Electronic Supplementary Material (ESI) for Dalton Transactions.


Supplementary Information

# Half-sandwich iron(II) complexes with protic acyclic diaminocarbene ligands: synthesis, deprotonation and metalation reactions

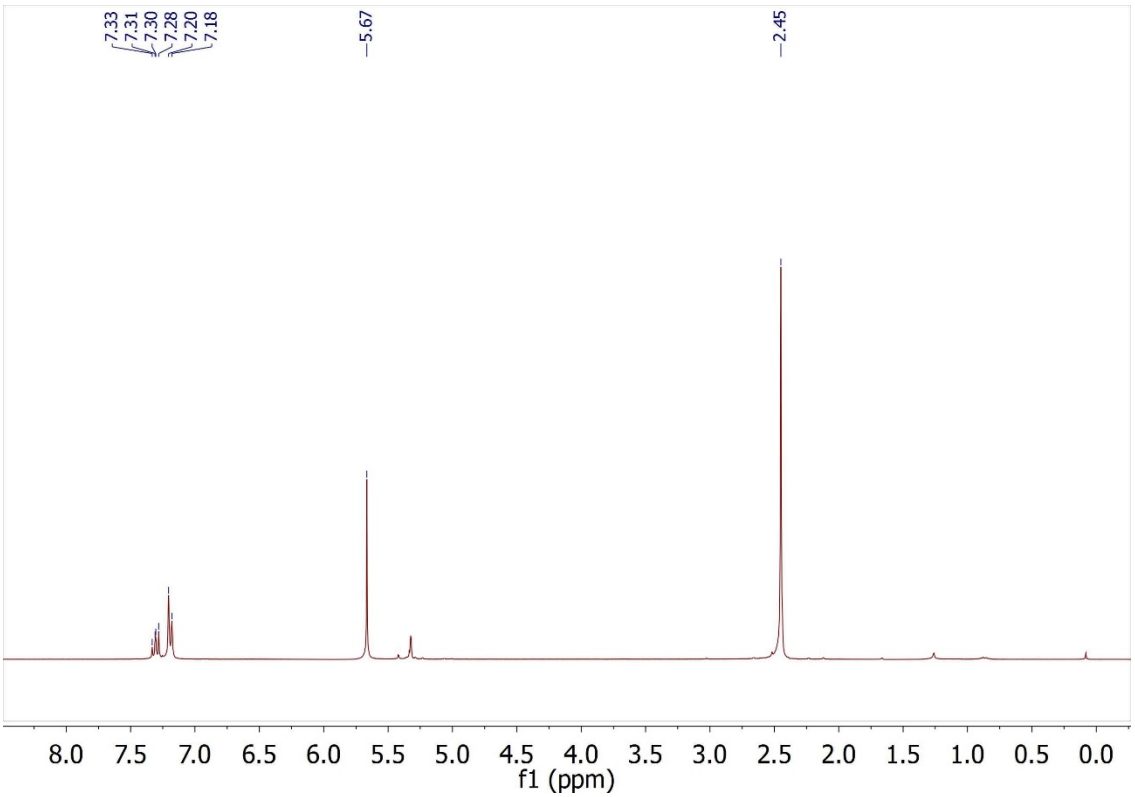
Javier Ruiz, Lucía García, Marilín Vivanco, Daniel Sol, and Santiago García-Granda

- Table S1 containing crystal data and structure refinements for the compounds **12a**, [**14**]$PF_6$ and [**16**]$PF_6$.
- NMR spectra of the new compounds.

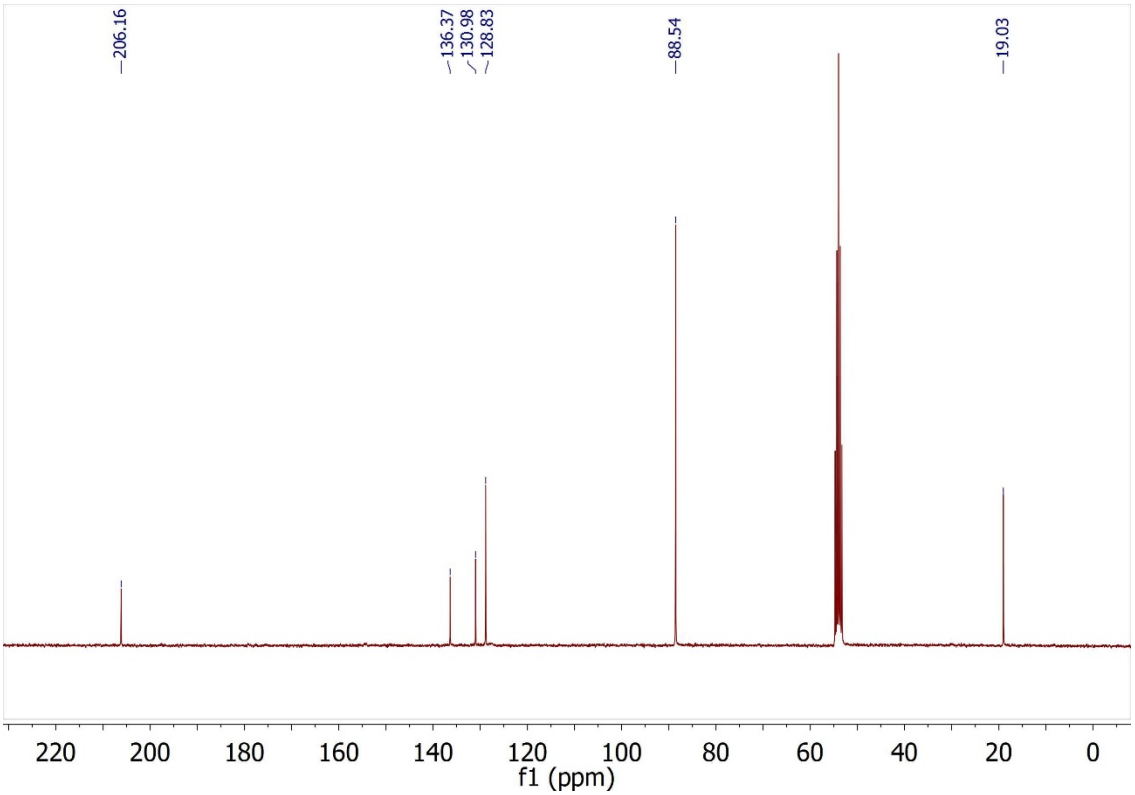
Table S1. Crystal data and structure refinements for the compounds **12a**, [**14**]$PF_6$ and [**16**]$PF_6$.

| | **12a** | [**14**]$PF_6$ | [**16**]$PF_6$* |
|---|---|---|---|
| Empirical formula | $C_{43}H_{41}N_3OPFeAu$ | $C_{44}H_{49}N_4OFeRuF_6P$ | $C_{48}H_{58}N_4O_2F_6PClFeRu$ |
| Formula weight | 899.57 | 951.76 | 1060.32 |
| Temperature/K | 100.0(2) | 120.0(1) | 150.0(2) |
| Crystal system | monoclinic | triclinic | orthorhombic |
| Space group | $P2_1/c$ | P-1 | $Pna2_1$ |
| a/Å | 14.9700(4) | 10.2798(9) | 25.0135(6) |
| b/Å | 11.9984(3) | 12.5670(10) | 10.8950(3) |
| c/Å | 23.0740(6) | 16.933(2) | 17.0457(4) |
| α/° | 90 | 102.774(8) | 90 |
| β/° | 115.888(3) | 99.633(7) | 90 |
| γ/° | 90 | 92.700(7) | 90 |
| Volume/$Å^3$ | 3728.56(19) | 2095.2(4) | 4645.3(2) |
| Z | 4 | 2 | 4 |
| $\rho_{calc}g/cm^3$ | 1.603 | 1.509 | 1.5160 |
| $\mu/mm^{-1}$ | 11.103 | 6.620 | 0.797 |
| F(000) | 1792.0 | 976.0 | 2184.0 |
| Crystal size/$mm^3$ | 0.155 × 0.089 × 0.033 | 0.07 × 0.04 × 0.02 | 0.152× 0.033× 0.030 |
| Radiation | CuKα (λ = 1.54184) | CuKα (λ = 1.5418) | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 8.174 to 141.39 | 7.24 to 141.49 | 6.52 to 62.96 |
| Index ranges | -18 ≤ h ≤ 16, -14 ≤ k ≤ 14, -20 ≤ l ≤ 27 | -12 ≤ h ≤ 12, -12 ≤ k ≤ 15, -20 ≤ l ≤ 20 | -35 ≤ h ≤ 21, -15 ≤ k ≤ 14, -23 ≤ l ≤ 24 |
| Reflections collected | 17805 | 14713 | 22674 |
| Independent reflections | 7024 [$R_{int}$ = 0.0344, $R_{sigma}$ = 0.0387] | 7815 [$R_{int}$ = 0.0937, $R_{sigma}$ = 0.1509] | 11236 [$R_{int}$ = 0.0591, $R_{sigma}$ = 0.1001] |
| Data/restraints/parameters | 7024/0/435 | 7815/0/533 | 11236/1/589 |
| Goodness-of-fit on $F^2$ | 1.163 | 0.892 | 1.058 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0636, $wR_2$ = 0.1498 | $R_1$ = 0.0539, $wR_2$ = 0.1085 | $R_1$ = 0.0632, $wR_2$ = 0.0944 |
| Final R indexes [all data] | $R_1$ = 0.0714, $wR_2$ = 0.1565 | $R_1$ = 0.0938, $wR_2$ = 0.1298 | $R_1$ = 0.0935, $wR_2$ = 0.1039 |
| Largest diff. peak/hole / e $Å^{-3}$ | 2.91/-0.68 | 0.69/-0.72 | 0.82/-0.71 |

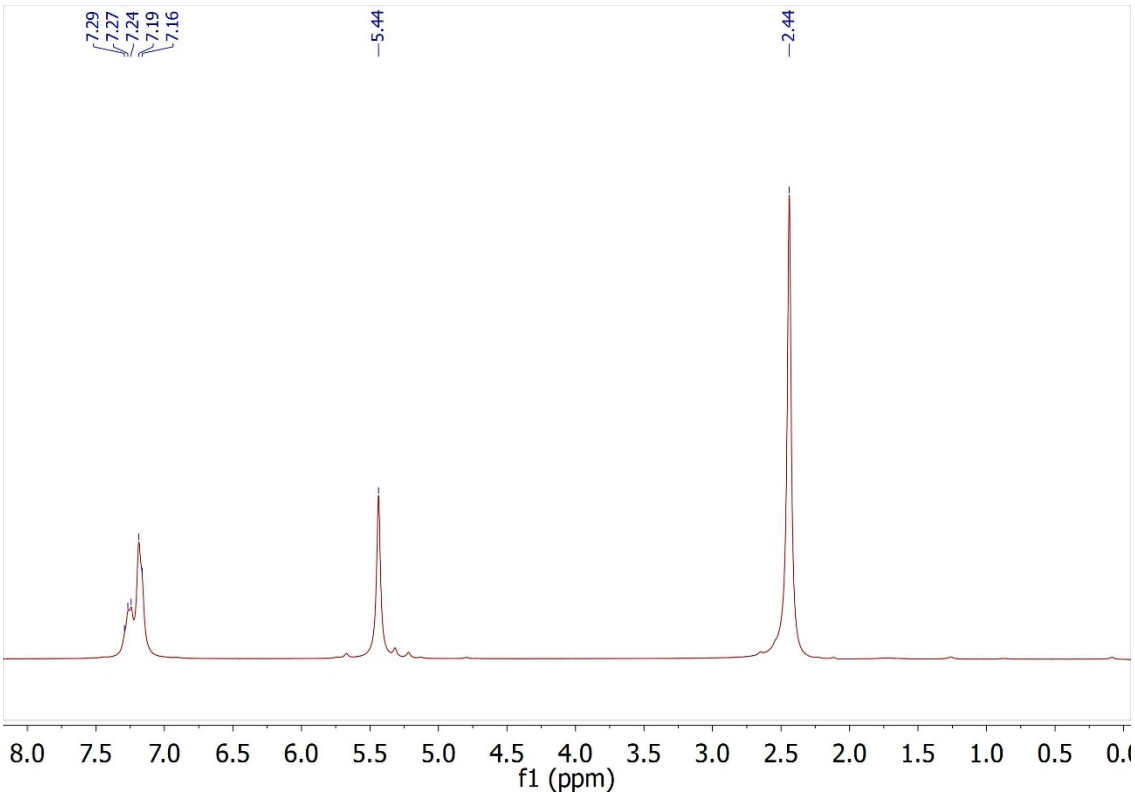
*structure reported: CCDC code: 951024



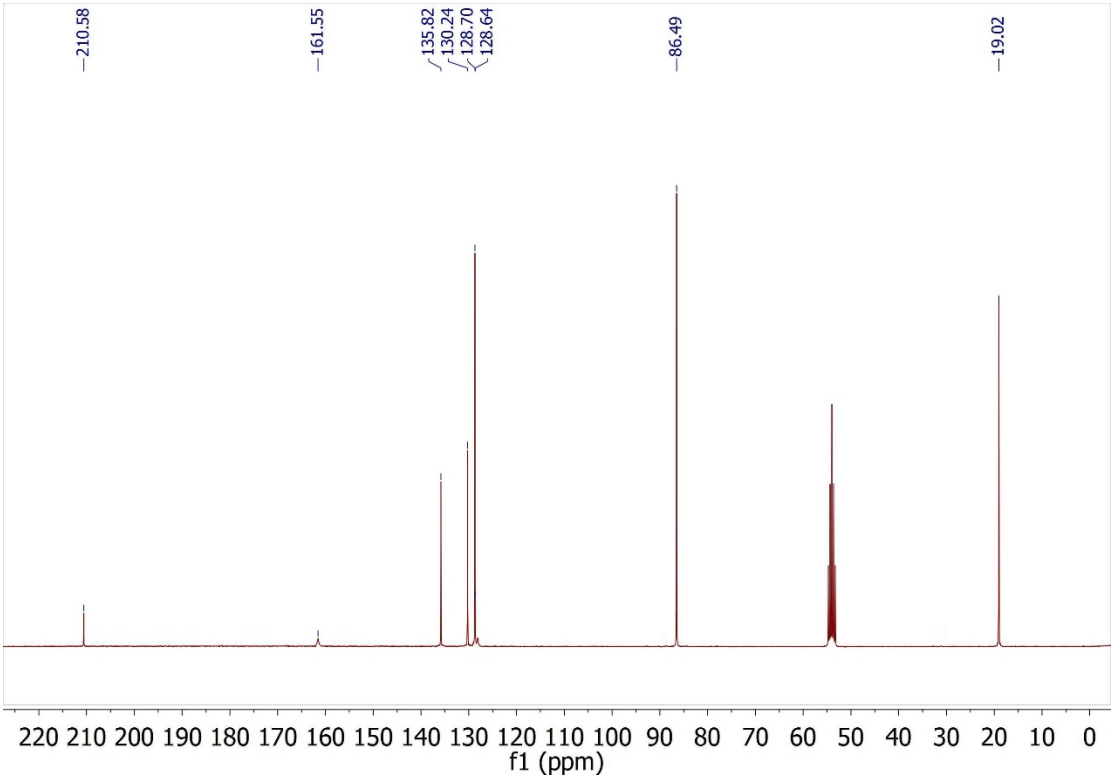

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **1**.



