Supporting Information

Direct Imide Formation from Thiophene Dicarboxylic Acids Gives Expanded Side-Chain Selection in Thienopyrrolediones

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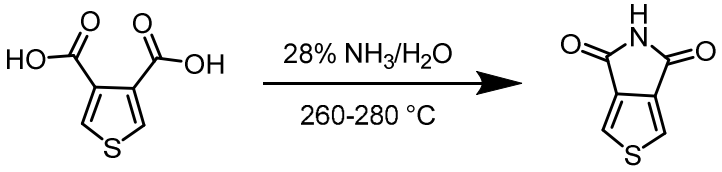
General Instrumentation:

Characterization: NMR spectra were collected on Varian Mercury Vx (300 MHz ^{1}H, 75 MHz ^{13}C), Bruker Avance III (376.5 MHz ^{19}F), or Bruker Avance III-HD (700 MHz ^{1}H, 176 MHz ^{13}C). Spectra were processed using MestReNova v6.0 and referenced to residual protonated solvent signals ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.16; CD_2Cl_2: ^{1}H 5.32 ppm, ^{13}C 54.00 ppm; DMSO-d_6: ^{1}H 2.50 ppm, ^{13}C 39.52 ppm). The ^{19}F spectrum is not referenced to an internal solvent signal. The solvent peak used as the internal reference is labeled in each spectrum as its deuterated parent solvent. Accurate mass spectra were collected by the Bioanalytical Mass Spectrometry Facility at Georgia Tech on either a MicroMass AutoSpec M (EI) or a Micromass Quattro LC (ESI). Elemental analyses were carried out by Atlantic Microlabs. Melting points were collected on a MEL-TEMP apparatus with digital thermometer at a 10 °C/min heating rate and are reported uncorrected.

Experimental Procedures:

3,4-thiophene carboxylic acid was purchased from Frontier Scientific and used without further purification. Heptadecan-9-ol,[1] 9-heptadecyl 4-toluenesulfonate,[1] 3,6,9-trioxadecyl 4-toluenesulfonate[2], and 3,3'-bithiophene dicarboxylic acid[3] were synthesized according to literature procedures. Silica gel (60 Å, 230-400 mesh) was purchased from Sorbtech (Norcross, GA). All other reagents were purchased from commercial suppliers and used without further purification.

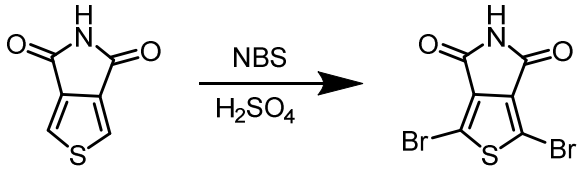


Thieno[3,4-c]pyrrole-4,6-dione (1):
Compound **1** has been previously synthesized by a different route.[4] A modified and more thorough account is given here. To a 50 mL 1-neck RBF was added 3,4-thiophene dicarboxylic acid (3.44 g, 20 mmol) and water (2-3 mL). Small pieces of glass were added as boiling stones. Concentrated aqueous ammonia (28%/14.8M, ~10 equivalents) was added slowly. The flask was heated gently to dissolve starting material, then to a boil until all water and excess ammonia were driven off. A white, crystalline material remained. NMR indicated complete conversion to the diammonium salt. A short (3-4") air-condenser was attached to the flask (use Teflon tape). In a sand bath, the flask was heated to 260-280 °C for 3-4 hours. During this time, the reaction became a homogenous melt, and product began to sublime to the top of the flask and into the condenser. Heating was continued until all material had sublimed. Solids were collected using excess hot acetonitrile (low solubility). Insoluble materials were filtered off. The solution was cooled in a -20 °C freezer to encourage precipitation. The precipitate was collected and washed with water then cold ACN. Drying under high vacuum gave the title compound (2.3g, 76%) as a beige solid, which can be used in subsequent reactions without further purification.
For obtaining high purity material, the product can be purified in multiple ways:

- Trituration or recrystallization in hot ACN
- Sublimation under vacuum (~10 mbar) at 160 °C.
- Brief sonication in water effectively removes starting material

^{1}H NMR (300 MHz, DMSO-d_6): δ 11.25 (bs, 1H), 8.26 (s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.29, 137.16, 127.32. HRMS (EI) *m/z* calculated for $C_6H_3NO_2S$ $[M]^+$ 152.9885; found

152.9881 EA: Anal. Calcd for $C_6H_3NO_2S$ (%): C, 47.05; H, 1.97; N, 9.15; S, 20.93. Found (%): C, 47.08; H, 2.15; N, 9.23; S, 20.69.



1,3-Dibromothieno[3,4-c]pyrrole-4,6-dione (2):

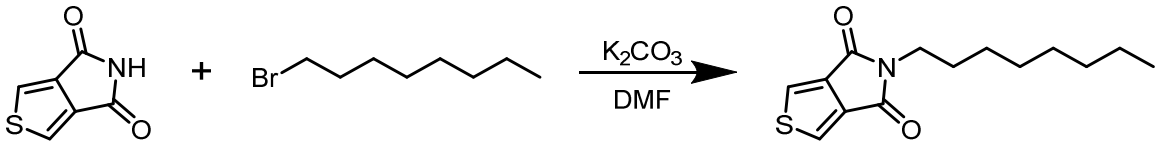
Compound **2** has been previously synthesized by a different route.[5] An alternate procedure from **1** is given here. **1** (710 mg, 4.6 mmol) was added to conc. H_2SO_4 (11 mL, 0.4M) at 0 °C. NBS (3.3 g, 18.5 mmol, 4.0 eq.) was added in one portion. The reaction was stirred for 30 min at 0 °C, then 3 hours at r.t. Reaction was poured onto a large excess of ice-water. The precipitated solid was collected on a nylon filter, washed with a large excess of DI water, then 1:1 water:methanol. The material can be used without further purification, or recrystallized from acetonitrile. Typical yields obtained were between 70-80%

^{1}H NMR (300 MHz, DMSO-d6): δ 11.57 (bs, 1H). ^{13}C NMR (75 MHz, DMSO-d6) δ 161.01, 135.96, 112.53.

HRMS (EI) *m/z* calculated for $C_6HBr_2NO_2S$ $[M]^+$ 308.8095; found 308.8098 EA: Anal. Calcd for $C_6HBr_2NO_2S$ (%): C, 23.18; H, 0.32; N, 4.50; S, 10.31; Br, 51.39. Found (%): C, 23.43; H, 0.52; N,4.54; S, 10.23; Br, 51.25.

General procedure for reaction of a thiophene imide with an electrophile:

To a reaction vessel charged with a thiophene imide (**1 or 2**) (1.0 eq.) and K_2CO_3 (2.0 eq) was added dry dimethylformamide to make a 0.1M solution of the imide. The electrophile (1.5 eq.) was introduced in one portion. The reaction was stirred at room temperature overnight, or until starting material is not present by TLC (10% EtOAc:DCM). The reaction was gravity filtered through a conical paper funnel (25 µm particle retention) with the aid of DCM or $CHCl_3$ and concentrated. The resulting material was dissolved in suitable solvent (often DCM), filtered to remove insoluble material, and concentrated. Further purification is described separately.

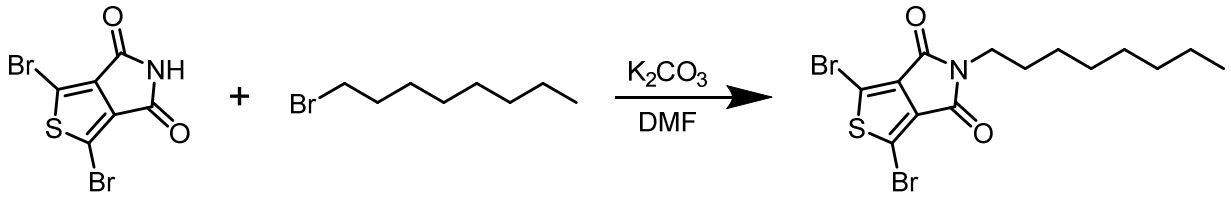


5-Octylthieno[3,4-c]pyrrole-4,6-dione (3a):

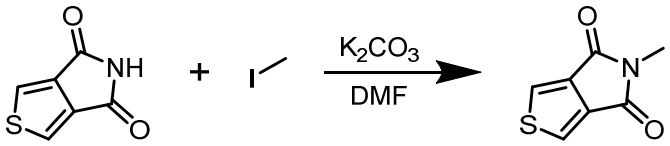
Compound **3a** has been previously synthesized by a different route.[6] 1 mmol scale with 1-bromooctane as the electrophile. Crude material was subjected to column chromatography (silica gel, 1:1 DCM:Hexanes) to give 252 mg (95%) of a white, crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (s, 2H), 3.60 (t, *J*=7.2 Hz, 2H), 1.63 (p, 2H), 1.39 – 1.15 (m, 10H), 0.92 – 0.80 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.81, 136.80, 125.60, 38.63, 31.91, 29.30 (2C), 28.61, 27.01, 22.76, 14.23. HRMS (EI) *m/z* calculated for $C_{14}H_{19}NO_2S$ $[M]^+$ 265.1137; found 265.1132. EA: Anal. Calcd for $C_{14}H_{19}NO_2S$ (%): C, 63.37; H, 7.22; N, 5.28; S,

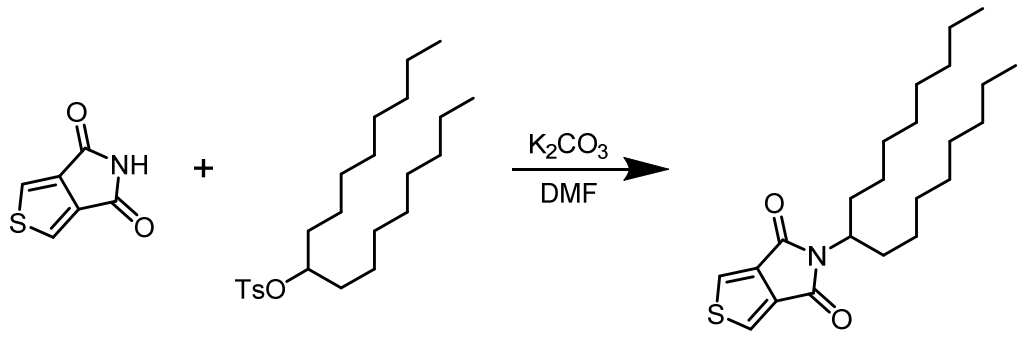
12.08. Found (%): C, 63.41; H, 7.05; N, 5.19; S, 12.03. Melting Point (°C): 121-122; Lit. 120-121.[6]



1,3-Dibromo-5-octylthieno[3,4-c]pyrrole-4,6-dione (4a):
Compound **4a** has been previously synthesized by a different route.[6] 0.5 mmol scale with 1-bromooctane as the electrophile. Crude red liquid was passed through silica pad with DCM to give beige crystals (202 mg). Further purification (silica gel, 1:1 DCM:Hexanes) yielded 177 mg (84%) of a white, crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, J = 7.2 Hz, 2H), 1.69 – 1.55 (m, 2H), 1.43 – 1.15 (m, 10H), 0.87 (t, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.53, 134.92, 113.06, 38.97, 31.91, 29.25, 28.39, 26.93, 22.76, 14.23. HRMS (EI) *m/z* calculated for $C_{14}H_{17}NO_2SBr_2$ $[M]^+$ 420.9347; found 420.9337. Melting Point (°C): 105-106; Lit. 104-105.[6]

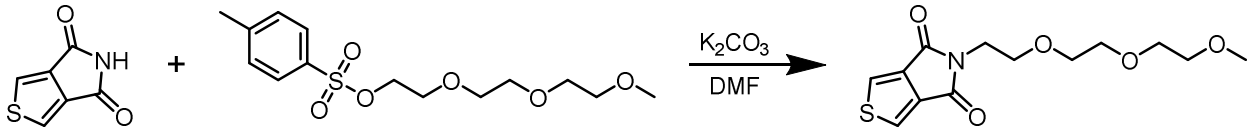


5-methylthieno[3,4-c]pyrrole-4,6-dione (3b):
1.0 mmol scale with methyl iodide as the electrophile. Column chromatography (silica gel, 0-5% Et_2O:$CHCl_3$) gave 92 mg (55%) of a white, crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 2H), 3.07 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.73, 136.58, 125.70, 24.42.
HRMS (ESI) *m/z* calculated for $C_7H_5NO_2S$ $[M + H]^+$ 168.0114; found 168.0113
Melting Point (°C): 149-151.EA: Anal. Calcd for $C_7H_5NO_2S$ (%): C, 50.29; H, 3.01; N, 8.38; S, 19.18. Found (%): C, 50.29; H, 3.06; N, 8.33; S, 19.02.

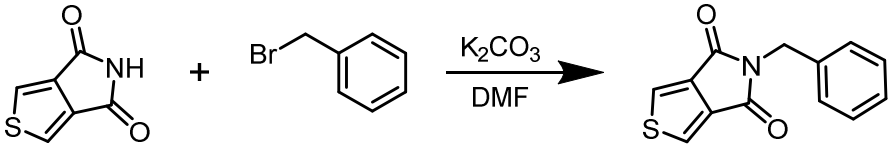


5-(heptadecan-9-yl)thieno[3,4-c]pyrrole-4,6-dione (3c):
Compound **3c** has been previously synthesized by a different route.[7] 1.0 mmol scale with 9-heptadecanyltosylate as the electrophile. Column chromatography (silica gel, 0-20%

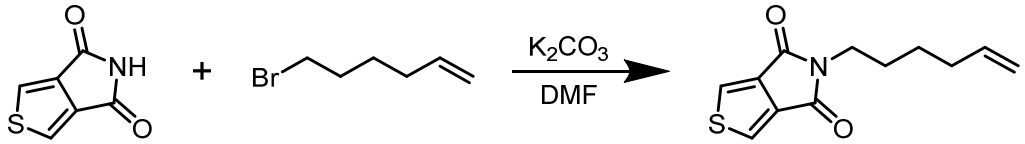
EtOAc:DCM) failed to separate tosylate starting material from product. To ease purification, the crude product was stirred with 1.0 eq LiBr in DMF (0.2M) to convert excess tosylate to bromide. Conversion was monitored by TLC and confirmed by NMR. Column chromatography (silica gel, 10% EtOAc:90% DCM) gave 236 mg (60%) of a waxy solid.
1H NMR (300 MHz, $CDCl_3$) δ 7.77 (s, 2H), 4.10 (hept, J = 5.3 Hz, 1H), 2.14 – 1.92 (m, 2H), 1.74 – 1.54 (m, 2H), 1.38 – 1.10 (m, 24H), 0.85 (t, J = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.19, 136.59, 125.40, 52.86, 32.40, 31.96, 29.59, 29.43, 29.36, 26.80, 22.78, 14.24. HRMS (EI) *m/z* calculated for $C_{23}H_{37}NO_2S$ $[M]^+$ 391.2545; found 391.2538. Melting Point (°C): 46-47 (Lit. 40-42)[7].



5-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-thieno[3,4-c]pyrrole-4,6-dione (3d):
1.0 mmol scale using 2-(2-(2-methoxyethoxy)ethoxy)ethyltosylate as the electrophile. Column chromatography (silica gel, 0-10% EtOAc:DCM) gave a colorless oil (90 mg, 30%). Purification may have been simplified by using LiBr, see **3c**. ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 2H), 3.82 – 3.75 (m, 2H), 3.70 – 3.63 (m, 2H), 3.63 – 3.41 (m, 8H), 3.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.47, 136.54, 125.73, 71.89, 70.58, 70.56, 70.08, 67.81, 59.03, 37.63. HRMS (EI) *m/z* calculated for $C_{13}H_{17}NO_5S$ $[M]^+$ 299.0827; found 299.0830. EA: Anal. Calcd for $C_{13}H_{17}NO_5S$ (%): C, 52.16; H, 5.72; N, 4.68; S, 10.71. Found (%): C, 52.02; H, 5.71; N, 4.57; S, 10.60.

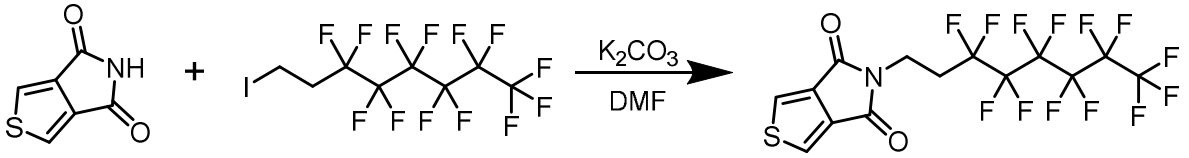


5-benzylthieno[3,4-c]pyrrole-4,6-dione (3e):
1.0 mmol scale with benzylbromide as the electrophile. Column chromatography (silica gel, 100% DCM) gave 210 mg (86%) of a white, crystalline solid. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.85 (s, 2H), 7.41 – 7.25 (m, 5H), 4.76 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.74, 137.18, 137.04, 129.10, 128.77, 128.20, 126.43, 42.36. HRMS (EI *m/z* calculated for $C_{13}H_9NO_2S$ $[M]^+$ 243.0354; found 243.0349. EA: Anal. Calcd for $C_{13}H_9NO_2S$ (%): C, 64.18; H, 3.73; N, 5.76; S, 13.18. Found (%): C, 63.97; H, 3.82; N, 5.79; S, 13.31. Melting Point (°C): 152-153.



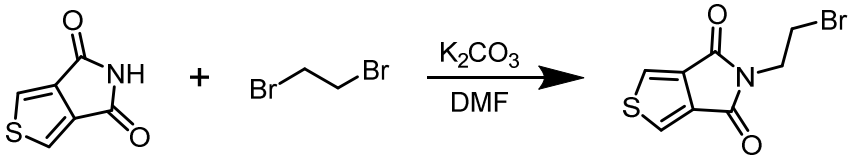
5-(hex-5-en-1-yl)thieno[3,4-c]pyrrole-4,6-dione (3f):

1.0 mmol scale with 6-bromohex-1-ene as the electrophile. Column chromatography (silica gel, 100% DCM) gave 222 mg (94%) of a white, crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 2H), 5.78 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.18 – 4.80 (m, 2H), 3.62 (t, J = 7.3 Hz, 2H), 2.09 (qt, J = 7.3, 1.3 Hz, 2H), 1.79 – 1.53 (m, 3H), 1.54 – 1.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.76, 138.40, 136.77, 125.64, 114.99, 38.41, 33.39, 28.04, 26.22. HRMS (EI) *m/z* calculated for $C_{12}H_{13}NO_2S$ $[M]^+$ 235.0667; Found 235.0665. EA: Anal. Calcd for $C_{12}H_{13}NO_2S$ (%): C, 61.25; H, 5.61; N, 5.95; S, 13.63. Found (%): C, 61.46; H, 5.61; N, 5.97; S, 13.78. Melting Point (°C): 98-99.



5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thieno[3,4-c]pyrrole-4,6-dione (3g):

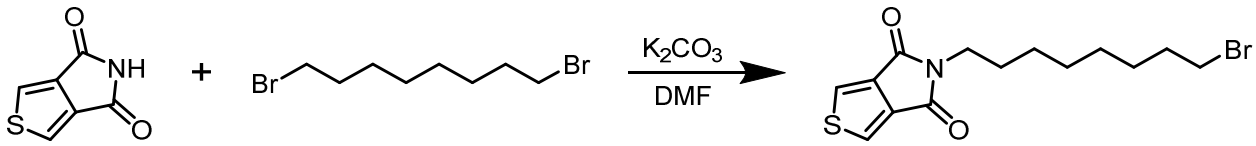
1 mmol scale. Column chromatography (silica gel, 100% DCM) gave 207 mg (42%) of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 2H), 3.97 (t, *J* = 7.3 Hz, 2H), 2.62 – 2.38 (m, 2H). 13C NMR (176 MHz, $CDCl_3$) δ 162.01, 136.25, 126.50, 30.70, 30.67, 30.64, 29.85, 29.58, 29.46, 29.33.. Note: Fluorine splits 13C signals. Additional peaks are shown in the NMR inset, but could not be assigned with certainty. HRMS (EI) *m/z* calculated for $C_{14}H_6F_{13}NO_2S$ $[M]^+$ 498.9912; Found 498.9911. EA: Anal. Calcd for $C_{14}H_6F_{13}NO_2S$ (%): C, 33.68; H, 1.21; F, 49.47; N, 2.81; S, 6.42. Found (%): C, 36.29; H, 1.60; F, 46.03; N, 2.97; S, 6.21. Melting Point (°C): 96-98.



