Supporting Information for:

C-H Arylation of Thiopyran Derivatives with Aryl Halides

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EXPERIMENTAL SECTION

1. Materials and reagents.

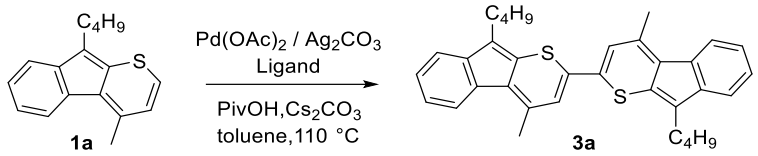
All chemicals and reagents were purchased from commercial sources and used as received unless otherwise specified. Anhydrous toluene was stilled from sodium benzophenone ketyl. Thiopyran derivatives **1a**, **1b**, and **1c** were synthesized according to previously reported method[S1] and all aryl bromide compounds were obtained through commercial sources and used without further purification. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.

2. Characterizations.

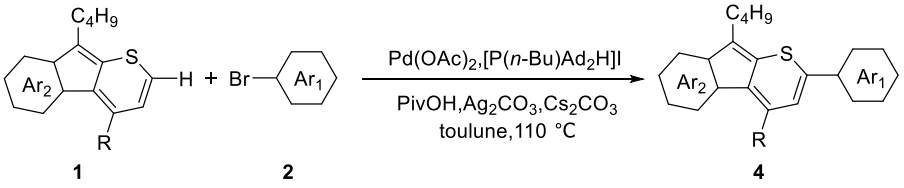
^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). High resolution mass (HRMS) spectra were recorded on an Agilent QTOF-6550 spectrometer using ESI for ionization. The single crystals suitable for X-ray analysis were obtained by the slow solvent volatilization method. The X-ray measurement of single crystals was recorded on a Bruker Sc XRD D8 venture.

3. Synthetic procedures.

Synthesis of 9,9'-dibutyl-4,4'-dimethyl-2,2'-biindeno[2,1-*b*]thiopyran (3a).



To a 25 mL Schlenk tube with a magnetic stir bar were sequentially added **1a** (130 mg, 0.5 mmol), pivalic acid (15.3 mg, 0.15 mmol), Ag_2CO_3 (137 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), [P(*n*-Bu)Ad_2H]I (24.3 mg, 0.05 mmol), toluene (5 mL). The reaction mixture was purged with nitrogen. Then, Cs_2CO_3 (489 mg, 1.5 mmol) was added to the reaction mixture. The reaction tube was moved to a pre-heated oil bath. After stirring for 22 h at 110 °C, the reaction mixture was cooled to room temperature. The residue was purified by column chromatography on silica gel (eluent: PE) to yield product **3a** (37 mg, 28%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.1 Hz, 1H), 7.25 (s, 1H), 2.91 – 2.84 (m, 5H), 1.73 (d, J = 5.1 Hz, 2H), 1.50 – 1.44 (m, 2H), 0.97 (d, J = 6.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.6, 136.9, 135.4, 130.5, 129.3, 127.5, 124.9, 124.9, 124.0, 121.6, 117.2, 30.4, 26.1, 23.3, 22.8, 14.4. HRMS (ESI) m/z: $[M]^+$ calcd. for $C_{34}H_{34}S_2$ 506.2102; found 506.2106.

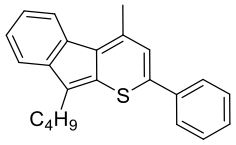


Scheme S1. Synthetic route for compounds **4a**-**4k** and **4m**.

General procedure for the synthesis of 4a-4k and 4m.

To a 25 mL Schlenk tube with a magnetic stir bar were sequentially added thiopyran derivatives **1** (0.5 mmol), bromo-substituted compound **2** (0.55 mmol), pivalic acid (0.15 mmol), Ag_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), [P(*n*-Bu)Ad_2H]I (0.05 mmol), toluene (5 mL). The reaction mixture was purged with nitrogen. Then, Cs_2CO_3 (1.5 mmol) was added to the reaction mixture. The reaction tube was moved to a pre-heated oil bath. After stirring for 22 h at 110 °C, the reaction mixture was cooled to room temperature. The residue was purified by column chromatography on silica gel to produce the target product.

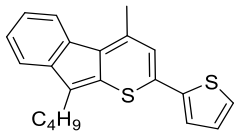
Synthesis of 9-butyl-4-methyl-2-phenylindeno[2,1-*b*]thiopyran (4a).



4a

Eluent: PE. Violet oil, 137 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 6.0 Hz, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.52 – 7.42(m, 4H), 7.30 (t, J = 7.6 Hz, 1H), 7.02 (s, 1H), 2.88 (d, J = 6.5 Hz, 5H), 1.73 (t, J = 7.8 Hz, 2H), 1.48 – 1.42 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.3, 140.9, 139.0, 138.5, 136.2, 129.5, 129.2, 127.3, 126.9, 124.6, 123.6, 122.1, 121.0, 119.9, 119.8, 117.0, 30.4, 26.1, 23.3, 23.0, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}S$ 331.1515; found 331.1516.

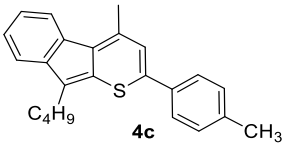
Synthesis of 9-butyl-4-methyl-2-(thienyl-2-)indeno[2,1-*b*]thiopyran (4b).



4b

Eluent:PE. Blue oil, 87 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 5.9 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 5.1 Hz, 1H), 7.03 (s, 1H), 2.84 (d, J = 11.3 Hz, 5H), 1.76 – 1.68 (m, 2H), 1.49 – 1.42 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.3, 141.6, 136.2, 133.8, 130.6, 128.4, 127.7, 127.6, 126.9, 125.6, 124.5, 124.2, 124.1, 121.3, 121.1, 117.1, 30.4, 26.1, 23.9, 22.8, 14.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{20}S_2$ 337.1080; found 337.1087.

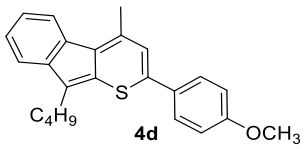
Synthesis of 9-butyl-4-methyl-2-(*p*-tolyl)indeno[2,1-*b*]thiopyran (4c).



4c

Eluent: PE. Violet oil, 138 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 7.7 Hz, 1H), 7.65 – 7.60 (m, 3H), 7.52 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.28 (s, 1H), 7.01 (s, 1H), 2.92 (t, J = 8.2 Hz, 2H), 2.87 (s, 3H), 2.44 (s, 3H), 1.77 (d, J = 7.2 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.03 – 0.96 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.2, 141.2, 139.7, 136.7, 135.7, 130.4, 129.9, 127.1, 126.8, 126.7, 125.4, 124.6, 123.5, 121.5, 121.0, 117.0, 30.5, 26.1, 23.3, 23.0, 21.6, 14.4. HRMS (ESI) m/z: $[M]^+$ calcd. for $C_{24}H_{24}S$ 344.1599; found 344.1609.

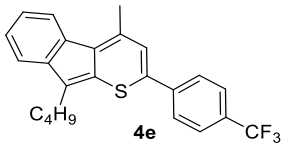
Synthesis of 9-butyl-2-(4-methoxyphenyl)-4-methylindeno[2,1-*b*]thiopyran (4d).



4d

Eluent: PE. Violet oil, 63 mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.17 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 6.9 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.03 – 6.93 (m, 3H), 3.88 (s, 3H), 2.88 (d, J = 19.1 Hz, 5H), 1.75 (t, J = 7.6 Hz, 2H), 1.50 – 1.44 (m, 2H), 1.00 – 0.98 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.6, 142.1, 140.9, 136.8, 131.0, 130.4, 128.5, 126.7, 126.4, 125.4, 124.5, 123.4, 121.0, 120.3, 117.5, 117.0, 114.6, 54.3, 31.6, 25.3, 23.3, 21.9, 17.7. HRMS (ESI) m/z: $[M]^+$ calcd. for $C_{24}H_{24}OS$ 360.1548; found 360.1565.

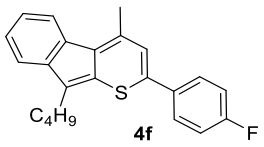
Synthesis of 9-butyl-4-methyl-2-(4-(trifluoromethyl)phenyl)indeno[2,1-*b*]thiopyran (4e).



4e

Eluent: PE. Blue-Violet oil, 190 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.17 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.02 (s, 1H), 2.90 (t, J = 7.5 Hz, 2H), 2.86 (s, 3H), 1.79 – 1.72 (m, 2H), 1.50 – 1.45 (m, 2H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.3, 141.8, 138.8, 135.8, 132.2, 131.2 (q, J = 32.7 Hz), 130.3, 127.8, 127.5, 127.3, 126.1 (q, J = 3.8 Hz), 124.8, 124.5, 124.2 (q, J = 270.7 Hz), 123.2, 121.4, 117.1, 30.4, 26.1, 23.3, 22.8, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -61.80. HRMS (ESI) m/z: $[M]^+$ calcd. for $C_{24}H_{21}F_3S$ 398.1316; found 398.1309.

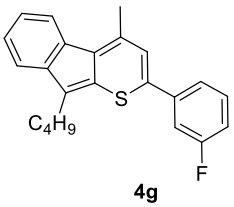
Synthesis of 9-butyl-2-(4-fluorophenyl)-4-methylindeno[2,1-*b*]thiopyran (4f).



4f

Eluent: PE. Blue-violet oil, 159 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.17 (d, J = 7.9 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.62 (d, J = 8.8 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 8.1 Hz, 1H), 7.16 (d, J = 15.1 Hz, 2H), 6.92 (s, 1H), 2.91 (t, J = 7.5 Hz, 2H), 2.84 (s, 3H), 1.83 – 1.72 (m, 2H), 1.53 – 1.44 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.7 (d, J = 248.7 Hz), 142.2, 139.7, 136.3, 134.7 (d, J = 3.2 Hz), 134.6, 130.4, 129.0 (d, J = 8.4 Hz), 127.0, 125.0, 124.7, 123.9, 122.1, 121.2, 117.1, 116.2 (d, J = 21.7 Hz), 30.5, 26.1, 23.3, 22.9, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -111.08. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{21}FS$ 349.1421; found 349.1437.

Synthesis of 9-butyl-2-(3-fluorophenyl)-4-methylindeno[2,1-*b*]thiopyran (4g).

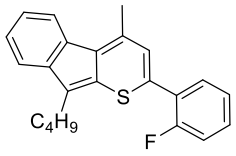


4g

Eluent: PE. Blue-violet oil, 162 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.16 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.9 Hz, 1H), 7.51 (d, J = 6.1 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.17 – 7.09 (m, 1H), 7.00 (s, 1H), 2.87 (d, J = 13.5 Hz, 5H), 1.80 – 1.69 (m, 2H), 1.51 – 1.43 (m, 2H), 0.99 – 0.96 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.3 (d, J = 245.6 Hz), 142.3, 140.6 (d, J = 7.9 Hz), 139.2 (d, J = 2.4 Hz), 136.0, 130.7 (d, J = 3.0 Hz), 130.4, 127.6, 127.1, 124.7, 124.2, 122.9 (d, J

= 8.4 Hz), 122.6, 121.3, 117.1, 116.4, 116.2, 114.2 (d, J = 23.3 Hz), 29.9, 26.4, 23.0, 22.9, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -111.27. HRMS (ESI) m/z: $[M]^+$ calcd. for $C_{23}H_{21}FS$ 348.1348; found 348.1355.

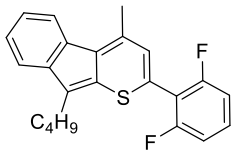
Synthesis of 9-butyl-2-(2-fluorophenyl)-4-methylindeno[2,1-*b*]thiopyran (4h).



4h

Eluent: PE. Blue-violet oil, 160 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 20.5 Hz, 2H), 7.54 (d, J = 8.3 Hz, 1H), 7.45 – 7.35 (m, 1H), 7.37 – 7.31 (m, 1H), 7.26 (s, 1H), 7.19 (d, J = 12.5 Hz, 1H), 7.03 (s, 1H), 2.88 (d, J = 10.6 Hz, 5H), 1.80 – 1.69 (m, 2H), 1.51 – 1.44 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.7 (d, J = 249.4 Hz), 142.2, 136.0, 134.2 (d, J = 2.3 Hz), 131.0 (d, J = 2.4 Hz), 130.8 (d, J = 8.4 Hz), 130.4, 127.1, 127.1, 126.3 (d, J = 7.5 Hz), 125.4 (d, J = 5.0 Hz), 125.2, 124.8, 124.7, 123.7, 121.1, 117.0, 116.7 (d, J = 22.1 Hz), 30.4, 26.1, 23.3, 22.9, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -114.02. HRMS (ESI) m/z: $[M]^+$ calcd. for $C_{23}H_{21}FS$ 348.1348; found 348.1348.

Synthesis of 9-butyl-2-(2,6-difluorophenyl)-4-methylindeno[2,1-*b*]thiopyran (4i).

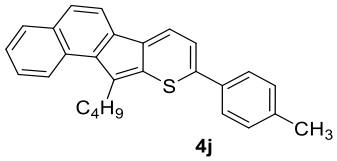


4i

Eluent: PE. Blue-violet oil, 154 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):

8.21 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.03 (t, J = 8.0 Hz, 2H), 6.83 (s, 1H), 2.87 (d, J = 6.3 Hz, 5H), 1.79 – 1.69 (m, 2H), 1.51 – 1.43 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.6 (dd, J = 250.1 Hz, 5.7 Hz), 142.2, 135.5, 131.1 (t, J = 10.3 Hz), 130.4, 127.7, 127.5, 127.2, 126.9, 125.0, 124.8, 123.8, 121.2, 117.0, 112.2 – 111.9 (m), 30.3, 26.1, 23.3, 22.8, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -110.48. HRMS (ESI) m/z: [M + H]$^+$ calcd. for $C_{23}H_{20}F_2S$ 366.1254; found 366.1266.

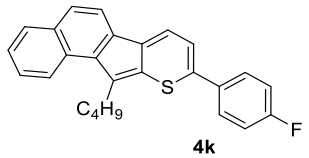
Synthesis of 11-butyl-9-(*p*-tolyl)benzo[4,5]indeno[2,1-*b*]thiopyran (4j).



4j

Eluent: PE. Green solid. 168 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.60 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 9.3 Hz, 1H), 8.00 (t, J = 8.2 Hz, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.63 (t, J = 8.1 Hz, 3H), 7.61 – 7.53 (m, 1H), 7.29 (d, J = 8.7 Hz, 3H), 3.35 (t, J = 7.7 Hz, 2H), 2.44 (s, 3H), 1.96 – 1.86 (m, 2H), 1.66 – 1.56 (m, 2H), 1.04 (t, J = 6.9 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.0, 140.6, 137.3, 135.9, 134.7, 130.0, 129.1, 129.0, 128.0, 127.4, 126.6, 125.7, 125.5, 125.4, 125.1, 124.8, 124.3, 121.6, 119.3, 115.5, 31.4, 29.2, 23.3, 21.6, 15.0. HRMS (ESI) m/z: [M + H]$^+$ calcd. for $C_{27}H_{24}S$ 381.1672; found 381.1673.

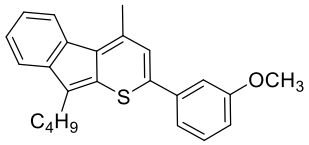
Synthesis of 11-butyl-9-(4-fluorophenyl)benzo[4,5]indeno[2,1-*b*]thiopyran (4k).



4k

Eluent: PE. Green solid. 173 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.58 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.73 – 7.54 (m, 5H), 7.15 (d, J = 9.0 Hz, 3H), 3.31 (t, J = 7.8 Hz, 2H), 1.91 (d, J = 15.5 Hz, 2H), 1.60 (t, J = 11.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.8 (d, J = 249.0 Hz), 142.4, 137.4, 134.8 (d, J = 3.4 Hz), 134.8, 129.4, 129.3, 129.3, 129.2, 128.0, 126.6, 126.1, 125.6 (d, J = 5.8 Hz), 125.0, 124.3, 123.9, 121.8, 119.3, 116.3 (d, J = 21.7 Hz), 116.0, 31.3, 29.2, 23.3, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -110.91. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{21}FS$ 385.1421; found 385.1438.

Synthesis of 9-butyl-2-(3-methoxyphenyl)-4-methylindeno[2,1-*b*]thiopyran (4m).

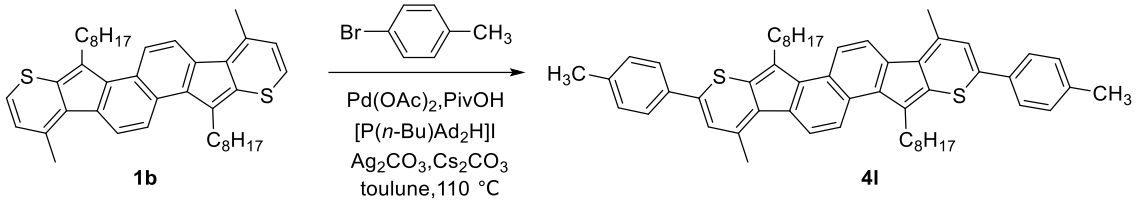


4m

Eluent: PE. Violet oil, 41 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.27 (d, J = 2.5 Hz, 1H), 7.03 (s, 1H), 6.99 (d, J = 9.4 Hz, 1H), 3.91 (s, 3H), 2.91 (t, J = 7.5 Hz, 2H), 2.87 (s, 3H), 1.76 (m, 2H), 1.48 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.2, 142.2, 140.8, 139.9, 136.4, 130.4, 130.2, 127.1, 126.9, 125.3, 124.6, 123.7, 122.2, 121.1, 119.8, 117.0, 115.0, 112.9, 55.7, 30.5, 26.1, 23.3, 22.9, 14.4. MALDI-TOF MS m/z: $[M]^+$ calcd. for

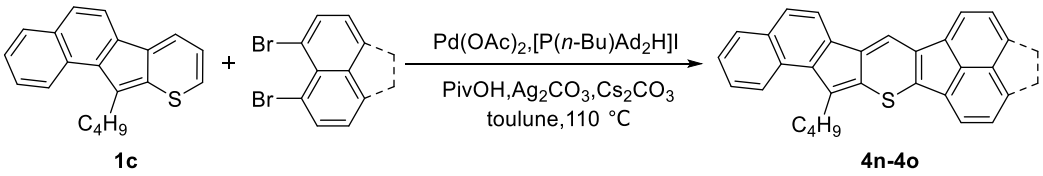
$C_{24}H_{24}OS$ 360.1548; found 360.1550.

