

Electronic Supplementary information

Photophysical properties of 4-4-(5-methylthiophen-2-yl)pyridinium–cyclic enolate betaine dyes tuned by control of twisted intramolecular transfer

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Table S1. Crystal data and structure refinement for **TPB-4**

	TPB-4
Formula	C ₂₀ H ₉ F ₅ N ₂ O ₃ S
Formula weight	452.35
Crystal system	monoclinic
Space group	P2 ₁ /c (#14)
Lattice Parameters <i>a</i> /Å	15.9055(9)
<i>b</i> /Å	7.1059(4)
<i>c</i> /Å	16.6403(11)
β /°	106.502(8)
Volume /Å ³	1803.3(2)
Z	4
Density ρ_{calc} /g cm ⁻³	1.666
μ /cm ⁻¹	2.575
<i>F</i> (000)	912.00
<i>T</i> /K	296.15
No. of refractions measured	16479
No. of refractions used (<i>R</i> _{int})	4116 (0.0373)
R1, wR2	0.0408, 0.0482
Goodness of fit on <i>F</i> ²	1.086
ρ_{fin} (max/min) /e Å ³	0.26/-0.34

Table S2. Photophysical properties of **TPB-1–4** in different solvents^a

Dye	Solvent	$\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / 10^2 \text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}} / \text{nm}$	Φ_{PL}
TPB-1	CHCl ₃	419 (270)	543	0.055
	CH ₂ Cl ₂	423 (250)	561	0.022
	THF	439 (283)	N.D. ^b	N.D. ^b
	acetone	427 (271)	N.D. ^b	N.D. ^b
	DMSO	426 (241)	N.D. ^b	N.D. ^b
	DMF	423 (239)	N.D. ^b	N.D. ^b
	TPB-2	CHCl ₃	347 (176), 424 (82)	593
CH ₂ Cl ₂		345 (158), 429 (75)	618	0.003
THF		337 (156), 452 (89)	N.D. ^b	N.D. ^b
acetone		337 (174), 439 (84)	N.D. ^b	N.D. ^b
DMSO		346 (168), 433 (71)	N.D. ^b	N.D. ^b
DMF		344 (183), 425 (75)	N.D. ^b	N.D. ^b
TPB-3		CHCl ₃	409 (300), 433 (270)	475
	CH ₂ Cl ₂	408 (300)	476	0.39
	THF	409 (273)	518	0.017
	acetone	404 (288)	516	0.010
	DMSO	406 (242)	503	0.004
	DMF	405 (237)	493	0.004
	TPB-4	CHCl ₃	425 (364), 448 (319)	491
CH ₂ Cl ₂		423 (358)	498	0.16
THF		424 (351)	536	0.014
acetone		419 (334)	537	0.009
DMSO		420 (289)	518	0.010
DMF		420 (264)	509	0.003

^a Measured at rt. ^b Not determined due to too weak emission.

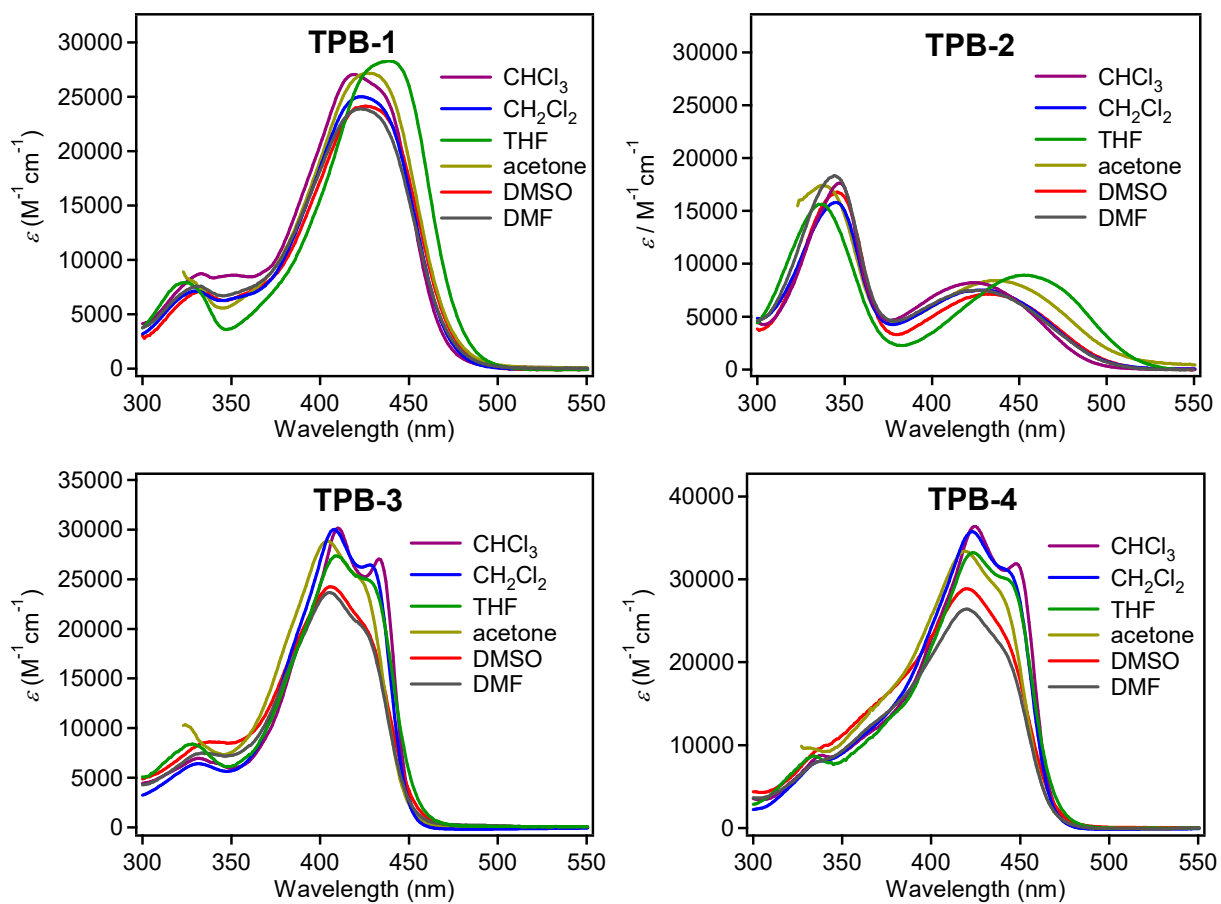


Fig. S1. Electronic absorption spectra of TPB-1–4 in different solvents (1.0×10^{-5} M).

