

Iodide-Mediated or Iodide-Catalyzed Demethylation and Friedel–Crafts C–H Borylative
Cyclization Leading to Thiophene-fused 1,2-Oxaborine Derivatives

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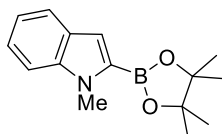
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1. Experimental Section

General

Nuclear magnetic resonance (NMR) spectra were recorded on Varian 600 System (^1H 600 MHz, ^{13}C 150 MHz), Varian 400-MR (^1H 400 MHz, ^{13}C 100 MHz), and JEOL JNM-ECS400 (^1H 400 MHz, ^{13}C 100 MHz) spectrometers. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to TMS (δ 0 ppm) or residual CHCl_3 in CDCl_3 (δ 7.26 ppm) or pyridine in pyridine- d_5 (δ 7.22 ppm) or DMSO in $\text{DMSO-}d_6$ (δ 2.50 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to CDCl_3 (δ 77.0 ppm) or $\text{DMSO-}d_6$ (δ 39.52 ppm). IR spectra were recorded on a JASCO FT/IR-4100 and Varian 7000e FT-IR spectrophotometers. Elemental analysis was obtained with Perkin-Elmer PE 2400 Series II CHNS/O analyzer. Analytic thin layer chromatography (TLC) was performed on Merck, pre-coated plate silica gel 60 F₂₅₄ (0.25 mm thickness). Column chromatography was performed on KANTO CHEMICAL silica gel 60N (40–50 μm). Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. High-resolution mass spectrometry was performed on JEOL JMS-700MStation (FAB-MS) or Bruker micrOTOF II-SKA (ESI). Dry tetrahydrofuran (THF) and dry diethyl ether (Et_2O) were purchased from Wako pure chemical industries. All reactions were performed under argon atmosphere. Chlorobenzene (PhCl) was dried over MS4A. Et_3N was distilled from CaH_2 . 3-Methoxybenzo[*b*]thiophene¹, 3-bromo-2-methoxythiophene² and 1,5-diiodo-2,4-dimethoxybenzene³ were synthesized according to the literatures. ^{13}C NMR of **4d** could not be measured due to its low solubility. In ^{13}C NMR of thienooxaborines, the carbon peaks bonded with the boron atom could not be observed.⁴ For the detection, we tried to increase the scanning time, but the corresponding carbon peaks could not be detected.



1-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole⁵

To a solution 1-methylindole (1.31 g, 10.0 mmol) in dry THF (20 mL) was added dropwise *t*-BuLi (1.62 M in pentane, 6.79 mL, 11.0 mmol) at -78°C . After stirring for 30 min, the reaction mixture was further stirred for 2 h at room temperature. To a mixture was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.4 mL, 12.0 mmol) at -78°C . After stirring for 30 min, the reaction mixture was further stirred for 2 h at room temperature. The reaction was quenched with H_2O (150 mL) and the resulting mixture was extracted with CH_2Cl_2 (2×200 mL). The combined organic phase was dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by recrystallization from Et_2O to afford the title compound as yellow solid (2.07 g, 8.06 mmol, 81%). ^1H NMR (600 MHz, CDCl_3) δ 1.38 (s, 12H), 3.99 (s, 3H), 7.10 (td, $J = 7.8, 0.6$ Hz, 1H), 7.16 (s, 1H), 7.28 (td, $J = 7.8, 1.2$ Hz, 1H), 7.36 (dd, $J = 7.8, 1.2$ Hz, 1H),

¹ Lemaire, M.; Fournier, J.; Chabert, D.; Joucla, L.; Daivid, E. *Tetrahedron* **2004**, *60*, 3221–3230.

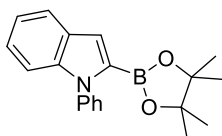
² Gronowitz, S.; Zhang, Y.; Hornfeldt, A. B. *Journal of Heterocyclic Chemistry* **1995**, *32*, 435–440.

³ Raminelli, C.; Gallo, R. D. C.; Ferreira, I. M.; Casagrande, G. A.; Pizzuiti, L.; Oliveira-S, D. *Tetrahedron Lett.* **2012**, *53*, 5372–5375.

⁴ Odom, J. D.; Moore, T. F. *J. Organomet. Chem.* **1979**, *173*, 15–32.

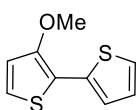
⁵ Furukawa, T.; Tobisu, M.; Chatani, N. *J. Am. Chem. Soc.* **2015**, *137*, 12211–12214.

7.66 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 24.8, 32.2, 83.6, 109.7, 114.2, 119.2, 121.5, 123.1, 127.8, 140.1; IR (KBr) 3055, 2980, 1522, 1292, 1142 cm^{-1} .



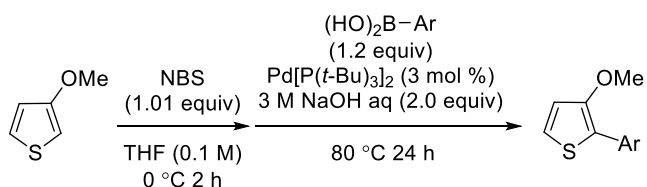
1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole

To a solution 1-phenyl-1H-indole (1.31 g, 10.0 mmol) in dry THF (20 mL) was added dropwise *t*-BuLi (1.62 M in pentane, 6.79 mL, 11.0 mmol) at -78 °C. After stirring for 30 min, the reaction was further stirred for 2 h at room temperature. To a mixture was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.4 mL, 12.0 mmol) at -78 °C. After stirring for 30 min, the reaction mixture was further stirred for 2 h at room temperature. The reaction was quenched with H_2O (150 mL) and the resulting mixture was extracted with CH_2Cl_2 (2×200 mL). The combined organic phase was dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by recrystallization from hexane/ Et_2O to afford the title compound as yellow solid (2.12 g, 6.66 mmol, 67%). ^1H NMR (600 MHz, CDCl_3) δ 1.22 (s, 12H), 7.14 (t, $J = 7.2$ Hz, 1H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.28 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.40–7.41 (m, 3H), 7.46–7.49 (m, 2H), 7.71 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 24.5, 83.6, 110.8, 115.7, 120.1, 21.5, 123.6, 127.0, 128.2, 128.5, 139.7, 140.3; IR (KBr) 3049, 2980, 2936, 1526, 1331, 1138 cm^{-1} .



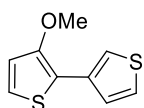
3-Methoxy-2,2'-bithiophene (1a)

To a solution of 3-methoxythiophene (1.15 g, 10.0 mmol) in dry THF (100 mL) was added NBS (1.37 g, 10.1 mmol) at 0 °C. The reaction mixture was then stirred at the same temperature for 2 h. To the mixture were added bis(*tri-tert*-butylphosphine)palladium (0.153 g, 0.3 mmol), 2-thienylboronic acid (1.54 g, 12.0 mmol) and 3 M NaOH aqueous solution (6.7 mL, 20 mmol), and then the mixture was stirred at 80 °C for 20 h. After cooling to room temperature, the reaction was quenched with H_2O (100 mL) and the resulting mixture was extracted with CH_2Cl_2 (3×50 mL). The combined organic phase was dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 10:1$) to afford 3-methoxy-2,2'-bithiophene (**1a**) as yellow oil (1.89 g, 9.63 mmol, 96%). ^1H NMR (400 MHz, CDCl_3) δ 3.94 (s, 3H), 6.86 (d, $J = 5.4$ Hz, 1H), 7.00 (dd, $J = 5.2, 3.8$ Hz, 1H), 7.06 (d, 5.4 Hz, 1H), 7.19 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.22 (dd, $J = 3.8, 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 58.8, 115.3, 116.9, 121.5, 122.8, 123.6, 126.8, 135.0, 153.2; IR (neat) 3105, 2934, 1558, 1261, 1070 cm^{-1} ; HRMS (FAB^+) m/z calcd for $\text{C}_9\text{H}_9\text{OS}_2$ [$\text{M}+\text{H}$] $^+$ 197.0089, found 197.0082.



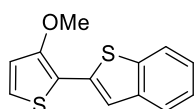
General Procedure for the bromination and Suzuki–Miyaura Coupling

To a solution of 3-methoxythiophene (343 mg, 3.0 mmol) in dry THF (30 mL) was added NBS (539 mg, 3.03 mmol) at 0 °C. The reaction mixture was then stirred at the same temperature for 2 h. To the mixture were added bis(*tri-tert*-butylphosphine)palladium (46 mg, 0.09 mmol), aryl boronic acid (3.6 or 6.0 mmol) and 3 M NaOH aqueous solution (6.7 mL, 20 mmol), and then the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (30 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 10:1).



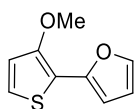
3-Methoxy-2,3'-bithiophene (1b)

The general procedure for the bromination and Suzuki–Miyaura coupling was performed with 3-thiopheneboronic acid (461 mg, 3.6 mmol) to afford the title compound as colorless oil (561 mg, 2.86 mmol, 95%). ¹H NMR (600 MHz, CDCl₃) δ 3.93 (s, 3H), 6.89 (d, *J* = 5.4 Hz, 1H), 7.07 (d, *J* = 5.4 Hz, 1H), 7.30 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.39 (dd, *J* = 4.8, 1.5 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 58.7, 116.0, 116.9, 119.5, 121.1, 125.2, 126.5, 133.4, 153.4; IR (neat) 3107, 2934, 1557, 1385, 1256, 1072 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₉H₉OS₂ [M+H]⁺ 197.0089, found 197.0084.



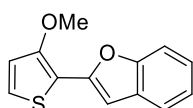
2-(3-Methoxythiophen-2-yl)benzo[*b*]thiophene (1f)

The general procedure for the bromination and Suzuki–Miyaura coupling was performed with benzo[*b*]thiophen-2-ylboronic acid (641 mg, 3.6 mmol) to afford the title compound as colorless solid (727 mg, 2.95 mmol, 98%). ¹H NMR (400 MHz, CDCl₃) δ 3.98 (s, 3H), 6.87 (d, *J* = 5.6 Hz, 1H), 7.13 (d, *J* = 5.6 Hz, 1H), 7.25 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.30 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.76 (dm, *J* = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 58.9, 115.0, 116.9, 118.7, 121.9, 122.9, 123.0, 123.7, 124.3, 135.2, 139.0, 139.9, 154.5; IR (KBr) 3107, 2930, 1549, 1385, 1065 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₃H₁₀BOS₂ [M+H]⁺ 247.0245, found 247.0235; mp 86.6–87.2 °C.



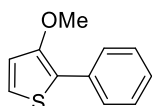
2-(3-Methoxythiophen-2-yl)furan (1h)

The general procedure for the bromination and Suzuki–Miyaura coupling was performed with furan-2-ylboronic acid (403 mg, 3.6 mmol) to afford the title compound as colorless oil (316 mg, 1.76 mmol, 59%). ¹H NMR (400 MHz, CDCl₃) δ 3.93 (s, 3H), 6.45 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 6.86 (d, *J* = 5.4 Hz, 1H), 7.10 (d, *J* = 5.4 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 58.6, 105.4, 111.2, 111.6, 116.2, 122.0, 140.2, 148.1, 153.1; IR (neat) 3113, 2936, 1547, 1387, 1238, 1067 cm⁻¹; HRMS (ESI⁺) *m/z* calcd for C₉H₉O₂S [M+H]⁺ 181.0318, found 181.0315.



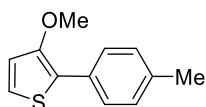
2-(3-Methoxythiophen-2-yl)benzofuran (1i)

The general procedure for the bromination and Suzuki–Miyaura coupling was performed with benzofuran-2-ylboronic acid (972 mg, 6.0 mmol) to afford the title compound as colorless solid (666 mg, 2.89 mmol, 96%). ¹H NMR (600 MHz, CDCl₃) δ 4.00 (s, 3H), 6.91 (d, *J* = 5.4 Hz, 1H), 7.02–7.03 (m, 1H), 7.18–7.24 (m, 3H), 7.46 (dm, *J* = 7.8 Hz, 1H), 7.53 (dm, *J* = 7.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 58.7, 101.5, 110.4, 110.7, 116.1, 120.5, 122.8, 123.5, 123.9, 129.7, 150.1, 153.6, 155.2; IR (KBr) 3109, 2968, 2853, 1585, 1454, 1074 cm⁻¹; HRMS (ESI⁺) *m/z* calcd for C₁₃H₁₀O₂SNa [M+Na]⁺ 253.0294, found 253.0288; mp 100.3–100.7 °C.



3-Methoxy-2-phenylthiophene (3f)⁶

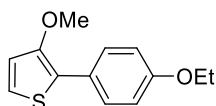
The general procedure for the bromination and Suzuki–Miyaura coupling was performed with phenylboronic acid (439 mg, 3.6 mmol) to afford the title compound as colorless oil (550 mg, 2.89 mmol, 96%). ¹H NMR 600 MHz, CDCl₃) δ 3.90 (s, 3H), 6.91 (d, *J* = 5.7 Hz, 1H), 7.14 (d, *J* = 5.7 Hz, 1H), 7.21 (tt, *J* = 8.4, 1.2 Hz, 1H), 7.35 (tt, *J* = 8.4, 1.2 Hz, 2H), 7.73 (dd, *J* = 8.4, 1.2 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 58.7, 117.5, 120.2, 122.1, 126.3, 126.9, 128.5, 133.4, 153.7; IR (neat) 3055, 2959, 2851, 1549, 1379, 1063 cm⁻¹.



⁶ Yanagisawa, S.; Uede, K.; Sekizawa, H.; Itami, K. *J. Am. Chem. Soc.* **2009**, *131*, 14622–14623

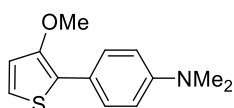
3-Methoxy-2-(*p*-tolyl)thiophene (3g)⁷

The general procedure for the bromination and Suzuki–Miyaura coupling was performed with 4-Methylphenylboronic acid (489 mg, 3.6 mmol) to afford the title compound as colorless oil (565 mg, 2.77 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 2.35 (s, 3H), 3.90 (s, 3H), 6.92 (d, *J* = 5.6 Hz, 1H), 7.11 (d, *J* = 5.6 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 21.1, 58.7, 117.5, 120.4, 121.6, 126.8, 129.2, 130.5, 136.1, 153.3; IR (neat) 3109, 2934, 2847, 1549, 1265, 1072 cm⁻¹.



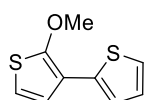
2-(4-Ethoxyphenyl)-3-methoxythiophene (3h)

The general procedure for the bromination and Suzuki–Miyaura coupling was performed with 4-ethoxyphenylboronic acid (598 mg, 3.6 mmol) to afford the title compound as colorless solid (636 mg, 2.72 mmol, 90%). ¹H NMR (600 MHz, CDCl₃) δ 1.41 (t, *J* = 6.6 Hz, 3H), 3.88 (s, 3H), 4.04 (q, *J* = 6.6 Hz, 2H), 6.895 (d, *J* = 8.7 Hz, 2H), 6.901 (d, *J* = 5.4 Hz, 1H), 7.08 (d, *J* = 5.4 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 14.8, 58.7, 63.4, 114.5, 117.5, 120.3, 121.0, 125.9, 128.2, 152.7, 157.6; IR (KBr) 3094, 2972, 2891, 1607, 1242, 1045 cm⁻¹; HRMS (ESI⁺) *m/z* calcd for C₁₃H₁₄O₂SNa [M+Na]⁺ 257.0607, found 257.0613; mp 37.5–38.3 °C.



4-(3-Methoxythiophen-2-yl)-*N,N*-diphenylaniline (3i)

The general procedure for the bromination and Suzuki–Miyaura coupling was performed with 4-(diphenylamino)phenylboronic acid (1.041 g, 3.6 mmol) to afford the title compound as colorless solid (1.070 g, 2.99 mmol, >99%). ¹H NMR (600 MHz, CDCl₃) δ 3.90 (s, 3H), 6.91 (d, *J* = 5.4 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 6.6 Hz, 2H), 7.09 (d, *J* = 5.4 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 4H), 7.24 (t, *J* = 7.8 Hz, 4H), 7.60 (d, *J* = 6.6 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 58.7, 117.4, 120.1, 121.4, 122.7, 123.9, 124.2, 127.6, 127.7, 129.2, 146.0, 147.6, 153.2; IR (KBr) 3001, 2936, 2849, 1587, 1275, 1067 cm⁻¹; HRMS (ESI⁺) *m/z* calcd for C₂₃H₁₉NOSNa [M+Na]⁺ 380.1080, found 380.1073; mp 87.2–87.8 °C.

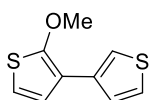


2'-Methoxy-2,3'-bithiophene (1c)

To a mixture of 3-bromo-2-methoxythiophene (579 mg, 3.0 mmol), bis(*tri-tert*-

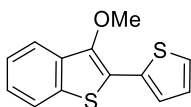
⁷ Tanaka, S.; Tanaka, D.; Tatsuta, G.; Murakami, K.; Tamda, S.; Sugie, A.; Mori, A. *Chem. Eur. J.* **2013**, *19*, 1658–1665.

butylphosphine)palladium (46 mg, 0.09 mmol), 2-thienylboronic acid (461 mg, 3.6 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol) in dry THF (30 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (30 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 10:1) to afford 2'-methoxy-2,3'-bithiophene (**1c**) as colorless oil (582 mg, 2.97 mmol, 99%). ¹H NMR (400 MHz, CDCl₃) δ 4.01 (s, 3H), 6.62 (d, *J* = 6.0 Hz, 1H), 7.03 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.06 (d, *J* = 6.0 Hz, 1H), 7.18 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.29 (dd, *J* = 3.6, 1.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 61.9, 111.5, 115.6, 122.9, 125.1, 126.9, 136.8, 159.5; IR (neat) 3107, 29959, 1566, 1269, 1101 cm⁻¹; HRMS (ESI⁺) *m/z* calcd for C₉H₈OS₂Na [M+Na]⁺ 218.9909, found 218.9903.



2-Methoxy-3,3'-bithiophene (**1d**)

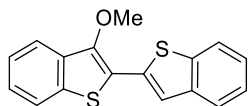
To a mixture of 3-bromo-2-methoxythiophene (579 mg, 3.0 mmol), bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), 3-thienylboronic acid (461 mg, 3.6 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol) in dry THF (30 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (30 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 10:1) to afford 2-methoxy-3,3'-bithiophene (**1d**) as colorless oil (576 mg, 2.93 mmol, 98%). ¹H NMR (400 MHz, CDCl₃) δ 3.99 (s, 3H), 6.61 (d, *J* = 6.0 Hz, 1H), 7.05 (d, *J* = 6.0 Hz, 1H), 7.31 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.43 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.52 (dd, *J* = 2.8, 1.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 61.7, 110.9, 116.4, 120.0, 124.9, 125.8, 126.7, 134.9, 160.3; IR (neat) 3107, 2940, 1580, 1269, 1011 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₉H₈OS₂ [M⁺] 196.0011, found 196.0009.



3-Methoxy-2-(thiophen-2-yl)benzo[*b*]thiophene (**1e**)

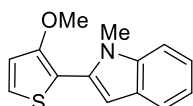
To a solution of 3-methoxybenzo[*b*]thiophene (493 mg, 3.0 mmol) in dry THF (30 mL) was added NBS (539 mg, 3.03 mmol) at 0 °C. The reaction mixture was then stirred at the same temperature for 2 h. To the mixture were added bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), 2-thienylboronic acid (461 mg, 3.6 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol), and then the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (50 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 7:1) to afford 3-methoxy-2-(thiophen-2-yl)benzo[*b*]thiophene (**1e**) as colorless solid (688

mg, 2.79 mmol, 93%). ¹H NMR (400 MHz, CDCl₃) δ 4.01 (s, 3H), 7.08 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.31–7.39 (m, 4H), 7.71–7.74 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 60.6, 120.7, 122.1, 122.8, 124.4, 125.0, 125.1, 126.0, 126.9, 133.8, 134.1, 135.3, 146.5; IR (KBr) 3096, 2961, 2837, 1437, 1344, 1053 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₃H₁₁OS₂ [M+H]⁺ 247.0245, found 247.0235; mp 66.4–67.2 °C.



3-Methoxy-2,2'-bibenzo[*b*]thiophene (**1g**)

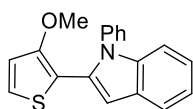
To a solution of 3-methoxybenzo[*b*]thiophene (493 mg, 3.0 mmol) in dry THF (30 mL) was added NBS (539 mg, 3.03 mmol) at 0 °C. The reaction mixture was then stirred at the same temperature for 2 h. To the mixture were added bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), benzo[*b*]thiophen-2-ylboronic acid (641 mg, 3.6 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol), and then the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (50 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 7:1) to afford 3-methoxy-2,2'-bibenzo[*b*]thiophene (**1g**) as colorless solid (826 mg, 2.79 mmol, 93%). ¹H NMR (400 MHz, CDCl₃) δ 4.05 (s, 3H), 7.31–7.39 (m, 4H), 7.54 (d, *J* = 0.4 Hz, 1H), 7.71–7.77 (m, 3H), 7.83 (dm, *J* = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 61.1, 121.0, 121.2, 122.0, 122.1, 122.9, 123.4, 124.6, 125.5, 133.7, 134.3, 135.9, 139.2, 140.1, 148.1; IR (KBr) 3055, 2926, 2833, 1454, 1358, 1061 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₇H₁₃OS₂ [M+H]⁺ 297.0402, found 297.0405; mp 130.0–130.7 °C.



2-(3-Methoxythiophen-2-yl)-1-methyl-1H-indole (**1j**)

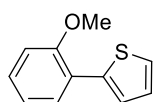
To a solution of 3-methoxythiophene (343 mg, 3.0 mmol) in dry THF (30 mL) was added NBS (539 mg, 3.03 mmol) at 0 °C. The reaction mixture was then stirred at the same temperature for 2 h. To the mixture were added bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), 1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (1.54 g, 6.0 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol), and then the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (50 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 5:1) to afford 2-(3-methoxythiophen-2-yl)-1-methyl-1H-indole (**1j**) as colorless solid (718 mg, 2.95 mmol, 98%). ¹H NMR (400 MHz, CDCl₃) δ 3.71 (s, 3H), 3.84 (s, 3H), 6.61 (s, 1H), 6.95 (d, *J* = 5.6 Hz, 1H), 7.11 (t, *J* = 7.4, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 5.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 30.8, 58.7, 103.4, 109.4, 110.3, 116.7, 119.6, 120.4, 121.6, 124.7, 127.8, 131.5, 137.8, 154.8; IR (KBr) 3094, 2932, 2849, 1526, 1379,

1072 cm⁻¹; HRMS (ESI⁺) *m/z* calcd for C₁₄H₁₄NOS [M+H]⁺ 244.0791, found 244.0795; mp 48.9–49.6 °C.



2-(3-Methoxythiophen-2-yl)-1-phenyl-1H-indole (**1k**)

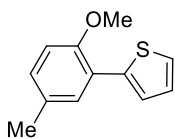
To a solution of 3-methoxythiophene (343 mg, 3.0 mmol) in dry THF (30 mL) was added NBS (539 mg, 3.03 mmol) at 0 °C. The reaction mixture was then stirred at the same temperature for 2 h. To the mixture were added bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), 1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (1.92 g, 6.0 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol), and then the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (50 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 5:1) to afford 2-(3-methoxythiophen-2-yl)-1-phenyl-1H-indole (**1k**) as colorless solid (865 mg, 2.83 mmol, 94%). ¹H NMR (600 MHz, CDCl₃) δ 3.61 (s, 3H), 6.75 (d, *J* = 5.7 Hz, 1H), 6.94 (s, 1H), 7.09 (d, *J* = 5.7 Hz, 1H), 7.13–7.14 (m, 2H), 7.18–7.20 (m, 1H), 7.32–7.33 (m, 2H), 7.38 (tt, *J* = 8.4, 1.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.64–7.65 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 58.4, 104.6, 110.3, 110.8, 116.1, 120.3, 120.4, 122.2, 124.2, 127.5, 128.1, 128.3, 129.0, 132.0, 138.36, 138.41, 155.0; IR (KBr) 3102, 2938, 1595, 1499, 1260, 1074 cm⁻¹; HRMS (ESI⁺) *m/z* calcd for C₁₉H₁₆NOS [M+H]⁺ 306.0947, found 306.0946; mp 81.9–82.7 °C.



2-(2-Methoxyphenyl)thiophene (**3a**)⁸

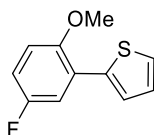
To a mixture of 1-bromo-2-methoxybenzene (561 mg, 3.0 mmol), bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), 2-thienylboronic acid (461 mg, 3.6 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol) in dry THF (30 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (30 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 10:1) to afford 2-(2-methoxyphenyl)thiophene (**3a**) as colorless oil (567 mg, 2.98 mmol, 99%). ¹H NMR (600 MHz, CDCl₃) δ 3.92 (s, 3H), 6.97–7.01 (m, 2H), 7.08–7.09 (m, 1H), 7.25 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.31–7.32 (m, 1H), 7.49–7.32 (m, 1H), 7.64 (dm, *J* = 8.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 55.5, 111.6, 120.9, 123.3, 125.3, 125.4, 126.7, 128.3, 128.6, 139.4, 155.6; IR (neat) 3071, 2936, 1580, 1258, 1024 cm⁻¹.

⁸ Pinxterhuis, E. B.; Giannerini, M.; Hornillos, V.; Feringa, B. L. *Nat. Commun.* **2016**, *7*, 11698–11705.



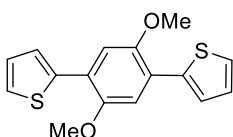
2-(2-Methoxy-5-methylphenyl)thiophene (**3b**)

To a mixture of 2-bromo-1-methoxy-4-methylbenzene (603 mg, 3.0 mmol), bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), 2-thienylboronic acid (461 mg, 3.6 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol) in dry THF (30 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (30 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 20:1) to afford 2-(2-methoxy-5-methylphenyl)thiophene (**3b**) as colorless oil (604 mg, 2.96 mmol, 99%). ¹H NMR (600 MHz, CDCl₃) δ 2.32 (s, 3H), 3.89 (s, 3H), 6.87 (d, *J* = 8.1 Hz, 1H), 7.05 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.07 (dd, *J* = 5.4, 2.4 Hz, 1H), 7.30 (dd, *J* = 5.4, 0.6 Hz, 1H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.48 (dd, *J* = 2.4, 0.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 20.5, 55.7, 111.7, 123.0, 125.2, 125.3, 126.7, 128.7, 129.2, 130.1, 139.6, 153.6; IR (neat) 2955, 2938, 2833, 1493, 1261, 1032 cm⁻¹; HRMS (EI⁺) *m/z* calcd for C₁₂H₁₃OS [M+H]⁺ 205.0682, found 205.0656.



2-(5-Fluoro-2-methoxyphenyl)thiophene (**3c**)

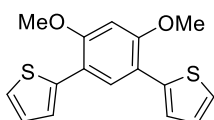
To a mixture of 2-bromo-4-fluoro-1-methoxybenzene (615 mg, 3.0 mmol), bis(tri-*tert*-butylphosphine)palladium (46 mg, 0.09 mmol), 2-thienylboronic acid (461 mg, 3.6 mmol) and 3 M NaOH aqueous solution (2.0 mL, 6 mmol) in dry THF (30 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (30 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 20:1) to afford 2-(5-fluoro-2-methoxyphenyl)thiophene (**3c**) as colorless oil (611 mg, 2.93 mmol, 98%). ¹H NMR (600 MHz, CDCl₃) δ 3.86 (s, 3H), 6.89–6.90 (m, 1H), 6.93–6.95 (m, 1H), 7.08–7.09 (m, 1H), 7.34–7.37 (m, 2H), 7.49 (d, *J* = 3.0 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 56.2, 112.8 (*J*_{C-F} = 8.1 Hz), 114.1 (*J*_{C-F} = 23.0 Hz), 114.7 (*J*_{C-F} = 24.2 Hz), 124.6 (*J*_{C-F} = 6.9 Hz), 125.8, 126.2, 126.8, 138.2, 151.7, 157.1 (*J*_{C-F} = 236.9 Hz); IR (neat) 3075, 2940, 2835, 1489, 1263, 1028 cm⁻¹; HRMS (EI⁺) *m/z* calcd for C₁₁H₉FOS [M]⁺ 208.0337, found 208.0356.



2,2'-(2,5-Dimethoxy-1,4-phenylene)dithiophene (**3d**)⁹

⁹ Lois, S.; Flores, J.-C.; Lere-Porte, J.-P.; Serein-Spirau, F.; Moreau, J. J. E.; Miqueu, K.; Sotiropoulos, J.-M.; Baylere,

To a mixture of 1,4-dibromo-2,5-dimethoxybenzene (888 mg, 3.0 mmol), bis(tri-*tert*-butylphosphine)palladium (92 mg, 0.18 mmol), 2-thienylboronic acid (921 mg, 7.2 mmol) and 3 M NaOH aqueous solution (4.0 mL, 6 mmol) in dry THF (60 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (100 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 1:1) to afford the title compound (**3d**) as colorless solid (895 mg, 2.96 mmol, 99%). ¹H NMR (600 MHz, CDCl₃) δ 3.94 (s, 6H), 7.11 (dd, *J* = 4.8, 3.0 Hz, 2H), 7.25 (s, 2H), 7.45 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.54 (dd, *J* = 3.0, 1.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 56.4, 112.3, 123.0, 125.5, 125.7, 126.9, 139.0, 149.9; IR (KBr) 3102, 2955, 1530, 1215, 1043 cm⁻¹.



2,2'-(4,6-Dimethoxy-1,3-phenylene)dithiophene (**3e**)

To a mixture of 1,5-diiodo-2,4-dimethoxybenzene (780 mg, 2.0 mmol), bis(tri-*tert*-butylphosphine)palladium (61 mg, 0.12 mmol), 2-thienylboronic acid (614 mg, 4.8 mmol) and 3 M NaOH aqueous solution (2.7 mL, 8 mmol) in dry THF (40 mL) was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with H₂O (50 mL) and the resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 1:1) to afford the title compound (**3e**) as colorless solid (593 mg, 1.96 mmol, 98%). ¹H NMR (600 MHz, CDCl₃) δ 3.95 (s, 6H), 6.60 (s, 1H), 7.08 (dd, *J* = 4.8, 3.6 Hz, 2H), 7.28 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.41 (dd, *J* = 3.6, 1.2 Hz, 2H), 7.85 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.8, 96.2, 116.4, 124.6, 124.7, 126.8, 128.9, 139.1, 156.0; IR (KBr) 3105, 3001, 1609, 1269, 1028 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₆H₁₄O₂S₂ [M]⁺ 302.0429, found 302.0436; mp 117.7–118.3 °C.

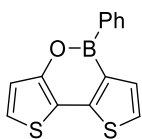
General Procedure A for the demethylation and cyclization (Bu₄NI 20 mol %)

To a mixture of cyclization precursor (0.2 mmol), tetrabutylammonium iodide (15 mg, 0.04 mmol) in chlorobenzene (1.4 mL) were added Et₃N (39 μL, 0.28 mmol) and PhBCl₂ (39 μL, 0.30 mmol), and the mixture was stirred at 135 °C for 24 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel.

General Procedure B for the demethylation and cyclization (Bu₄NI 1.2 equiv)

To a mixture of cyclization precursor (0.2 mmol), tetrabutylammonium iodide (89 mg, 0.24 mmol) in chlorobenzene (1.4 mL) were added Et₃N (28 μL, 0.20 mmol) and PhBCl₂ (39 μL, 0.30 mmol), and the mixture was stirred at 135 °C for 24 h. After cooling to room temperature, the resulting mixture was

concentrated under reduced pressure. The residue was purified by column chromatography on silica gel.

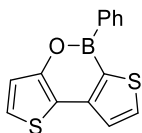


5-Phenyl-5H-dithieno[3,2-c:2',3'-e][1,2]oxaborinine (2a)

The general procedure A for the demethylation and cyclization was performed with 3-methoxy-2,2'-bithiophene (**1a**) (39 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane) to afford the title compound as colorless solid (50 mg, 0.186 mmol, 93%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 5.6 Hz, 1H), 7.35 (d, *J* = 5.2 Hz, 2H), 7.50–7.55 (m, 3H), 7.90 (d, *J* = 5.2 Hz, 1H), 8.18–8.24 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 118.3, 119.8, 122.99, 123.04, 128.1, 130.6, 131.6, 134.4, 150.7, 152.1; IR (KBr) 3105, 1526, 1304 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₄H₁₀BOS₂ [M+H]⁺ 269.0260, found 269.0244; mp 98.6–99.5 °C.

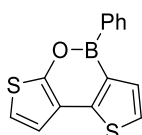
Synthesis of 5-phenyl-5H-dithieno[3,2-c:2',3'-e][1,2]oxaborinine (2a) in 1.0 mmol scale

To a mixture of 3-methoxy-2,2'-bithiophene (196 mg, 1.0 mmol), tetrabutylammonium iodide (74 mg, 0.2 mmol) in chlorobenzene (7.0 mL) were added Et₃N (194 μL, 1.4 mmol) and PhBCl₂ (195 μL, 1.5 mmol), and the mixture was stirred at 135 °C for 24 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to afford the title compound as colorless solid (221 mg, 0.823 mmol, 82%).



5-Phenyl-5H-dithieno[2,3-c:2',3'-e][1,2]oxaborinine (2b)

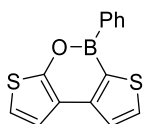
The general procedure A for the demethylation and cyclization was performed with 3-methoxy-2,3'-bithiophene (**1b**) (39 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 8:1) to afford the title compound as colorless solid (51 mg, 0.190 mmol, 95%). ¹H NMR (600 MHz, CDCl₃) δ 7.29 (d, *J* = 5.1 Hz, 1H), 7.34 (d, *J* = 5.1 Hz, 1H), 7.52–7.54 (m, 4H), 7.99 (d, *J* = 4.8 Hz, 1H), 8.29–8.31 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 118.9, 119.9, 122.5, 122.7, 128.1, 131.1, 134.5, 137.5, 146.6, 152.4; IR (KBr) 3111, 3049, 3013, 1425, 1300, 1121 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₄H₉BOS₂ [M]⁺ 268.0182, found 268.0182; mp 104.4–105.0 °C.



4-Phenyl-4H-dithieno[3,2-c:3',2'-e][1,2]oxaborinine (2c)

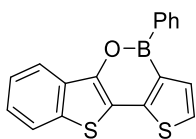
The general procedure A for the demethylation and cyclization was performed with 2'-methoxy-2,3'-bithiophene (**1c**) (39 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel

(hexane/CH₂Cl₂ = 10:1) to afford the title compound as colorless solid (49 mg, 0.184 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 6.95 (d, *J* = 6.0 Hz, 1H), 7.23 (d, *J* = 6.0 Hz, 1H), 7.36 (d, *J* = 5.0 Hz, 1H), 7.51–7.54 (m, 3H), 7.90 (d, *J* = 5.0 Hz, 1H), 8.20–8.22 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 115.2, 119.5, 120.1, 123.1, 128.1, 130.8, 131.5, 134.5, 152.4, 157.4; IR (KBr) 3102, 3080, 3040, 1537, 1352, 1142 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₄H₁₀BOS₂ [M+H]⁺ 268.0296, found 268.0283; mp 77.8–78.3 °C.



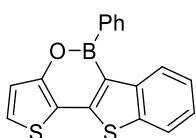
5-Phenyl-5H-dithieno[2,3-*c*:3',2'-*e*][1,2]oxaborinine (**2d**)

The general procedure for A the demethylation and cyclization was performed with 2'-methoxy-2,3'-bithiophene (**2d**) (39 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 10:1) to afford the title compound as colorless solid (49 mg, 0.183 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 6.93 (d, *J* = 6.0 Hz, 1H), 7.32 (d, *J* = 6.0 Hz, 1H), 7.53–7.55 (m, 3H), 7.63 (d, *J* = 5.0 Hz, 1H), 8.01 (d, *J* = 5.0 Hz, 1H), 8.29–8.31 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 114.5, 120.2, 120.3, 122.9, 128.2, 131.3, 134.6, 137.5, 148.3, 158.1; IR (KBr) 3109, 3049, 3013, 1549, 1391, 1103 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₄H₁₀BOS₂ [M+H]⁺ 269.0260, found 269.0249; mp 90.7–91.2 °C.



4-Phenyl-4H-benzo[4,5]thieno[2,3-*e*]thieno[3,2-*c*][1,2]oxaborinine (**2e**)

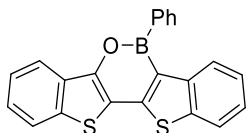
The general procedure A for the demethylation and cyclization was performed with 3-methoxy-2-(thiophen-2-yl)benzo[*b*]thiophene (**1e**) (49 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 10:1) to afford the title compound as colorless solid (51 mg, 0.161 mmol, 80%). ¹H NMR (600 MHz, CDCl₃) δ 7.44 (d, *J* = 4.8 Hz, 1H), 7.45 (td, *J* = 8.4, 1.2 Hz, 1H), 7.50 (td, *J* = 8.4, 1.2 Hz, 1H), 7.55–7.57 (m, 3H), 7.85 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.98 (d, *J* = 4.8 Hz, 1H), 8.21 (dt, *J* = 8.4, 1.2 Hz, 1H), 8.30–8.32 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 117.5, 121.3, 123.2, 124.1, 125.0, 126.4, 128.2, 130.8, 131.3, 131.8, 134.6, 135.9, 145.9, 150.8; IR (KBr) 3084, 3049, 1530, 1489, 1298, 1022 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₈H₁₁BOS₂ [M]⁺ 317.0375, found 317.0382; mp 154.5–155.0 °C.



5-Phenyl-5H-benzo[4,5]thieno[3,2-*c*]thieno[2,3-*e*][1,2]oxaborinine (**2f**)

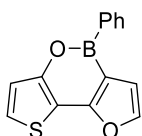
The general procedure A for the demethylation and cyclization was performed with 2-(3-methoxythiophen-2-yl)benzo[*b*]thiophene (**1f**) (49 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (CH₂Cl₂) to afford the title compound as colorless solid (56 mg, 0.176 mmol, 88%). ¹H NMR (600 MHz, CDCl₃) δ 7.26 (d, *J* = 4.5 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H),

7.43 (d, $J = 4.5$ Hz, 1H), 7.23–7.55 (m, 3H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.97–7.98 (m, 2H), 8.09 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 118.6, 119.8, 122.3, 124.9, 125.0, 125.1, 128.0, 129.8, 133.4, 138.9, 142.0, 152.3, 153.4; IR (KBr) 3109, 3049, 1524, 1420, 1256, 1233 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{BOS}_2$ $[\text{M}+\text{H}]^+$ 318.0338, found 318.0354; mp 172.2–172.9 $^\circ\text{C}$.



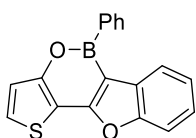
6-Phenyl-6H-benzo[4,5]thieno[3,2-c]benzo[4,5]thieno[2,3-e][1,2]oxaborinine (2g)

The general procedure A for the demethylation and cyclization was performed with 3-methoxy-2,2'-bibenzo[*b*]thiophene (**1g**) (59 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (CH_2Cl_2) and reprecipitation from CHCl_3 to afford the title compound as colorless solid (60 mg, 0.169 mmol, 84%). ^1H NMR (400 MHz, CDCl_3) δ 7.33 (td, $J = 7.6, 1.6$ Hz, 1H), 7.38 (td, $J = 7.6, 1.6$ Hz, 1H), 7.45–7.51 (m, 2H), 7.58–7.59 (m, 3H), 7.86–7.88 (m, 1H), 7.93 (d, $J = 7.2$ Hz, 1H), 8.06–8.08 (m, 2H), 8.17–8.20 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 117.7, 121.7, 122.4, 123.3, 125.06, 125.10, 125.2, 126.9, 128.0, 130.0, 131.0, 133.6, 136.8, 139.3, 142.0, 147.6, 152.5; IR (KBr) 3049, 1522, 1462, 1341, 1240, 1022 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{22}\text{H}_{13}\text{BOS}_2$ $[\text{M}]^+$ 368.0495, found 368.0482; mp 216.2–216.7 $^\circ\text{C}$.



4-Phenyl-4H-furo[3,2-c]thieno[2,3-e][1,2]oxaborinine (2h)

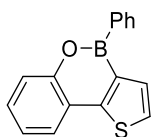
The general procedure A for the demethylation and cyclization was performed with 2-(3-methoxythiophen-2-yl)furan (**1h**) (36 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane) to afford the title compound as colorless solid (42 mg, 0.167 mmol, 83%). ^1H NMR (600 MHz, CDCl_3) δ 7.19 (d, $J = 1.8$ Hz, 1H), 7.30 (d, $J = 5.4$ Hz, 1H), 7.40 (d, $J = 5.4$ Hz, 1H), 7.51–7.53 (m, 3H), 7.63 (d, $J = 1.8$ Hz, 1H), 8.22–8.23 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 111.8, 112.9, 119.8, 124.1, 128.1, 130.9, 134.4, 142.5, 155.1, 161.4; IR (KBr) 3142, 3113, 3017, 1555, 1300, 1148 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{14}\text{H}_9\text{BO}_2\text{S}$ $[\text{M}]^+$ 251.0447, found 251.0449; mp 71.4–71.7 $^\circ\text{C}$.



5-Phenyl-5H-thieno[2',3':5,6][1,2]oxaborinino[4,3-b]benzofuran (2i)

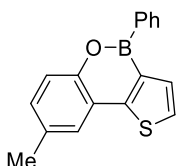
The general procedure A for the demethylation and cyclization was performed with 2-(3-methoxythiophen-2-yl)benzofuran (**1i**) (46 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel ((hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$) to afford the title compound as colorless solid (55 mg, 0.182 mmol, 91%). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (td, $J = 7.8, 1.2$ Hz, 1H), 7.35 (d, $J = 5.4$ Hz, 1H), 7.39 (td, $J = 7.8, 1.2$ Hz, 1H), 7.54 (d, $J = 5.4$ Hz, 1H), 7.57–7.59 (m, 3H), 7.65 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.09 (dd,

$J = 7.8, 1.2$ Hz, 1H), 8.21–8.23 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 111.4, 111.6, 119.9, 122.8, 123.9, 125.1, 126.5, 128.1, 129.0, 130.5, 134.0, 155.7, 157.2, 163.9; IR (KBr) 3107, 3048, 1553, 1441, 1242, 1101 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{BO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 303.0645, found 303.0654; mp 155.6–156.3 $^\circ\text{C}$.



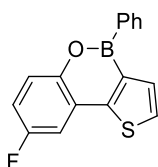
4-Phenyl-4H-furo[3,2-c]thieno[2,3-e][1,2]oxaborinine (4a)

The general procedure B for the demethylation and cyclization was performed with 2-(2-methoxyphenyl)thiophene (**3a**) (38 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 10:1$) to afford the title compound as colorless solid (49 mg, 0.187 mmol, 94%). ^1H NMR (600 MHz, CDCl_3) δ 7.29 (t, $J = 7.8$ Hz, 1H), 7.45–7.48 (m, 2H), 7.52–7.56 (m, 3H), 7.63 (d, $J = 7.2$ Hz, 1H), 7.89 (dd, $J = 7.8$ Hz, 1H), 7.91 (d, $J = 5.4$ Hz, 1H), 8.26–8.27 (m, 2); ^{13}C NMR (150 MHz, CDCl_3) δ 120.0, 121.8, 123.3, 124.5, 125.1, 128.1, 128.9, 130.9, 131.8, 134.7, 150.6, 154.1; IR (KBr) 3100, 3046, 1504, 1323, 1248 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{16}\text{H}_{11}\text{BOS}$ $[\text{M}]^+$ 261.0654, found 261.0658; mp 92.4–93.1 $^\circ\text{C}$.



8-Methyl-4-phenyl-4H-benzo[e]thieno[3,2-c][1,2]oxaborinine (4b)

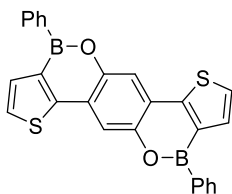
The general procedure B for the demethylation and cyclization was performed with 2-(2-methoxy-5-methylphenyl)thiophene (**3b**) (41 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 10:1$) to afford the title compound as colorless solid (51 mg, 0.184 mmol, 92%). ^1H NMR (400 MHz, CDCl_3) δ 2.46 (s, 3H), 7.56 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.45 (d, $J = 5.2$ Hz, 1H), 7.50–7.54 (m, 4H), 7.67 (bs, 1H), 7.89 (d, $J = 5.2$ Hz, 1H), 8.24–8.26 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 119.6, 121.4, 124.4, 124.9, 128.1, 130.0, 130.8, 131.8, 132.8, 134.6, 148.7, 154.1; IR (KBr) 3076, 3048, 1510, 1327, 1269 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{BOS}$ $[\text{M}+\text{H}]^+$ 277.0859, found 277.0850; mp 105.8–106.1 $^\circ\text{C}$.



