Electronic Supporting Information

Aggregation-Induced Enhanced Fluorescence by Hydrogen Bonding in π-Conjugated Tricarbocycles with a CF_2CF_2-containing Cyclohexa-1,3-diene skeleton

Haruka Ohsato,[a] Masato Morita,[a] Shigeyuki Yamada,* [a]
Tomohiro Agou,[b] Hiroki Fukumoto,[b] and Tsutomu Konno*[a]

[a] Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
[b] Department of Quantum Beam Science, Graduate School of Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

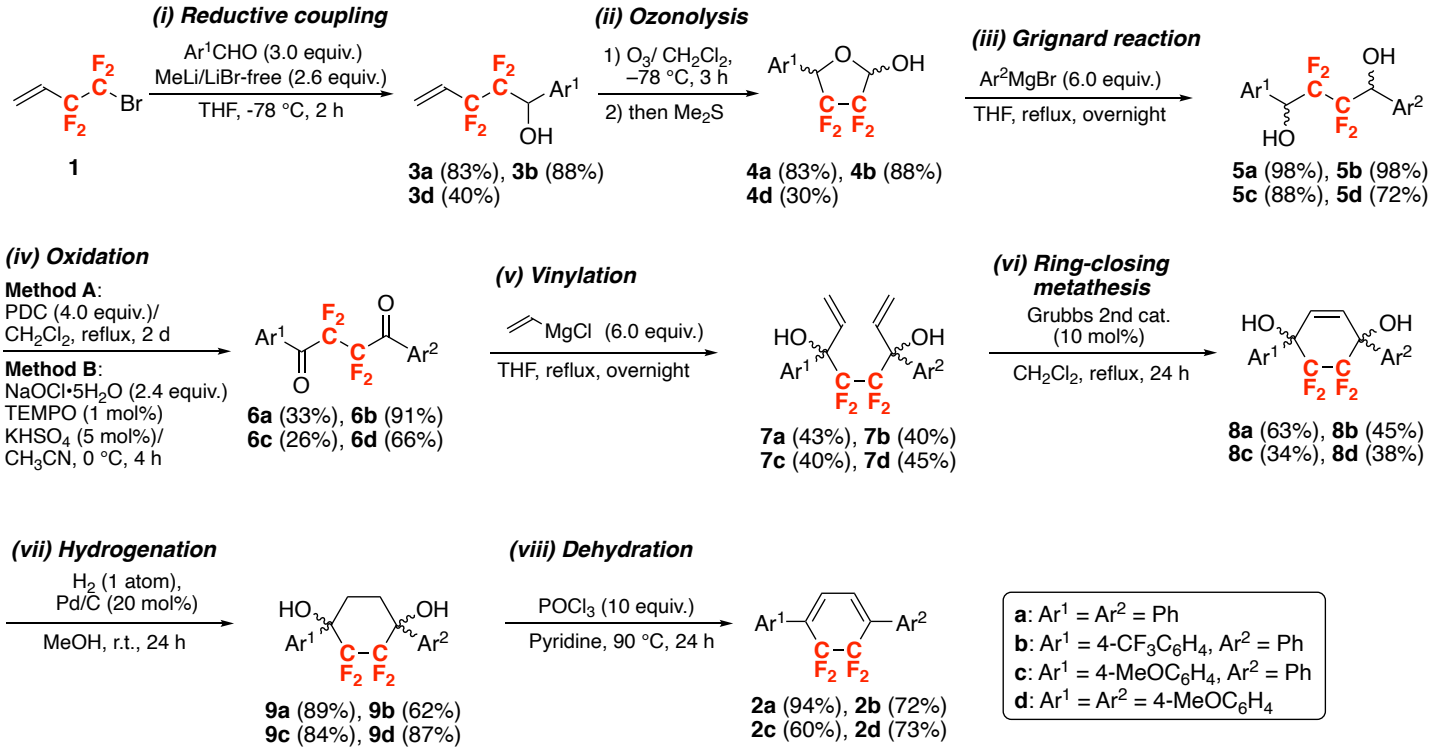
*Correspondence: syamada@kit.ac.jp (S.Y.) and konno@kit.ac.jp (T.K.)

Table of Contents:

1. Experimental

1.1. General

The progress of the reactions was monitored via thin-layer chromatography (TLC), which was performed on silica gel TLC plates (Merck, Silica gel, $60F_{254}$). Column chromatography was performed using silica gel (Fujifilm Wako Pure Chemical Corporation, Wako-gel® 60N, 38–100 mm). ^{1}H nuclear magnetic resonance (NMR) (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were acquired using a Bruker AVANCE III 400 NMR spectrometer in chloroform-*d* ($CDCl_3$) solution. The chemical shifts in ^{1}H and ^{13}C NMR spectra were reported in parts per million (ppm) based on the residual proton or carbon in the NMR solvent. The chemical shift in ^{19}F NMR spectra were also reported in ppm based on the internal standard, $CFCl_3$ (d_F = 0 ppm). Infrared (IR) spectra were recorded using the KBr method using a JASCO FTIR-4100 type A spectrometer. IR spectra are reported in wavenumber (cm^{-1}) units. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS700MS spectrometer using the fast atom bombardment (FAB) method. Characterization data for **3a–c** were reported in *Synthesis* **2011**, 33–44. In the molecules, **4**, **5**, **7**, **8**, and **9**, which may be produced as a diastereomeric mixture, characterization data of the major products were only described because the data could not be safely assigned as minor products.

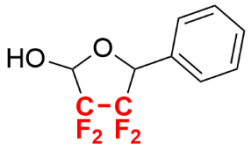


Scheme S1. Synthetic procedure of the desired molecules **2a–d** from the commercially available **1**.

1.2. Typical procedure for the synthesis of 5-phenyl-3,3,4,4-tetrafluorotetrahydrofuran-2-ol (4a)

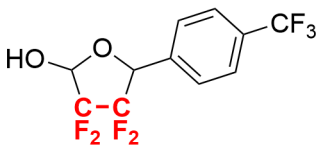
In a two-necked round-bottomed flask containing a Teflon®-coated magnetic stirring bar was placed bishomoallyl alcohol **3a** (1.16 g, 5.0 mmol) in CH_2Cl_2 (25 mL), and the whole solution was cooled to –78 °C. O_3 gas was bubbled through the solution at –78 °C for 3 h, followed by treating with Me_2S (3.7 mL, 50 mmol) after checking complete consumption of starting **3a** by the TLC analysis. After removing solvent using rotary evaporator, the crude product was purified by silica gel column chromatography to afford the corresponding lactol **4a** as a white solid in a diasteremeric mixture (0.98 g, 4.1 mmol, 83%).

1.3.1. 3,3,4,4-Tetrafluoro-5-phenyltetrahydrofuran-2-ol (4a)



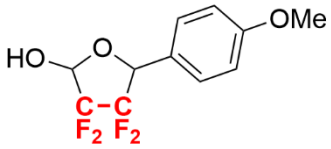
Yield: 83% (White solid) as a diastereomeric mixture; M.p.: 50.4–51.8 °C; ^{1}H NMR ($CDCl_3$): δ 3.54 (s, 1H), 5.37 (dd, J = 15.9, 8.8 Hz, 1H), 5.61 (dt,, J = 6.4, 2.8 Hz, 1H), 7.35–7.46 (m, 5H); ^{19}F NMR ($CDCl_3$): δ –129.53 (dm, J = 245.8 Hz, 1F), –128.59 (ddd, J = 239.8, 15.8, 2.7 Hz, 1F), –128.32 (dm, J = 246.6 Hz, 1F, C*F*), –120.28 (dm, 240.3 Hz, 1F); ^{13}C NMR ($CDCl_3$): δ 80.0 (dd, J = 29.2, 24.1 Hz), 94.2–95.2 (m, 1C), 113.0–119.0 (m, 2C for CF_2CF_2), 127.4, 127.5, 128.7, 129.8; IR (KBr): ν 3419, 3071, 2911, 2755, 2464, 1959, 1896, 1589, 1499, 1447, 1319, 1149, 1041, 917, 730 cm^{-1}; HRMS (FAB) Calcd for $C_{10}H_8F_4O_2$ [M]$^+$: 264.0773, found: 264.0777.

1.3.2. 3,3,4,4-Tetrafluoro-5-(*p*-(trifluoromethyl)phenyl)tetrahydrofuran-2-ol (4b)



Yield: 30% (White solid) as a diastereomeric mixture; M.p.: 89.2–89.4 °C; ^{1}H NMR ($CDCl_3$): δ 3.60 (s, 1H), 5.43 (dd, J = 15.6, 8.9 Hz, 1H), 5.64 (s, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –128.89 (dm, J = 246.3 Hz, 1F, CF_2), –128.37 (dd, J = 239.8, 15.3 Hz, 1F), –127.82 (dm, J = 246.3 Hz, 1F), –119.12 (dm, 239.8 Hz, 1F), –63.36 (s, 3F); ^{13}C NMR ($CDCl_3$): δ 79.4 (dd, J = 29.3, 24.2 Hz), 94.3–95.4 (m, 1C), 112.6–119.2 (m, 2C for CF2CF2), 123.8 (q, J = 272.1 Hz), 125.6, 127.5, 131.8 (q, J = 33.0 Hz), 134.7; IR (KBr): ν 3501, 2916, 2466, 2305, 1941, 1626, 1428, 1353, 1338, 1236, 1178, 1127, 1042, 859, 746 cm^{-1}; HRMS (FAB) Calcd for $C_{11}H_7F_7O_2$ [M]$^+$: 304.0334, found: 304.0343.

1.3.3. 3,3,4,4-Tetrafluoro-5-(*p*-methoxyphenyl)tetrahydrofuran-2-ol (4c)

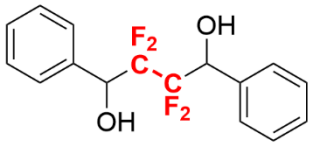


Yield: 88% (White solid) as a diastereomeric mixture; M.p.: 63.8–64.8 °C; ^{1}H NMR ($CDCl_3$): δ 3.49 (d, J = 5.2 Hz, 1H), 3.83 (s, 3H), 5.30 (dd, J = 15.9, 8.9 Hz, 1H), 5.59 (s, 1H), 6.95 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –129.28 (dm, J = 246.0 Hz, 1F), –128.77 (ddd, J = 240.1, 16.2, 3.3 Hz, 1F), –128.30 (dm, J = 246.0 Hz, 1F), –120.67 (dm, 240.1 Hz, 1F); ^{13}C NMR ($CDCl_3$): δ 55.4, 79.9 (dd, J = 29.5, 24.0 Hz), 94.6 (dd, J = 36.6, 23.3 Hz), 112.4–119.2 (m, 2C for CF2CF2), 114.1, 122.6, 129.0, 160.6; IR (KBr): ν 3466, 2973, 2914, 2557, 2433, 2041, 1903, 1615, 1469, 1443, 1353, 1262, 1014, 871, 785 cm^{-1}; HRMS (FAB) Calcd for $C_{11}H_{10}F_4O_2$ [M]$^+$: 266.0566, found: 266.0568.

1.4. Typical procedure for the synthesis of 1-phenyl-2,2,3,3-tetrafluoro-4-phenylbutan-1,4-diol (5a)

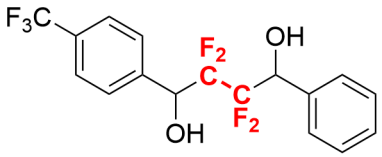
In a two-necked round-bottomed flask, equipped with a Teflon®-coated magnetic stirrer bar was put a solution of lactol **4a** (0.71 g, 3.0 mmol) and THF (3.0 mL), and the flask was dipped into an ice bath. To the solution was added dropwise a THF solution of phenylmagnesium bromide (0.85 mol L–1 THF solution, 22 mL, 18 mmol), prepared from Mg turning (0.69 g, 28.6 mmol) and bromobenzene (4.14 g, 26 mmol), at 0 °C, followed by continuous stirring at reflux temperature overnight. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (50 mL). The crude product was extracted with EtOAc (50 mL) three times, and the combined organic layer was dried over Na_2SO_4, followed by filtration, and concentration under high vacuum condition using a rotary evaporator. The residue was purified by silica gel column chromatography to afford the corresponding tetrafluorinated 1,4-diol **5a** as a white solid in a diastereomeric mixture (0.92 g, 2.9 mmol, 98%).

1.4.1. 2,2,3,3-Tetrafluoro-1,4-diphenylbutan-1,4-diol (5a)



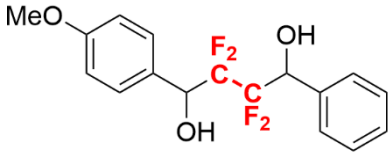
Yield: 98% (White solid) as a diastereomeric mixture; M.p.: 131.0–131.5 °C; ^{1}H NMR ($CDCl_3$): δ 3.22 (brs, 2H), 5.22 (d, J = 20.0 Hz, 2H), 7.39–7.47 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 72.6 (dd, J = 30.4, 11.5 Hz), 116.0 (tt, J = 263.4, 29.3 Hz), 128.1, 128.4, 129.3, 134.7; ^{19}F NMR ($CDCl_3$): δ –127.55 (dd, J = 274.0, 19.2 Hz, 2F), –116.18 (d, J = 274.0 Hz, 2F, CF_2); IR (KBr): ν 3379, 3090, 3066, 2927, 1958, 1889, 1587, 1496, 1421, 1342, 1003, 919, 831, 793, 725 cm^{-1}; HRMS (FAB) Calcd for $C_{16}H_{14}F_4NaO_2$ [M+Na]$^+$: 337.0828, Found: 337.0825.

1.4.2. 2,2,3,3-Tetrafluoro-1-phenyl-4-[*p*-(trifluoromethyl)phenyl]butan-1,4-diol (5b)



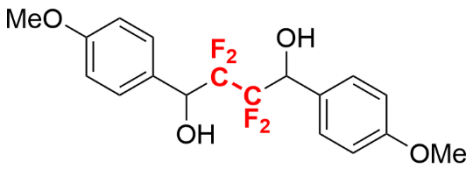
Yield: 72% (Pale yellow solid) as a diastereomeric mixture; M.p.: 145.6–146.7 °C; ^{1}H NMR ($CDCl_3$): δ 4.31 (brs, 1H), 4.49 (brs, 1H), 5.21 (d, J = 20.0 Hz, 1H), 5.32 (d, J = 20.0 Hz, 1H), 7.32–7.42 (m, 3H), 7.44–7.50 (m, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –115.94 (dd, J = 274.7, 19.7 Hz, 1F), –127.87 (dd, J = 274.7, 19.7, 5.3 Hz, 1F), –116.40 (d, J = 275.2 Hz, 1F), –116.01 (d, J = 275.2 Hz, 1F), –63.17 (s, 3F); ^{13}C NMR ($CDCl_3$): δ 72.2 (dd, J = 37.5, 22.9 Hz), 72.5 (dd, J = 38.2, 22.9 Hz), 112.8–119.1 (m, 2C for CF2CF2), 123.9 (q, J = 272.2 Hz), 127.4, 128.0, 128.5, 129.5, 131.2 (q, J = 32.2 Hz), 133.1, 134.5, 138.5; IR (KBr): ν 3395, 2959, 2874, 1727, 1496, 1334, 1203, 1126, 1070, 1017, 994, 860, 836, 737, 717 cm^{-1}; HRMS (FAB) Calcd for $C_{17}H_{13}F_7O_2Na$ [M+Na]$^+$: 405.0701, Found: 405.0691.

1.4.3. 2,2,3,3-Tetrafluoro-1-(*p*-methoxyphenyl)-4-phenylbutan-1,4-diol (5c)



Yield: 98% (White solid) as a diastereomeric mixture; M.p.: 95.3–96.7 °C; ^{1}H NMR ($CDCl_3$): δ 2.97 (brs, 1H), 3.03 (brs, 1H), 3.82 (s, 3H), 5.22 (t, J = 20.0 Hz, 1H), 5.23 (t, J = 20.0 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 7.39–7.42 (m, 5H), 7.47–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 55.4, 72.3 (dd, J = 41.9, 22.8 Hz), 72.6 (dd, J = 41.7, 22.7 Hz), 114.0, 112.5–119.0 (m, 2C for CF2CF2), 127.0, 128.2, 128.5, 129.3, 129.5, 134.9, 160.4; ^{19}F NMR ($CDCl_3$): δ –127.81 (dt, J = 275.2, 21.5 Hz, 2F), –116.47 (dd, J = 274.1, 59.5 Hz, 2F); IR (KBr): ν 3376, 2957, 2838, 1613, 1516, 1495, 1456, 1442, 1259, 1177, 1096, 1028, 917, 844, 731 cm^{-1}; HRMS (FAB) Calcd for $C_{17}H_{17}F_4O_3$ [M]$^+$: 344.1036, Found: 334.1045.

1.4.4. 2,2,3,3-Tetrafluoro-1,4-bis(*p*-methoxyphenyl)butan-1,4-diol (5d)



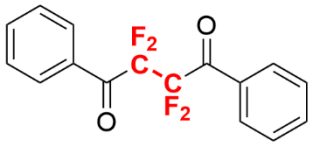
Yield: 88% (White solid) as a diastereomeric mixture; M.p.: 152.4–153.9 °C; ^{1}H NMR ($CDCl_3$): δ 3.07 (brs, 2H), 3.82 (s, 6H), 5.17 (d, J = 20.1 Hz, 2H), 6.92 (d, J = 8.6 Hz, 4H), 7.39 (d, J = 8.6 Hz, 4H); ^{19}F NMR ($CDCl_3$): δ –128.06 (dd, J = 273.1, 19.6 Hz, 2F), –116.46 (d, J = 273.1 Hz, 2F); ^{13}C NMR ($CDCl_3$): δ 55.4, 72.3 (dd, J = 30.5, 22.9 Hz), 113.0–120.0 (m, 1C for CF2), 113.8, 126.8, 129.4, 160.3; IR (KBr): ν 3468, 3399, 3008, 2848, 1727, 1610, 1581, 1444, 1353, 1280, 1257, 1177, 1081, 936, 785 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{20}F_4O_4$ [M+Na]$^+$: 374.1141, Found: 374.1134.

1.5. Typical procedure for the synthesis of 2,2,3,3-tetrafluoro-1-(*p*-methoxyphenyl)-4-phenylbutan-1,4-dione (6b)

[**Method A for the synthesis of 6a and 6c**] To a solution of pyridinium dichromate (PDC, 0.47 g, 1.2 mmol) in CH_2Cl_2 (2.0 mL) was added **5c** (0.10 g, 0.30 mmol) at room temperature, and the whole was heated at the reflux temperature for 2 d. After cooling the reaction mixture to room temperature, the mixture was passed through celite to give the crude solution, which was purified by silica gel column chromatography, affording the corresponding diketone derivative **6c** in 91% (0.093 g, 0.27 mmol) as a white solid.

