Supporting Information

Four-Component α-Bromo-β-Phosphoalkoxylation of Aromatic α,β-Unsaturated Carbonyl Compounds

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1.1 General Information

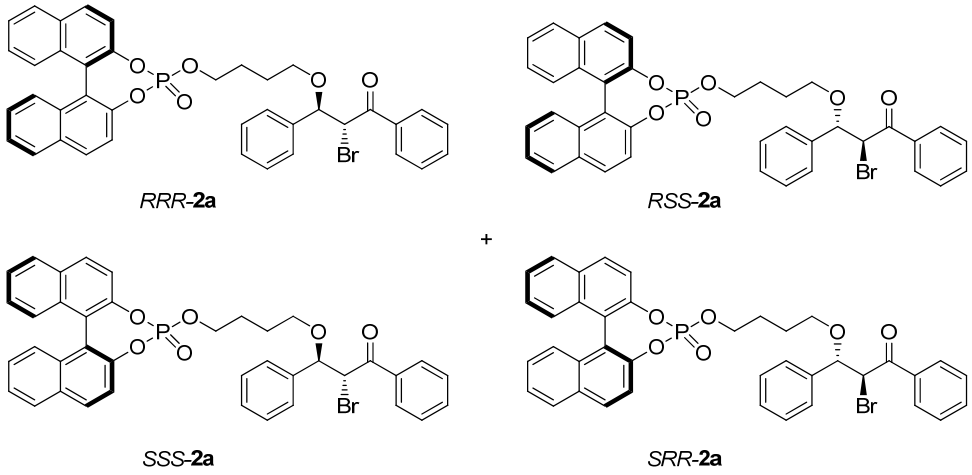
The reactions were conducted normally under an atmosphere of nitrogen using typical vacuum-line techniques unless otherwise noted. The analysis by thin layer chromatography (TLC) was performed using F254 *pre*-coated silica gel plate. Visualization of the spots on TLC was carried out with UV radiation (256 and 365 nm). Column chromatography was performed with silica gel (300-400 mesh). Petroleum ether used (B.P. = 60-90 ^{o}C). HRMS was recorded on *Bruker Apex IV FTMS*. Diastereomeric and enantiomeric ratios were determined by chiral HPLC on *Shimadzu LC-20A* apparatus with Chiralpak AS-H, OD-H, AD-H and IF. ^{1}H-NMR spectra were recorded on *Buruker Avance* 400 and *Varian Mercury* 400. Chemical shifts were reported in ppm downfield from tetramethylsilane ($CDCl_3$, δ = 7.26). The following abbreviations are used, b: broad, d: doublet, dd: doublet of doublet, m: multiplet, p: pentet q: quartet, s: singlet, t: triplet. The ^{13}C-NMR were recorded on a *Varian Mercury* 400 (100 MHz) with complete proton decoupling. Samples were run in $CDCl_3$ and are referenced to $CDCl_3$ as an internal standard at 77.0 ppm. The reagents in liquid state were used after direct distillation or distillation under reduced pressure. The reagents in solid state were used as supplied or after crystallization. Dry solvents were treated following routine method and *via* syringe into the reaction vessels though a rubber septum.

1.2 Phosphoalkoxylation of Enones

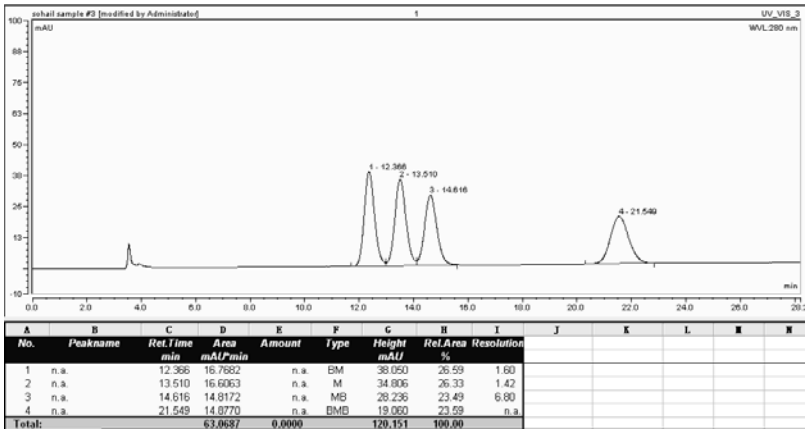
1.2.1 General Procedure

THF was added to the solid mixture of ketone (0.2 mmol) and acid (0.21 mmol, 1.01 Equiv.) and stirred for five minutes. NBS (0.4 mmol, 2 Equiv.) was added slowly (0.5 equiv.) as solution in THF (0.2 mL) at room temperature after each five hours and stirred for 24 h at room temperature under argon. The solvent was then removed under reduce pressure and residue was purified by flash column chromatography (EtoOAc : *n*-hexane; (1:10, V/V, 100 mL), (1:5, V/V 100 mL), (1:3, V/V, 200 mL) to yield the corresponding product.

4-(2-Bromo-3-oxo-1,3-diphenylpropoxy)butyl-1,1'-binaphthyl-2,2'-diyl phosphate (2a).



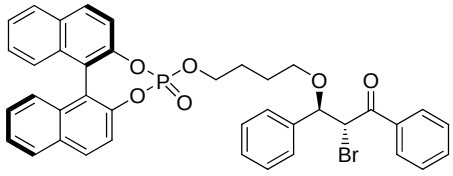
Organic phosphate *R*/*S*-**3a** was used as Brønsted acid, mixture of four isomers (*RRR*-**2a**, *RSS*-**2a**, *SSS*-**2a** and *SRR*-**2a**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.43-1.47 (m, 2H), 1.53-1.60 (m, 2H), 3.31-3.34 (m, 2H), 4.00-4.22 (m, 2H), 4.89 and 4.90 (two d, J = 9.8 Hz, total 1H), 5.11 and 5.12 (both d, J = 9.8 Hz, total 1H), 7.26-7.46 (m, 14H), 7.54-7.56 (m, 2H), 7.91-8.03 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.3, 27.0, 47.5, 69.1, 82.0, 120.2, 120.6, 121.2, 125.8, 126.7, 127.2, 128.1, 128.4, 128.9, 131.0, 131.4, 131.8, 132.2, 133.6, 135.4, 139.1, 146.5, 147.5, 193.2; ^{31}P NMR ($CDCl_3$): δ_P = 2.80. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $[C_{39}H_{33}BrO_6P]^+$ 709.1178; Found 709.1184. Four isomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 75/25, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 12.36 min, t_2 = 13.5 min, t_3 = 14.6 min, t_4 = 21.5 min.



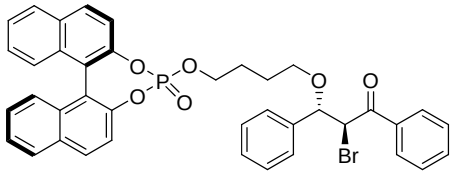
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	12.366	16.7682	n.a.	BM	38.050	26.59	1.60
2	n.a.	13.510	16.6063	n.a.	M	34.806	26.33	1.42
3	n.a.	14.616	14.8172	n.a.	MB	29.236	23.49	6.80
4	n.a.	21.549	14.8770	n.a.	BMB	19.060	23.59	n.a.
Total:			63.0687	0.0000		120.151	100.00	

Fig. S1. HPLC spectra of *RRR*-**2a**, *RSS*-**2a**, *SSS*-**2a** and *SRR*-**2a**

4-(2-Bromo-3-oxo-1,3-diphenylpropoxy)butyl-1,1'-binaphthyl-2,2'-diyl phosphate (2a).

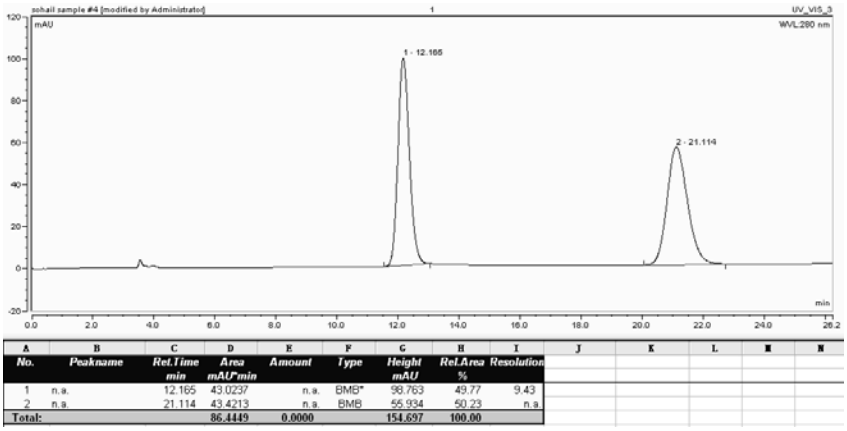


RRR-**2a**



RSS-**2a**

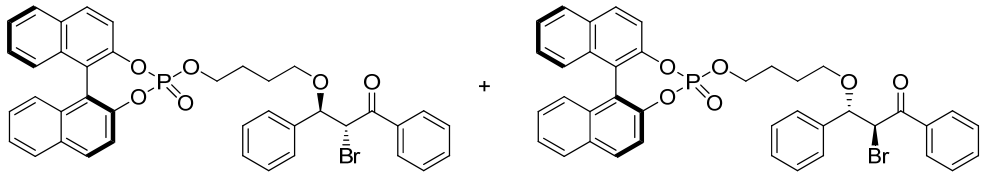
Enantiopure organic phosphate *R*-**3a** was used as Brønsted acid, mixture of two diastereomers (*RRR*-**2a** and *RSS*-**2a**); clear oil; mp 76-77 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.39-1.49 (m, 2H), 1.54-1.62 (m, 2H), 3.27-3.37 (m, 2H), 4.08-4.24 (m, 2H), 4.88 and 4.99 (both d, J = 9.8 Hz, total 1H), 5.11 and 5.12 (both d, J = 9.8 Hz, 1H), 7.24-7.67 (m, 16H), 7.90-8.03 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.2, 26.9, 47.4, 69.1, 69.4, 82.0, 120.2, 120.6, 121.4, 125.8, 126.7, 127.2, 128.1, 128.4, 128.9, 131.0, 131.5, 132.3,133.6, 135.4, 138.2, 146.3, 147.4, 193.3; ^{31}P NMR ($CDCl_3$): δ_P = 2.83. Two diastereomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 75/25, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 12.1 min, t_2 = 21.1 min.



No.	Peakname	Rel.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	12.165	43.0237	n.a.	BMB*	98.763	49.77	9.43
2	n.a.	21.114	43.4213	n.a.	BMB	55.934	50.23	n.a.
Total:			86.4449	0.0000		154.697	100.00	

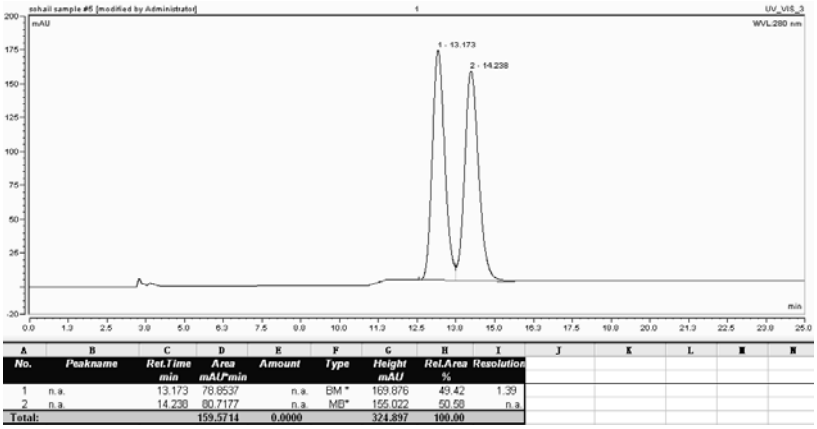
Fig. S2. HPLC spectra of *RRR*-**2a** and *RSS*-**2a**

4-(2-Bromo-3-oxo-1,3-diphenylpropoxy)butyl-1,1'-binaphthyl-2,2'-diyl phosphate (2a).



SSS-**2a** *SRR*-**2a**

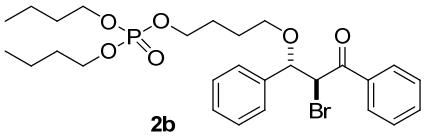
Enantiopure organic phosphate *S*-**3a** was used as Brønsted acid, mixture of two diastereomers (*SSS*-**2a**, *SRR*-**2a**); clear oil; mp 76-77 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.41-1.48 (m, 2H), 1.55-1.62 (m, 2H), 3.27-3.37 (m, 2H), 4.08-4.24 (m, 2H), 4.89 and 4.90 (both d, J = 9.8 Hz, total 1H), 5.11 and 5.12 (both d, J = 9.8 Hz, total 1H), 7.24-7.67 (m, 16H), 7.90-8.03 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.4, 27.0, 47.5, 69.1, 69.4, 82.0, 120.2, 120.6, 121.2, 121.4, 125.7, 126.7, 127.0, 127.2, 128.1, 128.3, 128.7, 128.8, 138.2, 138.2, 146.2, 146.3, 147.3, 147.4, 125.8, 126.7, 127.2, 128.1, 128.4, 128.9, 131.0, 131.5, 132.3,133.6, 135.4, 138.2, 146.3, 147.4, 193.4; ^{31}P NMR ($CDCl_3$): δ_P = 2.76. Two diastereomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 75/25, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 13.1 min, t_2 = 14.2 min.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	13.173	78.8537	n.a.	BM *	169.876	49.42	1.39
2	n.a.	14.238	80.7177	n.a.	MB*	155.022	50.58	n.a.
Total:			159.5714	0.0000		324.897	100.00	

Fig. S3. HPLC spectra of *SSS*-**2a**, *SRR*-**2a**

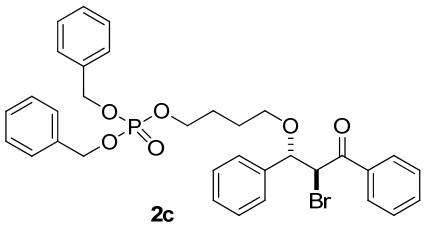
4-(2-Bromo-3-oxo-1,3-diphenylpropoxy)butyl-1,1'-dibutyl phosphate (2b).



2b

Organic phosphate **3b** was used as Brønsted acid, one diastereomer, clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.91 (t, J = 7.3, 6H), 1.34-1.40 (m, 4H), 1.44 1.47 (m, 4H), 1.49-1.63 (m, 4H), 3.31-3.37 (m, 2H), 3.85-3.90 (m, 2H), 3.94-3.99 (m, 4H), 4.90 (d, J = 9.9 Hz, 1H), 5.10 (d, J = 9.9 Hz, 1H), 7.36-7.52 (m, 7H), 7.61 (t, J = 7.3, 1H); 8.03 (d, J = 7.4, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 13.5, 18.6, 25.6, 26.8, 32.2, 32.3, 47.5, 67.0, 67.2, 67.3, 69.2, 81.9, 128.1, 128.3, 128.7, 133.6, 135.5, 138.2, 193.2. ^{31}P NMR ($CDCl_3$): δ_P = –3.03.

4-(2-Bromo-3-oxo-1,3-diphenylpropoxy)butyl-1,1'-dibenzyl phosphate (2c).

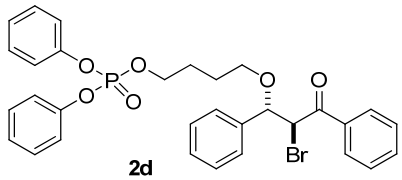


2c

Organic phosphate **3c** was used as Brønsted acid, one diastereomer, clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.36-1.45 (m, 4H), 3.26-3.30 (m, 2H), 3.81-3.86 (m, 2H), 4.88 (d, J = 9.8 Hz, 1H), 4.95 and 4.97 (both s, total 4H), 5.09 (d, J = 9.8 Hz, 1H), 7.30-7.49 (m, 17H), 7.56-

7.60 (m, 1H), 8.03 (d, J = 8.1, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.4, 26.7, 47.5, 69.0, 69.1, 69.2, 81.9, 127.8, 128.1, 128.3, 128.4, 128.5, 128.7, 133.6, 135.4, 135.8, 138.2, 193.2. ^{31}P NMR ($CDCl_3$): δ_P = –0.92.

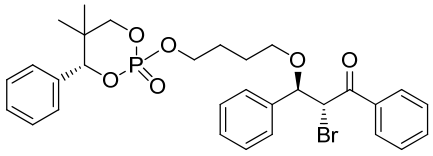
4-(2-Bromo-3-oxo-1,3-diphenylpropoxy)butyl-1,1'-diphenyl phosphate (2d).



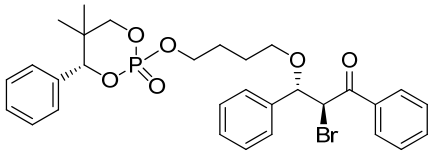
2d

Organic phosphate **3d** was used as Brønsted acid, one diastereomer, clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.41-1.44 (m, 2H), 1.50-1.57 (m, 2H), 3.28-3.33 (m, 2H), 4.07-4.12 (m, 2H), 4.89 (d, J = 9.8 Hz, 1H), 5.10 (d, J = 9.8 Hz, 1H), 7.16 (d, J = 7.7, 5H), 7.29 (t, J = 7.7, 4H), 7.37-7.49 (m, 8H), 7.58 (t, J = 7.5, 1H); 8.02 (d, J = 8.1, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.4, 26.8, 47.5, 68.9, 69.1, 82.03, 120.0, 125.2, 128.1, 128.3, 128.7, 128.8, 129.7, 133.7, 135.4, 138.2, 150.5, 150.6, 193.2; ^{31}P NMR ($CDCl_3$): δ_P = –11.96.

4-(2-Bromo-3-oxo-1,3-diphenylpropoxy)butyl-1,1'-2,2-dimethyl-3-phenylpropyl phosphate (2e).



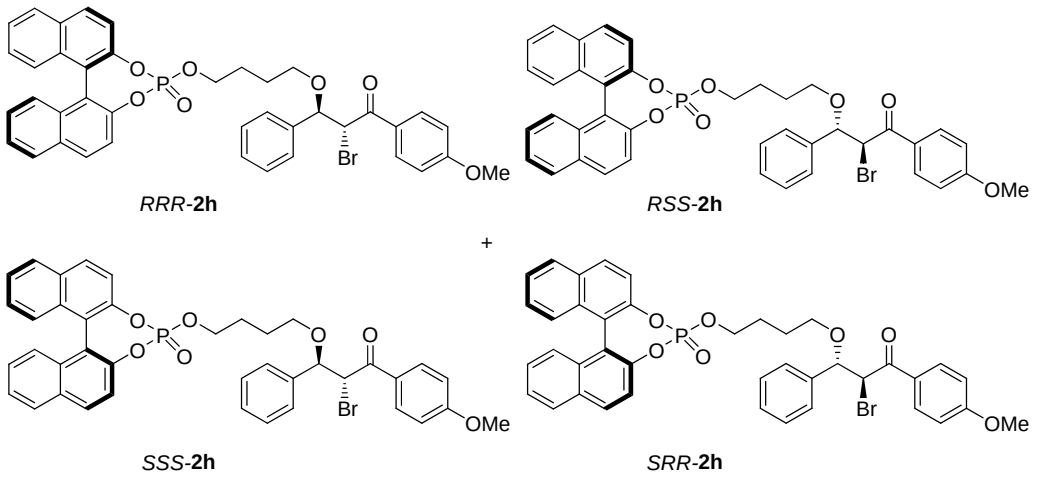
RRR-**2e**



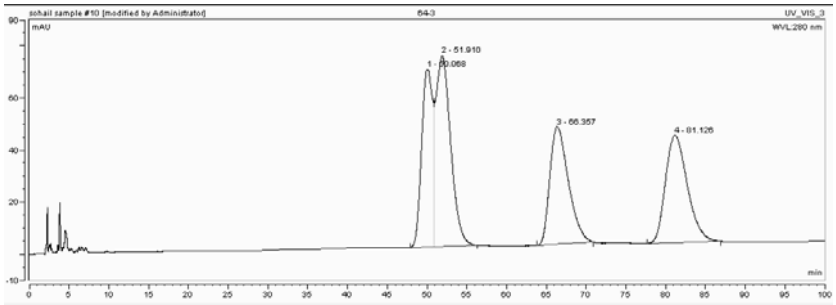
RSS-**2e**

Enantiopure organic phosphate *R*-**3e** was used as Brønsted acid, mixture of two diastereomers (*RRR*-**2e**, *RSS*-**2e**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.75 (s, 3H), 1.02 (s, 3H), 1.46-1.49 (m, 2H), 1.55-1.58 (m, 2H), 3.33-3.36 (m, 2H), 3.80-4.00 (m, 3H) 4.13 (d, J = 10.9, 1H), 4.90 and 4.91 (both d, J = 9.8, total 1H), 5.08-5.12 (m, 2H), 7.25-7.52 (m, 12H), 7.57-7.62 (m, 1H), 8.02 (d, J = 7.5, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 17.0, 20.9, 25.6, 26.1, 36.0, 47.5, 47.5, 67.1, 69.2, 78.5, 82.0, 87.8, 87.9, 127.3, 127.8, 128.1, 128.3, 128.5, 128.7, 128.8, 133.6, 135.5, 138.1, 193.3; ^{31}P NMR ($CDCl_3$): δ_P = –7.30.

4-(2-Bromo-3-(4-methoxyphenyl)-3-oxo-1-phenylpropoxy)butyl-1,1'-binaphthyl-2,2'-diyl phosphate (2h).



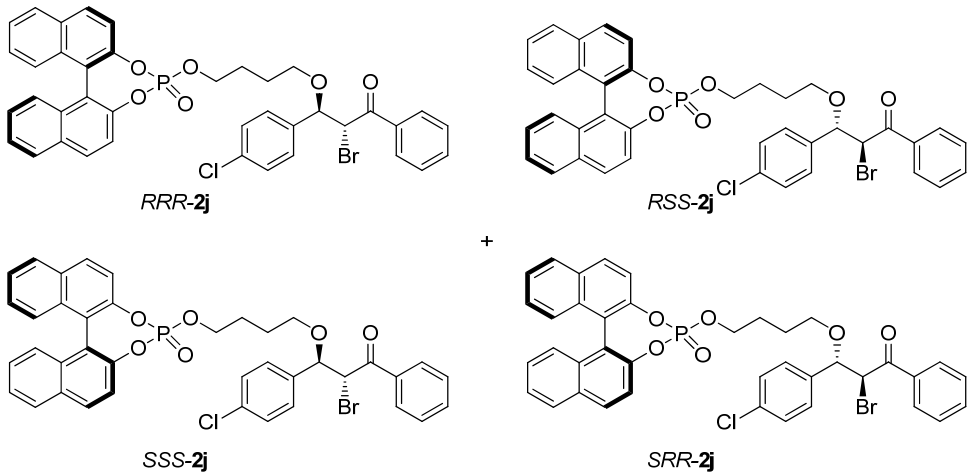
Organic phosphate *R*/*S*-**3a** was used as Brønsted acid, mixture of four isomers (*RRR*-**2h**, *RSS*-**2h**, *SSS*-**2h** and *SRR*-**2h**); clear oil; ^{1}H NMR (400MHz, $CDCl_3$): δ_H = 1.42-1.47 (m, 2H), 1.54-1.61 (m, 2H), 3.27-3.37 (m, 2H), 3.81-3.82 (both s, total 3H), 4.08-4.25 (m, 2H), 4.89 (both d, J = 9.8 Hz, total 1H), 5.09 and 5.10 (both d, J = 9.8 Hz, total 1H), 6.90-6.94 (m, 2H) 7.24-7.49 (m, 12H), 7.55 (dd, 1.7, 8.8 Hz, 1H), 7.90-8.03 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.2, 27.0, 47.4, 55.2, 69.1, 69.5, 82.1, 114.0, 120.2, 120.6, 120.7, 121.2, 121.4, 125.7, 126.7, 127.0, 127.1,128.1, 128.2, 128.3, 128.4, 128.5, 128.7,128.8, 130.8, 131.0, 131.1, 131.4, 131.6, 131.8, 132.2, 138.4, 146.3, 147.4,164.1, 192.0; ^{31}P NMR ($CDCl_3$): δ_P = 2.85. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{35}BrO_7P$ 739.1283; Found 739.1288. Four isomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/212, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 50.0 min, t_2 = 51.9 min, t_3 = 66.3 min, t_4 = 81.1 min.



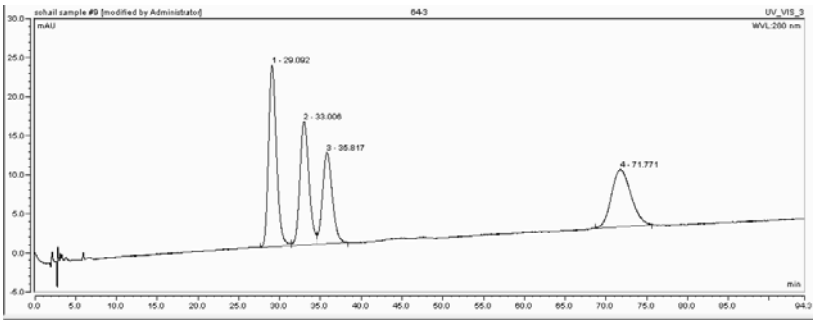
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	50.068	109.5214	n.a.	BM	68.390	21.03	n.a.
2	n.a.	51.910	157.8464	n.a.	MB	73.508	30.32	n.a.
3	n.a.	66.357	121.5047	n.a.	BMB	45.045	23.34	3.18
4	n.a.	81.126	131.8144	n.a.	BMB	41.212	25.32	n.a.
Total:			520.6869	0.0000		228.154	100.00	

Fig. S4. HPLC spectra of *RRR*-**2h**, *RSS*-**2h**, *SSS*-**2h** and *SRR*-**2h**

4-(2-Bromo1-(4-chlorophenyl)-3-oxo-3-phenylpropoxy)butyl-1,1'-binaphthyl-2,2'-diyl phosphate (2j).



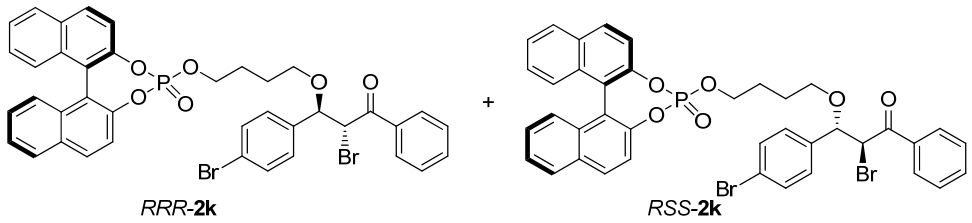
Organic phosphate *R*/*S*-**3a** was used as Brønsted acid, mixture of four isomers (*RRR*-**2j**, *RSS*-**2j**, *SSS*-**2j** and *SRR*-**2j**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.41-1.50 (m, 2H), 1.52-1.62 (m, 2H), 3.25-3.37 (m, 2H), 4.08-4.25 (m, 2H), 4.87 and 4.88 (both d, J = 9.8 Hz, total 1H), 5.05 and 5.06 (both d, J = 9.8 Hz, total 1H), 7.24-7.58 (m, 16H), 7.90-8.03 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.3, 27.01, 47.2, 69.3, 69.4, 81.3, 125.8, 126.7, 127.0, 127.1, 128.4, 128.5, 128.6, 128.7, 128.8, 129.4, 131.0, 131.4,131.5, 131.9,132.2, 133.7, 134.5, 135.2, 136.8,146.3, 147.4, 193.0; ^{31}P NMR ($CDCl_3$): δ_P = 3.03. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{32}BrClO_6P$ 743.0788; Found 743.0791. Four isomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/12, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 29.0 min, t_2 = 33.0 min, t_3 = 35.8 min, t_4 = 71.7 min.



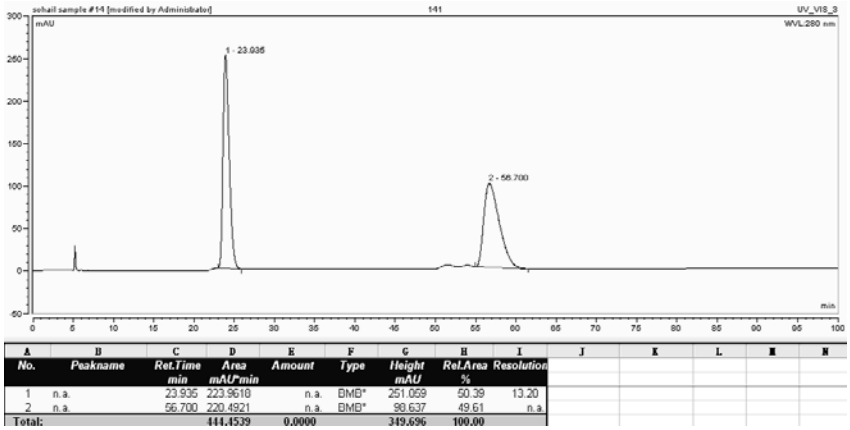
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	29.092	26.2735	n.a.	BM	23.275	31.62	2.09
2	n.a.	33.006	20.3951	n.a.	M	15.850	24.55	1.35
3	n.a.	35.817	16.3444	n.a.	MB*	11.716	19.67	11.02
4	n.a.	71.771	20.0686	n.a.	BMB	7.326	24.16	n.a.
Total:			83.0816	0.0000		58.167	100.00	

Fig. S5. HPLC spectra of *RRR*-**2j**, *RSS*-**2j**, *SSS*-**2j** and *SRR*-**2j**

4-(2-Bromo-1-(4-bromophenyl)-3-oxo-3-phenylpropoxy)butyl-1,1'-binaphthyl-2,2'-diyl phosphate (2k).



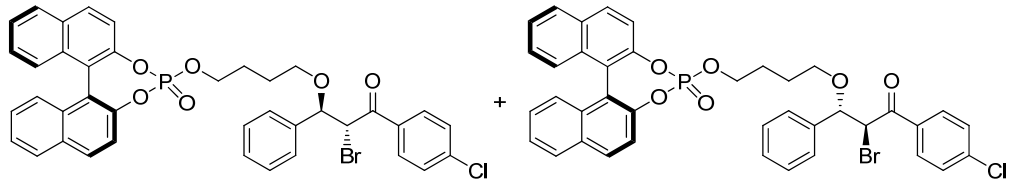
Enantiopure organic phosphate *R*-**3a** was used as Brønsted acid, mixture of two diastereomers (*SSS*-**2k** and *SRR*-**2k**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.45-1.51 (m, 2H), 1.55-1.63 (m, 2H), 3.26-3.39 (m, 2H), 4.11-4.27 (m, 2H), 4.87 and 4.88 (both d, J = 9.8 Hz, total 1H), 5.06 and 5.08 (both d, J = 9.8 Hz, total 1H), 7.25-7.59 (m, 15H), 7.92-7.95 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.3, 27.0, 47.2, 69.4, 81.4, 120.1, 120.2, 120.6, 121.2, 121.4, 122.7, 125.8, 126.7, 126.8, 127.0, 127.2, 128.4, 128.5, 128.7, 128.8, 129.8, 131.0, 131.4, 131.5, 131.6, 131.8, 133.7, 135.2, 137.3, 192.9; ^{31}P NMR ($CDCl_3$): δ = 2.78. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{32}BrO_6P$ 787.0283; Found 787.0279. Two diastereomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/212, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 23.9 min, t_2 = 56.7 min.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	23.935	223.9618	n.a.	BMB*	251.059	50.39	13.20
2	n.a.	56.700	220.4921	n.a.	BMB*	98.637	49.61	n.a.
Total:			444.4539	0.0000		349.696	100.00	

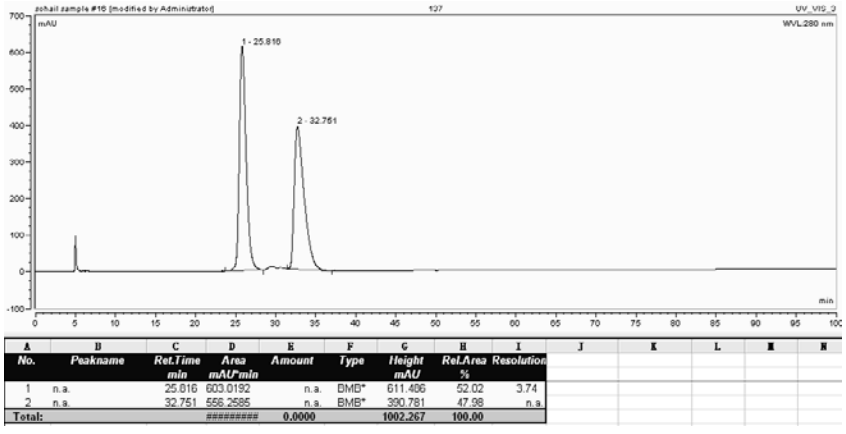
Fig. S6. HPLC spectra of *SSS*-**2k** and *SRR*-**2k**

4-(2-Bromo-3-(4-chlorophenyl)-3-oxo-1-phenylpropoxy)butyl-1,1'-binaphthyl-2,2'-diyl phosphate (2l).



