SUPPORTING INFORMATION

Chemodivergent, multicomponent domino reactions in aqueous media: L-Proline-catalyzed assembly of densely functionalized 4*H*-pyrano[2,3-*c*]pyrazoles and bispyrazolyl propanoates from simple, acyclic starting materials

Pitchaimani Prasanna,[a] Subbu Perumal[*a] and J. Carlos Menéndez [*b]

[a]*Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai – 625021, Tamil Nadu, India*
[b]*Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad Complutense, 28040 Madrid, Spain*

E-mail: subbu.perum@gmail.com; josecm@farm.ucm.es

Contents:

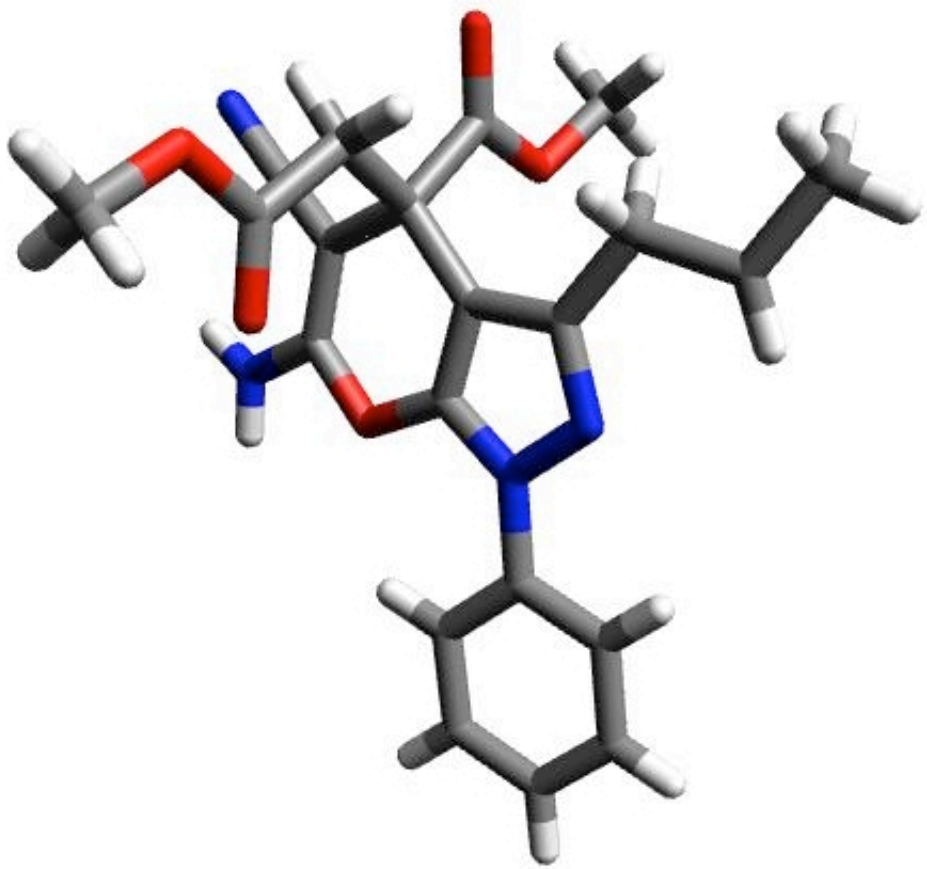

Figure 1. X-Ray structure of **5g**.

(CCDC number 894543)

Crystal data of **5g**

Empirical formula	$C_{21}H_{21}N_4O_5$
Formula weight	409.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 8.1356(9) Å α= 91.571(6)°.
	b = 10.6065(13) Å β= 105.781(6)°.
	c = 12.4620(15) Å γ= 100.384(6)°.
Volume	1014.5(2) $Å^3$
Z	2
Density (calculated)	1.340 kg/m^3
Absorption coefficient	0.098 mm^{-1}
F(000)	430
Crystal size	0.24 x 0.22 x 0.17 mm^3
Theta range for data collection	2.0 to 25.0°.
Index ranges	-9≤h≤9, -12≤k≤12, -14≤l≤14
Reflections collected/ unique	15163/ 3589 [R(int) = 0.0356]
Completeness to theta = 25.0°	100 %

Absorption correction	Psi scan
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3589 / 3 / 281
Goodness-of-fit on F2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1366
R indices (all data)	R1 = 0.0447, wR2 = 0.1293
Largest diff. peak and hole	0.479 and -0.243 e.Å^{-3}

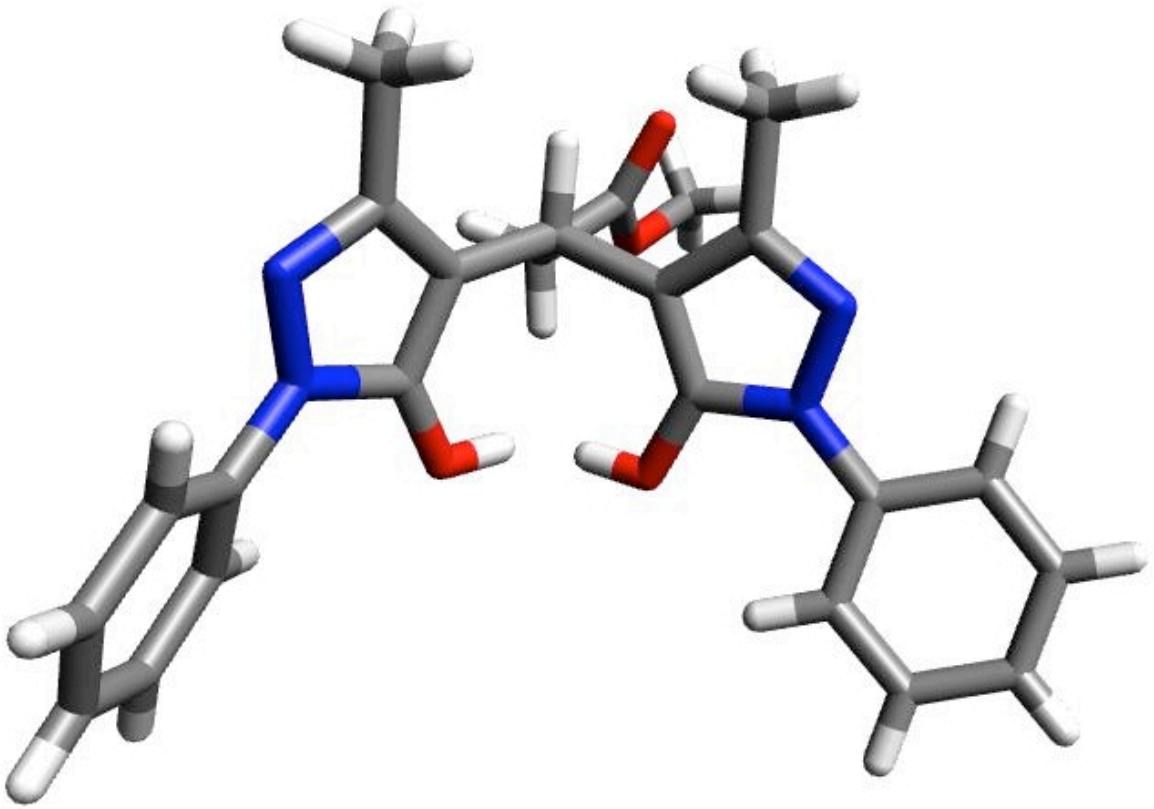

Figure 2. X-Ray structure of **7a**.

CCDC number 896612

Crystal data of **7a**

Empirical formula	$C_{24}H_{23}N_4O_4$
Formula weight	431.46
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 12.2016(5) Å α= 90°.
	b = 13.6995(5) Å β= 110.166(2)°.
	c = 15.4526(5) Å γ= 90°.
Volume	2424.65(16) $Å^3$
Z	4
Density (calculated)	1.182 kg/m^3
Absorption coefficient	0.082 mm^{-1}
F(000)	908
Crystal size	0.20 x 0.20 x 0.20 mm^3
Theta range for data collection	1.55 to 28.38°.
Index ranges	-13≤h≤16, -18≤k≤15, -20≤l≤20
Reflections collected/ unique	24003/ 6087 [R(int) = 0.0270]
Completeness to theta = 28.38°	100 %

Absorption correction	Psi scan
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6087 / 0 / 293
Goodness-of-fit on F2	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0799, wR2 = 0.2121
R indices (all data)	R1 = 0.0604, wR2 = 0.2001
Largest diff. peak and hole	0.740 and -0.427 e.Å^{-3}

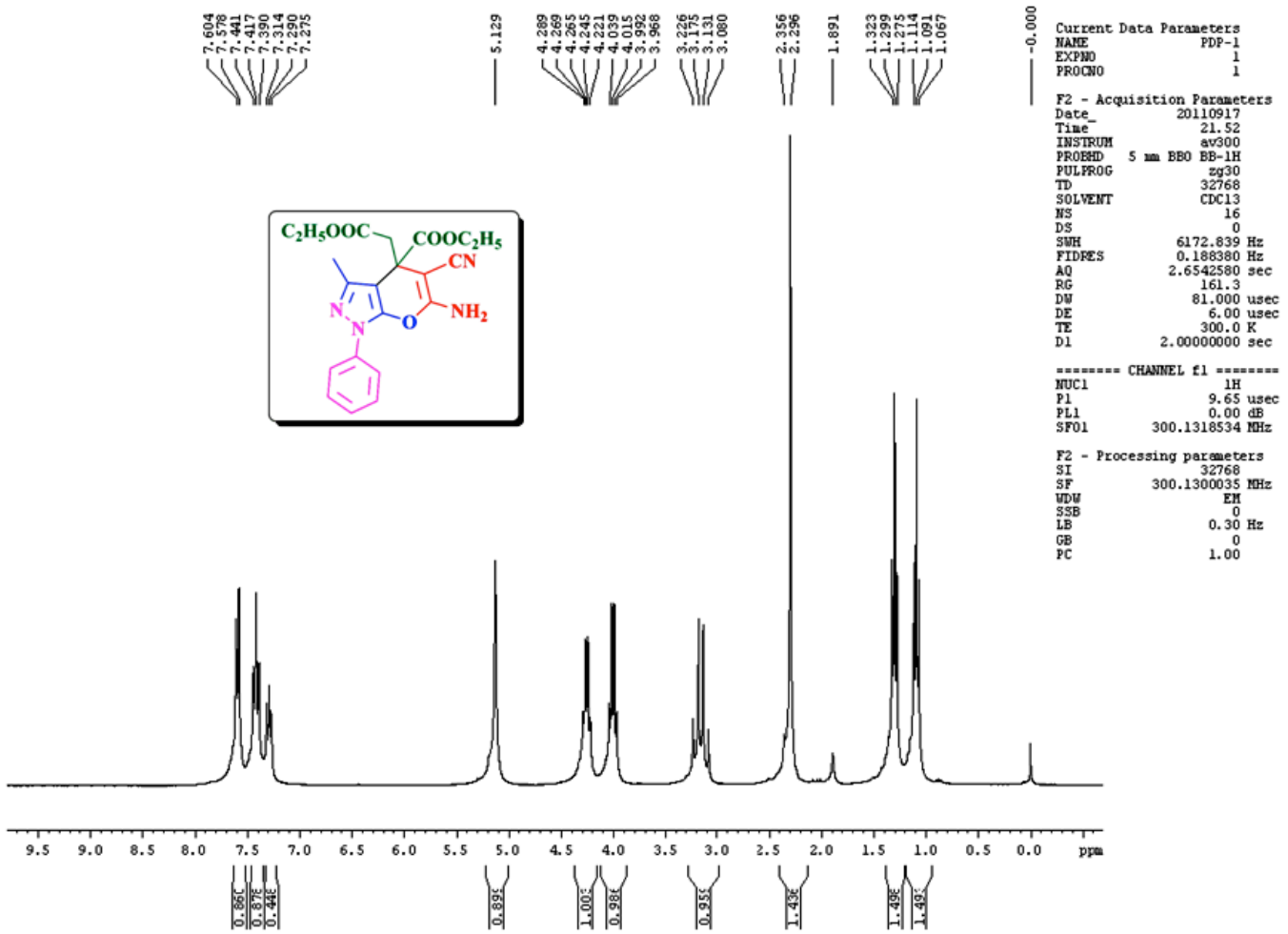

Figure 1. ^{1}H NMR Spectrum of 5a ($CDCl_3$)

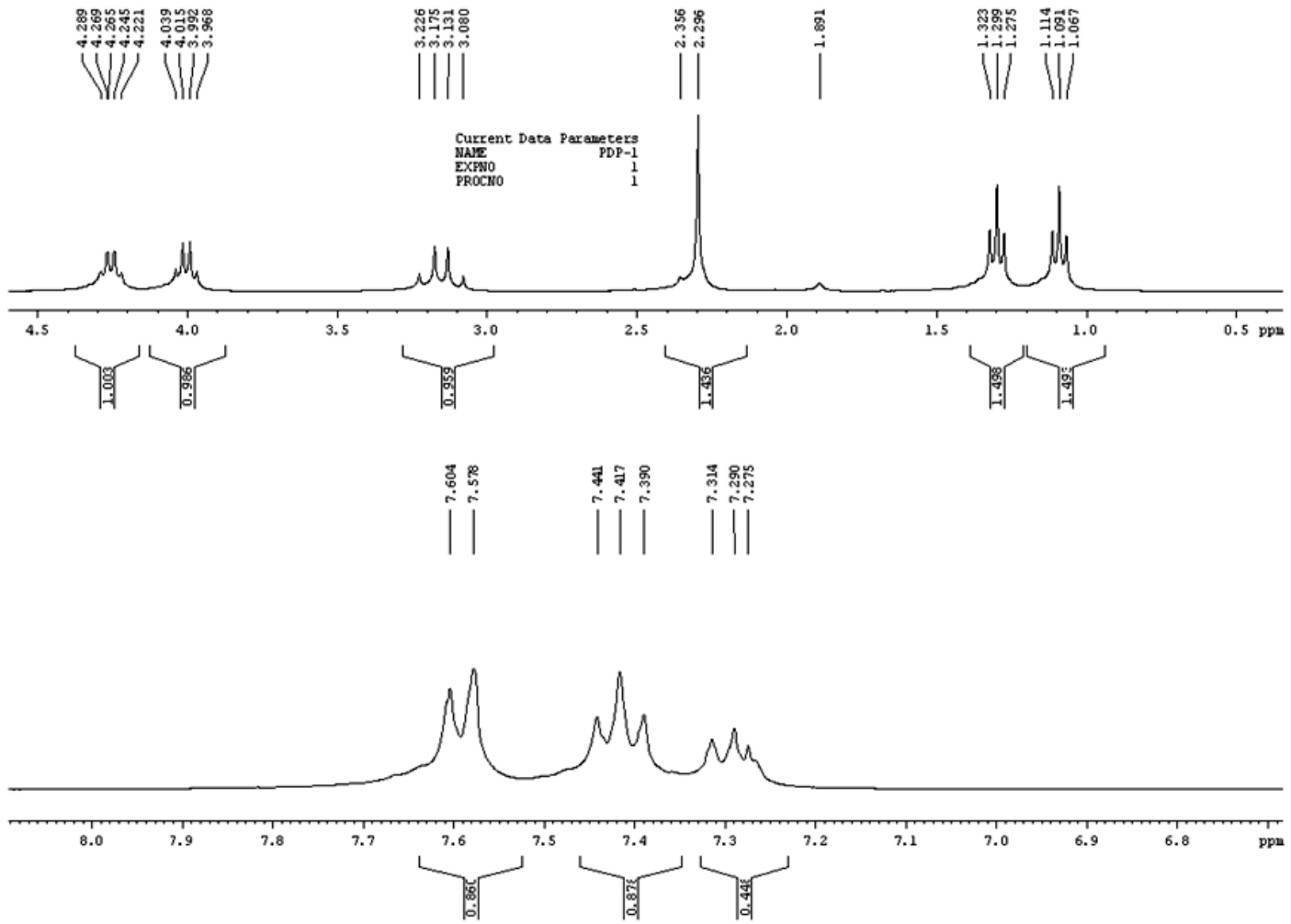

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Figure 2. ^{1}H NMR Spectrum of 5a (expanded**)**

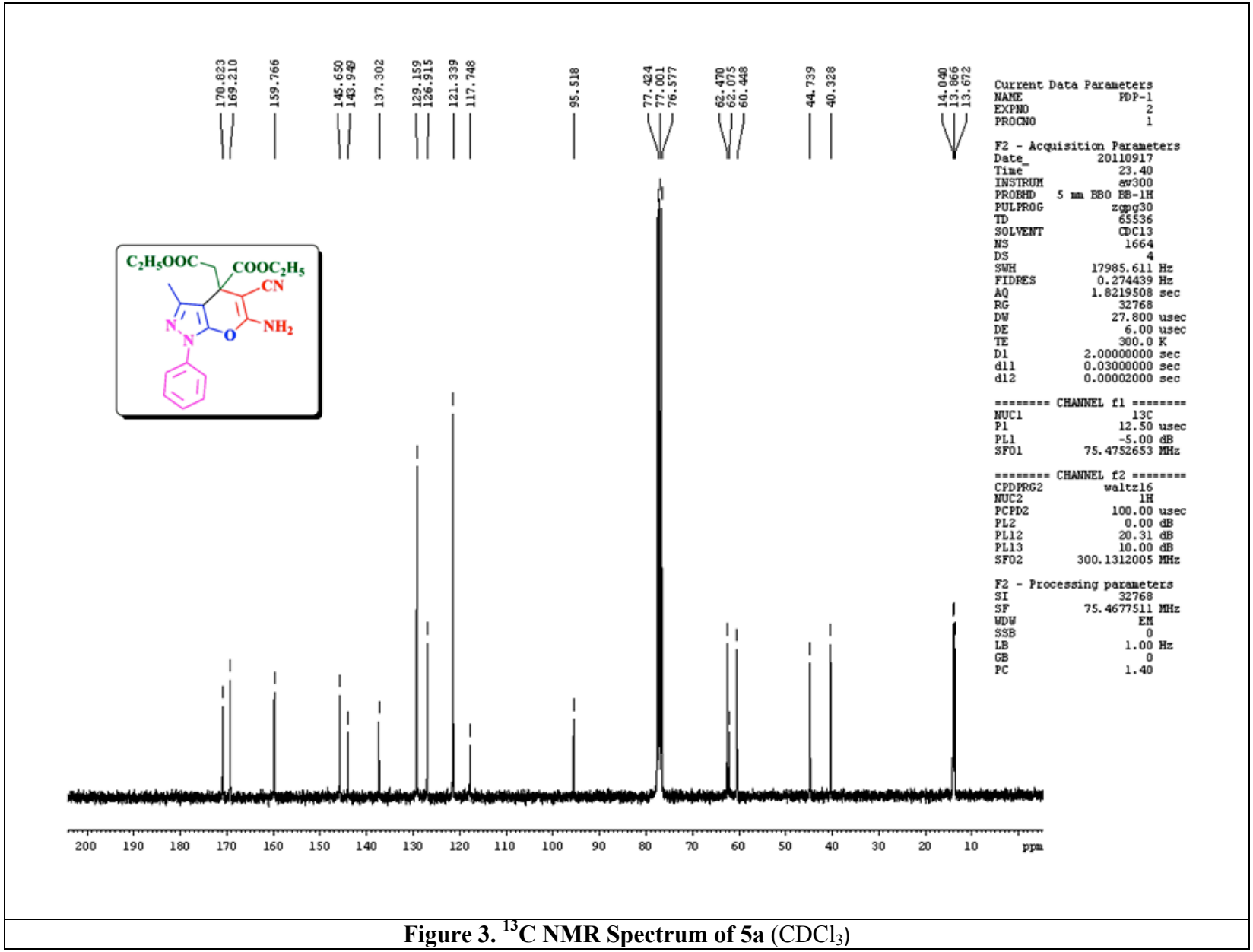

Figure 3. ^{13}C NMR Spectrum of 5a ($CDCl_3$)