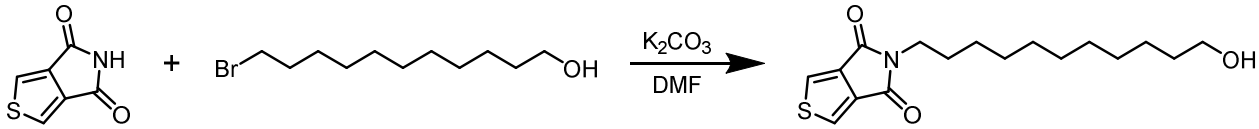
5-(2-bromoethyl)-thieno[3,4-c]pyrrole-4,6-dione (3h):

1.0 mmol scale. A substoichiometric amount of dibromoethane (94 mg, 0.5 mmol, 0.5 eq.) was used to encourage dimer formation. Dimer formation was not observed by TLC or NMR. Column chromatography (silica gel, 100% DCM) gave 190 mg (73%, calculated with imide as limiting reagent and represents a low estimate) of a white, crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 2H), 4.04 (t, J = 6.7 Hz, 2H), 3.58 (t, J = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.13, 136.25, 126.43, 39.79, 28.11. HRMS (EI) *m/z* calculated for $C_8H_6BrNO_2S$

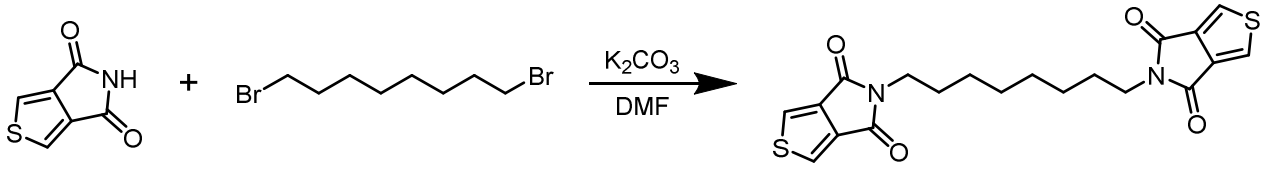
$[M]^+$ 258.9303; found 258.9294. EA: Anal. Calcd for $C_8H_6BrNO_2S$ (%): C, 36.94; H, 2.33; N, 5.39; S, 12.33. Found (%): C, 36.95; H, 2.33; N, 5.26; S, 12.34. Melting Point (°C): 142-143.



5-(8-bromooctyl)-thieno[3,4-c]pyrrole-4,6-dione (3i):
2 mmol scale. 1.0 eq. of 1,8-dibromooctane was used to allow for formation of dimer. Column chromatography (silica gel, 100% DCM, Rf=0.33) gave 396 mg (58%, overall conversion with **3k** was 92%) of a white, crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 2H), 3.60 (t, J = 7.4 Hz, 2H), 3.39 (t, J = 6.8 Hz, 2H), 1.83 (p, J = 7.1 Hz, 2H), 1.71 – 1.55 (m, 2H), 1.48 – 1.36 (m, 2H), 1.36 – 1.23 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.78, 136.75, 125.64, 38.51, 34.12, 32.85, 29.07, 28.71, 28.52, 28.17, 26.83. HRMS (EI) *m/z* calculated for $C_{14}H_{18}BrNO_2S$ $[M]^+$ 343.0242; found 343.0236. EA: Anal. Calcd for $C_{14}H_{18}BrNO_2S$ (%): C, 48.84; H, 5.27; N, 4.07; S, 9.31. Found (%): C, 49.01; H, 5.24; N, 4.04; S, 9.42. Melting Point (°C): 77-78.

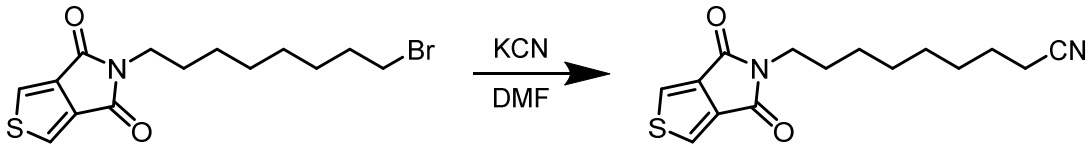


5-(11-hydroxyundecyl)thieno[3,4-c]pyrrole-4,6-dione (3j):
0.36 mmol scale. Column chromatography (silica gel, 10% MeOH:$CHCl_3$) gave 90 mg (78%) of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 2H), 3.67 – 3.52 (overlapping triplets, 4H), 1.70 – 1.47 (m, 4H), 1.40 – 1.15 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.81, 136.71, 125.65, 63.12, 38.58, 32.90, 29.61, 29.52 (2C), 29.46, 29.24, 28.54, 26.92, 25.82. HRMS (ESI) *m/z* calculated for $C_{17}H_{26}NO_3S^+$ Calc. $[M + H]^+$ 324.1628; found 324.1628. EA: Anal. Calcd for $C_{17}H_{25}NO_3S$ (%): C, 63.13; H, 7.79; N, 4.33; S, 9.91. Found (%): C, 63.24; H, 7.86; N, 4.20; S, 9.82. Melting Point (°C): 116-117



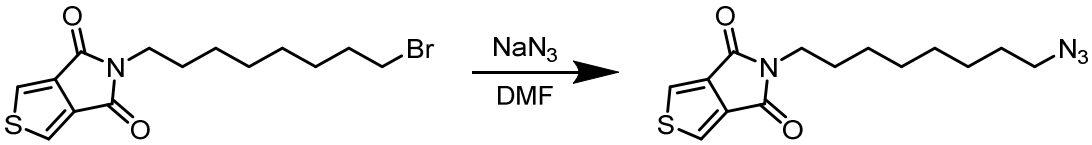
5,5'-(octane-1,8-diyl)bisthieno[3,4-c]pyrrole-4,6-dione (3k):
2 mmol scale. 1.0 eq. of 1,8-dibromooctane was used to allow for formation of dimer. Column chromatography (silica gel, 100% DCM to elute **3k** then 10% Et_2O:DCM) gave 143 mg (34%, overall conversion with **3k** was 92%) of a white, crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 4H), 3.60 (t, *J* = 7.3 Hz, 4H), 1.62 (p, *J* = 6.9 Hz, 4H), 1.37 – 1.22 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.81, 136.79, 125.62, 38.56, 29.20, 28.57, 26.92. HRMS (EI) *m/z* calculated for $C_{20}H_{20}N_2O_4S_2$ $[M]^+$ 416.0865; found 416.0866. EA: Anal. Calcd for

$C_{20}H_{20}N_2O_4S_2$ (%): C, 57.67; H, 4.84; N, 6.73; S, 15.39. Found (%): C, 57.42; H, 4.74; N, 6.57; S, 15.12. Melting Point (°C): 206-207



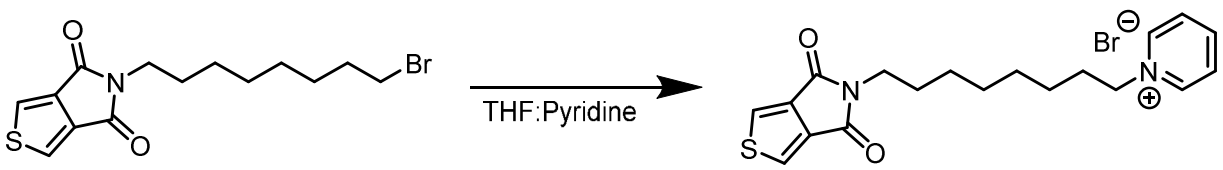
5-(9-nitrilononanyl)thieno[3,4-c]pyrrole-4,6-dione (3l):

3i (100 mg, 0.29 mmol, 1.0 eq) and potassium cyanide (28 mg, 0.44 mmol, 1.5 eq) were dissolved in 5 ml DMF. The mixture was heated at 50 °C for 4 hours at which point TLC indicated no starting material remained. The reaction was cooled, poured into 50 mL H_2O, extracted with DCM (3x). The combined organics were washed with H_2O, dried over $MgSO_4$, and concentrated. Residual DMF was removed on high vacuum overnight. Column chromatography (silica gel, 100% DCM, Rf=0.2) gave 74 mg (88 %) of a white, waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 2H), 3.57 (t, J = 7.3 Hz, 2H), 2.30 (t, J = 7.1 Hz, 2H), 1.70 – 1.54 (m, 4H), 1.47 – 1.35 (m, 2H), 1.35 – 1.24 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.69, 136.62, 125.64, 119.89, 77.16, 38.35, 28.84, 28.64, 28.59, 28.39, 26.70, 25.34, 17.13. HRMS (EI) *m/z* calculated for $C_{15}H_{18}N_2O_2S$ $[M]^+$ 290.1089; found 290.1094. EA: Anal. Calcd for $C_{15}H_{18}N_2O_2S$ (%): C, 62.04; H, 6.25; N, 9.65; S, 11.04. Found (%): C, 62.20; H, 6.22; N, 9.51; S, 10.95. Melting Point (°C): 51-52.



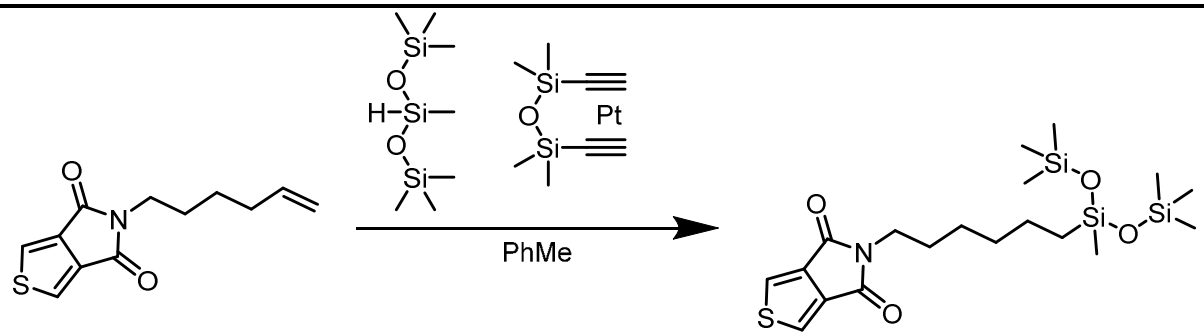
5-(8-azidooctyl)thieno[3,4-c]pyrrole-4,6-dione (3m):

3i (100 mg, 0.29 mmol, 1.0 eq) and sodium azide (28 mg, 0.44 mmol, 1.5 eq) were dissolved in 5 ml DMF. The mixture was heated at 50 °C for 4 hours at which point TLC indicated no starting material remained. The reaction was cooled, poured into 50 mL H_2O, extracted with DCM (3x). The combined organics were washed with H_2O, dried over $MgSO_4$, and concentrated. Residual DMF was removed on high vacuum overnight. Column chromatography (silica gel, 100% DCM, Rf=0.24) gave 78 mg (88%) of a white, waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 2H), 3.60 (t, J = 7.3 Hz, 2H), 3.23 (t, J = 6.9 Hz, 2H), 1.73 – 1.49 (m, 4H), 1.43 – 1.20 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.77, 136.74, 125.63, 51.54, 38.50, 29.10, 29.09, 28.89, 28.51, 26.82, 26.72. HRMS (EI) *m/z* calculated for $C_{14}H_{18}N_4O_2S$ $[M]^+$ 306.1150; found 306.1156. EA: Anal. Calcd for $C_{14}H_{18}N_4O_2S$ (%): C, 54.88; H, 5.92; N, 18.29; S, 10.46. Found (%): C, 55.14; H, 5.83; N, 18.18; S, 10.37. Melting Point (°C): 44-45.



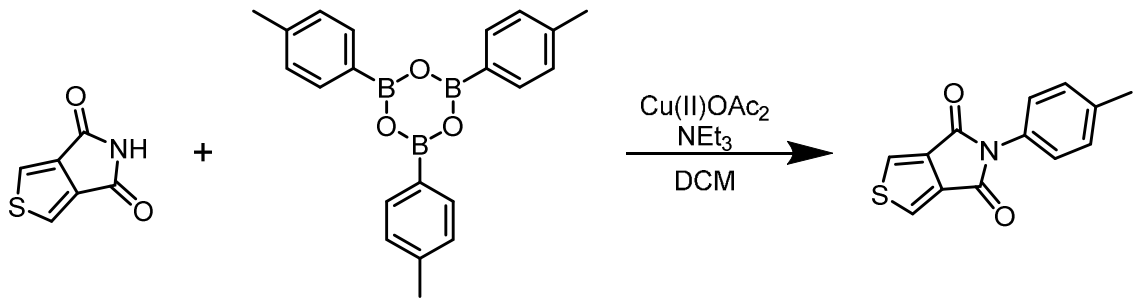
1-(8-(4,6-dioxothieno[3,4-c]pyrrol-5-yl)octyl)pyridinium bromide (3n):

3i (85 mg, 0.25 mmol, 1.0 eq) was dissolved in 1:1 THF:pyridine (6 mL). The mixture was heated at 65 °C for 3 hours at which point TLC indicated no starting material remained (100% DCM). The reaction was cooled and concentrated to a beige solid. The crude product was dissolved in H_2O and washed with $CHCl_3$ (3x). The combined organics were back extracted with H_2O. The organics were dried over MgSO4 and concentrated to give ~8 mg (0.03 mmol) of starting material indicating ~90% conversion. The combined aqueous washes were concentrated to 90 mg (86%) of a pale beige solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.51 (d, J = 5.7 Hz, 2H), 8.55 (t, J = 7.8 Hz, 1H), 8.14 (t, J = 7.0 Hz, 2H), 7.86 (s, 2H), 4.95 (t, J = 7.4 Hz, 2H), 3.52 (t, J = 7.3 Hz, 2H), 2.02 (p, J = 7.2 Hz, 2H), 1.56 (p, J = 7.1 Hz, 2H), 1.45 – 1.16 (m, 8H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.98, 145.76, 145.51, 136.93, 128.85, 126.20, 62.16, 38.52, 32.20, 29.17, 29.10, 28.64, 26.96, 26.20. HRMS (ESI) *m/z* calculated for $C_{19}H_{23}N_2O_2S^+$ Calc. $[M - - Br]^+$ 343.1475; found 343.1475. EA: Anal. Calcd for $C_{19}H_{23}BrN_2O_2S$ (%): C, 53.90; H, 5.48; N, 6.62; S, 7.57. Found (%): C, 53.63; H, 5.55; N, 6.51; S, 7.68. Melting Point (°C): 188-189.



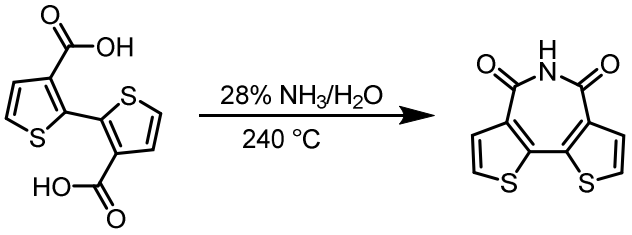
5-(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)thieno[3,4-c]pyrrole-4,6-dione (3o):

3f (71 mg, 0.30 mmol, 1.0 eq) was dissolved in dry toluene (3 mL). 1,1,1,3,5,5,5-Heptamethyltrisiloxane (0.2 mL, 2.3 eq) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's Catalyst, 2 wt% in xylenes, 0.17 mL, 5 mol% Pt) were added by syringe through a septum. The reaction was heated at 65 °C for 6 hours. TLC indicated starting material after 2 hours and no starting material after 6 hours. Reaction was concentrated to a brown oil and directly chromatographed (silica gel, 100% DCM, Rf=0.44) to give a light brown, waxy solid. 123 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 2H), 3.61 (t, 2H), 1.69 – 1.59 (m, 2H), 1.39 – 1.22 (m, 6H), 0.48 – 0.38 (m, 2H), 0.07 (s, 18H), -0.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.81, 136.83, 125.58, 38.68, 32.97, 28.62, 26.78, 23.14, 17.71, 2.02, -0.16. HRMS (EI) *m/z* calculated for $C_{19}H_{35}NO_4SSi$ $[M]^+$ 457.1595; found 457.1596. EA: Anal. Calcd for $C_{19}H_{35}NO_4SSi_3$ (%): C, 49.85; H, 7.71; N, 3.06; S, 7.00. Found (%): C, 49.66; H, 7.91; N, 2.86; S, 6.71.



5-(*p*-tolyl)thieno[3,4-c]pyrrole-4,6-dione (3p):

A reaction vessel was charged with **1** (115 mg, 0.75 mmol, 1.0 eq), triethylamine (0.23 mL, 1.5 mmol, 2.0 eq), anhydrous copper(II) acetate (137 mg, 0.75 mmol, 1.0 eq), 2,4,6-tri-*p*-tolylboroxine (178 mg, 0.5 mmol, 2.0 eq of boronic acid), and dry dichloromethane (10 mL). The reaction was stirred at r.t. and monitored by TLC (product has Rf 0.4 in 100% DCM, imide visualized in 10% Et_2O:DCM). After 36 hours, the reaction was quenched by pouring into H_2O. The mixture was extracted with DCM (3x). The combined organics were washed with H_2O, then brine, and dried over $MgSO_4$, and concentrated. Column chromatography (silica gel, 100% DCM) gave 156 mg (86%) of a white, crystalline solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.96 (s, *J* = 0.8 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.19 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.84, 138.61, 136.34, 129.92, 129.32, 126.71, 126.62, 21.38. HRMS (EI) *m/z* calculated for $C_{13}H_9NO_2S$ $[M]^+$ 243.0354; found 243.0353. EA: Anal. Calcd for $C_{13}H_9NO_2S$ (%): C, 64.18; H, 3.73; N, 5.76; S, 13.18. Found (%): C, 64.28; H, 3.83; N, 5.61; S, 13.08. Melting Point (°C): 246-248.



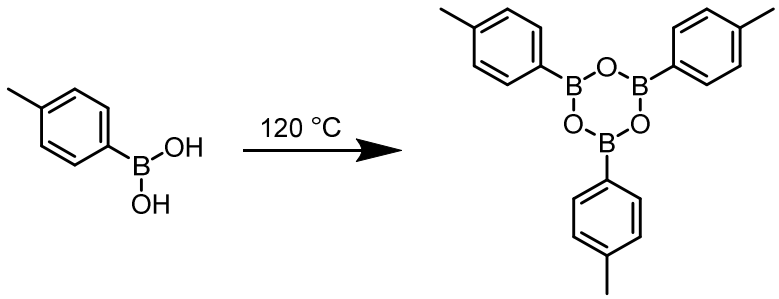
Dithieno[3,2-c:2',3'-e]azepine-4,6-dione (BTI) (5):

Synthesized in a similar fashion as **(1)** with equipment modifications. 2,2'-bithiophene- ,3'-dicarboxylic acid was treated with 28% ammonium hydroxide. After heating to dryness, the solid ammonium salt was placed on a small piece of aluminum foil (10 mm x 10 mm). The aluminum foil boat was slid into a 20 mm diameter glass tube lined with aluminum foil. Heating tape was wrapped around the glass tube to create a temperature gradient at least 200 mm in length. The temperature at the starting material was maintained at 240-260 °C for 8 hours. A continuous flow of argon (15 mL/min) was passed through the tube during the reaction. To prevent anhydride formation, the argon was bubbled through 28% ammonium hydroxide. An exit bubbler of hydrochloric acid was used to scrub the exiting gas. After 8 hours, the aluminum foil lining was removed and pure **(5)** can be directly collected as yellow crystals (62 mg, 52%) which are pure by NMR. Major impurities could include decarboxylated starting material (which can be removed by sublimation at 100 °C, <500 mTorr) and the anhydride (treating the anhydride in ethyl acetate with silica gel destroys the anhydride, **(5)** has an Rf of 0.8 in 100% ethyl acetate).