8-Fluoro-4-phenyl-4H-benzo[e]thieno[3,2-c][1,2]oxaborinine (4c)

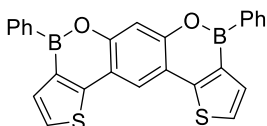
The general procedure B for the demethylation and cyclization was performed with 2-(5-fluoro-2-methoxyphenyl)thiophene (**3c**) (42 mg, 0.20 mmol). The residue was purified by column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 10:1$) to afford the title compound as colorless solid (47 mg, 0.169 mmol, 85%). ^1H NMR (400 MHz, CDCl_3) δ 7.14–7.19 (m, 1H), 7.50–7.57 (m, 6H), 7.90 (d, $J = 5.2$ Hz, 1H), 8.23–8.25 (m,

2H); ^{13}C NMR (100 MHz, CDCl_3) δ 109.8 (d, $J_{\text{C-F}} = 24.3$ Hz), 116.1 (d, $J_{\text{C-F}} = 24.3$ Hz), 121.3 (d, $J_{\text{C-F}} = 8.3$ Hz), 122.5 (d, $J_{\text{C-F}} = 9.1$ Hz), 125.9, 128.1, 131.1, 131.9, 134.6, 146.8, 153.0, 158.2 (d, $J_{\text{C-F}} = 240.5$ Hz); IR (KBr) 3086, 3049, 1510, 1265, 1175, 1009 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{16}\text{H}_{10}\text{BFOS}$ $[\text{M}]^+$ 280.0509, found 280.0529; mp 93.4–93.9 $^{\circ}\text{C}$.



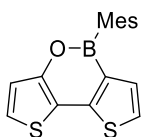
(4d)

To a mixture of 2,2'-(2,5-dimethoxy-1,4-phenylene)dithiophene (**3d**) (61 mg, 0.2 mmol), tetrabutylammonium iodide (177 mg, 0.48 mmol) in chlorobenzene (2.8 mL) were added Et_3N (56 μL , 0.40 mmol) and PhBCl_2 (78 μL , 0.60 mmol), and the mixture was stirred at 135 $^{\circ}\text{C}$ for 24 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by reprecipitation from CHCl_3 to afford the title compound as yellow solid (85 mg, 0.191 mmol, 96%). ^1H NMR (600 MHz, pyridine- d_5) δ 7.34 (t, $J = 7.2$ Hz, 2H), 7.43–7.47 (m, 8H), 7.76 (d, $J = 6.6$ Hz, 4H), 7.79 (s, 2H); IR (KBr) 3098, 3049, 3015, 1516, 1279, 1238 cm^{-1} ; HRMS (EI $^+$) m/z calcd for $\text{C}_{26}\text{H}_{16}\text{B}_2\text{O}_2\text{S}_2$ $[\text{M}]^+$ 445.0808, found 445.0809; mp >300 $^{\circ}\text{C}$; Anal. calcd for $\text{C}_{26}\text{H}_{16}\text{B}_2\text{O}_2\text{S}_2$: C, 70.00; H, 3.61; N, 0, found: C, 69.70; H, 3.25; N, 0.



(4e)

To a mixture of 2,2'-(4,6-dimethoxy-1,3-phenylene)dithiophene (**3e**) (61 mg, 0.2 mmol), tetrabutylammonium iodide (177 mg, 0.48 mmol) in chlorobenzene (2.8 mL) were added Et_3N (56 μL , 0.40 mmol) and PhBCl_2 (78 μL , 0.60 mmol), and the mixture was stirred at 135 $^{\circ}\text{C}$ for 24 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2) and reprecipitation from CHCl_3 to afford the title compound as yellow solid (85 mg, 0.191 mmol, 96%). ^1H NMR (600 MHz, CDCl_3) δ 7.47 (d, $J = 7.5$ Hz, 2H), 7.55–7.57 (m, 6H), 7.79 (s, 1H), 7.89 (d, $J = 7.5$ Hz, 2H), 8.24 (s, 1H), 8.27–8.29 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 110.2, 118.5, 119.2, 125.1, 128.1, 131.2, 131.9, 133.9, 134.8, 136.3, 151.0, 153.3; IR (KBr) 3082, 3042, 1560, 1499, 1329, 1269 cm^{-1} ; HRMS (FAB $^+$) m/z calcd for $\text{C}_{26}\text{H}_{17}\text{B}_2\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 446.0886, found 446.0884; mp 265.6–266.0 $^{\circ}\text{C}$.

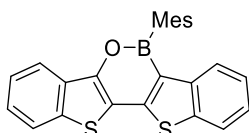


5-Phenyl-5H-dithieno[3,2-c:2',3'-e][1,2]oxaborinine (2l)

To a mixture of 3-methoxy-2,2'-bithiophene (**1a**) (39 mg, 0.20 mmol), tetrabutylammonium iodide (89 mg, 0.24 mmol) in chlorobenzene (1.4 mL) were added Et₃N (28 μ L, 0.20 mmol) and 1 M BCl₃ DCM solution (300 μ L, 0.30 mmol), and the mixture was stirred at 135 °C for 24 h. After cooling to 0 °C, to the mixture was added 1 M MesMgBr THF solution (1.0 mL, 1.0 mmol) and stirred for 30 min. The residue was purified by column chromatography on silica gel (hexane) to afford the title compound as colorless solid (52 mg, 0.194 mmol, 97%). ¹H NMR (600 MHz, CDCl₃) δ 2.22 (s, 6H), 2.34 (s, 3H), 6.92 (s, 2H), 7.23 (d, 5.4 Hz, 1H), 7.24 (d, *J* = 4.8 Hz, 1H), 7.31 (d, *J* = 4.8 Hz, 1H), 7.34 (d, *J* = 5.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 21.3, 22.5, 118.3, 112.0, 122.8, 122.9, 127.4, 131.9, 138.4, 140.4, 149.7, 152.4; IR (KBr) 3096, 2914, 2853, 1526, 1298, 1047 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₁₇H₁₆BOS₂ [M+H]⁺ 310.0766, found 310.0779; mp 63.8–64.4 °C.

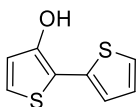
Synthesis of 5-phenyl-5H-dithieno[3,2-c:2',3'-e][1,2]oxaborinine (2l) in 1.0 mmol scale

To a mixture of 3-methoxy-2,2'-bithiophene (196 mg, 1.0 mmol), tetrabutylammonium iodide (443 mg, 1.2 mmol) in chlorobenzene (7.0 mL) were added Et₃N (139 μ L, 1.0 mmol) and 1 M BCl₃ DCM solution (1.5 mL, 1.5 mmol), and the mixture was stirred at 135 °C for 24 h. After cooling to 0 °C, to the mixture was added 1 M MesMgBr THF solution (5.0 mL, 5.0 mmol) and stirred for 30 min. The residue was purified by column chromatography on silica gel (hexane) to afford the title compound as colorless solid (287 mg, 0.926 mmol, 93%).



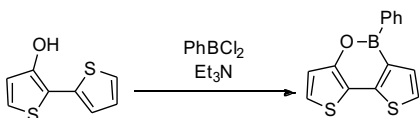
6-Mesityl-6H-benzo[4,5]thieno[3,2-c]benzo[4,5]thieno[2,3-e][1,2]oxaborinine (2m)

To a mixture of 3-methoxy-2,2'-bibenzo[*b*]thiophene (**1g**) (59 mg, 0.20 mmol), tetrabutylammonium iodide (89 mg, 0.24 mmol) in chlorobenzene (1.4 mL) were added Et₃N (28 μ L, 0.20 mmol) and 1 M BCl₃ DCM solution (300 μ L, 0.30 mmol), and the mixture was stirred at 135 °C for 24 h. After cooling to room temperature, to the mixture was added 1 M MesMgBr THF solution (1.0 mL, 1.0 mmol) and stirred for 30 min. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂) to afford the title compound as colorless solid (74 mg, 0.181 mmol, 91%). ¹H NMR (600 MHz, CDCl₃) δ 2.22 (s, 6H), 2.43 (s, 3H), 7.02 (s, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.47–7.51 (m, 2H), 7.88–7.90 (m, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 8.16–8.18 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 21.4, 22.3, 117.6, 121.8, 122.3, 123.3, 124.1, 125.1, 125.2, 125.5, 126.9, 127.6, 130.4, 131.2, 135.1, 136.5, 138.6, 139.3, 140.2, 142.1, 148.2, 151.6; IR (KBr) 3053, 2916, 2855, 1520, 1236, 1026 cm⁻¹; HRMS (FAB⁺) *m/z* calcd for C₂₅H₁₉BOS₂ [M]⁺ 409.1001, found 409.1015; mp 230.4–230.8 °C.



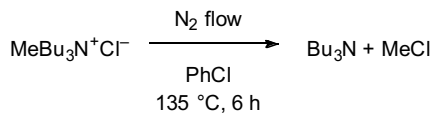
[2,2'-Bithiophen]-3-ol

To a solution of 3-bromo-2,2'-bithiophene (366 mg, 1.5 mmol) in dry Et₂O (7.5 mL) was added dropwise *n*-butyllithium (1.60 M in hexane, 1.03 mL, 1.7 mmol) at -78 °C. The mixture was then stirred at the same temperature for 1 h. To the mixture was added trimethoxyborane (0.50 mL, 4.5 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. To the mixture were added benzene (15 mL) and 30 v/v % hydrogen peroxide aq. (0.12 mL, 4.4 mmol) at room temperature. This mixture was stirred at 80 °C for 4 h. The reaction was quenched with aqueous saturated solution of Na₂SO₃ (30 mL), and the resulting mixture was extracted with Et₂O (3 × 20 mL). The combined organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/Et₂O = 2:1) to afford (2,2'-bithiophen)-3-ol as colorless solid (174 mg, 0.95 mmol, 64%). ¹H NMR (600 MHz, DMSO-*d*₆) δ 6.72 (d, *J* = 5.4 Hz, 1H), 7.01 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.14 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.25 (d, *J* = 5.4 Hz, 1H), 7.36 (dd, *J* = 5.1, 1.2 Hz, 1H), 10.23 (s, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 110.8, 120.8, 121.6, 122.0, 123.4, 127.0, 135.4, 150.8; IR (KBr) 687, 989, 1400, 3109, 3287 cm⁻¹; mp 88.2–88.4 °C; HRMS (ESI⁺) *m/z* calcd for C₈H₅OS₂ [M+H]⁺ 182.9934, found: 182.9918.



Synthesis of **2a** from [2,2'-Bithiophen]-3-ol

To a solution of [2,2'-bithiophen]-3-ol (36 mg, 0.20 mmol) in chlorobenzene (1.4 mL) were added dichlorophenylborane (39 μL, 0.28 mmol) and triethylamine (55 μL, 0.40 mmol), and the mixture was stirred at 145 °C for 48 h. After being allowed to cool to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/dichloromethane = 5:1) to afford **2a** as colorless solid (48 mg, 0.18 mmol, 91%).



Conversion of MeBu₃NCl to Bu₃N

A solution of MeBu₃N (97 mg, 0.41 mmol) in chlorobenzene (2.8 mL) was stirred at 135 °C for 6 h with N₂ flow. After cooled to room temperature, the resulting mixture was concentrated under reduced pressure. The residue (50 mg) was analyzed by ¹H NMR to determine the yields of Bu₃N (62%), MeBu₂N (4%), and MeBu₃NCl (2%).

2. X-ray Crystallography

Details of the crystal data and a summary of the intensity data collection parameters for **4d** are listed in Table S1 and Figure S1. X-ray single crystal analysis was conducted with a Rigaku VariMax with Saturn. Graphite-monochromated Mo K α radiation ($\lambda = 0.71075 \text{ \AA}$) was used. The structure was solved by direct methods with SIR2014¹⁰ and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. All calculations were performed by using Yadokari-XG¹¹ and the ORTEP illustration was drawn by ORTEP-3¹² and colored by Adobe Illustrator.

(10) *SIR2014*, Burla, M. C.; Caliandro, R.; Carrozzini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G. *J. Appl. Crystallogr.* **2015**, *48*, 306–309.

(11) Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, Kabuto, C.; Akine, S.; Nemoto, T.; Kwon, E. *J. Cryst. Soc. Jpn.* **2009**, *51*, 218–224.

(12) Farrugia, L. J. *J. Appl. Crystallogr.* **2012**, *45*, 849–854.

Table S1. Crystal data and structure refinement for **4d**

Identification code	CCDC 1895523
Empirical formula	C ₂₆ H ₁₆ B ₂ O ₂ S ₂
Formula weight	446.13
Temperature	100(2) K
Wavelength	0.71075 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c (#14)
Unit cell dimensions	$a = 10.658(14)$ Å $\alpha = 90^\circ$. $b = 4.886(7)$ Å $\beta = 91.78(2)^\circ$. $c = 19.54(3)$ Å $\gamma = 90^\circ$.
Volume	1017(3) Å ³
Z	2
Density (calculated)	1.457 Mg/m ³
Absorption coefficient	0.285 mm ⁻¹
F(000)	460
Crystal size	0.480 x 0.100 x 0.030 mm ³
Theta range for data collection	2.786 to 31.380°.
Index ranges	-4 ≤ h ≤ 14, -6 ≤ k ≤ 6, -28 ≤ l ≤ 26
Reflections collected	4521
Independent reflections	2820 [R(int) = 0.0384]
Completeness to theta = 25.242°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.650
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2820 / 0 / 145
Goodness-of-fit on F ²	0.932
Final R indices [I > 2σ(I)]	R ₁ = 0.0447, wR ₂ = 0.0915
R indices (all data)	R ₁ = 0.0788, wR ₂ = 0.1032
Extinction coefficient	n/a
Largest diff. peak and hole	0.330 and -0.480 e.Å ⁻³

4d)

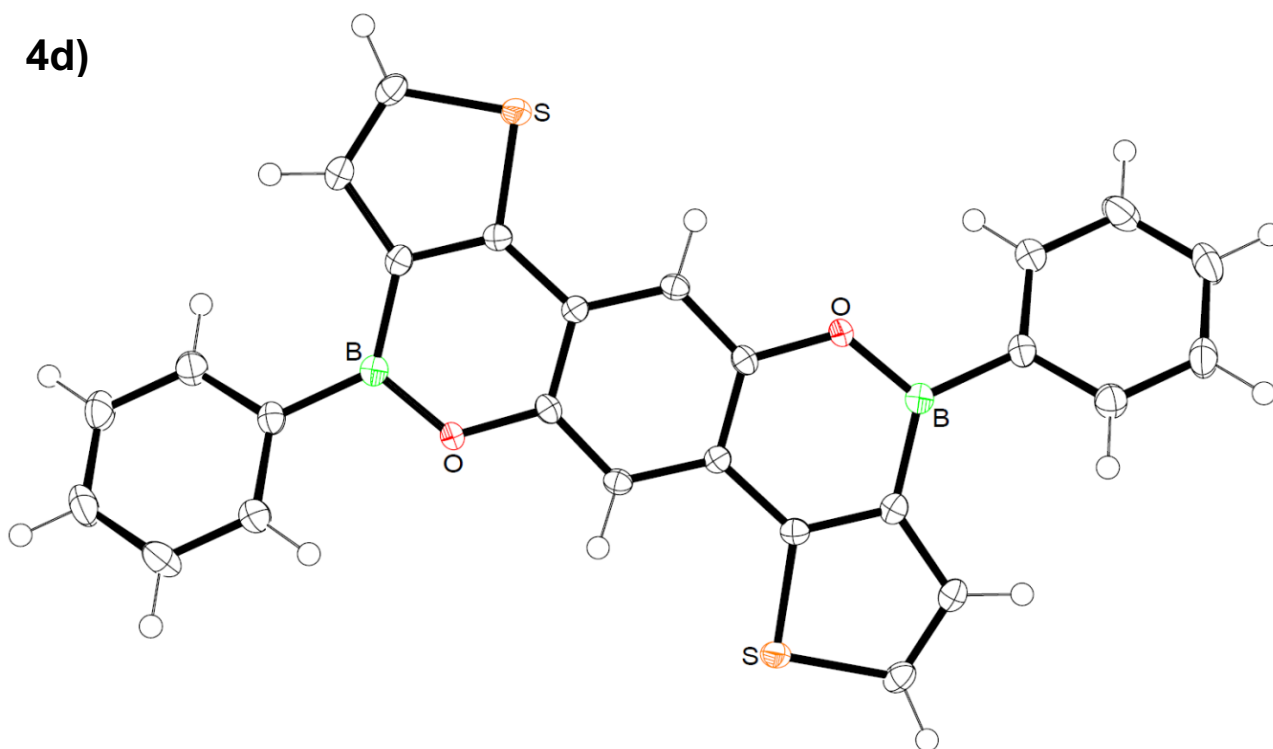


Figure S1. ORTEP drawing of **4d** with 50% thermal ellipsoids.

3. UV-Vis Absorption

UV-visible spectra were measured with HITACHI U-1900 UV-Vis Ratio Beam spectrophotometer. Dilute solution of **2a–m** and **4a–e** (1.0×10^{-5} M) in degassed spectral grade DCM in a 1 cm square quartz cell was used for measurements. The UV-vis absorption measurement was performed at a scan speed of 100 nm/min from 600 to 220 nm.

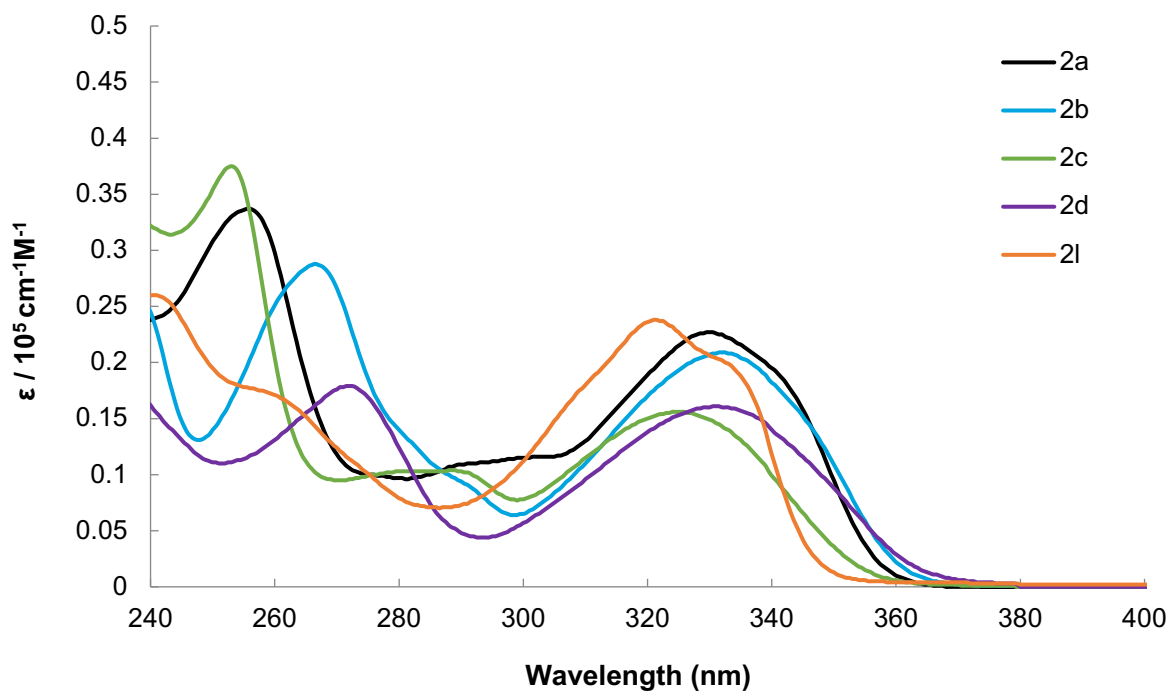


Figure S2. UV-Vis spectra of **2a–d** and **l** (1.0×10^{-5} M in DCM)

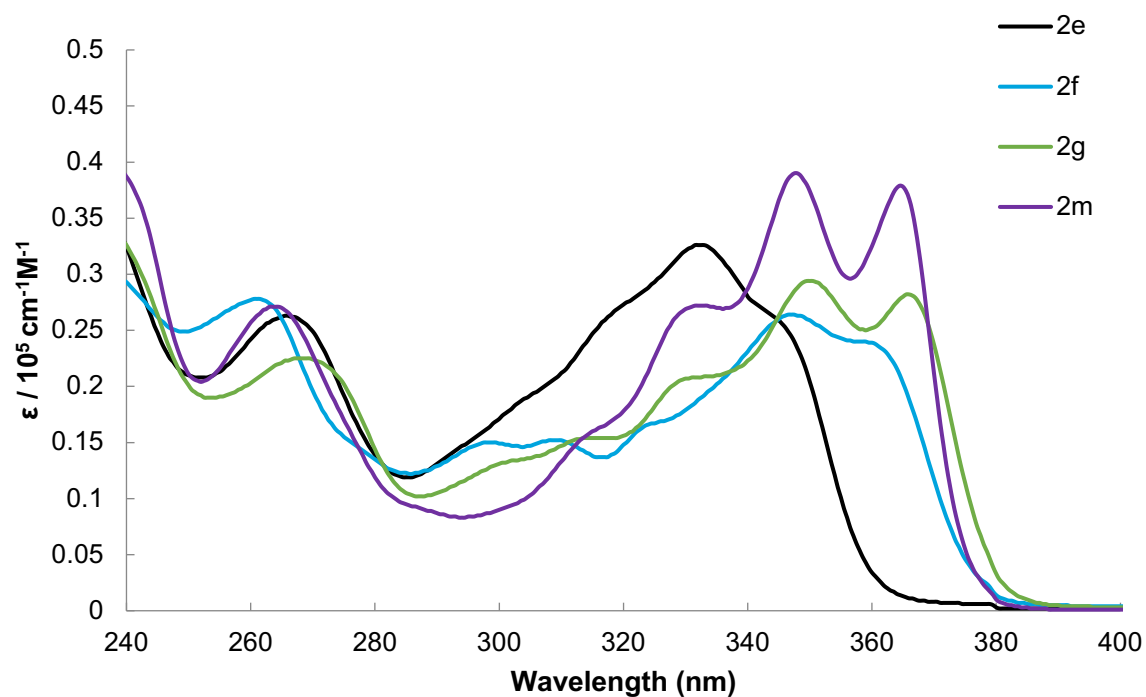


Figure S3. UV-Vis spectra of **2e-g** and **m** (1.0×10^{-5} M in DCM)

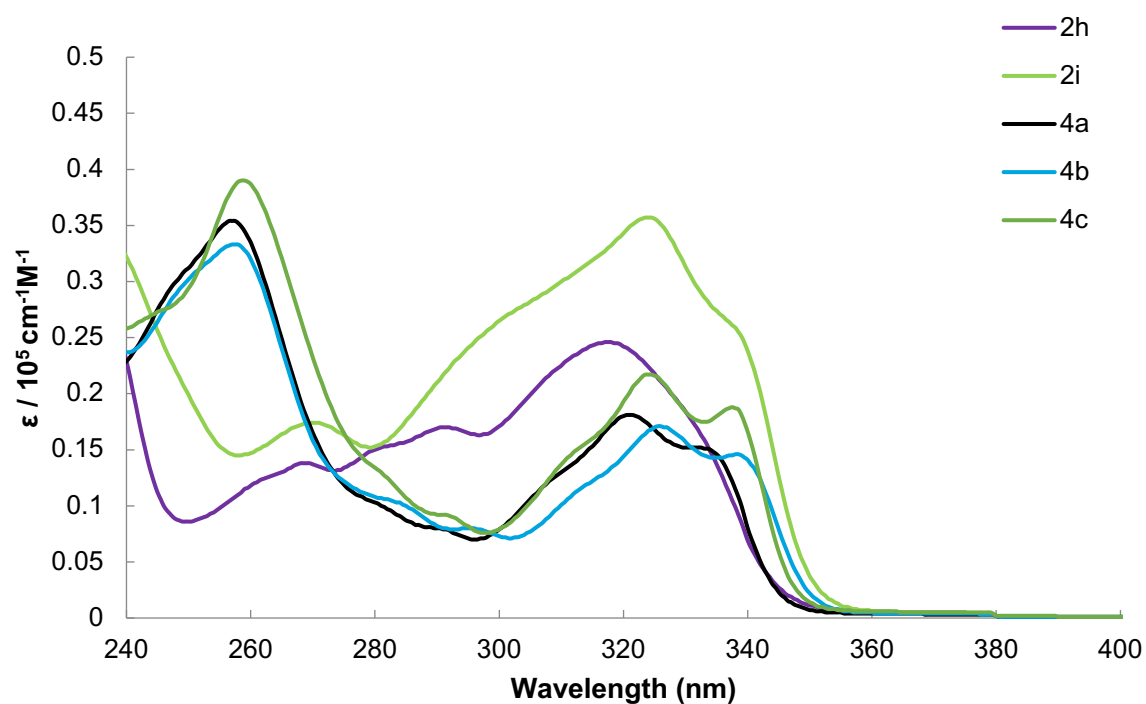


Figure S4. UV-Vis spectra of **2h-i** and **4a-c** (1.0×10^{-5} M in DCM)

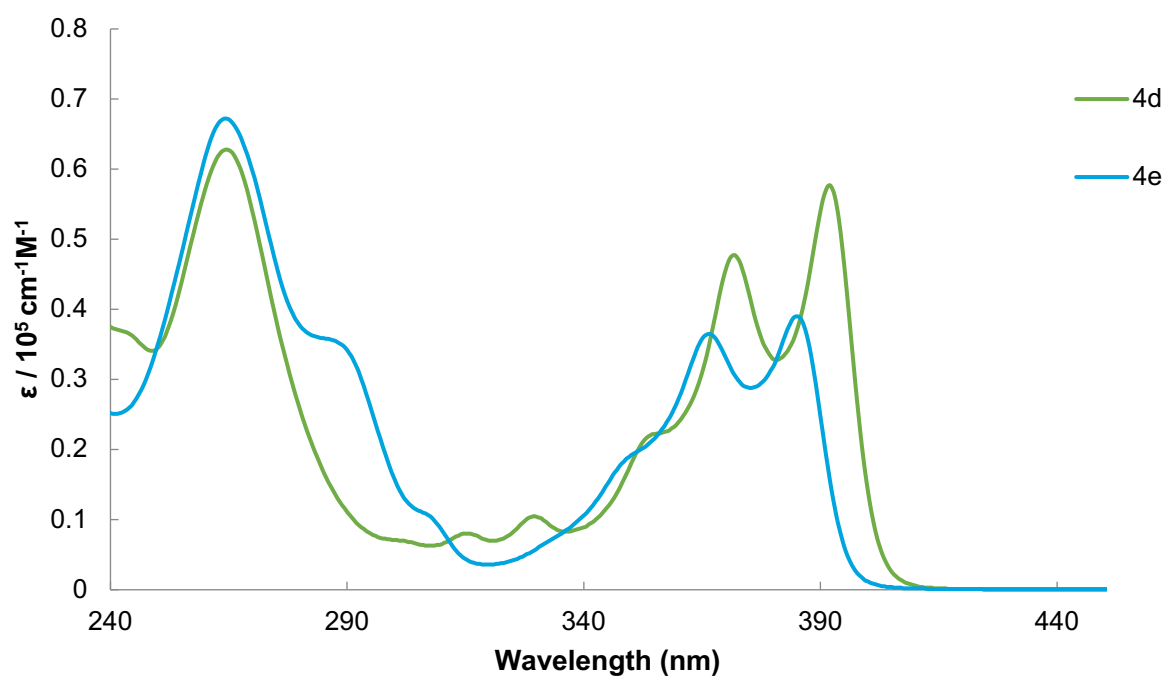


Figure S5. UV-Vis spectra of **4d** and **4e** (1.0×10^{-5} M in DCM)

4. FL spectra

FL spectra were measured with HITACHI F-2700 spectrophotometer. Dilute solution of **2a–m** and **4a–e** (1.0×10^{-5} M) in degassed spectral grade DCM in a 1 cm square quartz cell was used for measurements. The FL absorption measurement was performed at a scan speed of 60 nm/min from 580 to 280 nm.

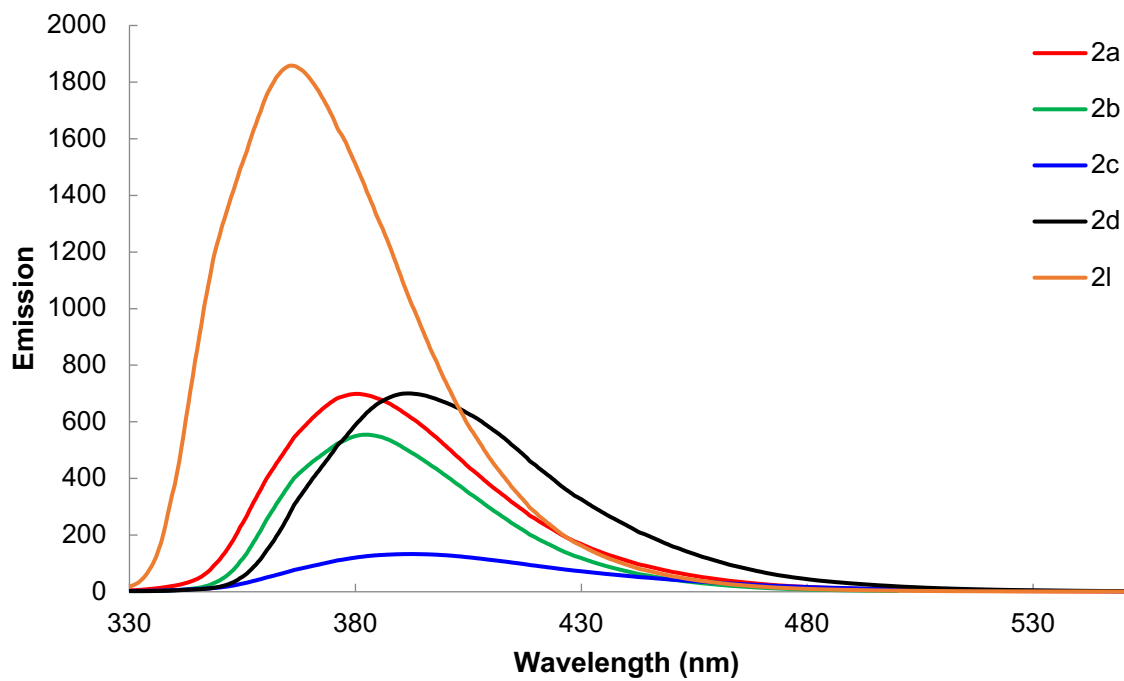


Figure S6. FL spectra of **2a–d** and **l** (1.0×10^{-5} M in DCM)

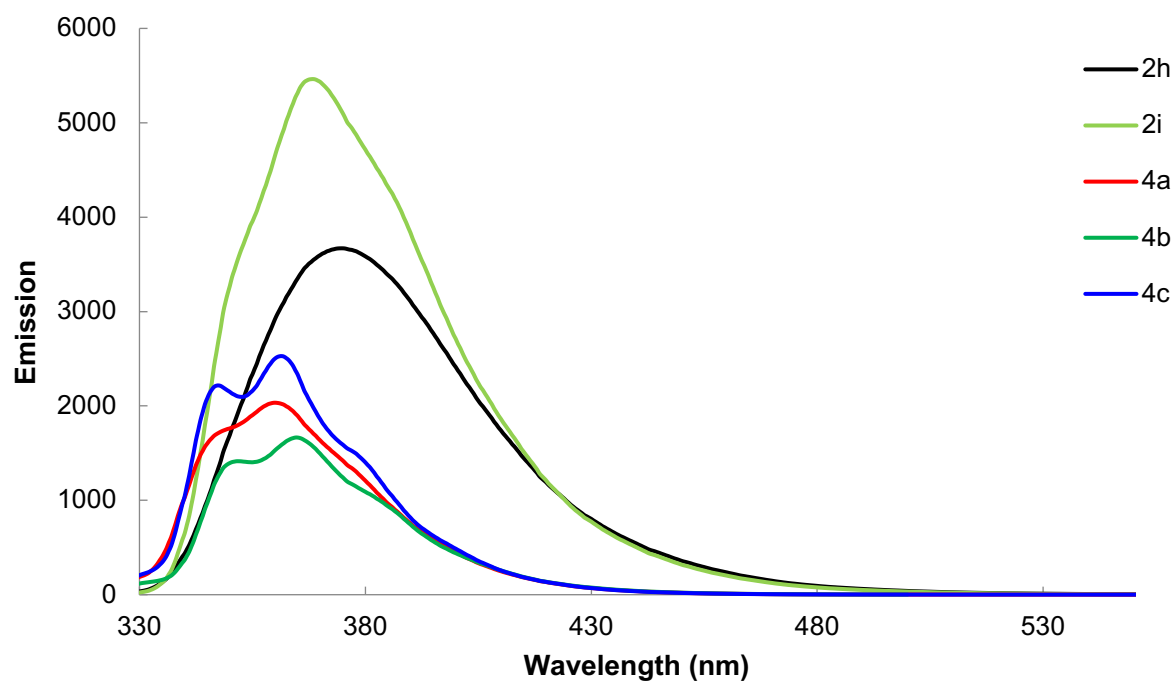


Figure S7. FL spectra of 2h-i and 4a-c (1.0×10^{-5} M in DCM)

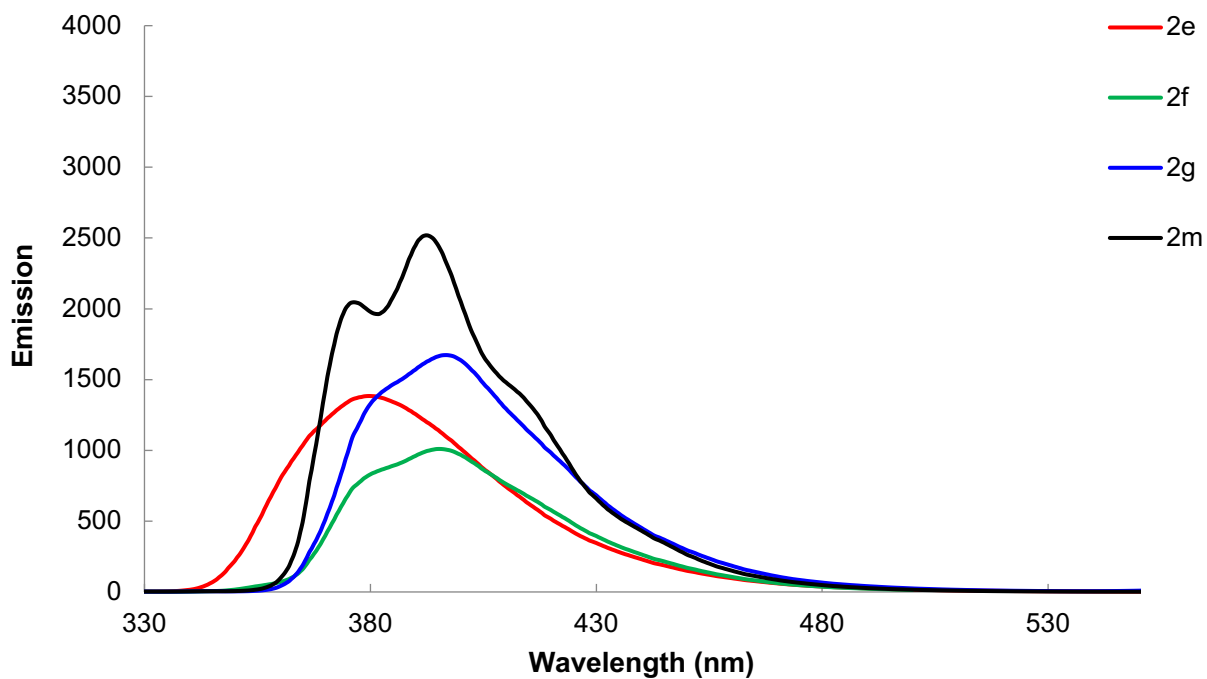


Figure S8. FL spectra of 2e-g and m (1.0×10^{-5} M in DCM)

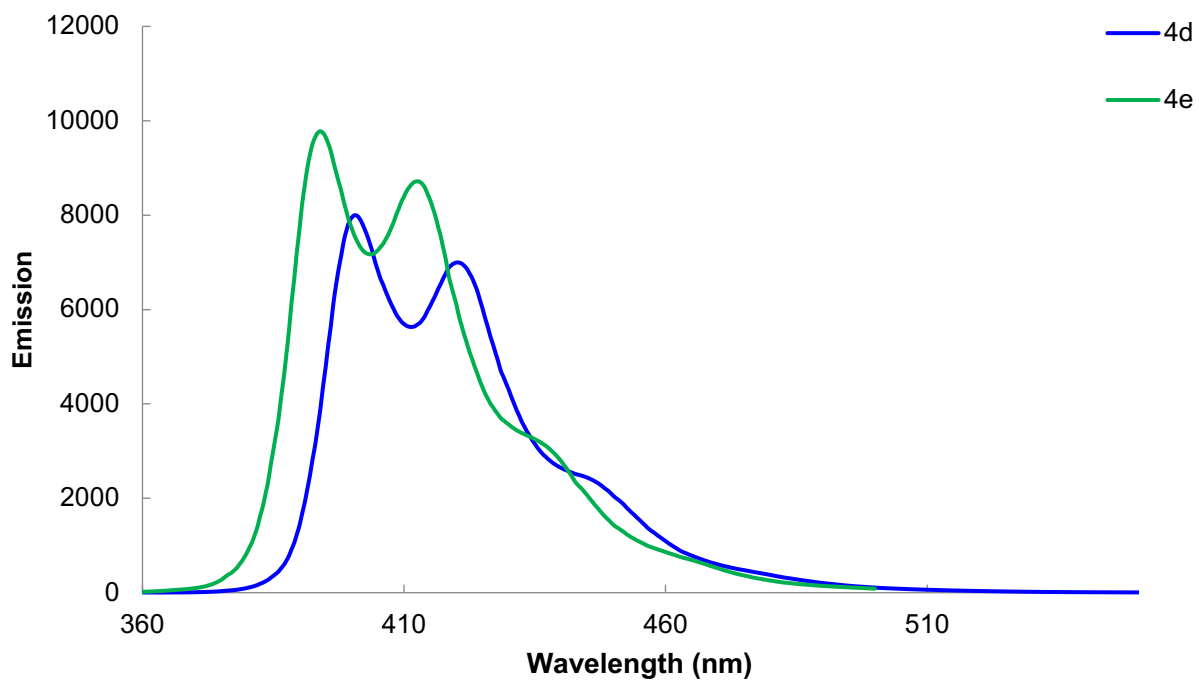


Figure S9. FL spectra of **4d–e** (1.0×10^{-5} M in DCM)

5. Cyclic Voltammetry

Cyclic Voltammograms (CVs) were recorded on Electrochemical Analyzer CHI-600B. A Pt electrode (surface area: $A = 0.071 \text{ cm}^2$, BAS), a Ag/Ag^+ (Ag wire in $0.01 \text{ M AgNO}_3/0.1 \text{ M Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$), and a Pt wire electrode were used as working, reference, and counter electrodes, respectively. The working electrode was polished with $5 \mu\text{m}$ diamond slurry and then with $0.5 \mu\text{m}$ alumina slurry. After polishing, it was washed with deionized water and acetone, and dried in an oven. A CH_2Cl_2 solution of sample including 1 mM of each sample and 0.1 M of Bu_4NPF_6 was prepared as an electrochemical solution. Using the electrodes and the solutions, beaker-typed three electrode electrochemical cells were constructed, and were connected with the potentiostat to perform cyclic voltammetry. The redox potentials were calibrated with ferrocene as an international standard.

