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Electronic Supplementary Information

Pd-Catalyzed site-specific heteroaromatic C-H/*peri*-C-H annulative coupling for synthesis of cyclopenta-fused polycyclic heteroarenes

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Contents

1. General information

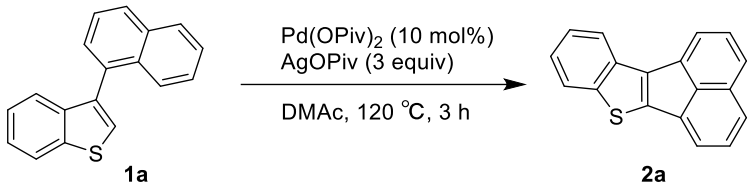
^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (400 MHz) and JEOL JNM AL 600 (600 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, CD_2Cl_2 at 5.32 ppm, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, bs = broad singlet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (100 MHz) spectrometer with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line for $CDCl_3$ at 77 ppm, and CD_2Cl_2 at 53.8 ppm. High-resolution mass spectra were obtained on a Bruker Daltonics SolariX spectrometer using dithranol (DIT) as an exact matrix and FT-ICR-MS analyzer. UV/Vis absorption spectra were recorded on a JASCO V-650DS spectrometer. Redox potential values are measured by cyclic voltammograms (CV), which are versus $Ag/AgNO_3$ reference electrode; Pt wire as a counter electrode and glassy carbon as a working electrode; 0.1 M $TBAPF_6$ as a supporting electrolyte in dichloromethane; scan rate is 50 mV s^{-1}, and the energy level of Fc/Fc+ as -4.80 eV. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~100 μm, KANTO Chemical Co.) and Silica gel 60 (Merck). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials

Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, LTD., Tokyo Chemical Industry Co., LTD., Kanto Chemical Co., Inc., Aldrich Inc., and other commercial suppliers and were used without purification. Tetrahydrofuran and diethyl ether were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. AcOH was purchased from Wako Pure Chemical Industries, LTD. Other solvents were purchased from commercial suppliers as dehydrated solvents, and used under argon or nitrogen atmosphere. $CDCl_3$ was purchased from KANTO Chemical Co., Inc. All air- and moisture-sensitive manipulations were performed under argon atmosphere using oven-dried glassware, including standard Schlenk and glovebox techniques. Compounds **2a**, **4k**, **6b**, and **6c** were conformed representatively according the reported literatures.[1-3] The structures of all starting substrates and products were determined by ^{1}H, ^{13}C NMR, and high resolution mass spectrometry (HRMS).

2. General procedures for the synthesis of 2a, 4a, and 6a

2-1. General procedure for Pd-catalyzed synthesis of benzothiophene-fused CP-PHA (2a)

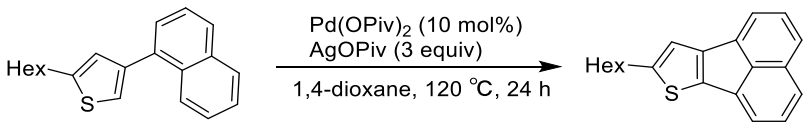


1a **2a**

0.1 mmol scale method for Pd-catalyzed synthesis of 2a: 3-(Naphthalen-1-yl)-benzo[*b*]thiophene (**1a**) (52 mg, 0.2 mmol), $Pd(OPiv)_2$ (6.2 mg, 0.02 mmol), and AgOPiv (126 mg, 0.6 mmol) in a 5 mL reactor vial with screwed cap were dissolved in dry DMAc (2 mL, 0.1 M) under Ar atmosphere. The mixture was heated on an aluminum-block at 120 °C for 3 h. After cooling to room temperature, the resulting mixture was filtered with celite and extracted with diethyl ether. Combined organic layers were washed with water (2 x 10 mL) and brine (1 x 10 mL), dried over anhydrous $MgSO_4$. After concentration, the resulting residue was purified by silica gel chromatography using a mixture of hexane/diethyl ether (30/1) as an eluent, affording corresponding product acenaphtho[1,2-*b*]benzo[d]thiophene (**2a**) in 72% (37.2 mg) yield as orange solid.

1.0 mmol scale method for Pd-catalyzed synthesis of 2a: 3-(Naphthalen-1-yl)-benzo[b]thiophene (**1a**) (260 mg, 1.0 mmol), $Pd(OPiv)_2$ (30.8 mg, 0.1 mmol), and AgOPiv (313 mg, 1.5 mmol) in a neck-flask equipped with an Ar ballon were dissolved in dry DMAc (10 mL, 0.1 M) under Ar atmosphere. The mixture was heated on an oil bath at 120 °C for 5 h. After cooling to room temperature, the resulting mixture was filtered with celite and extracted with diethyl ether. Combined organic layers were washed with water (2 x 30 mL) and brine (1 x 30 mL), dried over anhydrous $MgSO_4$. After concentration, the resulting residue was purified by silica gel chromatography using a mixture of hexane/diethyl ether (30/1) as an eluent, affording corresponding product acenaphtho[1,2-*b*]benzo[d]thiophene (**2a**) in 77% (198 mg) yield as orange solid.

2-2. General procedure for Pd-catalyzed synthesis of thiophene-fused CP-PHA (4a)

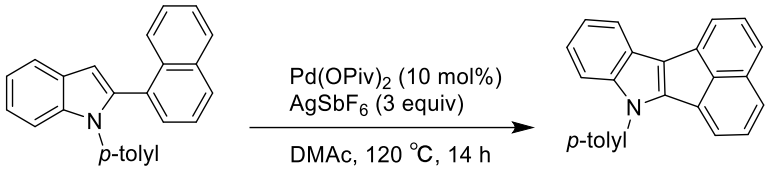


3a **4a**

2-Hexyl-4-(naphthalen-1-yl)thiophene (**3a**) (29 mg, 0.1 mmol), $Pd(OPiv)_2$ (3.1 mg, 0.01 mmol), and AgOPiv (63 mg, 0.3 mmol) in a 5 mL reactor vial with screwed cap were dissolved in dry

1,4-dioxane (1 mL, 0.1 M) under Ar atmosphere. The mixture was heated on an aluminum-block at 120 °C for 24 h. After cooling to room temperature, the resulting mixture was filtered with celite and extracted with diethyl ether. Combined organic layers were washed with water (2 x 10 mL) and brine (1 x 10 mL), dried over anhydrous $MgSO_4$. After concentration, the resulting residue was purified by silica gel chromatography using hexane as eluent, affording corresponding product 8-hexylacenaphtho[1,2-*b*]thiophene (**4a**) in 80% (23.4 mg) yield as orange oil.

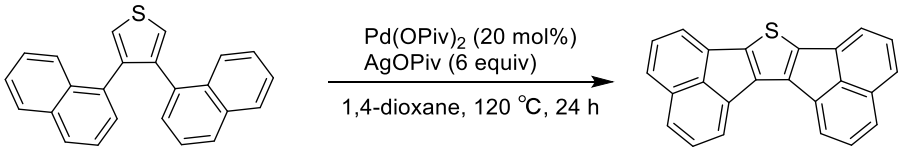
2-3. General procedure for Pd-catalyzed synthesis of indole-fused CP-PHA (6a)



5a **6a**

2-(Naphthalen-1-yl)-1-(*p*-tolyl)-1*H*-indole (**5a**) (66 mg, 0.2 mmol), $Pd(OPiv)_2$ (6.2 mg, 0.02 mmol), and $AgSbF_6$ (206 mg, 0.6 mmol) in a reactor vial with screwed cap were dissolved in dry DMAc (2 mL, 0.1 M) under Ar atmosphere. The mixture was heated on an aluminum-block at 120 °C for 14 h. After cooling to room temperature, the resulting mixture was filtered with celite and extracted with diethyl ether. Combined organic layers were washed with water (2 x 10 mL) and brine (1 x 10 mL), dried over anhydrous $MgSO_4$. After concentration, the resulting residue was purified by silica gel chromatography using a mixture of hexane/dichloromethane (5/1) as an eluent, affording corresponding product 7-(*p*-tolyl)-7*H*-acenaphtho[1,2-*b*]indole (**6a**) in 65% (21.5 mg) yield as red solid.

2-4. General procedure for Pd-catalyzed twofold annulative coupling for synthesis of 4j



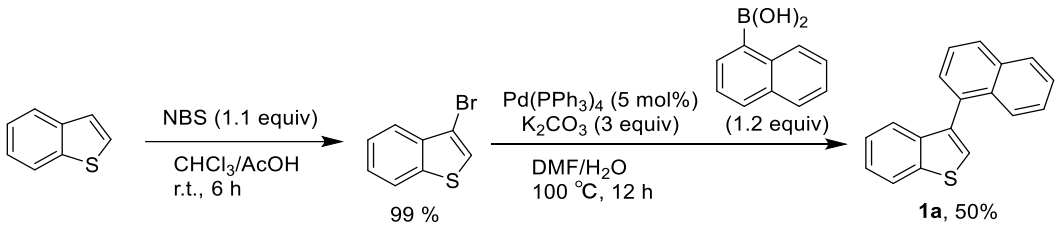
3k **4k**

3,4-Di(naphthalen-1-yl)thiophene (**3k**) (33 mg, 0.1 mmol), $Pd(OPiv)_2$ (6.2 mg, 0.02 mmol), and AgOPiv (125 mg, 0.6 mmol) in a reactor vial with screwed cap were dissolved in dry DMAc (2 mL, 0.05 M) under Ar atmosphere. The mixture was heated on an aluminum-block at 120 °C for 24 h. After cooling to room temperature, the resulting mixture was filtered with celite and extracted with diethyl ether. Combined organic layers were washed with water (2 x 10 mL) and brine (1 x 10 mL), dried over anhydrous $MgSO_4$. After concentration, the resulting residue was purified by silica gel chromatography using a mixture of hexane/dichloromethane (5/1) as an

eluent, affording corresponding product diacenaphtho[1,2-*b*:1',2'-*d*]thiophene (**4k**) in 58% (19.2 mg) yield as red solid.

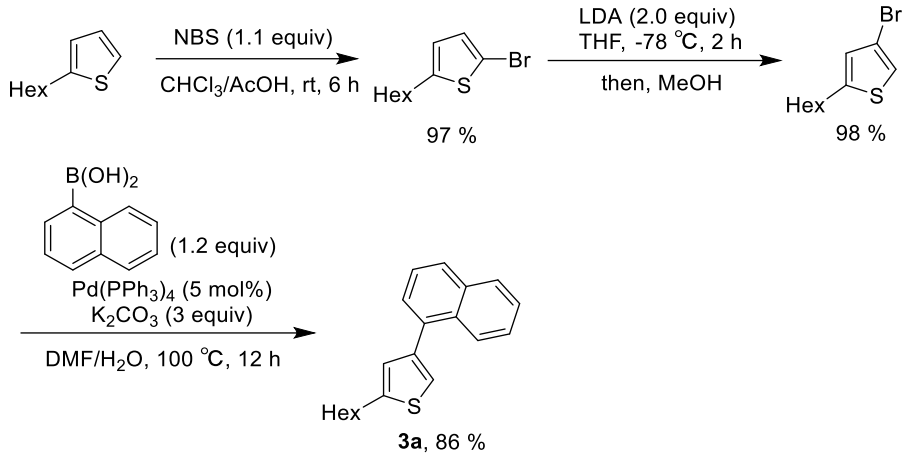
3. Synthetic methods of starting substrates

3-1. General synthetic methods of substrates 1 (benzothiophene)



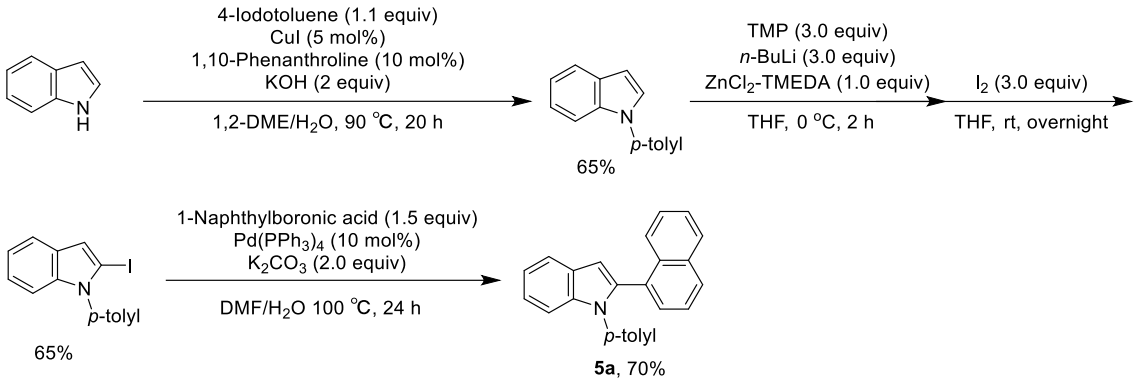
To a mixture of benzo[*b*]thiophene (671 mg, 5 mmol) and NBS (978 mg, 5.5 mmol) was added $CHCl_3$/AcOH = 1:1 (v/v, 0.5 M) under air. The mixture was stirred for 6 h at room temperature. The reaction was quenched with aq. $NaHCO_3$ and extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, removal of solvent on a rotary evaporator gave a brown oil. The crude product was purified by column chromatography using hexane as eluent, to give 3-bromobenzo[*b*]thiophene as clear colorless oil (99% yield, 1.044 g). Next, to a mixture of 3-bromobenzo[*b*]thiophene (1,044 g, 4.9 mmol), $Pd(PPh_3)_4$ (288 mg, 0.25 mmol), K_2CO_3 (1658 g, 12 mmol), and 1-naphthaleneboronic acid (1031 mg, 6 mmol) was added a mixture of DMF/H_2O = 5:1 (v/v, 0.2 M) under Ar atmosphere. The mixture was stirred for 12 h at 100 °C. The reaction was cooled to room temperature and extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration, removal of solvent on a rotary evaporator gave a brown oil. The crude product was purified by column chromatography using a mixture of hexane/Et_2O = 20:1(v/v) as an eluent, giving 3-(naphthalen-1-yl)benzo[*b*]thiophene (**1a**) as white solid (50% yield, 650 mg).

3-2. General synthetic methods of substrates 3 (2-hexyl thiophene)



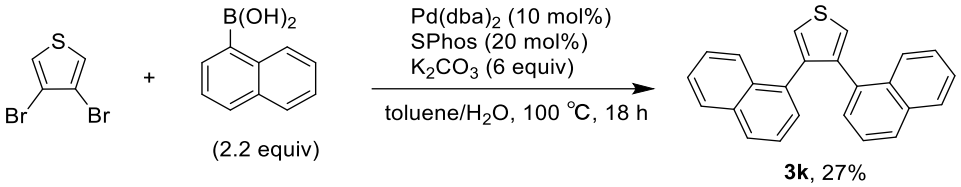
To a mixture of 2-hexylthiophene (841 mg, 5 mmol) and NBS (978 mg, 5.5 mmol) was added $CHCl_3$/AcOH = 1:1 (v/v, 0.5 M) under air. The mixture was stirred for 6 h at room temperature. The reaction was quenched with aq. $NaHCO_3$ and extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and removal of solvent on a rotary evaporator, the crude product was purified by column chromatography using hexane as eluent, to give 2-bromo-5-hexylthiophene as clear colorless oil (97% yield, 1.194 g). Next, to a solution of 2-bromo-5-hexylthiophene (494 mg, 2.0 mmol) in THF (25 mL) was added LDA (0.5 M THF solution, 8 mL, 4 mmol) at -78 °C under Ar atmosphere. After stirring for 2 h, the reaction was quenched by addition of MeOH (10 mL), and stirred at -78 °C for 1 h. The solution was warmed up to room temperature, and the reaction mixture was extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and removal of solvent on a rotary evaporator, the crude product was purified by column chromatography using hexane as an eluent, giving 4-bromo-2-hexylthiophene as yellow oil (98% yield, 483 mg).[4] Next, to a mixture of 4-bromo2-hexylthiophene (483 mg, 2 mmol), $Pd(PPh_3)_4$ (115 mg, 0.1 mmol), K_2CO_3 (691 mg, 5 mmol), and 1-naphthaleneboronic acid (378 mg, 2.2 mmol) was added a mixture of DMF/H_2O = 5:1 (v/v, 0.2 M) under Ar atmosphere. The mixture was stirred for 12 h at 100 °C. The reaction was cooled to room temperature and extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and removal of solvent on a rotary evaporator, the crude product was purified by column chromatography using a mixture of hexane/Et_2O = 20:1(v/v) as an eluent, giving 2-hexyl-4-(naphthalen-1-yl)thiophene (**3a**) as colorless oil (86% yield, 508 mg).

3-3. General synthetic methods of substrate 5 (indole)



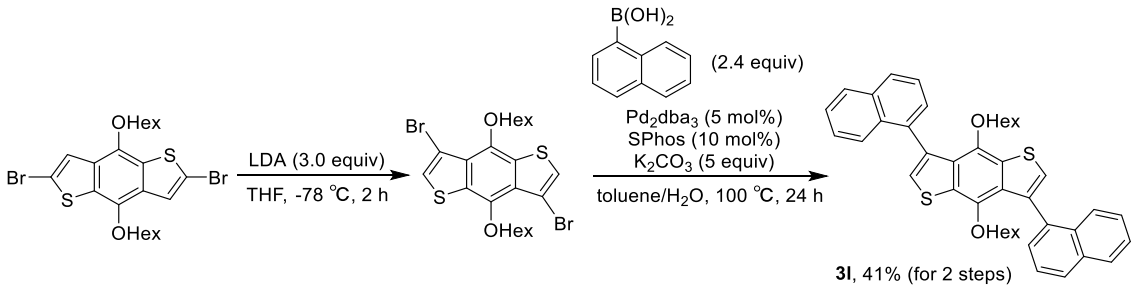
To a mixture of indole (2.3 g, 20 mmol), 4-iodotoluene (4.8 g, 22 mmol), CuI (190 mg, 1 mmol), 1,10-phenanthroline (360 mg, 2 mmol), and KOH (2.2 g, 40 mmol) was added a mixture of 1,2-DME/H_2O = 3:7 (v/v, 0.5 M) under Ar atmosphere. The mixture was heated at 90 °C for 20 h. After cooling to room temperature, the resulting mixture was quenched with aq. NH_4Cl and extracted with diethyl ether. The organic layer was separated and dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane as eluent, giving 1-(*p*-tolyl)-1*H*-indole in 65% yield (2.7 g, 13 mmol) as colorless oil. Next, *n*-BuLi (1.6 M hexanes solution, 25 mL, 39 mmol) was added successfully to a solution of 2,2,6,6-tetramethylpiperidine (6.6 mL, 39 mmol) in THF (40 mL) at 0 °C, and the rection mixture was stirred for 5 min before adding $ZnCl_2$·TMEDA (3.3 g, 13 mmol). The resulting mixture was stirred for 15 min at 0 °C and then 1-(*p*-tolyl)-1*H*-indole (2.7 g, 13 mmol) was added at 0 °C. After stirring for 2 h at room temperature, a solution of I_2 (10 g, 40 mmol) in THF (40 mL) was added. The mixture was stirred overnight before addition of aqueous saturated solution of $Na_2S_2O_3$ and extracted with diethyl ether (3 x 40 mL). The combined organic layers were dried over $MgSO_4$ and filtered. After concentration under reduced pressure, the residue was purified by flash silica gel chromatography using hexane as an eluent to give corresponding product 2-iodo-1-(*p*-tolyl)-1*H*-indole in 65% yield (2.9 g, 8.6 mmol) as brown solid. To a mixture of 2-iodo-1-(*p*-tolyl)-1*H*-indole (470 mg, 1.4 mmol), 1-naphthaleneboronic acid (364 mg, 2.1 mmol), $Pd(PPh_3)_4$ (163 mg, 0.14 mmol), and K_2CO_3 (387 mmol, 2.8 mmol) was added a mixture of DMF/H_2O (5:1, 7 mL, 0.2 M) under Ar atmosphere. After stirring for 24 h at 100 °C, the resulting mixture was cooled to room temperature and filtered through a Celite pad. The filtrate was extracted with diethyl ether (3 x 20 mL) and dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by flash silica gel chromatography using a mixture hexane/CH_2Cl_2 (5/1) as an eluent, affording 2-(naphthalen-1-yl)-1-(*p*-tolyl)-1*H*-indole (**5a**) in 70% yield (324 mg, 0.97 mmol) as white solid.

3-4. Synthetic method of substrates 3j



To a mixture of 3,4-dibromothiophene (483 mg, 2.0 mmol), $Pd(dba)_2$ (115 mg, 0.2 mmol), SPhos (312 mg, 0.048 mmol), K_2CO_3 (1658 mg, 12 mmol), and 1-naphthaleneboronic acid (756 mg, 4.4 mmol) was added a mixture of toluene/H_2O = 5:1 (v/v, 0.1 M) under Ar atmosphere. The mixture was stirred for 18 h at 100 °C. The reaction was cooled to room temperature and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and removal of solvent on a rotary evaporator, the crude product was purified by column chromatography using a mixture of hexane/Et_2O = 10:1(v/v) as an eluent, giving 3,4-di(naphthalen-1-yl)thiophene (**3k**) as white solid (27% yield, 185 mg).

3-5. Synthetic methods of substrates 3k

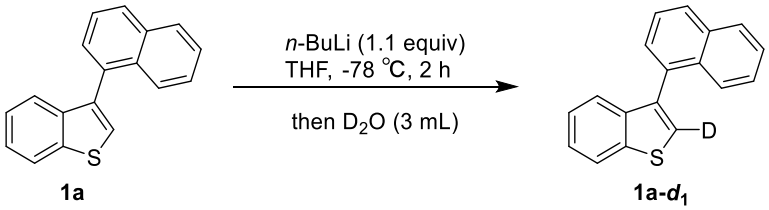


The known compound 2,6-dibromo-4,8-bis(hexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene was synthesized according to the literature.[5] To a solution of 2,6-dibromo-4,8-bis(hexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene (877 mg, 1.6 mmol) in THF (10 mL) was added LDA (0.5 M THF solution, 9.6 mL, 4.8 mmol) at -78 °C under Ar atmosphere. After stirring for 2 h, the reaction was stopped by addition of MeOH (20 mL) and stirred for 1 h at -78 °C. The solution was warmed up to room temperature and extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and removal of solvent on a rotary evaporator, the crude product was purified by column chromatography using a CH_2Cl_2 as an eluent, giving 3,7-dibromo-4,8-bis(hexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene.

Next, to a mixture of 3,7-dibromo-4,8-bis(hexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene (877 mg, 1.6 mmol), Pd_2dba_3 (92 mg, 0.16 mmol), SPhos (249 mg, 0.32 mmol), K_2CO_3 (4075 mg, 19.2 mmol), and 1-naphthaleneboronic acid (1.1 g, 6.4 mmol) was added a mixture of toluene/H_2O = 5:1 (v/v, 0.1 M) under Ar atmosphere. The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and

removal of solvent on a rotary evaporator, the crude product was purified by column chromatography using a mixture of hexane/CH_2Cl_2 = 5:1(v/v) as an eluent. The product was further purified by recrystallization ($CHCl_3$/hexane), giving 4,8-bis(hexyloxy)-3,7-di(naphthalen-1-yl)benzo[1,2-*b*:4,5-*b*']dithiophene (**3l**) as orange solid (41% yield for 2 steps, 430 mg).

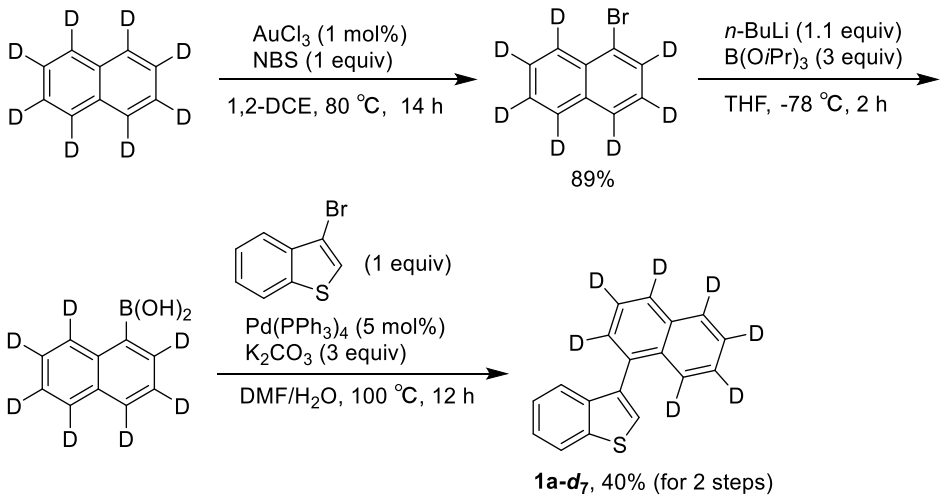
3-6. Synthetic method of substrates 1a-d_1



1a **1a-d_1**

To a solution of **1a** (520 mg, 2 mmol) in THF (10 mL) was added *n*-BuLi (1.6M hexane solution, 1.4mL, 2.2 mmol) at -78 °C. After stirring for 2 h, D_2O (3 mL) was added and the solution was allowed to room temperature. After stirring for 1 h, the solution was extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over MgSO4. After filtration and removal of solvent on a rotary evaporator, the crude product was purified by column chromatography using a mixture of hexane/Et_2O = 20:1(v/v) as eluent, giving 3-(naphthalen-1-yl)benzo[*b*]thiophene-2-*d* (**1a-d_1**) as white solid (99% yield, 520 mg)

3-7. Synthetic methods of substrates 1a-d_7



To a mixture of naphthalene-d_8 (408 mg, 3 mmol), $AuCl_3$ (9.1 mg, 0.03 mmol), and NBS (534 mg, 3 mmol) was added 1,2-dichloroethane (DCE) under Ar atmosphere. The mixture was stirred at 80 °C for 14 h. After cooling to room temperature, the resulting mixture was filtered with celite and extracted with diethyl ether (2 x 10 mL). Combined organic layers were washed with water (2 x 10 mL) and brine (1 x 10 mL), and dried over anhydrous $MgSO_4$. After concentration, the resulting residue was purified by silica gel chromatography using hexane as an eluent, affording corresponding product 1-bromonaphthalene-d_7 in 89% yield as pale yellow oil (575 mg). Next, to a solution of 1-bromonaphthalene-d_7 (428 mg, 2.0 mmol) in THF was added *n*-BuLi (1.6 M hexane solution, 1.4 mL) at -78 °C under Ar atmosphere. After stirring for 1 h, B(O-*i*-Pr)$_3$ was added and the reaction was stirred for 3 h at -78 °C. After warming to room temperature, the

reaction was quenched with 1N HCl and extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and removal of solvent on a rotary evaporator, the corresponding 1-naphthalene boronic acid-d_7 (white solid) was obtained, which used to the next step without further purification. Next, to a mixture of 3-bromobenzo [*b*]thiophene (426 mg, 2 mmol), $Pd(PPh_3)_4$ (115 mg, 0.1 mmol), K_2CO_3 (829 mg, 6 mmol), and 1-naphthaleneboronic acid-d_7 was added a mixture of DMF/H_2O = 4:1 (v/v, 0.2 M) under Ar atmosphere. The mixture was stirred for 12 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with Et_2O (3 x 20 mL). The combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and removal of solvent on a rotary evaporato, the crude product was purified by column chromatography using a mixture of hexane/Et_2O = 20:1(v/v) as an eluent, giving 3-(naphthalen-1-yl-d_7)benzo[*b*]thiophene (**1a-*d*$_7$**) as white solid (40% yield for , 216 mg).

4. References

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5. DFT Calculations

DFT Calculation details. The computational studies were conducted using the Gaussian09, Revision C.01.[1] The ground-state geometry of products was optimized at the B3LYP/6-31G(d) level, and the time-dependent DFT (TD-DFT) calculations were conducted at the B3LYP/6-31G(d) level for the excited state calculation using the ground-state geometry.

5-1. HOMO and LUMO contours of CP-PHA products

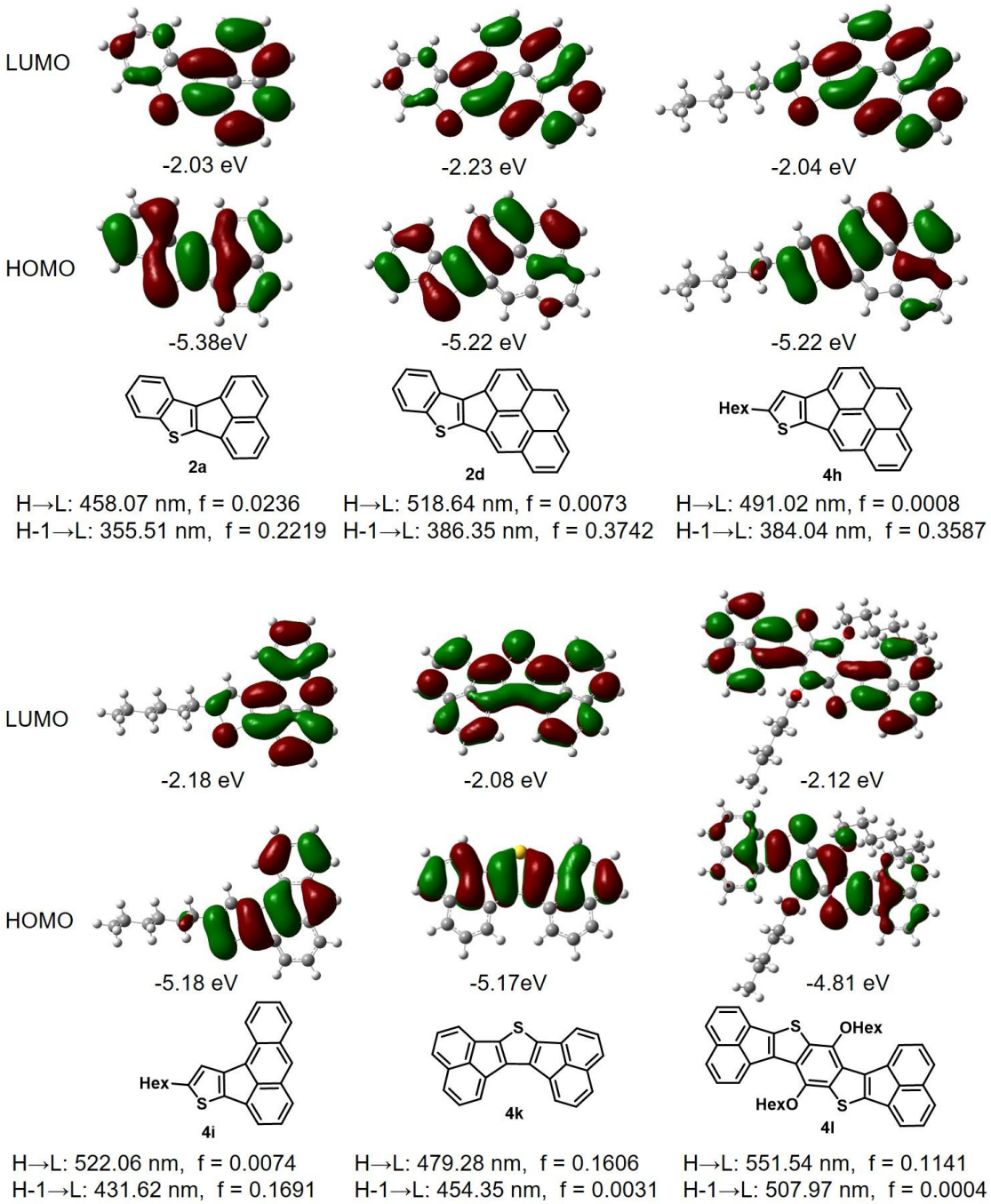
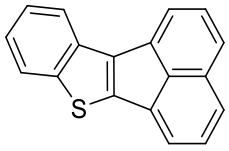


Figure S1. DFT Calculation of HOMO and LUMO contours of CP-PHA products.

5-2. Excited state density of CP-PHA products

Table S1



2a

Excited State 1: Singlet-A 2.7067 eV 458.07 nm f=0.0236 <S**2>=0.000
67 -> 68 0.69450
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1090.04746881
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.4875 eV 355.51 nm f=0.2219 <S**2>=0.000
66 -> 68 0.68489
67 -> 69 -0.12125

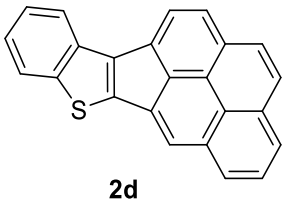
Excited State 3: Singlet-A 4.0465 eV 306.40 nm f=0.0312 <S**2>=0.000
64 -> 68 -0.17878
65 -> 68 0.64861

Excited State 4: Singlet-A 4.1523 eV 298.59 nm f=0.0393 <S**2>=0.000
64 -> 68 0.59593
65 -> 68 0.21294
65 -> 69 0.10228
66 -> 69 -0.22804
66 -> 70 0.11000

Excited State 5: Singlet-A 4.4446 eV 278.95 nm f=0.1825 <S**2>=0.000
66 -> 68 0.11908
67 -> 69 0.65457
67 -> 70 -0.18997

Excited State 6: Singlet-A 4.5854 eV 270.39 nm f=0.0377 <S**2>=0.000

63 -> 68 0.17223
66 -> 71 0.10777
67 -> 69 0.12924
67 -> 70 0.58663
67 -> 71 -0.26448



2d

Excited State 1: Singlet-A 2.3906 eV 518.64 nm f=0.0073 <S**2>=0.000
85 -> 87 0.10330
86 -> 87 0.69336
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1319.93830337
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.2091 eV 386.35 nm f=0.3742 <S**2>=0.000
84 -> 87 -0.11385
85 -> 87 0.65645
86 -> 87 -0.10365
86 -> 89 -0.14593

Excited State 3: Singlet-A 3.4207 eV 362.45 nm f=0.0363 <S**2>=0.000
83 -> 87 -0.15616
84 -> 87 0.59766
85 -> 88 -0.13430
86 -> 88 0.26656

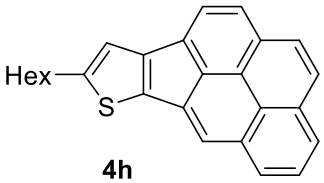
Excited State 4: Singlet-A 3.7053 eV 334.61 nm f=0.0102 <S**2>=0.000
83 -> 87 0.60144
84 -> 87 0.26343
86 -> 88 -0.19605

Excited State 5: Singlet-A 3.9440 eV 314.36 nm f=0.0637 <S**2>=0.000

83	-> 87	0.23075
84	-> 87	-0.12860
85	-> 88	0.23608
86	-> 88	0.58194

Excited State 6: Singlet-A 4.1337 eV 299.93 nm f=0.2777 <S**2>=0.000

83	-> 88	-0.10454
85	-> 87	0.13388
85	-> 88	0.23464
86	-> 88	-0.10622
86	-> 89	0.61368



4h

Excited State 1: Singlet-A 2.5250 eV 491.02 nm f=0.0008 <S**2>=0.000

96	-> 98	-0.15360
97	-> 98	0.68564

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1402.16963415

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.2284 eV 384.04 nm f=0.3587 <S**2>=0.000

95	-> 99	0.10674
96	-> 98	0.65808
97	-> 98	0.14675
97	->100	-0.14793

Excited State 3: Singlet-A 3.5223 eV 352.00 nm f=0.0241 <S**2>=0.000

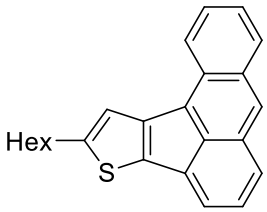
95	-> 98	0.59502
96	-> 99	-0.19010

97 -> 99 -0.30173

Excited State 4: Singlet-A 4.0158 eV 308.74 nm f=0.0252 <S**2>=0.000
97 -> 98 0.16864
96 -> 99 -0.36743
97 -> 99 0.56035

Excited State 5: Singlet-A 4.1966 eV 295.44 nm f=0.0127 <S**2>=0.000
93 -> 98 0.13108
94 -> 98 0.64581
96 ->100 -0.19176

Excited State 6: Singlet-A 4.2600 eV 291.04 nm f=0.1231 <S**2>=0.000
95 -> 98 0.13133
95 -> 99 0.14538
96 -> 98 0.11819
96 -> 99 0.36239
96 ->100 0.13689
97 -> 99 0.21410
97 ->100 0.47342



4i

Excited State 1: Singlet-A 2.3749 eV 522.06 nm f=0.0074 <S**2>=0.000
90 -> 92 -0.26141
91 -> 92 0.65072
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1325.93325179
Copying the excited state density for this state as the 1-particle RhoCI density.

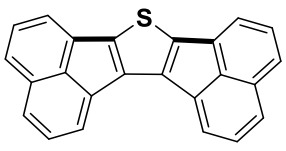
Excited State 2: Singlet-A 2.8725 eV 431.62 nm f=0.1691 <S**2>=0.000
90 -> 92 0.64606
91 -> 92 0.26141

Excited State 3: Singlet-A 3.7224 eV 333.08 nm f=0.0580 <S**2>=0.000
89 -> 92 0.59023
90 -> 93 -0.17064
90 -> 94 0.17823
91 -> 93 -0.10136
91 -> 94 0.26742

Excited State 4: Singlet-A 4.0061 eV 309.49 nm f=0.0112 <S**2>=0.000
88 -> 92 0.68002
90 -> 93 -0.11769
91 -> 94 -0.10503

Excited State 5: Singlet-A 4.1796 eV 296.64 nm f=0.1212 <S**2>=0.000
91 -> 93 0.67683

Excited State 6: Singlet-A 4.4027 eV 281.61 nm f=0.0627 <S**2>=0.000
87 -> 92 -0.26699
88 -> 92 0.13152
90 -> 93 0.35035
90 -> 94 -0.21186
91 -> 94 0.47119



4k

Excited State 1: Singlet-A 2.5869 eV 479.28 nm f=0.1606 <S**2>=0.000
85 -> 88 0.13840
86 -> 87 0.68221

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1319.89381239
Copying the excited state density for this state as the 1-particle RhoCI density.

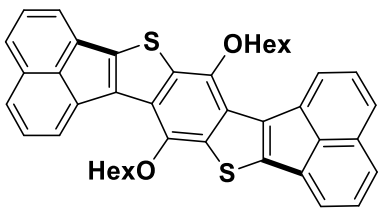
Excited State 2: Singlet-A 2.7288 eV 454.35 nm f=0.0031 <S**2>=0.000
86 -> 88 0.69425

Excited State 3: Singlet-A 3.1744 eV 390.58 nm f=0.0202 <S**2>=0.000
85 -> 87 0.68649

Excited State 4: Singlet-A 3.5076 eV 353.48 nm f=0.4325 <S**2>=0.000
85 -> 88 0.68457
86 -> 87 -0.14492

Excited State 5: Singlet-A 3.7541 eV 330.27 nm f=0.0944 <S**2>=0.000
84 -> 87 0.69644

Excited State 6: Singlet-A 3.9378 eV 314.85 nm f=0.0223 <S**2>=0.000
82 -> 88 -0.12484
83 -> 87 0.58321
84 -> 88 -0.29762
85 -> 89 -0.10479
86 -> 90 0.12801



4l

Excited State 1: Singlet-A 2.2480 eV 551.54 nm f=0.1141 <S**2>=0.000
169 ->170 0.69668
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2570.14008658

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.4408 eV 507.97 nm f=0.0004 <S**2>=0.000
169 ->171 0.69590

Excited State 3: Singlet-A 3.1025 eV 399.63 nm f=0.3021 <S**2>=0.000
167 ->171 0.12239
168 ->170 0.66559

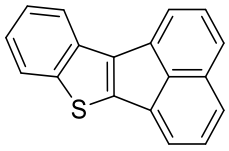
Excited State 4: Singlet-A 3.1747 eV 390.53 nm f=0.0191 <S**2>=0.000
166 ->170 0.11772
167 ->170 0.66382
168 ->170 -0.10310

Excited State 5: Singlet-A 3.4320 eV 361.26 nm f=0.0021 <S**2>=0.000
168 ->171 0.67978

Excited State 6: Singlet-A 3.4518 eV 359.18 nm f=0.3067 <S**2>=0.000
165 ->170 0.22321
167 ->171 0.61388
168 ->170 -0.16201

5-3. Ground-state geometry of CP-PHA products

Table S2



2a

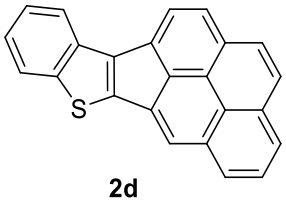
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.596407	-0.737137	-0.000029

2	6	0	1.895180	0.501789	-0.000021
3	6	0	2.643265	1.694216	-0.000031
4	6	0	4.030487	1.638954	-0.000046
5	6	0	4.703258	0.404634	-0.000053
6	6	0	3.991421	-0.791409	-0.000046
7	6	0	0.127884	-1.055111	-0.000008
8	6	0	0.475760	0.287311	-0.000012
9	1	0	2.133402	2.653342	-0.000028
10	1	0	4.604418	2.561513	-0.000053
11	1	0	5.789326	0.381548	-0.000064
12	1	0	4.510476	-1.745722	-0.000049
13	16	0	1.499452	-2.127738	-0.000007
14	6	0	-2.481985	2.779798	0.000036
15	6	0	-3.498386	1.842272	0.000045
16	6	0	-3.183696	0.450847	0.000035
17	6	0	-1.823477	0.124926	0.000015
18	6	0	-0.766090	1.077703	0.000006
19	6	0	-1.103775	2.416141	0.000017
20	1	0	-5.166765	-0.457282	0.000060
21	1	0	-2.735949	3.836441	0.000045
22	1	0	-4.537146	2.163123	0.000061
23	6	0	-4.095879	-0.645045	0.000045
24	6	0	-1.324816	-1.208999	0.000006
25	1	0	-0.350500	3.199212	0.000010
26	6	0	-2.230768	-2.250659	0.000017
27	6	0	-3.621071	-1.945367	0.000036
28	1	0	-1.910285	-3.289166	0.000012
29	1	0	-4.330531	-2.768374	0.000045

HOMO : -0.19768 a.u. = -5.37915 eV

LUMO : -0.07458 a.u. = -2.02943 eV



2d

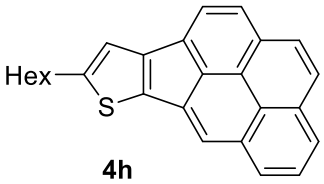
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.335291	2.565403	-0.000002
2	6	0	0.990769	3.032705	0.000003
3	6	0	2.100478	2.161935	-0.000003
4	6	0	1.840123	0.759964	-0.000016
5	6	0	0.523507	0.327744	-0.000031
6	6	0	-0.587003	1.188132	-0.000018
7	6	0	3.482568	2.561217	0.000008
8	6	0	2.869255	-0.218415	-0.000007
9	6	0	4.222982	0.212043	0.000006
10	6	0	4.486176	1.632452	0.000012
11	6	0	5.231680	-0.765786	0.000017
12	1	0	6.275194	-0.459813	0.000028
13	6	0	4.903407	-2.122957	0.000016
14	6	0	3.572130	-2.542800	0.000005
15	6	0	2.521152	-1.608447	-0.000006
16	6	0	1.130768	-2.012682	-0.000011
17	6	0	0.144011	-1.061849	-0.000024
18	1	0	0.904833	-3.076669	-0.000003
19	1	0	3.723784	3.621647	0.000015
20	1	0	-1.146732	3.288154	0.000007
21	1	0	1.167292	4.105705	0.000013
22	1	0	5.523730	1.958019	0.000020
23	1	0	5.696945	-2.865099	0.000025
24	1	0	3.340117	-3.605154	0.000007
25	6	0	-1.761964	0.299025	-0.000010
26	6	0	-1.314259	-1.017448	-0.000013

27	6	0	-3.193482	0.403921	-0.000003
28	16	0	-2.603828	-2.189011	-0.000002
29	6	0	-3.800035	-0.884033	0.000008
30	6	0	-5.187372	-1.041681	0.000019
31	6	0	-4.027832	1.537878	-0.000002
32	6	0	-5.985649	0.098303	0.000019
33	1	0	-5.634116	-2.031902	0.000023
34	6	0	-5.406882	1.379702	0.000009
35	1	0	-3.590030	2.531956	-0.000009
36	1	0	-7.067028	-0.005381	0.000028
37	1	0	-6.048166	2.256746	0.000012

HOMO : -0.19182 a.u. = -5.21969 eV

LUMO : -0.08193 a.u. = -2.22943 eV



4h

Standard orientation:

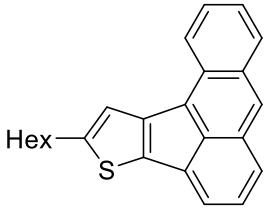
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.242677	-1.056905	0.475185
2	6	0	0.096833	0.329147	0.564900
3	6	0	1.579266	-1.486490	0.700712
4	16	0	1.601674	1.103922	0.926730
5	6	0	2.441948	-0.447864	0.959250
6	1	0	1.909333	-2.520395	0.681473
7	6	0	3.920681	-0.513861	1.218674
8	1	0	4.172205	0.052402	2.126552
9	1	0	4.174562	-1.560519	1.431581
10	6	0	4.794940	-0.007137	0.052547
11	1	0	4.543495	1.040816	-0.160726

12	1	0	4.541368	-0.573204	-0.853840
13	6	0	6.296364	-0.128095	0.340756
14	1	0	6.537796	0.432925	1.256014
15	1	0	6.541817	-1.178893	0.555883
16	6	0	7.179984	0.373241	-0.808618
17	1	0	6.936930	1.424644	-1.022571
18	1	0	6.937399	-0.186033	-1.724450
19	6	0	8.682439	0.249521	-0.523643
20	1	0	8.924207	0.807972	0.391976
21	1	0	8.924710	-0.801479	-0.310714
22	6	0	9.559126	0.753002	-1.674760
23	1	0	9.362911	1.810887	-1.888696
24	1	0	10.624949	0.653051	-1.439749
25	1	0	9.366809	0.189061	-2.595865
26	6	0	-1.077791	-1.639513	0.176066
27	6	0	-1.612488	-2.915657	-0.030904
28	6	0	-1.955084	-0.545182	0.102785
29	6	0	-2.984813	-3.060574	-0.299163
30	1	0	-0.984992	-3.802279	0.012433
31	6	0	-3.311656	-0.658937	-0.159391
32	6	0	-1.291225	0.714469	0.335145
33	6	0	-3.861538	-1.957597	-0.369994
34	1	0	-3.385837	-4.058954	-0.457519
35	6	0	-4.090723	0.527690	-0.203205
36	6	0	-2.036805	1.863293	0.293158
37	6	0	-5.273796	-2.024305	-0.636847
38	6	0	-5.482398	0.424068	-0.468925
39	6	0	-3.458246	1.793594	0.021783
40	1	0	-1.593996	2.842687	0.460129
41	6	0	-6.038571	-0.891751	-0.682716
42	1	0	-5.732187	-2.996405	-0.803465
43	6	0	-6.242122	1.605275	-0.509205
44	6	0	-4.267643	2.942063	-0.030848
45	1	0	-7.104215	-0.966949	-0.886089
46	6	0	-5.635794	2.843795	-0.292321
47	1	0	-7.309271	1.550449	-0.711126

48	1	0	-3.818061	3.918176	0.135592
49	1	0	-6.238104	3.747538	-0.327030

HOMO : -0.19194 a.u. = -5.22296 eV

LUMO : -0.07513 a.u. = -2.04439 eV



4i

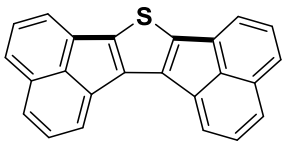
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.227957	-3.826560	0.097598
2	6	0	-2.397220	-2.741263	0.209552
3	6	0	-2.882645	-1.414644	0.007358
4	6	0	-4.290891	-1.235239	-0.323673
5	6	0	-5.113833	-2.401016	-0.427420
6	6	0	-4.604358	-3.656130	-0.224723
7	6	0	-2.084498	-0.259793	0.106750
8	6	0	-4.834506	0.045053	-0.537828
9	6	0	-4.034875	1.195801	-0.439859
10	6	0	-2.678014	0.993663	-0.118306
11	6	0	-1.730684	2.063226	0.019149
12	6	0	-2.165950	3.353656	-0.172523
13	6	0	-3.540647	3.580585	-0.499866
14	6	0	-4.450055	2.554100	-0.631470
15	1	0	-2.836459	-4.827972	0.255678
16	1	0	-1.349527	-2.882070	0.455401
17	1	0	-6.164542	-2.267219	-0.674173
18	1	0	-5.247229	-4.527976	-0.308890

19	1	0	-5.890911	0.132304	-0.782998
20	1	0	-1.494077	4.203276	-0.081843
21	1	0	-3.870585	4.605257	-0.648461
22	1	0	-5.486123	2.768868	-0.880931
23	6	0	-0.667094	0.015195	0.408760
24	6	0	-0.480367	1.396008	0.350656
25	6	0	0.530451	-0.682284	0.738842
26	16	0	1.154669	1.840234	0.697724
27	6	0	1.607320	0.150459	0.928083
28	1	0	0.619308	-1.758501	0.843444
29	6	0	3.023421	-0.227008	1.260508
30	1	0	3.377614	0.352825	2.124605
31	1	0	3.021617	-1.277828	1.578534
32	6	0	4.020068	-0.051027	0.095885
33	1	0	4.020800	0.999719	-0.224974
34	1	0	3.666912	-0.633660	-0.765543
35	6	0	5.446266	-0.477097	0.465259
36	1	0	5.785535	0.104029	1.335803
37	1	0	5.439830	-1.529289	0.787153
38	6	0	6.450404	-0.304589	-0.681598
39	1	0	6.458266	0.747568	-1.002923
40	1	0	6.111145	-0.884664	-1.552632
41	6	0	7.877624	-0.731746	-0.314800
42	1	0	8.216279	-0.151715	0.555528
43	1	0	7.869391	-1.783275	0.006041
44	6	0	8.874922	-0.556496	-1.464535
45	1	0	8.932103	0.491537	-1.783453
46	1	0	9.883243	-0.870604	-1.171525
47	1	0	8.581395	-1.151469	-2.338215

