Supporting Information

Synthesis, Structure-Property Relationships and Absorbance Modulation of Highly Asymmetric Photochromes with Variable Oxidation and Substitution Patterns

Kakishi Uno[a#], Dojin Kim[a#], Jonas Bucevicius[b], Mariano L. Bossi[c], Vladimir N. Belov[a], and Stefan W. Hell[a,c]

[a]Department of NanoBiophotonics, Max Planck Institute for Multidisciplinary Sciences (MPI NAT), Am Fassberg 11, 37077 Göttingen, Germany
[b]Chromatin Labeling and Imaging group, Department of NanoBiophotonics, MPI NAT, Am Fassberg 11, 37077 Göttingen, Germany.
[c]Department of Optical Nanoscopy, Max Planck Institute for Medical Research (MPI-MR), Jahnstrasse 29, 69120 Heidelberg, Germany.

# equal contribution

Abbreviations

anti-parallel (ap), aqueous (aq.), argon (Ar), brine (aq. NaCl), catalyst/catalysis (cat.), closed form (CF), diarylethene (DAE), dichloromethane (DCM), equivalent (equiv.), electrospray ionization (ESI), ethyl acetate (EtOAc), high performance liquid chromatography (HPLC), high resolution mass-spectrometry (HR-MS), m-CPBA (*meta*-chloroperoxybenzoic acid), methanol (MeOH), NBS (*N*-bromosuccinimide), *N*-hydroxysuccinimide (NHS), *N,N*-diisopropyl ethyl amine (DIEA), , nitrogen (N_2), nuclear magnetic resonance (NMR), open form (OF), parallel (p), phosphate buffer saline (PBS), photostationary state (PSS), reversed phase (RP), room temperature (r.t.), saturated (sat.), tetrahydrofurane (THF), thin layer chromatography (TLC), ultraviolet (UV), visible (Vis), volume ratio of two solvents (v/v).

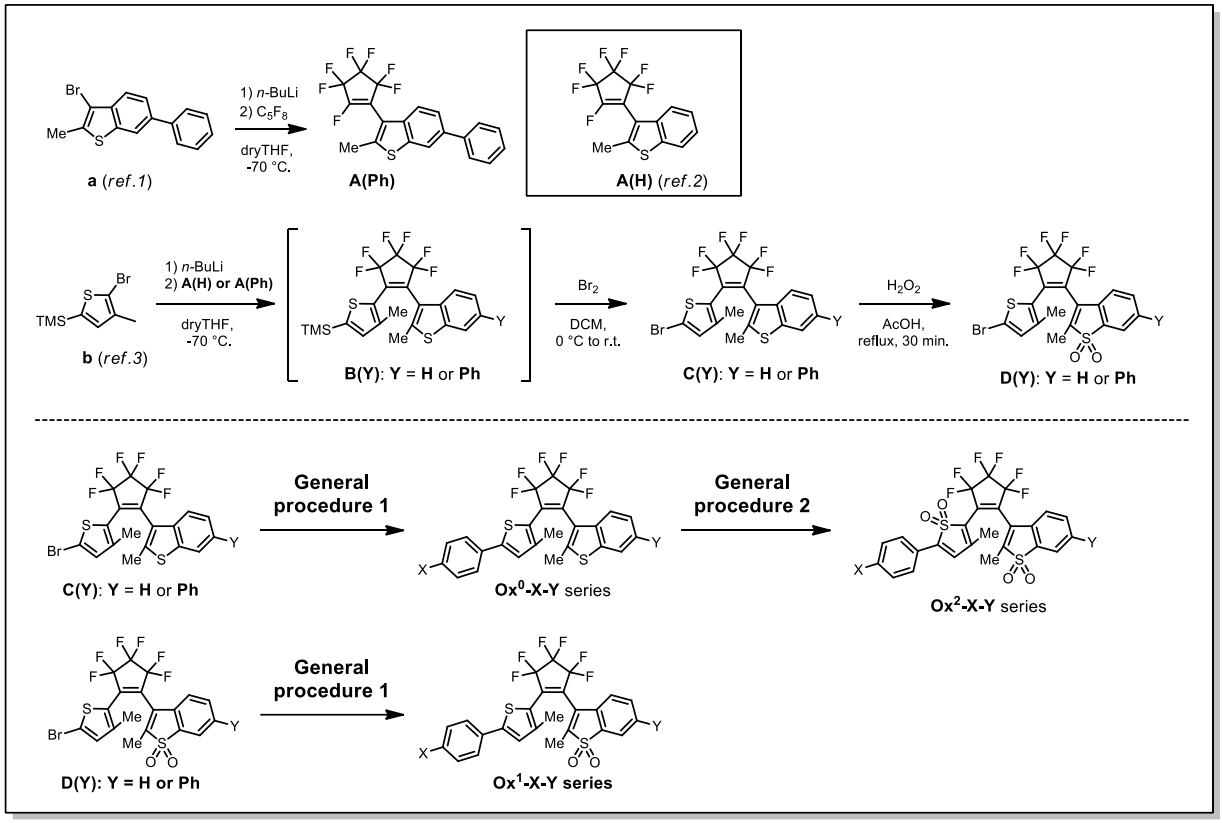
Materials
The key precursors **a**,[S1] **A(H)**,[S2] and **b**[S3] were synthesized according to previously reported procedures. Other chemicals were purchased from TCI Deutschland (Tokyo Chemical Industry Co.) or Sigma-Aldrich and used without further purification.

Nuclear Magnetic Resonance (NMR)
NMR Spectra (^{1}H, ^{13}C and ^{19}F) were recorded on an *Agilent 400MR DD2* spectrometer. All ^{1}H- and ^{13}C-NMR spectra are referenced to the signals of the residual protons and ^{13}C in $CDCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.00 ppm). Multiplicities of the signals are described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, br = broad. Coupling constants (*J*) are given in Hz.

ESI and high resolution mass-spectrometry (ESI-MS)
ESI-MS were recorded on a Varian 500-MS spectrometer (Agilent). ESI-HRMS were recorded on a MICROTOF spectrometer (Bruker) equipped with an *Apollo* ion source and a direct injector as an LC-autosampler (Agilent RR 1200).

High-performance liquid chromatography (HPLC)
Analytical HPLC was performed on a KNAUER Azura system with a 20 µL injection loop, a 150 × 4 mm column (Knauer, Eurospher II 100-10 C18A with precolumn, Vertex Plus), and a photodiode array detector. Flowrate was 1.2 mL/min with water/MeCN gradient (both solvents containing 0.1% of TFA).

Synthesis

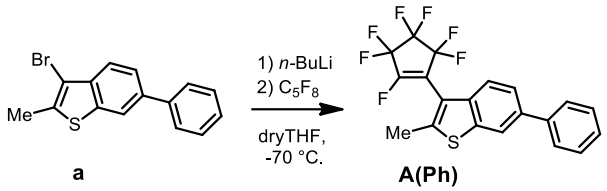


Scheme S1. Upper: The synthesis of precursors. Bottom: The general procedures for the synthesis of diarylethenes studied in this work.

General procedure 1 (GP-1)
Starting material (e.g. **C(H)**, **C(Ph)**, **D(H)**, or **D(Ph)** (1 equiv.) and boronic acids (phenyl boronic acid, 4-methoxyphenylboronic acid, or 4-cyanophenylboronic acid) (1.1-1.3 equiv.) were dissolved in a THF solution (15-20 mL). To this solution, saturated aqueous Na_2CO_3 (15-20 mL) and $Pd(PPh_3)_4$ (0.2 equiv.) were added. The mixture were heated to reflux for 1.5-3.0 h. After cooling to r.t., the mixture was poured into brine and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by silica gel column chromatography with EtOAc/*n*-hexane with noted gradient. The product yields, R_f values and appearance of each products are noted in the experiment section separately. For some substances, lyophilization with dioxane was performed to give light powders.

General procedure 2 (GP-1)
Ox^0-X-Y (e.g. **Ox^0-MeO-H**, **Ox^0-H-H**, **Ox^0-CN-H**, **Ox^0-MeO-Ph**, **Ox^0-H-Ph**, and **Ox^0-CN-Ph**) (1.0 equiv.) dissolved in DCM (10 mL per 0.1 g of **Ox^0-X-Y**) was added with 77 % m-CPBA (10 equiv.). The reaction mixture was stirred for 24-72 h. The reaction solution was poured into sat. aq. $Na_2S_2O_3$ solution, and stirred for 1 h. The DCM layer was extracted and poured into sat. aq. Na_2CO_3 solution, then stirred for 1 h. The organic layer was extracted and dried over Na_2SO_4. The crude products were purified by silica gel column chromatography with EtOAc/*n*-hexane with noted gradient. The product yields, R_f values and appearance of each products are noted in the experiment section separately. For some substances, lyophilization with dioxane was performed to give light powders.

A(Ph)



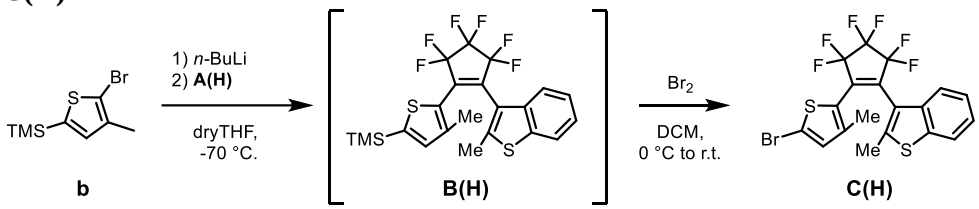
a **A(Ph)**

Starting material **a** (5.7 g, 19 mmol) [S1] was dissolved in dry THF (120 mL) under N_2. The reaction solution was cooled to -70℃. 1.6 M *n*-BuLi (13 mL, 21 mmol, 1.1 equiv.) was slowly added with stirring over 1 h. The reaction solution was further stirred for 2 h at -70℃. Octafluorocyclopentene (5.8 g mL, 28 mmol, 1.5 equiv.) was slowly added by syringe, and the reaction solution was gradually warmed-up to r.t. overnight. The reaction mixture was poured into sat. brine (250 mL) and extracted with ether (2×250 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was subjected to chromatography on regular silica gel (eluent: *n*-hexane/DCM = 95/5) to afford 6.0 g (76 % yield) of **b** as a white solid. R_f (*n*-hexane) = 0.40.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.00 (d, *J* = 1.6, 0.4 Hz, 1H), 7.66-7.62 (m, 3H), 7.57-7.53 (m, 1H), 7.50-7.45 (m, 2H), 7.38 (tt, *J* = 1.6, 0.4 Hz, 1H), 2.54 (s, 3H), ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 144.43, 140.56, 138.97, 138.27, 128.91, 127.52, 127.34, 124.83, 121.80, 120.50, 14.78. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = -107.6 (m, 2F), -118.8 (m, 2F), -125.1 (m, 1F), -130.3 (m, 2F).

ESI-MS: positive mode, *m/z* = $[M]^+$ calcd. for $C_{20}H_{11}F_7S^+$, 416.0464; found, 416.0460.

C(H)



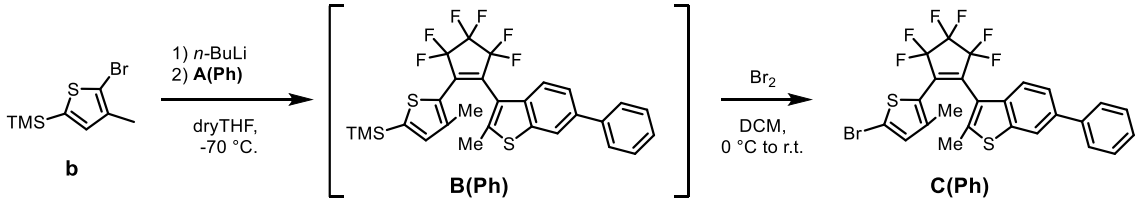
b **B(H)** **C(H)**

Starting material **b** [S3] (5.8 g, 23 mmol, 1.0 equiv.) was dissolved in dry THF (50 mL) under N_2. The reaction solution was cooled to -70℃. 1.6 M *n*-BuLi (16 mL, 26 mmol, 1.1 equiv.) was slowly added via syringe over 2 h. A dry THF solution (8 mL) containing **A(H)** [S2] (6.6 g, 19 mmol, 0.83 equiv.) was slowly added below -65℃, and the reaction solution was then gradually warmed-up to r.t. overnight. The reaction mixture was poured into sat. brine (250 mL) and extracted with ether (2×250 mL). The combined organic solutions were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude **B(H)** was subjected to chromatography on silica gel (eluent: *n*-hexane) to afford compound **B(H)** as a pale yellow oil (6.0 g, 53 %). The freshly prepared **B(H)** was dissolved in DCM (180 mL) and cooled to 0℃ by ice bath. Br_2 (2.4 g, 15 mmol, 1.2 equiv. relative to **B(H)**) was slowly added to the reaction solution, which was further stirred for 2 h at r.t. The reaction mixture was poured into combined brine (200 mL) and sat. aq. $Na_2S_2O_3$, (200 mL) which was then extracted with DCM (2×200 mL). The organic solutions were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was subjected to chromatography on silica gel (eluent: *n*-hexane) to give 3.5 g (30% two step yield) of **C(H)** as a pale yellow oil. R_f (*n*-hexane) = 0.44.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.78-7.74 (m, 1H), 7.49-7.45 (m, 1H), 7.35-7.31 (m, 2H), 6.72 (s, 1H), 2.36 (d, *J* = 0.4 Hz, 3H), 1.89 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 143.18, 141.23, 138.37, 138.12, 125.00, 124.59, 122.10, 121.87, 121.83, 119.87, 116.85, 15.76, 14.87. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = -109.7 (m, 4F), -132.4 (m, 2F).

ESI-MS: positive mode, *m/z* = ([M, ^{81}Br]$^+$ calcd. for $C_{19}H_{11}BrF_6S_2^+$) 497.9364, ([M, ^{79}Br]$^+$ calcd. for $C_{25}H_{15}BrF_6S_2^+$) 495.9385; found, 497.9362, 495.9383.

C(Ph)

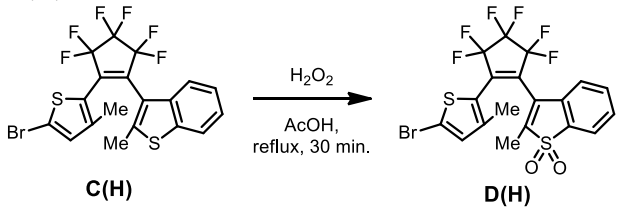


Starting material **b** [S3] (5.8 g, 23 mmol, 1.0 equiv.) was dissolved in dry THF (50 mL) under N_2. The reaction solution was cooled to -70℃. 1.6 M *n*-BuLi (16 mL, 26 mmol, 1.1 equiv.) was slowly added via syringe over 2 h. A dry THF solution (10 mL) containing **A(Ph)** (8.0 g, 19 mmol, 0.83 equiv.) was slowly added below -65℃, and the reaction solution was then gradually warmed-up to r.t. overnight. The reaction mixture was poured into sat. brine (250 mL) and extracted with ether (2×250 mL). The organic solutions were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude **B(Ph)** was subjected to chromatography on silica gel (eluent: *n*-hexane) to afford compound **B(Ph)** as a pale yellow oil (8.5 g, 64 %). The freshly prepared **B(Ph)** was dissolved in DCM (240 mL) and cooled to 0℃ by ice bath. Br_2 (3.1 g, 19 mmol, 1.3 equiv. relative to **B(Ph)**) was slowly added to the reaction solution, which was further stirred for 2 h at r.t. The reaction mixture was poured into combined brine (200 mL) and sat. aq. $Na_2S_2O_3$, which was then extracted with DCM (2×200 mL). The organic solutions were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was subjected to chromatography on silica gel (eluent: *n*-hexane) to give 4.4 g (33% two step yield) of **C(Ph)** as a white solid. R_f (*n*-hexane) = 0.27.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98-7.94 (m, 1H), 7.66-7.61 (m, 2H), 7.61-7.56 (m, 1H), 7.55-7.50 (m, 1H), 7.49-7.43 (m, 2H), 7.40-7.34 (m, 1H), 6.75 (s, 1H) , 2.38 (s, 3H) , 1.92 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 149.65, 143.53, 141.98, 140.56, 139.10, 137.97, 137.50, 137.23, 133.94, 128.88, 127.44, 127.27, 124.66, 122.06, 122.01, 120.40, 119.71, 116.93, 15.86, 15.83, 15.80, 15.00, 14.98.^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = -109.6 (m, 4F), -132.4 (m, 2F).

ESI-MS: positive mode, *m/z* = ([M, ^{81}Br]$^+$ calcd. for $C_{25}H_{15}BrF_6S_2^+$) 571.9698, ([M, ^{79}Br]$^+$ calcd. for $C_{25}H_{15}BrF_6S2^+$) 573.9677; found, 571.9699, 571.9675.

D(H)

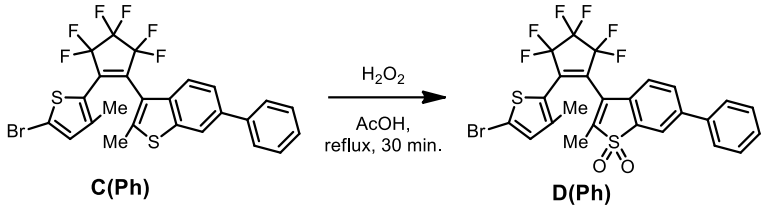


C(H) (1.5 g, 2.8 mmol, 1 equiv.) was dissolved in a acetic acid solution (30 mL). To this solution, 2.7 mL of 50% hydrogen peroxide in water (2.7 mL, excess) was added. The mixture was stirred at 130 ℃ for 30 min. After cooling to r.t., the mixture was poured into brine and stirred for 10 min. The generated precipitate was filtered and washed with water. The precipitate was subjected to silica chromatography with EtOAc/*n*-hexane (gradient: 10/90 to 40/60, v/v) to give 0.93 g (62%) of **D(H)** as a pale yellow powder. R_f (EtOAc/*n*-hexane = 1/3) = 0.40.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.80-7.76 (m, 1H), 7.57-7.49 (m, 2H), 7.14-7.10 (m, 1H), 6.84 (s, 1H), 2.11 (s, 3H), 2.06 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 143.37, 135.52, 134.68, 134.31, 134.15, 130.61, 130.44, 129.95, 126.26, 122.93, 122.89, 122.81, 122.73, 122.50, 122.33, 118.73, 16.21, 16.19, 16.16, 8.63, 8.60. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = -109.4 (m, 4F), -132.0 (m, 2F).

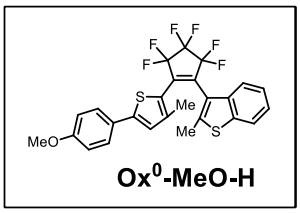
ESI-MS: positive mode, *m/z* = [M+Na]$^+$ calcd. for $C_{19}H_{11}BrF_6NaO_2S_2^+$, 550.9180; found, 550.9176.

D(Ph)



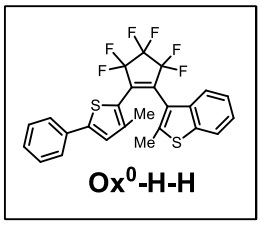
Compound **C(H)** (1.5 g, 2.6 mmol, 1 equiv.) was dissolved in a acetic acid solution (30 mL). To this solution, 50% hydrogen peroxide in water (3.0 mL, excess) was added. The mixture was stirred at 130 °C for 30 min. After cooling to r.t., the mixture was poured into brine and stirred for 10 min. The generated precipitate was filtered and washed with water. The precipitate was subjected to silica chromatography with EtOAc/*n*-hexane (gradient: 10/90 to 40/60, v/v) to give 0.81 g (51%) of **D(Ph)** as a pale yellow powder. R_f (EtOAc/*n*-hexane = 2/8) = 0.37.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.99 (d, *J* = 1.6 Hz, 1H), 7.74 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60-7.56 (m, 2H), 7.51-7.40 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H) , 6.86 (s, 1H) , 2.13 (s, 3H) , 2.09 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 143.83, 143.26, 143.08, 138.25, 136.19, 134.57, 132.35, 129.21, 128.83, 128.38, 127.03, 126.04, 123.06, 123.02, 120.83, 118.64, 16.13, 16.10, 16.08, 8.57, 8.54. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.3 (m, 4F), –132.1 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{25}H_{16}BrF_6O_2S_2^+$, 604.9674; found, 604.9662.

Ox^0-MeO-H: The synthesis was performed followed by **GP-1**.



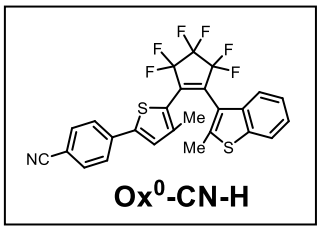
C(H) (0.30 g, 0.60 mmol) and 4-methoxyphenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (5/95, v/v) and lyophilization from dioxane gave 0.22 g (73%) of the titled compound as a pale yellow powder. R_f (*n*-hexane) = 0.10.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.77-7.73 (m, 1H), 7.56-7.52 (m, 1H), 7.40-7.28 (m, 4H), 6.8-6.83 (m, 3H), 3.81 (s, 3H), 2.38 (s, 3H), 1.89 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 160.10, 147.78, 143.19, 142.70, 138.54, 138.47, 127.29, 126.35, 125.88, 125.05, 124.58, 122.26, 122.22, 122.14, 120.96, 120.73, 114.49, 55.50, 16.24, 15.08. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = -109.5 (m, 4F), -132.4 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{26}H_{19}F_6OS_2^+$, 525.0776; found, 525.0760.

Ox^0-H-H: The synthesis was performed followed by **GP-1**.



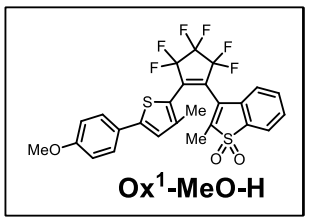
C(H) (0.30 g, 0.60 mmol) and phenylboronic acid were used in the synthesis. Purification by column chromatography with *n*-hexane and lyophilization from dioxane gave 0.21 g (71%) of the titled compound as a white powder. R_f (*n*-hexane) = 0.25.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.77-7.73 (m, 1H), 7.57-7.53 (m, 1H), 7.47-7.43 (m, 2H), 7.37-7.28 (m, 5H), 6.96 (s, 1H), 2.38 (s, 3H), 1.90 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 143.23, 142.57, 138.47, 133.09, 129.10, 128.63, 127.30, 125.97, 125.07, 124.62, 122.24, 122.19, 122.16, 120.59, 16.22, 16.19, 16.16, 15.10, 15.08. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.7 (m, 4F), –132.5 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M–F]^+$ calcd. for $C_{25}H_{16}F_5S_2^+$, 475.0608; found, 475.0595.

Ox^0-CN-H: The synthesis was performed followed by **GP-1**.



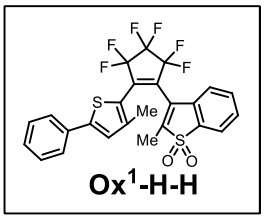
C(H) (0.45 g, 0.90 mmol) and 4-cyanophenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 0/100 to 15/85, v/v) and lyophilization from dioxane gave 0.37 g (79%) of the titled compound as a white powder. R_f (EtOAc/*n*-hexane) = 0.20.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.77-7.73 (m, 1H), 7.63-7.59 (m, 2H), 7.55-7.50 (m, 3H), 7.37-7.29 (m, 2H), 7.05 (s, 1H), 2.38 (s, 3H), 1.91 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 144.77, 143.33, 142.74, 138.47, 138.30, 137.26, 132.88, 129.01, 126.23, 125.16, 124.74, 123.95, 122.23, 122.11, 122.06, 120.23, 118.61, 111.75, 16.10, 16.07, 16.05, 15.12, 15.10. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.6 (m, 4F), –132.4 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+Na]^+$ calcd. for $C_{26}H_{15}F_6NNaS_2^+$, 542.0442; found, 542.0428.

Ox^1-MeO-H: The synthesis was performed followed by **GP-1**.



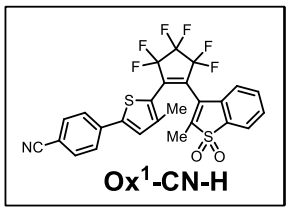
D(H) (0.30 g, 0.57 mmol) and 4-methoxyphenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 10/90 to 30/70, v/v) gave 0.37 g (79%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 1/3) = 0.20.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.79-7.75 (m, 1H), 7.54-7.46 (m, 2H), 7.46-7.40 (m, 2H), 7.18-7.13 (m, 1H), 6.95 (s, 1H), 6.91-6.86 (m, 2H), 3.82 (s, 3H), 2.15 (s, 3H), 2.14 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 160.55, 149.72, 144.32, 143.17, 135.65, 134.08, 130.39, 130.22, 127.52, 127.07, 126.99, 125.25, 123.04, 123.00, 122.14, 114.66, 55.53, 16.70, 16.67, 16.63, 8.63, 8.59. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –108.9 (m, 4F), –131.8 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{26}H_{19}F_6O_3S_2^+$, 557.0674; found, 557.0663.

Ox^1-H-H: The synthesis was performed followed by **GP-1**.



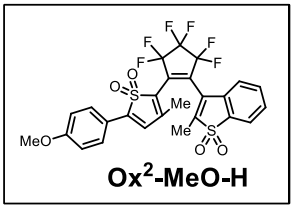
D(H) (0.30 g, 0.57 mmol) and phenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 20/80, v/v) gave 0.21 g (79%) the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 1/3) = 0.35.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.79-7.76 (m, 1H), 7.54-7.46 (m, 4H), 7.40-7.30 (m, 3H), 7.18-7.14 (m, 1H), 7.06 (s, 1H), 2.16 (s, 3H), 2.14 (d, J = 0.9 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 149.51, 144.08, 143.23, 135.63, 134.09, 132.51, 130.27, 129.26, 129.20, 127.94, 126.88, 126.15, 123.02, 122.98, 122.18, 16.63, 16.60, 16.57, 8.65, 8.62. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –108.6 (m, 4F), –131.9 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{25}H_{17}F_6O_2S_2^+$, 527.0569; found, 527.0564.

Ox^1-CN-H: The synthesis was performed followed by **GP-1**.



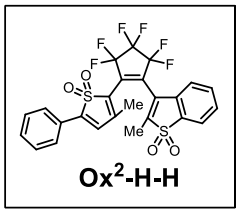
D(H) (0.30 g, 0.57 mmol) and 4-cyanophenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 10/90 to 30/70, v/v) gave 0.18 g (58%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 1/3) = 0.20.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.80-7.76 (m, 1H), 7.67-7.62 (m, 2H), 7.61-7.56 (m, 2H), 7.56-7.48 (m, 2H), 7.18-7.13 (m, 2H), 2.17 (s, 3H), 2.15 (d, J = 0.5 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 146.42, 144.06, 143.43, 136.68, 135.59, 134.17, 133.03, 130.44, 130.11, 129.58, 126.49, 122.94, 122.91, 122.31, 118.45, 112.37, 16.51, 16.48, 16.45, 8.66, 8.63. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.4 (m, 4F), –131.9 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{26}H_{16}F_6NO_2S_2^+$, 552.0521; found, 552.0506.

Ox^2-MeO-H: The synthesis was performed followed by **GP-2**.



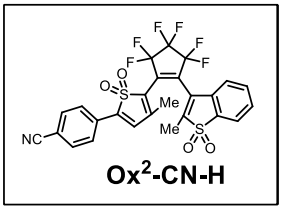
Ox^0-MeO-H (0.18 g, 0.34 mmol) was used in as starting material. The reaction time was 24 h. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 30/70, v/v) and lyophilization from dioxane gave 59 mg (29%) of the titled compound as an orange powder. R_f (EtOAc/*n*-hexane = 2/3) = 0.20.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.77-7.74 (m, 1H), 7.64-7.60 (m, 2H), 7.57 (td, *J* = 7.6, 1.2 Hz, 1H), 7.50 (td, *J* = 7.6, 1.0 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 6.95-6.90 (m, 2H), 6.53 (s, 1H), 3.83 (s, 3H), 2.24 (s, 3H), 2.06 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.47, 146.23, 145.03, 143.60, 135.17, 134.25, 130.39, 130.25, 129.14, 125.56, 123.44, 123.39, 123.37, 122.17, 119.64, 118.31, 115.18, 55.67, 18.25, 18.23, 18.21, 8.96, 8.93. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.7 (m, 4F), –131.9 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{26}H_{19}F_6O_5S_2^+$, 589.0573; found, 589.0558.

Ox^2-H-H: The synthesis was performed followed by **GP-2**.



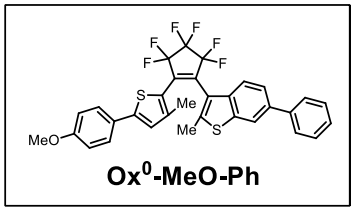
Ox^0-H -H (0.15 g, 0.30 mmol) was used in as starting material. The reaction time was 24 h. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 30/70, v/v) and lyophilization from dioxane gave 47 mg (28%) the titled compound as a yellow powder. R_f (EtOAc/*n*-hexane = 2/3) = 0.40.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.78-7.74 (m, 1H), 7.68-7.64 (m, 2H), 7.58 (td, *J* = 7.6, 1.2 Hz, 1H), 7.51 (td, *J* = 7.6, 1.0 Hz, 1H), 7.48-7.39 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 2.24 (s, 3H), 2.08 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 145.40, 145.08, 143.67, 135.15, 134.25, 131.74, 130.44, 130.22, 130.20, 129.55, 127.26, 125.75, 125.38, 124.55, 123.36, 123.33, 122.44, 122.21, 30.46, 18.13, 18.11, 18.09, 8.96, 8.93. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.3 (m, 4F), –131.9 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{25}H_{17}F_6O_4S_2^+$, 559.0467; found, 559.0455.

Ox^2-CN-H: The synthesis was performed followed by **GP-2**.



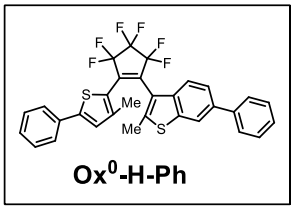
Ox^0-CN-H (0.28 g, 0.54 mmol) was used in as starting material. The reaction time was 72 h. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 35/65, v/v) and lyophilization from dioxane gave 87 mg (27%) of the titled compound as a yellow powder. R_f (EtOAc/*n*-hexane = 2/3) = 0.15.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.79-7.69 (m, 5H), 7.59 (td, *J* = 7.6, 1.3 Hz, 1H), 7.52 (td, *J* = 7.6, 1.0 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 6.84 (s, 1H), 2.23 (d, *J* = 0.9 Hz, 3H), 2.13 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 144.60, 143.81, 143.00, 135.13, 134.26, 133.12, 130.55, 130.17, 129.77, 127.66, 125.63, 125.09, 123.23, 123.21, 122.30, 117.81, 114.92, 18.04, 18.02, 18.00, 8.95, 8.92. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.4 (m, 4F), –132.0 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{26}H_{16}F_6NO_4S_2^+$, 584.0419; found, 584.0414.

Ox^0-MeO-Ph: The synthesis was performed followed by **GP-1**.



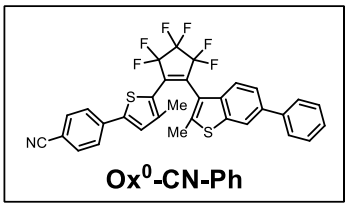
C(Ph) (0.30 g, 0.52 mmol) and 4-methoxyphenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 15/85, v/v) and lyophilization from dioxane gave 0.22 g (70%) of the titled compound as a yellow powder. R_f (EtOAc/*n*-hexane = 1/9) = 0.27.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97-7.94 (m, 1H), 7.65-7.61 (m, 2H), 7.60-7.57 (m, 2H), 7.48-7.42 (m, 2H), 7.41-7.33 (m, 3H), 6.89-6.83 (s, 3H), 3.81 (s, 3H), 2.38 (s, 3H), 1 .92 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 159.96, 140.66, 139.04, 137.75, 128.85, 127.26, 126.24, 125.72, 124.55, 124.04, 122.29, 122.24, 120.30, 119.72, 114.35, 77.20, 55.36, 16.17, 15.03. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.2 (m, 4F), –132.4 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{32}H_{23}F_6OS_2^+$, 601.1089; found, 601.1059.

Ox^0-MeO-Ph: The synthesis was performed followed by **GP-1**.



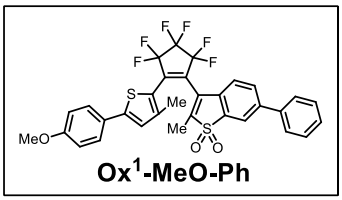
C(Ph) (0.30 g, 0.52 mmol) and phenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 15/85, v/v) and lyophilization from dioxane gave 0.24 g (80%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 1/9) = 0.40.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97-7.94 (m, 1H), 7.65-7.60 (m, 2H), 7.60-7.55 (m, 2H), 7.49-7.42 (m, 4H), 7.39-7.27 (m, 4H), 6.98 (s, 1H), 2.39 (s, 3H), 1.93 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 147.58, 143.43, 142.47, 140.62, 139.04, 137.79, 137.45, 132.92, 128.95, 128.84, 128.49, 127.37, 127.25, 127.18, 125.82, 124.57, 122.25, 122.20, 121.76, 120.31, 120.28, 16.13, 16.10, 16.08, 15.05, 15.03. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.6 (m, 4F), –132.4 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M]^+$ calcd. for $C_{31}H_{20}F_6S_2^+$, 570.0905; found, 570.0905.

Ox^0-CN-Ph: The synthesis was performed followed by **GP-1**.



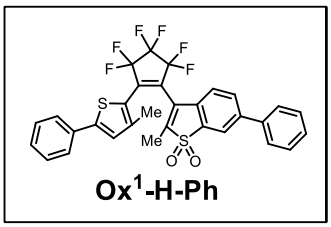
C(Ph) (0.30 g, 0.60 mmol) and 4-cyanophenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95, 30/70) and lyophilization from dioxane gave 0.18 g (58%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 2/8) = 0.33.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.96 (s, 1H), 7.66-7.59 (m, 4H), 7.59-7.51 (m, 4H), 7.49-7.42 (m, 2H), 7.39-7.31 (m, 1H), 7.07 (s, 1H), 2.40 (s, 3H), 1.94 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 144.68, 143.52, 142.65, 140.45, 13 9.05, 137.92, 137.25, 137.10, 132.74, 128.89, 127.48, 127.20, 126.10, 124.64, 123.77, 122.13, 122.0 9, 120.33, 119.93, 118.45, 111.62, 16.02, 15.99, 15.97, 15.09, 15.06. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.4 (m, 4F), –132.4 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{32}H_{20}F_6NS_2^+$, 596.0936; found, 596.0921.

Ox^1-MeO-Ph: The synthesis was performed followed by **GP-1**.



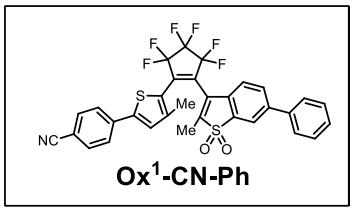
D(Ph) (0.30 g, 0.50 mmol) and 4-methoxyphenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 30/70, v/v) and lyophilization from dioxane gave 0.20 g (64%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 3/7) = 0.43.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.99 (d, *J* = 1.6 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59-7.54 (m, 2H), 7.50-7.38 (m, 5H), 7.21 (m, 1H), 6.97 (s, 1H),), 6.91-6.86 (m, 2H), 3.81 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 160.39, 143.57, 142.89, 138.37, 136.32, 132.31, 129.15, 128.71, 127.39, 127.01, 126.87, 125.11, 123.13, 120.64, 114.50, 55.38, 16.58, 8.54. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –108.6 (m, 4F), –132.1 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{32}H_{23}F_6O_3S_2^+$, 633.0987; found, 633.0968.

Ox[1]-H-Ph: The synthesis was performed followed by **GP-1**.



