

Supplementary information

Synthesis of novel π -extended D–A–D-type dipyrido[3,2-*a*:2',3'-*c*]phenazine derivatives and their photosensitized singlet oxygen generation

Yuichiro Hayashi,^a Ami Morimoto,^a Takeshi Maeda,^a Toshiaki Enoki,^b
Yousuke Ooyama,^b Yasunori Matsui,^a Hiroshi Ikeda^a and Shigeyuki Yagi^{a*}

^aDepartment of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

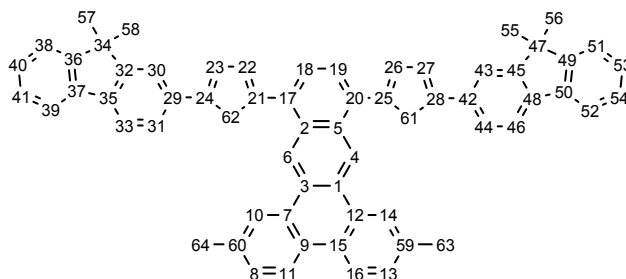
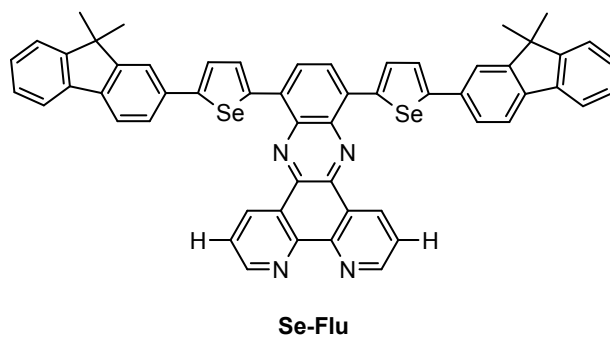
^bDepartment of Applied Chemistry, Graduate School of Engineering, Hiroshima University,
1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

Corresponding author: Prof. Dr. Shigeyuki Yagi
TEL: +81-72-254-9320 FAX: +81-72-254-9910
E-mail: yagi@chem.osakafu-u.ac.jp

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Table S1. HOMO and LUMO composition analysis of **Se-Flu** showing the percent contribution of each atom.*



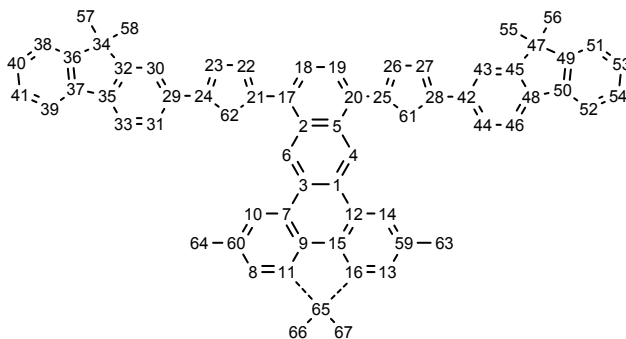
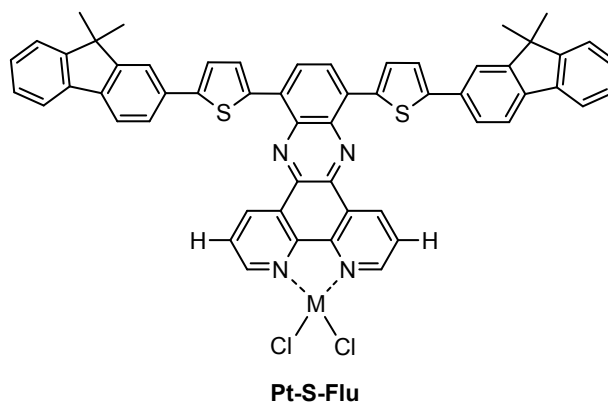
HOMO			LUMO		
Atom	1(C) :	0.39%	Atom	1(C) :	4.88%
Atom	2(C) :	1.01%	Atom	2(C) :	1.36%
Atom	3(C) :	0.39%	Atom	3(C) :	4.88%
Atom	4(N) :	0.69%	Atom	4(N) :	13.30%
Atom	5(C) :	1.01%	Atom	5(C) :	1.36%
Atom	6(N) :	0.69%	Atom	6(N) :	13.30%
Atom	7(C) :	0.14%	Atom	7(C) :	1.98%
Atom	8(C) :	0.16%	Atom	8(C) :	2.14%
Atom	9(C) :	0.16%	Atom	9(C) :	2.17%
Atom	10(C) :	0.08%	Atom	10(C) :	1.41%
Atom	11(N) :	0.01%	Atom	11(N) :	0.08%
Atom	12(C) :	0.14%	Atom	12(C) :	1.98%
Atom	13(C) :	0.16%	Atom	13(C) :	2.14%
Atom	14(C) :	0.08%	Atom	14(C) :	1.41%
Atom	15(C) :	0.16%	Atom	15(C) :	2.17%
Atom	16(N) :	0.01%	Atom	16(N) :	0.08%

Atom	17(C) :	4.48%	Atom	17(C) :	8.05%
Atom	18(C) :	3.13%	Atom	18(C) :	5.54%
Atom	19(C) :	3.13%	Atom	19(C) :	5.54%
Atom	20(C) :	4.48%	Atom	20(C) :	8.05%
Atom	21(C) :	6.91%	Atom	21(C) :	0.35%
Atom	22(C) :	4.66%	Atom	22(C) :	2.39%
Atom	23(C) :	3.97%	Atom	23(C) :	0.09%
Atom	24(C) :	7.12%	Atom	24(C) :	2.15%
Atom	25(C) :	6.91%	Atom	25(C) :	0.35%
Atom	26(C) :	4.66%	Atom	26(C) :	2.39%
Atom	27(C) :	3.97%	Atom	27(C) :	0.09%
Atom	28(C) :	7.12%	Atom	28(C) :	2.15%
Atom	29(C) :	2.19%	Atom	29(C) :	0.13%
Atom	30(C) :	1.71%	Atom	30(C) :	0.48%
Atom	31(C) :	2.42%	Atom	31(C) :	0.39%
Atom	32(C) :	0.90%	Atom	32(C) :	0.01%
Atom	33(C) :	0.61%	Atom	33(C) :	0.05%
Atom	34(C) :	0.01%	Atom	34(C) :	0.00%
Atom	35(C) :	3.50%	Atom	35(C) :	0.51%
Atom	36(C) :	1.30%	Atom	36(C) :	0.10%
Atom	37(C) :	0.74%	Atom	37(C) :	0.02%
Atom	38(C) :	0.04%	Atom	38(C) :	0.02%
Atom	39(C) :	1.06%	Atom	39(C) :	0.14%
Atom	40(C) :	1.73%	Atom	40(C) :	0.15%
Atom	41(C) :	0.25%	Atom	41(C) :	0.00%
Atom	42(C) :	2.19%	Atom	42(C) :	0.13%
Atom	43(C) :	1.71%	Atom	43(C) :	0.48%
Atom	44(C) :	2.42%	Atom	44(C) :	0.39%
Atom	45(C) :	0.90%	Atom	45(C) :	0.01%
Atom	46(C) :	0.61%	Atom	46(C) :	0.05%
Atom	47(C) :	0.01%	Atom	47(C) :	0.00%
Atom	48(C) :	3.50%	Atom	48(C) :	0.51%
Atom	49(C) :	1.30%	Atom	49(C) :	0.10%
Atom	50(C) :	0.74%	Atom	50(C) :	0.02%

Atom	51(C) :	0.04%	Atom	51(C) :	0.02%
Atom	52(C) :	1.06%	Atom	52(C) :	0.14%
Atom	53(C) :	1.73%	Atom	53(C) :	0.15%
Atom	54(C) :	0.25%	Atom	54(C) :	0.00%
Atom	55(C) :	0.01%	Atom	55(C) :	0.00%
Atom	56(C) :	0.00%	Atom	56(C) :	0.00%
Atom	57(C) :	0.01%	Atom	57(C) :	0.00%
Atom	58(C) :	0.00%	Atom	58(C) :	0.00%
Atom	59(C) :	0.06%	Atom	59(C) :	0.53%
Atom	60(C) :	0.06%	Atom	60(C) :	0.53%
Atom	61(Se) :	0.46%	Atom	61(Se) :	1.45%
Atom	62(Se) :	0.46% □	Atom	62(Se) :	1.45%
Atom	63(H) :	0.00%	Atom	63(H) :	0.00%
Atom	64(H) :	0.00%	Atom	64(H) :	0.00%

* The values for the hydrogen atoms are not shown except for atoms 63 and 64 due to their low percent contributions.