Synthesis of 4,4′-methyl-2,2′-(*p*-toly)7,14-dioctylnaphtho[2,1-*f*:6,5-*f*′]bis-(cyclopenta[*b*]thiopyran) (4l).



To a 25 mL Schlenk tube with a magnetic stir bar were sequentially added 4,4′7,14-dioctylnaphtho[2,1-*f*:6,5-*f*′]bis-(cyclopenta[*b*]thiopyran) **1b** (100 mg, 0.18 mmol), 4-bromotoluene (32 mg, 0.38 mmol), pivalic acid (6 mg, 0.15 mmol), Ag_2CO_3 (49 mg, 0.18 mmol), $Pd(OAc)_2$ (1.5 mg, 0.01 mmol), [P(*n*-Bu)Ad_2H]I (8.8 mg, 0.02 mmol), toluene (5 mL). The reaction mixture was purged with nitrogen. Then, Cs_2CO_3 (176 mg, 1.5 mmol) was added to the reaction mixture. The reaction tube was moved to a pre-heated oil bath. After stirring for 22 h at 110 °C, the reaction mixture was cooled to room temperature. The residue was purified by column chromatography on silica gel (PE/DCM = 8/1). to yield product **4l** (24 mg, 44%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.48 (t, J = 14.0 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.20 (s, 1H), 3.43 (s, 2H), 3.08 (s, 3H), 2.44 (s, 3H), 2.00 – 1.95 (m, 2H), 1.67 – 1.61 (m, 2H), 1.50 – 1.41 (m, 2H), 1.37 – 1.27 (m, 6H), 0.94 – 0.84 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.7, 140.1, 139.0, 138.1, 136.2, 130.3, 127.8, 127.7, 126.6, 125.8, 125.0, 122.5, 122.2, 118.4, 32.6, 30.6, 30.5, 30.2, 30.0, 29.4, 24.0, 23.3, 21.9, 14.8. HRMS (ESI) *m*/*z*: $[M]^+$ calcd. for $C_{54}H_{60}S_2$ 772.4136; found 772.4140.

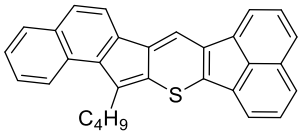
General procedure for the synthesis of 4n and 4o.



1c **4n-4o**

To a 25 mL Schlenk tube with a magnetic stir bar were sequentially added thiopyran derivatives **1c** (0.5 mmol), dibromo-substituted compounds (0.55 mmol), pivalic acid (0.15 mmol), Ag_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), [P(*n*-Bu)Ad_2H]I (0.05 mmol), toluene (5 mL). The reaction mixture was purged with nitrogen. Then, Cs_2CO_3 (1.5 mmol) was added to the reaction mixture. The reaction tube was moved to a pre-heated oil bath. After stirring for 22 h at 110 °C, the reaction mixture was cooled to room temperature. The residue was purified by column chromatography on silica gel to produce the target product.

Synthesis of 8-butylacenaphtho[1,2-*b*]benzo[4,5]indeno[1,2-*e*]thiopyran (4n).

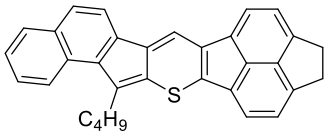


4n

Eluent: PE/DCM = 15/1. Brown solid, 107 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.49 (d, J = 8.2 Hz, 1H), 8.36 (s, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.83 (t, J = 8.5 Hz, 2H), 7.75 (d, J = 6.8 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.58 – 7.50 (m, 4H), 3.24 (t, J = 7.8 Hz, 2H), 1.93 – 1.85 (m, 2H), 1.65 – 1.59 (m, 2H), 1.06 – 1.02 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.0, 137.1, 136.7, 134.6, 130.0, 129.7, 129.2, 129.1, 128.9, 128.4, 128.3, 128.0, 128.0,

127.4, 126.5, 126.4, 125.4, 125.2, 124.9, 122.9, 121.7, 121.5, 119.7, 119.2, 119.2, 31.3, 29.3, 23.4, 14.4. HRMS (ESI) *m*/*z*: $[M]^+$ calcd. for $C_{30}H_{22}S$ 414.1442; found 414.1442.

Synthesis of 6-butyl-1,2-dihydrobenzo[4,5]indeno[2,1-*b*]cyclopenta[5,6]-acenaphtho[1,2-*e*]thiopyran (4o).

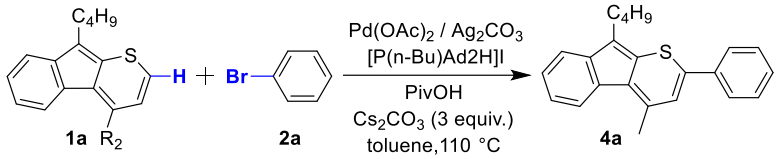


4o

Eluent: PE/DCM = 12/1. Brown solid, 105 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.52 (d, J = 8.3 Hz, 1H), 8.42 (s, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 6.9 Hz, 1H), 7.80 (d, J = 6.7 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.37 (d, J = 7.1 Hz, 2H), 3.36 (s, 4H), 3.28 (d, J = 7.8 Hz, 2H), 1.93 (t, J = 7.8 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.4, 146.0, 138.0, 136.8, 135.7, 134.5, 132.8, 132.5, 129.0, 129.0, 128.5, 128.0, 127.2, 125.8, 125.4, 125.1, 124.9, 124.1, 123.2, 122.1, 121.4, 121.2, 121.2, 120.9, 119.1, 33.0, 32.5, 31.3, 29.3, 23.4, 14.5. HRMS (ESI) *m*/*z*: $[M]^+$ calcd. for $C_{32}H_{24}S$ 440.1599; found 440.1592.

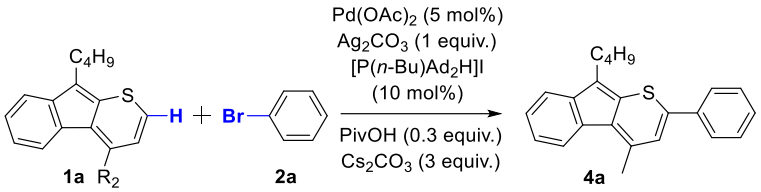
3. Optimization of the C-H arylation conditions.

Table S1. Optimization of the amount of $Pd(OAc)_2$, Ag_2CO_3, and PivOH in the C-H arylation reaction (the amount of the ligand is 2 equiv. of [Pd]).



Entry	[Pd] (mol %)	[Ag] (equiv.)	[PivOH] (equiv.)	Yield (%)
1	2	1.0	0.3	58
2	5	1.0	0.3	83
3	10	1.0	0.3	82
4	5	0	0.3	0
5	5	0.5	0.3	72
6	5	0.8	0.3	79
7	5	1.5	0.3	82
8	5	1.0	0.1	41
9	5	1.0	0.2	69
10	5	1.0	0.4	81
11	5	1.0	0.5	80

Table S2. Optimization of the solvent and the reaction temperature in the C-H arylation.



Entry	Solvent	*T* (℃)	Yield (%)
1	Toluene	80	47
2	Toluene	90	62
3	Toluene	100	74
4	Toluene	110	83
5	*o*-Xylene	140	66
6	Mesitylene	160	80
7	DMF	110	0
8	DMA	110	0
9	DMSO	110	0
10	1,4-Dioxane	110	11

5. X-ray crystallographic data.

Fig. S1 ORTEP drawing of **3a** with ellipsoid contour probability level of 50%.

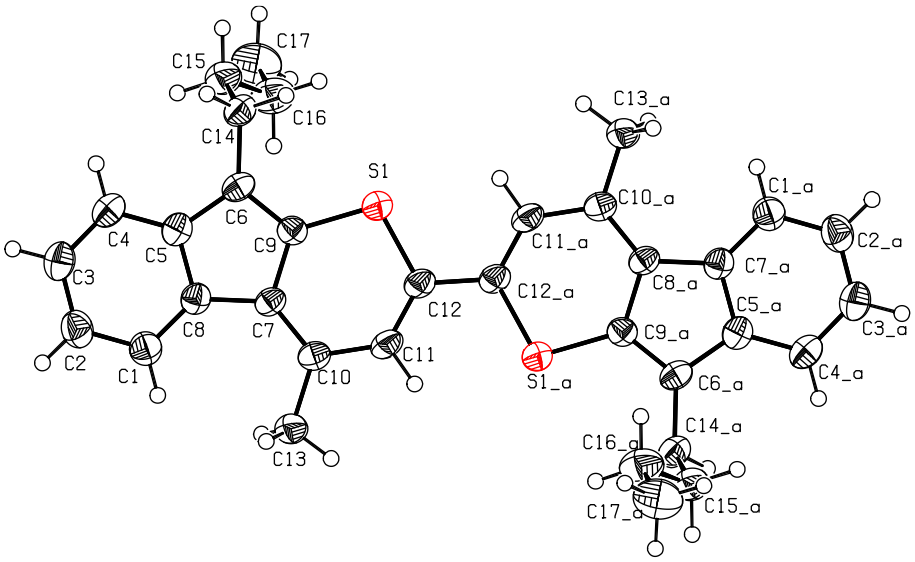


Fig. S2 ORTEP drawing of **4j** with ellipsoid contour probability level of 50%.

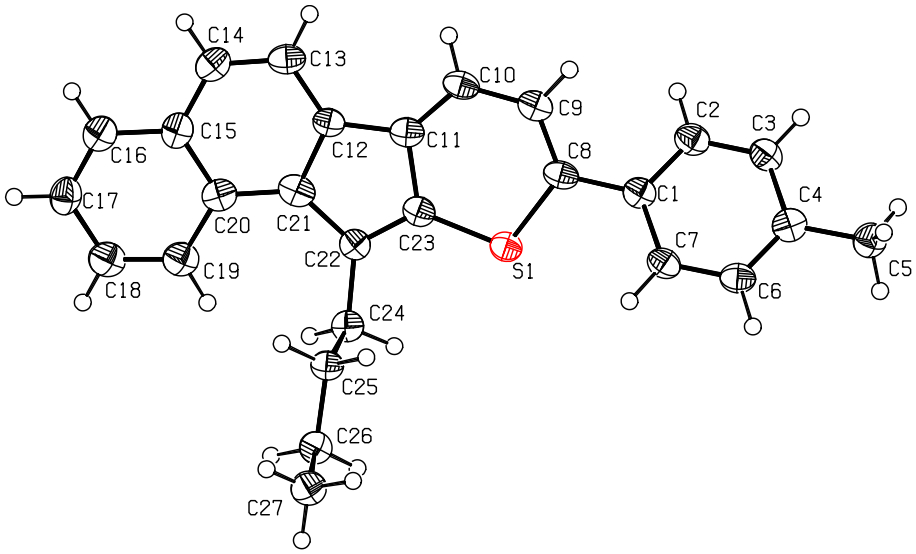


Fig. S3 ORTEP drawing of **4n** with ellipsoid contour probability level of 50%.

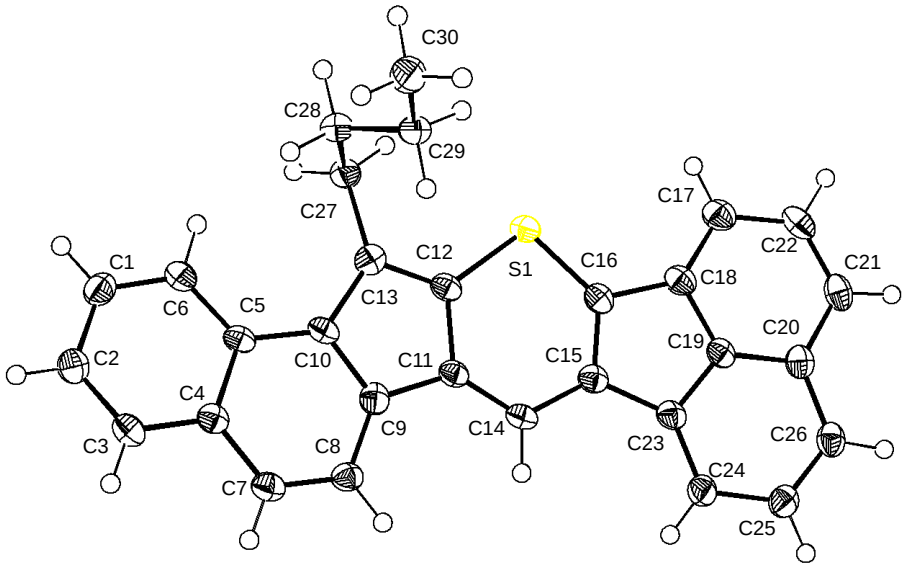


Table S3. Single crystal data and structure refinements for **3a**, **4j**, and **4n**.

	3a	**4j**	**4n**
CCDC No.	2310535	2310536	2310537
formula	$C_{34}H_{34}S_2$	$C_{27}H_{24}S$	$C_{30}H_{22}S$
formula wt.	506.73	380.52	414.57
T (K)	170	100	100
wavelength (Å)	0.71073	1.54178	1.54184
crystal size(mm)	0.12 × 0.07 × 0.04	0.15 × 0.09 × 0.08	0.25 × 0.04 × 0.01
crystal syst.	trigonal	triclinic	monoclinic
space group	$R\bar{3}$	$P\bar{1}$	$P2_1/C$
a (Å)	37.256(6)	12.0192(7)	14.9168(3)
b (Å)	37.256(6)	13.1986(7)	5.12150(10)
c (Å)	5.1212(11)	13.5978(7)	80.8465(18)
α (deg.)	90	91.326(2)	90
β (deg.)	90	92.661(3)	92.323(2)
γ (deg.)	120	113.371(3)	90
V (Å^3)	6156(2)	1975.96(19)	6171.3(2)
Z / $D_{calcd.}$ (mg/m^3)	9/1.230	4/1.279	12/1.338
μ (mm^{-1})	0.216	1.501	1.494
F(000)	2430	808	2616
R indices	$R1$ = 0.0694	$R1$ = 0.1065	$R1$ = 0.0778
	$wR2$ = 0.1313	$wR2$ = 0.2886	$wR2$ = 0.1630
[$I > 2\theta(I)$]	$R1$ = 0.1364	$R1$ = 0.1175	R = 0.1025
	$wR2$ = 0.1663	$wR2$ = 0.2967	$wR2$ = 0.1717

Table S4. Selected bond lengths for **3a**.

Bond	Length/Å	Bond	Length/Å
S1-C9	1.739(3)	C8-C1	1.391(5)
S1-C12	1.740(3)	C6-C14	1.501(5)
C9-C7	1.465(4)	C11-C12	1.363(5)
C9-C6	1.361(4)	C12-C12	1.478(6)
C7-C10	1.369(4)	C1-C2	1.399(5)
C7-C8	1.467(4)	C14-C15	1.538(5)
C5-C8	1.409(5)	C4-C3	1.388(5)
C5-C6	1.466(5)	C3-C2	1.382(5)
C5-C4	1.394(4)	C15-C16	1.492(5)
C10-C11	1.445(4)	C16-C17	1.537(5)
C10-C13	1.505(4)		

Table S5. Selected bond lengths for **4j**.

Bond	Length/Å	Bond	Length/Å
S1-C23	1.726(6)	C20-C15	1.435(8)
S1-C8	1.731(5)	C20-C15	1.424(8)
C4-C6	1.370(8)	C1-C8	1.480(8)
C7-C6	1.388(8)	C7-C1	1.408(8)
C4-C5	1.508(8)	C1-C2	1.390(8)
C4-C3	1.403(8)	C15-C16	1.424(8)
C25-C24	1.534(7)	C15-C14	1.421(8)
C25-C26	1.530(7)	C13-C14	1.355(8)
C12-C13	1.411(8)	C16-C17	1.356(9)
C23-C22	1.338(8)	C10-C9	1.412(8)
C21-C20	1.424(8)	C8-C9	1.373(8)
C21-C12	1.417(7)	C3-C2	1.387(8)
C21-20	1.463(8)	C24-C22	1.514(7)
C11-C12	1.447(8)	C26-C27	1.525(7)
C11-C23	1.493(7)	C19-C18	1.362(9)
C11-C10	1.352(8)	C18-C17	1.416(9)

Table S6. Selected bond lengths for **4n**.

Bond	Length/Å	Bond	Length/Å
S1-C16	1.714(5)	C12-C13	1.372(6)
S1-C12	1.751(4)	C13-C10	1.472(6)
C16-C18	1.483(6)	C10-C9	1.406(7)
C18-C17	1.365(6)	C9-C11	1.451(6)
C17-C22	1.417(6)	C9-C8	1.414(6)
C22-C21	1.376(6)	C8-C7	1.366(7)
C21-C20	1.425(6)	C7-C4	1.427(6)
C20-C19	1.396(6)	C4-C5	1.428(6)
C19-C18	1.414(6)	C5-C10	1.437(6)
C20-C26	1.425(6)	C4-C3	1.423(6)
C26-C25	1.378(6)	C3-C2	1.367(7)
C25-C24	1.434(6)	C2-C1	1.395(6)
C24-C23	1.373(6)	C1-C6	1.377(7)
C23-C19	1.411(6)	C6-C5	1.413(6)
C23-C15	1.475(7)	C12-C27	1.497(6)
C15-C16	1.388(6)	C27-C28	1.543(6)
C15-C14	1.432(7)	C28-C29	1.524(7)
C14-C11	1.354(6)	C29-C30	1.528(6)
C11-C12	1.463(6)		

6. Mechanism studies.

Fig. S4 ^{1}H NMR spectra of (a) L•HI, PdL_2, ArBr, mixture of ArBr and PdL_2, $ArPdL_2Br$, and (b) the zoomed aromatic region (L = [P(*n*-Bu)Ad_2], Ar = *p*-CF_3Ph).

