

Electronic Supporting Information for

Short and modular synthesis of tetraarylsalicylaldehydes

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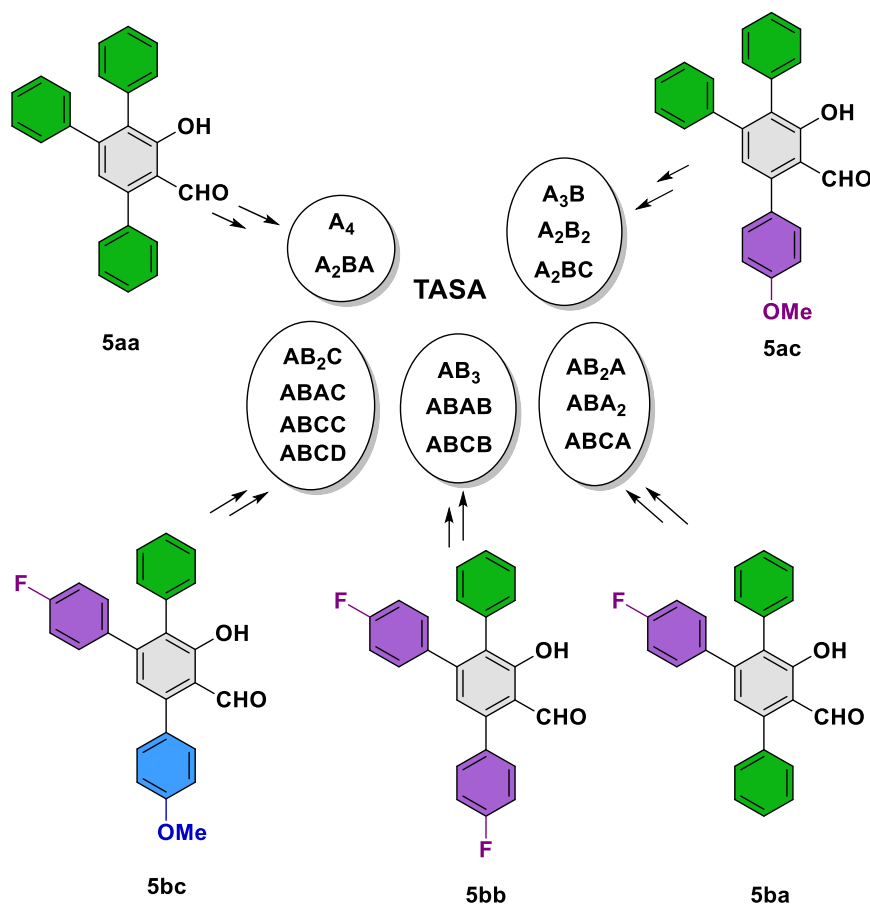
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1 General remarks

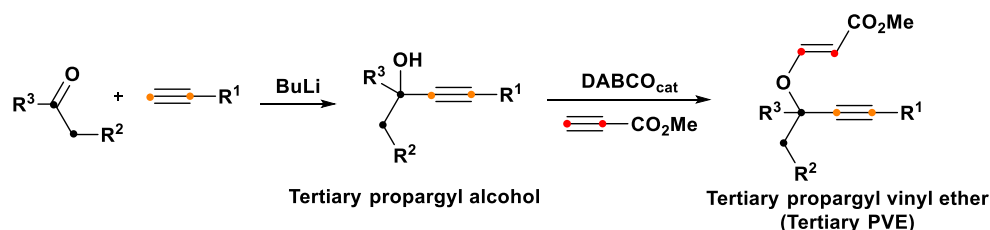
^1H NMR and ^{13}C NMR spectra of CDCl_3 solutions were recorded either at 400 and 100 MHz or at 500 and 125 MHz (Bruker Ac 200 and AMX2-500), respectively. Microwave reactions were conducted in sealed glass vessels (capacity 10 mL) using a CEM Discover microwave reactor. Mass spectra (low resolution) (EI/CI) were obtained with a Hewlett-Packard 5995 gas chromatograph/mass spectrometer. High-resolution mass spectra were recorded with a Micromass Autospec mass spectrometer. Microanalyses were performed with a Fisons Instruments EA 1108 carbon, hydrogen, and nitrogen analyzer. Analytical thin-layer chromatography plates used were E. Merck Brinkman UV-active silica gel (Kieselgel 60 F254) on aluminum. Flash column chromatography was carried out with E. Merck silica gel 60 (particle size less than 0.020 mm) using appropriate mixtures of ethyl acetate and hexanes, or hexanes and dichloromethane as eluents. All reactions were performed in oven-dried glassware. All materials were obtained from commercial suppliers and used as received. The fluorescence spectroscopic studies were performed on a Cary Eclipse Varian spectrofluorimeter (Mulgrave, Victoria, Australia), according to the following protocol: 1 mg of TASA was weighed using a digital scale and dissolved into 1 mL of MeCN. The slit width was fixed to 5 nm for both excitation and emission experiments using a quartz cell for the measurements.



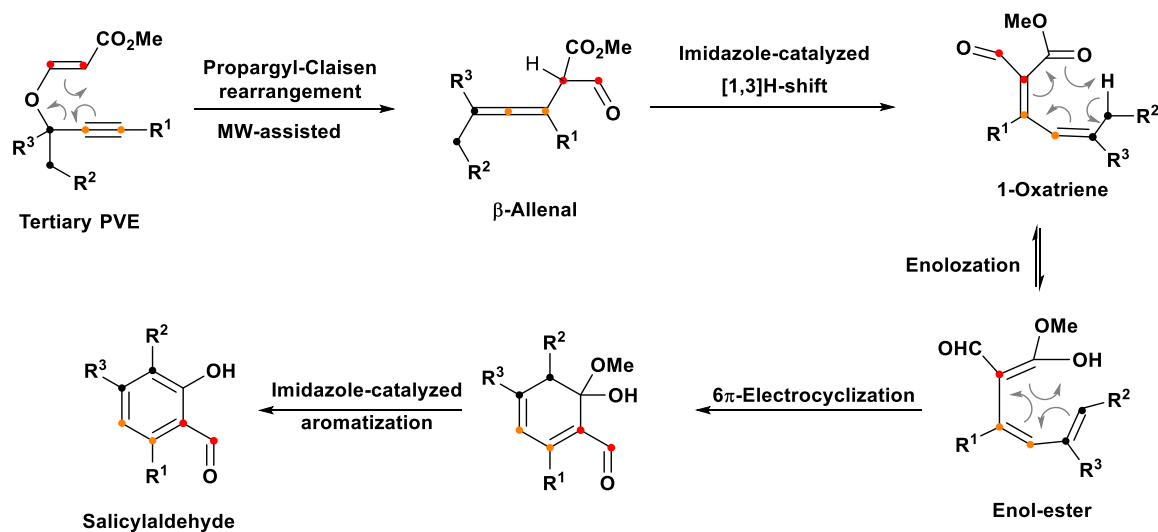
Scheme S1. All possible substitution geometries of tetraarylsalicylaldehydes (TASAs) and their salicylaldehyde precursors.

2 Three-step synthesis of salicylaldehydes from ketones and terminal alkynes.

a) Synthesis of tertiary propargyl vinyl ethers from ketones and terminal alkynes

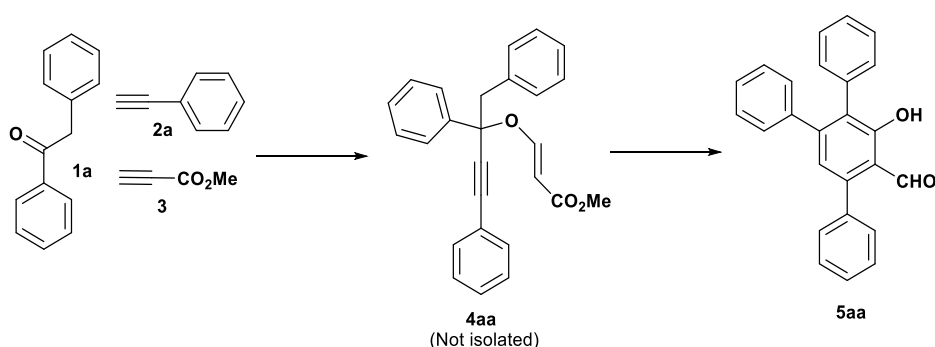


b) Imidazole-catalyzed domino transformation of tertiary propargyl vinyl ethers into salicylaldehydes



Scheme S2.

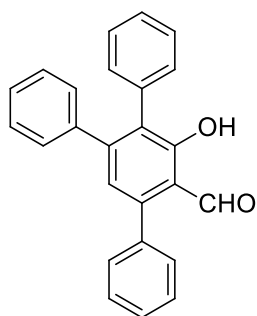
3 General procedure for the synthesis of salicylaldehydes 5.



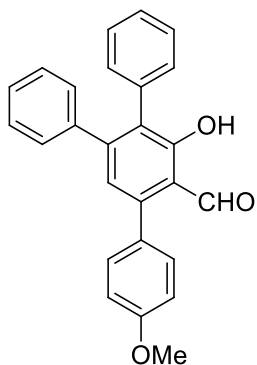
Phenylacetylene (**2a**) (204 mg, 2.0 mmol) was dissolved in 10 mL of dry THF in a round-bottomed flask. After the mixture was cooled to -40°C , a 1.6M solution of $BuLi$ in hexanes (1.54 mL, 2.0 mmol) was added dropwise. The temperature was maintained for 1 hr with stirring of the solution. 2-Phenylacetophenone (**1a**) (196 mg, 1.0 mmol) was then added slowly (dissolved in THF) and the stirring was continued overnight allowing the reaction mixture to warm up to room temperature slowly without additional cooling. After completion, the reaction was quenched with saturated NH_4Cl solution, extracted with CH_2Cl_2 , dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by flash chromatography (silica gel, eluent: n-hexane/EtOAc 90/10 v/v) to yield the corresponding

propargyl alcohol (226 mg, 76%) and **1a** (49 mg, 24%). To a solution of propargyl alcohol (226 mg, 0.76 mmol) in dry CH₂Cl₂ (5 mL) was added DABCO (8.5 mg, 0.076 mmol) and methyl propiolate (**3**) (96 mL, 1.14 mmol) (dropwise addition, 10 minutes) and the reaction mixture was stirred at room temperature for 5 min (TLC control). The solvent was removed under reduced pressure and the crude residue was placed into a sealed microwave vial using dry xylene (1 mL). Imidazole (5.2 mg, 0.076 mmol) was added and the reaction mixture was irradiated for 1 hour in a single-mode microwave oven (200 W, 190 °C). The solvent was evaporated and the crude residue was flash chromatographed (silica gel, eluent: n-hexane/EtOAc, 97/3 v/v) to yield pure salicylaldehyde **5aa** (175.6 mg, 66%).

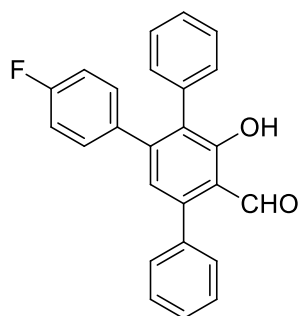
3'-Hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-4'-carbaldehyde 5aa (175.6 mg, 66%). Yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ = 7.04 (s, 1H), 7.13-7.17 (m, 2H), 7.18-7.23 (m, 5H), 7.24-7.30 (m, 3H), 7.48 (m, 5H), 9.94 (s, 1H), 12.45 (s, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 116.9, 123.5, 127.1, 127.4, 127.7 (2C), 127.8 (2C), 128.4, 128.5 (2C), 128.6, 129.5 (2C), 130.1 (2C), 131.1 (2C), 134.9, 137.3, 140.2, 146.3, 149.4, 160.8, 196.9 ppm. IR (CHCl₃, cm⁻¹) 3690.7, 3023.2, 1636.2, 1609.0, 1542.3, 1445.4, 1386.7, 1359.9, 129.1. MS (70 eV): *m/z* (%): 350 (100) [*M*⁺], 332 (7), 331 (10), 215 (12), 181 (7), 105 (6). Elemental analysis calcd (%) for C₂₅H₁₈O₂: C 85.69; H 5.18; found: C 85.77; H 5.50.



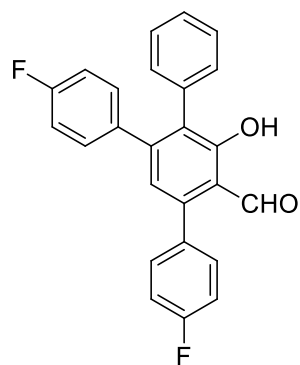
3'-Hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4'-carbaldehyde (5ac) (271.9 mg, 47%). Yellow solid. ¹H NMR (CDCl₃, 500 MHz): δ = 3.90 (s, 3H), 7.03-7.06 (m, 3H), 7.15-7.17 (m, 2H), 7.19-7.24 (m, 5H), 7.26-7.31 (m, 3H), 7.42 (d, 2H, ³*J*(H,H) = 8.6 Hz), 9.97 (s, 1H), 12.46 (s, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 55.4, 114.0 (2C), 117.0, 123.5, 127.0, 127.3, 127.7 (2C), 127.8 (2C), 128.1, 129.5 (2C), 129.6, 131.1 (2C), 131.3 (2C), 135.0, 140.2, 146.0, 149.3, 159.9, 160.8, 197.0 ppm. HRMS (EI-TOF) *m/z*: [*M*⁺] Calcd for C₂₆H₂₀O₃ 403.1310; Found 403.1312.



