

SUPPORTING INFORMATION

Diethyl 2,7-Dibromo-4*H*,5*H*-thieno[3,2-*b*:4,5-*b'*]dipyrrole-3,6-dicarboxylate: A Key Intermediate for a Diversity Oriented Synthesis of 2,7,12,17- Tetraarylporphycenes

Ofir Arad, Jordi Morros, Xavier Batllori, Jordi Teixidó, Santiago Nonell, and José I. Borrell*

Grup d'Enginyeria Molecular, Institut Químic de Sarrià,
Universitat Ramon Llull, Via Augusta, 390, E-08017 Barcelona,
Spain

j.i.borrell@iqs.url.edu

Experimental Section

All melting points were determined with a Büchi 530 capillary apparatus and are uncorrected. Infrared spectra were recorded in a Nicolet Magna 560 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were determined in a Varian Gemini-300 operating in a field strength of 300 and 75.5 MHz, respectively. Elemental microanalyses were obtained in a Carlo-Erba CHNS-O/EA 1108. All MS were registered at the Unidade de Espectrometria de Masas (Universidade de Santiago de Compostela) using a Micromass Autospec spectrometer. MALDI-TOF experiments were realized with a Bruker Autoflex spectrometer. Flash chromatography was performed using silica gel 60 A C.C 35-70 μm(SDS ref. 2000027).

Bis(azido-2'-ethoxycarbonyl-2'-vinyl)-2,5-tiophene (**18**)

A solution of 16.2 g (0.12 mol) of 2,5-tiophenedicarboxaldehyde (**16**) and 119 g (0.93 mol) of ethyl azidoacetate (**17**) in 500 mL of dry absolute ethanol was added dropwise to 300 mL of a sodium ethoxide solution (21% in ethanol) at -40 °C. The resulting mixture was poured into a cold ammonium chloride solution. The yellow solid obtained was separated by filtration to give 21.1 g (50%) of **18**. The filtrate was extracted with diethyl ether, washed with water, dried (MgSO₄), and concentrated *in vacuo* to give an extra crop of 2.4 g (4%) of **18**. Mp: 134 °C.¹

¹³C NMR (CDCl₃): δ: 162.6, 140.5, 131.6, 123.4, 118.3, 62.2, 14.2 (see page S6).

Diethyl 4*H*,5*H*-thieno[3,2-*b*:4,5-*b'*]dipyrrole-3,6-dicarboxylate (**15**)

32.0 g (88 mmol) of bis(azido-2'-ethoxycarbonyl-2'-vinyl)-2,5-tiophene **18** were suspended in 1500 mL of xylene (mixture of isomers). The suspension was heated to 115 °C (nitrogen evolution) and then maintained at such temperature for 12 hours. The white solid obtained was separated by filtration, washed with hexane, and dried (P₂O₅) to give 23 g (85%) of **15**. Mp: 254 °C.¹

IR (KBr): 3420, 3045, 2807, 1699, 1659

¹³C NMR 300 MHz (DMSO): δ 160.1, 126.9, 126.8, 124.4, 109.1, 60.1, 14.5

Anal. Calcd for C₁₄H₁₄N₂O₄S: C, 54.89; H, 4.61; N, 9.14; S, 10.47. Found: C, 55.12; H, 4.64; N, 9.19; S, 10.33.

¹ Farnier, M.; Soth, S.; Fournari, P. *Can. J. Chem.* **1976**, *54*, 1074.

Diethyl 2,7-dibromo-4*H*,5*H*-thieno[3,2-*b*:4,5-*b'*]dipyrrole-3,6-dicarboxylate (**19**)

A solution of 3 mL of Br₂ in 45 mL of AcOH was added dropwise to a suspension of 3.0 g (9.7 mmol) of **15** in a mixture of 250 mL of AcOEt and 100 mL of AcOH. The resulting mixture was stirred for 8 h at room temp. The resulting precipitate was filtered, washed with 3x50 mL of an aqueous NaHCO₃ solution, and dried over P₂O₅ *in vacuo* (50 °C) to yield 4.1 g (8.7 mmol, 89%) of **19** as a white solid. Mp: > 290 °C (d).

IR (KBr): ν_{\max} : 3417, 3327, 2924, 2853, 1686, 1649, 1375, 1230 cm⁻¹.

¹H NMR (DMSO-*d*₆): δ 11.52 (s, 2H, NH), 4.34 (q, 4H, *J*=7.2Hz, O-CH₂CH₃), 1.35 (t, 6H, *J*=7.2Hz, O-CH₂CH₃).

¹³C NMR (DMSO-*d*₆): δ 158.9, 127.7, 125.2, 121.9, 96.1, 60.6, 14.3.

MS (70 eV): *m/z* = 463.6 ([M+2H]⁺), 419.6, 371.6, 264.7.

HRMS: calcd for C₁₄H₁₂Br₂N₂O₄S, 461.8884, found 461.8892;

Anal. Calcd for C₁₄H₁₂Br₂N₂O₄S: C, 36.23; H, 2.61; N, 6.04; S, 6.91. Found: C, 36.11; H, 2.54; N, 5.98; S, 6.59.

Diethyl 2,7-dibromo-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno[3,2-*b*:4,5-*b'*]dipyrrole-3,6-dicarboxylate (**20**)

2.1 g (525 mmol) of NaH (60% in mineral oil) were added portionwise to a suspension of 11.0 g (24 mmol) of **19** in 50 mL of anhydrous THF under Ar atmosphere. The resulting mixture was stirred for 15 min at room temp. Then, 15 mL (80 mmol) of trimethylsilylethoxymethyl chloride (SEM-Cl) were added dropwise and the resulting solution was stirred for 1 h at room temp. 100 g of crushed ice were added and the resulting mixture was stirred until a precipitate appeared. The solid was filtered, washed with MeOH until it became white, and dried (P₂O₅) *in vacuo* (50 °C) to yield 13.4 g (18 mmol, 77%) of **20**. The mother liquor was extracted with hexane, washed (MgSO₄), and concentrated *in vacuo* to yield an extra crop of 3.0 g (4 mmol, 17%) of **20**. Mp: 127-129°C.

IR (KBr): ν_{\max} : 2952, 2902, 1705, 1382, 1319, 1228, 1088, 920, 859, 835 cm⁻¹.

¹H NMR (CDCl₃): δ : 6.27 (s, 4H, N-CH₂), 4.41 (q, 4H, *J*=7.2Hz, O-CH₂CH₃), 3.51 (t, 4H, *J*=8.4Hz, O-CH₂), 1.45 (t, 6H, *J*=7.2Hz, O-CH₂CH₃), 0.83 (t, 4H, *J*=8.4 Hz, Si-CH₂), -0.07 (s, 18H, Si-(CH₃)₃).

