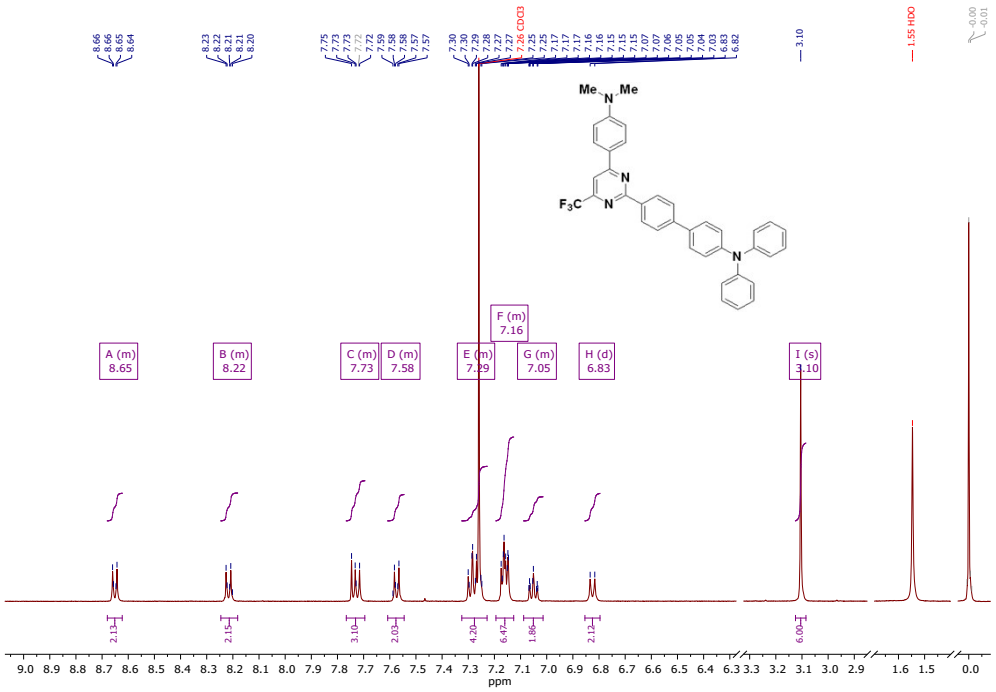


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7a**

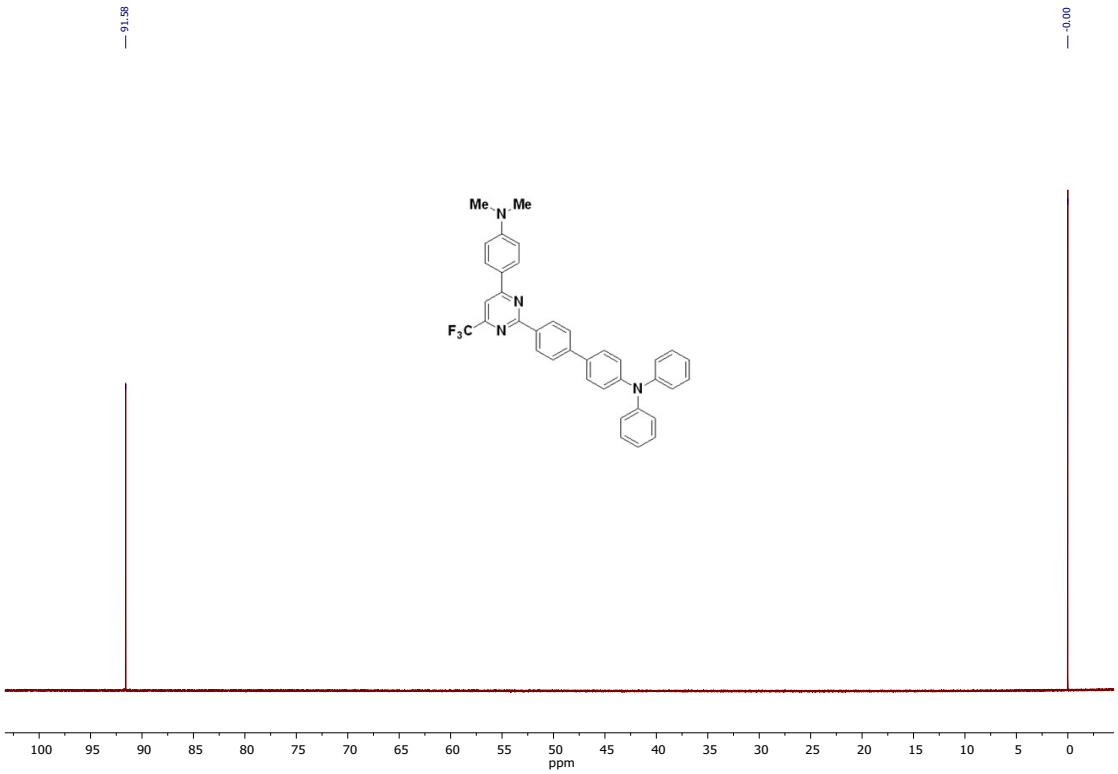


Figure S14. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **7a**

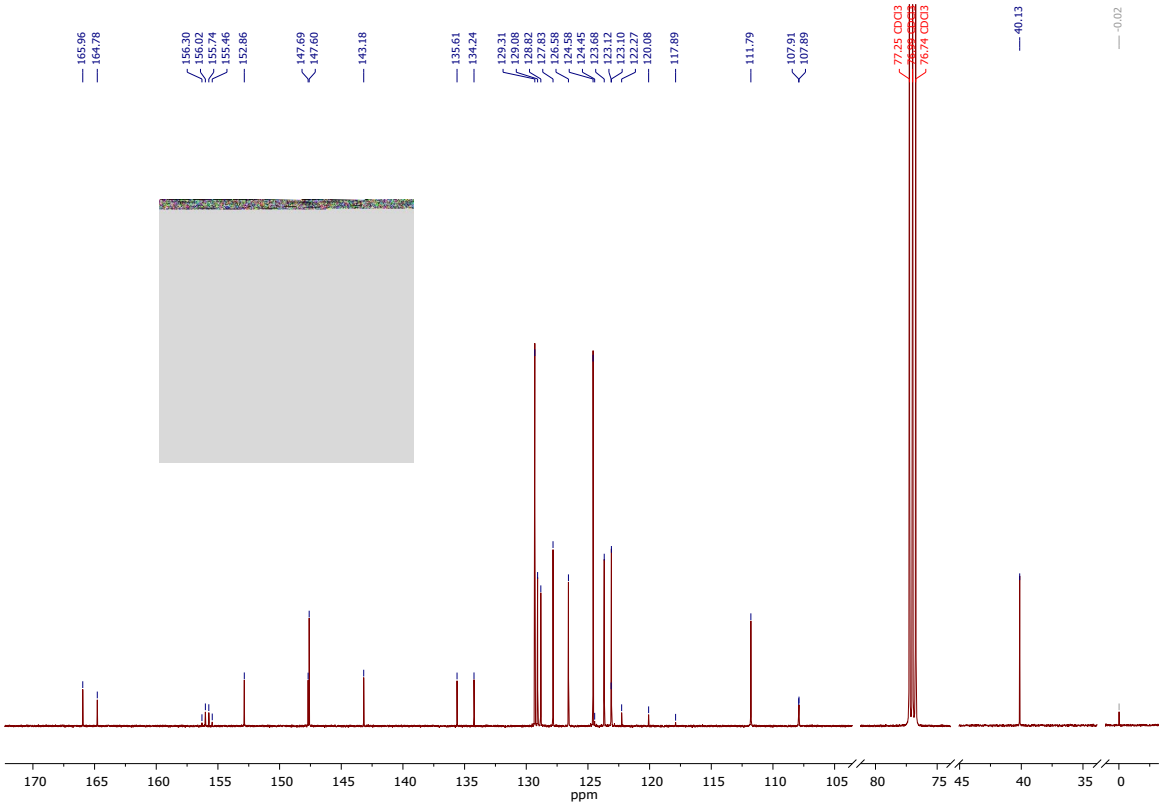


Figure S15. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **7a**

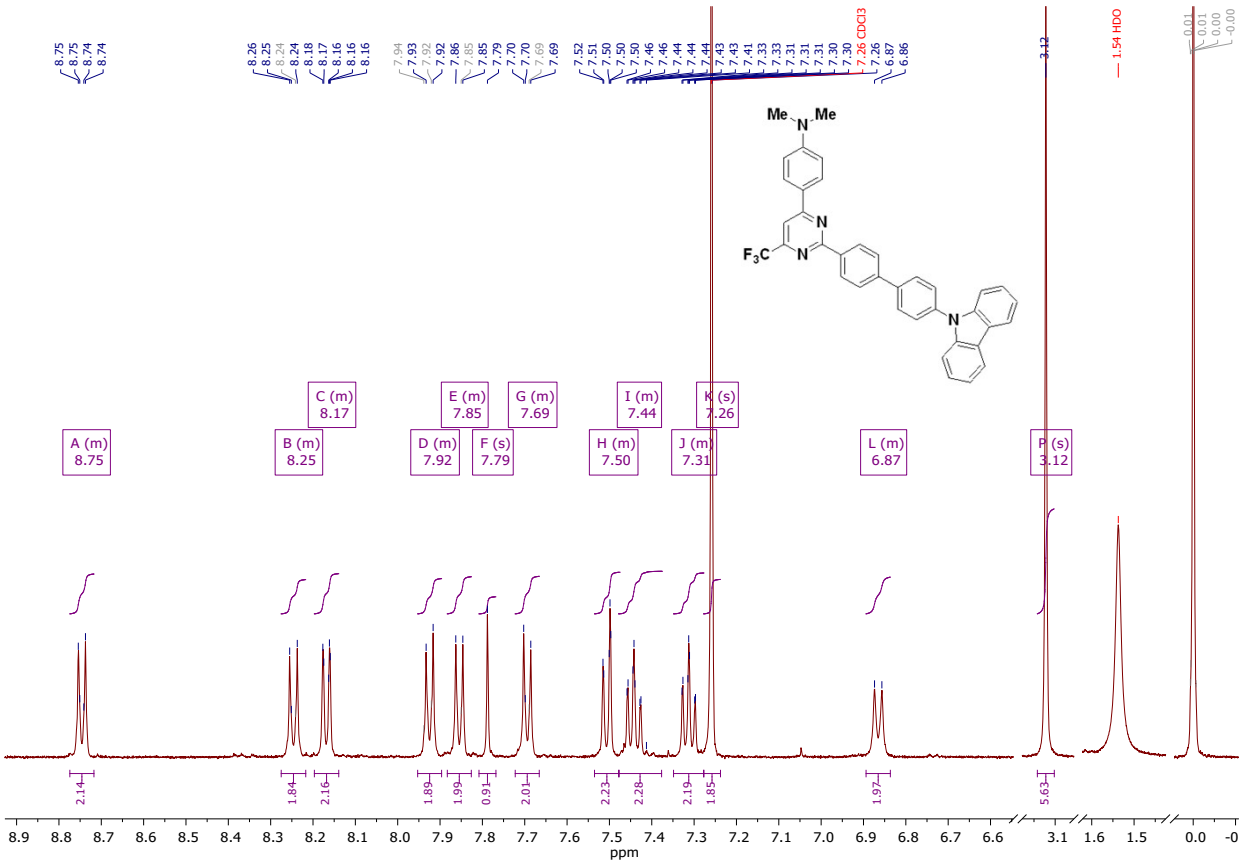


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7b**

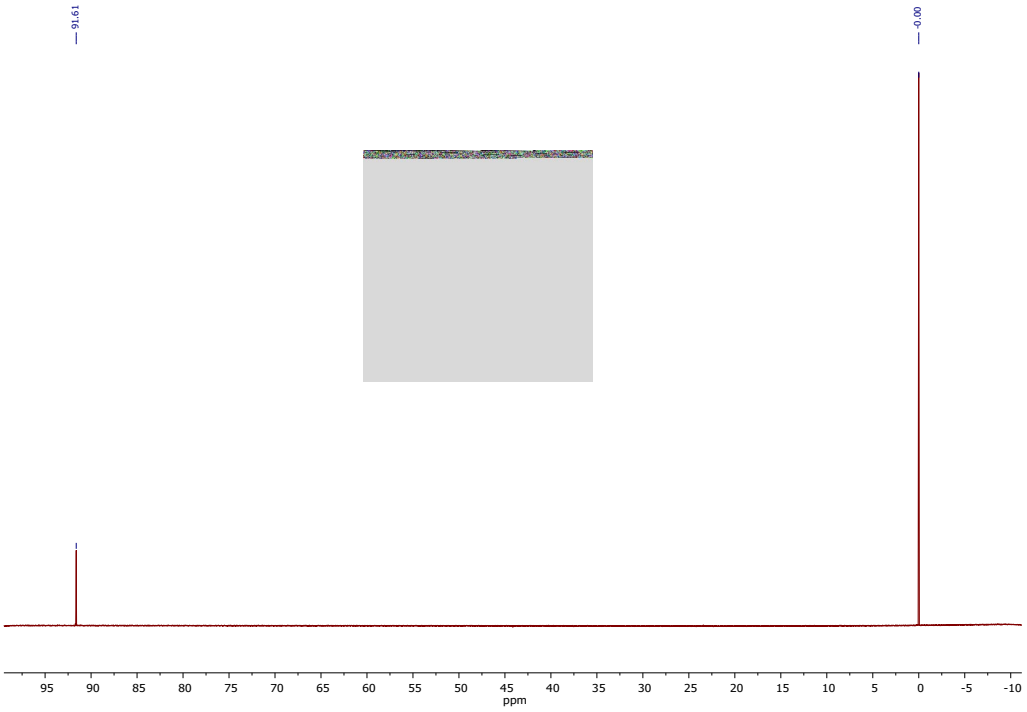