4-Fluoro-3'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-4'-carbaldehyde (5ba) (111.2 mg, 35%). Yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ = 6.85 (t, 2H, ³*J*(H,H) = 8.6 Hz), 6.97 (s, 1H), 7.06-7.20 (m, 2H), 7.15-7.17 (m, 2H), 7.23-7.29 (m, 3H), 7.44-7.48 (m, 5H), 9.90 (s, 1H), 12.40 (s, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 114.9 (d, 2C, *J*_{CF} = 21.5 Hz), 116.9, 123.4, 127.2, 127.9 (2C), 128.4, 128.5 (2C), 128.6, 130.1 (2C), 131.1 (2C), 131.2 (d, 2C, *J*_{CF} = 8.2 Hz), 134.8, 136.1 (d, *J*_{CF} = 3.1 Hz), 137.2, 146.4, 148.2, 160.8, 162.0 (d, *J*_{CF} = 247.3 Hz), 196.9 ppm. HRMS (EI-TOF) *m/z*: [*M*⁺] Calcd for C₂₅H₁₇FO₂ 391.1105; Found 391.1110.

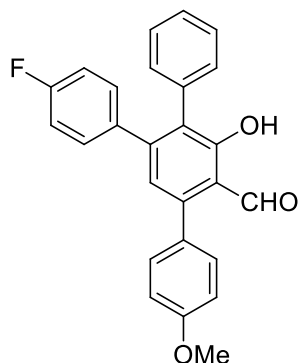


4-Fluoro-5'-(4-fluorophenyl)-3'-hydroxy-[1,1':2',1''-terphenyl]-4'-carbaldehyde (5bb) (137.2 mg, 40%). Yellow solid. ^1H



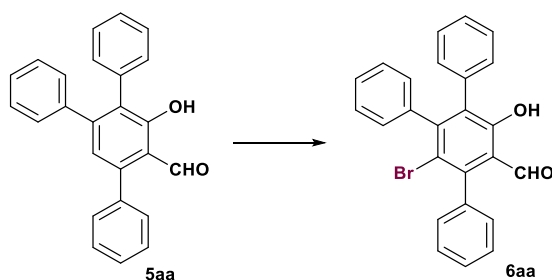
NMR (CDCl_3 , 400 MHz): δ = 6.88 (t, 2H, $^3J(\text{H,H})$ = 8.6 Hz), 6.96 (s, 1H), 7.10 (dd, 2H, $^3J(\text{H,H})$ = 8.4 and 5.7 Hz), 7.17-7.21 (m, 4H), 7.25-7.31 (m, 3H), 7.45 (dd, 2H, $^3J(\text{H,H})$ = 8.4 and 5.7 Hz), 9.90 (s, 1H), 12.43 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 114.9 (d, 2C, J_{CF} = 21.7 Hz), 115.6 (d, 2C, J_{CF} = 21.7 Hz), 116.9, 123.4, 127.3, 128.0 (2C), 128.8, 130.0 (2C), 131.2 (d, 2C, J_{CF} = 8.2 Hz), 131.7 (d, 2C, J_{CF} = 8.2 Hz), 133.2 (d, J_{CF} = 3.3 Hz), 134.6, 136.0 (d, J_{CF} = 3.3 Hz), 145.1, 148.3, 160.9, 162.1 (d, J_{CF} = 249.2 Hz), 162.9 (d, J_{CF} = 248.6 Hz), 196.5 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{25}\text{H}_{16}\text{F}_2\text{O}_2$ 409.1017; Found 409.1016.

4-Fluoro-3'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4'-carbaldehyde (5bc) (189.3 mg, 49%). Yellow solid.



^1H NMR (CDCl_3 , 400 MHz): δ = 3.87 (s, 3H), 6.86 (t, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 6.95 (s, 1H), 7.01 (d, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 7.07-7.10 (m, 2H), 7.15-7.17 (m, 2H), 7.23-7.29 (m, 3H), 7.38 (d, 2H, $^3J(\text{H,H})$ = 8.6 Hz), 9.92 (s, 1H), 12.40 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.4, 114.1 (2C), 114.9 (d, 2C, J_{CF} = 21.8 Hz), 117.1, 123.4, 127.2, 127.9 (2C), 128.2, 129.5, 131.1 (2C), 131.2 (d, 2C, J_{CF} = 8.0 Hz), 131.3 (2C), 134.8 (2C), 136.2 (d, 1C, J_{CF} = 3.8 Hz), 146.1, 148.2, 160.0, 160.8, 162.1 (d, 1C, J_{CF} = 247.2 Hz), 197.0 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{FO}_3$ 421.1216; Found 421.1218.

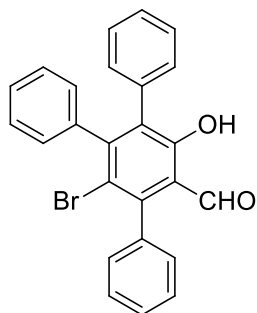
4 General procedure for the synthesis of Bromines 6.



To a stirred solution of Br_2 (227 mg, 1.43 mmol) in CH_2Cl_2 (2 mL) 1 at 0 °C was added dropwise a solution of salicylaldehyde **5aa** (200 mg, 0.57 mmol) in CH_2Cl_2 (3 mL). After stirring at room temperature for 12 h, the reaction mixture was washed with saturated Na_2SO_3 solution until it became colorless, dried over anhydrous MgSO_4 and concentrated. Flash chromatography of the crude reaction residue (silica gel, eluent: *n*-hexane/EtOAc, 97/3 v/v) yielded pure bromine **6aa** as yellow solid (221 mg, 90%).

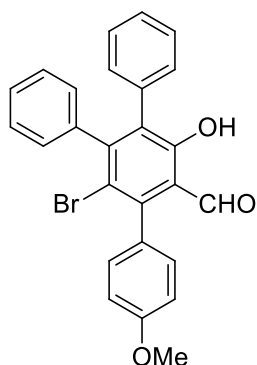
Note: In the case of salicylaldehydes **5ac** and **5bc**, which have an electron rich aromatic substituent, only a slight excess of Br_2 (1.3 equiv.) was used to avoid overbromination.

6'-Bromo-3'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-4'-carbaldehyde (6aa). Yield: 221 mg (90%). Yellow solid. ¹H



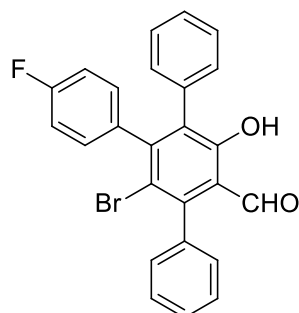
NMR (CDCl₃, 400 MHz): δ = 7.10-7.14 (m, 4H), 7.19-7.25 (m, 6H), 7.40-7.44 (m, 2H), 7.52-7.56 (m, 3H), 9.61 (s, 1H), 12.34 (s, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 116.0, 119.3, 127.0, 127.3, 127.4 (2C), 127.5 (2C), 128.3 (2C), 128.5, 129.5 (2C), 130.0 (2C), 130.4 (2C), 132.2, 134.7, 137.0, 139.9, 146.2, 150.7, 159.3, 197.1 ppm. IR (CHCl₃, cm⁻¹) 3062.7, 3010.1, 2893.4, 1640.9, 1594.0, 1494.6, 1443.9, 1384.0, 1355.6, 1279.3, 1010.3. MS (70 eV): *m/z* (%): 431 (98), 428 (100) [*M*⁺], 349 (20), 331 (39), 289 (28), 215 (30), 213 (13), 165 (19), 151 (16), 150 (10). Elemental analysis calcd (%) for C₂₅H₁₇O₂Br: C 69.94; H 3.99; found: C 69.69; H 4.33.

6'-Bromo-3'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4'-carbaldehyde (6ac) Yield: 184 mg (93%). Yellow



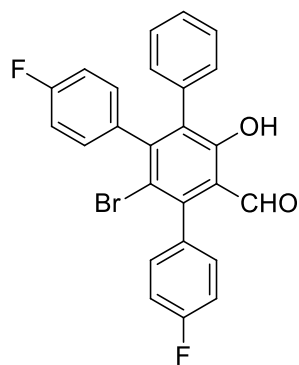
solid. ¹H NMR (CDCl₃, 500 MHz): δ = 3.88 (s, 3H), 7.03-7.09 (m, 6H), 7.14-7.21 (m, 6H), 7.29-7.31 (m, 2H), 7.26-7.31 (m, 3H), 9.61 (s, 1H), 12.27 (s, 1H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ = 55.3, 113.8 (2C), 116.6, 119.7, 127.1, 127.3, 127.5 (2C), 127.6 (2C), 129.2, 129.6 (2C), 130.5 (2C), 131.4 (2C), 132.1, 134.9, 140.1, 146.1, 150.7, 159.4, 159.7, 197.50 ppm. HRMS (EI-TOF) *m/z*: [*M*⁺] Calcd for C₂₆H₁₉O₃Br 481.0415; Found 481.0411.

6'-Bromo-4-fluoro-3'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-4'-carbaldehyde (6ba). Yield: 420 mg (92%). Yellow



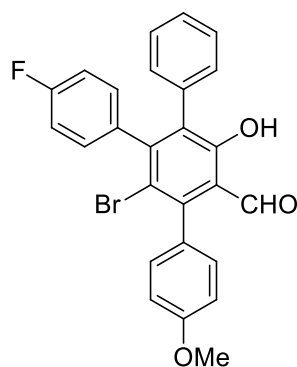
solid. ¹H NMR (CDCl₃, 400 MHz): δ = 6.87 (t, 2H, ³*J*(H,H) = 8.6 Hz), 6.99-7.03 (m, 2H), 7.05 (d, 2H, ³*J*(H,H) = 7.0 Hz), 7.16-7.24 (m, 3H), 7.36 (d, 2H, ³*J*(H,H) = 7.0 Hz), 7.47-7.52 (m, 3H), 9.55 (s, 1H), 12.25 (s, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 114.7 (d, 2C *J*_{CF} = 21.7 Hz), 116.2, 119.5, 127.3, 127.8 (2C), 128.5 (2C), 128.6, 130.1 (2C), 130.4 (2C), 131.4 (d, 2C, *J*_{CF} = 8.6 Hz), 132.5, 134.7, 135.8, (d, 1C *J*_{CF} = 3.5 Hz), 137.1, 146.3, 149.7, 159.4, 159.7, 161.9 (d, 1C, *J*_{CF} = 247.3 Hz), 197.2 ppm. HRMS (EI-TOF) *m/z*: [*M*⁺] Calcd for C₂₅H₁₆BrFO₂ 469.0215; Found 469.0232.

6'-Bromo-4-fluoro-5'-(4-fluorophenyl)-3'-hydroxy-[1,1':2',1''-terphenyl]-4'-carbaldehyde (6bb). Yield: 264 mg (95%).

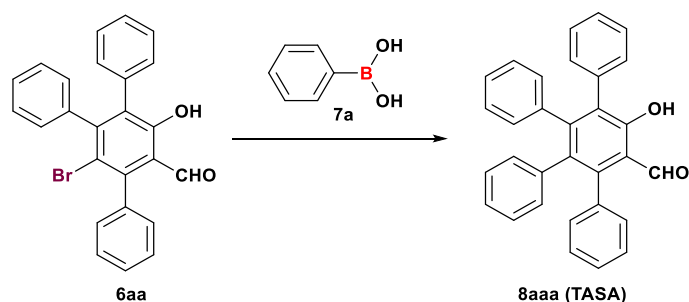


Yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ = 6.88 (t, 2H, ³*J*(H,H) = 8.7 Hz), 7.00 (dd, 2H, ³*J*(H,H) = 8.4 and 5.73 Hz), 7.04-7.06 (m, 2H), 7.17-7.24 (m, 5H), 7.35 (dd, 2H, ³*J*(H,H) = 8.4 and 5.3 Hz), 9.57 (s, 1H), 12.25 (s, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 114.7 (d, 2C *J*_{CF} = 22.3 Hz), 115.6 (d, 2C *J*_{CF} = 21.7 Hz), 116.4, 119.6, 127.3, 127.8 (2C), 130.3 (2C), 131.3 (d, 2C, *J*_{CF} = 8.6 Hz), 131.9 (d, 2C, *J*_{CF} = 8.6 Hz), 132.7, 132.9 (d, *J*_{CF} = 3.6 Hz), 134.6, 135.7 (d, *J*_{CF} = 3.5 Hz), 145.2, 149.8, 159.5, 161.9 (d, *J*_{CF} = 247.3 Hz), 162.7 (d, *J*_{CF} = 249.1 Hz), 196.9 ppm. HRMS (EI-TOF) *m/z*: [*M*⁺] Calcd for C₂₅H₁₅BrF₂O₂ 487.0121; Found 487.0121.

6'-Bromo-4-fluoro-3'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4'-carbaldehyde (6bc). Yield: 120 mg (84%). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.88 (s, 3H), 6.89 (t, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 7.01-7.07 (m, 6H), 7.15-7.22 (m, 3H), 7.29 (d, 2H, $^3J(\text{H,H})$ = 8.6 Hz), 9.61 (s, 1H), 12.28 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.3, 113.8 (2C), 114.6 (d, 2C J_{CF} = 21.7 Hz), 116.7, 119.8, 127.2, 127.7 (2C), 129.1, 130.4 (2C), 131.3 (2C), 131.4 (d, 2C, J_{CF} = 8.0 Hz), 132.2, 134.7, 135.9, (d, J_{CF} = 3.4 Hz), 146.1, 149.6, 159.3, 159.7, 161.8 (d, J_{CF} = 248.4 Hz), 197.4 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{26}\text{H}_{18}\text{BrFO}_3$ 499.0321; Found 499.0324.