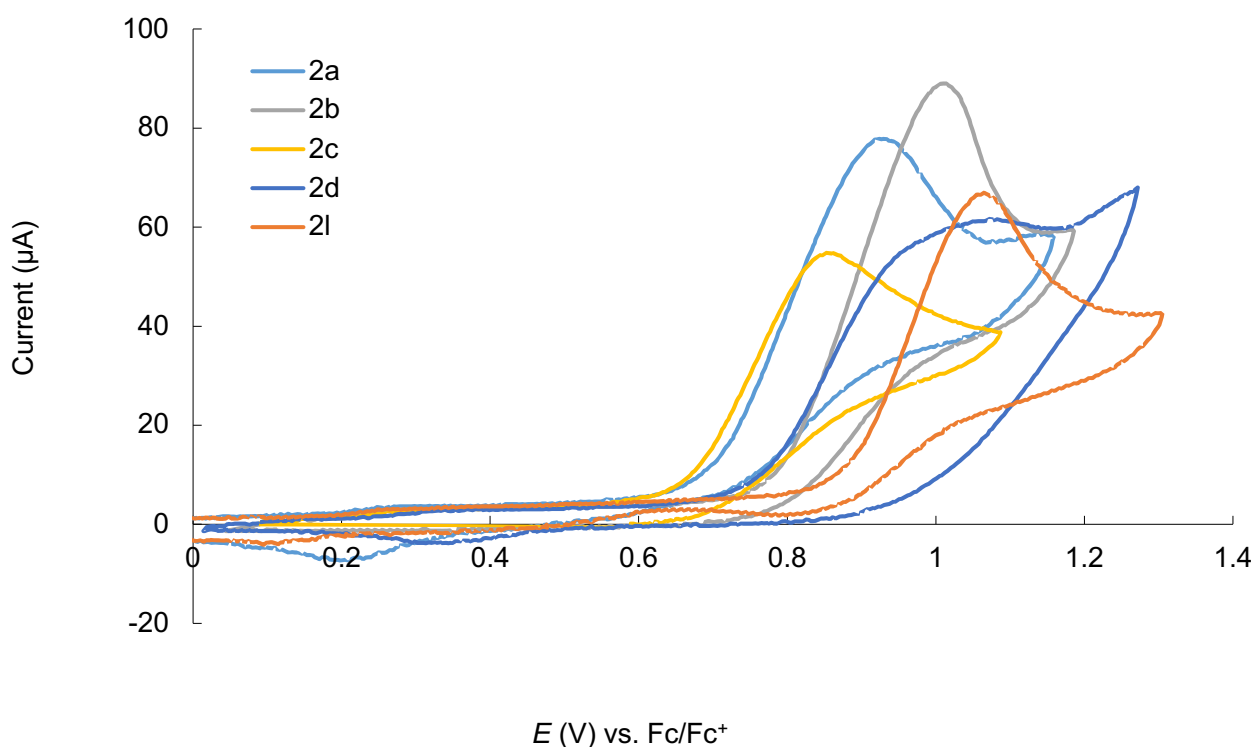


Figure S10. Cyclic voltammograms of **2a–d** and **I** (scan rate = 100 mVs^{-1})

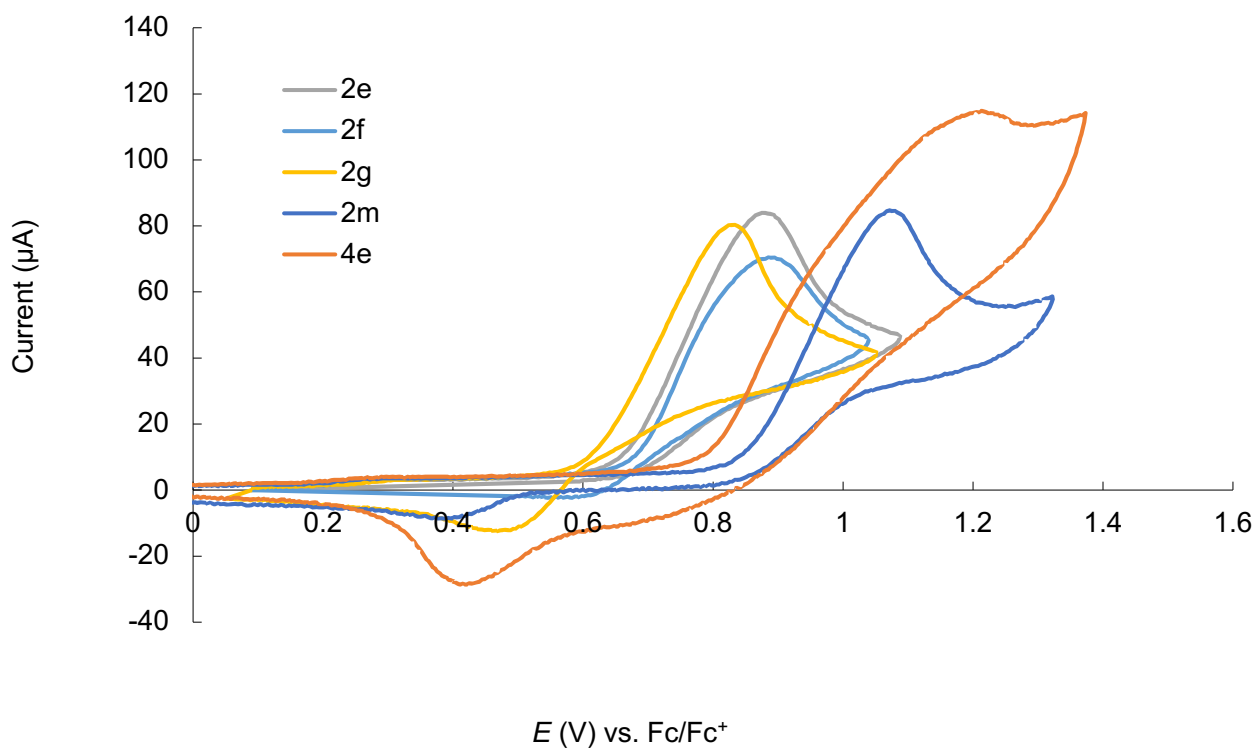


Figure S11. Cyclic voltammograms of **2e-g, m** and **4e** (scan rate = 100 mVs⁻¹)

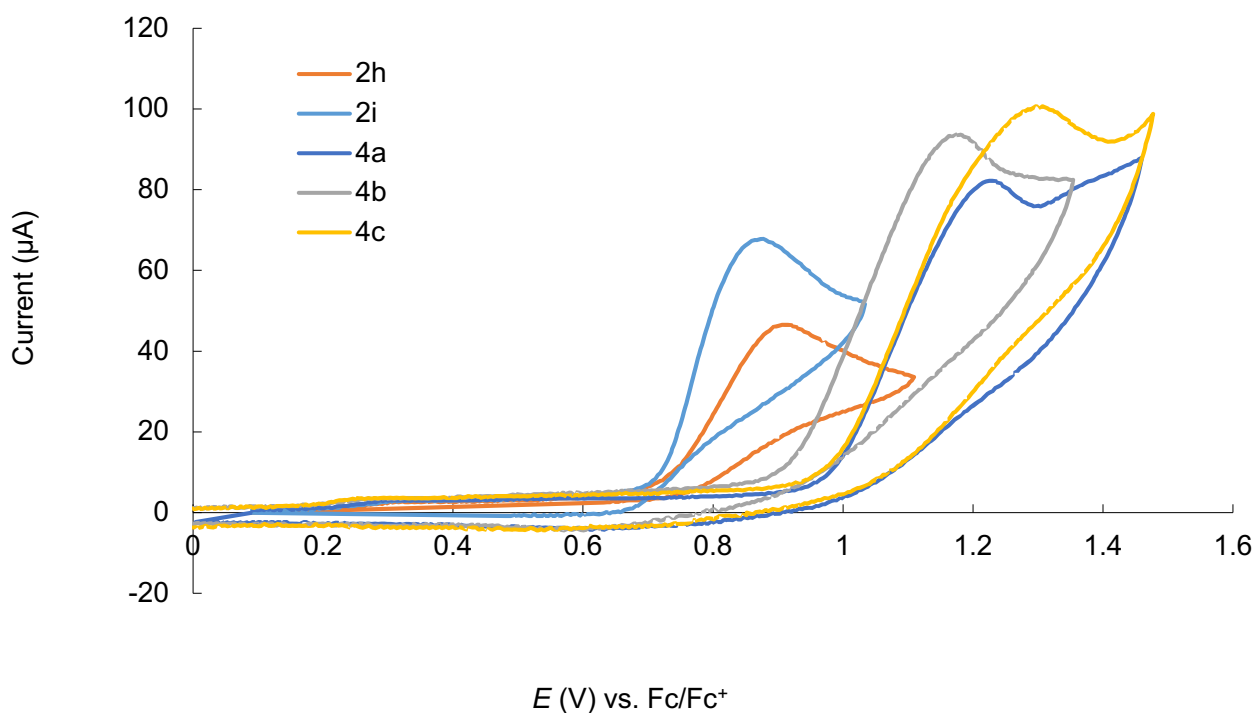


Figure S12. Cyclic voltammograms of **2h-i** and **4a-c** (scan rate = 100 mVs⁻¹)

6. Summary of Physical Data for DT-1,2-OBs

Table S2. Electrochemical and Optical Data for DT-1,2-OBs^a

DTAB	λ_{\max} (nm)	$\log \varepsilon$	$\lambda_{\text{onset}}/E_{\text{g}}^{\text{opt}}$ (nm/eV)	λ_{em} (nm)	Φ	E_{pa} (V)	E_{onset} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
2a	330	4.36	357, 3.47	381	0.05	0.93	0.74	-5.54	-2.07
2b	332	4.32	360, 3.44	383	0.05	1.01	0.80	-5.60	-2.16
2c	335	4.19	354, 3.50	393	0.02	0.86	0.67	-5.47	-1.97
2d	331	4.21	362, 3.43	392	0.11	1.07	0.77	-5.57	-2.14
2e	332	4.51	359, 3.45	380	0.10	0.89	0.67	-5.47	-2.02
2f	347	4.42	376, 3.30	395	0.09	0.90	0.69	-5.49	-2.19
2g	350	4.47	380, 3.26	397	0.17	0.85	0.62	-5.42	-2.16
2h	318	4.39	344, 3.60	375	0.23	0.93	0.74	-5.54	-1.94
2i	324	4.55	349, 3.55	368	0.24	0.89	0.72	-5.52	-1.97
2l	321	4.38	345, 3.59	366	0.09	1.07	0.89	-5.69	-2.10
2m	348	4.59	372, 3.33	393	0.19	1.09	0.85	-5.65	-2.32
4a	321	4.26	344, 3.60	360	0.11	1.24	0.99	-5.79	-2.19
4b	326	4.23	349, 3.55	365	0.11	1.18	0.93	-5.73	-2.18
4c	324	4.34	347, 3.57	362	0.12	1.31	0.99	-5.79	-2.22
4d	392	4.76	405, 3.06	401	0.52	– ^b	– ^b	– ^b	– ^b
4e	385	4.59	397, 3.12	394	0.52	1.21	0.79	-5.59	-2.47

^a E_{onset} values were determined by the onset of CV in CH_2Cl_2 . All potentials were calibrated with reference to Fc/Fc^+ . E_{HOMO} values were determined with reference to ferrocene (4.8 eV vs vacuum).¹³ Optical band gap: $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$. $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$. ^b Not determined.

7. DFT Calculations

Density functional theory (DFT) calculations were performed using Gaussian 09 program.¹⁴ Geometries were optimized at the B3LYP/6-31G(d) level of theory.¹⁵ TD-DFT calculations were carried out at the same level of theory. The data were summarized in Figure S13–15.

(14) *Gaussian 09, Revision E.01*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(15) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

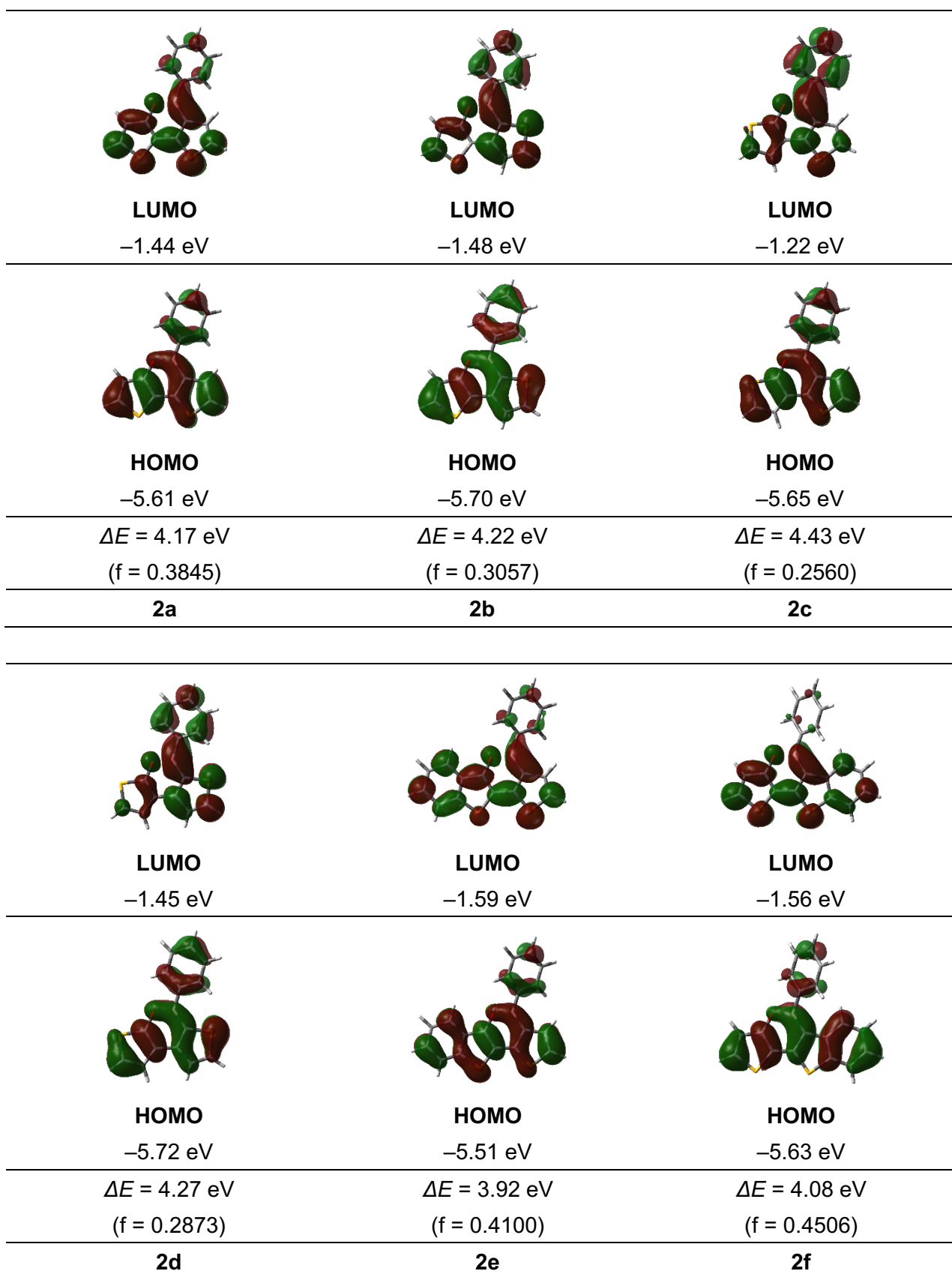


Figure S13. Kohn–Sham HOMO–LUMO orbitals of **2a–f**

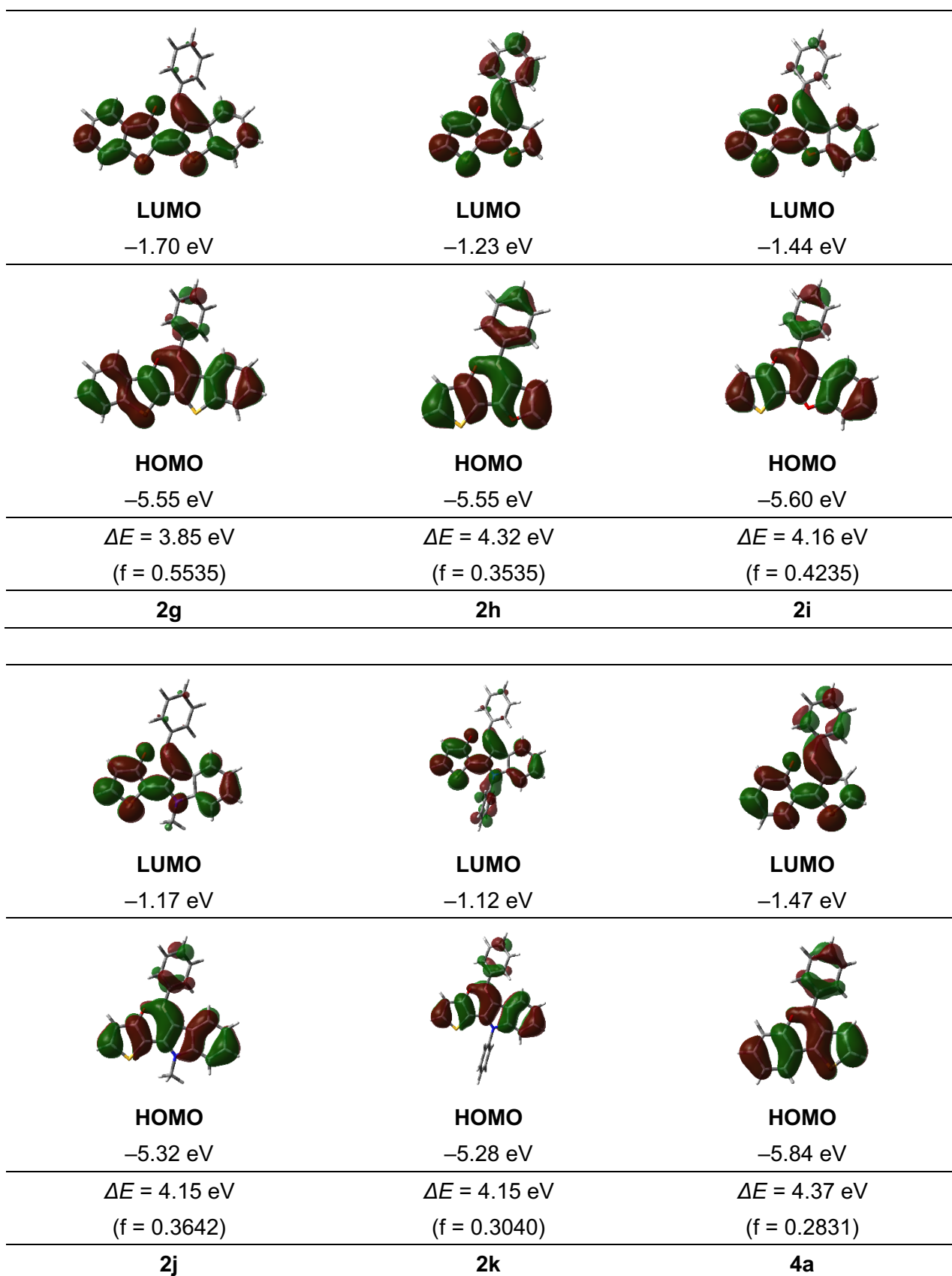


Figure S14. Kohn–Sham HOMO–LUMO orbitals of **2g–k**, and **4a**

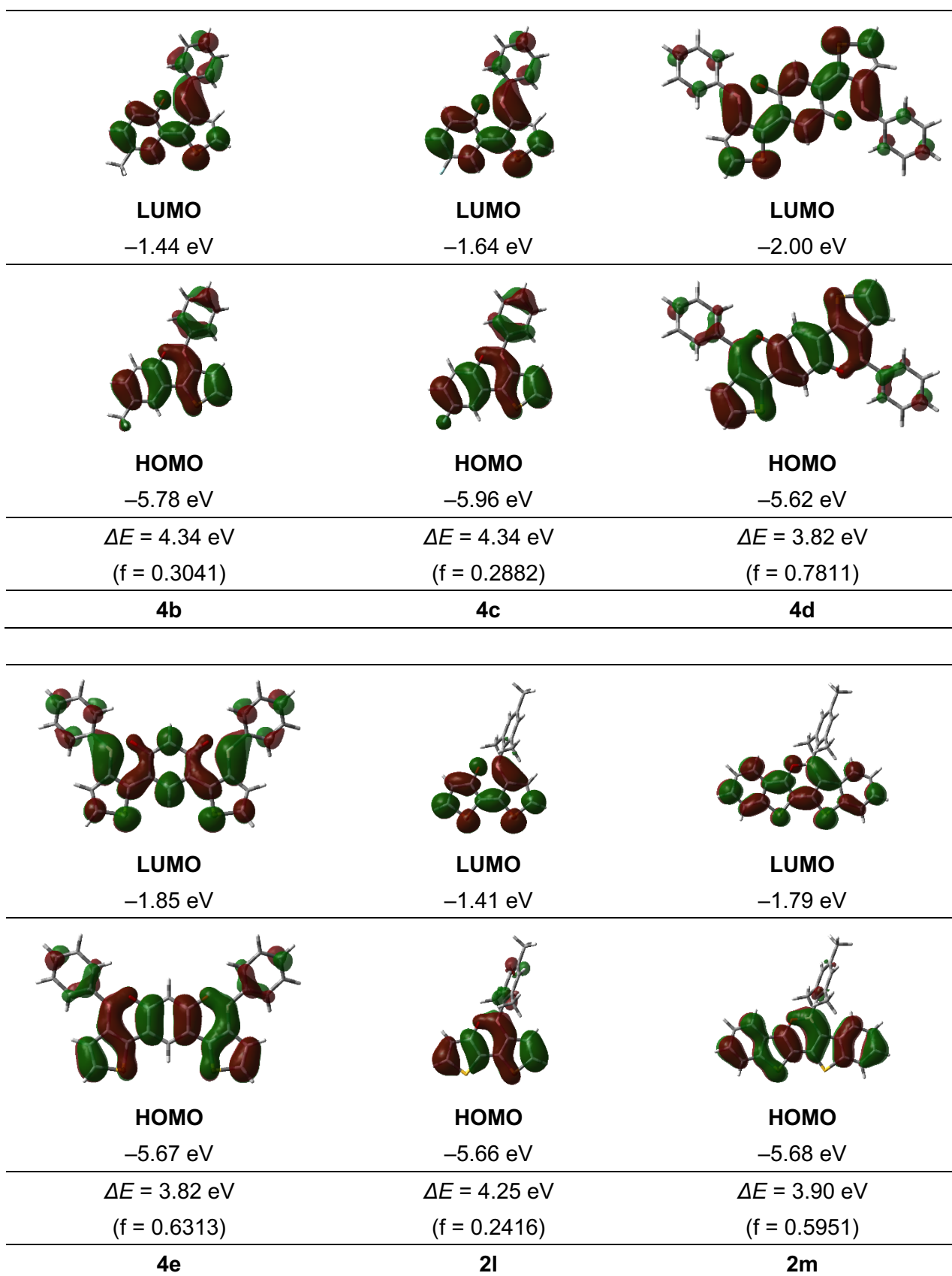


Figure S15. Kohn–Sham HOMO–LUMO orbitals of **4b–e**, **2l**, and **2m**

Computed Geometries and Energies

2a

C	3.522996517406	-1.394191471251	-0.205745112740
C	3.938517060760	-2.694298908675	-0.201890960388
C	2.103067419526	-1.296678569079	-0.131083648528
C	1.454846564454	-2.523024702391	-0.071680822176
S	2.616691923151	-3.827723724352	-0.107229052575
O	1.437602235092	-0.125012851628	-0.113140236890
B	0.041440416350	-0.047253690002	-0.022783892549
C	-0.720667404417	-1.381590616329	0.003864953809
C	0.033613961426	-2.564930782681	-0.014516055522
C	-2.127912827795	-1.679709909349	0.011892098155
C	-2.412596043572	-3.011318857810	0.017671622209
S	-0.966454844284	-3.993001752191	0.003217332772
C	-0.535148881838	1.404012438933	0.021232884784
C	-1.761922217719	1.710328947627	0.641161905241
C	-2.255647811621	3.014543034377	0.675938883762
C	-1.533451136533	4.049570597698	0.079186391544
C	-0.311116457675	3.774213804172	-0.538806535086
C	0.180951764043	2.470513072681	-0.558768305284
H	4.180052037155	-0.534364522608	-0.256643943919
H	4.952478599576	-3.067723905472	-0.246359066956
H	-2.901170677517	-0.920480676039	-0.004879701408
H	-3.381491996627	-3.492476979578	0.022512678940
H	-2.328538348956	0.922177217048	1.129693709731
H	-3.201158109927	3.224303120874	1.169756494588
H	-1.918292462141	5.066113883797	0.099535878599
H	0.257796201197	4.577135657872	-1.001020282362
H	1.137364520484	2.267322144358	-1.033197217752

2b

C	1.283613402152	-3.110086152061	-1.590940555557
C	2.528995518007	-2.870312637516	-1.085228184842
S	2.603942307245	-1.397749270527	-0.175608749480
C	0.353337707758	-2.081224407948	-1.238331031495
C	0.910384885937	-1.061148254293	-0.449900438732
B	0.066928116397	0.133844165346	0.005324378411
O	-1.261663254046	0.125069609628	-0.437652015383
S	-2.010761318920	-3.047082443568	-2.550477773843

C	-1.028805488908	-1.961315858564	-1.595574818424
C	-1.777566776912	-0.868442182577	-1.191691829998
C	-3.397351841223	-2.004204615078	-2.380617198479
C	-3.131465112348	-0.890062150508	-1.638592188212
C	0.473753212062	1.366831659709	0.871593467834
C	-0.322226454908	2.530636862161	0.858144433043
C	0.016197084975	3.653299120822	1.610676582734
C	1.162428420173	3.638591165086	2.409392461490
C	1.962771291127	2.495495798384	2.450000222341
C	1.620675519637	1.378247075071	1.688439214349
H	1.034771223921	-3.977584058739	-2.192530792162
H	3.415030867486	-3.481504321139	-1.200525226169
H	-4.332915460276	-2.285620329804	-2.844427147512
H	-3.850744373783	-0.112899086534	-1.409739788920
H	-1.217896852168	2.548451998953	0.243449879489
H	-0.612337666521	4.539752466581	1.577273131704
H	1.428424414002	4.512309321341	2.999140069654
H	2.851392008831	2.474121152728	3.075702338041
H	2.250408050302	0.494550993046	1.750592570118

2c

S	1.062140148765	-3.547307714084	-1.376405539565
C	2.450971796710	-2.494502296010	-1.252447700677
C	2.111487665739	-1.250068397756	-0.817209378649
C	0.009226621361	-2.272402110782	-0.824122833958
C	0.703456904304	-1.082124602790	-0.568726672641
B	-0.102343690941	0.122024048093	-0.063468234070
O	-1.479469413277	-0.096594965969	0.146482612231
C	-2.315908679239	-3.486796771370	-0.797241547087
C	-1.403020487906	-2.392162346337	-0.612897181502
C	-2.051235367417	-1.271456671540	-0.122347335291
C	-3.594783575567	-3.175307729359	-0.451212047202
S	-3.760524381220	-1.528078793652	0.118741471290
C	0.385583822952	1.565656848450	0.269689422051
C	1.515752964126	2.137527178632	-0.346405726723
C	1.934926841182	3.432368136064	-0.041237748938
C	1.234228916408	4.188234754112	0.900541419499
C	0.107047100375	3.646710679040	1.523486477385
C	-0.312408976179	2.356482606001	1.204776149890

H	3.432045074168	-2.874151538016	-1.504872504287
H	2.846694106797	-0.470072994462	-0.656774155978
H	-2.020522657472	-4.460821692762	-1.171670649424
H	-4.469640850358	-3.809437529118	-0.492519124337
H	2.061398786271	1.572829217590	-1.097422683115
H	2.805283879466	3.852770161649	-0.538687110354
H	1.561743527120	5.195669244385	1.144628869116
H	-0.444845286815	4.232507012483	2.254263174406
H	-1.195718019354	1.947589907507	1.688043437929

2d

C	0.525112081019	-3.407914091716	0.520907373534
C	1.845885005651	-3.164914816037	0.770562383422
S	2.240523857560	-1.481909031775	0.668442215378
C	-0.201805135768	-2.208318228986	0.238968106920
C	0.589144840567	-1.050028661808	0.287113164600
B	-0.005458576145	0.327507028280	-0.005718409694
O	-1.375248362716	0.316600010136	-0.334506803136
C	-2.637246310463	-3.068865304751	-0.210207698662
C	-1.600785822586	-2.080184956838	-0.091590721924
C	-2.085567663099	-0.814395519161	-0.362235880253
C	-3.843392078988	-2.540717986950	-0.556498370153
S	-3.784516064250	-0.802625961268	-0.758391266900
C	0.663980429398	1.734981514601	-0.016200894538
C	0.031571611517	2.813833575634	-0.667948352165
C	0.607758319374	4.081735238787	-0.703292409400
C	1.835367611624	4.308225672691	-0.075894824784
C	2.478423928929	3.260310238155	0.585455269436
C	1.898627619460	1.992260534043	0.610680234567
H	0.085824132658	-4.399223883328	0.532141865480
H	2.615593964689	-3.888294558909	1.007611484672
H	-2.481869370152	-4.128820241109	-0.042003212423
H	-4.780345455044	-3.058348611702	-0.709594648026
H	-0.925658726227	2.648282226703	-1.154472220418
H	0.101226640642	4.894497371069	-1.217732673433
H	2.286668392206	5.296970615665	-0.100043862782
H	3.429757662897	3.431609271690	1.082582477055
H	2.410318477246	1.197037686885	1.146358173628

2e

S	1.969463990504	-3.762715896476	0.280221423713
C	3.432901083431	-2.810124526958	0.331169980705
C	3.180022562686	-1.474422870954	0.243518712321
C	1.003629109808	-2.317672983125	0.141356338717
C	1.784680889705	-1.150675754687	0.122151410366
B	1.053027184217	0.195612648314	0.019313681477
O	-0.348161365006	0.140017754868	-0.002307225409
S	-1.584325601868	-3.570448536802	0.092274214431
C	-0.415435169718	-2.250903858635	0.081057758910
C	-1.033285465486	-1.018200478383	0.021304882663
C	-2.920350833250	-2.416486905047	0.014898651105
C	-2.467644456396	-1.076600059812	-0.018984575146
C	-3.400311775852	-0.028369342940	-0.085104438549
C	-4.754759505796	-0.331027823870	-0.114033048435
C	-5.193174582980	-1.667032151034	-0.078784080951
C	-4.283111719091	-2.719054161261	-0.014879046030
C	1.659912084803	1.632848102861	-0.045966239504
C	0.929516864814	2.737013593061	0.437400728967
C	1.450375169600	4.028971806586	0.396327289442
C	2.717876738187	4.253454184752	-0.146669553957
C	3.456604635580	3.179564784530	-0.646784642328
C	2.933255602292	1.887730715736	-0.590807179425
H	4.388046333542	-3.308512893339	0.429842648162
H	3.966596328841	-0.729714783364	0.281596230304
H	-3.051144210589	0.999233872221	-0.114684590629
H	-5.485269188517	0.471219225223	-0.165296896279
H	-6.257313316515	-1.884280426684	-0.102450278765
H	-4.626123936946	-3.749250215037	0.011169451005
H	-0.060622460494	2.573163180851	0.854542721224
H	0.869372146312	4.862020857690	0.784146025390
H	3.125553579086	5.260565041299	-0.183529821441
H	4.438270172364	3.349475202582	-1.081849971908
H	3.514672872729	1.067543097835	-1.003511590146

2f

S	-0.003941133587	-3.645644664872	0.240630775653
C	1.513730957920	-2.750463710464	0.173023391450
C	1.295037675722	-1.356167492404	0.035966394452

C	-0.912237023099	-2.154747397650	0.081583700152
C	-0.119142717255	-1.004008035148	0.012994428411
B	-0.853051584648	0.343673201337	-0.093577184447
O	-2.249043791238	0.294791418282	-0.231171587974
S	-3.518351228633	-3.364308579468	0.021444787652
C	-2.328471963266	-2.083868928050	-0.009032643262
C	-2.945683157586	-0.854069687306	-0.188683143133
C	-4.807952223893	-2.214102018731	-0.210620902328
C	-4.363831561372	-0.926656066145	-0.305403104030
C	2.790785256023	-3.311802764273	0.217801526598
C	3.889079928995	-2.464739996190	0.105777993423
C	3.703912290320	-1.083432205850	-0.058873342287
C	2.429000806156	-0.531340531088	-0.095946128315
C	-0.291918148920	1.805940076345	-0.049244615586
C	-0.823549006674	2.794425631929	-0.900397745988
C	-0.376477280313	4.114115620056	-0.851330195404
C	0.602605764521	4.485613074479	0.073016556131
C	1.129666928221	3.530098799706	0.943627520244
C	0.690422569025	2.207015894354	0.875887912694
H	-5.828661078441	-2.568497095101	-0.258157417288
H	-4.998886179285	-0.060578040366	-0.447035573530
H	2.924224075507	-4.384104309741	0.328274789771
H	4.892822562255	-2.879221328511	0.135956008642
H	4.569325532613	-0.434824734179	-0.163383840821
H	2.304476185103	0.535662281997	-0.238283730593
H	-1.600417166226	2.521514644481	-1.610251906658
H	-0.794563219412	4.854854065643	-1.528431638785
H	0.948865935225	5.515140090817	0.117738549776
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H	1.106229635528	1.477173661998	1.566119476149

2g

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C	1.646510475187	-0.425909412692	0.049632498877
C	2.994885622023	-0.912525919472	0.129167923869
C	3.920854743522	0.153155574700	0.038331008060
S	3.124192988794	1.719256234644	-0.144287897377
C	0.255729441860	1.542176160555	-0.149502198960
C	-0.914619238830	0.776707885786	-0.075709863044

B	-0.744973360934	-0.748764338240	-0.001544263031
O	0.571720312993	-1.228628185630	0.097367735981
S	-0.021558089334	3.268768968688	-0.268678690624
C	-1.763424953908	3.014602498555	-0.176832666274
C	-2.088675852587	1.639008159293	-0.061698950597
C	-2.732909852247	4.018915818369	-0.185552432483
C	-4.068229102492	3.649346955357	-0.058727221036
C	-4.418788622543	2.297788379020	0.084789231918
C	-3.448693264554	1.302934441884	0.085708827012
C	3.459307179238	-2.230410153527	0.273180184011
C	4.826937107832	-2.460754440105	0.325903081511
C	5.738902813812	-1.393371147172	0.235604240094
C	5.296580919523	-0.081153928307	0.090497834046
C	-1.815796412902	-1.891095665640	-0.042171615119
C	-1.684071513531	-3.017364490110	0.793506154792
C	-2.596641177100	-4.070317235483	0.745058430808
C	-3.657392633407	-4.033609322993	-0.163016514468
C	-3.798300891181	-2.938750690674	-1.017552274136
C	-2.891279246596	-1.880085175984	-0.950556029370
H	-2.451510291898	5.063736177700	-0.280016313768
H	-4.839967983048	4.413941019617	-0.060858355474
H	-5.463793582382	2.024084722244	0.201271011203
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H	2.745798794456	-3.046055353950	0.339002888504
H	5.199010171805	-3.475129309801	0.437116433444
H	6.805781521818	-1.593514915690	0.278646451400
H	6.005009728600	0.738999363172	0.019995749843
H	-0.852216494902	-3.065855887684	1.491928329574
H	-2.478882465087	-4.922106357536	1.410285389597
H	-4.367108799261	-4.855855827569	-0.207397240173
H	-4.613021658645	-2.909989513400	-1.736734656100
H	-3.011868681538	-1.038418603189	-1.628181762337

2h

C	-1.385272875492	-2.516416486411	0.002750868927
C	-1.987099281428	-1.322694332875	-0.376648322205
C	-3.349458855963	-1.472490674796	-0.768499594309
C	-3.757716695647	-2.772687465048	-0.681018104608
S	-2.502169430147	-3.848090509122	-0.121569641142

C	-0.028340254458	-2.471768317269	0.399603656974
C	0.718115707008	-1.296557405500	0.435698043168
B	0.010231592876	-0.001831001712	0.027868431287
O	-1.332810243673	-0.144925952244	-0.367466147299
O	0.699874636601	-3.553338038034	0.765837045846
C	1.964758539973	-3.076344217253	1.044516254999
C	2.028837657040	-1.734163071085	0.860459204787
C	0.567019514983	1.454168991951	-0.023822725359
C	1.762963319659	1.817006008148	0.624850865755
C	2.254937354281	3.120857095533	0.572843228762
C	1.559710982661	4.099384199068	-0.140407290413
C	0.368859658479	3.767502129609	-0.791487001096
C	-0.119430474522	2.463937855413	-0.727954853928
H	-3.973853494408	-0.648843879817	-1.093020150213
H	-4.733719260912	-3.177118569186	-0.912256625863
H	2.677716873715	-3.825464052747	1.352302845769
H	2.911515067862	-1.126019951150	0.998852315594
H	2.310267936097	1.072792590161	1.196896215580
H	3.177942481118	3.374969114550	1.087986028542
H	1.942120321217	5.116044168358	-0.186502037241
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2i

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C	-4.662465477224	-2.248345157264	-0.263509003854
S	-3.329658851903	-3.350162782441	-0.036376175772
C	-0.796582594015	-1.999627413496	0.079967235753
C	-0.046396029691	-0.827302240954	0.050574959446
B	-0.814982202886	0.487878210338	-0.082798708762
O	-2.211840847420	0.370316882121	-0.230313583004
O	-0.047113622858	-3.129675358787	0.193206512312
C	1.267196720381	-2.700009619780	0.219981177300
C	1.331707743862	-1.295361323428	0.126393867032
C	2.370562046496	-3.533303654966	0.309066833300
C	3.620236240648	-2.911200307955	0.292120995661
C	3.730216707526	-1.515310505224	0.182239589190

C	2.602487299059	-0.700163952333	0.097769161060
C	-0.287064759661	1.957221114189	-0.077081159450
C	-0.945751391673	2.959990305826	-0.815316697144
C	-0.494092604933	4.278718466010	-0.813986752414
C	0.622974640829	4.633637283609	-0.053661402143
C	1.281675310616	3.662979709833	0.703364472966
C	0.832826400932	2.341903251905	0.684157683033
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H	-5.667166139057	-2.643567485048	-0.328764161409
H	2.259639884107	-4.610125988199	0.381200878994
H	4.518631844207	-3.518040175025	0.358118913085
H	4.717002239551	-1.061274579128	0.159276957780
H	2.708033526224	0.374511306940	-0.002262581654
H	-1.824111619388	2.696730834205	-1.398997695774
H	-1.013800682881	5.031789135936	-1.401170065500
H	0.974665545196	5.662290293413	-0.047566839510
H	2.142109497924	3.935692729315	1.309311853239
H	1.345995665870	1.601298403190	1.291872651124

2j

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C	2.213100635410	-3.612495138412	-0.672129424224
C	1.464770330565	-4.749029586223	-0.586196303255
S	-0.161666382139	-4.442630466317	-0.043159957880
C	-0.687868665431	-1.630415340194	0.444992305206
C	-0.200191349042	-0.305634114118	0.425131172711
B	1.261771128734	-0.077840014045	0.073295283544
O	1.997416704354	-1.220250046837	-0.299493282959
C	-2.447073550820	-0.339783605800	0.978411541577
C	-1.342486544094	0.524364036685	0.750931346346
C	-3.719909773784	0.135917650962	1.302821174459
C	-3.888317500034	1.514607701566	1.398329673095
C	-2.815487830186	2.392373828494	1.164016717485
C	-1.551304067194	1.910988888225	0.840685511106
N	-2.017451650642	-1.655798151176	0.803433952365
C	-2.863844373238	-2.827698505542	0.936145067279
C	2.103532656183	1.242241676312	0.068701480594
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C	3.890372597577	2.600940034616	-0.901275022620
C	3.114476523666	1.442567499529	-0.891413056913
H	3.248926316694	-3.574781177721	-0.987293389232
H	1.766077439899	-5.764298935651	-0.805309126963
H	-4.559097264422	-0.534688659310	1.461919333205
H	-4.867205517524	1.915332832324	1.646695438781
H	-2.979320539200	3.464451598650	1.230678572150
H	-0.737171875660	2.600156931379	0.644637010737
H	-3.240388964988	-3.173628492191	-0.034092029244
H	-2.312459384018	-3.639826228036	1.416063803947
H	-3.713633185696	-2.581590387355	1.575584160949
H	1.172409211569	2.113118556816	1.812125651764
H	2.553182816844	4.157506492344	1.811781281431
H	4.294286881024	4.487842879898	0.066384472517
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H	3.292138218589	0.675257386438	-1.640767553128

2k

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C	-4.312177508966	-0.015870670886	-4.659065991466
S	-4.885956959392	-0.949772085976	-3.304836203991
C	-4.004369959580	0.105266442889	-0.754972560088
C	-3.270199905885	1.084347654152	-0.054285789124
B	-2.632160849647	2.212002067917	-0.853186467179
O	-2.755257884466	2.129804340365	-2.253579049156
C	-4.090328341612	-0.510431272653	1.410780508100
C	-3.312439585929	0.674020648285	1.336646399504
C	-4.348851858416	-1.177766597853	2.608762830272
C	-3.787957152768	-0.650129421686	3.768648696555
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C	-2.748914269579	1.169975584917	2.524894885929
N	-4.509872498673	-0.840760690358	0.116244874558
C	-5.334451439877	-1.964077006752	-0.204909409416
C	-6.687353641233	-1.773357767915	-0.504559301855
C	-7.490257029847	-2.873820785769	-0.806140122821

C	-6.949243891076	-4.160842512766	-0.793992950942
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C	-1.854796189843	3.478898650428	-0.361129760765
C	-0.785400972716	3.999507880605	-1.115688315238
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H	-7.577501601438	-5.016403829886	-1.025601758731
H	-5.177082157447	-5.349183452751	-0.472717657301
H	-3.737844431038	-3.382669098208	0.045849868306
H	-0.496146768753	3.500651440927	-2.037257484892
H	0.737621062741	5.511838600417	-1.302783695382
H	0.070480177612	6.691547829172	0.782776999735
H	-1.843012431718	5.838134615735	2.123615435419
H	-3.055287756930	3.814816442904	1.402805826502

21

C	-1.805989273916	-3.184482955916	0.041512253950
C	-2.241171128179	-2.077164543418	-0.675943226239
C	-3.439744343533	-2.299731320837	-1.414127790601
C	-3.902968351919	-3.573082560907	-1.250384648253
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C	-0.616647690366	-3.096618564113	0.817845250186
C	0.110178240013	-1.899197913342	0.866278558541
B	-0.408594424560	-0.698521279034	0.067071891815
O	-1.582019638840	-0.898298336225	-0.669125890180
S	0.120170510875	-4.354711985572	1.774400752648
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H	-0.478232869757	2.089488765966	3.058278086422
H	-1.613957184193	1.105299115960	2.127997271317
H	-0.157787706131	0.369622012944	2.792606370760
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H	1.674754556284	0.581609963136	-3.174149886721
H	1.440162039722	-0.808956658876	-2.106376002215
H	3.052021761356	4.600565726987	-0.931408361280
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2m

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C	3.187711179893	-1.225425706826	0.048096144191
C	4.274169097773	-0.319418960250	0.037679100810
S	3.741410419614	1.364595672301	0.000862564061
C	0.882803922489	1.654468996442	-0.025579071191
C	-0.388739317937	1.073192600128	-0.021131004572
B	-0.474942838136	-0.455827080016	0.015608063728
O	0.744860076368	-1.149668532004	0.031135181983
S	0.863972962268	3.407989031662	-0.068995056270
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C	5.817979163046	-2.149784713941	0.086733823275
C	5.593777820914	-0.775963102724	0.056850627302
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C	-4.089416024814	-2.983960500113	0.030657017894
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C	-2.216610825905	-1.969892211823	-1.164472331318
C	-1.460966483403	-1.778675192789	-2.463604699516
C	-2.033212586482	-0.948496716513	2.523152015437
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H	2.596741020658	-3.300930284386	0.088072151670
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4a			
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O	-1.084522451265	0.288225481113	0.044708504249
C	-1.232454833979	-2.090295422254	0.465331035894
C	-1.832626034380	-0.830134918400	0.239341216418
C	-3.223864262317	-0.692582778070	0.200172062028
C	-4.032885305700	-1.806552287827	0.382180857859
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C	-6.025059299079	-0.694690064464	-1.063601329865
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H	2.035910187642	-1.235132585152	0.536411080565
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4c

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4d

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B	3.817630446904	-0.574833021835	-0.009716531195
C	3.820698437033	0.914446775710	-0.403346979890
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O	-2.214461983054	1.088760472570	-1.432784799621
B	-3.445438438844	0.443187185781	-1.467418195067
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C	-2.202554417655	-1.637784566351	-0.840051557328
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C	-4.473006428367	-2.057846686750	-1.198996865467
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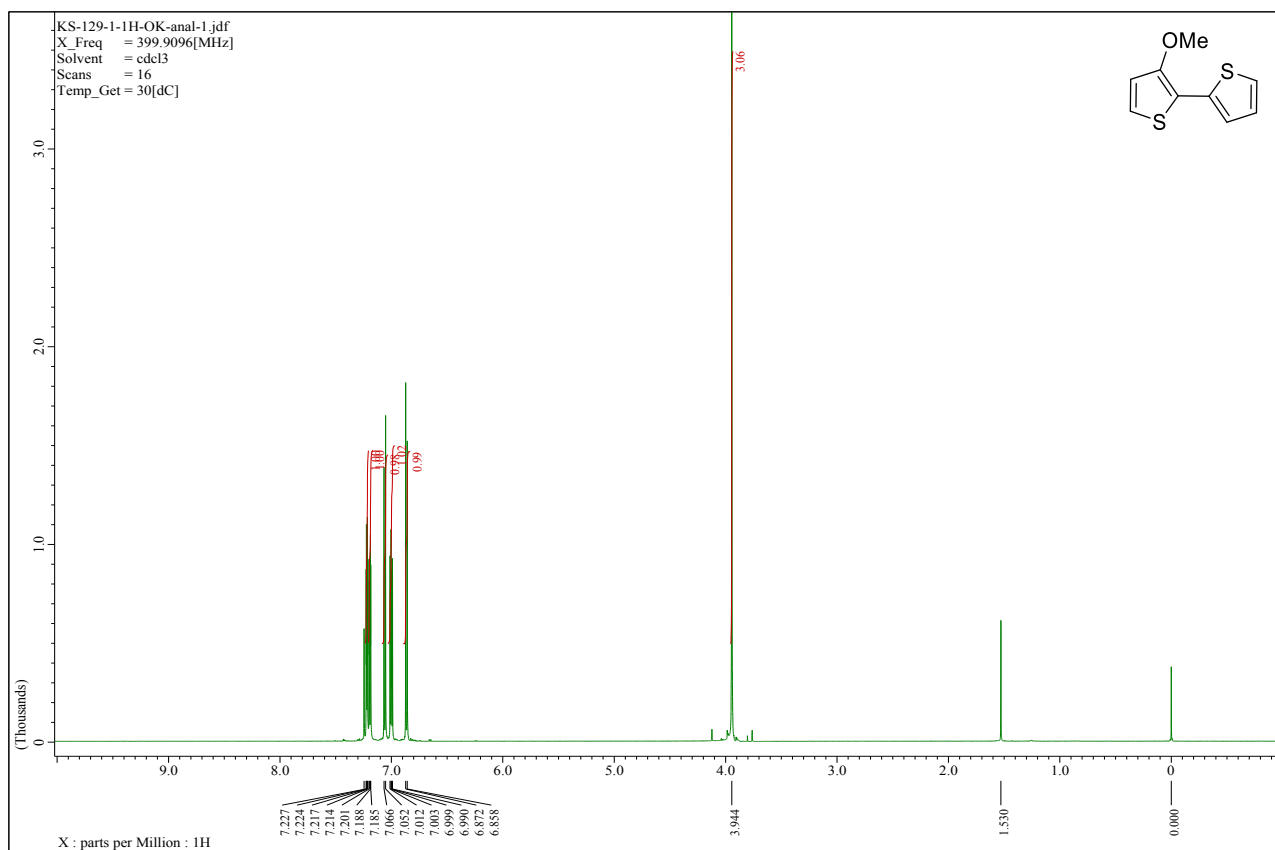
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C	0.417201776871	-2.147450840942	-0.970275702814
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C	0.958910064799	-0.752122089880	0.928983463309
C	-0.380699419854	-0.400303231389	1.060790545894
C	2.792123209981	-1.962326076411	-0.142853085288
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B	3.213267217052	-0.443574496823	1.799822819893