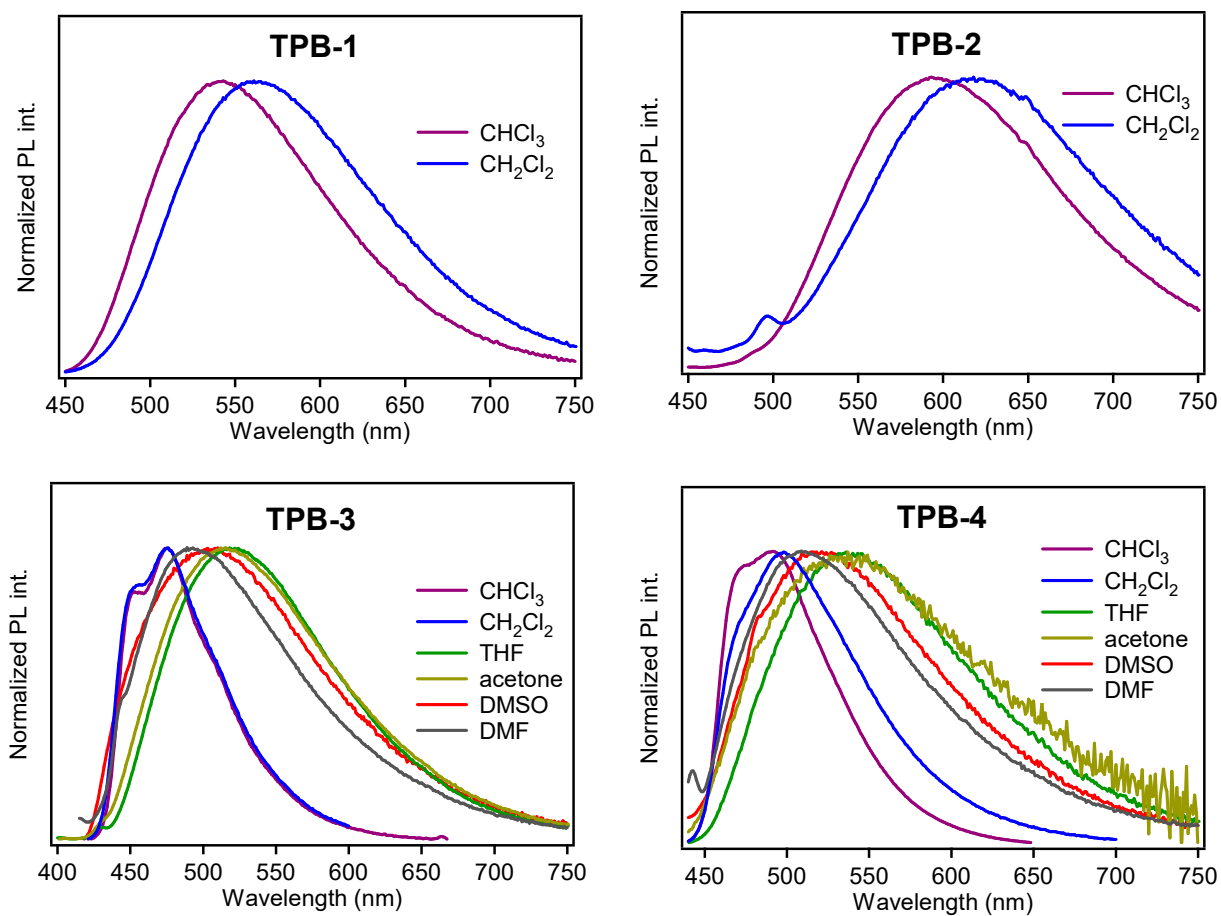


Fig. S2. Fluorescence spectra of TPB-1–4 in different solvents (1.0×10^{-5} M).