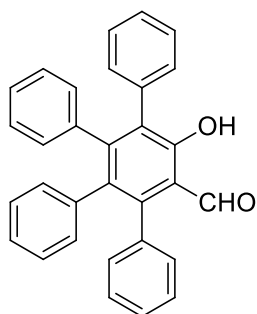


5 General procedure for the synthesis of tetraarylsalicylaldehydes 8

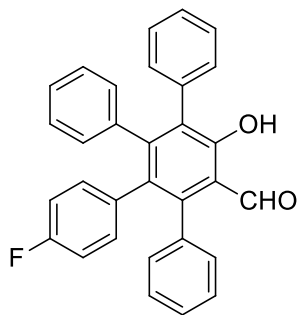


An oven-dried, N_2 -filled, round bottomed flask was charged with bromine **6aa** (100 mg, 0.23 mmol), phenylboronic acid (**7a**) (84.8 mg, 0.70 mmol), Na_2CO_3 (901 mg, 8.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (107 mg, 93 μmol) and DMF (6 mL). The reaction mixture was heated at 90 $^\circ\text{C}$ for 16 h under a nitrogen atmosphere. After cooling to 25 $^\circ\text{C}$, water was added and the aqueous layer was extracted with CH_2Cl_2 . The combined organic phases were dried (MgSO_4) and concentrated in vacuo. Flash chromatography of the crude reaction residue (silica gel, eluent: *n*-hexane/EtOAc, 95/5 v/v) delivered pure **8aaa (A₄)** as a yellow solid (63 mg, 64%, 70% brsm).

4'-Hydroxy-5',6'-diphenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8aaa). Yield: 76.4 mg (64%, 70% brsm). Yellow solid. ^1H NMR (CDCl_3 , 500 MHz): δ = 6.72-6.74 (m, 2H), 6.76-6.78 (m, 2H), 6.83-6.88 (m, 6H), 7.14-7.16 (m, 5H), 7.19-7.22 (m, 5H), 9.70 (s, 1H), 12.42 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 117.8, 125.6, 126.1, 126.7, 126.8 (4C), 127.3, 127.5 (2C), 127.6 (2C), 130.0, 130.4 (2C), 130.8 (2C), 131.0 (2C), 131.5 (2C), 133.4, 135.4, 136.2, 138.5, 139.0, 145.2, 149.8, 159.4, 197.7 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{31}\text{H}_{22}\text{O}_2$ 449.1517; Found 449.1509. Elemental analysis calcd (%) for $\text{C}_{31}\text{H}_{22}\text{O}_2$: C 87.30; H 5.20; found: C 87.30; H 5.36.

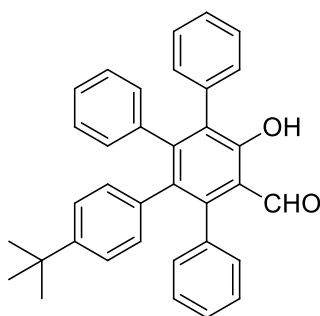


4-Fluoro-4'-hydroxy-5',6'-diphenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8aab). Yield: 48.8 mg (76%, 97% brsm).



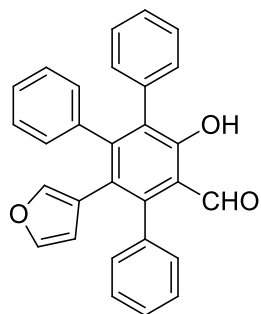
Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 6.44 (t, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 6.56-6.59 (m, 2H), 6.63-6.65 (m, 2H), 6.77-6.79 (m, 3H), 7.02-7.14 (m, 10H), 9.58 (s, 1H), 12.30 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 113.9 (d, 2C, J_{CF} = 21.1 Hz), 117.8, 126.2, 126.8, 127.0 (2C), 127.5, 127.6 (2C), 127.7 (2C), 130.1, 130.4 (2C), 130.8 (2C), 130.9 (2C), 132.3, 132.9 (d, 2C, J_{CF} = 7.5 Hz), 134.5 (d, J_{CF} = 3.3 Hz), 135.3, 136.1, 138.9, 145.3, 149.9, 159.6, 160.7 (d, J_{CF} = 245.1 Hz), 197.7 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{31}\text{H}_{21}\text{O}_2\text{F}$ 467.1423; Found 467.1425.

4-(tert-Butyl)-4'-hydroxy-5',6'-diphenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8aae). Yield: 76.4 mg (50%). Yellow solid.



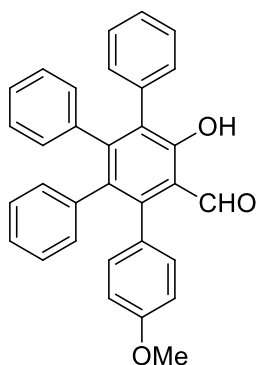
^1H NMR (CDCl_3 , 500 MHz): δ = 1.09 (s, 9H), 6.58-6.60 (m, 2H), 6.72-6.74 (m, 2H), 6.82-6.85 (m, 5H), 7.11-7.15 (m, 5H), 7.17-7.21 (m, 5H), 9.69 (s, 1H), 12.40 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 31.1 (3C), 34.1, 117.8, 123.6 (2C), 125.9, 126.7 (3C), 127.2, 127.4 (2C), 127.5 (2C), 129.8, 130.5 (2C), 130.9 (2C), 131.0 (2C), 131.1 (2C), 133.5, 135.3, 135.6, 136.4, 139.1, 145.3, 148.4, 150.0, 159.3, 197.8, ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{35}\text{H}_{30}\text{O}_2$ 439.1310; Found 439.1305.

6'-(Furan-3-yl)-3'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-4'-carbaldehyde (8aaf). Yield: 76.6 mg (79%). Yellow solid.



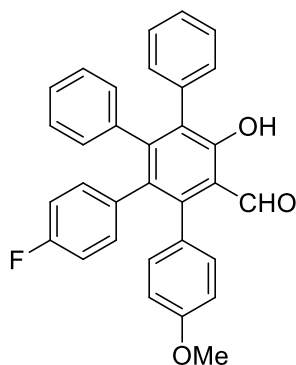
^1H NMR (CDCl_3 , 500 MHz): δ = 5.65-5.66 (m, 1H), 6.56-6.57 (m, 1H), 6.85-6.87 (m, 2H), 6.88 (t, 1H, $^3J(\text{H,H})$ = 1.7 Hz), 6.97-7.00 (m, 3H), 7.11-7.13 (m, 3H), 7.14-7.17 (m, 2H), 7.20-7.22 (m, 2H), 7.27-7.28 (m, 3H), 9.67 (s, 1H), 12.31 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 113.0, 118.0, 122.1, 124.0, 126.5, 126.8, 127.1 (2C), 127.6 (2C), 127.7, 127.8 (2C), 130.1 (2C), 130.3, 130.6 (2C), 130.8 (2C), 135.3, 136.5, 139.2, 141.2, 141.7, 145.9, 150.4, 159.5, 197.7 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{29}\text{H}_{20}\text{O}_3$ 505.2144; Found 505.2142.

4'-Hydroxy-4''-methoxy-5',6'-diphenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8aca). Yield: 53 mg (40%, 58% brsm).



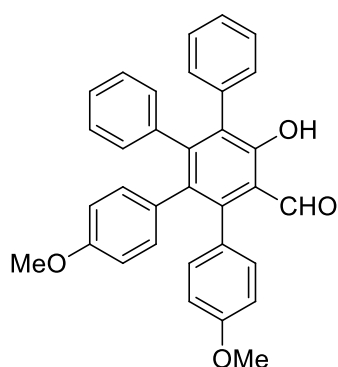
Yellow solid. ^1H NMR (CDCl_3 , 500 MHz): δ = 3.74 (s, 3H), 6.72-6.76 (m, 6H), 6.86-6.88 (m, 6H), 7.03 (d, 1H, $^3J(\text{H,H})$ = 8.3 Hz), 7.12-7.15 (m, 3H), 7.18-7.21 (m, 3H), 9.71 (s, 1H), 12.42 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 55.2, 113.1 (2C), 118.2, 125.6, 126.1, 126.7, 126.8 (2C), 126.9 (2C), 127.6 (2C), 128.4, 129.8, 130.5 (2C), 130.9 (2C), 131.6 (2C), 132.2 (2C), 133.7, 135.6, 135.7, 139.1, 145.0, 149.8, 158.8, 159.5, 198.0 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{32}\text{H}_{24}\text{O}_3$ 479.1623; Found 479.1617.

4-Fluoro-4'-hydroxy-4''-methoxy-5',6'-diphenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8acb). Yield: 51.5 mg (44%,



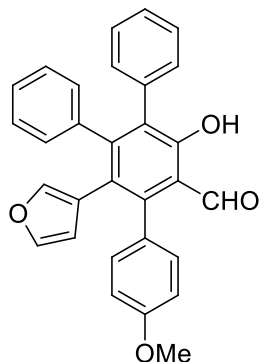
78% brsm). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.77 (s, 3H), 6.57 (t, 2H, $^3J(\text{H,H})$ = 8.8 Hz), 6.66-6.70 (m, 2H), 6.72-6.76 (m, 4H), 6.88-6.89 (m, 3H), 7.02 (d, 2H, $^3J(\text{H,H})$ = 8.8 Hz), 7.11-7.21 (m, 5H), 9.71 (s, 1H), 12.42 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.2, 113.2 (2C), 114.9 (d, 2C, J_{CF} = 21.3 Hz), 118.1, 126.2, 126.8, 126.9 (2C), 127.5 (2C), 128.2, 129.8, 130.3 (2C), 130.8 (2C), 132.1 (2), 132.5, 132.9 (d, 2C, J_{CF} = 7.9 Hz), 134.7 (d, J_{CF} = 3.5 Hz), 135.4, 139.0, 145.1, 149.9, 158.8, 159.5, 160.7 (d, J_{CF} = 243.9 Hz), 197.8 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{32}\text{H}_{23}\text{O}_3\text{F}$ 497.1529; Found 497.1526.

4'-Hydroxy-4,4''-dimethoxy-5',6'-diphenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8acc) Yield: 35 mg (43%, 69% brsm).



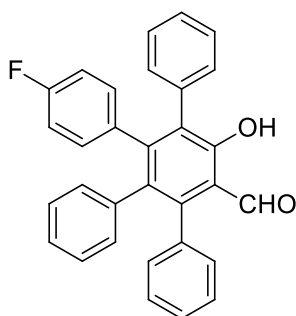
Yellow solid. ^1H NMR (CDCl_3 , 500 MHz): δ = 3.60 (s, 3H), 3.76 (s, 3H), 6.40 (d, 2H, $^3J(\text{H,H})$ = 8.8 Hz), 6.61 (d, 2H, $^3J(\text{H,H})$ = 8.8 Hz), 6.73-6.75 (m, 4H), 6.86-6.88 (m, 3H), 7.02 (d, 2H, $^3J(\text{H,H})$ = 8.8 Hz), 7.11-7.14 (m, 3H), 7.17-7.19 (m, 2H), 9.69 (s, 1H), 12.38 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 54.9, 55.2, 112.4 (2C), 113.1 (2C), 118.2, 126.0, 126.7, 126.8 (2C), 127.5 (2C), 128.6, 129.7, 130.4 (2C), 130.9 (2C), 131.0, 132.2 (2C), 132.5 (2C), 133.2, 135.6, 139.3, 145.3, 150.1, 157.2, 158.7, 159.3, 198.0 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{33}\text{H}_{26}\text{O}_4$ 502.1729; Found 502.1730.

6'-(Furan-3-yl)-3'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4'-carbaldehyde (8acf). Yield: 52.1 mg (53%,



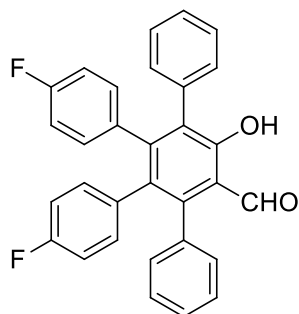
62% brsm). Yellow solid. Melting point: 197-198°C. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.81 (s, 3H), 5.65 (s, 1H), 6.56 (s, 1H), 6.84 (m, 4H), 6.93 (t, 1H, $^3J(\text{H,H})$ = 1.7 Hz), 6.97-6.99 (m, 3H), 7.09-7.13 (m, 4H), 7.15-7.21 (m, 3H), 9.71 (s, 1H), 12.38 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.2, 113.1, 113.3 (2C), 118.4, 122.2, 124.3, 126.5, 126.8, 127.1 (2C), 127.6 (2C), 128.6, 130.0, 130.1 (2C), 130.8 (2C), 131.9 (2C), 135.4, 139.3, 141.3, 141.7, 145.8, 150.4, 159.2, 159.6, 197.9 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{30}\text{H}_{22}\text{O}_4$ 469.1416; Found 469.1413.

