Supplementary Information

Synergistic Alginate/Iota-Carrageenan Hybrid Microspheres as Cu^{2+} Catalytic Platforms for Recyclable Paal-Knorr Reactions

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Energy-dispersive X-ray analysis information

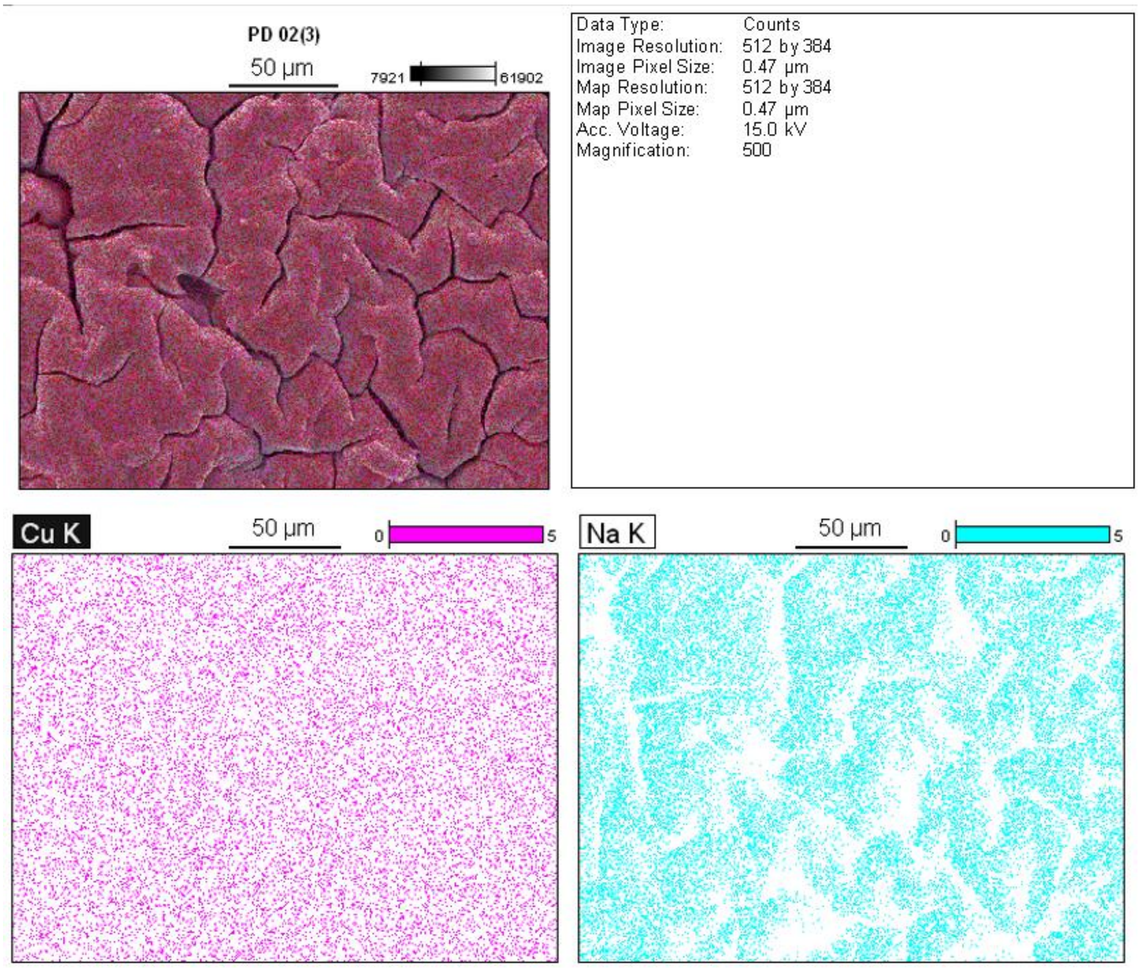

Figure S1. EDX analysis of Alg/ι-CAR-Cu^{2+} microspheres.

