Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Pyrrolyl-, 2-(2-thienyl)pyrrolyl- and 2,5-bis(2-thienyl)pyrrolyl-nucleosides: Synthesis, molecular and electronic structure, and redox behaviour of C5-thymidine derivatives.

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Contents:

Cyclic voltammetry:

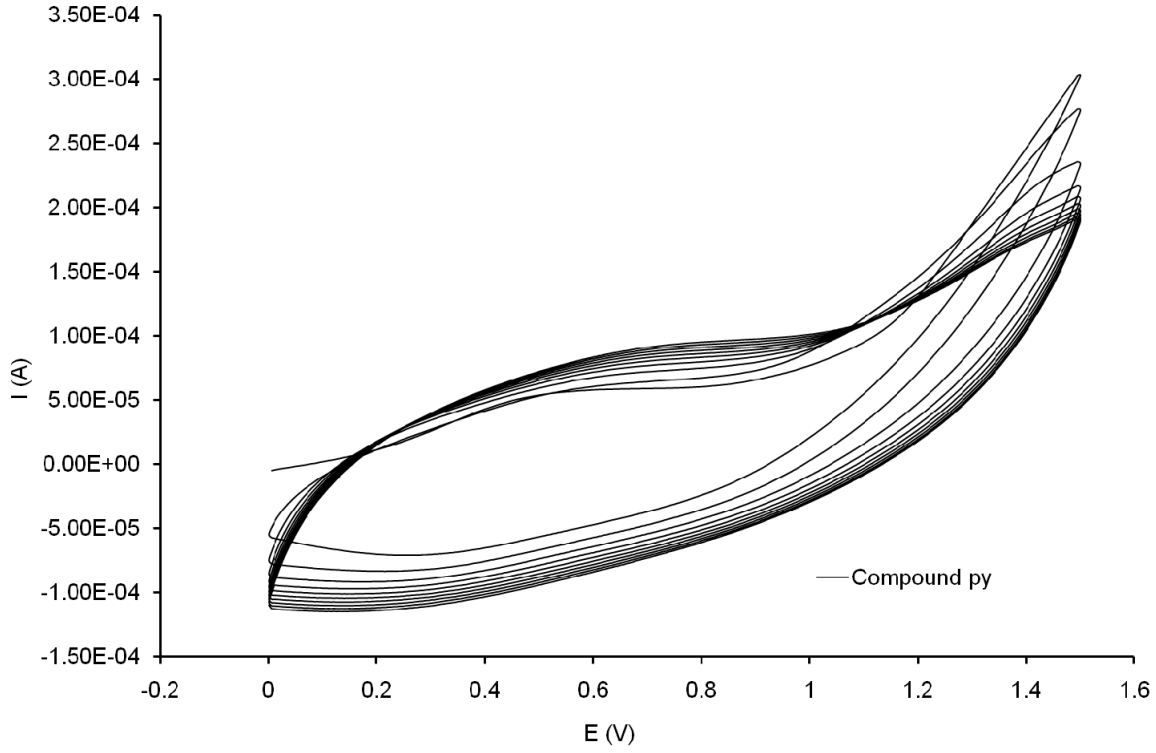


Fig. S1 CV for compound **py.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

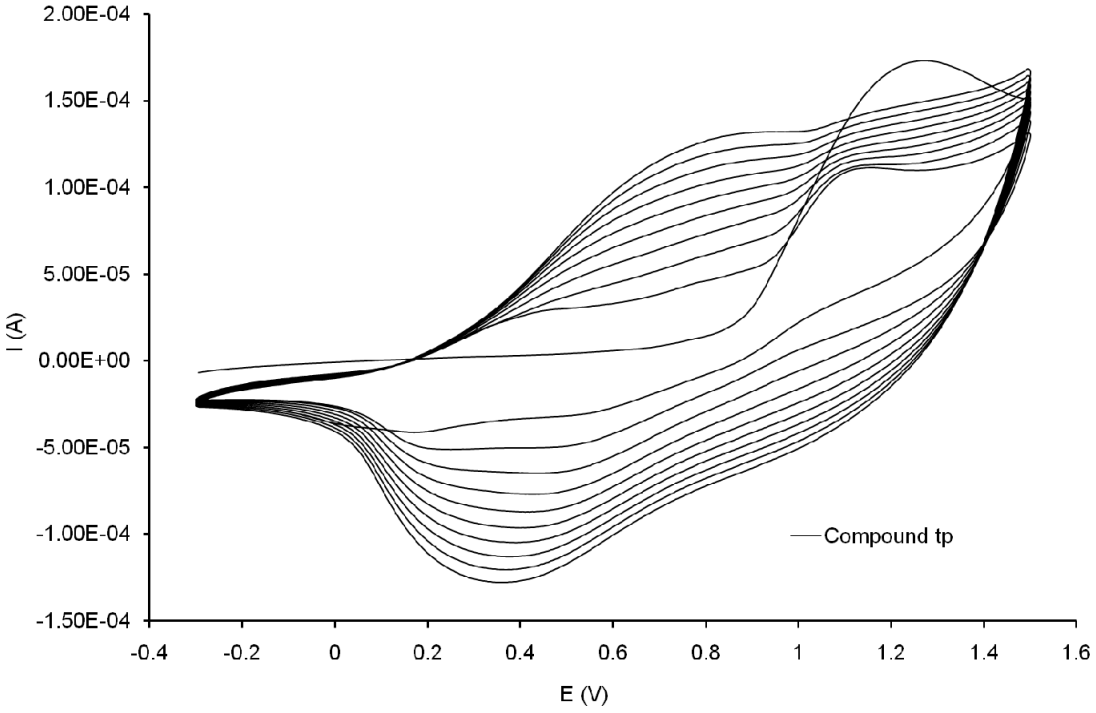


Fig. S2 CV for compound **tp.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

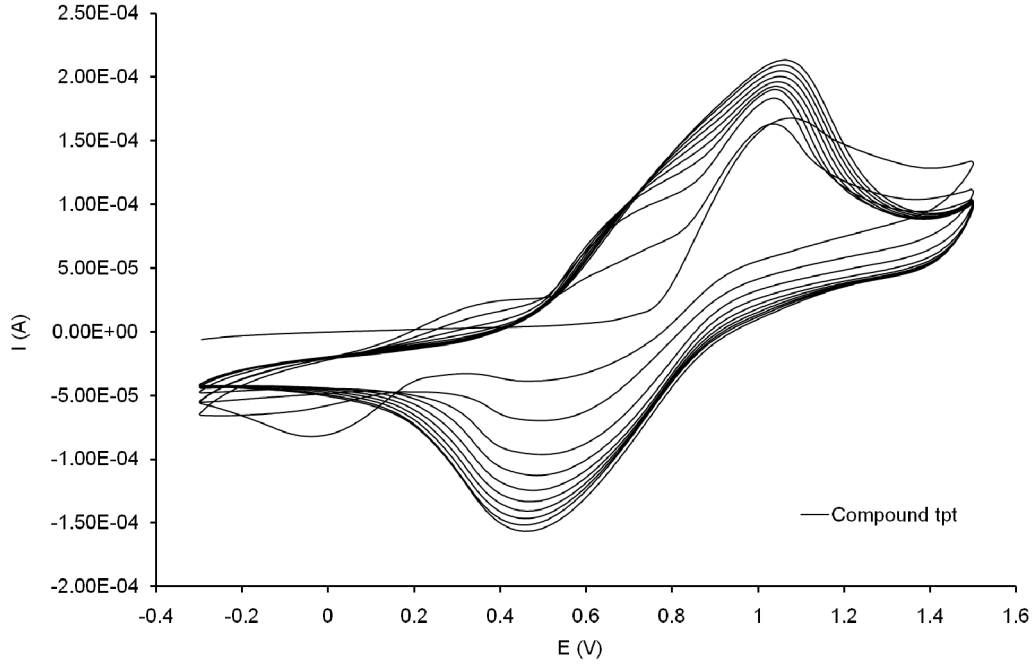


Fig. S3 CV for compound **tpt.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

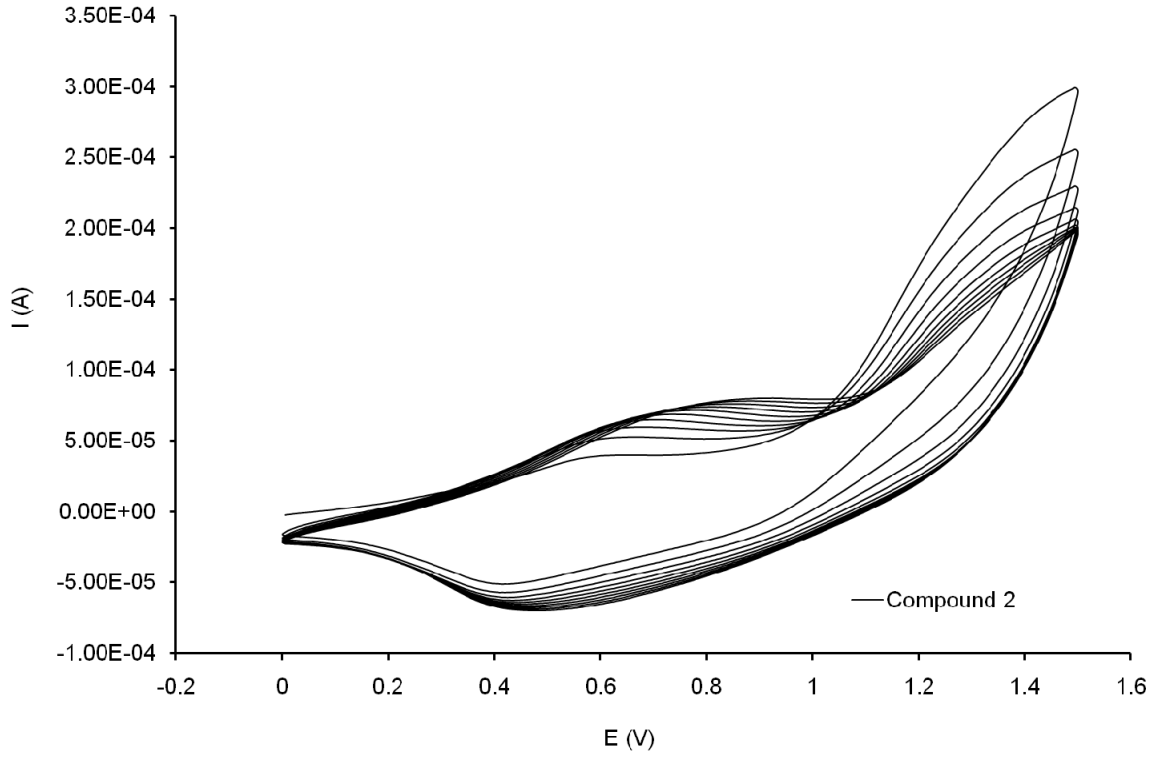


Fig. S4 CV for compound **2.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

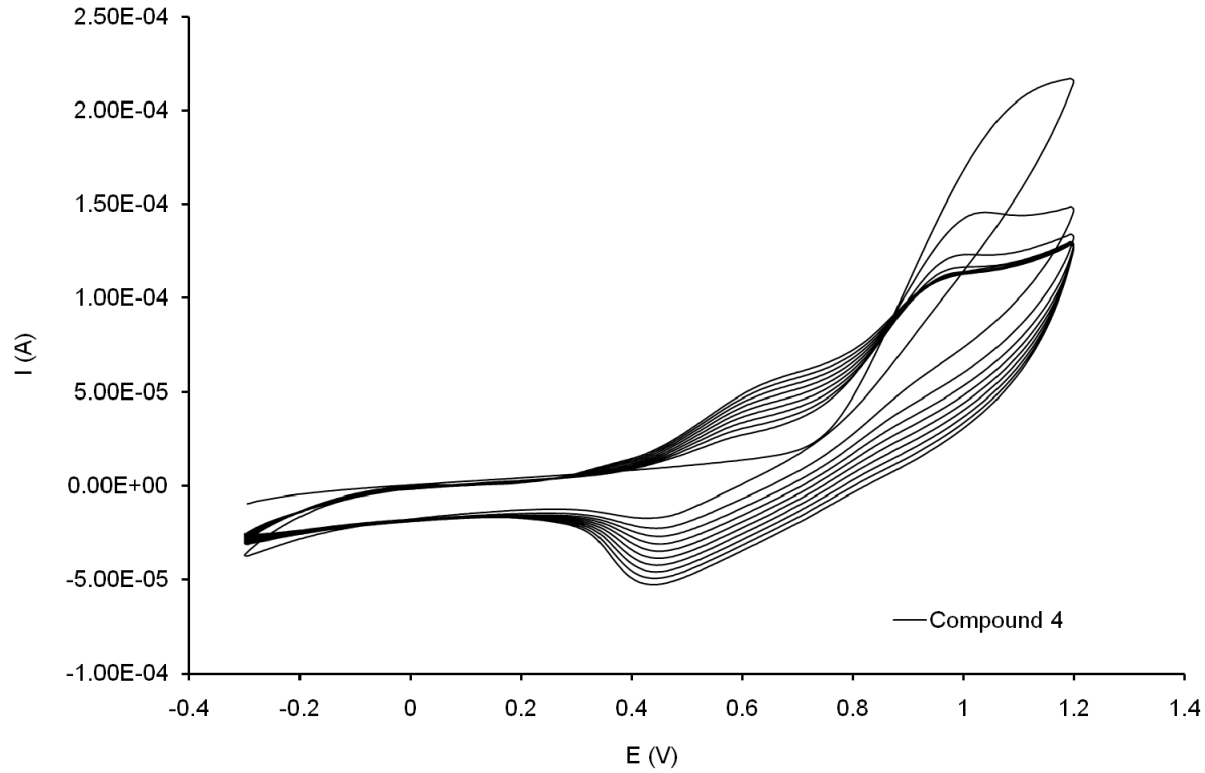


Fig. S5 CV for compound **4.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