¹³C NMR (CDCl₃): δ : 160.5, 130.7, 128.5, 123.9, 99.6, 75.0, 65.9, 61.1, 17.9, 14.4, -1.4.

MS (ESI-TOF): *m/z* = 747.0 ([M+Na+2H]⁺), 337.3, 236.1, 218.2, 163.0.

HRMS (MALDI-TOF): calcd for C₂₆H₄₀Br₂N₂O₆SSi₂+Na 745.041, found 745.040.

Anal. Calcd for C₂₆H₄₀Br₂N₂O₆SSi₂: C, 43.09; H, 5.56; N, 3.87; S, 4.42. Found: C, 43.25; H, 5.37; N, 3.64; S, 4.21.

Synthesis of diethyl 2,7-diaryl-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno[3,2-*b*:4,5-*b'*]dipyrrole-3,6-dicarboxylates (**21**)

General Procedure

An aqueous solution of 57 mg (412 μ mol) of Na₂CO₃ in 1 mL of water was added to a solution of 100 mg (138 μ mol) of **20**, 410 μ mol of the corresponding arylboronic acid in 60 mL of 1,4-dioxane. The resulting mixture was deoxygenated with N₂ for 30 min. Then, 25 mg (22 μ mol) of Pd(PPh₃)₄ were added and the resulting mixture was refluxed for 16 h under Ar atmosphere. Then, 30 mL of water were added to the cooled mixture and it was extracted with 3x50 mL of hexane. The organic extracts were dried (MgSO₄) and concentrated *in vacuo* to afford the corresponding compound **21**.

Diethyl 2,7-diphenyl-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno[3,2-*b*:4,5-*b'*]dipyrrole-3,6-dicarboxylate (**21**{5}, R = Ph)

As above using phenylboronic acid. The residue obtained was column chromatographed using a 1:10 AcOEt/hexane mixture as eluent to give 76 mg (77%) of **21**{5} (R = Ph) as a white solid. Mp: 90-92 °C.

IR (KBr): ν_{\max} : 3061, 3029, 2980, 2953, 2897, 1948, 1882, 1698 1397, 1382, 1317, 1249, 1238, 1179, 1101, 1078, 860, 836, 699 cm^{-1} .

^1H NMR (CDCl_3): δ 7.5-7.3 (m, 10H, Ph), 6.33 (s, 4H, N- CH_2), 4.14 (q, 4H, $J=6.9\text{Hz}$, O- CH_2CH_3), 3.61 (t, 4, $J=8.4\text{Hz}$, O- CH_2), 1.05 (t, 2H, $J=6.9\text{Hz}$, O- CH_2CH_3), 0.91 (t, 4H, $J=8.4\text{Hz}$, Si- CH_2), -0.04 (s, 18H, Si-(CH_3) $_3$).

^{13}C NMR (CDCl_3): δ 161.8, 134.5, 129.9, 129.2, 128.7, 127.8, 127.2, 126.8, 122.5, 74.6, 65.7, 60.5, 18.0, 13.8, -1.3.

MS (ESI-TOF): $m/z = 741.5$ ($[\text{M}+\text{Na}]^+$), 601.4, 416.5, 368.5, 288.4.

HRMS (ESI-TOF): calcd for $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_6\text{SSi}_2+\text{Na}$ 741.282, found 741.285.

Anal. Calcd for $\text{C}_{26}\text{H}_{40}\text{Br}_2\text{N}_2\text{O}_6\text{SSi}_2$: C, 43.09; H, 5.56; N, 3.87; S, 4.42. Found: C, 43.25; H, 5.37; N, 3.64; S, 4.21.

Diethyl 2,7-di(pyridin-4-yl)-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno [3,2-*b*,4,5-*b'*]dipyrrole-3,6-dicarboxylate (**21{6}**, R = $\text{C}_6\text{H}_4\text{N}$)

As above using (pyridin-4-yl)boronic acid. The residue obtained was crystallized from water/EtOH to give 95 mg (95%) of **21{6}** (R = $\text{C}_6\text{H}_4\text{N}$) as a white solid. Mp: 128-130 °C.

IR (KBr): ν_{\max} 3069, 3030, 2980, 2953, 2897, 1937, 1702, 1601, 1397, 1382, 1317, 1241, 1182, 1102, 1077, 860, 834, cm^{-1} .

^1H NMR (CDCl_3): δ 8.65 (dd, $J=1.7\text{Hz}$, $J=4.5\text{Hz}$, 4H, CH(Py)), 7.40 (dd, $J=1.7\text{Hz}$, $J=4.5\text{Hz}$, 4H, CH(Py)), 6.34 (s, 4H, N- CH_2), 4.21 (q, 4H, $J=7.1\text{Hz}$, O- CH_2CH_3), 3.61 (m, 4H, O- CH_2), 1.10 (t, 2H, $J=7.2\text{Hz}$, O- CH_2CH_3), 0.91 (m, 4H, Si- CH_2), -0.04 (s, 18H, Si-(CH_3) $_3$).

^{13}C NMR (CDCl_3): δ 161.2, 149.4, 142.6, 129.1, 128.7, 124.0, 123.5, 123.1, 74.7, 65.9, 61.0, 18.0, 13.8, -1.4.

MS (ESI-TOF): $m/z = 721.5$ ($[\text{M}]^+$), 681.5, 642.4, 591.4, 524.3, 448.3.

Anal. Calcd for $\text{C}_{36}\text{H}_{48}\text{N}_4\text{O}_6\text{SSi}_2$: C, 59.97; H, 6.71; N, 7.77; S, 4.45. Found: C, 60.13; H, 6.84; N, 7.66; S, 4.45.

Diethyl 2,7-di(*p*-methoxyphenyl)-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno[3,2-*b*,4,5-*b'*]dipyrrole-3,6-dicarboxylate (**21{7}**, R = *p*- MeOC_6H_4)

As above using *p*-methoxyphenylboronic acid. The residue obtained was column chromatographed using a 1:10 AcOEt/hexane mixture as eluent, and then crystallized from MeOH to give 138 mg (100%) of **21{7}** (R = *p*- MeOC_6H_4) as a white solid. Mp: 77-79 °C.

IR (KBr): ν_{\max} 3035, 2986, 2958, 2898, 2860, 2838, 1703, 1686, 1381, 1242, 1079, 833, 777 cm^{-1} .

^1H NMR (CDCl_3): δ 7.42 (dd, $J=2.1\text{Hz}$, $J=6.7\text{Hz}$, 4H, CH(Ar)), 6.92 (dd, $J=2.1\text{Hz}$, $J=6.7\text{Hz}$, 4H, CH(Ar)), 6.30 (s, 4H, N- CH_2), 4.19 (q, 4H, $J=7.2\text{Hz}$, O- CH_2CH_3), 3.59 (m, 4H, O- CH_2), 1.11 (t, 2H, $J=7.2\text{Hz}$, O- CH_2CH_3), 0.91 (m, 4H, Si- CH_2), -0.05 (s, 18H, Si-(CH_3) $_3$).

