Supplementary Information (SI) for ChemComm.

Supporting information

2,9-Diaryl-6,13-bs(triisopropylsilylethynyl)pentacene drivatives: synthesis and application in cancer sonodynamic therapy

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contents:

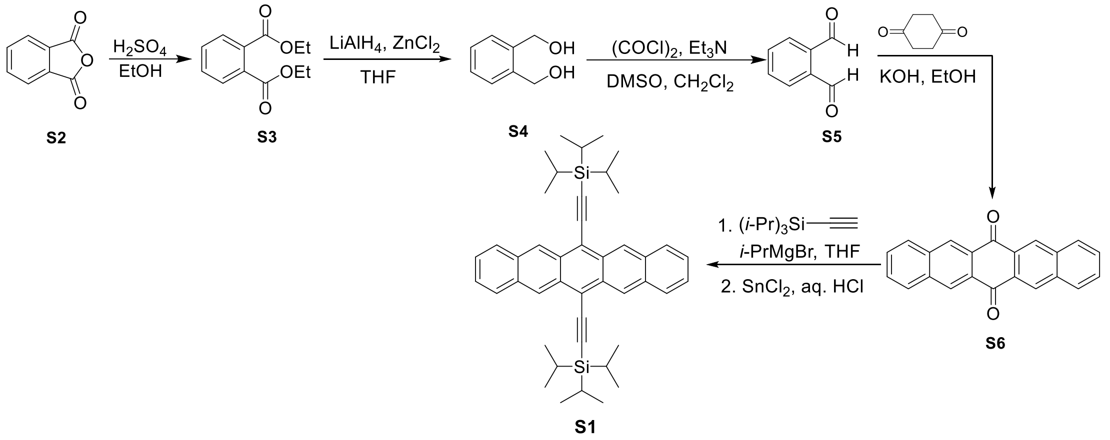
1. Materials and Instruments

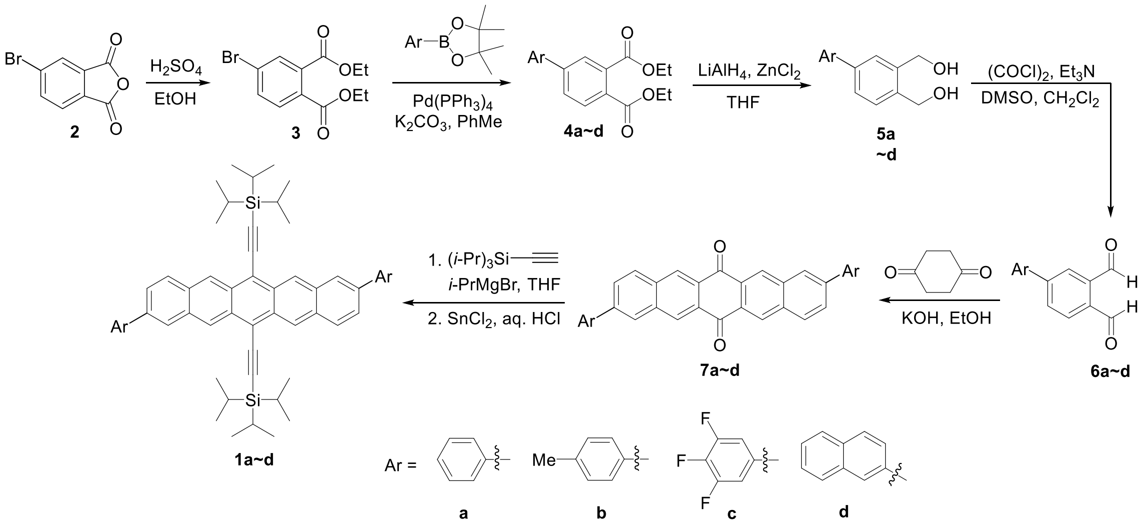
Phthalic anhydride, 4-bromo phthalic anhydride, tetrakis(triphenylphosphine) palladium, stannous chloride, (triisopropylsilyl)acetylene, phenylboronic acid pinacol ester, 4-methylphenylboronic acid pinacol ester, 3,4,5-trifluorophenylboronic acid pinacol ester, 2-naphthaleneboronic acid pinacol ester, tetramethylbenzidine(TMB) and 2,2,6,6-tetramethyl-4-piperidone hydrochloride were purchased from Bide Pharmatech Co., Ltd. Lithium aluminum hydride, potassium hydroxide and potassium carbonate were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Zinc chloride, oxalyl chloride, PBS, SOSG, 1,4-cyclohexanedione and diphenylisobenzofuran (DPBF) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Triethylamine and isopropyl magnesium bromide were purchased from Shanghai Titan Scientific Co., Ltd. Superoxide anion radical detection kit were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. Methyl thiazolyl tetrazolium(MTT), Hoechst33342 and 2’-7’dichlorofluorescin diacetate (DCFH-DA) were purchased from Beyotime Institute of Biotechnology Co. LLC. All starting chemicals and solvents were purchased from commercial suppliers without further purification. 4T1, NCTC 1469 and L02 cell lines were obtained from Cell Bank of Chinese Academy of Sciences and cultured in RPMI 1640 medium supplemented with 10% FBS (Gibco) and penicillin/streptomycin (1%, w/v). Female BALB/c mice and Sprague Dawley rats were purchased from Nanjing Qinglongshan Experimental Animal Center. Mice used in experiments were 6-8 weeks old and SD rats used in experiments were 3-4 weeks. All animal experiments were performed in accordance with the National Institute of Health Guidelines under the protocols approved by the Animal Ethical and Welfare Committee of Nanjing University of Science and Technology (Approval No: AUCU-NUST2023012).

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance-III DRX spectrometer operating at 500 MHz and 126 MHz respectively. High resolutions mass spectrometry (HRMS) data were obtained by a Thermo-Fisher Scientific high-performance liquid chromatography-high resolution mass spectrometry (HPLC/HRMS) system. The FTIR were measured by a Thermo-Fisher NICOLETIS20 Fourier transform infrared spectroscopy. The UV-Vis spectra were measured by a Thermo-Fisher Evolution 220 UV-Vis spectrophotometer. The ESR spectra were measured by a Bruker EMXplus-9 electron paramagnetic resonance (EPR) spectrometer. The fluorescence spectra were scanned with an excitation wavelength of 500 nm using a Hamamatsu Quantaurus-Tau fluorescence lifetime spectrometer. MTT assays were performed on a microplate reader (Tecan Group). Fluorescent images were taken by an inverted fluorescence microscope (Nikon Instruments, Japan).

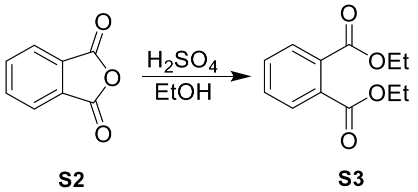
2. Experimental section

2.1 Synthesis





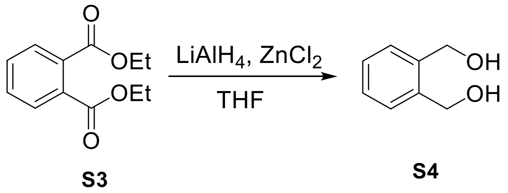
Synthesis of diethyl phthalate (S3)



S2 **S3**

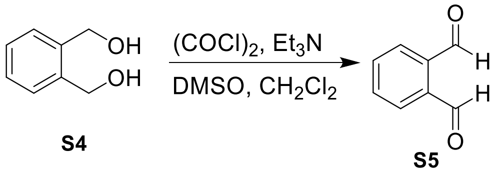
Phthalic anhydride (**S2)** (5 g, 33.8 mmol) and sulfuric acid 0.5 mL were dissolved in 40 mL ethanol under nitrogen atmosphere. The reaction mixture was refluxed for 24 h and then concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using petroleum ether (PE) : ethyl acetate (EA) = 100 : 1 as eluent to obtain the colorless oily liquid (7.3 g, 97% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 7.72 - 7.69 (m, 2H), 7.52 - 7.48 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 4H), 1.35 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 167.50, 132.23, 130.91, 128.76, 61.50, 14.02.

Synthesis of 1,2-benzenedimethanol (S4)



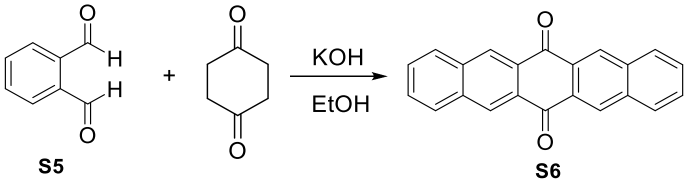
Lithium aluminum hydride (1.8 g, 47.4 mmol) and zinc chloride (1.8 g, 13.2 mmol) were dispersed in 100 mL dry tetrahydrofuran, then solution of diethyl phthalate (**S3**, 3 g, 13.5mmol) in 80 mL of tetrahydrofuran was added dropwise at 0°C. The reaction mixture returned to room temperature and stirred for 24 h. Subsequently, the reaction mixture was quenched with water at 0°C and filtered with celite. Filter residue was washed with ethanol and methanol and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 2 : 1 as eluent to obtain the white solid (1.66 g, 89% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 7.41 (dd, J = 5.5, 3.5 Hz, 2H), 7.25 (dd, J = 5.6, 3.4 Hz, 2H), 5.14 (t, J = 5.5 Hz, 2H), 4.58 (d, J = 5.6 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ = 139.84, 127.28, 127.09, 60.95.

Synthesis of *o*-phthalaldehyde (S5)



To a stirred solution of oxalyl chloride (5 mL, 59.1 mmol) in dichloromethane (60 mL) at -78°C was added dimethyl sulfoxide (5 mL, 70.9 mmol) in dichloromethane (10 mL). After 2 h, a solution of 1,2-benzenedimethanol (**S4**, 1.63 g, 11.8mmol) in dichloromethane (60 mL) and dimethyl sulfoxide (3 mL) was added over 30 min to the reaction mixture. After 2 h, triethylamine (24.6 mL, 177.3 mmol) was added over 20 min. After 1 h at -78°C, the reaction mixture was allowed to warm to room temperature then washed with water. The reaction mixture was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 20 : 1 as eluent to obtain the light yellow solid (1.3 g, 80% yield). ^{1}H NMR (500 MHz, chloroform-d) δ 10.53 (s, 2H), 8.00 - 7.96 (m, 2H), 7.80 (dd, J = 5.7, 3.3 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-d) δ = 192.43, 136.41, 133.81, 131.14.

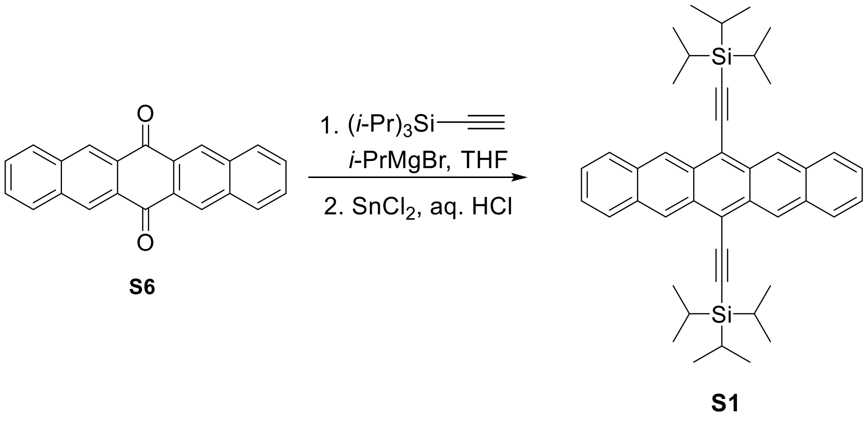
Synthesis of pentacene-6,13-dione (S6)



Aqueous KOH (15%, 1.2 g, 30 mmol) was slowly added to a solution of *o*-phthalaldehyde (**S5**)

(2 g, 14.9 mmol) and 1,4-cyclohexanedione (0.84 g, 7.45 mmol) in ethanol (90 mL) under a N_2 atmosphere. The solution turned from yellow to golden brown to dark brown before a yellow solid corresponding to pentacene-6,13-dione precipitated. After stirring the reaction mixture for 3 h, the crude reaction mixture was filtered and washed with ethanol, water, and methanol until the washings were colorless. The solid residue was dried under reduced pressure to obtain 1.74 g (76% yield) of bright yellow pentacene-6,13-dione. The product was used for next reaction without further purification because of poor solubility.

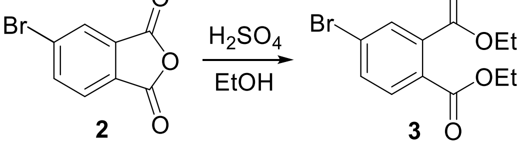
Synthesis of 6,13-Bis(triisopropylsilylethynyl)pentacene (S1)



6,13-Bis(triisopropylsilylethynyl)pentacene (S1) were synthesized based on reference with slight modifications as described below.[1]

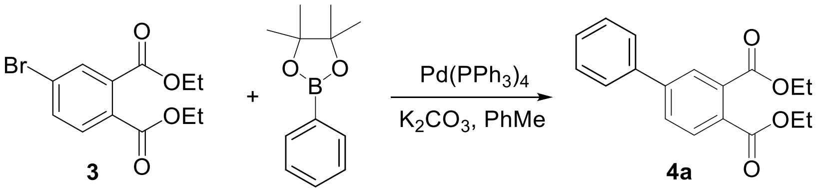
Triisopropylsilylacetylene (1.4 mL, 6.24 mmol) was dissolved in 20 mL tetrahydrofuran under nitrogen atmosphere, then 2.6 mL of a 2.8 M solution of isopropyl magnesium bromide in tetrahydrofuran was added slowly. The reaction mixture was stirred for 4 h at 38°C , pentacene-6,13-dione (**S6**, 0.2 g, 0.65 mmol) was added to the solution when the solution was allowed to cool. The reaction was stirred overnight at 38°C again. The reaction was combined with 1 mL of a stannous chloride (0.32 g, 1.7 mmol) solution in 10% HCl and was stirred for 5 min in the dark. The reaction mixture concentrated under reduced pressure then was purified in silica gel column chromatography using petroleum ether as eluent to obtain the dark blue solid (0.16 g, 38.5% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 9.30 (s, 4H), 7.97 (dd, *J* = 6.6, 3.3 Hz, 4H), 7.41 - 7.24 (m, 4H), 1.37 (s, 42H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 132.33, 130.68, 128.73, 126.36, 126.07, 118.41, 107.22, 104.76, 19.05, 11.74.

Synthesis of diethyl 4-bromophthalate (3)



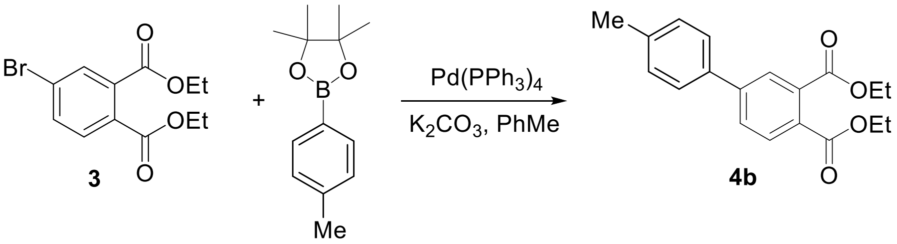
4-Bromophthalic anhydride (**2**, 10 g, 44.3 mmol) and sulfuric acid 0.8 mL were dissolved in 55 mL ethanol under nitrogen atmosphere. The reaction mixture was refluxed for 24 h and then concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 100 : 1 as eluent to obtain the colorless oily liquid (12.76 g, 96% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 7.83 (d, *J* = 1.9 Hz, 1H), 7.66 - 7.61 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 4H), 1.39 - 1.35 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 166.59, 166.36, 134.32, 133.86, 131.75, 130.64, 130.57, 125.57, 62.03, 61.85, 14.08.

Synthesis of diethyl 4-phenylphthalate (4a)



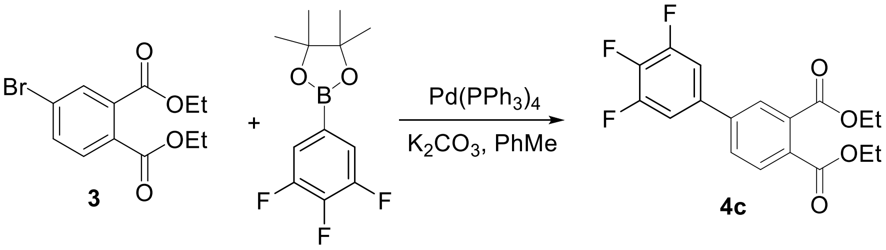
Diethyl 4-bromophthalate (**3**, 3.6 g, 12 mmol), potassium carbonate (5.1 g, 36.9 mmol), 2-naphthaleneboronic acid pinacol ester (3.7 g, 18 mmol) and tetrakis(triphenylphosphine) palladium (1.3 g) were dispersed in 50 mL 1,4-dioxane, then the reaction mixture was refluxed for 24 h. Subsequently, the reaction mixture returned to room temperature and was filtered with celite. Filter cake was washed with dichloromethane and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 80 : 1 as eluent to obtain the colorless oily liquid (3.2 g, 90% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 7.90 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.60 - 7.59 (m, 2H), 7.46 - 7.43 (m, 2H), 7.40 - 7.37 (m, 1H), 4.42 - 4.36 (m, 4H), 1.40 - 1.36 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 167.97, 167.26, 144.24, 139.15, 133.45, 130.29, 129.75, 129.21, 129.06, 128.45, 127.38, 127.28, 61.79, 61.65, 14.20, 14.18.

Synthesis of diethyl 4'-methyl-[1,1'-biphenyl]-3,4-dicarboxylate (4b)



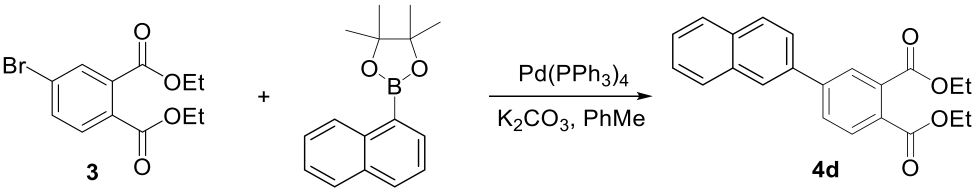
Diethyl 4-bromophthalate (**3**, 2.4 g, 8 mmol), potassium carbonate (3.4 g, 24.6 mmol), 4-methylbenzeneboronic acid pinacol ester (2.6 g, 12 mmol) and tetrakis(triphenylphosphine) palladium (0.86 g) were dispersed in 30 mL 1,4-dioxane, then the reaction mixture was refluxed for 24 h. Subsequently, the reaction mixture returned to room temperature and was filtered with celite. Filter cake was washed with dichloromethane and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 80 : 1 as eluent to obtain the colorless oily liquid (2.35 g, 94% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 7.87 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 4.42 - 4.35 (m, 4H), 2.38 (s, 3H), 1.39 - 1.36 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 168.11, 167.26, 144.20, 138.45, 136.22, 133.52, 129.87, 129.79, 129.76, 128.90, 127.09, 127.07, 61.77, 61.61, 21.19, 14.20, 14.18.

Synthesis of diethyl 3',4',5'-trifluoro-[1,1'-biphenyl]-3,4-dicarboxylate (4c)



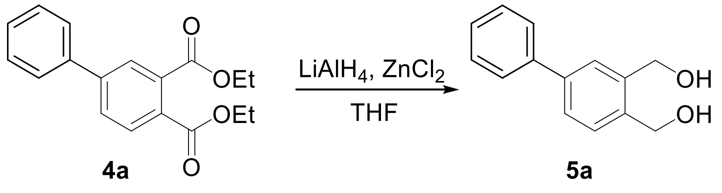
Diethyl 4-bromophthalate (**3**, 3 g, 10 mmol), potassium carbonate (4.2 g, 30.7 mmol), 3,4,5-trifluorophenylboronic acid pinacol ester (3.9 g, 15 mmol) and tetrakis(triphenylphosphine) palladium (1.1 g) were dispersed in 45 mL 1,4-dioxane, then the reaction mixture was refluxed for 24 h. Subsequently, the reaction mixture returned to room temperature and was filtered with celite. Filter cake was washed with dichloromethane and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 80 : 1 as eluent to obtain the colorless oily liquid (3.2 g, 92% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 7.84 - 7.81 (m, 2H), 7.65 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.27 - 7.20 (m, 2H), 4.40 (p, *J* = 7.2 Hz, 4H), 1.39 (td, *J* = 7.1, 3.5 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 167.35, 166.92, 152.63, 150.59, 140.93, 135.26, 133.56, 131.61, 129.95, 128.99, 127.19, 111.52, 62.00, 61.85, 14.12.

Synthesis of diethyl 4-(naphthalen-2-yl)phthalate (4d)



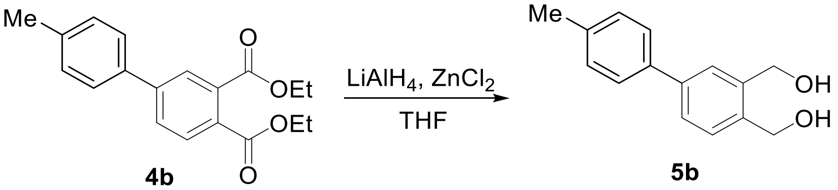
Diethyl 4-bromophthalate (**3**, 2.4 g, 8 mmol), potassium carbonate (3.4 g, 24.6 mmol), 2-naphthaleneboronic acid pinacol ester (3.1 g, 12 mmol) and tetrakis(triphenylphosphine) palladium (0.86 g) were dispersed in 30 mL 1,4-dioxane, then the reaction mixture was refluxed for 24 h. Subsequently, the reaction mixture returned to room temperature and was filtered with celite. Filter cake was washed with dichloromethane and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 80 : 1 as eluent to obtain the white solid (2.6 g, 93% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 8.04 (d, *J* = 19.1 Hz, 2H), 7.92 - 7.82 (m, 5H), 7.71 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.53 - 7.48 (m, 2H), 4.44 - 4.38 (m, 4H), 1.41 - 1.38 (m, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 168.10, 167.28, 144.17, 136.40, 133.59, 133.56, 133.11, 130.24, 129.86, 129.42, 128.88, 128.42, 127.75, 127.58, 126.69, 126.66, 126.47, 125.05, 61.88, 61.71, 14.23, 14.22.

Synthesis of 4-phenyl-1,2-benzenedimethanol (5a)



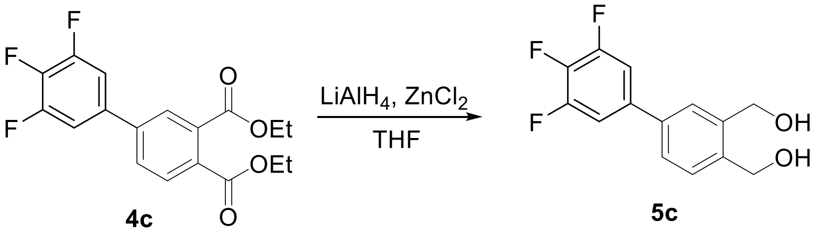
Lithium aluminum hydride (1.35 g, 35.5 mmol) and zinc chloride (1.35 g, 9.9 mmol) were dispersed in 80 mL tetrahydrofuran, then 60 mL tetrahydrofuran dissolved with diethyl 4-phenylphthalate (**4a**, 3 g, 10.1 mmol) was added dropwise at 0°C. The reaction mixture returned to room temperature and stirred for 24 h. Subsequently, the reaction mixture was quenched with water at 0°C and filtered with celite. Filter residue was washed with ethanol and methanol and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 2 : 1 as eluent to obtain the white solid (1.9 g, 87% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 7.66 - 7.60 (m, 3H), 7.50 - 7.40 (m, 4H), 7.31 (t, *J* = 7.1 Hz, 1H), 5.14 (dt, *J* = 19.1, 5.5 Hz, 2H), 4.57 (dd, *J* = 16.4, 5.5 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ = 140.81, 140.45, 139.13, 138.92, 129.39, 127.95, 127.68, 126.97, 125.53, 125.20, 60.93, 60.66.

Synthesis of (4'-methyl-[1,1'-biphenyl]-3,4-diyl)dimethanol (5b)



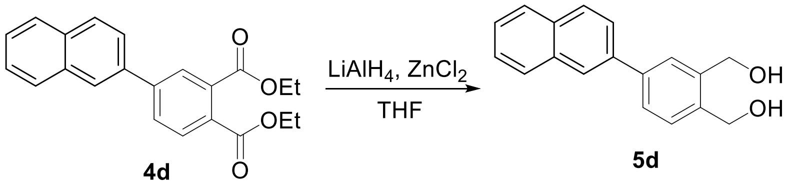
Lithium aluminum hydride (1.5 g, 39.3 mmol) and zinc chloride (1.5 g, 11 mmol) were dispersed in 80 mL tetrahydrofuran, then 60 mL tetrahydrofuran dissolved with diethyl 4'-methyl-[1,1'-biphenyl]-3,4-dicarboxylate (**4b**, 3.5 g, 11.2 mmol) was added dropwise at 0°C. The reaction mixture returned to room temperature and stirred for 24 h. Subsequently, the reaction mixture was quenched with water at 0°C and filtered with celite. Filter residue was washed with ethanol and methanol and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 2 : 1 as eluent to obtain the white solid (2.2 g, 86% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 7.67 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.50 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 5.14 (dt, *J* = 19.9, 5.5 Hz, 2H), 4.60 (dd, *J* = 16.6, 5.5 Hz, 4H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ = 140.40, 138.82, 138.79, 137.89, 136.91, 129.98, 127.92, 126.77, 125.26, 124.89, 60.94, 60.66, 21.13.

Synthesis of (3',4',5'-trifluoro-[1,1'-biphenyl]-3,4-diyl)dimethanol (5c)



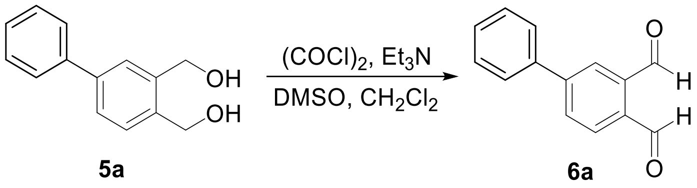
Lithium aluminum hydride (1.6 g, 41.8 mmol) and zinc chloride (1.6 g, 11.6 mmol) were dispersed in 90 mL tetrahydrofuran, then 70 mL tetrahydrofuran dissolved with diethyl 3',4',5'-trifluoro-[1,1'-biphenyl]-3,4-dicarboxylate (**4c**, 4.2 g, 11.9 mmol) was added dropwise at 0°C. The reaction mixture returned to room temperature and stirred for 24 h. Subsequently, the reaction mixture was quenched with water at 0°C and filtered with celite. Filter residue was washed with ethanol and methanol and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 2 : 1 as eluent to obtain the white solid (2.8 g, 88% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 7.73 - 7.68 (m, 1H), 7.61 - 7.57 (m, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.39 - 7.15 (m, 2H), 5.21 (t, *J* = 5.4 Hz, 2H), 4.61 (t, *J* = 5.6 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ = 164.26, 162.31, 144.49, 140.52, 136.31, 127.90, 125.66, 111.32, 109.97, 102.79, 60.89, 60.55.

Synthesis of (4-(naphthalen-2-yl)-1,2-phenylene)dimethanol (5d)



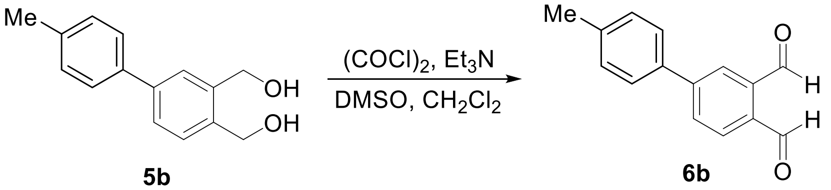
Lithium aluminum hydride (1.5 g, 39.3 mmol) and zinc chloride (1.5 g, 11 mmol) were dispersed in 90 mL tetrahydrofuran, then 70 mL tetrahydrofuran dissolved with diethyl 4-(naphthalen-2-yl)phthalate (**4d**, 4 g, 11.5 mmol) was added dropwise at 0°C. The reaction mixture returned to room temperature and stirred for 24 h. Subsequently, the reaction mixture was quenched with water at 0°C and filtered with celite. Filter residue was washed with ethanol and methanol and filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 2 : 1 as eluent to obtain the white solid (2.6 g, 85% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.22 (d, *J* = 1.9 Hz, 1H), 8.02 - 7.85 (m, 6H), 7.71 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.57 - 7.50 (m, 2H), 5.28 - 5.2 (m, 2H), 4.67 (dd, *J* = 20.7, 5.5 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ = 140.56, 139.33, 138.66, 138.13, 133.86, 132.64, 128.94, 128.62, 128.04, 127.97, 126.87, 126.47, 125.79, 125.53, 125.51, 125.31, 60.99, 60.69.

Synthesis of 4-phenylphthalaldehyde (6a)



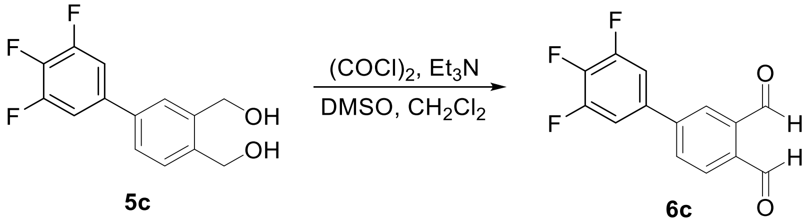
To a stirred solution of oxalyl chloride (4 mL, 46.8 mmol) in dichloromethane (50 mL) at -78°C was added dimethyl sulfoxide (4 mL, 56.1 mmol) in dichloromethane (8 mL). After 2 h, a solution of 4-phenyl-1,2-benzenedimethanol (**5a**, 2 g, 9.3 mmol) in dichloromethane (50 mL) and dimethyl sulfoxide (3mL) was added over 30 min to the reaction mixture. After 2 h, triethylamine (19.5 mL, 140.3 mmol) was added over 20 min. After 1 h at -78°C, the reaction mixture was allowed to warm to room temperature then washed with water. The reaction mixture was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 20 : 1 as eluent to obtain the light yellow solid (1.6 g, 82% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 10.62 (s, 1H), 10.54 (s, 1H), 8.18 (d, *J* = 1.9 Hz, 1H), 8.05 - 7.96 (m, 2H), 7.67 - 7.66 (m, 2H), 7.52 - 7.44 (m, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 192.40, 192.02, 146.70, 138.40, 136.96, 134.86, 132.19, 131.81, 129.49, 129.29, 129.15, 127.34.

Synthesis of 4-(4'-methyl)phenyl phthalaldehyde (6b)



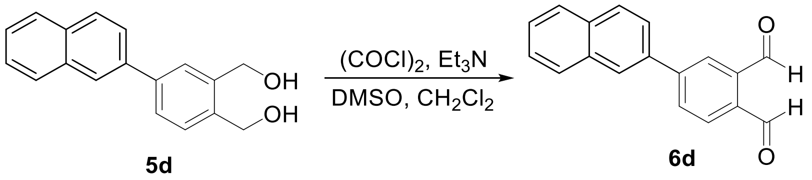
To a stirred solution of oxalyl chloride (5 mL, 59.1 mmol) in dichloromethane (60 mL) at -78℃ was added dimethyl sulfoxide (5 mL, 70.9 mmol) in dichloromethane (10 mL). After 2 h, a solution of (4'-methyl-[1,1'-biphenyl]-3,4-diyl)dimethanol (**5b**, 2.6 g, 11.4 mmol) in dichloromethane (60 mL) and dimethyl sulfoxide (3 mL) was added over 30 min to the reaction mixture. After 2 h, triethylamine (24.6 mL, 177.3 mmol) was added over 20 min. After 1 h at -78℃, the reaction mixture was allowed to warm to room temperature then washed with water. The reaction mixture was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 20 : 1 as eluent to obtain the light yellow solid (2.1 g, 82% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 10.62 (s, 1H), 10.52 (s, 1H), 8.16 (d, *J* = 1.8 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.57 - 7.56 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 192.49, 192.01, 146.63, 139.35, 136.95, 135.45, 134.59, 132.21, 131.47, 130.01, 129.18, 127.17, 21.27.

Synthesis of 3',4',5'-trifluoro-[1,1'-biphenyl]-3,4-dicarbaldehyde (6c)



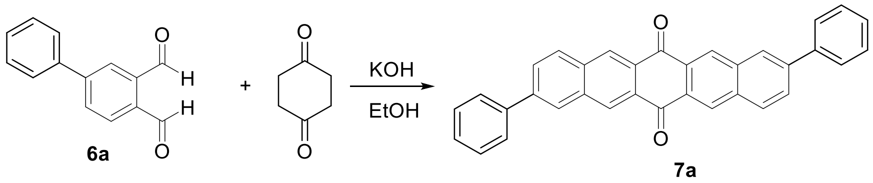
To a stirred solution of oxalyl chloride (3.2 mL, 37.6 mmol) in dichloromethane (40 mL) at -78℃ was added dimethyl sulfoxide (3.2 mL, 45 mmol) in dichloromethane (6 mL). After 2 h, a solution of (3',4',5'-trifluoro-[1,1'-biphenyl]-3,4-diyl)dimethanol (**5c**, 2 g, 7.5 mmol) in dichloromethane (40 mL) and dimethyl sulfoxide (2 mL) was added over 30 min to the reaction mixture. After 2 h, triethylamine (15 mL, 112.1 mmol) was added over 20 min. After 1 h at -78℃, the reaction mixture was allowed to warm to room temperature then washed with water. The reaction mixture was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 20 : 1 as eluent to obtain the light yellow solid (1.6 g, 81% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 10.64 (s, 1H), 10.55 (s, 1H), 8.15 (d, *J* = 1.9 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.27 - 7.18 (m, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 191.84, 191.71, 164.59, 162.50, 144.17, 141.66, 137.07, 135.76, 132.38, 131.81, 129.32, 110.54, 110.33, 104.42.