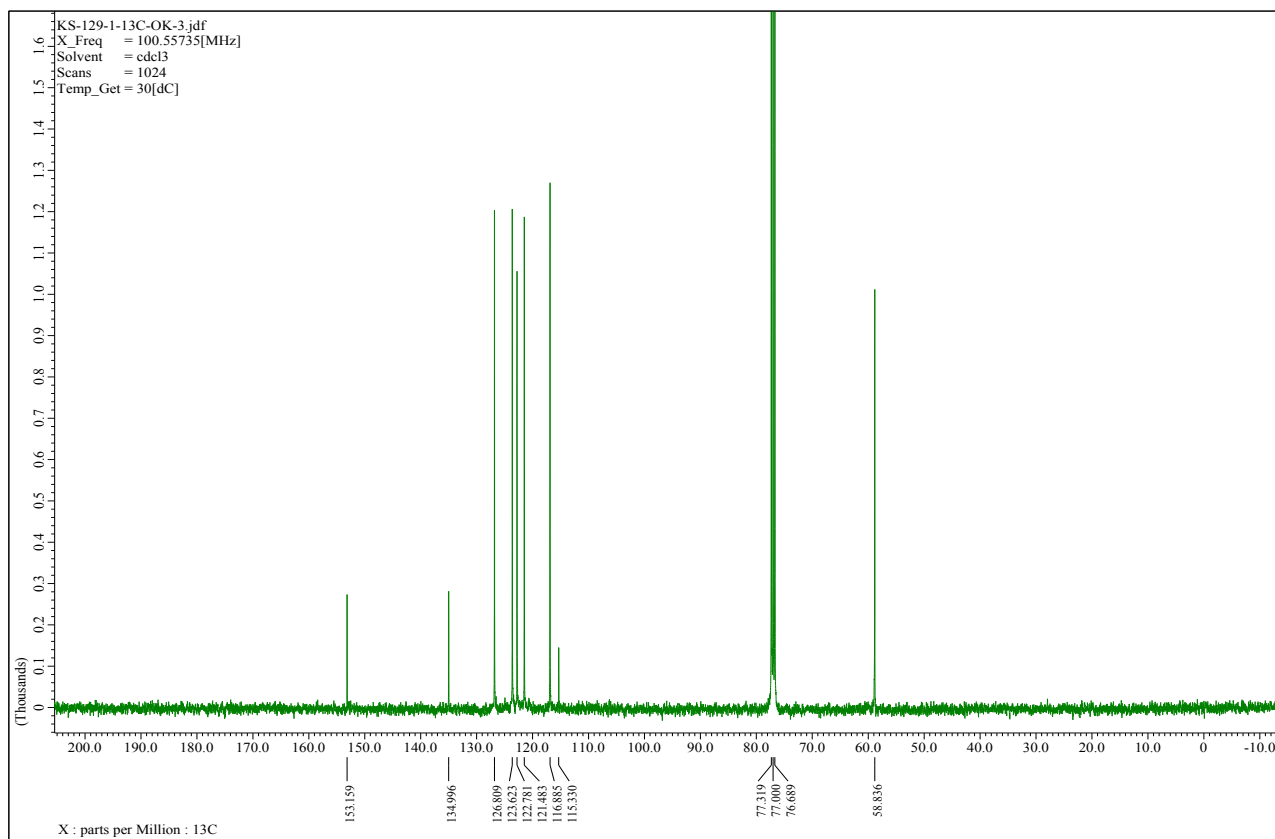
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C	-3.325632428236	-1.953359865920	-1.583074603377
C	-1.985671513216	-2.314424625946	-1.716920169604
S	3.516477957263	-3.081232923120	-1.271958599706
C	5.083973357432	-2.851207513031	-0.544113643252
C	5.041312221749	-1.970138199990	0.494001183053
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C	-3.453611968405	-3.480421319707	-3.356836420032
S	-1.745885923835	-3.469065644638	-3.005626739340
C	-5.060068610669	-0.339669527415	-0.103357266685
C	-5.316928125219	0.102300225472	1.210196959496
C	-6.549789271974	0.644965222642	1.567037127588
C	-7.557965992608	0.776036982534	0.608678760500
C	-7.324088476227	0.362839939899	-0.704239436051
C	-6.092180339890	-0.192359917162	-1.050191196184
C	4.021744671228	0.329771877179	2.888558307514
C	3.390606409006	0.744311099264	4.078750596615
C	4.088338860742	1.429337324510	5.071562791791
C	5.439755150788	1.734236449278	4.890559988104
C	6.084990058469	1.351205006656	3.713214382596
C	5.383233640630	0.653416906306	2.730281080532
H	0.727004503334	-2.828999480252	-1.758161004831
H	-0.689291570880	0.281334267197	1.844999092010
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H	5.915644176523	-1.720731391842	1.083646124718
H	-5.227482485725	-2.541922210591	-2.587522422894
H	-3.830477204695	-4.112709594938	-4.149805423218
H	-4.533968754173	0.014242099432	1.958532180400
H	-6.725535019400	0.970090536254	2.589398760422
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H	-8.100305335852	0.474868434412	-1.456995360874
H	-5.922041358567	-0.489869887745	-2.081295272211
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H	7.132814392056	1.597607692223	3.561377549969
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8. ¹H and ¹³C NMR Spectra of Products

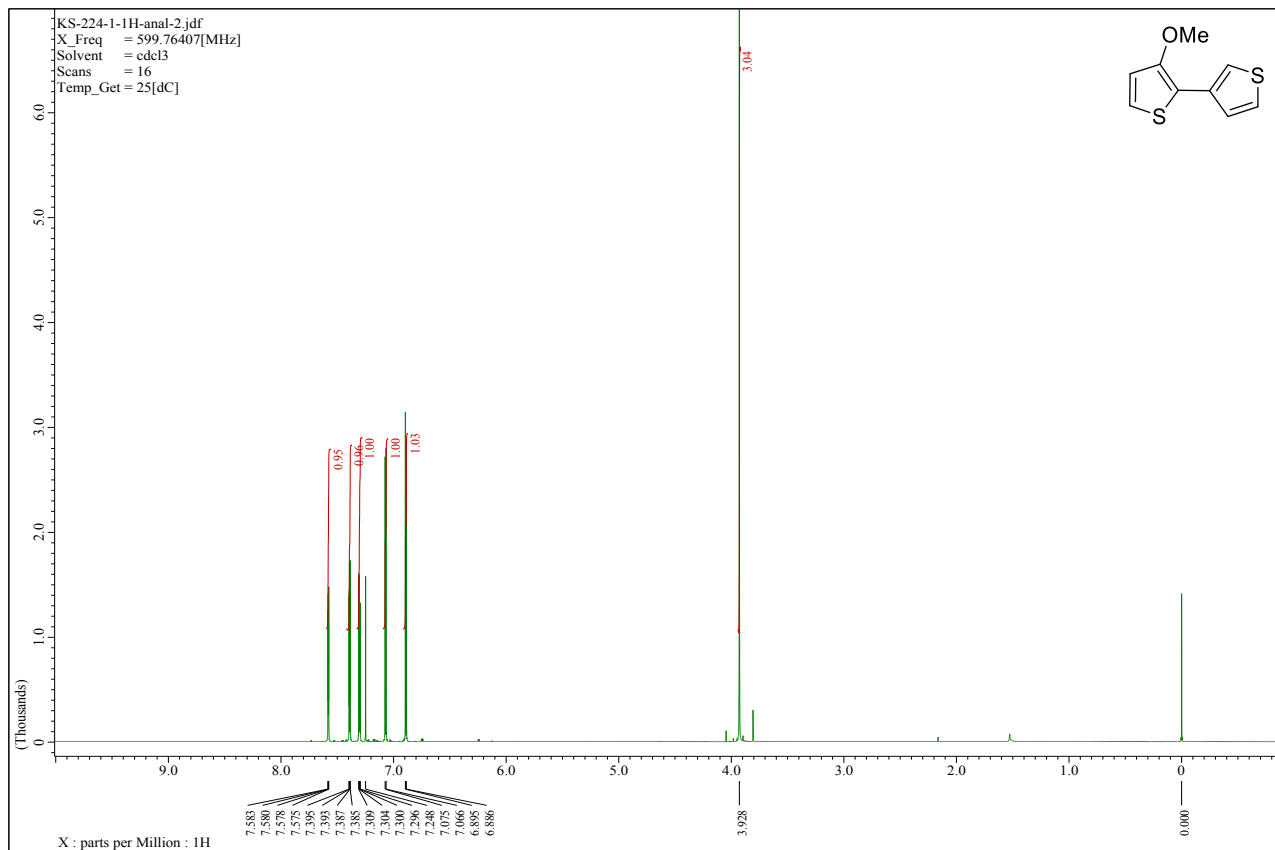
3-Methoxy-2,2'-bithiophene (1a) ¹H



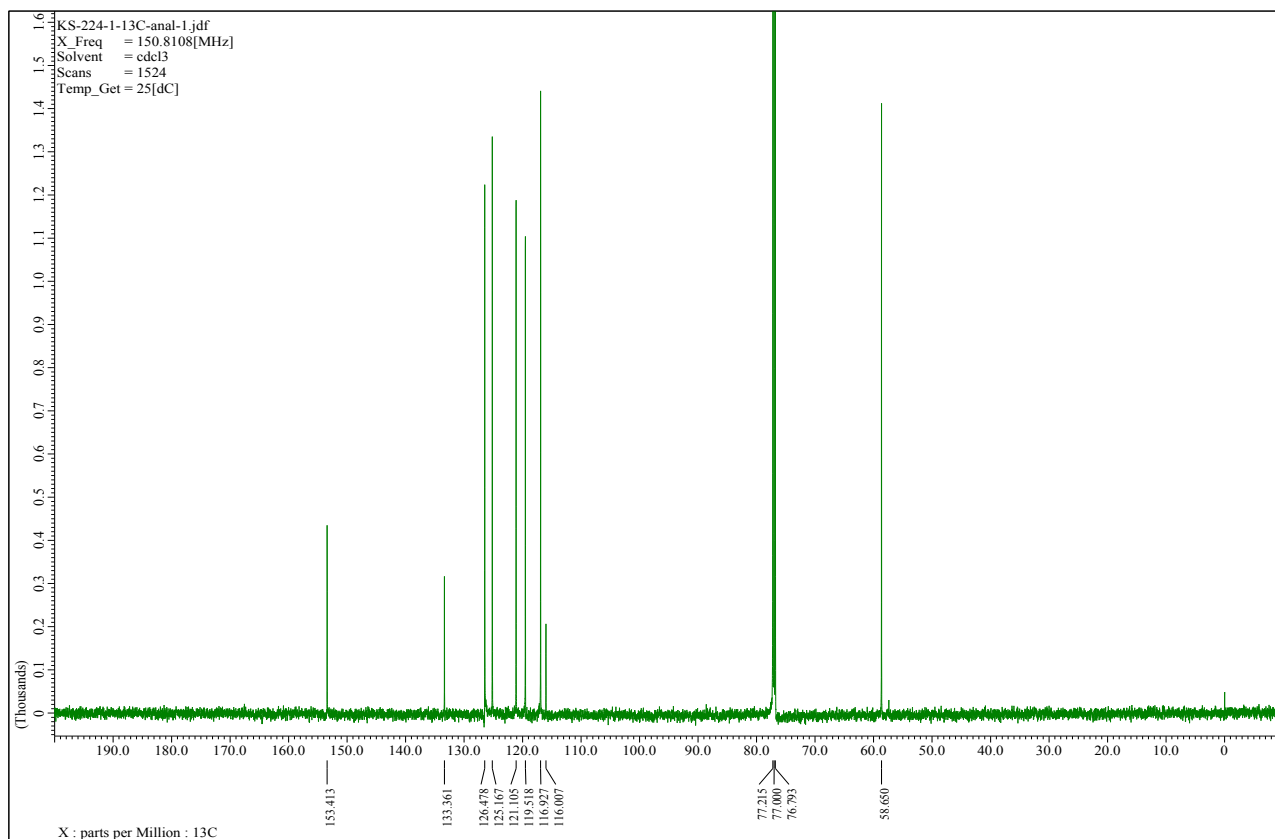
3-Methoxy-2,2'-bithiophene (1a) ¹³C



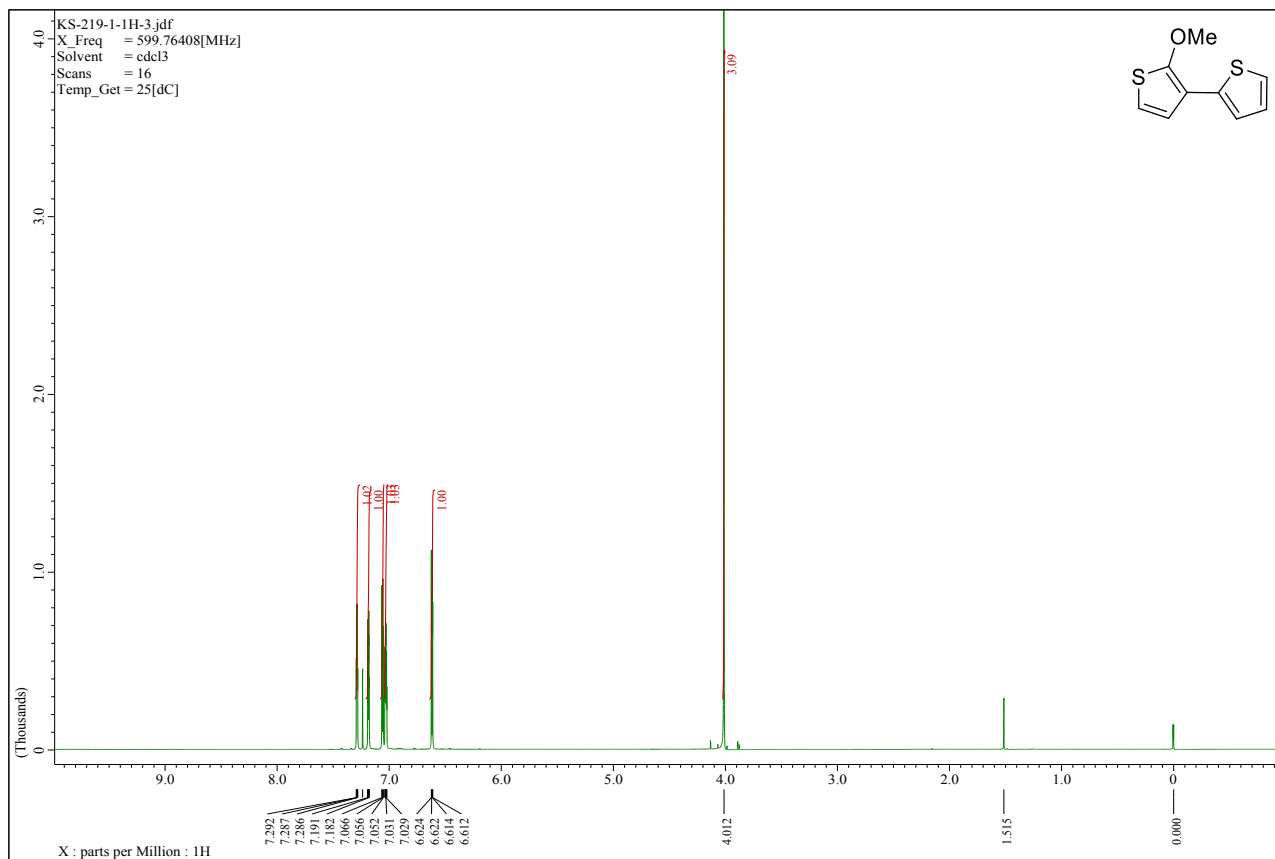
5-Phenyl-5*H*-dithieno[2,3-*c*:2',3'-*e*][1,2]oxaborinine (2b) ¹H



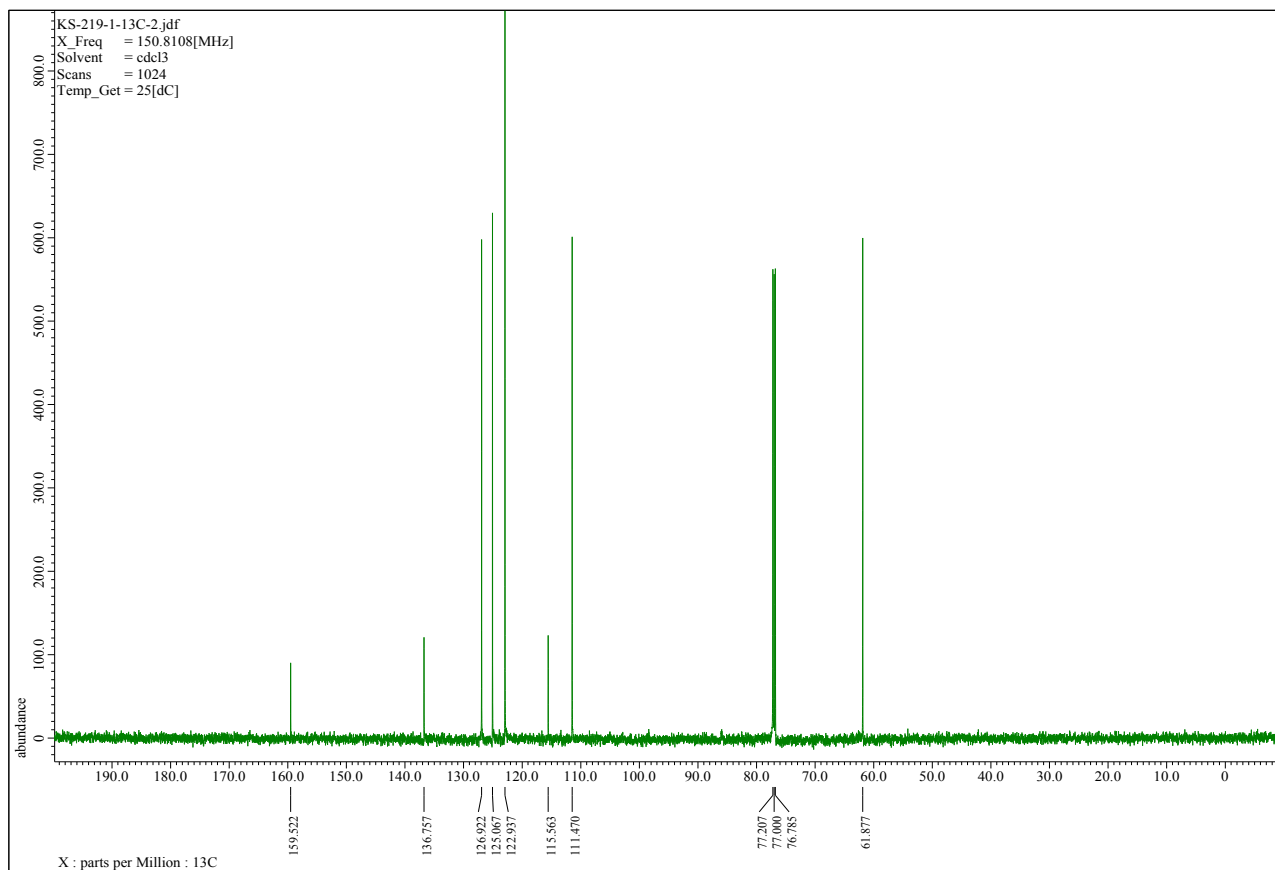
5-Phenyl-5*H*-dithieno[2,3-*c*:2',3'-*e*][1,2]oxaborinine (2b) ¹³C



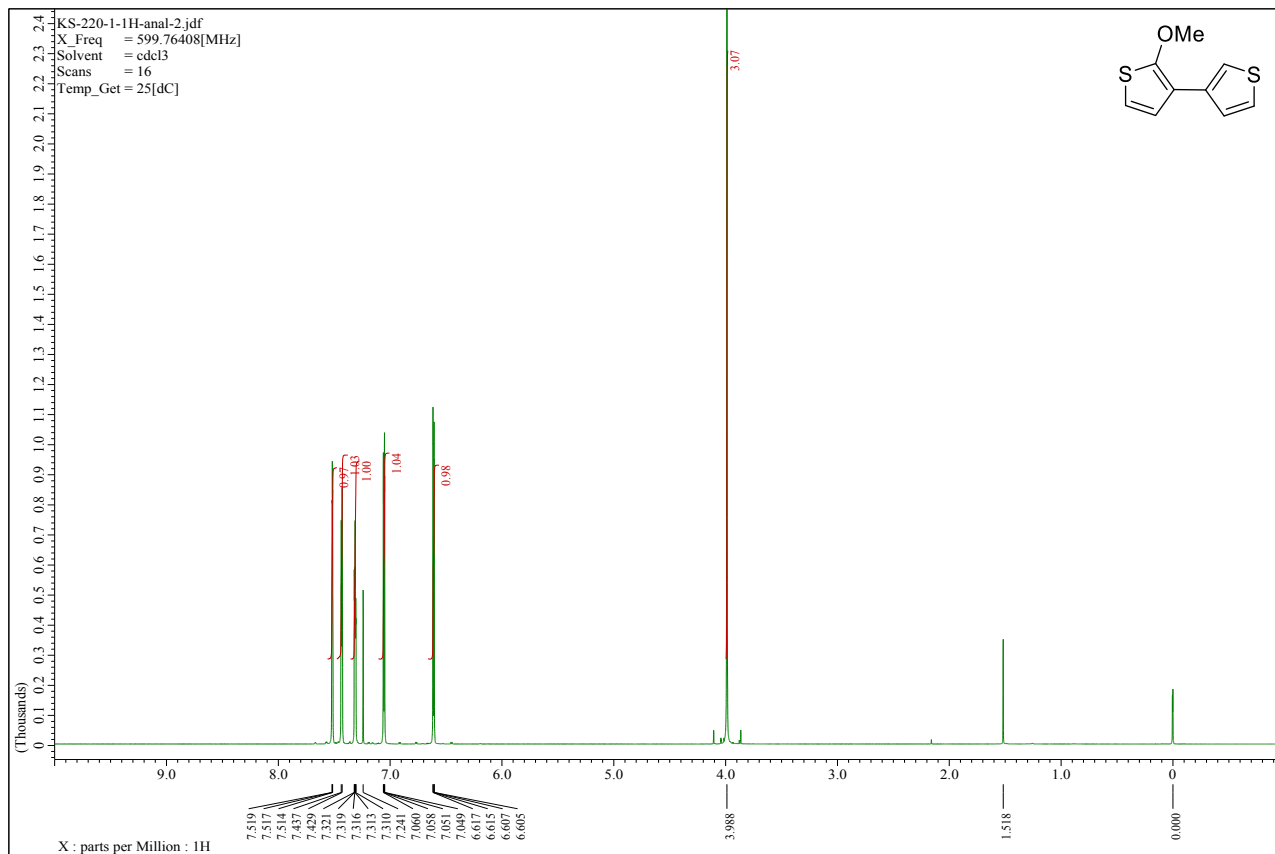
2'-Methoxy-2,3'-bithiophene (1c) ¹H



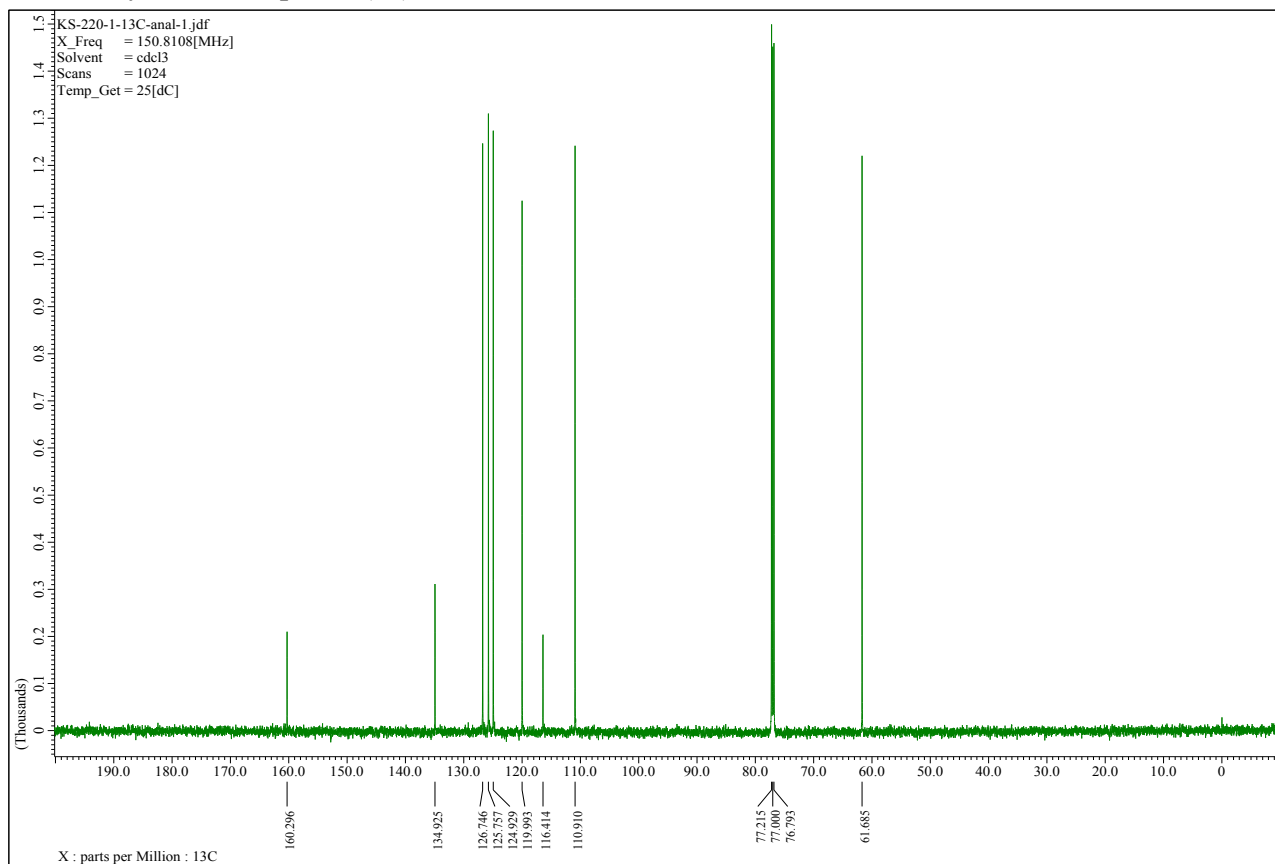
2'-Methoxy-2,3'-bithiophene (1c) ¹³C



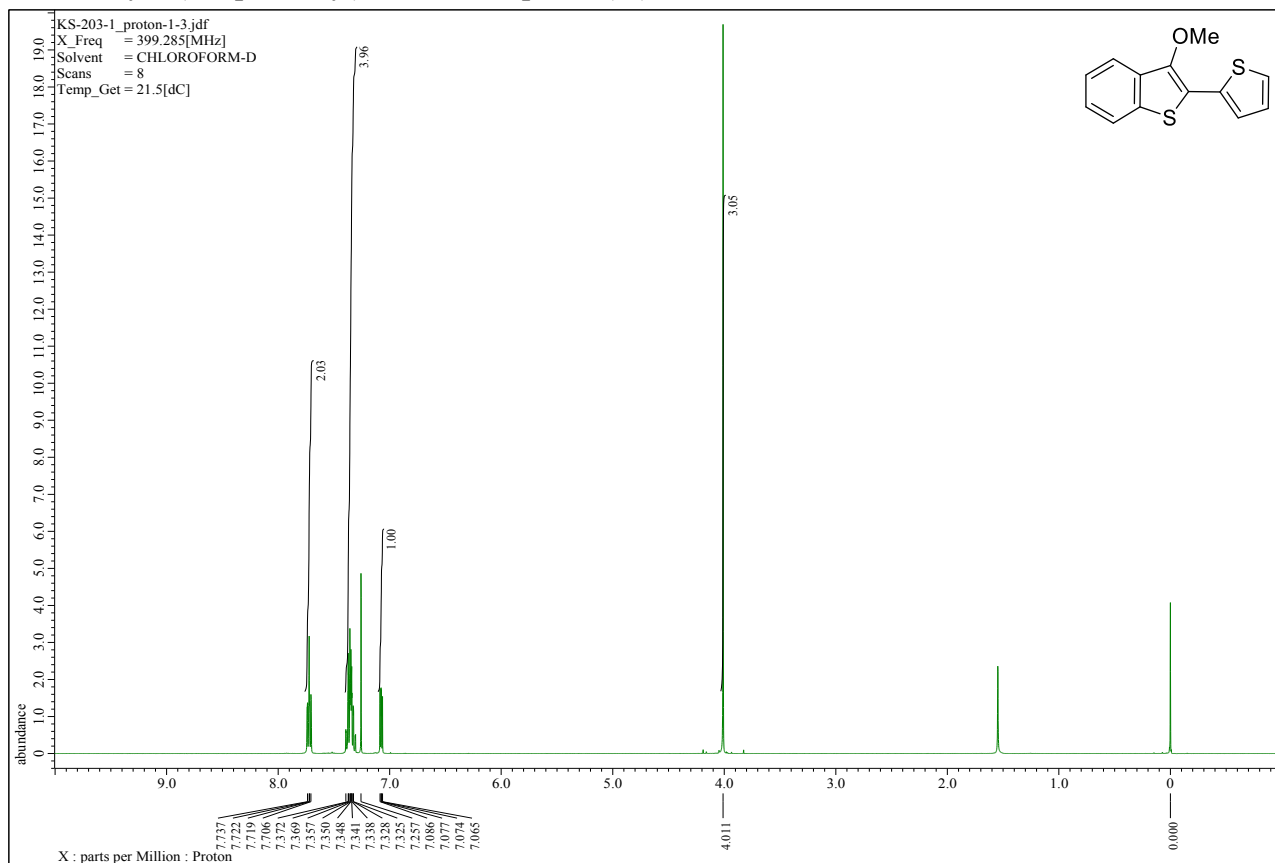
2-Methoxy-3,3'-bithiophene (1d) ¹H



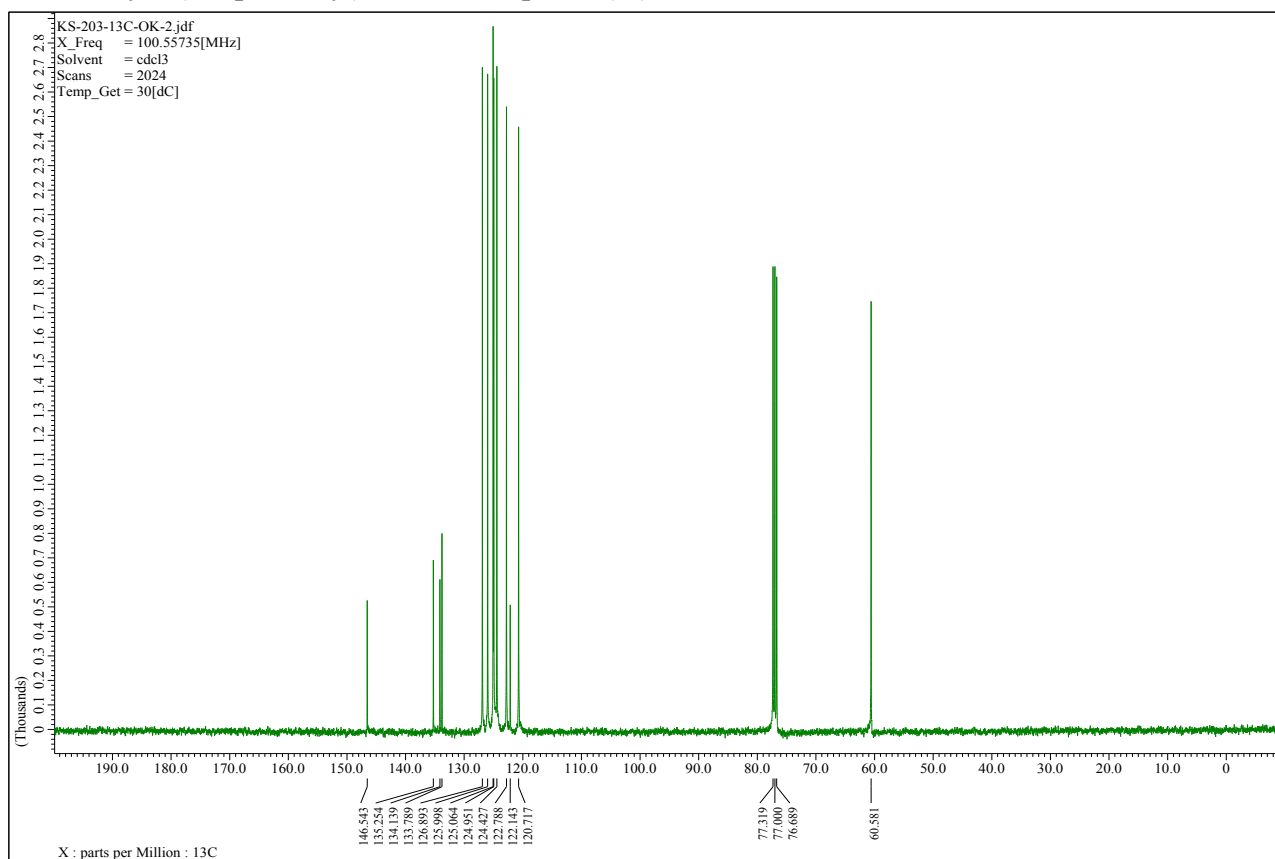
2-Methoxy-3,3'-bithiophene (1d) ¹³C



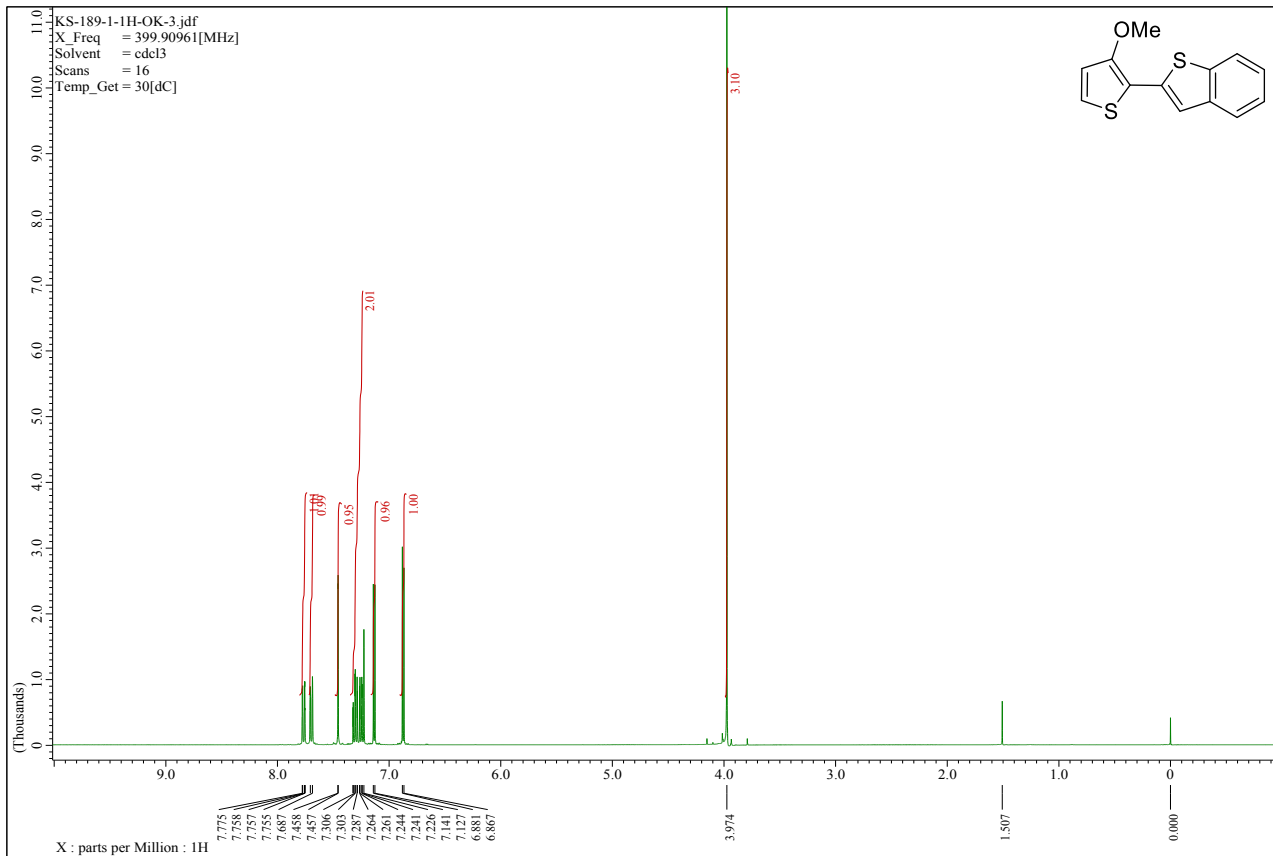
3-Methoxy-2-(thiophen-2-yl)benzo[b]thiophene (1e) ¹H



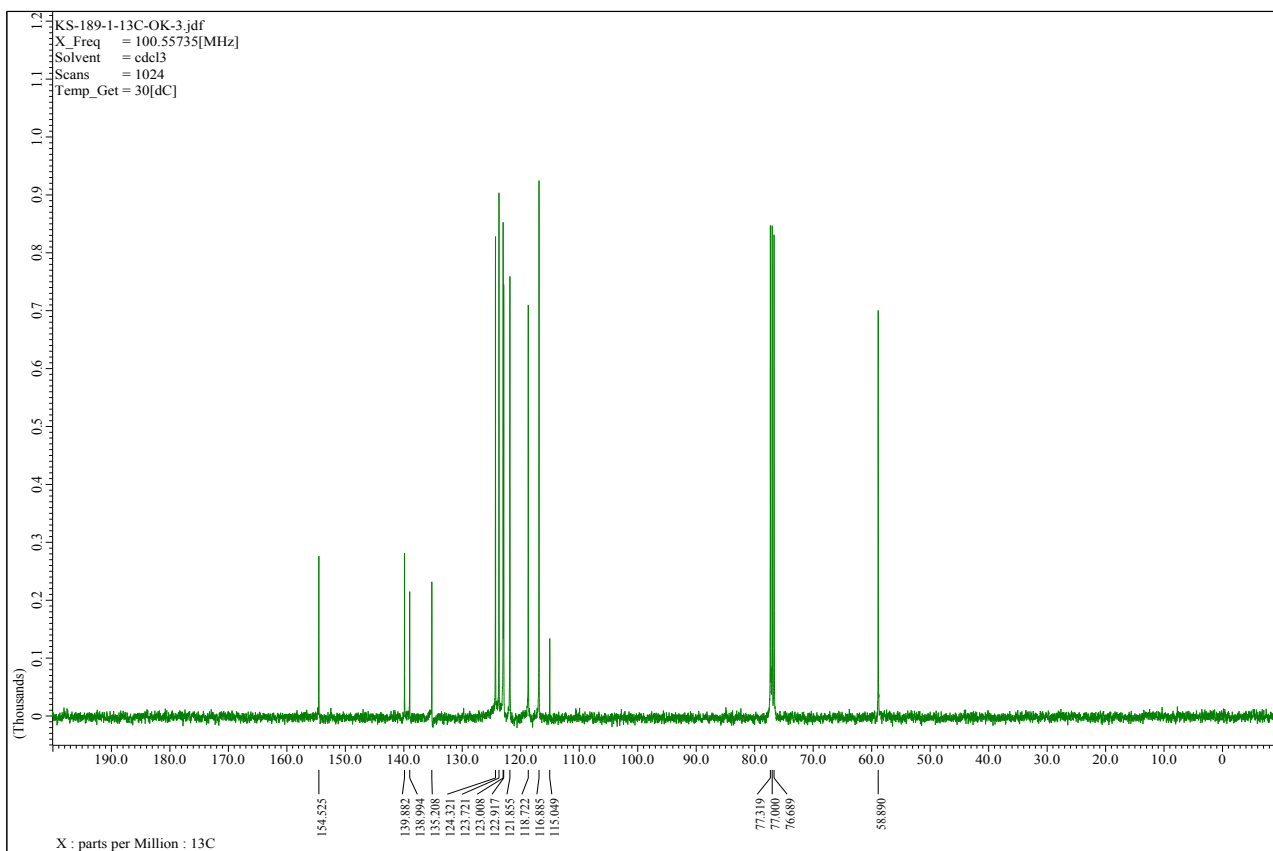
3-Methoxy-2-(thiophen-2-yl)benzo[b]thiophene (1e) ¹³C



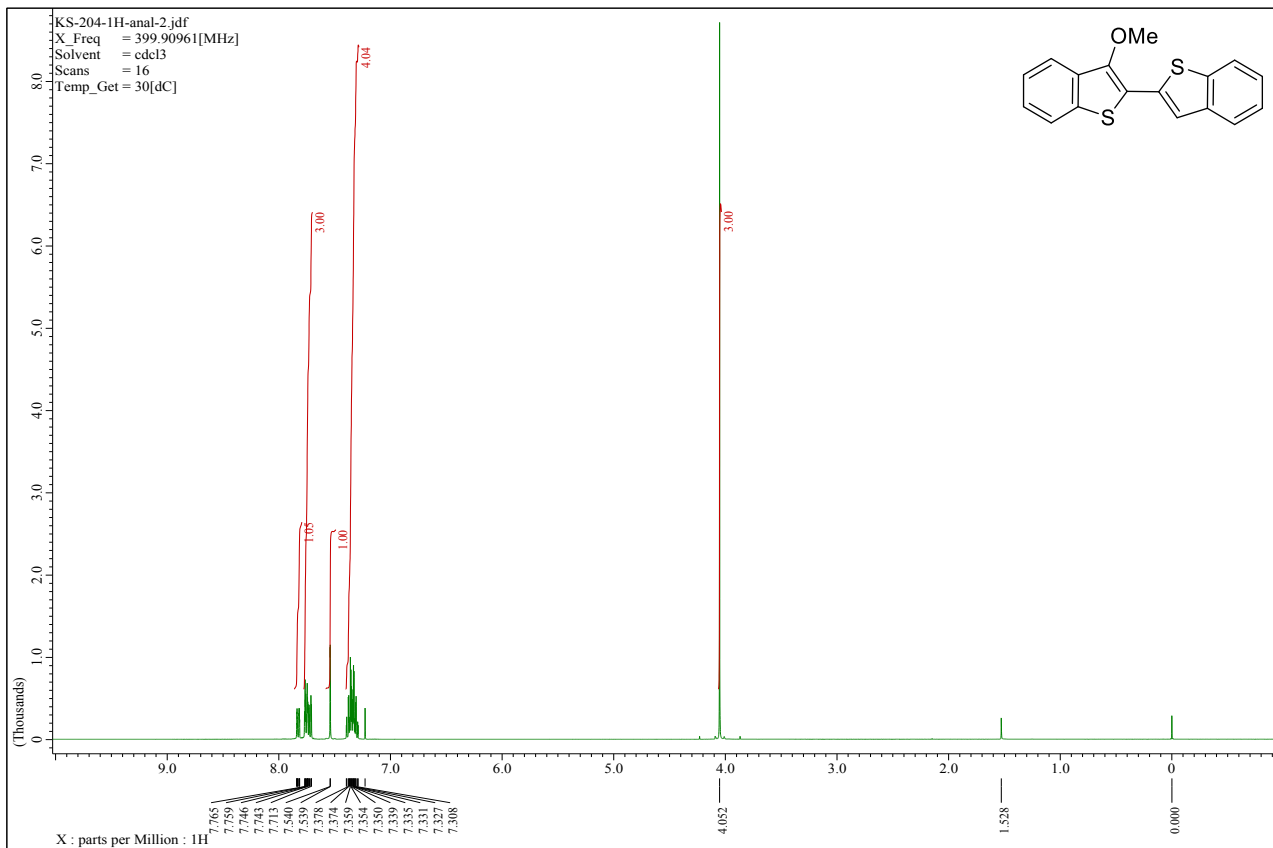
2-(3-Methoxythiophen-2-yl)benzo[b]thiophene (1f) ¹H