6'-(4-Fluorophenyl)-4'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8baa). Yield: 56 mg (57%). Yellow



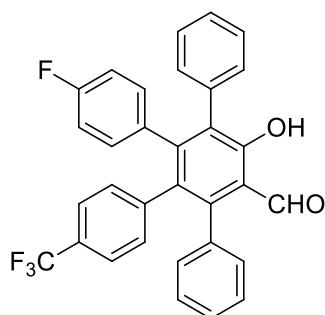
solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 6.57 (t, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 6.70-6.74 (m, 4H), 6.86-6.88 (m, 3H), 7.12-7.14 (m, 4H), 7.17-7.26 (m, 6H), 9.69 (s, 1H), 12.42 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 113.9 (d, 2C, J_{CF} = 21.3 Hz), 117.8, 125.8, 126.9, 127.0 (2C), 127.4, 127.6 (2C), 127.7 (2C), 130.1, 130.8 (2C), 130.9 (2C), 131.4 (2C), 132.0 (d, 2C, J_{CF} = 7.9 Hz), 133.4, 134.9 (d, J_{CF} = 3.6 Hz), 135.3, 136.1, 138.4, 145.2, 148.6, 159.4, 161.0 (d, J_{CF} = 247.0 Hz), 191.7 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{31}\text{H}_{21}\text{FO}_2$ 467.1423; Found 467.1423.

4-Fluoro-6'-(4-fluorophenyl)-4'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8bab). Yield: 40 mg (41%,



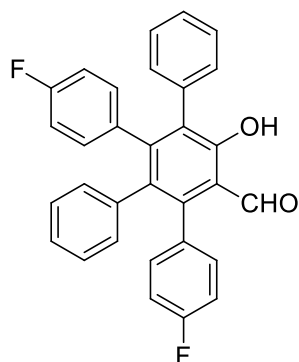
81% brsm). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 6.55-6.62 (m, 4H), 6.65-6.72 (m, 4H), 7.10-7.12 (m, 4H), 7.17-7.23 (m, 6H), 9.68 (s, 1H), 12.41 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 114.0 (d, 2C, J_{CF} = 21.3 Hz), 114.1 (d, 2C, J_{CF} = 21.2 Hz), 117.9, 126.9, 127.5, 127.7 (2C), 127.8 (2C), 130.2, 130.7 (2C), 130.8 (2C), 131.9 (d, 2C, J_{CF} = 8.1 Hz), 132.3, 132.8 (d, 2C, J_{CF} = 8.1 Hz), 134.3 (d, J_{CF} = 3.7 Hz), 134.8 (d, J_{CF} = 3.5 Hz), 135.1, 135.9, 145.4, 148.7, 159.5, 160.8 (d, J_{CF} = 245.4 Hz), 161.0 (d, J_{CF} = 246.0 Hz), 197.6 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{31}\text{H}_{20}\text{F}_2\text{O}_2$ 485.1329; Found 485.1328.

6'-(4-Fluorophenyl)-4'-hydroxy-5'-phenyl-4-(trifluoromethyl)-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8bad). Yield: 50



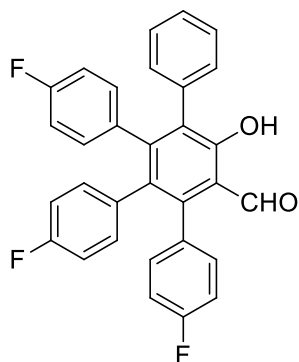
mg (46%, 70% brsm). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 6.59 (t, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 6.68-6.71 (m, 2H), 6.84 (d, 2H, $^3J(\text{H,H})$ = 8.1 Hz), 7.09-7.15 (m, 6H), 7.17-7.22 (m, 6H), 9.68 (s, 1H), 12.44 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 114.2 (d, 2C, J_{CF} = 21.5 Hz), 117.9, 123.9 (q, 2C, J_{CF} = 3.6 Hz), 124.0 (q, J_{CF} = 270.3 Hz), 127.0, 127.7 (q, 2C, J_{CF} = 31.4 Hz), 127.8, 127.9 (2C), 132.0 (d, J_{CF} = 8.1 Hz), 130.5, 130.7 (2C), 130.8 (2C), 131.8 (2C), 132.0 (d, 2C, J_{CF} = 8.1 Hz), 134.5 (d, J_{CF} = 3.5 Hz), 135.0, 135.5, 142.5, 145.2, 148.3, 159.9, 161.2 (d, J_{CF} = 246.5 Hz), 197.5 ppm. One carbon signal buried under the aromatic region. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{32}\text{H}_{20}\text{F}_4\text{O}_2$ 535.1297; Found 535.1293.

4''-Fluoro-6'-(4-fluorophenyl)-4'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8bba). Yield: 37.5 mg



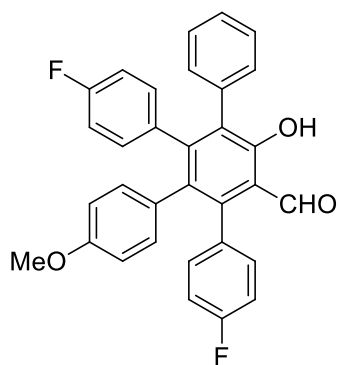
(37%, 46% brsm). Yellow solid. ^1H NMR (CDCl_3 , 500 MHz): δ = 6.57 (t, 2H, $^3J(\text{H,H})$ = 8.6 Hz), 6.68-6.72 (m, 4H), 6.68-6.92 (m, 5H), 7.08-7.12 (m, 4H), 7.16-7.18 (m, 1H), 7.20-7.23 (m, 2H), 9.69 (s, 1H), 12.39 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 113.9 (d, 2C, J_{CF} = 21.1 Hz), 114.7 (d, 2C, J_{CF} = 21.8 Hz), 117.9, 125.9, 126.9, 127.1 (2C), 127.7 (2C), 127.8, 130.4 (d, J_{CF} = 4.3 Hz), 130.8 (2C), 131.4 (2C), 132.0 (d, 2C, J_{CF} = 8.2 Hz), 132.5 (d, 2C, J_{CF} = 8.0 Hz), 133.7, 134.9 (d, J_{CF} = 3.4 Hz), 135.2, 138.2, 144.0, 148.8, 159.5, 161.0 (d, J_{CF} = 245.3 Hz), 161.9 (d, J_{CF} = 248.5 Hz), 197.3 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{31}\text{H}_{20}\text{F}_2\text{O}_2$ 485.1329; Found 485.1329.

4,4''-Difluoro-6'-(4-fluorophenyl)-4'-hydroxy-5'-phenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8bbb). Yield: 26 mg



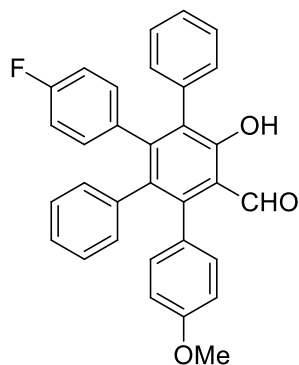
(33%, 81% brsm). Yellow solid. ^1H NMR (CDCl_3 , 500 MHz): δ = 6.58-6.62 (m, 4H), 6.63-6.66 (m, 2H), 6.67-6.70 (m, 2H), 6.93 (t, 2H, $^3J(\text{H,H})$ = 8.5 Hz), 7.07-7.10 (m, 4H), 7.17-7.23 (m, 3H), 9.68 (s, 1H), 12.39 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 114.2 (d, 2C, J_{CF} = 21.5 Hz), 114.3 (d, 2C, J_{CF} = 21.5 Hz), 114.9 (d, 2C, J_{CF} = 21.5 Hz), 118.0, 127.0, 127.8 (2C), 130.6, 130.7 (2C), 131.9, 132.0 (d, 2C, J_{CF} = 8.2 Hz), 132.5 (d, 2C, J_{CF} = 8.2 Hz), 132.6, 132.8 (d, 2C, J_{CF} = 8.2 Hz), 134.3 (d, J_{CF} = 3.4 Hz), 134.8 (d, J_{CF} = 4.1 Hz), 135.0 (d, J_{CF} = 6.0 Hz), 144.2, 148.9, 159.7, 160.9 (d, J_{CF} = 247.5 Hz), 161.1 (d, J_{CF} = 247.5 Hz), 162.0 (d, J_{CF} = 248.5 Hz), 197.3 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{31}\text{H}_{19}\text{F}_3\text{O}_2$ 503.1235; Found 503.1230.

4''-Fluoro-6'-(4-fluorophenyl)-4'-hydroxy-4-methoxy-5'-phenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8bbc). Yield:



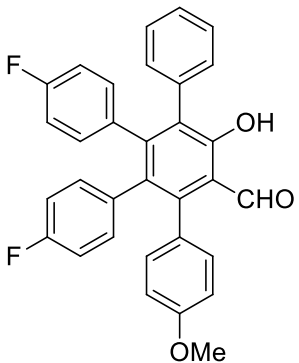
63 mg (84%). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.63 (s, 3H), 6.44 (d, 2H, $^3J(\text{H,H})$ = 8.6 Hz), 6.57-6.61 (m, 4H), 6.70 (dd, 2H, $^3J(\text{H,H})$ = 8.6 and 5.5 Hz), 6.92 (t, 2H, $^3J(\text{H,H})$ = 8.6 Hz), 7.08-7.12 (m, 4H), 7.17-7.25 (m, 3H), 9.68 (s, 1H), 12.39 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 54.9, 112.6 (2C), 114.0 (d, 2C, J_{CF} = 21.6 Hz), 114.7 (d, 2C, J_{CF} = 21.6 Hz), 117.9, 126.9, 127.7 (2C), 130.3, 130.4, 130.7 (2C), 131.9 (d, 2C, J_{CF} = 8.1 Hz), 132.2 (d, J_{CF} = 3.4 Hz), 132.4 (2C), 132.5 (d, 2C, J_{CF} = 8.0 Hz), 133.3, 135.0 (d, J_{CF} = 3.4 Hz), 135.3, 144.3, 149.1, 157.4, 159.4, 161.0 (d, J_{CF} = 246.2 Hz), 161.9 (d, J_{CF} = 247.9 Hz), 197.4 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{F}_2\text{O}_3$ 515.1435; Found 515.1436.

6'-(4-Fluorophenyl)-4'-hydroxy-4''-methoxy-5'-phenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8bca). Yield: 25.9 mg



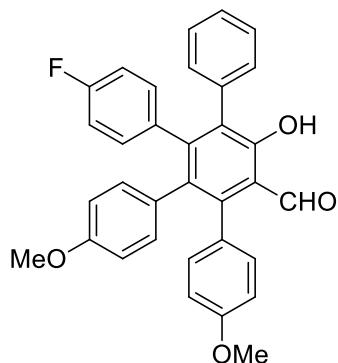
(85%). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.74 (s, 3H), 6.56 (t, 2H, $^3J(\text{H,H})$ = 8.8 Hz), 6.68-6.73 (m, 6H), 6.87-6.90 (m, 3H), 7.02 (d, 2H, $^3J(\text{H,H})$ = 8.5 Hz), 7.10-7.11 (m, 2H), 7.15-7.24 (m, 3H), 9.70 (s, 1H), 12.40 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.1, 113.1 (2C), 113.9 (d, 2C, J_{CF} = 21.7 Hz), 118.2, 125.7, 126.8, 127.0 (2C), 127.7 (2C), 128.2, 129.9, 130.8 (2C), 131.5 (2C), 132.0 (d, 2C, J_{CF} = 8.0 Hz), 132.2 (2C), 133.7, 135.1 (d, J_{CF} = 3.2 Hz), 135.4, 138.6, 145.1, 148.6, 158.8, 159.4, 161.0 (d, J_{CF} = 246.4 Hz), 197.9 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{32}\text{H}_{23}\text{FO}_3$ 497.1529; Found 497.1523.

4-Fluoro-6'-(4-fluorophenyl)-4'-hydroxy-4''-methoxy-5'-phenyl-[1,1':2',1''-terphenyl]-3' carbaldehyde (8bcb). Yield:



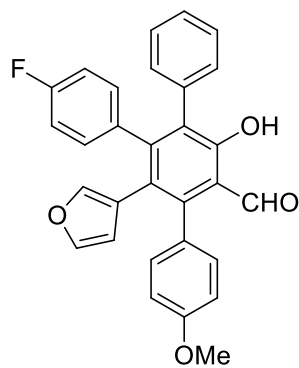
39 mg (52%, 90% brsm). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.77 (s, 3H), 6.57-6.62 (m, 4H), 6.65-6.71 (m, 4H), 6.75 (d, 2H, $^3J(\text{H,H})$ = 8.2 Hz), 7.01 (d, 2H, $^3J(\text{H,H})$ = 8.5 Hz), 7.09-7.11 (m, 2H), 7.16-7.23 (m, 3H), 9.71 (s, 1H), 12.41 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.2, 113.2 (2C), 114.0 (d, 2C, J_{CF} = 21.6 Hz), 114.1 (d, 2C, J_{CF} = 21.1 Hz), 118.2, 126.9, 127.7 (2C), 128.0, 130.0, 130.8 (2C), 131.9 (d, 2C, J_{CF} = 8.2 Hz), 132.1 (2C), 132.6, 132.9 (d, 2C, J_{CF} = 7.9 Hz), 134.5 (d, J_{CF} = 3.4 Hz), 134.9 (d, J_{CF} = 3.4 Hz), 135.2, 145.2, 148.7, 158.9, 159.6, 160.8 (d, J_{CF} = 245.7 Hz), 161.1 (d, J_{CF} = 246.4 Hz), 197.8 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{32}\text{H}_{22}\text{F}_2\text{O}_4$ 515.1435; Found 515.1440.