Figure S17. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **7b**

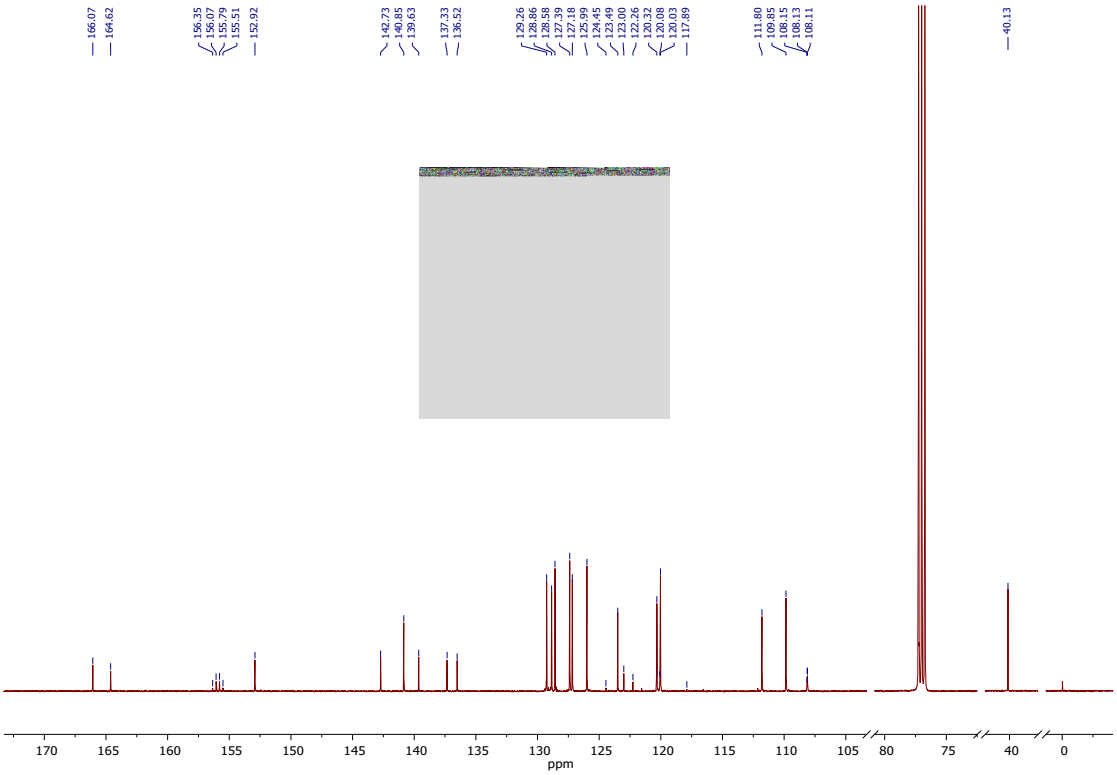


Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **7b**

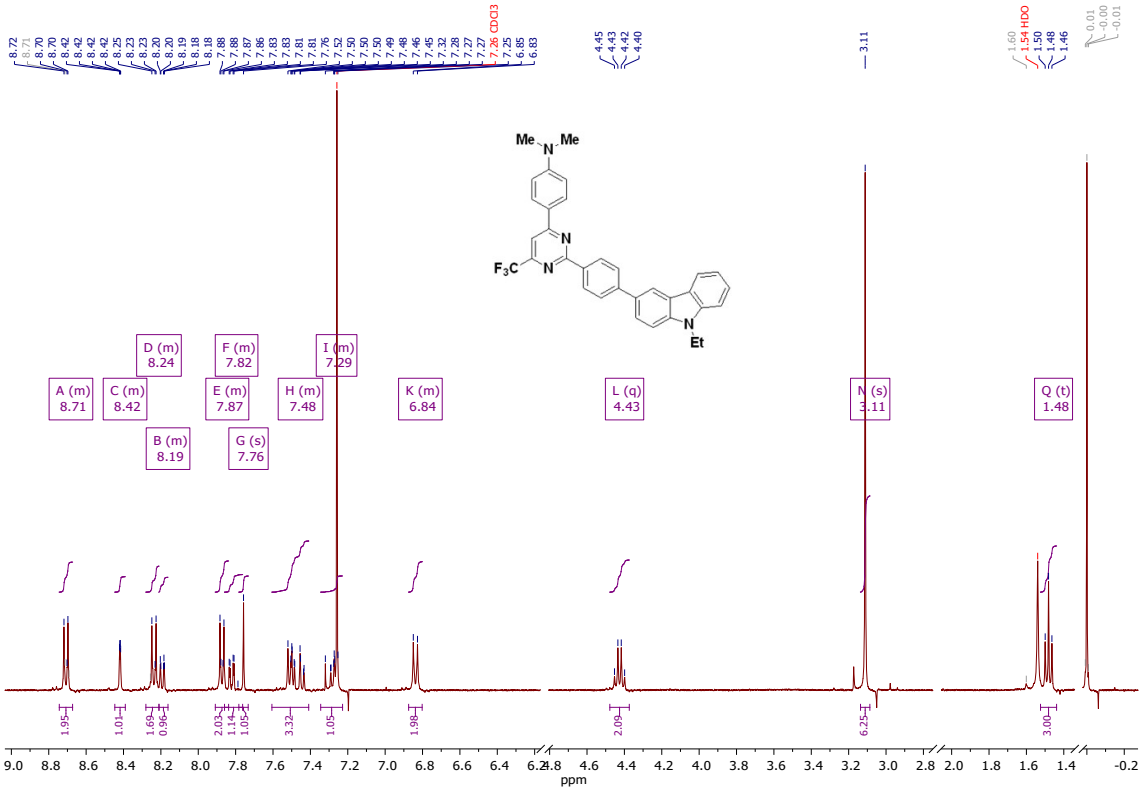


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7c**

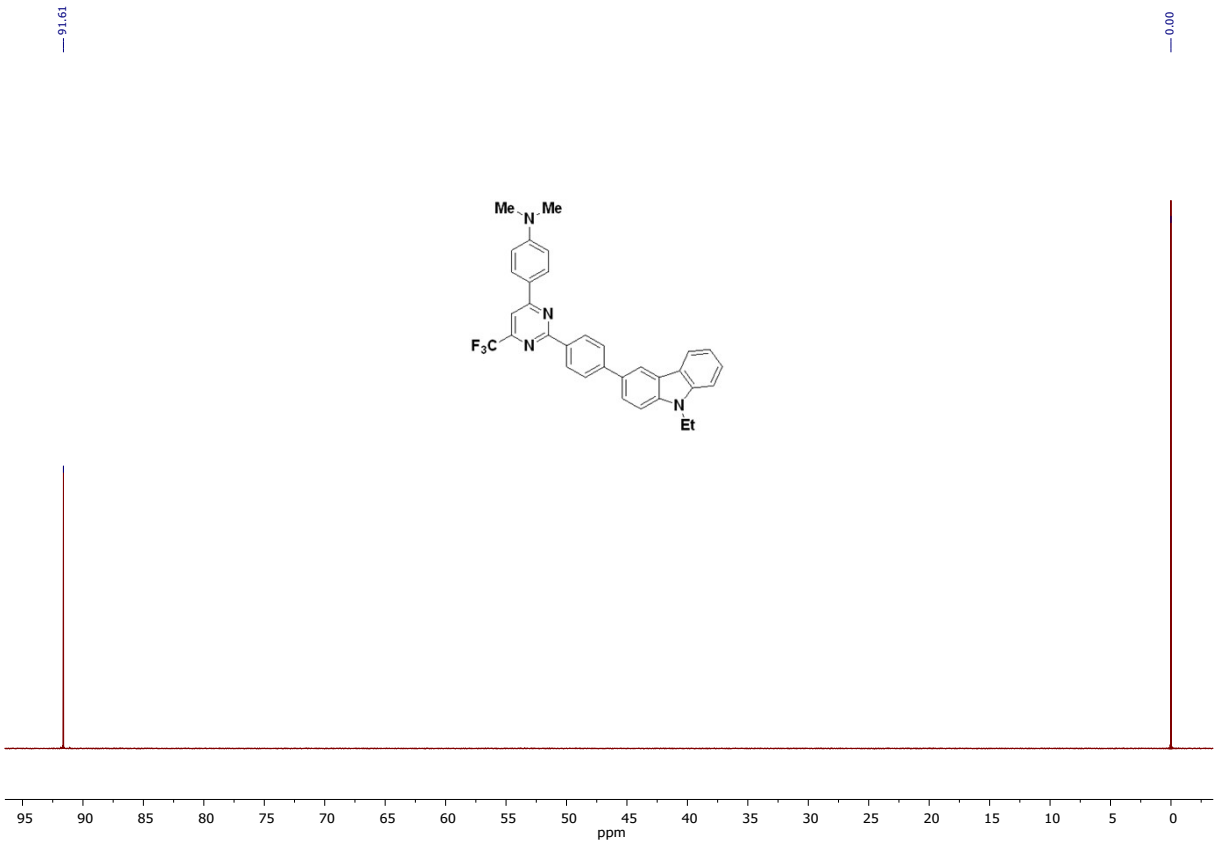


Figure S20. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **7c**

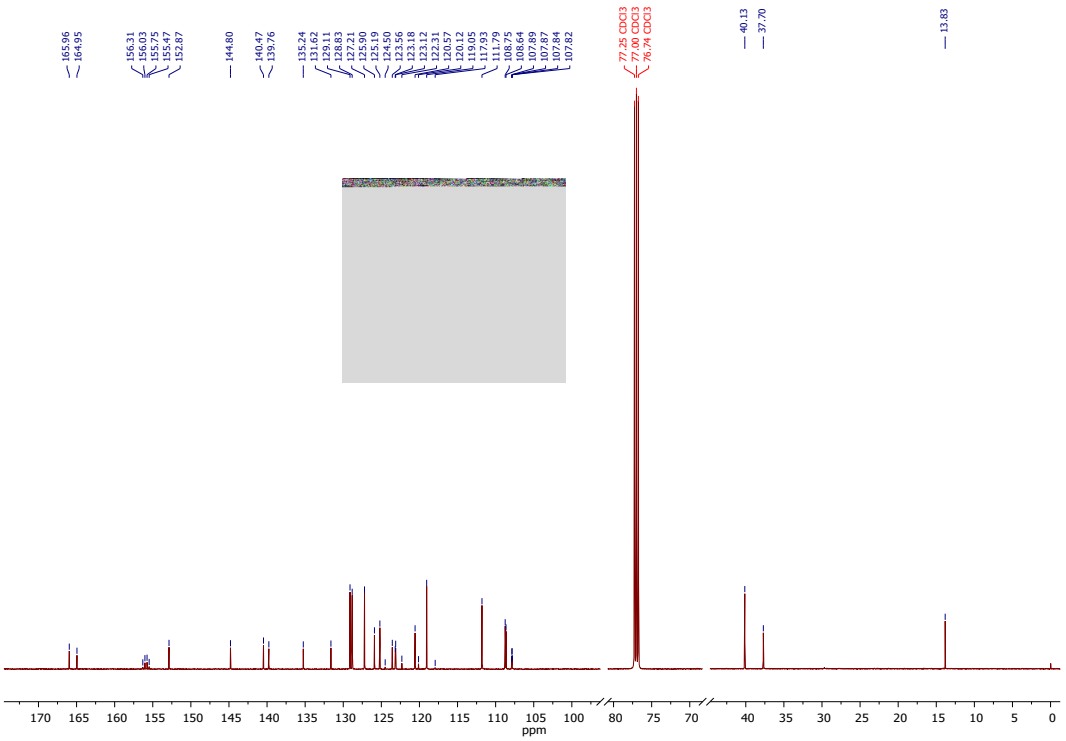


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **7c**

