

Electronic Supplementary Materials

Fluorinated tolane-based fluorophores bearing a branched flexible unit with aggregation-induced emission enhancement characteristics

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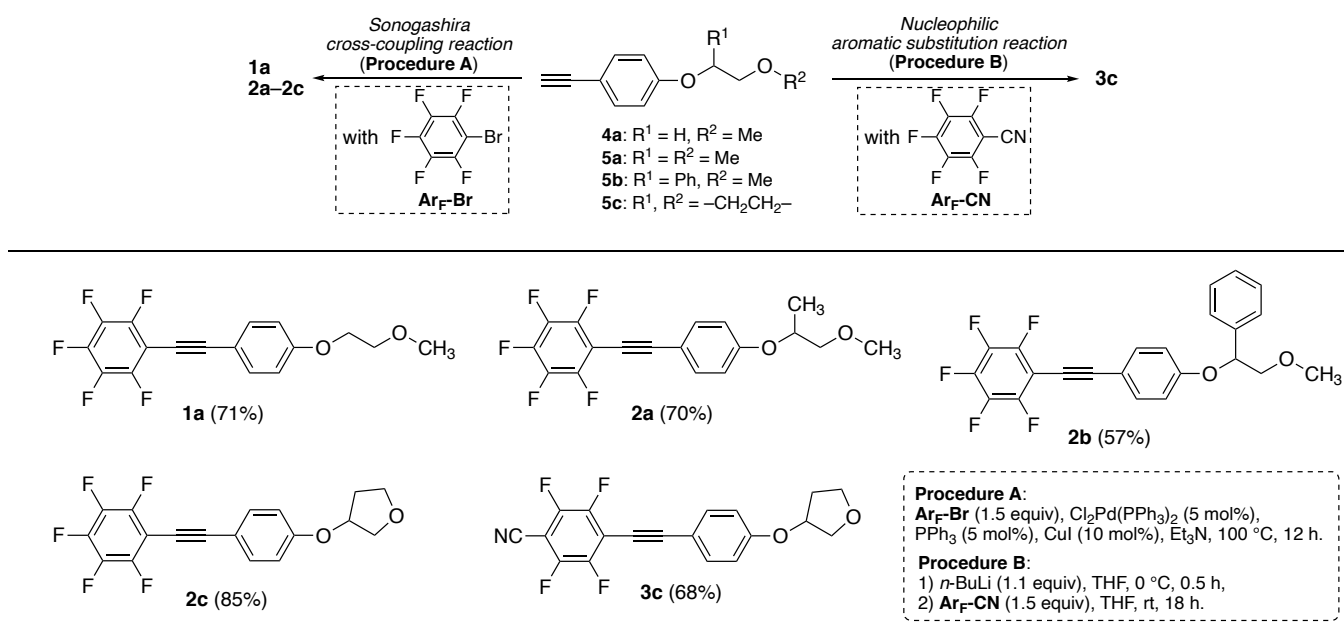
1. Experimental

1.1. Genral

The progress of the reactions was monitored via thin-layer chromatography (TLC), which was performed on silica gel TLC plates (Merck, Silica gel, 60F₂₅₄; New Jersey, NJ, USA). Column chromatography was performed using silica gel (Fujifilm Wako Pure Chemical Corporation, Wako-gel® 60N, 38–100 µm; Osaka, Japan). ¹H nuclear magnetic resonance (NMR) (400 MHz), ¹³C NMR (100 MHz), and ¹⁹F NMR (376 MHz) spectra were acquired using an AVANCE III 400 NMR spectrometer (Bruker, Rheinstetten, Germany) in chloroform-*d* (CDCl₃) solution. The chemical shifts in ¹H and ¹³C NMR spectra were reported in parts per million (ppm) based on the residual proton or carbon in the NMR solvent. The chemical shift in ¹⁹F NMR spectra were also reported in ppm based on the internal standard, CFCl₃ (δ_F = 0 ppm). Infrared (IR) spectra were recorded using the KBr method using an FTIR-4100 type A spectrometer (JASCO, Tokyo, Japan). IR spectra are reported in wavenumber (cm⁻¹) units. High-resolution mass spectra (HRMS) were recorded on a JMS700MS spectrometer (JEOL, Tokyo, Japan) using the fast atom bombardment (FAB) method.

1.2. Synthesis

Fluorinated tolane-based fluorophores **1a**, **2a–c**, and **3c** were readily synthesized from the corresponding phenylacetylenes **4a** and **5a–c** bearing a suitable flexible unit at the *para*-position. According to the reported literature, the precursors **4a** and **5a–c** were prepared from easily available 2-bromoethanol for **4a** and methyl lactate for **5a**, ethyl mandelate for **5b**, and 3-hydroxytetrahydrofuran for **5c**. The detailed experimental procedures and structural characterization for the synthesis of **1a**, **2a–c**, and **3c** were described below.



Scheme S1. Synthetic procedure of fluorinated tolane-based fluorophores **1a**, **2a–c**, and **3c**.

1.2.1. Typical synthetic procedure for 2,3,4,5,6-pentafluoro-1-[2-[4-(methoxyethoxy)phenyl]ethyn-1-yl]benzene (**1a**) via Pd(0)-catalyzed Sonogashira cross-coupling reaction

In a two-necked round-bottomed flask, equipped with a Teflon®-coated stirrer bar and reflux condenser, was placed 4-methoxyethoxyphenyl acetylene (1.55 g, 5.3 mmol), Cl₂Pd(PPh₃)₂ (0.19 g, 0.3 mmol), PPh₃ (0.07 g, 0.3 mmol), bromopentafluorobenzene (1.6 g, 0.8 mL, 7.6 mmol), and Et₃N (15 mL). To the resultant solution was added CuI (0.10 g, 0.5 mmol) and Et₃N (5 mL), and the whole was stirred at 100 °C overnight. After being stirred at the temperature for 18 h, precipitate formed in the reaction mixture was separated by atmospheric filtration and the filtrate was

poured into saturated aqueous NH_4Cl solution (30 mL). Crude product was extracted with EtOAc (30 mL, three times) and organic layer combined was washed with brine (once). The collected organic layer was dried over anhydrous Na_2SO_4 , which was separated by filtration. The filtrate was evaporated in vacuo and subjected to silica-gel column chromatography (eluent: hexane/EtOAc = 15/1), followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (v/v = 1/1), to obtain the title compound in 71% (0.70 g, 1.5 mmol) as a white crystal.

2,3,4,5,6-Pentafluoro-1-[2-{4-(methoxyethoxy)phenyl}ethyn-1-yl]benzene (1a)

Yield: 71%; M.p.: 86.1–87.3 °C; ^1H NMR (CDCl_3): δ 3.45 (s, 3H), 3.76 (t, J = 4.8 Hz, 2H), 4.14 (t, J = 4.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H); ^{13}C NMR (CDCl_3): δ 59.2, 67.4, 70.8, 71.9 (q, J = 3.6 Hz), 100.6 (td, J = 19.0, 3.6 Hz), 101.8 (q, J = 3.0 Hz), 113.8, 114.7, 133.4, 136.0–139.2 (dm, J = 240.5 Hz), 139.5–142.6 (dm, J = 256.7 Hz), 145.5–148.4 (dm, J = 252.2 Hz), 159.9; ^{19}F NMR (CDCl_3): δ –137.06 (dd, J = 21.8, 6.8 Hz, 2F), –154.19 (t, J = 21.8 Hz, 1F), –162.68 (ddd, J = 21.8, 21.8, 6.8 Hz, 2F); IR (KBr): ν 3002, 2878, 2809, 2223, 1604, 1444, 1415, 1289, 1247, 1122, 1058, 987 cm^{-1} ; HRMS: (FAB+) m/z $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{F}_5\text{O}_2$: 342.0679; found: 342.0690.

2,3,4,5,6-Pentafluoro-1-[2-{4-(1-methoxy-2-propoxy)phenyl}ethyn-1-yl]benzene (2a)

Yield: 70%; M.p.: 45.5–46.2 °C; ^1H NMR (CDCl_3): δ 1.33 (d, J = 6.4 Hz, 3H), 3.41 (s, 3H), 3.45–3.53 (m, 1H), 3.56–3.62 (m, 1H), 4.54–4.64 (m, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H); ^{13}C NMR (CDCl_3): δ 16.6, 59.3, 71.8, 73.1, 75.7, 100.6 (td, J = 18.3, 3.6 Hz), 101.9 (q, J = 2.9 Hz), 113.5, 115.9, 133.4, 136.1–139.2 (dm, J = 247.9 Hz), 139.5–142.6 (dm, J = 255.9 Hz), 145.4–148.5 (dm, J = 248.0 Hz), 159.1; ^{19}F NMR (CDCl_3): δ –136.9 to –137.2 (m, 2F), –154.0 to –154.4 (m, 1F), –162.5 to –162.8 (m, 2F); IR (KBr): ν 3089, 2982, 2933, 2223, 1602, 1523, 1500, 1446, 1247, 1116, 989, 837 cm^{-1} ; HRMS: (FAB+) m/z $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{13}\text{F}_5\text{O}_2$: 356.0836; found: 356.0839.

2,3,4,5,6-Pentafluoro-1-[2-{4-(2-methoxy-1-phenylethoxy)phenyl}ethyn-1-yl]benzene (2b)

Yield: 57%; M.p.: 92.6–93.4 °C; ^1H NMR (CDCl_3): δ 3.48 (s, 3H), 3.68 (dd, J = 10.8, 3.2 Hz, 1H), 3.86 (dd, J = 10.8, 7.6 Hz, 1H), 5.42 (dd, J = 7.6, 3.6 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 7.28–7.46 (m, 7H); ^{13}C NMR (CDCl_3): δ 59.3, 71.8 (q, J = 3.7 Hz), 76.9, 79.6, 100.6 (td, J = 18.3, 3.6 Hz), 101.8 (q, J = 2.9 Hz), 113.7, 116.1, 126.2, 128.1, 128.6, 133.2, 136.0–139.1 (dm, J = 248.6 Hz), 137.8, 139.4–142.6 (dm, J = 256.7 Hz), 145.4–148.4 (dm, J = 248.0 Hz), 159.0; ^{19}F NMR (CDCl_3): δ –137.05 (dd, J = 21.8, 6.8 Hz, 2F), –154.22 (t, J = 21.8 Hz, 1F), –162.66 (td, J = 21.8, 21.8, 6.8 Hz, 2F); IR (KBr): ν 3000, 2904, 2829, 2220, 1600, 1497, 1447, 1285, 1243, 1174, 1019, 964, 834 cm^{-1} ; HRMS: (FAB+) m/z $[\text{M}]^+$ calcd for $\text{C}_{23}\text{H}_{15}\text{F}_5\text{O}_2$: 418.0992; found: 418.0983.

2,3,4,5,6-Pentafluoro-1-[2-{4-[(tetrahydrofuran-3-yl)oxy]phenyl}ethyn-1-yl]benzene (2c)

Yield: 85%; M.p.: 106.1–107.9 °C; ^1H NMR (CDCl_3): δ 2.10–2.19 (m, 1H), 2.19–2.30 (m, 1H), 3.88–3.95 (m, 1H), 3.95–4.04 (m, 3H), 4.92–4.98 (m, 1H), 6.85 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H); ^{13}C NMR (CDCl_3): δ 32.9, 67.1, 72.1 (q, J = 3.6 Hz), 72.9, 77.5, 100.5 (td, J = 17.6, 3.6 Hz), 101.6 (q, J = 2.9 Hz), 113.8, 115.4, 133.5, 136.1–139.1 (dm, J = 250.8 Hz), 139.5–142.8 (dm, J = 256.8 Hz), 145.5–148.4 (dm, J = 252.3 Hz), 158.4; ^{19}F NMR (CDCl_3): δ –137.01 (dd, J = 21.8, 6.8 Hz, 2F), 154.02 (t, J = 20.3 Hz, 1F), –162.59 (ddd, J = 21.8, 20.3, 6.8 Hz, 2F); IR (KBr): ν 2991, 2959, 2864, 2229, 1604, 125, 1496, 1252, 1176, 1075, 987, 837 cm^{-1} ; HRMS: (FAB+) m/z $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{11}\text{F}_5\text{O}_2$: 354.0679; found: 354.0681.

1.2.1. Synthetic procedure for 2,3,5,6-tetrafluoro-4-[2-{4-((tetrahydrofuran-3-yl)oxy)phenyl}ethyn-1-yl]benzonitrile (3c) via a nucleophilic aromatic substitution reaction

In a two-necked round-bottomed flask, equipped with a Teflon®-coated stirrer bar, was placed 4-((tetrahydrofuran-3-yl)oxy)phenylacetylene (0.38 g, 2.0 mmol), and THF (20 mL). To the solution was added slowly a hexane solution of *n*-BuLi (1.6 mol L⁻¹; 1.4 mL, 2.2 mmol) at 0 °C, and stirred at the temperature for 0.5 h. To the resultant solution was added pentafluorobenzonitrile (3.4 g, 2.2 mL, 34.8 mmol) and the whole was stirred room temperature for 18 h. After 18 h, the resultant solution was poured into saturated aqueous NH₄Cl solution (20 mL) and the crude product was extracted with EtOAc (30 mL, three times) and organic layer combined was washed with brine (once). The collected organic layer was dried over anhydrous Na₂SO₄, which was separated by filtration. The filtrate was evaporated in vacuo and subjected to silica-gel column chromatography (eluent: hexane/EtOAc = 5/1), followed by recrystallization from CH₂Cl₂/MeOH (v/v = 1/1), to obtain the title compound in 68% (0.49 g, 1.36 mmol) as a white crystal.