Table S2. HOMO and LUMO composition analysis of **Pt-S-Flu** showing the percent contribution of each atom.*



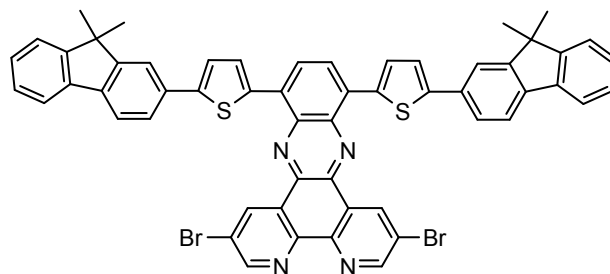
HOMO			□	LUMO		
Atom	1(C) :	0.39%		Atom	1(C) :	3.75%
Atom	2(C) :	1.02%		Atom	2(C) :	2.58%
Atom	3(C) :	0.39%		Atom	3(C) :	3.75%
Atom	4(N) :	0.39%		Atom	4(N) :	14.80%
Atom	5(C) :	1.02%		Atom	5(C) :	2.58%
Atom	6(N) :	0.39%		Atom	6(N) :	14.80%
Atom	7(C) :	0.04%		Atom	7(C) :	4.02%
Atom	8(C) :	0.11%		Atom	8(C) :	1.79%
Atom	9(C) :	0.10%		Atom	9(C) :	3.87%
Atom	10(C) :	0.07%		Atom	10(C) :	0.62%
Atom	11(N) :	0.00%		Atom	11(N) :	0.52%
Atom	12(C) :	0.04%		Atom	12(C) :	4.02%
Atom	13(C) :	0.11%		Atom	13(C) :	1.79%
Atom	14(C) :	0.07%		Atom	14(C) :	0.62%

Atom	15(C) :	0.10%	Atom	15(C) :	3.87%
Atom	16(N) :	0.00%	Atom	16(N) :	0.52%
Atom	17(C) :	3.18%	Atom	17(C) :	6.22%
Atom	18(C) :	2.37%	Atom	18(C) :	4.96%
Atom	19(C) :	2.37%	Atom	19(C) :	4.96%
Atom	20(C) :	3.18%	Atom	20(C) :	6.22%
Atom	21(C) :	6.90%	Atom	21(C) :	0.09%
Atom	22(C) :	3.67%	Atom	22(C) :	1.56%
Atom	23(C) :	4.09%	Atom	23(C) :	0.04%
Atom	24(C) :	6.42%	Atom	24(C) :	1.37%
Atom	25(C) :	6.90%	Atom	25(C) :	0.09%
Atom	26(C) :	3.67%	Atom	26(C) :	1.56%
Atom	27(C) :	4.09%	Atom	27(C) :	0.04%
Atom	28(C) :	6.42%	Atom	28(C) :	1.37%
Atom	29(C) :	3.08%	Atom	29(C) :	0.02%
Atom	30(C) :	1.65%	Atom	30(C) :	0.25%
Atom	31(C) :	2.56%	Atom	31(C) :	0.23%
Atom	32(C) :	1.33%	Atom	32(C) :	0.01%
Atom	33(C) :	0.92%	Atom	33(C) :	0.01%
Atom	34(C) :	0.02%	Atom	34(C) :	0.00%
Atom	35(C) :	4.06%	Atom	35(C) :	0.27%
Atom	36(C) :	1.75%	Atom	36(C) :	0.06%
Atom	37(C) :	1.23%	Atom	37(C) :	0.00%
Atom	38(C) :	0.07%	Atom	38(C) :	0.00%
Atom	39(C) :	1.35%	Atom	39(C) :	0.07%
Atom	40(C) :	2.42%	Atom	40(C) :	0.07%
Atom	41(C) :	0.41%	Atom	41(C) :	0.00%
Atom	42(C) :	3.08%	Atom	42(C) :	0.02%
Atom	43(C) :	1.65%	Atom	43(C) :	0.25%
Atom	44(C) :	2.56%	Atom	44(C) :	0.23%
Atom	45(C) :	1.33%	Atom	45(C) :	0.01%
Atom	46(C) :	0.92%	Atom	46(C) :	0.01%
Atom	47(C) :	0.02%	Atom	47(C) :	0.00%
Atom	48(C) :	4.06%	Atom	48(C) :	0.27%

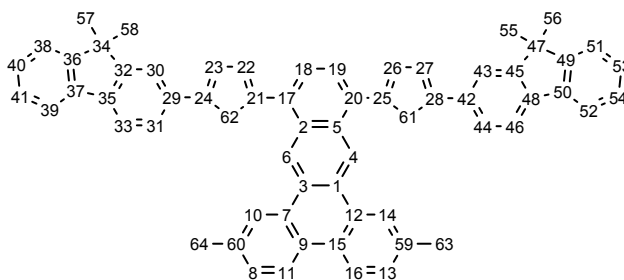
Atom	49(C) :	1.75%	Atom	49(C) :	0.06%
Atom	50(C) :	1.23%	Atom	50(C) :	0.00%
Atom	51(C) :	0.07%	Atom	51(C) :	0.00%
Atom	52(C) :	1.35%	Atom	52(C) :	0.07%
Atom	53(C) :	2.42%	Atom	53(C) :	0.07%
Atom	54(C) :	0.41%	Atom	54(C) :	0.00%
Atom	55(C) :	0.01%	Atom	55(C) :	0.00%
Atom	56(C) :	0.01%	Atom	56(C) :	0.00%
Atom	57(C) :	0.01%	Atom	57(C) :	0.00%
Atom	58(C) :	0.01%	Atom	58(C) :	0.00%
Atom	59(C) :	0.02%	Atom	59(C) :	1.98%
Atom	60(C) :	0.02%	Atom	60(C) :	1.98%
Atom	61(S) :	0.26%	Atom	61(S) :	0.66%
Atom	62(S) :	0.26%	Atom	62(S) :	0.66%
Atom	63(H) :	0.00%	Atom	63(H) :	0.00%
Atom	64(H) :	0.00%	Atom	64(H) :	0.00%
Atom	65(Pt) :	0.01%	Atom	65(Pt) :	0.08%
Atom	66(Cl) :	0.01%	Atom	66(Cl) :	0.04%
Atom	67(Cl) :	0.01% □	Atom	67(Cl) :	0.04%

* The values for the hydrogen atoms are not shown except for atoms 63 and 64 due to the quite low percentage contributions.

Table S3. HOMO and LUMO composition analysis of **S-Flu-Br** showing the percent contribution of each atom.*



S-Flu-Br



HOMO			□	LUMO		
Atom	1(C) :	0.38%		Atom	1(C) :	4.65%
Atom	2(C) :	1.03%		Atom	2(C) :	2.00%
Atom	3(C) :	0.38%		Atom	3(C) :	4.65%
Atom	4(N) :	0.55%		Atom	4(N) :	14.65%
Atom	5(C) :	1.03%		Atom	5(C) :	2.00%
Atom	6(N) :	0.55%		Atom	6(N) :	14.65%
Atom	7(C) :	0.09%		Atom	7(C) :	2.70%
Atom	8(C) :	0.14%		Atom	8(C) :	2.47%
Atom	9(C) :	0.14%		Atom	9(C) :	2.38%
Atom	10(C) :	0.06%		Atom	10(C) :	1.50%
Atom	11(N) :	0.01%		Atom	11(N) :	0.07%
Atom	12(C) :	0.09%		Atom	12(C) :	2.70%
Atom	13(C) :	0.14%		Atom	13(C) :	2.47%
Atom	14(C) :	0.06%		Atom	14(C) :	1.50%
Atom	15(C) :	0.14%		Atom	15(C) :	2.38%
Atom	16(N) :	0.01%		Atom	16(N) :	0.07%
Atom	17(C) :	3.94%		Atom	17(C) :	7.23%
Atom	18(C) :	2.83%		Atom	18(C) :	5.35%

Atom	19(C) :	2.83%	Atom	19(C) :	5.35%
Atom	20(C) :	3.94%	Atom	20(C) :	7.23%
Atom	21(C) :	7.10%	Atom	21(C) :	0.16%
Atom	22(C) :	4.18%	Atom	22(C) :	1.91%
Atom	23(C) :	3.96%	Atom	23(C) :	0.04%
Atom	24(C) :	7.06%	Atom	24(C) :	1.69%
Atom	25(C) :	7.10%	Atom	25(C) :	0.16%
Atom	26(C) :	4.18%	Atom	26(C) :	1.91%
Atom	27(C) :	3.96%	Atom	27(C) :	0.04%
Atom	28(C) :	7.06%	Atom	28(C) :	1.69%
Atom	29(C) :	2.52%	Atom	29(C) :	0.06%
Atom	30(C) :	1.71%	Atom	30(C) :	0.34%
Atom	31(C) :	2.50%	Atom	31(C) :	0.29%
Atom	32(C) :	1.04%	Atom	32(C) :	0.01%
Atom	33(C) :	0.71%	Atom	33(C) :	0.03%
Atom	34(C) :	0.01%	Atom	34(C) :	0.00%
Atom	35(C) :	3.74%	Atom	35(C) :	0.36%
Atom	36(C) :	1.46%	Atom	36(C) :	0.07%
Atom	37(C) :	0.89%	Atom	37(C) :	0.01%
Atom	38(C) :	0.05%	Atom	38(C) :	0.01%
Atom	39(C) :	1.17%	Atom	39(C) :	0.09%
Atom	40(C) :	1.96%	Atom	40(C) :	0.10%
Atom	41(C) :	0.30%	Atom	41(C) :	0.00%
Atom	42(C) :	2.52%	Atom	42(C) :	0.06%
Atom	43(C) :	1.71%	Atom	43(C) :	0.34%
Atom	44(C) :	2.50%	Atom	44(C) :	0.29%
Atom	45(C) :	1.04%	Atom	45(C) :	0.01%
Atom	46(C) :	0.71%	Atom	46(C) :	0.03%
Atom	47(C) :	0.01%	Atom	47(C) :	0.00%
Atom	48(C) :	3.74%	Atom	48(C) :	0.36%
Atom	49(C) :	1.46%	Atom	49(C) :	0.07%
Atom	50(C) :	0.89%	Atom	50(C) :	0.01%
Atom	51(C) :	0.05%	Atom	51(C) :	0.01%
Atom	52(C) :	1.17%	Atom	52(C) :	0.09%

