Electronic Supporting Information

Effects of Tetrafluorocyclohexa-1,3-diene Ring Position on Photoluminescence and Liquid-Crystalline Properties of Tricyclic π-Conjugated Molecules

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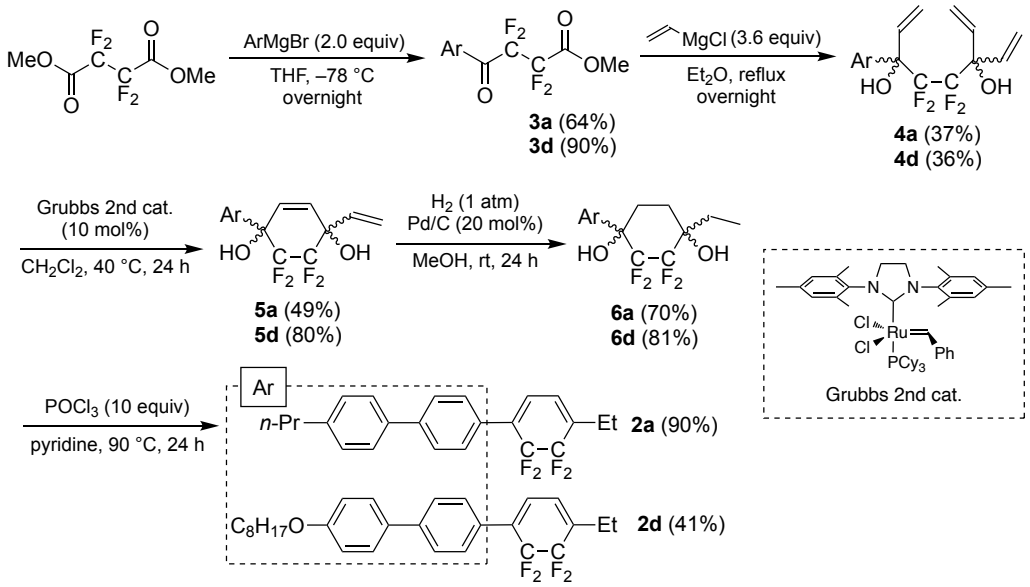
1. Synthesis of 2a and 2d



Scheme S1. Synthetic procedure of **2a** and **2d** starting from commercially available dimethyl 2,2,3,3-tetrafluorosuccinate.

1-1. Typical procedure for the preparation of methyl 2,2,3,3-tetrafluoro-4-oxo-4-[4-(4-n-propylphenyl)phenyl]butanoate (3a)

To a solution of dimethyl 2,2,3,3-tetrafluorosuccinate (3.27 g, 15 mmol) in THF (30 mL) was added a THF solution of 4-(4-propylphenyl)phenylmagnesium bromide, prepared from 4-(4-propylphenyl)phenyl bromide (30 mmol) and magnesium turnings(33 mmol) at −78 °C. Then, the mixture was stirred at that temperature overnight. The reaction mixture was poured into aqueous NH_4Cl solution, then the whole was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the *β*-keto ester **3a** in 64% yield (3.55 g, 9.60 mmol).

Methyl 2,2,3,3-tetrafluoro-4-oxo-4-[4-(4-n-propylphenyl)phenyl]butanoate (3a)

Yield: 64% (3.55 g, 9.60 mmol); ^{1}H NMR ($CDCl_3$): δ 1.96 (t, J = 7.4 Hz, 3H), 1.69 (sext., J = 7.4 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H), 3.97 (s, 3H), 7.31 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H);^{13}C NMR ($CDCl_3$): δ 13.8, 24.4, 37.7, 54.0, 108.2 (tt, J = 262.7, 27.8 Hz), 111.2 (tt, J = 270.1, 28.5 Hz), 127.2, 127.3, 129.2, 130.8 (two carbons were overlaped), 136.4, 143.8, 148.2, 160.4 (t, J = 30.0 Hz), 184.9 (t, J = 27.1 Hz); ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –120.97 (t, J = 4.9 Hz, 2F), –113.46 (t, J = 4.9 Hz, 2F). The compound characterization data were consistent with those described in previously published reports.[1]

Methyl 2,2,3,3-tetrafluoro-4-oxo-4-[4-(4-octyloxyphenyl)phenyl]butanoate (3d)

Yield: 90% (5.06 g, 10.8 mmol); White solid; M.p.: 42.3-43.8 ℃; 1H NMR ($CDCl_3$): δ0.90 (t, J = 7.2 Hz, 3H), 1.25–1.43 (m, 8H), 1.49 (quin, J = 6.8 Hz, 2H), 1.82 (quin, J = 6.4 Hz, 2H), 3.97 (s, 3H), 4.02 (t, J = 6.4 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8

Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.0, 29.20, 29.22, 29.3, 31.8, 54.0, 68.2, 108.2 (tt, J = 302.3, 27.9 Hz), 110.8 (tt, J = 231.9, 27.9 Hz), 115.1, 126.7, 128.5, 128.8, 130.9, 131.1, 147.8, 160.1, 160.3 (t, J = 30.0 Hz), 184.8 (t, J = 27.2 Hz); ^{19}F NMR (CDCl3): δ –112.99 (s, 2F), –120.67 (s, 2F); IR (KBr): ν 2926, 2855, 2532, 2362, 1789, 1685, 1593, 1428, 1408, 1391, 1200, 1175, 1012, 832, 752, 731 cm^{-1}; HRMS (FAB) Calcd for $C_{25}H_{28}F_4O_4$ $[M]^+$: 468.1924, Found: 468.1932.

1-2. Typical procedure for the synthesis of 3-ethenyl-4,4,5,5-tetrafluoro-6-[4-(4-propylphenyl)phenyl]-1,7-octadien-3,6-diol (4a)

To a solution of β-keto ester (**3a**, 3.55 g, 9.3 mmol) in Et_2O (90 mL) was added a THF solution of vinylmagnesium chloride (2.1 M, 16 mL, 33.5 mmol) at room temperature and continuously stirred at reflux temperature overnight. The reaction mixture was poured into aqueous NH_4Cl solution and the whole was extracted with Et_2O three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the desired diol **4a** in 37% yield (1.48 g, 3.44 mmol).

3-Ethenyl-4,4,5,5-tetrafluoro-6-[4-(4-*n*-propylphenyl)phenyl]-1,7-octadien-3,6-diol (4a)

Yield: 37% (1.48 g, 3.44 mmol); ^{1}H NMR ($CDCl_3$): δ 1.03 (t, J = 7.4 Hz, 3H), 1.73 (sext., J = 7.4 Hz, 2H), 2.68 (t, J = 7.4 Hz, 2H), 3.75 (s, 1H), 4.75 (s, 1H), 5.42 (d, J = 10.8 Hz, 1H), 5.43 (d, J = 10.8 Hz, 1H), 5.45 (d, J = 10.8 Hz, 1H), 5.57 (d, J = 17.2 Hz, 2H), 5.58 (d, J = 17.2 Hz, 1H), 6.15 (dd, J = 17.2, 10.8 Hz, 1H), 6.23 (dd, J = 17.2, 10.8 Hz, 1H), 6.69 (dd, J = 17.2, 10.8 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 13.8, 24.5, 37.6, 77.27 (t, J = 24.9 Hz), 77.33 (t, J = 24.9 Hz), 116.0, 117.1, 117.4, 117.6 (tt, J = 265.0, 28.5 Hz), 117.8 (tt, J = 264.3, 29.2 Hz), 126.3, 126.9, 127.4, 128.8, 133.7, 134.5, 137.1, 137.3, 137.8, 140.8, 142.0; ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –116.23 to –116.19 (m, 2F), –114.45 (d, J = 278.3 Hz, 1F), –113.36 (d, J = 278.3 Hz, 1F). The compound characterization data were consistent with those described in previously published reports.[1]

3-Ethenyl-4,4,5,5-tetrafluoro-6-[4-(4-octyloxyphenyl)phenyl]-1,7-octadien-3,6-diol (4d)

Yield: 36% (2.25 g, 4.32 mmol); Yellow liquid; ^{1}H NMR ($CDCl_3$): δ 0.91 (t, J = 7.6 Hz, 3H), 1.28–1.43 (m, 8H), 1.49 (quin, J = 7.6 Hz, 2H), 1.82 (quin, J = 7.6 Hz, 2H), 3.48 (s, 1H), 3.96–4.08 (m, 2H), 4.53 (s, 1H), 5.36–5.48 (m, 3H), 5.50–5.60 (m, 3H), 6.06–6.24 (m, 2H), 6.60–6.73 (m, 1H), 6.92–7.03 (m, 3H), 7.49–7.68 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.0, 29.2, 29.3, 29.4, 31.8, 68.1, 114.8, 115.9, 116.2, 117.1, 117.4, 126.1, 127.1, 127.4, 128.1, 132.7, 133.7, 134.5, 136.3, 136.9, 137.1, 140.6, 158.8, several carbons coupled with F atoms were not detected due to the presence of diastereomer mixture; ^{19}F NMR ($CDCl_3$): δ –111.28 (d, J = 279.3 Hz, 0.5F), –112.58 (d, J = 279.3 Hz, 0.5F), –112.39 (d, J = 278.9 Hz, 1F), –113.66 (d, J = 278.9 Hz, 1F), –115.33 (m, 2F); IR (neat): ν 3362, 3036, 2927, 2856, 1709, 1608, 1581, 1525, 1401, 1376, 1177, 1119, 859, 836 cm^{-1}; HRMS (FAB) Calcd for $C_{30}H_{36}F_4O_3$ $[M]^+$: 520.2601, Found: 520.2603.

1-3. Typical procedure for the preparation of *cis*-1-ethenyl-5,5,6,6-tetrafluoro-4-[4-(4-*n*-propylphenyl)phenyl]-2-cyclohexen-1,4-diol (5a)

To a solution of 10 mol% of Grubbs 2nd generation catalyst (0.28 g, 0.34 mmol) in CH_2Cl_2 (17 mL) was

added 1,7-octadiene-3,6-diol **4a** (1.48 g, 3.4 mmol) at room temperature and stirred at that temperature for 40 h. The reaction mixture was passed through a short plug of silica gel using EtOAc as an eluent and concentrated in vacuo to give the crude mixture. Purification by silica gel column chromatography using a mixed solvent system (hexane/EtOAc = 3/1) afforded the desired product **5a** in 49% yield (0.68 g, 1.39 mmol).

***cis*-1-Ethenyl-5,5,6,6-tetrafluoro-4-[4-(4-*n*-propylphenyl)phenyl]-2-cyclohexen-1,4-diol (5a)**

Yield: 49% (0.68 g, 1.39 mmol); ^{1}H NMR ($CDCl_3$): δ 0.98 (t, J = 7.2 Hz, 3H), 1.68 (sext., J = 7.2 Hz, 2H), 2.59 (d, J = 5.2 Hz, 1H), 2.63 (t, J = 7.2 Hz, 2H), 2.74 (d, J = 4.0 Hz, 1H), 5.49 (d, J = 10.7 Hz, 1H), 5.67 (d, J = 16.8 Hz, 1H), 5.92–6.09 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 7.50–7.53 (m, 4H), 7.61 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 13.8, 24.5, 37.7, 74.4–75.0 (m, 2C), 111.0–119.1 (m, 2C), 126.6, 127.0, 127.8, 128.9, 130.7, 131.65, 131.69, 133.4 (t, J = 5.0 Hz), 134.6, 137.6, 141.9, 142.3; ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –132.24 to –131.45 (m, 1F), –130.93 to –130.17 (m, 1F), –122.33 (ddd, J = 263.6, 19.6, 4.9 Hz, 1F), –116.18 (ddd, J = 268.5, 17.3, 6.1 Hz, 1F). The compound characterization data were consistent with those described in previously published reports.[1]

***cis*-1-Ethenyl-5,5,6,6-tetrafluoro-4-[4-(4-octyloxyphenyl)phenyl]-2-cyclohexen-1,4-diol (5d)**

Yield: 80% (0.79 g, 1.6 mmol); dark liquid; ^{1}H NMR ($CDCl_3$): δ 0.91 (t, J = 7.2 Hz, 3H), 1.22–1.41 (m, 8H), 1.48 (quin, J = 7.2 Hz, 2H), 1.82 (quin, J = 6.8 Hz, 2H), 2.99 (brs, 1H), 3.04 (brs, 1H), 4.00 (t, J = 6.4 Hz, 2H), 5.47 (d, J = 10.8 Hz, 1H), 5.66 (d, J = 17.2 Hz, 1H), 5.90–5.95 (m, 1H), 6.00–6.12 (m, 1H), 6.98 (d, J = 8.8 Hz, 2H), 7.44–7.68 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.0, 29.22, 29.25, 29.3, 31.8, 68.1, 74.7 (td, J = 20.5, 9.4 Hz), 114.8, 119.0, 126.3, 127.8, 128.1, 132.1 (dt, J = 278.0, 4.3 Hz), 132.6, 133.0 (dt, J = 262.6, 4.63 Hz), 141.5, 158.9; ^{19}F NMR ($CDCl_3$): δ –115.52 (dd, J = 262.8, 13.6 Hz, 1F), –121.40 (dd, J = 264.3, 13.6 Hz, 1F), –132.14 (dd, J = 262.8, 17.6 Hz, 1F), –131.19 (dd, J = 268.4, 17.6 Hz, 1F); IR (neat): ν 3417, 3035, 2927, 2855, 1888, 1708, 1607, 1497, 1470, 1402, 1293, 1140, 879, 783 cm^{-1}; HRMS (FAB) Calcd for $C_{28}H_{32}F_4O_3$ $[M]^+$: 492.2288, Found: 492.2282.

1-4. Typical procedure for the synthesis of 1-ethyl-2,2,3,3-tetrafluoro-4-[4-(4-*n*-propylphenyl)phenyl]cyclohexan-1,4-diol (6a)

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 (0.16 g, 0.15 mmol), tetrafluorinated cyclohexen-1,4- diol **5a** (0.65 g, 1.5 mmol) and MeOH (15 mL). To the suspension was bubbled hydrogen gas (1 atm) 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 ash, after which the crude product was purified by column chromatography using hexane/EtOAc = 3/1 as an eluent to obtain the corresponding tetrafluorinated cyclohexan-1,4-diol **6a** in 70% yield (0.43 g, 1.05 mmol).

1-Ethyl-2,2,3,3-tetrafluoro-4-[4-(4-*n*-propylphenyl)phenyl]cyclohexan-1,4-diol (6a)

Yield: 70% (0.43 g, 1.05 mmol); White solid; m.p.: 139–140 °C; ^{1}H NMR ($CDCl_3$): δ 0.98 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.6 Hz, 3H), 1.68 (sext, J = 7.61 Hz, 2H), 1.74–2.00 (m, 5H), 2.11 (t, J = 13.2 Hz), 2.54 (d, J = 2.0 Hz, 1H), 2.63 (t, J = 7.6 Hz, 2H), 2.78 (t, J = 13.2 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.61–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 13.9, 24.5, 26.7 (d, J = 4.1 Hz), 27.1, 29.5 (d, J = 3.3 Hz), 37.7, 74.4 (ddd, J = 24.8, 22.2, 1.7 Hz), 75.4 (ddd, J = 24.8, 20.7, 1.7 Hz), 113.6–119.1 (m, 2C), 126.7, 126.9, 127.1 (d, J = 2.5 Hz), 128.9, 137.2 (d, J = 1.6 Hz), 137.7, 141.4, 142.2; ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –135.63 (ddd, J = 268.3, 14.7, 8.6 Hz, 1F), –134.65 (ddd, J = 268.3, 12.0, 6.1 Hz, 1F), –116.1 (dt, J = 268.5, 9.8 Hz, 1F), –112.33 (ddd, J = 268.3, 14.3, 9.8 Hz, 1F); The compound characterization data were consistent with those described in previously published reports.[1]

1-Ethyl-2,2,3,3-tetrafluoro-4-[4-(4-octyloxyphenyl)phenyl]cyclohexan-1,4-diol (6d)

Yield: 77% (0.38 g, 0.77 mmol); M.p.: 73.5-74.5 ℃; ^{1}H NMR ($CDCl_3$): δ 0.91 (t, J = 6.8 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H), 1.22–1.41 (m, 11H), 1.41–1.52 (m, 3H), 1.73–1.92 (m, 5H), 2.86 (brs, 1H), 4.00 (t, J = 6.4 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.59 (s, 4H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.0, 29.2, 29.3, 29.4, 31.8, 68.1, 74.8 (t, J = 20.5 Hz), 75.2 (dd, J = 26.4, 21.2 Hz), 114.8, 126.4, 127.1, 128.1, 128.3, 132.4, 136.3, 141.2, 158.9, The two carbons assigned as CF_2CF_2 unit were not found in the spectrum due to low intensities caused by spin-spin coupling with fluorine atom; ^{19}F NMR ($CDCl_3$): δ –113.09 (d, J = 276.3 Hz, 1F), –116.96 (dd, J = 274.1 Hz, 1F), –131.82 (d, J = 252.2 Hz, 1F), –134.35 (d, J = 258.6 Hz, 2F); IR (KBr): ν 3457, 3037, 2934, 2853, 1890, 1711, 1607, 1581, 1560, 1527, 1392, 1255, 1203, 1158, 997, 897, 760 cm^{-1}; HRMS (FAB) Calcd for $C_{28}H_{36}F_4O_3$ $[M]^+$: 496.2601, Found: 496.2601.

1-5. Typical procedure for the synthesis of 4-ethyl-5,5,6,6-tetrafluoro-1-[4-(4-*n*-propylphenyl)phenyl]cyclohexa-1,3-diene (2a)

In a two-necked round-bottomed flask containing a teflon®- coated magnetic stirring bar, tetrafluorinated cyclohexan-1,4- diol **6a** (0.30 g, 0.74 mmol) and pyridine (7.4 mL) were placed. To the solution was added freshly distilled $POCl_3$ (0.70 mL, 7.4 mmol) at room temperature, and the whole solution was heated at 90 °C (bath temp.) for 24 h. After cooling the reaction mixture to room temperature, the resultant solution was poured into saturated aqueous NH_4Cl solution and acidified by adding 3N 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 gel column chromatography (eluent: hexane/EtOAc = 10/1) to afford the corresponding tetrafluorinated cyclohexa-1,3-diene **2a** in 90% yield (0.25 g, 0.67 mmol).

4-Ethyl-5,5,6,6-tetrafluoro-1-[4-(4-*n*-propylphenyl)phenyl]cyclohexa-1,3-diene (2a)

Yield 90% (0.25 g, 0.67 mmol); M.p.: 92 ℃ determined by DSC; ^{1}H NMR ($CDCl_3$): δ 0.98 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.6 Hz, 3H), 1.69 (sext, J = 7.6 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 6.09 (d, J = 6.0 Hz, 1H), 6.39 (d, J = 6.0 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 11.4, 13.8, 21.6, 24.5, 37.7, 114.0 (tt, J = 251.87, 26.82 Hz), 114.1 (tt, J = 251.9, 26.8 Hz), 123.1 (t, J = 9.2 Hz), 125.8 (t, J = 8.79 Hz), 126.8, 126.9, 127.4, 129.0, 131.7, 133.6 (t, J = 22.0 Hz), 137.6, 137.8 (t, J = 21.9 Hz), 141.5, 142.3; ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –126.57 (d,

J = 4.76 Hz, 2F), –122.23 (d, J = 4.86 Hz, 2F); The compound characterization data were consistent with those described in previously published reports.[1]

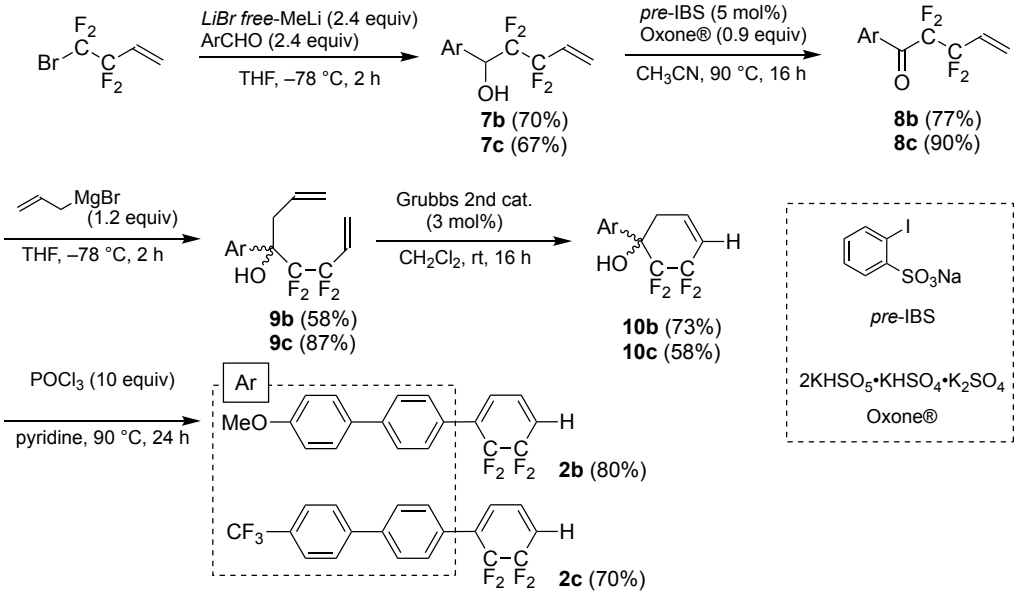
4-Ethyl-5,5,6,6-tetrafluoro-1-[4-(4-octyloxyphenyl)phenyl]cyclohexa-1,3-diene (2d)

Yield: 83% (0.32 g, 0.69 mmol); Pale yellow solid; M.p.: 71 ℃ determined by DSC; ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J = 6.8 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.26–1.42 (m, 8H), 1.48 (quin, J = 8.0 Hz, 2H), 1.81 (quin, J = 7.2 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 6.09 (d, J = 6.0 Hz, 1H), 6.38 (d, J = 6.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 7.48–7.62 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 11.5, 14.1, 21.7, 22.7, 26.1, 29.26, 29.31, 29.4, 31.8, 68.1, 114.9, 126.7, 127.5, 128.0, 124.4 (dt, J = 253.8, 8.8 Hz), 131.3, 132.6, 133.7 (t, J = 23.1 Hz), 137.8 (t, J = 21.2 Hz), 141.3, 159.1; ^{19}F NMR ($CDCl_3$): δ –123.55 (s, 2F), –127.90 (s, 2F); IR (KBr): ν 3038, 2926, 2852, 1885, 1654, 1606, 1579, 1529, 1500, 1253, 1132, 907, 864 cm^{-1}; HRMS (FAB) Calcd for $C_{28}H_{32}F_4O$ $[M]^+$: 460.2389, Found: 460.2382.

Reference:

[1] Kumon, T.; Hashishita, S.; Kida, T.; Yamada, S.; Ishihara, T.; Konno, T. *Beilstein J. Org. Chem.* **2018**, *14*, 148–154.

2. Synthesis of 2b and 2c



Scheme S2. Synthetic procedure of **2b** and **2c** starting from commercially available 4-bromo-3,3,4,4-tetrafluorobut-1-ene.

2-1. Typical procedure for the synthesis of 2,2,3,3-Tetrafluoro-1-[4-(4-trifluoromethylphenyl)phenyl]pent-4-en-1-ol (7c)

In a two-necked round-bottomed flask, equipped with a magnetic stirrer bar and inlet tube for argon, 4-bromo-3,3,4,4-tetrafluorobut-1-ene (3.15 g, 15 mmol), 4-{4-(trifluoromethyl)phenyl}benzaldehyde (9.01 g, 36 mmol) and THF (30 mL) were placed, and then the reaction flask was immersed in a cooling bath to be cooled to –78 ℃. To the solution was added dropwise MeLi (LiBr-free, 1.06 M in Et_2O, 22 mL) at –78 ℃ and the whole solution was stirred at that temperature. After stirring for 2 h, an aqueous saturated solution of NH_4Cl was a added to the resultant, after which the resulting solution was allowed to warm to room temperature. The reaction mixture was extracted with EtOAc three times and the combined organic layers were washed with brine, and then dried over anhydrous Na_2SO_4. The crude product was obtained after filtration, followed by removing solvent using a rotary evaporator. The residue was purified by silica gel column chromatography (eluent: hexane/AcOEt = 10/1) to afford the corresponding bishmoallyl alcohol **7c** in 67% yield (3.89 g, 10.0 mmol).

2,2,3,3-Tetrafluoro-1-[4-(4-trifluoromethylphenyl)phenyl]pent-4-en-1-ol (7c)

Yield: 67% (3.89 g, 10.0 mmol); White solid; M.p.: 108.0–109.5 ℃; ^{1}H NMR ($CDCl_3$): δ 2.54 (brs, 1H), 5.24 (dd, J = 17.2, 7.2 Hz, 1H), 5.70 (d, J = 10.8 Hz, 1H), 5.89 (d, J = 15.2 Hz, 1H), 5.97–6.13 (m, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.70 (s, 4H); ^{13}C NMR ($CDCl_3$): δ 71.7 (dd, J = 29.3, 23.5 Hz), 123.8 (t, J = 9.6 Hz), 125.8 (q, J = 3.6 Hz), 126.8 (t, J = 24.1 Hz), 127.2, 127.4, 128.7, 129.6 (d, J = 33.0 Hz), 135.0, 140.6, 143.9; ^{19}F NMR ($CDCl_3$): δ –63.31 (s, 3F), –113.22 (dd, J = 264.3, 12.0 Hz, 1F), –114.07 (dd, J = 264.3, 12.0 Hz, 1F), –120.02 (d, J = 275.2 Hz, 1F), –128.00 (dd, J = 275.2, 16.2 Hz, 1F); IR (KBr): ν 3419, 2362, 2357, 1923, 1617, 1566, 1503, 1421, 1400, 1006, 861, 835, 733 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{13}F_7O$ $[M]^+$: 378.0855, Found: 378.0849.

2,2,3,3-Tetrafluoro-1-[4-(4-methoxyphenyl)phenyl]pent-4-en-1-ol (7b)

Yield: 70% (4.76 g, 14.0 mmol); M.p.: 172.3–173.5 ℃; ^{1}H NMR ($CDCl_3$): δ 3.73 (brs, 1H), 3.83 (s, 3H), 5.16 (dd, J = 17.56, 7.00 Hz, 1H), 5.63 (d, J = 11.08 Hz, 1H), 5.85 (dt, J = 8.68, 1.98 Hz, 1H), 5.98–6.11(m, 1H), 6.76 (s, 2H), 6.95 (t, J = 8.56 Hz, 2H), 7.45–7.56 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 55.5, 72.0 (dd, J = 29.1, 22.8 Hz), 114.4, 115.6 (tm, J = 255.76 Hz), 115.9 (tm, J = 257.0 Hz), 123.7 (t, J = 9.6 Hz), 126.8, 127.1 (t, J = 24.0 Hz), 128.3, 128.6, 133.1, 133.6, 141.8, 159.5; ^{19}F NMR ($CDCl_3$, C_6F_6): δ −128.66 (dd, J = 274.1, 18.1 Hz, 1F), –120.25 (dt, J = 135.9, 5.8 Hz, 1F), –115.08 (ddd, J = 262.4, 12.5, 4.2 Hz, 1F), –113.70 (dd, J = 262.5, 11.4 Hz, 1F); IR (KBr): ν 3421, 3036, 2956, 2839, 1919, 1718, 1649, 1609, 1583, 1565, 1442, 1339, 1270, 1013, 991, 827 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{16}F_4O_2$ $[M]^+$: 340.1086, Found: 340.1096.

2-2. Typical procedure for the synthesis of 2,2,3,3-tetrafluoro-1-[4-(4-trifluoromethylphenyl)phenyl]pent-4-en-1-one (8c)

A solution of tetrafluorinated alcohol (**7c**) (2.09 g, 5.5 mmol) and Oxone® (3.04 g, 4.95 mmol) in CH_3CN (27.5 mL) was heated at 90 ºC in the presence of *pre*-IBS (0.095 g, 0.27 mmol). After stirring for 16 h, the resulting mixture was cooled to room temperature and filtered by silica gel, which was successively washed with EtOAc, then concentrated in *vacuo*. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 10/1) to afford the corresponding ketone **8c** in 90% yield (1.86 g, 4.95 mmol).

2,2,3,3-tetrafluoro-1-[4-(4-trifluoromethylphenyl)phenyl]pent-4-en-1-one (8c)

Yield: 90% (1.86 g, 4.95 mmol); Pale yellow liquid; ^{1}H NMR ($CDCl_3$): δ 5.78 (d, J = 11.2 Hz, 1H), 5.96 (d, J = 17.6 Hz, 1H), 6.08–6.24 (m, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.74 (s, 4H), 8.21 (d, J = 8.0 Hz, 2H); $_{13}$C NMR ($CDCl_3$): δ 112.0 (tt, J = 265.6, 36.7 Hz), 114.7 (tt, J = 250.8, 29.4 Hz), 124.1 (q, J = 271.4 Hz), 124.8 (t, J = 9.6 Hz), 125.95, 125.98, 127.5, 127.6, 130.6 (q, J = 32.3 Hz), 131.0, 131.7, 142.8, 145.8, 185.4 (t, J = 26.4 Hz); ^{19}F NMR ($CDCl_3$): δ –62.70 (s, 3F), –113.34 (d, J = 10.9 Hz, 2F), –114.34 (s, 2F); IR (neat): ν 3396, 3055, 2946, 1932, 1701, 1606, 1558, 1112, 1017, 964, 828, 737 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{12}F_7O$ $[M+H]^+$: 377.0771, Found: 377.0781.

2,2,3,3-tetrafluoro-1-[4-(4-methoxyphenyl)phenyl]pent-4-en-1-one (8b)

Yield: 77% (0.78 g, 2.31 mmol); White solid; M.p.: 53.2-54.7 ℃; ^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3H), 5.77 (d, J = 11.2 Hz, 1H), 5.95 (dt, J = 17.2, 2.0 Hz, 1H), 6.06–6.23 (m, 1H), 7.02 (d, J = 9.2 Hz, 2H), 7.60 (d, J = 9.2 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.4, 112.1 (tt, J = 265.6, 35.9 Hz), 114.5, 114.6 (tt, J = 250.8, 30.8 Hz), 124.7 (t, J = 9.6 Hz), 126.3 (t, J = 23.4 Hz), 126.6, 128.5, 130.3, 131.0, 131.6, 146.9, 160.3, 185.4 (t, J = 26.5 Hz); ^{19}F NMR ($CDCl_3$): δ –113.38 (d, J = 9.4 Hz, 2F), –114.19 (s, 2F); IR (KBr): ν 2971, 2843, 1697, 1601, 1577, 1555, 1528, 1459, 1444, 1278, 1253, 1183, 1012, 825 cm^{-1}; HRMS (FAB) Calcd for $C_{18}H_{14}F_4O_2$ $[M]^+$: 338.0930, Found: 338.0924.

2-3. Typical procedure for the synthesis of 5,5,6,6-tetrafluoro-4-(4-trifluoromethylphenyl)phenylocta-1,7-dien-4-ol (9c)

To a solution of tetrafluorinated ketone **8c** (1.88 g, 5.0 mmol) in Et_2O (20 mL) was added dropwise allyl magnesium bromide (0.60 M in diethyl ether, 10 mL, 6.0 mmol) at –78 ºC and the whole was stirred at the same temperature for 2 h. The reaction mixture was quenched with saturated NH_4Cl aqueous and then the whole was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4, then filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (hexane : EtOAc = 10 : 1, R_f = 0.12) to give the corresponding 1,7-octadiene **9c** in 87% yield (1.82 g, 4.35 mmol).

5,5,6,6-tetrafluoro-4-(4-trifluoromethylphenyl)phenylocta-1,7-dien-4-ol (9c)

Yield: 87% (1.82 g, 4.35 mmol); Pale yellow liquid; ^{1}H NMR ($CDCl_3$): δ 2.67 (brs, 1H), 2.98 (dd, J = 14.0, 8.0 Hz, 1H), 3.11 (dd, J = 14.0, 6.0 Hz, 1H), 5.21 (d, J = 10.4 Hz, 1H), 5.26 (d, J = 17.2 Hz, 1H), 5.44–5.59 (m, 2H), 5.70 (dt, J = 17.2, 2.4 Hz, 1H), 5.88–6.04 (m, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.72 (s, 4H); ^{13}C NMR ($CDCl_3$): δ 40.9, 76.6 (t, J = 24.9 Hz), 115.8 (tt, J = 251.5, 33.8 Hz), 116.6 (tt, J = 261.9, 30.8 Hz), 121.6, 122.0 (t, J = 10.3 Hz), 124.3 (q, J = 272.1 Hz), 125.7 (q, J = 3.6 Hz), 126.8, 127.3, 127.4, 127.9 (t, J = 23.4 Hz), 129.5 (q, J = 32.2 Hz), 130.8, 138.0, 139.3, 143.9; ^{19}F NMR ($CDCl_3$, C_6F_6): δ –63.32 (s, 3F), –109.24 (d, J = 261.6 Hz, 1F), –111.96 (d, J = 261.6 Hz, 1F), –120.63 (s, 1F), –120.69 (s, 1F); IR (neat): ν 3548, 3090, 2985, 1924, 1617, 1398, 1235, 1168, 1071, 978, 733 cm^{-1}; HRMS (FAB) Calcd for $C_{21}H_{17}F_7O$ $[M]^+$: 418.1168, Found: 418.1166.