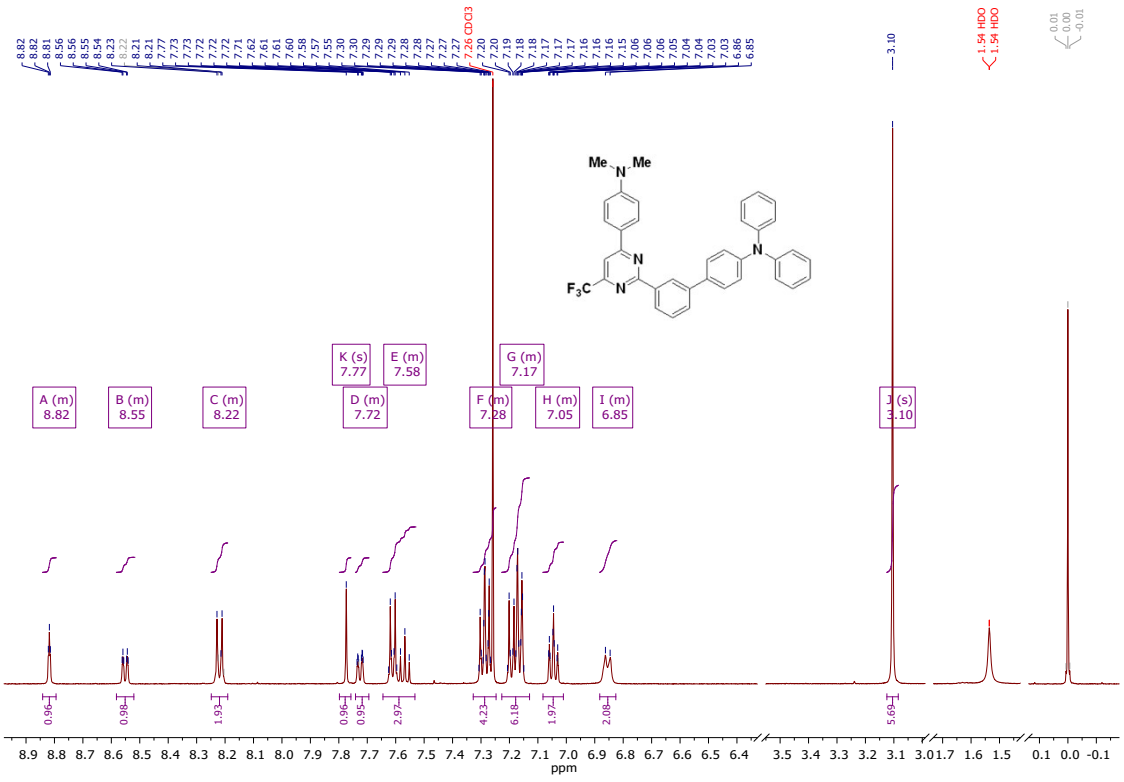


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8a**

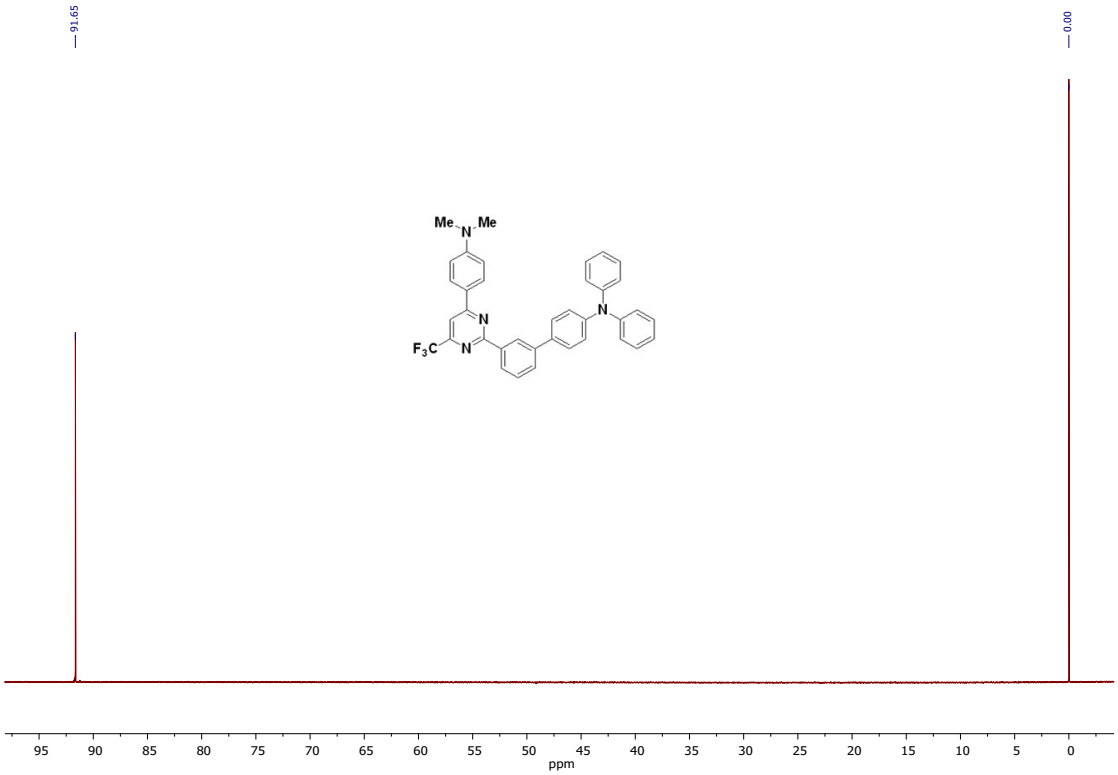


Figure S23. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **8a**

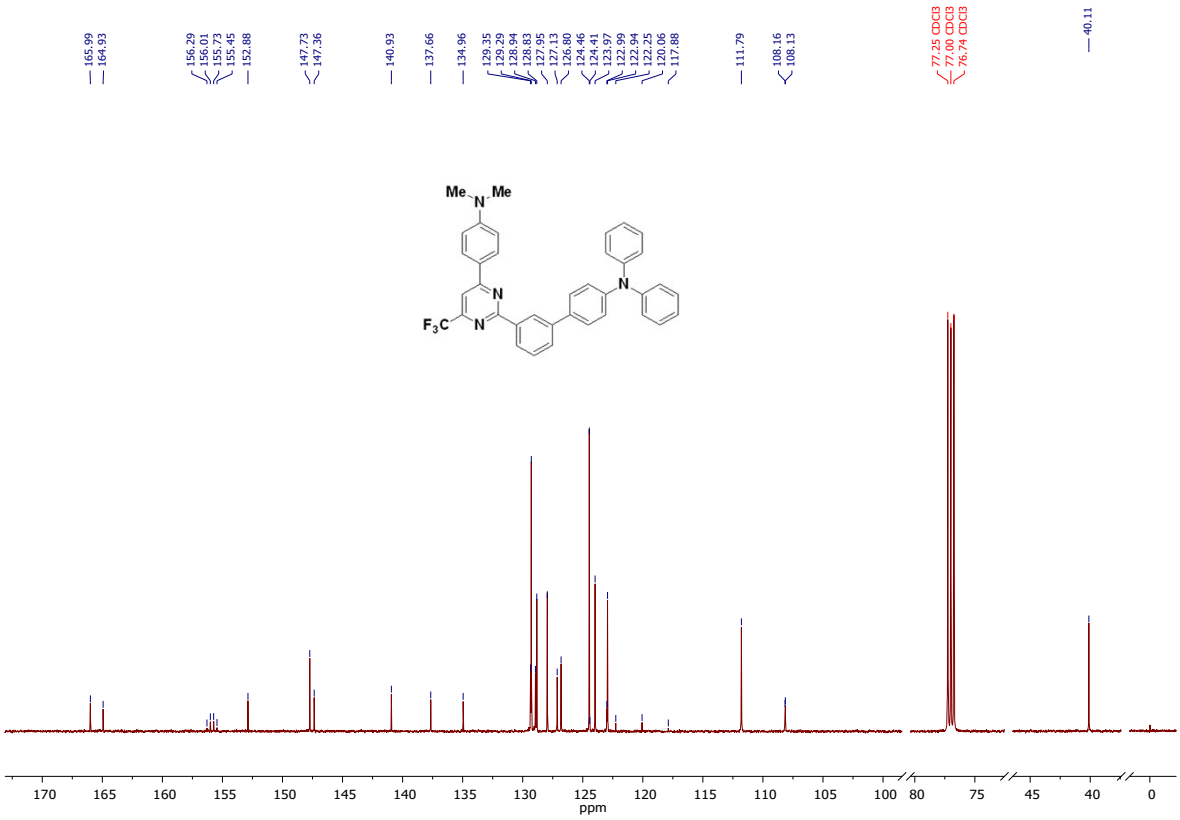


Figure S24. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **8a**

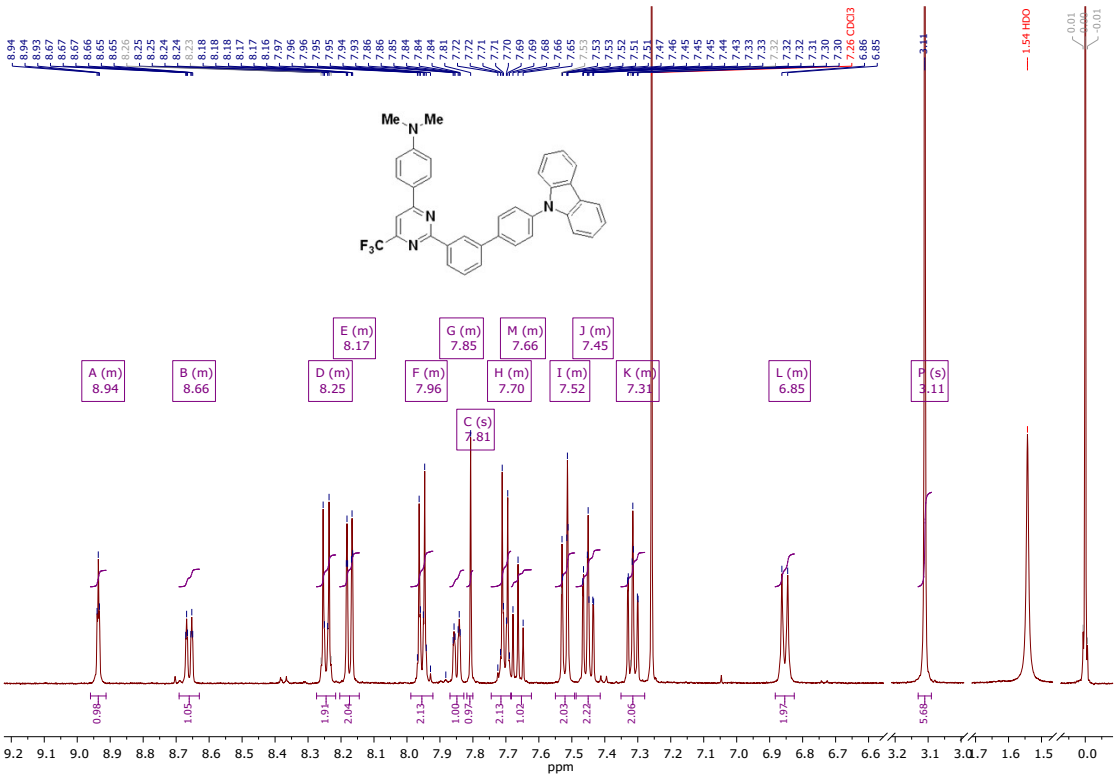


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8b**

Figure S26. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **8b**