Atom	53(C) :	1.96%	Atom	53(C) :	0.10%
Atom	54(C) :	0.30%	Atom	54(C) :	0.00%
Atom	55(C) :	0.01%	Atom	55(C) :	0.00%
Atom	56(C) :	0.01%	Atom	56(C) :	0.00%
Atom	57(C) :	0.01%	Atom	57(C) :	0.00%
Atom	58(C) :	0.01%	Atom	58(C) :	0.00%
Atom	59(C) :	0.04%	Atom	59(C) :	0.67%
Atom	60(C) :	0.04%	Atom	60(C) :	0.67%
Atom	61(S) :	0.28%	Atom	61(S) :	0.91%
Atom	62(S) :	0.28%	Atom	62(S) :	0.91%
Atom	63(Br) :	0.02%	Atom	63(Br) :	0.12%
Atom	64(Br) :	0.02% □	Atom	64(Br) :	0.12%

* The values for the hydrogen atoms are not shown except for atoms 63 and 64 due to the quite low percentage contributions.

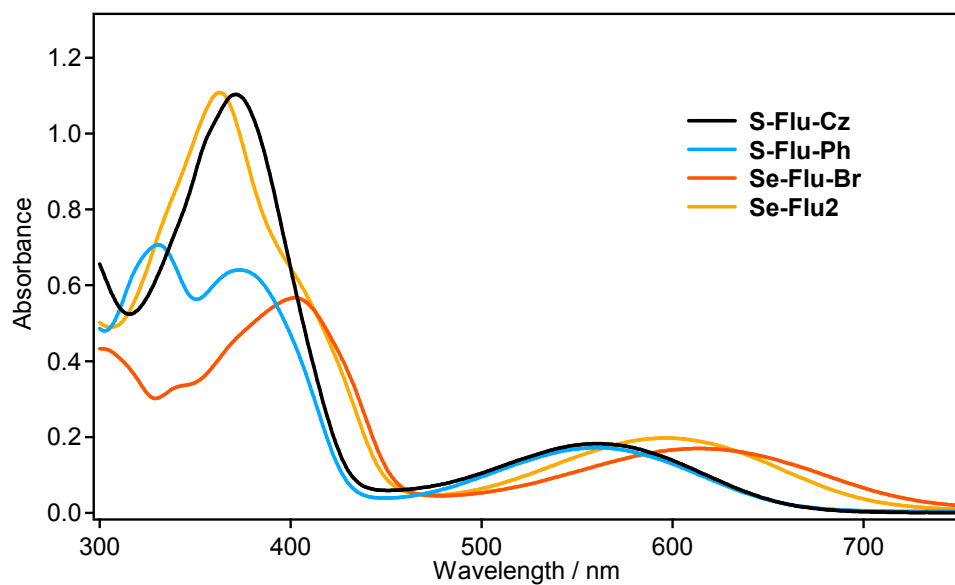


Fig. S1. UV-Vis absorption spectra (10 μM) of **S-Flu-Cz**, **S-Flu-Ph**, **Se-Flu-Br** and **Se-Flu2** in dichloromethane at rt.

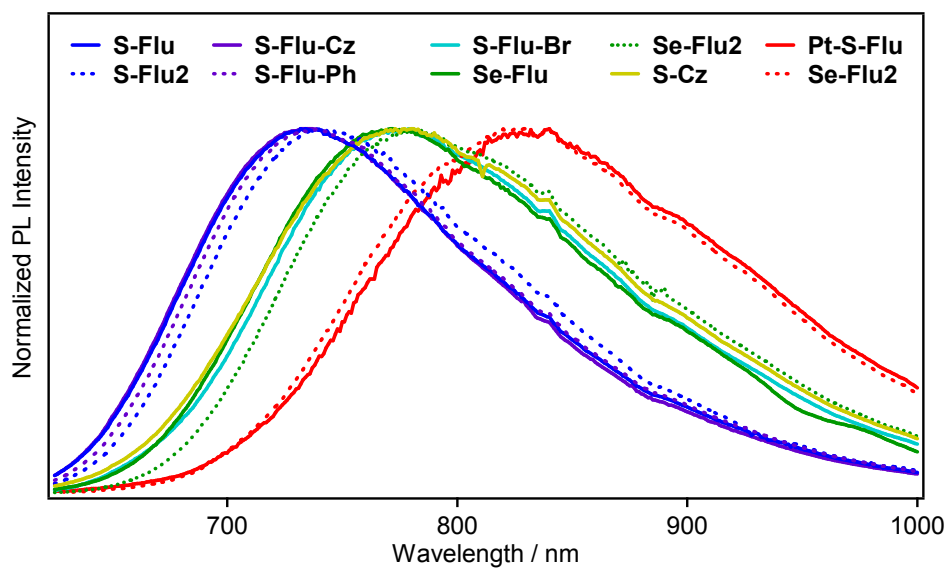


Fig. S2. Normalized PL spectra of dppz derivatives (10 μM) in dichloromethane at rt.

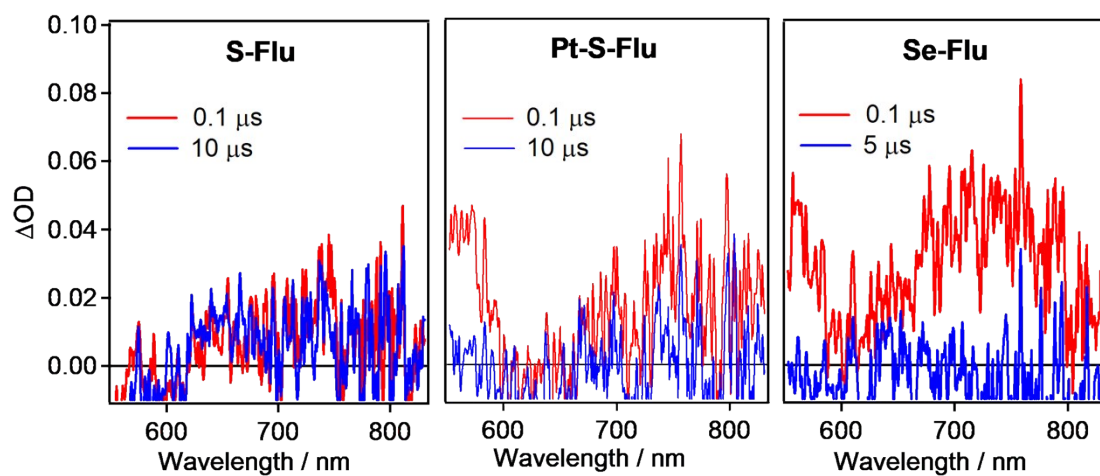


Fig. S3. Differential spectra of nanosecond transient absorption of **S-Flu** (left), **Pt-S-Flu** (middle) and **Se-Flu** (right).