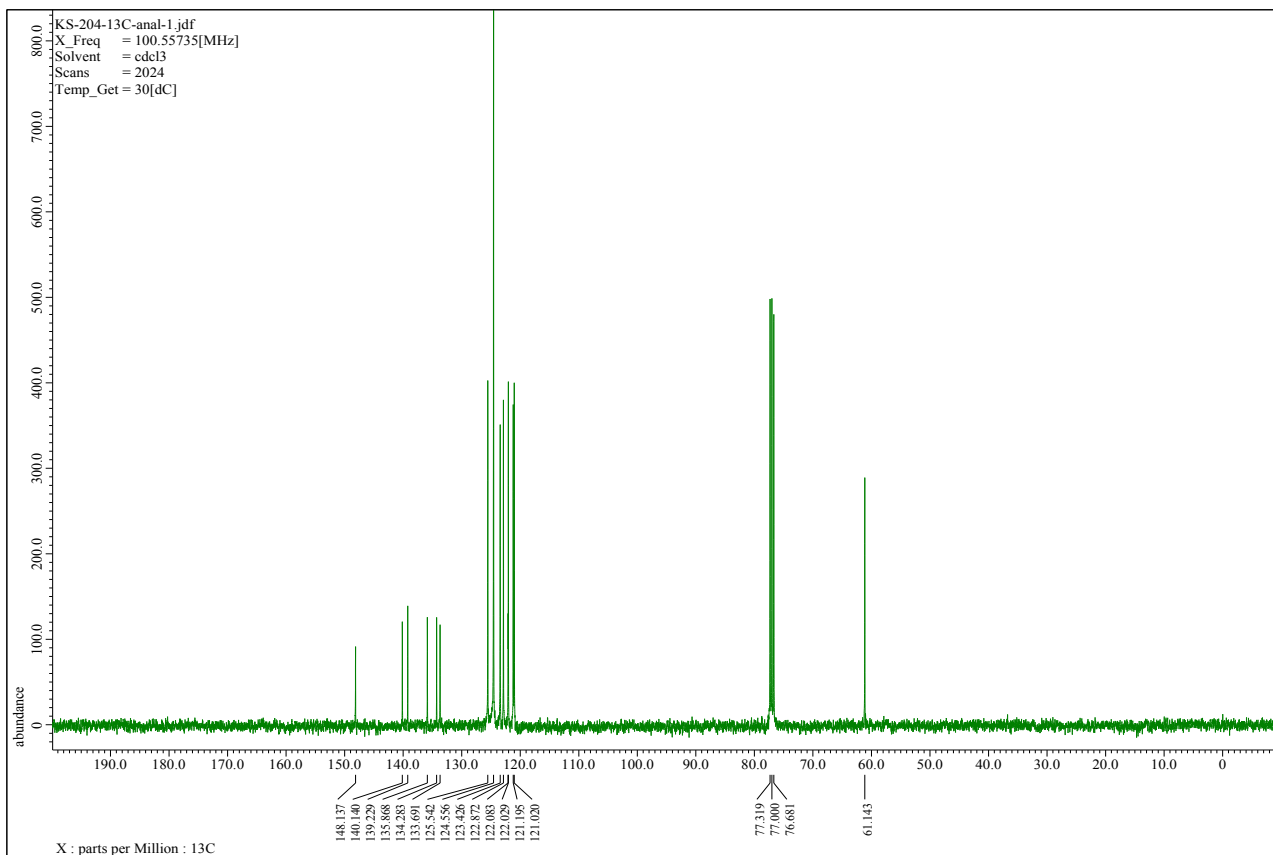
2-(3-Methoxythiophen-2-yl)benzo[b]thiophene (1f) ¹³C



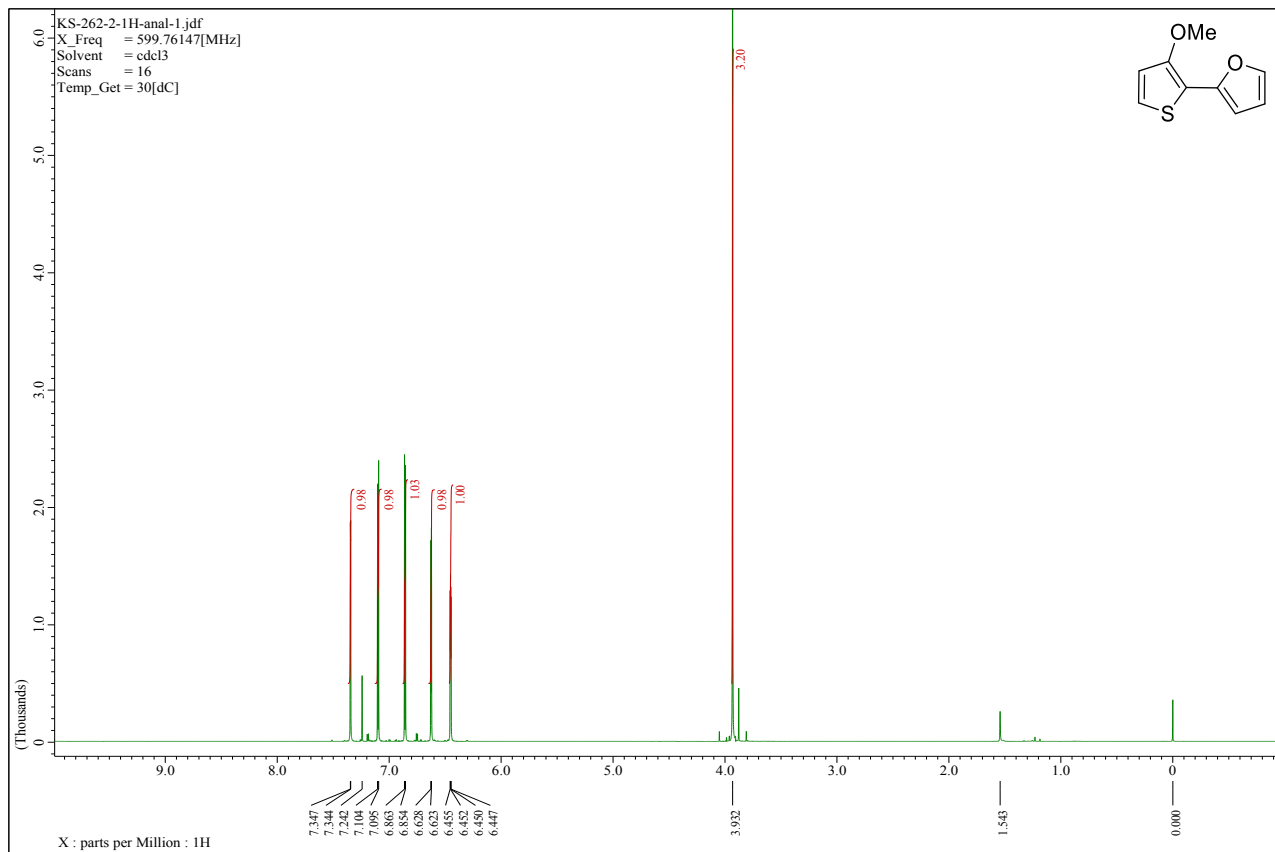
3-Methoxy-2,2'-bibenzo[b]thiophene (1g) ¹H



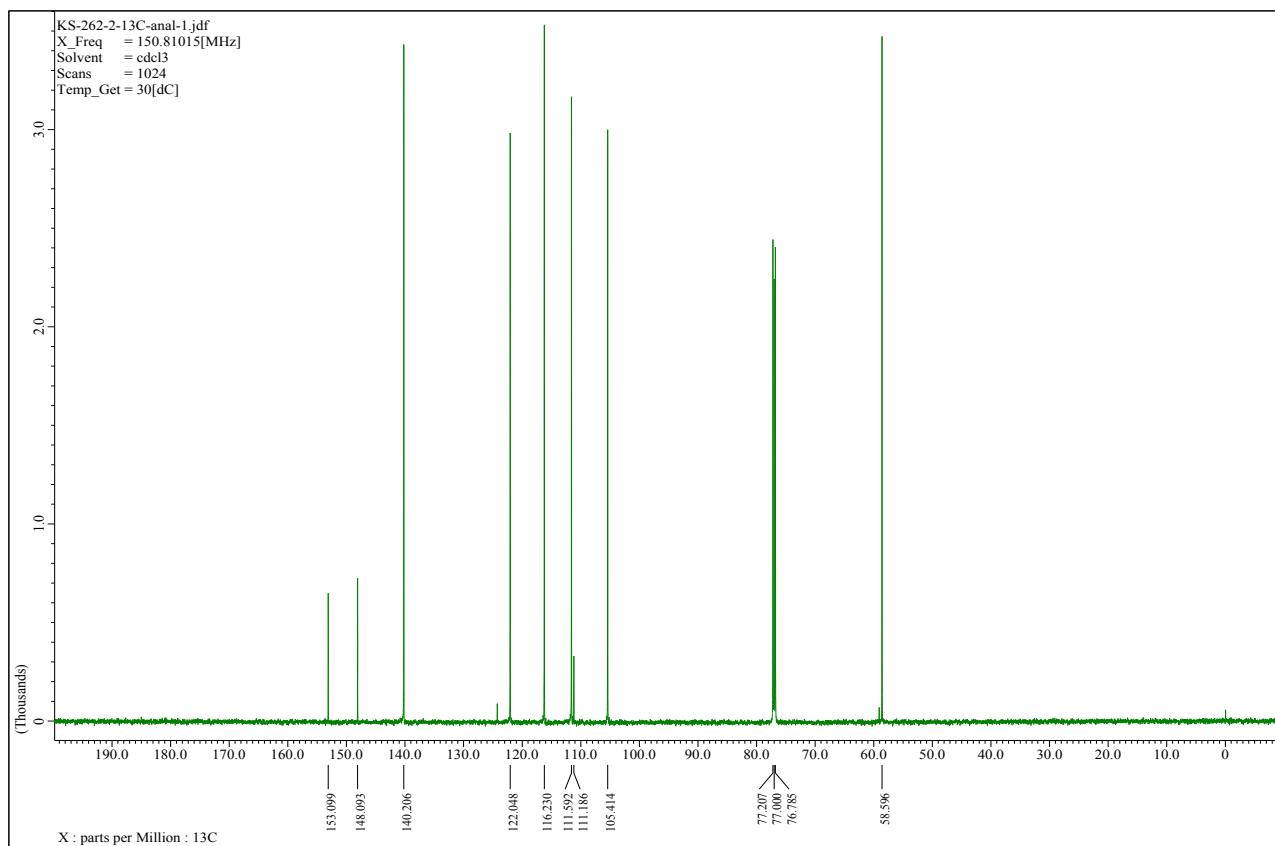
3-Methoxy-2,2'-bibenzo[b]thiophene (1g) ¹³C



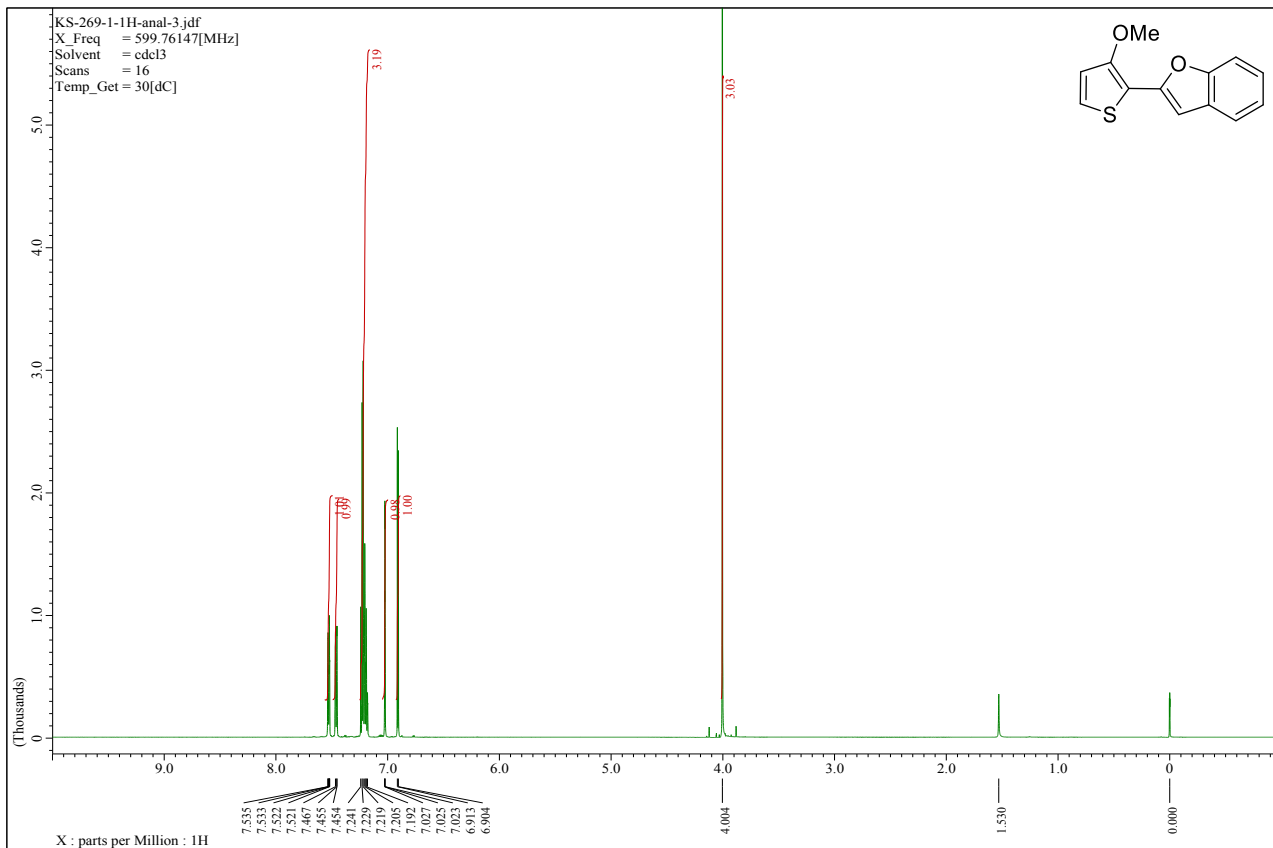
2-(3-Methoxythiophen-2-yl)furan (1h) ¹H



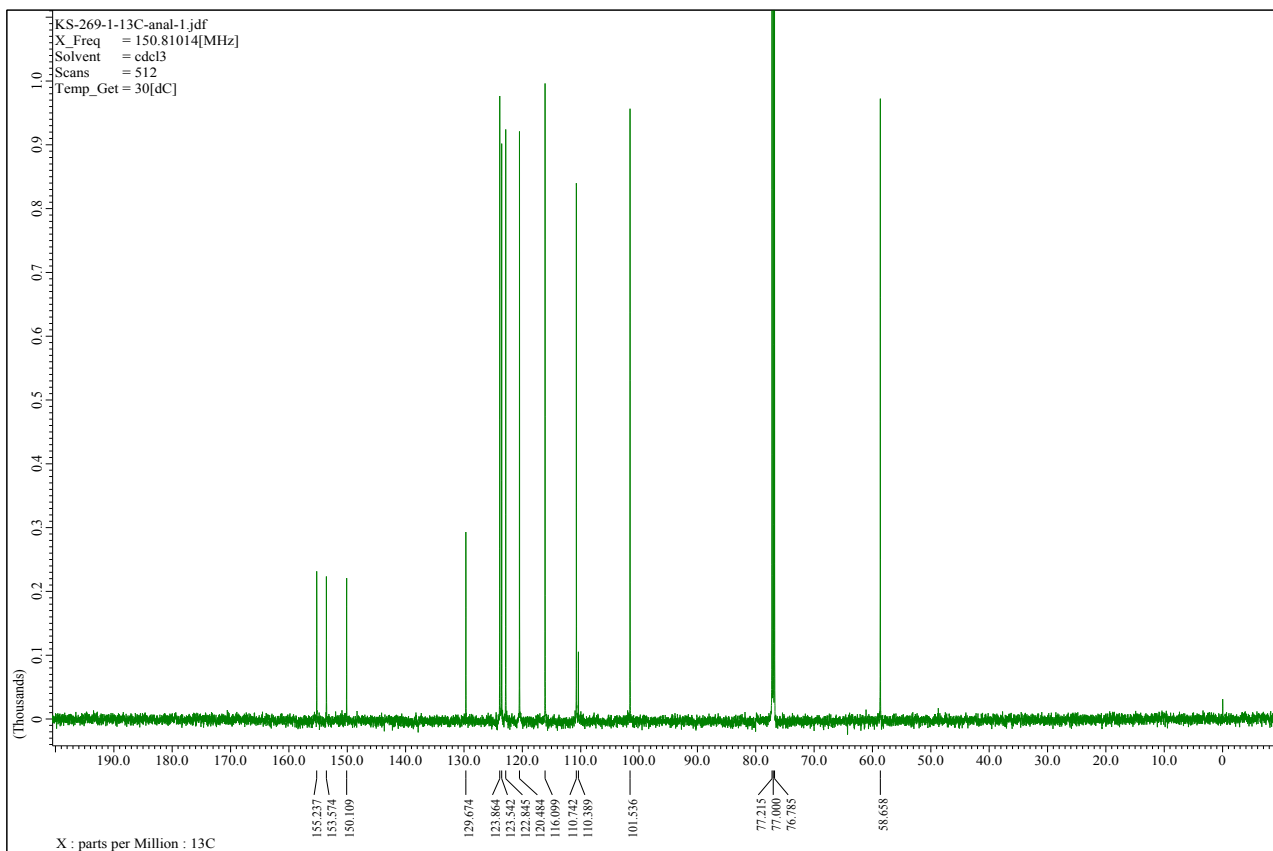
2-(3-Methoxythiophen-2-yl)furan (1h) ¹³C



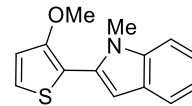
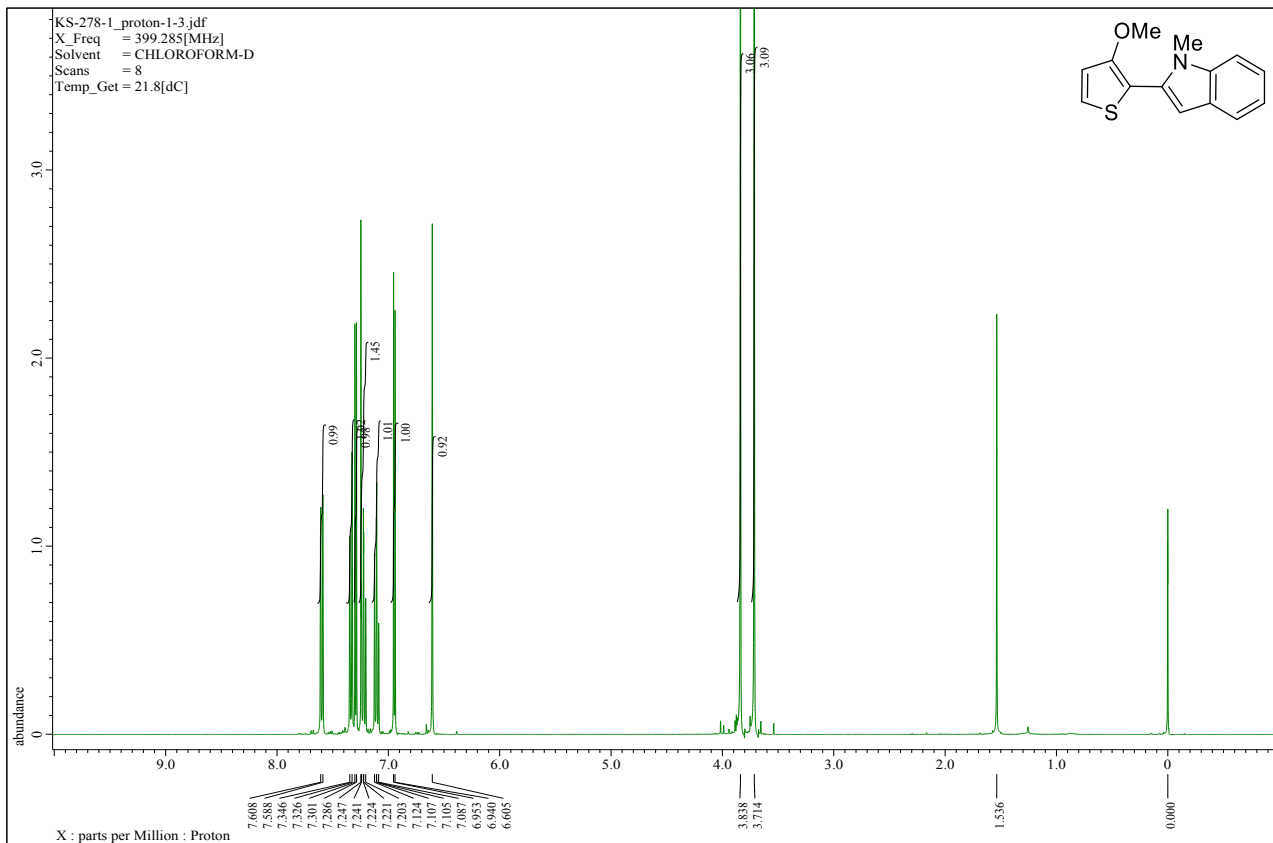
2-(3-Methoxythiophen-2-yl)benzofuran (1i) ¹H



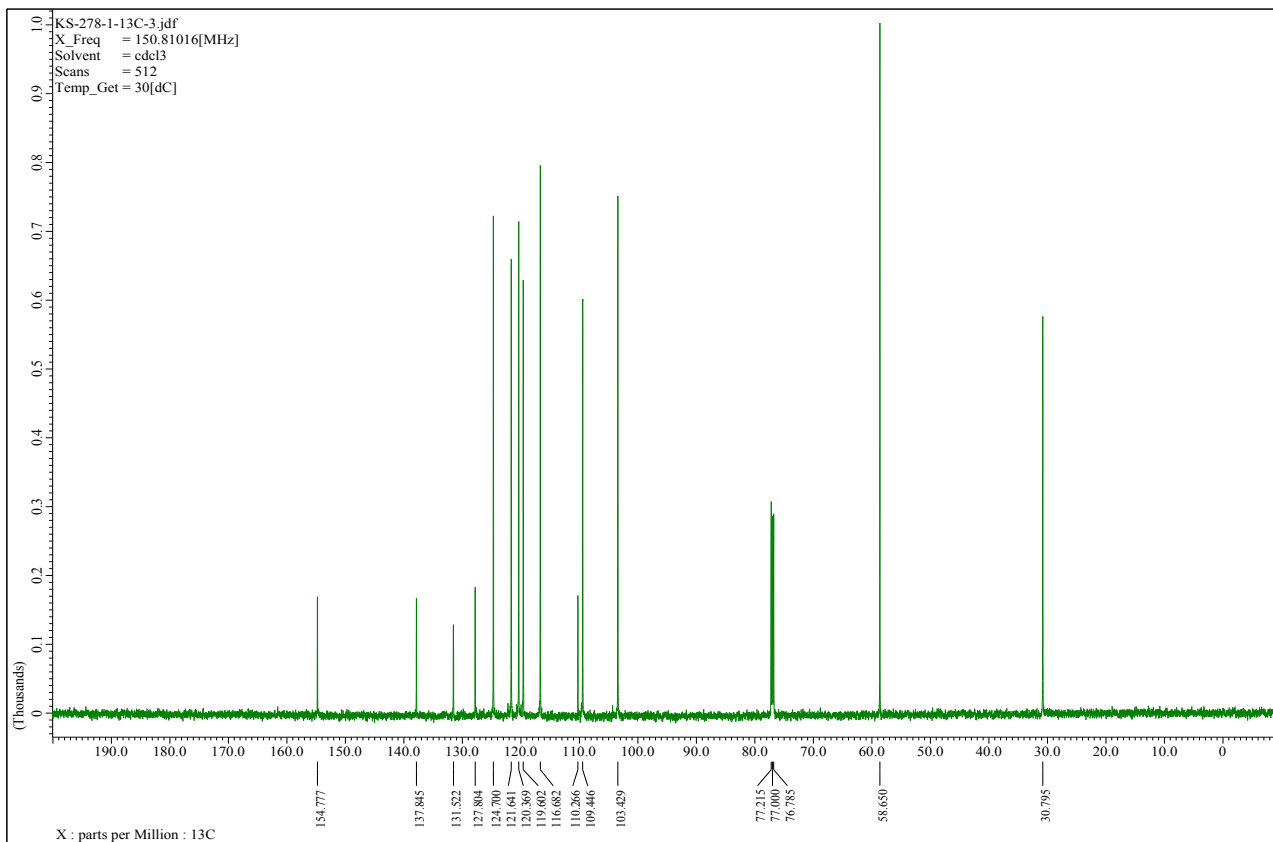
2-(3-Methoxythiophen-2-yl)benzofuran (1i) ¹³C



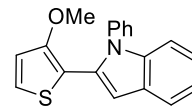
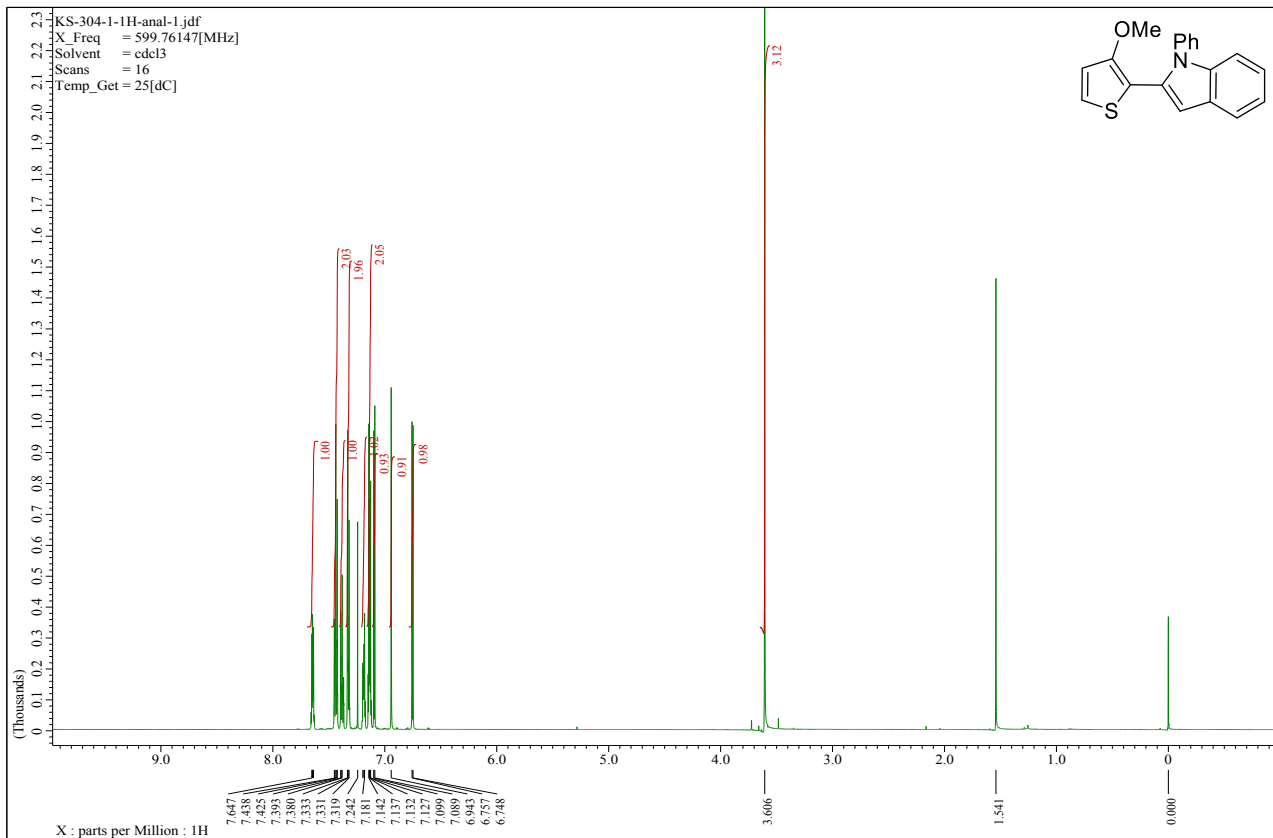
2-(3-Methoxythiophen-2-yl)-1-methyl-1H-indole (1j) ¹H



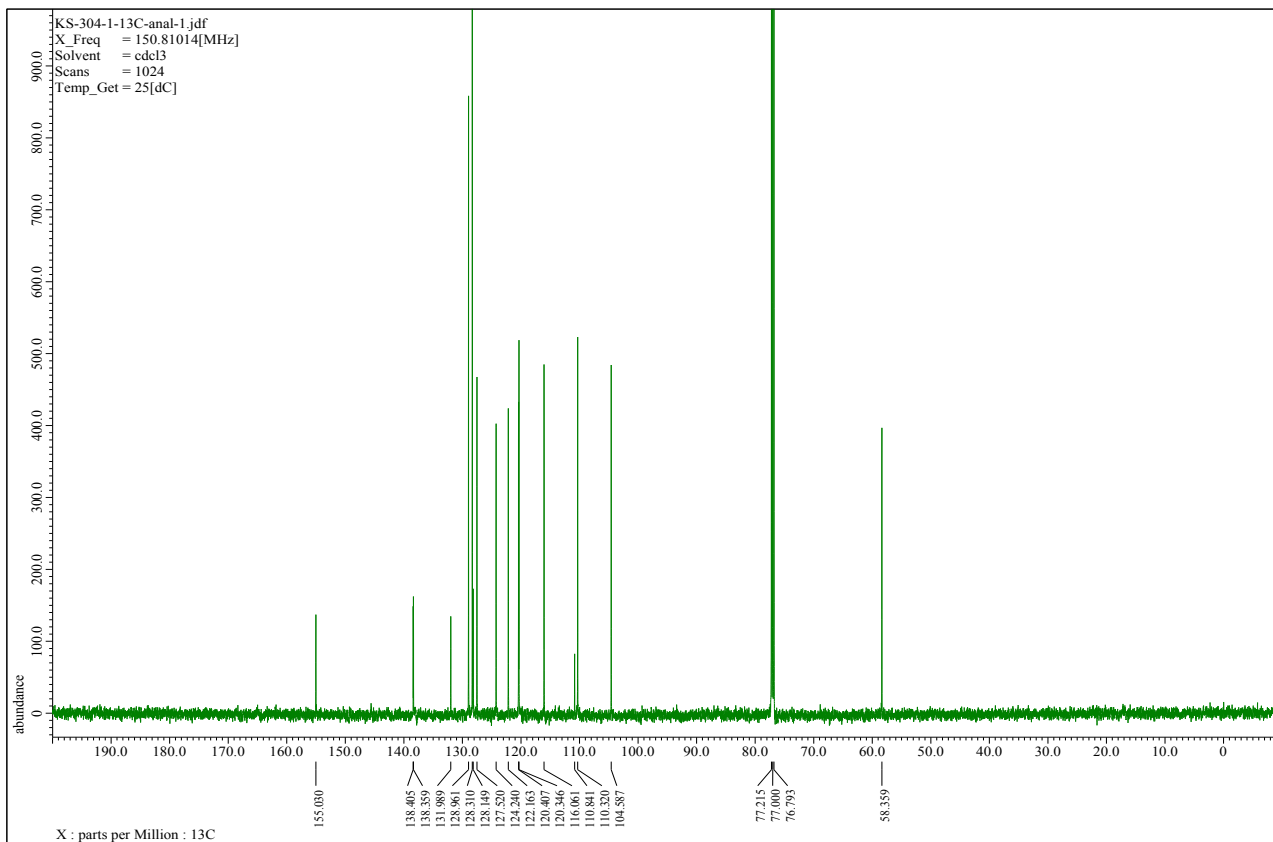
2-(3-Methoxythiophen-2-yl)-1-methyl-1H-indole (1j) ¹³C



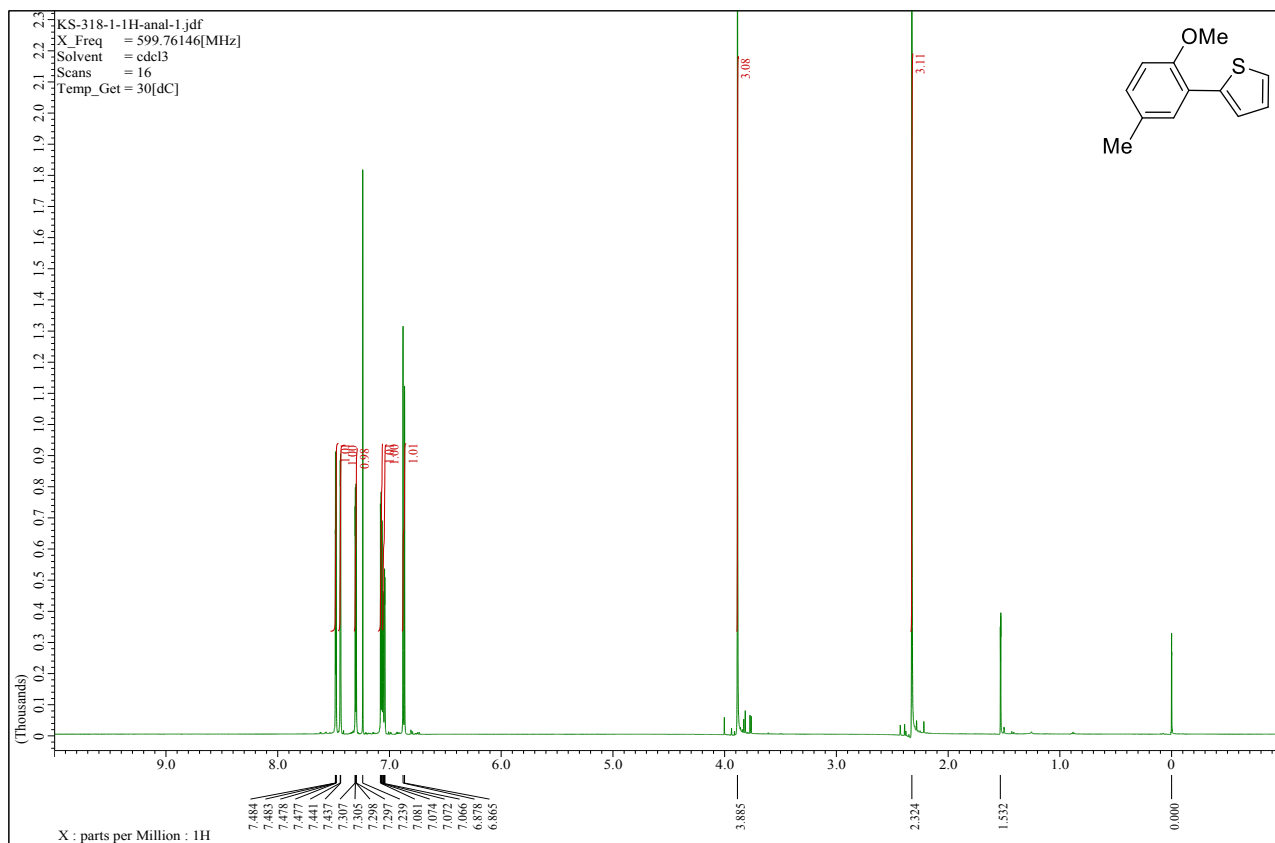
2-(3-Methoxythiophen-2-yl)-1-phenyl-1H-indole (1k) ¹H



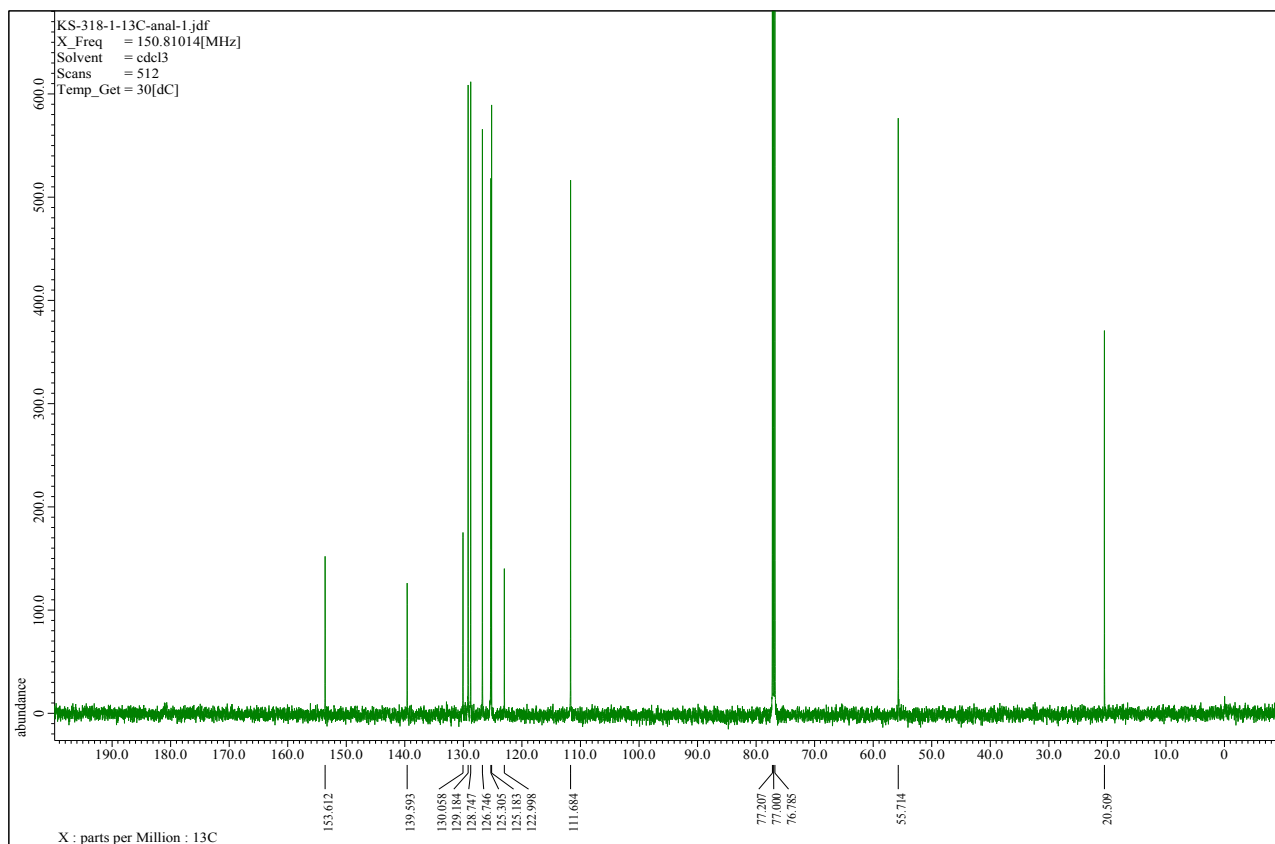
2-(3-Methoxythiophen-2-yl)-1-phenyl-1H-indole (1k) ¹³C



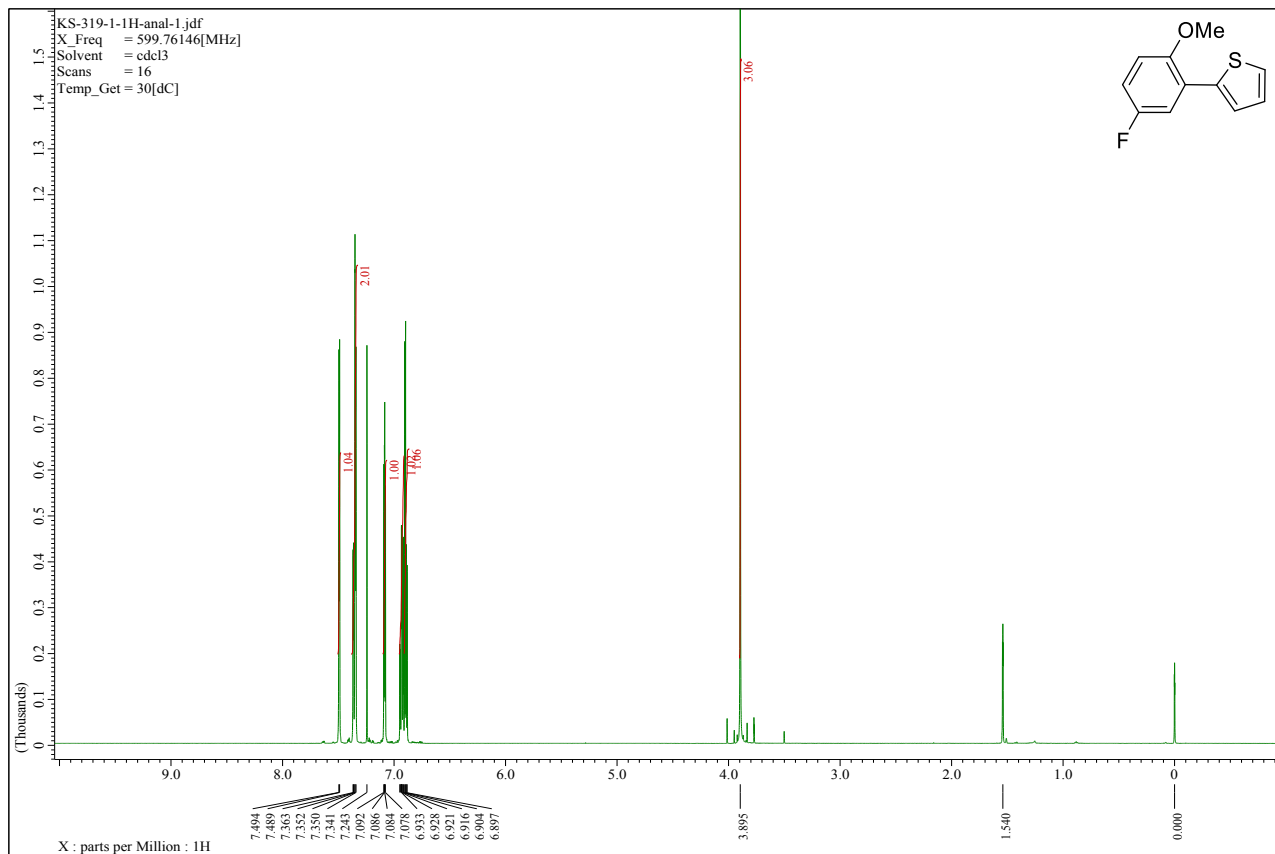
2-(2-Methoxy-5-methylphenyl)thiophene (3b) ¹H



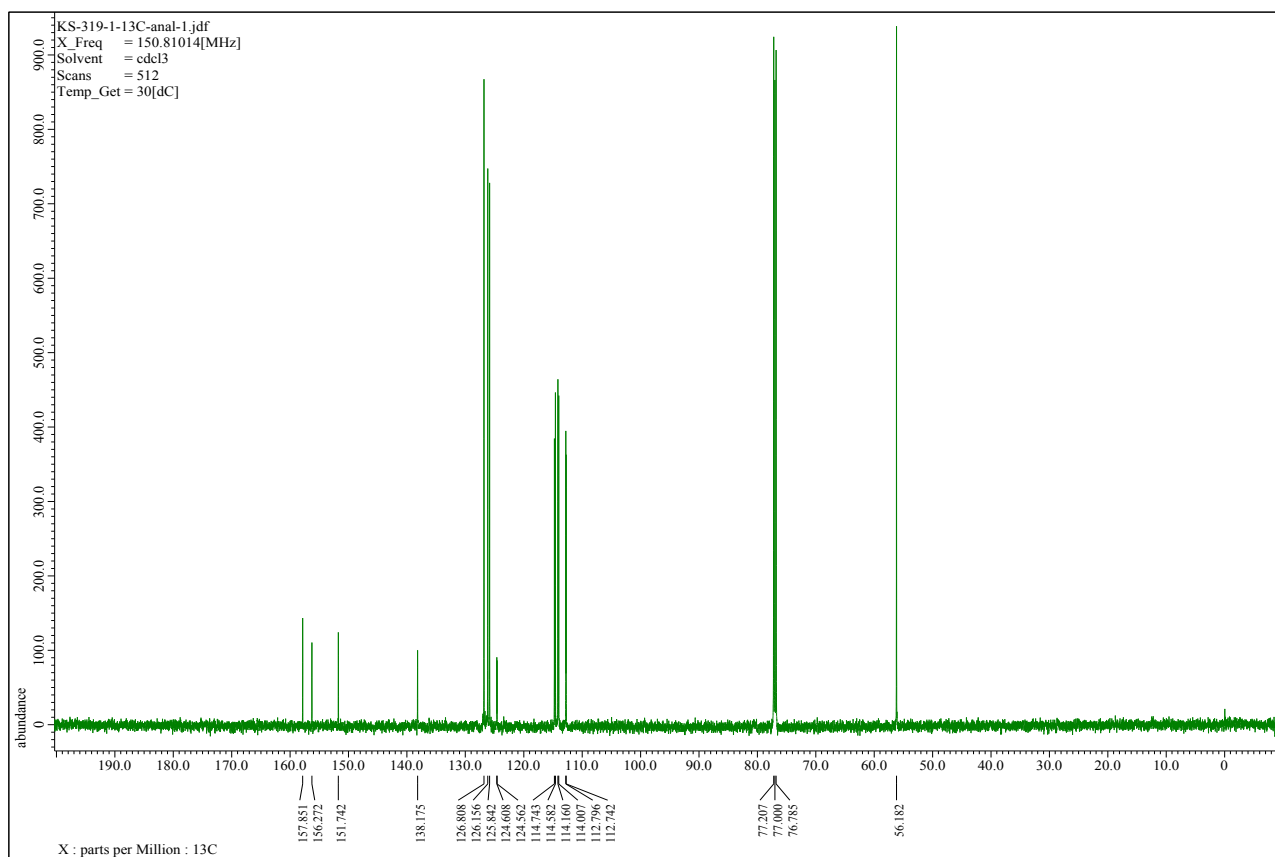
2-(2-Methoxy-5-methylphenyl)thiophene (3b) ¹³C