HOMO : -0.19059 a.u. = -5.18622 eV

LUMO : -0.08016 a.u. = -2.18127 eV



4k

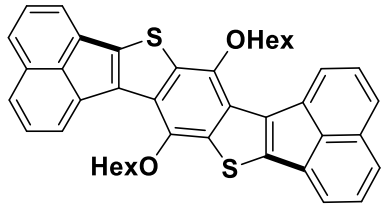
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.231524	-1.249211	0.000014
2	6	0	-0.708914	0.051851	0.000010
3	6	0	0.708914	0.051851	-0.000007
4	6	0	1.231524	-1.249211	-0.000011
5	16	0	0.000000	-2.476171	0.000005
6	6	0	2.688183	-1.217717	-0.000007
7	6	0	3.014379	0.170698	-0.000002
8	6	0	4.323798	0.665214	0.000001
9	6	0	5.368473	-0.305639	-0.000001
10	6	0	5.061172	-1.655029	-0.000006
11	6	0	3.721321	-2.134673	-0.000009
12	6	0	1.848111	0.985863	-0.000002
13	6	0	2.015681	2.355600	0.000003
14	6	0	3.336401	2.889036	0.000008
15	6	0	4.461332	2.084405	0.000006
16	6	0	-2.688183	-1.217717	0.000006
17	6	0	-3.721321	-2.134673	0.000006
18	6	0	-5.061172	-1.655029	0.000000
19	6	0	-5.368473	-0.305639	-0.000005
20	6	0	-4.323798	0.665214	-0.000003
21	6	0	-3.014379	0.170698	0.000002
22	6	0	-4.461332	2.084405	-0.000009
23	6	0	-3.336401	2.889036	-0.000007
24	6	0	-2.015681	2.355600	0.000000
25	6	0	-1.848111	0.985863	0.000005
26	1	0	6.406681	0.016812	0.000001

27	1	0	5.868946	-2.381944	-0.000008
28	1	0	3.536597	-3.205665	-0.000014
29	1	0	1.169330	3.036806	0.000005
30	1	0	3.456889	3.969061	0.000013
31	1	0	5.452188	2.531910	0.000010
32	1	0	-3.536597	-3.205665	0.000010
33	1	0	-5.868946	-2.381944	-0.000001
34	1	0	-6.406682	0.016812	-0.000009
35	1	0	-5.452188	2.531910	-0.000014
36	1	0	-3.456889	3.969061	-0.000013
37	1	0	-1.169330	3.036806	-0.000001

HOMO : -0.18987 a.u. = -5.16663 eV

LUMO : -0.07658 a.u. = -2.08385 eV



4l

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	-1.108567	0.476643	-0.713669
4	6	0	0.244066	0.766203	-0.850710
5	6	0	1.275698	-0.214364	-0.725794
6	6	0	0.909061	-1.533333	-0.382588
7	16	0	-1.133419	-3.468902	-0.082868
8	6	0	-2.743914	-2.829799	-0.225196
9	16	0	0.874366	2.384028	-1.182864

10	6	0	2.494234	1.744985	-1.191335
11	6	0	2.567649	0.376926	-0.961586
12	6	0	-2.789174	-1.464753	-0.463855
13	6	0	4.690538	1.178360	-1.394808
14	6	0	3.981266	-0.023254	-1.113330
15	6	0	6.069331	1.253335	-1.622934
16	6	0	6.785064	0.020718	-1.572126
17	6	0	6.106118	-1.157998	-1.325066
18	6	0	4.699453	-1.202678	-1.097390
19	6	0	-4.944225	-2.291070	-0.452658
20	6	0	3.816189	2.299391	-1.455299
21	6	0	4.350730	3.541666	-1.735979
22	6	0	5.752935	3.646753	-1.951322
23	6	0	6.595060	2.548666	-1.901628
24	6	0	-4.205490	-1.089041	-0.640080
25	6	0	-6.337064	-2.389610	-0.542695
26	6	0	-7.035858	-1.184594	-0.850118
27	6	0	-6.329915	-0.014137	-1.056892
28	6	0	-4.909132	0.054348	-0.962109
29	6	0	-4.086752	-3.397720	-0.196852
30	6	0	-4.652257	-4.643594	-0.008181
31	6	0	-6.067856	-4.765912	-0.076492
32	6	0	-6.894056	-3.685255	-0.335757
33	8	0	1.909952	-2.443359	-0.154440
34	6	0	1.830712	-3.271474	1.029423
35	6	0	3.207973	-3.393026	1.671271
36	6	0	3.707140	-2.108537	2.343653
37	6	0	5.112021	-2.249233	2.942317
38	6	0	5.614737	-0.970364	3.624070
39	6	0	7.016665	-1.117960	4.224075
40	8	0	-2.033042	1.497162	-0.803681
41	6	0	-2.353599	2.109134	0.467081
42	6	0	-3.084725	3.417169	0.204168
43	6	0	-3.468608	4.140469	1.502273
44	6	0	-4.209025	5.462121	1.259576
45	6	0	-4.592428	6.193308	2.552475

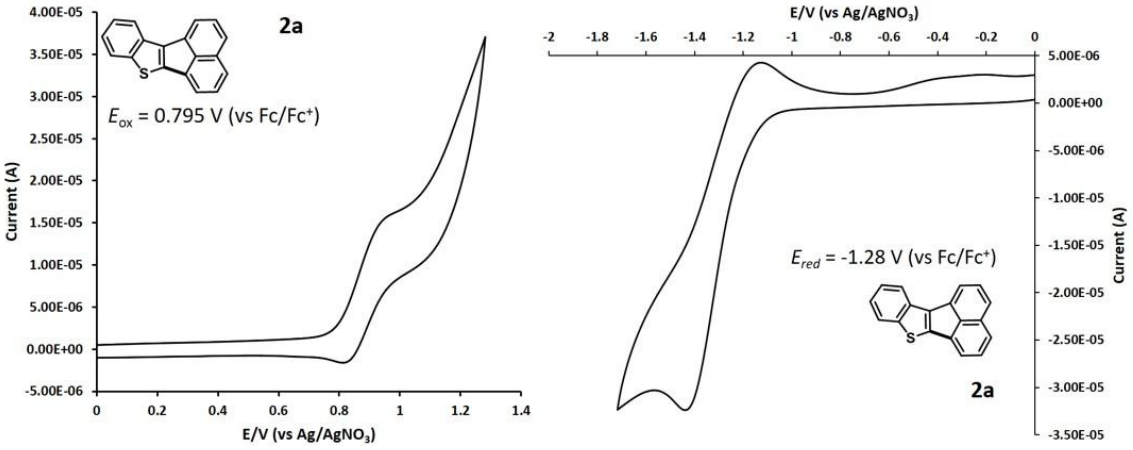
46	6	0	-5.332150	7.511670	2.303251
47	1	0	7.859046	0.009743	-1.741120
48	1	0	6.659252	-2.093514	-1.306826
49	1	0	4.207438	-2.153023	-0.928066
50	1	0	3.730223	4.431809	-1.798854
51	1	0	6.170960	4.625841	-2.169077
52	1	0	7.660182	2.672103	-2.081814
53	1	0	-8.119851	-1.192743	-0.933652
54	1	0	-6.872253	0.893868	-1.307335
55	1	0	-4.396501	0.987489	-1.165605
56	1	0	-4.046560	-5.524796	0.186531
57	1	0	-6.510109	-5.746827	0.074940
58	1	0	-7.971073	-3.824905	-0.387502
59	1	0	1.116794	-2.830960	1.734341
60	1	0	1.459994	-4.261291	0.737512
61	1	0	3.148725	-4.201236	2.414722
62	1	0	3.924754	-3.730969	0.910794
63	1	0	3.703602	-1.290720	1.613594
64	1	0	2.999531	-1.821202	3.135831
65	1	0	5.121616	-3.076425	3.668474
66	1	0	5.816866	-2.533943	2.146951
67	1	0	5.612463	-0.149265	2.894059
68	1	0	4.907439	-0.678499	4.413557
69	1	0	7.347613	-0.188748	4.701888
70	1	0	7.042665	-1.910200	4.982717
71	1	0	7.752611	-1.375645	3.452352
72	1	0	-2.973805	1.417269	1.053276
73	1	0	-1.424644	2.291174	1.022921
74	1	0	-2.442659	4.059974	-0.411743
75	1	0	-3.986323	3.214553	-0.388900
76	1	0	-4.097744	3.480891	2.117814
77	1	0	-2.562335	4.336895	2.093670
78	1	0	-3.581900	6.121568	0.641636
79	1	0	-5.117054	5.266927	0.670009
80	1	0	-5.218322	5.533173	3.169748
81	1	0	-3.684446	6.388007	3.140710

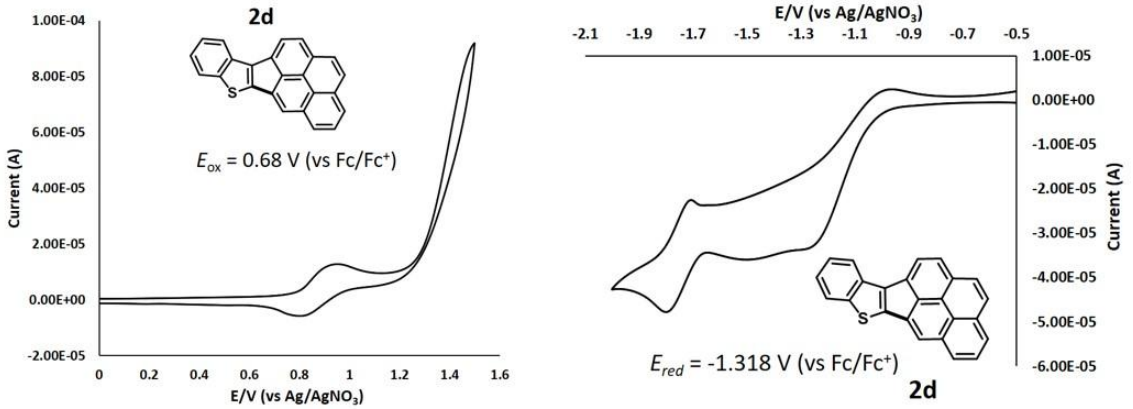
82	1	0	-5.593442	8.008176	3.244676
83	1	0	-4.716950	8.207246	1.719216
84	1	0	-6.261833	7.345002	1.745266

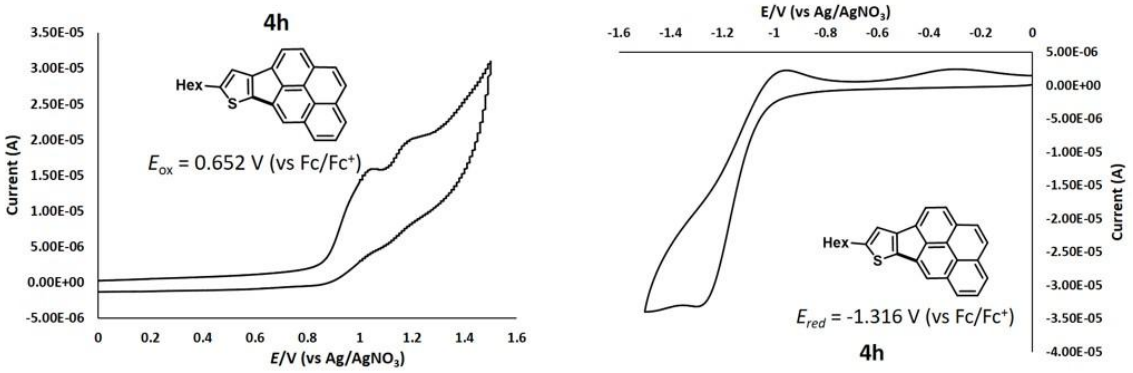
HOMO : -0.17662 a.u. = -4.80607 eV

LUMO : -0.07797 a.u. = -2.12167 eV

6. Cyclic voltammetry (CV) of products







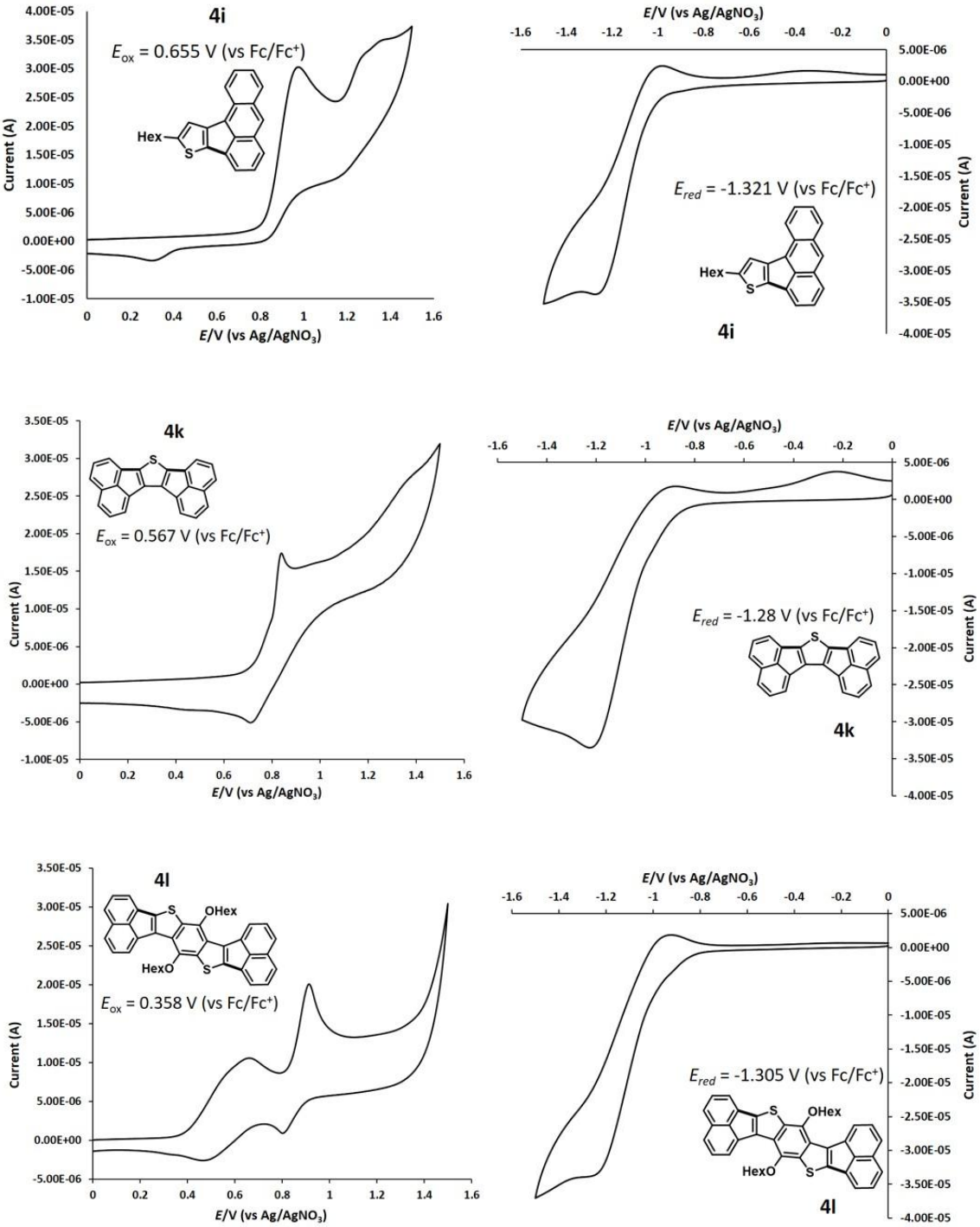
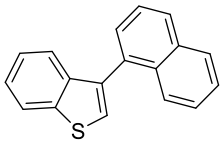


Figure S2. Cyclic voltammograms (CV) of CP-PHA products. First oxidation potentials measured by CV using $Ag/AgNO_3$ as a reference electrode, Pt wire as a counter electrode, glassy carbon as a working electrode, and Bu_4NPF_6 (0.1 M) as a supporting electrolyte in dichloromethane. The scan rate is 50 mV s-1 and the Fc/Fc^+ (-4.80 eV) was used as an external standard.

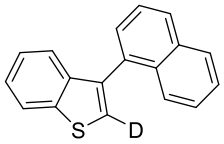
7. Analytical data of starting substrates and products

3-(Naphthalen-1-yl)benzo[*b*]thiophene (1a)



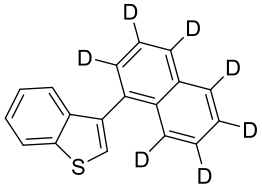
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **1a** as white solid (2.5 mmol, 650 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.94 (m, 3H), 7.73 (d, J = 8.2 Hz, 1H), 7.60-7.49 (m, 4H), 7.44-7.37 (m, 3H), 7.29 (td, J = 7.6, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.5, 136.3, 133.7, 133.6, 132.4, 128.2, 127.8, 126.1, 126.0, 125.9, 125.4, 124.9, 124.4, 124.1, 123.4, 122.6, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{18}H_{12}S$, 260.0659; Found 260.0658; Mp. 90-92 °C.

3-(Naphthalen-1-yl)benzo[*b*]thiophene-2-*d* (1a-d_1)



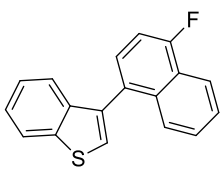
Purified by column chromatography (silica gel), [hexane/Et_2O = 20:1(v/v)] to give **1a-d_1** white solid (2.0 mmol, 520 mg, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.94 (m, 3H), 7.73 (d, J = 8.7 Hz, 1H), 7.60-7.49 (m, 3H), 7.43-7.36 (m, 3H), 7.29 (td, J = 7.6, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.5, 136.2, 133.7, 133.6, 132.4, 128.2, 127.8, 126.1, 126.0, 125.9, 125.4, 124.7 (t, J_D = 28.6 Hz), 124.4, 124.2, 123.4, 122.7, one sp^2 peak is not shown due to superimposition. HRMS [APCI] m/z: [M+nH] calc For $C_{18}H_{11}DS$, 262.0795; Found 262.0795; Mp. 91-92 °C.

3-(Naphthalen-1-yl-d_7)benzo[*b*]thiophene (1a-d_7)



Purified by column chromatography (silica gel), [hexane/Et_2O = 20:1(v/v)] to give **1a-d_7** white solid (0.8 mmol, 216 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.42 (q, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$ δ 139.9, 139.5, 136.3, 133.5, 133.4, 132.3, 124.9, 124.3, 124.1, 123.4, 122.6, sp^2 carbons adjacent to D cannot be identified due to their weal intensity and superimposition. HRMS [APCI] m/z: [M+nH] calc For $C_{18}H_5D_7S$, 268.1171; Found 268.1172; Mp. 90-92 °C.

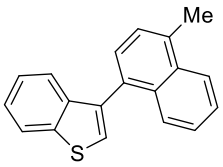
3-(4-Fluoronaphthalen-1-yl)benzo[*b*]thiophene (1b)



Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **1b** as white solid (0.35 mmol, 97.7 mg, 18% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 1H), 7.98-7.96 (m, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.48-7.35 (m, 5H), 7.31-7.28 (m, 1H), 7.24-7.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (d, J_F = 254.2 Hz), 139.9, 139.4, 135.6,

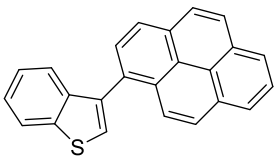
133.7 (d, J_F = 4.9 Hz), 129.6 (d, J_F = 4.7 Hz), 127.5 (d, J_F = 8.6 Hz), 127.0, 126.2, 126.2 (d, J_F = 1.9 Hz), 125.2, 124.5, 124.2, 123.8 (d, J_F = 16.4 Hz), 123.3, 122.7, 120.7 (d, J_F = 4.9 Hz), 109.1 (d, J_F = 20.3 Hz). HRMS [FD+(eiFi)] m/z: [M] calc For $C_{18}H_{11}FS$, 278.0565; Found 278.0564; Mp. 74-76 °C.

3-(4-Methylnaphthalen-1-yl)benzo[*b*]thiophene (1c)



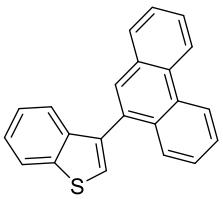
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **1c** as white solid (0.51 mmol, 142 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.57-7.53 (m, 1H), 7.46-7.37 (m, 6H), 7.30-7.26 (m, 1H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.7, 136.6, 134.6, 132.8, 132.5, 131.9, 127.5, 126.8, 126.2, 125.8, 125.7, 124.9, 124.4, 124.4, 124.1, 123.5, 122.7, 19.6. HRMS [APCI] m/z: [M+nH] calc For $C_{19}H_{14}S$, 275.0889; Found 275.0889; Mp. 59-61 °C.

3-(Pyren-1-yl)benzo[*b*]thiophene (1d)



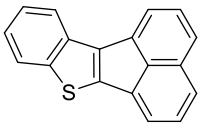
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **1d** as white solid (0.30 mmol, 98.3 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.22 (m, 2H), 8.19-8.15 (m, 3H), 8.08-7.98 (m, 5H), 7.61 (s, 1H), 7.46-7.40 (m, 2H), 7.30 (td, *J* = 7.6, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.6, 136.7, 131.2, 130.9, 130.8, 130.8, 129.6, 128.0, 127.5, 127.4, 127.2, 125.9, 125.4, 125.3, 125.1, 125.0, 124.8, 124.6, 124.6, 124.4, 124.3, 123.4, 122.7. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{14}S$, 334.0816; Found 334.0815; Mp. 164-166 °C.

3-(Phenanthren-9-yl)benzo[*b*]thiophene (1e)



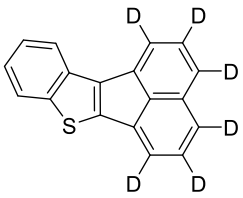
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **1e** as white solid (2.1 mmol, 656 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (m, 2H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.84 (s, 1H), 7.76-7.63 (m, 4H), 7.56 (s, 1H), 7.50-7.39 (m, 3H), 7.28 (td, *J* = 7.6, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.6, 136.4, 132.3, 131.5, 131.5, 130.5, 130.3, 128.7, 127.0, 126.9, 126.6, 126.6, 125.1, 124.5, 124.2, 123.5, 122.9, 122.7, 122.6. two sp^2 peak is not shown due to superimposition. HRMS [APCI] m/z: [M+nH] calc For $C_{22}H_{14}S$, 311.0889; Found 311.0889; Mp. 146-148 °C.

Acenaphtho[1,2-*b*]benzo[*d*]thiophene (2a)



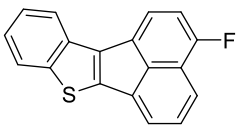
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **2a** as orange solid (0.07 mmol, 18.6 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 6.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.81-7.74 (m, 3H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.9, 139.0, 134.1, 133.6, 133.5, 133.3, 129.0, 127.7, 127.7, 127.6, 126.3, 125.1, 124.0, 124.0, 122.0, 121.9, 121.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{18}H_{10}S$, 258.0503; Found 258.0502; Mp. 120-122 °C.

Acenaphtho[1,2-*b*]benzo[*d*]thiophene-1,2,3,4,5,6-*d*$_6$ (2a-*d*$_6$)



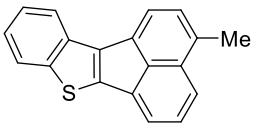
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **2a-*d*$_6$** as orange solid (0.057 mmol, 15.1 mg, 57% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.89 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.34 (td, *J* = 7.7, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.9, 138.9, 133.9, 133.5, 133.3, 128.8, 127.3 (t, J_D = 24.0 Hz), 127.2 (t, J_D = 24.0 Hz), 125.9 (t, J_D = 25.0 Hz), 125.1, 124.0, 123.9, 121.9, 121.6 (t, J_D = 25.0 Hz), 120.7 (t, J_D = 25.0 Hz), one singlet sp^2 and one triplet sp^2 peaks are not shown due to superimposition. HRMS [APCI] m/z: [M+nH] calc For $C_{18}H_4D_6S$, 265.0952; Found 265.0952; Mp. 121-123 °C.

3-Fluoroacenaphtho[1,2-*b*]benzo[*d*]thiophene (2b)



Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **2b** as orange solid (0.079 mmol, 21.8 mg, 79% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.83-7.77 (m, 2H), 7.59 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.48-7.44 (m, 1H), 7.36-7.32 (m, 1H), 7.15 (dd, *J* = 10.8, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, J_F = 260.1 Hz), 144.6, 141.1 (d, J_F = 3.8 Hz), 138.7, 134.7 (d, J_F = 5.7 Hz), 133.4 (d. J_F = 2.92 Hz), 133.2, 130.4 (d, J_F = 4.8 Hz), 128.0, 125.2, 124.2, 124.1, 122.5, 121.9, 121.5, 121.4, 120.3 (d, J_F = 19.3 Hz), 111.3 (d, J_F = 21.1 Hz). HRMS [FD+(eiFi)] m/z: [M] calc For $C_{18}H_9FS$, 276.0409; Found 276.0408; Mp. 160-162 °C.

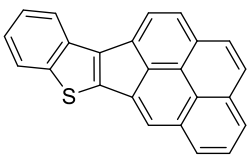
3-Methylacenaphtho[1,2-*b*]benzo[*d*]thiophene (2c)



Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **2c** as orange solid (0.075 mmol, 20.4 mg, 75% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.8 Hz,

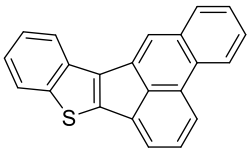
1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 6.8 Hz, 1H), 7.56 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.46 (td, *J* = 7.6, 0.8 Hz, 1H), 7.34-7.30 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.1, 139.0, 135.2, 133.9, 133.6, 133.5, 132.3, 129.2, 127.7, 127.2, 125.0, 124.6, 124.0, 123.9, 121.9, 121.6, 121.2, 18.0. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{19}H_{12}S$, 272.0659; Found 272.0658; Mp. 141-143 °C.

Benzo[*b*]benzo[10,1]acephenanthryleno[4,5-*d*]thiophene (2d)



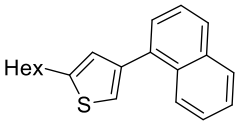
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **2d** as red solid (0.048 mmol, 15.9 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.36 (t, *J* = 7.3 Hz, 2H), 8.31-8.24 (m, 2H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.08-7.93 (m, 4H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 142.5, 139.6, 133.5, 132.3, 131.9, 131.4, 130.4, 130.1, 130.0, 129.7, 128.2, 126.8, 126.7, 126.6, 125.1, 124.4, 124.1, 123.7, 122.4, 122.3, 121.3, 119.9, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{12}S$, 332.0659; Found 332.0658; Mp. 230-232 °C.

Acephenanthryleno[4,5-*b*]benzo[*d*]thiophene (2e)



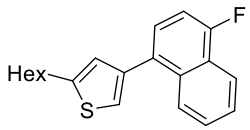
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **2e** as orange solid (0.078 mmol, 24.0 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.8 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.27-8.25 (m, 2H), 8.05 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 6.9 Hz, 1H), 7.71-7.62 (m, 3H), 7.51 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38-7.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 137.8, 133.9, 133.6, 133.6, 132.0, 130.3, 130.3, 128.0, 127.3, 127.0, 126.9, 125.3, 124.1, 124.1, 123.1, 122.7, 122.1, 122.0, 120.5, two sp^2 peaks are not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{22}H_{12}S$, 308.0659; Found 308.0659; Mp. 214-215 °C.

2-Hexyl-4-(naphthalen-1-yl)thiophene (3a)



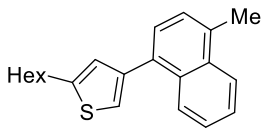
Purified by column chromatography (silica gel), [Hexane only] to give **3a** as colorless oil (1.7 mmol, 508.1 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 1H), 7.90-7.80 (m, 2H), 7.51-7.44 (m, 4H), 7.16 (d, *J* = 1.2 Hz, 1H), 7.00-6.98 (m, 1H), 2.91-2.87 (m, 2H), 1.79-1.72 (m, 2H), 1.45-1.32 (m, 6H), 0.94-0.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 140.6, 135.4, 133.8, 131.7, 128.2, 127.5, 126.7, 126.7, 126.0, 125.7, 125.3, 120.9, 31.6, 31.6, 30.1, 28.8, 22.6, 14.1 one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{20}H_{22}S$, 294.1442; Found 294.1441.

4-(4-Fluoronaphthalen-1-yl)-2-hexylthiophene (3b)



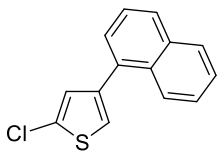
Purified by column chromatography (silica gel), [Hexane only] to give **3b** as colorless oil (1.1 mmol, 346.2 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) 1H-NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 1H), 8.07 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.58-7.50 (m, 2H), 7.39 (dd, *J* = 7.8, 5.6 Hz, 1H), 7.18-7.12 (m, 2H), 6.96-6.94 (m, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 1.76 (quint, *J* = 7.6 Hz, 2H), 1.46-1.33 (m, 6H), 0.92 (t, J = 7.1 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, J_F = 252.3 Hz), 145.9, 140.0, 133.0 (d, J_F = 4.8 Hz), 131.6 (d, J_F = 4.8Hz), 126.9, 126.6, 126.4 (d, J_F = 8.7 Hz), 126.0, 126.0 (d, J_F = 4.7 Hz), 123.8 (d, J_F = 15.5 Hz), 121.0, 120.7 (d, J_F = 5.8 Hz), 108.9 (d, J_F = 20.3 Hz), 31.7, 31.6, 30.1, 28.9, 22.6, 14.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{20}H_{21}FS$, 312.1348; Found 312.1347.

2-Hexyl-4-(4-methylnaphthalen-1-yl)thiophene (3c)



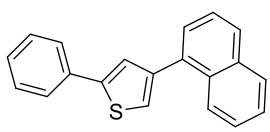
Purified by column chromatography (silica gel), [Hexane only] to give **3c** as colorless oil (0.79 mmol, 244 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.09 (m, 1H), 8.05-8.03 (m, 1H), 7.55-7.44 (m, 2H), 7.38-7.32 (m, 2H), 7.12 (d, *J* = 1.6 Hz, 1H), 6.97-6.95 (m, 1H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.72 (s, 3H), 1.75 (quint, *J* = 7.6 Hz, 2H), 1.45-1.31 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 140.9, 133.8, 133.7, 132.8, 131.8, 126.8, 126.6, 126.4, 126.2, 125.6, 124.3, 120.7, 31.7, 31.6, 30.2, 28.9, 22.6, 19.6, 14.1, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{21}H_{24}S$, 308.1598; Found 308.1598.

2-Chloro-4-(naphthalen-1-yl)thiophene (3d)



Purified by column chromatography (silica gel), [Hexane only] to give **3d** as colorless oil (1.4 mmol, 342 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 1H), 7.91-7.84 (m, 2H), 7.52-7.43 (m, 4H), 7.15-7.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 134.3, 133.9, 131.6, 130.0, 128.6, 128.5, 128.3, 127.0, 126.5, 126.1, 125.6, 125.5, 121.9. HRMS [APCl positive] m/z: [M] calc For $C_{14}H_9ClS$, 244.0108; Found 244.0108.

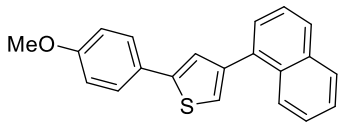
4-(Naphthalen-1-yl)-2-phenylthiophene (3e)



Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **3e** as yellow oil (1.5 mmol, 429 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.94-7.83 (m, 2H), 7.72-7.69 (m, 2H), 7.57-7.48 (m, 5H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 142.0, 135.0, 134.3, 133.8, 131.7, 128.9, 128.3, 127.9,

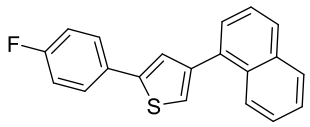
127.6, 126.8, 126.2, 125.9, 125.8, 125.6, 125.4, 122.9, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{20}H_{14}S$, 286.0816; Found 286.0815.

2-(4-Methoxyphenyl)-4-(naphthalen-1-yl)thiophene (3f)



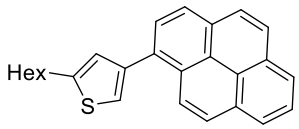
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **3f** as yellow oil (1.7 mmol, 528 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 7.8, 1.4 Hz, 1H), 7.93-7.85 (m, 2H), 7.61 (dt, J = 8.8, 2.5 Hz, 2H), 7.55-7.46 (m, 4H), 7.42 (d, J = 1.6 Hz, 1H), 7.28 (d, J = 1.2 Hz, 1H), 6.95 (dt, J = 8.4, 2.6 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 144.1, 141.9, 135.1, 133.8, 131.7, 128.3, 127.8, 127.2, 126.8, 126.2, 125.9, 125.8, 125.4, 124.7, 121.9, 114.3, 55.4, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{21}H_{16}OS$, 316.0921; Found 316.0921.

2-(4-Fluorophenyl)-4-(naphthalen-1-yl)thiophene (3g)



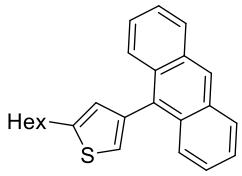
Purified by column chromatography (silica gel), [Hexane/Et_2O = 10:1 (v/v)] to give **3g** as yellow solid (1.5 mmol, 456 mg, 50% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2 Hz, 1H), 7.95-7.88 (m, 2H), 7.67-7.63 (m, 2H), 7.56-7.47 (m, 5H), 7.34 (s, 1H), 7.12 (t, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_F = 248.5 Hz), 143.1, 142.1, 134.8, 133.8, 131.7, 130.6 (d, J_F = 2.8 Hz), 128.4, 127.9, 127.5 (d, J_F = 8.7 Hz), 126.8, 126.2, 125.9, 125.8, 125.6, 125.4, 122.8, 115.9 (d, J_F = 21.2 Hz). HRMS [APCI] m/z: [M+nH] calc For $C_{20}H_{13}FS$, 305.0794; Found 305.0795; Mp. 48-50 °C.

2-Hexyl-4-(pyren-1-yl)thiophene (3h)



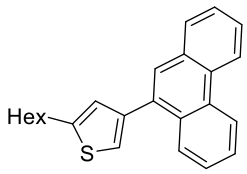
Purified by column chromatography (silica gel), [Hexane only] to give **3h** as white solid (0.76 mmol, 280 mg, 76% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 9.2 Hz, 1H), 8.20-8.16 (m, 3H), 8.09-7.99 (m, 5H), 7.29 (d, J = 1.4 Hz, 1H), 7.14-7.12 (m, 1H), 2.95 (t, J = 7.8 Hz, 2H), 1.80 (quint, J = 7.6 Hz, 2H), 1.49-1.34 (m, 6H), 0.92 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 146.0, 141.1, 132.9, 131.5, 131.0, 130.4, 128.6, 127.4, 127.3, 127.1, 126.0, 125.3, 125.0, 125.0, 124.9, 124.8, 124.6, 121.4, 31.7, 31.6, 30.2, 28.9, 22.6, 14.1, two sp^2 peaks are not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{26}H_{24}S$, 368.1598; Found 368.1598; Mp. 50-53 °C.

4-(Anthracen-9-yl)-2-hexylthiophene (3i)



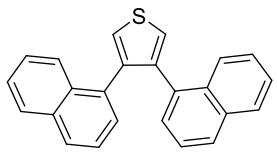
Purified by column chromatography (silica gel), [Hexane only] to give **3i** as pale orange solid (0.2 mmol, 70.1 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.86 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.48-7.36 (m, 4H), 7.14 (d, *J* = 1.4 Hz, 1H), 6.90-6.89 (m, 1H), 2.94 (t, *J* = 7.3 Hz, 2H), 1.80 (quint, *J* = 7.6 Hz, 2H), 1.48-1.33 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 137.9, 132.6, 131.3, 130.7, 128.3, 127.9, 126.8, 126.5, 125.3, 125.1, 122.5, 31.7, 31.6, 30.1, 28.8, 22.6, 14.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{24}S$, 344.1598; Found 344.1598; Mp. 60-62 °C.

2-Hexyl-4-(phenanthren-9-yl)thiophene (3j)



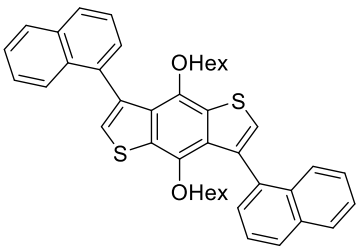
Purified by column chromatography (silica gel), [Hexane only] to give **3j** as colorless oil (2.1 mmol, 709 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.71 (d, *J* = 8.7 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.75 (s, 1H), 7.70-7.56 (m, 4H), 7.23 (d, *J* = 1.4 Hz, 1H), 7.03 (d, *J* = 0.8 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 1.77 (quint, *J* = 8.0 Hz, 2H), 1.47-1.27 (m, 6H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 140.7, 134.0, 131.6, 131.2, 130.6, 129.9, 128.5, 127.3, 126.8, 126.7, 126.5, 126.4, 122.8, 122.5, 121.1, 31.7, 31.6, 30.2, 28.9, 22.6, 14.1, two sp^2 peaks are not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{24}S$, 344.1598; Found 344.1598.

3,4-Di(naphthalen-1-yl)thiophene (3k)



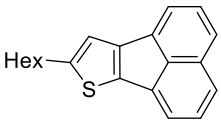
Purified by column chromatography (silica gel), [Hexane/Et_2O = 10:1 (v/v)] to give **3k** as white solid (0.55 mmol, 185 mg, 27% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.49 (s, 2H), 7.37-7.28 (m, 4H), 7.19-7.12 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 134.2, 133.4, 132.3, 128.0, 127.7, 127.4, 126.0, 125.7, 125.4, 125.0, 124.9. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{16}S$, 336.0972; Found 336.0971; Mp. 232-233 °C.

4,8-Bis(hexyloxy)-3,7-di(naphthalen-1-yl)benzo[1,2-*b*:4,5-*b*']dithiophene (3l)



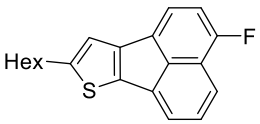
Purified by recrystallization [Hexane/$CHCl_3$] to give **3l** as pale yellow solid (0.67 mmol, 430 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.92 (m, 4H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.61-7.48 (m, 6H), 7.44-7.37 (m, 2H), 7.30 (s, 2H), 3.48-3.38 (m, 4H), 1.18-1.09 (m, 4H), 0.98-0.91 (m, 4H), 0.85-0.59 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 135.2, 134.7, 133.3, 132.7, 130.8, 127.9, 127.9, 127.6, 127.5, 126.4, 126.4, 126.1, 126.0, 125.7, 125.0, 74.5, 31.4, 29.0, 24.9, 22.4, 14.0. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{42}H_{42}O_2S_2$, 642.2626; Found 642.2624; Mp. 150-152 °C.

8-Hexylacenaphtho[1,2-*b*]thiophene (4a)



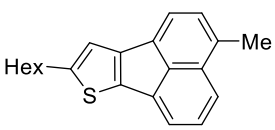
Purified by column chromatography (silica gel), [Hexane only] to give **4a** as orange oil (0.08 mmol, 23.4 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.65 (d, *J* = 6.9 Hz, 1H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.52-7.48 (m, 2H), 7.10 (s, 1H), 2.90 (t, *J* = 7.3 Hz, 2H), 1.76 (quint, *J* = 7.6 Hz, 2H), 1.45-1.29 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 145.1, 138.6, 134.3, 134.0, 133.0, 129.2, 127.6, 127.5, 126.0, 125.9, 120.5, 119.7, 117.3, 31.7, 31.6, 31.1, 28.7, 22.6, 14.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{20}H_{20}S$, 292.1285; Found 292.1285.

3-Fluoro-8-hexylacenaphtho[1,2-*b*]thiophene (4b)



Purified by column chromatography (silica gel), [Hexane only] to give **4b** as orange oil (0.082 mmol, 25.7 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.54-7.48 (m, 2H), 7.10-7.04 (m, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 1.75 (quint, *J* = 7.6 Hz, 2H), 1.45-1.32 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 159.2 (d, J_F = 259.1 Hz), 150.7, 144.7, 138.0 (d, J_F = 2.9 Hz), 134.5 (d, J_F = 6.7 Hz), 133.7(d, J_F = 2.9 Hz), 130.6 (d, J_F = 3.8 Hz), 127.9, 120.8 (d, J_F = 8.6 Hz), 120.4 (d, J_F = 18.3 Hz), 120.3, 119.6, 117.1, 111.2 (d, J_F = 22.1 Hz), 31.7, 31.6, 31.1, 28.7, 22.6, 14.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{20}H_{19}FS$, 310.1191; Found 310.1190.

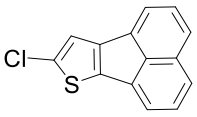
8-Hexyl-3-methylacenaphtho[1,2-*b*]thiophene (4c)



Purified by column chromatography (silica gel), [Hexane only] to give **4c** as orange oil (0.07 mmol, 21.4 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.06 (s, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.74 (s, 3H), 1.76 (quint, *J* = 7.6 Hz, 2H), 1.45-1.32 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

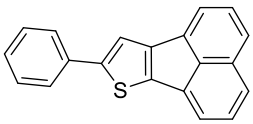
δ 149.9, 145.1, 138.0, 134.7, 134.3, 133.3, 132.5, 129.4, 127.5, 127.2, 122.9, 120.6, 119.4, 117.2, 31.7, 31.6, 31.1, 28.8, 22.6, 18.1, 14.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{21}H_{22}S$, 306.1442; Found 306.1441.

8-Chloroacenaphtho[1,2-*b*]thiophene (4d)



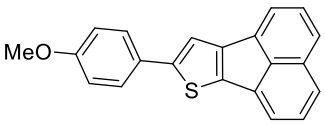
Purified by column chromatography (silica gel) [Hexane only], then further purified by gel permeation chromatography (GPC) to give **4d** as yellow solid (0.04 mmol, 9.0 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.53 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.2, 133.7, 133.4, 132.1, 131.9, 129.4, 127.9, 127.8, 126.9, 126.8, 121.3, 120.6, 119.9. HRMS [APCl positive] m/z: [M] calc For $C_{14}H_7ClS$, 241.9951; Found 241.9951; Mp. 108-110 °C.

8-Phenylacenaphtho[1,2-*b*]thiophene (4e)



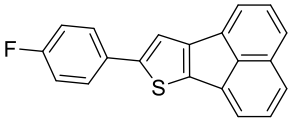
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **4e** as yellow solid (0.085 mmol, 24.1 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.70 (m, 6H), 7.66 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.1, 140.2, 135.0, 133.9, 133.6, 133.2, 129.3, 129.0, 127.8, 127.6, 127.5, 126.5, 126.3, 125.5, 120.8, 120.4, 116.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{20}H_{12}S$, 284.0659; Found 284.0659; Mp. 156-158 °C.

8-(4-Methoxyphenyl)acenaphtho[1,2-*b*]thiophene (4f)



Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **4f** as yellow solid (0.082 mmol, 25.7 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.72 (m, 3H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.64-7.60 (m, 2H), 7.56-7.52 (m, 3H), 6.96 (dt, *J* = 9.2, 2.8 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 147.8, 146.2, 139.3, 134.0, 133.7, 133.1, 129.3, 127.9, 127.8, 127.6, 126.8, 126.3, 126.3, 120.8, 120.1, 115.2, 114.4, 55.4. HRMS [APCI] m/z: [M+nH] calc For $C_{21}H_{14}OS$, 315.0838; Found 315.0838; Mp. 188-190 °C.

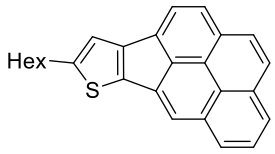
8-(4-Fluorophenyl)acenaphtho[1,2-*b*]thiophene (4g)



Purified by column chromatography (silica gel), [Hexane/Et_2O = 5:1 (v/v)] to give **4f** as yellow solid (0.086 mmol, 26.0 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.73 (m, 3H), 7.70 (d, *J* = 6.9 Hz, 1H), 7.67-7.62 (m, 2H), 7.57-7.53 (m, 3H), 7.15-7.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

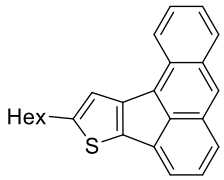
162.3 (d, J_F = 248.5 Hz), 146.5, 146.1, 140.1, 133.8, 133.5, 133.1, 131.3 (d, J_F = 3.8Hz), 129.3, 127.7 (d, J_F = 11.5 Hz), 127.2, 127.1, 126.6, 126.4, 120.9, 120.4, 116.1, 115.9 (d, J_F = 22.1 Hz). HRMS [APCI] m/z: [M+nH] calc For $C_{20}H_{11}FS$, 303.0638; Found 303.0638; Mp. 175-176 °C.

8-Hexylbenzo[10,1]acephenanthryleno[5,4-*b*]thiophene (4h)



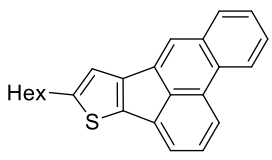
Purified by column chromatography (silica gel), [Hexane/Et_2O = 10:1 (v/v)] to give **4h** as orange solid (0.05 mmol, 18.3 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.8 Hz, 1H), 8.27 (s, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.11-7.97 (m, 5H), 7.23 (s, 1H), 2.97 (t, *J* = 7.6 Hz, 2H), 1.81 (quint, *J* = 7.6 Hz, 2H), 1.51-1.33 (m, 6H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 148.4, 136.8, 132.5, 131.9, 131.7, 130.6, 130.1, 129.8, 129.0, 127.2, 126.7, 126.5, 126.4, 124.2, 121.9, 121.5, 120.8, 119.6, 117.5, 31.7, 31.6, 31.3, 28.8, 22.6, 14.1. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{26}H_{22}S$, 366.1442; Found 366.1441; Mp. 80-82 °C.

2-Hexylaceanthryleno[2,1-*b*]thiophene (4i)



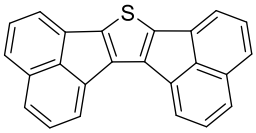
Purified by column chromatography (silica gel), [Hexane/Et_2O = 10:1 (v/v)] to give **4i** as red solid (0.066 mmol, 17.1 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.7 Hz, 1H), 8.34 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 6.4 Hz, 1H), 7.61-7.51 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.8 Hz, 2H), 1.82 (quint, *J* = 7.6 Hz, 2H), 1.51-1.34 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 145.3, 136.9, 134.1, 133.9, 130.6, 130.2, 129.9, 127.6, 127.4, 127.1, 126.6, 126.5, 124.7, 124.6, 120.5, 118.6, 31.8, 31.6, 31.3, 28.8, 22.6, 14.1, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{22}S$, 342.1442; Found 344.1441; Mp. 85-87 °C.

10-Hexylacephenanthryleno[4,5-*b*]thiophene (4j)



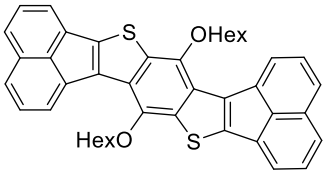
Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **4j** as yellow solid (0.086 mmol, 29.4 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.6 Hz, 1H), 8.31-8.27 (m, 1H), 7.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.93 (s, 1H), 7.67-7.57 (m, 4H), 7.15 (s, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 1.78 (quint, *J* = 7.6, 2H), 1.49-1.32 (m, 6H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.9, 141.1, 134.1, 133.9, 133.1, 132.2, 130.3, 130.1, 128.0, 126.9, 126.7, 123.1, 121.9, 120.4, 118.6, 117.4, 31.7, 31.6, 31.1, 28.8, 22.6, 14.1, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{22}S$, 342.1442; Found 342.1441; Mp. 70-72 °C.

Diacenaphtho[1,2-*b*:1',2'-*d*]thiophene (4k)



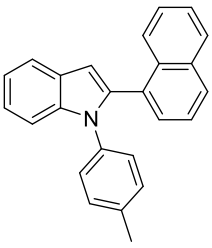
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 5:1 (v/v)] to give **4k** as red solid (0.058 mmol, 19.2 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.8 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 6.4 Hz, 2H), 7.67 (d, *J* = 6.8 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 138.3, 134.3, 133.5, 133.3, 129.4, 127.9, 127.7, 126.7, 126.5, 122.2, 120.2. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{12}S$, 332.0659; Found 332.0659; Mp. 270-272 °C.

Compound 4l



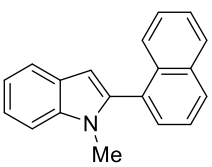
Purified by recrystallization [Hexane/$CHCl_3$] to give **4l** as red solid (0.027 mmol, 17.2 mg, 27% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.9 Hz, 2H), 7.85-7.78 (m, 6H), 7.66-7.59 (m, 4H), 4.42-4.36 (m, 4H), 2.12 (quint, *J* = 7.2 Hz, 4H), 1.68 (quint, *J* = 7.6 Hz, 4H), 1.49-1.42 (m, 9H), 0.98 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.0, 141.5, 137.4, 136.3, 133.9, 133.1(8), 133.1(2), 128.8, 128.0, 127.7, 127.4, 126.3, 126.0, 123.9, 121.6, 74.5, 31.9, 30.6, 25.8, 22.9, 14.2. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{42}H_{38}O_2S_2$, 638.2313; Found 638.2312; Mp. 204-206 °C.

2-(Naphthalen-1-yl)-1-(*p*-tolyl)-1*H*-indole (5a)



Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 5:1 (v/v)] to give **5a** as white solid (0.97 mmol, 324 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.84-7.72 (m, 3H), 7.47-7.31 (m, 5H), 7.24-7.20 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.82 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.2, 136.5, 135.5, 133.4, 132.6, 130.5, 129.4, 129.1, 128.2, 128.1, 128.0, 127.1, 126.2, 126.1, 125.8, 124.8, 122.1, 120.5, 120.4, 110.7, 105.5, 20.9. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{25}H_{19}N$,333.1517; Found 333.1517; Mp. 101-103 °C.

