Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Electronic Supporting Information

Thiophene-functionalized isoindigo dyes bearing electron donor substituents with absorptions approaching the near infrared region

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Table of contents

1. Computational Details

The isoindigo derivatives were calculated with the DFT method in combination with the B3-LYP[S1] functional. All calculations were performed with the TURBOMOLE program (version 5.10).[S2] The TZVP[S3] basis for C, N, O, and S atoms was combined with the TZV[S2] basis for the H atom. This basis is designated as TZV(P) and was found to be an excellent compromise between accuracy and computational effort for systems of similar size.[S4] All dyes were fully geometry-optimized, emanating from structures computed on semi-empirical AM1 level. Long alkyl chains were replaced by methyl groups.

Transition densities were calculated on CC2 level with the TZV(P) basis based on the previously geometry-optimized structures using the TURBOMOLE program (version 5.9). In all CC2 computations, the resolution-of-the-identity (RI) approximation was employed.[S5] Corresponding auxiliary basis sets were applied for fitting the charge density.[S6] The frozen core approximation was used to freeze orbitals with eigenvalues smaller than −3.0 a. u. in the calculation of the correlation and excitation energies.

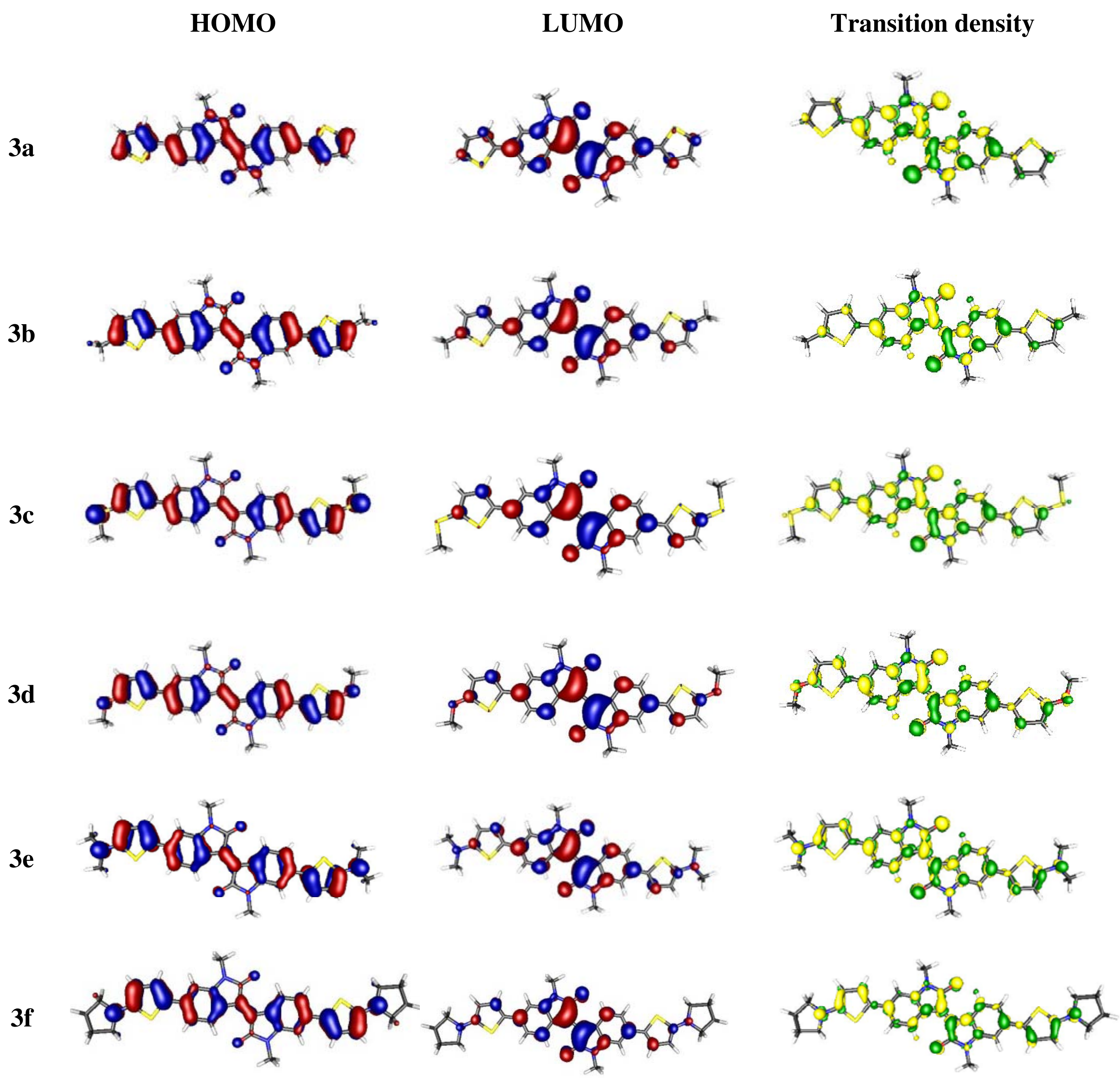

Fig. S 1 HOMO, LUMO according to DFT (B3-LYP) calculations and transition density (CC2 level) of **3a-f**.

2. Cyclic voltammetry

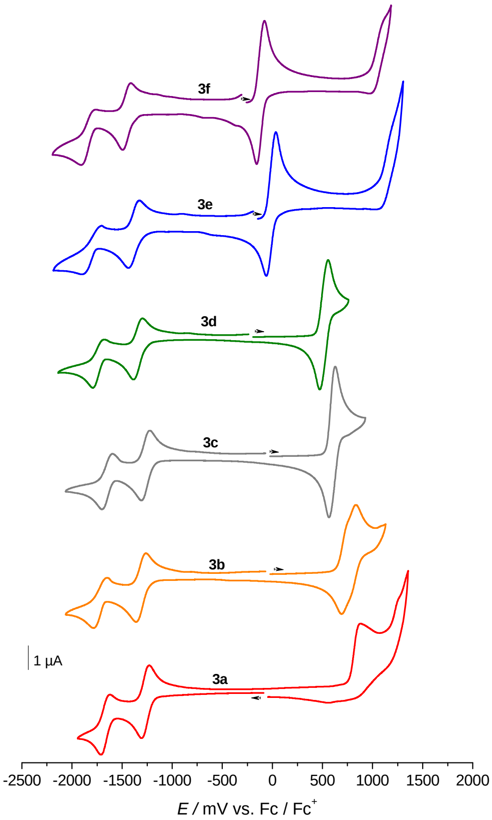

Fig. S 2 Cyclic voltammograms of **3a-f** in dry dichloromethane (10^{-4} M); scan rate 100 mV s^{-1}; supporting electrolyte: tetrabutylammonium hexafluorophosphate (NBu_4PF_6, 0.1 M).

