Supporting information

Synthesis and Fluorescence Properties of Unsymmetrical 1,4-Dihydropyrrolo[3,2-*b*]pyrrole Dyes

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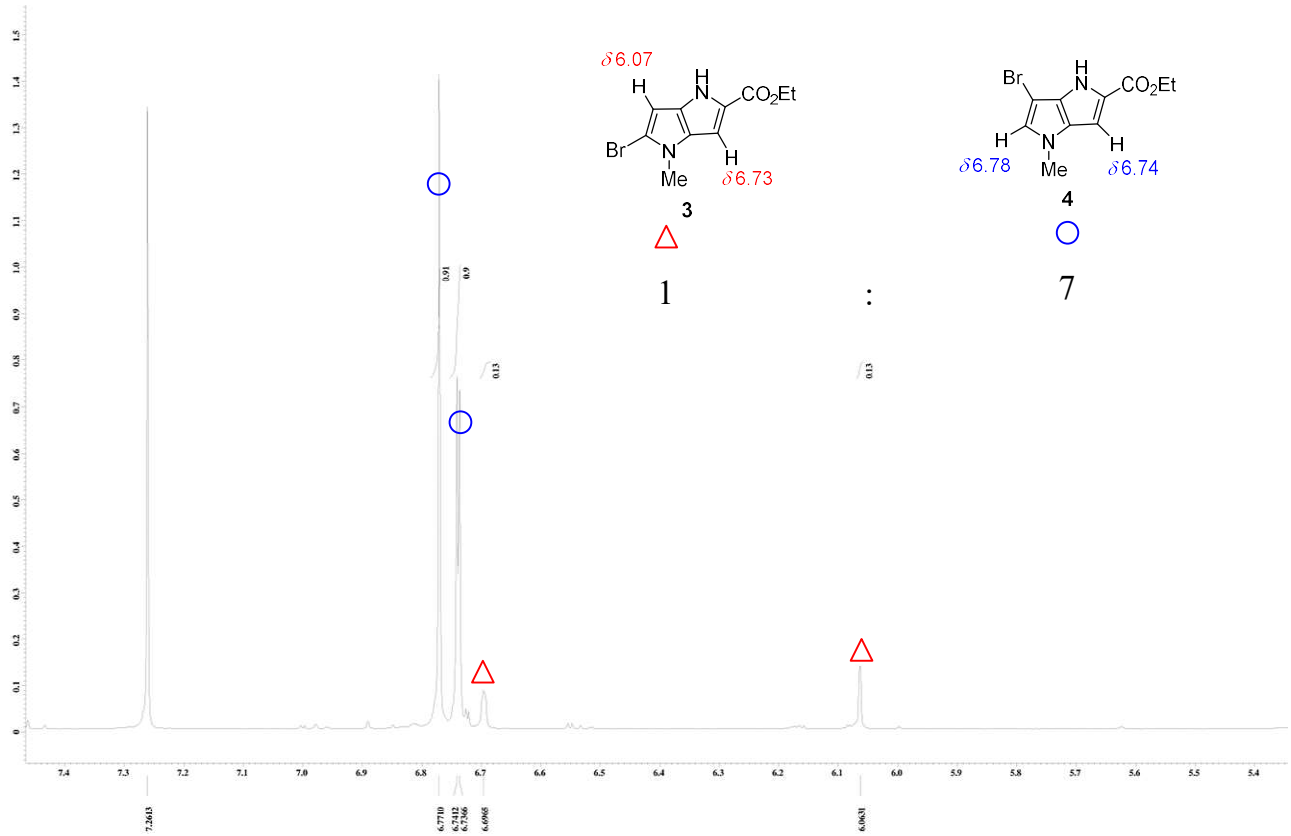

Figure S1. ^{1}H NMR spectrum of bromination of **2** in $CDCl_3$.

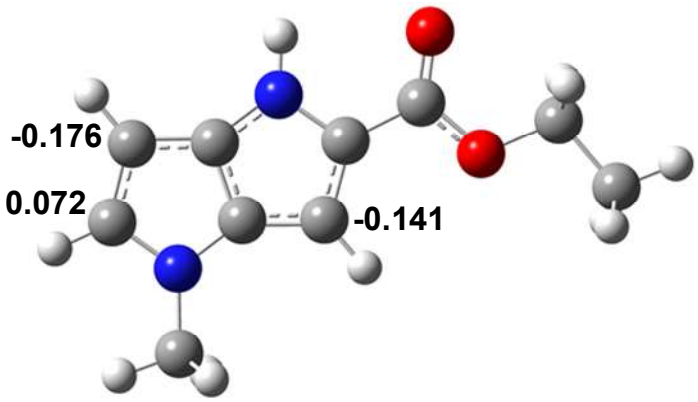

Figure S2. Mulliken charge distribution of **2**. The geometry optimization was performed using the B3LYP/6-31G(d,p) with THF as solvent.

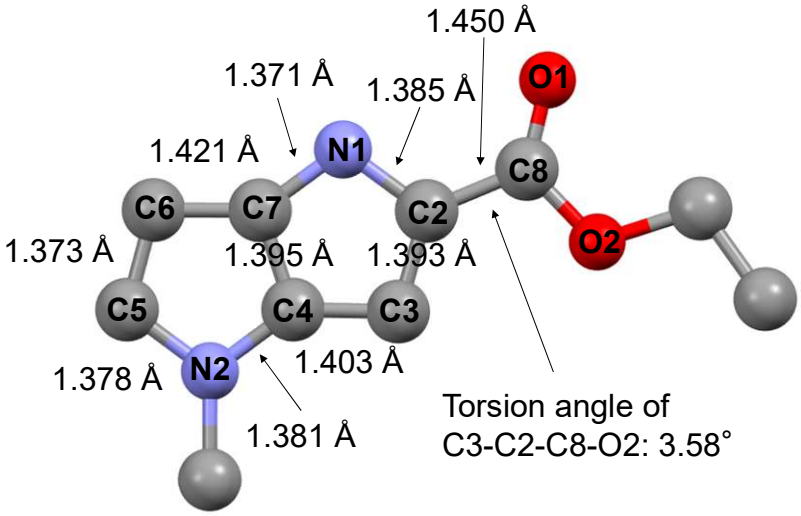

Figure S3. Experimentally obtained bond lengths and torsion angle in the crystalline state.