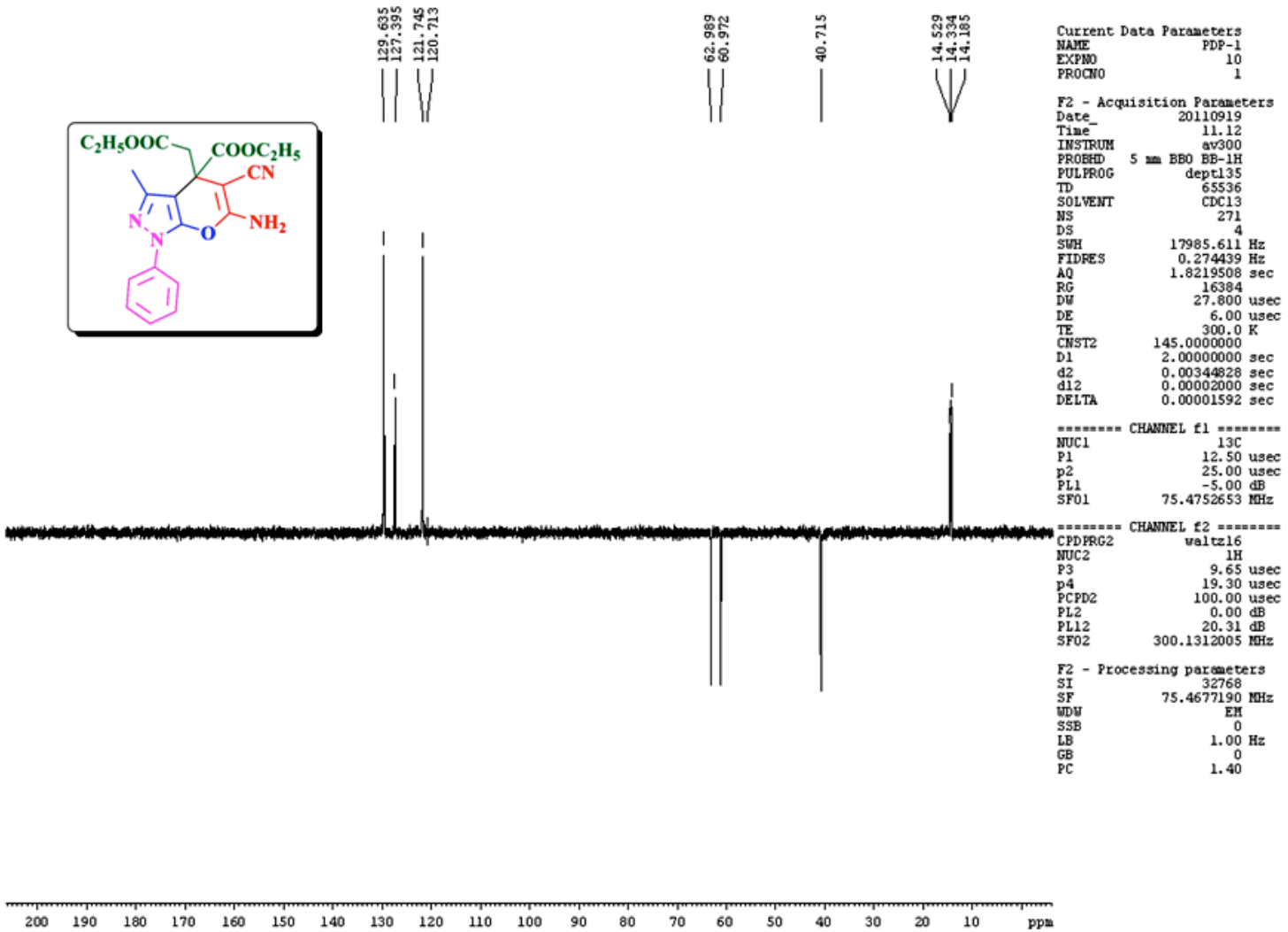

Figure 4. DEPT - 135 NMR Spectrum of 5a ($CDCl_3$)

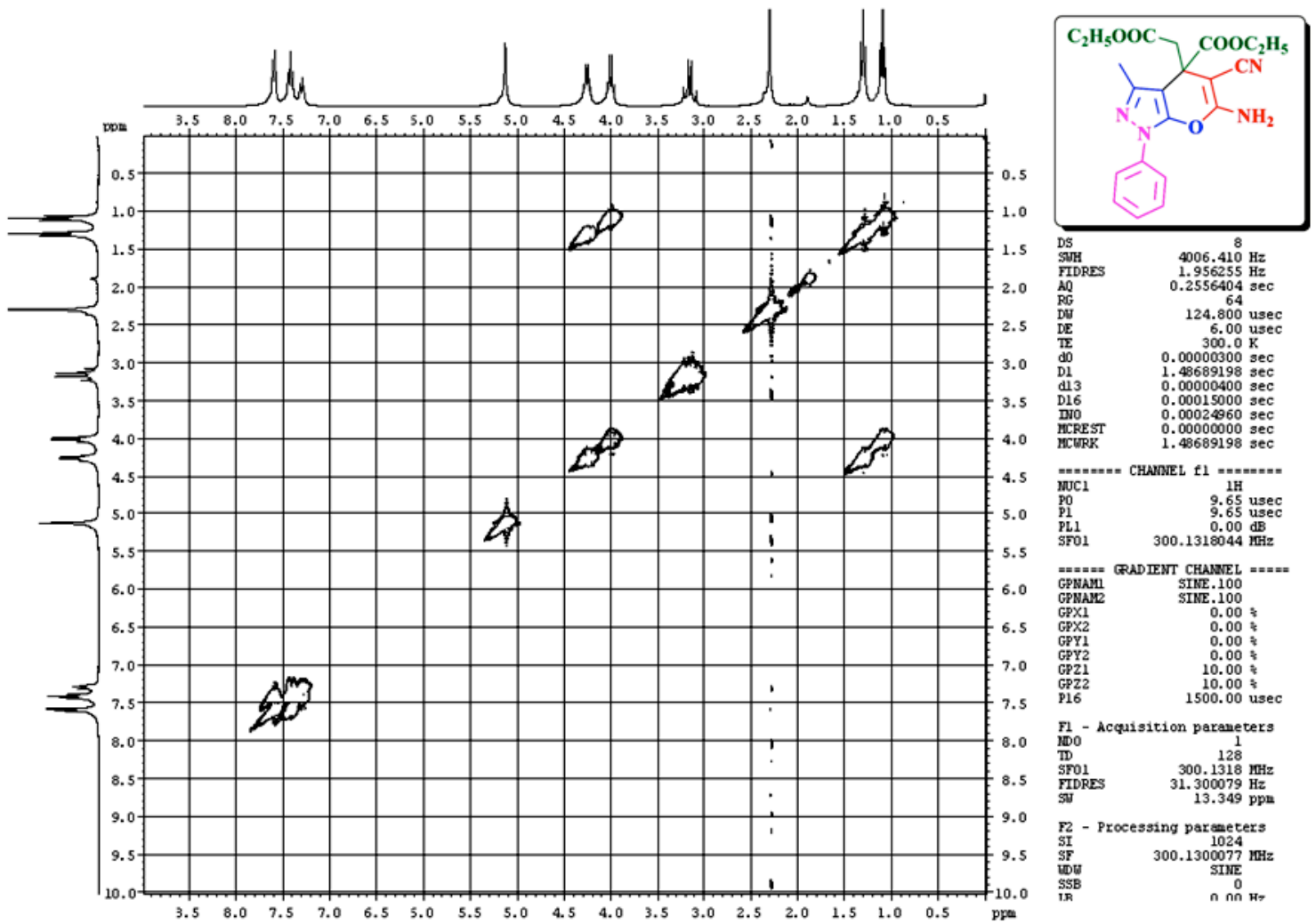

Figure 5. H,H - COSY Spectrum of 5a ($CDCl_3$)

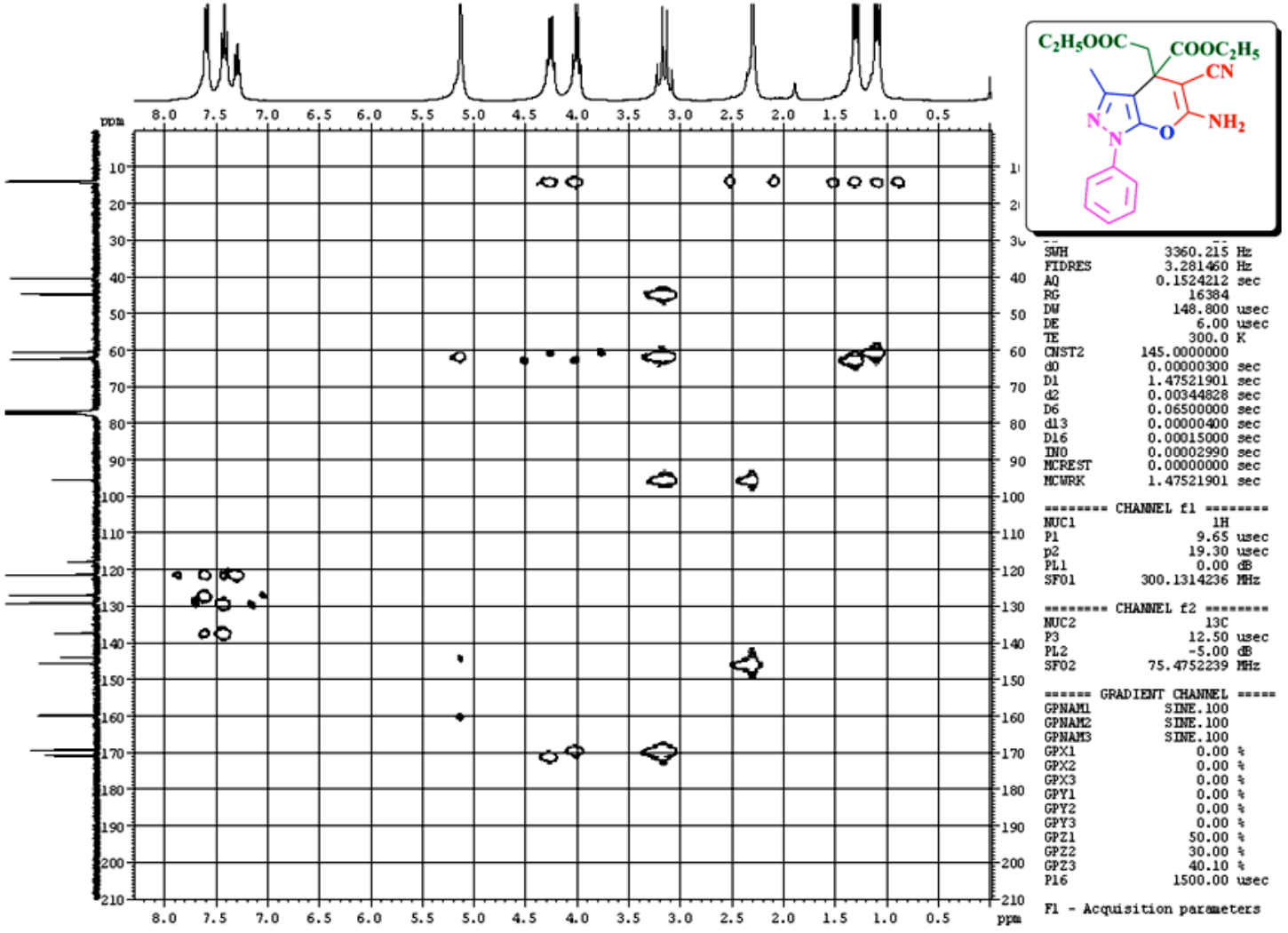

Figure 6. HMBC Spectrum of 5a ($CDCl_3$)

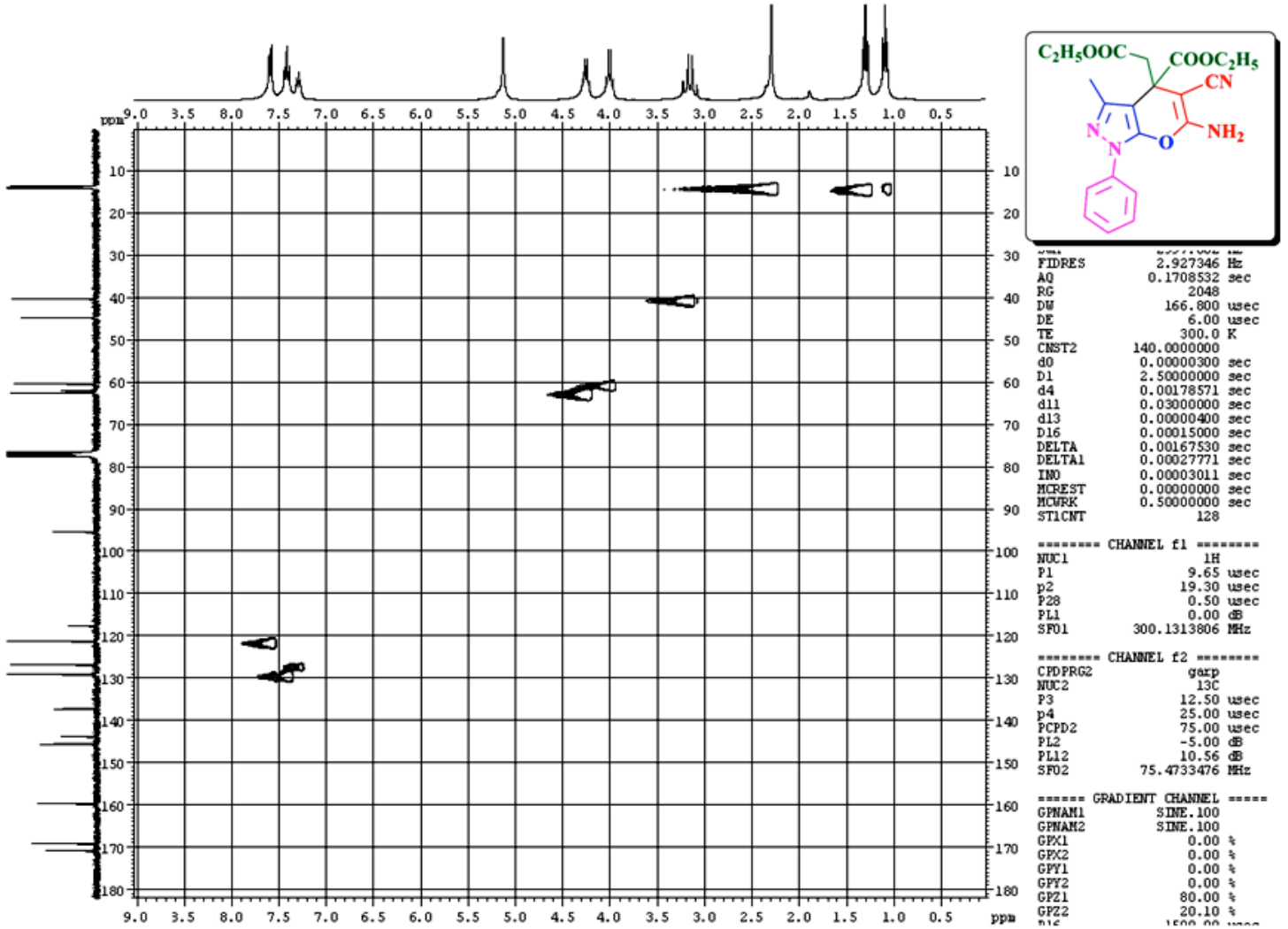

Figure 7. C,H-COSY Spectrum of 5a ($CDCl_3$)

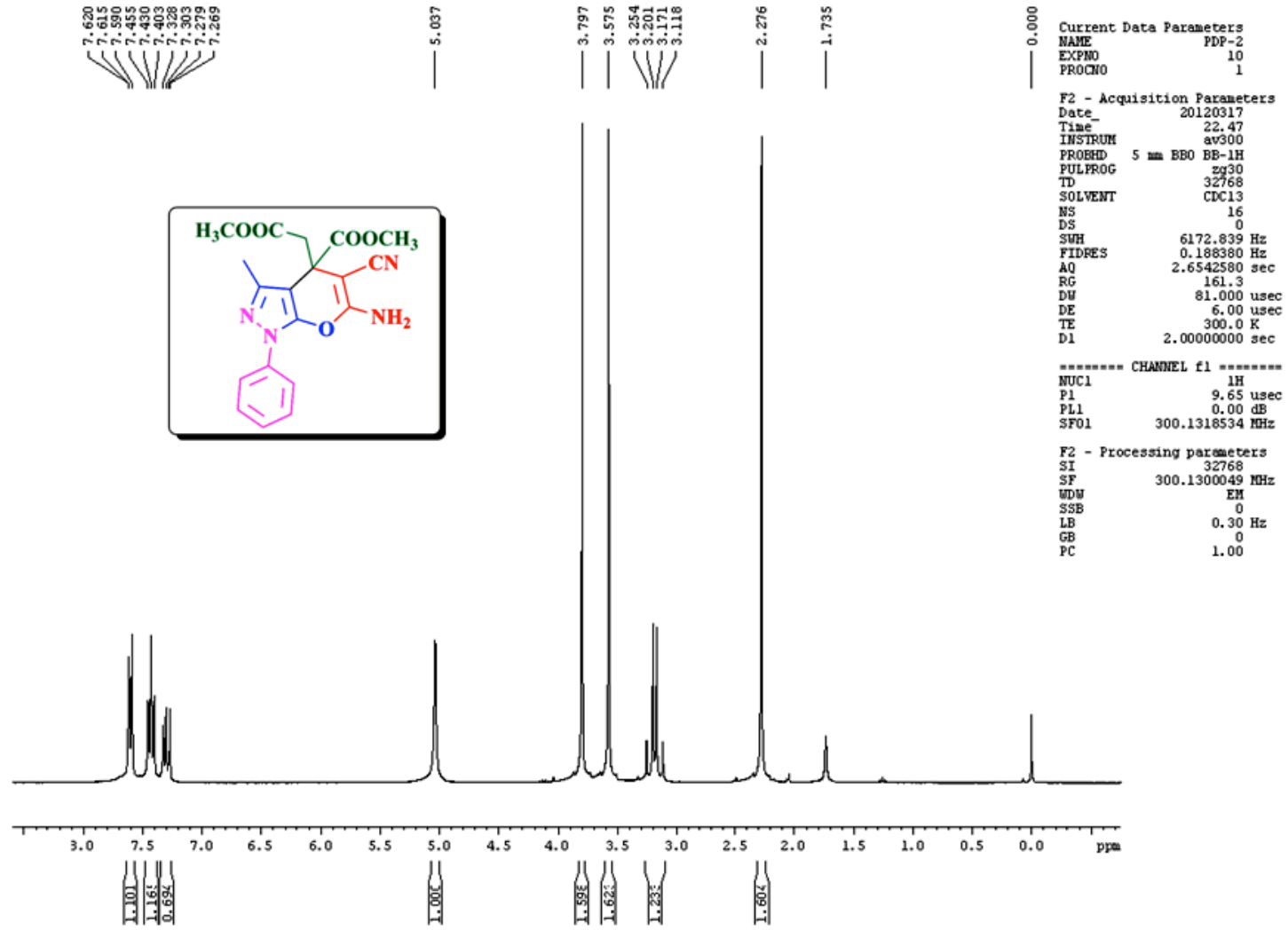

Figure 8. ^{1}H NMR Spectrum of 5b ($CDCl_3$)