3. NMR-spectra

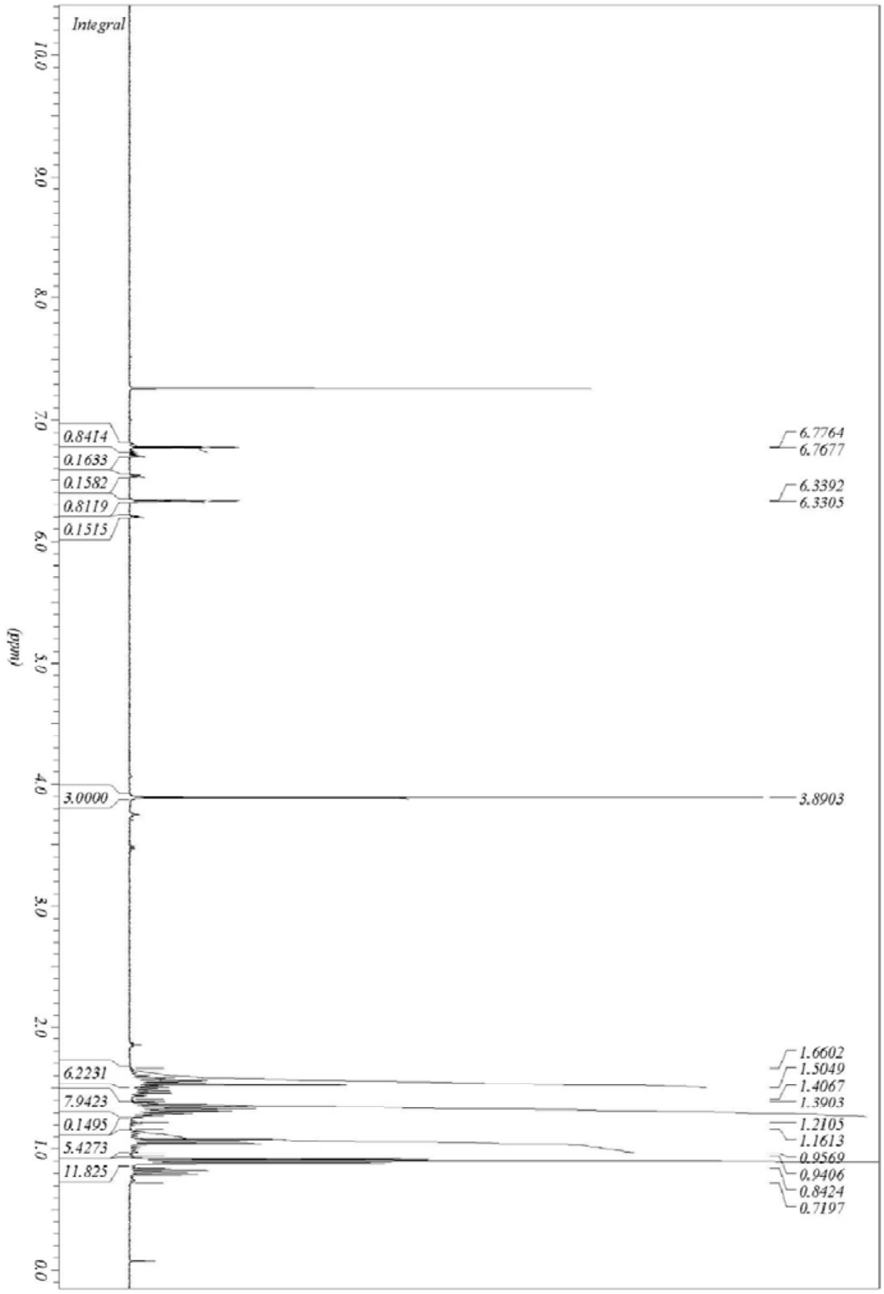

Fig. S 3 400 MHz ^{1}H NMR spectrum of **2d** in $CDCl_3$.

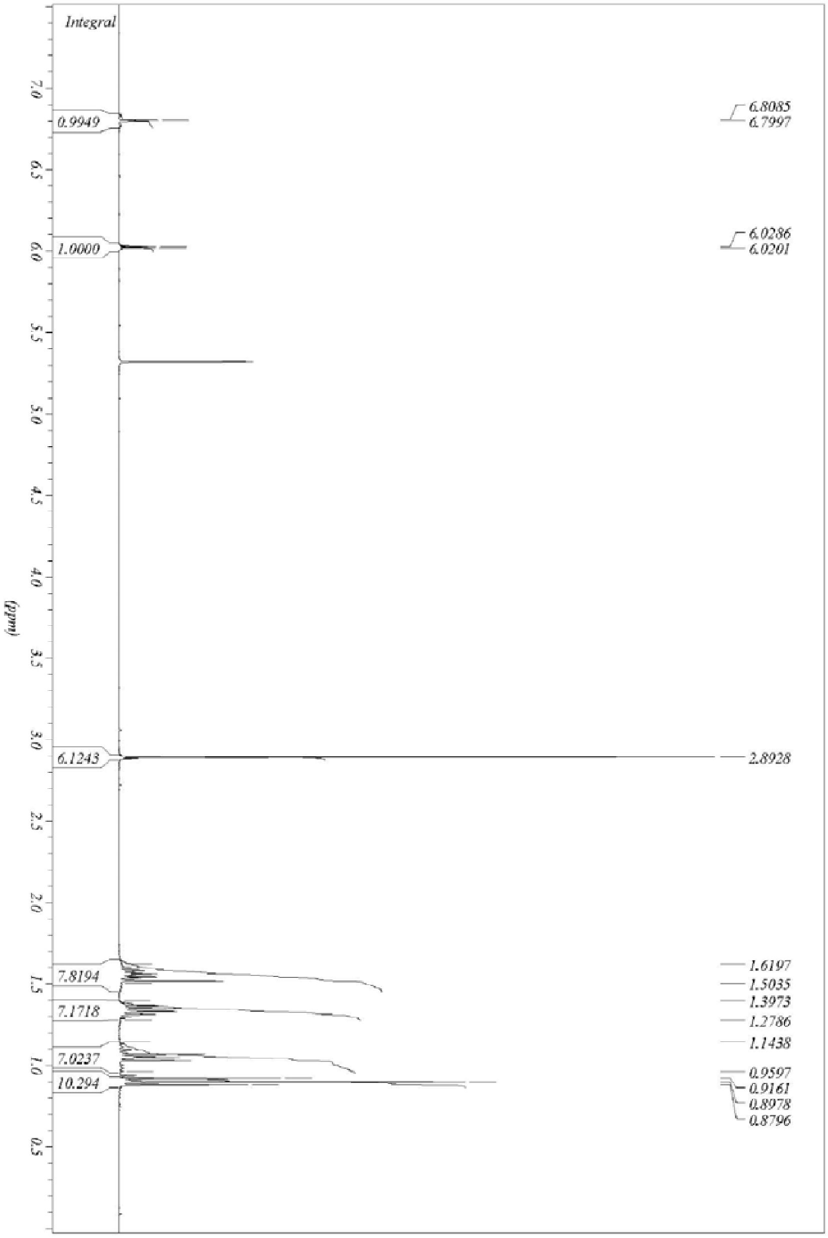

Fig. S 4 400 MHz ^{1}H NMR spectrum of **2e** in CD_2Cl_2.