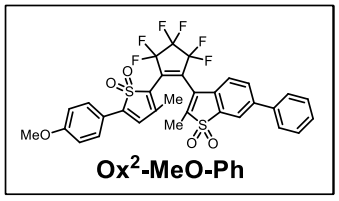
D(Ph) (0.30 g, 0.50 mmol) and 4-methoxyphenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 30/70, v/v) and lyophilization from dioxane gave 0.24 g (80%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 3/7) = 0.50.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.01-7.97 (m, 1H), 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59-7.54 (m, 2H), 7.54-7.49 (m, 2H), 7.49-7.29 (m, 2H), 7.22 (s, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 2.18 (s, 3H), 2.16 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 149.39, 143.97, 143.63, 142.96, 138.33, 136.29, 132.36, 132.31, 129.16, 129.10, 129.04, 128.73, 127.82, 127.01, 126.65, 126.01, 123.15, 123.11, 120.68, 16.54, 16.51, 16.49, 8.58, 8.55. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –108.9 (m, 4F), –132.0 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{31}H_{21}F_6O_2S_2^+$, 603.0882; found, 603.0874.

Ox[1]-CN-Ph: The synthesis was performed followed by **GP-1.**



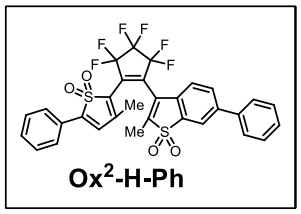
D(Ph) (0.30 g, 0.50 mmol) and 4-cyanophenylboronic acid were used in the synthesis. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 5/95 to 30/70, v/v) and lyophilization from dioxane gave 0.19 g (61%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 3/7) = 0.33.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.99 (d, *J* = 1.6 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67-7.62 (m, 2H), 7.62-7.53 (m, 4H), 7.50-7.38 (m, 3H), 7.21 (d, *J* = 8.0 Hz,1H) , 7.18 (s, 1H) , 2.20 (s, 3H) , 2.15 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 146.30, 143.96, 143.78, 143.14, 138.16, 136.51, 136.25, 132.86, 132.33, 129.45, 129.21, 128.85, 128.52, 126.96, 126.34, 126.23, 123.06, 123.02, 122.38, 120.77, 118.28, 112.20, 16.41, 16.38, 16.35, 8.59, 8.56. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.0 (m, 4F), –132.3 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{32}H_{20}F_6NO_2S_2^+$, 628.0834; found, 628.0809.

Ox[2]-MeO-Ph: The synthesis was performed followed by **GP-2**.



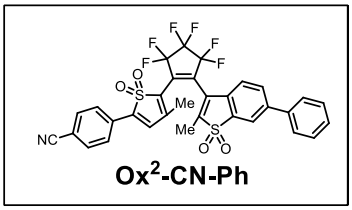
Ox[0]-MeO-Ph (0.15 g, 0.25 mmol) was used in as starting material. The reaction time was 24 h. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 10/90 to 40/60, v/v) and lyophilization from dioxane gave 95 g (57%) of the titled compound as an orange powder. R_f (EtOAc/*n*-hexane = 40/60) = 0.33.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (dd, *J* = 1.6, 0.4 Hz, 1H), 7.77 (dd, *J* = 2.0, 8.4 Hz, 1H),7.66-7.61 (m, 2H), 7.59-7.54 (m, 2H), 7.49-7.38 (m, 3H), 7.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.96 –6.90 (m, 2H), 6.55 (s, 1H), 3.83 (s, 3H), 2.27 (d, , *J* = 1.2 Hz, 3H), 2.09 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.32, 146.12, 144.90, 143.74, 143 .32, 138.30, 135.84, 132.45, 129.16, 129.01, 128.75, 128.66, 127.02, 125.35, 123.52, 123.50, 123.36 , 120.67, 119.50, 118.16, 115.03, 55.51, 18.14, 8.91, 8.87. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.3 (m, 4F), –132.2 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{32}H_{23}F_6O_5S_2^+$, 665.0886; found, 665.0877.

Ox^2-H-Ph: The synthesis was performed followed by **GP-2**.



Ox^0-H-Ph (0.15 g, 0.26 mmol) was used in as starting material. The reaction time was 24 h. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 10/90 to 40/60, v/v) and lyophilization from dioxane gave 63 mg (38%) of the titled compound as a yellow powder. R_f (EtOAc/*n*-hexane = 40/60) = 0.33.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, *J* = 1.6 Hz, 1H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70-7.65 (m, 2H), 7.59-7.54 (m, 2H), 7.49-7.38 (m, 6H), 7.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.71 (s, 1H), 2.27 (d, *J* =1.2 Hz, 3H), 2.11 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 145.27, 144.96, 143.81, 143.38, 138.27, 135.82, 132.45, 131.59, 129.40, 129.17, 128.78, 128.63, 127.13, 127.02, 125.61, 125.17, 124.48, 123.48, 123.46, 122.29, 120.72, 18.04, 18.02, 18.00, 8.91, 8.88. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.4 (m, 4F), –132.2 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{31}H_{21}F_6O_4S_2^+$, 635.0780; found, 635.0771.

Ox^2-CN-Ph: The synthesis was performed followed by **GP-2**.



Ox^0-CN-Ph (0.15 g, 0.25 mmol) was used in as starting material. The reaction time was 72 h. Purification by column chromatography with mixed eluent of EtOAc/*n*-hexane (gradient: 10/90 to 40/60, v/v) and lyophilization from dioxane gave 47 m (28%) of the titled compound as a pale yellow powder. R_f (EtOAc/*n*-hexane = 40/60) = 0.17.
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.99 (d, *J* = 1.6 Hz, 1H), 7.80-7.75 (m, 3H), 7.75-7.69 (m, 2H), 7.59-7.55 (m, 2H), 7.50-7.39 (m, 3H), 7.29 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.85 (s, 1H), 2.26 (s, 3H), 2.15 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 144.46, 143.94, 143.51, 142.88, 138.16, 135.81, 132.98, 132.44, 129.61, 129.23, 128.88, 128.56, 127.52, 126.99, 125.58, 125.46, 124.89, 123.36, 120.79, 117.66, 114.80, 17.95, 17.93, 17.91, 8.91, 8.88. ^{19}F-NMR (367 MHz, $CDCl_3$): δ (ppm) = –109.4 (m, 4F), –132 (m, 2F).
ESI-MS: positive mode, *m/z* = $[M+H]^+$ calcd. for $C_{32}H_{20}F_6NO_4S_2^+$, 660.0732; found, 660.0720.

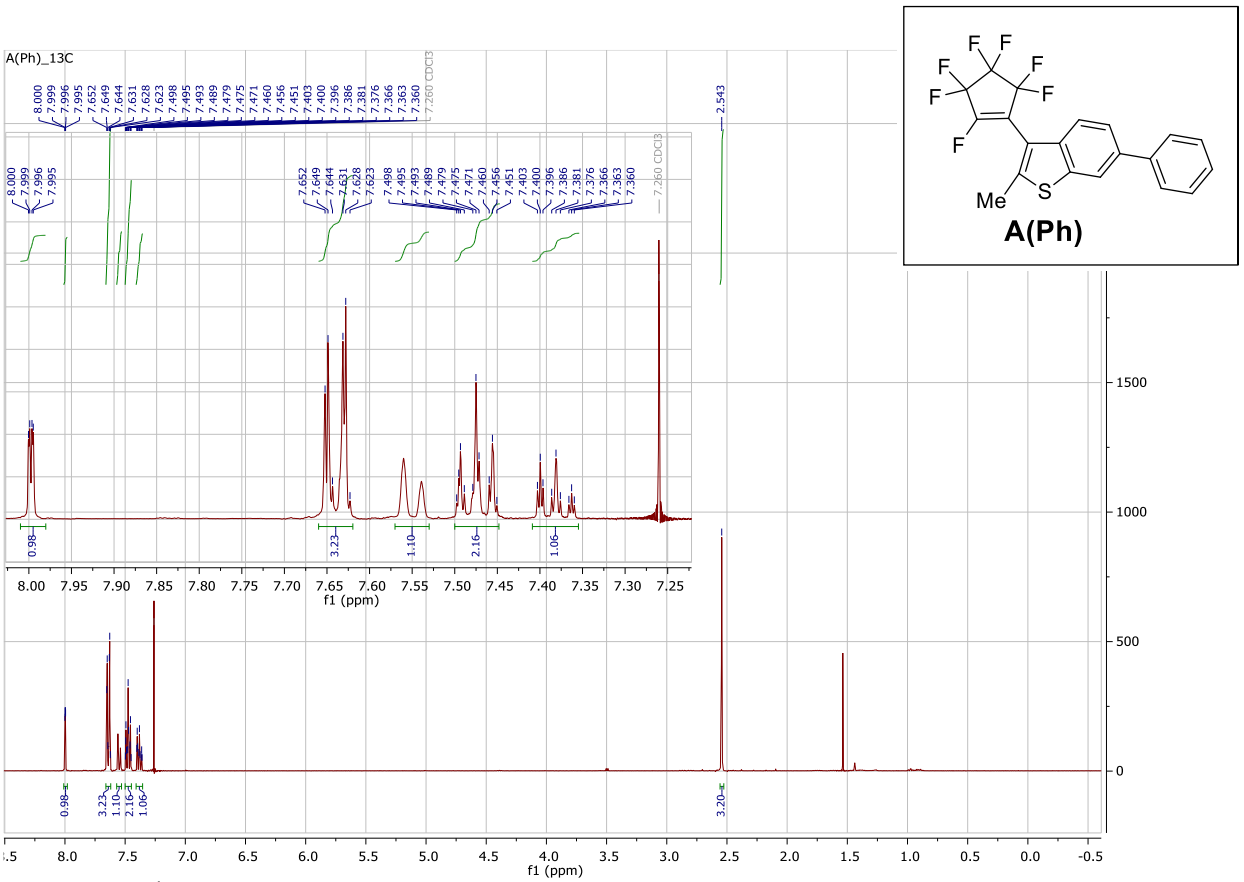


Figure S1a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **A(Ph)**.

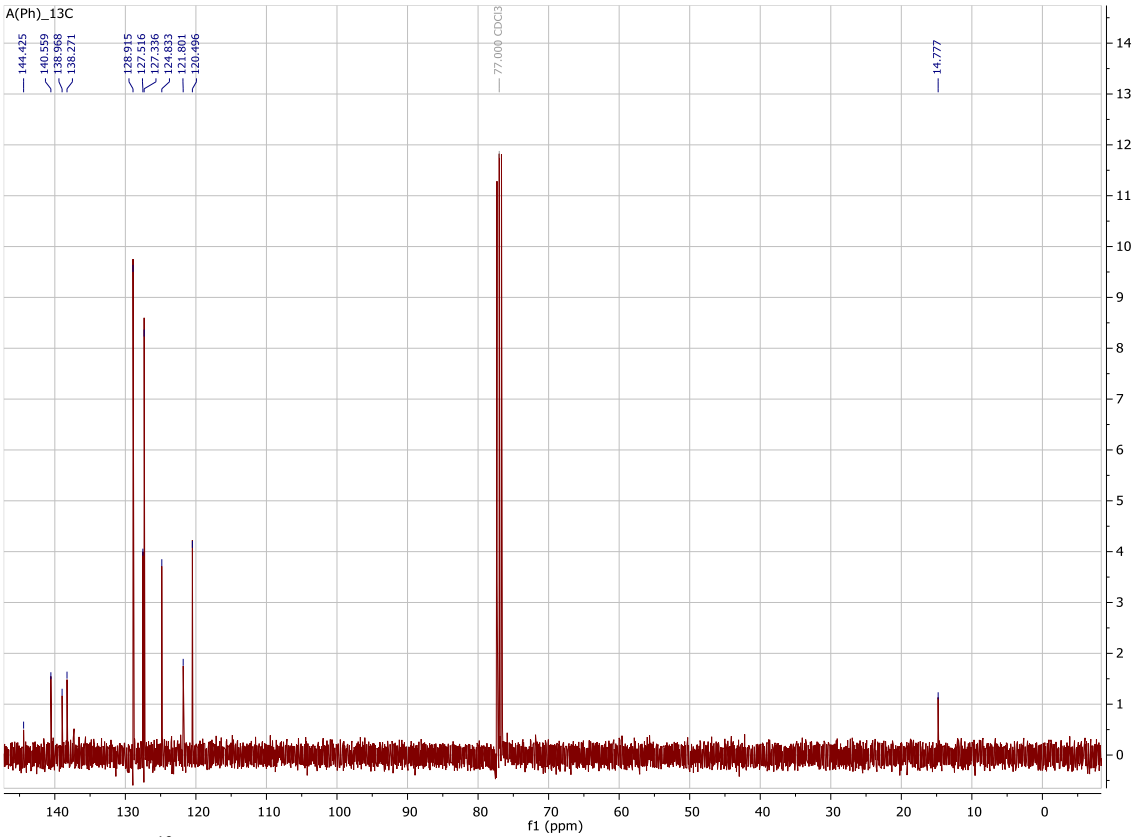


Figure S1b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **A(Ph)**.

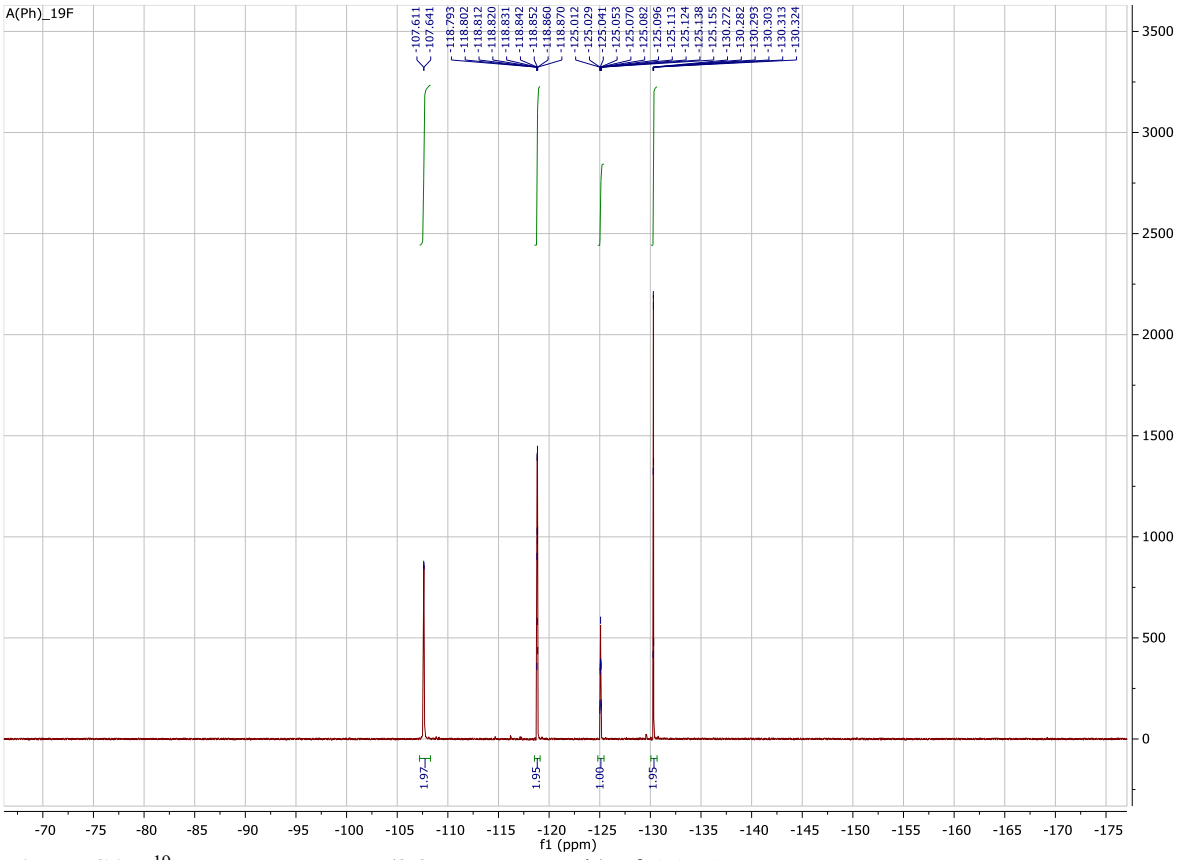


Figure S1c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **A(Ph)**.

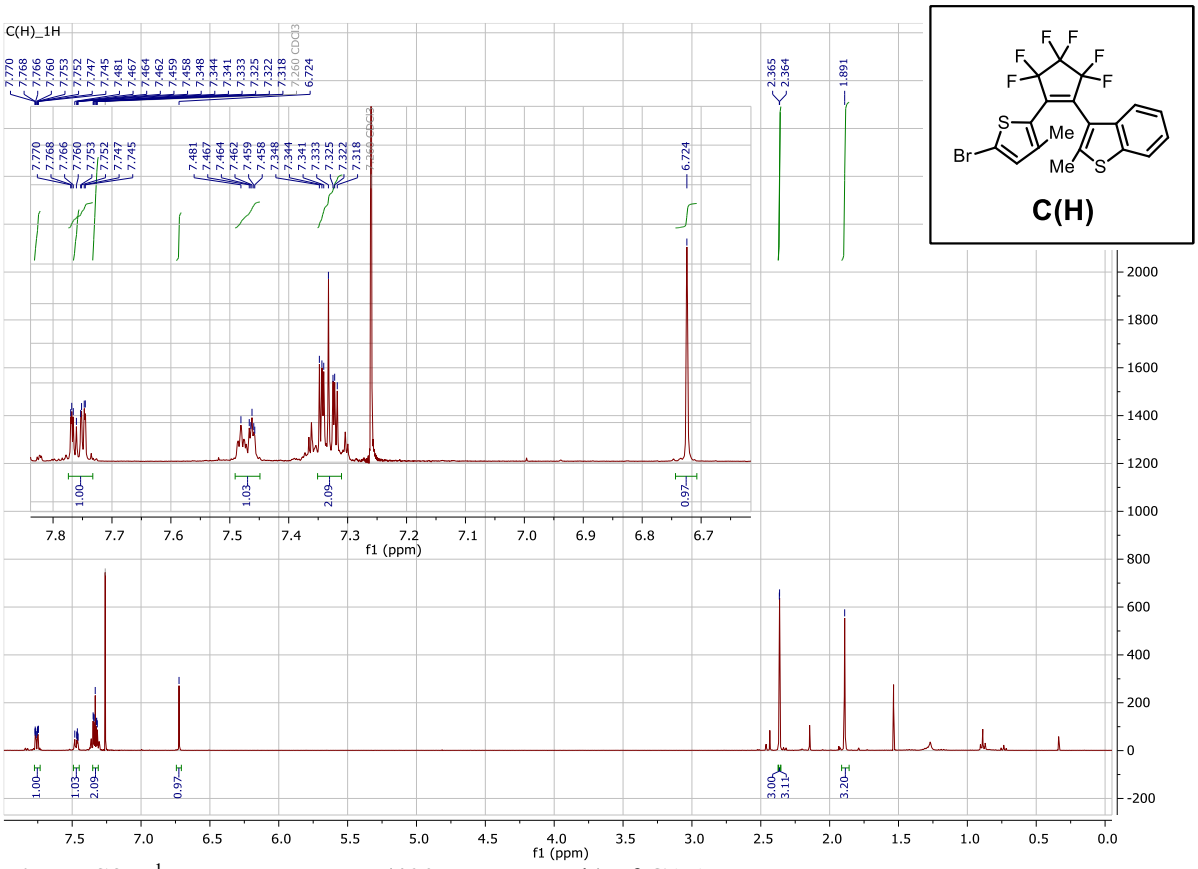


Figure S2a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **C(H)**.

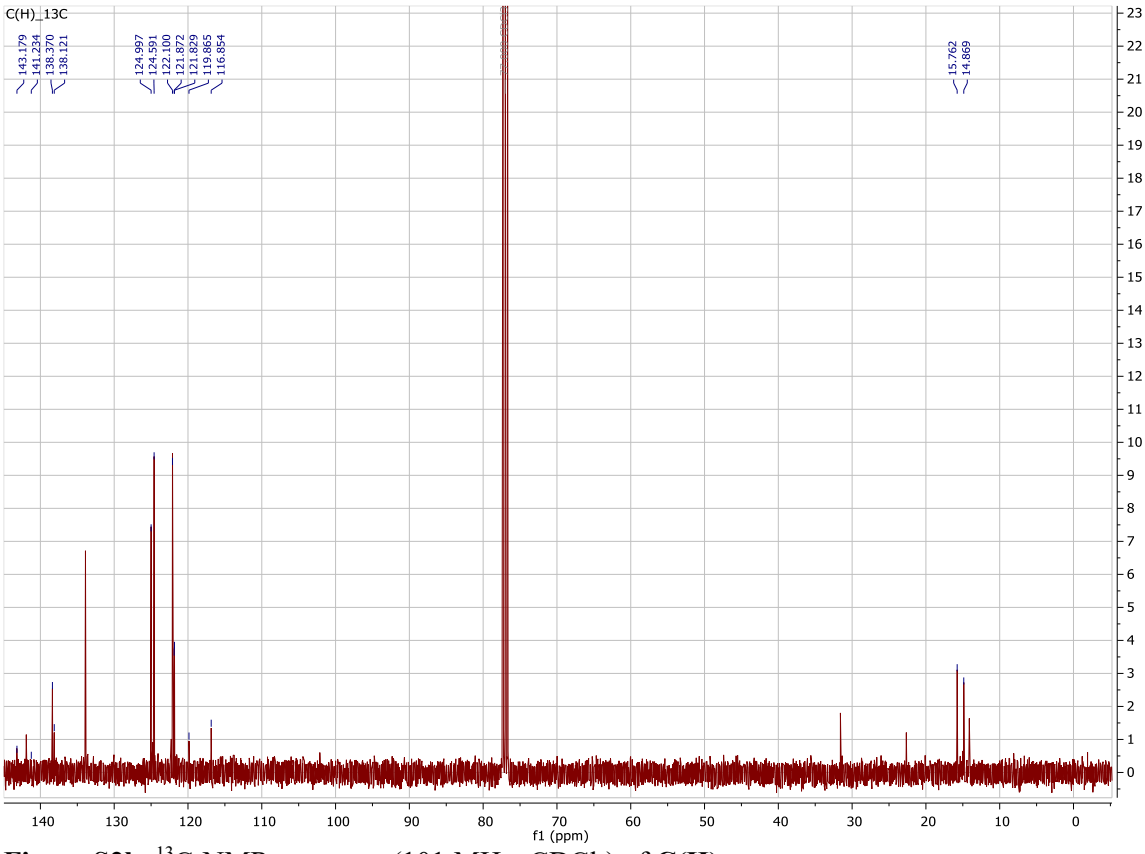


Figure S2b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **C(H)**.

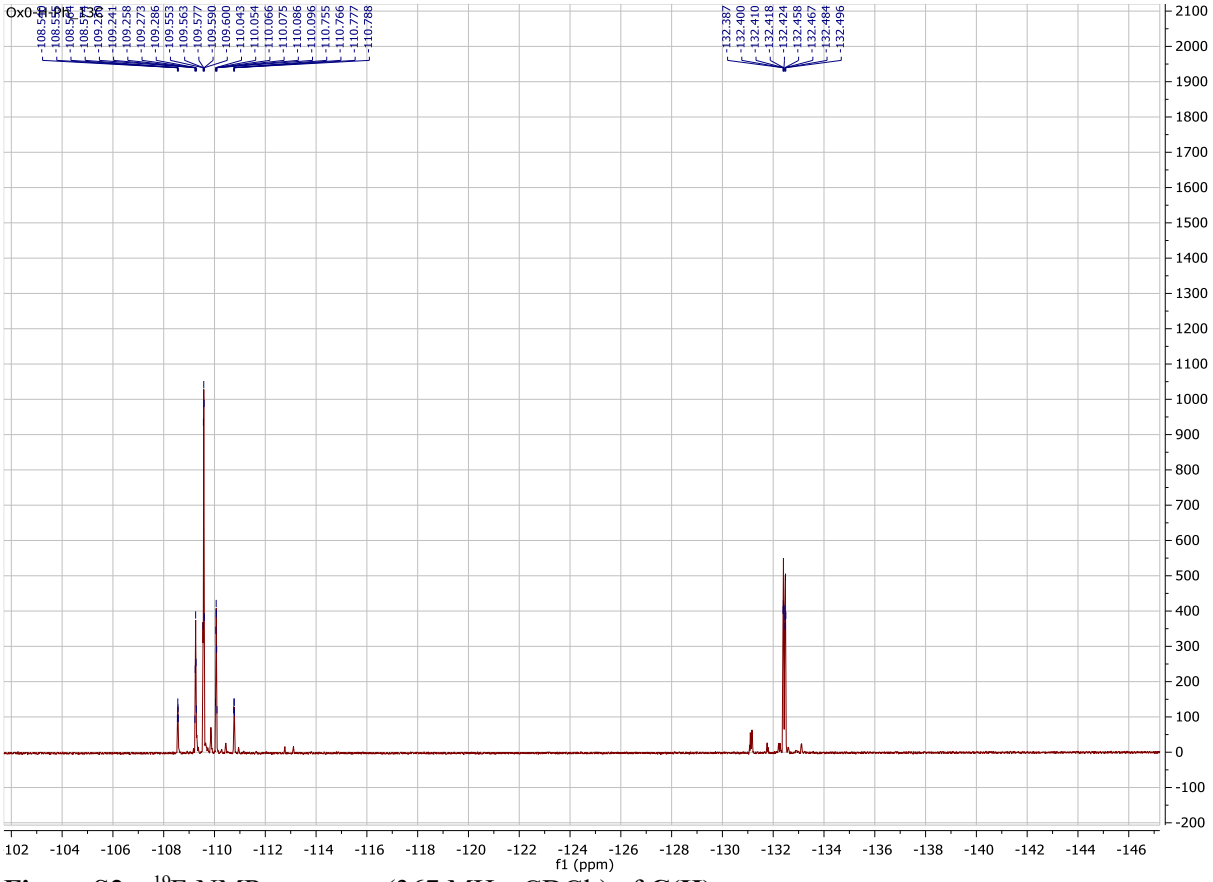


Figure S2c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **C(H)**.

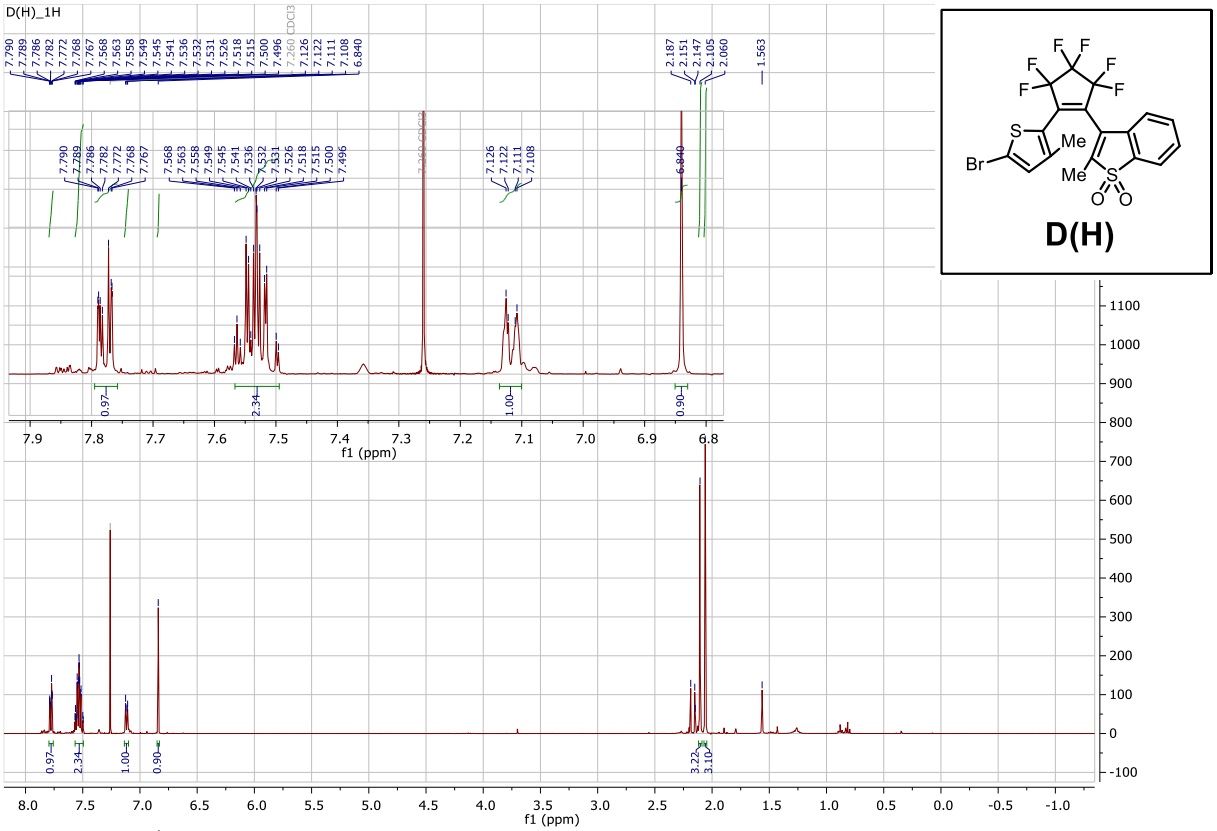


Figure S3a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **D(H)**.

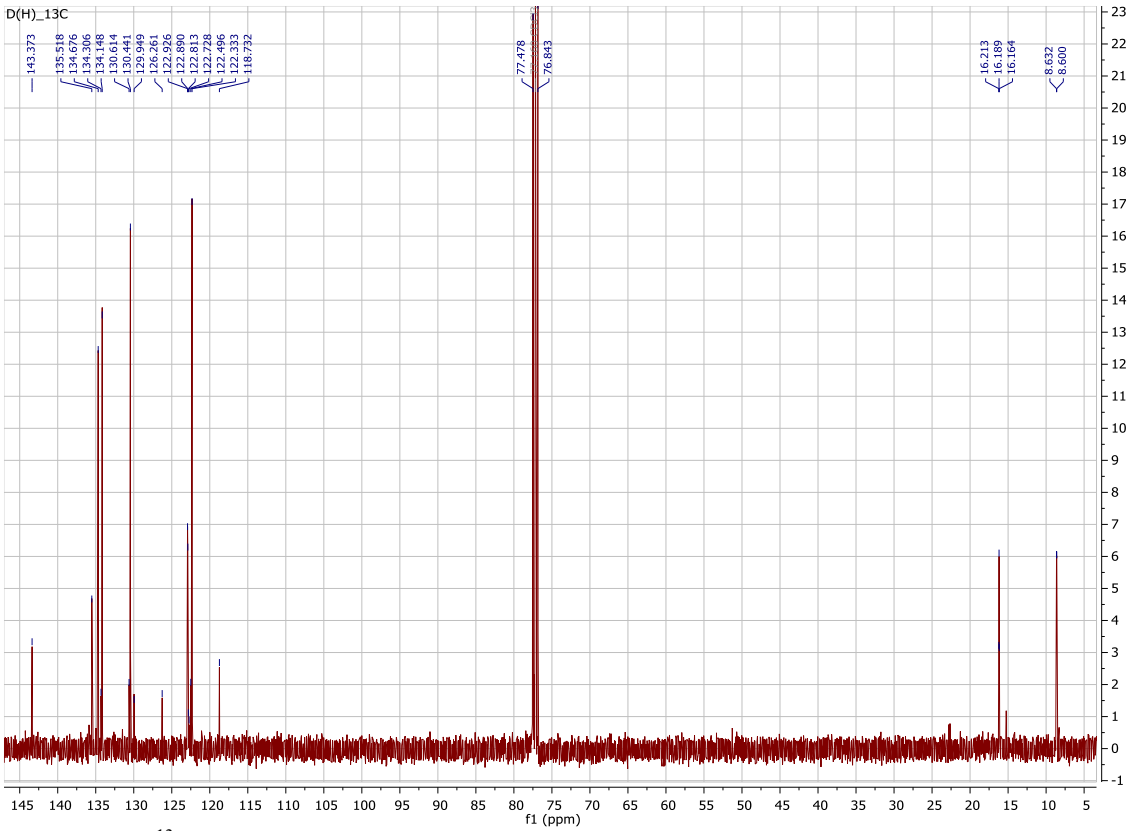


Figure S3b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **D(H)**.

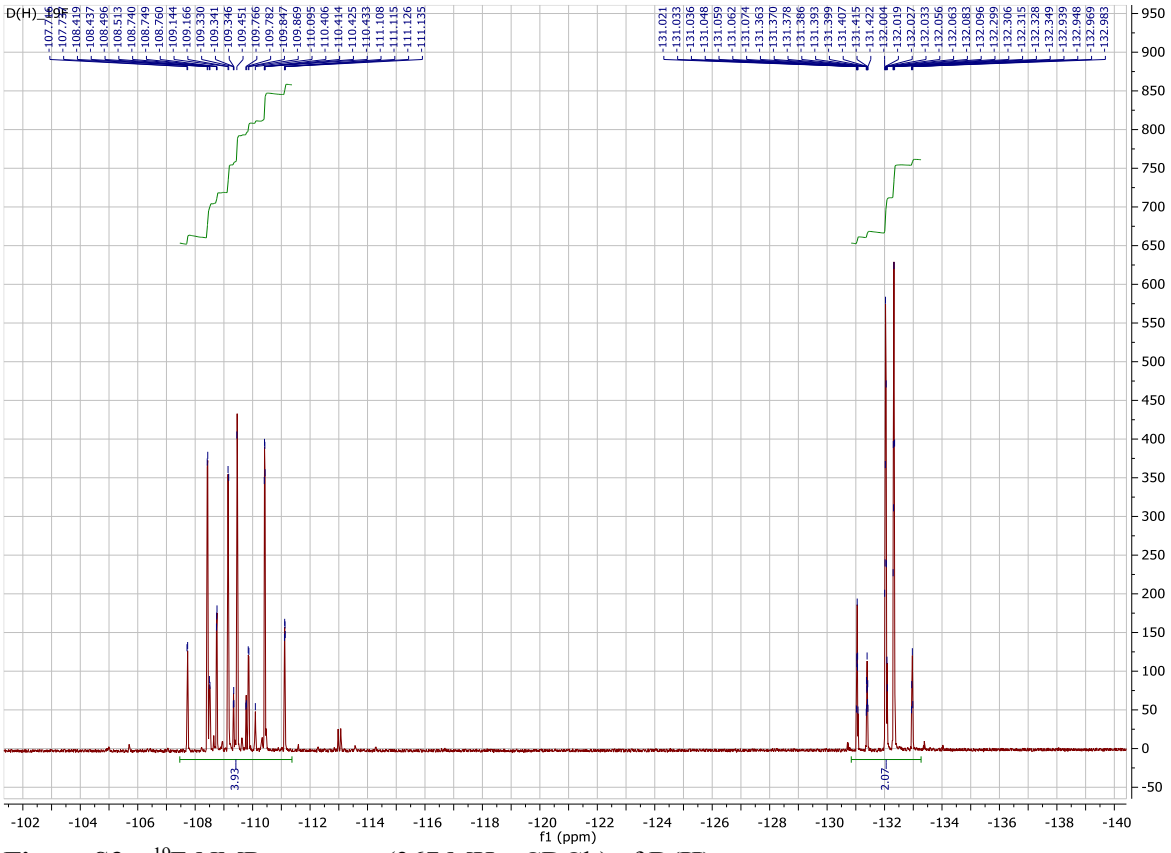


Figure S3c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **D(H)**.