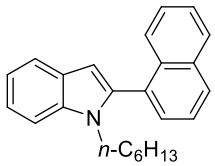
1-Methyl-2-(naphthalen-1-yl)-1*H*-indole (5b)



Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 5:1 (v/v)] to give **5b** as white solid (1.7 mmol, 435.1 mg, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.94 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.60-7.51 (m, 3H), 7.48-7.42 (m, 2H), 7.32 (td, *J* = 7.7, 1.1 Hz, 1H), 7.23-7.20 (m, 1H), 6.65 (s, 1H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 137.6, 133.5, 132.9, 130.5, 128.9, 128.2, 128.0, 126.6, 126.1, 125.2, 121.5, 120.5, 119.8, 109.5, 103.0, 30.8. HRMS [FD+(eiFi)]

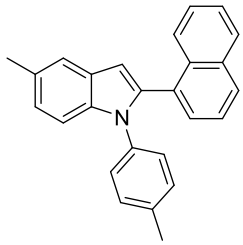
m/z: [M] calc For $C_{19}H_{15}N$, 257.1204; Found 257.1204; Mp. 109-110 °C.

1-Hexyl-2-(naphthalen-1-yl)-1*H*-indole (5c)



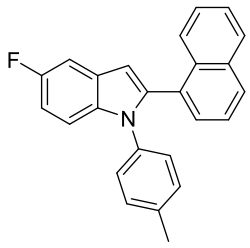
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 10:1 (v/v)] to give **5c** as colorless oil (5.2 mmol, 1711 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.94 (m, 1H), 7.93 (d, J = 8.4 Hz, 1H) 7.71 (d, J = 8.4 Hz, 2H), 7.59-7.55 (m, 2H), 7.52-7.50 (m, 1H), 7.45-7.41 (m, 2H), 7.28 (t, J = 7.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.60 (d, J = 1.2 Hz, 1H), 4.04 (quint, J = 7.2 Hz, 1H), 3.77 (quint, J = 7.2 Hz, 1H), 1.55-1.50 (m, 2H), 1.06-0.95 (m, 6H), 0.71 (td, J = 7.2, 1.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.8, 136.7, 133.5, 133.0, 130.8, 128.9, 128.9, 128.2, 128.2, 126.5, 126.1, 126.1, 125.1, 121.3, 120.5, 119.6, 109.9, 103.3, 44.0, 31.1, 29.8, 26.3, 22.3, 13.8. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{24}H_{25}N$, 327.1987; Found 327.1986.

5-Methyl-2-(naphthalen-1-yl)-1-(*p*-tolyl)-1*H*-indole (5d)



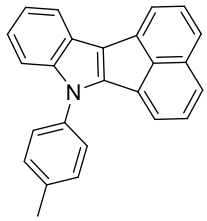
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 5:1 (v/v)] to give **5d** as white solid (0.3 mmol, 113 mg, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.53-7.51 (m, 1H), 7.46-7.30 (m, 4H), 7.26 (d, J = 8.8 Hz, 1H), 7.07-6.97 (m, 5H), 6.73 (s, 1H), 2.51 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.6, 136.4, 135.7, 133.4, 132.7, 130.7, 129.8, 129.5, 129.1, 128.4, 128.2, 128.0, 127.0, 126.3, 126.2, 125.8, 124.8, 123.7, 120.1, 110.4, 105.2, 21.4, 21.0. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{26}H_{21}N$, 347.1674; Found 347.1673; Mp. 111-113 °C.

5-Fluoro-2-(naphthalen-1-yl)-1-(*p*-tolyl)-1*H*-indole (5e)



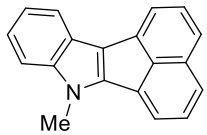
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 5:1 (v/v)] to give **5e** as white solid (0.48 mmol, 168 mg, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H),7.47-7.30 (m, 5H), 7.26 (dd, J = 9.2, 4.6 Hz, 1H), 7.04-6.93 (m, 5H), 6.76 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4 (d, J_F = 235.9 Hz), 140.2, 136.8, 135.3, 134.8, 133.4, 132.5, 130.2, 129.6, 129.1, 128.5, 128.3 (d, J_F = 10.6 Hz), 128.1, 127.0, 126.3, 126.1, 125.9, 124.8, 111.4 (d, J_F = 9.7 Hz), 110.3 (d, J_F = 26.1 Hz), 105.4 (d, J_F = 3.9 Hz), 105.1 (d, J_F = 24.0 Hz), 21. 0. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{25}H_{18}FN$, 351.1423; Found 351.1422; Mp. 103-104 °C.

7-(*p*-Tolyl)-7*H*-acenaphtho[1,2-*b*]indole (6a)



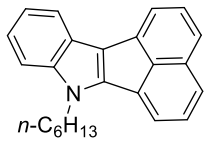
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 2:1 (v/v)] to give **6a** as red solid (0.065 mmol, 21.5 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 6.5 Hz, 1H), 7.70 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.61 (t, *J* = 8.2 Hz, 3H), 7.53 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.44-7.36 (m, 5H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.18 (td, *J* = 7.7, 1.0 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.5, 142.1, 137.7, 135.4, 133.5, 132.8, 130.4, 129.4, 129.2, 128.0, 127.5, 126.9, 125.7, 124.7, 123.2, 122.0, 121.4, 120.8, 120.7, 120.3, 119.6, 111.5, 21.3. HRMS [APCI] m/z: [M+nH] calc For $C_{25}H_{17}N$, 332.1433; Found 332.1434; Mp. 114-115 °C.

7-Methyl-7*H*-acenaphtho[1,2-*b*]indole (6b)



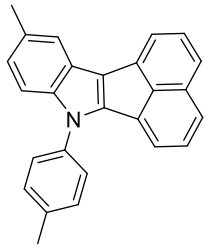
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 5:1 (v/v)] to give **6b** as red solid (0.039 mmol, 9.9 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85-7.73 (m, 4H), 7.60-7.50 (m, 3H), 7.38-7.36 (m, 1H), 7.24-7.19 (m, 2H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.0, 133.8, 132.9, 129.6, 129.2, 128.1, 127.3, 126.9, 124.1, 122.8, 121.4, 120.6, 119.8(4), 119.8(1), 119.5, 119.1, 110.2, 31.5. HRMS [APCI] m/z: [M+nH] calc For $C_{19}H_{13}N$, 256.1120; Found 256.1121; Mp. 191-193 °C.

7-Hexyl-7*H*-acenaphtho[1,2-*b*]indole (6c)



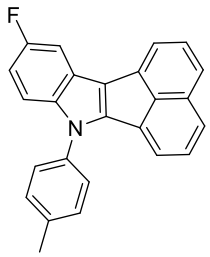
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 10:1 (v/v)] to give **6c** as red solid (0.03 mmol, 9.7 mg, 30% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86-7.83 (m, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 6.9 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.53-7.50 (m, 2H), 7.39-7.36 (m, 1H), 7.22-7.19 (m, 2H), 4.43 (t, *J* = 7.2 Hz, 2H), 2.00 (quint, *J* = 7.5 Hz, 2H), 1.46 (quint, *J* = 7.5 Hz, 2H), 1.36-1.26 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 141.5, 134.0, 133.0, 129.7, 129.3, 128.2, 127.3, 127.0, 124.1, 123.0, 121.3, 120.6, 120.0, 119.8, 119.7, 119.4, 110.5, 45.5, 31.5, 29.9, 26.9, 22.5, 14.0. HRMS [APCI] m/z: [M+nH] calc For $C_{24}H_{23}N$, 326.1903; Found 326.1903; Mp. 83-85 °C.

10-Methyl-7-(*p*-tolyl)-7*H*-acenaphtho[1,2-*b*]indole (6d)



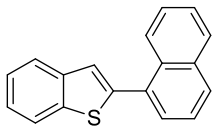
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 2:1 (v/v)] to give **6d** as red solid (0.061 mmol, 21.0 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.4 Hz, 1H), 7.69 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.61-7.58 (m, 3H), 7.53 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.43-7.34 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 8.8, 1.2 Hz, 1H), 2.54 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 140.6, 137.5, 135.7, 133.6, 132.9, 130.8, 130.3, 129.6, 129.3, 128.0, 127.3, 126.9, 125.6, 124.5, 123.6, 123.5, 120.5, 120.4, 120.1, 119.4, 111.2, 21.5, 21.2. HRMS [APCI] m/z: [M+nH] calc For $C_{26}H_{19}N$, 346.1590; Found 346.1590; Mp. 130-131 °C.

10-Fluoro-7-(*p*-tolyl)-7*H*-acenaphtho[1,2-*b*]indole (6e)



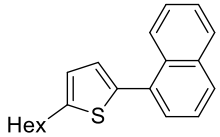
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 2:1 (v/v)] to give **6e** as red solid (0.06 mmol, 20.9 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.70 (m, 2H), 7.63-7.50 (m, 5H), 7.44-7.35 (m, 4H), 7.30 (dd, *J* = 8.8, 4.4 Hz, 1H), 6.90 (td, *J* = 8.8, 2.8 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, J_F = 237.9 Hz), 146.0, 138.7, 138.0, 135.3, 133.1, 132.8, 130.5, 129.4, 129.1, 128.1, 127.8, 126.9, 125.7, 124.8, 123.4 (d, J_F = 9.6 Hz), 120.8, 120.4 (d, J_F = 4.8 Hz), 120.2, 112.2 (d, J_F = 9.6 Hz), 110.0 (d, J_F = 26.1 Hz), 104.6 (d, J_F = 24.0 Hz), 21.3. HRMS [APCI] m/z: [M+nH] calc For $C_{25}H_{16}FN$, 350.1339; Found 350.1339; Mp. 146-148 °C.

2-(Naphthalen-1-yl)benzo[*b*]thiophene (1a')



Purified by column chromatography (silica gel), [Hexane/Et_2O = 20:1 (v/v)] to give **1a'** as white solid (2.9 mmol, 777 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 6.9 Hz, 1H), 7.95-7.85 (m, 4H), 7.67 (d, *J* = 6.9 Hz, 1H), 7.56-7.37 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.2, 140.1, 133., 132.3, 131.7, 128.8, 128.4, 128.3, 126.6, 126.1, 125.7, 125.1, 124.4, 124.2, 124.0, 123.5, 122.0. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{18}H_{12}S$, 260.0659; Found 260.0659; Mp. 121-122 °C.

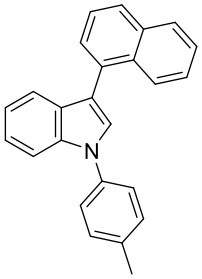
2-Hexyl-5-(naphthalen-1-yl)thiophene (3a')



Purified by column chromatography (silica gel), [Hexane only]to give **3a'** as colorless oil (0.89 mmol, 263 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.31 (m, 1H), 7.92-7.88 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.59-7.47 (m, 4H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.87 (d, *J* = 3.7 Hz, 1H), 2.91 (t, *J* = 7.8 Hz, 2H), 1.78 (quint, *J* = 7.6 Hz, 2H), 1.50-1.35 (m, 6H), 0.94 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100

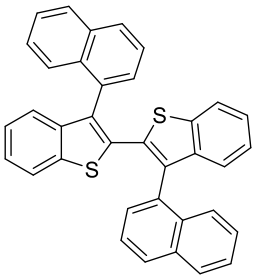
MHz, $CDCl_3$) δ 146.4, 139.0, 133.9, 132.9, 131.8, 128.3, 128.0, 127.9, 127.0, 126.3, 125.9, 125.2, 124.2, 31.7, 31.6, 30.2, 28.9, 22.6, 14.1 one sp2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{20}H_{22}S$, 294.1442; Found 294.1441.

3-(Naphthalen-1-yl)-1-(*p*-tolyl)-1*H*-indole (5a')



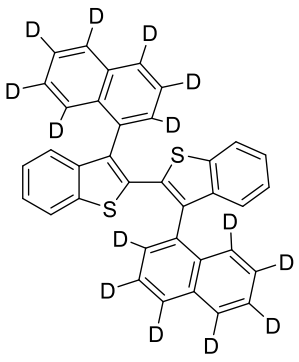
Purified by column chromatography (silica gel), [Hexane/CH_2Cl_2 = 10:1 (v/v)] to give **5a'** as white solid (2.3 mmol, 777 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.68-7.64 (m, 2H), 7.59-7.50 (m, 6H), 7.45-7.41 (m, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31-7.27 (m, 1H), 7.17 (td, *J* = 7.6, 0.9 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 136.4, 136.1, 133.9, 132.5, 132.4, 130.2, 128.8, 128.2, 127.7, 127.2(9), 127.2(4), 126.5, 125.7, 125.5, 124.3, 122.6, 120.6, 120.4, 117.1, 110.7, 21.0, one sp^2 peak is not shown due to superimposition. HRMS [FD+(eiFi)] m/z: [M] calc For $C_{25}H_{19}N$, 333.1517; Found 333.1516; Mp. 62-64 °C.

3,3'-Di(naphthalen-1-yl)-2,2'-bibenzo[*b*]thiophene (1a/1a dimer)



Purified by GPC to give **1a/1a dimer** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.50-7.36 (m, 4H), 7.30-7.14 (m, 8H), 7.12-7.07 (m, 2H), 7.02-7.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.2, 139.7, 139.6, 134.9, 134.5, 133.6, 133.5, 133.3, 132.6(9), 132.6(6), 132.3(7), 132.3(2), 129.1, 128.7, 128.3, 128.1, 128.0, 125.9, 125.8(5), 125.8(1), 125.7(4), 125.7(2), 125.5, 125.2, 124.7, 124.2, 123.8, 121.7, 121.6. HRMS (MALDI): calcd for $C_{36}H_{22}S_2^+[M]^+$, 518.1157; Found 518.1157; Mp. 242-244 °C.

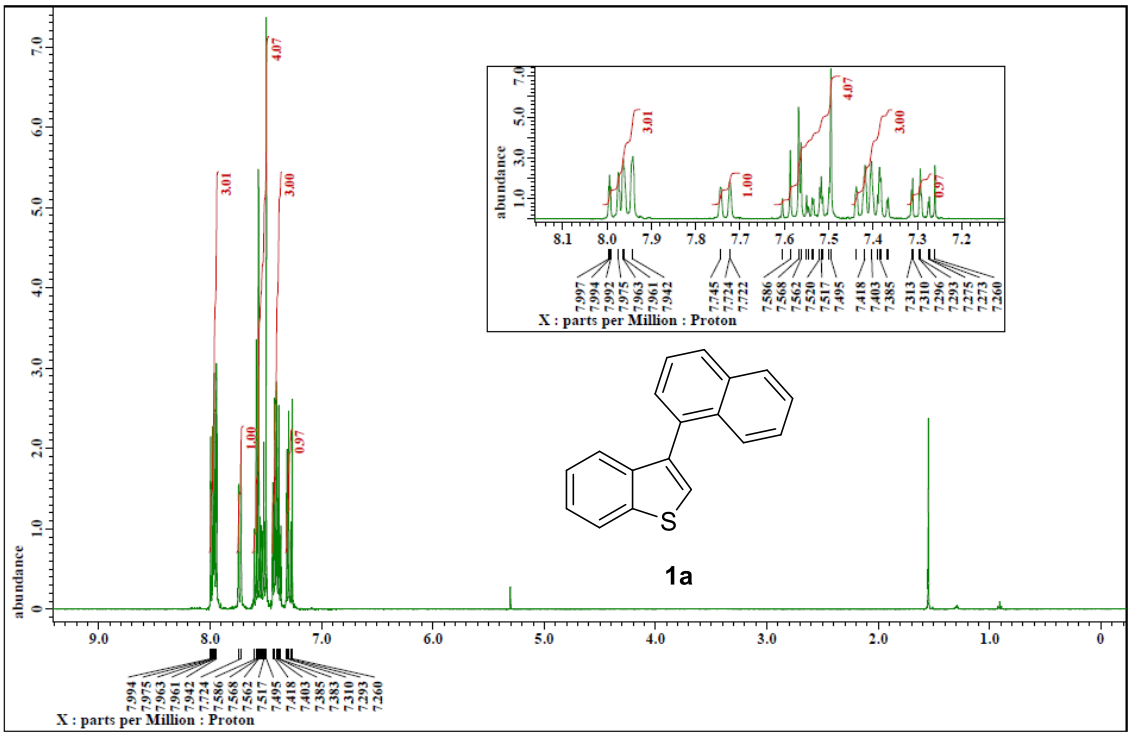
3,3'-Bis(naphthalen-1-yl-*d*$_7$)-2,2'-bibenzo[*b*]thiophene (1a-*d*$_7$/1a-*d*$_7$ dimer)



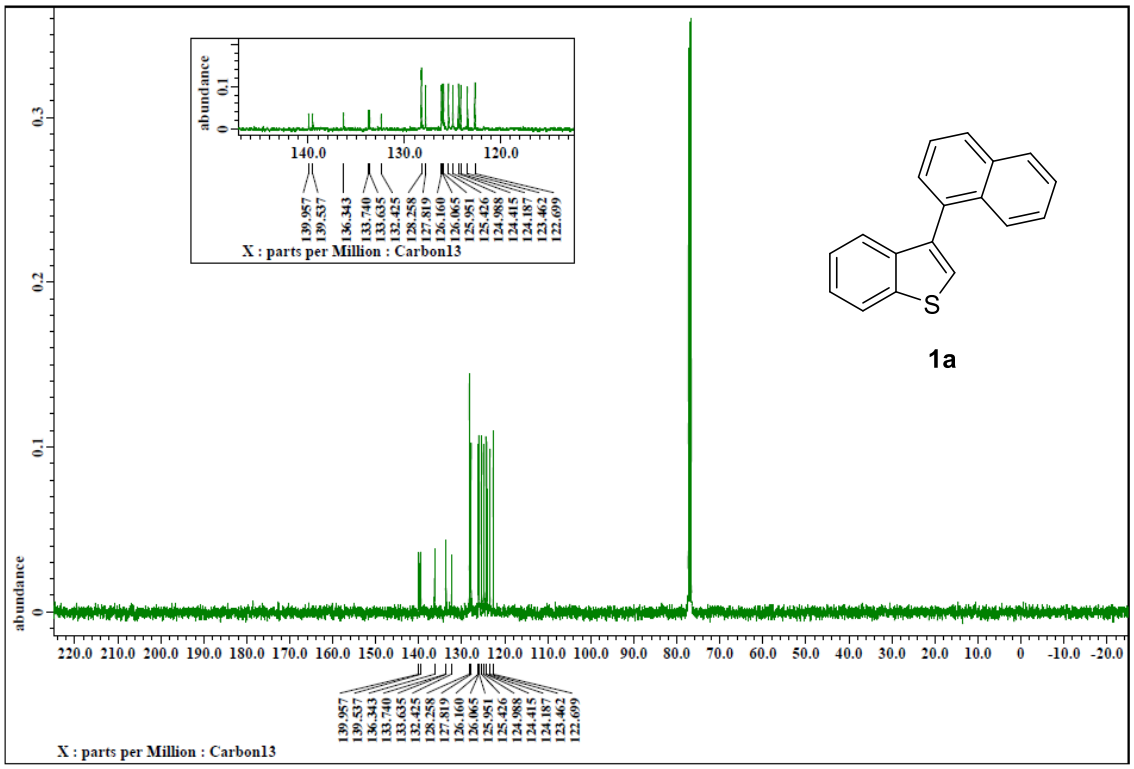
Purified by GPC to give **1a-*d*$_7$/1a-*d*$_7$ dimer** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 2H), 7.11-7.07 (m, 2H), 7.01 (d, *J* = 9.2 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.3, 139.7, 139.6, 134.9, 134.5, 133.5, 133.4, 133.2(9), 133.2(6) 132.5(9), 132.5(2), 132.2, 132.1, 124.7, 124.2, 123.8, 121.7, 121.6, sp^2 carbons adjacent to D cannot be identified due to their weal intensity and superimposition. HRMS (MALDI): calcd for $C_{36}H_8D_{14}S_2^+[M]^+$, 532.2036; Found 532.2036; Mp. 243-245 °C.

8. ^{1}H and ^{13}C NMR spectra of starting substrates and products

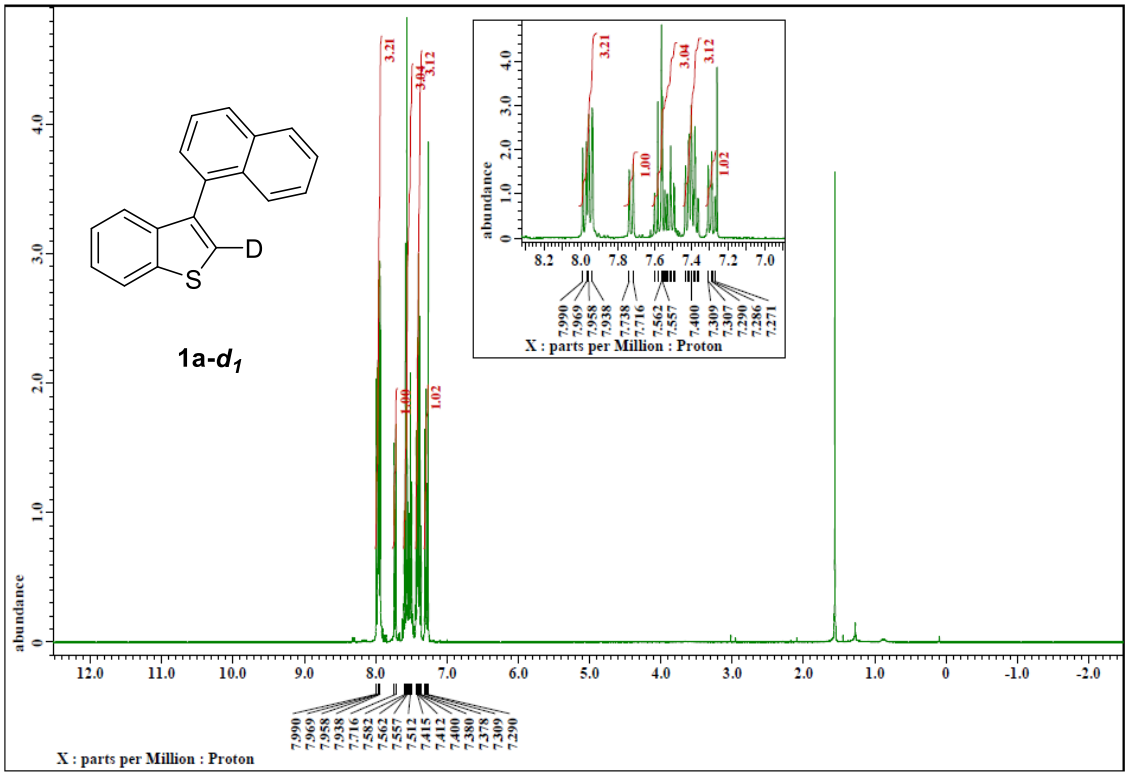
^{1}H NMR (400 MHz, $CDCl_3$)



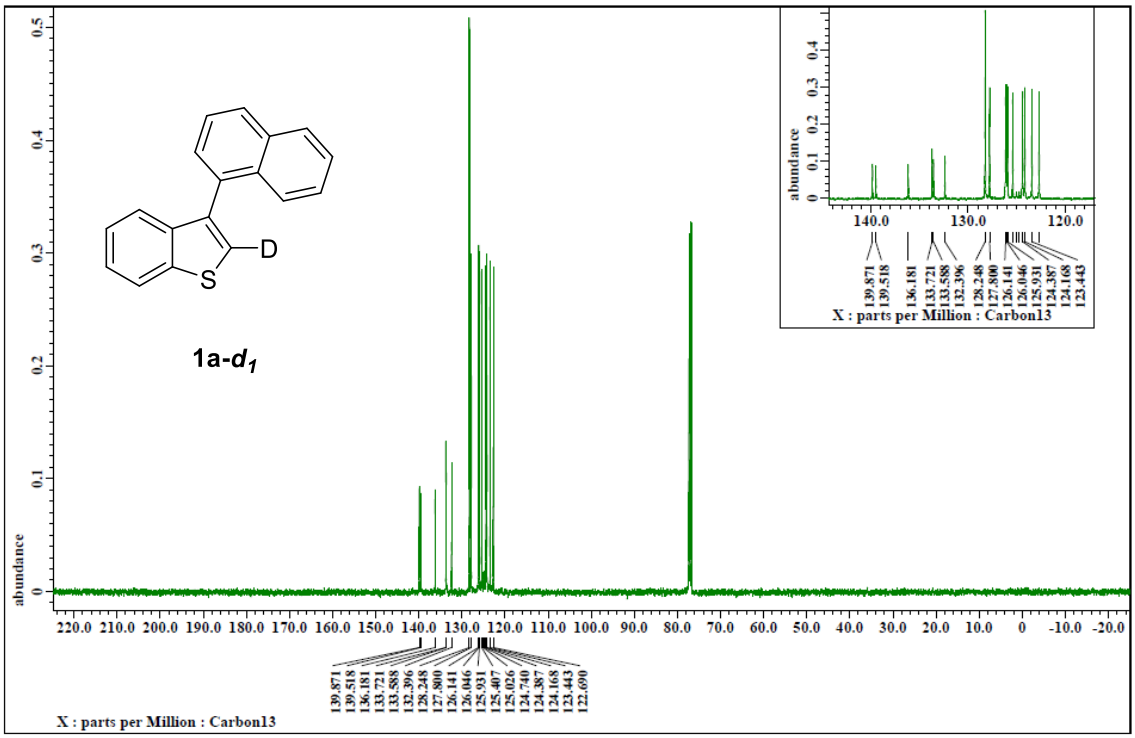
^{13}C NMR (100 MHz, $CDCl_3$)



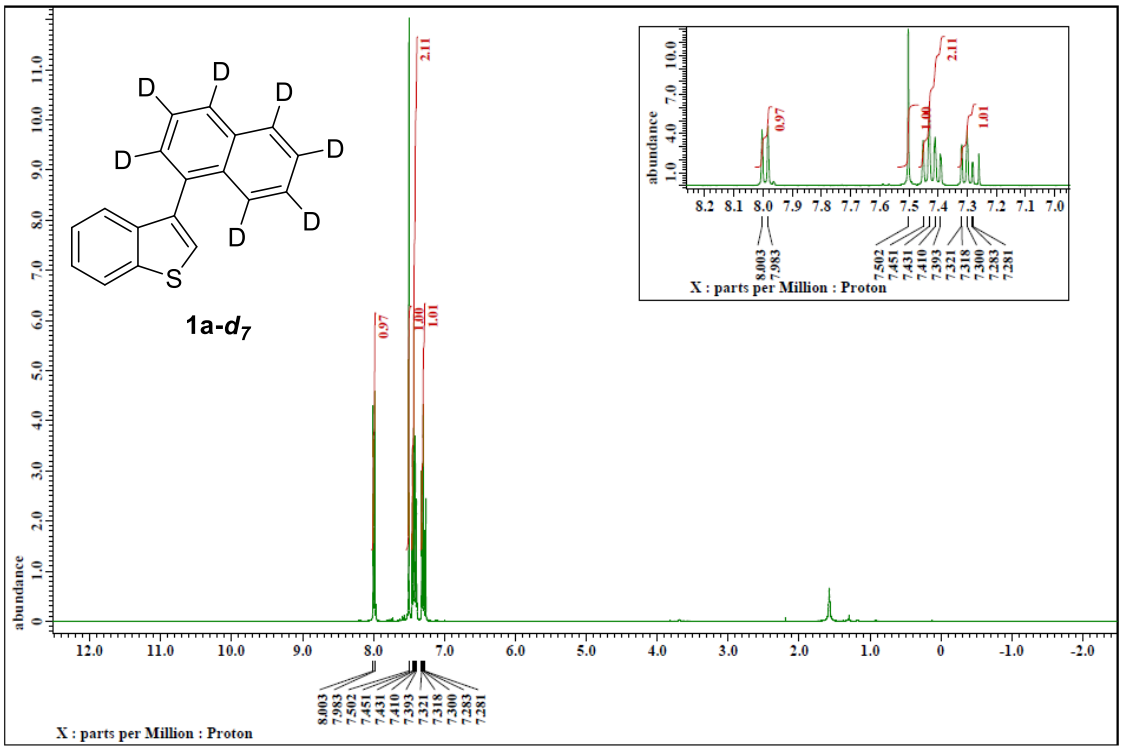
^{1}H NMR (400 MHz, $CDCl_3$)



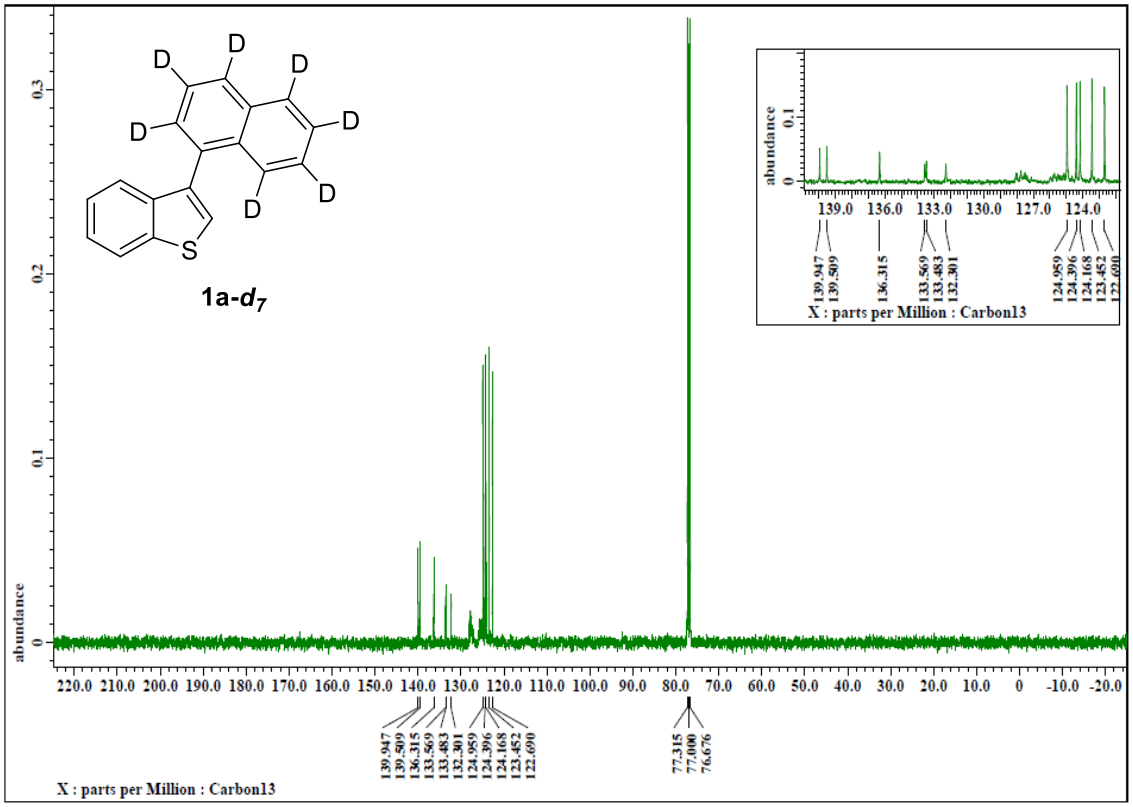
^{13}C NMR (100 MHz, $CDCl_3$)



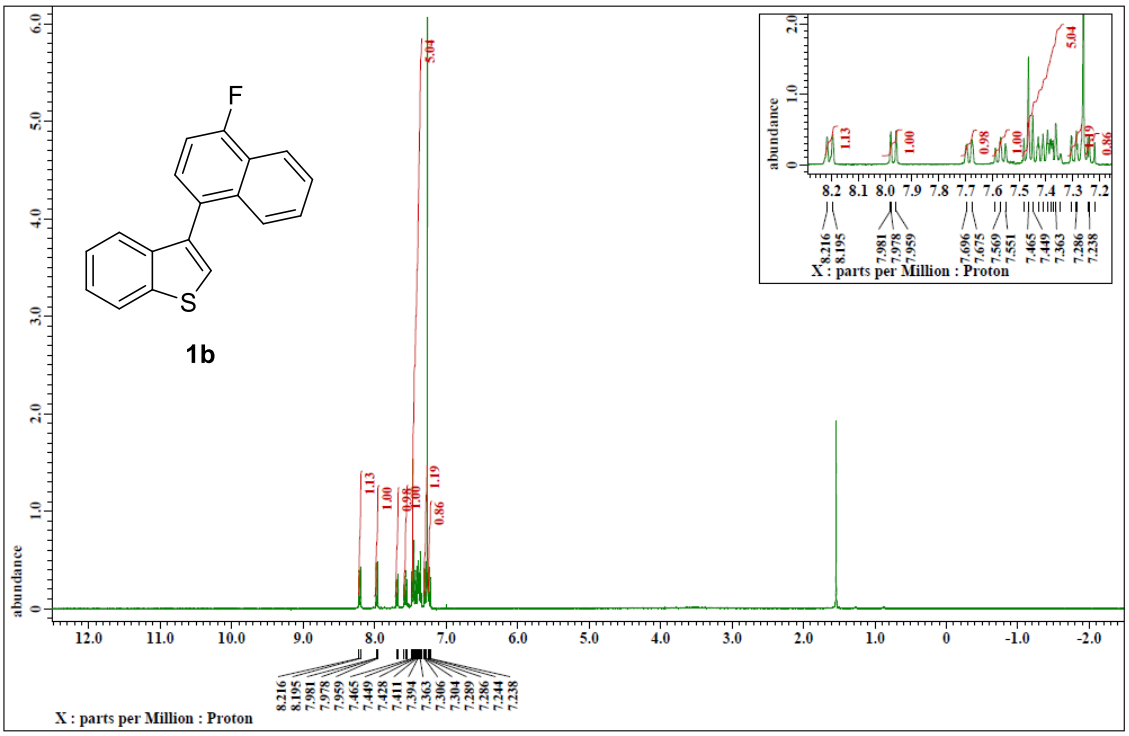
^{1}H NMR (400 MHz, $CDCl_3$)



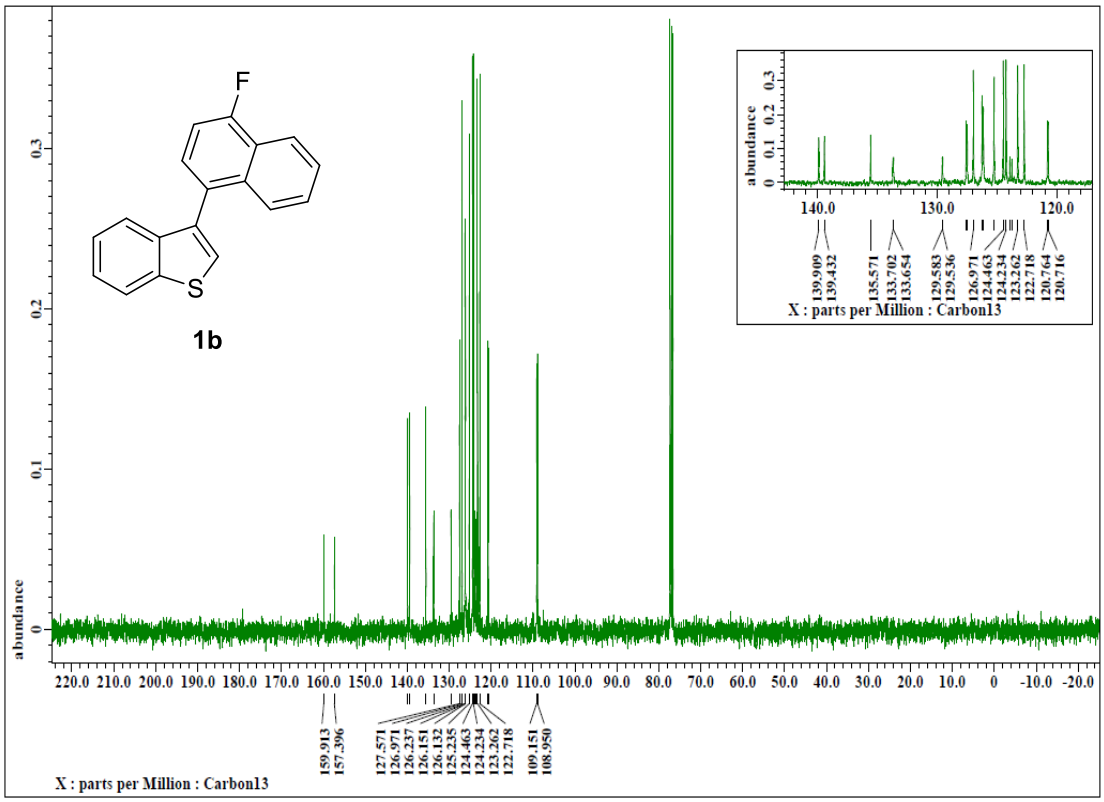
^{13}C NMR (100 MHz, $CDCl_3$)

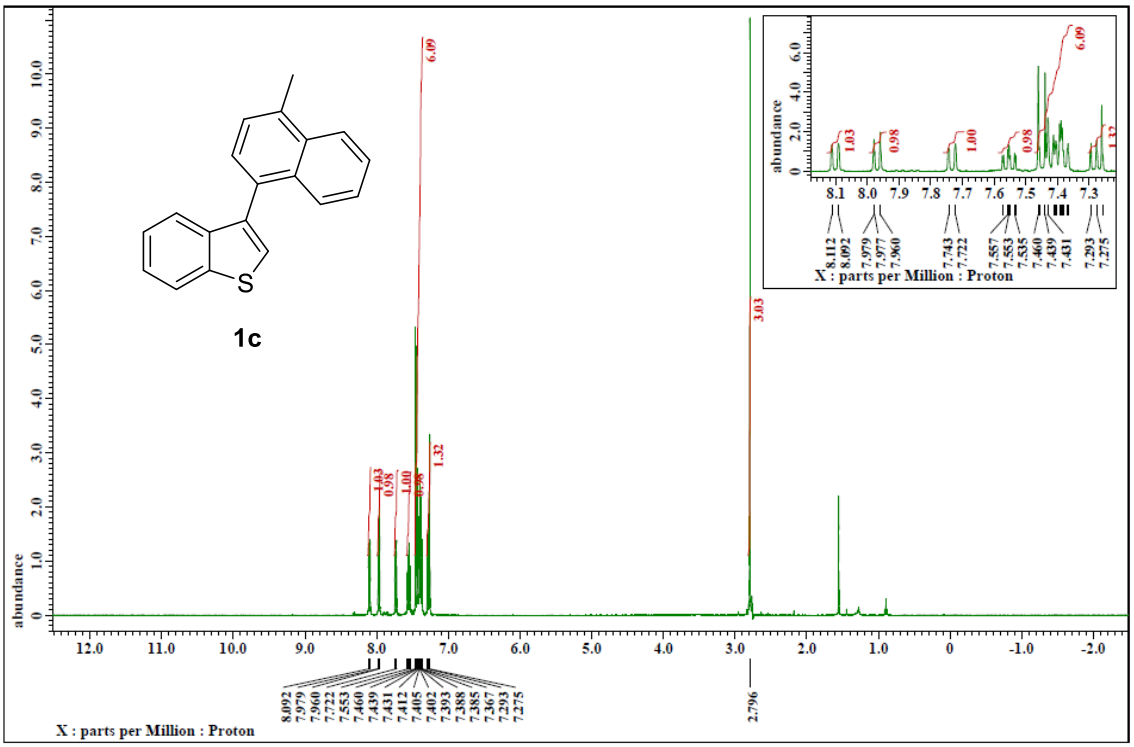


^{1}H NMR (400 MHz, $CDCl_3$)



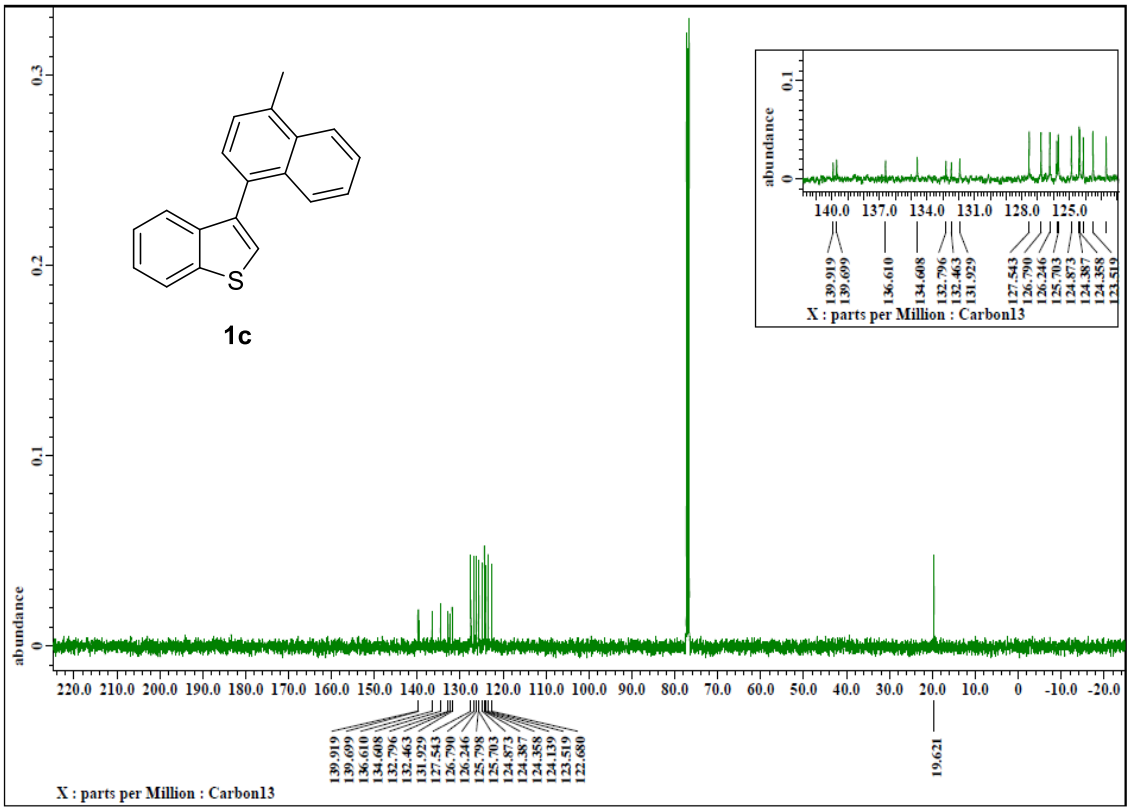
^{13}C NMR (100 MHz, $CDCl_3$)





^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)



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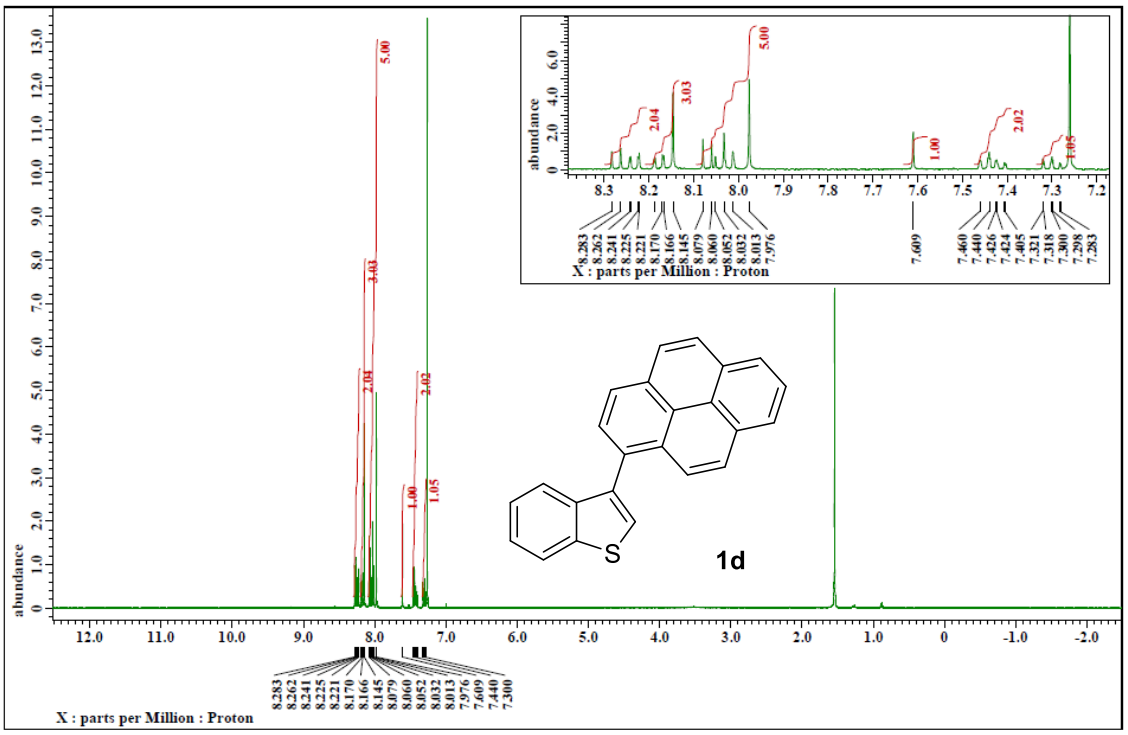
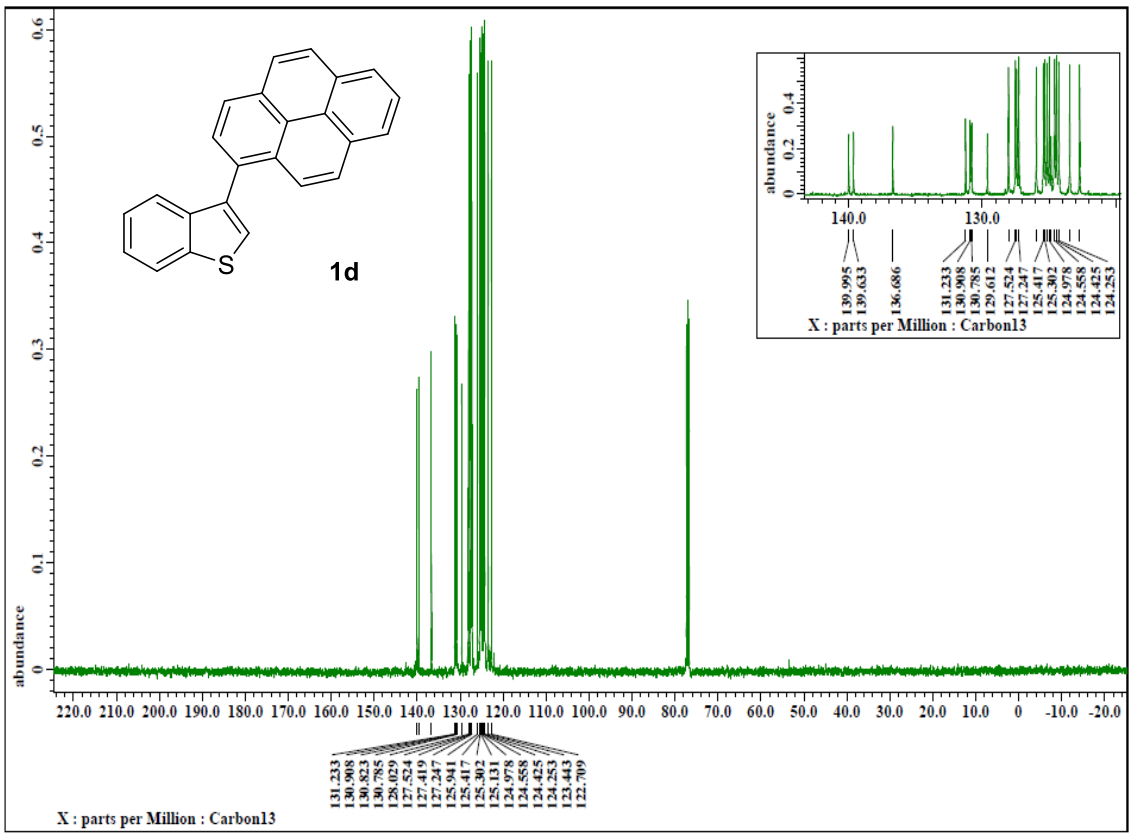
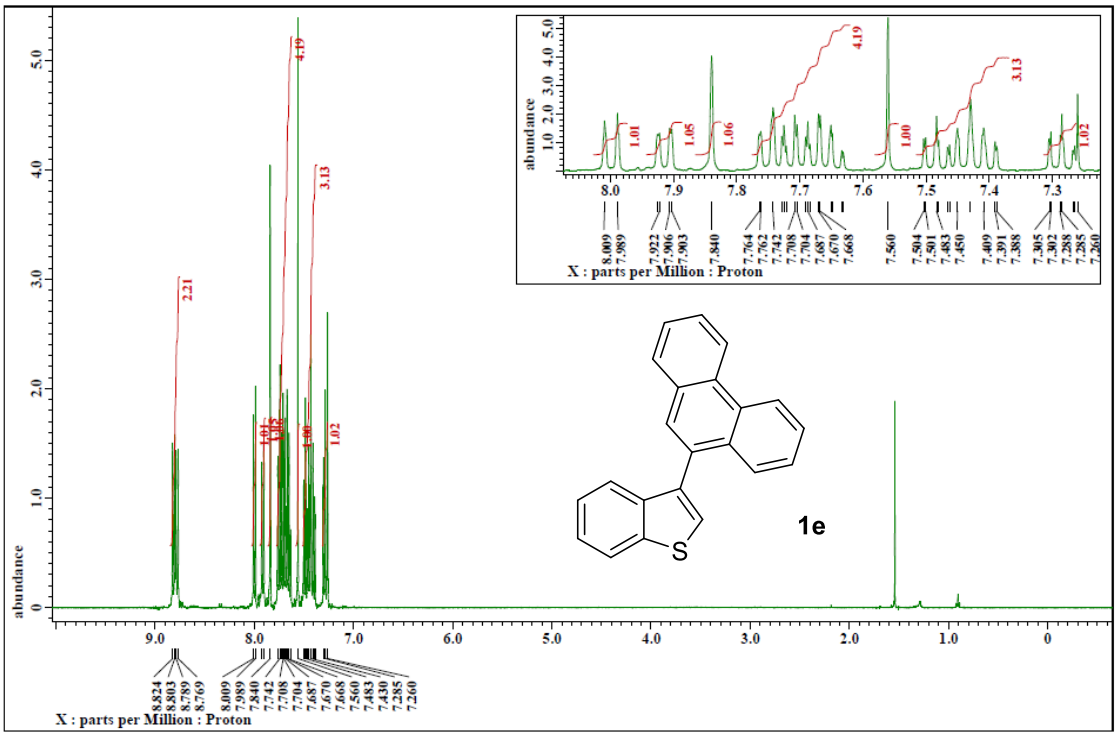