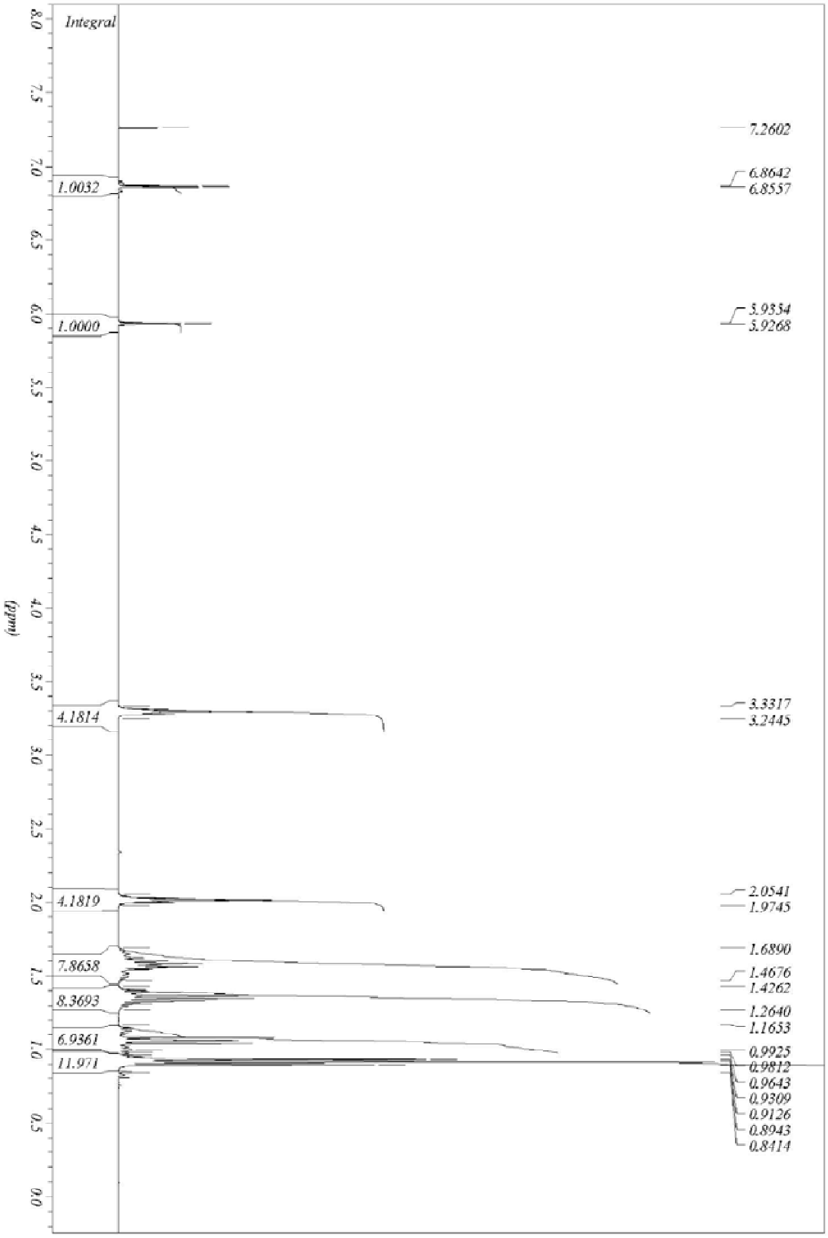

Fig. S 5 400 MHz ^{1}H NMR spectrum of **2f** in $CDCl_3$.

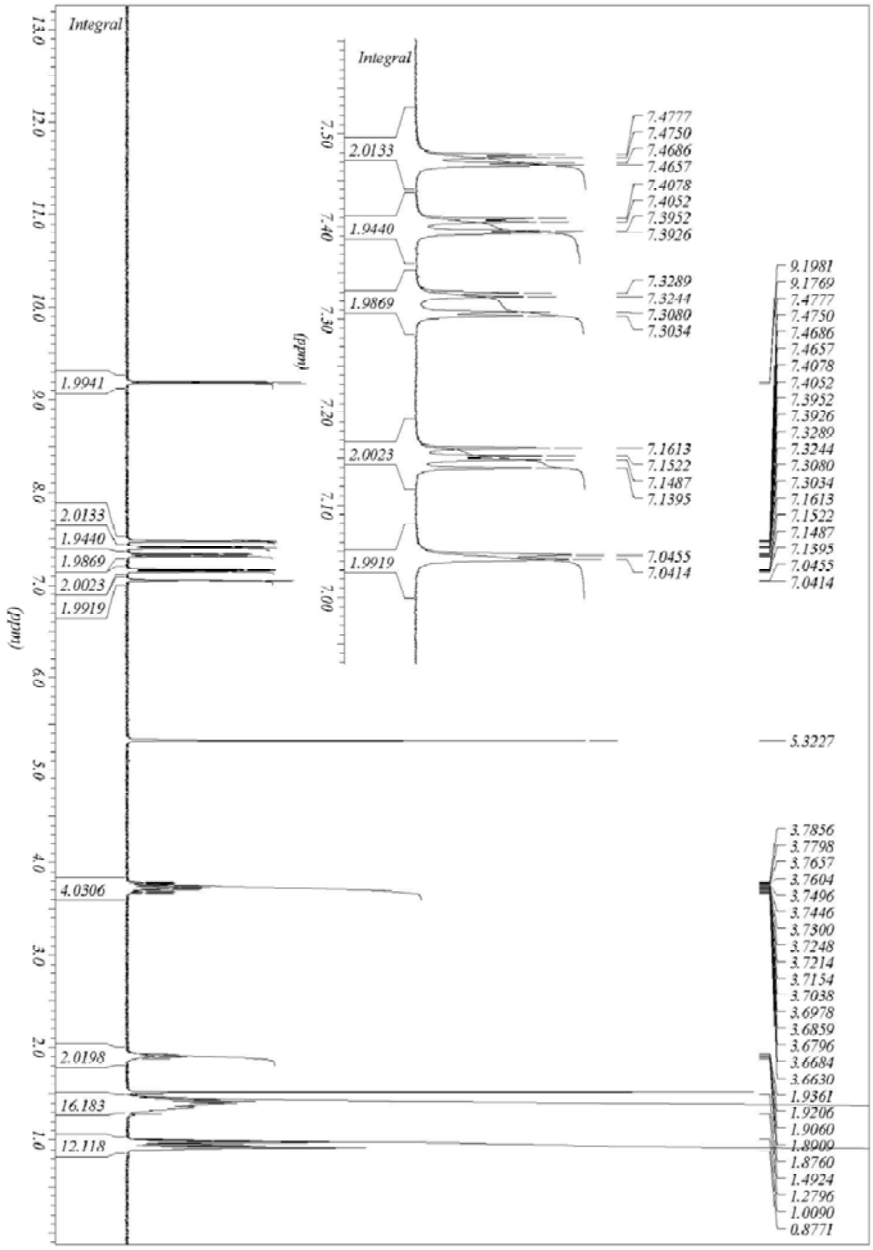

Fig. S 6 400 MHz ^{1}H NMR spectrum of **3a** in CD_2Cl_2.