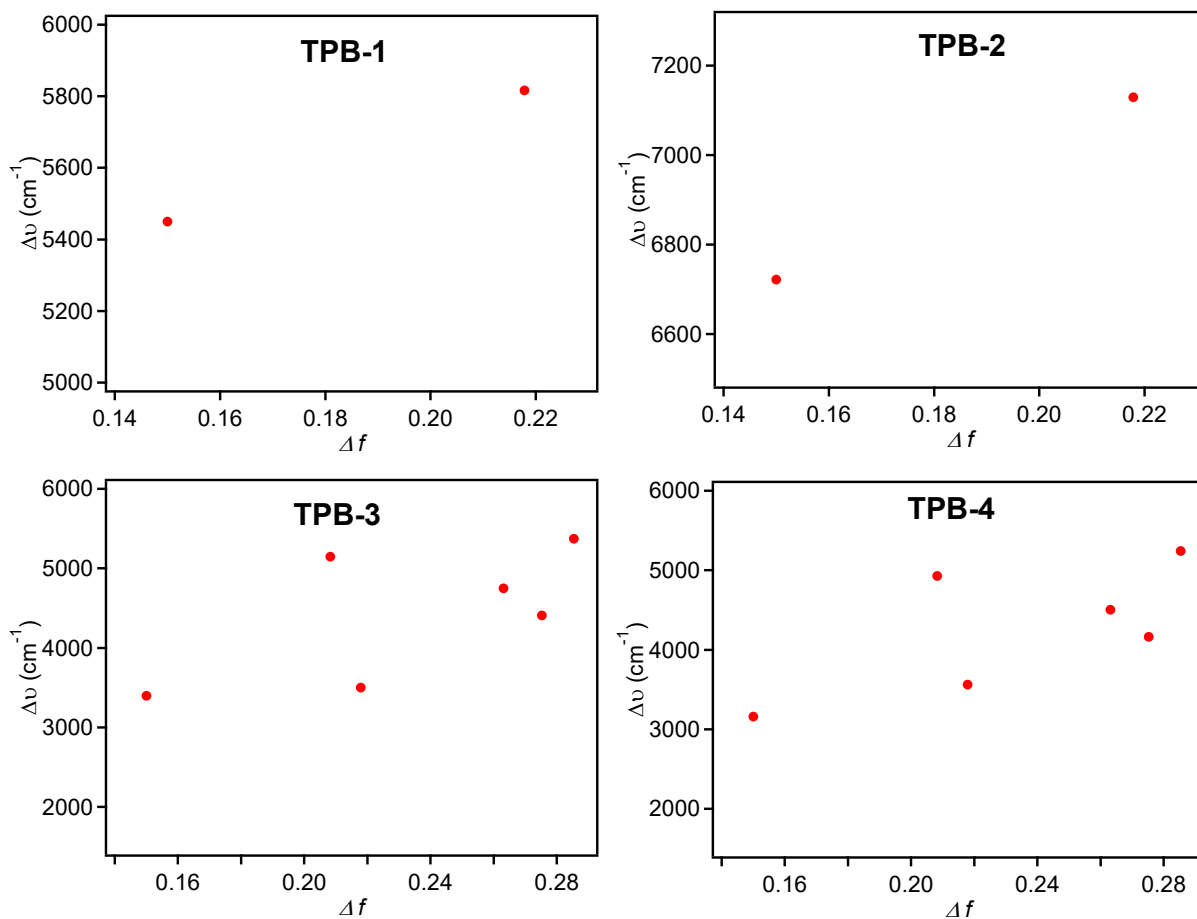


Fig. S3. Lippert-Mataga plots for TPB-1-4.

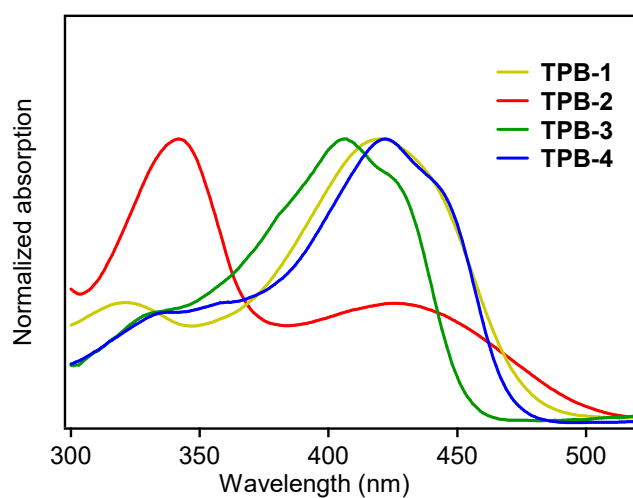