5,5,6,6-tetrafluoro-4-(4-methoxyphenyl)phenylocta-1,7-dien-4-ol (9b)

Yield: 58% (0.51 g, 1.33 mmol); colorless liquid; ^{1}H NMR ($CDCl_3$): δ 2.70 (brs, 1H), 2.97 (dd, J = 14.4, 8.4 Hz, 1H), 3.13 (dd, J = 14.4, 6.0 Hz, 1H), 3.87 (s, 3H), 5.21 (d, J = 10.0 Hz, 1H), 5.26 (d, J = 17.2 Hz, 1H), 5.48–5.61 (m, 2H), 5.71 (d, J = 15.6 Hz, 1H), 5.87–6.03 (m, 1H), 7.02 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.61 (s, 4H); ^{13}C NMR ($CDCl_3$): δ 40.8, 55.2, 76.6 (t, J = 24.2 Hz), 114.2, 115.7 (tt, J = 251.5, 33.0 Hz), 116.7 (tt, J = 261.9, 31.6 Hz), 121.3, 121.8 (t, J = 10.3 Hz), 126.1, 127.1, 127.9 (t, J = 22.4 Hz), 128.0, 131.0, 132.8, 136.1, 140.3, 159.2; ^{19}F NMR ($CDCl_3$): δ –108.41 (dd, J = 261.6, 10.9 Hz, 1F), –110.94 (dd, J = 261.6, 12.0 Hz, 1F), –119.68 (s, 2F); IR (neat): ν 3558, 3082, 3059, 2962, 2909, 2838, 1925, 1887, 1712, 1639, 1561, 1399, 1211, 1000, 859, 740 cm^{-1}; HRMS (FAB) Calcd for $C_{21}H_{20}F_4O_2$ $[M]^+$: 380.1399, Found: 380.1407.

2-4. Typical procedure for the synthesis of 5,5,6,6-tetrafluoro-1-(4-trifluoromethylphenyl)phenylcyclohex-3-en-1-ol (10c)

A solution of 1,7-octadiene **9c** (1.67 g, 4.0 mmol) in CH_2Cl_2 (20 mL) in the presence of Grubbs 2nd Generation cat. (0.10 g, 0.12 mmol) was stirred at room temperature for 16 h. The reaction mixture was passed through silica gel, eluting with EtOAc, and the filtrate was concentrated in *vacuo*. The residue was purified by silica gel column chromatography (hexane : EtOAc = 3 : 1, R_f = 0.32) to give the corresponding alcohol **10c** in 58% yield (0.90 g, 2.32 mmol).

5,5,6,6-tetrafluoro-1-(4-trifluoromethylphenyl)phenylcyclohex-3-en-1-ol (10c)

Yield: 58% (0.90 g, 2.32 mmol); White solid; M.p.: 140.5–141.7 ℃; ^{1}H NMR ($CDCl_3$): δ 2.65–2.77 (m, 2H), 3.08–3.20 (m, 1H), 5.93–6.03 (m, 1H), 6.28–6.36 (m, 1H), 7.66 (d, J = 8.8 Hz, 2H), 7.71 (s, 4H), 7.73 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 38.6, 75.1 (t, J = 24.1 Hz), 109.5–118.0 (m, 2C for CF_2CF_2), 121.3 (t, J = 27.1 Hz), 124.2 (q, J = 272.2 Hz), 125.8 (q, J = 3.7 Hz), 127.2, 127.3, 127.4, 129.7 (q, J = 32.2 Hz), 134.2 (t, J = 10.3 Hz), 137.2, 140.2, 143.7; ^{19}F NMR ($CDCl_3$): δ –62.42 (s, 3F), –99.74 (d, J = 287.6 Hz, 1F), –116.47 (d, J = 287.6 Hz, 1F), –120.74 (dd, J = 261.6, 10.9 Hz, 1F), –137.46 (d, J = 261.6 Hz, 1F); IR (KBr): ν 3664, 3474, 3047, 2935, 1929, 1663, 1586, 1503, 1272, 1016, 957, 942, 789, 738 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{13}F_7O$ $[M]^+$: 390.0855, Found: 390.0862.

5,5,6,6-tetrafluoro-1-(4-methoxyphenyl)phenylcyclohex-3-en-1-ol (10b)

Yield: 73% (0.31 g, 0.88 mmol); White solid; M.p.: 147.7–148.9 ℃; ^{1}H NMR ($CDCl_3$): δ 2.71 (s, 2H), 3.13 (m, 1H), 3.87 (s, 3H), 5.92–6.02 (m, 1H), 6.27–6.35 (m, 1H), 7.00 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 38.5, 55.3, 75.1 (t, J = 24.9 Hz), 112–118 (m, 2C for CF_2CF_2), 114.3, 121.2 (t, J = 26.3 Hz), 126.6, 126.9 (d, J = 2.9 Hz), 128.1, 132.7, 134.3 (t, J = 10.9 Hz), 135.5, 141.3, 159.4; ^{19}F NMR ($CDCl_3$): δ –99.81 (d, J = 286.1 Hz, 1F), –116.38 (d, J = 286.1 Hz, 1F), –120.67 (dd, J = 261.6, 19.6 Hz, 1F), –137.5 (d, J = 261.6 Hz, 1F); IR (KBr): ν 3601, 3039, 2961, 2936, 2912, 2842, 1926, 1868, 1710, 1667, 1501, 1460, 1359, 1117, 1013, 901, 873 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{16}F_4O_2$ $[M]^+$: 352.1086, Found: 352.1084.

2-5. Typical procedure for the synthesis of 5,5,6,6-Tetrafluoro-1-(4-trifluoromethylphenyl)phenylcyclohexa-1,3-diene (2c)

In a two-necked round-bottomed flask containing a teflon®-coated magnetic stirring bar, tetrafluorinated cyclohexan-1,4-diol **10c** (0.78 g, 2.0 mmol) and pyridine (10 mL) were placed. To the solution was added freshly distilled $POCl_3$ (0.54 mL, 6.0 mmol) at room temperature, the whole solution was heated at 90 ℃ for 24 h. After cooling the reaction mixture to room temperature, the resultant solution was poured into saturated aqueous NH_4Cl solution and acidified by adding 3M HCl solution. The whole solution was extracted with AcOEt 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 (Hexane : CH_2Cl_2 = 10 : 1) to afford the corresponding tetrafluorinated cyclohexa-1,3-diene **2c** in 70% (0.15 g, 1.4 mmol) as a white solid.

5,5,6,6-Tetrafluoro-1-(4-trifluoromethylphenyl)phenylcyclohexa-1,3-diene (2c)

Yield: 70% (0.15 g, 1.4 mmol); White solid; M.p.: 138 ℃ determined by DSC; ^{1}H NMR ($CDCl_3$): δ 6.06–6.18 (m, 1H), 6.40–6.54 (m, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.72 (s, 4H); ^{13}C NMR ($CDCl_3$): δ 112.7 (tt, J = 249.4, 27.2 Hz), 113.4 (tt, J = 253.0, 26.5 Hz), 124.2 (q, J = 272.1 Hz), 123.4 (t, J = 25.6 Hz), 125.5 (t, J = 8.0 Hz), 125.8 (q, J = 3.6 Hz), 127.3, 127.4, 127.9, 129.7 (q, J = 32.3 Hz), 129.8 (t, J = 11.8 Hz), 132.6, 136.1 (t, J = 22.7 Hz), 140.4, 143.6; ^{19}F NMR ($CDCl_3$): δ –62.43 (s, 3F), –121.31

(s, 2F), –121.72 (s, 2F); IR (KBr): ν 3088, 2362, 1919, 1690, 1616, 1502, 1425, 1274, 1210, 968, 875, 794, 739, 729 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{11}F_7$ $[M]^+$: 372.0749, Found: 372.0759.

5,5,6,6-Tetrafluoro-1-(4-methoxyphenyl)phenylcyclohexa-1,3-diene (2b)

Yield: 80% (0.53 g, 1.6 mmol); White solid; M.p.: 130 ℃ determined by DSC; ^1H NMR ($CDCl_3$): δ 3.86 (s, 3H), 6.03–6.12 (m, 1H), 6.37–6.46 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 7.51–7.63 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 55.3, 110.0–116.0 (m, 2C for CF_2CF_2), 114.3, 122.9 (t, J = 25.8 Hz), 124.7 (t, J = 8.0 Hz), 126.7, 127.7, 128.1, 129.9 (t, J = 11.8 Hz), 130.9, 132.6, 136.4 (t, J = 22.0 Hz), 141.6, 159.5; ^{19}F NMR ($CDCl_3$): δ –121.29 (s, 2F), –121.67 (s, 2F); IR (KBr): ν 3026, 2968, 2844, 1649, 1604, 1576, 1530, 1445, 1399, 1312, 1289, 1202, 1183, 1021, 1011, 879, 787 cm^{-1}; HRMS (FAB) Calcd for $C_{19}H_{14}F_4O$ $[M]^+$: 334.0980, Found: 334.0980.

3. NMR spectrum

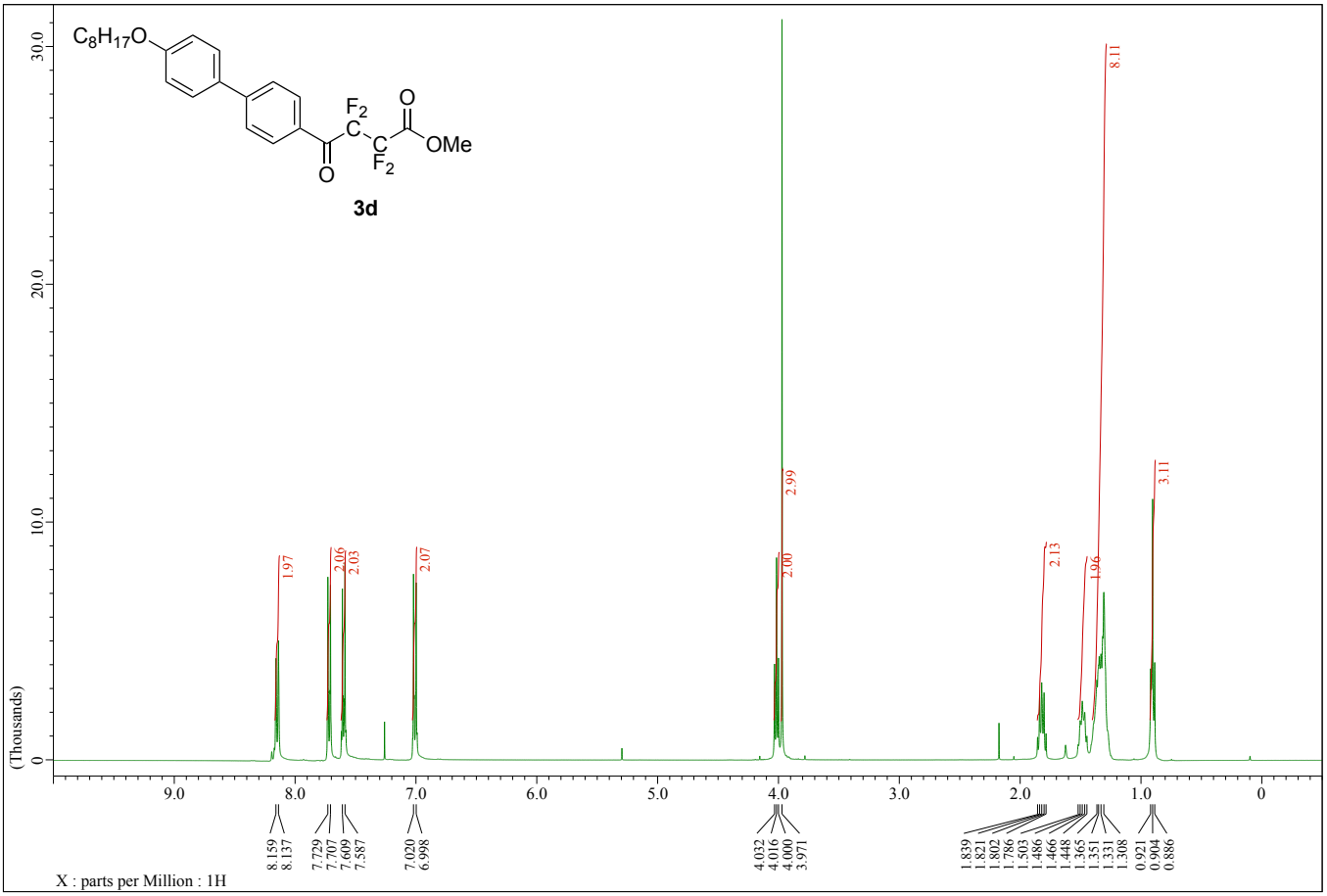


Figure S1. ^{1}H NMR spectrum of **3d** ($CDCl_3$, 400 MHz).

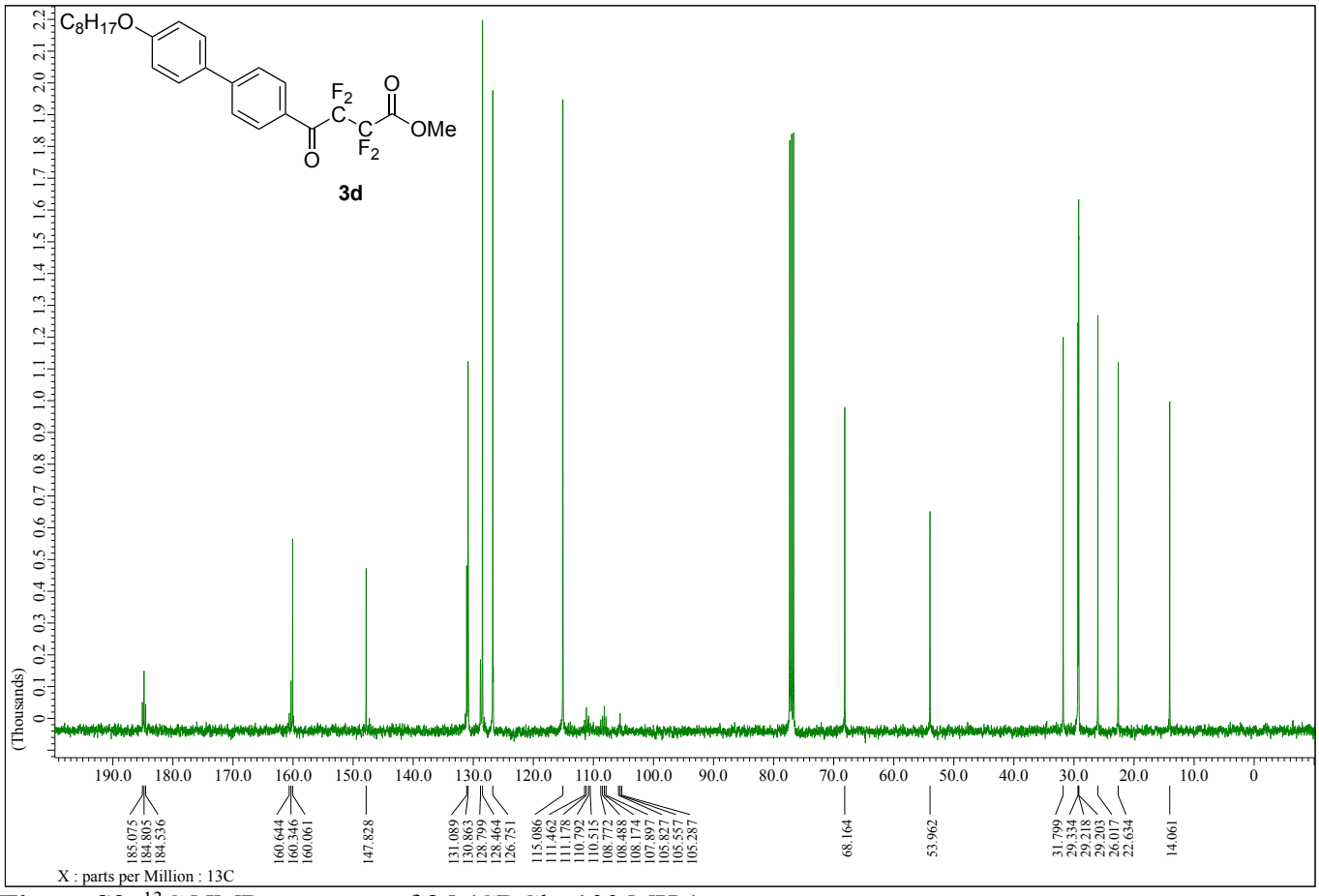


Figure S2. ^{13}C NMR spectrum of **3d** ($CDCl_3$, 100 MHz).

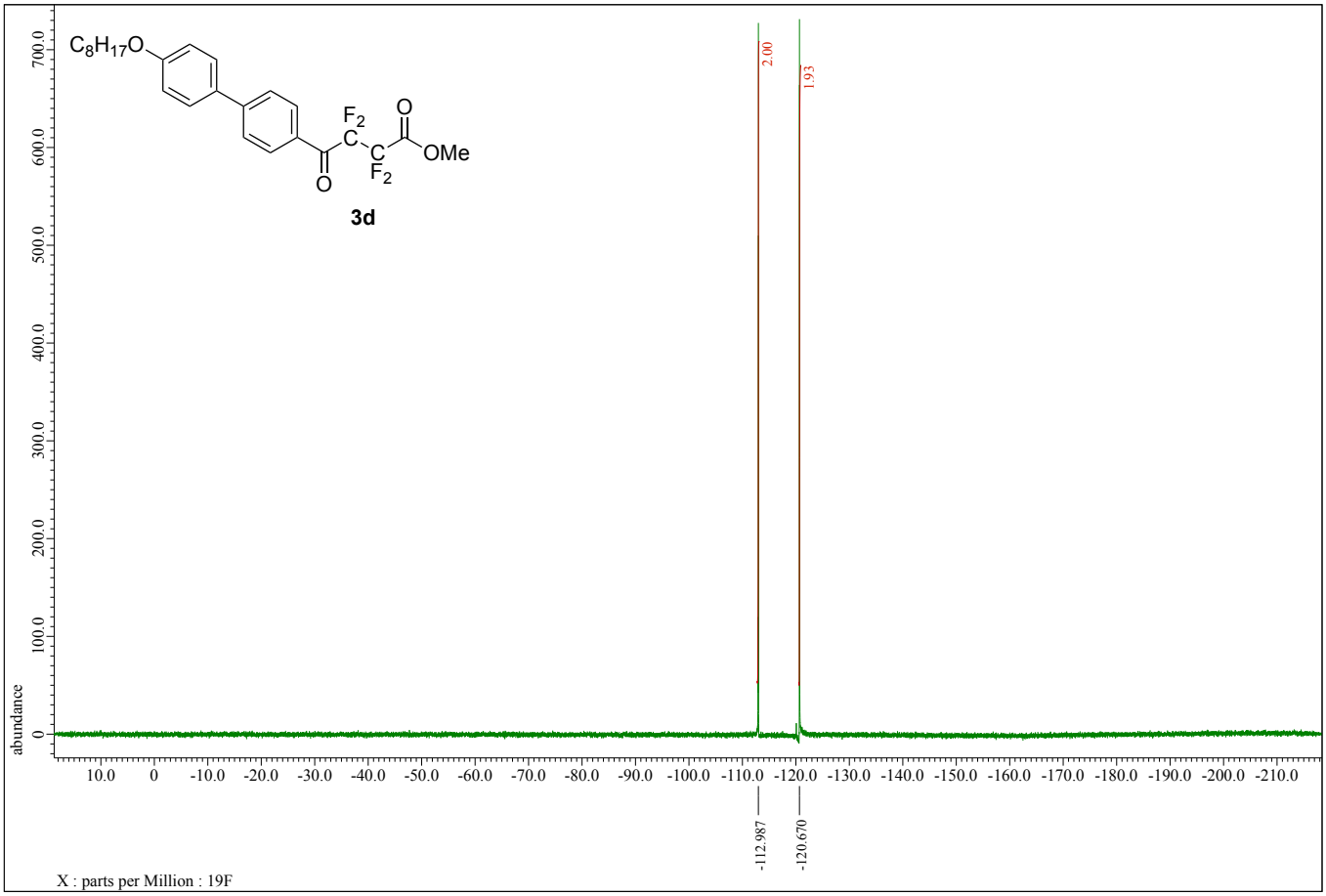


Figure S3. ^{19}F NMR spectrum of **3d** ($CDCl_3$, 376 MHz).

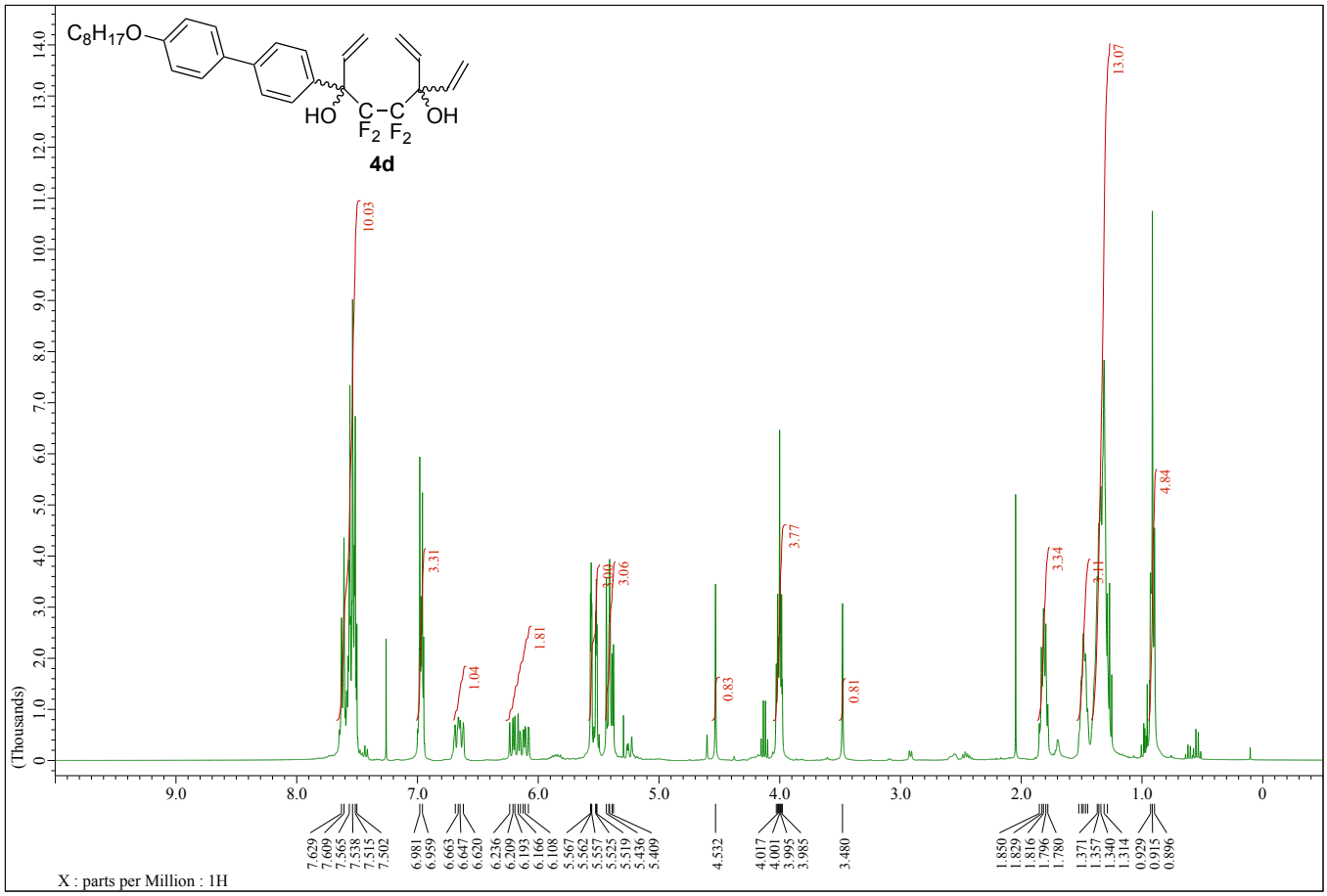


Figure S4. ^{1}H NMR spectrum of **4d** ($CDCl_3$, 400 MHz).

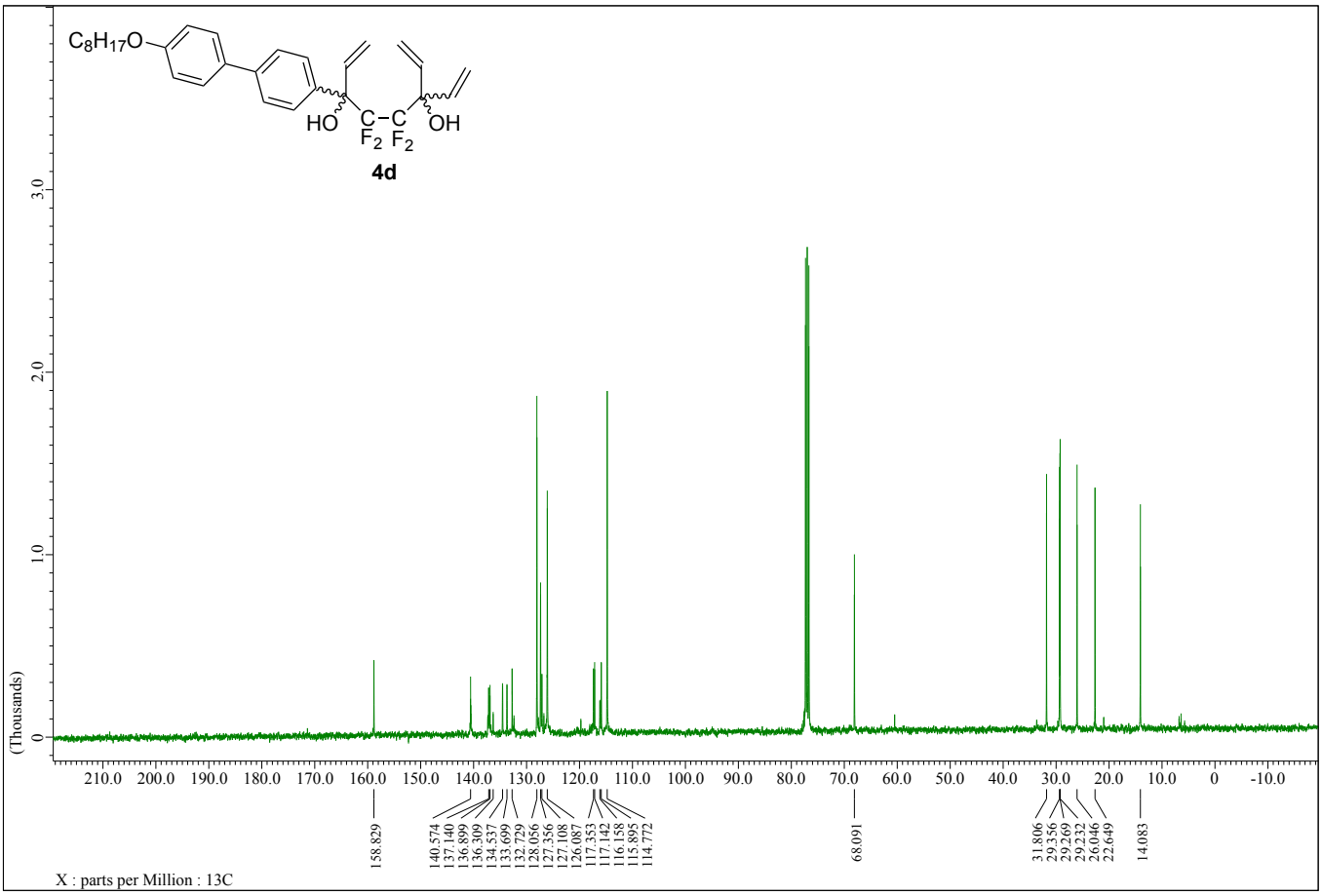


Figure S5. ^{13}C NMR spectrum of **4d** ($CDCl_3$, 100 MHz).

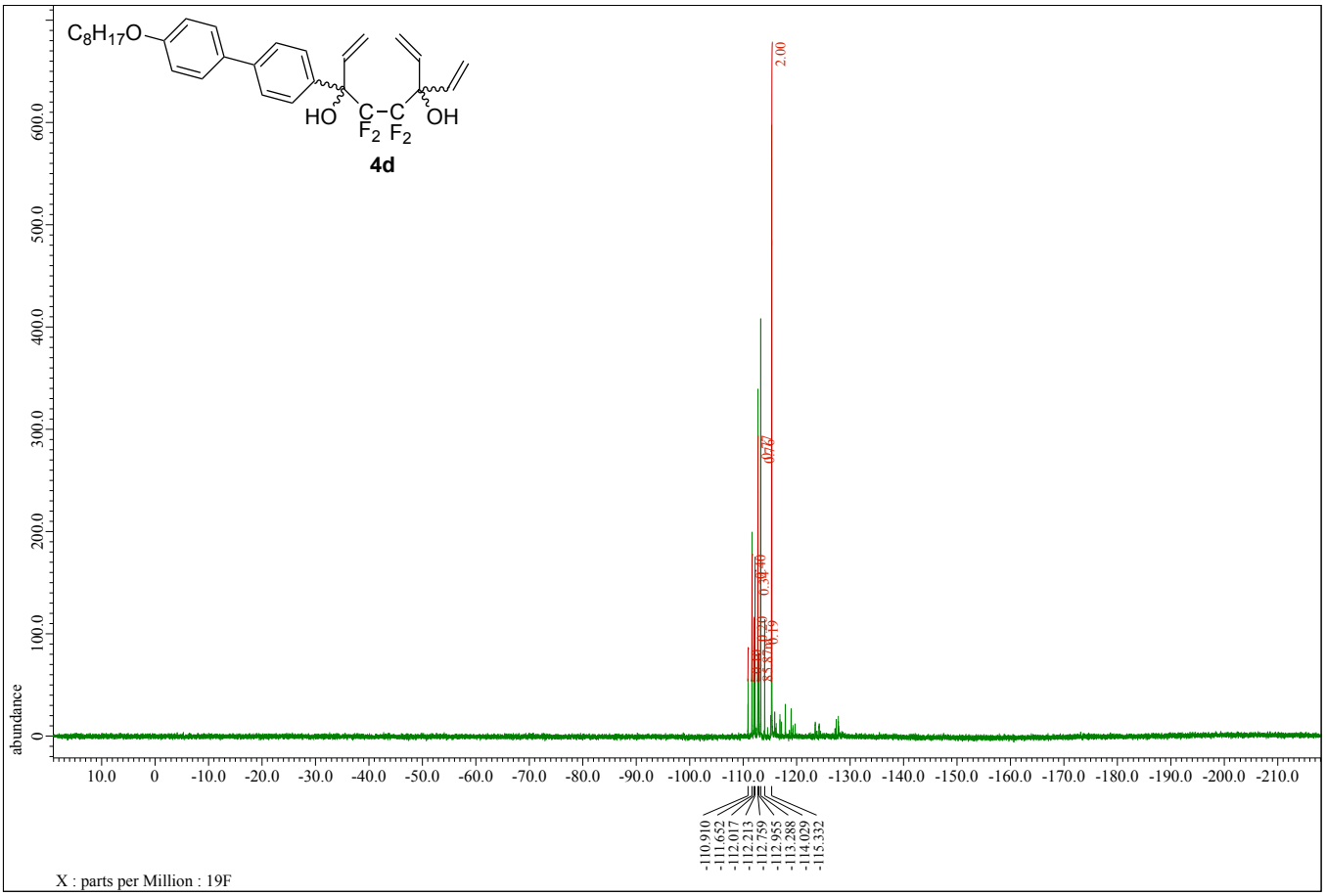


Figure S6. ^{19}F NMR spectrum of **4d** ($CDCl_3$, 376 MHz).

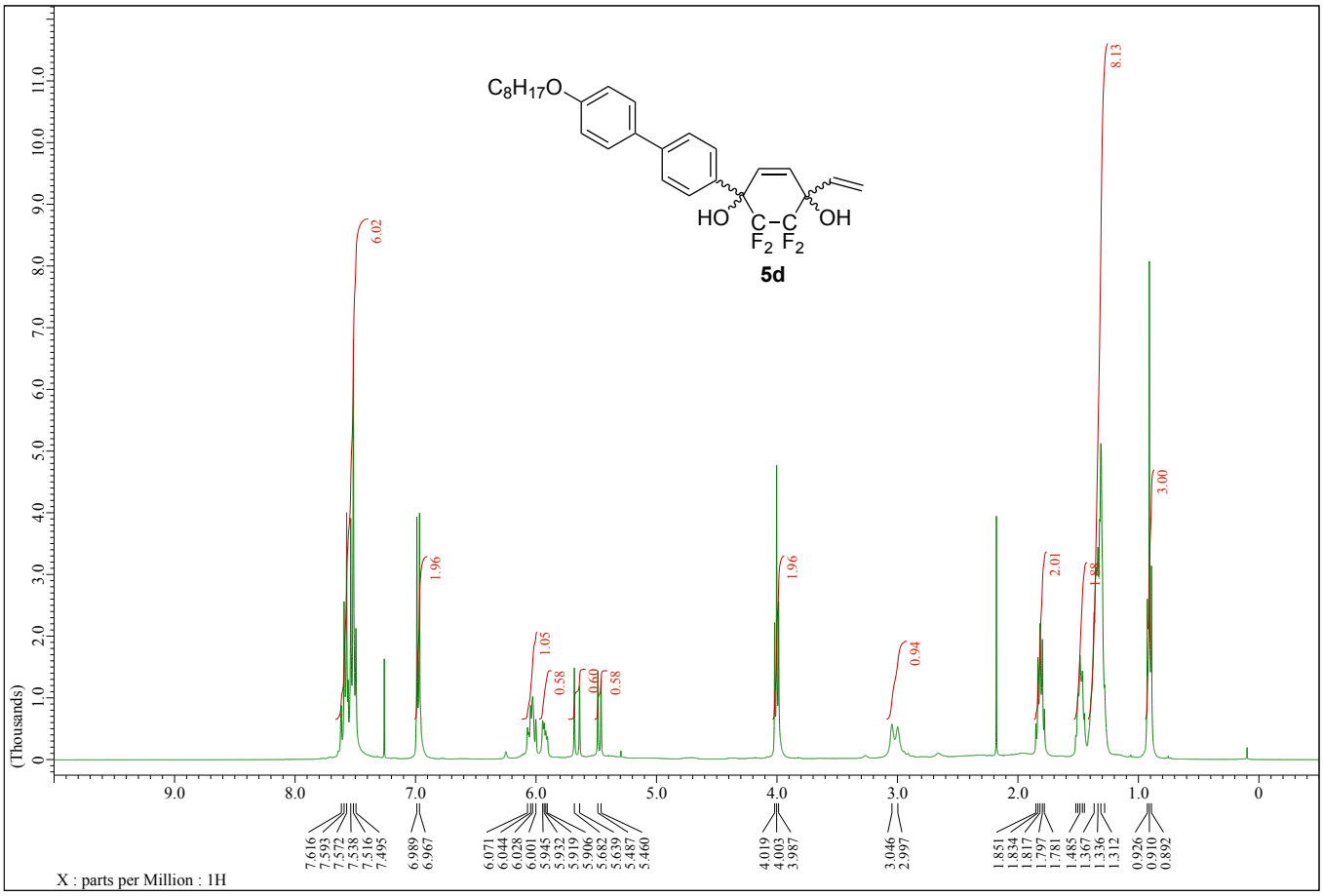


Figure S7. ^{1}H NMR spectrum of **5d** ($CDCl_3$, 400 MHz).