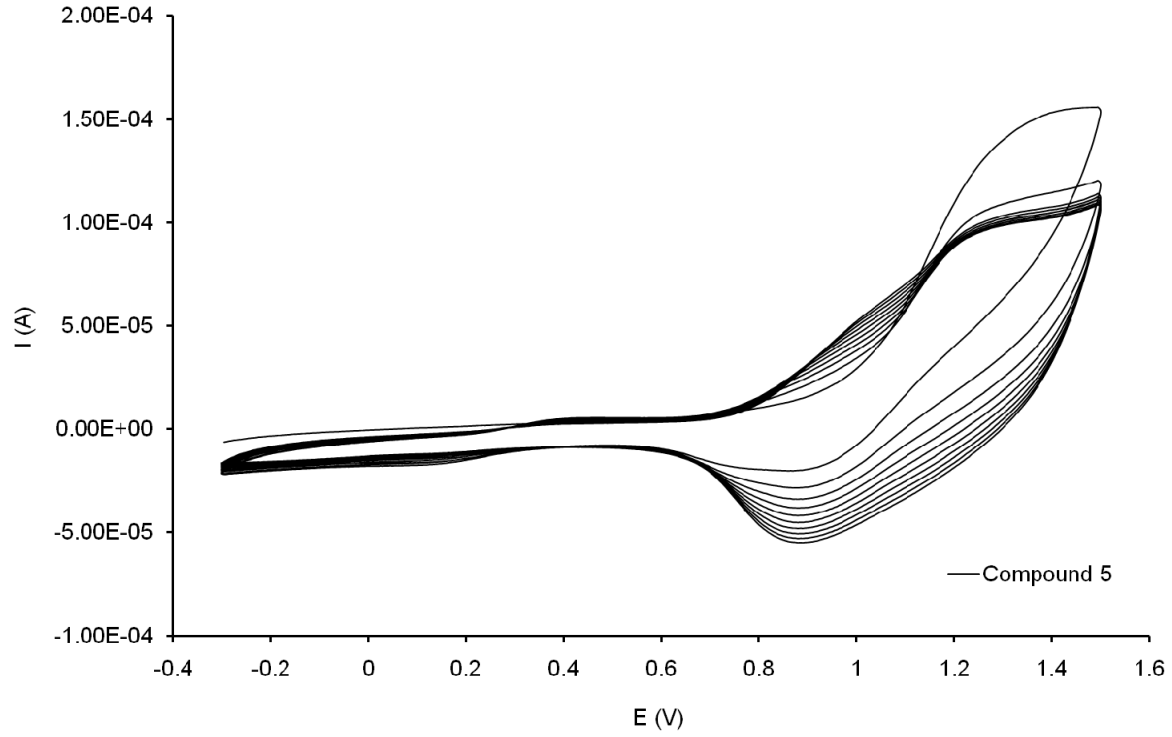


Fig. S6 CV for compound **5.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

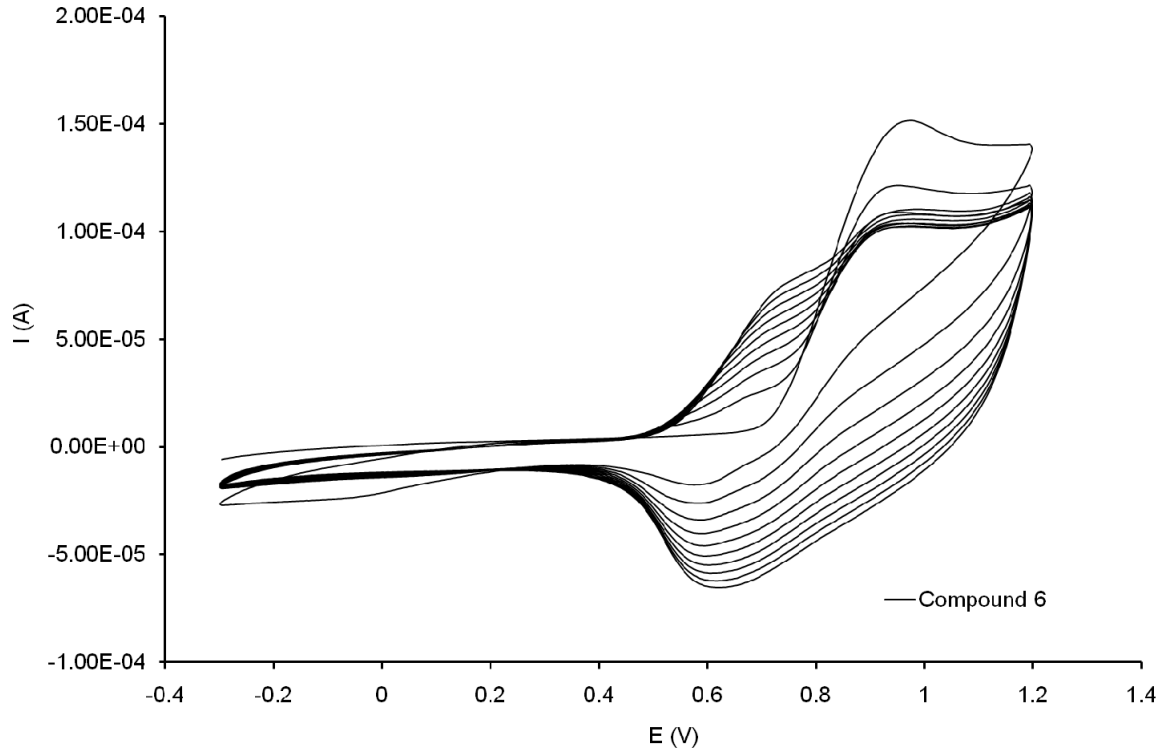


Fig. S7 CV for compound **6.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

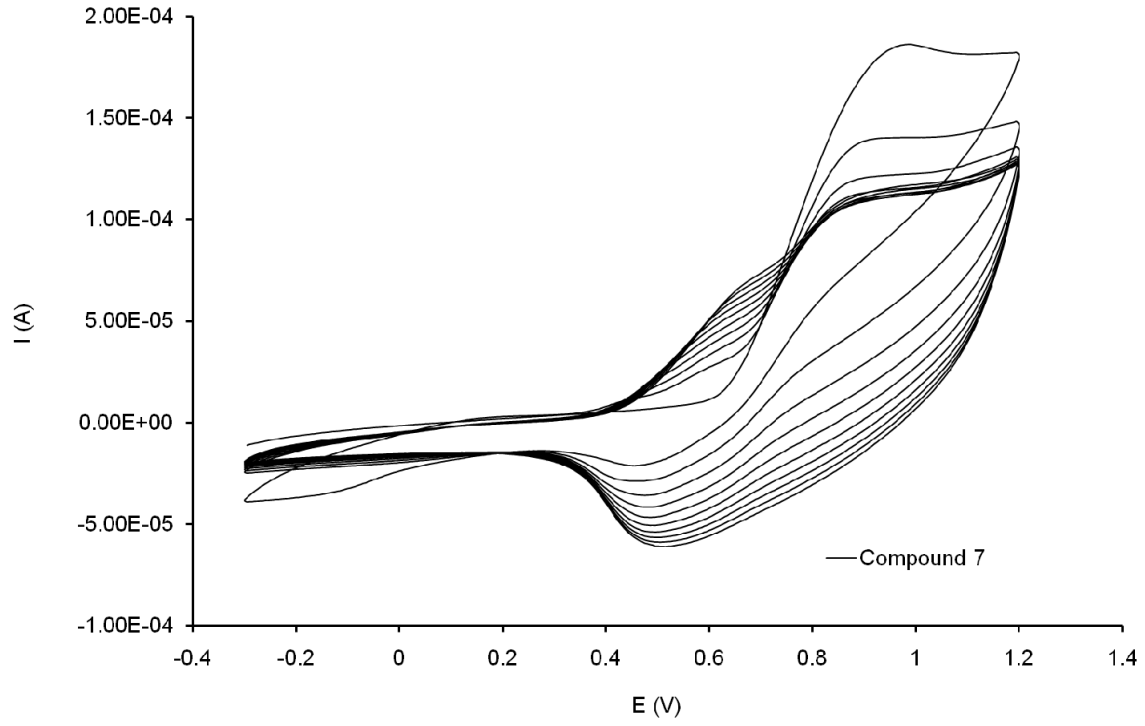


Fig. S8 CV for compound **7.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

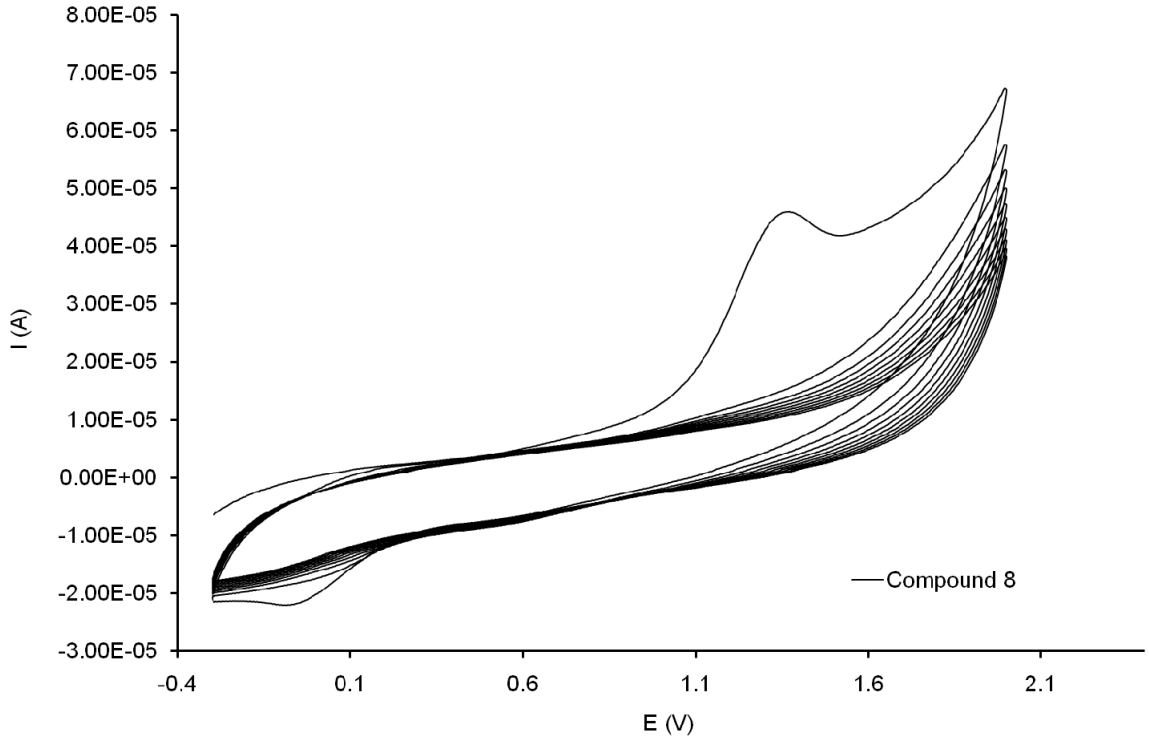


Fig. S9 CV for compound **8.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

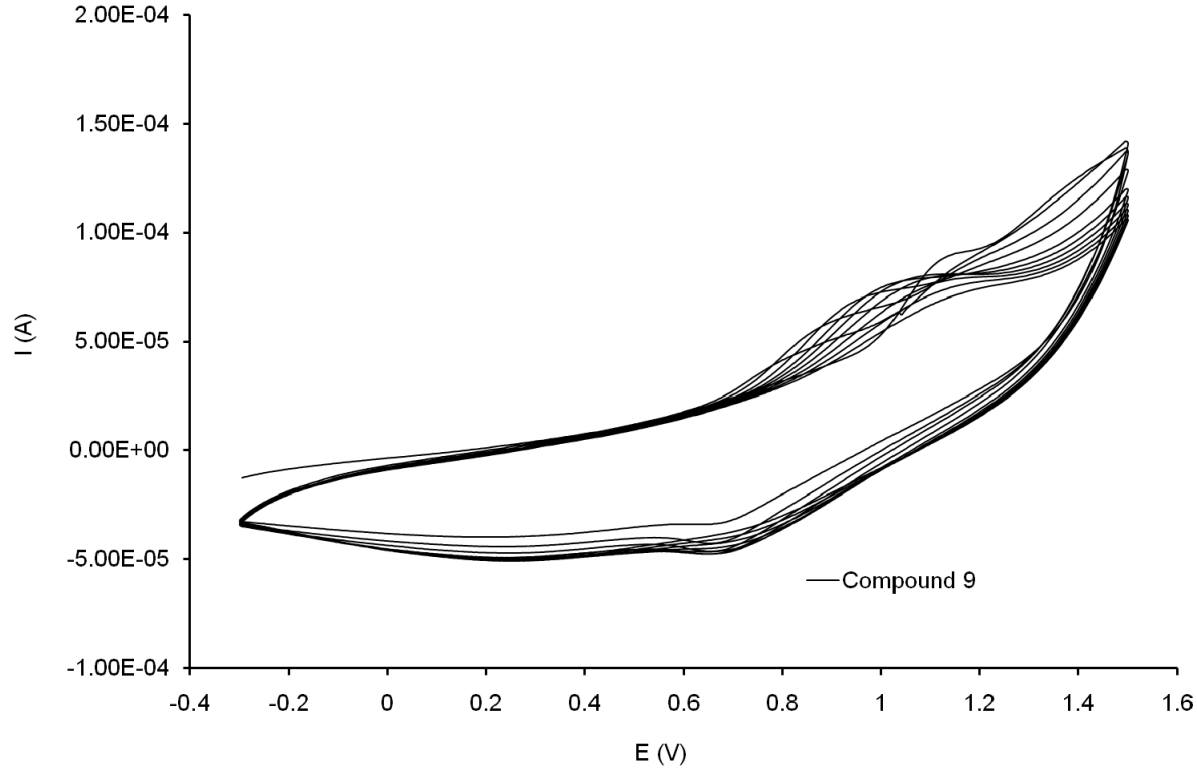


Fig. S10 CV for compound **9.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