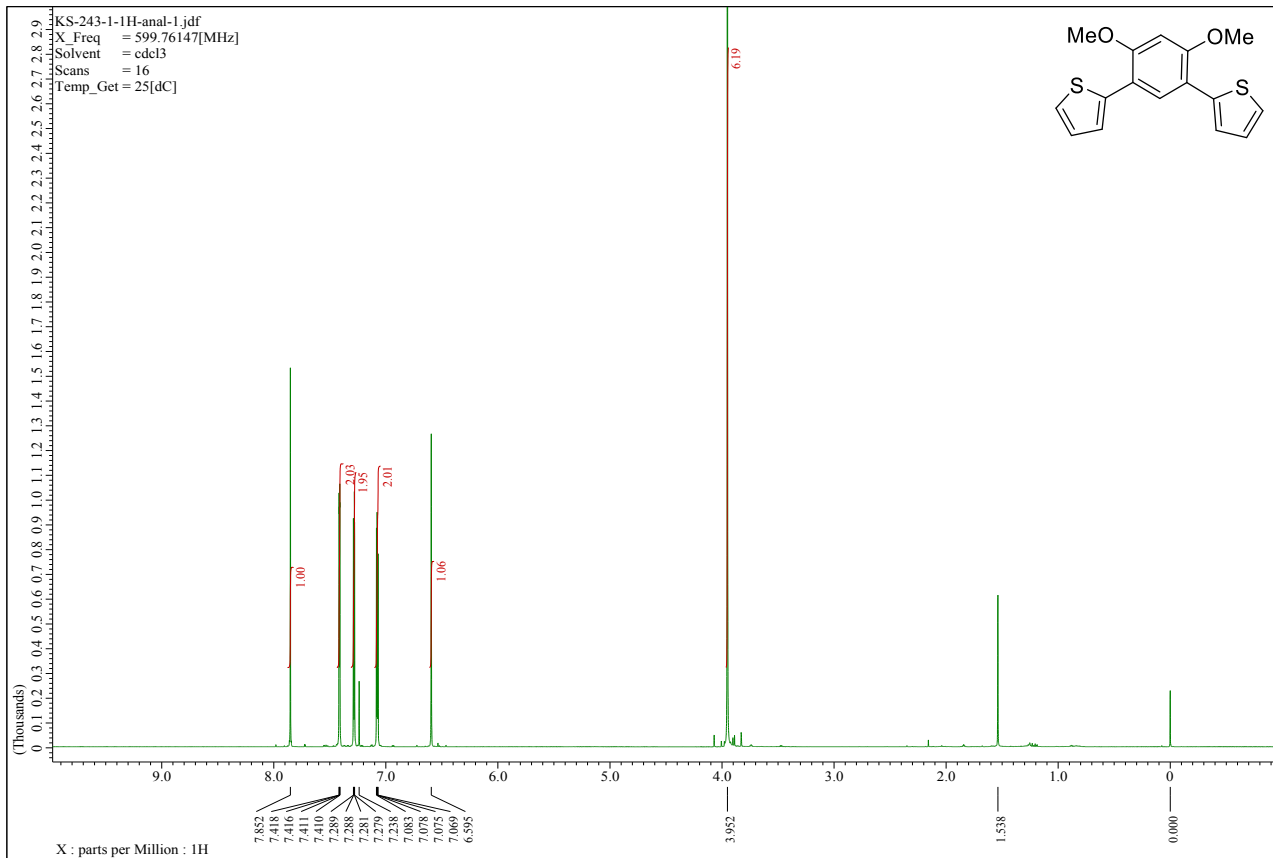
2-(5-Fluoro-2-methoxyphenyl)thiophene (3c) ¹H



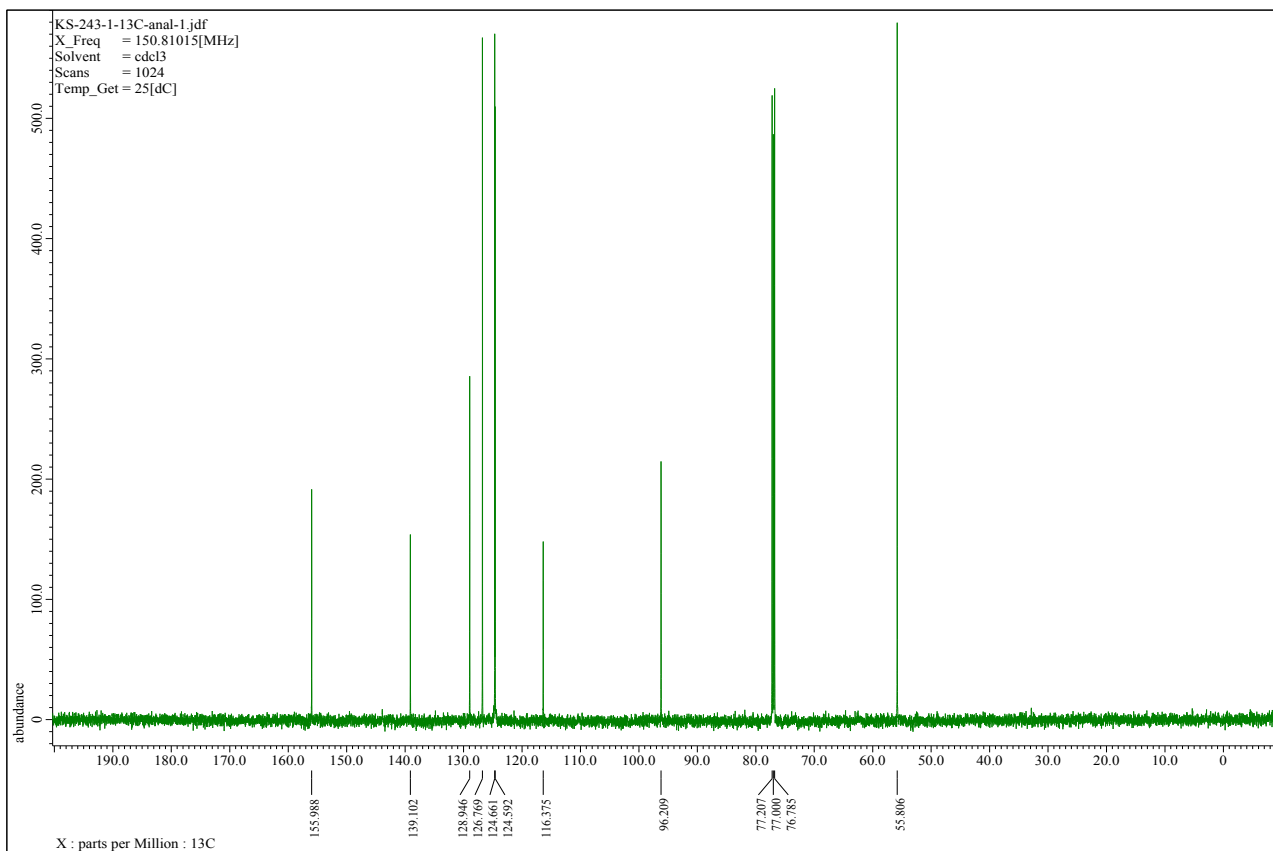
2-(5-Fluoro-2-methoxyphenyl)thiophene (3c) ¹³C



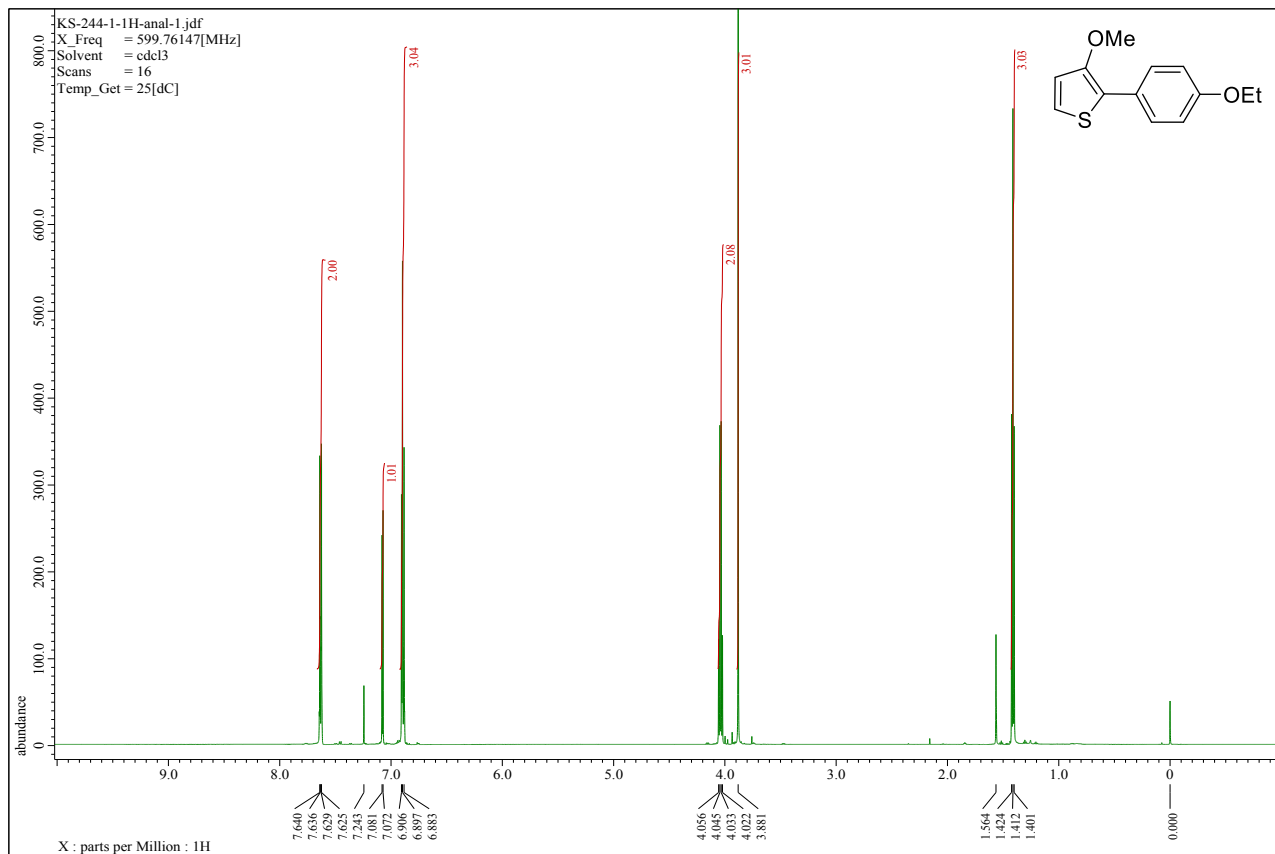
2,2'-(4,6-Dimethoxy-1,3-phenylene)dithiophene (3e) ¹H



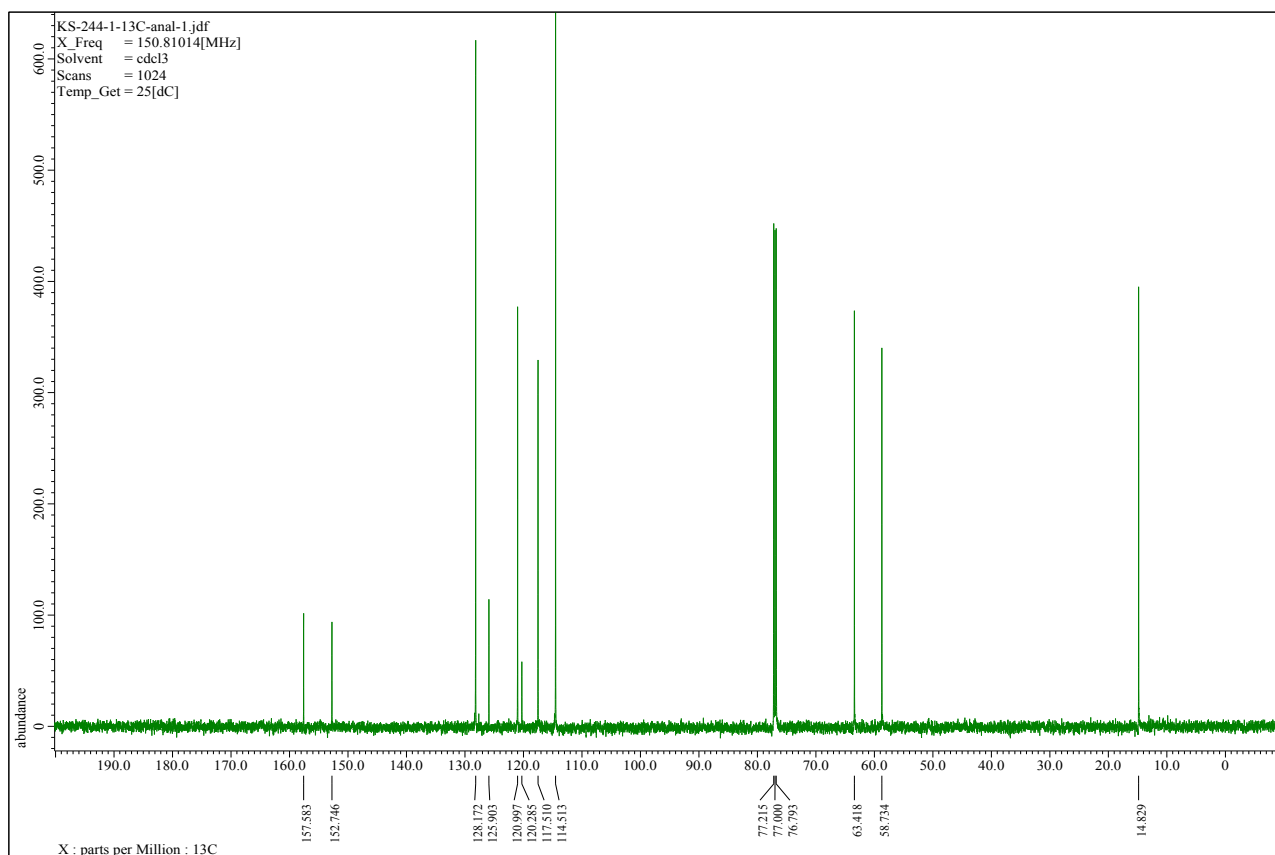
2,2'-(4,6-Dimethoxy-1,3-phenylene)dithiophene (3e) ¹³C



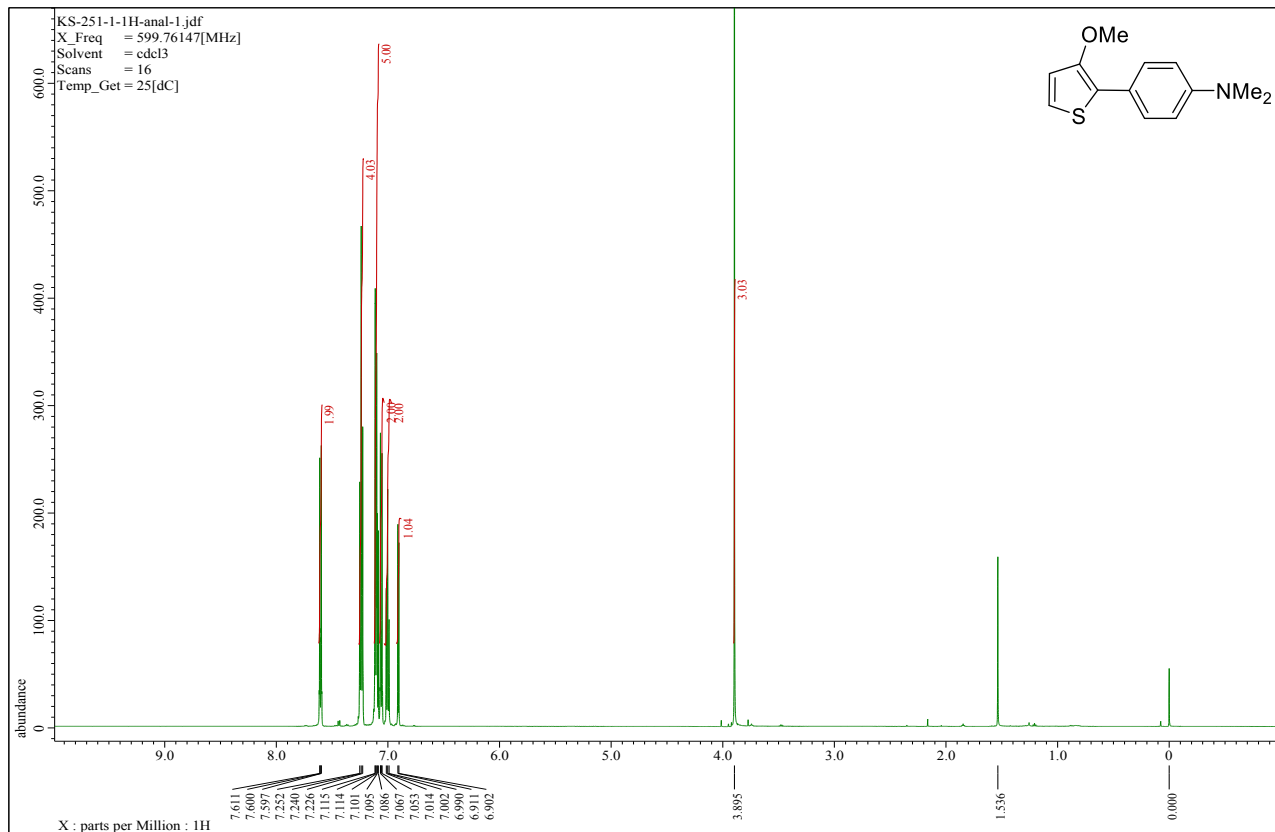
2-(4-Ethoxyphenyl)-3-methoxythiophene (3h) ¹H



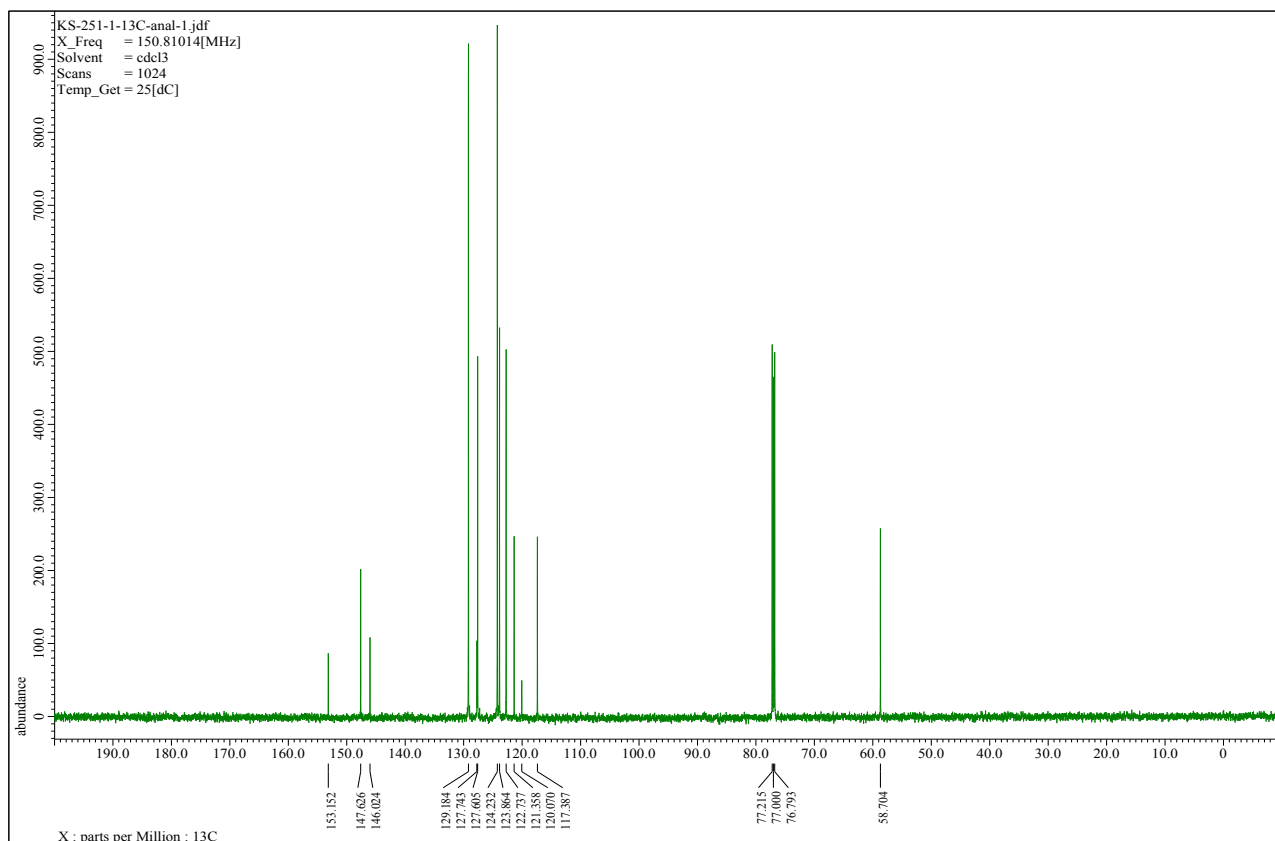
2-(4-Ethoxyphenyl)-3-methoxythiophene (3h) ¹³C



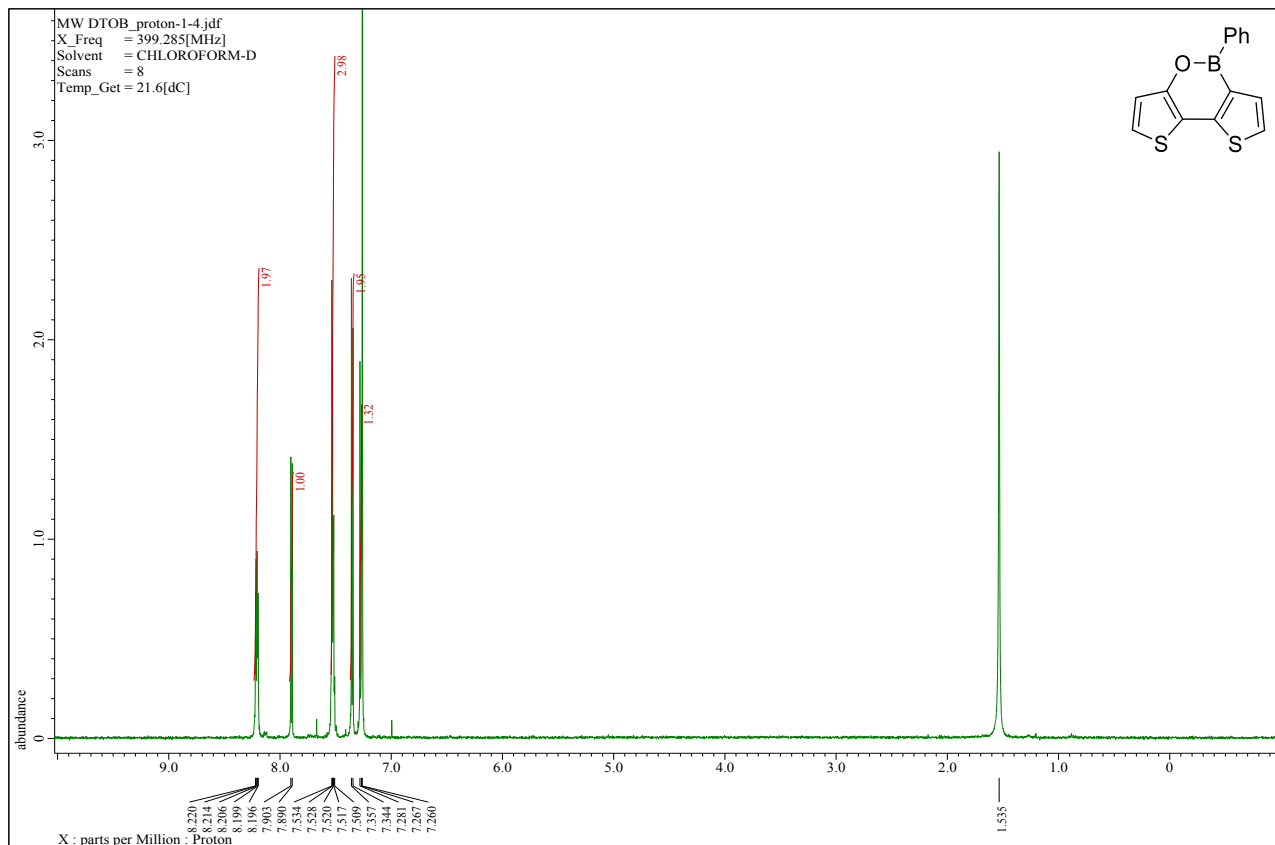
4-(3-Methoxythiophen-2-yl)-N,N-diphenylaniline (3i) ¹H



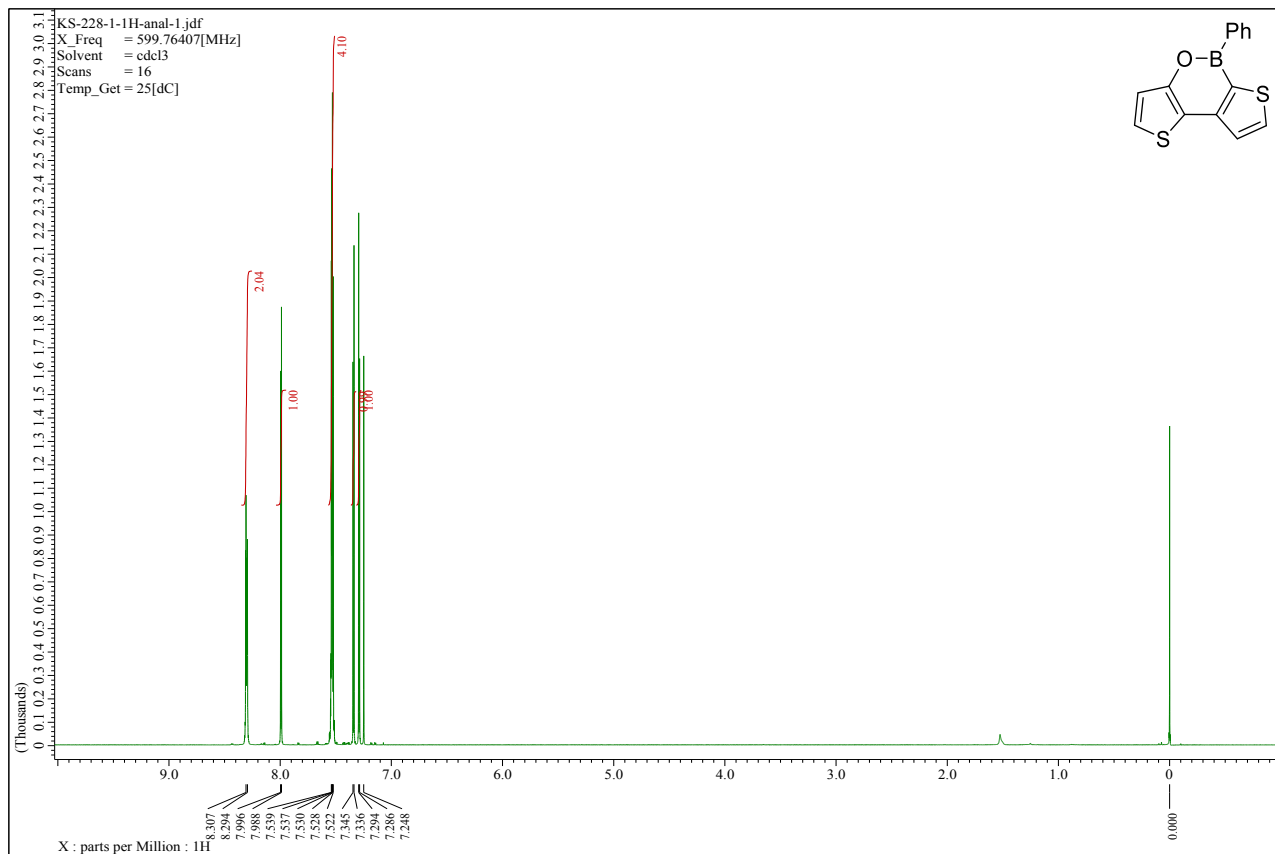
4-(3-Methoxythiophen-2-yl)-N,N-diphenylaniline (3i) ¹³C



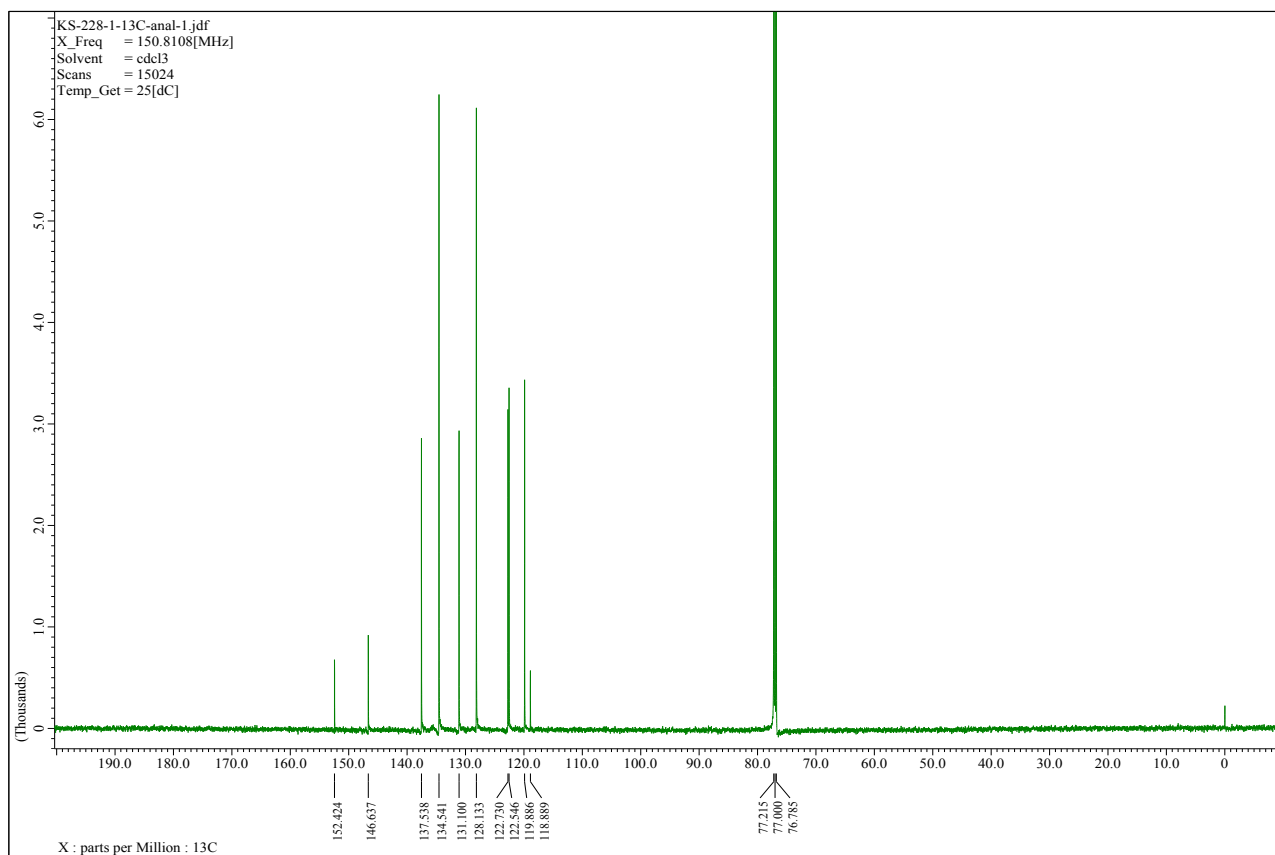
5-Phenyl-5*H*-dithieno[3,2-c:2',3'-e][1,2]oxaborinine (2a) ¹H



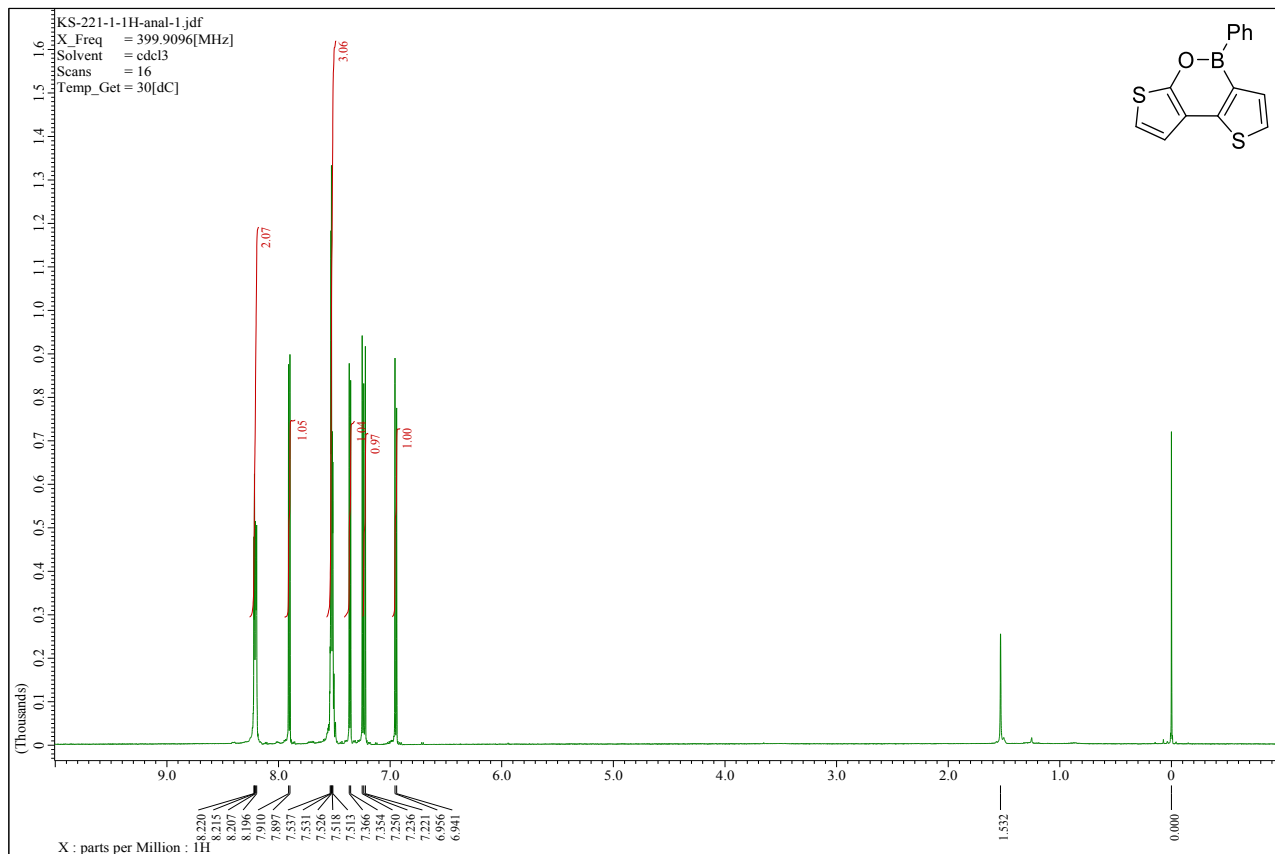
5-Phenyl-5*H*-dithieno[2,3-*c*:2',3'-*e*][1,2]oxaborinine (2b) ¹H



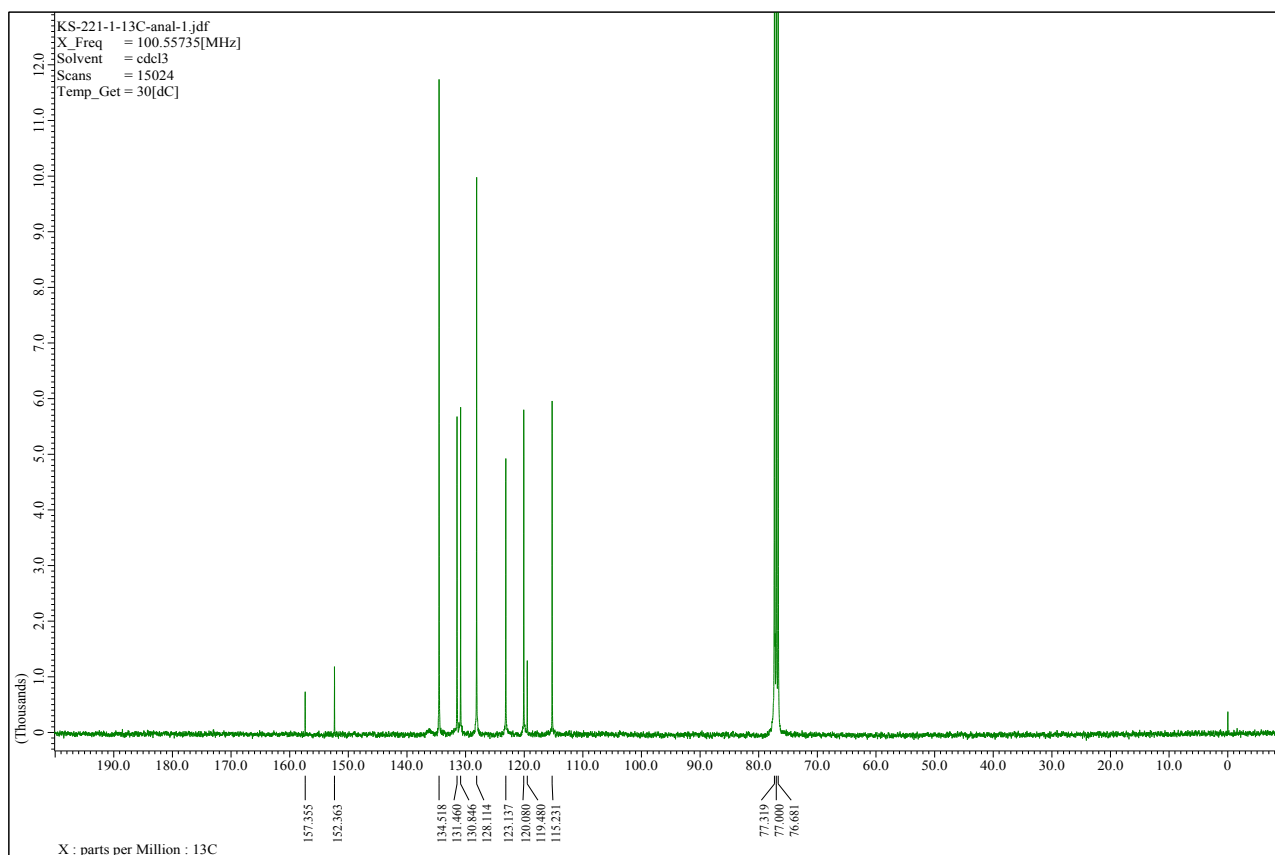
5-Phenyl-5*H*-dithieno[2,3-*c*:2',3'-*e*][1,2]oxaborinine (2b) ¹³C



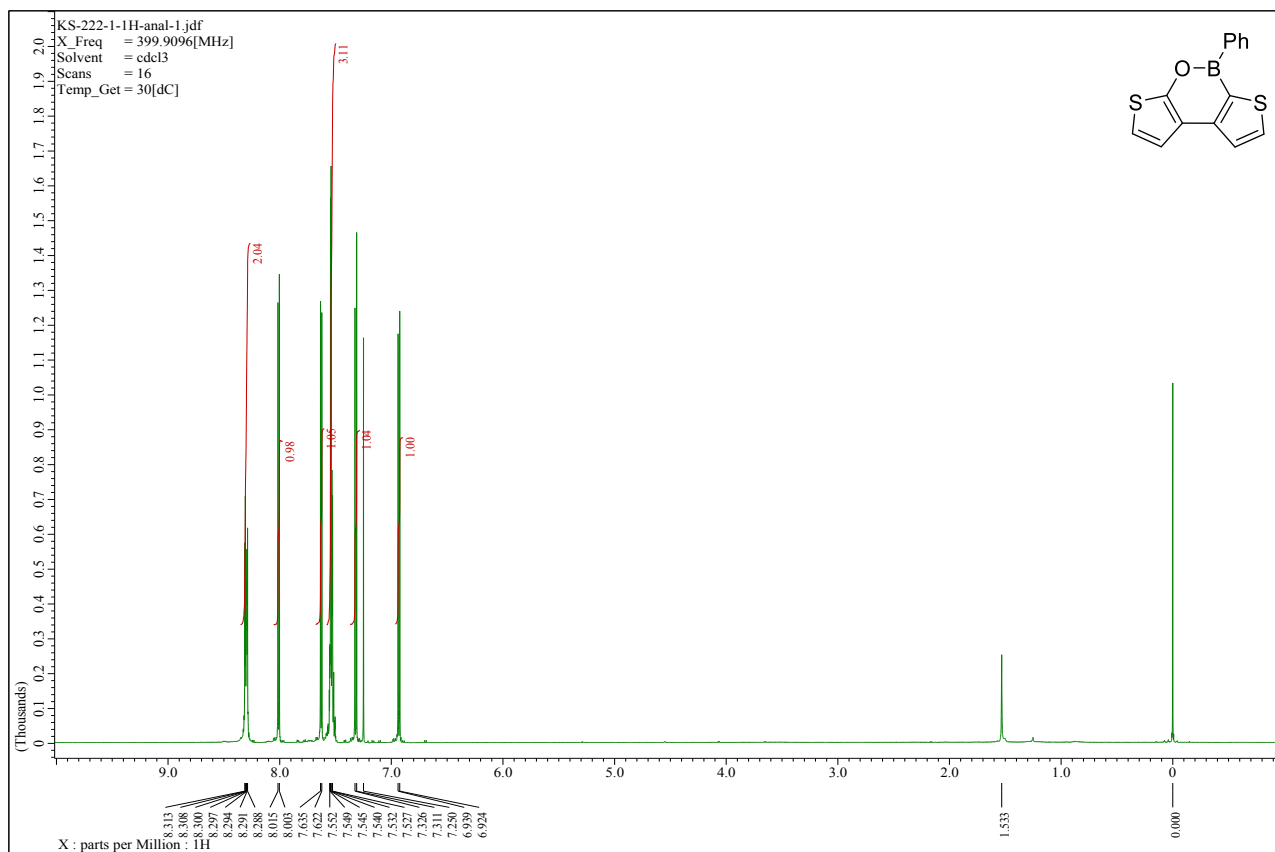
4-Phenyl-4*H*-dithieno[3,2-*c*:3',2'-*e*][1,2]oxaborinine (2c) ¹H



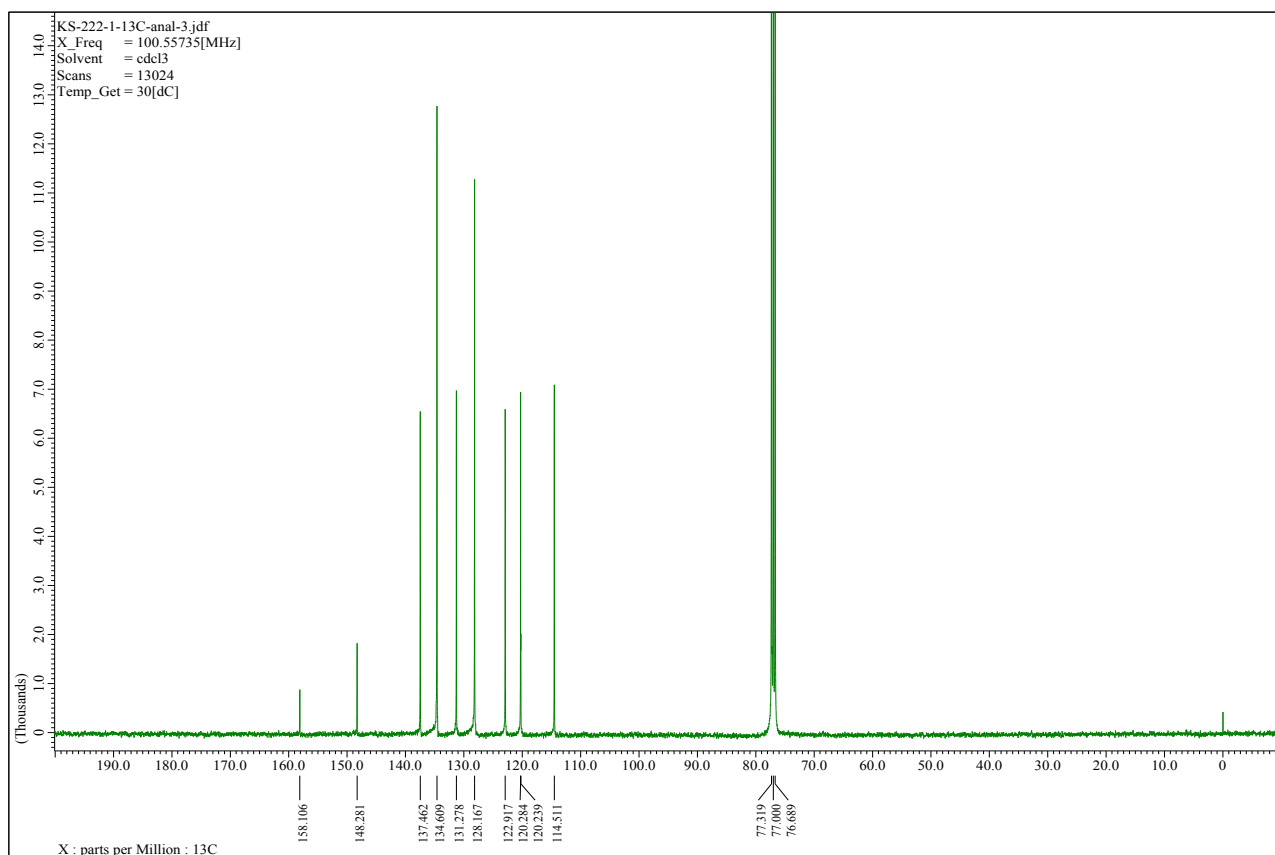
4-Phenyl-4*H*-dithieno[3,2-*c*:3',2'-*e*][1,2]oxaborinine (2c) ¹³C