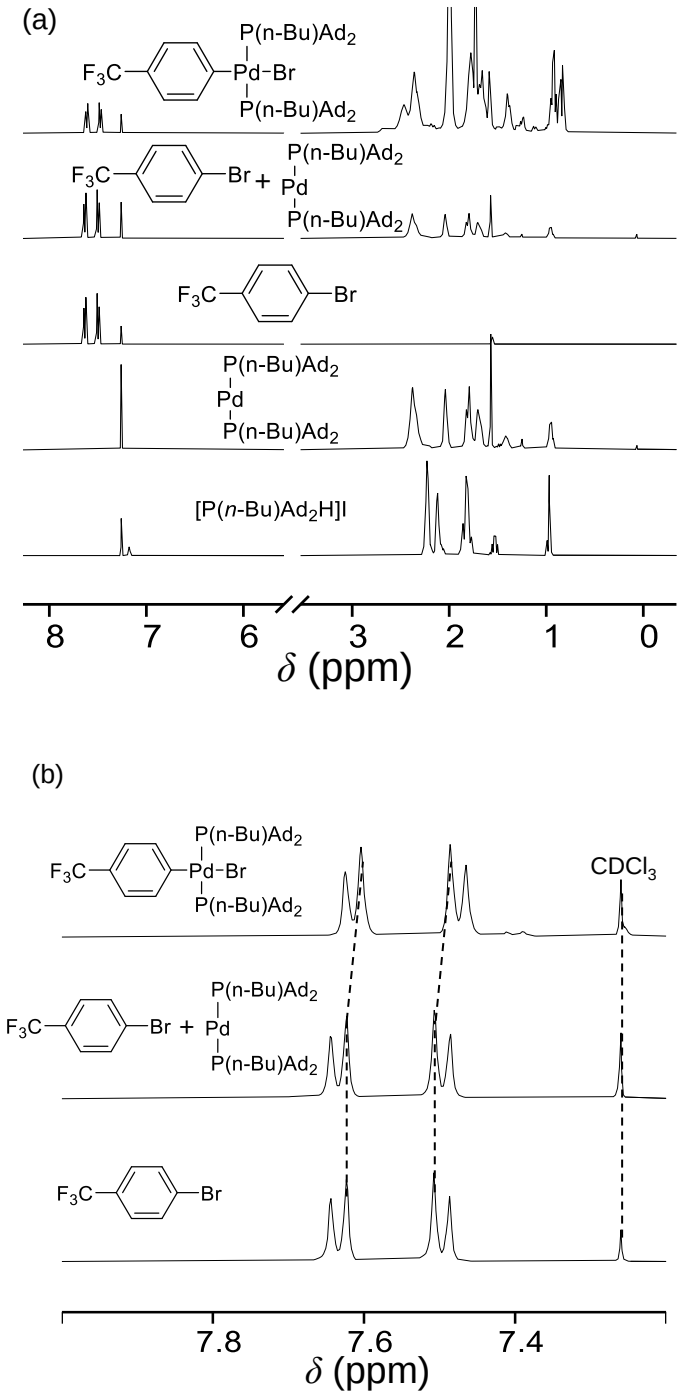
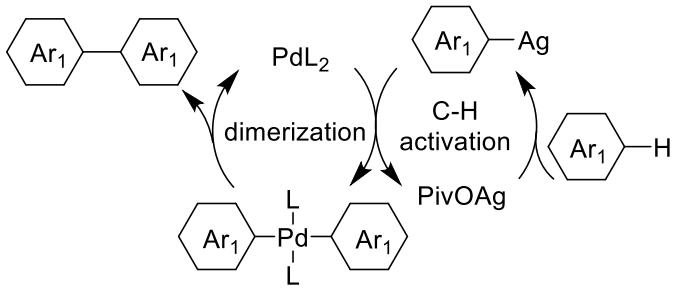


Fig. S5 Proposed mechanism of the dimerization.



7. NMR spectra of the products.

Fig. S6 ^{1}H NMR spectrum of **3a** in $CDCl_3$.

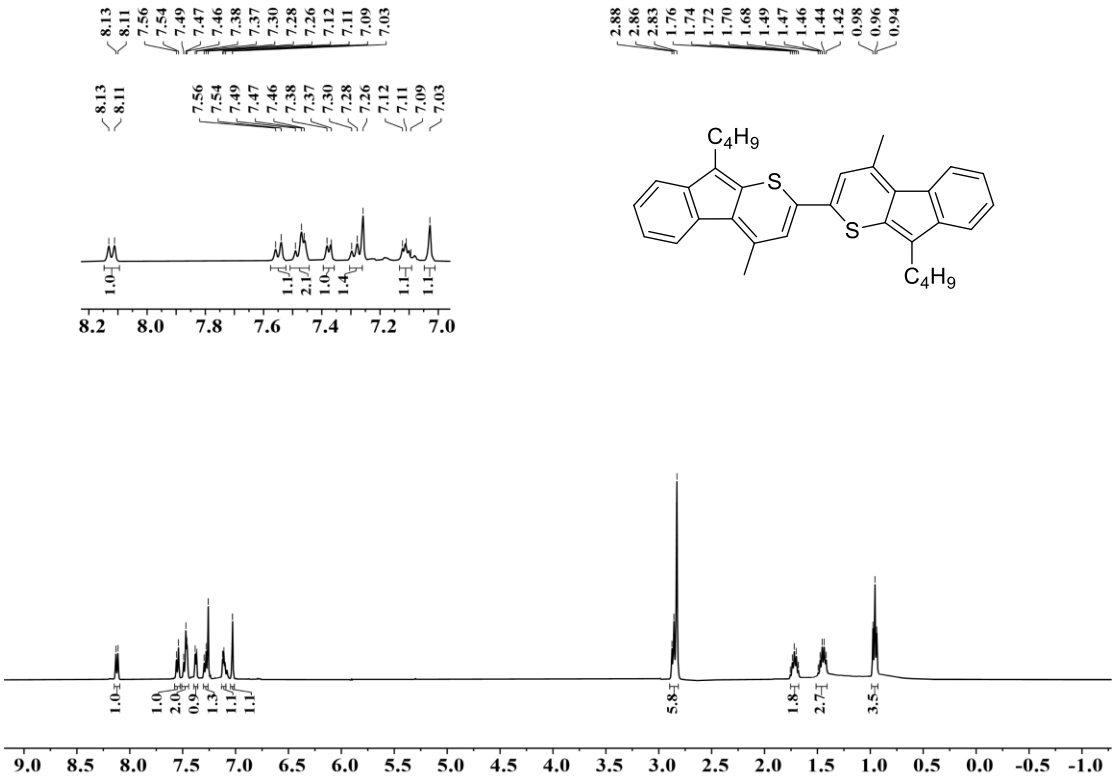


Fig. S7 ^{13}C NMR spectrum of **3a** in $CDCl_3$.

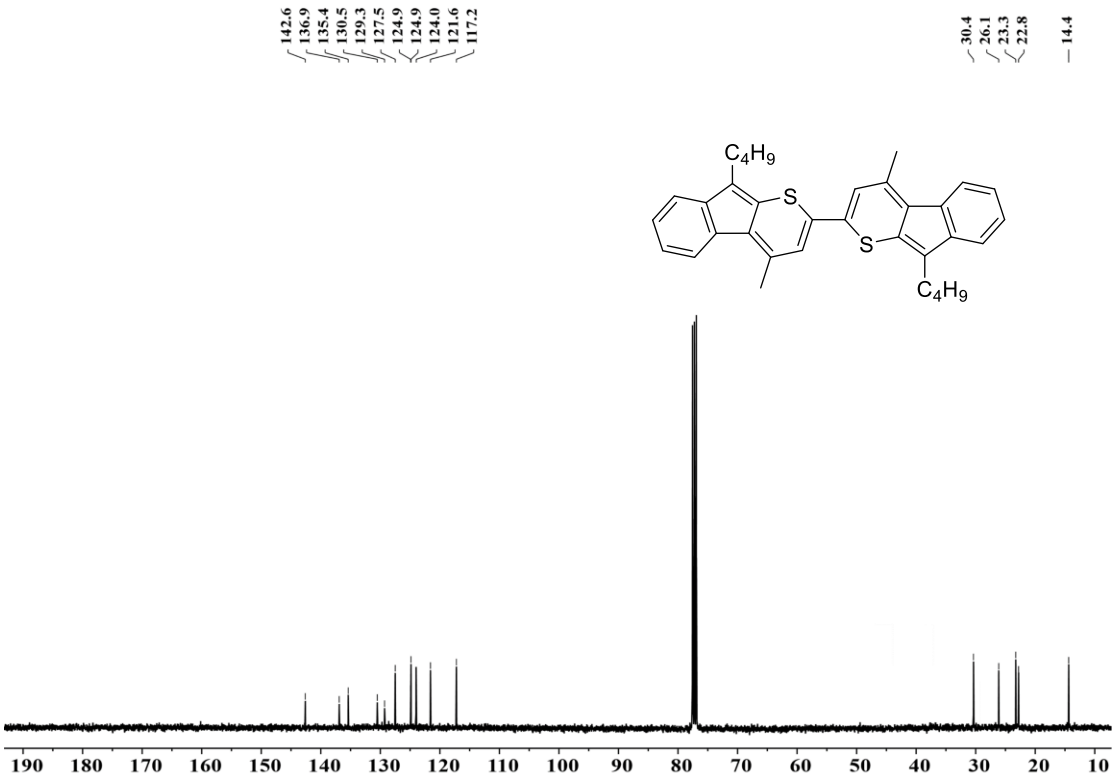


Fig. S8 ^{1}H NMR spectrum of **4a** in $CDCl_3$.

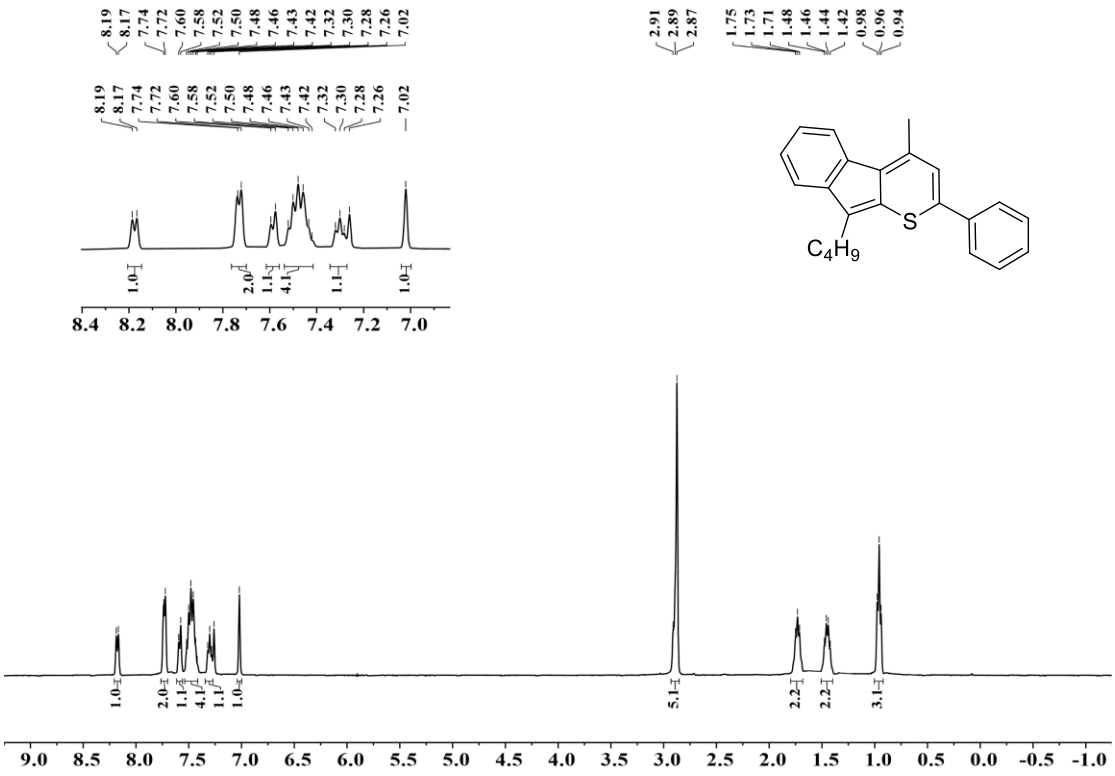


Fig. S9 ^{13}C NMR spectrum of **4a** in $CDCl_3$.

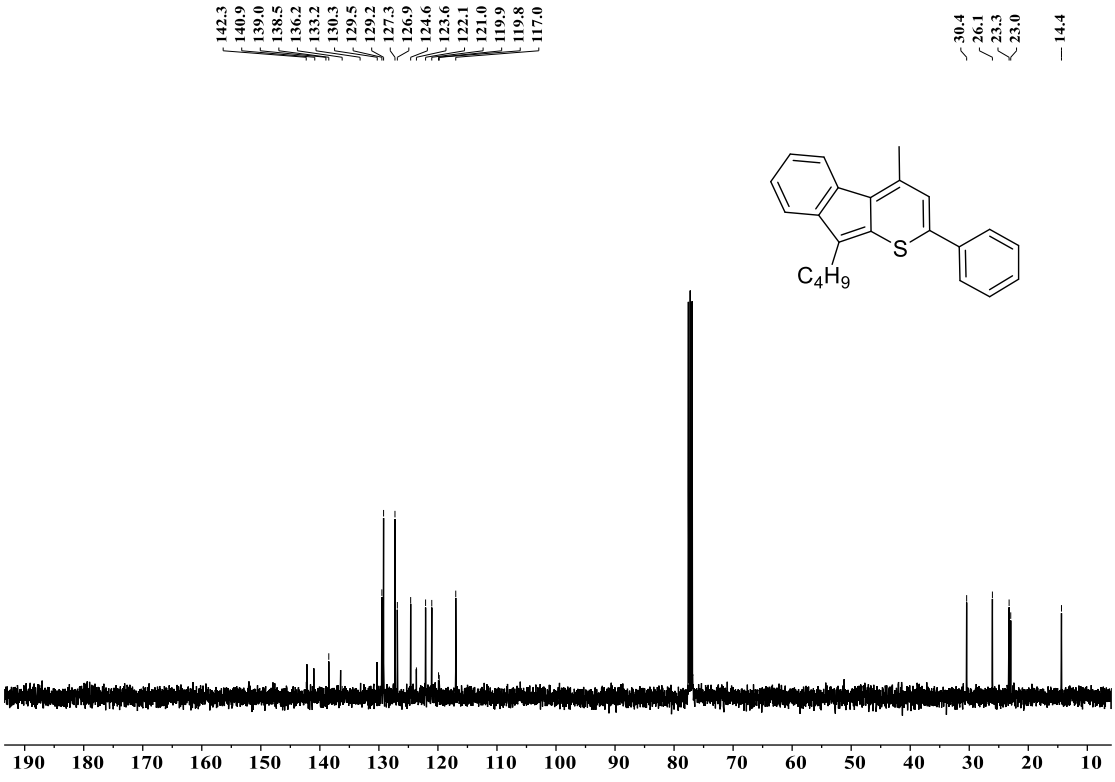


Fig. S10 ^{1}H NMR spectrum of **4b** in $CDCl_3$.

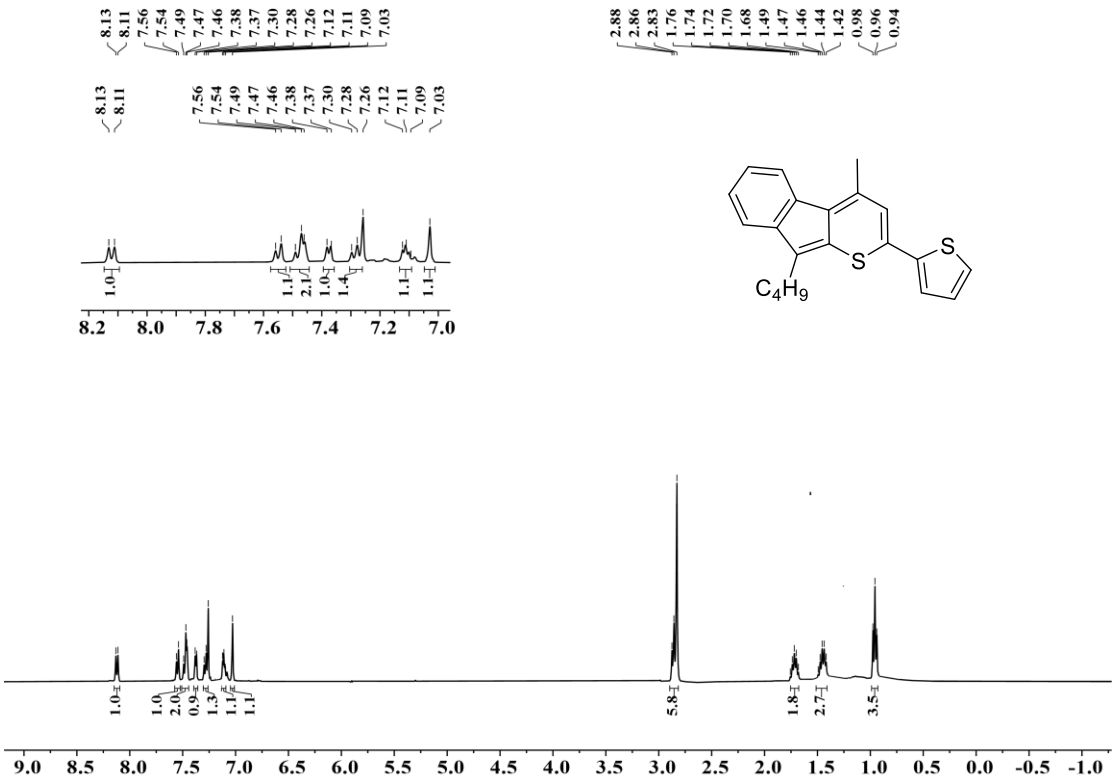


Fig. S11 ^{13}C NMR spectrum of **4b** in $CDCl_3$.