Synthesis of 4-(naphthalen-2-yl)phthalaldehyde (6d)



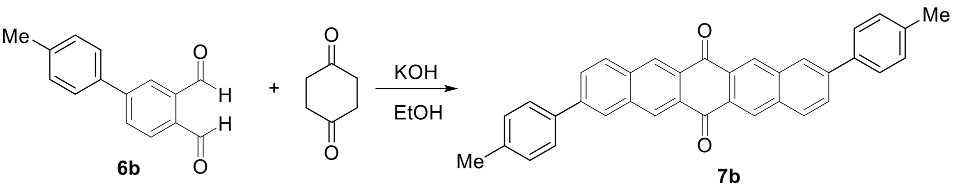
To a stirred solution of oxalyl chloride (5 mL, 59.1 mmol) in dichloromethane (60 mL) at -78℃ was added dimethyl sulfoxide (5 mL, 70.9 mmol) in dichloromethane (10 mL). After 2 h, a solution of (4-(naphthalen-2-yl)-1,2-phenylene)dimethanol (**5d**, 3 g, 11.4 mmol) in dichloromethane (60 mL) and dimethyl sulfoxide (3mL) was added over 30 min to the reaction mixture. After 2 h, triethylamine (24.6 mL, 177.3 mmol) was added over 20 min. After 1 h at -78℃, the reaction mixture was allowed to warm to room temperature then washed with water. The reaction mixture was concentrated under reduced pressure to afford the crude product. The crude product was purified in silica gel column chromatography using PE : EA = 20 : 1 as eluent to obtain the light yellow solid (2.4 g, 81% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 10.64 (s, 1H), 10.52 (s, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 8.11 (d, *J* = 1.9 Hz, 1H), 8.07 - 8.02 (m, 2H), 7.95 - 7.85 (m, 3H), 7.75 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.55 - 7.53 (m, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 192.43, 192.01, 146.58, 136.99, 135.59, 134.81, 133.51, 133.37, 132.30, 131.96, 129.59, 129.16, 128.54, 127.80, 127.08, 126.94, 126.86, 124.71.

Synthesis of 2,9-diphenylpentacene-6,13-dione (7a)



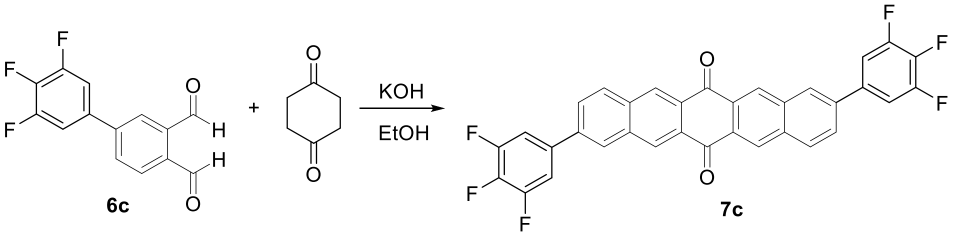
Aqueous KOH (15%, 2.98 g, 53.12 mmol) was slowly added to a solution of 4-phenylphthalaldehyde (**6a**, 5.58 g, 26.56 mmol) and 1,4-cyclohexanedione (1.49 g, 13.28 mmol) in ethanol (160 mL) under a N_2 atmosphere. The solution turned from yellow to golden brown to dark brown before a brown solid corresponding to 2,9-diphenylpentacene-6,13-dione precipitated. After stirring the reaction mixture for 3h, the crude reaction mixture was filtered and washed with ethanol, water, and methanol until the washings were colorless. The solid residue was dried under reduced pressure to obtain 4.52 g (74% yield) of brown 2,9-diphenylpentacene-6,13-dione. The product was used for next reaction without further purification because of poor solubility.

Synthesis of 2,9-di-*p*-tolylpentacene-6,13-dione (7b)



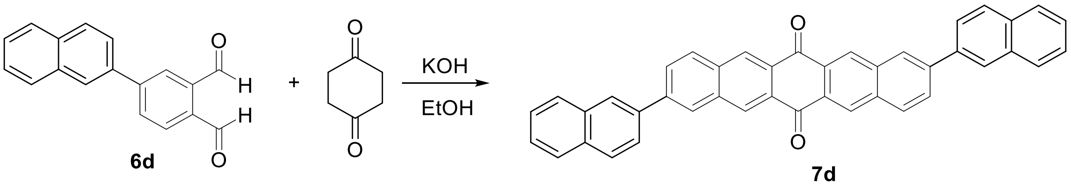
Aqueous KOH (15%, 2.1 g, 37.5 mmol) was slowly added to a solution of 4-(4'-methyl)phenyl phthalaldehyde (**6b**, 4.2 g, 18.74 mmol) and 1,4-cyclohexanedione (1.05 g, 9.38 mmol) in ethanol (110 mL) under a N_2 atmosphere. The solution turned from yellow to golden brown to dark brown before a brown solid corresponding to 2,9-di-*p*-tolylpentacene-6,13-dione precipitated. After stirring the reaction mixture for 3h, the crude reaction mixture was filtered and washed with ethanol, water, and methanol until the washings were colorless. The solid residue was dried under reduced pressure to obtain 3.38 g (74% yield) of brown 2,9-di-*p*-tolylpentacene-6,13-dione. The product was used for next reaction without further purification because of poor solubility.

Synthesis of 2,9-bis(3,4,5-trifluorophenyl)pentacene-6,13-dione (7c)



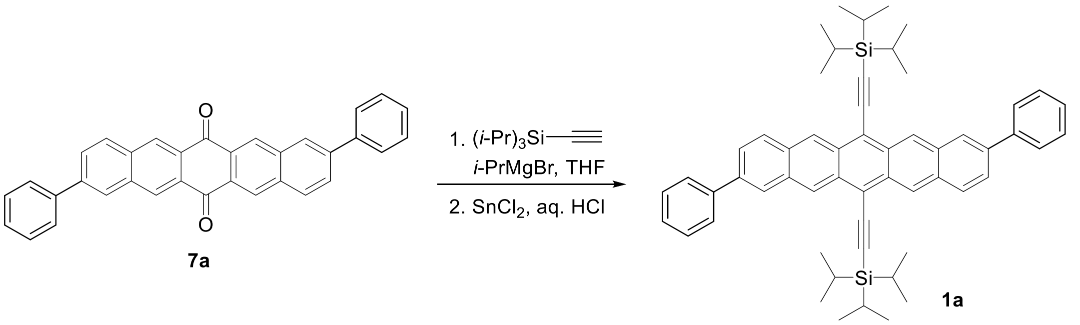
Aqueous KOH (15%, 1.7 g, 30.3 mmol) was slowly added to a solution of 3',4',5'-trifluoro-[1,1'-biphenyl]-3,4-dicarbaldehyde (**6c**, 4 g, 15.15 mmol) and 1,4-cyclohexanedione (0.847 g, 7.57 mmol) in ethanol (90 mL) under a N_2 atmosphere. The solution turned from yellow to golden brown to dark brown before a brown solid corresponding to 2,9-bis(3,4,5-trifluorophenyl)pentacene-6,13-dione precipitated. After stirring the reaction mixture for 3h, the crude reaction mixture was filtered and washed with ethanol, water, and methanol until the washings were colorless. The solid residue was dried under reduced pressure to obtain 3.1g (72% yield) of brown 2,9-bis(3,4,5-trifluorophenyl)pentacene-6,13-dione. The product was used for next reaction without further purification because of poor solubility.

Synthesis of 2,9-di(naphthalen-2-yl)pentacene-6,13-dione (7d)



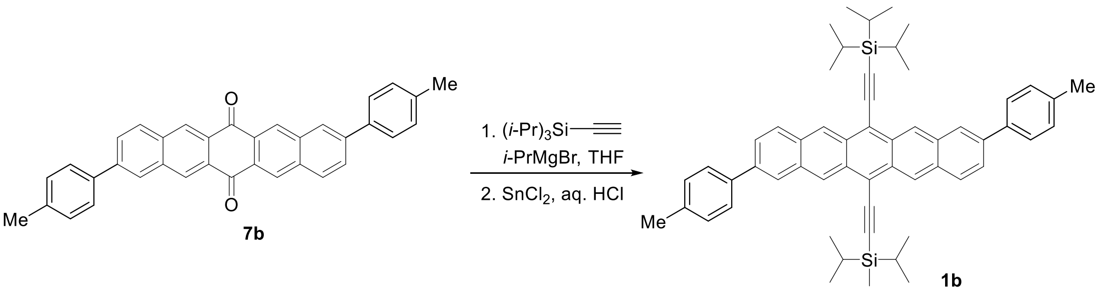
Aqueous KOH (15%, 2.15 g, 38.44 mmol) was slowly added to a solution of 4-(naphthalen-2-yl)phthalaldehyde (**6d**, 5 g, 19.22 mmol) and 1,4-cyclohexanedione (1.08 g, 9.61 mmol) in ethanol (110 mL) under a N_2 atmosphere. The solution turned from yellow to golden brown to dark brown before a brown solid corresponding to 2,9-di(naphthalen-2-yl)pentacene-6,13-dione precipitated. After stirring the reaction mixture for 3h, the crude reaction mixture was filtered and washed with ethanol, water, and methanol until the washings were colorless. The solid residue was dried under reduced pressure to obtain 4.04 g (75% yield) of brown 2,9-di(naphthalen-2-yl)pentacene-6,13-dione. The product was used for next reaction without further purification because of poor solubility.

Synthesis of 2,9-diphenyl-6,13-bis(triisopropylsilylethynyl)pentacene (1a)



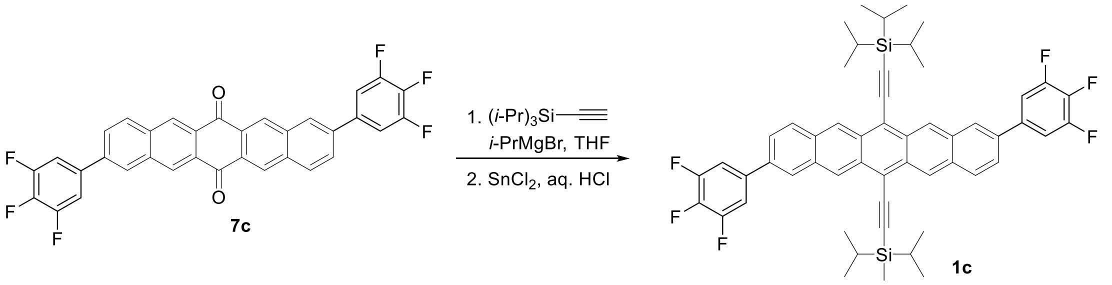
(Triisopropylsilyl)acetylene (1.4 mL, 6.24mmol) was dissolved in 20 mL tetrahydrofuran under nitrogen atmosphere, then 2.6 mL of a 2.8 M solution of isopropyl magnesium bromide in tetrahydrofuran was added slowly. The reaction mixture was stirred for 4 h at 38℃ , 2,9-diphenylpentacene-6,13-dione (**7a**, 0.3 g, 0.65 mmol) was added to the solution when the solution was allowed to cool. The reaction was stirred overnight at 38℃ again. The reaction was combined with 1 mL of a stannous chloride (0.32 g, 1.7 mmol) solution in 10% HCl and was stirred for 5 min in the dark. The reaction mixture concentrated under reduced pressure then was purified in silica gel column chromatography using petroleum ether (PE) as eluent to obtain the dark green solid (0.2 g, 39% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 9.33 (dd, *J* = 11.7, 3.3 Hz, 4H), 8.14 (s, 2H), 8.06 (d, *J* = 8.9 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 4H), 7.71 (dd, *J* = 9.0, 1.7 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 4H), 7.41 (t, *J* = 7.4 Hz, 2H), 1.39 (d, *J* = 5.6 Hz, 42H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 140.87, 138.39, 132.54, 131.59, 130.99, 129.40, 129.03, 127.73, 127.33, 126.66, 126.53, 126.22, 125.94, 118.43, 107.31, 104.75, 19.11, 11.76. IR (ν cm^{-1}): 3062, 3033, 2940, 2857, 2131, 1627, 1590, 1460, 1365, 1014, 875, 744, 674. HRMS (APCI) m/z calculated for [$C_{56}H_{62}Si_2$] 791.4390; found 791.4465 (M+H$^+$).

Synthesis of 2,9-di-*p*-tolyl-6,13-bis(triisopropylsilylethynyl)pentacene (1b)



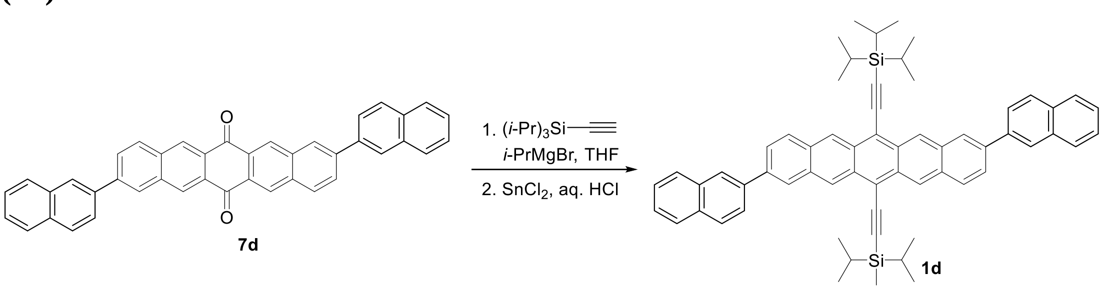
(Triisopropylsilyl)acetylene (1.4 mL, 6.24mmol) was dissolved in 20 mL tetrahydrofuran under nitrogen atmosphere, then 2.6 mL of a 2.8 M solution of isopropyl magnesium bromide in tetrahydrofuran was added slowly. The reaction mixture was stirred for 4 h at 38℃ , 2,9-di-*p*-tolylpentacene-6,13-dione (**7b,** 0.32 g, 0.65 mmol) was added to the solution when the solution was allowed to cool. The reaction was stirred overnight at 38℃ again. The reaction was combined with 1 mL of a stannous chloride (0.32 g, 1.7 mmol) solution in 10% HCl and was stirred for 5 min in the dark. The reaction mixture concentrated under reduced pressure then was purified in silica gel column chromatography using petroleum ether (PE) as eluent to obtain the dark green solid (0.21 g, 40% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 9.32 - 9.30 (m, 4H), 8.10 (s, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.71 - 7.68 (m, 6H), 7.33 (d, *J* = 7.7 Hz, 4H), 2.44 (s, 6H), 1.38 (d, *J* = 5.9 Hz, 42H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 138.27, 137.98, 137.59, 132.60, 131.50, 131.10, 129.72, 127.13, 126.44, 126.12, 125.42, 118.33, 107.16, 104.82, 21.23, 19.07, 11.76. IR (ν cm^{-1}): 3027, 2945, 2890, 2133, 1627, 1567, 1462, 1367, 1018, 875, 746, 672. HRMS (APCI) m/z calculated for [$C_{58}H_{66}Si_2$] 819.4703; found 819.4784 (M+H$^+$).

Synthesis of 2,9-bis(3,4,5-trifluorophenyl)-6,13-bis(triisopropylsilylethynyl) pentacene (1c)



(Triisopropylsilyl)acetylene (1.4 mL, 6.24mmol) was dissolved in 20 mL tetrahydrofuran under nitrogen atmosphere, then 2.6 mL of a 2.8 M solution of isopropyl magnesium bromide in tetrahydrofuran was added slowly. The reaction mixture was stirred for 4 h at 38℃ , 2,9-bis(3,4,5-trifluorophenyl)pentacene-6,13-dione (**7c**, 0.37 g, 0.65 mmol) was added to the solution when the solution was allowed to cool. The reaction was stirred overnight at 38℃ again. The reaction was combined with 1 mL of a stannous chloride (0.32 g, 1.7 mmol) solution in 10% HCl and was stirred for 5 min in the dark. The reaction mixture concentrated under reduced pressure then was purified in silica gel column chromatography using petroleum ether (PE) as eluent to obtain the dark blue solid (0.23 g, 39% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 9.34 - 9.30 (m, 4H), 8.09 - 8.01 (m, 4H), 7.62 - 7.53 (m, 2H), 7.37 (dd, *J* = 8.3, 6.2 Hz, 2H), 7.30 - 7.26 (m, 2H), 1.40 (dd, *J* = 5.1, 3.4 Hz, 42H). ^{13}C NMR (126 MHz, Acetone-d_6) δ = 131.47, 131.13, 130.01, 129.86, 127.15, 126.58, 126.38, 125.57, 125.28, 118.65, 111.11, 109.99, 19.10 - 19.06 (m), 11.73. IR (ν cm^{-1}): 3047, 2939, 2860, 2133, 1621, 1588, 1500, 1367, 1245, 1014, 878, 746, 665. HRMS (APCI) m/z calculated for [$C_{56}H_{56}F_6Si_2$] 899.3825; found 899.3887 (M+H$^+$).

Synthesis of 2,9-di(naphthalen-2-yl-6,13-bis(triisopropylsilylethynyl)pentacene (1d)



(Triisopropylsilyl)acetylene (1.4 mL, 6.24mmol) was dissolved in 20 mL tetrahydrofuran under nitrogen atmosphere, then 2.6 mL of a 2.8 M solution of isopropyl magnesium bromide in tetrahydrofuran was added slowly. The reaction mixture was stirred for 4 h at 38℃ , 2,9-di(naphthalen-2-yl)pentacene-6,13-dione (**7d**, 0.36 g, 0.65 mmol) was added to the solution when the solution was allowed to cool. The reaction was stirred overnight at 38°C again. The reaction was combined with 1 mL of a stannous chloride (0.32 g, 1.7 mmol) solution in 10% HCl and was stirred for 5 min in the dark. The reaction mixture concentrated under reduced pressure then was purified in silica gel column chromatography using petroleum ether (PE) as eluent to obtain the dark green solid (0.23 g, 40% yield). ^{1}H NMR (500 MHz, chloroform-*d*) δ = 9.35 - 9.31 (m, 4H), 8.22 (d, *J* = 8.1 Hz, 4H), 8.09 (d, *J* = 9.0 Hz, 2H), 8.00 - 7.92 (m, 6H), 7.86 (dd, *J* = 21.4, 8.4 Hz, 4H), 7.54 - 7.48 (m, 4H), 1.41 (d, *J* = 5.9 Hz, 42H). ^{13}C NMR (126 MHz, chloroform-*d*) δ = 138.18, 138.05, 133.75, 132.86, 131.13, 130.82, 129.47, 128.69, 128.37, 127.73, 126.68, 126.47, 126.22, 126.07, 125.39, 118.63, 107.30, 104.82, 19.13, 19.10, 11.78. IR (ν cm^{-1}): 3054, 2923, 2860, 2133, 1630, 1590, 1457, 1369, 1012, 876, 742, 676. HRMS (APCI) m/z calculated for [$C_{64}H_{66}Si_2$] 891.4703; found 891.4791 (M+H$^+$).

2.2 Evaluation tests

Evaluation of sonodynamic effects

DPBF was used as a probe to detect the production of ROS. DPBF was dispersed in DMF solution (1 mg/mL), and then 100 µL of DPBF solution was mixed with 8 mL of **S1**, **1a**, **1b**, **1c** and **1d** aqueous solutions. 200 µL mixed solution was contained in each well in a 96-wells plates. Each well was treated different times with US (1 W/cm^2, 1 MHz, 50% duty cycle). Then the absorbance of DPBF at 410 nm was measured for ROS detection after US.

Fig. S1. The picture of for microplate reader for ROS determination

The exploration of the US stability of 1d in a simulated *in vivo* environment.

1d was dispersed in PBS solution (0.4 mg/mL), and 8mL **1d** PBS solution was mixed with 100 µL of DPBF (1 mg/mL) DMF solution. 200 µL mixed solution was contained in each well in a 96-wells plates. Each well was treated different times with US (1 W/cm^2, 1 MHz, 50% duty cycle). Then the absorbance of DPBF at 410 nm was measured after US. After 24 h, 8mL **1d** PBS solution was mixed with 100 µL of DPBF (1 mg/mL) DMF solution (freshly prepared). 200 µL mixed solution was contained in each well in a 96-wells plates. Each well was treated different times with US (1 W/cm^2, 1 MHz, 50% duty cycle). Then the absorbance of DPBF at 410 nm was measured after US. After 48 h, 8mL **1d** PBS solution was mixed with 100 µL of DPBF (1 mg/mL) DMF solution (freshly prepared). 200 µL mixed solution was contained in each well in a 96-wells plates. Each well was treated different times with US (1 W/cm^2, 1 MHz, 50% duty cycle). Then the absorbance of DPBF at 410 nm was measured after US.

Detection of $^1O_2$

The fluorescent probe singlet oxygen sensor green (SOSG) was used to detect $^1O_2$. 18 μL of the SOSG storage solution (5 mM) was diluted to 1800 μL with water to obtain the SOSG working solution (50 μM). Subsequently, 20 μL SOSG working solution was mixed with 180 μL of H_2O, **S1**, **1a**, **1b**, **1c** and **1d** aqueous solutions in each well in a 96-wells plates. Each well was treated different times with US (1 W/cm^2, 1 MHz, 50% duty cycle). The fluorescence intensity of the mixed solution was measured (λ_{ex} = 504 nm, λ_{em} = 525 nm) after US.

ESR measurements of $^1O_2$

2,2,6,6-Tetramethylpiperidine (TEMP) was employed as spin-trapping agents to detect $^1O_2$. Compound **1d** was dissolved in water at a dilution of 10 μM, and then 25 mM TEMP was added into water with US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle). The EPR signal was recorded at room temperature. As a comparison, the control group was detected too.

Detection of •OH

TMB was used as a probe to detect •OH. TMB was dispersed in DMF solution (5 mg/mL), and then 40 μL of TMB solution was mixed with 3 mL of H_2O, **S1**, **1a**, **1b**, **1c** and **1d** aqueous solutions. 200 μL mixed solution was contained in each well in a 96-wells plates. Each well was treated different times with US (1 W/cm^2, 1 MHz, 50% duty cycle). Then the absorbance of TMB at 652 nm was measured for •OH detection after US.

Detection of $O_2^{\bullet-}$

20 μL of H_2O, **S1**, **1a**, **1b**, **1c** and **1d** aqueous solutions in each well in a 96-wells plates. Each well was treated different times with US (1 W/cm^2, 1 MHz, 50% duty cycle). $O_2^{\bullet-}$ lysis buffer (1 eq.) and hydroxylamine solution (2 eq.) were added and mixed. After 20 min, sulfanilic acid solution (2 eq.) and naphthylamine solution (2 eq.) were added. Then the absorbance at 530 nm was measured after 30 min for $O_2^{\bullet-}$ detection.

In vitro cytotoxicity

4T1 cells were seeded into 96-wells plates with 100 μL of culture medium at a density of 5000 cells per well and cultured for 12 h. Each well was washed 3 times with PBS, the medium of the cells was replaced with a serum-free medium containing different concentrations of **S1**, **1a**, **1b**, **1c** and **1d** for 8 h and then treated with US (1 min, 1 W/cm^2, 1 MHz, 50% duty cycle). After 16 h of incubation, MTT solution (20 μL) was added to the culture medium and continue to incubate for 4 h. The medium was removed, following dimethyl sulfoxide (200μL) was added to completely dissolve the product (formazan) and the absorbance was measured at 570 nm using the microplate reader.

Evaluation of the biocompatibility

NCTC 1469 cells and L02 cells were seeded into 96-wells plates with 100 μL of culture medium at a density of 5000 cells per well and cultured for 12 h. Each well was washed 3 times with PBS, the medium of the cells was replaced with a serum-free medium containing different concentrations of **S1**, **1a**, **1b**, **1c** and **1d** for 24 h of incubation. Then, MTT solution (20 μL) was added to the culture medium and continue to incubate for 4 h. The medium was removed, following dimethyl sulfoxide (200 μL) was added to completely dissolve the product (formazan) and the absorbance was measured at 570 nm using the microplate reader.

Live/dead staining assay

4T1 cells were seeded into 6-wells plates with 2 mL of culture medium at a density of 6×10^5 cells per well and cultured for 12 h. Each well was washed 3 times with PBS, followed by incubating with **S1** (85 μM), **1a** (85 μM), **1b** (85 μM), **1c** (85 μM) and **1d**(85 μM) for 8 h. Cells were treated with US (1 min, 1 W/cm^2, 1 MHz, 50% duty cycle) and continue to incubate for 16 h. Afterwards, cells were washed with PBS, and stained with calcein-AM (2 μM) and propidium iodide (PI, 8 μM) for 30 min. Finally, the 4T1 cells were observed by an inverted fluorescence microscope.

Measurement of intracellular ROS levels

4T1 cells were seeded into 6-wells plates with 2 mL of culture medium at a density of 6×10^5 cells per well and cultured for 12 h. Each well was washed 3 times with PBS, followed by incubating with **S1** (85 μM), **1a** (85 μM), **1b** (85 μM), **1c** (85 μM) and **1d**(85 μM) for 10 h. After washing with PBS, DCFH-DA probe was added and incubated for 15 min, then, the US, **S1**+US, **1a**+US, **1b**+US, **1c**+US and **1d**+US groups were treated with US (1 min, 1 W/cm^2, 1 MHz, 50% duty cycle). Finally, the 4T1 cells were observed by an inverted fluorescence microscope.

Pharmacokinetic studies in rats

Sprague Dawley rats were used to evaluate the pharmacokinetics of **S1**, **1a**, **1b**, **1c** and **1d**. The concentrations of **S1**, **1a**, **1b**, **1c** and **1d** in plasma were measured using HPLC. **S1** (5.4 mg/kg), **1a** (5.5 mg/kg), **1b** (5.0 mg/kg), **1c** (7.0 mg/kg) and **1d** (4.8 mg/kg) were separately injected through the tail vein (n = 6), and blood samples were collected at predetermined intervals. Plasma was obtained by centrifugation at 10 000 rpm for 10 min, followed by adding 200 μL of acetonitrile. The mixture was vortexed for 2 min, centrifuged at 12 000 rpm for 10 min, and measured by HPLC. Pharmacokinetic parameters were calculated by PKSolver V2.0.

In vivo antitumor effects

For *in vivo* experiments, 1×10^7 4T1 cells were subcutaneously injected into female BALB/c mice. When tumor volume reached ≈ 100 mm^3, mice were assigned into three groups at random (n = 6 for each group) as following: Control (saline) + US; S1 (135 μM) + US; 1d (85 μM) + US. The treatment process was after intratumoral injection of corresponding drugs and US treatment (2 min, 1 W/cm^2, 1 MHz, 50% duty cycle) was performed in each group, every 2 days for 14 days. Tumor volumes and body weights were measured every 2 days. At the end of treatment, mice were sacrificed, and tumors were collected, weighted, imaged, and analyzed by H&E and TUNEL stains. The major organs, including heart, liver, spleen, lung, and kidneys were also harvested and analyzed by H&E stains.

2.3 Statistical analysis

All experimental results shown in this article were based on data from at least three separate experiments, and all data are presented as mean ± SD. Graphpad Prism 9.5 software was used for all statistical comparisons and data were analyzed via Student’s t-test: $^{**}p<0.005$, $^{***}p<0.0005$.

3. DFT Calculations

The Gaussian 09 program was used for all the DFT calculations [2]. The ground-state (S_0) geometry of the complexes was using restricted DFT at M06-2X/def2-SVP level. For all the vertical excitation (S_1) energy was performed with TDDFT method with M06-2X/def2-SVP level.

Table S1. Cartesian coordinates for all optimized geometries of **S1**.

The excitation energy of **S1** is 2.0330 eV.

C	-0.76981800	-1.08453000	0.04695300
C	-1.52291300	0.11419500	0.02755700
C	-0.88156500	1.37523400	0.00275100
C	0.56035100	1.44152200	-0.00233900
C	1.31388400	0.24393000	0.01449400
C	0.67194500	-1.01821200	0.03876100
C	-1.61795900	2.57888900	-0.01685700
C	1.18300700	2.70784500	-0.02398800
C	0.44859400	3.87975700	-0.03644400
C	-0.99454700	3.81288200	-0.03329000
C	-1.74053000	5.04127800	-0.04731700
H	-2.82591900	4.98258300	-0.04348700
C	-1.10452300	6.24143600	-0.06255500
C	0.32990800	6.30823900	-0.06572300
C	1.07577000	5.17306800	-0.05329200
H	-2.70323700	2.52427300	-0.02244900
H	2.26869100	2.75276300	-0.03423300
H	-1.67720700	7.16355600	-0.07180900
H	0.81375300	7.28001400	-0.07788800
H	2.16171900	5.21727000	-0.05436700
C	-0.54248100	-5.95027500	0.14430100
C	-1.28787000	-4.81478600	0.12602000
C	-0.65948400	-3.52245400	0.09451500
C	0.78327300	-3.45628500	0.08422600
C	1.52879000	-4.68474700	0.10445600
C	0.89198500	-5.88433400	0.13277500
H	-2.47957300	-2.39627900	0.07642300
H	-1.02664400	-6.92165700	0.16927600
H	-2.37404400	-4.85728500	0.13668200

C	-1.39365700	-2.35041600	0.07372800
C	1.40772900	-2.22271900	0.05571900
H	2.61428600	-4.62624600	0.09772000
H	1.46405800	-6.80677300	0.14796800
H	2.49308700	-2.17123700	0.04589500
C	-2.94630400	0.04501100	0.02899500
C	-4.16359100	-0.03057300	0.02473500
Si	-5.99902900	-0.21345600	-0.03652400
C	2.73857700	0.29521100	0.00604800
C	3.95808800	0.30076800	-0.00055800
Si	5.80140300	0.17261800	-0.06209200
C	-6.45919600	-0.79497500	-1.79356500
H	-7.51438900	-0.51013800	-1.93215400
C	-6.78632600	1.47630800	0.35542400
H	-7.81032300	1.25257200	0.69443200
C	-6.50456900	-1.52642400	1.25040300
H	-7.44787800	-1.95251100	0.87390700
C	6.53480300	1.88391200	0.31941500
H	6.49803300	2.45351600	-0.62137300
C	6.19055400	-0.35764600	-1.84393700
H	5.60502000	0.34539700	-2.45548800
C	6.30998100	-1.08982200	1.27086100
H	6.36589300	-0.50981700	2.20541300
C	7.99913000	1.79891900	0.77460600
H	8.63935900	1.28328700	0.05110300
H	8.41447900	2.80182400	0.93017900
H	8.07845900	1.26423600	1.72917500
C	5.70856800	2.63565000	1.37070400
H	5.68079000	2.08189900	2.31757600
H	6.14855200	3.61818600	1.58081200
H	4.67347500	2.78454000	1.04966600
C	7.66339200	-0.20310500	-2.24430500
H	7.80855800	-0.48981300	-3.29317300
H	8.00810500	0.83076400	-2.13530200
H	8.31839300	-0.84054900	-1.63987100
C	5.67548100	-1.77013700	-2.14676200
H	4.61537100	-1.87812400	-1.88992500
H	5.78815000	-2.00656500	-3.21178900
H	6.23673800	-2.52576600	-1.58490000
C	5.26612400	-2.19697900	1.47533800
H	5.13129300	-2.78661400	0.55954600
H	5.58715200	-2.88835300	2.26422300
H	4.29086800	-1.78874200	1.75594700
C	7.69246900	-1.71012800	1.01756100

H	8.47659900	-0.95866900	0.88145800
H	7.98660500	-2.34845500	1.85946200
H	7.67931100	-2.34203900	0.12205100
C	-6.35269300	-2.31530600	-1.96776900
H	-6.97003000	-2.86876800	-1.25280300
H	-6.66733500	-2.60816900	-2.97678800
H	-5.31390500	-2.64586000	-1.84525800
C	-5.62017900	-0.10713600	-2.87983600
H	-5.69109900	0.98308000	-2.84636100
H	-4.56294500	-0.37046300	-2.76629300
H	-5.94168100	-0.43297500	-3.87660400
C	-6.88746300	2.39318300	-0.86991500
H	-7.45256600	1.93797100	-1.68957400
H	-7.38352200	3.33468400	-0.60425600
H	-5.88965500	2.64692600	-1.24904100
C	-6.05471900	2.21698200	1.48363400
H	-6.55494800	3.16735100	1.70702900
H	-6.00724100	1.63932300	2.41020500
H	-5.02391700	2.44483700	1.18848200
C	-5.47266500	-2.65845300	1.36192200
H	-5.82283500	-3.43292100	2.05516200
H	-5.26736600	-3.13870700	0.40038800
H	-4.52333000	-2.26945100	1.74774300
C	-6.77490700	-0.95044500	2.64583900
H	-7.53190300	-0.15935100	2.63515000
H	-7.12574000	-1.73769800	3.32412700
H	-5.85744000	-0.53509900	3.07885800

Table S2. Cartesian coordinates for all optimized geometries of **1a**.
The excitation energy of **1a** is 2.0360 eV.