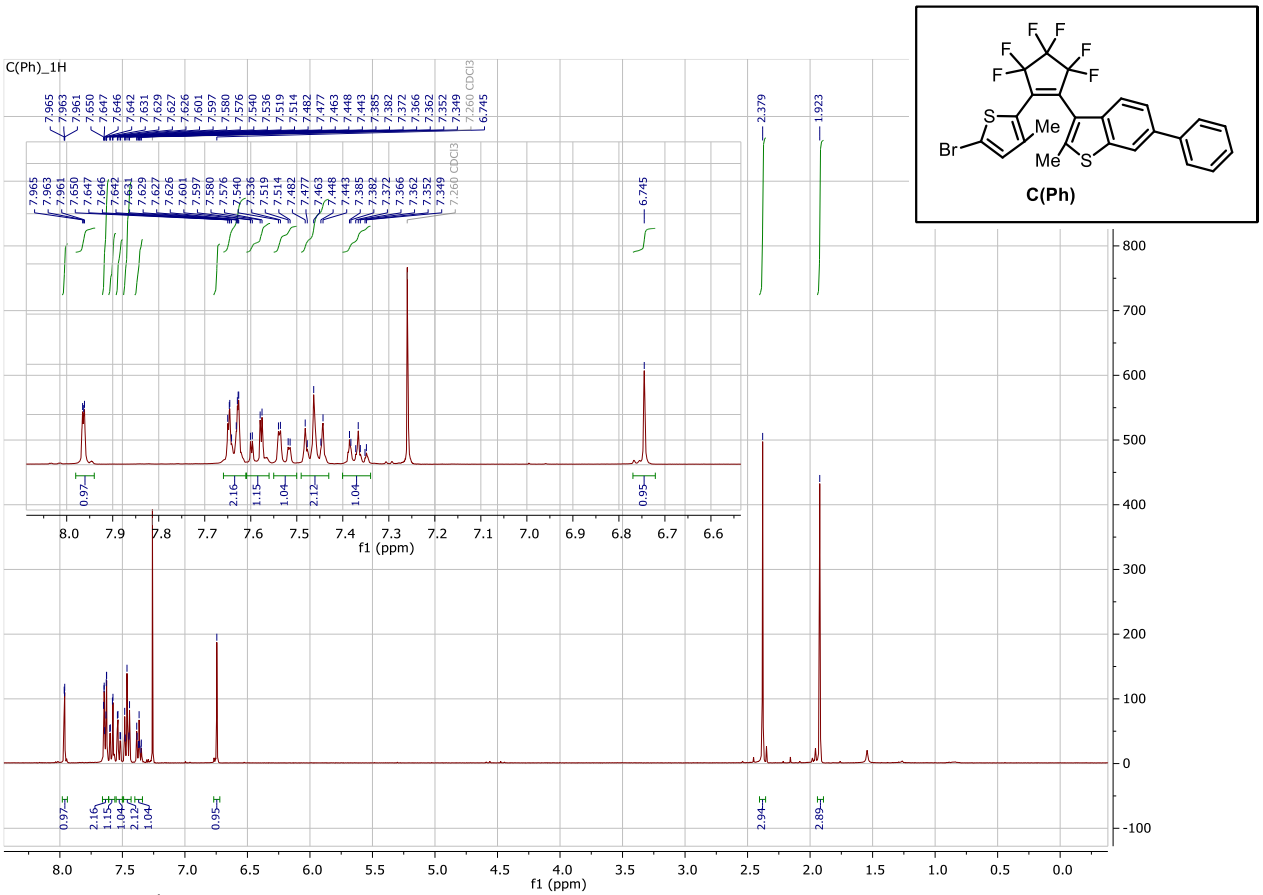


Figure S4a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **C(Ph)**.

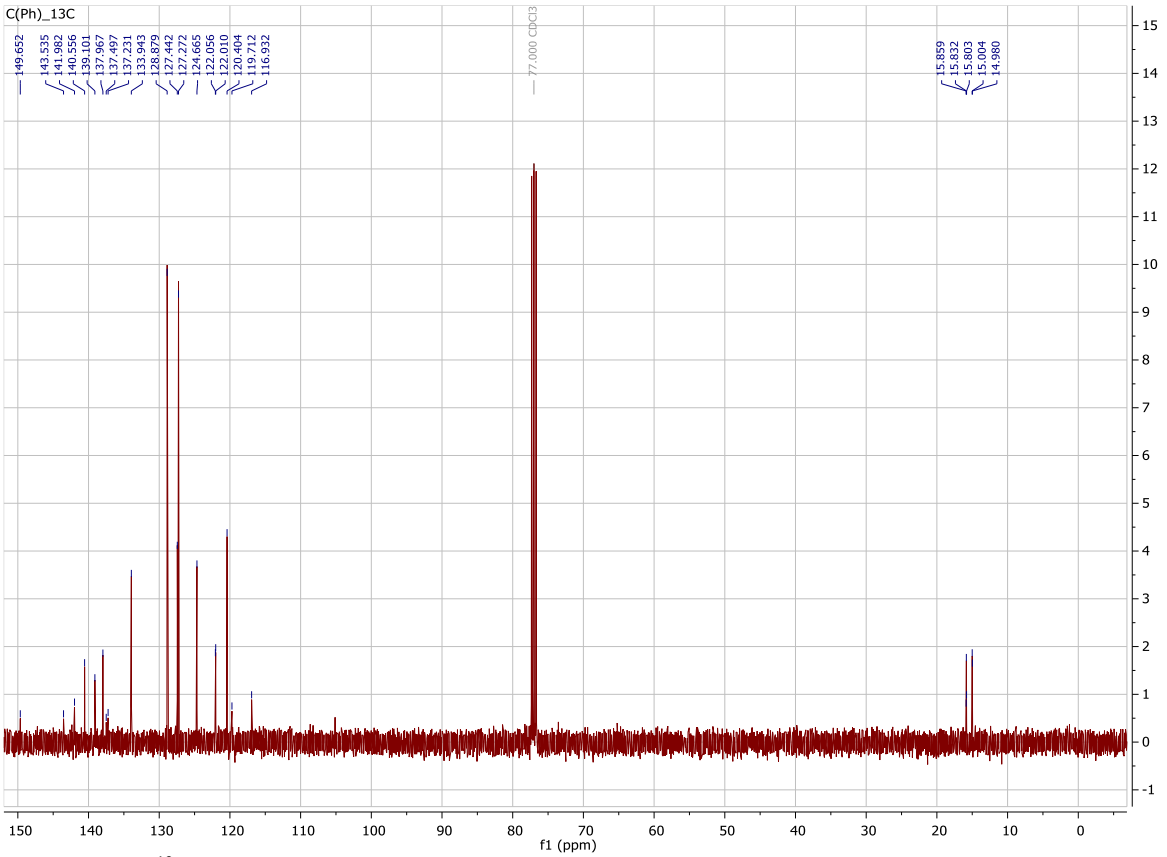


Figure S4b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **C(Ph)**.

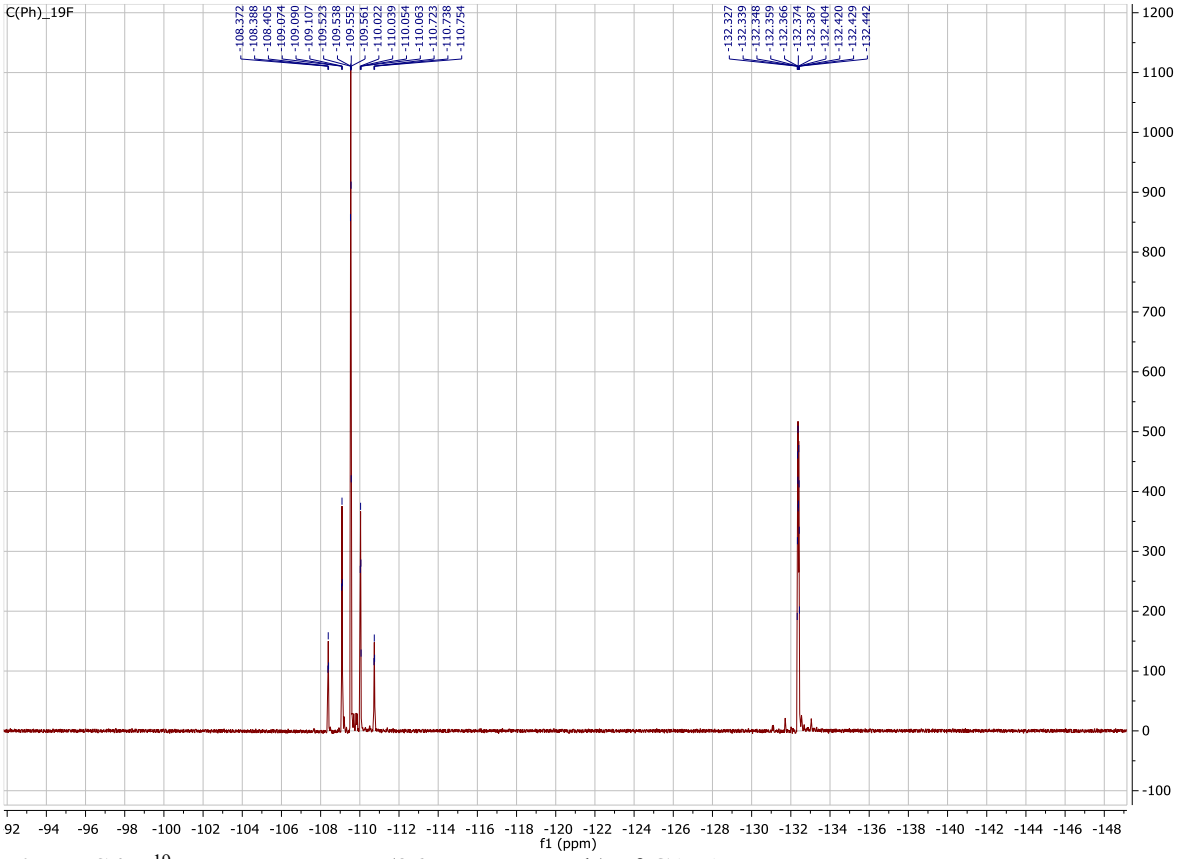


Figure S4c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **C(Ph)**.

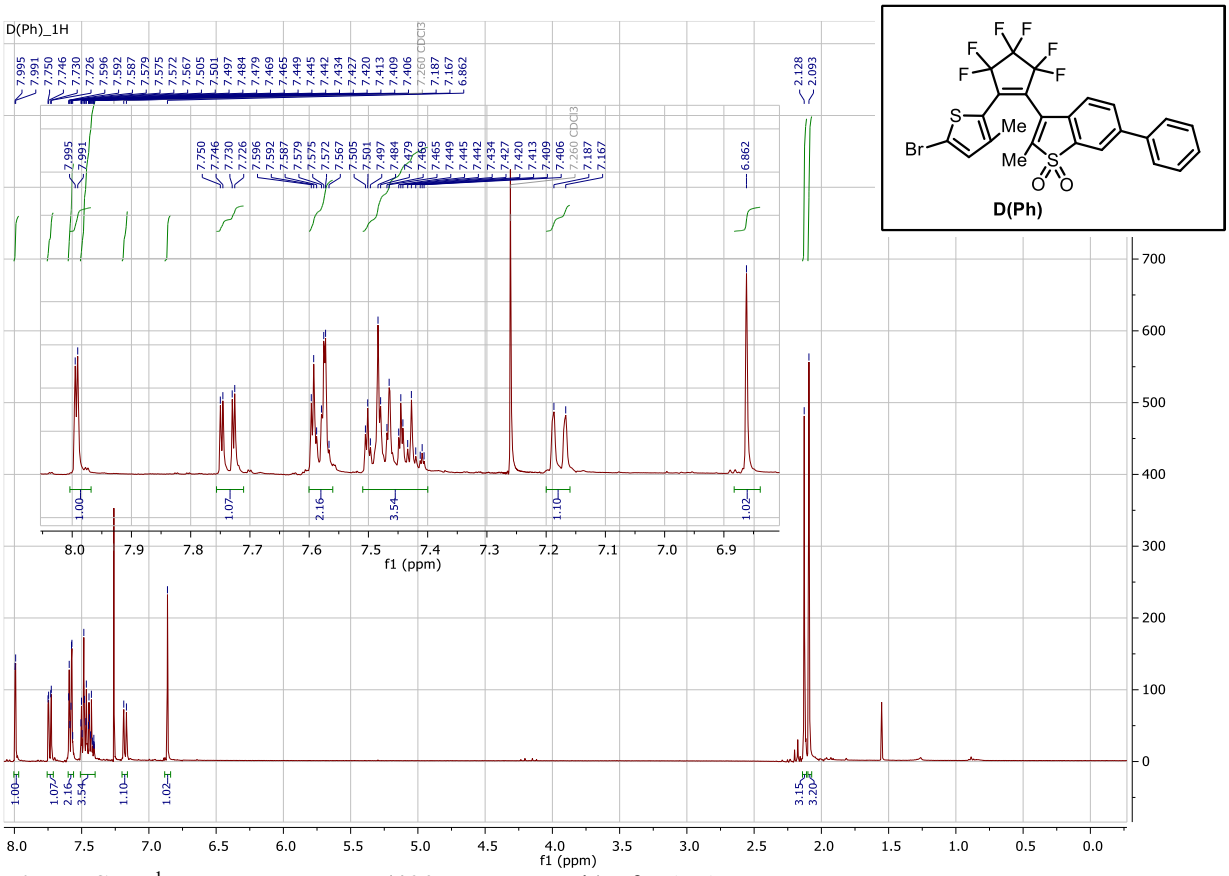


Figure S5a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **D(Ph)**.

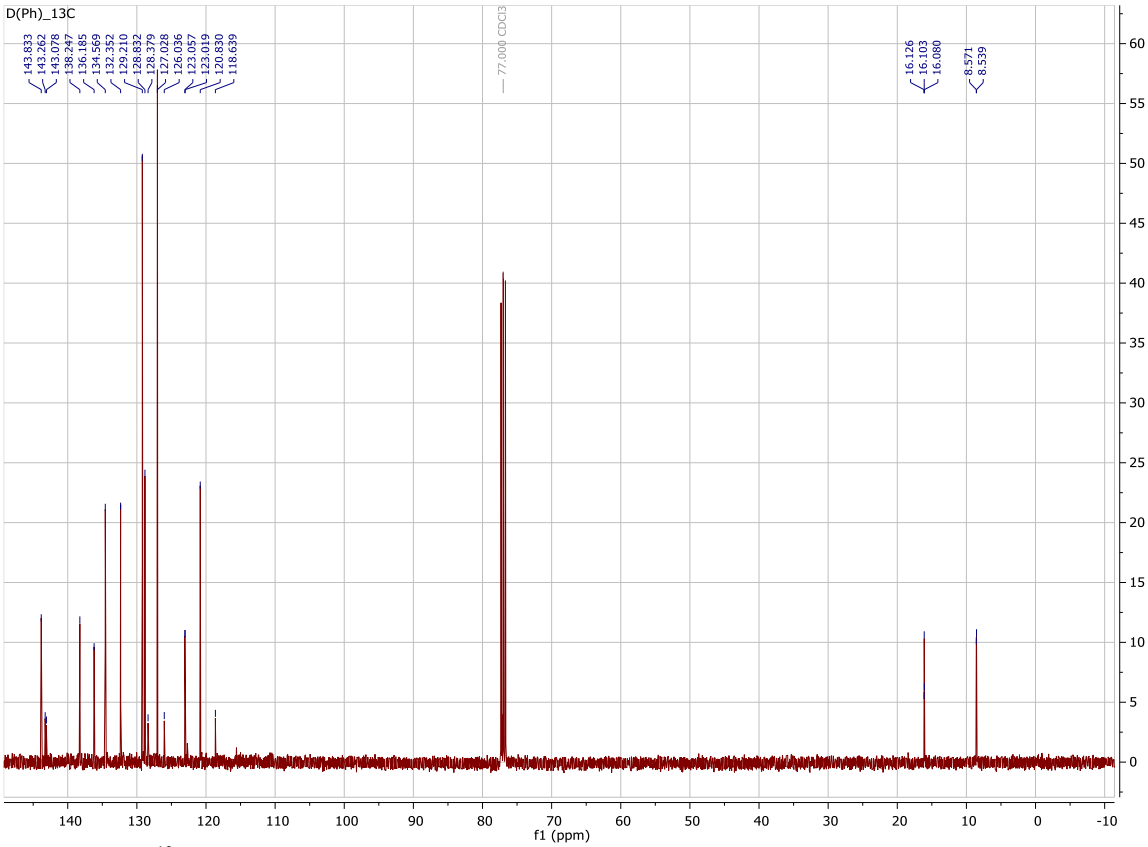


Figure S5b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **D(Ph)**.

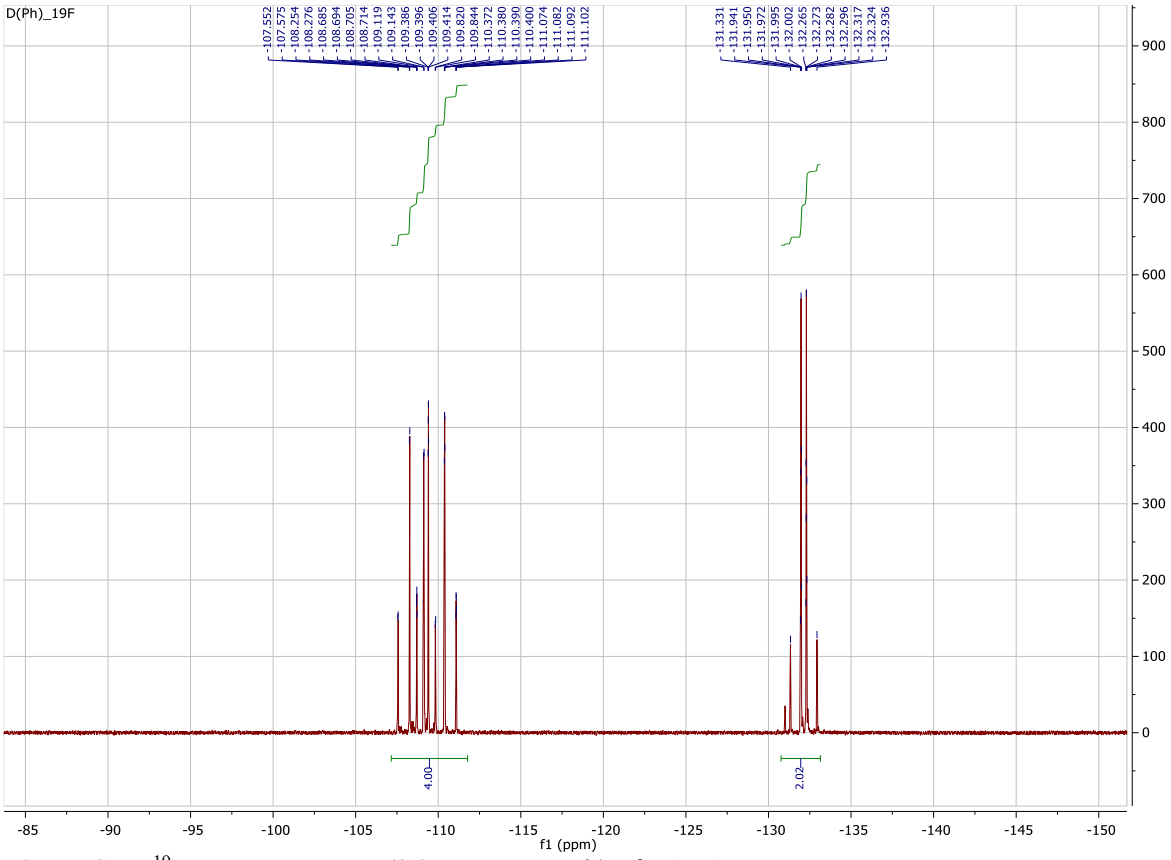


Figure S5c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **D(Ph)**.

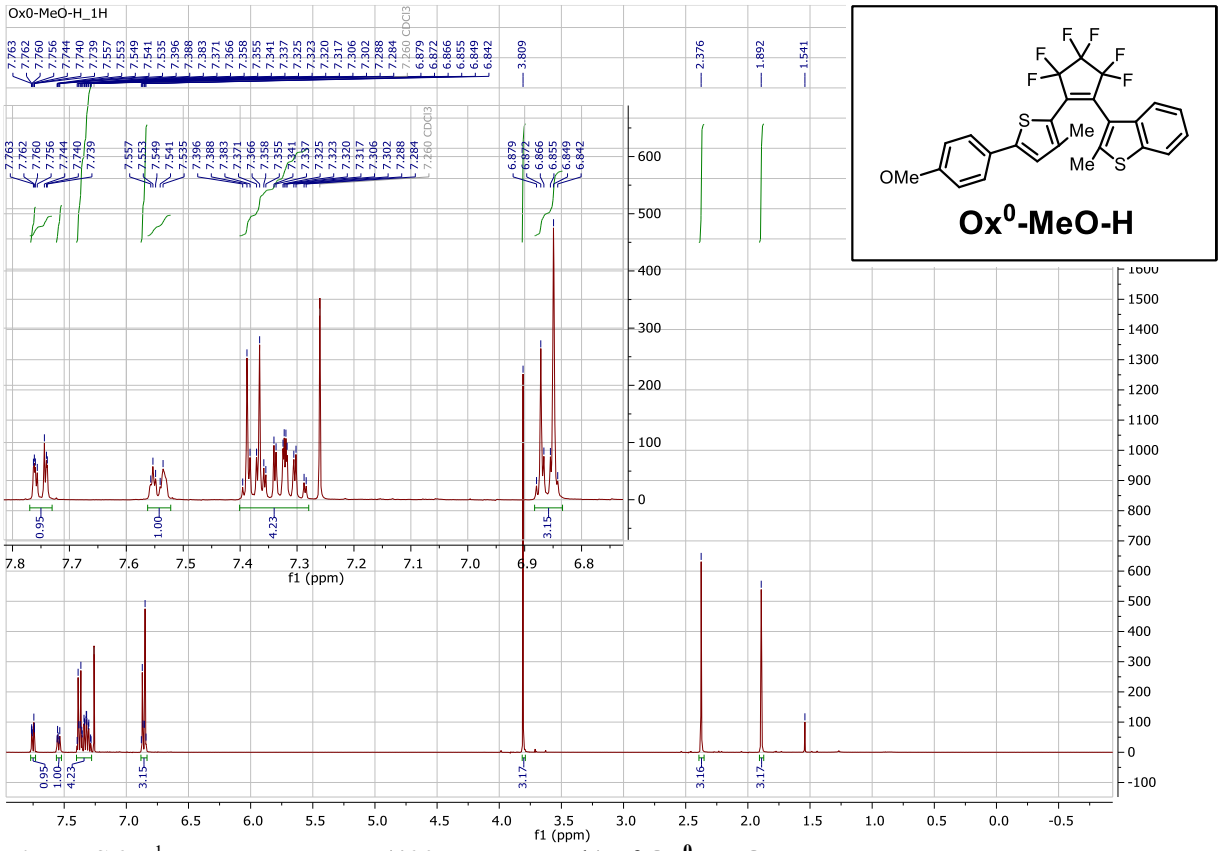


Figure S6a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^0-MeO-H**.

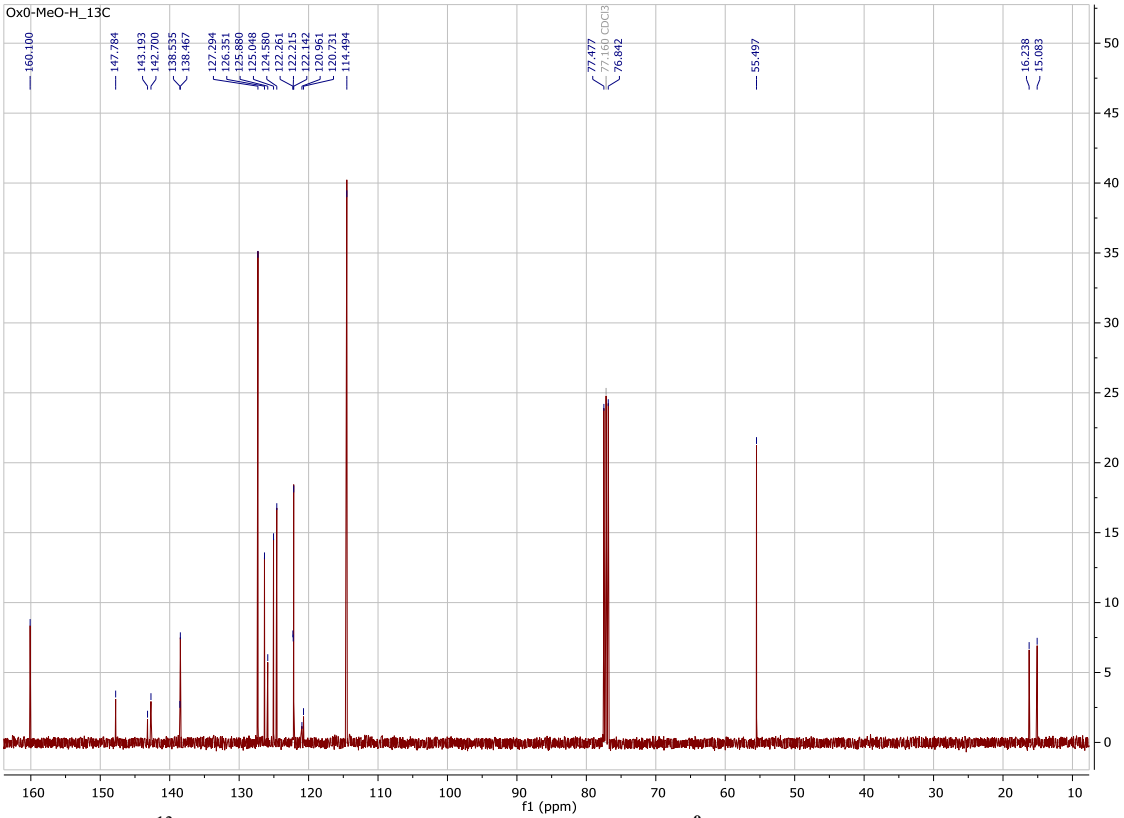


Figure S6b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^0-MeO-H**.

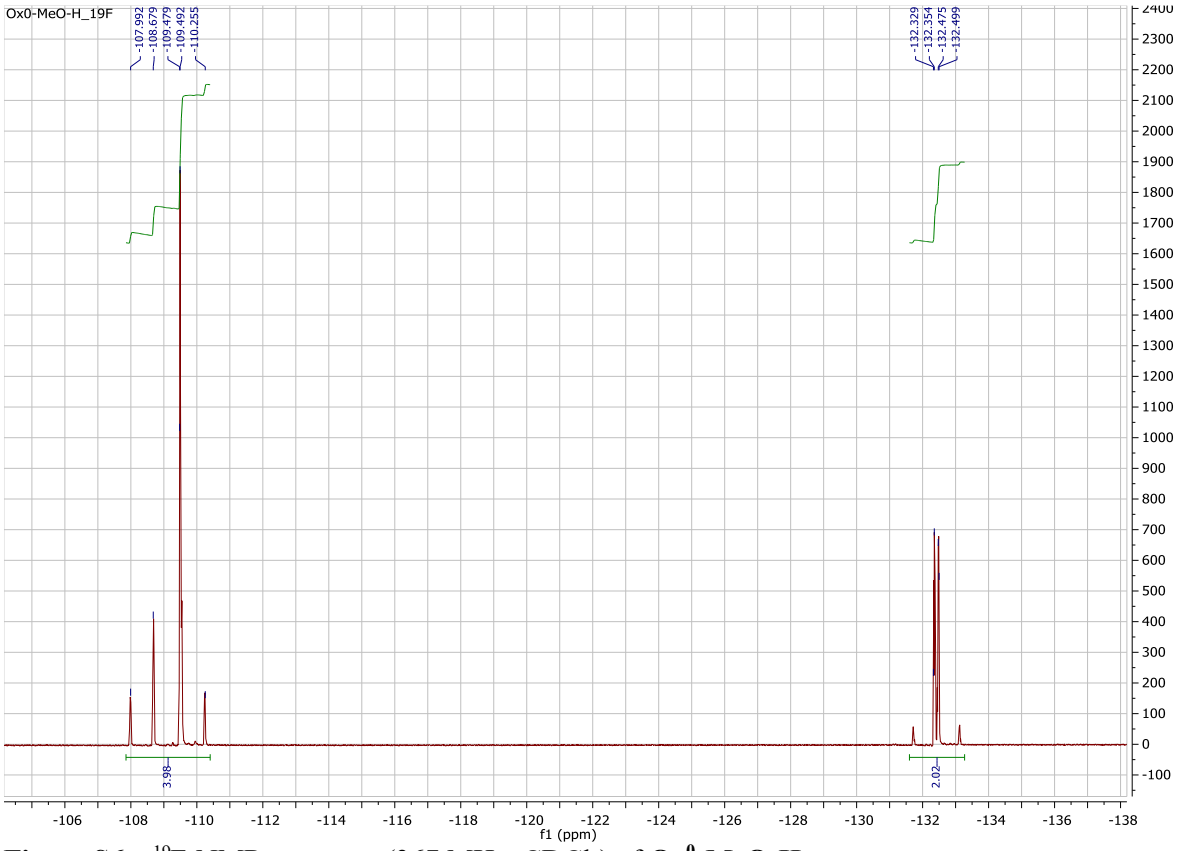


Figure S6c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^0-MeO-H**.

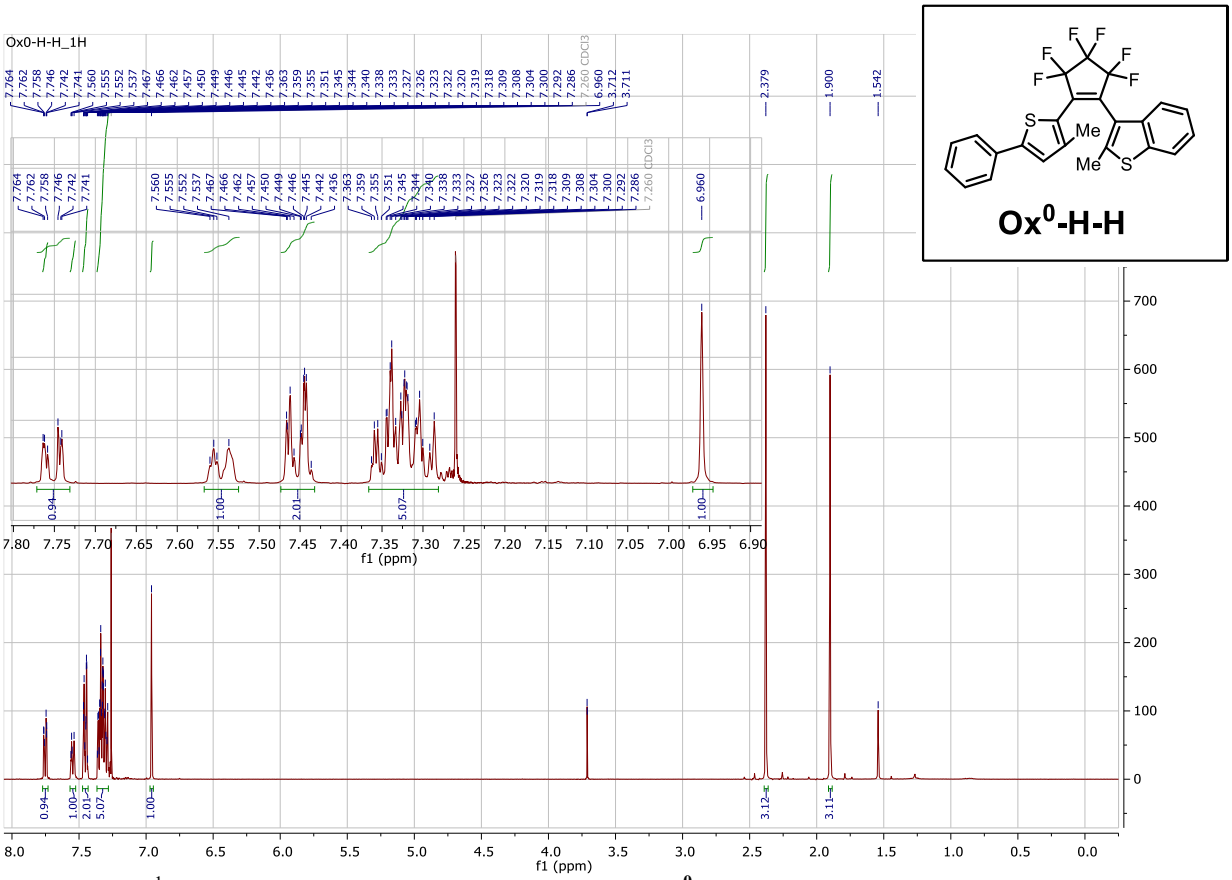


Figure S7a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^0-H-H**.

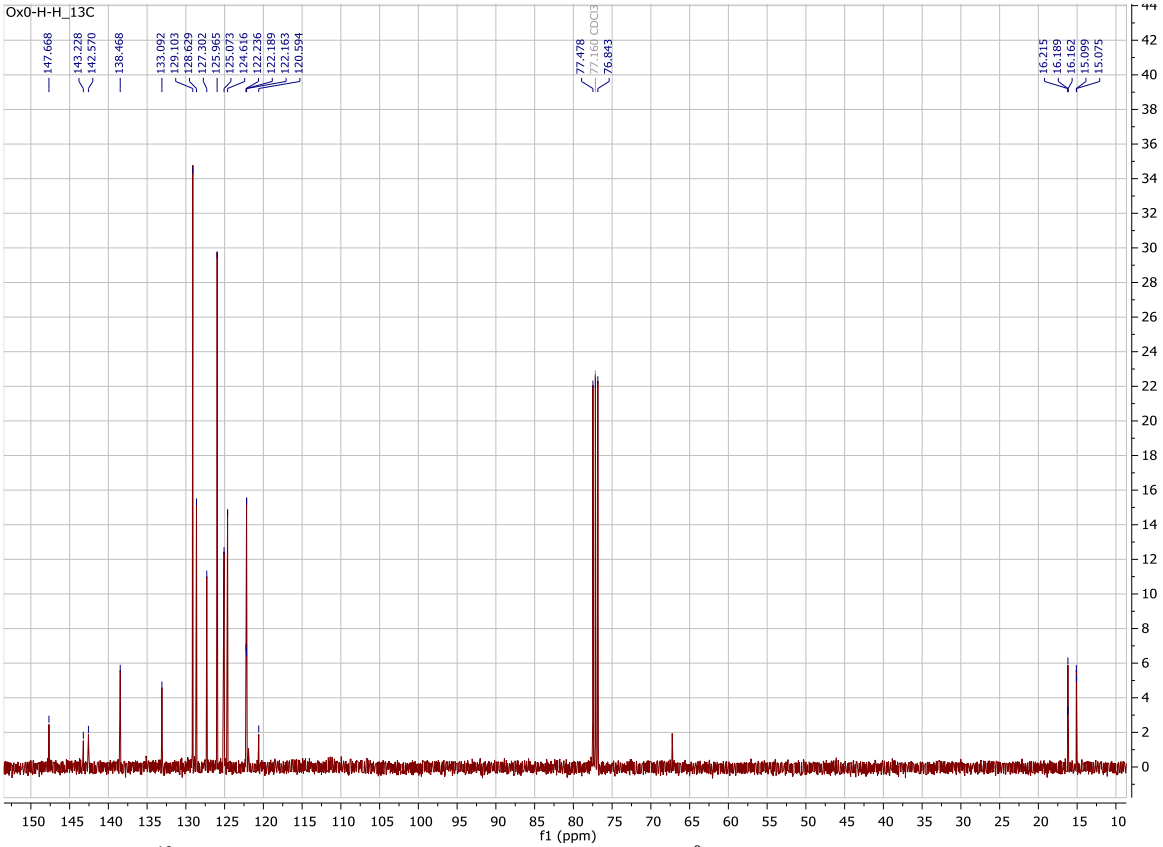


Figure S7b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^0-H-H**.

