1. **SYNTHESIS AND CHARACTERIZATION**
   1. **Overview of compounds**

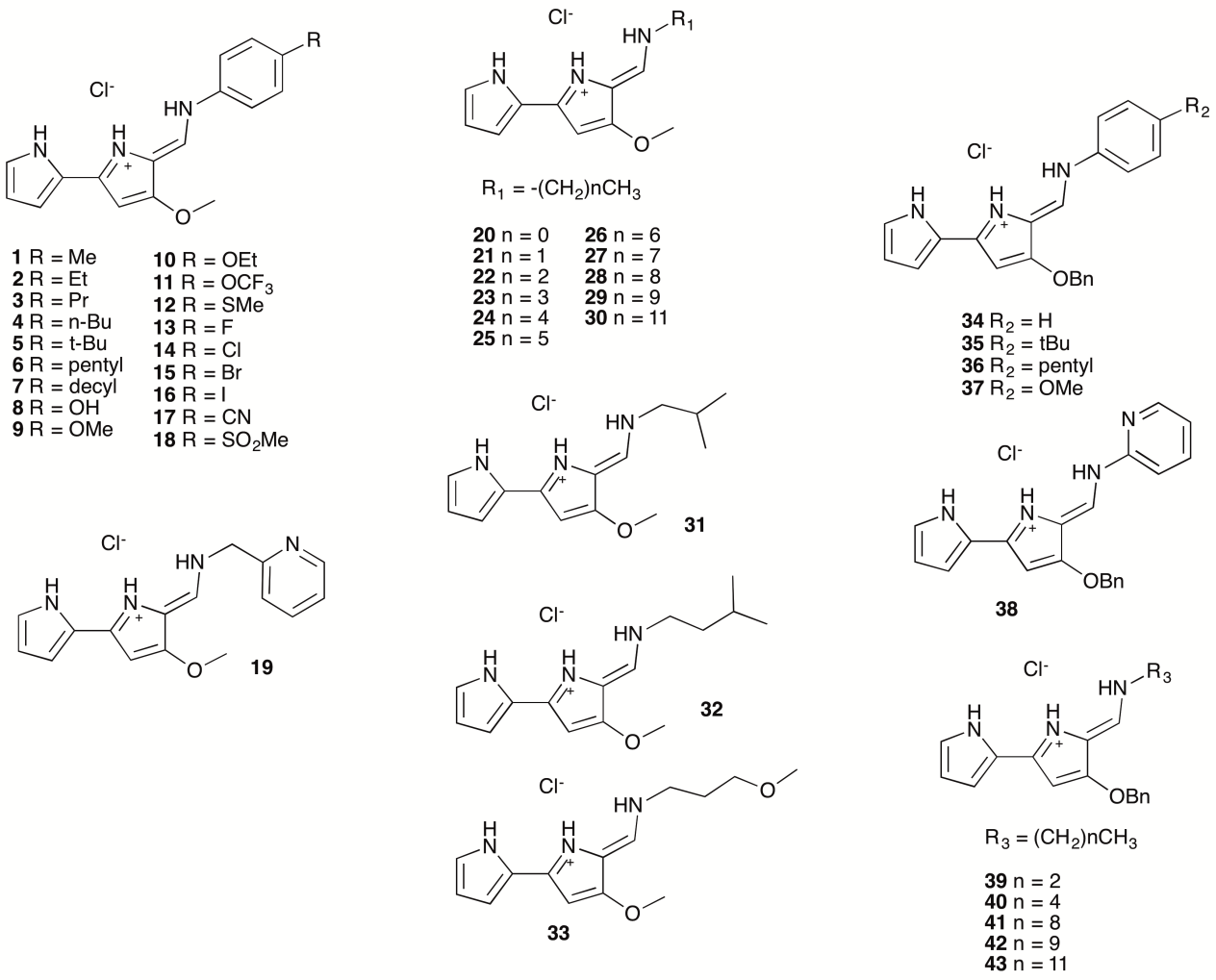
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Chart S1. Overview of tambjamine derivatives included in this study.

* 1. **Experimental procedures**

**General**. NMR spectra were recorded on Varian Mercury-300 MHz and Varian Unity-400 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and calibrated to the residual solvent peak in CDCl3 and DMSO-*d6*. High resolution mass spectra (HRMS) were recorded on a MicromassAutospec S-2 spectrometer using EI at 70 eV. Commercial reagents were used as provided by the supplier. 4-methoxy-1H,1'H-[2,2'-bipyrrole]-5-carbaldehyde and 4-(benzyloxy)-1H,1'H-[2,2'-bipyrrole]-5-carbaldehyde[[1]](#footnote-1) were prepared as described in the bibliography. Compounds **5**, **9**, **34**, **35**, **37**, **38**[[2]](#footnote-2) and **20**, **21**, **22**, **23**, **24**, **25**, **26**, **27**, **28**, **29**, **30**, **31**, **32**, **39**, **40, 42**[[3]](#footnote-3) were previously reported by us.

Compounds **1–43** were synthesized using modifications of the previously reported method.[[4]](#footnote-4) 4-methoxy-1H,1'H-[2,2'-bipyrrole]-5-carbaldehyde (190 mg, 1 mmol) or 4-(benzyloxy)-1H,1'H-[2,2'-bipyrrole]-5-carbaldehyde (266 mg, 1 mmol) and the corresponding amine (1.6–8 mmol, 1.6–8 mmol equivalents) were dissolved in 10 ml chloroform (or 1,2-dichloroethane; compounds **11**, **13**, **14**, **15**, **16**, **17**, **18**, **30**, **31** and **32**), 40 µL of acetic acid were added. The mixture was stirred at 60 ºC until TLC showed disappearance of the staring material. The reaction mixture was diluted with 40 mL of dichloromethane and washed with HCl 1M (3 × 25 mL). The organic fraction was dried over Na2SO4 and the solvent evaporated to yield **1**–**43** as yellow–orange solids in good to excellent yields.

**4'-methoxy-5'-((p-tolylamino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (1).** Yield: 100%;1H NMR (300 MHz, CDCl3): δ = 13.86 (s, 1H), 11.17 (d, *J* = 14.5 Hz, 1H), 10.67 (s, 1H), 7.75 (d, *J* = 14.7 Hz, 1H), 7.31–7.10 (m, 5H), 6.80 (s, 1H), 6.30 (d, *J* = 3.7 Hz, 1H), 5.98 (d, *J* = 2.1 Hz, 1H), 3.96 (s, 3H, OCH3), 2.33 (s, 3H); 13C NMR (75 MHz, CDCl3): δ = 165.09 (C), 144.12 (C), 136.18 (C), 136.04 (C), 130.53 (2CH), 130.31 (CH), 125.34 (CH), 122.64 (C), 117.19 (2CH), 114.77 (CH), 113.29 (C), 111.39 (CH), 92.01 (CH), 58.85 (OCH3), 21.09 (CH3); HRMS (EI) m/z [M]+ calcd for [C17H17N3O] 279.1372; found: 279.1376.

**5'-(((4-ethylphenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (2).** Yield: 95%;1H NMR (300 MHz, CDCl3): δ = 13.90 (s, 1H), 11.20 (d, *J* = 14.3 Hz, 1H), 10.69 (s, 1H), 7.76 (d, *J* = 14.7 Hz, 1H), 7.41–7.10 (m, 5H), 6.81 (s, 1H), 6.32 (s, 1H), 5.99 (s, 1H), 3.97 (s, 3H, OCH3), 2.64 (app q, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ = 165.07 (C), 144.05 (C), 142.38 (C), 136.32 (C), 130.29 (CH), 129.31 (2CH), 125.21 (CH), 122.63 (C), 117.26 (2CH), 114.73 (CH), 113.26 (C), 111.35 (CH), 92.04 (CH), 58.84 (OCH3), 28.42 (CH2), 15.62 (CH3); HRMS (EI) m/z [M]+ calcd for [C18H19N3O] 293.1528; found: 293.1521.

**4'-methoxy-5'-(((4-propylphenyl)amino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (3).** Yield: 92%; 1H NMR (300 MHz, CDCl3): δ = 13.55 (s, 1H), 11.08 (d, *J* = 14.6 Hz, 1H), 10.61 (s, 1H), 7.62 (d, *J* = 14.7 Hz, 1H), 7.26–7.06 (m, 4H), 7.01 (d, *J* = 1.2 Hz, 1H), 6.75 (s, 1H), 6.21 (d, *J* = 3.7 Hz, 1H), 5.95 (d, *J* = 2.1 Hz, 1H), 3.86 (s, 3H, OCH3), 2.50 (t, *J* = 7.1 Hz, 2H), 1.65–1.49 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ = 164.97 (C), 143.87 (C), 140.65 (C), 136.20 (C), 130.05 (CH), 129.75 (2CH), 124.93 (CH), 122.51 (C), 117.00 (2CH), 114.62 (CH), 113.08 (C), 111.24 (CH), 92.06 (CH), 58.78 (OCH3), 37.41 (CH2), 24.49 (CH2), 13.75 (CH3); HRMS (EI) m/z [M]+ calcd for [C19H21N3O] 307.1685; found: 307.1690.

**5'-(((4-butylphenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (4).** Yield: 97%; 1H NMR (300 MHz, CDCl3): δ = 13.59 (s, 1H), 11.08 (d, *J* = 14.6 Hz, 1H), 10.62 (s, 1H), 7.64 (d, *J* = 14.7 Hz, 1H), 7.26–7.09 (m, 4H), 7.06–7.01 (m, 1H), 6.83–6.71 (m, 1H), 6.23 (d, *J* = 3.8 Hz, 1H), 5.95 (d, *J* = 2.2 Hz, 1H), 3.88 (s, 3H, OCH3), 2.54 (t, *J* = 7.8 Hz, 2H), 1.61–1.46 (m, 2H), 1.37–1.24 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ = 164.99 (C), 143.90 (C), 140.93 (C), 136.18 (C), 130.10 (CH), 129.73 (2CH), 125.01 (CH), 122.53 (C), 117.06 (2CH), 114.65 (CH), 113.10 (C), 111.26 (CH), 92.06 (CH), 58.79 (OCH3), 35.09 (CH2), 33.57 (CH2), 22.33 (CH2), 13.98 (CH3); HRMS (EI) m/z [M]+ calcd for [C20H23N3O] 321.1841; found: 321.1841.

**4'-methoxy-5'-(((4-pentylphenyl)amino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (6).**

Yield: 100%; 1H NMR (300 MHz, CDCl3): δ = 13.58 (s, 1H), 11.08 (d, *J* = 14.6 Hz, 1H), 10.62 (s, 1H), 7.62 (d, *J* = 14.6 Hz, 1H), 7.26–7.05 (m, 4H), 7.01 (s, 1H), 6.75 (s, 1H), 6.21 (d, *J* = 1.6 Hz, 1H), 5.94 (s, 1H), 3.86 (s, 3H, OCH3), 2.51 (t, *J* = 7.7 Hz, 2H), 1.62–1.47 (m, 2H), 1.30–1.20 (m, 4H), 0.86 (t, *J* = 6.5 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ = 164.96 (C), 143.86 (C), 140.91 (C), 136.17 (C), 130.06 (CH), 129.68 (2CH), 124.90 (CH), 122.53 (C), 117.01 (2CH), 114.59 (CH), 113.08 (C), 111.24 (CH), 92.05 (CH), 58.77 (OCH3), 35.33 (CH2), 31.43 (CH2), 31.07 (CH2), 22.52 (CH2), 14.06 (CH3); HRMS (EI) m/z [M]+ calcd for [C21H25N3O] 335.1998; found: 335.1981.

**5'-(((4-decylphenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (7).** Yield: 95%; 1H NMR (400 MHz, CDCl3): δ = 13.90 (s, 1H), 11.20 (d, *J* = 14.5 Hz, 1H), 10.68 (s, 1H), 7.75 (d, *J* = 14.6 Hz, 1H), 7.32–7.16 (m, 4H), 7.12 (s, 1H), 6.81 (s, 1H), 6.31 (d, *J* = 3.6 Hz, 1H), 5.99 (d, *J* = 2.1 Hz, 1H), 3.97 (s, 3H, OCH3), 2.58 (t, *J* = 5.7 Hz, 2H), 1.64–1.52 (m, 4H), 1.30–1.24 (m, 12H), 0.87 (t, *J* = 6.7 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ = 165.03 (C), 143.98 (C), 141.09 (C), 136.25 (C), 130.23 (CH), 129.81 (2CH), 125.14 (CH), 122.61 (C), 117.15 (2CH), 114.69 (CH), 113.21 (C), 111.32 (CH), 92.03 (CH), 58.82 (OCH3), 35.47 (CH2), 31.99 (CH2), 31.51 (CH2), 29.70 (2CH2), 29.57 (CH2), 29.42 (CH2), 29.33 (CH2), 22.78 (CH2), 14.23 (CH3); HRMS (EI) m/z [M]+ calcd for [C26H35N3O] 405.2780; found: 405.2776.

**5'-(((4-hydroxyphenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (8).** Yield: 38%; 1H NMR (300 MHz, DMSO-*d6*): δ = 13.09 (s, 1H), 12.52 (d, *J* = 14.1 Hz, 1H), 11.96 (s, 1H), 9.74 (s, 1H), 8.17 (d, *J* = 13.9 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.19 (s, 2H, OH), 6.83 (d, *J* = 8.4 Hz, 2H), 6.56 (s, 1H), 6.31 (s, 1H), 3.98 (s, 3H, OCH3); 13C NMR (75 MHz, DMSO-*d6*): δ = 164.36 (C), 155.85 (C), 142.16 (C), 132.53 (CH), 130.45 (C), 124.39 (CH), 122.24 (C), 119.09 (2CH), 116.20 (2CH), 111.95 (CH), 111.89 (C), 110.81 (CH), 92.19 (CH), 58.75 (OCH3); HRMS (EI) m/z [M]+ calcd for [C16H15N3O2] 281.1164; found: 281.1166.

**5'-(((4-ethoxyphenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride**

**(10).** Yield: 92%; 1H NMR (300 MHz, CDCl3): δ = 13.75 (s, 1H), 11.23 (d, *J* = 14.7 Hz, 1H), 10.61 (s, 1H), 7.69 (d, *J* = 14.8 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.13–7.07 (m, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.82–6.75 (m, 1H), 6.38–6.22 (m, 1H), 5.97 (d, *J* = 2.2 Hz, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 3.95 (s, 3H, OCH3), 1.40 (t, *J* = 7.0 Hz, 3H); 13C NMR (75 MHz, CDCl3): δ = 164.75 (C), 157.40 (C), 143.54 (C), 131.83 (C), 130.59 (CH), 125.04 (CH), 122.71 (C), 118.73 (2CH), 115.71 (2CH), 114.40 (CH), 112.99 (C), 111.29 (CH), 91.91 (CH), 63.98 (CH2), 58.79 (OCH3), 14.88 (CH3); HRMS (EI) m/z [M]+ calcd for [C18H19N3O2] 309.1477; found: 309.1483.

**4'-methoxy-5'-(((4-(trifluoromethoxy)phenyl)amino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (11).** Yield: 95%; 1H NMR (300 MHz, CDCl3): δ = 13.68 (s, 1H), 11.18 (d, *J* = 14.1 Hz, 1H), 10.64 (s, 1H), 7.66 (d, *J* = 14.3 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.10 (s, 1H), 6.82 (s, 1H), 6.29 (s, 1H), 5.94 (s, 1H), 3.89 (s, 3H, OCH3); 13C NMR (75 MHz, CDCl3): δ = 165.71 (C), 146.51 (q, *J* = 1.7 Hz, C), 145.27 (C), 137.32(C), 129.65 (CH), 125.97 (CH), 122.70 (2CH), 122.43 (C), 120.5 (q, *J* = 256.0 Hz, CF3) 118.30 (2CH), 115.69 (CH), 114.06 (C), 111.72 (CH), 92.34 (CH), 58.94 (OCH3); HRMS (EI) m/z [M]+ calcd for [C17H14F3N3O2] 349.1038; found: 349.1039.

**4'-methoxy-5'-(((4-(methylthio)phenyl)amino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (12).** Yield: 87%;1H NMR (300 MHz, DMSO*-d6*): δ = 13.16 (s, 1H), 12.52 (d, *J* = 14.1 Hz, 1H), 12.06 (s, 1H), 8.27 (d, *J* = 14.2 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 2H), 6.60 (s, 1H), 6.35 (s, 1H), 4.01 (s, 3H, OCH3), 2.50 (s, 3H); 13C NMR (75 MHz, DMSO*-d6*): δ = 165.21 (C), 143.58 (C), 135.94 (C), 135.40 (C), 131.90 (CH), 127.29 (2CH), 125.10 (CH), 122.15 (2C), 118.02 (2CH), 112.79 (CH), 111.14 (CH), 92.54 (CH), 58.92 (OCH3), 15.06 (CH3); HRMS (EI) m/z [M]+ calcd for [C17H17N3OS] 311.1092; found: 311.1098.

**5'-(((4-fluorophenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (13).** Yield: 82%;1H NMR (300 MHz, DMSO-*d6*): δ = 13.19 (s, 1H), 12.58 (d, *J* = 14.1 Hz, 1H), 12.05 (s, 1H), 8.25 (d, *J* = 14.0 Hz, 1H), 7.72–7.59 (m, 2H), 7.38–7.16 (m, 4H), 6.59 (s, 1H), 6.34 (s, 1H), 4.00 (s, 3H, OCH3); 13C NMR (75 MHz, DMSO-*d6*): δ = 165.53 (C), 159.78 (C, d, *J* = 241.5 Hz ), 143.87 (C), 135.30 (C, d, *J* = 2.3 Hz), 132.58 (CH), 125.21 (CH), 122.12 (C), 119.35 (2CH, d, *J* = 8.3 Hz), 116.60 (2CH, d, *J* = 23.1 Hz), 112.92 (CH), 111.83 (C), 111.20 (CH), 92.61 (CH), 58.99 (OCH3); HRMS (EI) m/z [M]+ calcd for [C16H14FN3O] 283.1121; found: 283.1130.