SSS-**2l** *SRR*-**2l**

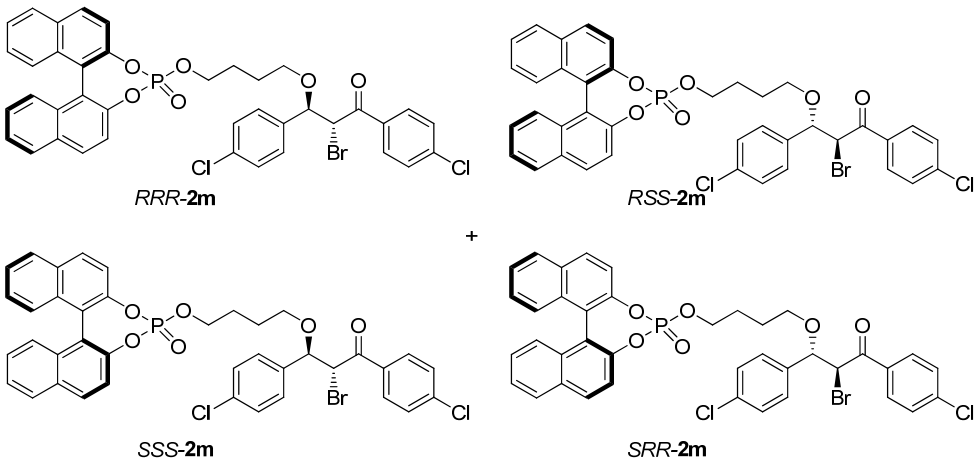
Enantiopure organic phosphate *S*-**3a** was used as Brønsted acid, mixture of two diastereomers (*SSS*-**2l** and *SRR*-**2l**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.42-1.50 (m, 2H), 1.55-1.63 (m, 2H), 3.27-3.37 (m, 2H), 4.08-4.26 (m, 2H), 4.87 and 4.88 (both d, J=9.8 Hz, total 1H), 5.04 and 5.06 (both d, J = 9.8 Hz, total 1H), 7.23-7.48 (m, 14H), 7.54-7.57 (m, 1H), 7.90-8.02 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.3, 27.1, 47.3, 69.1, 69.5, 81.9, 120.2, 120.6, 121.2, 125.8, 126.7, 127.0, 127.2, 128.1, 128.6, 128.9, 129.2, 130.2, 131.0, 131.4, 131.6, 131.8, 132.3, 133.7, 138.0, 140.2, 146.4, 147.4, 192.0; ^{31}P NMR ($CDCl_3$): δ_P = 2.79. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{32}BrClO_6P$ 743.0788; Found 743.0791. Two diastereomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/212, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 25.8 min, t_2 = 32.7 min.



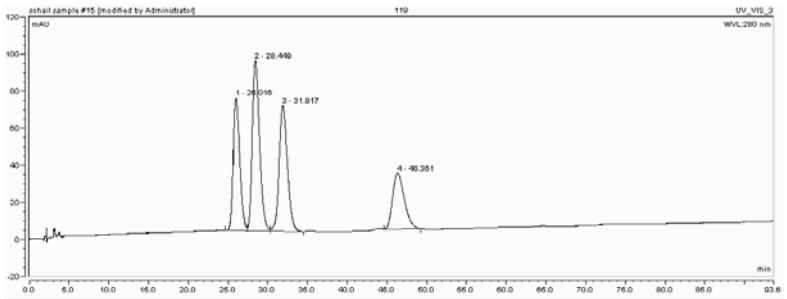
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	25.816	603.0192	n.a.	BMB*	611.486	52.02	3.74
2	n.a.	32.751	556.2585	n.a.	BMB*	390.781	47.98	n.a.
Total:			########	0.0000		1002.267	100.00	

Fig. S7. HPLC spectra of *SSS*-**2l** and *SRR*-**2l**

4-(2-Bromo-1,3-bis(4-chlorophenyl)-3-oxopropoxy)butyl-1,1'-binaphthyl 2,2'diyl phosphate (2m).



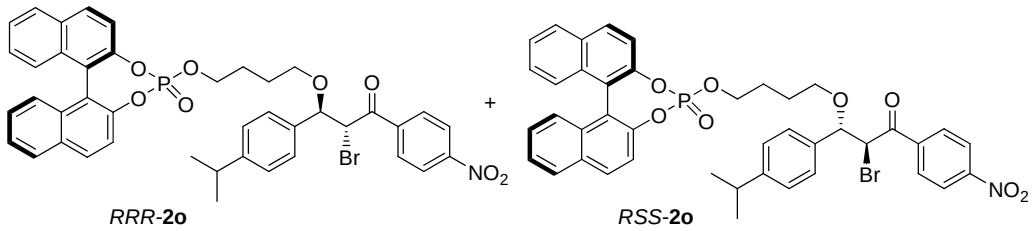
Organic phosphate *R*/*S*-**3a** was used as Brønsted acid, mixture of four isomers (*RRR*-**2m**, *RSS*-**2m**, *SSS*-**2m** and *SRR*-**2m**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.34-1.43 (m, 2H), 1.47-1.55 (m, 2H), 3.18-3.28 (m, 2H), 4.03-4.16 (m, 2H), 4.77 and 4.78 (both d, J = 9.8 Hz, total 1H), 4.90 and 4.92 (both d, J=9.8 Hz, total 1H), 7.16-7.49 (m, 14H) 7.84-7.95 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.4, 27.1, 47.0, 69.3, 69.4, 81.2, 120.1, 120.6, 121.2, 121.3, 121.4, 125.8, 126.8, 127.0, 127.2, 128.4, 128.5,128.6, 129.1, 129.2, 129.4, 130.1, 131.0, 131.4, 131.6, 131.8, 132.2, 133.5, 134.7, 136.6, 140.4, 146.3, 147.4, 191.7; ^{31}P NMR ($CDCl_3$) δ_P = 2.86. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{31}BrCl_2O_6P$ 777.0398; Found 777.0391. Four isomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/212, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 26.0 min, t_2 = 28.4 min, t_3 = 31.9 min, t_4 = 46.3 min.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	26.016	68.0550	n.a.	BM *	71.488	22.86	1.54
2	n.a.	28.449	96.9015	n.a.	M *	91.760	32.51	1.99
3	n.a.	31.917	81.7958	n.a.	MB*	67.904	27.47	6.37
4	n.a.	46.351	51.0622	n.a.	BMB	30.053	17.15	n.a.
Total:			297.7146	0.0000		261.206	100.00	

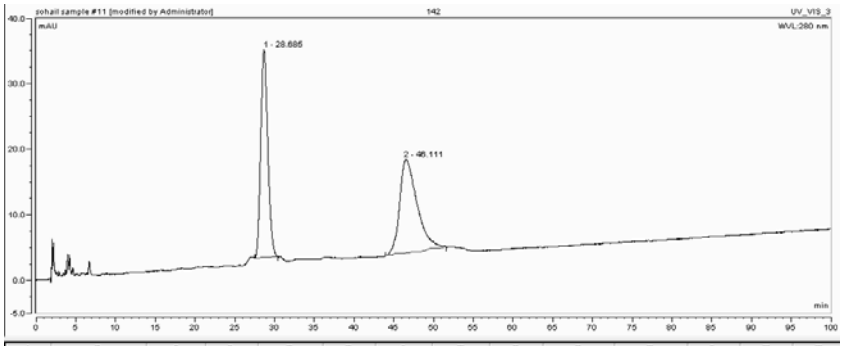
Fig. S8. HPLC spectra of *RRR*-**2m**, *RSS*-**2m**, *SSS*-**2m** and *SRR*-**2m**

4-(2-bromo-1-(4-isopropylphenyl)-3-(4-nitrophenyl)-3-oxopropoxy)butyl-*1,1'-binaphthyl-2,2'-diyl phosphate (2o).*



RRR-**2o** *RSS*-**2o**

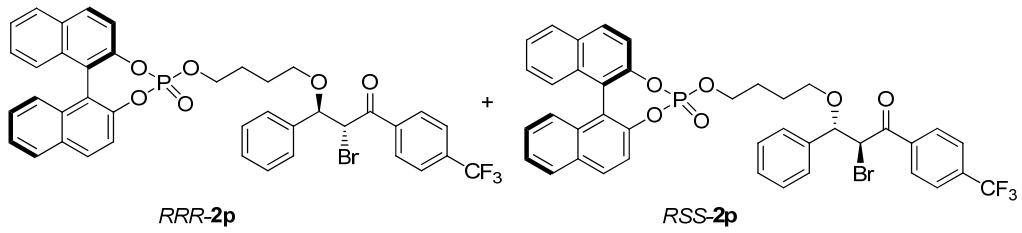
Enantiopure organic phosphate *R*-**3a** was used as Brønsted acid, mixture of two diastereomers (*RRR*-**2o** and *RSS*-**2o**); clear oil; ^{1}H NMR (400MHz, $CDCl_3$) δ = 1.26-1.28 (m, 6H), 1.44-1.52 (m, 2H), 1.57-1.64 (m, 2H), 2.90-2.97 (m, 1H), 3.31-3.36 (m, 2H), 4.11-4.28 (m, 2H), 4.86 (d, J=9.8 Hz, 1H), 5.05 and 5.08 (both d, J = 9.8 Hz, total 1H), 7.25-7.40 (m, 10H), 7.46-7.50 (m, 2H) , 7.53-7.57 (m, 1H) , 7.92-8.04 (m, 4H) , 8.12-8.14 (m, 2H) , 8.21-8.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.9, 25.3, 27.1, 33.9, 47.9, 69.2, 69.4, 81.8, 120.1, 120.5, 121.3, 123.8, 123.9, 125.8, 126.5, 126.8, 127.1,127.9, 128.4, 128.5, 131.0, 131.4, 132.5, 134.8, 140.0, 140.1, 146.2, 146.3, 147.2, 147.4, 149.7, 150.4, 192.0; ^{31}P NMR ($CDCl_3$): δ = 2.86. . HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{42}H_{38}BrNO_8P$ 796.1498; Found 796.1496. Two diastereomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/212, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 28.6 min, t_2 = 46.1 min.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	28.686	32.7474	n.a.	BMB	31.769	51.18	8.27
2	n.a.	46.111	31.2345	n.a.	BMB*	13.556	48.82	n.a.
Total:			63.9819	0.0000		45.325	100.00	

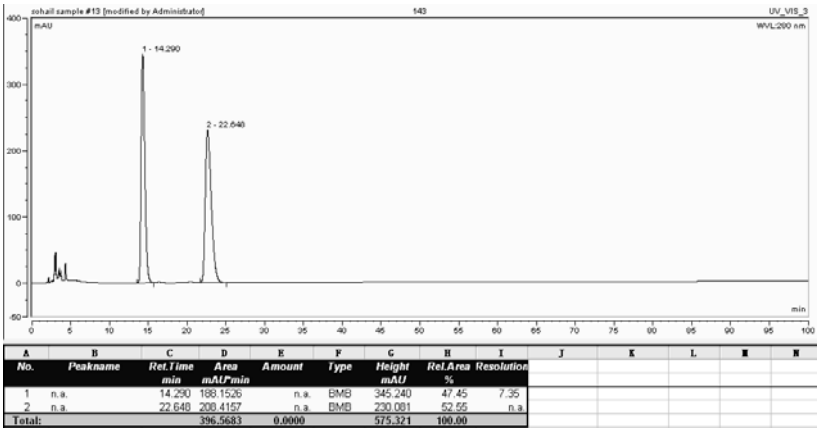
Fig. S9. HPLC spectra of *RRR*-**2o** and *RSS*-**2o**

4-(2-bromo-3-oxo-1-phenyl-3-(4-(trifluoromethyl)phenyl)propoxy)butyl-*1,1'-binaphthyl-2,2'-diyl phosphate (2p).*



RRR-**2p** *RSS*-**2p**

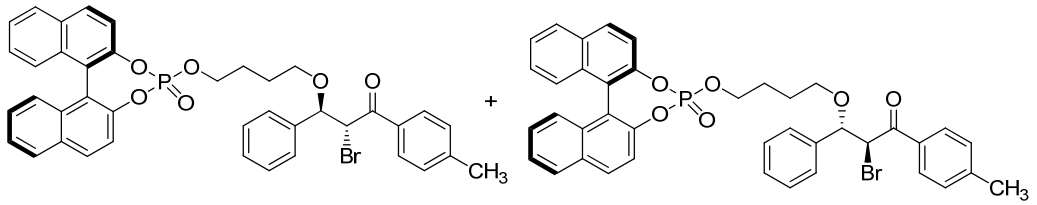
Enantiopure organic phosphate *R*-**3a** was used as Brønsted acid, mixture of two diastereomers (*RRR*-**2p** and *RSS*-**2p**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46-1.53 (m, 2H), 1.57-1.65 (m, 2H), 3.30-3.42 (m, 2H), 4.10-4.28 (m, 2H), 4.92 (two d, J = 9.8 Hz, total 1H), 5.10 and 5.11 (both d, J = 9.8 Hz, total 1H), 7.25-7.60 (m, 14H), 7.74-7.83 (m, 1H), 7.92-8.04 (m, 4H) , 8.20 (d, J = 7.8 Hz, 1H), 8.29 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.3, 26.9, 47.6, 69.2, 69.4, 82.0, 120.1, 120.6, 125.5, 125.8, 126.7, 126.8, 127.0, 127.1, 128.1, 128.4, 129.5, 129.5, 129.9, 131.0, 131.5,131.6, 131.8, 132.3, 135.9, 137.8,146.3, 147.4, 191.9; ^{31}P NMR ($CDCl_3$): δ = 2.82. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{32}BrF_3O_6P$ 777.1052; Found 777.1056. Two diastereomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/212, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 14.2 min, t_2 = 22.6 min.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	14.290	188.1526	n.a.	BMB	345.240	47.45	7.35
2	n.a.	22.648	208.4157	n.a.	BMB	230.081	52.55	n.a.
Total:			396.5683	0.0000		575.321	100.00	

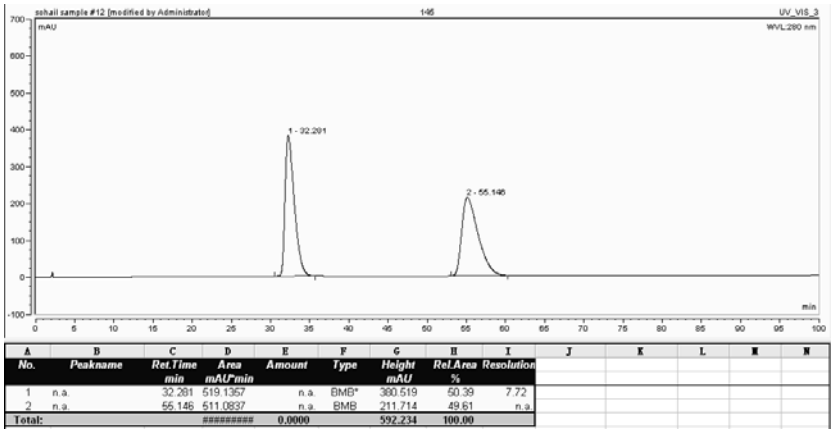
Fig. S10. HPLC spectra of *RRR*-**2p** and *RSS*-**2p**

4-(2-bromo-3-oxo-1-phenyl-3-(4-(methyl)phenyl)propoxy)butyl-*1,1'-binaphthyl-2,2'-diyl phosphate (2q)*.



RRR-**2q** *RSS*-**2q**

Enantiopure organic phosphate *R*-**3a** was used as Brønsted acid, mixture of two diastereomers (*RRR*-**2q** and *RSS*-**2q**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42-1.51 (m, 2H), 1.54-1.65 (m, 2H), 2.38 and 2.39 (both s, total 3H) 3.28-3.39 (m, 2H), 4.10-4.27 (m, 2H), 4.92 and 4.93 (both d, J = 9.8 Hz, total 1H), 5.13 and 5.14 (both d, J = 9.8 Hz, total 1H), 7.24-7.59 (m, 14H), 7.92-7.96 (m, 1H), 7.99-8.04 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.3, 25.4, 26.9, 47.5, 69.1, 69.5, 82.0, 120.1,120.2, 120.6, 120.7, 121.2, 121.4, 125.8, 126.7,126.8, 127.0, 127.2, 128.1, 128.3, 128.4, 128.5, 128.7, 128.9, 129.5, 131.1, 131.4, 131.6, 131.8, 132.2, 132.3, 132.9, 138.3, 144.7, 146.2, 147.3, 192.8; ^{31}P NMR ($CDCl_3$): δ = 2.77. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{35}BrO_6P$ 723.1334; Found 796.1330. Two diastereomers were recognized by HPLC on *Chiralpak* IF (*n*-hexane/*iso*-propanol = 88/212, V/V, 1.0 mL min^{-1}, 254 nm), t_1 = 32.2 min, t_2 = 55.1 min.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	32.281	519.1357	n.a.	BMB*	380.519	50.39	7.72
2	n.a.	55.146	511.0837	n.a.	BMB	211.714	49.61	n.a.
Total:			########	0.0000		592.234	100.00	

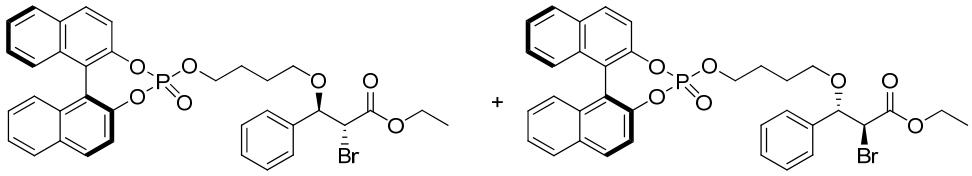
Fig. S11. HPLC spectra of *RRR*-**2q** and *RSS*-**2q**

1.3 Phosphoalkoxylation of Esters

3.2.1 General Procedure

Cyclic ether was added to the solid mixture of unsaturated carbonyl esters (0.2 mmol) and an acid **3a** (0.21 mmol, 1.01 Equiv.) and stirred for five minutes. NBS (0.4 mmol, 2 Equiv.) was added slowly (0.5 equiv.) as solution in cyclic ether (0.2 mL) at room temperature after each five hours and stirred at room temperature for 48 h. The solvent was then removed under reduce pressure and residue was purified by flash column chromatography (EtoOAc : *n*-hexane; (1:10, V/V, 100 mL), (1:5, V/V 100 mL), (1:3, V/V, 200 mL) to yield the corresponding product.

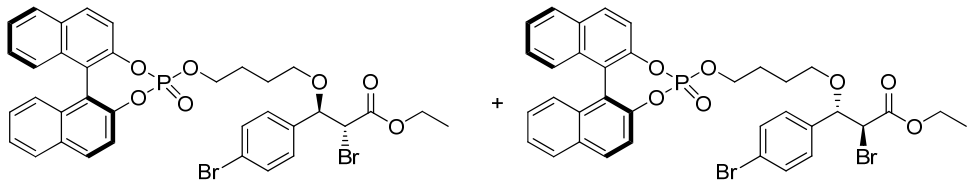
Ethyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)butoxy)-2-bromo-3-phenylpropanoate (5a)



SSS-**5a** + *SRR*-**5a**

Enantiopure organic phosphate *S*-**3a** was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5a** and *SRR*-**5a**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.18 (t, J = 7.8 Hz, 3H), 1.44-1.51 (m, 2H), 1.53-1.69 (m, 2H), 3.23-3.27 (m, 2H), 4.09-4.24 (m, 5H), 4.52 and 4.53 (both d, J = 10 Hz, total 1H), 7.17-7.42 (m, 12H), 7.51 (d, J = 8.8 1H) 7.85-7.96 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 18.9, 25.5, 27.1, 47.4, 62.0, 69.0, 69.5, 82.7, 120.1, 120.2, 120.6, 121.2, 121.4, 125.7, 126.7, 126.8, 127.0, 127.2, 128.0, 128.3, 128.4, 128.5, 128.8, 131.0, 131.1, 131.4, 131.6, 131.8, 132.2, 132.3, 137.3, 146.3, 147.4, 168.9; ^{31}P NMR ($CDCl_3$): δ_P = 2.79. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{33}BrO_7P$ 677.1127; Found 677.1129.

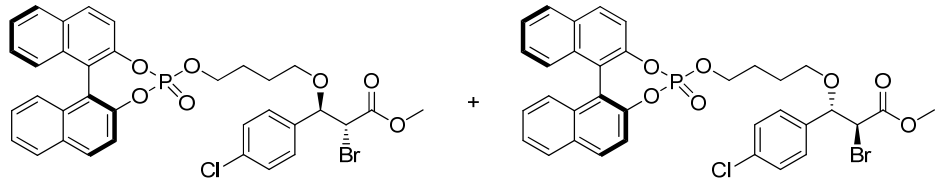
Ethyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)butoxy)-2-bromo-3-(4 bromophenyl)propanoate (5b).



SSS-**5b** *SRR*-**5b**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5b** and *SRR*-**5b**); clear oil; ^{1}HNMR (400 MHz, $CDCl_3$): δ_H = 1.26 (t, J = 7.8 3H), 1.53-1.58 (m, 2H), 1.68-1.76 (m, 2H), 3.29-3.33 (m, 2H), 4.12 (d, J = 9.9 1H), 4.20-4.30 (m, 4H), 4.56 and 4.57 (both d, J = 9.9 Hz, total 1H), 7.19-7.50 (m, 12H), 7.58 (d, J = 8.8 1H) 7.94-8.05 (m, 4H); ^{13}CNMR (125 MHz, $CDCl_3$): δ_C 10.9, 25.5, 27.0, 47.2, 62.1, 69.2, 82.0, 120.1, 120.6, 121.3, 121.4, 122.9, 125.8, 126.7, 126.8, 127.0, 127.2, 128.4, 128.5, 129.6, 131.0, 131.4, 131.6, 132.2, 132.3, 136.4, 146.2, 146.3, 147.3, 147.4, 168.6; ^{31}P NMR ($CDCl_3$): δ_P = 2.81. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{32}Br_2O_7P$ 755.0232; Found 755.0251.

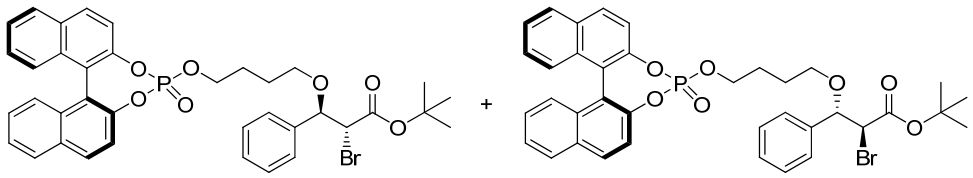
Methyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)-2-bromo-3-(4-chlorophenyl)propanoate (5c).



SSS-**5c** *SRR*-**5c**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5c** and *SRR*-**5c**); ^{1}HNMR (400 MHz, $CDCl_3$): δ_H = 1.51-1.58 (m, 2H), 1.69-1.76 (m, 2H), 3.29-3.33 (m, 2H), 3.76 (s, 3H), 4.14 (d, J = 9.8 Hz, 1H), 4.22-4.33 (m, 2H), 4.58 and 4.59 (both d, J = 9.8 Hz, total 1H), 7.24-7.39 (m, 8H), 7.43-7.50 (m, 3H), 7.58 (d, J = 8.8 Hz, 1H), 7.93-7.99 (m, 2H), 8.01-8.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.5, 27.1, 46.8, 53.0, 69.2, 69.4, 82.1, 120.2, 120.6, 121.2, 121.4, 125.8, 126.7, 126.8, 127.0, 127.2, 128.7, 129.3, 131.1, 131.5, 131.9, 132.3, 134.8, 135.8, 146.4, 147.4, 169.1; ^{31}P NMR ($CDCl_3$): δ = 2.82. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{30}BrClO_7P$ 697.0581; Found 697.0605.

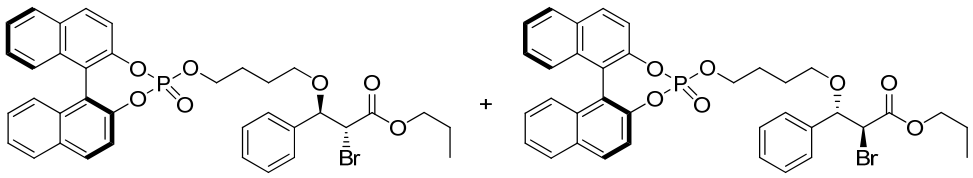
Tert-butyl 3-(4-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)butoxy)-2-bromo-3-phenylpropanoate (5d)



SSS-**5d** *SRR*-**5d**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5d** and *SRR*-**5d**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.25 (s, 9H), 1.54-1.56 (m, 2H), 1.69-1.73 (m, 2H), 3.31-3.32 (m, 2H), 4.13-4.15 (m, 1H), 4.22-4.35 (m, 2H), 4.59 (d, J = 10 Hz, 1H), 7.24-7.58 (m, 14H), 7.93-8.03 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 21.6, 25.5, 27.3, 48.0, 65.7, 69.1, 69.9, 82.8, 120.1, 120.2, 120.6, 121.2, 121.4, 125.7, 126.7, 126.8, 127.0, 127.2, 128.0, 128.3, 128.4, 128.5, 128.8, 130.8, 131.1, 131.6, 131.8, 132.2, 132.3, 137.7, 146.4, 147.7, 168.4; ^{31}P NMR ($CDCl_3$): δ_P = 2.89. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{35}BrO_7P$ 689.1304; Found 689.1299.

Propyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)butoxy)-2-bromo-3-phenylpropanoate (5e).

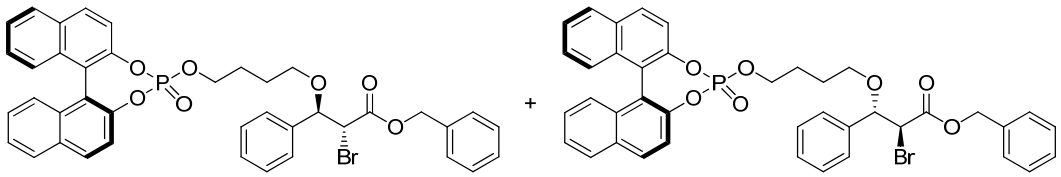


SSS-**5e** *SRR*-**5e**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5e** and *SRR*-**5e**); clear oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.90-0.99 (m, 2H), 1.55-1.56 (m, 2H), 1.63-1.74 (m, 2H), 3.30-3.34 (m, 2H), 4.13-4.21 (m, 3H), 4.25-4.32 (m, 2H), 4.59 and 4.60 (both d, J = 9.9 Hz, total 1H),), 5.13-5.14 (m, 2H), 7.25-7.59 (m, 14H), 7.93-8.04 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 10.2, 19.3, 25.7, 27.1, 47.7, 65.5, 67.5, 69.2, 82.8, 120.1, 120.6, 121.2, 121.4, 125.7, 126.7, 127.0, 127.2, 128.0, 128.3, 128.4, 128.5, 128.8, 130.8, 131.1, 131.4, 131.6, 131.8, 132.2, 132.3, 132.4, 137.7, 146.5, 147.5, 169.1; ^{31}P NMR

($CDCl_3$): δ_P = 2.84. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{35}BrO_7P$ 689.1304; Found 689.1299.

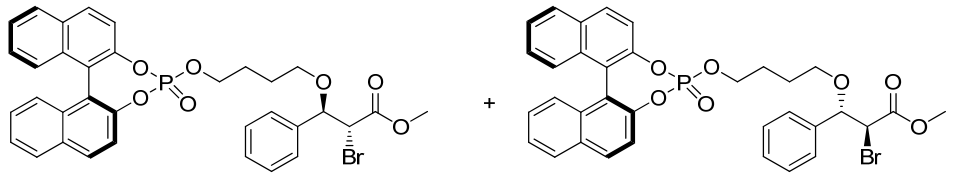
Benzyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)butoxy)-2-bromo-3-phenylpropanoate (5f)



SSS-**5f** *SRR*-**5f**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5f** and *SRR*-**5f**); clear oil; ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.34-1.41 (m, 2H), 1.54-1.60 (m, 2H), 3.15-3.20 (m, 2H), 4.10-4.17 (m, 3H), 4.52 and 4.53 (both d, J = 10 Hz, total 1H), 5.13-5.14 (m, 2H), 7.16-7.40 (m, 17H), 7.50 (d, J = 8.8 1H) 7.83-7.95 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 24.4, 26.0, 46.1, 66.5, 67.9, 68.5, 81.7, 119.3, 119.6, 120.8, 124.7, 125.7, 125.9, 126.1, 126.9, 127.2, 127.3, 127.4, 127.7, 127.8, 129.8, 130.0, 130.1, 130.4, 130.5, 130.8, 131.2, 131.4, 134.2, 136.2, 145.4, 146.4, 167.6; ^{31}P NMR ($CDCl_3$): δ_P = 2.84. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{35}BrO_7P$ 739.1283; Found 739.1302.

Methyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)butoxy)-2-bromo-3-phenylpropanoate (5g).

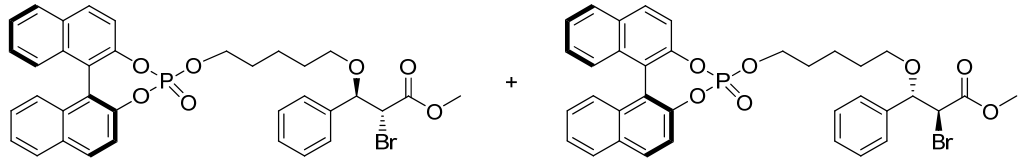


SSS-**5g** *SRR*-**5g**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5g** and *SRR*-**5g**); clear oil; ^1H NMR (400 MHz, $CDCl_3$) δ_H = 1.51-1.58 (m, 2H), 1.70-1.77 (m, 2H), 3.31-3.33 (m, 2H), 3.76-3.77 (both s, total 3H), 4.18-4.30 (m, 3H), 4.59-4.60 (both d, J = 10 Hz, total 1H), 4.59 (d, J = 10 Hz, 1H), 7.25-7.39 (m, 9H), 7.42-7.49 (m, 4H), 7.59 (d, J = 8.8 Hz, 1H), 7.93-8.04 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.5, 27.0, 47.1, 52.8, 69.0,

69.5, 82.6, 120.1, 120.6, 121.3, 125.8, 126.7, 126.8, 127.0, 127.2, 127.9, 128.4, 128.5, 128.9, 131.0, 131.4, 131.7, 131.9, 132.3, 137.2, 146.4, 147.4, 169.4; ^{31}P NMR ($CDCl_3$): δ_P = 2.81. . HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}BrO_7P$ 663.0970; Found 663.1005.

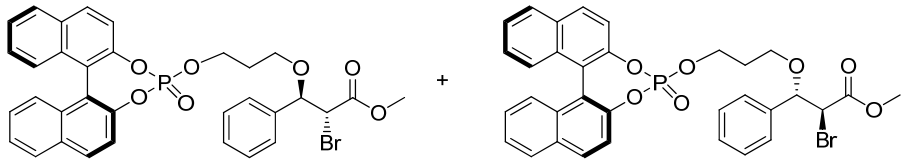
Ethyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)pentyloxy)-2-bromo-3-phenylpropanoate (5h).



SSS-**5h** + *SRR*-**5h**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5h** and *SRR*-**5h**); ^{1}HNMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.27-1.35 (m, 3H), 1.45-1.58 (m, 3H), 1.64-1.77 (m, 2H), 3.27-3.34 (m, 2H), 4.15-4.34 (m, 5H), 4.59 and 4.60 (both d, *J* = 10 Hz, total 1H), 7.29-7.39 (m, 12H), 7.44-7.50 (m, 1H), 7.93-8.04 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 14.0, 19.1, 25.5, 27.1, 47.5, 62.0, 69.0, 69.5, 82.7, 120.1, 120.2, 120.6, 121.2, 121.4, 125.7, 126.7, 127.0, 127.2, 128.0, 128.3, 128.4, 128.5, 128.8, 131.1, 131.4, 131.6, 131.8, 132.2, 132.3, 137.3, 146.3, 147.4, 168.8; ^{31}P NMR ($CDCl_3$): δ_P = 2.83. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{33}BrO_7P$, 677.1127; Found 677.1163.

Ethyl 3-(1,1'-binaphthyl-2,2'-diyl phosphoryloxy)pentyloxy)-2-bromo-3-phenylpropanoate (5i).

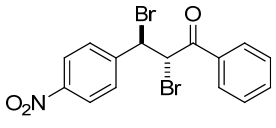


SSS-**5i** + *SRR*-**5i**

Enantiopure *S*-(**3a**) was used as Brønsted acid, mixture of two diastereomers (*SSS*-**5i** and *SRR*-**5i**); ^{1}HNMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 1.71-1.75 (m, 2H), 3.32-3.35 (m, 2H), 3.76 and 3.77 (both s, total 3H), 4.18-4.30 (m, 3H), 4.59 and 4.61 (both d, *J* = 10 Hz, total 1H), 7.29-7.37 (m, 9H), 7.42-7.49 (m, 3H), 7.59 (d, *J* = 8.7 1H), 7.57-8.04 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 25.4, 47.0, 52.9, 69.0, 69.5, 82.7, 120.1, 120.6, 121.4,

125.8, 126.7, 126.8, 127.0, 127.2, 128.4, 128.9, 131.1, 132.2, 132.3, 137.2, 146.3, 147.5, 169.4; ^{31}P NMR ($CDCl_3$): δ_P = 2.82.

2,3-dibromo-1,3-diphenylpropan-1-one



6

THF was added to the solid mixture of 4-NO_2 chalcone **2k** (0.2 mmol) and **3a** (0.21 mmol, 1.01 Equiv.) and stirred for five minutes. NBS (0.4 mmol, 2 Equiv.) was added slowly (0.5 equiv.) at room temperature after each five hours and stirred for 24 h at room temperature under argon. The solvent was then removed under reduce pressure and residue was purified by flash column chromatography (EtoOAc : *n*-hexane; (1:100, V/V) yielded 2,3-dibromo-1,3-diphenylpropan-1-one **6**. White solid ^{1}HNMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 5.69 (d, *J* = 11.2 Hz, 1H), 5.77 (d, *J* = 11.2 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.66-7.71 (m, 3H), 8.09 (d, *J* = 7.6 Hz, 2H), 8.29 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 45.9, 47.2, 124.1, 128.9, 129.1, 129.4, 134.1, 134.4, 145.1, 148.1, 190.3.

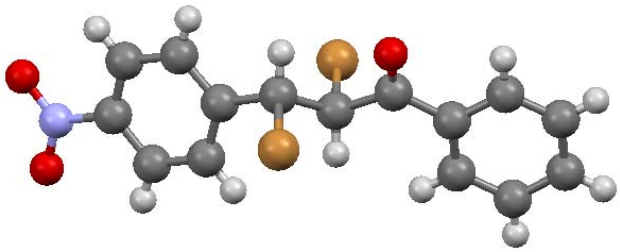
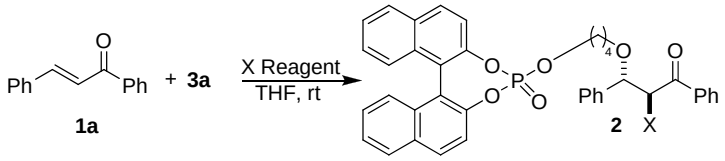


Fig. S12. Single-crystal structure of **6**

1.4 Effect of Different Halogen Reagents on the Phosphoalkoxylation

The addition of suitable electrophile was important to capture the resulting nucleophilic enol. As shown below (Table S1), a series of suitable halogen reagent were screened.