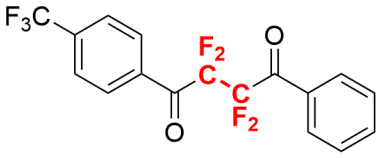
[Method B for the synthesis of 6b–d] Potassium hydrogen sulfate (4.5 mg, 0.025 mmol) and TEMPO (0.90 mg, 0.005 mmol) was added to a stirred solution of **5c** (0.16 g, 0.50 mmol) in acetonitrile (5.0 mL) at room temperature, and the resulting mixture was cooled to 0 °C. Sodium hypochlorite pentahydrate (0.22 mg, 1.2 mmol) was added to the reaction mixture and continuously stirred at that temperature for 4 h. After 4 h, the crude product was extracted with ethyl acetate, and the combined organic extract was washed with brine, dried over sodium sulfate, and removed the solvent *in vacuo*. The residue was purified by silica column chromatography to afford the corresponding **6c** in 82% (0.14 g, 0.41 mmol) as a white solid.

1.5.1. 2,2,3,3-Tetrafluoro-1,4-diphenylbutan-1,4-dione (6a)



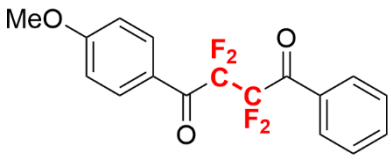
Yield: 61% (White solid); M.p.: 73.8–74.2 °C; ^{1}H NMR ($CDCl_3$): δ 7.53–7.56 (m, 4H), 7.69 (tt, J = 7.5, 1.3 Hz, 2H), 8.12 (d, J = 7.5 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 111.7 (tt, J = 270.2, 26.2 Hz) 129.0, 130.3, 131.8, 135.1, 185.8 (t, J = 29.3 Hz); ^{19}F NMR ($CDCl_3$): δ –113.51 (s, 4F); IR (KBr): ν 3376, 3085, 3077, 2011, 1988, 1924, 1595, 1578, 1449, 1324, 1308, 1192, 1078, 990, 938, 764 cm^{-1}; HRMS (FAB) Calcd for $C_{16}H_{14}F_4NaO_2$ [M+Na]$^+$: 311.0695, Found: 311.0705.

1.5.2. 1-(*p*-Trifluoromethylphenyl)-2,2,3,3-tetrafluoro-4-phenyl butan-1,4-dione (6b)



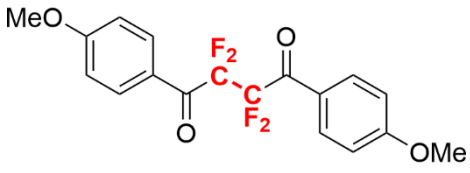
Yield: 77% (Colorless liquid); ^{1}H NMR ($CDCl_3$): δ 7.54 (t, J = 7.9 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 2H), 8.12 (d, J = 7.9 Hz, 2H), 8.22 (d, J = 8.2 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –114.75 to –114.73 (m, 2F), –112.84 to –112.82 (m, 2F), –64.03 (s, 2F); ^{13}C NMR ($CDCl_3$): δ 111.3 (tt, J = 268.5, 25.6 Hz), 111.7 (tt, J = 271.1, 26.4 Hz), 123.3 (q, J = 272.9 Hz), 125.9 (q, J = 3.7 Hz), 128.9, 130.2 (t, J = 2.9 Hz), 130.4 (t, J = 2.9 Hz), 131.1, 134.6, 135.4, 135.9 (q, J = 33.0 Hz), 185.2 (t, J = 27.9 Hz), 185.7 (t, J = 27.5 Hz); IR (KBr): ν 3503, 3403, 3068, 1699, 1599, 1451, 1319, 1292, 1258, 1177, 1056, 1017, 889, 856, 770 cm^{-1}; HRMS (FAB) Calcd for $C_{17}H_{10}F_7O_2$ [M+H]$^+$: 379.0569, Found: 379.0565.

1.5.3. 2,2,3,3-Tetrafluoro-1-(*p*-Methoxyphenyl)-4-phenylbutan-1,4-dione (6c)



Yield: 91% (White solid); M.p.: 104.5–105.3 °C; ^{1}H NMR ($CDCl_3$): δ 3.91 (s, 3H), 7.00 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.68 (tdd, J = 7.4, 2.5, 1.6 Hz, 1H), 8.10–8.12 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 55.8, 112.1 (tt, J = 270.2, 26.9 Hz), 111.5 (tt, J = 269.1, 26.3 Hz), 111.9 (tt, J = 269.9, 27.2 Hz), 114.4, 124.4, 128.9, 130.2 (t, J = 3.1 Hz), 132.0, 132.9 (t, J = 3.1 Hz), 134.9, 165.3, 183.9 (t, J = 26.9 Hz), 185.8 (t, 27.2 Hz); ^{19}F NMR ($CDCl_3$): δ –114.05 (s, 2F), –112.54 (s, 2F); IR (KBr): ν 3067, 3019, 2961, 2850, 1707, 1599, 1453, 1429, 1295, 1179, 1103, 1018, 886, 795, 718 cm^{-1}; HRMS (FAB) Calcd for $C_{17}H_{13}F_4O_3$ [MH]$^+$: 341.0801, Found: 341.0802.

1.5.4. 2,2,3,3-Tetrafluoro-1,4-bis(*p*-methoxyphenyl)butan-1,4-dione (6d)

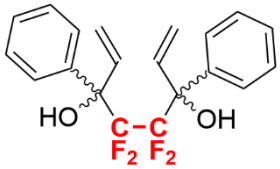


Yield: 35% (Yellow solid); M.p.: 101.3–101.8 °C; ^{1}H NMR ($CDCl_3$): δ 3.91 (s, 6H), 6.99 (d, J = 9.0 Hz, 4H), 8.12 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –113.06 (s, 4F, CF_2); ^{13}C NMR ($CDCl_3$): δ 55.8, 111.8 (tt, J = 269.2, 27.2 Hz), 114.3, 124.7, 132.9, 165.2, 183.9 (t, J = 28.4 Hz); IR (KBr): ν 2979, 2944, 2846, 2650, 2592, 1696, 1601, 1512, 1428, 1323, 1275, 1172, 1055, 821, 775 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{15}F_4O_4$ [MH]$^+$: 371.0906, Found: 371.0893.

1.6. Typical procedure for the synthesis of 3,6-diphenyl-4,4,5,5-tetrafluoroocta-1,7-dien-3,6-diol (7a)

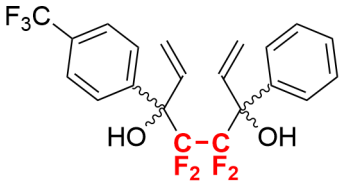
In a two-necked round-bottomed flask containing a Teflon®-coated magnetic stirring bar was put the diketone **6a** (0.16 g, 0.50 mmol) and THF (2.0 mL). To the solution was slowly added vinylmagnesium chloride (2.1 M in THF, 1.8 mL, 3.0 mmol) at 0 °C, and the resultant was stirred at reflux temperature. After being stirred for 14 h, the whole was quenched by pouring into ice-cooled saturated NH_4Cl solution. The organic layer was extracted with Et_2O three times and washed with brine, and then dried over anhydrous Na_2SO_4. After filtration, the filtrate was evaporated *in vacuo* to remove the organic solvent, and the residue was purified by silica gel column chromatography to give the corresponding **7a** in 43% yield (0.079 g, 0.22 mmol) as yellow solid.

1.6.1. 4,4,5,5-Tetrafluoro-3,6-diphenylocta-1,7-dien-3,6-diol (7a)



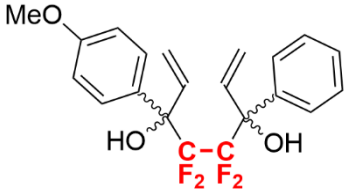
Yield: 43% (Yellow solid) as a diastereomeric mixture; M.p.: 97.8–98.7 °C; ^{1}H NMR ($CDCl_3$): δ3.82 (s, 1H), 3.85 (s, 1H), 5.40 (d, J = 10.4 Hz, 2H), 5.49 (d, J = 16.8 Hz, 2H), 6.54–6.66 (m, 2H), 7.31–7.38 (m, 6H), 7.51–7.57 (m, 4H); ^{13}C NMR: δ77.7 (dd, J = 51.6, 25.0 Hz), 116.3, 117.9 (tt, J = 266.0, 30.0 Hz), 126.9, 128.0, 128.3, 137.6, 138.2; ^{19}F NMR ($CDCl_3$): δ–113.71 (d, J = 278.8 Hz, 2F), –112.45 (d, J = 278.8 Hz, 2F); IR (KBr): ν3589, 3482, 3244, 2925, 1720, 1642, 1494, 1449, 1261, 1109, 1004, 996, 873, 754, 738 cm^{-1}; HRMS (FAB) Calcd for $C_{20}H_{18}F_4NaO_2$ [M+Na]$^+$: 389.1141, Found: 389.1151.

1.6.2. 4,4,5,5-Tetrafluoro-3-[*p*-(trifluoromethyl)phenyl]-6-phenylocta-1,7-dien-3,6-diol (7b)



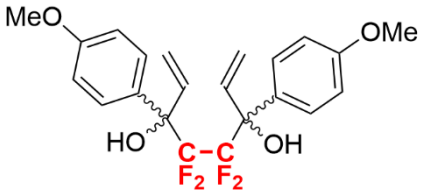
Yield: 45% (Yellow liquid) as a diastereomeric mixture; ^{1}H NMR ($CDCl_3$): δ3.58 (s, 1H), 4.19 (s, 1H), 5.40–5.50 (m, 2H), 5.50–5.58 (m, 2H), 6.52–6.67 (m, 2H), 7.32–7.40 (m, 3H), 7.51–7.71 (m, 6H); ^{19}F NMR ($CDCl_3$): δ–113.96 (d, J = 279.9 Hz, 2F), –113.09 (d, J = 279.9 Hz, 2F), –63.73 (s, 3F); ^{13}C NMR ($CDCl_3$): δ77.5 (t, J = 23.8 Hz), 77.9 (t, J = 24.2 Hz), 116.8, 114.2–121.0 (m, 2C for CF2C2), 124.0 (q, J = 272.2 Hz), 124.7, 126.6, 127.4, 128.0, 128.3, 130.1, 136.1, 137.0, 137.5, 138.3, 142.2; IR (neat): ν3252, 2896, 1931, 1891, 1619, 1496, 1450, 1414, 1331, 1166, 1119, 997, 838, 757, 731 cm^{-1}; HRMS (FAB) Calcd for $C_{21}H_{17}F_7NaO_2$ [M+Na]$^+$: 457.1014, Found: 457.1026.

1.6.3. 4,4,5,5-Tetrafluoro-3-(*p*-methoxyphenyl)-6-phenylocta-1,7-dien-3,6-diol (7c)



Yield: 40% (Yellow liquid) as a diastereomeric mixture; ^{1}H NMR ($CDCl_3$): δ3.82 (s, 3H), 4.64 (s, 1H), 4.76 (s, 1H), 5.40 (d, J = 10.4 Hz, 2H), 5.49 (d, J = 16.8 Hz, 2H), 6.54–6.66 (m, 2H), 6.87 (d, J = 8.8 Hz, 2H), 7.31–7.41 (m, 3H), 7.49 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ55.2, 77.7 (t, J = 24.0 Hz), 77.8 (t, J = 24.2 Hz), 113.3, 116.1, 116.2, 116.4, 118.0 (tt, J = 265.6, 29.7 Hz), 118.0 (tt, J = 265.8, 30.2 Hz), 126.9, 127.9, 128.27, 128.31, 130.3, 137.5, 138.2, 159.3; ^{19}F NMR ($CDCl_3$): δ–113.76 (ddd, J = 279.4, 113.2, 5.6 Hz, 2F), –113.47 (dd, J = 279.4, 26.4 Hz, 2F); IR (neat): ν3434, 2936, 2839, 2046, 1895, 1641, 1607, 1584, 1508, 1348, 1132, 931, 831, 790, 754 cm^{-1}; HRMS (FAB) Calcd for $C_{21}H_{20}F_4NaO_3$ [M + Na]$^+$: 419.1246, Found: 419.1253.

1.6.4. 4,4,5,5-Tetrafluoro-3,6-bis(*p*-methoxyphenyl)octa-1,7-dien-3,6-diol (7d)

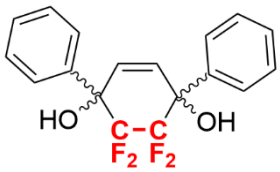


Yield: 40% (Yellow solid) as a diastereomeric mixture; M.p.: 114.8–115.2 °C; ^{1}H NMR ($CDCl_3$): δ3.79 (s, 6H), 3.82 (s, 2H), 5.37 (d, J = 10.8 Hz, 2H), 5.47 (d, J = 17.1 Hz, 2H), 6.53–6.63 (m, 2H), 6.84–6.89 (m, 4H), 7.42–7.49 (m, 4H); ^{13}C NMR ($CDCl_3$): δ55.3, 77.7 (t, J = 24.5 Hz), 113.4, 116.1, 118.1 (tt, J = 266.1, 29.5 Hz), 128.2, 130.4, 137.7, 159.4; ^{19}F NMR ($CDCl_3$): δ–114.14 (dd, J = 111.4, 5.6 Hz, 1F), –113.39 (dd, J = 113.7, 2.2 Hz, 1F), –112.8 (d, J = 37.6 Hz, 1F), –112.1 (d, J = 26.5 Hz, 1F); IR (KBr): ν3611, 3509, 2942, 2845, 1610, 1510, 1445, 1303, 1251, 1157, 1022, 981, 931, 804, 754 cm^{-1}; HRMS (FAB) Calcd for $C_{22}H_{22}F_4O_4$ [M]$^+$: 426.1454, Found: 426.1453.

1.7. Typical procedure for the synthesis of 4,4,5,5-tetrafluoro-3,6-diphenylcyclohex-1-en-3,6-diol (8a)

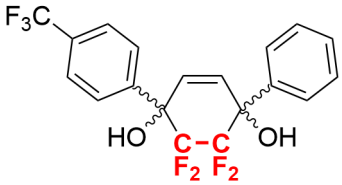
In a two-necked round-bottomed flask, equipped with a Teflon®-coated magnetic stirring bar, reflux condenser and an inlet tube for argon, was placed Grubbs 2nd generation catalyst (6.7 mg, 7.1 mmol) and CH_2Cl_2 (2.0 mL). To the solution was added **7a** (0.026 g, 0.071 mmol) at room temperature, and the whole was heated at reflux temperature. After refluxing for 24 h, the reaction mixture was allowed to cool to room temperature. The whole solution was purified by silica column chromatography to afford the corresponding **8a** in 63% yield (15 mg, 0.04 mmol) as a white solid.

1.7.1. 4,4,5,5-Tetrafluoro-1,4-diphenylcyclohex-2-en-1,4-diol (8a)



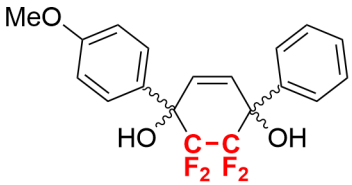
Yield: 63% (White solid) as a diastereomeric mixture; M.p.: 185.6–185.9 °C; ^{1}H NMR ($CDCl_3$): δ 2.91 (s, 2H), 6.24 (s, 2H), 7.39–7.59 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 75.5 (dd, J = 21.0, 19.3 Hz), 107.0–118.0 (m, 1C for CF2), 127.7, 128.3, 129.2, 132.2, 136.2; ^{19}F NMR ($CDCl_3$): δ –125.80 (d, J = 264.9 Hz, 2F), –121.14 (d, J = 264.9 Hz, 2F); IR (KBr): ν 3432, 3334, 2854, 1725, 1495, 1451, 1340, 1298, 1212, 1156, 1145, 1120, 994, 871, 759 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{14}F_4NaO_2$ $[M+Na]^+$: 361.0828, Found: 361.0828.

1.7.2. 4,4,5,5-Tetrafluoro1-1-[*p*-(trifluoromethyl)phenyl]-4-phenylcyclohex-2-en-1,4-diol (8b)



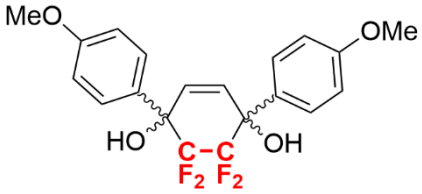
Yield: 38% (white solid) as a diastereomeric mixture; M.p.: 183.8–184.6 °C; ^{1}H NMR ($CDCl_3$): δ 2.98 (s, 1H), 2.88 (s, 1H), 6.22 (dt, J = 5.3, 3.4 Hz, 1H), 6.31 (dt, J = 5.3, 3.4 Hz, 1H), 7.41–7.47 (m, 3H), 7.56 (d, J = 6.8 Hz, 2H), 7.67–7.72 (m, 4H); ^{19}F NMR ($CDCl_3$): δ –126.05 (dd, J = 264.9, 18.0 Hz, 1F), –124.61 (dd, J = 264.9, 18.0 Hz, 1F), –121.13 (dd, J = 264.9, 19.1 Hz, 1F), –119.97 (dd, J = 264.9, 19.1 Hz, 1F), –63.14 (s, 3F): ^{13}C NMR ($CDCl_3$): δ 75.3 (t, J = 22.0 Hz), 75.4 (t, J = 22.3 Hz), 117.3 (tt, J = 274.1, 38.5 Hz), 117.4 (tt, J = 274.4, 38.8 Hz), 125.4, 127.6, 128.5, 129.5, 131.5, 131.7, 133.0, 133.2, 136.0, 139.9, one carbon of CF_3 cannot be assigned due to significant low intensity; IR (KBr): ν 3389, 3069, 3045, 1621, 1452, 1327, 1233, 1183, 1169, 1139, 1014, 988, 881, 832, 763 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{13}F_7NaO_2$ $[M+Na]^+$: 429.0701, Found: 429.0704.