**5'-(((4-chlorophenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride** **(14).** Yield: 74%;1H NMR (300 MHz, DMSO-*d6*): δ = 13.21 (s, 1H), 12.55 (d, *J* = 13.8 Hz, 1H), 12.08 (s, 1H), 8.25 (d, *J* = 13.5 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.26 (s, 2H), 6.59 (s, 1H), 6.35 (s, 1H), 4.00 (s, 3H, OCH3); 13C NMR (75 MHz, DMSO-*d6*): δ = 165.66 (C), 144.33 (C), 137.72 (C), 131.85 (CH), 129.58 (2CH), 129.32 (C), 125.41 (CH), 122.03 (C), 118.95 (2CH), 113.18 (CH, C), 111.22 (CH), 92.66 (CH), 58.94 (OCH3); HRMS (EI) m/z [M]+ calcd for [C16H14ClN3O] 299.0825; found: 299.0828.

**5'-(((4-bromophenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (15).** Yield: 95%;1H NMR (300 MHz, DMSO-*d6*): δ = 13.06 (s, 1H), 12.37 (d, *J* = 12.1 Hz, 1H), 12.07 (s, 1H), 8.18 (d, *J* = 8.9 Hz, 1H), 7.62–7.48 (m, 4H), 7.23 (s, 2H), 6.56 (s, 1H), 6.34 (s, 1H), 3.97 (s, 3H, OCH3); 13C NMR (75 MHz, DMSO-*d6*): δ = 165.84 (C), 144.55 (C), 138.19 (C), 132.58 (2CH), 131.65 (CH), 125.58 (CH), 122.11 (C), 119.33 (2CH), 117.59 (C), 113.34 (CH, C), 111.39 (CH), 92.80 (CH), 59.09 (OCH3); HRMS (EI) m/z [M]+ calcd for [C16H14BrN3O] 343.0320; found: 343.0328.

**5'-(((4-iodophenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (16).** Yield: 72%;1H NMR (300 MHz, DMSO*-d6*): δ = 13.19 (s, 1H), 12.47 (d, *J* = 14.1 Hz, 1H), 12.08 (s, 1H), 8.24 (d, *J* = 13.8 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.26 (s, 2H), 6.59 (s, 1H), 6.35-6.33 (m, 1H), 4.00 (s, 3H, OCH3); 13C NMR (75 MHz, DMSO*-d6*): δ = 165.70 (C), 144.42 (C), 138.56 (C), 138.28 (2CH), 131.52 (CH), 125.49 (CH), 122.04 (C), 119.43 (2CH), 113.25 (CH, C), 111.27 (CH), 92.69 (CH), 89.79 (C), 58.97 (OCH3); HRMS (EI) m/z [M]+ calcd for [C16H14IN3O] 391.0182; found: 391.0179.

**5'-(((4-cyanophenyl)amino)methylene)-4'-methoxy-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (17).** Yield: 100%;1H NMR (300 MHz, CDCl3): δ = 13.99 (s, 1H), 11.34 (d, *J* = 13.7 Hz, 1H), 10.72 (s, 1H), 7.71 (d, *J* = 13.9 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.24–7.18 (m, 1H), 6.96–6.89 (m, 1H), 6.43–6.32 (m, 1H), 6.03 (d, *J* = 2.0 Hz, 1H), 4.02 (s, 3H; OCH3); 1H NMR (300 MHz, DMSO*-d6*): δ = 13.28 (s, 1H), 12.56 (d, *J* = 13.7 Hz, 1H), 12.19 (s, 1H), 8.32 (d, *J* = 0.6 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.34 (s, 2H), 6.64 (s, 1H), 6.39 (s, 1H), 4.03 (s, 3H; OCH3); 13C NMR (75 MHz, DMSO*-d6*): δ = 166.52 (C), 145.92 (C), 142.69 (C), 133.97 (2CH), 130.70 (CH), 126.39 (CH), 121.86 (C), 118.77 (C), 117.58 (2CH), 114.47 (C), 114.20 (CH), 111.65 (CH), 106.61 (C), 93.09 (CH), 59.13 (OCH3); HRMS (EI) m/z [M]+ calcd for [C17H14N4O] 290.1168; found: 290.1165.

**4'-methoxy-5'-(((4-(methylsulfonyl)phenyl)amino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (18).** Yield: 66%;1H NMR (300 MHz, DMSO-*d6*): δ = 13.32 (s, 1H), 12.60 (d, *J* = 13.7 Hz, 1H), 12.20 (s, 1H), 8.34 (d, *J* = 13.6 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.33 (s, 2H), 6.65 (s, 1H), 6.39 (s, 1H), 4.04 (s, 3H, OCH3), 3.23 (s, 3H); 13C NMR (75 MHz, DMSO-*d6*): δ = 166.49 (C), 145.80 (C), 143.04 (C), 136.37 (C), 130.89 (CH), 128.95 (2CH), 126.31 (CH), 121.89 (C), 117.35 (2CH), 114.34 (CH), 114.13 (C), 111.64 (CH), 93.08 (CH), 59.14 (OCH3), 43.70 (CH3); HRMS (EI) m/z [M]+ calcd for [C17H17N3O3S] 343.0991; found: 343.0986.

**1-(4'-methoxy-1H,5'H-[2,2'-bipyrrol]-5'-ylidene)-N-(pyridin-2-ylmethyl)methanamine (19).** Yield: 19%; 1H NMR (300 MHz, CDCl3): δ = 13.70 (s, 1H), 10.67 (s, 1H), 9.83 (s, 1H), 8.57 (d, *J* = 4.8 Hz, 1H), 7.73 (td, *J* = 7.9, 1.5 Hz, 1H), 7.58–7.45 (m, 2H), 7.30–7.20 (m, 1H), 7.06 (s, 1H), 6.80–6.71 (m, 1H), 6.31–6.24 (m, 1H), 5.95 (s, 1H), 4.73 (s, 2H), 3.92 (s, 3H, OCH3). 13C NMR (75 MHz, CDCl3): δ = 164.63 (C), 155.37 (C), 149.91 (CH), 143.34 (C), 140.75 (CH), 137.61 (CH), 124.63 (CH), 123.41 (CH), 122.71 (C), 122.51 (CH), 113.86 (CH), 111.79 (C), 111.04 (CH), 91.46 (CH), 58.66 (OCH3), 55.19 (CH2). HRMS (EI) m/z [M]+ calcd for [C16H16N4O4] 280.1324; found: 280.1325.

**4'-methoxy-5'-(((3-methoxypropyl)amino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (33).** Yield: 88%; 1H NMR (300 MHz, CDCl3): δ = 13.63 (s, 1H), 10.61 (s, 1H), 9.40 (s, 1H), 7.35 (d, *J* = 14.4 Hz, 1H), 7.05 (td, *J* = 2.7, 1.4 Hz, 1H), 6.76–6.71 (m, 1H), 6.31–6.25 (m, 1H), 5.94 (d, *J* = 1.9 Hz, 1H), 3.92 (s, 3H, OCH3), 3.61 (app q, 2H), 3.50 (t, *J* = 5.7 Hz, 2H), 3.35 (s, 3H, OCH3), 1.99 (app quin, 2H). 13C NMR (75 MHz, CDCl3): δ = 164.00 (C), 142.51 (C), 140.79 (CH), 124.23 (CH), 122.77 (C), 113.32 (CH), 110.97 (C), 110.87 (CH), 91.24 (CH), 68.50 (CH2), 58.83 (OCH3), 58.60 (OCH3), 47.77 (CH2), 30.13 (CH2). HRMS (EI) m/z [M]+ calcd for [C14H19N3O2] 261.1417; found: 261.1475.

**4'-(benzyloxy)-5'-(((4-pentylphenyl)amino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (36).** Yield:95%;1H NMR (300 MHz, CDCl3): δ = 13.90 (s, 1H), 11.26 (d, *J* = 14.7 Hz, 1H), 10.70 (s, 1H), 7.76 (d, *J* = 14.4 Hz, 1H), 7.53–7.35 (m, 5H), 7.33–7.12 (m, 4H), 7.09 (s, 1H), 6.79 (s, 1H), 6.29 (s, 1H), 6.06 (s, 1H), 5.19 (s, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.58 (app quin, 2H), 1.36–1.24 (m, 4H), 0.89 (t, *J* = 6.6 Hz, 3H). 13C NMR (75 MHz, CDCl3): δ = 163.90 (C), 144.04 (C), 141.26 (C), 136.34 (C), 134.91 (C), 130.64 (CH), 129.87 (2CH), 129.08 (CH), 129.00 (2CH), 128.22 (2CH), 125.29 (CH), 122.67 (C), 117.40 (2CH), 114.75 (CH), 113.57 (C), 111.35 (CH), 92.98 (CH), 73.84 (CH2), 35.47 (CH2), 31.50 (CH2), 31.17 (CH2), 22.62 (CH2), 14.14 (CH3). HRMS (EI) m/z [M]+ calcd for [C27H29N3O] 411.2311; found: 411.2310.

**4'-(benzyloxy)-5'-((nonylamino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (41).** Yield:74%;1H NMR (300 MHz, CDCl3): δ = 13.44 (s, 1H), 10.48 (s, 1H), 9.37 (d, *J* = 14.9 Hz, 1H), 7.37–7.08 (m, 6H), 6.85 (s, 1H), 6.60 (s, 1H), 6.14–6.07 (m, 1H), 5.89 (d, *J* = 2.0 Hz, 1H), 4.96 (s, 2H), 3.28 (app q, 2H), 1.58 (app quin, 2H), 1.28–1.03 (m, 12H), 0.72 (t, *J* = 6.6 Hz, 3H). 13C NMR (75 MHz, CDCl3): δ = 162.55 (C), 142.11 (C), 140.55 (CH), 135.05 (C), 128.85 (CH), 128.82 (2CH), 128.02 (2CH), 123.96 (CH), 122.72 (C), 113.11 (CH), 111.01 (C), 110.74 (CH), 92.10 (CH), 73.43 (CH2), 51.04 (CH2), 31.82 (CH2), 30.31 (CH2), 29.40 (CH2), 29.23 (CH2), 29.12 (CH2), 26.53 (CH2), 22.66 (CH2), 14.13 (CH3). HRMS (EI) m/z [M]+ calcd for [C25H33N3O] 391.2624; found: 391.2530.

**4'-(benzyloxy)-5'-((undecylamino)methylene)-1H,5'H-[2,2'-bipyrrol]-1'-ium chloride (43).** Yield:59%; 1H NMR (300 MHz, CDCl3): δ = 13.61 (s, 1H), 10.62 (s, 1H), 9.51 (d, *J* = 14.7 Hz, 1H), 7.43–7.31 (m, 6H), 7.01 (s, 1H), 6.72 (s, 1H), 6.29–6.21 (m, 1H), 6.01 (d, *J* = 1.9 Hz, 1H), 5.11 (s, 2H), 3.43 (app q, 2H), 1.72 (app quin, 2H), 1.41–1.17 (m, 18H), 0.86 (t, *J* = 6.6 Hz, 3H). 13C NMR (75 MHz, CDCl3): δ = 162.60 (C), 142.21 (C), 140.59 (CH), 135.09 (C), 128.93 (CH), 128.89 (2CH), 128.07 (2CH), 124.10 (CH), 122.76 (C), 113.18 (CH), 111.07 (C), 110.79 (CH), 92.11 (CH), 73.49 (CH2), 51.12 (CH2), 31.98 (CH2), 30.38 (CH2), 29.68 (2CH2), 29.64 (CH2), 29.51 (CH2), 29.41 (CH2), 29.19 (CH2), 26.60 (CH2), 22.76 (CH2), 14.20 (CH3). HRMS (EI) m/z [M]+ calcd for [C28H39N3O] 433.3093; found: 433.3112.

* 1. **Characterization data**

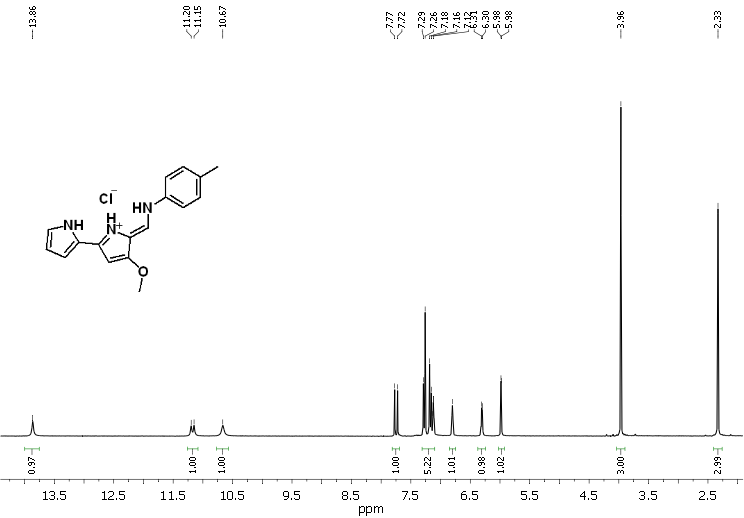


Figure S1. 1H NMR (CDCl3) of compound **1**. HCl.

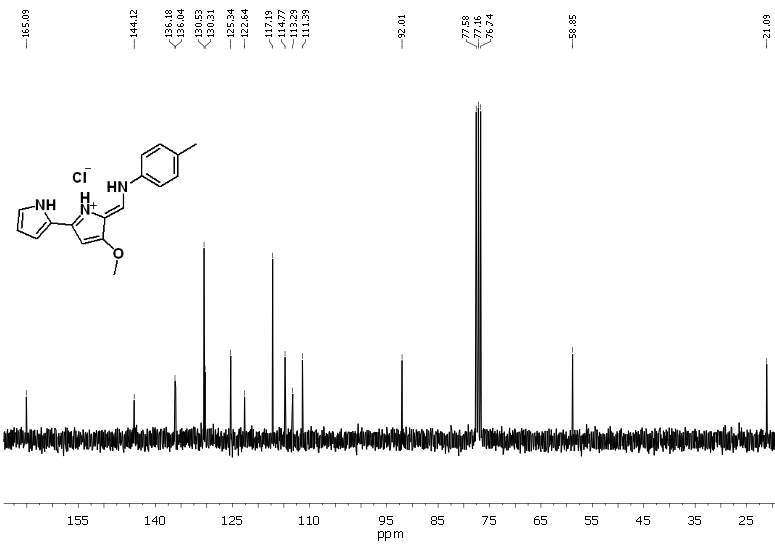


Figure S2. 13C NMR (CDCl3) of compound **1**. HCl.

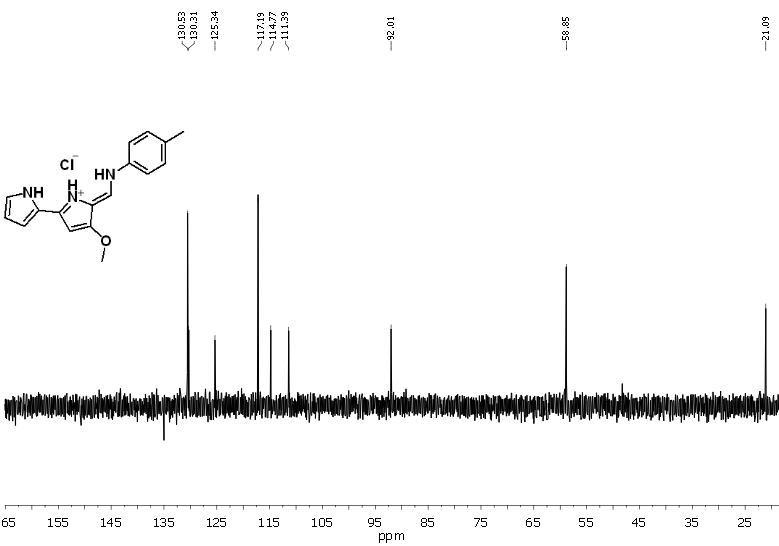
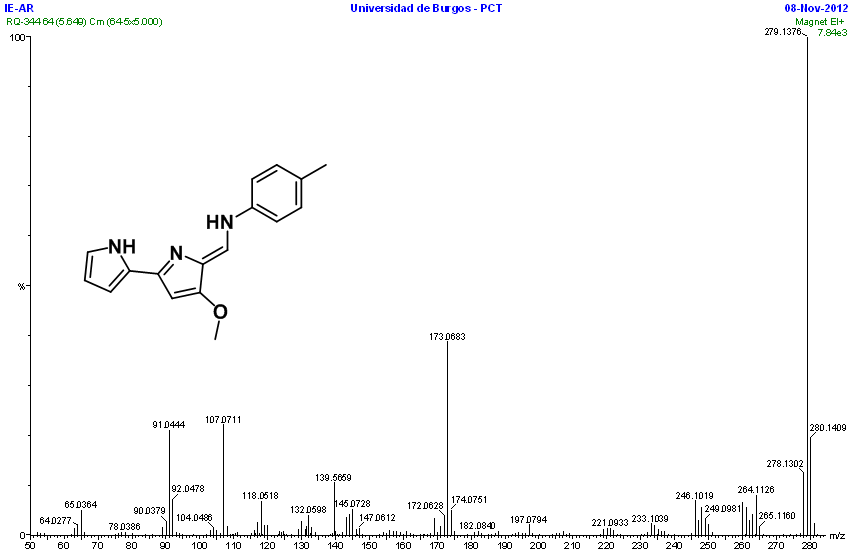
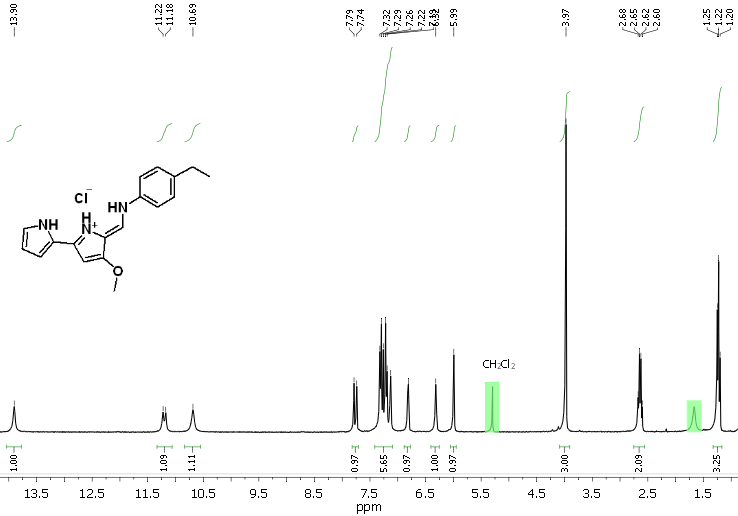
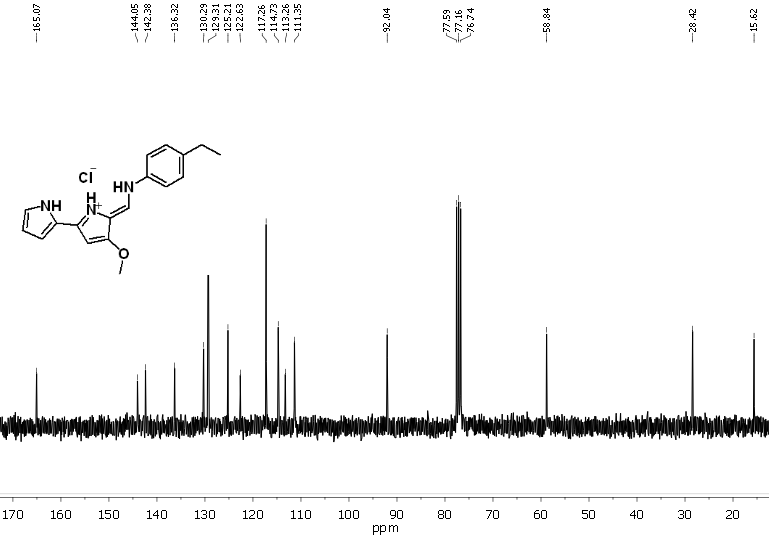
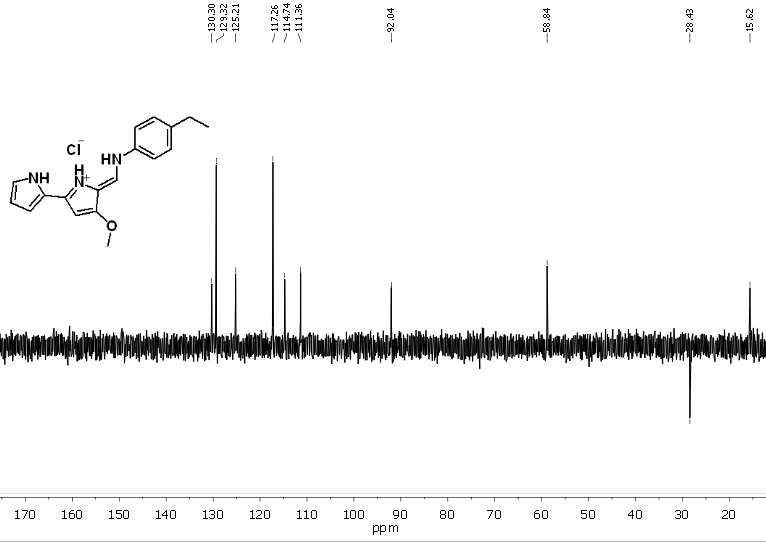