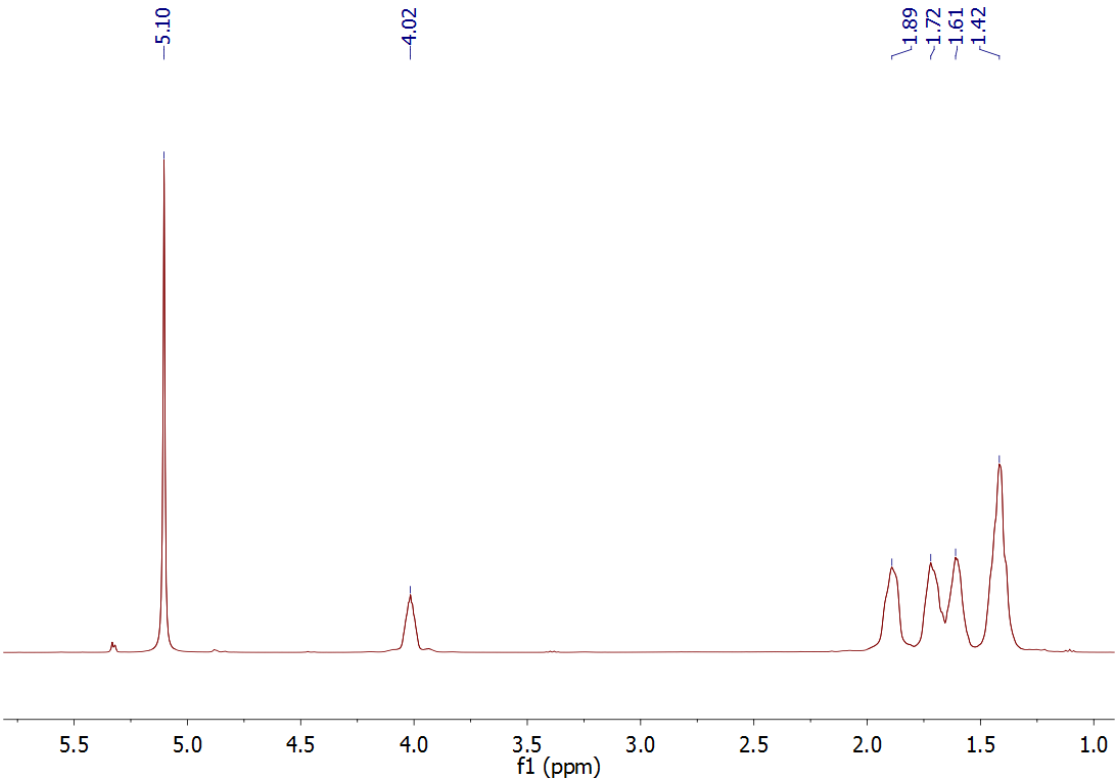

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **1**.



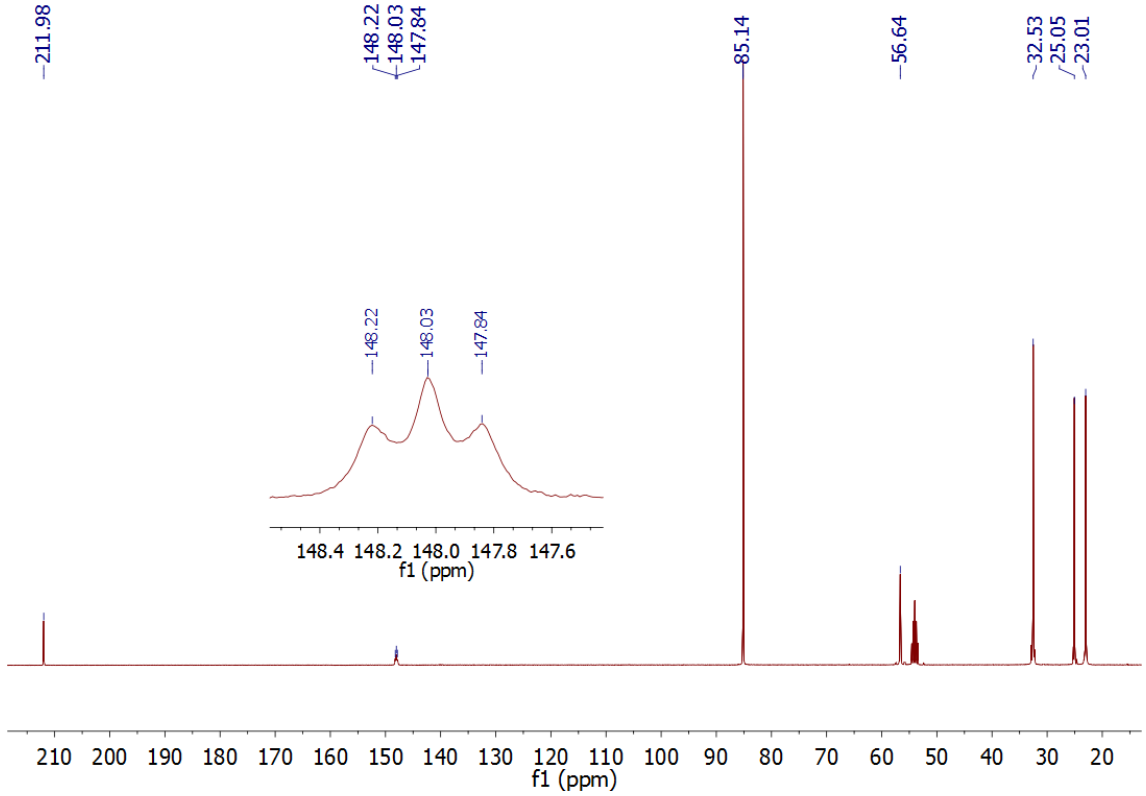

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **2a**.



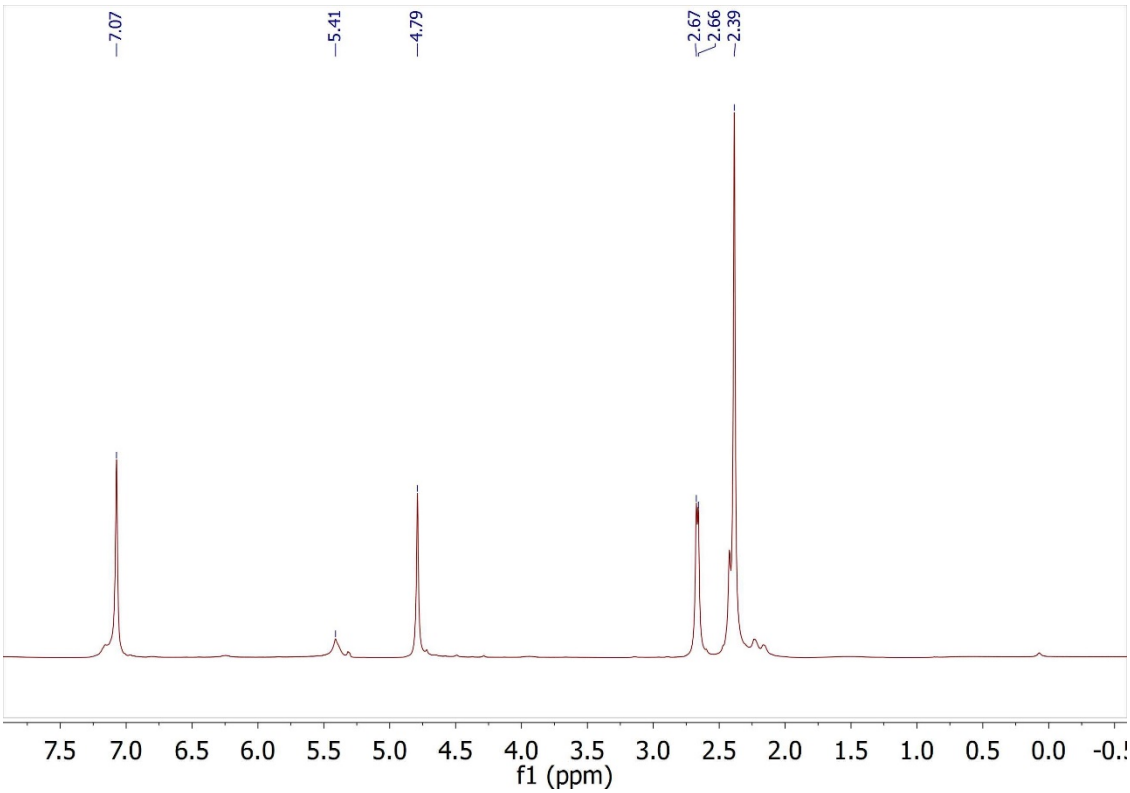

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **2a**.



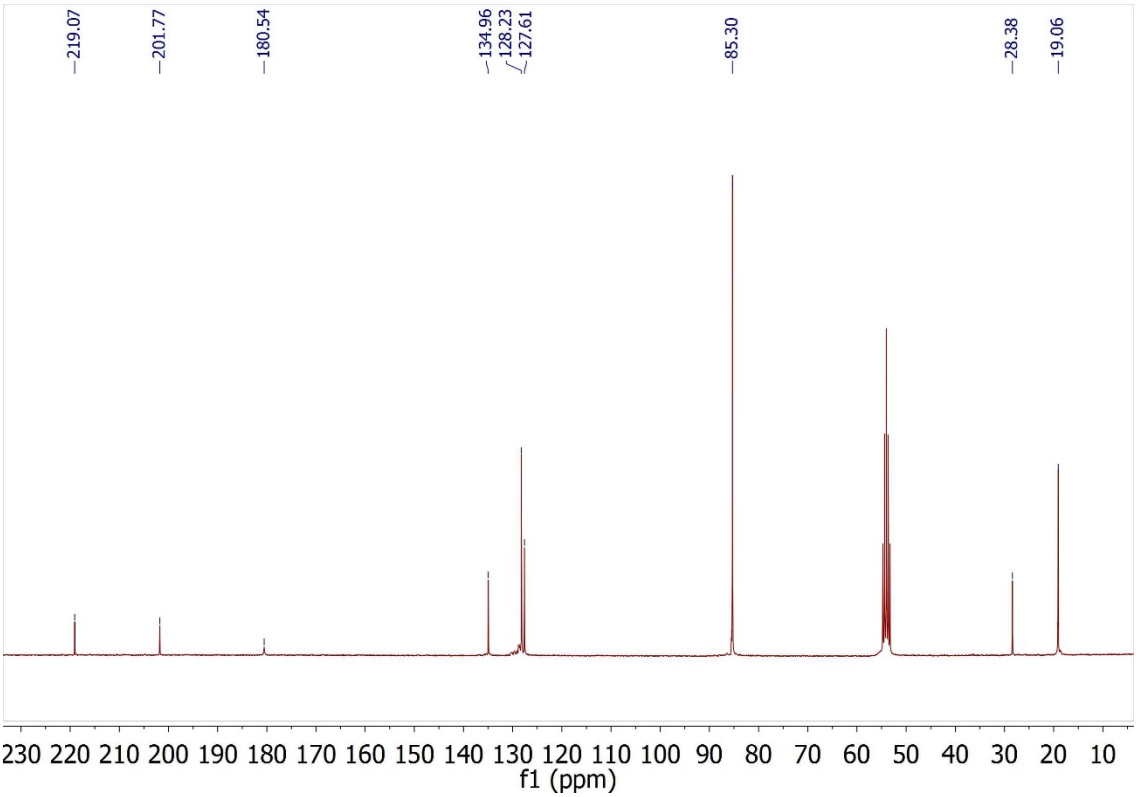

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **2b**



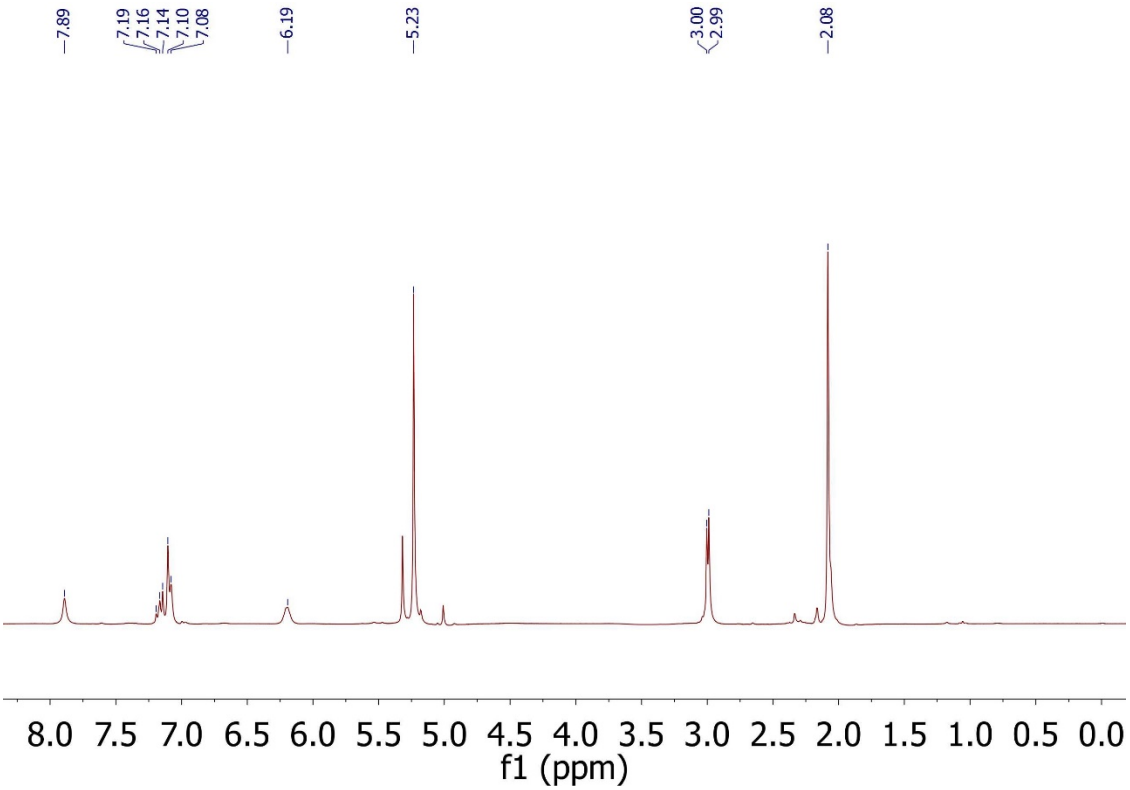

$^{13}$C{$^{1}$H} NMR ($CD_2Cl_2$, 298K) spectra of compound **2b**



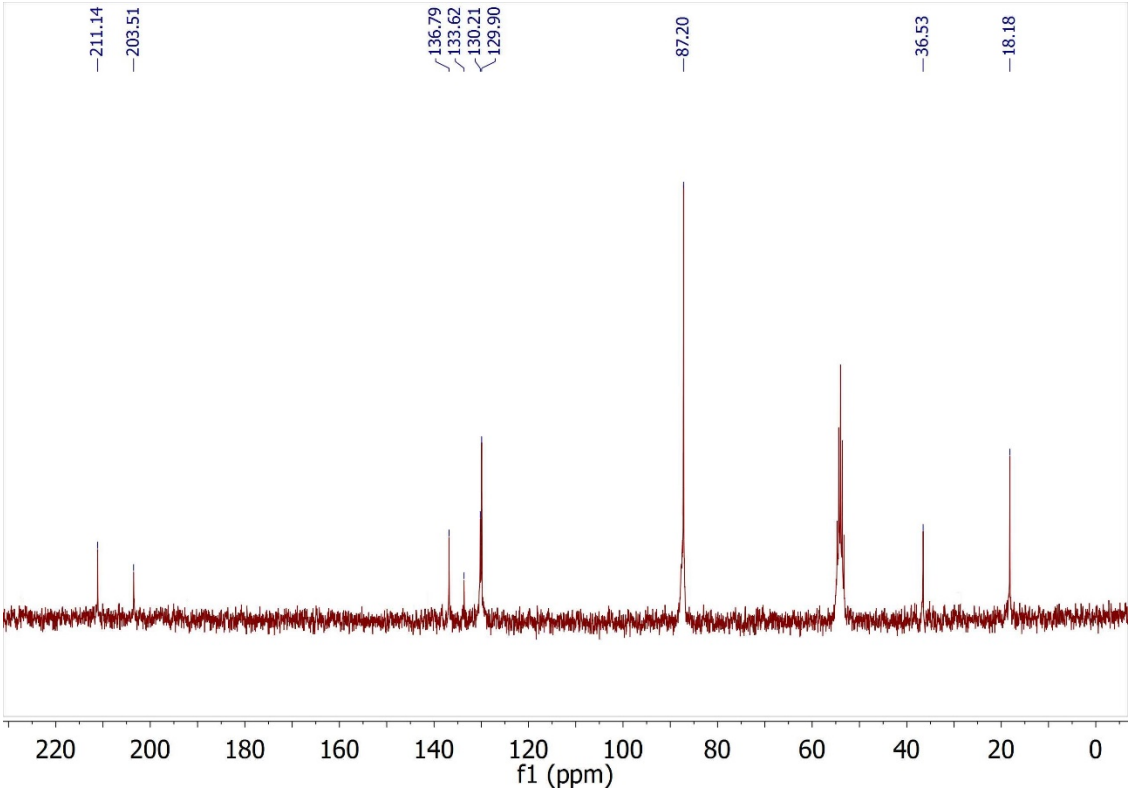

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **3**.