1.7.3. 4,4,5,5-Tetrafluoro-1-(*p*-Methoxyphenyl)-4-phenylcyclohex-2-en-1,4-diol (8c)



Yield: 45% (White solid) as a diastereomeric mixture; M.p.: 181.9–182.3 °C; ^{1}H NMR ($CDCl_3$): δ 2.90 (brs, 1H), 2.91 (brs, 1H), 3.82 (s, 3H), 6.21 (s, 2H), 6.92–6.96 (m, 2H), 7.40–7.45 (m, 3H), 7.49 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.4, 75.4 (t, J = 37.9 Hz), 75.5 (t, J = 38.8 Hz), 113.7, 114.5 (tm, J = 287.1 Hz), 114.8 (tm, J = 286.4 Hz), 127.7, 128.3, 129.0, 129.3, 131.9, 132.0, 132.5, 136.2, 160.3; ^{19}F NMR ($CDCl_3$): δ –126.15 (dd, J = 263.7, 19.5 Hz, 1F), –125.00 (dd, J = 263.7, 19.5 Hz, 1F), –121.65 (dd, J = 264.3, 19.9 Hz, 1F), –120.11 (dd, J = 264.3, 19.9 Hz, 1F); IR (KBr): ν 3537, 3398, 2974, 2844, 1872, 1701, 1609, 1515, 1450, 1405, 1293, 1184, 992, 836, 764 cm^{-1}; HRMS (FAB) Calcd for $C_{21}H_{20}F_4NaO_3$ $[M+Na]^+$: 391.0933, Found: 391.0941.

1.7.4. 1,4-Di(*p*-methoxyphenyl)-5,5,6,6-tetrafluorocyclohex-2-en-1,4-diol (8d)



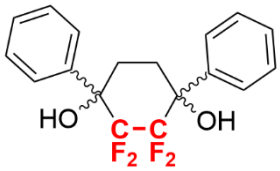
Yield: 34% (White solid) as a diastereomeric mixture; M.p.: 71.2–71.5 °C; ^{1}H NMR ($CDCl_3$): δ 3.71 (s, 6H), 3.93 (s, 2H), 6.06 (s, 2H), 6.83 (d, J = 8.8 Hz, 4H), 7.41 (d, J = 8.8 Hz, 4H); ^{19}F NMR ($CDCl_3$): δ –125.64 (d, J = 262.0 Hz, 2F), –120.7 (d, J = 262.0 Hz, 2F); ^{13}C NMR (MeOH-d_4): δ 55.7, 75.8 (t, J = 21.9 Hz), 114.1, 116.1 (tt, J = 214.4, 28.0 Hz), 130.2, 131.5, 132.8, 161.3; IR (KBr): ν 3443, 2936, 2840, 1611, 1513, 1464, 1420, 1303, 1255, 1108, 1017, 986, 902, 831, 768 cm^{-1}; HRMS (FAB) Calcd for $C_{20}H_{18}F_4O_4$ $[M]^+$: 398.1141, Found: 398.1145.

1.8. Typical procedure for the synthesis of 2,2,3,3-tetrafluoro-1,4-diphenylcyclohexan-1,4-diol (9a)

In a two-necked round-bottomed flask, equipped with a teflon®-coated magnetic stirring bar and three-way stopcock attached to a balloon filled with hydrogen gas, were added 10% Pd/C (0.024 g, 0.02 mmol), tetrafluorinated cyclohexen-1,4-diol **8a** (0.039 g, 0.10 mmol) and methanol (10 mL). The hydrogen gas was bubbled into the solution using a vacuum aspirator three times, then the whole solution was vigorously stirred at room temperature for 24 h. The crude product was passed through silica gel to remove palladium residues, after which the crude product was purified by silica column chromatography to afford the corresponding **9a** in 89% (0.030 g, 0.09 mmol) as a white solid

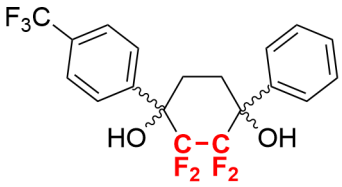
as a diastereomeric mixture.

1.8.1. 2,2,3,3-Tetrafluoro-1,4-diphenylcyclohexan-1,4-diol (9a)



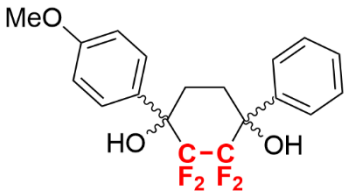
Yield: 89% (White solid) as a diastereomeric mixture; M.p.: 184.1–184.3 °C; ^{1}H NMR (MeOH-d_4): δ 2.29–2.35 (m, 2H), 2.55–2.60 (m, 2H), 2.93 (brs, 2H), 7.29–7.38 (m, 6H), 7.64 (d, J = 7.4 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 32.1, 75.7 (t, J = 21.1 Hz), 116.3 (t, J = 25.8 Hz), 127.2, 128.5, 129.0, 138.0; ^{19}F NMR (MeOH-d_4): δ –115.56 to –127.57 (brs, 4F); IR (KBr): ν 3473, 3097, 3062, 2956, 2922, 2851, 1728, 1497, 1455, 1447, 1240, 1189, 992, 763, 747 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{16}F_4NaO_2$ [M+Na]$^+$: 363.0984, Found: 363.0994.

1.8.2. 2,2,3,3-Ttetrafluoro-1-[*p*-(trifluoromethyl)phenyl)-4-phenylcyclohexan-1,4-diol (9b)



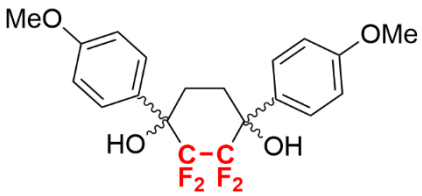
Yield: 87% (Pale yellow solid) as a diastereomeric mixture; M.p.: 160.1–160.4 °C; ^{1}H NMR (MeOH-d_4): δ 2.33–2.38 (m, 2H), 2.57–2.63 (m, 2H), 3.31 (brs, 2H), 7.31–7.40 (m, 3H), 7.67 (t, J = 7.4 Hz, 4H), 7.85 (d, J = 8.2 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –124.41 to –112.75 (brs, 4F), –63.31 (s, 3F); ^{13}C NMR (Acetone-d_6): δ 31.8, 31.9, 76.3 (t, J = 21.0 Hz), 76.4 (t, J = 21.1 Hz), 117.5 (tt, J = 259.4, 25.4 Hz), 117.7 (tt, J = 259.6, 25.7 Hz), 124.2 (q, J = 270.7 Hz), 124.4, 128.8, 129.0, 129.3, 129.6, 129.9 (q, J = 32.3 Hz), 140.4, 145.1; IR (KBr): ν 3464, 3355, 1621, 1499, 1411, 1330, 1217, 1179, 1116, 1094, 1070, 1017, 995, 842, 744 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{15}F_7NaO_2$ [M+Na]$^+$: 431.0858, Found: 431.0850.

1.8.3. 2,2,3,3-Tetrafluoro-1-(*p*-methoxyphenyl)-4-phenylcyclohexan-1,4-diol (9c)



Yield: 62% (White solid) as a diastereomeric mixture; M.p.: 161.5–162.3 °C; ^{1}H NMR ($CDCl_3$): δ 2.26–2.38 (m, 2H), 2.52–2.57 (m, 2H), 2.70 (s, 1H), 2.81 (s, 1H), 3.82 (s, 3H), 6.92 (d, J = 8.9 Hz, 2H), 7.35–7.42 (m, 3H), 7.54–7.60 (m, 4H); ^{19}F NMR ($CDCl_3$): δ –111.90 to –125.45 (brs, 4F); ^{13}C NMR ($CDCl_3$): δ 31.2, 31.3, 55.4, 75.5 (t, J = 20.6 Hz), 75.7 (t, J = 20.7 Hz), 113.9, 116.2 (tt, J = 263.3, 25.3 Hz), 116.5 (tt, J = 263.3, 25.4 Hz), 127.2, 128.5, 128.7, 129.0, 129.9, 138.0, 159.9; IR (KBr): ν 3468, 3318, 2955, 1613, 1515, 1379, 1258, 1188, 1135, 1116, 1088, 992, 860, 753, 704 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{18}F_4O_3$ [M]$^+$: 370.1192, Found: 370.1203.

1.8.4. 2,2,3,3-Tetrafluoro-1,4-bis(*p*-methoxyphenyl)cyclohexan-1,4-diol (9d)

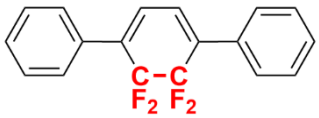


Yield: 84% (White solid) as a diastereomeric mixture; M.p.: 74.9–76.2 °C; ^{1}H NMR ($CDCl_3$): δ 2.26–2.32 (m, 2H), 2.48–2.54 (m, 2H), 2.76 (s, 2H), 3.81 (s, 6H), 6.90 (d, J = 8.9 Hz, 4H), 7.52 (d, J = 8.9 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 31.2, 55.4, 75.5 (t, J = 21.0 Hz), 113.8, 117.3 (tt, J = 261.4, 27.3 Hz), 128.6, 130.0, 159.9; ^{19}F NMR ($CDCl_3$): δ –110.85 to –125.14 (brs, 4F); IR (KBr): ν 3445, 2939, 2840, 1611, 1516, 1464, 1302, 1258, 1184, 1120, 1031, 948, 830, 806, 752 cm^{-1}; HRMS (FAB) Calcd for $C_{20}H_{20}F_4O_4$ [M]$^+$: 400.1298, Found: 400.1294.

1.9. Typical procedure for the synthesis of 5,5,6,6-tetrafluoro-1,4-diphenylcyclohexa-1,3-diene (2a)

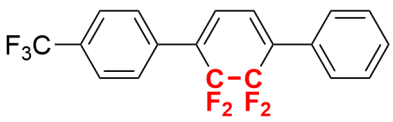
In a two-necked round-bottomed flask containing a teflon®-coated magnetic stirring bar was placed **9a** (0.034 g, 0.1 mmol) and pyridine (2.0 mL). To the solution was added freshly distilled $POCl_3$ (0.1 mL, 1.0 mmol) at room temperature. The whole solution was heated at 90 °C for 24 h. After 24 h, the resultant solution was poured into saturated aqueous NH_4Cl solution and acidified by adding 3M HCl solution. The whole solution was extracted with EtOAc three times, and the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica column chromatography to afford the corresponding **2a** in 94% (0.029 g, 0.10 mmol) as a white solid.

1.9.1. 5,5,6,6-Tetrafluoro-1,4-diphenylcyclohexa-1,3-diene (2a)



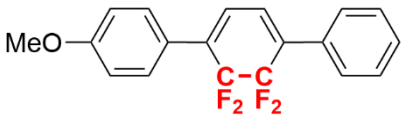
Yield: 94% (White solid); M.p. = 185 °C (determined by DSC); ^{1}H NMR (Acetone-d_6): δ 6.83 (s, 2H), 7.46–7.50 (m, 6H), 7.59 (d, J = 6.8 Hz, 4H); ^{13}C NMR (Acetone-d_6): δ 115.3 (tt, J = 252.2, 27.0 Hz, 2C for CF_2CF_2), 128.2, 129.8, 130.2, 133.8, 135.4 (t, J = 23.7 Hz); ^{19}F NMR ($CDCl_3$): δ –121.73 (s, 4F); IR (KBr): ν 3051, 2962, 2924, 1966, 1910, 1817, 1571, 1494, 1446, 1377, 1355, 1078, 1055, 1028, 768 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{12}F_4$ [M]$^+$: 304.0875, Found: 304.0882.

1.9.2. 5,5,6,6-Tetrafluoro-1-[*p*-(trifluoromethyl)phenyl)]-4-phenylcyclohexa-1,3-diene (2b)



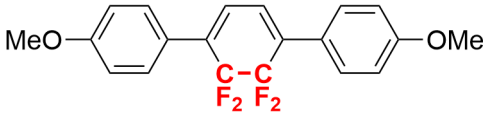
Yield: 73% (Pale yellow solid); M.p. = 98 °C (determined by DSC); ^{1}H NMR ($CDCl_3$): δ 6.54 (d, J = 6.1 Hz, 1H), 6.60 (d, J = 6.1 Hz, 1H), 7.42–7.45 (m, 3H), 7.52–7.54 (m, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 113.7 (tt, J = 253.5, 27.1 Hz), 113.8 (tt, J = 253.8, 27.8 Hz), 122.7, 125.6, 125.70, 125.74, 127.5, 127.7, 127.8, 128.8, 129.6, 131.1 (q, J = 54.5 Hz), 132.7, 134.0 (t, J = 22.0 Hz), 136.5 (t, J = 22.3 Hz); ^{19}F NMR ($CDCl_3$): δ –63.30 (s, 3F), –121.67 (d, J = 6.9 Hz, 2F), –121.88 (d, J = 6.9 Hz, 2F); IR (KBr): ν 3108, 3087, 3073, 2938, 2646, 1951, 1928, 1619, 1499, 1448, 1377, 1199, 959, 863, 743 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{11}F_7$ [M]$^+$: 372.0749, Found: 372.0750.

1.9.3. 5,5,6,6-Tetrafluoro-1-(*p*-methoxyphenyl)-4-phenylcyclohexa-1,3-diene (2c)



Yield: 72% (Pale yellow solid); M.p. = 165 °C (determined by DSC); ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 3H), 6.44 (d, J = 6.4 Hz, 1H), 6.50 (d, J = 6.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 7.37–7.44 (m, 3H), 7.46–7.52 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 55.5, 114.0 (tt, J = 253.2, 26.7 Hz), 114.1 (tt, J = 253.2, 26.7 Hz), 114.2, 124.4, 125.4, 126.4, 127.3, 128.7, 128.8, 129.1, 133.1, 134.4 (t, J = 22.3 Hz), 134.9 (t, J = 23.1 Hz, *C*H=C-Ar), 160.6; ^{19}F NMR ($CDCl_3$): δ –121.71 (d, J = 42.9 Hz, 4F); IR (KBr): ν 3048, 2967, 2940, 2841, 1605, 1516, 1354, 1285, 1254, 1186, 1152, 1098, 1054, 1027, 790 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{14}F_4O$ [M]$^+$: 334.0981, Found: 334.0977.

1.9.4. 5,5,6,6-Tetrafluoro-1,4-bis(*p*-methoxyphenyl)cyclohexa-1,3-diene (2d)



Yield: 60% (Pale yellow solid); M.p. = 208 °C (determined by DSC); ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 6H), 6.42 (s, 2H), 6.93–6.95 (m, 4H), 7.46 (d, J = 8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 55.5, 114.2, 114.3 (tm, J = 242.2 Hz), 124.7, 125.5, 128.7, 134.1, 160.5; ^{19}F NMR ($CDCl_3$,): δ –121.49 (s, 4F); IR (KBr): ν 3045, 2967, 2939, 2841, 1604, 1513, 1459, 1441, 1250, 1183, 1155, 1098, 1053, 1028, 816, 785 cm^{-1}; HRMS (FAB) Calcd for $C_{20}H_{16}F_4O_2$ [M]$^+$: 364.1086, Found: 364.1083.

2. NMR Spectrum

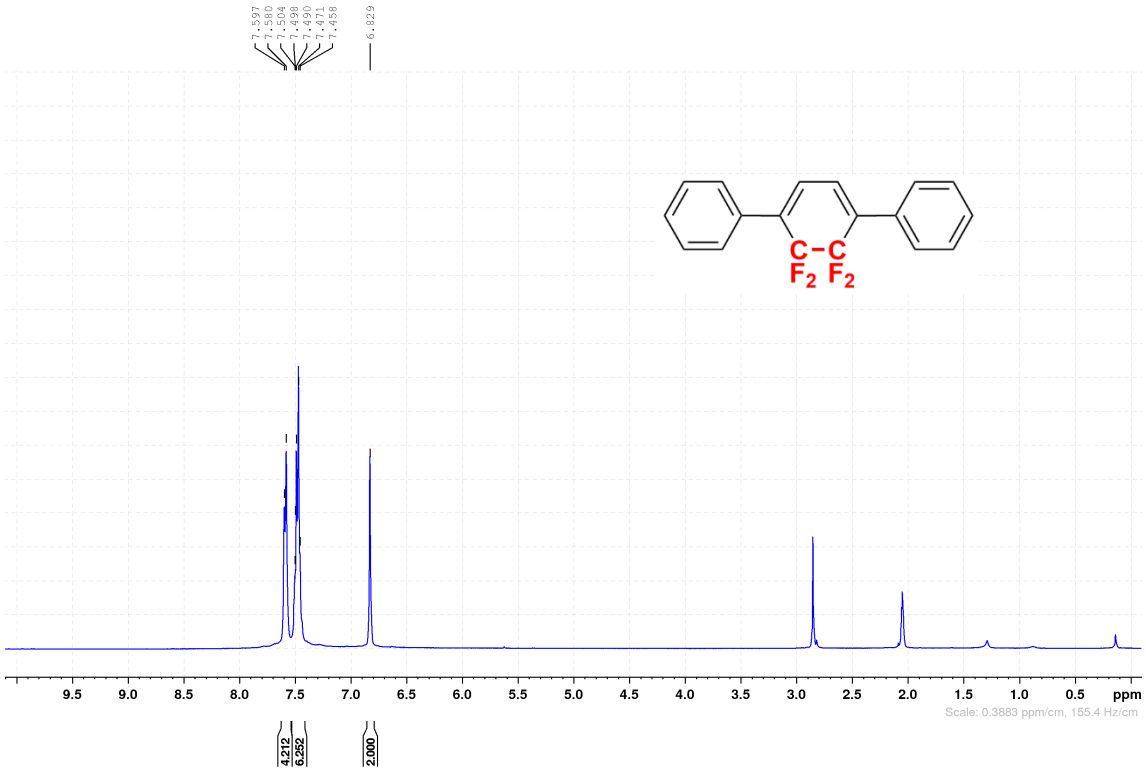


Figure S1. ^{1}H NMR spectrum of **2a** (Acetone-d_6, 400 MHz)