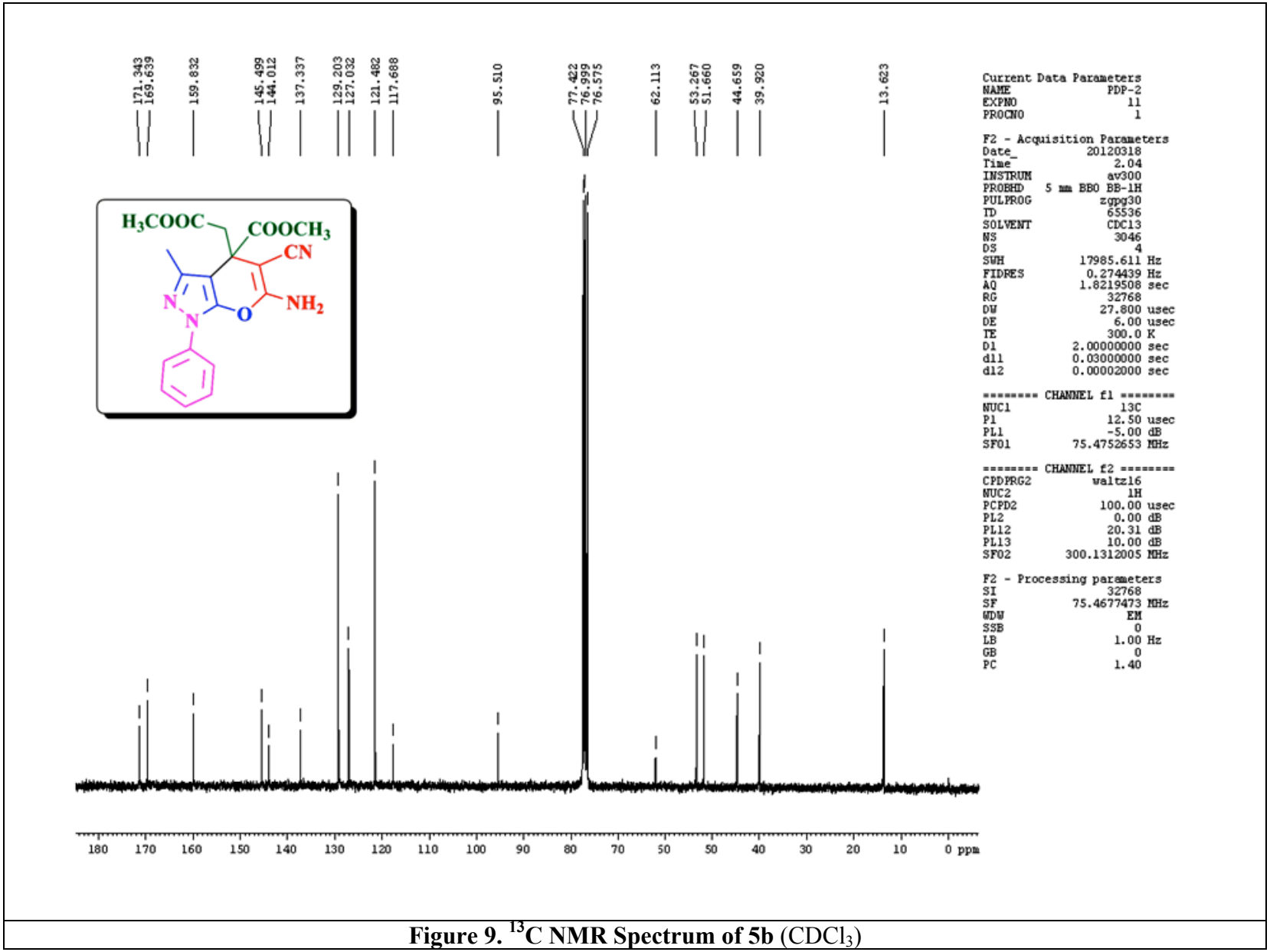

Figure 9. ^{13}**C NMR Spectrum of 5b** ($CDCl_3$)

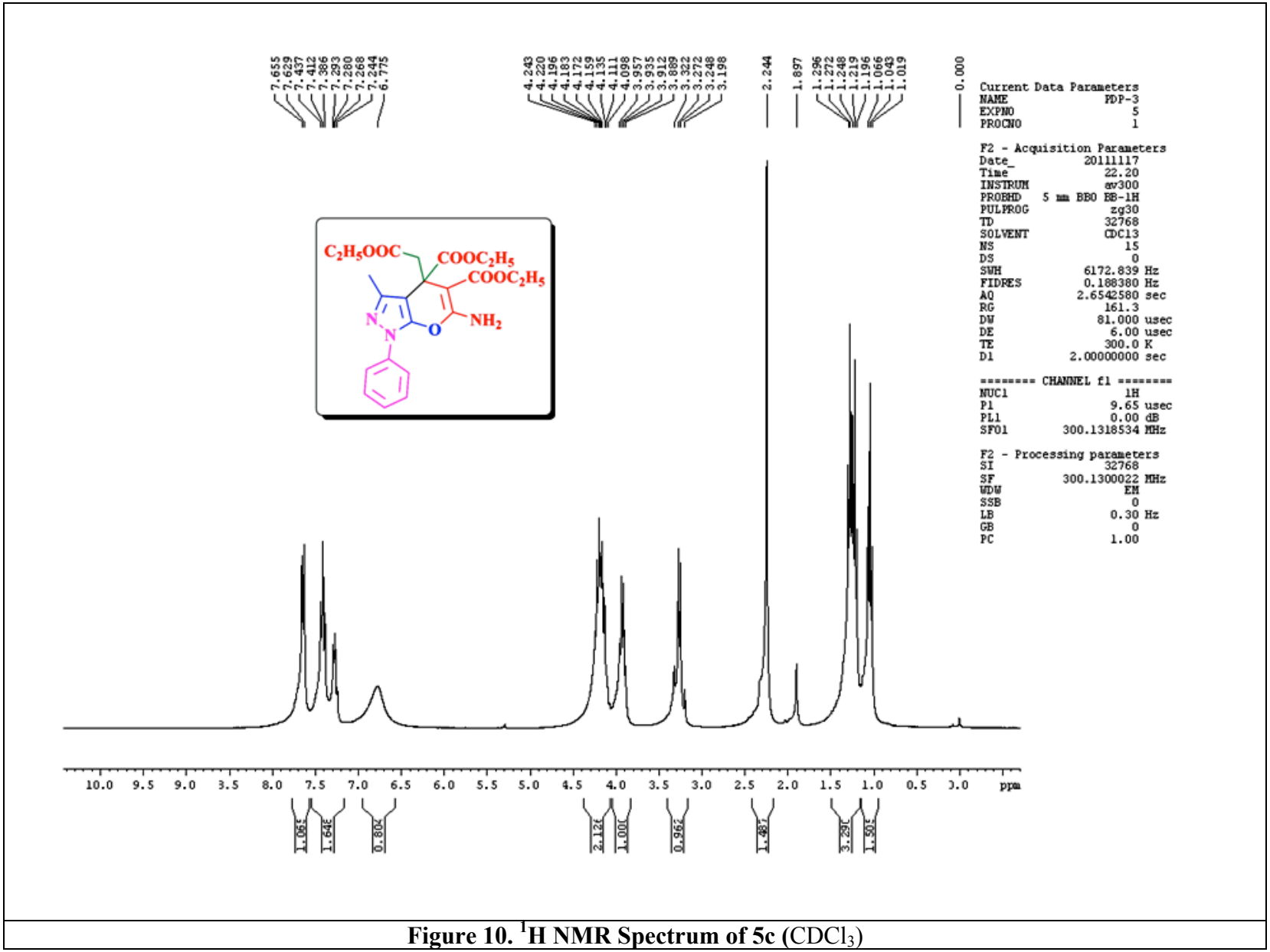

Figure 10. ^{1}H NMR Spectrum of 5c ($CDCl_3$)

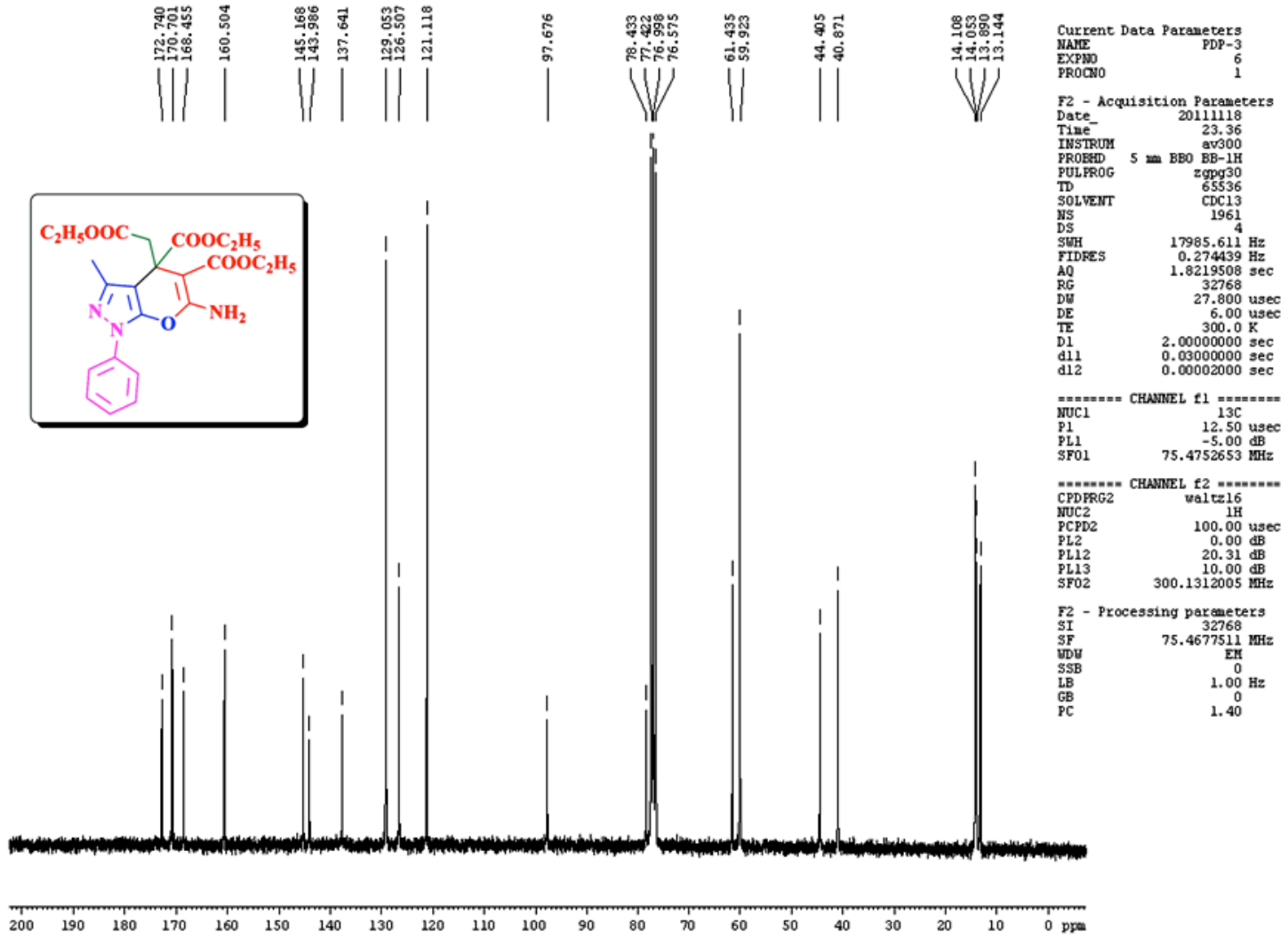

Figure 11. ^{13}C NMR Spectrum of 5c ($CDCl_3$)

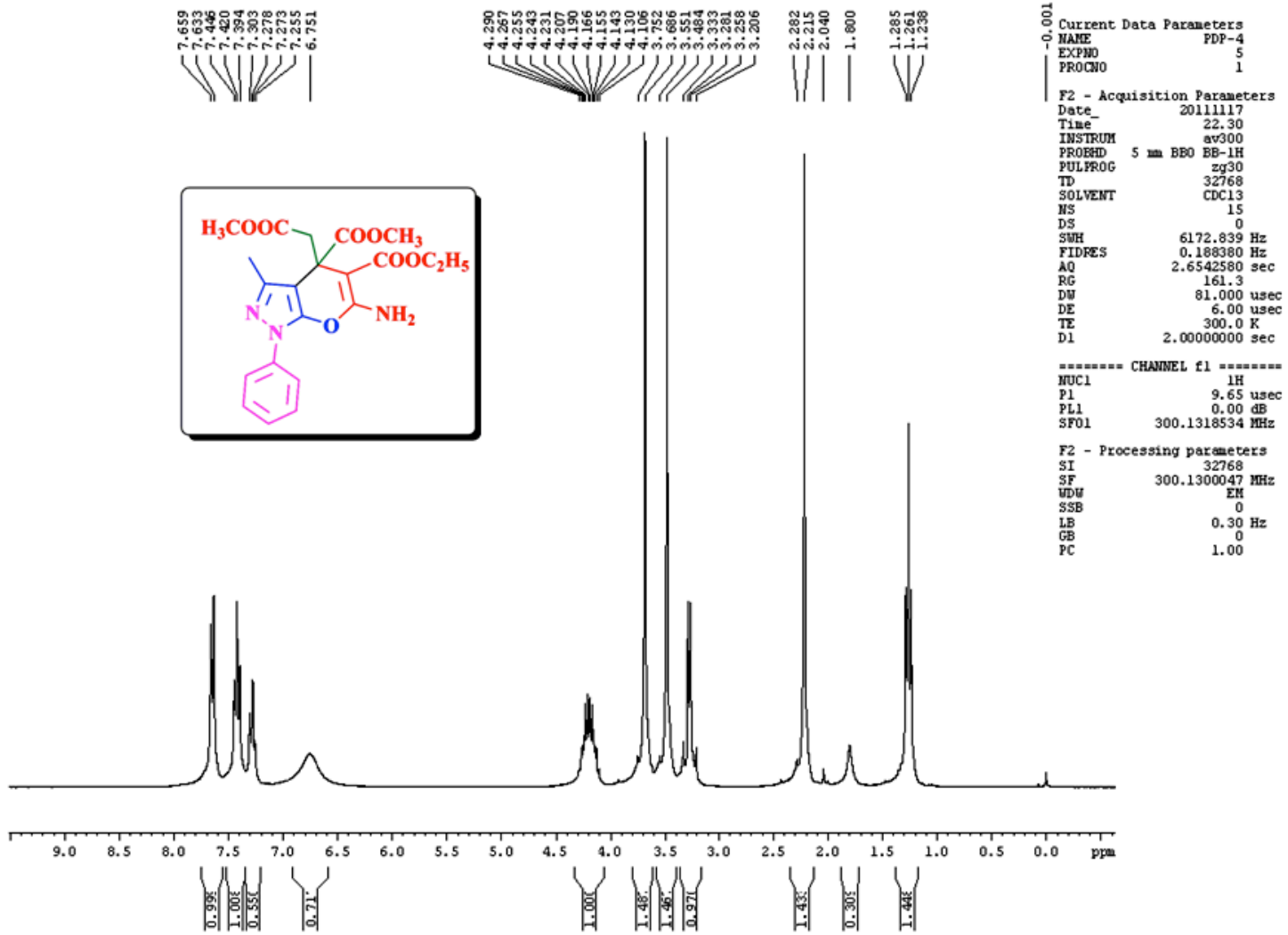

Figure 12. ^{1}H NMR Spectrum of 5d ($CDCl_3$)

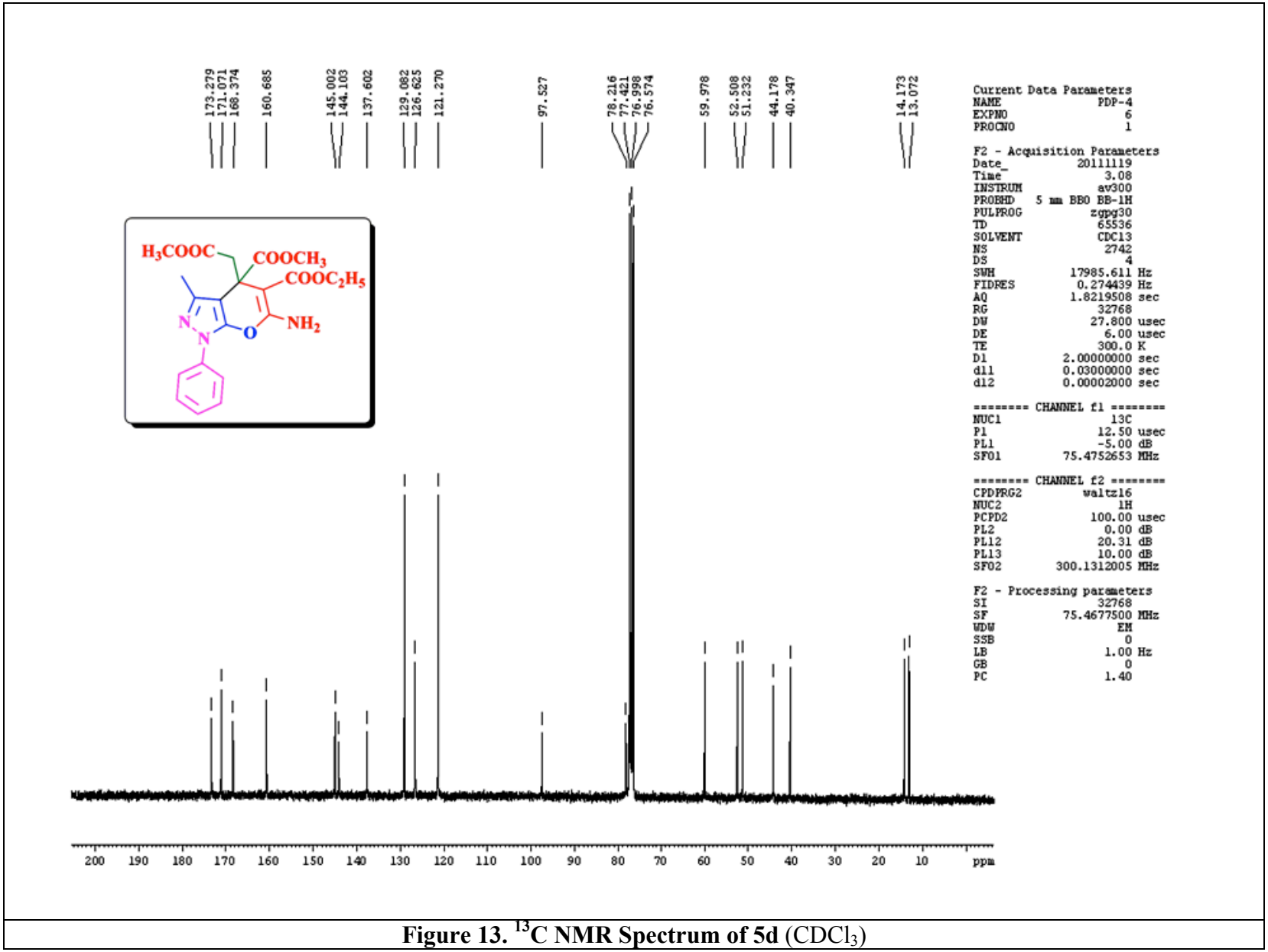

Figure 13. ^{13}C NMR Spectrum of 5d ($CDCl_3$)