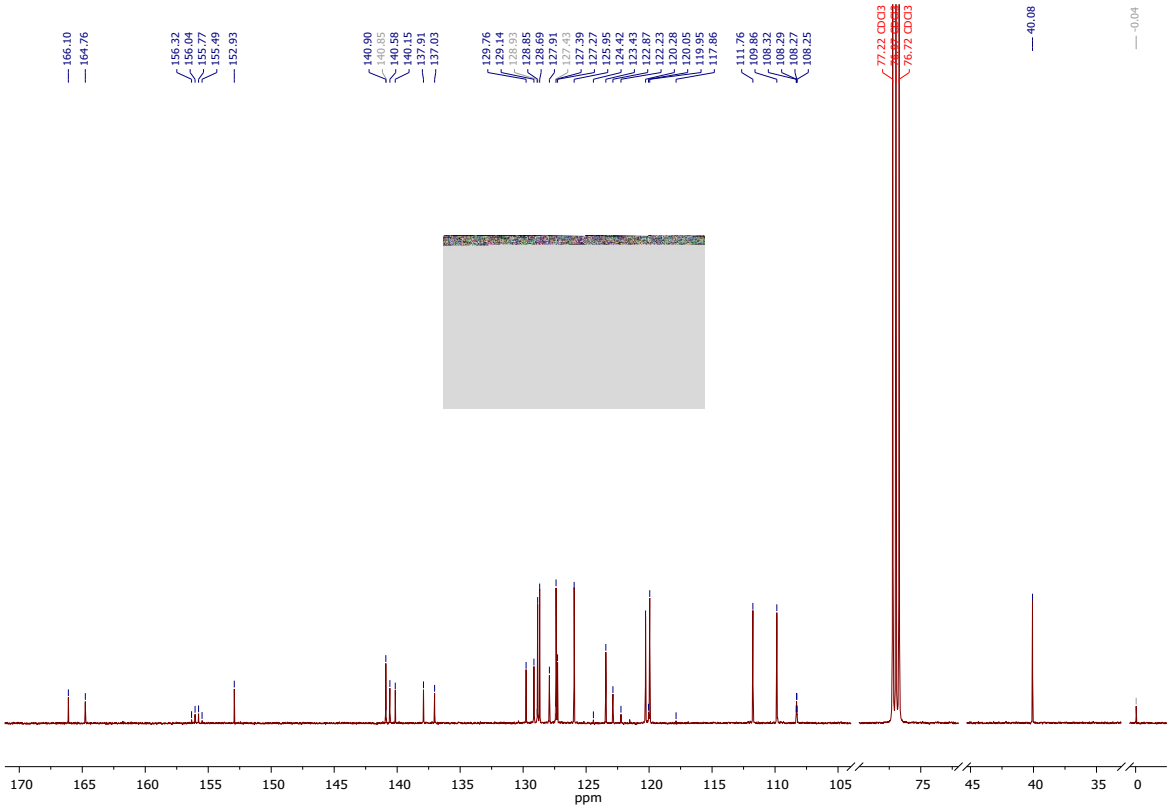


Figure S27. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **8b**

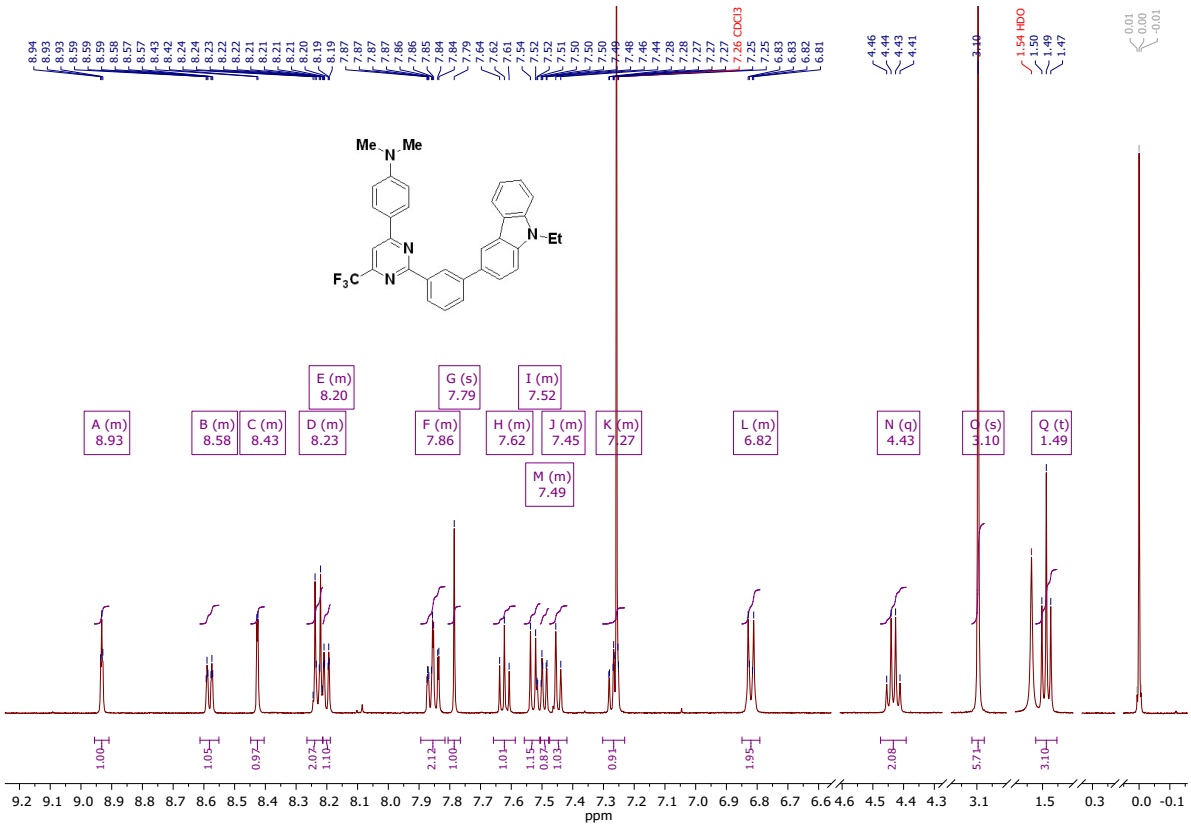


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8c**

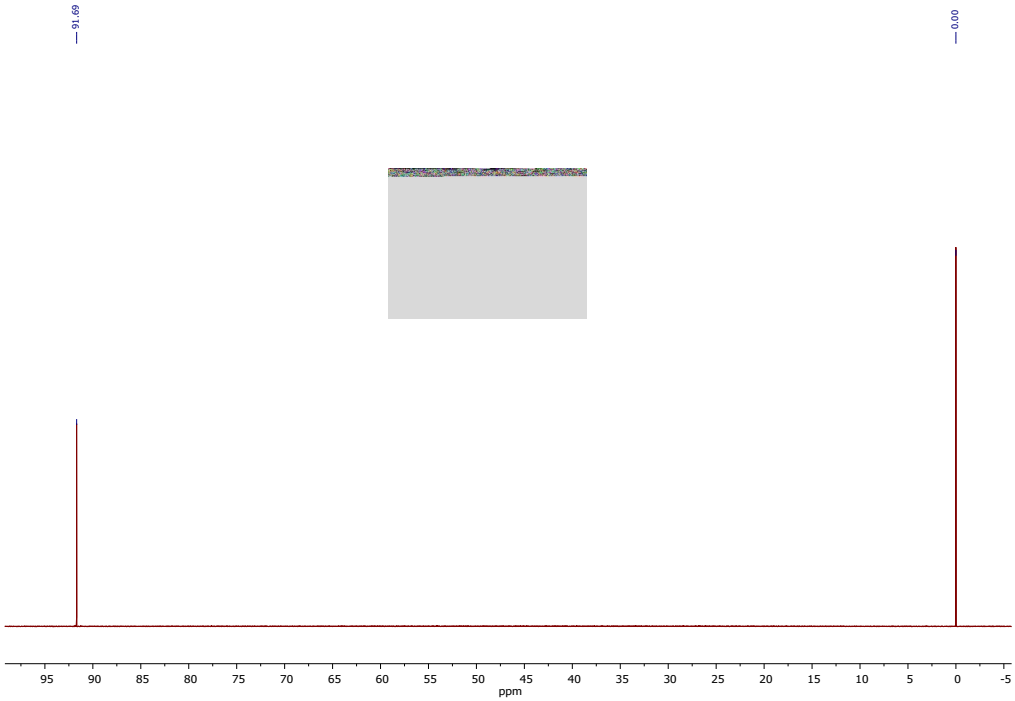


Figure S29. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **8c**

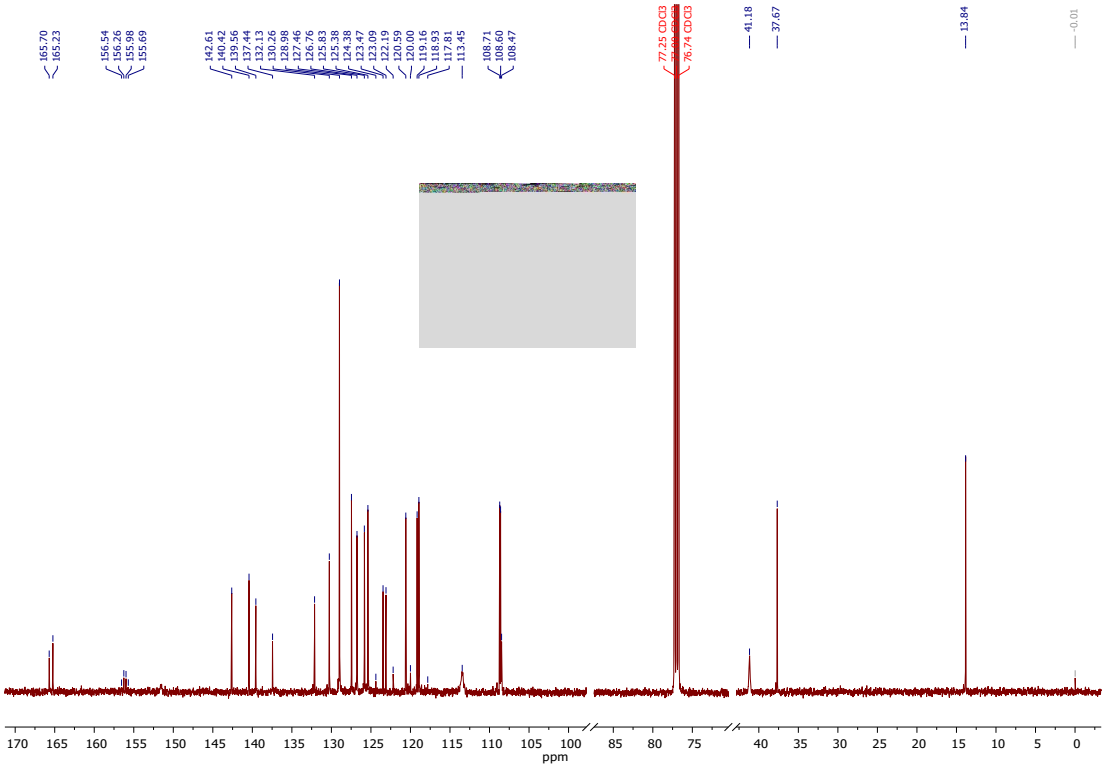


Figure S30. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **8c**

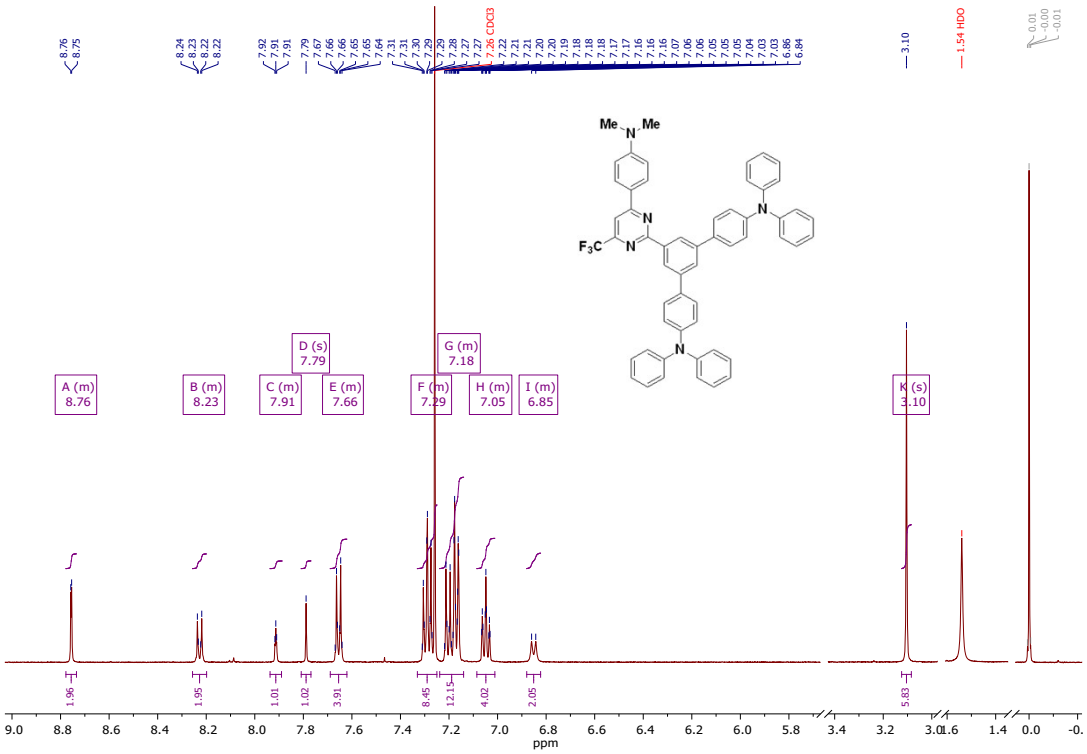