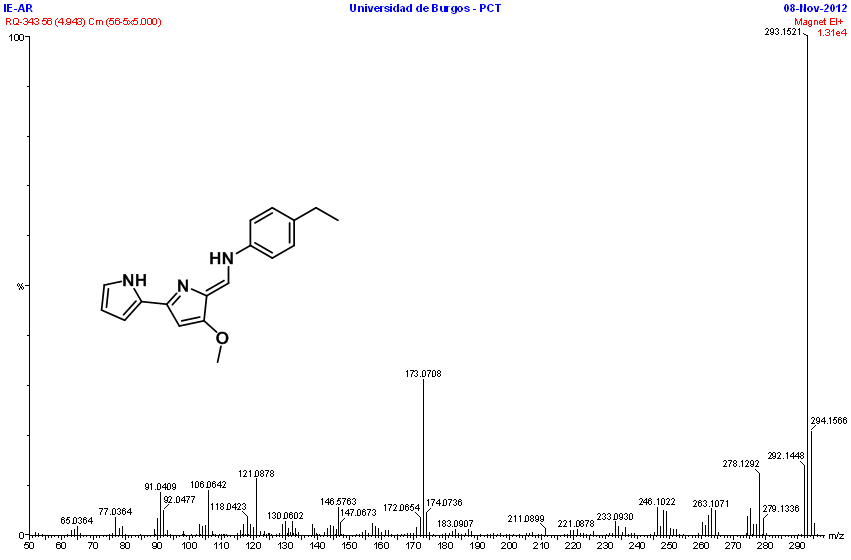
Figure S3. DEPT 13C NMR (CDCl3) of compound **1**. HCl.

Figure S4. HRMS (EI) of compound **1**.

 Figure S5. 1H NMR (CDCl3) of compound **2**. HCl.

Figure S6. 13C NMR (CDCl3) of compound **2**. HCl.

Figure S7. DEPT 13C NMR (CDCl3) of compound **2**. HCl.

Figure S8. HRMS (EI) of compound **2**.

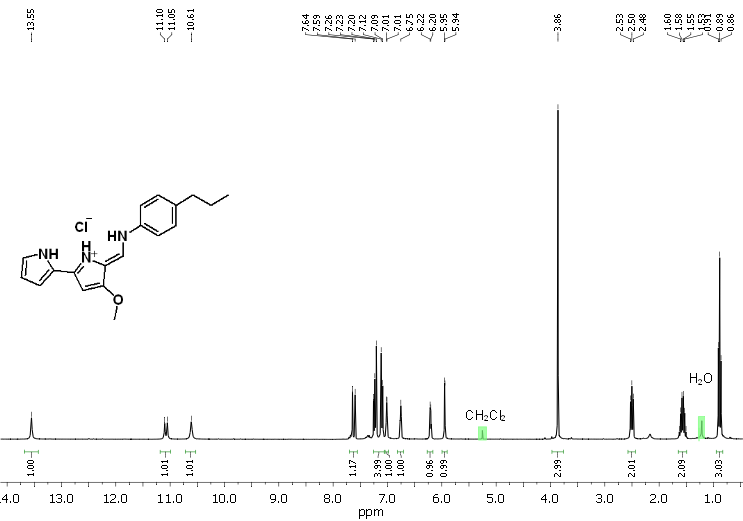
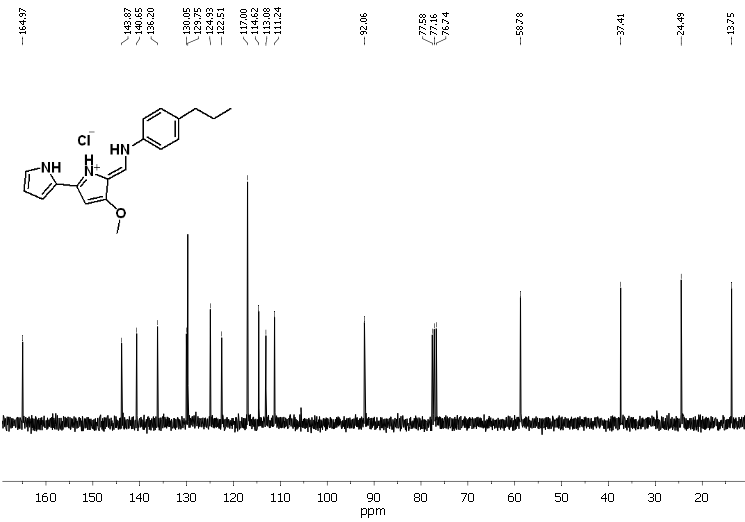
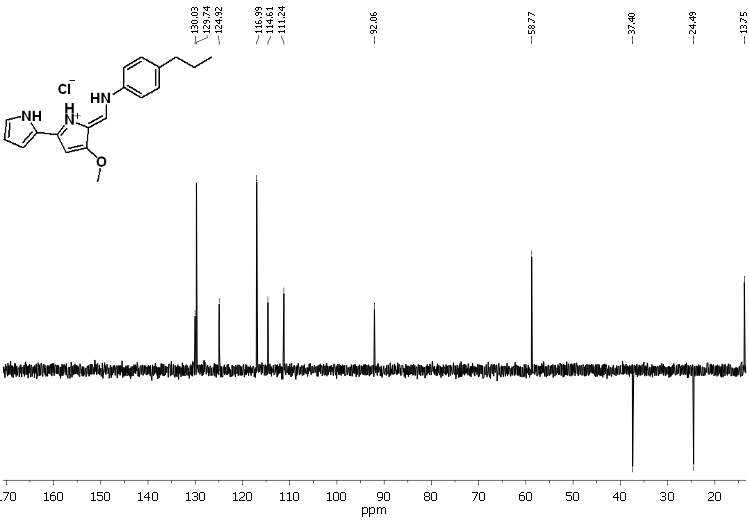
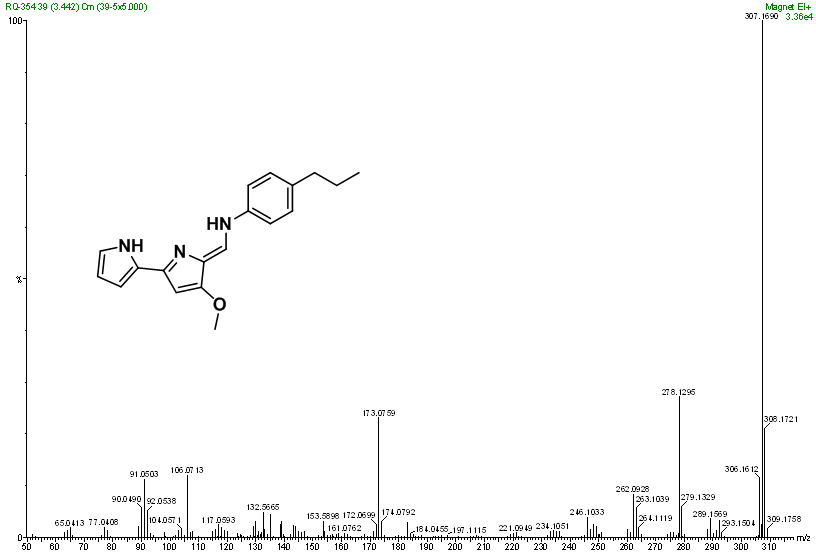


Figure S9. 1H NMR (CDCl3) of compound **3**. HCl.

 Figure S10. 13C NMR (CDCl3) of compound **3**. HCl.

 Figure S11. DEPT 13C NMR (CDCl3) of compound **3**. HCl.

Figure S12. HRMS (EI) of compound **3**.

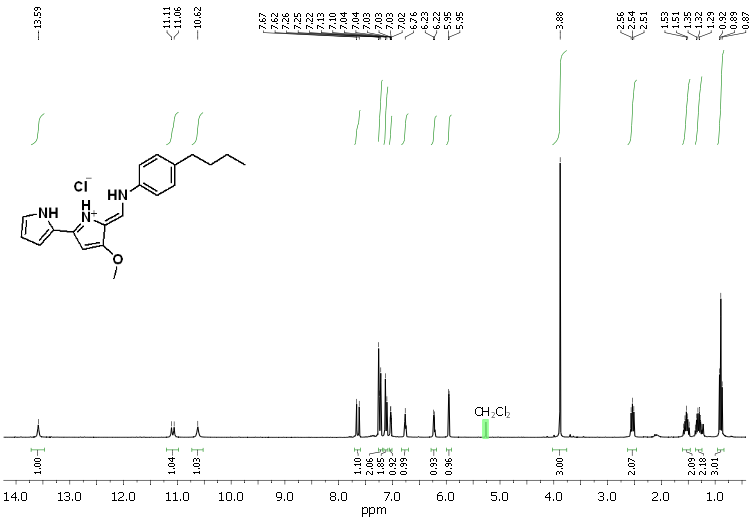
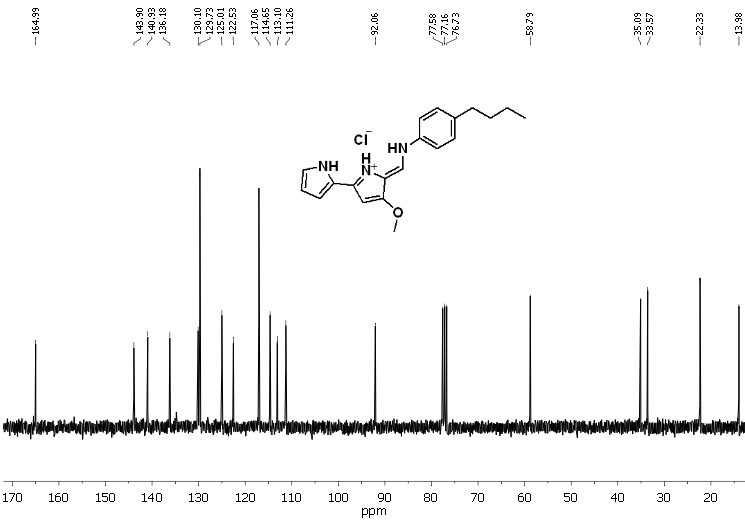
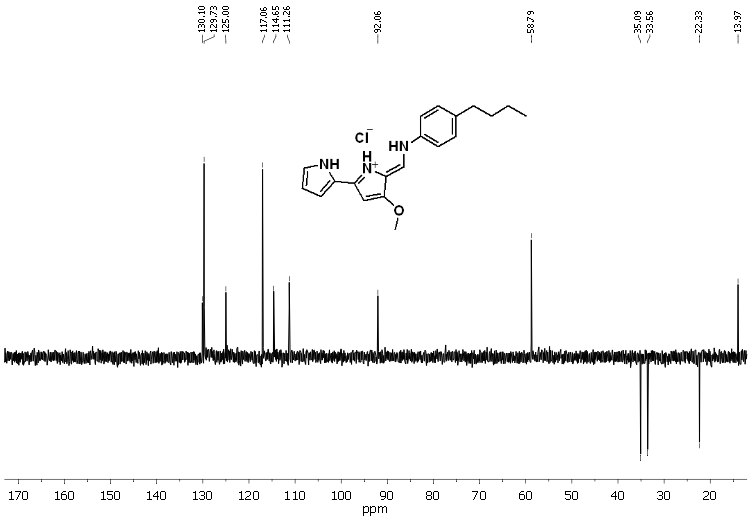
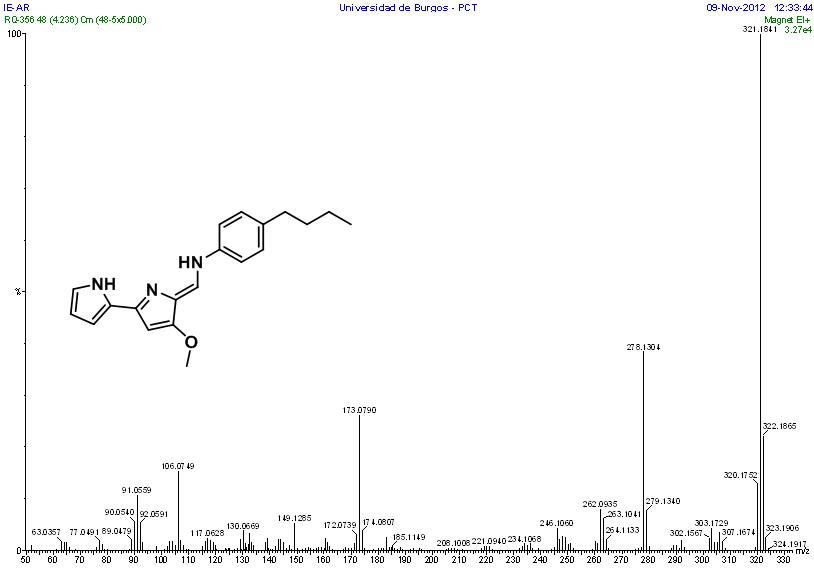


Figure S13. 1H NMR (CDCl3) of compound **4**. HCl.

 Figure S14. 13C NMR (CDCl3) of compound **4**. HCl.

 Figure S15. DEPT 13C NMR (CDCl3) of compound **4**. HCl.

Figure S16. HRMS (EI) of compound **4**.

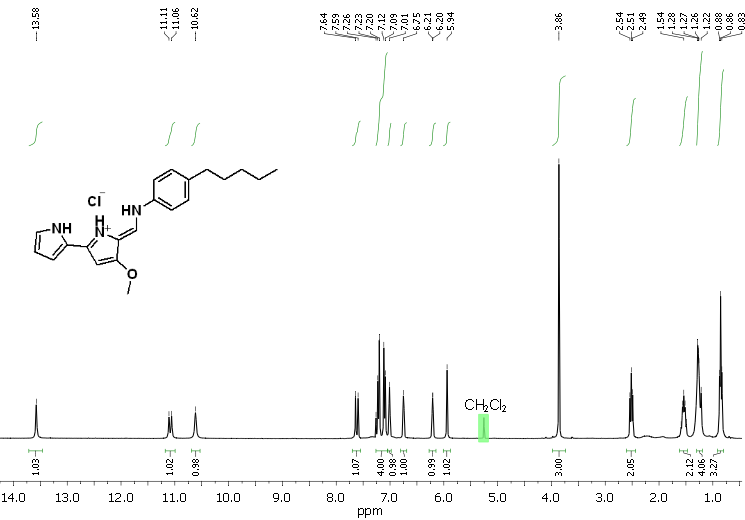


Figure S17. 1H NMR (CDCl3) of compound **6**. HCl.