2,3,5,6-Tetrafluoro-4-[2-{4-((tetrahydrofuran-3-yl)oxy)phenyl}ethyn-1-yl]benzonitrile (3c)

Yield: 68%; M.p.: 157.4–158.1 °C; ¹H NMR (CDCl₃): δ 2.11–2.20 (m, 1H), 2.20–2.31 (m, 1H), 3.92 (td, *J* = 8.4, 4.4 Hz, 1H), 3.96–4.05 (m, 3H), 4.97 (tq, *J* = 4.4, 4.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (CDCl₃): δ 32.9, 67.2, 72.9, 73.1 (q, *J* = 3.7 Hz), 77.6, 92.9 (t, *J* = 17.6 Hz), 107.3 (t, *J* = 3.7 Hz), 107.5 (t, *J* = 3.6 Hz), 111.6 (q, *J* = 17.6 Hz), 112.9, 115.6, 134.1, 146.3 (ddt, *J* = 254.5, 12.5, 4.0 Hz), 147.0 (ddt, *J* = 260.4, 15.4, 3.7 Hz), 159.2; ¹⁹F NMR (CDCl₃): δ –133.60 (ddd, *J* = 24.4, 15.0, 6.8 Hz, 2F), –134.54 (ddd, *J* = 24.4, 16.6, 6.8 Hz); IR (KBr): ν 3065, 2975, 2874, 2245, 2216, 1646, 1601, 1490, 1331, 1249, 1075, 984 cm⁻¹; HRMS: (FAB+) *m/z* [M]⁺ calcd for C₁₉H₁₁F₄NO₂: 361.0726; found: 361.0734.

2. NMR Spectra

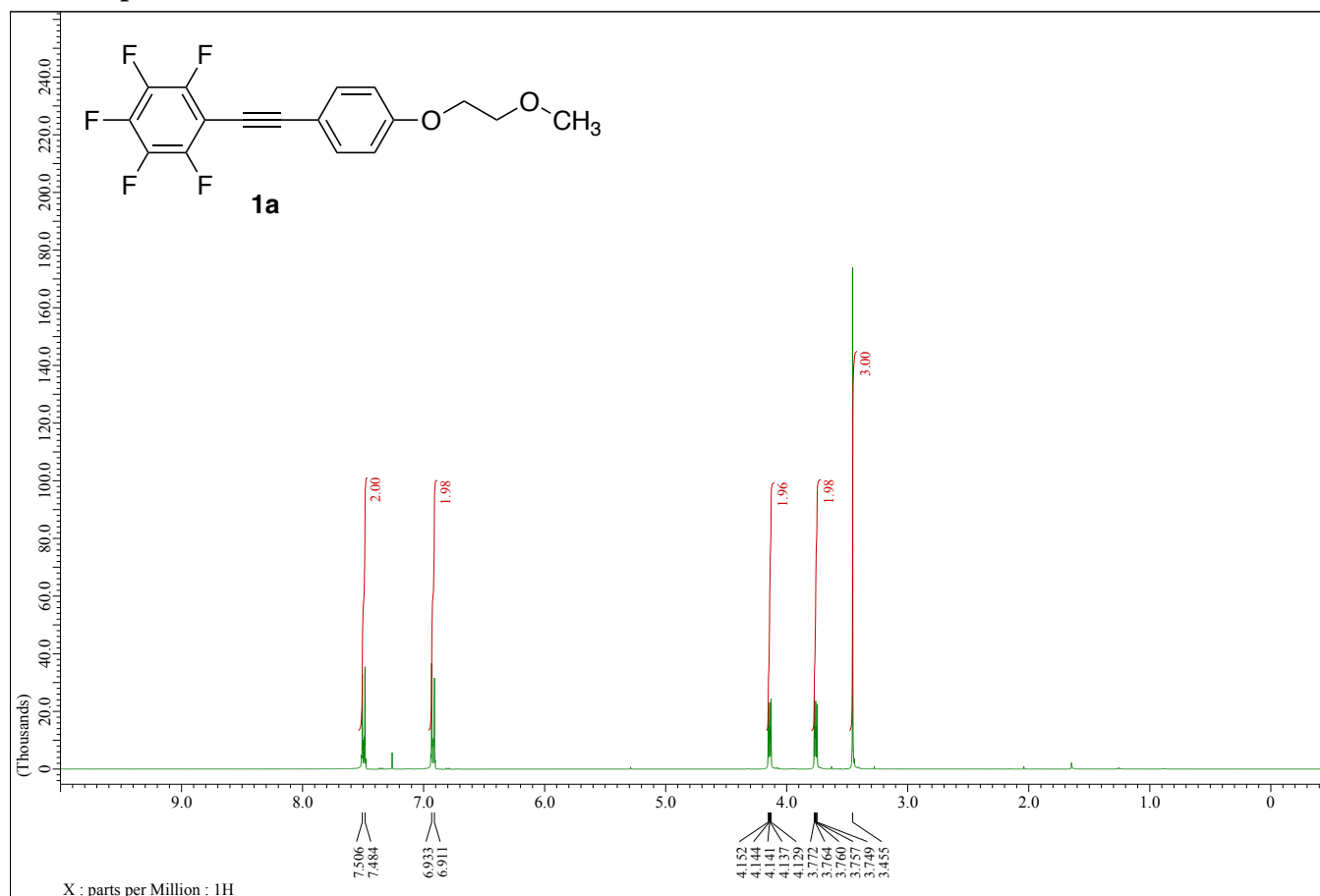


Figure S1. ¹H NMR spectrum of **1a** (400 MHz, CDCl₃)

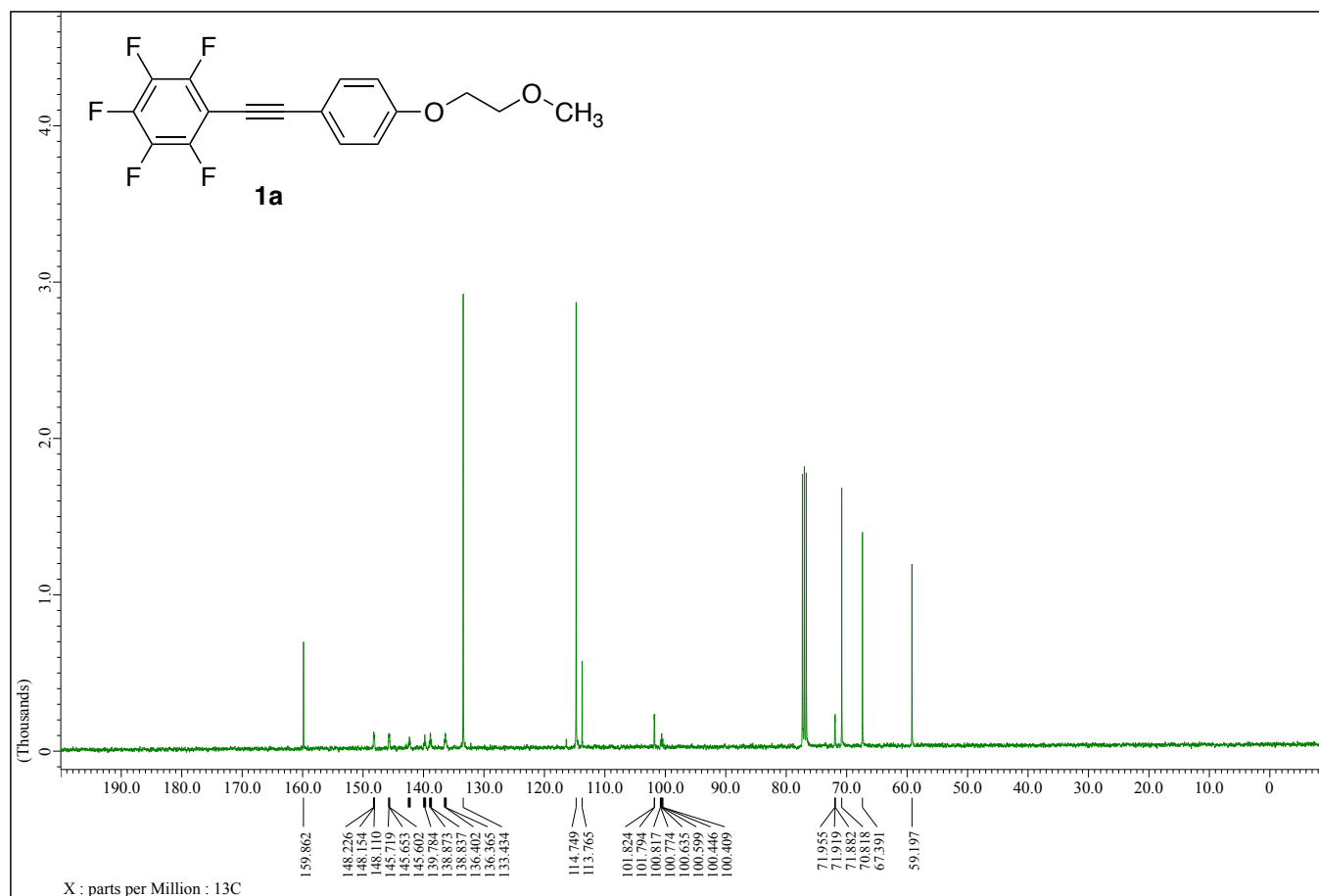


Figure S2. ¹³C NMR spectrum of **1a** (100 MHz, CDCl₃)

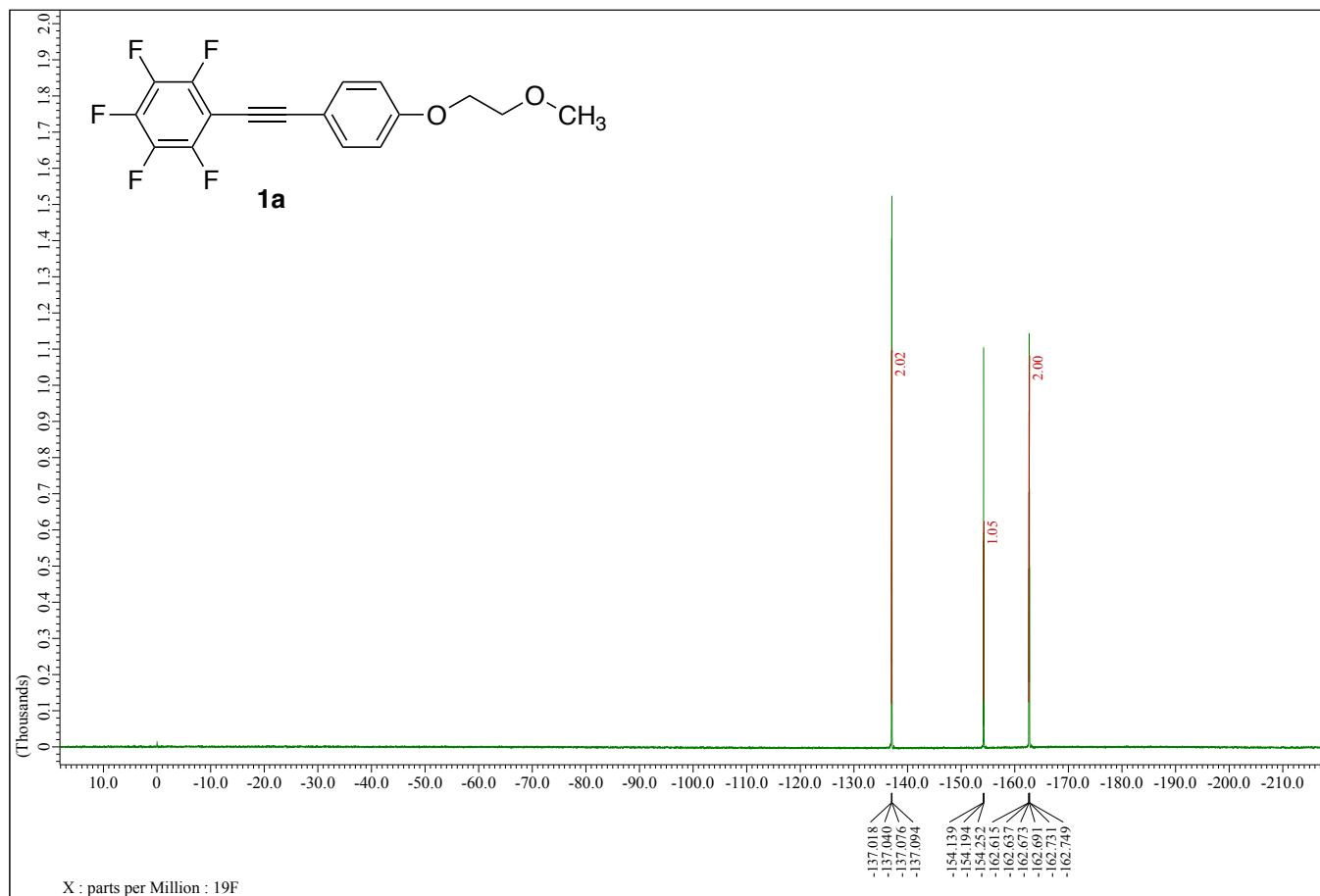


Figure S3. ^{19}F NMR spectrum of **1a** (376 MHz, CDCl_3 , CFCl_3)