6'-(4-Fluorophenyl)-4'-hydroxy-4,4''-dimethoxy-5'-phenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (8bcc). Yield: 33 mg



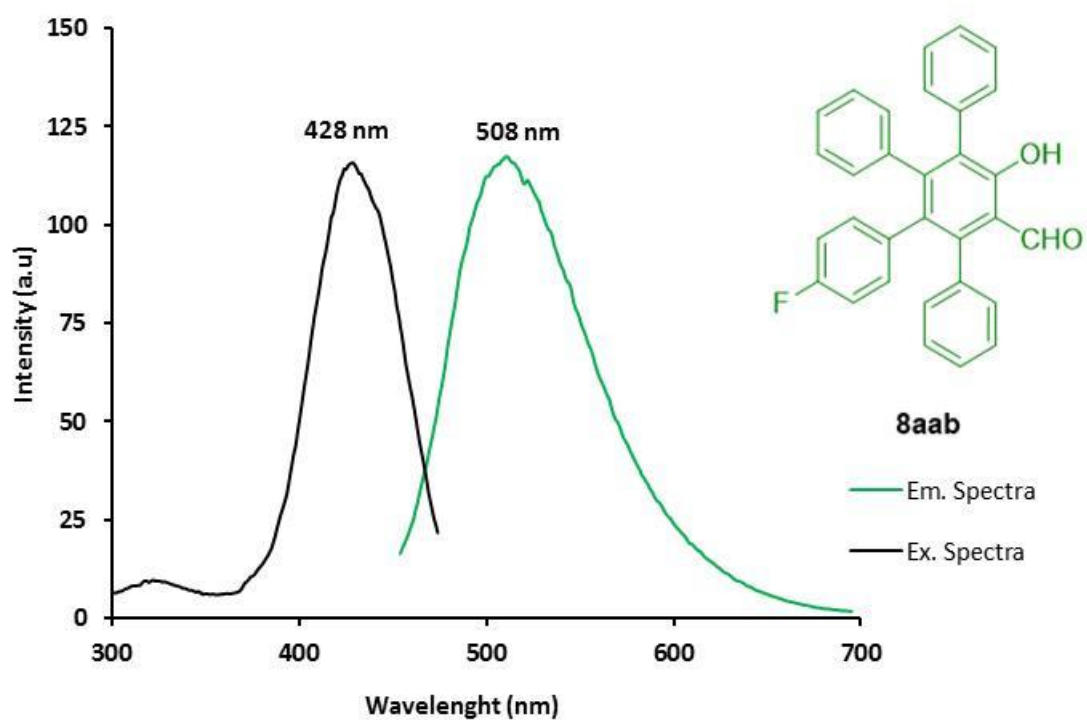
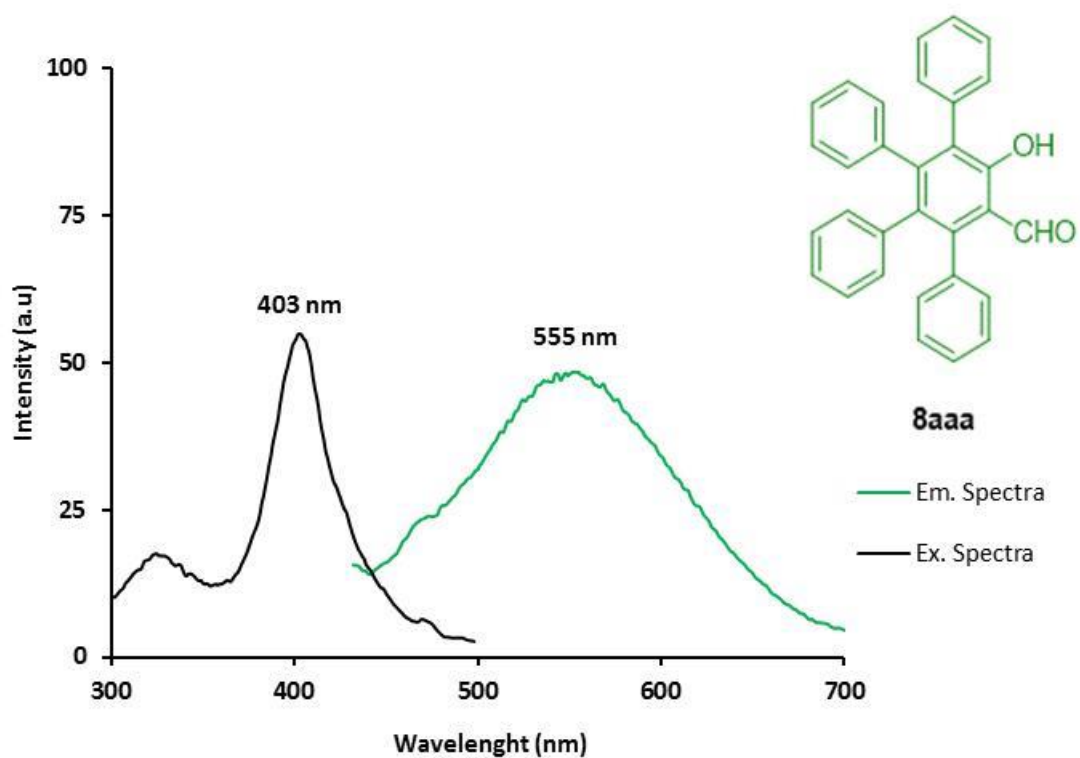
(50%). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.62 (s, 3H), 3.76 (s, 3H), 6.43 (d, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 6.55-6.60 (m, 4H), 6.68-6.71 (m, 2H), 6.74 (d, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 7.02 (d, 2H, $^3J(\text{H,H})$ = 8.7 Hz), 7.08-7.11 (m, 2H), 7.17-7.22 (m, 3H), 9.96 (s, 1H), 12.38 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 54.9, 55.2, 112.5 (2C), 113.1 (2C), 114.0 (d, 2C, J_{CF} = 21.5 Hz), 118.2, 126.8, 127.6 (2C), 128.4, 129.8, 130.8 (3C), 132.0 (d, 2C, J_{CF} = 8.1 Hz), 132.1 (2C), 132.4 (2C), 133.3, 135.2 (d, J_{CF} = 3.4 Hz), 135.5, 145.3, 149.0, 157.3, 158.7, 159.3, 161.0 (d, J_{CF} = 244.5 Hz), 197.9 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{33}\text{H}_{25}\text{FO}_4$ 527.1635; Found 527.1637.

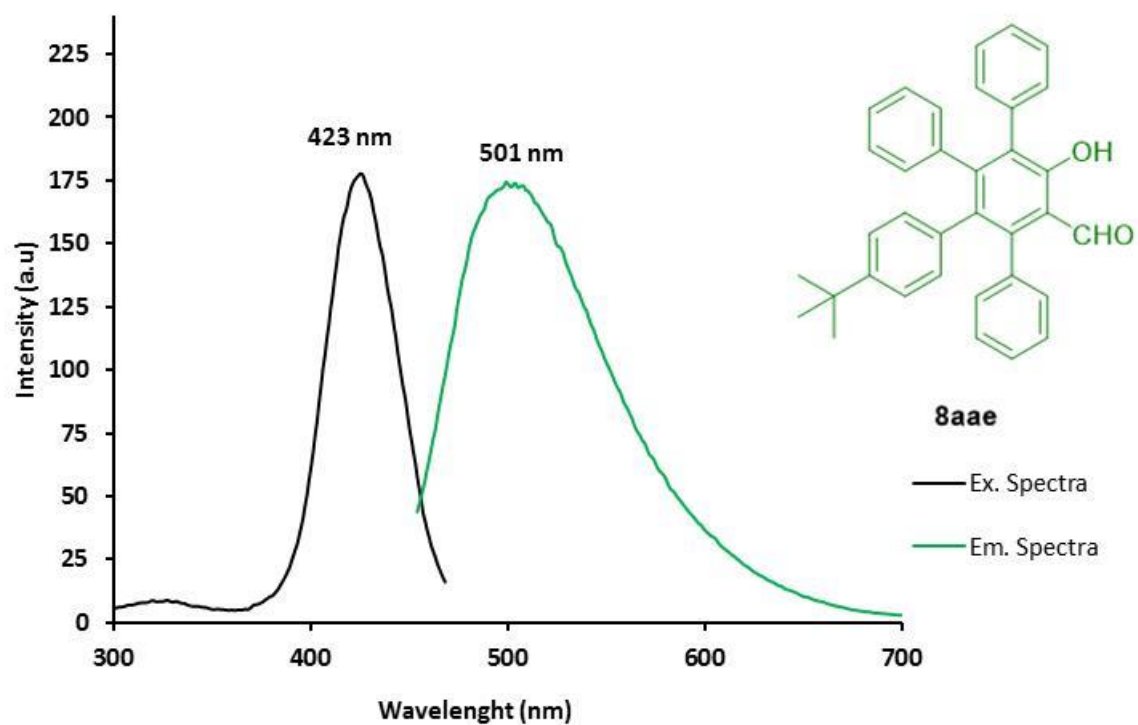
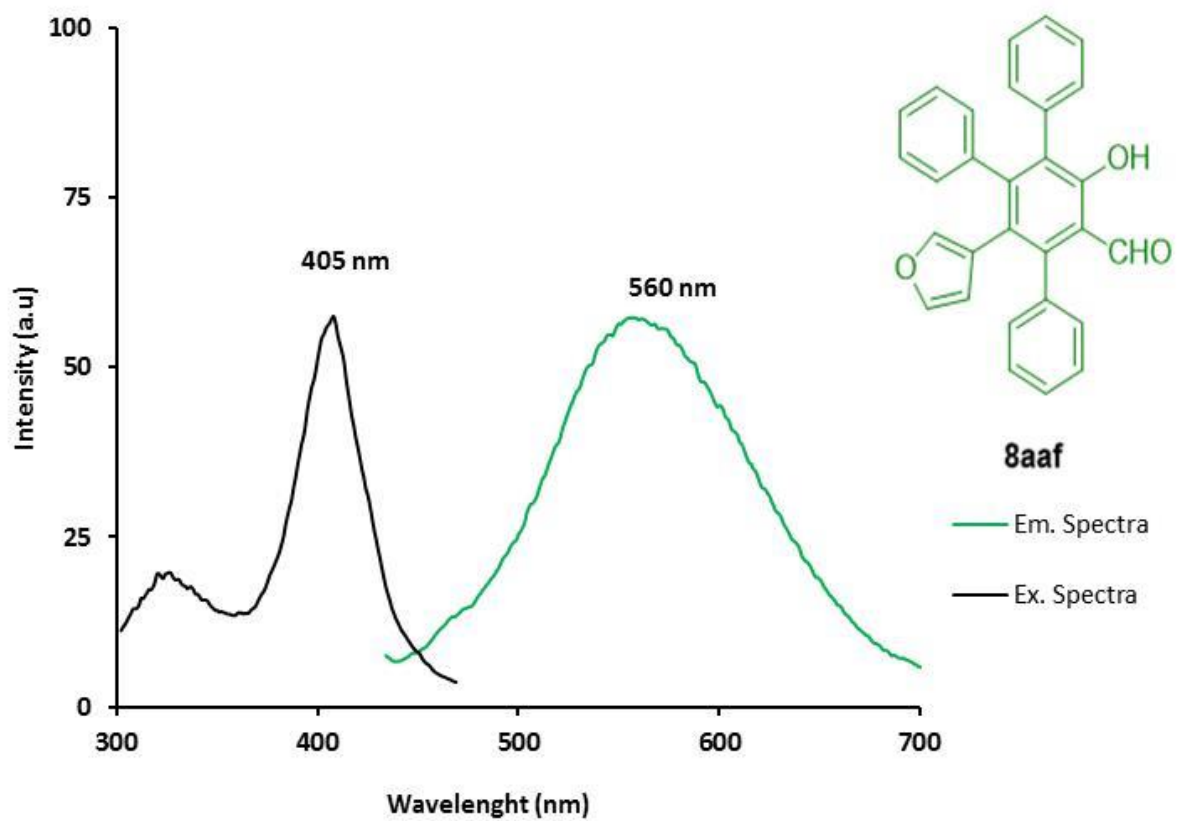
4-Fluoro-6'-(furan-3-yl)-3'-hydroxy-5'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4'-carbaldehyde (8bcf). Yield: 54.8 mg