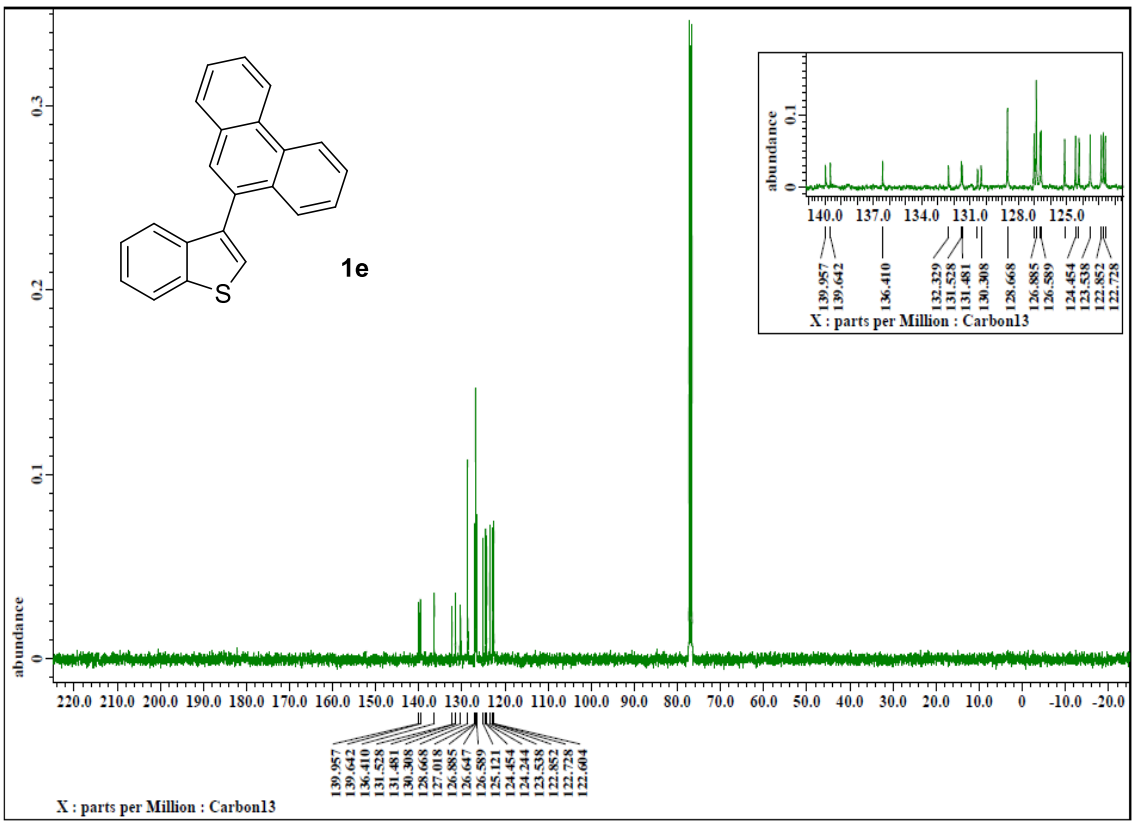
^{13}C NMR (100 MHz, $CDCl_3$)



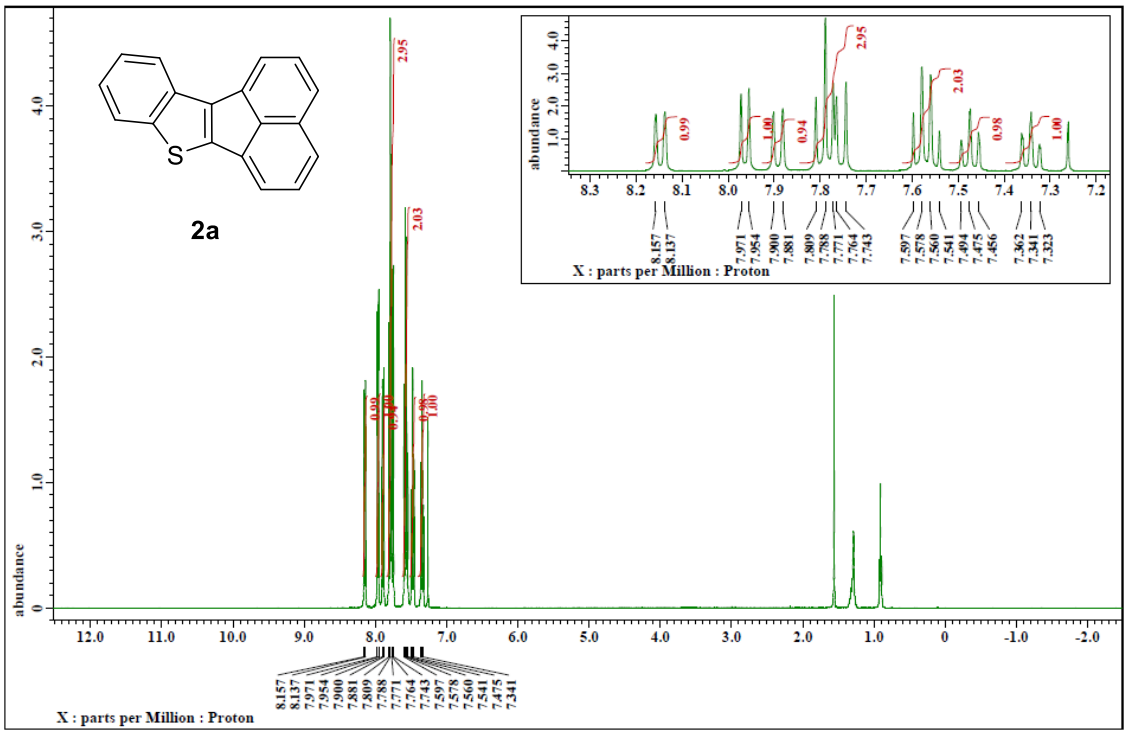
^{1}H NMR (400 MHz, $CDCl_3$)



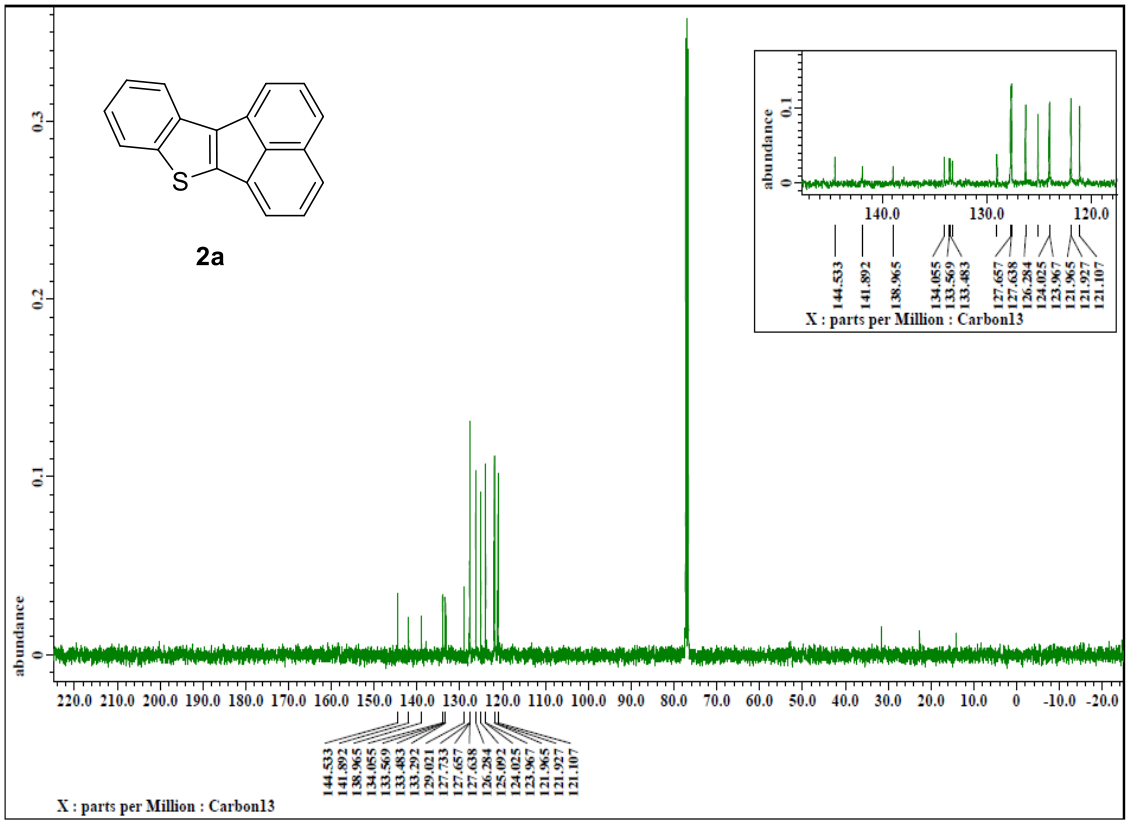
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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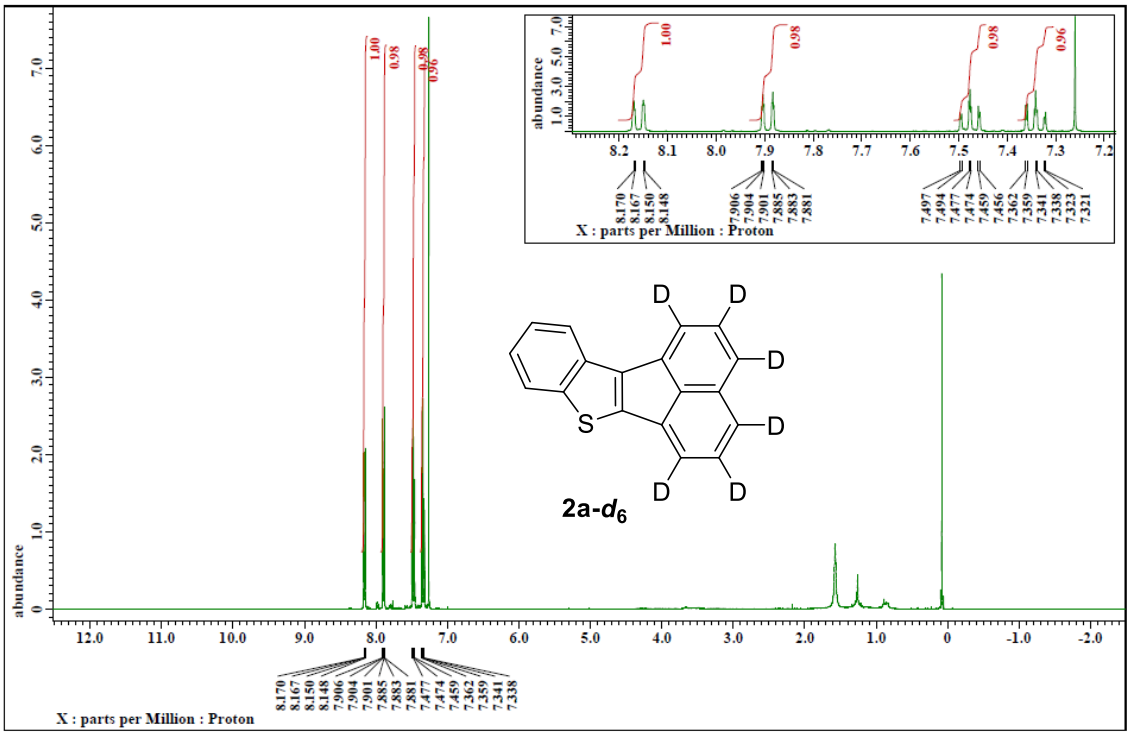

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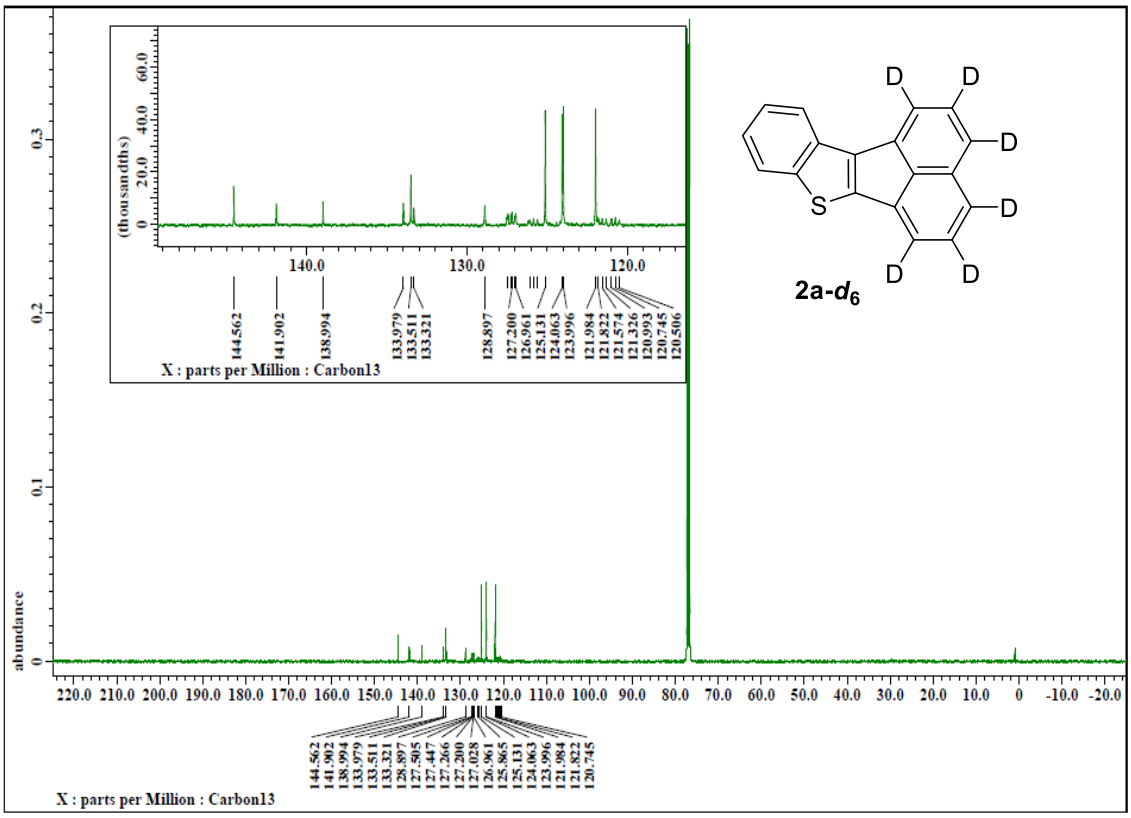

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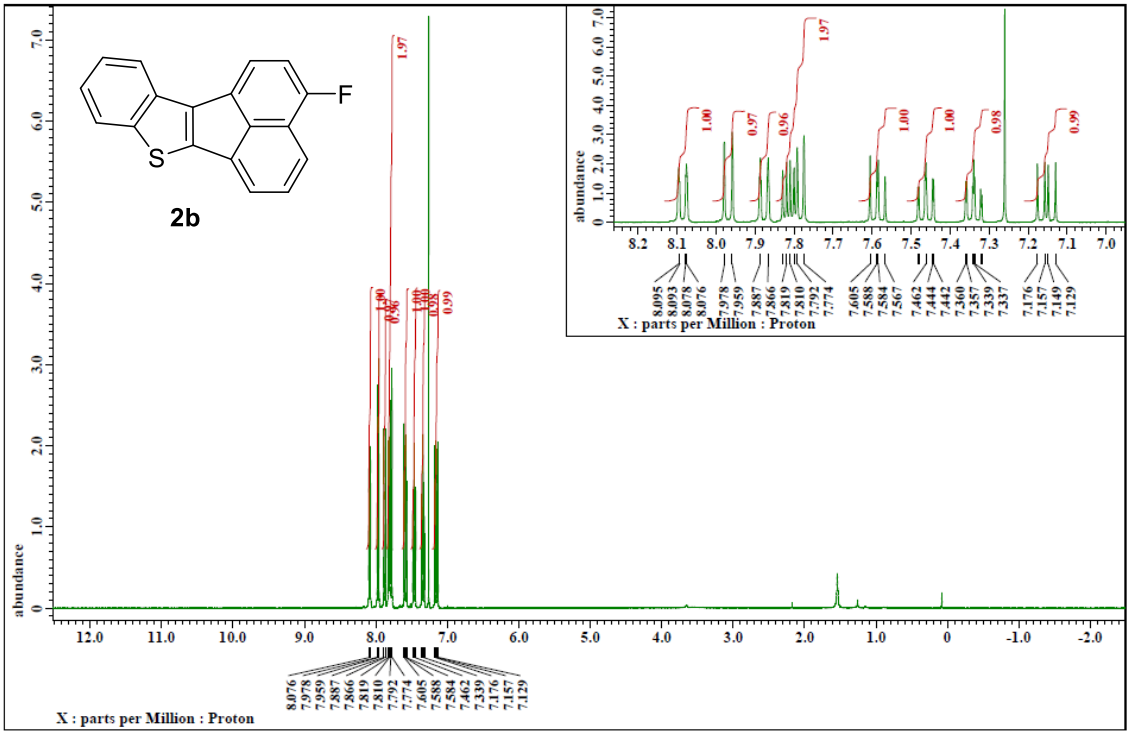

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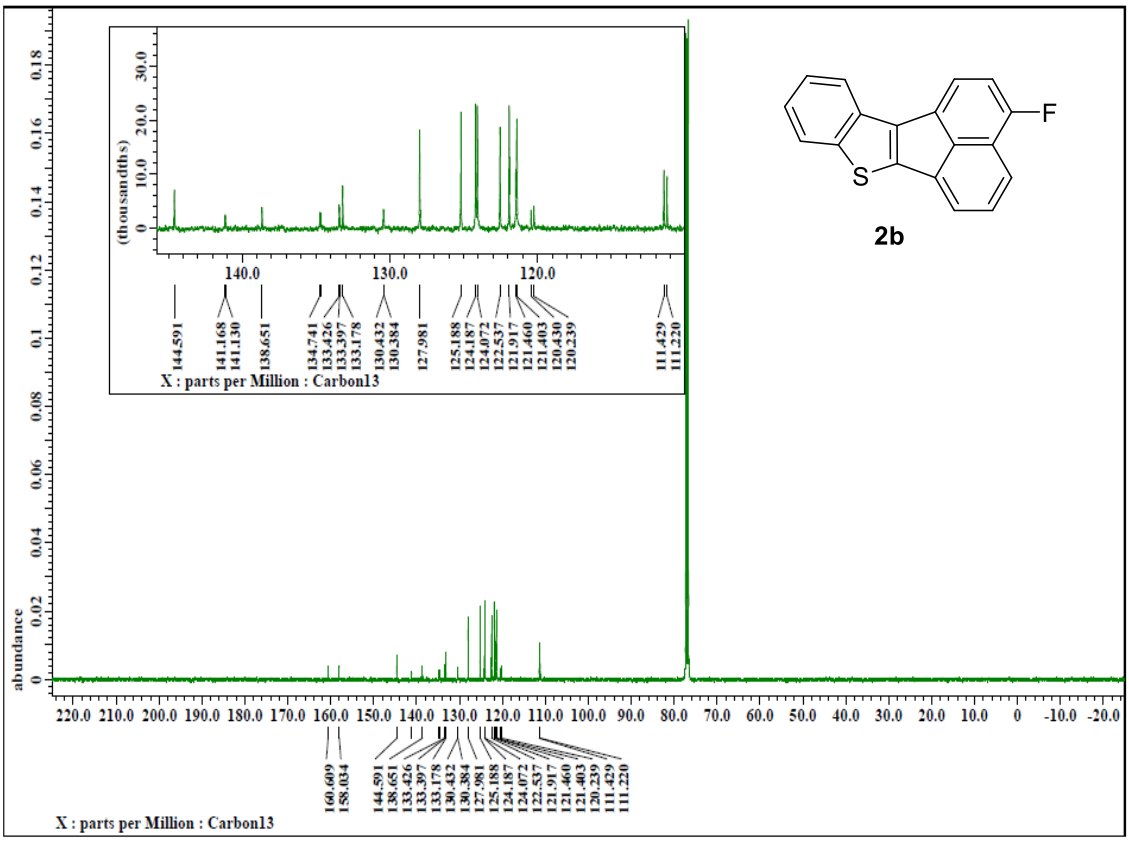
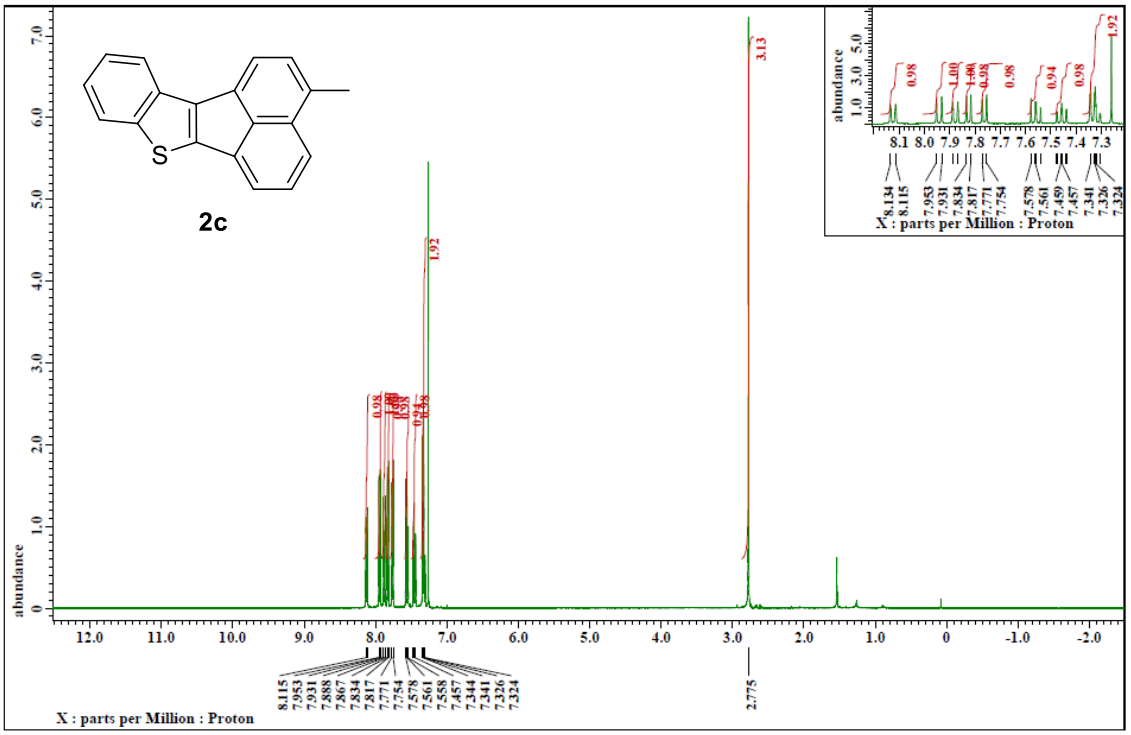
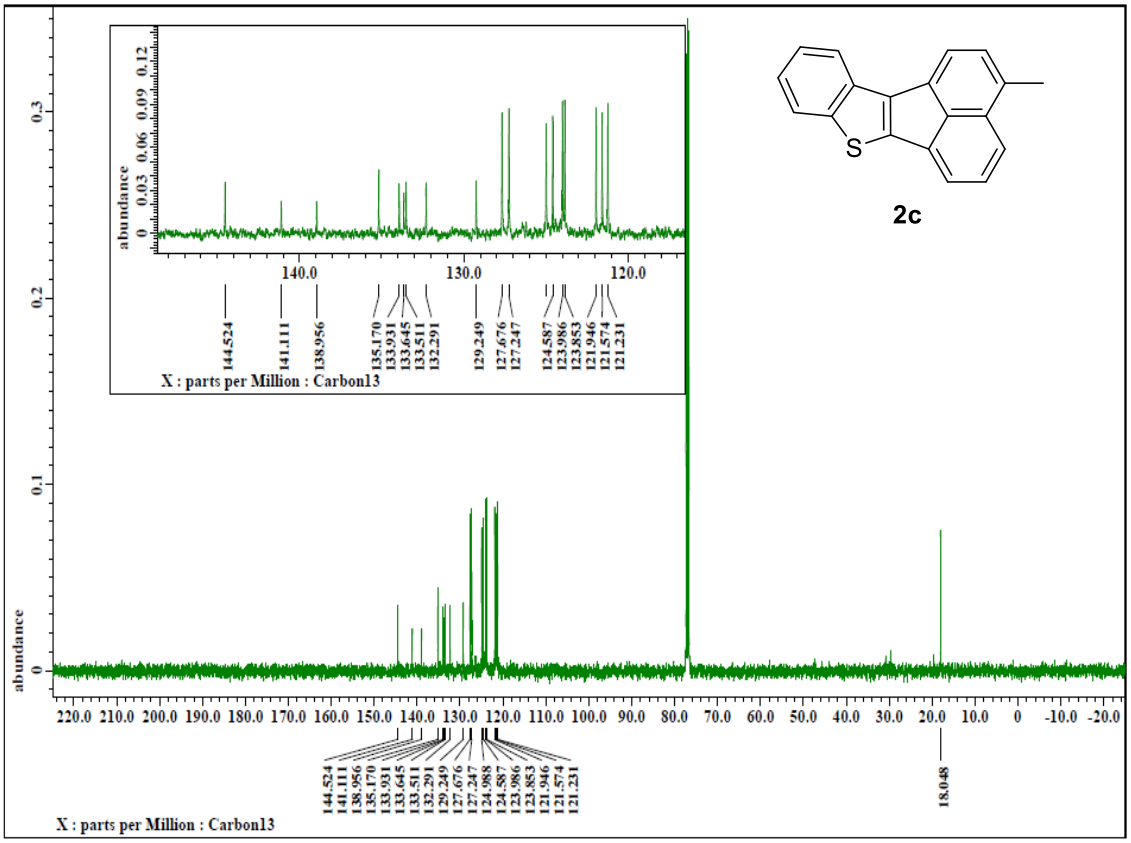


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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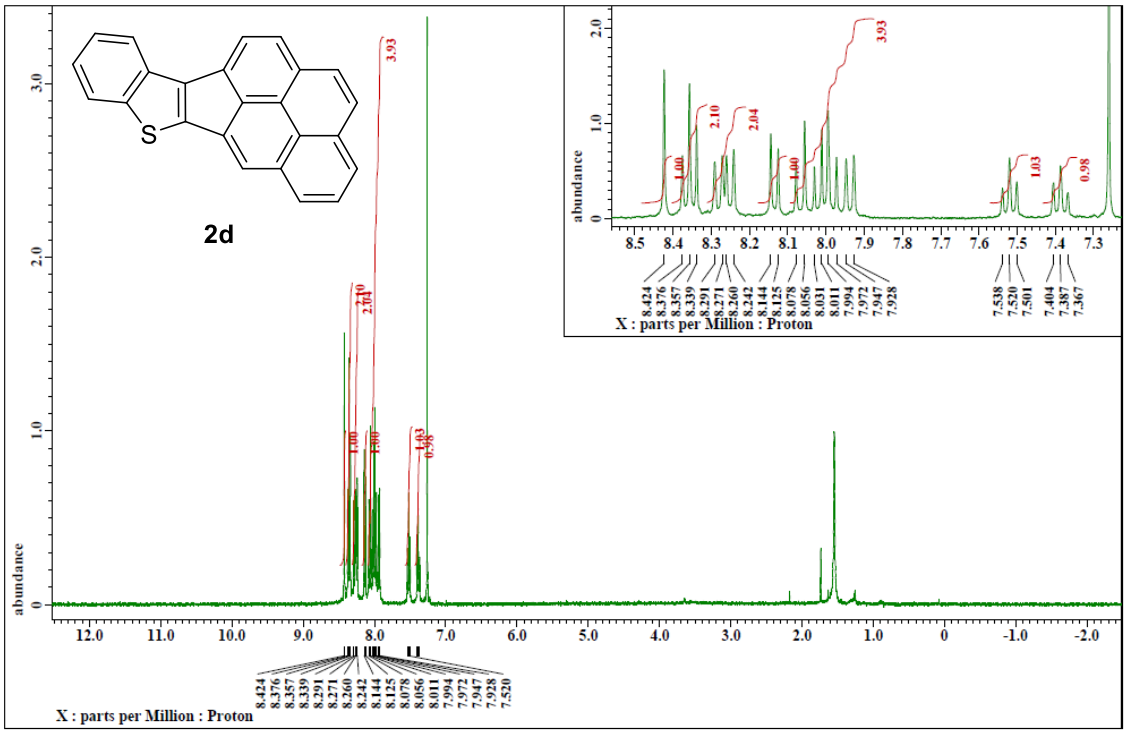

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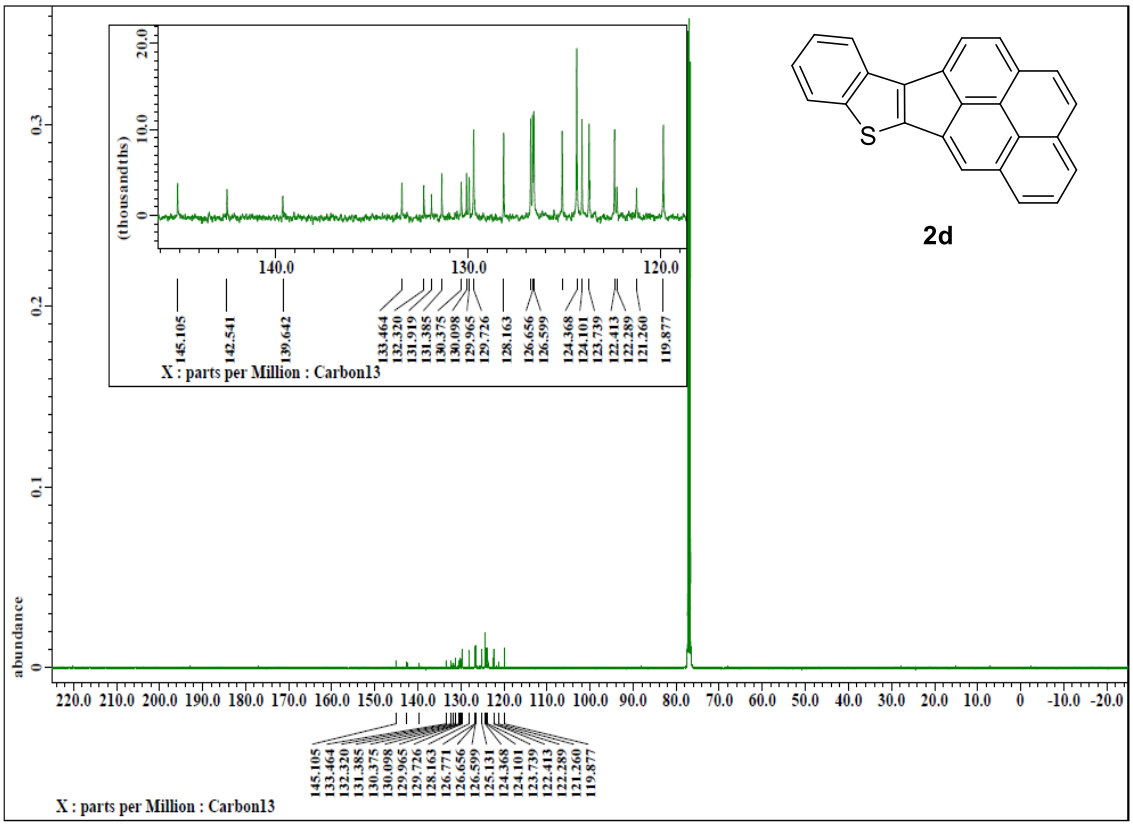

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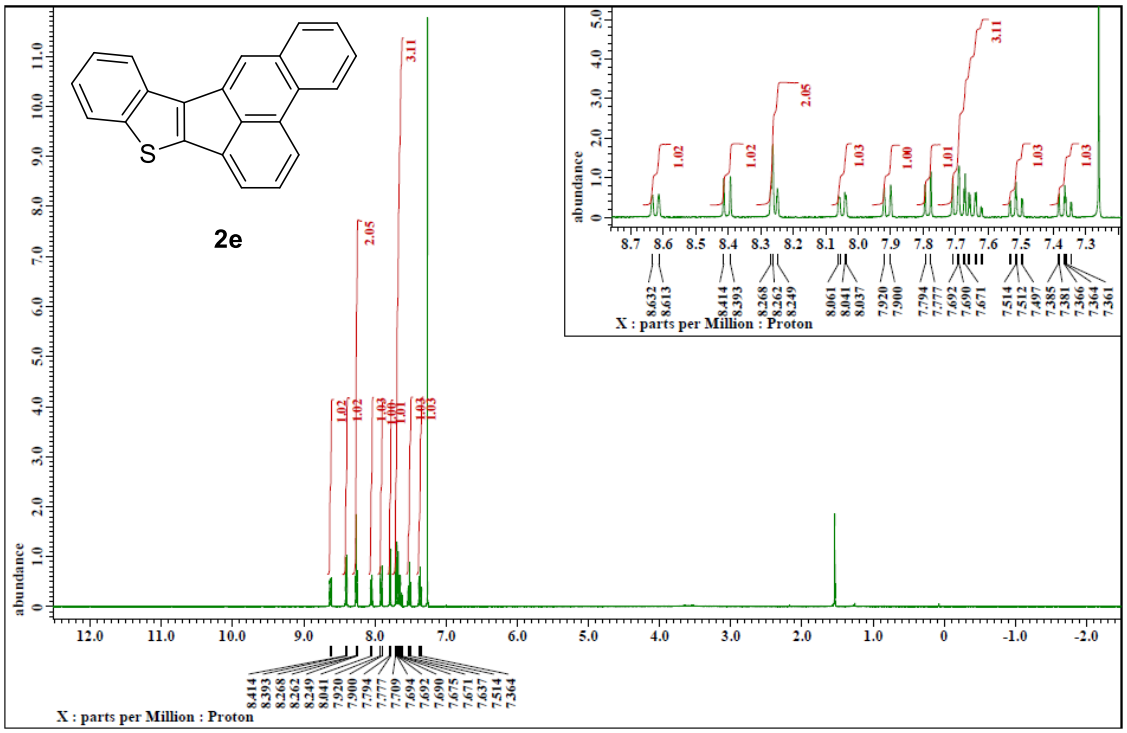
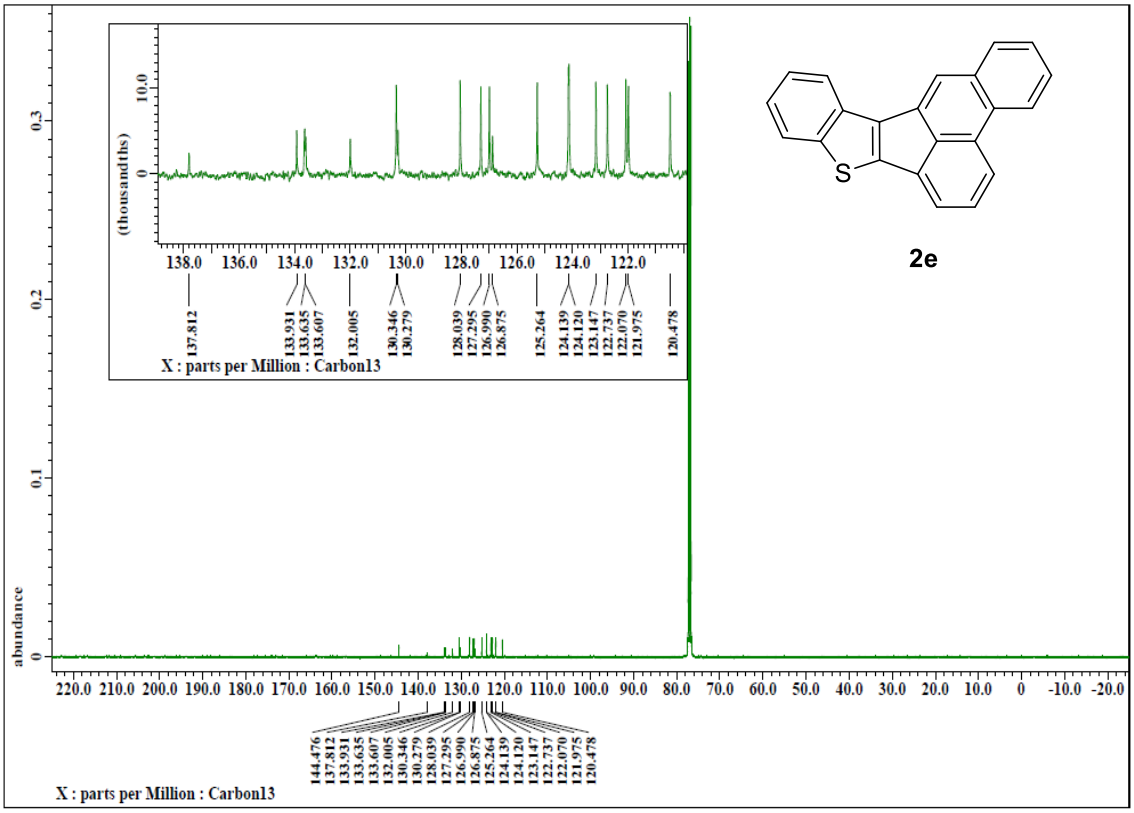
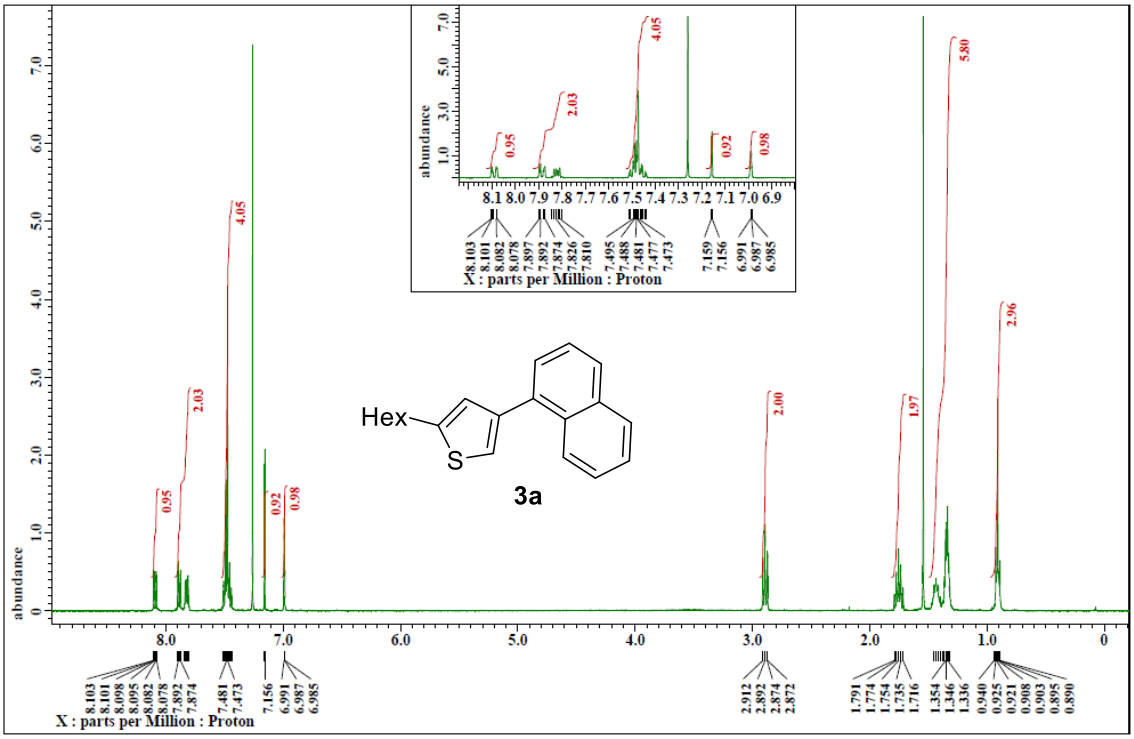


^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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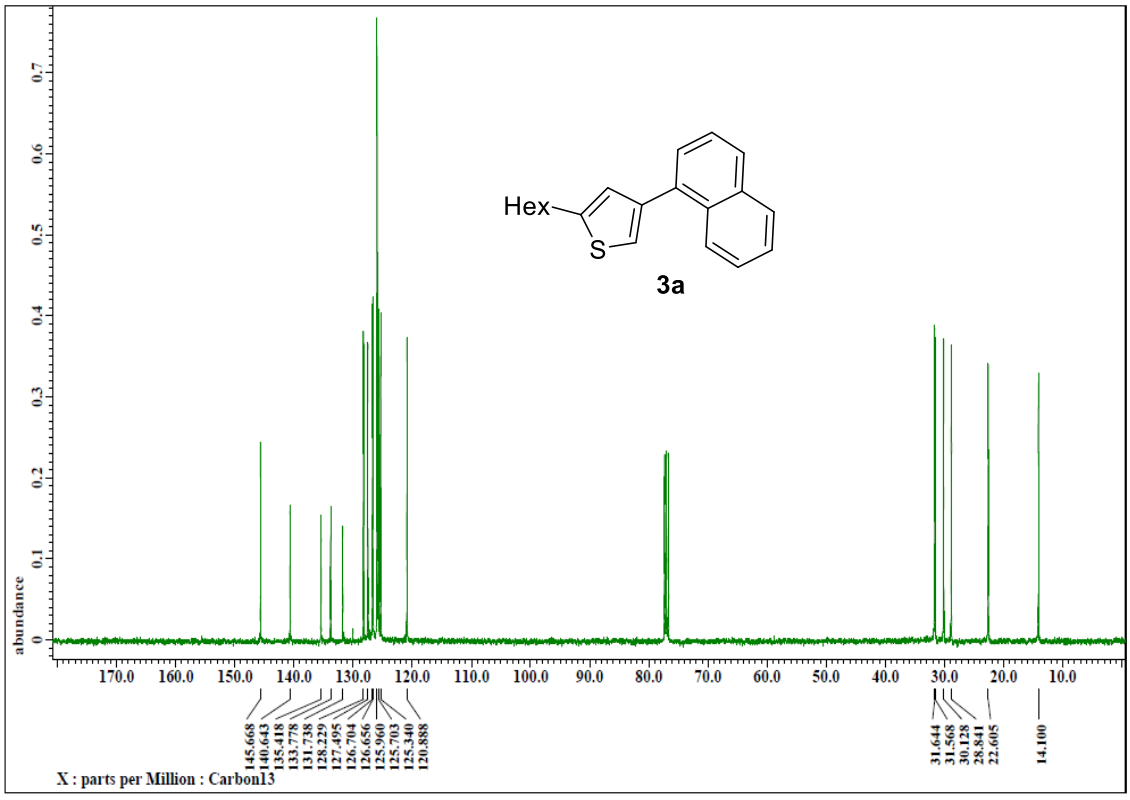

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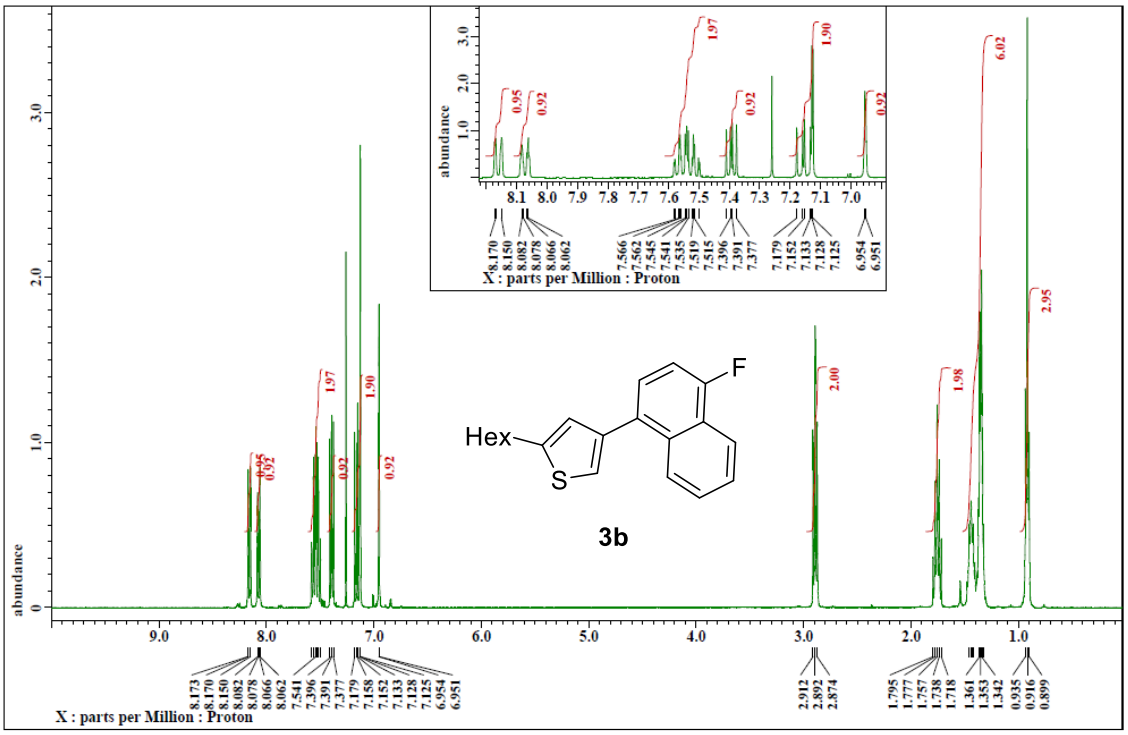

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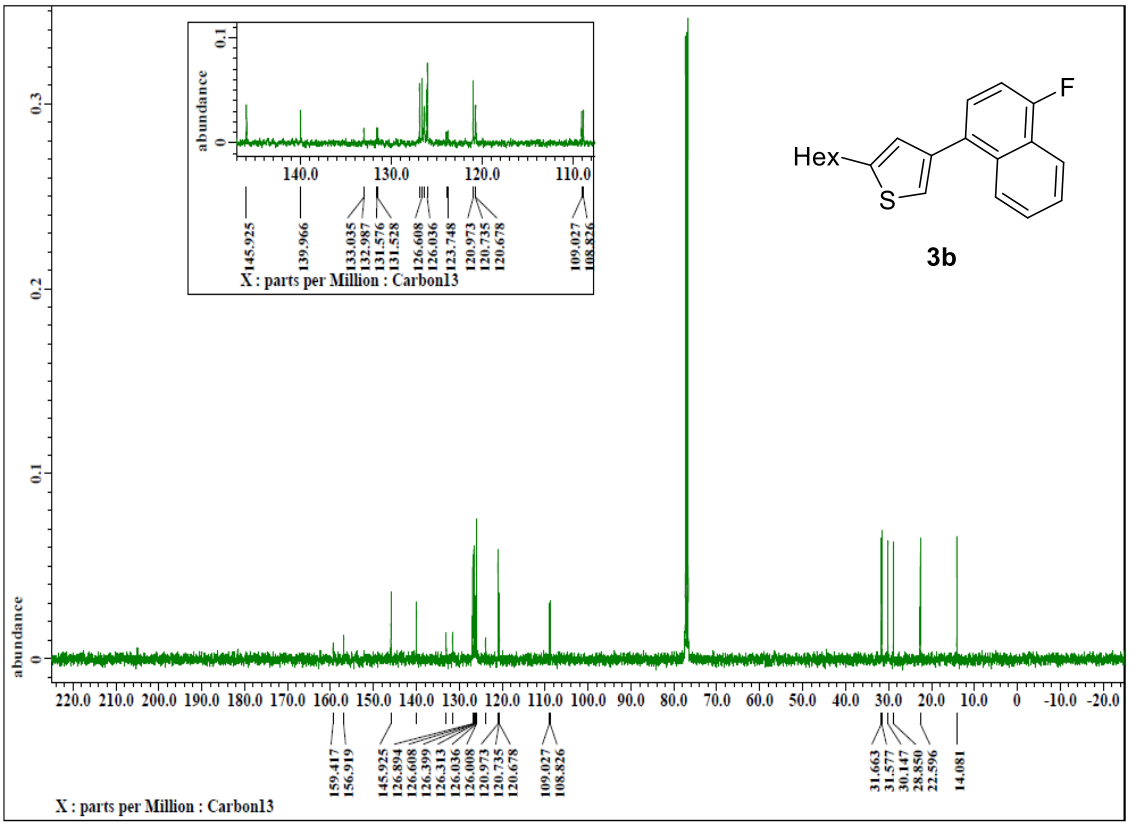