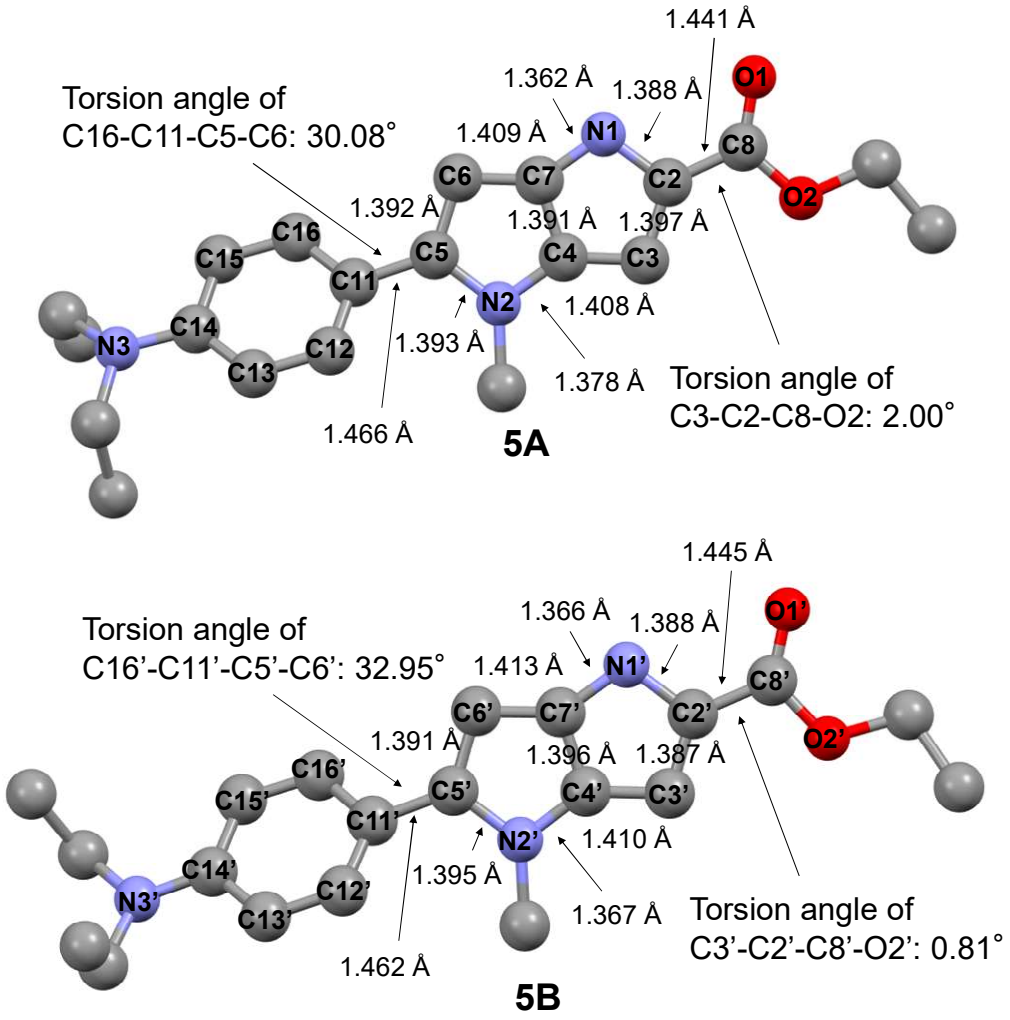

Figure S4. (a) Experimentally obtained bond lengths and torsion angles of **5A** and **5B** in the crystalline state.

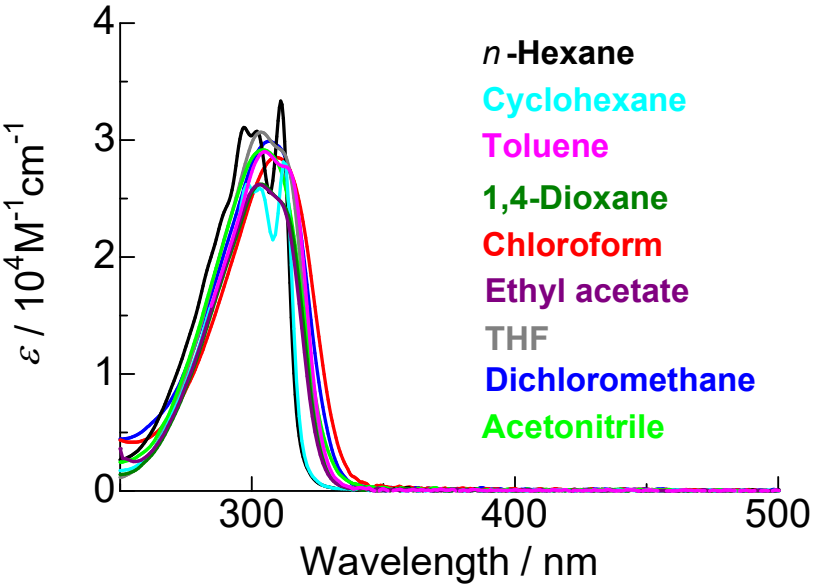

Figure S5. UV−visible absorption spectra of **2** in various solvents (1.0×10^{-5} M).