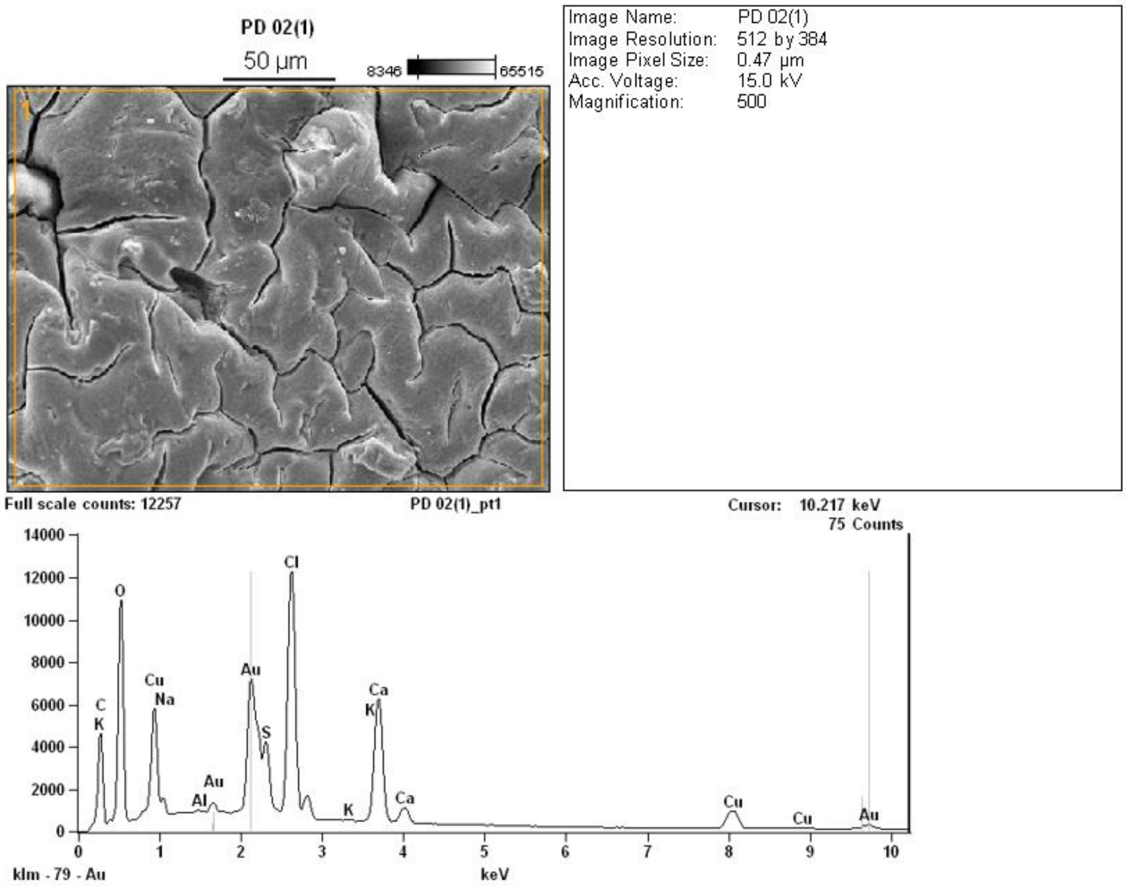

Figure S2. EDX analysis and elemental mapping of Alg/ι-CAR-Cu^{2+} microspheres.

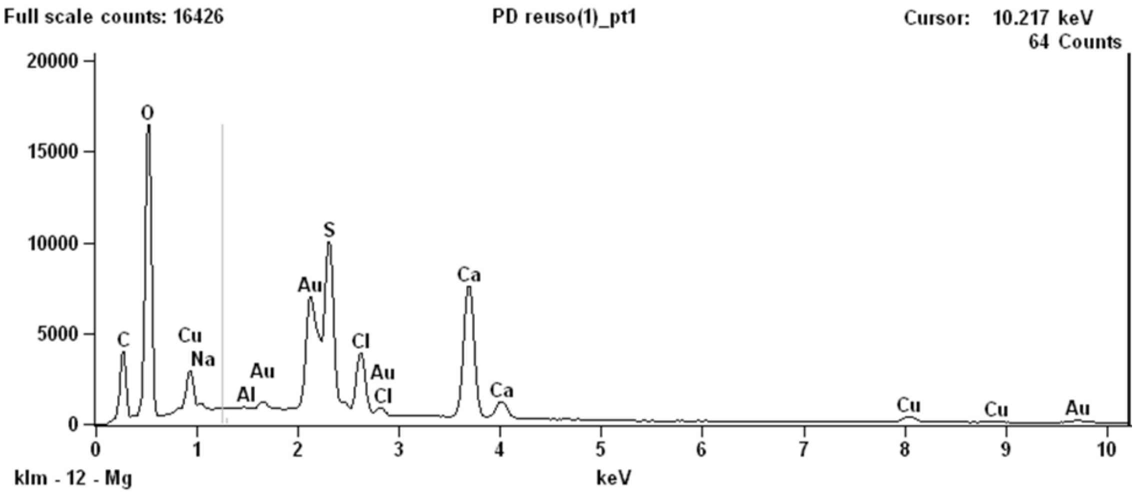

Figure S3. EDX analysis and elemental mapping of Alg/ι-CAR-Cu^{2+} reused microspheres.