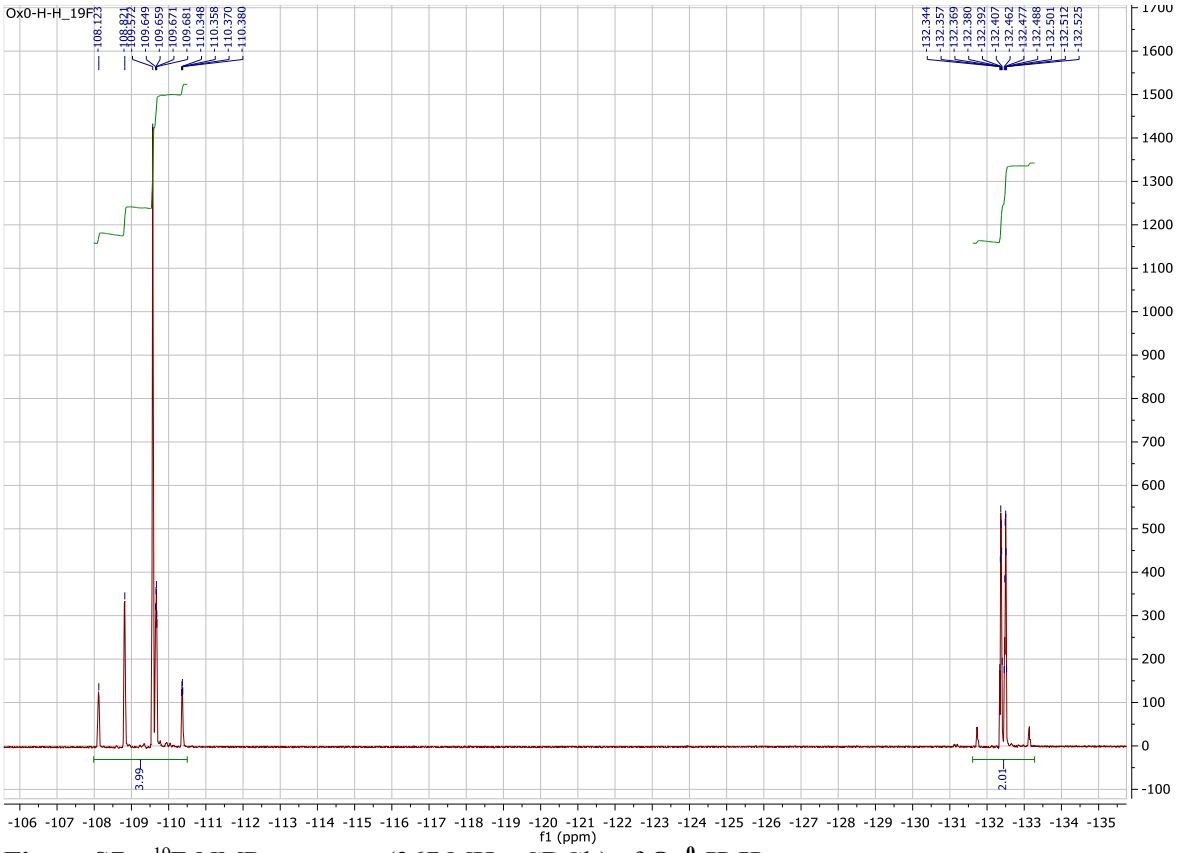


Figure S7c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^0-H-H**.

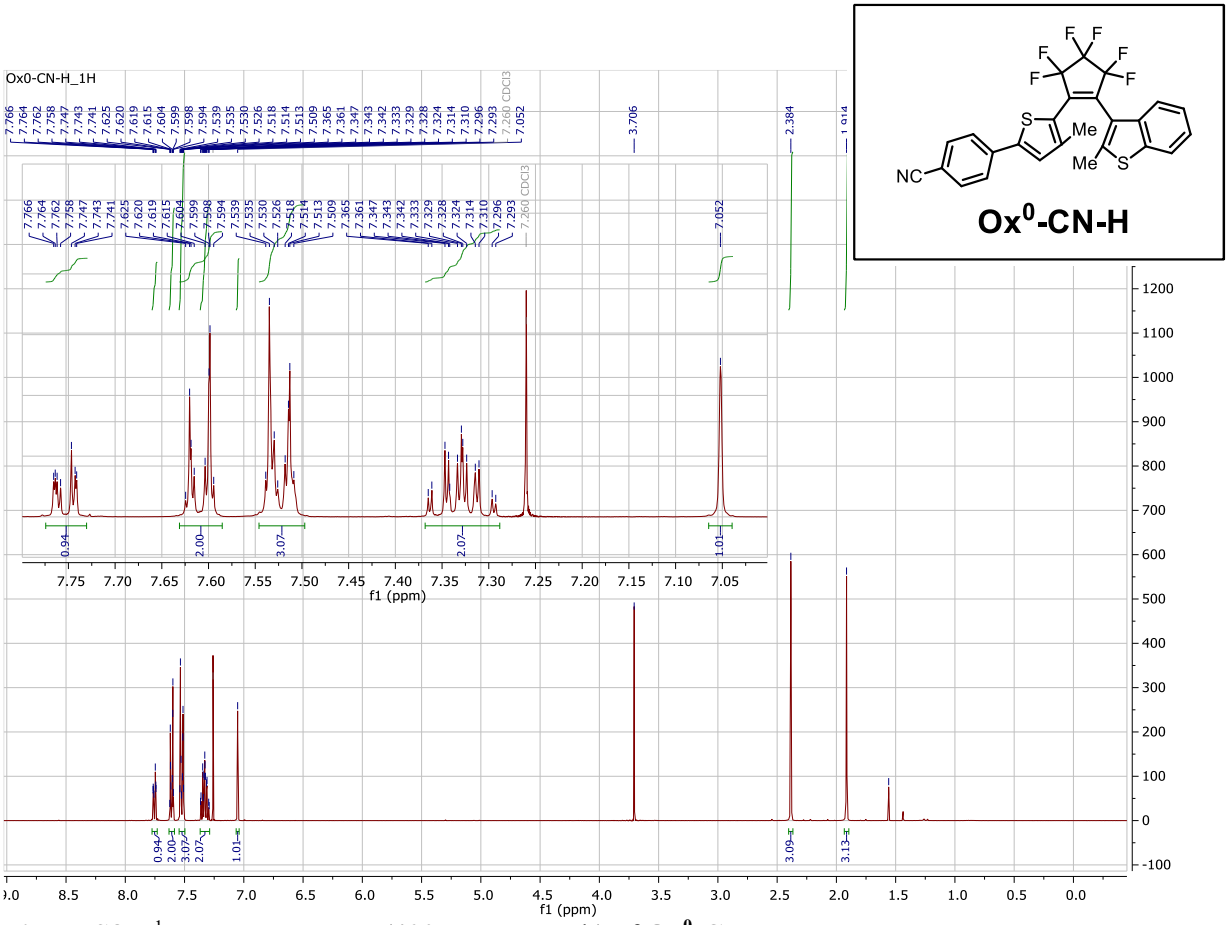


Figure S8a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^0-CN-H**.

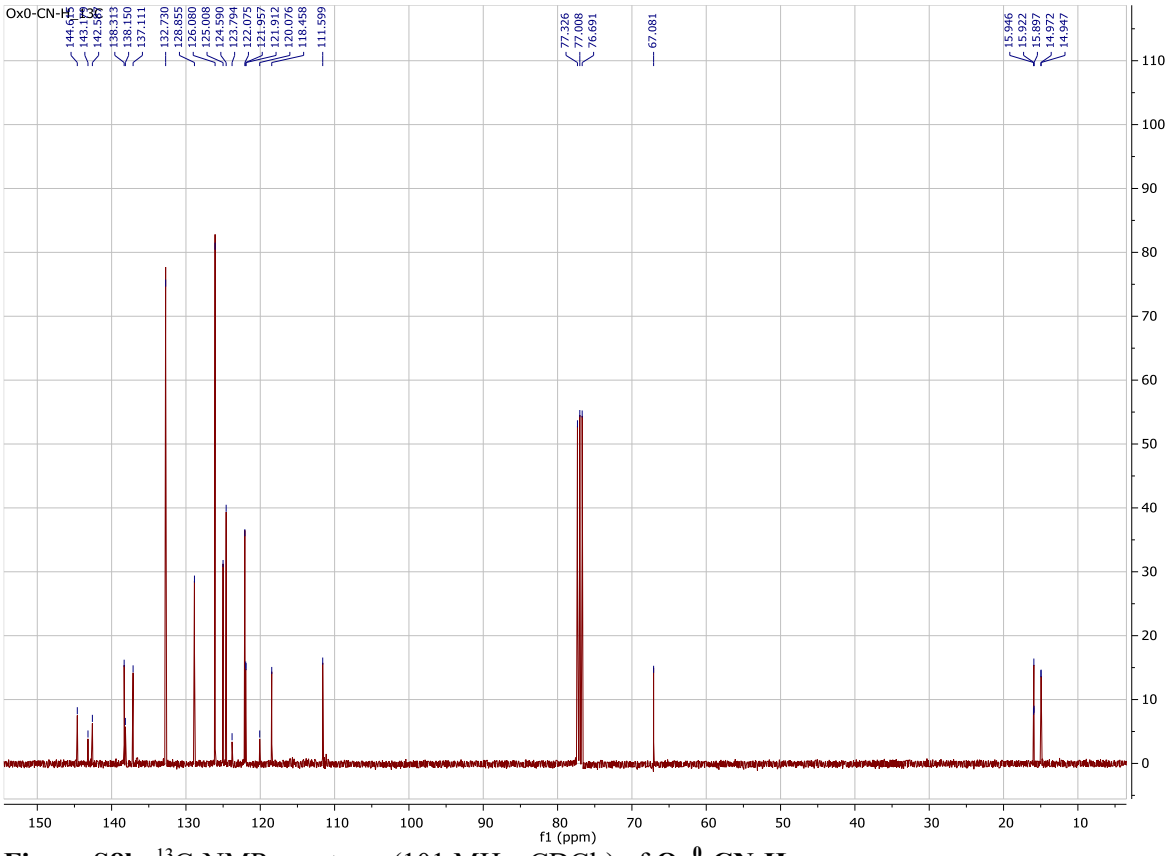


Figure S8b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^0-CN-H**.

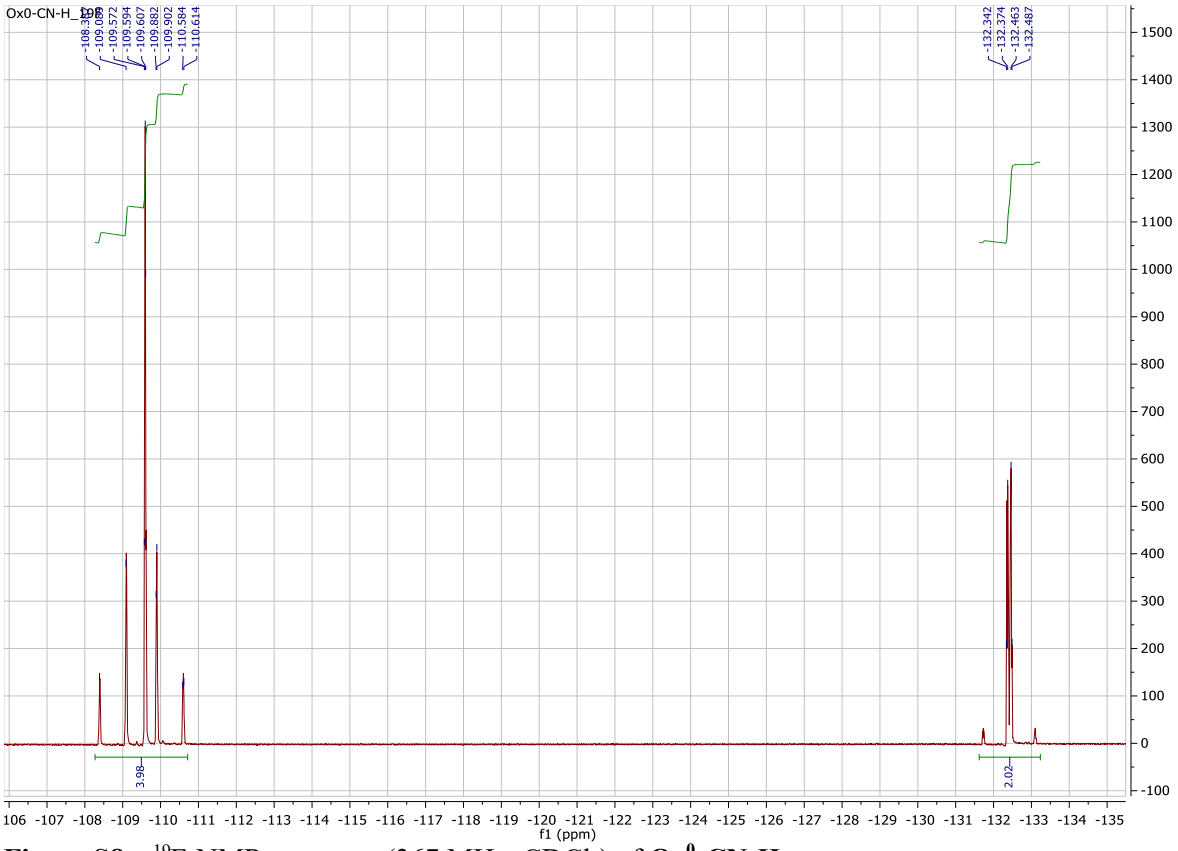


Figure S8c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^0-CN-H**.

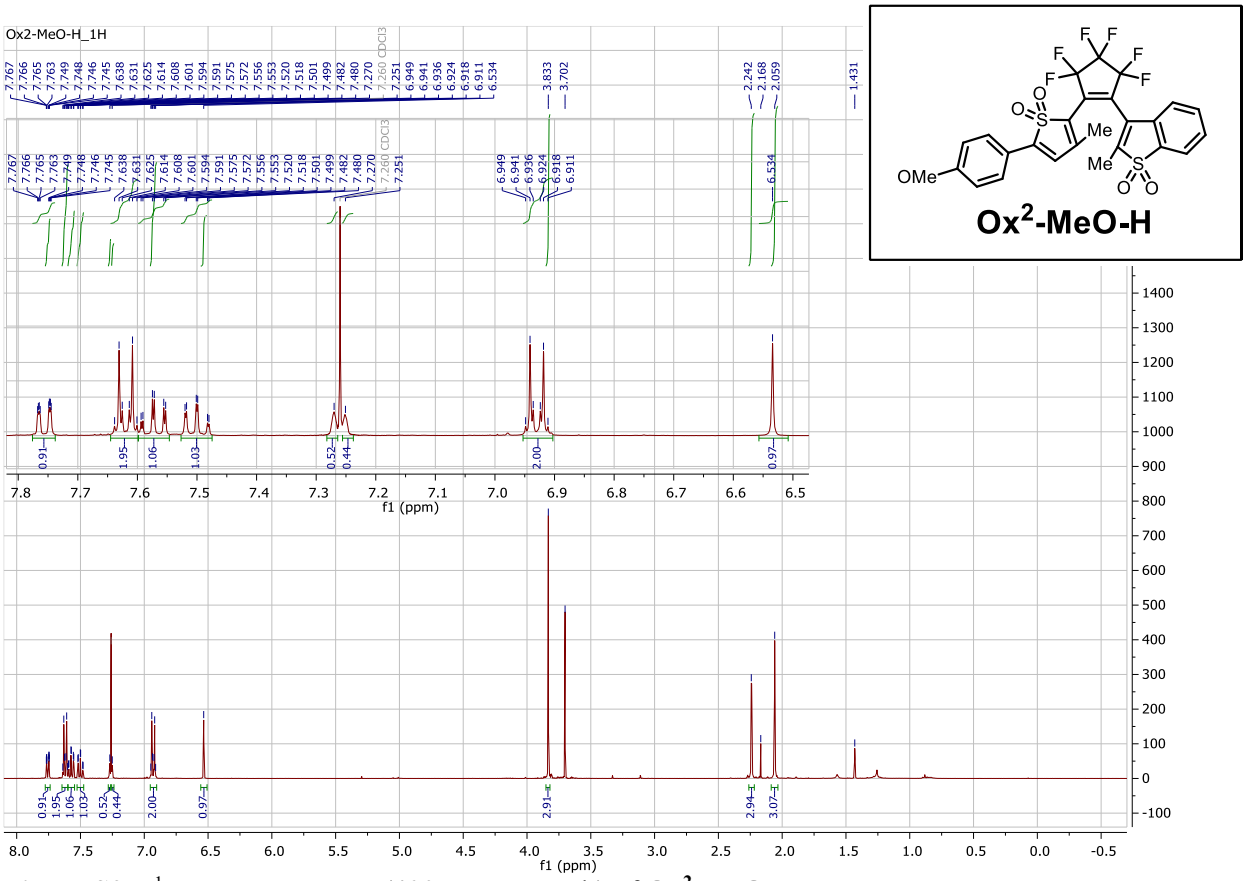


Figure S9a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^2-MeO-H**.

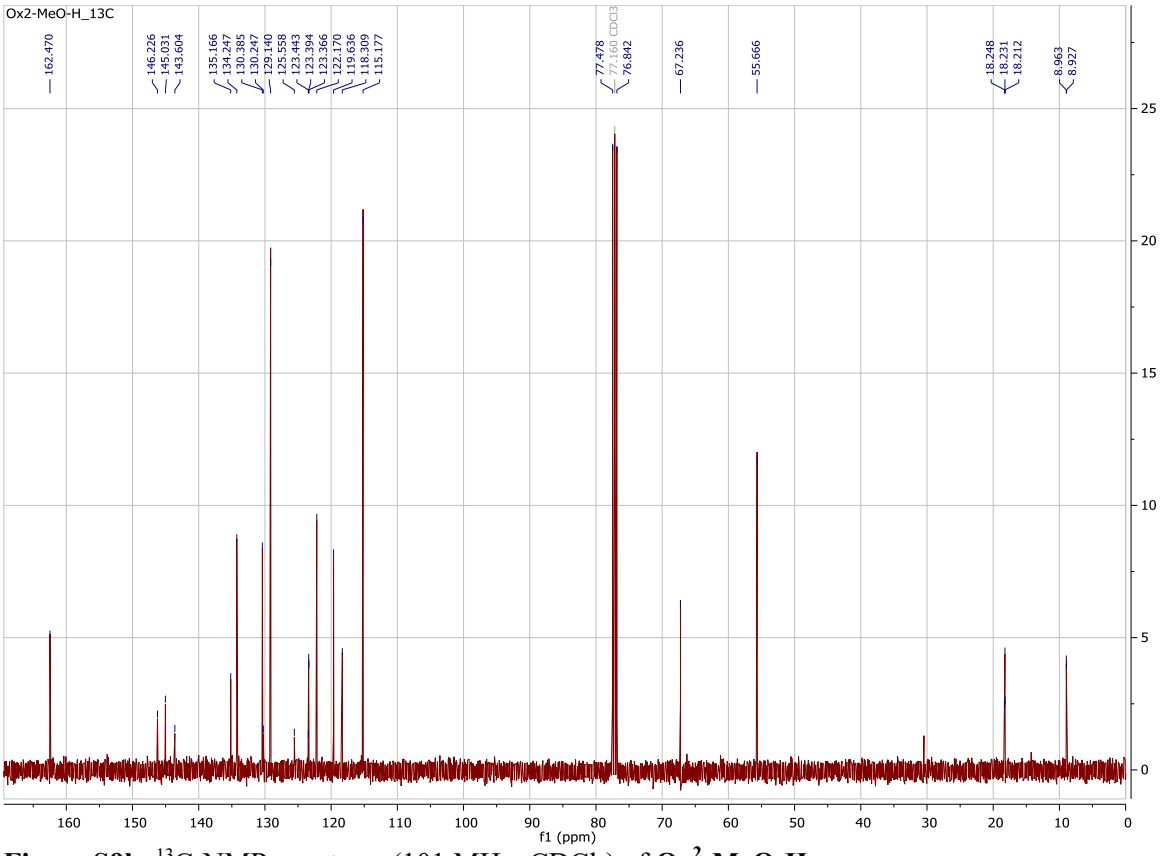


Figure S9b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^2-MeO-H**.

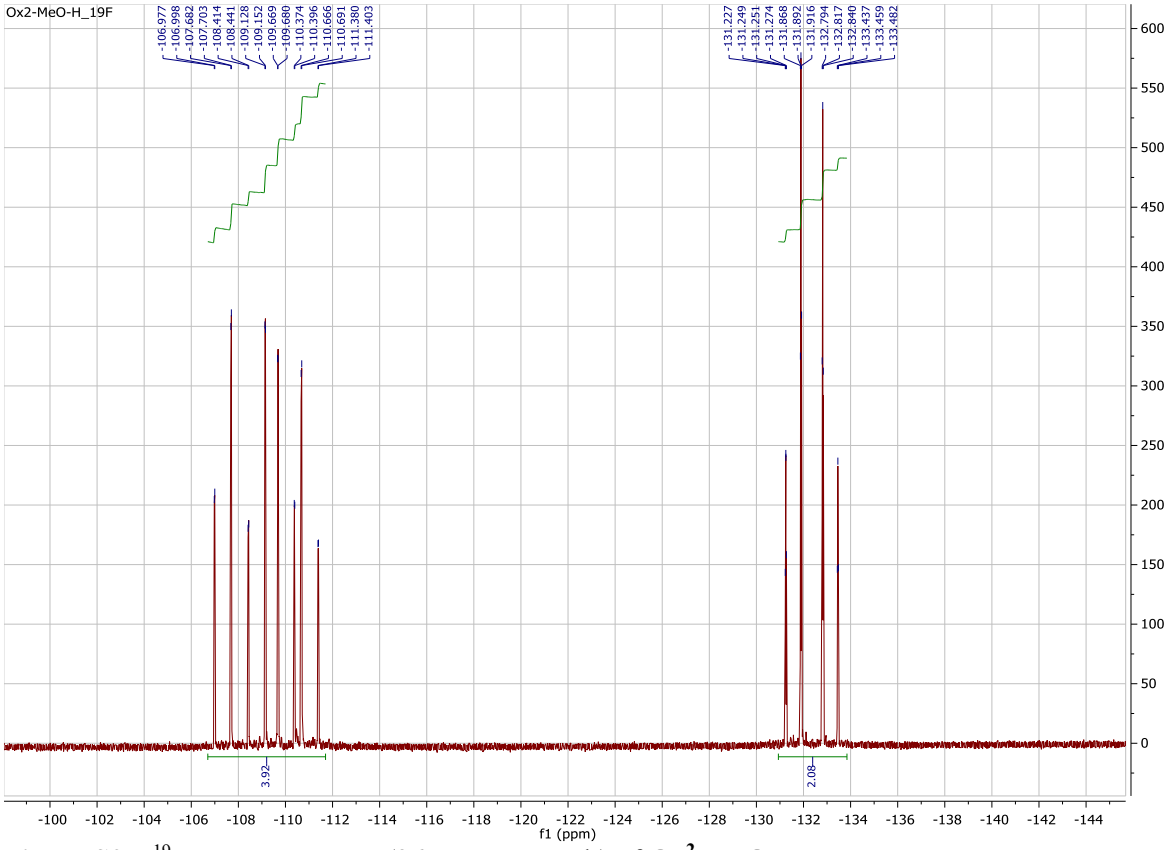


Figure S9c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^2-MeO-H**.

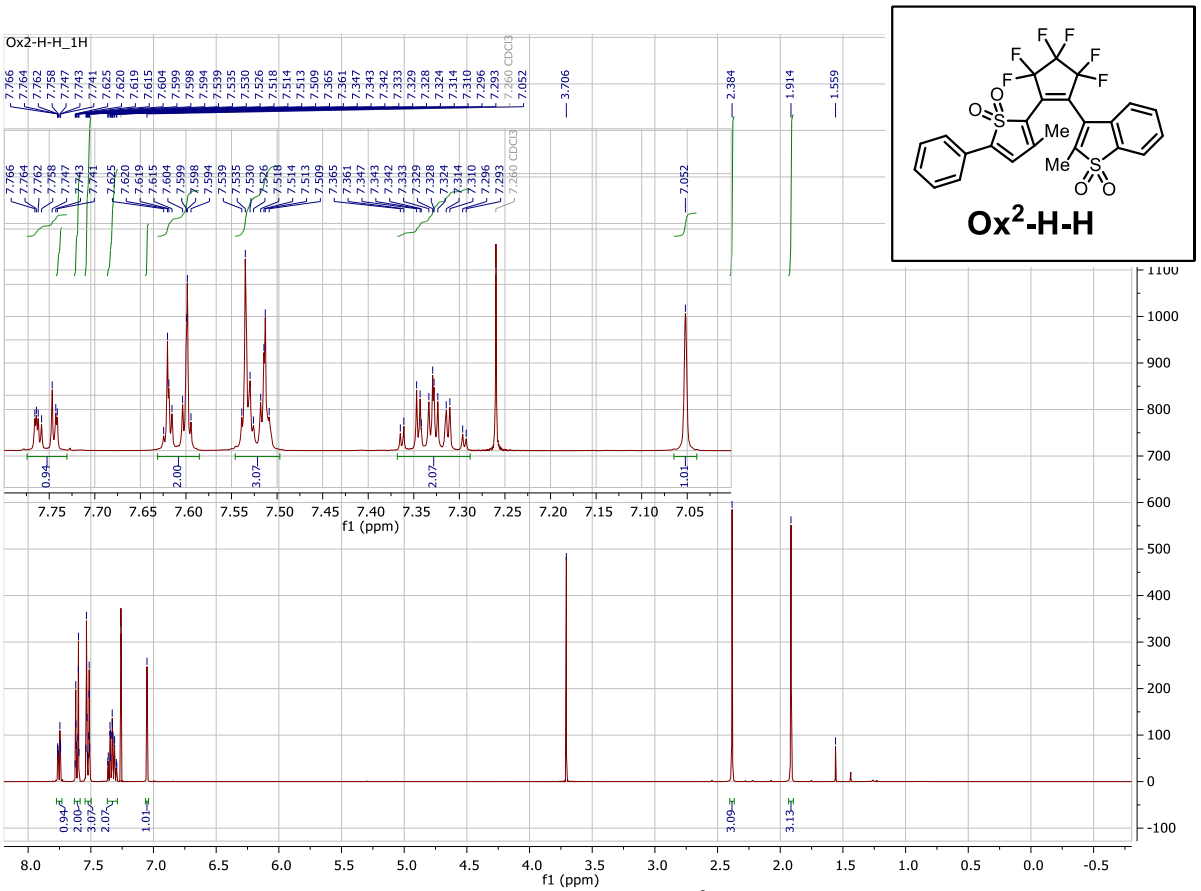


Figure S10a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^2-H-H**.

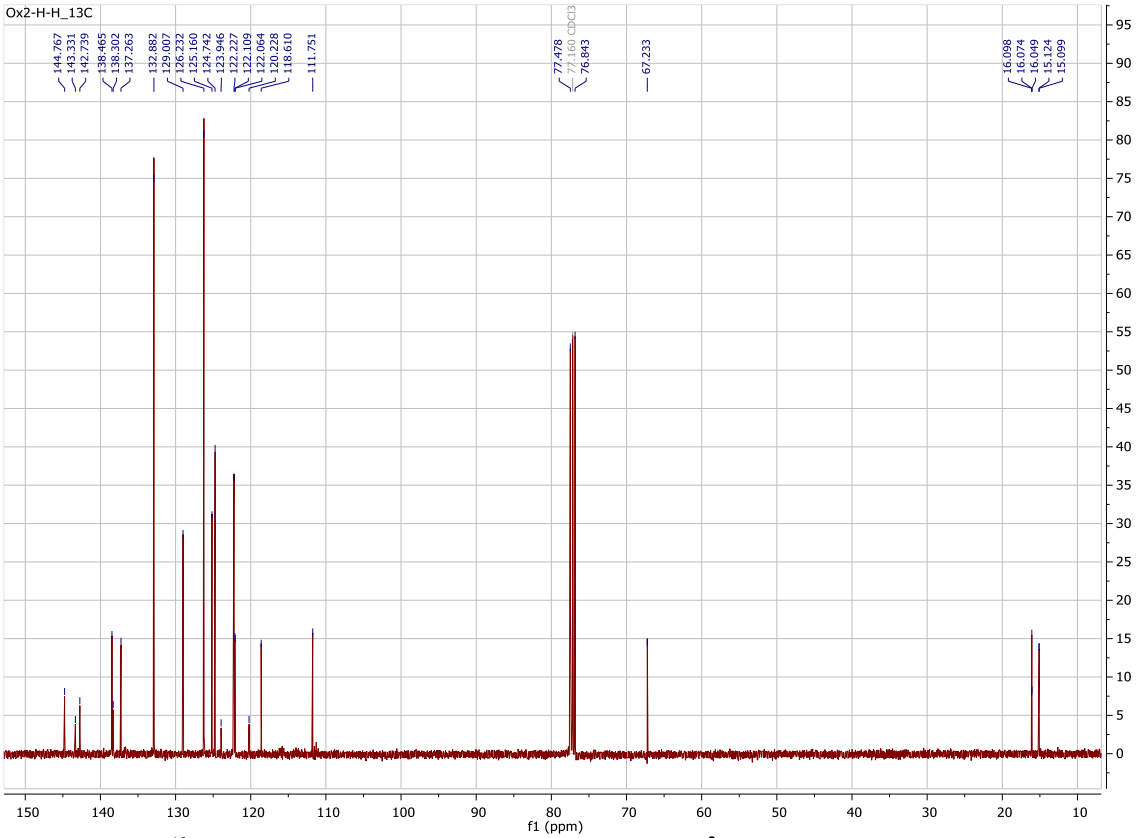


Figure S10b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^2-H-H**.

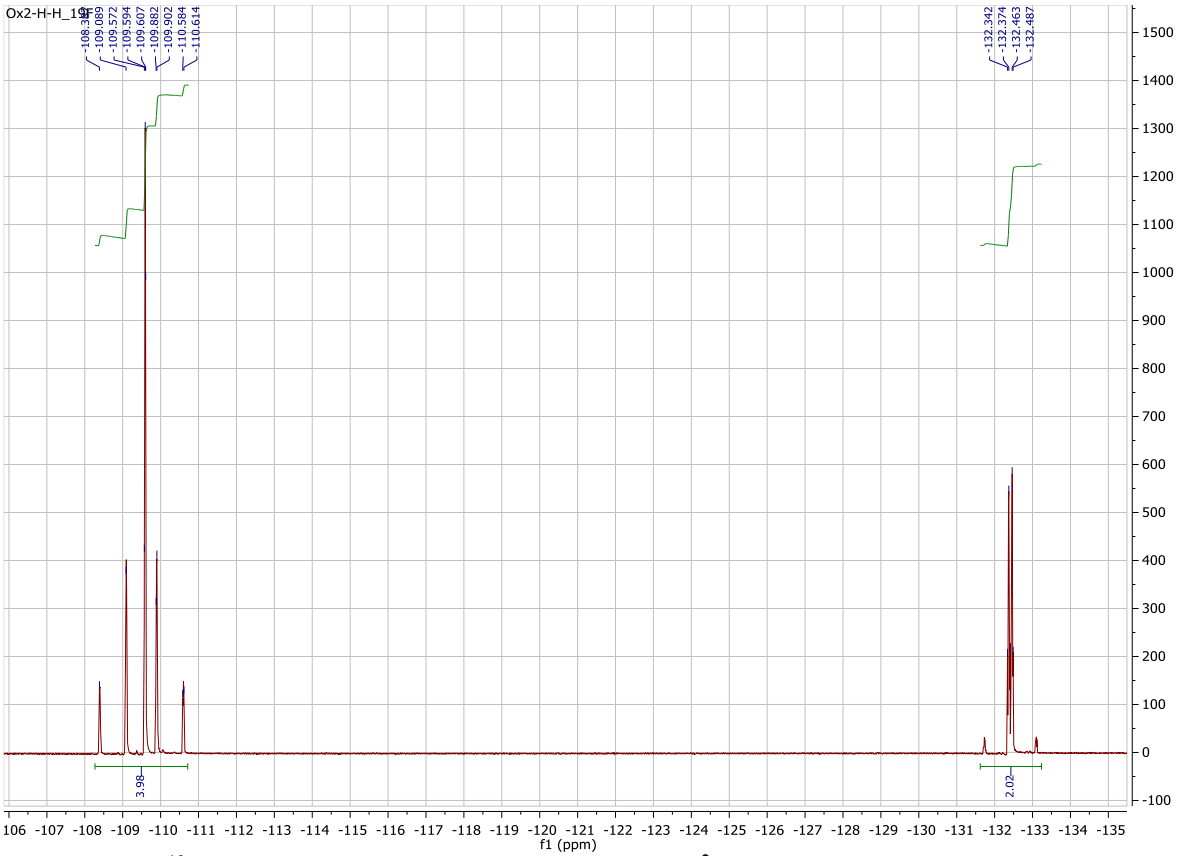


Figure S10c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^2-H-H**.

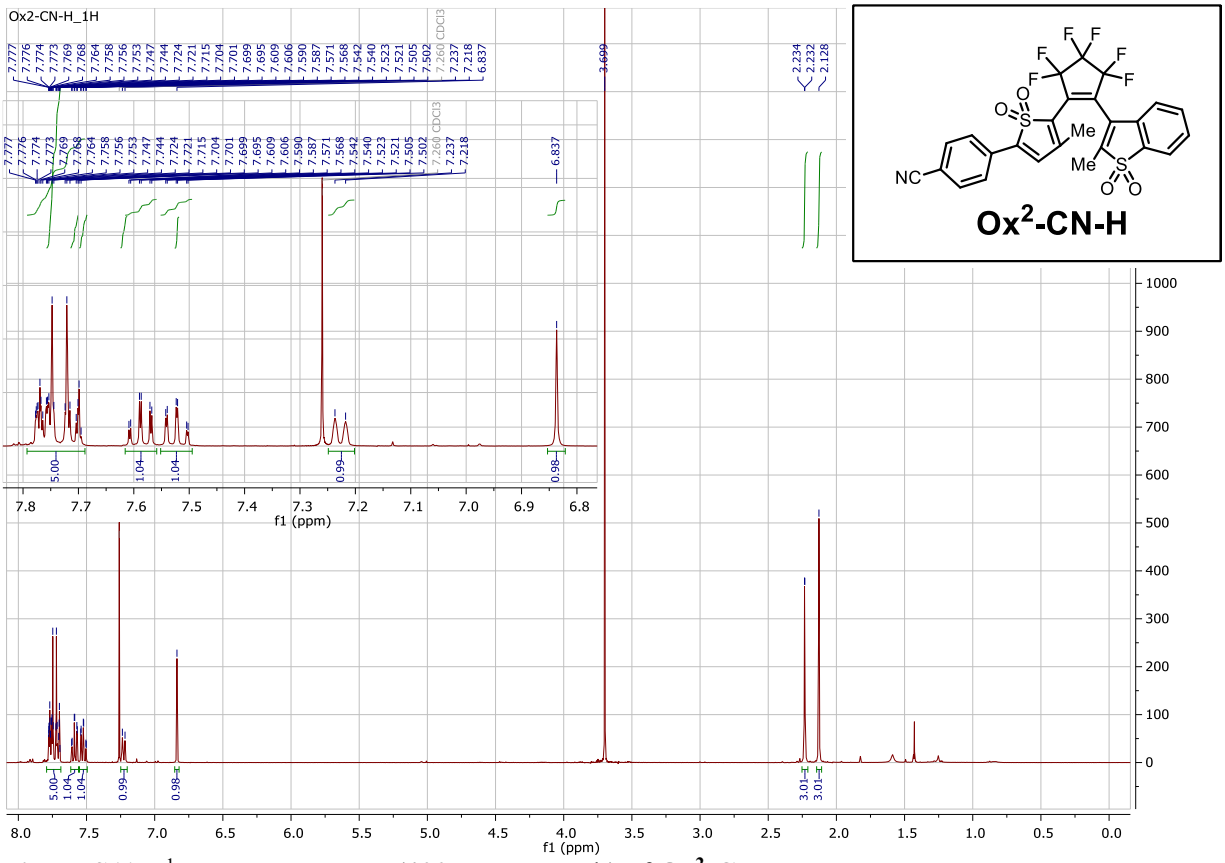


Figure S11a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^2-CN-H**.