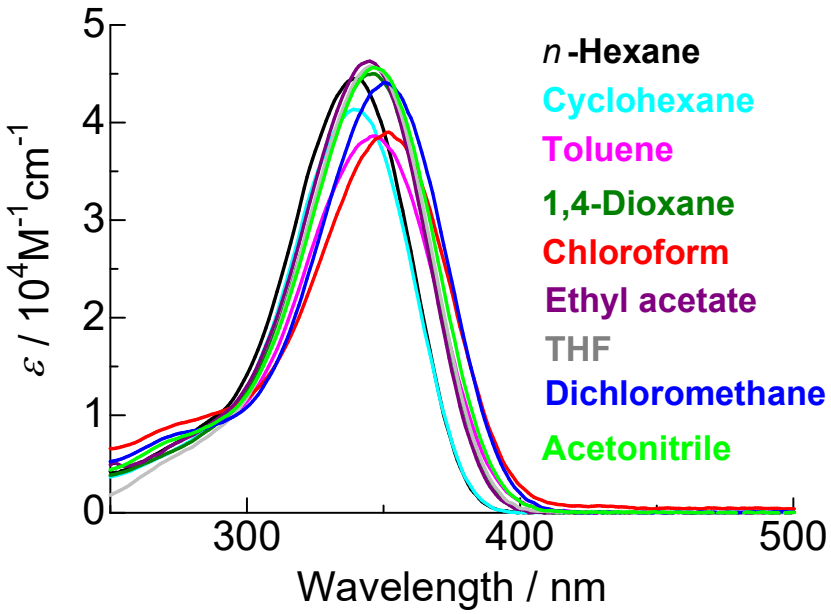

Figure S6. UV−visible absorption spectra of **5** in various solvents (1.0×10^{-5} M).

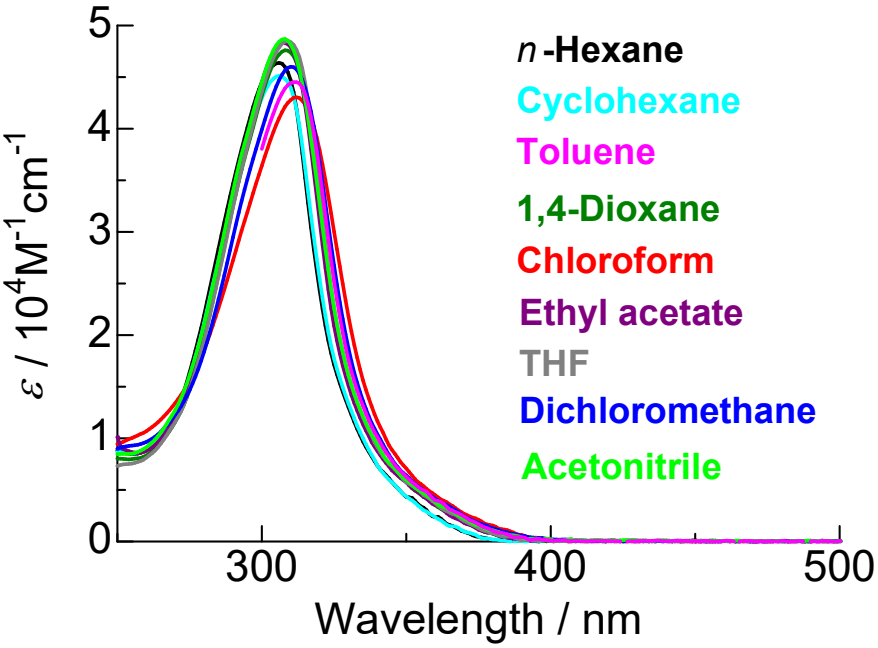

Figure S7. UV−visible absorption spectra of **6** in various solvents (1.0×10^{-5} M).

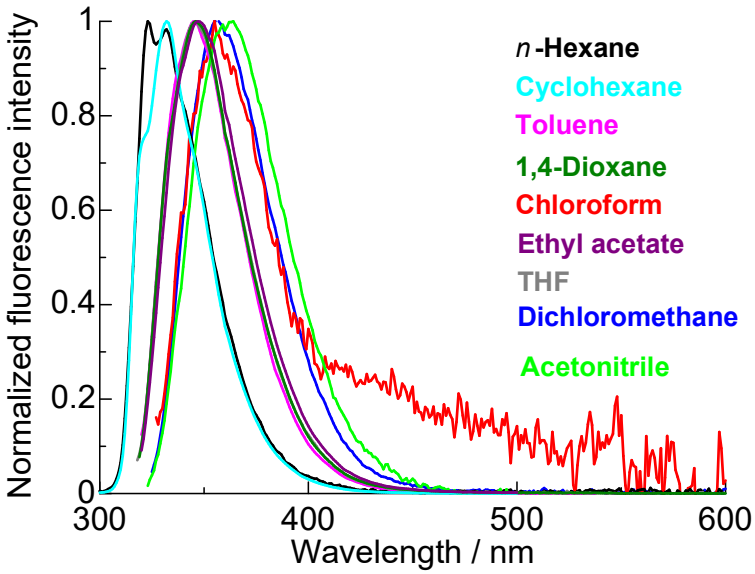

Figure S8. Normalized fluorescence spectra of **2** in various solvents (1.0×10^{-5} M).

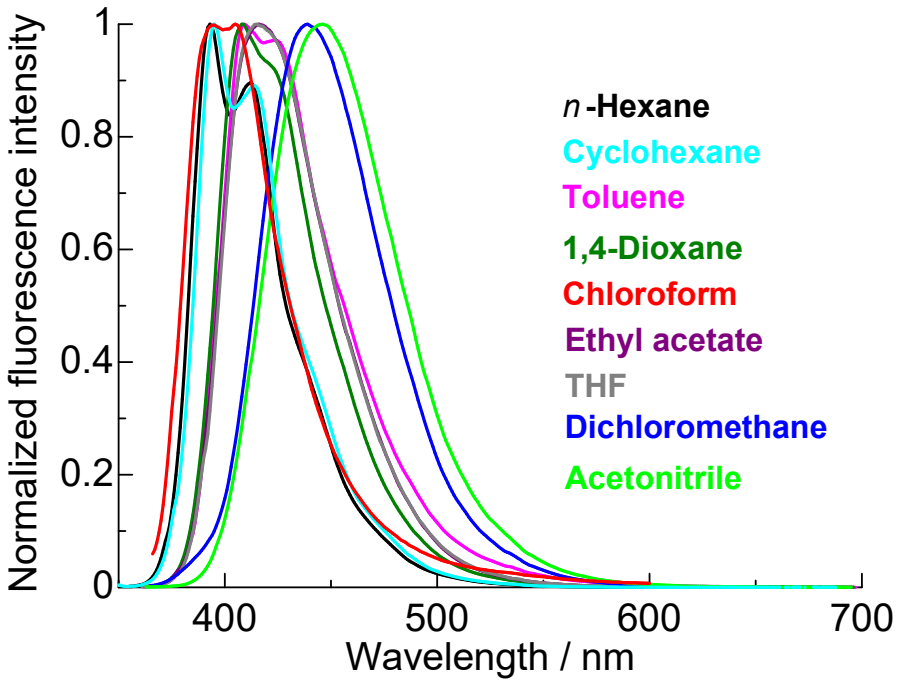

Figure S9. Normalized fluorescence spectra of **5** in various solvents (1.0×10^{-5} M).