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.76 (d, J = 5.4 Hz, 2H), 7.29 (d, J = 5.4 Hz, 2H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 159.66, 139.97, 132.39, 131.17, 125.15.

HRMS (EI) *m/z* calculated for $C_{10}H_6NO_2S_2^+$ Calc. $[M + H]^+$ 234.9762, Found 234.9765. Melting Point (°C): 247-250 (melts, sublimes decomposition products).



2,4,6-tri-*p*-tolylboroxine

From a commercial bottle of *p*-tolylboronic acid, the NMR shows both boroxine and boronic acid species. The free acid is only slightly soluble in $CDCl_3$, so a quantitative comparison is not practical. Dehydration was performed in an open Erlenmeyer flask placed a standard laboratory oven (~120 °C) for six hours.[8] The resulting material was fully soluble in $CDCl_3$ and NMR shows no free acid. Product was stored in a desiccator until use to prevent hydrolysis back to the boronic acid.

Boroxine NMR:

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.9 Hz, 6H), 7.32 (d, *J* = 7.6 Hz, 6H), 2.45 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.08, 135.85, 128.92, 22.09.

Boronic Acid NMR:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 3H).

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^{1}H- and ^{13}C-NMR Spectra:

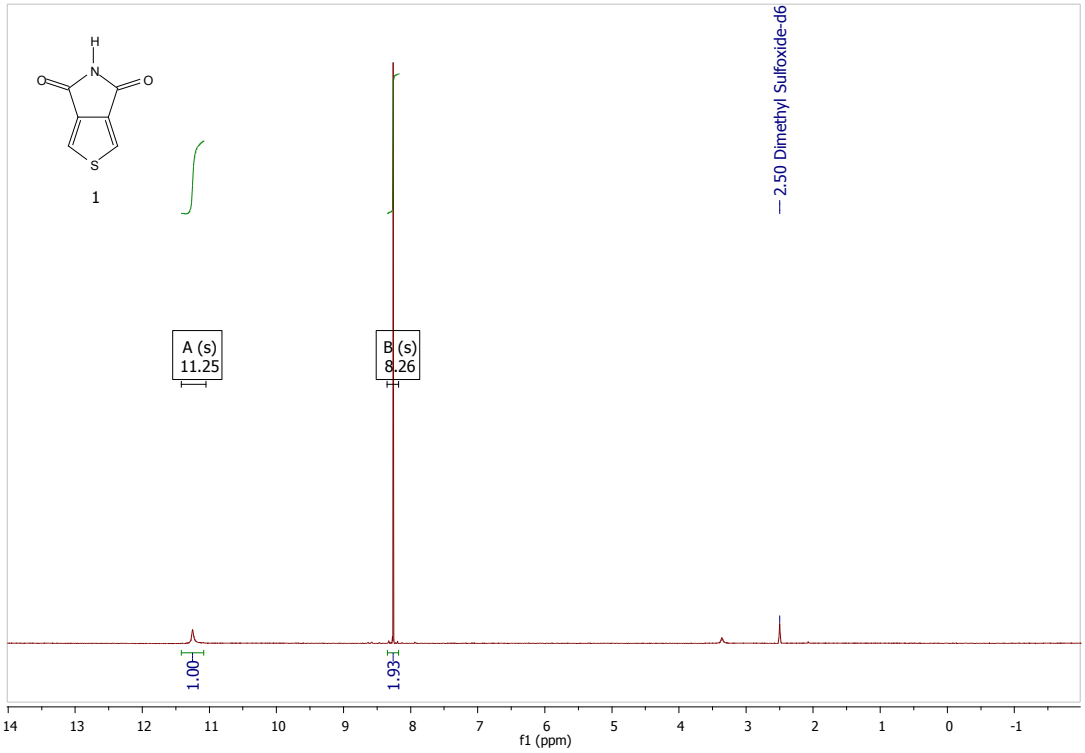

Figure 1. 300 MHz ^{1}H-NMR of Thieno[3,4-c]pyrrole-4,6-dione (1) in DMSO-d6

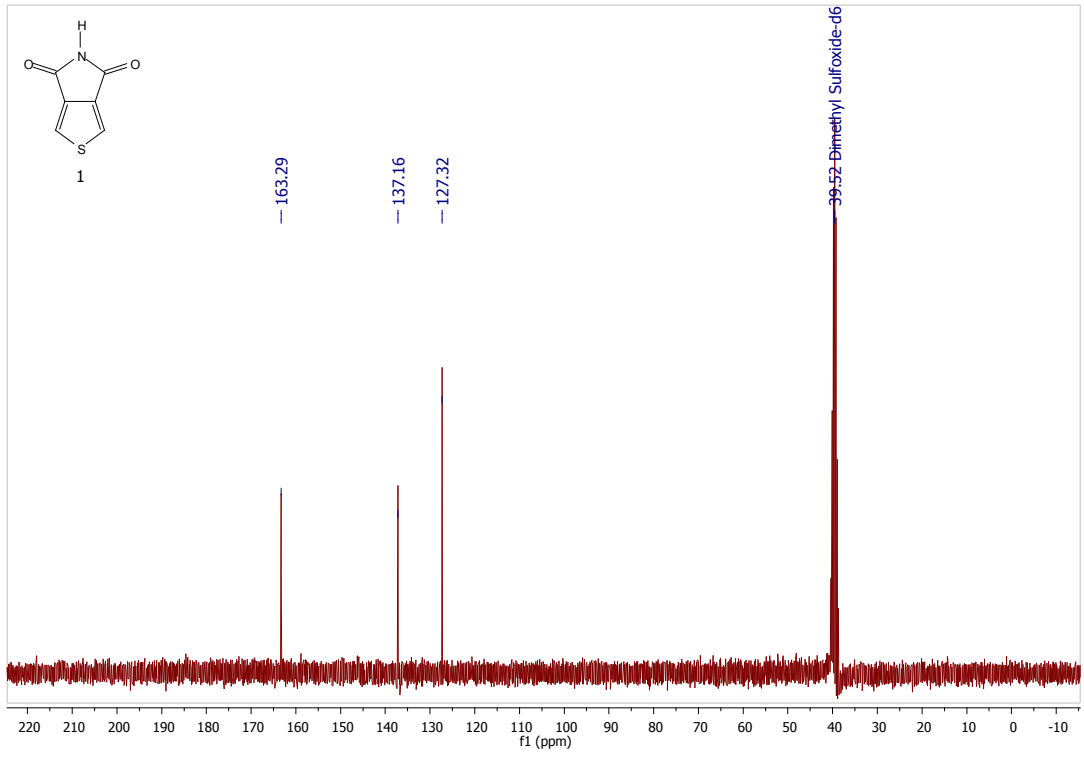

Figure 2. 75 MHz ^{13}C-NMR of Thieno[3,4-c]pyrrole-4,6-dione (1) in DMSO-d6

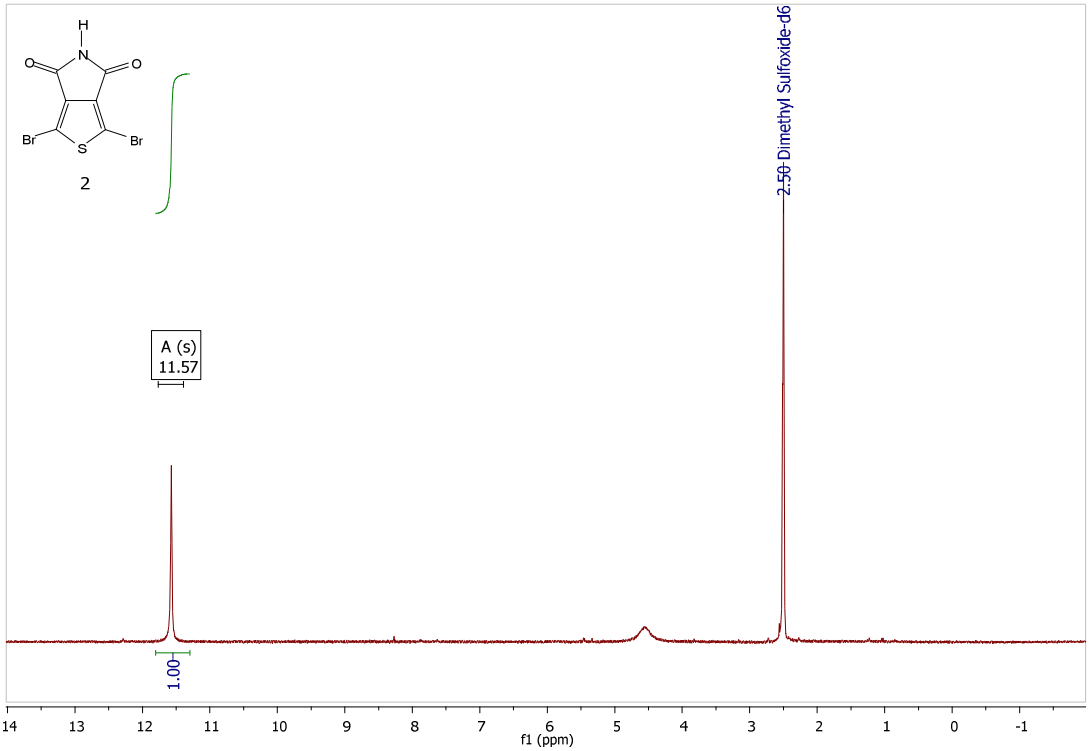

Figure 3. 300 MHz ^{1}H-NMR of 1,3-Dibromothieno[3,4-c]pyrrole-4,6-dione (2) in DMSO-d6

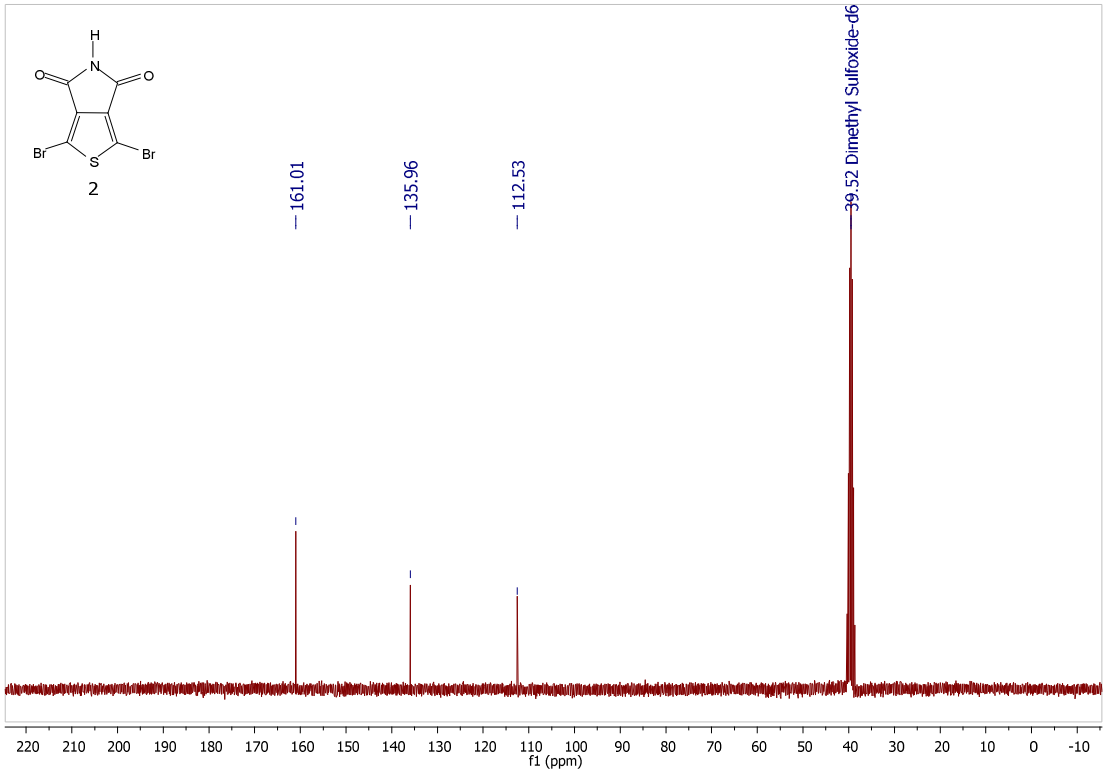

Figure 4. 75 MHz ^{13}C-NMR of 1,3-Dibromothieno[3,4-c]pyrrole-4,6-dione (2) in DMSO-d6

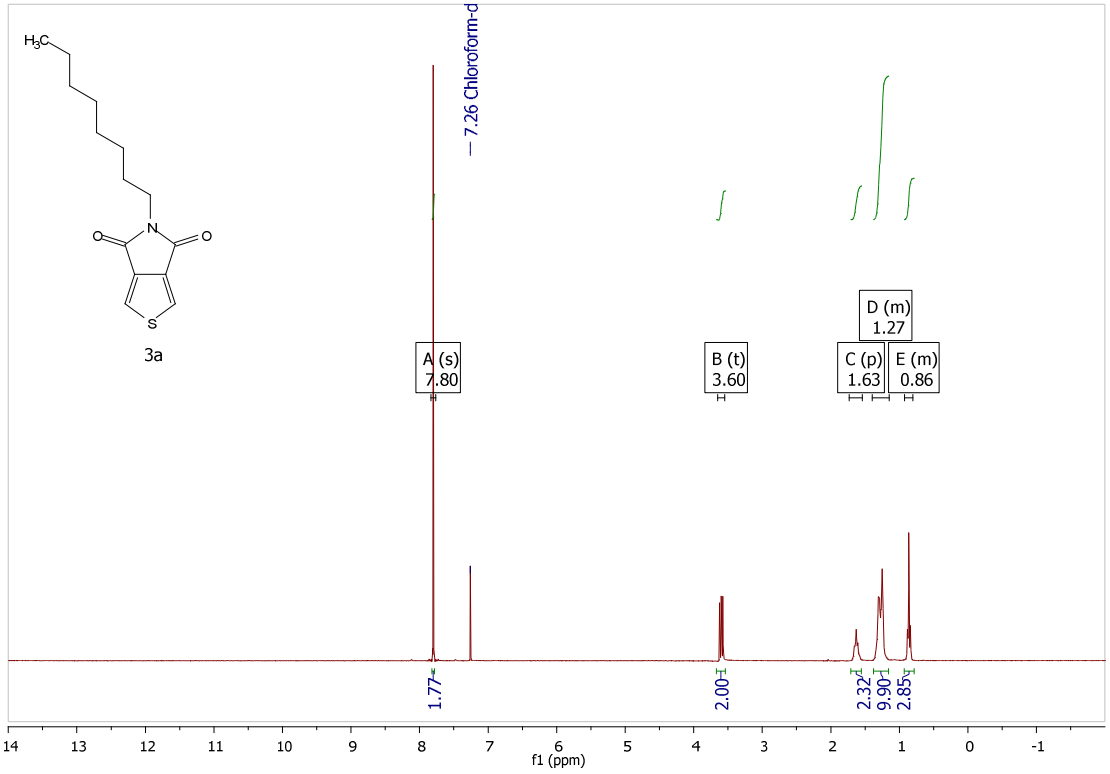

Figure 5. 300 MHz ^{1}H-NMR of 5-Octylthieno[3,4-c]pyrrole-4,6-dione (3a)

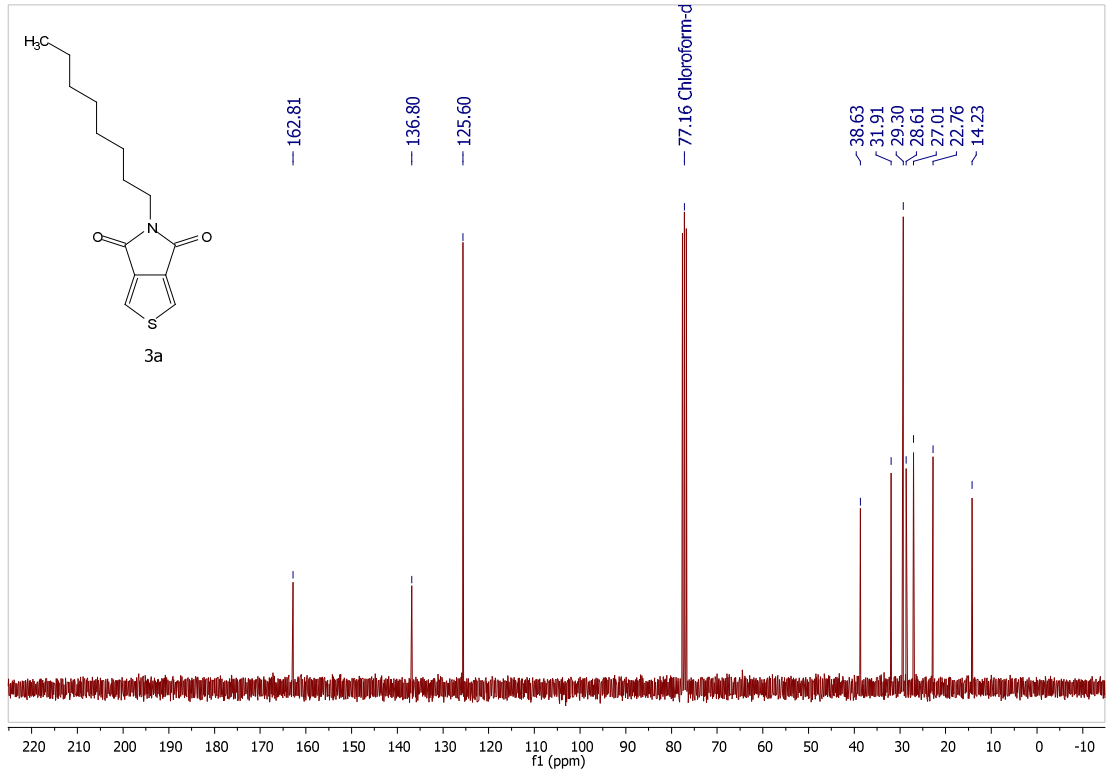

Figure 6. 75 MHz ^{13}C-NMR of 5-Octylthieno[3,4-c]pyrrole-4,6-dione (3a)

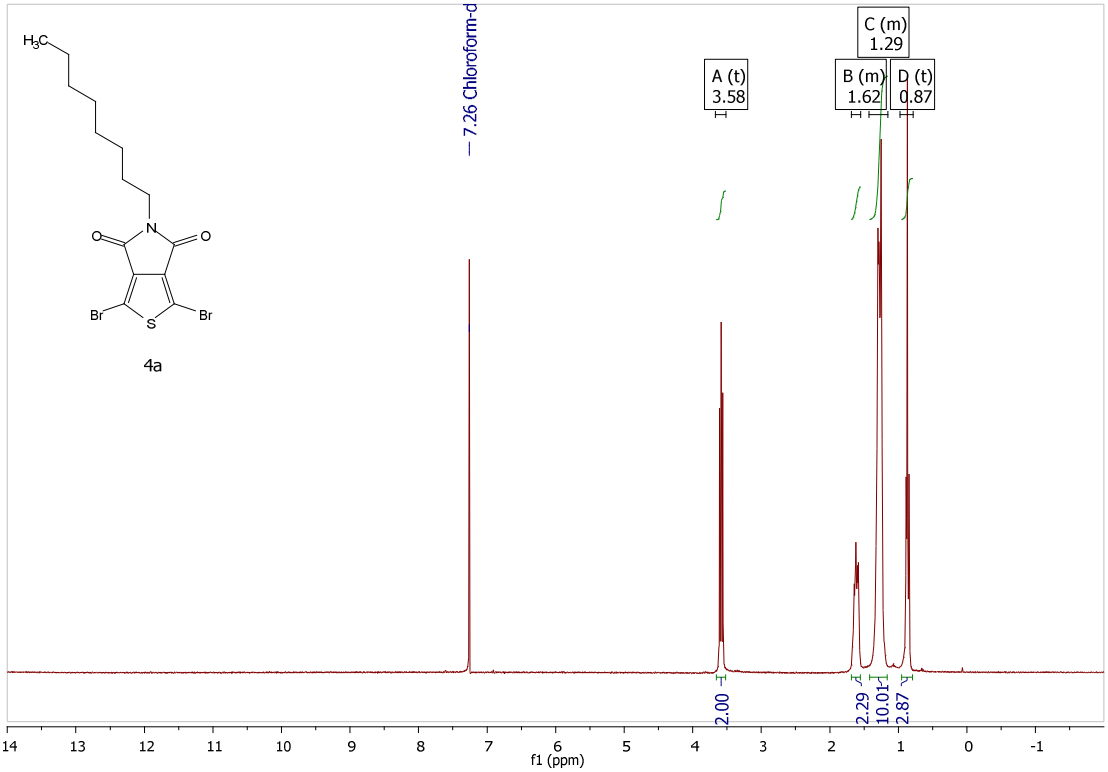

Figure 7. 300 MHz ^{1}H-NMR of 1,3-Dibromo-5-octylthieno[3,4-c]pyrrole-4,6-dione (4a)