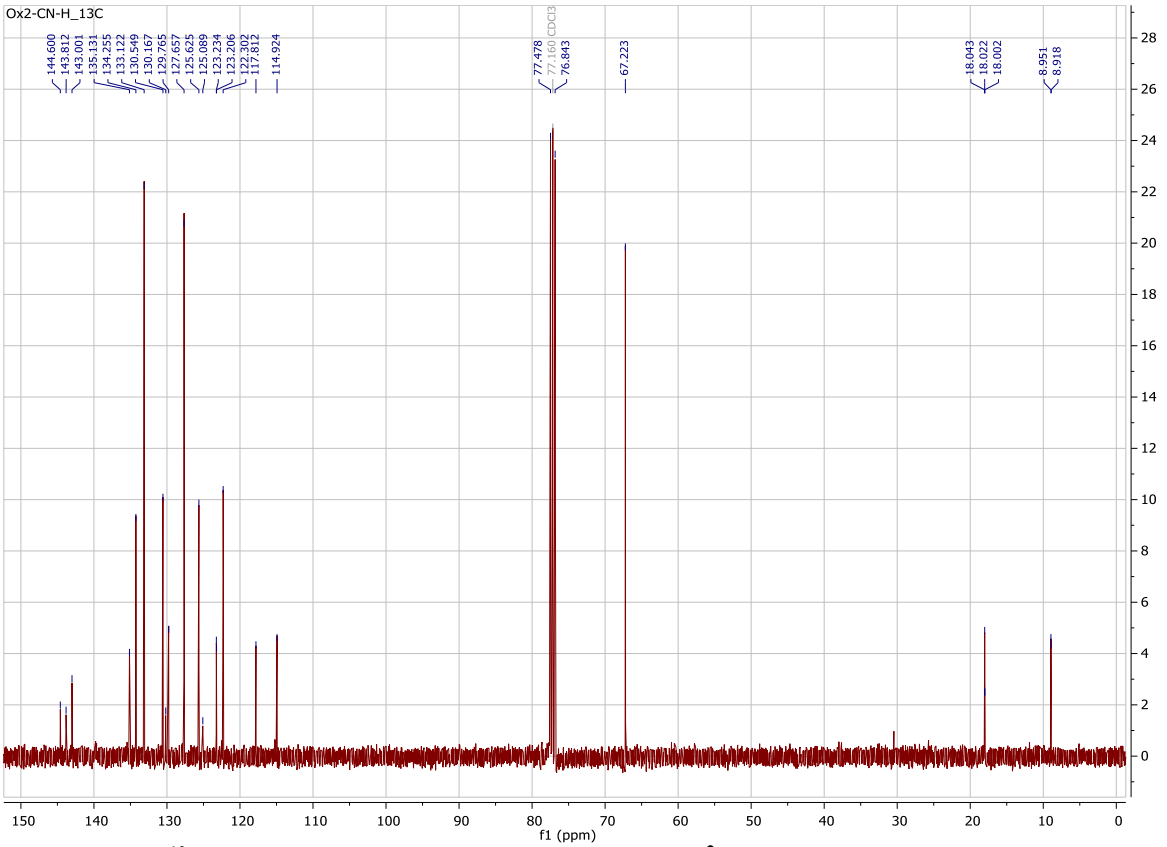


Figure S11b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^2-CN-H**.

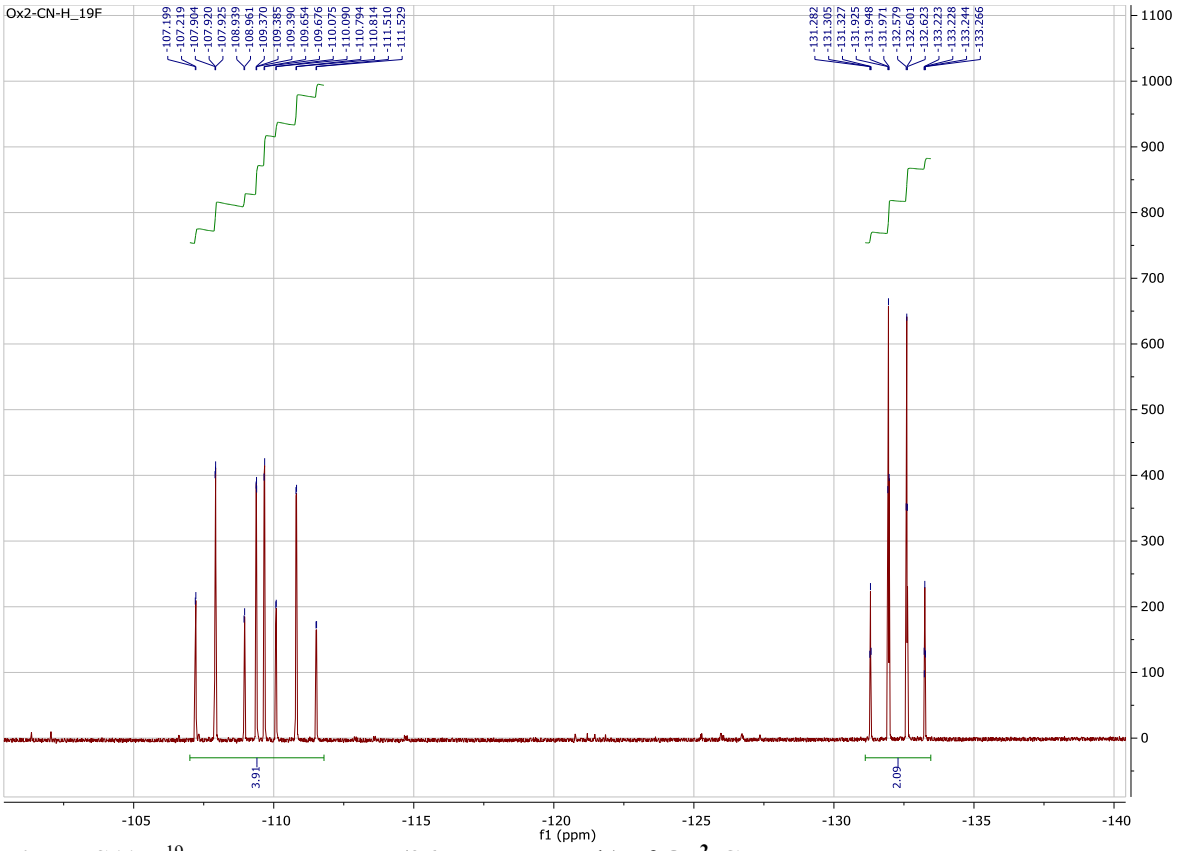


Figure S11c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^2-CN-H**.

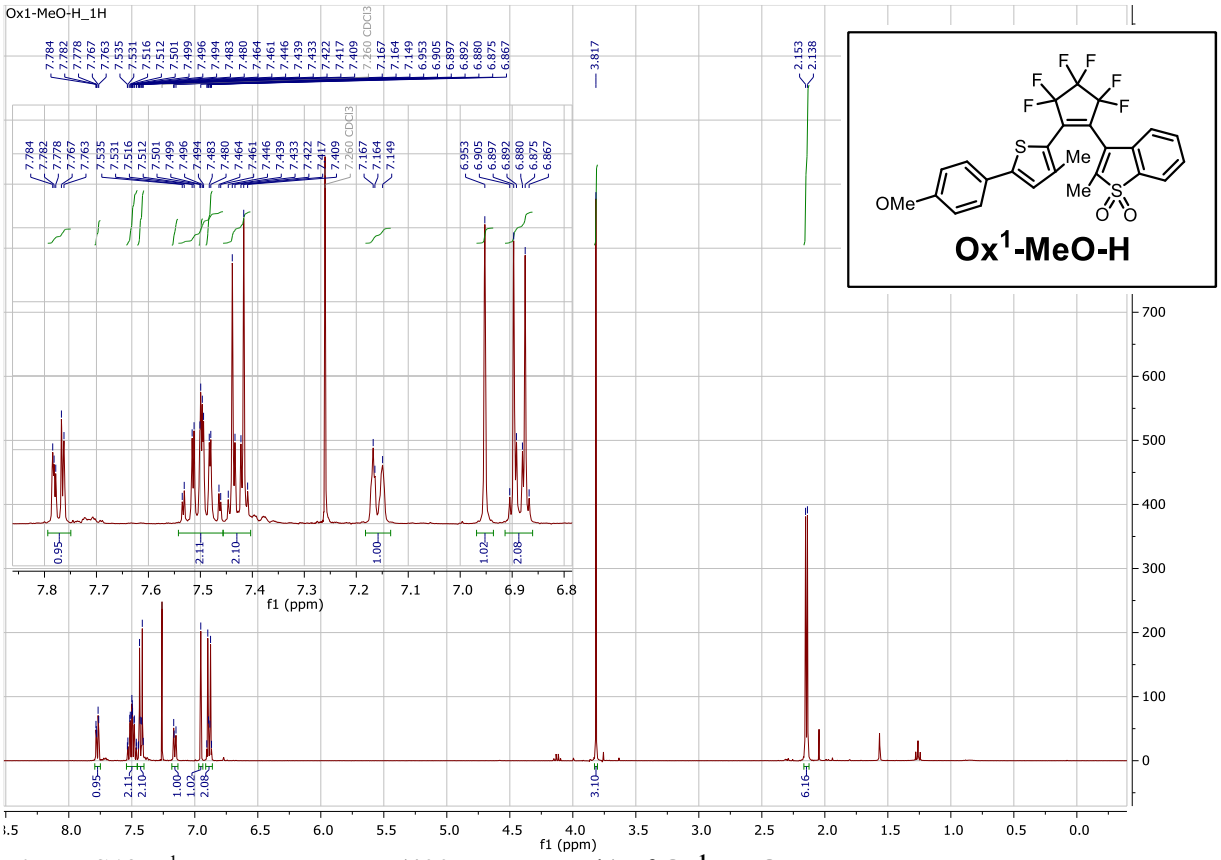


Figure S12a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^{1}-MeO-H**.

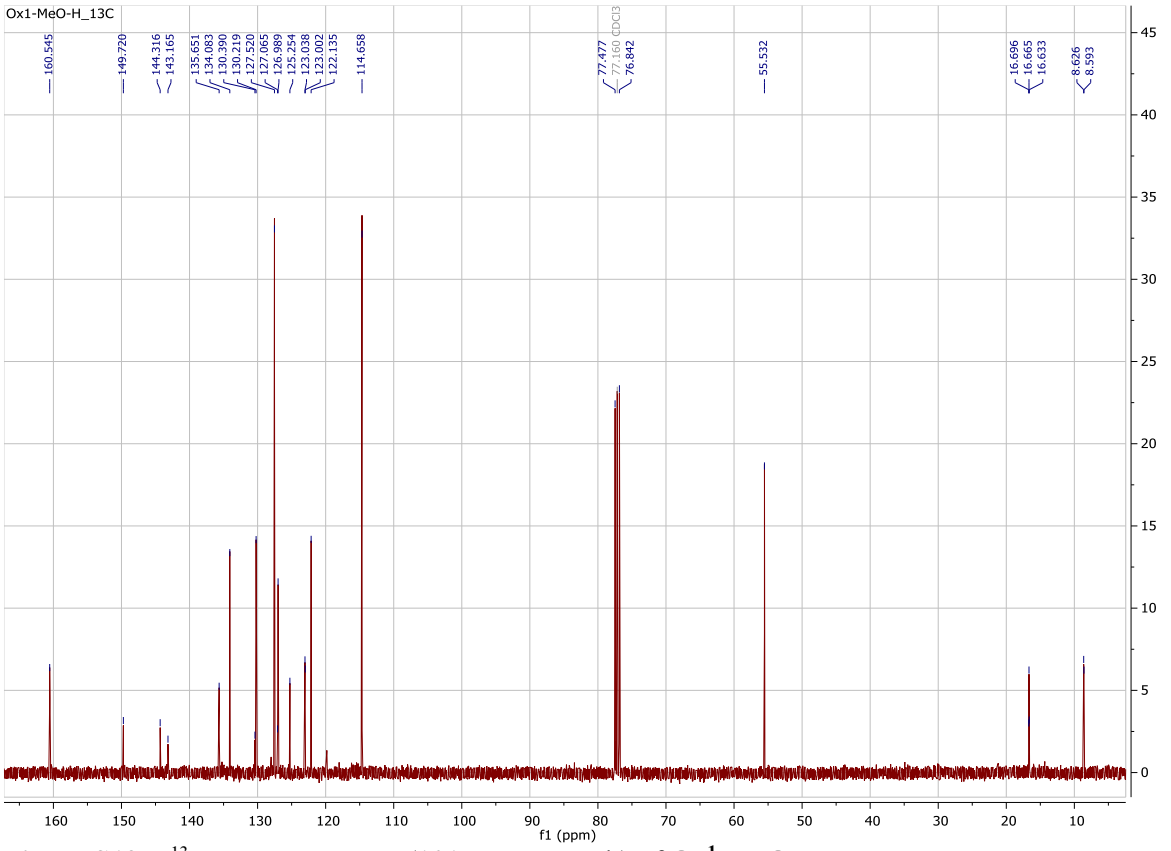


Figure S12b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^{1}-MeO-H**.

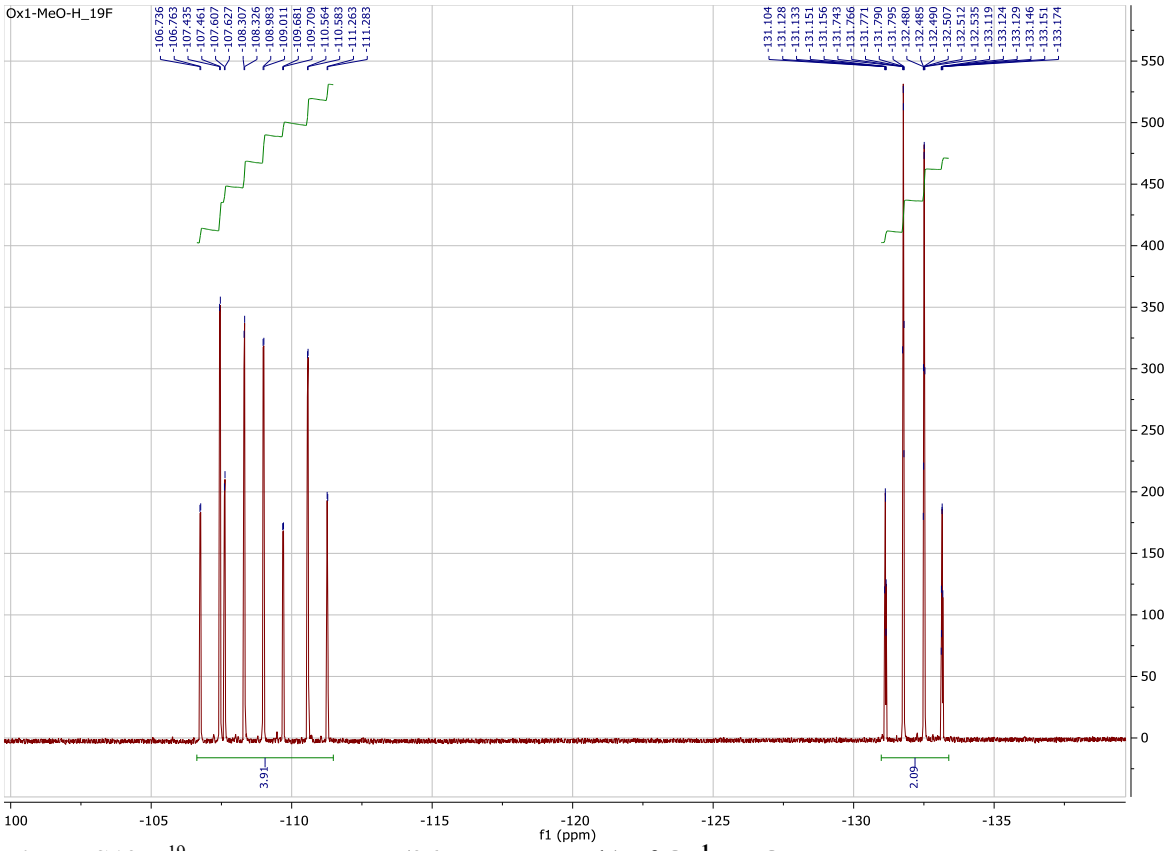


Figure S12c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^1-MeO-H**.

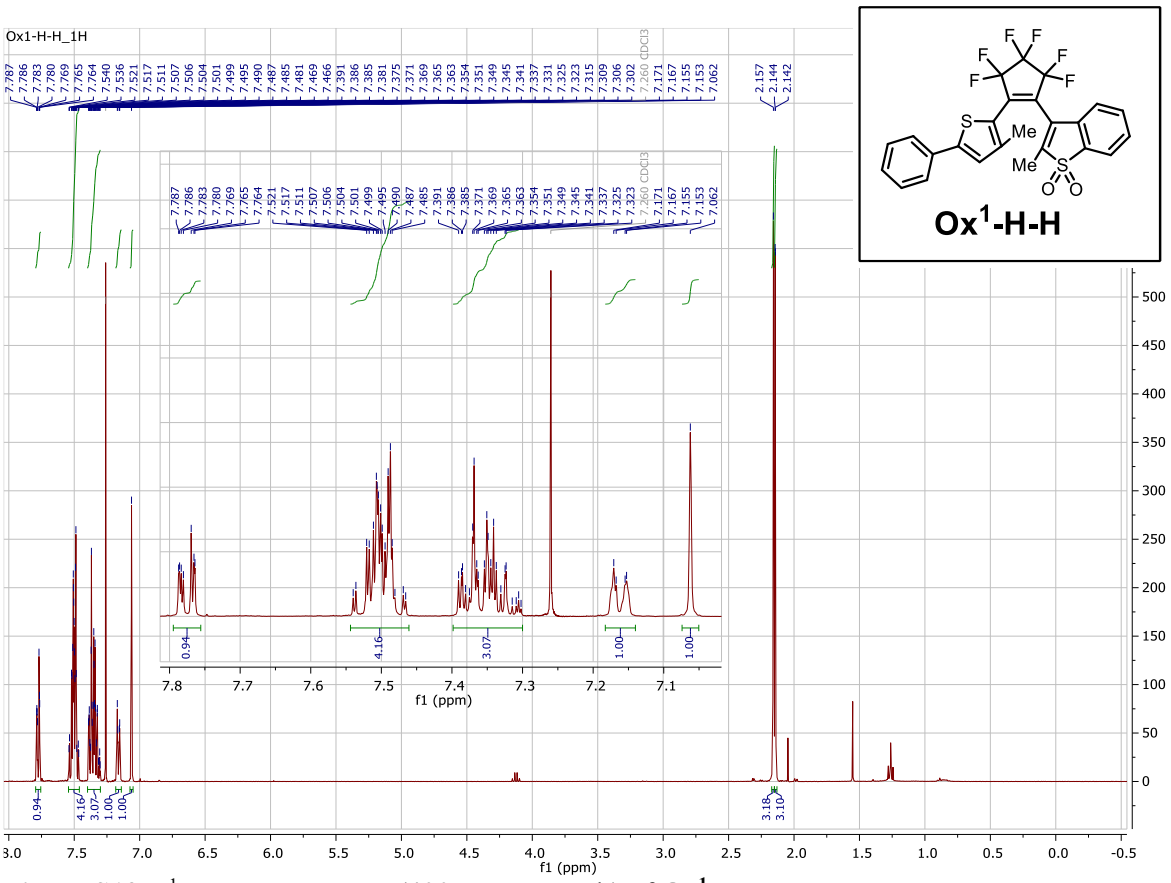


Figure S13a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^{1}-H-H**.

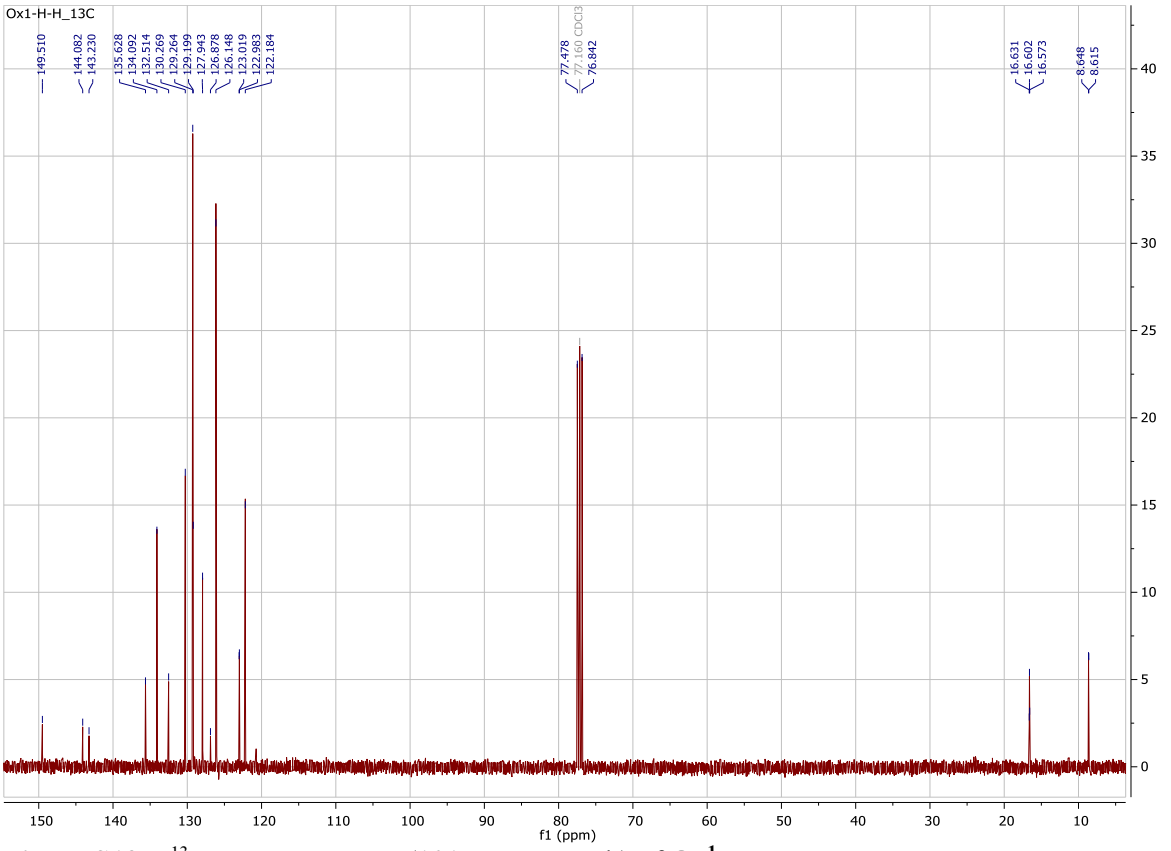


Figure S13b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^{1}-H-H**.

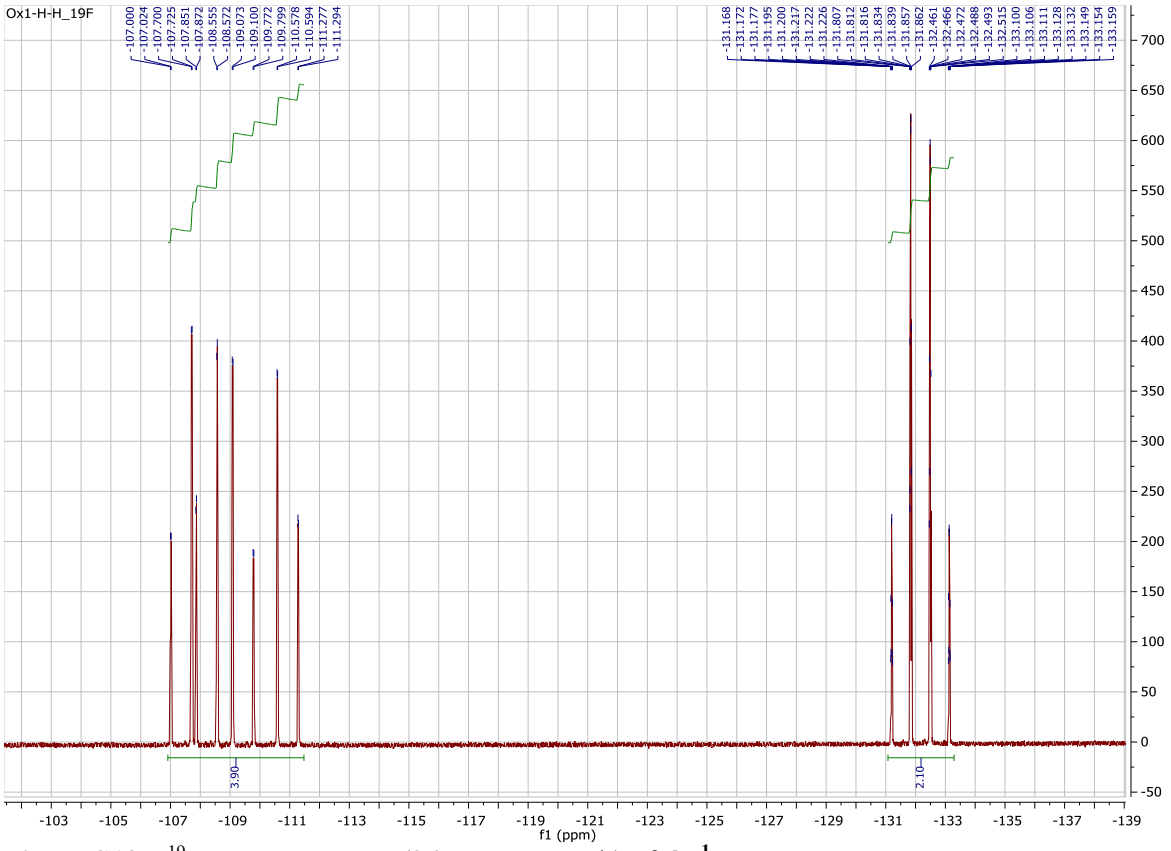


Figure S13c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^1-H-H**.

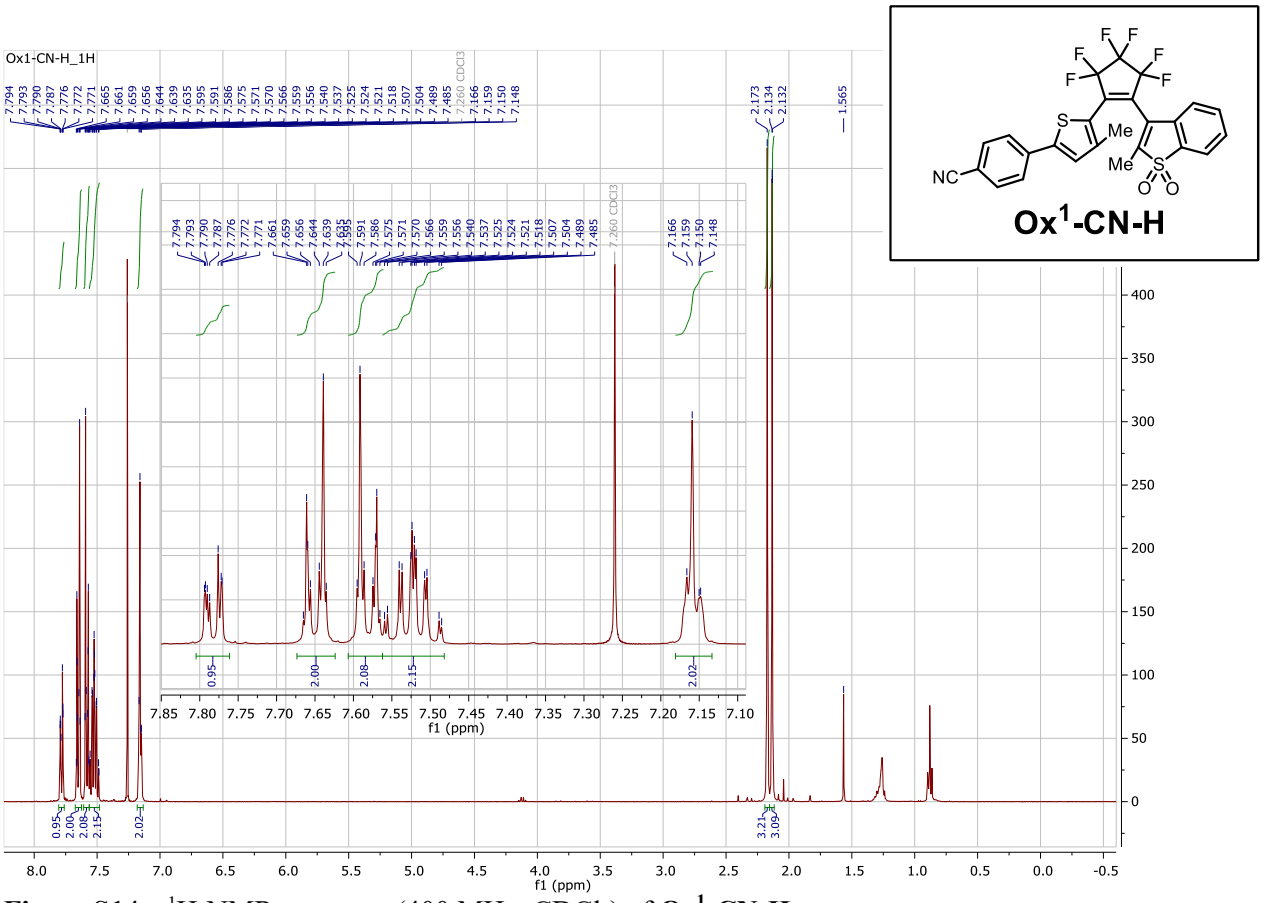


Figure S14c. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^{1}-CN-H**.

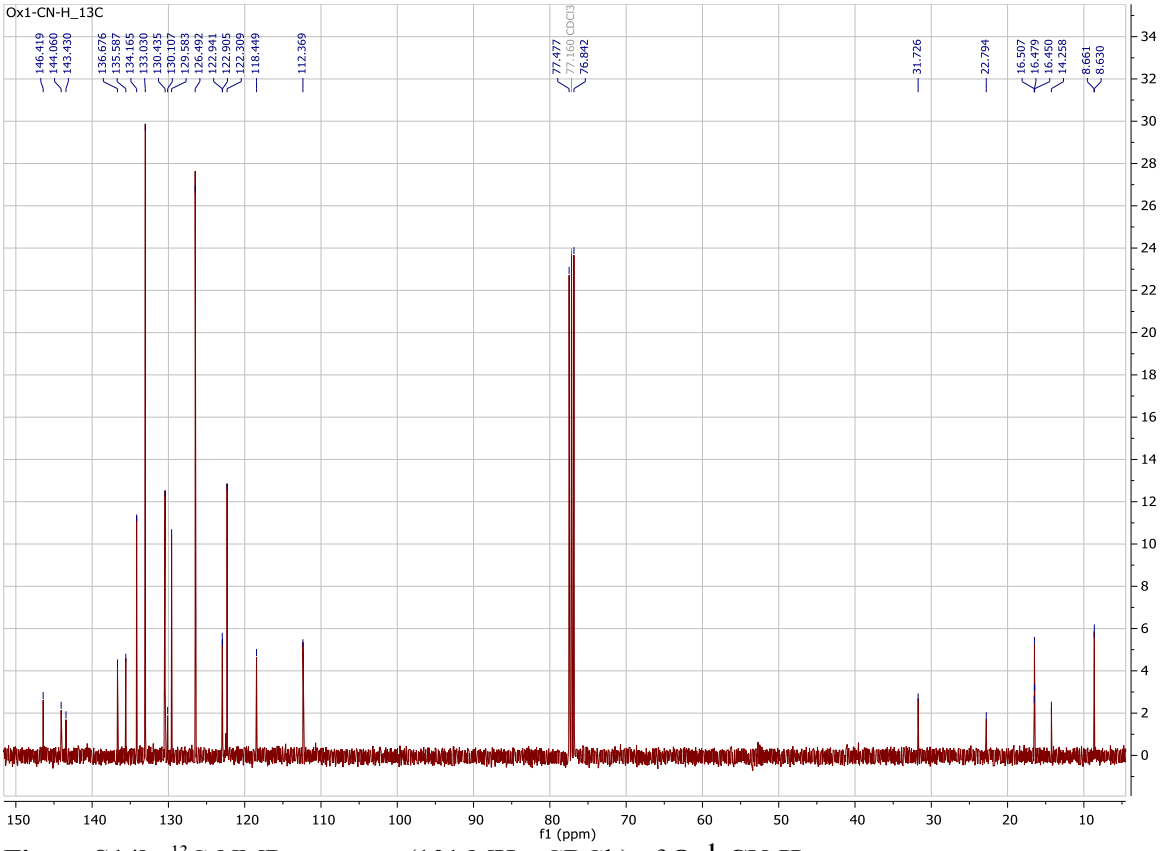


Figure S14b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^{1}-CN-H**.

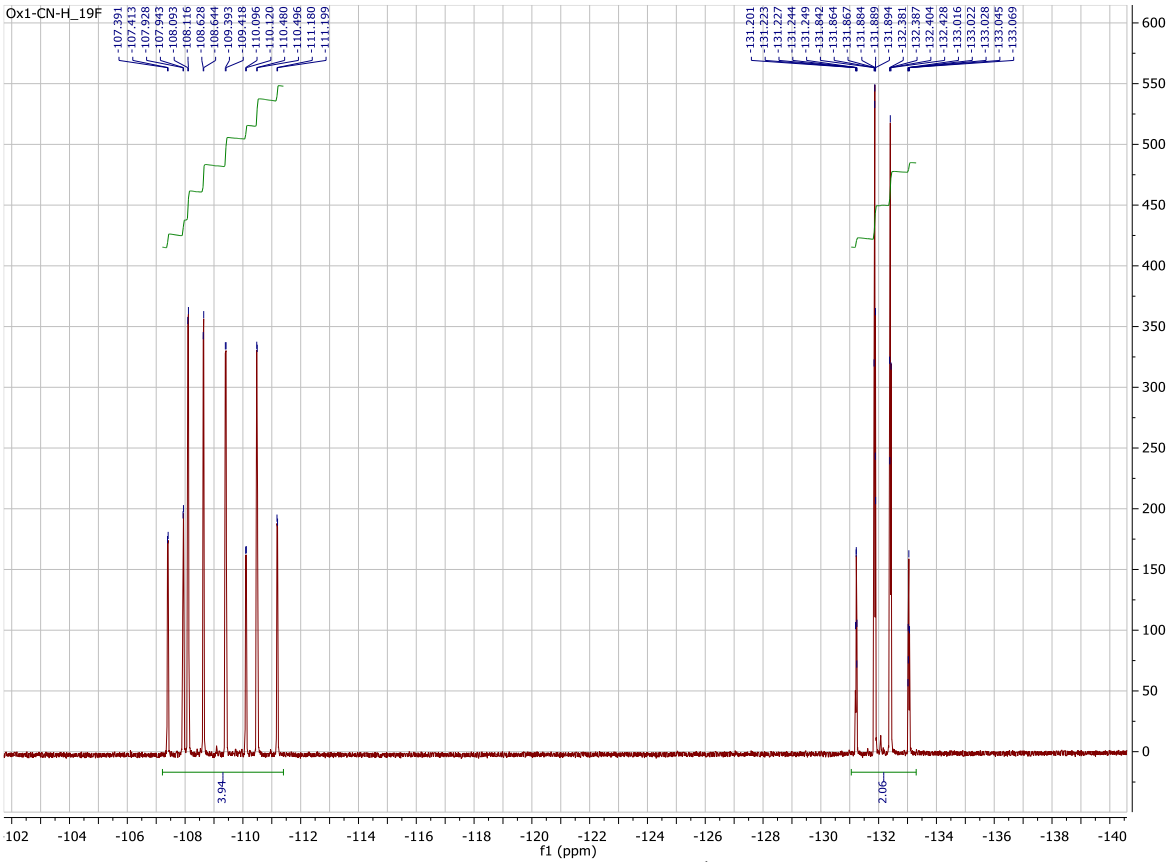


Figure S14c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^1-CN-H**.