Fig. S4. Electronic absorption spectra of TPB-1-4 in PMMA doped film.

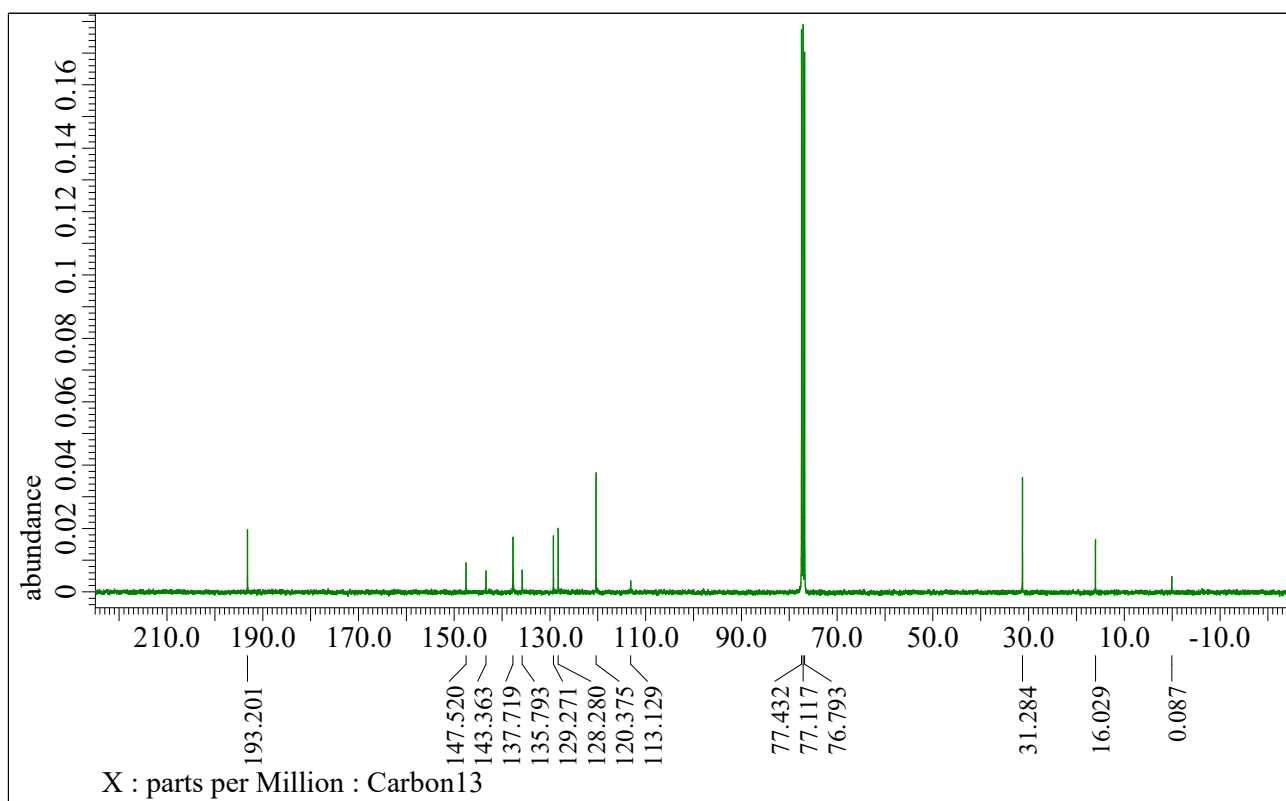
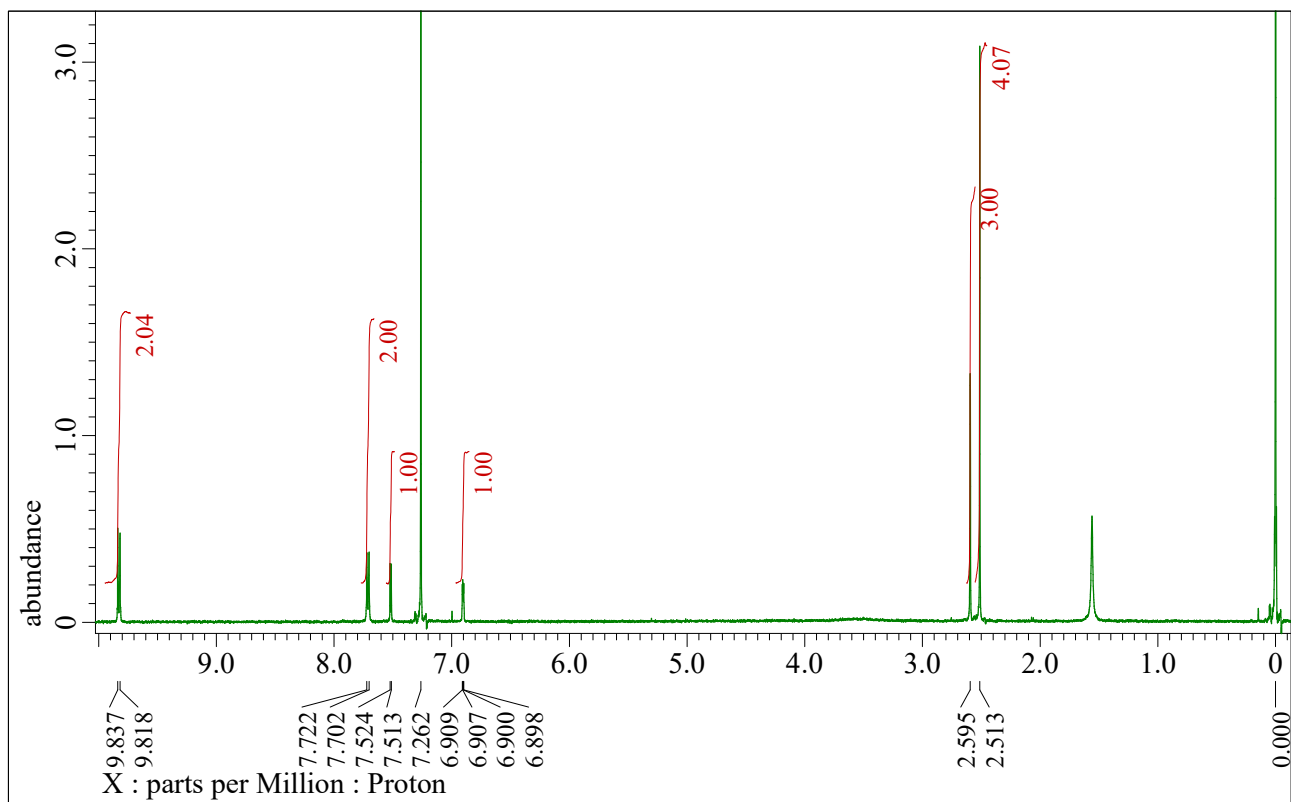