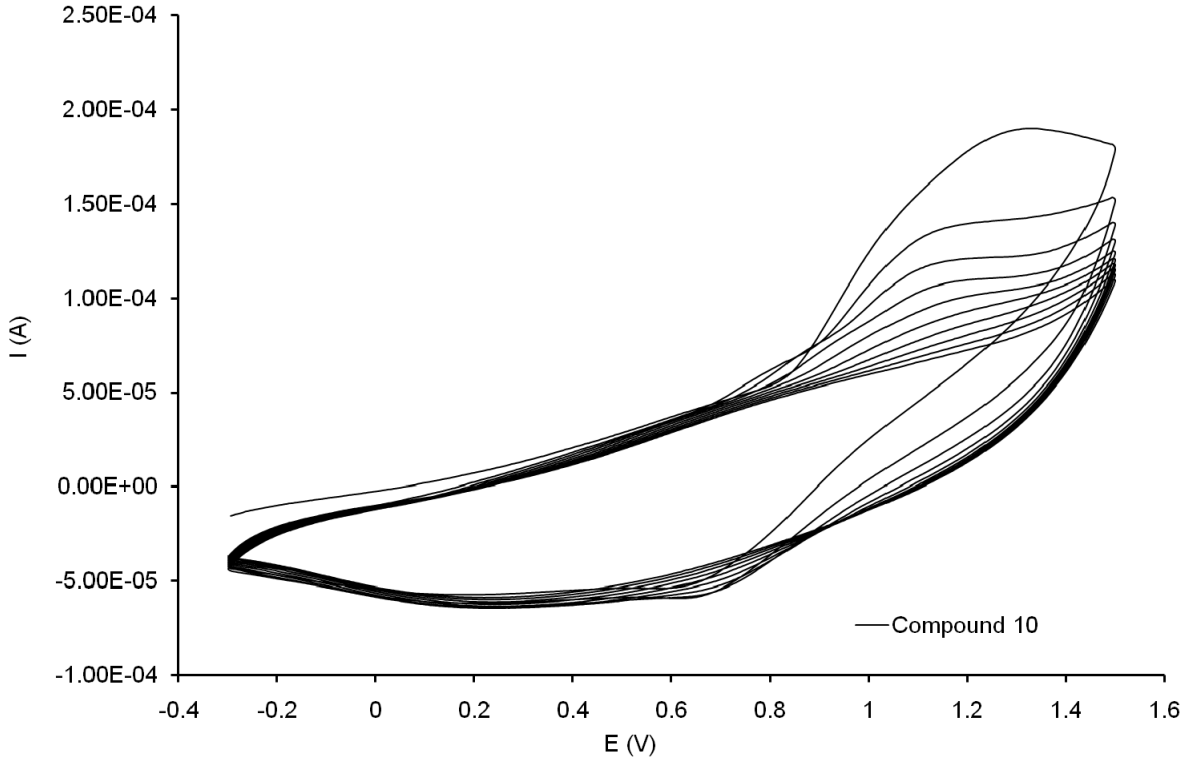


Fig. S11 CV for compound **10.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

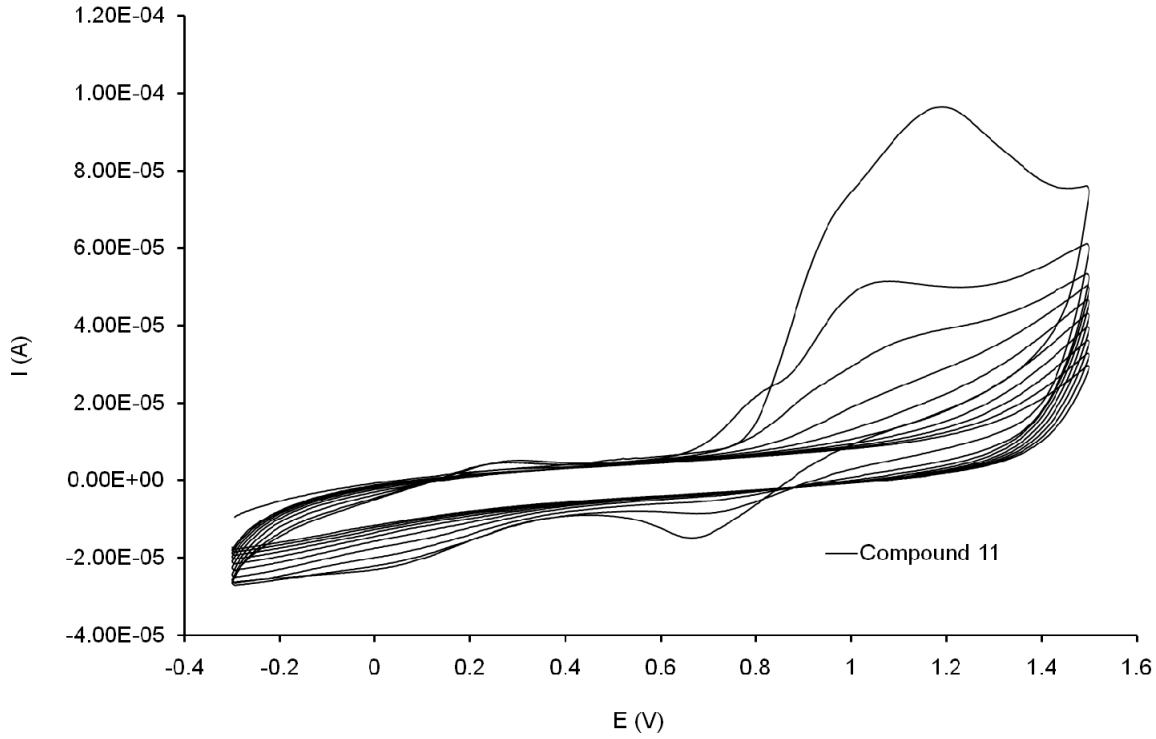


Fig. S12 CV for compound **11.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

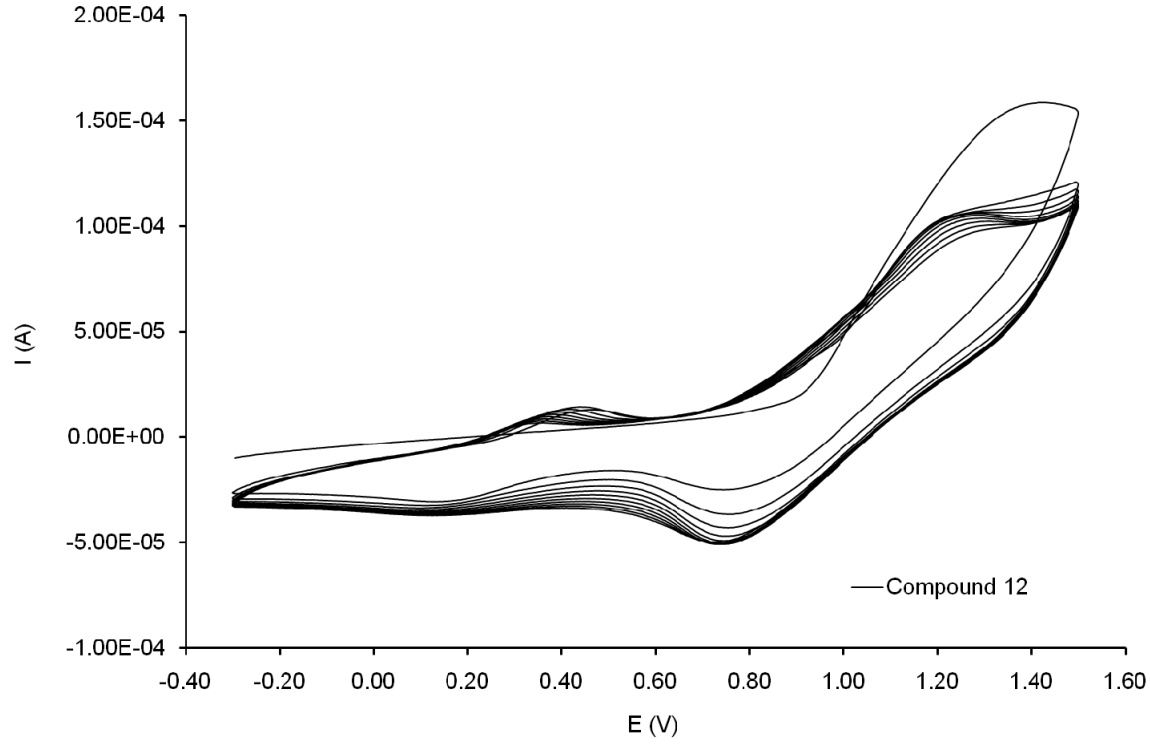


Fig. S13 CV for compound **12.** Conditions: 10mM of sample, 100mM $LiClO_4$, acetonitrile, r.t., working electrode Pt, counter electrode Au and Ag quasi-reference electrode. Scan rate 0.2 V/s.

Table S1. DFT-calculated C-C distances (Å) between pyrrolyl and thienyl rings for neutral modified nucleobases and cationic modified nucleobases.

	TP	**TP$^+$**				
	d(C_{th}-C_{py})	d(C_{th}-C_{py})	**TPT**	d(C_{th}-C_{py})	**TPT$^+$**	d(C_{th}-C_{py})
9	1.458	1.412				
dT_4C_tp	1.458	1.412				
dT_3C_tp	1.458	1.412				
10			1.457 - 1.457		1.427 - 1.423	
11			1.457 - 1.457		1.431 - 1.422	
12			1.456 - 1.455		1.432 - 1.421	