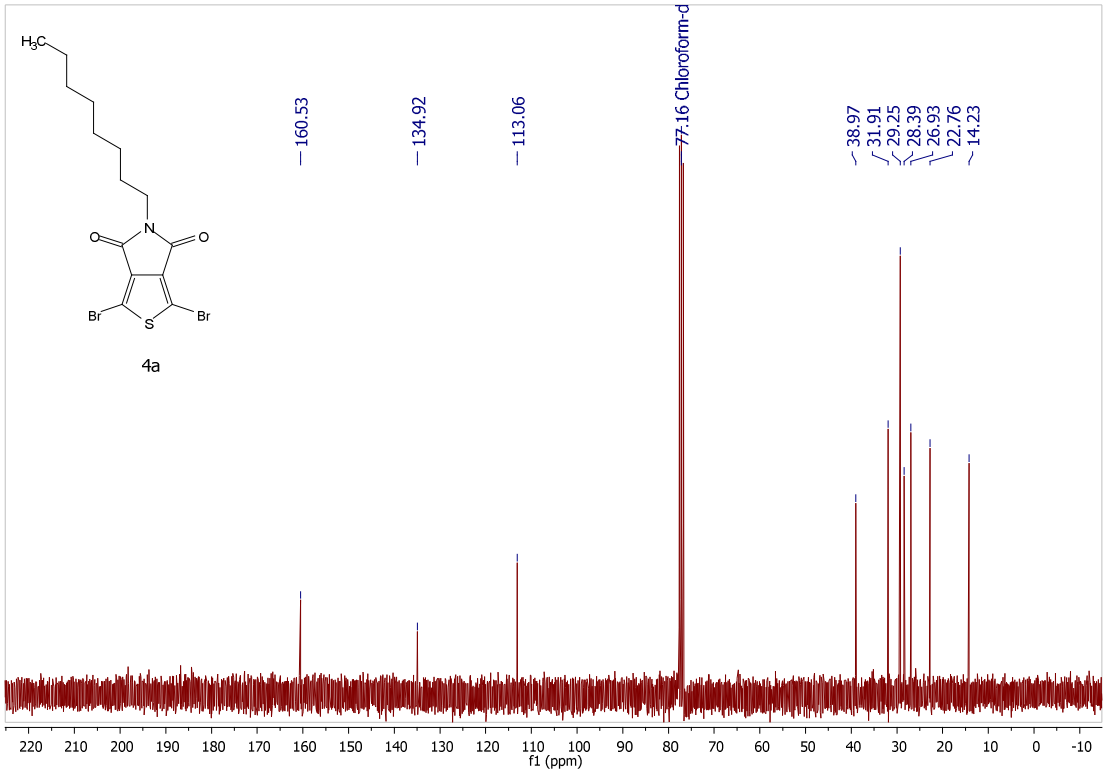

Figure 8. 75 MHz ^{13}C-NMR of 1,3-Dibromo-5-octylthieno[3,4-c]pyrrole-4,6-dione (4a)

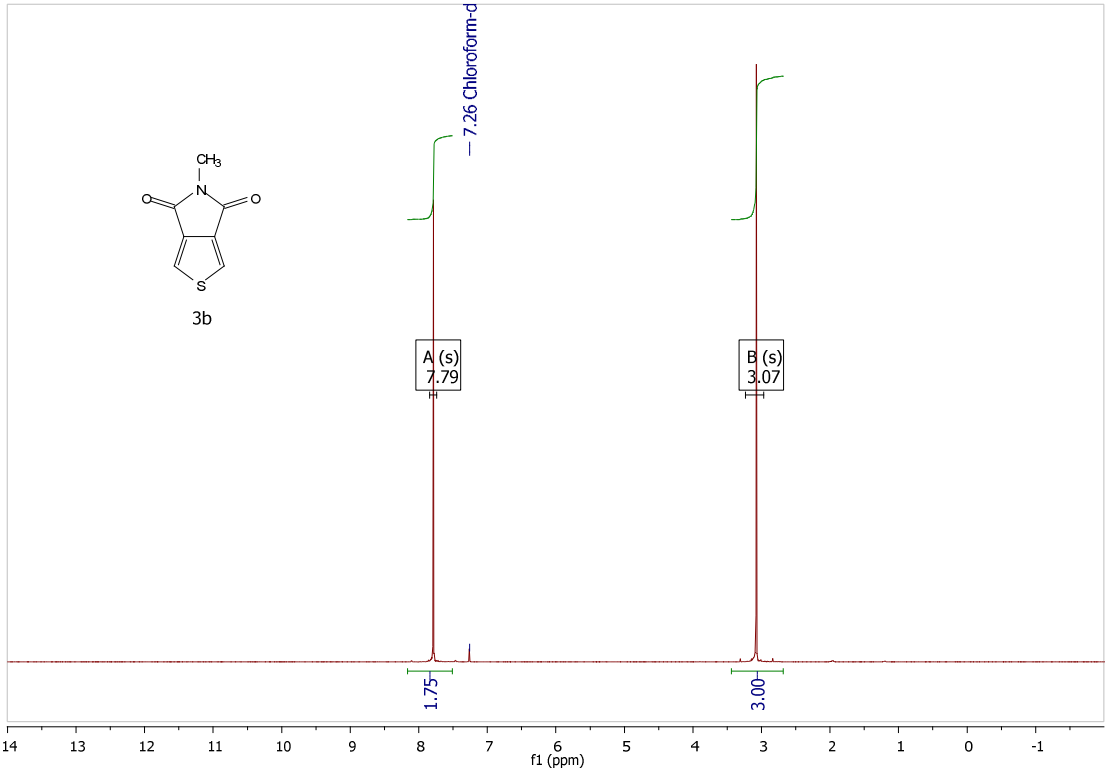

Figure 9. 300 MHz ^{1}H-NMR of 5-methylthieno[3,4-c]pyrrole-4,6-dione (3b)

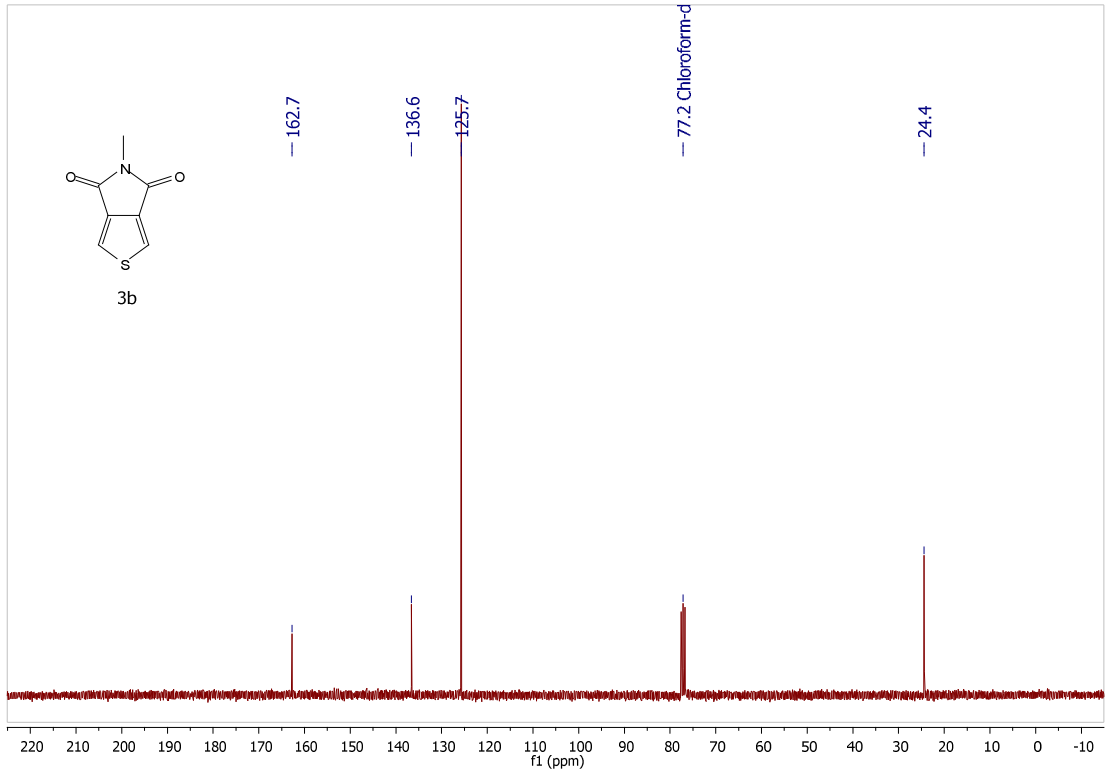

Figure 10. 75 MHz ^{13}C-NMR of 5-methylthieno[3,4-c]pyrrole-4,6-dione (3b)

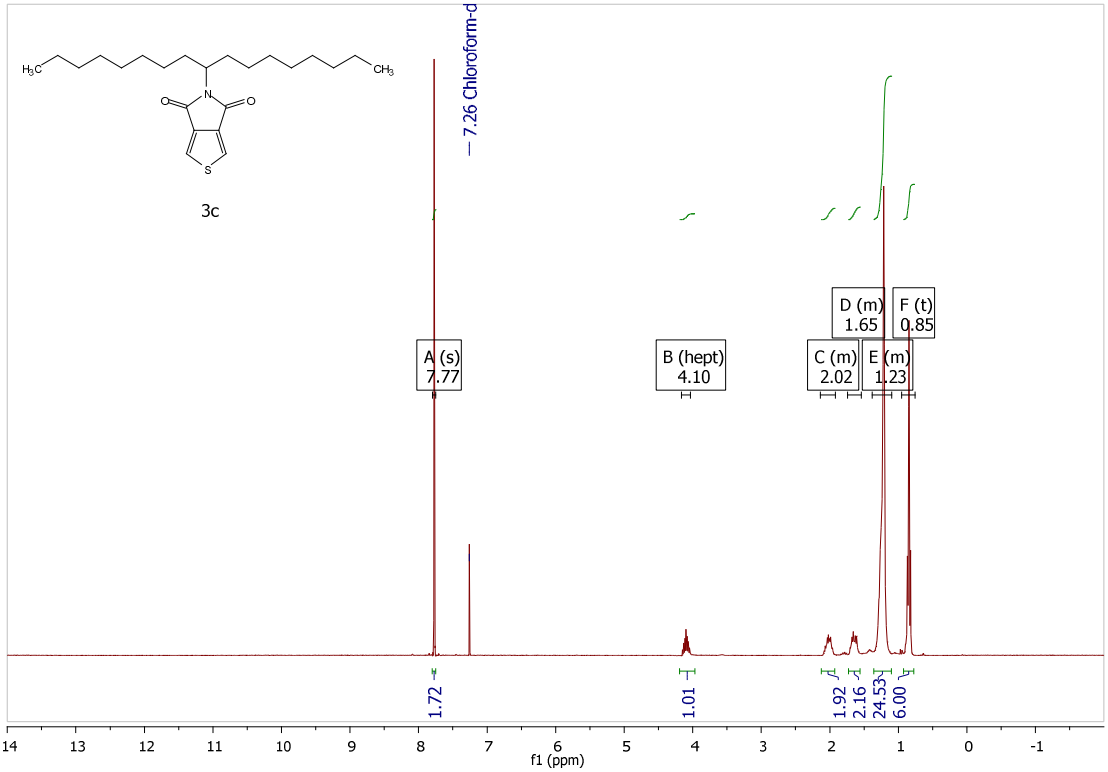

Figure 11. 300 MHz ^{1}H-NMR of 5-(heptadecan-9-yl)thieno[3,4-c]pyrrole-4,6-dione (3c)

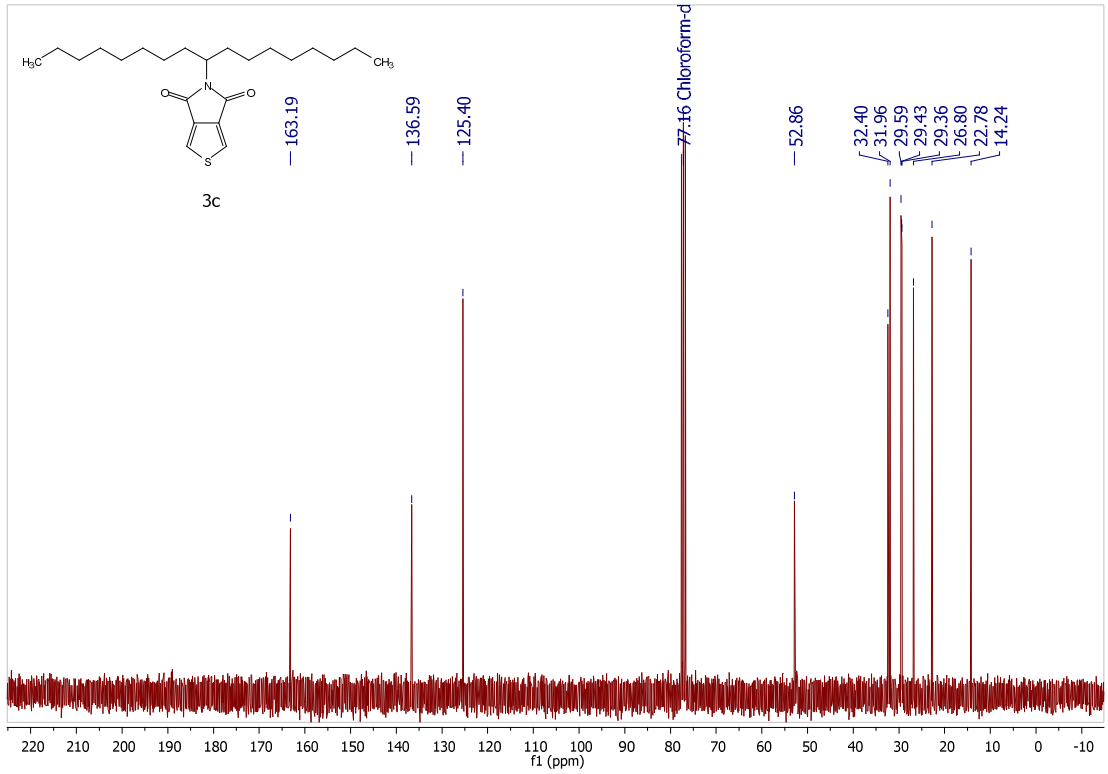

Figure 12. 75 MHz ^{13}C-NMR of 5-(heptadecan-9-yl)thieno[3,4-c]pyrrole-4,6-dione (3c)

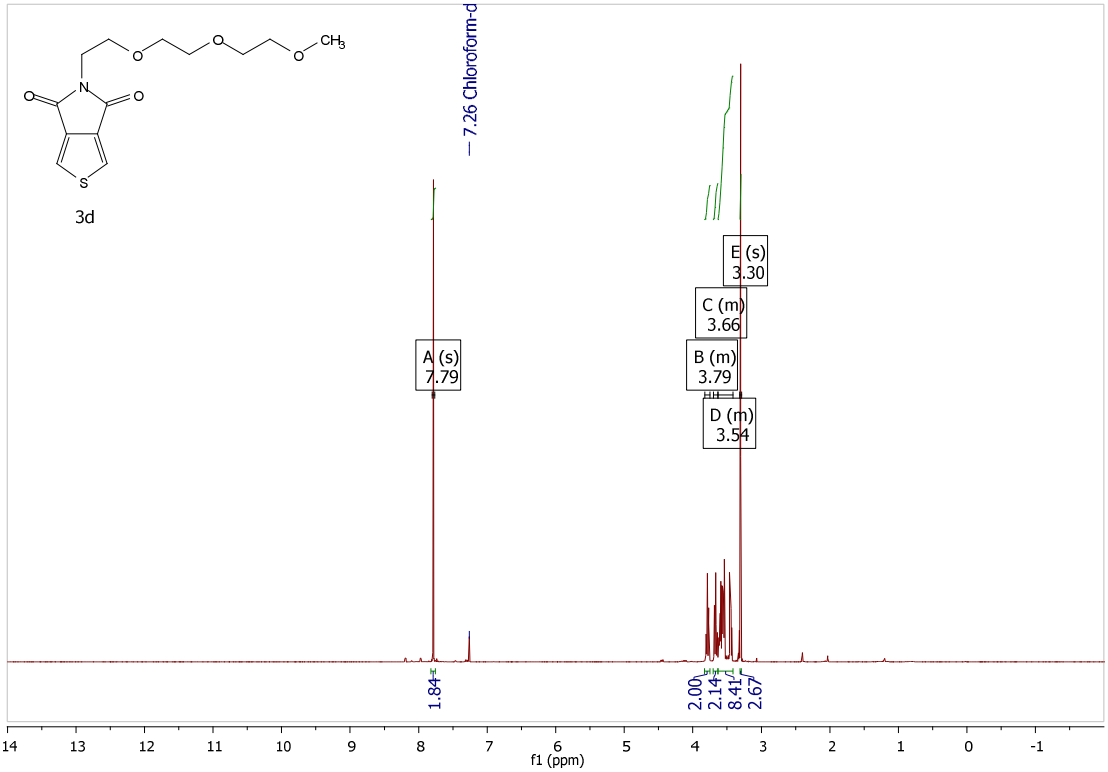

Figure 13. 300 MHz ^{1}H-NMR of 5-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-thieno[3,4-c]pyrrole-4,6-dione (3d)

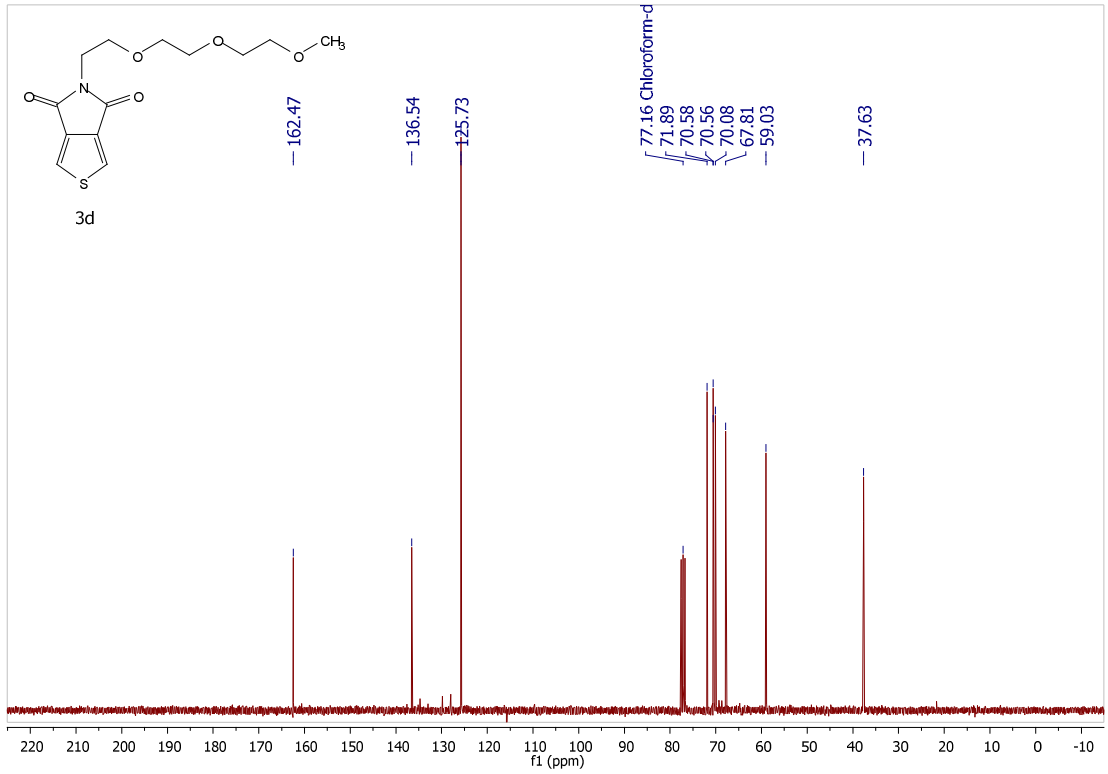

Figure 14. 75 MHz ^{13}C-NMR of 5-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-thieno[3,4-c]pyrrole-4,6-dione (3d)