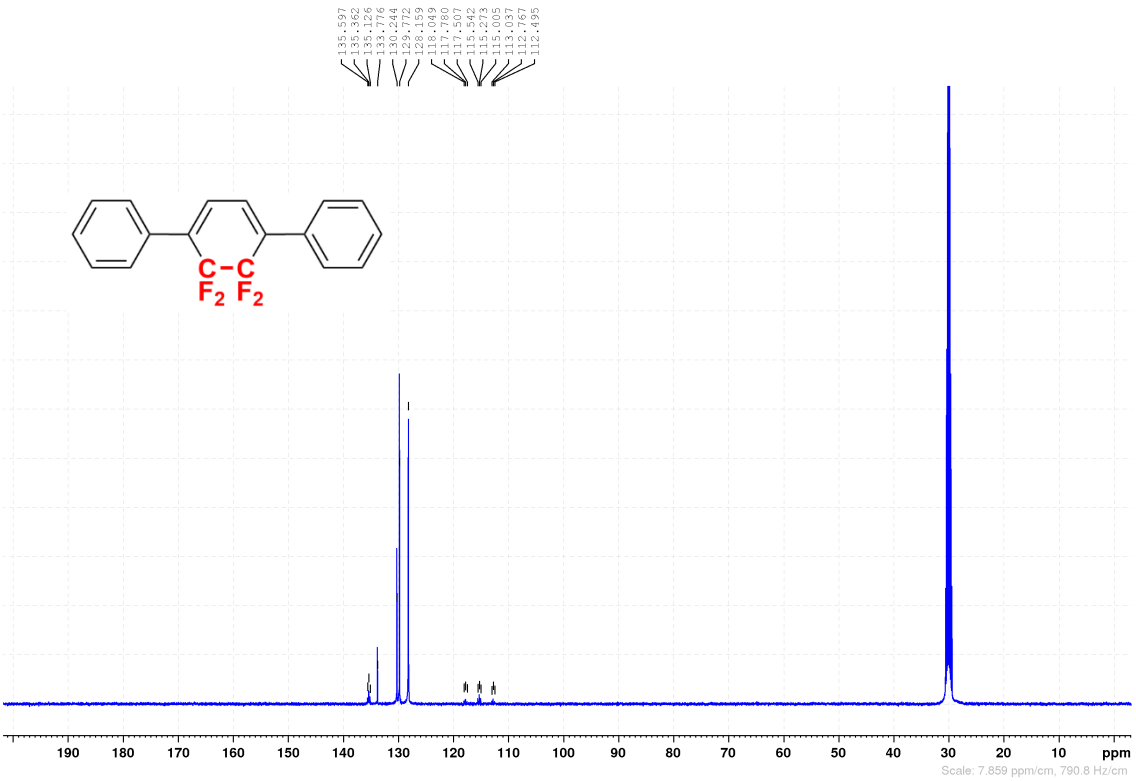


Figure S2. ^{13}C NMR spectrum of **2a** (Acetone-d_6, 100 MHz)

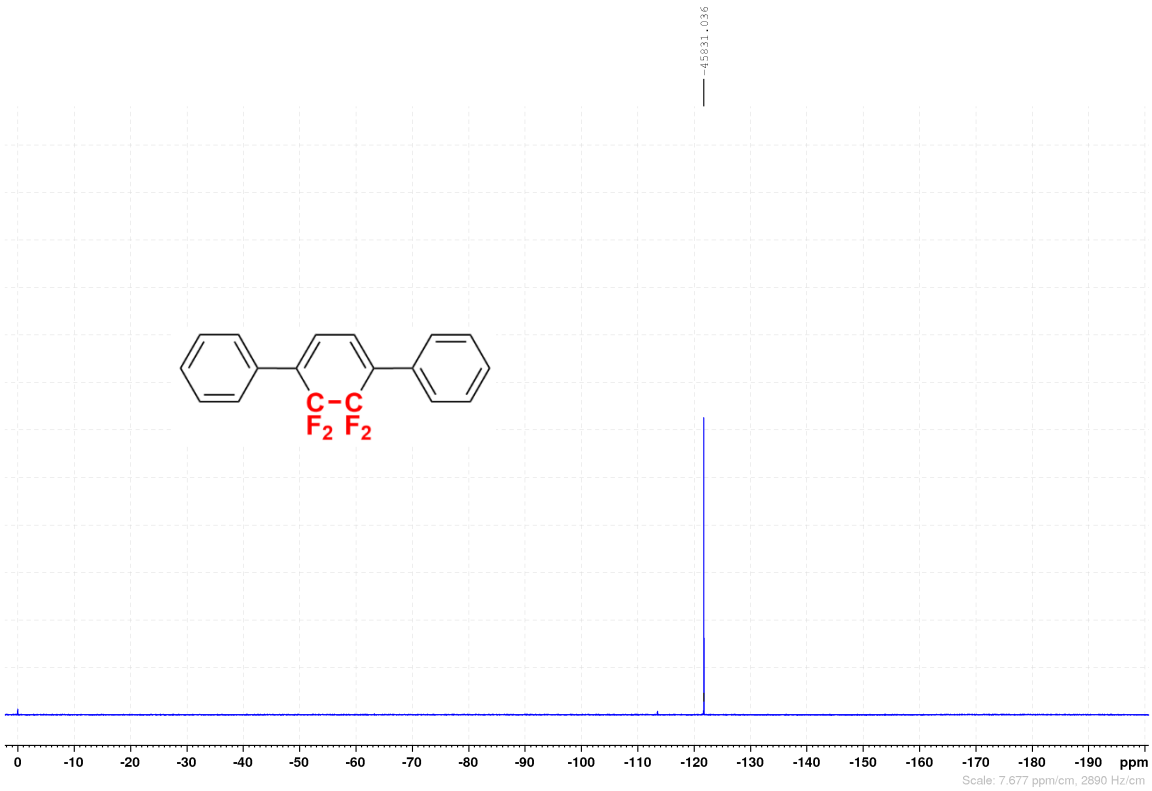


Figure S3. ^{19}F NMR spectrum of **2a** (Acetone-d_6, 376 MHz)

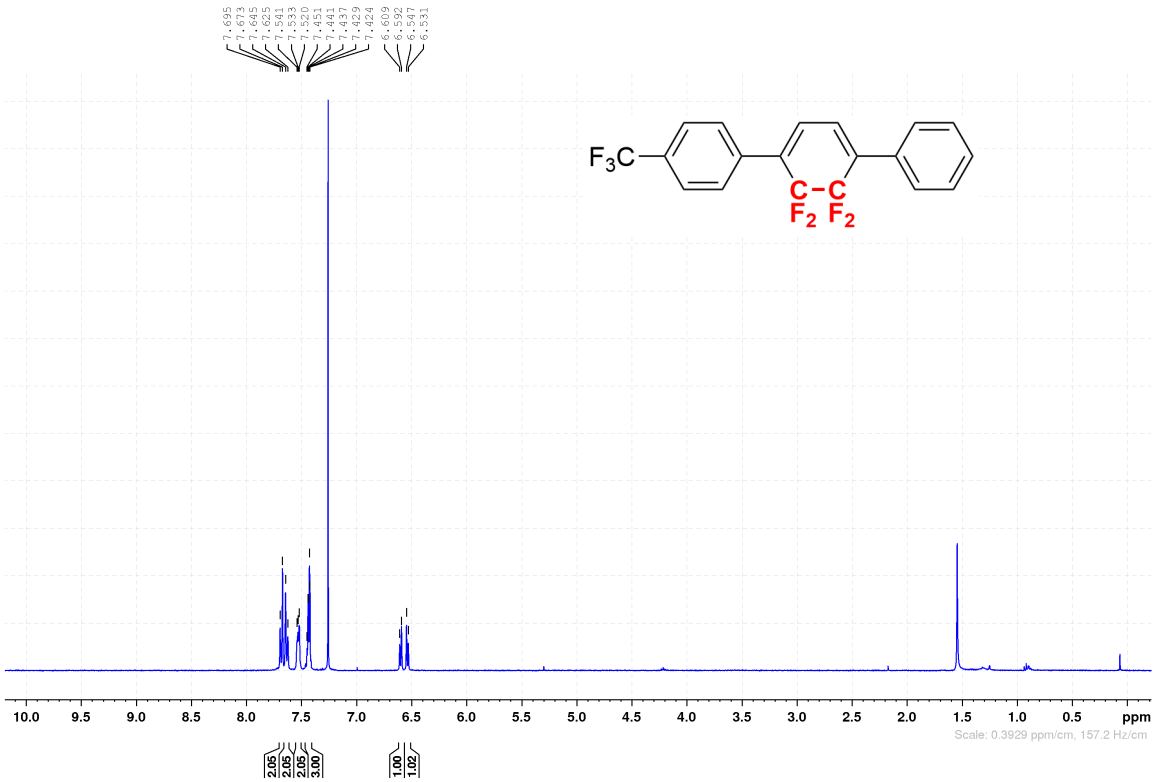


Figure S4. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 400 MHz)

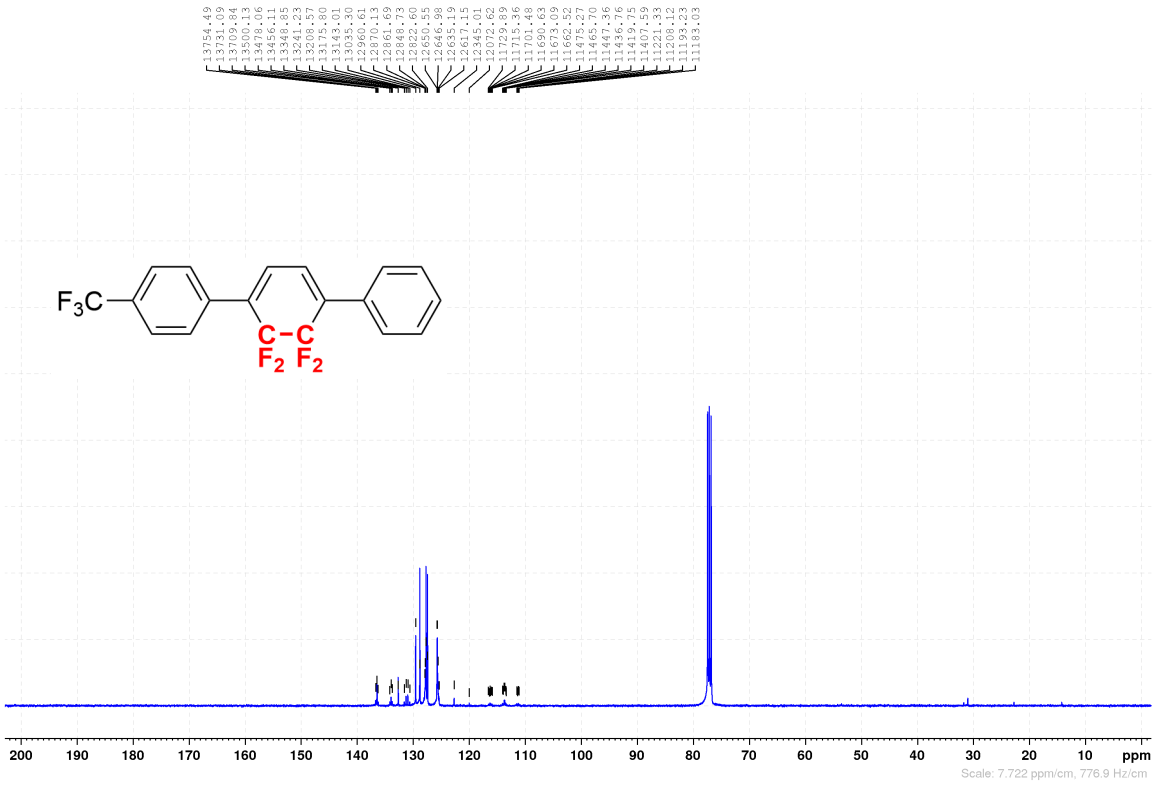


Figure S5. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 100 MHz)

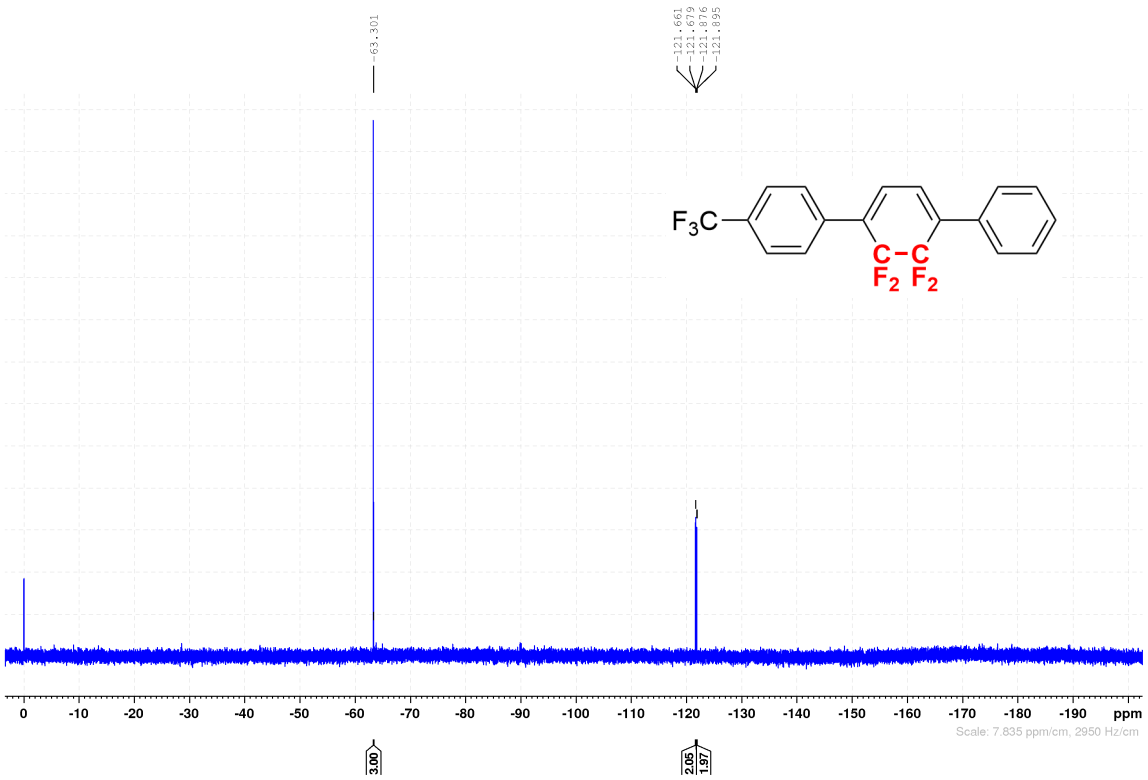


Figure S6. ^{19}F NMR spectrum of **2b** ($CDCl_3$, 376 MHz)

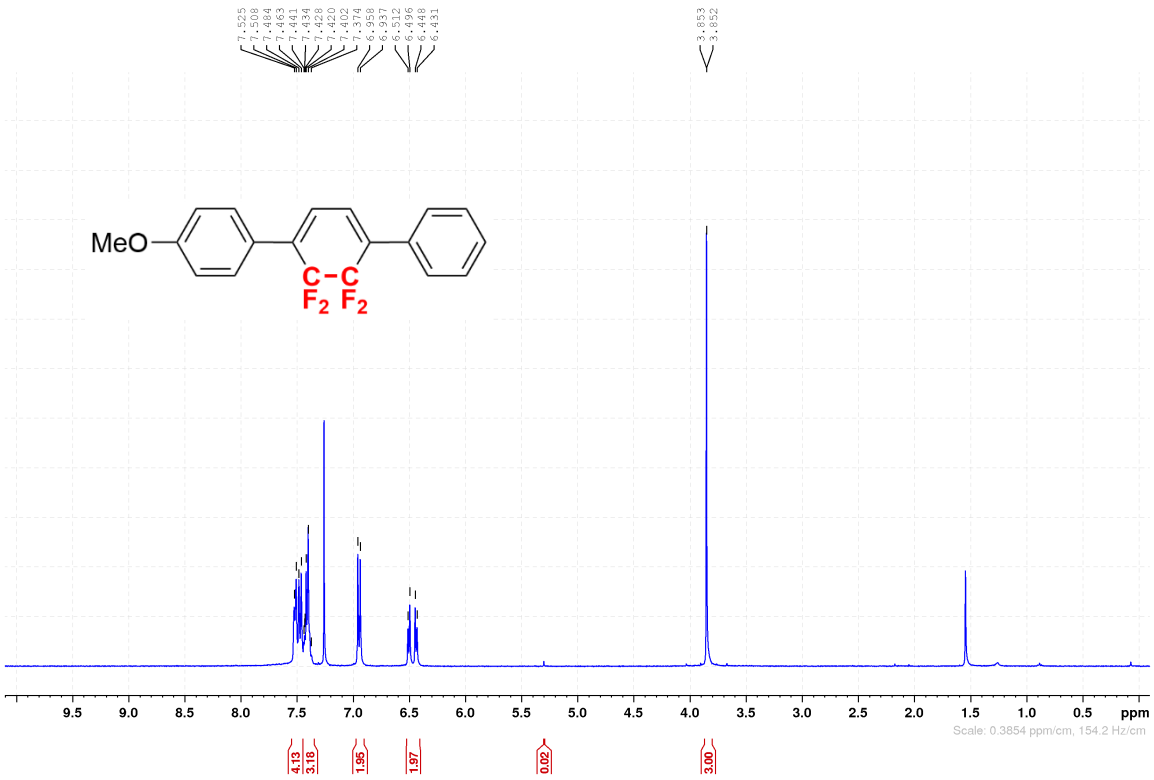


Figure S7. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 400 MHz)

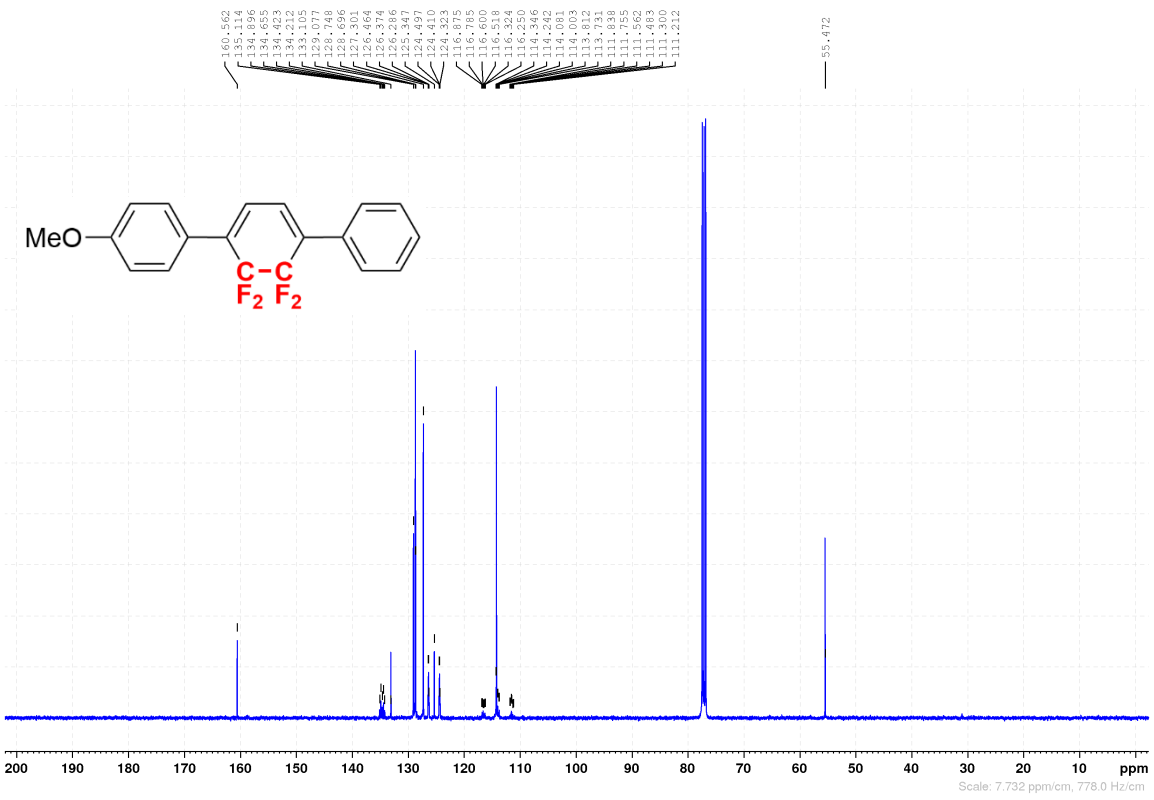


Figure S8. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 100 MHz)