Single-crystal X-Ray diffraction

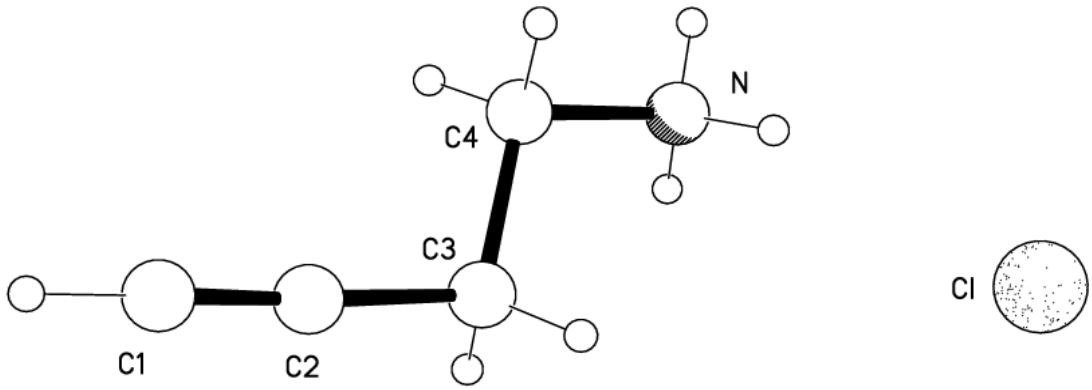
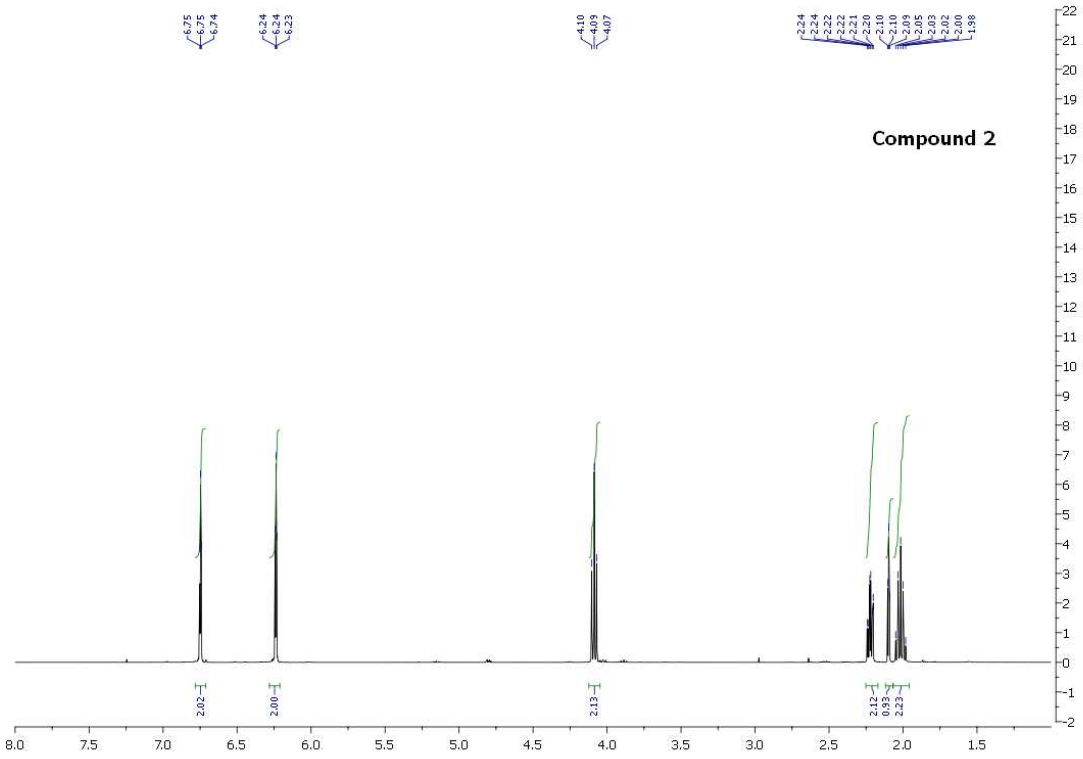
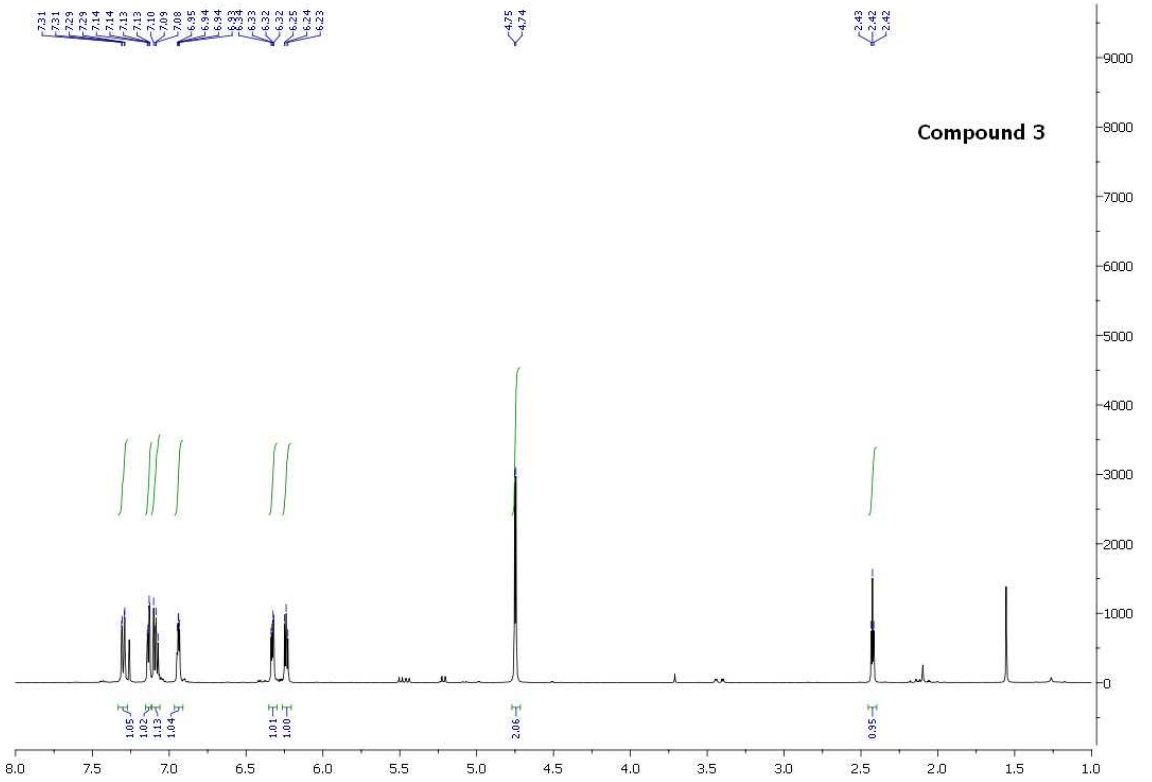
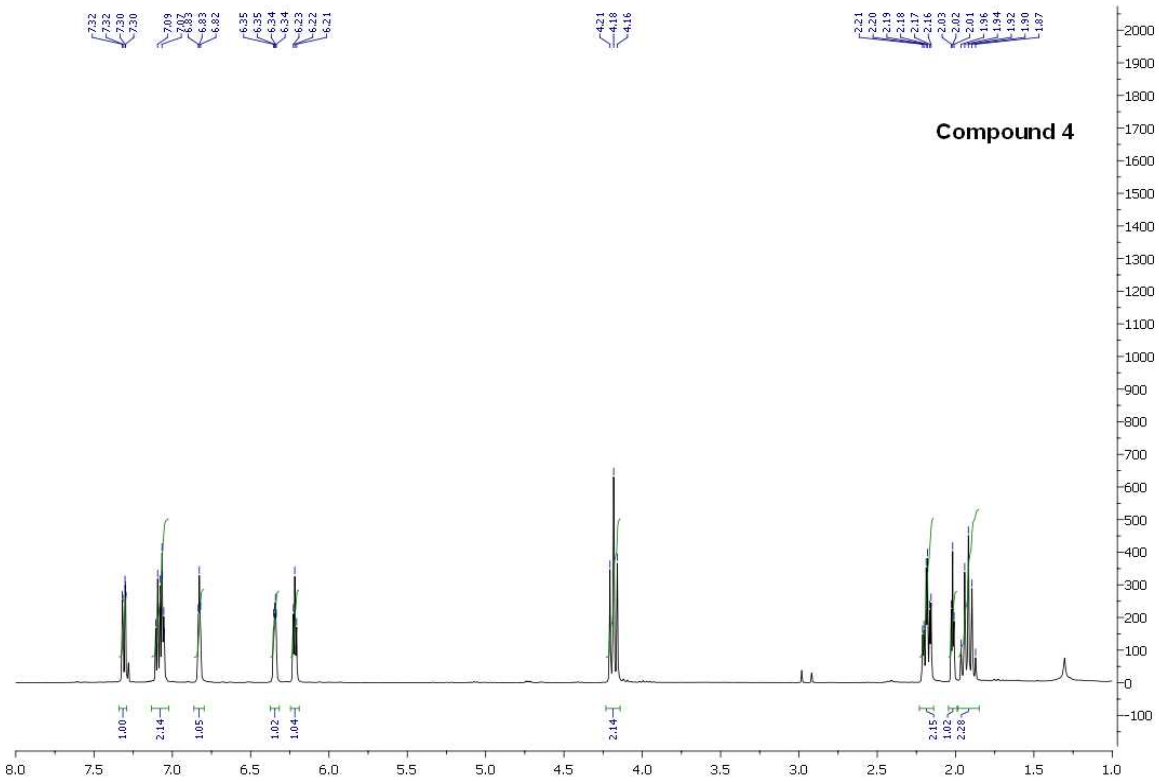


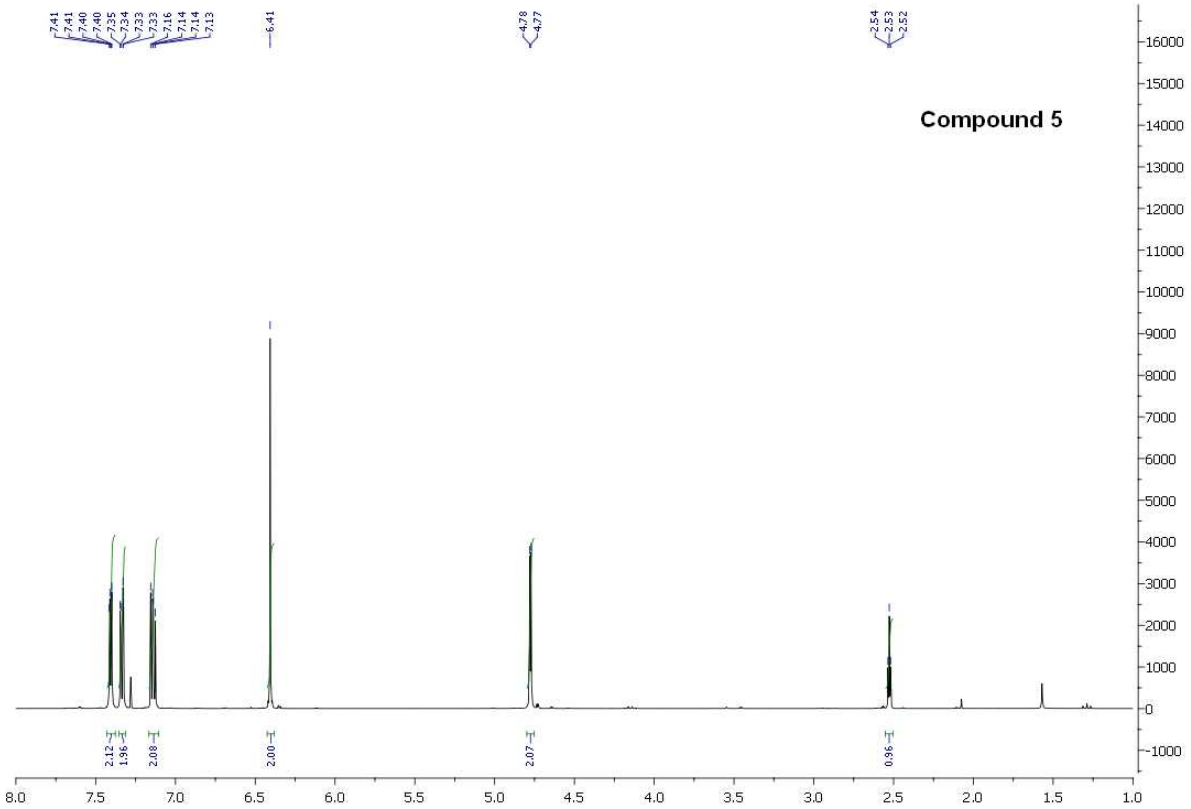
Fig. S14 Molecular structure of 4-amino-1-butyne. Distances (Å): C1–C2 1.176(2), C2–C3 1.466(2), C3–C4 1.513(2), C4–N 1.4798(18). Selected angles C3–C4–N 110.58(12)°, C2–C3–C4 110.44(13)°.