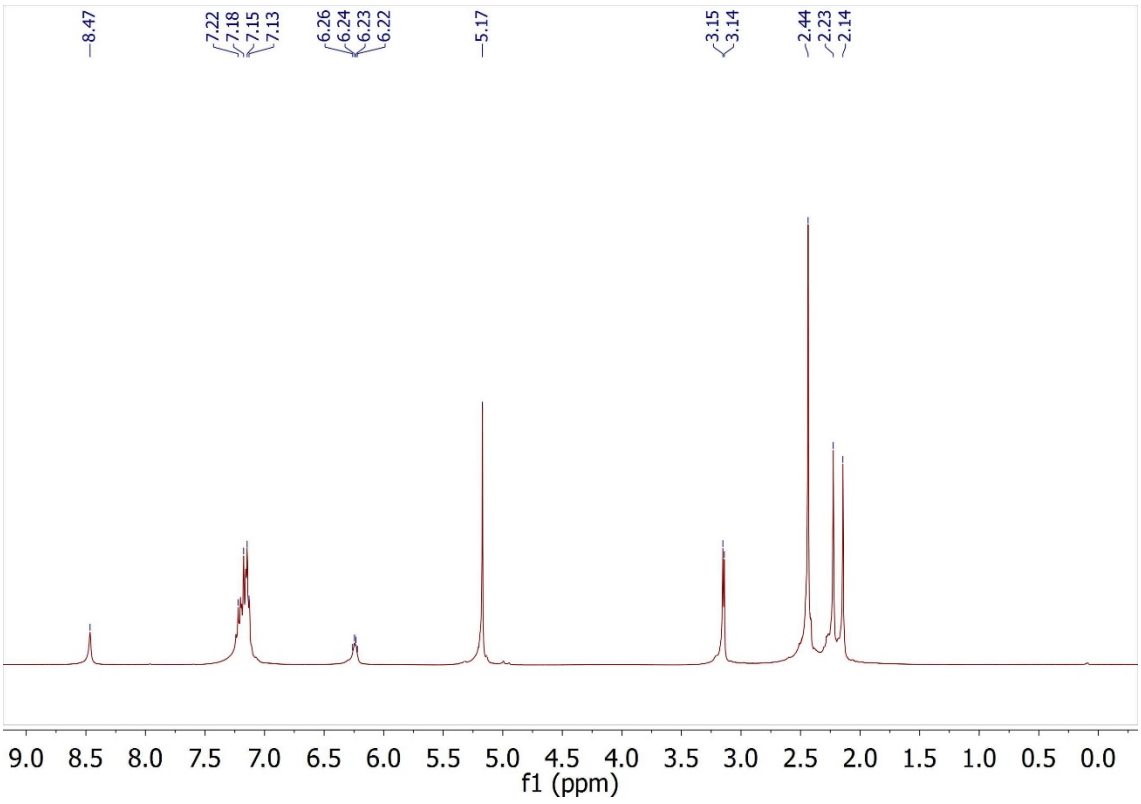

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **3**.



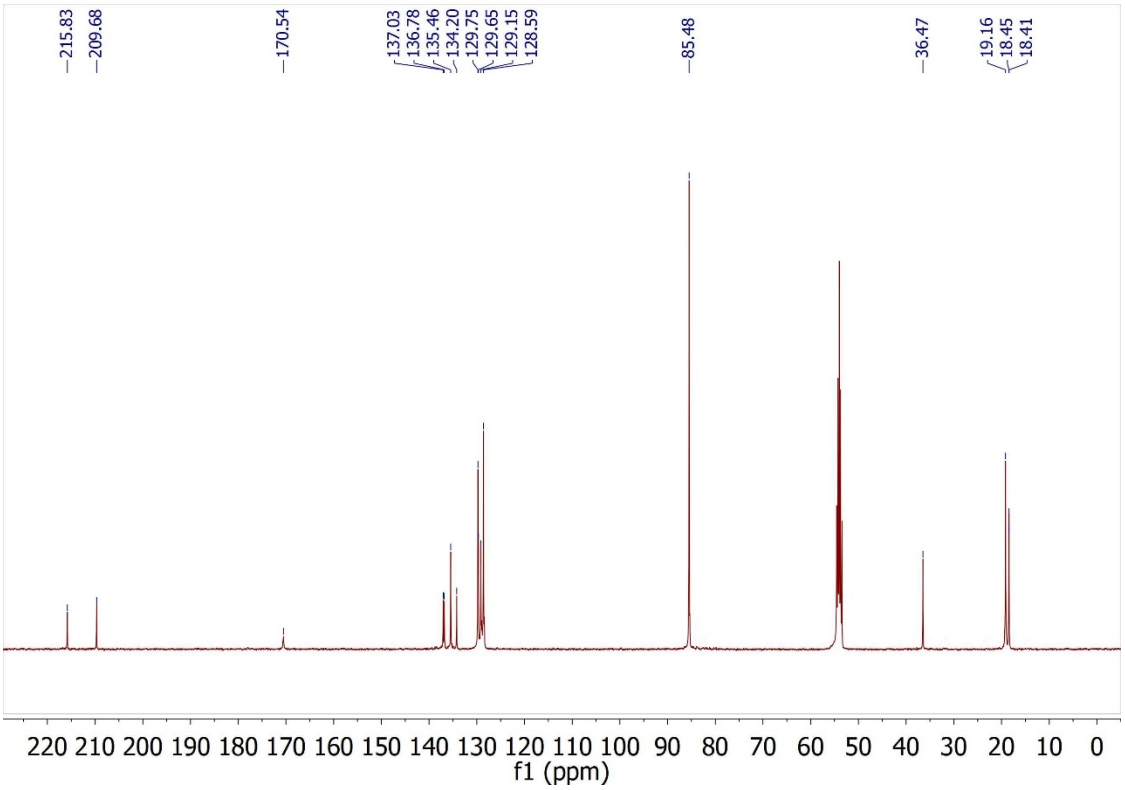

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **4**.



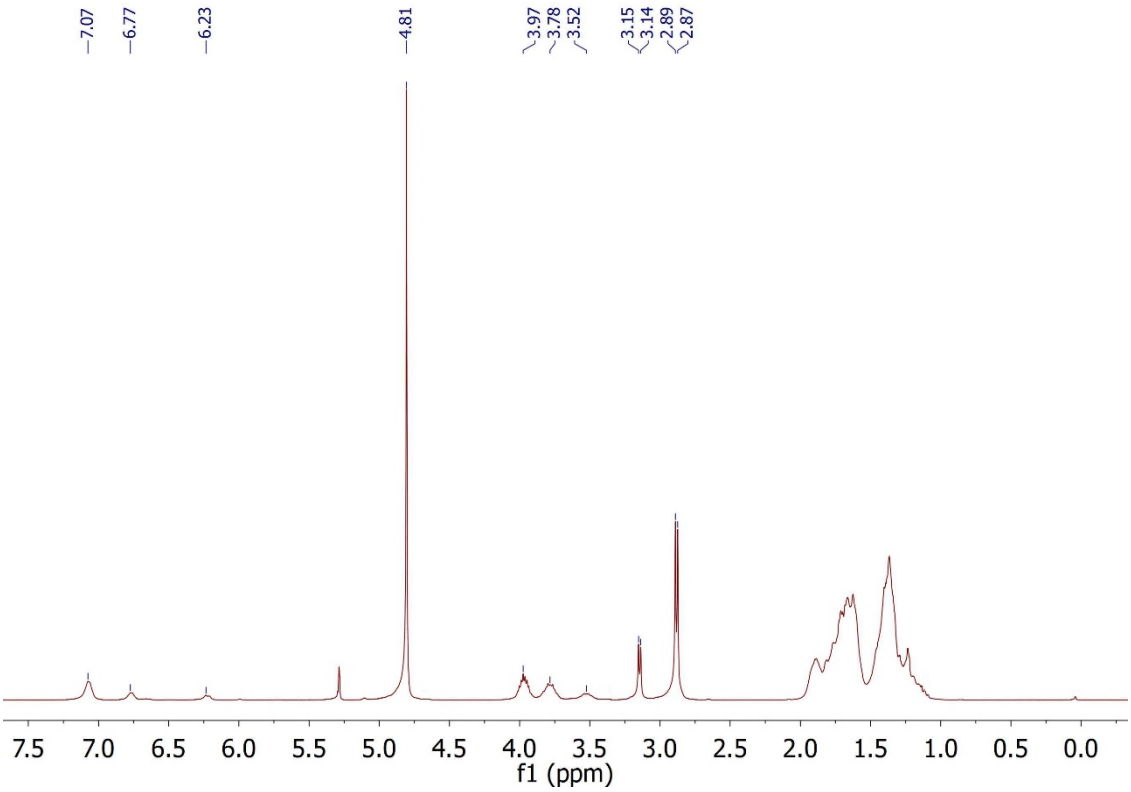

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **4**.



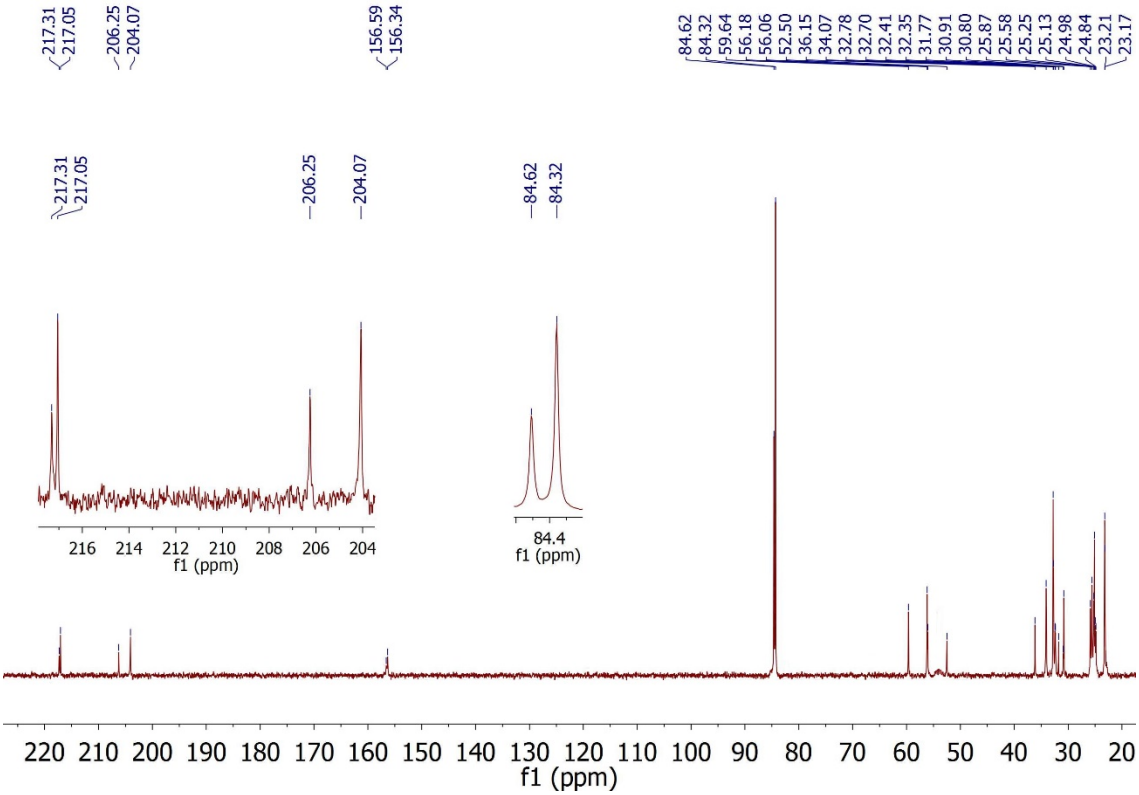

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **5a**.



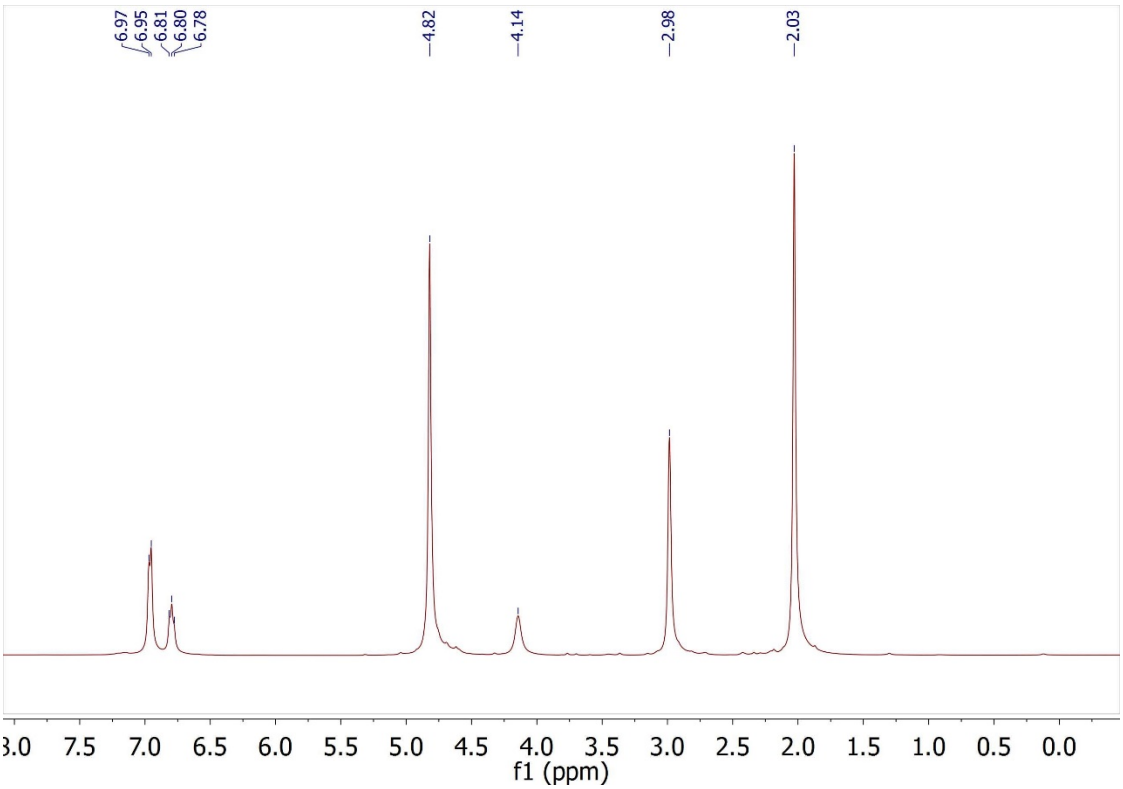

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **5a**.



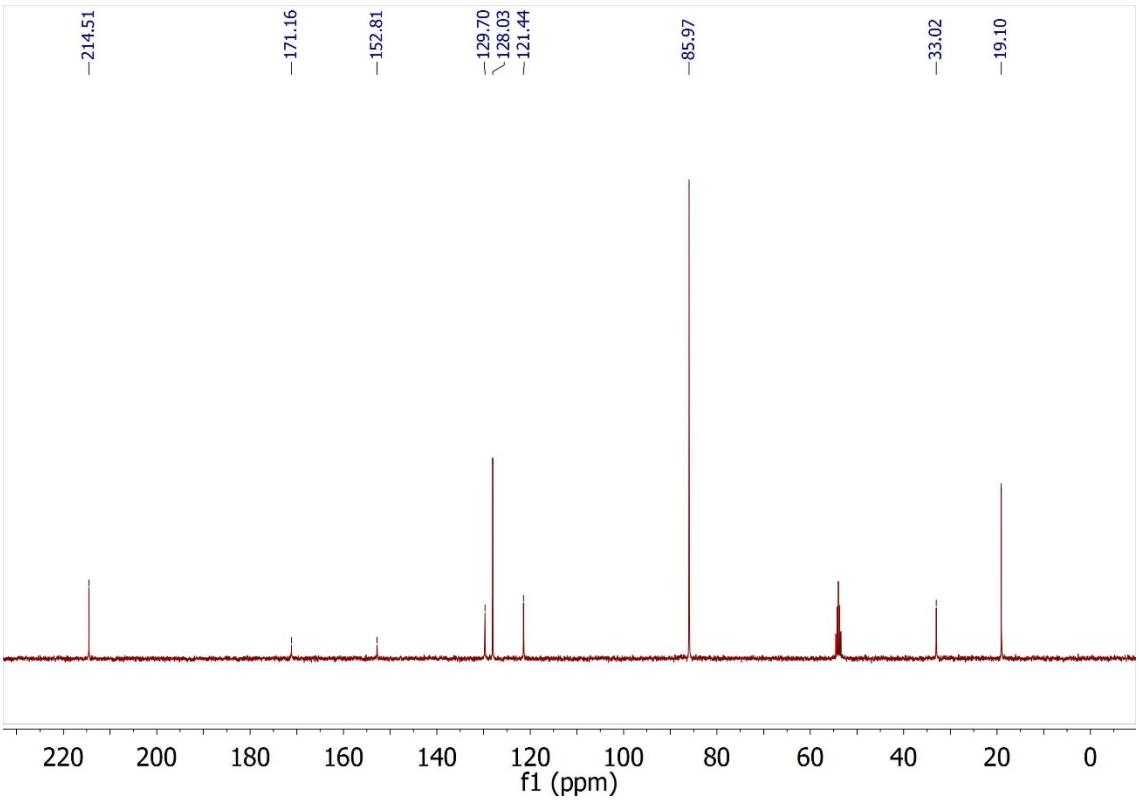

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **5b**.