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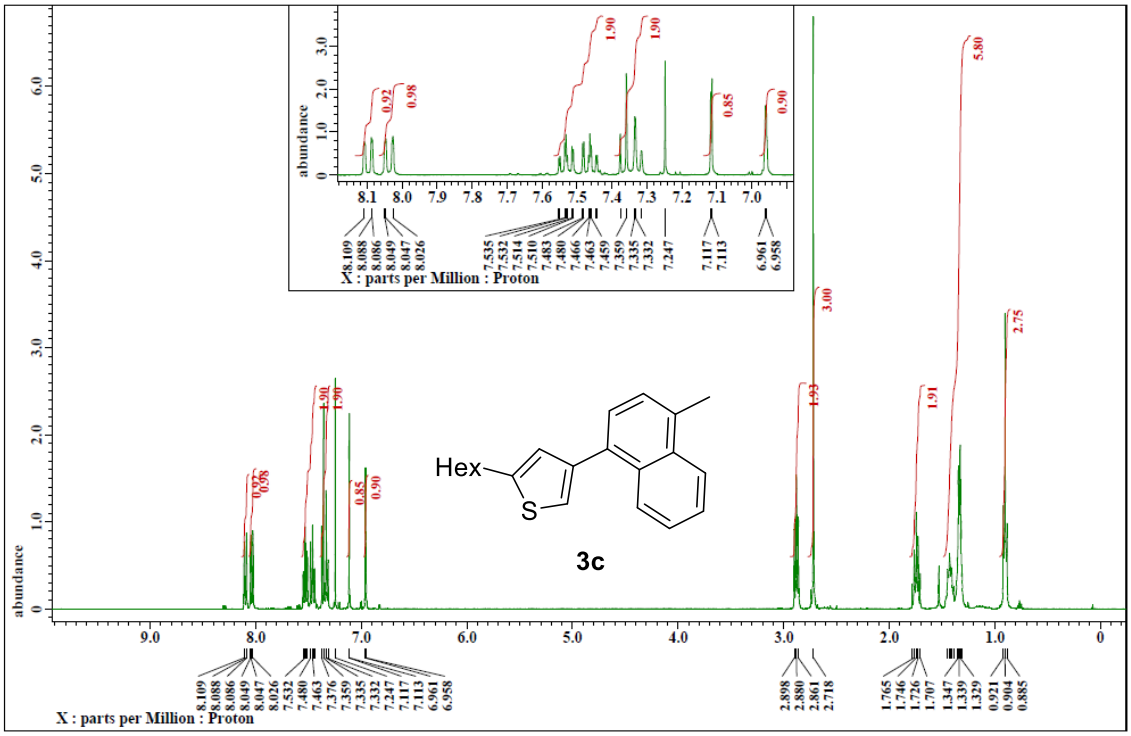

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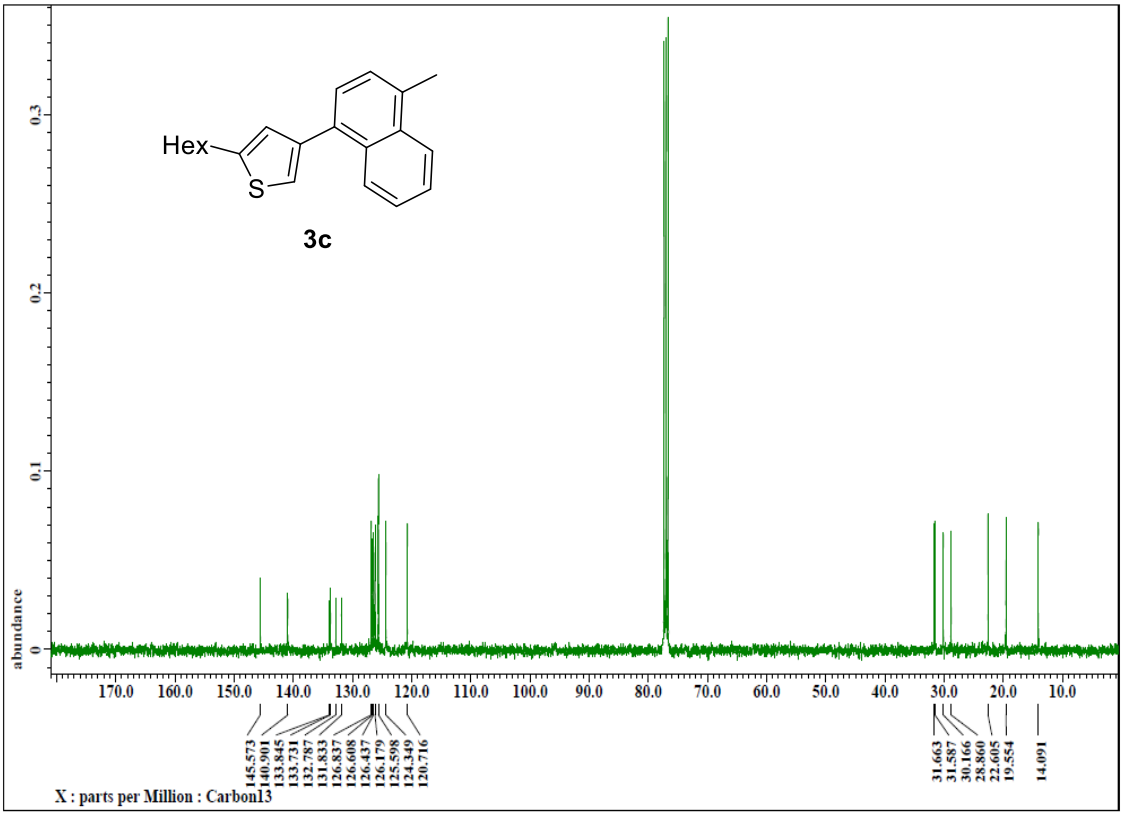

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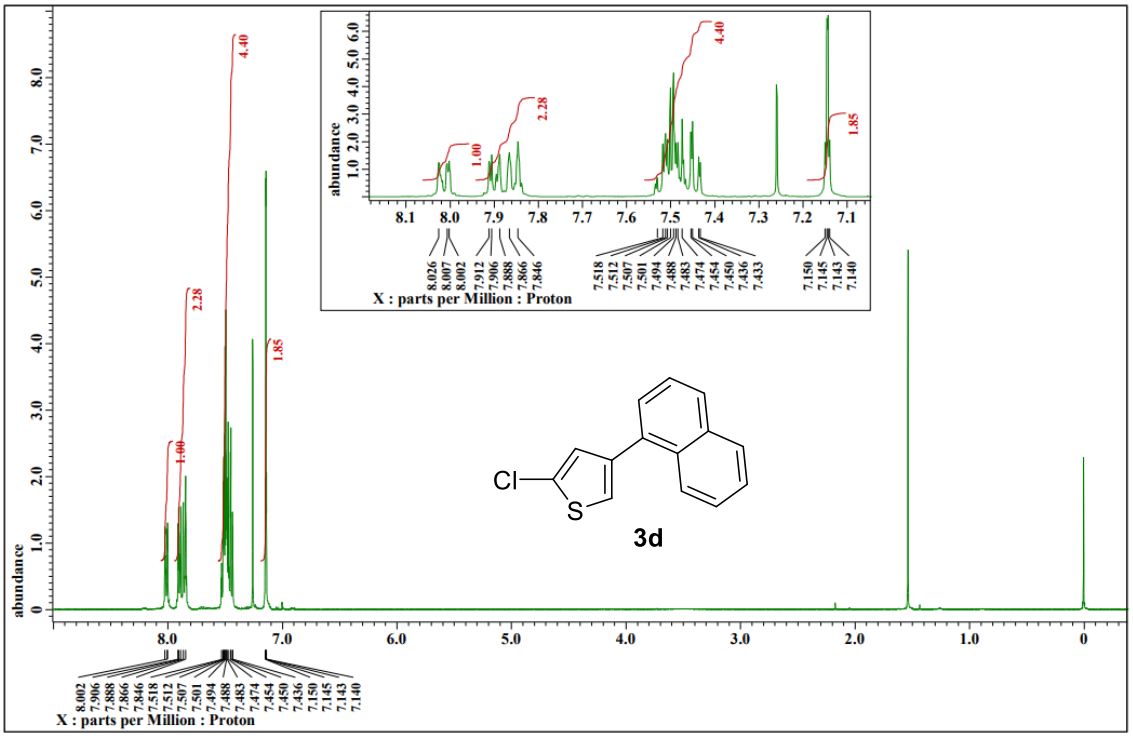

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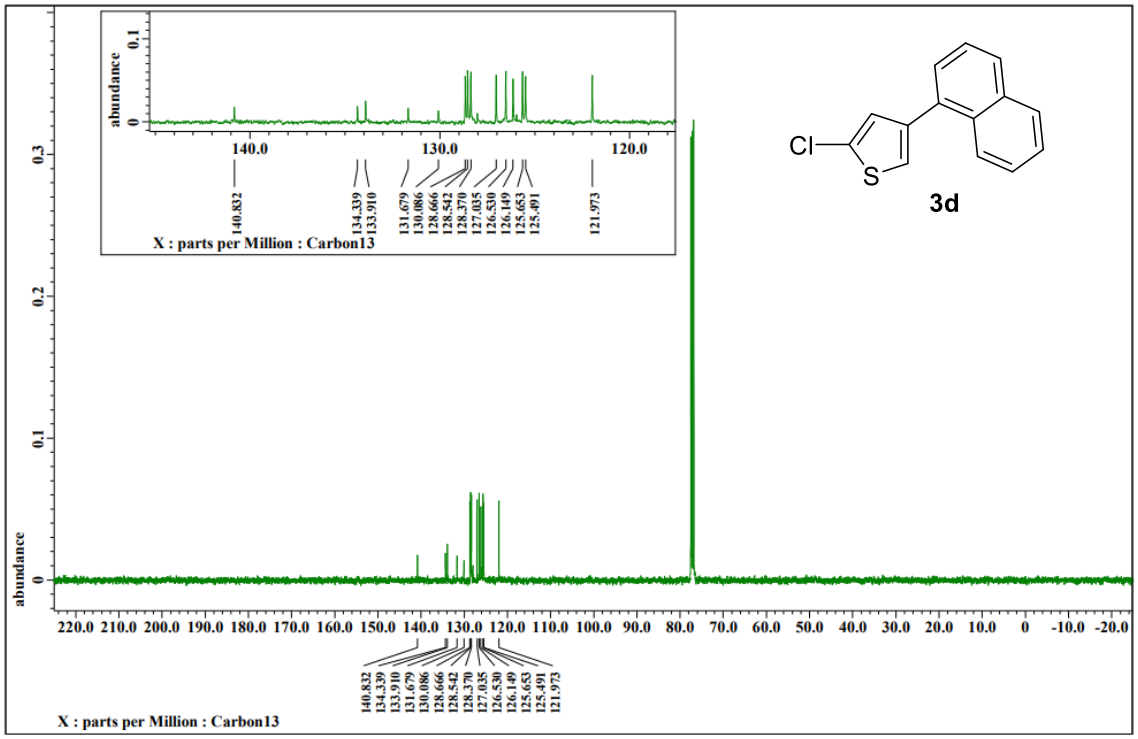

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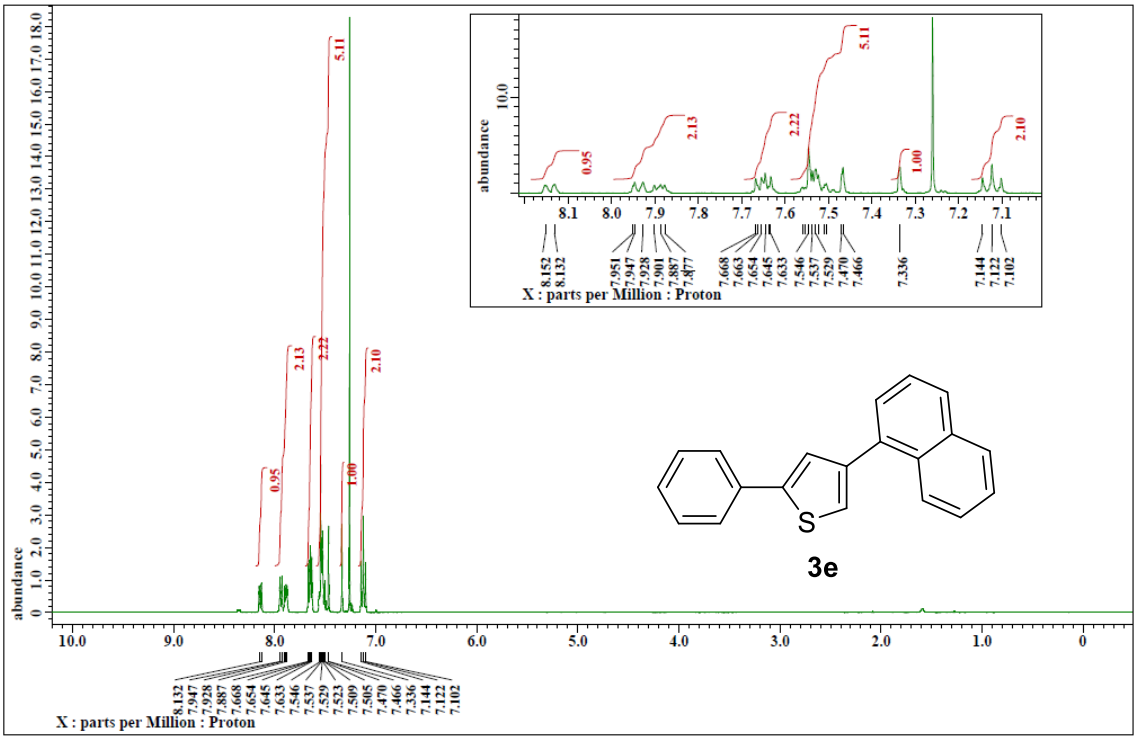

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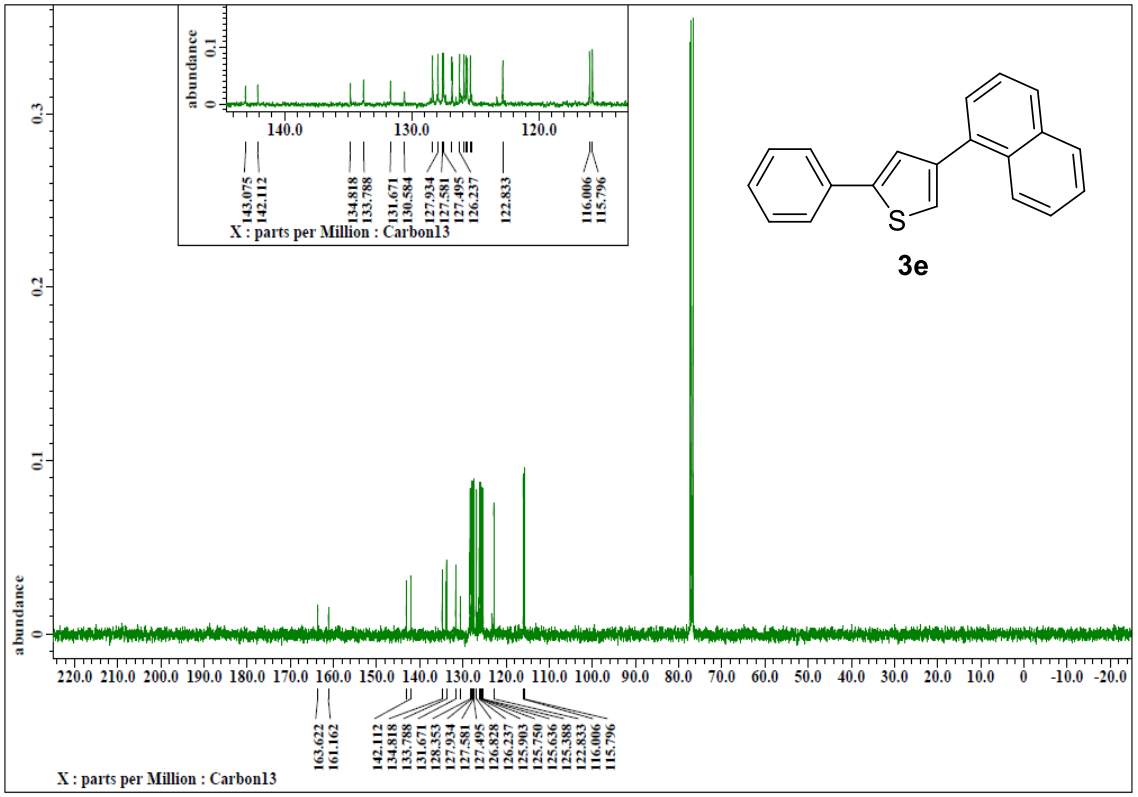

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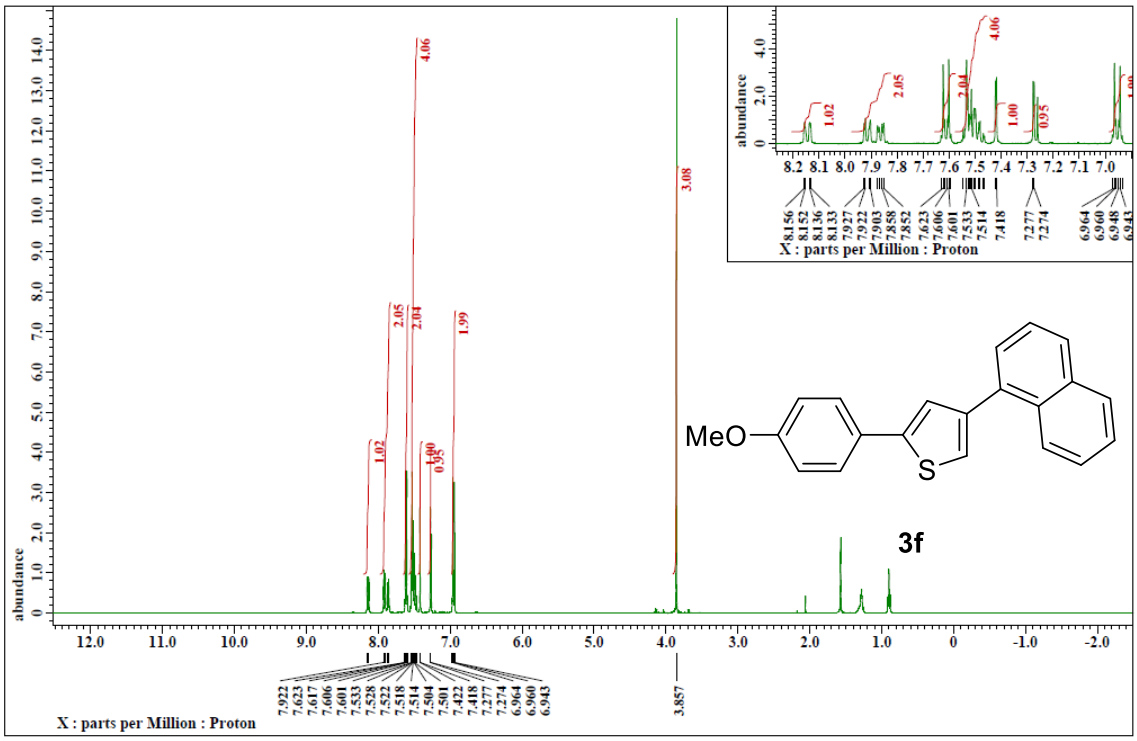

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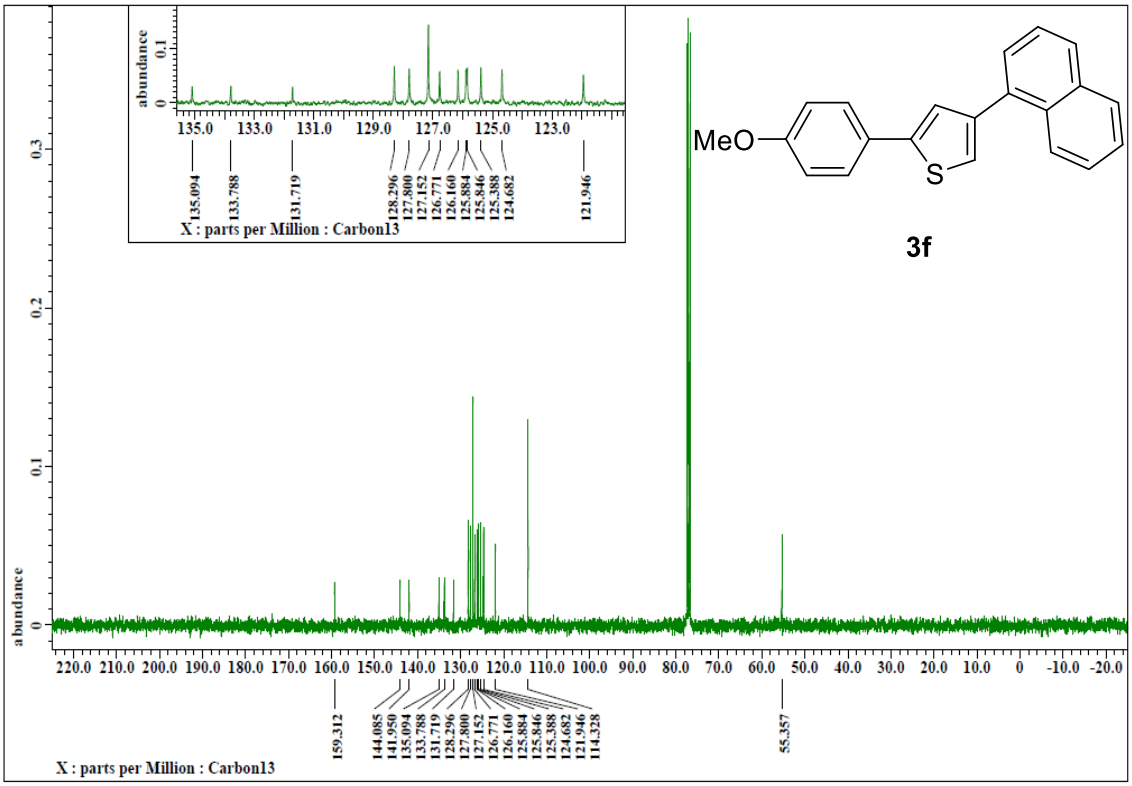

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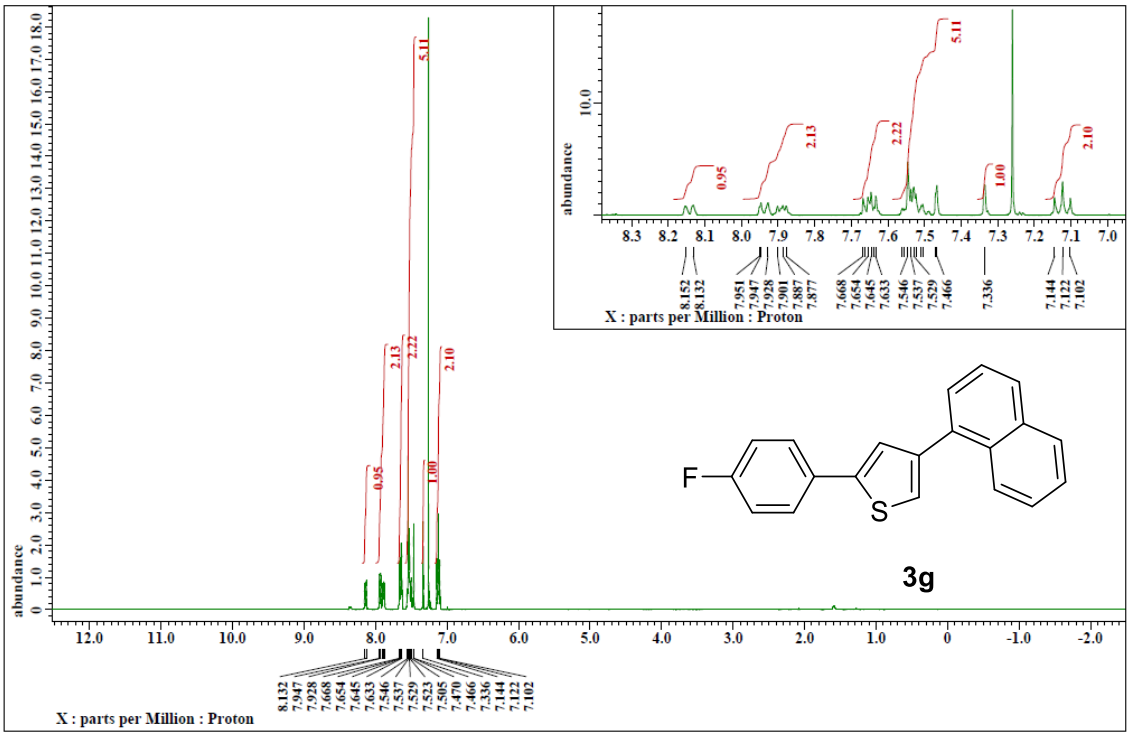

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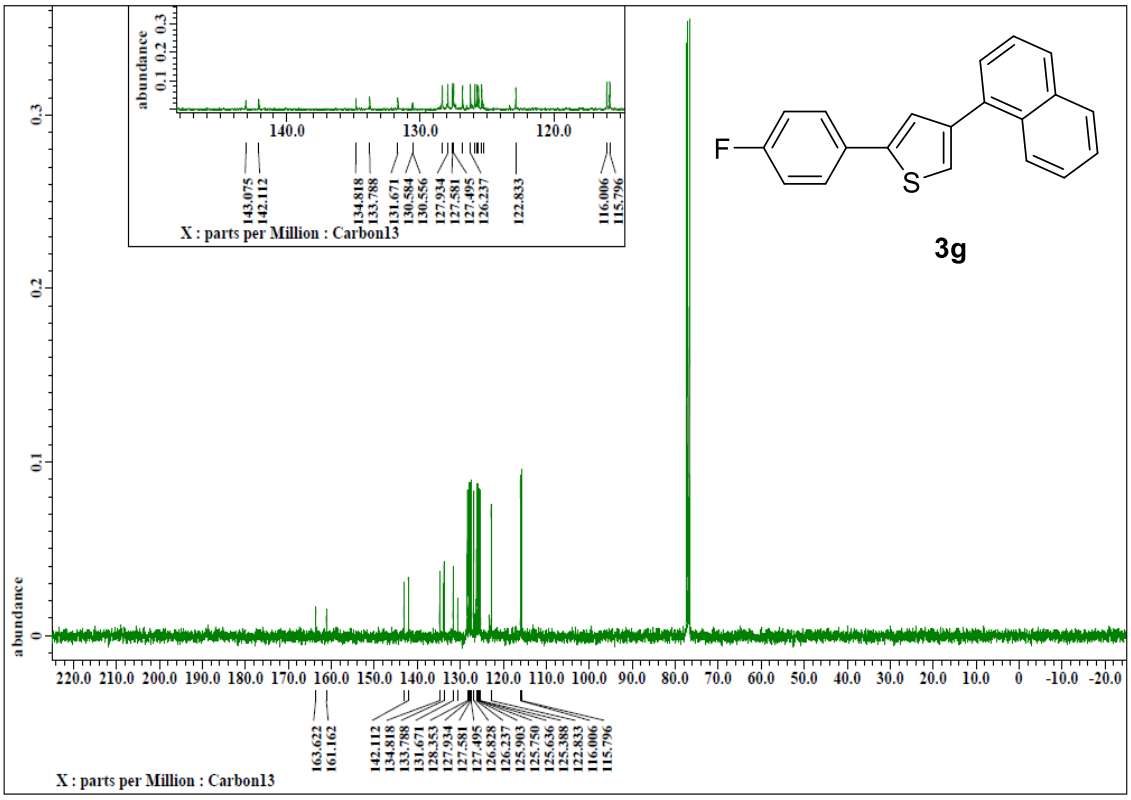

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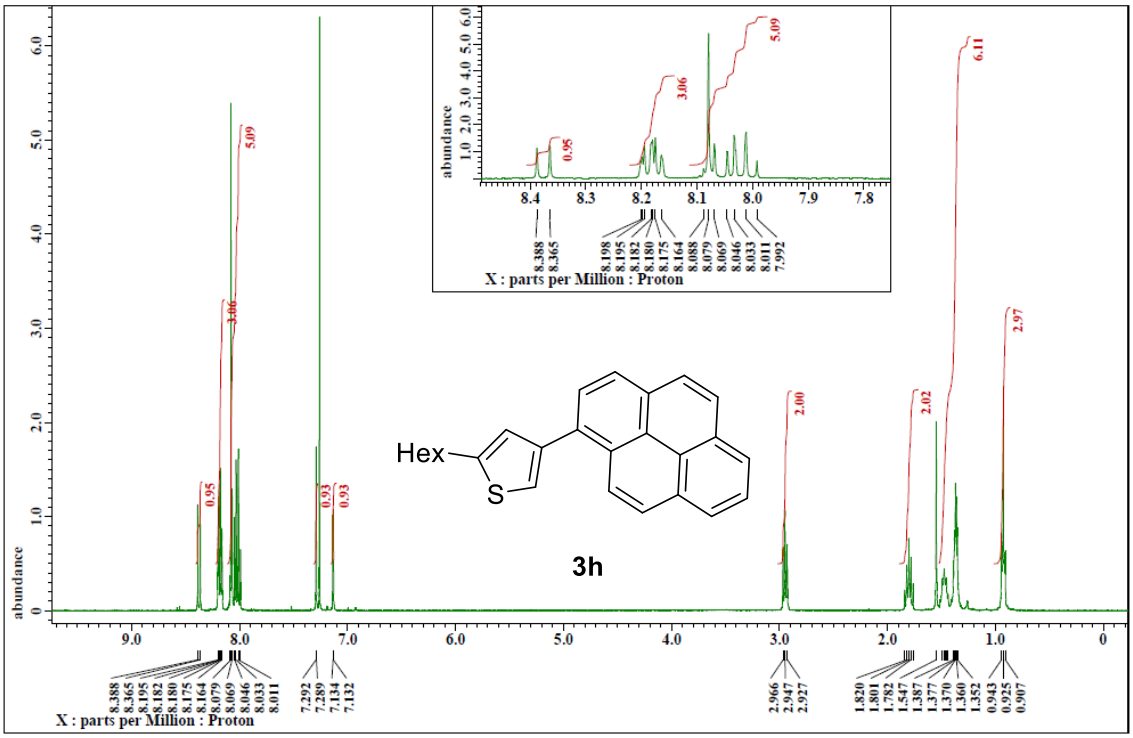

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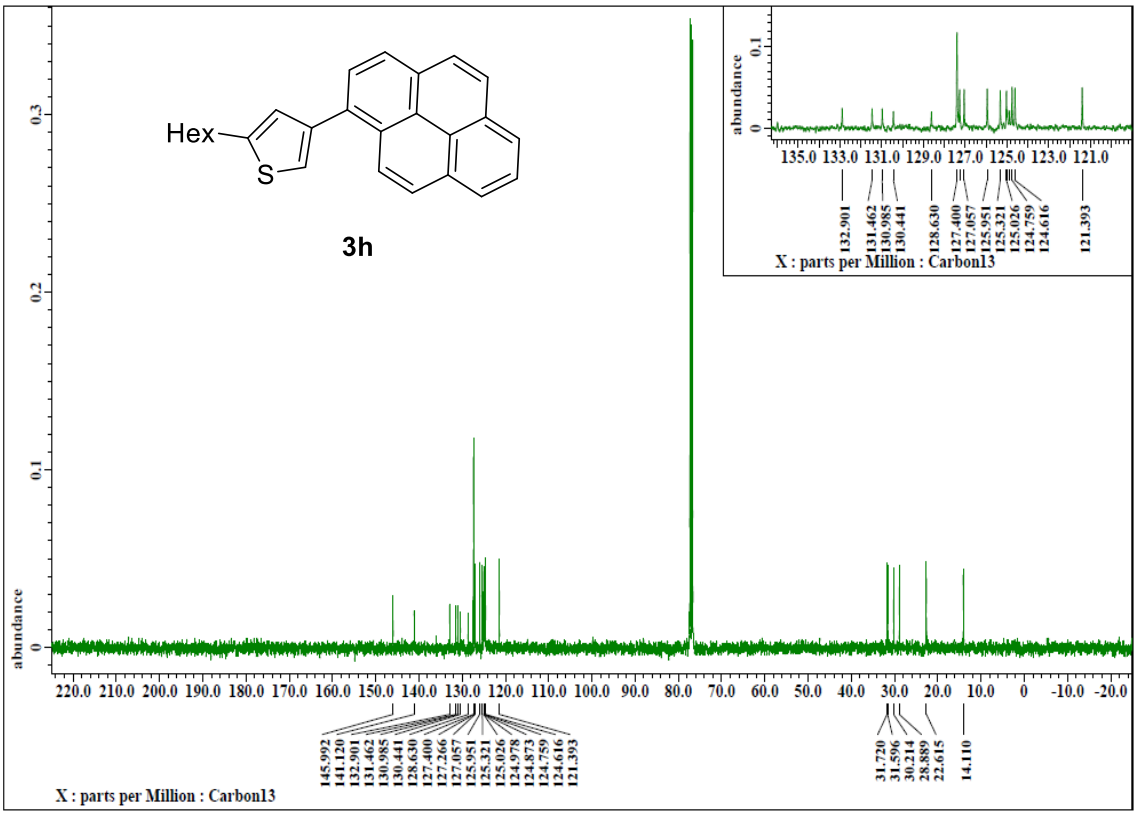

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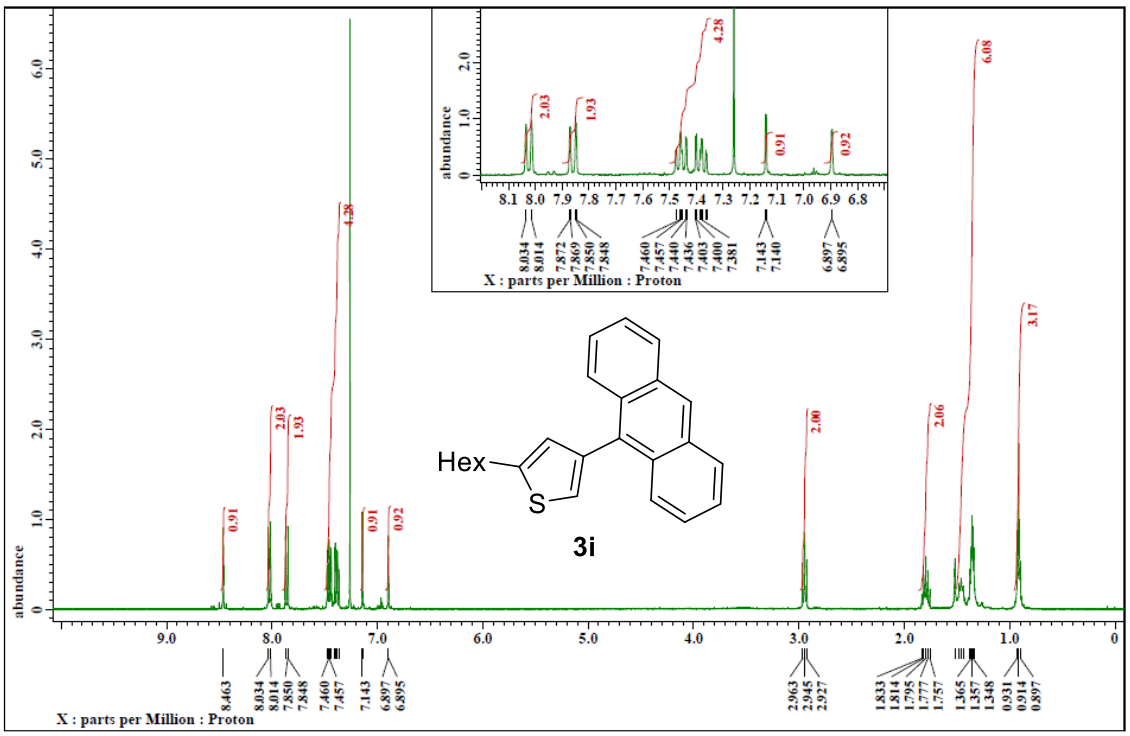

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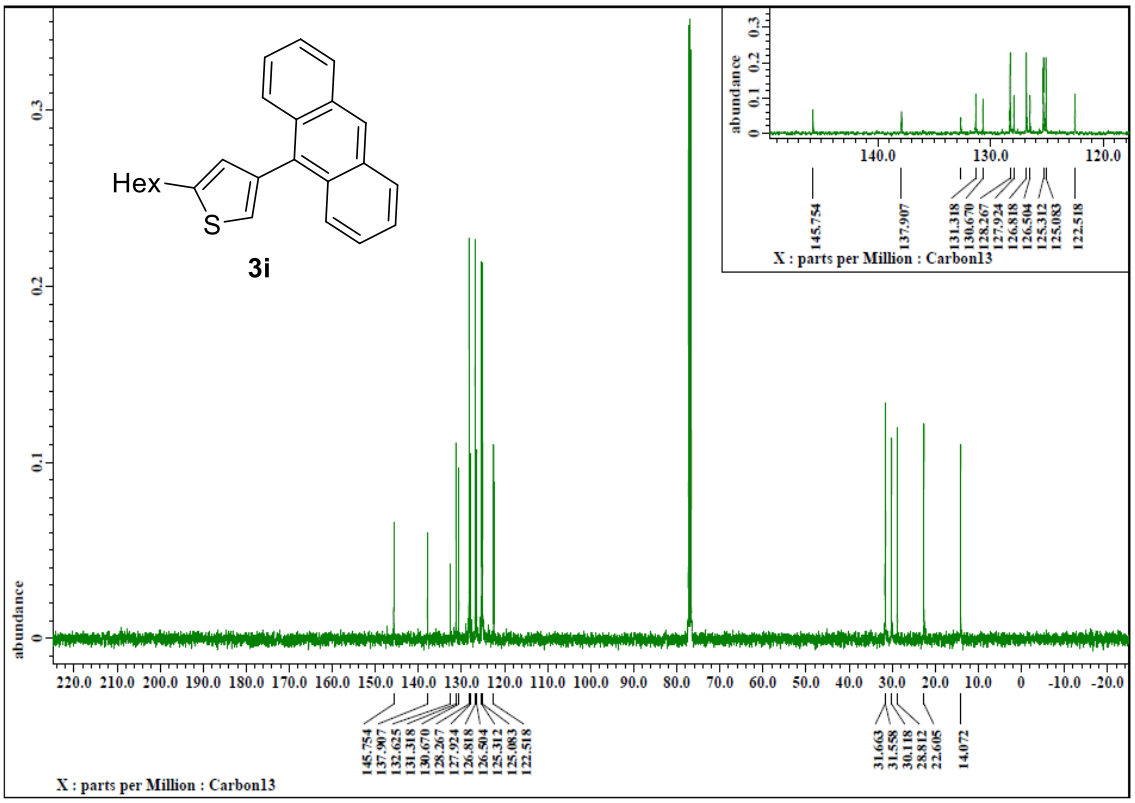

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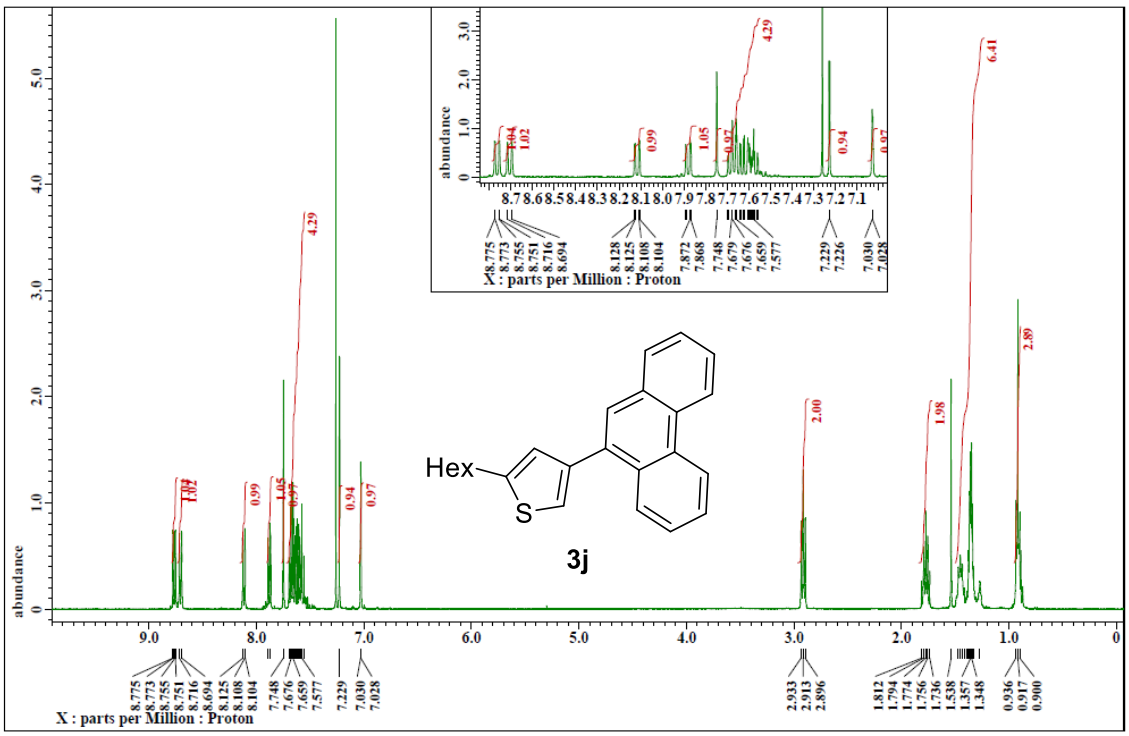

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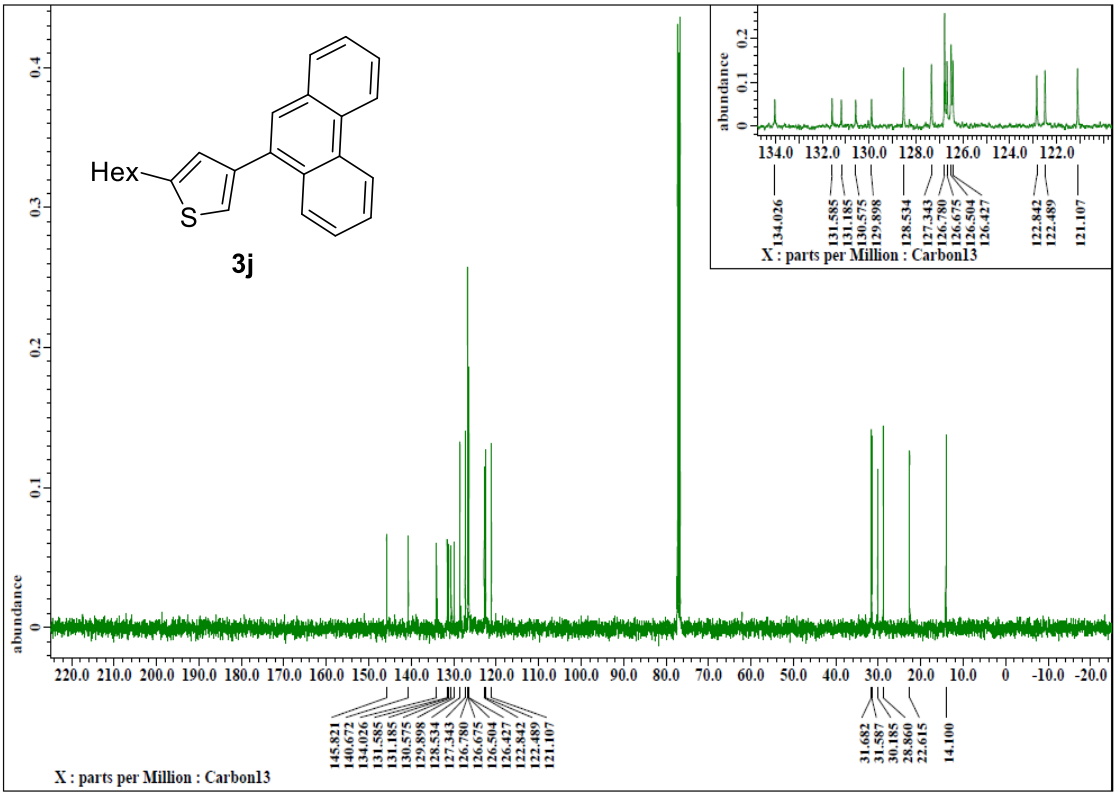

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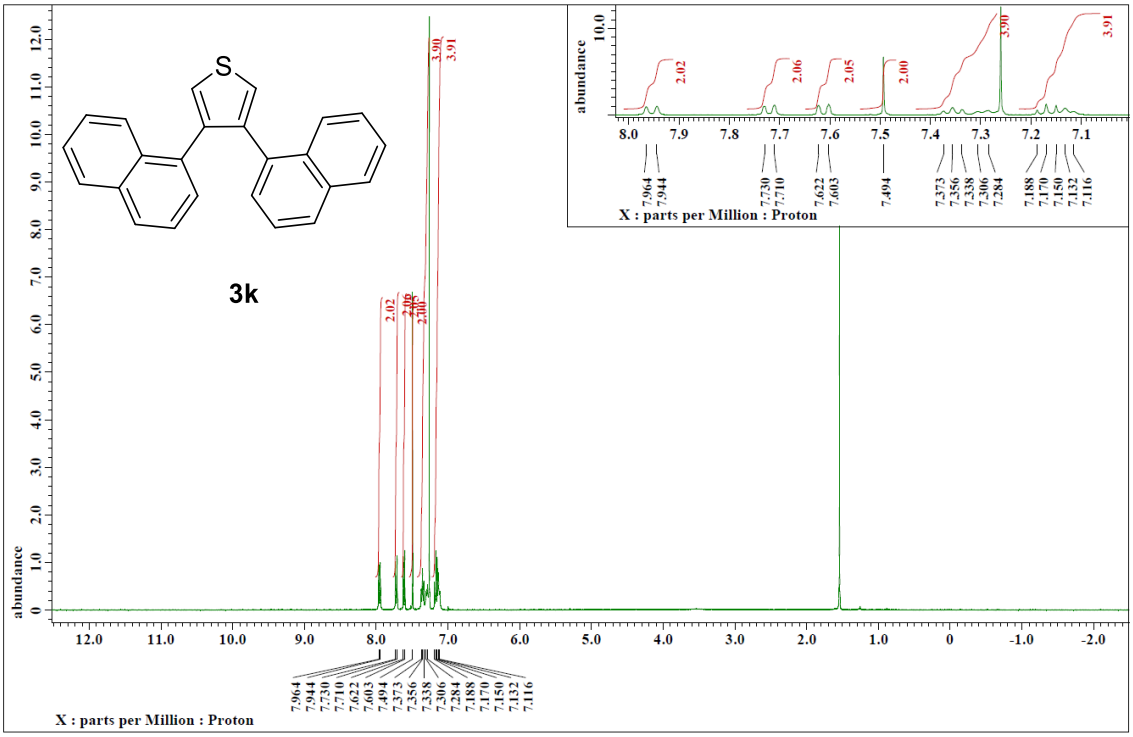
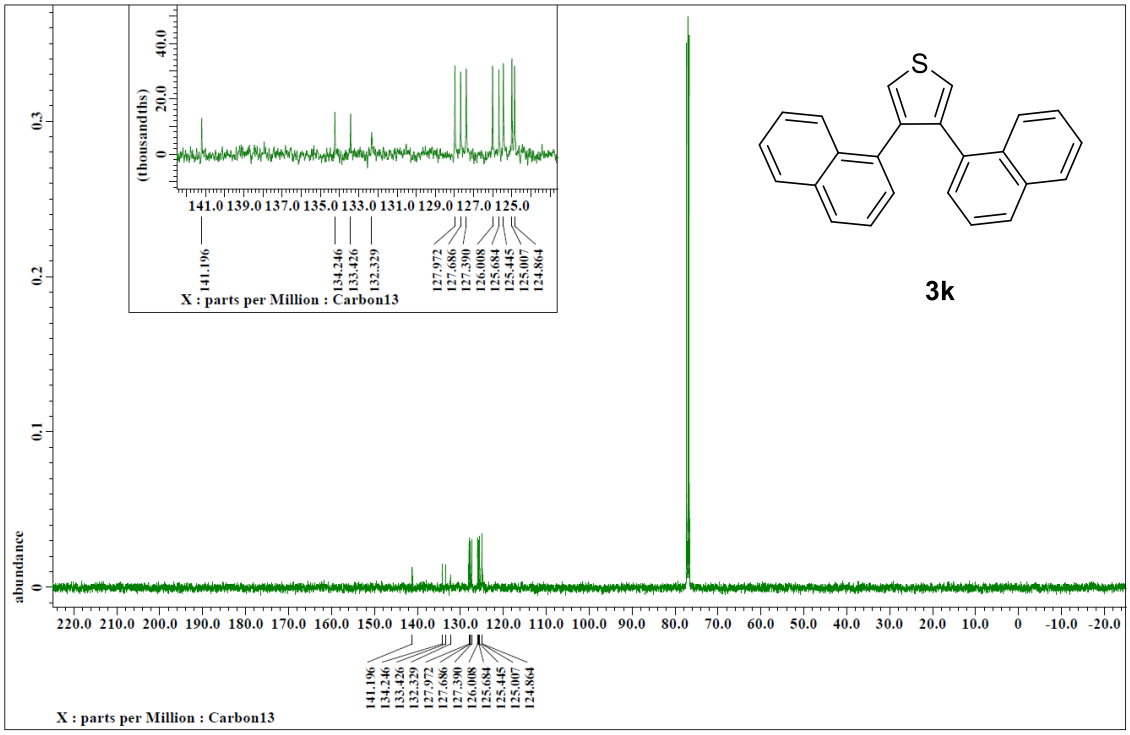


^{13}C NMR (100 MHz, $CDCl_3$)