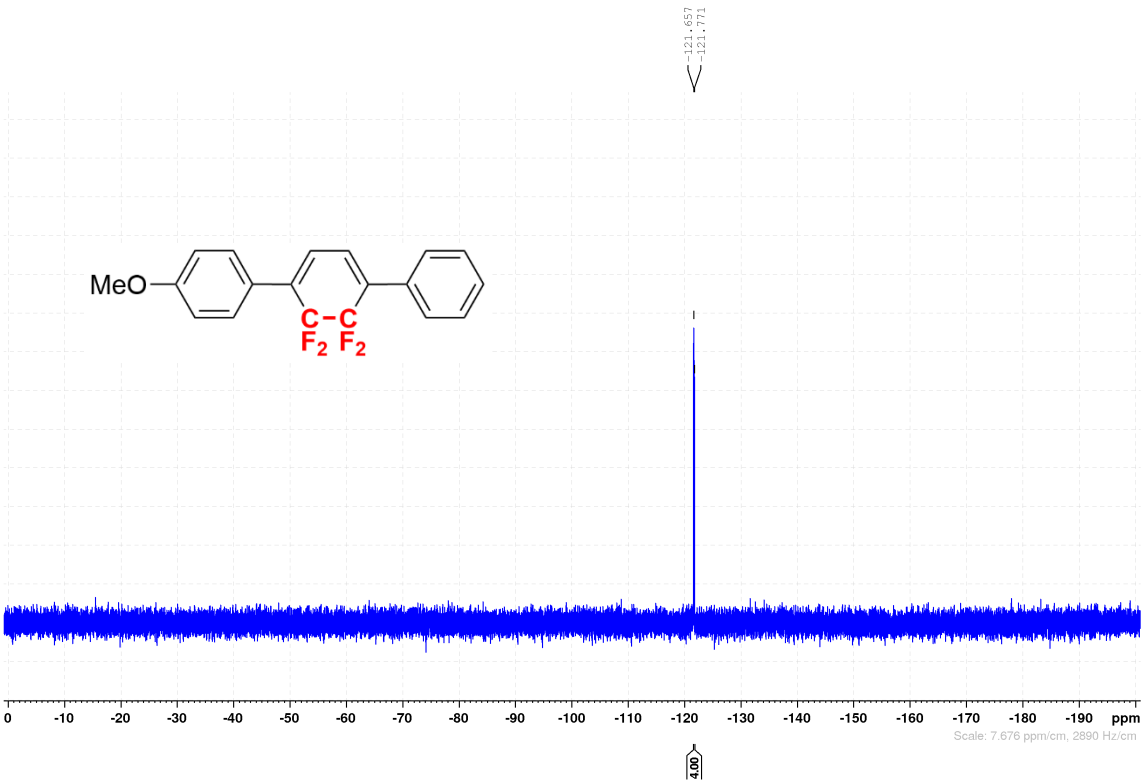


Figure S9. ^{19}F NMR spectrum of **2c** ($CDCl_3$, 376 MHz)

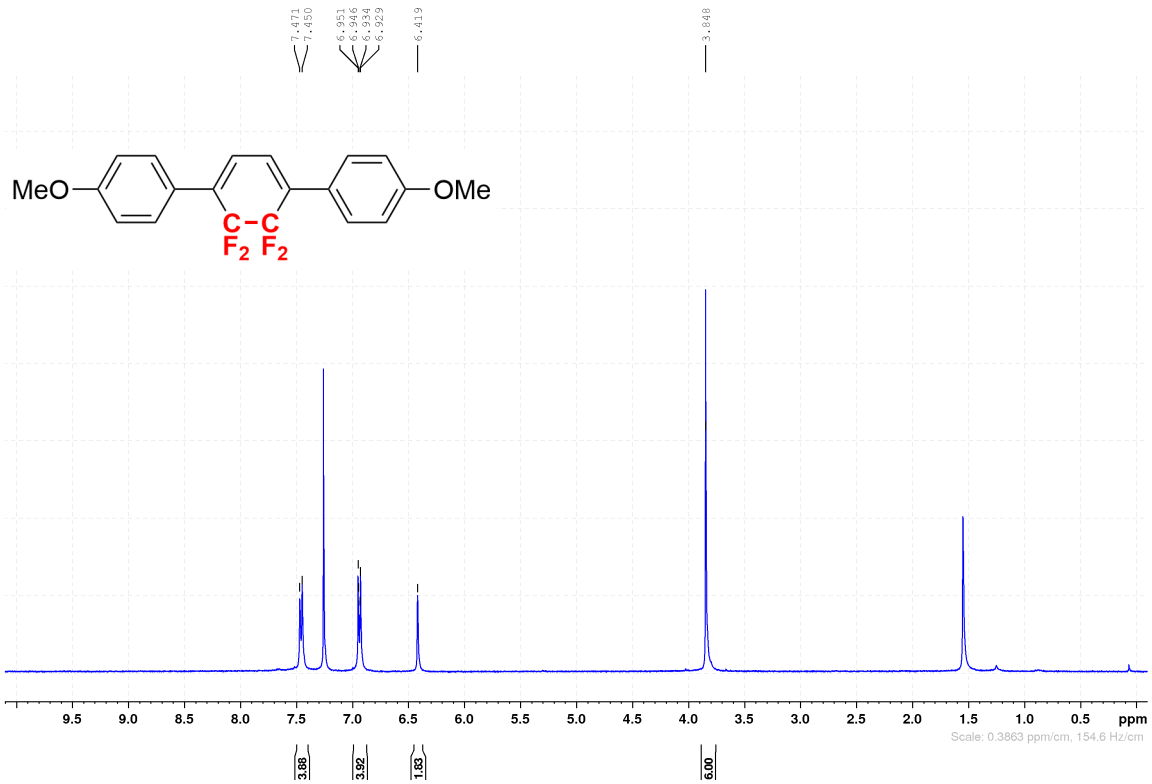


Figure S10. ^{1}H NMR spectrum of **2d** ($CDCl_3$, 400 MHz)

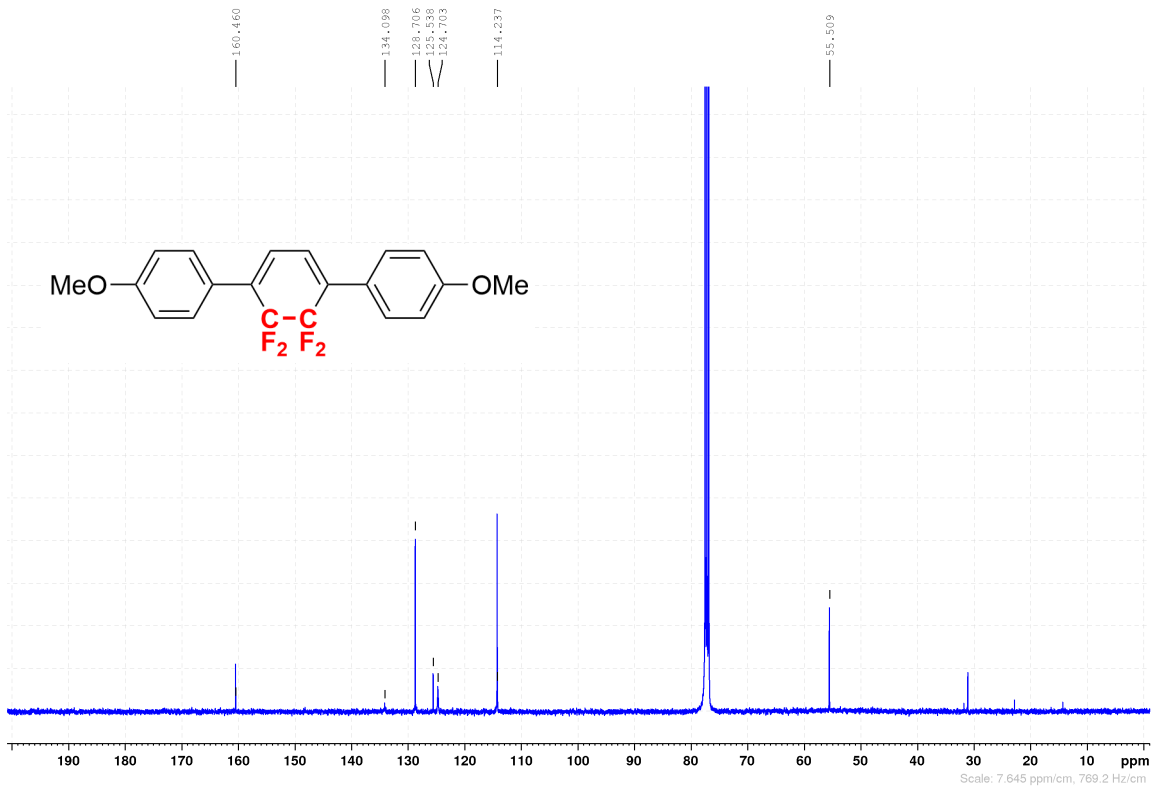


Figure S11. ^{13}C NMR spectrum of **2d** ($CDCl_3$, 100 MHz)

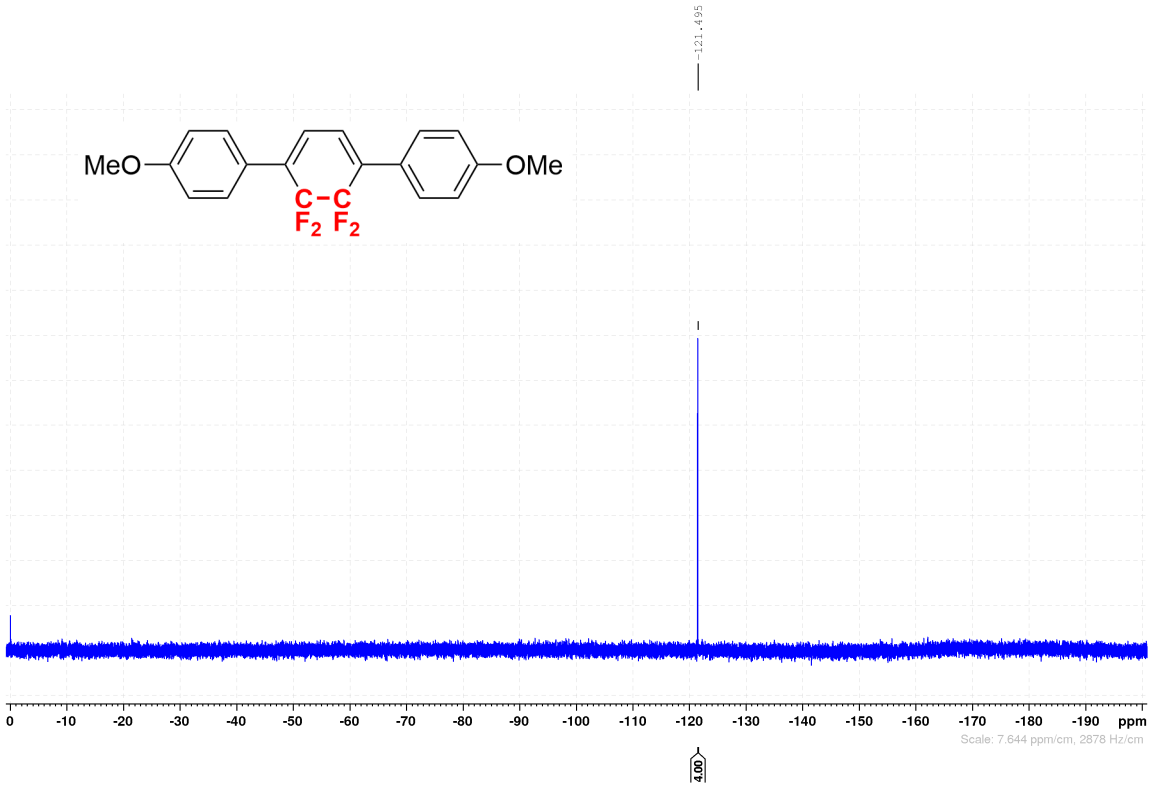


Figure S12. ^{19}F NMR spectrum of **2d** ($CDCl_3$, 376 MHz)

3. X-ray Crystallographic Analysis

Single crystal X-ray diffractions were recorded on an XtaLab AFC11 diffractometer (Rigaku). The reflection data were integrated, scaled, and averaged using CrysAlisPro (ver. 1.171.39.43a, Rigaku). Empirical absorption corrections were applied using the SCALE 3 ABSPACK scaling algorithm (CrysAlisPro). The structure were identified by a direct method (SHELXT-2018/2) and refined using a full matrix least square method (SHELXL-2014/7) visualized by Olex2. The crystallographic data were deposited into the Cambridge Crystallographic Data Centre (CCDC) database. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data of **2a–d**

	2a	**2b**	**2c**	**2d**
CCDC #	2144835	2144836	2144837	2144838
Empirical Formula	$C_{18}H_{12}F_4$	$C_{19}H_{11}F_7$	$C_{19}H_{14}F_4O$	$C_{20}H_{16}F_4O_2$
Formula weight	304.28	372.28	334.40	364.33
Temperature [K]	299	298	173	173
Crystal Color / Habit	Colourless / Block	Colourless / Block	Yellow / Block	Colourless / Block
Crystal Size [mm]	0.64 x 0.46 x 0.24	0.55 x 0.42 x 0.18	0.45 x 0.35 x 0.27	0.37 x 0.27 x 0.17
Crystal System	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space Group	*Pbcn*	*P* –1	*Pbca*	*C* 2/*c*
a [Å]	15.9027(7)	6.5391(2)	9.0280(5)	19.8807(11)
b [Å]	9.8059(3)	8.9883(3)	35.5954(16)	9.3734(5)
c [Å]	9.1193(4)	14.4828(5)	9.5477(5)	8.9806(5)
α [°]	90	94.851(3)	90	90
β [°]	90	94.118(3)	90	94.599(5)
γ [°]	90	109.620(3)	90	90
V [Å^3]	1422.07(10)	794.37(5)	3068.2(3)	1668.14(16)
Z	4	2	8	4
R [$F^2 > 2\sigma(F^2)$] [a]	0.0441	0.0424	0.0405	0.0350
wR_2 (F^2) [b]	0.1330	0.1210	0.1497	0.0889

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR = \{[\Sigma w(|F_o| - |F_c|)]/\Sigma w|F_o|\}^{1/2}$.

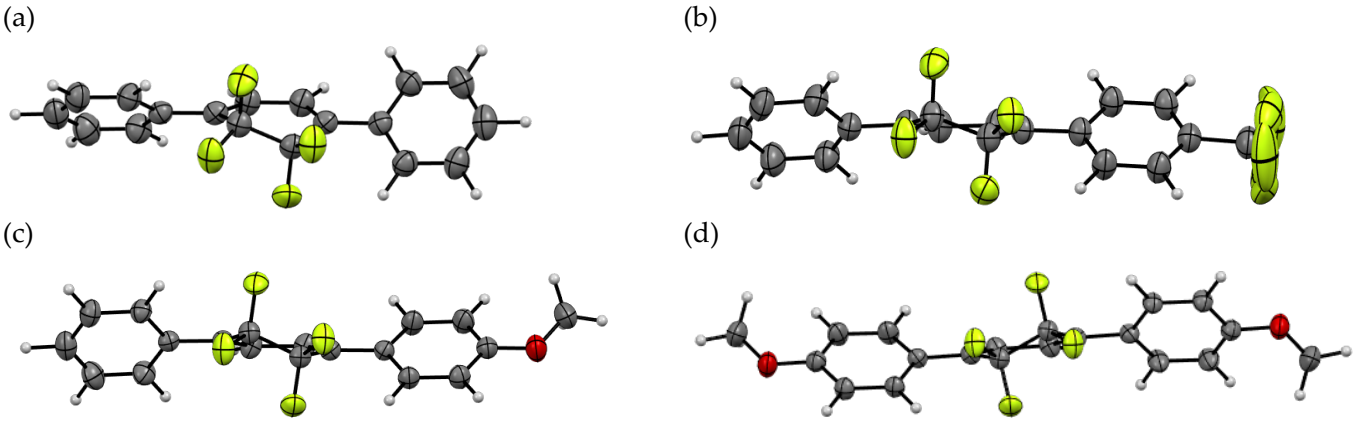


Figure S13. ORTEP Drawing of (a) **2a**, (b) **2b**, (c) **2c**, and (d) **2d**.