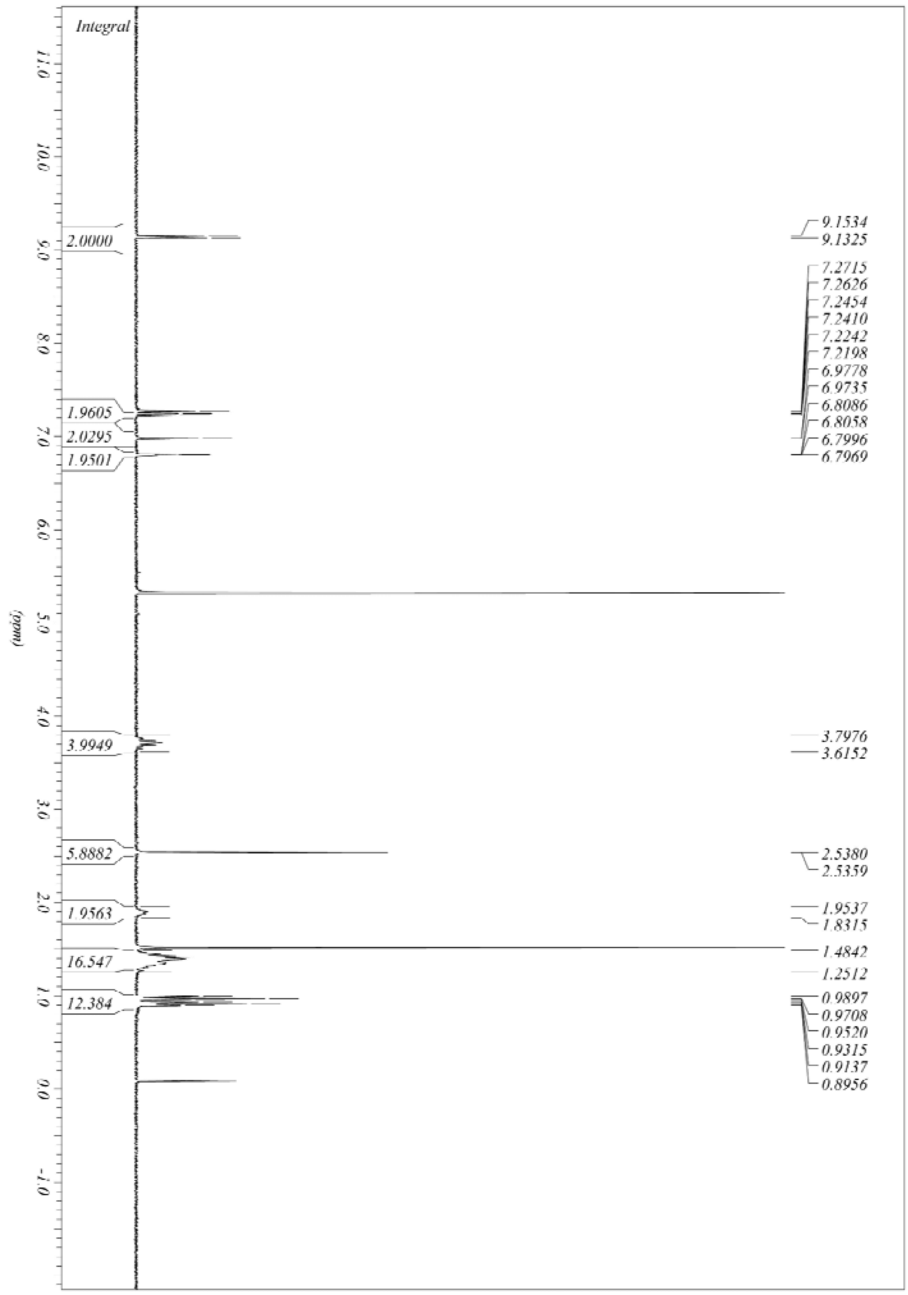

Fig. S 7 400 MHz [1]H NMR spectrum of **3b** in CD_2Cl_2.

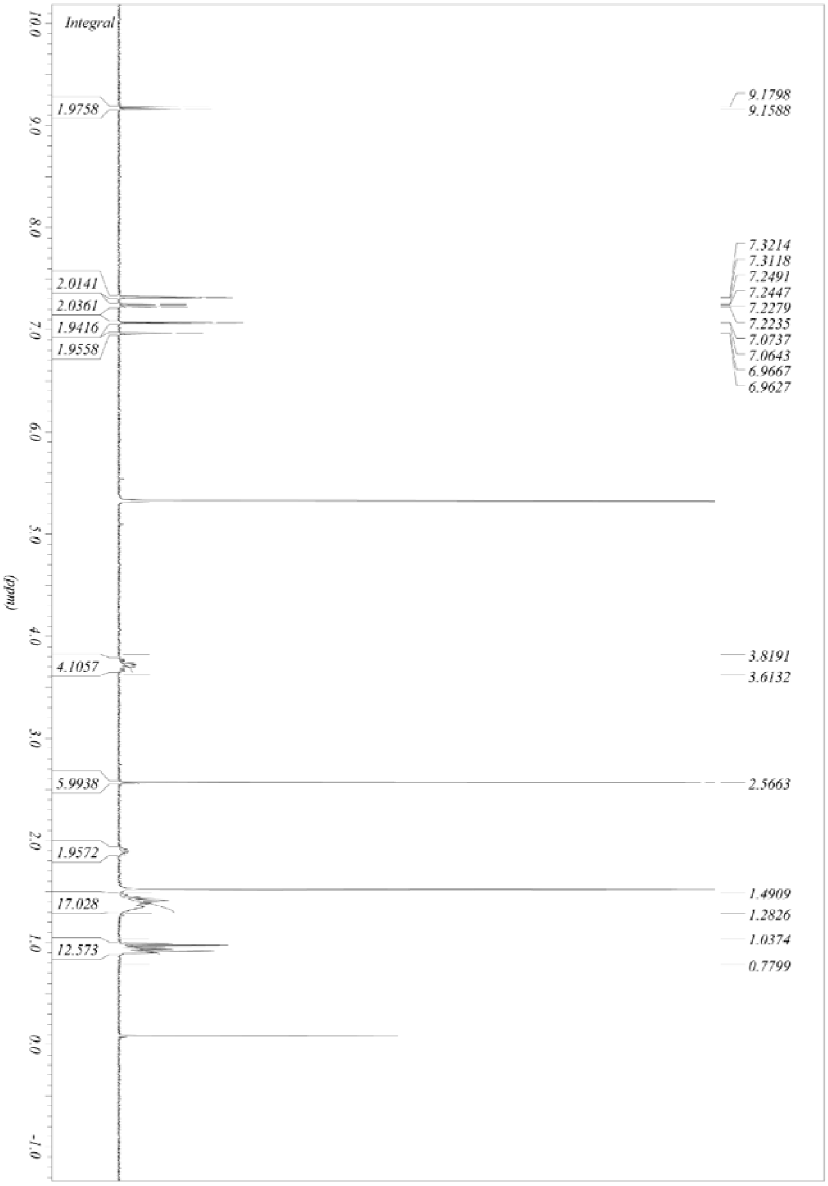

Fig. S 8 400 MHz ^{1}H NMR spectrum of **3c** in CD_2Cl_2.