C	-1.34674900	0.03912600	0.03524200
C	-0.81566000	-1.27418100	0.04169400
C	0.58145200	-1.49278000	0.05151100
C	1.47958300	-0.36267200	0.05233000
C	0.94968300	0.94995100	0.04482100
C	-0.44864300	1.16915000	0.04080500
C	1.12674700	-2.79503900	0.05525800
C	2.87072700	-0.59867700	0.05859400
C	3.39148000	-1.88061600	0.06136200
C	2.49160500	-3.00992300	0.05676600
C	3.05937100	-4.33020500	0.05663600
H	2.38389100	-5.18165200	0.06647300
C	4.40342300	-4.51216100	0.05577800
C	5.31439600	-3.39191700	0.05802900

C	4.80488900	-2.12531800	0.06025100
H	0.44725900	-3.64289000	0.05684100
H	3.54235300	0.25526800	0.06719300
H	4.81701100	-5.51603300	0.08198700
H	5.47165700	-1.26675400	0.03067700
C	-5.18239100	3.06626000	-0.00596000
C	-4.67212400	1.79992700	-0.00080600
C	-3.25879000	1.55661000	0.01623300
C	-2.35957700	2.68591800	0.02320000
C	-2.92774900	4.00590100	0.01684000
C	-4.27197600	4.18697400	0.00166500
H	-3.41072900	-0.57871400	0.01642400
H	-5.33770400	0.94039900	-0.03809700
C	-2.73802600	0.27466400	0.02146400
C	-0.99435900	2.47174300	0.03811700
H	-2.25228300	4.85745700	0.03310300
H	-4.68646700	5.19058700	0.02365200
H	-0.31683300	3.32128200	0.05043700
C	-1.71256100	-2.38198100	0.03351900
C	-2.51299600	-3.30223900	0.02429400
Si	-3.82834000	-4.59747900	-0.01171200
C	1.83153700	2.07017400	0.03202300
C	2.57089400	3.03984400	0.01258500
Si	3.63110400	4.55375500	0.01701300
C	-4.88862900	-4.39779600	1.56047100
H	-5.36708600	-5.37768800	1.71720700
C	-3.00102400	-6.31231300	-0.06213600
H	-3.74652700	-6.98296700	-0.51791600
C	-4.87814100	-4.29980500	-1.57523800
H	-5.85891200	-4.75323800	-1.36102100
C	5.37001400	4.05302200	-0.56793200
H	5.87728300	3.61512300	0.30512000
C	3.65686100	5.12846200	1.82734200
H	3.89371400	4.20917100	2.38409900
C	2.84399900	5.78768300	-1.20277800
H	3.23562600	5.50057700	-2.19142700
C	6.19265800	5.25642000	-1.05024200
H	6.28634000	6.03964800	-0.29092300
H	7.20522100	4.94360900	-1.33215500
H	5.73470600	5.70789600	-1.93885000
C	5.30963200	2.99160100	-1.67391000
H	4.77908500	3.37414200	-2.55508100
H	6.31856900	2.70991300	-1.99885700
H	4.78844000	2.08663300	-1.34842600

C	4.74760800	6.15716700	2.15010600
H	4.73017900	6.41433500	3.21636300
H	5.74767100	5.77401500	1.92101300
H	4.60768400	7.08827000	1.58954100
C	2.27851100	5.60957600	2.29863000
H	1.49902300	4.86722800	2.09261400
H	2.28090900	5.80281900	3.37812200
H	1.99267900	6.54423300	1.80222000
C	1.31425900	5.67625100	-1.26095100
H	0.86323400	5.89706000	-0.28522200
H	0.90268200	6.39369800	-1.98142300
H	0.99293700	4.67352100	-1.55754500
C	3.26029400	7.24203500	-0.93737100
H	4.34674200	7.37414500	-0.91623400
H	2.86099600	7.90431400	-1.71517300
H	2.86477400	7.59543700	0.02166100
C	-6.00095500	-3.35184400	1.41433700
H	-6.66731000	-3.56013200	0.57119900
H	-6.61307300	-3.31453100	2.32361600
H	-5.57515500	-2.35094400	1.27034900
C	-4.04241100	-4.06429500	2.79761600
H	-3.25526800	-4.79945200	2.98441400
H	-3.55831000	-3.08910100	2.67482900
H	-4.67352700	-4.01485900	3.69337000
C	-2.66028900	-6.86653200	1.32661100
H	-3.53459100	-6.92304900	1.98295500
H	-2.23986500	-7.87614800	1.24365800
H	-1.90736600	-6.24123300	1.82131500
C	-1.74026700	-6.32526200	-0.93752100
H	-1.32080800	-7.33698500	-0.99644000
H	-1.92760300	-5.98034100	-1.95781100
H	-0.97330200	-5.67086800	-0.50704800
C	-5.08700200	-2.80629900	-1.86621600
H	-5.73496400	-2.67200500	-2.74101900
H	-5.54534700	-2.27068900	-1.02953600
H	-4.12832400	-2.32206700	-2.08363100
C	-4.30881300	-4.98158200	-2.82611400
H	-4.17862500	-6.06080500	-2.69514900
H	-4.97607200	-4.82765600	-3.68284900
H	-3.33519700	-4.55340500	-3.09270100
C	-6.64437200	3.31107500	-0.02480500
C	-7.18130700	4.37291300	-0.76241300
C	-7.51972900	2.48455800	0.68968600
C	-8.55369100	4.59638500	-0.79195600

H	-6.51942600	5.01218200	-1.34027300
C	-8.89184000	2.70735900	0.66037100
H	-7.11407200	1.67766600	1.29367300
C	-9.41438800	3.76430400	-0.08095300
H	-8.95208600	5.41945100	-1.37761300
H	-9.55362800	2.06080700	1.22872800
H	-10.48532000	3.94073900	-0.10114300
C	6.77629000	-3.63785300	0.05051400
C	7.31785200	-4.69836200	-0.68568300
C	7.64698300	-2.81365400	0.77330500
C	8.69026700	-4.92263200	-0.70592300
H	6.65976400	-5.33574400	-1.26990000
C	9.01915000	-3.03721400	0.75325400
H	7.23728100	-2.00812600	1.37632700
C	9.54635500	-4.09268700	0.01311400
H	9.09242100	-5.74450900	-1.29068100
H	9.67729200	-2.39251200	1.32790100
H	10.61730500	-4.26967000	0.00004900

Table S3. Cartesian coordinates for all optimized geometries of **1b**.
The excitation energy of **1b** is 2.0023 eV.

C	-1.35210100	-0.17471000	0.07462300
C	-0.59837900	-1.37355600	0.06821900
C	0.81591000	-1.34312100	0.07174000
C	1.50119000	-0.07241800	0.07283000
C	0.74798900	1.12624900	0.06102200
C	-0.66718100	1.09551700	0.06431300
C	1.58257900	-2.52911600	0.06955600
C	2.91202300	-0.05930300	0.08052300
C	3.65093000	-1.22947400	0.08258600
C	2.96405400	-2.49957200	0.07093100
C	3.75536600	-3.69912200	0.06422600
H	3.23960200	-4.65594400	0.06623700
C	5.11050600	-3.64166100	0.06658700
C	5.80996000	-2.37852200	0.08182900
C	5.08531900	-1.22136800	0.08798600
H	1.06350600	-3.48410400	0.07136800
H	3.42310200	0.89959500	0.09082700
H	5.69467500	-4.55702500	0.08592200
H	5.59154400	-0.25897300	0.06686600
C	-5.66233400	2.12638800	0.04348100
C	-4.93682500	0.96999500	0.06999500
C	-3.50257500	0.98048800	0.07111400
C	-2.81666400	2.25048400	0.04624500

C	-3.60864900	3.44922600	0.01974100
C	-4.96382900	3.38999300	0.01525300
H	-3.27385700	-1.14749400	0.11017100
H	-5.44106000	0.00602800	0.05809500
C	-2.76287000	-0.18901100	0.08498000
C	-1.43501700	2.28105300	0.05088400
H	-3.09324200	4.40637600	0.01018700
H	-5.54919400	4.30479600	0.01871700
H	-0.91807500	3.23693100	0.04307400
C	-1.27880100	-2.62563200	0.04139400
C	-1.87181700	-3.69078600	0.00452100
Si	-2.78373800	-5.29438300	-0.05894600
C	1.41387100	2.38664000	0.03547800
C	1.95417000	3.47962200	0.00314900
Si	2.64983700	5.19270700	-0.01355300
C	-3.13745800	-5.84153000	1.73093300
H	-3.29671000	-6.93043100	1.67945800
C	-1.68573700	-6.56187900	-0.96349200
H	-2.37667300	-7.33243000	-1.34008800
C	-4.41914100	-5.00713600	-0.99779900
H	-5.11578400	-5.76256900	-0.60216800
C	4.48391900	5.08976800	-0.50429100
H	5.03574800	4.81290900	0.40656900
C	2.45168300	5.81254500	1.77088700
H	2.86980200	4.99202500	2.37373400
C	1.66306300	6.17498500	-1.31423900
H	2.15765600	5.95533100	-2.27347400
C	5.02850300	6.43521500	-1.00698000
H	4.90094000	7.24347500	-0.27910100
H	6.09878400	6.35808500	-1.23345900
H	4.52281400	6.73719000	-1.93233400
C	4.72469900	4.00570500	-1.56304900
H	4.16470200	4.22410700	-2.48102700
H	5.78620800	3.95546800	-1.83430000
H	4.41110900	3.01622900	-1.21793800
C	3.25386700	7.07904400	2.09540000
H	3.11866200	7.36096000	3.14686200
H	4.32647700	6.93334800	1.92924000
H	2.93284000	7.93155600	1.48649100
C	0.97780700	5.96813700	2.16439100
H	0.40507400	5.05829600	1.95131300
H	0.87966400	6.18321200	3.23532800
H	0.50741400	6.79670000	1.62231800
C	0.20370600	5.71418800	-1.43068800

H	-0.33467300	5.86332600	-0.48595200
H	-0.32285100	6.29026900	-2.20152700
H	0.13390000	4.65382100	-1.69008700
C	1.72332100	7.69327100	-1.09056400
H	2.74845600	8.07068200	-1.01849100
H	1.23144100	8.22312200	-1.91526700
H	1.20074600	7.97432900	-0.16901400
C	-4.40654300	-5.20632200	2.31509700
H	-5.29851600	-5.40957600	1.71363400
H	-4.59318800	-5.58684300	3.32666400
H	-4.29283600	-4.11841900	2.39465100
C	-1.95900500	-5.56336600	2.67496900
H	-1.02572200	-6.02356500	2.33976900
H	-1.78301900	-4.48506800	2.75420100
H	-2.17560500	-5.94173300	3.68149800
C	-0.67006100	-7.25445900	-0.04686500
H	-1.14467600	-7.76498300	0.79724300
H	-0.09552100	-8.00165200	-0.60799100
H	0.04816300	-6.53061200	0.35806400
C	-0.95142700	-5.94229300	-2.16037800
H	-0.36762400	-6.70471800	-2.69056600
H	-1.63138700	-5.48155000	-2.88181000
H	-0.25740000	-5.16400100	-1.82251600
C	-5.00478800	-3.61524700	-0.72049500
H	-5.99586300	-3.51113300	-1.17876300
H	-5.10501100	-3.40299400	0.34853800
H	-4.35629500	-2.84431200	-1.15282200
C	-4.31294400	-5.21872000	-2.51297700
H	-3.92466100	-6.20888700	-2.77331200
H	-5.29715400	-5.11189800	-2.98499200
H	-3.65407100	-4.46857600	-2.96561500
C	-7.14399200	2.11042100	0.03748000
C	-7.86891100	3.02687500	-0.73317300
C	-7.85874400	1.17506400	0.79317700
C	-9.25779200	3.00032200	-0.75203300
H	-7.33746600	3.74845800	-1.34788400
C	-9.24817600	1.15440700	0.77239700
H	-7.31692800	0.47185000	1.41965900
C	-9.97222900	2.06700600	0.00264500
H	-9.79938700	3.71320900	-1.36934300
H	-9.78233200	0.42110100	1.37179700
C	7.29163700	-2.36411600	0.08668200
C	8.02117700	-3.29032600	-0.66783600
C	8.00184000	-1.42157800	0.83763900

C	9.41015600	-3.26613900	-0.67591100
H	7.49346000	-4.01814600	-1.27838800
C	9.39147900	-1.40326400	0.82766300
H	7.45625300	-0.71101700	1.45241500
C	10.12011400	-2.32546300	0.07394300
H	9.95546800	-3.98692700	-1.28062600
H	9.92204700	-0.66420700	1.42316000
C	11.62716000	-2.32744100	0.09040300
H	12.02269400	-1.34103300	0.34731600
H	12.01006700	-3.04005600	0.82967300
H	12.03374000	-2.61559200	-0.88326900
C	-11.47936200	2.06656400	0.00731400
H	-11.86915200	2.78128400	0.74092300
H	-11.87883900	2.35025900	-0.97057700
H	-11.87527000	1.08048400	0.26498100

Table S4. Cartesian coordinates for all optimized geometries of **1c**.
The excitation energy of **1c** is 1.9997 eV.

C	-1.35164000	-0.27944000	0.00127600
C	-0.49648300	-1.40764100	-0.01469300
C	0.90948400	-1.25120100	-0.00761400
C	1.48022200	0.07502600	0.00239100
C	0.62553700	1.20346500	-0.00226100
C	-0.78115100	1.04654800	0.00350000
C	1.77713100	-2.36526100	-0.00786400
C	2.88422100	0.21293200	0.01919400
C	3.72201900	-0.88827600	0.02825600
C	3.15039800	-2.21385300	0.00862500
C	4.04407100	-3.33898300	0.01644300
H	3.61527400	-4.33769200	0.01085900
C	5.38888800	-3.16403300	0.04619000
C	5.97092100	-1.84320800	0.07208600
C	5.14902200	-0.75349100	0.05722500
H	1.34497700	-3.36237400	-0.01198100
H	3.30817900	1.21323700	0.03725200
H	6.04902200	-4.02556400	0.08150800
H	5.56715300	0.25030900	0.04118600
C	-5.84401100	1.63278200	0.06187500
C	-5.02090200	0.54389100	0.04681300
C	-3.59405600	0.68117700	0.02889900
C	-3.02338100	2.00701000	0.02122600
C	-3.91801400	3.13125800	0.03155800
C	-5.26287300	2.95438100	0.05039400
H	-3.17881900	-1.41995200	0.02886400

H	-5.43659500	-0.46095700	0.01918000
C	-2.75545300	-0.41925700	0.01648100
C	-1.65000400	2.16003900	0.01197600
H	-3.48976500	4.13035000	0.03501800
H	-5.92411300	3.81501900	0.08673500
H	-1.22056500	3.15825300	0.01638600
C	-1.05961900	-2.71650300	-0.04060800
C	-1.54149500	-3.83646700	-0.06882400
Si	-2.27614700	-5.53217500	-0.08483500
C	1.17687900	2.51798600	-0.01734500
C	1.61563000	3.65554000	-0.04066300
Si	2.17537200	5.41940900	-0.05359600
C	-2.53581000	-6.06476000	1.72623400
H	-2.58126800	-7.16540400	1.70667600
C	-1.06256600	-6.69497600	-0.98048000
H	-1.67405500	-7.54079000	-1.33257100
C	-3.94581300	-5.44547900	-0.99856700
H	-4.54414600	-6.26908300	-0.57830200
C	4.00823600	5.45022800	-0.55703200
H	4.58282600	5.20511800	0.34889700
C	1.94208600	6.01603300	1.73423400
H	2.41736100	5.22499200	2.33395000
C	1.10614900	6.32525900	-1.34396600
H	1.60630100	6.14187100	-2.30782300
C	4.45388400	6.83438000	-1.05171200
H	4.28072600	7.62602100	-0.31513600
H	5.52410400	6.83198300	-1.29048200
H	3.91875000	7.10908700	-1.96888500
C	4.31895900	4.39525600	-1.62660600
H	3.74337300	4.58397100	-2.54158500
H	5.38068200	4.42012800	-1.90044100
H	4.07451500	3.38317300	-1.29092500
C	2.65740200	7.33389500	2.05642100
H	2.50905600	7.60479900	3.10887400
H	3.73643700	7.26236000	1.88384200
H	2.27450400	8.16243300	1.45023300
C	0.46236000	6.07245900	2.13379600
H	-0.04910500	5.12516600	1.92782600
H	0.35516800	6.28510800	3.20430000
H	-0.06489400	6.86547400	1.59078600
C	-0.31718500	5.75985400	-1.44679000
H	-0.85655100	5.87402400	-0.49788100
H	-0.88982300	6.29431800	-2.21464200
H	-0.31323800	4.69640900	-1.70343900

C	1.05728000	7.84432300	-1.12062100
H	2.05240000	8.29555600	-1.05498500
H	0.52304200	8.33651800	-1.94213400
H	0.52192700	8.08727100	-0.19563700
C	-3.85352000	-5.54783800	2.31808600
H	-4.72825600	-5.85250100	1.73466500
H	-3.98758700	-5.92307900	3.33974200
H	-3.84865100	-4.45249200	2.37371600
C	-1.37439900	-5.64094900	2.63662200
H	-0.40790400	-6.02350500	2.29827400
H	-1.30018600	-4.54866400	2.67647600
H	-1.53702600	-6.00271200	3.65917200
C	0.02977000	-7.25981700	-0.06399100
H	-0.38018300	-7.79579300	0.79811100
H	0.67066700	-7.95704200	-0.61722400
H	0.67476700	-6.45688700	0.31446600
C	-0.40971000	-6.02914000	-2.19991700
H	0.24379600	-6.73853300	-2.72205700
H	-1.14146800	-5.65616900	-2.92130500
H	0.20434400	-5.17641300	-1.88821500
C	-4.68664600	-4.12600500	-0.73665500
H	-5.68596900	-4.14747600	-1.18823500
H	-4.80507600	-3.90859400	0.32942500
H	-4.13595000	-3.29250900	-1.18852400
C	-3.83891800	-5.67066100	-2.51191600
H	-3.34483900	-6.61450500	-2.76395500
H	-4.83614900	-5.68492100	-2.96828600
H	-3.27730800	-4.85814400	-2.98753200
C	-7.31763600	1.47752200	0.08352600
C	-8.13639700	2.37104700	-0.61662700
C	-7.90813400	0.43100300	0.80162000
C	-9.51046000	2.20449100	-0.59888900
H	-7.72176300	3.18184500	-1.20552200
C	-9.28390300	0.28460400	0.80025900
H	-7.31260500	-0.25809300	1.38982500
C	-10.10293400	1.16418600	0.10462100
C	7.44432700	-1.68980200	0.11167100
C	8.27023500	-2.57549100	-0.59005300
C	8.02734400	-0.65411400	0.85113800
C	9.64425900	-2.41181500	-0.55252600
H	7.86172600	-3.37761900	-1.19490700
C	9.40329600	-0.51065900	0.86965300
H	7.42546600	0.02739400	1.44170600
C	10.22951800	-1.38259400	0.17292800

F	11.55203900	-1.23927300	0.20605000
F	10.44382300	-3.24257500	-1.22363400
F	9.97323300	0.46451900	1.57970800
F	-9.86079800	-0.70214500	1.48840700
F	-11.42546700	1.01722900	0.11742400
F	-10.30286800	3.04278600	-1.26920900

Table S5. Cartesian coordinates for all optimized geometries of **1d**.
The excitation energy of **1d** is 2.0007 eV.

C	-1.33489100	-0.38292100	0.20531900
C	-0.39632800	-1.44322500	0.21100500
C	0.99404900	-1.18259300	0.22251500
C	1.46296400	0.18253100	0.21518100
C	0.52506400	1.24286400	0.20458900
C	-0.86599800	0.98206000	0.20494400
C	1.94342900	-2.22775200	0.23380700
C	2.85304300	0.42520500	0.21230100
C	3.77239400	-0.60891800	0.21446900
C	3.30152200	-1.97365000	0.22649200
C	4.27814500	-3.02785600	0.23272600
H	3.92610300	-4.05579500	0.26220200
C	5.60529500	-2.75025500	0.21330400
C	6.09035800	-1.39008100	0.18714900
C	5.18605500	-0.36672400	0.19413200
H	1.58720000	-3.25430400	0.25107900
H	3.20086500	1.45453700	0.21223200
H	6.33024300	-3.55804900	0.24612500
H	5.52433100	0.66579500	0.14836000
C	-5.96214800	1.18661600	0.13373300
C	-5.05723300	0.16388500	0.15427200
C	-3.64404800	0.40765200	0.17996200
C	-3.17373300	1.77240300	0.18108400
C	-4.15073300	2.82612400	0.16896600
C	-5.47767600	2.54730200	0.14665900
H	-3.07363400	-1.65567100	0.20188700
H	-5.39362900	-0.86980700	0.11680100
C	-2.72485300	-0.62656000	0.19466300
C	-1.81568600	2.02739000	0.19727100
H	-3.79894300	3.85451700	0.18752700
H	-6.20305000	3.35512100	0.16688900
H	-1.46088400	3.05464900	0.20409400
C	-0.86470300	-2.78912500	0.18893900
C	-1.28130900	-3.93498400	0.15921000
Si	-1.96382100	-5.64951100	0.10345000

C	0.98253600	2.59288700	0.18230100
C	1.35857300	3.75268000	0.15506200
Si	1.86748200	5.52960100	0.13647900
C	-2.52629000	-6.11515700	1.86448100
H	-2.53137100	-7.21645400	1.88854300
C	-0.58887600	-6.81724700	-0.50978200
H	-1.11057000	-7.69832300	-0.91552400
C	-3.45102100	-5.64297300	-1.09075600
H	-4.09646200	-6.47057000	-0.75713100
C	3.69877600	5.60421000	-0.37096700
H	4.27958000	5.37216600	0.53458600
C	1.62806600	6.12690200	1.92367600
H	2.12246000	5.34743700	2.52304300
C	0.77466800	6.40882300	-1.15204500
H	1.27577400	6.23480400	-2.11720200
C	4.11226000	6.99778800	-0.86624500
H	3.92098200	7.78584900	-0.13033600
H	5.18219200	7.01981200	-1.10584100
H	3.57052400	7.25943400	-1.78336300
C	4.03360700	4.55706800	-1.44089600
H	3.45209100	4.73163200	-2.35499200
H	5.09406600	4.60764300	-1.71646600
H	3.81433700	3.53921700	-1.10547100
C	2.31558200	7.46049300	2.24102400
H	2.16625600	7.72963700	3.29389000
H	3.39512700	7.41288000	2.06330000
H	1.91141600	8.27954600	1.63564000
C	0.14900800	6.15194300	2.32892700
H	-0.34201000	5.19300700	2.12791300
H	0.04128100	6.36583600	3.39920000
H	-0.39788200	6.93124000	1.78535600
C	-0.63535700	5.80953100	-1.24813800
H	-1.17577400	5.91761300	-0.29937000
H	-1.22147300	6.32498300	-2.01887300
H	-0.60705700	4.74457600	-1.49687800
C	0.69084400	7.92677700	-0.93238200
H	1.67530200	8.40186300	-0.87371100
H	0.14016200	8.40413900	-1.75194600
H	0.15544300	8.15930100	-0.00478300
C	-3.94453300	-5.63028900	2.19111800
H	-4.69068200	-5.99280700	1.47673900
H	-4.24543900	-5.97057000	3.18943700
H	-3.98724400	-4.53425100	2.19746800
C	-1.56017200	-5.60654900	2.94368200

H	-0.53385600	-5.95071700	2.79201200
H	-1.54105000	-4.51127300	2.95001600
H	-1.88245300	-5.94186000	3.93701300
C	0.34137500	-7.29933800	0.61038100
H	-0.19902000	-7.80352600	1.41788400
H	1.08386300	-8.00313800	0.21502000
H	0.89255400	-6.45800700	1.04868200
C	0.25004000	-6.19183400	-1.63262800
H	1.00403100	-6.90310100	-1.99170200
H	-0.35178400	-5.88318400	-2.49114300
H	0.77715000	-5.30250400	-1.26825400
C	-4.25365800	-4.33670500	-1.00577800
H	-5.15504000	-4.39320500	-1.62809000
H	-4.56672100	-4.09843900	0.01553900
H	-3.64906700	-3.49843700	-1.37114900
C	-3.06930600	-5.90766900	-2.55225600
H	-2.52954900	-6.85154300	-2.68148600
H	-3.96672200	-5.94848100	-3.18139400
H	-2.43762200	-5.10052900	-2.94117600
C	-7.42026600	0.92861100	0.08314000
C	-8.26399500	1.76164800	-0.61926700
C	-7.97722100	-0.19758800	0.75474200
C	-9.65830700	1.51798700	-0.69330400
H	-7.86100200	2.61533700	-1.15950300
C	-9.31944200	-0.45828000	0.70158700
H	-7.32260400	-0.83707600	1.33949400
C	-10.53132500	2.36858700	-1.42204200
C	-10.20056300	0.38721500	-0.02334600
H	-9.73293800	-1.31532500	1.22726400
C	-11.87654000	2.10983400	-1.47678100
H	-10.11163000	3.23025200	-1.93499300
C	-11.59628900	0.14515400	-0.09644700
C	-12.41614100	0.98552400	-0.80547500
H	-12.53486600	2.76653700	-2.03713000
H	-12.00420100	-0.72025400	0.41972900
H	-13.48304100	0.79164700	-0.85651400
C	7.54867900	-1.13345500	0.13623900
C	8.39144700	-1.97135000	-0.56148700
C	8.10641300	-0.00340700	0.80050900
C	9.78569900	-1.72840800	-0.63861100
H	7.98739900	-2.82820800	-1.09590600
C	9.44873200	0.25642200	0.74463700
H	7.45226000	0.63973100	1.38181200
C	10.65763000	-2.58329700	-1.36362200

C	10.32885300	-0.59362900	0.02381000
H	9.86308600	1.11648200	1.26467000
C	12.00270100	-2.32468200	-1.42210000
H	10.23719100	-3.44796200	-1.87085600
C	11.72447700	-0.35196000	-0.05283900
C	12.54324400	-1.19639500	-0.75827500
H	12.66022400	-2.98452700	-1.97970300
H	12.13317200	0.51654500	0.45745500
H	13.61002800	-1.00268200	-0.81227700

4. Identification and Testing Spectra of Compounds

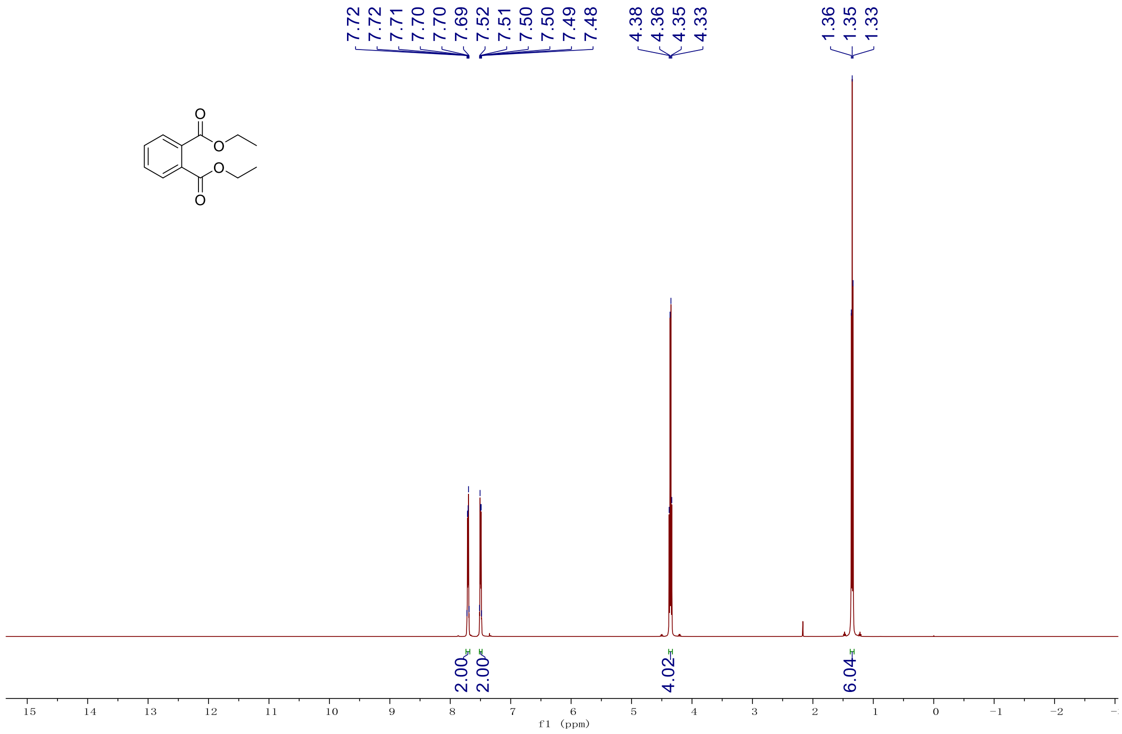


Fig. S2. ^{1}H NMR spectrum of compound S3.

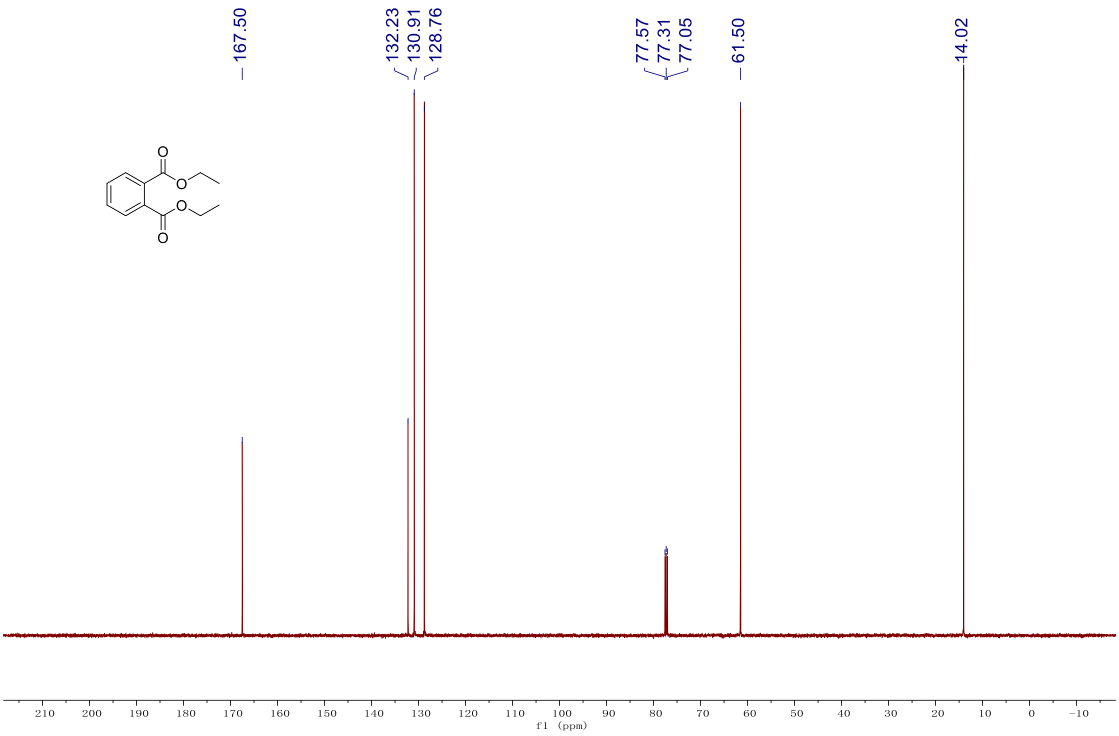


Fig. S3. ^{13}C NMR spectrum of compound S3.

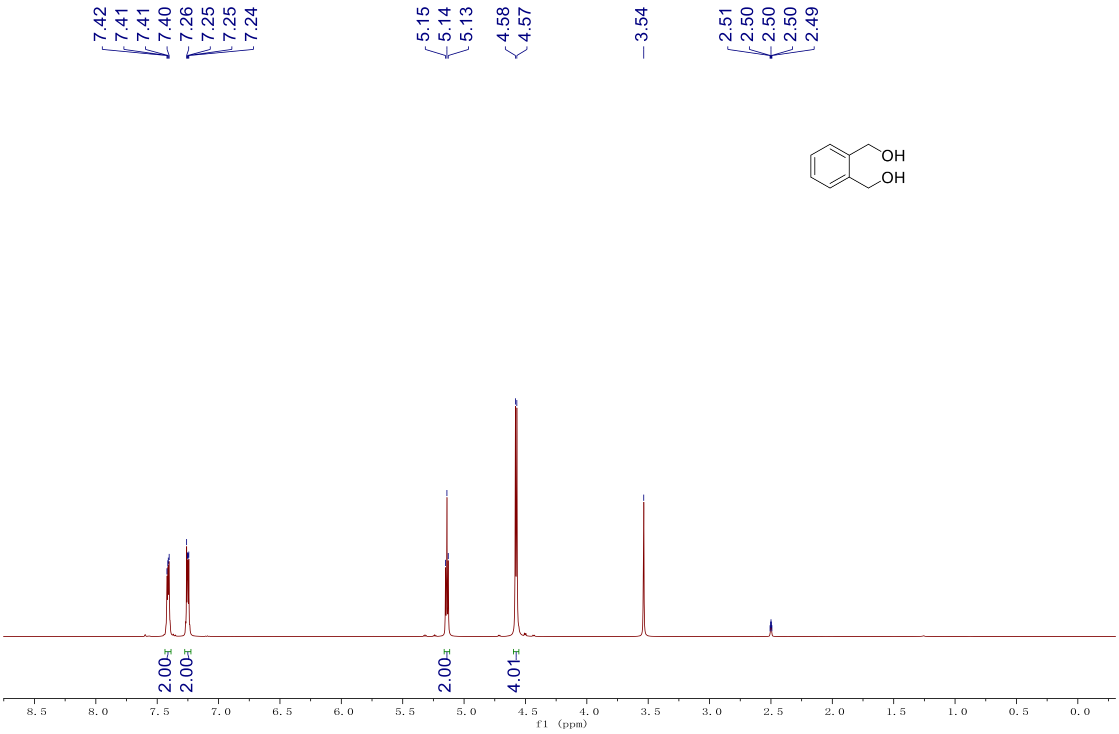


Fig. S4. ^{1}H NMR spectrum of compound **S4**.