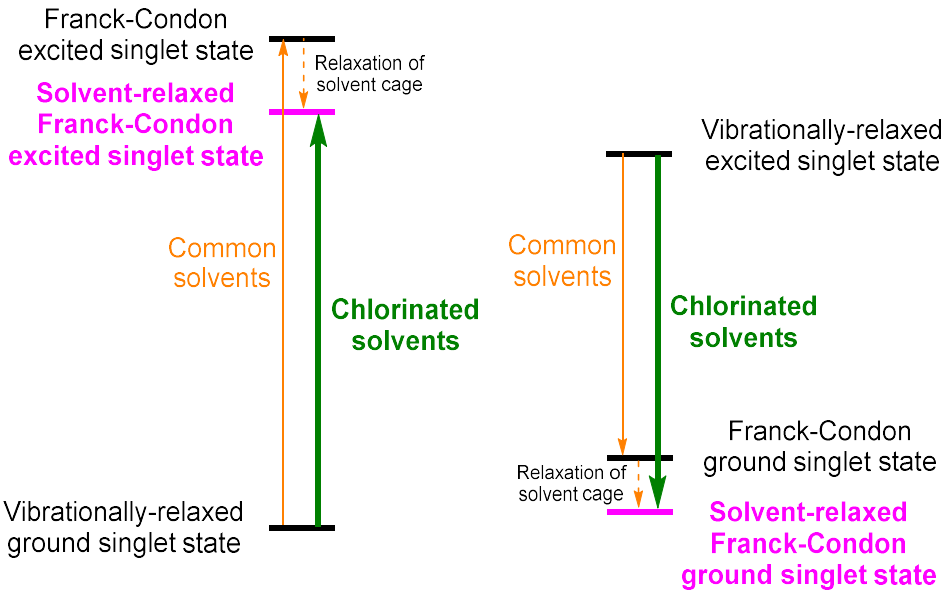

Figure S10. Representation of solvent-relaxed Franck-Condon (FC) excited state and solvent-relaxed FC ground state in chlorinated solvents.

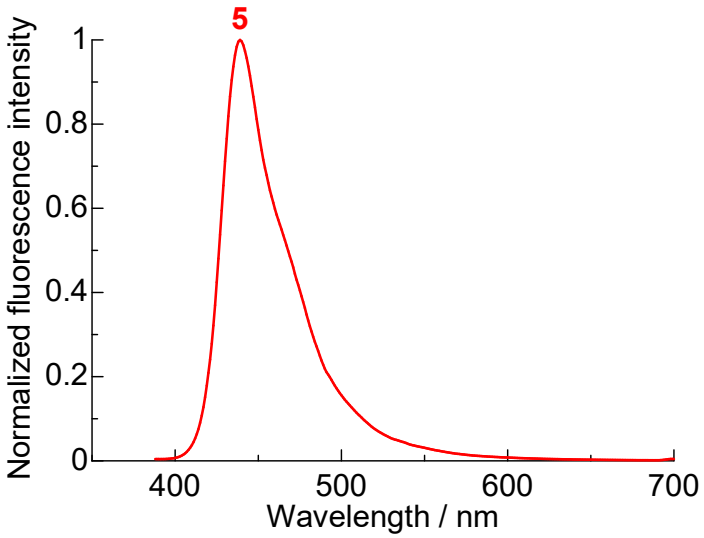

Figure S11. Fluorescence spectra of **5** in the crystalline state.

Table S1. Optical properties of **2** in various solvents[a]

Solvent	λ_{ab} (ε) / nm	λ_{fl}[b] / nm	Φ_f[c]
n-Hexane	297 (31,100), 302 (30,800), 311 (33,300)	323	0.21
Cyclohexane	298 (26,200), 303 (25,900), 312 (28,100)	332	0.34
Toluene	305 (29,000)	345	0.49
1,4-Dioxane	303 (26,200)	346	0.06
$CHCl_3$	309 (28,500)	355	< 0.01
Ethyl acetate	303 (26,200)	347	0.04
THF	304 (30,700)	346	0.05
CH_2Cl_2	307 (29,900)	356	0.03
MeCN	305 (29,200)	364	0.01

[a]Measured at a concentration of 1.0 x 10^{-5} M. [b]The excitation wavelengths (λ_{ex}) were as follows: hexane (321 nm), cyclohexane (311 nm), 1,4-dioxane (313 nm), toluene (315 nm), chloroform (319 nm), ethyl acetate (313 nm), THF (313 nm), dichloromethane (316 nm), and acetonitrile (314 nm). [c]Measured using an integrating sphere method.

Table S2. Optical properties of **5** in various solvents[a]

Solvent	λ_{ab} (ε) / nm	λ_{fl}[b] / nm	Φ_f[c]
n-Hexane	340 (44,500)	393, 412	0.72
Cyclohexane	339 (41,400)	395	0.84
Toluene	347 (38,600)	409, 423	0.93
1,4-Dioxane	346 (45,000)	408	0.98
$CHCl_3$	351 (37,600)	395, 405	0.09
Ethyl acetate	345 (46,300)	416	0.86
THF	345 (45,800)	415	0.94
CH_2Cl_2	350 (44,100)	439	0.87
MeCN	346 (45,600)	446	0.98

[a]Measured at a concentration of 1.0 x 10^{-5} M. The excitation wavelengths (λ_{ex}) were as follows: *n*-hexane (350 nm), cyclohexane (349 nm), 1,4-dioxane (356 nm), toluene (357 nm), chloroform (361 nm), ethyl acetate (355 nm), THF (355 nm), dichloromethane (360 nm) and acetonitrile (356 nm). [c]Measured using an integrating sphere method.