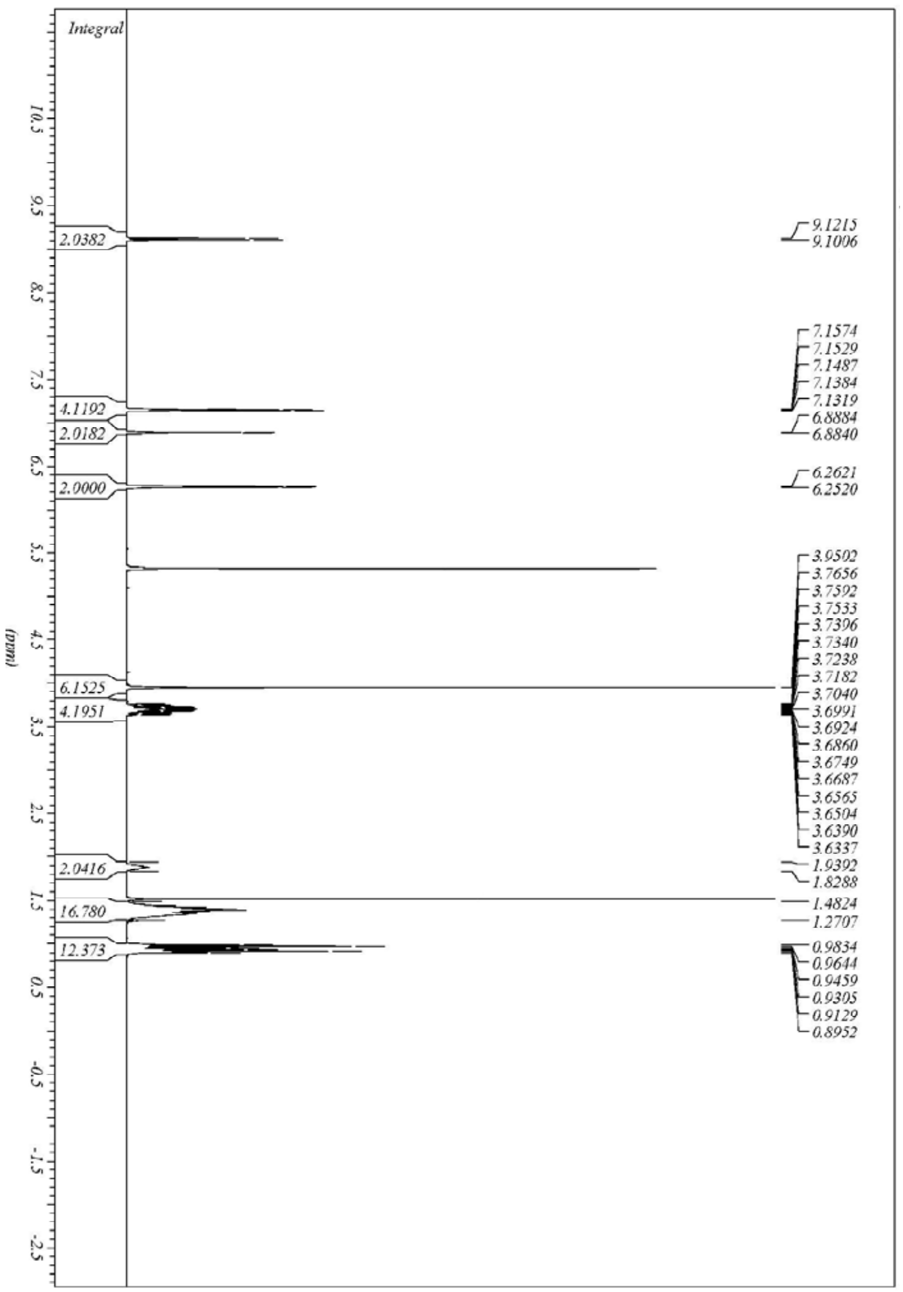

Fig. S 9 400 MHz ^{1}H NMR spectrum of **3d** in CD_2Cl_2.

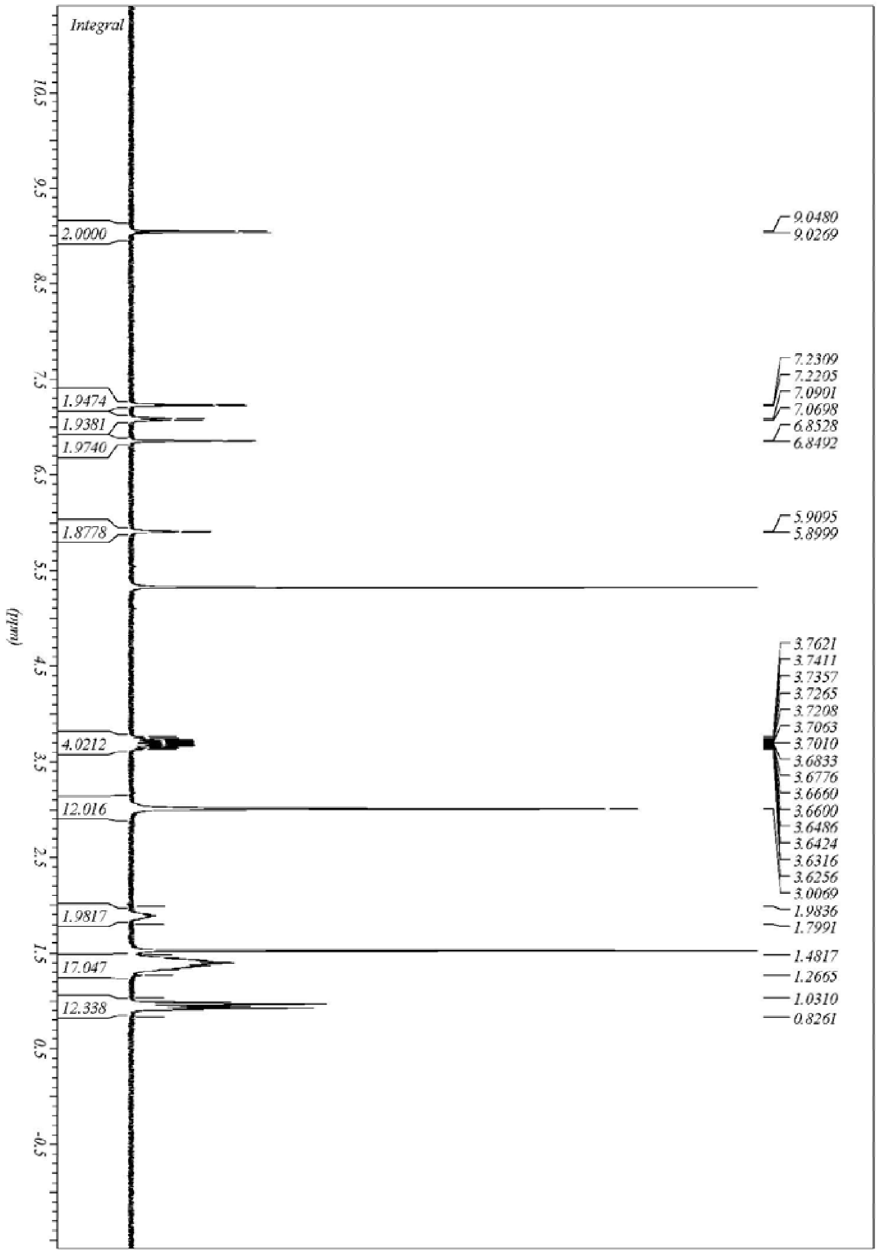

Fig. S 10 400 MHz ^{1}H NMR spectrum of **3e** in CD_2Cl_2.

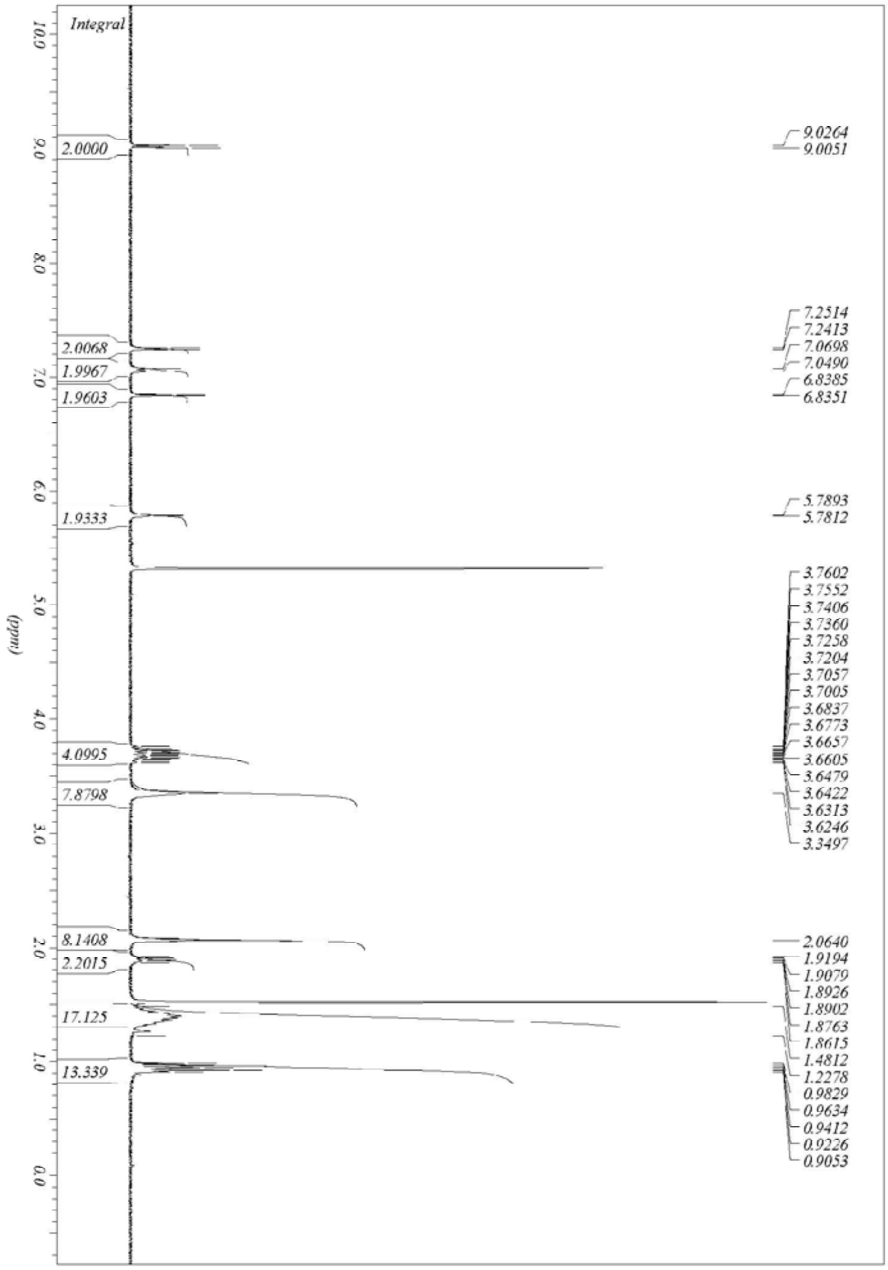

Fig. S 11 400 MHz [1]H NMR spectrum of **3f** in CD_2Cl_2.