Fig. S5. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) spectra of TPB-1 (CDCl₃, 25 °C).

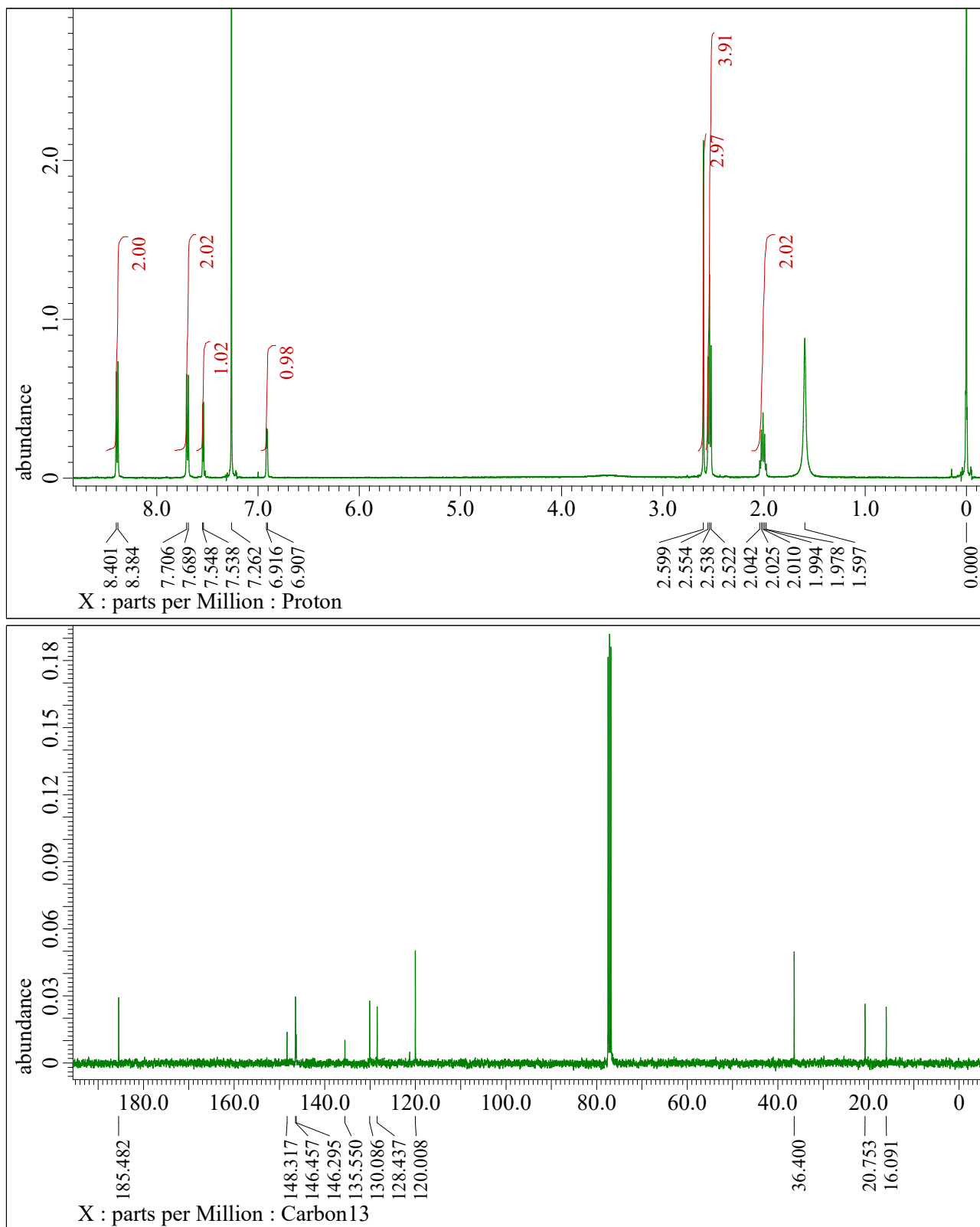


Fig. S6. ^1H (upper, 400 MHz) and ^{13}C (lower, 100 MHz) spectra of **TPB-2** (CDCl_3 , 25 $^\circ\text{C}$).

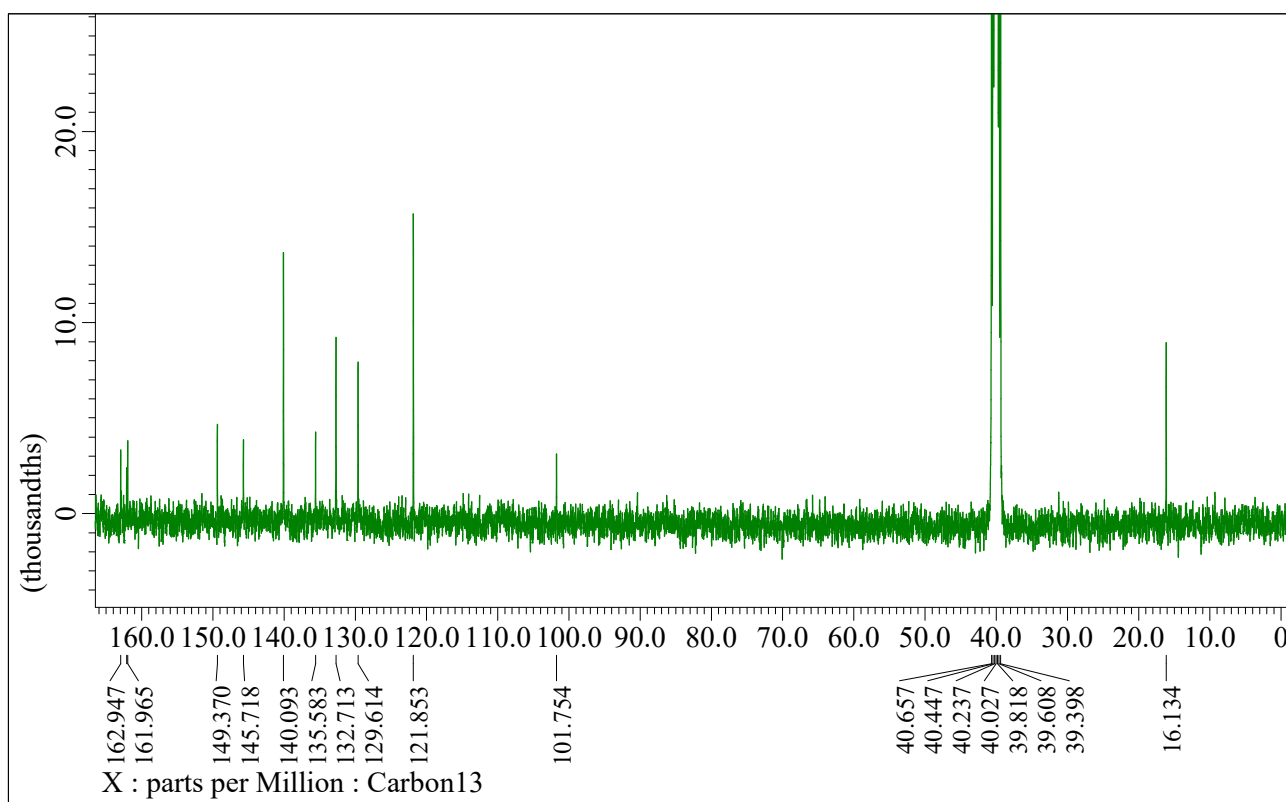
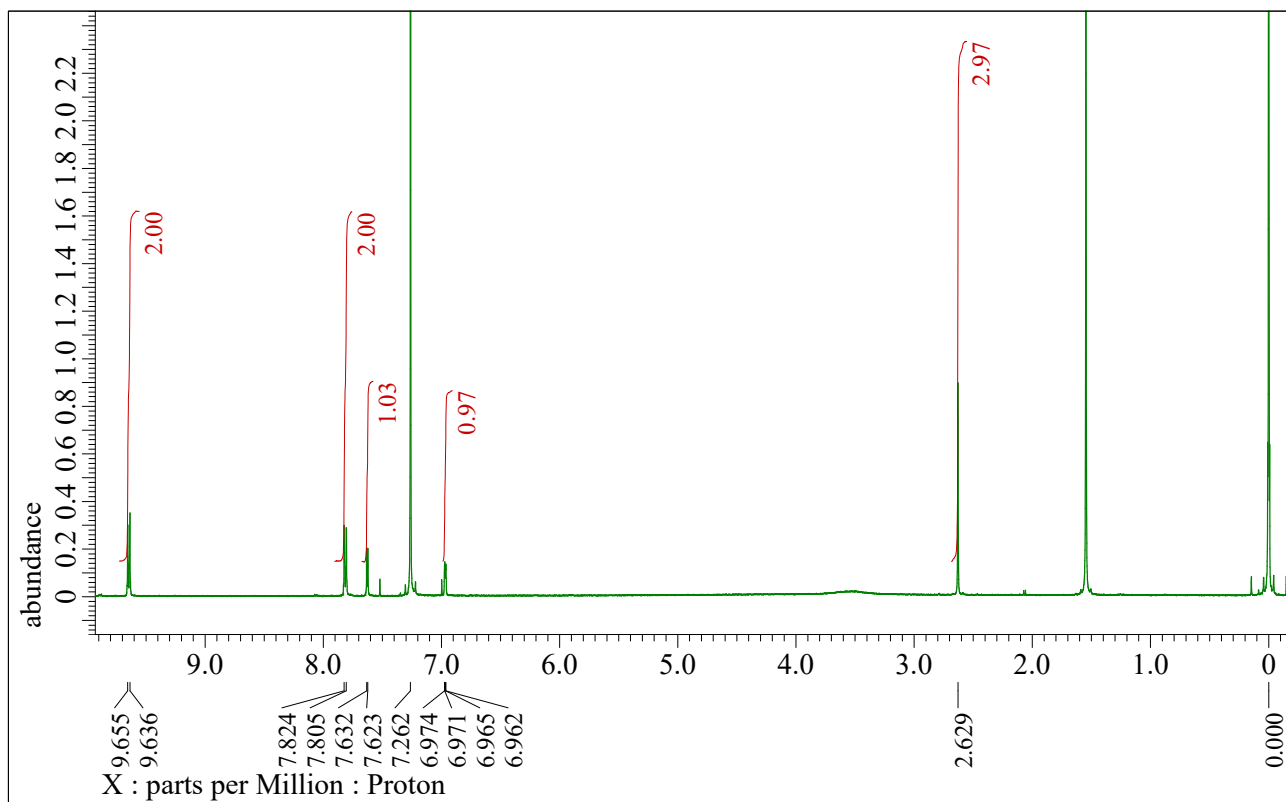