^{13}C NMR (CDCl_3): δ 161.9, 158.7, 130.4, 130.0, 128.8, 126.8, 126.6, 122.3, 113.3, 74.7, 65.6, 60.4, 55.3, 18.0, 14.0, -1.3.

MS (ESI-TOF): $m/z = 801.3$ ($[\text{M}]^+$), 671.2, 456.2, 337.2, 301.1, 236.0.

HRMS (MALDI-TOF): calcd for $\text{C}_{40}\text{H}_{54}\text{N}_2\text{O}_8\text{SSi}_2+\text{Na}$ 801.303, found 801.303.

Anal. Calcd for $\text{C}_{40}\text{H}_{54}\text{N}_2\text{O}_8\text{SSi}_2$: C, 61.66; H, 6.99; N, 3.60; S, 4.12. Found: C, 61.83; H, 7.09; N, 3.40; S, 4.54.

Synthesis of Diethyl 4,4'-diaryl-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-3,6-dicarboxylates (**22**)

General Procedure

0.13 mmol of the corresponding diethyl 2,7-diaryl-4*H*,5*H*-bis(trimethylsilylethoxymethyl)-thieno[3,2-*b*,4,5-*b'*]dipyrrole-3,6-dicarboxylate **21** were added to a suspension of 0.5 g of Raney Nickel (caution pyrophoric) in 25 mL of deoxygenated EtOH. The Raney Nickel was previously washed with deoxygenated EtOH. The mixture was heated at reflux for 4 hours. The resulting suspension was filtered

on Celite®, the residue was washed with acetone and the combined organic solvent was concentrated *in vacuo* to give the corresponding compound **22**.

Diethyl 4,4'-diphenyl-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-5,5'-dicarboxylate (22{5}, R = Ph)

As above using diethyl 2,7-diphenyl-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno[3,2-*b*,4,5-*b'*]dipyrrole-3,6-dicarboxylate (**21{5}**, R = Ph). The crude material obtained was crystallized from water/EtOH (1:9) to give 90 mg (100%) of **22{5}** (R = Ph) as a white solid. Mp: 101-103 °C.

IR (KBr): ν_{\max} 3058, 3030, 2953, 2926, 2898, 1944, 1875, 1802, 1670, 1416, 1239, 1098, 1078, 836, 762, 698 cm^{-1} .

¹H NMR (CDCl₃): δ 7.41-7.29 (m, 10H, Ph), 6.50 (s, 2H, C_{pyrrole}-H), 5.57 (s, 4H, N-CH₂), 4.15 (q, 4H, *J*=6.0Hz, O-CH₂CH₃), 1.41 (m, 4H, O-CH₂), 1.06 (t, 6H, *J*=6.0 Hz, O-CH₂CH₃), 0.86 (m, 4H, *J*=8.4 Hz, Si-CH₂), -0.062 (s, 18H, Si-(CH₃)₃).

¹³C NMR (CDCl₃): δ 161.5, 135.9, 133.6, 129.3, 129.1, 127.5, 126.7, 115.0, 74.3, 65.7, 60.3, 55.3, 18.0, 13.8, -1.4.

MS (ESI-TOF): *m/z* = 711.3 ([M+Na]⁺), 635.3, 543.2.

HRMS (ESI-TOF): calcd for C₃₈H₅₂N₂O₆Si₂+Na 711.326, found 711.324.

Anal. Calcd for C₃₈H₅₂N₂O₆Si₂: C, 66.24; H, 7.61; N, 4.07. Found: C, 66.66; H, 7.86; N, 4.04.

Diethyl 4,4'-(di(pyridin-4-yl)-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-3,6-dicarboxylate (22{6}, R = C₆H₄N)

As above using diethyl 2,7-di(pyridin-4-yl)-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno[3,2-*b*,4,5-*b'*]dipyrrole-3,6-dicarboxylate (**21{6}**, R = C₆H₄N). The crude material obtained was treated with acetic acid, extracted with AcOEt and neutralized with sodium carbonate, dried (MgSO₄) and evaporated *in vacuo* to give 125 mg (100%) of **22{6}** (R = C₆H₄N) as a white solid. Mp: 144-145 °C.

¹H NMR (CDCl₃): δ 8.61 (d, 4H, *J*=5.7 Hz, Py), 7.33 (d, 4H, *J*=5.7Hz, Py), 6.55 (s, 2H, C_{pyrrole}-H), 5.58 (s, 2H, N-CH₂), 4.20 (q, 4H, *J*=7.2Hz, O-CH₂CH₃), 3.50 (m, 4H, O-CH₂), 1.12 (t, 6H, *J*=7.2 Hz, O-CH₂CH₃), 0.87 (m, 4H, Si-CH₂), -0.05 (s, 18H, Si-(CH₃)₃) (see page S7).

¹³C NMR (CDCl₃): δ 161.0, 149.0, 143.9, 130.5, 129.1, 124.2, 121.2, 114.6, 113.0, 74.3, 66.0, 60.0, 18.1, 13.8, -1.4.

MS (MALDI-TOF): *m/z* = 691.3 ([M+H]⁺)

HRMS (MALDI-TOF): calcd for C₃₆H₅₀N₄O₆Si₂+H 691.335, found 691.334.

Diethyl 4,4'-(*p*-methoxyphenyl)-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-3,6-dicarboxylate (22{7}, R = *p*-MeOC₆H₄)

As above using diethyl 2,7-di(*p*-methoxyphenyl)-4*H*,5*H*-bis(trimethylsilylethoxymethyl)thieno[3,2-*b*,4,5-*b'*]dipyrrole-3,6-dicarboxylate (**21{7}**, R = *p*-MeOC₆H₄). The crude material obtained was washed with water and dried (P₂O₅) to give 92 mg (94%) of **22{7}** (R = *p*-MeOC₆H₄) as a white solid. Mp: 77-78 °C.

IR (KBr): ν_{\max} 2952, 2900, 2835, 1697, 1501, 1247, 836 cm^{-1} .

¹H NMR 300 MHz (CDCl₃): δ 7.35 (d, *J* = 8.4 Hz, 4H, Ph), 6.90 (d, *J* = 8.4 Hz, 4H, Ph), 6.46 (s, 2H, C_{pyrrole}-H), 5.57 (s, 4H, N-CH₂), 4.19 (q, 4H, *J*=6.0Hz, O-CH₂CH₃), 3.85 (s, 6H, O-CH₃), 3.46 (m, 4H, O-CH₂), 1.13 (t, 6H, *J*=6.0 Hz, O-CH₂CH₃), 0.86 (m, 4H, *J*=8.4 Hz, Si-CH₂), -0.05 (s, 18H, Si-(CH₃)₃).