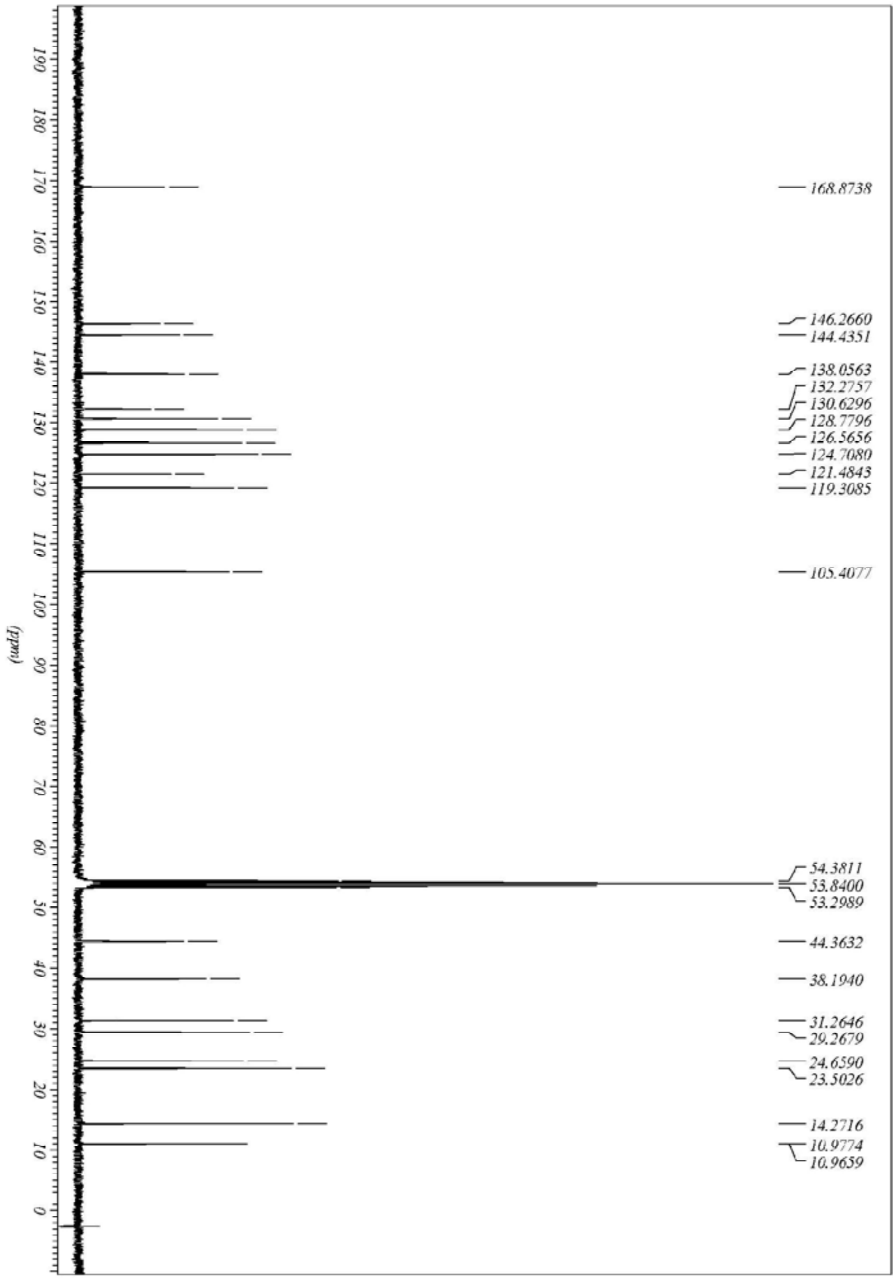

Fig. S 12 101 MHz ^{13}C NMR spectrum of **3a** in CD_2Cl_2.

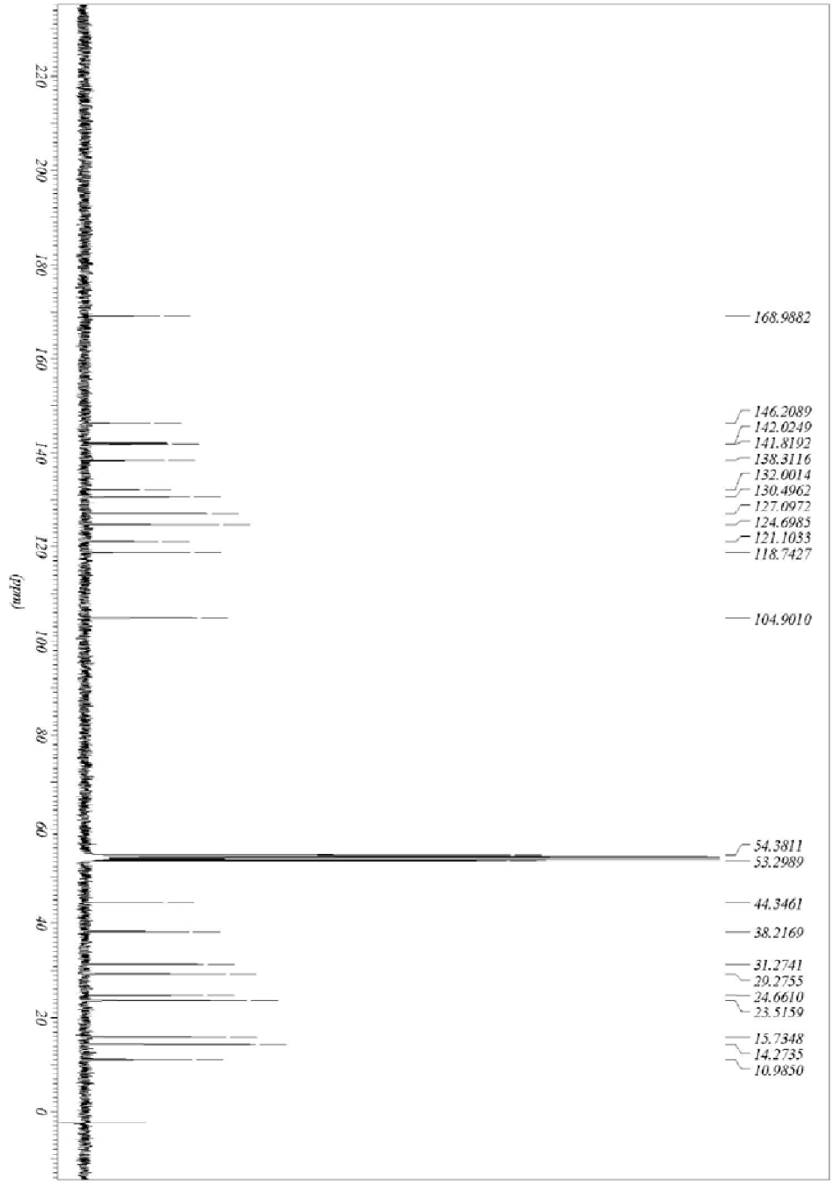

Fig. S 13 101 MHz ^{13}C NMR spectrum of **3b** in CD_2Cl_2.