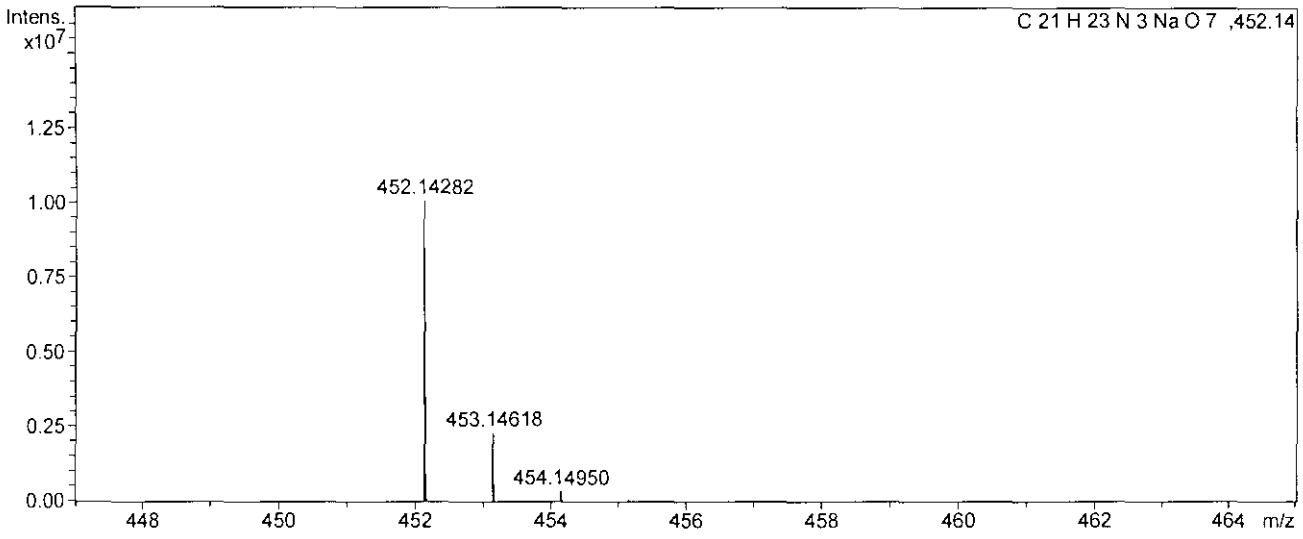

Figure 14. HRMS Spectrum of 5d

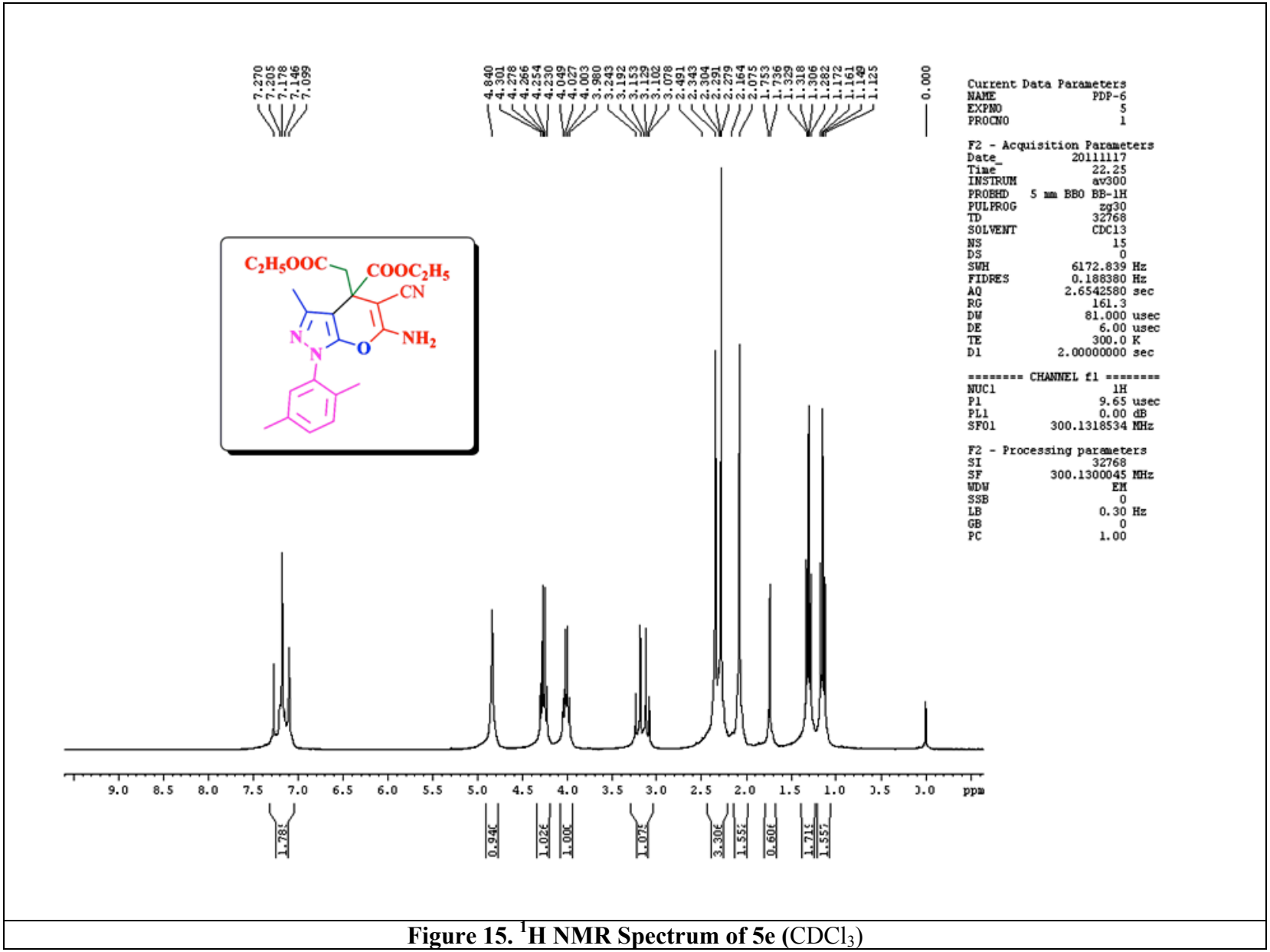

Figure 15. ^{1}H NMR Spectrum of 5e ($CDCl_3$)

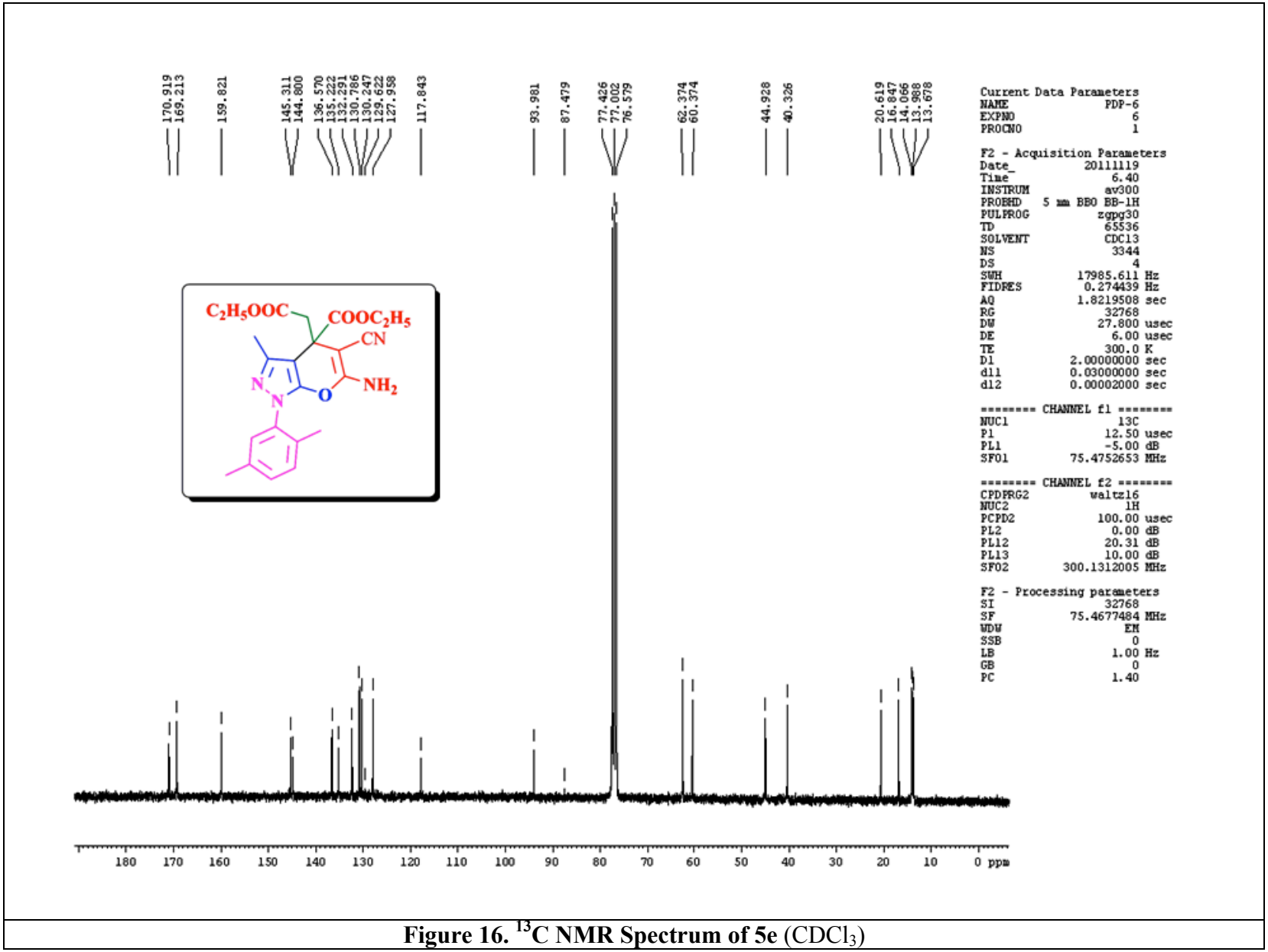

Figure 16. ^{13}C NMR Spectrum of 5e ($CDCl_3$)

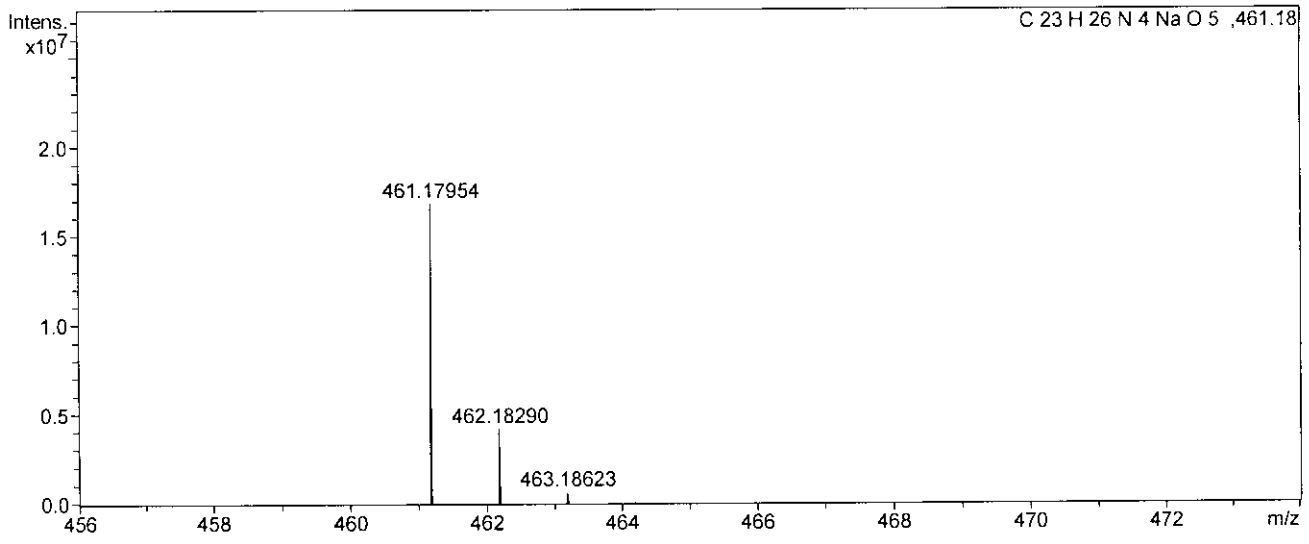

Figure 17. HRMS Spectrum of 5e

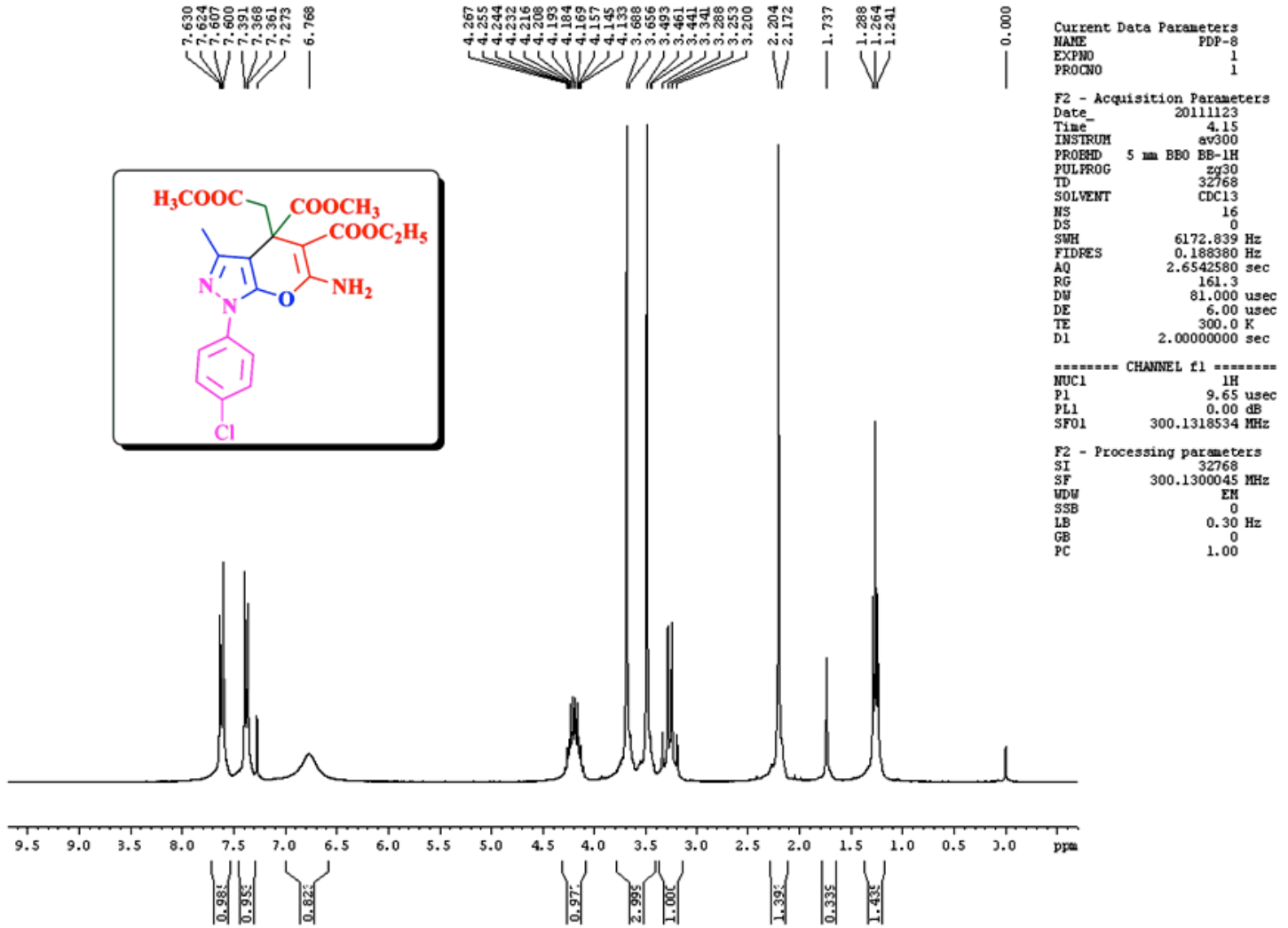

Figure 18. ^{1}H NMR Spectrum of 5f ($CDCl_3$)

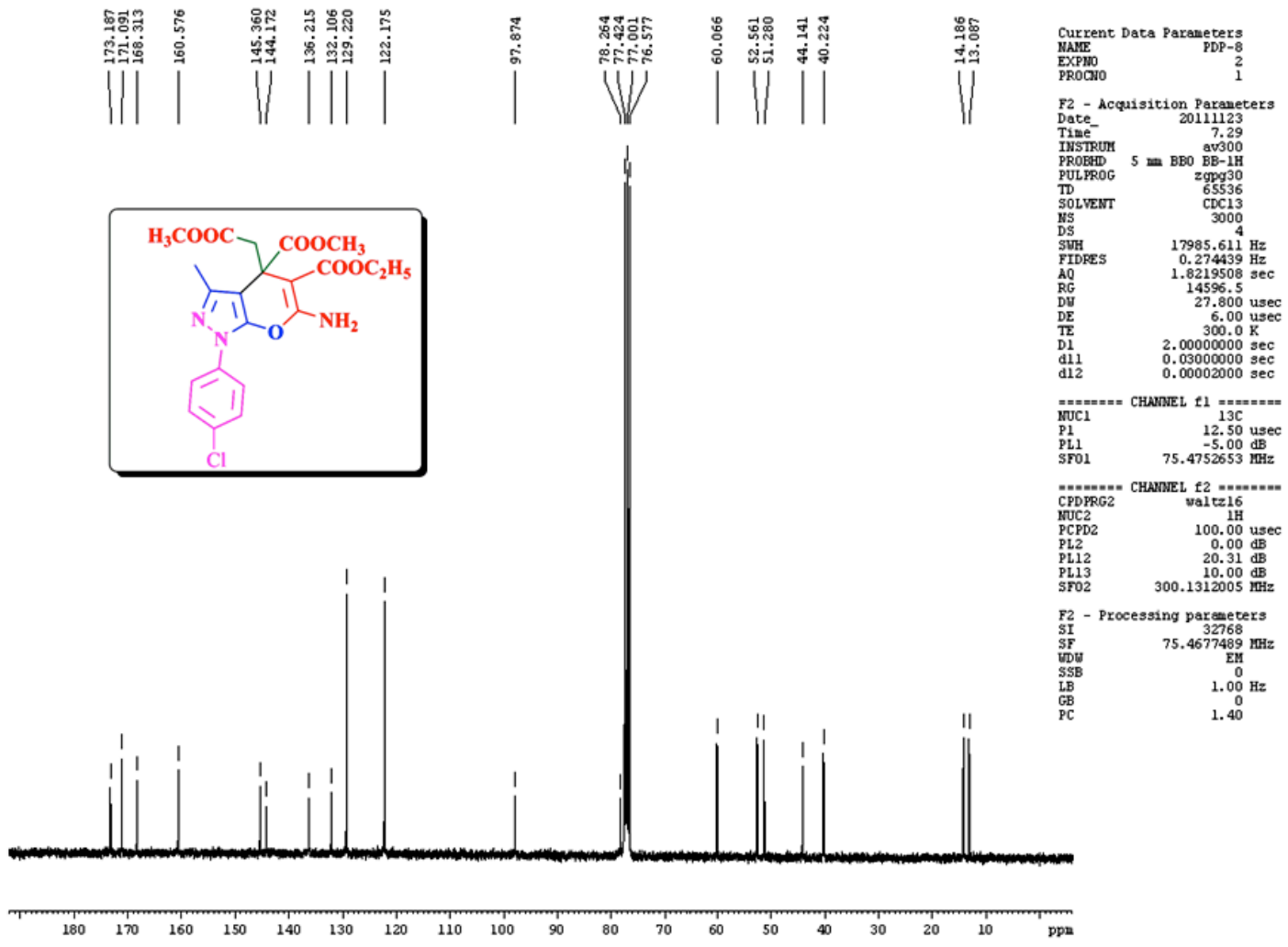

Figure 19. ^{13}C NMR Spectrum of 5f ($CDCl_3$)