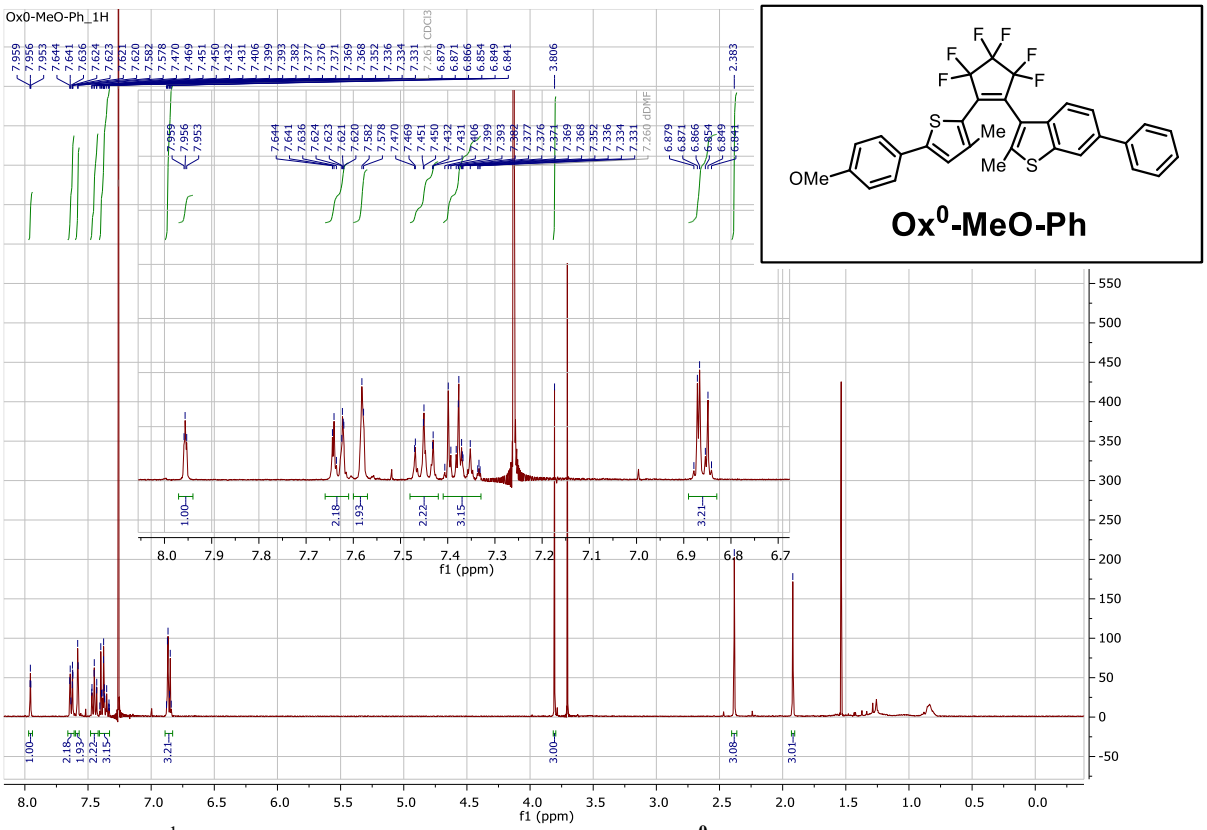


Figure S15a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^0-MeO-Ph**.

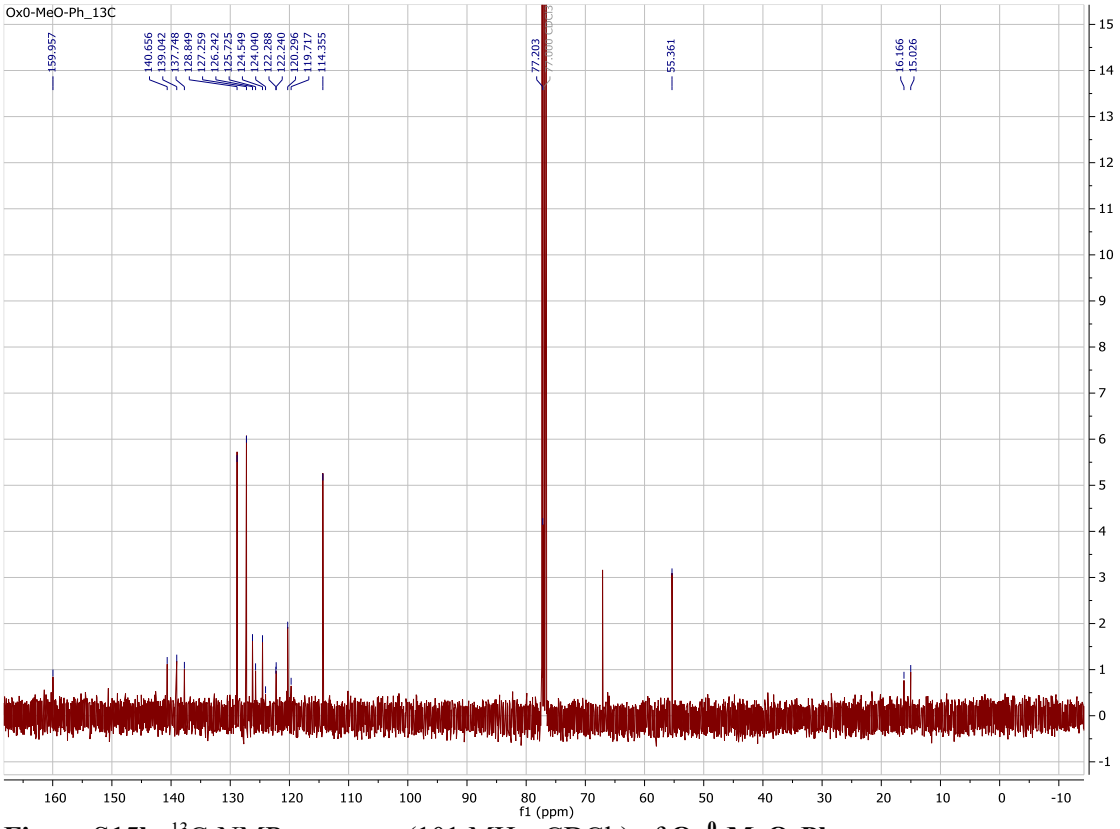


Figure S15b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^0-MeO-Ph**.

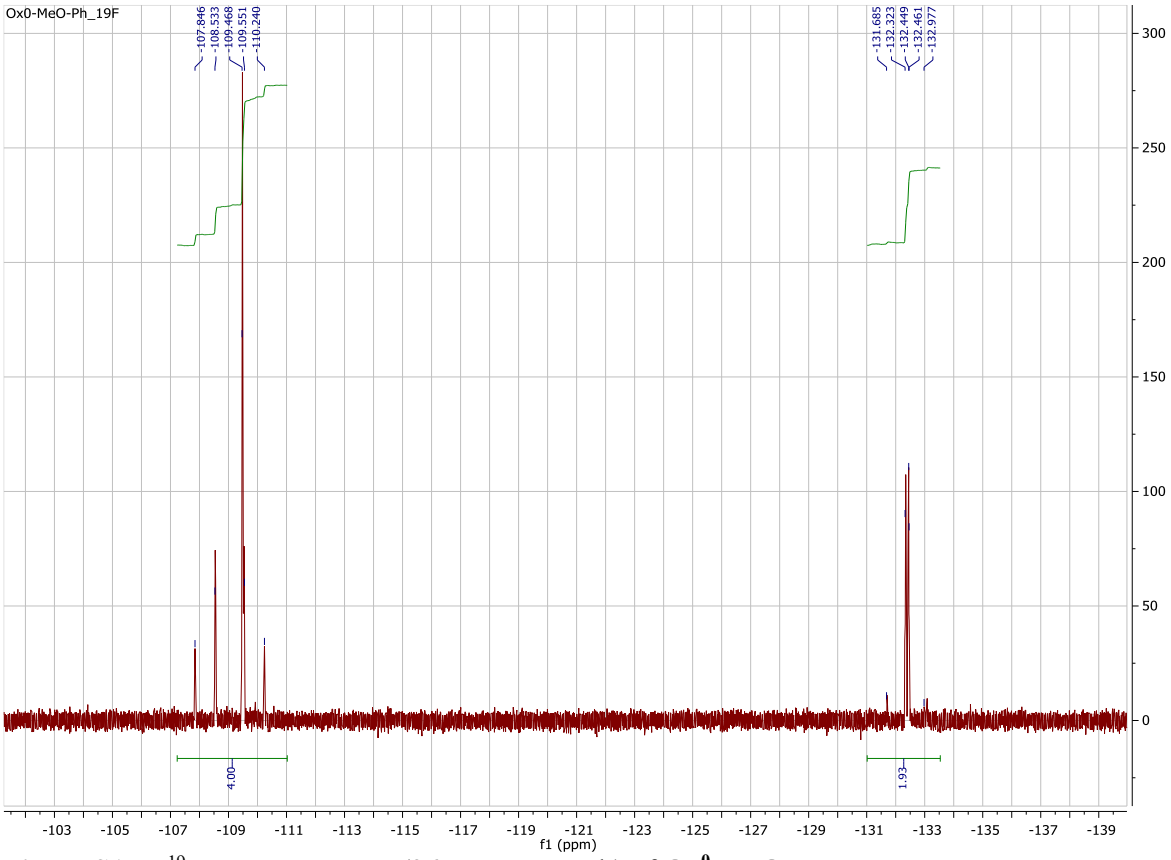


Figure S15c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^0-MeO-Ph**.

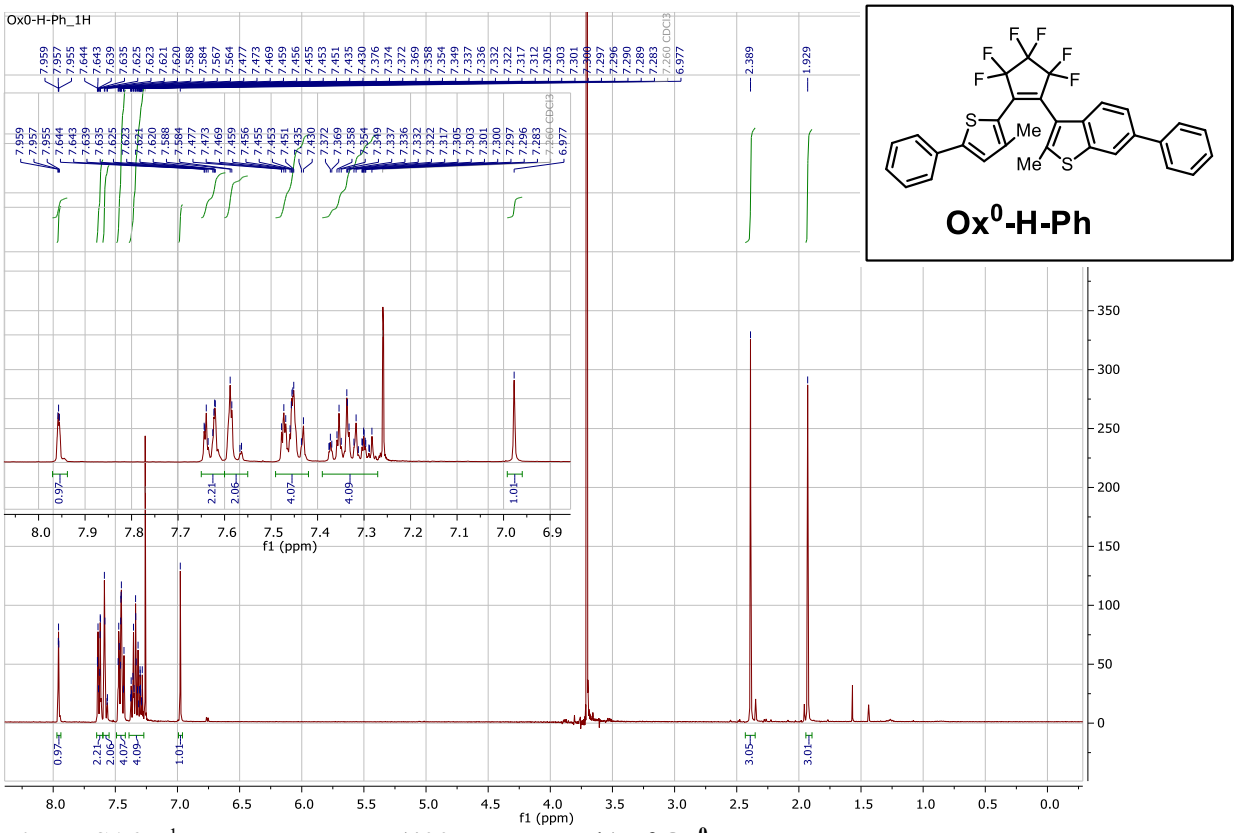


Figure S16a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^0-H-Ph**.

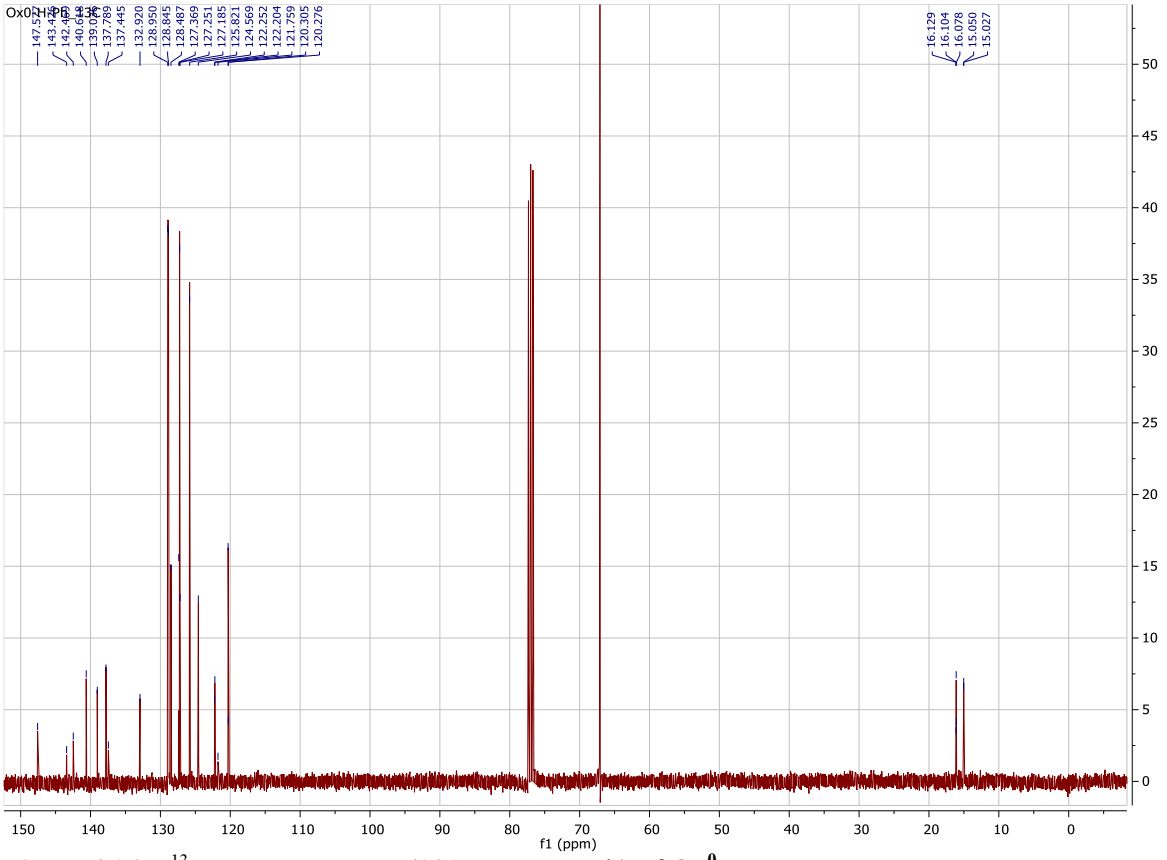


Figure S16b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^0-H-Ph**.

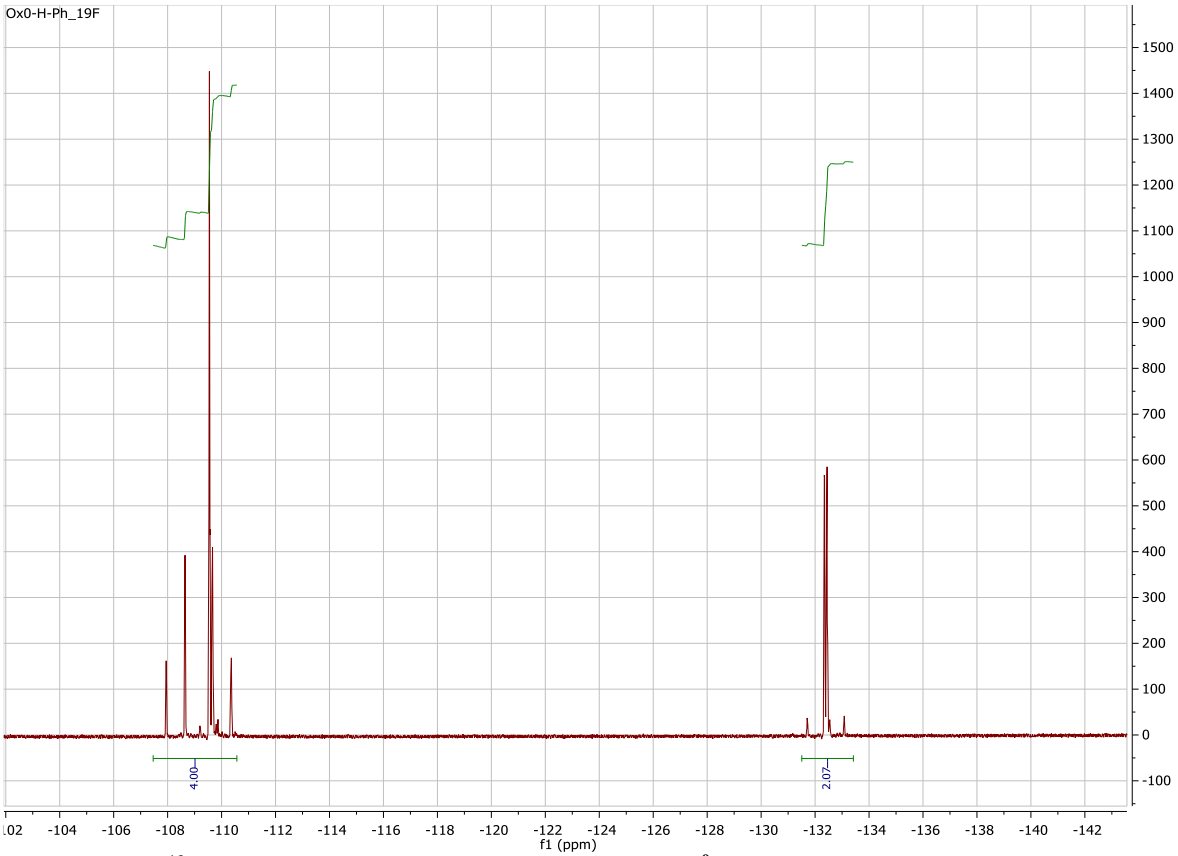


Figure S16c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^0-H-Ph**.

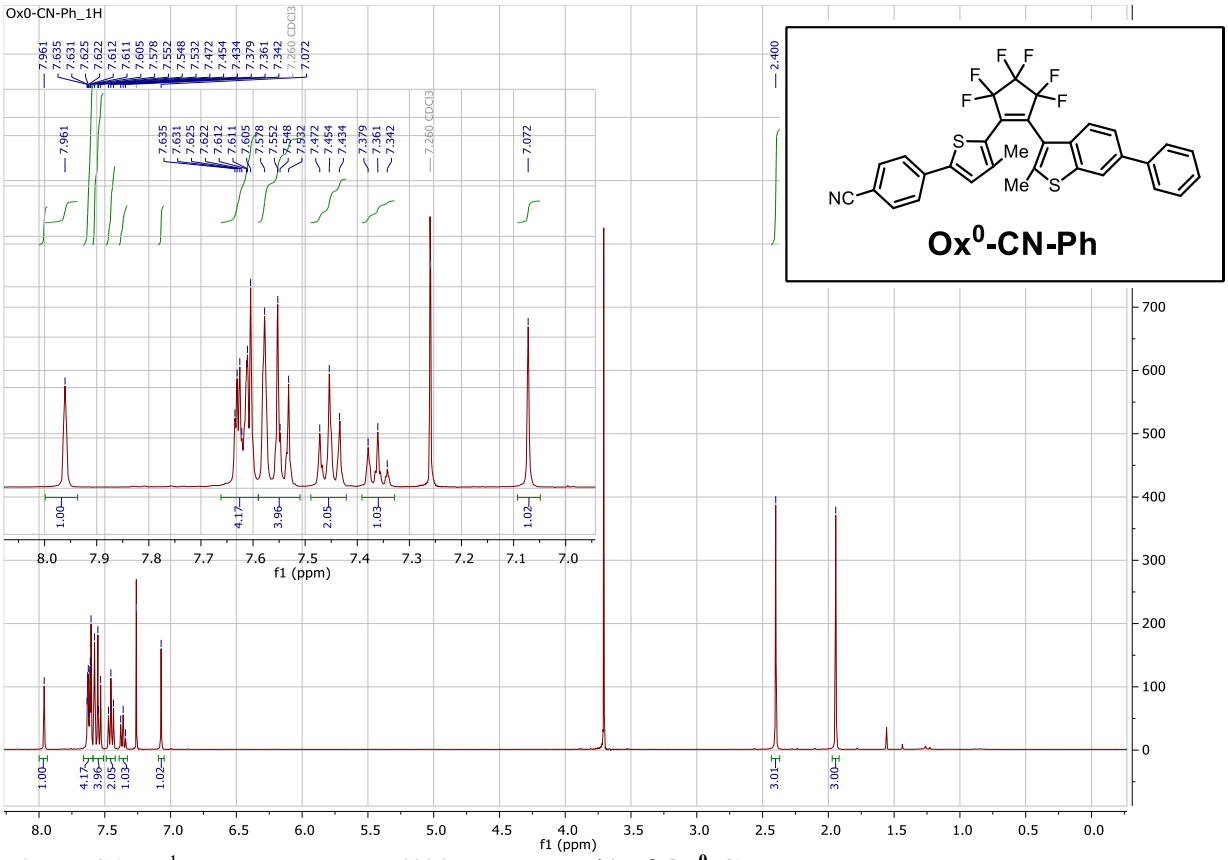


Figure S17a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^0-CN-Ph**.

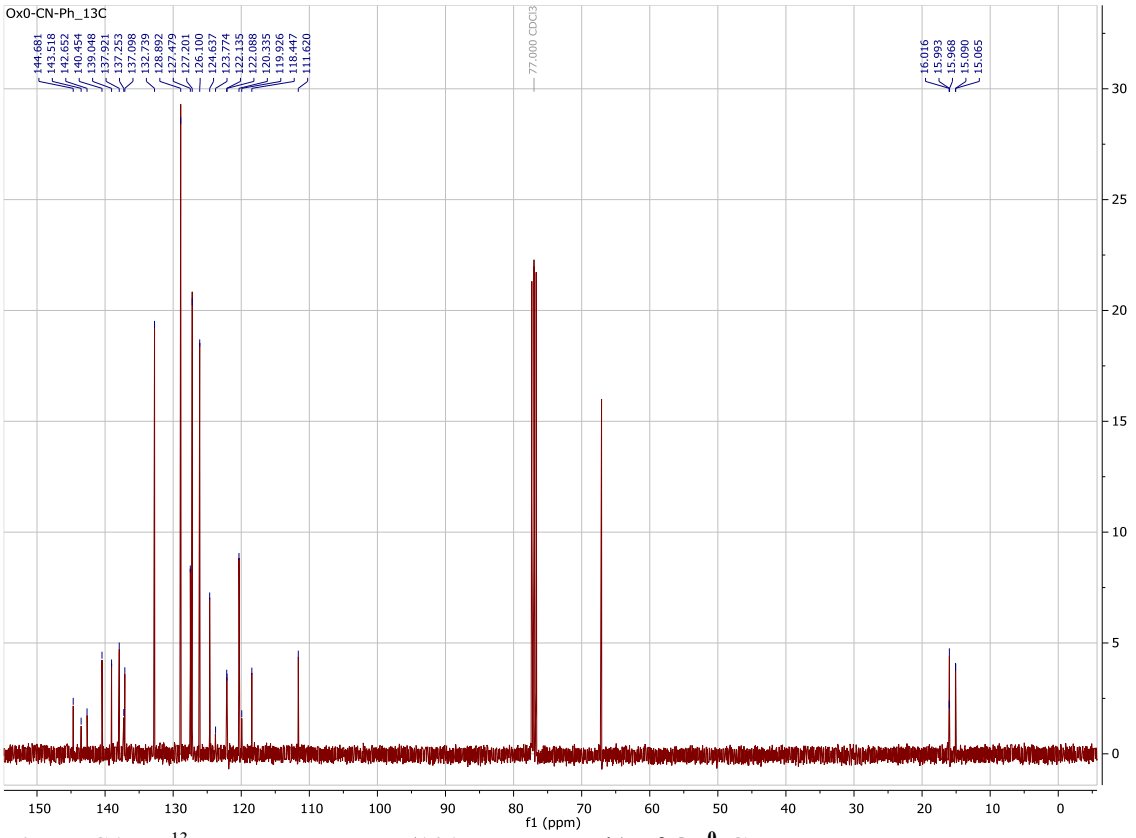


Figure S17b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^0-CN-Ph**.

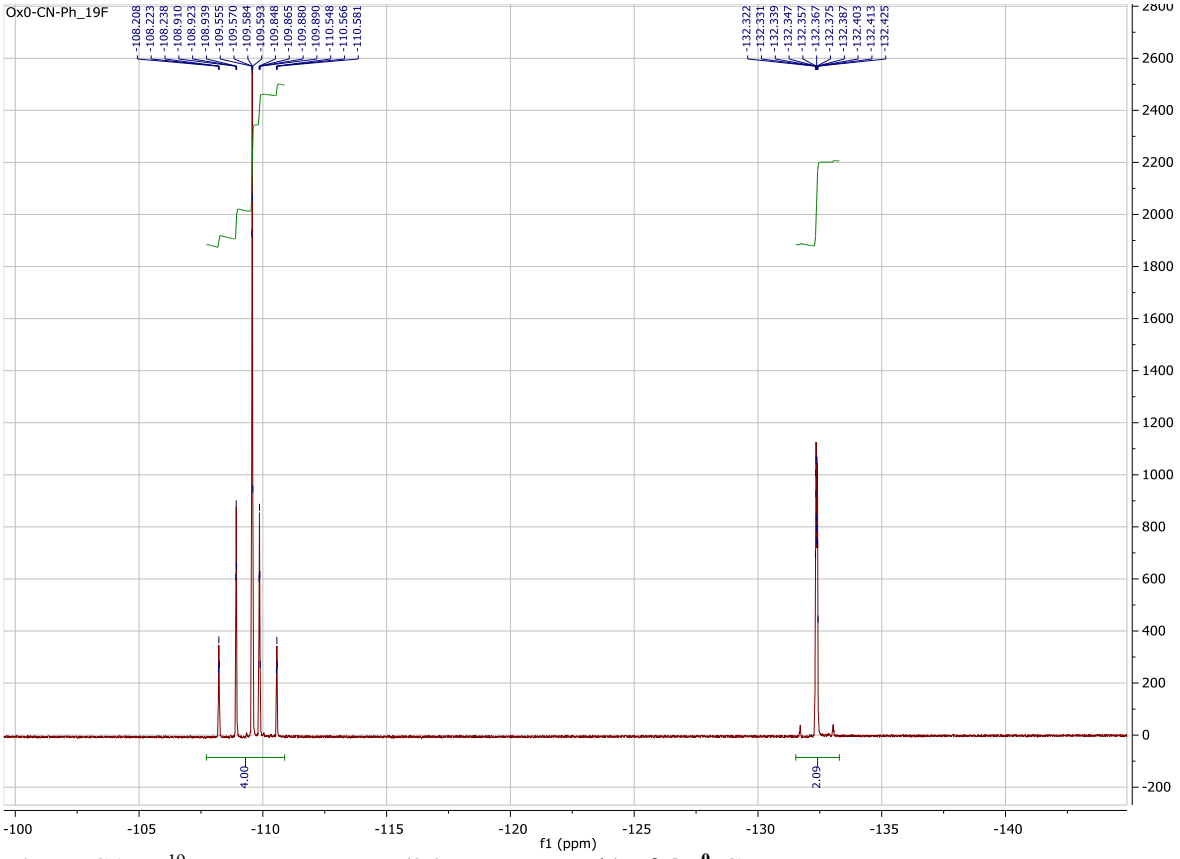


Figure S17c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^0-CN-Ph**.

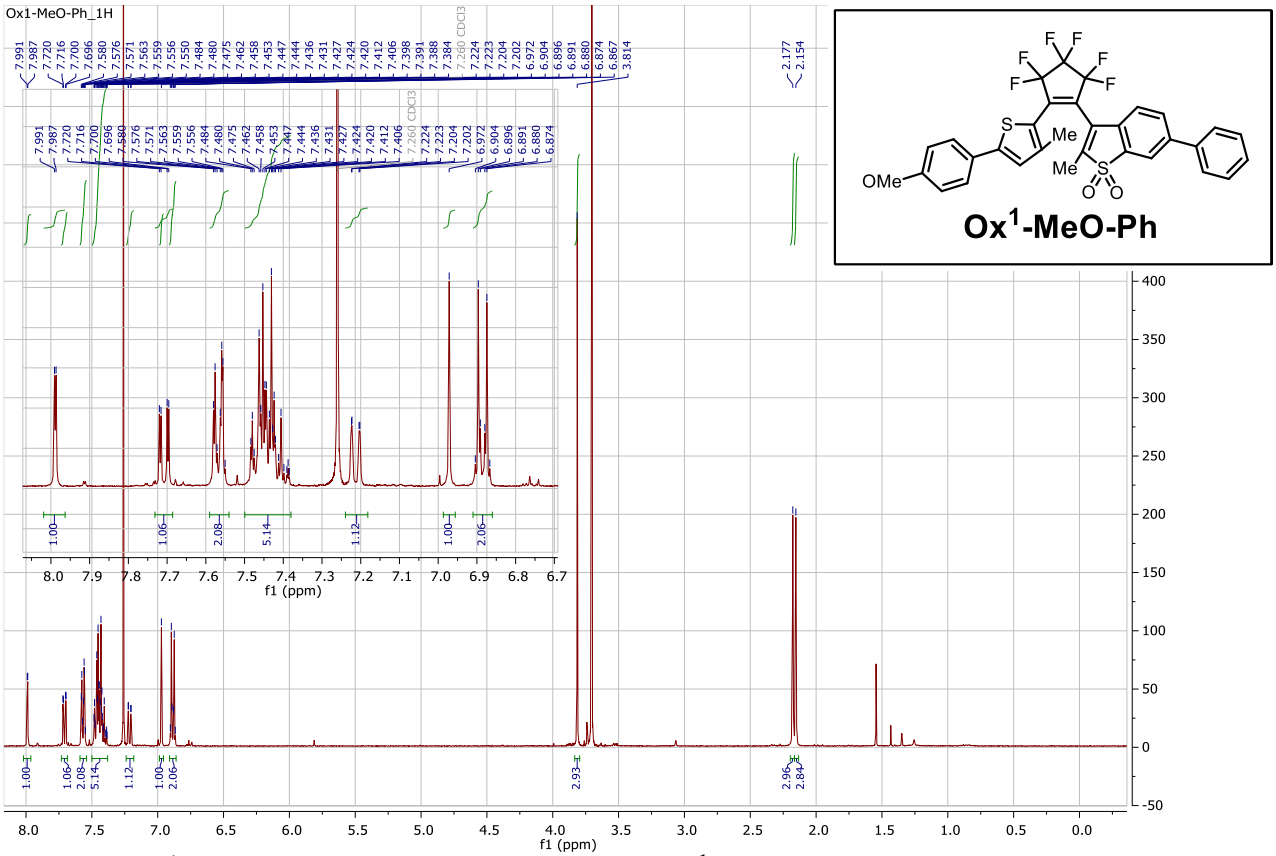


Figure S18a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^{1}-MeO-Ph**.

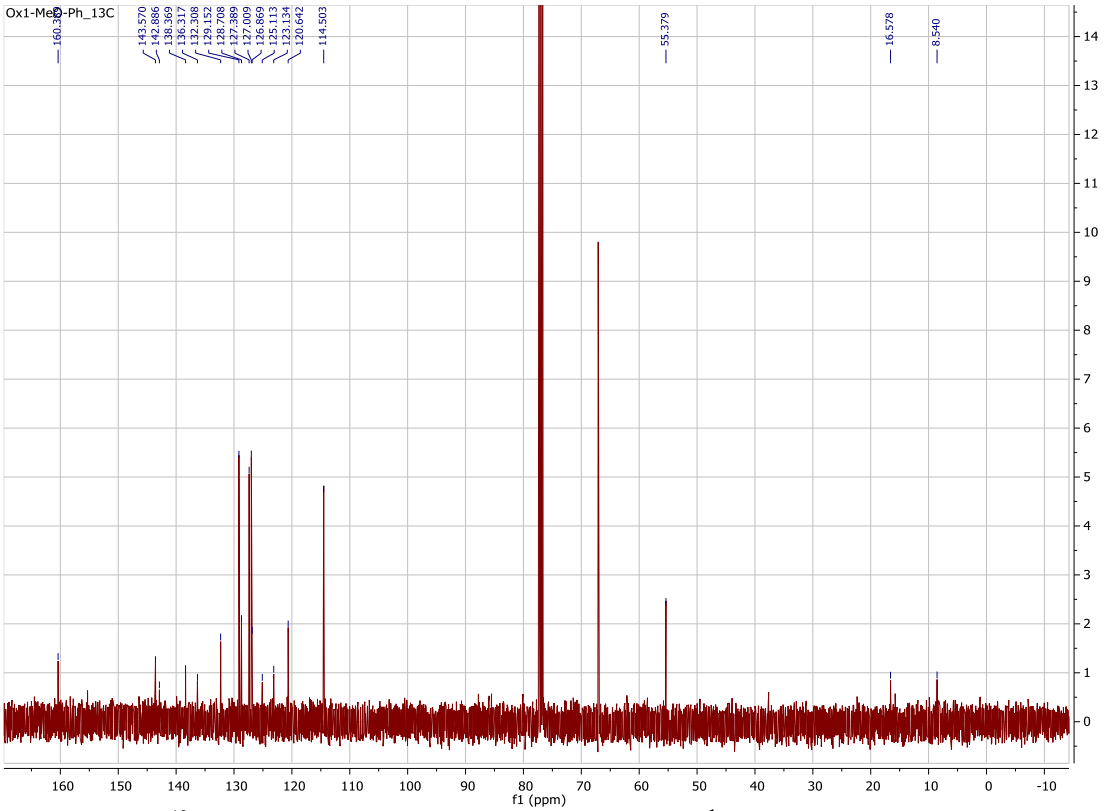


Figure S18b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^{1}-MeO-Ph**.