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **9a**

Figure S32. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **9a**

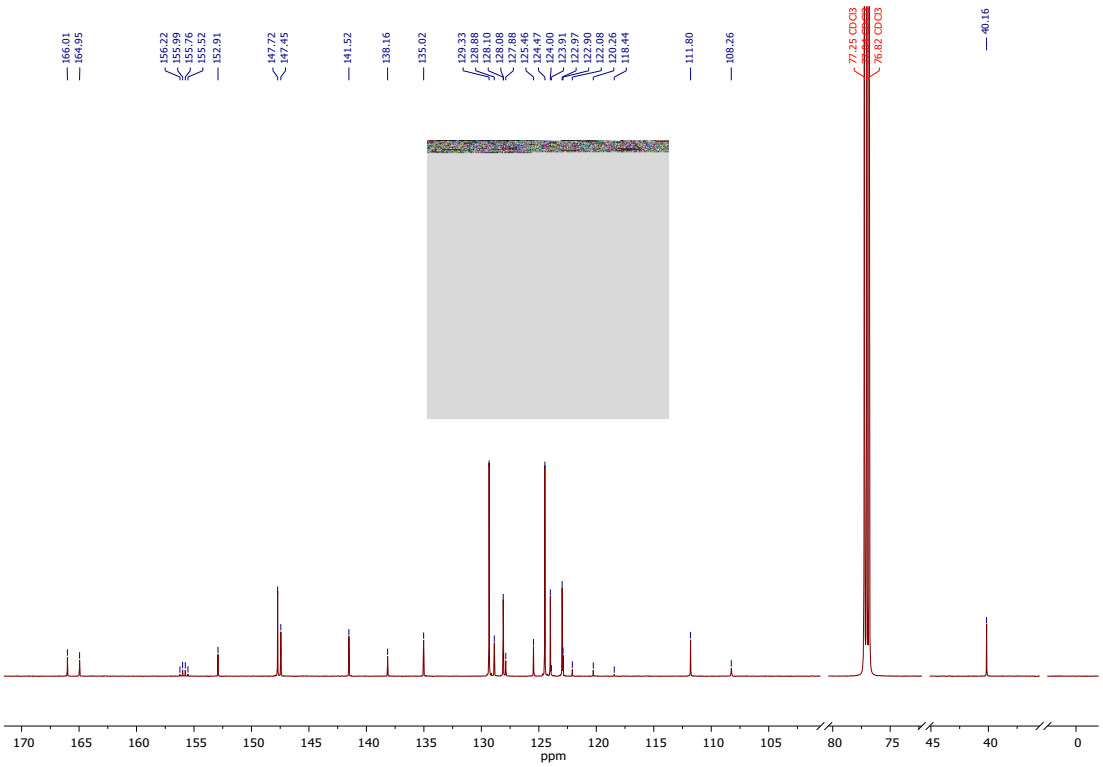


Figure S33. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9a**

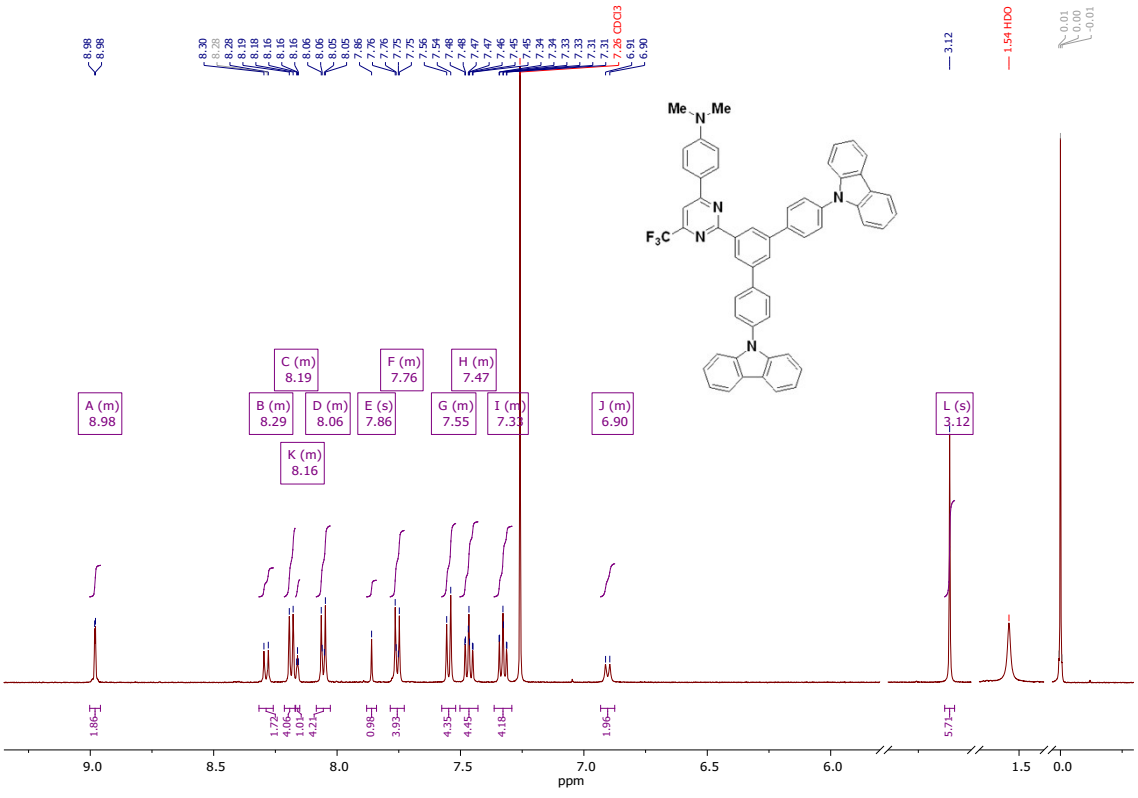


Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **9b**

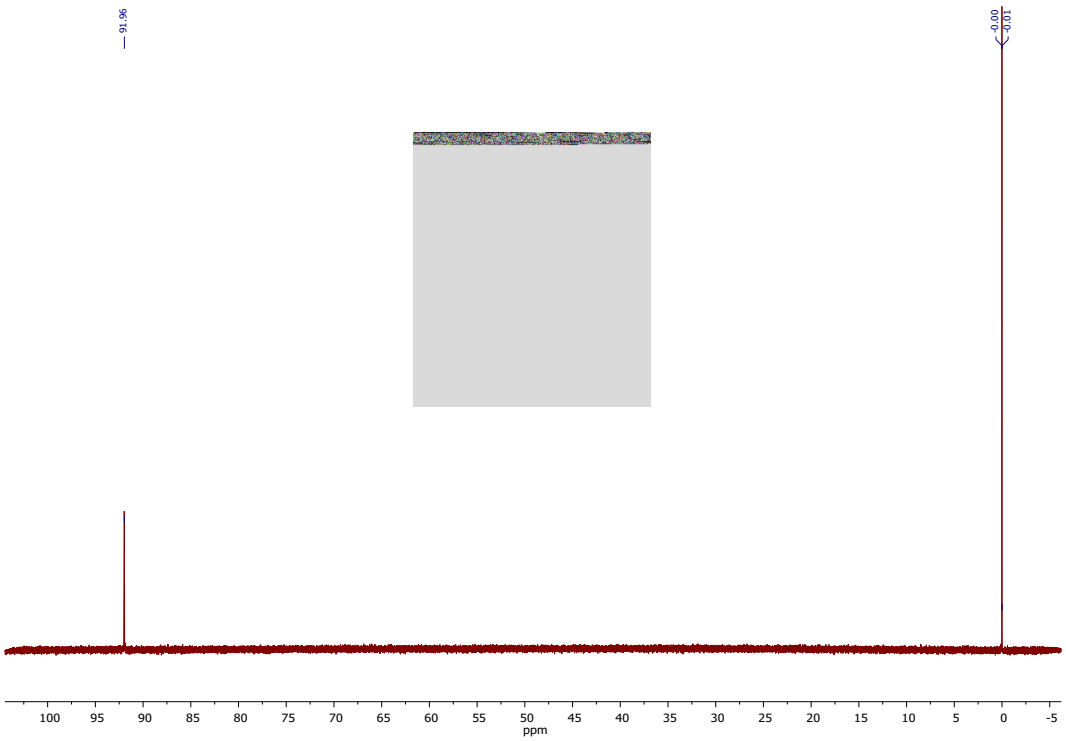


Figure S35. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **9b**

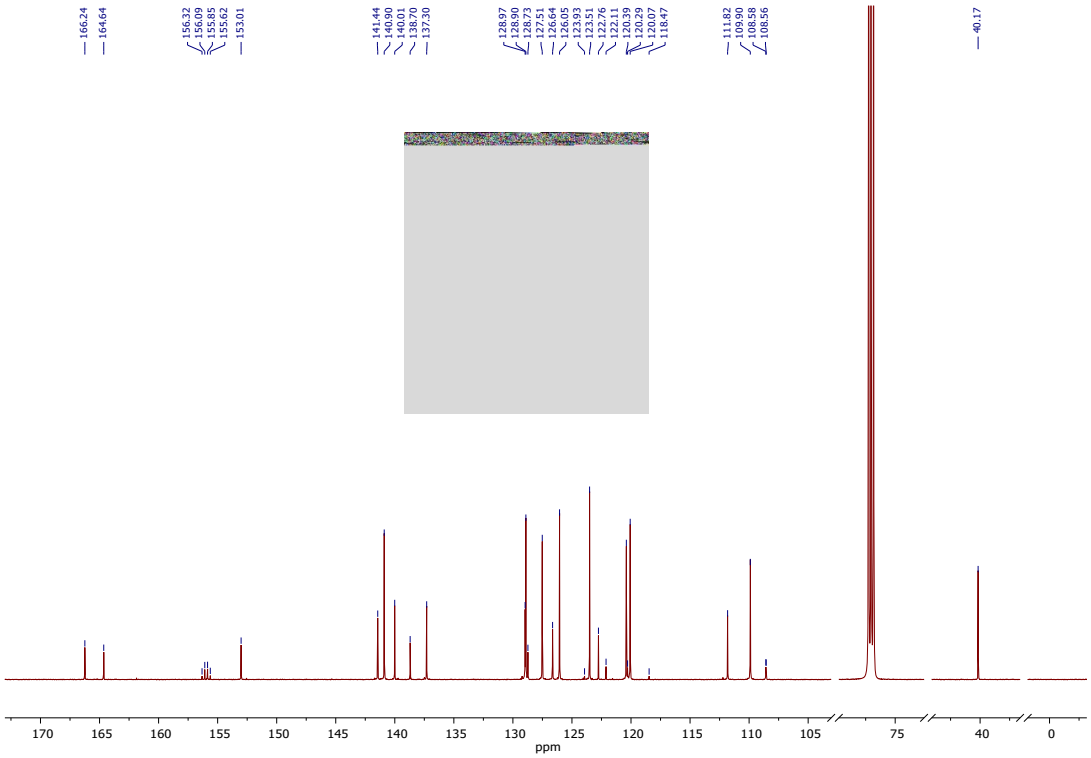