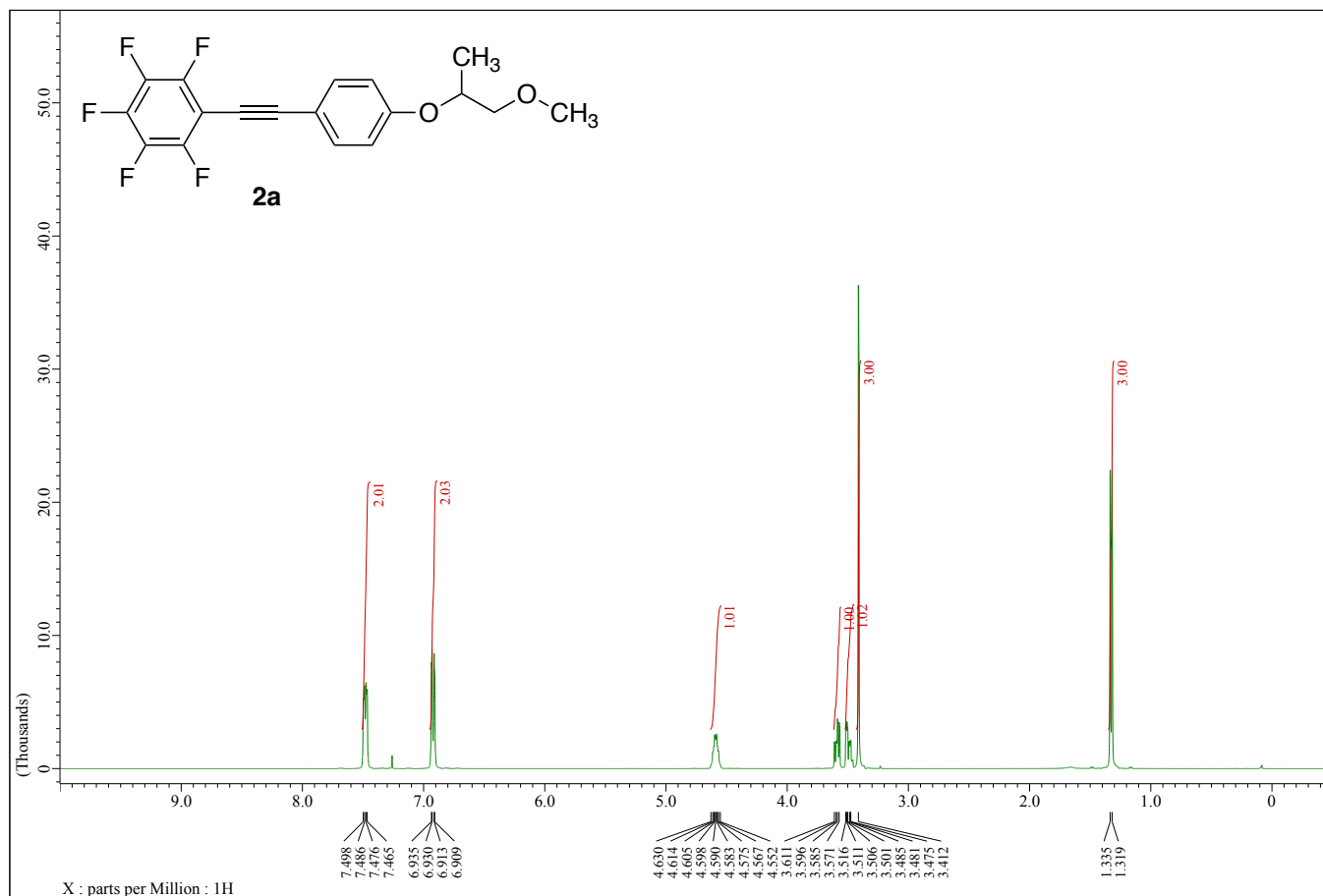


Figure S4. ¹H NMR spectrum of **2a** (400 MHz, CDCl₃)

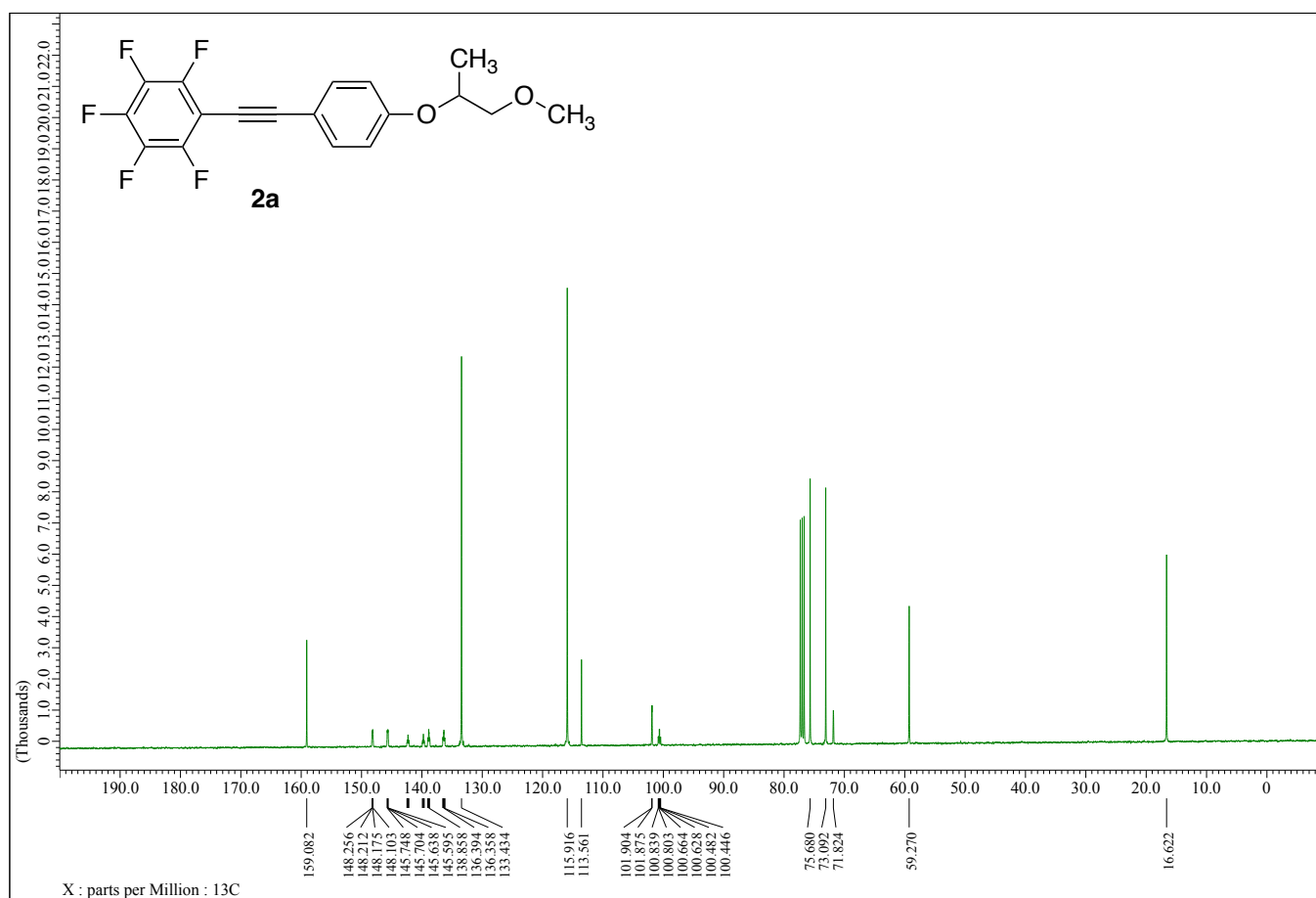


Figure S5. ¹³C NMR spectrum of **2a** (100 MHz, CDCl₃)

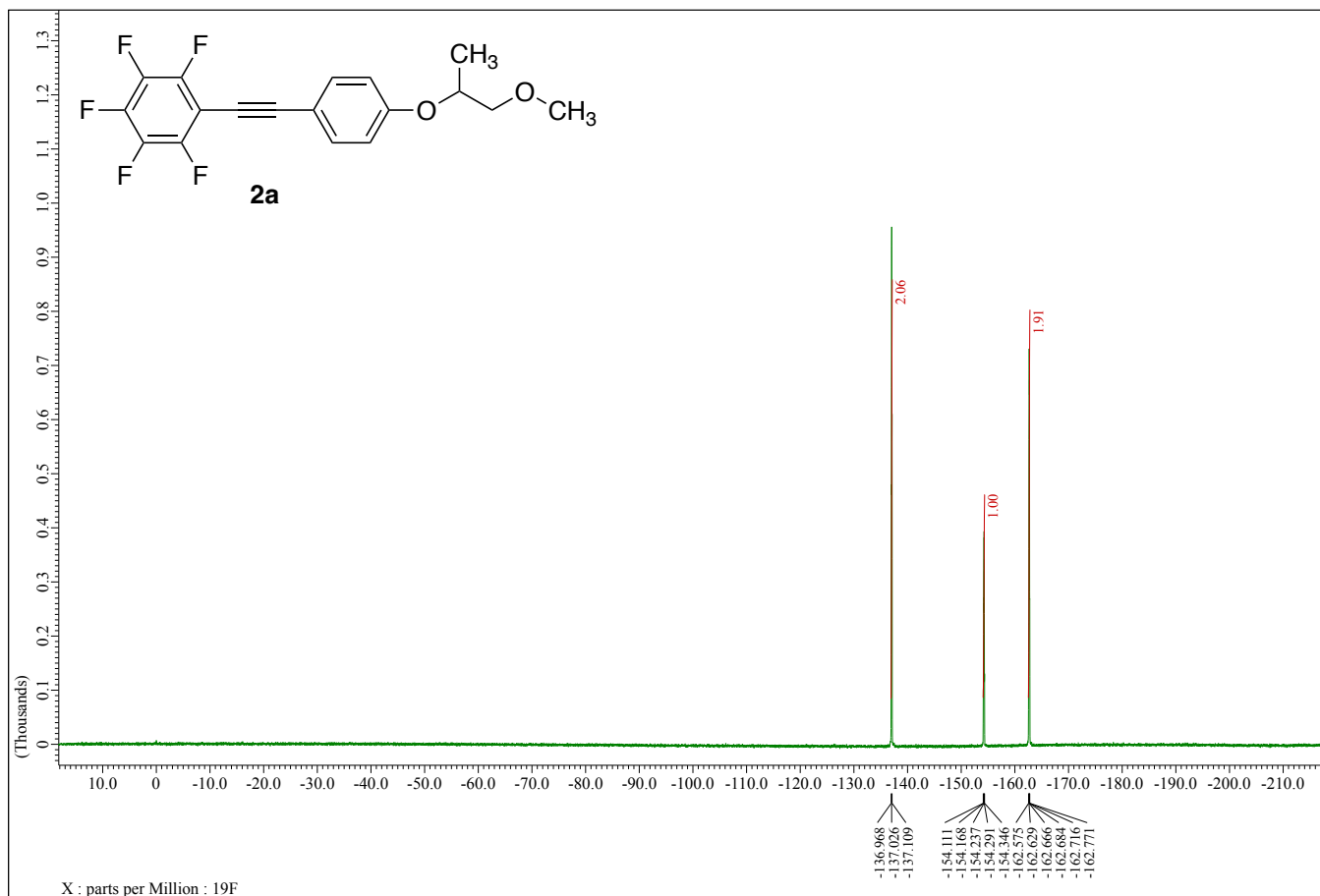


Figure S6. ¹⁹F NMR spectrum of **2a** (376 MHz, CDCl₃, CFC₃)