Table S3. Optical properties of **6** in various solvents[a]

Solvent	λ_{ab} (ε) / nm	λ_{fl}[b] / nm	Φ_f[c]
n-Hexane	306 (46,400)	406[d]	0.16
Cyclohexane	306 (45,100)	407[d]	0.21
Toluene	312 (44,500)	459[e]	0.59
1,4-Dioxane	308 (47,600)	457[e]	0.38
$CHCl_3$	312 (43,000)	388[d], 488[e]	0.07
Ethyl acetate	307 (48,300)	469[e]	0.19
THF	309 (48,500)	464[e]	0.26
CH_2Cl_2	310 (46,000)	392[d], 517[e]	0.14
MeCN	308 (48,700)	538[e]	0.05

[a]Measured at a concentration of 1.0 x 10^{-5} M. [b]The excitation wavelengths (λ_{ex}) were as follows: *n*-hexane (316 nm), cyclohexane (316 nm), 1,4-dioxane (318 nm), toluene (322 nm), chloroform (322 nm), ethyl acetate (317 nm), THF (319 nm), dichloromethane (320 nm) and acetonitrile (318 nm). [c]Measured using an integrating sphere method. [d]Fluorescence from LE state. [e]Fluorescence from TICT state.

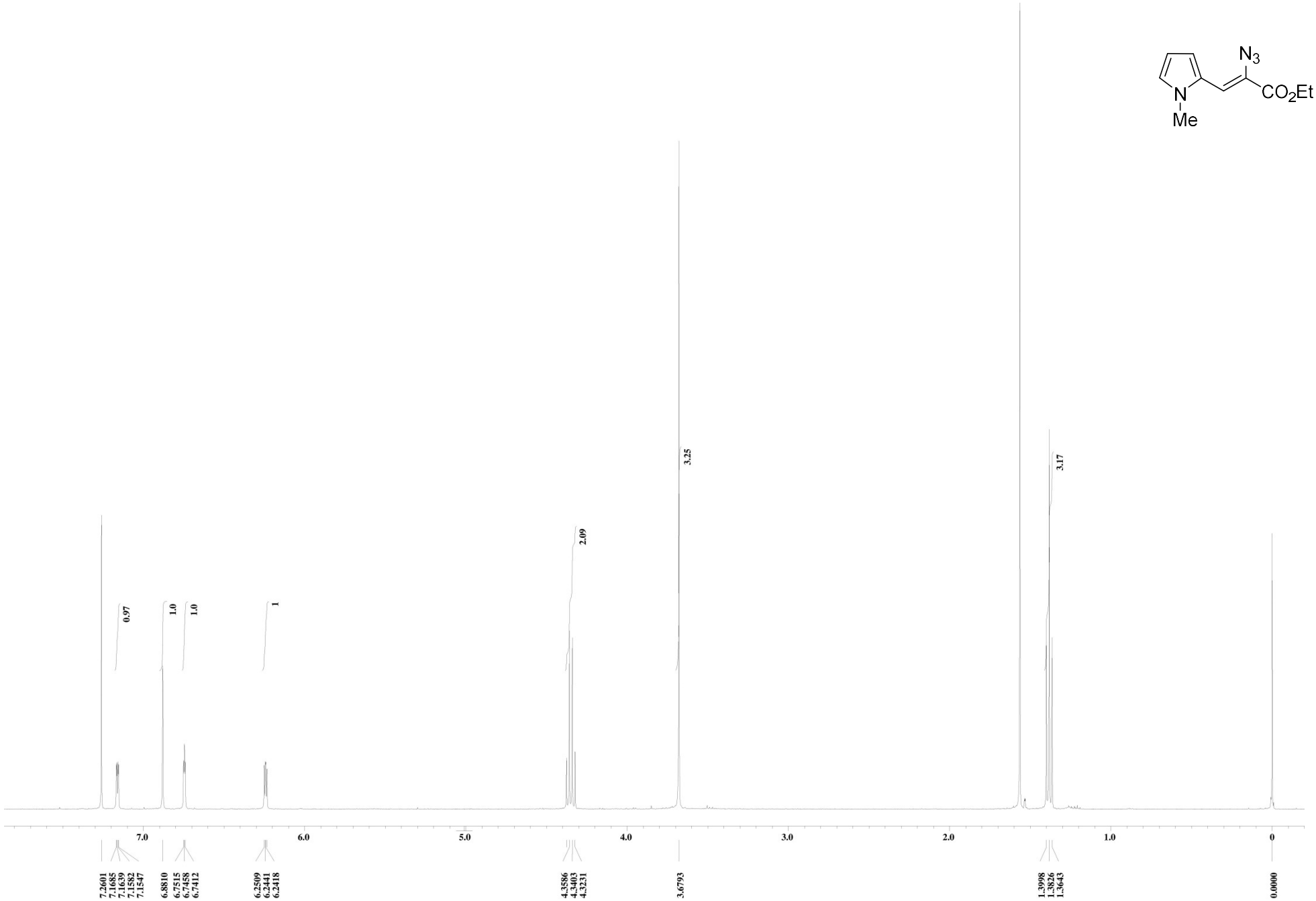

Figure S12. ^{1}H NMR spectrum of **1**.