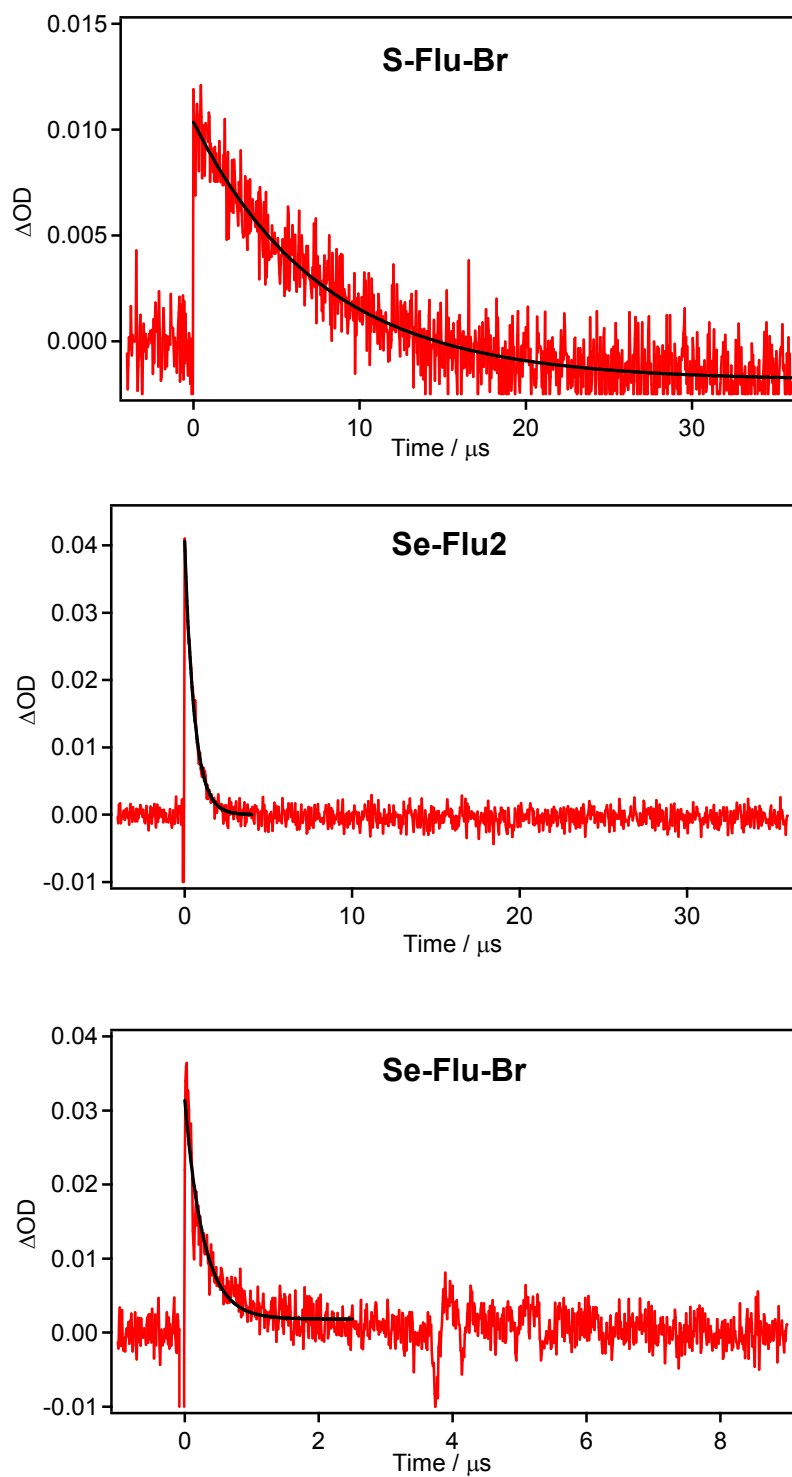


Fig. S4. Nanosecond transient absorption decay curves for **S-Flu-Br** (upper), **Se-Flu2** (middle) and **S-Flu-Br** (lower).

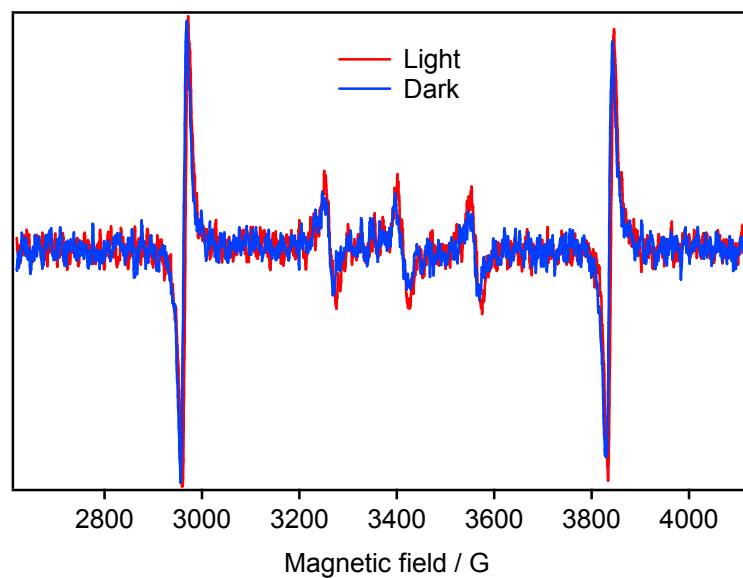


Fig. S5. ESR spectra of 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TEMP). The triplet signal between 3200 G and 3600 G is assigned to nitroxyl radical based on 4-oxo-TEMPO. Red line: a dichloromethane solution of **Se-Flu2** (0.01 mM) and 4-oxo-TEMP (50 mM) irradiated with light (> 510 nm, 14 mW cm^{-2}) for 30 minutes. Blue line: an identical dichloromethane solution left in the dark for 30 minutes.

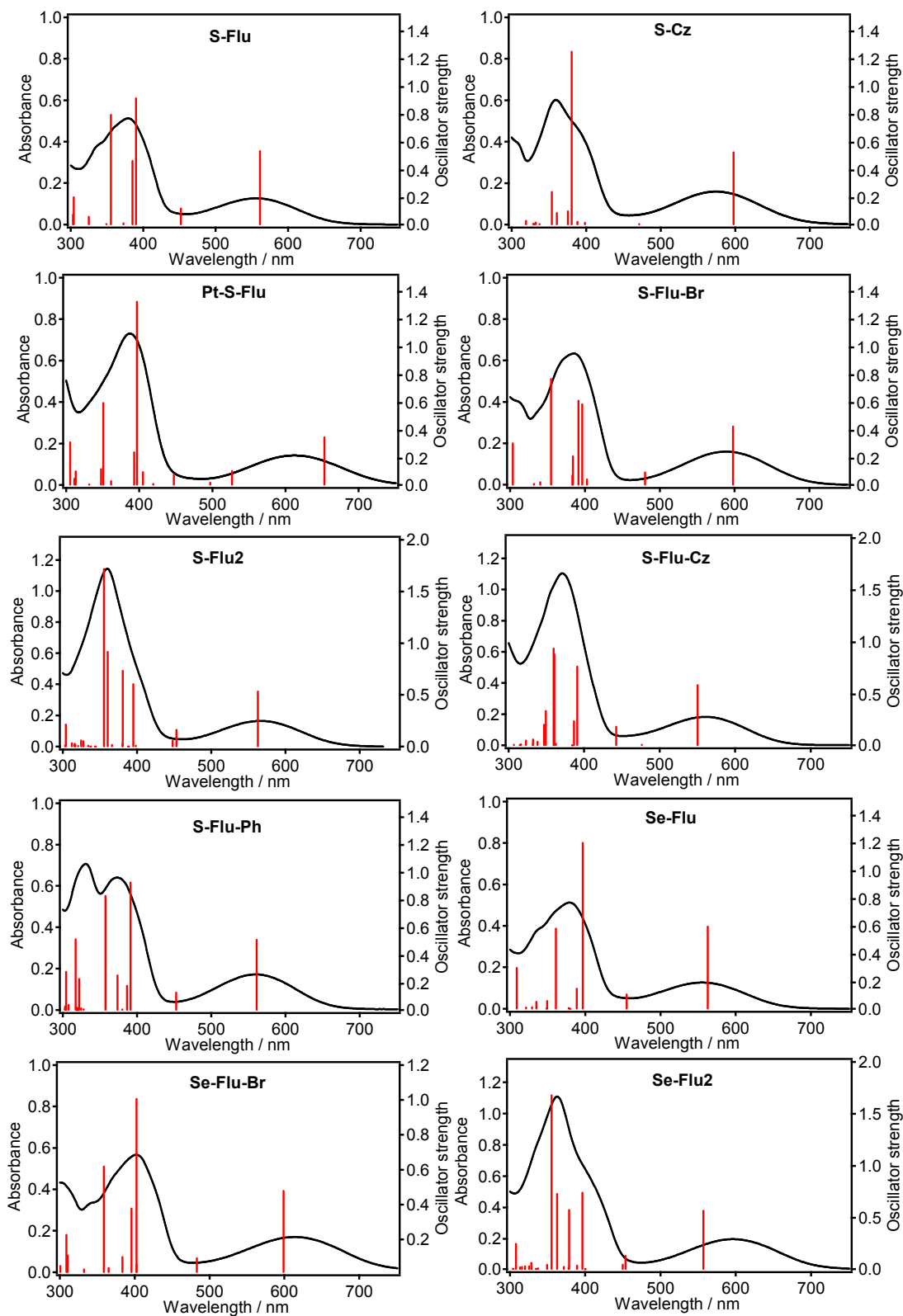


Fig. S6. Calculated oscillator strength (red bars) and electronic absorption spectra (solid lines) of the dppz derivatives obtained in dichloromethane (10 μ M) at rt.