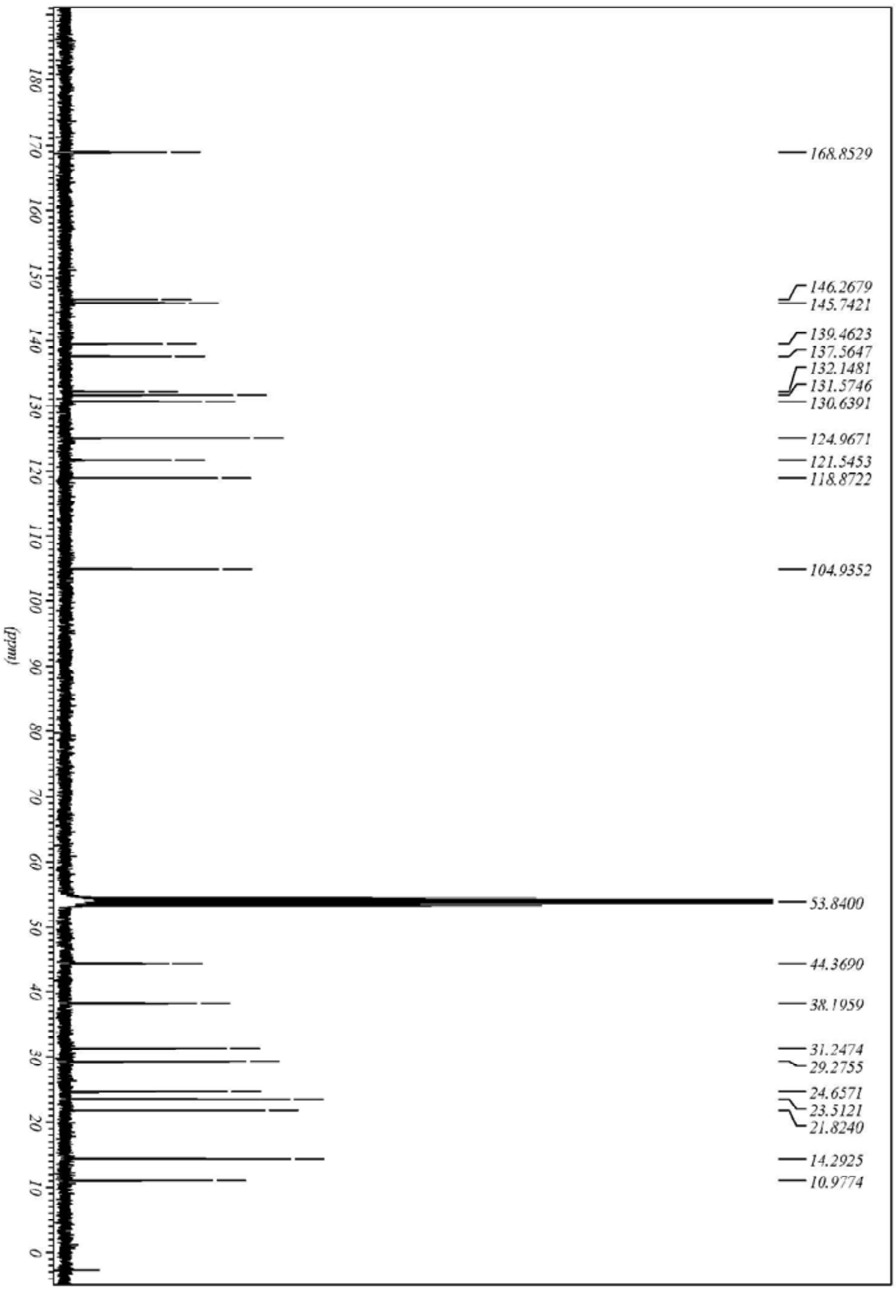

Fig. S 14 101 MHz 13C NMR spectrum of **3c** in CD_2Cl_2.

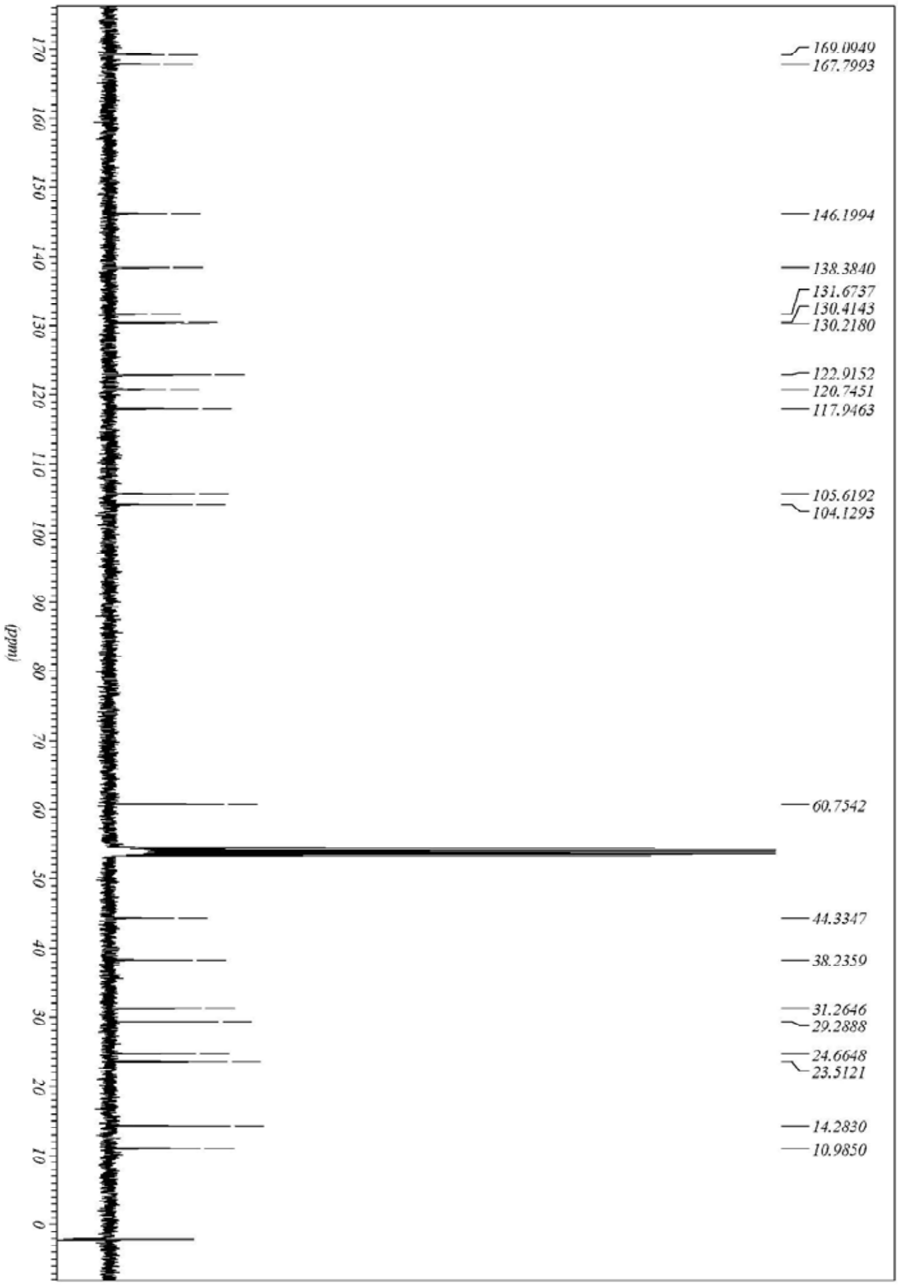

Fig. S 15 101 MHz ^{13}C NMR spectrum of **3d** in CD_2Cl_2.