4. DFT Calculation

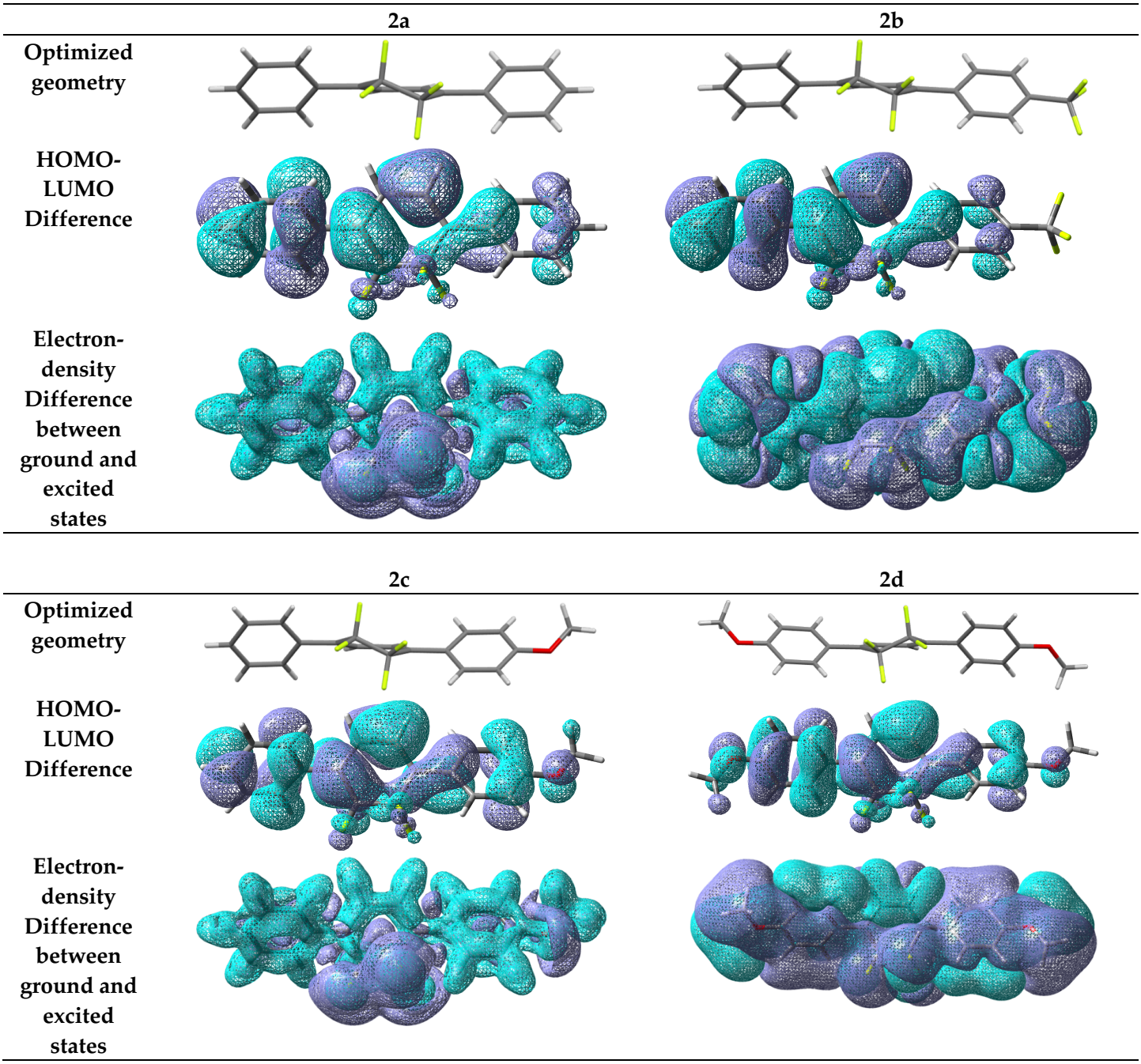


Figure S14. Optimized geometry, HOMO-LUMO difference distribution, and electron-density difference between ground and excited states for **2a**–**d**.

Table S2. Energy (hartree) and dipole moment (debye) of **2a**–**d** at S_0 state. (CPCM for $CHCl_3$)

	E(RCAM-B3LYP) [hartree]	Dipole moment (debye)			
2a	-1092.06854376	X= 0.0000	Y= 4.0414	Z= 0.0001	Tot= 4.0414
2b	-1429.05470941	X= 3.5042	Y= -4.2261	Z= 0.1373	Tot= 5.4916
2c	-1206.55353350	X= 1.5588	Y= -5.1445	Z= 0.6751	Tot= 5.4177
2d	-1321.03851299	X= 0.0843	Y= -4.0323	Z= 1.7336	Tot= 4.3899

Table S3. Theoretical vertical transition behavior calculated by TD-DFT calculation. (CPCM for $CHCl_3$)

	Transition	Transition Energy (eV)	Theoretical Absorption (nm)	Oscillator strength / *f*
2a	HOMO → LUMO	3.5494	349.31	0.8058
2b	HOMO → LUMO	3.5643	347.85	0.8556
2c	HOMO → LUMO	3.4014	364.51	0.8688
2d	HOMO → LUMO	3.3025	375.43	0.9498

Table S4. Cartesian coordinate for **2a** at the optimized geometry in S_0 state.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-5.072078	-0.467469	-0.749409
2	6	0	-3.681747	-0.481744	-0.773343
3	6	0	-2.946772	0.419431	0.010668
4	6	0	-3.642238	1.321932	0.82656
5	6	0	-5.032842	1.333721	0.848262
6	6	0	-5.753364	0.439639	0.059468
7	1	0	-5.627835	-1.171186	-1.371322
8	1	0	-3.161341	-1.188224	-1.419241
9	1	0	-3.08622	2.007791	1.467591
10	1	0	-5.556584	2.040254	1.494359
11	6	0	-1.470298	0.443499	-0.034401
12	6	0	-0.729811	1.564237	0.030015
13	6	0	0.729782	1.564253	-0.030055
14	1	0	-1.225439	2.532665	0.108144
15	6	0	1.47029	0.44353	0.034381
16	1	0	1.22538	2.532694	-0.108204
17	6	0	2.946766	0.419459	-0.01068
18	6	0	3.64226	1.321979	-0.82653
19	6	0	3.68172	-0.481758	0.773301
20	6	0	5.03286	1.333736	-0.848207
21	1	0	3.08627	2.00787	-1.467548
22	6	0	5.072056	-0.467518	0.749387
23	1	0	3.161295	-1.18826	1.41916
24	6	0	5.753363	0.43961	-0.05944
25	1	0	5.556659	2.040272	-1.494258
26	1	0	5.627752	-1.171291	1.371288
27	6	0	-0.72393	-0.843808	-0.266442
28	6	0	0.72394	-0.843786	0.266439
29	9	0	-1.359656	-1.902564	0.297373
30	9	0	0.665277	-1.102304	1.610429
31	9	0	1.359693	-1.902539	-0.29735
32	9	0	-0.665277	-1.102349	-1.610425
33	1	0	6.844412	0.44581	-0.079269
34	1	0	-6.844415	0.445758	0.079213

Table S5. Cartesian coordinate for **2b** at the optimized geometry in S_0 state.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-6.384927	-0.362438	-0.773512
2	6	0	-4.995441	-0.414277	-0.789207
3	6	0	-4.241646	0.464594	0.00219
4	6	0	-4.916993	1.383301	0.816911
5	6	0	-6.306791	1.432001	0.830793
6	6	0	-7.046115	0.560023	0.034653
7	1	0	-6.955749	-1.048802	-1.401055
8	1	0	-4.490599	-1.132498	-1.43446
9	1	0	-4.346651	2.052115	1.463301
10	1	0	-6.815323	2.150077	1.476229
11	6	0	-2.765068	0.449262	-0.033979
12	6	0	-1.995673	1.549714	0.04112
13	6	0	-0.536484	1.509228	-0.010534
14	1	0	-2.464608	2.530983	0.120826
15	6	0	0.171235	0.367841	0.05362
16	1	0	-0.014176	2.464256	-0.080298
17	6	0	1.646741	0.30579	0.024567
18	6	0	2.37534	1.198492	-0.772503
19	6	0	2.347431	-0.622456	0.807893
20	6	0	3.763476	1.175283	-0.779617
21	1	0	1.848957	1.909961	-1.409459
22	6	0	3.735409	-0.648595	0.801388
23	1	0	1.803246	-1.31883	1.444111
24	6	0	4.444687	0.247873	0.005287
25	1	0	4.318546	1.876974	-1.402033
26	1	0	4.269413	-1.364888	1.42547
27	6	0	-2.052776	-0.857725	-0.267957
28	6	0	-0.608876	-0.900592	0.273952
29	9	0	-2.720593	-1.9006	0.286621
30	9	0	-0.680973	-1.166099	1.615367
31	9	0	0.003834	-1.970755	-0.293579
32	9	0	-1.99241	-1.109386	-1.612459
33	1	0	-8.136684	0.595368	0.048157
34	6	0	5.941575	0.188606	-0.038439
35	9	0	6.385339	-0.638889	-1.006024
36	9	0	6.464573	-0.259162	1.116914
37	9	0	6.488341	1.392639	-0.285789

Table S6. Cartesian coordinate for **2c** at the optimized geometry in S_0 state.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-5.779803	0.261653	0.851783
2	6	0	-4.391088	0.334871	0.845344
3	6	0	-3.637729	-0.492167	-0.000635
4	6	0	-4.31487	-1.381104	-0.84643
5	6	0	-5.703869	-1.452594	-0.837176
6	6	0	-6.442121	-0.631974	0.012731
7	1	0	-6.349173	0.908233	1.521623
8	1	0	-3.885331	1.029475	1.51531
9	1	0	-3.746533	-2.008509	-1.534812
10	1	0	-6.212927	-2.147639	-1.507088
11	6	0	-2.160859	-0.453834	0.009946
12	6	0	-1.374461	-1.535786	-0.132337
13	6	0	0.084345	-1.477729	-0.107224
14	1	0	-1.831455	-2.51887	-0.253085
15	6	0	0.777521	-0.324202	-0.121591
16	1	0	0.62057	-2.427397	-0.099201
17	6	0	2.248684	-0.233174	-0.099755
18	6	0	3.009196	-1.156231	0.623344
19	6	0	2.934888	0.760261	-0.82121
20	6	0	4.40099	-1.11488	0.628583
21	1	0	2.506587	-1.919275	1.219771
22	6	0	4.316772	0.811021	-0.825307
23	1	0	2.376561	1.494068	-1.401567
24	6	0	5.064976	-0.126679	-0.101688
25	1	0	4.951977	-1.848797	1.21379
26	1	0	4.850089	1.575692	-1.391146
27	6	0	7.214393	-0.912791	0.545275
28	1	0	7.052457	-1.944499	0.192779
29	1	0	8.253585	-0.623264	0.351512
30	1	0	7.019968	-0.865192	1.629149
31	6	0	-1.464037	0.849161	0.2969
32	6	0	-0.029547	0.940266	-0.263852
33	9	0	-2.155472	1.909452	-0.194945
34	9	0	-0.128439	1.270787	-1.589742
35	9	0	0.57261	1.993518	0.346223
36	9	0	-1.385865	1.038424	1.651939
37	8	0	6.409988	0.010795	-0.166967
38	1	0	-7.532097	-0.68454	0.017205

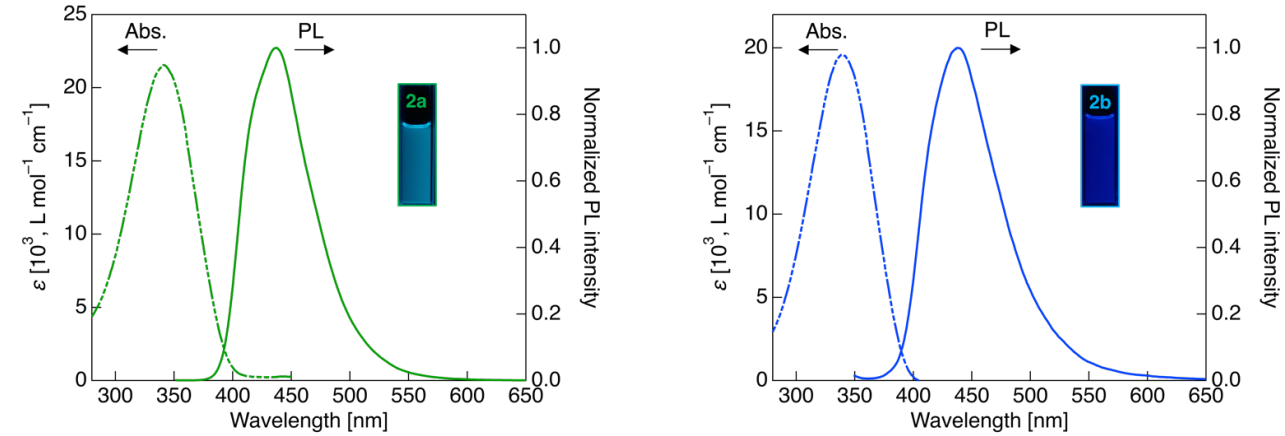
Table S7. Cartesian coordinate for **2d** at the optimized geometry in S_0 state.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	5.091381	0.373985	-0.696921
2	6	0	3.69999	0.424788	-0.702445
3	6	0	2.931702	-0.445868	0.077796
4	6	0	3.612102	-1.373214	0.885269
5	6	0	4.993785	-1.433514	0.900079
6	6	0	5.748715	-0.560221	0.106534
7	1	0	5.648314	1.066137	-1.325733
8	1	0	3.208395	1.153131	-1.34646
9	1	0	3.04554	-2.046109	1.530762
10	1	0	5.520977	-2.14734	1.534057
11	6	0	1.457994	-0.4223	0.041893
12	6	0	0.675429	-1.511472	0.158081
13	6	0	-0.782656	-1.462483	0.113951
14	1	0	1.135984	-2.493703	0.270925
15	6	0	-1.486346	-0.315203	0.129579
16	1	0	-1.311647	-2.416032	0.087591
17	6	0	-2.95802	-0.236309	0.086628
18	6	0	-3.700105	-1.15786	-0.657177
19	6	0	-3.66367	0.743582	0.807813
20	6	0	-5.09215	-1.128628	-0.682256
21	1	0	-3.182204	-1.910344	-1.253963
22	6	0	-5.04599	0.782876	0.791621
23	1	0	-3.120299	1.47597	1.403977
24	6	0	-5.775398	-0.153703	0.047857
25	1	0	-5.628039	-1.861402	-1.282756
26	1	0	-5.594107	1.537286	1.357141
27	8	0	7.093307	-0.694034	0.191793
28	8	0	-7.122799	-0.028436	0.094731
29	6	0	-7.908089	-0.952592	-0.63747
30	1	0	-7.741234	-1.986144	-0.292641
31	1	0	-8.952717	-0.674936	-0.455804
32	1	0	-7.698986	-0.892951	-1.718055
33	6	0	7.903744	0.173087	-0.58199
34	1	0	7.715722	0.045661	-1.660537
35	1	0	7.741351	1.228278	-0.308097
36	1	0	8.941243	-0.102622	-0.36082
37	6	0	0.752994	0.878823	-0.238748
38	6	0	-0.691747	0.952684	0.298291
39	9	0	1.425114	1.940143	0.278317
40	9	0	-0.617277	1.271344	1.629237
41	9	0	-1.291148	2.008698	-0.310774
42	9	0	0.697273	1.084942	-1.592567

5. Photophysical Characteristics

5-1. Solution state

(a) **2a** (b) **2b**



(c) **2c** (d) **2d**

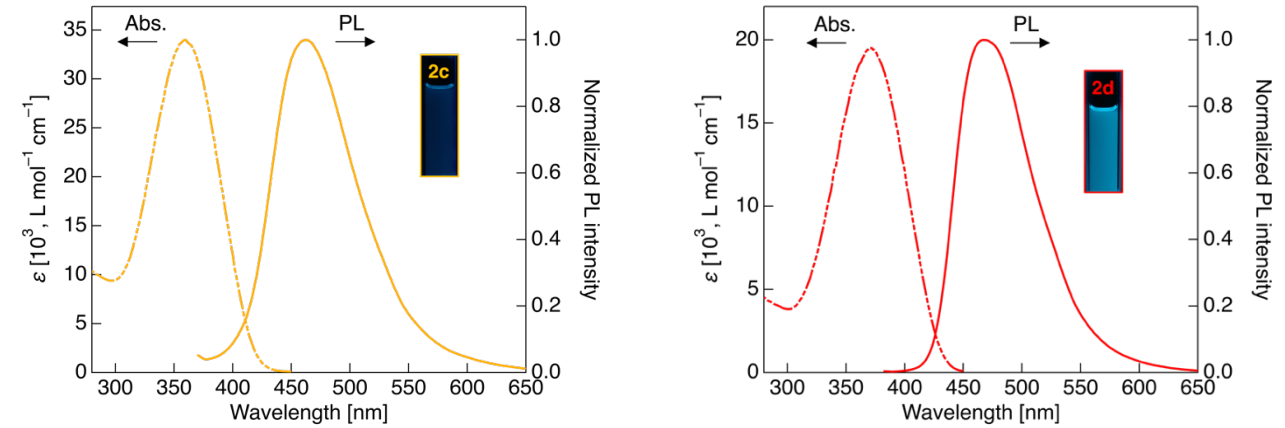


Figure S15. UV-vis and PL spectra of **2a–d** in $CHCl_3$ solution. Concentration: 1.0×10^{-5} mol L^{-1} for UV-vis and PL measurement.

(a) **2a** (b) **2b** (c) **2c** (d) **2d**

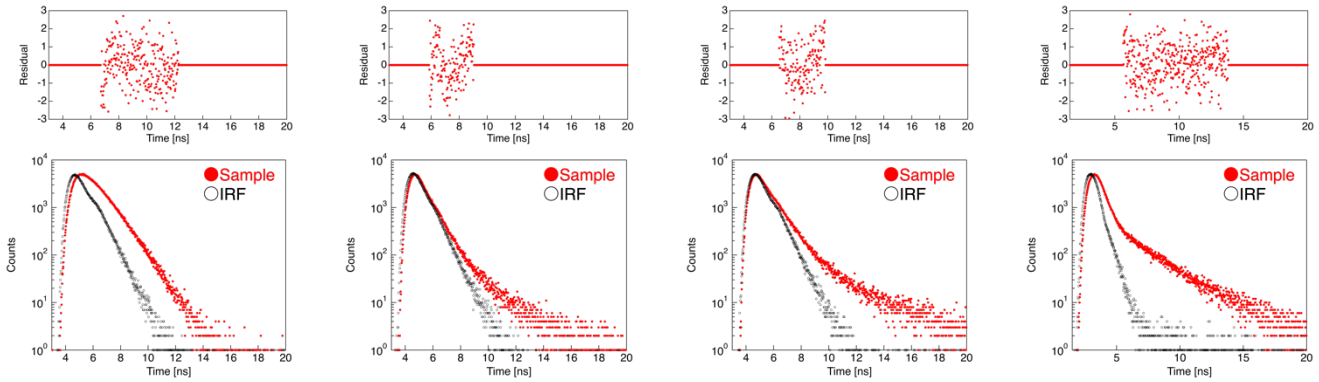


Figure S16. PL decay profiles of (a) **2a** (λ_{ex} = 340 nm. λ_{PL} = 437 nm), (b) **2b** (λ_{ex} = 340 nm. λ_{PL} = 437 nm), (c) **2c** (λ_{ex} = 340 nm. λ_{PL} = 468 nm), and (d) **2d** (λ_{ex} = 340 nm. λ_{PL} = 467 nm) in $CHCl_3$ solution.