Table S1. Effect of different halogen reagent on phosphoetherification[a]



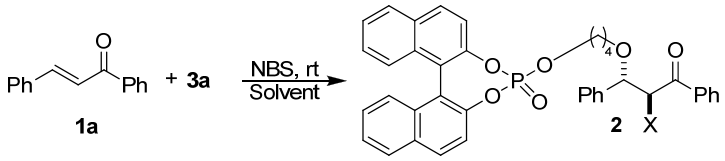
Ent.	Halogen Reagent	Yield (%)[b]
1	$KBrO_3$ (10 Equiv.)	NR
2	$KBrO_3$ / KBr (10:5 Equiv.)	NR
3	n-Bu_4NBr_3	NR
4	NIS	Product was not stable
5	NCS	trace
6	1,3-Dichloro-5,5-dimethylhydantoin	41
7	1,3-Dibromo-5,5-dimethylhydantoin	68
8[c]	NBS	78

[a] Chalcone **1a** (0.2 mmol) and **3a** (0.21 mmol, 1.01 Equiv.) were mixed and stired in THF (2 mL) for 5 minutes followed by slow addition of halogen reagent (0.5 Equiv. after each 5 hours) at room temperature and stirred for 24 h under argon, [b] Isolate yield, [c] Reactoin was performed with 0.1 M of the substrate. Notes: NR, No reaction.

1.5 Effect of Mixed Co-Solvent on Phosphoalkoxylation

Reaction was also tested in different mixed co-solvent under optimized reaction conditions. MeOH/THF (competition nucleophile) the yield of product was decreased without any methanol-associated product. Chlorinated solvents were found more effective than other regarding yields, CH_3CN, DMSO and toluene produced desired product in very low yield (Table S2, entries 1, 7, 8). DMF and chlorinated solvents were found more effective than others and moderate yields were obtained (Table S2, entries 1, 7, 8). However Pure THF itself was found best and exhibited the best results regarding yield (Table S3, entry 9). No conversion was observed when THF was replaced with Et_2O (Table S2, entry 10).

Table S2. Effect of mixed co-solvent on phosphoalkoxylation



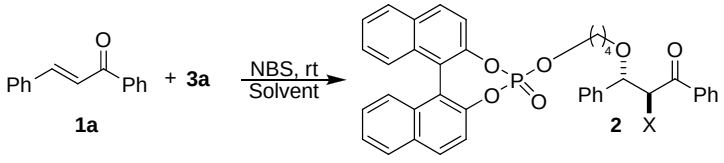
Ent.	Solvent	Co-Solvent	Ratio (mL)	Yield (%)[b]
1	THF / CH_2Cl_2	CH_2Cl_2	1:1 (2 mL)	39
2	THF /	CCl_4	1:1 (2 mL)	32
3	THF /	$CHCl_3$	1:1 (2 mL)	26
4	THF /	DMF	1:1 (2 mL)	33
5	THF /	MeOH	1:1 (2 mL)	13
6	THF / /	CH_3CN	1:1 (2 mL)	15
7	THF /	DMSO	1:1 (2 mL)	20
8	THF /	Toluene	1:1 (2 mL)	12
9	THF	---	1:1 (2 mL)	59
10	Et_2O	---	1:1 (2 mL)	NR

[a] Chalcone **1a** (0.2 mmol) and acid **3a** (0.21 mmol, 1.01 Equiv.) were stirred in cosolvent, NBS (0.4 mmol, 2 Equiv.) was added in THF and stirred at room temperature for 24 h under argon, [b] Isolate yield.

1.6 Effect of Concentration and Stoichiometric Amount of THF on Phosphoalkoxylation

The reaction was briefly investigated in stoichiometric amount (0.1, 0.2 and 0.4 Equiv.) of THF and very low yield of desired product was observed (Table S3, entries 1-3). Further investigation showed that the reaction was also highly dependent on the concentration, in which a higher reaction yield (86%) of the desired product was obtained when reaction was conducted under concentrated (0.04 mol in 2 mL THF) conditions. (Table S3, entry 7). This also favours the Brønsted acid catalysis mechanism because concentrated reaction is more acidic than diluted.

Table S3. Effect of concentration and stoichiometric amount of THF on phosphoalkoxylation



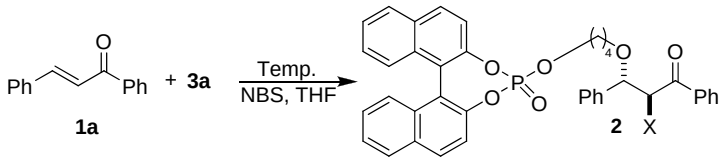
Ent.	Substrate (mmol.)	Solvent	Co-Solvent (2 mL)	Yield (%)[b]
1	0.2	16 µL	CH_2Cl_2	5
2	0.2	32 µL	CH_2Cl_2	5
3	0.2	64 µL	CH_2Cl_2	6
4	0.2	128 µL	CH_2Cl_2	7
5	0.1	2 mL	---	40
6	0.2	2 mL	---	63
7	0.4	2 mL	---	86

[a] Chalcone **1a** (0.2 mmol) and acid **3a** (0.21 mmol, 1.01 Equiv.) were stirred in THF, NBS (0.4 mmol, 2 Equiv.) was added in THF/cosolvent and stirred at room temperature for 24 h under argon, [b] Isolate yield.

1.7 Effect of Temperature on the Phosphoalkoxylation

Conditions were also optimized regarding temperature, interestingly, low yields were observed at both higher and lower temperatures (Table S4, entries 1-4); however, moderate yield was obtained at room temperature.

Table S4. Effect of temperature on phosphoalkoxylation



Entry	Temp. (^oC)	Yield (%)[b]
1	0	23
2	-25	10
3	-78	NR
4	65	24
5	rt	82

Enones **1a** (0.2 mmol) and **3a** (0.21 mmol) were added and stirred in THF followed by slow addition of NBS (0.1 mmol, 0.5 Equiv.) after each five hours and stirred for 24 h at respective temperature under argon. [b] Isolate yields of all possible isomers

1.8 Structural Characterization of 2a

In ^{1}H NMR, the appearance of twenty two protons in aromatic region confirmed the attachment of BNPH. Four protons in aliphatic region at 1.39-1.62 ppm and a set of multiplets, two protons each, at 3.31 and 4.16 respectively confirmed the ring opening of THF. Moreover, all analytical data of **2a**, HRMS, HSQC COESY, NOESY and ^{13}C NMR suggested the desired transformation. Profoundly, In ^{1}H NMR the appearance of two sets of doublets at 4.88-4.91 and 5.09-5.13 respectively with coupling constant of *J*= 9.8 Hz each between the protons at C-1 and C-2 position suggested the product as mixture of two diastereomers and assured *anti*-diastereoselectivity around the double bond (Fig. S13). The appearance of some peaks as a pair in ^{13}C NMR also confirmed the product as a mixture of diastereomers (Fig. S14). Further, the results on chiral high-performance liquid chromatography (CHIRAL PAK IF) confirmed the product as a mixture of diastereomers (Fig. S1). Each *R*-**3a** and *S*-**3a** produced two diasteromers (Fig. S2 and S3), while racemic **3a** produced four isomers (Fig. S1).

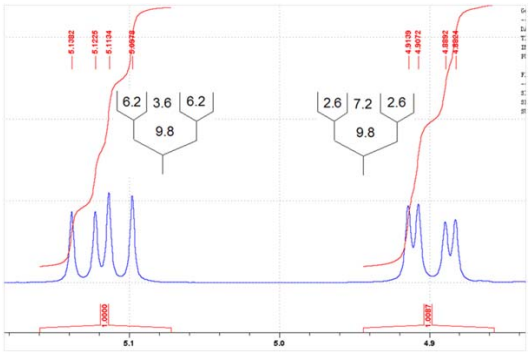


Fig. S13. Magnified ^{1}H NMR spectrum (4.8 ppm to 5.2 ppm) of **2a**.

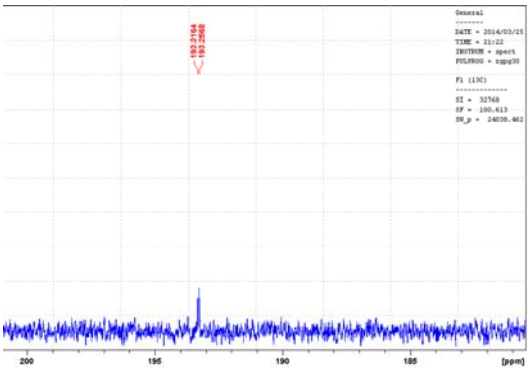


Fig. S14. Magnified ^{13}C NMR spectrum (185-200 ppm) of **2a**.

1.9 Other Features of Phosphoalkoxylation

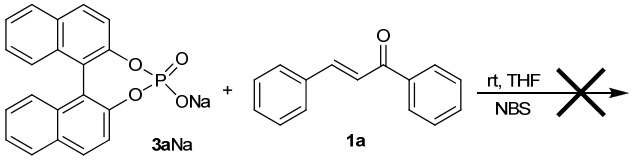
There are several features in this novel phosphoalkoxylation reaction which led us to design the reaction mechanism (Table S6).

Table S5. The Effect of nucleophile and anion on the rate of the reaction[a]

Ent.	Nucleophile / Acid	Solvent	Product (R)	Yield (%) [b]
1	$NH_2CH_2CH_2NH_2$	THF	NR	…
2	**3a**Na	THF	NR	…
3	**3a**	THF / MeOH	NR	10

[a]Enones **1a** (0.2 mmol) and acid / nucleophile (0.21 mmol) were added and stirred in THF followed by slow addition of NBS (0.1 mmol, 0.5 Equiv.) at room temperature after each five hours and stirred for 24 h under argon. [b]Isolate yields of all possible isomers.

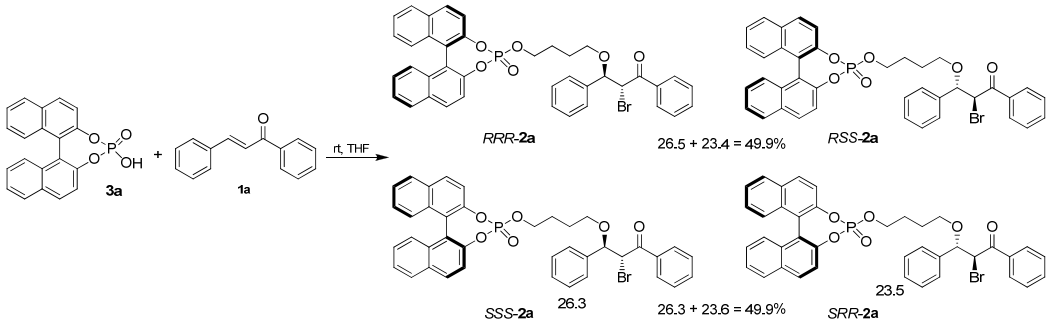
1.9.1 Importance of Bronstated Acid



3a was added to the stirred suspension of NaH in THF (2 mL), and mixture was stirred at room temperature for one hour. Chalcone **1a** was added to the reaction mixture, followed by the slow addition of NBS (0.5 Equiv.) after each 5 hours and stirred at room temperature for 24 hours. The reaction was monitored by TLC and interestingly, no conversion was observed. Importantly, the colour of solution was gets changed to slight reddish brown and succinimide was also separated even though there was no conversion.[1] These results confirmed the activation of NBS but ruled out the formation of bromonium ion as an intermediate. It also confirmed that acidic proton is not important for NBS activation while important for the reaction and it could be the carbonyl activation for conjugate addition.

[1] U. Hennecke, C. H. M€uller, R. Fr€ohlich, *Org. Lett.* **2011**, *13*, 860-863

1.9.2 Chiral matched/mismatched



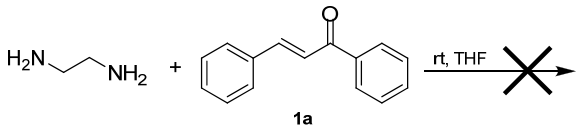
When racemic **3a** was used, it produces four isomers of different ratios *RRR*, *RSS* (26.7 : 23.8) and *SSS*, *SRR* (26.3 : 23.06). Importantly, when the retention time of these four isomers were compared with the diastereomers obtained from enantiomerically pure **3a** (Fig. S1, S2 and S3), the results were of great importance. *R* enantiomer of **3a** in a racemic mixture react in a different manner with the transition state thus producing diastereomers of different ratios (*RSS* and *RRR* 26.7 : 23.8) and vice versa. From these preliminarily results, it can be concluded that the spectacular case of a matched/mismatched ion pairing interaction of phosphate ion with diastereomeric transition may exist, resulting energetically different TS's, and thus produces different diastereomeric ratios.[2-4]

[2] J. Lacour, D. Linder, *Science*, **2007**, *317*, 462-463.

[3] S. E. Reisman, A. G. Doyle, E. N. Jacobsen, *J. Am. Chem. Soc.* **2008**, 130, 7198-7199.

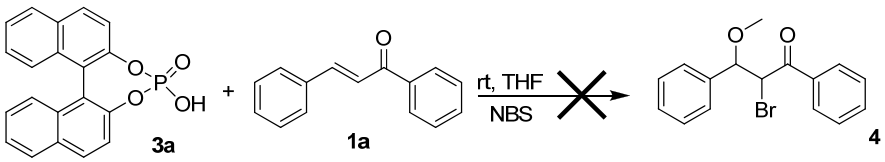
[4] C. Li, C. Wang, B. Villa-Marcos, J. Xiao, *J. Am. Chem. Soc.* **2008**, *130*, 14450-14451.

1.9.3 No reaction with ethane-1,2-diamine



Second, the reaction was performed in the presence of ethane-1,2-diamine instead of BNPH, no conversion was observed, also and ruled out the formation of bromonium ion as an intermediate.

1.9.4 Competition Reaction (MeOH)



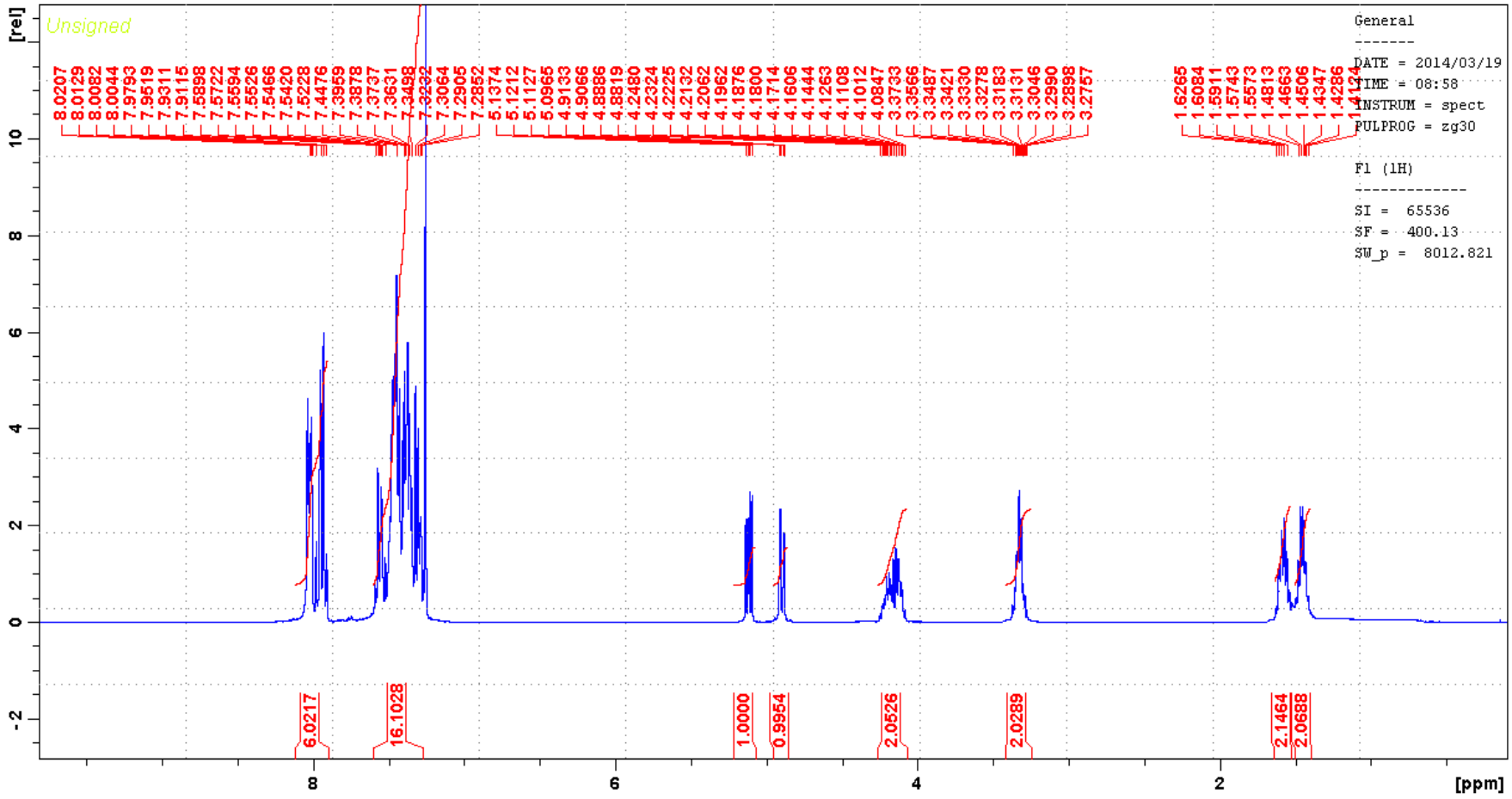
The use of equal amount of MeOH as a competition nucleophile with THF (co-solvent, Table S3 entry 5). After 24 h, yield decreased and only 10% of the phosphate derived-adduct was obtained, while no bromomethoxy product **4** was detected. It also confirms the dearth of halonium ion. (S. Bar, Can. J. Chem. **2010**, *88*, 605-612.)

1.9.5 Radical Scavenger,

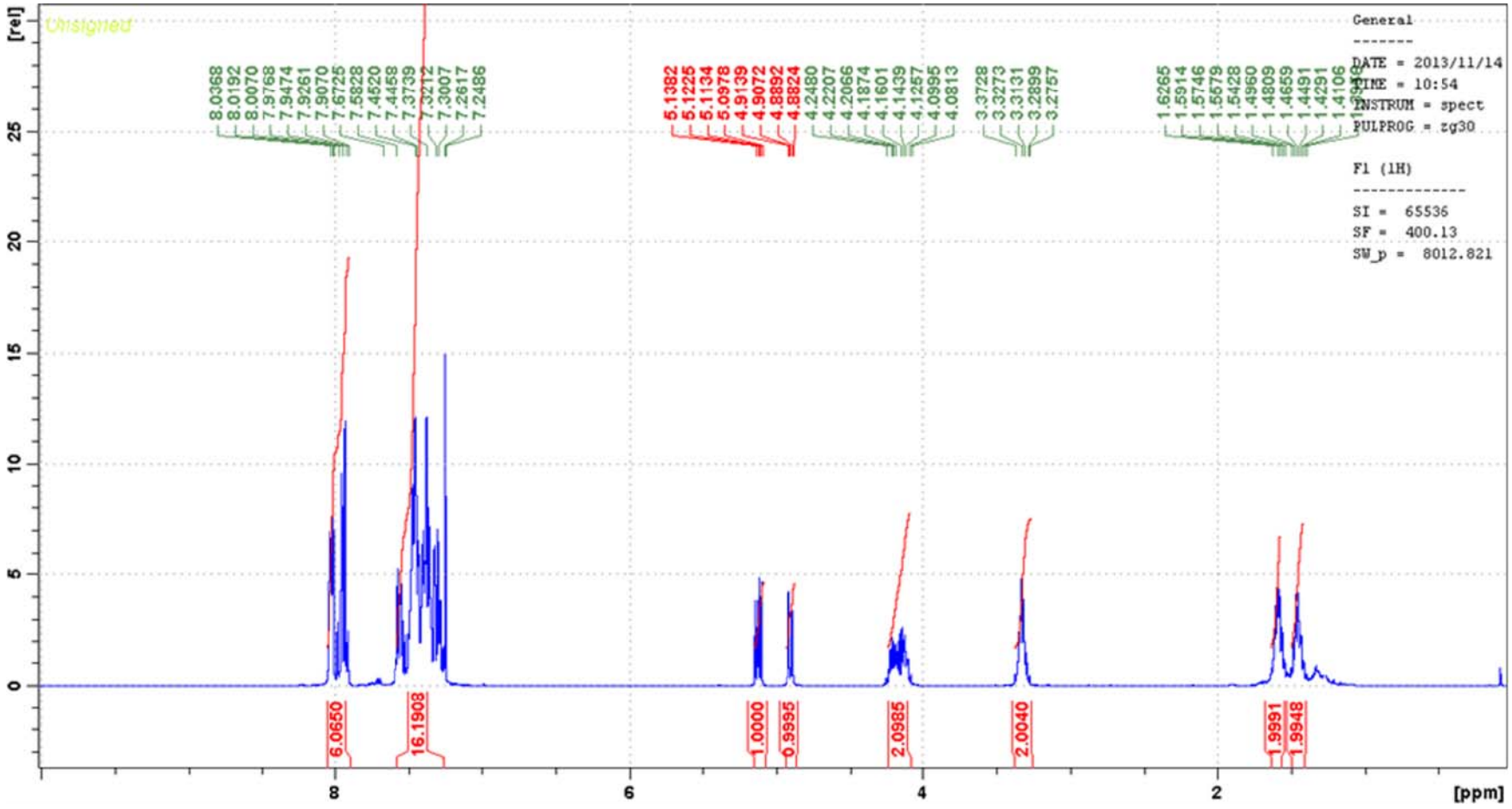
A 10 mol% 5 of radical scavenger, 2,6-di-ter-butyl-4-methylphenol (BHT), was added to the reaction mixture under optimized conditions. After 24 hours 78% of the desired product was obtained, which was identical to the reaction without the addition of BHT. Since phosphoalkoxlation of α,β-unsaturated aromatic carbonyl compounds seemed not be a radical type- reaction.

1.10 NMR Spectra

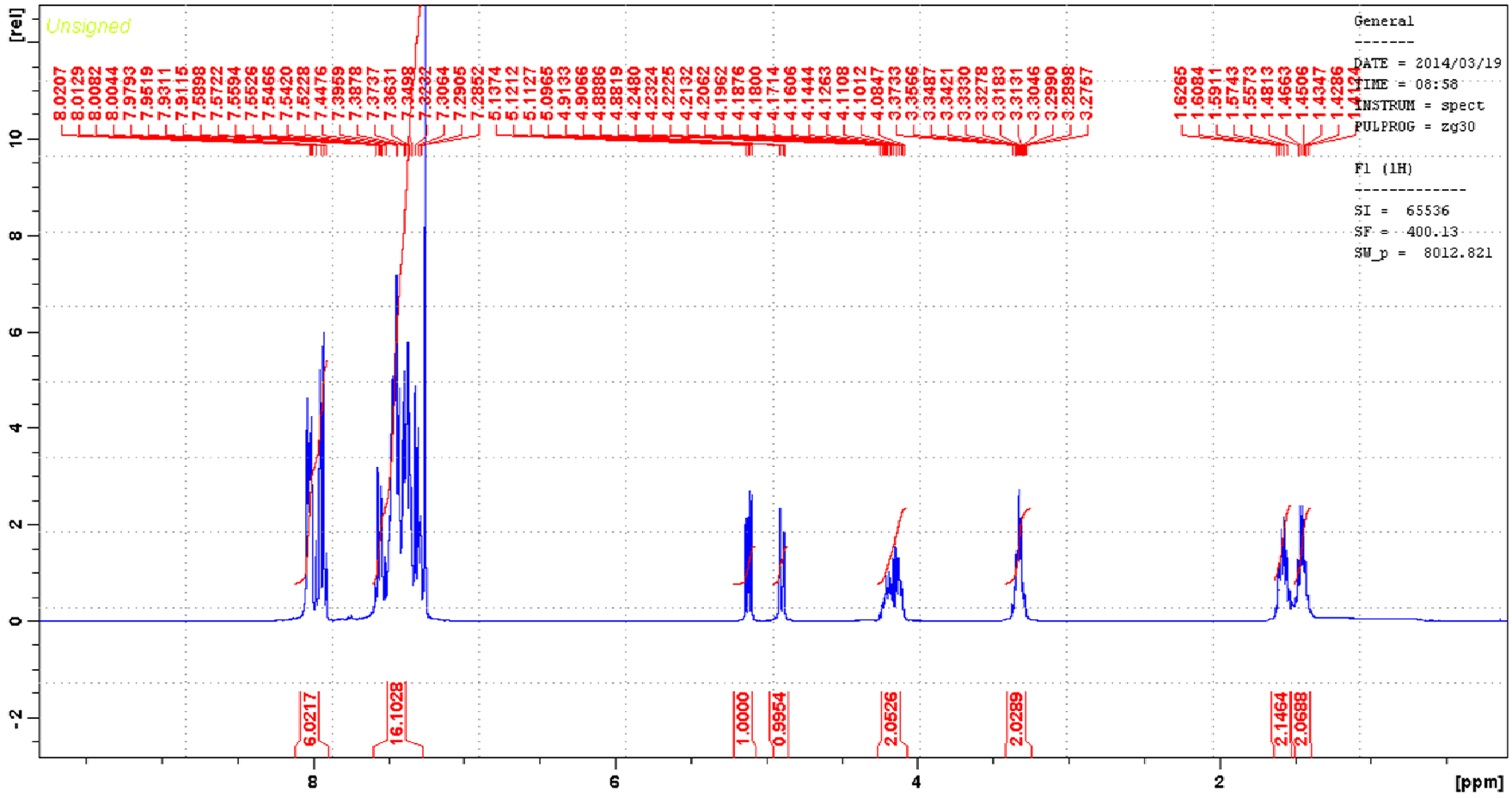
^{1}H NMR spectrum of *RRR*-**2a**, *RSS*-**2a**, *SSS*-**2a** and *SRR*-**2a**



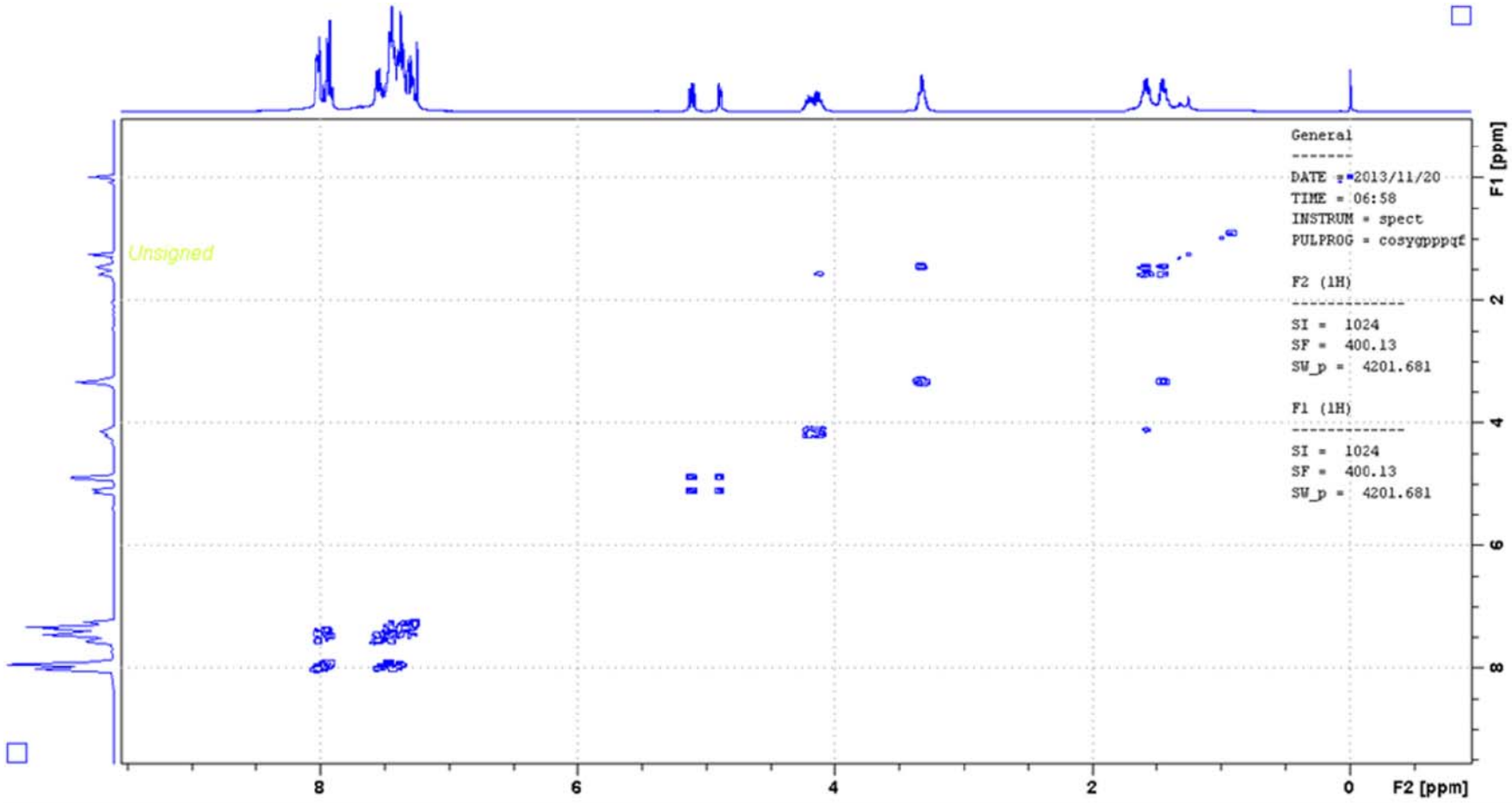
^{1}H NMR spectrum of *RRR*-**2a** and *RSS*-**2a**



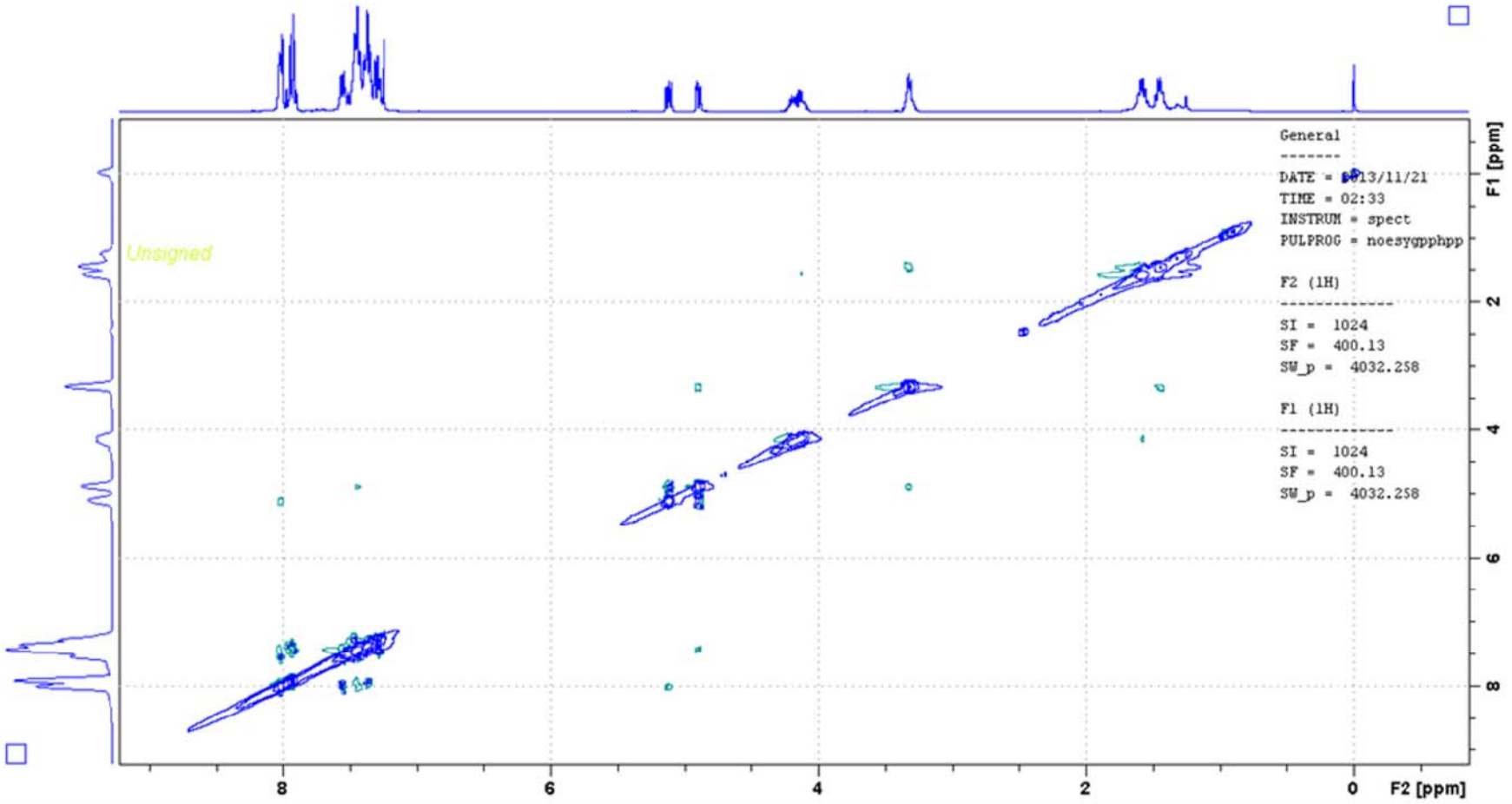
^{1}H NMR spectrum of *SSS*-**2a**, *SRR*-**2a**