Scanning electron microscopy images

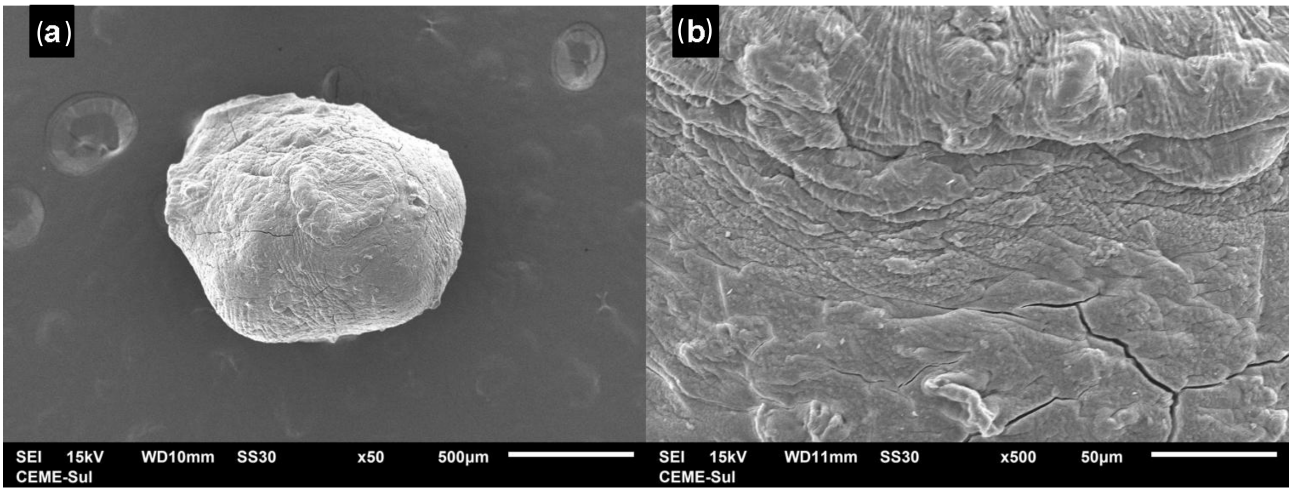

Figure S4. SEM images of Alg/ι-CAR-Cu^{2+} reuse microspheres.

Thermogravimetric analysis (TGA)

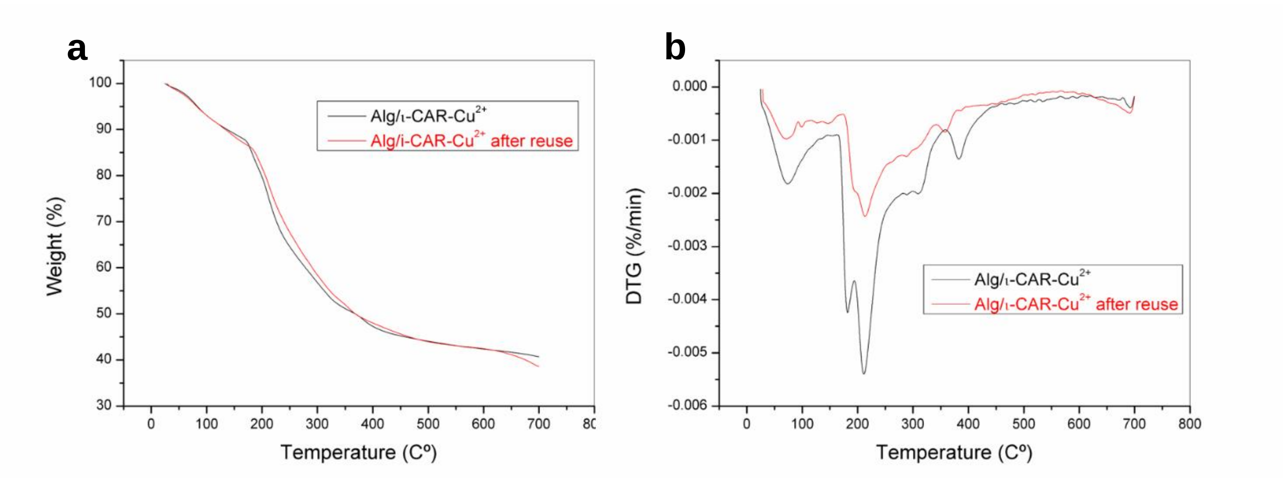

Figure S5. (a) TGA and (b) DTG curves of Alg/ι-CAR-Cu^{2+} and reuse microspheres.

Zero charge point (PCZ) analysis graph

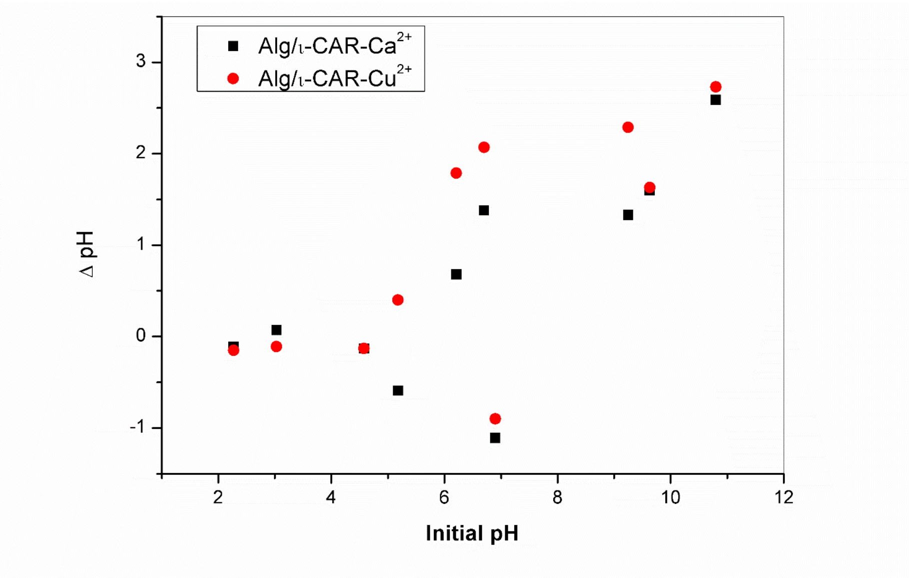

Figure S6. Point of zero charge graph (PCZ) for Alg/ι-CAR-Ca^{2+} and Alg/ι-CAR-Cu^{2+}.