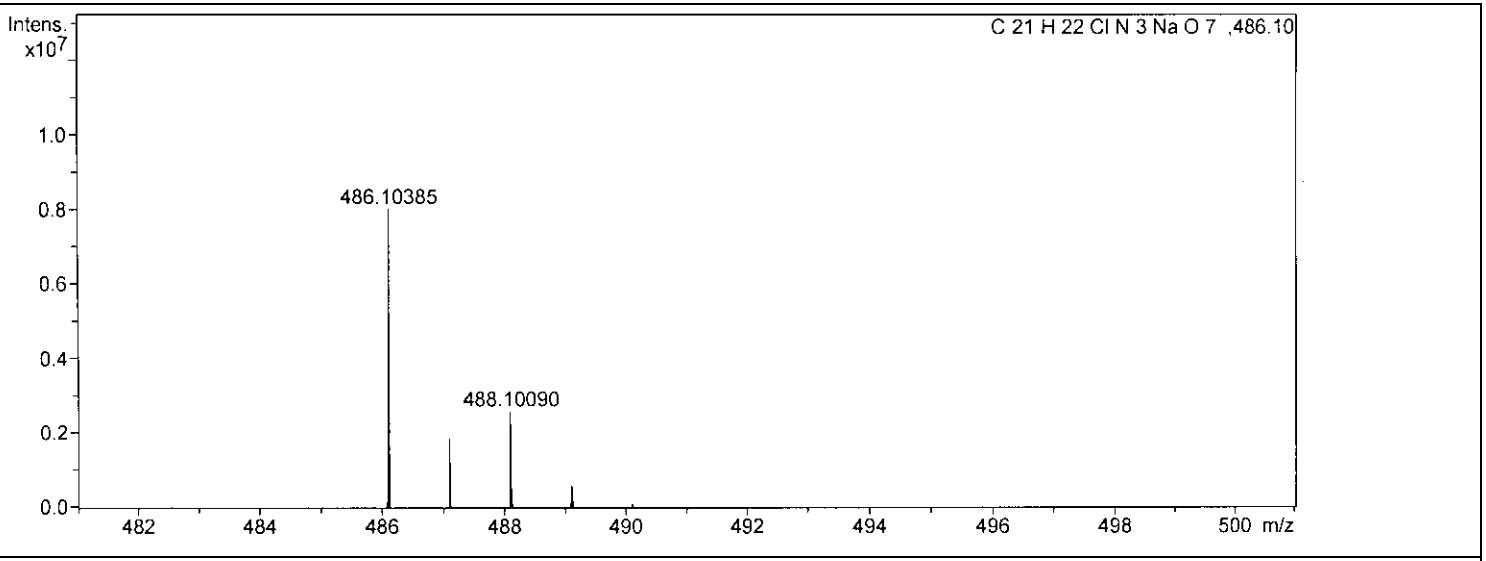

Figure 20. HRMS Spectrum of 5f

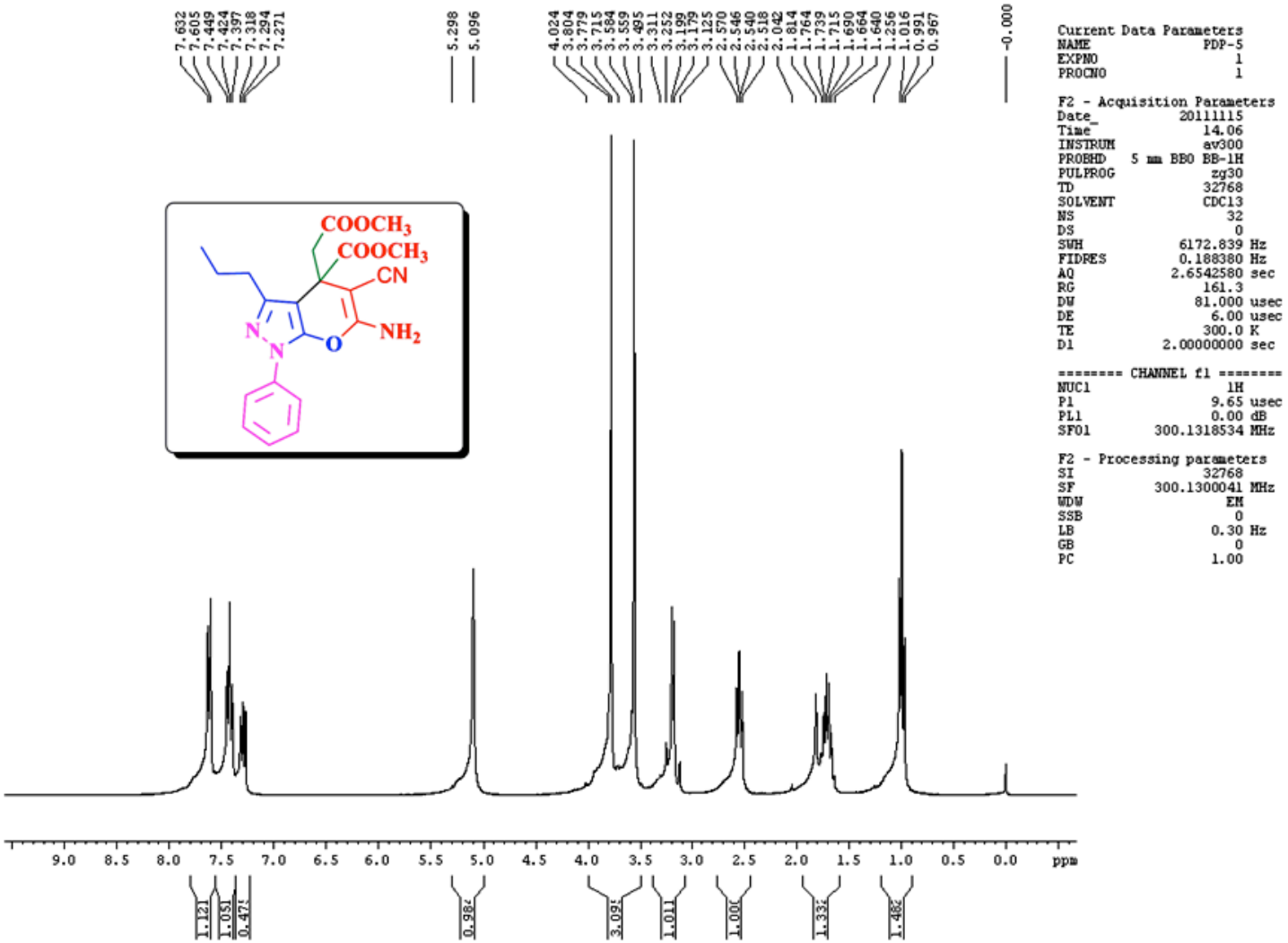

Figure 21. ^{1}H NMR Spectrum of 5g ($CDCl_3$)

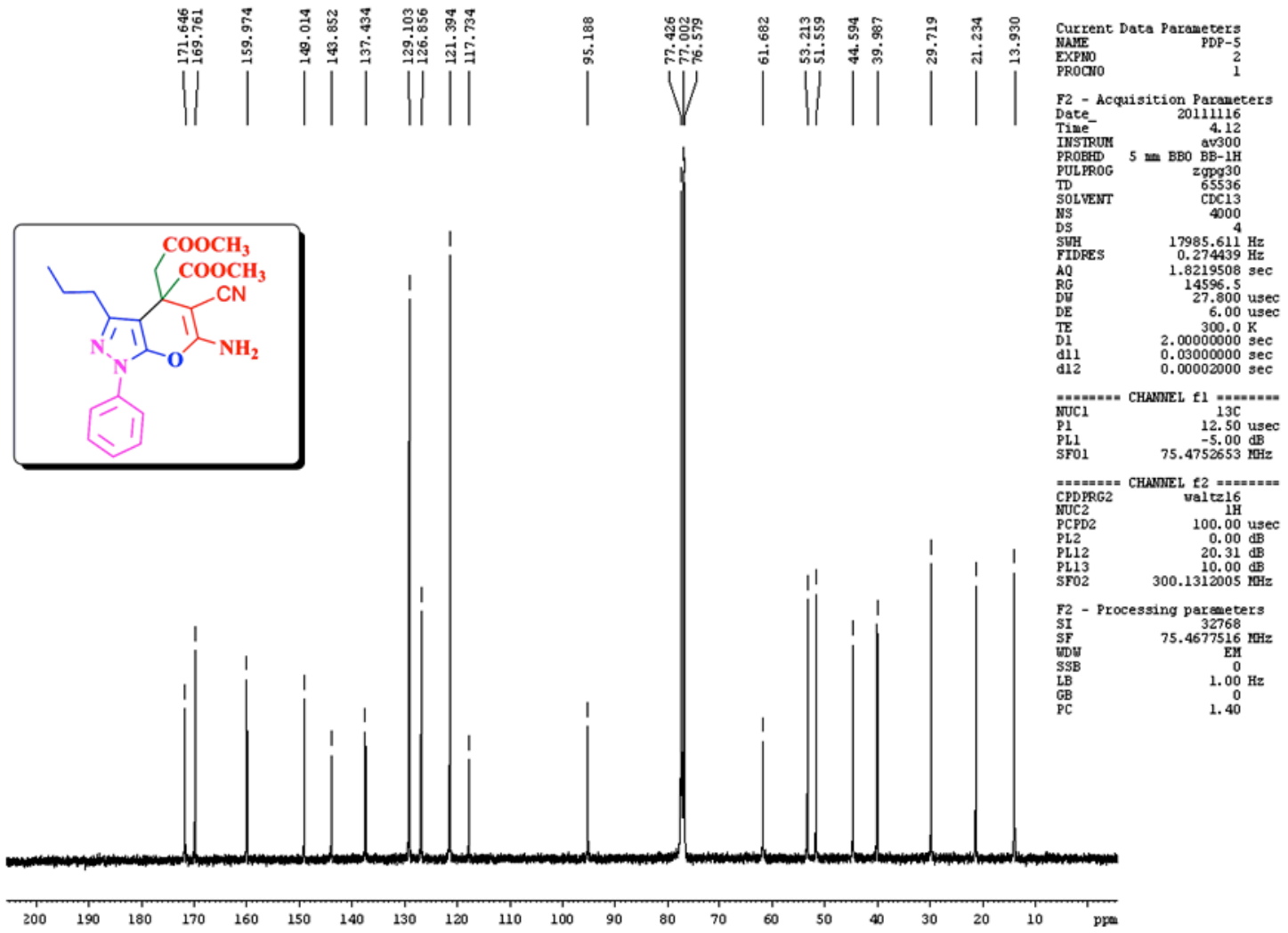

Figure 22. ^{13}C NMR Spectrum of 5g ($CDCl_3$)

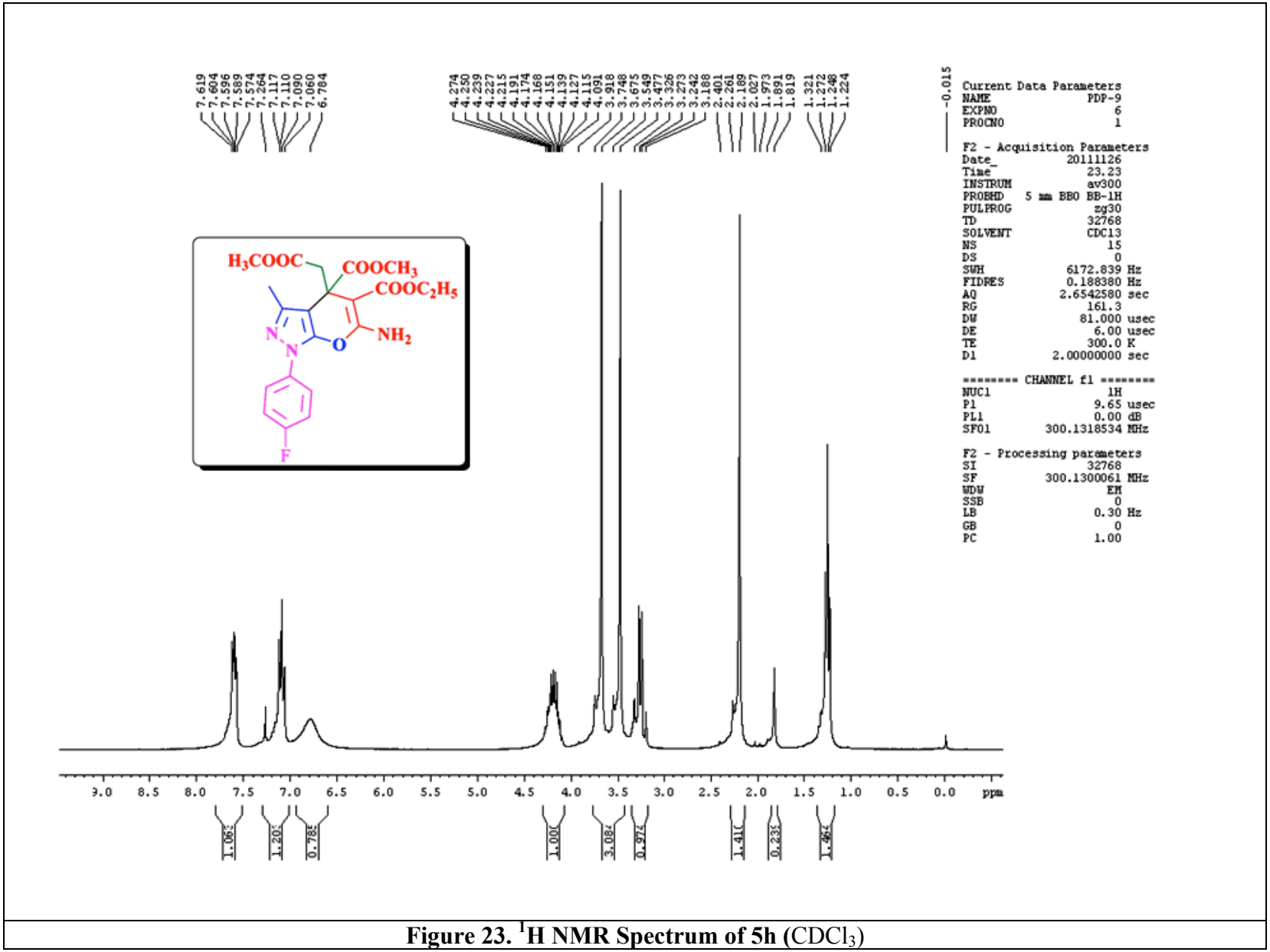

Figure 23. ^{1}H NMR Spectrum of 5h ($CDCl_3$)

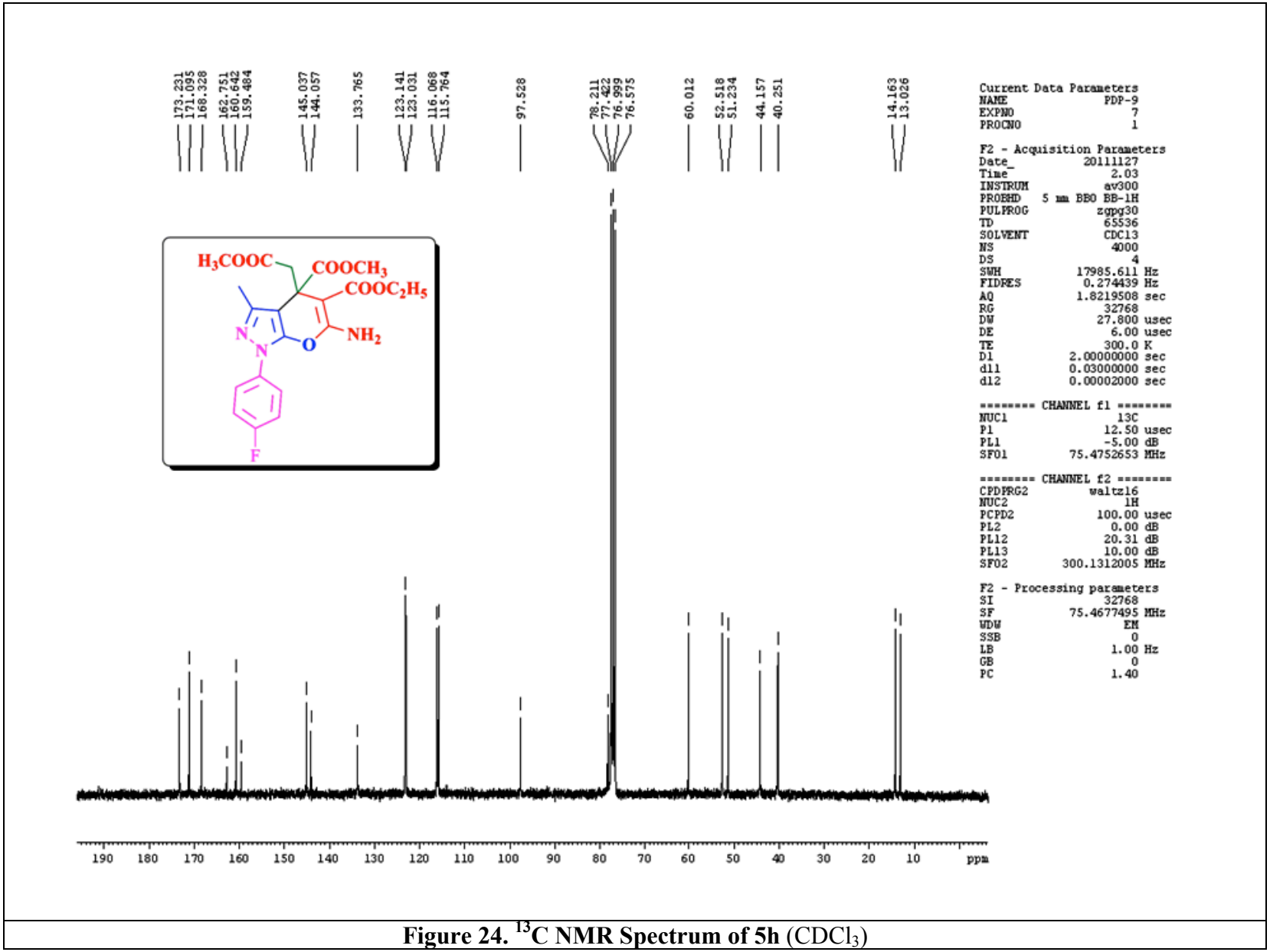

Figure 24. ^{13}C NMR Spectrum of 5h ($CDCl_3$)