Figure S36. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9b**

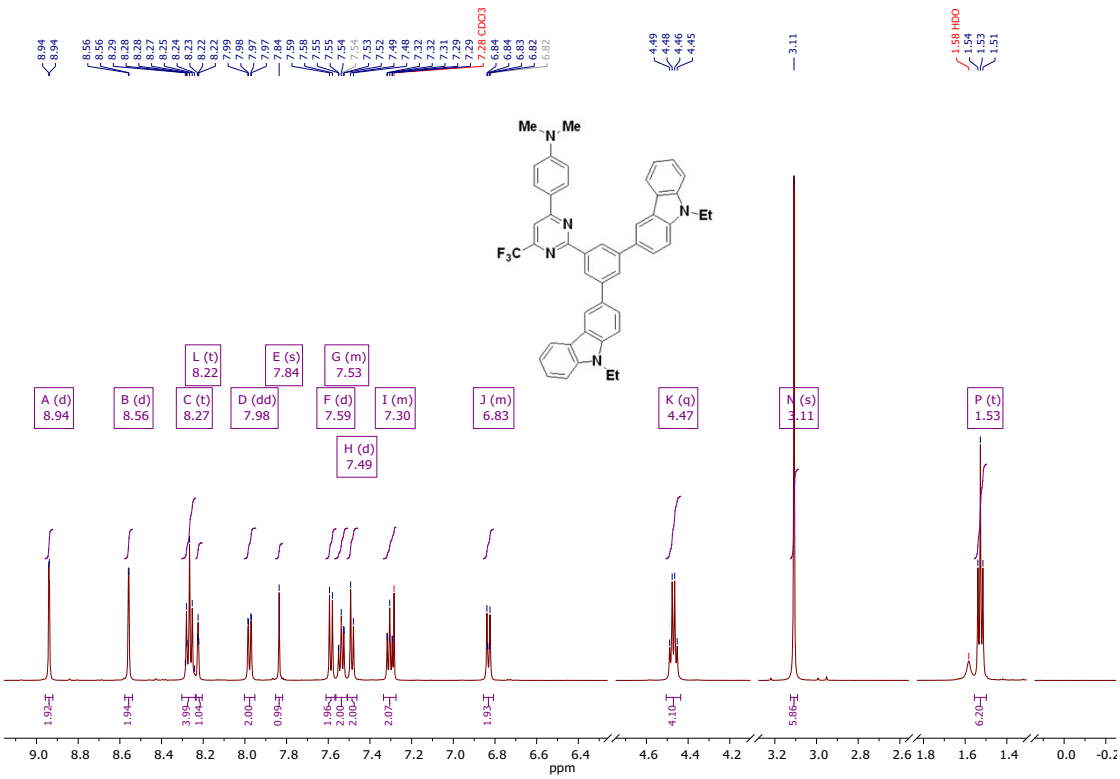


Figure S37. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **9c**

Figure S38. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **9c**

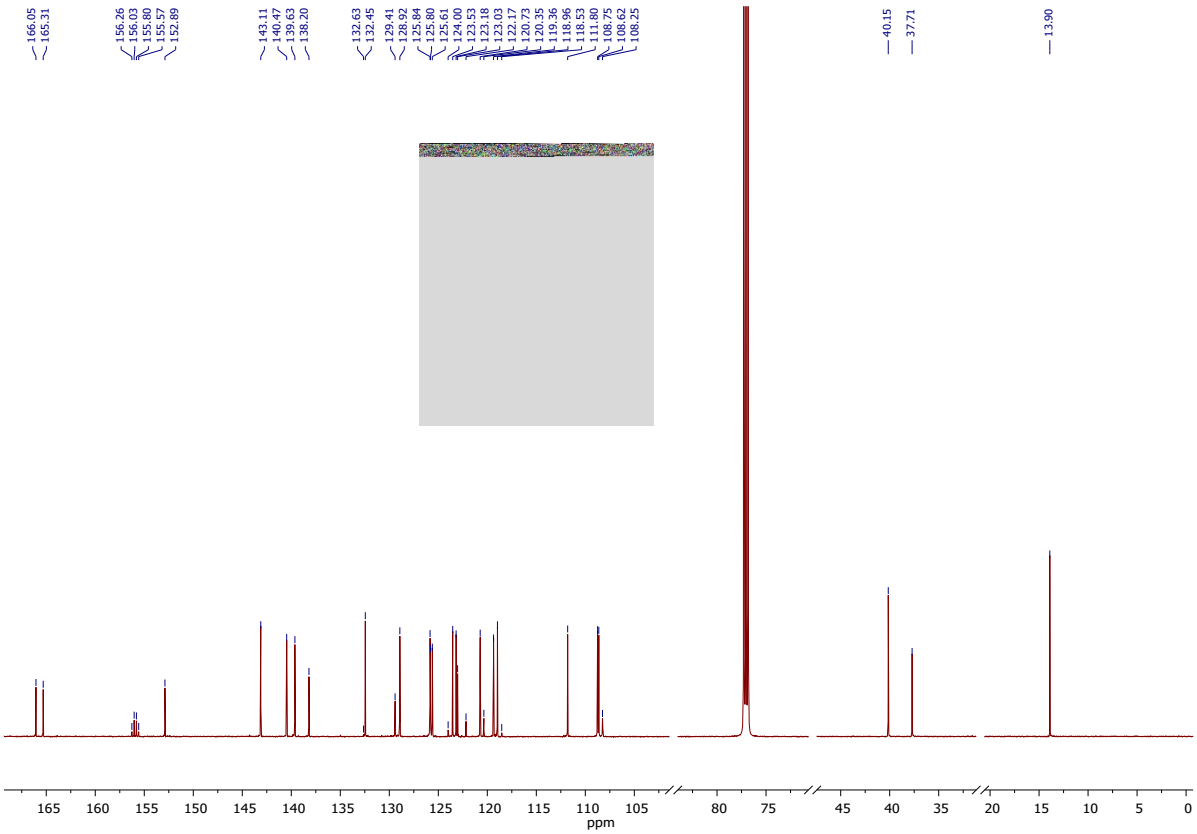


Figure S39. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9c**

Table S1. Calculated fluorescence emission wavelengths obtained using MN15 and CAM-B3LYP functionals

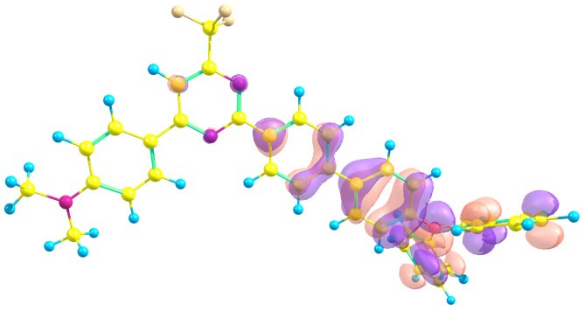