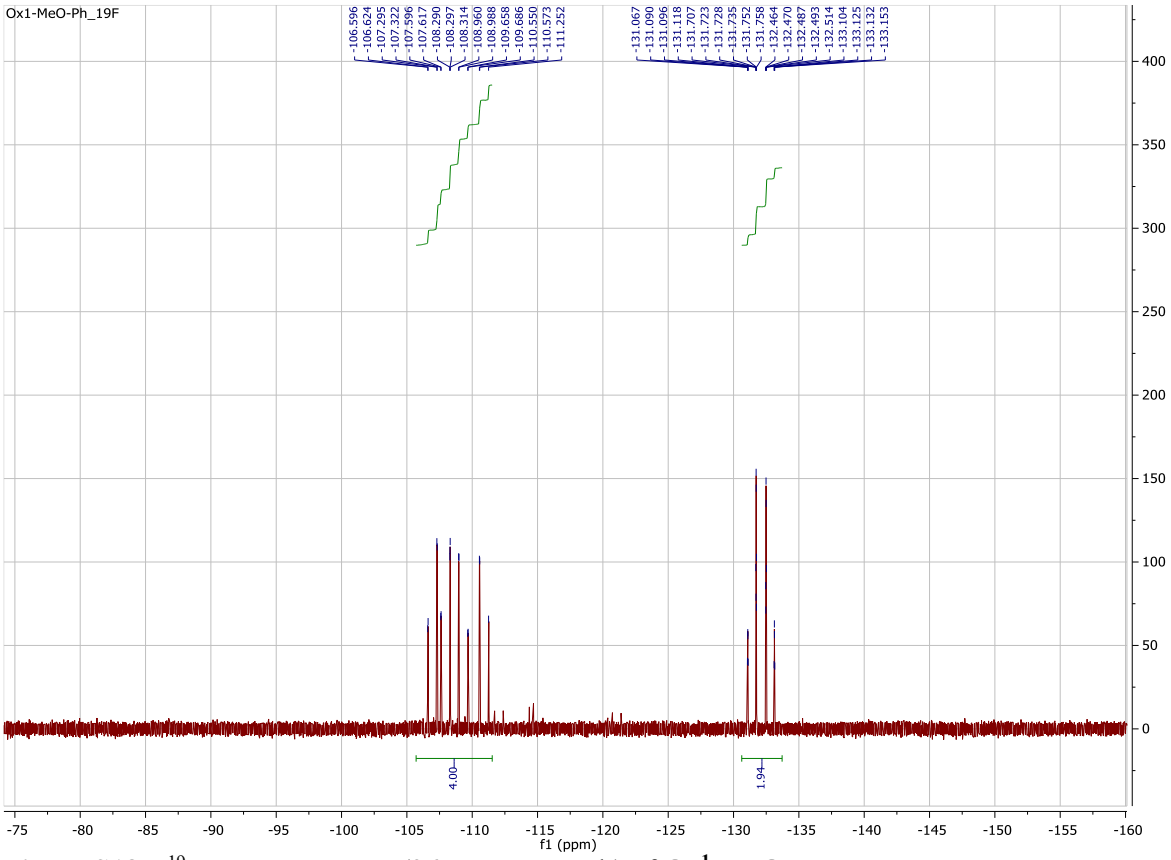


Figure S18c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^1-MeO-Ph**.

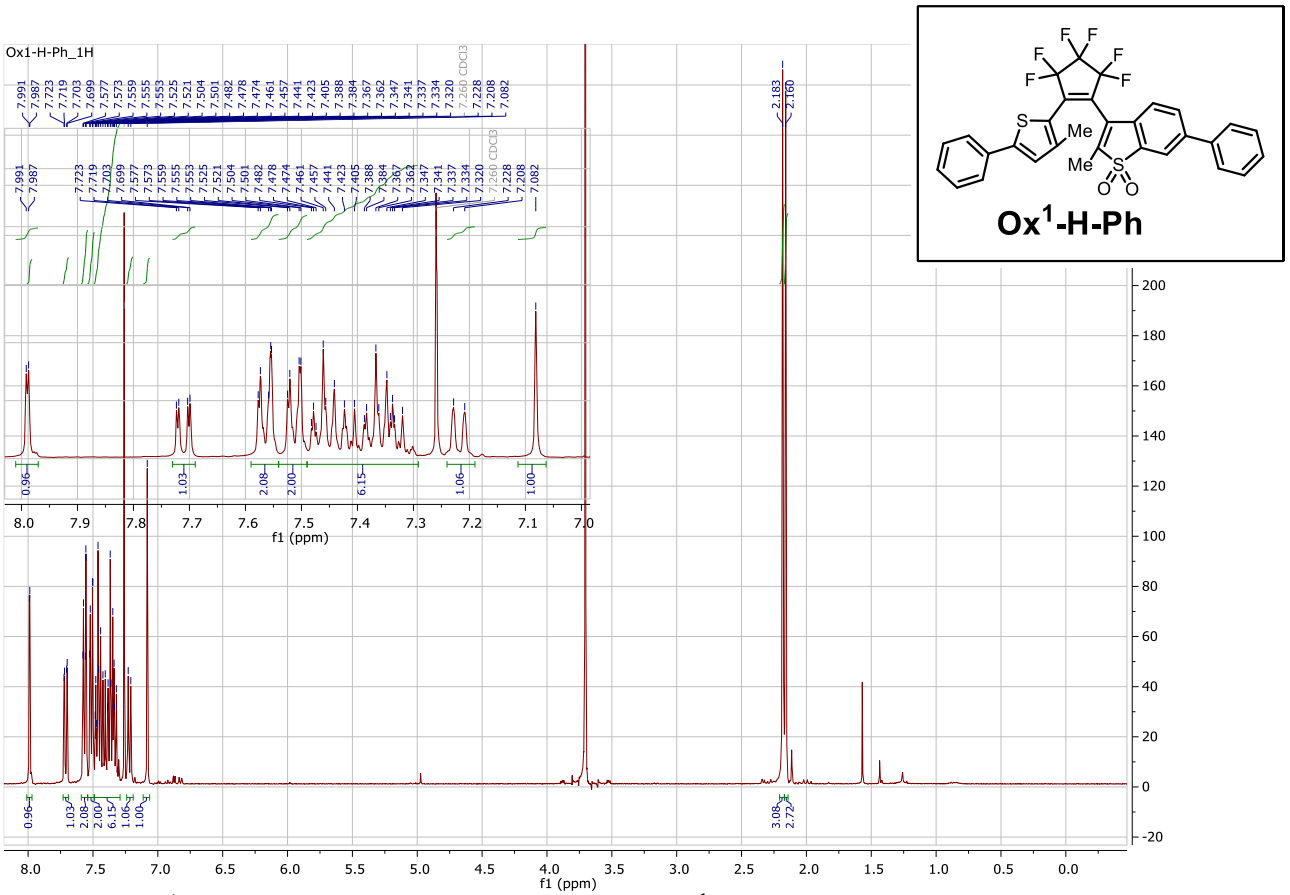


Figure S19a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^{1}-H-Ph**.

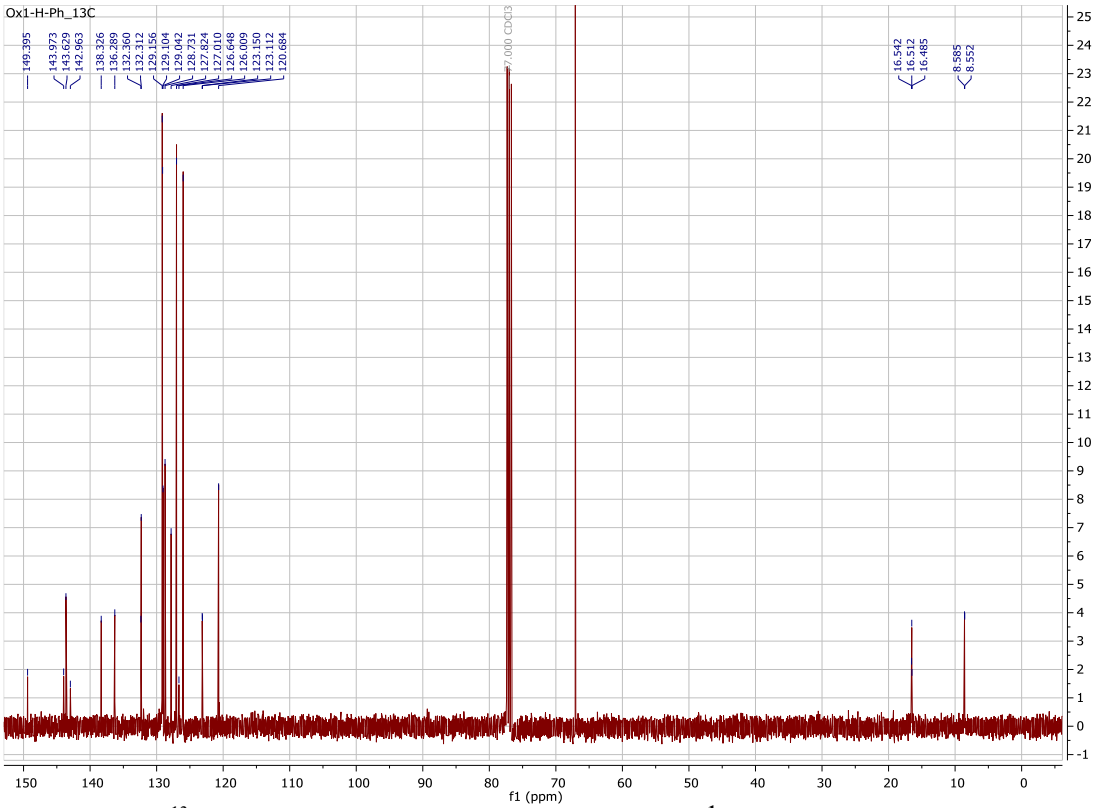


Figure S19b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^{1}-H-Ph**.

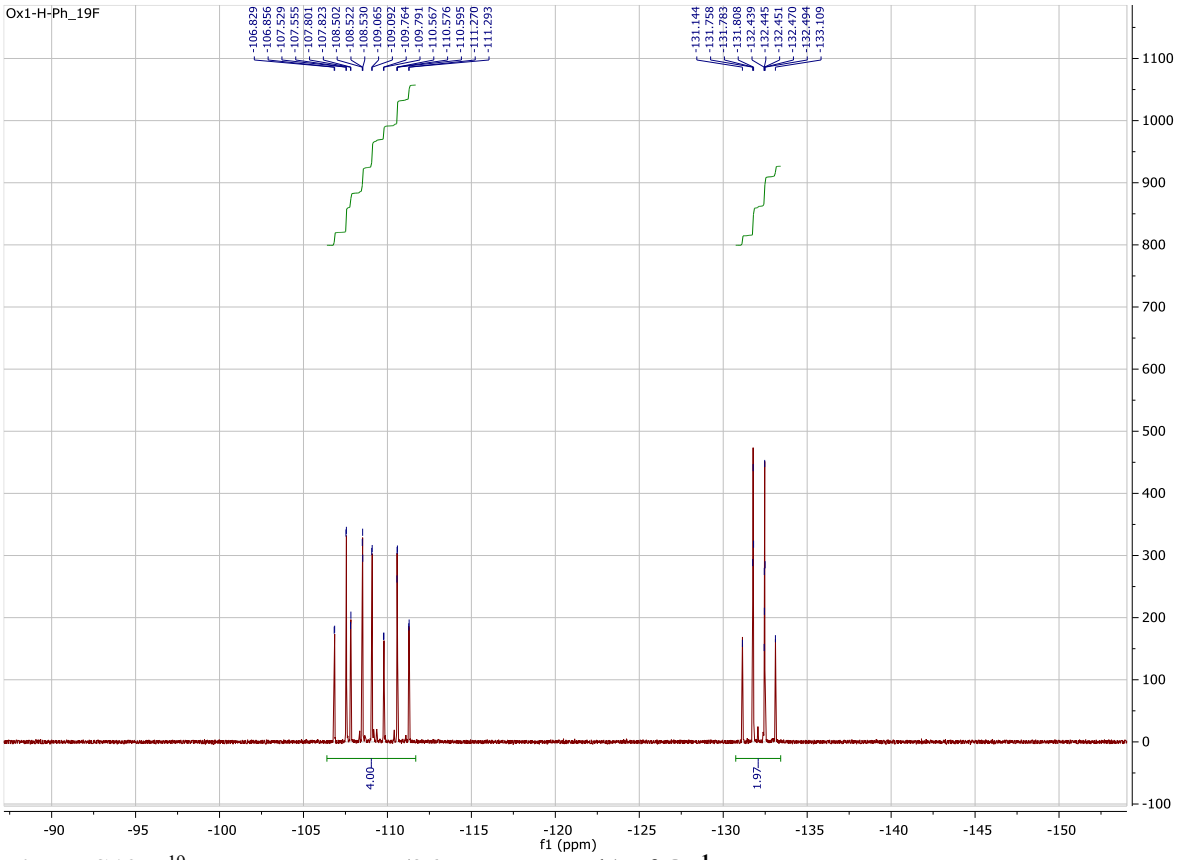


Figure S19c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^1-H-Ph**.

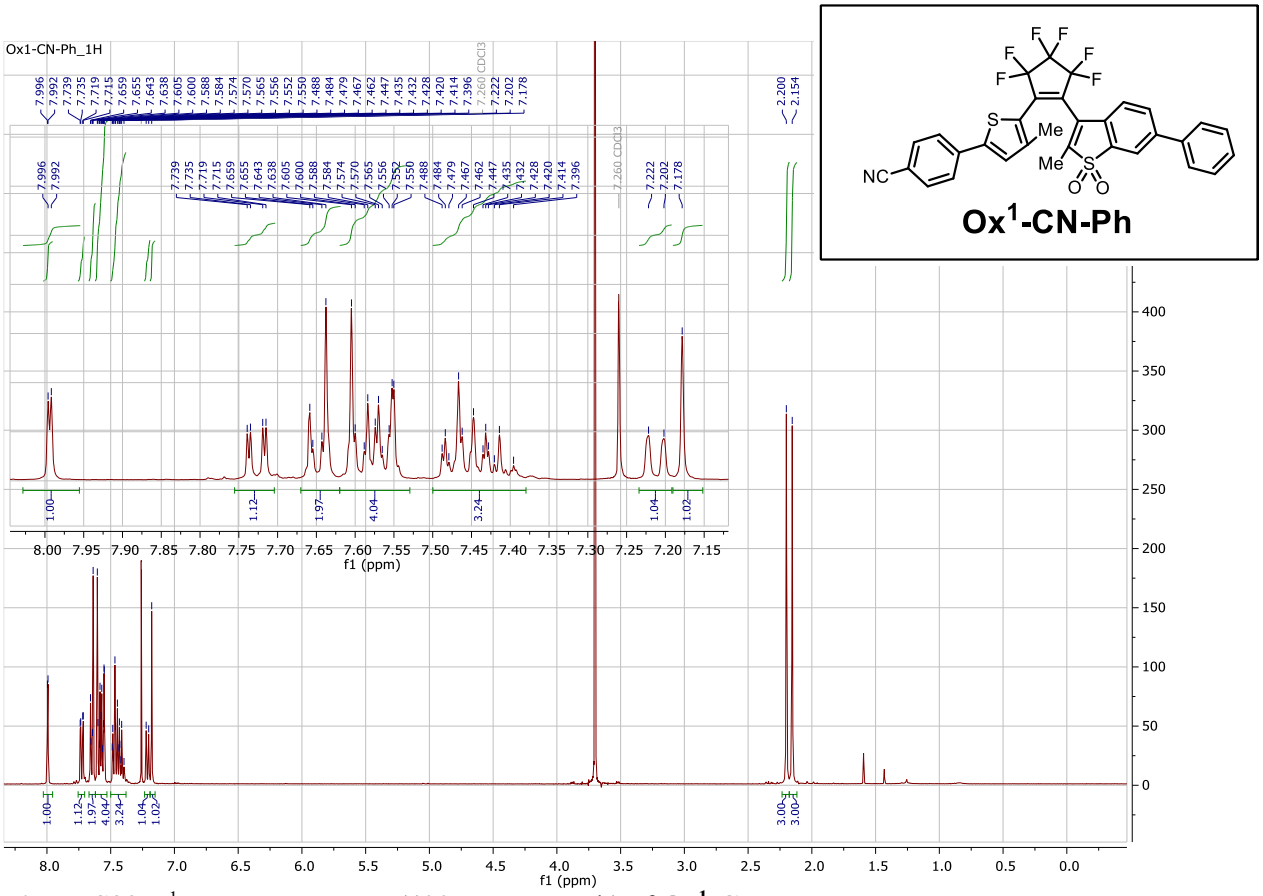


Figure S20a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^{1}-CN-Ph**.

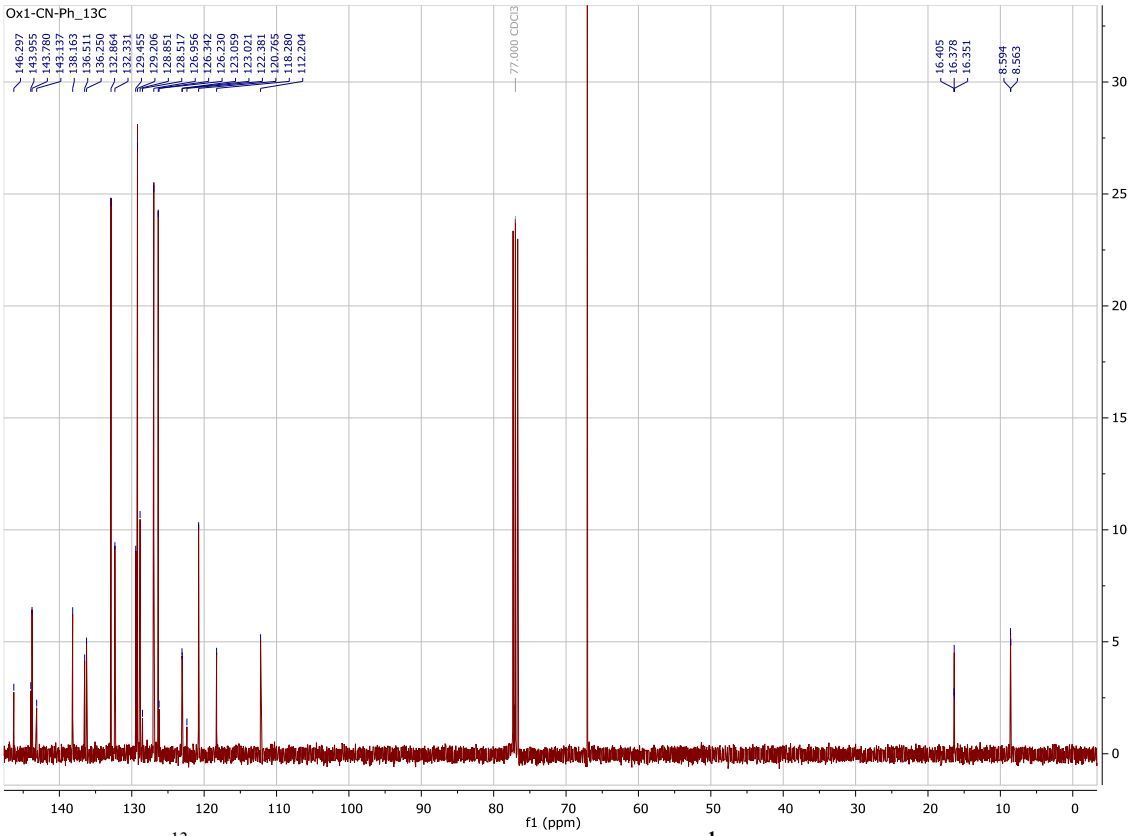


Figure S20b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^{1}-CN-Ph**.

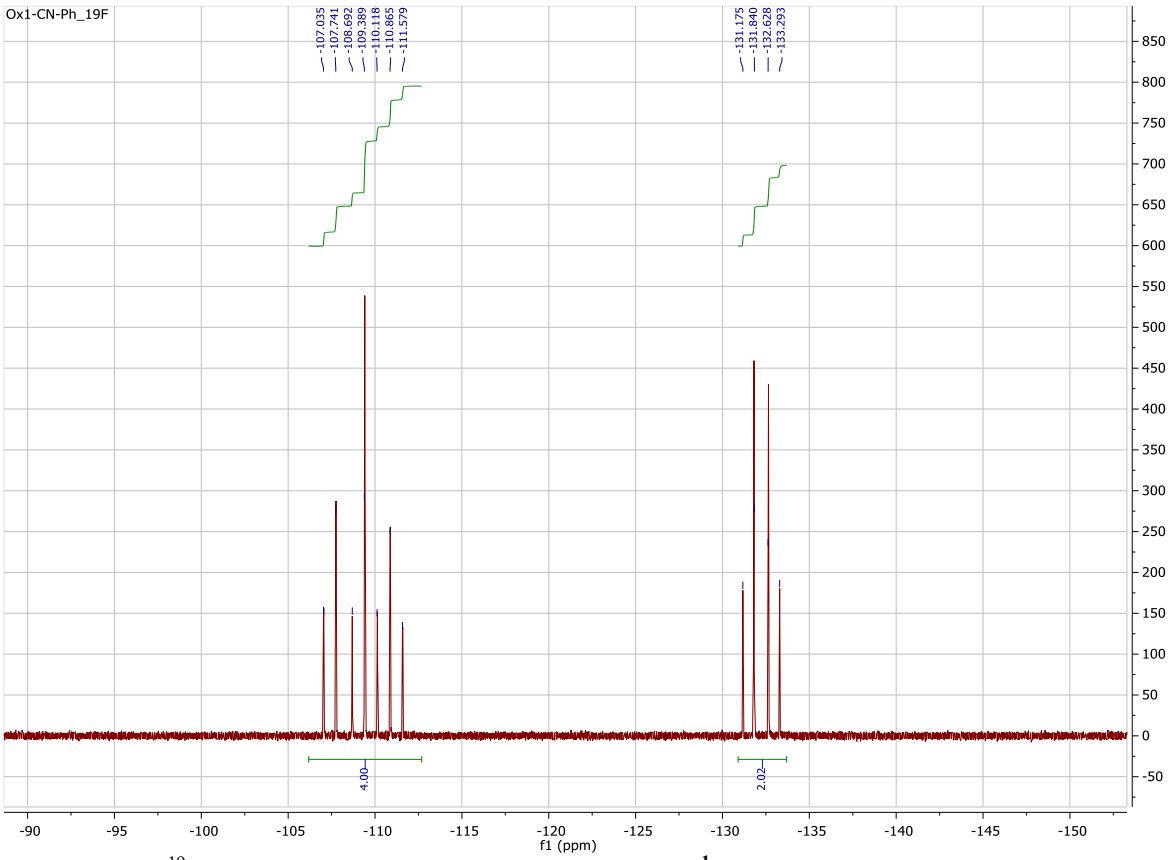


Figure S20c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^1-CN-Ph**.

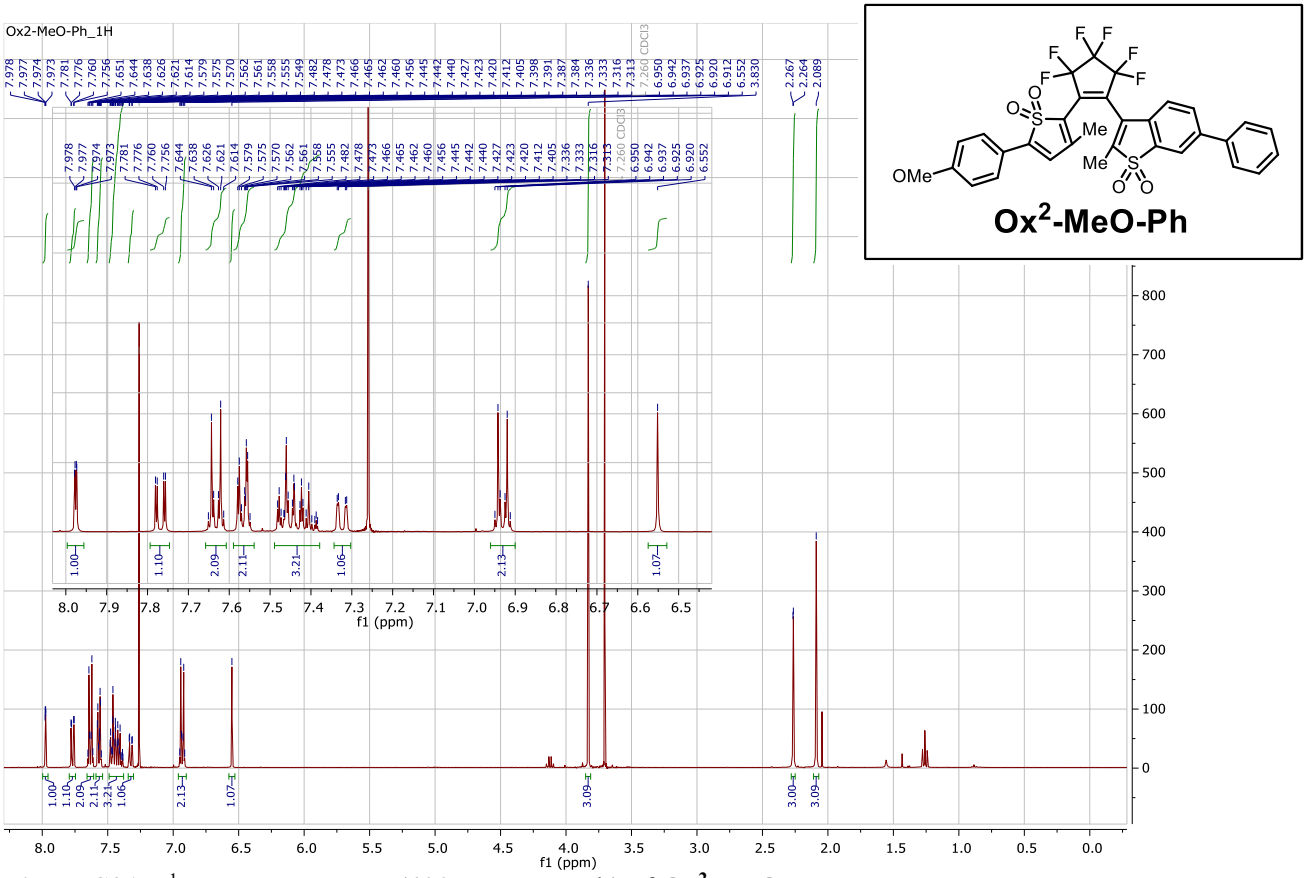


Figure S21a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^2-MeO-Ph**.

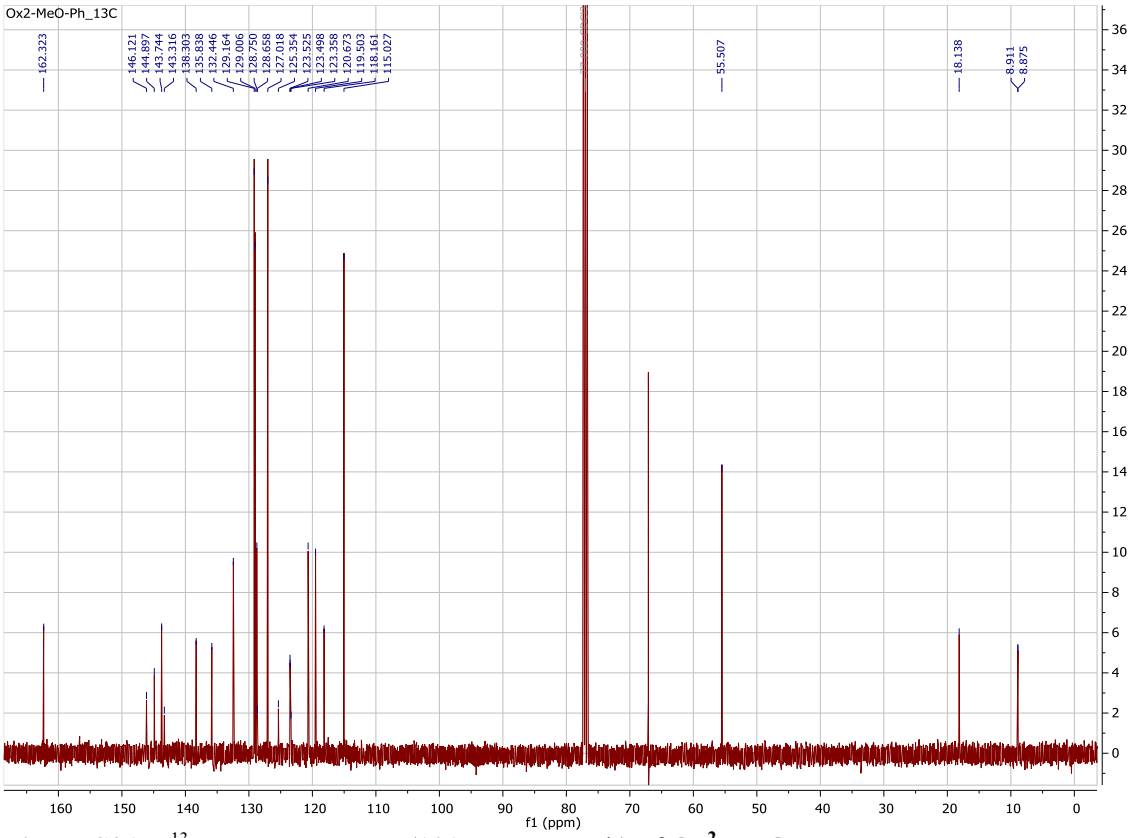


Figure S21b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^2-MeO-Ph**.

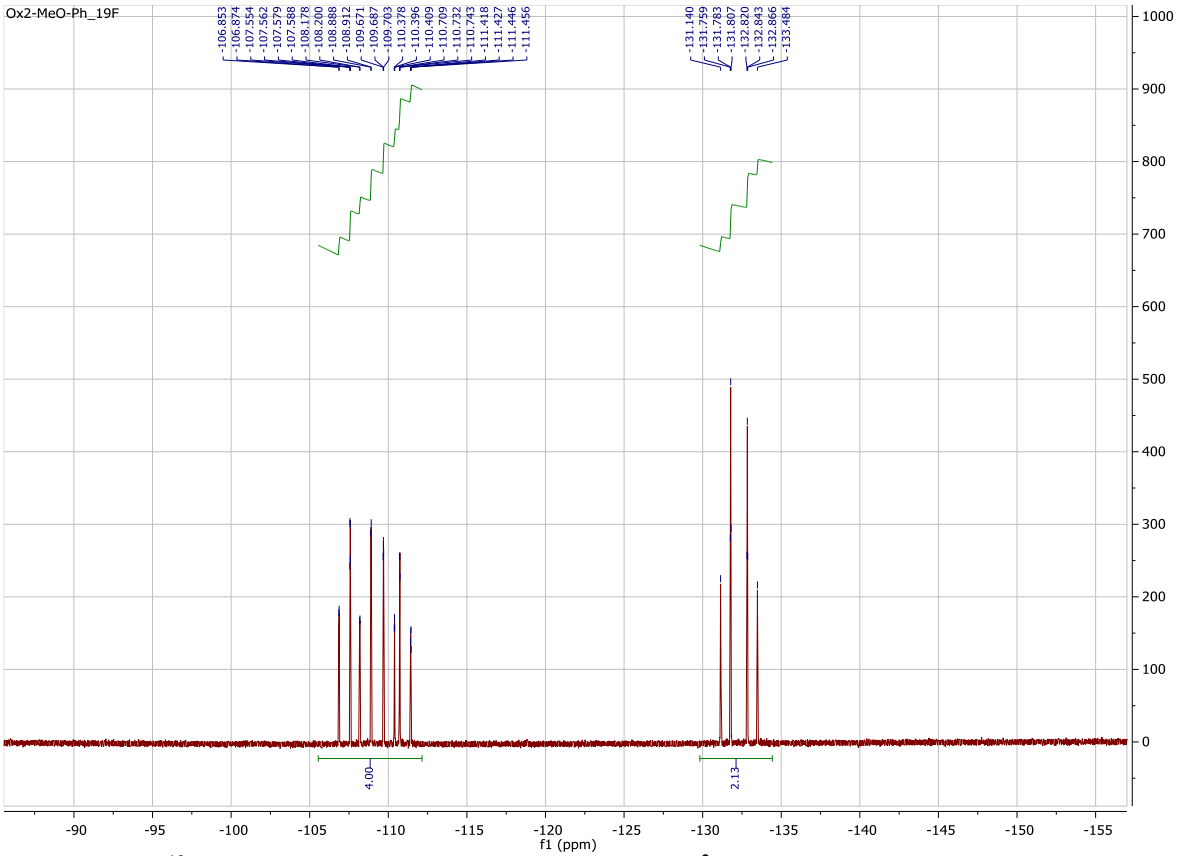


Figure S21c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^2-MeO-Ph**.

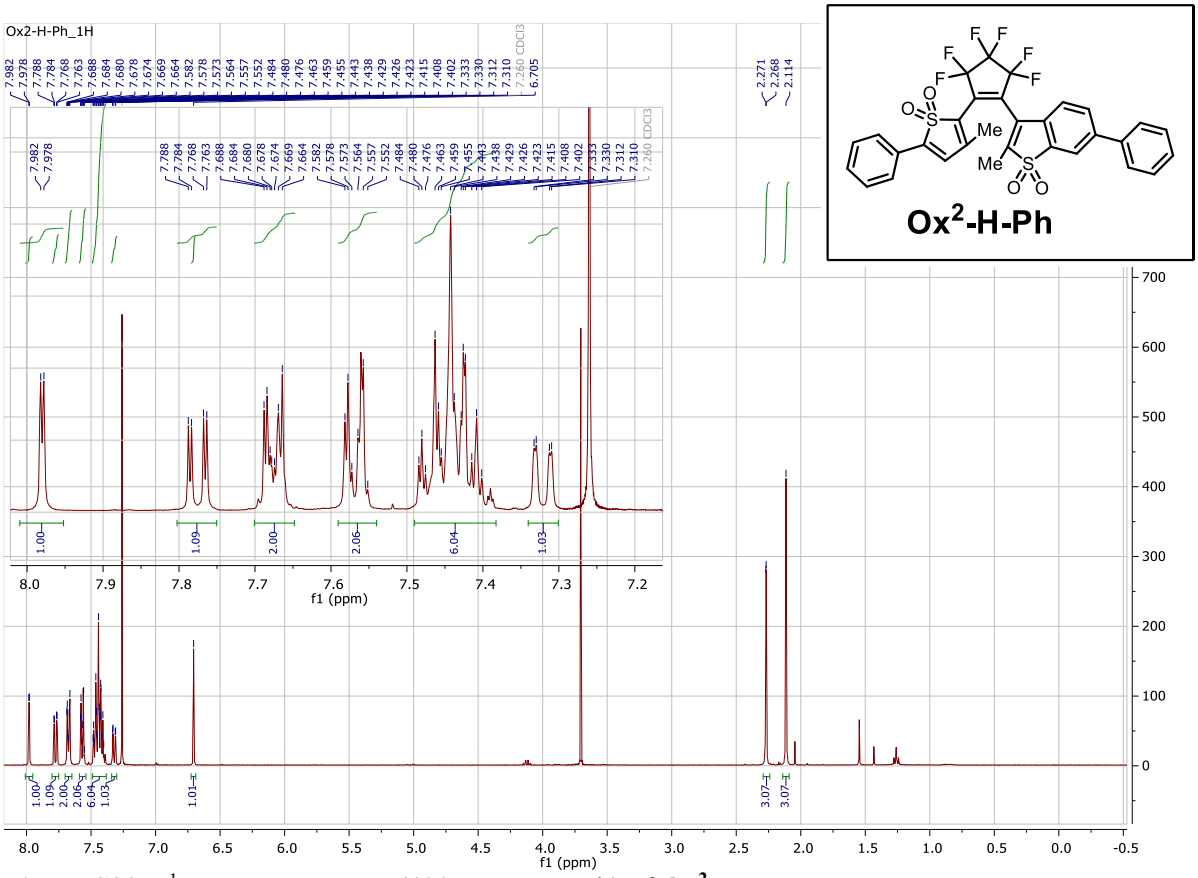


Figure S22a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^2-H-Ph**.