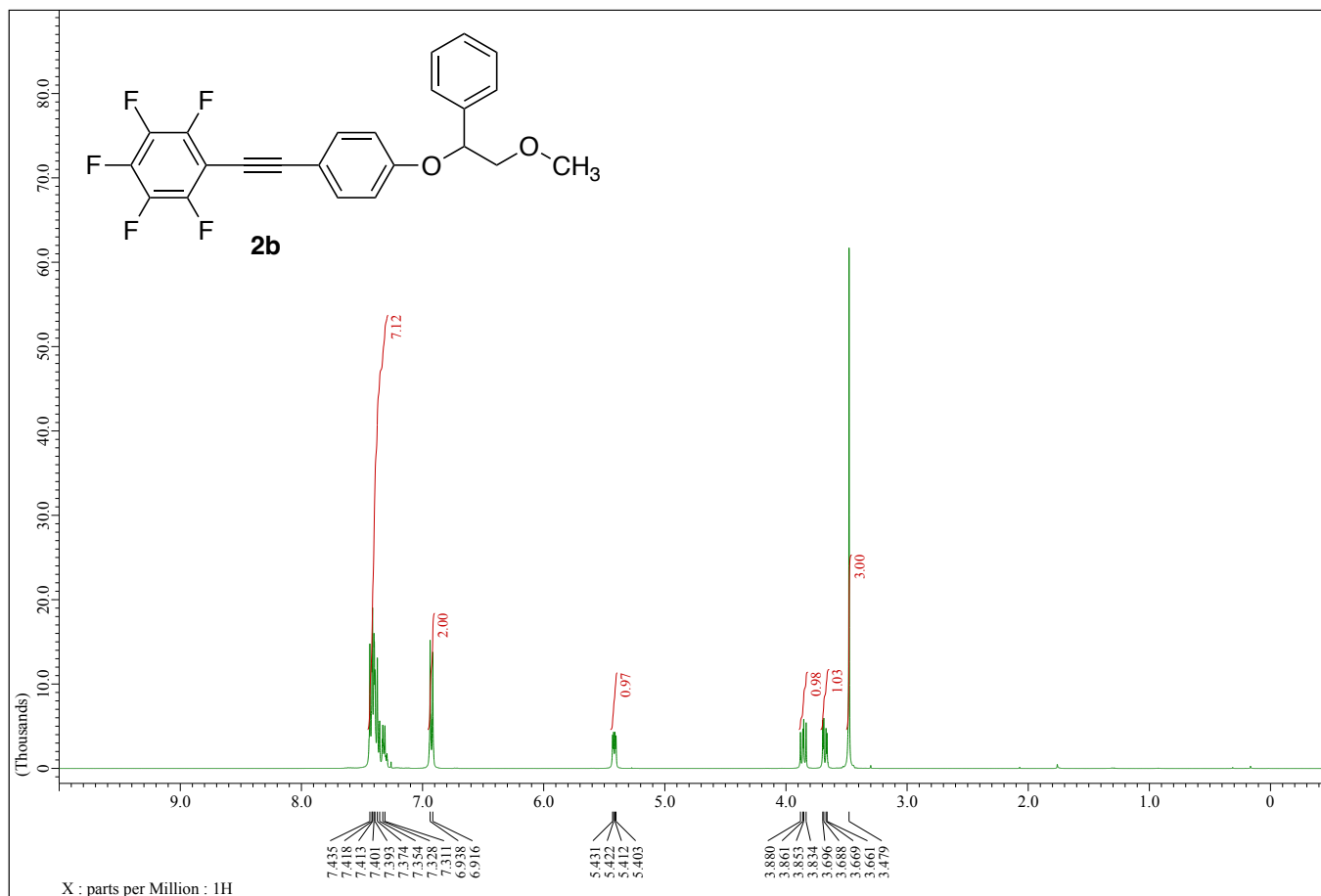


Figure S7. ¹H NMR spectrum of **2b** (400 MHz, CDCl₃)

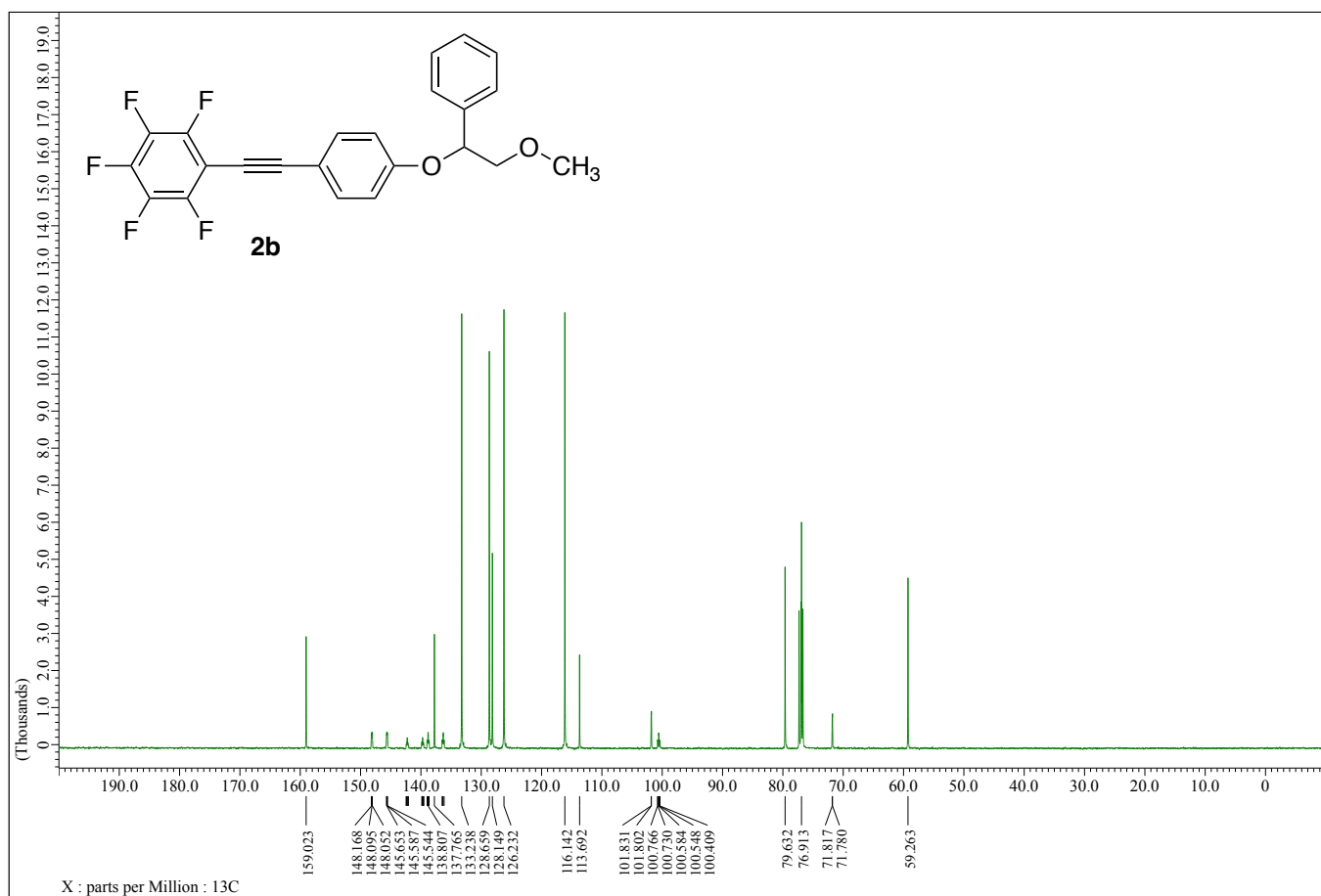


Figure S8. ¹³C NMR spectrum of **2b** (100 MHz, CDCl₃)

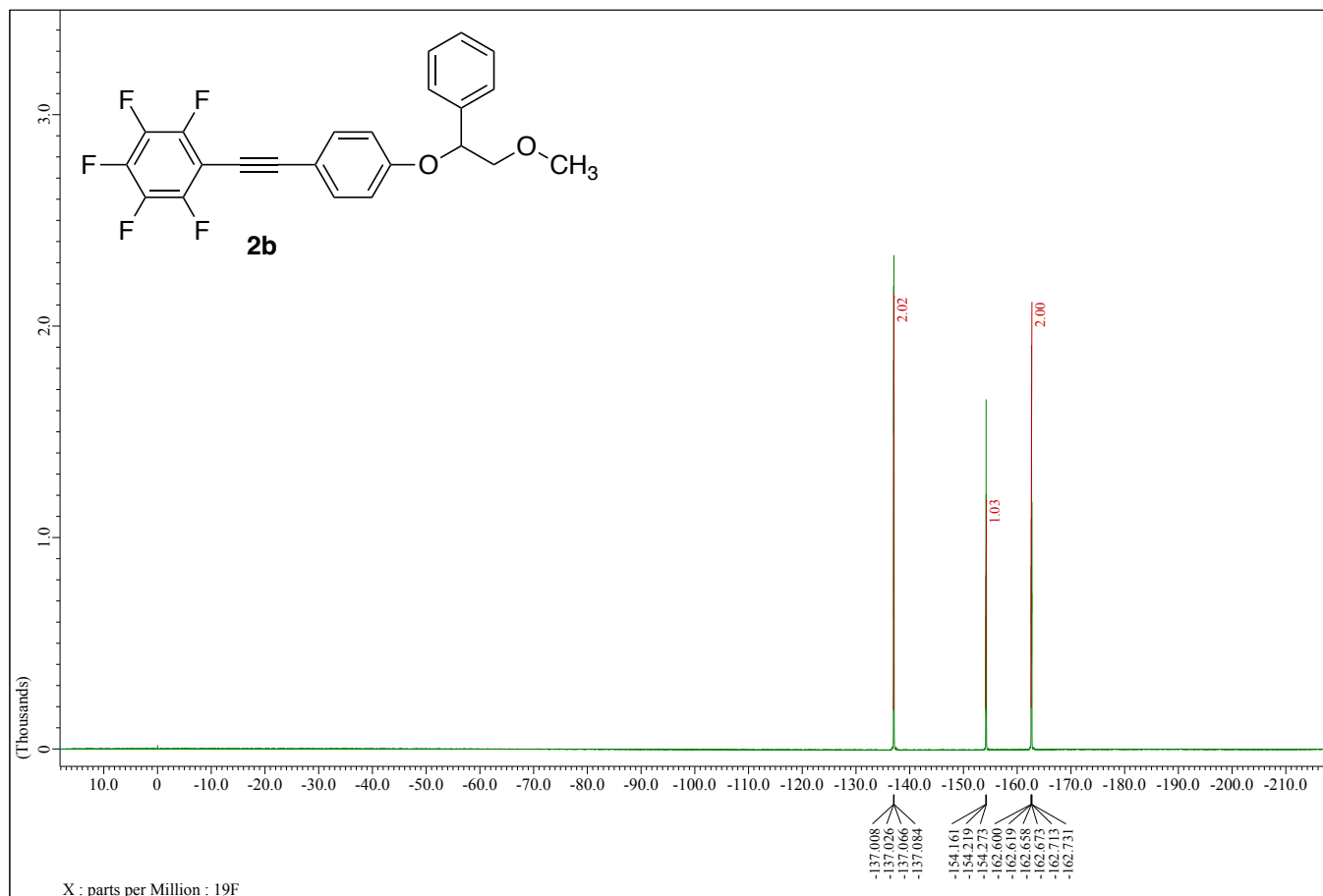


Figure S9. ^{19}F NMR spectrum of **2b** (376 MHz, CDCl_3 , CFCl_3)

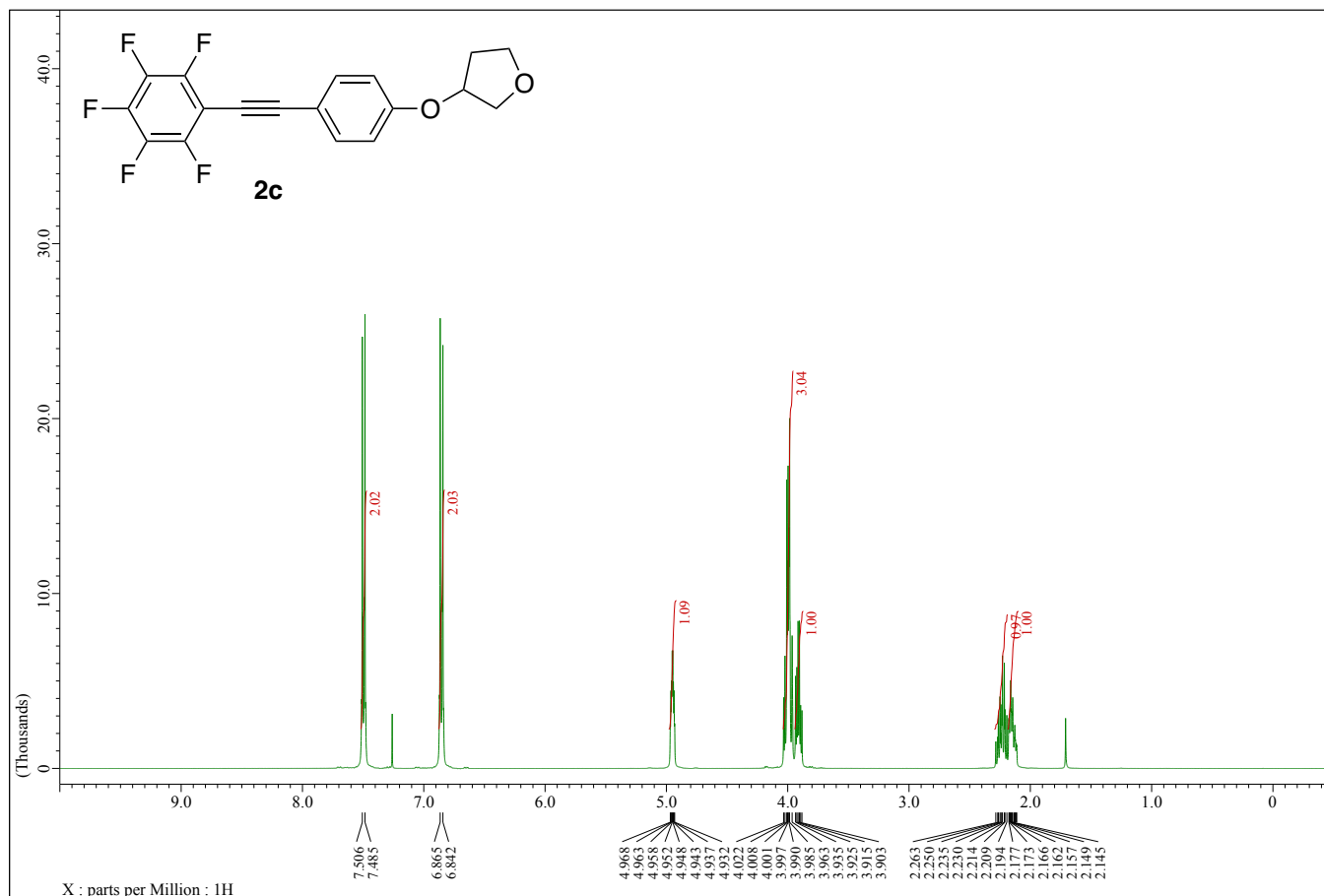


Figure S10. ¹H NMR spectrum of **2c** (400 MHz, CDCl₃)