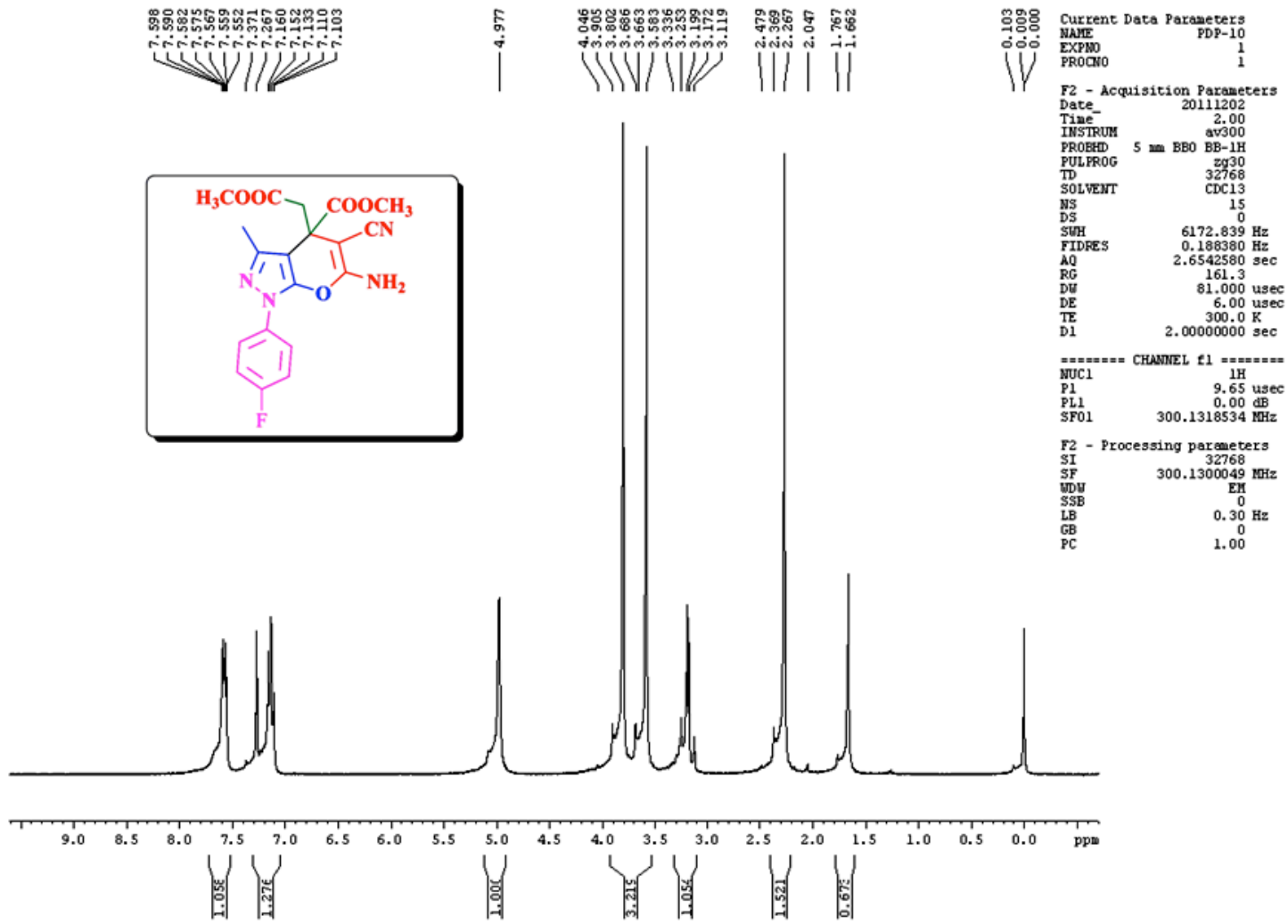

Figure 25. ^{1}H NMR Spectrum of 5i ($CDCl_3$)

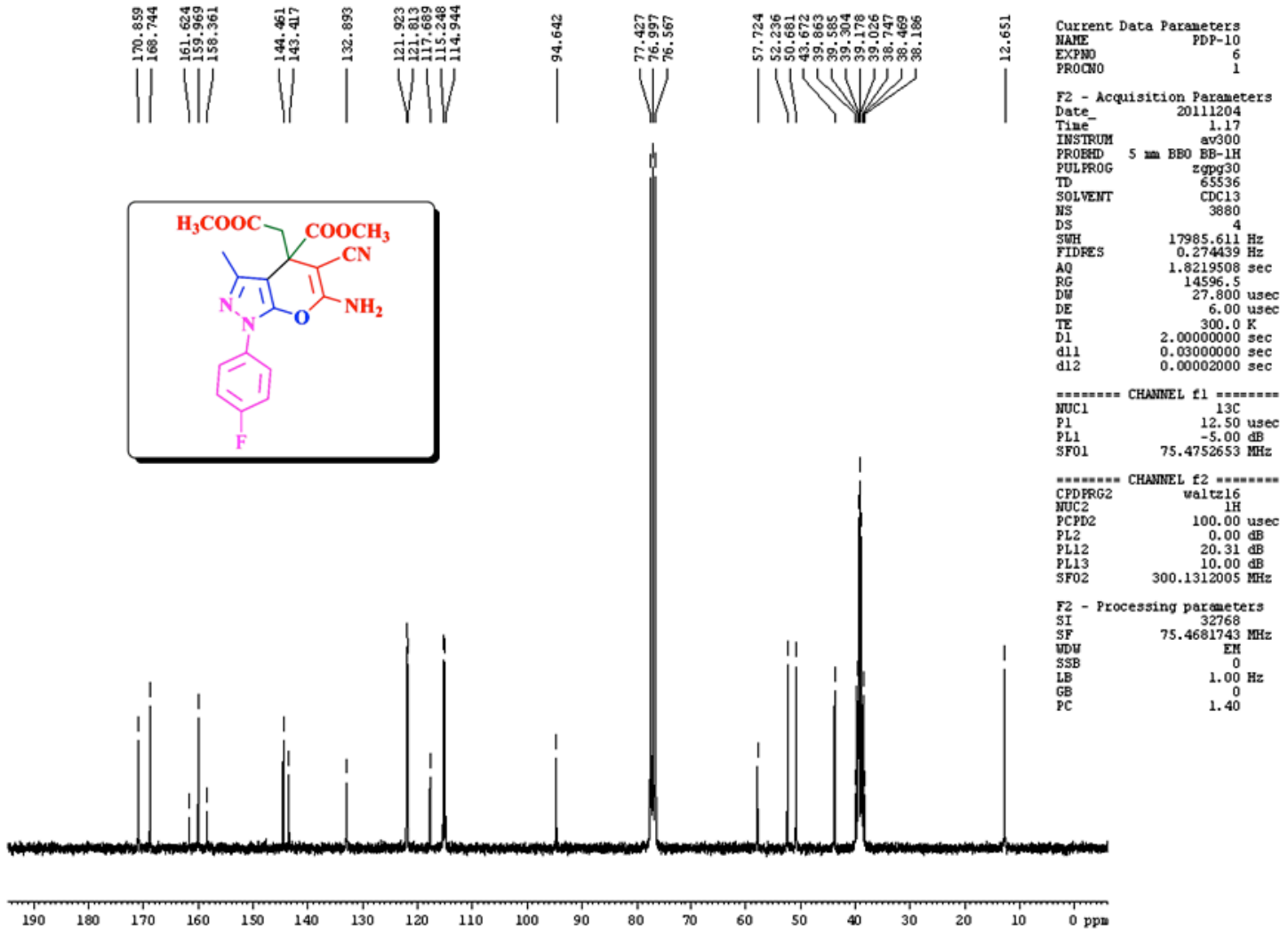

Figure 26. ^{13}C NMR Spectrum of 5i ($CDCl_3$)

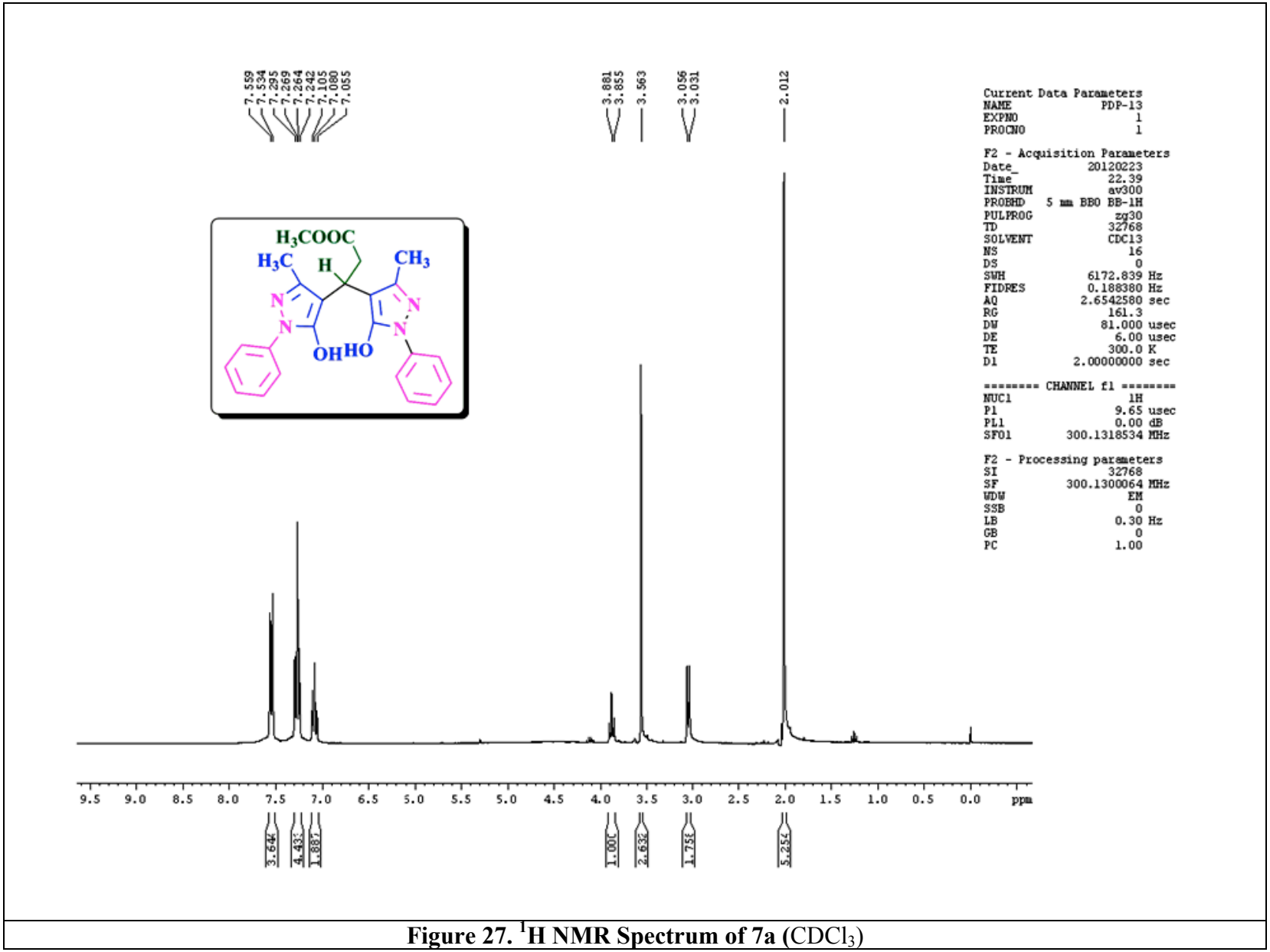

Figure 27. ^{1}H NMR Spectrum of 7a ($CDCl_3$)

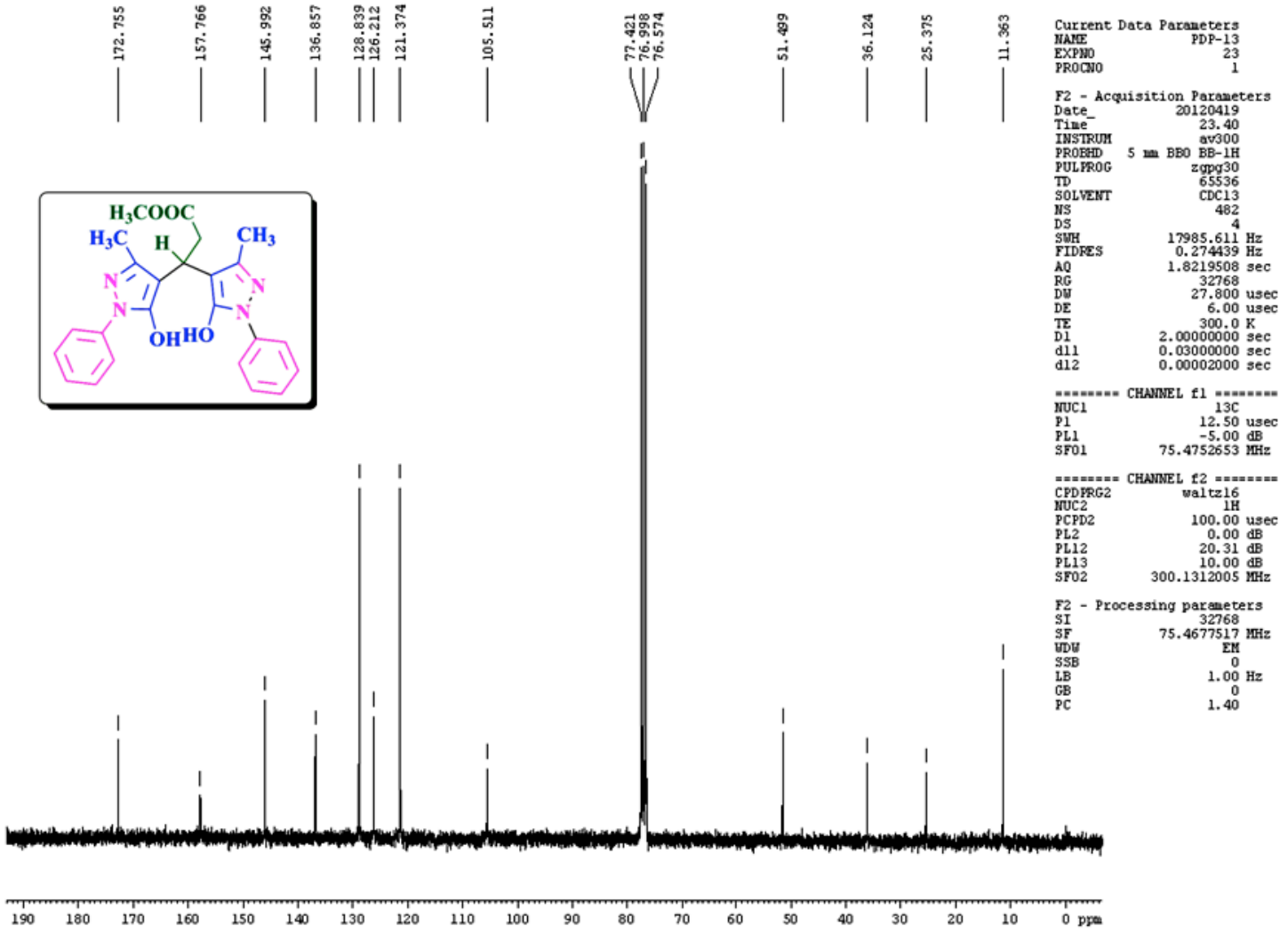

Figure 28. ^{13}C NMR Spectrum of 7a ($CDCl_3$)

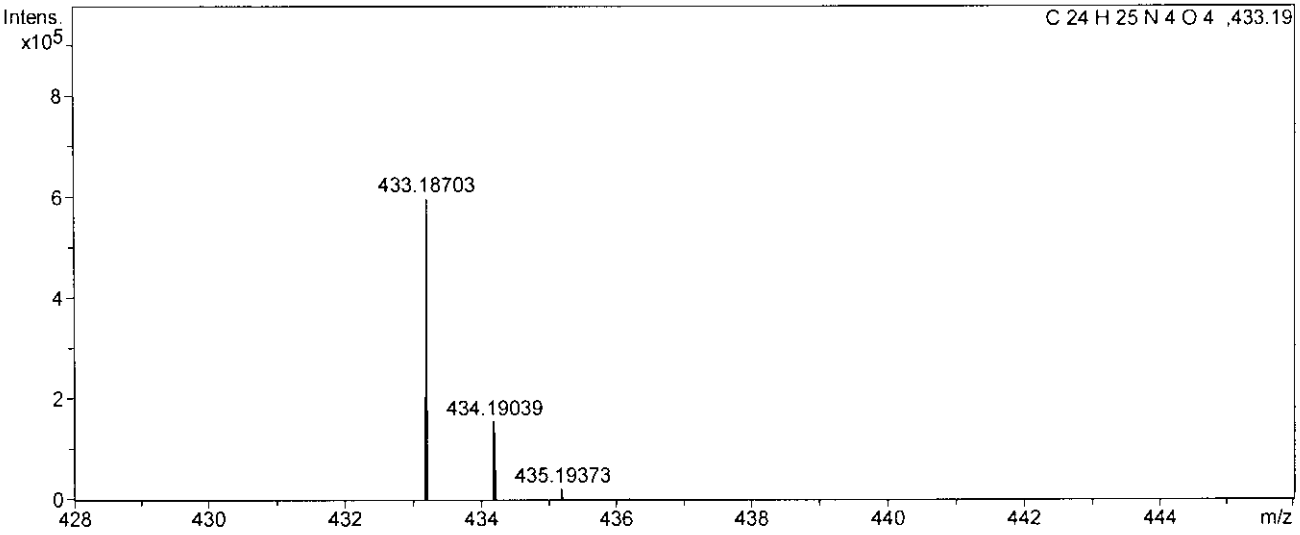

Figure 29. HRMS Spectrum of 7a

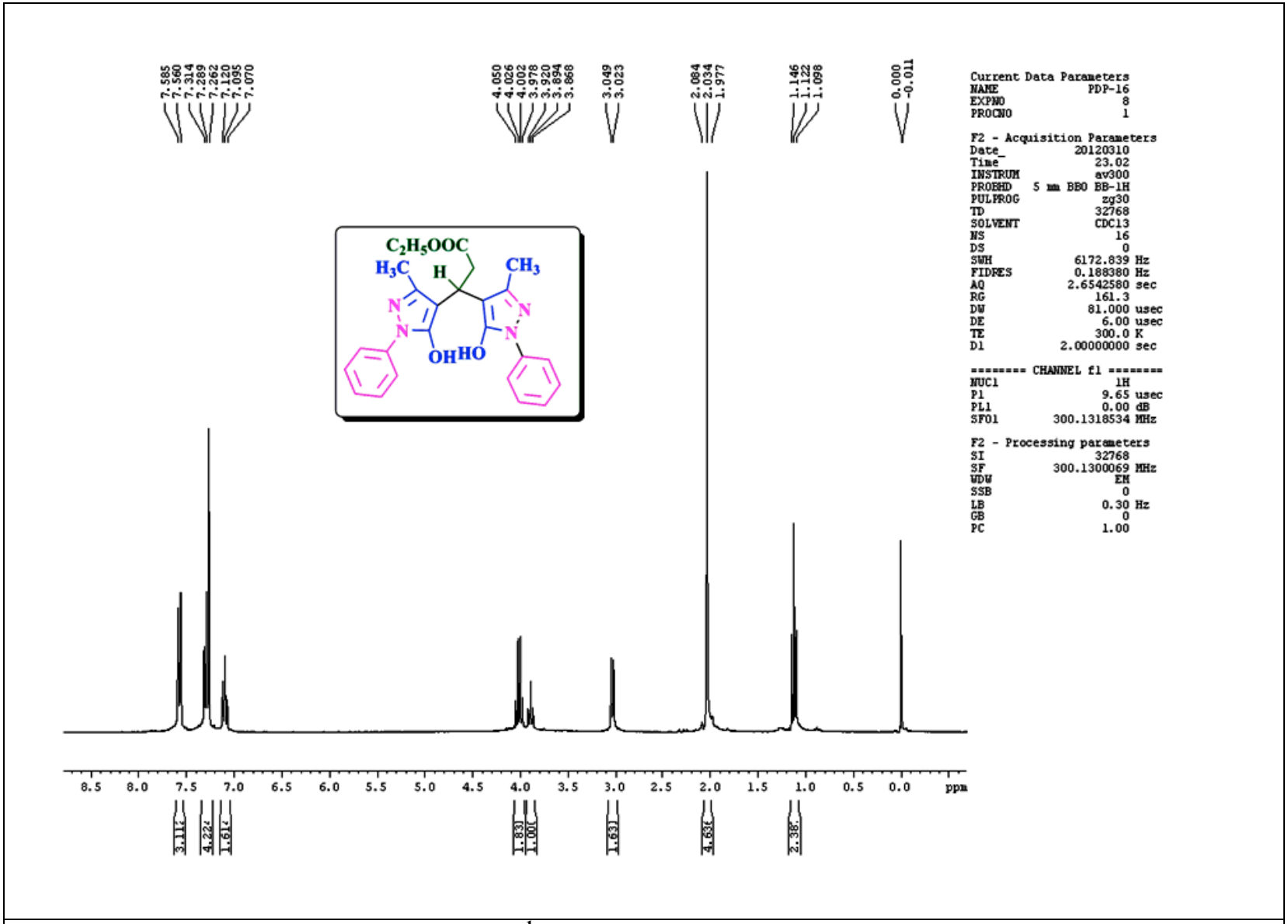

Figure 30. ^{1}H NMR Spectrum of 7b ($CDCl_3$)