¹³C NMR 300 MHz (CDCl₃): δ 161.5, 158.5, 133.3, 130.4, 129.2, 128.3, 120.4, 115.0, 113.0, 74.3, 65.7, 60.2, 55.3, 18.0, 14.0, -1.4 (see page S8).

MS (ESI-TOF): *m/z* = 771.6 ([M+Na]⁺), 701.6, 631.5, 603.4.

HRMS (ESI): calcd for C₄₀H₅₆N₂O₈Si₂+Na 771.347, found 771.344.

Synthesis of Diethyl 4,4'-diaryl-2,2'-bipyrrole-3,6-dicarboxylates (**10**)

General Procedure

A solution of the corresponding diethyl 4,4'-diaryl-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-3,6-dicarboxylate **22** (770 μmol) in 10 mL of dry 1,4-dioxane containing 0.8 mL (380 μmol) of ethylenediamine was heated at reflux and then 32 mL (168 μmol) of tetrabutylammonium fluoride (TBAF) (1M in THF) were added dropwise. The evolution of the reaction was monitored by TLC (24-48 h). The resulting mixture was poured into water and extracted with AcOEt (3 x 25 mL). The organic extracts were dried (MgSO_4) and concentrated *in vacuo* to give the corresponding compound **10**.

Diethyl 4,4'-diphenyl-2,2'-bipyrrole-3,6-dicarboxylate (**10{5}**, R = Ph)

As above using diethyl 4,4'-diphenyl-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-5,5'-dicarboxylate (**22{5}**, R = Ph). The crude material obtained was recrystallized from MeOH to give 424 mg (80%) of **10{5}** (R = Ph) as a white solid. Mp: 265 $^\circ\text{C}$ (d)² (see page S9).

Diethyl 4,4'-(di(pyridin-4-yl))-2,2'-bipyrrole-3,6-dicarboxylate (**10{6}**, R = C₆H₄N)

As above using 4,4'-(di(pyridin-4-yl))-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-3,6-dicarboxylate (**22{6}**, R = C₆H₄N). The crude material obtained was washed with pentane and with MeOH yielding 295 mg (89%) of **10{6}** (R = C₆H₄N) as a white solid. Mp: 275 $^\circ\text{C}$ (d).

¹H NMR (d₆-DMSO): δ 12.32 (s, 2H, NH), 8.63 (d, J = 5.8 Hz, 4H, Py), 7.61 (d, J = 5.8 Hz, 4H, Ph), 7.04 (d, 2H, , J = 2.0 Hz, C_{pyrrole}-H), 4.27 (q, 4H, J = 7.0 Hz, O-CH₂CH₃), 1.24 (t, 6H, J = 7.0 Hz, O-CH₂CH₃).

¹³C NMR (CDCl₃): δ 160.2, 149.1, 142.5, 129.2, 127.8, 124.1, 118.6, 110.5, 60.4, 14.4 (see p/ S10)

MS (ESI-TOF): m/z = 437.3 ([M+Li]⁺), 316.4, 288.4, 158.1.

HRMS (ESI-TOF): calcd for C₂₄H₂₃N₄O₄ 431.171, found 431.173.

Diethyl 4,4'-(*p*-methoxyphenyl)-2,2'-bipyrrole-3,6-dicarboxylate (**10{7}**, R = *p*-MeOC₆H₄)

As above using diethyl 4,4'-(*p*-methoxyphenyl)-1,1'-bis(trimethylsilylethoxymethyl)-2,2'-bipyrrole-3,6-dicarboxylate (**22{7}**, R = *p*-MeOC₆H₄). The crude material obtained was column chromatographed using a 1:2 AcOEt/hexane mixture as eluent to give 342 mg (91%) of **10{7}** (R = *p*-MeOC₆H₄) as a white solid. Mp: 245 $^\circ\text{C}$ (d).

¹H NMR (CDCl₃): δ 9.44 (s, 2H, NH), 7.52 (d, J = 8.8 Hz, 4H, Ph), 6.93 (d, J = 8.8 Hz, 4H, Ph), 6.53 (d, 2H, , J = 3.0 Hz, C_{pyrrole}-H), 4.27 (q, 4H, J = 7.1 Hz, O-CH₂CH₃), 1.28 (t, 6H, J = 7.1 Hz, O-CH₂CH₃).