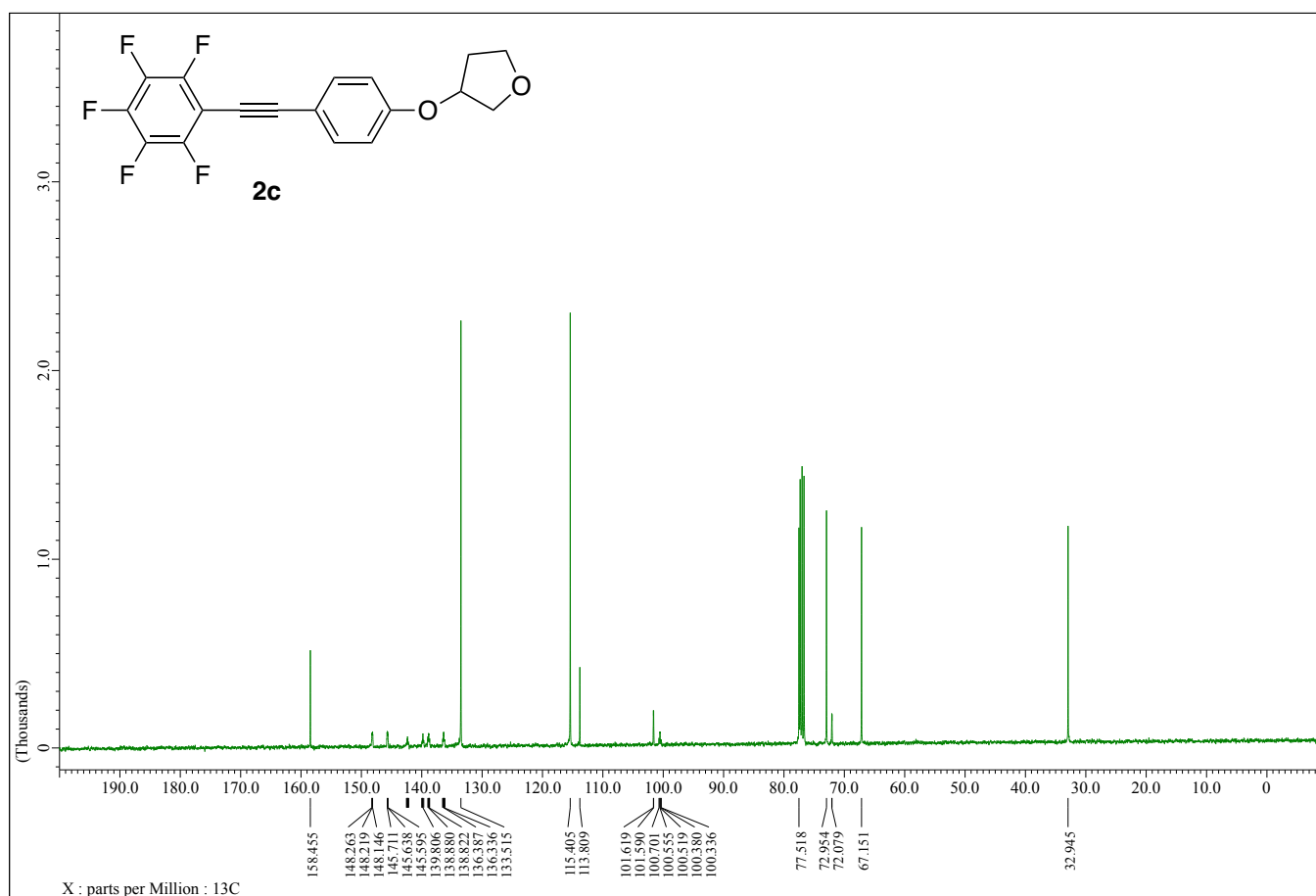


Figure S11. ¹³C NMR spectrum of **2c** (100 MHz, CDCl₃)

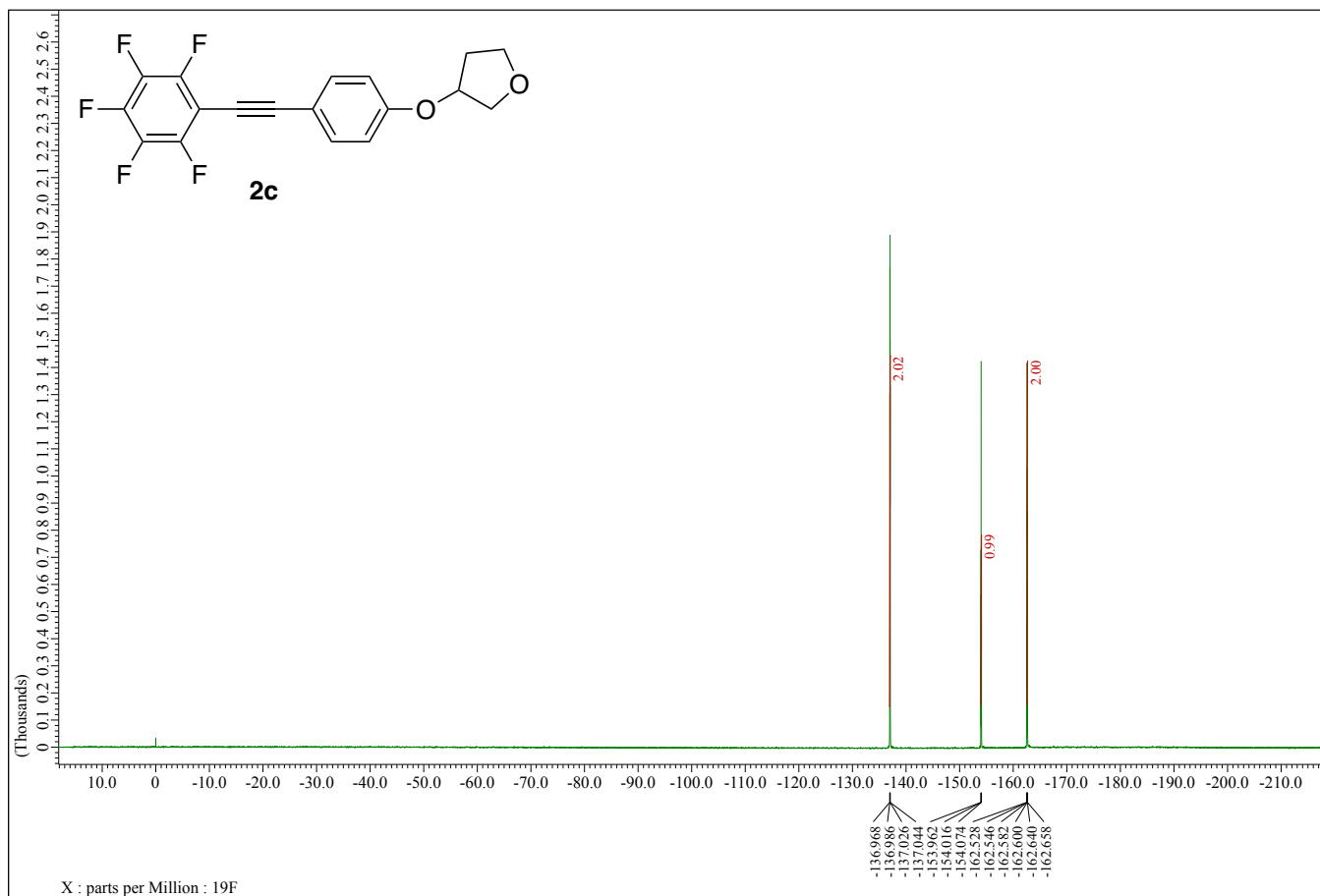


Figure S12. ^{19}F NMR spectrum of **2c** (376 MHz, CDCl_3 , CFCl_3)

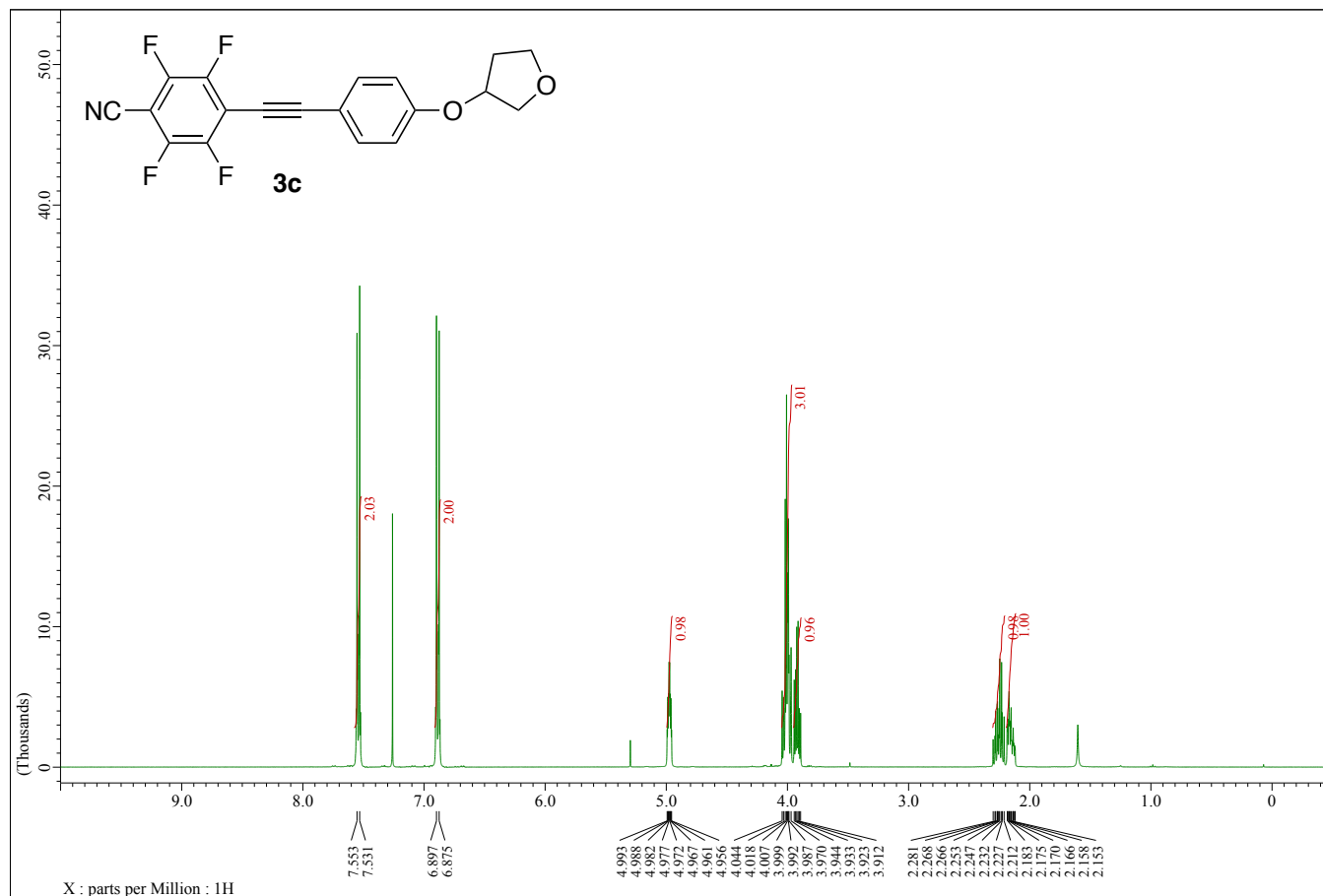


Figure S13. ¹H NMR spectrum of **3c** (400 MHz, CDCl₃)