Fig. S7. ¹H (upper, 400 MHz, CDCl₃) and ¹³C (lower, 100 MHz, DMSO-D₆) spectra of TPB-3 (25 °C).

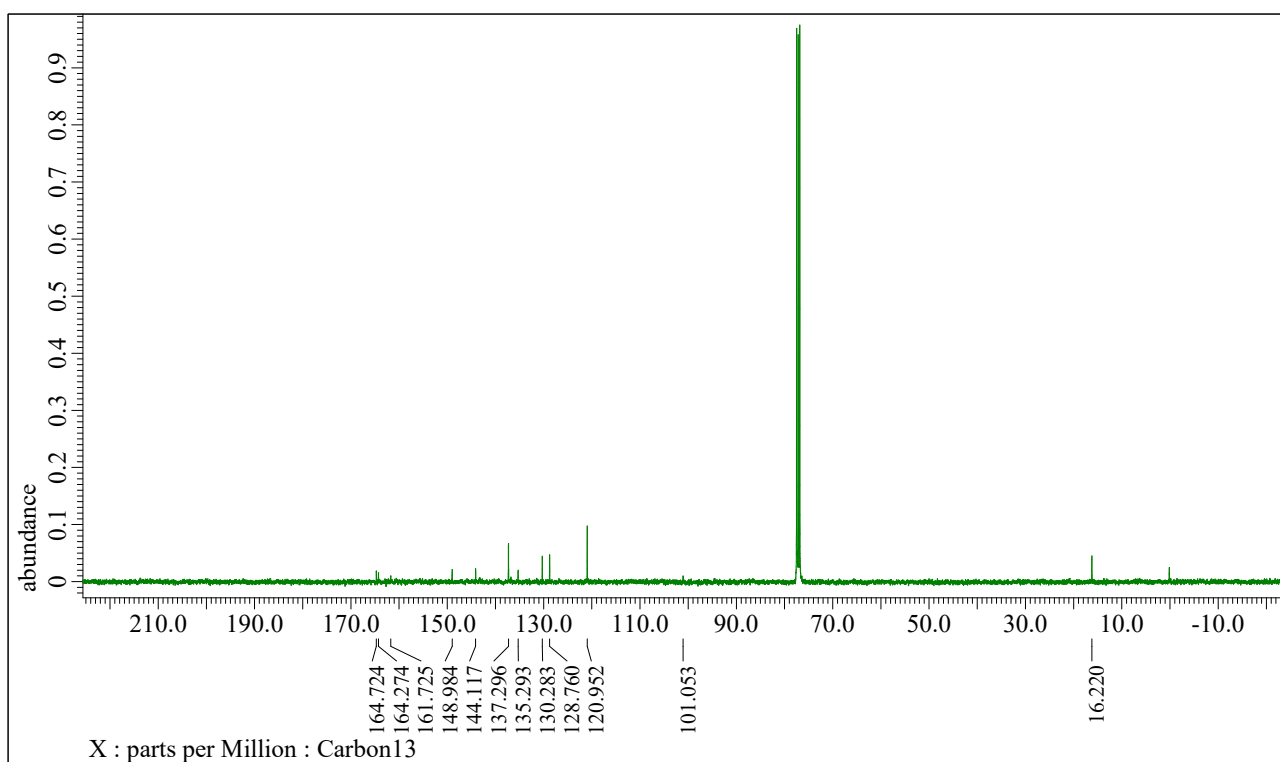
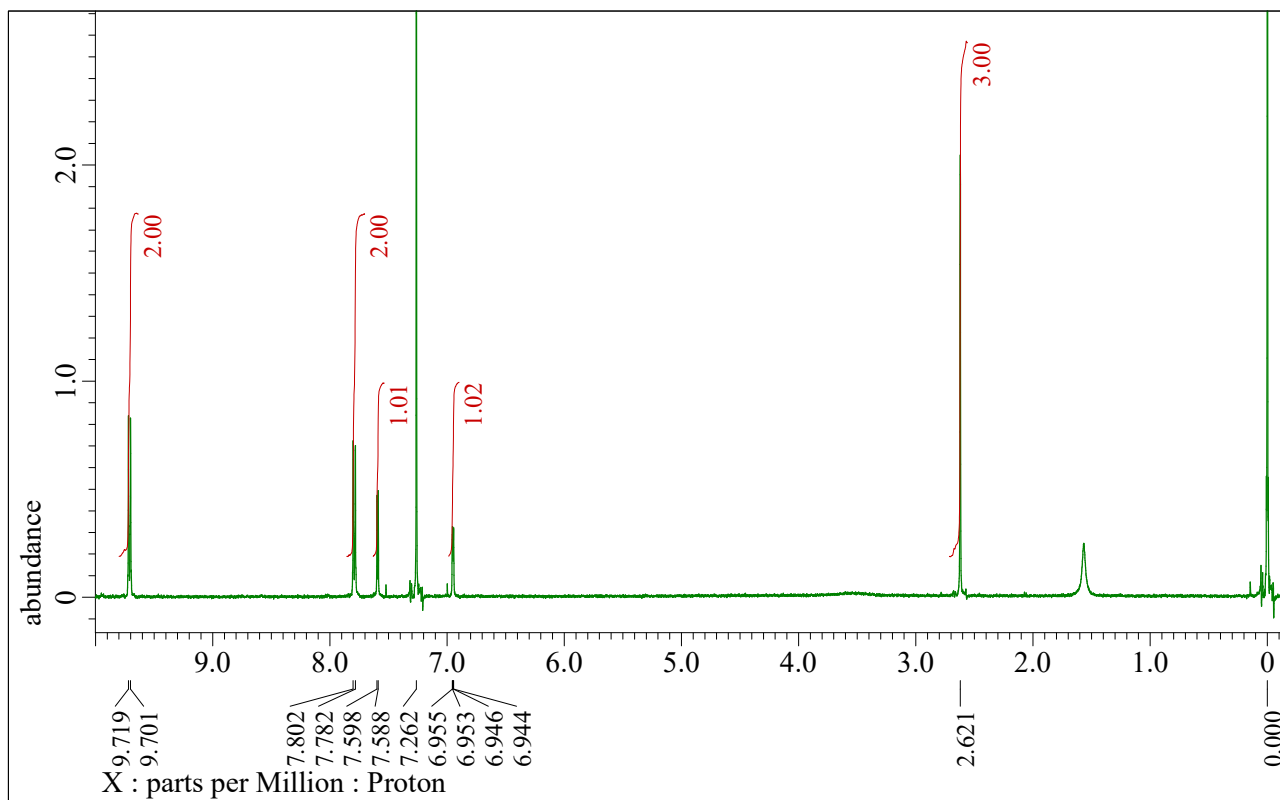