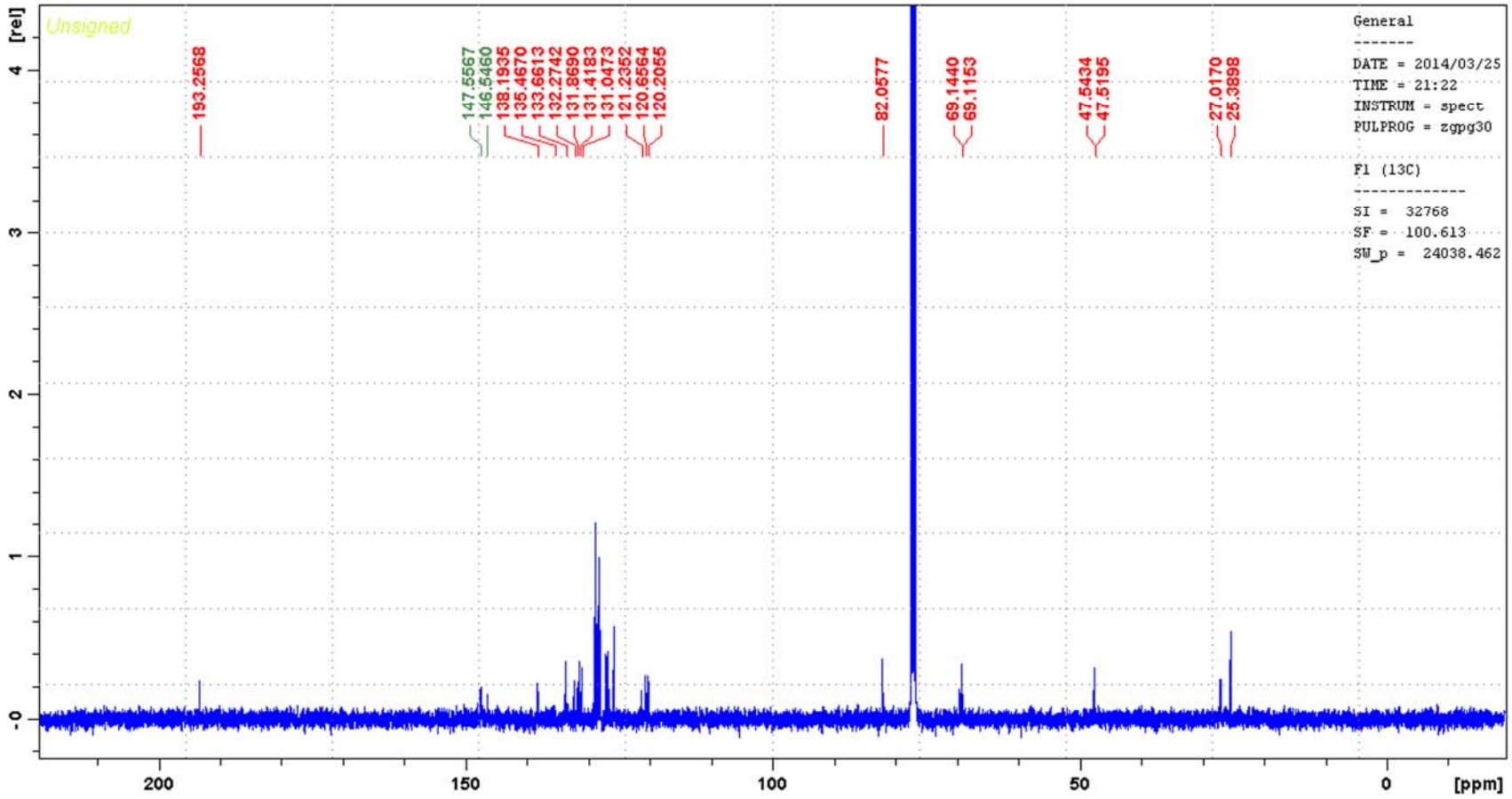
COESY spectrum of **2a**



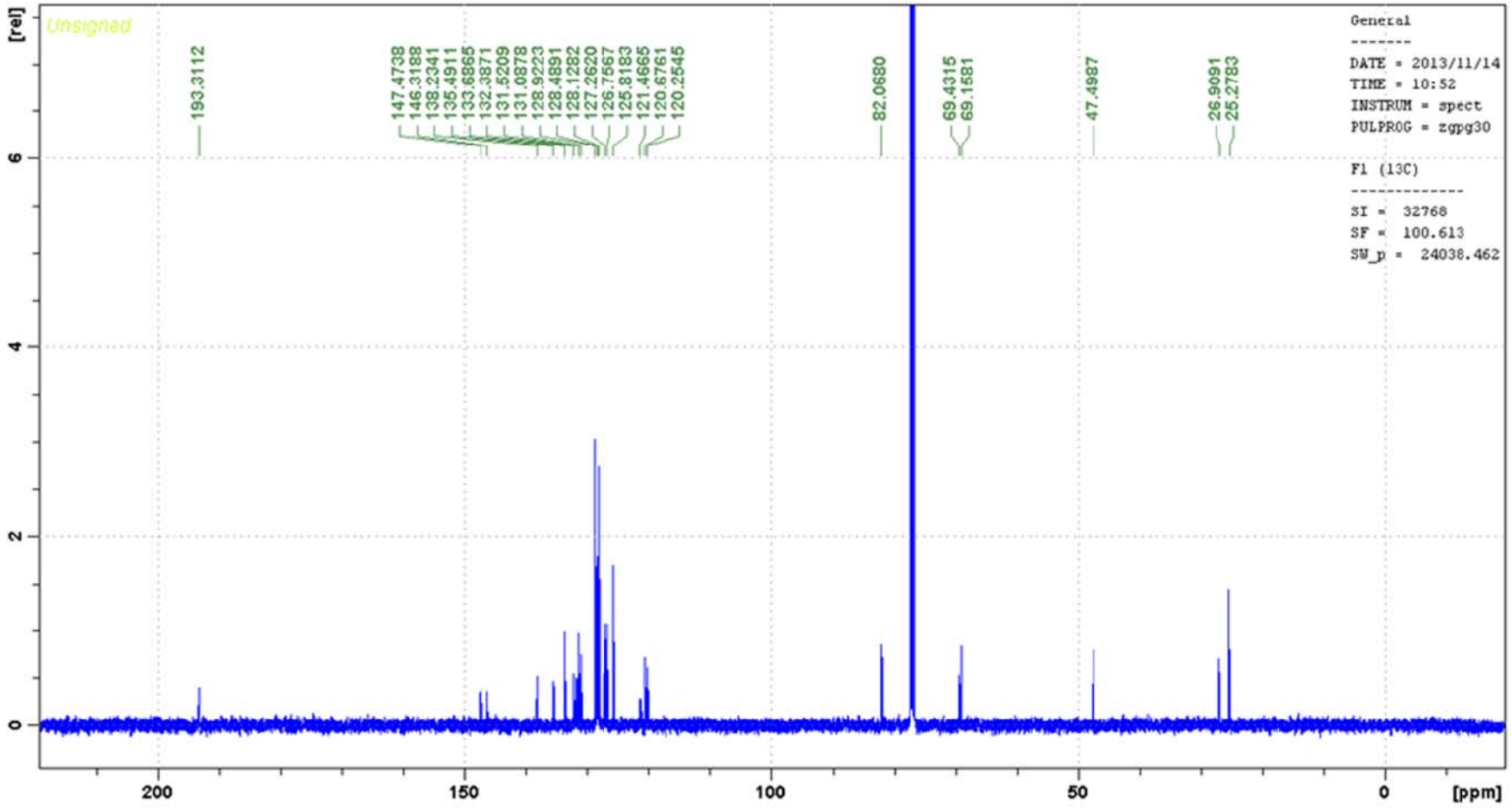
NOESY spectrum of **2a**



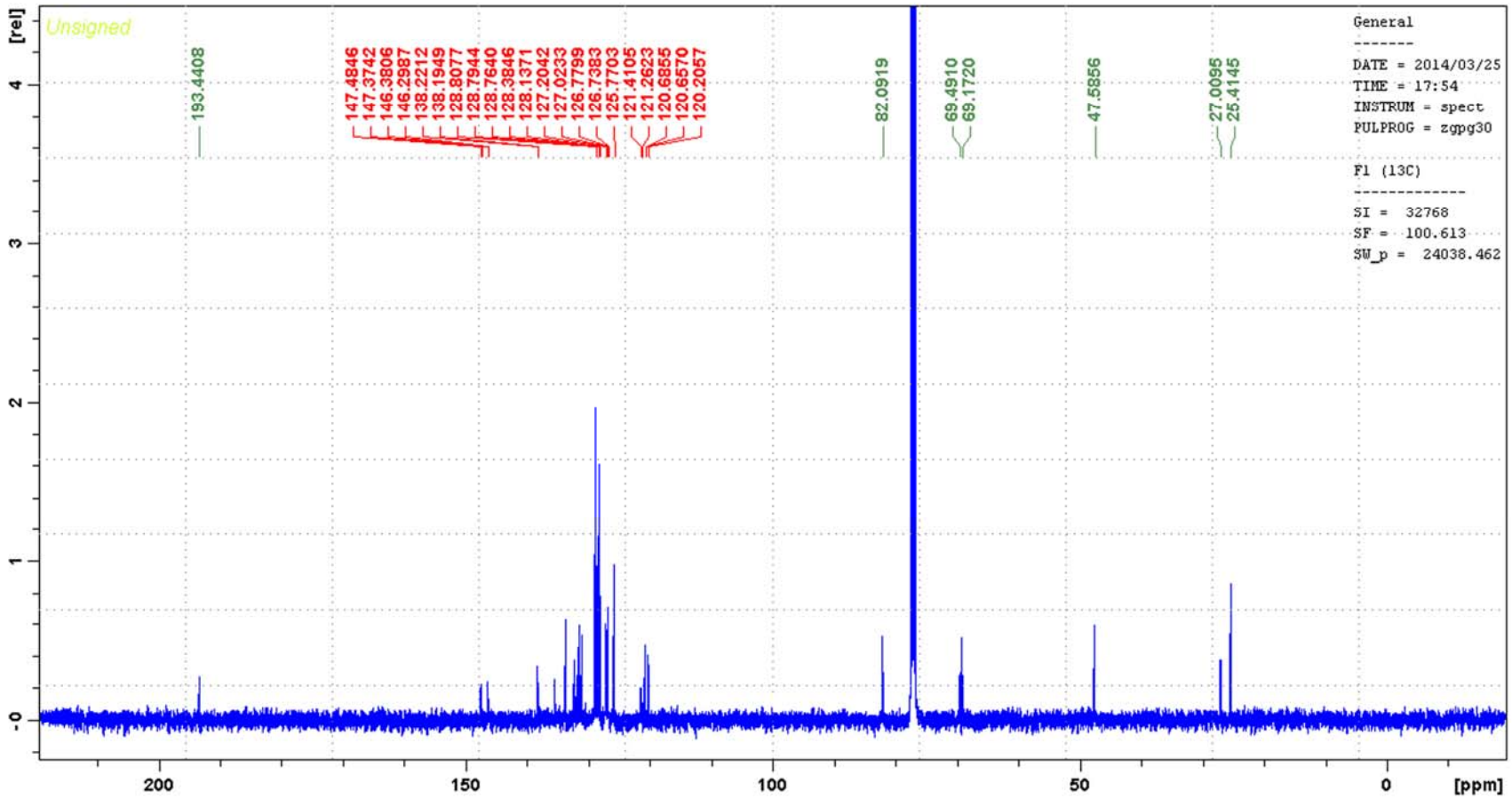
^{1}H NMR spectrum of *RRR*-**2a**, *RSS*-**2a**, *SSS*-**2a** and *SRR*-**2a**



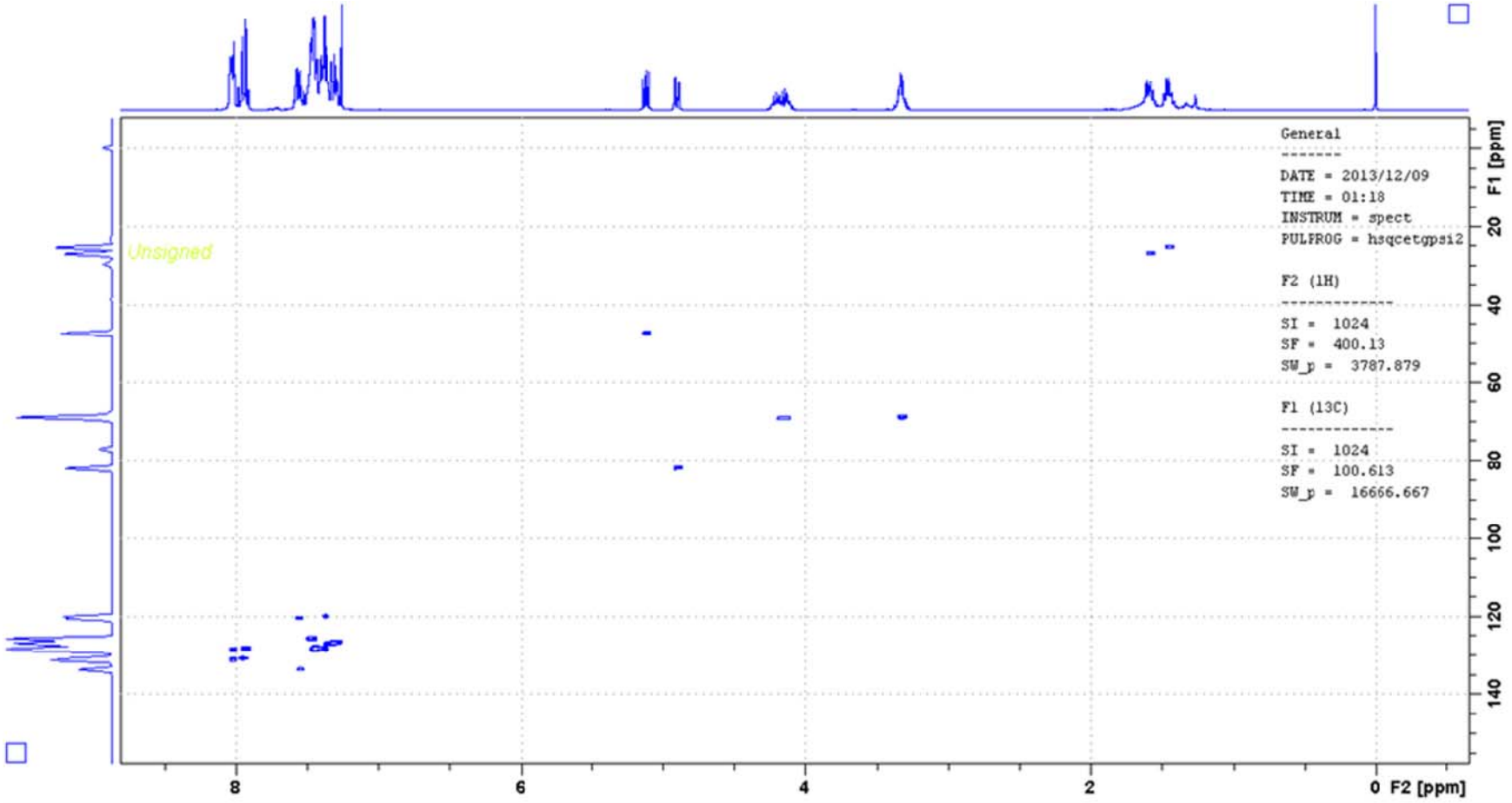
^{13}C NMR spectrum of *RRR*-**2a** and *RSS*-**2a**



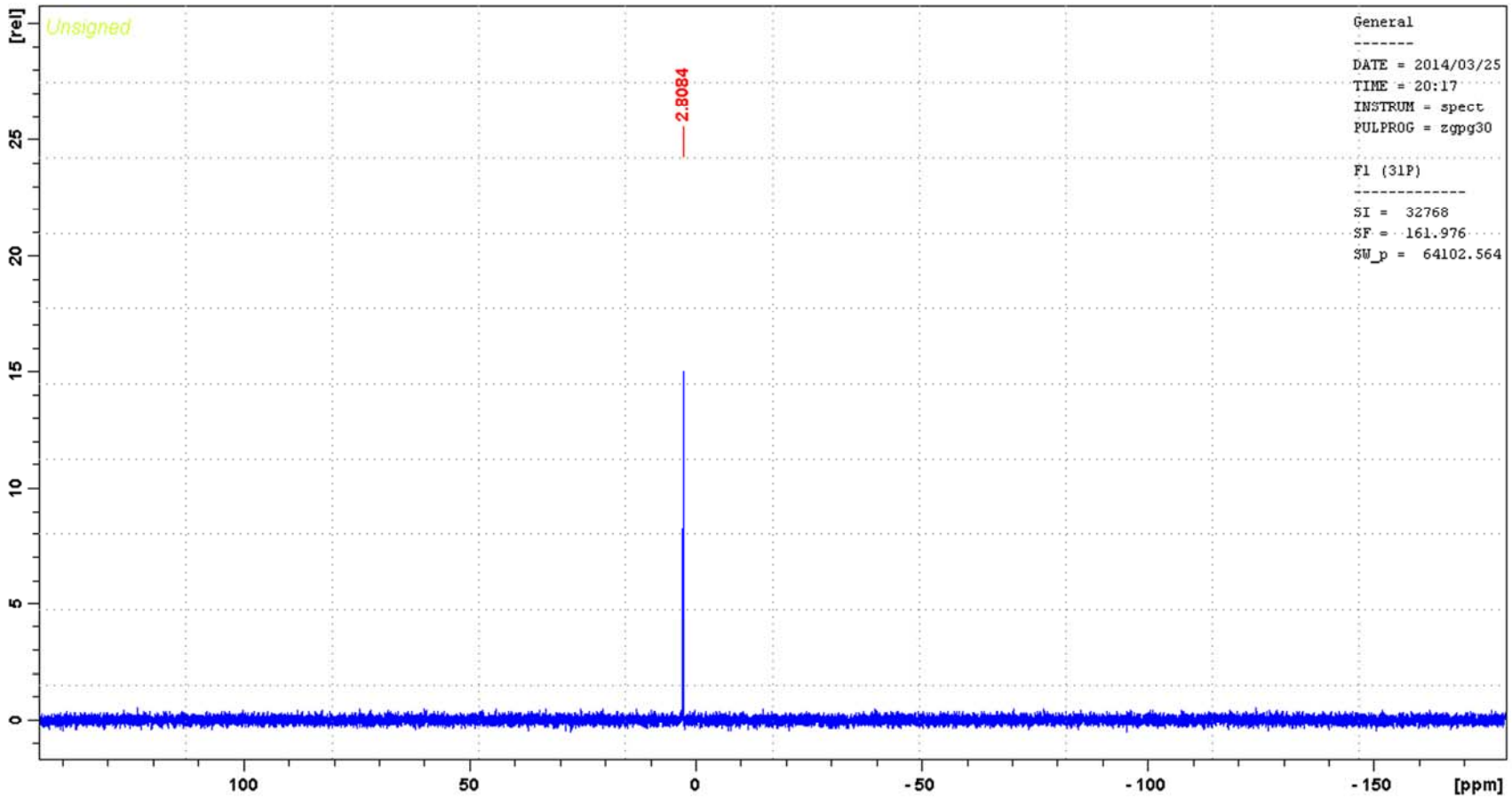
^{13}C NMR spectrum of *SSS*-**2a**, *SRR*-**2a**



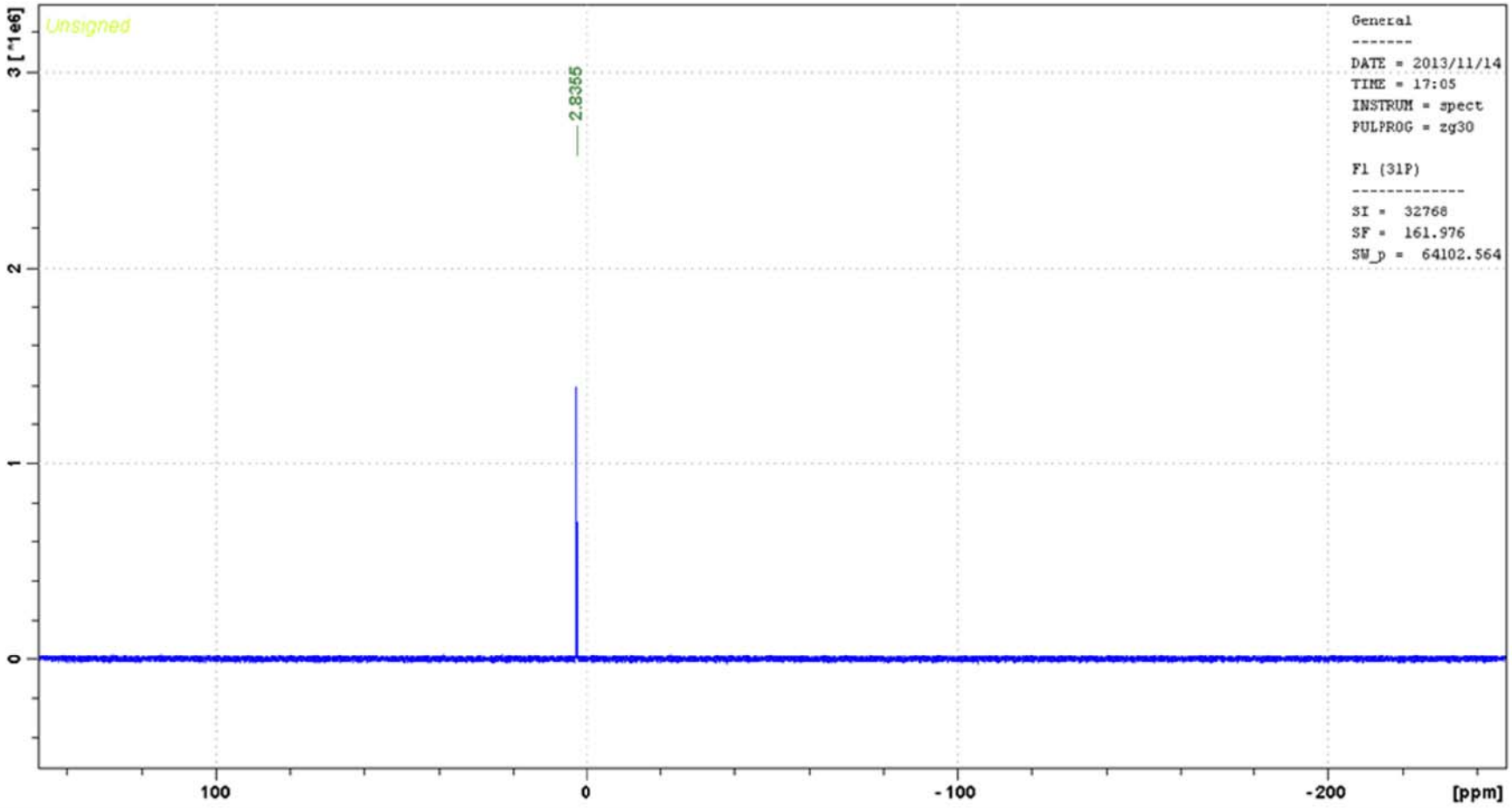
HSQC spectrum of **2a**



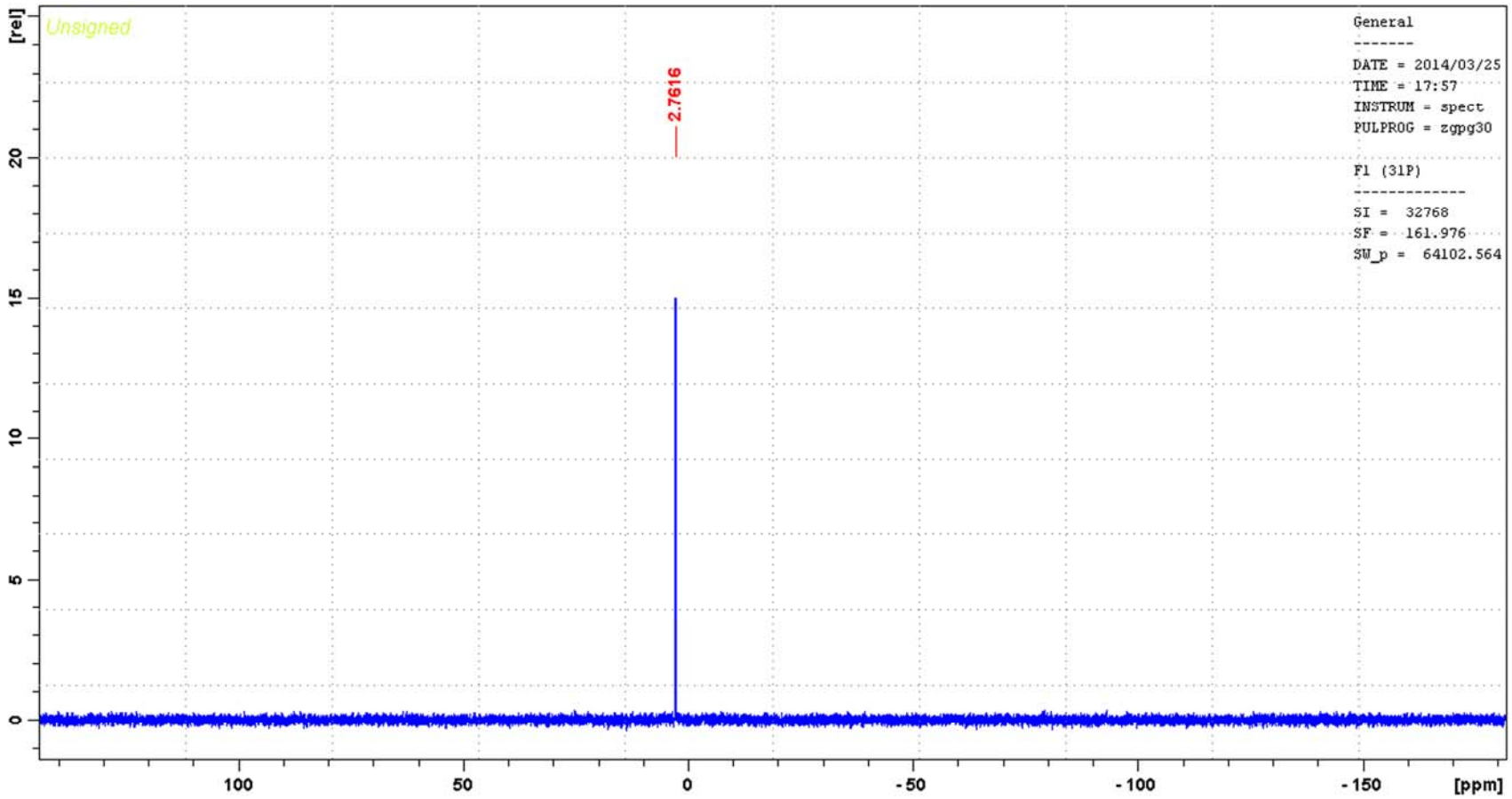
^{31}P NMR spectrum of *RRR*-**2a**, *RSS*-**2a**, *SSS*-**2a** and *SRR*-**2a**



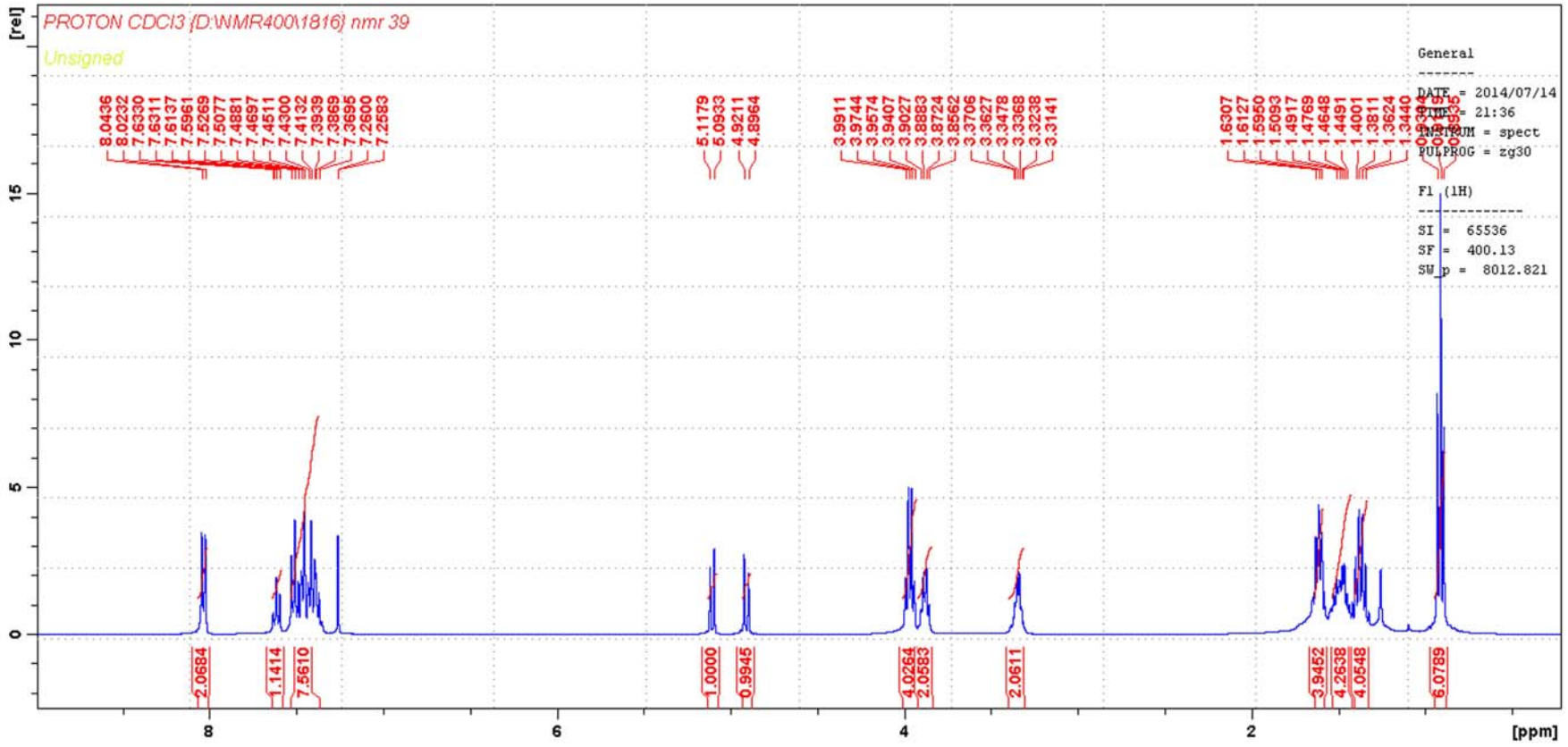
^{31}P NMR spectrum of *RRR*-**2a** and *RSS*-**2a**



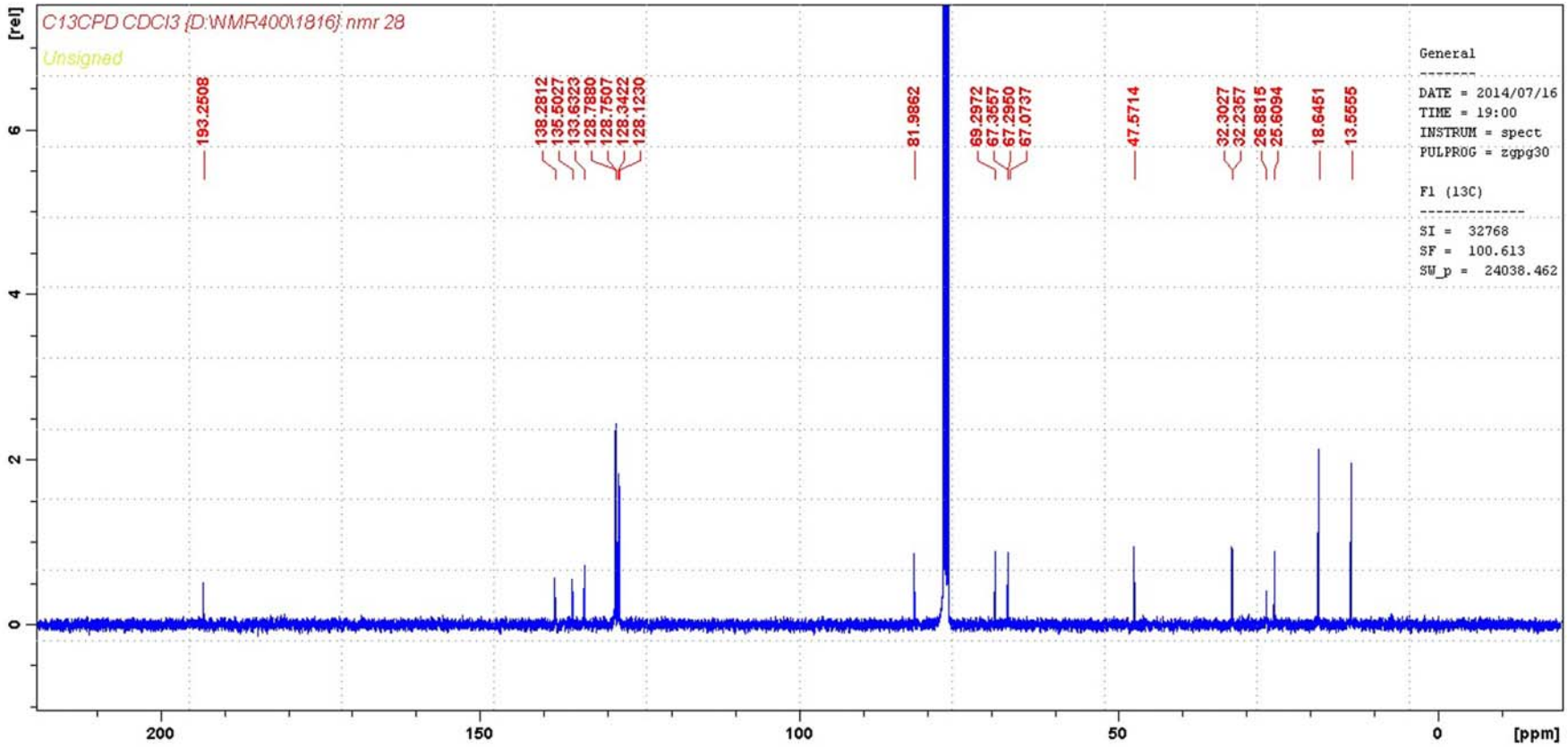
^{31}P NMR spectrum *SSS*-**2a**, *SRR*-**2a**