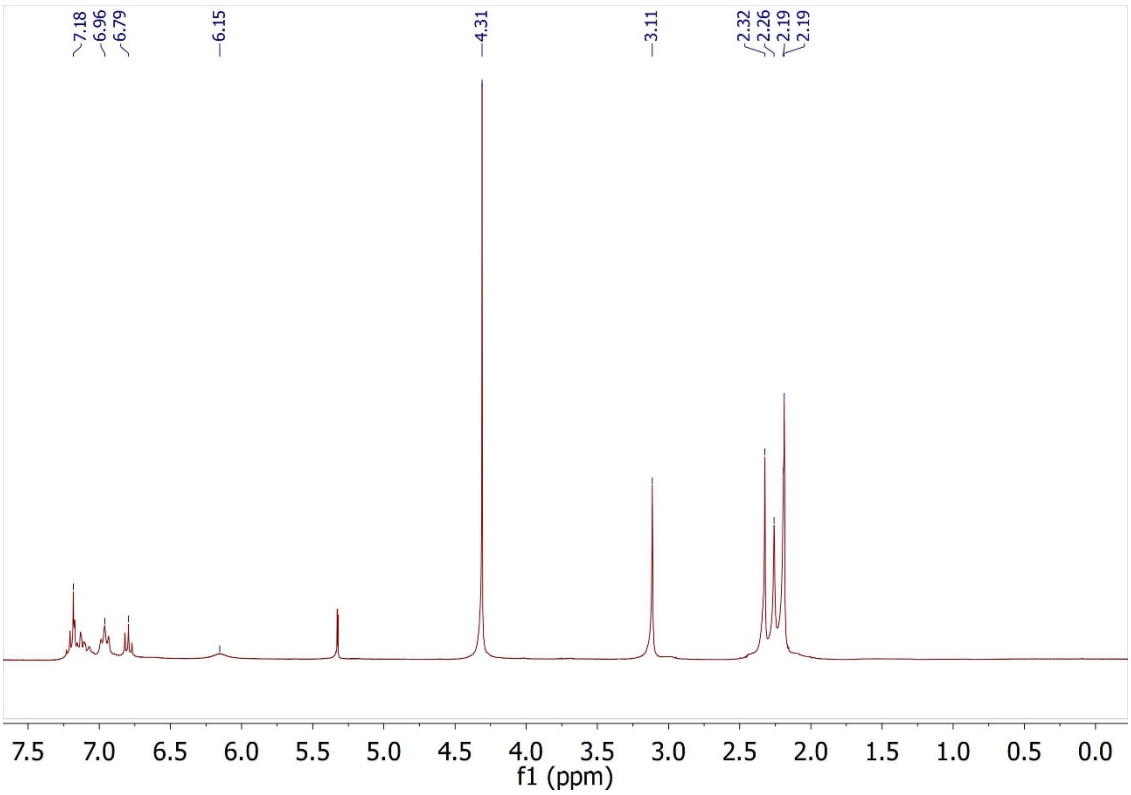

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **5b**.



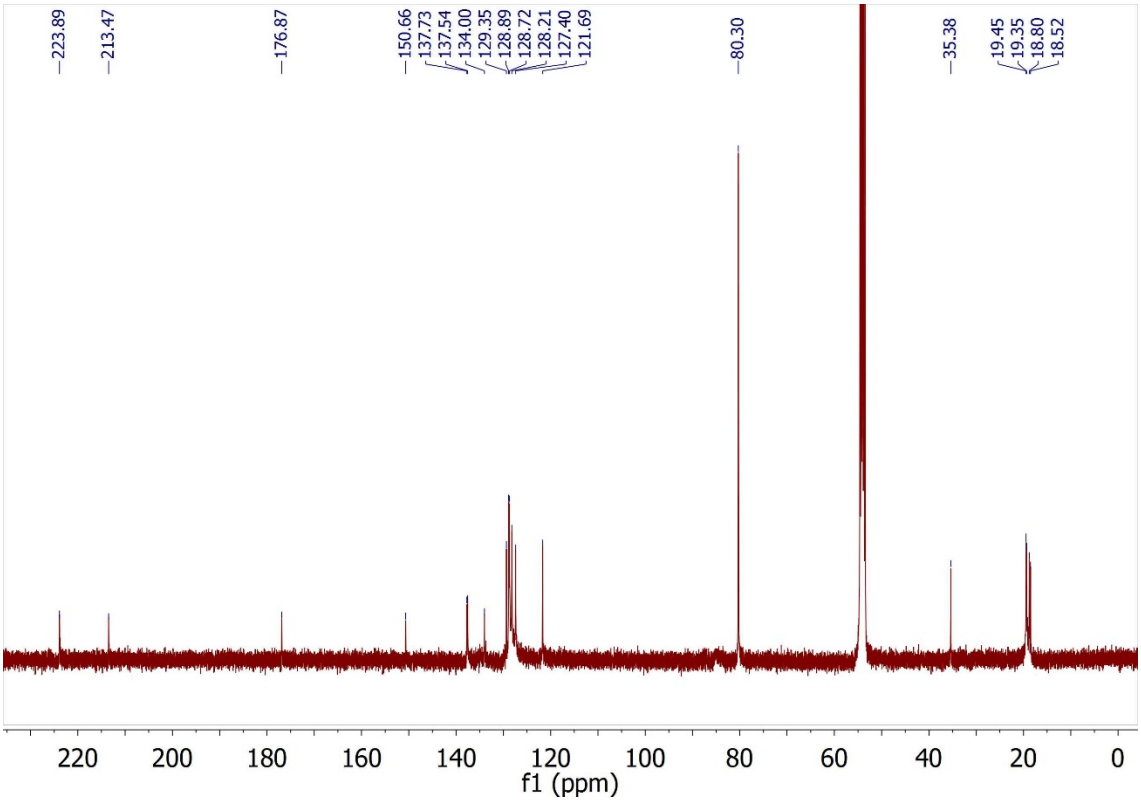

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **6**.



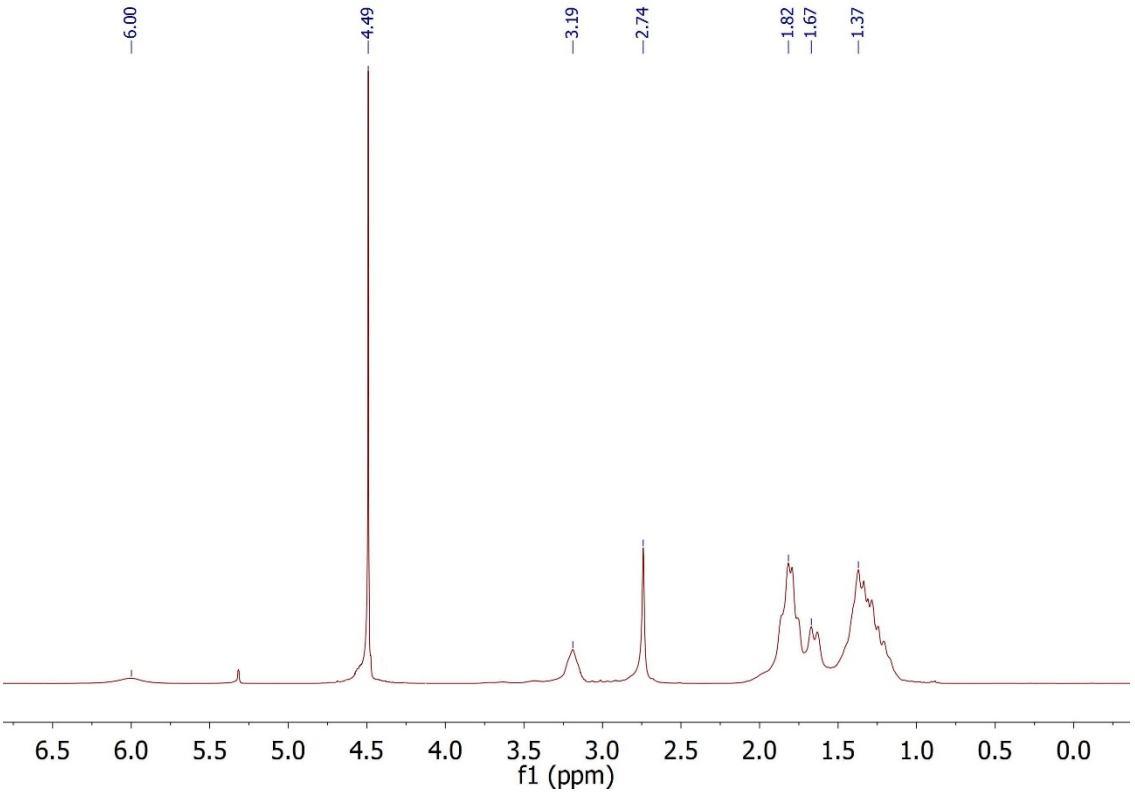

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **6**.



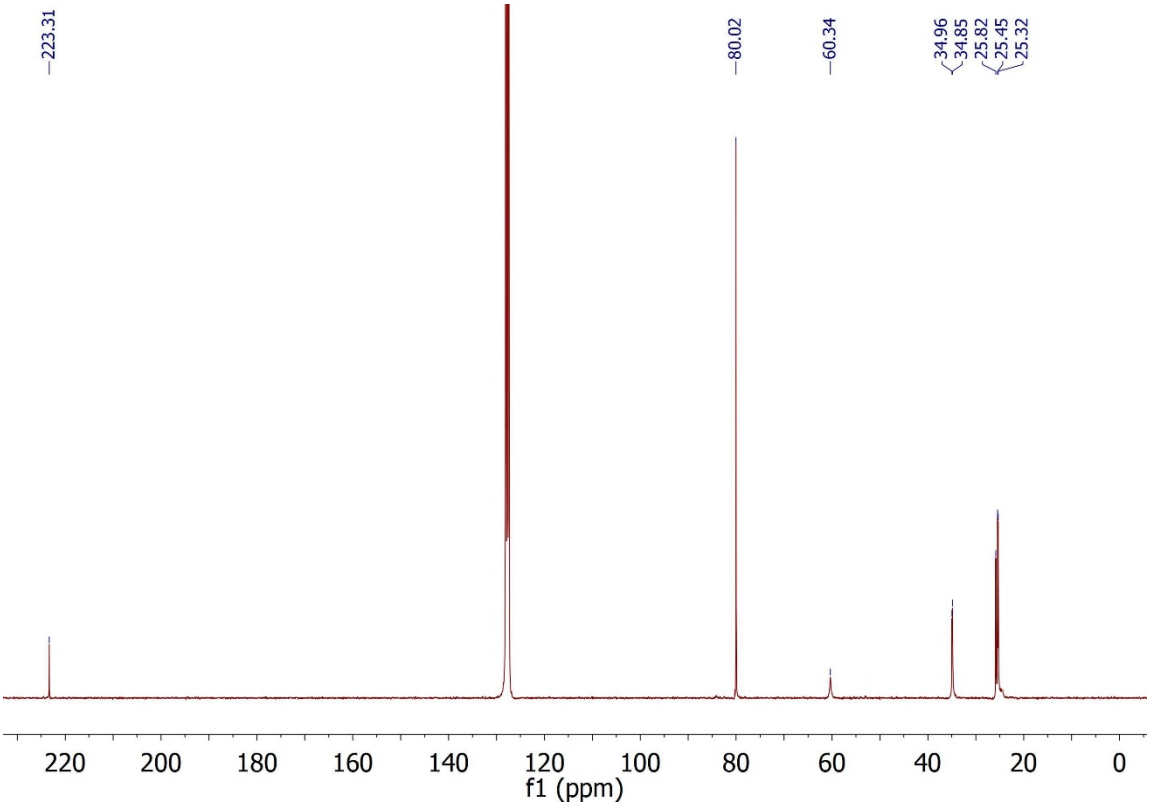

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **8a**.



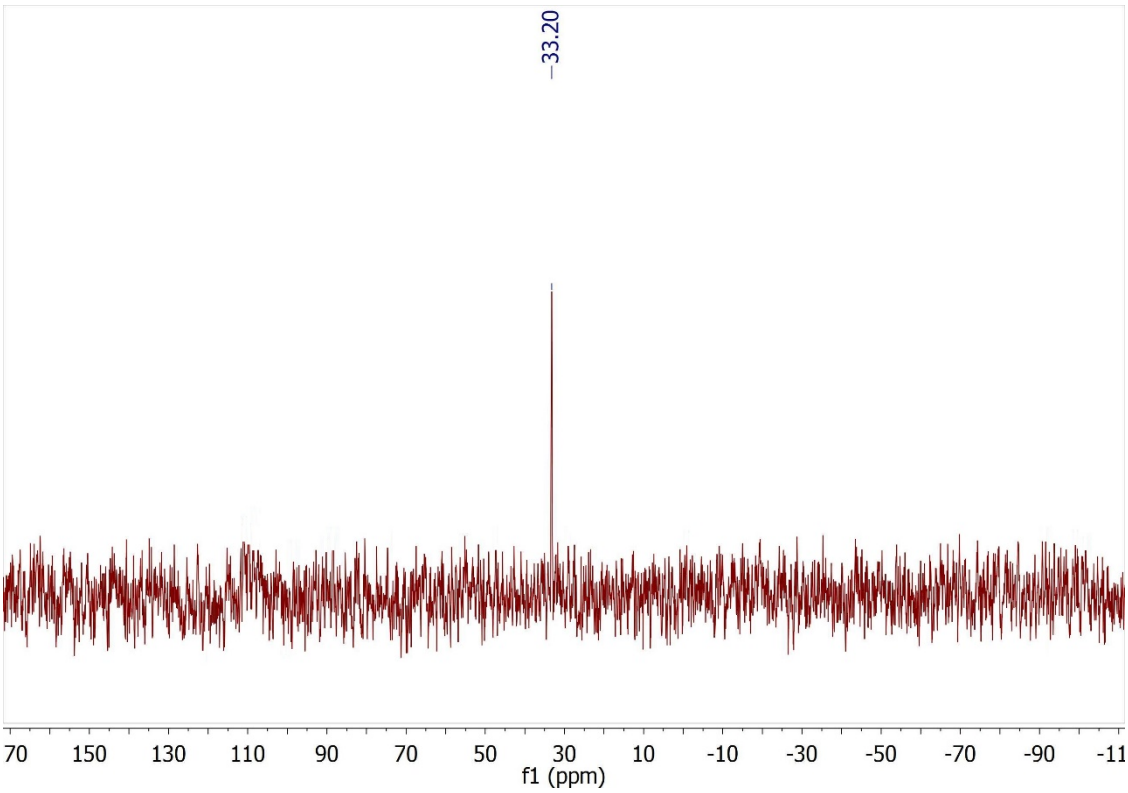

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **8a**.