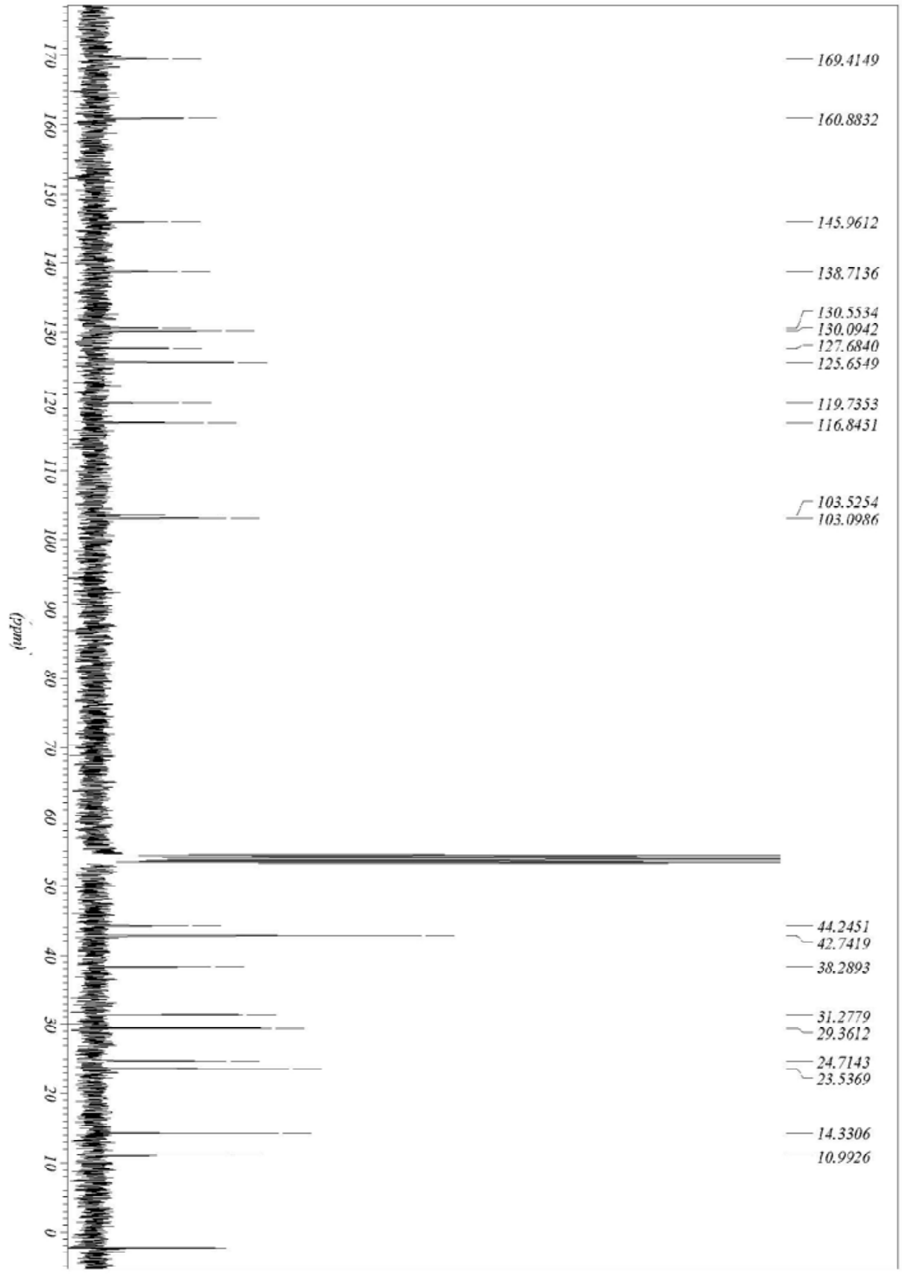

Fig. S 16 101 MHz ^{13}C NMR spectrum of **3e** in CD_2Cl_2.

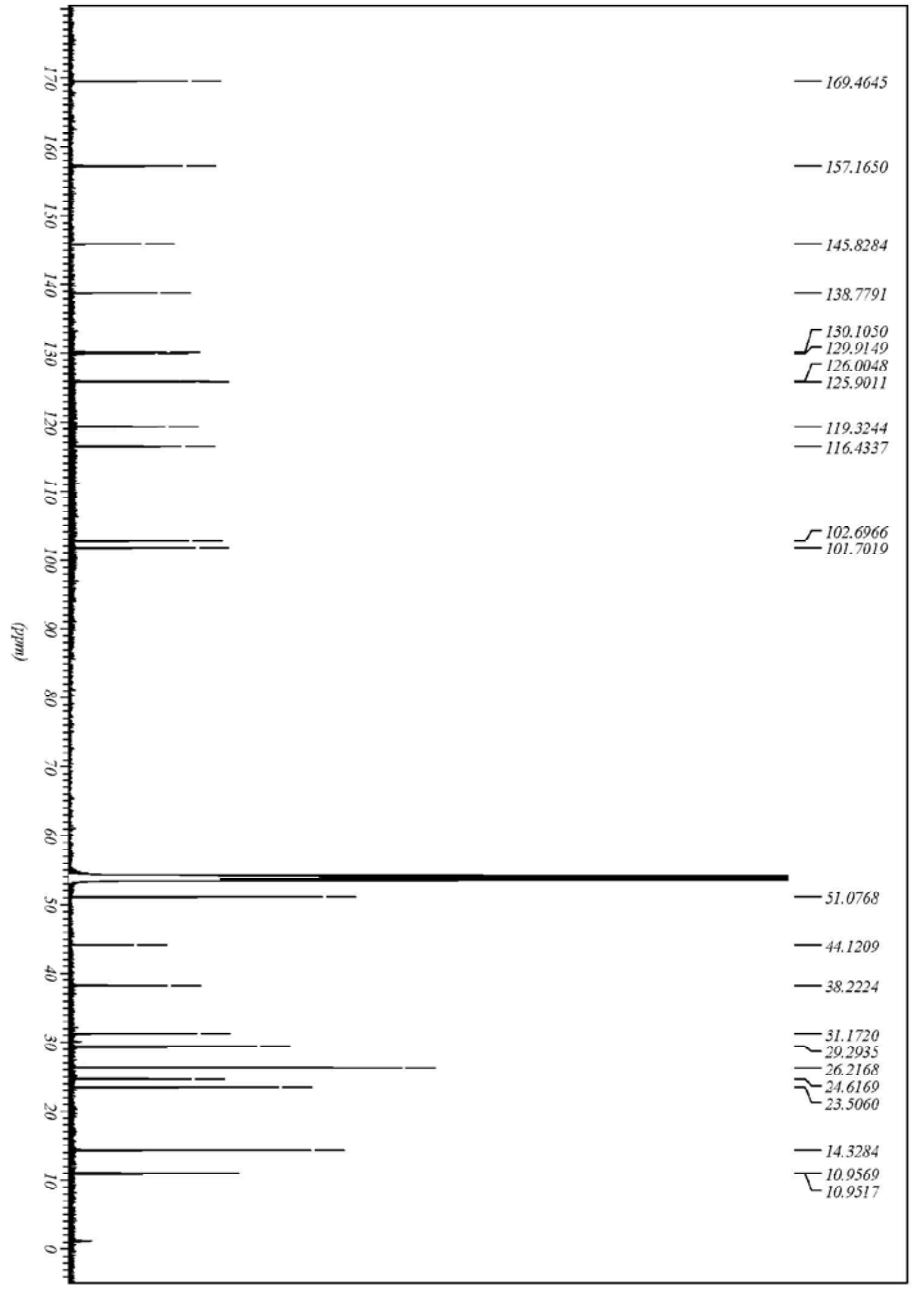

Fig. S 17 151 MHz ^{13}C NMR spectrum of **3f** in CD_2Cl_2.

4. References

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