Fig. S8. ^1H (upper, 400 MHz) and ^{13}C (lower, 100 MHz) spectra of **TPB-4** (CDCl_3 , 25 °C).

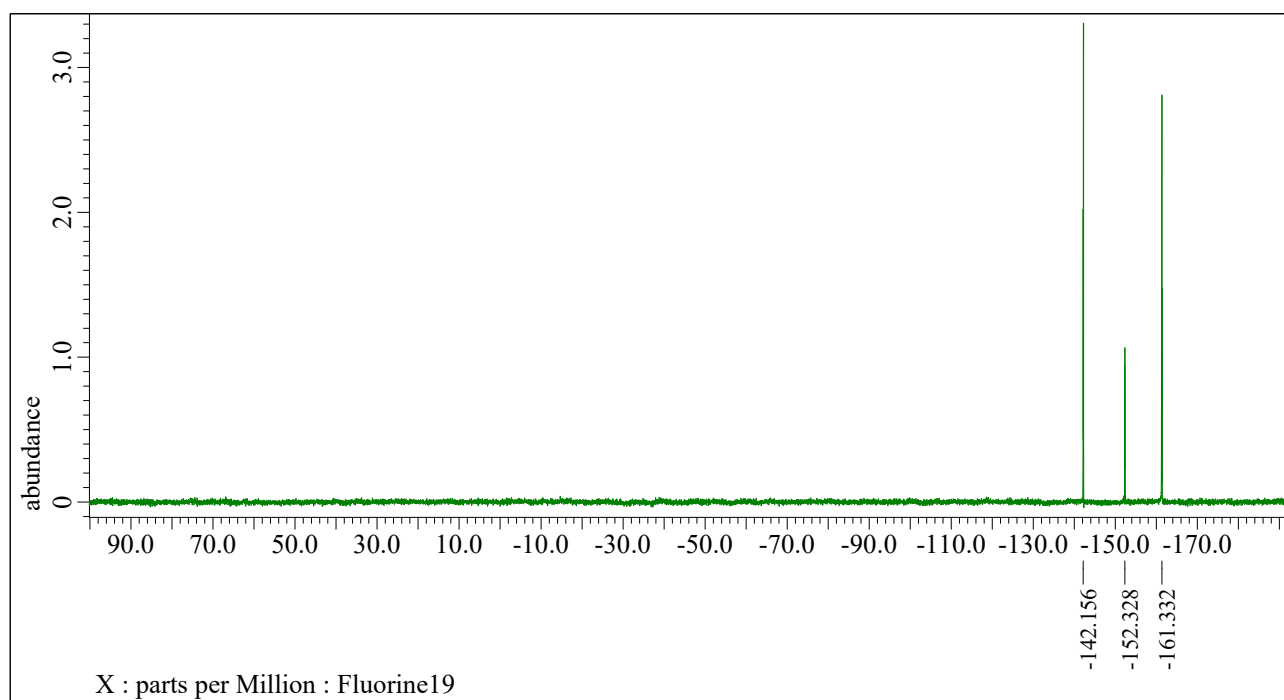


Fig. S9. ^{19}F (376 MHz) spectra of **TPB-4** (CDCl_3 , $25\text{ }^\circ\text{C}$).