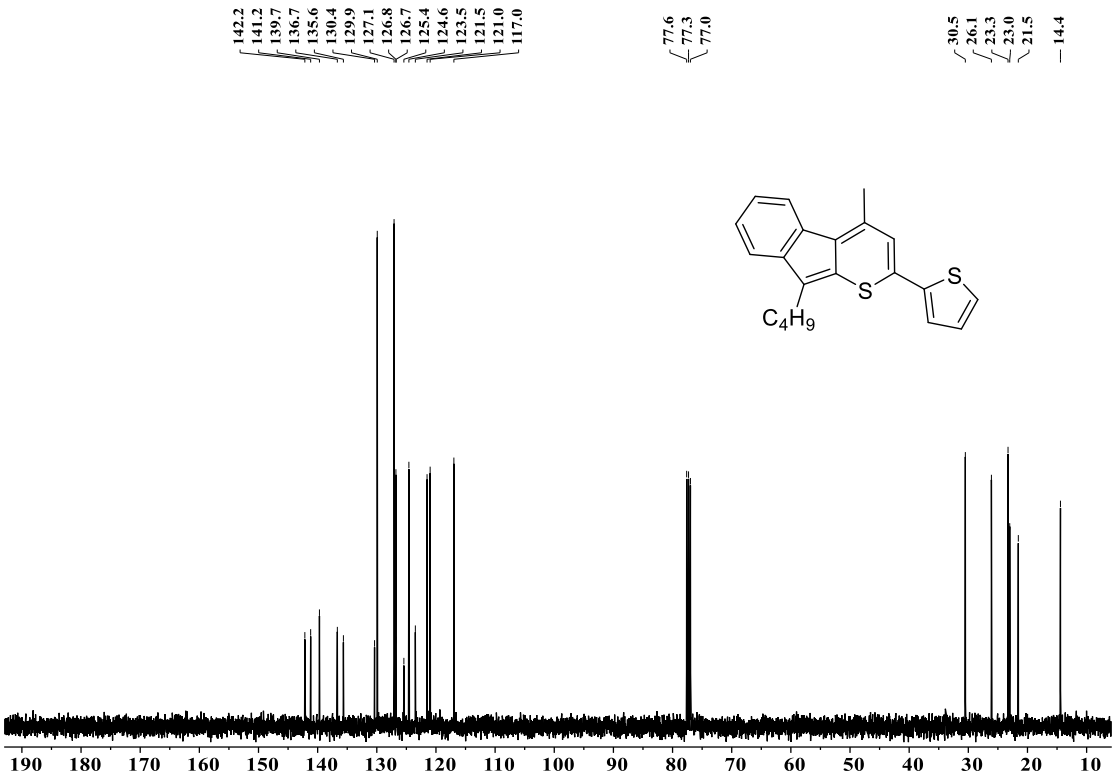


Fig. S12 ^{1}H NMR spectrum of **4c** in $CDCl_3$.

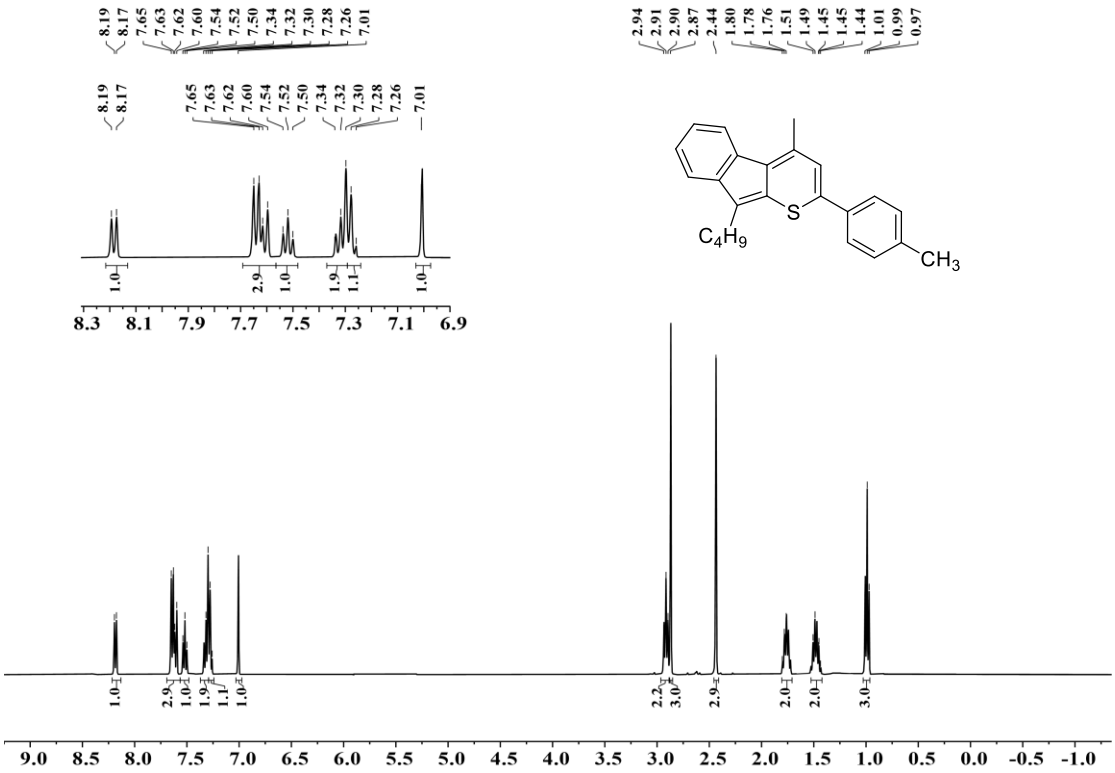


Fig. S13 ^{13}C NMR spectrum of **4c** in $CDCl_3$.

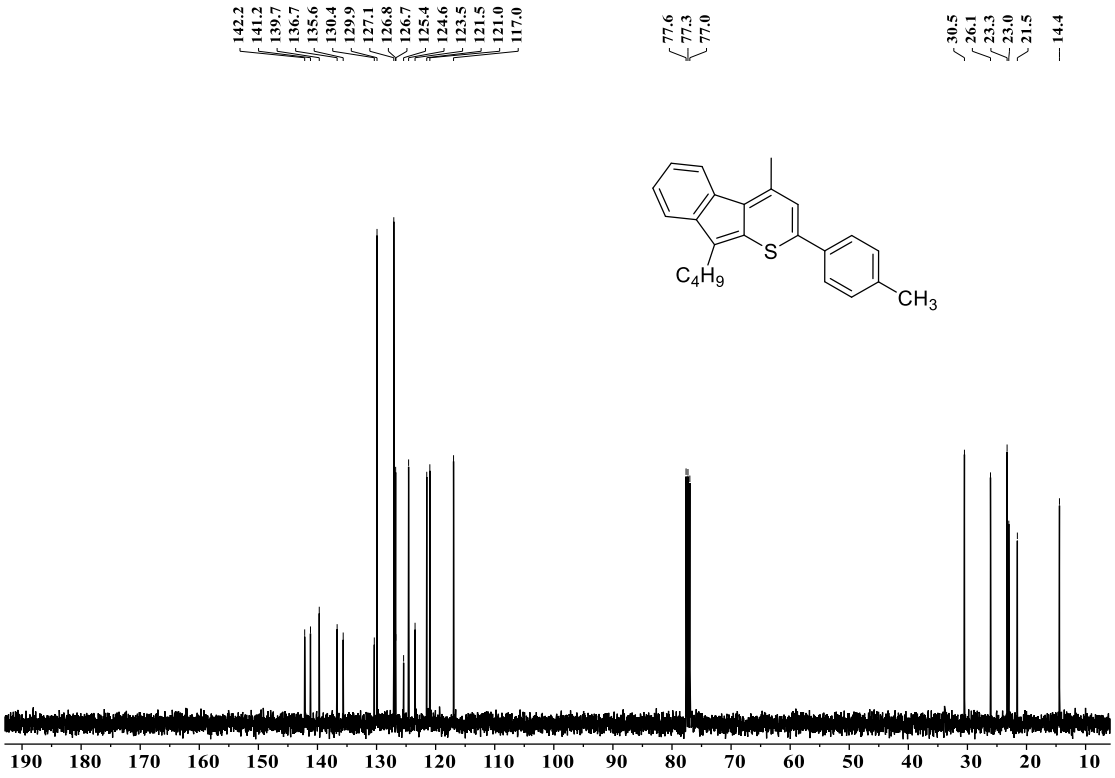


Fig. S14 ^{1}H NMR spectrum of **4d** in $CDCl_3$.

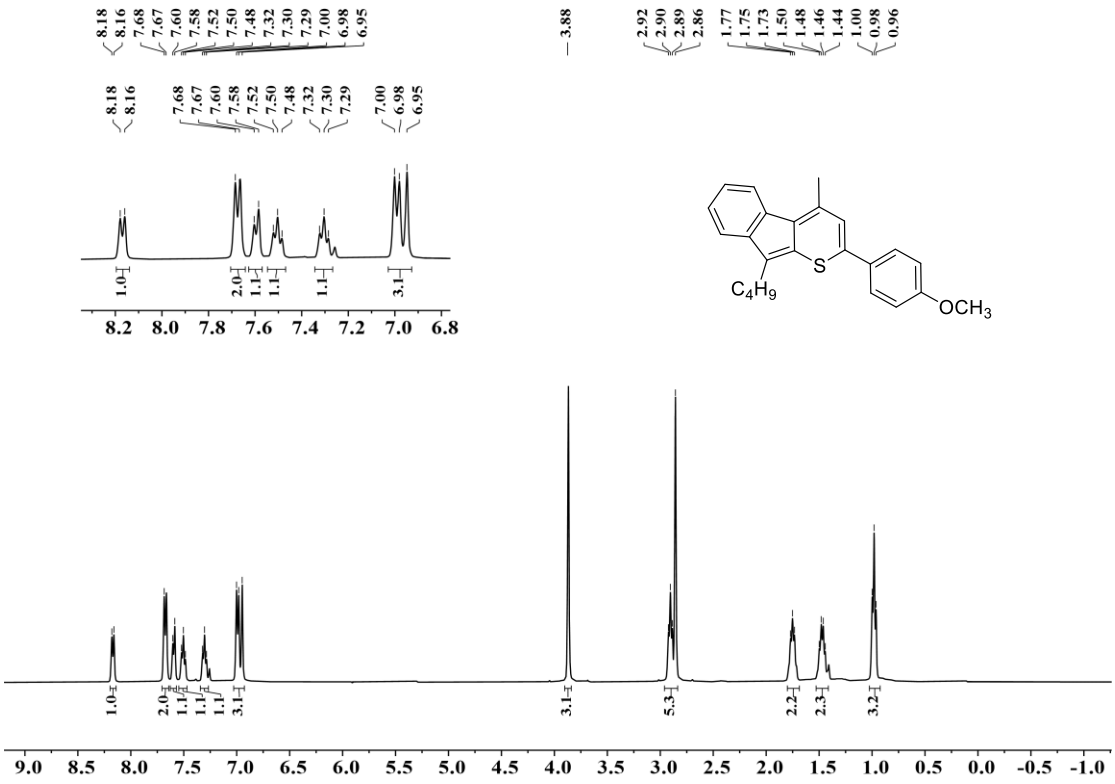


Fig. S15 ^{13}C NMR spectrum of **4d** in $CDCl_3$.

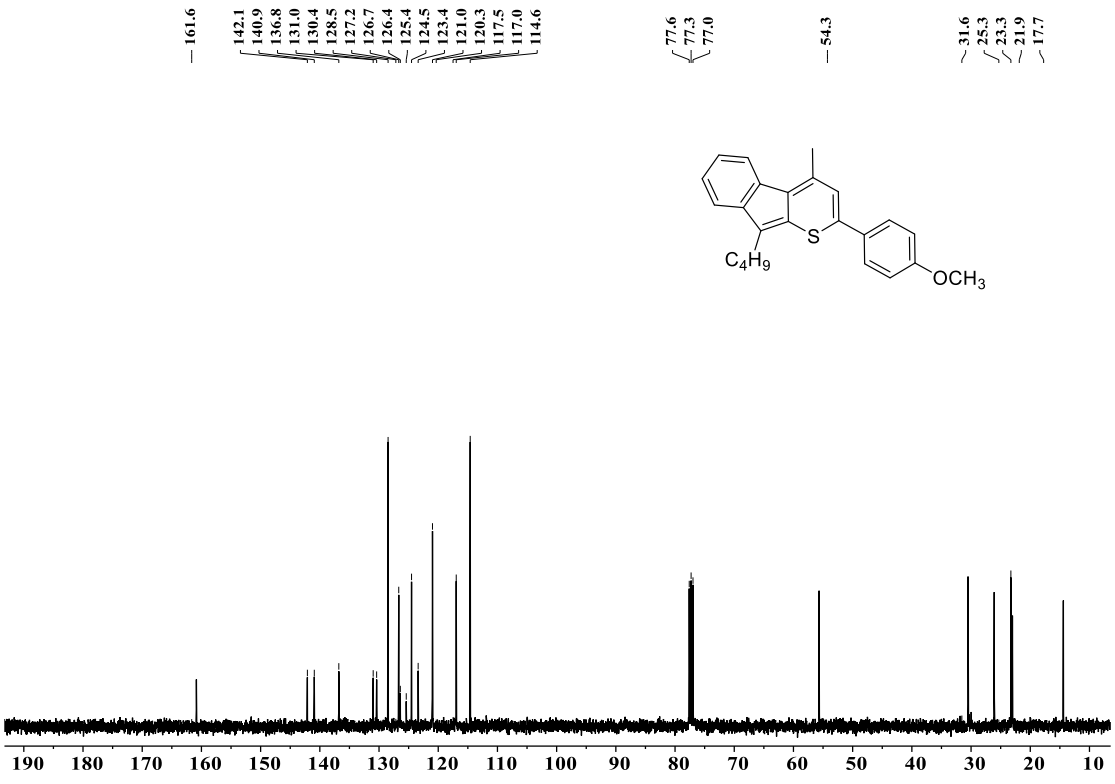


Fig. S16 ^{1}H NMR spectrum of **4e** in $CDCl_3$.

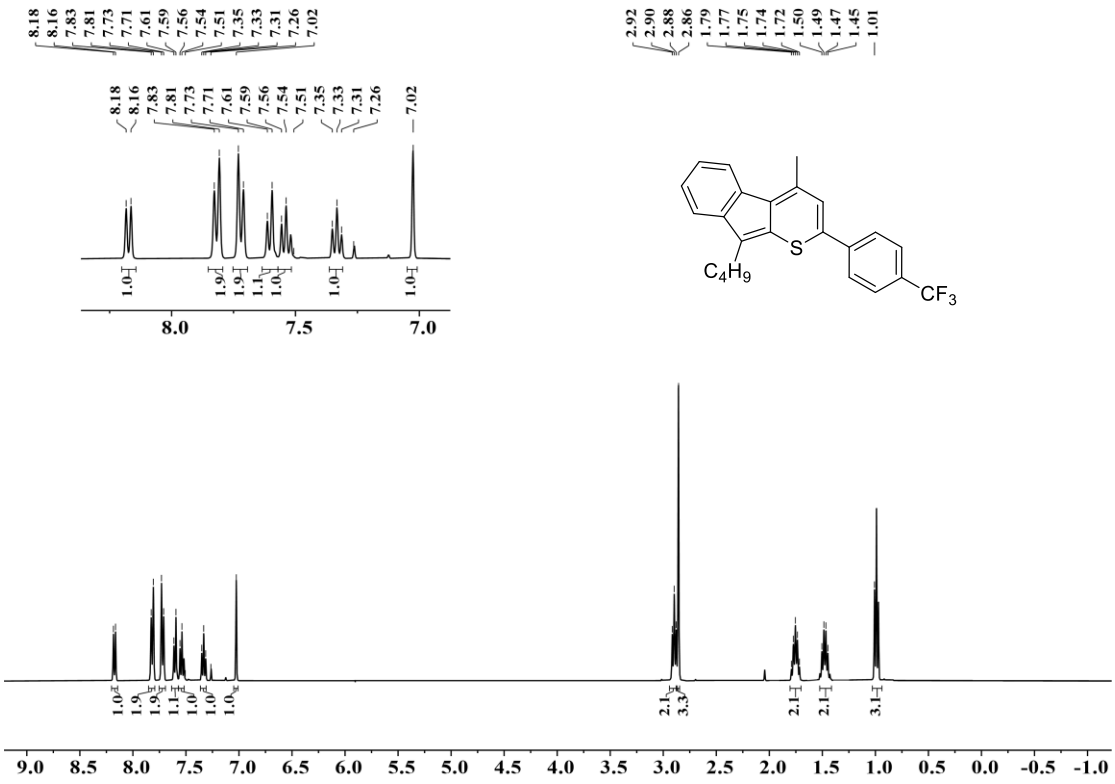


Fig. S17 ^{13}C NMR spectrum of **4e** in $CDCl_3$.

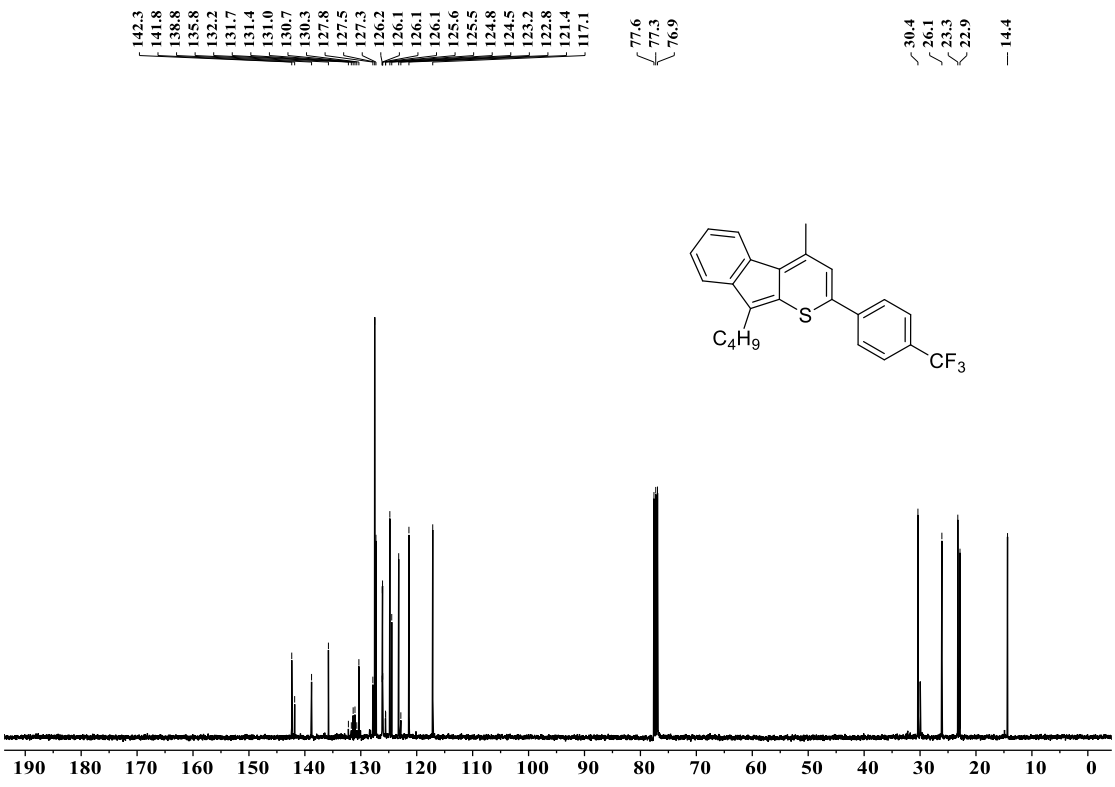


Fig. S18 ^{19}F NMR spectrum of **4e** in $CDCl_3$.