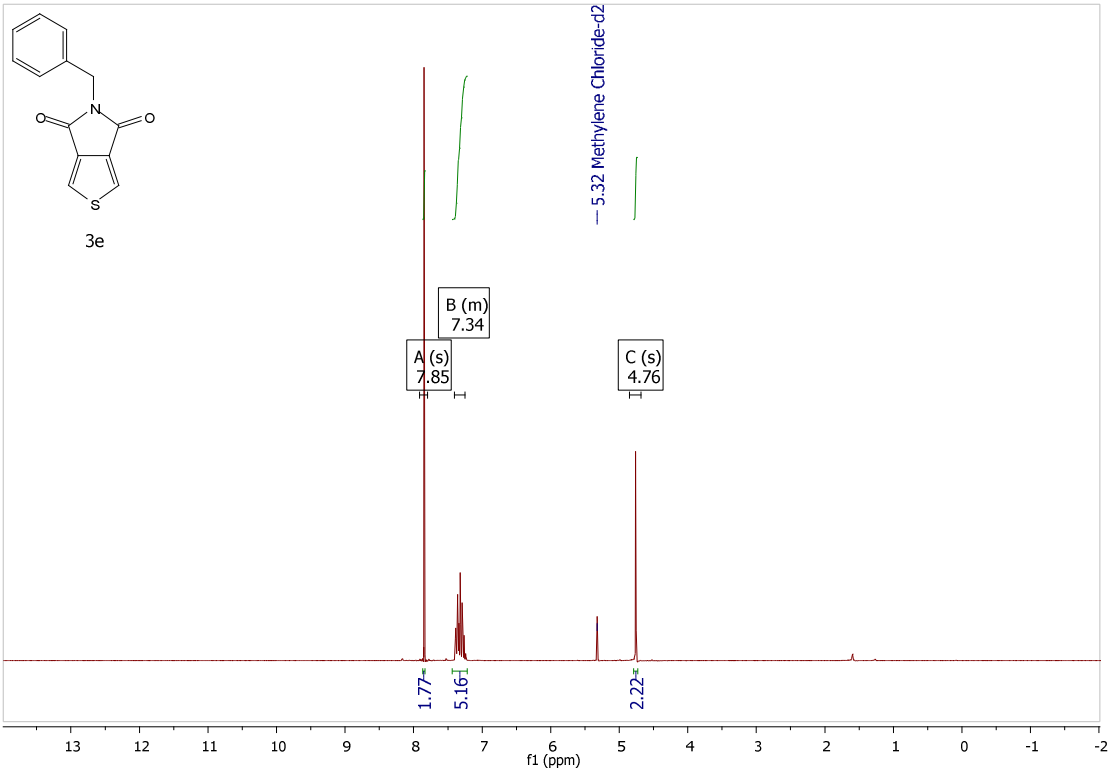

Figure 15. 300 MHz ^{1}H-NMR of 5-benzylthieno[3,4-c]pyrrole-4,6-dione (3e)

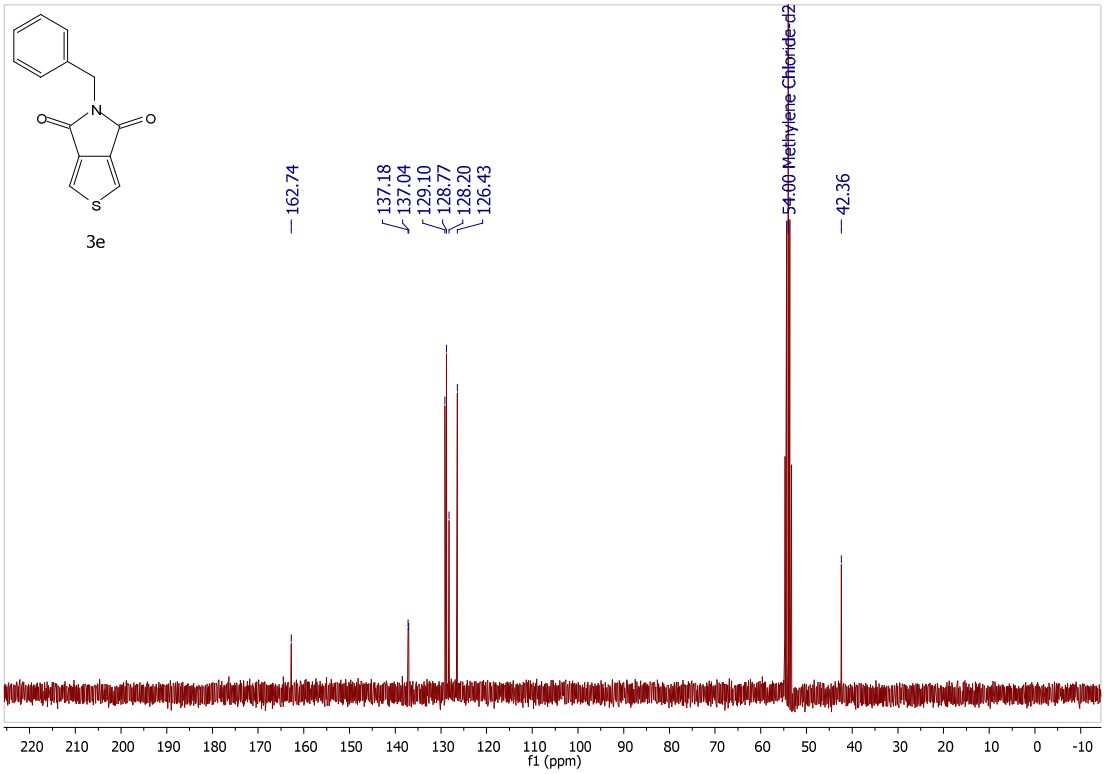

Figure 16. 75 MHz ^{13}C-NMR of 5-benzylthieno[3,4-c]pyrrole-4,6-dione (3e)

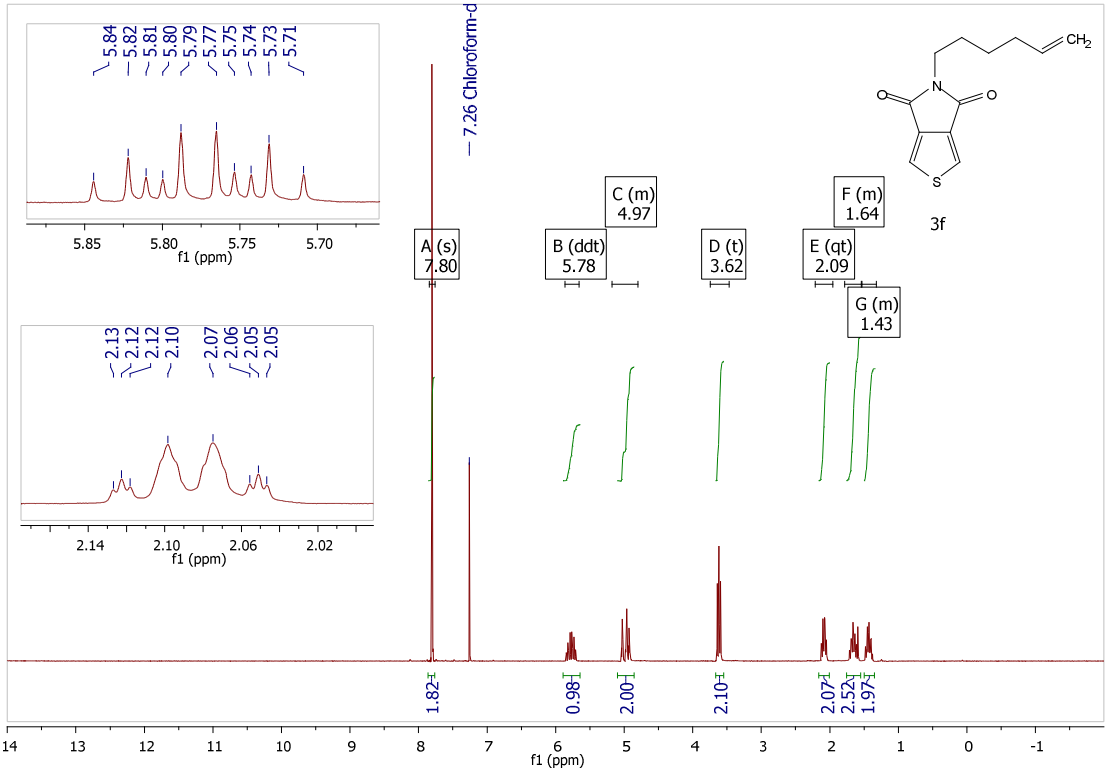

Figure 17. 300 MHz ^{1}H-NMR of 5-(hex-5-en-1-yl)thieno[3,4-c]pyrrole-4,6-dione (3f)

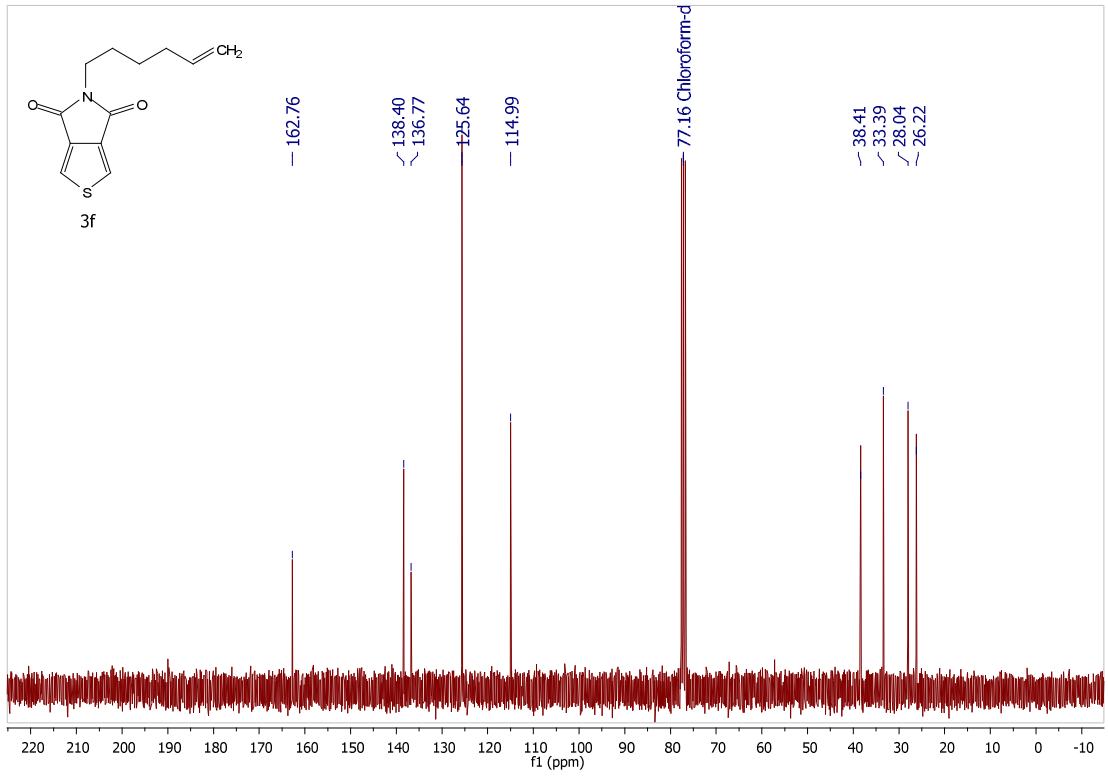

Figure 18. 75 MHz ^{13}C-NMR of 5-(hex-5-en-1-yl)thieno[3,4-c]pyrrole-4,6-dione (3f)

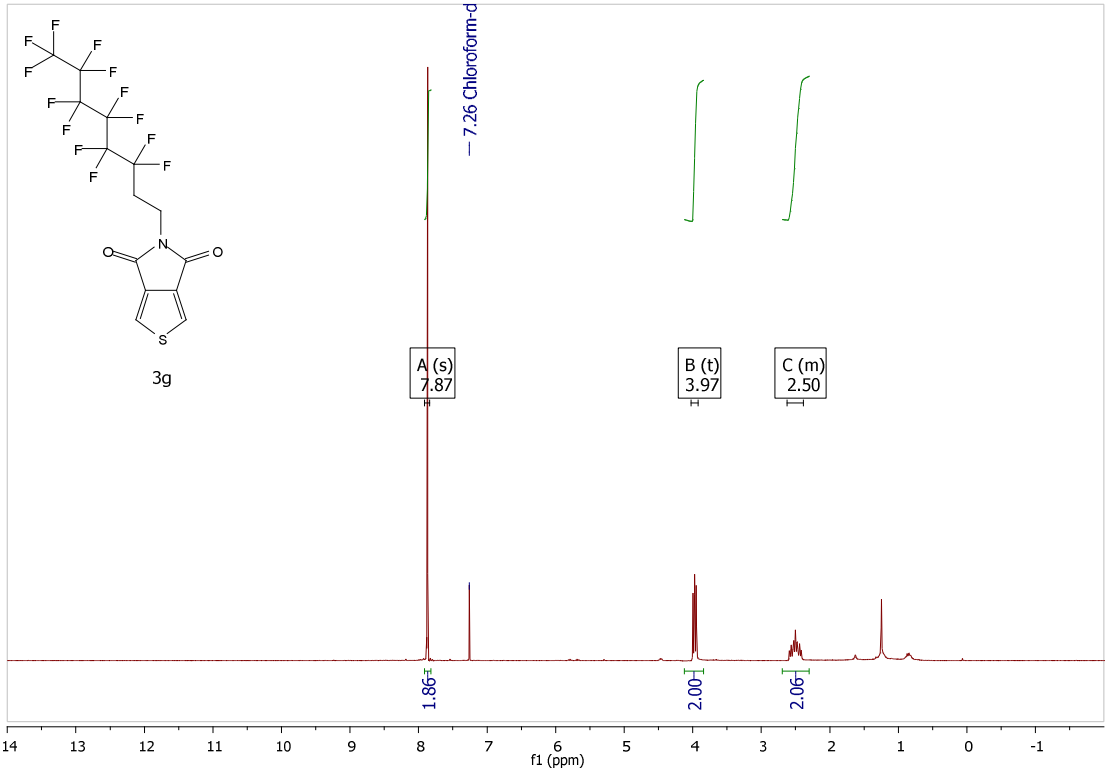

Figure 19. 300 MHz ^{1}H-NMR of 5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thieno[3,4-c]pyrrole-4,6-dione (3g)

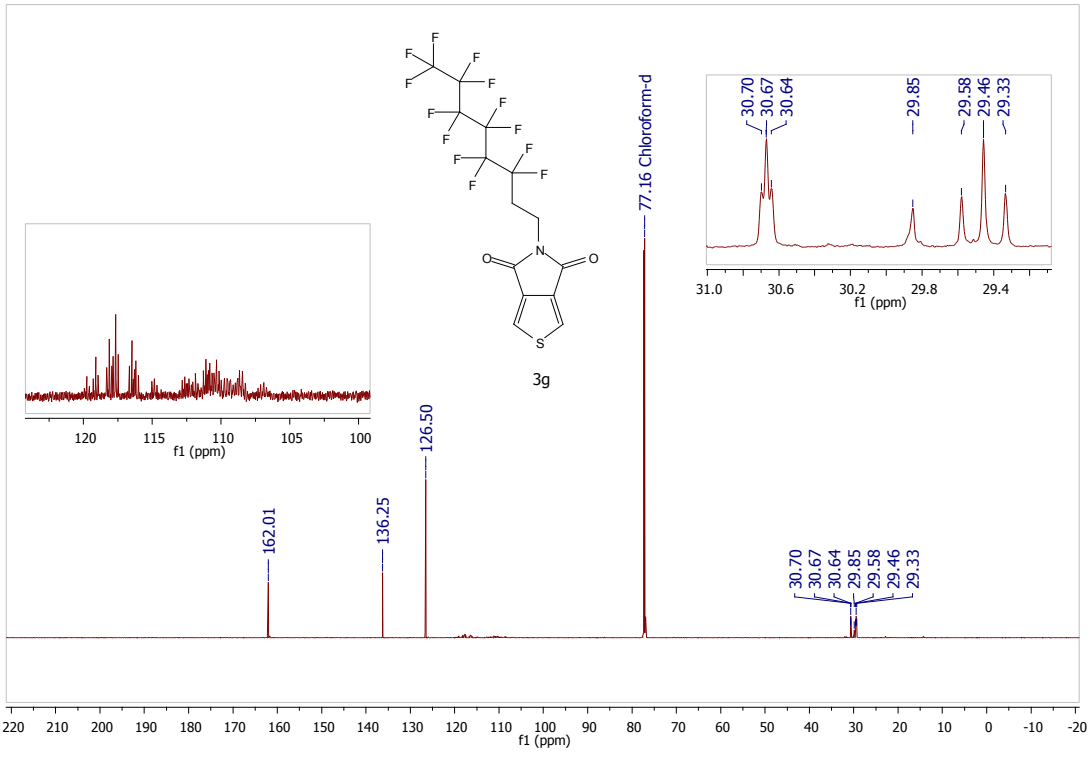

Figure 20. Figure . 176 MHz 13C-NMR of 5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thieno[3,4-c]pyrrole-4,6-dione (3g)