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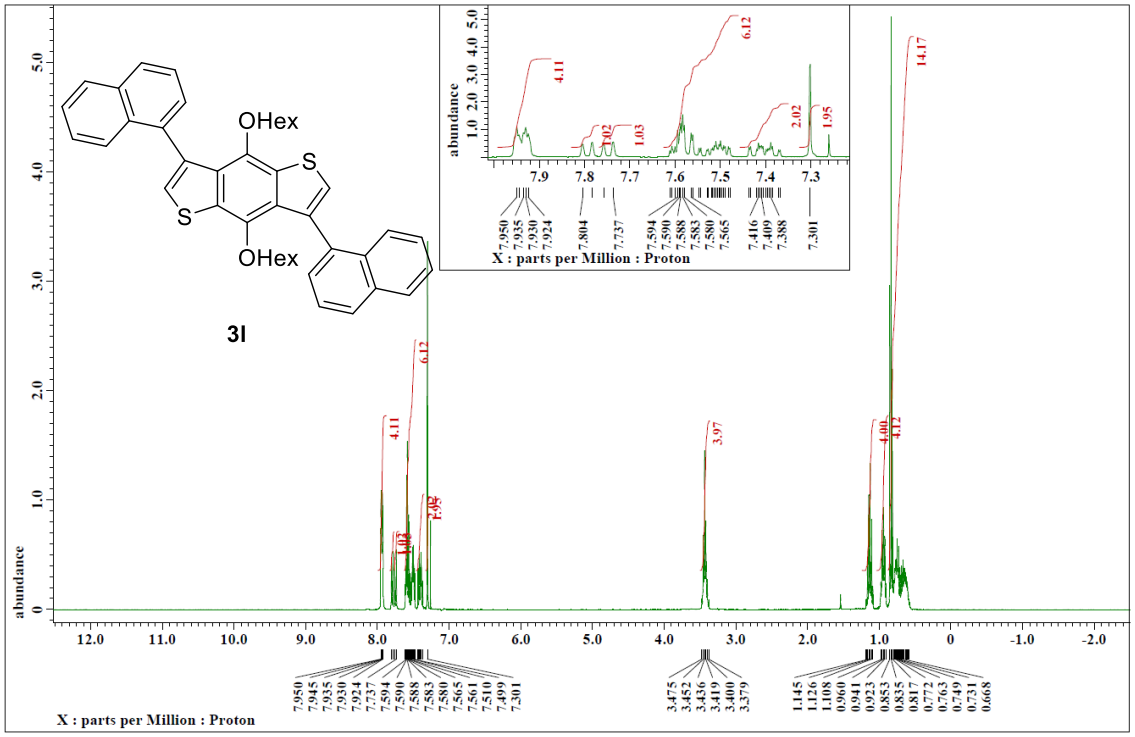
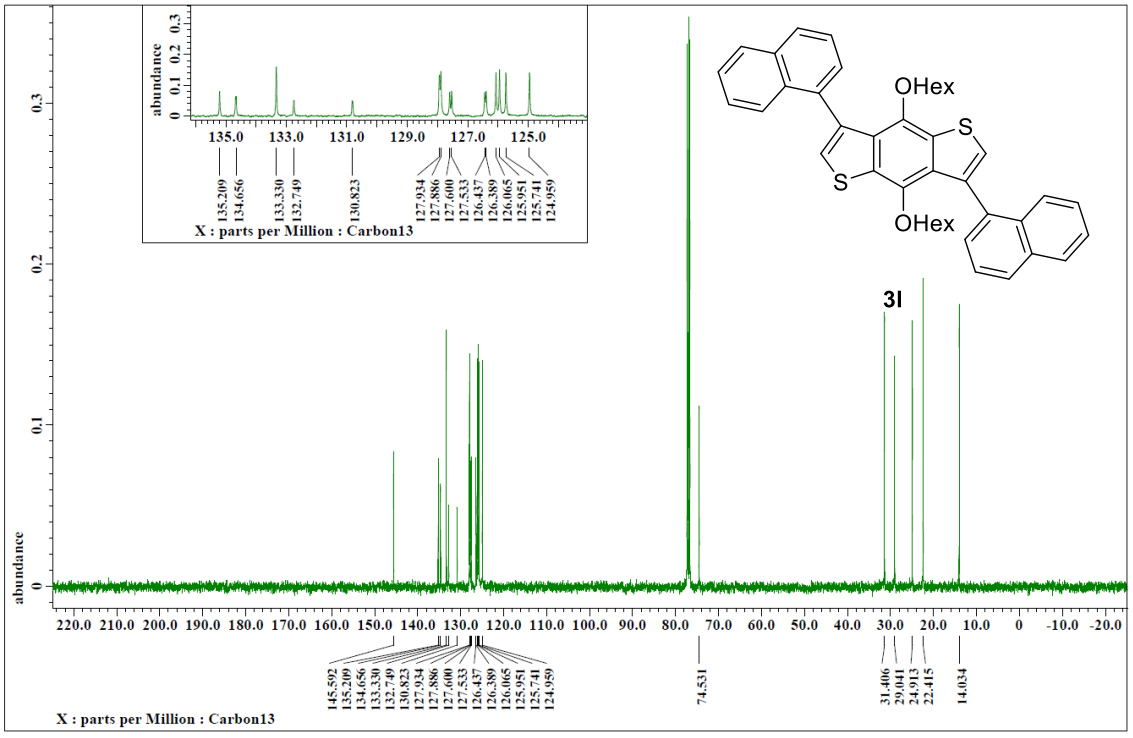


^{13}C NMR (100 MHz, $CDCl_3$)



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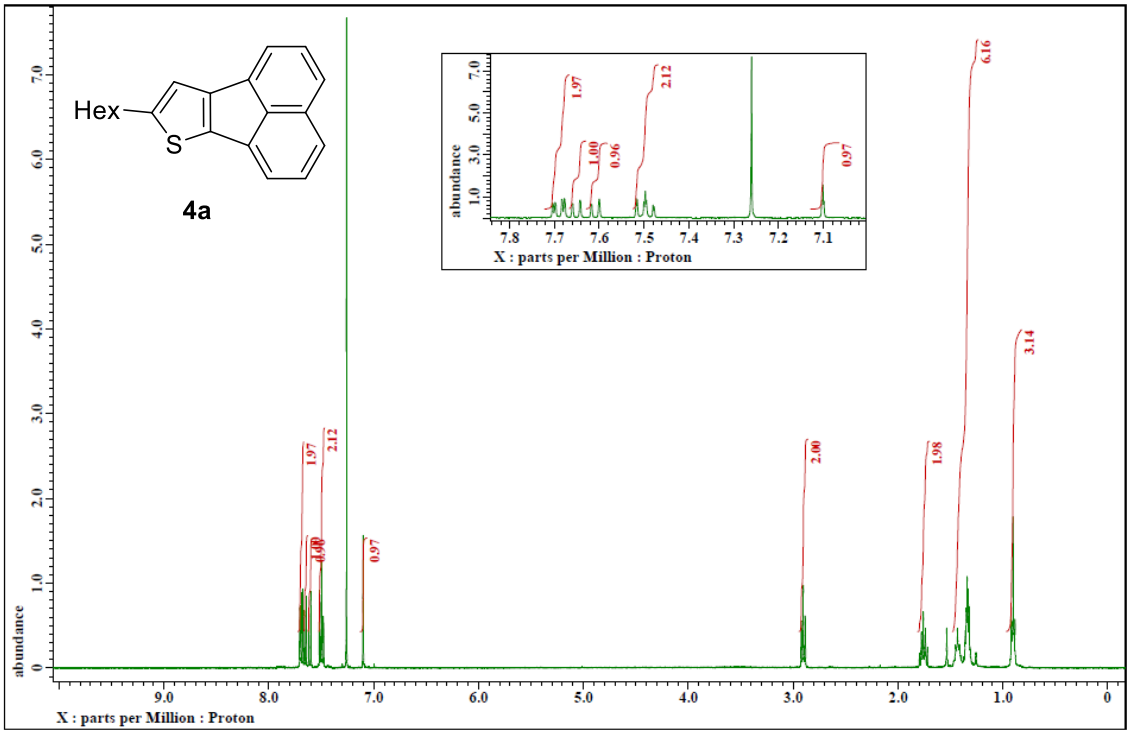

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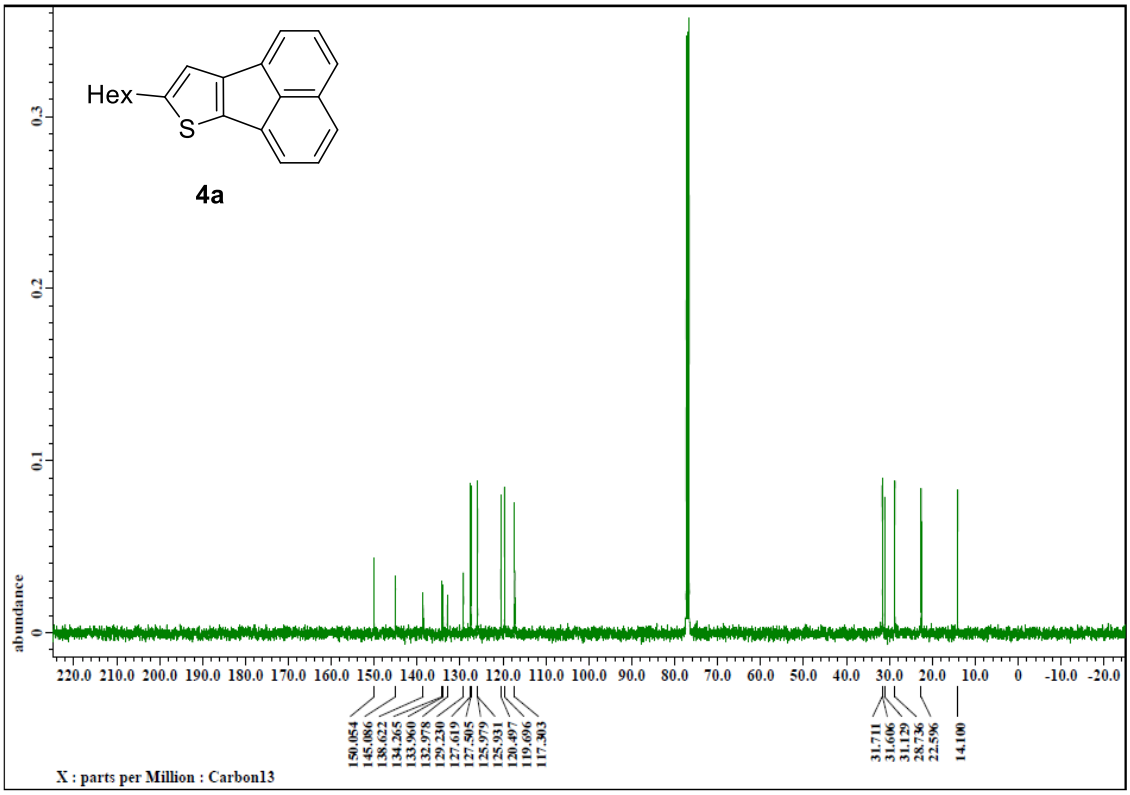

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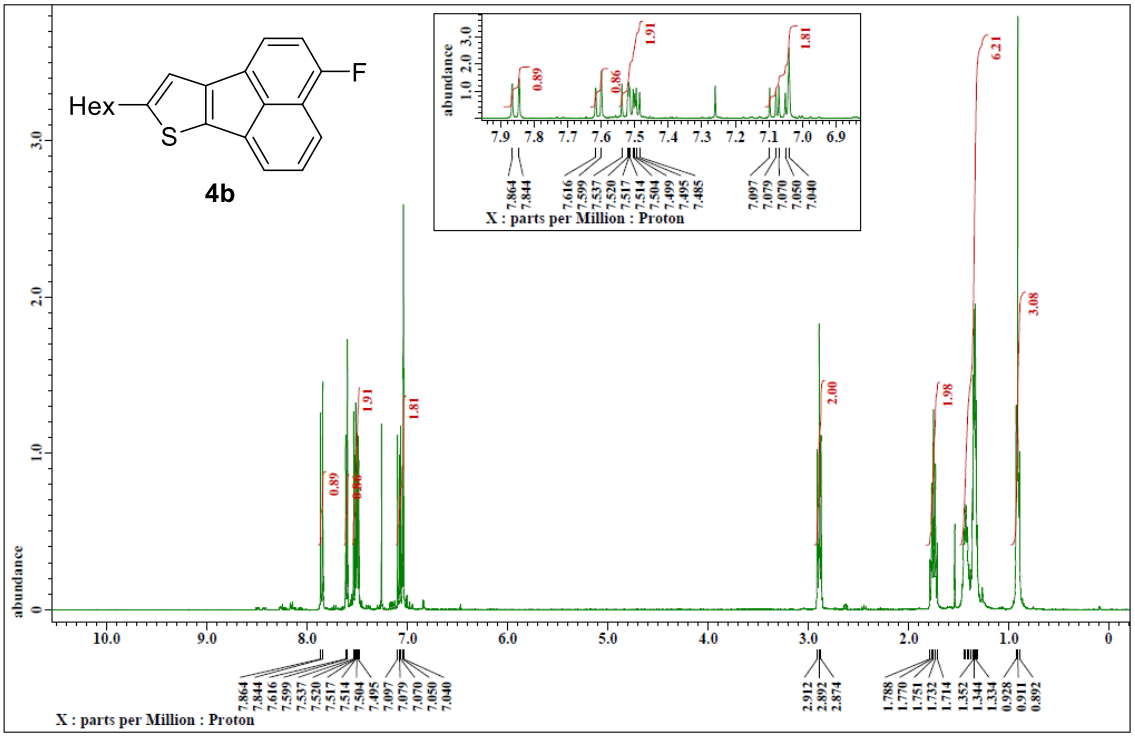

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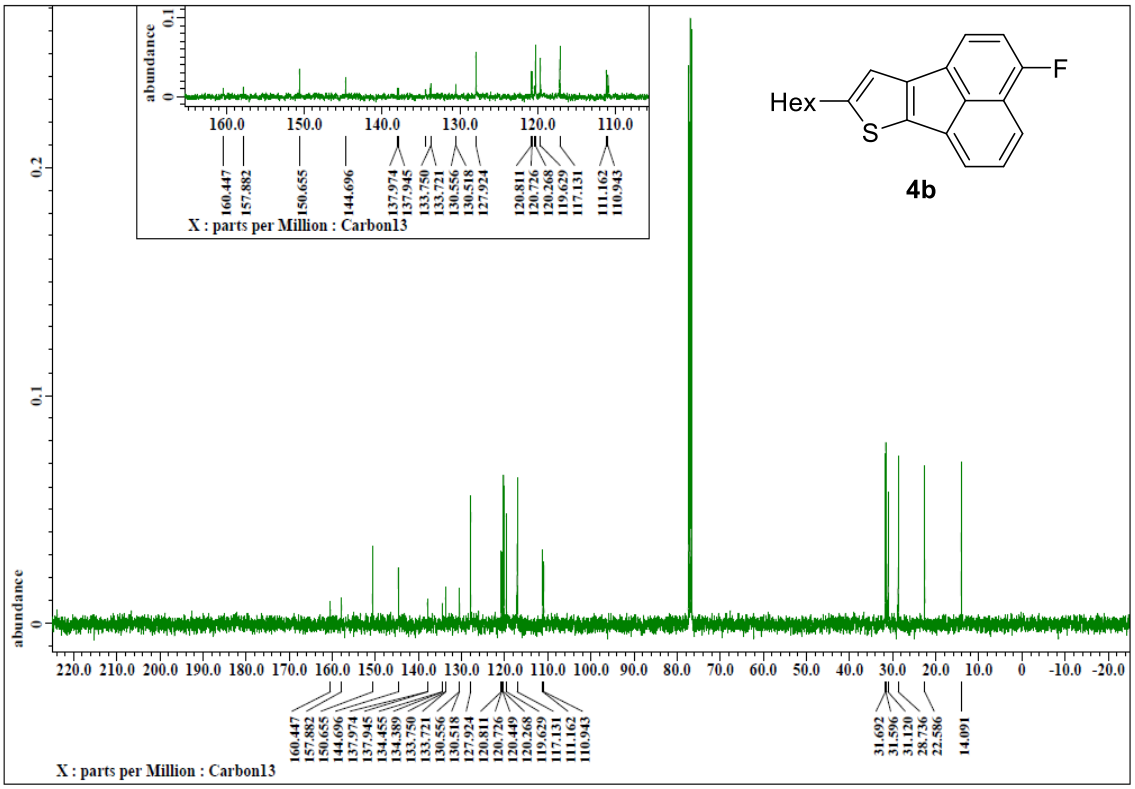
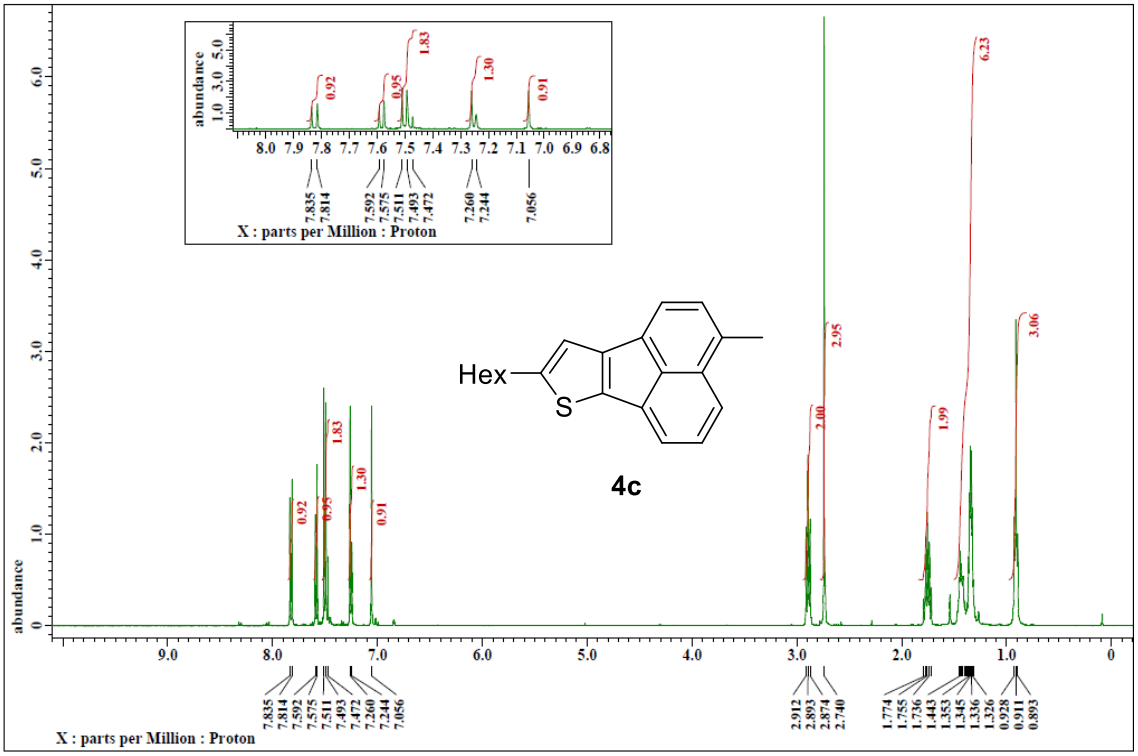
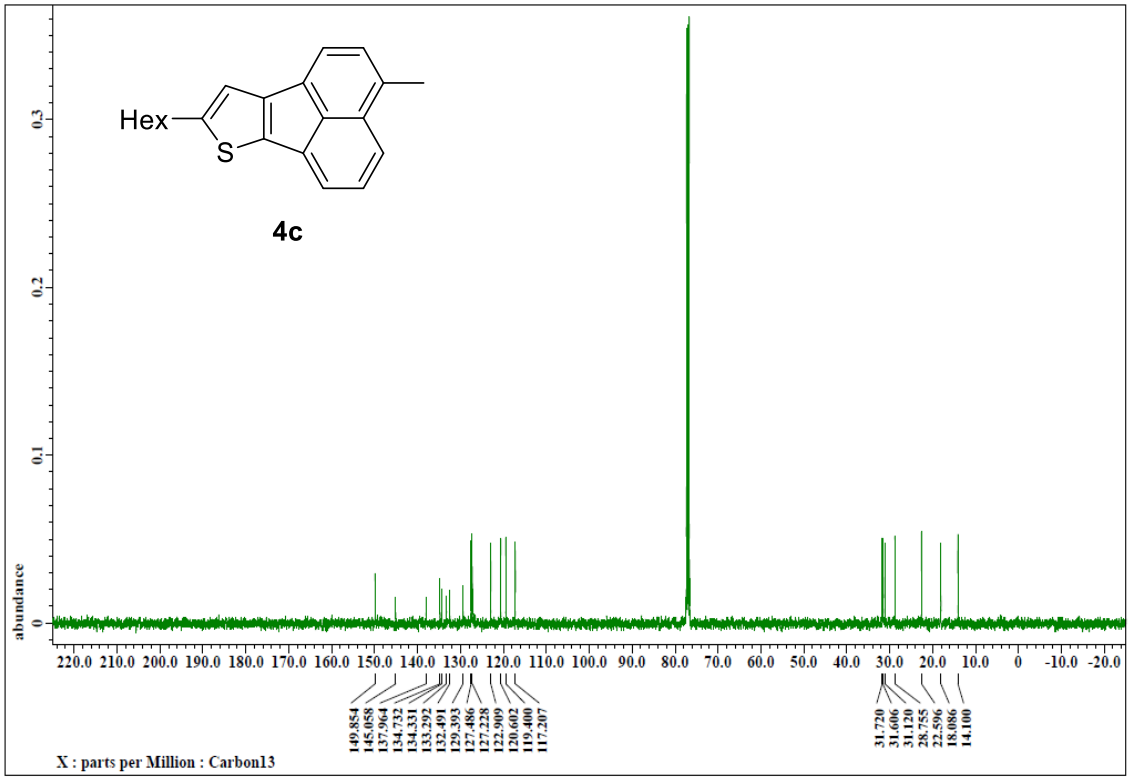


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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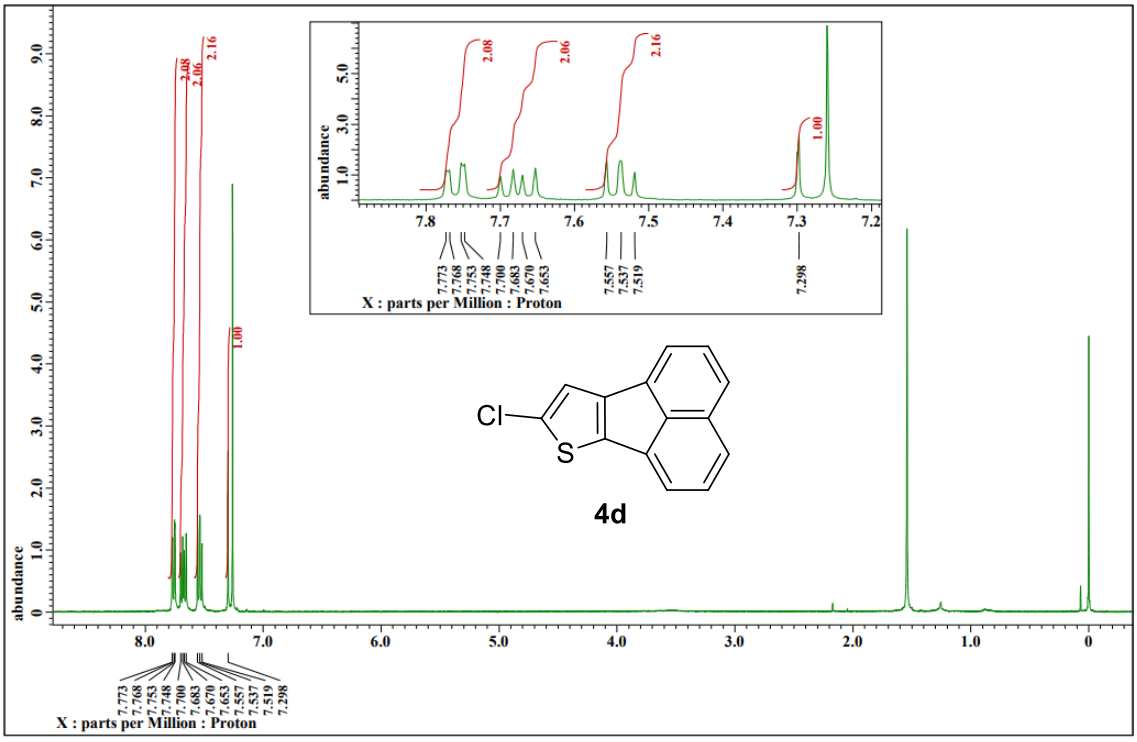

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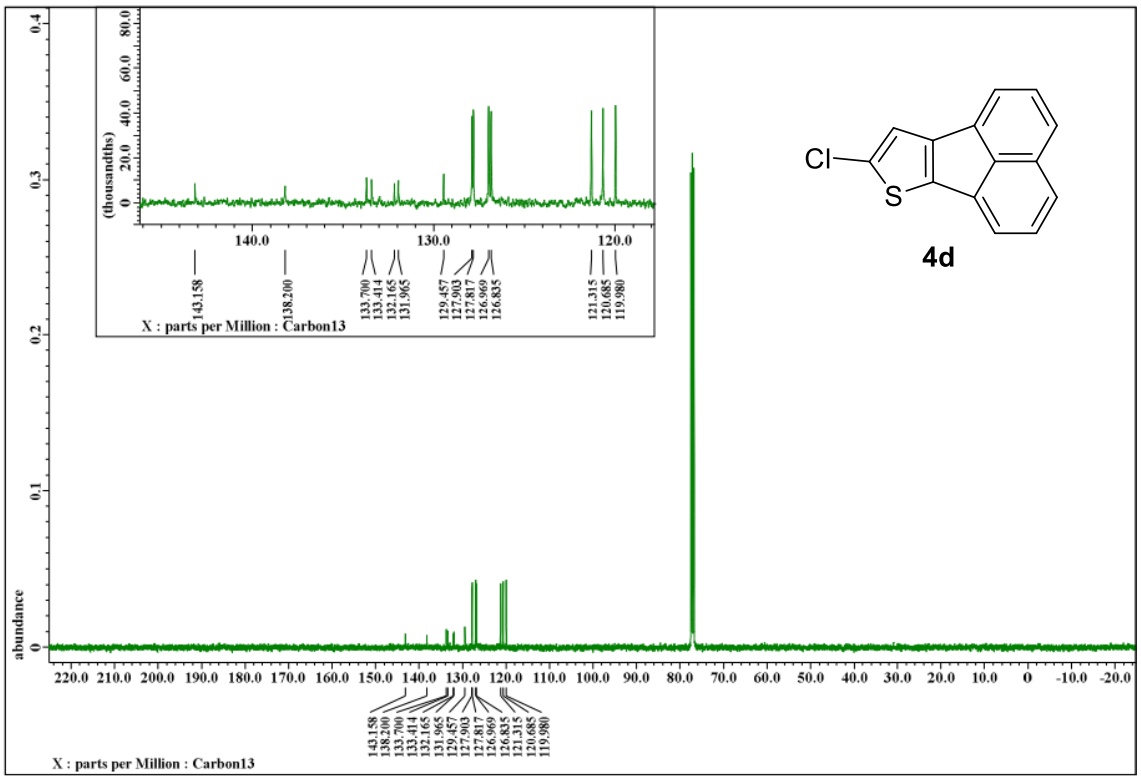

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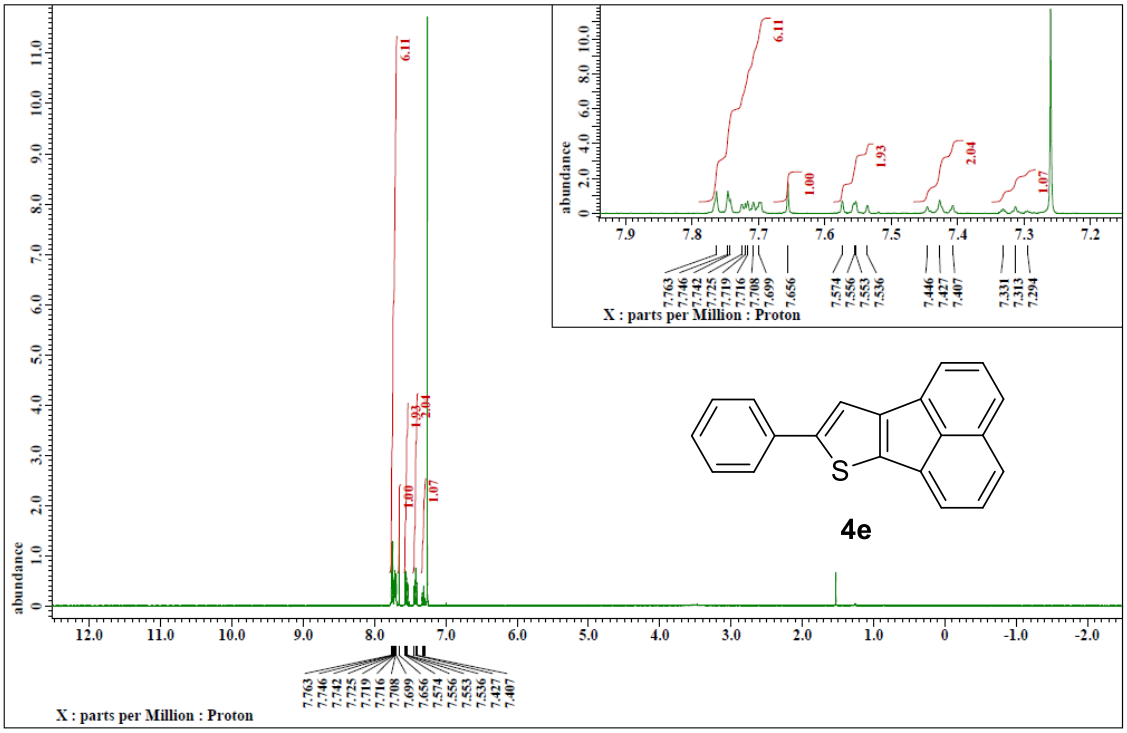
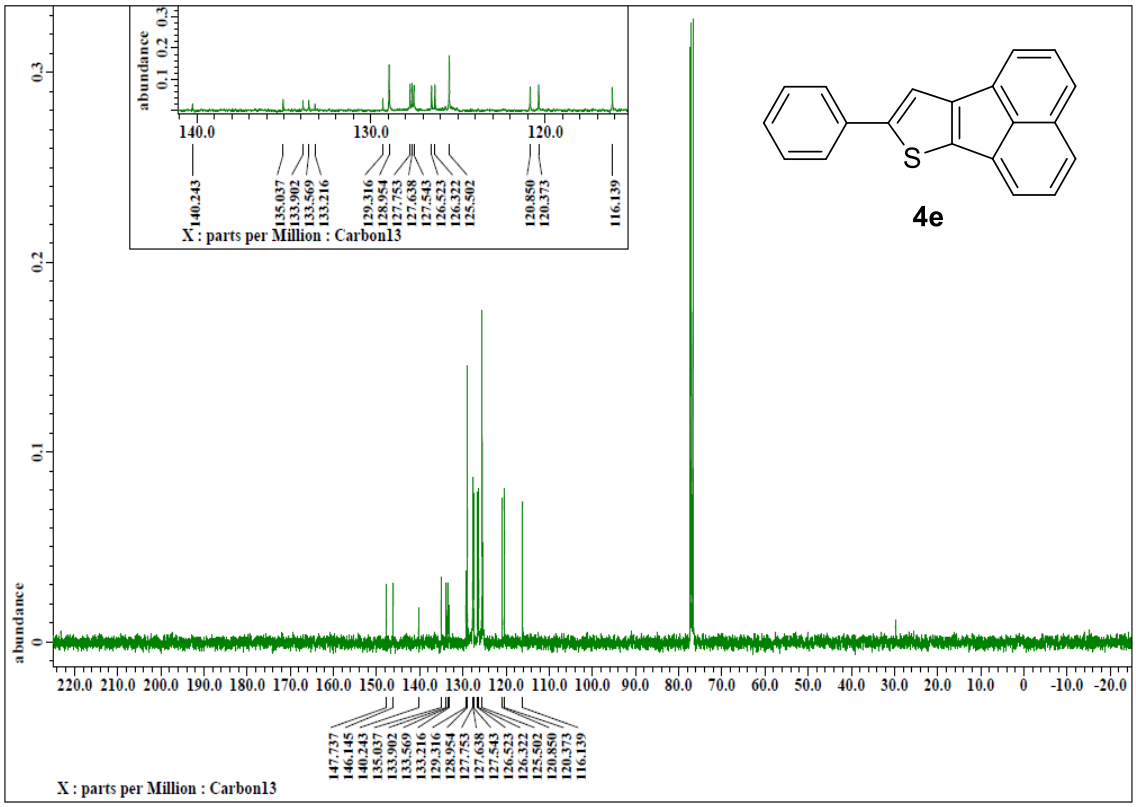


^{13}C NMR (100 MHz, $CDCl_3$)



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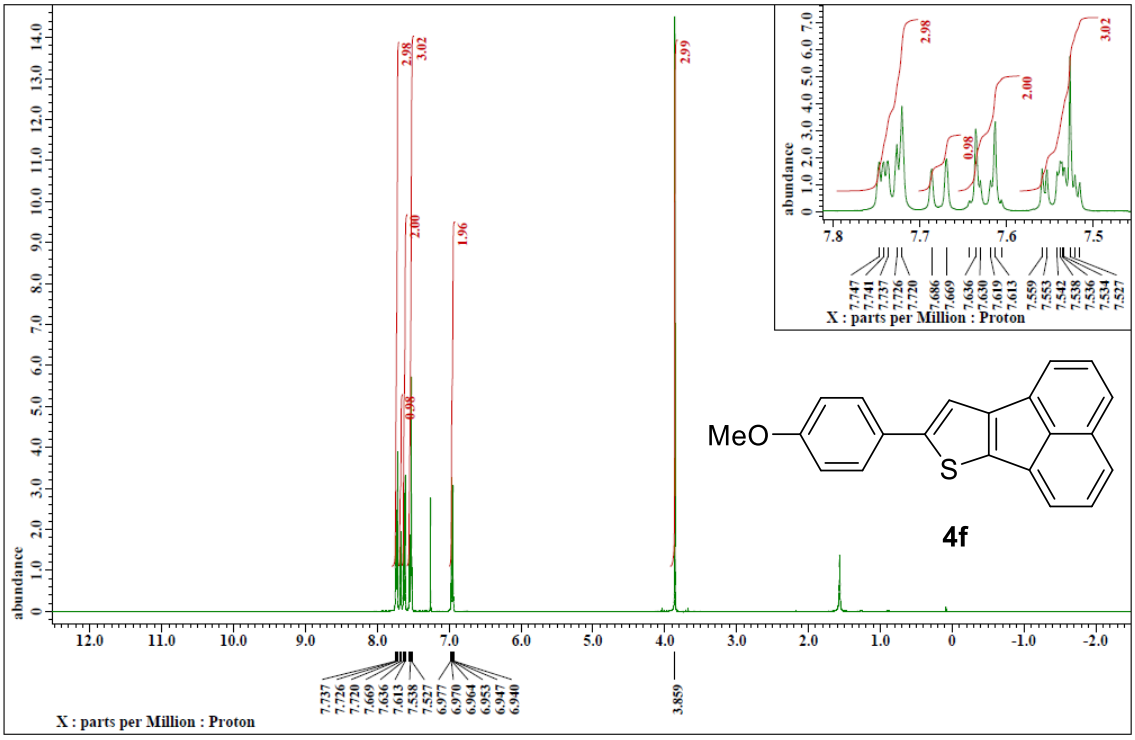
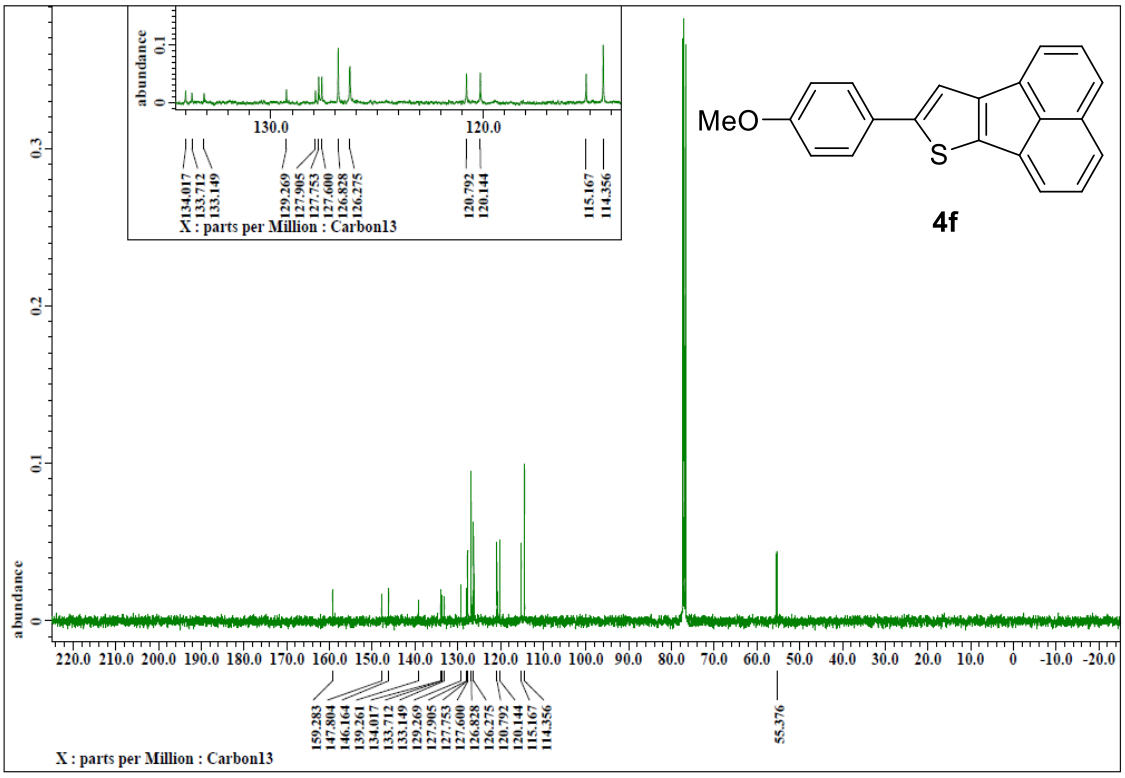
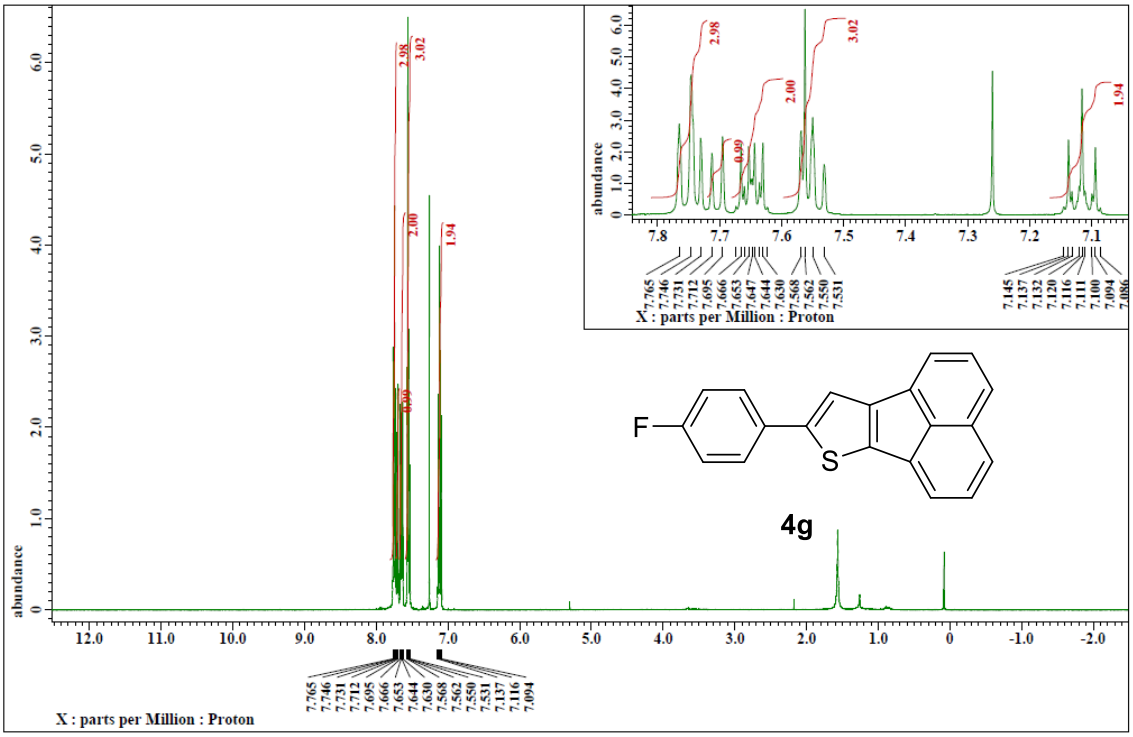


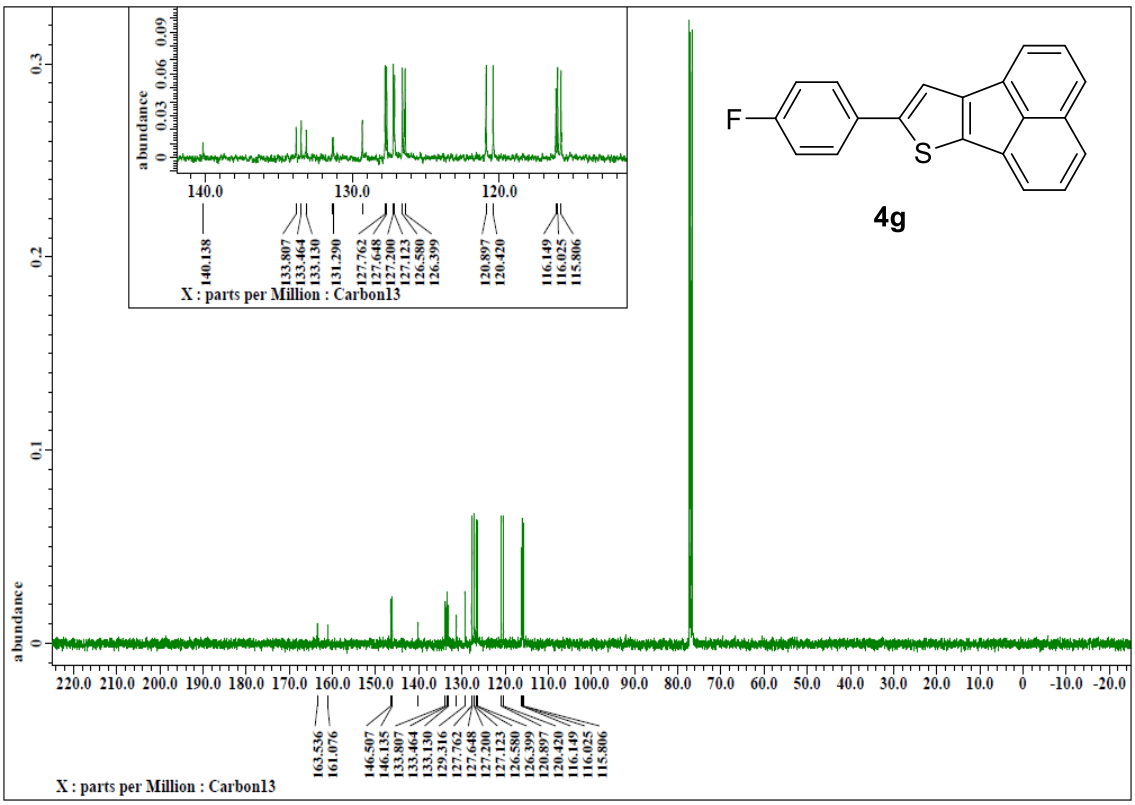
^{13}C NMR (100 MHz, $CDCl_3$)



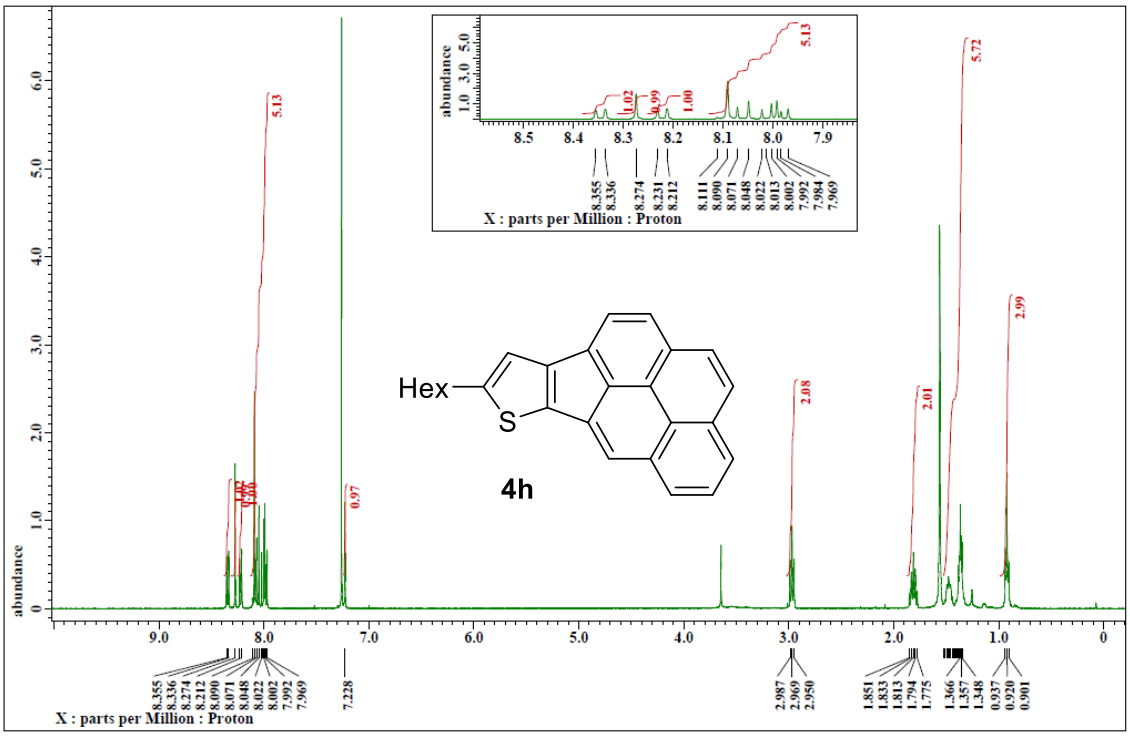
^{1}H NMR (400 MHz, $CDCl_3$)



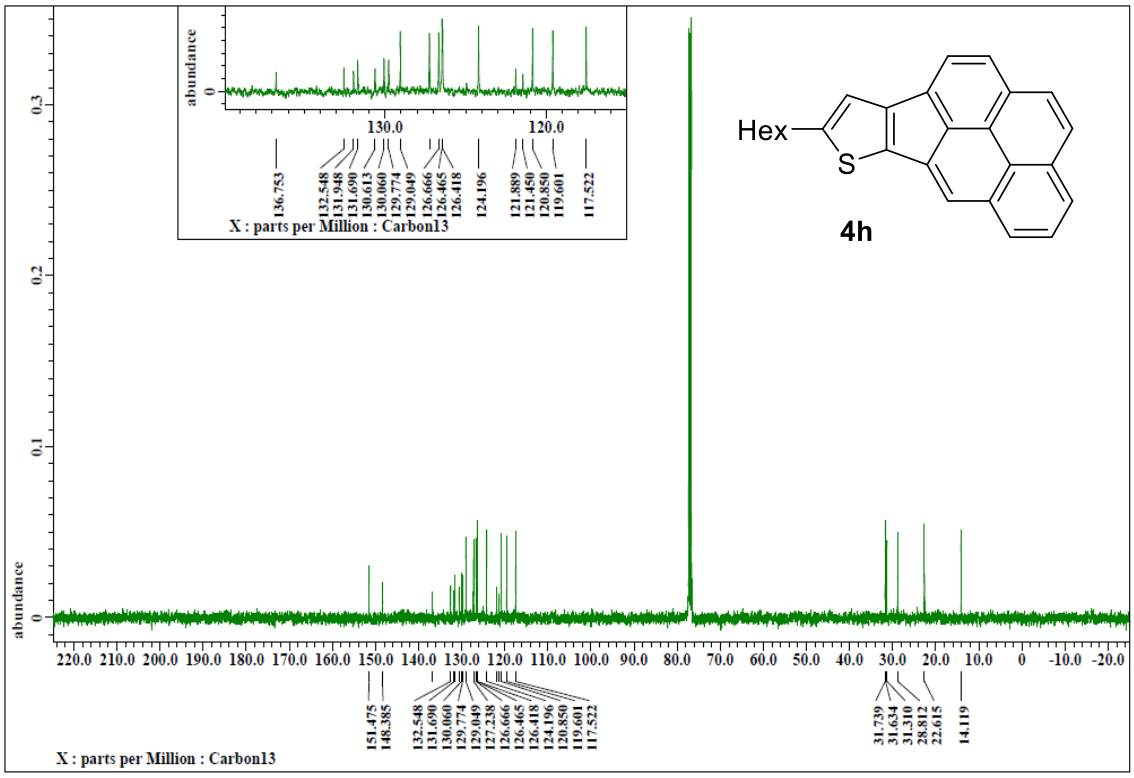
^{13}C NMR (100 MHz, $CDCl_3$)



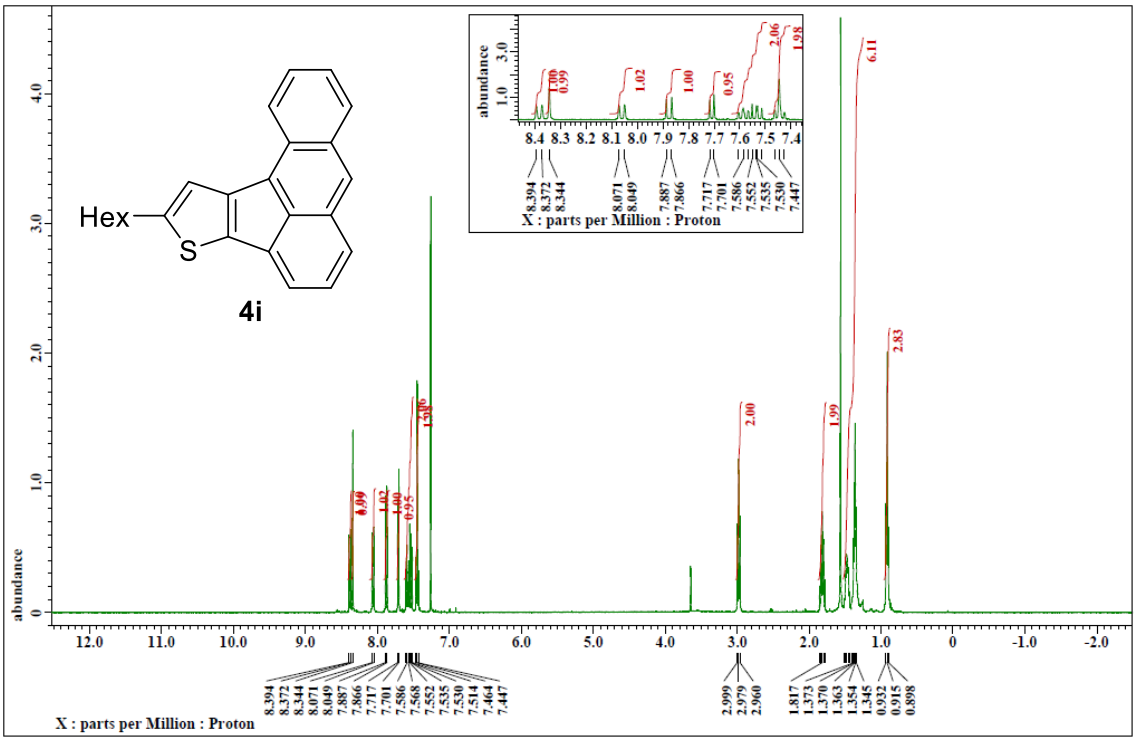
^{1}H NMR (400 MHz, $CDCl_3$)