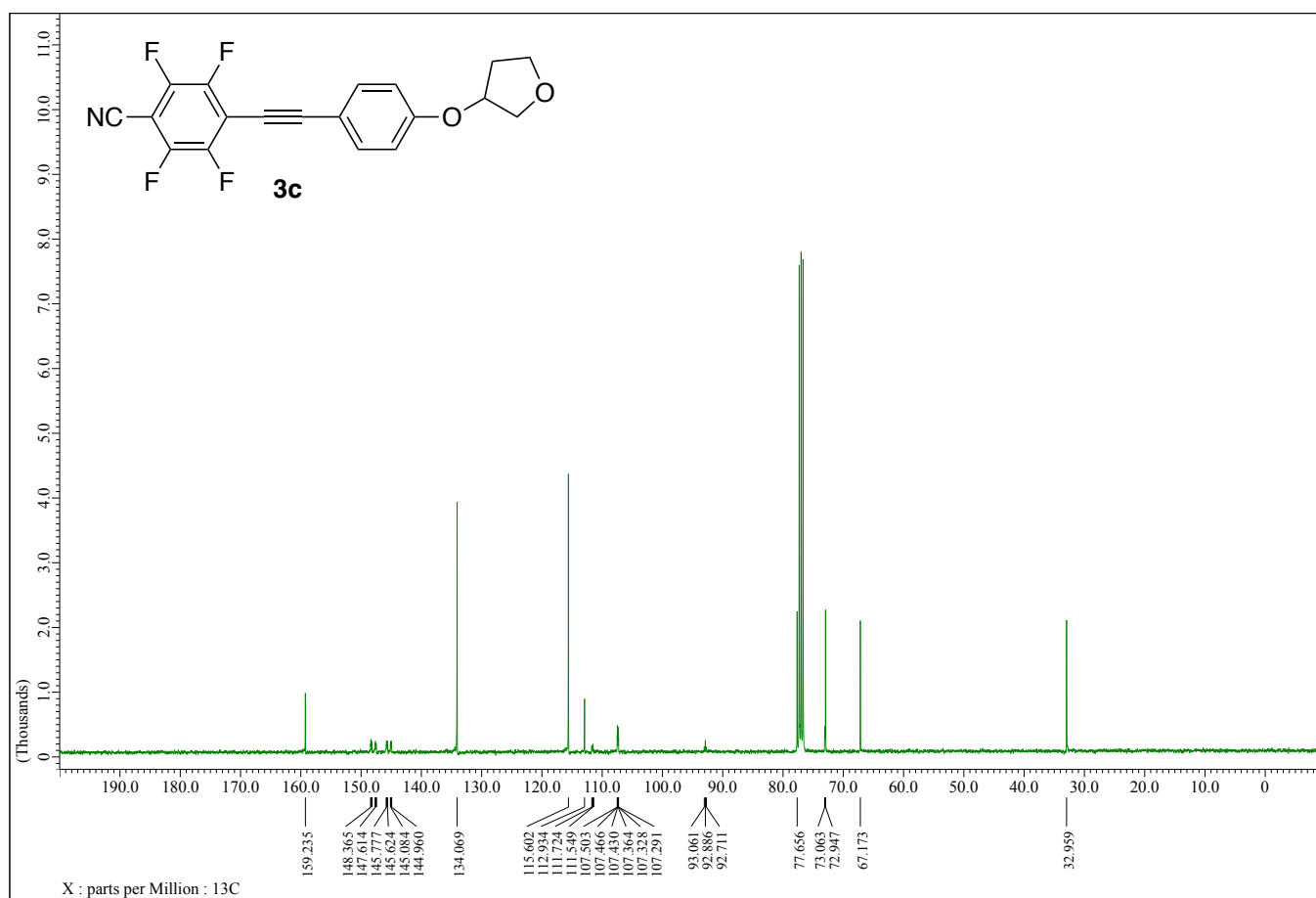


Figure S14. ¹³C NMR spectrum of **3c** (100 MHz, CDCl₃)

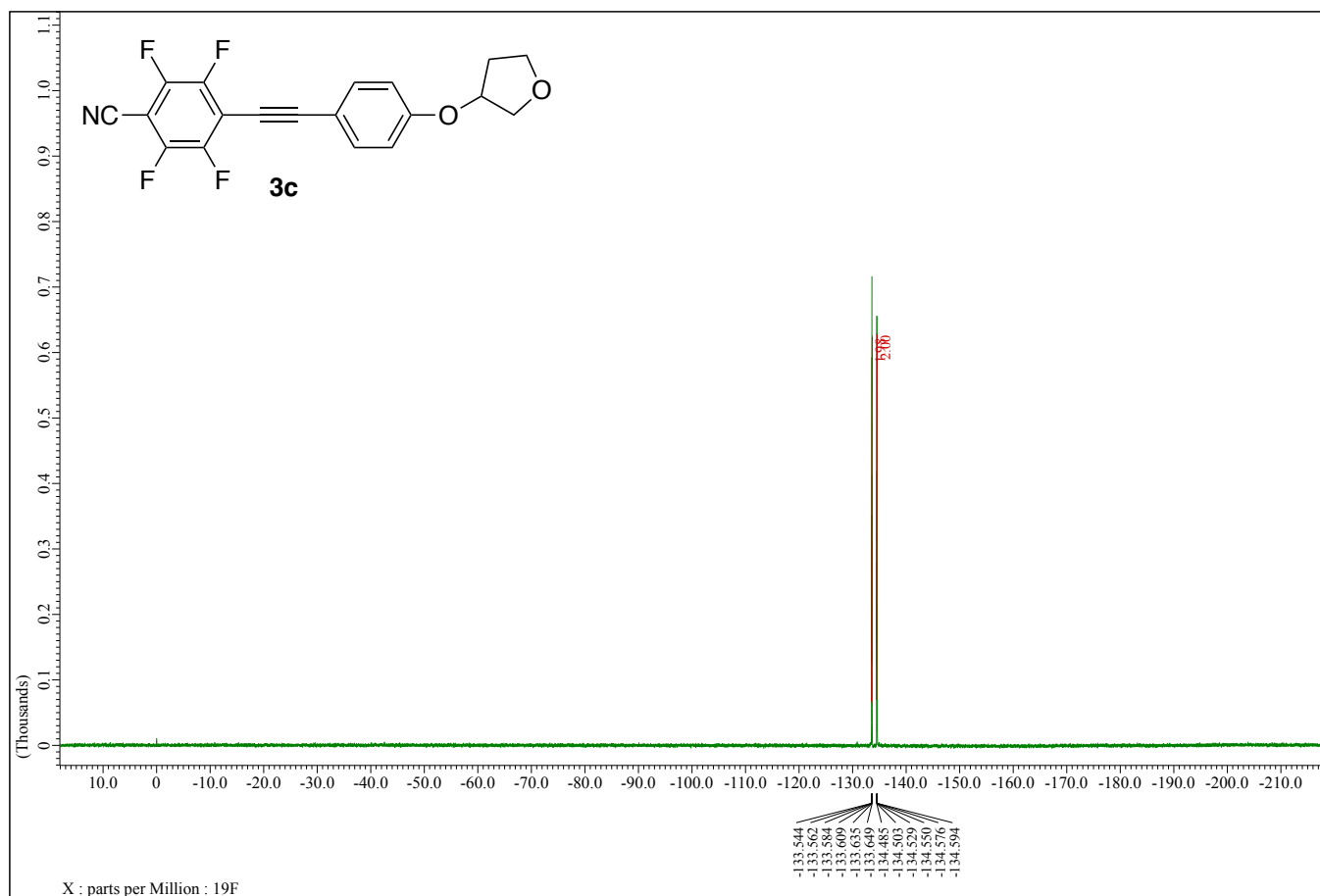


Figure S15. ^{19}F NMR spectrum of **3c** (376 MHz, CDCl_3 , CFCl_3)

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 **1a**, **2a**, **2b**, and **3c**

	1a	2a	2b	3c
CCDC #	2118480	2118481	2118482	2118483
Empirical Formula	C ₁₇ H ₁₁ F ₅ O ₂	C ₁₈ H ₁₃ F ₅ O ₂	C ₂₃ H ₁₅ F ₅ O ₂	C ₁₉ H ₁₁ F ₄ NO ₂
Formula weight	342.26	356.28	418.35	361.29
Temperature [K]	299	293	299	298
Crystal Color / Habit	Colorless / Block	Colorless / Block	Colorless / Block	Colorless / Block
Crystal Size [mm]	0.94 x 0.67 x 0.26	0.55 x 0.48 x 0.43	0.55 x 0.48 x 0.43	0.52 x 0.34 x 0.20
Crystal System	Monoclinic	Triclinic	Triclinic	Monoclinic
Space Group	<i>P</i> 1 2 ₁ / <i>c</i> 1	<i>P</i> –1	<i>P</i> –1	<i>P</i> 1 2 ₁ / <i>n</i> 1
<i>a</i> [Å]	8.9965(3)	7.5715(6)	8.9679(5)	6.1206(3)
<i>b</i> [Å]	7.9831(3)	10.6727(6)	9.2898(4)	22.0913(10)
<i>c</i> [Å]	21.5960(9)	11.9855(7)	11.8018(5)	11.8054(6)
α [°]	90	65.696(6)	88.321(4)	90
β [°]	94.474(4)	71.888(6)	83.008(4)	97.582(5)
γ [°]	90	76.943(6)	84.421(4)	90
<i>V</i> [Å ³]	1546.30(10)	833.57(11)	971.12(8)	1582.28(13)
<i>Z</i>	4	2	2	4
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] [a]	0.0510	0.1432	0.0447	0.0485
<i>wR</i> ₂ (<i>F</i> ²) [b]	0.1624	0.5001	0.1381	0.1503

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

4. DFT calculation

All computations were performed using the Gaussian 16 software package (Revision B.01). Geometry optimizations were carried out using the CAM-B3LYP hybrid functional and the 6-31+G(d) basis set with an implicit solvation model (conductor-like polarizable continuum model; CPCM) for CH₂Cl₂. The vertical excitation energies and dipole moments of the optimized structures were calculated using the time-dependent self-consistent field approximation at the same level of theory.

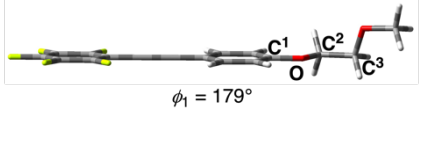
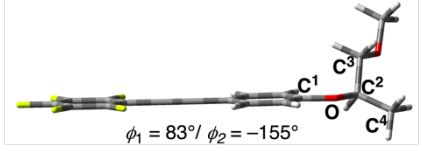
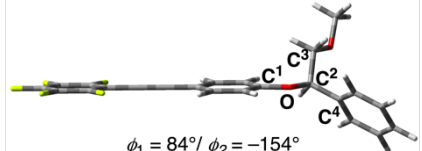
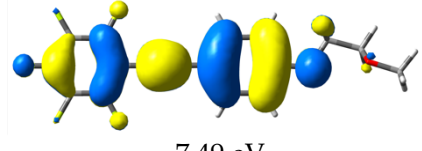
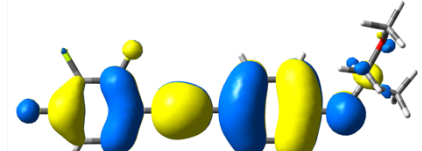
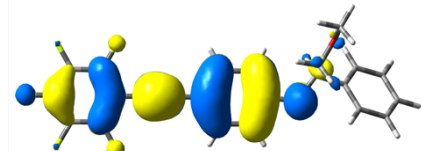
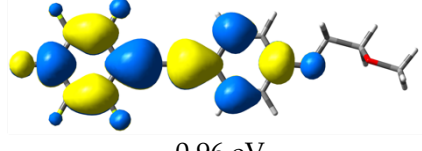
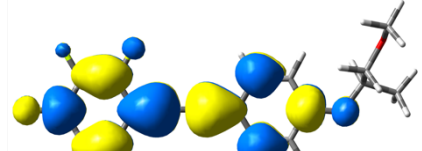
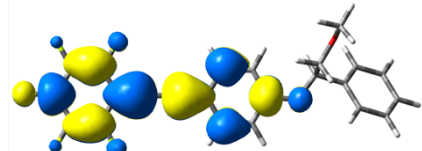
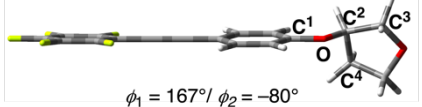
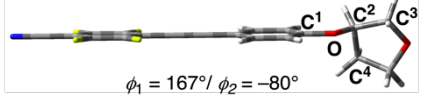
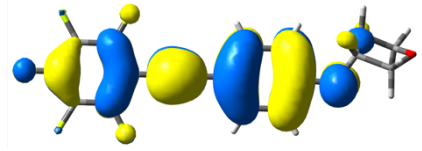
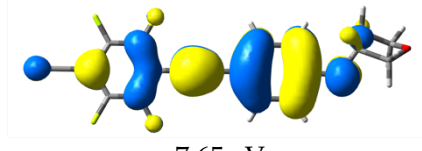
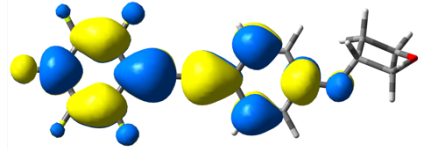
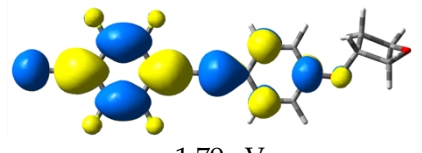
(a) 1a	(b) 2a	(c) 2b
 $\phi_1 = 179^\circ$	 $\phi_1 = 83^\circ / \phi_2 = -155^\circ$	 $\phi_1 = 84^\circ / \phi_2 = -154^\circ$
 -7.49 eV	 -7.49 eV	 -7.52 eV
 -0.96 eV	 -0.97 eV	 -0.98 eV
(d) 2c	(e) 3c	
 $\phi_1 = 167^\circ / \phi_2 = -80^\circ$	 $\phi_1 = 167^\circ / \phi_2 = -80^\circ$	
 -7.52 eV	 -7.65 eV	
 -0.98 eV	 -1.79 eV	

Figure S16. Optimized geometry, HOMO and LUMO distributions for **1a**, **2a–c**, and **3c** at S_0 state.