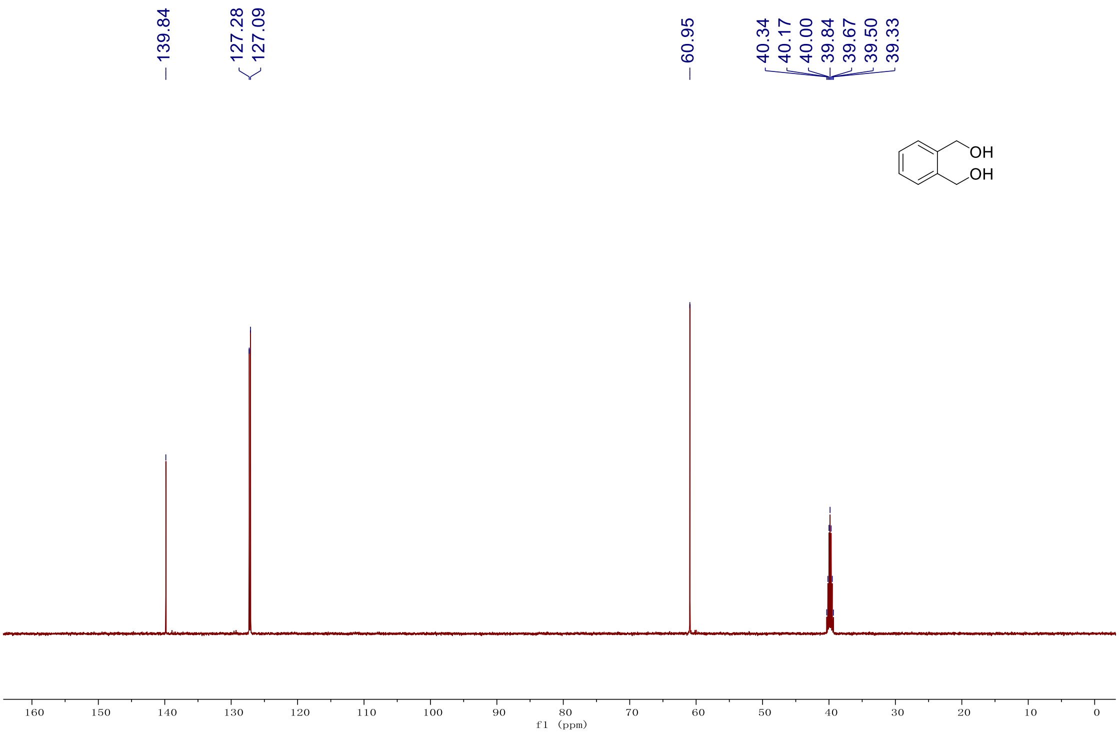


Fig. S5. ^{13}C NMR spectrum of compound **S4**.

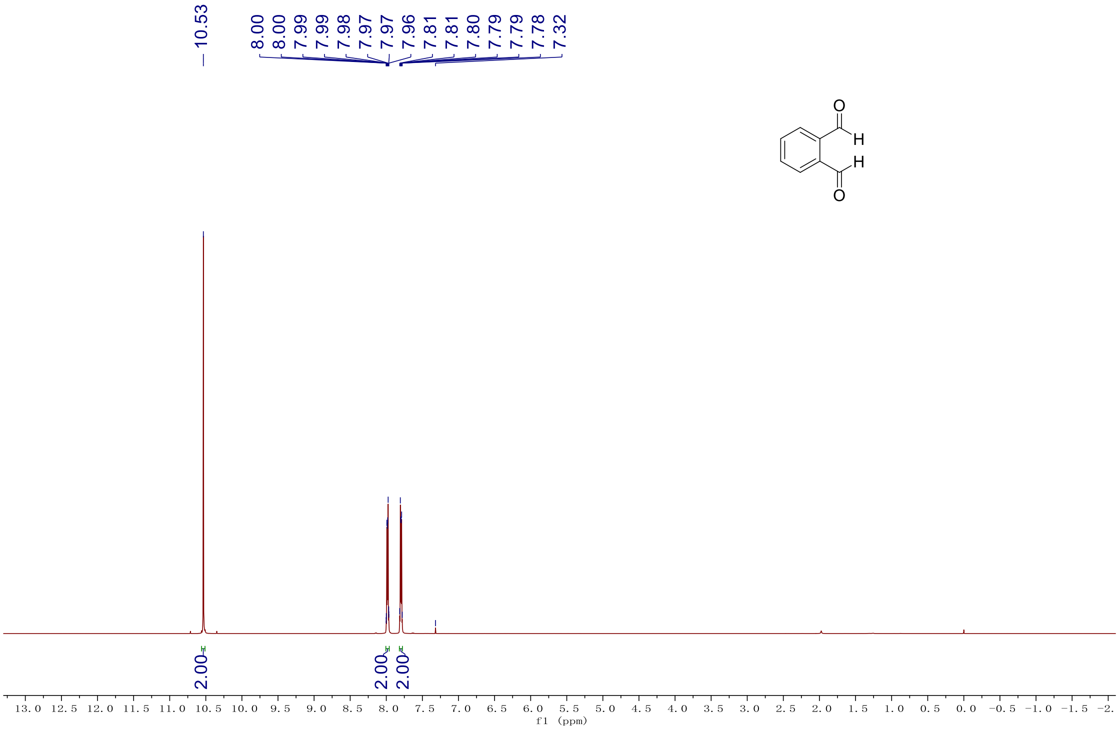


Fig. S6. ^{1}H NMR spectrum of compound **S5**.

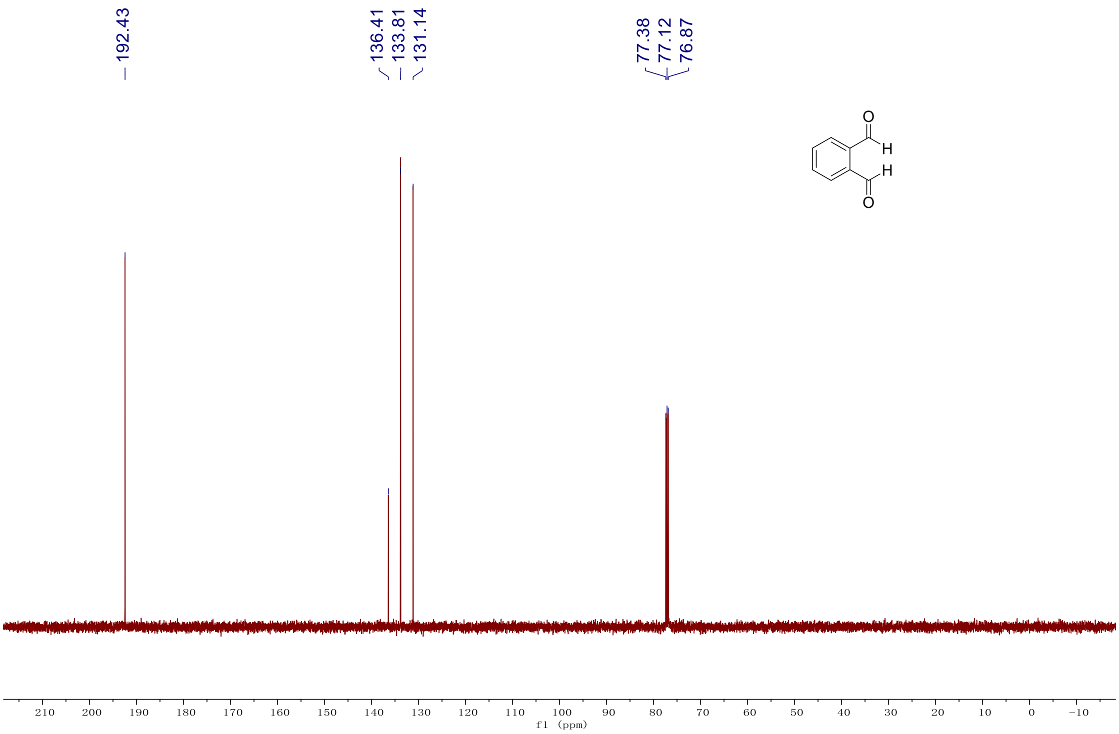


Fig. S7. ^{13}C NMR spectrum of compound **S5**.

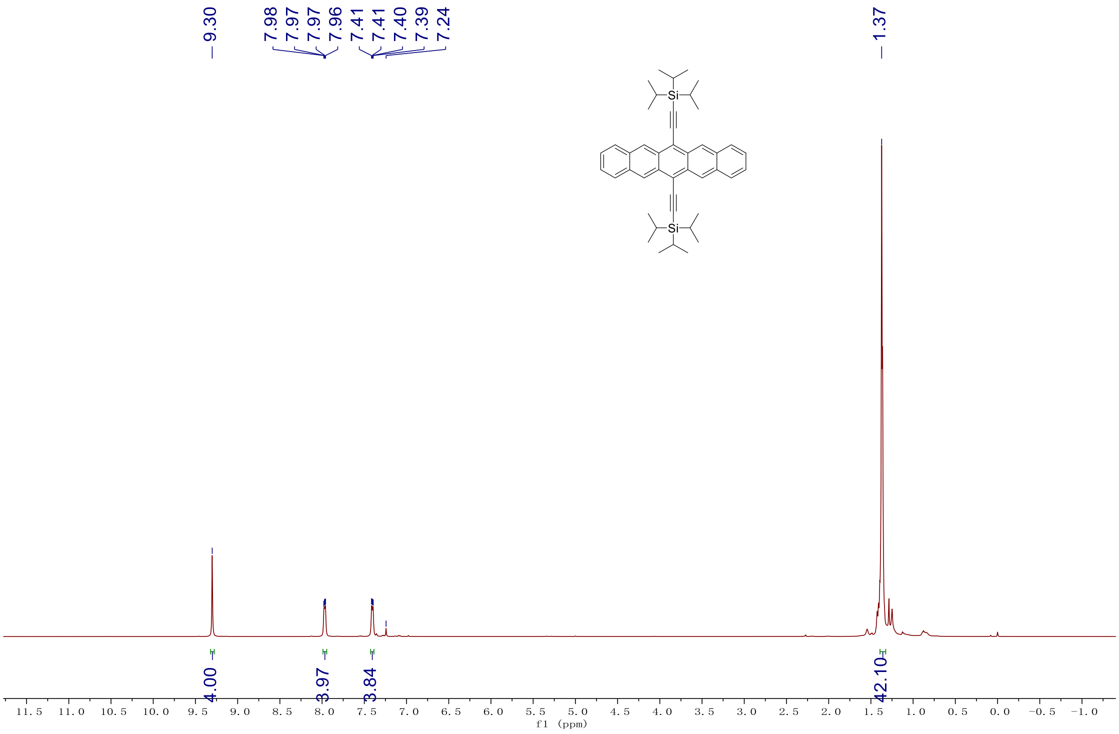


Fig. S8. ^{1}H NMR spectrum of compound **S1**.

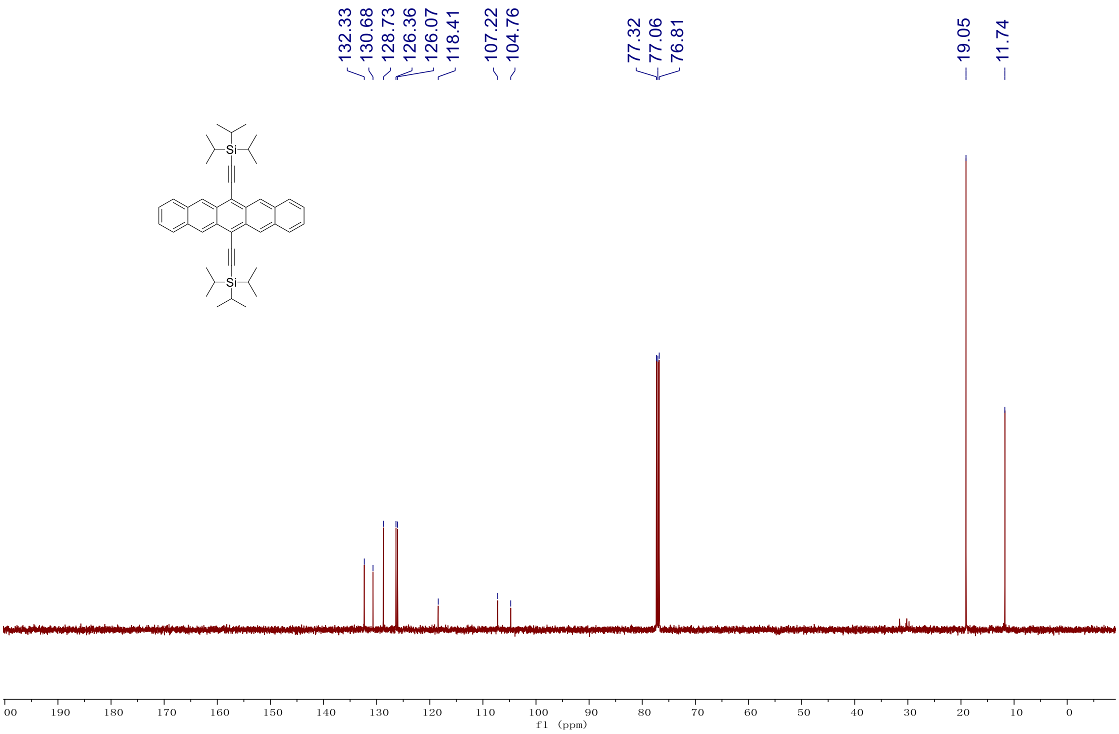


Fig. S9. ^{13}C NMR spectrum of compound **S1**.

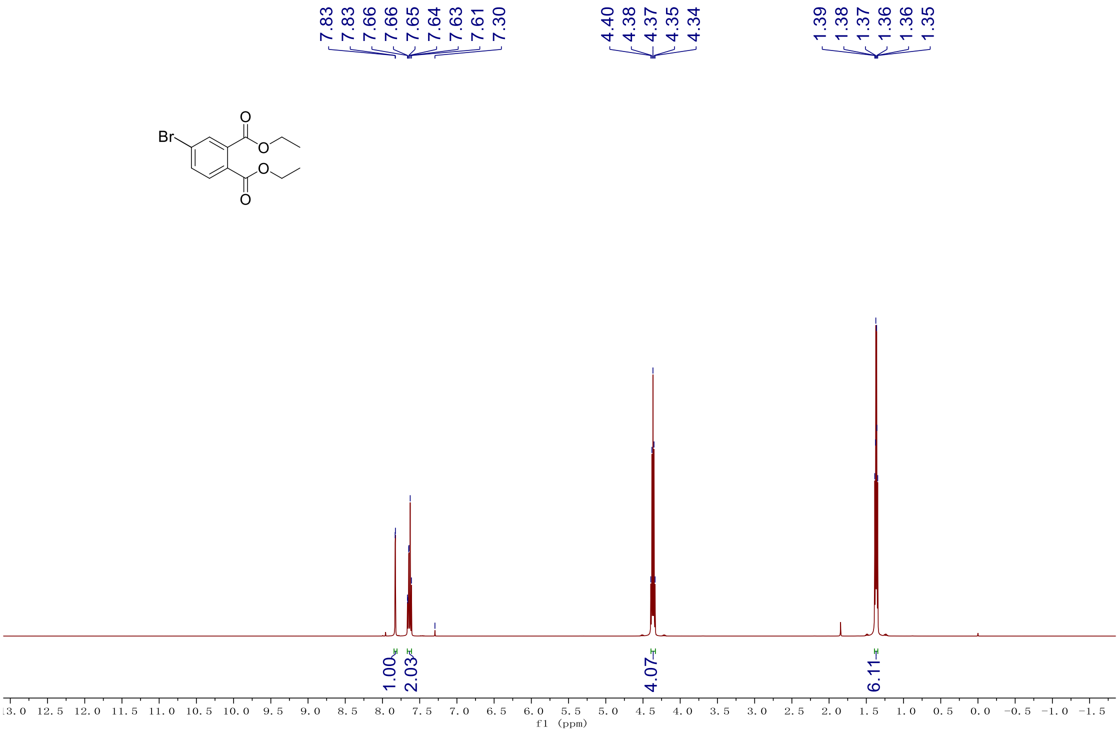


Fig. S10. ^{1}H NMR spectrum of compound **3**.

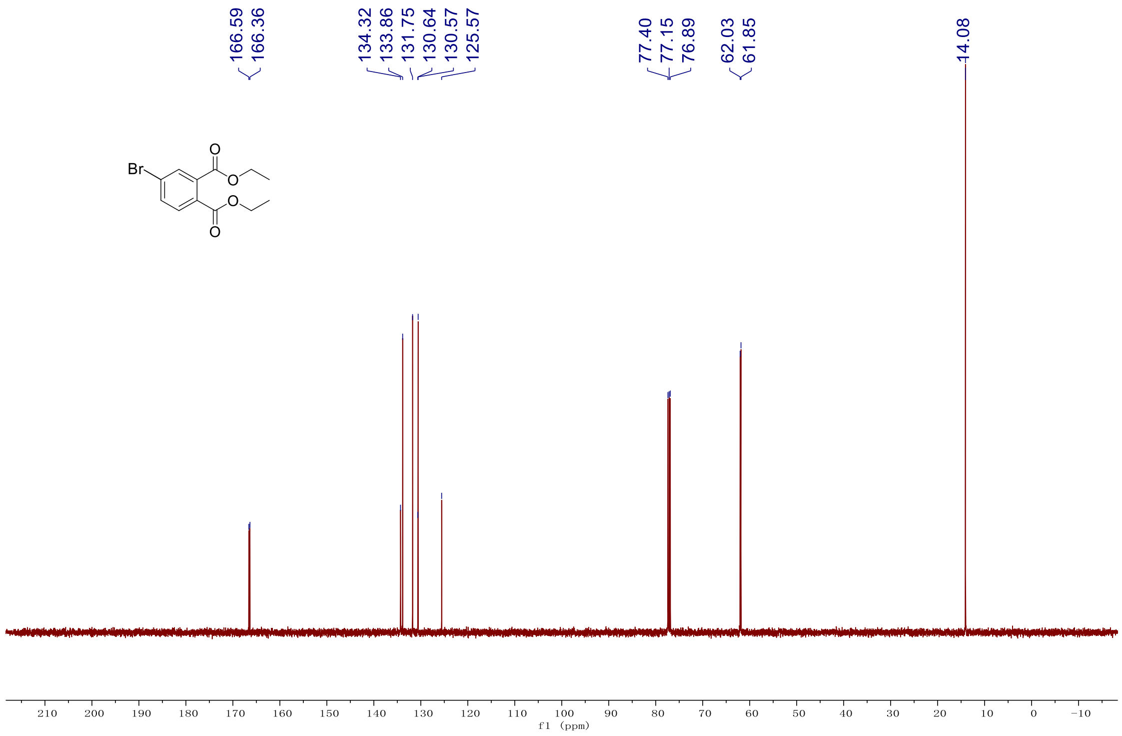


Fig. S11. ^{13}C NMR spectrum of compound **3**.

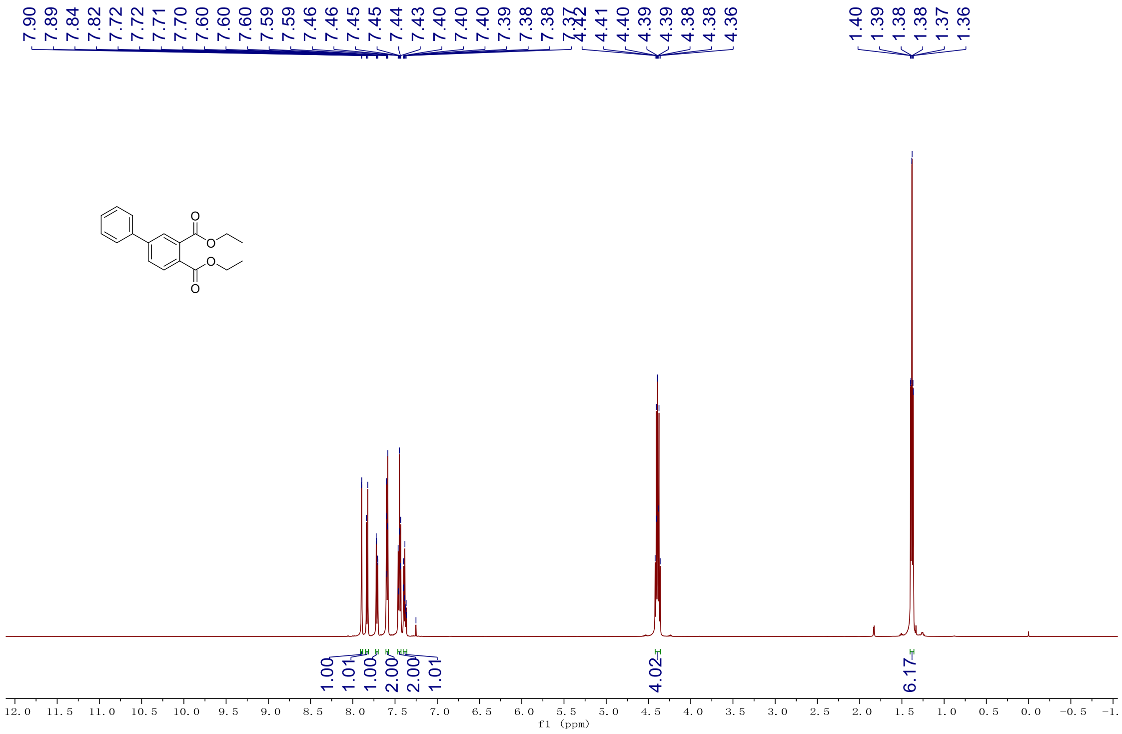


Fig. S12. ^{1}H NMR spectrum of compound **4a**.

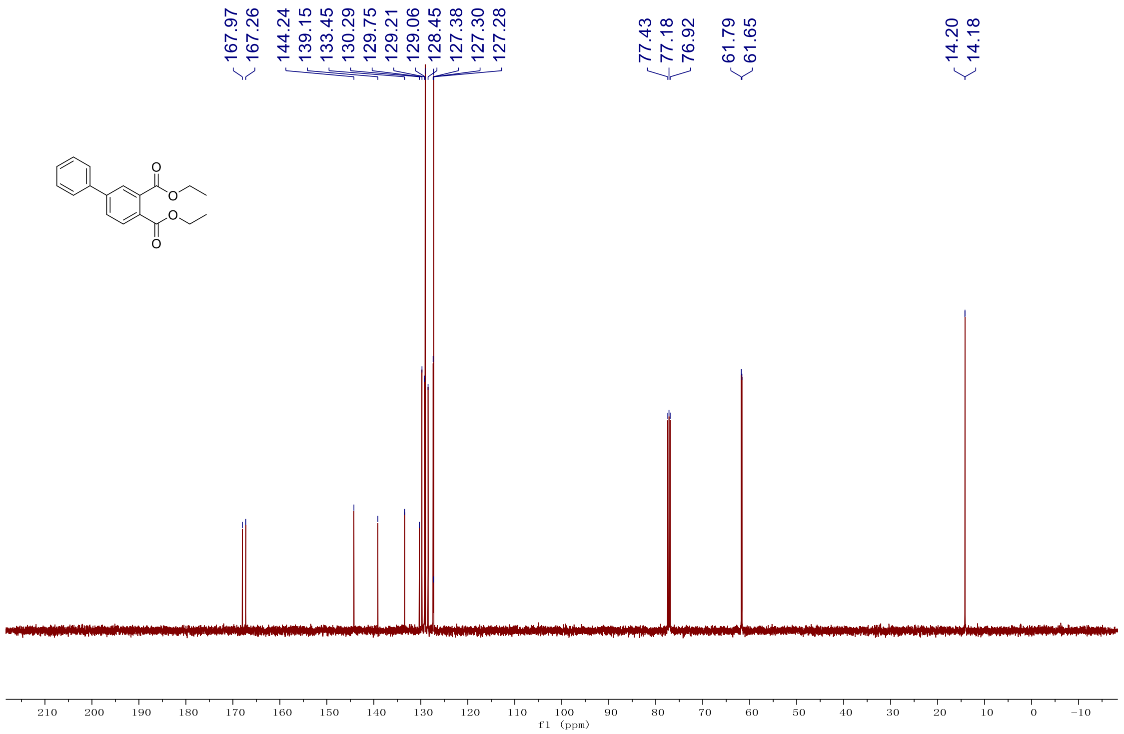


Fig. S13. ^{13}C NMR spectrum of compound **4a**.

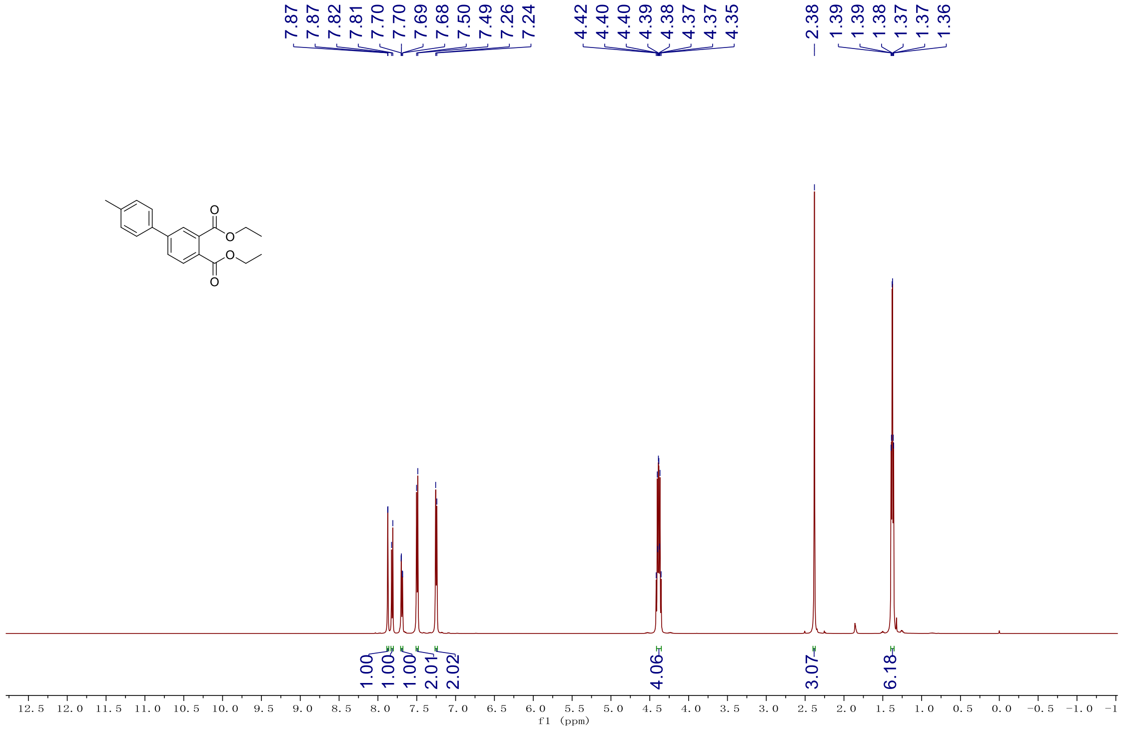


Fig. S14. ^{1}H NMR spectrum of compound **4b**.

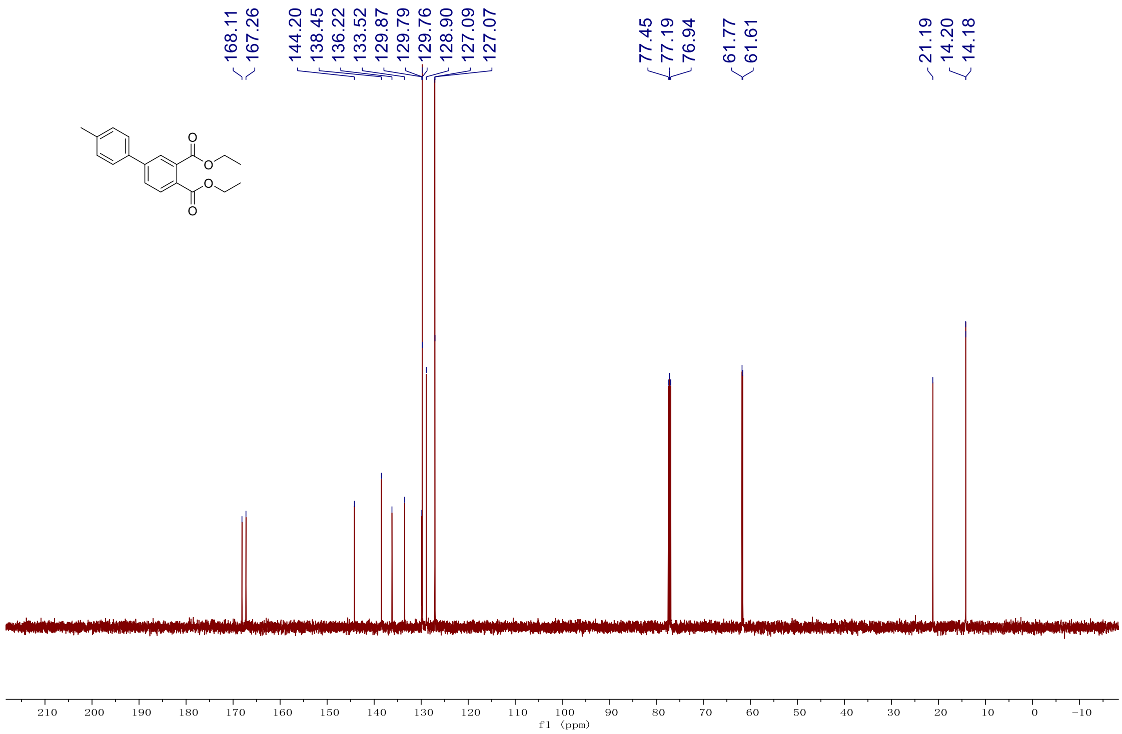


Fig. S15. ^{13}C NMR spectrum of compound **4b**.

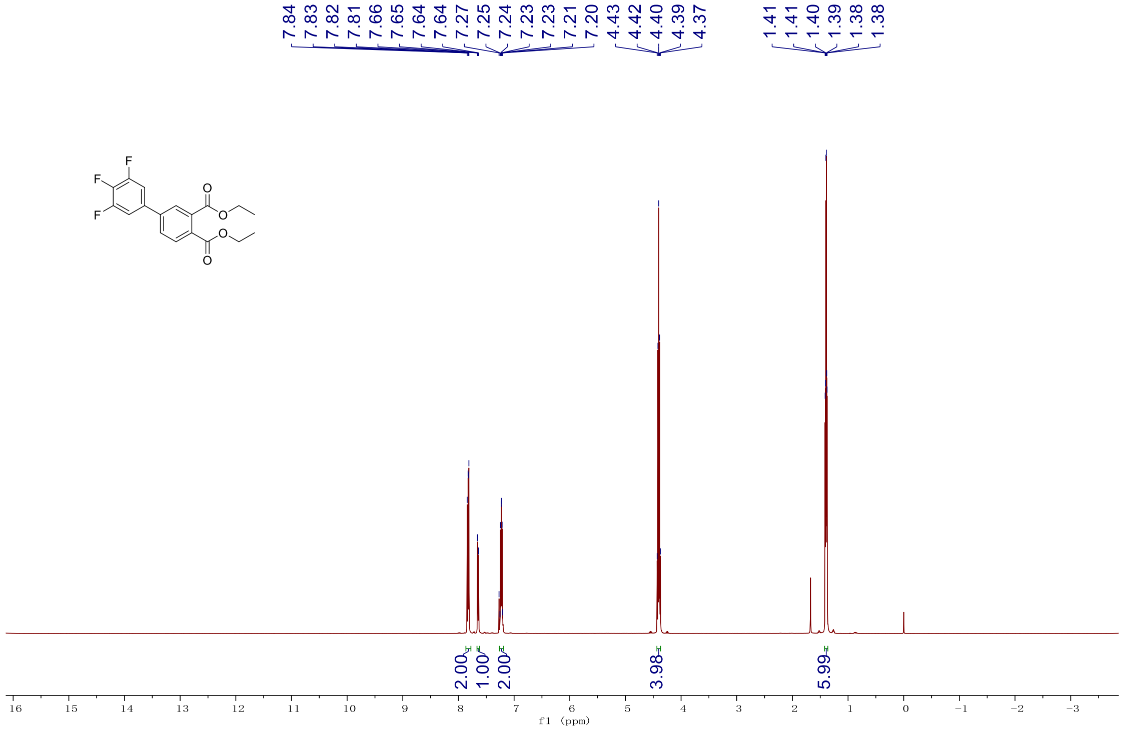


Fig. S16. ^{1}H NMR spectrum of compound **4c**.