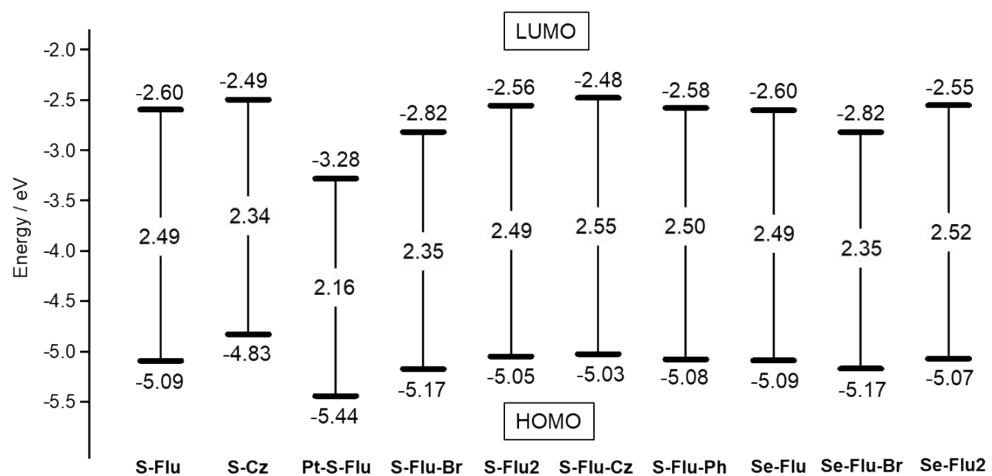


Fig. S7. Calculated HOMO and LUMO energy levels for the dppz derivatives

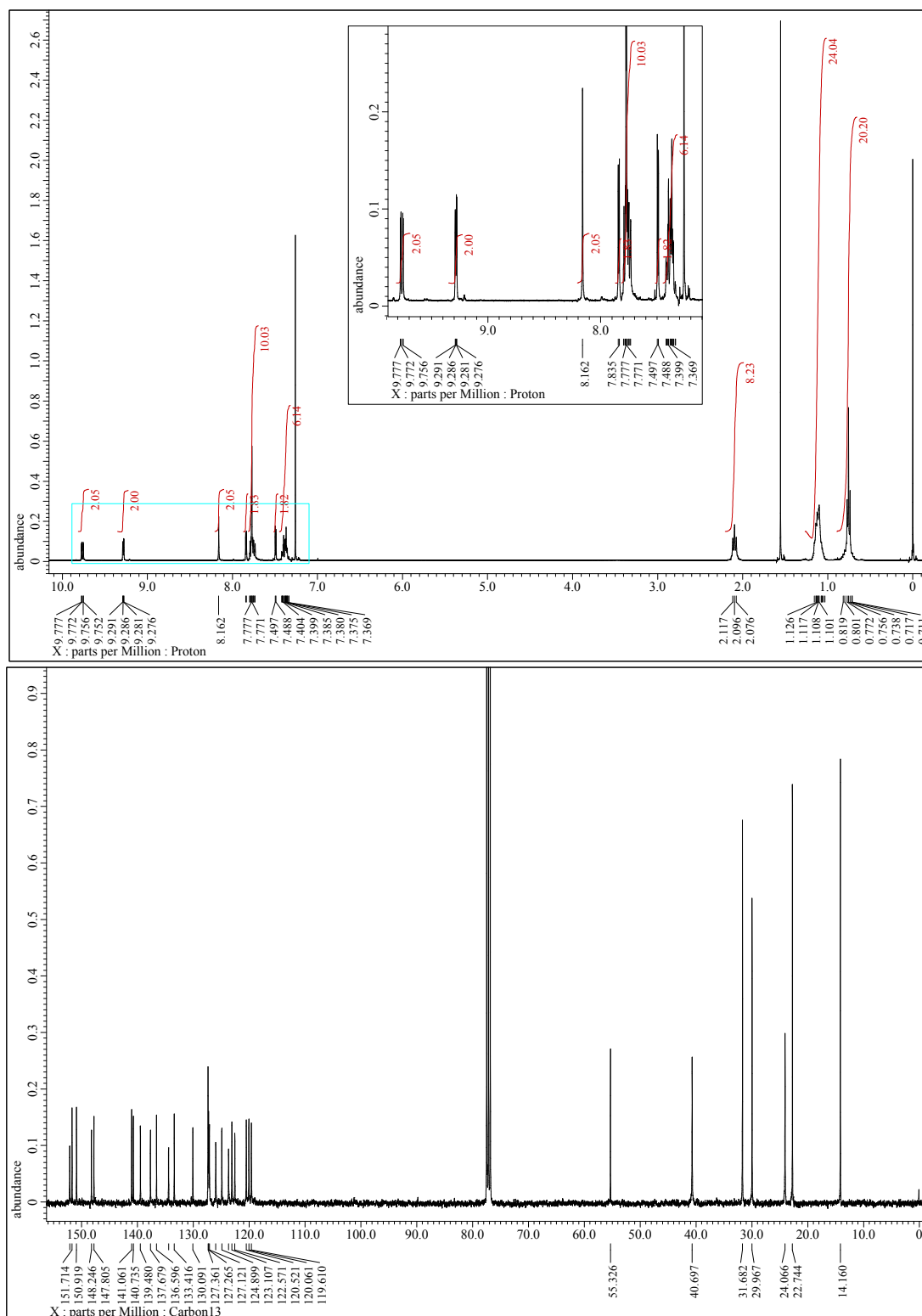


Fig. S8. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of **S-Flu** (CDCl₃, 25 °C).

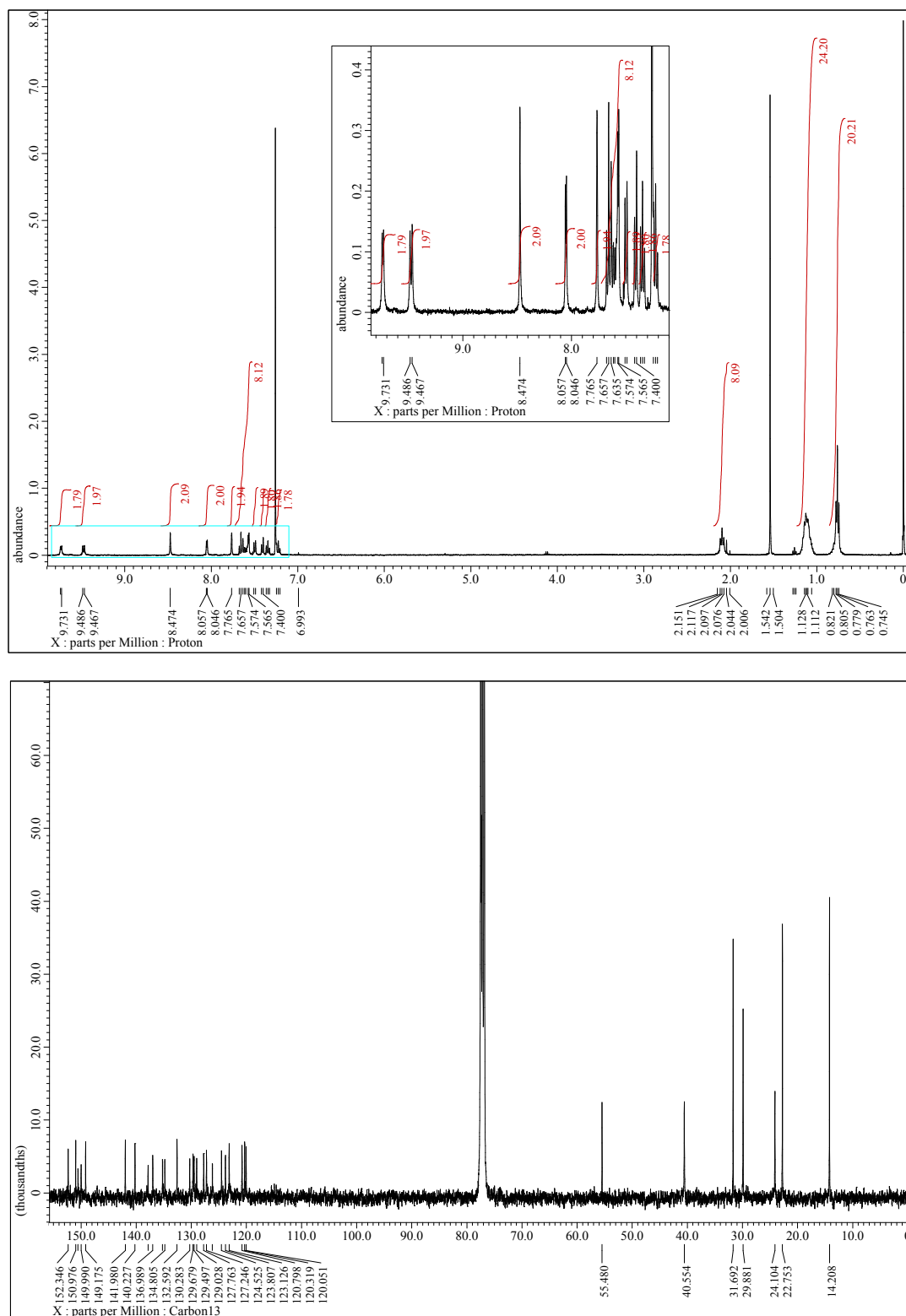


Fig. S9. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of **Pt-S-Flu** (CDCl₃, 25 °C).