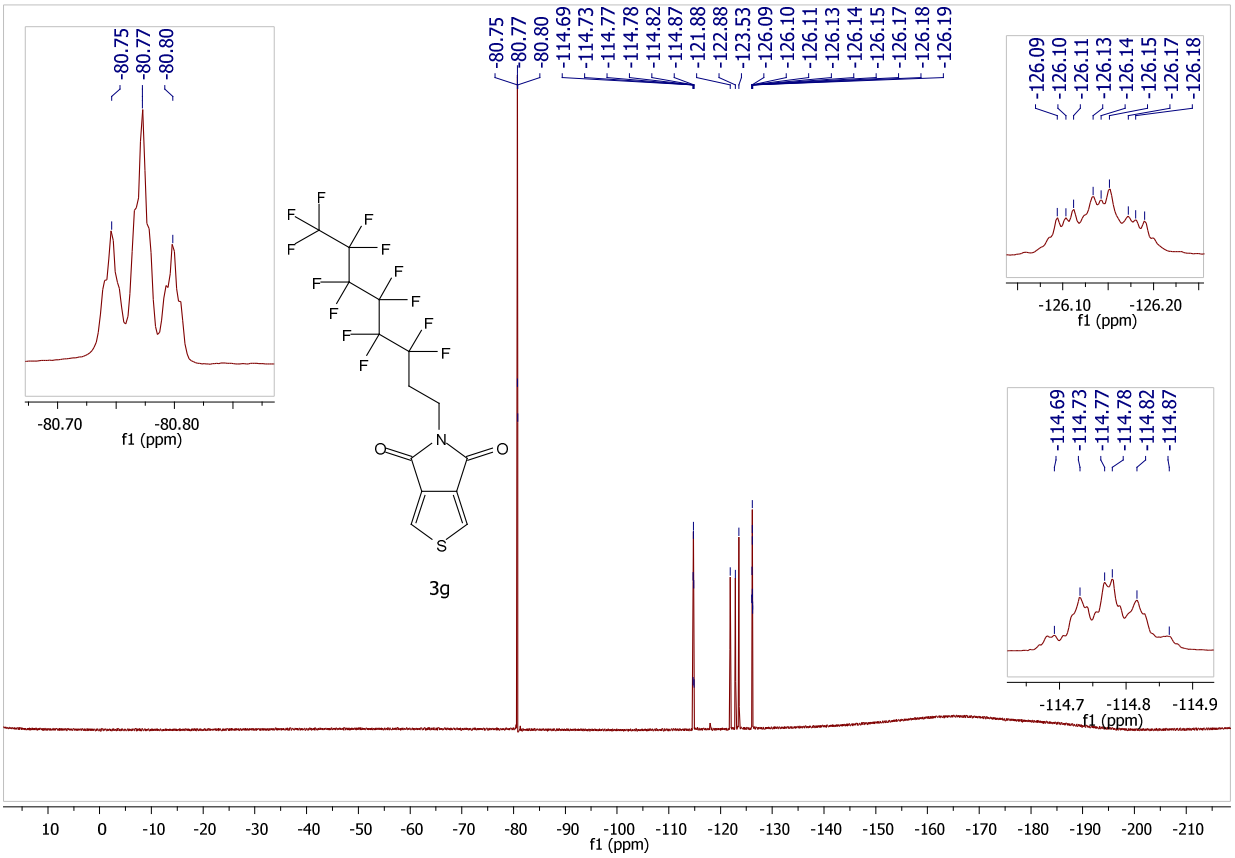

Figure 21. 376.5 MHz ^{19}F-NMR of 5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thieno[3,4-c]pyrrole-4,6-dione (3g)

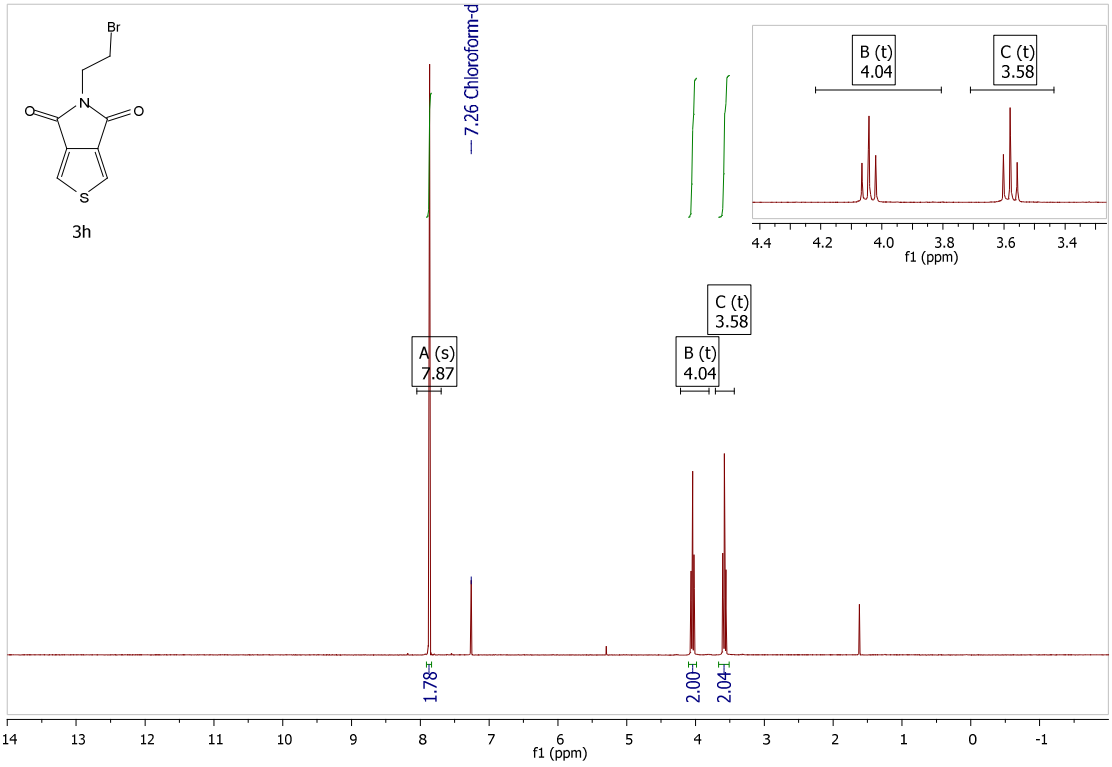

Figure 22. 300 MHz ^{1}H-NMR of 5-(2-bromoethyl)-thieno[3,4-c]pyrrole-4,6-dione (3h)

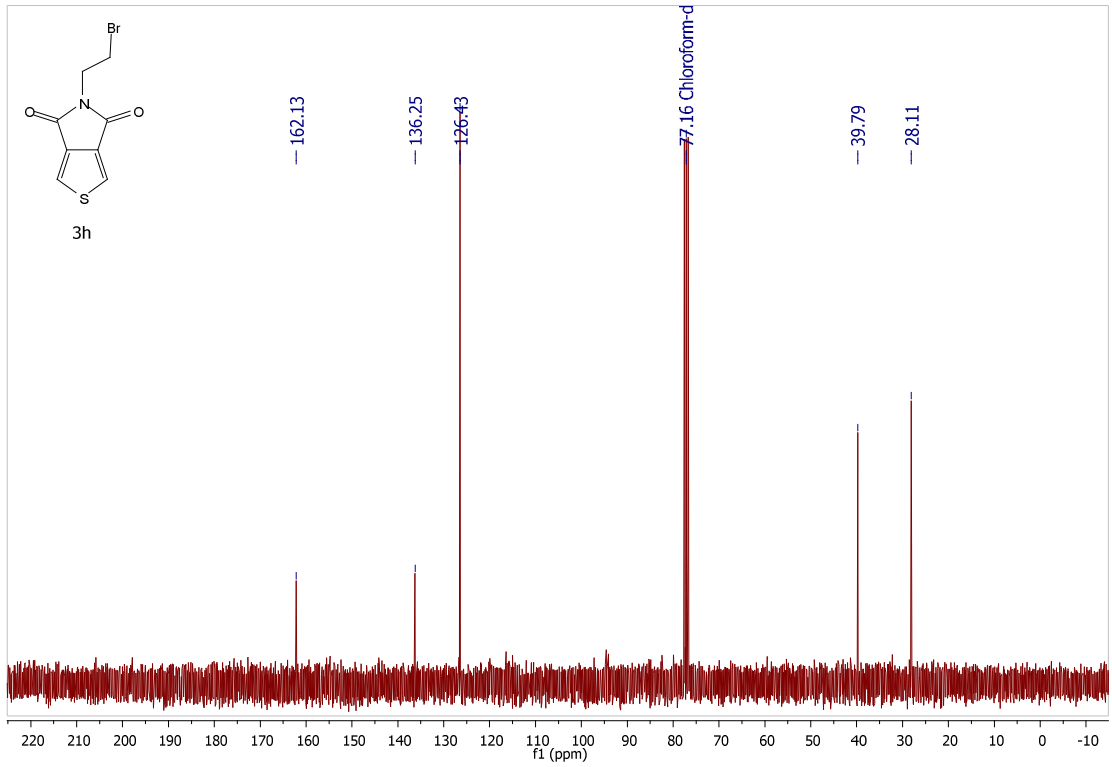

Figure 23. 75 MHz ^{13}C-NMR of 5-(2-bromoethyl)-thieno[3,4-c]pyrrole-4,6-dione (3h)

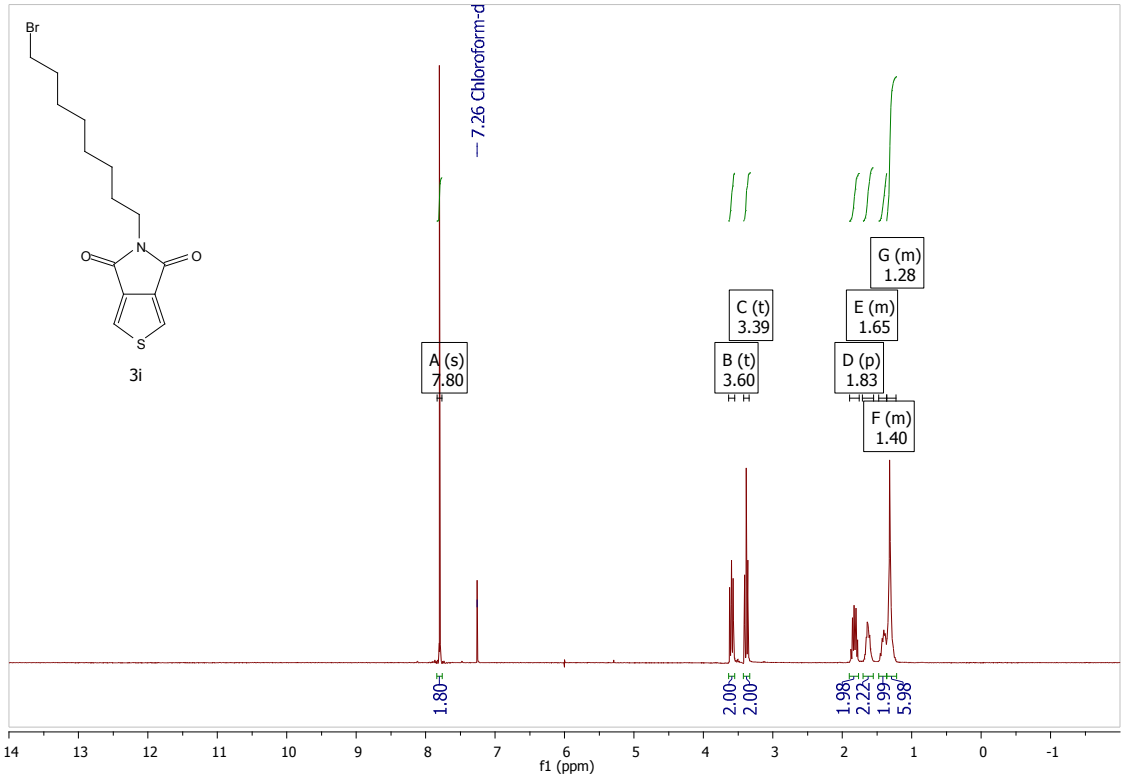

Figure 24. 300 MHz ^{1}H-NMR of 5-(8-bromooctyl)-thieno[3,4-c]pyrrole-4,6-dione (3i)

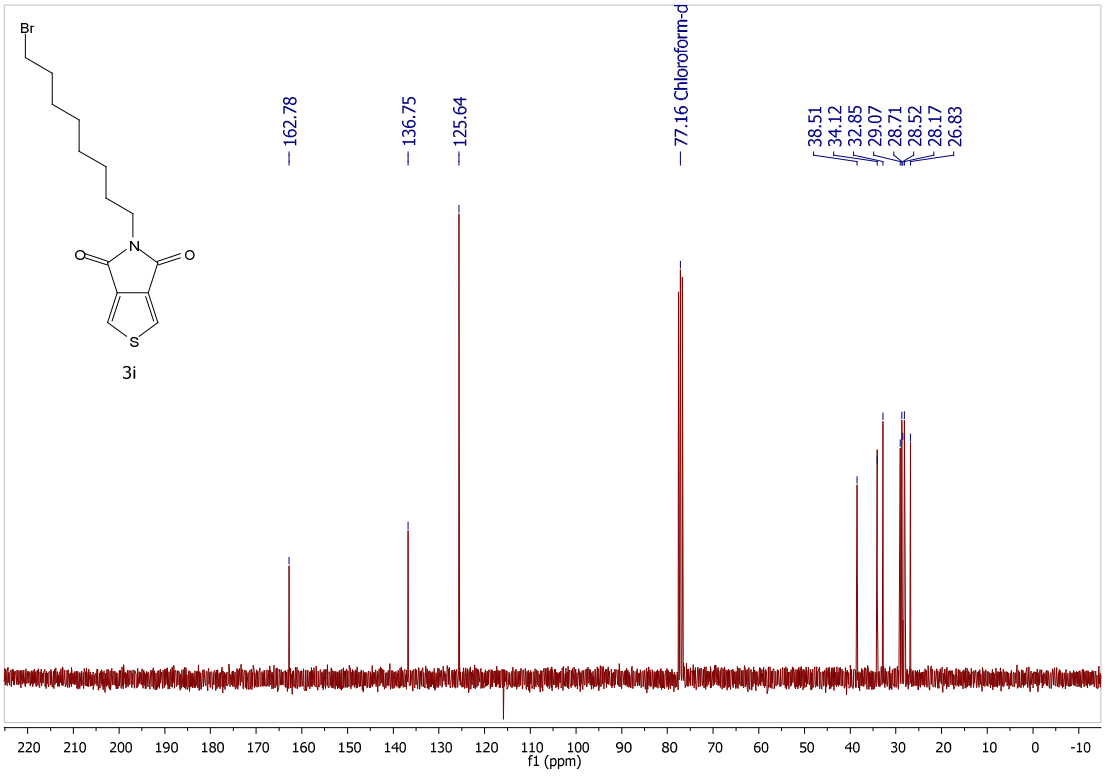

Figure 25. 75 MHz ^{13}C-NMR of 5-(8-bromooctyl)-thieno[3,4-c]pyrrole-4,6-dione (3i)

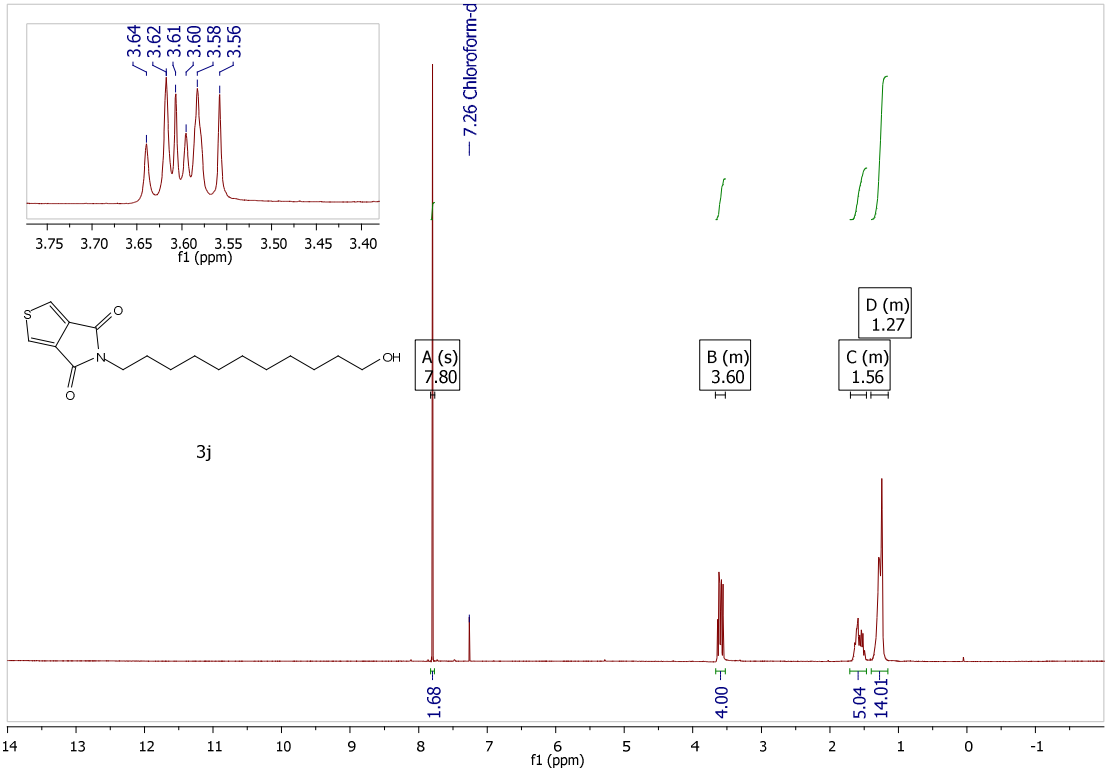

Figure 26. 300 MHz ^{1}H-NMR of 5-(11-hydroxyundecyl)thieno[3,4-c]pyrrole-4,6-dione (3j)

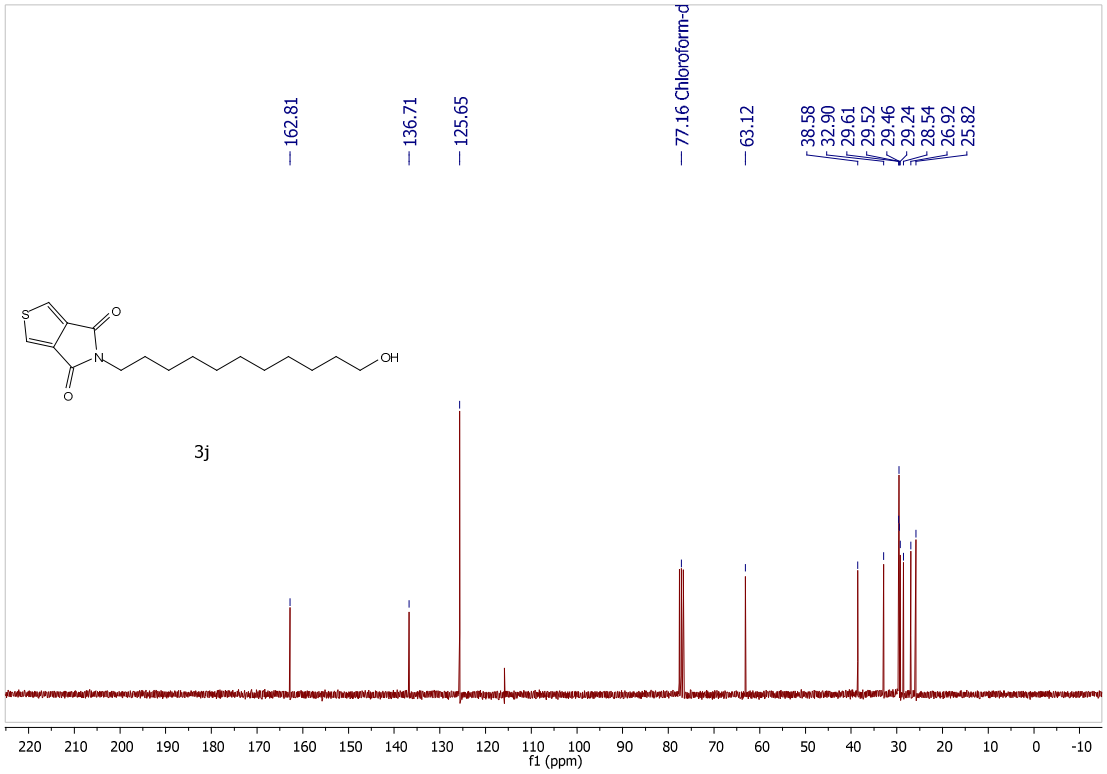

Figure 27. 75 MHz ^{13}C-NMR of 5-(11-hydroxyundecyl)thieno[3,4-c]pyrrole-4,6-dione (3j)