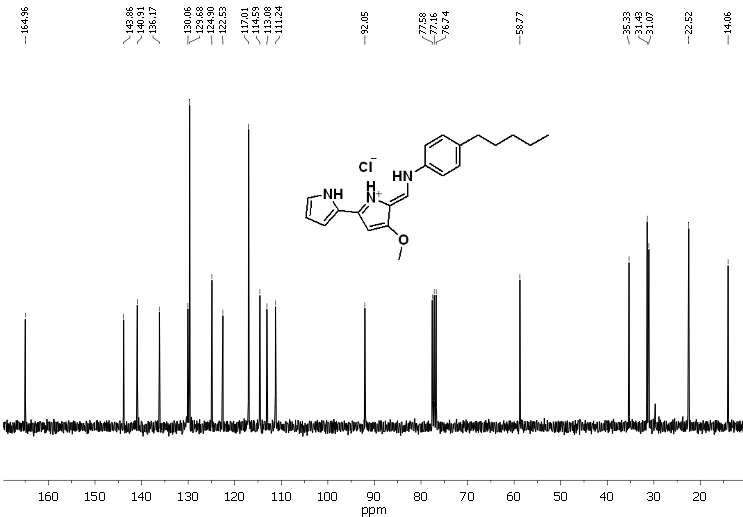


Figure S18. 13C NMR (CDCl3) of compound **6**. HCl.

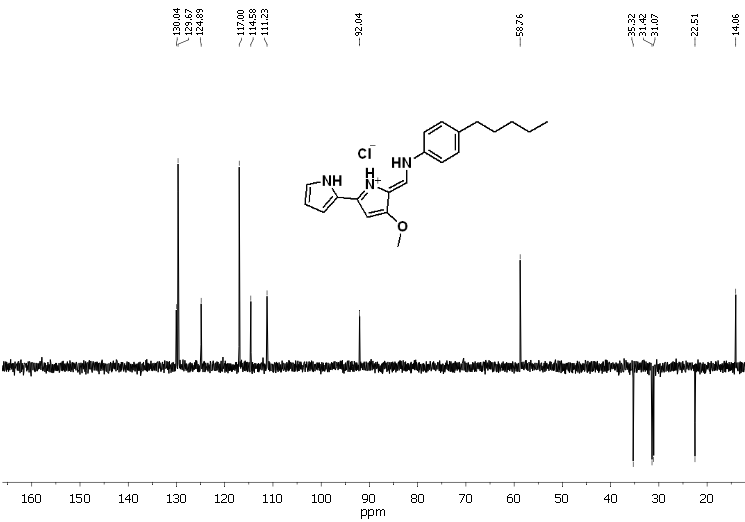
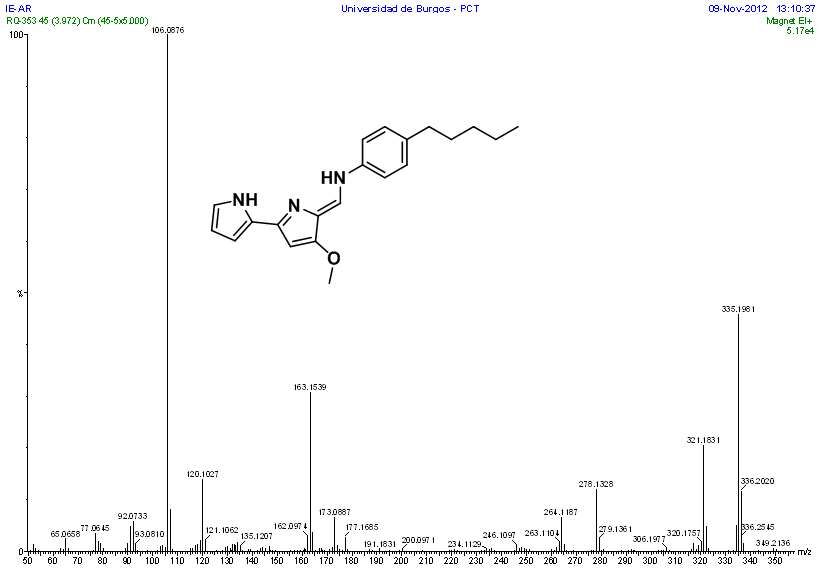
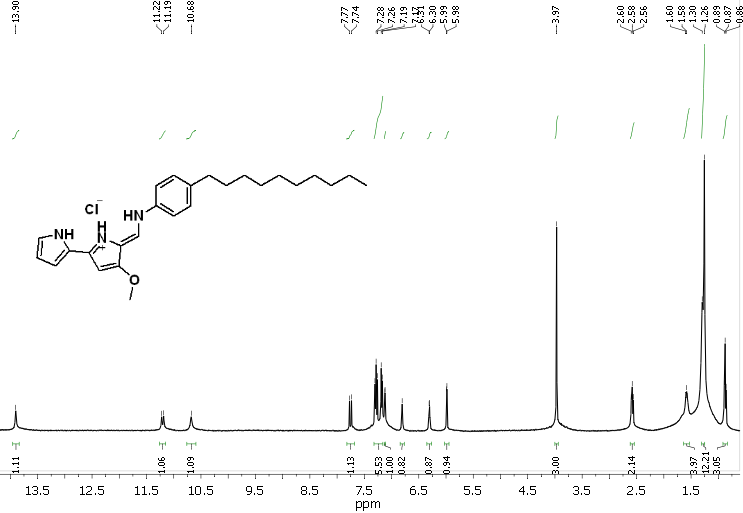
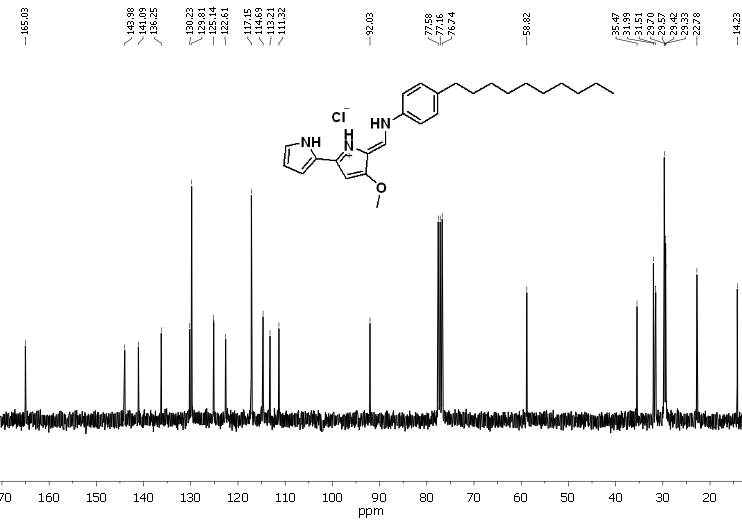
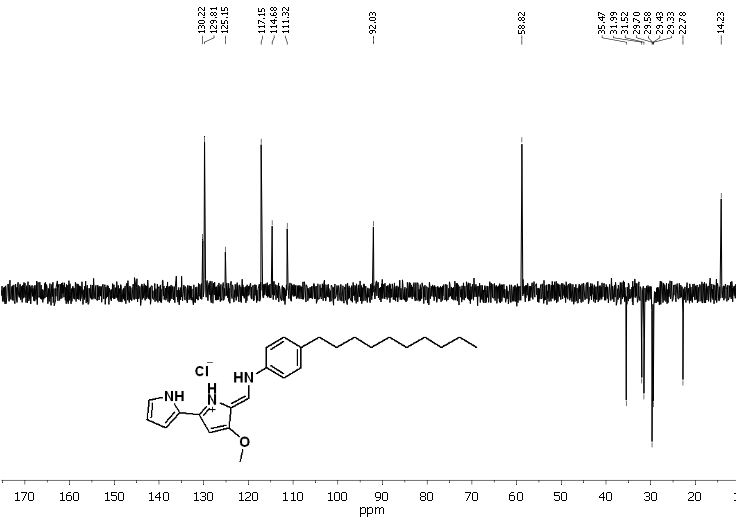


Figure S19. DEPT 13C NMR (CDCl3) of compound **6**. HCl.

Figure S20. HRMS (EI) of compound **6**.

Figure S21. 1H NMR (CDCl3) of compound **7**. HCl.

 Figure S22. 13C NMR (CDCl3) of compound **7**. HCl.

 Figure S23. DEPT 13C NMR (CDCl3) of compound **7**. HCl.

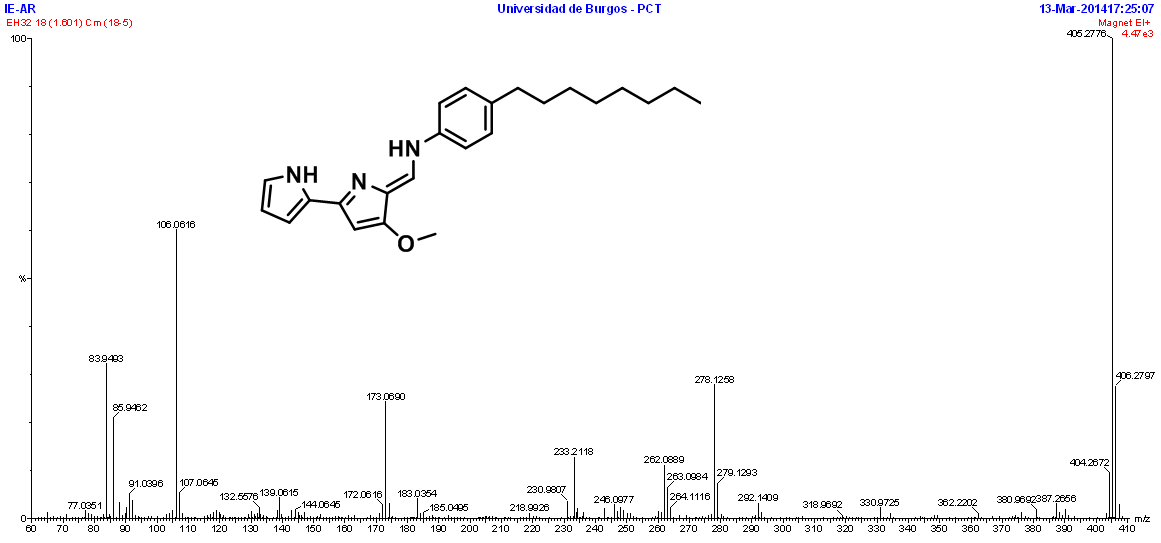
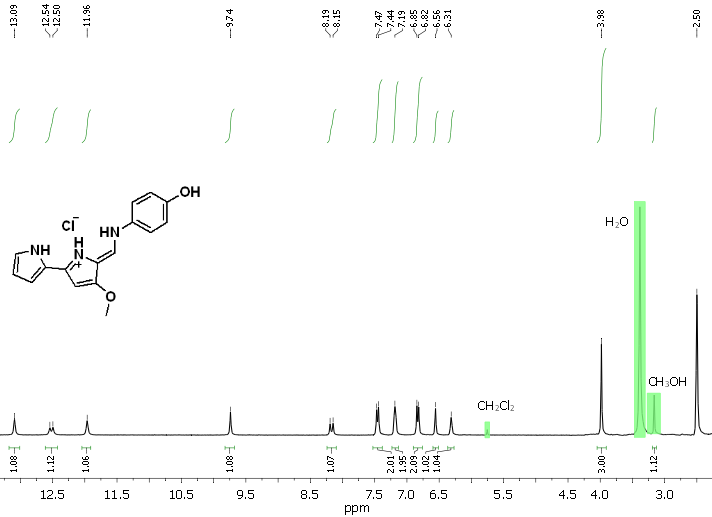
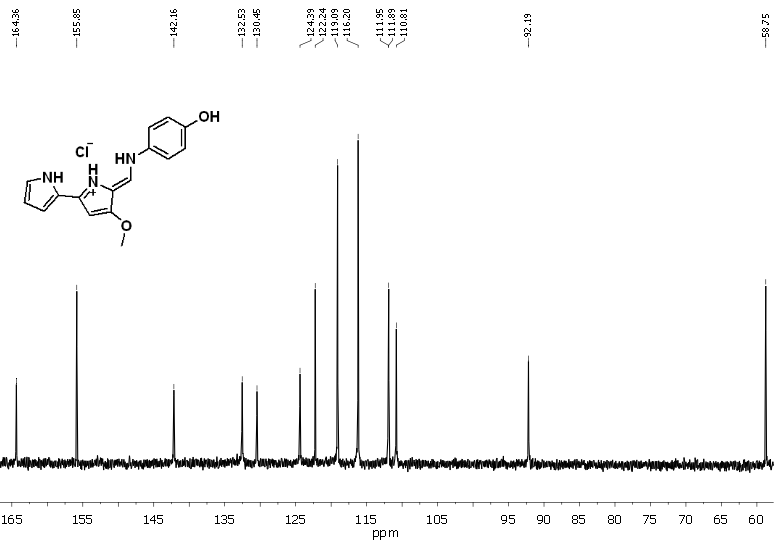
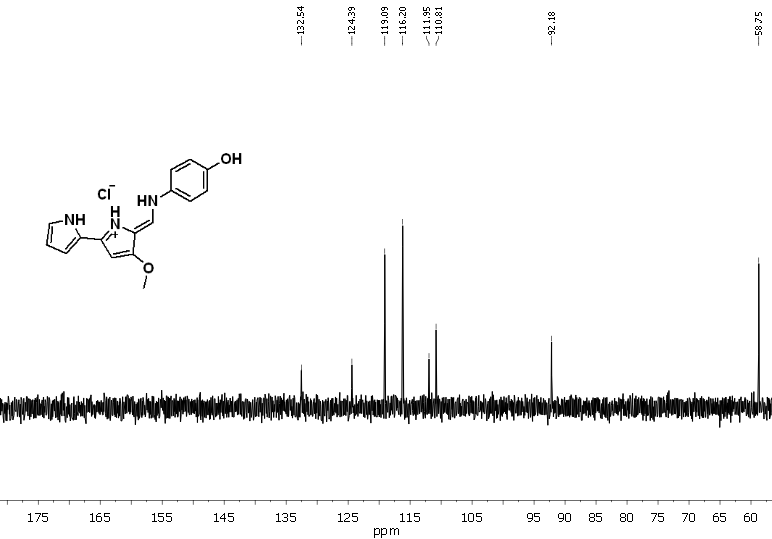
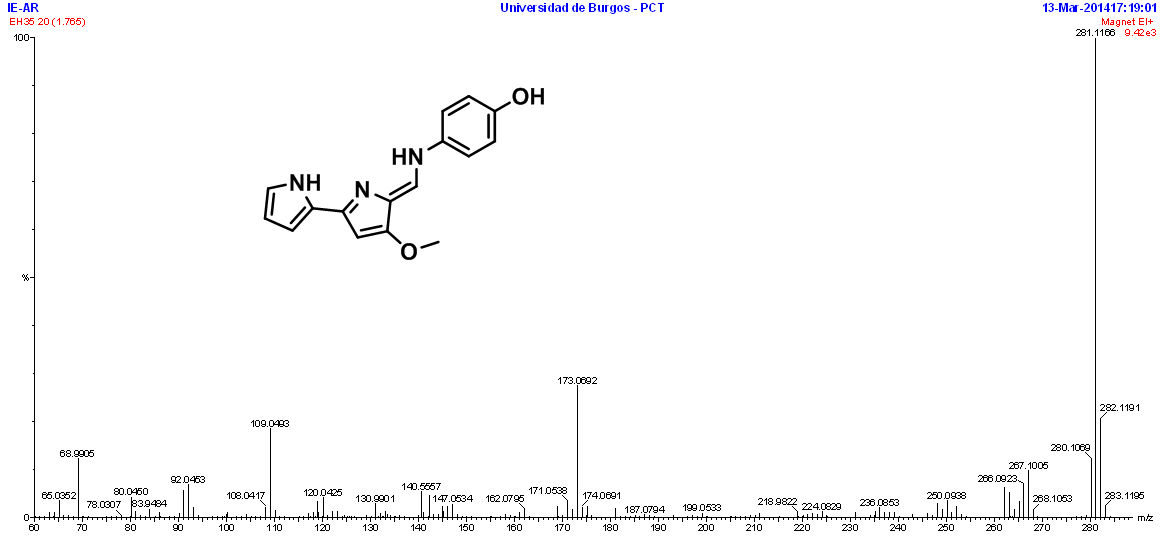


Figure S24. HRMS (EI) of compound **7**.

 Figure S25. 1H NMR (DMSO-*d6*) of compound **8**. HCl.

Figure S26. 13C NMR (DMSO-*d6*) of compound **8**. HCl.

Figure S27. DEPT 13C NMR (DMSO-*d6*) of compound **8**. HCl.

Figure S28. HRMS (EI) of compound **8**.