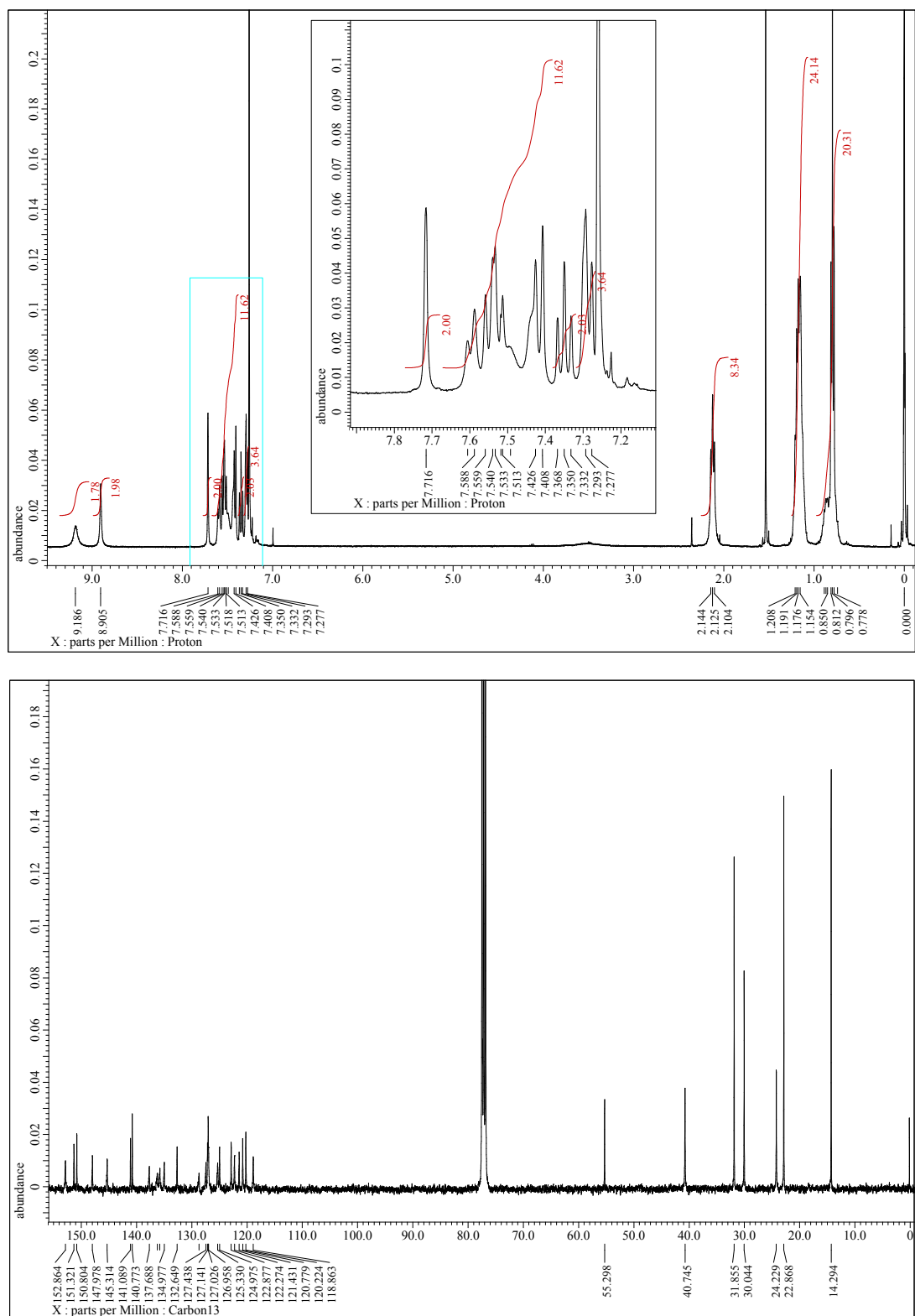


Fig. S10. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of **S-Flu-Br** (CDCl₃, 25 °C).

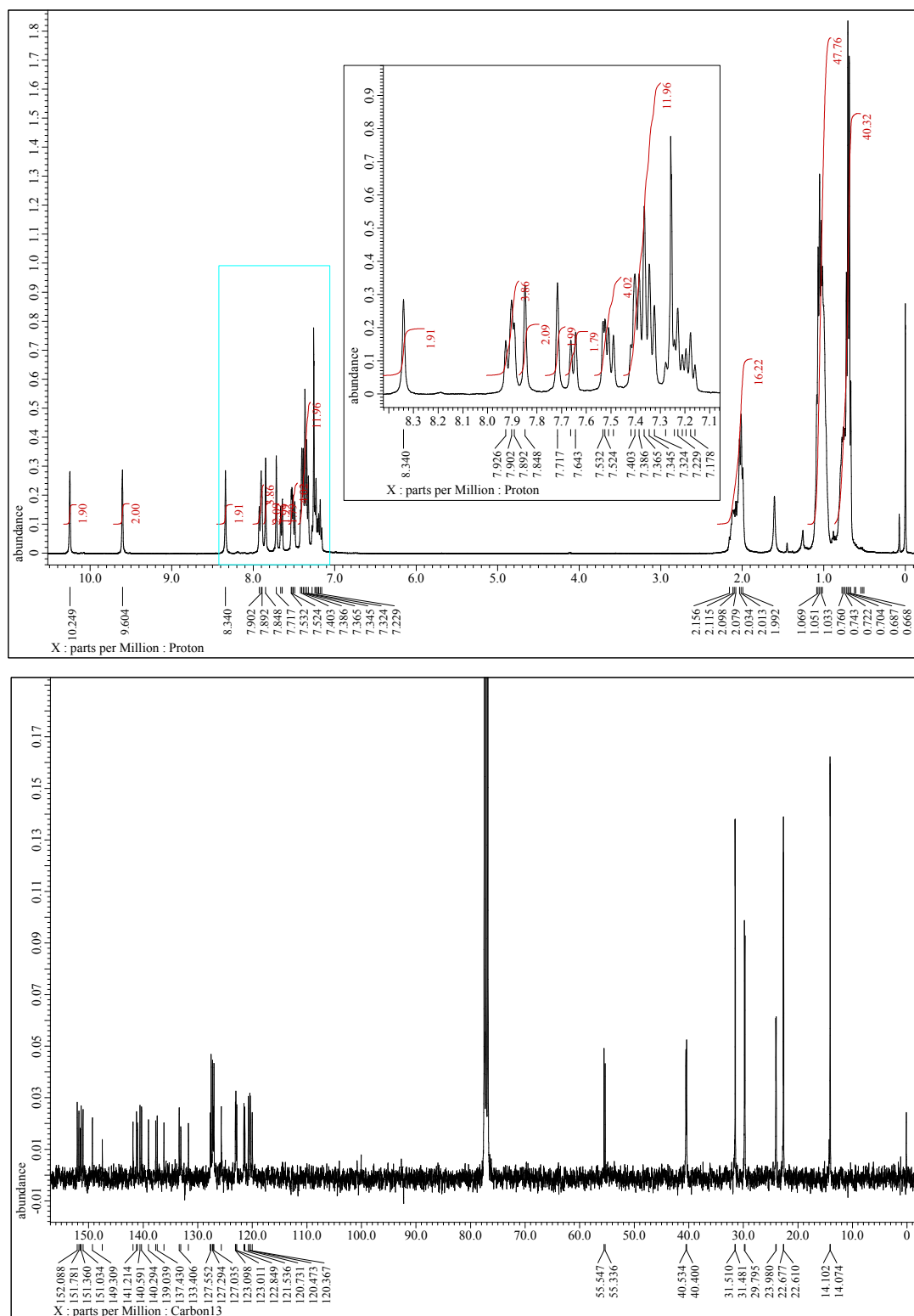


Fig. S11. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of **S-Flu2** (CDCl₃, 25 °C).

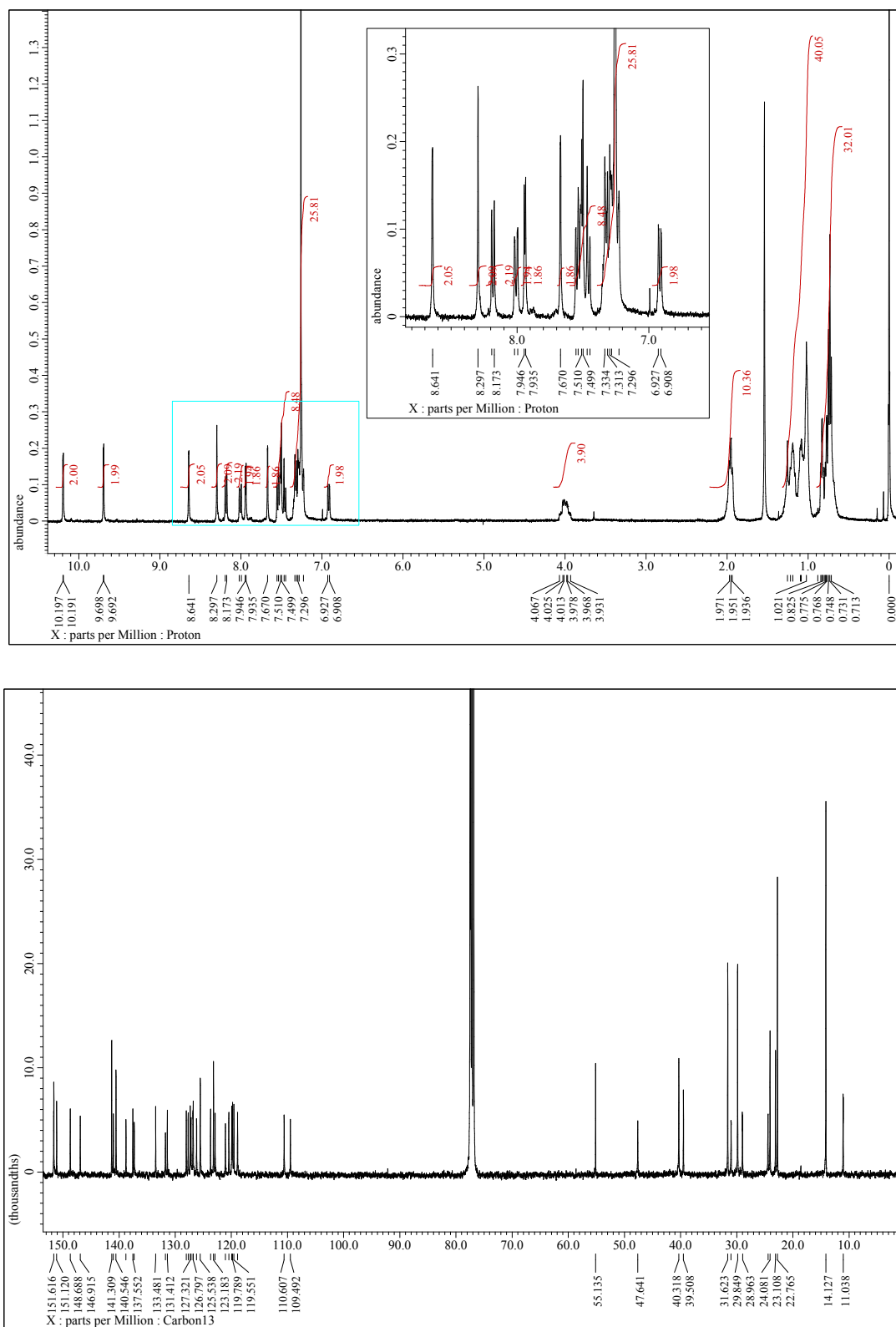


Fig. S12. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of **S-Flu-Cz** (CDCl₃, 25 °C).