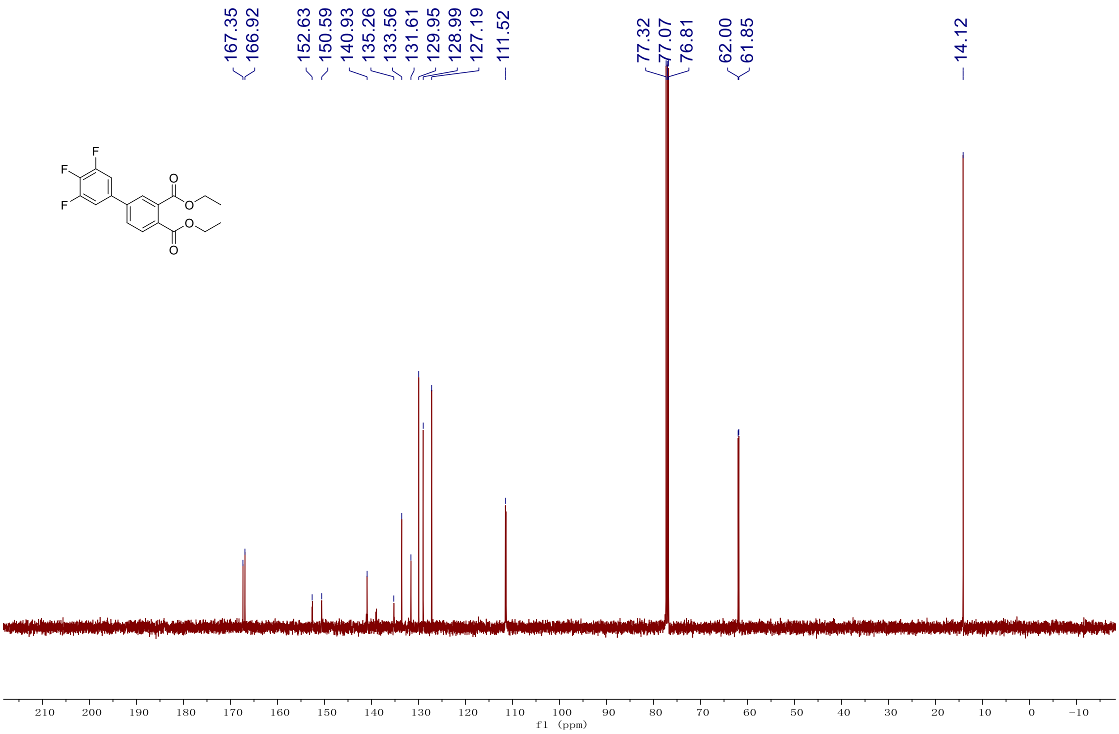


Fig. S17. ^{13}C NMR spectrum of compound **4c**.

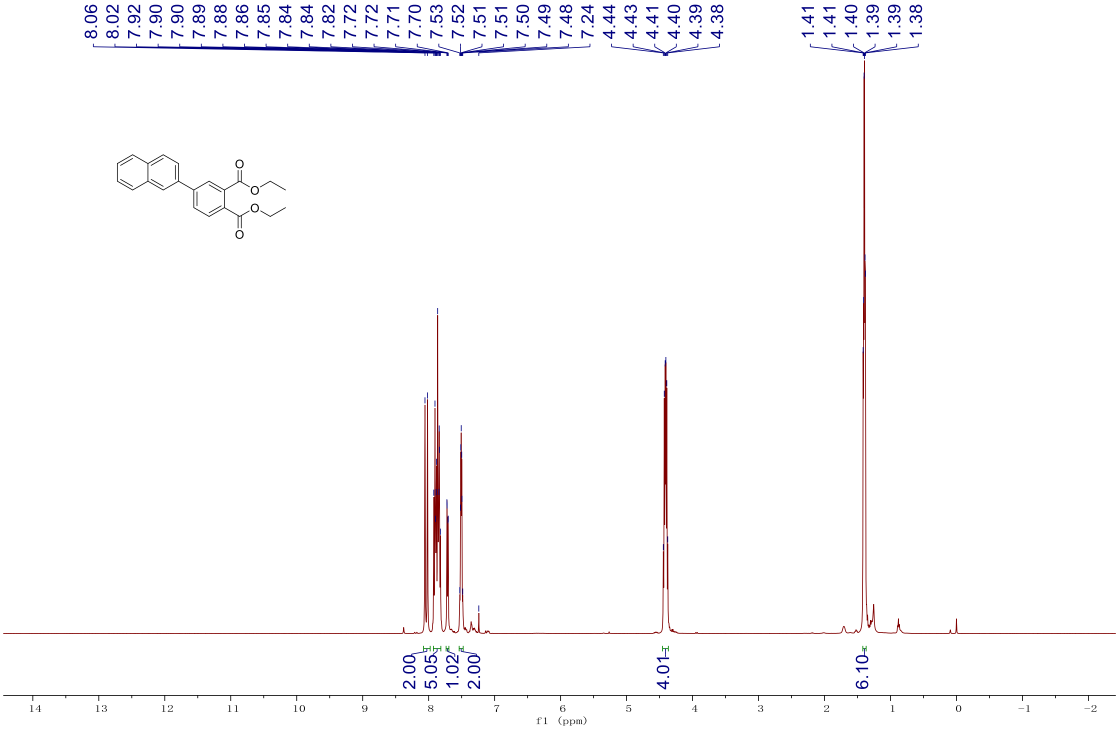


Fig. S18. ^{1}H NMR spectrum of compound **4d**.

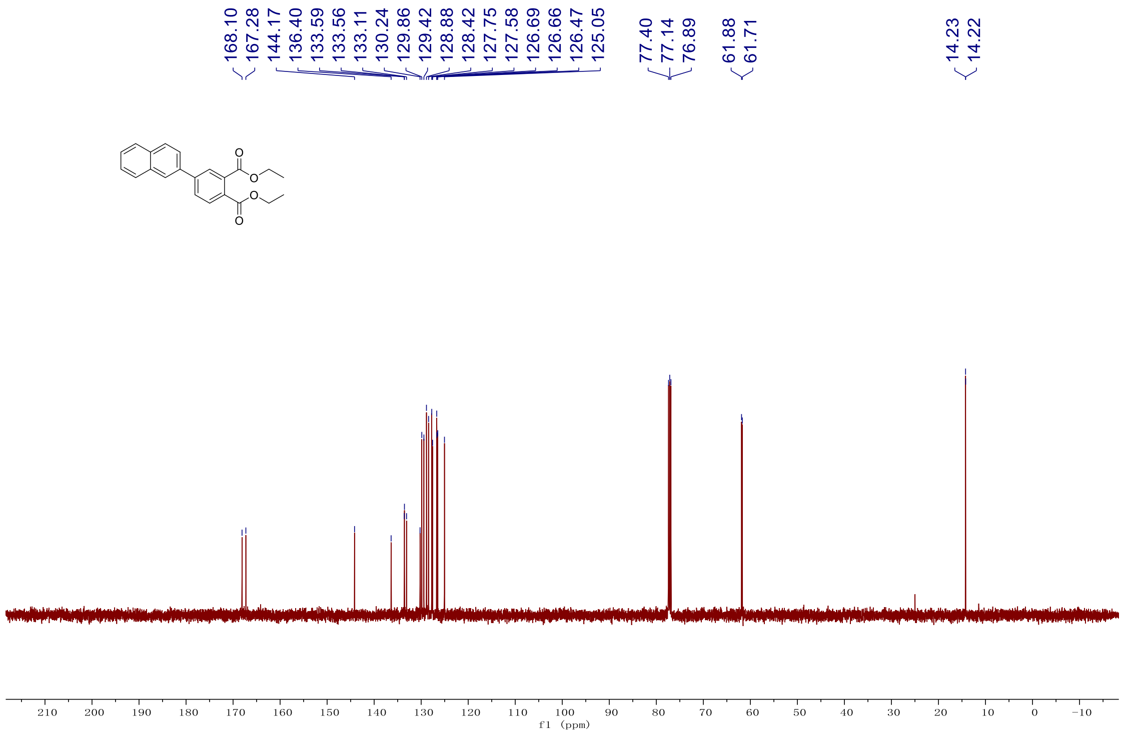


Fig. S19. ^{13}C NMR spectrum of compound **4d**.

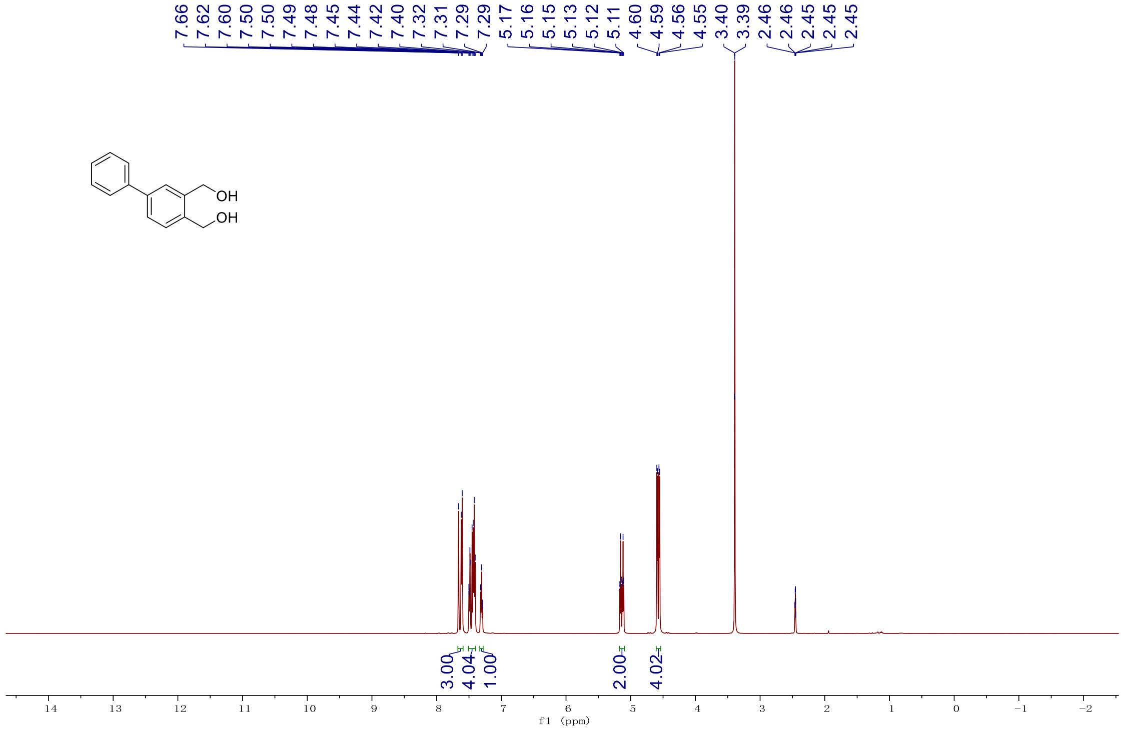


Fig. S20. ^{1}H NMR spectrum of compound **5a**.

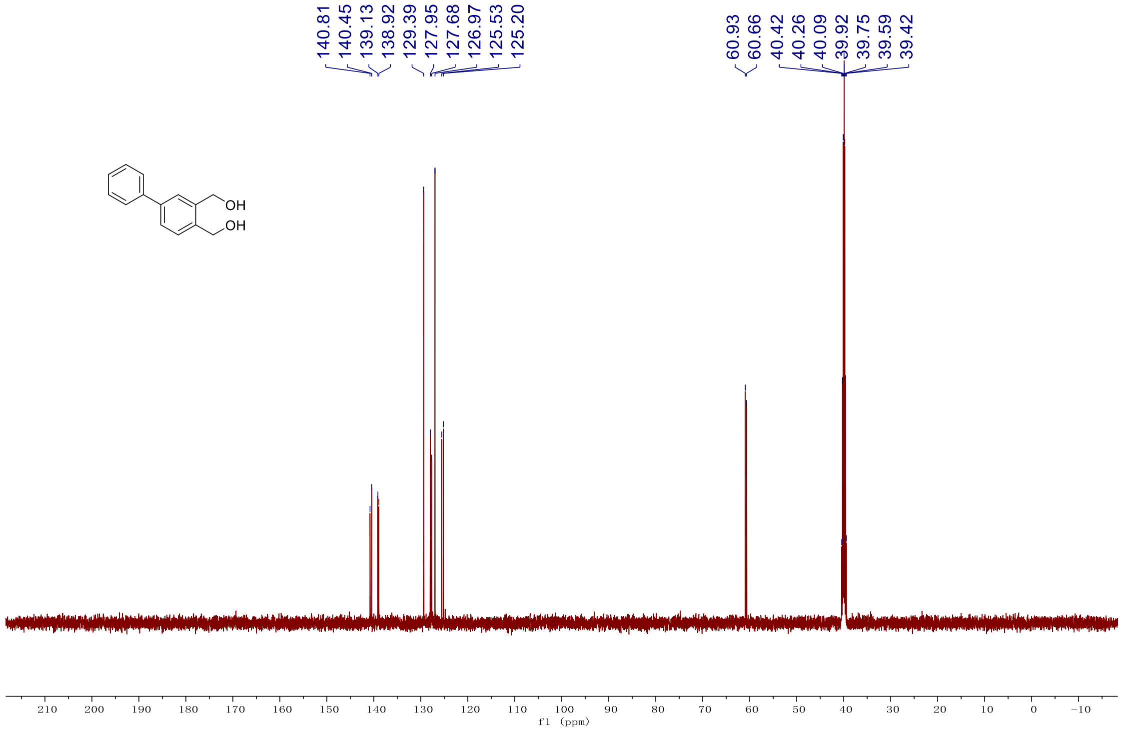


Fig. S21. ^{13}C NMR spectrum of compound **5a**.

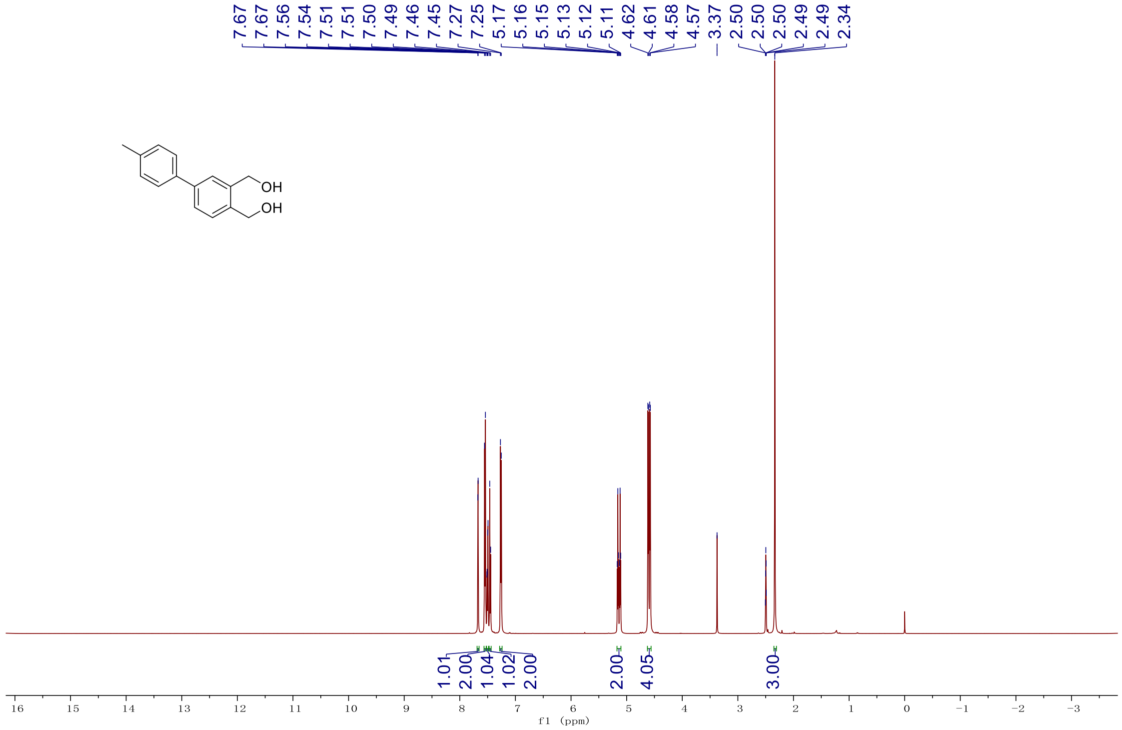


Fig. S22. ^{1}H NMR spectrum of compound **5b**.

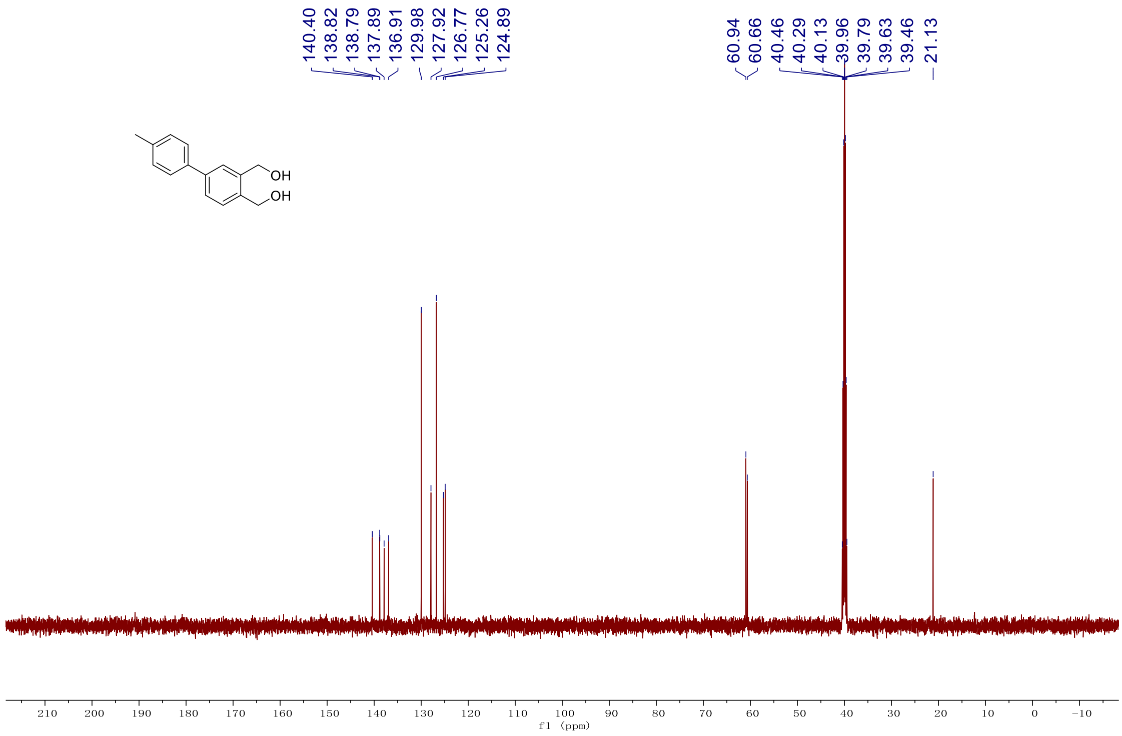


Fig. S23. ^{13}C NMR spectrum of compound **5b**.

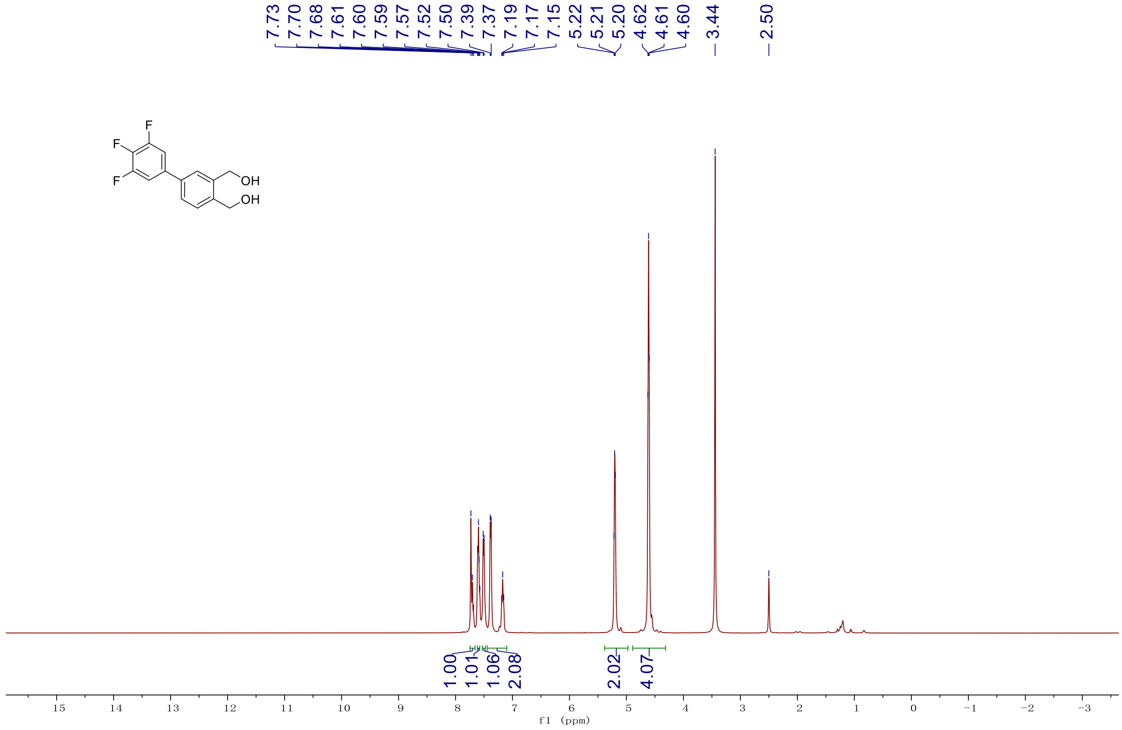


Fig. S24. ^{1}H NMR spectrum of compound **5c**.

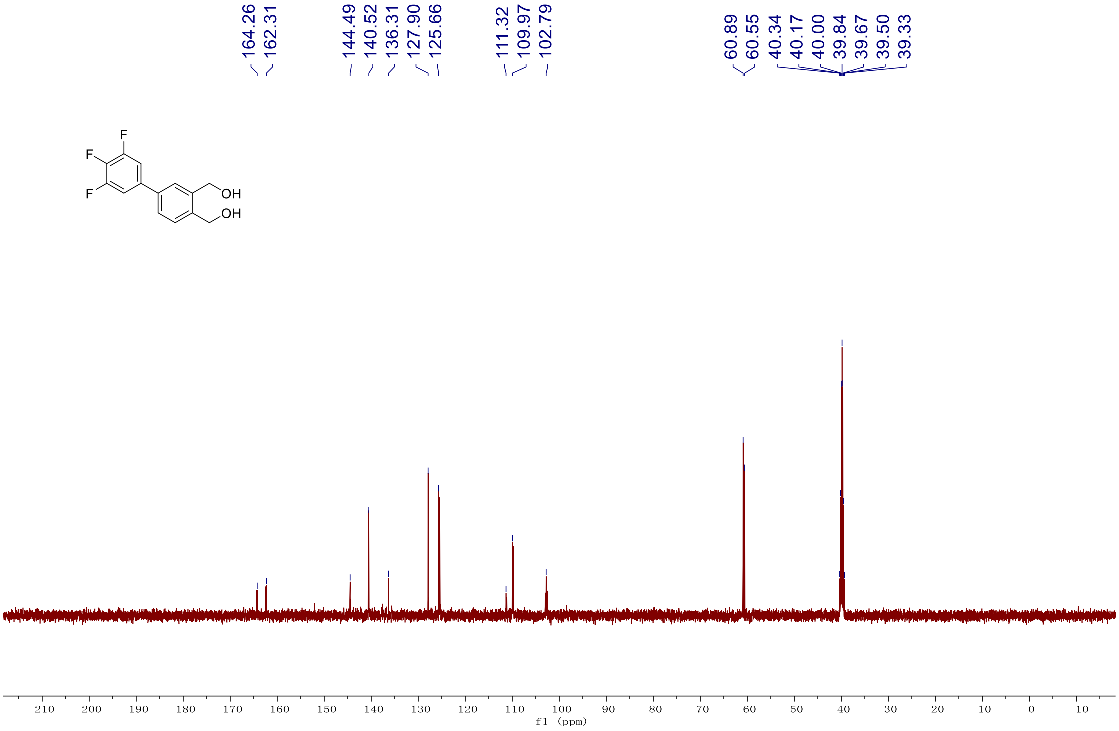


Fig. S25. ^{13}C NMR spectrum of compound **5c**.

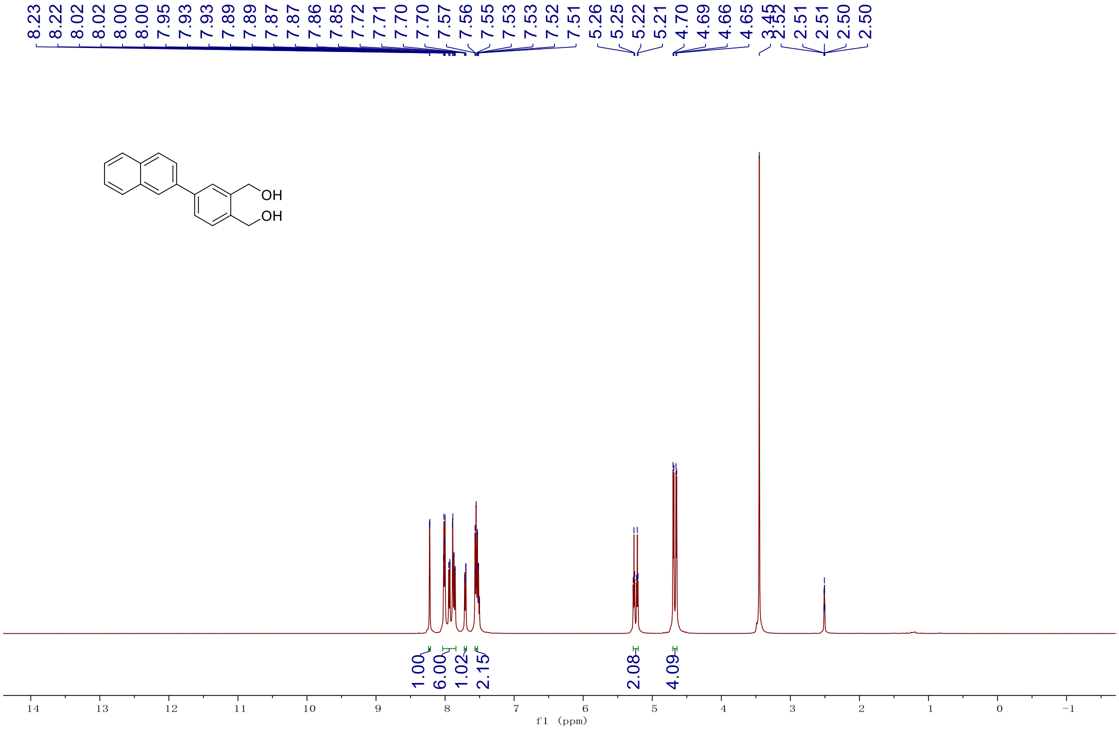


Fig. S26. ^{1}H NMR spectrum of compound **5d**.

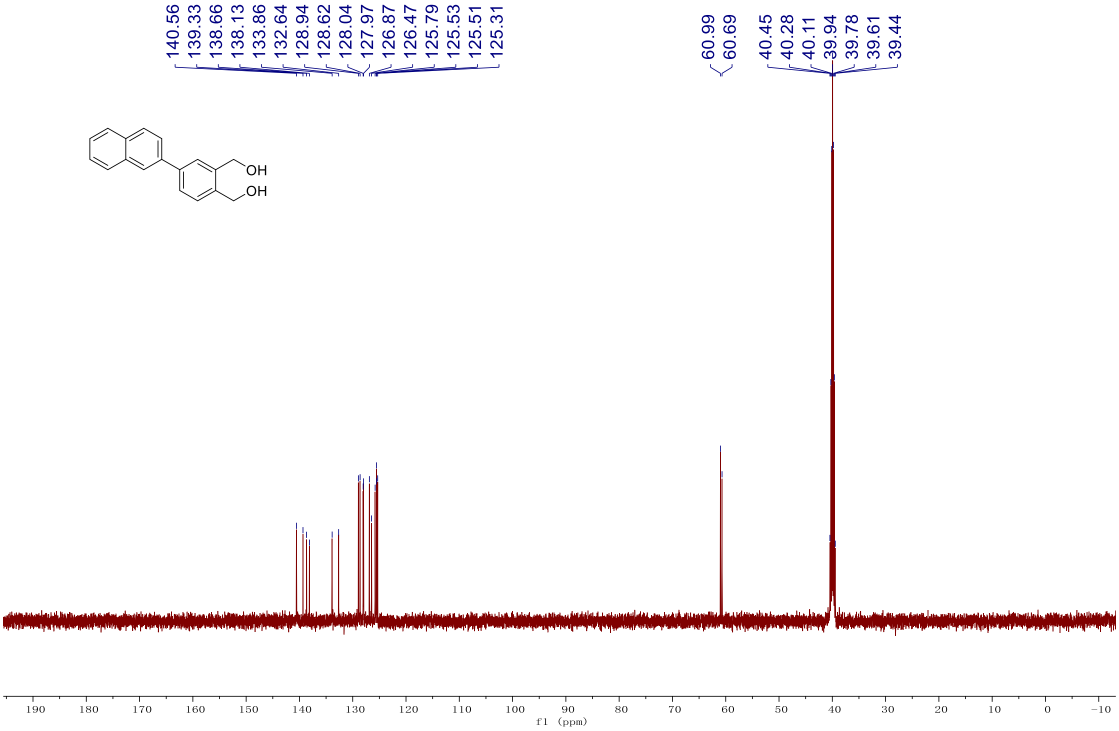


Fig. S27. ^{13}C NMR spectrum of compound **5d**.

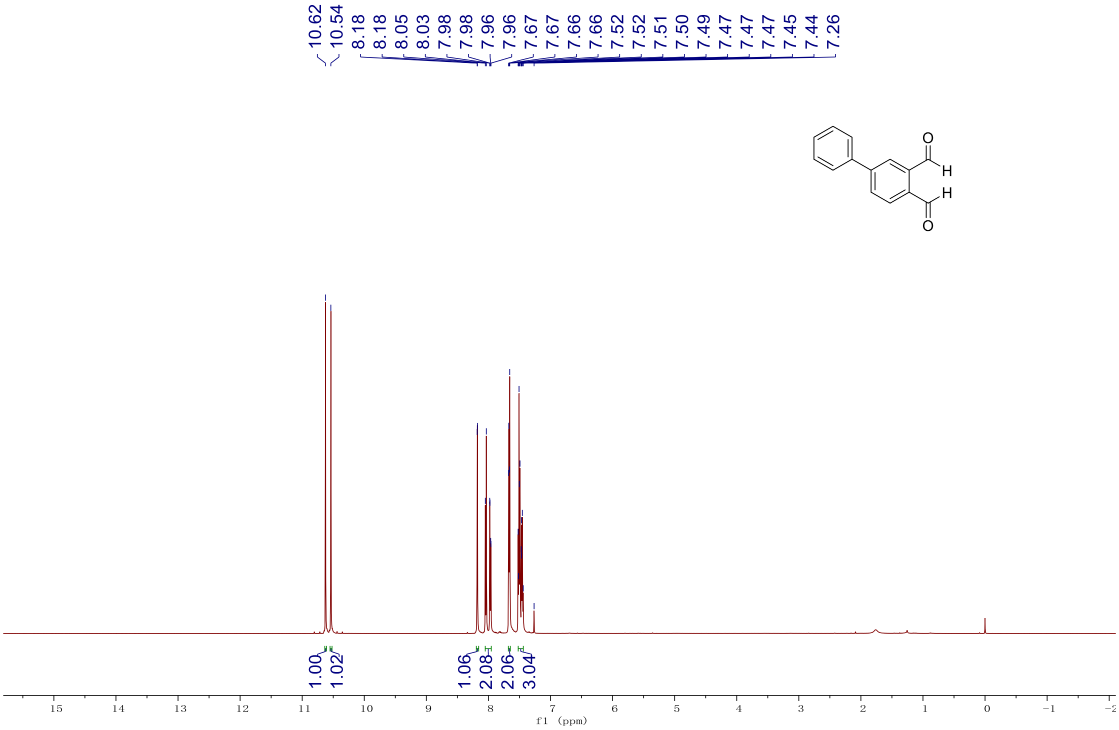


Fig. S28. ^{1}H NMR spectrum of compound **6a**.

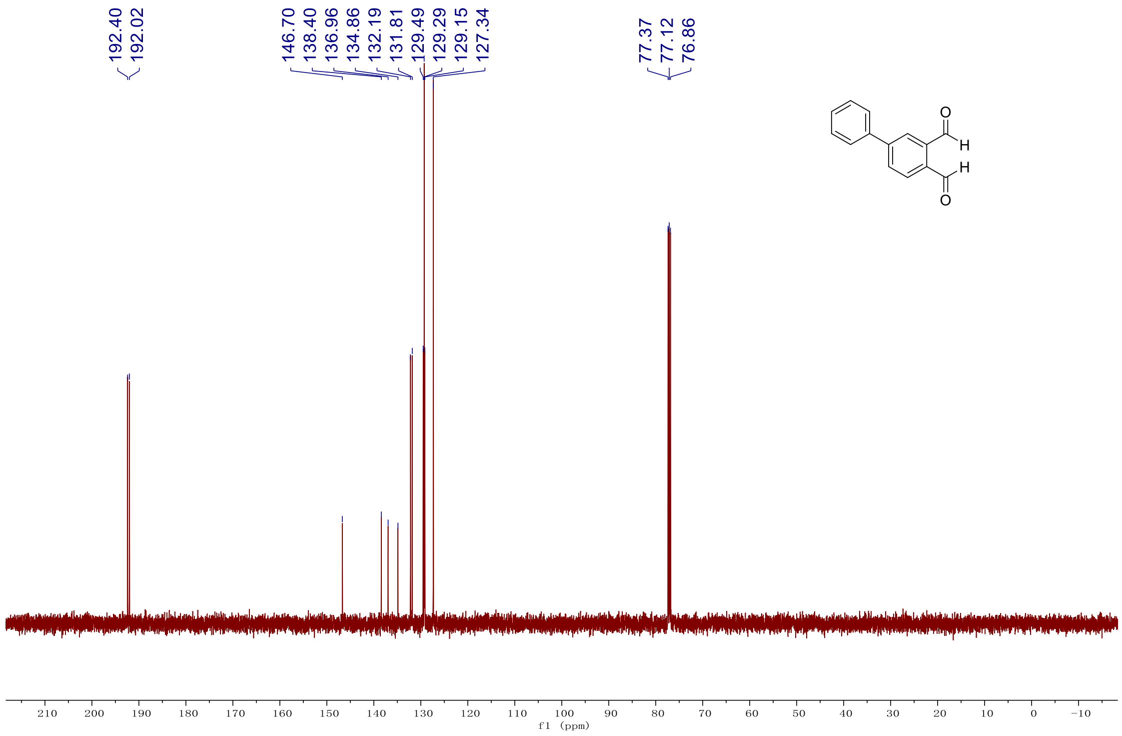


Fig. S29. ^{13}C NMR spectrum of compound **6a**.