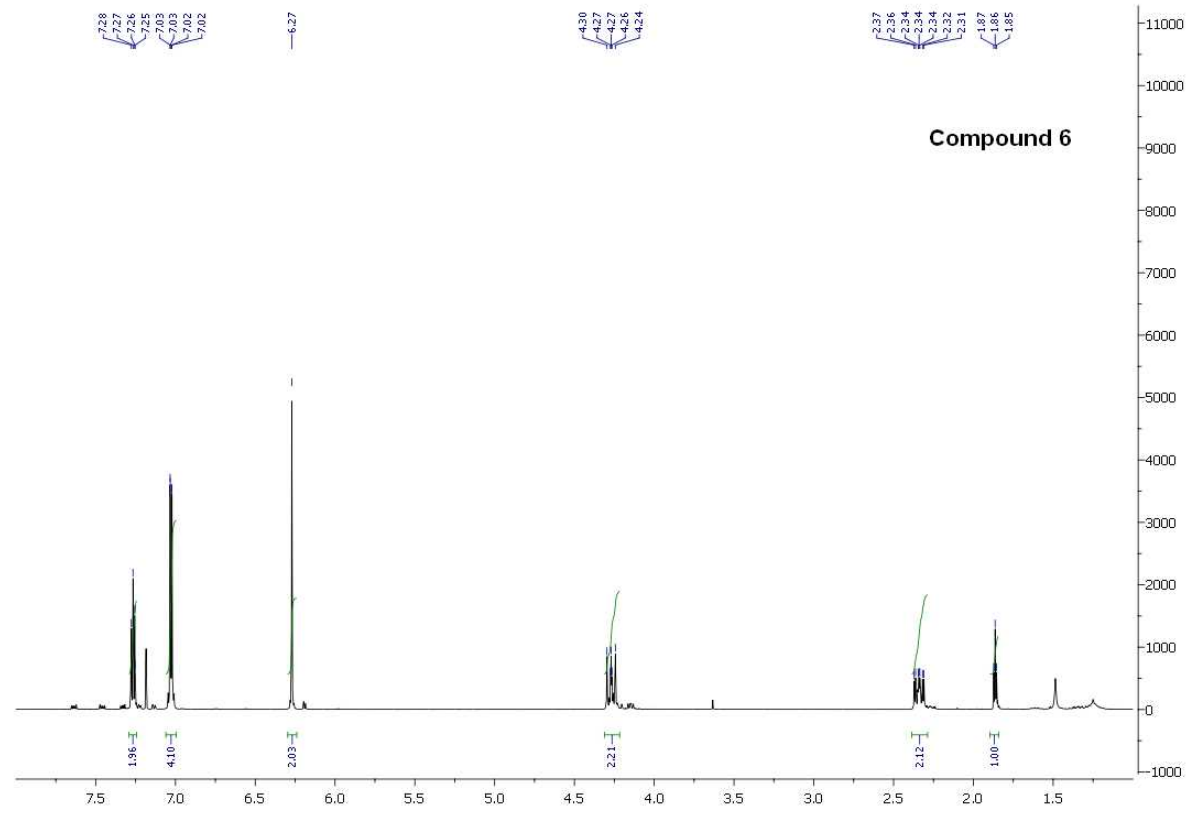
^{1}H NMR spectra

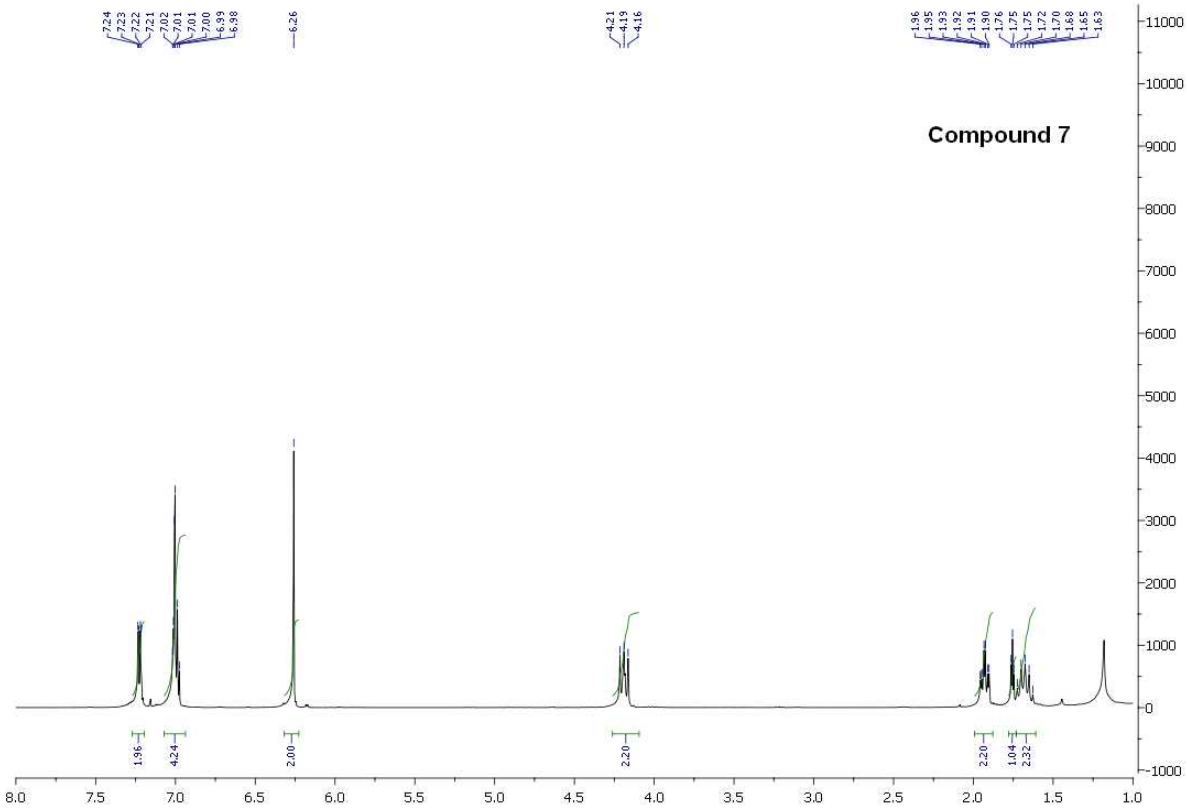


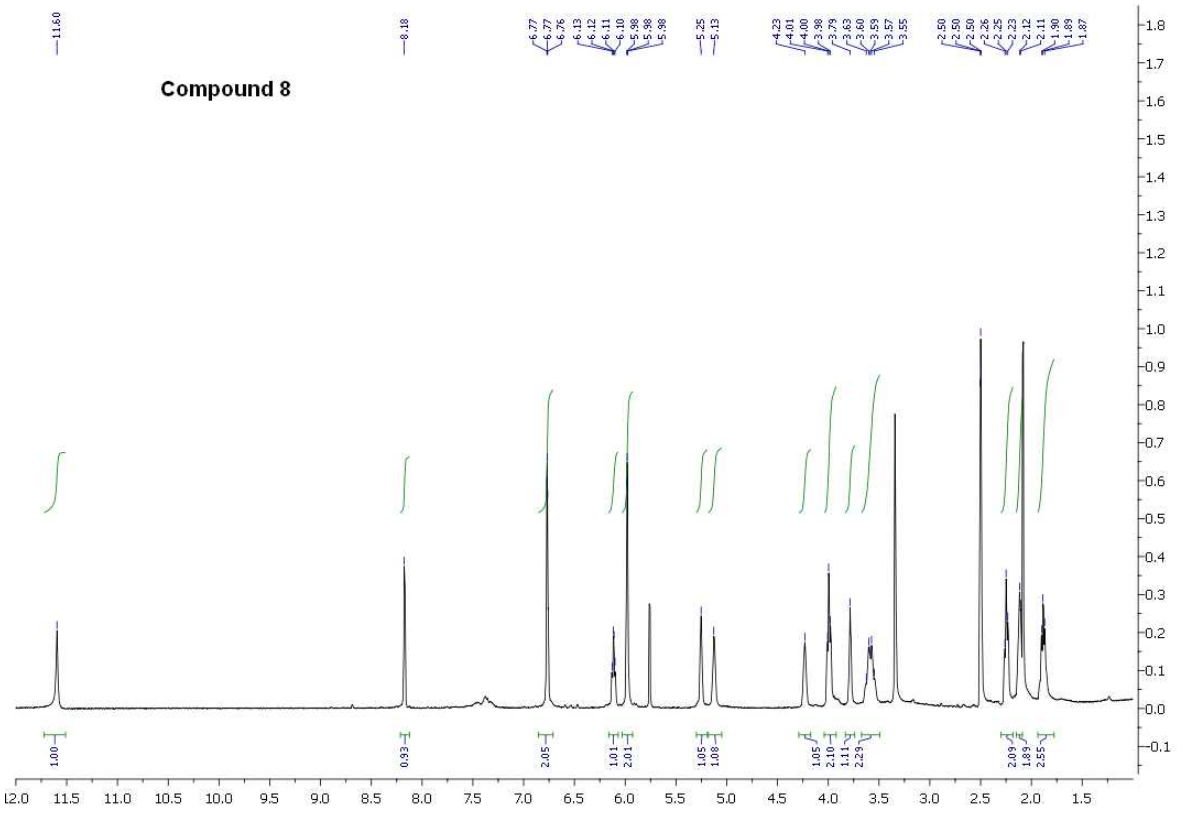




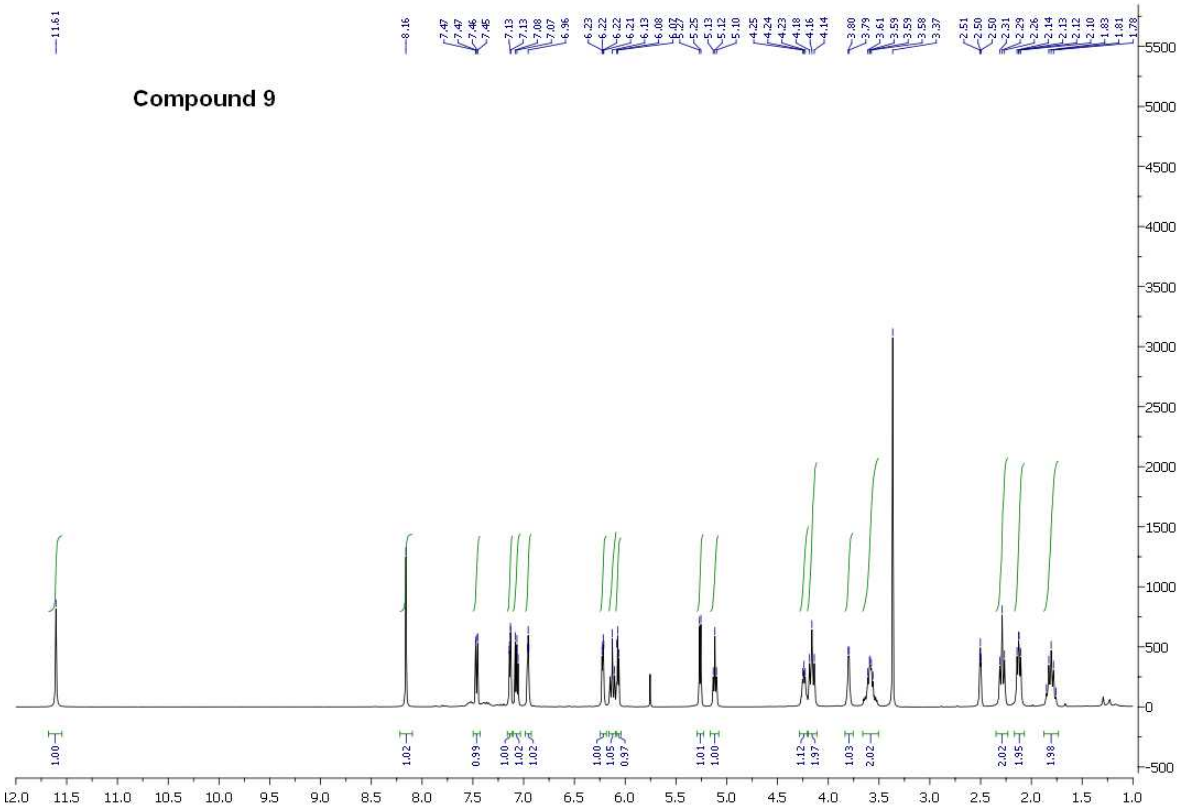




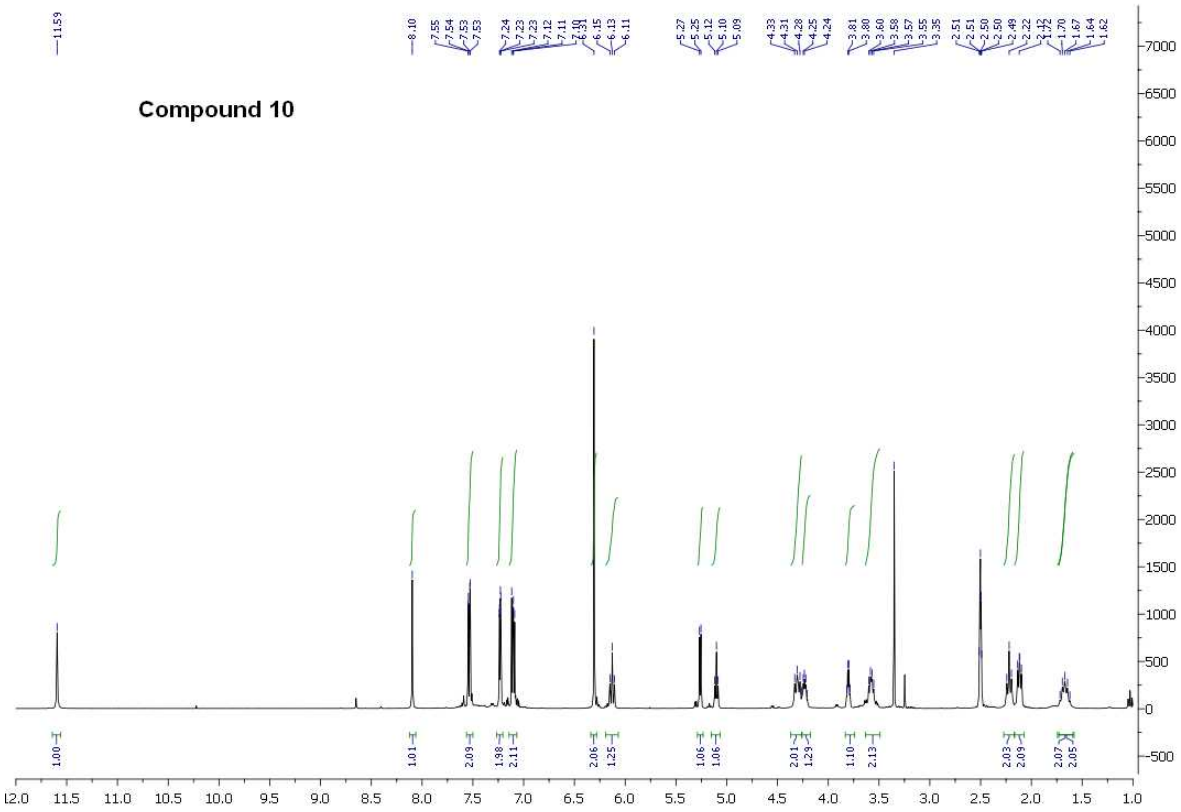


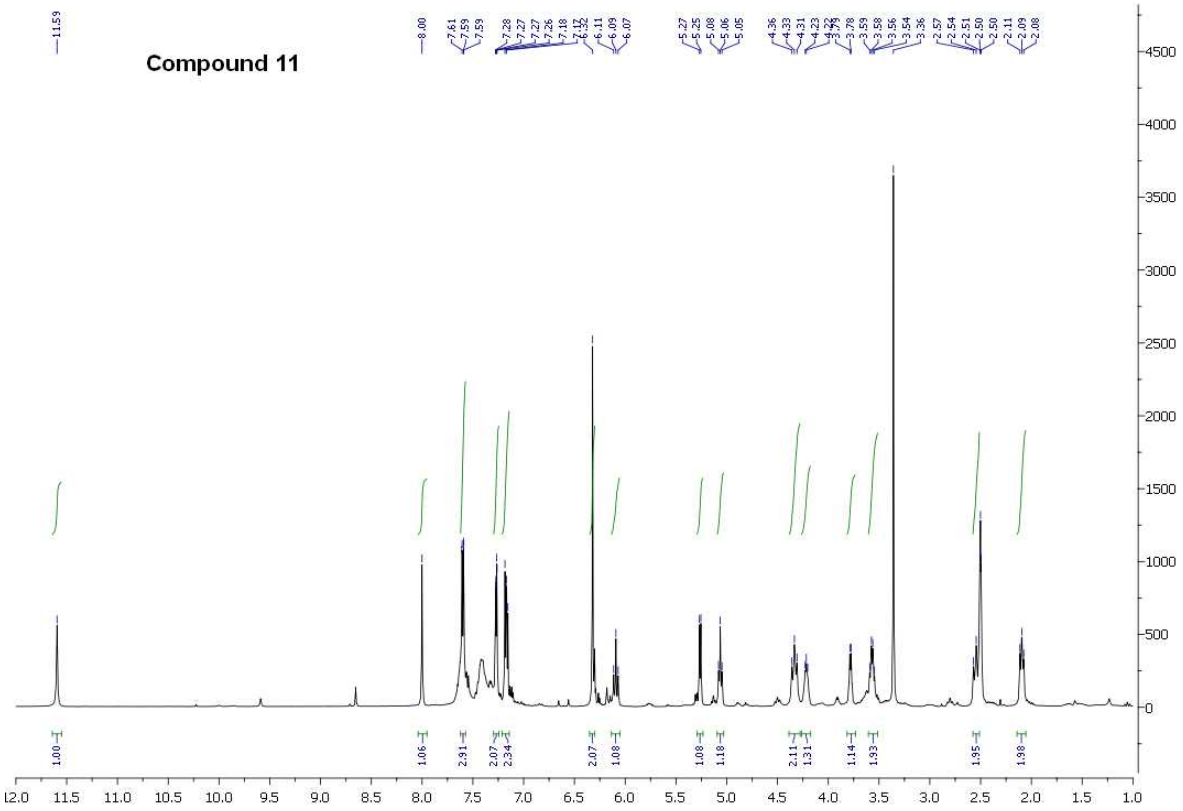


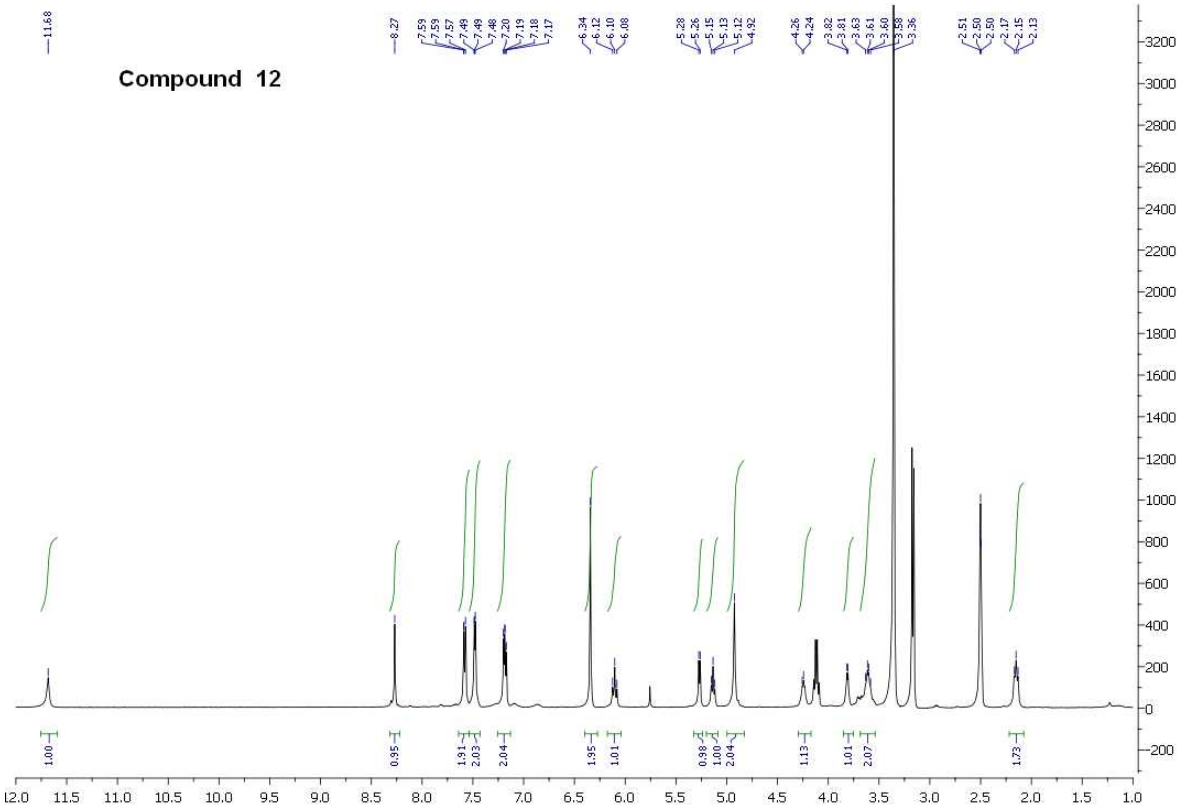
Compound 9



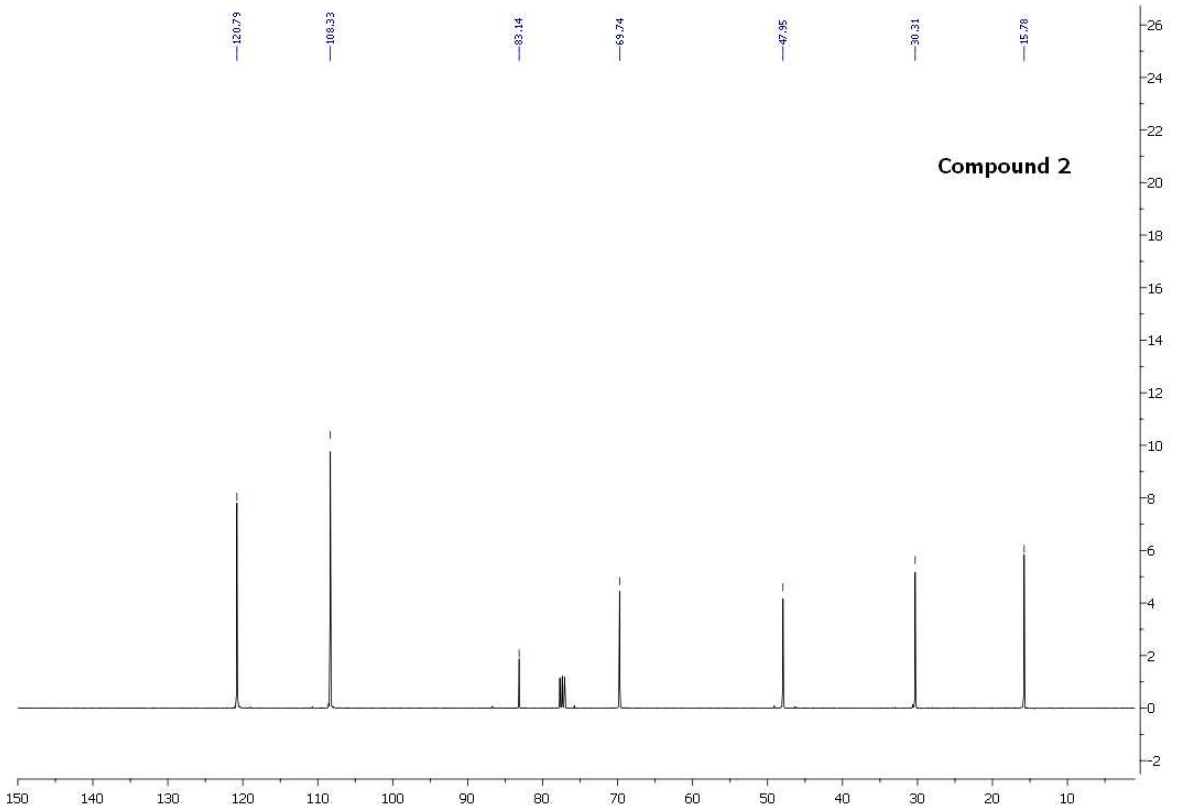
Compound 10

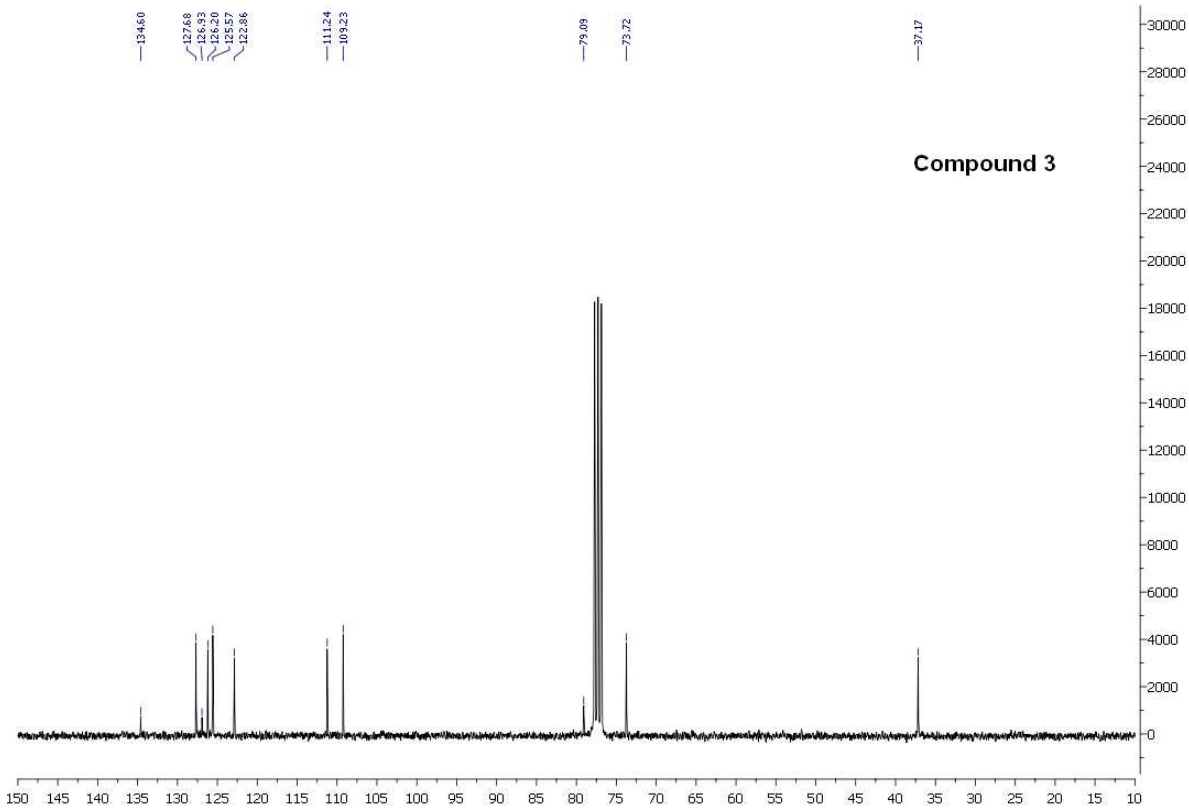


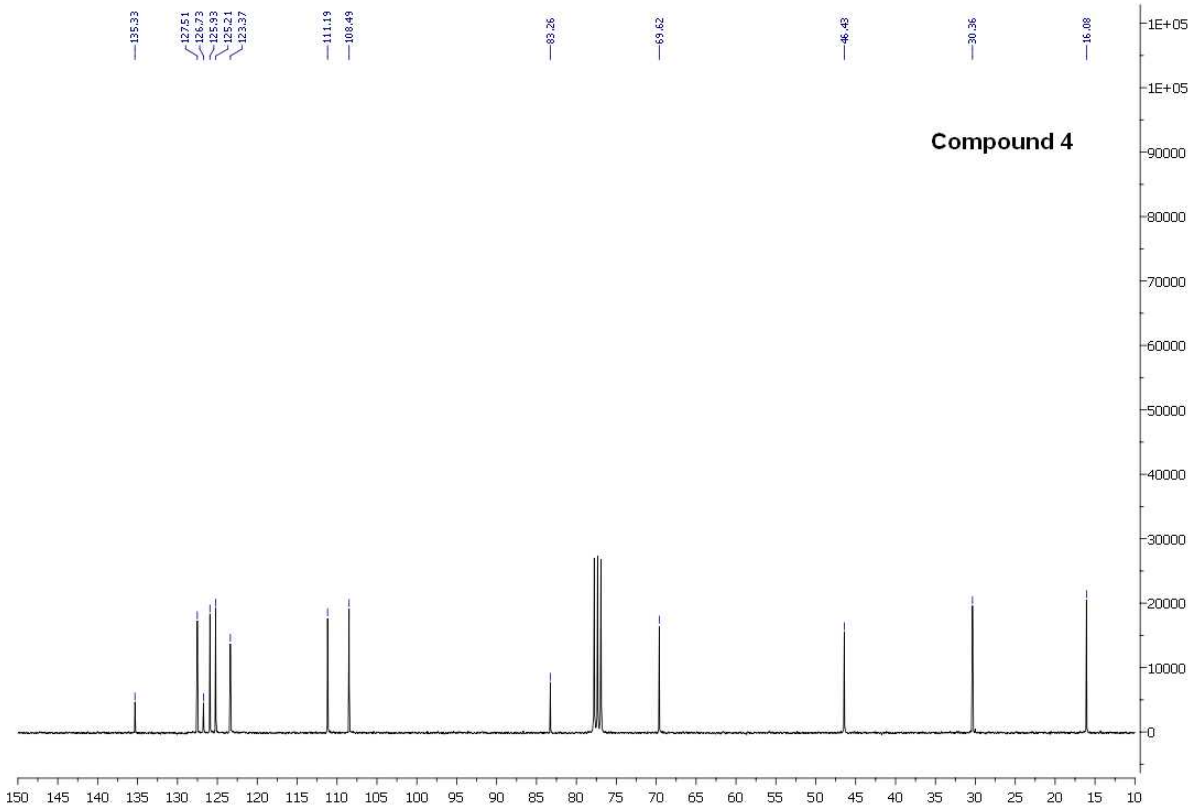


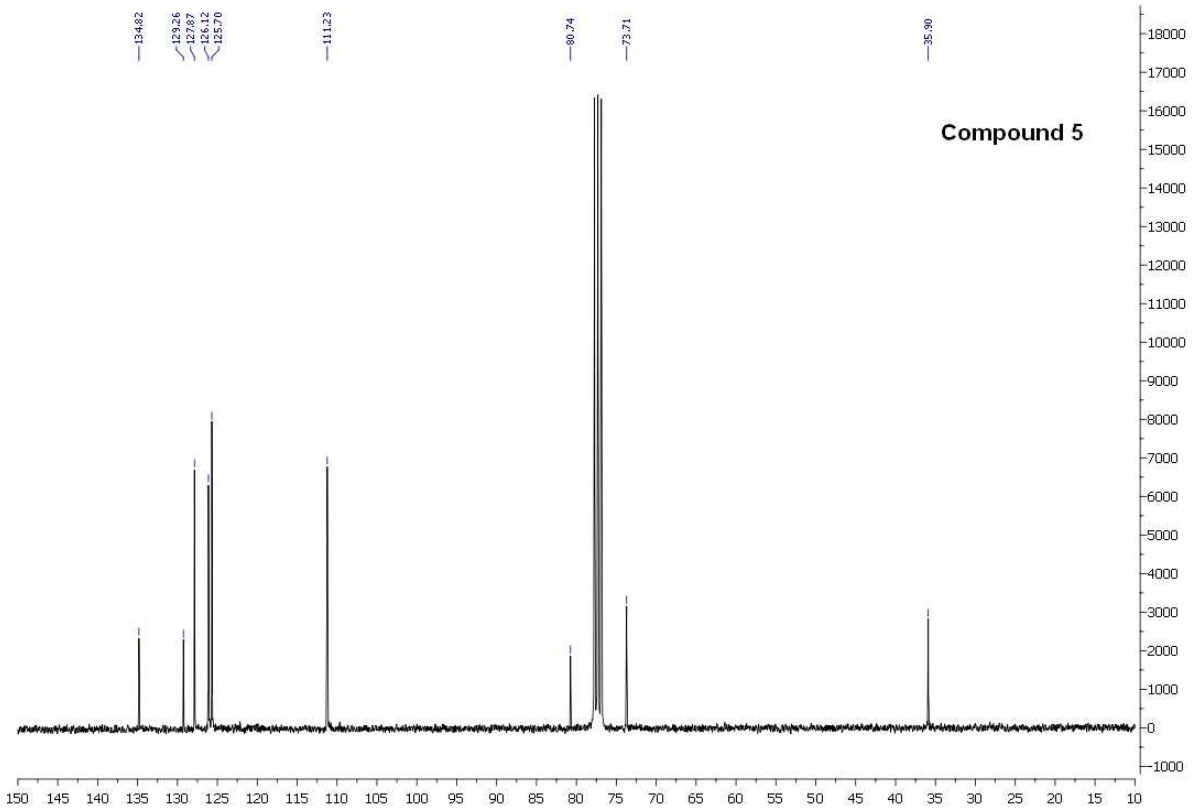


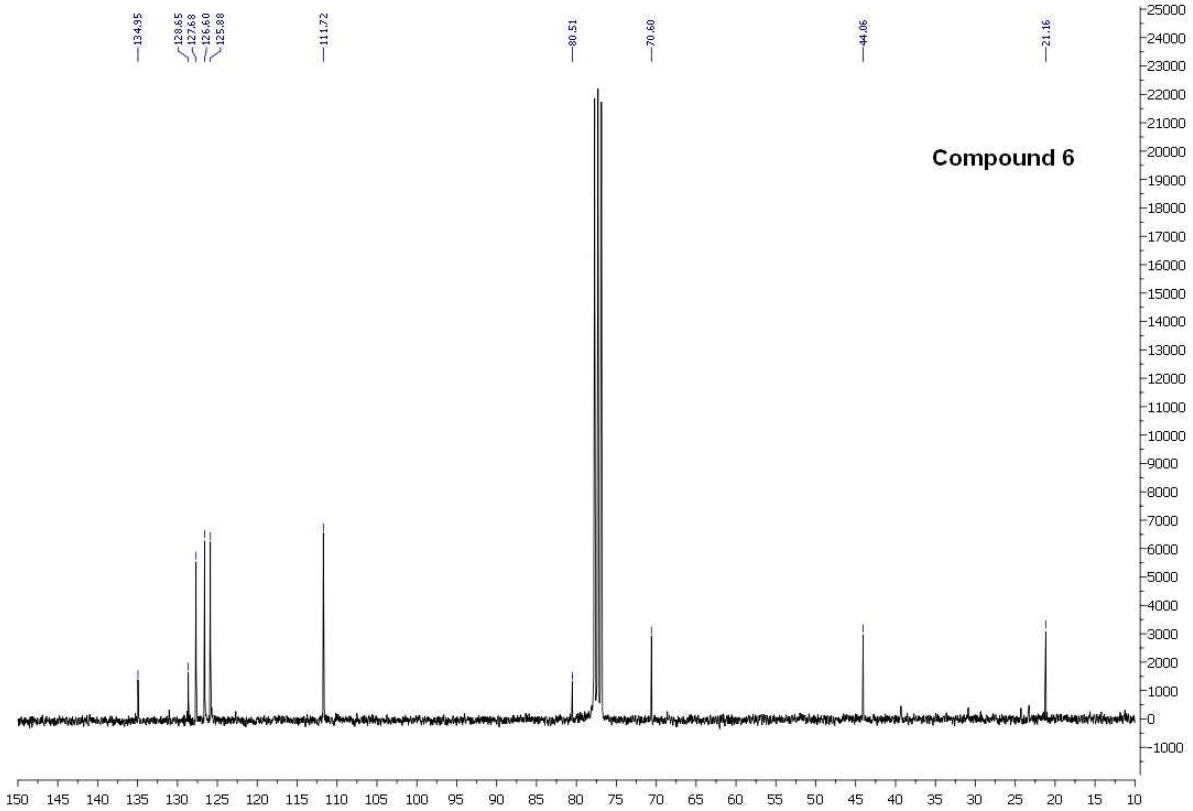
^{13}C NMR spectra

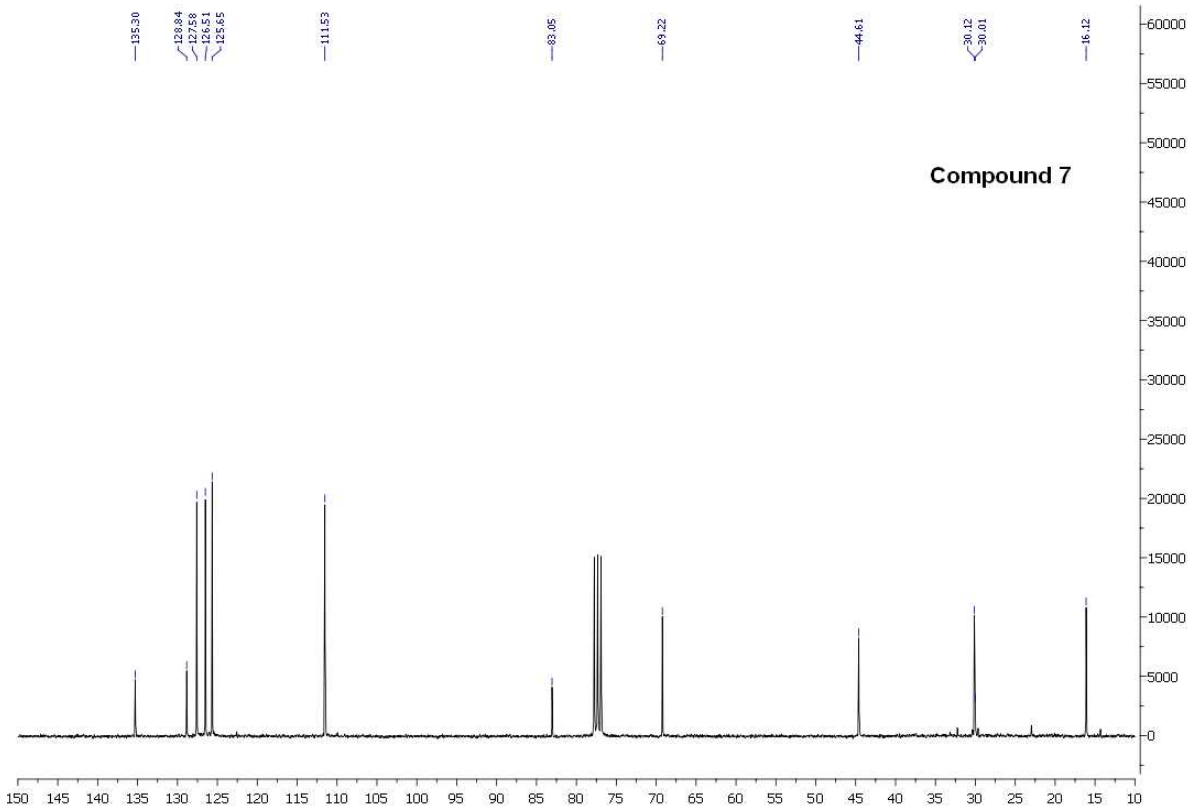


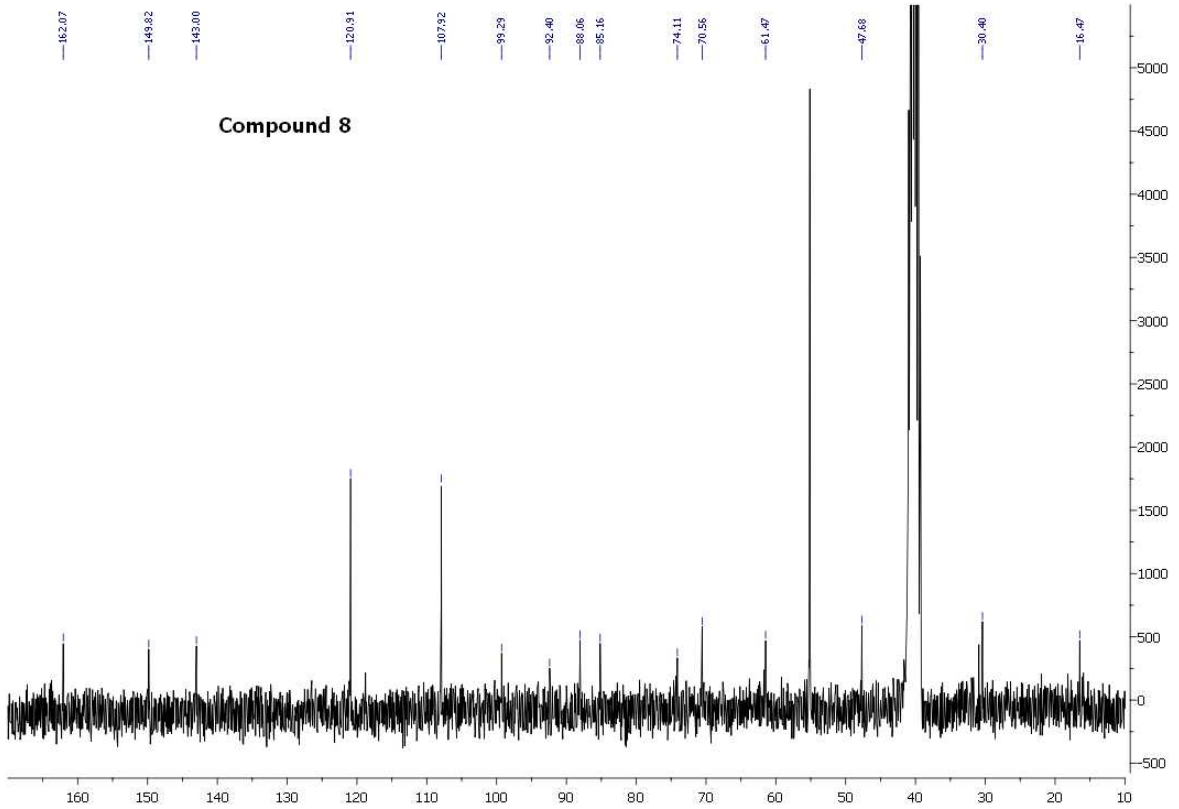


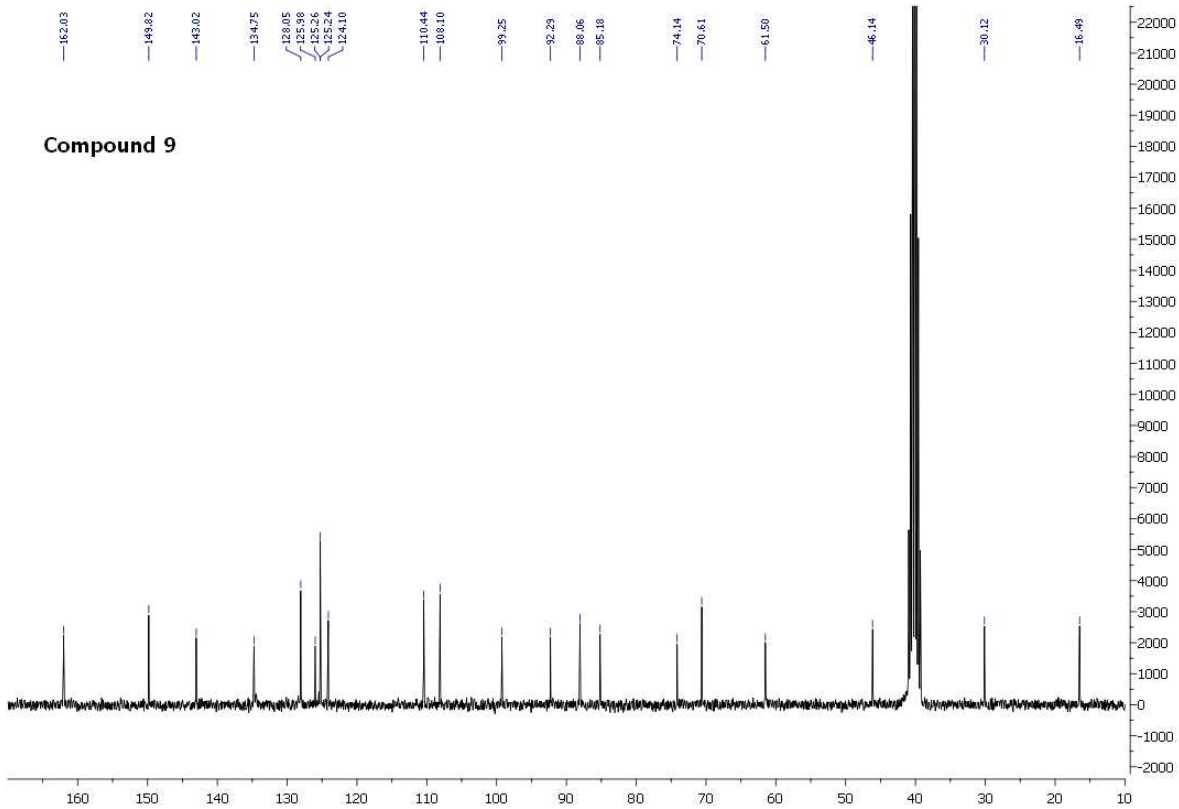


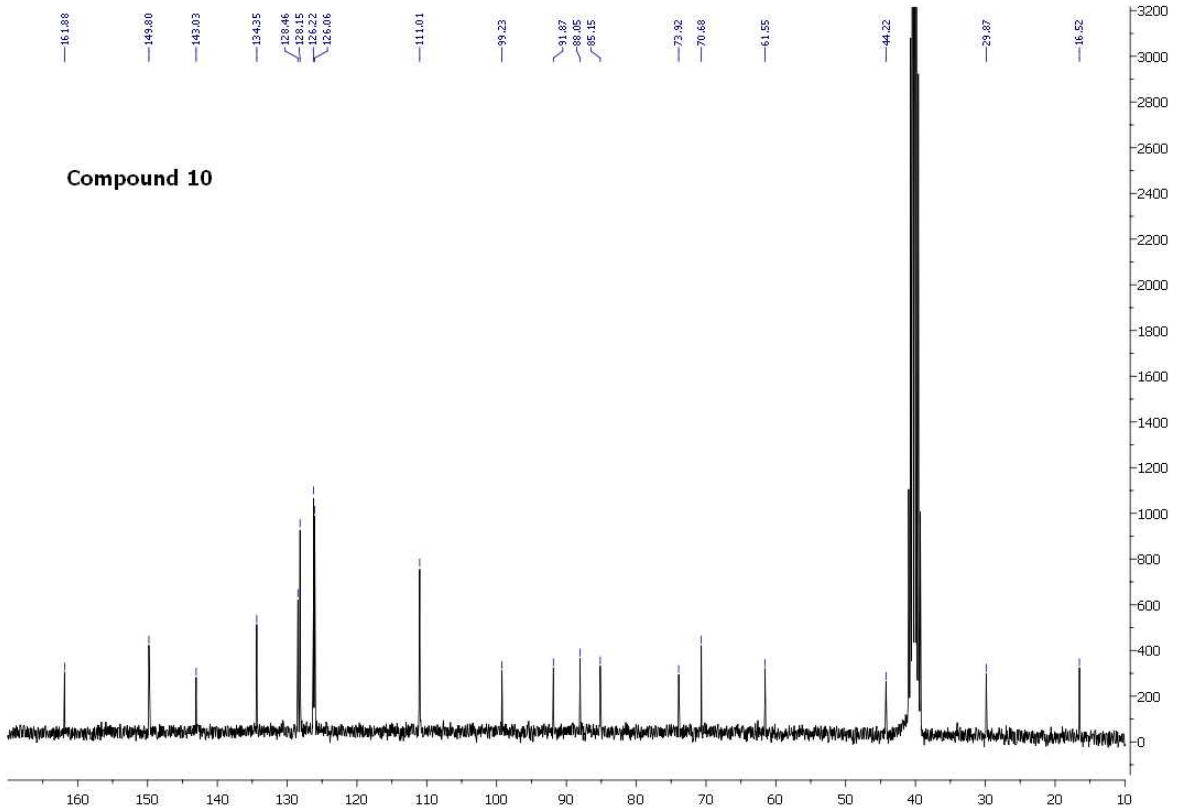


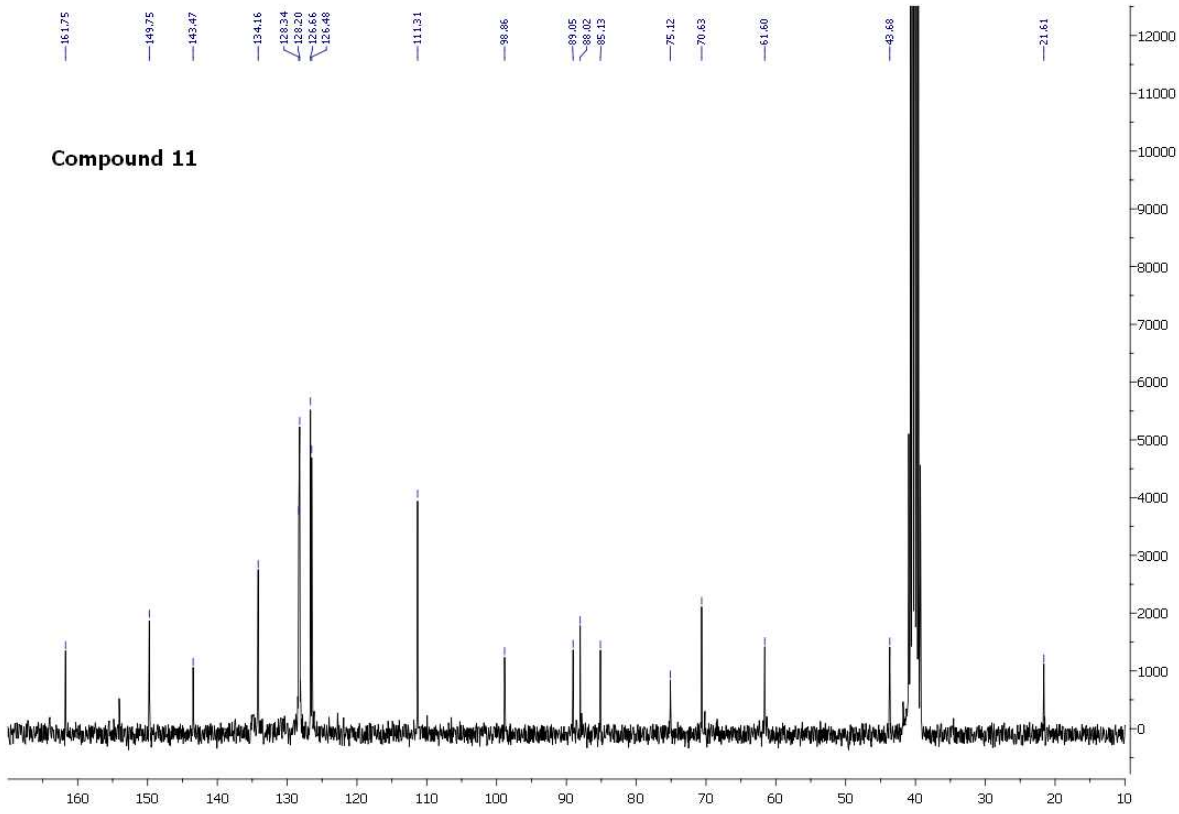


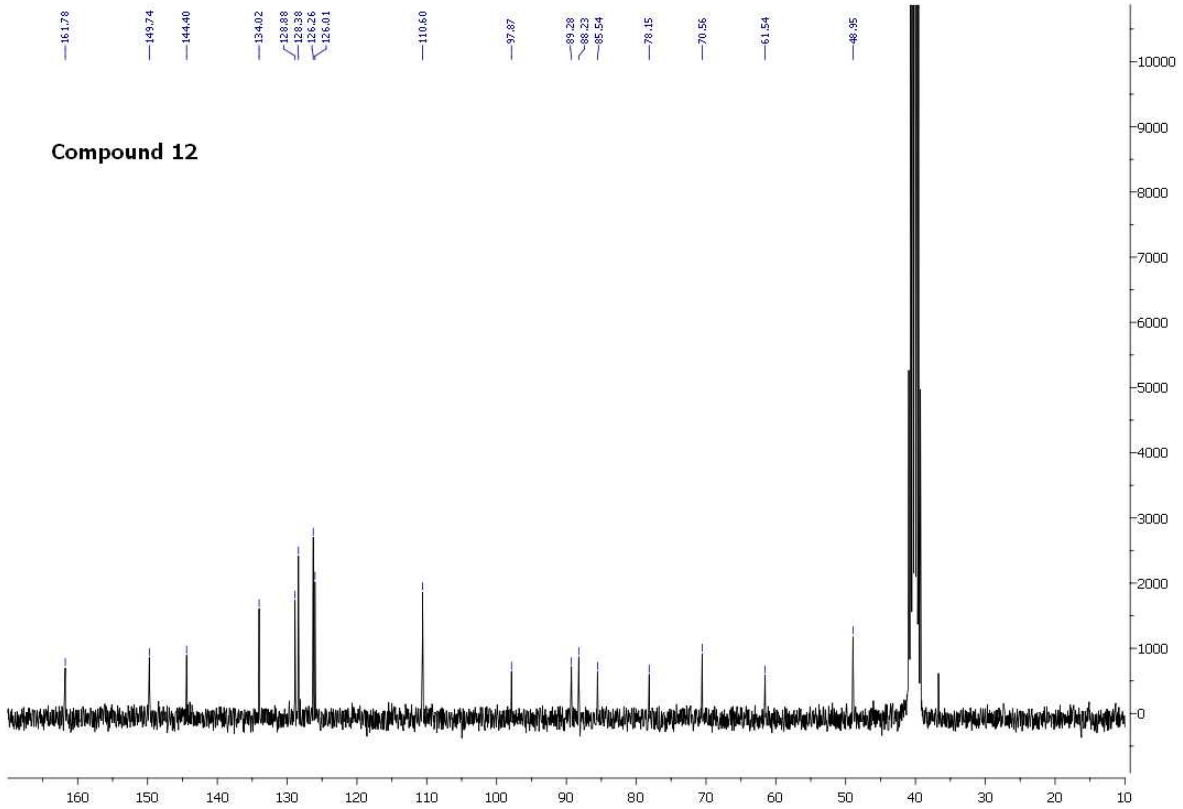






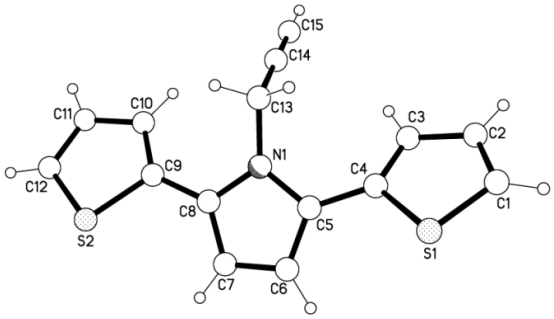