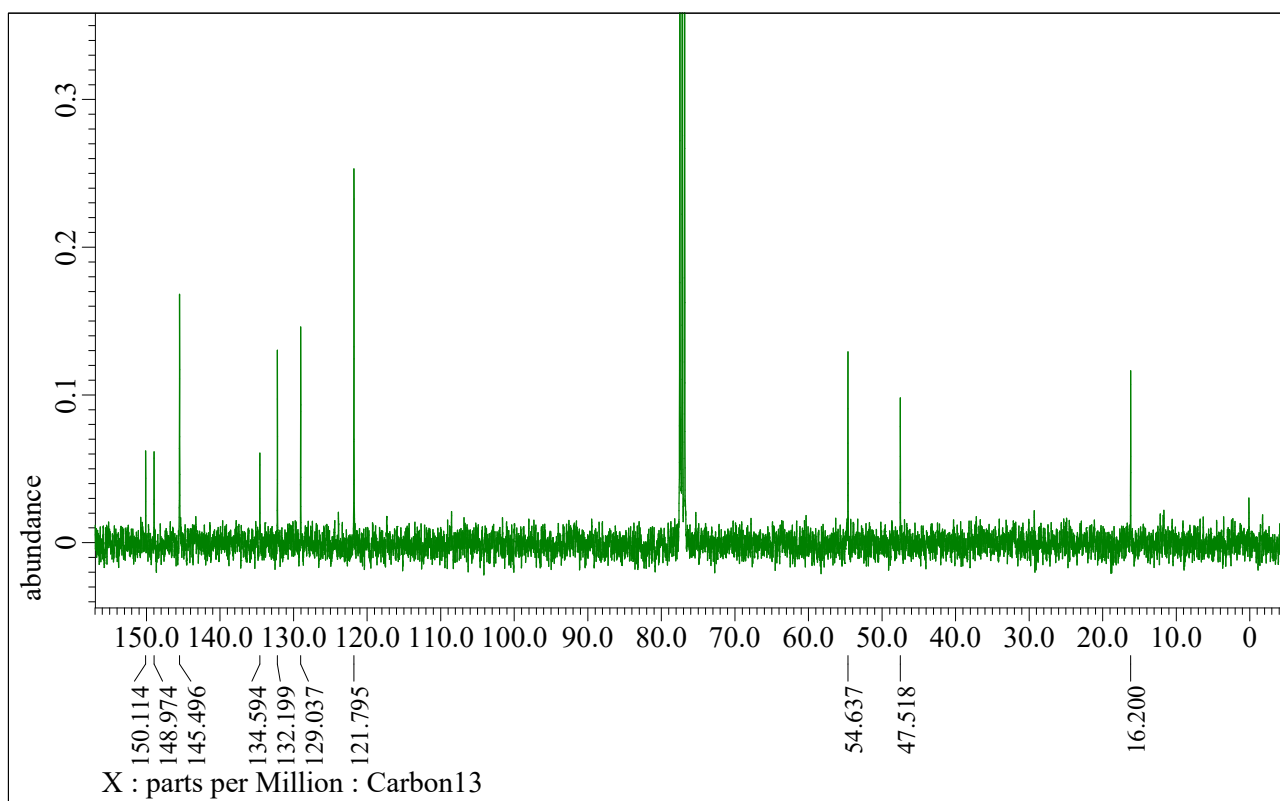
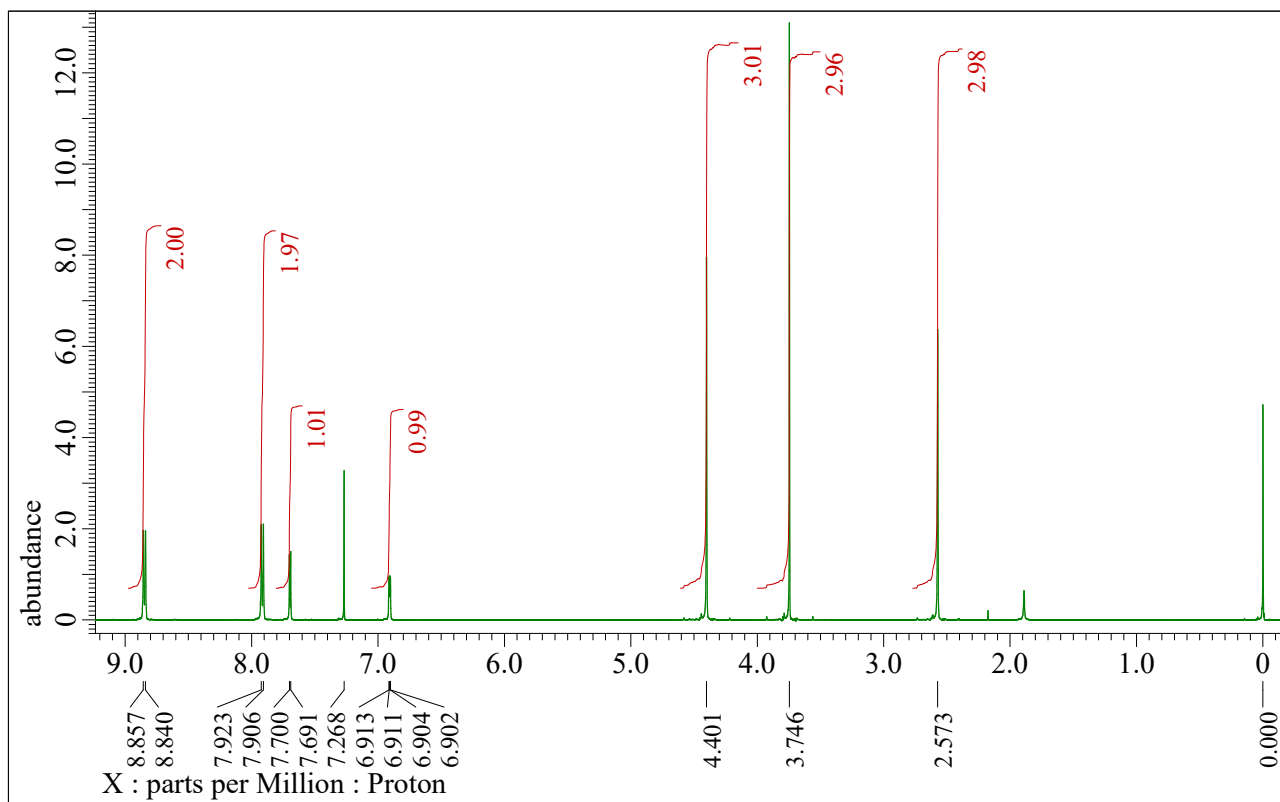


Fig. S10. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) spectra of TP-Me (CDCl₃, 25 °C).