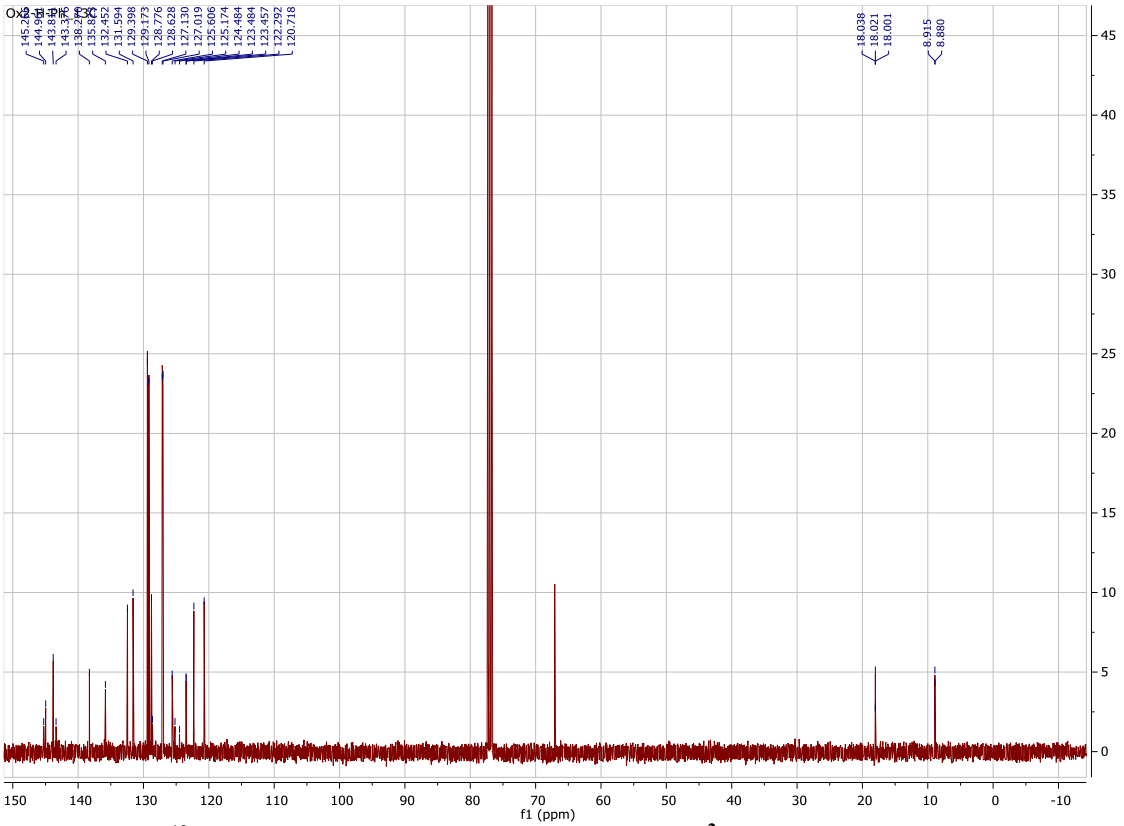


Figure S22b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^2-H-Ph**.

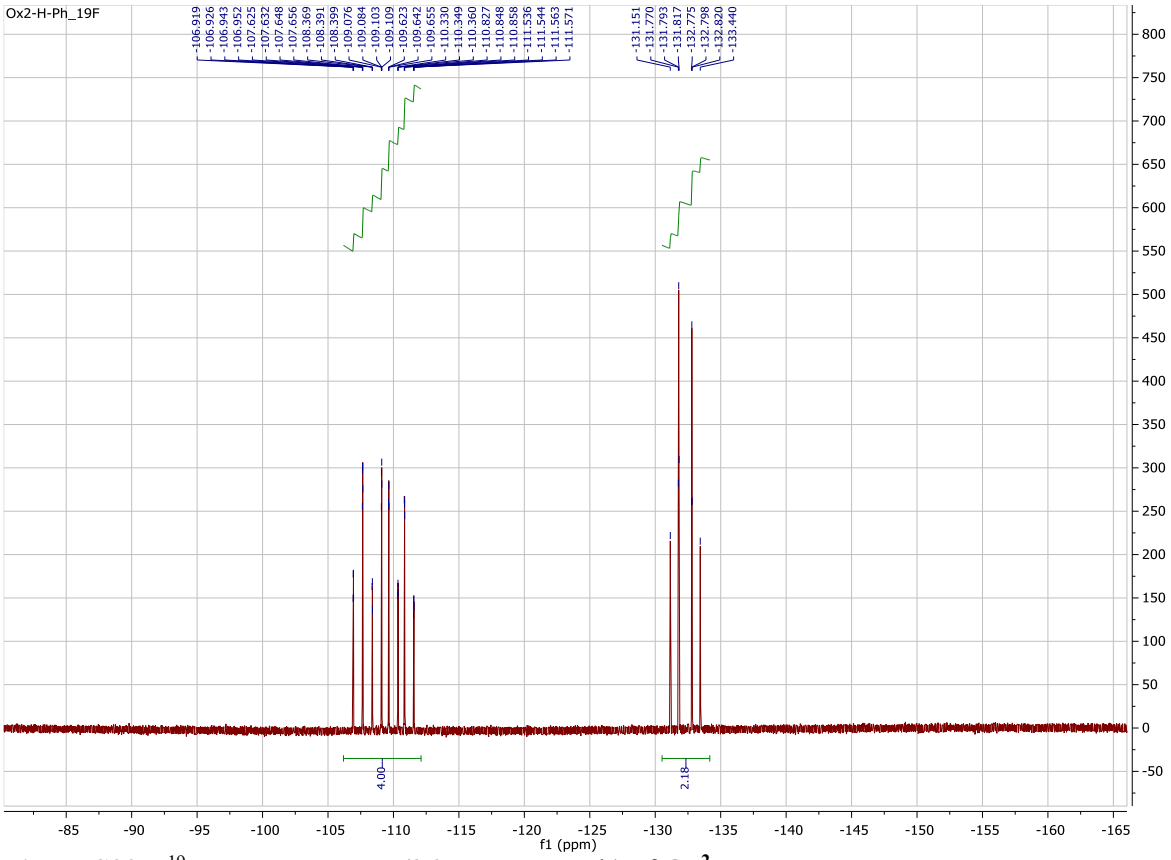


Figure S22c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^2-H-Ph**.

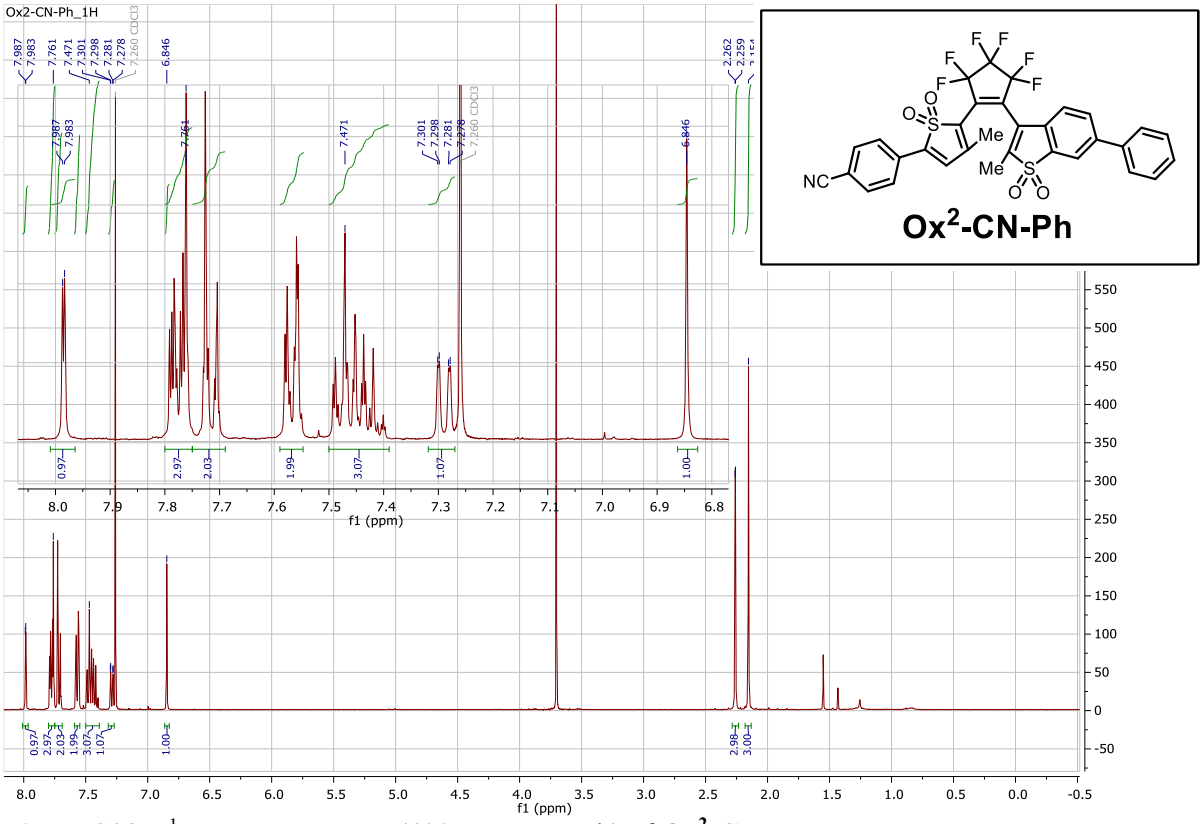


Figure S23a. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Ox^2-CN-Ph**.

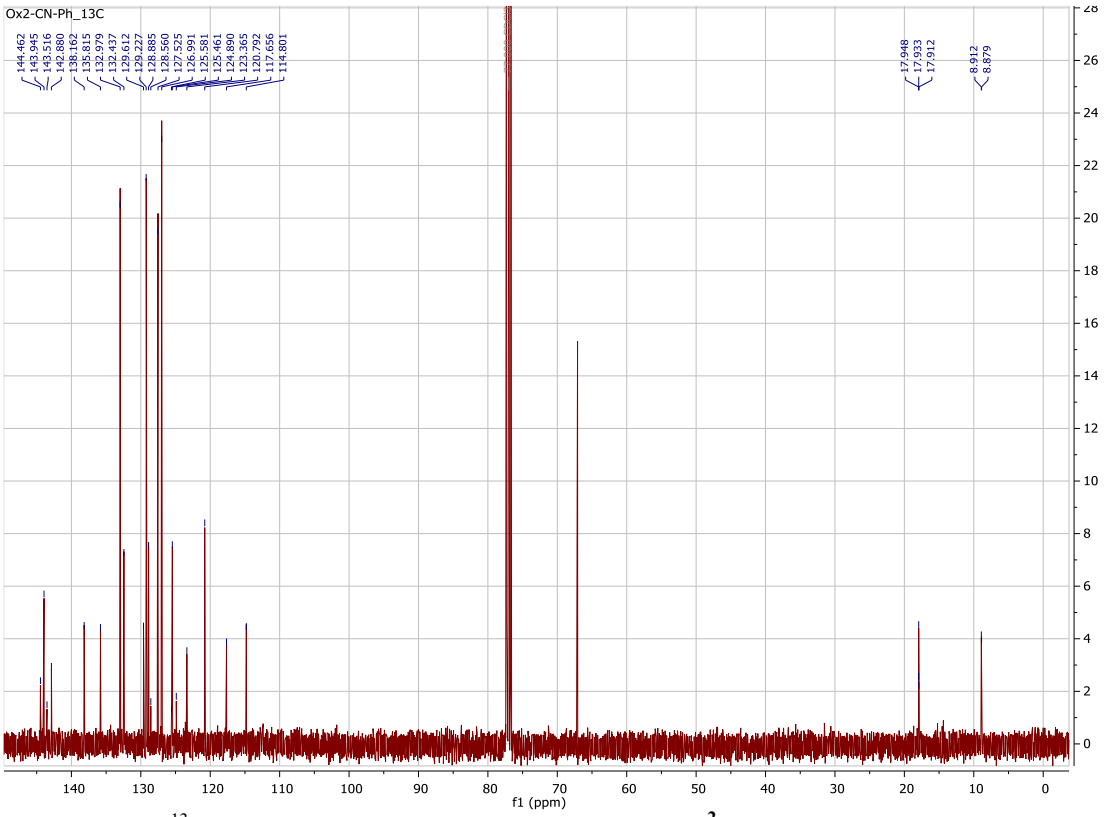


Figure S23b. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Ox^2-CN-Ph**.

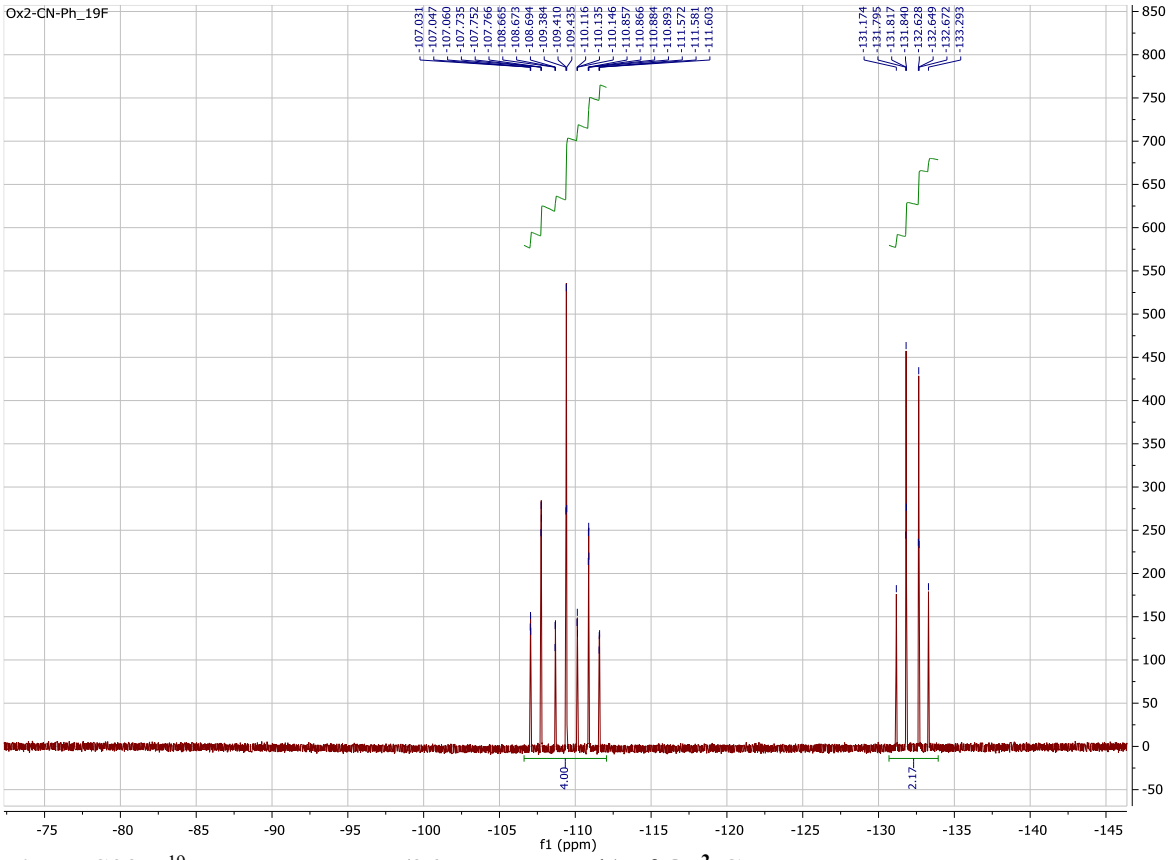


Figure S23c. ^{19}F-NMR spectrum (367 MHz, $CDCl_3$) of **Ox^2-CN-Ph**.

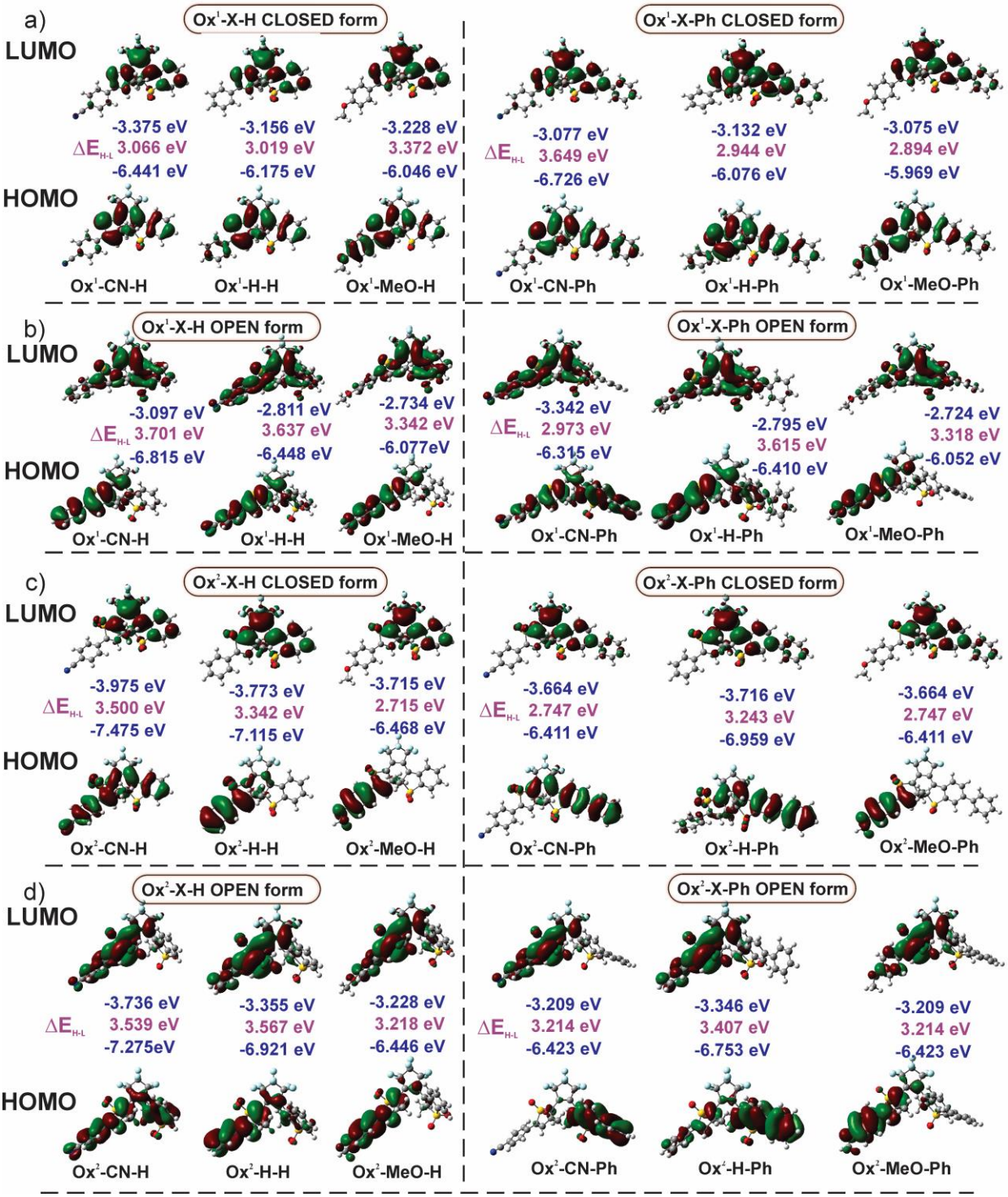
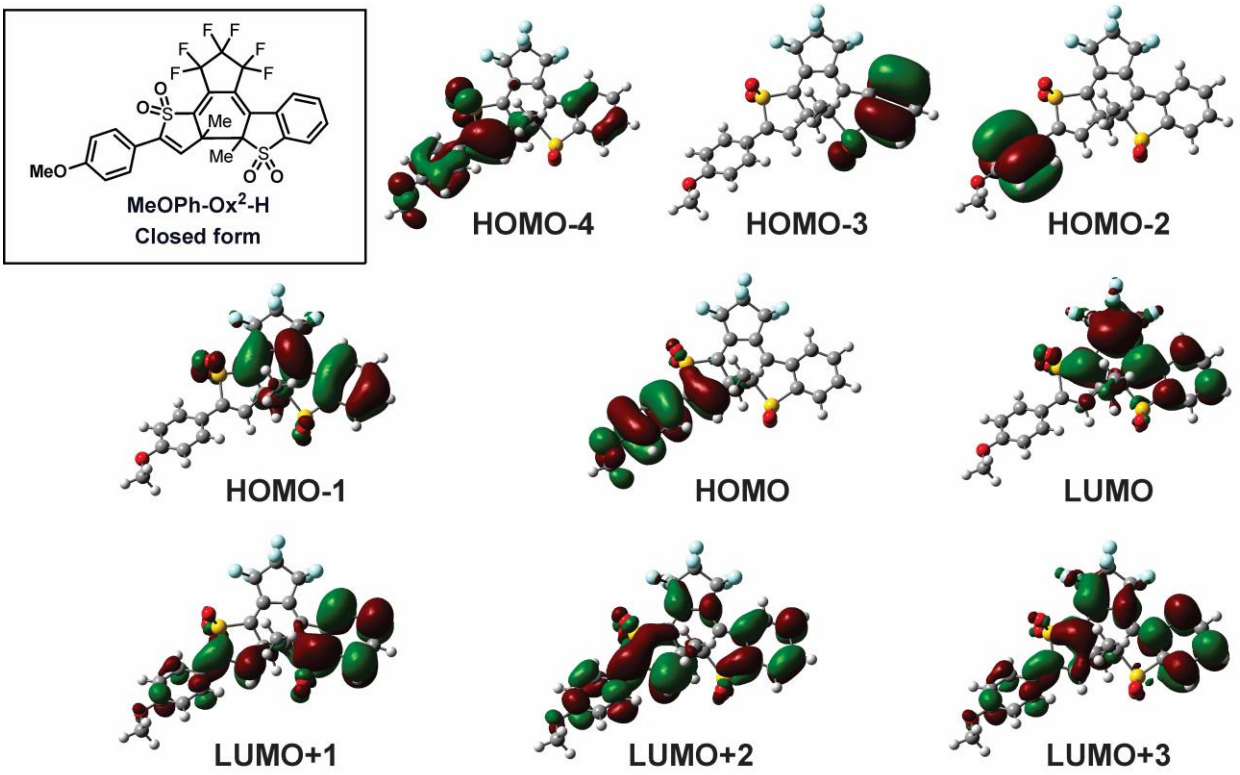
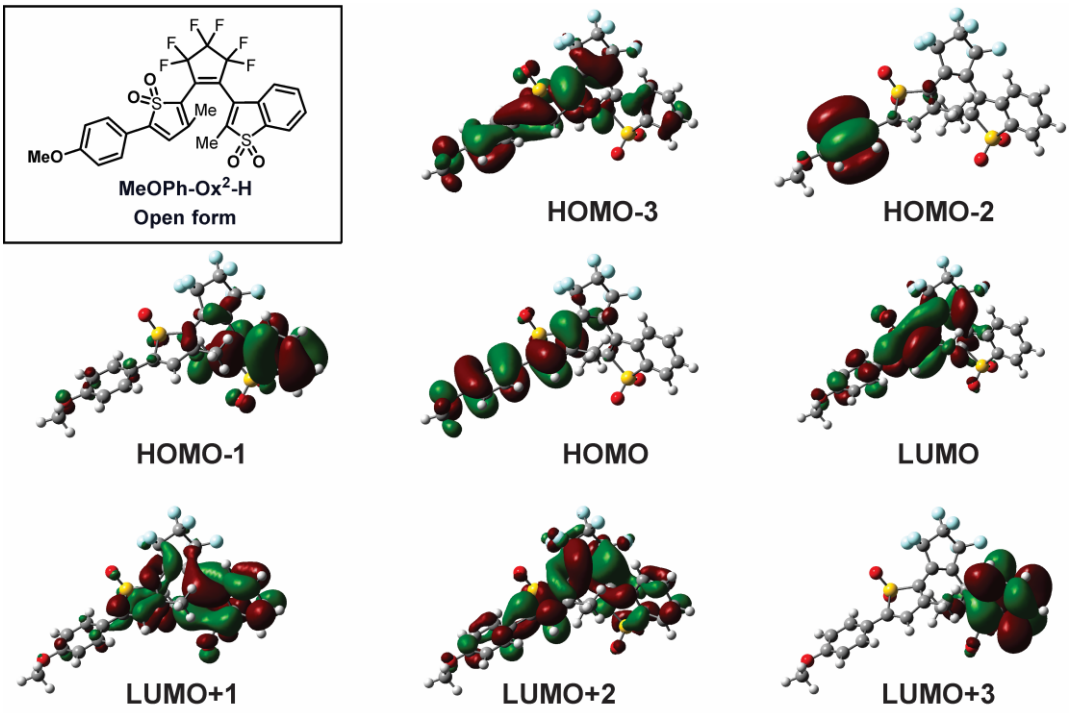


Figure S24. The DFT calculated ground state isodensity surface plots of the FMOs in **a)** closed forms **b)** open forms of **OX^1-X-Y** series and **c**) closed forms **d**) open forms of **OX^2-X-Y** series



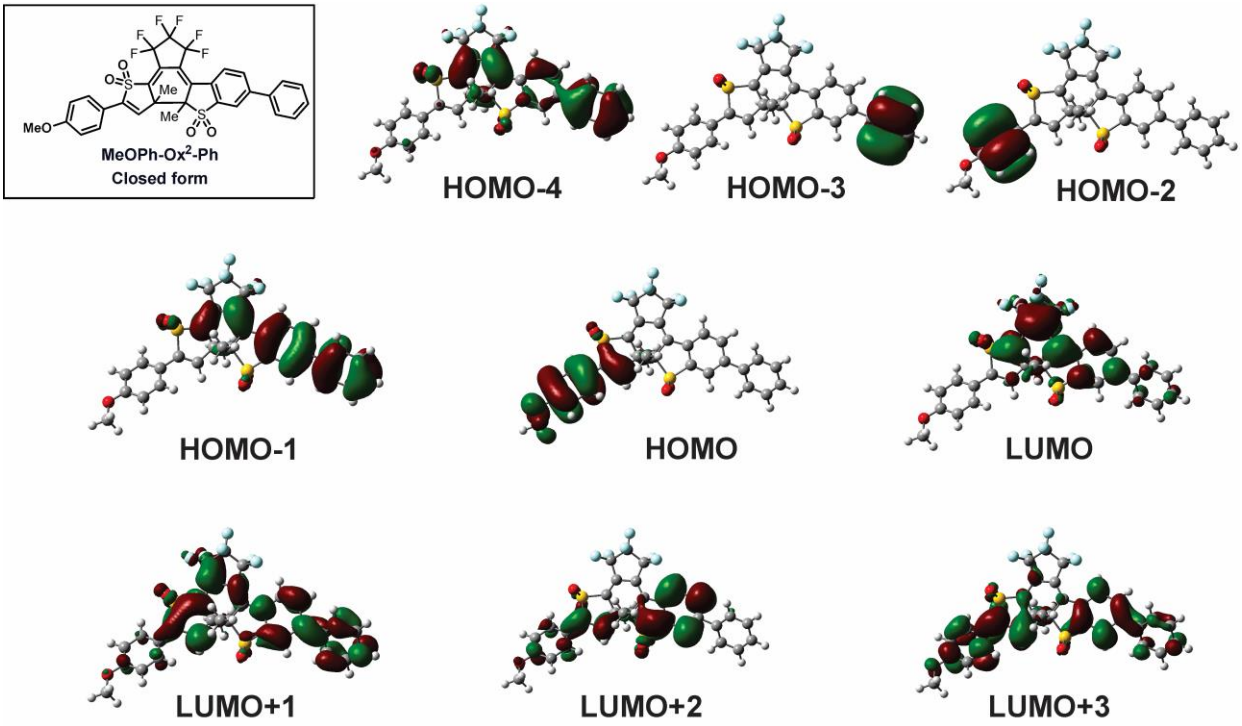
Transition	Major contribution	*f* (Oscillator strength)	Energy, eV	Wavelength, nm
$S_0 \rightarrow S_1$	HOMO-1 -> LUMO (100%)	0.3824	3.3880	365.96
$S_0 \rightarrow S_2$	HOMO-4 -> LUMO (15%) HOMO-1 -> LUMO (25%) HOMO -> LUMO (60%)	0.1615	3.5770	346.62
$S_0 \rightarrow S_3$	HOMO-3 -> LUMO (63%) HOMO-3 -> LUMO+3 (13%) HOMO-1 -> LUMO+1 (24%)	0.0319	4.4639	277.75
$S_0 \rightarrow S_4$	HOMO-5 -> LUMO (100%)	0.0079	4.5451	272.79
$S_0 \rightarrow S_5$	HOMO -> LUMO+2 (100%)	0.6831	4.6322	267.66
$S_0 \rightarrow S_6$	HOMO-4 -> LUMO (25%) HOMO-2 -> LUMO (63%) HOMO-2 -> LUMO+2 (22%)	0.0089	4.9148	252.27

Figure S25. Electronic absorption spectra of closed form of **OX²-MeO-H** computed using TDDFT, B3LYP/6-311++G(d,p)/IEFPCM (1,4-dioxane) and DFT calculated isodensity surface plots of the FMOs and neighboring molecular orbitals involved in calculated transitions.



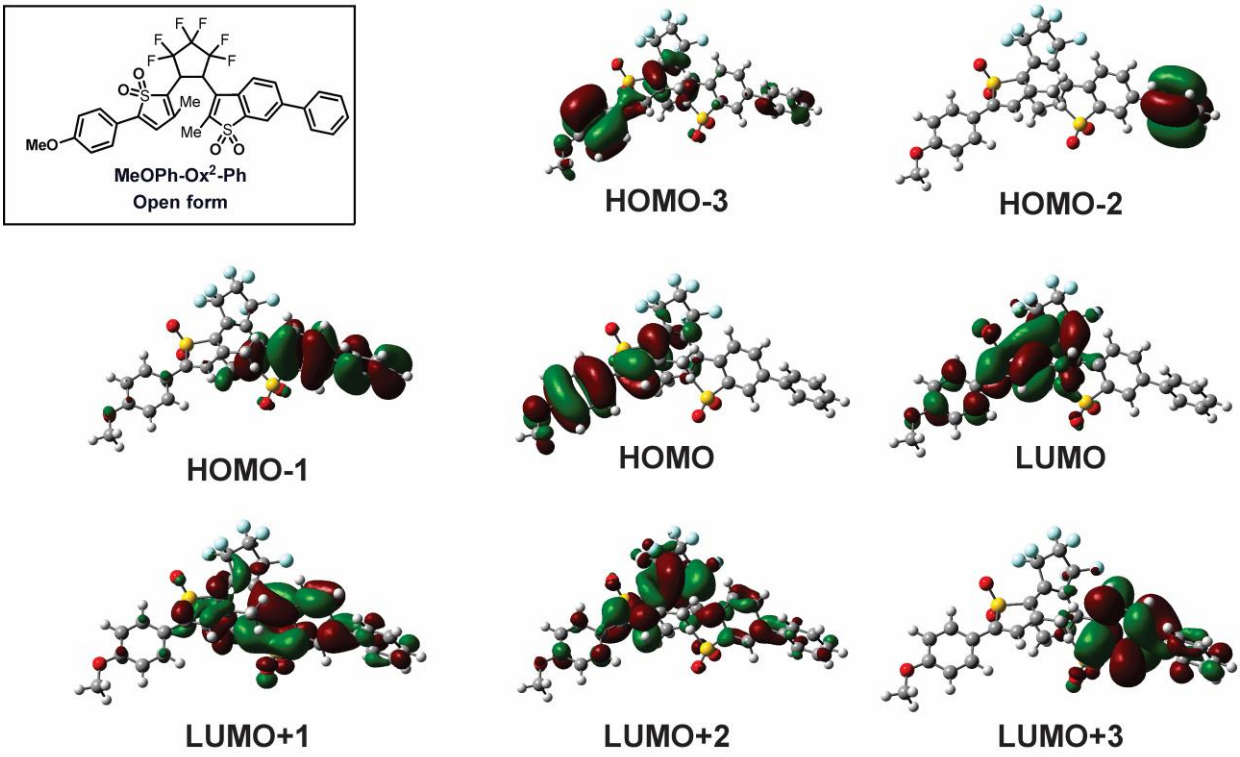
Transition	Major contribution	*f* (Oscillator strength)	Energy, eV	Wavelength, nm
S_0 –> S_1	HOMO -> LUMO (79%) HOMO-3 -> LUMO (21%)	0.6300	3.1146	398.07
S_0 –> S_2	HOMO-1 -> LUMO (46%) HOMO-1 -> LUMO+1 (40%) HOMO -> LUMO+2 (14%)	0.0896	4.1260	300.49
S_0 –> S_3	HOMO-3 -> LUMO+1 (21%) HOMO-1 -> LUMO (30%) HOMO -> LUMO+1 (49%)	0.0032	4.3852	282.73
S_0 –> S_4	HOMO-5 -> LUMO (13%) HOMO-3 -> LUMO (22%) HOMO-1 -> LUMO+1 (44%) HOMO-1 -> LUMO+2 (21%)	0.0280	4.4213	280.43
S_0 –> S_5	HOMO-2 -> LUMO (50%) HOMO-2 -> LUMO+2 (16%) HOMO-2 -> LUMO+8 (9%) HOMO -> LUMO+6 (25%)	0.0000	4.6133	268.75
S_0 –> S_6	HOMO-8 -> LUMO (11%) HOMO-5 -> LUMO (19%) HOMO-3 -> LUMO (46%) HOMO -> LUMO+6 (11%)	0.0404	4.6599	266.07

Figure S26. Electronic absorption spectra of open form of **OX^2-MeO-H** computed using TDDFT, B3LYP/6-311++G(d,p)/IEFPCM (1,4-dioxane) and DFT calculated isodensity surface plots of the FMOs and neighboring molecular orbitals involved in calculated transitions.



Transition	Major contribution	Oscilator strength, *f*	Energy, eV	Wavelength, nm
S_0 –> S_1	HOMO-4 -> LUMO (28%) HOMO-1 -> LUMO (72%	0.8429	3.1872	389.00
S_0 –> S_2	HOMO-6 -> LUMO (19%) HOMO -> LUMO (81%)	0.0891	3.5440	349.84
S_0 –> S_3	HOMO-4 -> LUMO (85%) HOMO-1 -> LUMO+3 (15%)	0.1318	4.3371	285.87
S_0 –> S_4	HOMO-5 -> LUMO (69%) HOMO -5 -> LUMO+1 (14%) HOMO-4 -> LUMO (17%)	0.0312	4.4027	281.61
S_0 –> S_5	HOMO-7 -> LUMO (100%)	0.0200	4.5464	272.71
S_0 –> S_6	HOMO -> LUMO+1 (38%) HOMO -> LUMO+3 (62%)	0.6893	4.6285	267.87

Figure S27. Electronic absorption spectra of closed form of **OX²-MeO-Ph** computed using TDDFT, B3LYP/6-311++G(d,p)/IEFPCM (1,4-dioxane) and DFT calculated isodensity surface plots of the FMOs and neighboring molecular orbitals involved in calculated transitions.



Transition	Major contribution	*f* (Oscillator strength)	Energy, eV	Wavelength, nm
$S_0 \rightarrow S_1$	HOMO -3 -> LUMO (14%) HOMO -> LUMO (86%)	0.6787	3.1105	398.60
$S_0 \rightarrow S_2$	HOMO-1 -> LUMO (39%) HOMO-1 -> LUMO+1 (47%) HOMO -> LUMO+1 (14%)	0.2642	3.8985	318.03
$S_0 \rightarrow S_3$	HOMO-3 -> LUMO (22%) HOMO-1 -> LUMO (78%)	0.1412	4.2149	294.16
$S_0 \rightarrow S_4$	HOMO -> LUMO+2 (100%)	0.0286	4.3416	285.58
$S_0 \rightarrow S_5$	HOMO-4 -> LUMO (20%) HOMO-3 -> LUMO (63%) HOMO-3 -> LUMO+2 (17%)	0.0120	4.6060	269.18
$S_0 \rightarrow S_6$	HOMO-7 -> LUMO (22%) HOMO-6 -> LUMO (13%) HOMO-5 -> LUMO (21%) HOMO-4 -> LUMO (25%) HOMO -> LUMO (10%) HOMO -> LUMO+1 (9%)	4.6272	0.0942	267.95

Figure S28. Electronic absorption spectra of open form of **OX²-MeO-Ph** computed using TDDFT, B3LYP/6-311++G(d,p)/IEFPCM (1,4-dioxane) and DFT calculated isodensity surface plots of the FMOs and neighboring molecular orbitals involved in calculated transitions.

Supplementary References

S1. B. Kim, K. T. Lee, J. Cho, N. A. Darshanoju, K. Jung, I. H. Ahn, J. M. Shin, H. Oh, Y. Ki, H. Lee, S. J. Kwon, I. S. Kim, W. Cai, K.H. Ahn, D. H. Ko, *Adv. Optical Mater.* **2021***, 9,* 2100776.

S2. G. Liu, M. Liu, S. Z. Pu, C. B. Fan and S. Q. Cui, *Dyes Pigm.* **2012**, *95*, 553-562.

S3. Y. Shoji , A. Yagi , M. Horiuchi , M. Morimoto and M. Irie, *Isr. J. Chem.* **2013**, *53* , 303-311.