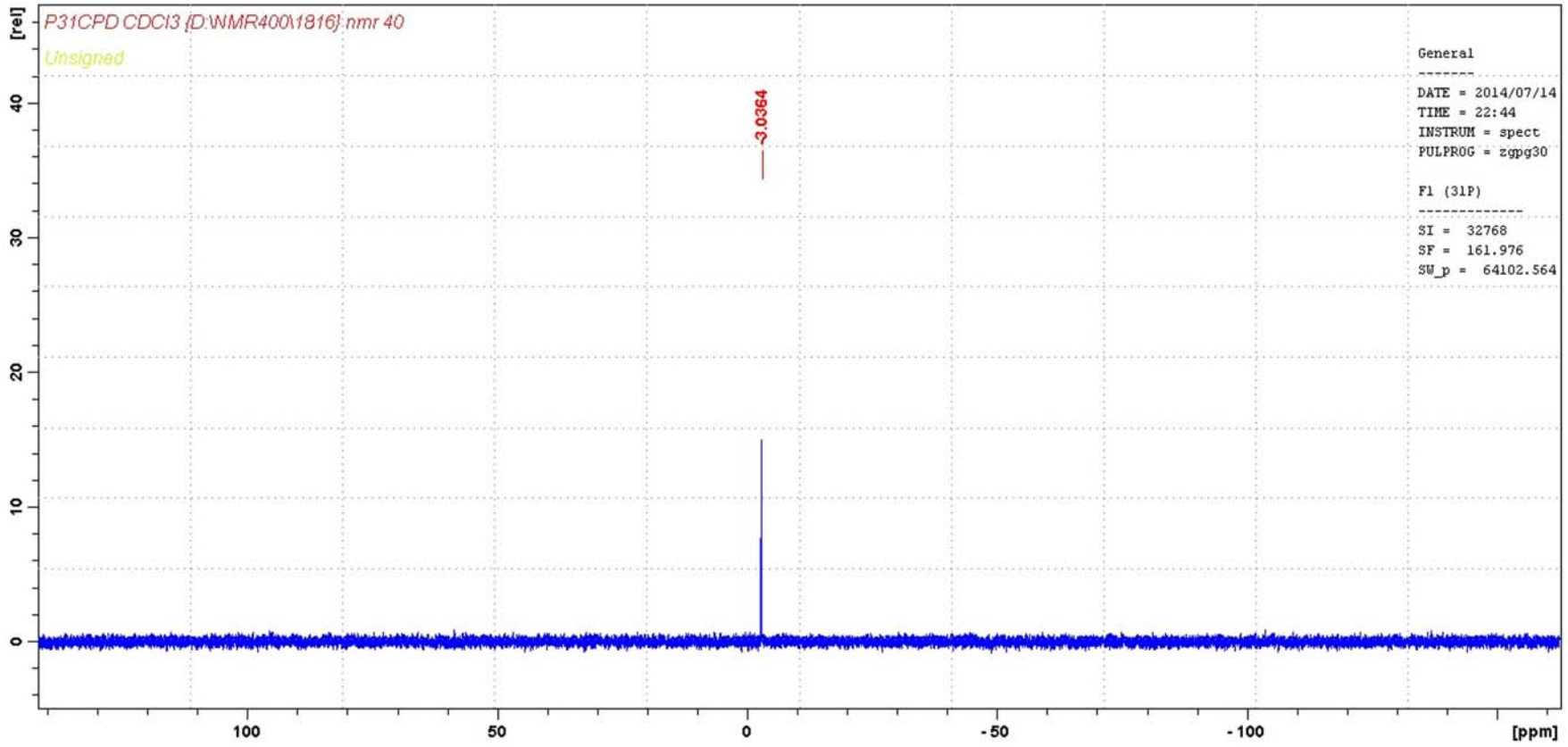
^{1}H NMR spectrum of **2b**



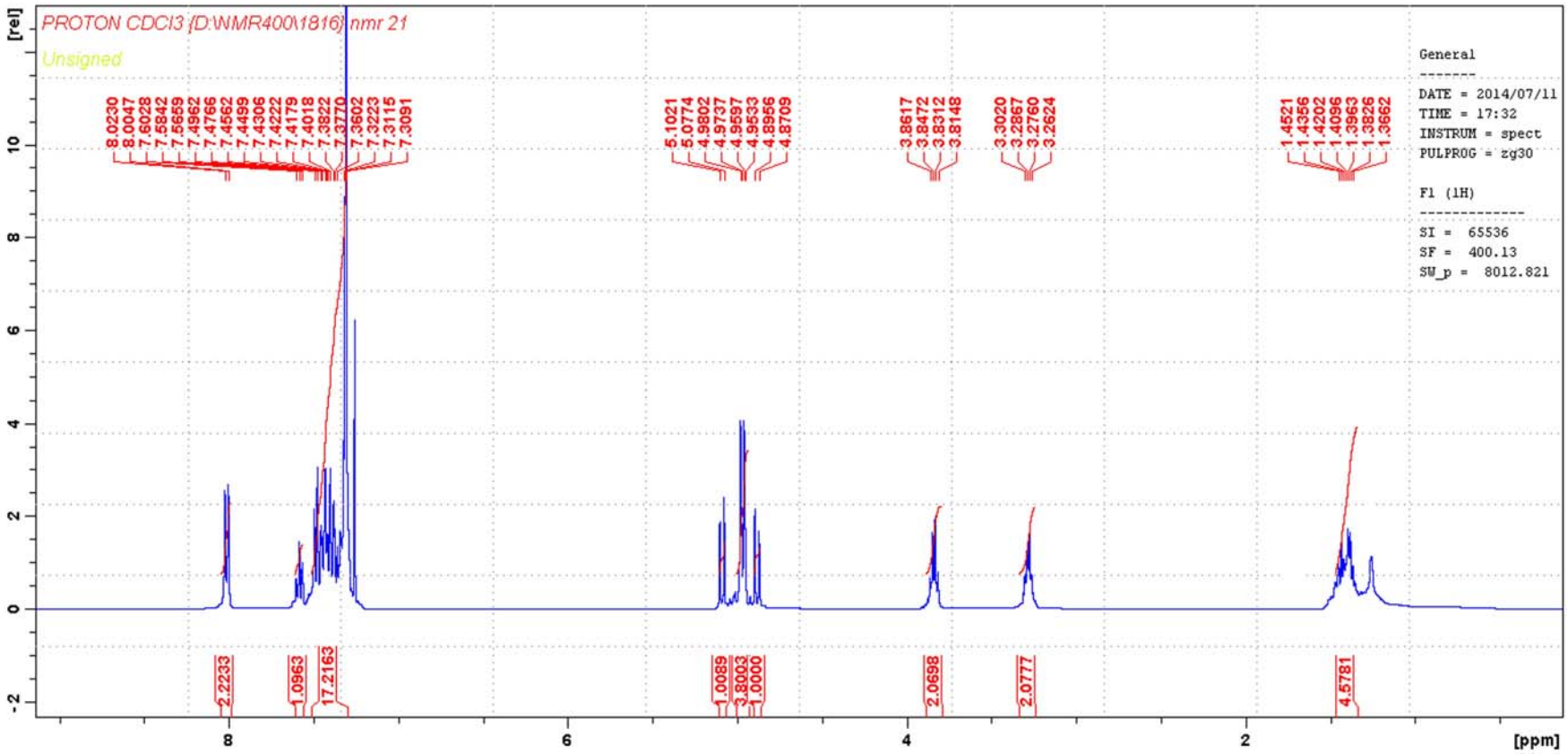
^{13}C NMR spectrum of **2b**



P NMR spectrum of **2b**



^{1}H NMR spectrum of **2c**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7.4222
7.4179
7.4018
7.3822
7.3770
7.3602
7.3223
7.3115
7.3091
5.1021
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4.9597
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3.8617
3.8472
3.8312
3.8148
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3.2760
3.2624
1.4521
1.4356
1.4202
1.4096
1.3963
1.3826
1.3662
2.2233
1.0963
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1.0000
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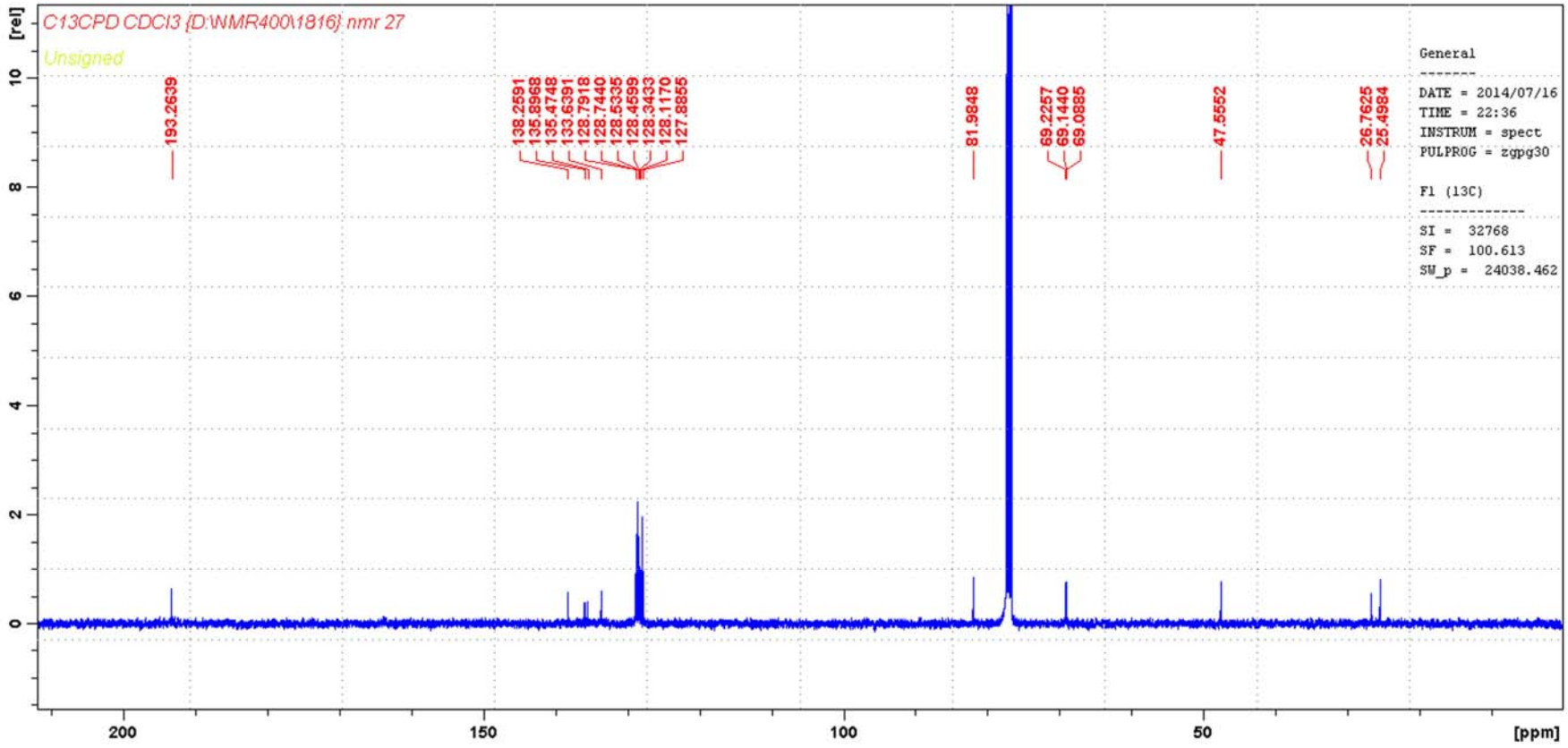
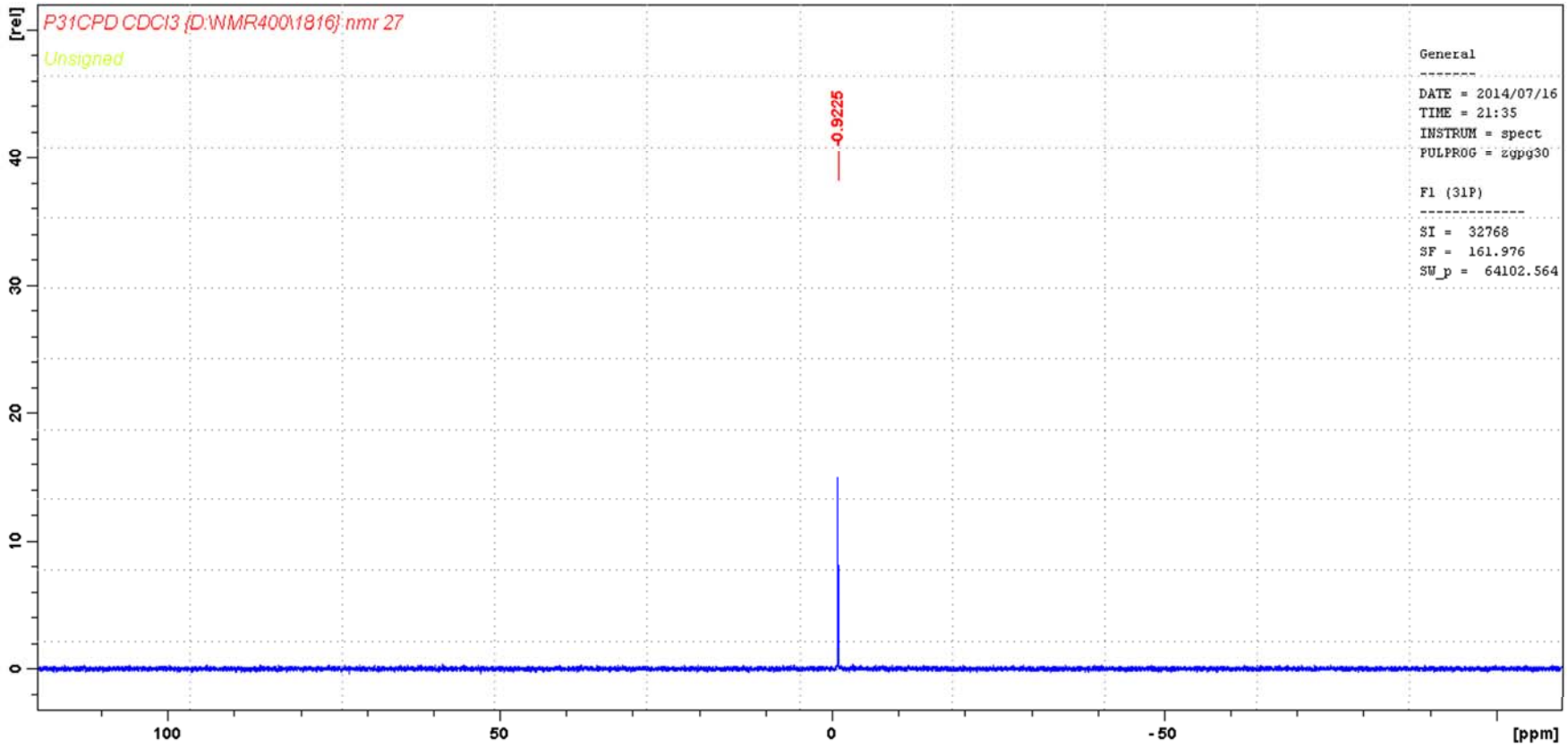
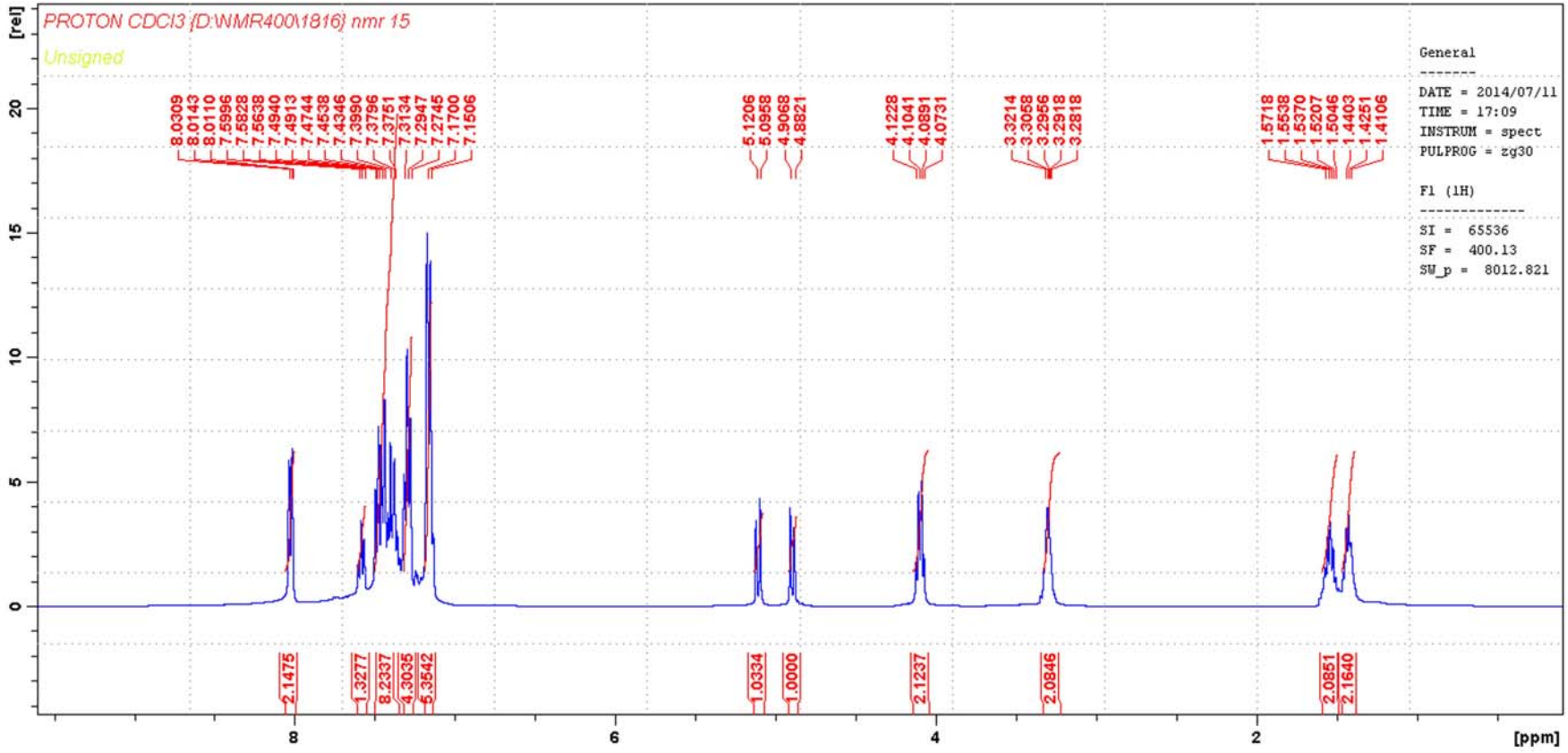
^{13}C NMR spectrum of **2c**



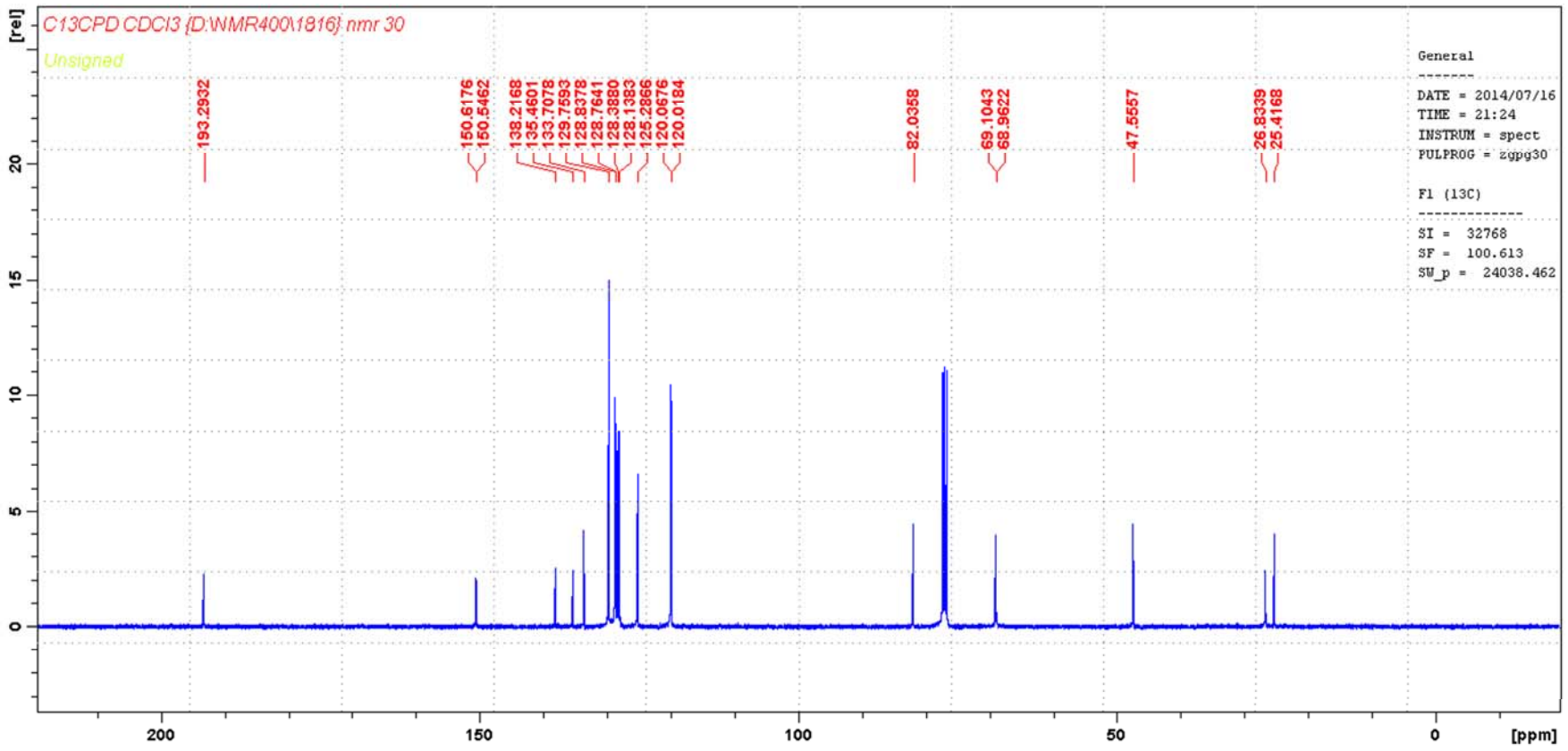
P NMR spectrum of **2c**



^{1}H NMR spectrum of **2d**



^{13}C NMR spectrum of **2d**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128.3880
128.1383
125.2866
120.0676
120.0184
82.0358
69.1043
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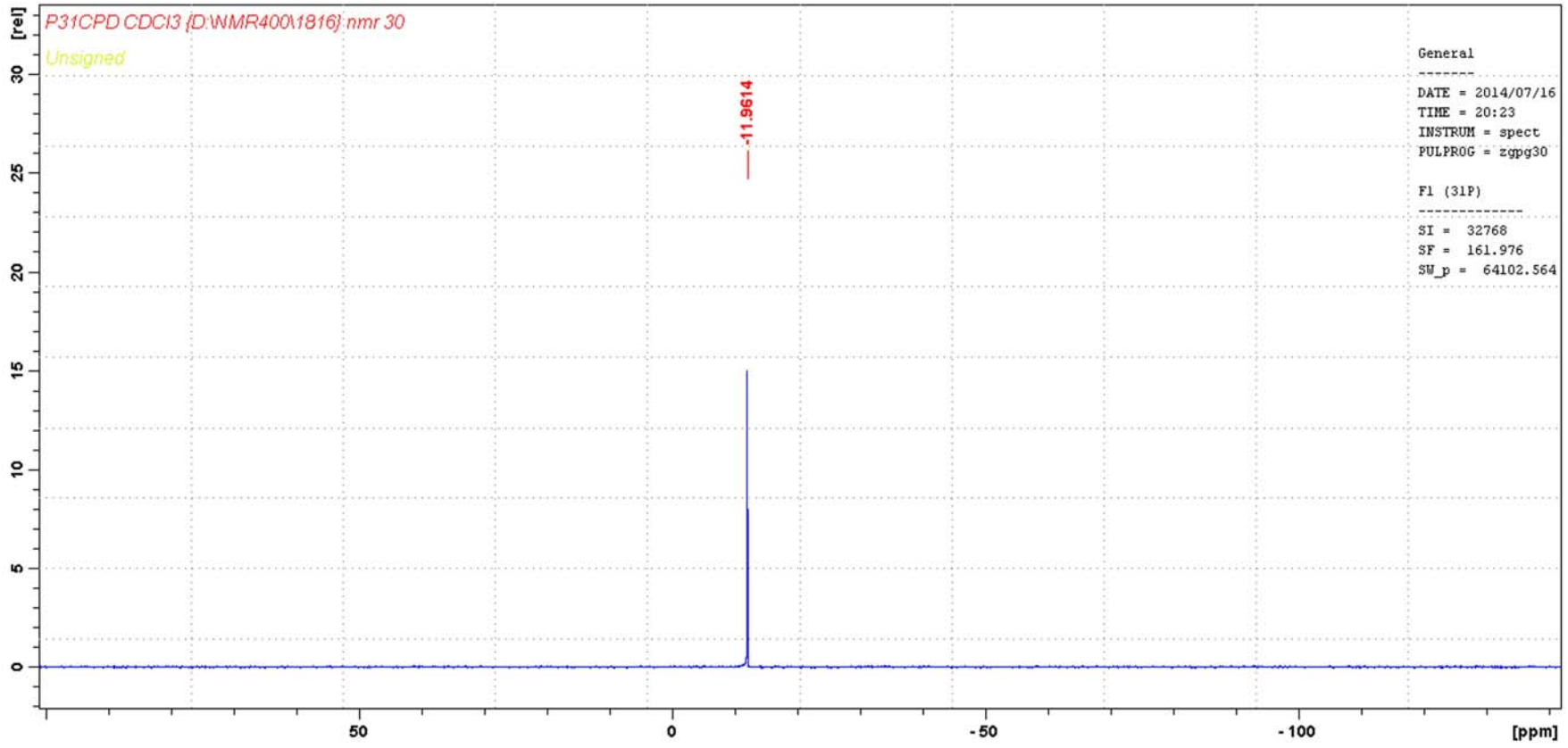
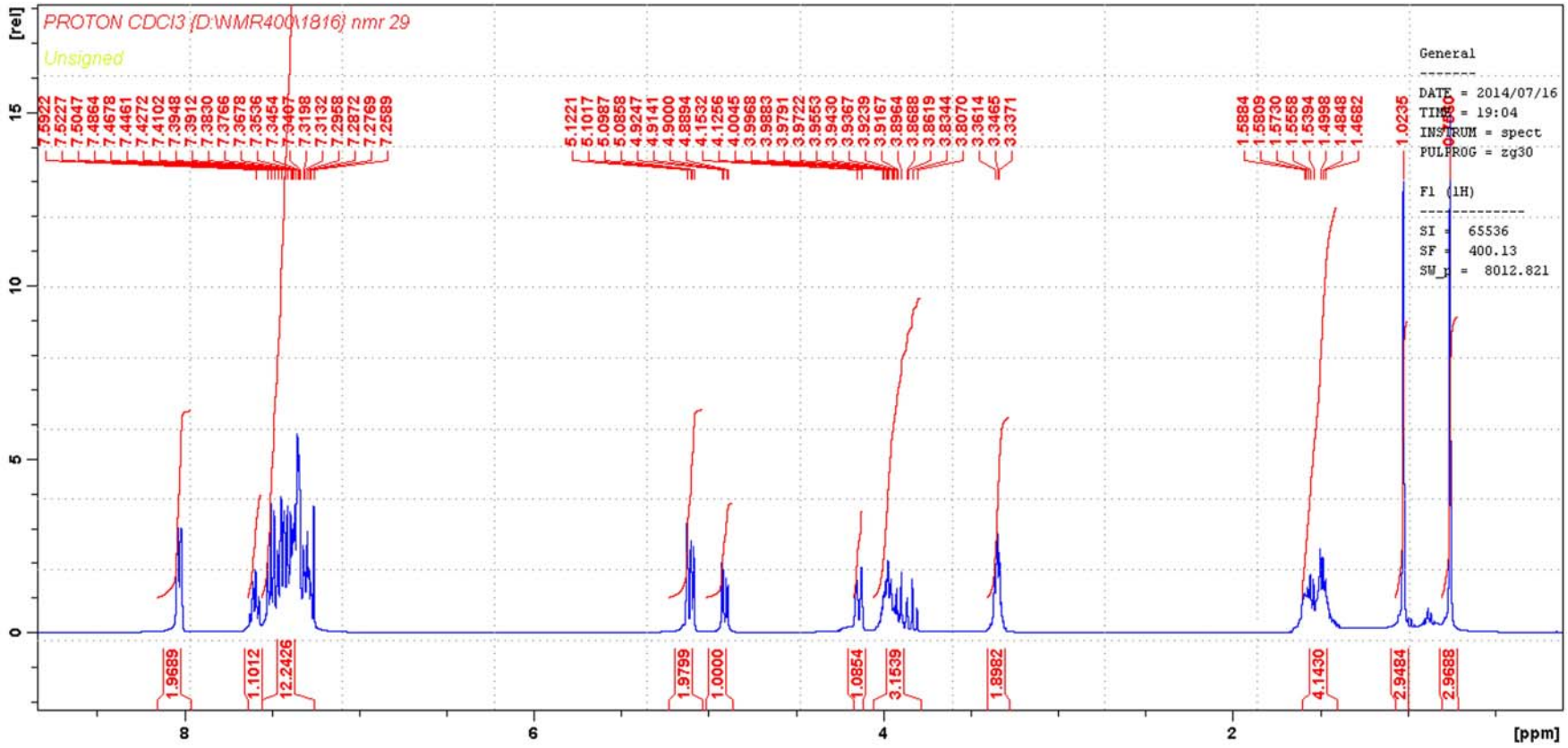
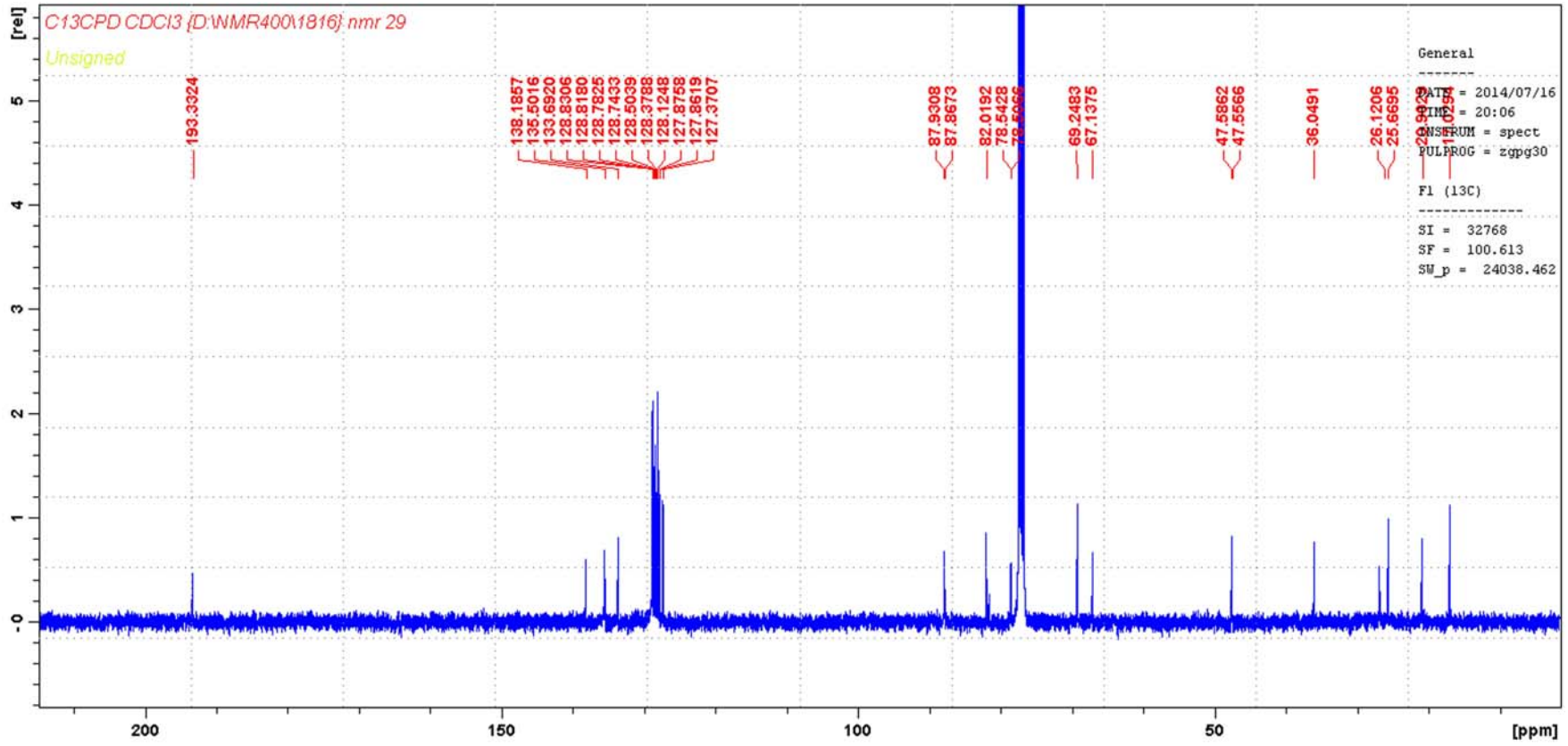