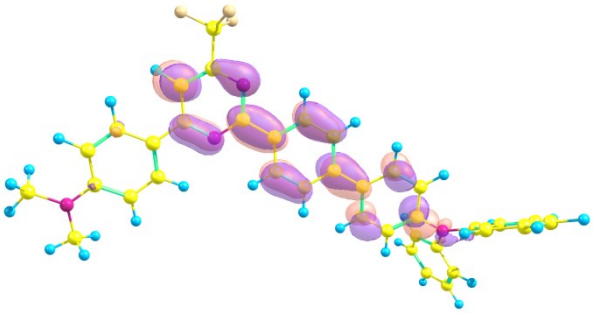
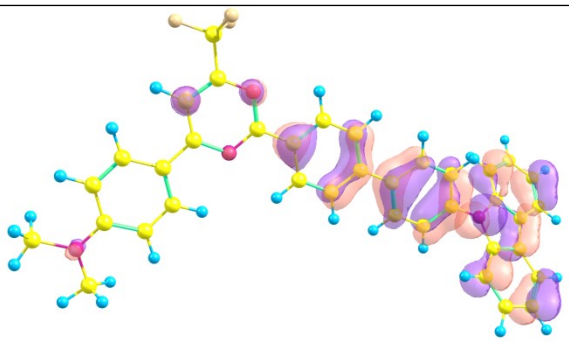
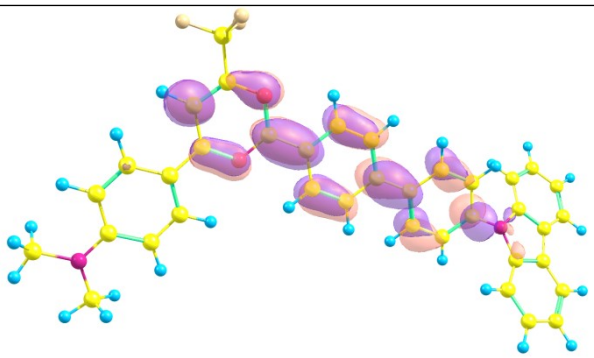
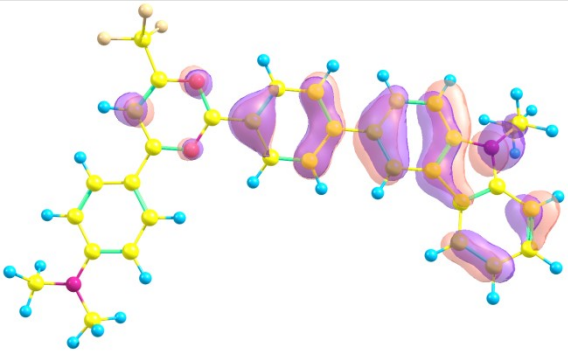
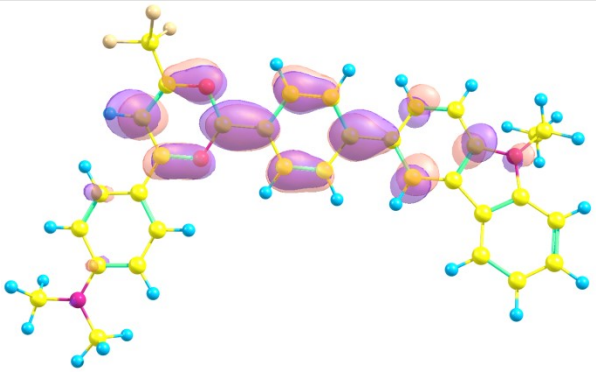
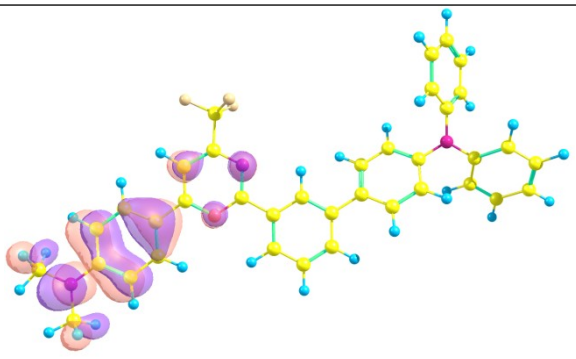
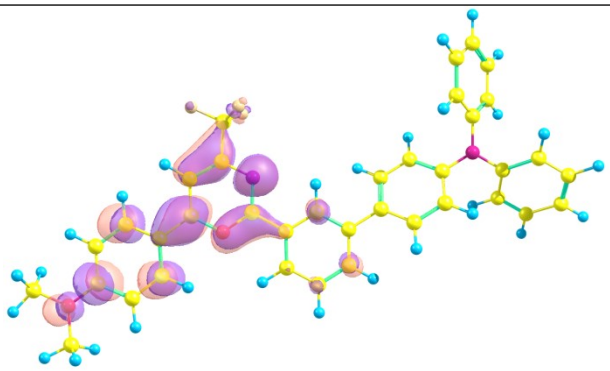
		Fluorescence, nm		
		MN15	CAM-B3LYP	Experiment
Chloroform	7a	429	392	480
	8a	441	398	451
	8b	443	400	447
	9a	442	398	450
	9c	433	341	447
Cyclohexane	7a	414	390	434
	8a	431	390	406
	9c	428	339	407