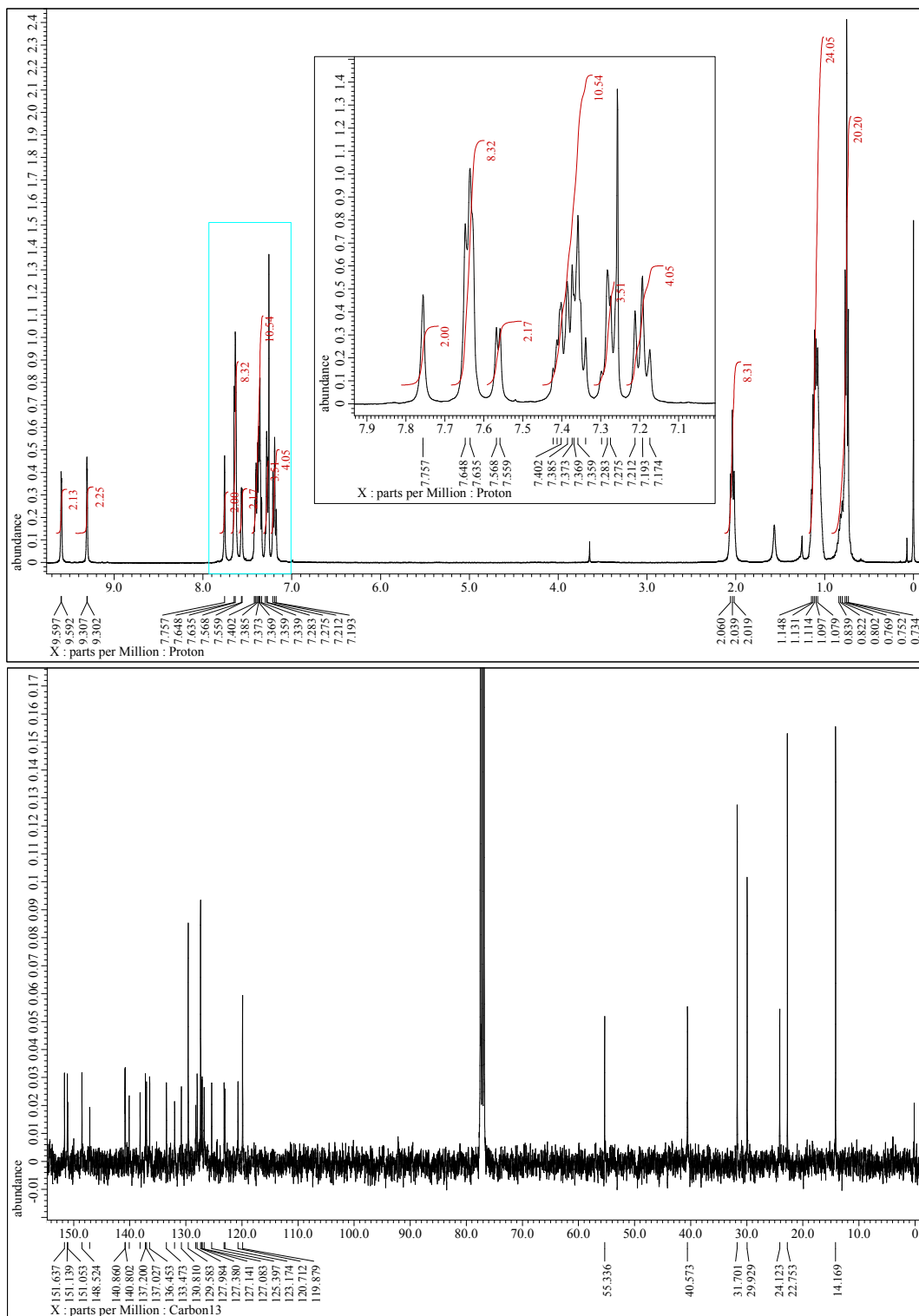


Fig. S13. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of **S-Flu-Ph** (CDCl₃, 25 °C).

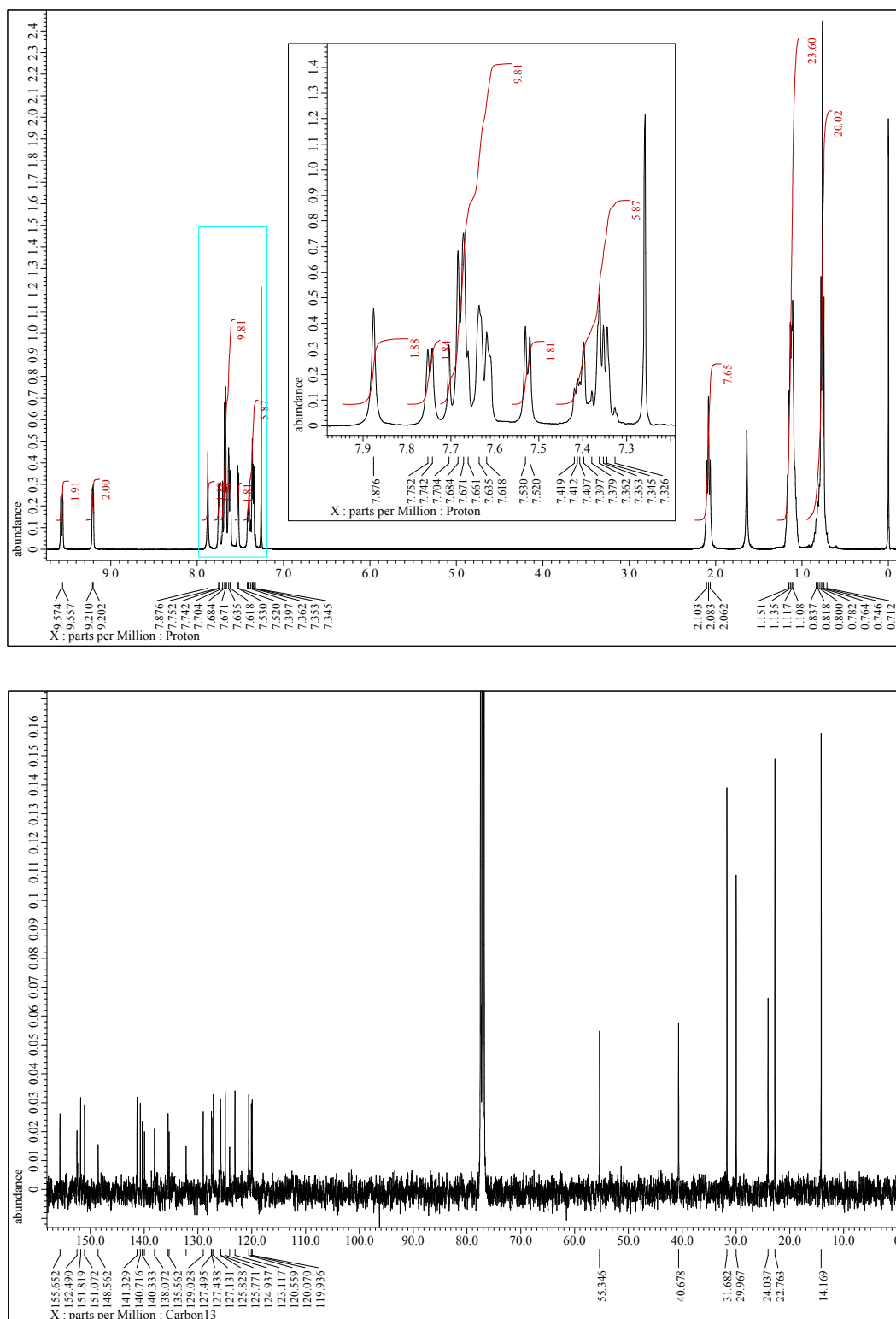


Fig. S14. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of Se-Flu (CDCl₃, 25 °C).