Copper leaching

Table S1. Quantification of copper leaching by flame atomic absorption spectroscopy (FAAS) in the reuse cycles of Alg/ι-CAR-Cu^{2+} microspheres in the Paal-Knorr reaction

Reuse cycle	Copper leaching / mg	Remaining copper / mg
1	0.07	0.59986
2	0.29	0.59957
3	4.19	0.59538
4	13.25	0.58213
5	0.77	0.58136

NMR analysis data

2,5-Dimethyl-1-phenyl-1*H*-pyrrole (**3a**): yellow solid, mp: 50-52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 3H), 7.22-7.19 (m, 2H), 5.90 (s, 2H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 129.1, 128.8, 128.3, 127.7, 105.7, 13.0.

1-(4-Methoxyphenyl)-2,5-dimethyl-1*H*-pyrrole (**3b**): brown solid, mp: 58-59 °C lit.:[1] 55-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.11 (m, 2H), 6.97-6.95 (m, 2H), 5.88 (s, 2H), 3.85 (s, 3H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 131.9, 129.3, 129.1, 114.3, 105.4, 55.6, 13.1.

1-(4-Chlorophenyl)-2,5-dimethyl-1*H*-pyrrole (**3c**): brown solid, mp: 56-57 °C lit.:[1] 56-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.15-7.13 (m, 2H), 5.90 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 133.7, 129.6, 129.4, 128.8, 106.2, 13.1.

Spectral data

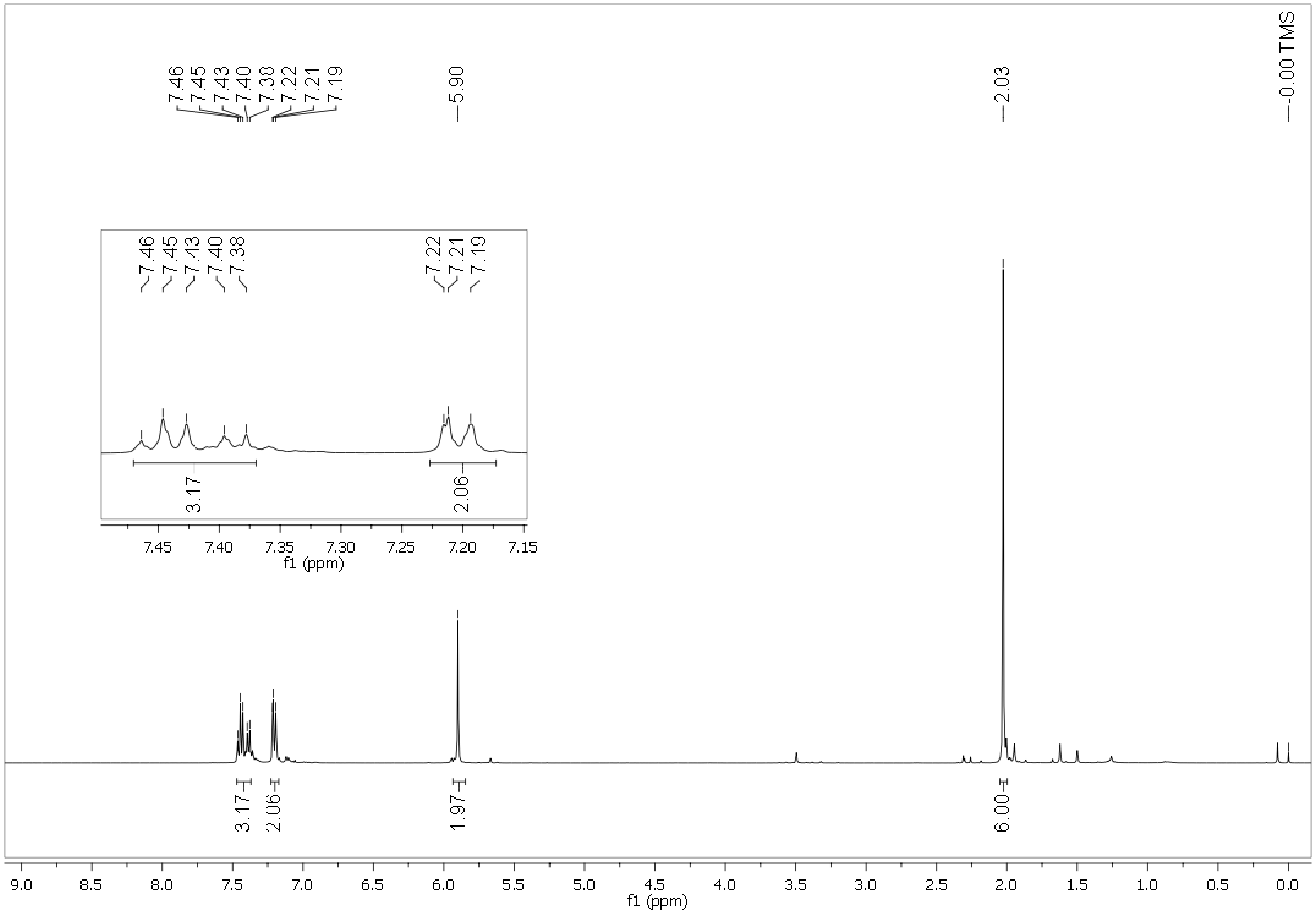

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,5-dimethyl-1-phenyl-1*H*-pyrrole (**3a**).