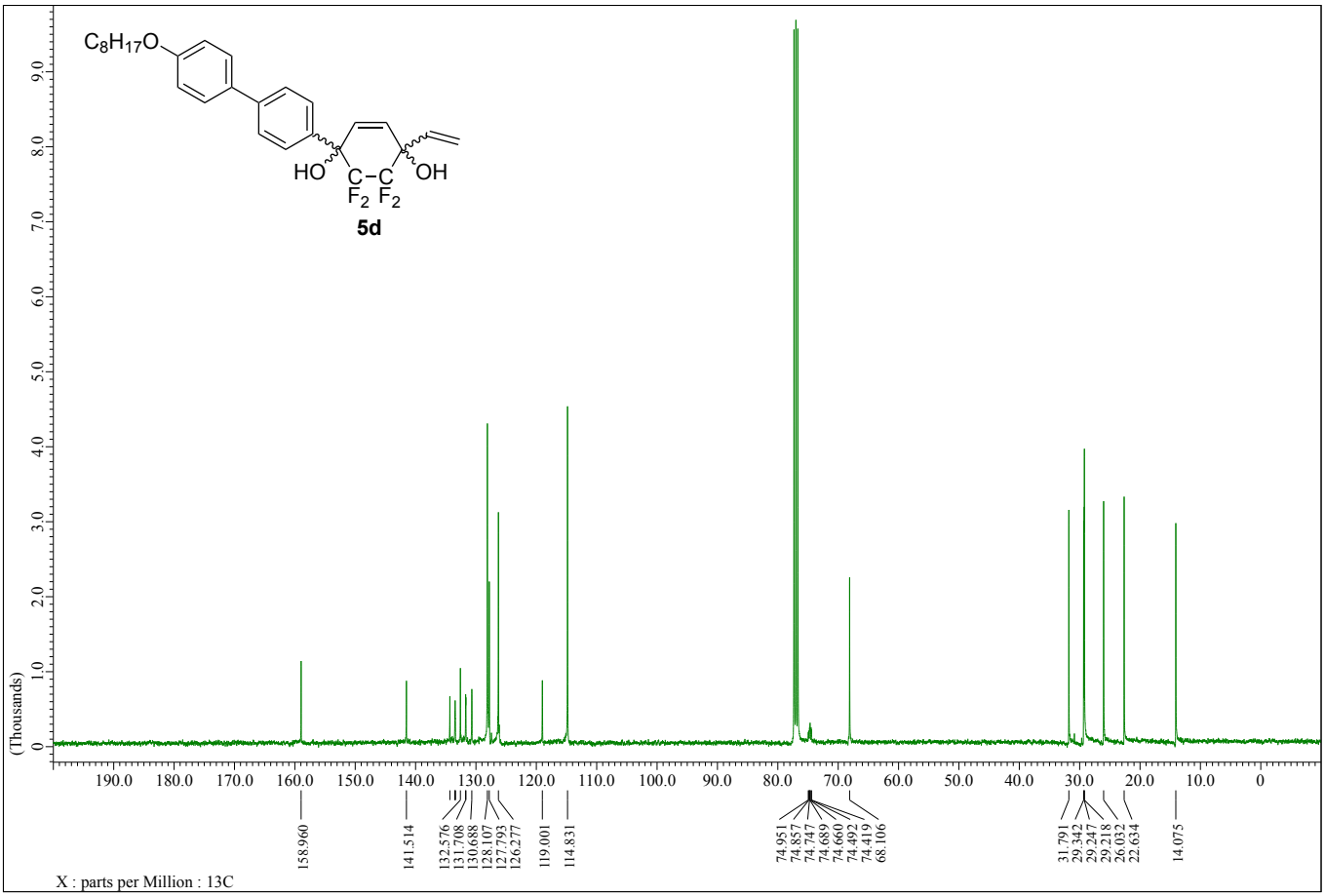


Figure S8. ^{13}C NMR spectrum of **5d** ($CDCl_3$, 100 MHz).

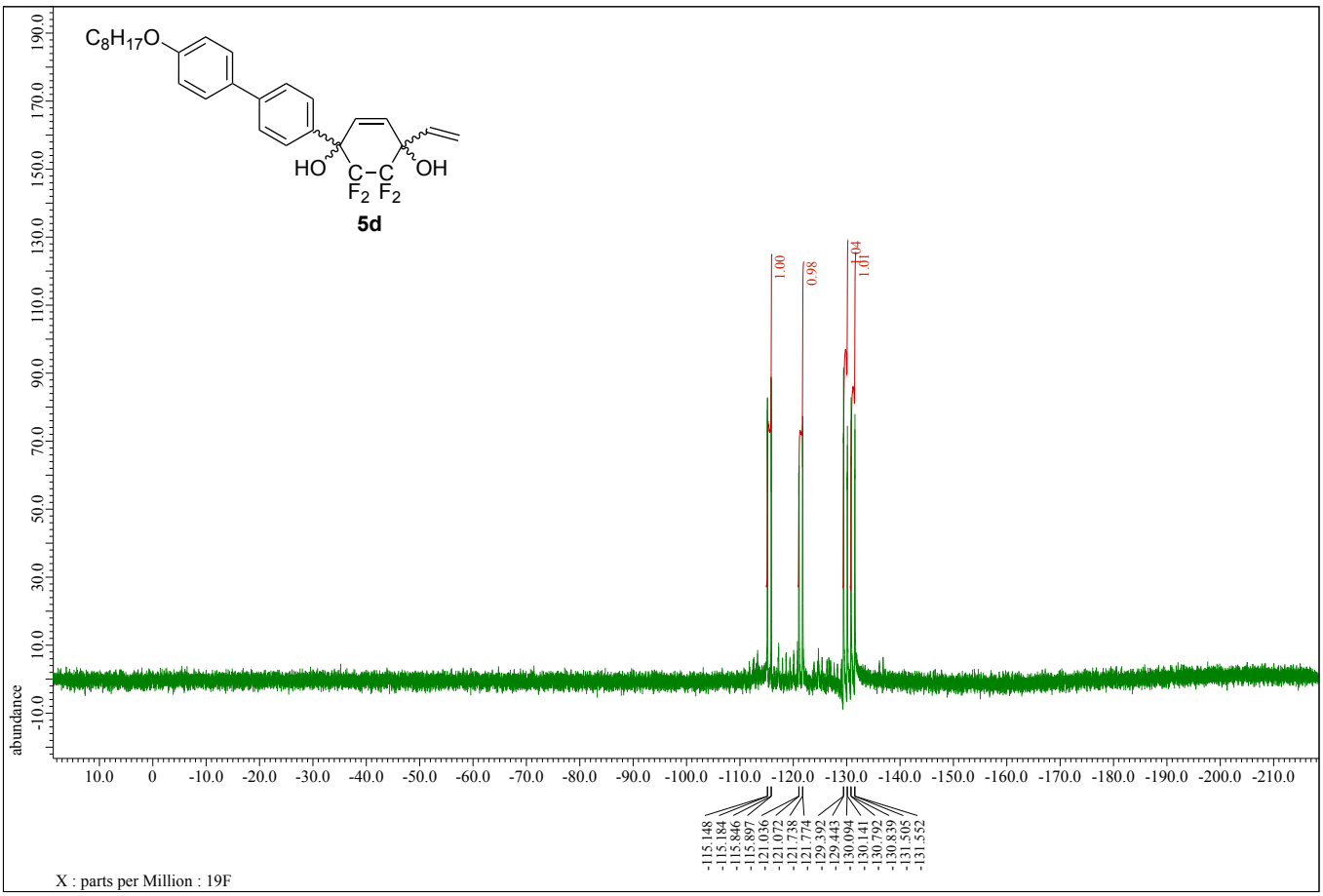


Figure S9. ^{19}F NMR spectrum of **5d** ($CDCl_3$, 376 MHz).

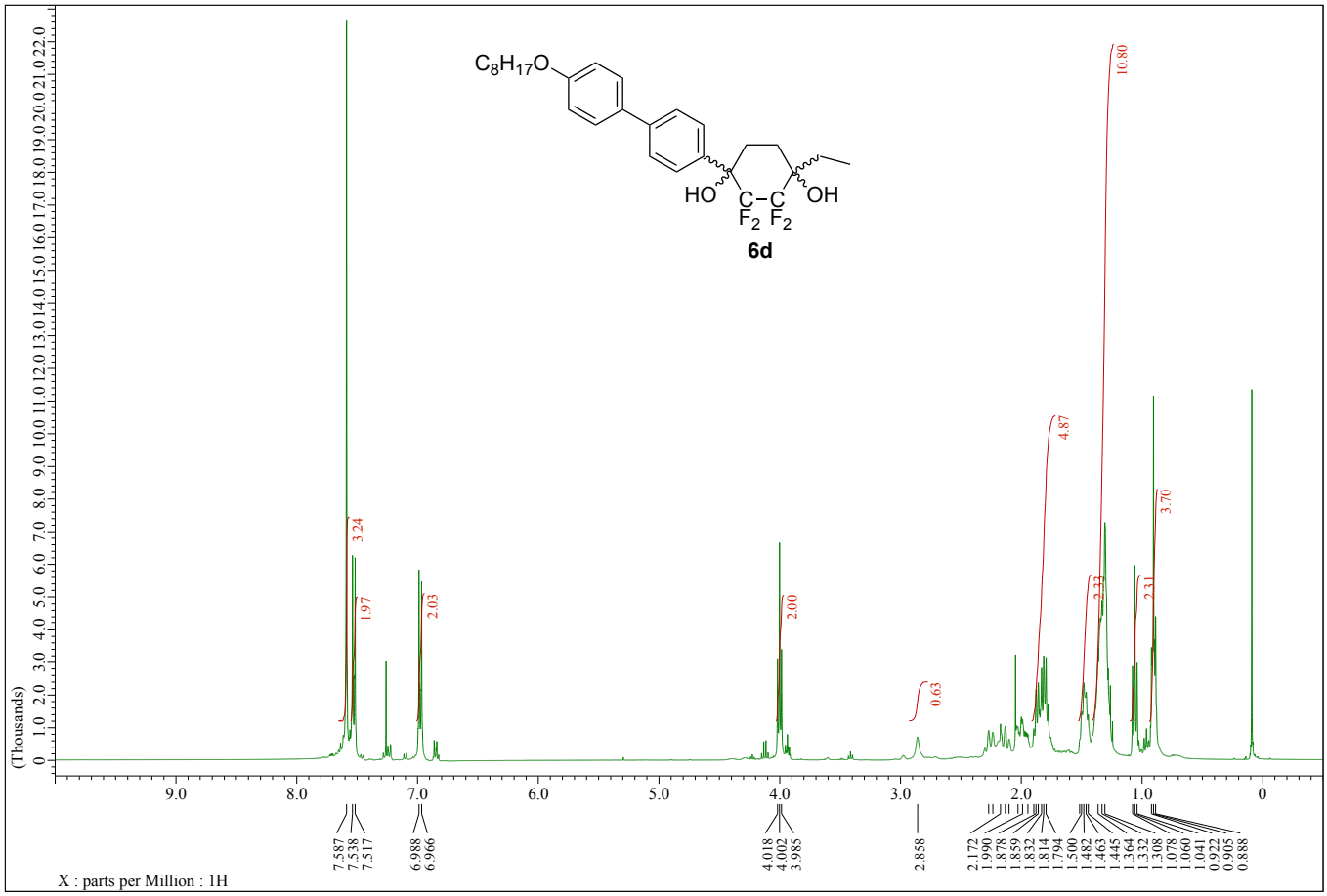


Figure S10. ^{1}H NMR spectrum of **6d** ($CDCl_3$, 400 MHz).

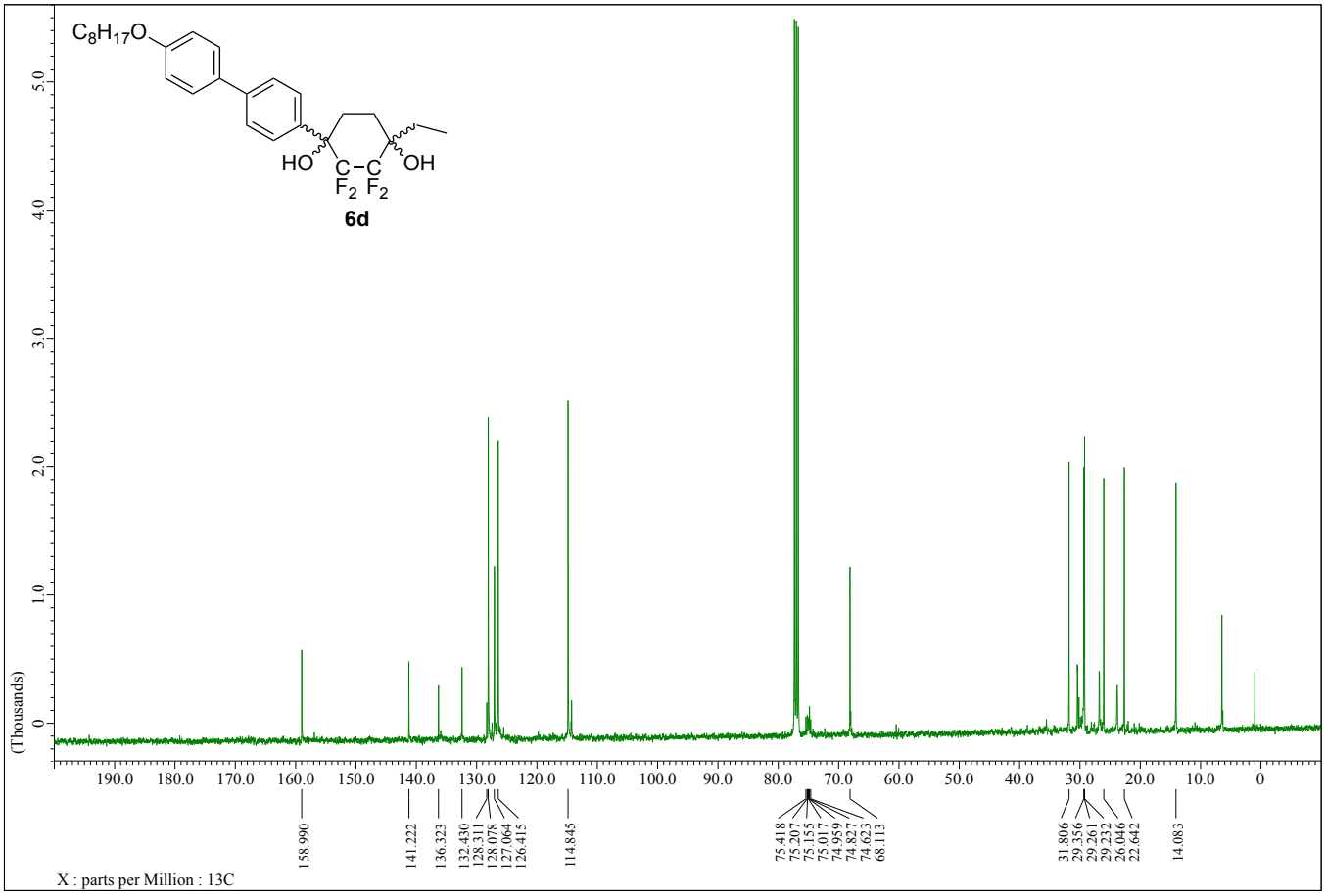


Figure S11. ^{13}C NMR spectrum of **6d** ($CDCl_3$, 100 MHz).

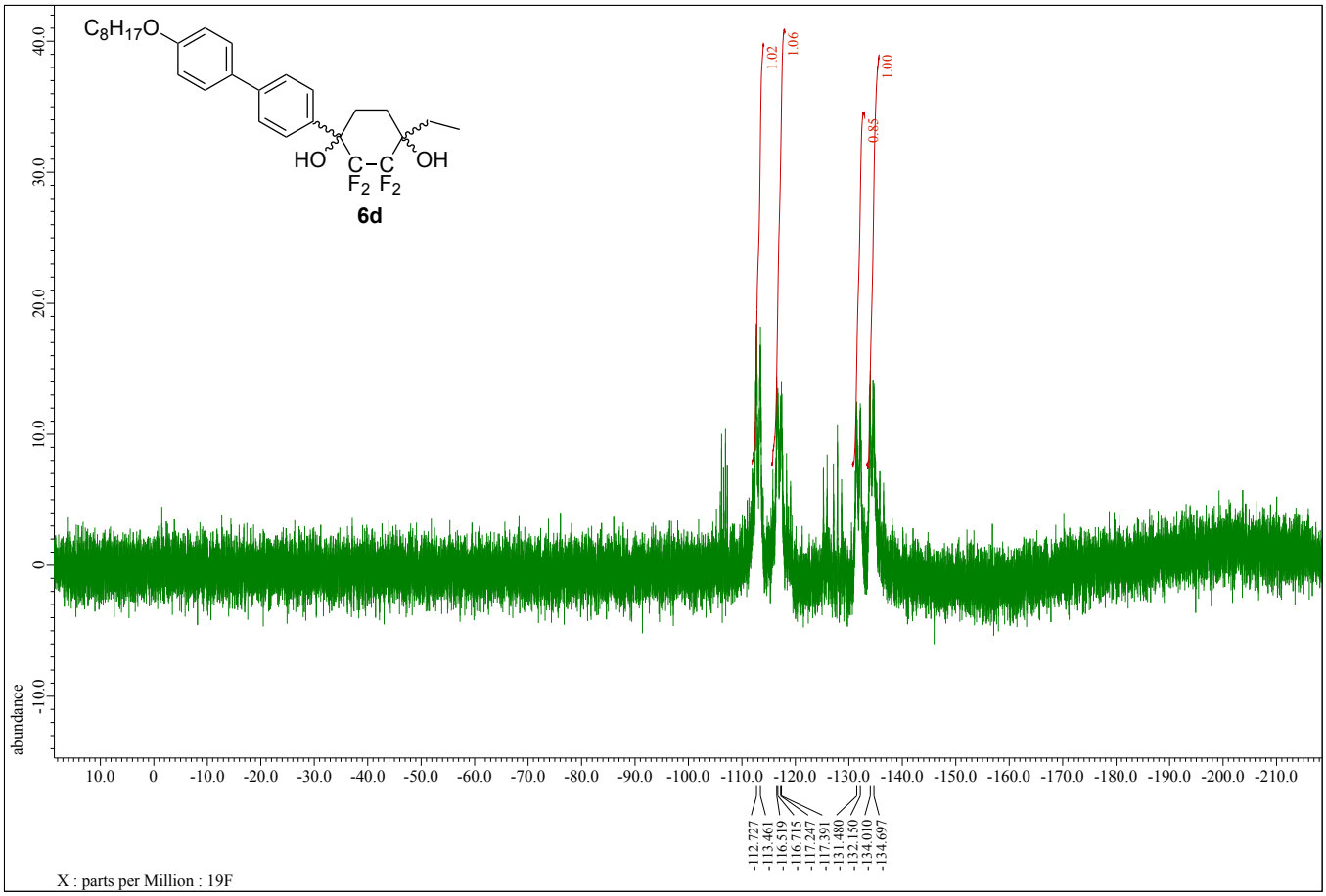


Figure S12. ^{19}F NMR spectrum of **6d** ($CDCl_3$, 376 MHz).

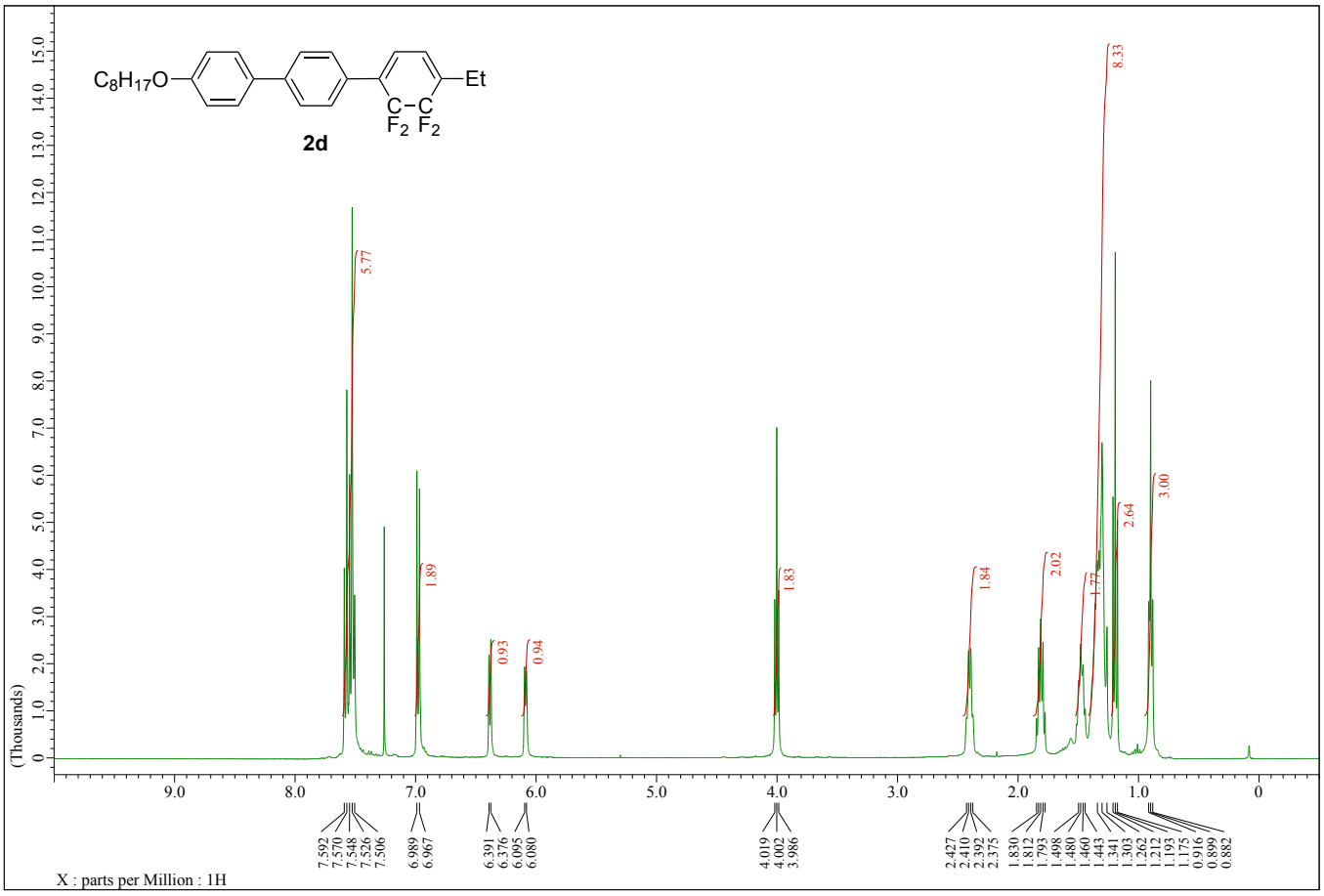


Figure S13. ^{1}H NMR spectrum of **2d** ($CDCl_3$, 400 MHz).

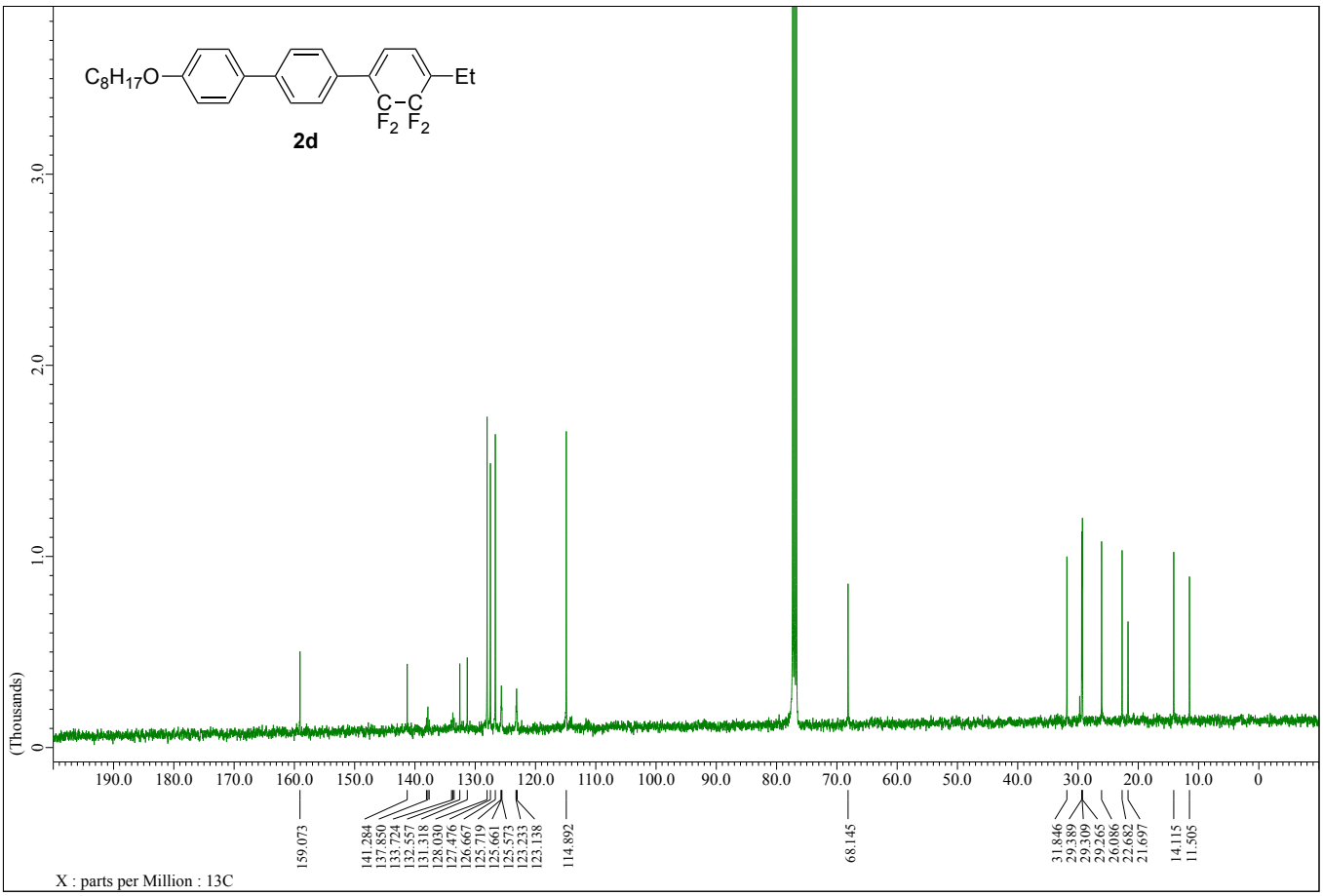


Figure S14. ^{13}C NMR spectrum of **2d** ($CDCl_3$, 100 MHz).

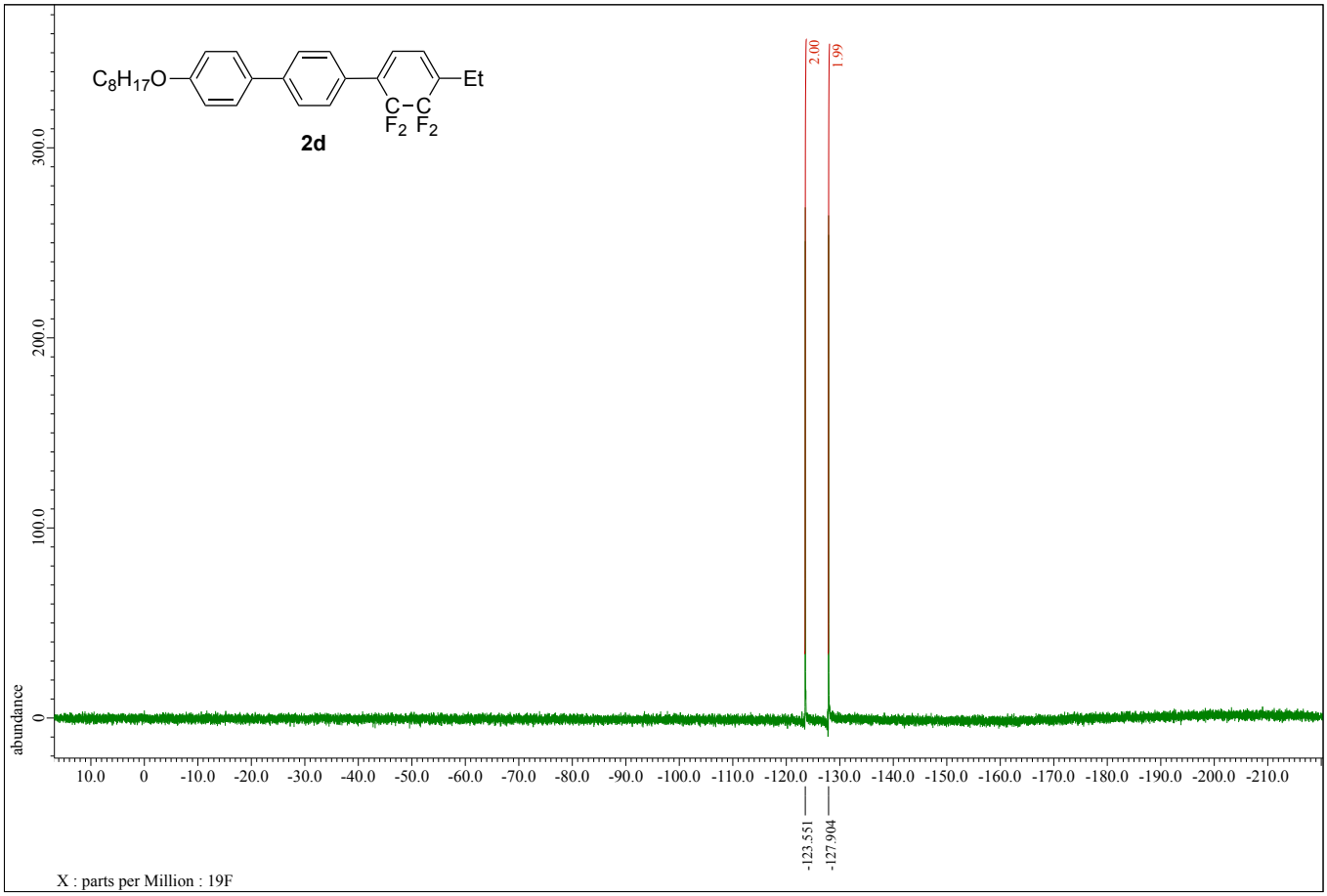


Figure S15. ^{19}F NMR spectrum of **2d** ($CDCl_3$, 376 MHz).