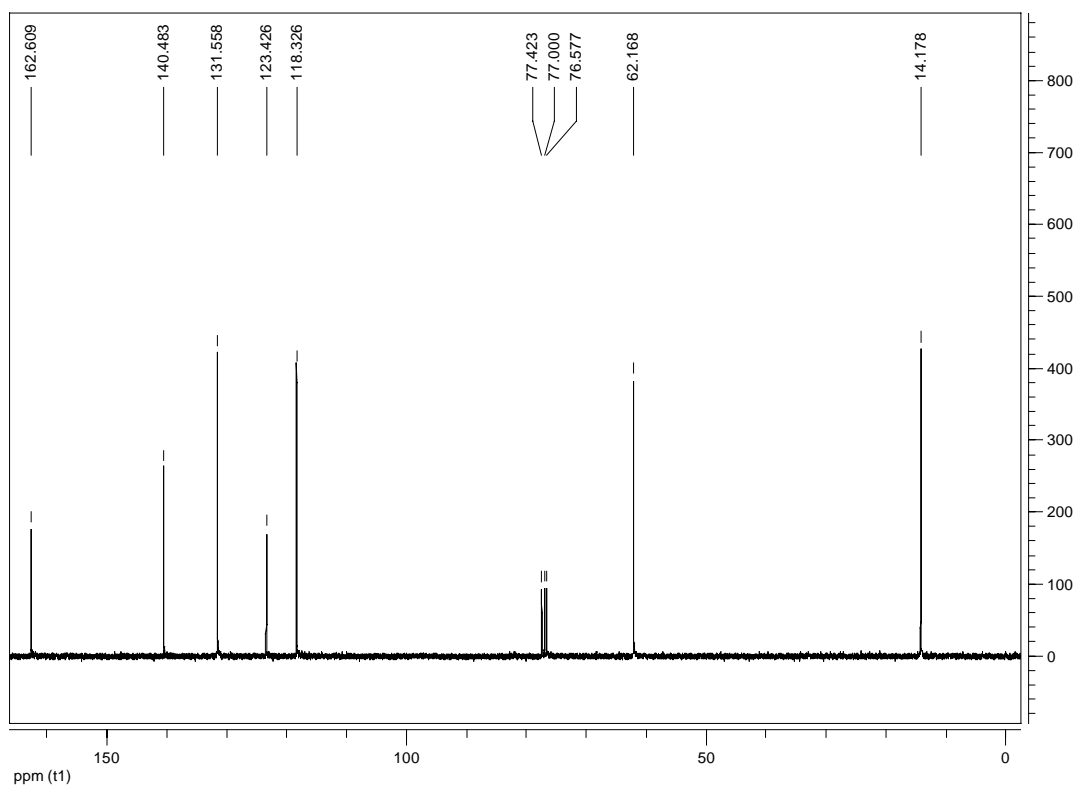
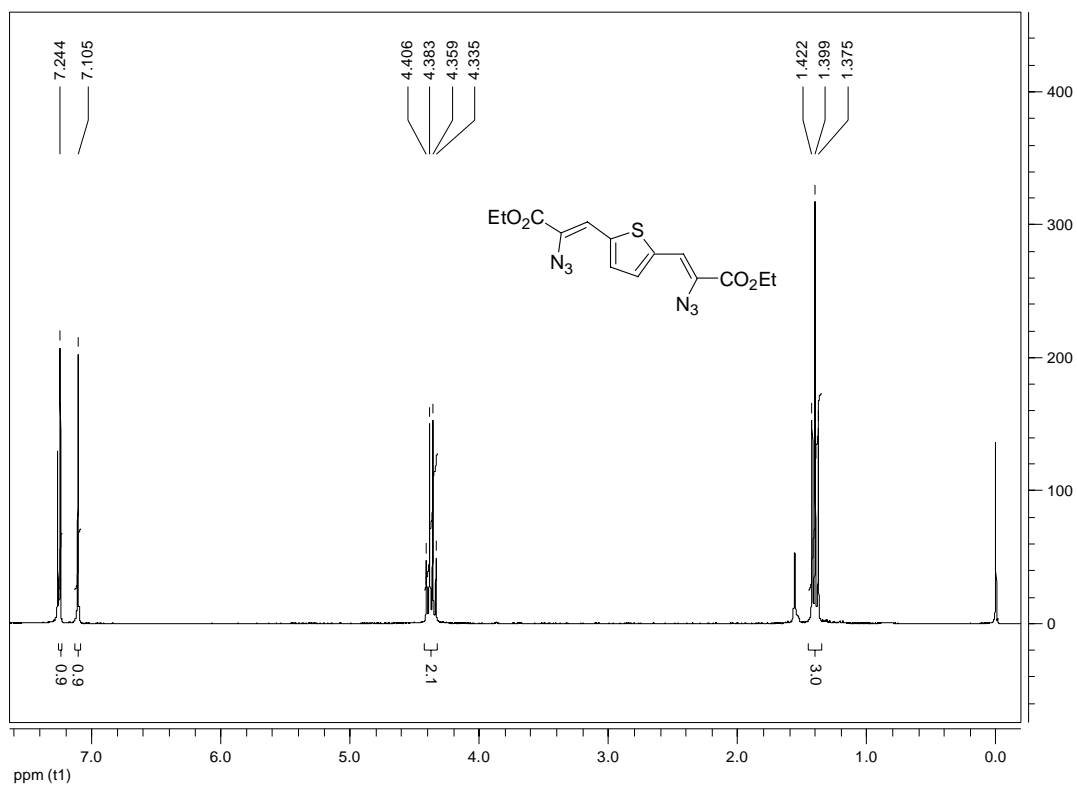
¹³C NMR (d₆-DMSO): δ 160.2, 158.1, 131.9, 130.3, 127.5, 127.0, 117.1, 112.1, 110.0, 59.6, 55.0, 14.3 (see p/S11)

MS (MALDI-TOF): m/z = 489.6 ([M+H]⁺)

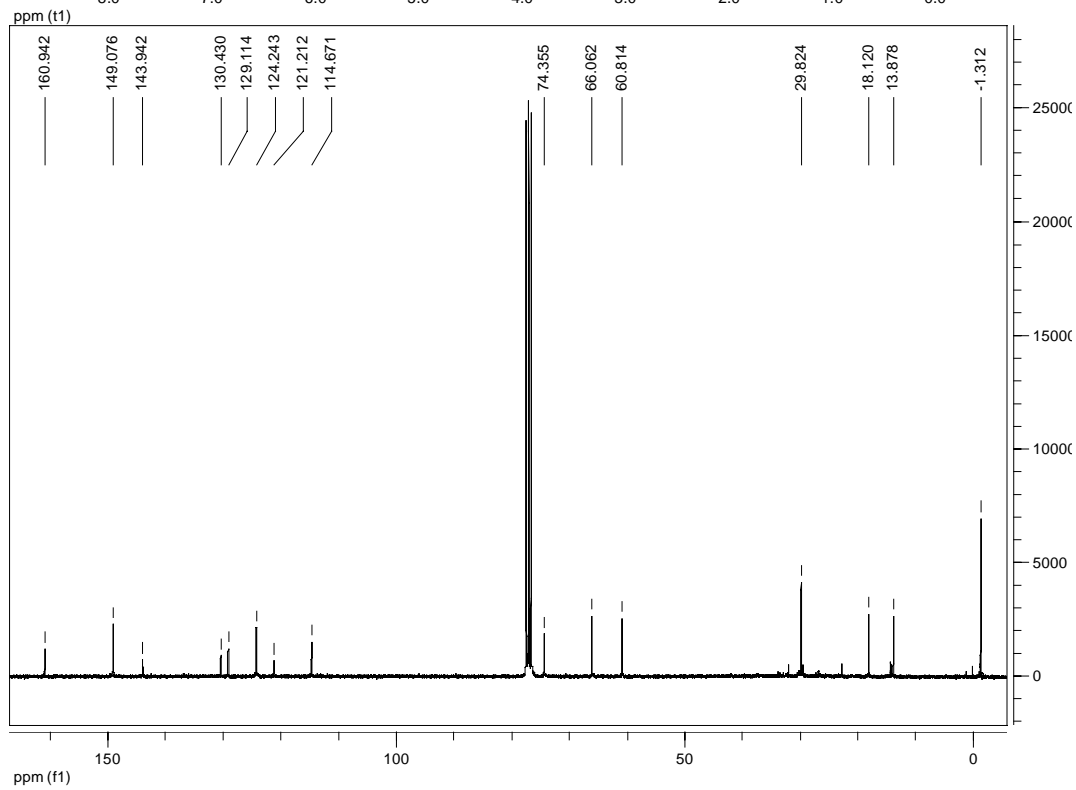
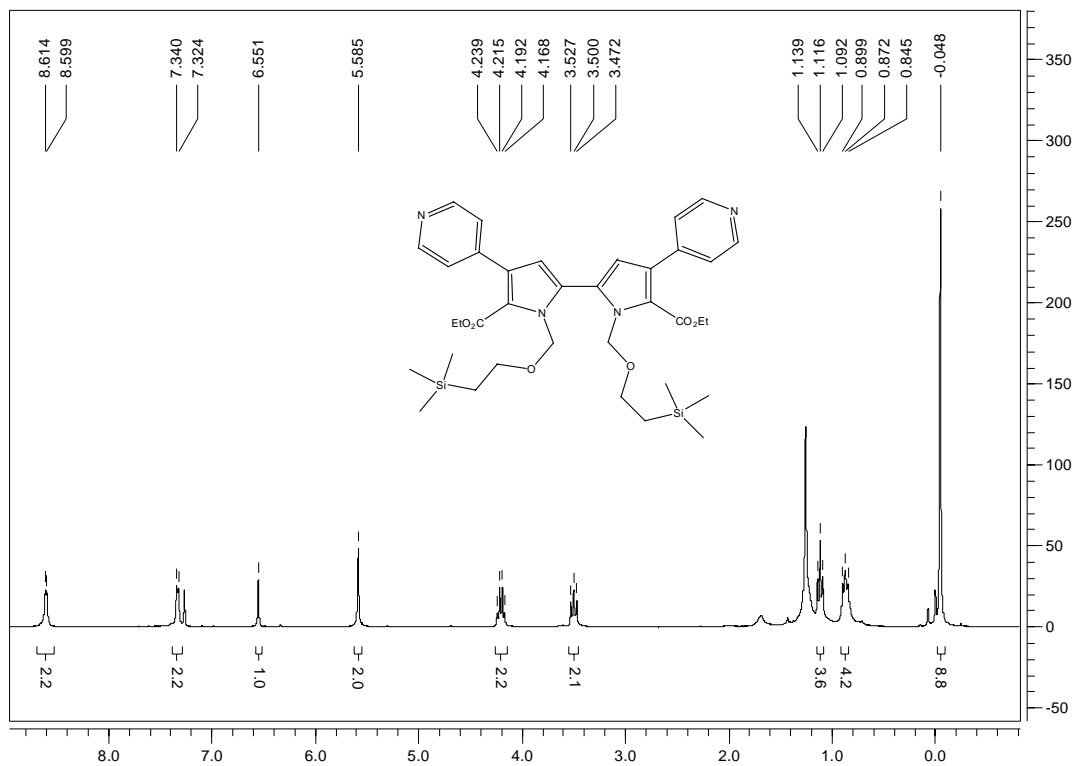
Anal. Calcd for C₂₈H₂₈N₂O₆: C, 68.84; H, 5.78; N, 5.73. Found: C, 68.69; H, 6.00; N, 5.55.