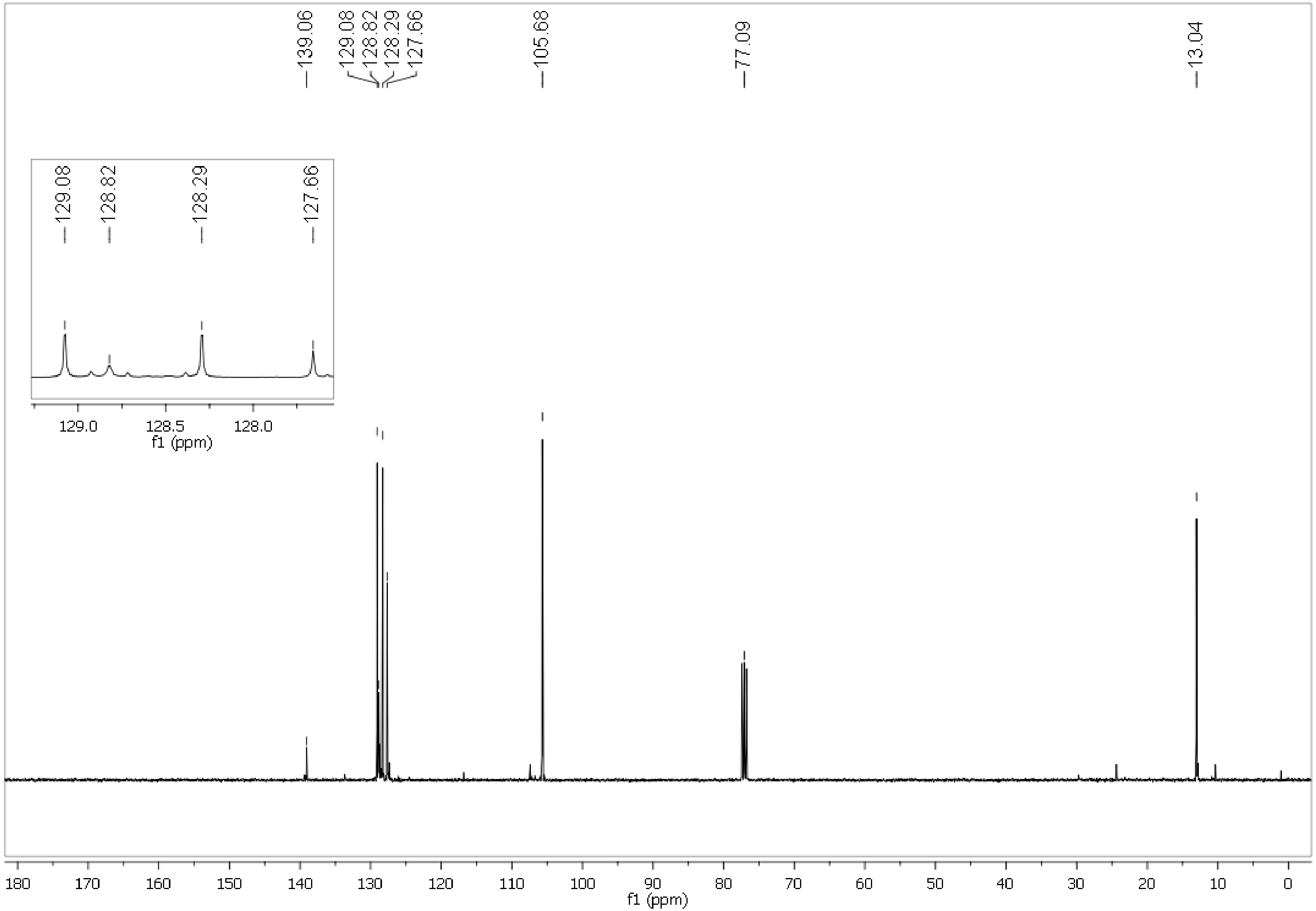

Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2,5-dimethyl-1-phenyl-1*H*-pyrrole (**3a**).