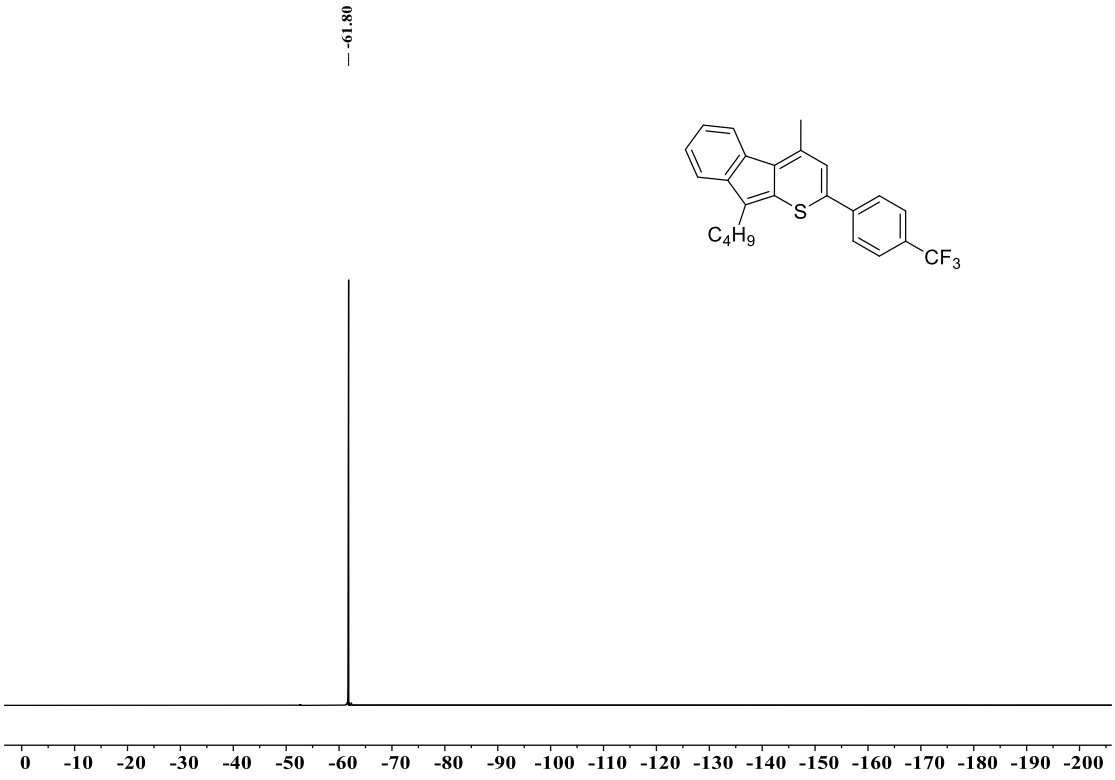


Fig. S19 ^{1}H NMR spectrum of **4f** in $CDCl_3$.

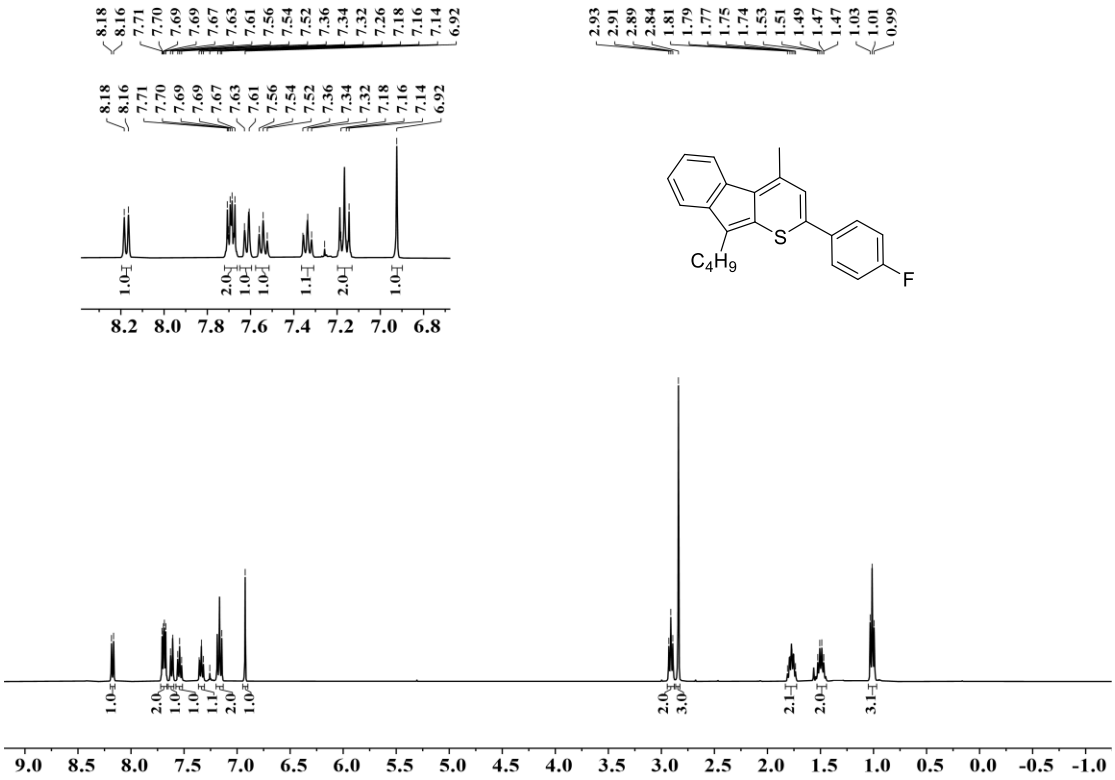


Fig. S20 ^{13}C NMR spectrum of **4f** in $CDCl_3$.

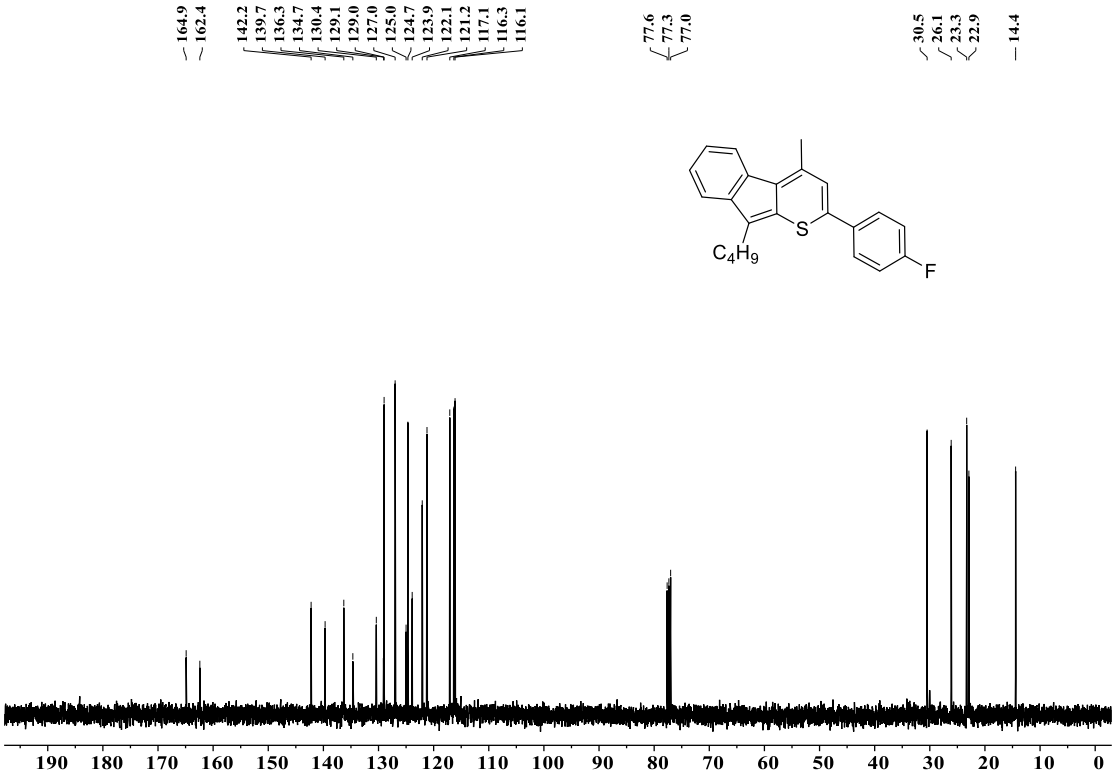


Fig. S21 ^{19}F NMR spectrum of **4f** in $CDCl_3$.

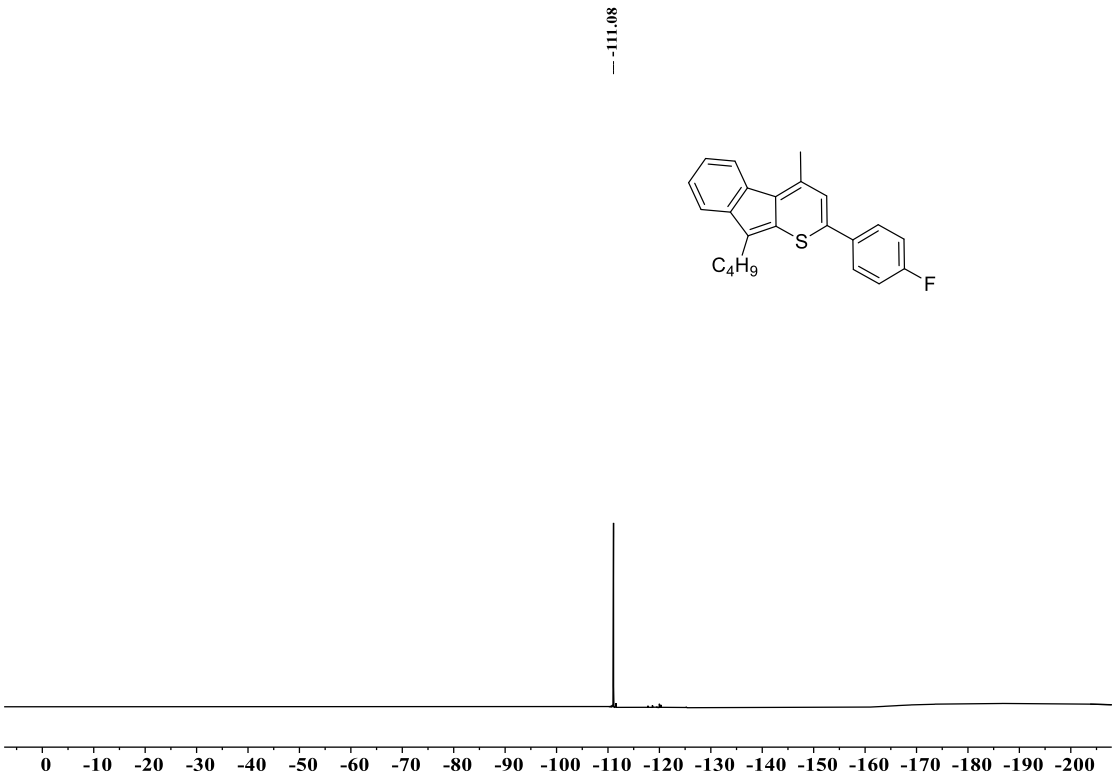


Fig. S22 ^{1}H NMR spectrum of **4g** in $CDCl_3$.

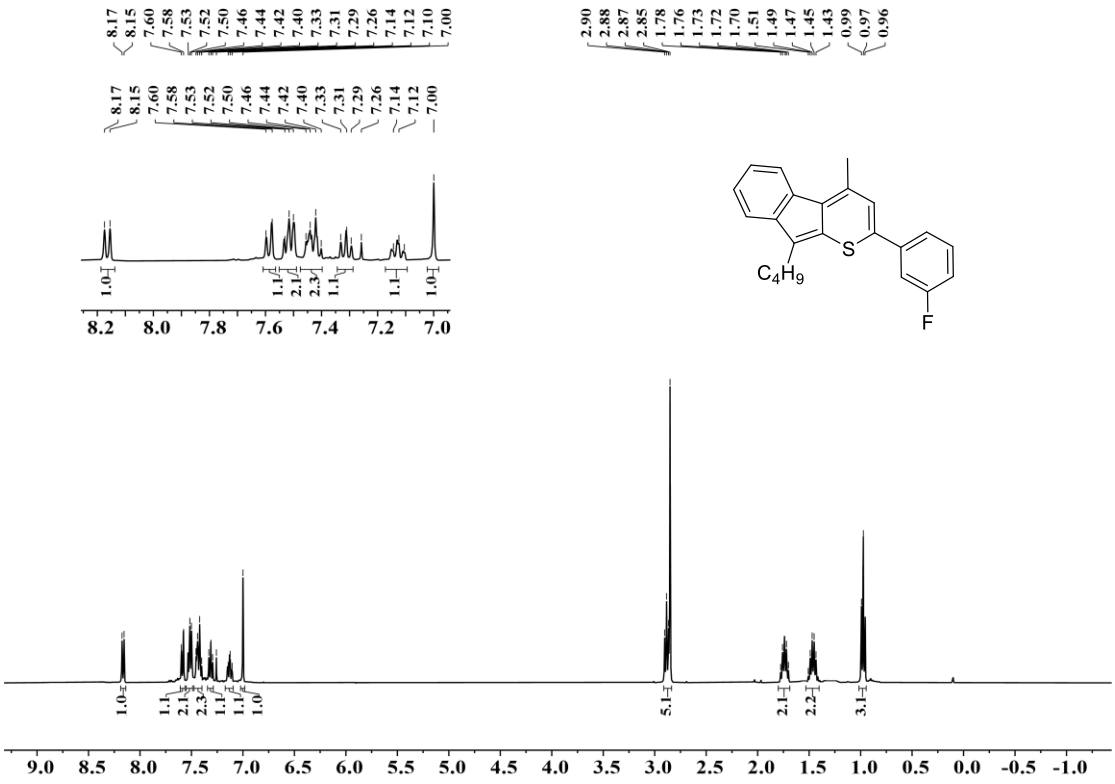


Fig. S23 ^{13}C NMR spectrum of **4g** in $CDCl_3$.

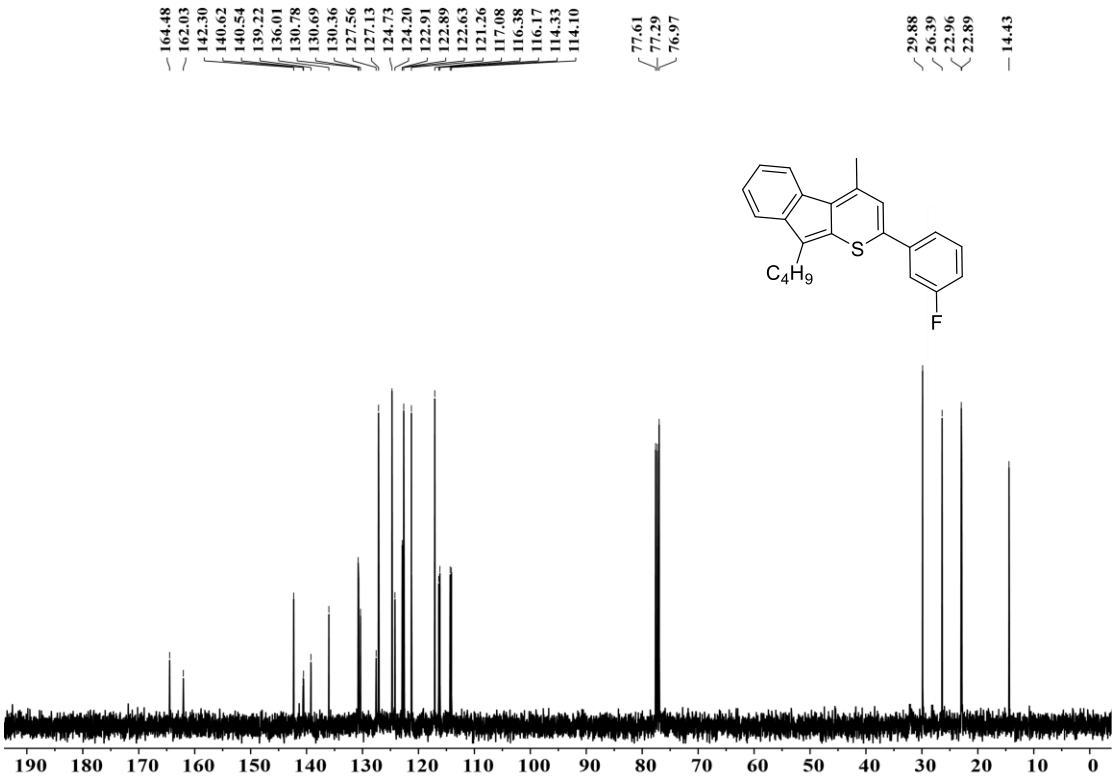


Fig. S24 ^{19}F NMR spectrum of **4g** in $CDCl_3$.