Table S8. Photophysical data of **2a–d** in $CHCl_3$ solution (concentration: 1.0 x 10^{-5} mol L^{-1})

	λ_{abs} [nm] (ε, 10^3 [L mol^{-1} cm^{-1}])	λ_{PL} [nm]	Φ_{PL}	τ_{PL} [ns]	k_r [10^8, s^{-1}]	k_{nr} [10^8, s^{-1}]
2a	341 (21.6)	437	0.31	1.1	2.8	6.3
2b	339 (19.6)	437	0.03	0.88	0.34	11.0
2c	360 (34.0)	462	0.01	1.1	0.09	9.0
2d	371 (19.4)	467	0.11	0.64	1.7	13.9

Radiation rate constant: $k_r = \Phi_{PL}/\tau_{PL}$, Nonradiation rate constant: $k_{nr} = (1-\Phi_{PL})/\tau_{PL}$

5-2. Solvent effect

(a) **2a** (b) **2b**

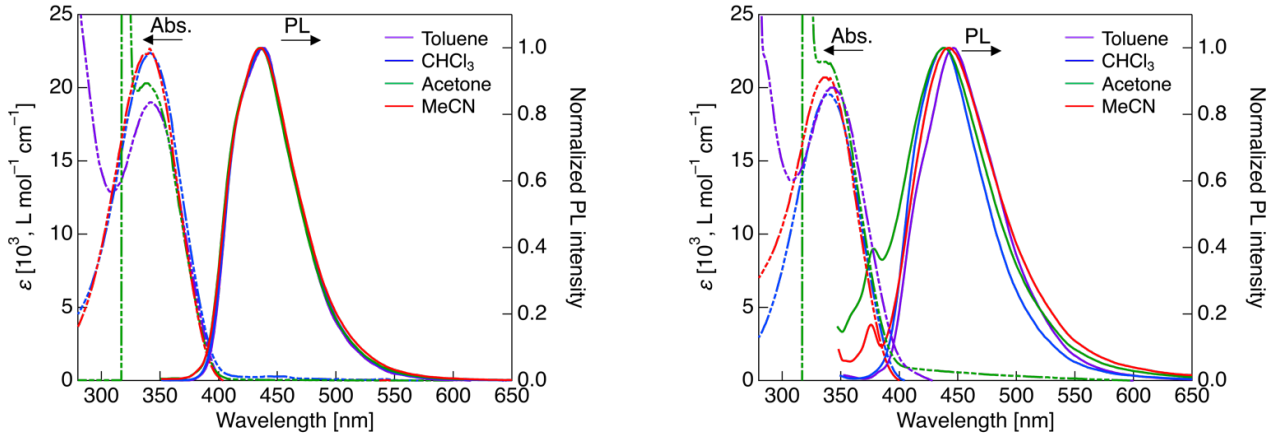


Figure S17. UV-vis and PL spectra of **2a** and **2b** in various solvent (toluene, $CHCl_3$, acetone, and MeCN). Concentration: 1.0×10^{-5} mol L^{-1} for UV-vis and PL measurement. *The short-wavelength PL band for **2b** at around 400 nm is maybe originated from the impurities.

(a) in acetone (b) in MeCN

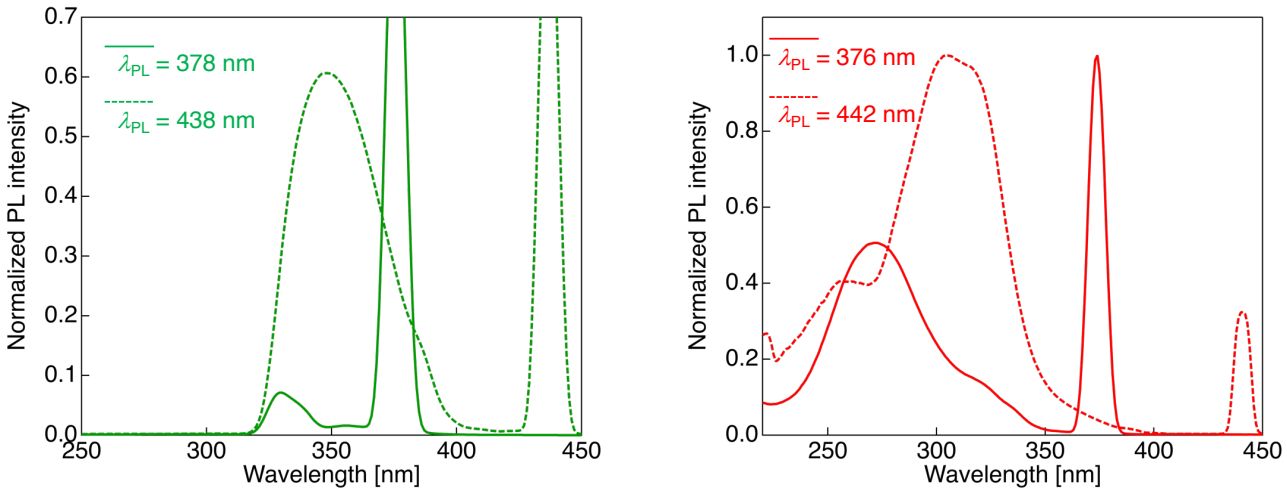


Figure S18. Excitation spectra of **2b** in (a) acetone and (b) MeCN.

(a) Toluene (b) $CHCl_3$ (c) Acetone (d) MeCN

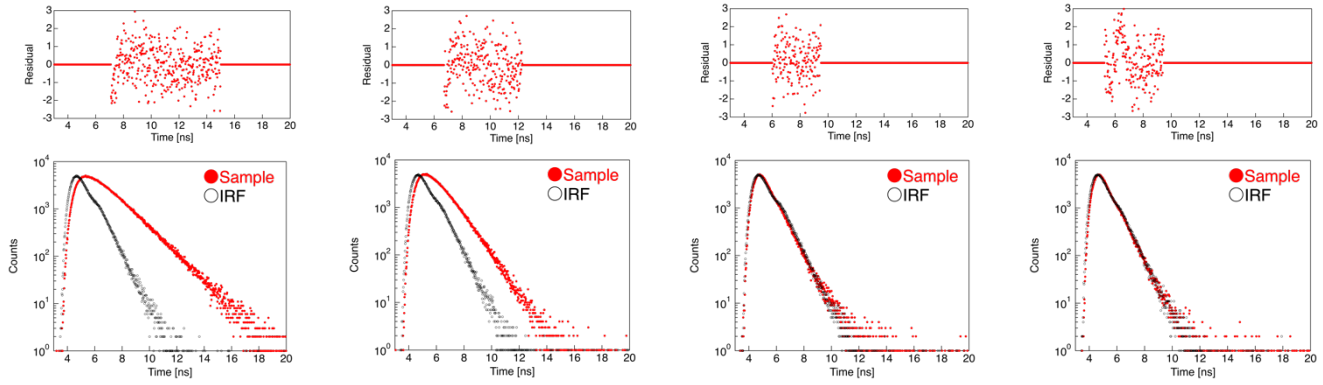


Figure S19. PL decay profiles monitored at λ_{PL} of **2a** in various solvent: (a) toluene (λ_{ex} = 340 nm. λ_{PL} = 436 nm), (b) $CHCl_3$ (λ_{ex} = 340 nm. λ_{PL} = 437 nm), (c) acetone (λ_{ex} = 340 nm. λ_{PL} = 435 nm), and (d) MeCN (λ_{ex} = 340 nm. λ_{PL} = 432 nm).

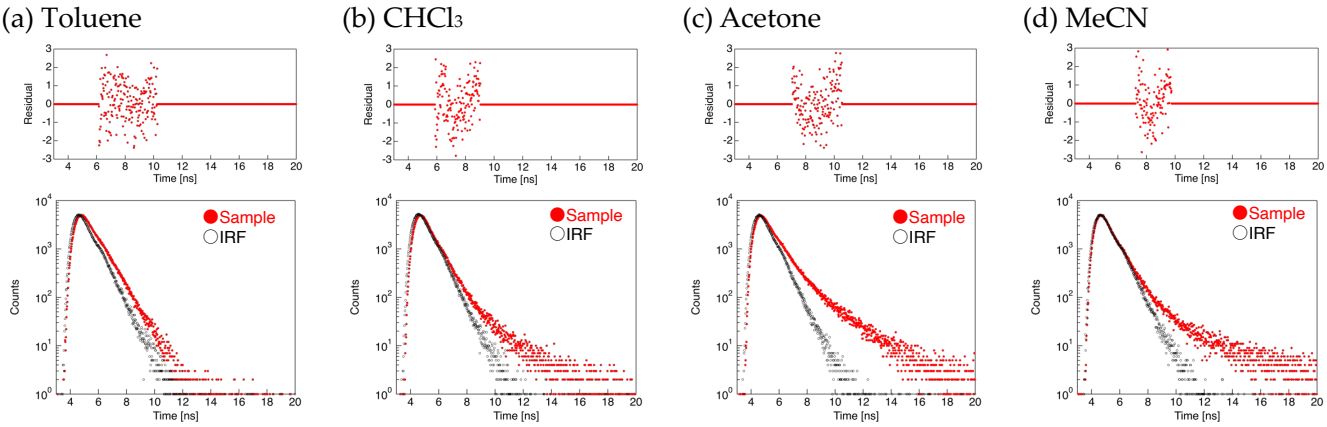


Figure S20. PL decay profiles monitored at λ_{PL} of **2b** in various solvent: (a) toluene (λ_{ex} = 340 nm. λ_{PL} = 446 nm), (b) $CHCl_3$ (λ_{ex} = 340 nm. λ_{PL} = 437 nm), (c) acetone (λ_{ex} = 340 nm. λ_{PL} = 438 nm), and (d) MeCN (λ_{ex} = 340 nm. λ_{PL} = 442 nm).

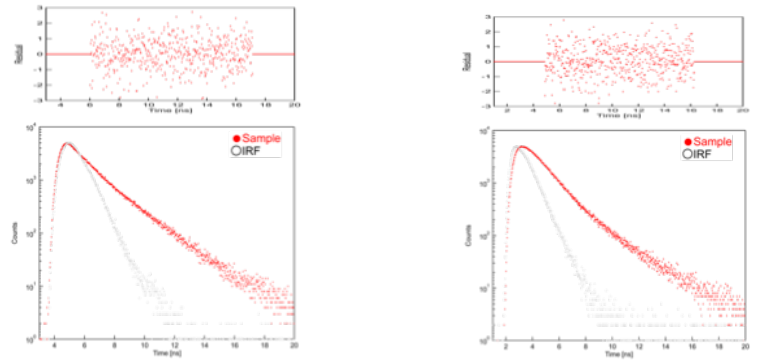


Figure S21. PL decay profiles monitored at λ_{PL} of **2b** in (a) acetone and (b) MeCN for short-wavelength PL peak.

Table S9. Photophysical data of **2a** and **2b** in various solvent.

	Dielectric constant (ε)	Reflective index (n)	Δf	ν_{abs} [cm^{-1}]	ν_{PL} [cm^{-1}]	$\Delta\nu$ [cm^{-1}]
2a						
Toluene	2.381	1.496	0.0136	29155	22831	6324
$CHCl_3$	4.806	1.443	0.149	29326	22883	6443
Acetone	20.56	1.359	0.284	29499	22989	6510
MeCN	35.94	1.344	0.305	29412	22936	6476
2b						
Toluene	2.381	1.496	0.0136	29070	22422	6648
$CHCl_3$	4.806	1.443	0.149	29499	22883	6616
Acetone	20.56	1.359	0.284	29674	22831	6843
MeCN	35.94	1.344	0.305	29674	22624	7050

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

(a) **2a** (b) **2b**

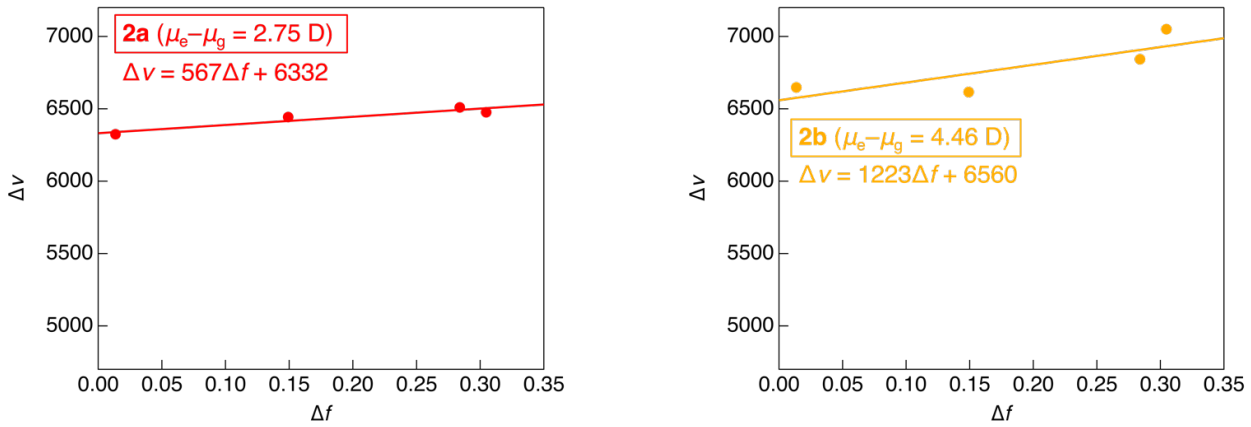


Figure S22. Lippert-Mataga plot of **2a** and **2b** calculated from photophysical behavior in various solvent.

(a) **2c** (b) **2d**

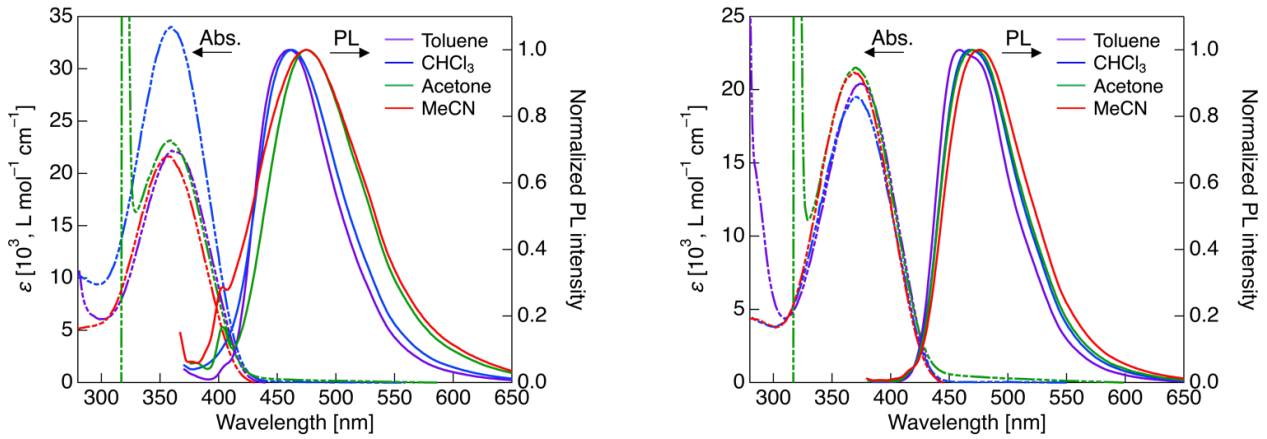


Figure S23. UV-vis and PL spectra of **2c** and **2d** in various solvent (toluene, $CHCl_3$, acetone, and MeCN). Concentration: 1.0 × 10^{-5} mol L^{-1} for UV-vis and PL measurement. *The short-wavelength PL band at around 400 nm for **2c** is maybe originated from the impurities.

(a) in acetone (b) in MeCN

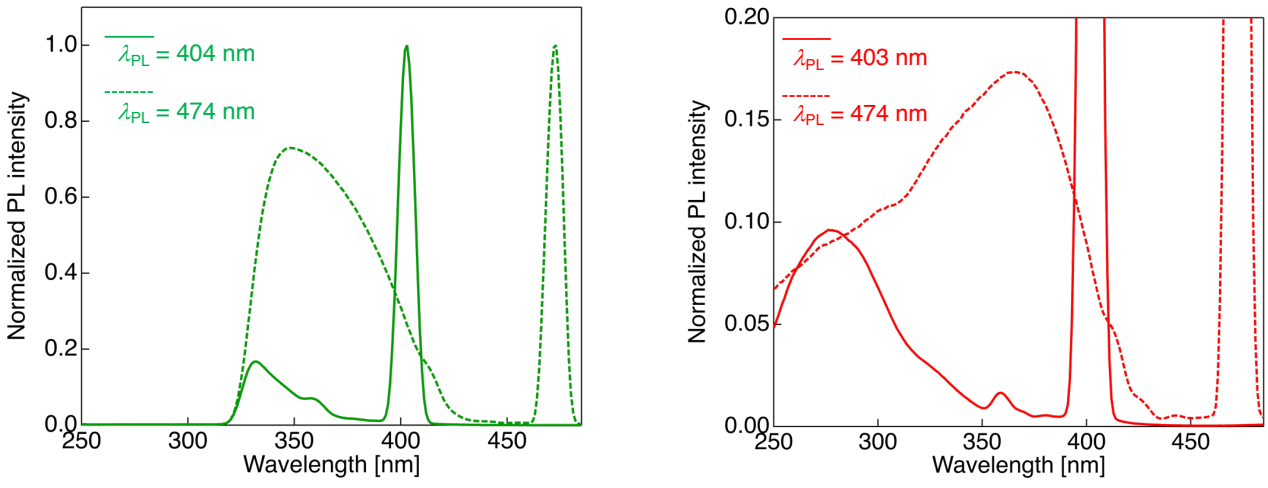


Figure S24. Excitation spectra of **2b** in (a) acetone and (b) MeCN.