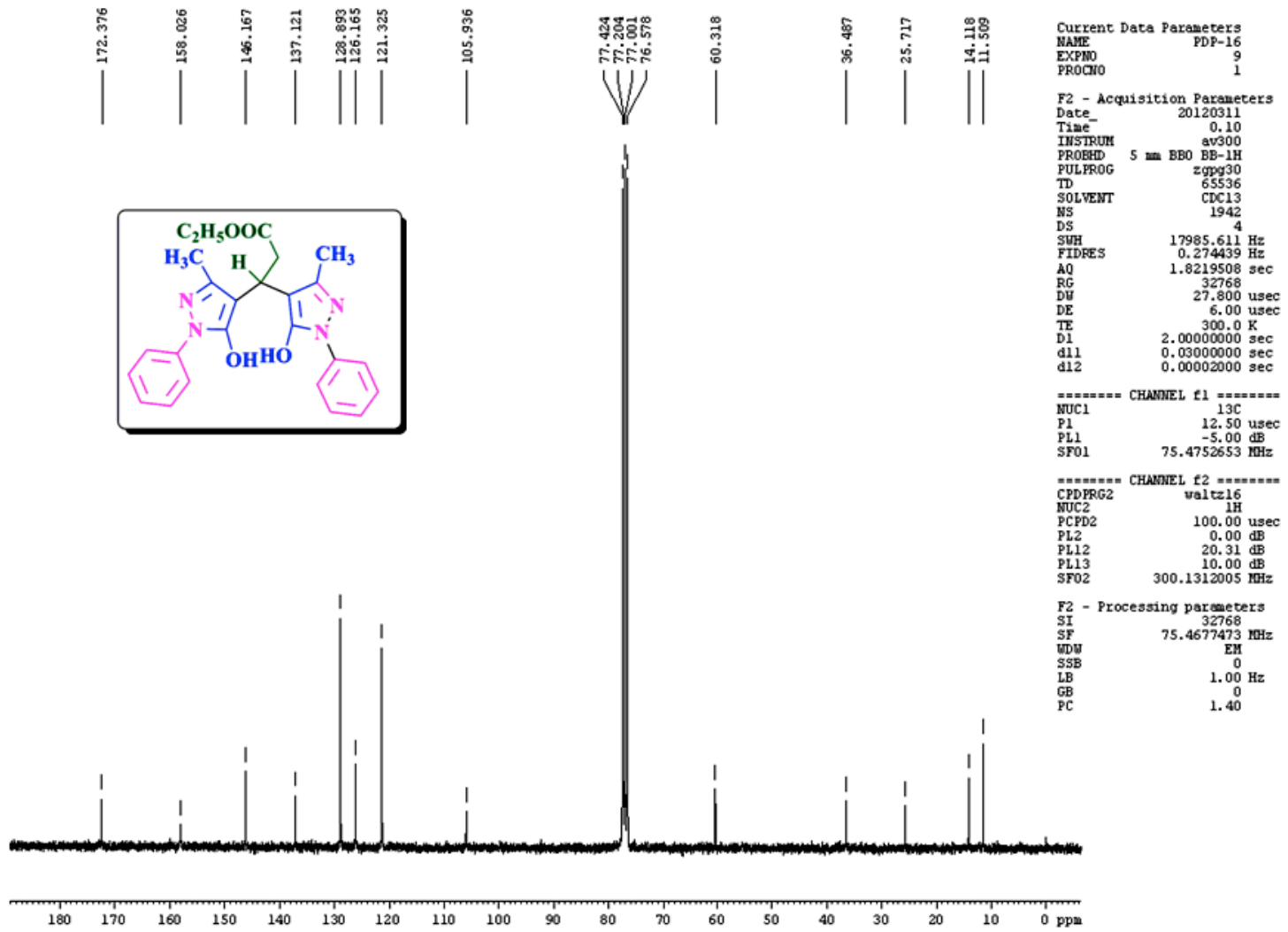

Figure 31. ^{13}C NMR Spectrum of 7b ($CDCl_3$)

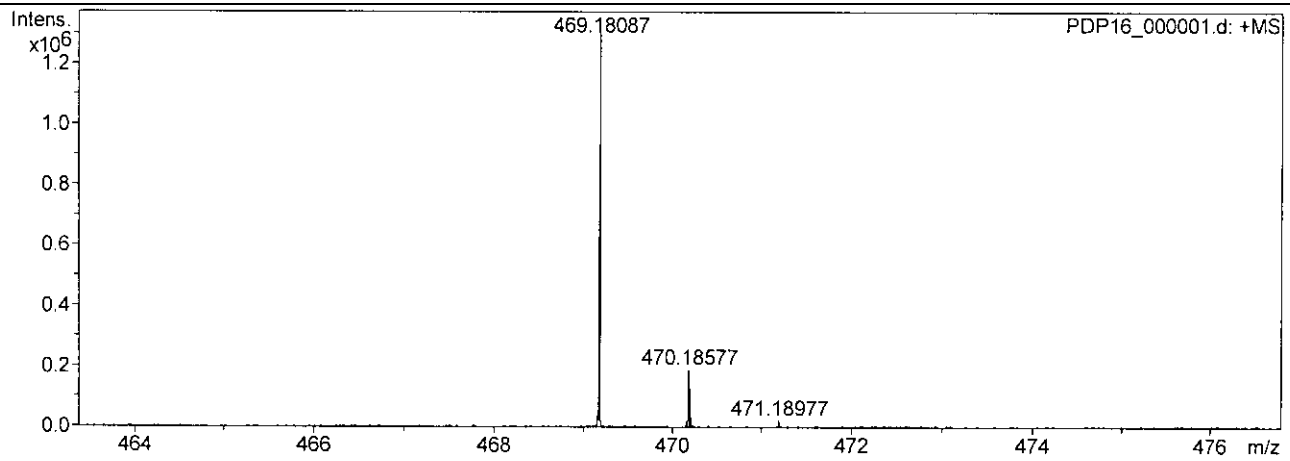

Figure 32. HRMS Spectrum of 7b

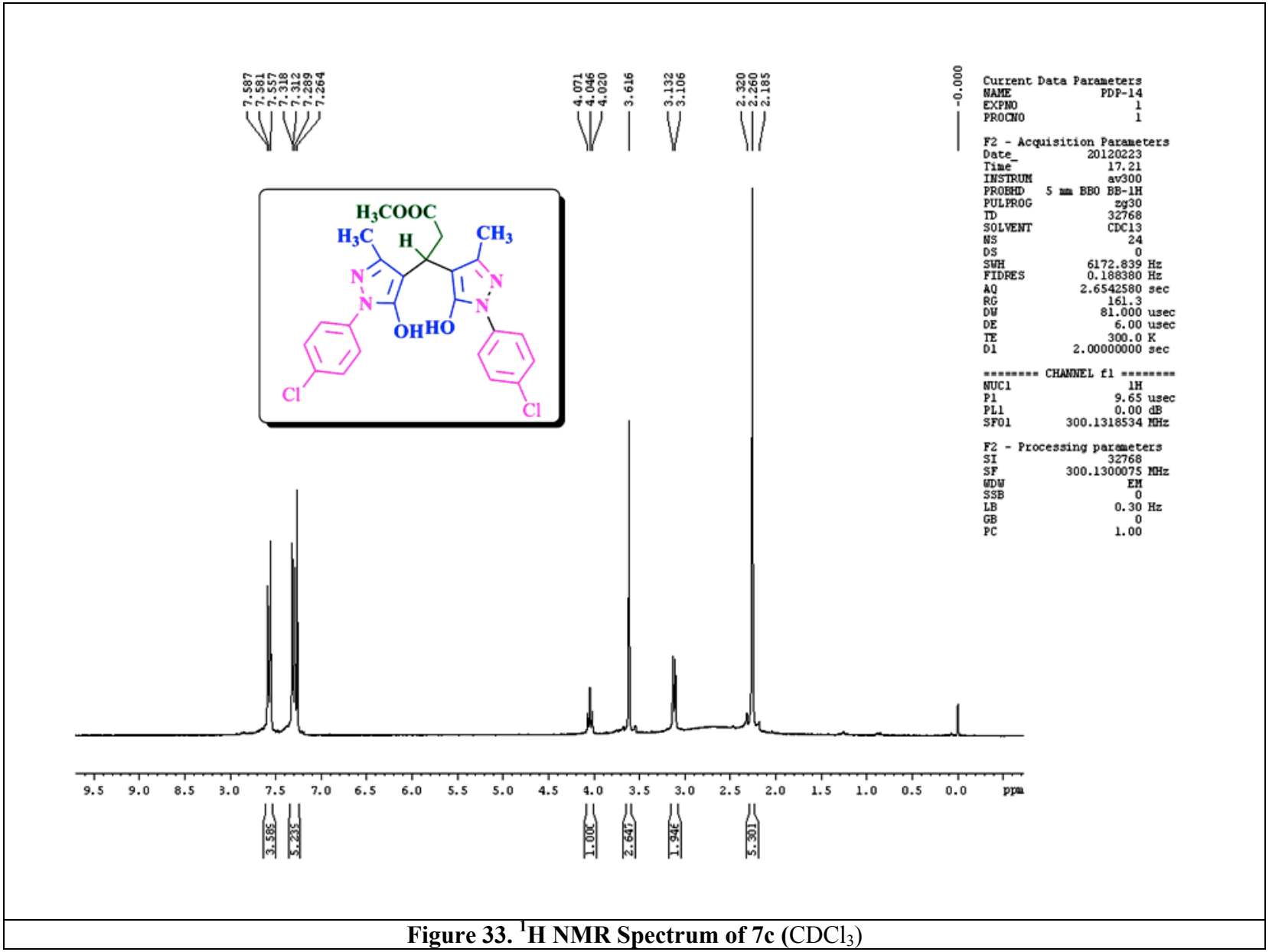

Figure 33. ^{1}H NMR Spectrum of 7c ($CDCl_3$)

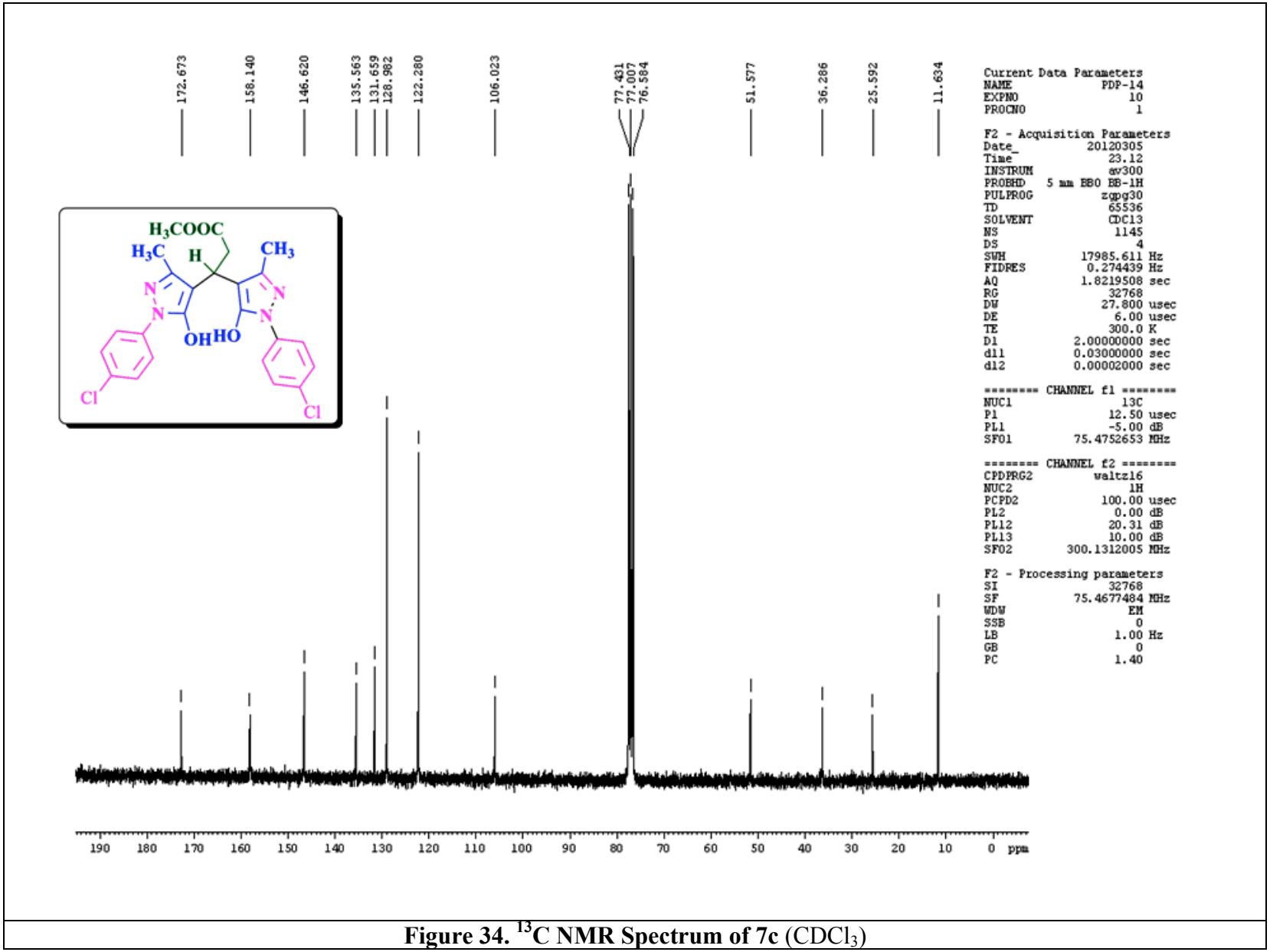

Figure 34. ^{13}C NMR Spectrum of 7c ($CDCl_3$)

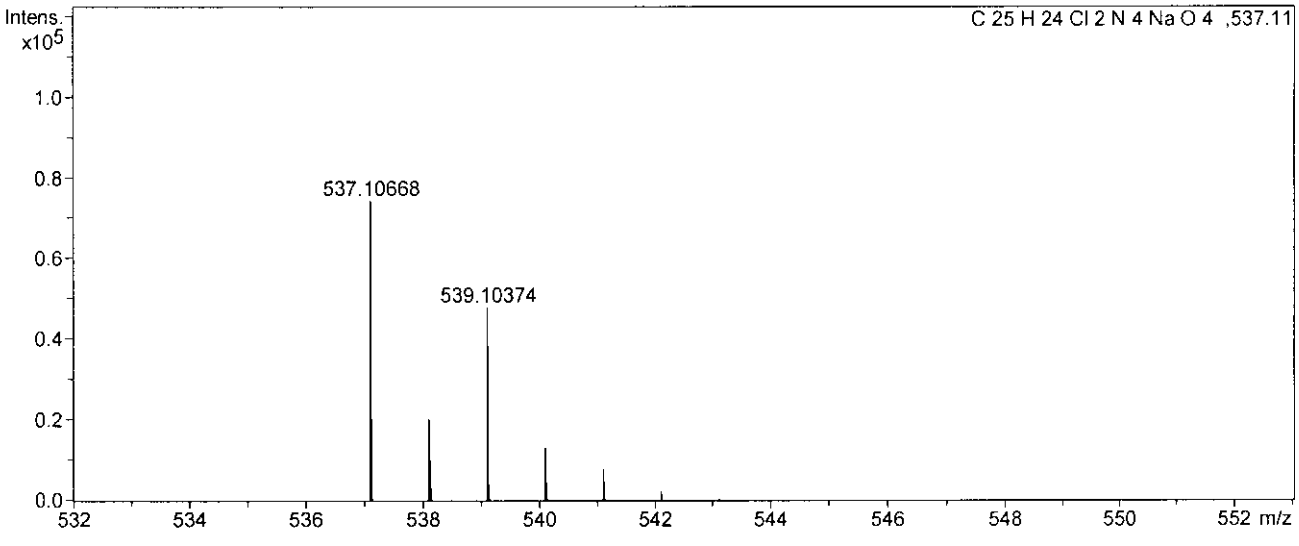

Figure 35. HRMS Spectrum of 7c

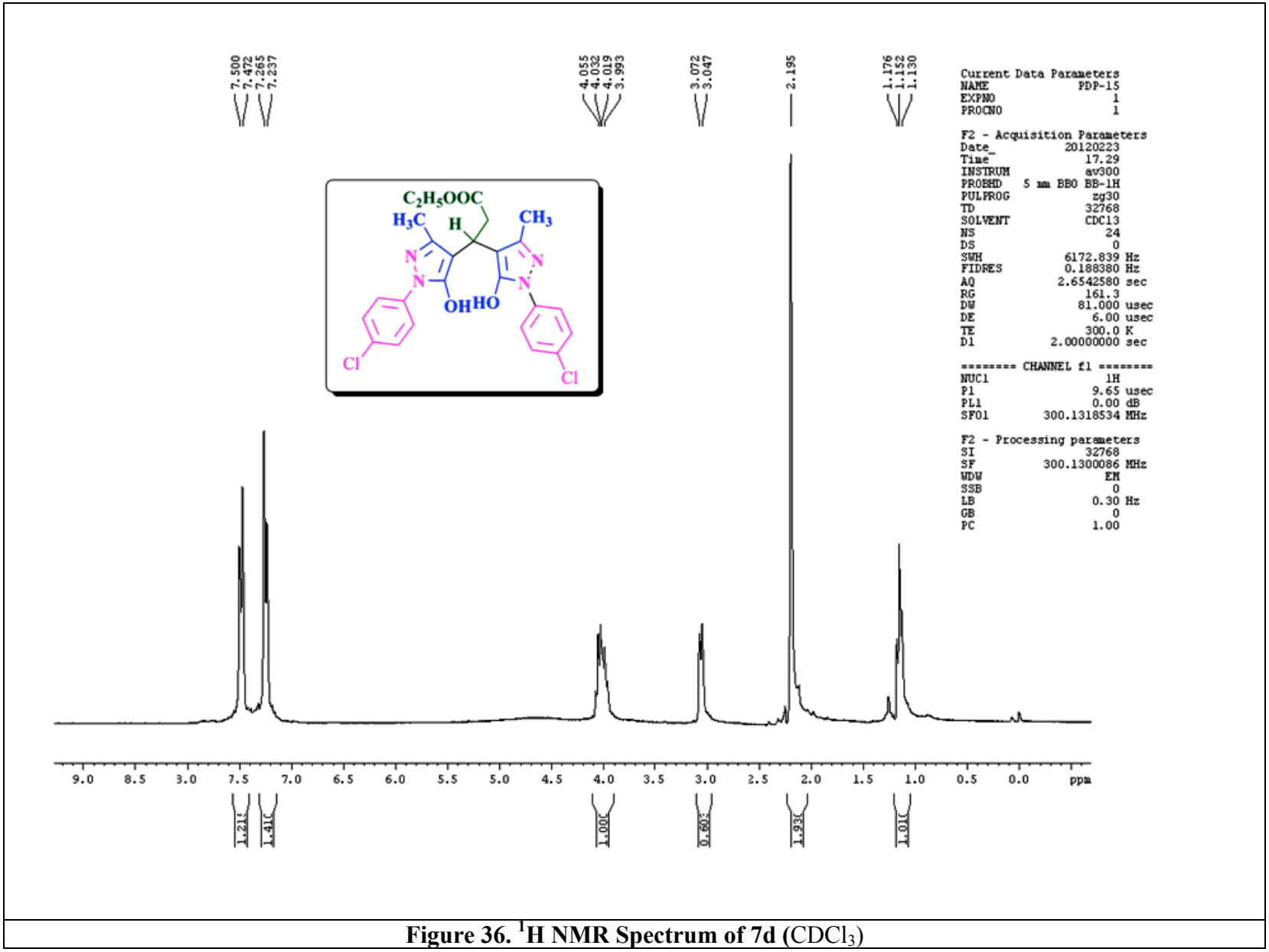

Figure 36. ^{1}H NMR Spectrum of 7d ($CDCl_3$)