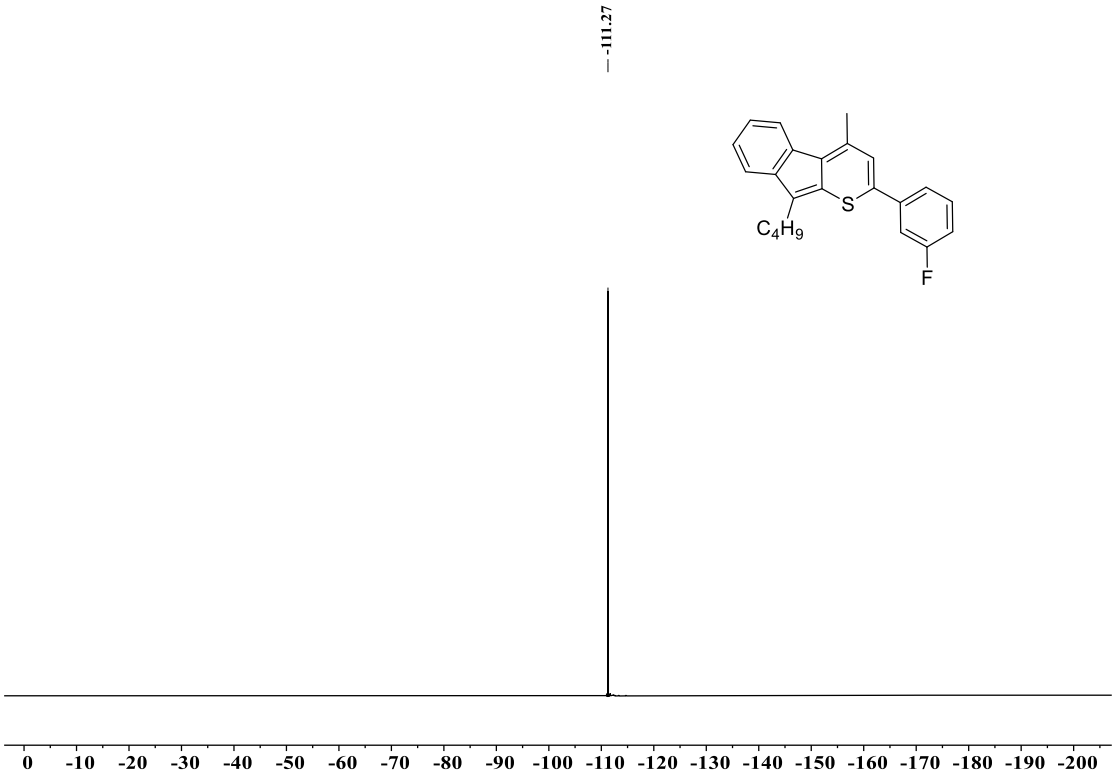


Fig. S25 ^{1}H NMR spectrum of **4h** in $CDCl_3$.

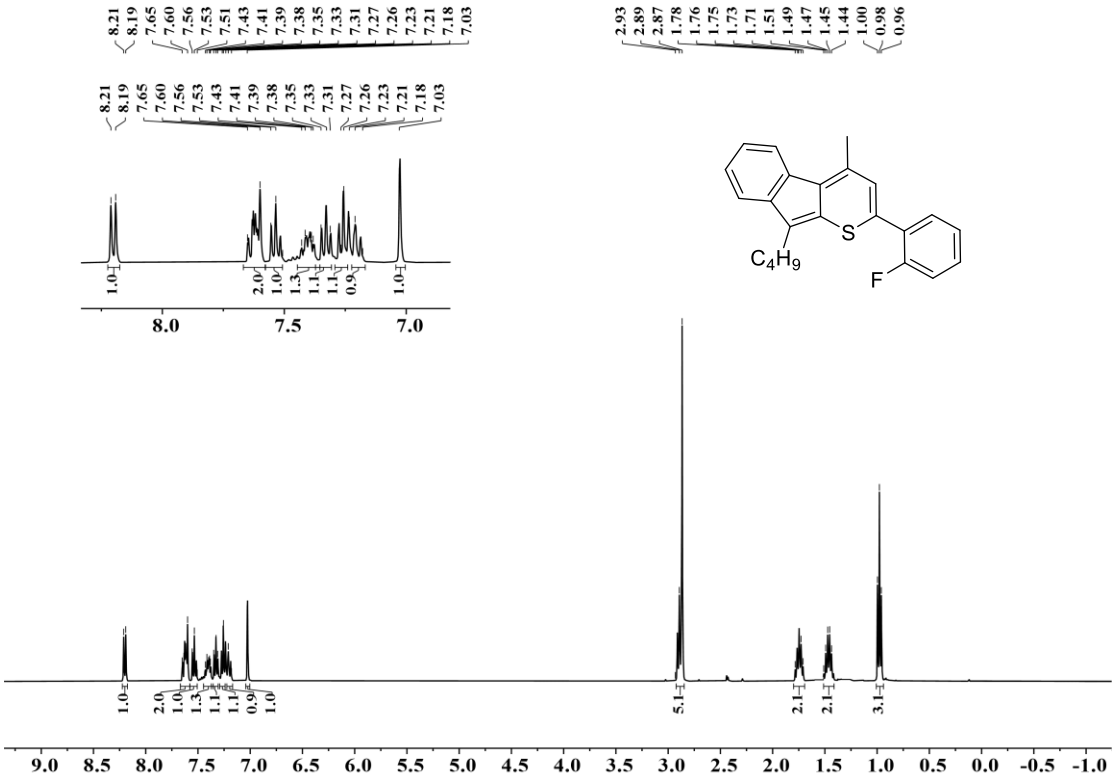


Fig. S26 ^{13}C NMR spectrum of **4h** in $CDCl_3$.

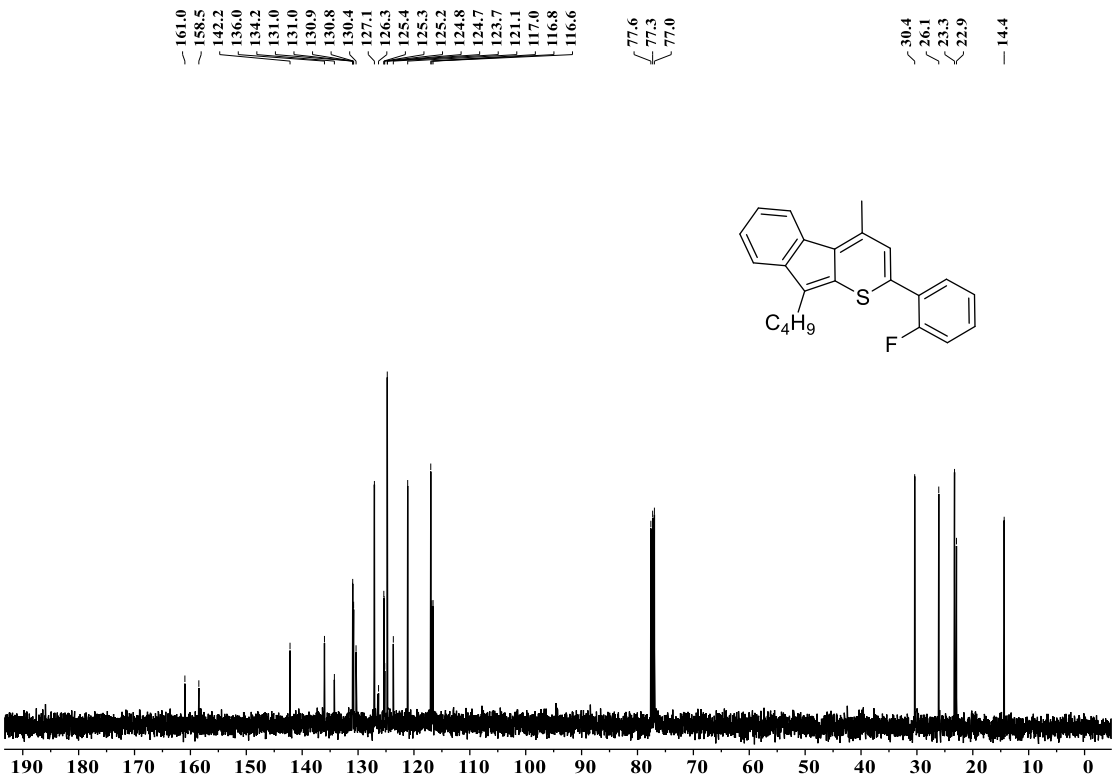


Fig. S27 ^{19}F NMR spectrum of **4h** in $CDCl_3$.

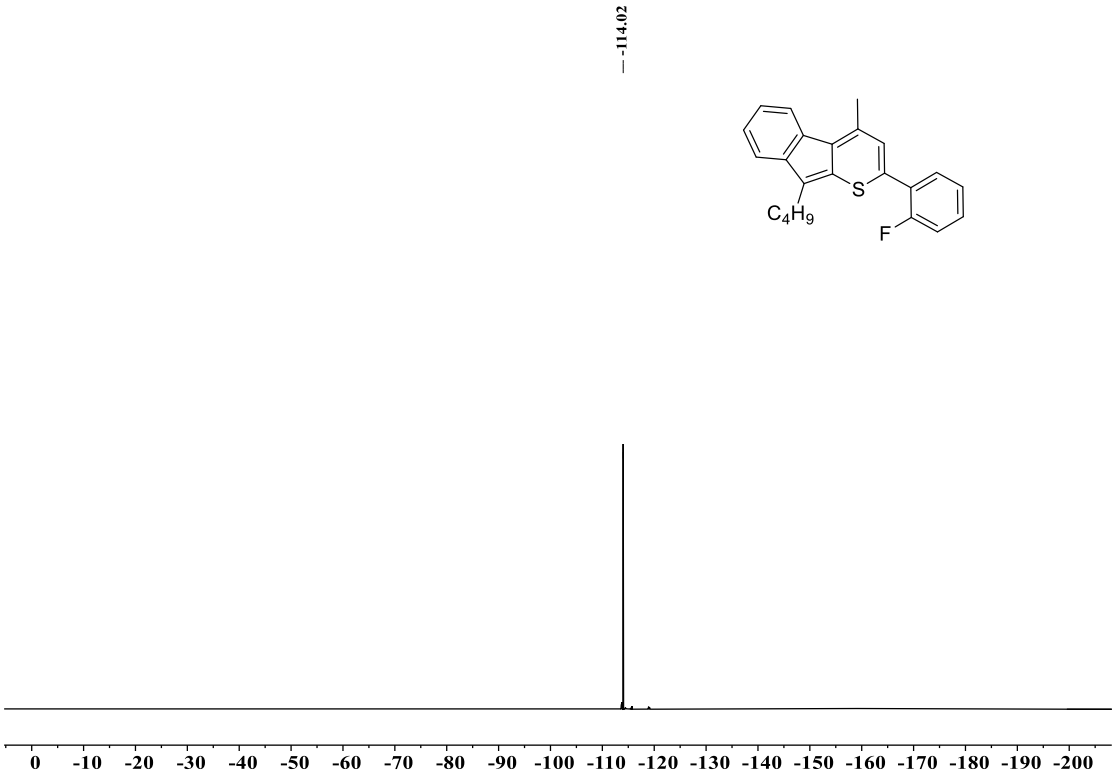


Fig. S28 ^{1}H NMR spectrum of **4i** in $CDCl_3$.

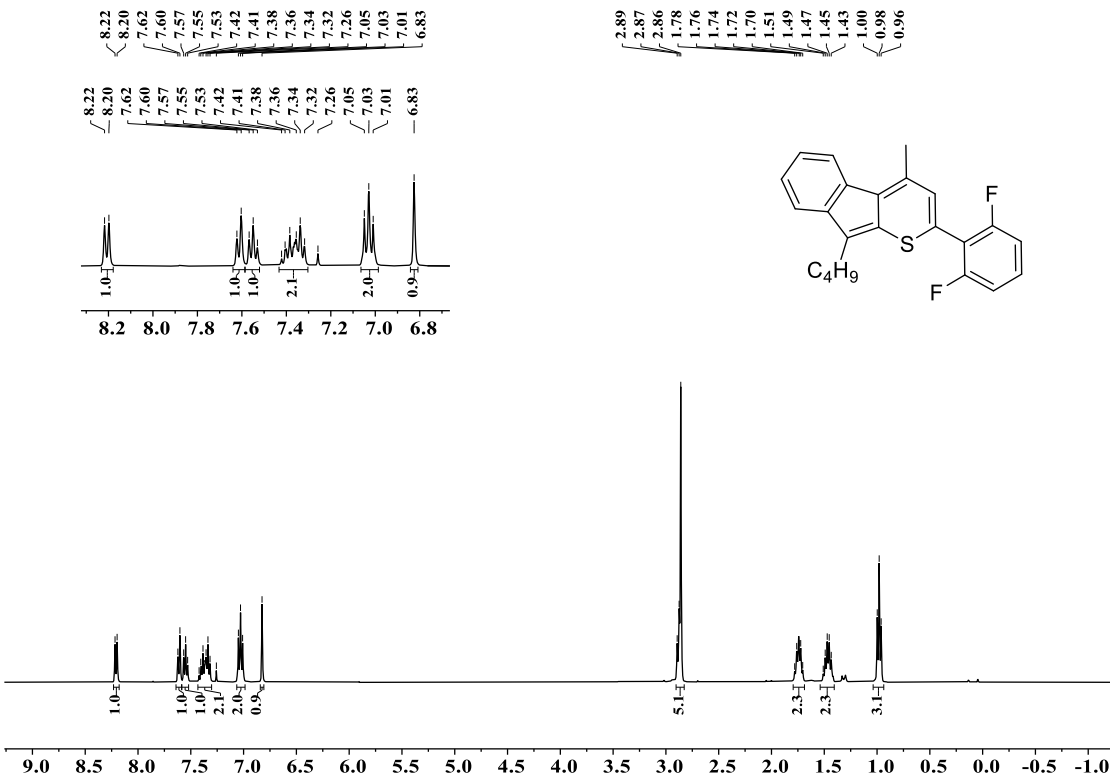


Fig. S29 ^{13}C NMR spectrum of **4i** in $CDCl_3$.

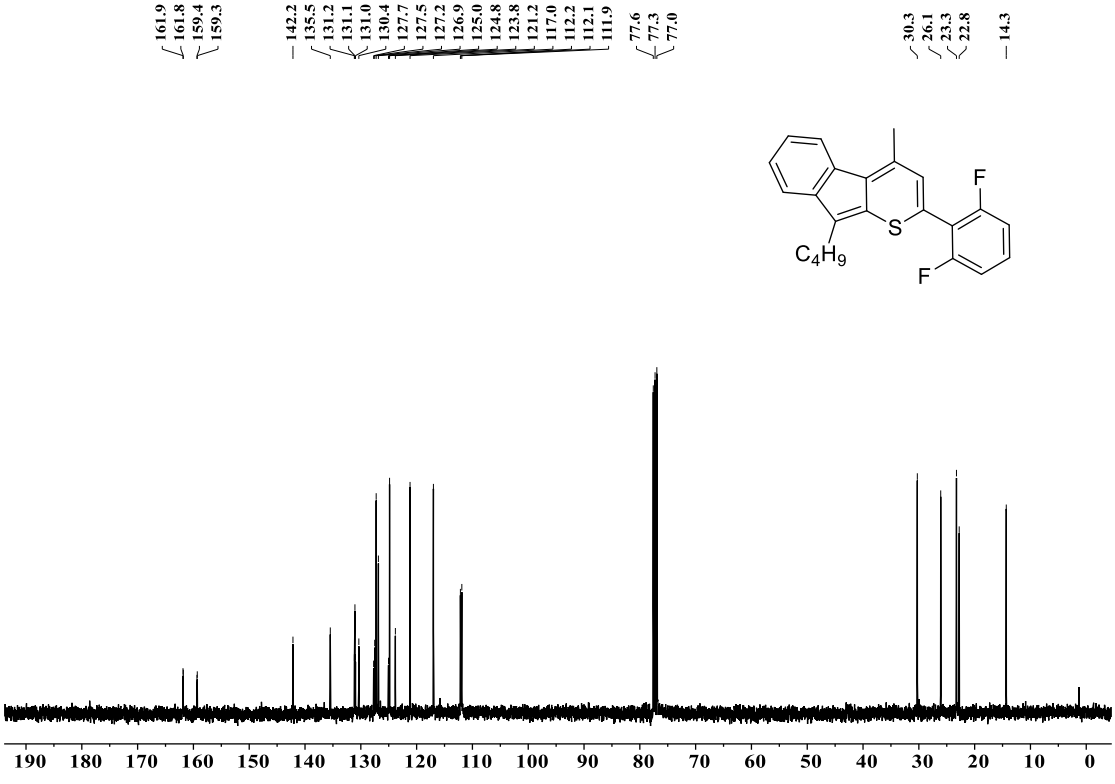


Fig. S30 ^{19}F NMR spectrum of **4i** in $CDCl_3$.

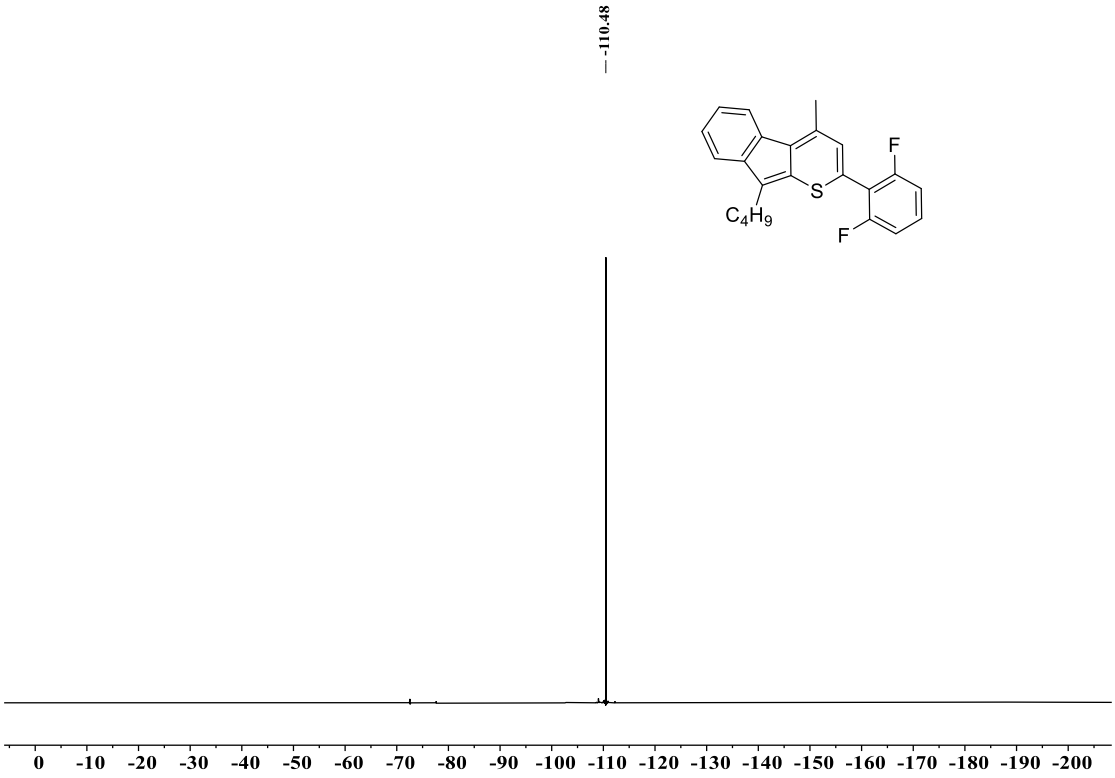


Fig. S31 ^{1}H NMR spectrum of **4j** in $CDCl_3$.