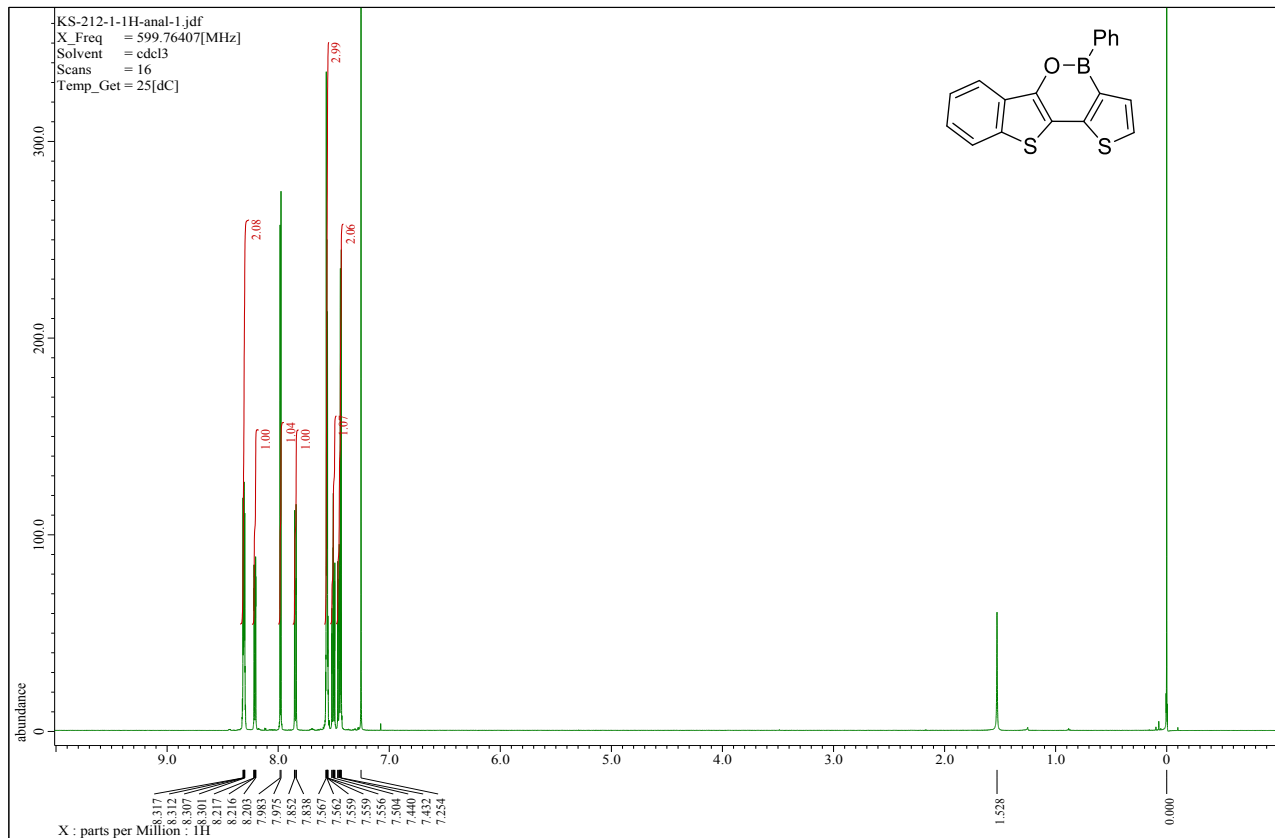
5-Phenyl-5*H*-dithieno[2,3-*c*:3',2'-*e*][1,2]oxaborinine (2d) ¹H



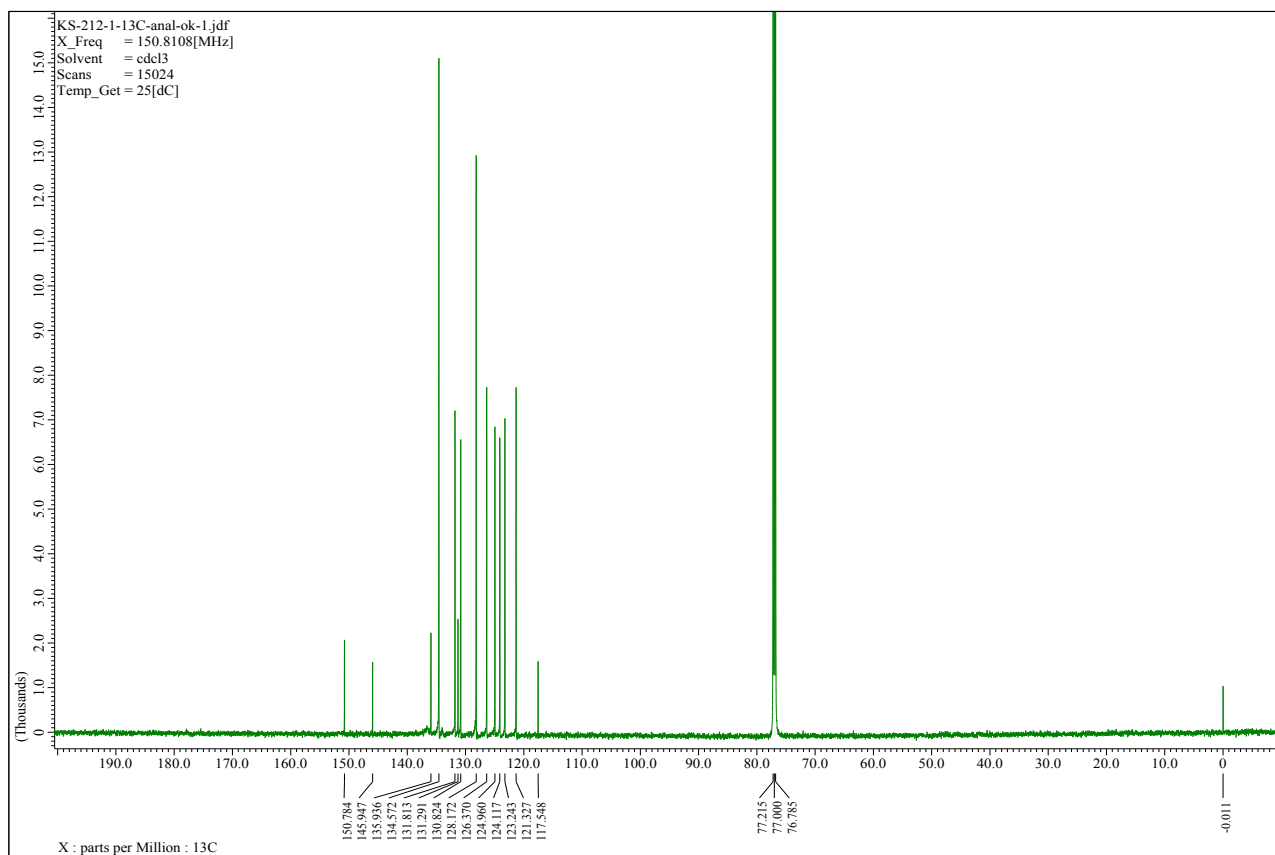
5-Phenyl-5*H*-dithieno[2,3-*c*:3',2'-*e*][1,2]oxaborinine (2d) ¹³C



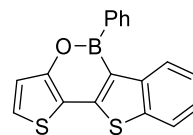
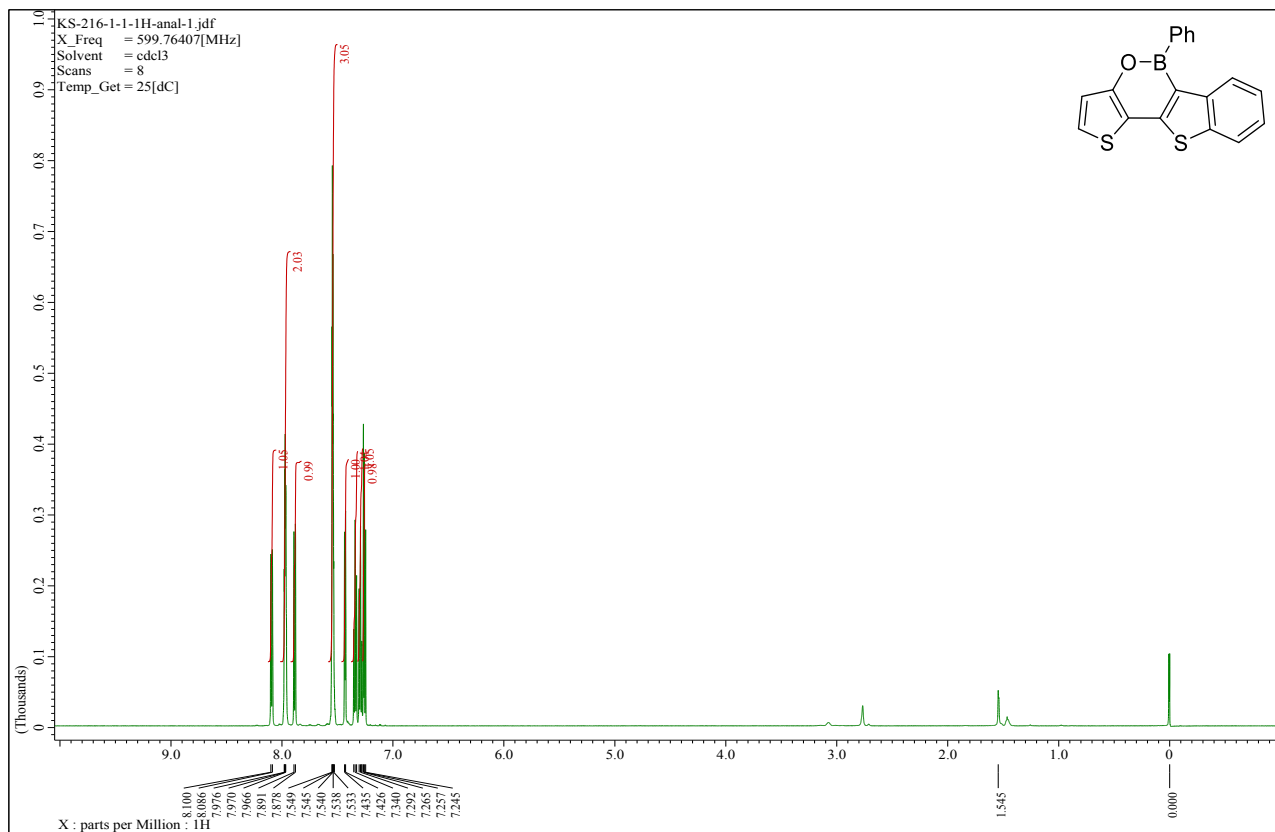
4-Phenyl-4*H*-benzo[4,5]thieno[2,3-*e*]thieno[3,2-*c*][1,2]oxaborinine (2e) ¹H



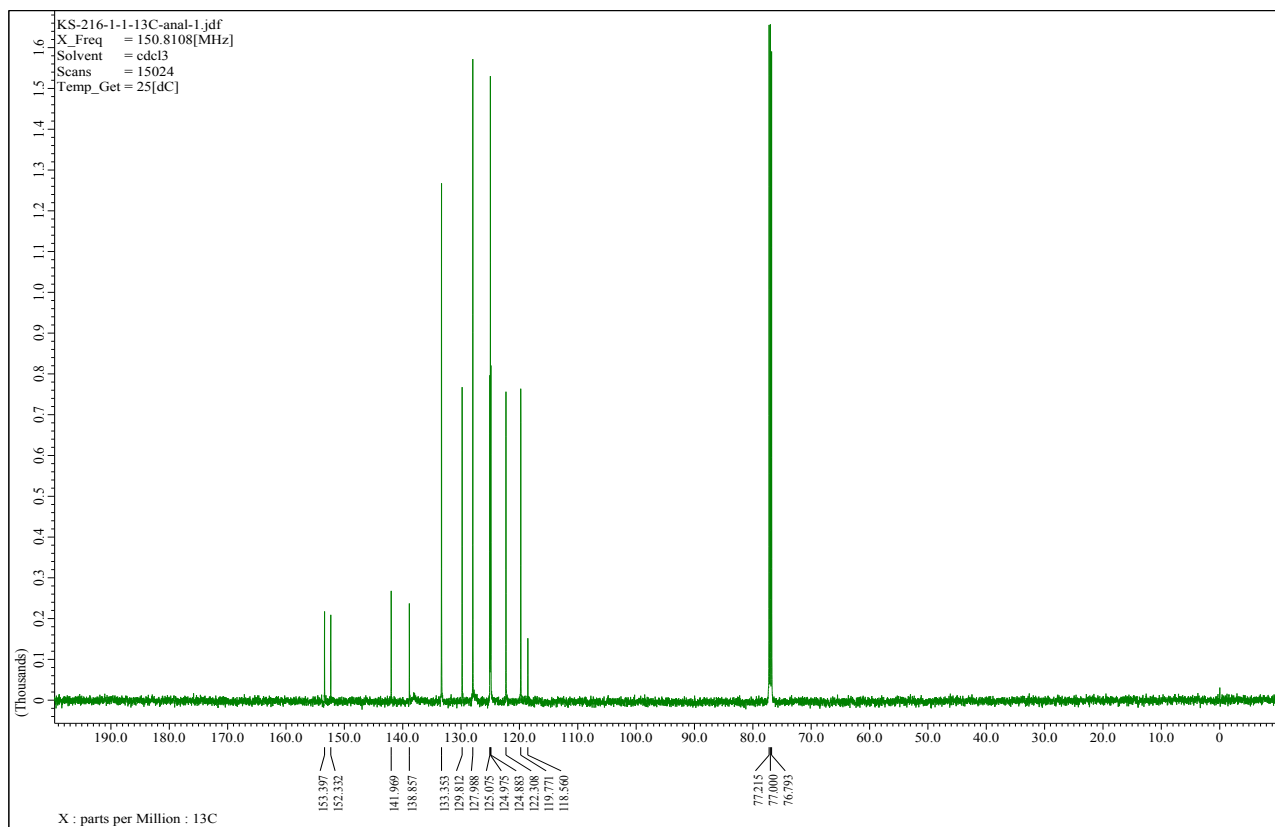
4-Phenyl-4*H*-benzo[4,5]thieno[2,3-*e*]thieno[3,2-*c*][1,2]oxaborinine (2e) ¹³C



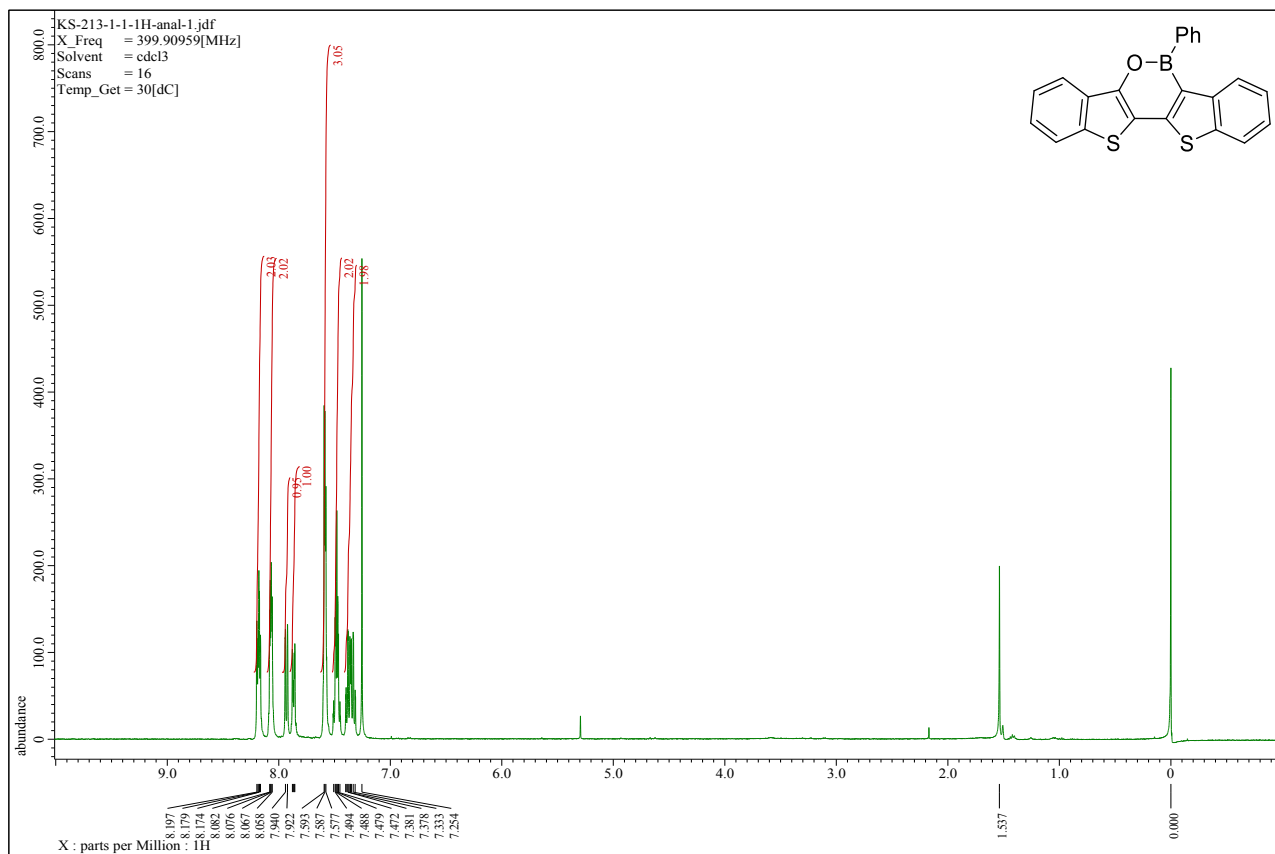
5-Phenyl-5*H*-benzo[4,5]thieno[3,2-c]thieno[2,3-e][1,2]oxaborinine (2f) ¹H



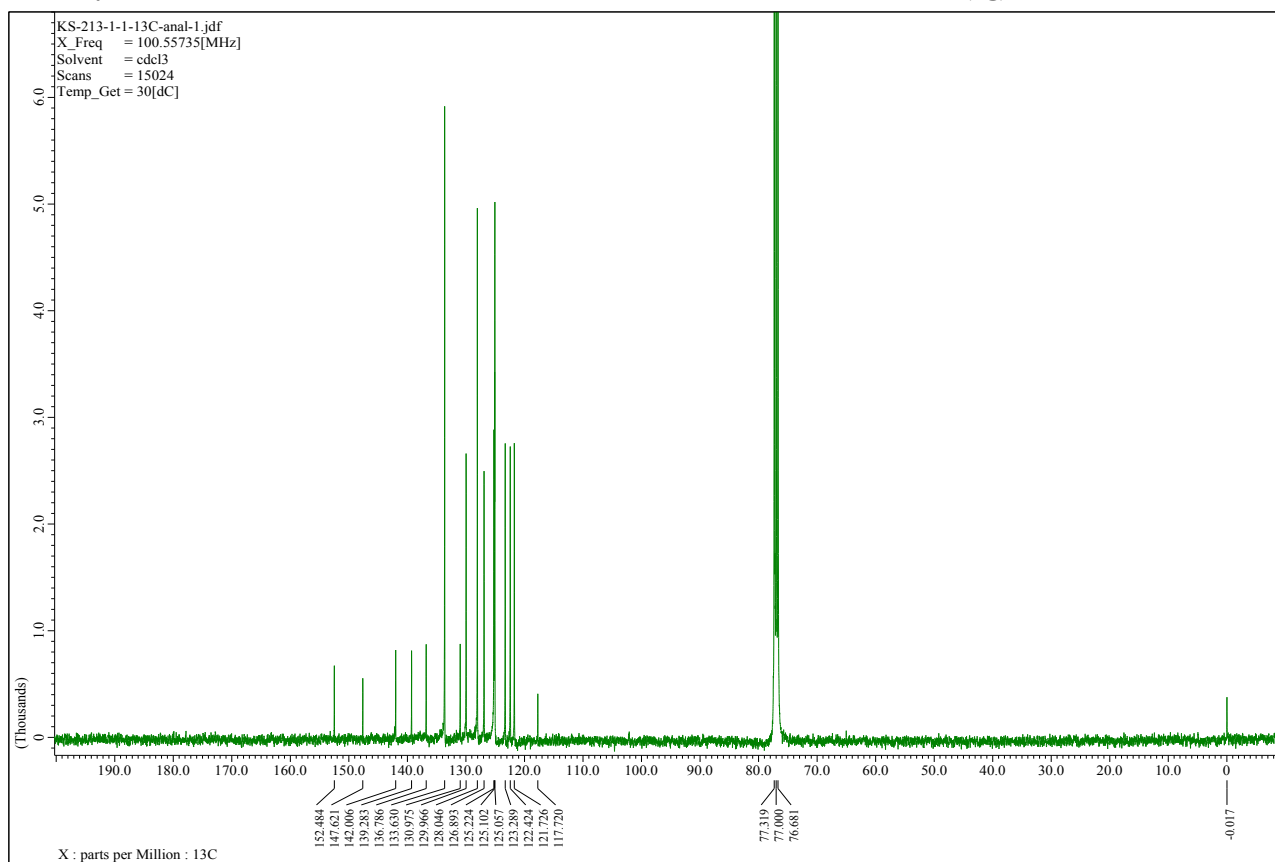
5-Phenyl-5*H*-benzo[4,5]thieno[3,2-c]thieno[2,3-e][1,2]oxaborinine (2f) ¹³C



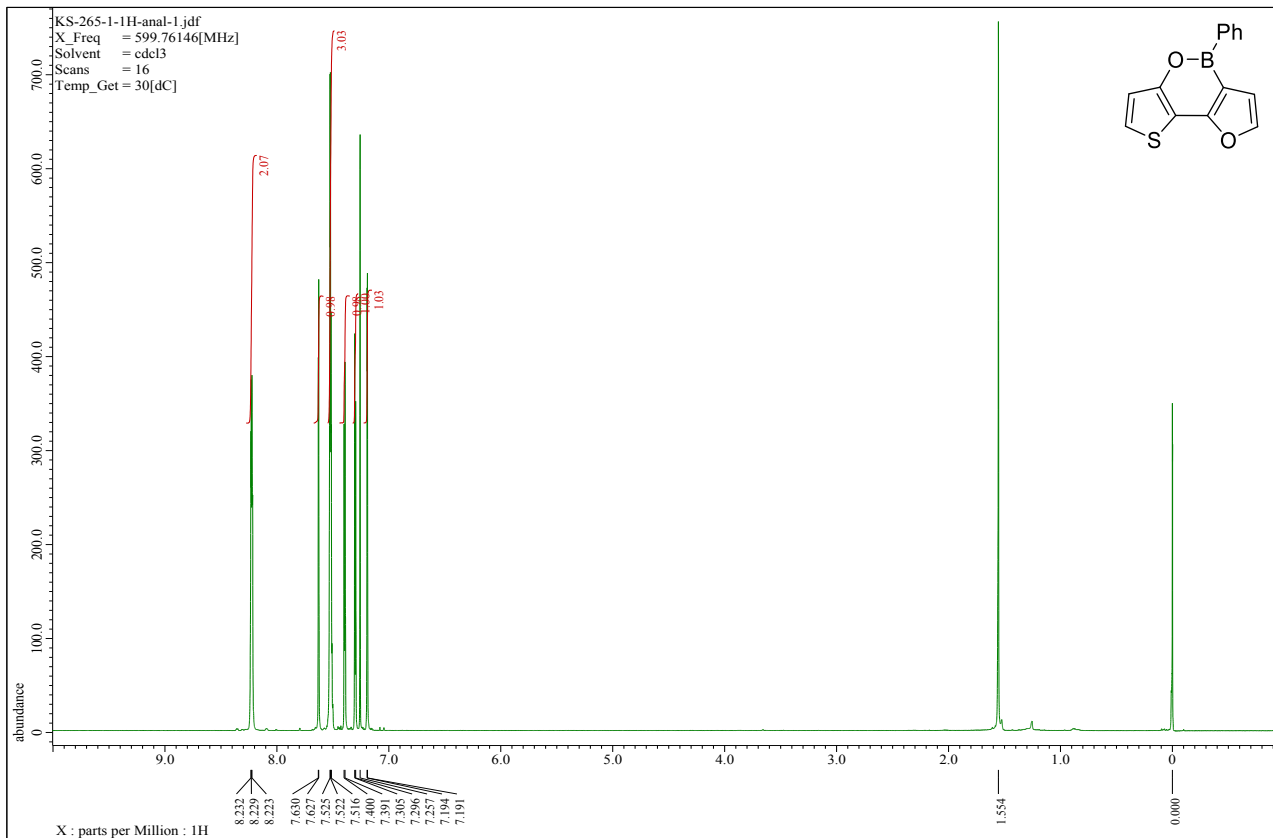
6-Phenyl-6H-benzo[4,5]thieno[3,2-c]benzo[4,5]thieno[2,3-e][1,2]oxaborinine (2g) ¹H



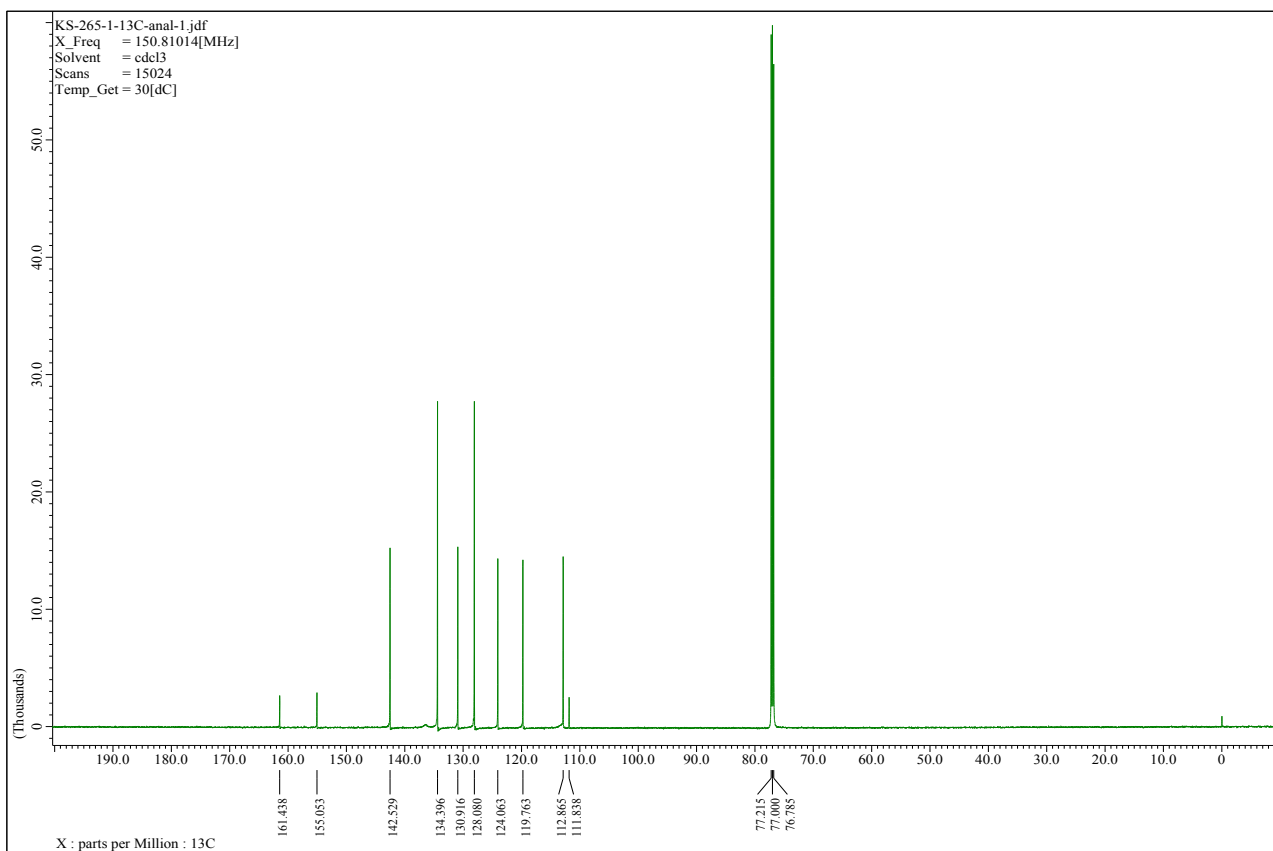
6-Phenyl-6H-benzo[4,5]thieno[3,2-c]benzo[4,5]thieno[2,3-e][1,2]oxaborinine (2g) ¹³C



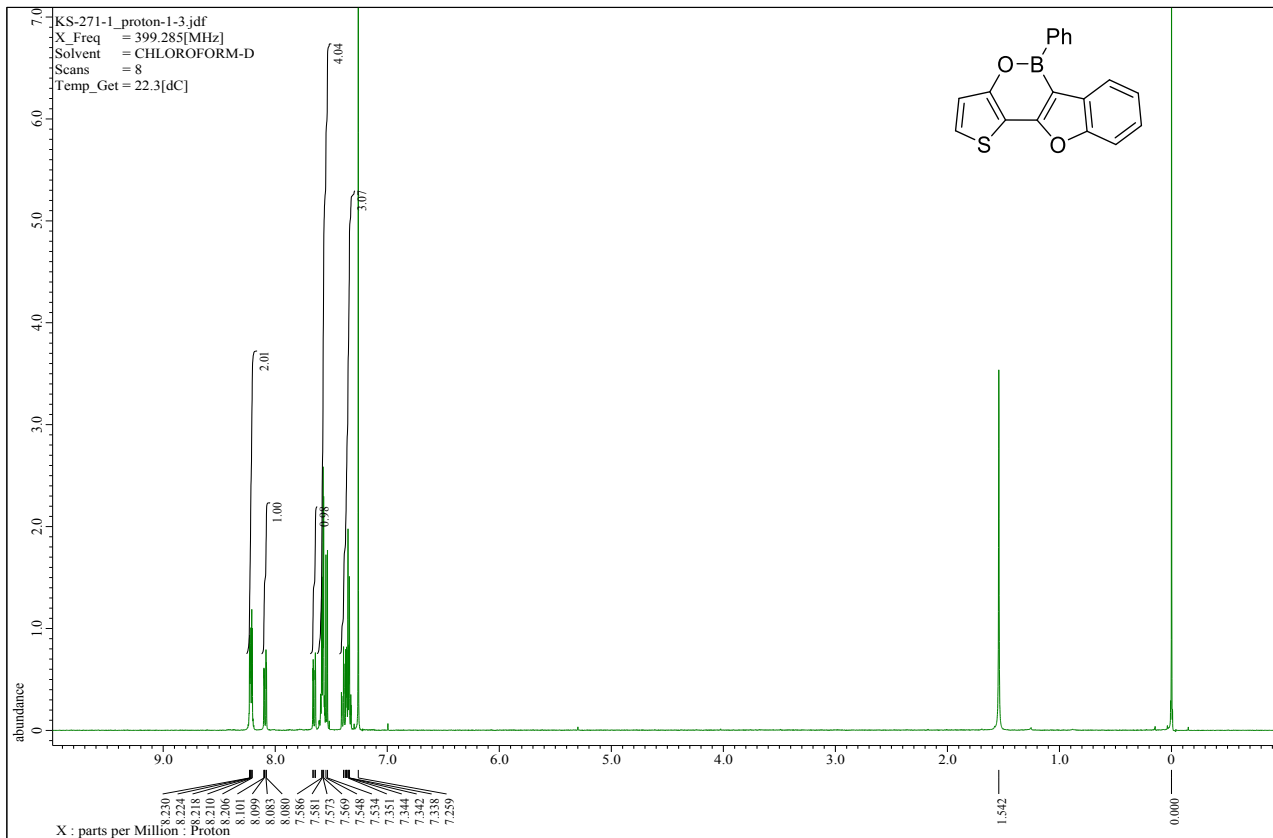
4-Phenyl-4*H*-furo[3,2-*c*]thieno[2,3-*e*][1,2]oxaborinine (2h) ¹H



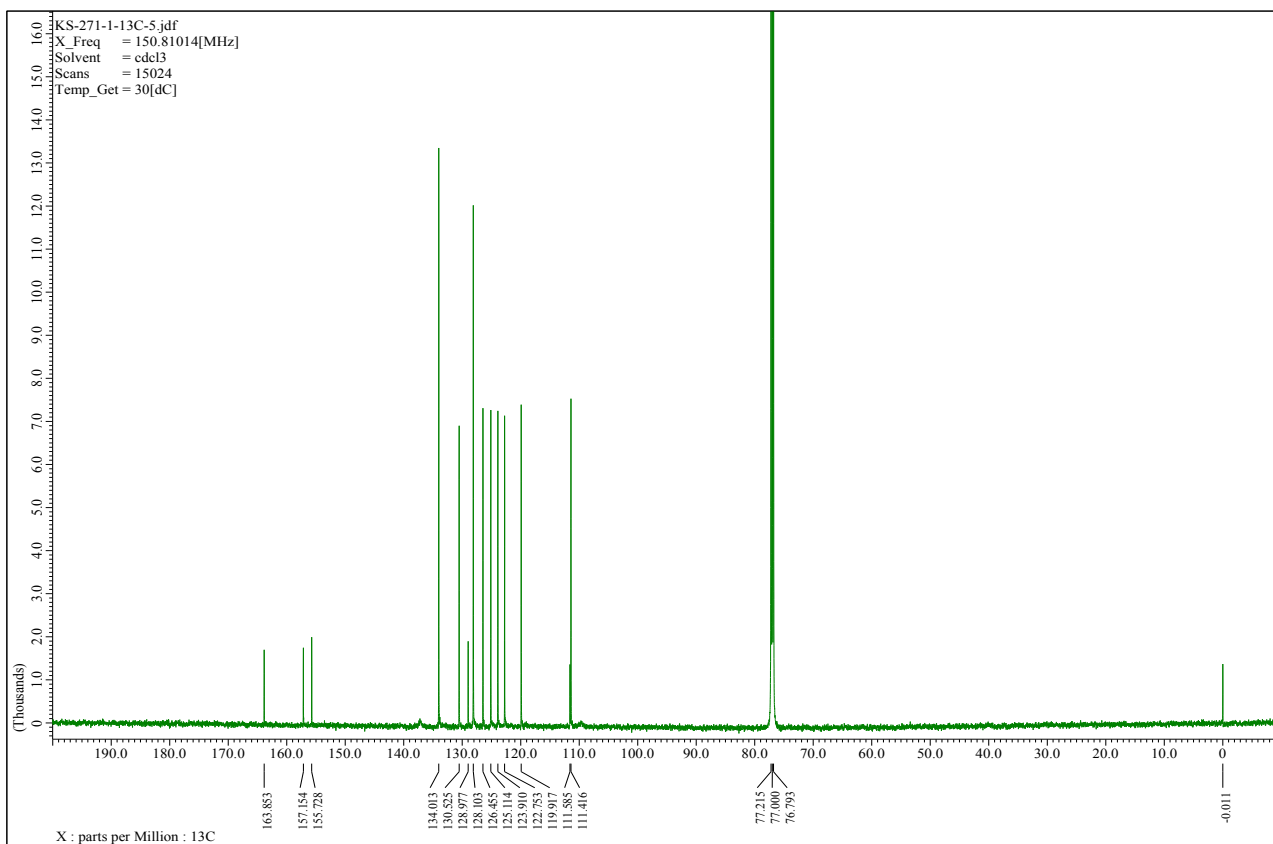
4-Phenyl-4*H*-furo[3,2-*c*]thieno[2,3-*e*][1,2]oxaborinine (2h) ¹³C



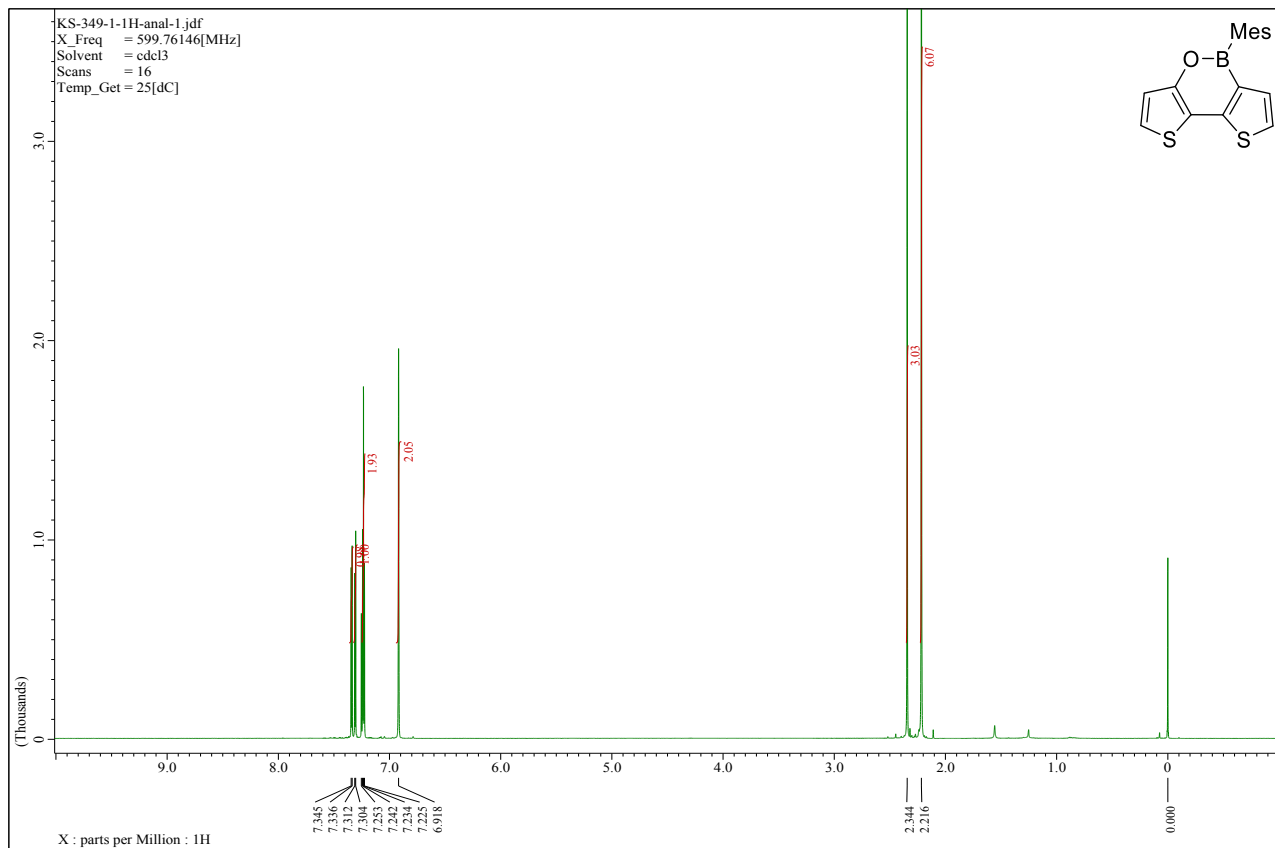
5-Phenyl-5H-thieno[2',3':5,6][1,2]oxaborinino[4,3-b]benzofuran (2i) ¹H



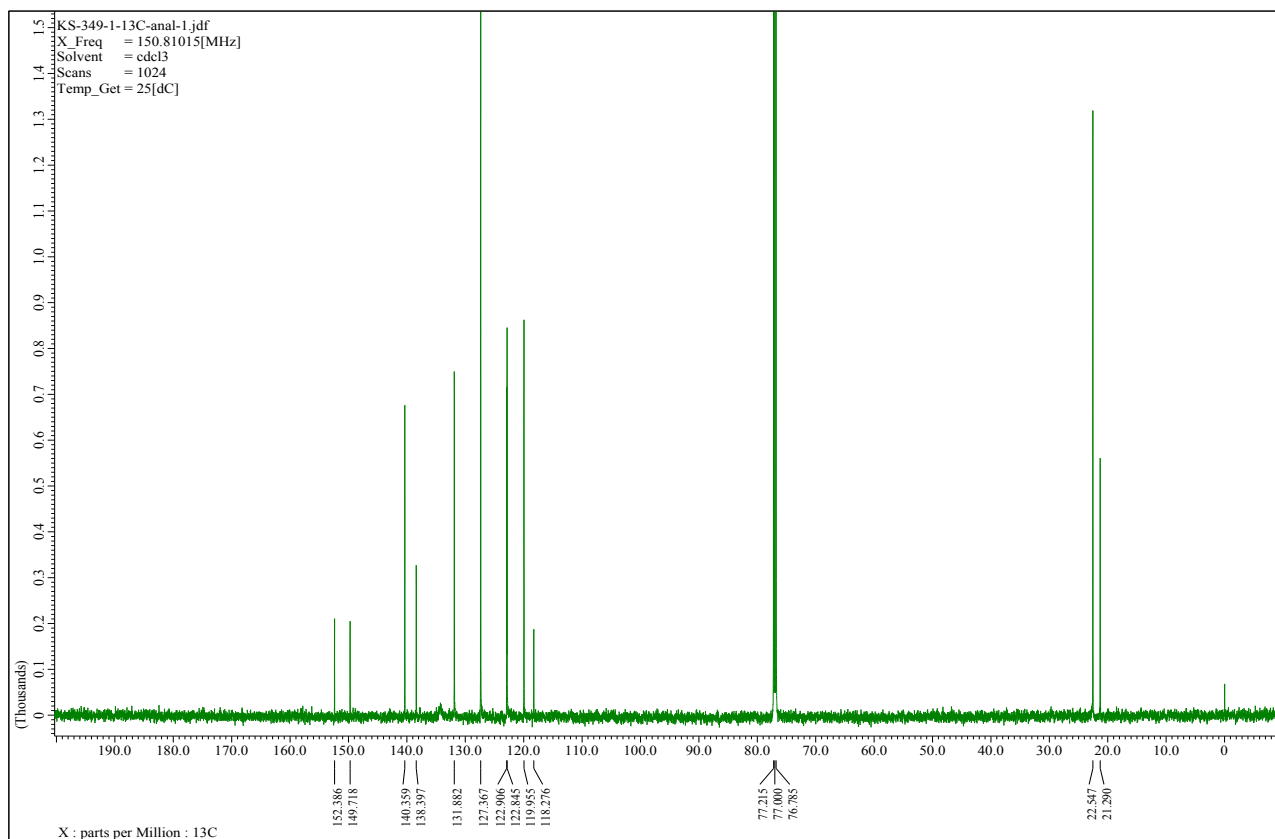
5-Phenyl-5H-thieno[2',3':5,6][1,2]oxaborinino[4,3-b]benzofuran (2i) ¹³C