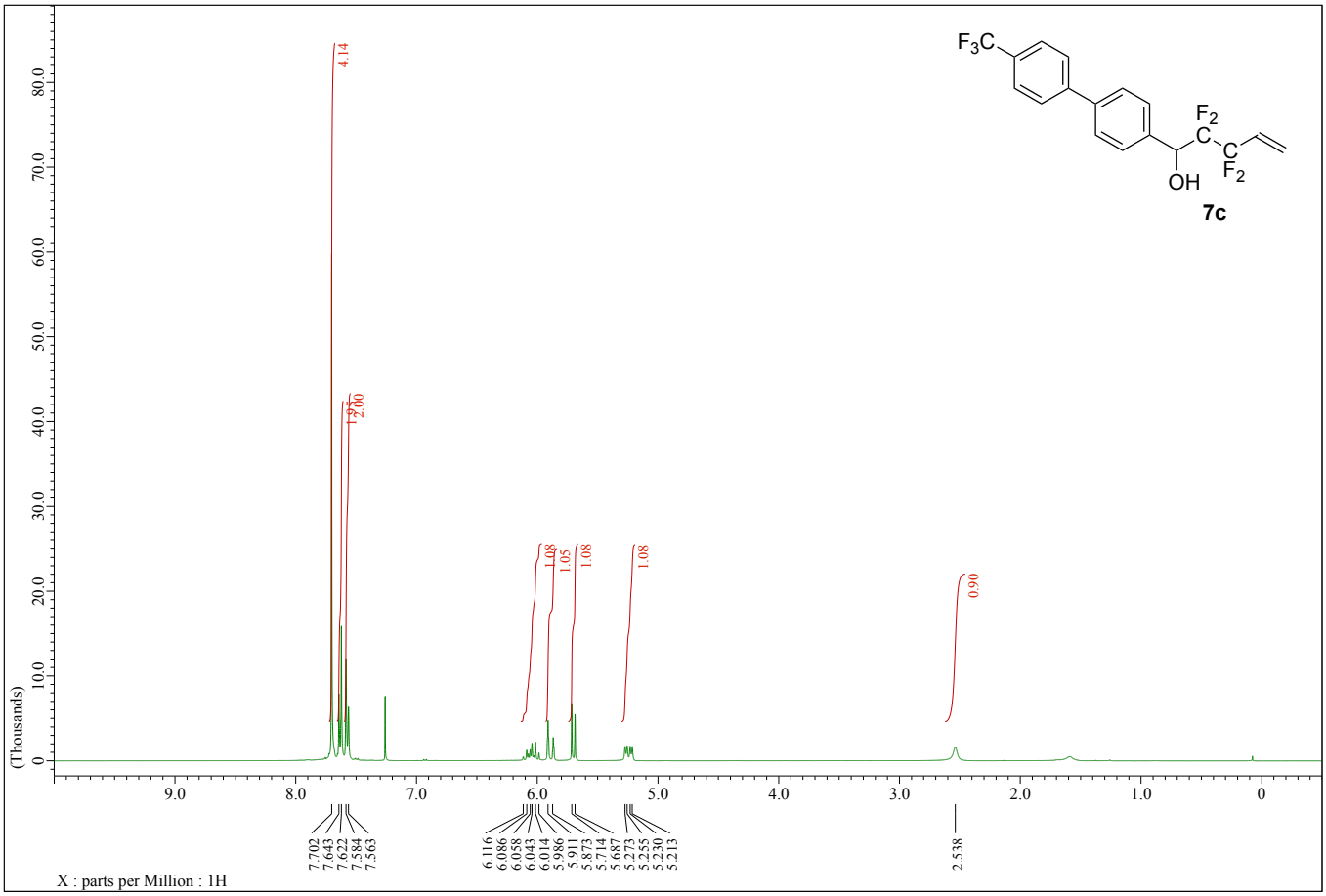


Figure S16. ^{1}H NMR spectrum of **7c** ($CDCl_3$, 400 MHz).

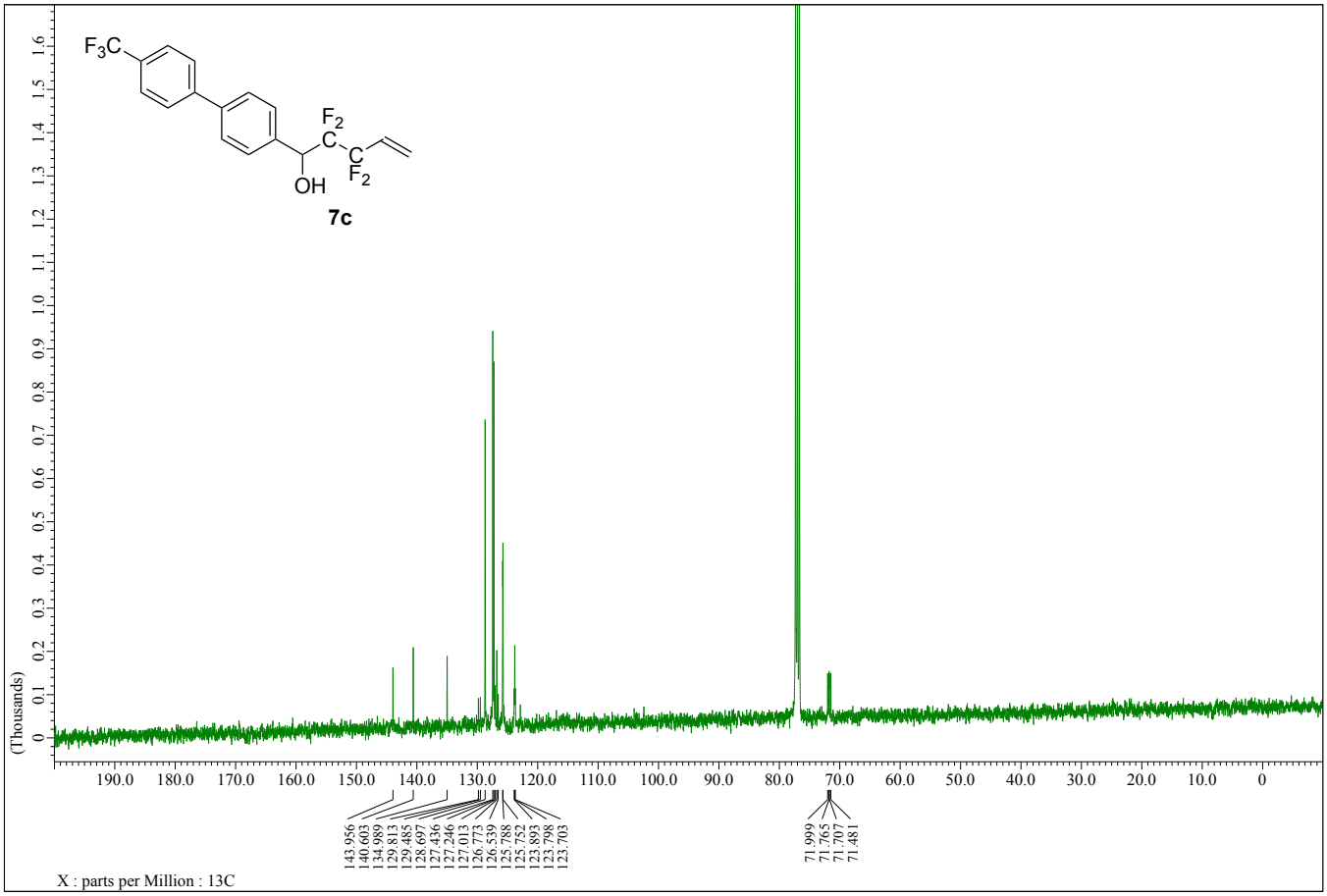


Figure S17. ^{13}C NMR spectrum of **7c** ($CDCl_3$, 100 MHz).

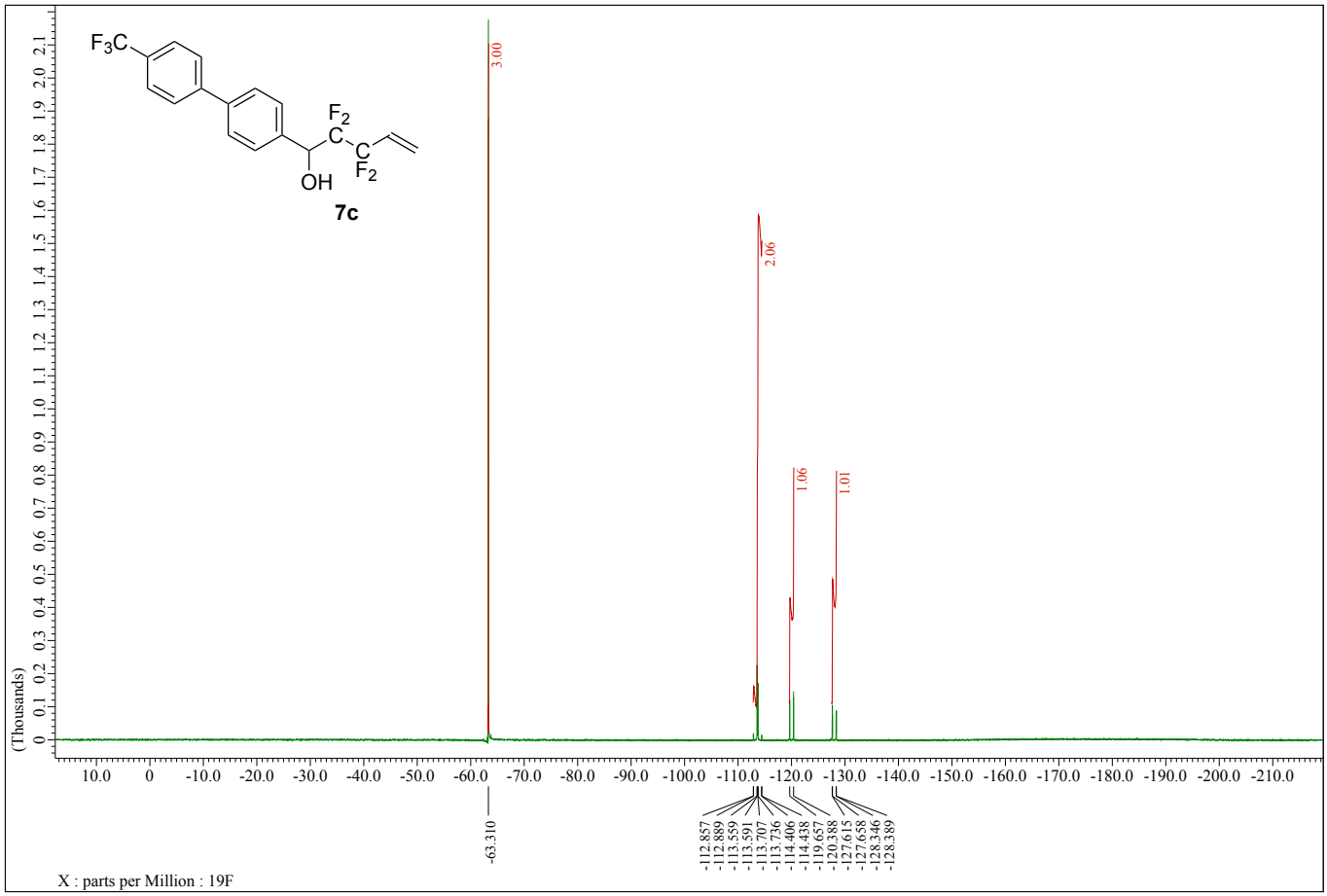


Figure S18. ^{19}F NMR spectrum of **7c** ($CDCl_3$, 376 MHz).

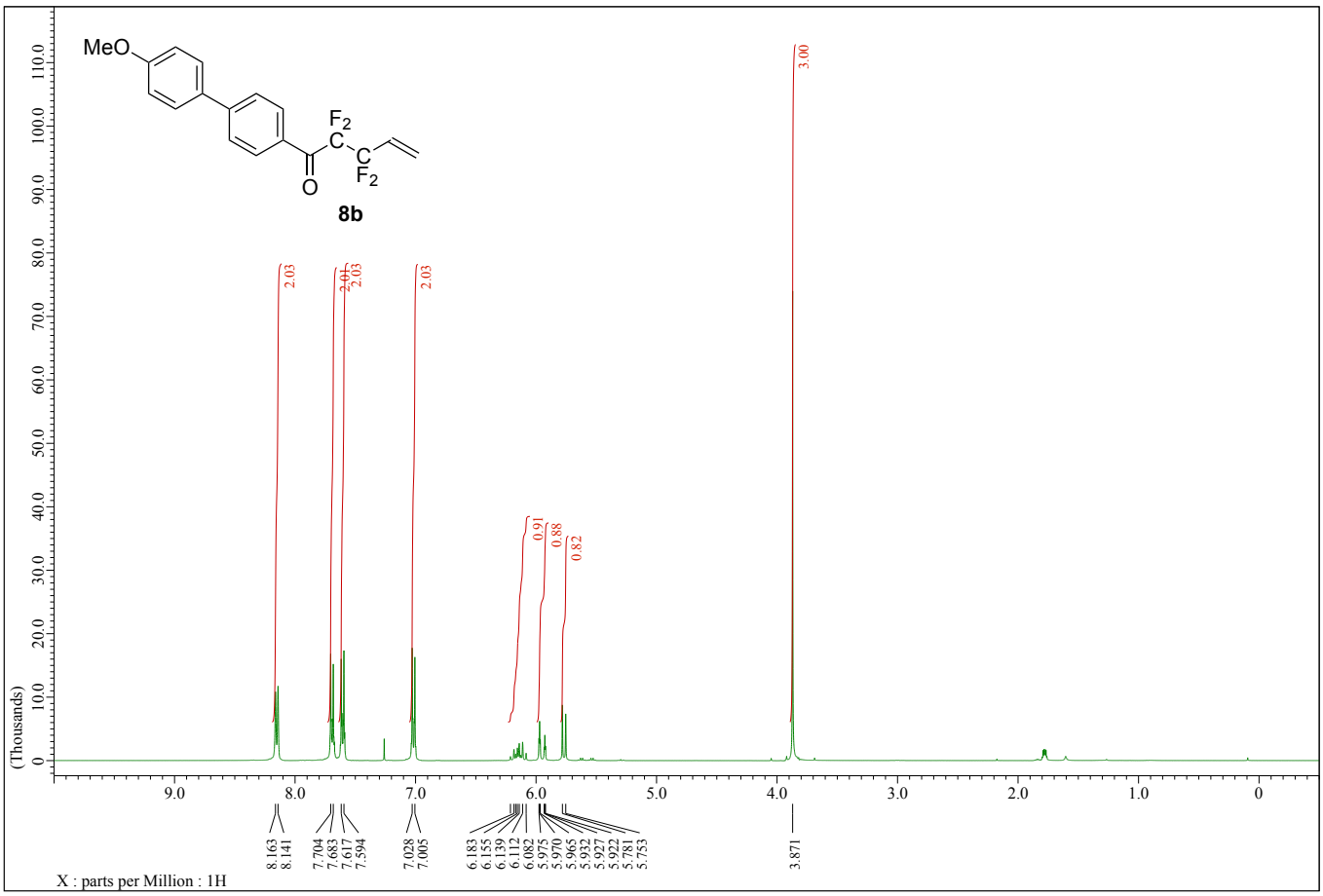


Figure S19. ^{1}H NMR spectrum of **8b** ($CDCl_3$, 400 MHz).

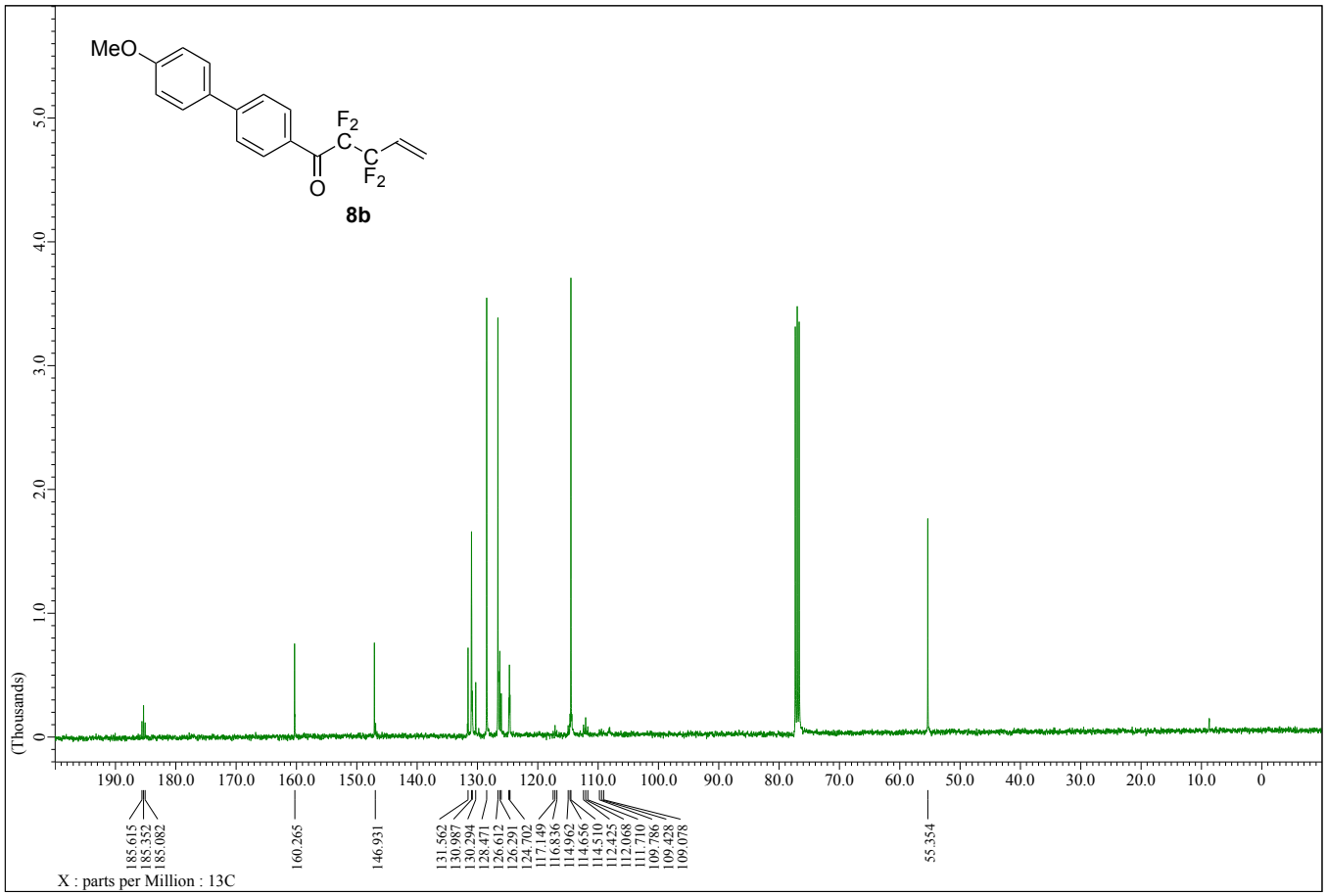


Figure S20. ^{13}C NMR spectrum of **8b** ($CDCl_3$, 100 MHz).

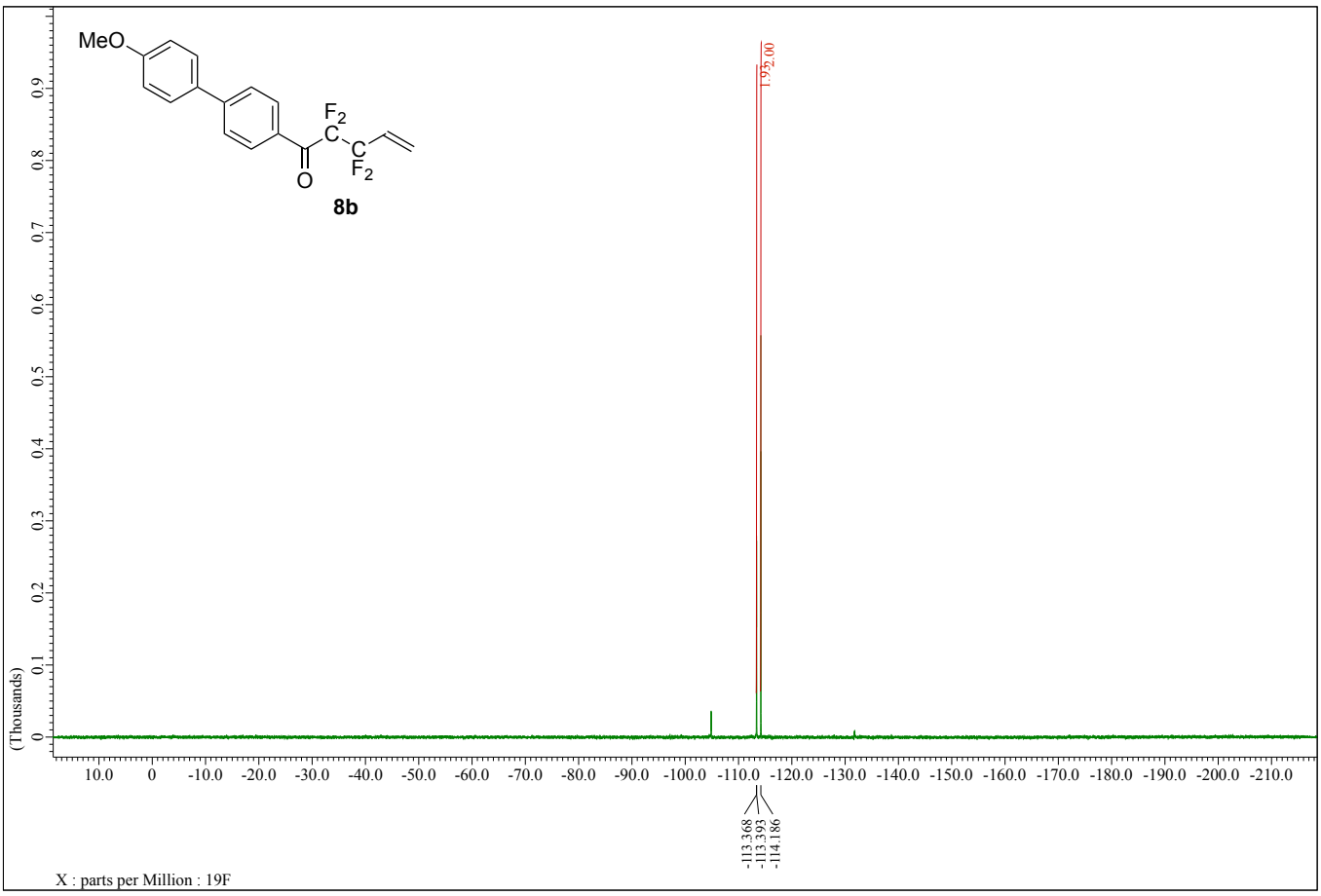


Figure S21. ^{19}F NMR spectrum of **8b** ($CDCl_3$, 376 MHz).

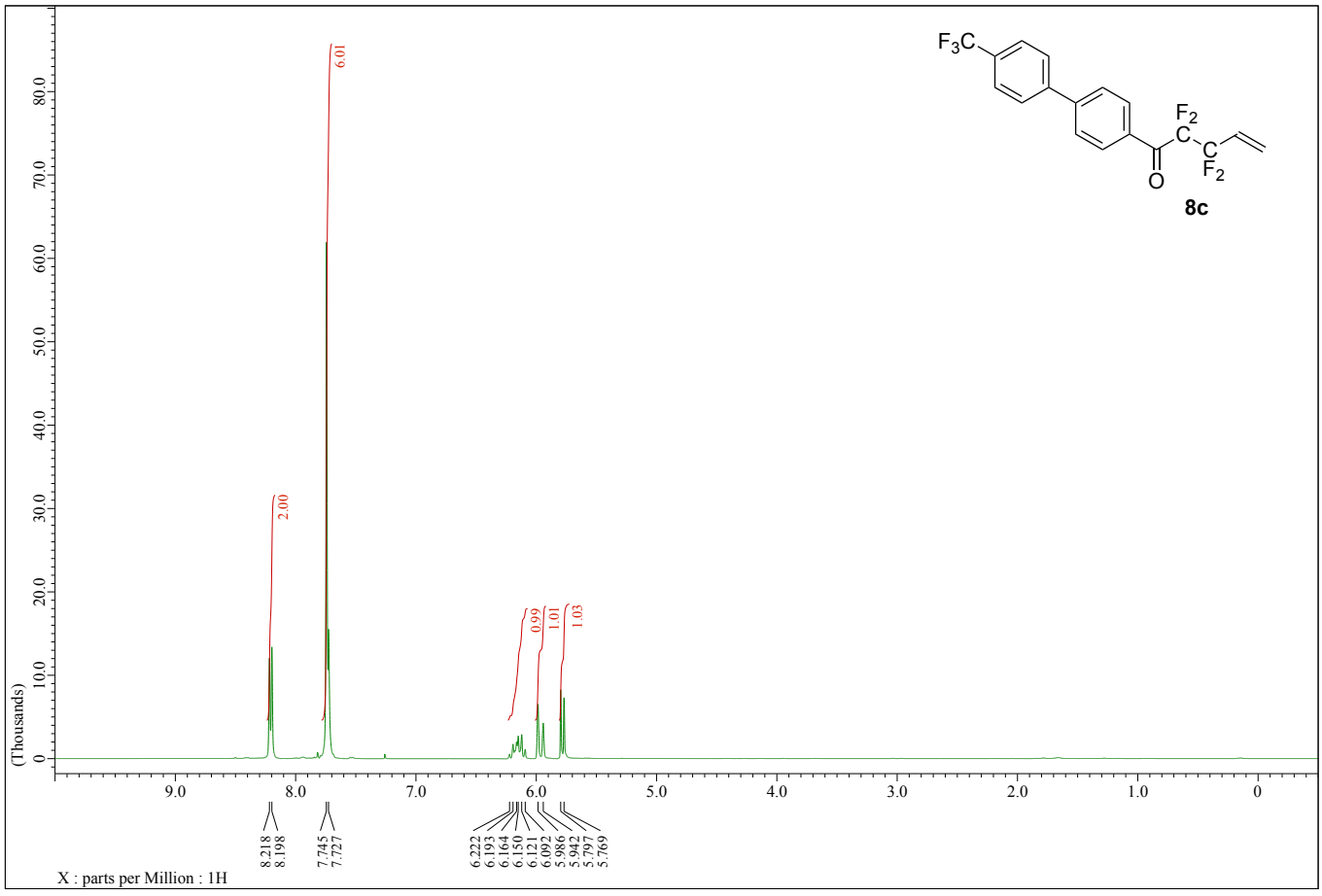


Figure S22. ^{1}H NMR spectrum of **8c** ($CDCl_3$, 400 MHz).

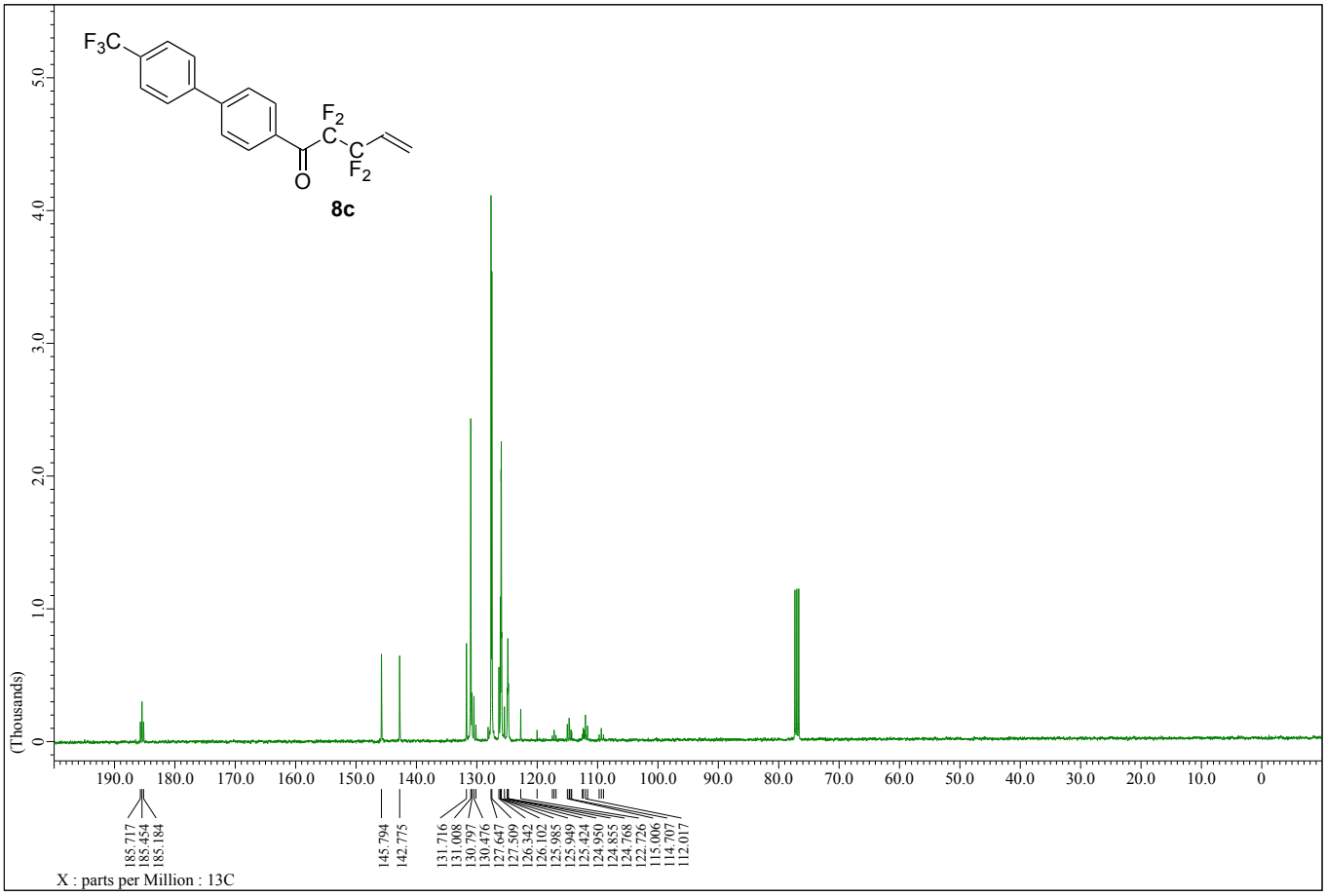


Figure S23. ^{13}C NMR spectrum of **8c** ($CDCl_3$, 100 MHz).

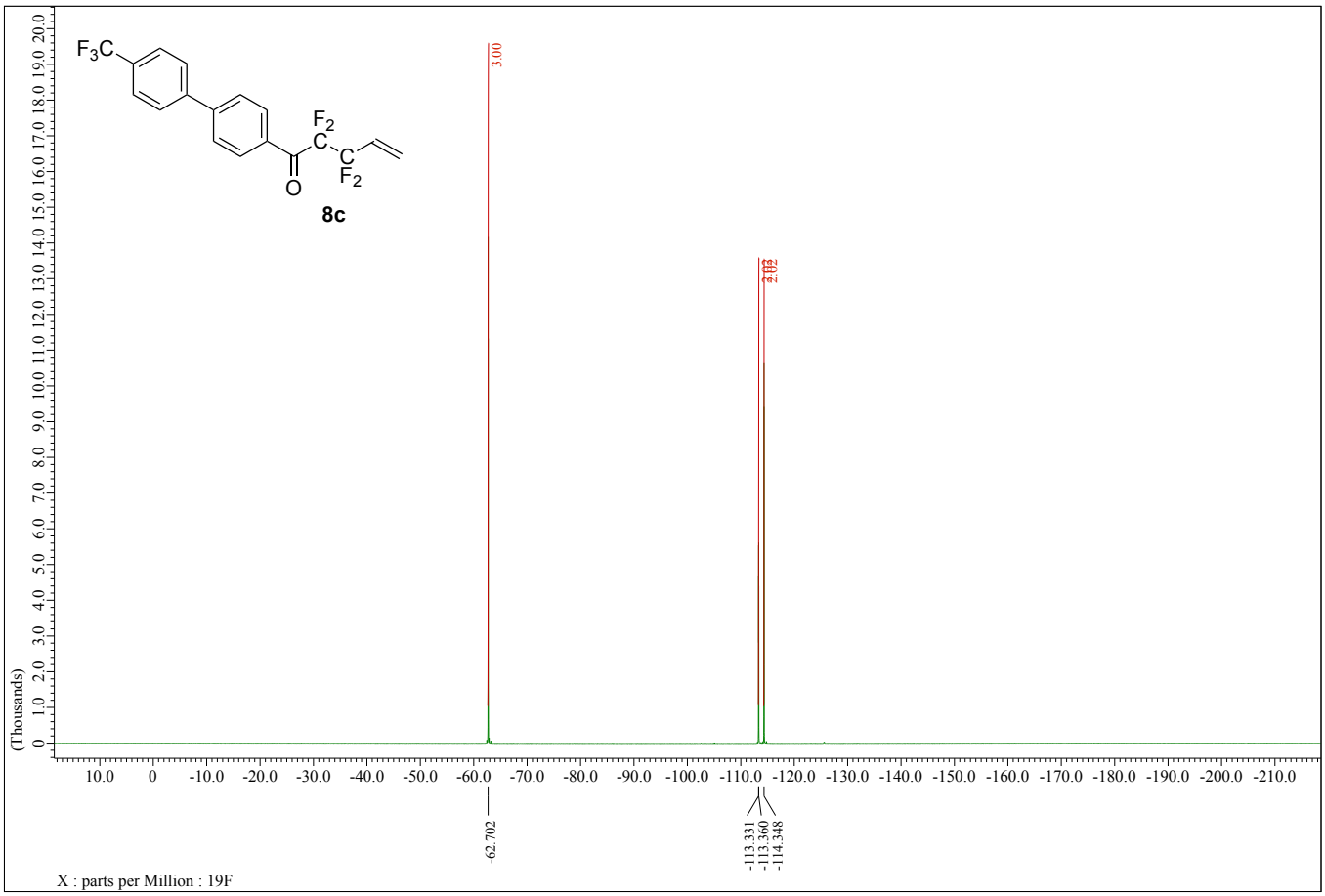


Figure S24. ^{19}F NMR spectrum of **8c** ($CDCl_3$, 376 MHz).