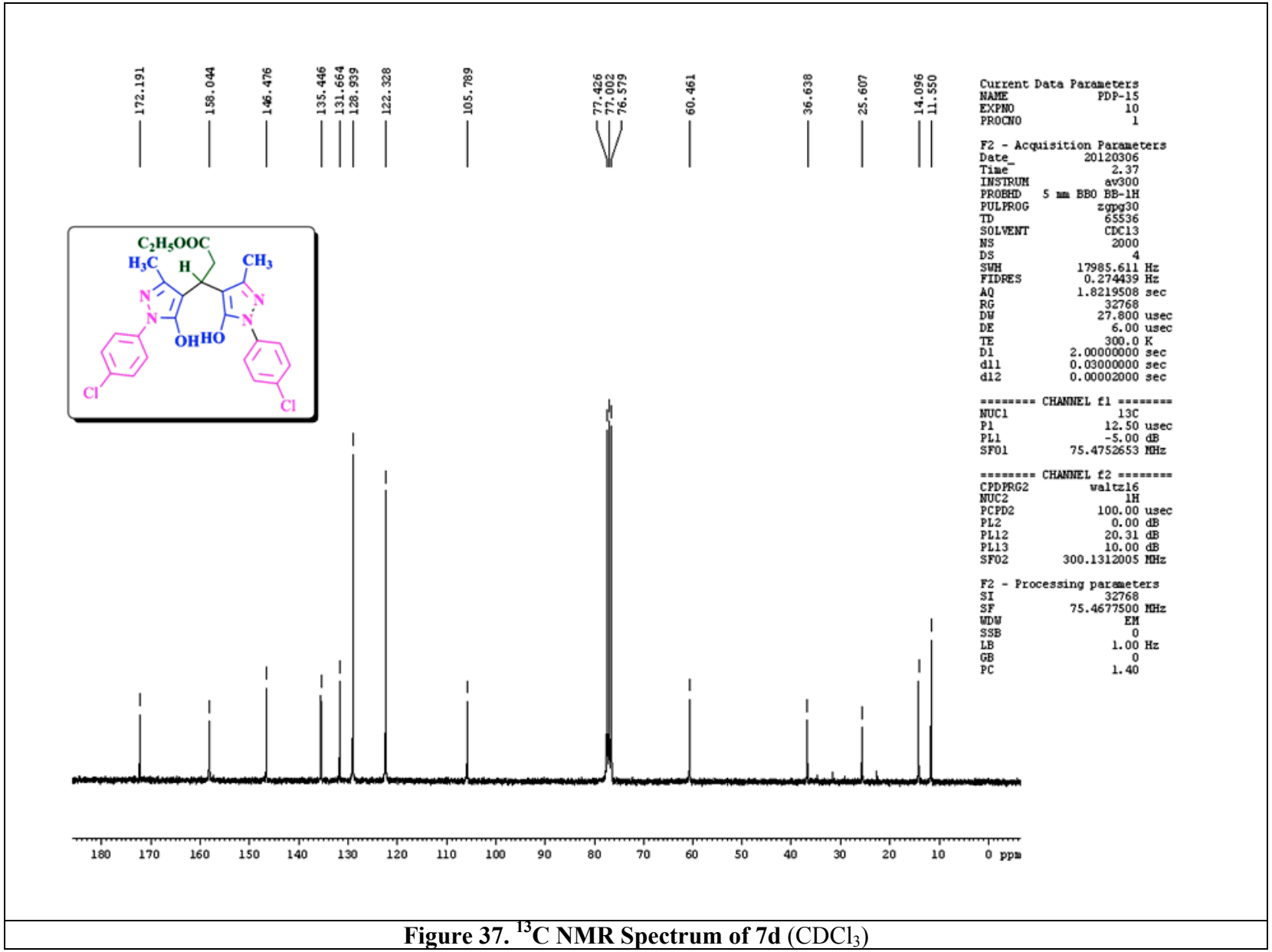

Figure 37. ^{13}C NMR Spectrum of 7d ($CDCl_3$)

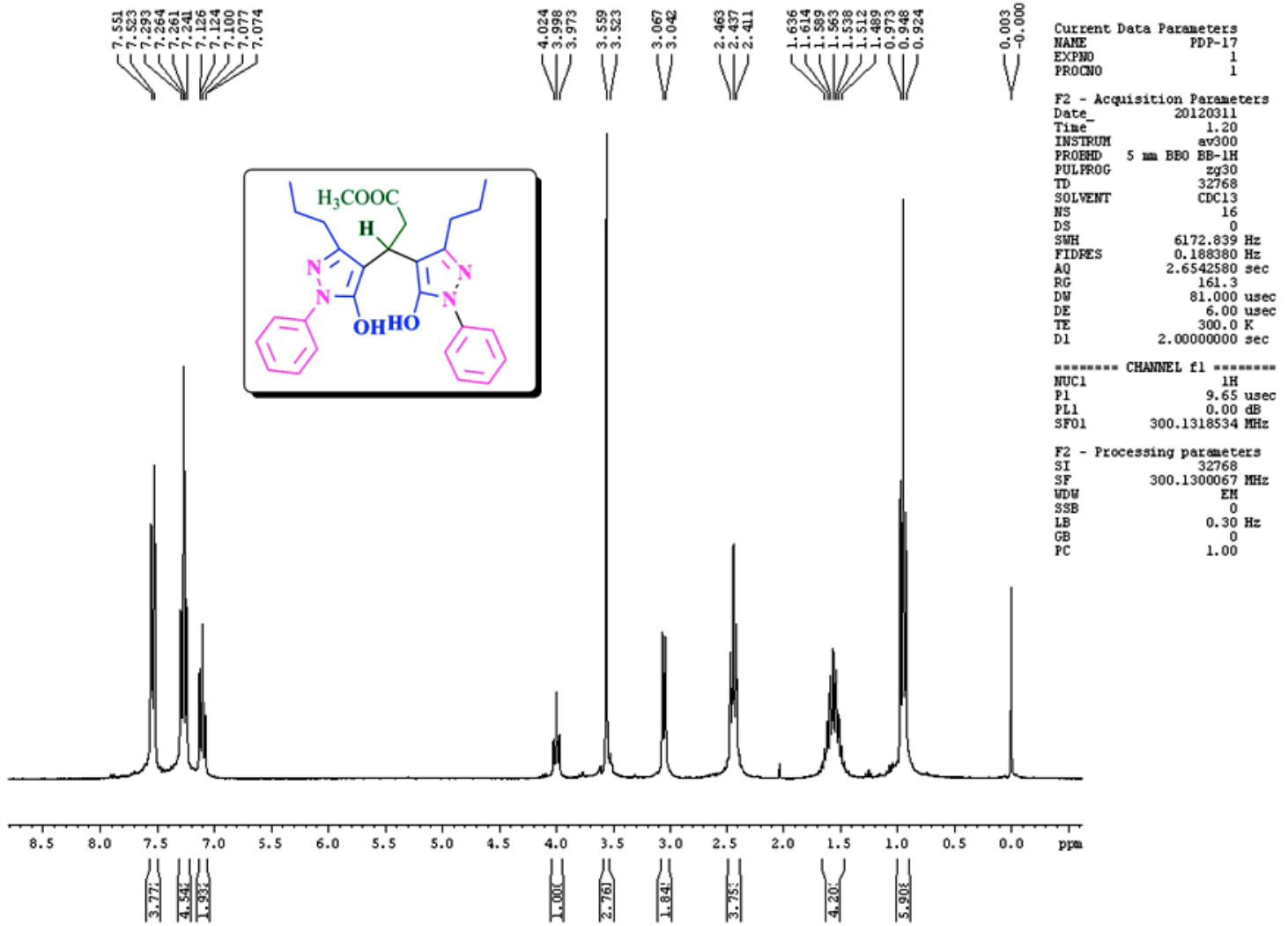

Figure 38. ^{1}H NMR Spectrum of 7e ($CDCl_3$)

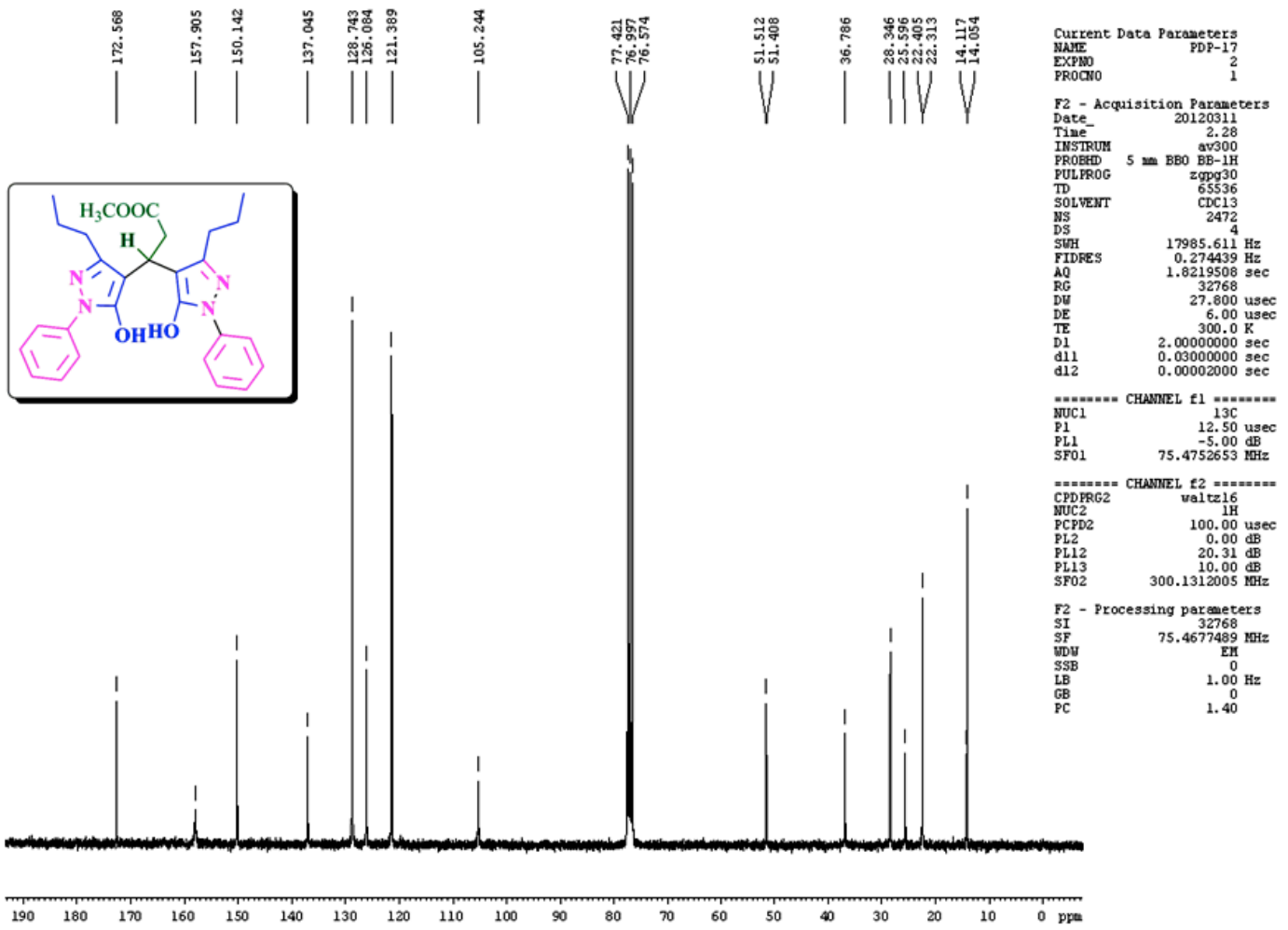

Figure 39. ^{13}C NMR Spectrum of 7e ($CDCl_3$)

HPLC profile of 5a (Chiralcel OD-H column, 90% Hexane: 10% 2-propanol, 0.5 mL/min)

Compound **5a** obtained in the D,L-proline-catalyzed reaction

Shimadzu CLASS-VP V6.14 SP1 *Area % Report* **Page 1 of 1**

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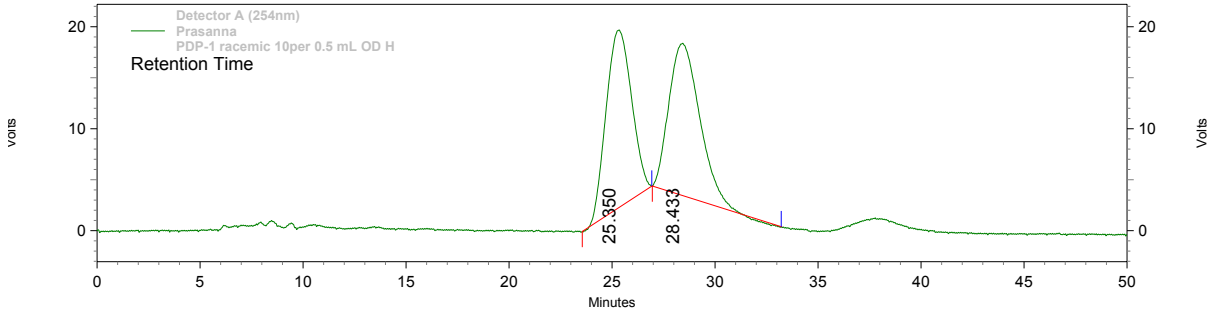

Detector A (254nm)

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2	28.433	1551170	50.887	14942	46.214
Totals		3048284	100.000	32332	100.000

HPLC profile of 5a (Chiralcel OD-H column, 90% Hexane: 10% 2-propanol, 0.5 mL/min)

Compound **5a** obtained in the L-proline-catalyzed reaction

Shimadzu CLASS-VP V6.14 SP1 *Area % Report* **Page 1 of 1**

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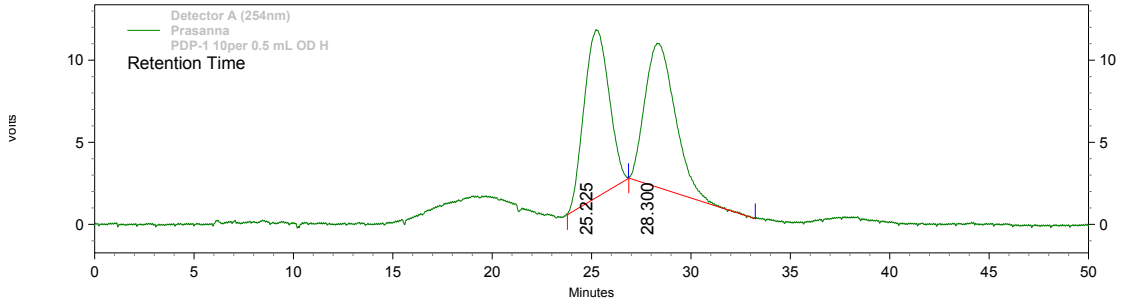

Detector A (254nm)

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2	28.300	933015	51.200	8773	46.140
Totals		1822304	100.000	19014	100.000

HPLC profile of 5f (Chiralcel OD-H column, solvent: 90% Hexane-10% 2-propanol, flow rate = 0.5 mL/min)

Compound **5f** obtained in the D,L-proline-catalyzed reaction

Shimadzu CLASS-VP V6.14 SP1 *Area % Report* **Page 1 of 1**

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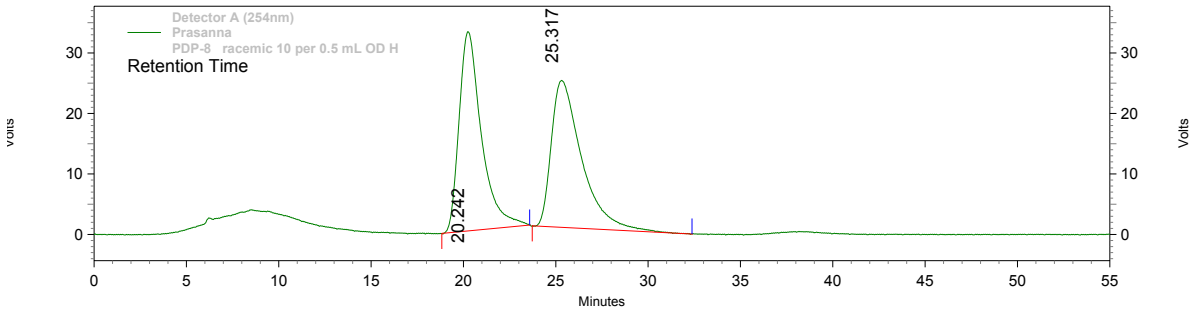


Detector A (254nm)

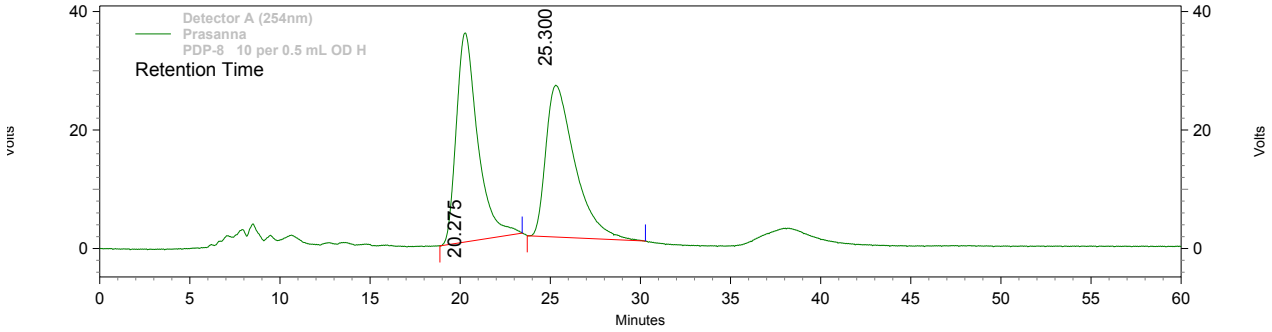
Pk #	Retention Time	Area	Area %	Height	Height %
1	20.242	2769414	50.073	32943	57.561
2	25.317	2761387	49.927	24288	42.439
Totals		5530801	100.000	57231	100.000

HPLC profile of 5f (Chiralcel OD-H column, 90% Hexane: 10% 2-propanol, 0.5 mL/min)

Compound **5f** obtained in the L-proline-catalyzed reaction

Shimadzu CLASS-VP V6.14 SP1 *Area % Report* **Page 1 of 1**

Method Name: C:\CLASS-VP\untitled.met
Data Name: E:\Class VP\Data\prasanna\PDP-8 10 per 0.5 mL OD H
User: System
Acquired: 2/22/2013 14:57:17
Printed: 2/23/2013 11:31:06



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	20.275	2918721	50.424	35271	57.913
2	25.300	2869623	49.576	25632	42.087
Totals		5788344	100.000	60903	100.000