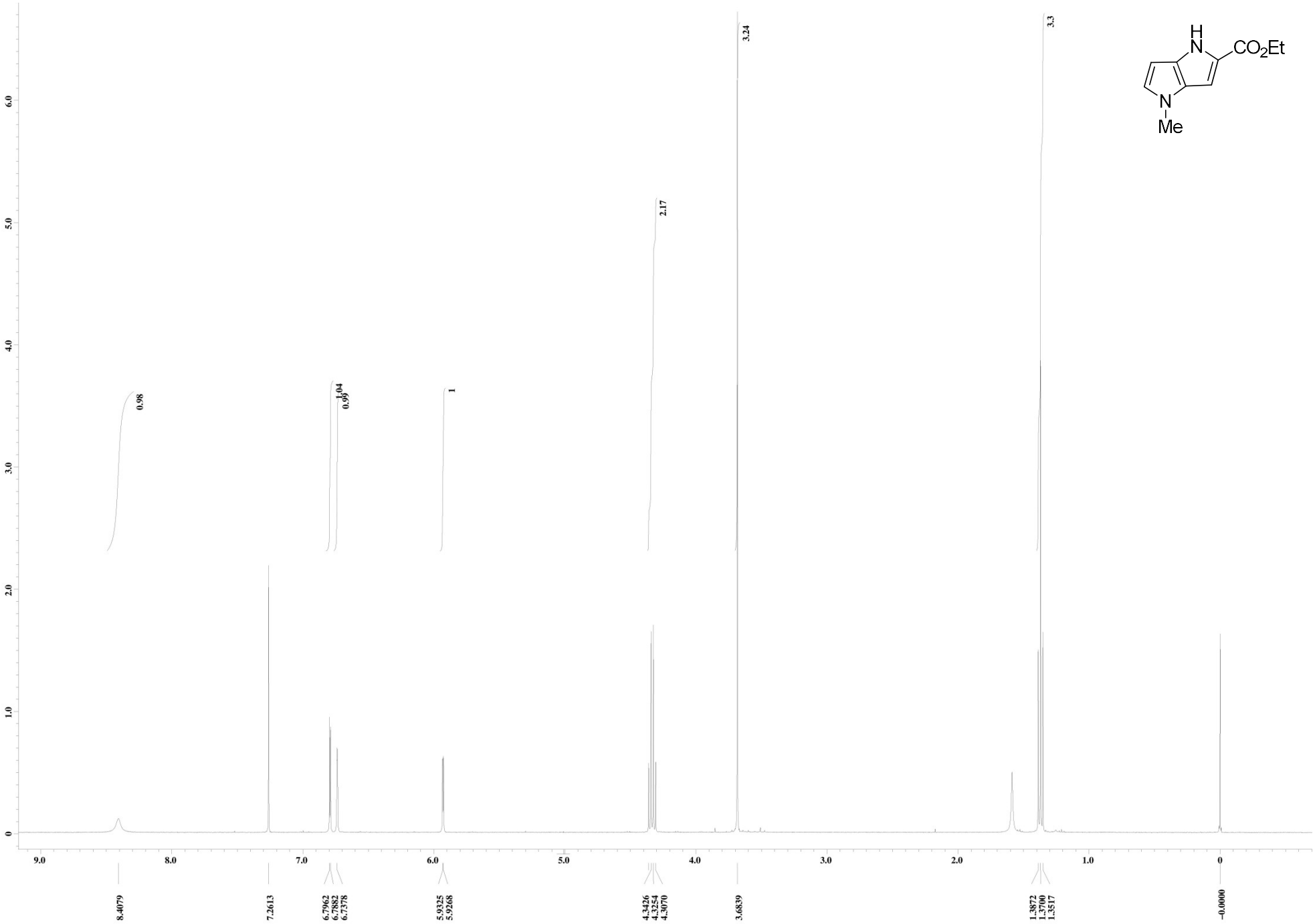

Figure S13. ^{1}H NMR spectrum of **2**.

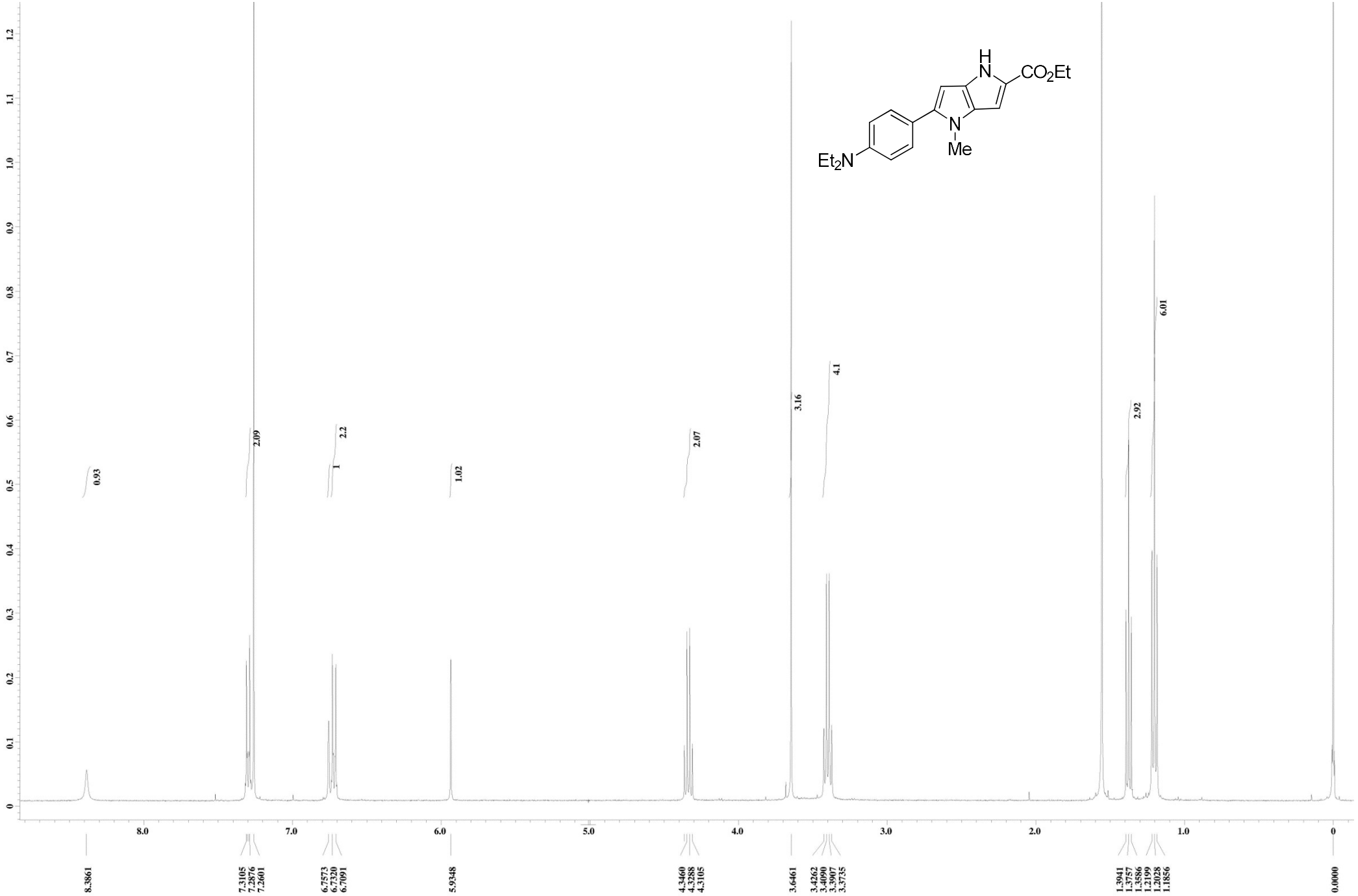

Figure S14. ^{1}H NMR spectrum of **5**.