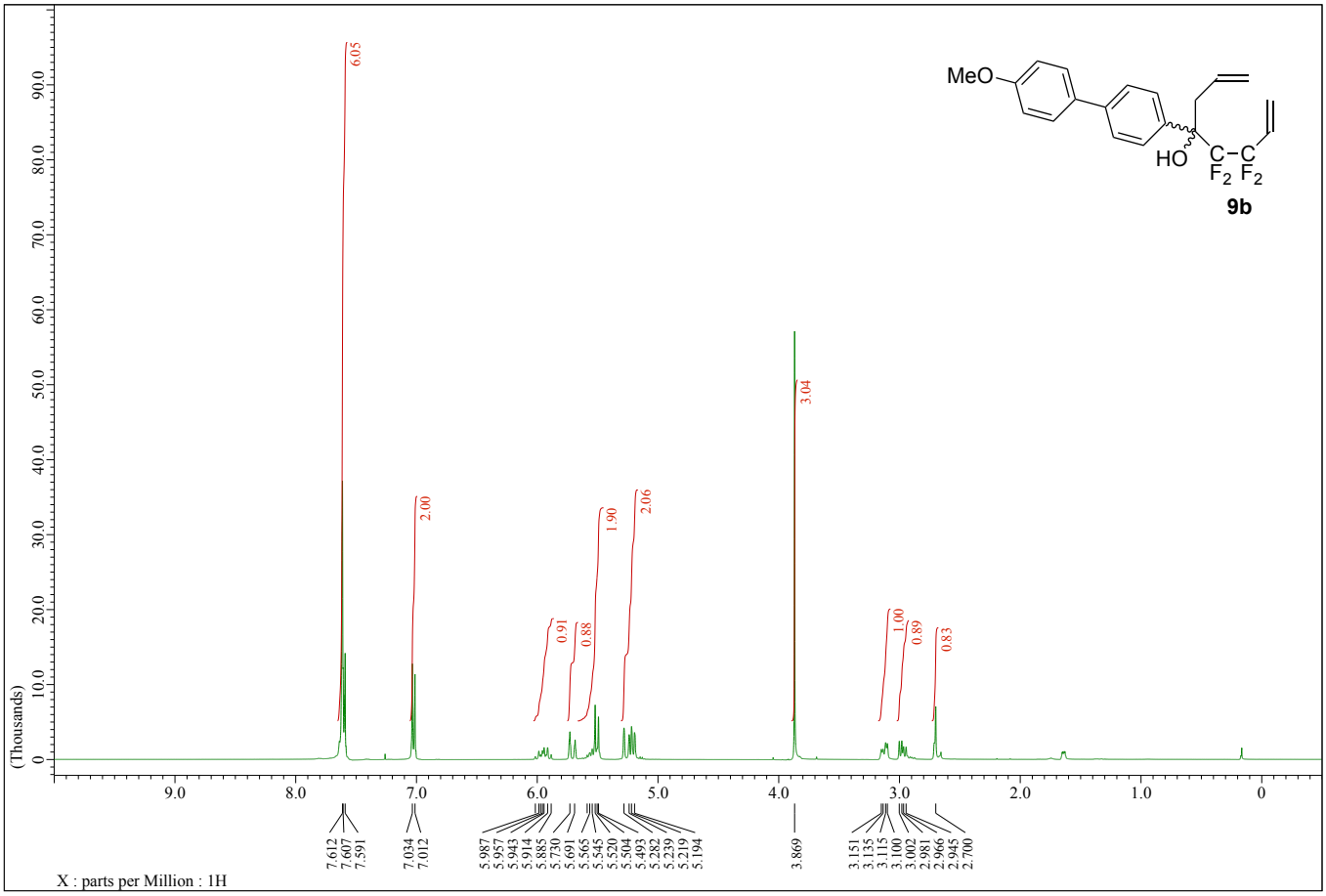


Figure S25. ^{1}H NMR spectrum of **9b** ($CDCl_3$, 400 MHz).

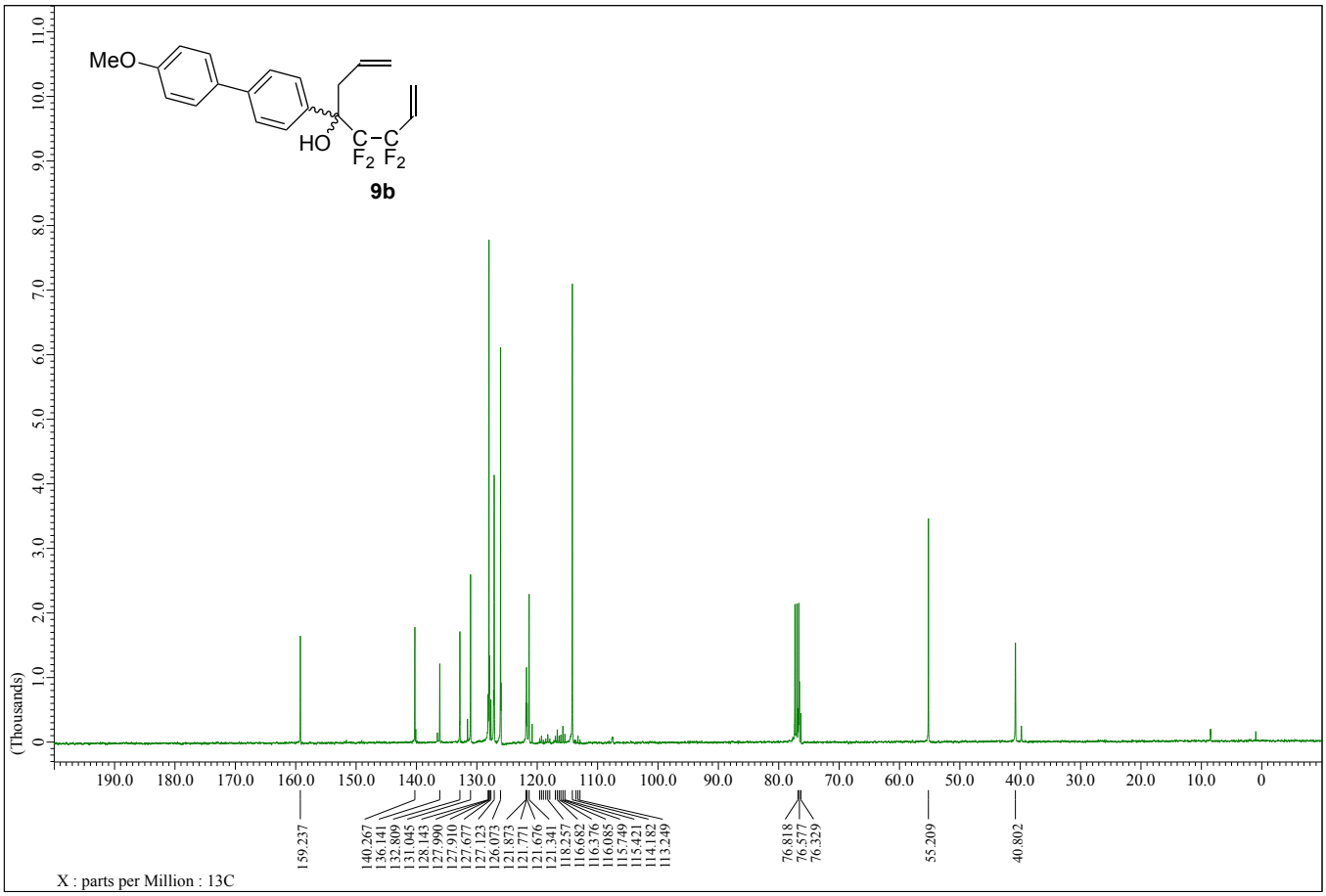


Figure S26. ^{13}C NMR spectrum of **9b** ($CDCl_3$, 100 MHz).

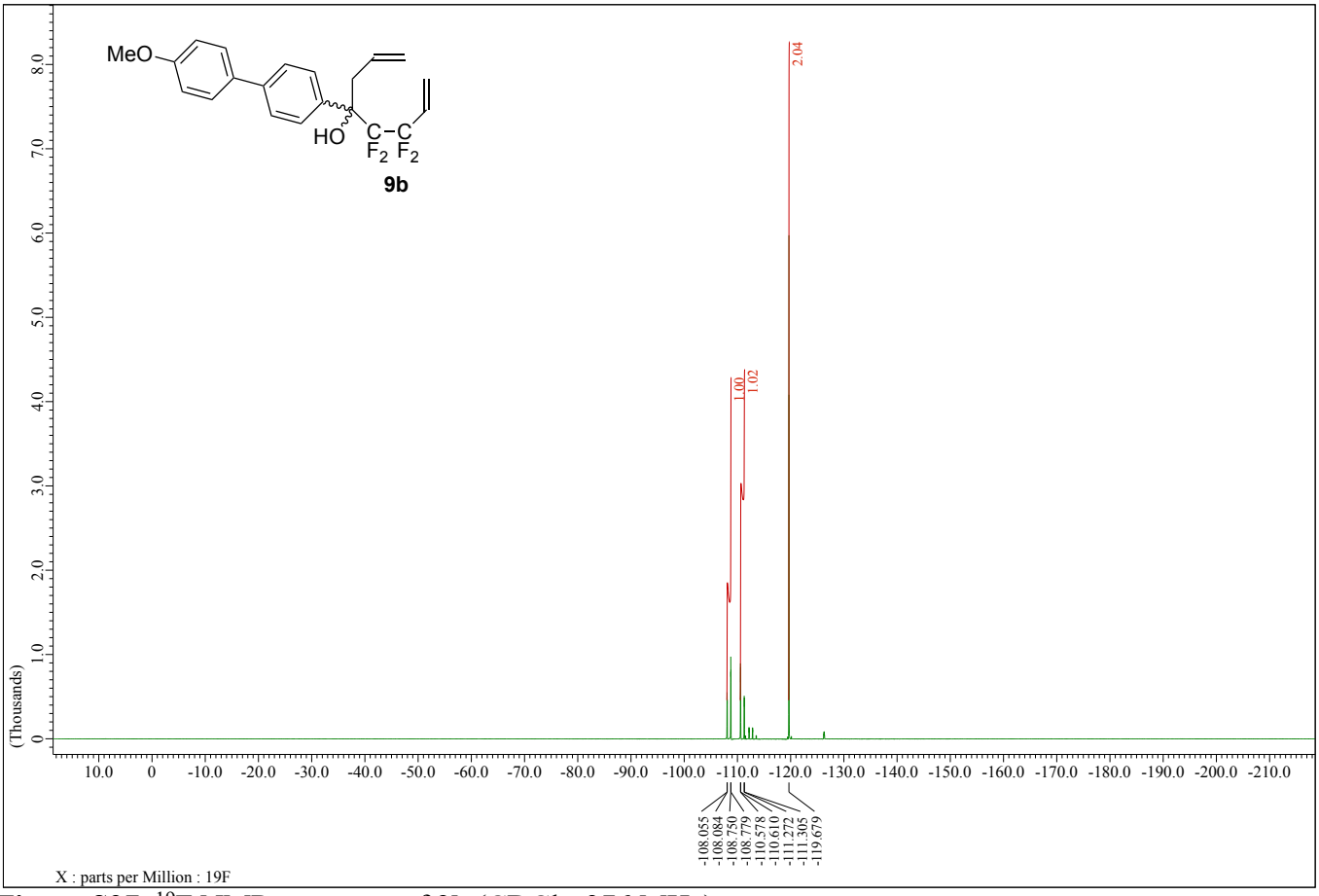


Figure S27. ^{19}F NMR spectrum of **9b** ($CDCl_3$, 376 MHz).

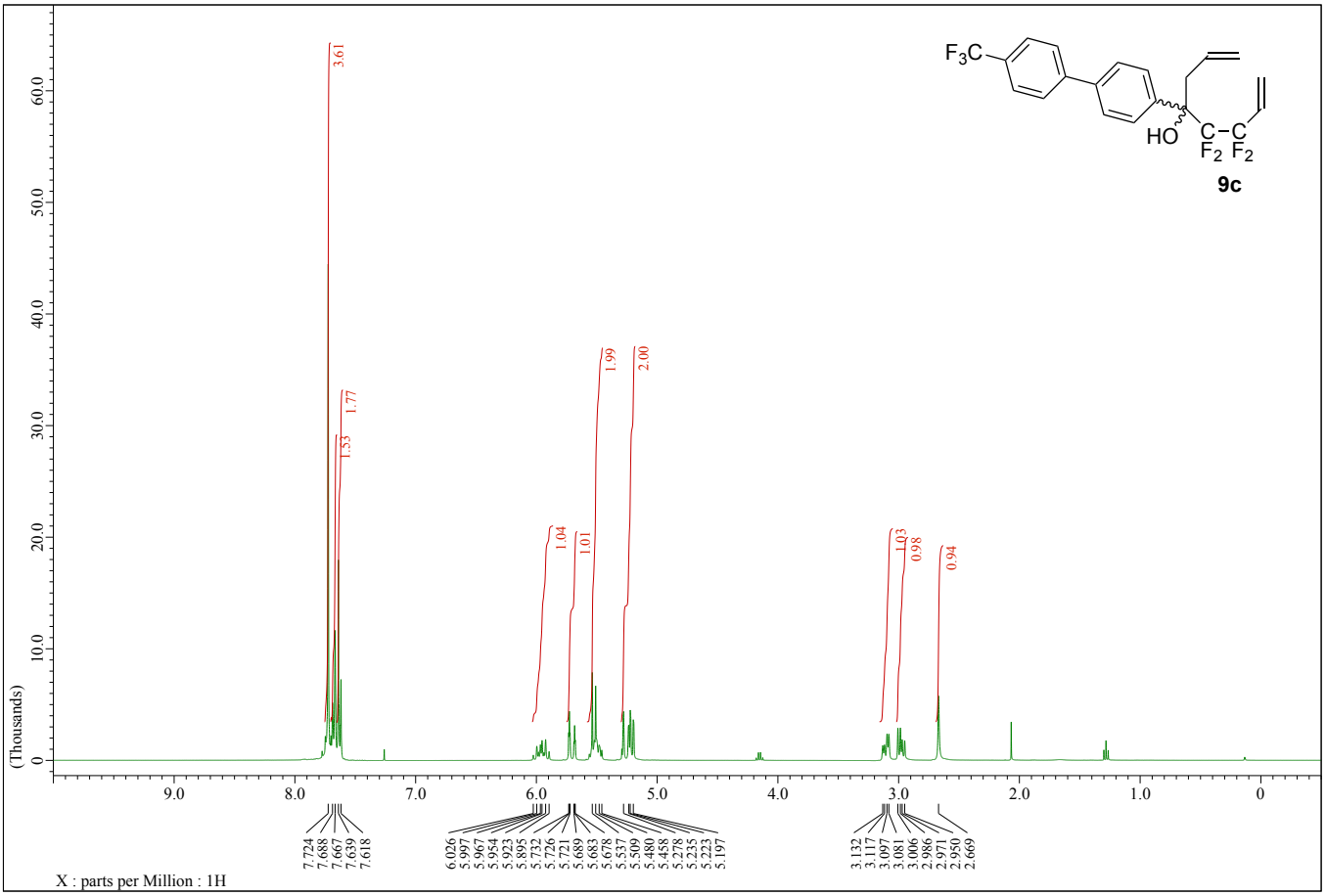


Figure S28. ^{1}H NMR spectrum of **9c** ($CDCl_3$, 400 MHz).

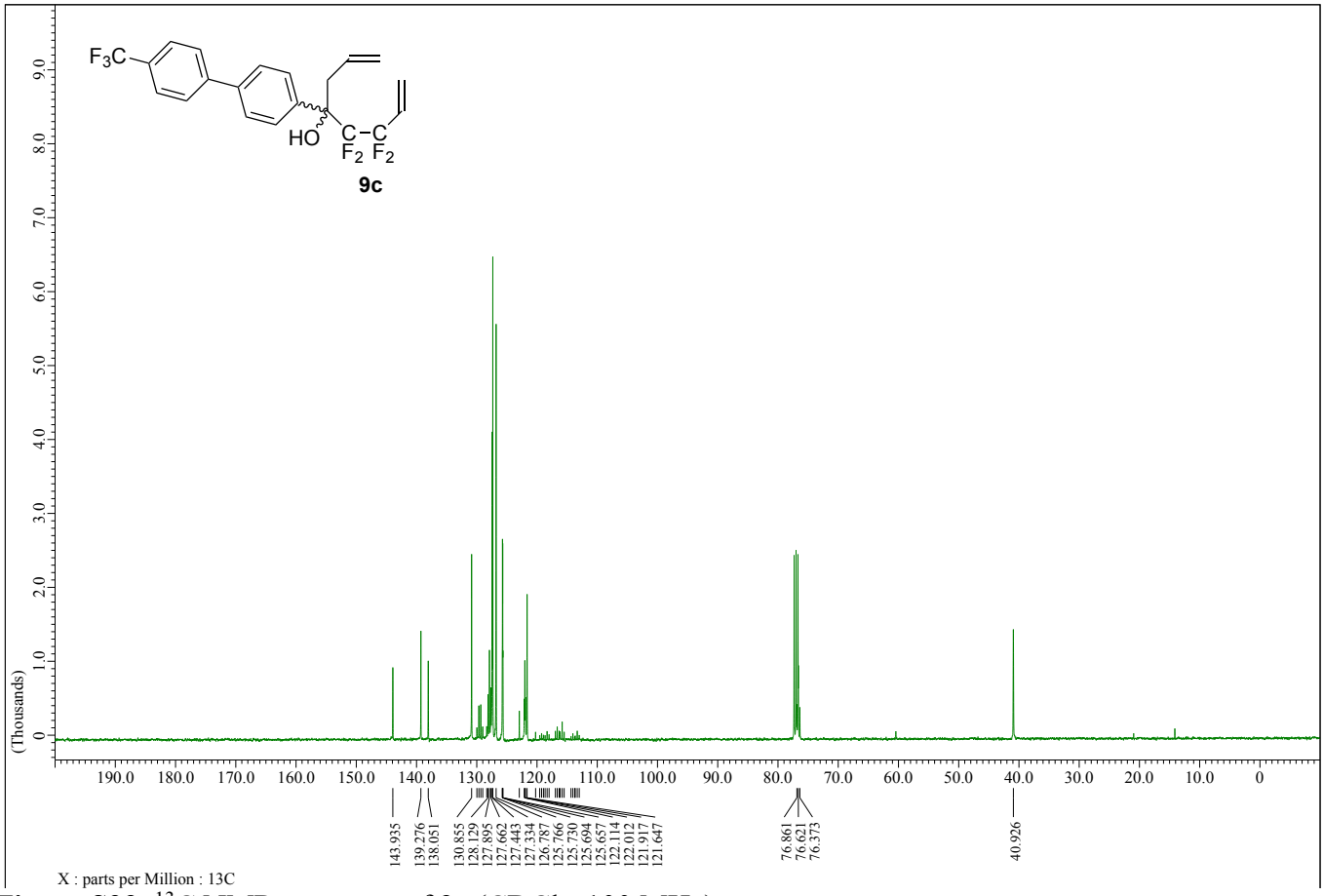


Figure S29. ^{13}C NMR spectrum of **9c** ($CDCl_3$, 100 MHz).

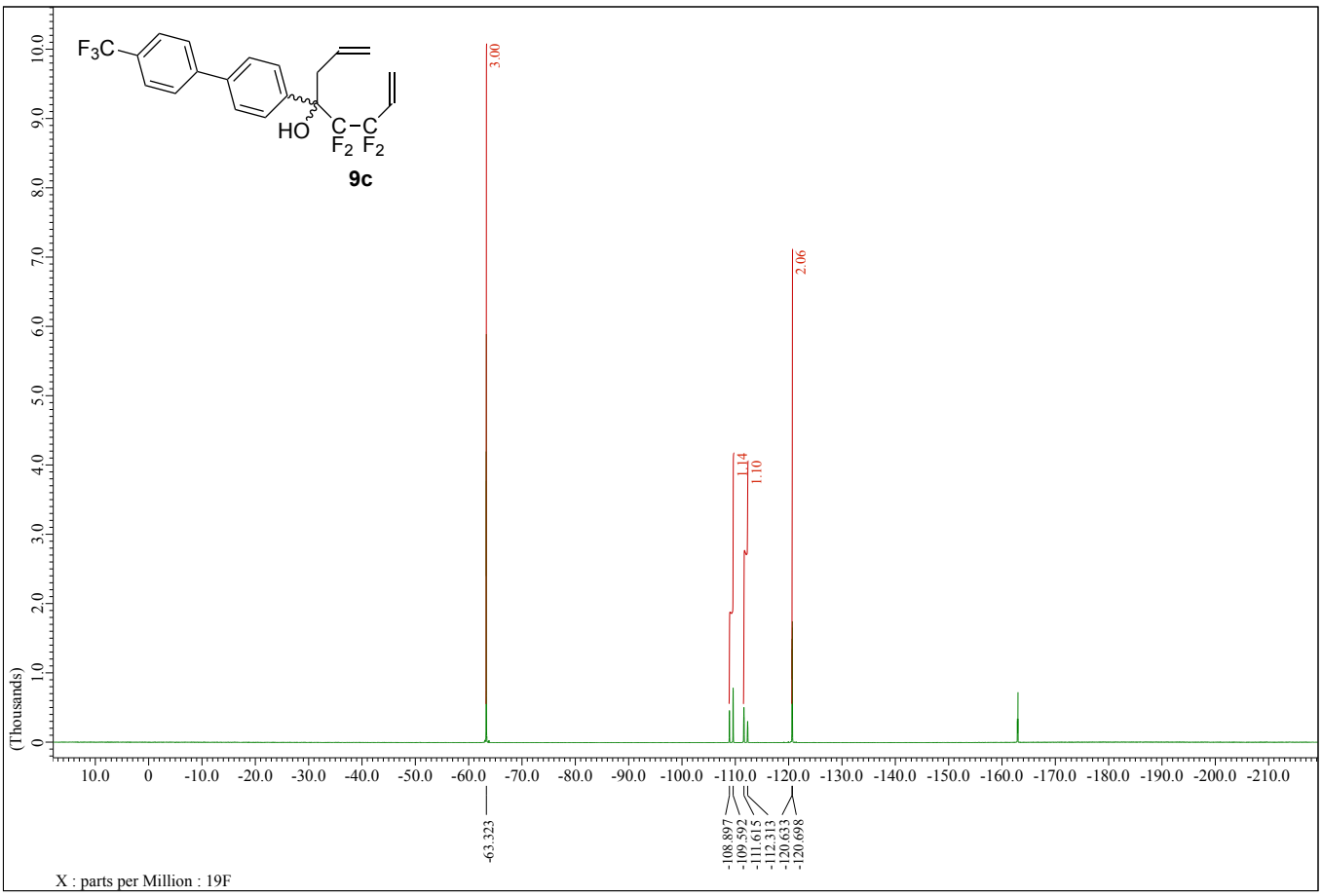


Figure S30. ^{19}F NMR spectrum of **9c** ($CDCl_3$, 376 MHz).

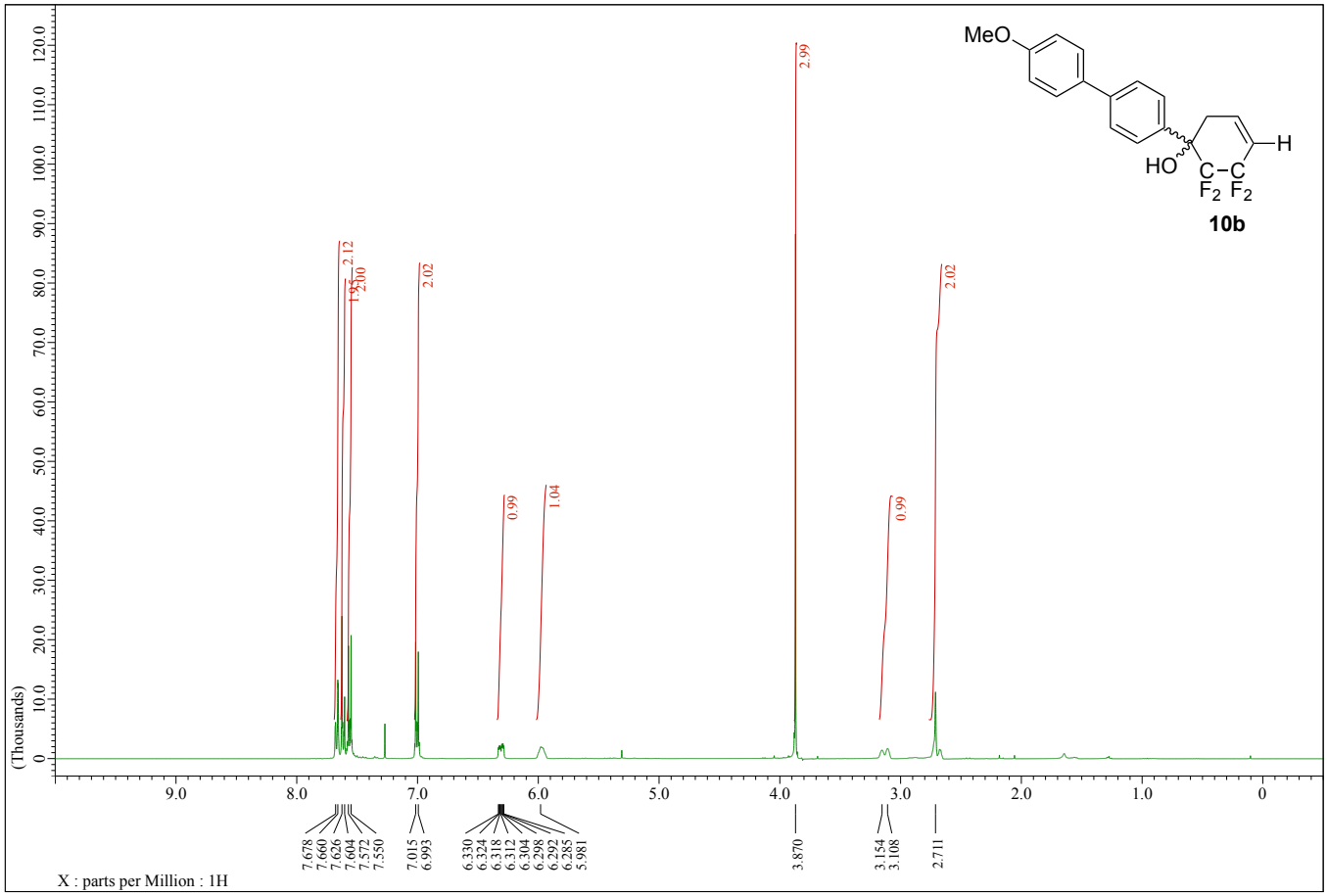


Figure S31. ^{1}H NMR spectrum of **10b** ($CDCl_3$, 400 MHz).

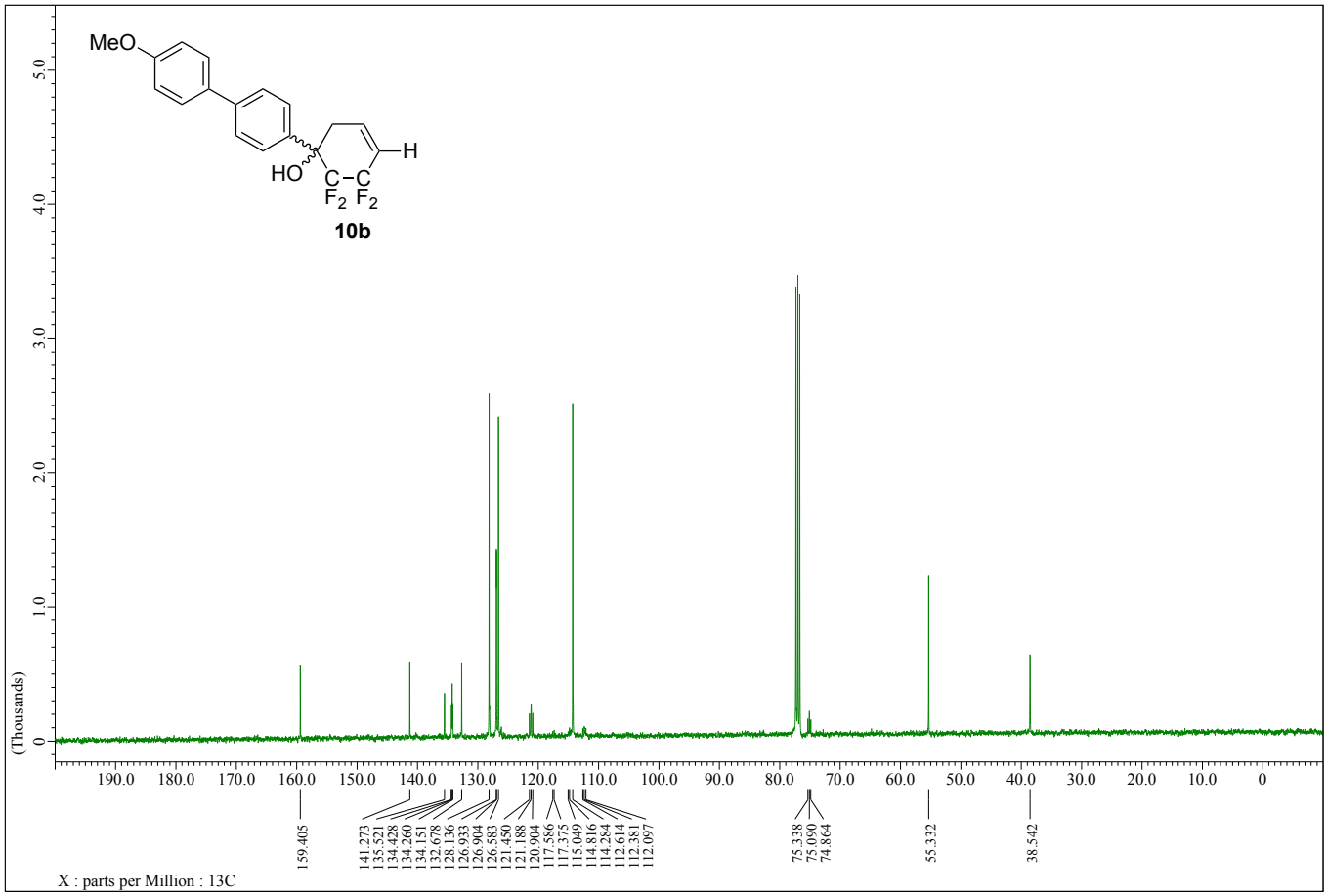


Figure S32. ^{13}C NMR spectrum of **10b** ($CDCl_3$, 100 MHz).

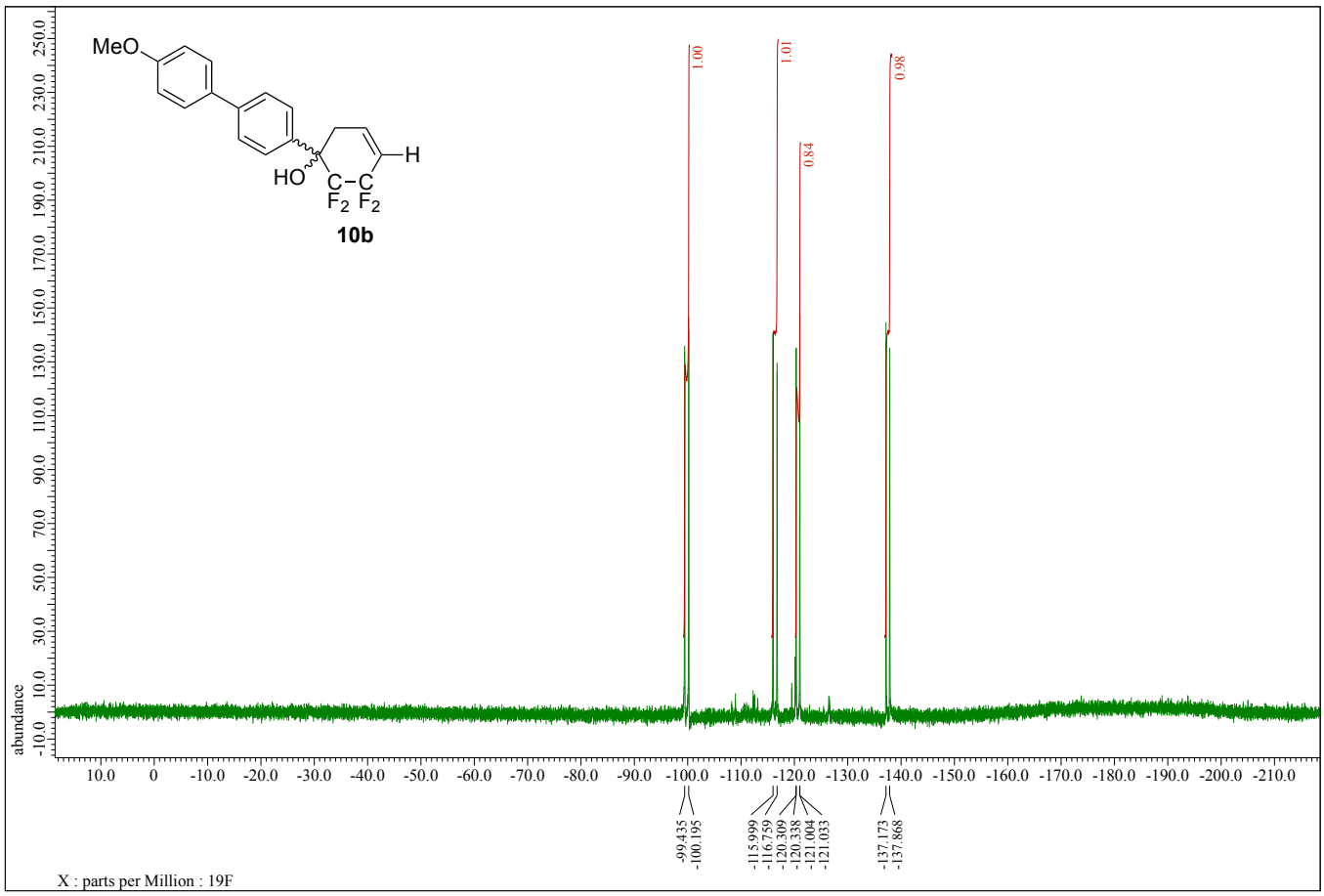


Figure S33. ^{19}F NMR spectrum of **10b** ($CDCl_3$, 376 MHz).