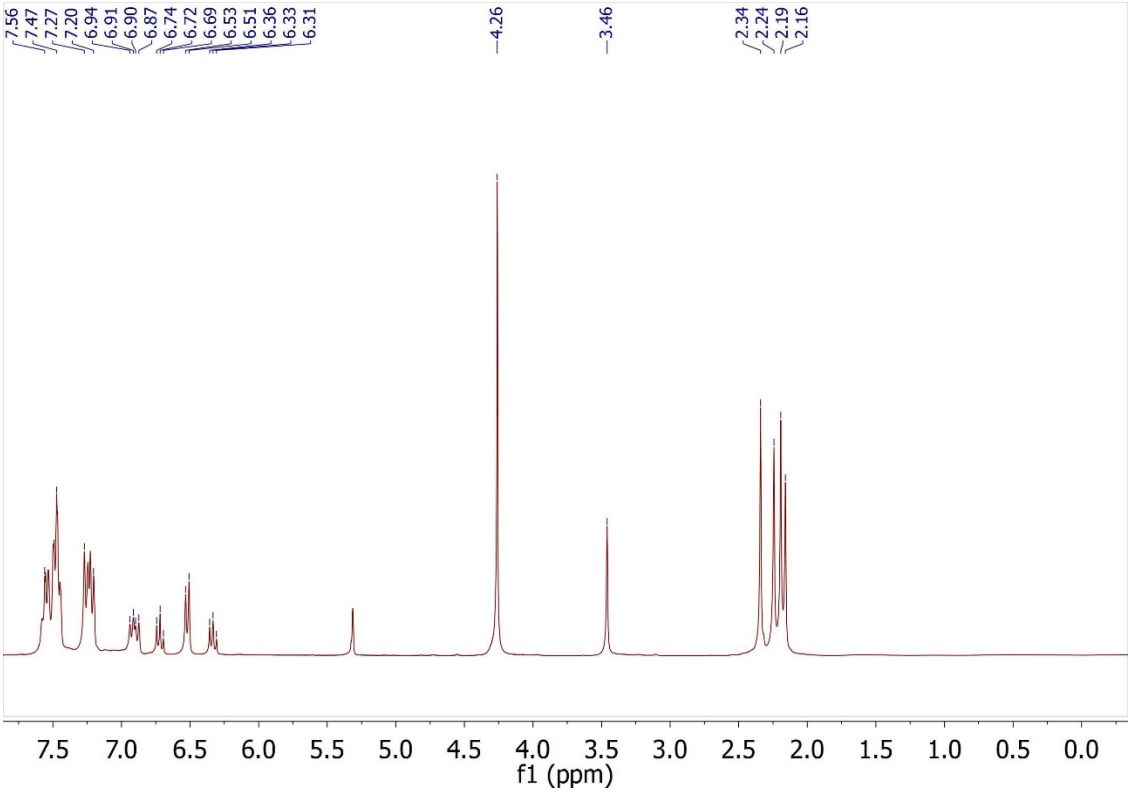

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **8b**.



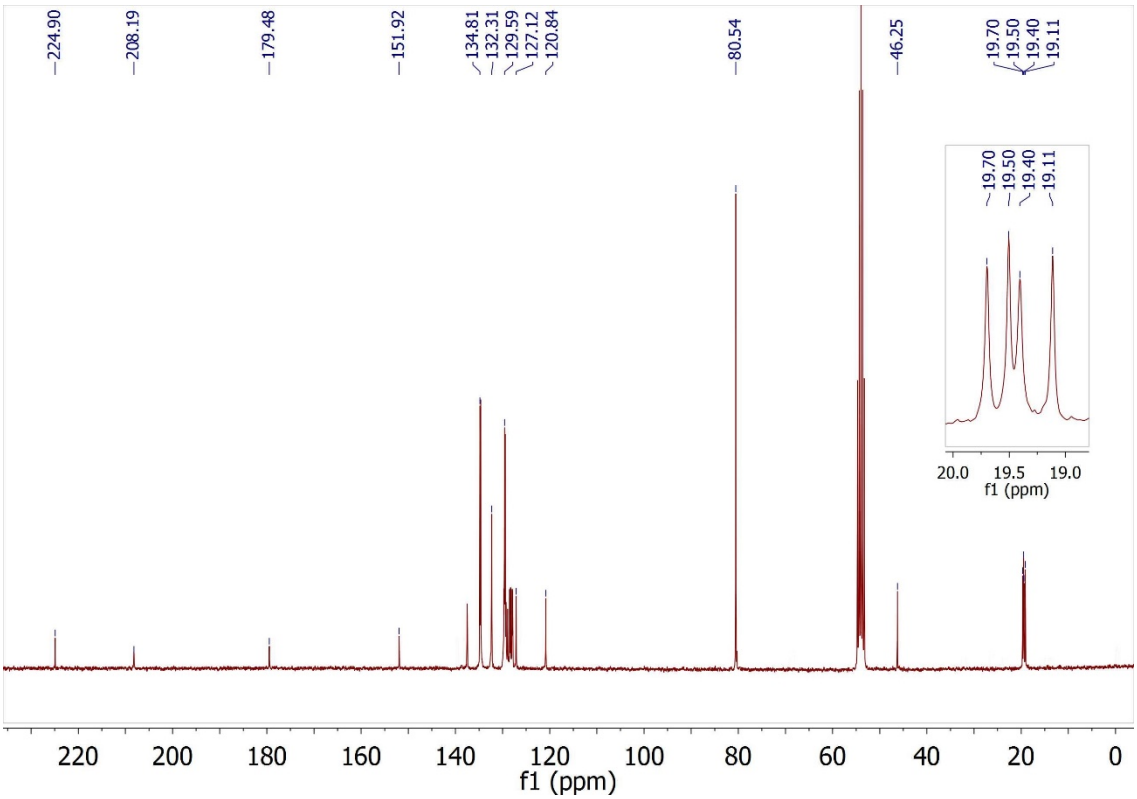

$^{13}$C NMR ($C_6D_6$, 298K) spectra of compound **8b**.



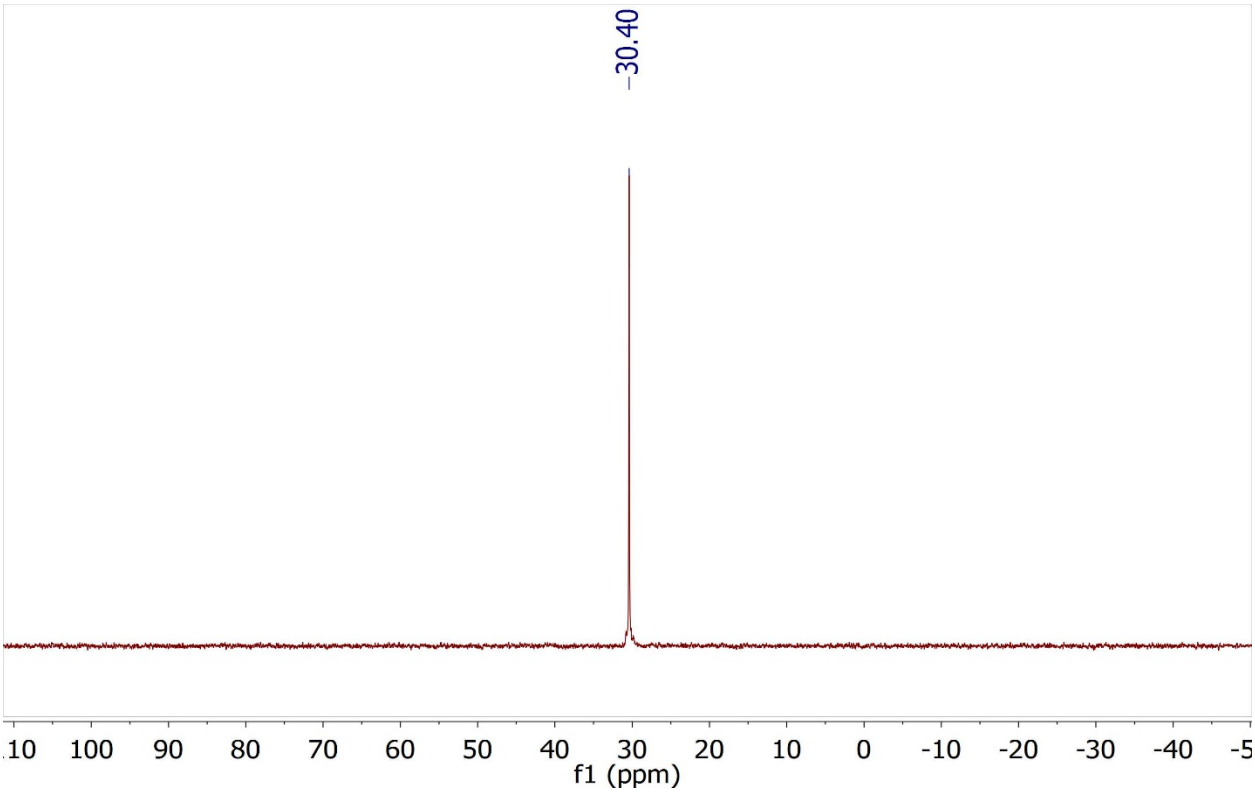

$^{31}P$ NMR ($CD_2Cl_2$, 298K) spectra of compound **11**.



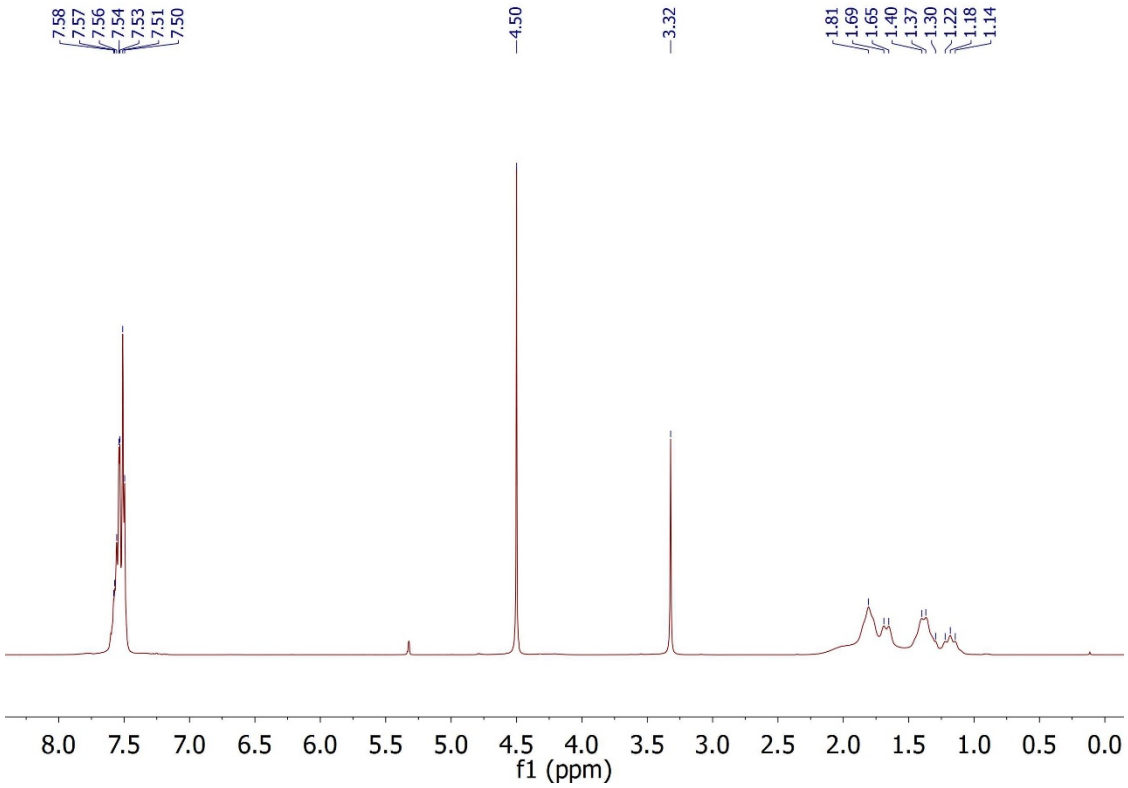

$^{1}H$ NMR ($CD_2Cl_2$, 298K) spectra of compound **12a**.



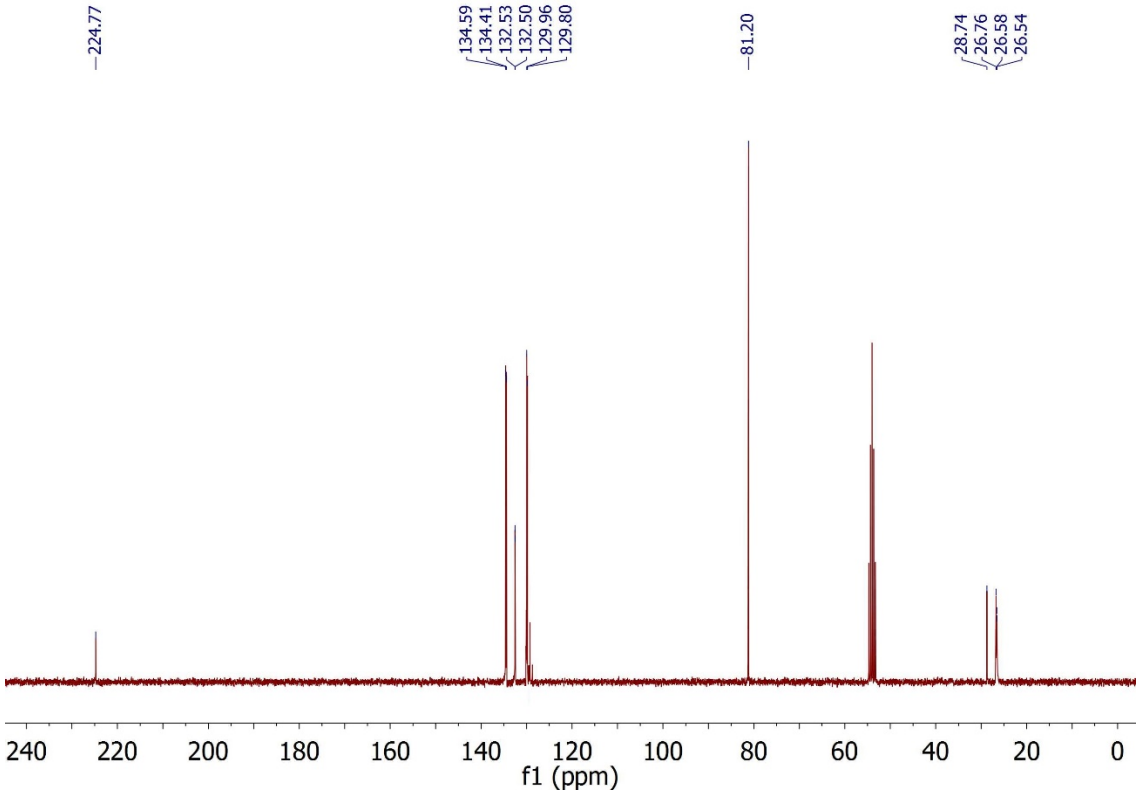

$^{13}C$ NMR ($CD_2Cl_2$, 298K) spectra of compound **12a**.



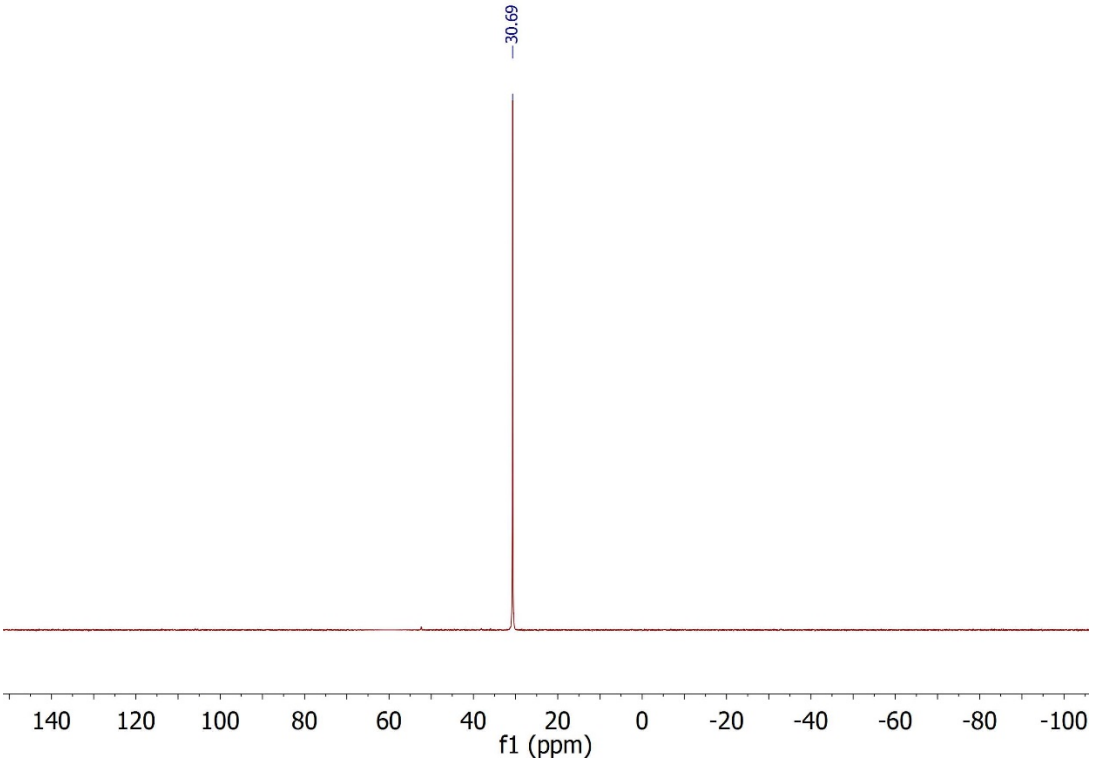

$^{31}P$ NMR ($CD_2Cl_2$, 298K) spectra of compound **12a**.