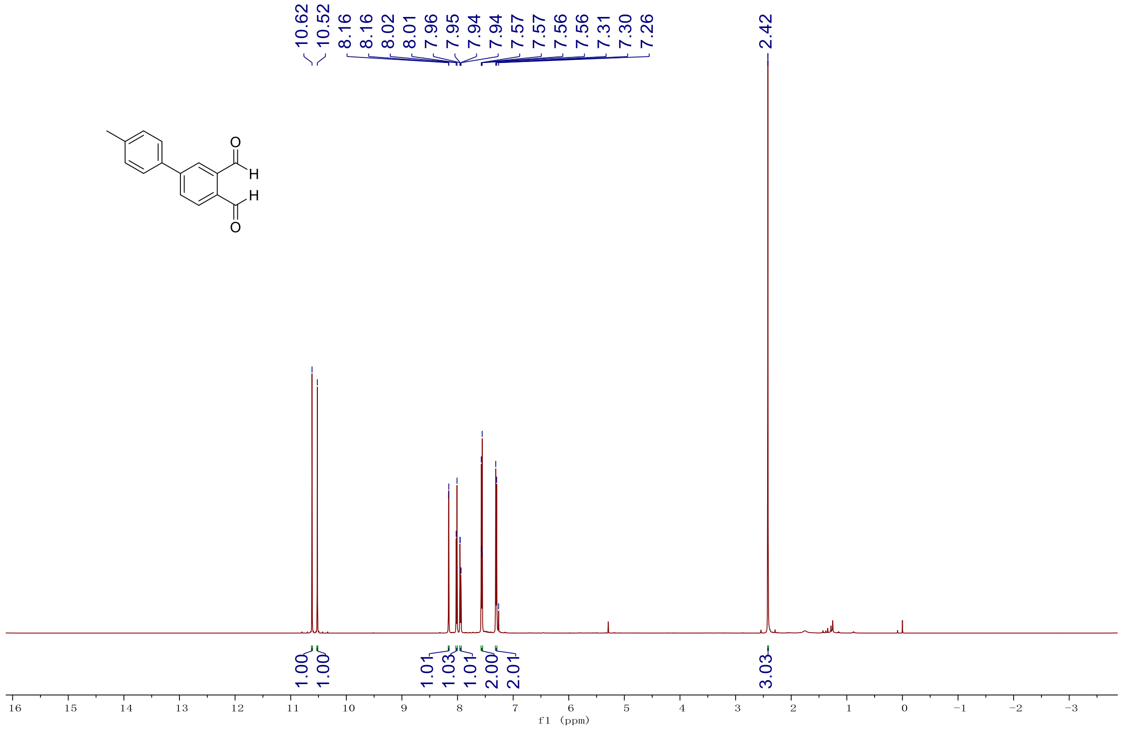


Fig. S30. ^{1}H NMR spectrum of compound **6b**.

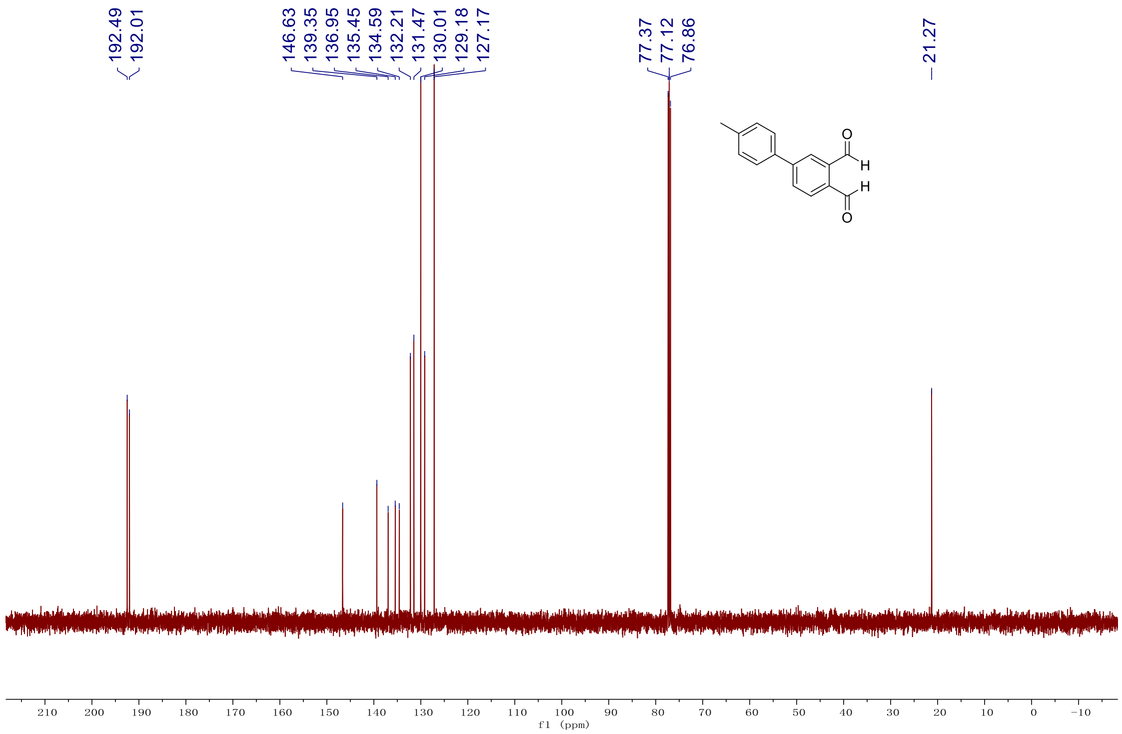


Fig. S31. ^{13}C NMR spectrum of compound **6b**.

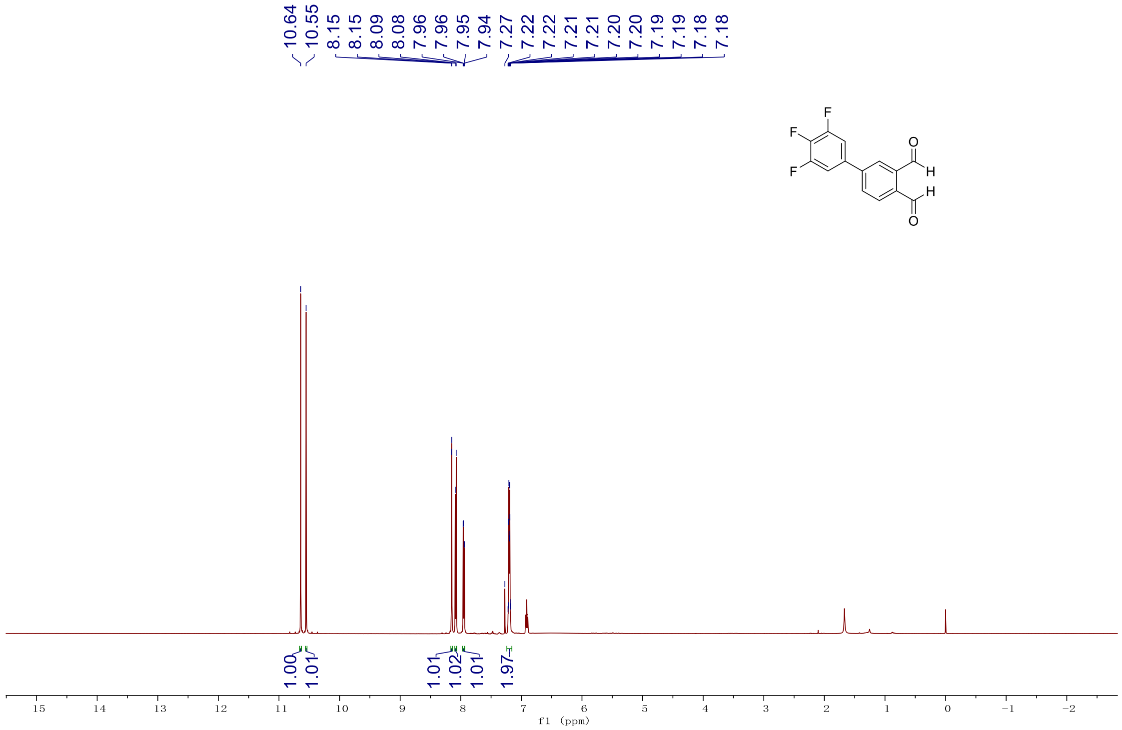


Fig. S32. ^{1}H NMR spectrum of compound **6c**.

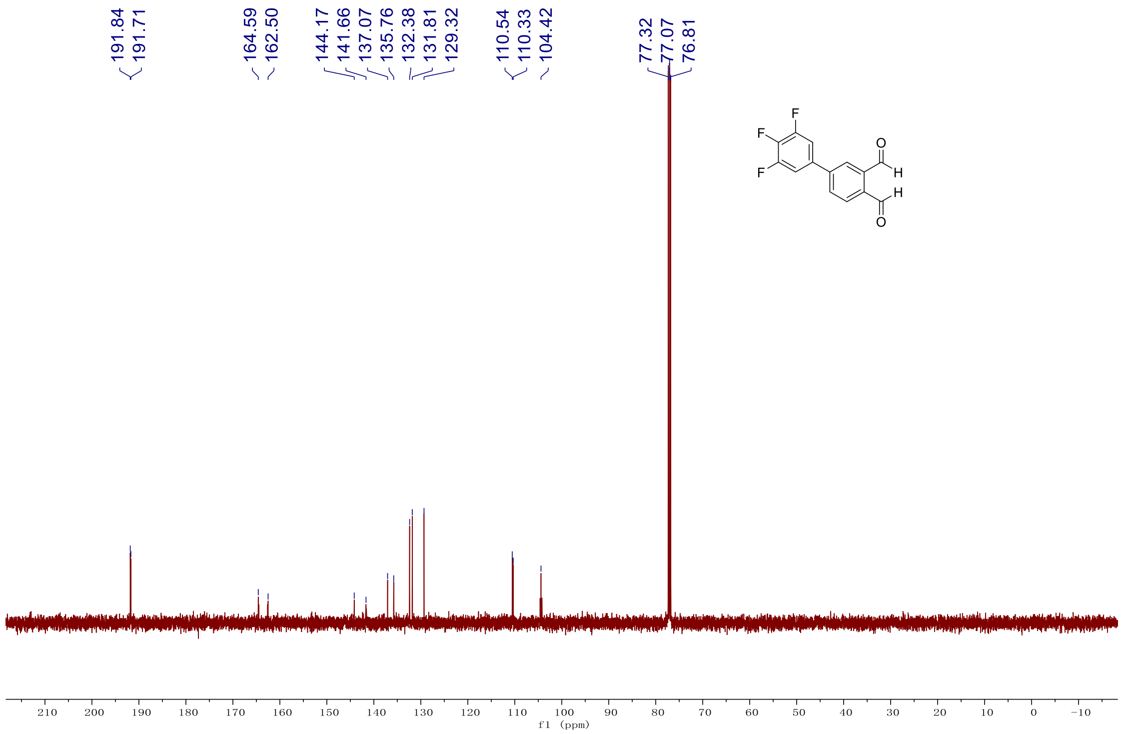


Fig. S33. ^{13}C NMR spectrum of compound **6c**.

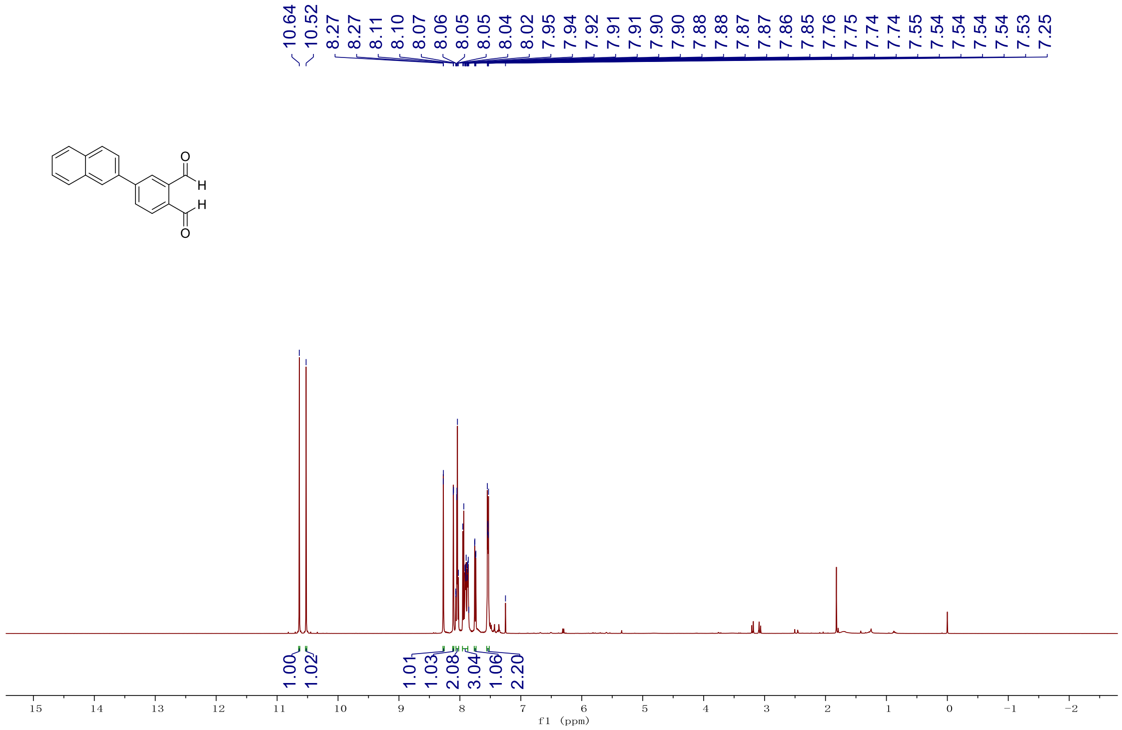


Fig. S34. ^{1}H NMR spectrum of compound **6d**.

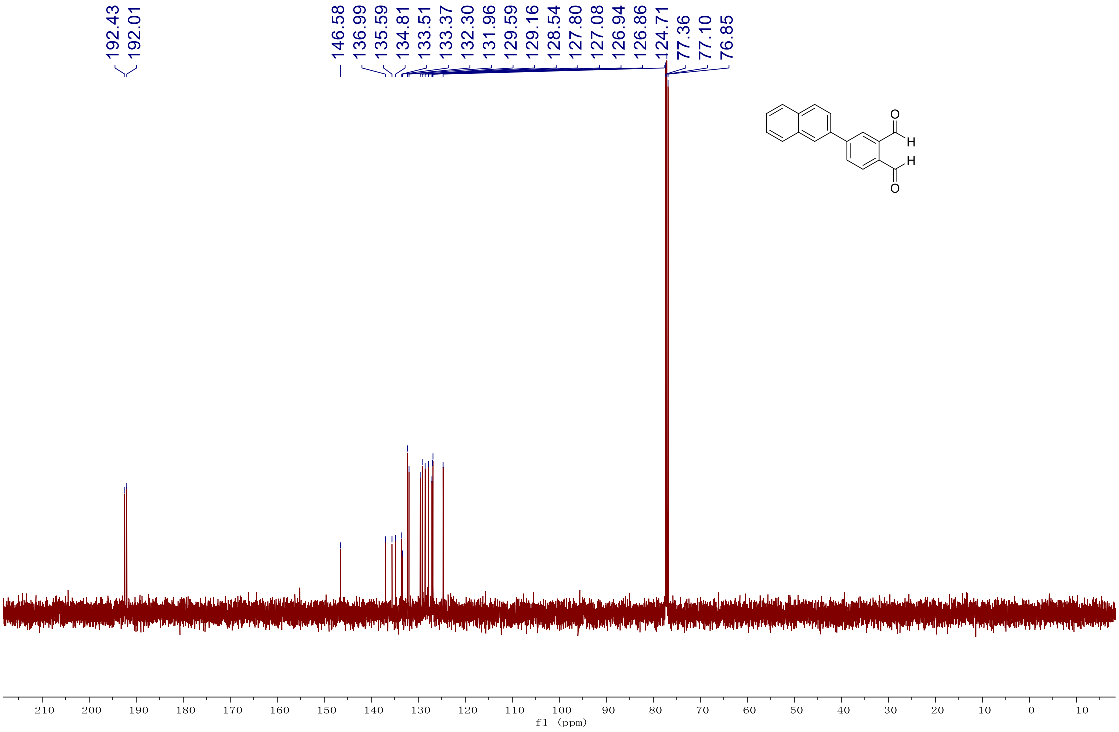


Fig. S35. ^{13}C NMR spectrum of compound **6d**.

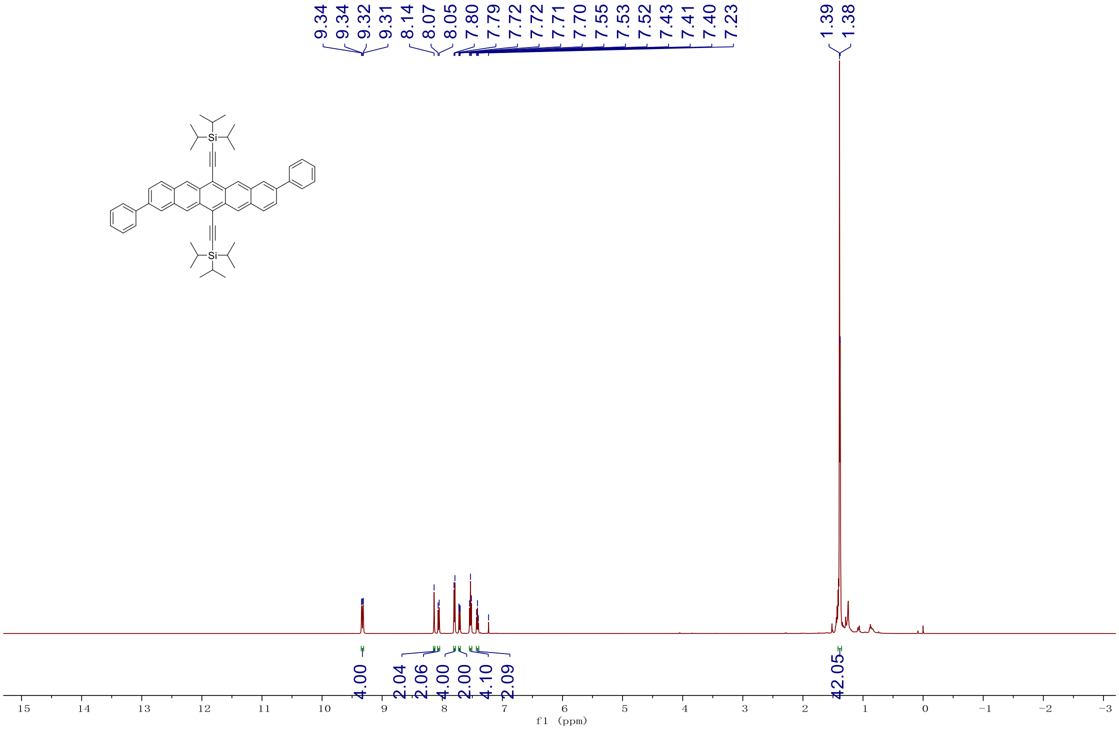


Fig. S36. ^{1}H NMR spectrum of compound **1a**.

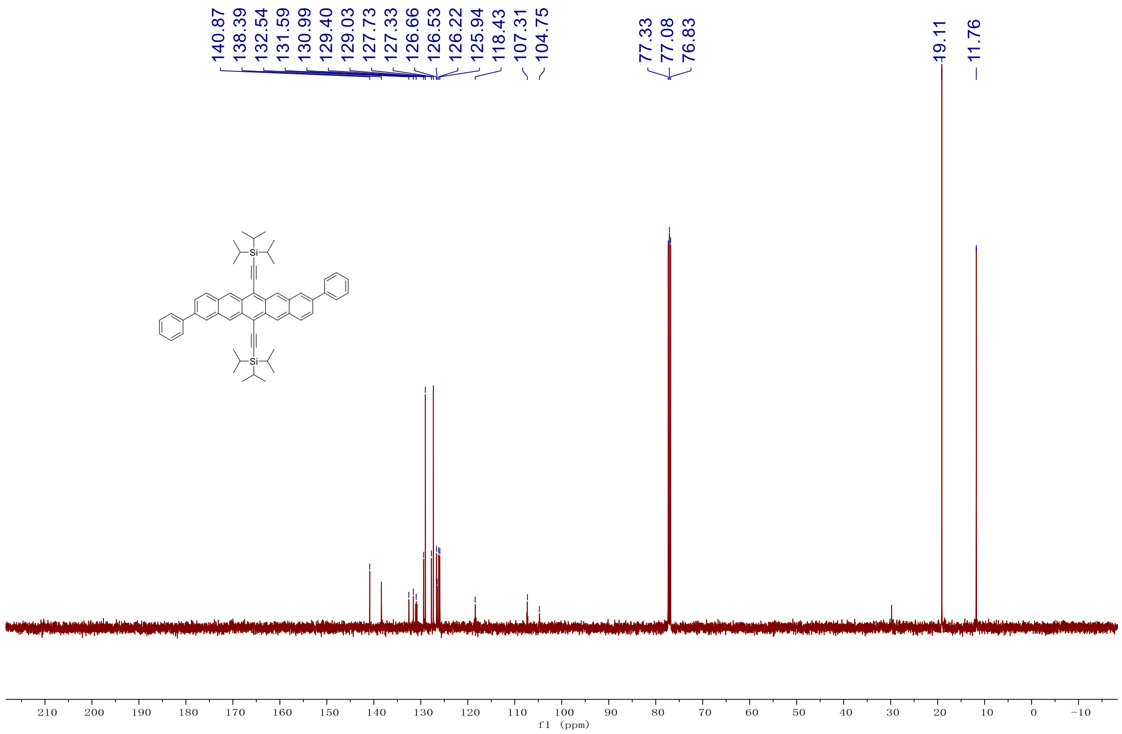


Fig. S37. ^{13}C NMR spectrum of compound **1a**.

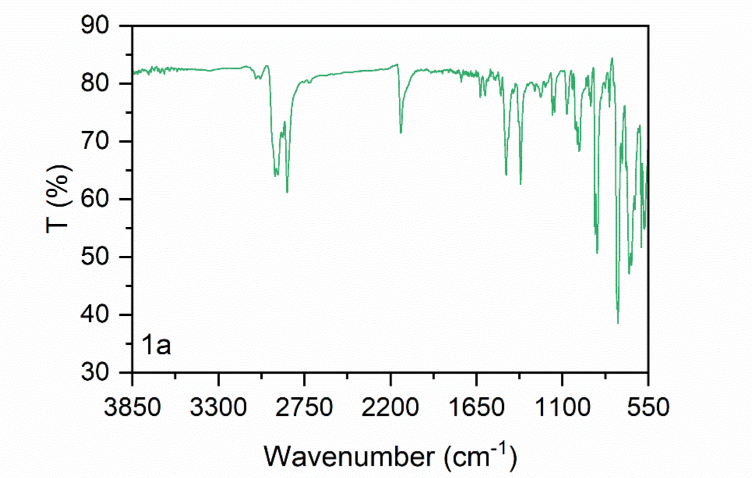


Fig. S38. FTIR spectrum of compound **1a**.

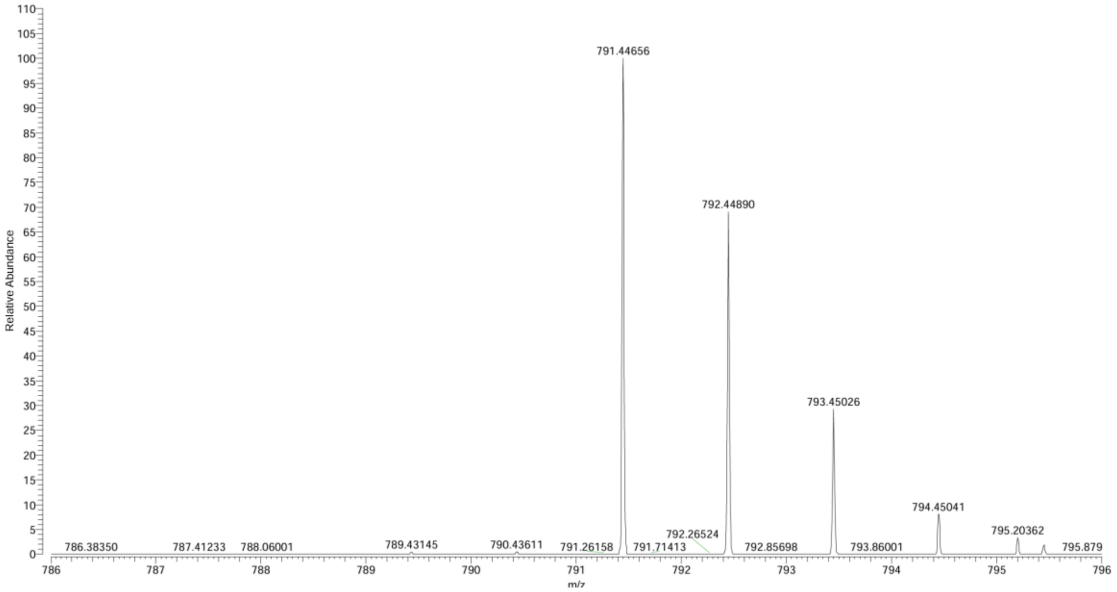


Fig. S39. HRMS (APCI) of compound **1a**.

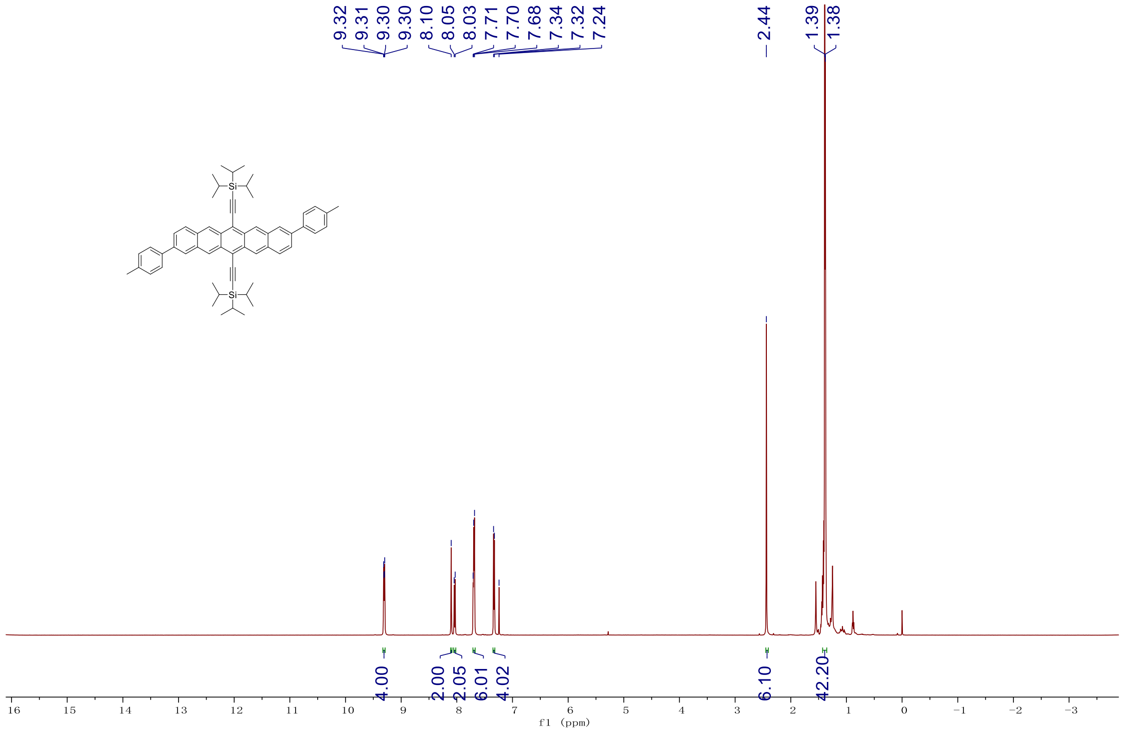


Fig. S40. ^{1}H NMR spectrum of compound **1b**.

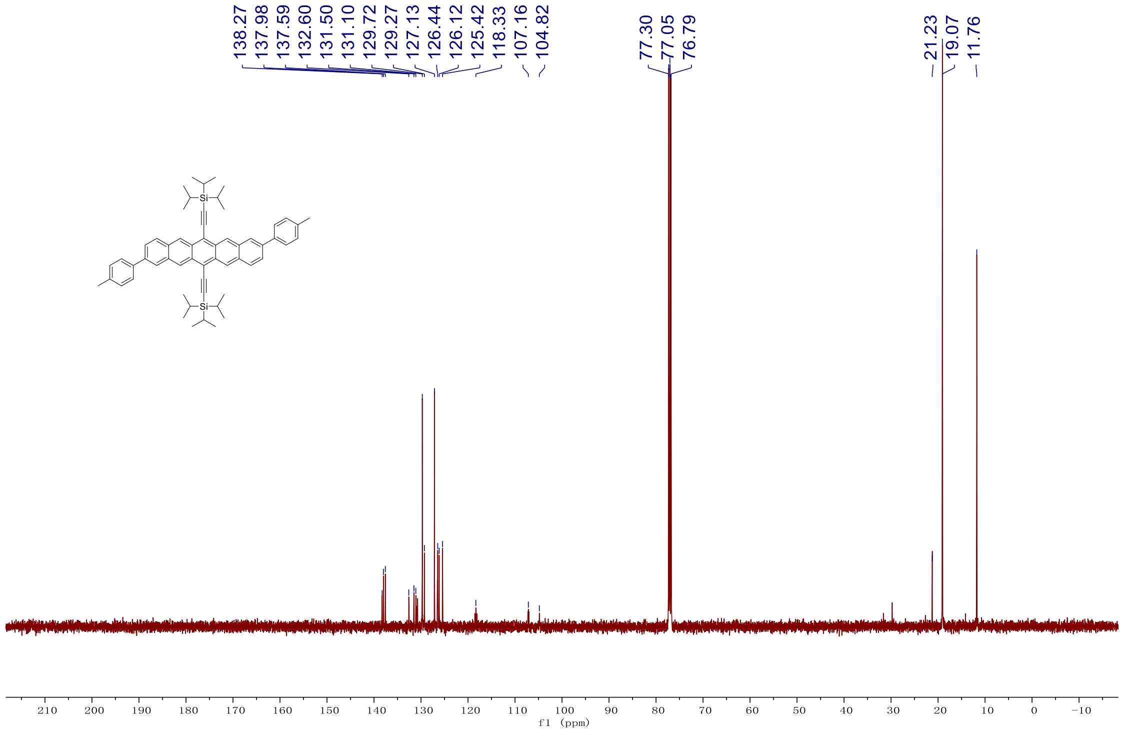


Fig. S41. ^{13}C NMR spectrum of compound **1b**.

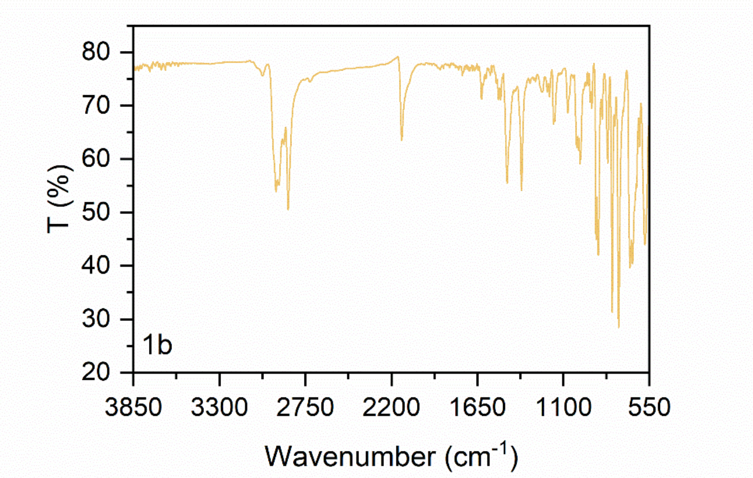


Fig. S42. FTIR spectrum of compound **1b**.