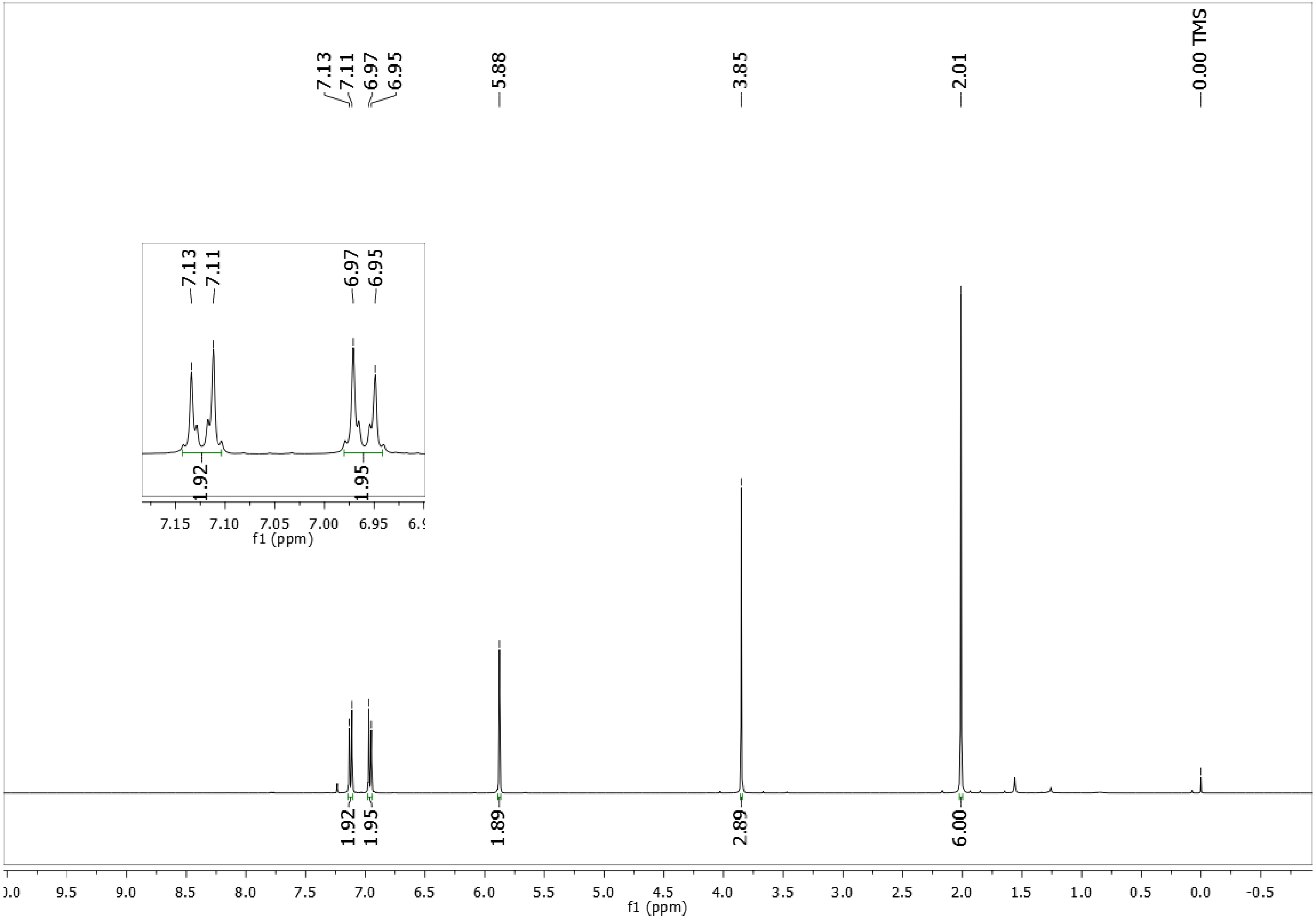

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(4-methoxyphenyl)-2,5-dimethyl-1*H*-pyrrole (**3b**).