Table S2. Energy (hartree) and dipole moment (debye) of **1a**, **2a–c**, and **3c** at S_0 state.

	E(RCAM-B3LYP) [hartree]	Dipole moment (debye)
1a	–1303.82476447	X= –6.1818/ Y= –1.8659/ Z= –1.4624/ Tot= 6.6208
2a	–1343.12614784	X= 4.8136/ Y= 0.7952/ Z= 1.0909/ Tot= 4.9994
2b	–1534.79588633	X= –4.5082/ Y= 1.2126/ Z= –1.3888/ Tot= 4.8706
2c	–1341.92350211	X= –2.7877/ Y= 1.3028/ Z= –0.0075/ Tot= 3.0780
3c	–1334.90603360	X= 7.2520/ Y= –1.0002/ Z= –0.0879/ Tot= 7.3212

Table S3. Theoretical vertical transition behavior calculated by TD-DFT calculation.

	Transition	Transition Energy (eV)	Theoretical Absorption (nm)	Oscillator strength f
1a	HOMO → LUMO	4.1422	299.32	1.3106
2a	HOMO → LUMO	4.1375	299.66	1.3205
2b	HOMO → LUMO	4.1424	299.30	1.4127
2c	HOMO → LUMO	4.1484	298.87	1.3183
3c	HOMO → LUMO	3.7157	333.68	1.4966

Table S4. Cartesian coordinate for **1a** at the optimized geometry in S₀ state.

No.	Atom	Type	Coordinates (Angstroms)			18	1	0	-3.721218	-2.028557	-0.164329
	No.		x	y	z						
1	8	0	-5.203326	0.256400	-0.357394	19	6	0	5.805044	-0.029489	0.119288
2	9	0	3.044482	-2.345669	0.050790	20	6	0	0.368940	0.060387	-0.112360
3	9	0	5.736243	-2.384312	0.166235	21	6	0	-1.793459	-1.104108	-0.136206
4	9	0	7.137053	-0.052237	0.176137	22	1	0	-1.273990	-2.053927	-0.061096
5	9	0	3.129055	2.379295	-0.045803	23	6	0	1.577332	0.042016	-0.061410
6	9	0	5.820602	2.326158	0.069924	24	6	0	3.749555	1.195638	0.005877
7	6	0	-3.856030	0.130249	-0.291407	25	6	0	-6.010546	-0.917129	-0.313918
8	8	0	-7.825354	0.138468	0.815661	26	1	0	-5.823210	-1.465389	0.616275
9	6	0	-3.128852	1.326994	-0.328413	27	1	0	-5.773032	-1.564169	-1.166381
10	1	0	-3.669092	2.264932	-0.403283	28	6	0	5.131536	1.181100	0.064968
11	6	0	-1.748967	1.304921	-0.270004	29	6	0	-7.457291	-0.501549	-0.387149
12	1	0	-1.192389	2.235994	-0.299119	30	1	0	-7.611230	0.172547	-1.242386
13	6	0	2.995963	0.018339	-0.001015	31	1	0	-8.072628	-1.399997	-0.544460
14	6	0	-1.056918	0.084556	-0.172633	32	6	0	-9.169302	0.577830	0.808485
15	6	0	3.707054	-1.183833	0.054577	33	1	0	-9.341440	1.308062	0.006037
16	6	0	5.088648	-1.216445	0.114044	34	1	0	-9.359925	1.050836	1.773081
17	6	0	-3.182585	-1.089816	-0.194678	35	1	0	-9.860064	-0.266362	0.675697

Table S5. Cartesian coordinate for **2a** at the optimized geometry in S₀ state.

No.	Atom	Type	Coordinates (Angstroms)								
	No.		x	y	z						
1	8	0	4.947143	-1.279564	-0.294053	19	6	0	-1.761056	-0.215441	-0.079901
2	9	0	-2.960945	2.269344	-0.585529	20	6	0	1.400673	-1.853119	0.064927
3	9	0	-7.268236	0.555491	0.146469	21	1	0	0.746058	-2.690226	0.284577
4	9	0	-3.551640	-2.282563	0.542631	22	6	0	5.936142	-0.280603	-0.583798
5	6	0	-3.166494	-0.019055	-0.024870	23	1	0	5.550676	0.407130	-1.343187
6	6	0	3.624913	-0.972092	-0.263955	24	6	0	-5.948872	0.370578	0.090938
7	9	0	-6.217040	-1.902021	0.652102	25	6	0	-5.410386	-0.880781	0.348186
8	6	0	0.848470	-0.582617	-0.172666	26	6	0	-5.110775	1.429041	-0.224305
9	9	0	-5.628328	2.635837	-0.472901	27	6	0	6.241554	0.492340	0.695380
10	6	0	3.089456	0.297181	-0.498328	28	1	0	5.313068	0.862025	1.153201
11	1	0	3.723189	1.148742	-0.711042	29	1	0	6.733473	-0.175143	1.419109
12	6	0	-4.040548	-1.063837	0.288843	30	6	0	7.145060	-1.011773	-1.131703
13	6	0	1.712479	0.481331	-0.453646	31	1	0	7.506105	-1.749104	-0.407391
14	1	0	1.302837	1.469486	-0.636266	32	1	0	7.948094	-0.298489	-1.333544
15	6	0	-3.743194	1.228611	-0.279229	33	1	0	6.892500	-1.527986	-2.061898
16	6	0	2.768381	-2.043587	0.019732	34	8	0	7.085285	1.573876	0.365454
17	1	0	3.200754	-3.022291	0.199670	35	6	0	7.447071	2.349168	1.492081
18	6	0	-0.563826	-0.382303	-0.123986	36	1	0	7.995328	1.743788	2.226471
						37	1	0	6.559471	2.779136	1.975737
						38	1	0	8.090448	3.155375	1.136221

Table S6. Cartesian coordinate for **2b** at the optimized geometry in S₀ state.

No.	Atom	Type	Coordinates (Angstroms)								
	No.		x	y	z						
1	8	0	-3.714414	-0.705217	-0.339212	23	1	0	-4.247963	0.910628	0.854644
2	9	0	4.379697	2.125493	0.896651	24	6	0	7.271533	0.100671	0.170252
3	9	0	8.600786	0.185344	0.231593	25	6	0	6.668937	-1.058433	-0.293921
4	9	0	4.737587	-2.268937	-0.806667	26	6	0	6.487220	1.171653	0.570261
5	6	0	4.468392	-0.077461	0.040802	27	6	0	-4.814847	1.252986	-1.194426
6	6	0	-2.372676	-0.501629	-0.256506	28	1	0	-3.833437	1.599363	-1.548133
7	9	0	7.423660	-2.091345	-0.680426	29	1	0	-5.294629	0.699128	-2.014211
8	6	0	0.423123	-0.329585	-0.138967	30	8	0	-5.607788	2.348471	-0.800567
9	9	0	7.066742	2.289549	1.017937	31	6	0	-5.851531	3.255336	-1.859341
10	6	0	-1.763753	0.688942	0.146519	32	1	0	-6.390806	2.764562	-2.680546
11	1	0	-2.344998	1.562723	0.412870	33	1	0	-4.911199	3.670216	-2.246822
12	6	0	5.289203	-1.137654	-0.354391	34	1	0	-6.464066	4.063405	-1.456699
13	6	0	-0.376996	0.765272	0.204575	35	6	0	-5.925411	-0.332153	0.444018
14	1	0	0.090572	1.692711	0.518774	36	6	0	-6.513696	0.004409	1.661753
15	6	0	5.108940	1.075651	0.503268	37	6	0	-6.547232	-1.280192	-0.372352
16	6	0	-1.581360	-1.603010	-0.605507	38	6	0	-7.710367	-0.589300	2.059444
17	1	0	-2.071536	-2.519485	-0.916720	39	1	0	-6.035361	0.737960	2.305290
18	6	0	1.846350	-0.240175	-0.076669	40	6	0	-7.737299	-1.880320	0.025333
19	6	0	3.052476	-0.166969	-0.023431	41	1	0	-6.093877	-1.558149	-1.319471
20	6	0	-0.203421	-1.519409	-0.547854	42	6	0	-8.323882	-1.533876	1.242185
21	1	0	0.401111	-2.378972	-0.818306	43	1	0	-8.158647	-0.315655	3.009931
22	6	0	-4.640436	0.332745	0.013314	44	1	0	-8.209117	-2.619355	-0.615478
						45	1	0	-9.254275	-2.001038	1.551152

Table S7. Cartesian coordinate for **2c** at the optimized geometry in S₀ state.

No.	Atom	Type	Coordinates (Angstroms)								
	No.		x	y	z						
1	9	0	3.416456	-2.366132	0.123979	18	1	0	-3.392814	-2.660364	0.125672
2	9	0	5.728198	2.548625	-0.062987	19	6	0	0.518548	-0.228911	-0.072184
3	9	0	3.042434	2.339054	-0.125104	20	6	0	-1.704331	0.786828	-0.316167
4	9	0	6.101202	-2.142178	0.185298	21	1	0	-1.238004	1.758958	-0.438857
5	8	0	-5.036189	-0.781509	-0.237621	22	6	0	1.723908	-0.134475	-0.038350
6	8	0	-8.230855	0.276904	0.079540	23	6	0	-3.090383	0.686323	-0.358809
7	6	0	3.139150	-0.020828	-0.002850	24	1	0	-3.677389	1.583978	-0.506497
8	6	0	-0.903793	-0.342252	-0.113789	25	6	0	-5.927004	0.303089	-0.524791
9	6	0	-3.696940	-0.562437	-0.202606	26	1	0	-5.537280	0.856271	-1.382602
10	6	0	5.941115	0.205308	0.061314	27	6	0	-7.305020	-0.318566	-0.822164
11	6	0	3.963667	-1.146724	0.077095	28	1	0	-7.655367	-0.125350	-1.837385
12	6	0	5.342864	-1.044457	0.109148	29	1	0	-7.247362	-1.402008	-0.658086
13	6	0	5.153032	1.343209	-0.017479	30	6	0	-6.186471	1.196119	0.697908
14	6	0	-1.528263	-1.591350	0.048399	31	1	0	-5.365023	1.160810	1.416961
15	1	0	-0.922288	-2.477412	0.206973	32	1	0	-6.323469	2.233604	0.378222
16	6	0	3.775355	1.222963	-0.048554	33	6	0	-7.496170	0.639114	1.246432
17	6	0	-2.904920	-1.698849	0.004828	34	1	0	-7.322206	-0.246917	1.873416
						35	1	0	-8.091112	1.361769	1.806938
						36	9	0	7.269778	0.312729	0.091660

Table S8. Cartesian coordinate for **3c** at the optimized geometry in S₀ state.