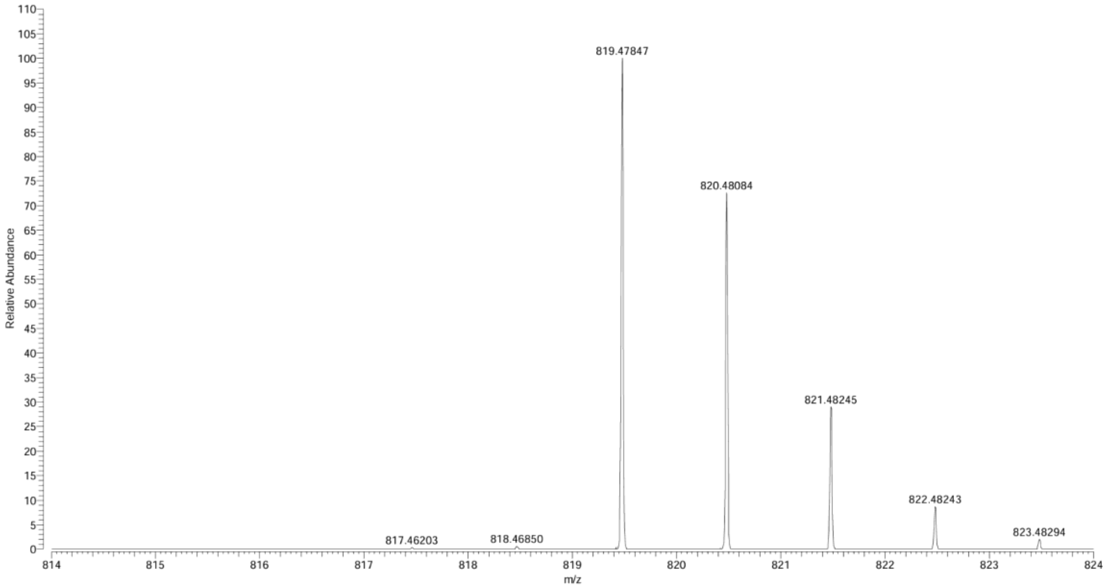


Fig. S43. HRMS (APCI) of compound **1b**.

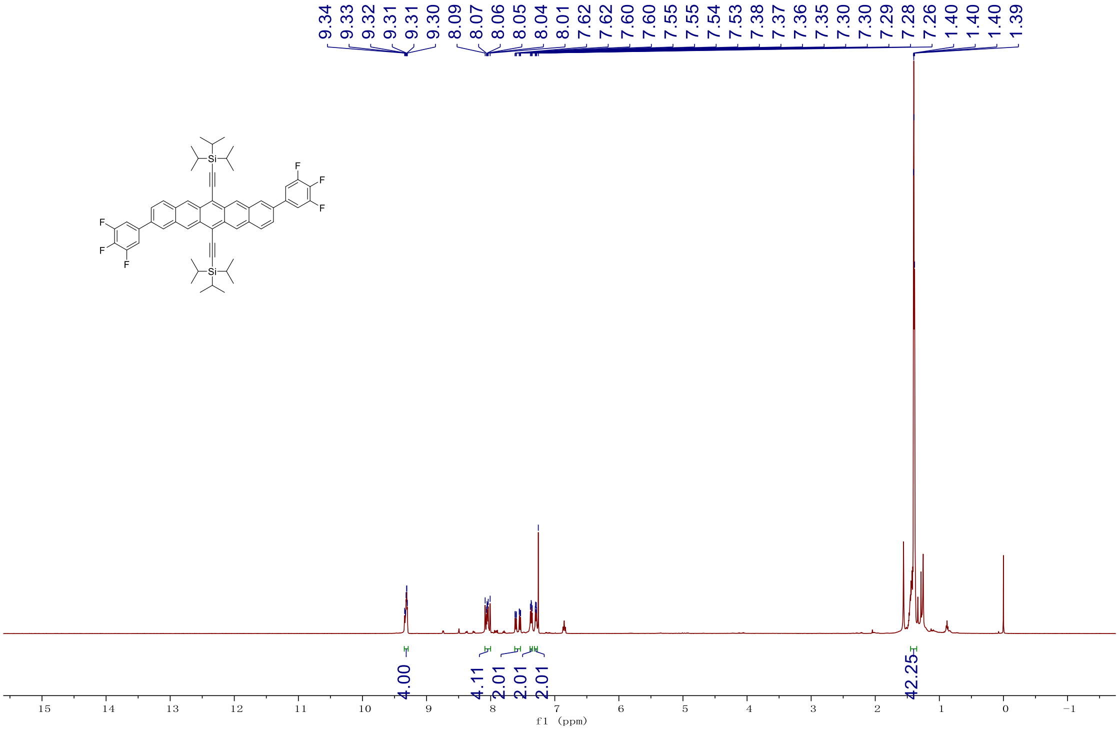


Fig. S44. ^{1}H NMR spectrum of compound **1c**.

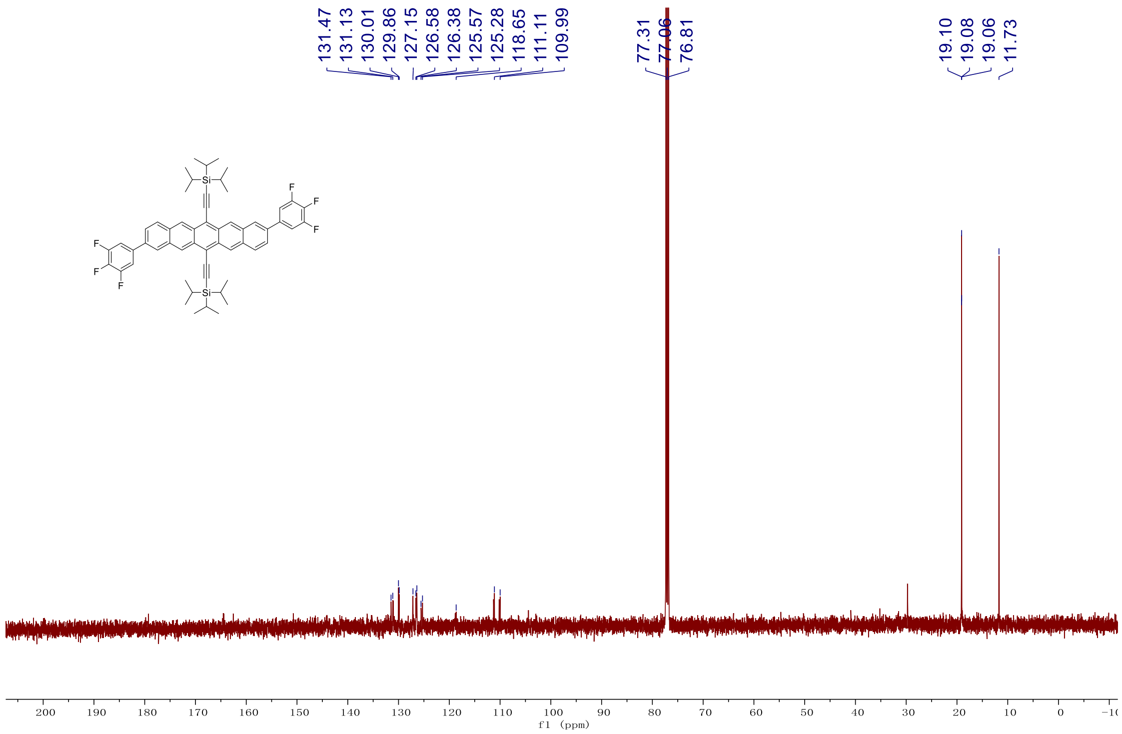


Fig. S45. ^{13}C NMR spectrum of compound **1c**.

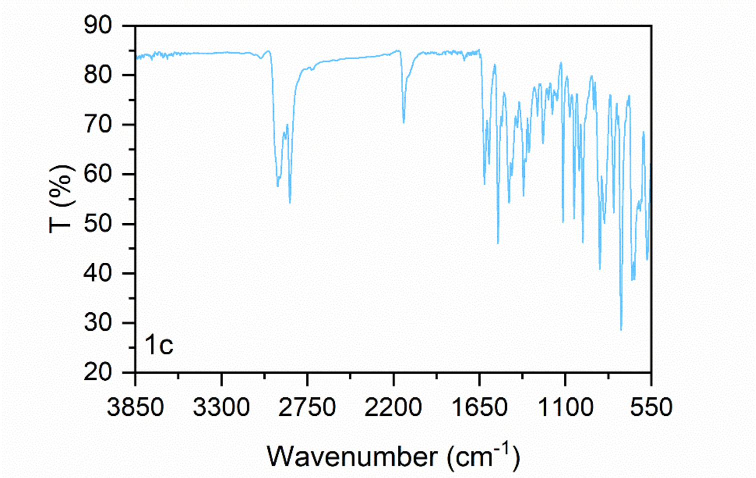


Fig. S46. FTIR spectrum of compound **1c**.

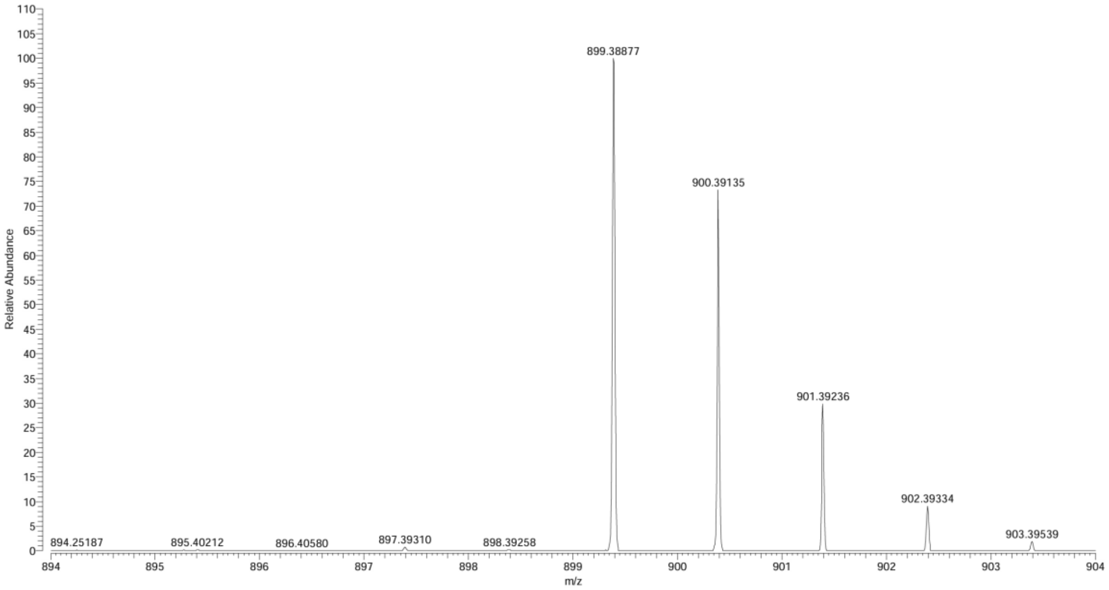


Fig. S47. HRMS (APCI) of compound **1c**.

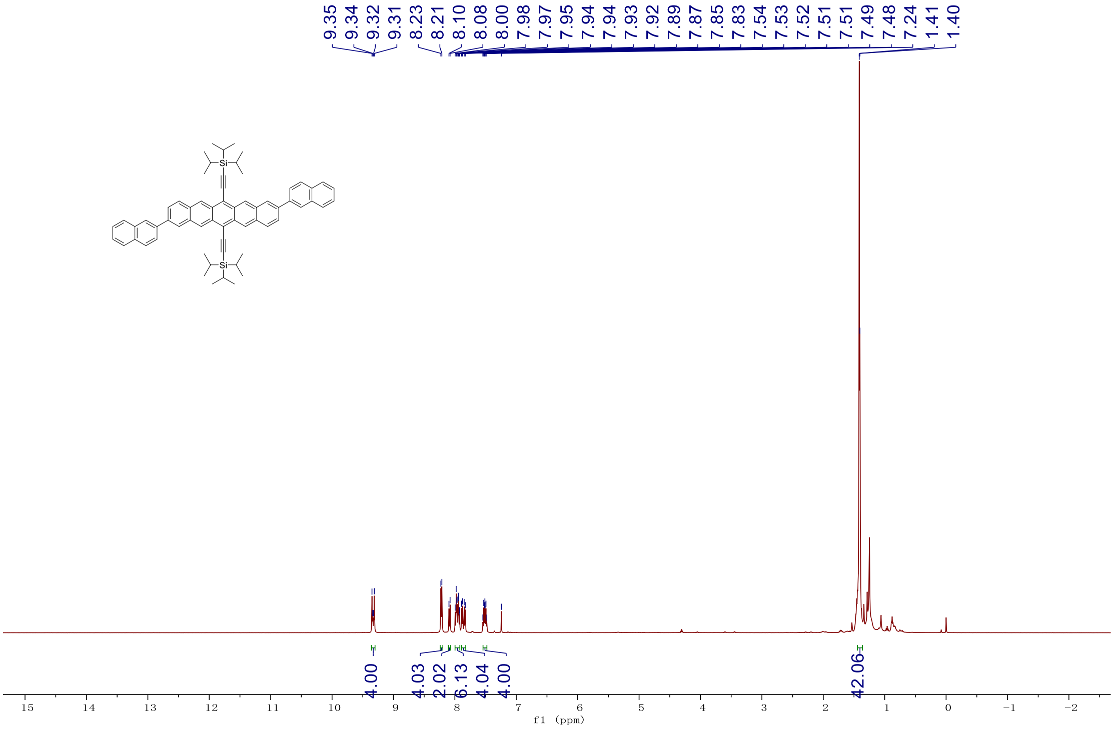


Fig. S48. ^{1}H NMR spectrum of compound **1d**.

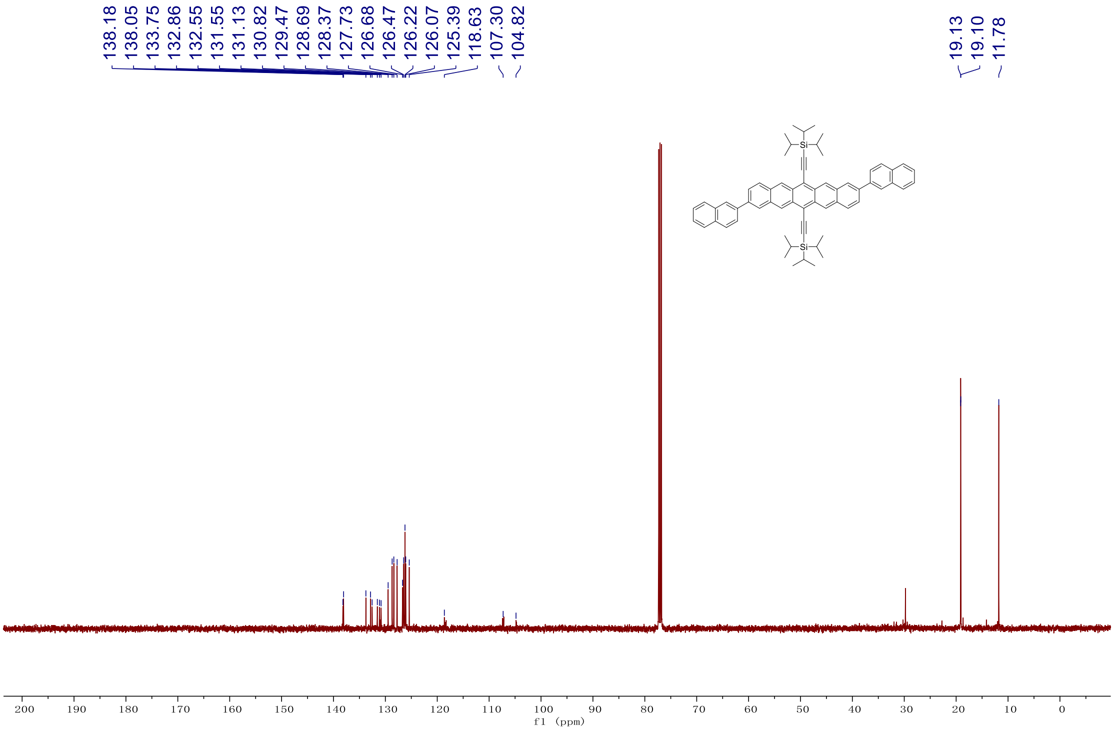


Fig. S49. ^{13}C NMR spectrum of compound **1d**.

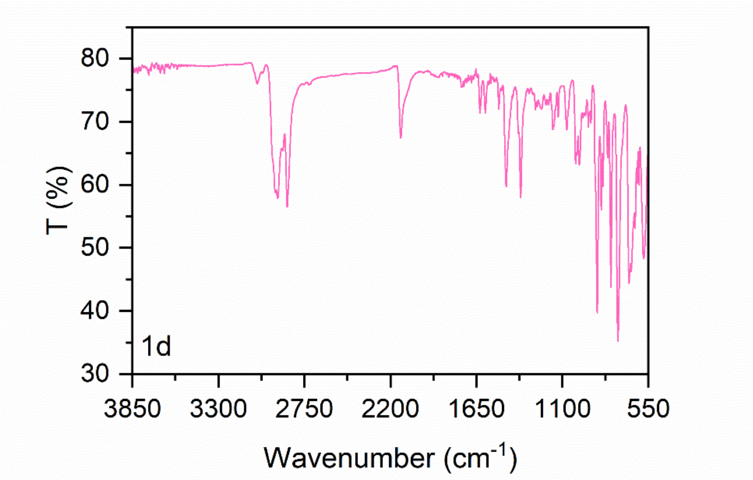


Fig. S50. FTIR spectrum of compound **1d**.

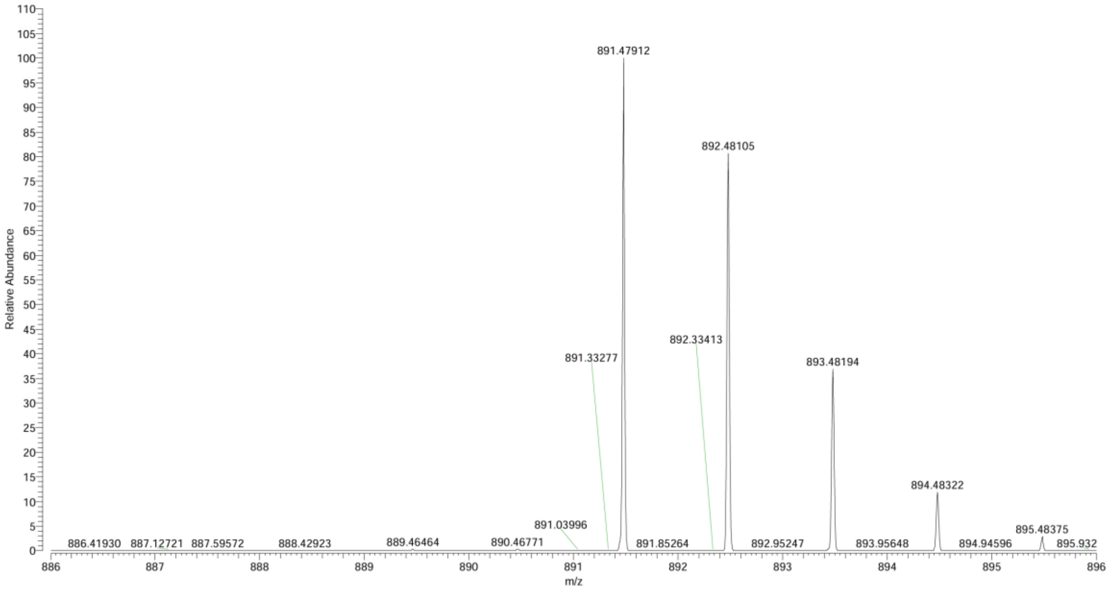


Fig. S51. HRMS (APCI) of compound **1d**.

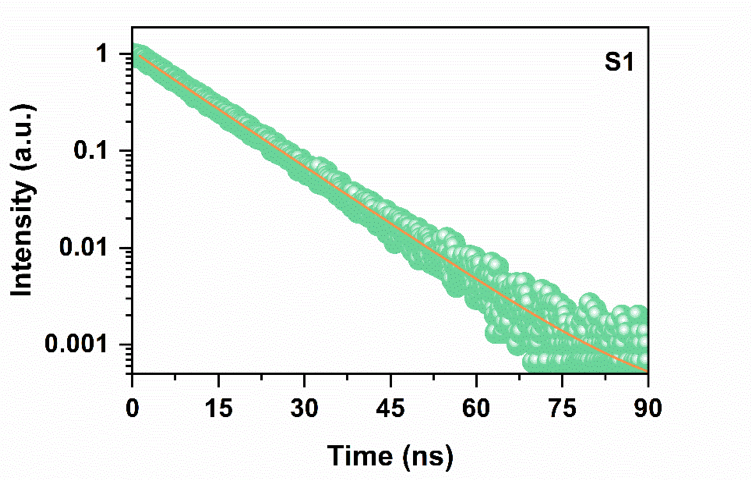


Fig. S52. Fluorescence decays of compound **S1** at 500nm.

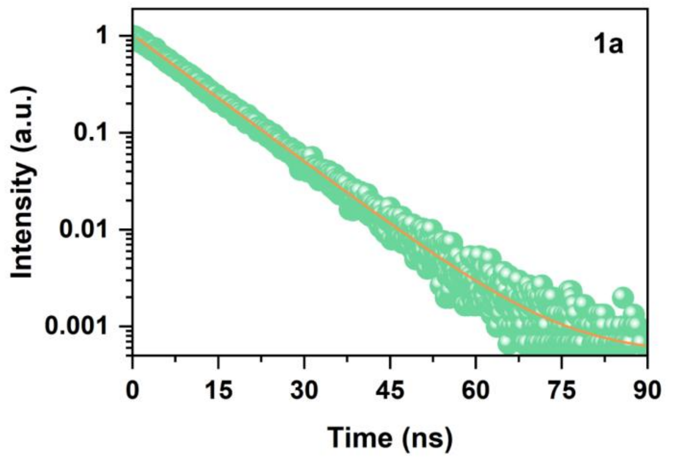


Fig. S53. Fluorescence decays of compound **1a** at 500nm.

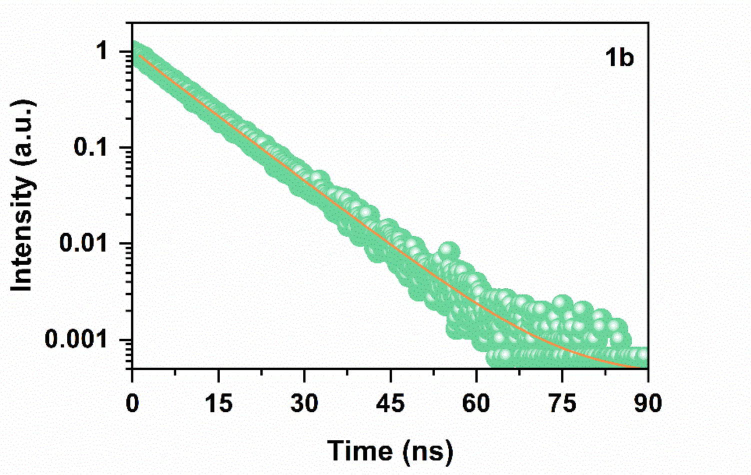


Fig. S54. Fluorescence decays of compound **1b** at 500nm.

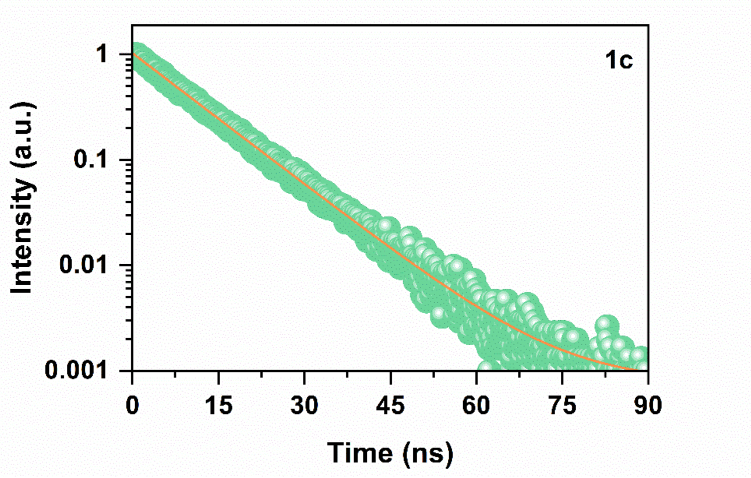


Fig. S55. Fluorescence decays of compound **1c** at 500nm.

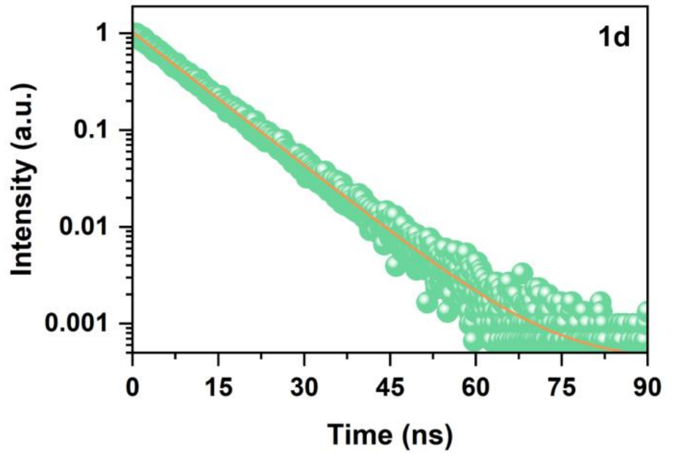


Fig. S56. Fluorescence decays of compound **1d** at 500nm.

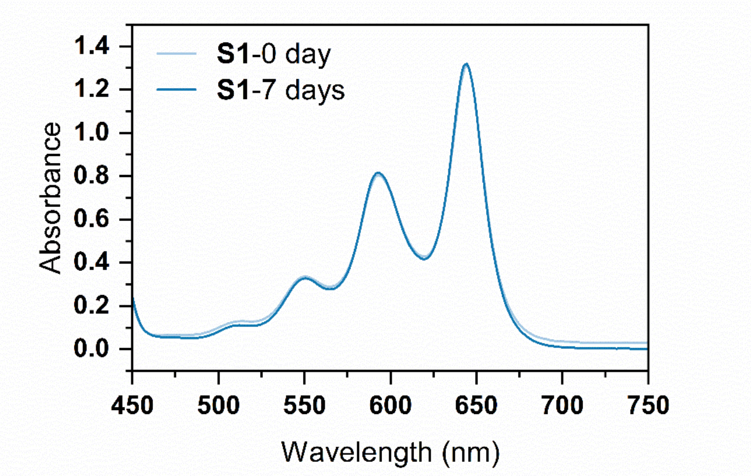


Fig. S57. UV-Vis absorption spectra of **S1**, freshly prepared and after 7 days respectively.

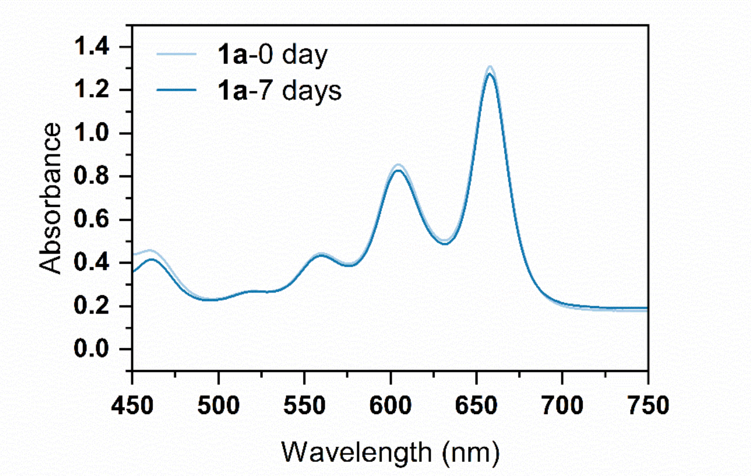


Fig. S58. UV-Vis absorption spectra of **1a**, freshly prepared and after 7 days respectively.

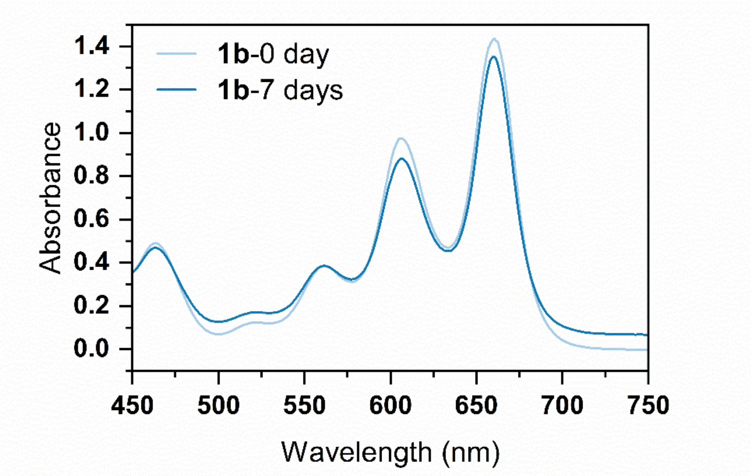


Fig. S59. UV-Vis absorption spectra of **1b**, freshly prepared and after 7 days respectively.

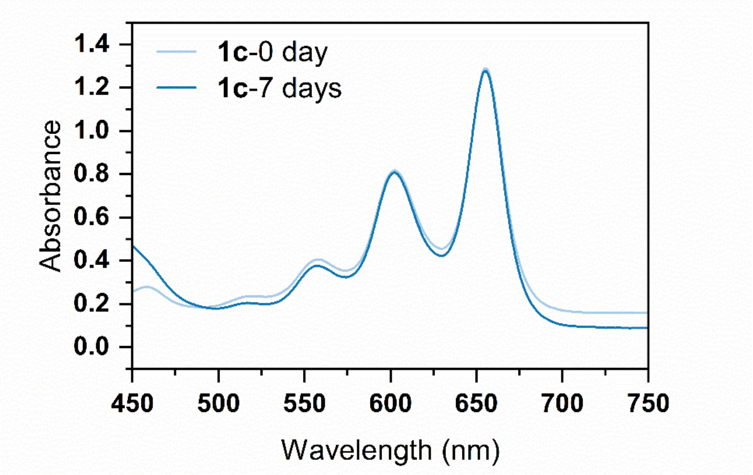


Fig. S60. UV-Vis absorption spectra of **1c**, freshly prepared and after 7 days respectively.

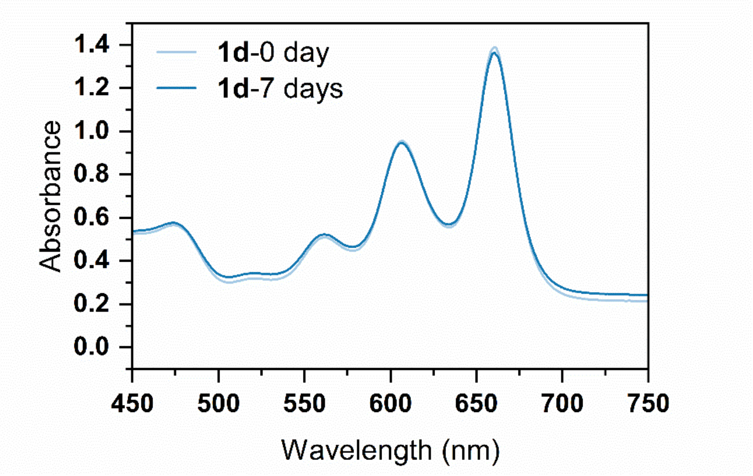
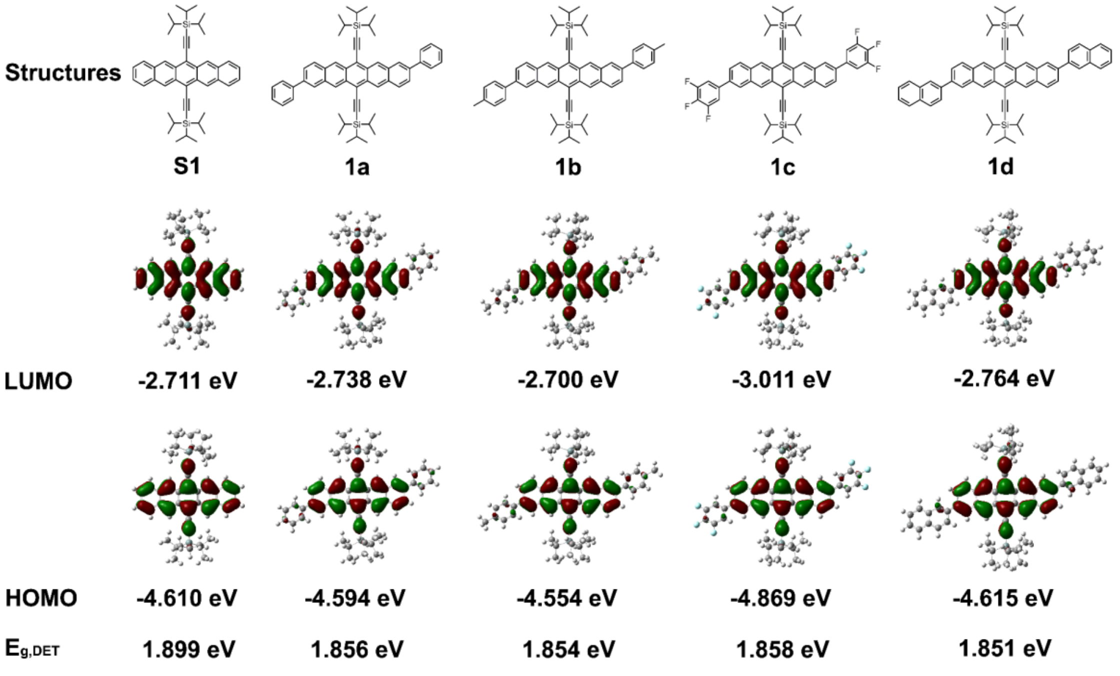


Fig. S61. UV-Vis absorption spectra of **1d**, freshly prepared and after 7 days respectively.