Crystal structure information for 5, 6 and 7.

The crystal structures of compounds **5** and **6** contain two independent molecules in the asymmetric unit, with bond lengths and angles lying within the expected ranges. In the molecular structure of **5**, the three heterocyclic rings are oriented such that the hetero atoms alternate in an up-down-up arrangement (Figure 2). Furthermore, the thienyl rings are almost coplanar (dihedral angle 12.7°) with respect to one another, but are twisted by 29.1° and 40.7° individually with respect to the pyrrolyl group.



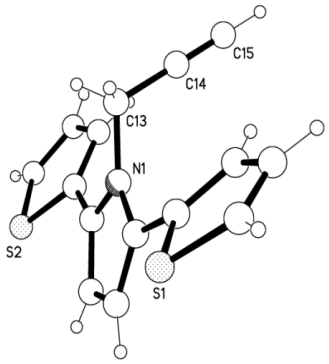


Fig. 2 Two views of the molecular structure of one of the independent molecules of **5**. Selected angles N1–C13–C14 115.2°, and interplanar angles; a–b 40.7°, b–c 29.1°, a–c 12.7°. Planes defined as follows: (a) S1/C1/C2/C3/C4, (b) N1/C5/C6/C7/C8, (c) S2/C9/C10/C11/C12.

The crystal structure of **6** (Figure 3) also contains two independent molecules differing primarily with regard to the orientations of the thienyl rings, disordered over two positions. Subsequent discussion refers to the major conformation. In the N1-containing independent molecule the heteroatoms lie on the same side i.e. an up-up-up conformation, though the thienyl rings are twisted in opposite directions relative to the central pyrrolyl group. The inter-planar angles between the thienyl and pyrrolyl rings are 48.4° and 65.8°. In the N2-containing independent molecule, the hetero atoms show an up-up-down arrangement and a more coplanar arrangement, with thienyl-pyrrolyl interplanar angles of 33.2° and 31.1°.

The molecular structure of compound 7 (Figure 4), the **tpt**-derivative with a C_5 chain, reveals an up-up-down arrangement of the heteroatoms, though again there is some disorder in the thienyl S1-ring. Here the thienyl-pyrrolyl interplanar angles are slightly larger, 40.0° and 41.1°, than is seen in one of the independent molecules of **6**.