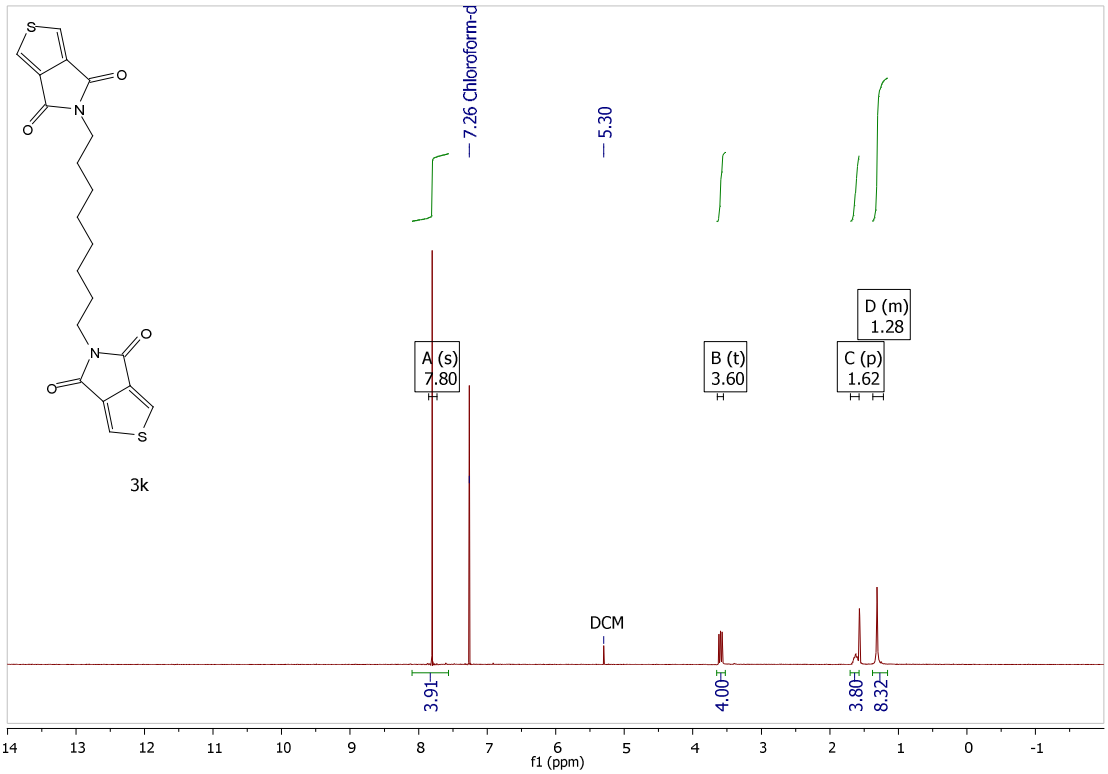

Figure 28. 300 MHz ^{1}H-NMR of 5,5'-(octane-1,8-diyl)bisthieno[3,4-c]pyrrole-4,6-dione (3k)

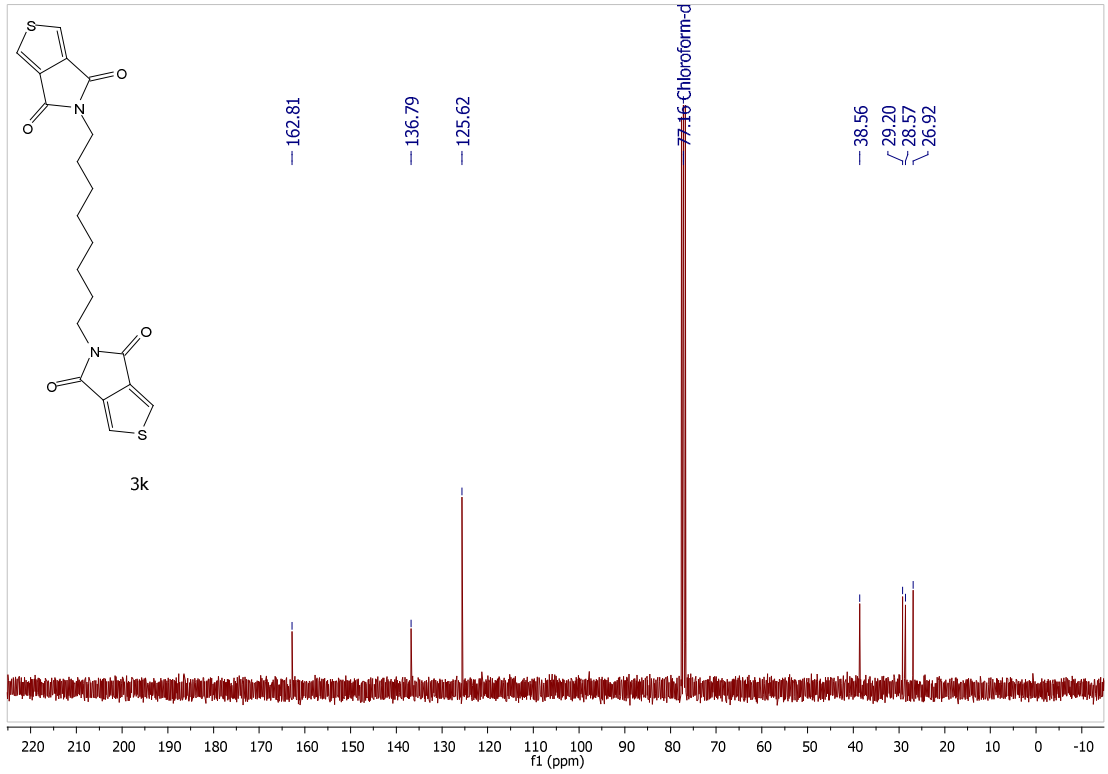

Figure 29. 75 MHz ^{13}C-NMR of 5,5'-(octane-1,8-diyl)bisthieno[3,4-c]pyrrole-4,6-dione (3k)

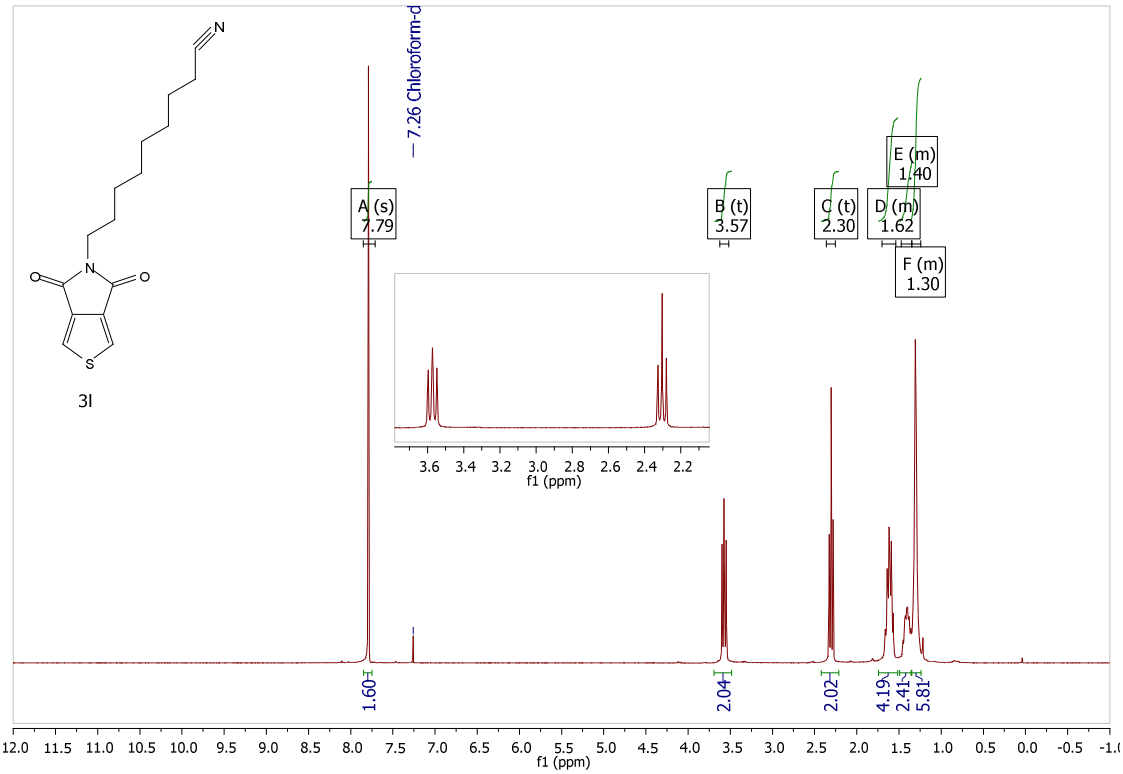

Figure 30. 300 MHz ^{1}H-NMR of 5-(9-nitrilononanyl)thieno[3,4-c]pyrrole-4,6-dione (3l)

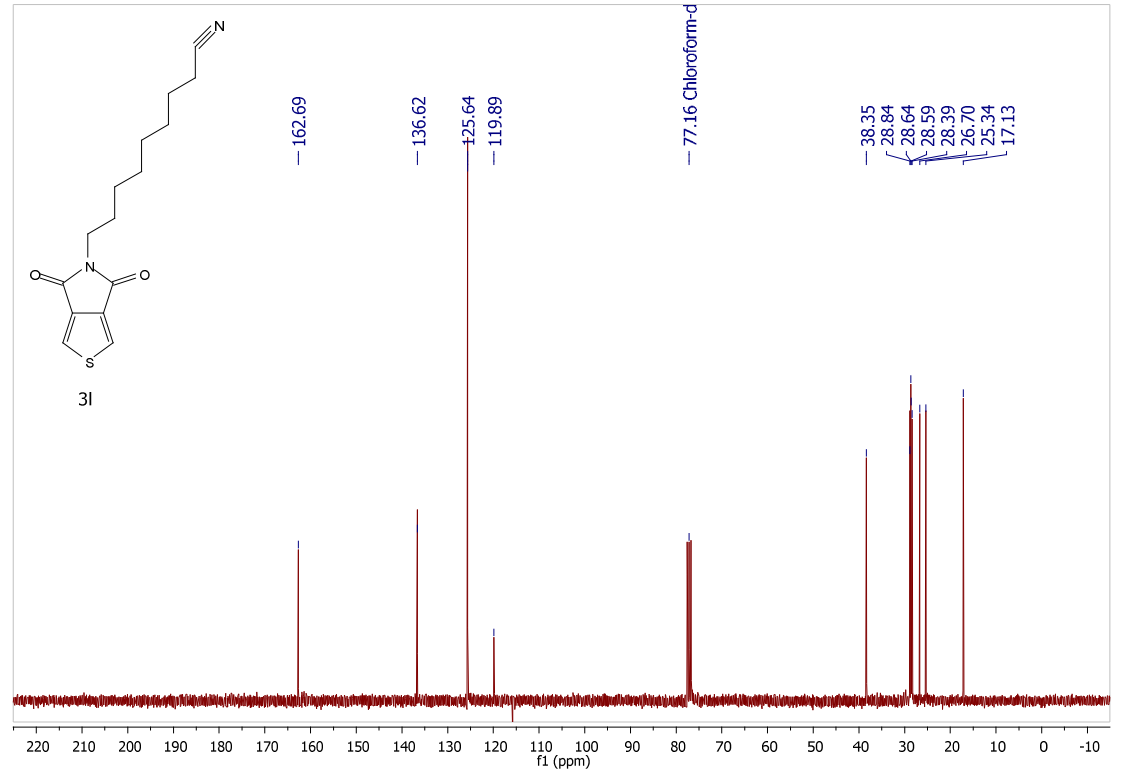

Figure 31. 75 MHz ^{13}C-NMR of 5-(9-nitrilononanyl)thieno[3,4-c]pyrrole-4,6-dione (3l)

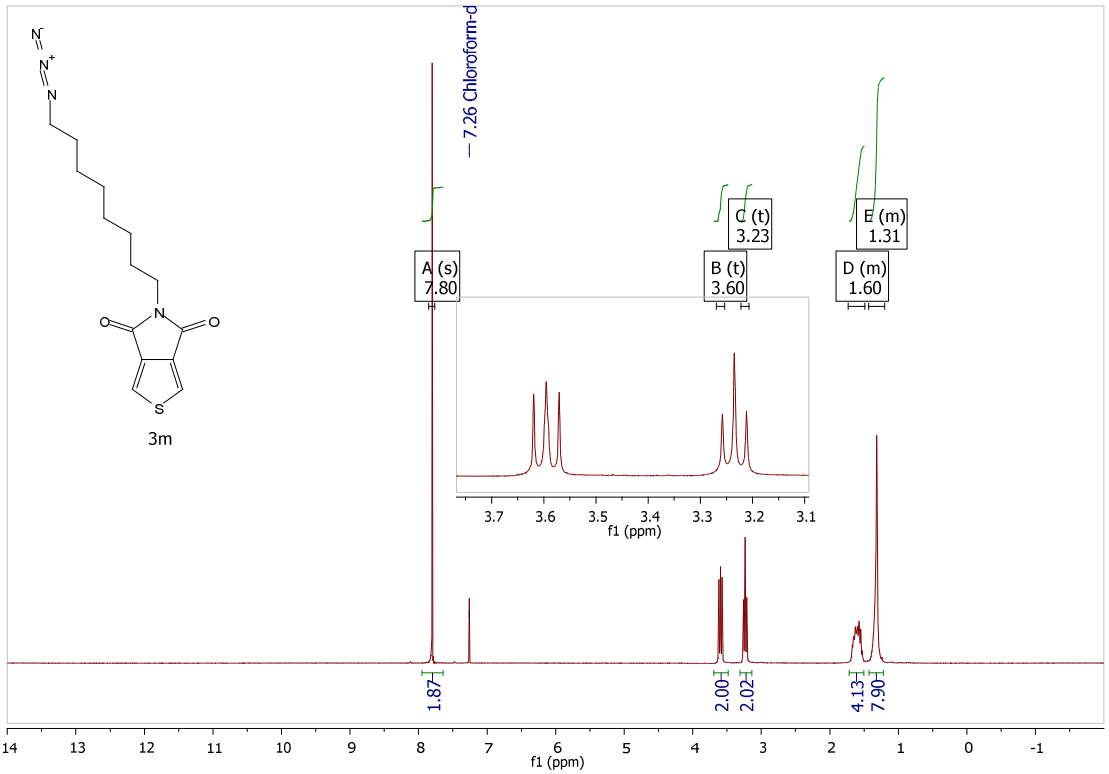

Figure 32. 300 MHz ^{1}H-NMR of 5-(8-azidooctyl)thieno[3,4-c]pyrrole-4,6-dione (3m)

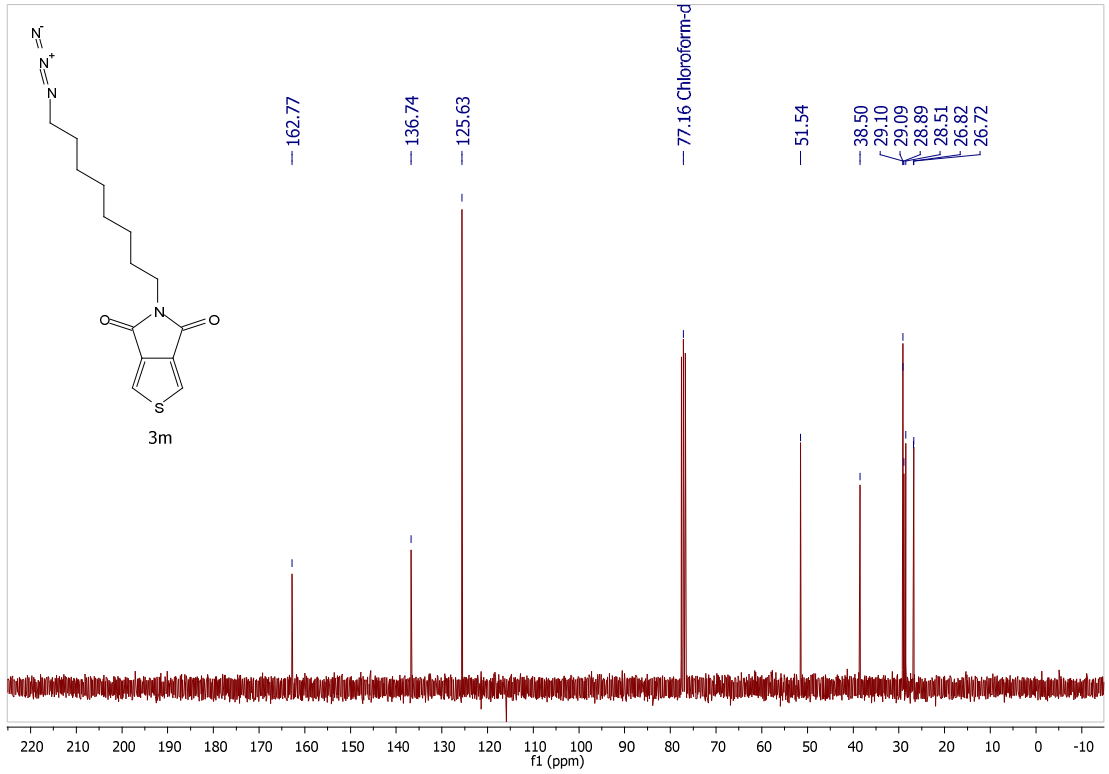

Figure 33. 75 MHz ^{13}C-NMR of 5-(8-azidooctyl)thieno[3,4-c]pyrrole-4,6-dione (3m)

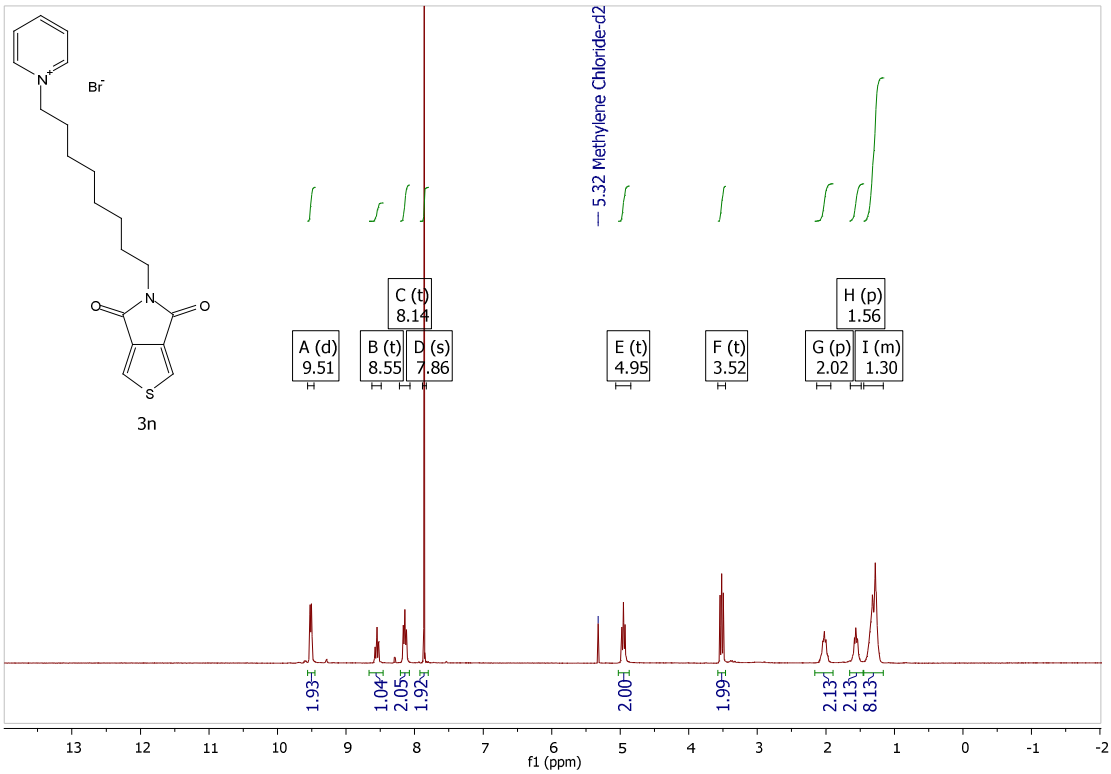

Figure 34. 300 MHz ^{1}H-NMR of 1-(8-(4,6-dioxothieno[3,4-c]pyrrol-5-yl)octyl)pyridinium bromide (3n)