No.	Atom	Type	Coordinates (Angstroms)			19	6	0	-0.309465	0.241216	-0.088235
	No.		x	y	z						
1	9	0	-3.188937	2.389880	0.134412	20	6	0	1.905106	-0.793523	-0.296783
2	9	0	-5.504752	-2.514775	-0.088141	21	1	0	1.433331	-1.766291	-0.389306
3	9	0	-2.835455	-2.314104	-0.157968	22	6	0	-1.515978	0.151961	-0.052914
4	9	0	-5.857703	2.180696	0.203095	23	6	0	3.290764	-0.701200	-0.340375
5	8	0	5.241460	0.760565	-0.261570	24	1	0	3.874101	-1.605457	-0.458767
6	8	0	8.430344	-0.294364	0.105363	25	6	0	-7.170674	-0.281360	0.098081
7	6	0	-2.927095	0.044443	-0.014014	26	7	0	-8.323075	-0.370102	0.129484
8	6	0	1.110656	0.346705	-0.131369	27	6	0	6.129566	-0.337132	-0.509041
9	6	0	3.902970	0.549778	-0.222195	28	1	0	5.740046	-0.917117	-1.348902
10	6	0	-5.748940	-0.172218	0.059558	29	6	0	7.510663	0.269268	-0.822672
11	6	0	-3.744957	1.175945	0.078996	30	1	0	7.865042	0.036579	-1.828177
12	6	0	-5.120621	1.072651	0.114686	31	1	0	7.455558	1.358298	-0.700219
13	6	0	-4.941760	-1.306897	-0.033166	32	6	0	6.381187	-1.188187	0.744481
14	6	0	1.740213	1.598352	-0.007581	33	1	0	5.556332	-1.127787	1.457955
15	1	0	1.137818	2.491484	0.121751	34	1	0	6.518123	-2.235969	0.460454
16	6	0	-3.566548	-1.198970	-0.068712	35	6	0	7.689073	-0.614767	1.280286
17	6	0	3.116679	1.697165	-0.051943	36	1	0	7.513622	0.292529	1.875620
18	1	0	3.610051	2.659030	0.039444	37	1	0	8.279664	-1.318851	1.868304

5. Photophysical Characteristics

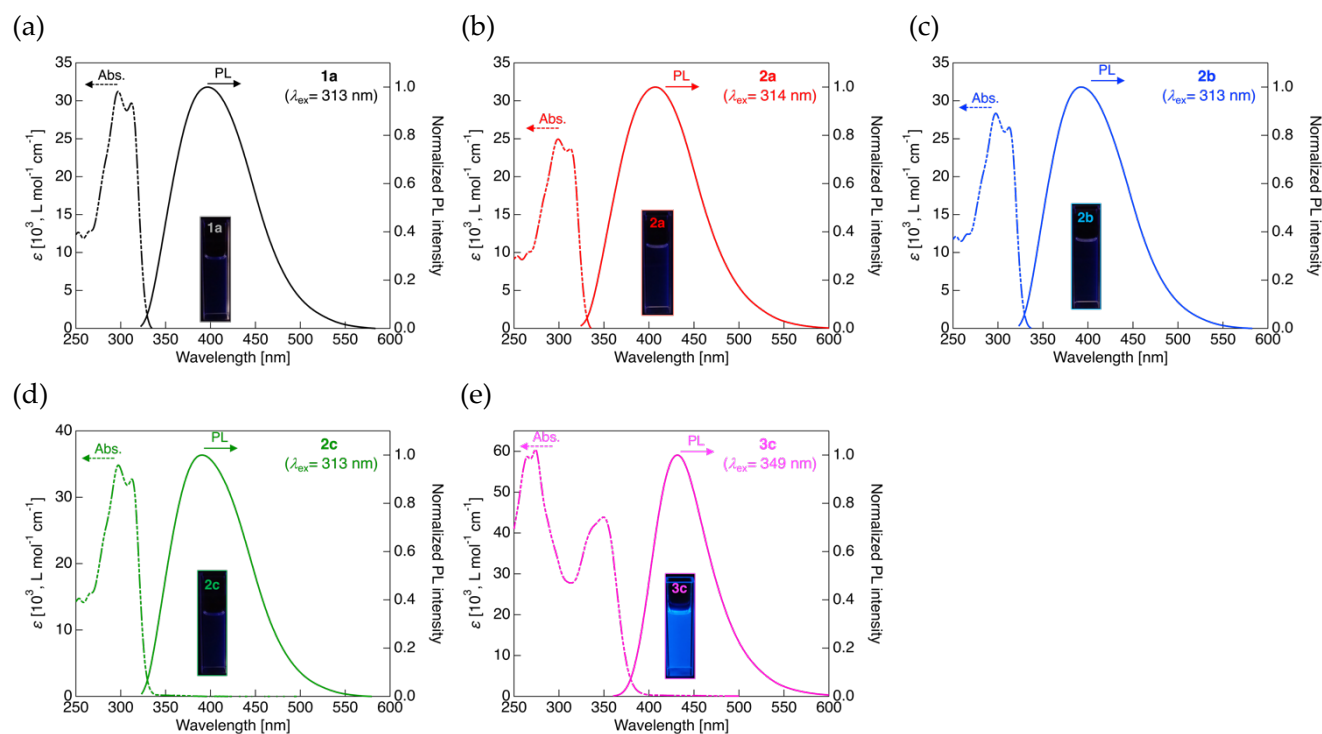


Figure S17. UV-vis and PL spectra of **1a**, **2a–c**, and **3c** in CH_2Cl_2 solution. Concentration: $1.0 \times 10^{-5} \text{ mol L}^{-1}$ for UV-vis and $1.0 \times 10^{-6} \text{ mol L}^{-1}$ for PL.

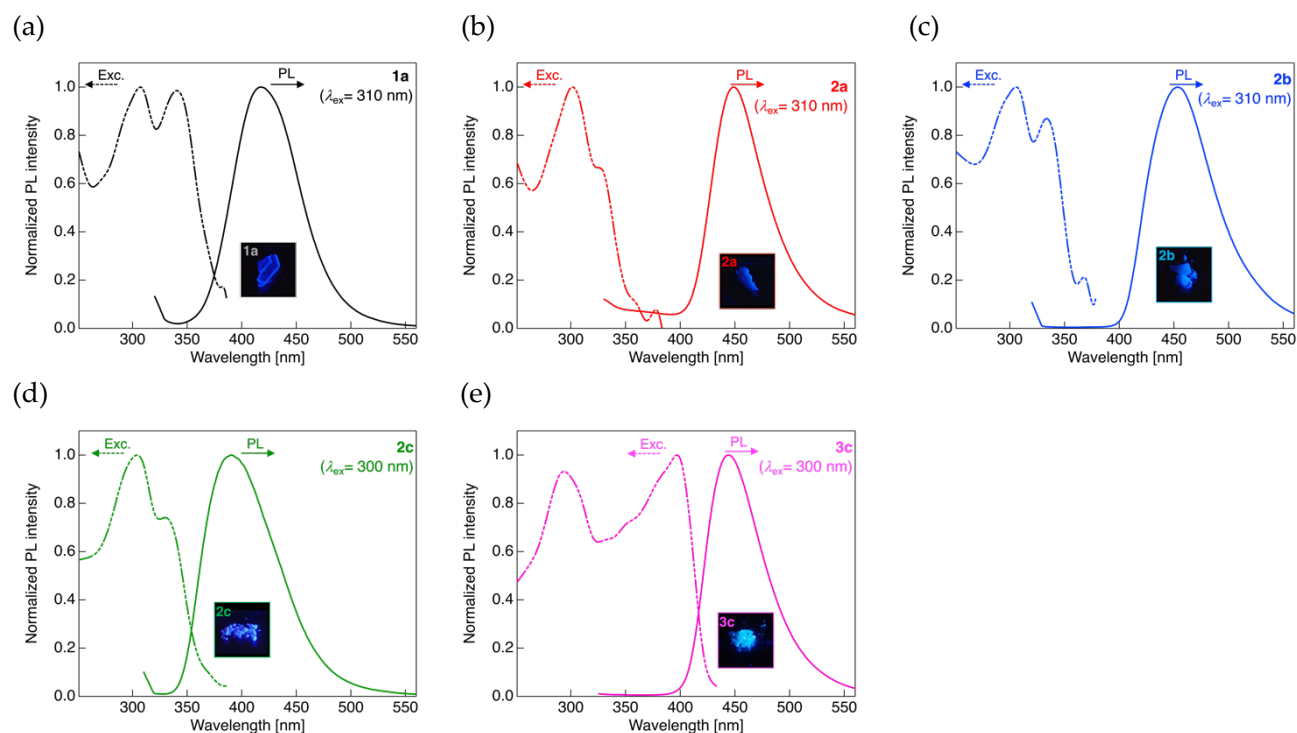


Figure S18. Excitation and PL spectra of **1a**, **2a–c**, and **3c** in crystalline state. Excitation spectra were obtained by monitoring PL at the maximum PL wavelength ($\lambda_{\text{em}} = 418 \text{ nm}$ for **1a**, 449 nm for **2a**, 453 nm for **2b**, 390 nm for **2c**, and 444 nm for **3c**).

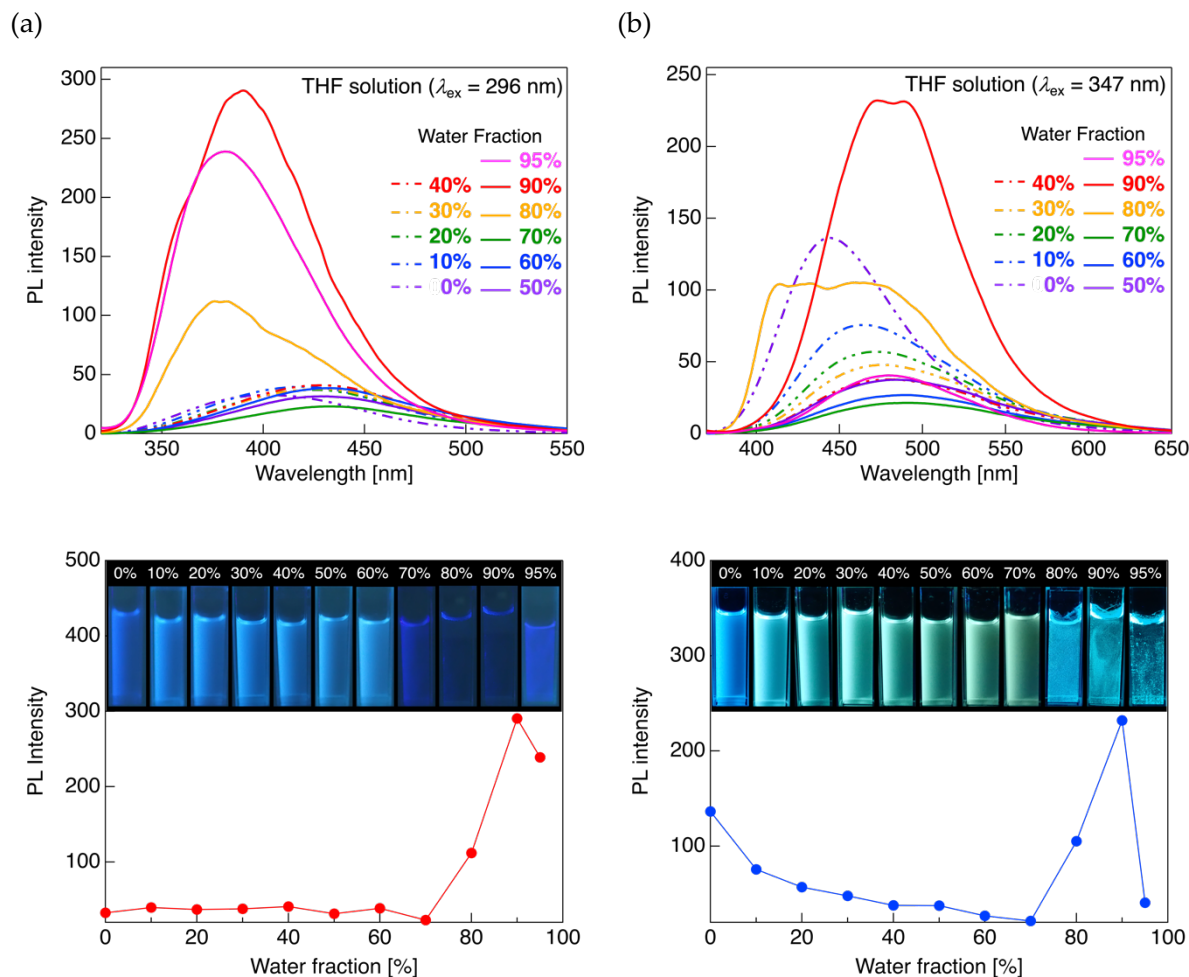


Figure S19. PL spectra and AIE characteristics of **2c** and **3c** in THF/H₂O mixed solvent system.

Table S9. Photophysical data of **2c** and **3c** in THF/H₂O mixed solvent system.

Water ratio [%]	2c ($\lambda_{\text{ex}} = 296 \text{ nm}$)		3c ($\lambda_{\text{ex}} = 347 \text{ nm}$)	
	λ_{PL} [nm]	PL intensity	λ_{PL} [nm]	PL intensity
0	402	32.56	444	136.37
10	419	39.69	462	75.60
20	423	37.01	473	56.90
30	428	37.87	476	47.81
40	430	40.93	480	37.73
50	429	31.47	485	37.52
60	433	38.53	490	26.84
70	434	23.00	493	21.40
80	382	111.91	459	105.14
90	390	290.50	473	232.03
95	381	238.89	479	40.55