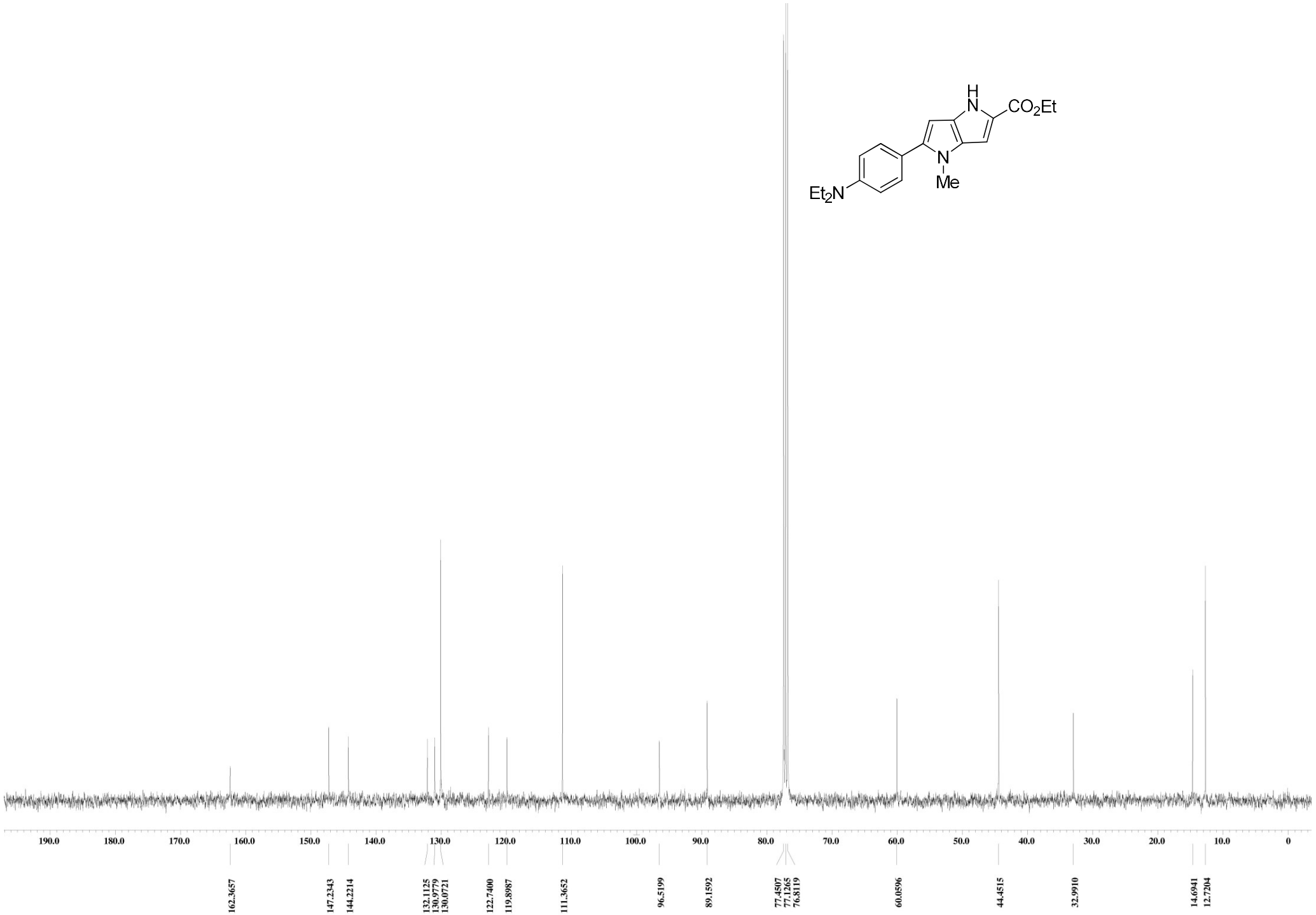

Figure S15. ^{13}C NMR spectrum of **5**.