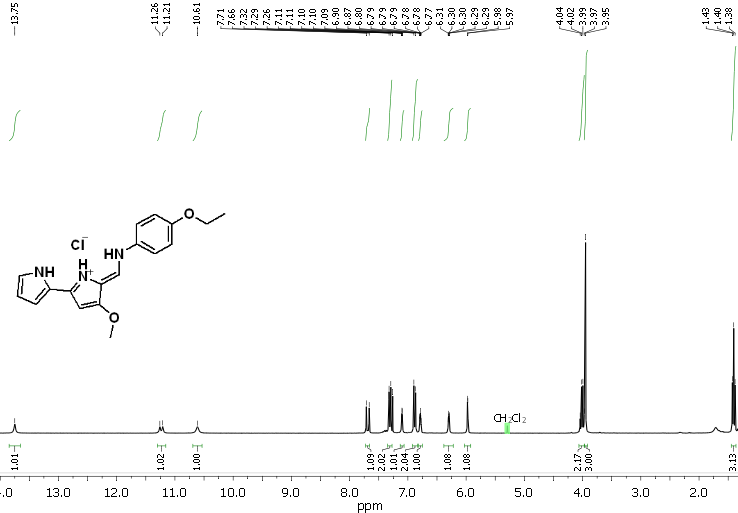
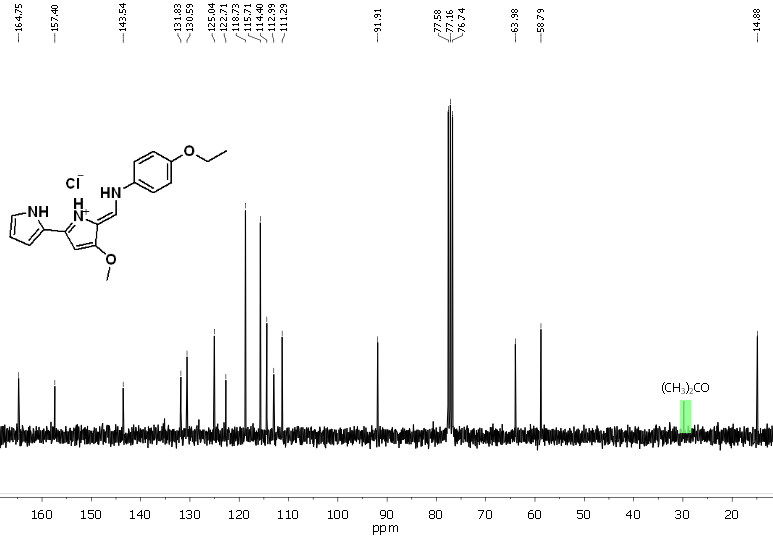
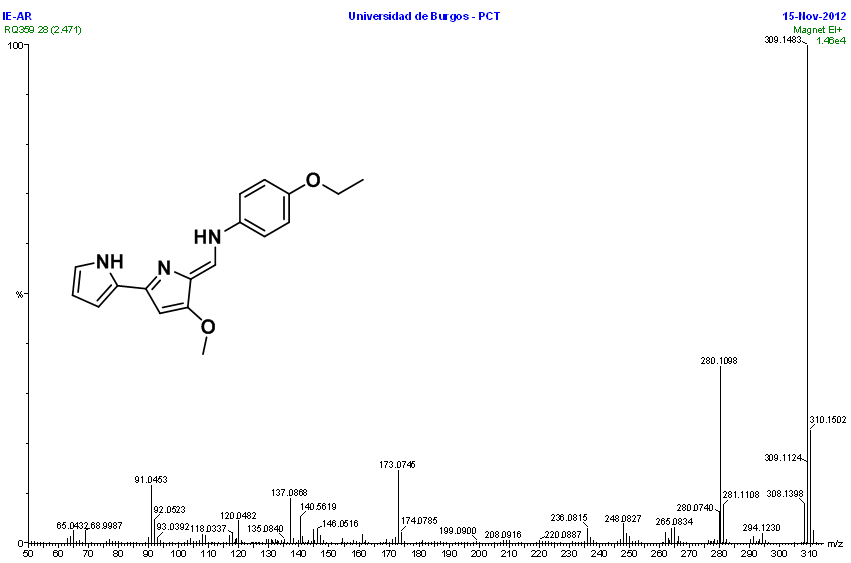


Figure S29. 1H NMR (CDCl3) of compound **10**. HCl.

Figure S30. 13C NMR (CDCl3) of compound **10**. HCl.

Figure S31. HRMS (EI) of compound **10**.

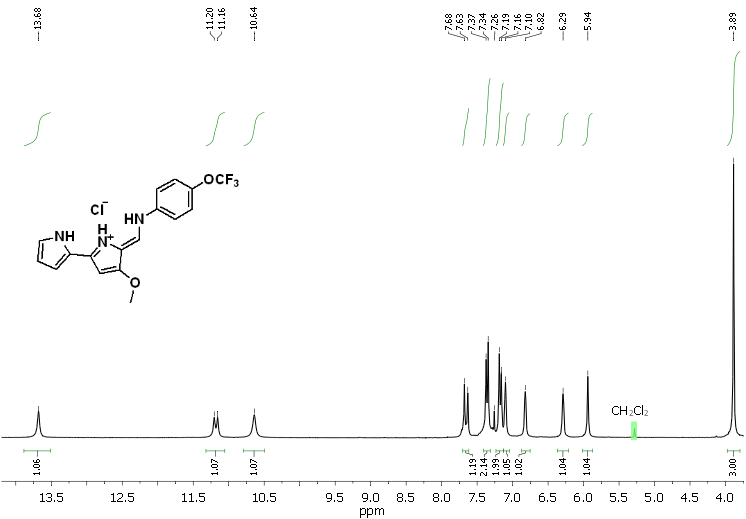


Figure S32. 1H NMR (CDCl3) of compound **11**. HCl.

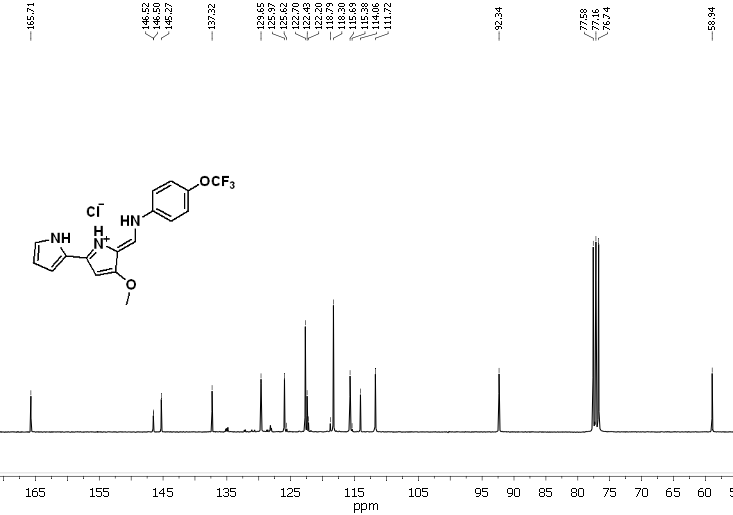
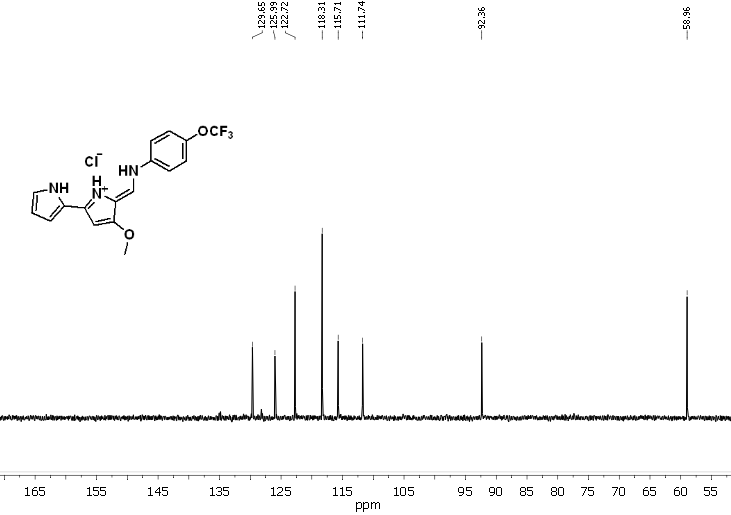


Figure S33. 13C NMR (CDCl3) of compound **11**. HCl.

Figure S34. DEPT 13C NMR (CDCl3) of compound **11**. HCl.

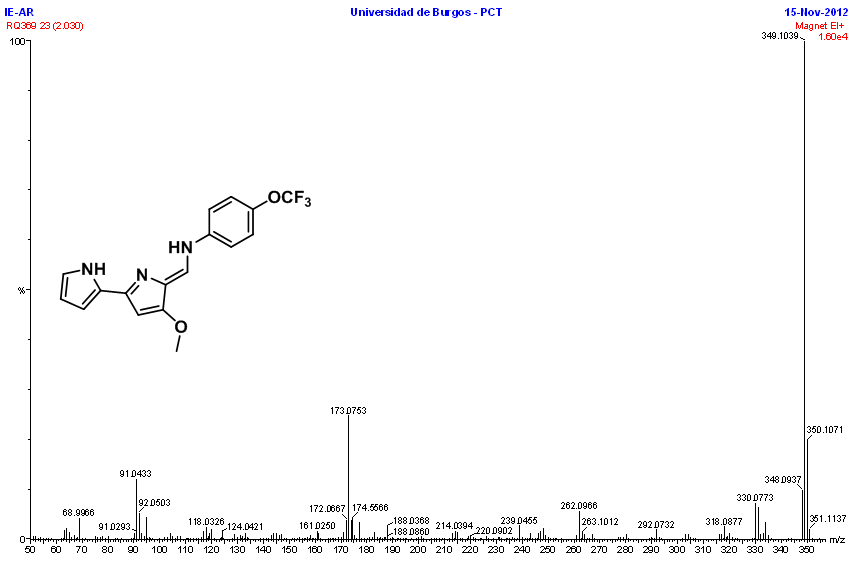


Figure S35. HRMS (EI) of compound **11**.

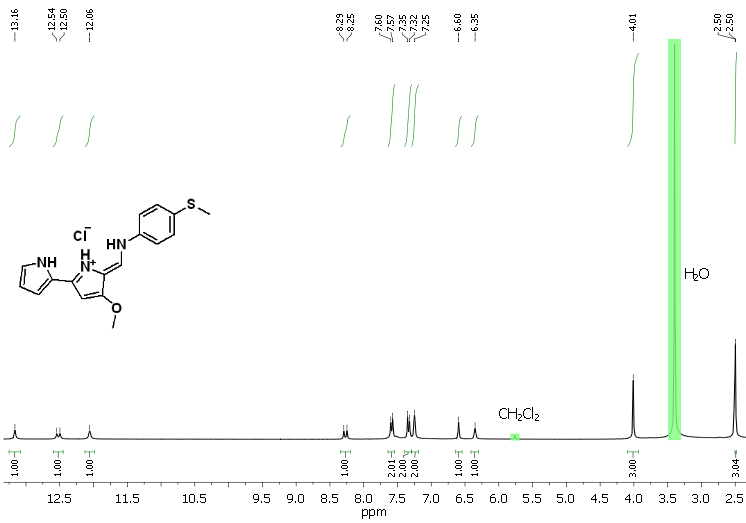
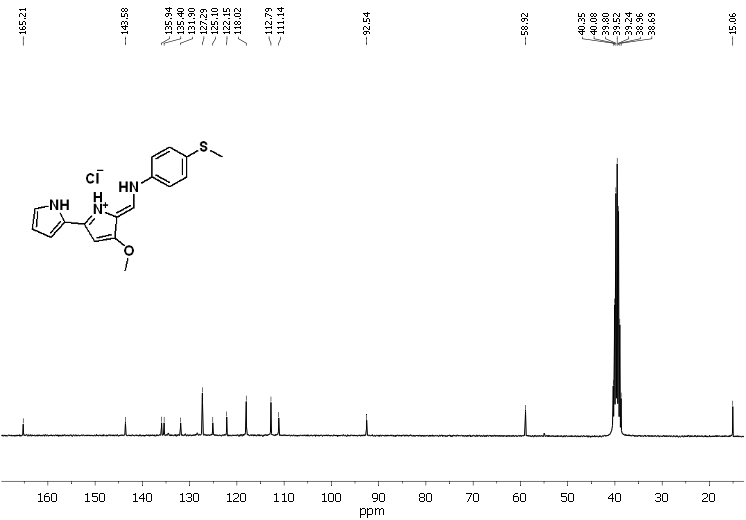


Figure S36. 1H NMR (DMSO-*d6*) of compound **12**. HCl.

 Figure S37. 13C NMR (DMSO-*d6*) of compound **12**. HCl.

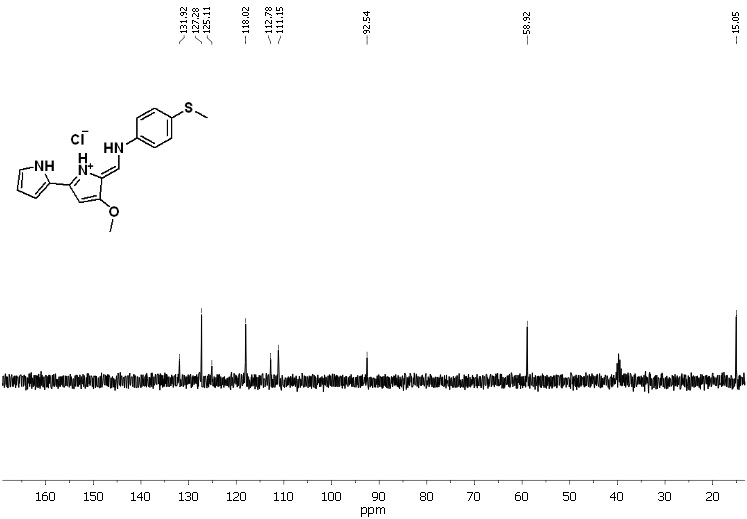
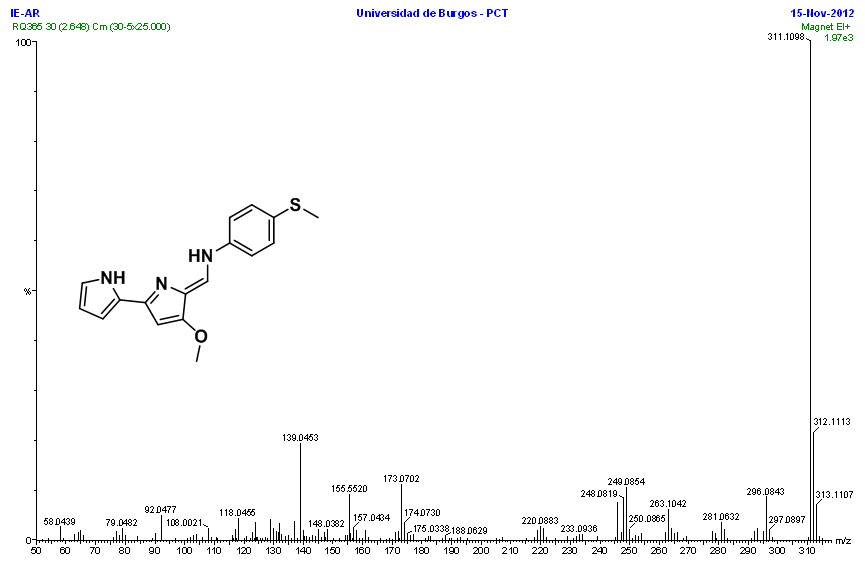


Figure S38. DEPT 13C NMR (DMSO-*d6*) of compound **12**. HCl.

Figure S39. HRMS (EI) of compound **12**.

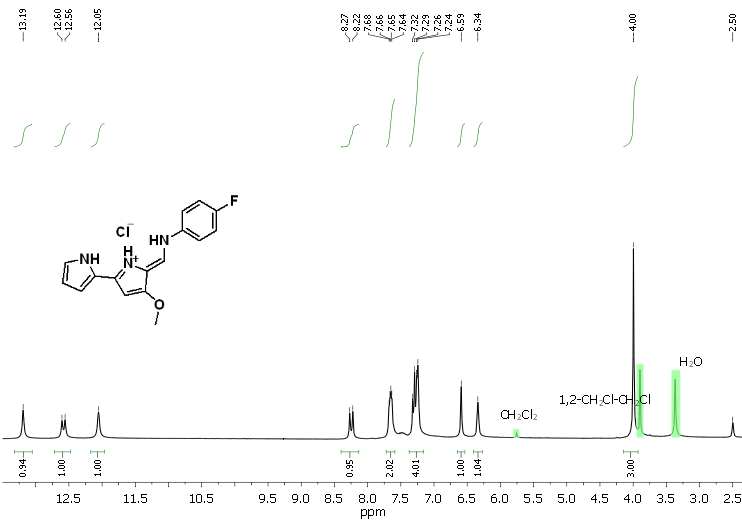
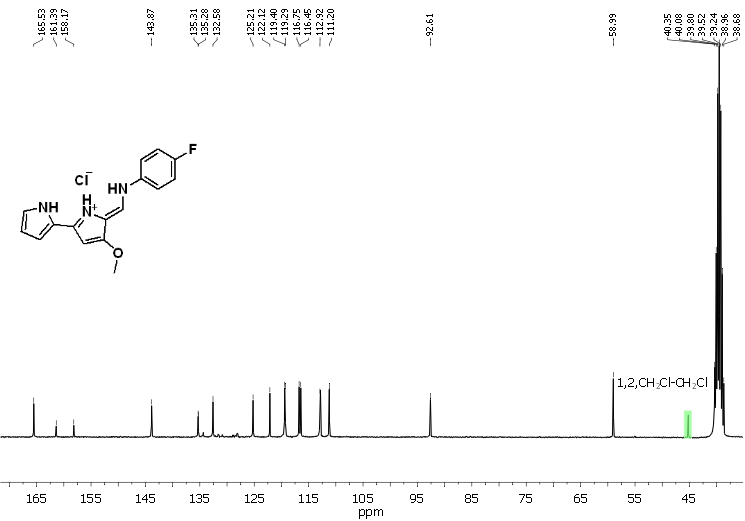


Figure S40. 1H NMR (DMSO-*d6*) of compound **13**. HCl.

Figure S41. 13C NMR (DMSO-*d6*) of compound **13**. HCl.