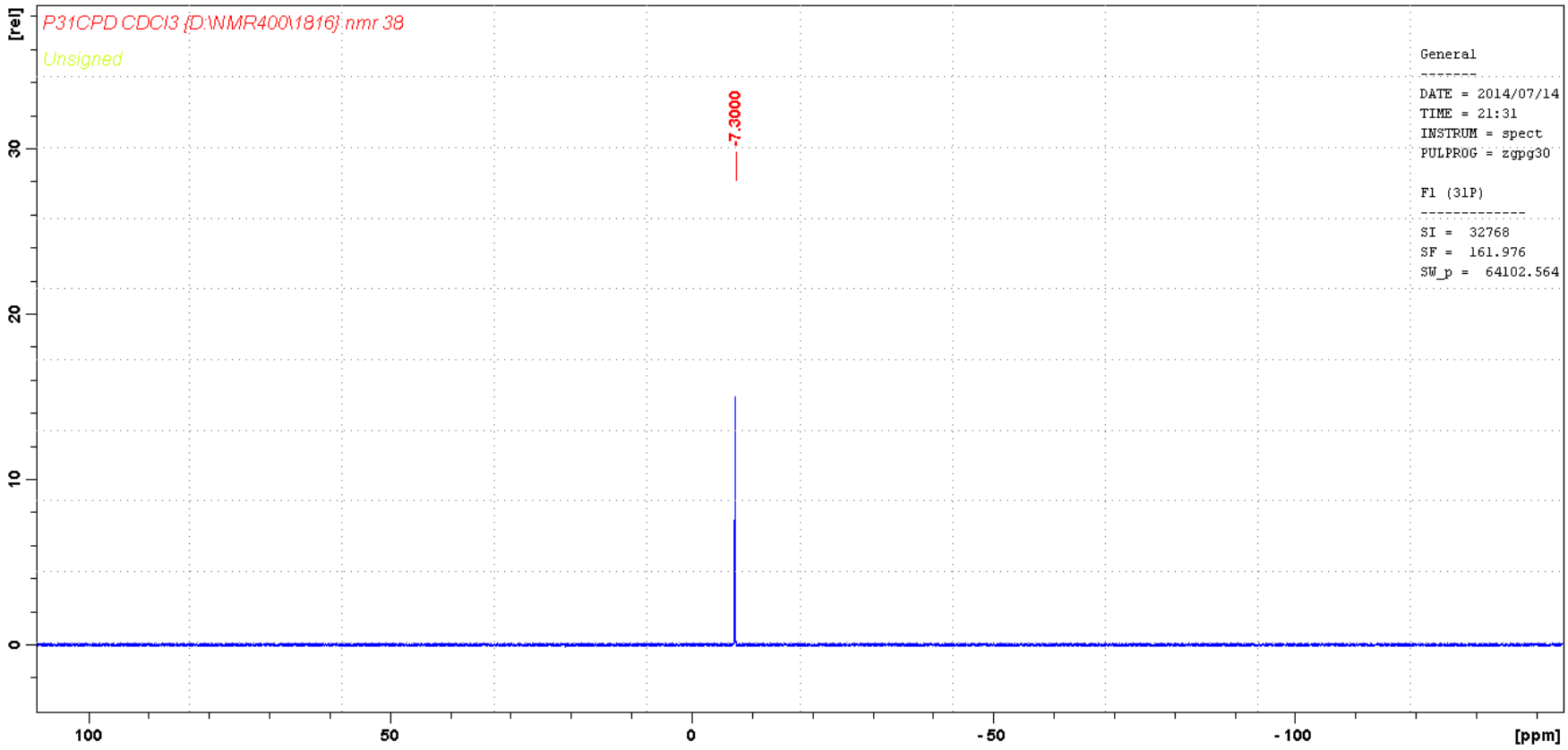
^{1}H NMR spectrum of **2e**



^{13}C NMR spectrum of **2e**



P NMR spectrum of **2e**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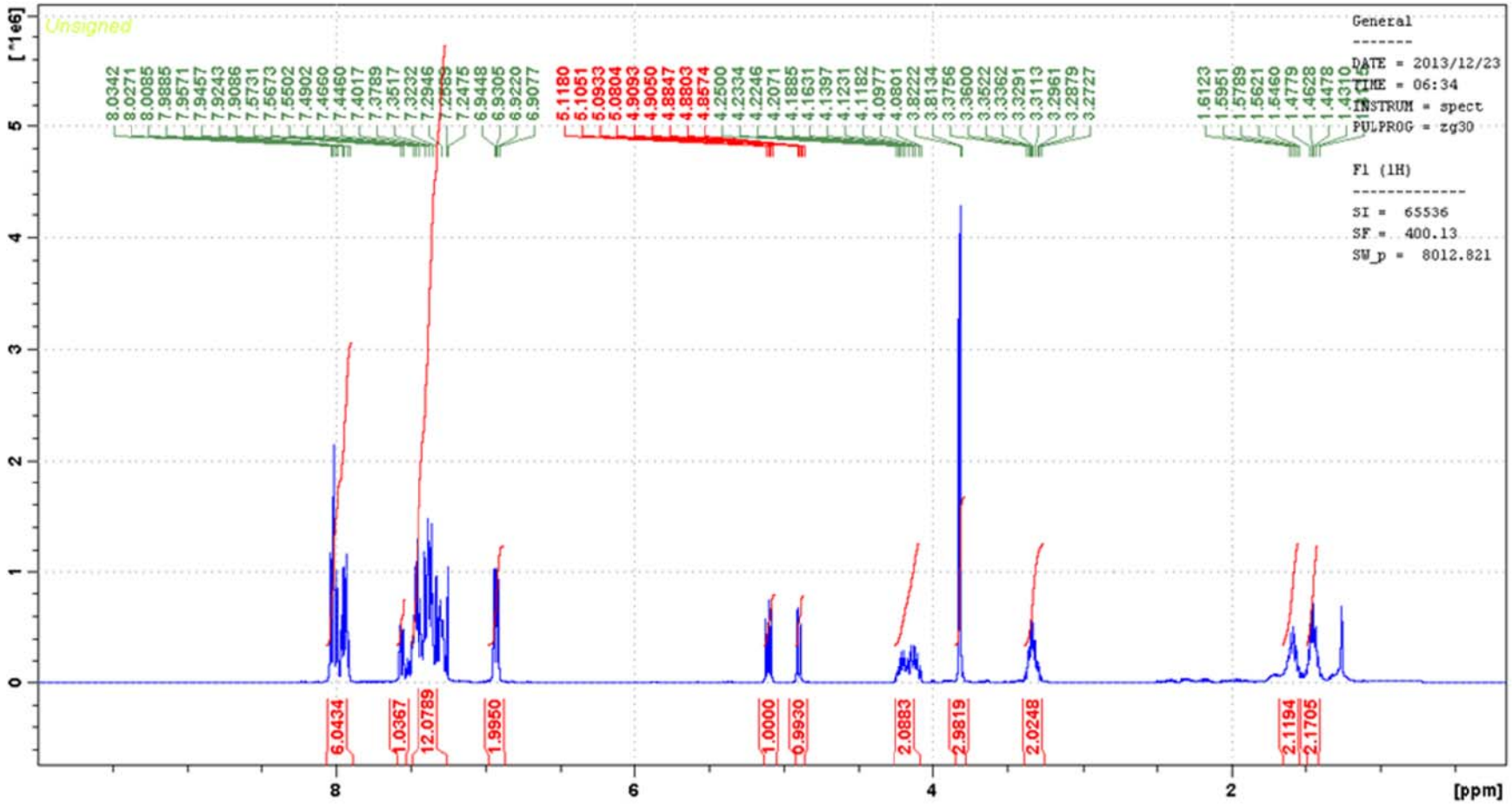
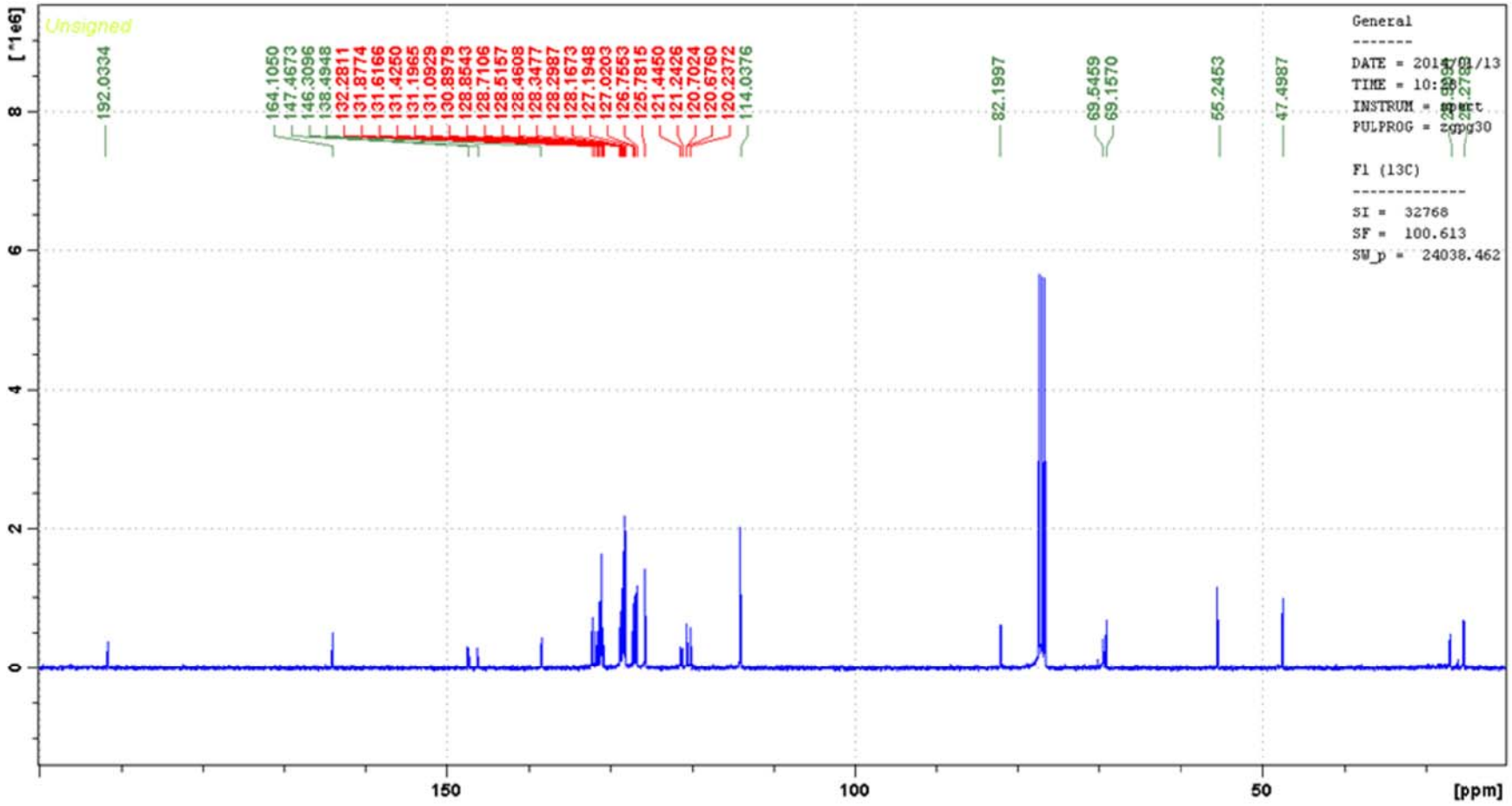
50
0
-50
-100
[ppm]