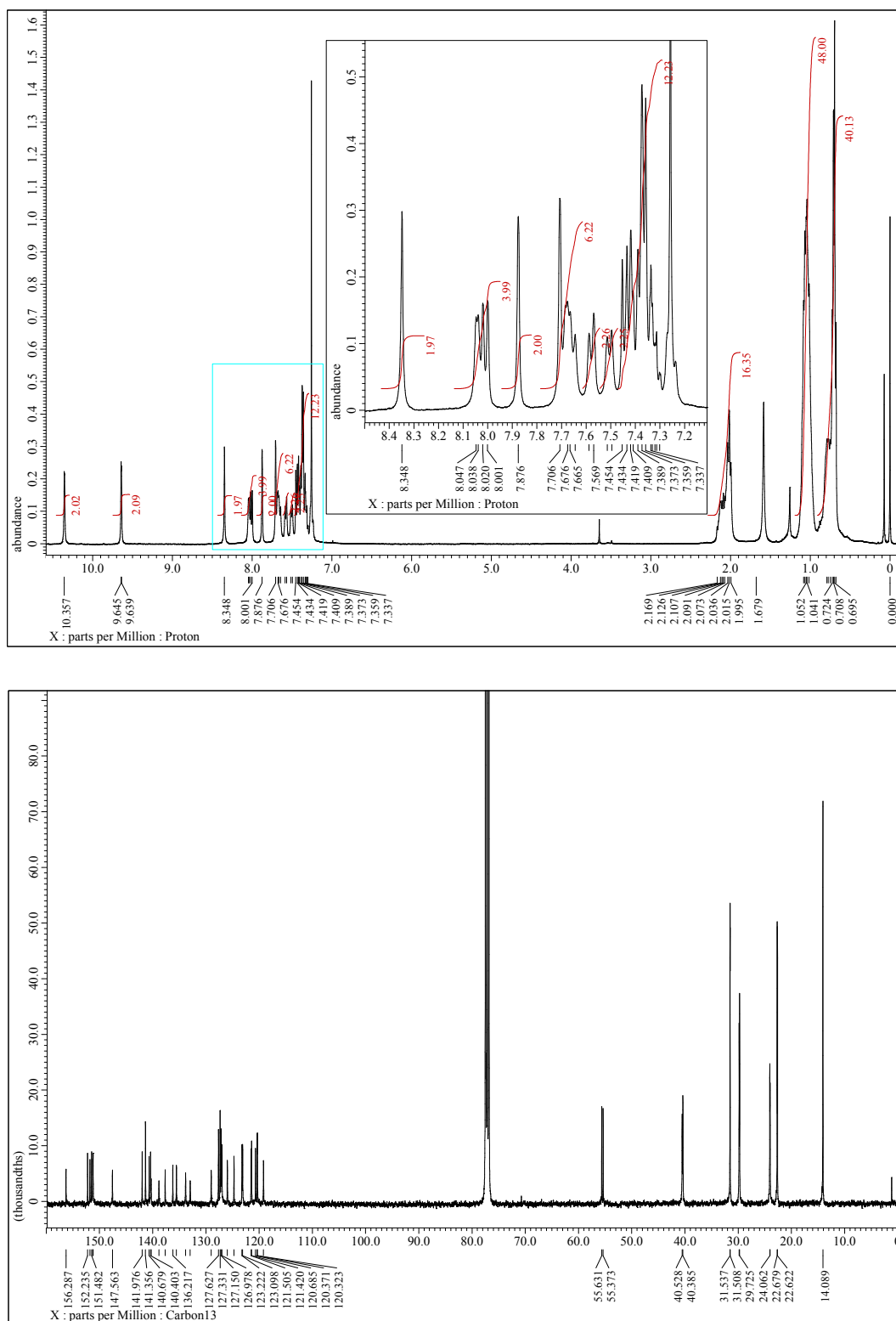


Fig. S15. ¹H (upper, 400 MHz) and ¹³C (lower, 100 MHz) NMR spectra of **Se-Flu2** (CDCl₃, 25 °C).

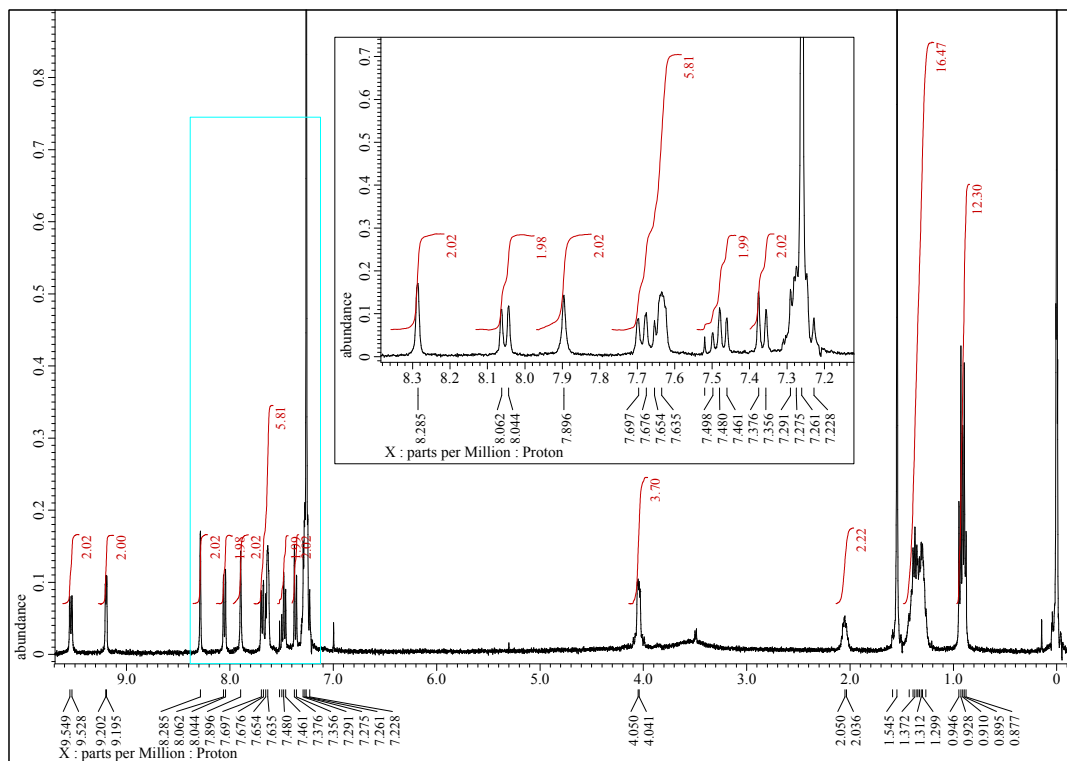


Fig. S16. ^1H (400 MHz) spectrum of **S-Cz** (CDCl_3 , 25 $^\circ\text{C}$).

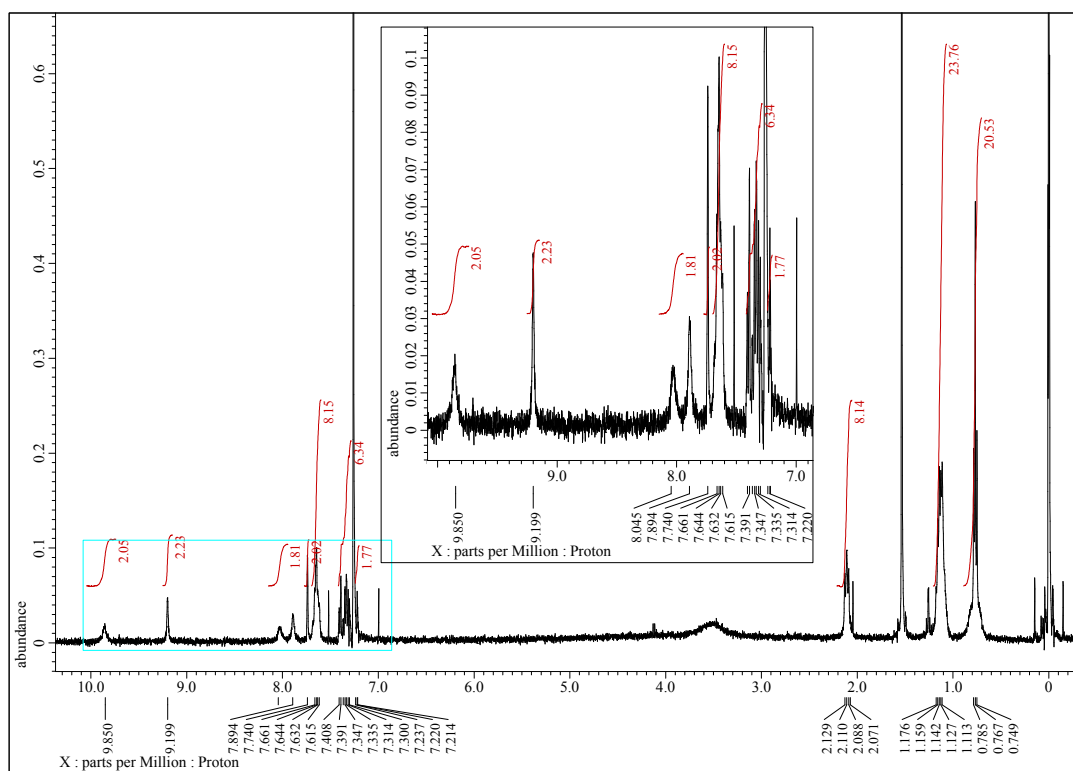


Fig. S17. ^1H (400 MHz) NMR spectrum of **Se-Flu-Br** (CDCl_3 , 25 $^\circ\text{C}$).