(a) Toluene (b) $CHCl_3$ (c) Acetone (d) MeCN

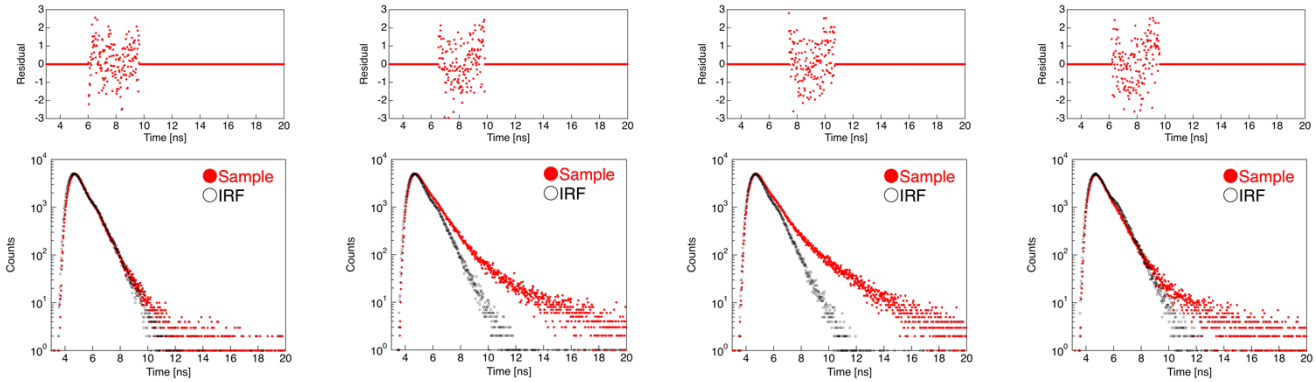


Figure S25. PL decay profiles monitored at λ_{PL} of **2c** in various solvent: (a) toluene (λ_{ex} = 340 nm. λ_{PL} = 468 nm), (b) $CHCl_3$ (λ_{ex} = 340 nm. λ_{PL} = 468 nm), (c) acetone (λ_{ex} = 340 nm. λ_{PL} = 468 nm), and (d) MeCN (λ_{ex} = 340 nm. λ_{PL} = 469 nm).

(a) Acetone (λ_{em} = 404 nm) (b) MeCN (λ_{em} = 403 nm)

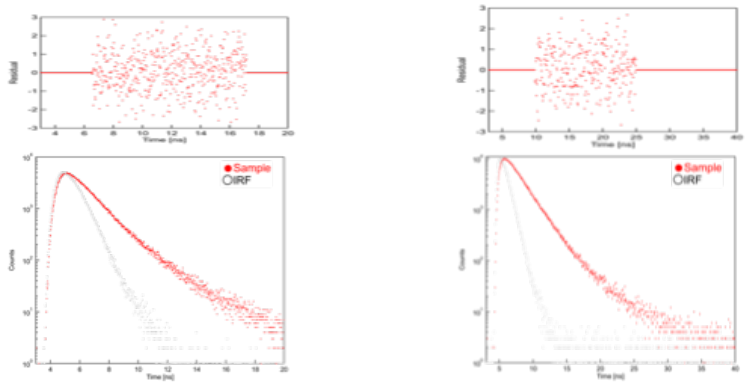


Figure S26. PL decay profiles monitored at λ_{PL} of **2c** in (a) acetone and (b) MeCN for short-wavelength PL peak.

(a) Toluene (b) $CHCl_3$ (c) Acetone (d) MeCN

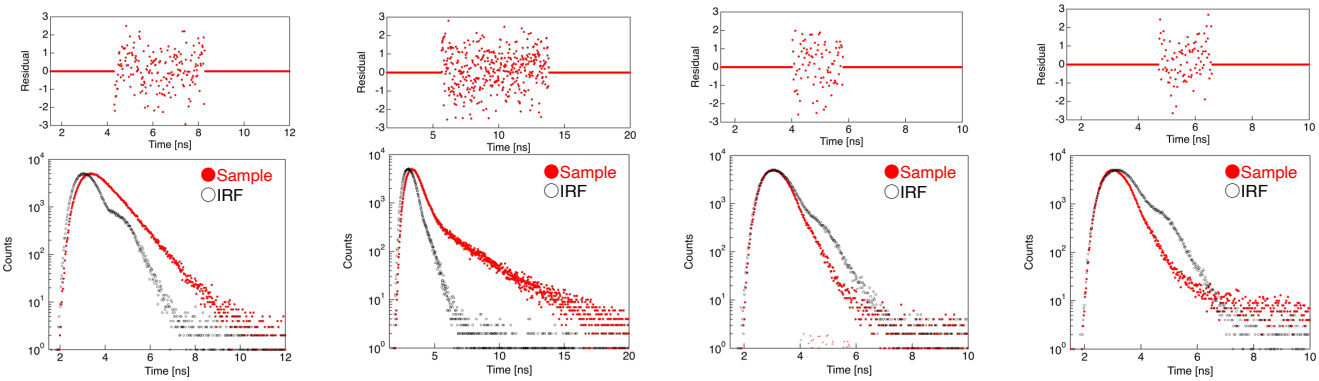


Figure S27. PL decay profiles monitored at λ_{PL} of **2d** in various solvent: (a) toluene (λ_{ex} = 340 nm. λ_{PL} = 459 nm), (b) $CHCl_3$ (λ_{ex} = 340 nm. λ_{PL} = 467 nm), (c) acetone (λ_{ex} = 340 nm. λ_{PL} = 470 nm), and (d) MeCN (λ_{ex} = 340 nm. λ_{PL} = 476 nm).

Table S10. Photophysical data of **2c** and **2d** in various solvent.

	Dielectric constant (ε)	Reflective index (n)	Δf	ν_{abs} [cm^{-1}]	ν_{PL} [cm^{-1}]	$\Delta\nu$ [cm^{-1}]
2c						
Toluene	2.381	1.496	0.0136	27628	21736	5885
$CHCl_3$	4.806	1.443	0.149	27778	21645	6133
Acetone	20.56	1.359	0.284	27855	21097	6758
MeCN	35.94	1.344	0.305	28090	21097	6993
2d						
Toluene	2.381	1.496	0.0136	26667	21786	4881
$CHCl_3$	4.806	1.443	0.149	26954	21413	5541
Acetone	20.56	1.359	0.284	27027	21277	5750
MeCN	35.94	1.344	0.305	27100	21008	6092

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

(a) **2c** (b) **2d**

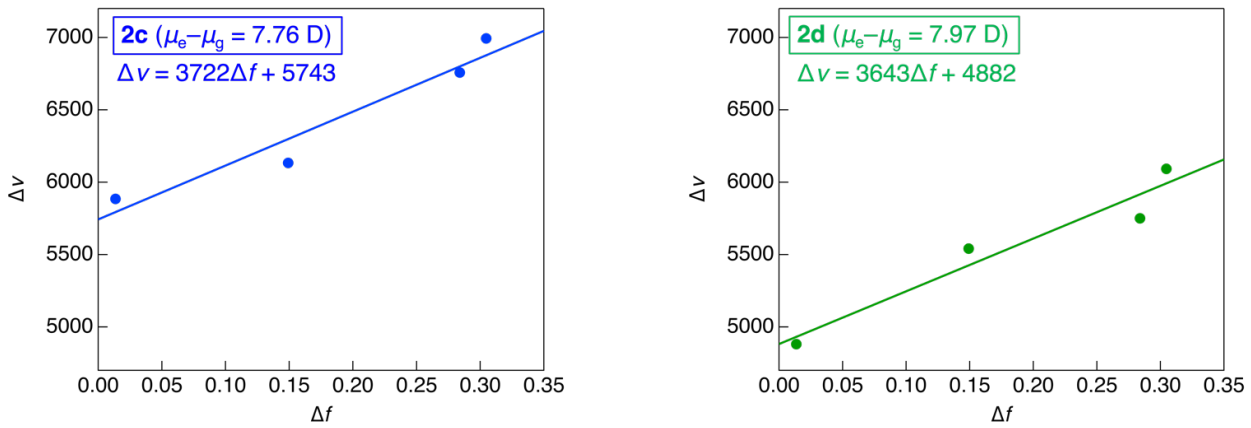
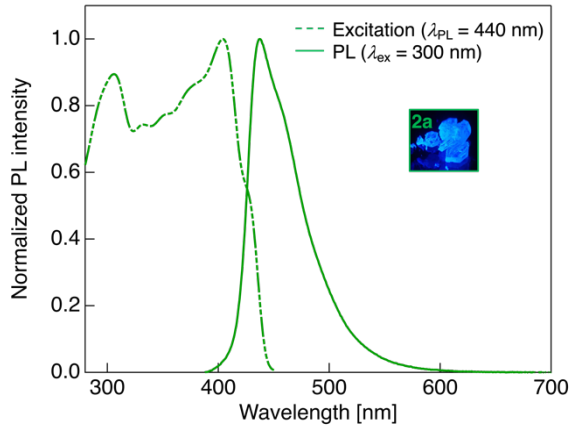


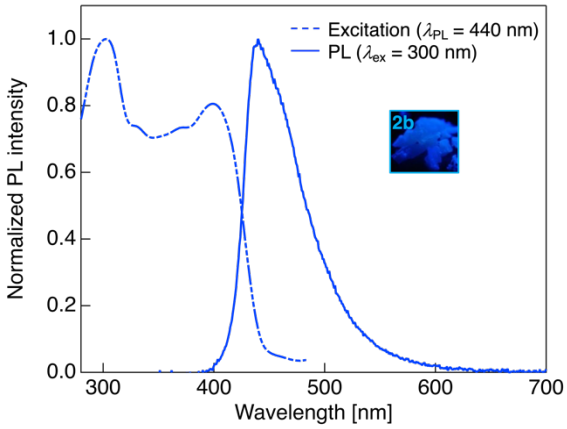
Figure S28. Lippert-Mataga plot of **2c** and **2d** calculated from photophysical behavior in various solvent.

5-3. Crystalline state

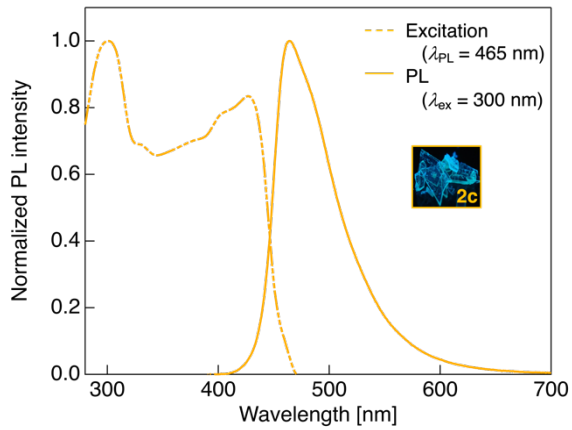
(a) **2a**



(b) **2b**



(c) **2c**



(d) **2d**

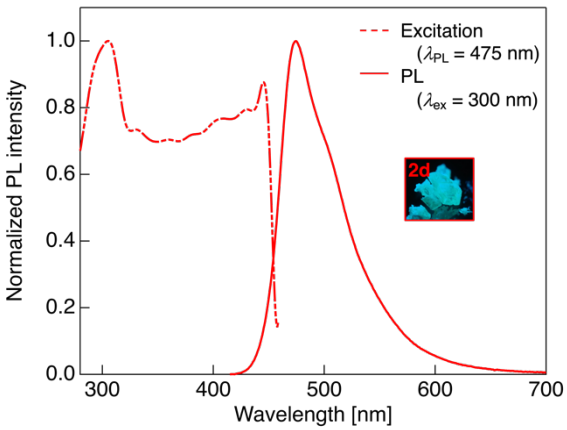


Figure S29. Excitation and PL spectra of (a) **2a**, (b) **2b**, (c) **2c**, and (d) **2d** in crystal.

(a) **2a** (b) **2b** (c) **2c** (d) **2d**

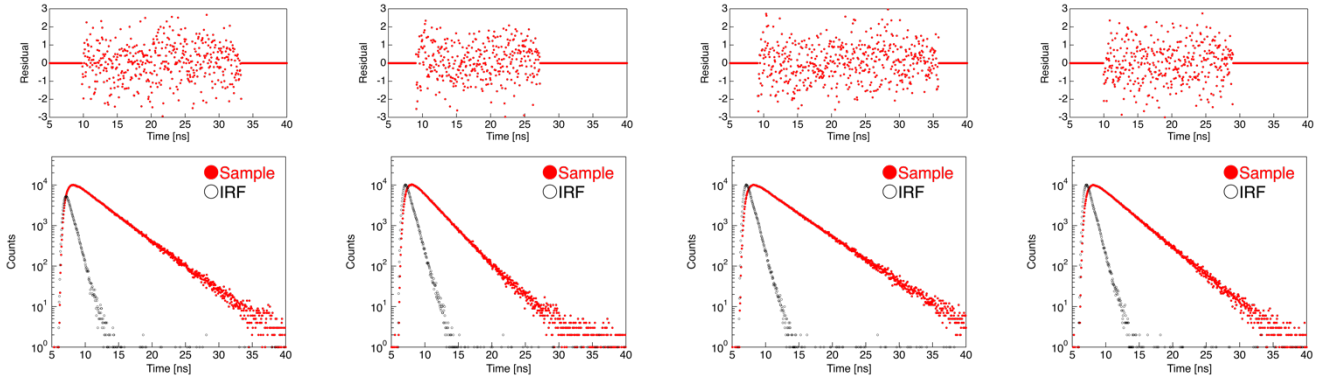


Figure S30. PL decay profiles of (a) **2a** (λ_{ex} = 340 nm. λ_{PL} = 437 nm), (b) **2b** (λ_{ex} = 340 nm. λ_{PL} = 439 nm), (c) **2c** (λ_{ex} = 340 nm. λ_{PL} = 464 nm), and (d) **2d** (λ_{ex} = 340 nm. λ_{PL} = 474 nm) in crystal.

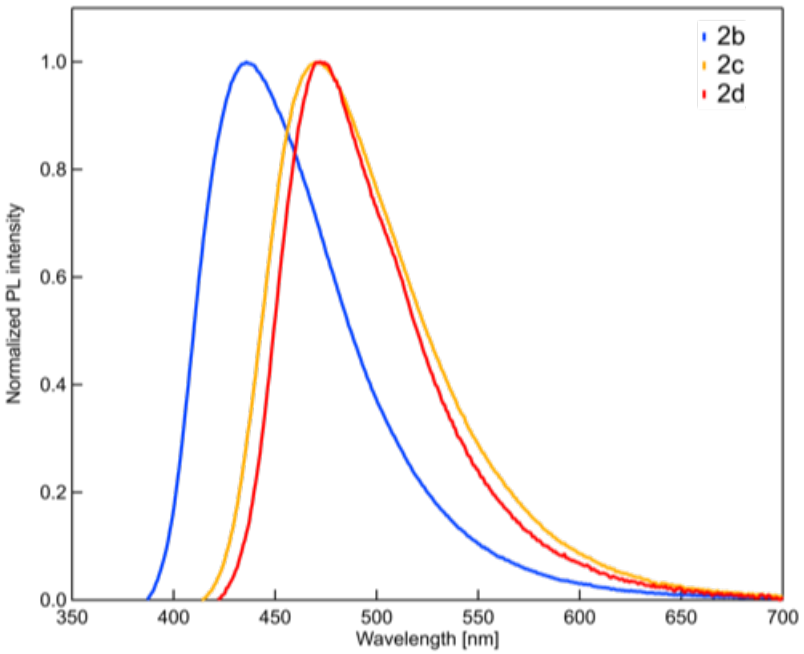


Figure S31. PL spectra of**2b**, **2c**, and **2d** in the PMMA film (1 wt%).

Table S11. Photophysical data of **2a–d** in PMMA film

1% PMMA film	λ_{PL}	Φ_{PL}
2a	–	0
2b	436 nm	0.62
2c	464 nm	0.51
2d	472 nm	0.16

5-4. AIEE Behavior

(a) **2a** (b) **2c**

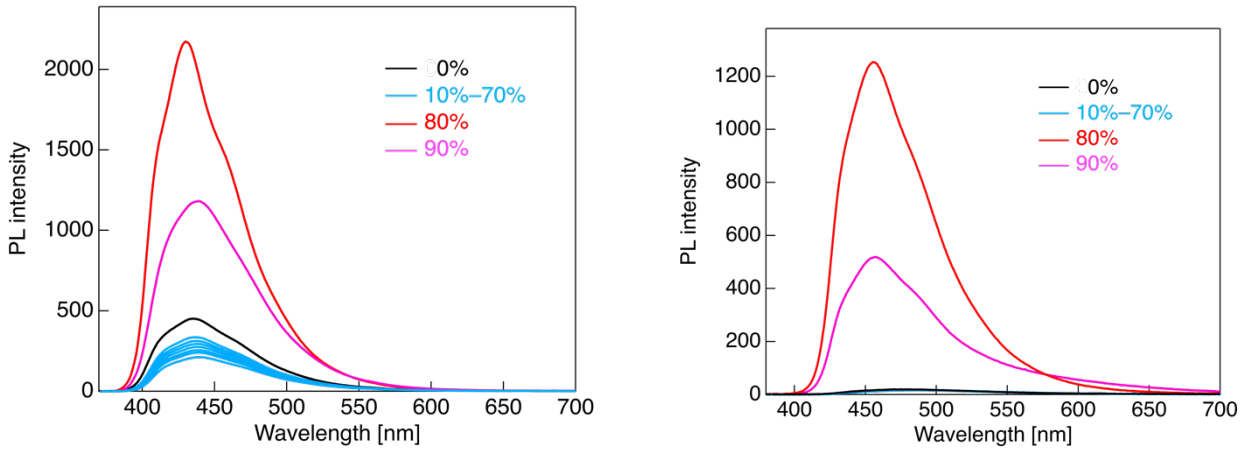


Figure S32. PL spectra and AIE characteristics of **2a** and **2c** in THF/H_2O mixed solvent system.

Table S12. Photophysical data of **2a** and **2c** in THF/H_2O mixed solvent system.

	2a (λ_{ex} = 296 nm)		**3c** (λ_{ex} = 347 nm)	
Water ratio [%]	λ_{PL} [nm]	PL intensity / Φ_{PL}	λ_{PL} [nm]	PL intensity / Φ_{PL}
0	436	451.36 / 0.186	469	19.65 / 0.011
10	437	335.87 / 0.141	479	18.27 / 0.011
20	437	312.72 / 0.133	480	17.13 / 0.010
30	438	293.78 / 0.127	479	16.77 / 0.010
40	437	275.74 / 0.120	481	17.28 / 0.010
50	437	255.01 / 0.113	484	17.34 / 0.010
60	439	240.97 / 0.107	485	17.23 / 0.010
70	438	212.48 / 0.096	488	17.72 / 0.010
80	430	2172.8 / 1.0	455	1253.8 / 0.545
90	439	1181.3 / 0.71	457	518.9 / 0.253