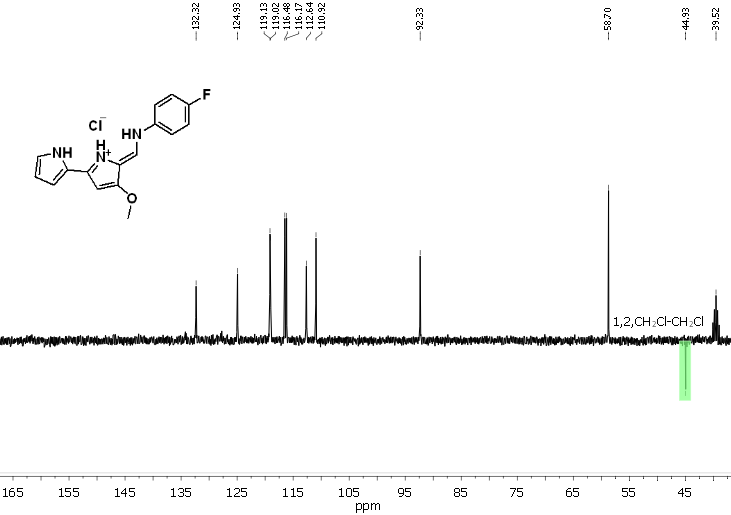
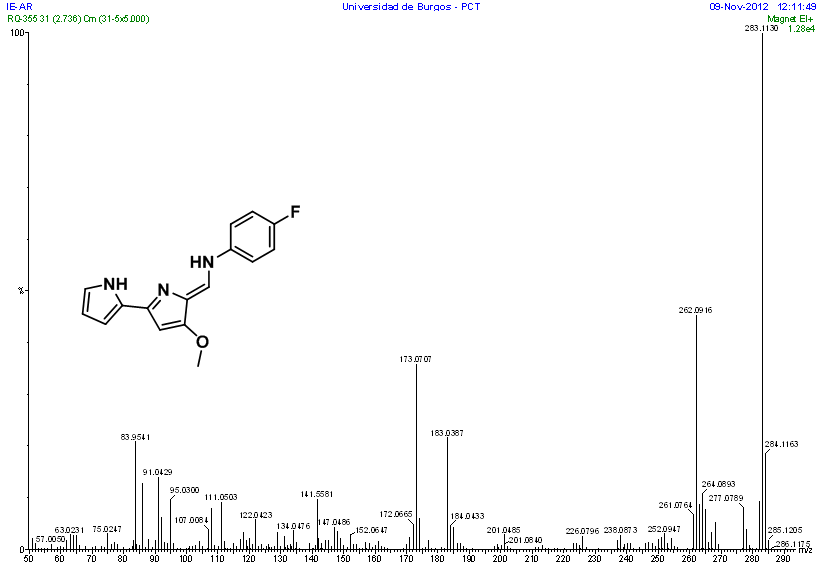
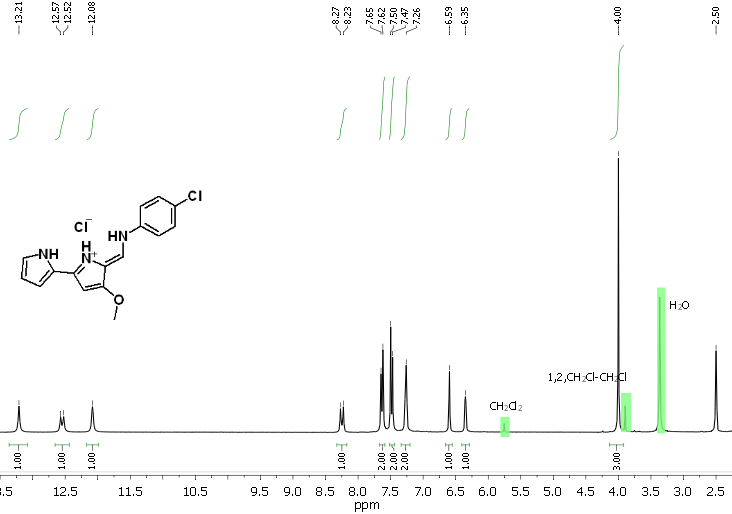
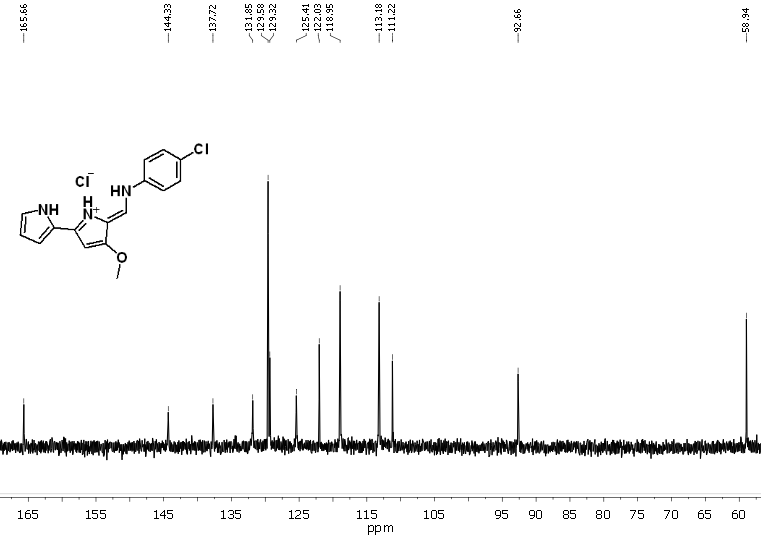
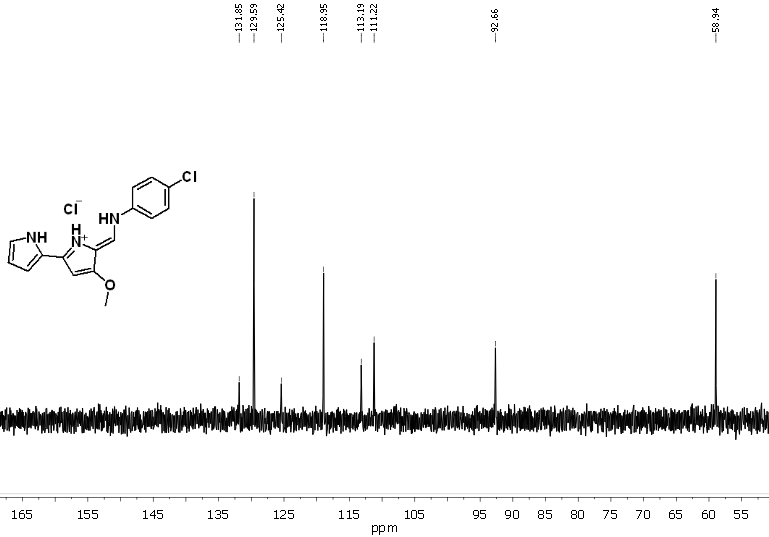


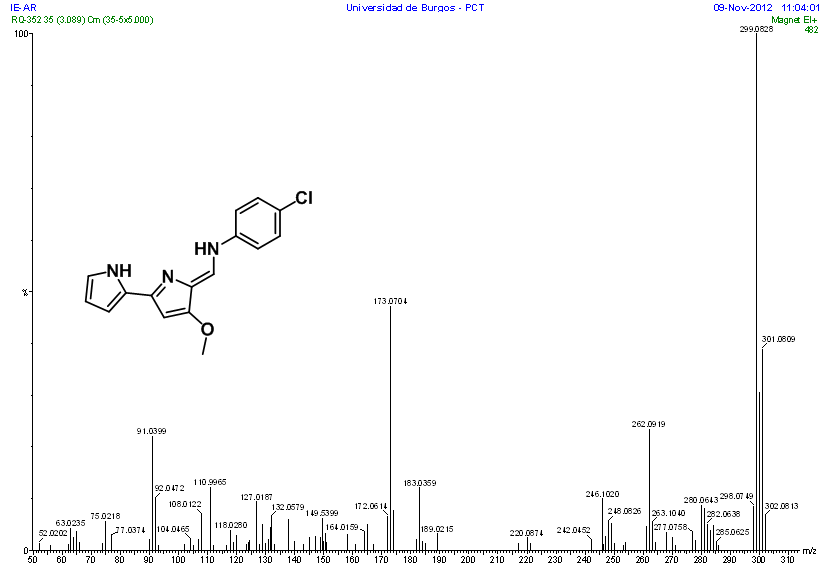
Figure S42. DEPT 13C NMR (DMSO-*d6*) of compound **13**. HCl.

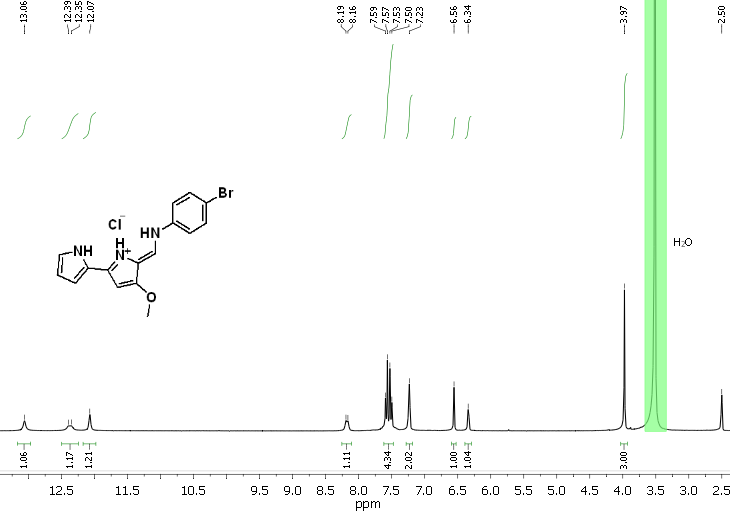
Figure S43. HRMS (EI) of compound **13**.

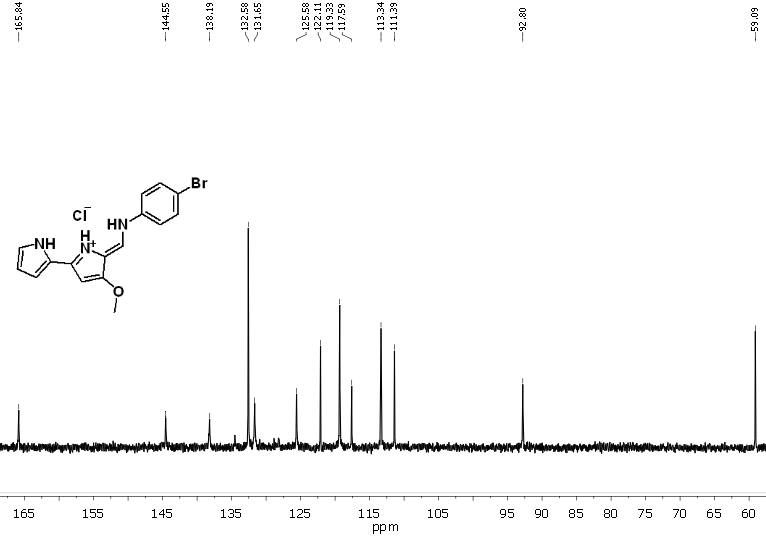
Figure S44. 1H NMR (DMSO-*d6*) of compound **14**. HCl.

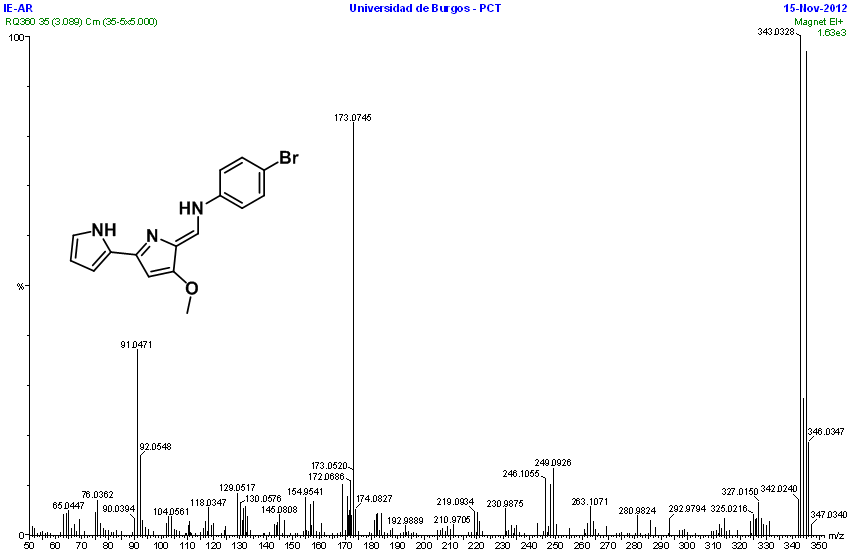
Figure S43. 13C NMR (DMSO-*d6*) of compound **14**. HCl.

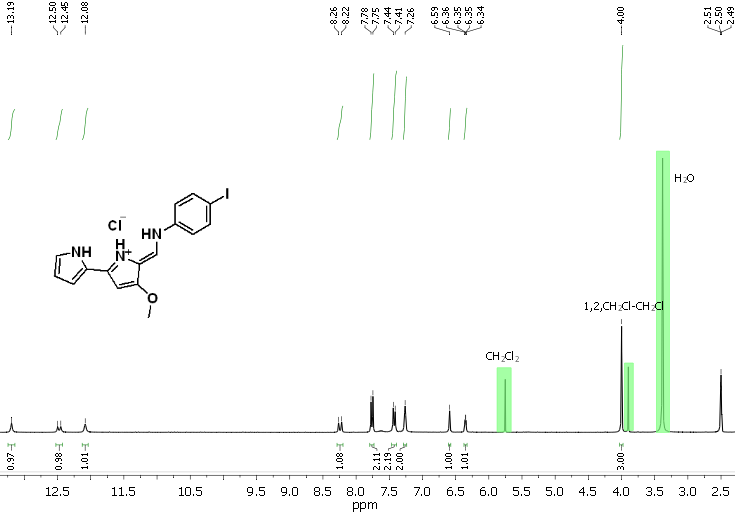
Figure S45. DEPT 13C NMR (DMSO-*d6*) of compound **14**. HCl.

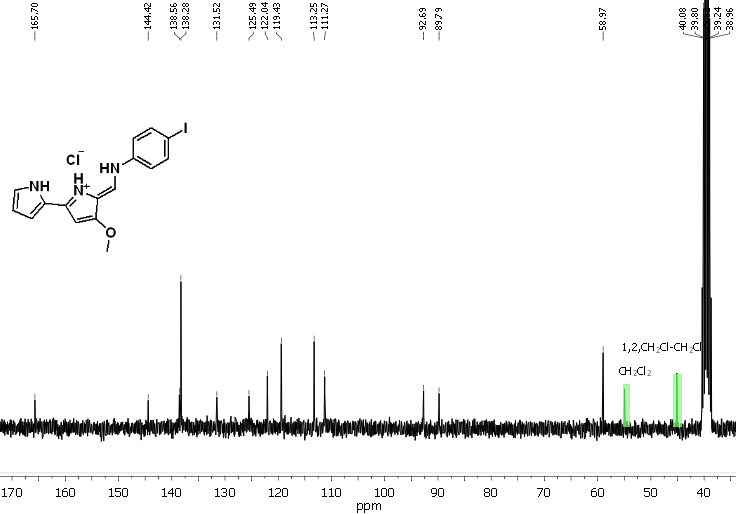
Figure S46. HRMS (EI) of compound **14**.

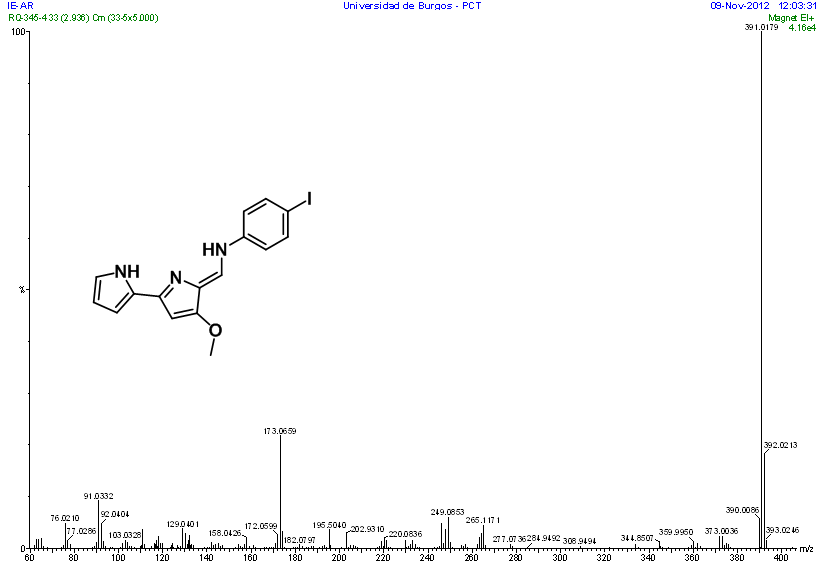
Figure S47. 1H NMR (DMSO-*d6*) of compound **15**. HCl.

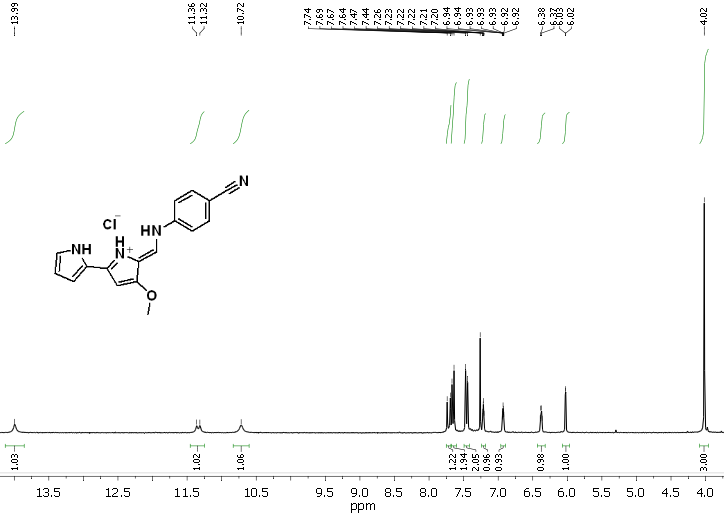
Figure S48. 13C NMR (DMSO-*d6*) of compound **15**. HCl.

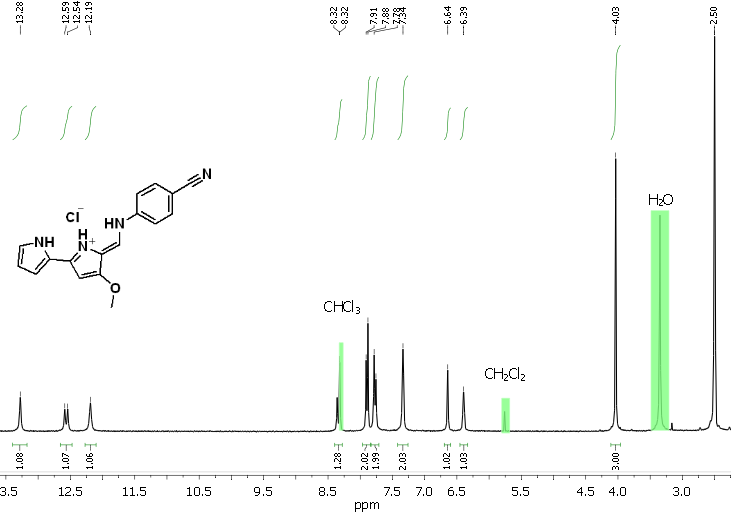
Figure S49. HRMS (EI) of compound **15**.