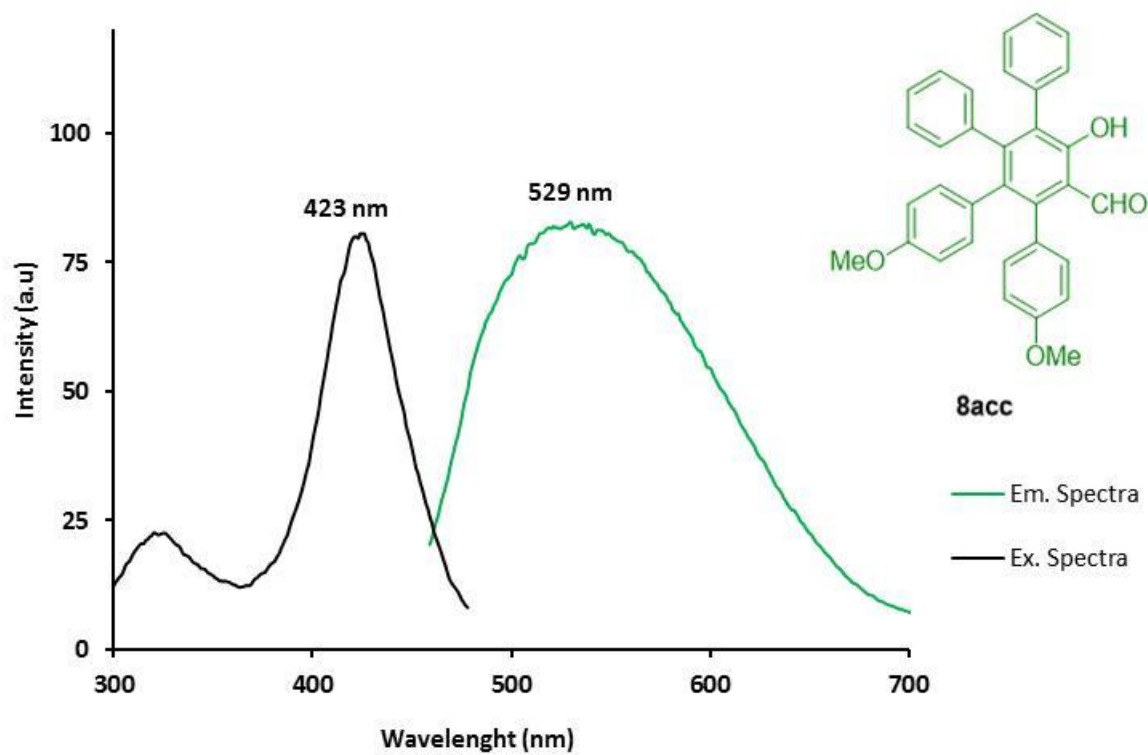
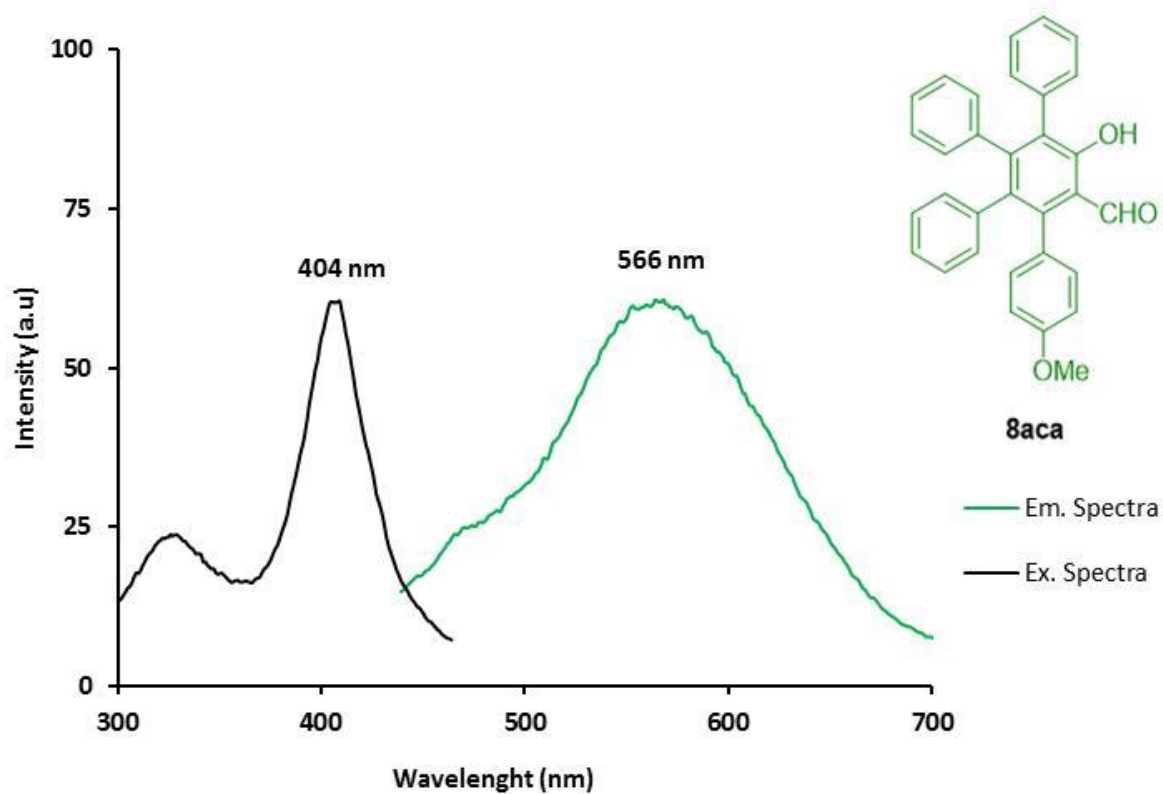


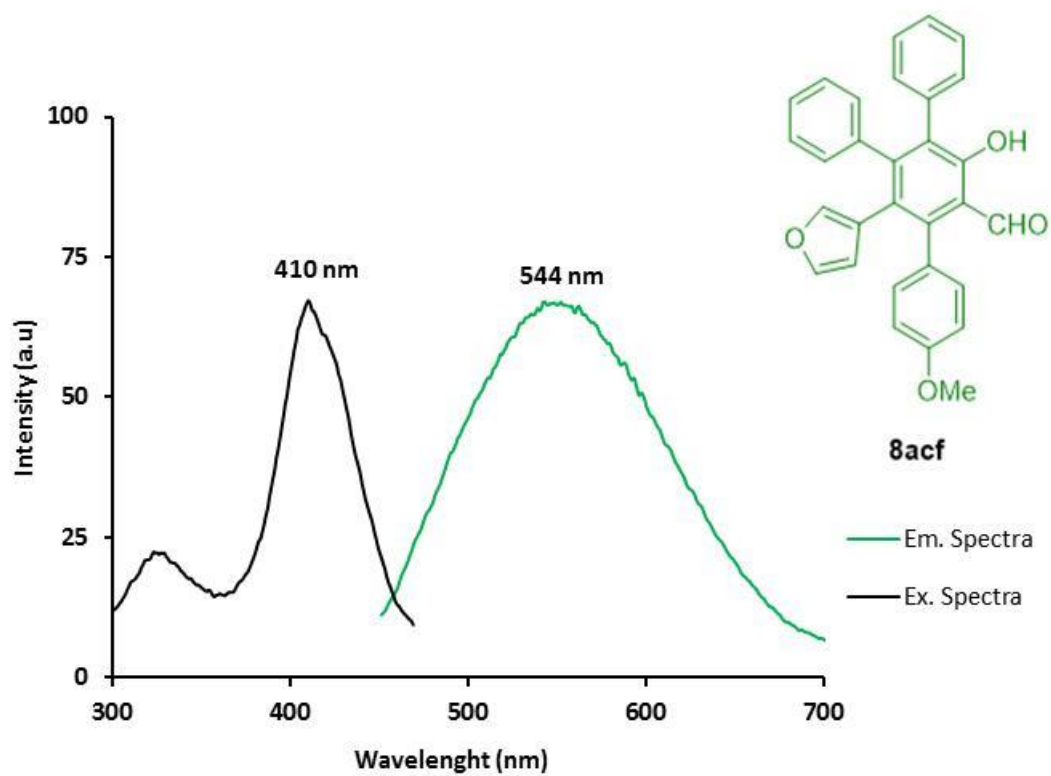
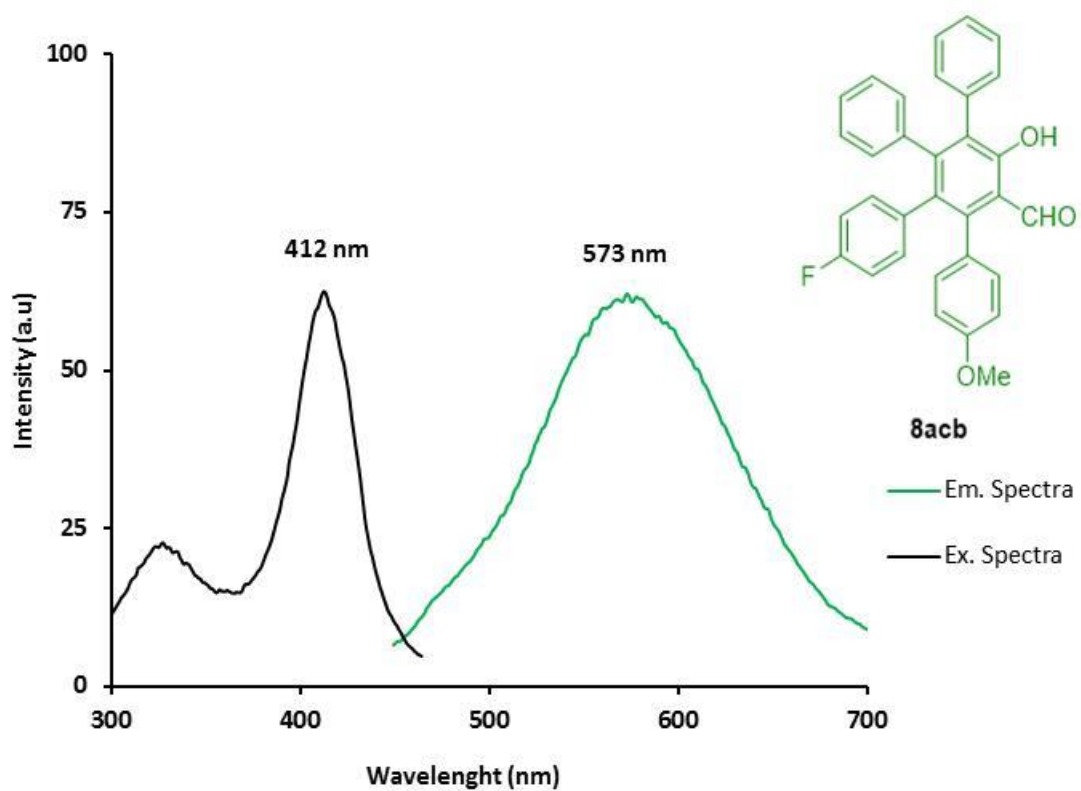
(73%). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.81 (s, 3H), 5.66 (s, 1H), 6.58 (s, 1H), 6.68 (t, 2H, $^3J(\text{H,H})$ = 8.8 Hz), 6.80-6.86 (m, 4H), 6.97 (s, 1H), 7.08-7.13 (m, 4H), 7.17-7.25 (m, 3H), 9.71 (s, 1H), 12.40 (s, 1H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.2, 113.0, 113.3 (2C), 114.1 (d, 2C, J_{CF} = 21.4 Hz), 118.4, 122.1, 124.3, 126.9, 127.7 (2C), 128.4, 130.2, 130.7 (2C), 131.7 (d, 2C, J_{CF} = 8.3 Hz), 131.8 (2C), 135.2 (d, J_{CF} = 3.5 Hz), 135.3, 141.5, 141.6, 145.9, 149.2, 159.1, 159.5, 161.3 (d, J_{CF} = 246.3 Hz), 197.8 ppm. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{30}\text{H}_{21}\text{FO}_4$ 487.1322; Found 487.1324.