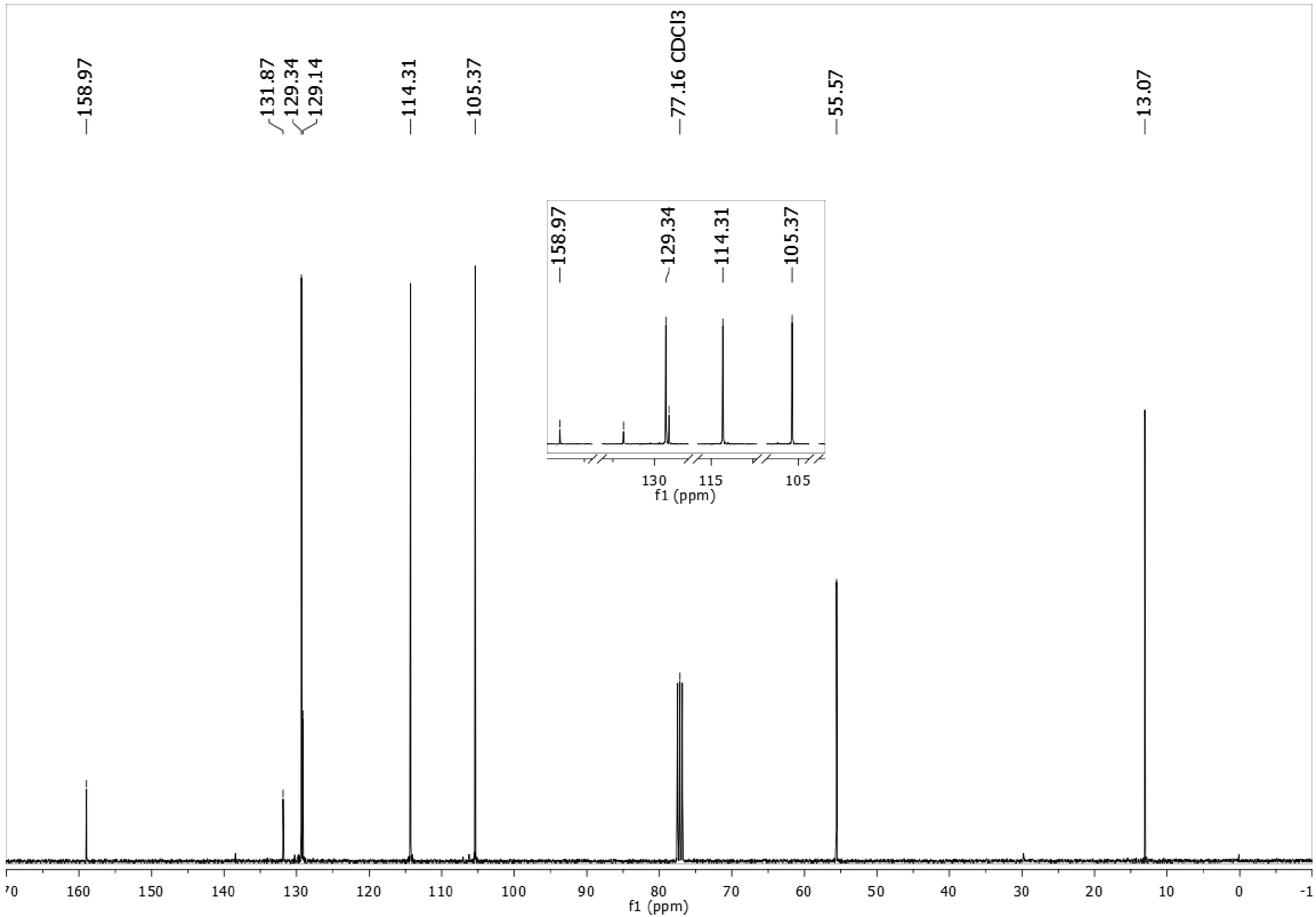

Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1-(4-methoxyphenyl)-2,5-dimethyl-1*H*-pyrrole (**3b**).