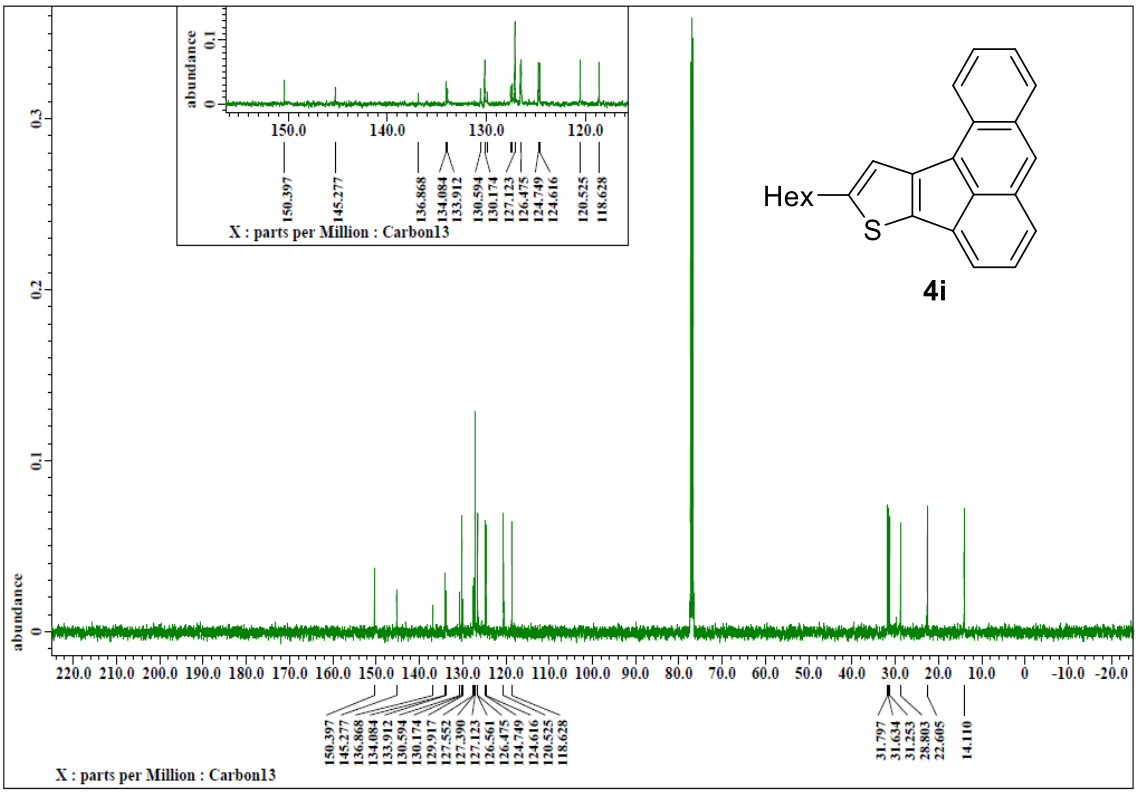
^{13}C NMR (100 MHz, $CDCl_3$)



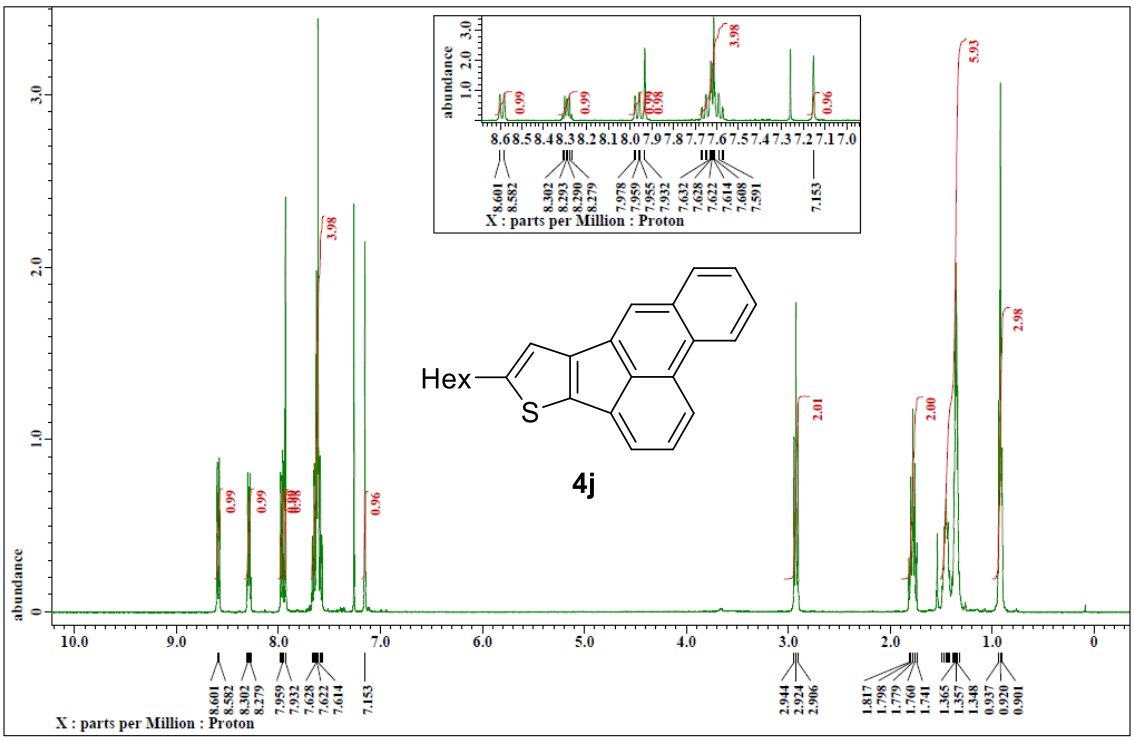
^{1}H NMR (400 MHz, $CDCl_3$)



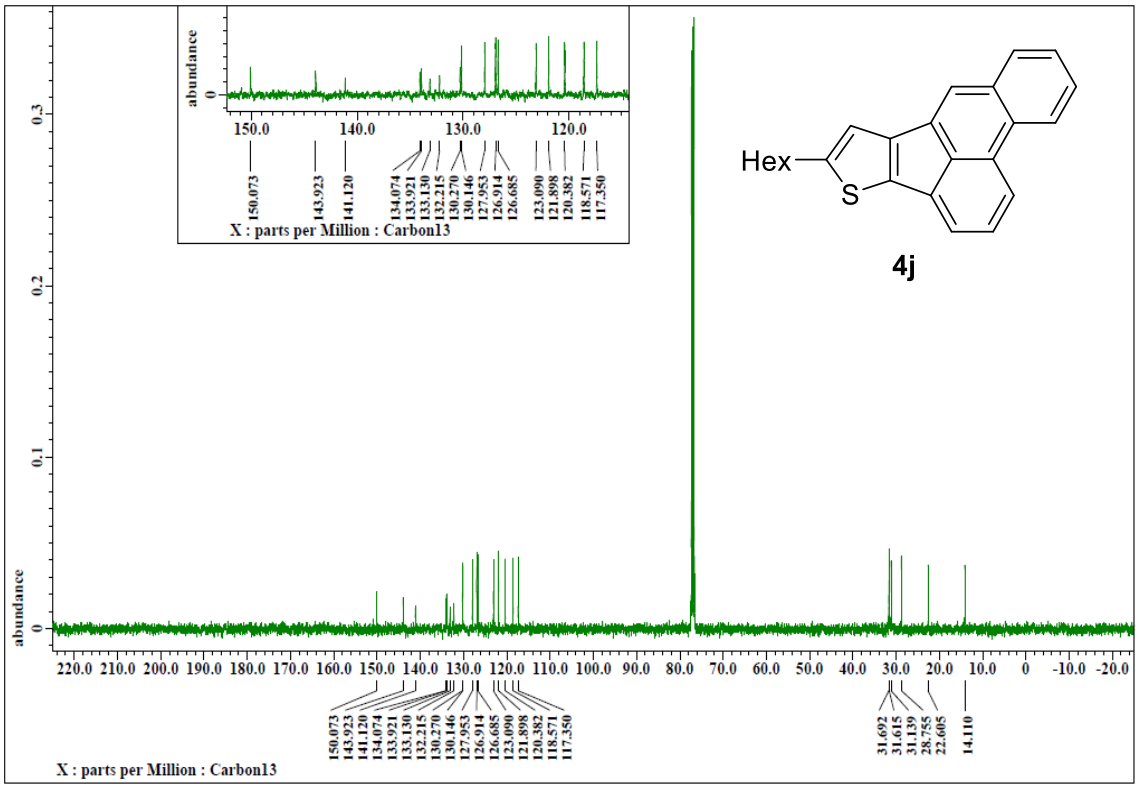
^{13}C NMR (100 MHz, $CDCl_3$)



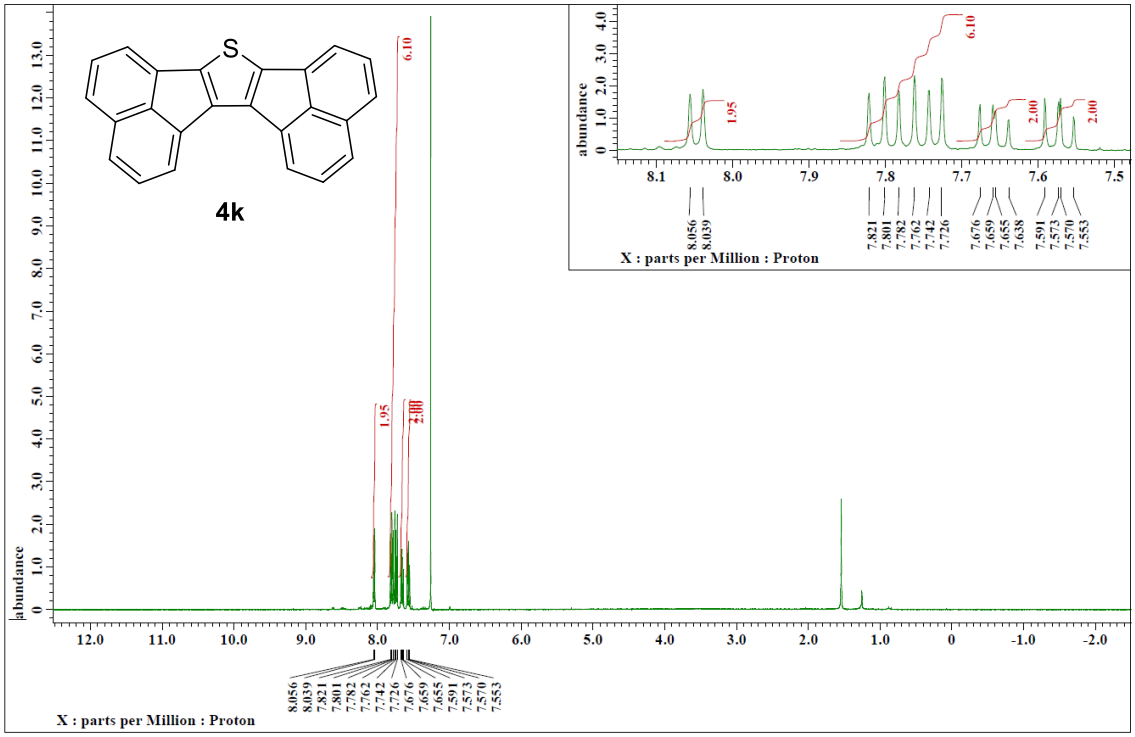
^{1}H NMR (400 MHz, $CDCl_3$)



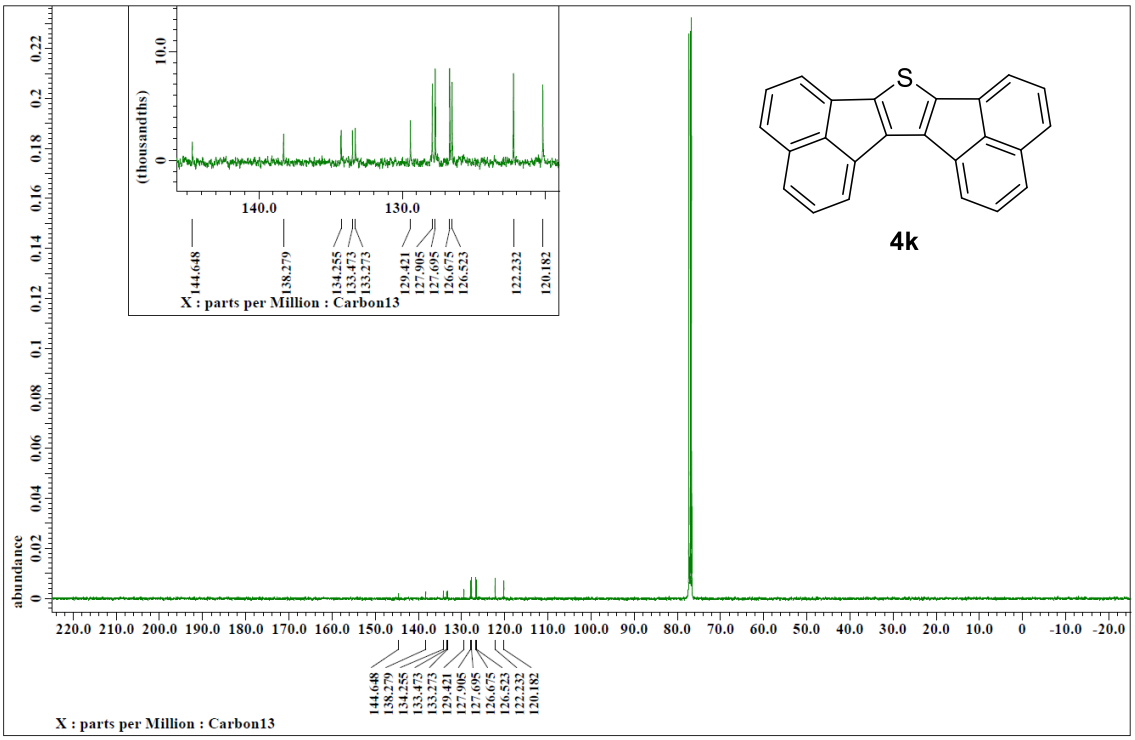
^{13}C NMR (100 MHz, $CDCl_3$)



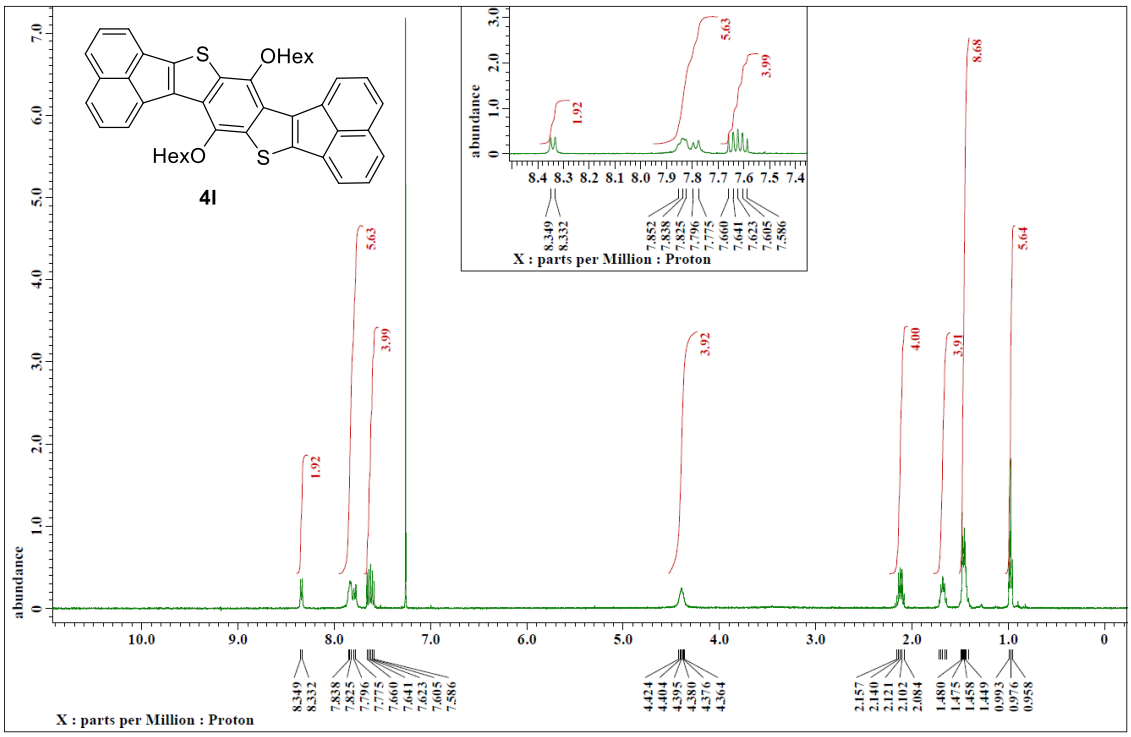
^{1}H NMR (400 MHz, $CDCl_3$)



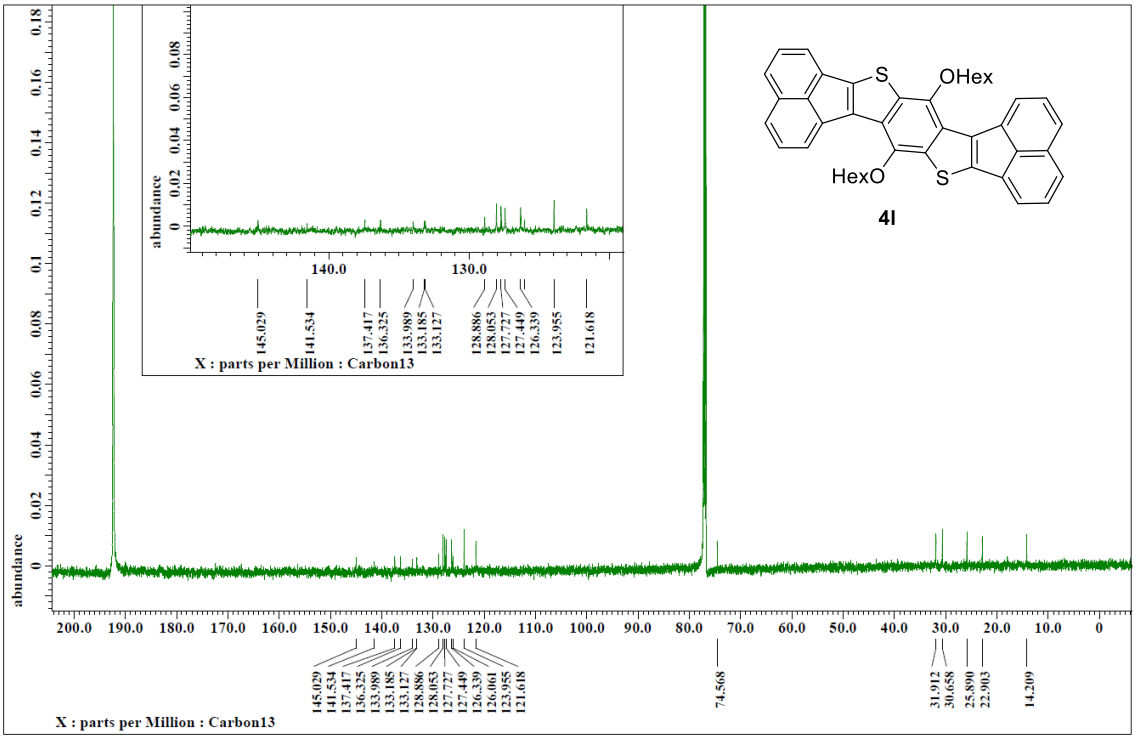
^{13}C NMR (100 MHz, $CDCl_3$)



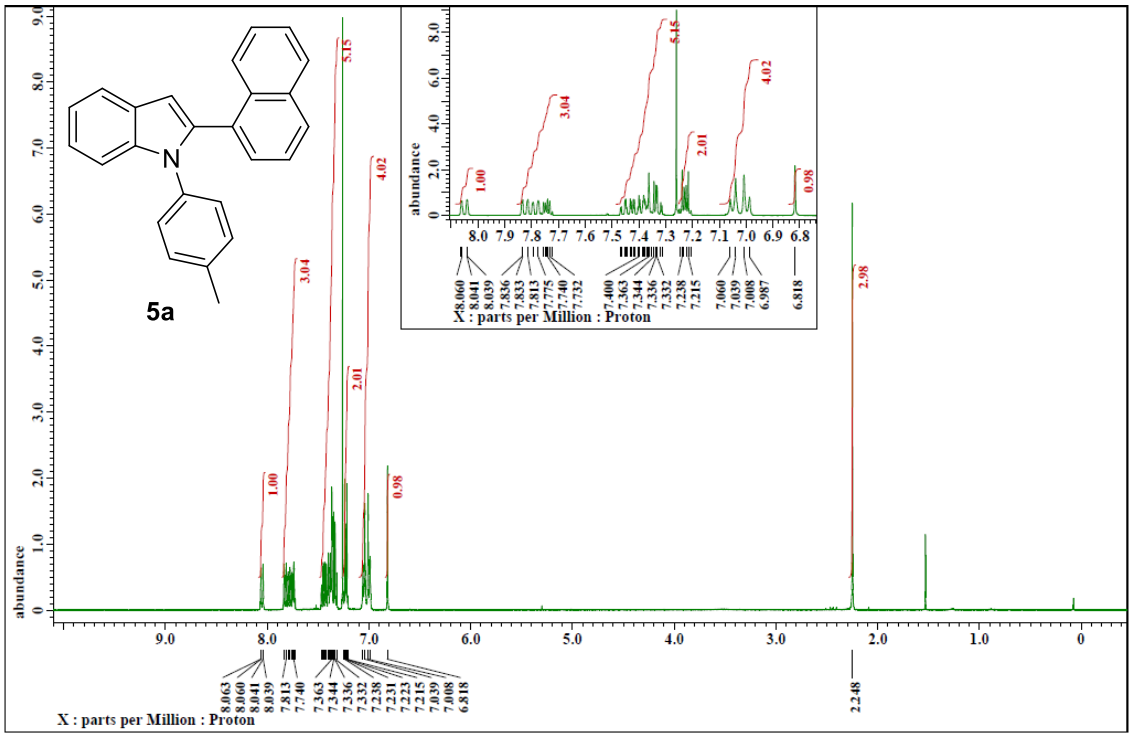
^{1}H NMR (400 MHz, $CDCl_3$:CS_2)



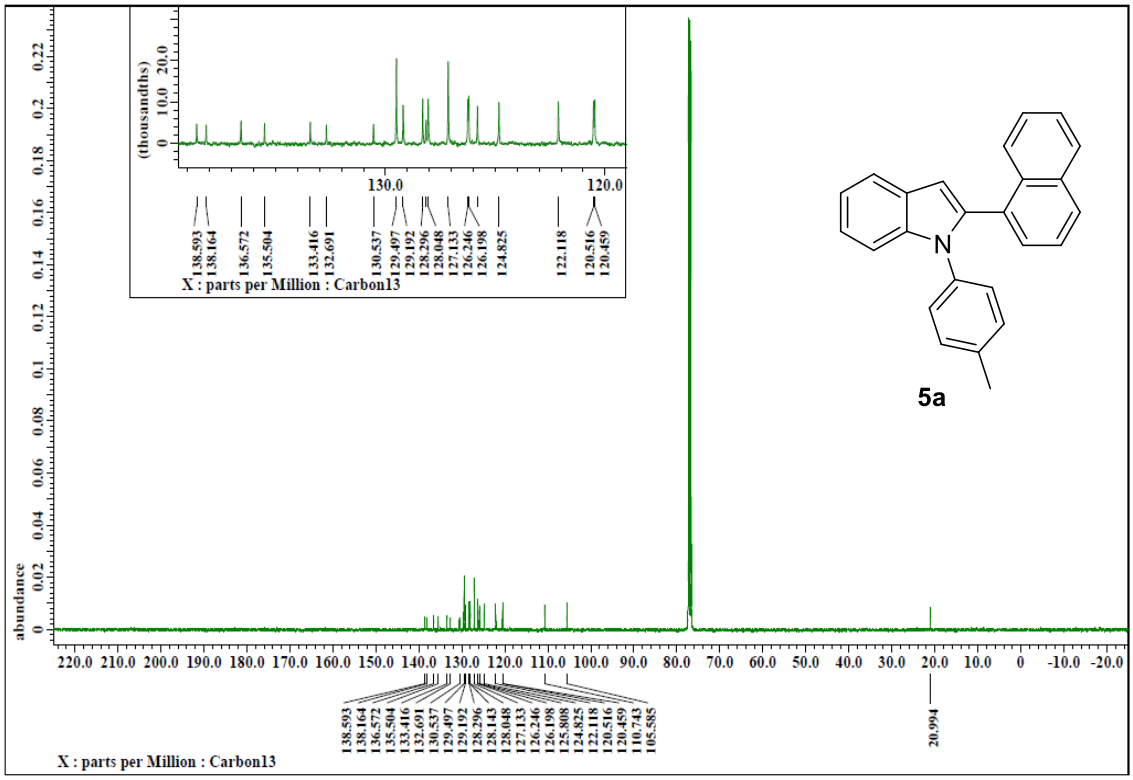
^{13}C NMR (150 MHz, $CDCl_3$:CS_2)



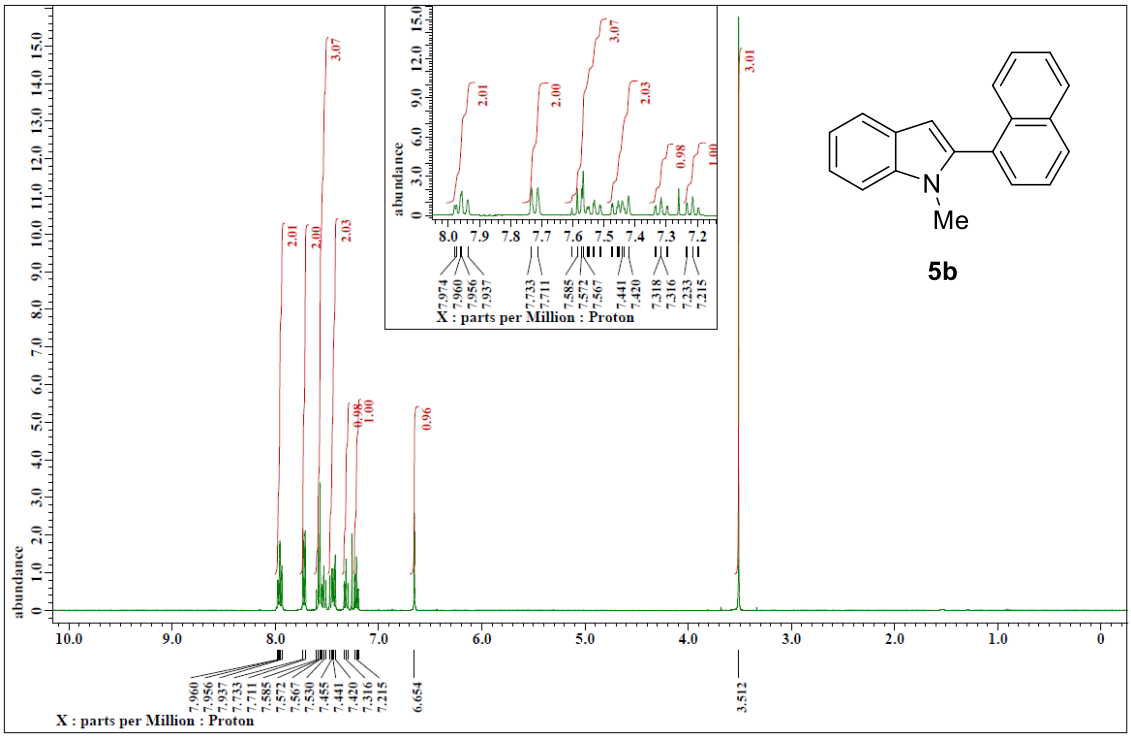
^{1}H NMR (400 MHz, $CDCl_3$)



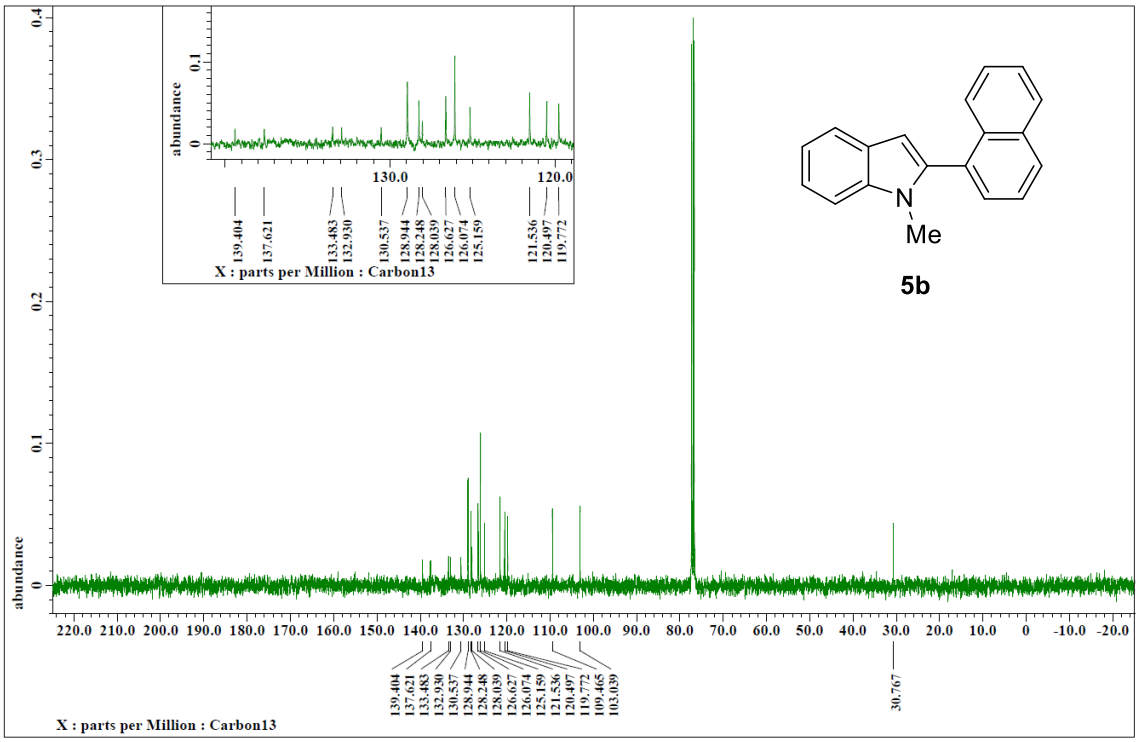
^{13}C NMR (100 MHz, $CDCl_3$)



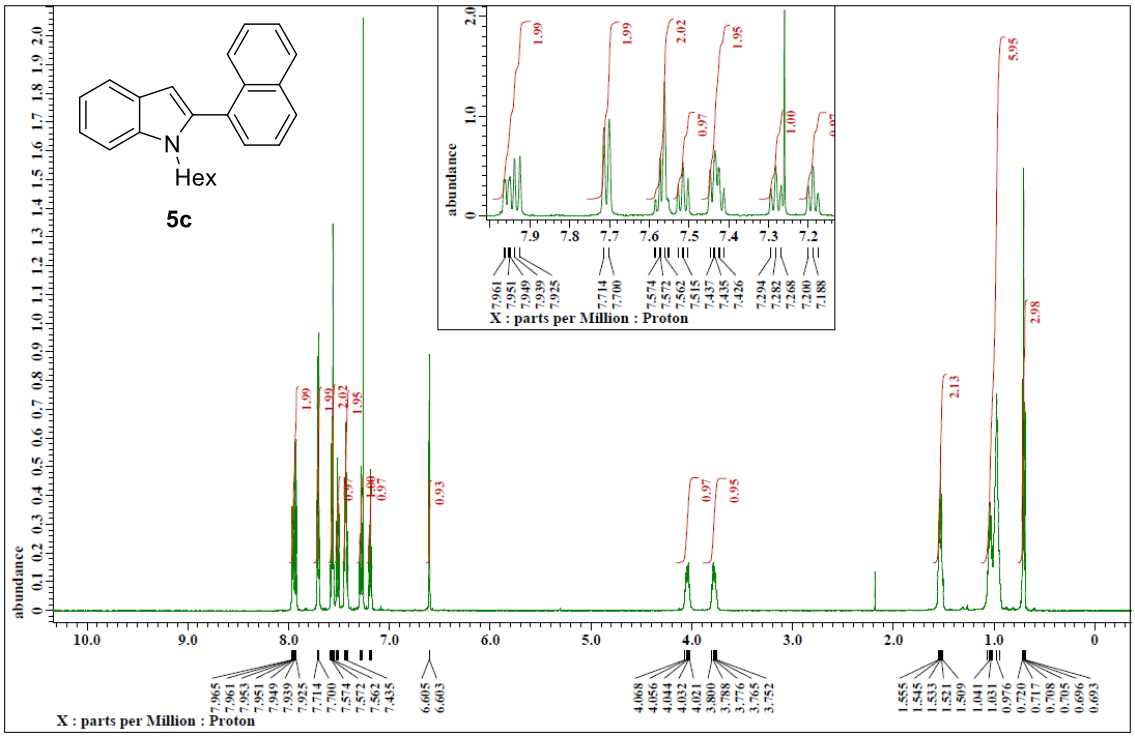
^{1}H NMR (400 MHz, $CDCl_3$)



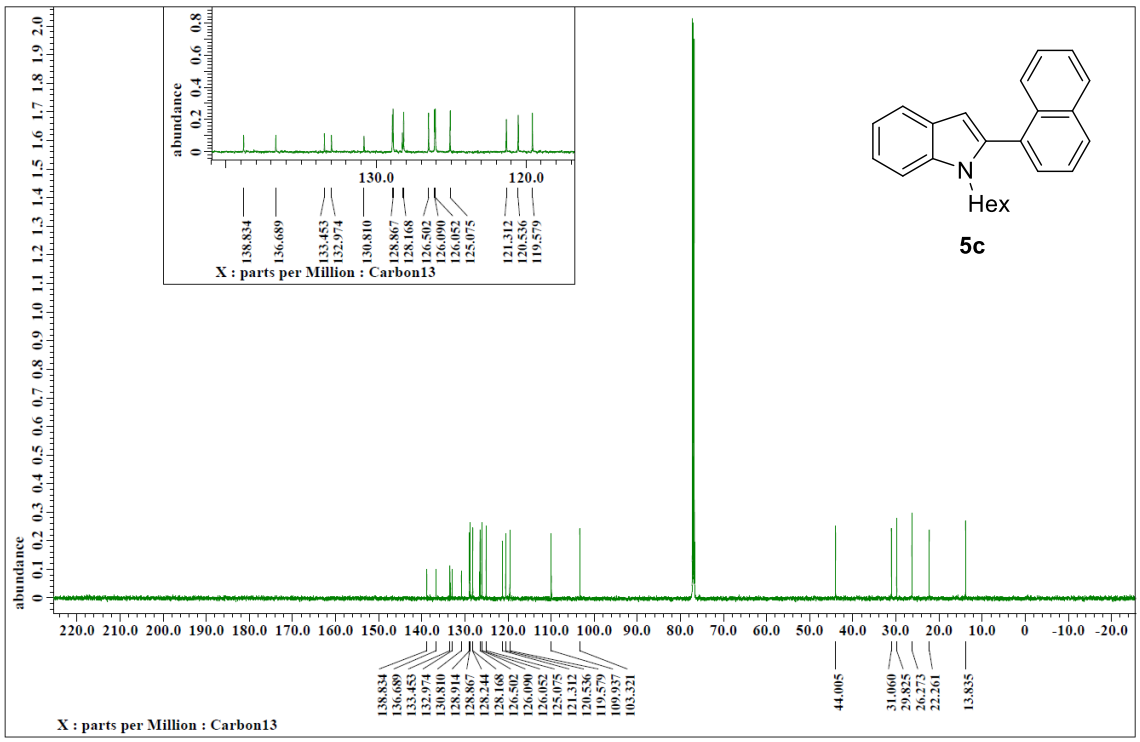
^{13}C NMR (100 MHz, $CDCl_3$)



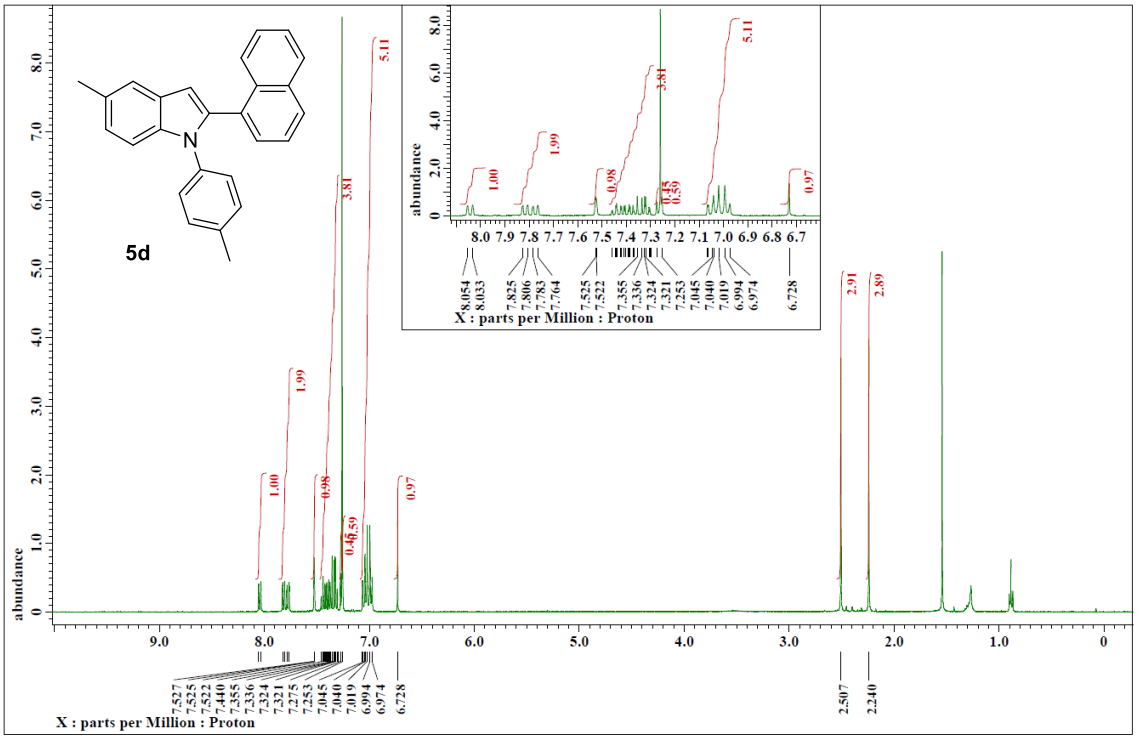
^{1}H NMR (600 MHz, $CDCl_3$)



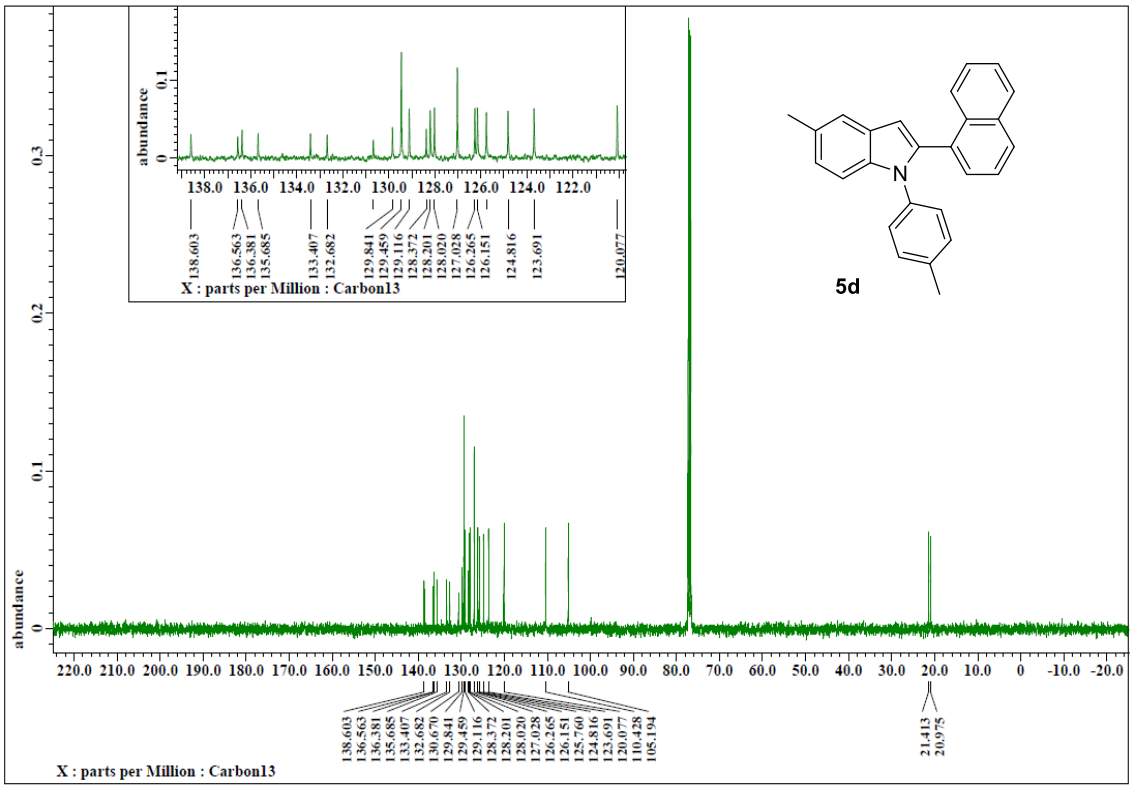
^{13}C NMR (150 MHz, $CDCl_3$)



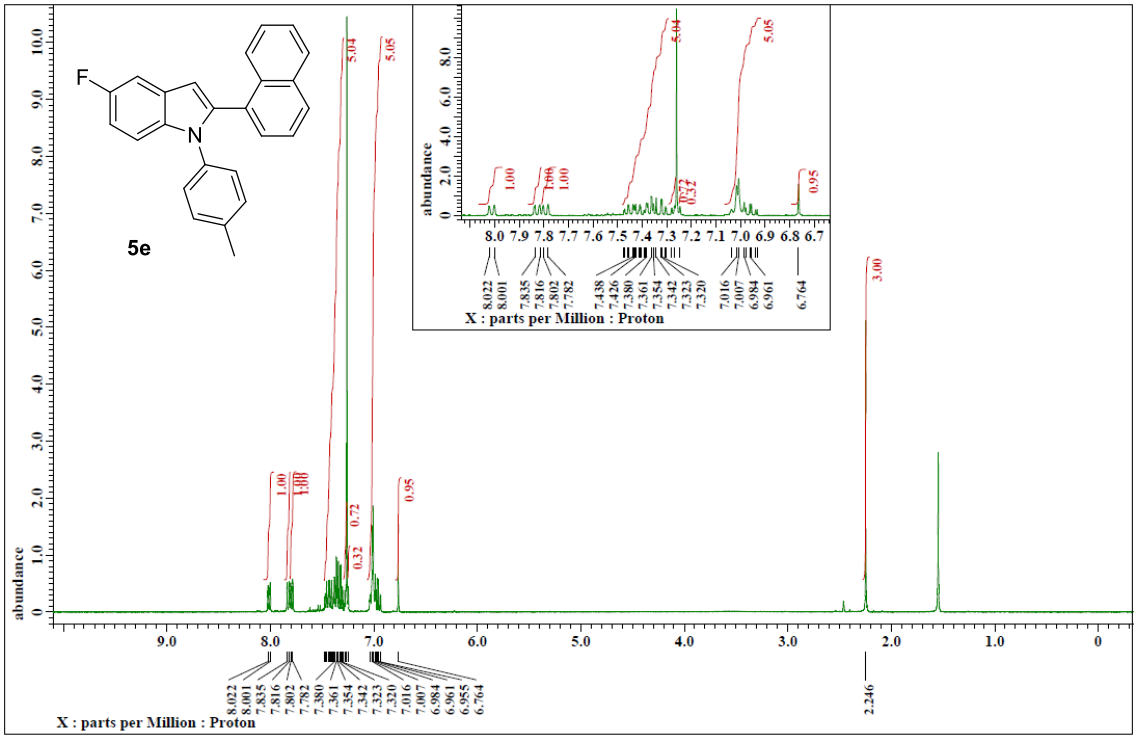
^{1}H NMR (400 MHz, $CDCl_3$)



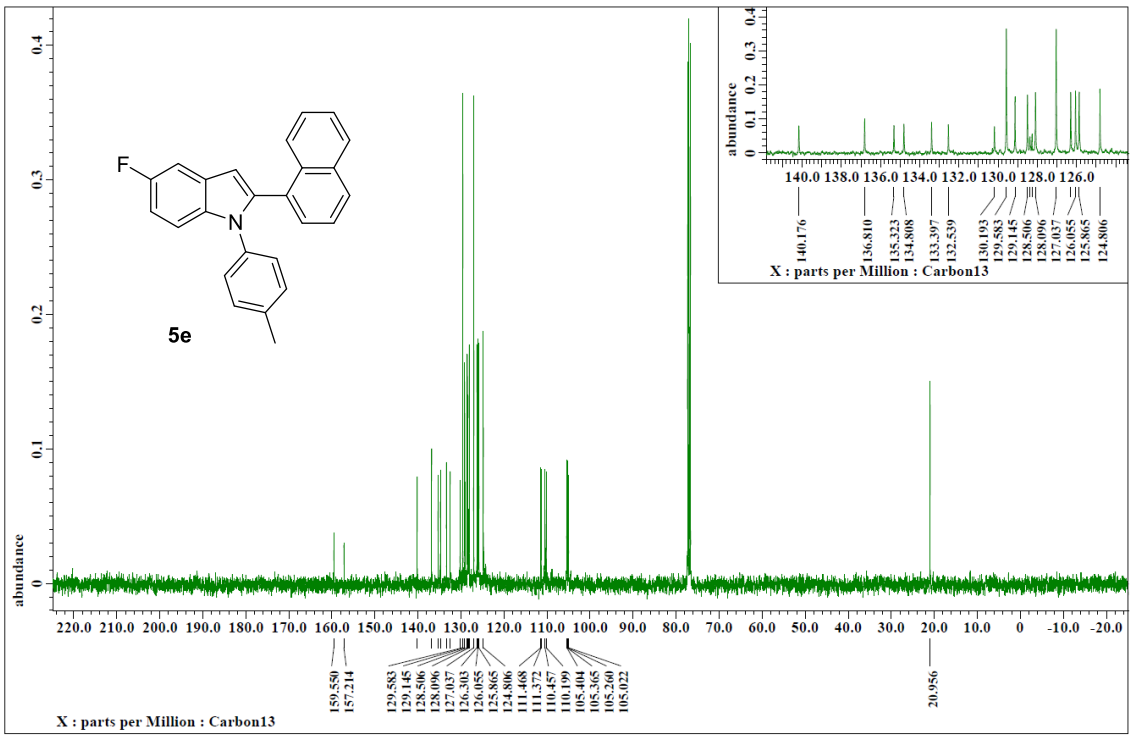
^{13}C NMR (100 MHz, $CDCl_3$)



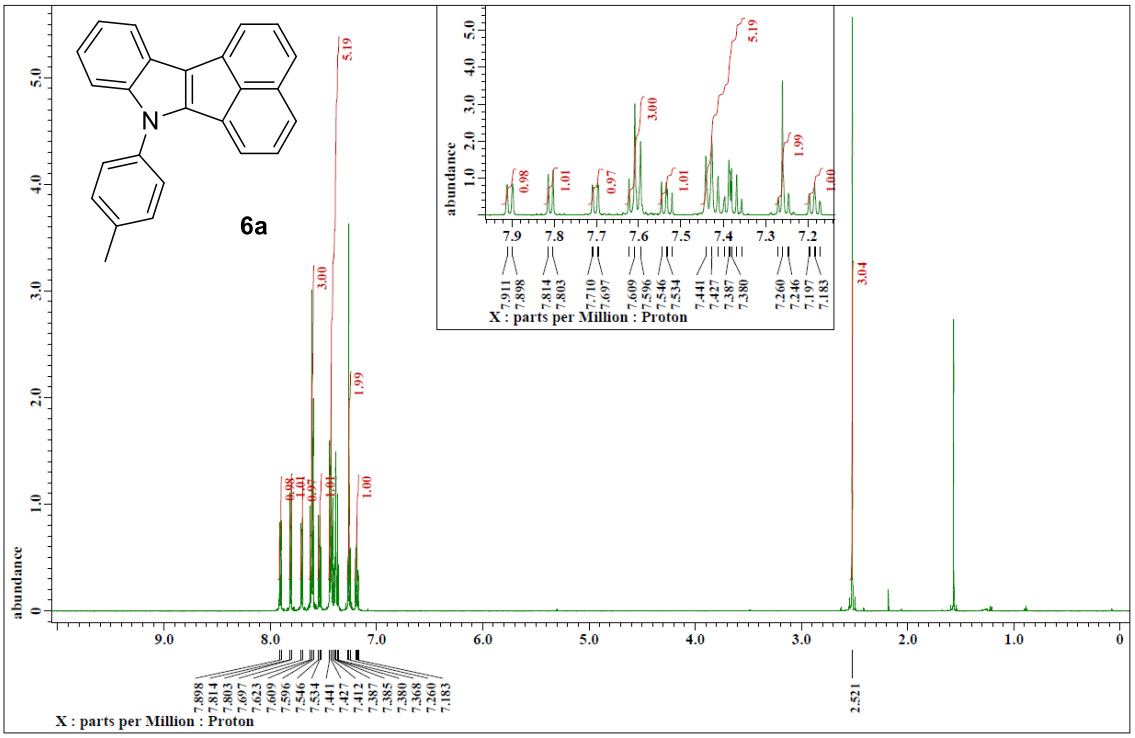
^{1}H NMR (400 MHz, $CDCl_3$)