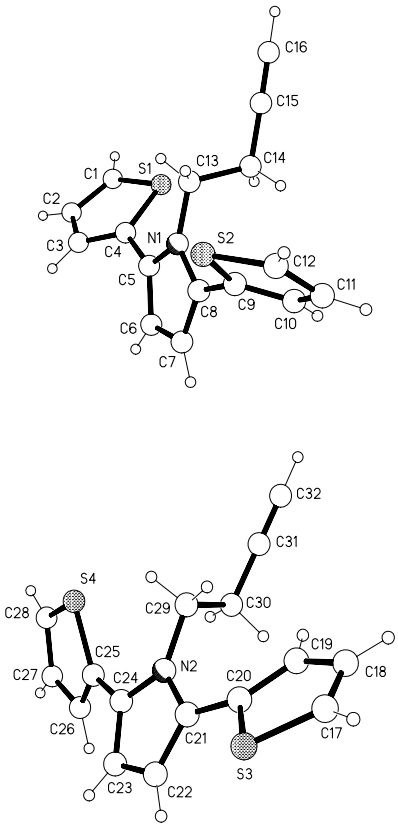


Fig. 3 Molecular structures of the two independent molecules in the crystal structure of **6**. Selected angles N1–C13–C14 111.0°, N2–C29–C30 110.7° and interplanar angles a–b 48.4°, b–c 65.8°, a–c 69.2°, a′–b′ 33.2°, b′–c′ 31.1°, a′–c′ 62.6°. Planes defined as follows: (a) S1/C1/C2/C3/C4, (b) N1/C5/C6/C7/C8, (c) S2/C9/C10/C11/C12, (a′) S3/C17/C18/C19/C20, (b′) N2/C21/C22/C23/C24, (c′) S4/C25/C26/C27/C28.

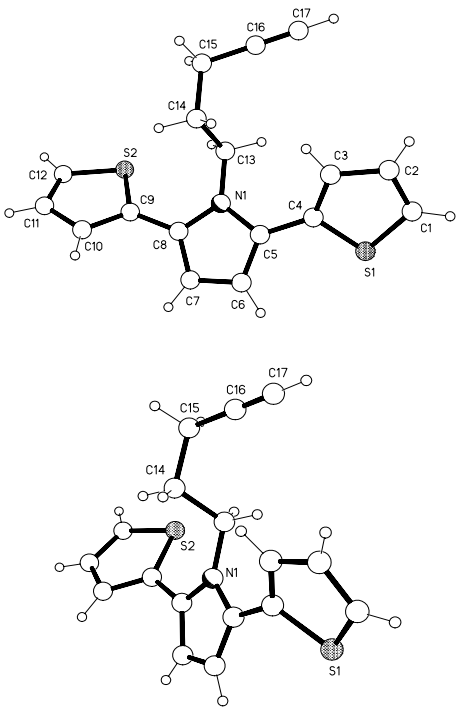


Fig. 4 Two views of the molecular structure of **7**. The major component of the disordered molecule is shown. Selected angles: N1–C13–C14 112.8°, and interplanar angles: a–b 40.0°, b–c 41.1°, a–c 76.4°. Planes defined as follows: (a) S1/C1/C2/C3/C4, (b) N1/C5/C6/C7/C8, (c) S2/C9/C10/C11/C12.