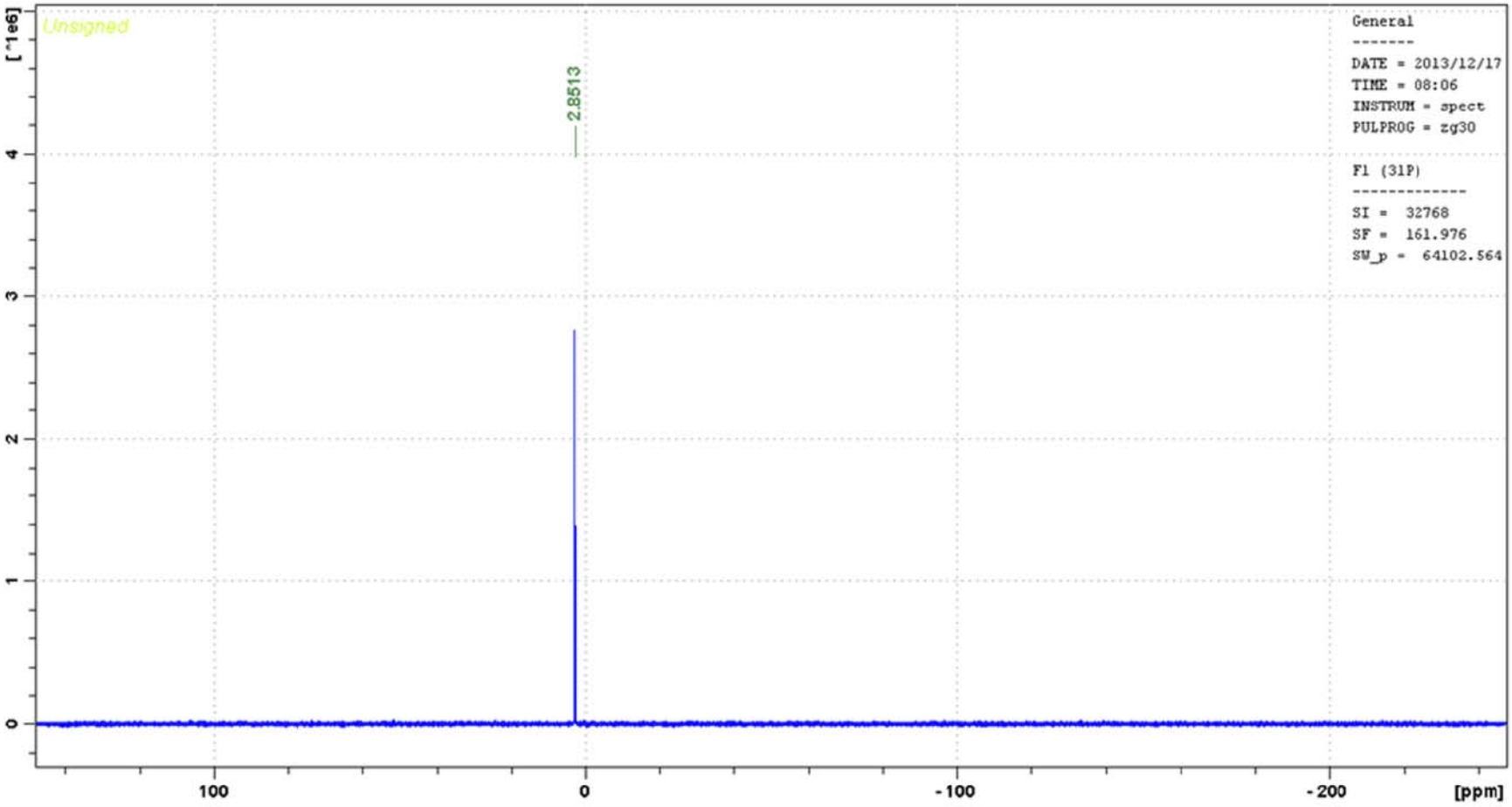
^{1}H NMR spectrum of **2h**



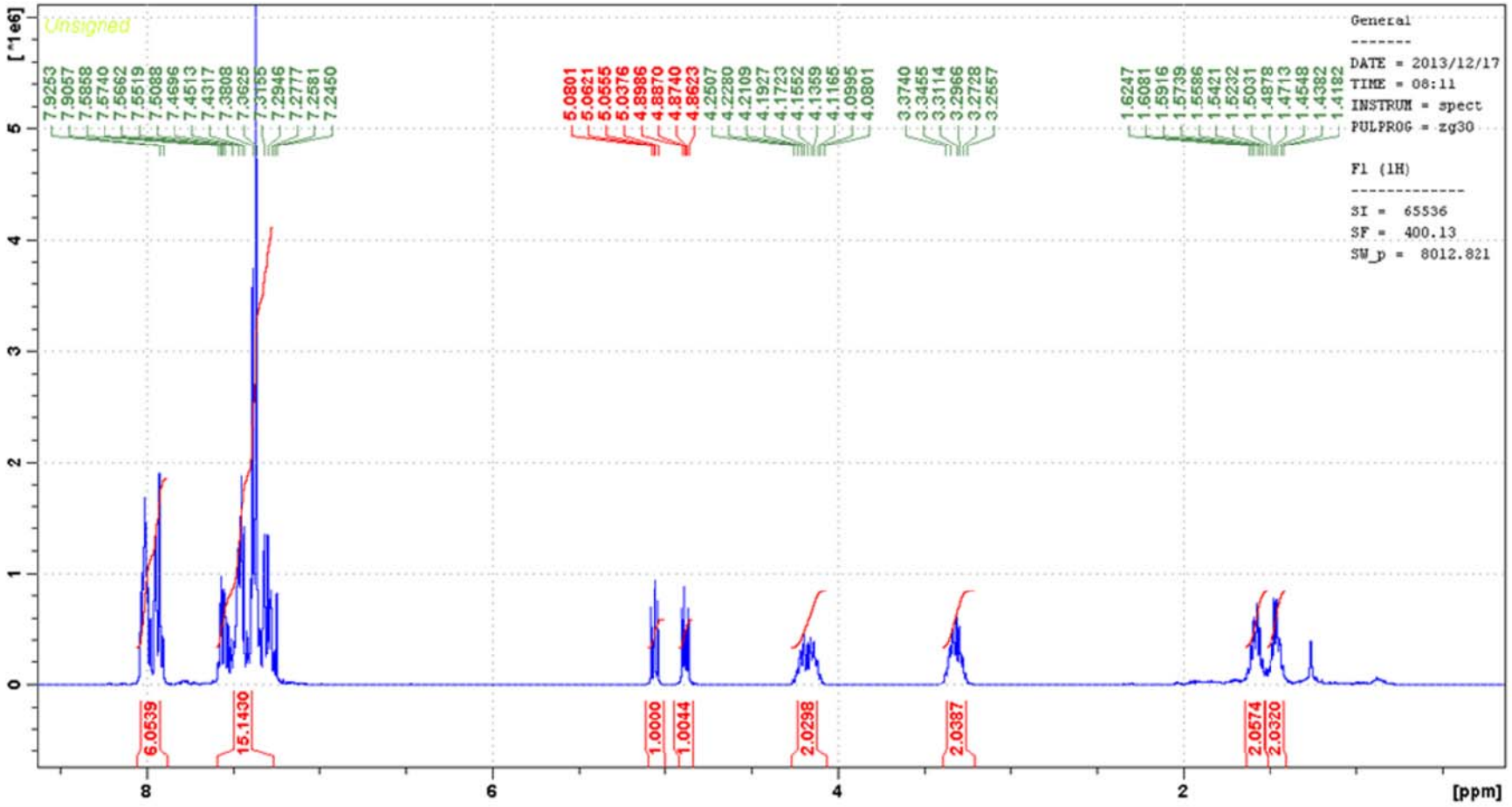
^{13}C NMR spectrum of **2h**



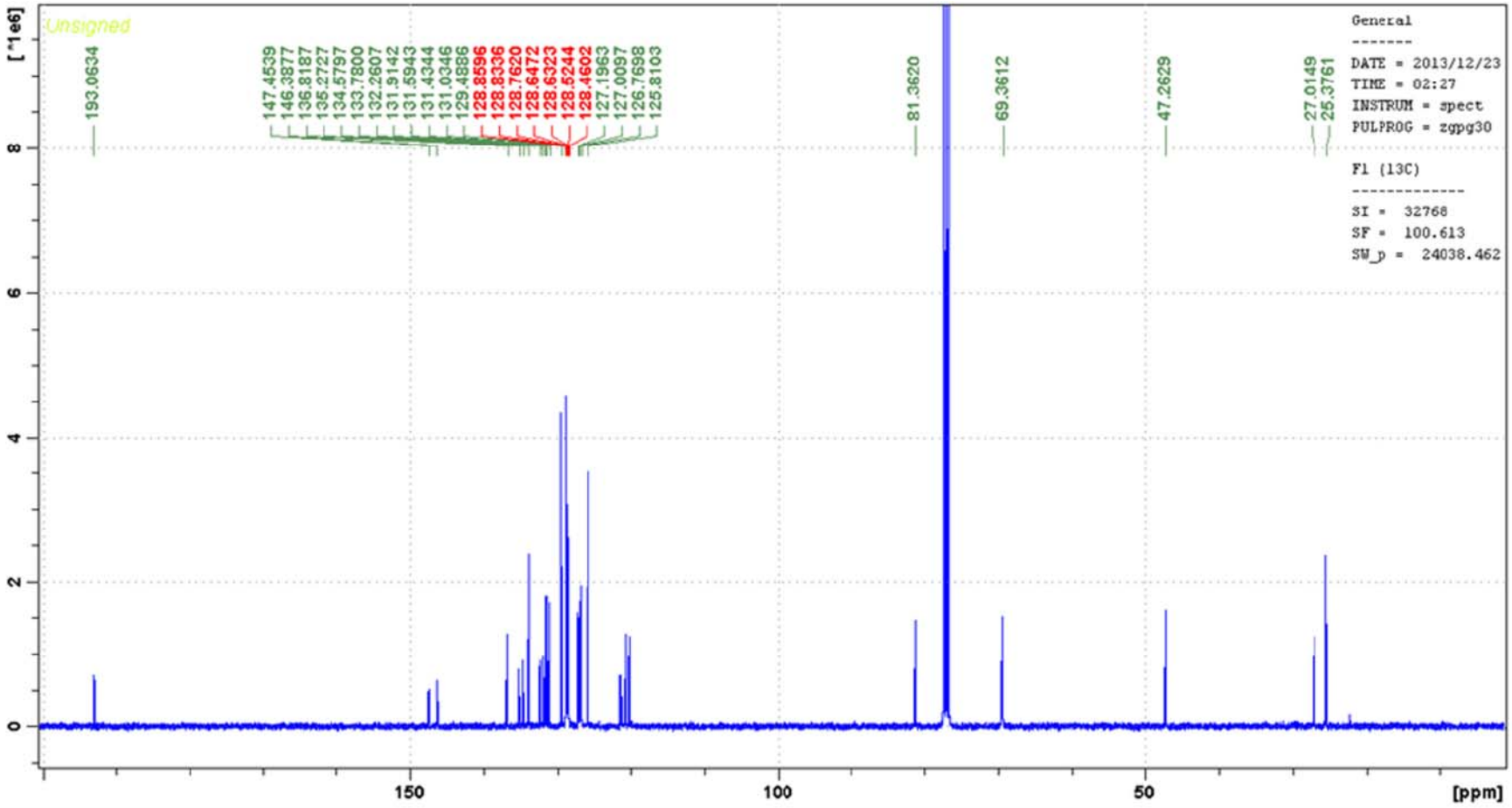
^{31}P NMR spectrum of **2h**



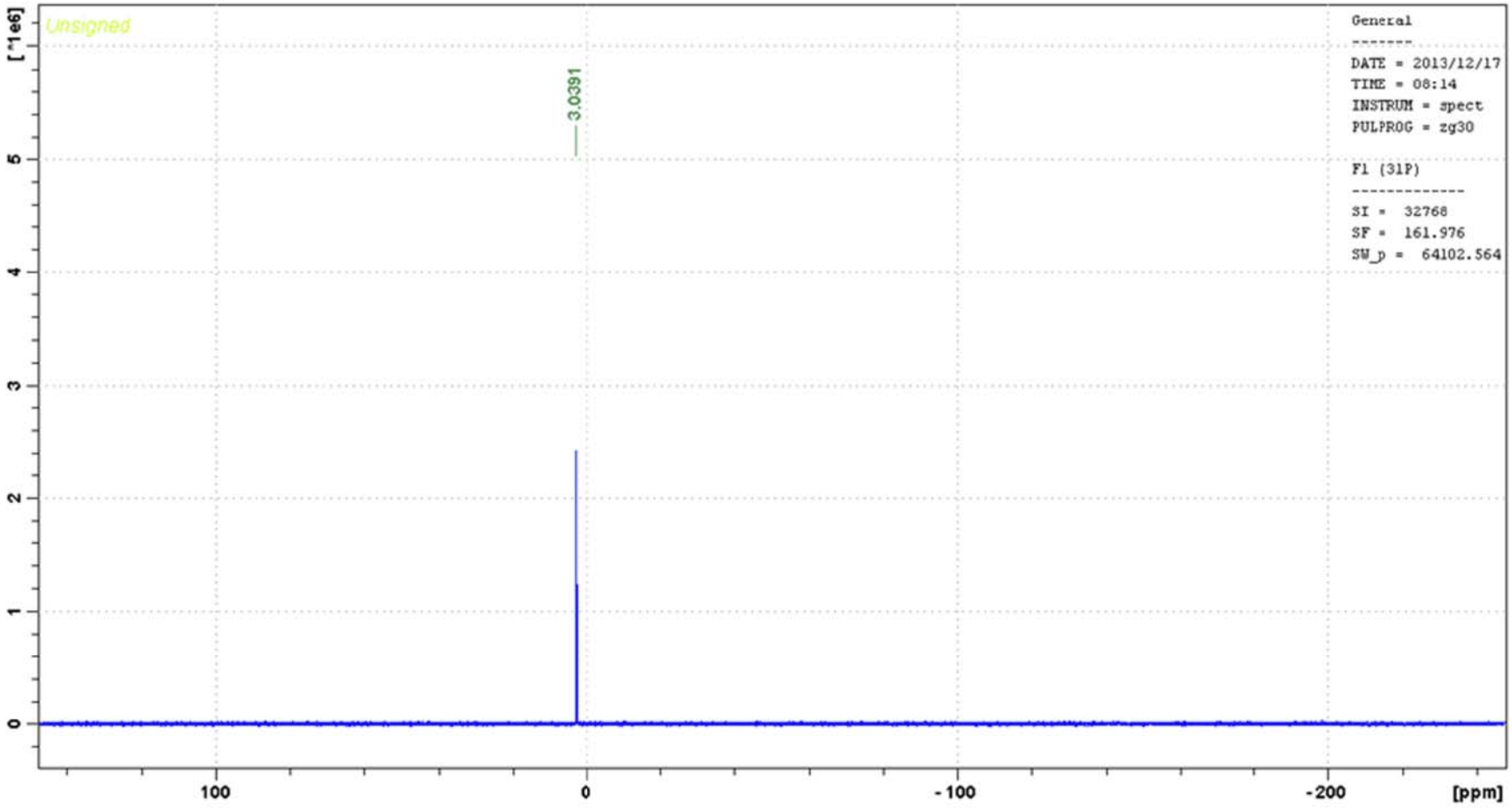
^{1}H NMR spectrum of **2j**



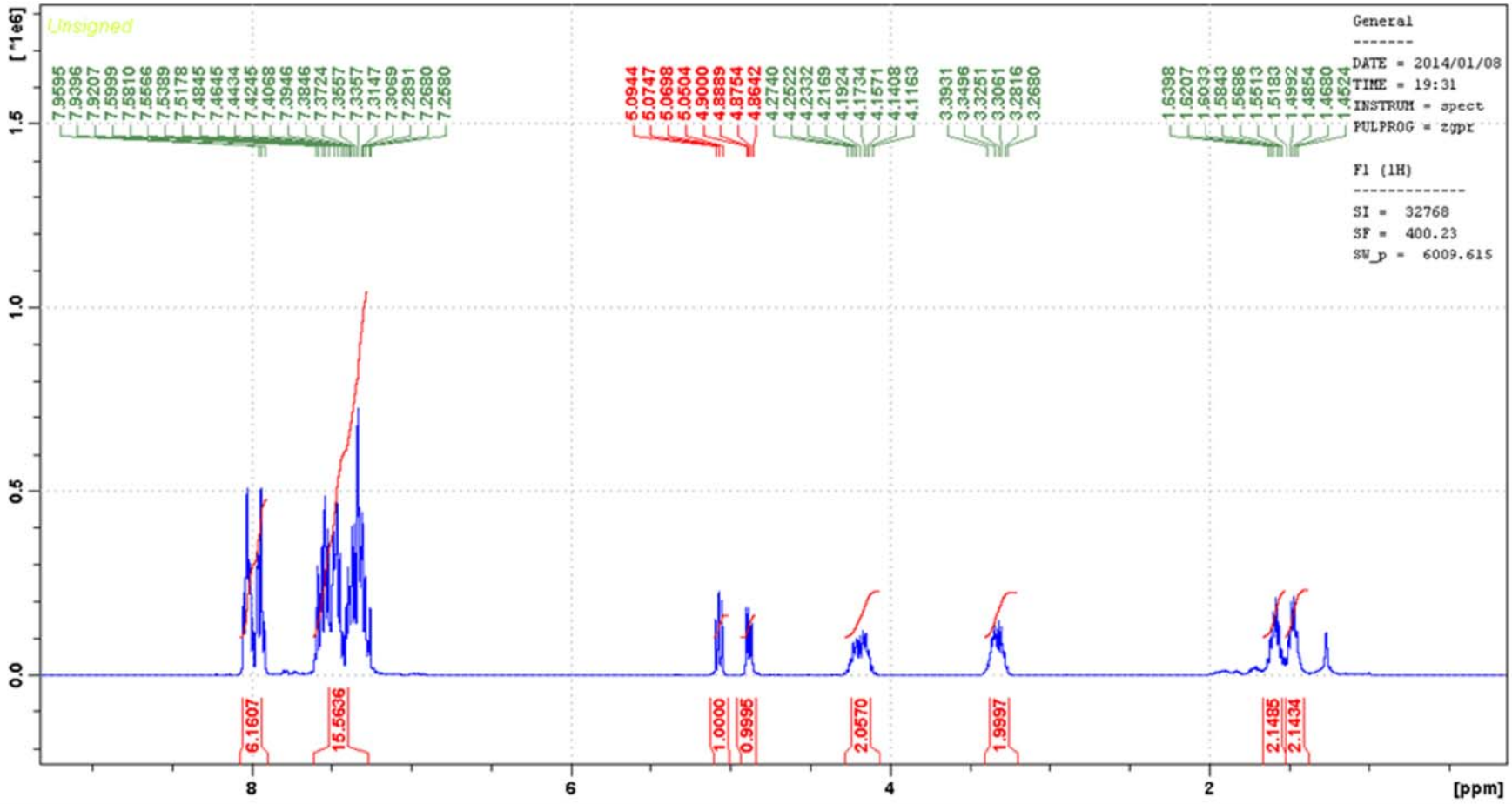
^{13}C NMR spectrum of **2j**



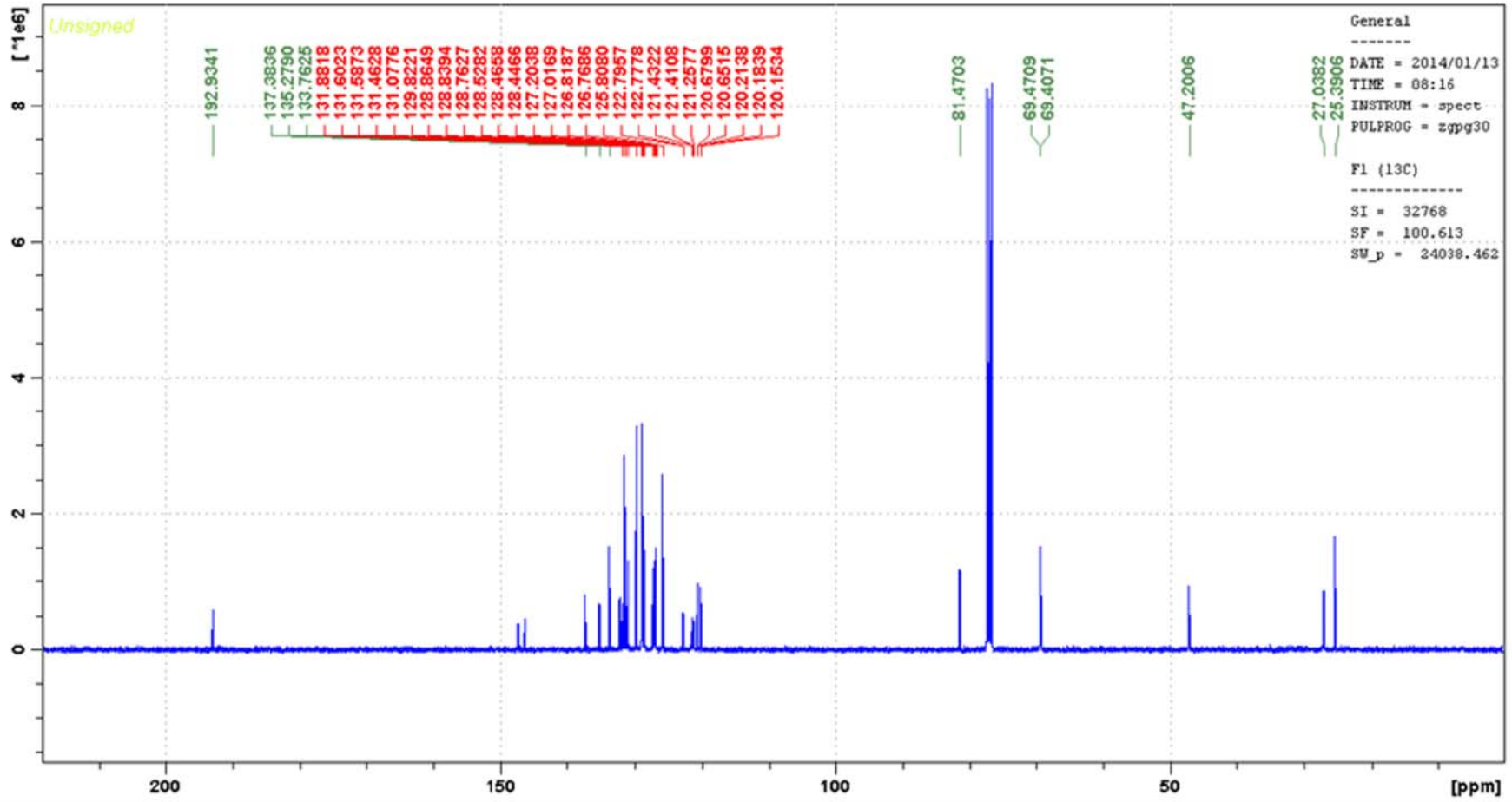
^{31}P NMR spectrum of **2j**



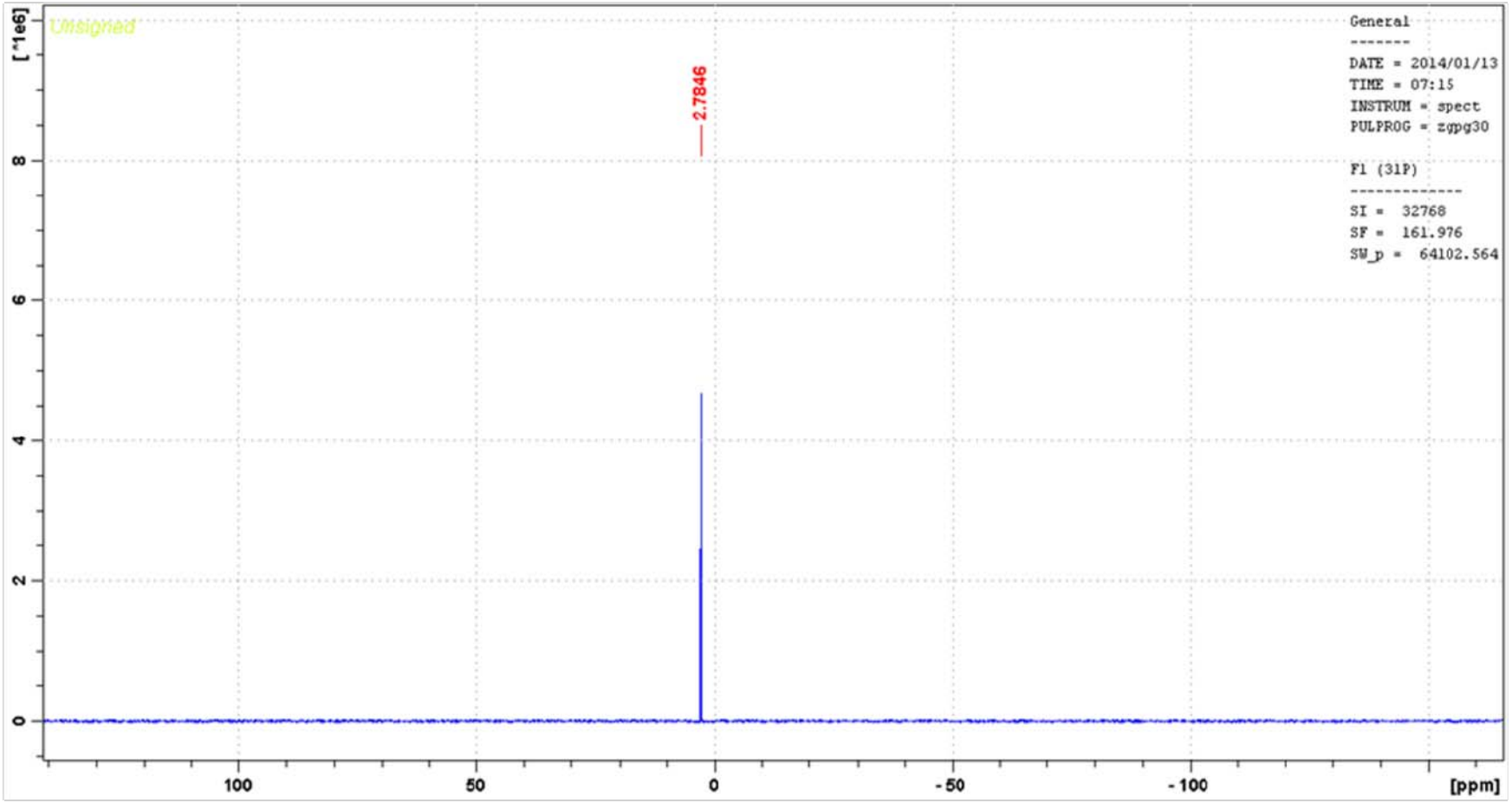
^{1}H NMR spectrum of **2k**



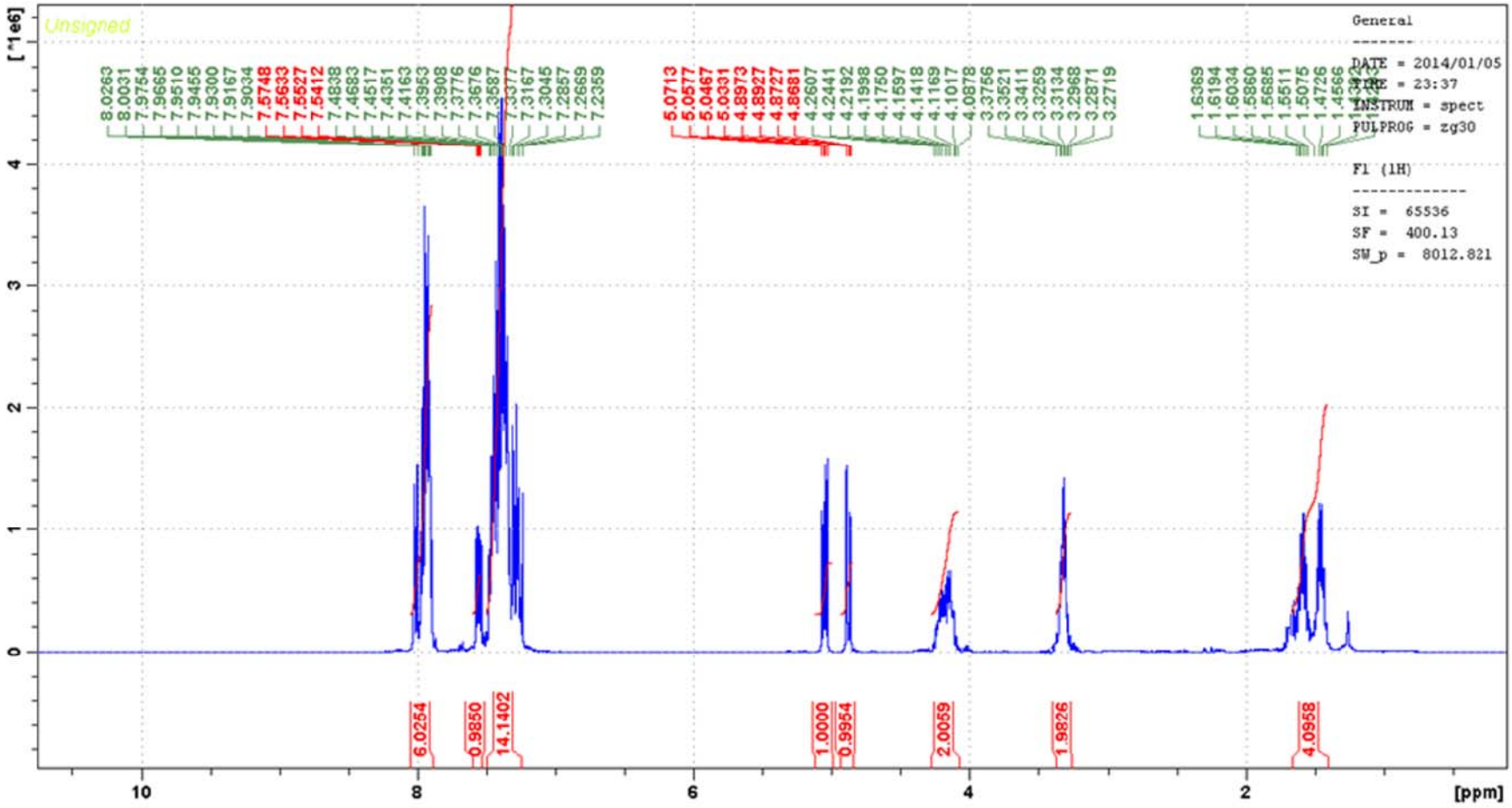
^{13}C NMR spectrum of **2k**



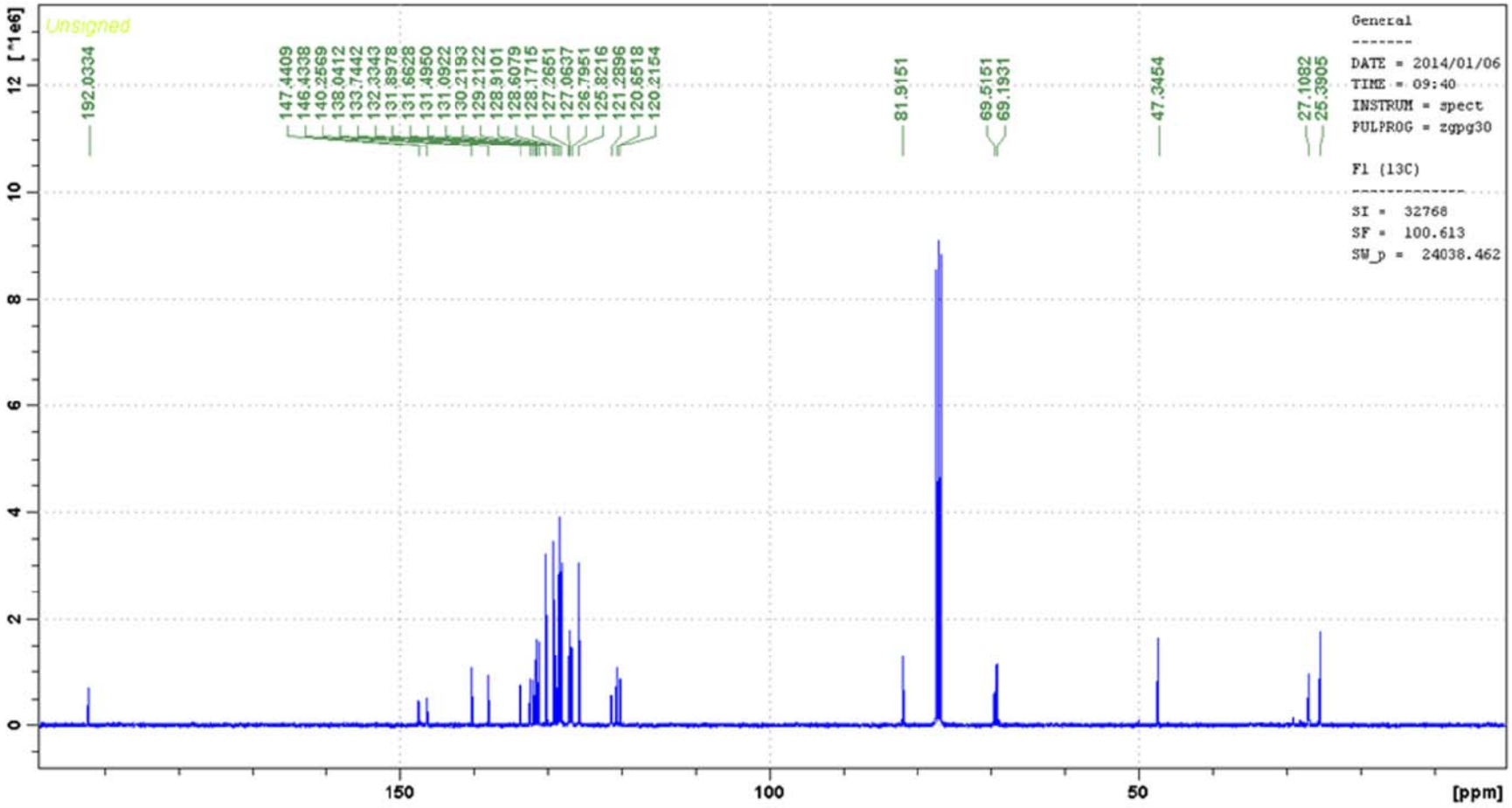
^{31}P NMR spectrum of **2k**



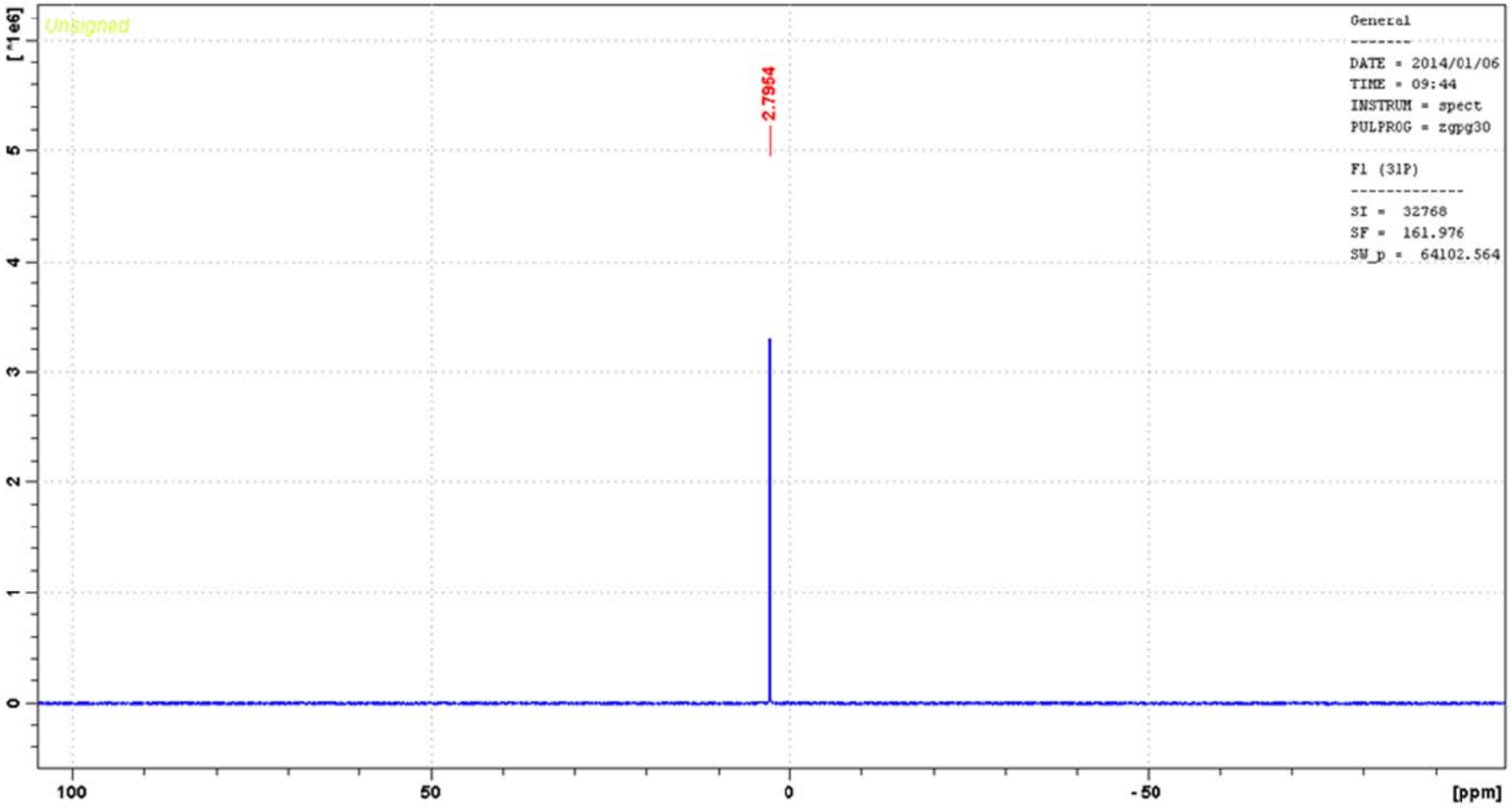
^{1}H NMR spectrum of **2l**



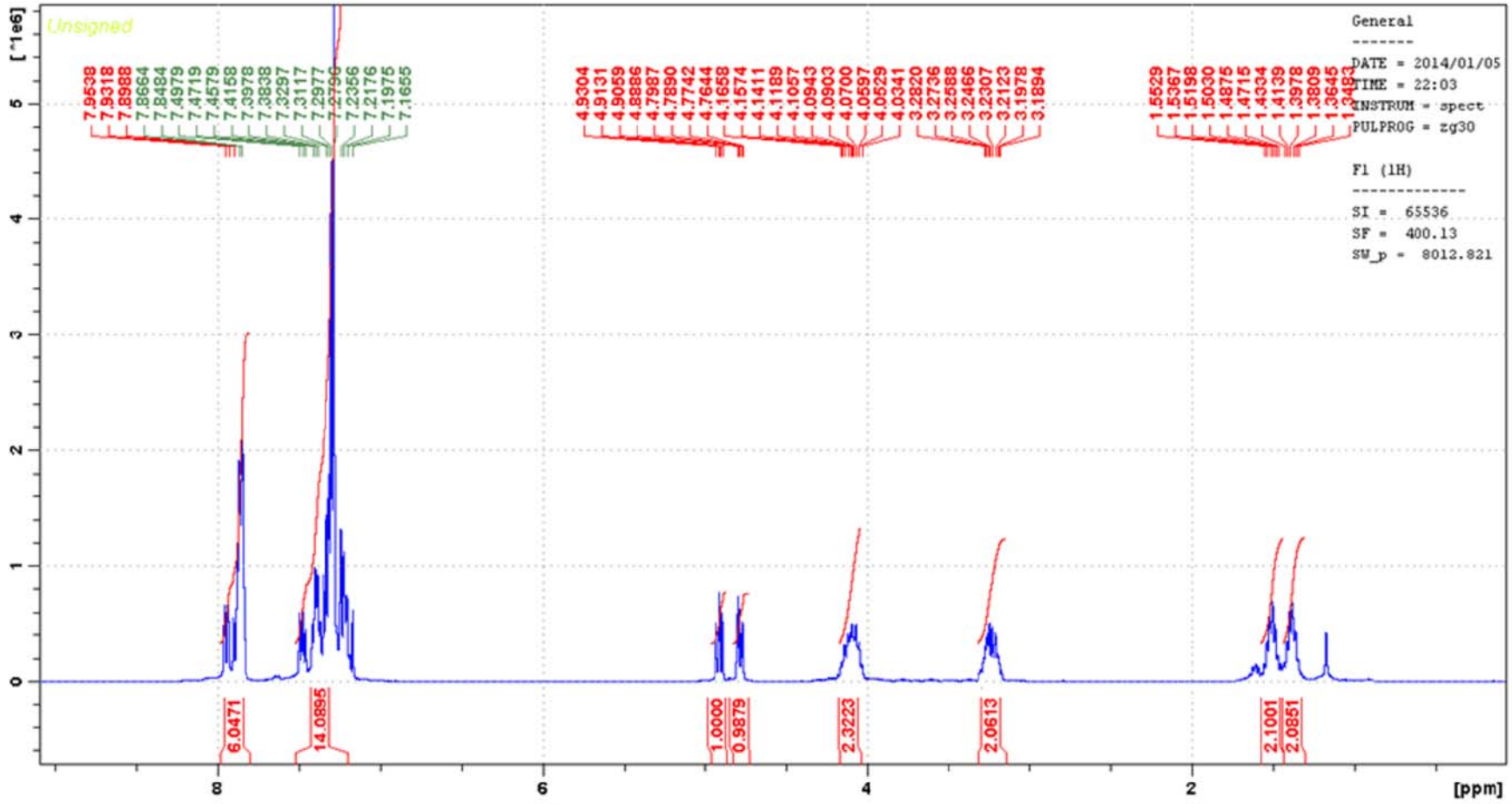
^{13}C NMR spectrum of **2l**



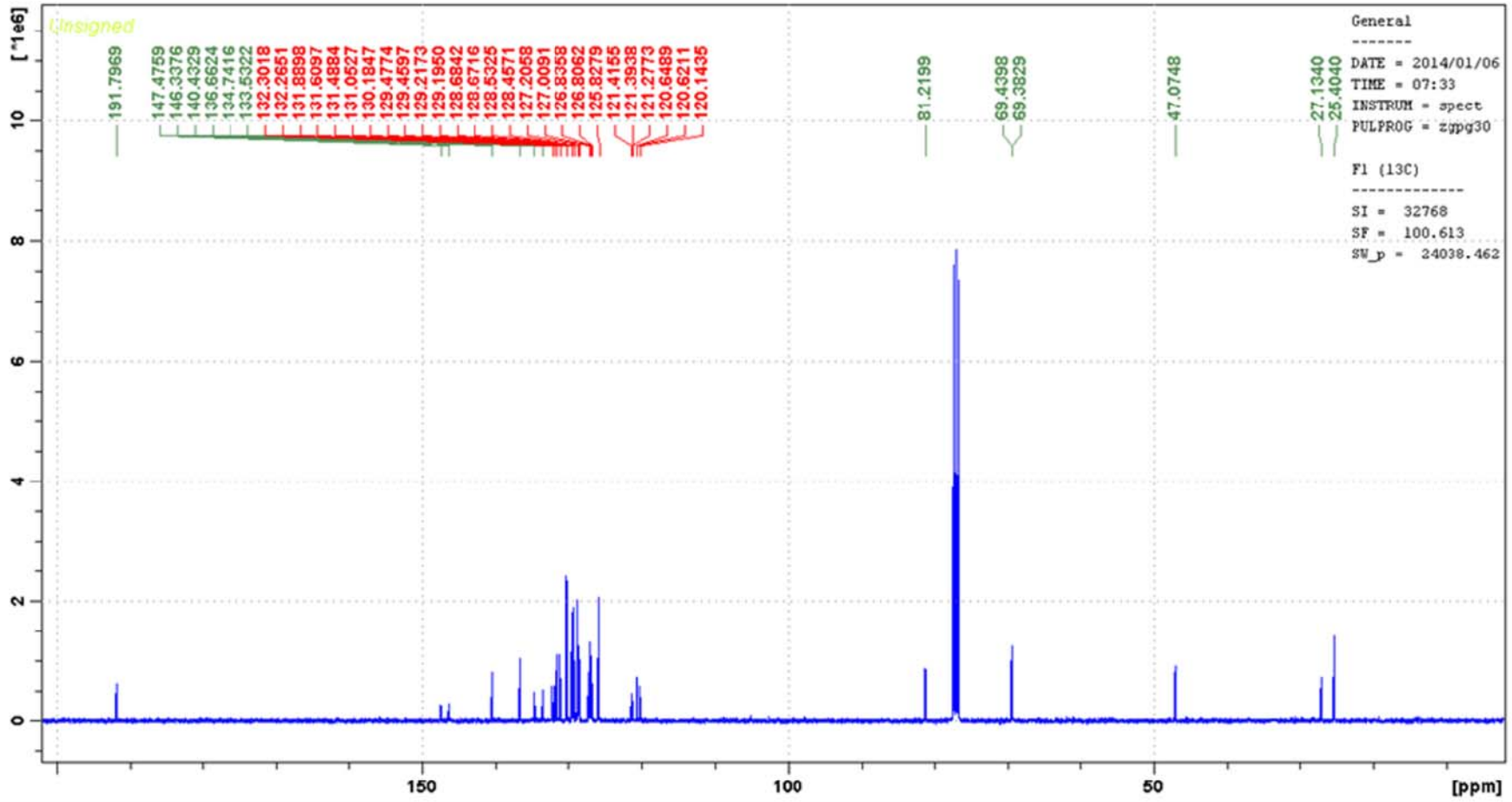
^{31}P NMR spectrum of **2l**