² Gavalda, A.; Borrell, J. I.; Teixidó, J.; Nonell, S.; Arad, O.; Grau, R.; Cañete, M.; Juarranz, A.; Villanueva, A.; Stockert, J. C. *J. Porphyrins. Phthalocyanines*. **2001**, *5*, 846.

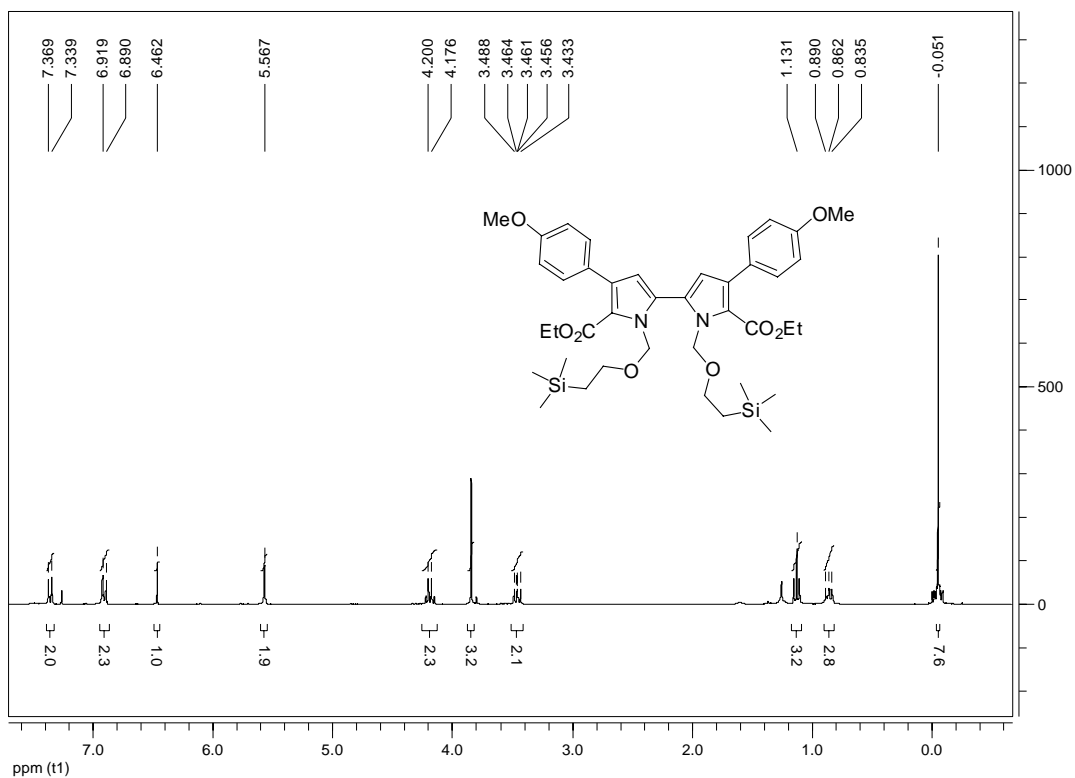
Bis(azido-2'-ethoxycarbonyl-2'-vinyl)-2,5-thiophene (18)