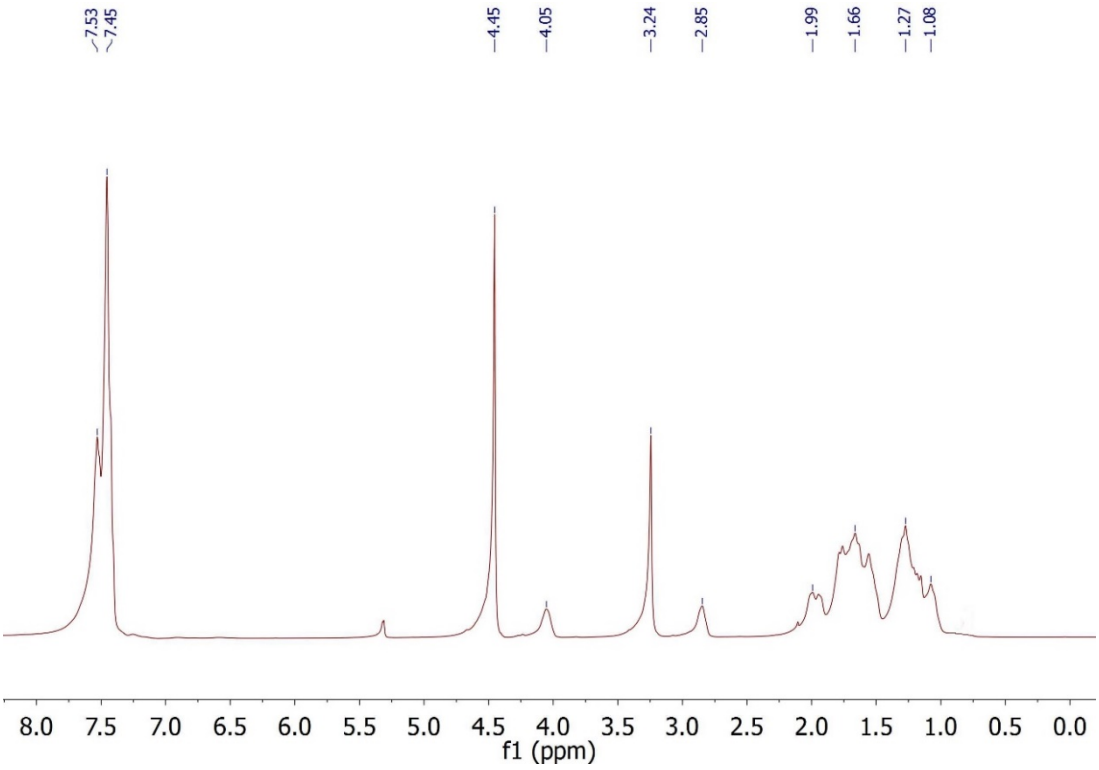

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **12b**.



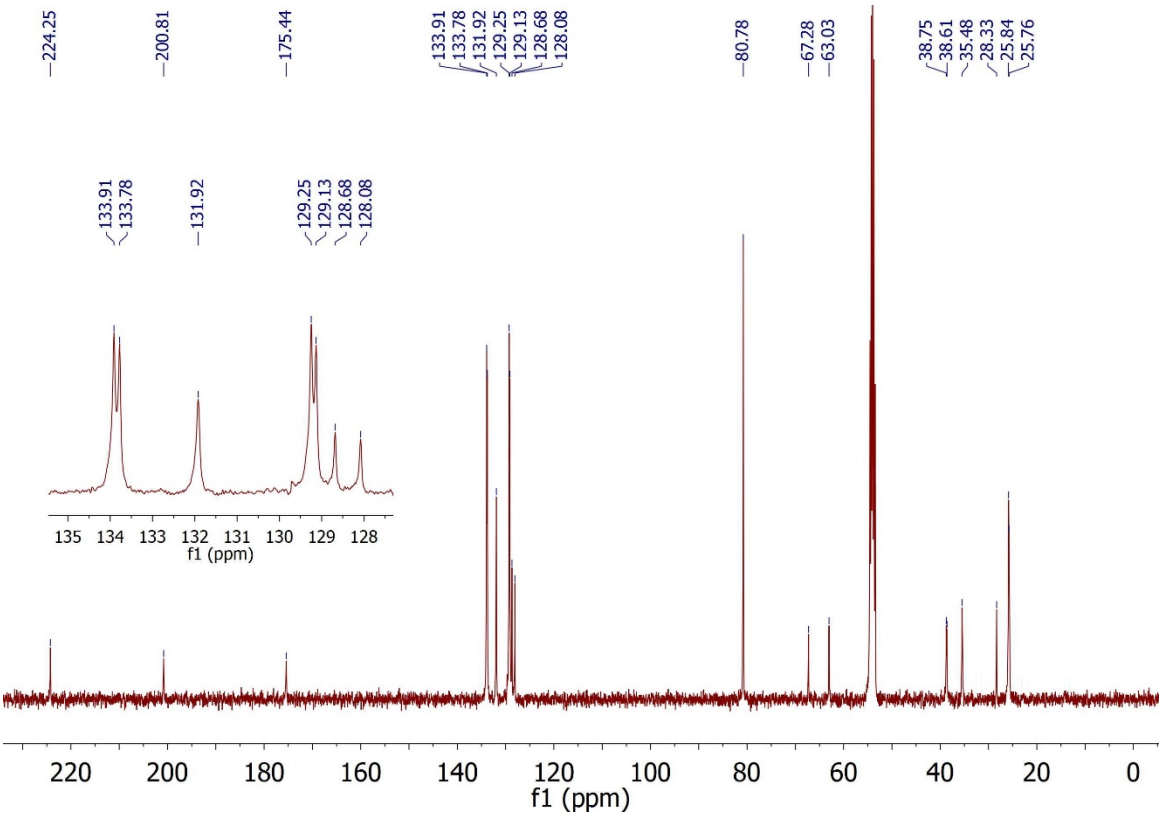

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **12b**.



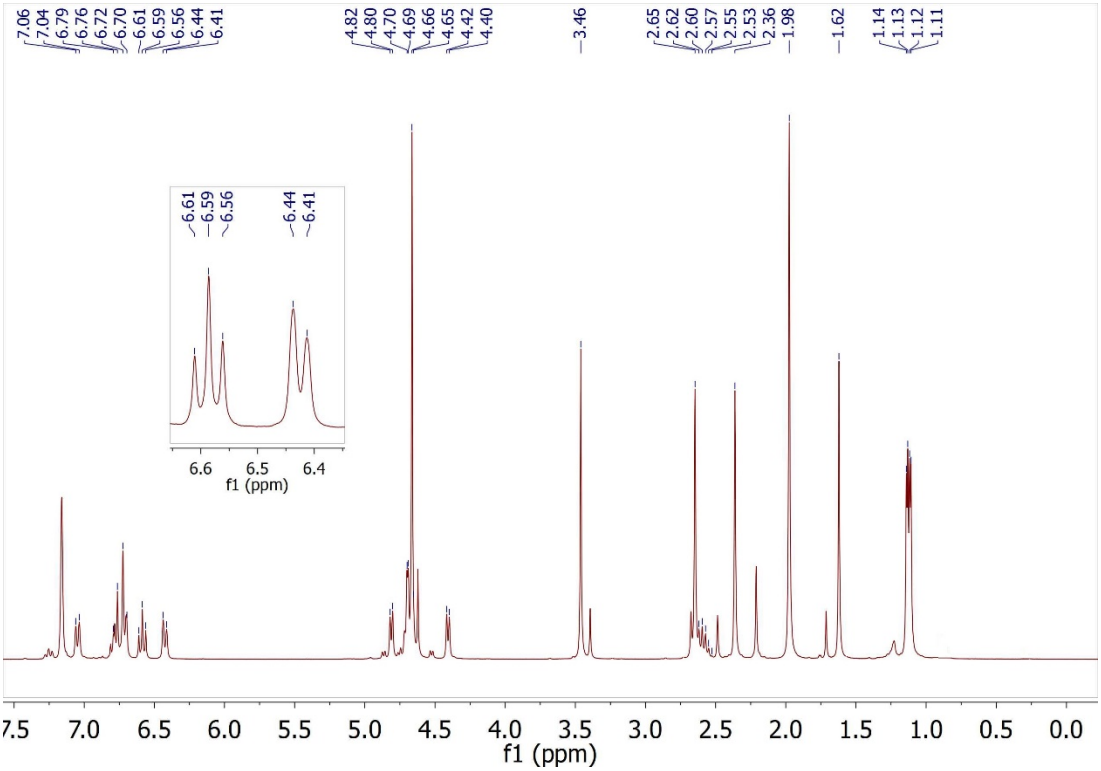

$^{31}P$ NMR ($CD_2Cl_2$, 298K) spectra of compound **12b**.



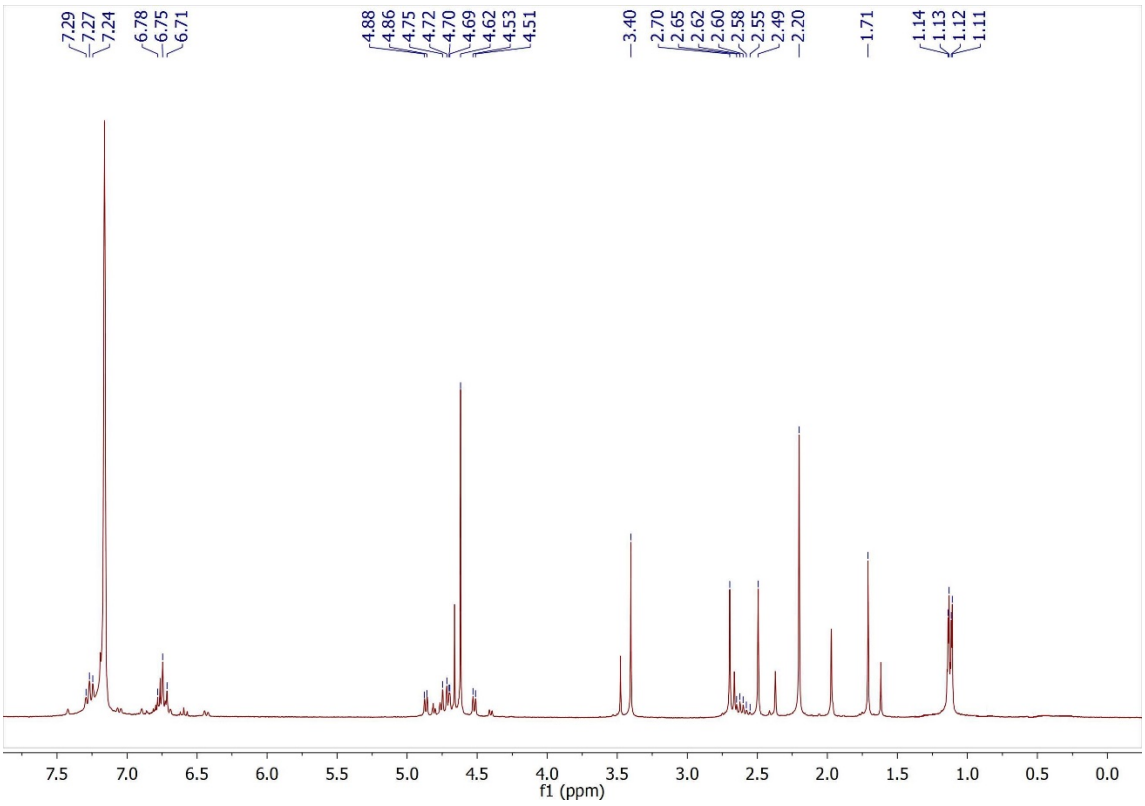

$^{1}H$ NMR ($CD_2Cl_2$, 183K) spectra of compound **12b**.



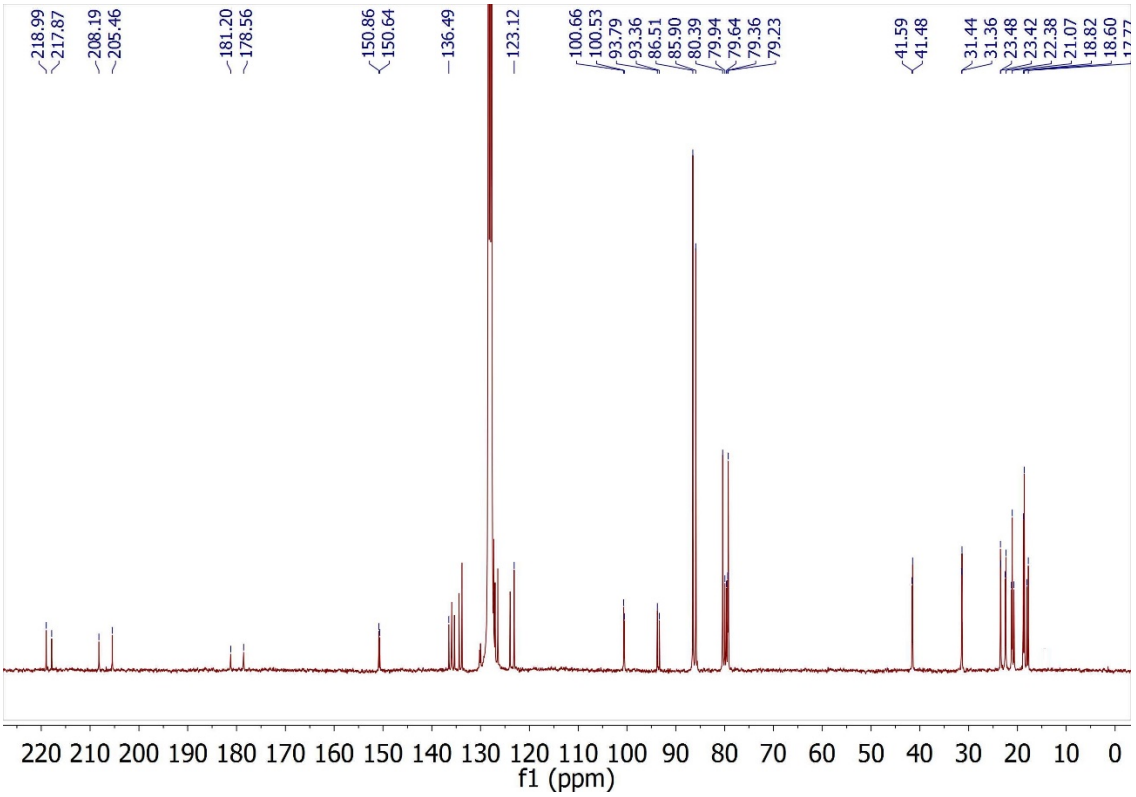

$^{13}C$ NMR ($CD_2Cl_2$, 183K) spectra of compound **12b**.