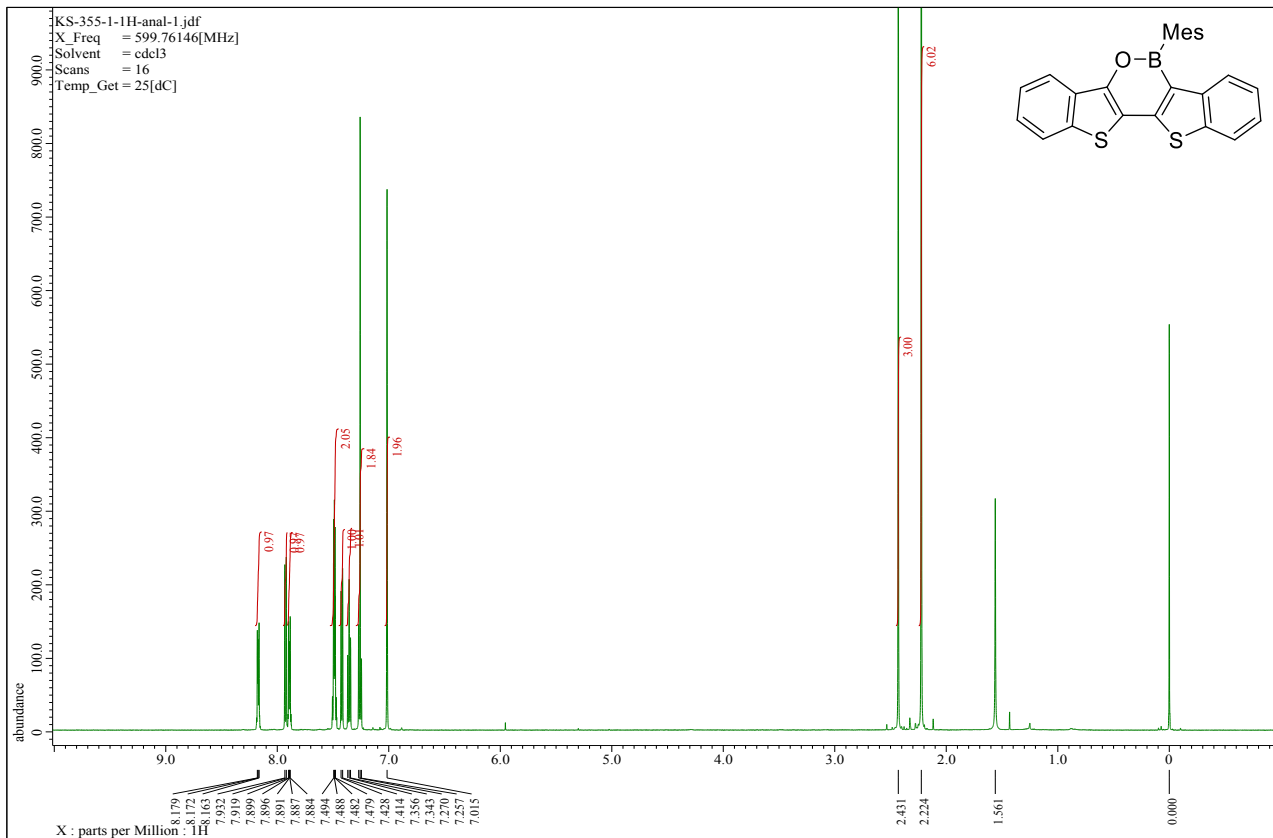
5-Phenyl-5*H*-dithieno[3,2-c:2',3'-e][1,2]oxaborinine (2I) ¹H



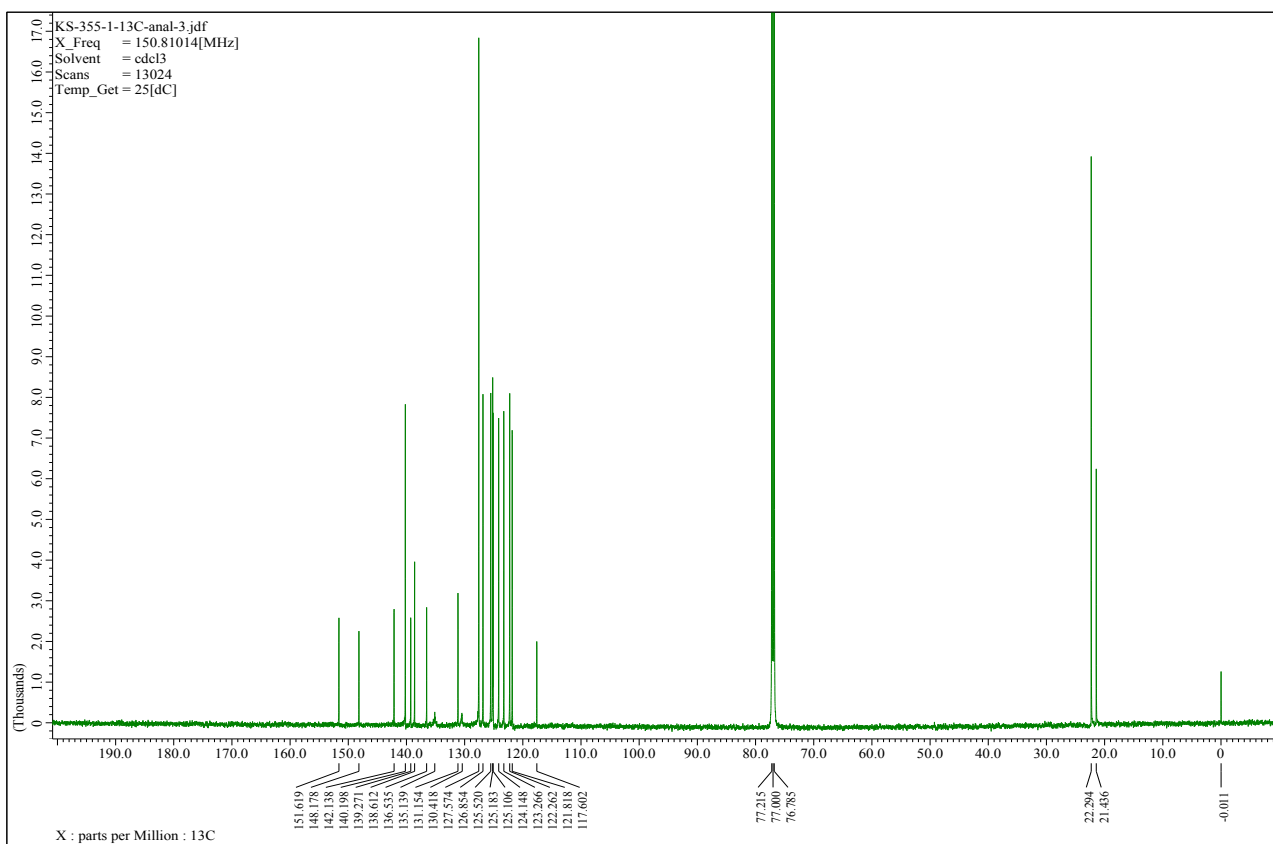
5-Phenyl-5*H*-dithieno[3,2-c:2',3'-e][1,2]oxaborinine (2I) ¹³C



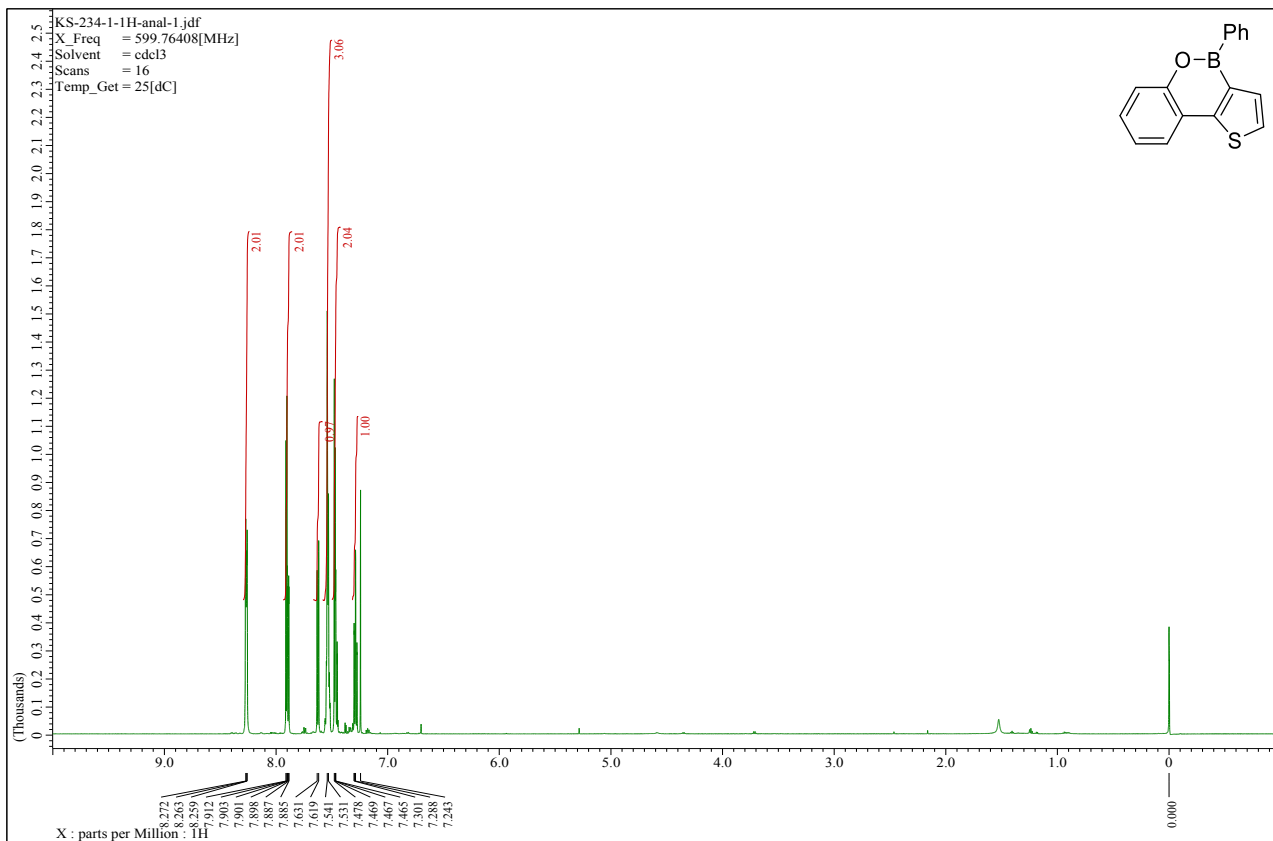
6-Mesityl-6H-benzo[4,5]thieno[3,2-c]benzo[4,5]thieno[2,3-e][1,2]oxaborinine (2m) ¹H



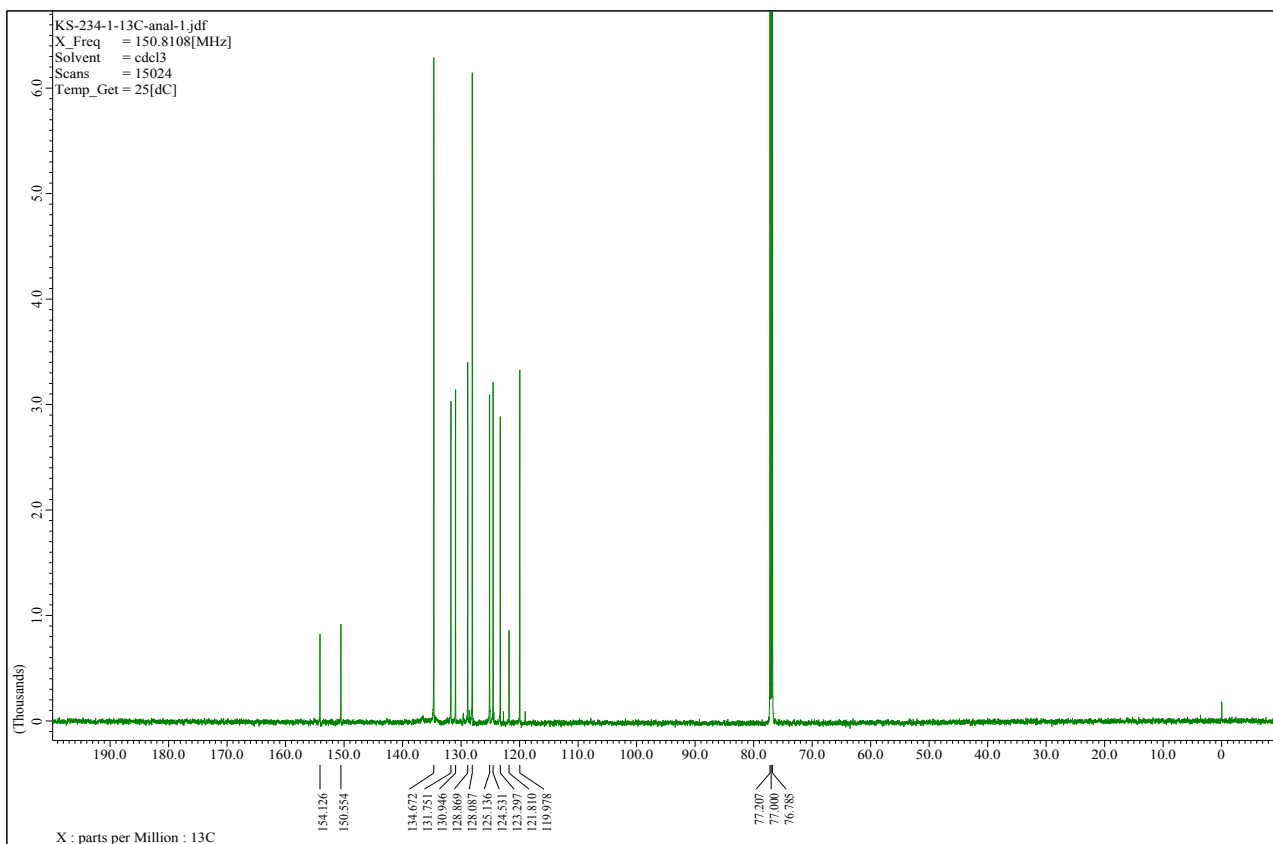
6-Mesityl-6H-benzo[4,5]thieno[3,2-c]benzo[4,5]thieno[2,3-e][1,2]oxaborinine (2m) ¹³C



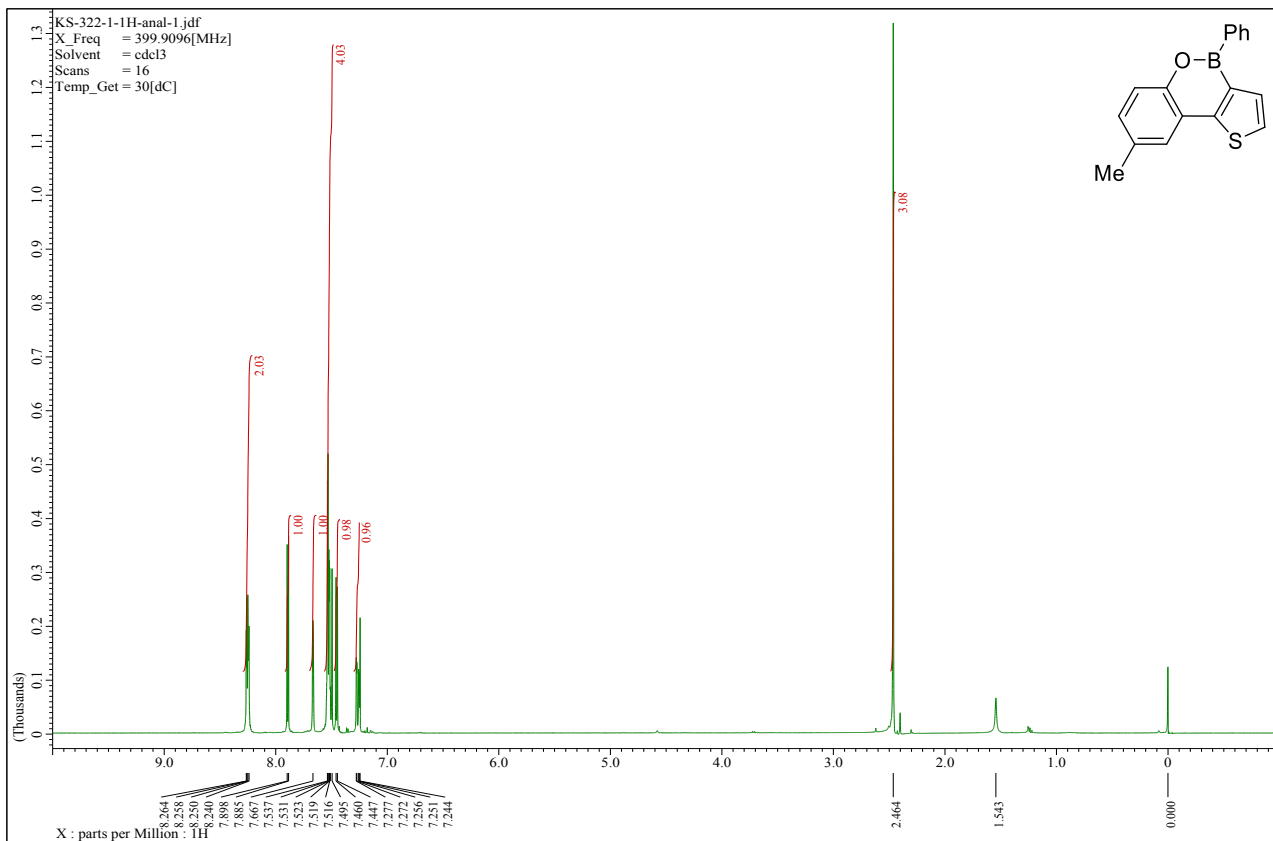
4-Phenyl-4*H*-furo[3,2-*c*]thieno[2,3-*e*][1,2]oxaborinine (4a) ¹H



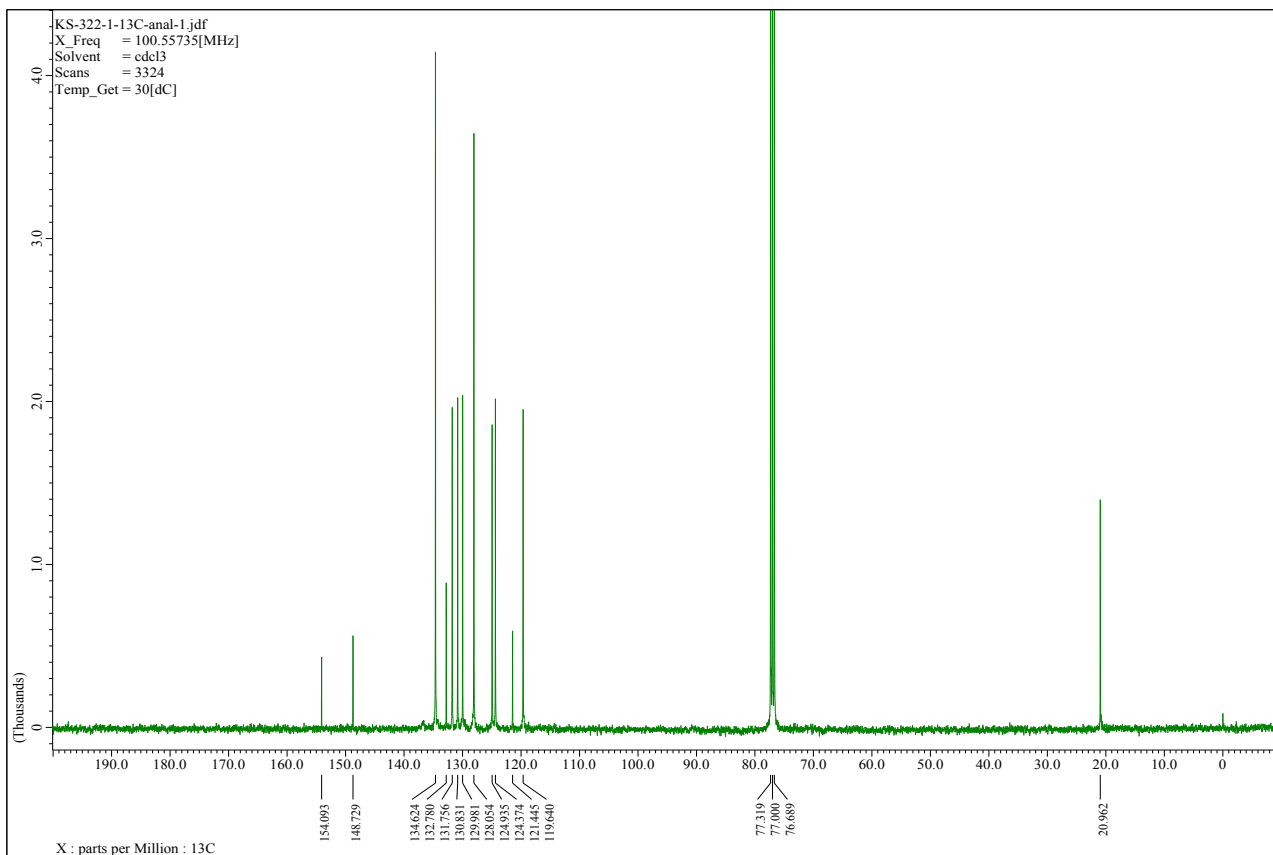
4-Phenyl-4*H*-furo[3,2-*c*]thieno[2,3-*e*][1,2]oxaborinine (4a) ¹³C



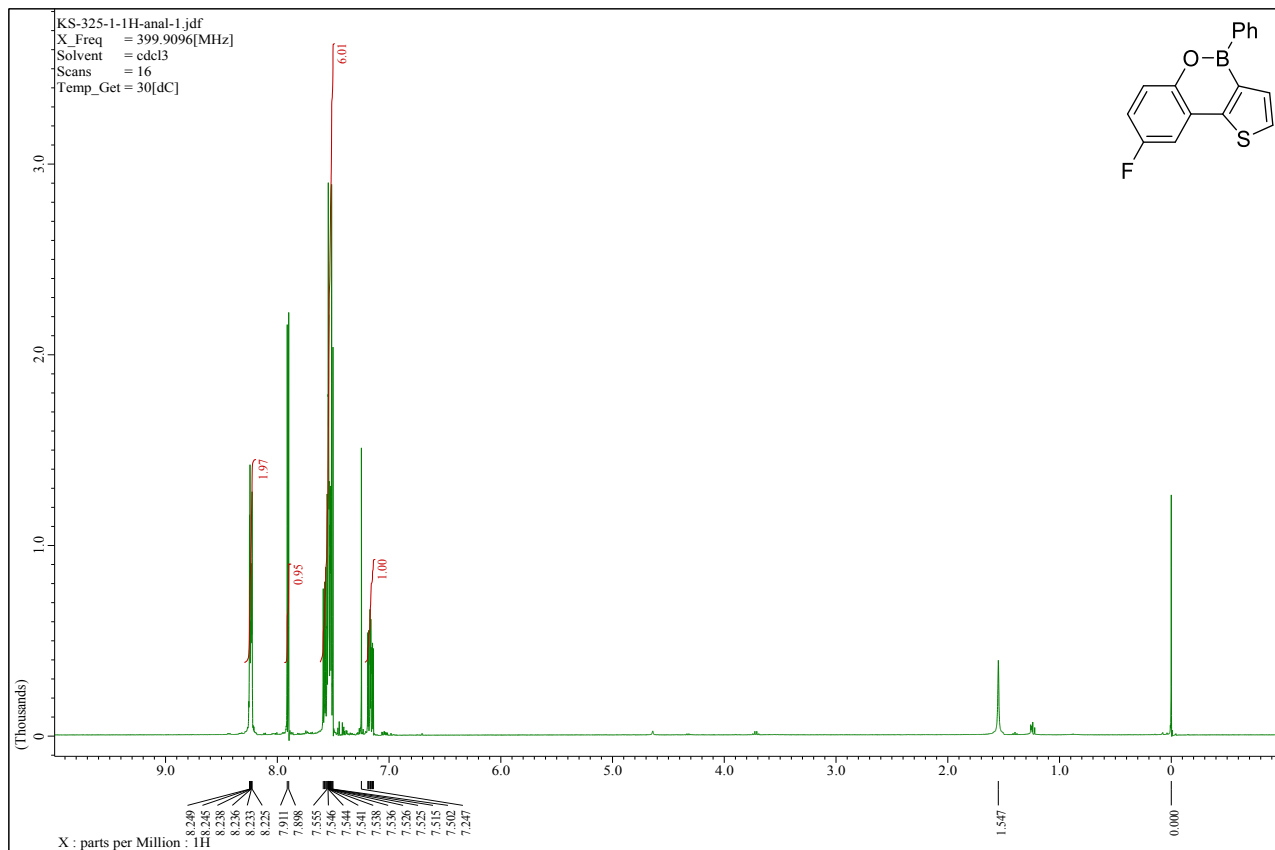
8-Methyl-4-phenyl-4*H*-benzo[e]thieno[3,2-c][1,2]oxaborinine (4b) ¹H



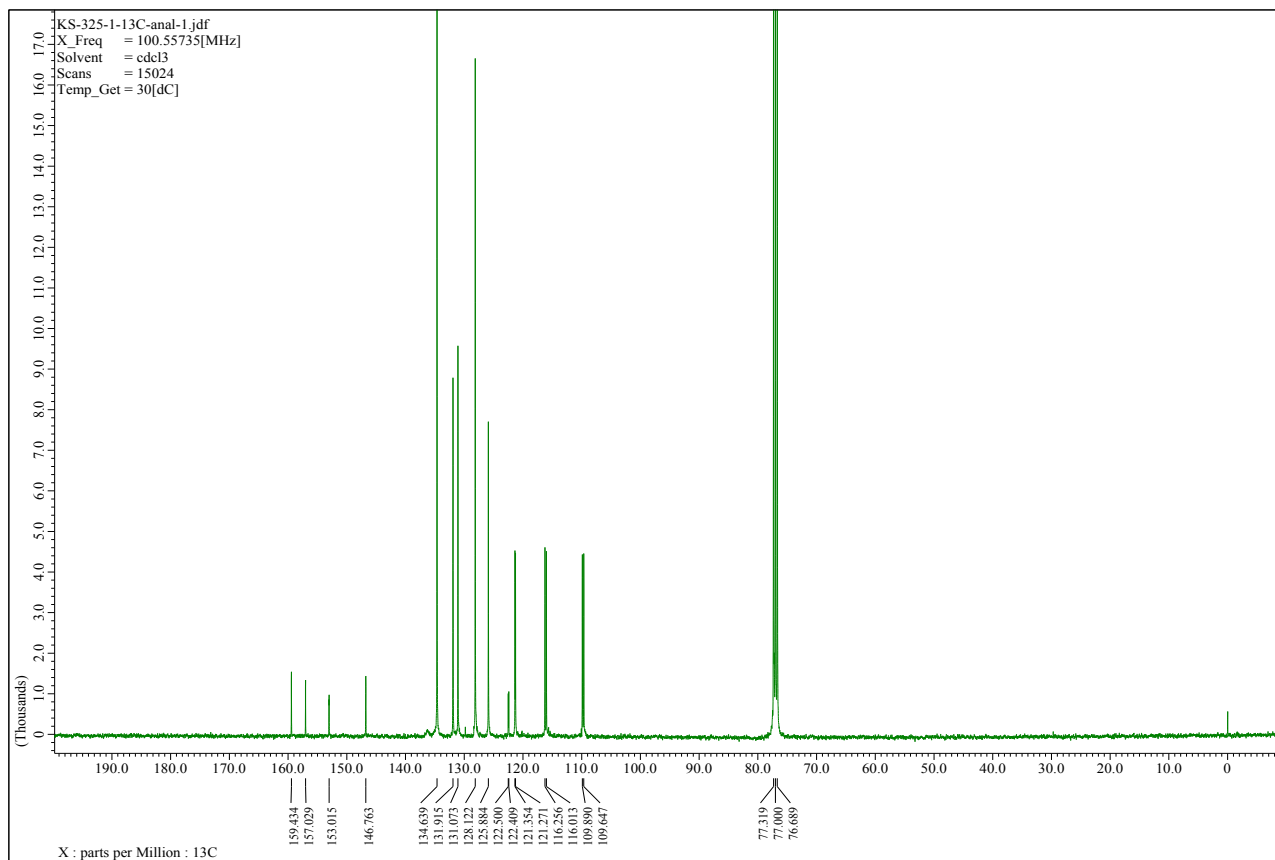
8-Methyl-4-phenyl-4*H*-benzo[e]thieno[3,2-c][1,2]oxaborinine (4b) ¹³C



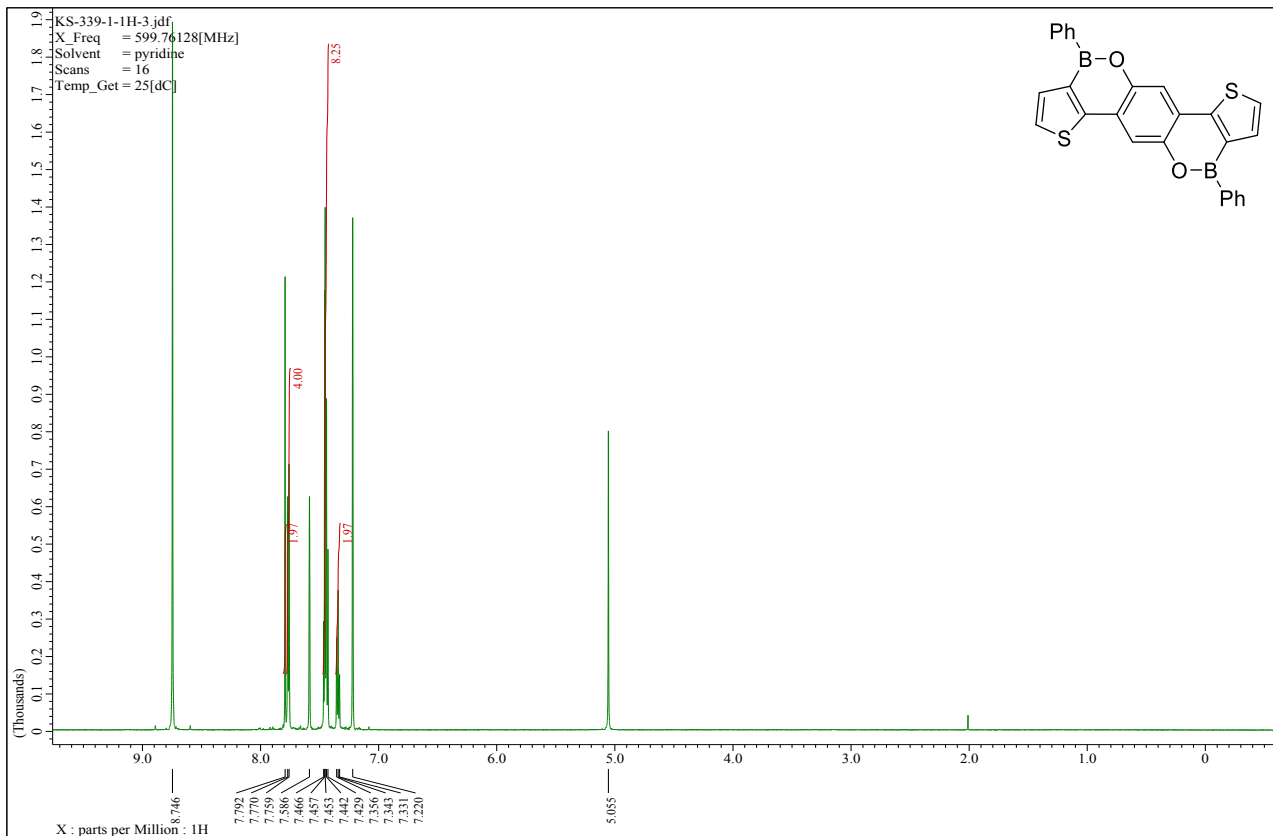
8-Fluoro-4-phenyl-4*H*-benzo[e]thieno[3,2-*c*][1,2]oxaborinine (4c) ¹H



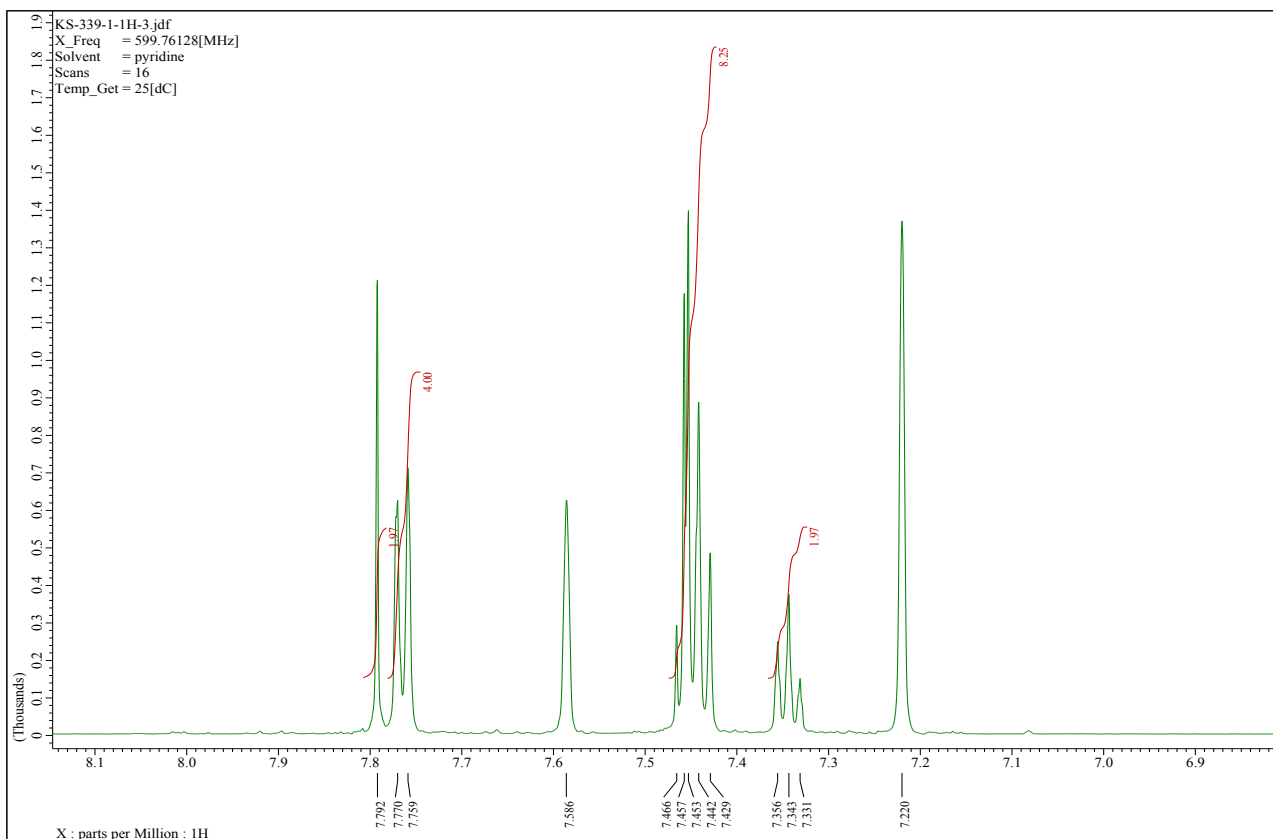
8-Fluoro-4-phenyl-4*H*-benzo[e]thieno[3,2-*c*][1,2]oxaborinine (4c) ¹³C



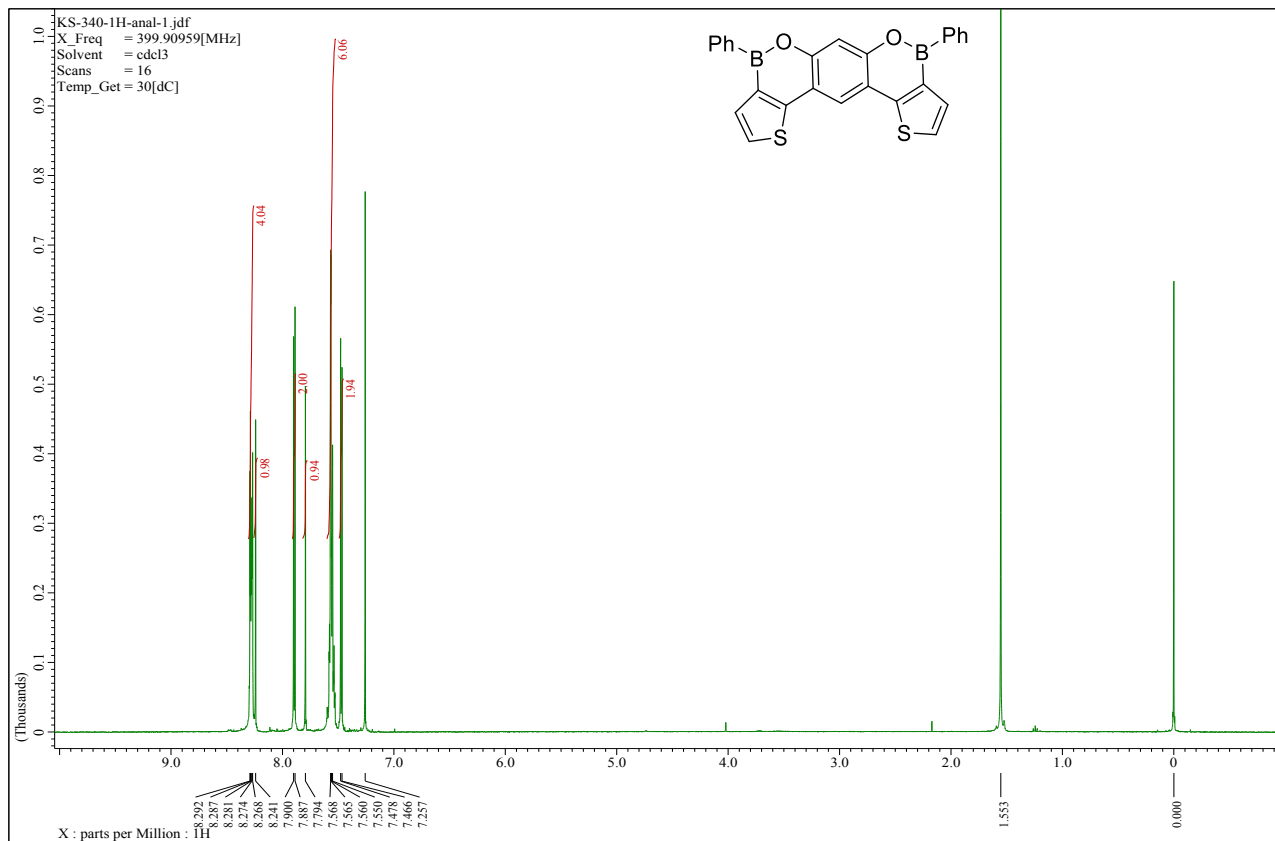
(4d) ¹H



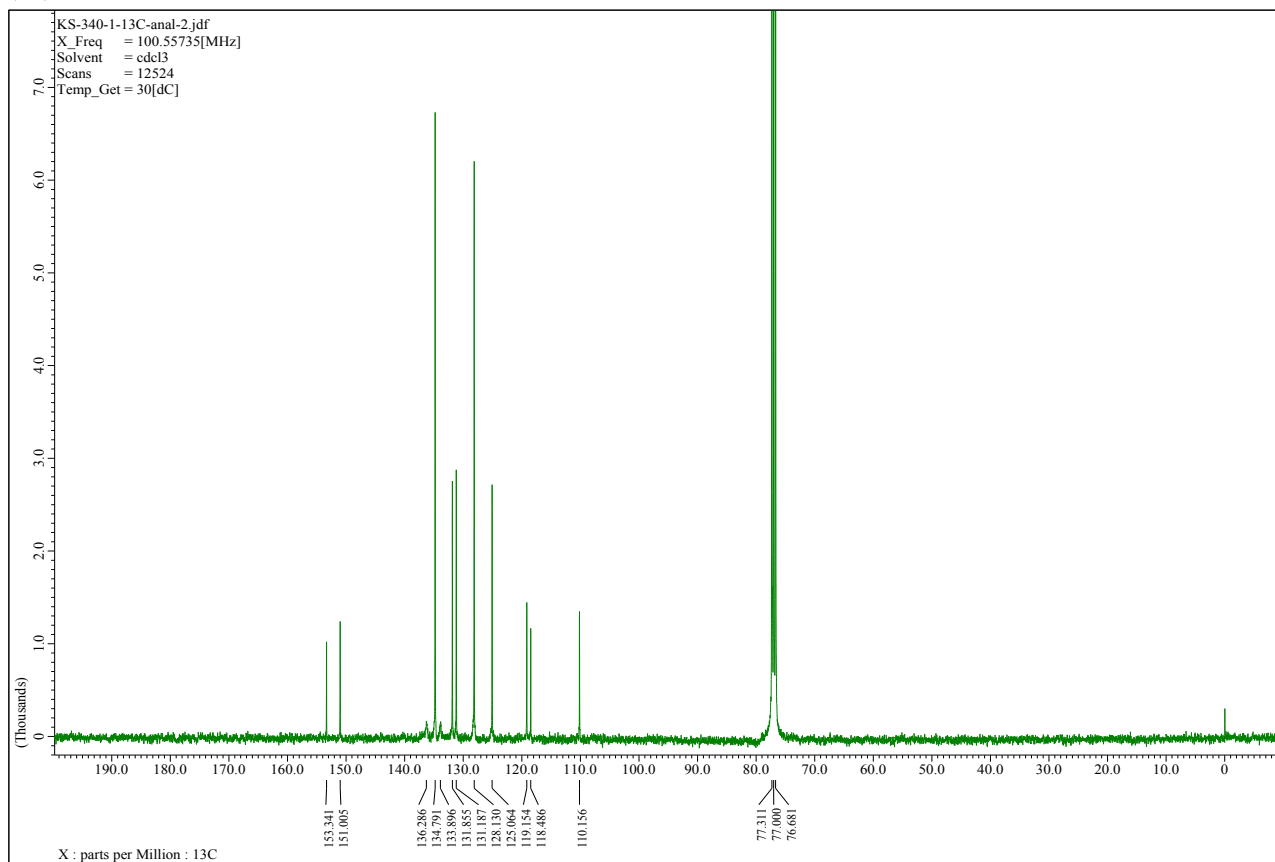
(4d)



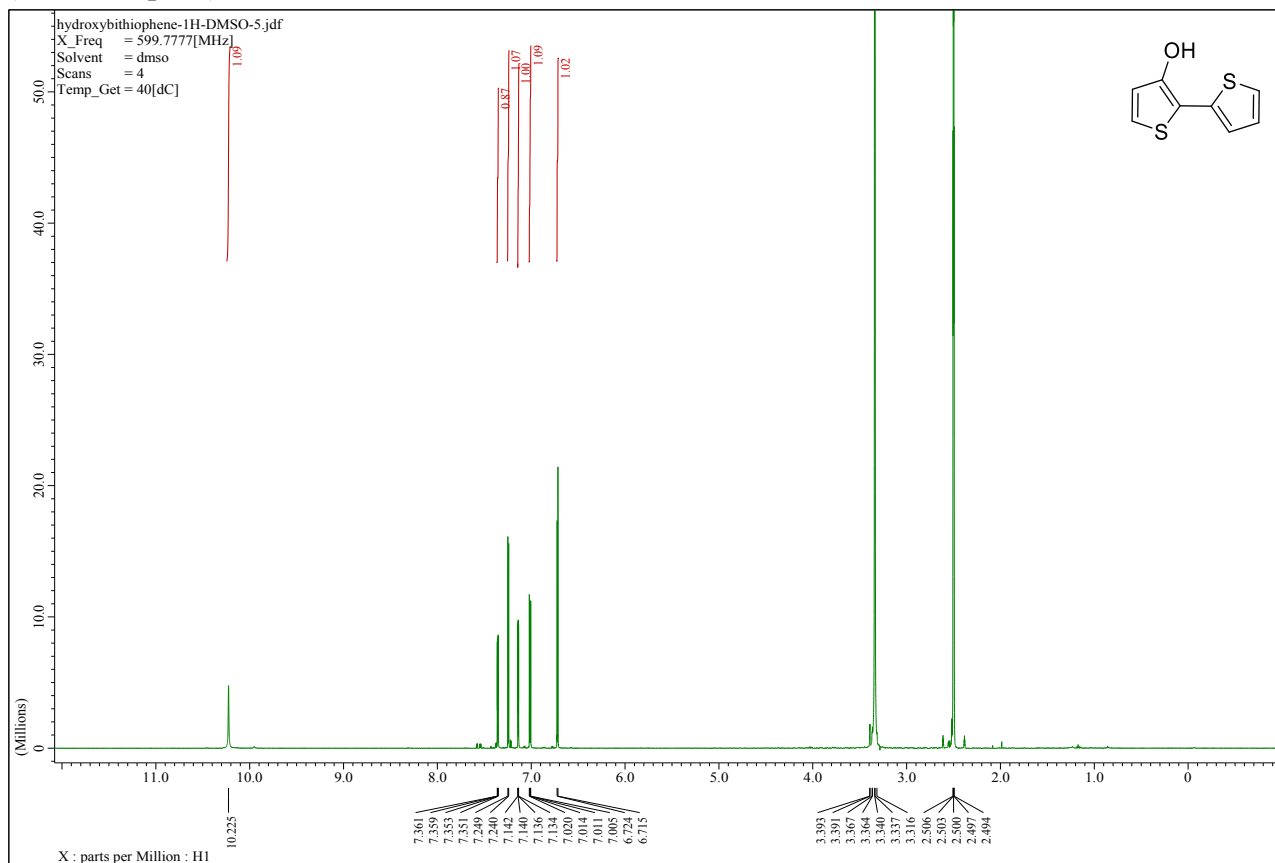
(4e) ¹H



(4e) ¹³C



(2,2'-Bithiophen)-3-ol ¹H



(2,2'-Bithiophen)-3-ol ¹³C