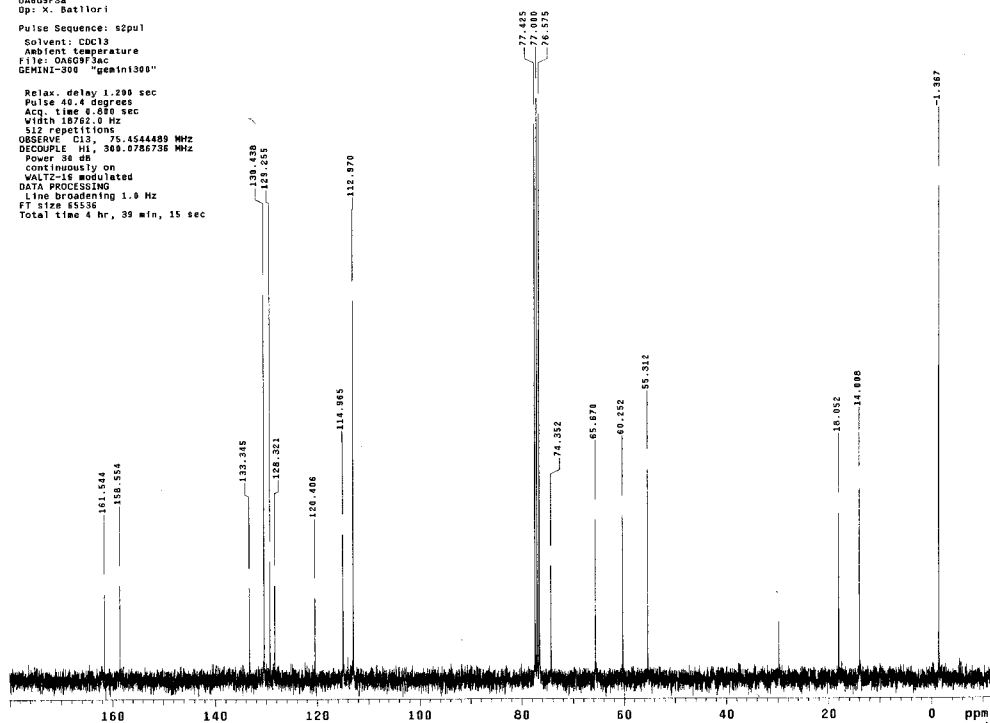
Diethyl 4,4'-(di(pyridin-4-yl)-1,1'-bis(trimethylsilyloxyethyl)-2,2'-bipyrrole-3,6-dicarboxylate (22{6}, R = C₆H₄N)



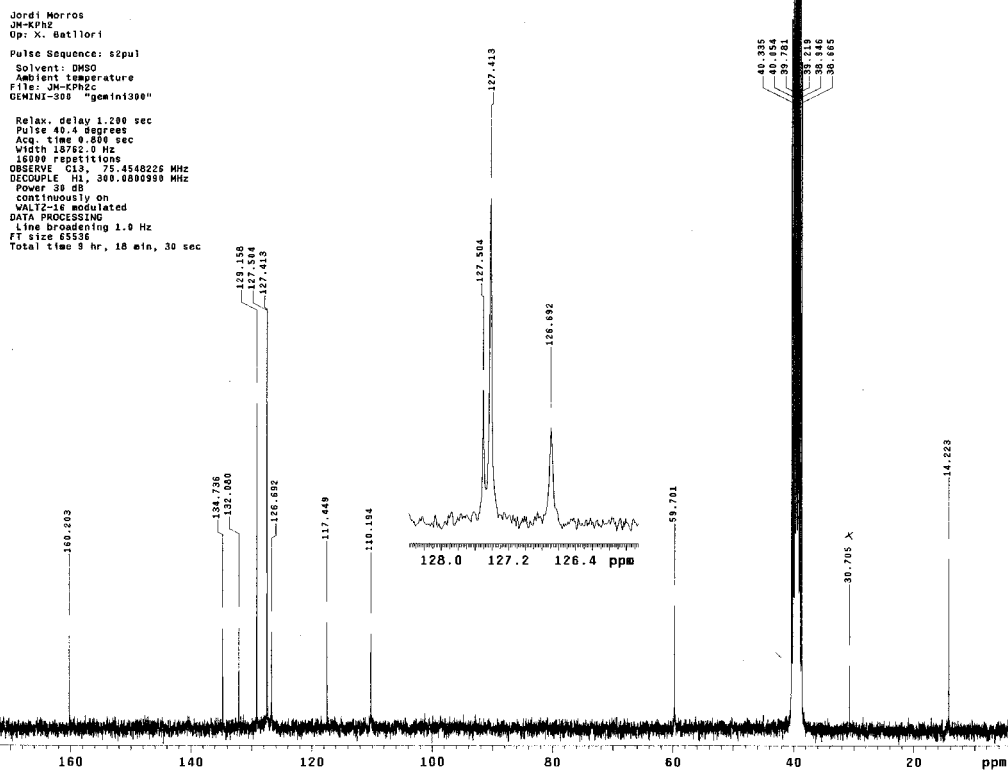
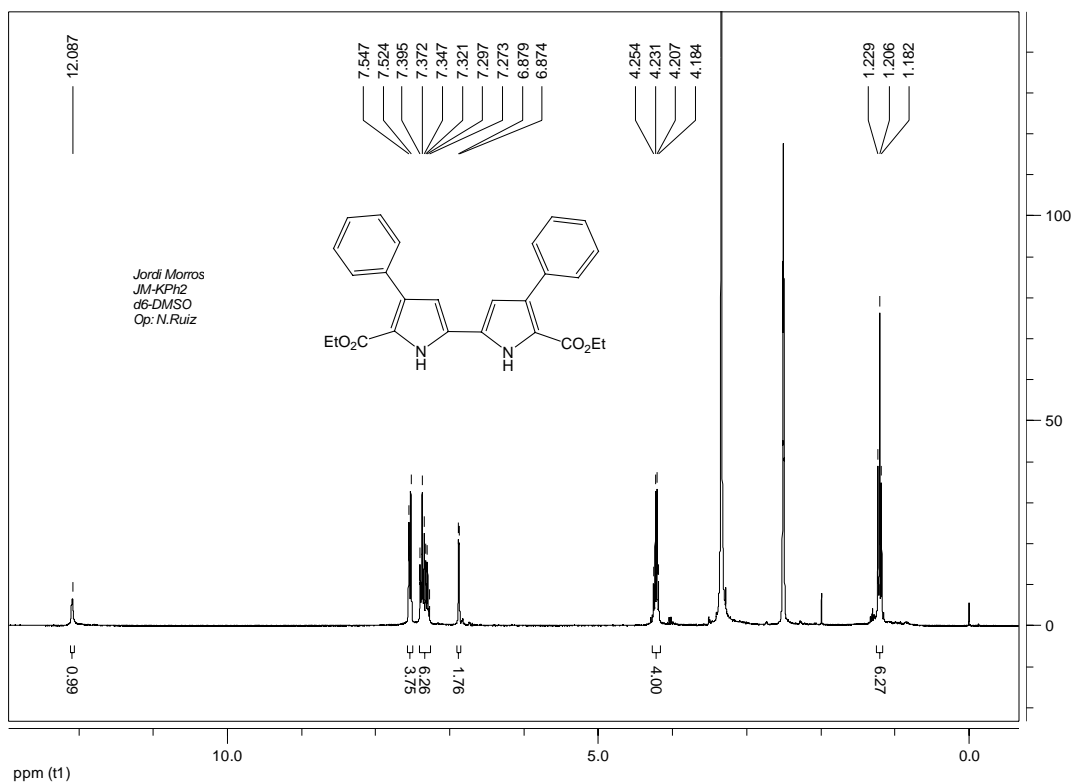
Diethyl 4,4'-(*p*-methoxyphenyl)-1,1'-bis(trimethylsilyloxyethyl)-2,2'-bipyrrole-3,6-dicarboxylate (22{7}, R = *p*-MeOC₆H₄)