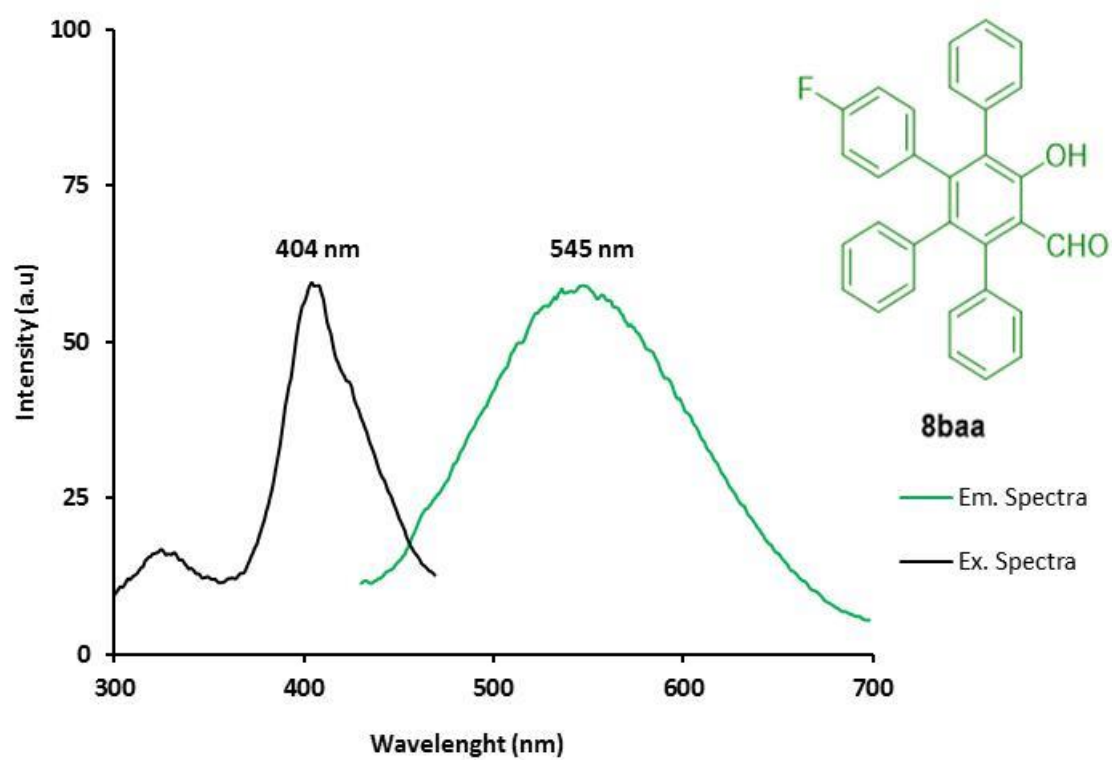
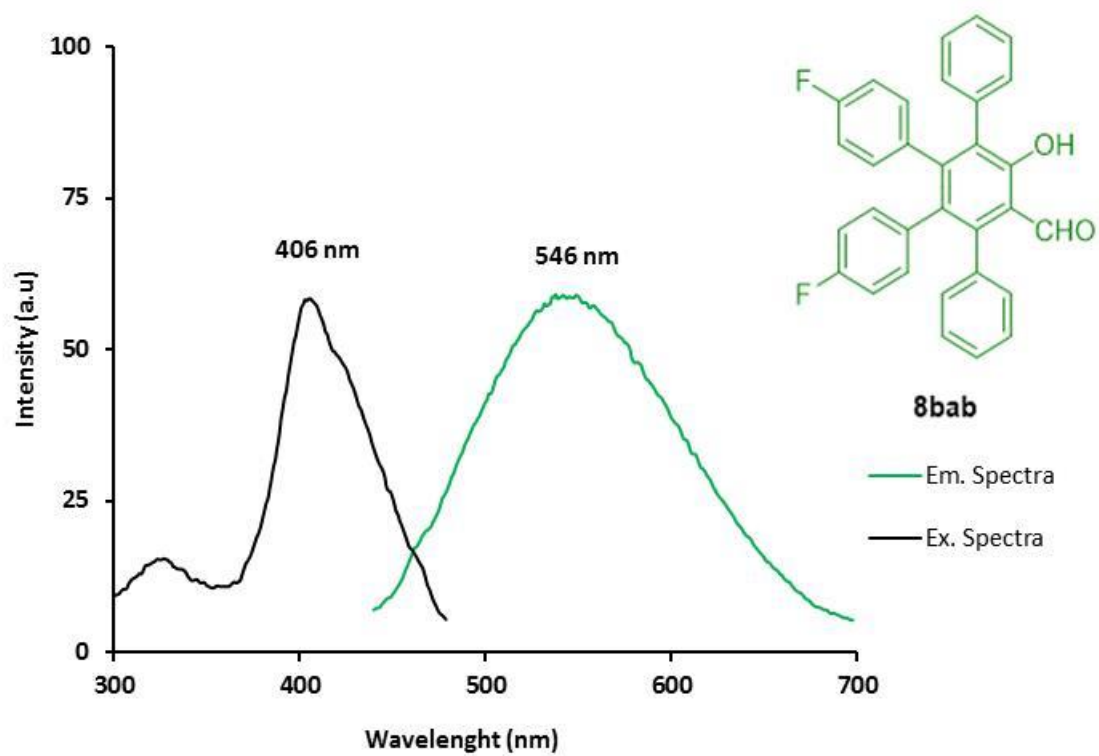
6 Fluorescence spectra of tetraarylsalicylaldehydes 8

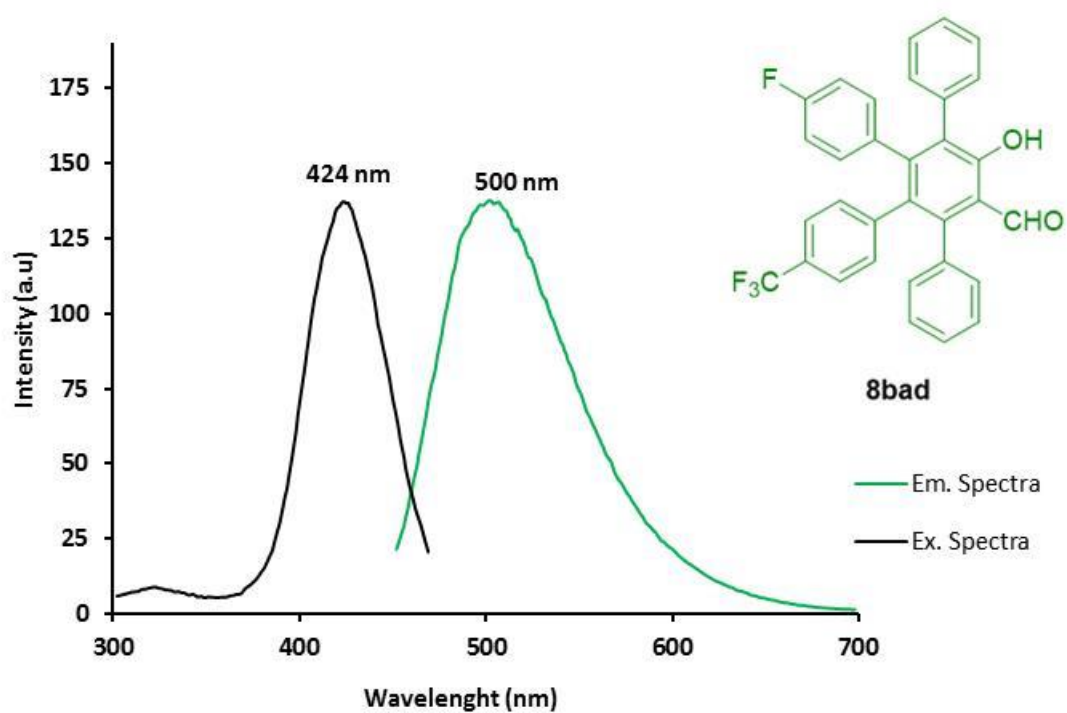
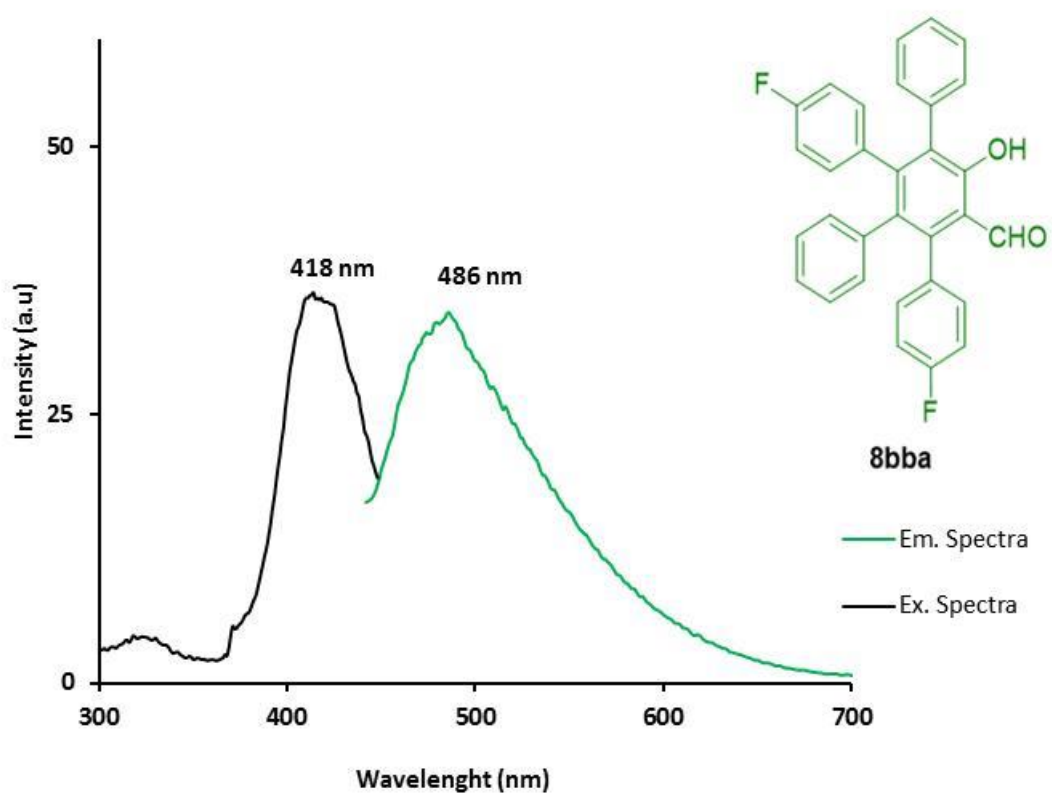


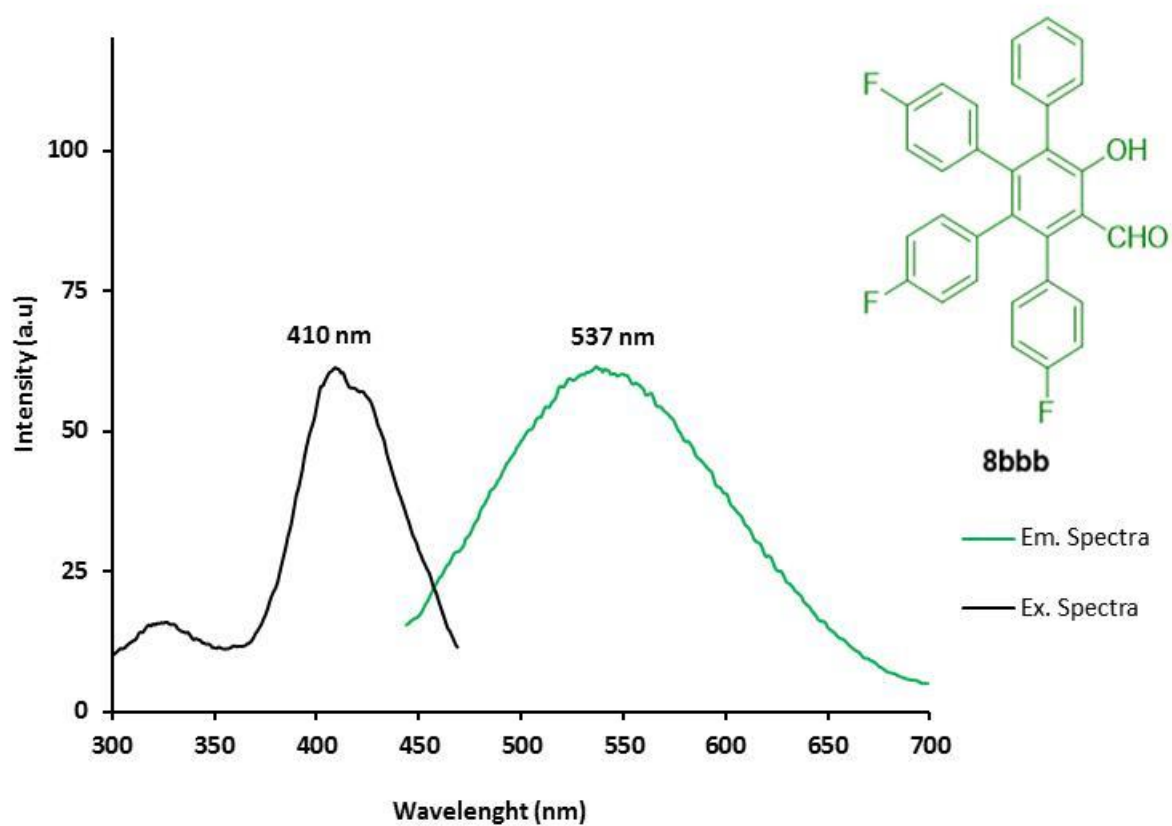
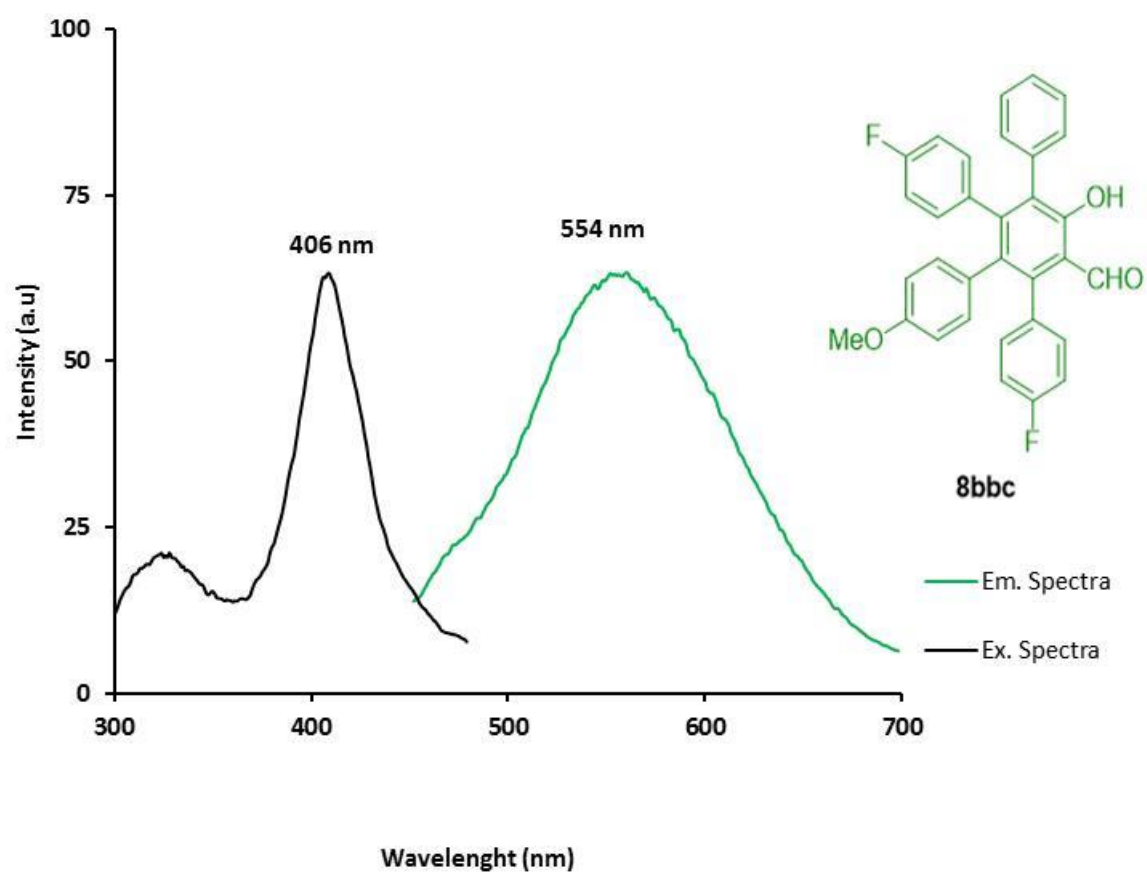