	S1	1a	1b	1c	1d
LUMO	-2.711 eV	-2.738 eV	-2.700 eV	-3.011 eV	-2.764 eV
HOMO	-4.610 eV	-4.594 eV	-4.554 eV	-4.869 eV	-4.615 eV
$E_{g,DET}$	1.899 eV	1.856 eV	1.854 eV	1.858 eV	1.851 eV

Fig. S62. Calculation(B3LYP/6-31G*) and frontier molecular orbitals of **S1** and **1a~d**.

Table S6 Photophysical properties and computational results for **S1** and **1a~d**.

compound	$\lambda_{abs,max}$ (nm)	$\lambda_{em,max}$ (nm)	λ_{onset} (nm)	τ (ns) [a]	$E_{g,opt}$ (eV) [b]	$E_{g,DFT}$ (eV) [c]	ΔE_{ST} (eV) [d]
S1	646	665	670	10.949	1.850	1.899	1.970
1a	658	677	684	10.468	1.813	1.856	1.940
1b	659	682	688	9.937	1.802	1.854	1.936
1c	655	675	682	9.571	1.818	1.858	1.940
1d	660	684	690	9.434	1.797	1.851	1.936

[a] Fluorescence lifetimes excited at 500 nm. [b] Optical gap calculated by λ_{onset}, $E_{g,opt} = 1240/\lambda_{onset}$. [c] $E_{g,DFT}$ from DFT calculations with B3LYP/6-31G* level. [d] ΔE_{ST} from TD-DFT calculations with M06-2X/def2-SVP level.

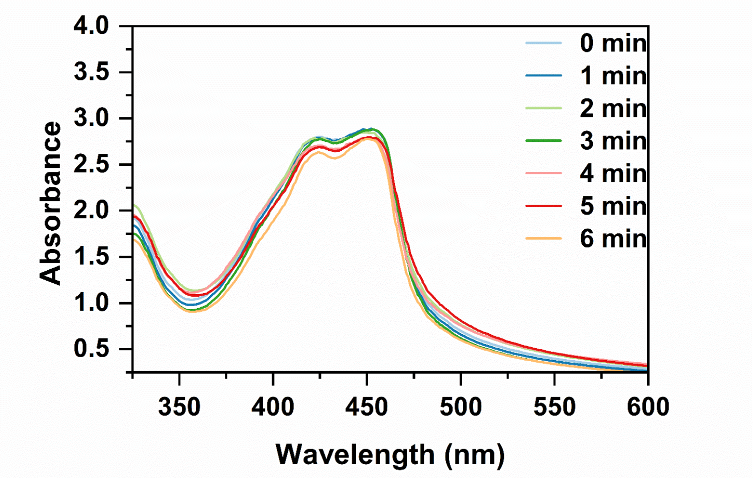


Fig. S63. UV-Vis spectra of DPBF solution mixed with **S1** under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

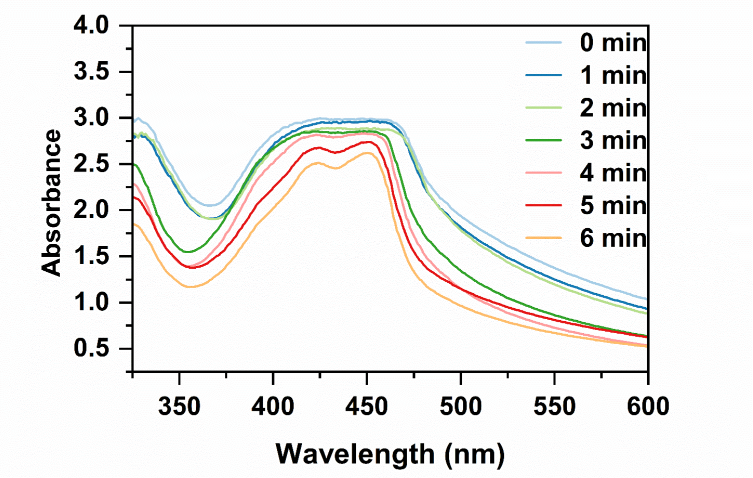


Fig. S64. UV-Vis spectra of DPBF solution mixed with **1a** under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

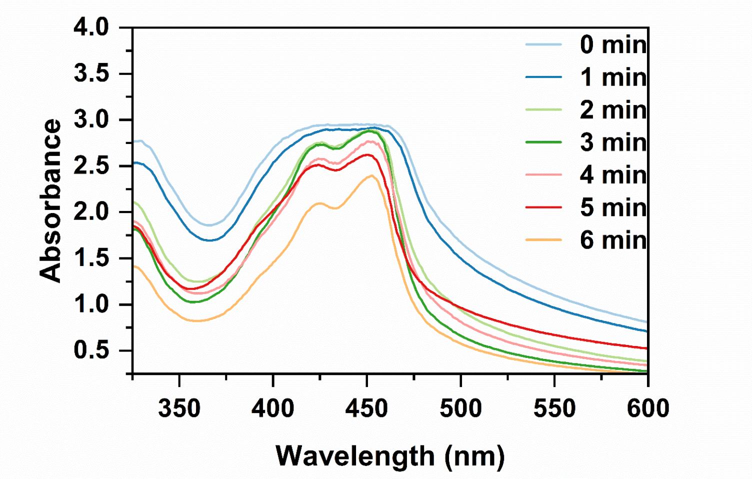


Fig. S65. UV-Vis spectra of DPBF solution mixed with **1b** under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

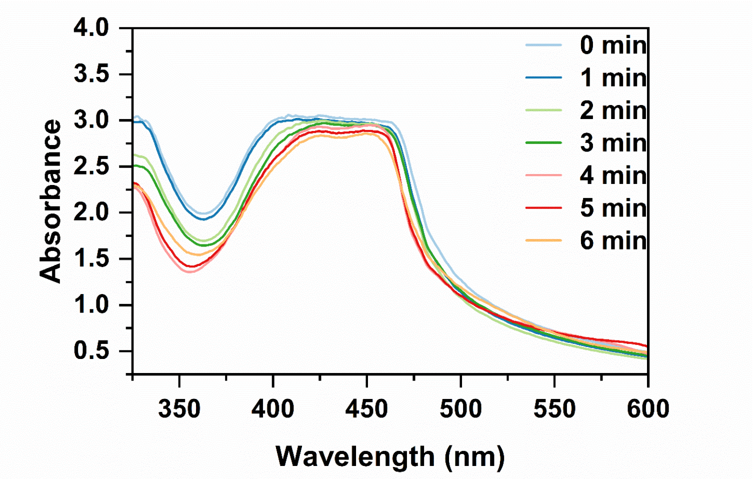


Fig. S66. UV-Vis spectra of DPBF solution mixed with **1c** under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

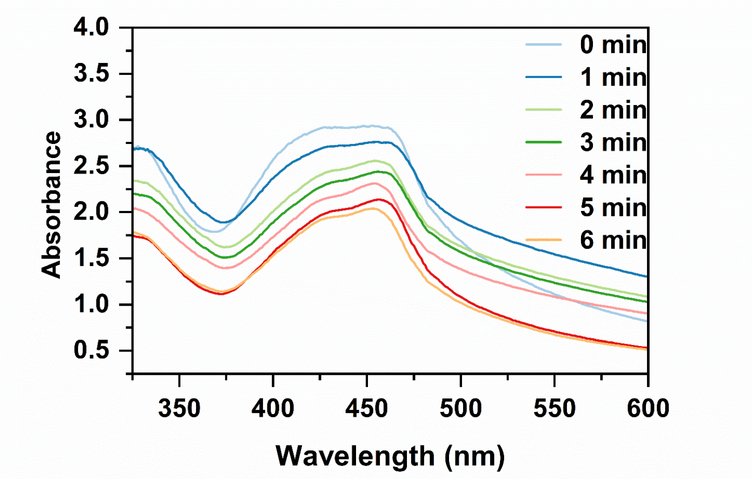


Fig. S67. UV-Vis spectra of DPBF solution mixed with **1d** under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

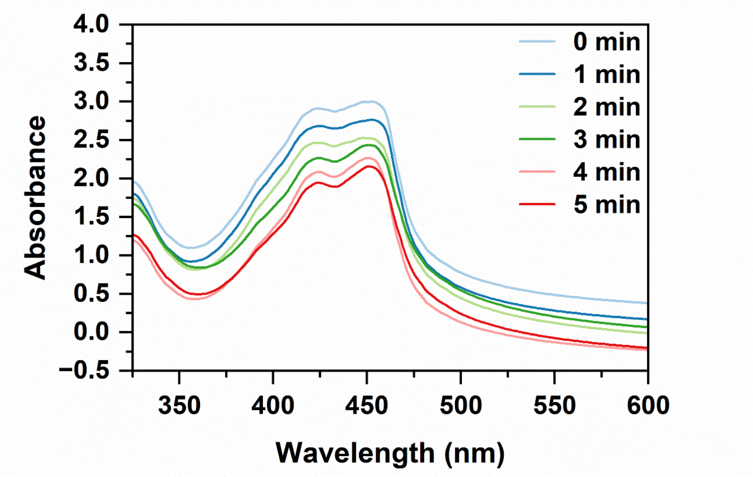


Fig. S68. UV-Vis spectra of DPBF solution mixed with the PBS solution of **1d** under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

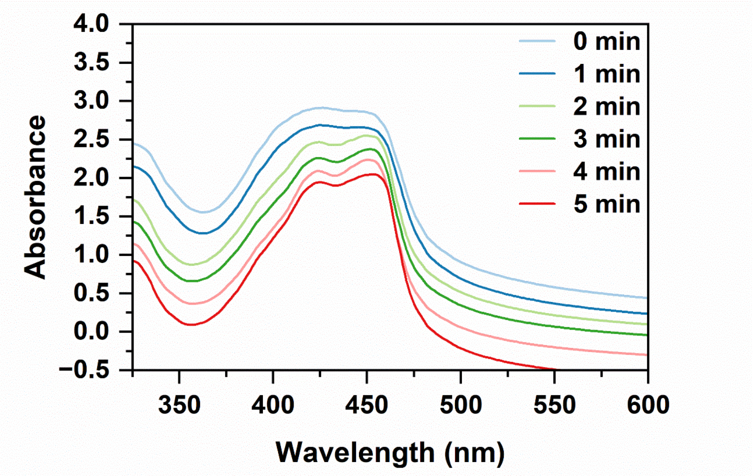


Fig. S69. UV-Vis spectra of DPBF solution mixed with the PBS solution of **1d** after 24 h under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

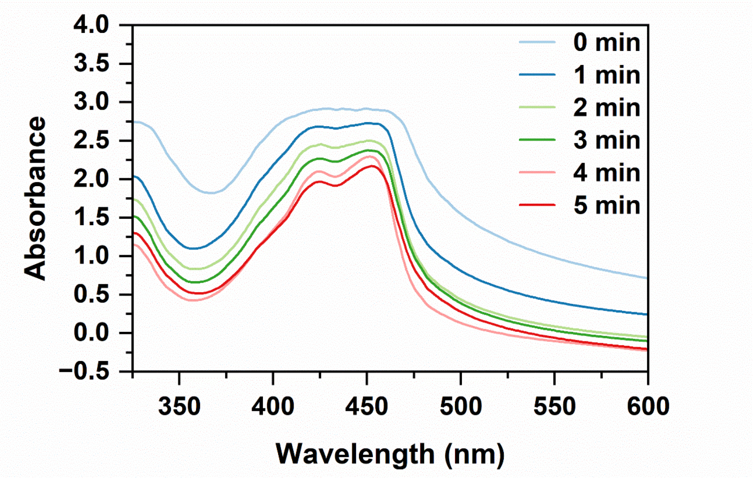


Fig. S70. UV-Vis spectra of DPBF solution mixed with the PBS solution of **1d** after 48 h under US irradiation (1 W/cm^2, 1 MHz, 50% duty cycle).

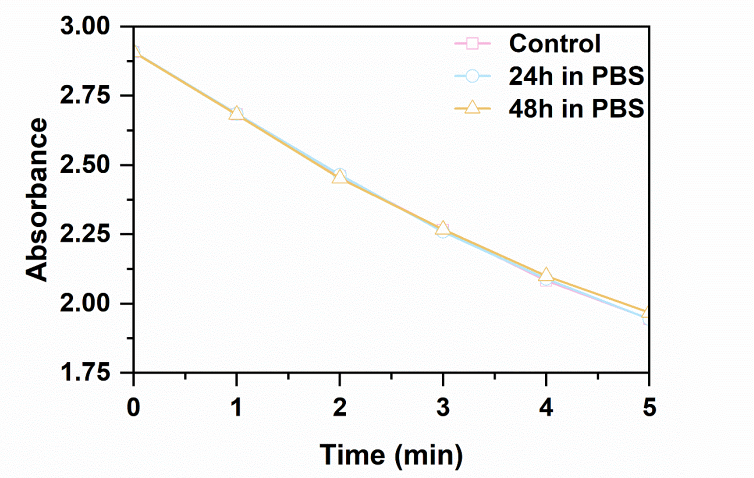


Fig. S71. Oxidation rates of DPBF under US irradiation under different conditions.

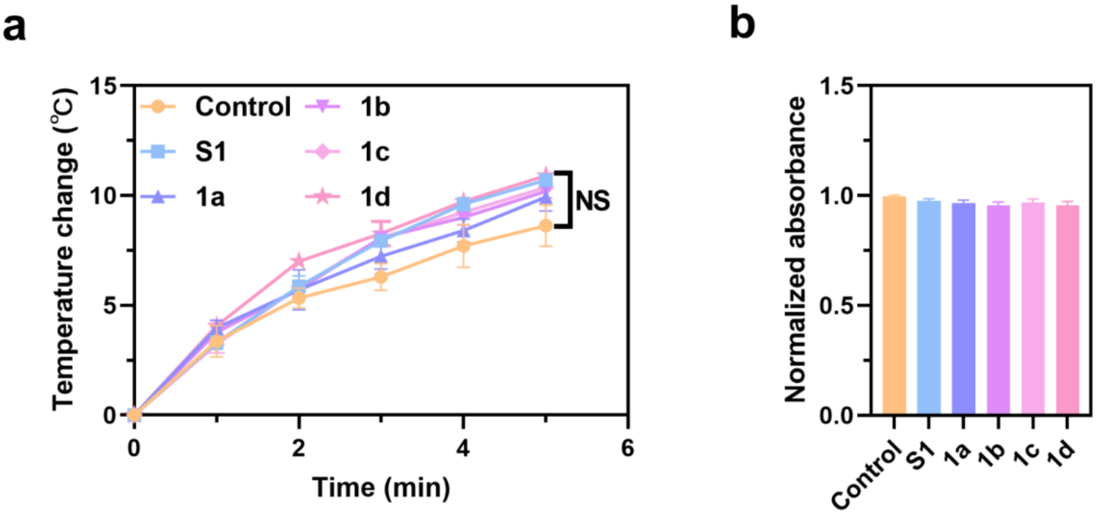


Fig. S72. (a) Temperature changes of Control, **S1**, **1a**, **1b**, **1c** and **1d** under US irradiation (1.0 W/cm^2, 1.0 MHz, 50% duty cycle) for different time intervals. NS: no significance. (b) Absorbance changes of DPBF at 410 nm in the presence of **S1**, **1a**, **1b**, **1c** and **1d** after heating at 80 °C for 30 min.

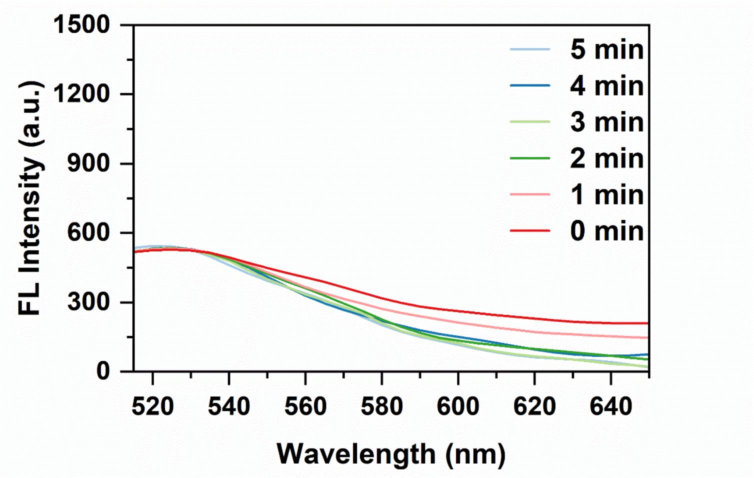


Fig. S73. Fluorescence spectra of SOSG solution mixed with H_2O under US treatment.

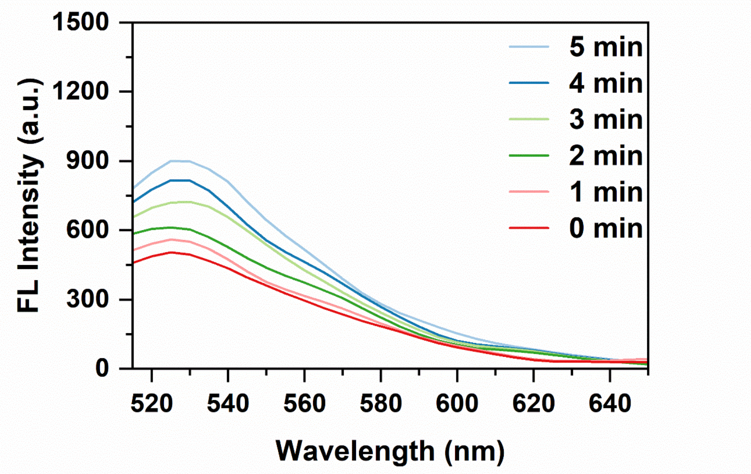


Fig. S74. Fluorescence spectra of SOSG solution mixed with **S1** under US treatment.

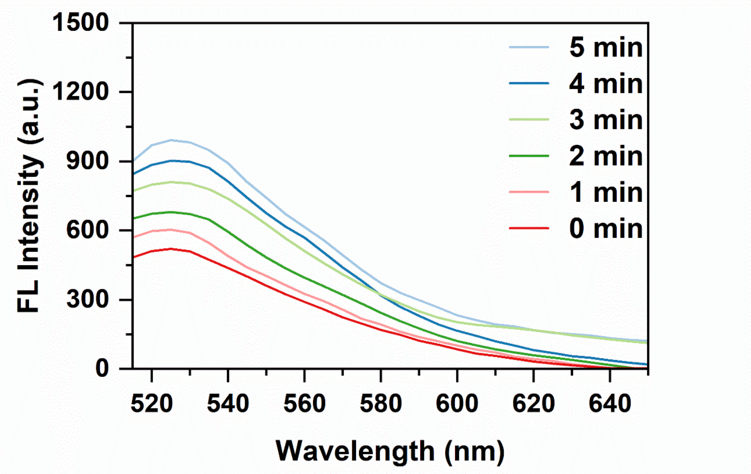


Fig. S75. Fluorescence spectra of SOSG solution mixed with **1a** under US treatment.

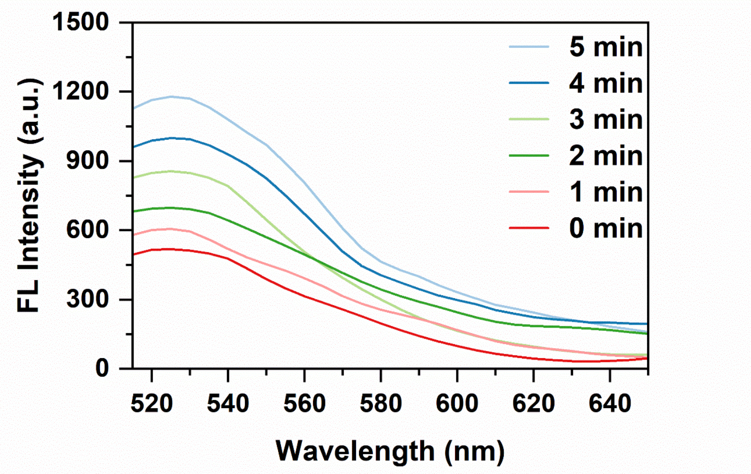


Fig. S76. Fluorescence spectra of SOSG solution mixed with **1b** under US treatment.

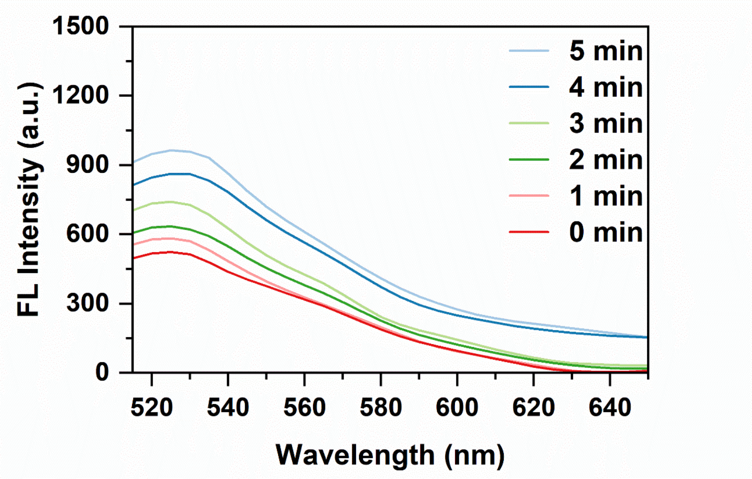


Fig. S77. Fluorescence spectra of SOSG solution mixed with **1c** under US treatment.

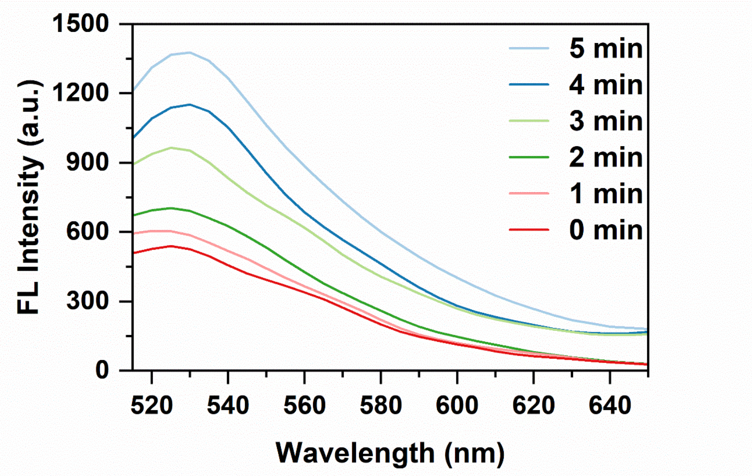


Fig. S78. Fluorescence spectra of SOSG solution mixed with **1d** under US treatment.

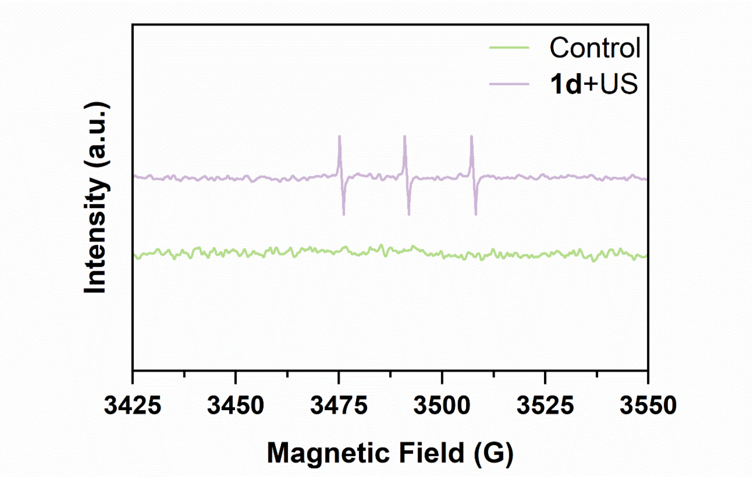


Fig. S79. ESR spectra of $^1O_2$ generation by **1d** under US irradiation captured by TEMP.

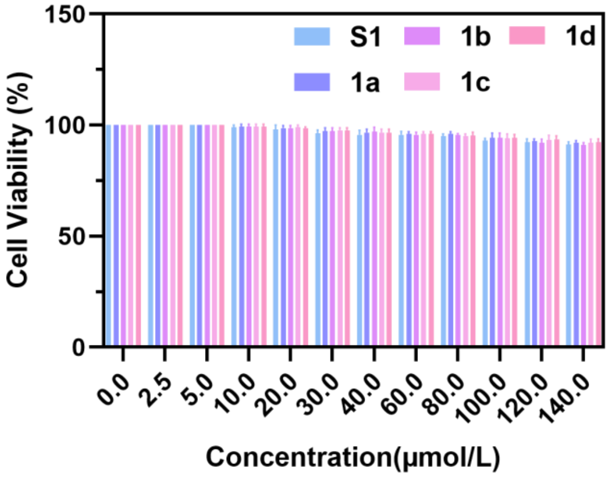


Fig. S80. Cytotoxicity of **S1**, **1a**, **1b**, **1c** and **1d** against NCTC 1469 cells.

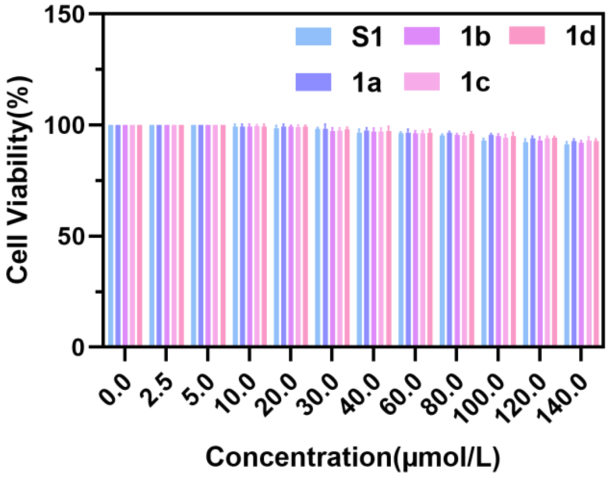


Fig. S81. Cytotoxicity of **S1**, **1a**, **1b**, **1c** and **1d** against L02 cells.

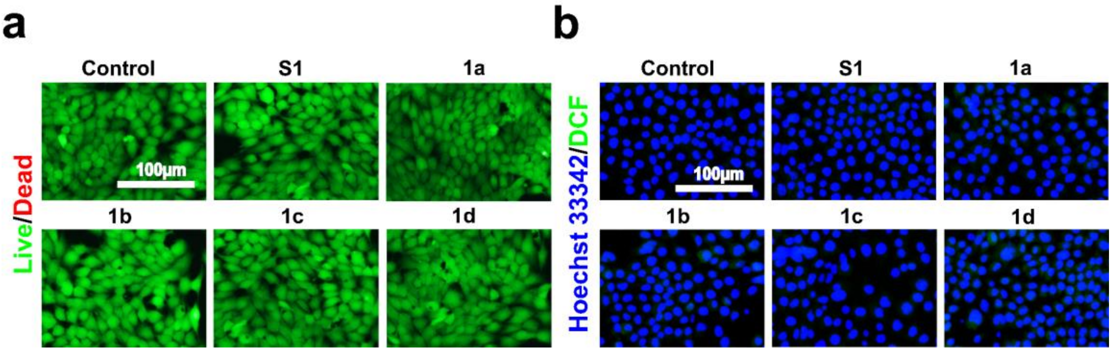


Fig. S82. (a) Fluorescent images of 4T1 cells stained with calcein AM (green) and propidium iodide (PI, red). (b) Fluorescent images of 4T1 cells stained with Hoechst 33342 and DCFH-DA to detect ROS.

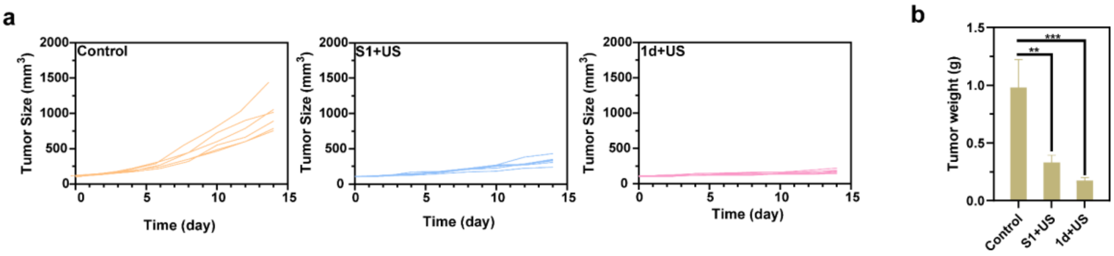


Fig. S83. (a) Tumor volume of each mouse in each group changing during treatment (n=6, mean ± SD). (b) Tumor weights on average at the end of the treatment.

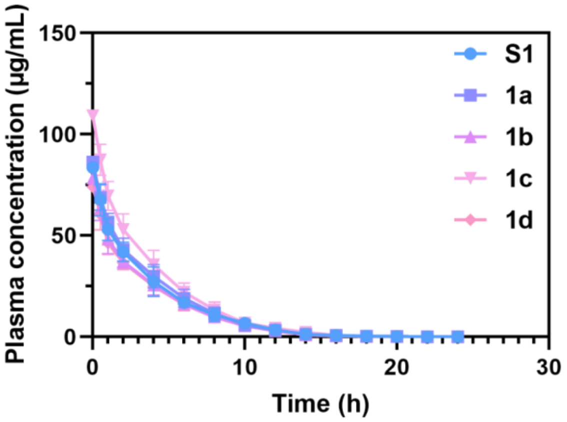


Fig.S84. Time-dependent plasma concentrations of **S1** and **1a~d** after intravenous injection.

Table S7 Pharmacokinetic parameters of **S1** and **1a~d**. Parameters were calculated by PKSolver V2.0. The data are presented as mean ± SD (n = 6).

PK Parameters	**S1**	**1a**	**1b**	**1c**	**1d**
$T_{1/2}$ (h)	1.97 ± 0.12	2.06 ± 0.15	1.79 ± 0.29	2.01 ± 0.15	1.79 ± 0.29
$AUC_{0\text{-}inf}$ (μg•h•mL^{-1})	293.23 ± 8.54	307.20 ± 37.07	267.07 ± 25.80	374.11 ± 47.09	259.97 ± 20.71
$MRT_{0\text{-}inf}$ (h)	3.68 ± 0.08	3.62 ± 0.14	3.60 ± 0.03	3.59 ± 0.13	3.63 ± 0.06

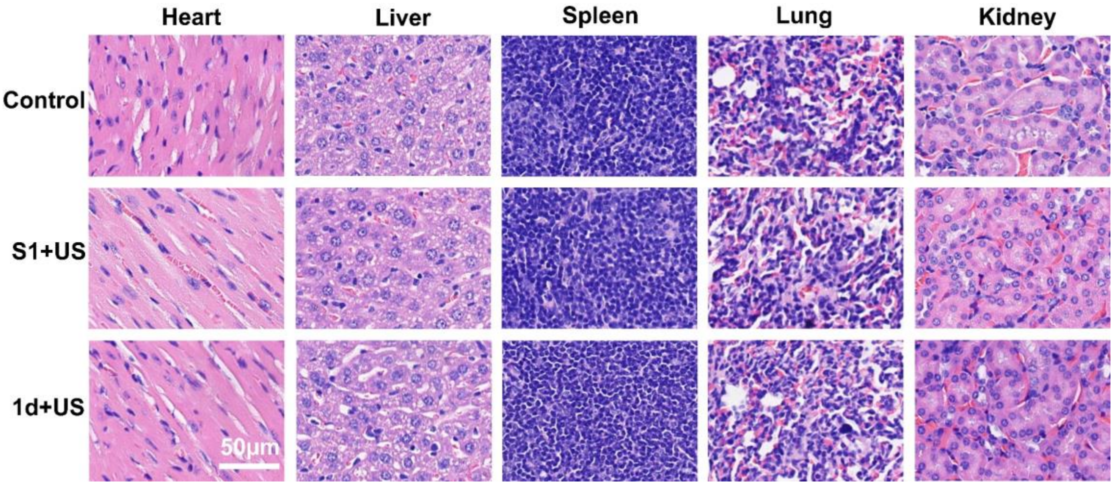


Fig. S85. H&E staining major organ tissues (heart, liver, spleen, lung, and kidney) of mice after 14 days of treament.

5. References

[1] C. D. Sheraw, T. N. Jackson, D. L. Eaton and J. E. Anthony, *Adv. Mater.*, 2003, **15**, 2009–2011.

[2] M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; G. A. Petersson; H. Nakatsuji; X. Li; M. Caricato; A. Marenich; Bloino; J. B. Janesko; G. R. Gomperts; B. Mennucci; H. P. Hratchian; J. V. Ortiz; A. F. Izmaylov; J. L. Sonnenberg; D. Williams-Young; F. Ding; F. Lipparini; F. Egidi; J. Goings; B. Peng; A. Petrone; T. Henderson; D. Ranasinghe; V. G. Zakrzewski; J. Gao; N. Rega; G. Zheng; W. Liang; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; K. Throssell; J. A. Montgomery; Jr.; J. E. Peralta; F. Ogliaro; M. Bearpark; J. J. Heyd; E. K. Brothers; N. Kudin; V. N. Staroverov; T. Keith; R. Kobayashi; J. Normand; K. Raghavachari; A. Rendell; J. C. Burant; S. S. Iyengar; J. Tomasi; M. Cossi; J. M. Millam; M. Klene; C. Adamo; R. Cammi; J. W. Ochterski; R. L. Martin; K. Morokuma; O. Farkas; J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford, CT, 2016.