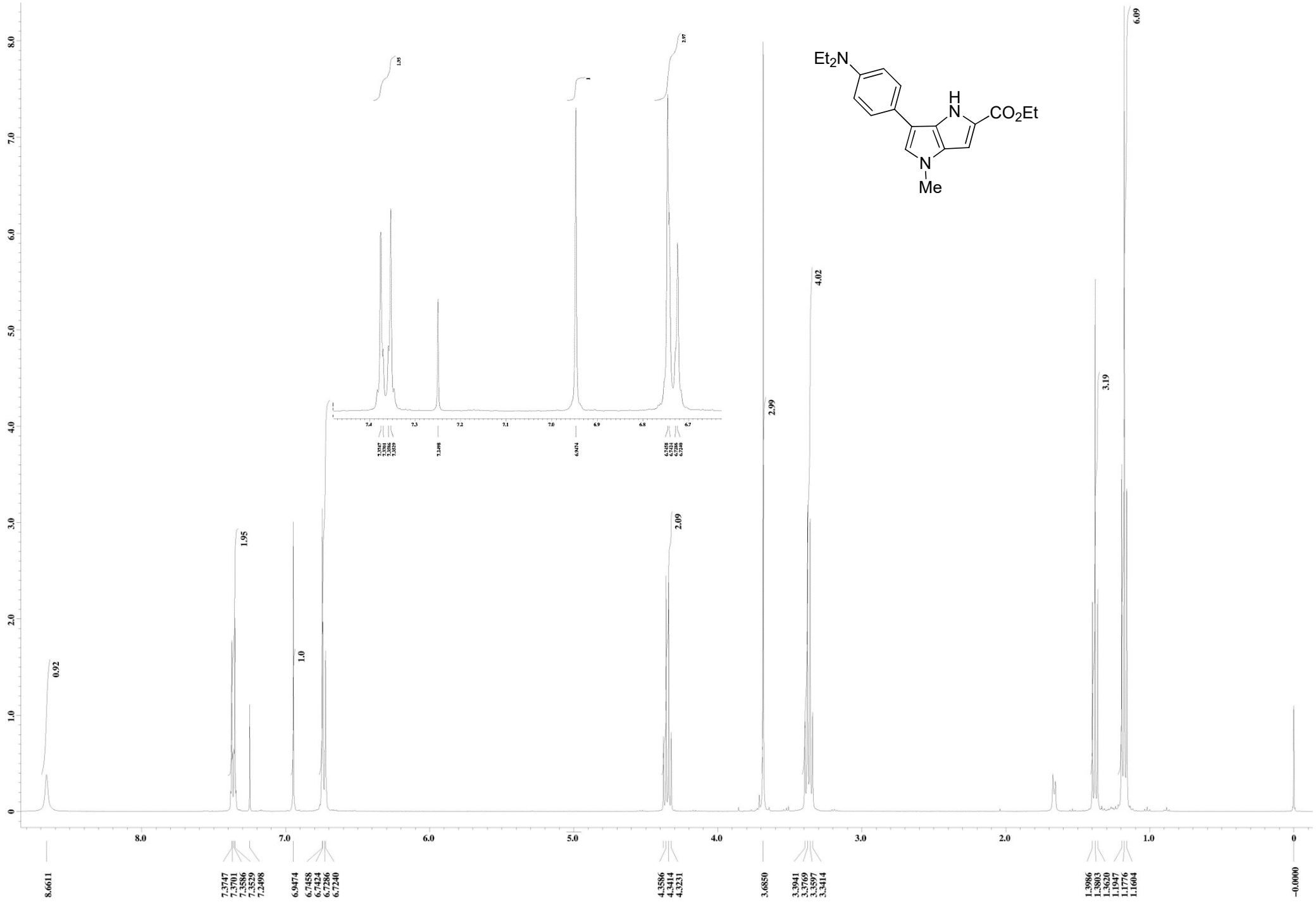

Figure S16. ^{1}H NMR spectrum of **6**.

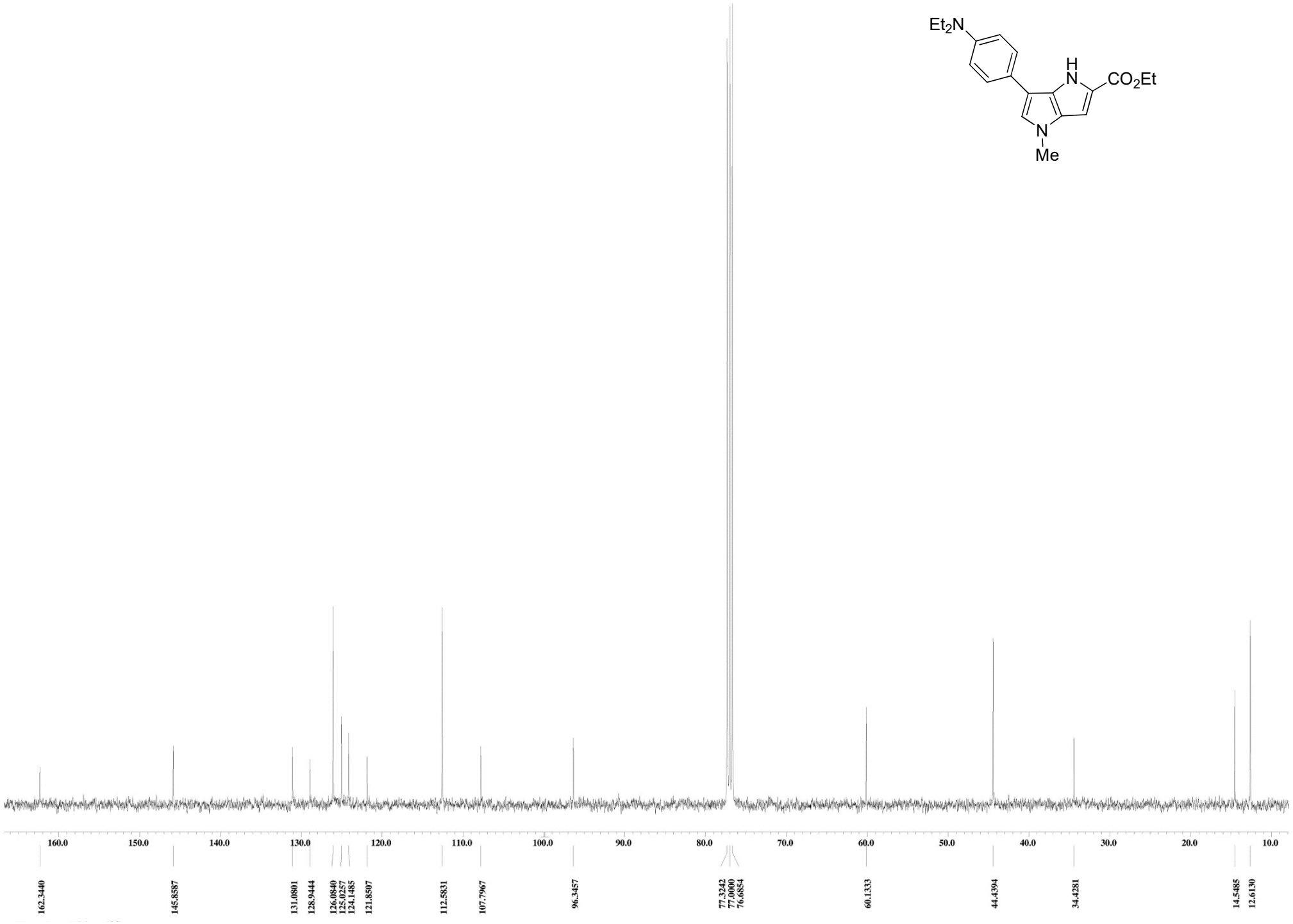

Figure S17. ^{13}C NMR spectrum of **6**.