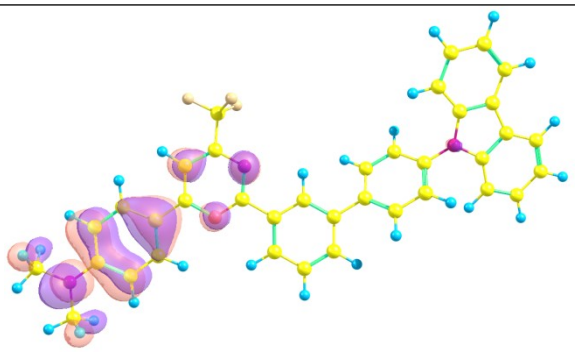
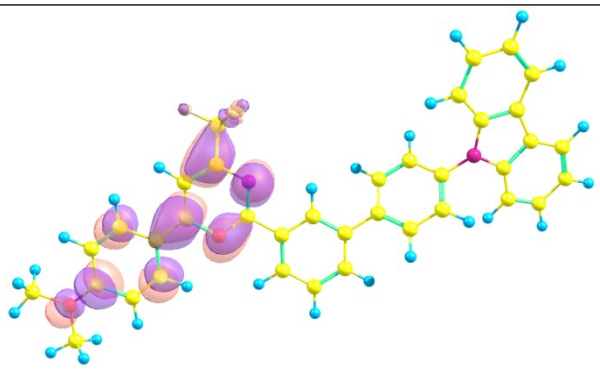
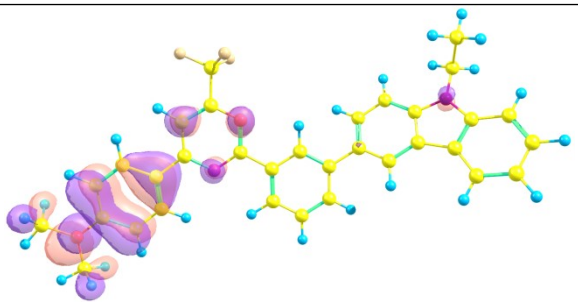
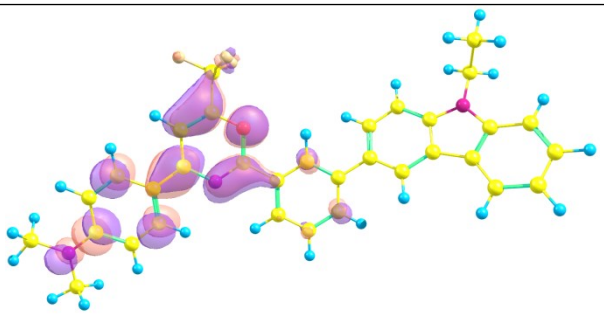
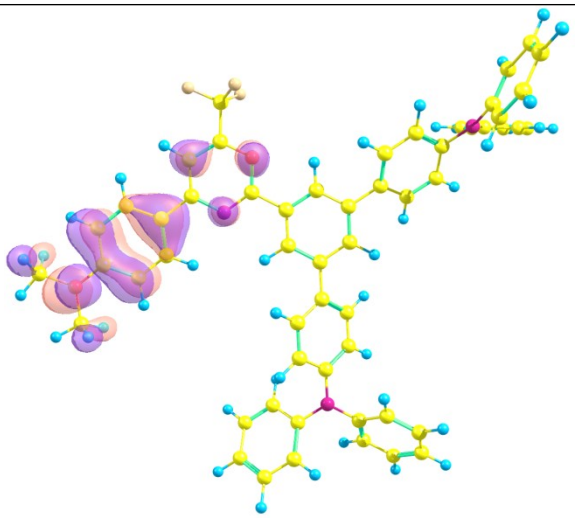
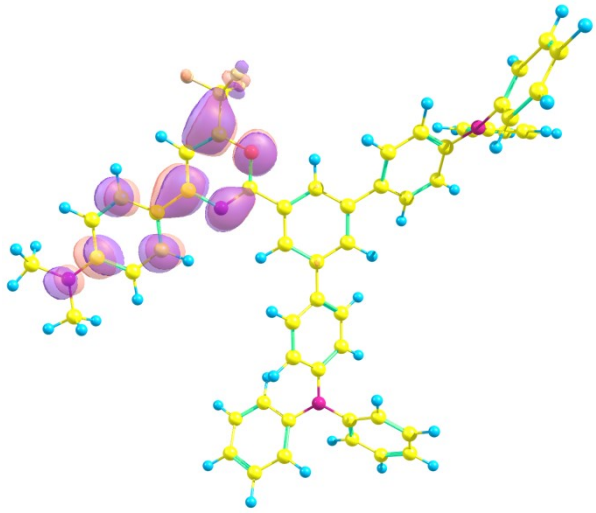
Table S2. Spectral characteristics of the studied push-pull systems in different solvents

	Cyclohexane (ε = 2)			Toluene (ε = 2.4)			Chloroform (ε = 4.5)			Acetonitrile (ε = 38)		
	λ_{abs}, nm	λ_{fl}, nm	φ	λ_{abs}, nm	λ_{fl}, nm	φ	λ_{abs}, nm	λ_{fl}, nm	φ	λ_{abs}, nm	λ_{fl}, nm	φ
7a	376 288 261	411 434	0.85	381	442	0.66	381	480	0.96	380	554	0.024
7b	364 345 292	389 407	0.51	376 346	430	0.34	376 347 293 243	450	0.43	376 343 291 259 234	~560	0.024
7c	369 302 259	385 406	0.57	374 307	426	0.47	373 305 244	446	0.54	375 303 246	527-550	0.1
8a	360 314 247	394 406	0.45	374 315	428	0.50	374 315 242	451	0.18	378 344 310 253	526	0.06
8b	350 242	387 405	0.52	377	427	0.50	377 283 244	447	0.63	380 280	~524	0.10
8c	375 351 311 245	390 405	0.33	380 352 313	431	0.42	350 315 245	456	0.12	381 350 310	502	0.066
9a	368 345	387 406	0.54	379 345 330 294	429	0.49	378 346 331 294 245	450	0.57	379 343	~514	0.088
9b	370 342 293 260	391 410	0.47	382 343 329 294	437	0.42	381 344 295 248	452	0.56	383 341 327 292	~520	0.076
9c	372 355	386 404	0.25	380	430	0.59	380 290 265	447	0.65	381 264	533	0.085

λ_{abs} - absorption maximum; λ_{fl} -fluorescence maximum; φ - quantum yield; ε - permittivity

Table S3. Contour plots of the frontier orbitals of the studied push-pull systems with the largest contributions to the $S_0 \rightarrow S_1$ transition

7a	 HOMO ⟶ LUMO (0.665)	
7b	 HOMO ⟶ LUMO (0.645)	
7c	 HOMO ⟶ LUMO (0.659)	
8a	 HOMO-1 ⟶ LUMO (0.651)	

8b	 HOMO ⟶ LUMO (0.684)	
8c	 HOMO-1 ⟶ LUMO (0.643)	
9a	 HOMO-2 ⟶ LUMO (0.664)	

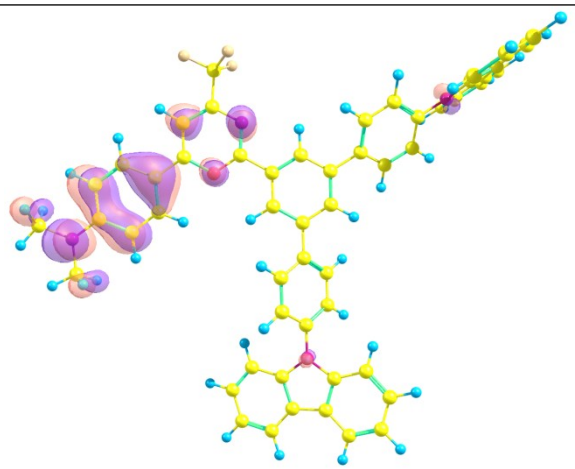
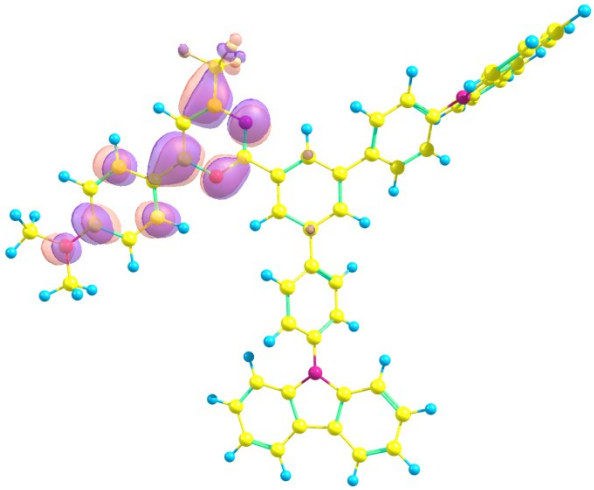
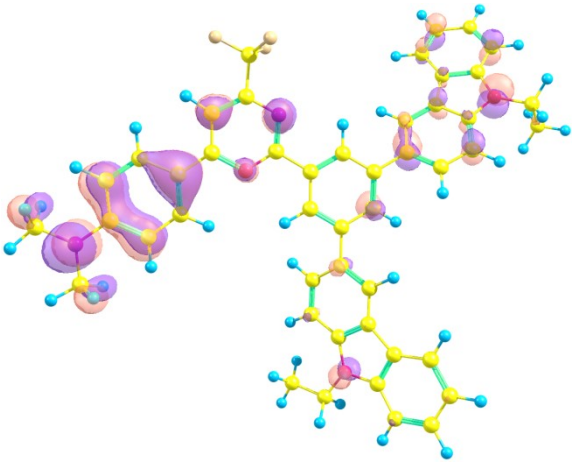
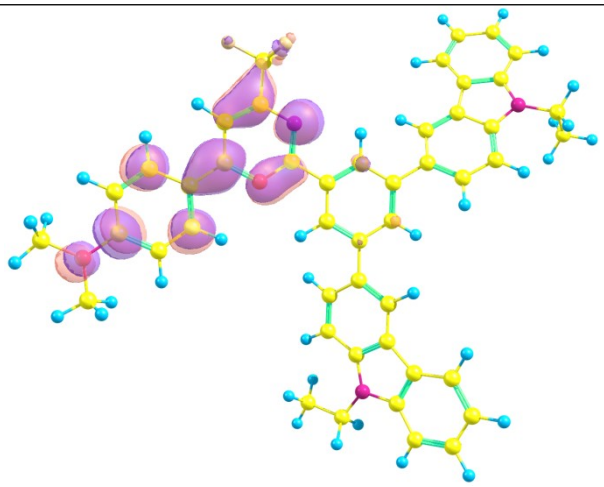
9b	 HOMO ⟶ LUMO (0.664)	
9c	 HOMO-1 ⟶ LUMO (0.560)	

Table S4. External Quantum Efficiency (EQE) of OLEDs based on push-pull systems

	E_ph_avg, 10^{-19} J	L_e, W/m²	J/S, A/m²	EQE
7a	3.80	0.623	6382	0.0001
7b	4.75	0.931	6056	0.0001
7c	5.40	0.757	6765	0.0002
8a	3.70	0.247	1561	0.0002
8b	3.74	1.108	3926	0.0001
8c	3.61	0.146	3807	0.0004
9a	3.94	1.111	4202	0.0003
9b	3.81	2.051	3858	0.0005
9c	3.73	0.997	2516	0.0007

EQE was determined based on measurements of the average photon energy (Eph_avg), current density (J/S), and radiance (Le).

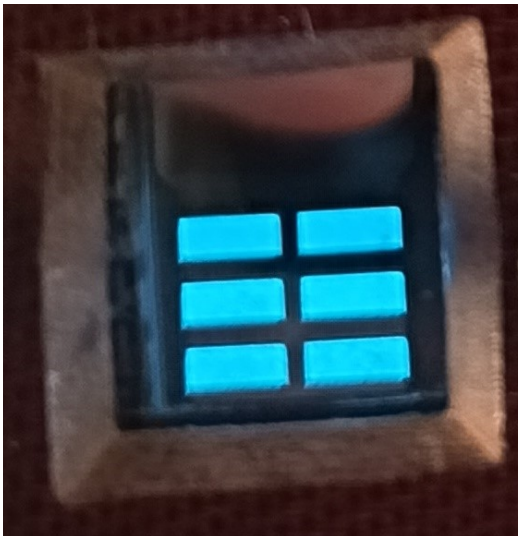


Figure S40. The photo of the emission for device based on the compound **9b**