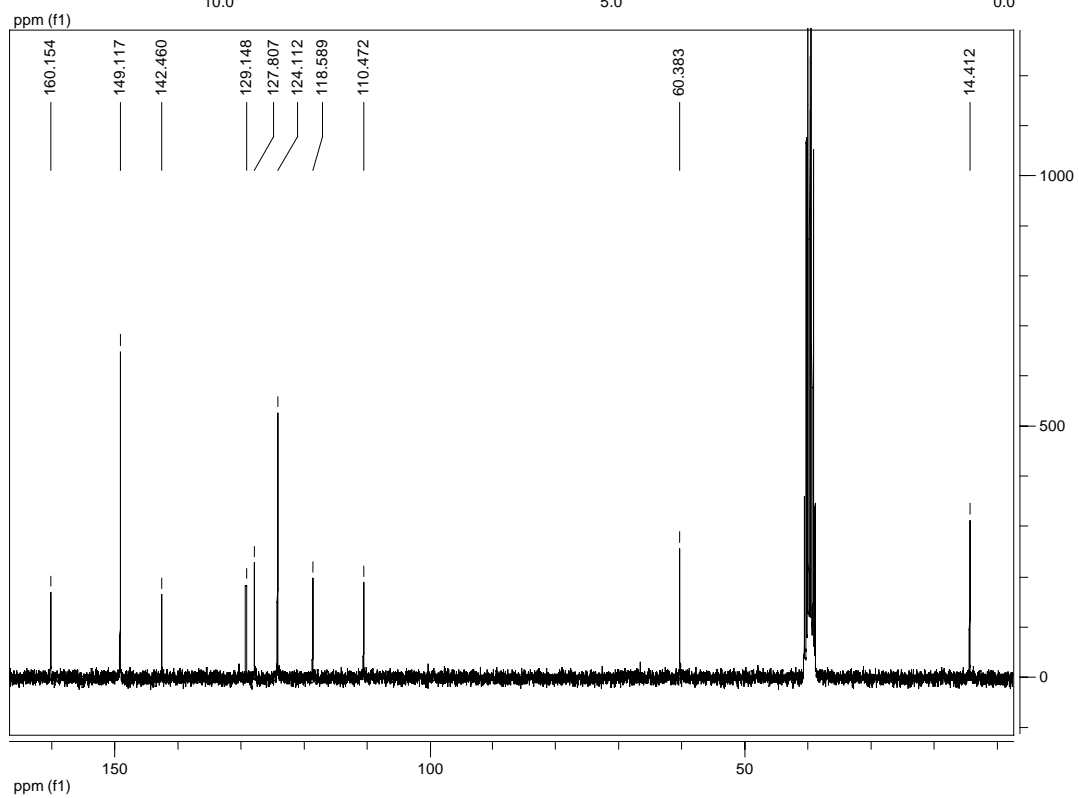
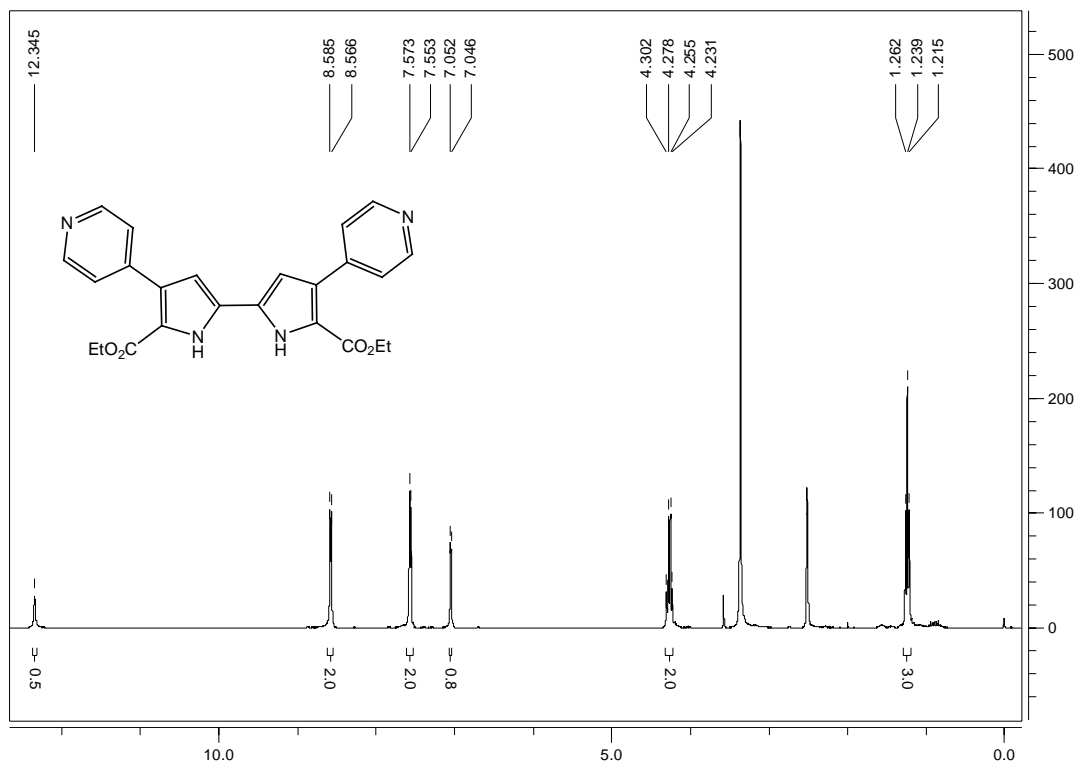
Ofir Arad
 DA6095a
 Op: K. Battlori
 Pulse Sequence: s2pul
 solvent: CDCl3
 Ambient temperature
 File: GAD09F5ec
 GEMINI-300 "gemini300"
 Relax delay 1.200 sec
 Pulse 40.4 degrees
 Acq. time 0.680 sec
 Width 10762.0 Hz
 SIZ repetitions
 OBSERVE f13 75.4544489 MHz
 DECOUPLE H1 309.0786736 MHz
 Power 36 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line Broadening 1.0 Hz
 FT size 65536
 Total time 4 hr, 39 min, 15 sec



Diethyl 4,4'-diphenyl-2,2'-bipyrrrole-3,6-dicarboxylate (10{5}, R = Ph)



Diethyl 4,4'-(di(pyridin-4-yl)-2,2'-bipyrrole-3,6-dicarboxylate (10{6}, R = C₆H₄N)



Diethyl 4,4'-(*p*-methoxyphenyl)-2,2'-bipyrrole-3,6-dicarboxylate (10{7}, R = *p*-MeOC₆H₄)