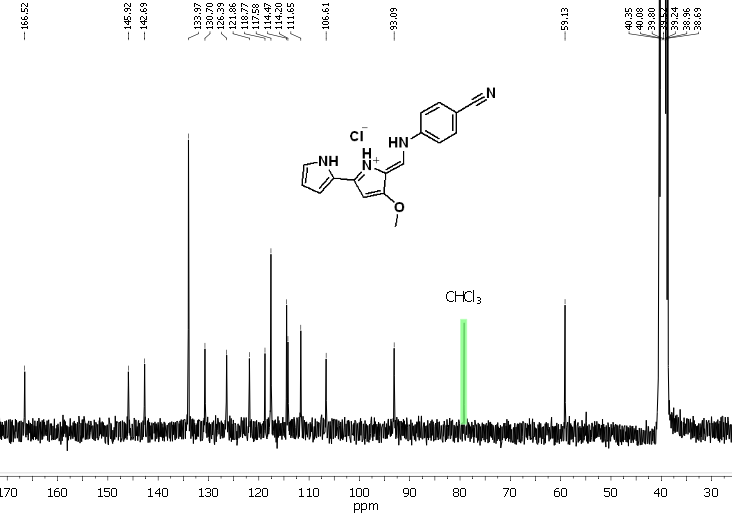
Figure S50. 1H NMR (DMSO-*d6*) of compound **16**. HCl.

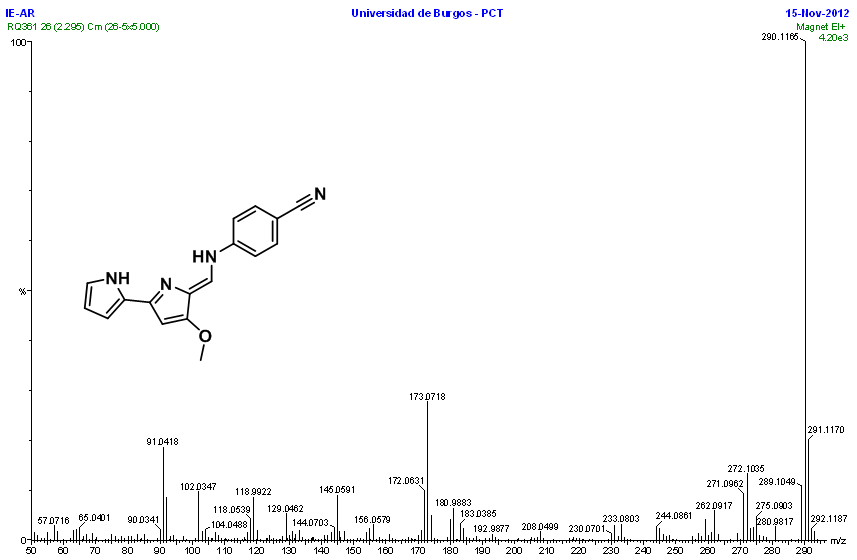
Figure S51. 13C NMR (DMSO-*d6*) of compound **16**. HCl.

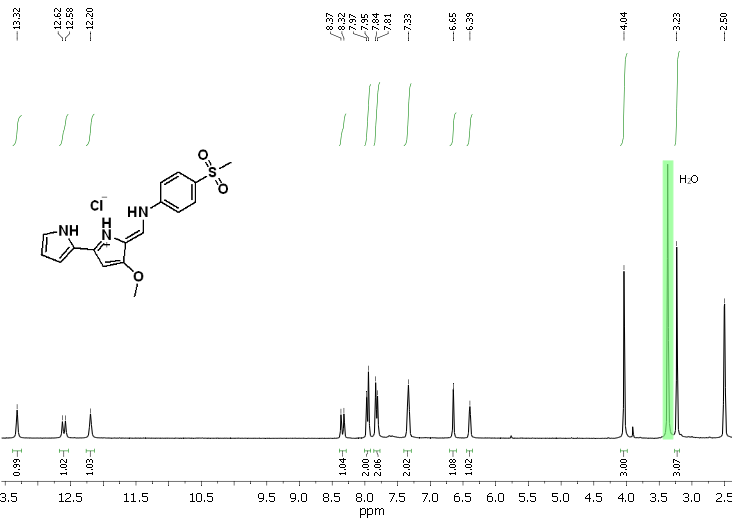
Figure S52. HRMS (EI) of compound **16**.

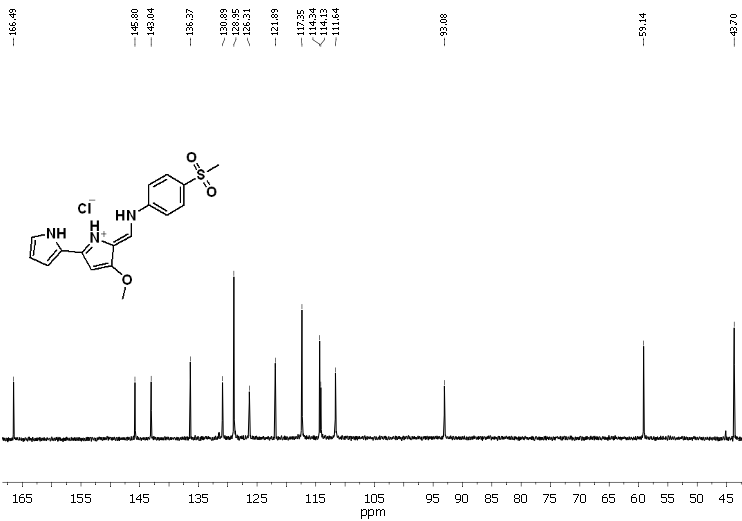
 Figure S53. 1H NMR (CDCl3) of compound **17**. HCl.

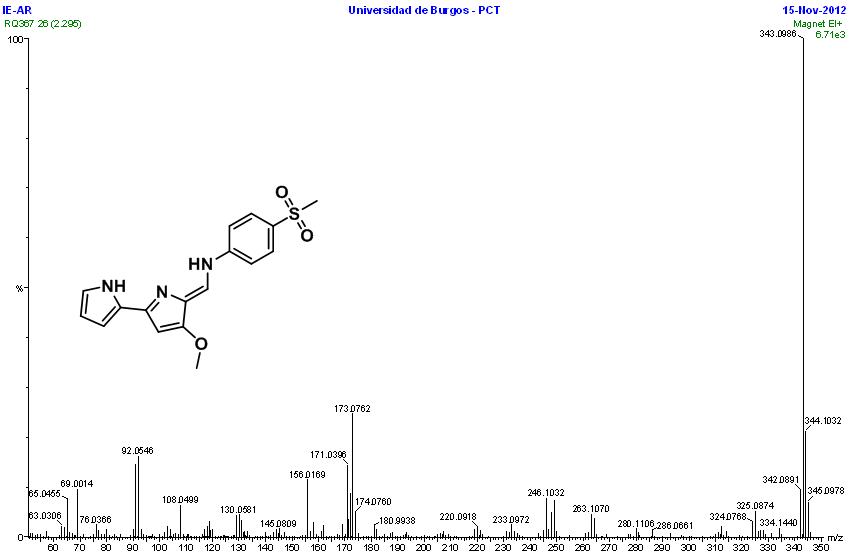
 Figure S54. 1H NMR (DMSO-*d6*) of compound **17**. HCl.

 Figure S55. 13C NMR (DMSO-*d6*) of compound **17**. HCl.

Figure S56. HRMS (EI) of compound **17**.

Figure S57. 1H NMR (DMSO-*d6*) of compound **18**. HCl.

Figure S58. 13C NMR (DMSO-*d6*) of compound **18**. HCl.

Figure S59. HRMS (EI) of compound **18**.

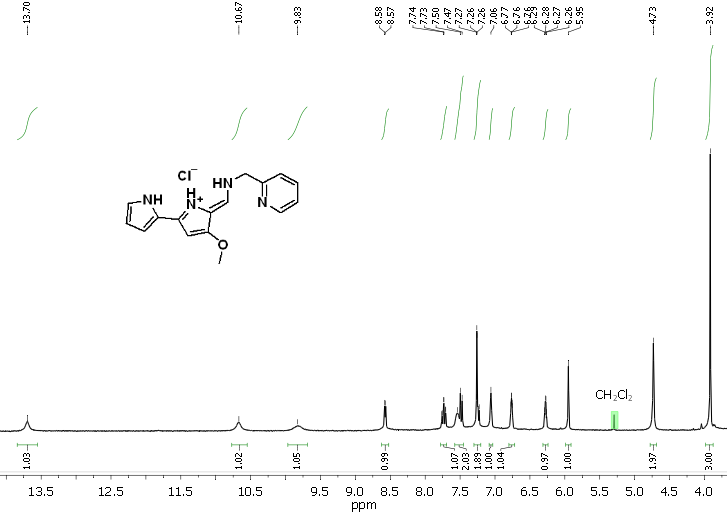


Figure S60. 1H NMR (CDCl3) of compound **19**. HCl.

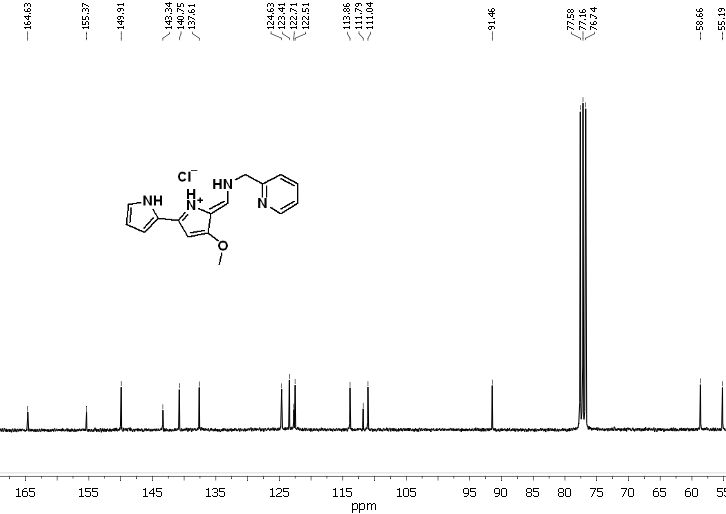


Figure S61. 13C NMR (CDCl3) of compound **19**. HCl.

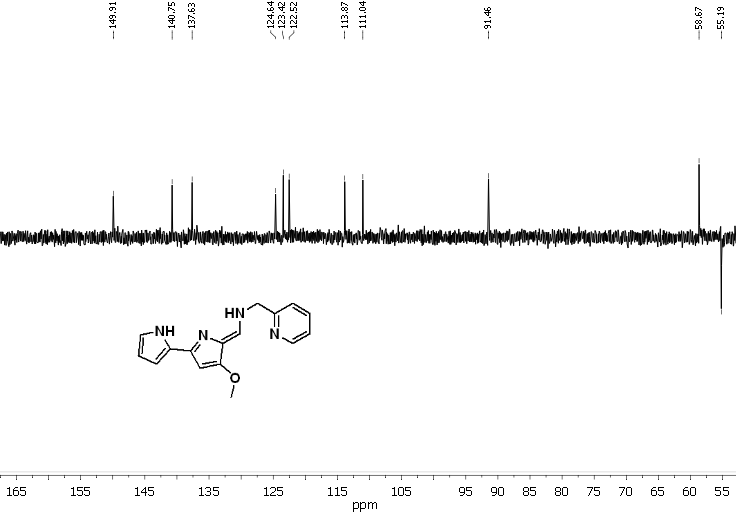


Figure S62. DEPT 13C NMR (CDCl3) of compound **19**. HCl.

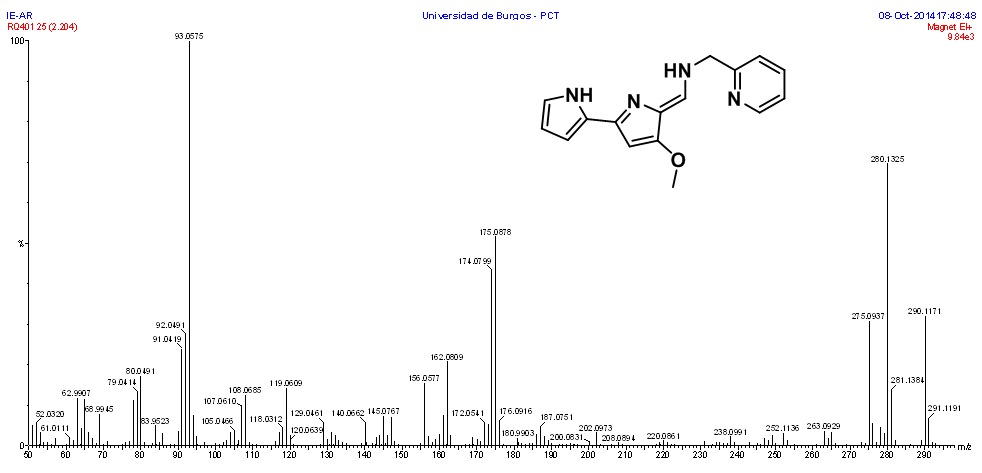


Figure S63. HRMS (EI) of compound **19**.

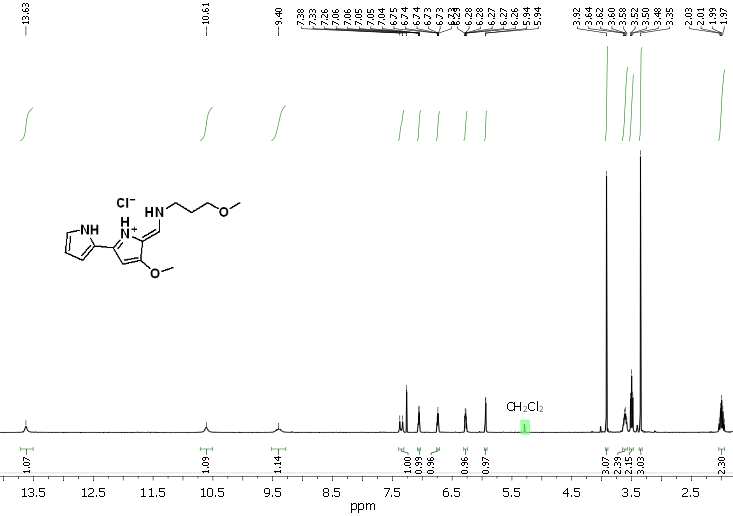


Figure S64. 1H NMR (CDCl3) of compound **33**. HCl.

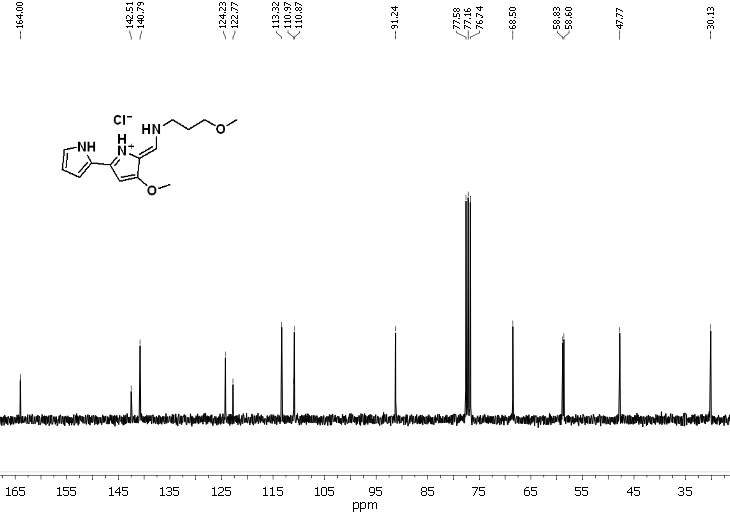


Figure S65. 13C NMR (CDCl3) of compound **33**. HCl.

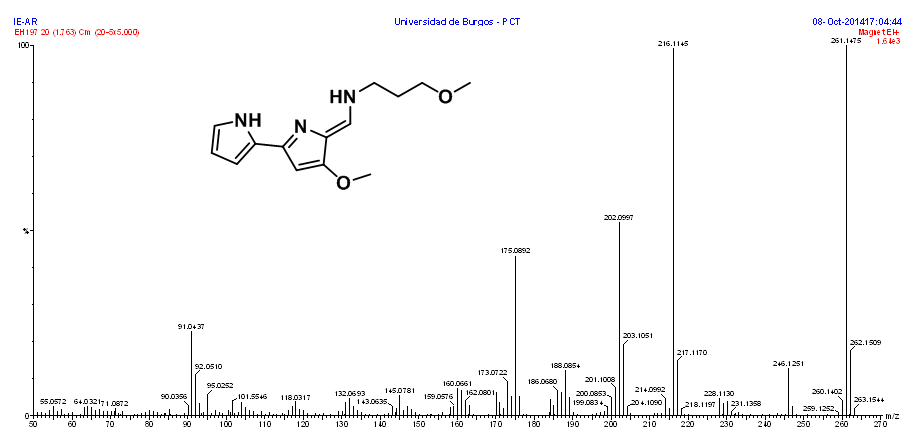


Figure S66. HRMS (EI) of compound **33**.