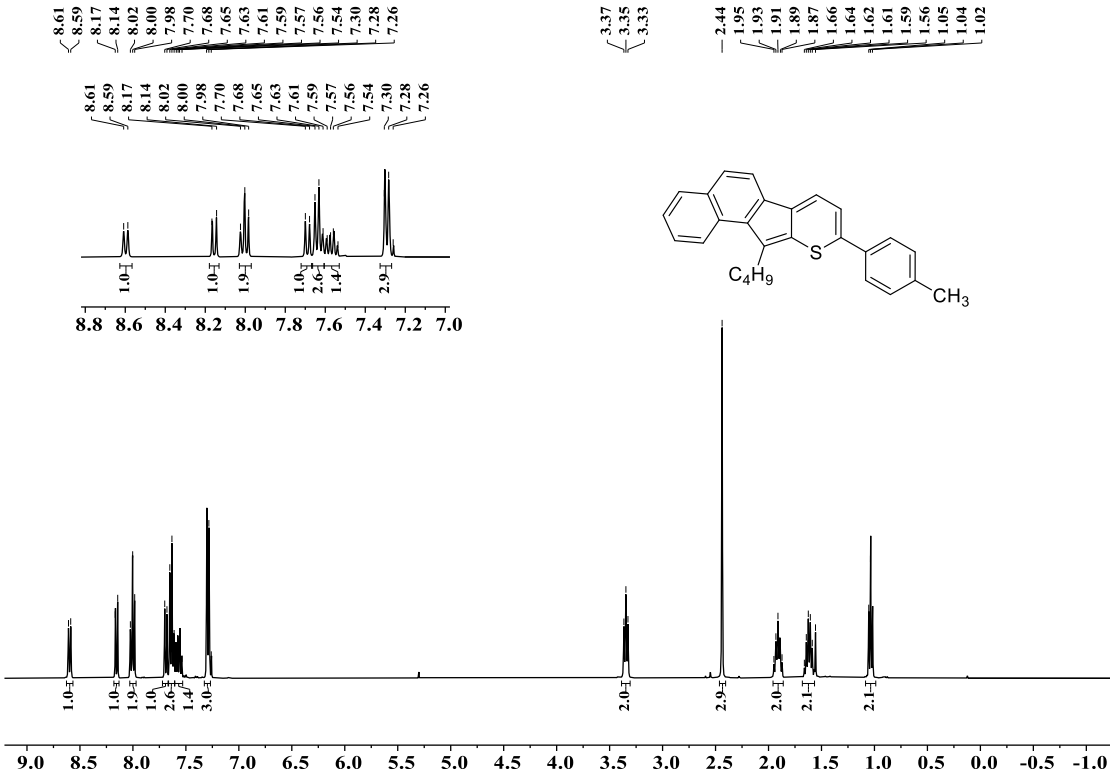


Fig. S32 ^{13}C NMR spectrum of **4j** in $CDCl_3$.

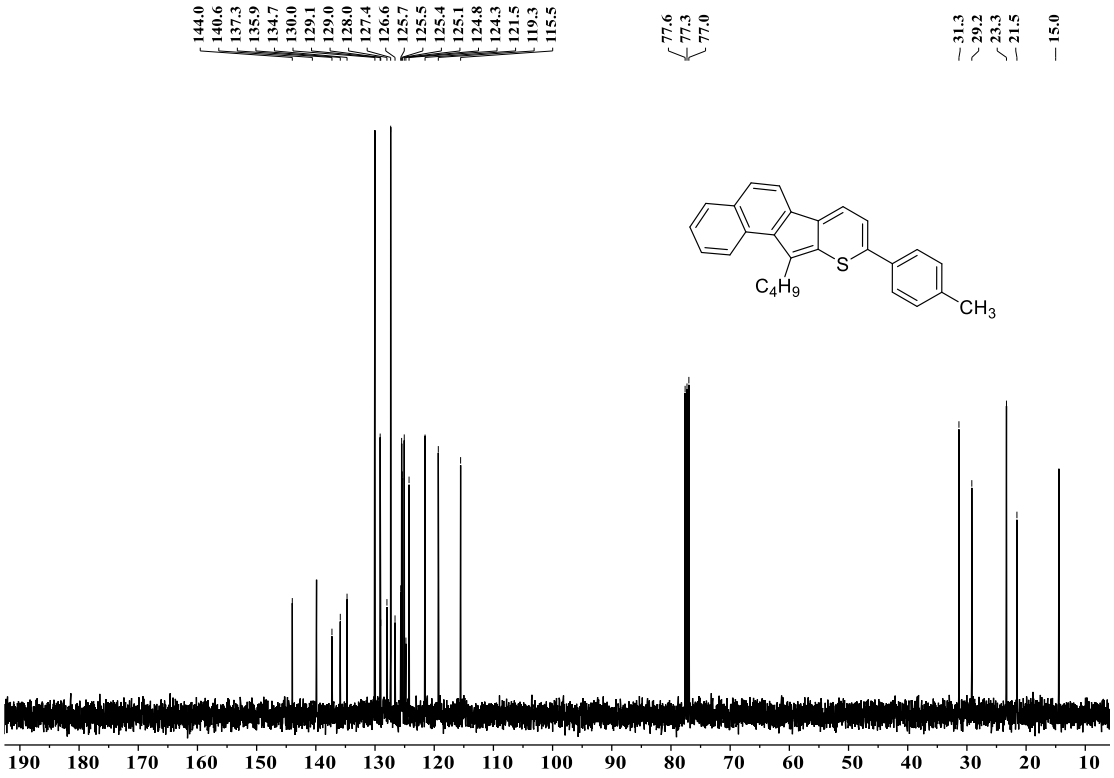


Fig. S33 ^{1}H NMR spectrum of **4k** in $CDCl_3$.

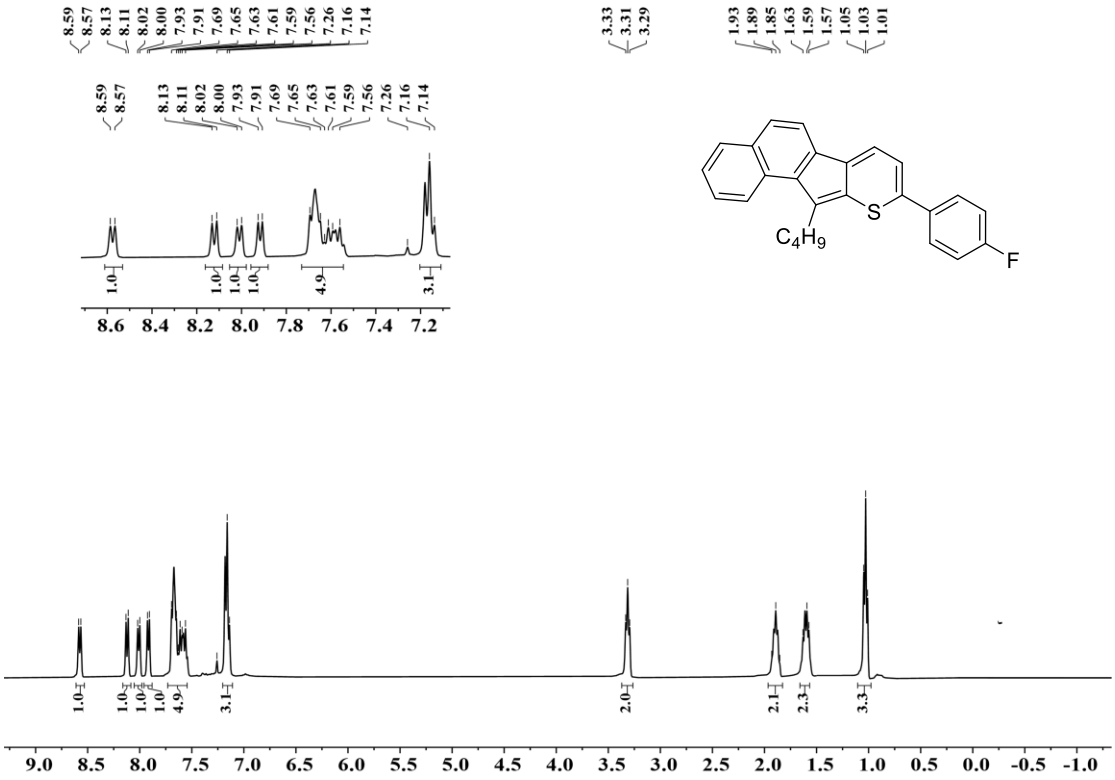


Fig. S34 ^{13}C NMR spectrum of **4k** in $CDCl_3$.

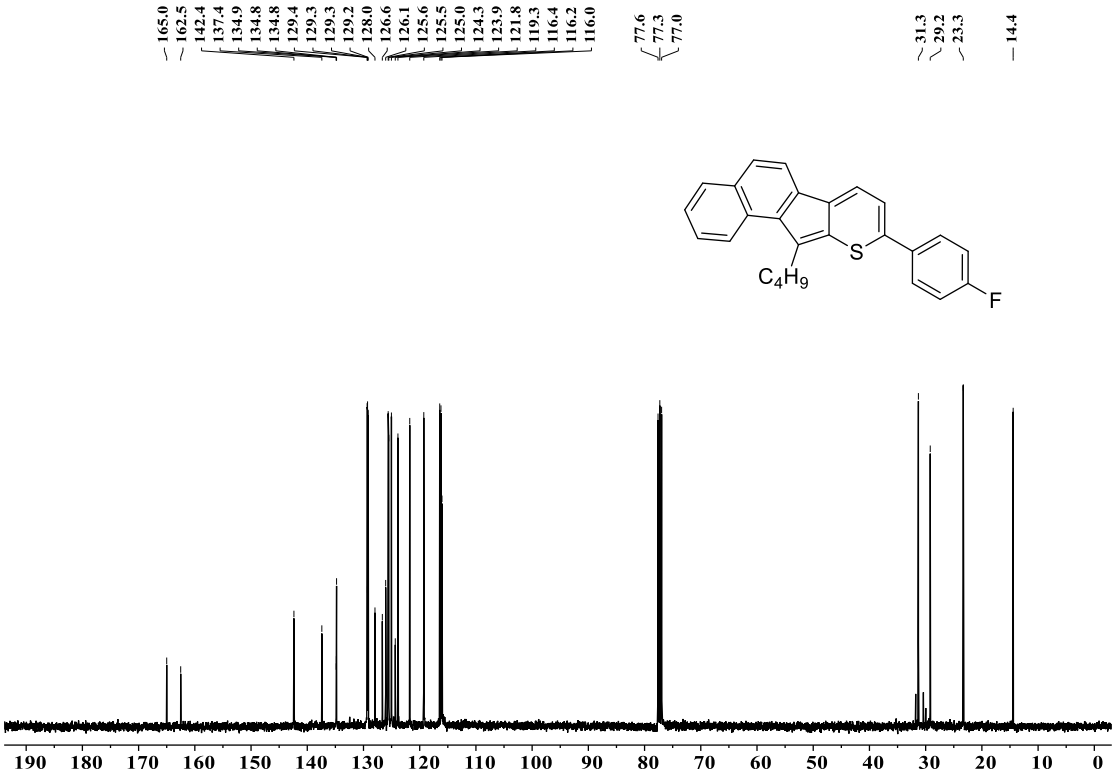


Fig. S35 ^{19}F NMR spectrum of **4k** in $CDCl_3$.

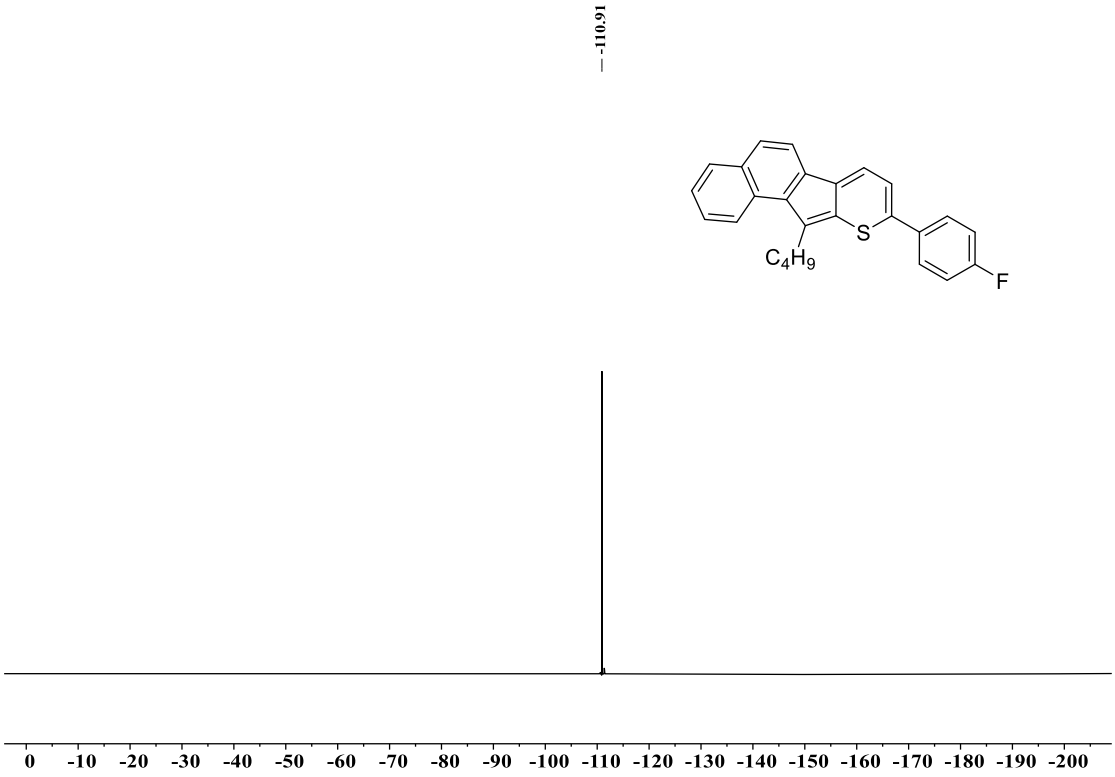


Fig. S36 ^{1}H NMR spectrum of **4l** in $CDCl_3$.

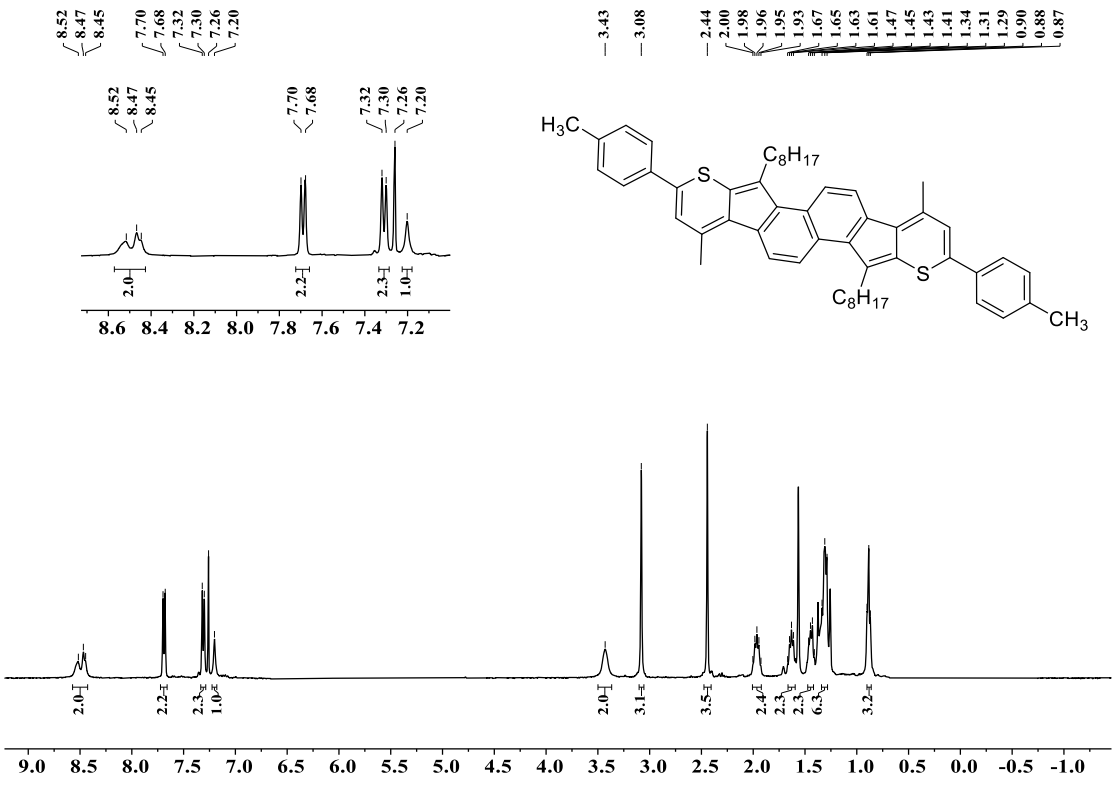


Fig. S37 ^{13}C NMR spectrum of **4l** in $CDCl_3$.