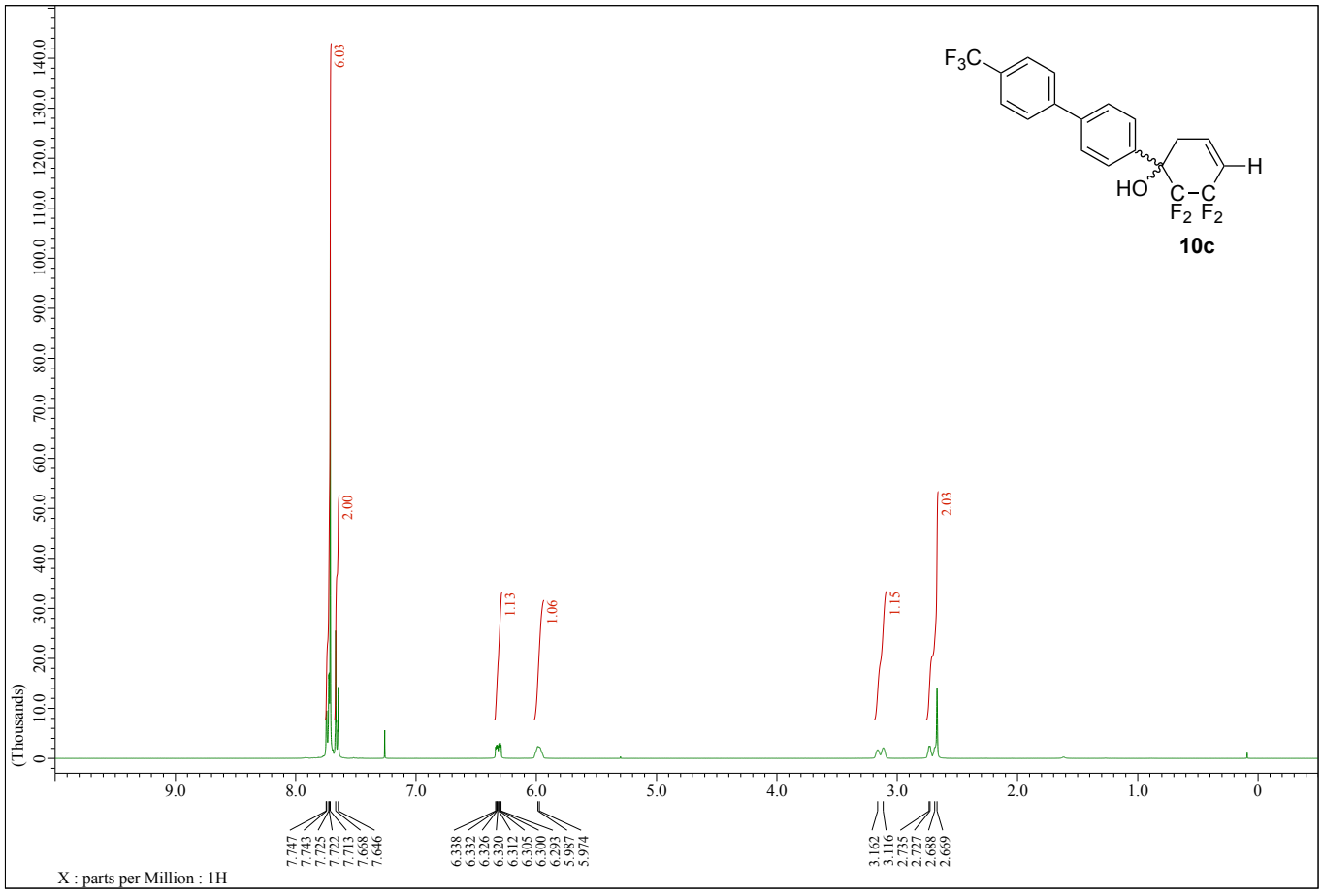


Figure S34. ^{1}H NMR spectrum of **10c** ($CDCl_3$, 400 MHz).

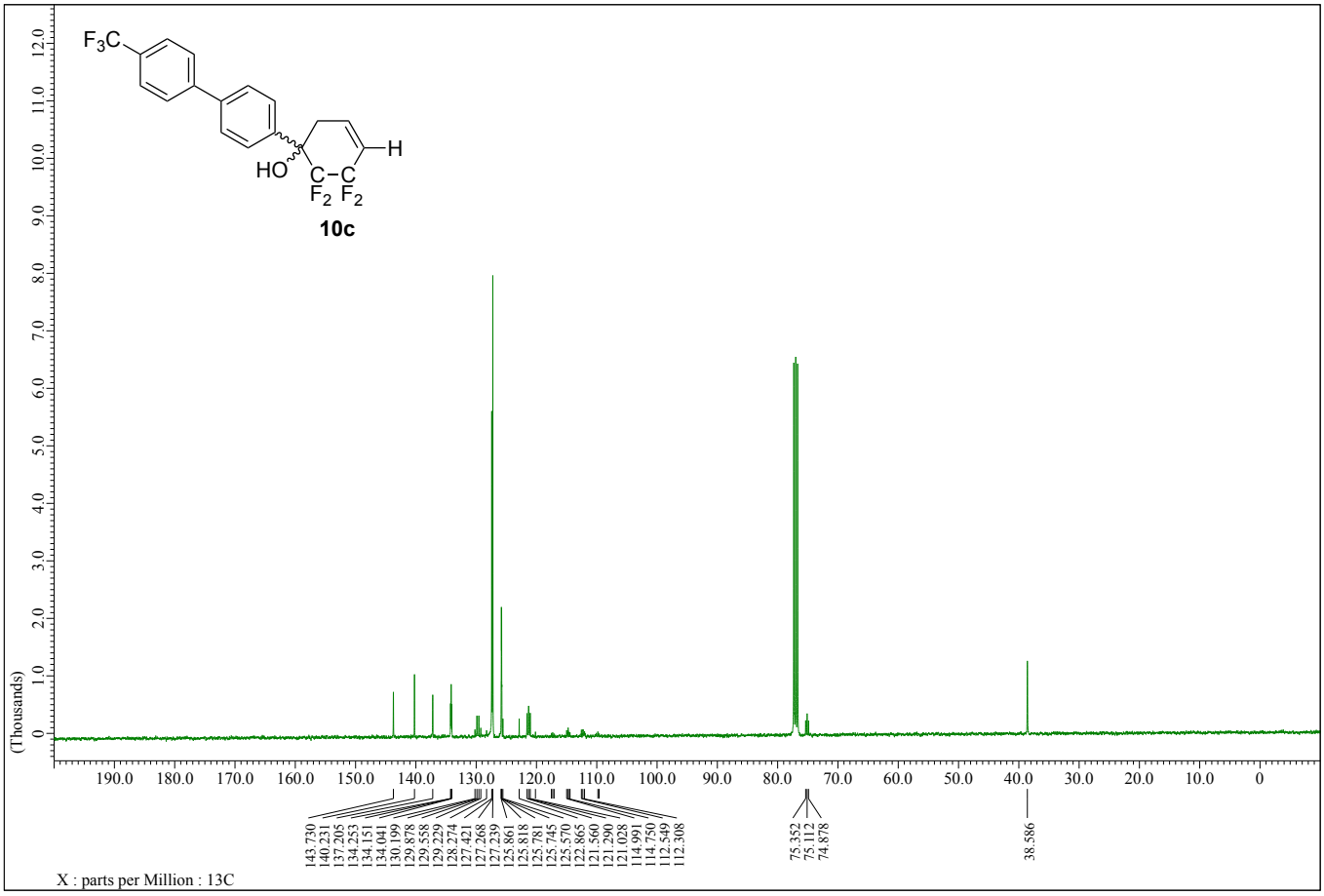


Figure S35. ^{13}C NMR spectrum of **10c** ($CDCl_3$, 100 MHz).

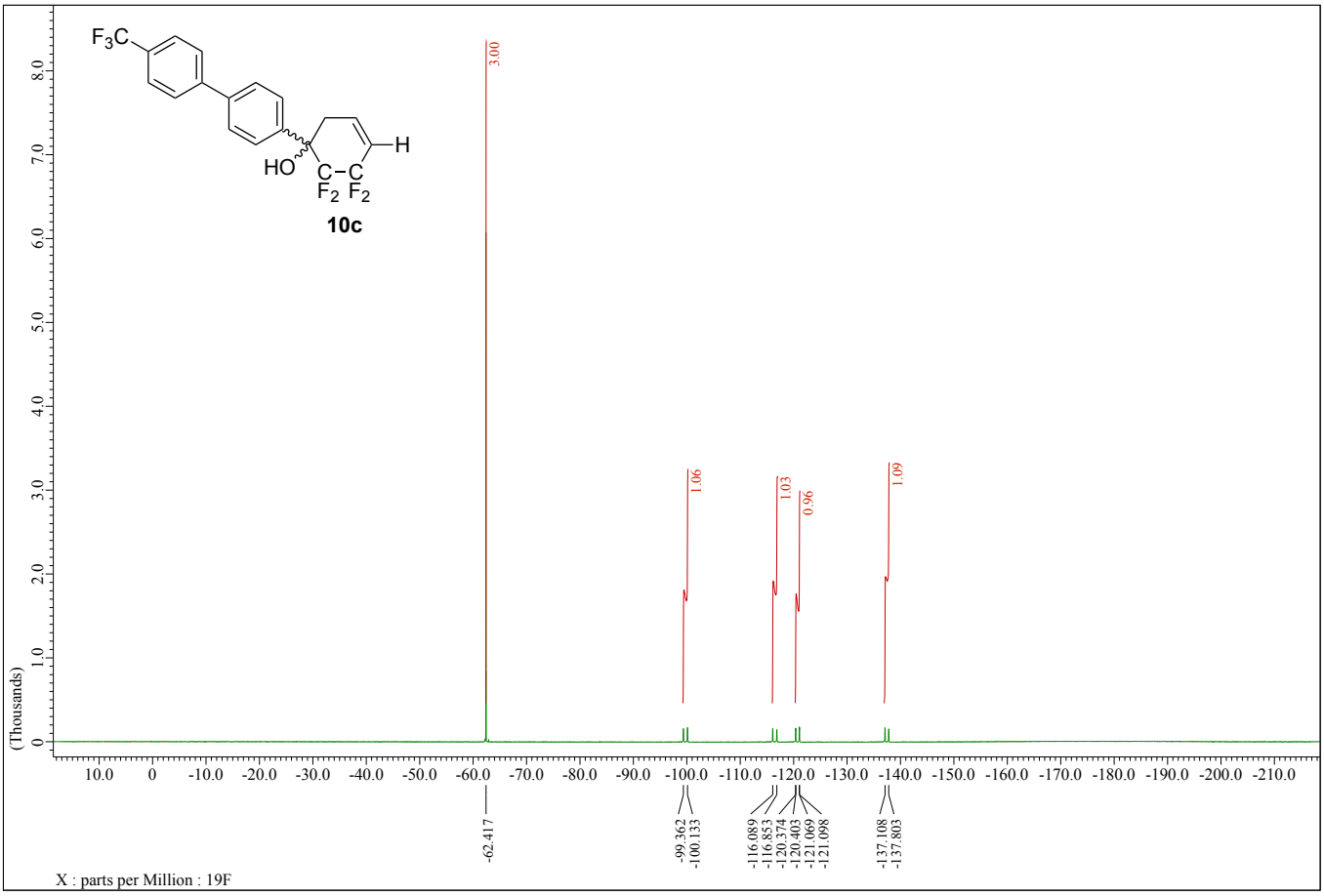


Figure S36. ^{19}F NMR spectrum of **10c** ($CDCl_3$, 376 MHz).

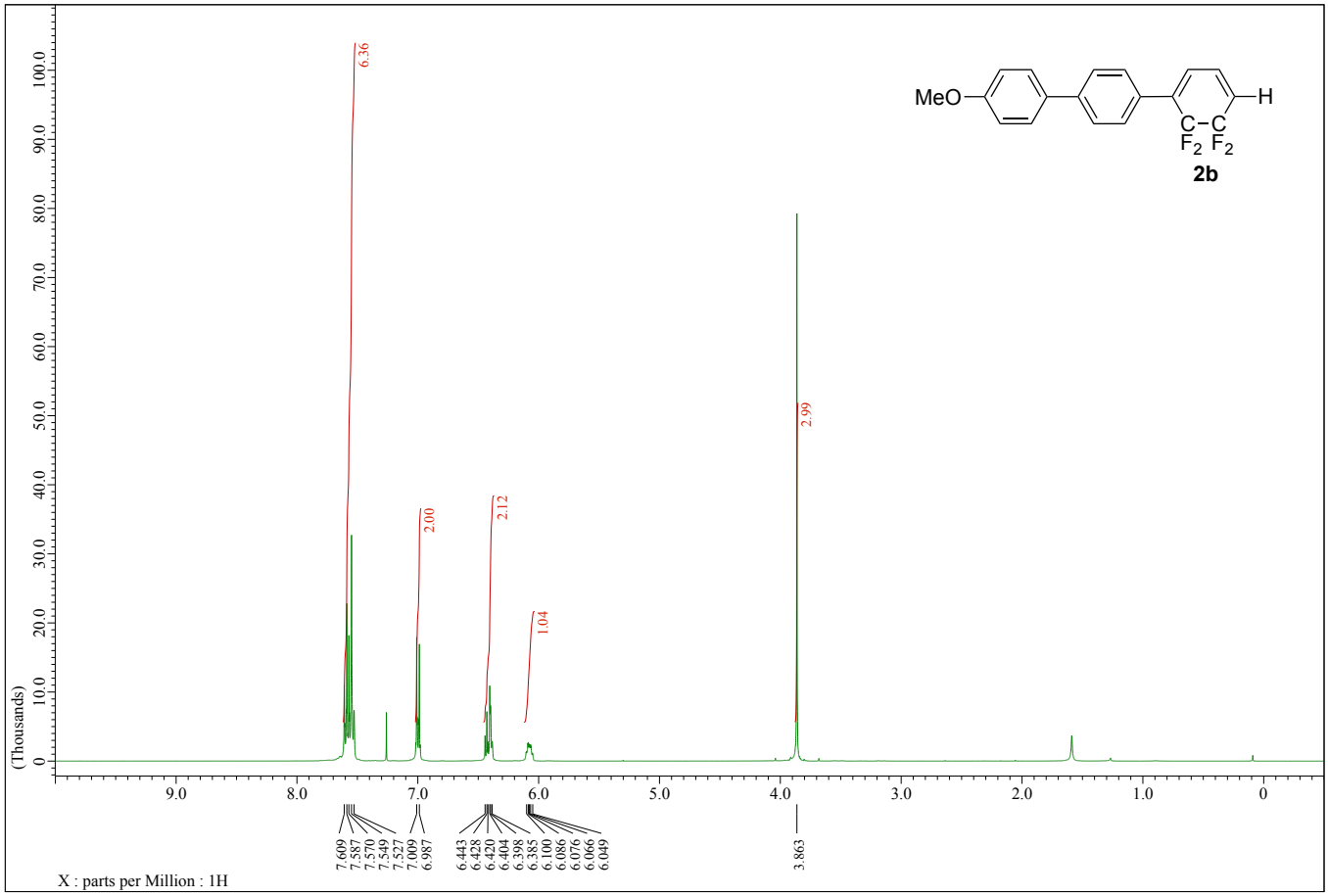


Figure S37. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 400 MHz).

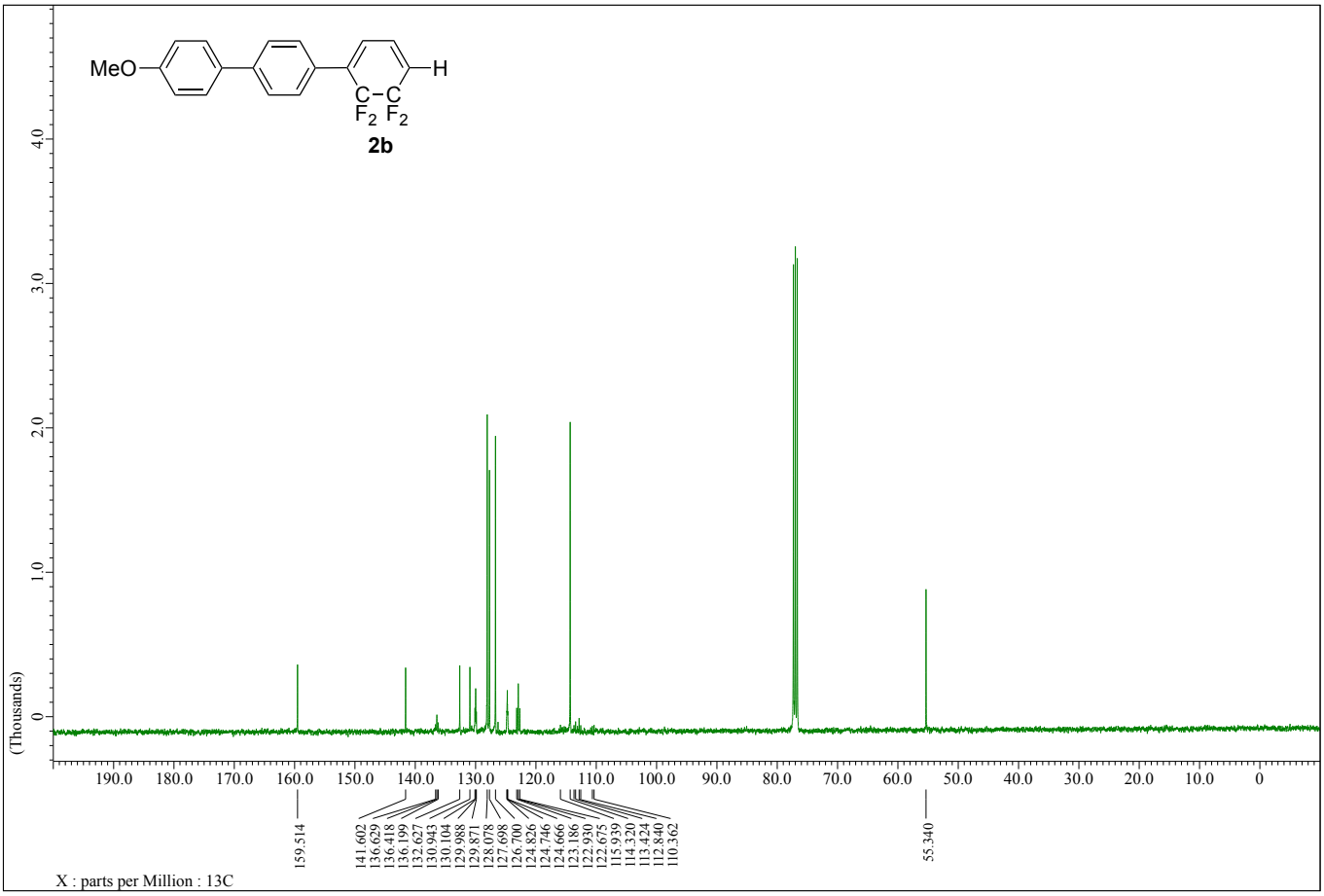


Figure S38. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 100 MHz).

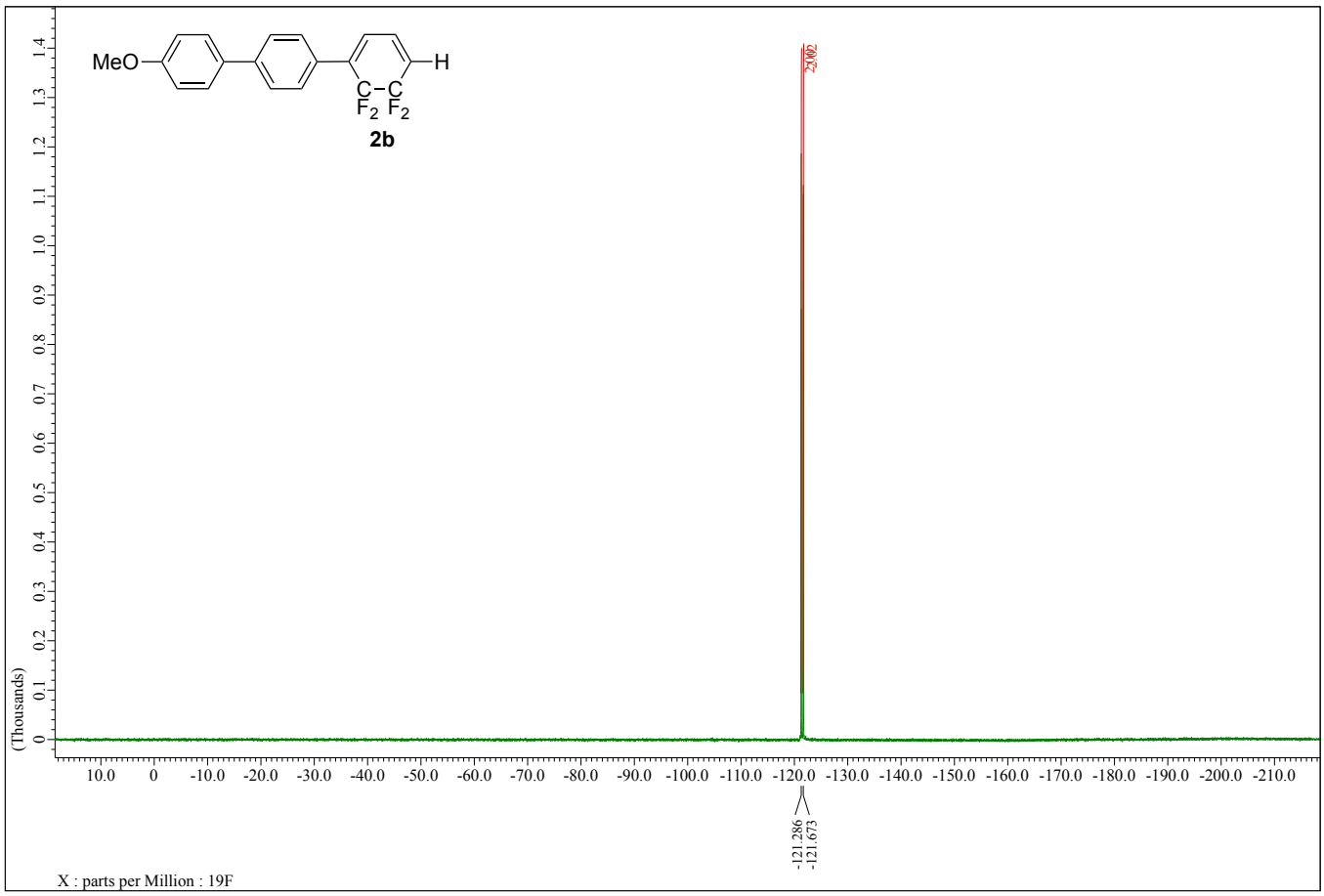


Figure S39. ^{19}F NMR spectrum of **2b** ($CDCl_3$, 376 MHz).

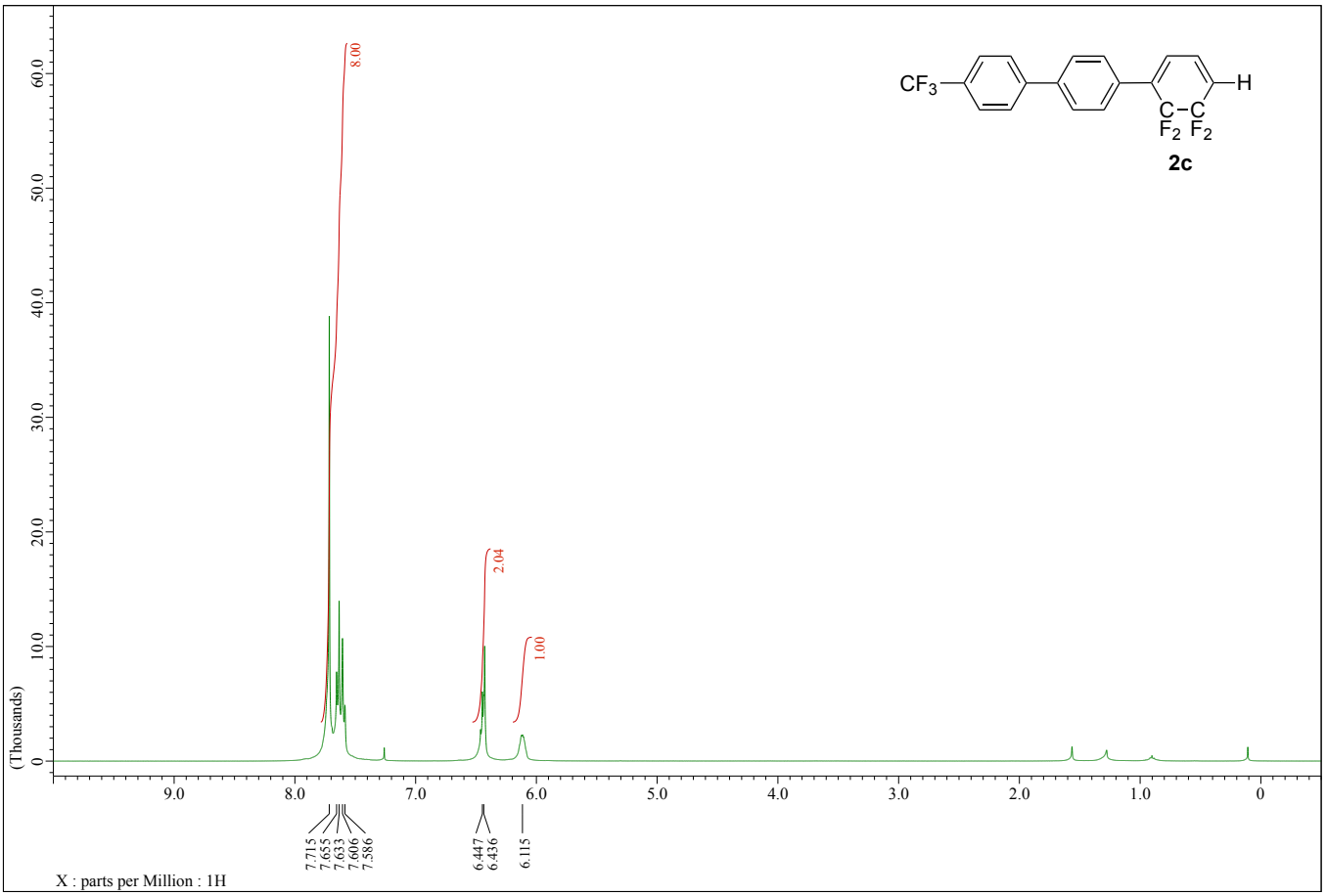


Figure S40. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 400 MHz).

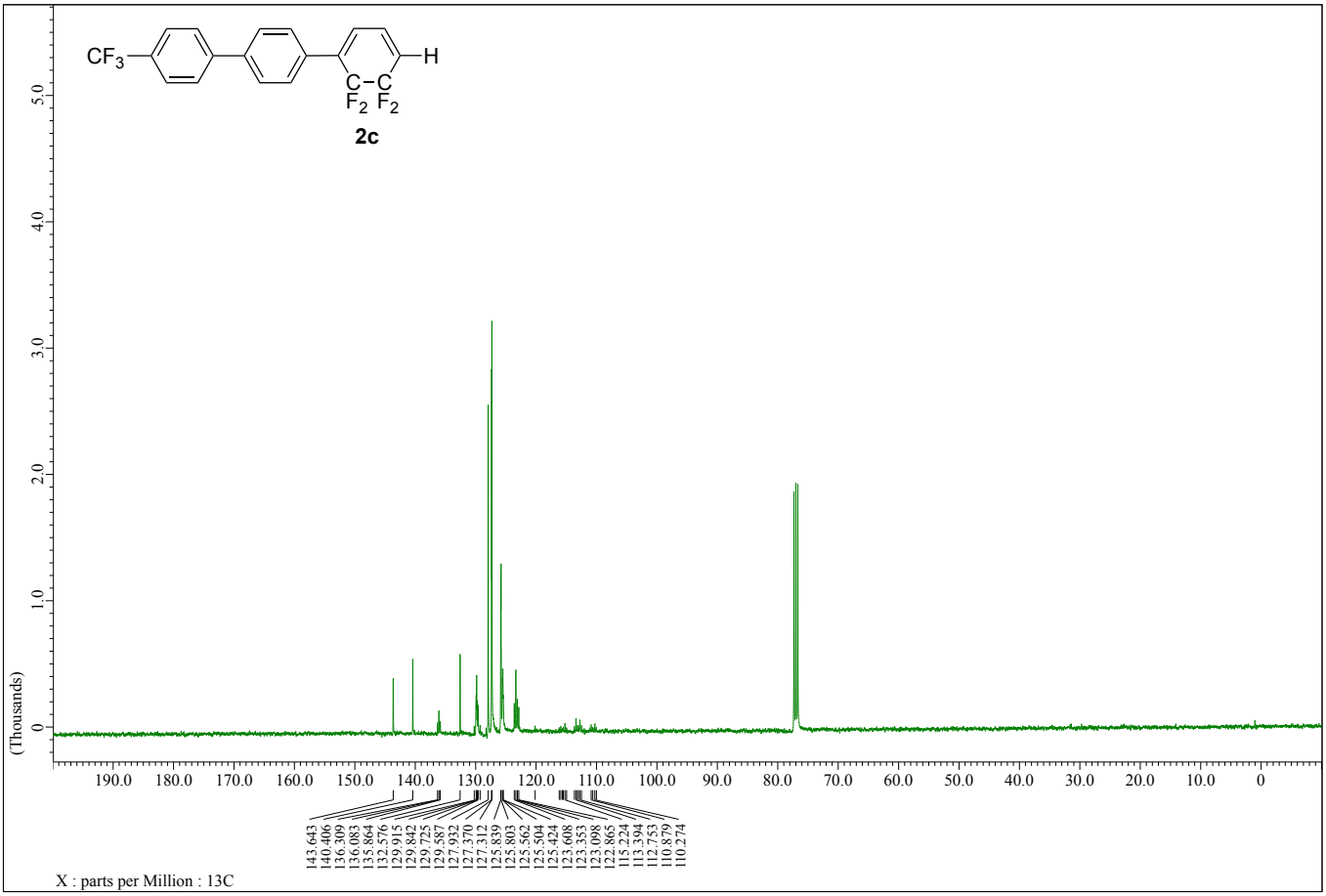


Figure S41. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 100 MHz).

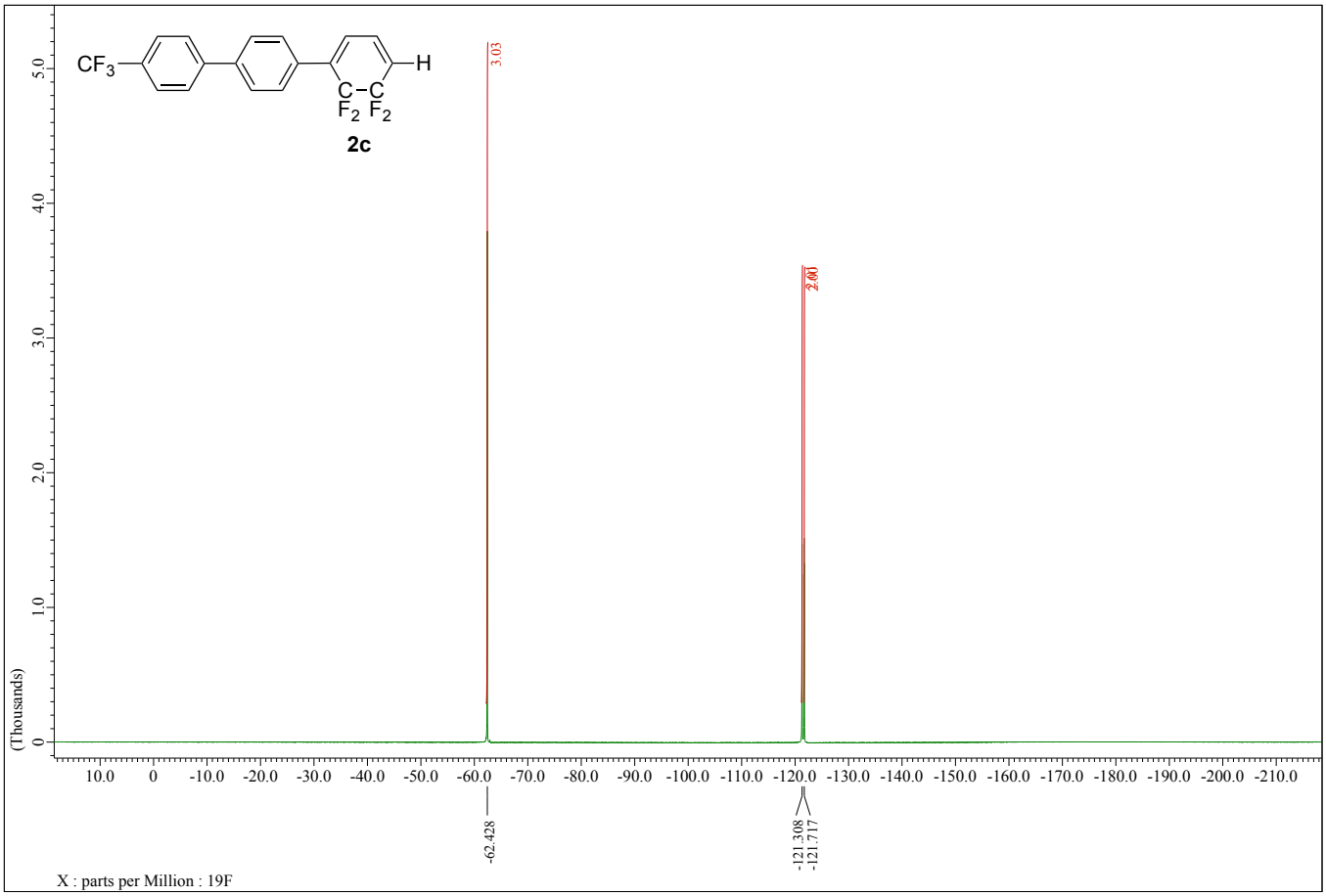


Figure S42. ^{19}F NMR spectrum of **2c** ($CDCl_3$, 376 MHz).