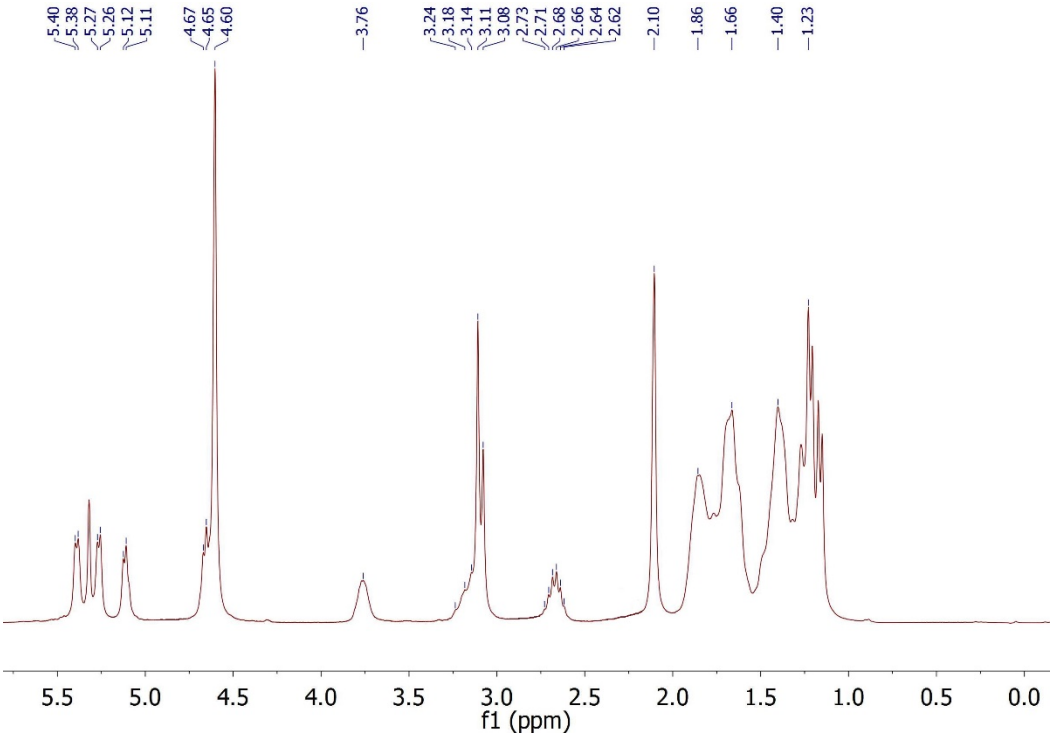

$^{1}H$ NMR ($C_6D_6$, 298K) spectra of compound **13a** (Enriched in the A isomer).



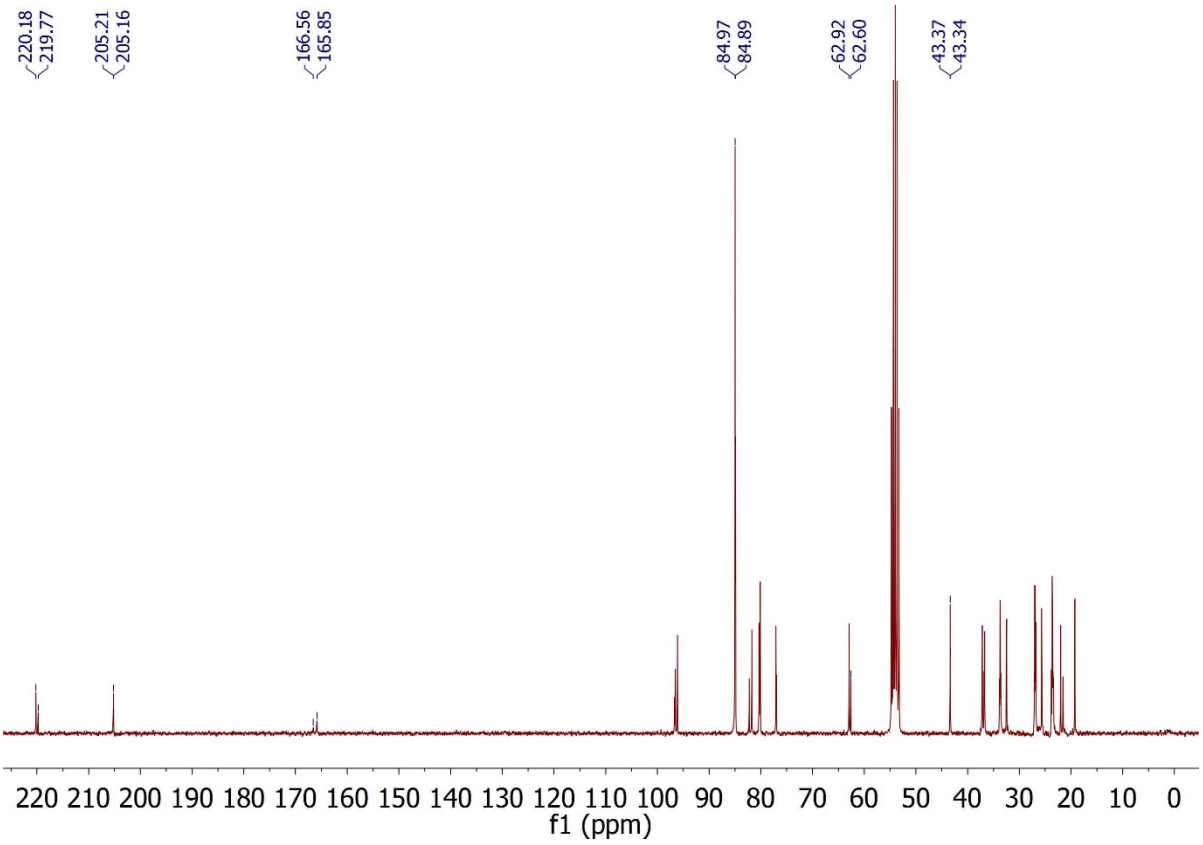

$^{1}$H NMR ($C_6D_6$, 298K) spectra of compound **13a** (Enriched in the B isomer).



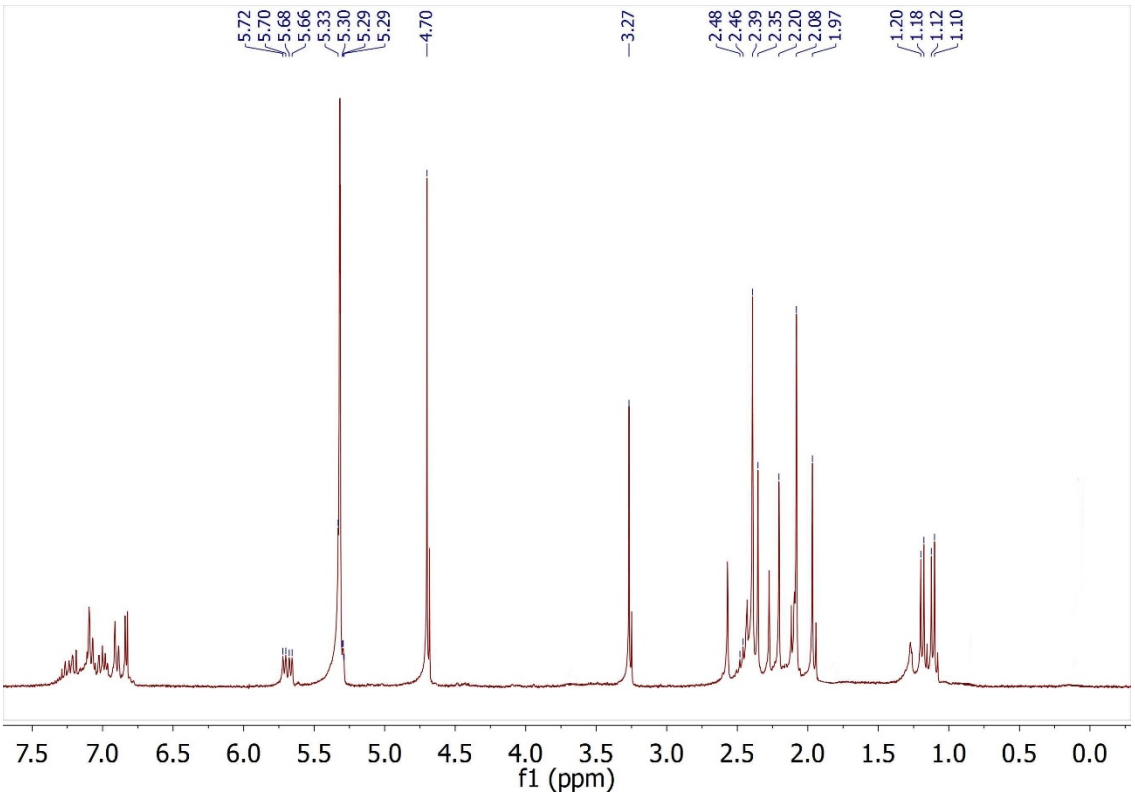

$^{13}$C NMR ($C_6D_6$, 298K) spectra of compound **13a**.



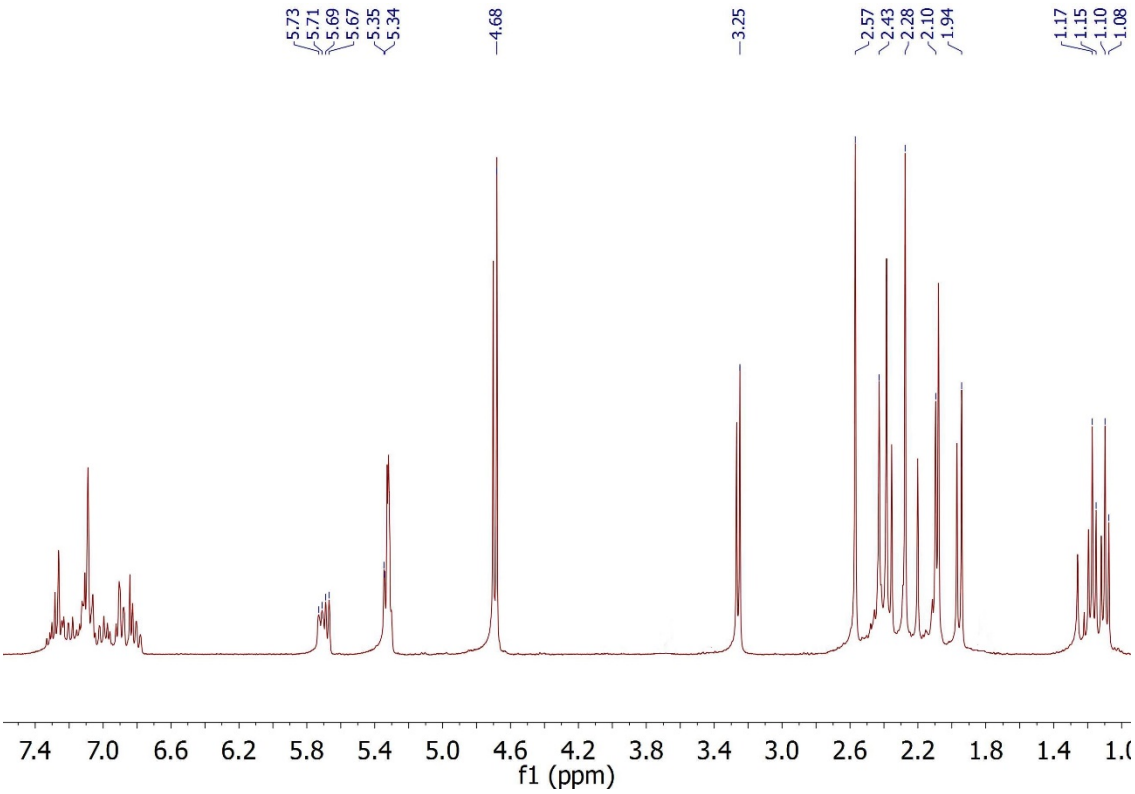

$^{1}$H NMR ($CD_2Cl_2$, 298K) spectra of compound **13b**.



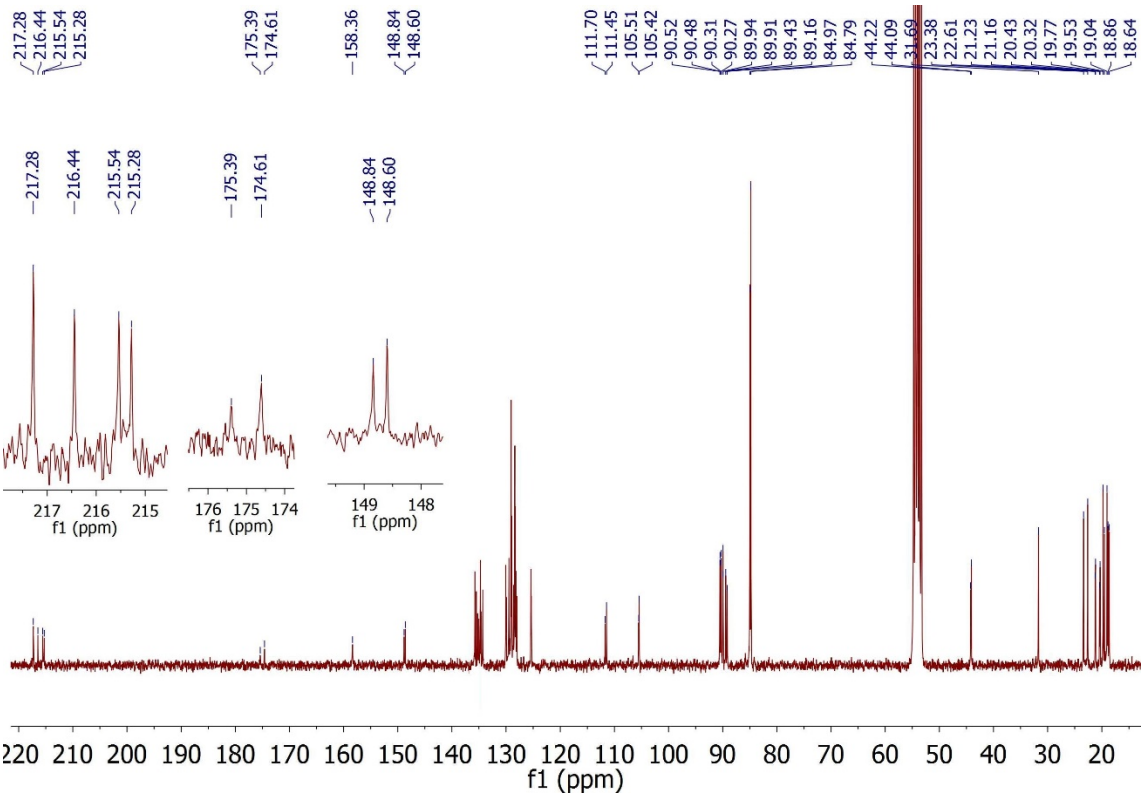

$^{13}$C NMR ($CD_2Cl_2$, 298K) spectra of compound **13b**.



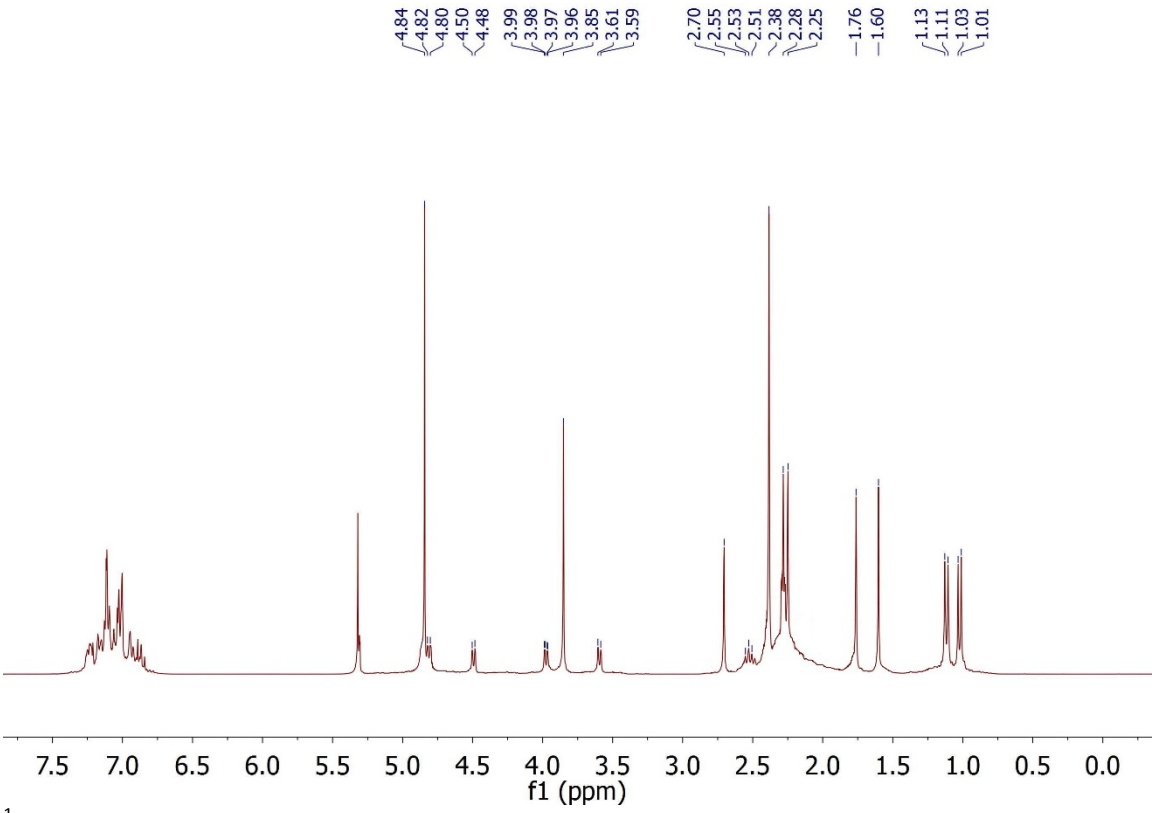

$^1$H NMR ($CD_2Cl_2$, 298K) spectra of compound **14** (Enriched in the isomer A).