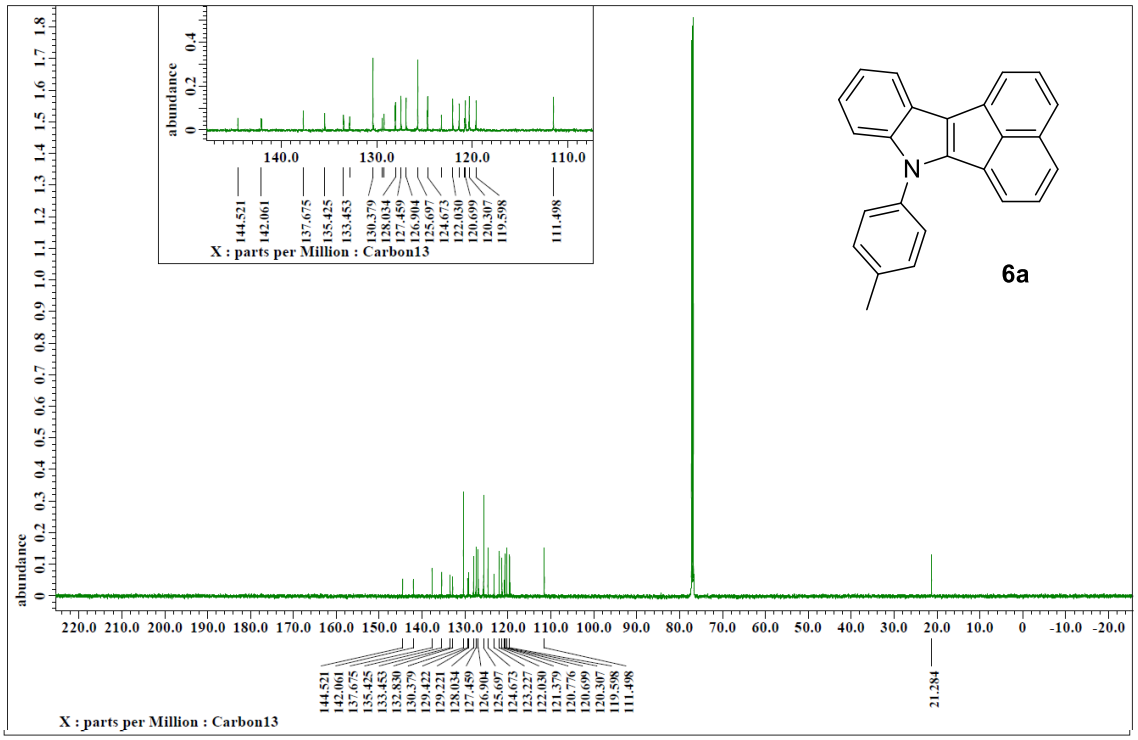
^{13}C NMR (100 MHz, $CDCl_3$)



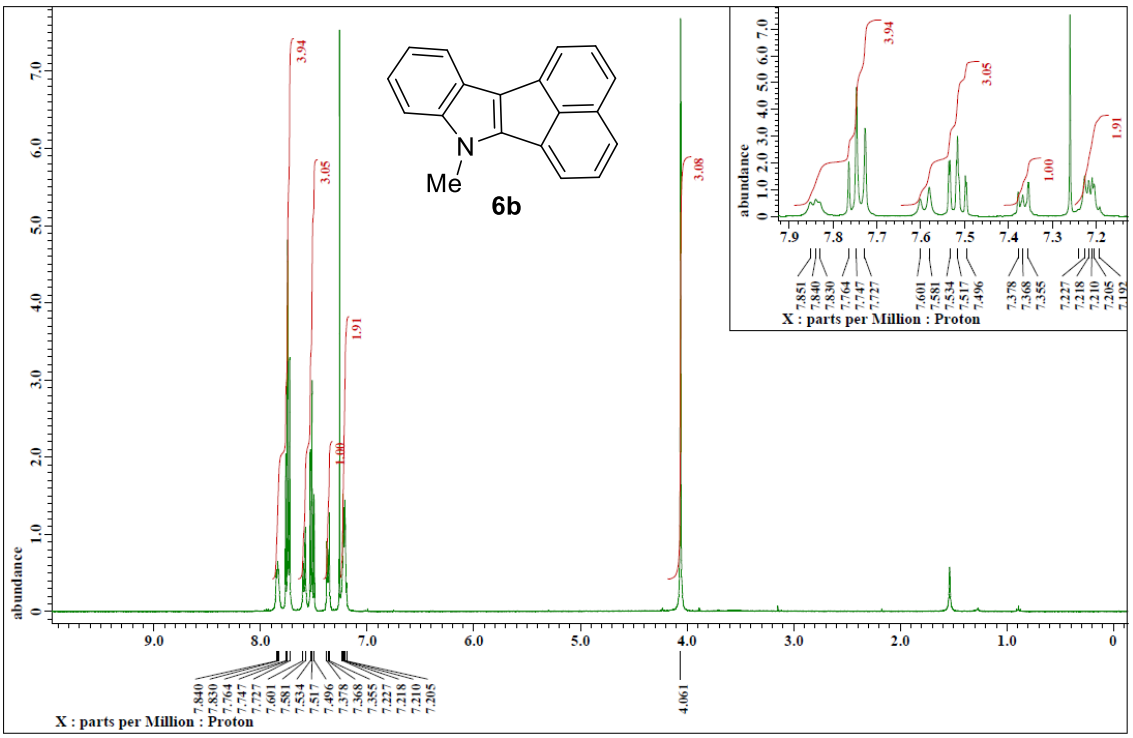
^{1}H NMR (600 MHz, $CDCl_3$)



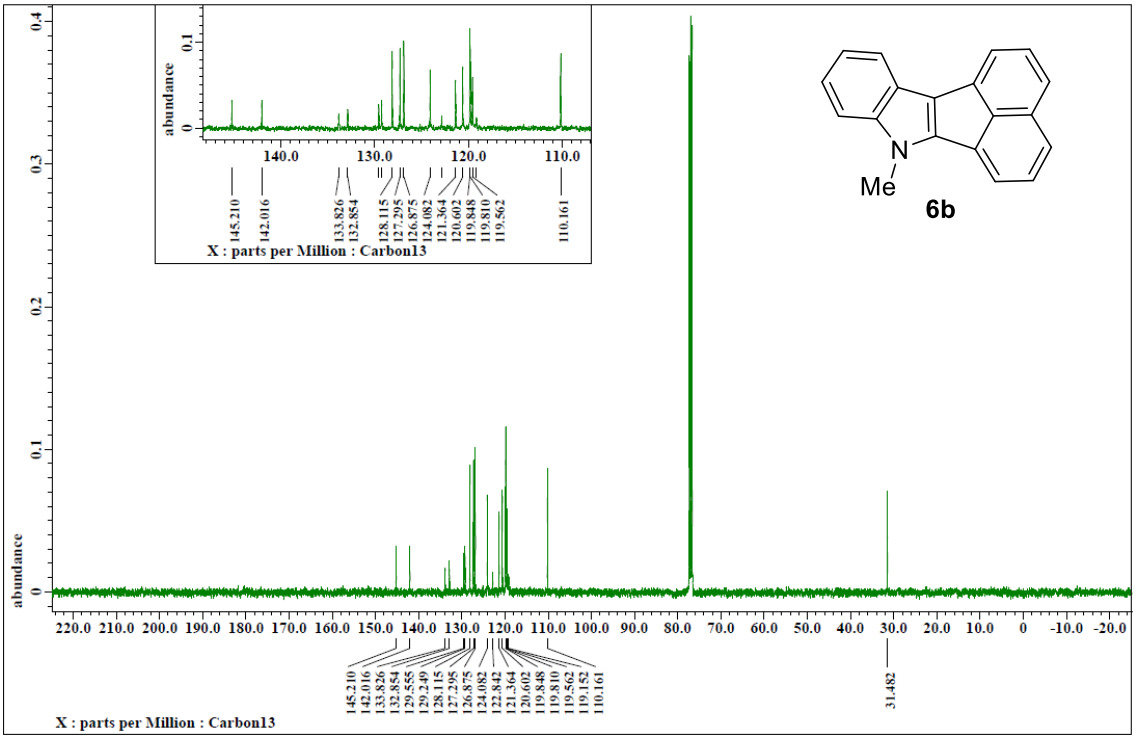
^{13}C NMR (150 MHz, $CDCl_3$)



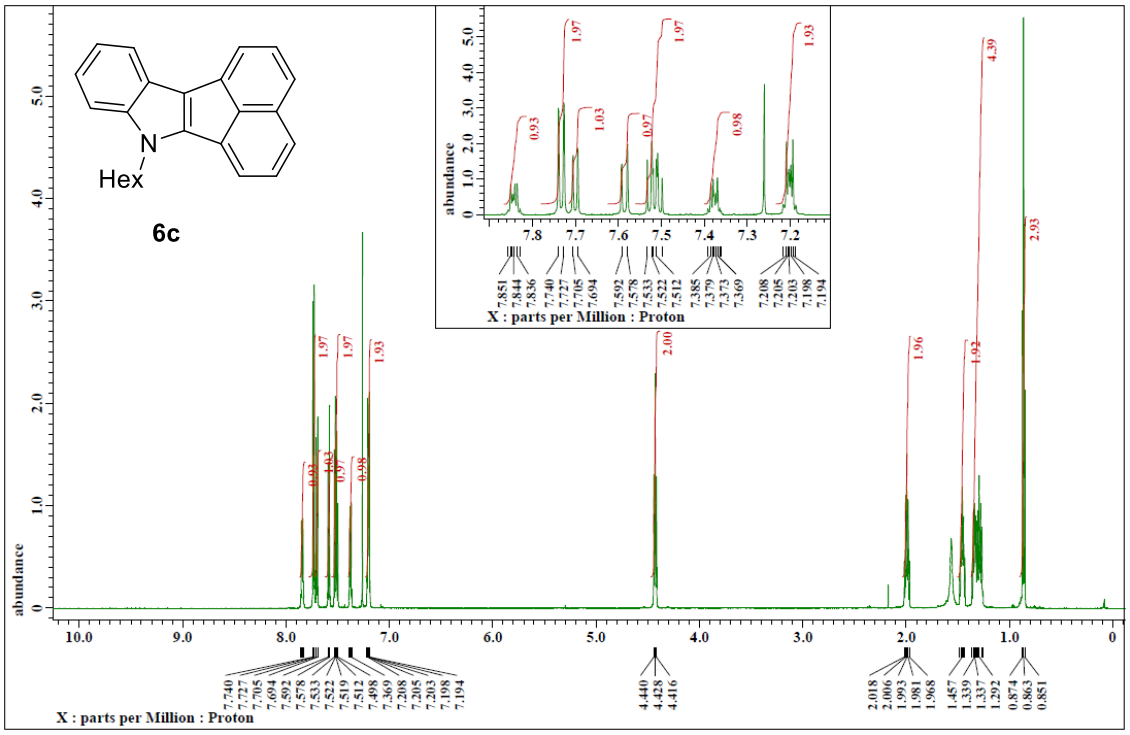
^{1}H NMR (400 MHz, $CDCl_3$)



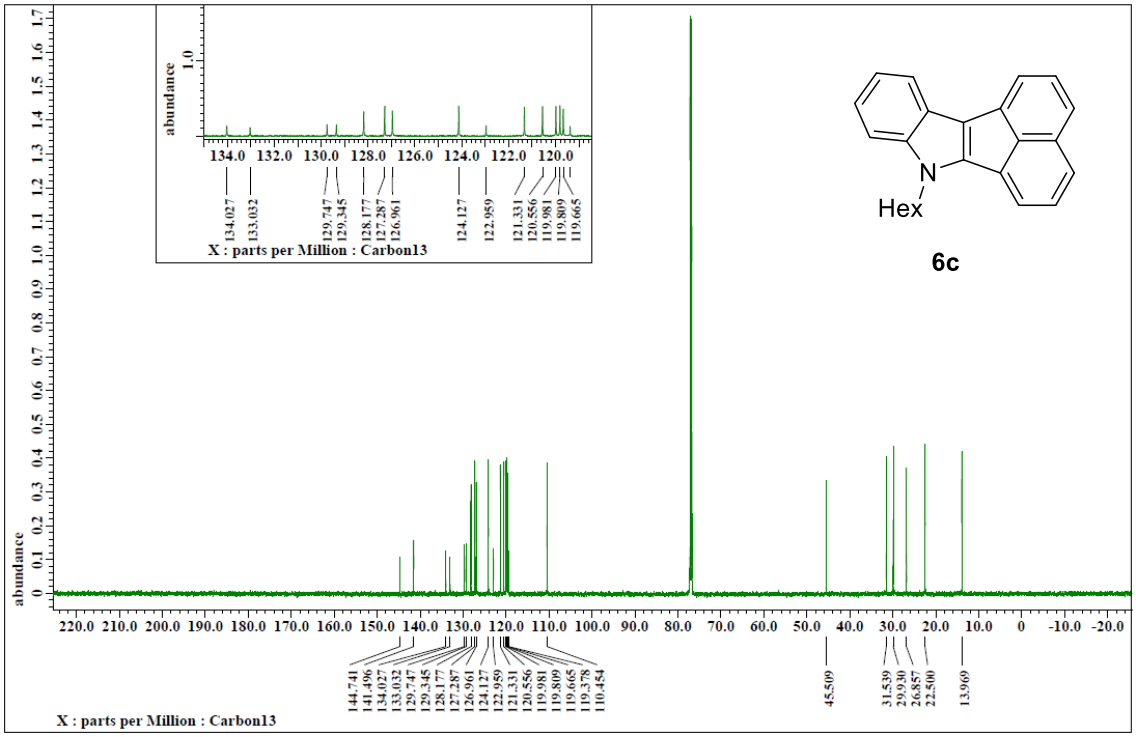
^{13}C NMR (100 MHz, $CDCl_3$)



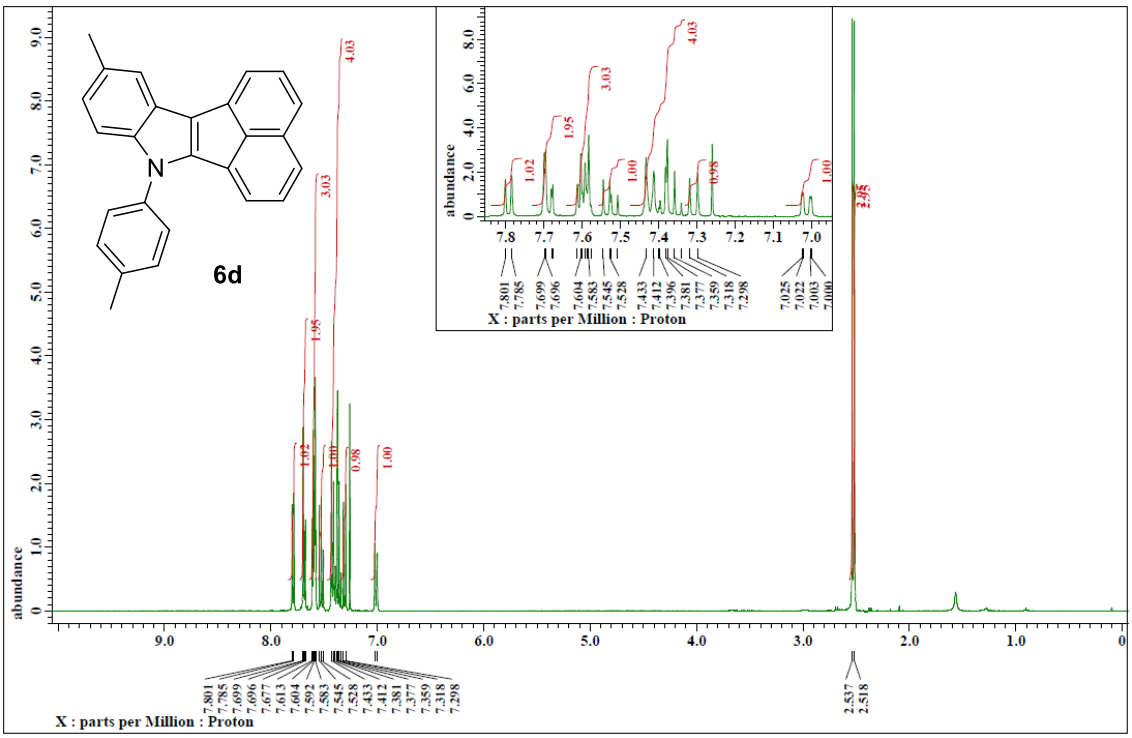
^{1}H NMR (600 MHz, $CDCl_3$)



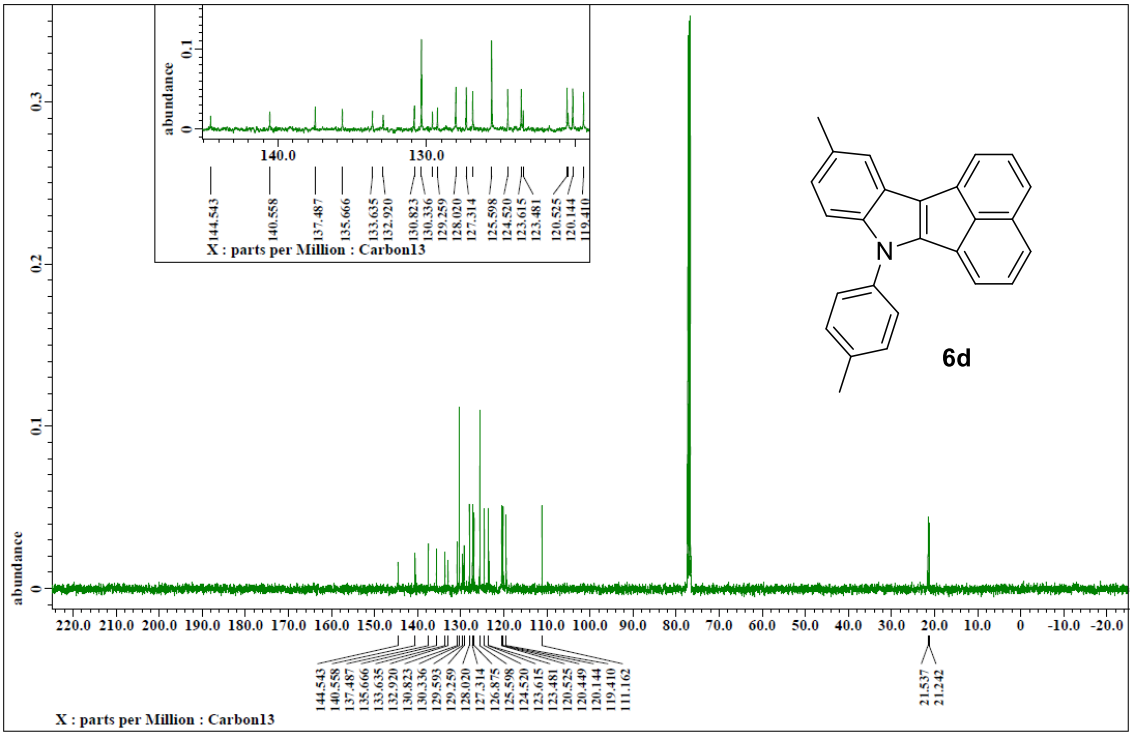
^{13}C NMR (150 MHz, $CDCl_3$)



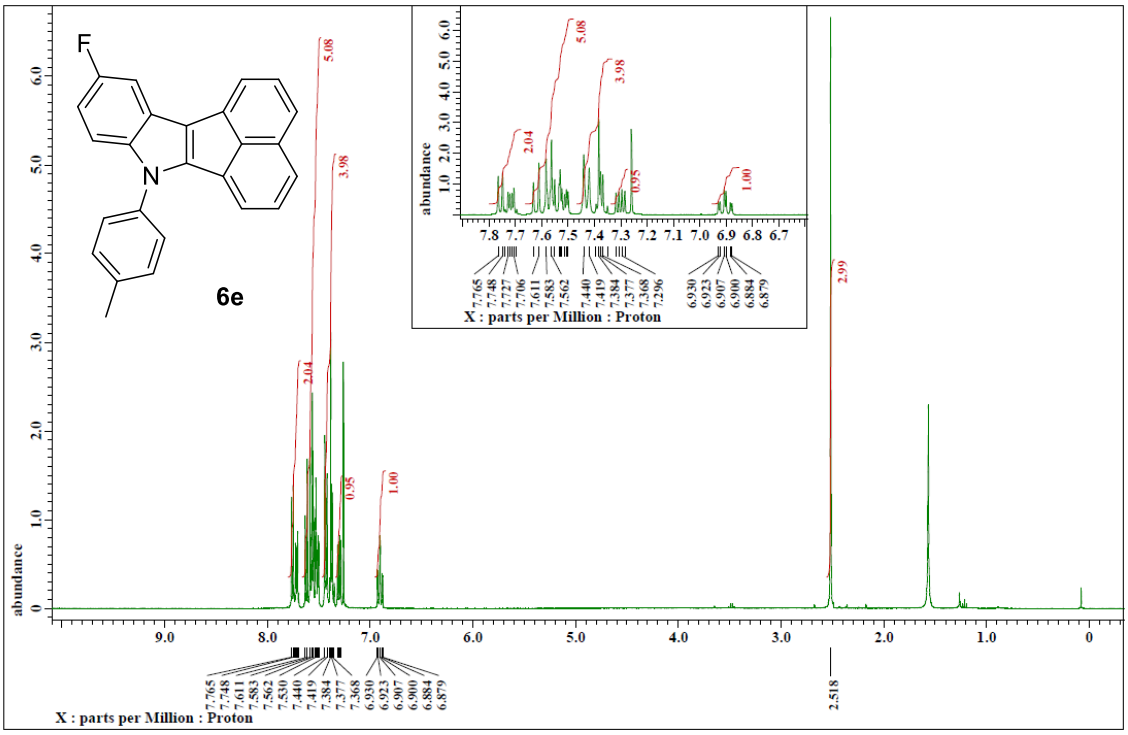
^{1}H NMR (400 MHz, $CDCl_3$)



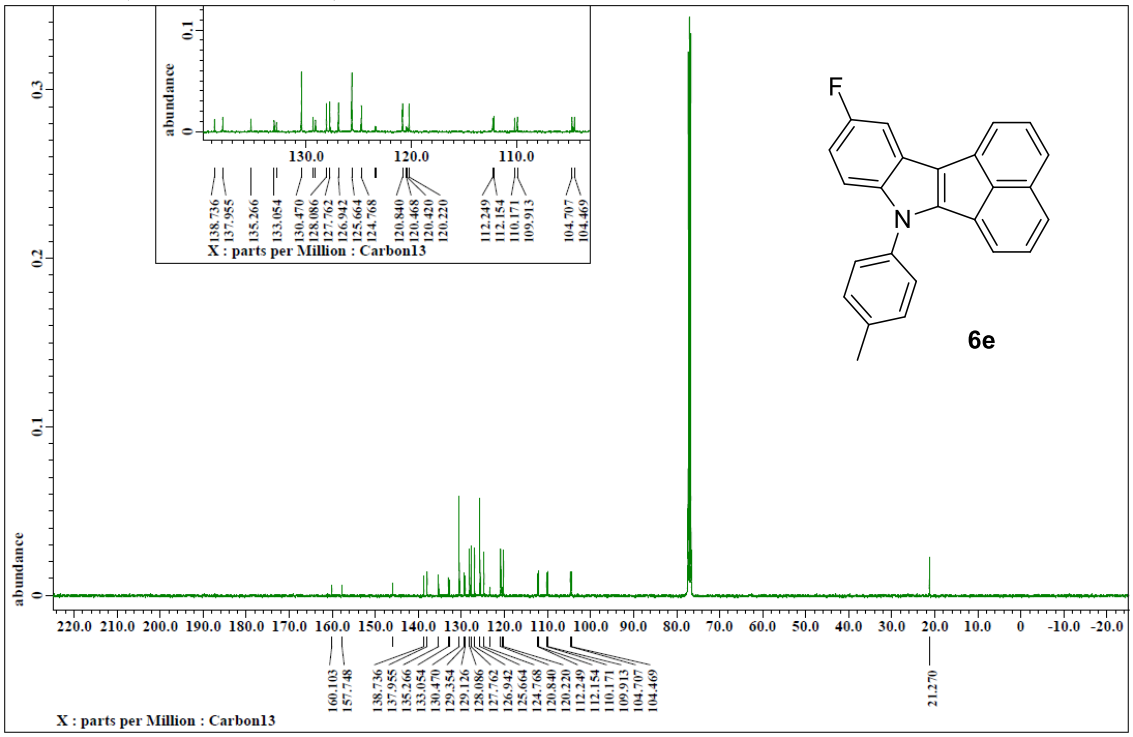
^{13}C NMR (100 MHz, $CDCl_3$)



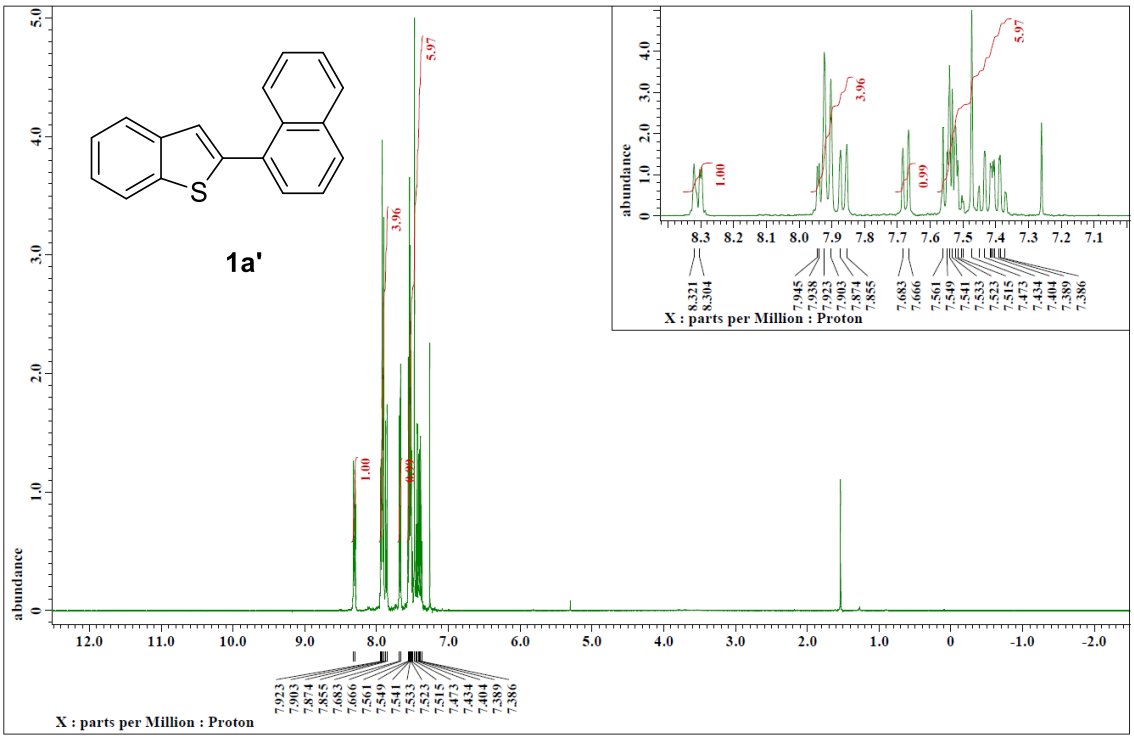
^{1}H NMR (400 MHz, $CDCl_3$)



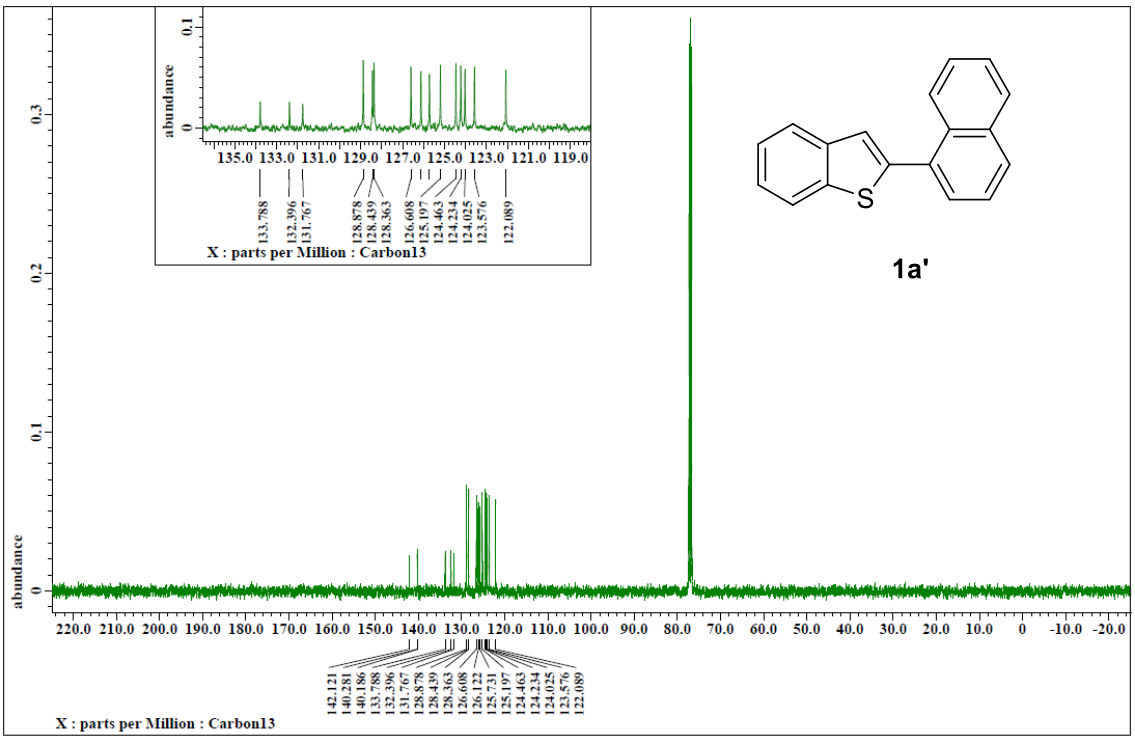
^{13}C NMR (100 MHz, $CDCl_3$)



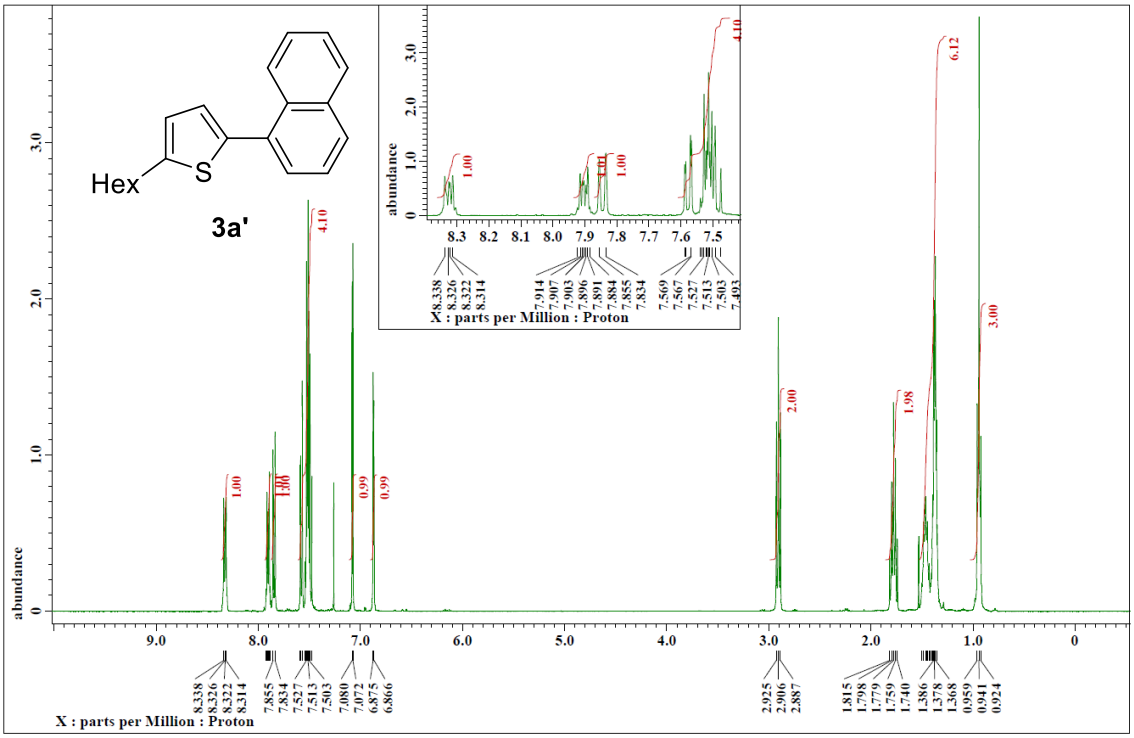
^{1}H NMR (400 MHz, $CDCl_3$)



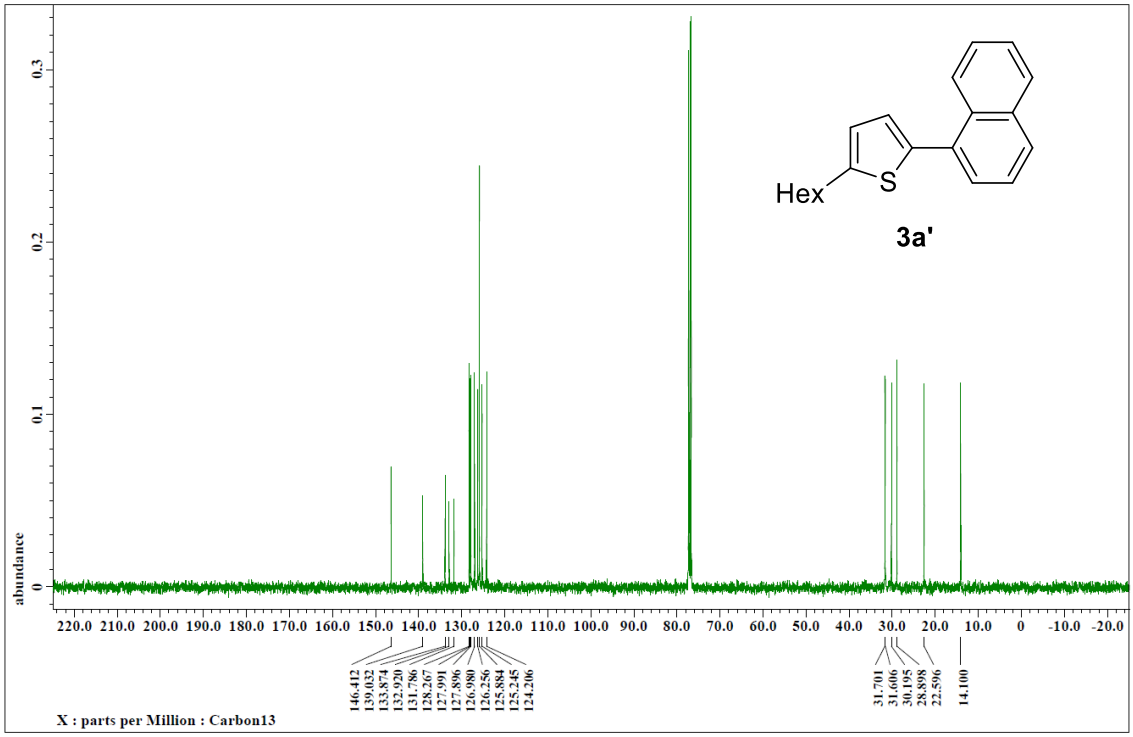
^{13}C NMR (100 MHz, $CDCl_3$)



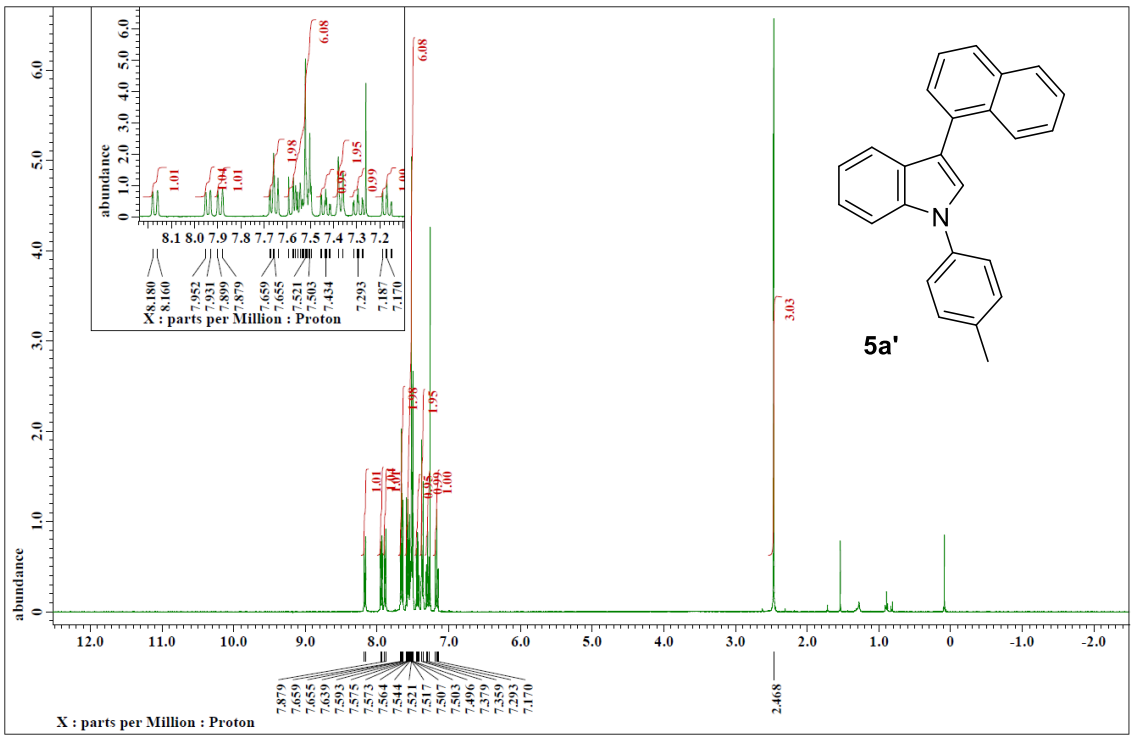
^{1}H NMR (400 MHz, $CDCl_3$)



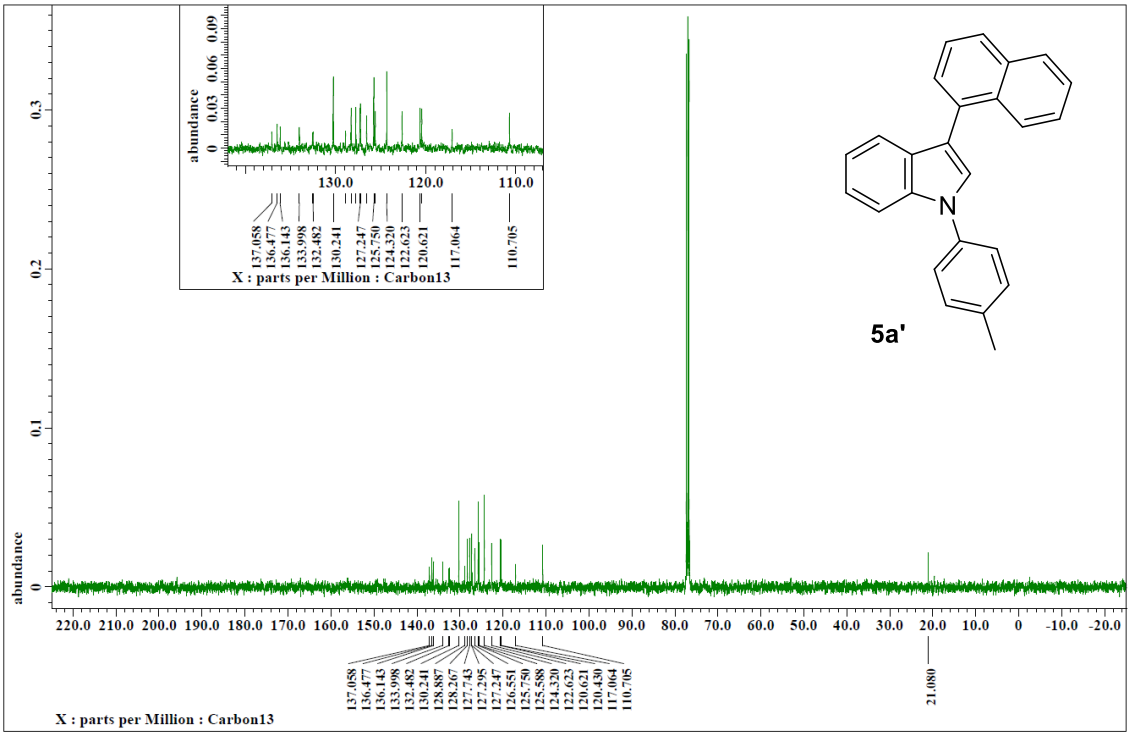
^{13}C NMR (100 MHz, $CDCl_3$)



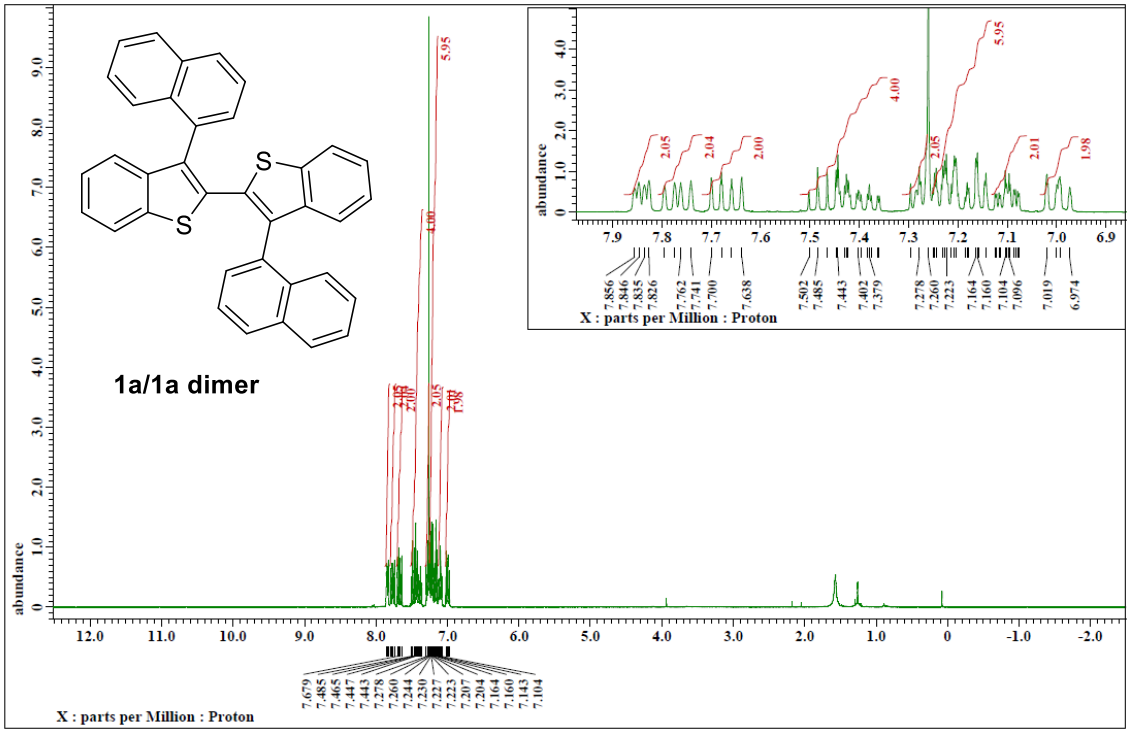
^{1}H NMR (400 MHz, $CDCl_3$)



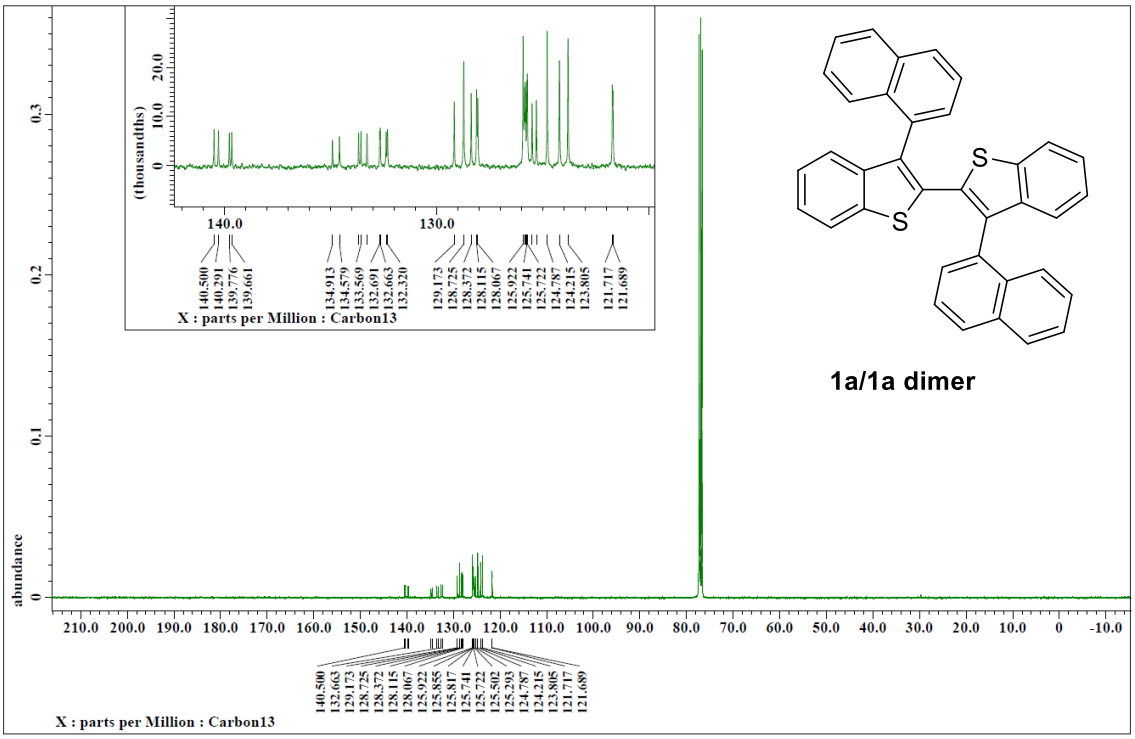
^{13}C NMR (100 MHz, $CDCl_3$)



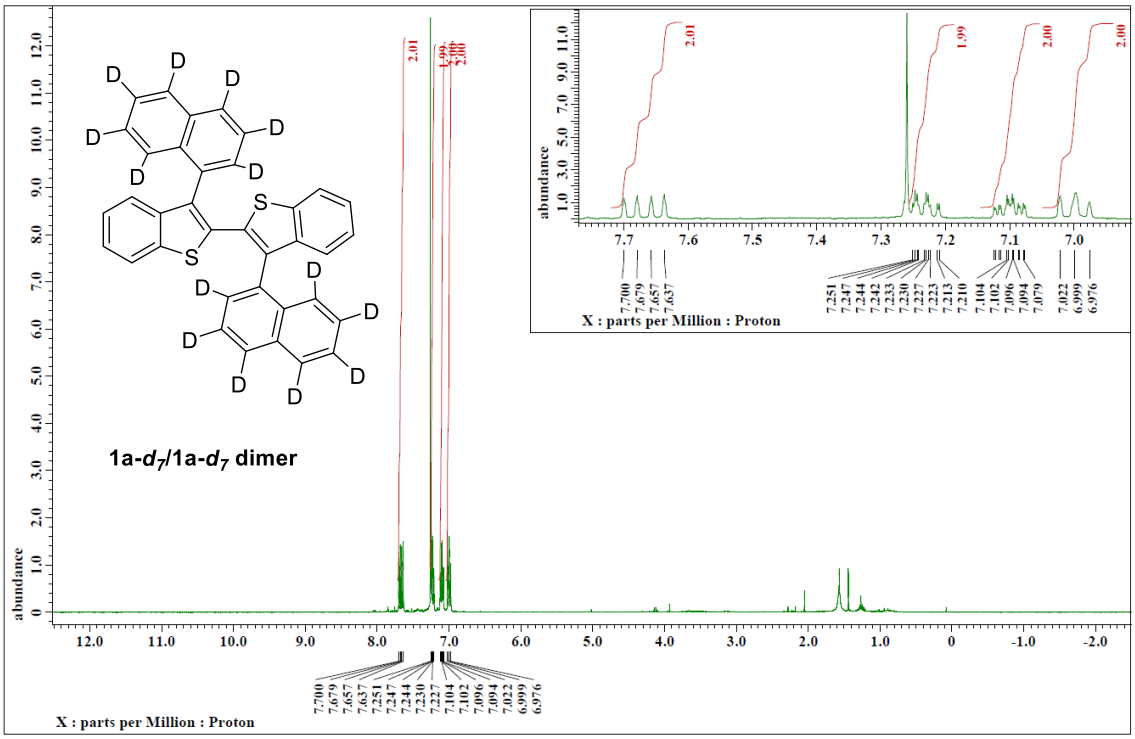
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)