3. Single crystal 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 was 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 **2b**

	2b
CCDC #	2269760
Empirical Formula	$C_{19}H_{14}F_4O$
Formula weight	334.30
Temperature [K]	173
Crystal Color / Habit	Colourless / Plate
Crystal Size [mm]	0.305 × 0.275 × 0.153
Crystal System	Orthorhombic
Space Group	$P\ 2_1\ 2_1\ 2_1$
a [Å]	5.5586(7)
b [Å]	9.2038(15)
c [Å]	29.282(4)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	1498.1(4)
Z	4
R [$F^2 > 2s(F^2)$] [a]	0.0631
wR_2 (F^2) [b]	0.1269

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

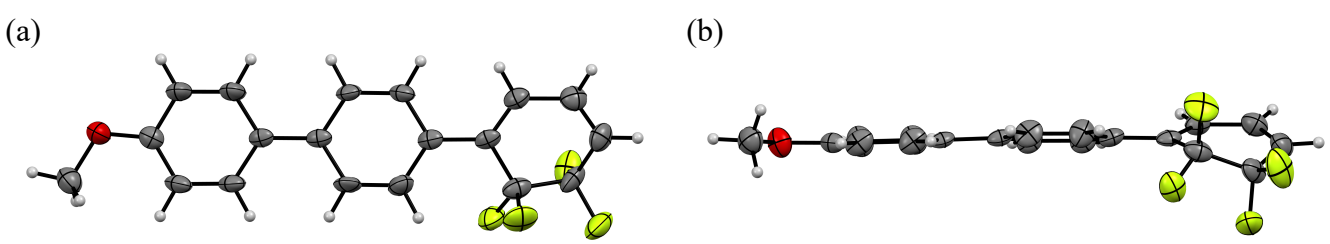


Figure S43. ORTEP type crystal structure of **2b** viewed from (a) top and (b) side.

4. Theoretical calculations

All computations were performed using Gaussian 16 program set with the density functional theory (DFT) at the M06-2X hybrid functional and 6-31+G(d) (for all atoms) basis set with a conductor-like polarizable continuum model (CPCM) for $CHCl_3$. Theoretical vertical transitions were also calculated using the time-dependent DFT (TD-DFT) method at the same theory level using the same solvation model.

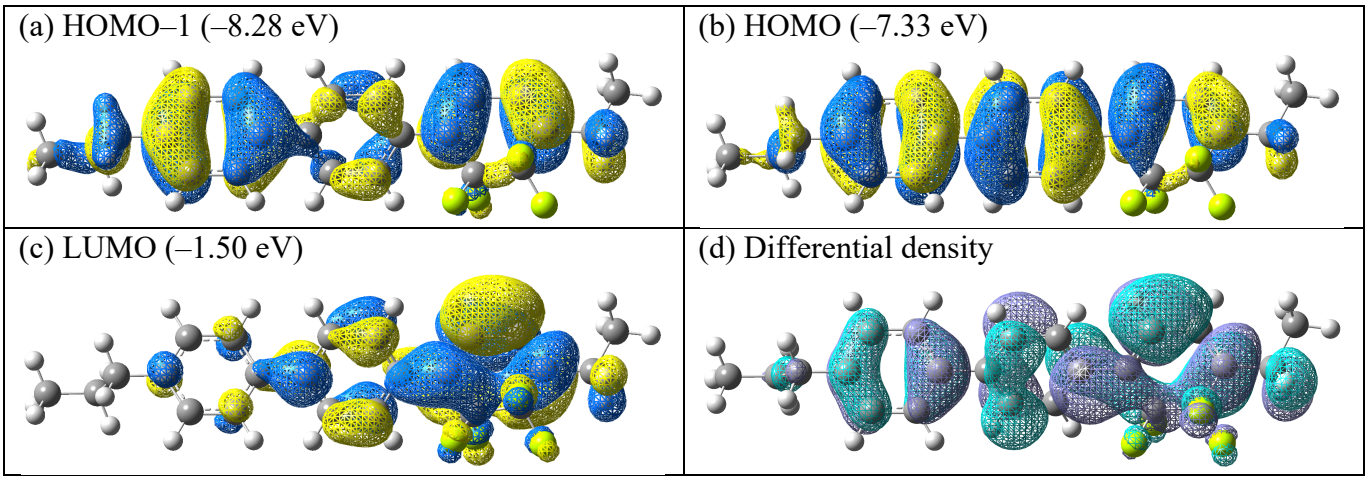


Figure S44. Orbital distributions for **2a** of (a) HOMO–1, (b) HOMO, (c) LUMO, and (d) differential density between HOMO and LUMO.

<Results for optimization>
SCF Done: E(RM062X) = -1288.59491896 A.U. after 9 cycles
Dipole moment (field-independent basis, Debye):
X= -0.7390 Y= 4.4663 Z= -0.9453 Tot= 4.6247

<Results for TD-SCF>
Excited State 1: Singlet-A 3.7466 eV 330.92 nm f=1.0035 <S**2>=0.000
97 -> 99 0.24354
98 -> 99 0.65329
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1288.45723314
Copying the excited state density for this state as the 1-particle RhoCI density.

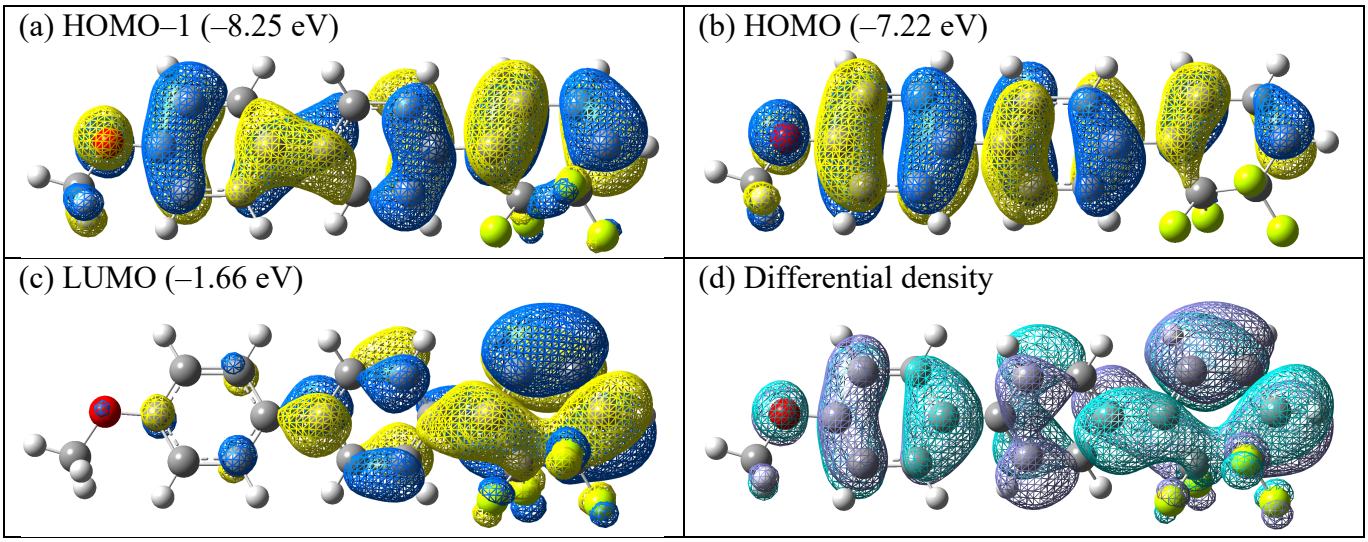


Figure S45. Orbital distributions for **2b** of (a) HOMO–1, (b) HOMO, (c) LUMO, and (d) differential density between HOMO and LUMO.

<Results for optimization>
SCF Done: E(RM062X) = -1206.59862518 A.U. after 9 cycles
Dipole moment (field-independent basis, Debye):
X= -2.2446 Y= 2.9557 Z= -0.6624 Tot= 3.7701

<Results for TD-SCF>
Excited State 1: Singlet-A 3.6729 eV 337.56 nm f=0.9058 <S**2>=0.000
85 -> 87 0.31347
86 -> 87 0.62094
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1206.46364755
Copying the excited state density for this state as the 1-particle RhoCI density.

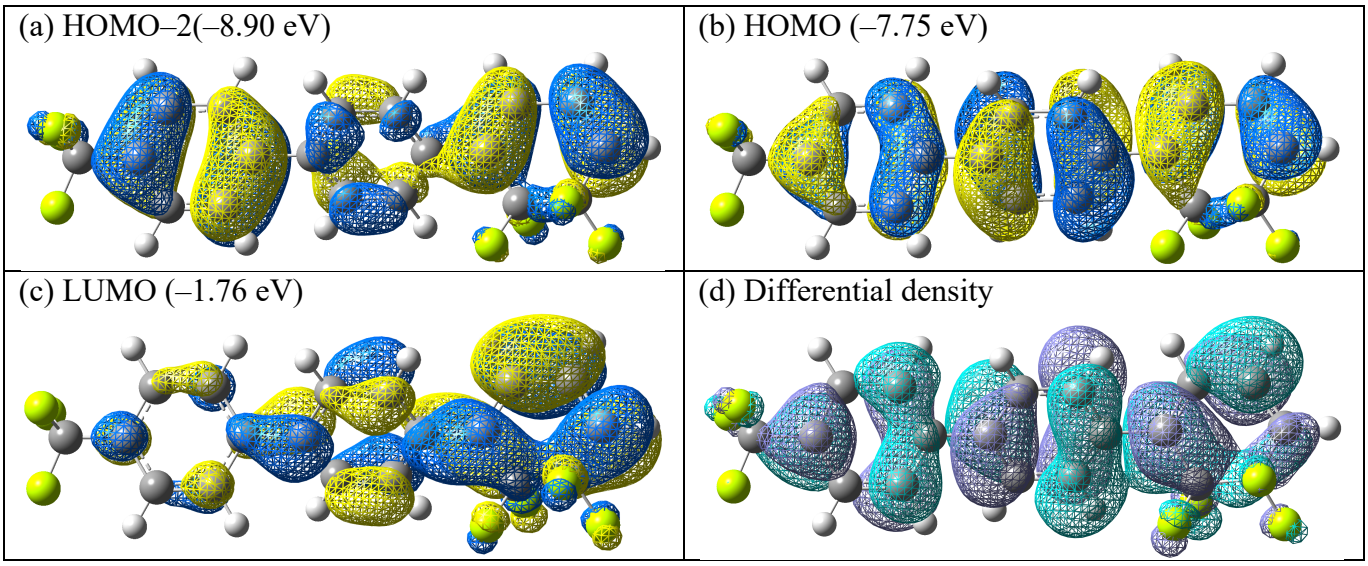


Figure S46. Orbital distributions for **2c** of (a) HOMO–1, (b) HOMO, (c) LUMO, and (d) differential density between HOMO and LUMO.

<Results for optimization>
SCF Done: E(RM062X) = -1429.07310820 A.U. after 9 cycles
Dipole moment (field-independent basis, Debye):
X= 2.5502 Y= 4.7785 Z= -1.0073 Tot= 5.5093

<Results for TD-SCF>
Excited State 1: Singlet-A 3.8175 eV 324.78 nm f=0.8715 <S**2>=0.000
92 -> 95 0.16765
94 -> 95 0.67582
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1428.93281657
Copying the excited state density for this state as the 1-particle RhoCI density.

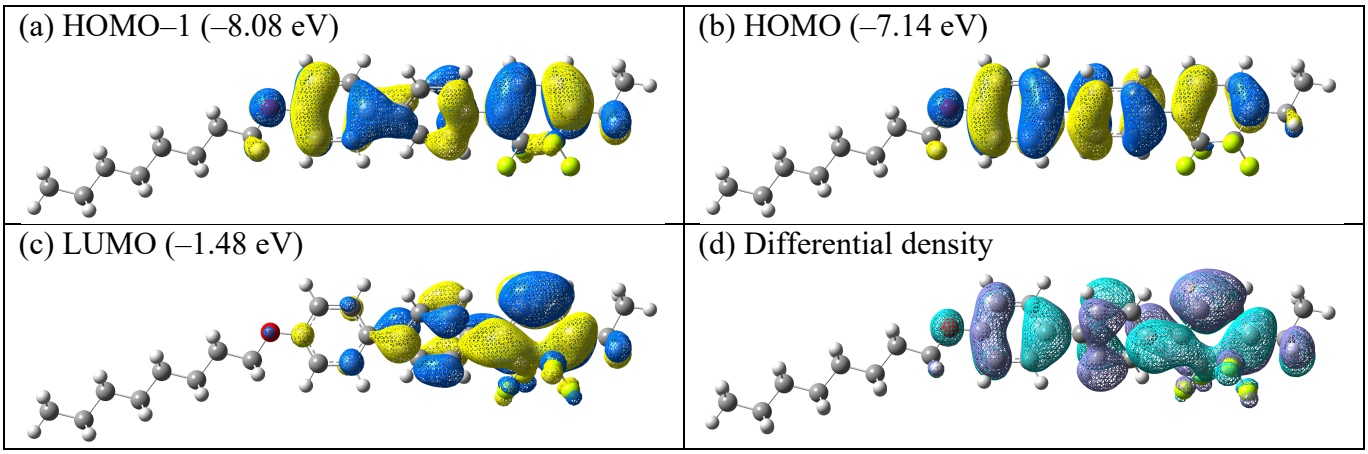


Figure S47. Orbital distributions for **2d** of (a) HOMO–1, (b) HOMO, (c) LUMO, and (d) differential density between HOMO and LUMO.

<Results for optimization>
SCF Done: E(RM062X) = -1560.25169787 A.U. after 8 cycles
Dipole moment (field-independent basis, Debye):
X= -0.8627 Y= 2.9669 Z= -0.4738 Tot= 3.1259

<Results for TD-SCF>
Excited State 1: Singlet-A 3.7026 eV 334.86 nm f=1.0401 <S**2>=0.000
121 ->123 -0.30957
122 ->123 0.62317
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1560.11563017
Copying the excited state density for this state as the 1-particle RhoCI density.

Table S2. Cartesian coordinates of **2a**.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-5.440033	1.331344	0.238184
2	6	0	-4.050677	1.367674	0.153628
3	6	0	-3.29405	0.193146	0.261131
4	6	0	-3.974887	-1.016202	0.456332
5	6	0	-5.36415	-1.046345	0.541669
6	6	0	-6.121125	0.125342	0.434305
7	1	0	-6.006759	2.255621	0.145341
8	1	0	-3.549568	2.317107	-0.017272
9	1	0	-3.411521	-1.938906	0.569688
10	1	0	-5.870257	-1.995636	0.705313
11	6	0	-1.813436	0.229986	0.174557
12	6	0	-1.102343	-0.792029	-0.468956
13	6	0	-1.083668	1.28446	0.741252
14	6	0	0.285338	-0.763292	-0.54806
15	1	0	-1.642499	-1.610832	-0.936157
16	6	0	0.303278	1.317808	0.663307
17	1	0	-1.604947	2.070704	1.280423
18	6	0	1.011325	0.300203	0.00827
19	1	0	0.802627	-1.562829	-1.069518
20	1	0	0.845925	2.126908	1.144349
21	6	0	2.480217	0.373096	-0.105776
22	6	0	3.174387	1.516052	-0.255268
23	6	0	4.635352	1.564601	-0.38968
24	1	0	2.639578	2.459804	-0.315798
25	6	0	5.421513	0.500706	-0.171628
26	1	0	5.074371	2.517716	-0.668207
27	6	0	6.920671	0.453699	-0.251032
28	1	0	7.303591	0.078162	0.70798
29	1	0	7.204134	-0.301905	-0.994858
30	6	0	7.57336	1.789305	-0.588077
31	1	0	7.337409	2.548843	0.164191
32	1	0	8.659699	1.675482	-0.623904
33	1	0	7.242432	2.158781	-1.564032
34	6	0	-7.62815	0.080846	0.472208
35	1	0	-7.958586	-0.723146	1.142127
36	1	0	-8.017012	1.021039	0.883307
37	6	0	-8.236459	-0.146541	-0.919175
38	1	0	-7.842918	-1.084646	-1.330911
39	1	0	-7.900966	0.654849	-1.58973
40	6	0	3.278002	-0.90645	-0.163103
41	6	0	4.735072	-0.749901	0.310831
42	9	0	2.712375	-1.896783	0.574128
43	9	0	4.716721	-0.752198	1.68017
44	9	0	5.413842	-1.868176	-0.05891
45	9	0	3.320874	-1.366321	-1.453373
46	6	0	-9.762026	-0.191909	-0.880055
47	1	0	-10.181702	-0.355165	-1.877437
48	1	0	-10.111749	-1.002045	-0.230343
49	1	0	-10.170649	0.747814	-0.491871

Table S3. Cartesian coordinates of **2b**.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-5.270113	1.315999	-0.140799
2	6	0	-3.886559	1.390381	-0.168061
3	6	0	-3.092506	0.239076	-0.031783
4	6	0	-3.74325	-0.986146	0.134215
5	6	0	-5.135429	-1.079363	0.166242
6	6	0	-5.904863	0.078338	0.027536
7	1	0	-5.882313	2.205055	-0.257402
8	1	0	-3.412975	2.35655	-0.321229
9	1	0	-3.15833	-1.892609	0.266405
10	1	0	-5.598565	-2.048915	0.307996
11	6	0	-1.612934	0.324757	-0.061176
12	6	0	-0.841936	-0.675888	-0.66907
13	6	0	-0.941672	1.406729	0.526651
14	6	0	0.545975	-0.602097	-0.690564
15	1	0	-1.334556	-1.514198	-1.153818
16	6	0	0.445065	1.48754	0.502544
17	1	0	-1.509509	2.177942	1.039844
18	6	0	1.21252	0.489421	-0.114449
19	1	0	1.109691	-1.387045	-1.185198
20	1	0	0.940137	2.318392	0.997641
21	6	0	2.681254	0.613139	-0.170581
22	6	0	3.335428	1.781218	-0.306876
23	6	0	4.800072	1.871758	-0.382082
24	1	0	2.77037	2.703655	-0.403012
25	6	0	5.590646	0.828006	-0.112096
26	1	0	5.232788	2.826363	-0.664211
27	6	0	3.520898	-0.646056	-0.178752
28	6	0	4.955911	-0.443983	0.348757
29	9	0	2.951878	-1.640768	0.547886
30	9	0	4.886311	-0.461781	1.715661
31	9	0	5.694625	-1.526609	-0.008667
32	9	0	3.621794	-1.11466	-1.461226
33	8	0	-7.26321	0.102715	0.042567
34	6	0	-7.944028	-1.130688	0.203905
35	1	0	-7.69157	-1.595393	1.163342
36	1	0	-9.006447	-0.891613	0.182307
37	1	0	-7.705616	-1.819847	-0.613729
38	1	0	6.674227	0.861445	-0.143736

Table S4. Cartesian coordinates of **2c**.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-4.611513	1.161191	-0.169042
2	6	0	-3.227119	1.266254	-0.199091
3	6	0	-2.418198	0.131977	-0.030615
4	6	0	-3.033135	-1.109838	0.168622
5	6	0	-4.420745	-1.22344	0.199985
6	6	0	-5.205163	-0.086268	0.030827
7	1	0	-5.229372	2.04374	-0.309167
8	1	0	-2.768567	2.234424	-0.377786
9	1	0	-2.423714	-1.995239	0.323879
10	1	0	-4.884732	-2.19042	0.362708
11	6	0	-0.939391	0.248479	-0.062957
12	6	0	-0.153722	-0.741282	-0.667441
13	6	0	-0.29377	1.347792	0.518572
14	6	0	1.232091	-0.637382	-0.694706
15	1	0	-0.630966	-1.592446	-1.144975
16	6	0	1.091321	1.454337	0.494131
17	1	0	-0.877263	2.110281	1.027146
18	6	0	1.875814	0.469385	-0.122149
19	1	0	1.811235	-1.412039	-1.187403
20	1	0	1.571158	2.295831	0.985828
21	6	0	3.342655	0.620475	-0.17908
22	6	0	3.97289	1.79972	-0.327466
23	6	0	5.43582	1.918147	-0.40437
24	1	0	3.389707	2.709962	-0.431827
25	6	0	6.245574	0.892834	-0.121568
26	1	0	5.84998	2.87762	-0.697338
27	6	0	4.205701	-0.622412	-0.173644
28	6	0	5.635447	-0.386375	0.353501
29	9	0	3.6537	-1.619395	0.562792
30	9	0	5.564171	-0.389104	1.720119
31	9	0	6.39552	-1.457902	0.009153
32	9	0	4.317529	-1.102552	-1.450674
33	1	0	7.328361	0.946795	-0.152806
34	6	0	-6.702801	-0.167211	0.06315
35	9	0	-7.225109	0.569234	1.066253
36	9	0	-7.256553	0.305493	-1.07274
37	9	0	-7.152187	-1.422087	0.225297

Table S5. Cartesian coordinates of **2d**.

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-2.454075	2.279396	-0.115227
2	6	0	-1.076261	2.129284	-0.121481
3	6	0	-0.481722	0.857394	-0.064422
4	6	0	-1.326196	-0.253965	0.00074
5	6	0	-2.71545	-0.121408	0.00939
6	6	0	-3.285318	1.153203	-0.048912
7	1	0	-2.911455	3.262621	-0.170163
8	1	0	-0.449532	3.014159	-0.195375
9	1	0	-0.899033	-1.25094	0.07049
10	1	0	-3.33202	-1.010512	0.07137
11	6	0	0.992626	0.702309	-0.070131
12	6	0	1.605451	-0.367461	-0.737489
13	6	0	1.81702	1.617199	0.600675
14	6	0	2.987134	-0.520609	-0.736246
15	1	0	0.995009	-1.079094	-1.286549
16	6	0	3.198788	1.47039	0.60062
17	1	0	1.370321	2.434815	1.159853
18	6	0	3.808899	0.404337	-0.075383
19	1	0	3.427824	-1.352302	-1.277519
20	1	0	3.810471	2.172864	1.16011
21	6	0	5.278849	0.285757	-0.101695
22	6	0	6.124694	1.331344	-0.146035
23	6	0	7.585173	1.190028	-0.191332
24	1	0	5.722327	2.339789	-0.18426
25	6	0	8.209287	0.021258	0.013833
26	1	0	8.162482	2.087644	-0.390916
27	6	0	9.691345	-0.222885	0.02059
28	1	0	9.957655	-0.69263	0.977518
29	1	0	9.922053	-0.972657	-0.747006
30	6	0	10.534208	1.027675	-0.200736
31	1	0	10.350568	1.774602	0.578273
32	1	0	11.596273	0.770927	-0.178775
33	1	0	10.319724	1.485171	-1.171892
34	6	0	5.904548	-1.085021	-0.182504
35	6	0	7.334831	-1.14715	0.385332
36	9	0	5.166495	-2.024002	0.463916
37	9	0	7.225738	-1.210652	1.74901
38	9	0	7.884759	-2.32785	-0.003791
39	9	0	5.972499	-1.485905	-1.491334
40	8	0	-4.621587	1.397558	-0.047028
41	6	0	-5.508419	0.285243	0.00957
42	1	0	-5.32226	-0.2866	0.929203
43	1	0	-5.325961	-0.373721	-0.850606
44	6	0	-6.928569	0.81599	-0.013628
45	1	0	-7.069371	1.492835	0.838327
46	1	0	-7.071152	1.408706	-0.92585
47	6	0	-7.956061	-0.313796	0.041152
48	1	0	-7.800164	-0.908582	0.952187
49	1	0	-7.798451	-0.994661	-0.807192
50	6	0	-9.395756	0.197324	0.014458
51	1	0	-9.555268	0.877261	0.863406
52	1	0	-9.551663	0.79415	-0.895468
53	6	0	-10.42943	-0.926413	0.065269
54	1	0	-10.267391	-1.606837	-0.783218
55	1	0	-10.272565	-1.52311	0.975487
56	6	0	-11.870279	-0.419538	0.036841
57	1	0	-12.033514	0.260613	0.885511
58	1	0	-12.027615	0.177911	-0.87299
59	6	0	-12.905226	-1.542655	0.086235
60	1	0	-12.740927	-2.221418	-0.761376
61	1	0	-12.747634	-2.138186	0.995442
62	6	0	-14.340663	-1.020953	0.056108
63	1	0	-15.06759	-1.838475	0.092651
64	1	0	-14.533404	-0.361114	0.909684
65	1	0	-14.527025	-0.445666	-0.8579

Photophysical properties

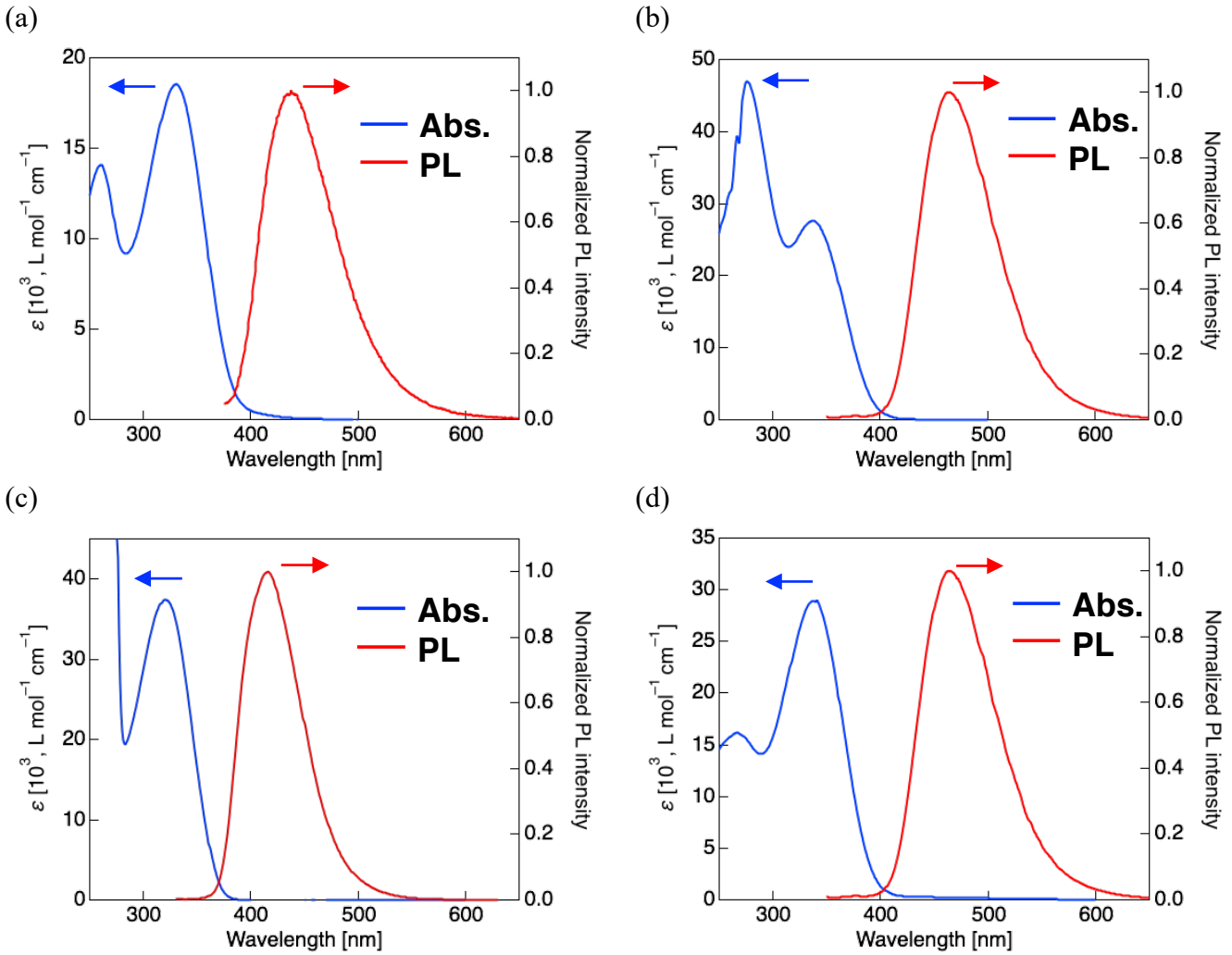
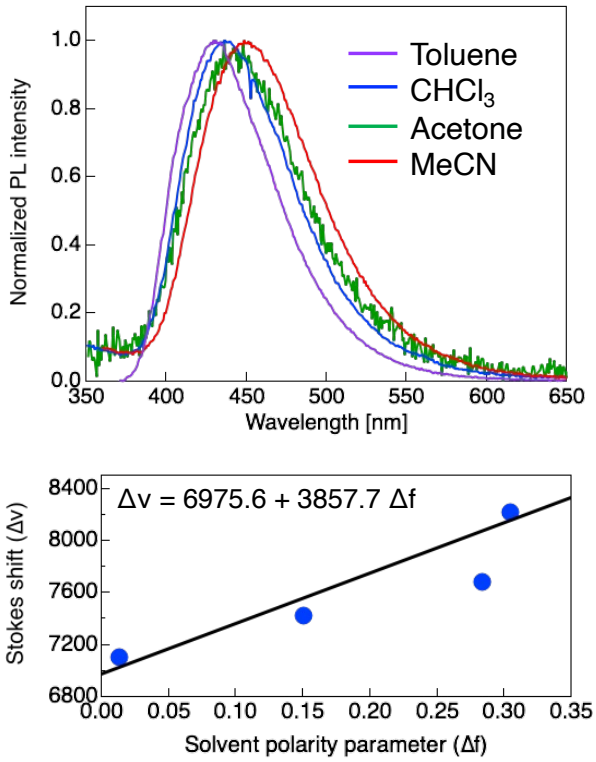
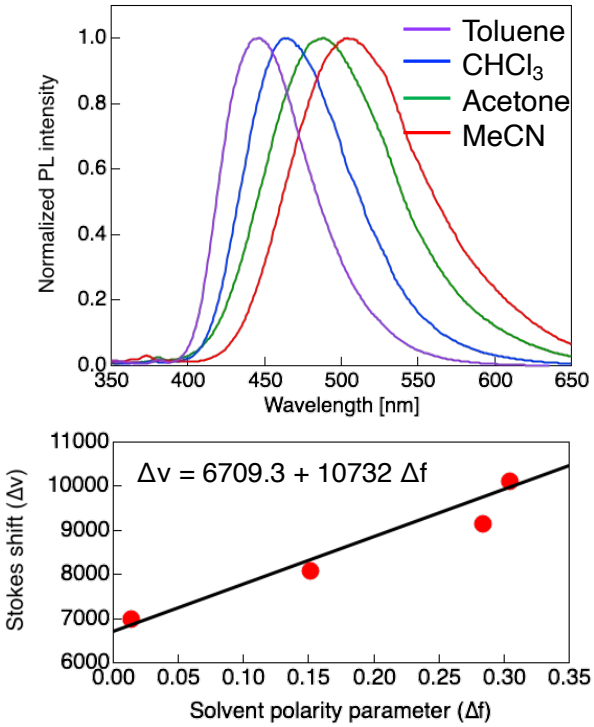


Figure S48. UV-vis absorption and PL spectra of (a) **2a**, (b) **2b**, (c) **2c**, and (d) **2d** in $CHCl_3$ solution. Concentration: 1.0×10^{-5} mol L^{-1} for Abs. and 1.0×10^{-6} mol L^{-1} for PL measurement.

(a)



(b)



(c)

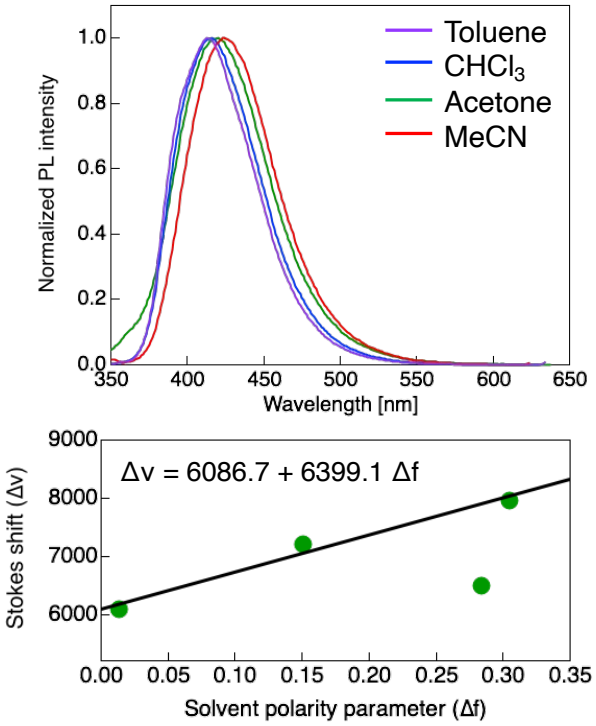


Figure S49. PL spectra of (a) **2a**, (b) **2b**, and (c) **2c** in a different solvent. Lippert-Mataga plot obtained from Stokes shift and solvent polarity parameter (Δ*f*).