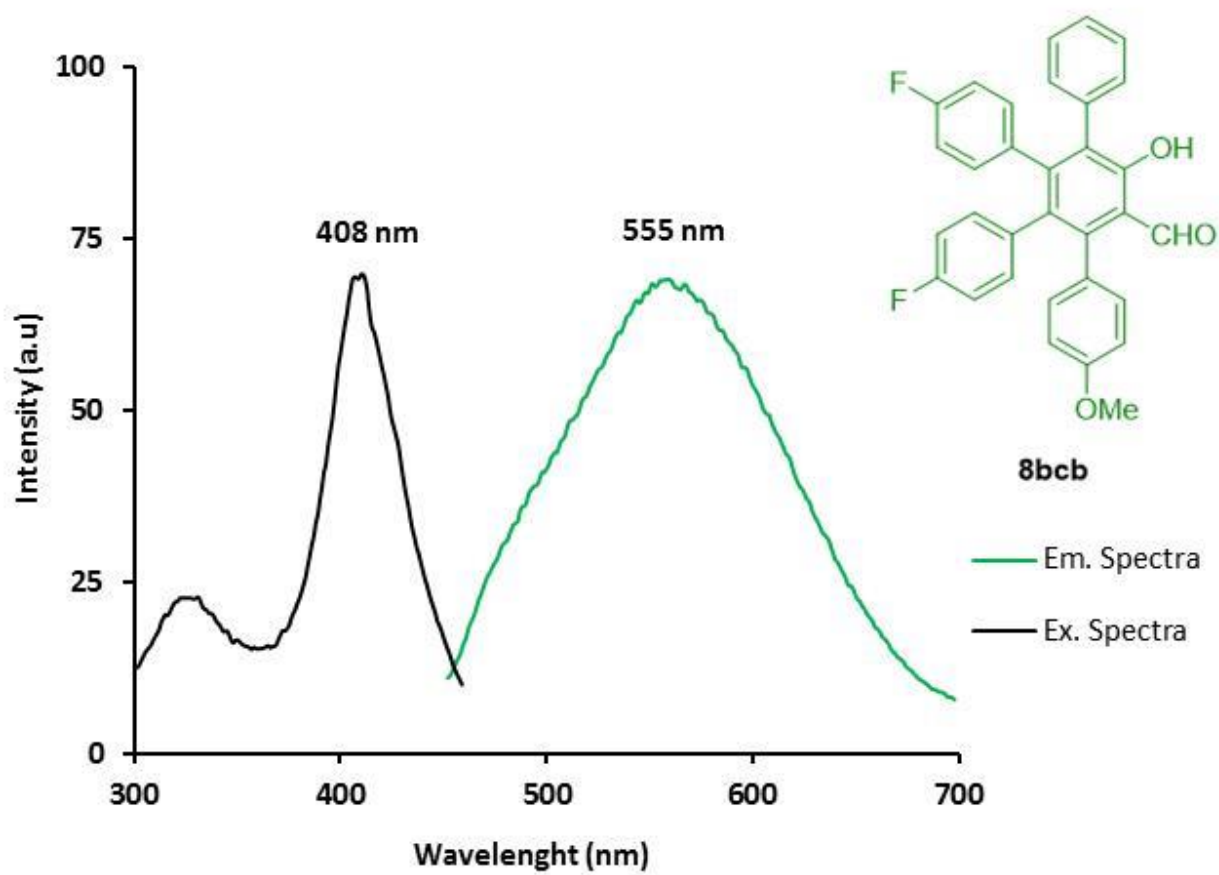
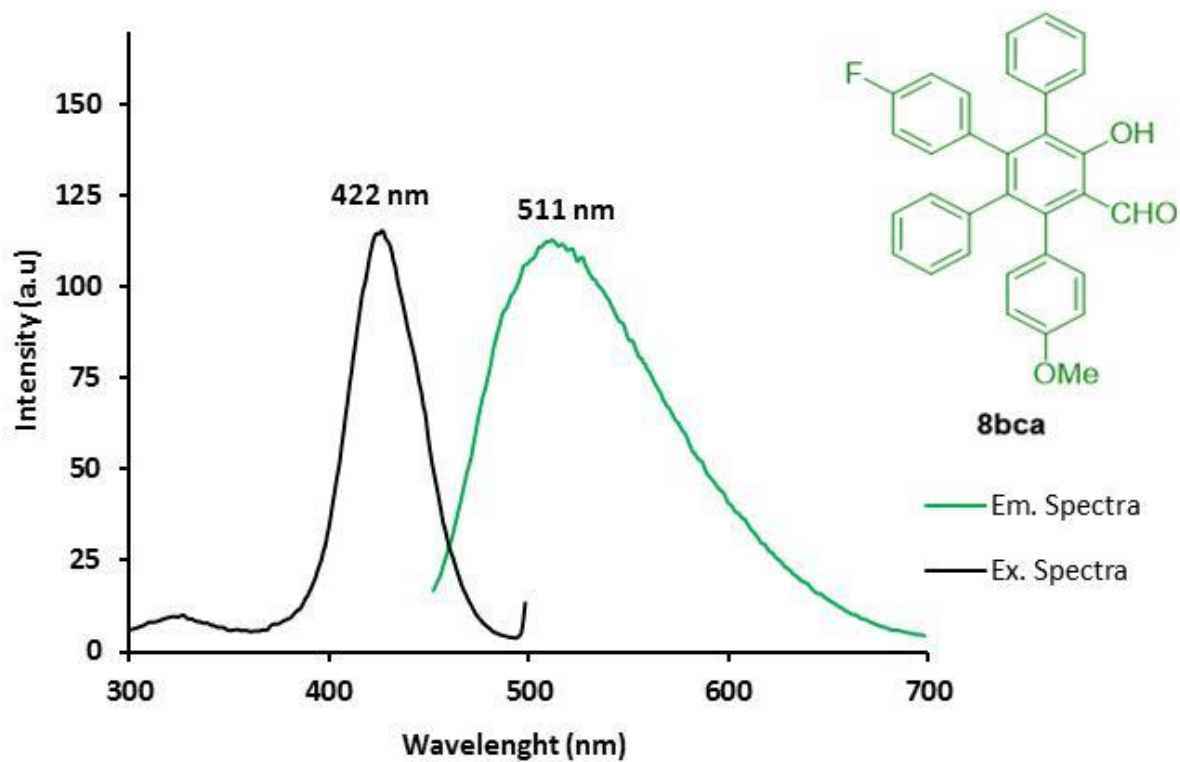


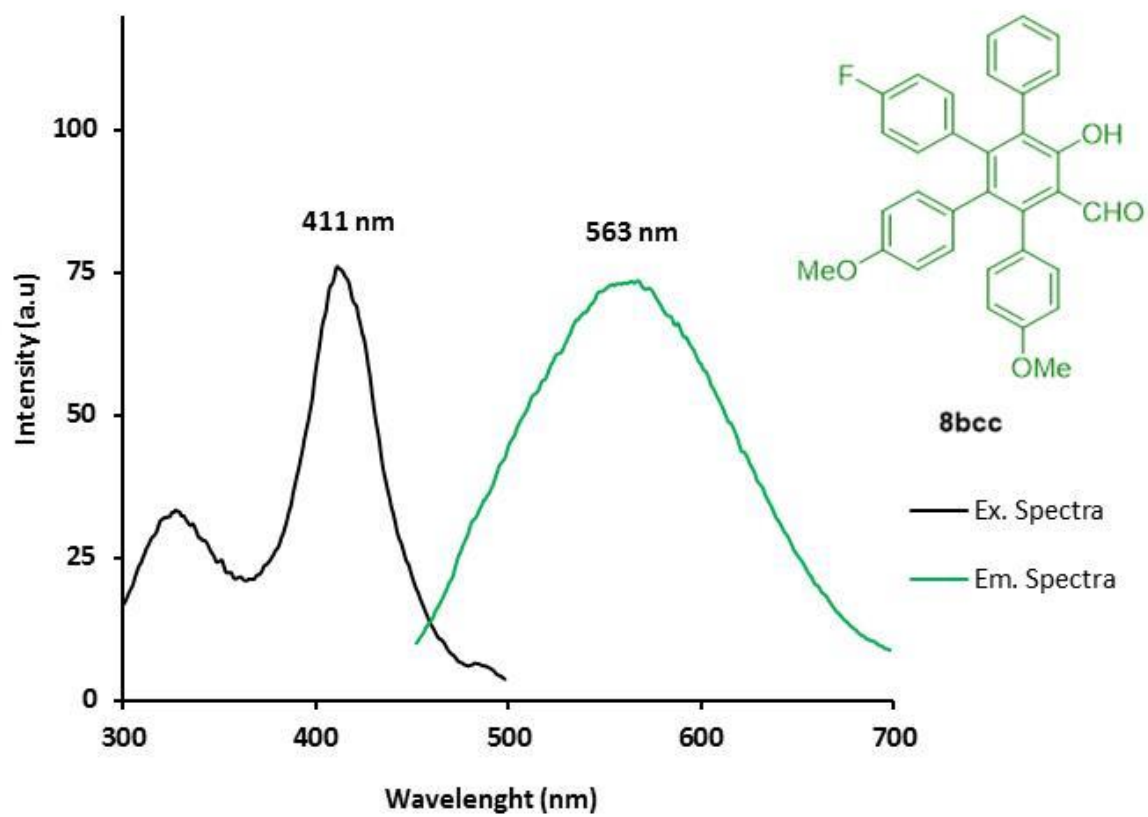
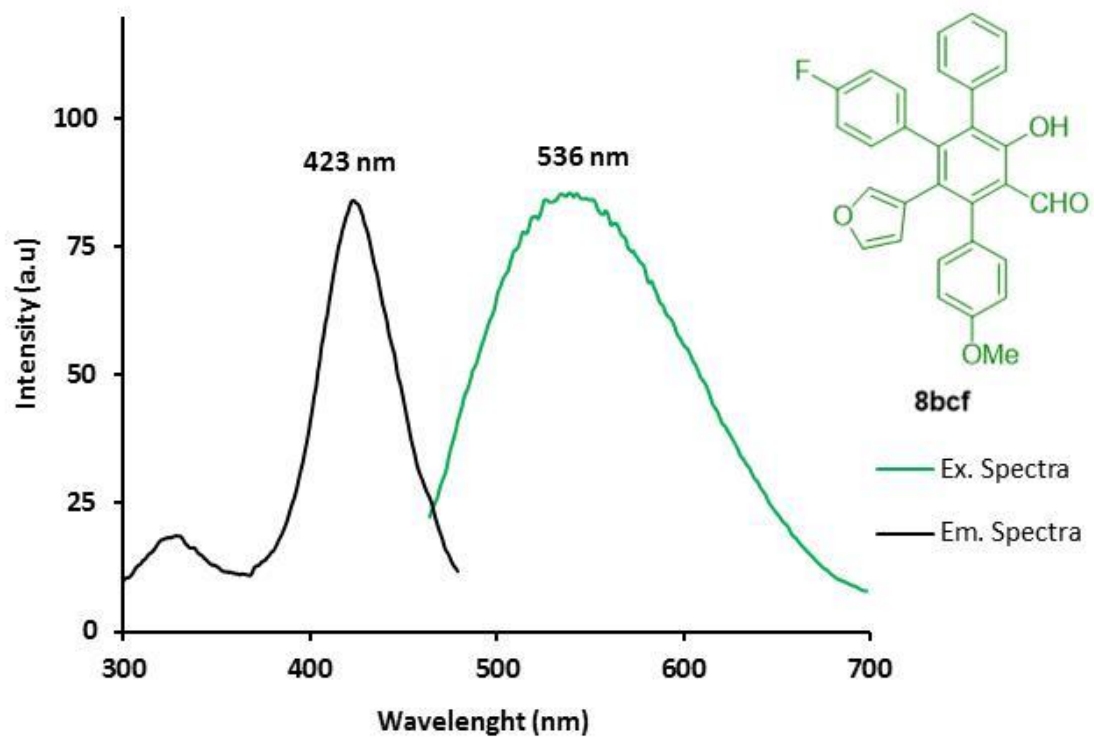












7 ^1H and ^{13}C NMR spectra