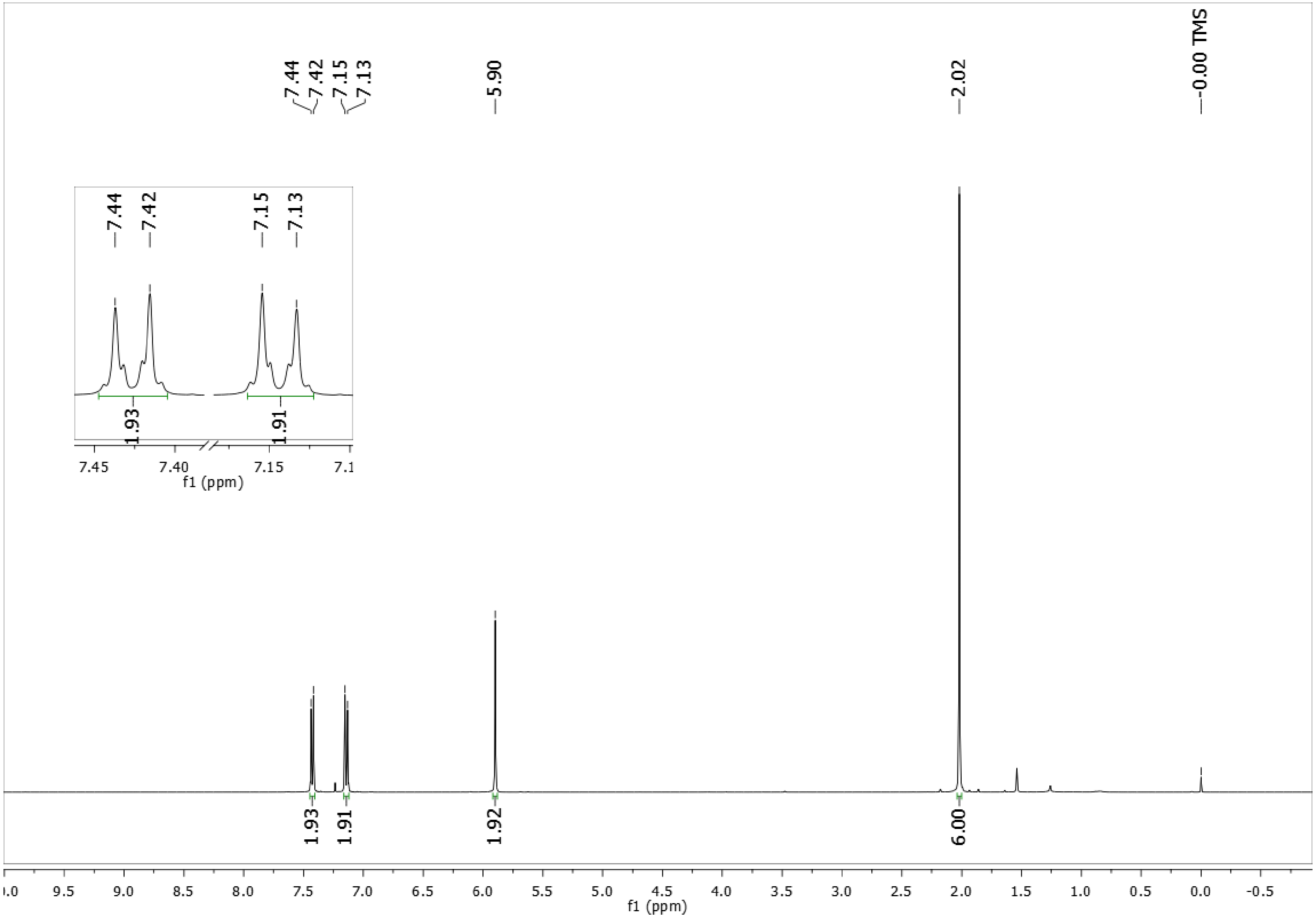

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(4-chlorophenyl)-2,5-dimethyl-1*H*-pyrrole (**3c**).

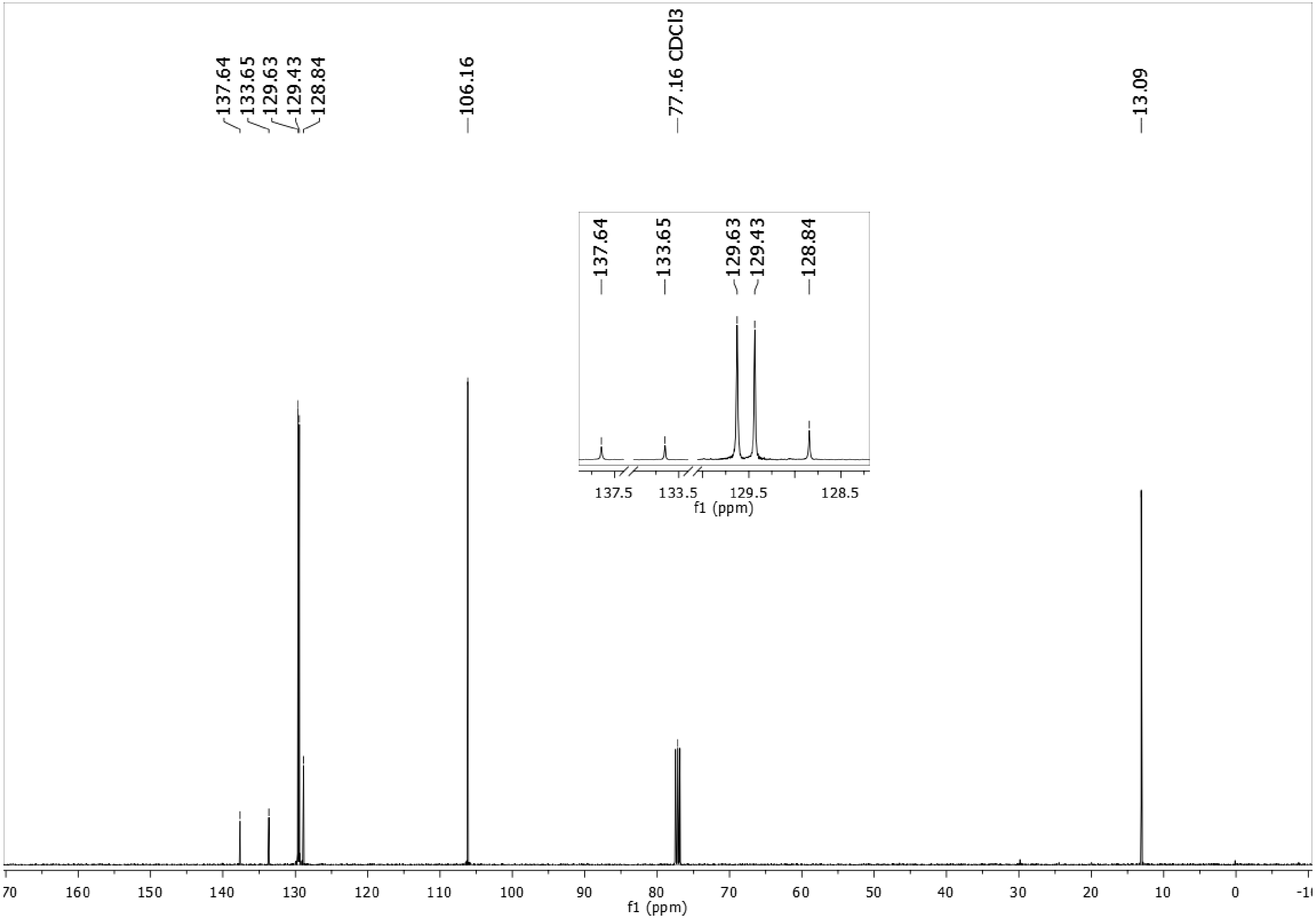

Figure S12. ^{13}C NMR (100 MHz, CDC_{l3}) spectrum of 1-(4-chlorophenyl)-2,5-dimethyl-1*H*-pyrrole (**3c**).

References

1. Lee, H.; Kim, B. H.; *Tetrahedron* **2013**, *69*, 6698. [Crossref]