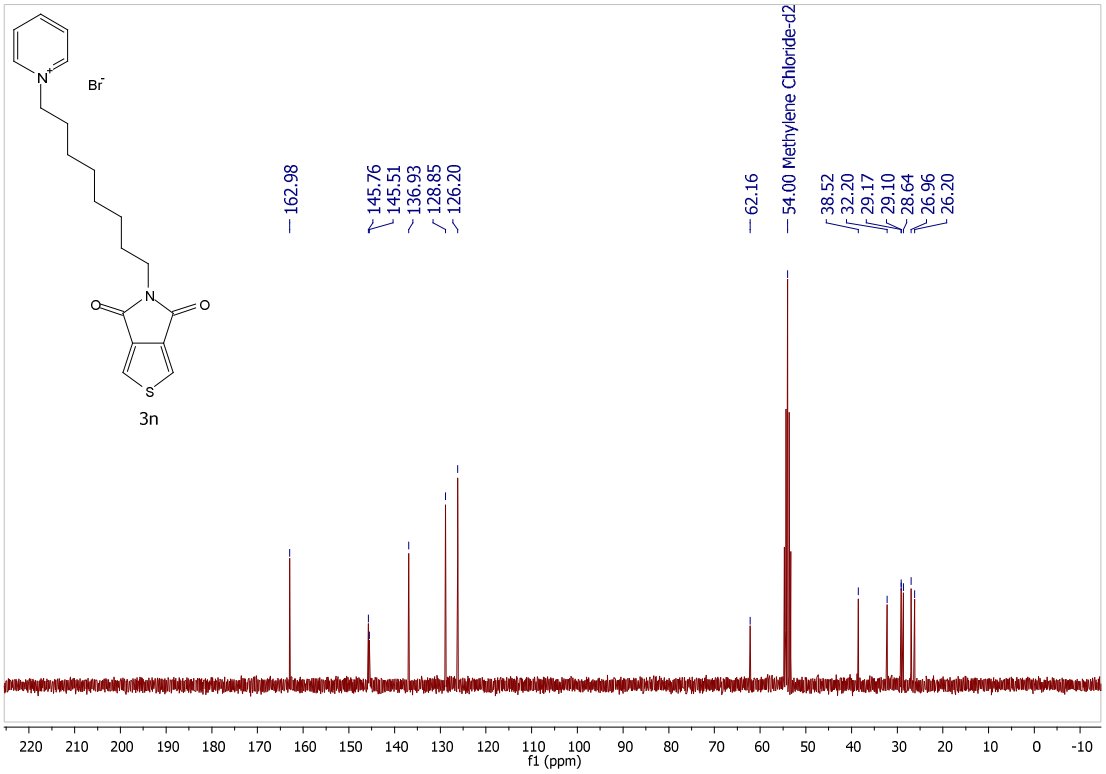

Figure 35. 75 MHz ^{13}C-NMR of 1-(8-(4,6-dioxothieno[3,4-c]pyrrol-5-yl)octyl)pyridinium bromide (3n)

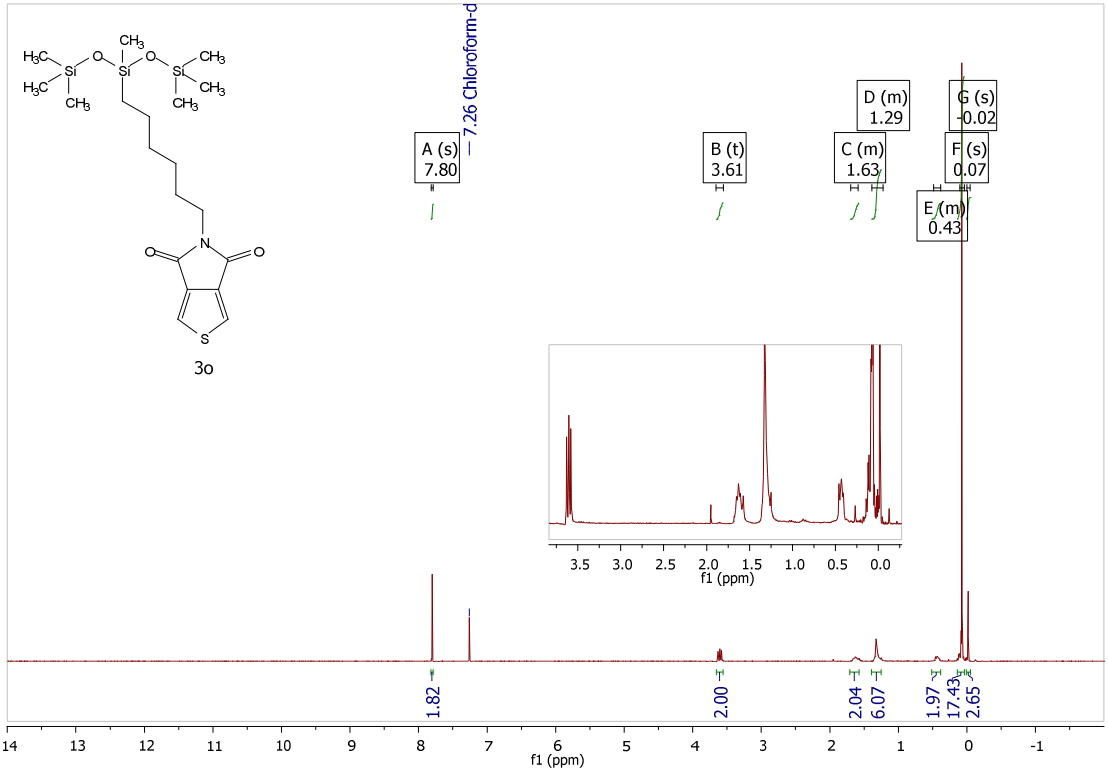

Figure 36. 300 MHz ^{1}H-NMR of 5-(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3o)

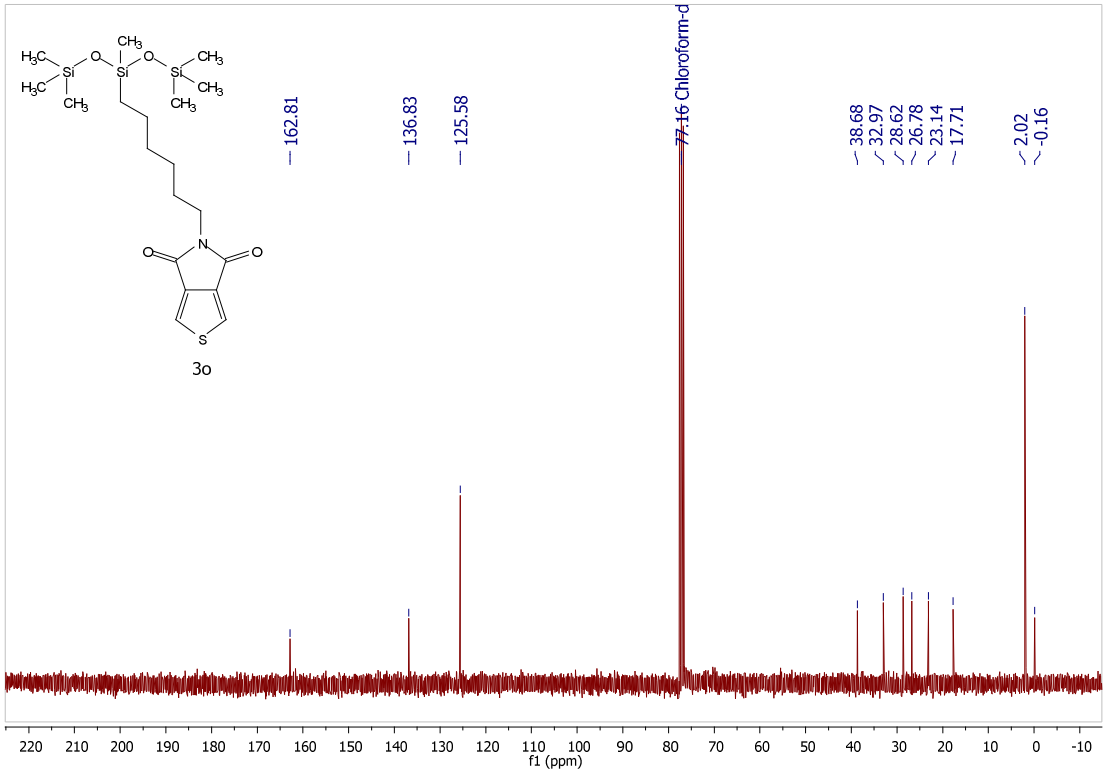

Figure 37. 75 MHz ^{13}C-NMR of 5-(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3o)

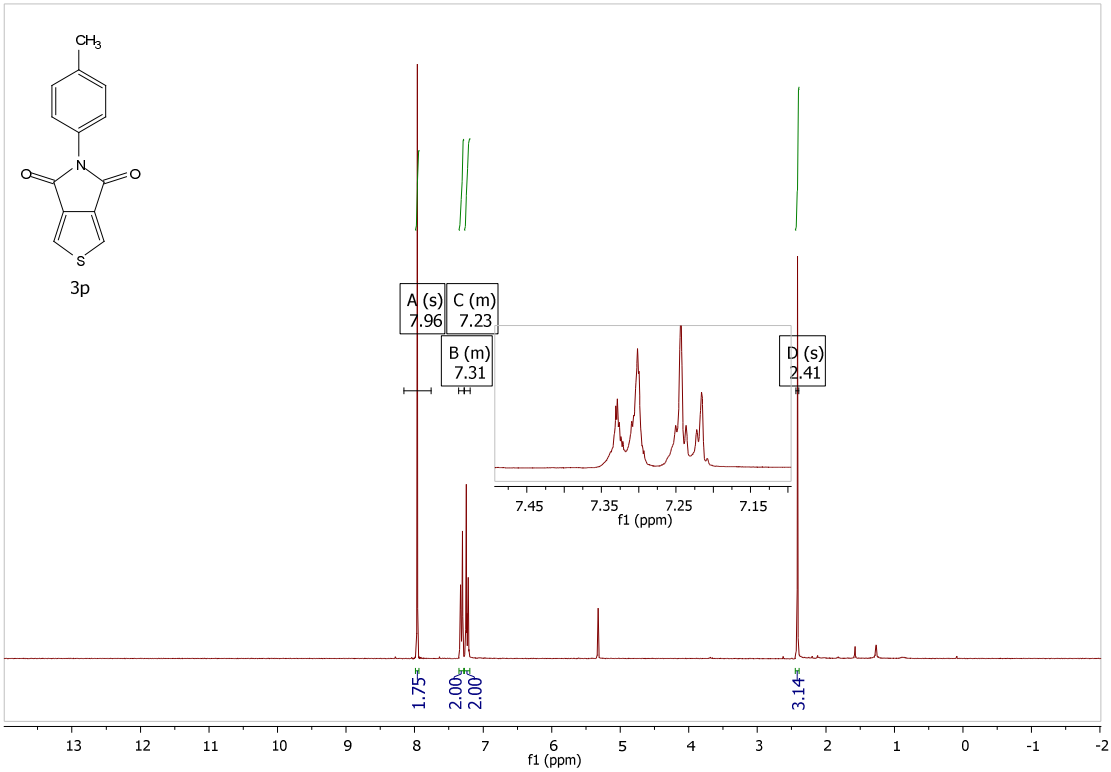

Figure 38. 300 MHz ^{1}H-NMR of 5-(p-tolyl)thieno[3,4-c]pyrrole-4,6-dione (3p)

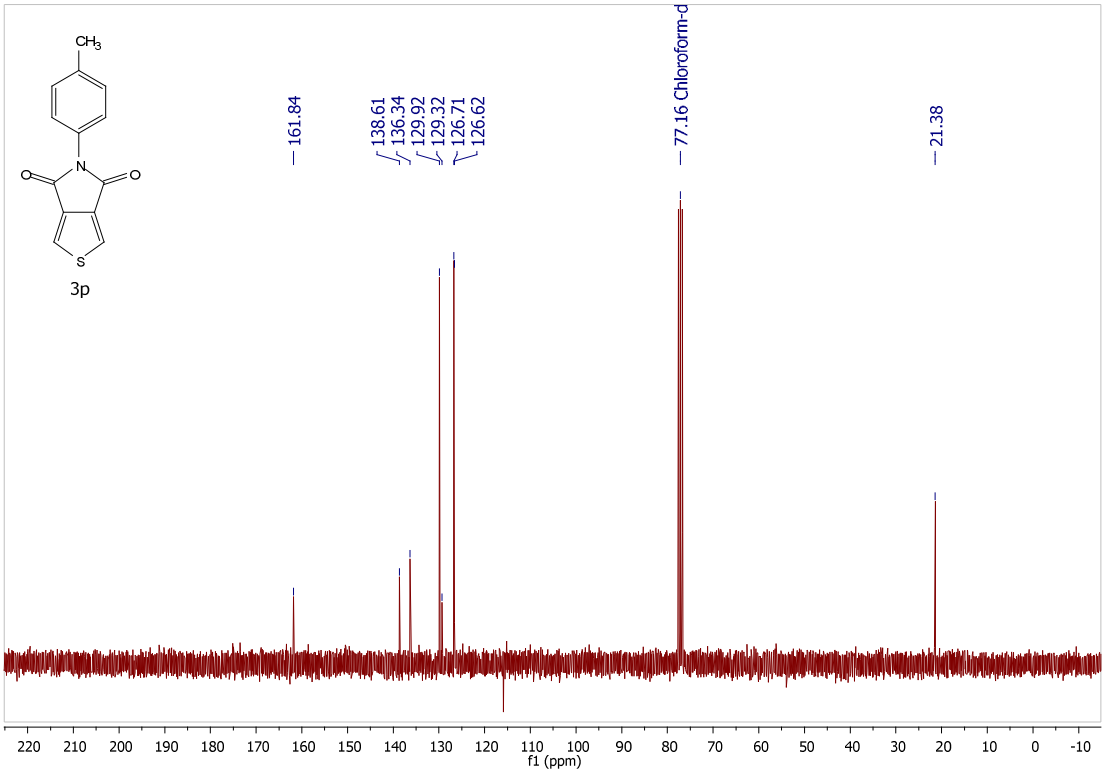

Figure 39. 75 MHz ^{13}C-NMR of 5-(p-tolyl)thieno[3,4-c]pyrrole-4,6-dione (3p)

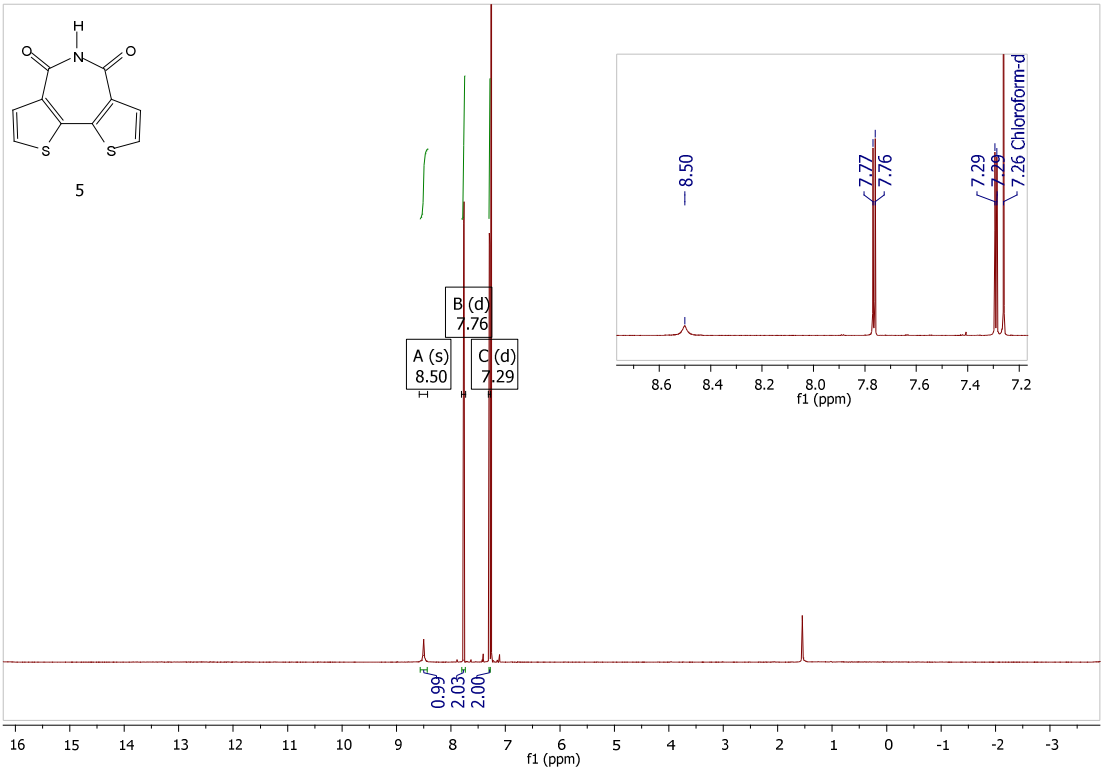

Figure 40. 700 MHz ^{1}H-NMR of Dithieno[3,2-c:2',3'-e]azepine-4,6-dione (BTI) (5)

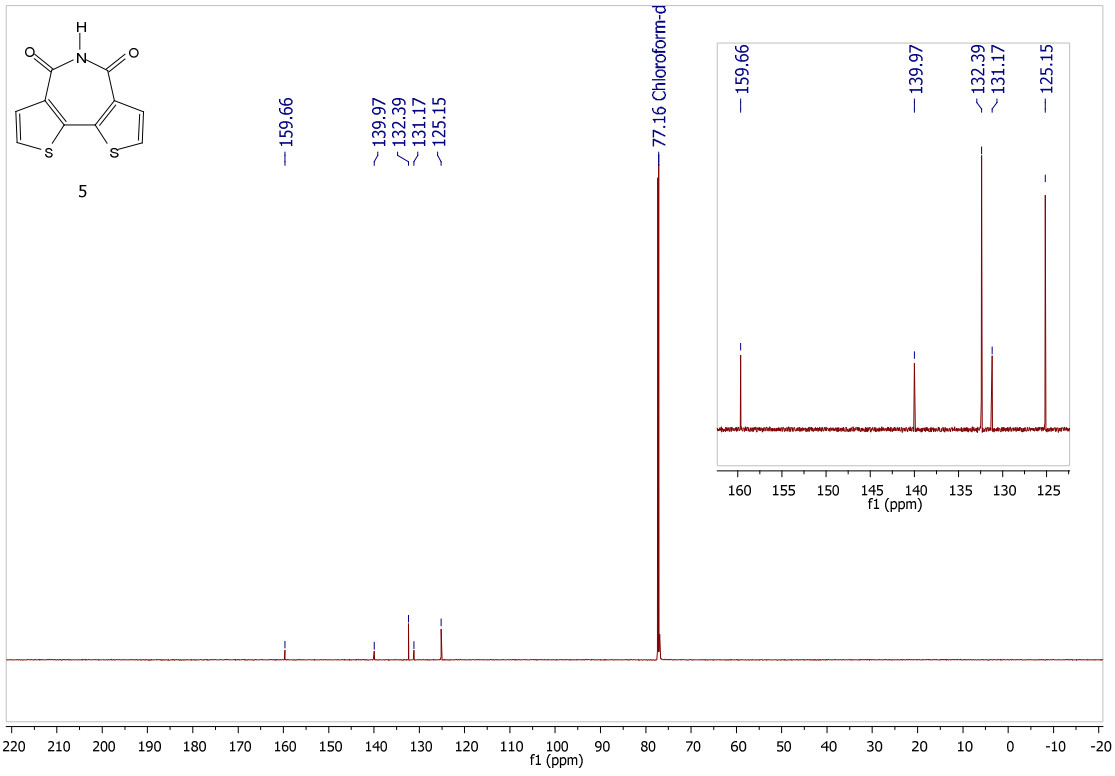

Figure 41. 176 MHz ^{13}C-NMR of Dithieno[3,2-c:2',3'-e]azepine-4,6-dione (BTI) (5)

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