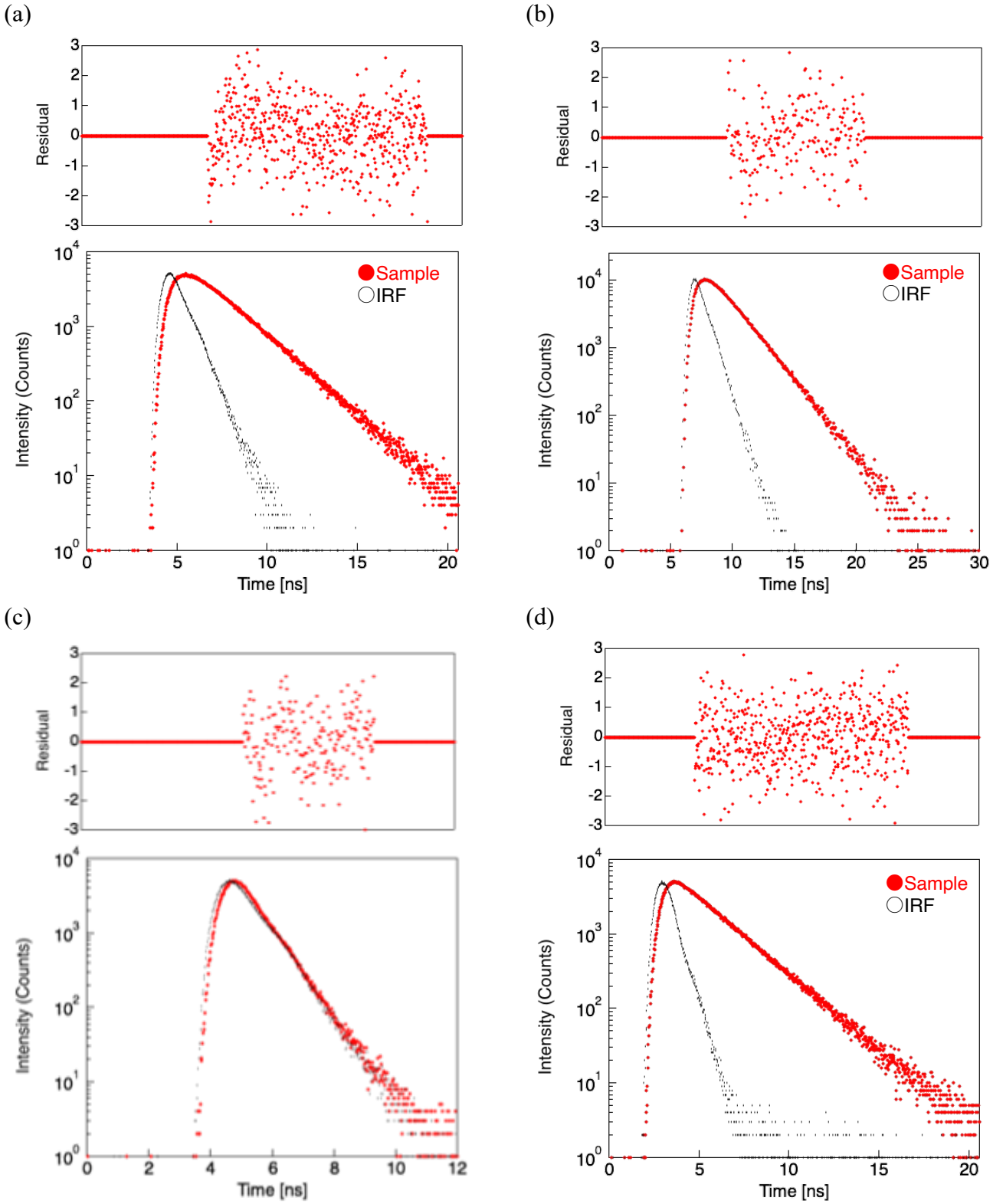


Figure S50. PL decay profiles of (a) **2a** (λ_{ex} = 340 nm, λ_{PL} = 450 nm), (b) **2b** (λ_{ex} = 340 nm, λ_{PL} = 470 nm), (c) **2c** (λ_{ex} = 340 nm, λ_{PL} = 416 nm), and (d) **2d** (λ_{ex} = 365 nm, λ_{PL} = 460 nm) in $CHCl_3$ solution.

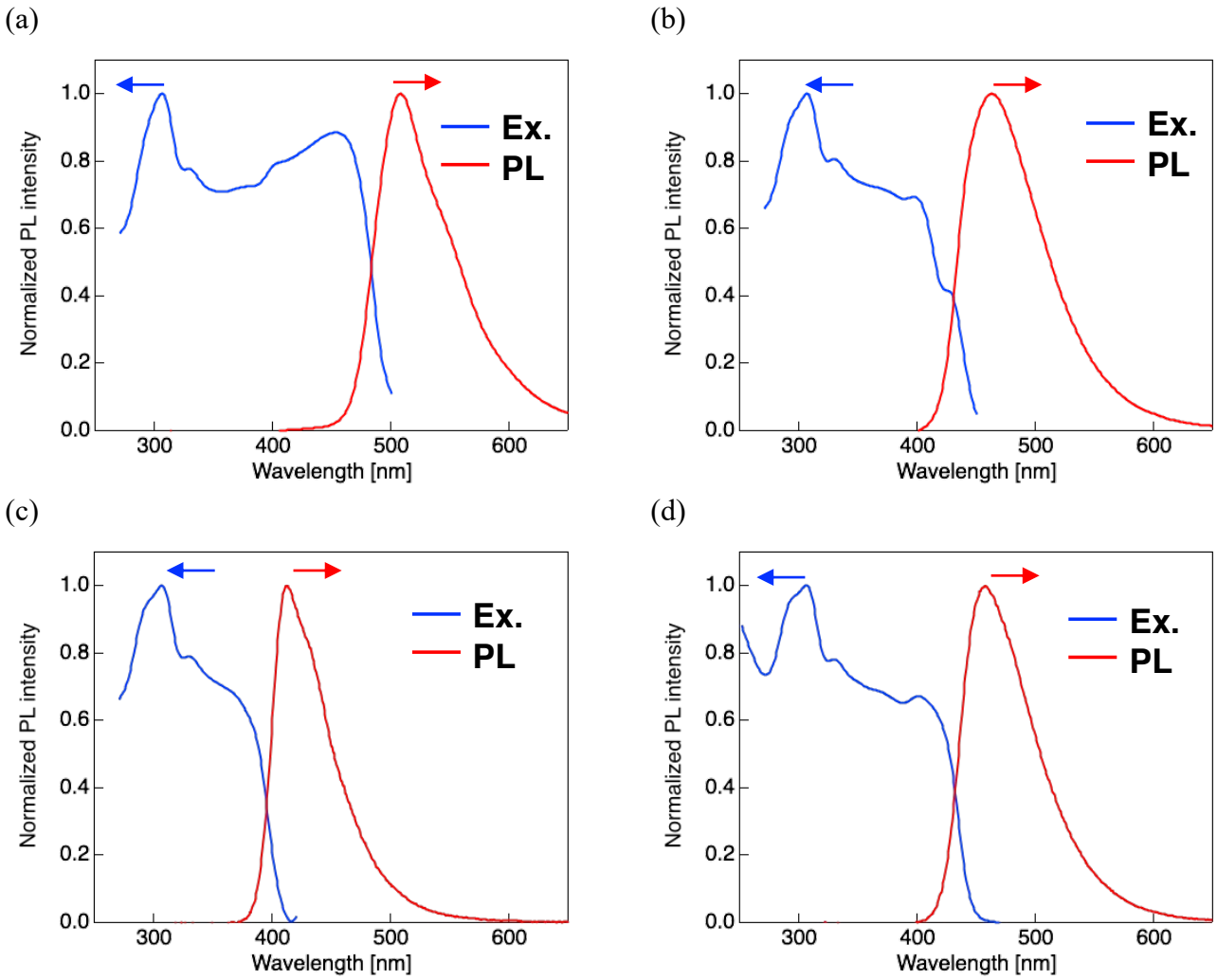


Figure S51. Excitation and PL spectra of (a) **2a**, (b) **2b**, (c) **2c**, and (d) **2d** in crystalline states. Detected lPL for excitation spectra was 307 nm for **2a**–**c**, and 306 nm for **2d**.

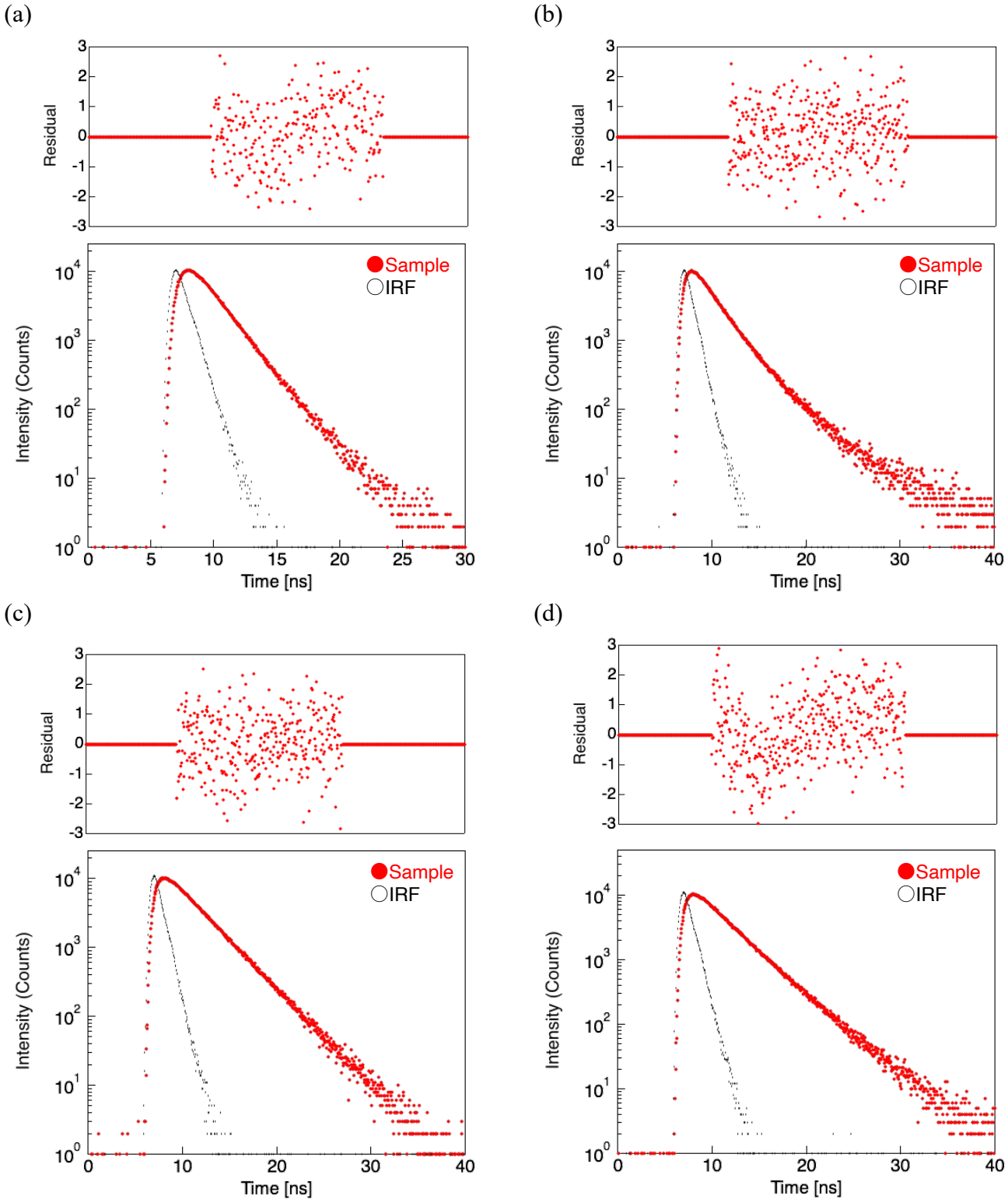


Figure S52. PL decay profiles of (a) **2a** (λ_{ex} = 340 nm, λ_{PL} = 500 nm), (b) **2b** (λ_{ex} = 340 nm, λ_{PL} = 445 nm), (c) **2c** (λ_{ex} = 340 nm, λ_{PL} = 415 nm), and (d) **2d** (λ_{ex} = 340 nm, λ_{PL} = 450 nm) in crystalline states.

Phase transition properties

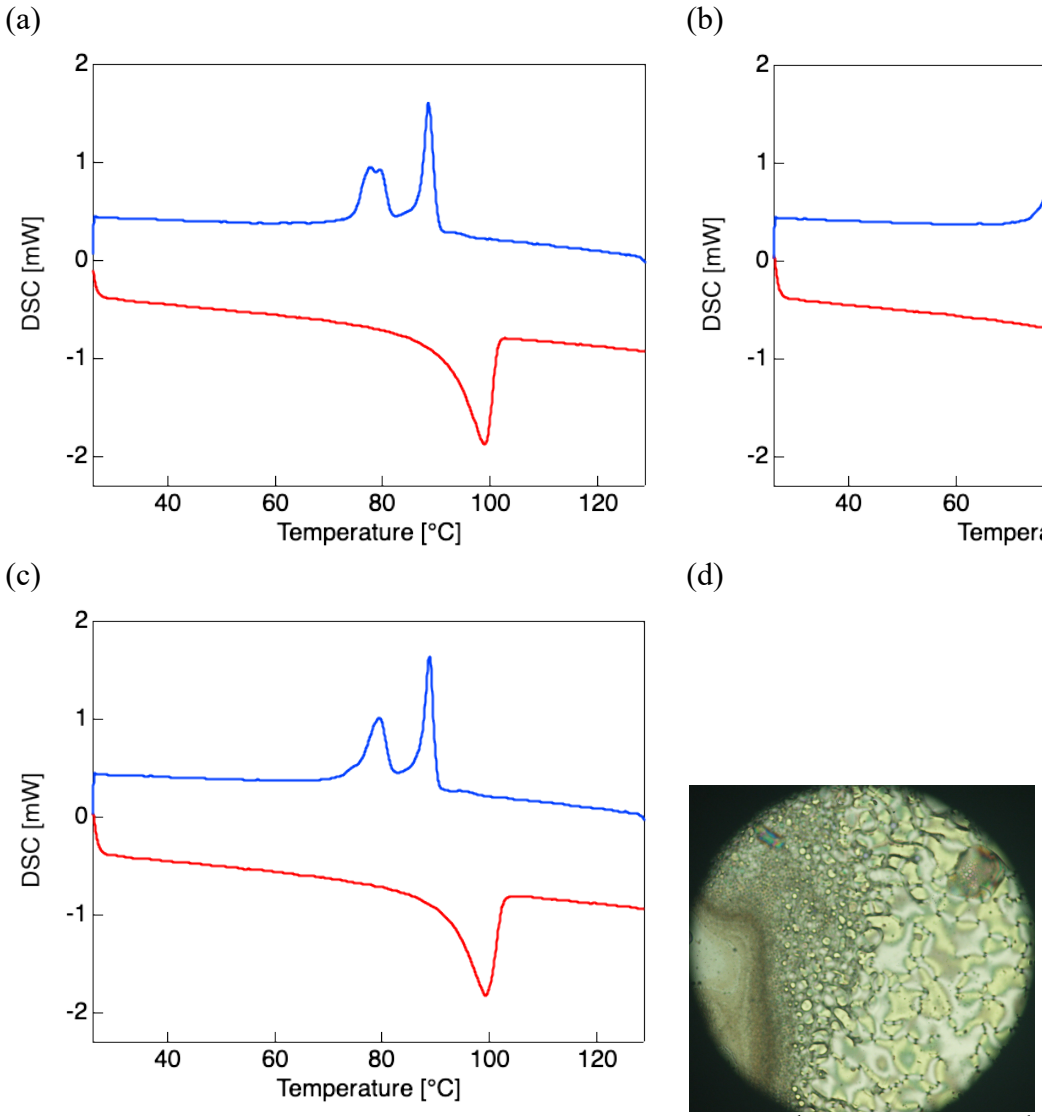


Figure S53. DSC thermograms for **2a** in (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle. (d) Optical texture image observed by POM at 93 °C (N phase).

Table S6. Phase transition behavior of **2a** observed by DSC measurement.

Molecule	Phase sequence		Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
2a	1st Heating	Cry-Iso	92	17.1	46.8
	1st Cooling	Iso-N	90	−6.2	−17.1
		N-Cry	81	−4.9	−13.9
	2nd Heating	Cry-Iso	91	17.2	47.3
	2nd Cooling	Iso-N	90	−6.4	−17.6
		N-Iso	81	−5.1	−14.5
	3rd Heating	Cry-Iso	92	17.2	47.2
	3rd Cooling	Iso-N	90	−6.0	−16.5
		N-Cry	81	−4.82	−13.6

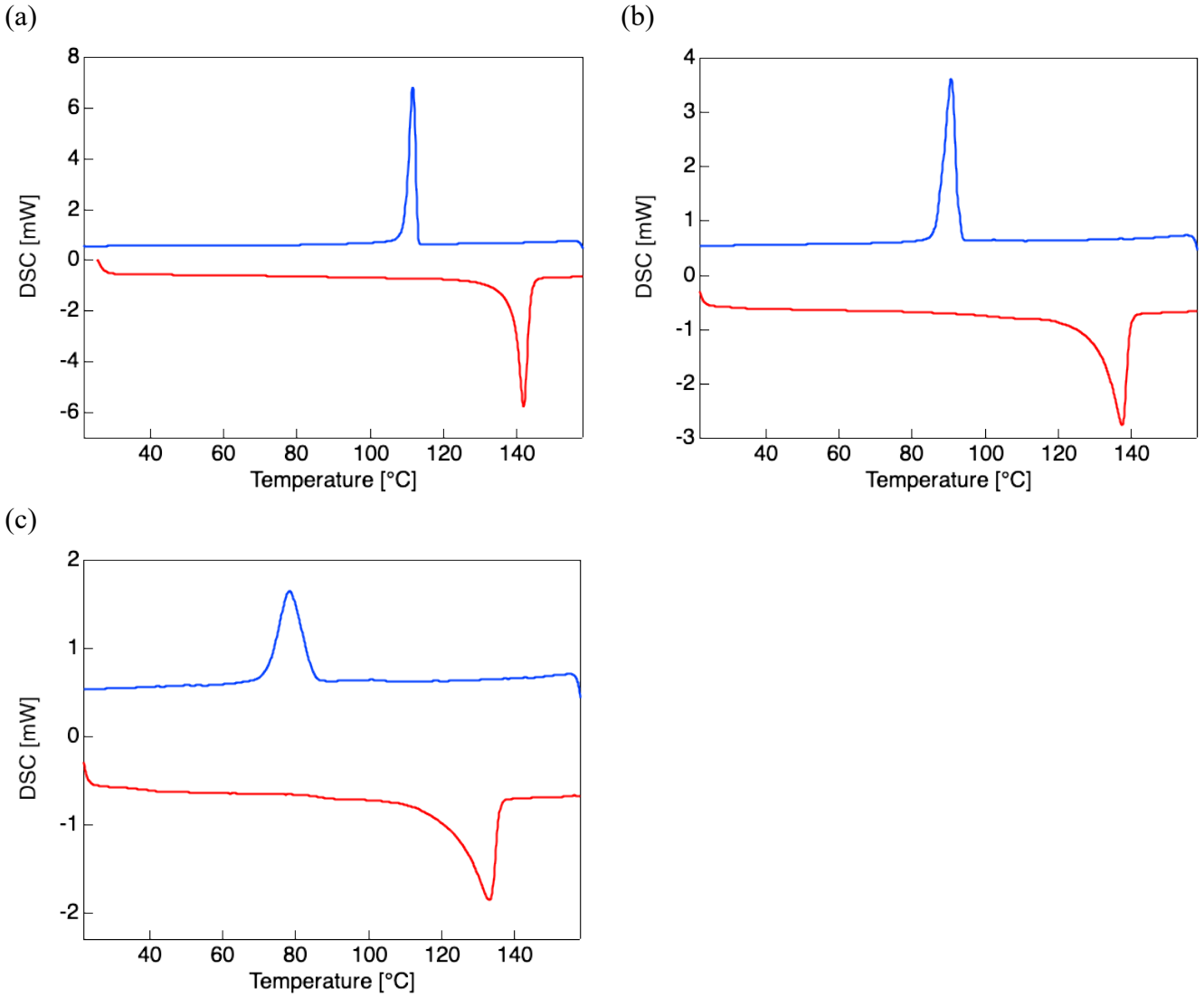


Figure S54. DSC thermograms for **2b** in (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle.

Table S7. Phase transition behavior of **2b** observed by DSC measurement.

Molecule	Phase sequence		Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
2b	1st Heating	Cry-Iso	139	23.6	57.3
	1st Cooling	Iso-Cry	113	−15.5	−40.1
	2nd Heating	Cry-Iso	130	16.4	40.6
	2nd Cooling	Iso-Cry	93	−12.1	−33.0
	3rd Heating	Cry-Iso	122	13.3	33.7
	3rd Cooling	Iso-Cry	85	−8.6	−23.9

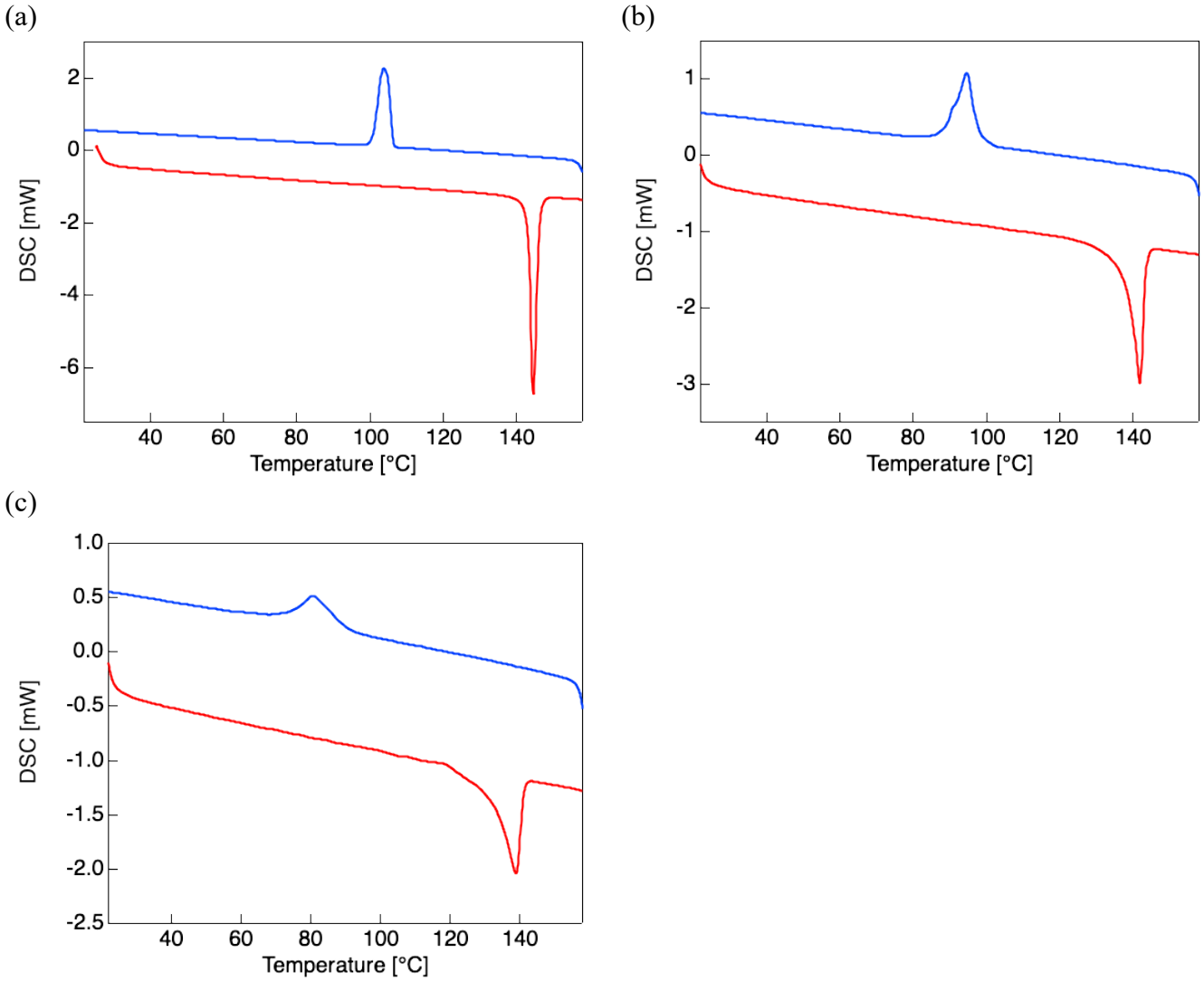


Figure S55. DSC thermograms for **2c** in (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle.

Table S8. Phase transition behavior of **2c** observed by DSC measurement.

Molecule	Phase sequence		Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
2c	1st Heating	Cry-Iso	143	16.3	39.2
	1st Cooling	Iso-Cry	106	−11.4	−30.2
	2nd Heating	Cry-Iso	138	11.8	28.6
	2nd Cooling	Iso-Cry	98	−8.16	−22.0
	3rd Heating	Cry-Iso	132	9.70	23.9
	3rd Cooling	Iso-Cry	90	−4.22	−11.6

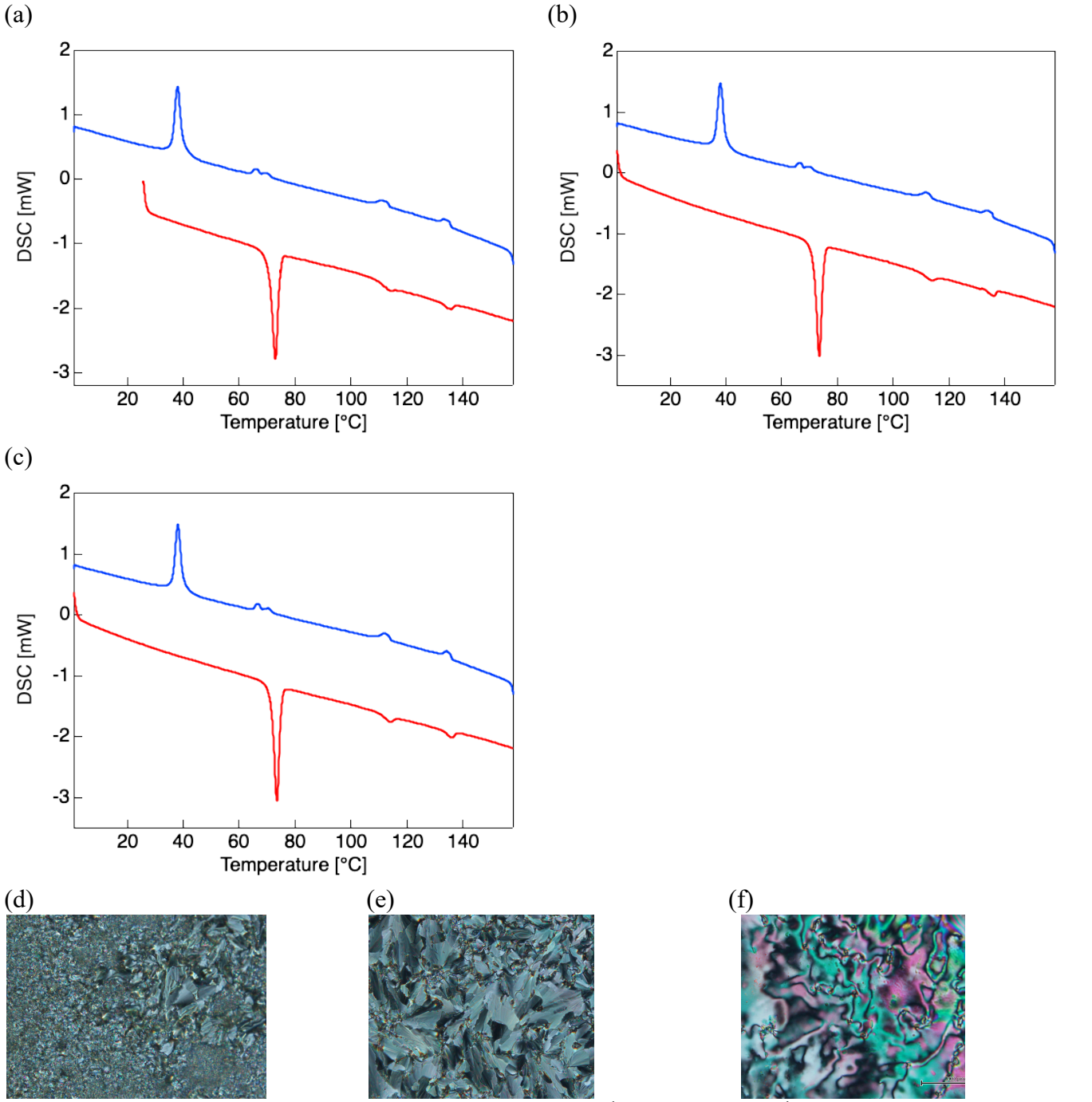


Figure S56. DSC thermograms for **2d** in (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle. Optical texture images observed by POM at (d) 73 °C (SmC phase), (e) 110 °C (SmA phase), and (f) 133 °C (N phase).

Table S9. Phase transition behavior of **2d** observed by DSC measurement.

Molecule	Phase sequence		Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
2d	1st Heating	Cry-SmA	71	12.3	35.8
		SmA-N	111	0.93	2.43
		N-Iso	133	0.58	1.24
	1st Cooling	Iso-N	136	–0.78	−1.91
		N-SmA	114	−1.06	−2.74
		SmA-SmC	68	−1.14	−3.35
		SmC-Cry	40	−8.23	−26.30
	2nd Heating	Cry-SmA	71	12.6	36.5
		SmA-N	110	0.88	2.28
		N-Iso	133	0.72	1.77
	2nd Cooling	Iso-N	136	−0.85	−2.08
		N-SmA	114	−1.02	−2.63
		SmA-SmC	68	−1.12	−3.28
		SmC-Cry	40	−8.09	−25.84
	3rd Heating	Cry-SmA	71	12.49	36.26
		SmA-N	110	0.94	2.45
		N-Iso	134	0.70	1.72
	3rd Cooling	Iso-N	136	−0.76	−1.84
		N-SmA	114	−0.98	−2.53
		SmA-SmC	68	−1.13	−3.32
		SmC-Cry	40	−7.69	−24.57

VT-PXRD measurements of 2a and 2d

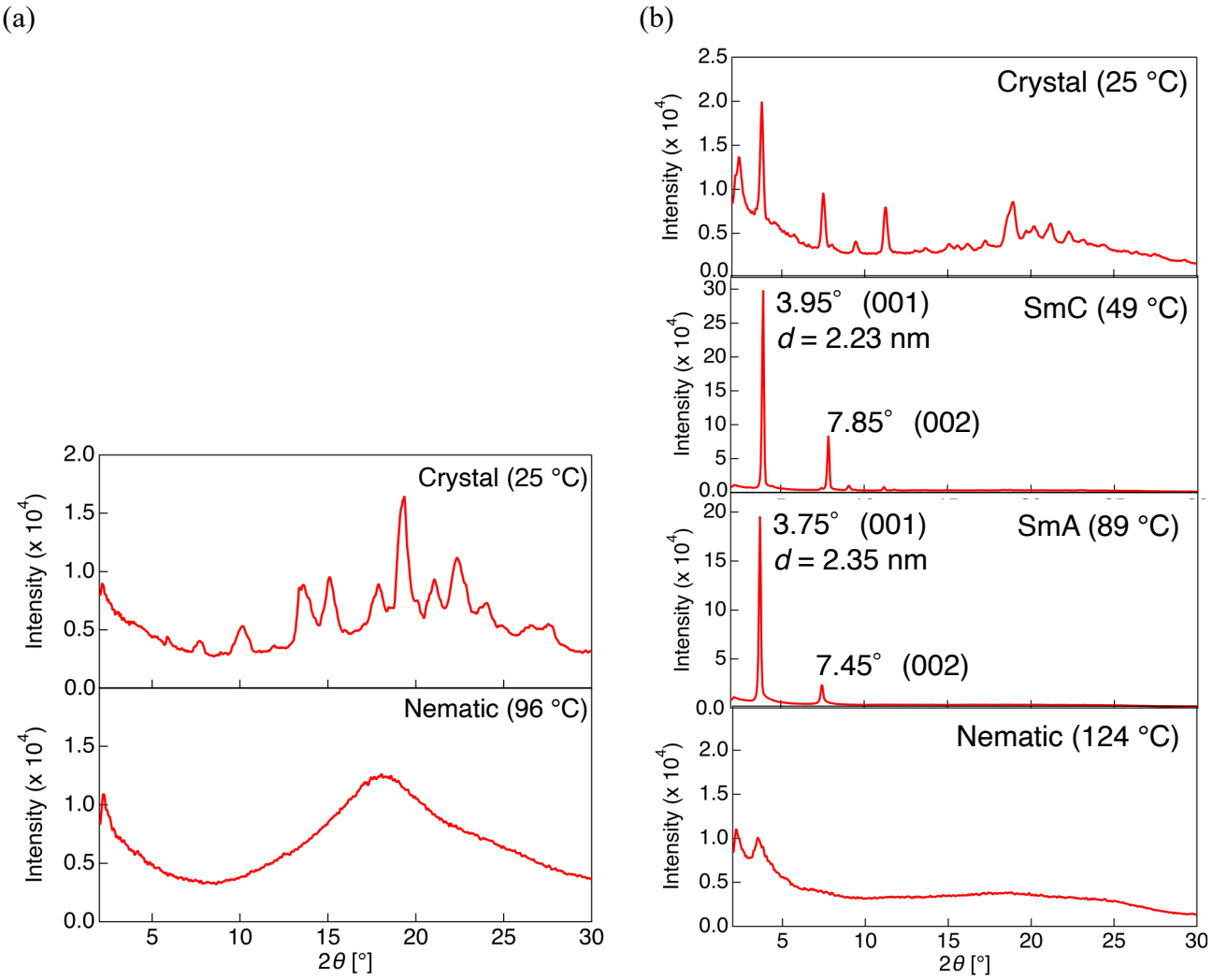


Figure S57. (a) Diffraction patterns of **2a** measured in crystalline and N phases. (b) Diffraction patterns of **2d** measured in crystalline, SmC, SmA, and N phases.