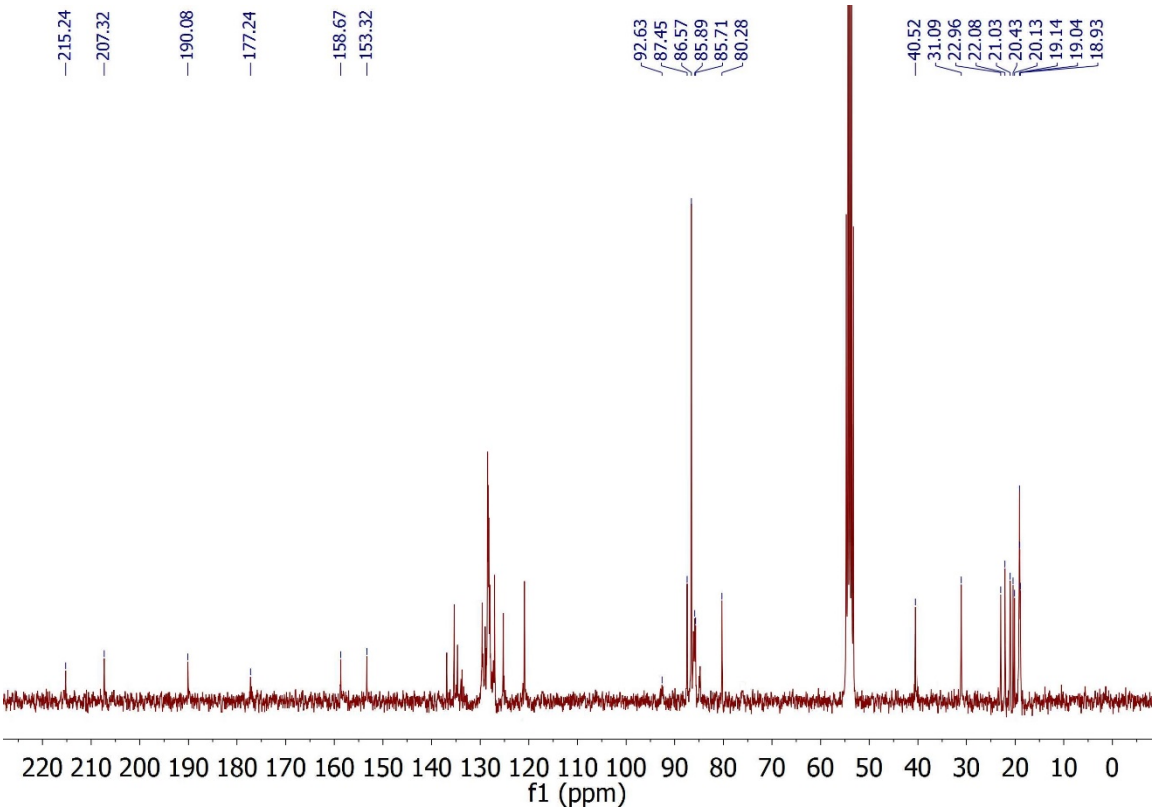

$^1$H NMR ($CD_2Cl_2$, 298K) spectra of compound **14** (Enriched in the isomer B).



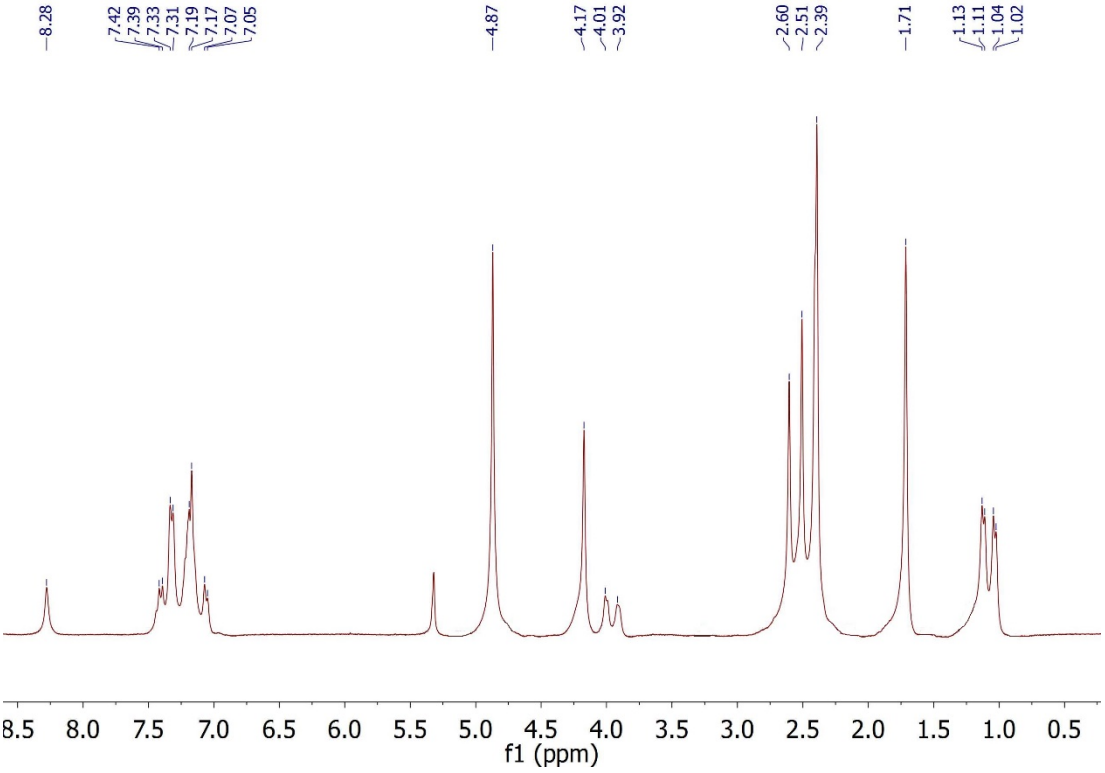

$^{13}C$ NMR ($CD_2Cl_2$, 298K) spectra of compound **14**.



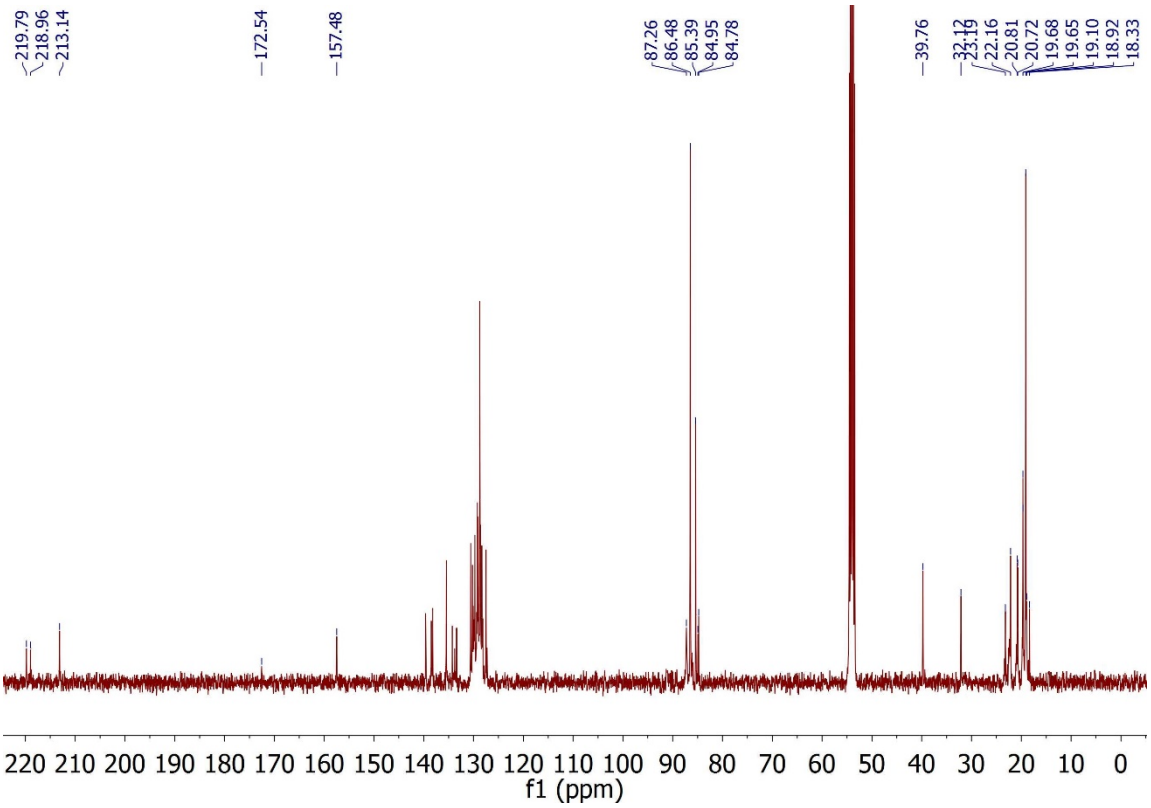

$^{1}H$ NMR ($CD_2Cl_2$, 298K) spectra of compound **15**.



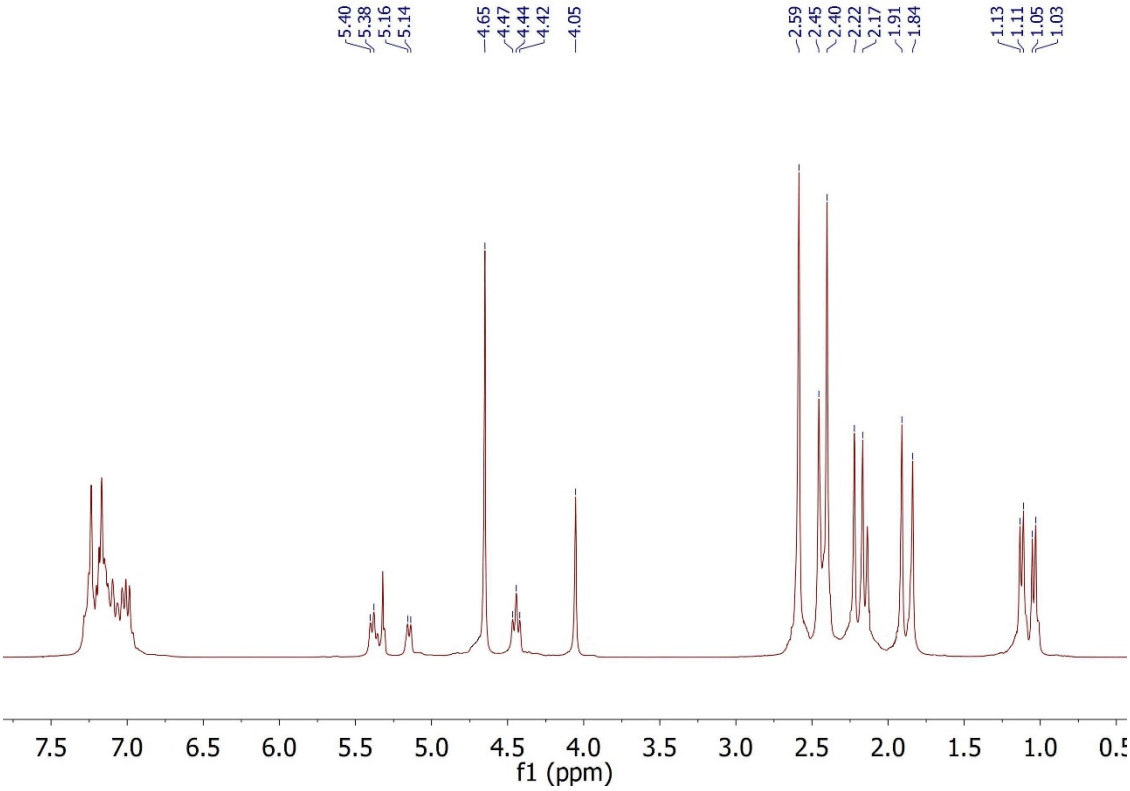

$^{13}C$ NMR ($CD_2Cl_2$, 298K) spectra of compound **15**.



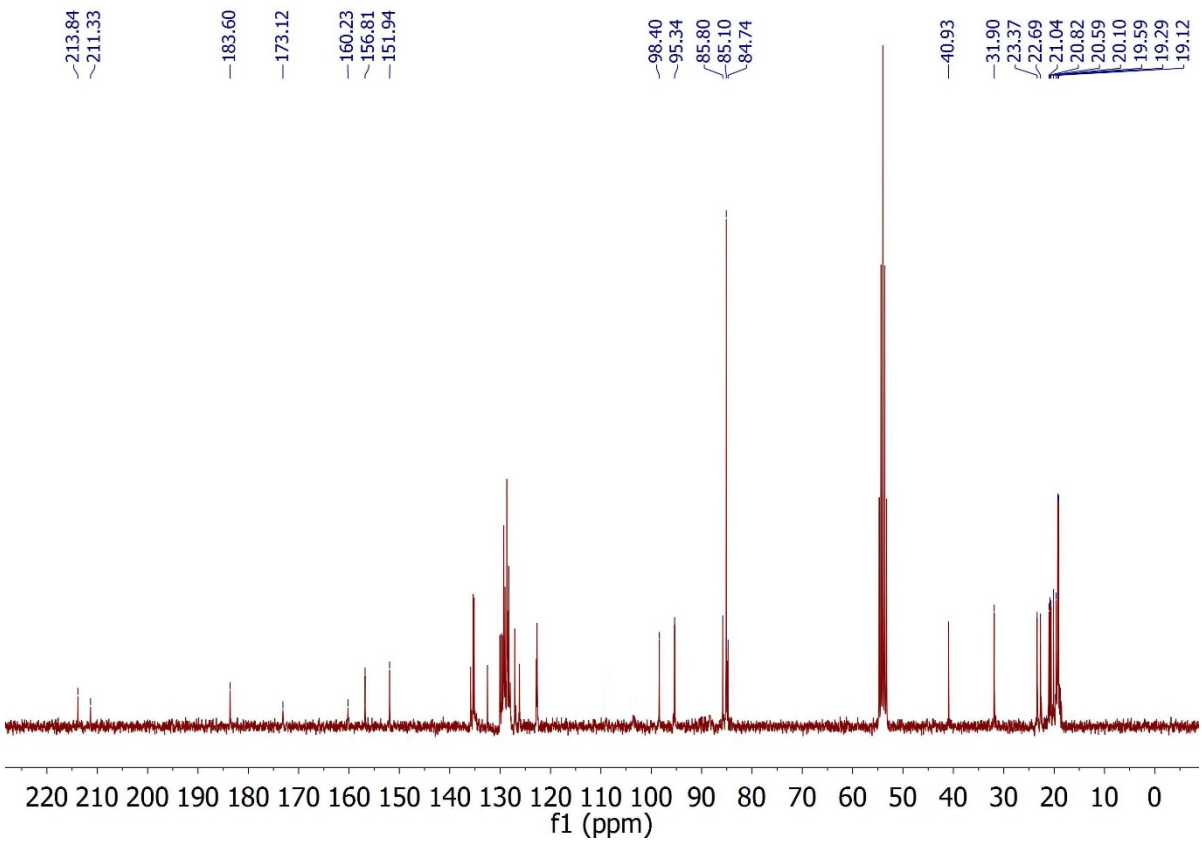

$^{1}H$ NMR ($CD_2Cl_2$, 298K) spectra of compound **16**.




$^{13}C$ NMR ($CD_2Cl_2$, 298K) spectra of compound **16**.




$^{1}H$ NMR ($CD_2Cl_2$, 298K) spectra of compound **17**.




$^{13}C$ NMR ($CD_2Cl_2$, 298K) spectra of compound **17**.