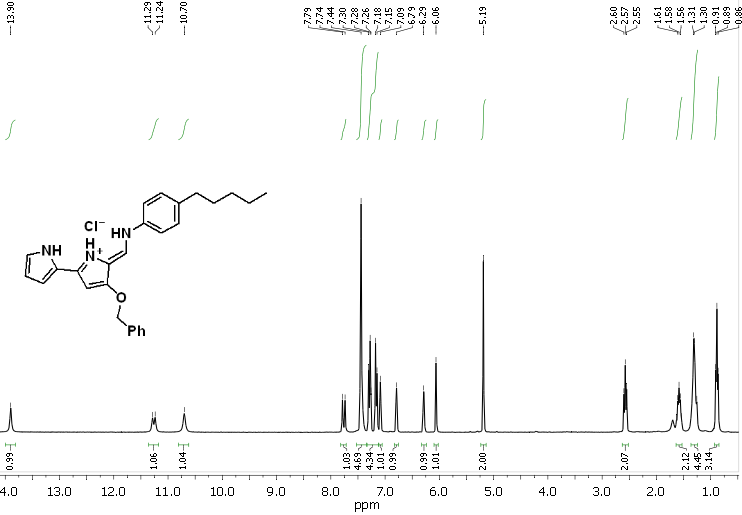


Figure S67. 1H NMR (CDCl3) of compound **36**. HCl.

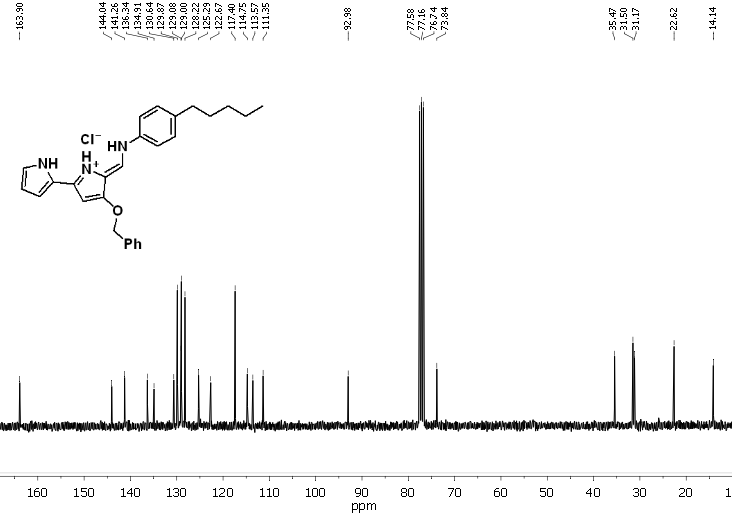


Figure S68. 13C NMR (CDCl3) of compound **36**. HCl.

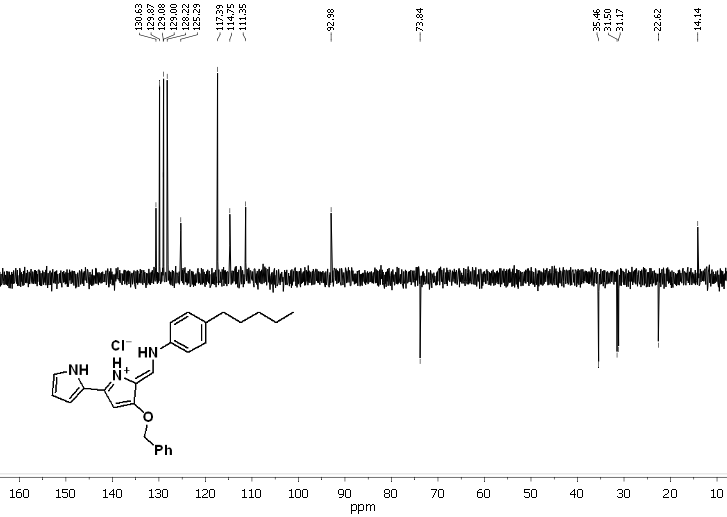


Figure S69. DEPT 13C NMR (CDCl3) of compound **36**. HCl.

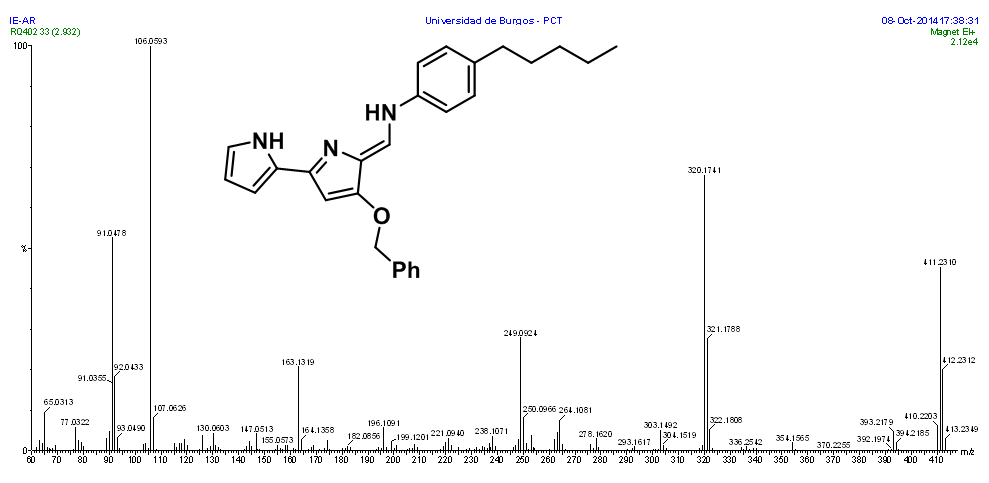


Figure S70. HRMS (EI) of compound **36**.

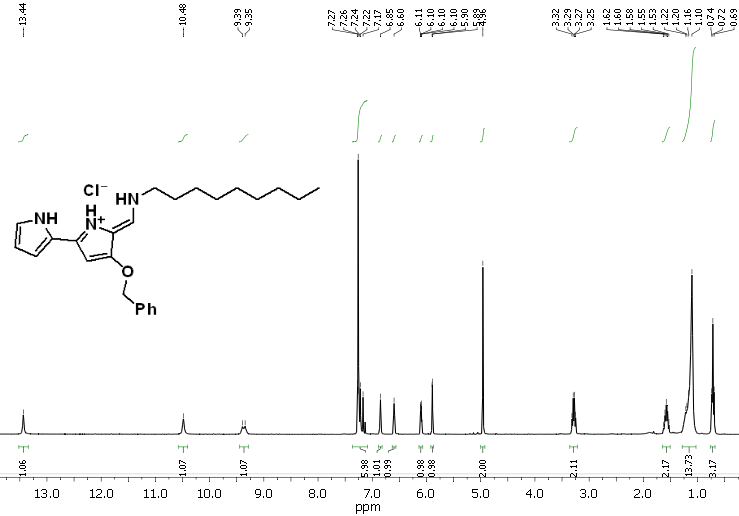


Figure S71. 1H NMR (CDCl3) of compound **41**. HCl.

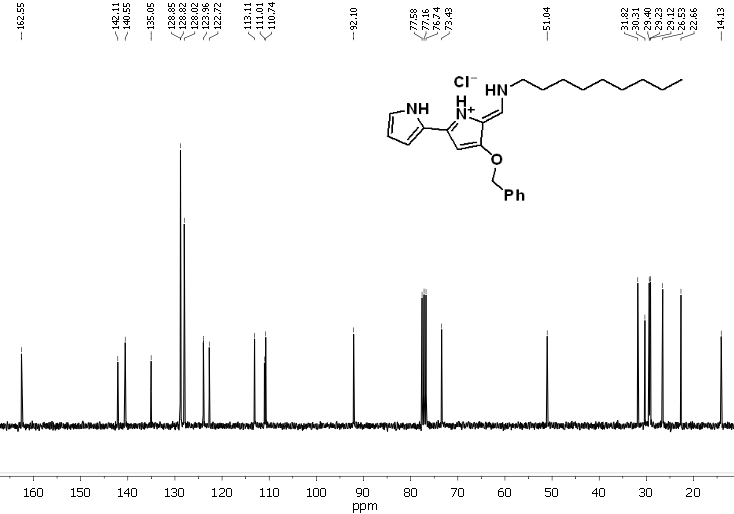


Figure S72. 13C NMR (CDCl3) of compound **41**. HCl.

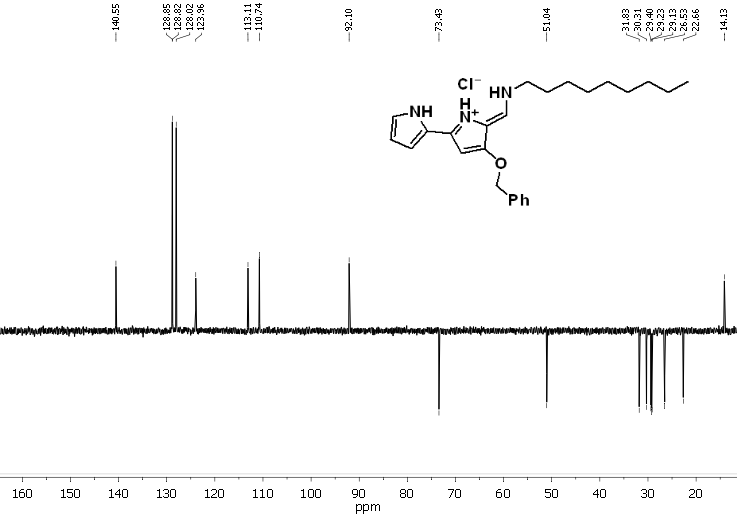


Figure S73. DEPT 13C NMR (CDCl3) of compound **41**. HCl.

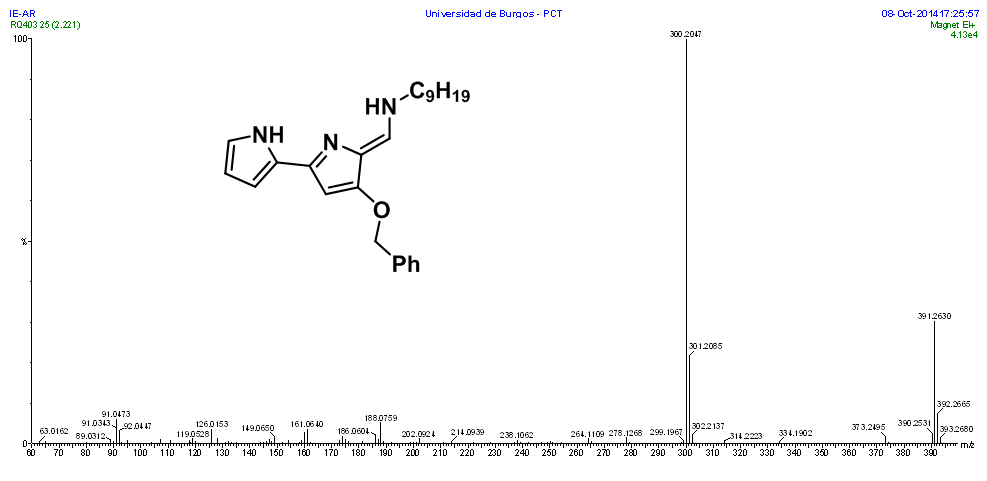


Figure S74. HRMS (EI) of compound **41**.

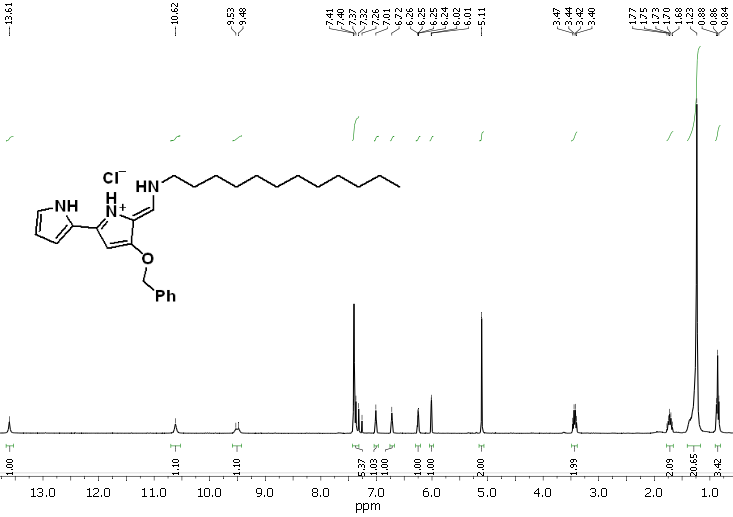


Figure S75. 1H NMR (CDCl3) of compound **43**. HCl.

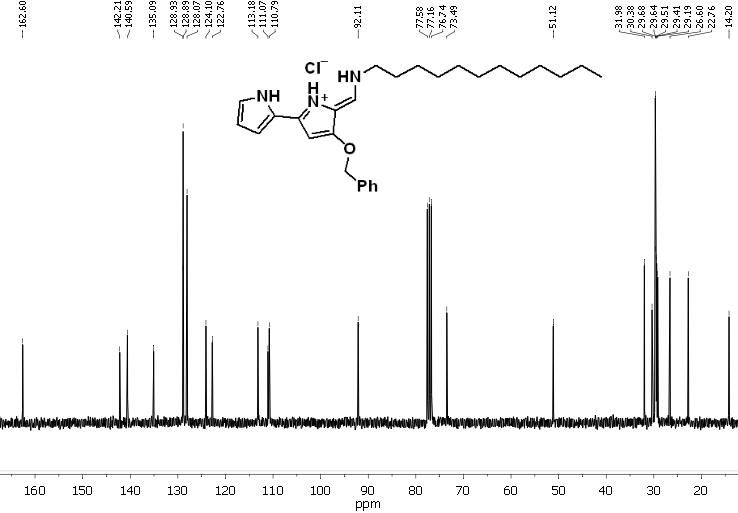


Figure S76. 13 CNMR (CDCl3) of compound **43**. HCl.

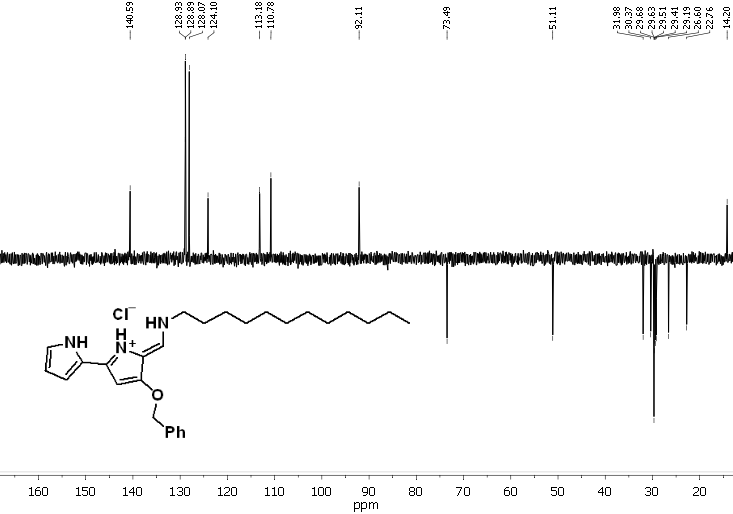


Figure S77. DEPT 13 CNMR (CDCl3) of compound **43**. HCl.

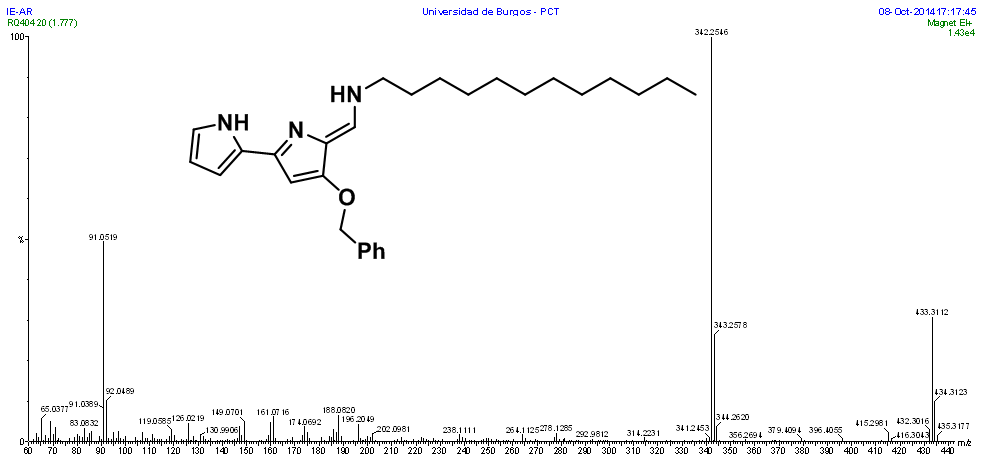


Figure S78. HRMS (EI) of compound **43**.

1. a) K. Dairi, S. Tripathy, G. Attardo and J.–F. Lavallee, *Tetrahedron Lett*., 2006, **47**, 2605–2606; b) P. Iglesias Hernández, D. Moreno, A. Araujo Javier, T. Torroba, R. Pérez-Tomás, R. Quesada, *Chem. Commun.*, 2012, **48**, 1556-1558 [↑](#footnote-ref-1)
2. E. Hernando, V. Soto-Cerrato, S. Cortés-Arroyo, R. Pérez-Tomás and R. Quesada, ***Org. Biomol. Chem.***, 2014, **12**, 1771–1778 [↑](#footnote-ref-2)
3. [V. Saggiomo](http://pubs.rsc.org/en/results?searchtext=Author%3AVittorio%20Saggiomo), [S. Otto](http://pubs.rsc.org/en/results?searchtext=Author%3ASijbren%20Otto), [I. Marques](http://pubs.rsc.org/en/results?searchtext=Author%3AIgor%20Marques), [V. Félix](http://pubs.rsc.org/en/results?searchtext=Author%3AV%C3%ADtor%20F%C3%A9lix), [T. Torroba](http://pubs.rsc.org/en/results?searchtext=Author%3ATom%C3%A1s%20Torroba) and [R. Quesada](http://pubs.rsc.org/en/results?searchtext=Author%3ARoberto%20Quesada), ***Chem. Commun.***, 2012, **48**, 5274–5276 [↑](#footnote-ref-3)
4. D. M. Pinkerton, M. G. Banwell and A. C. Willis, *Org. Lett*., 2007, **9**, 5127–5130 [↑](#footnote-ref-4)