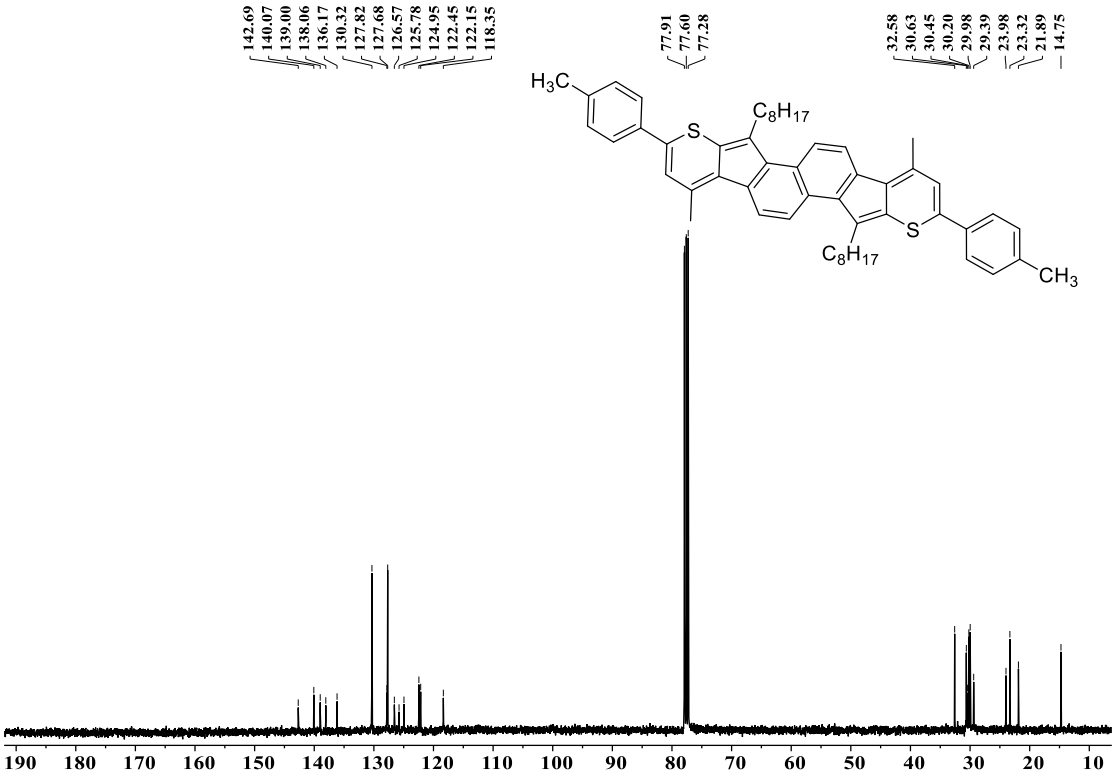


Fig. S38 ^{1}H NMR spectrum of **4m** in $CDCl_3$.

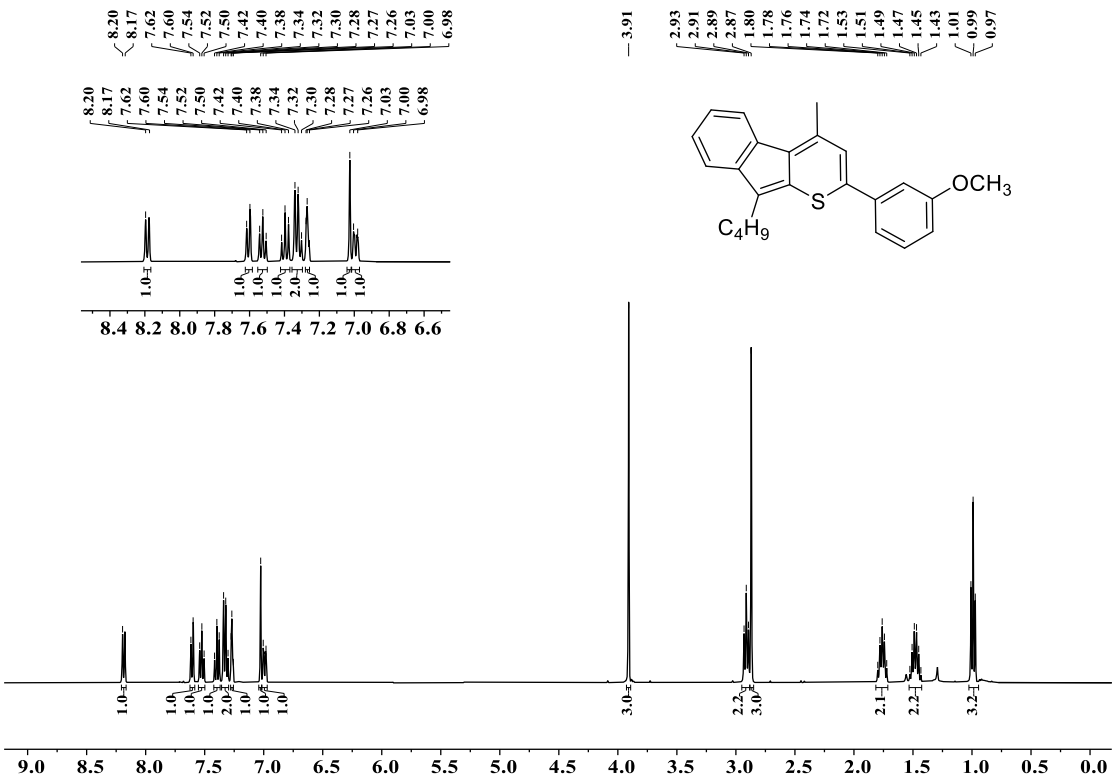


Fig. S39 ^{13}C NMR spectrum of **4m** in $CDCl_3$.

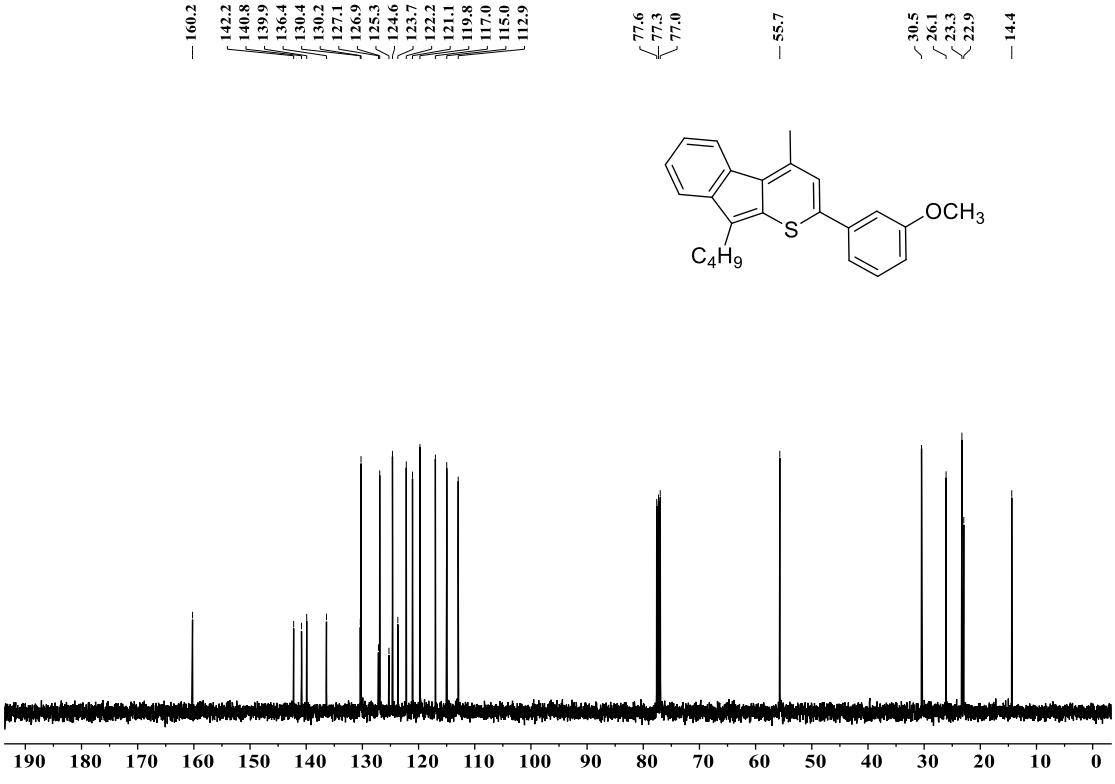


Fig. S40 ^{1}H NMR spectrum of **4n** in $CDCl_3$.

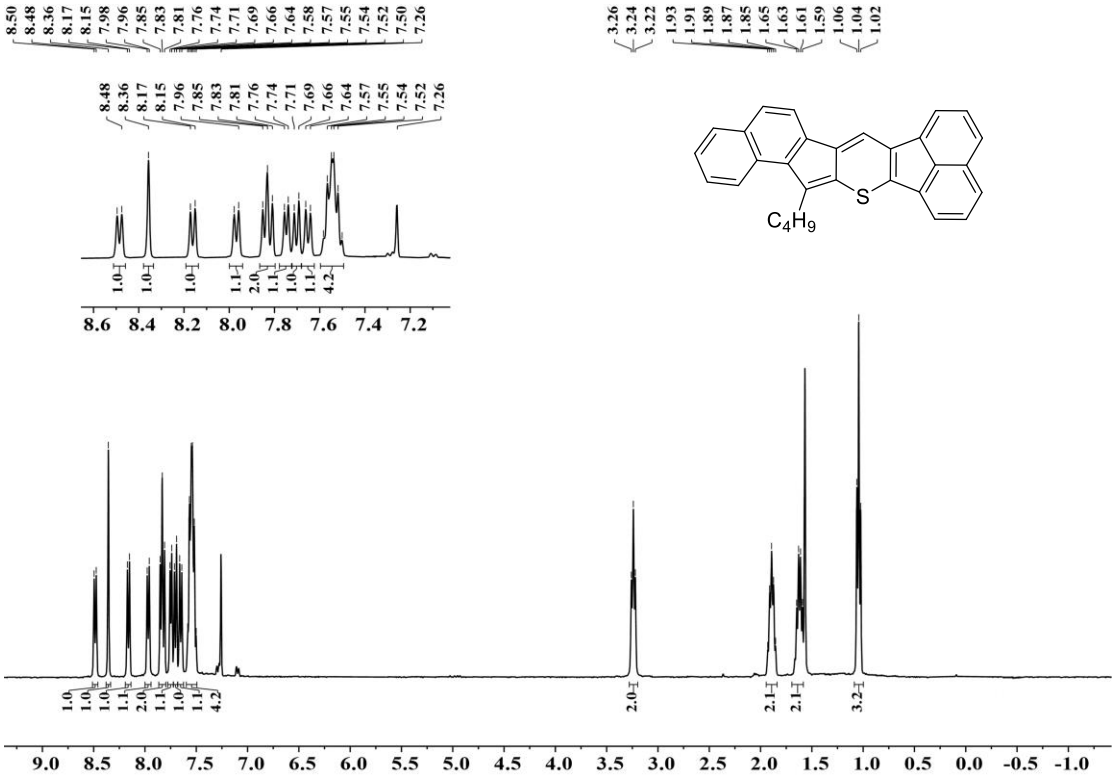


Fig. S41 ^{13}C NMR spectrum of **4n** in $CDCl_3$.

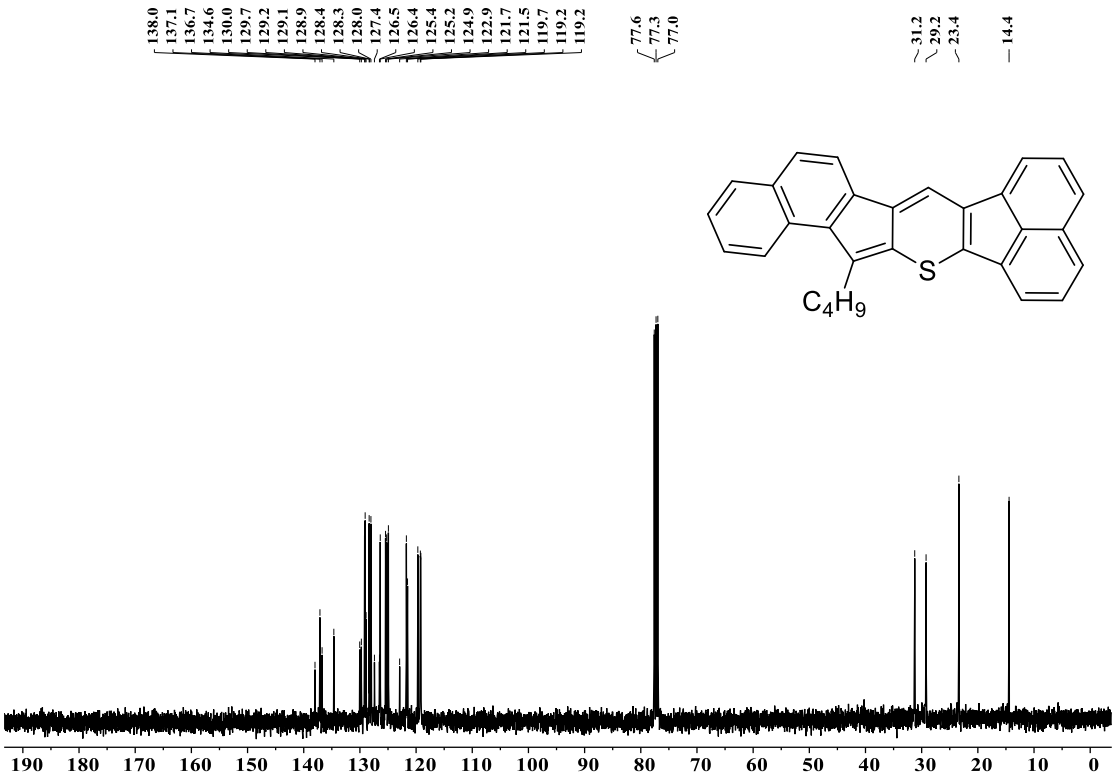


Fig. S42 ^{1}H NMR spectrum of **4o** in $CDCl_3$.

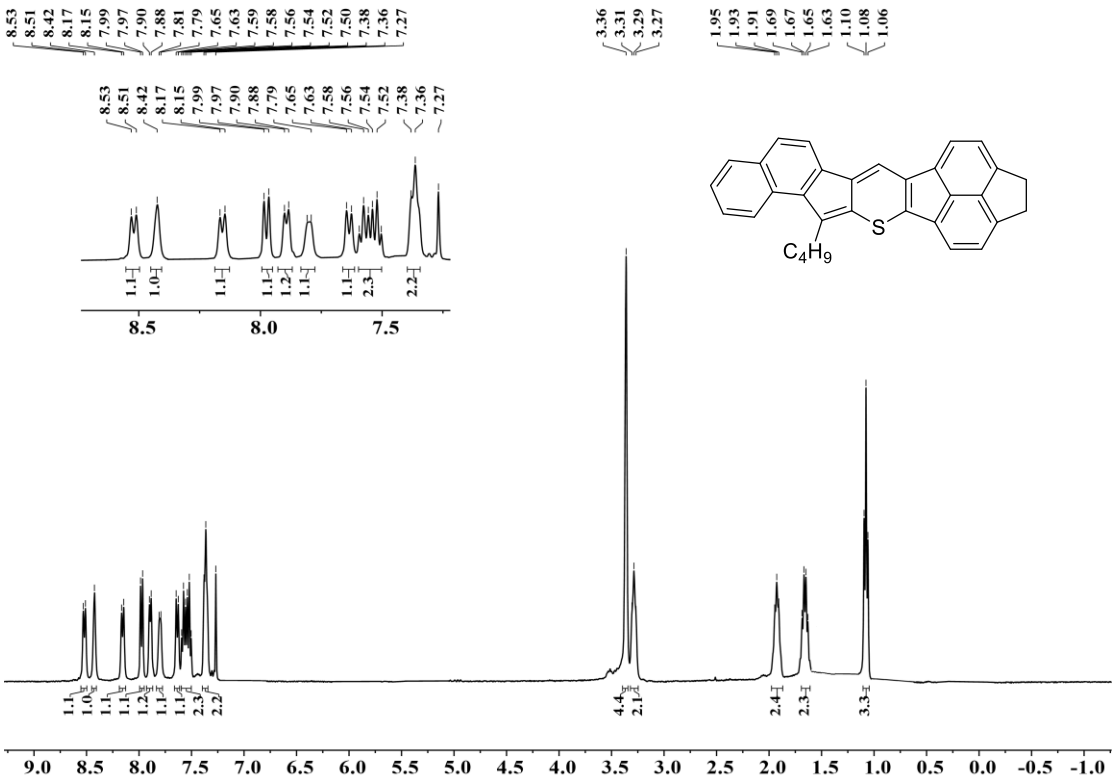
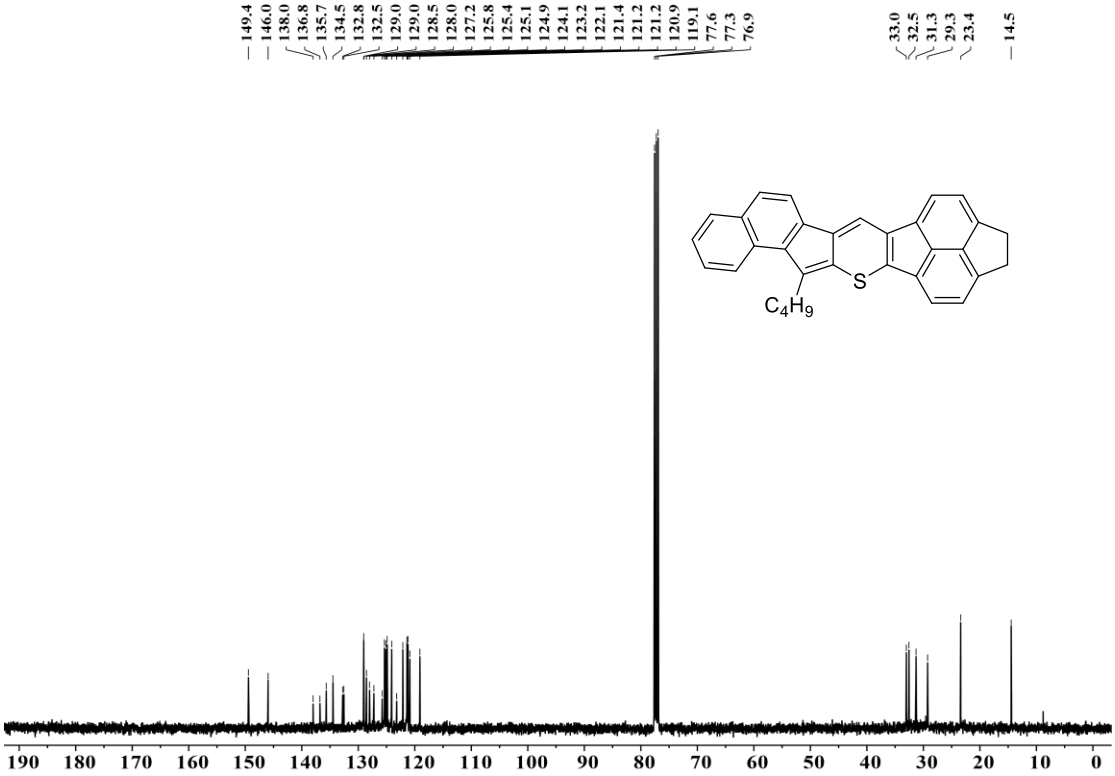


Fig. S43 ^{13}C NMR spectrum of **4o** in $CDCl_3$.



8. Reference.

S1. Y. Lu, Y. Qiao, H. Xue and G. Zhou, *Org. Lett.*, 2018, **20**, 6632-6635.