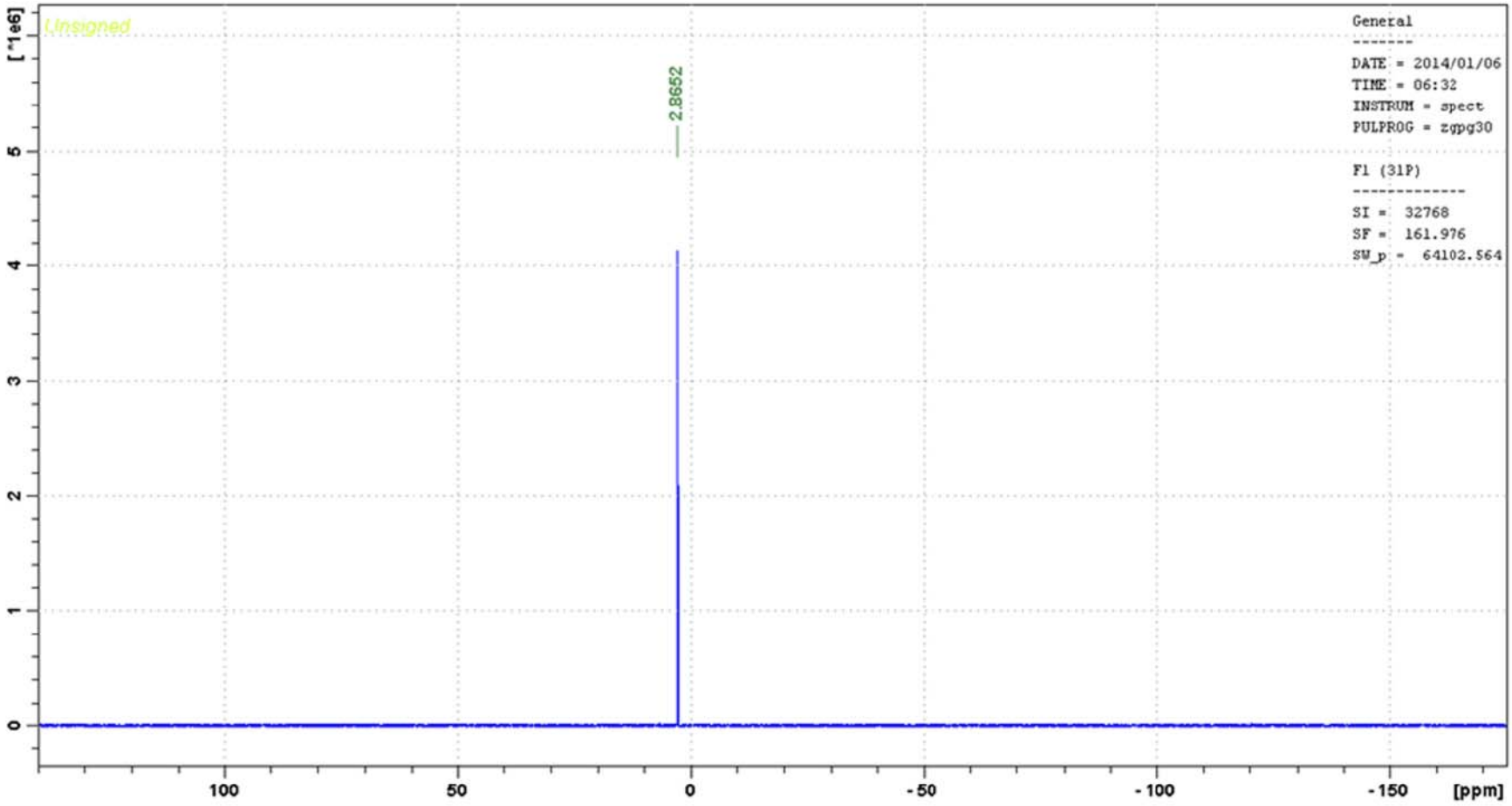
^{1}H NMR spectrum of **2m**



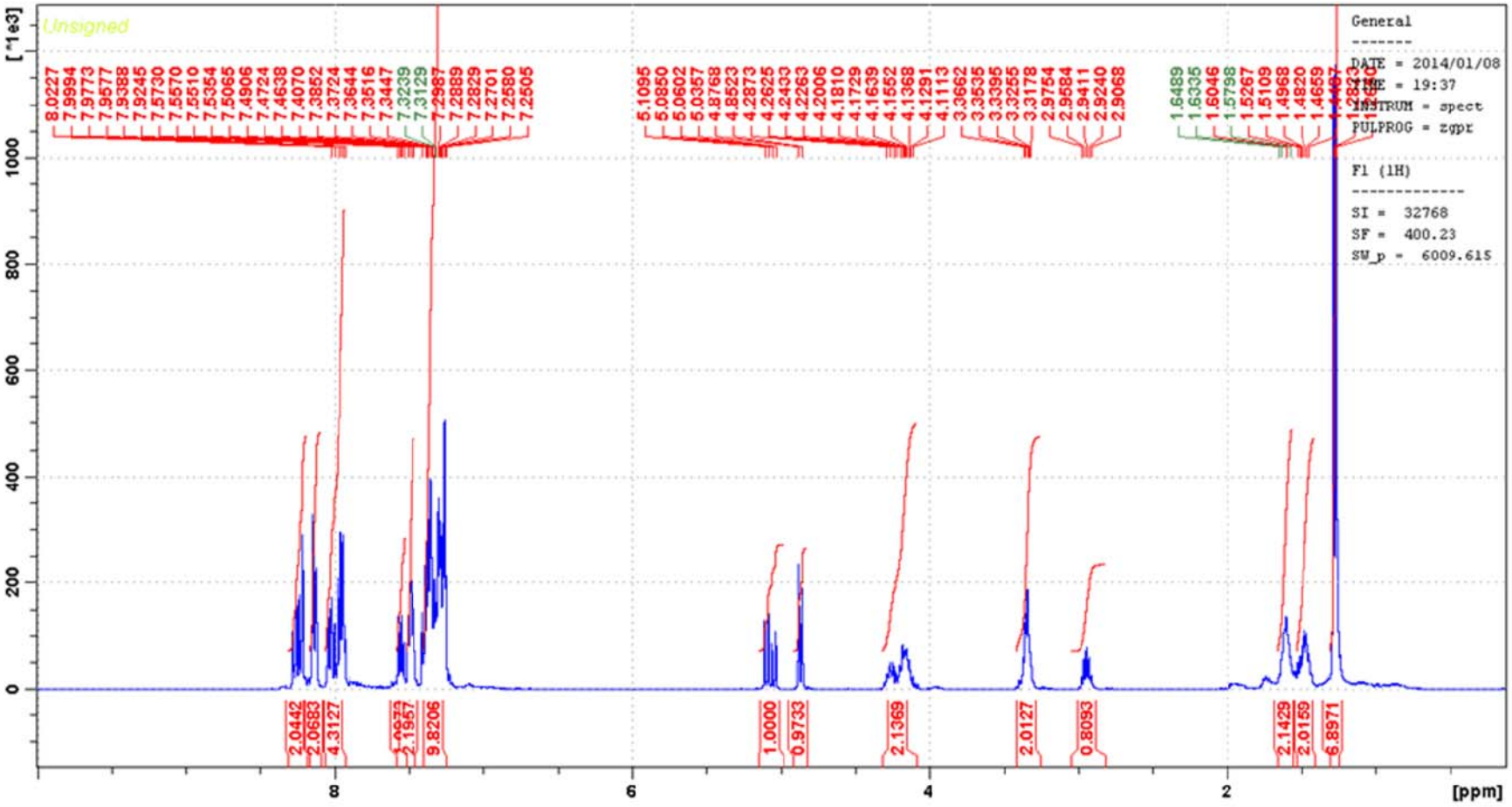
^{13}C NMR spectrum of **2m**



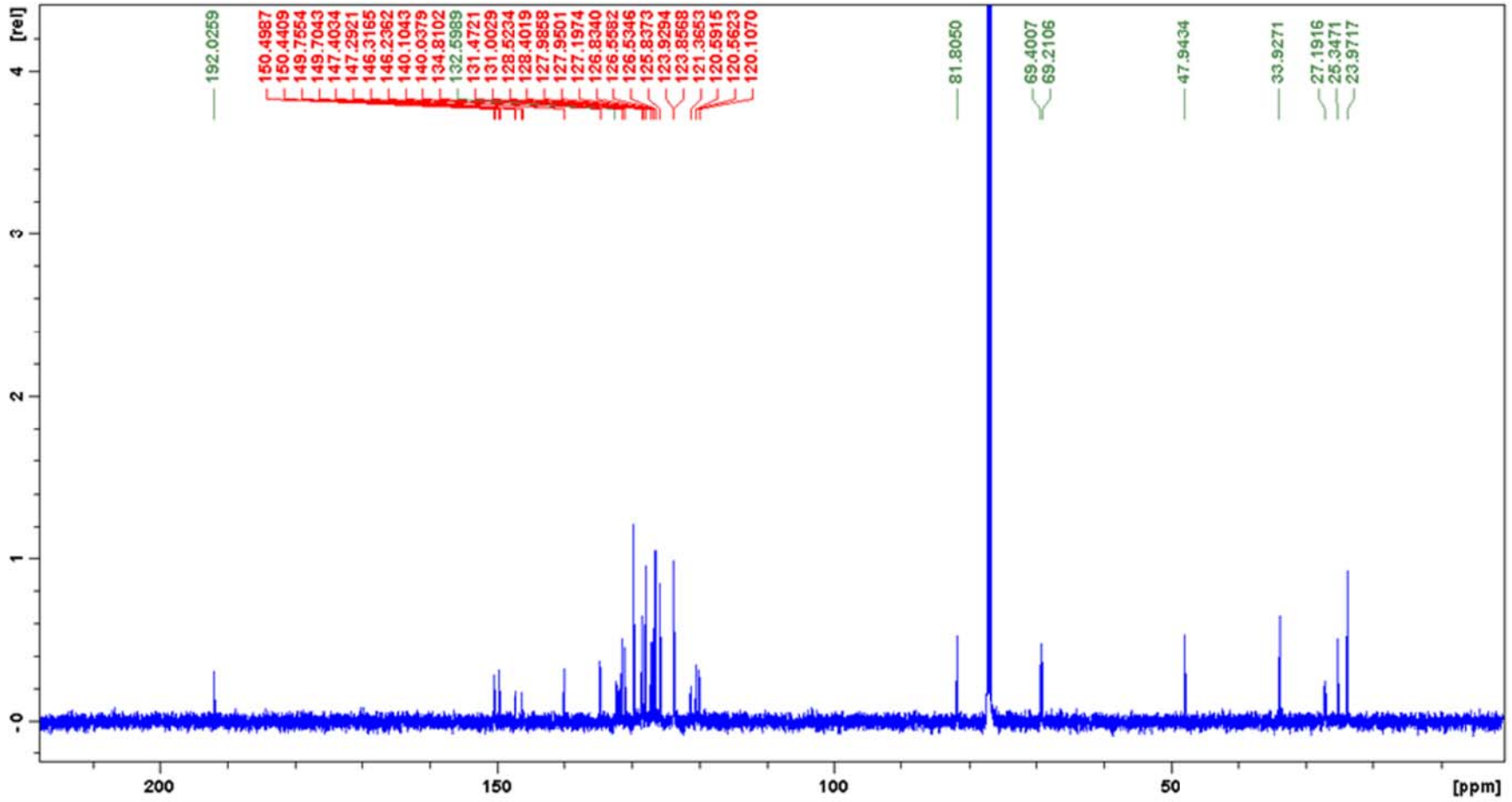
^{31}P NMR spectrum of **2m**



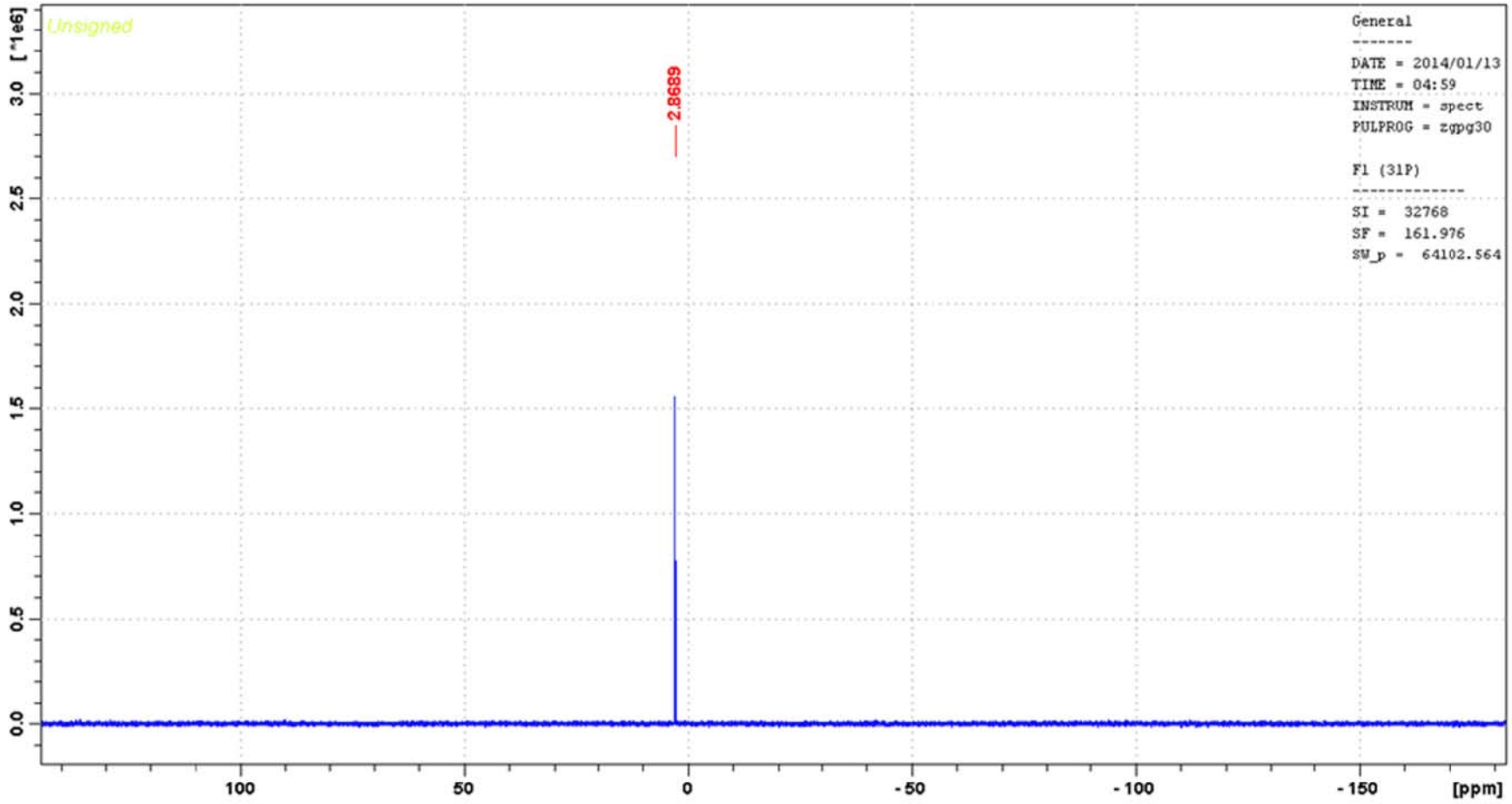
^{1}H NMR spectrum of **2o**



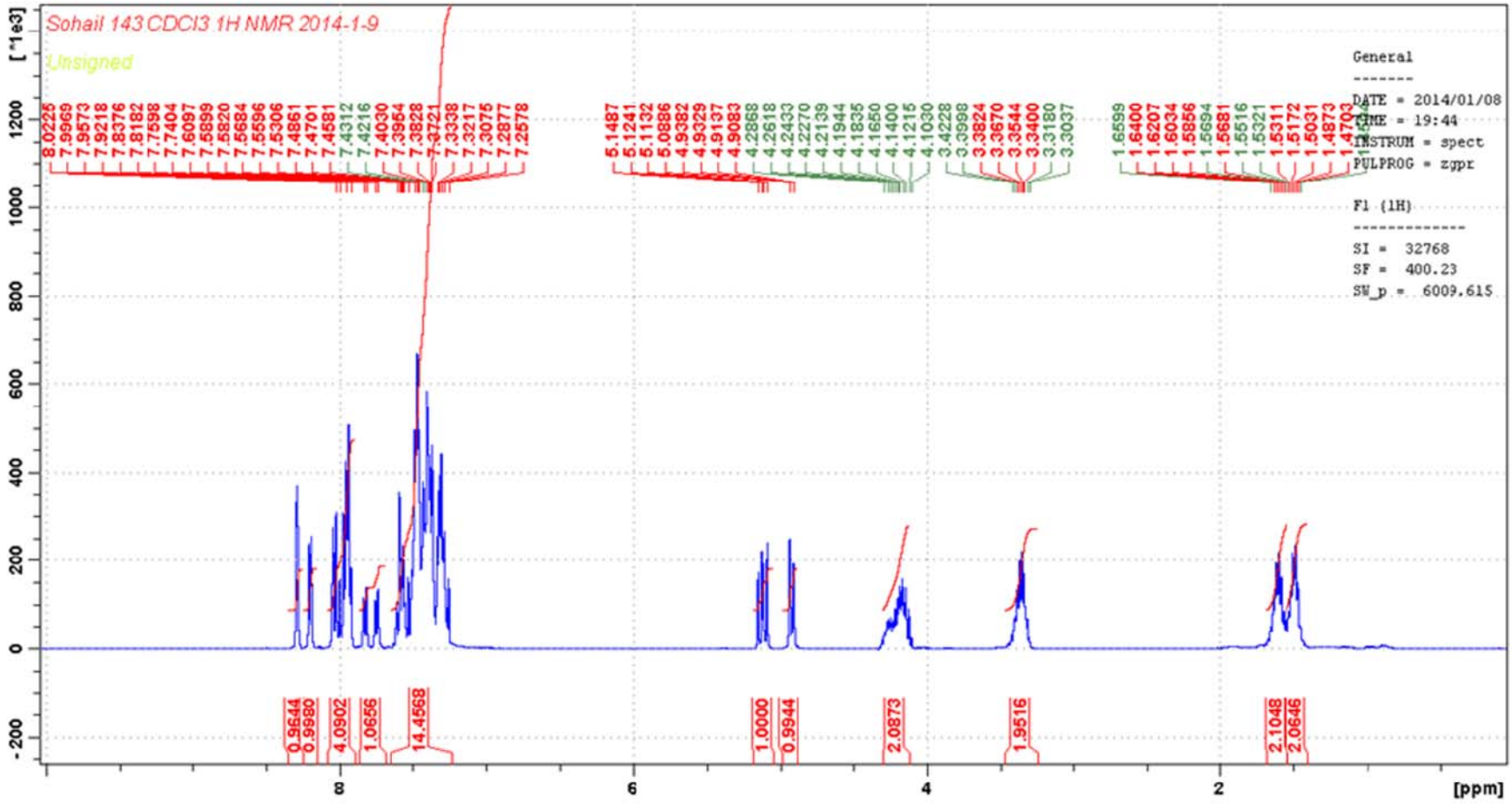
^{13}C NMR spectrum of **2o**



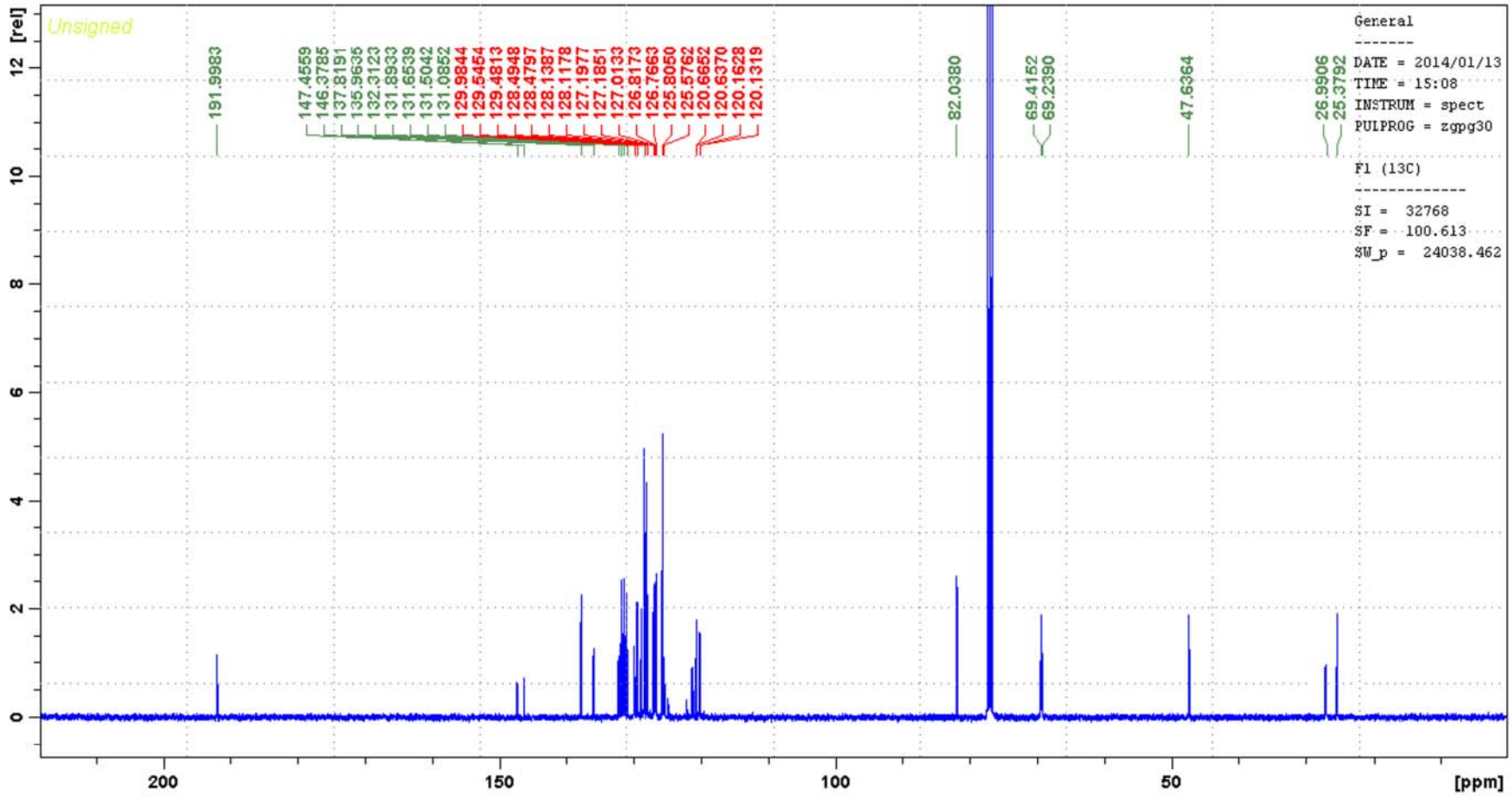
^{31}P NMR spectrum of **2o**



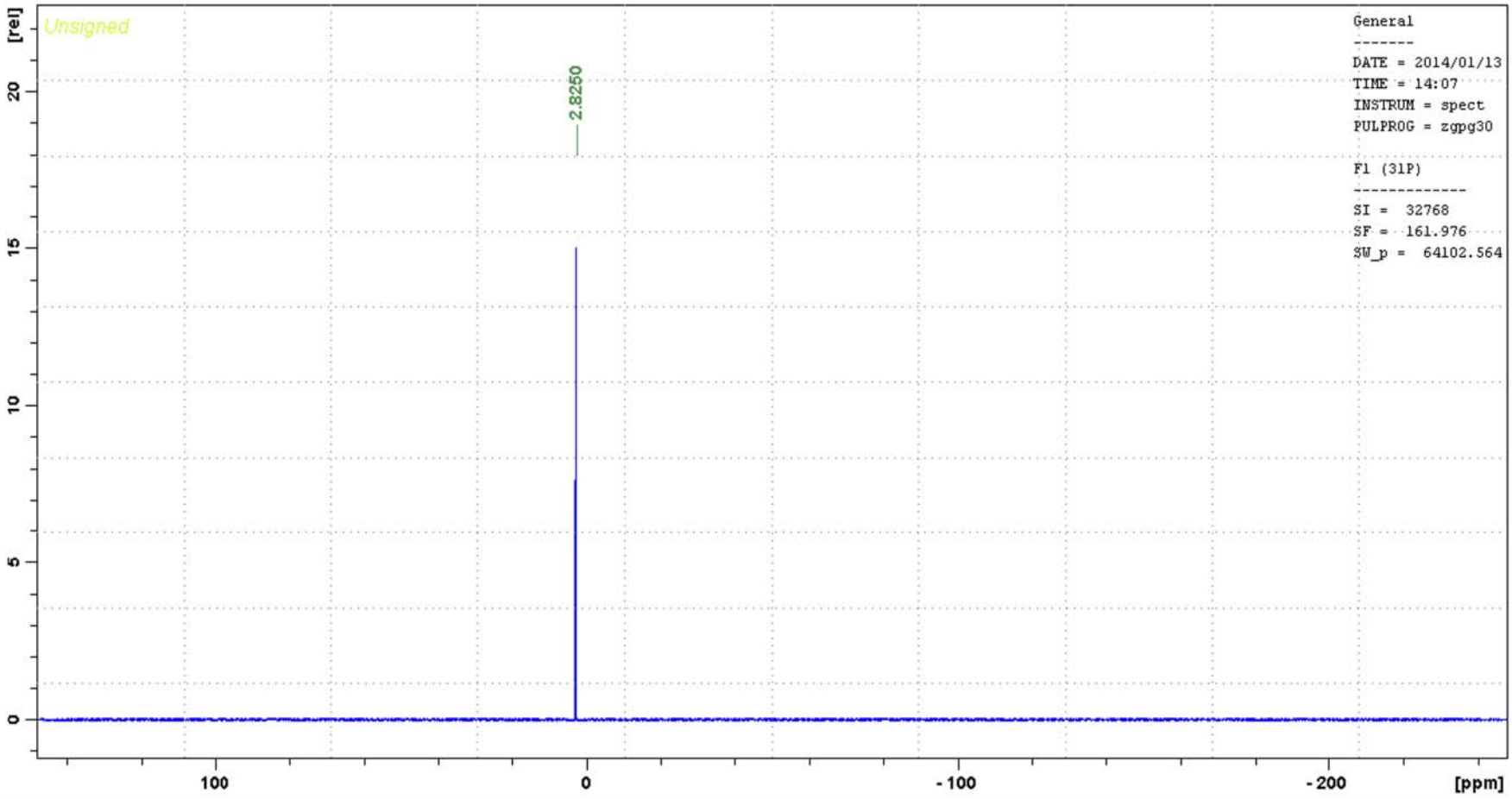
^{1}H NMR spectrum of **2p**



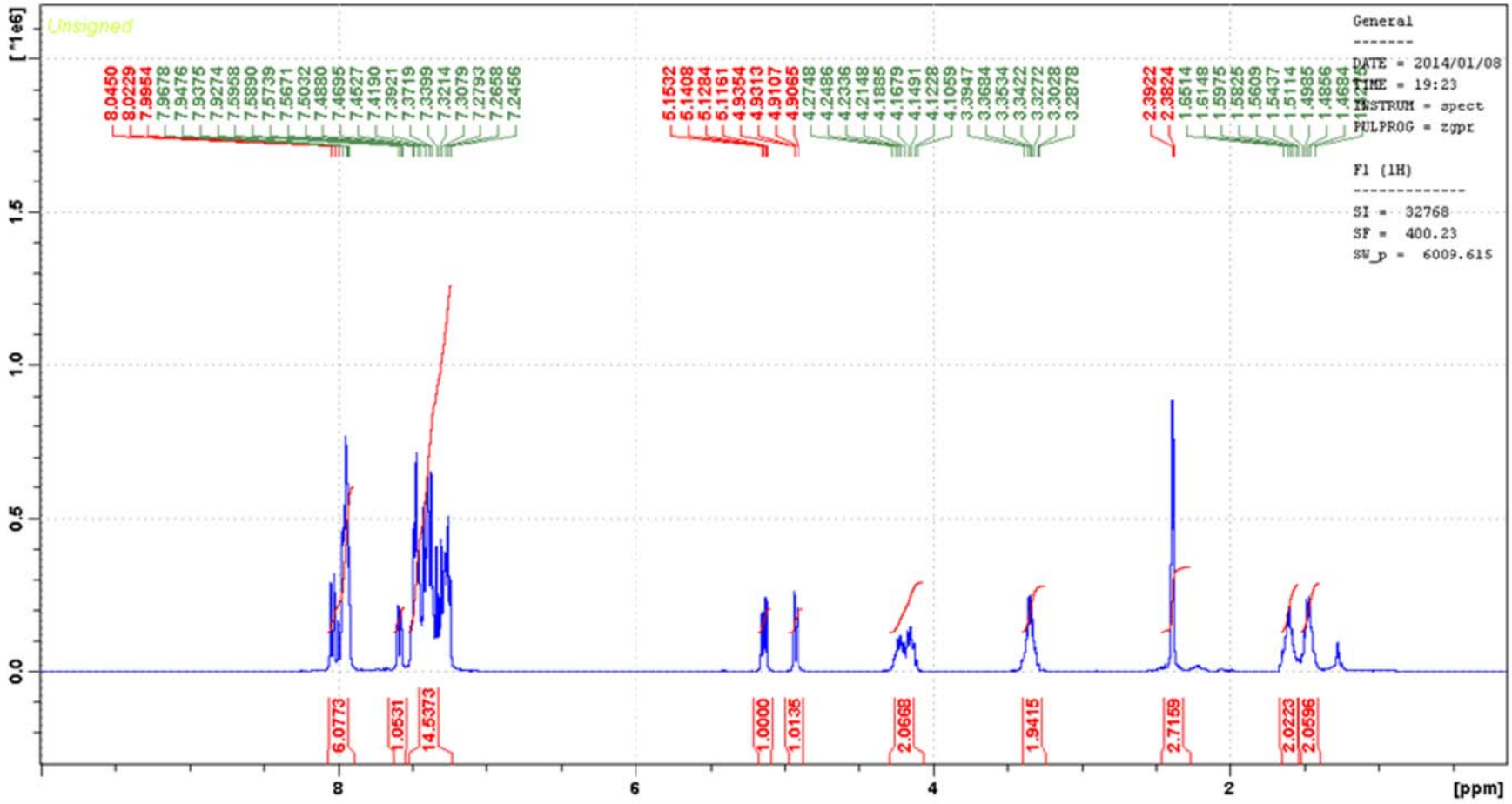
^{13}C NMR spectrum of **2p**



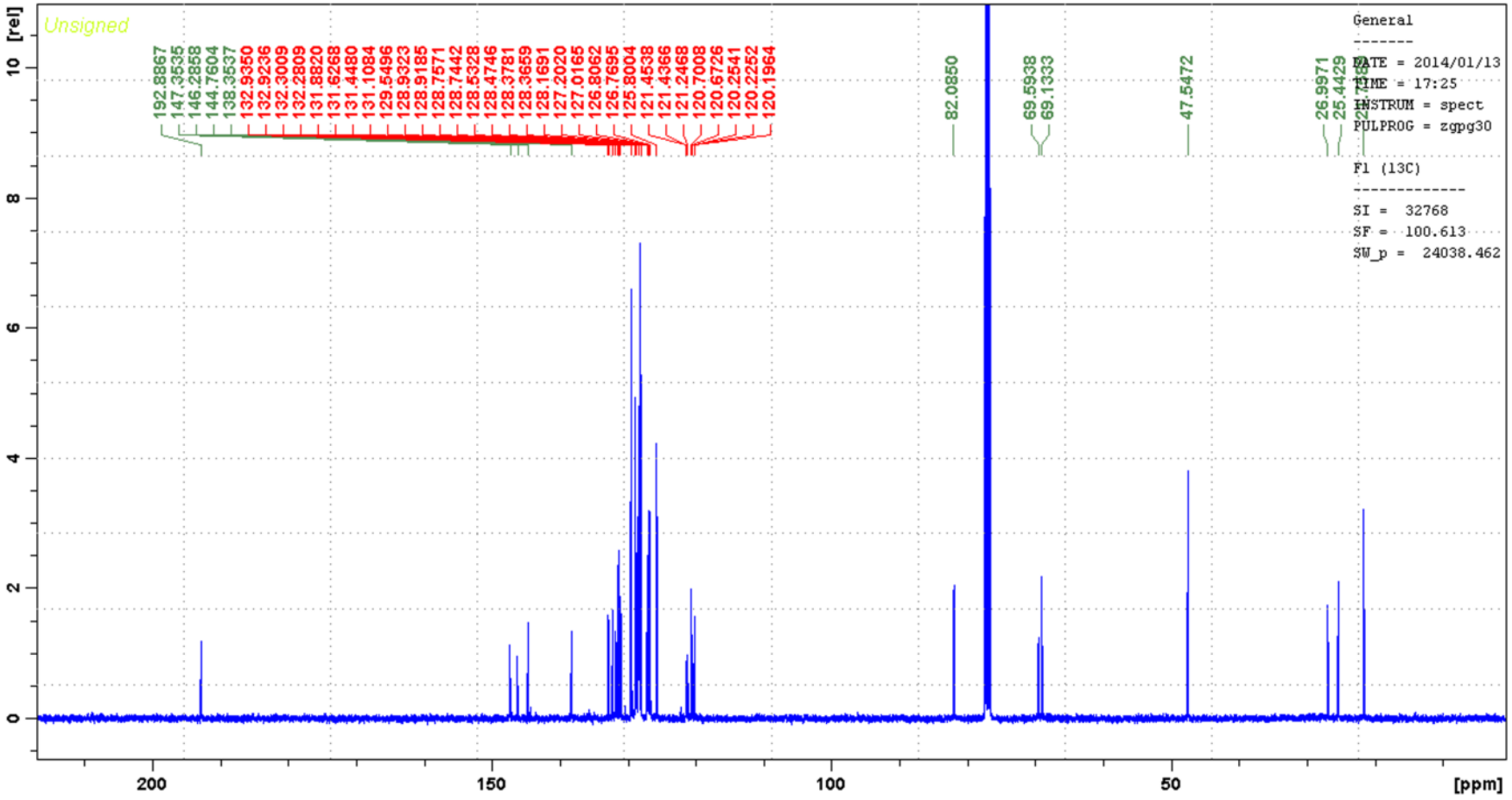
^{31}P NMR spectrum of **2p**



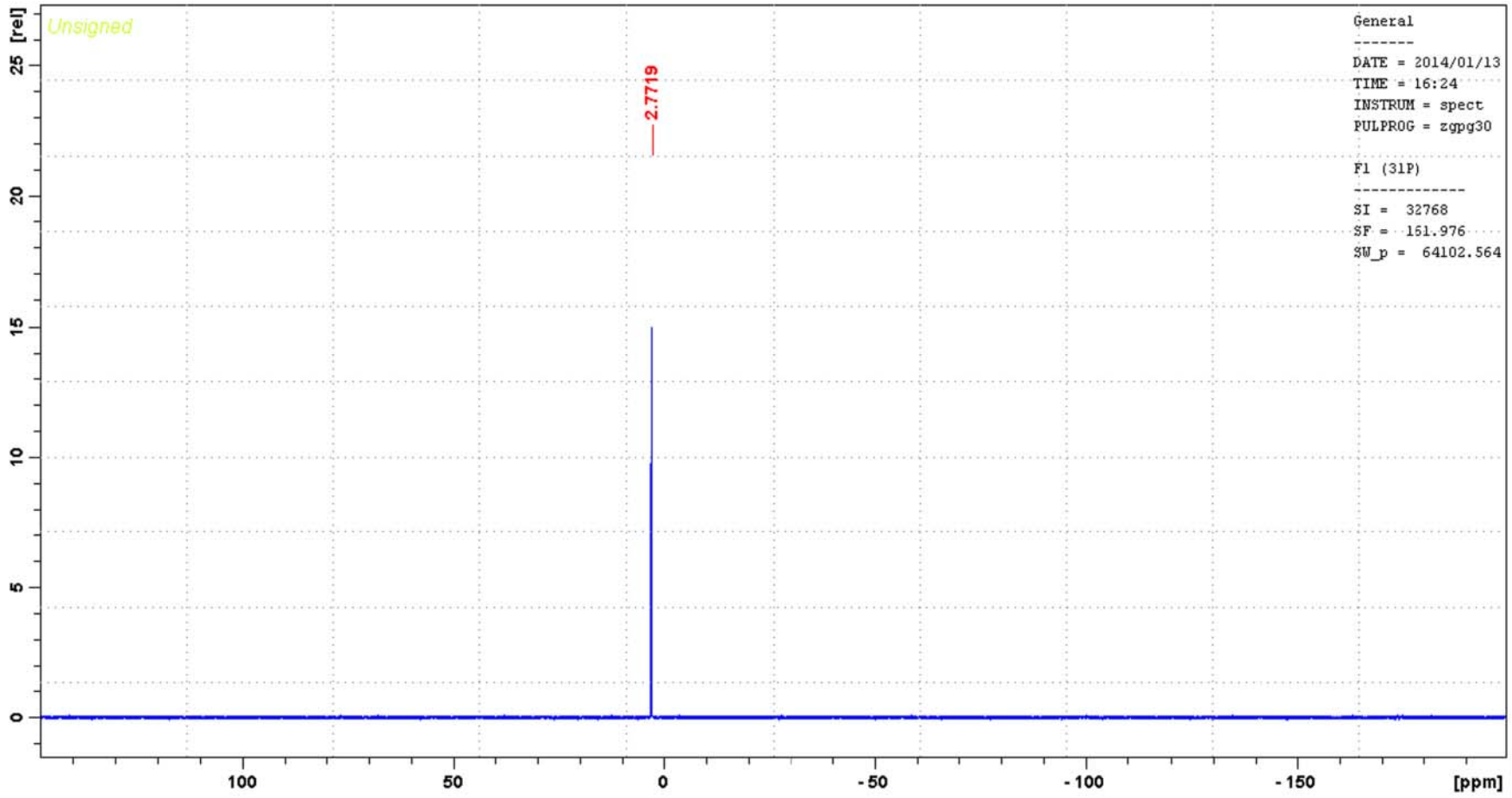
^{1}H NMR spectrum of **2q**



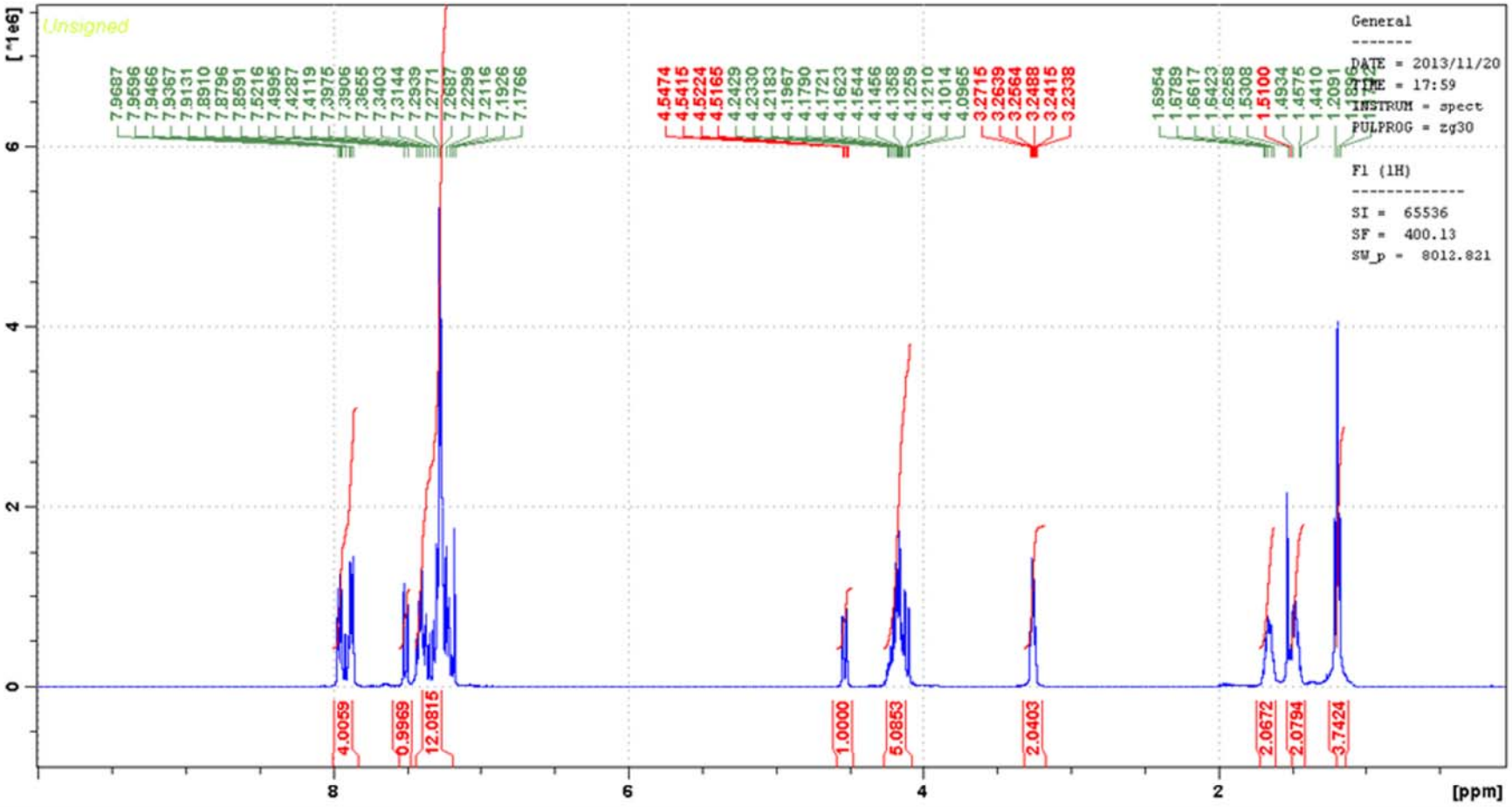
^{13}C NMR spectrum of **2q**



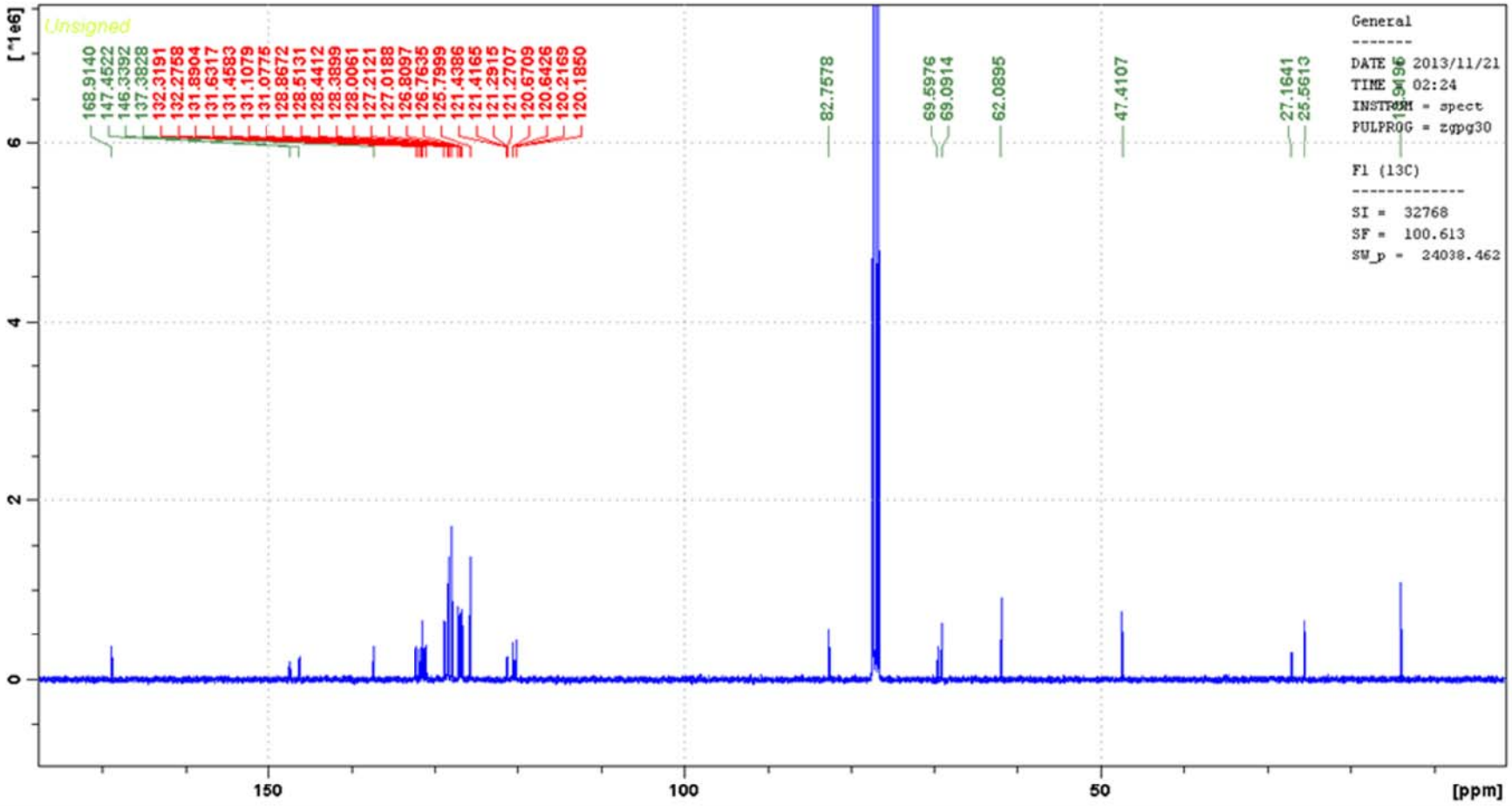
^{31}P NMR spectrum of **2q**



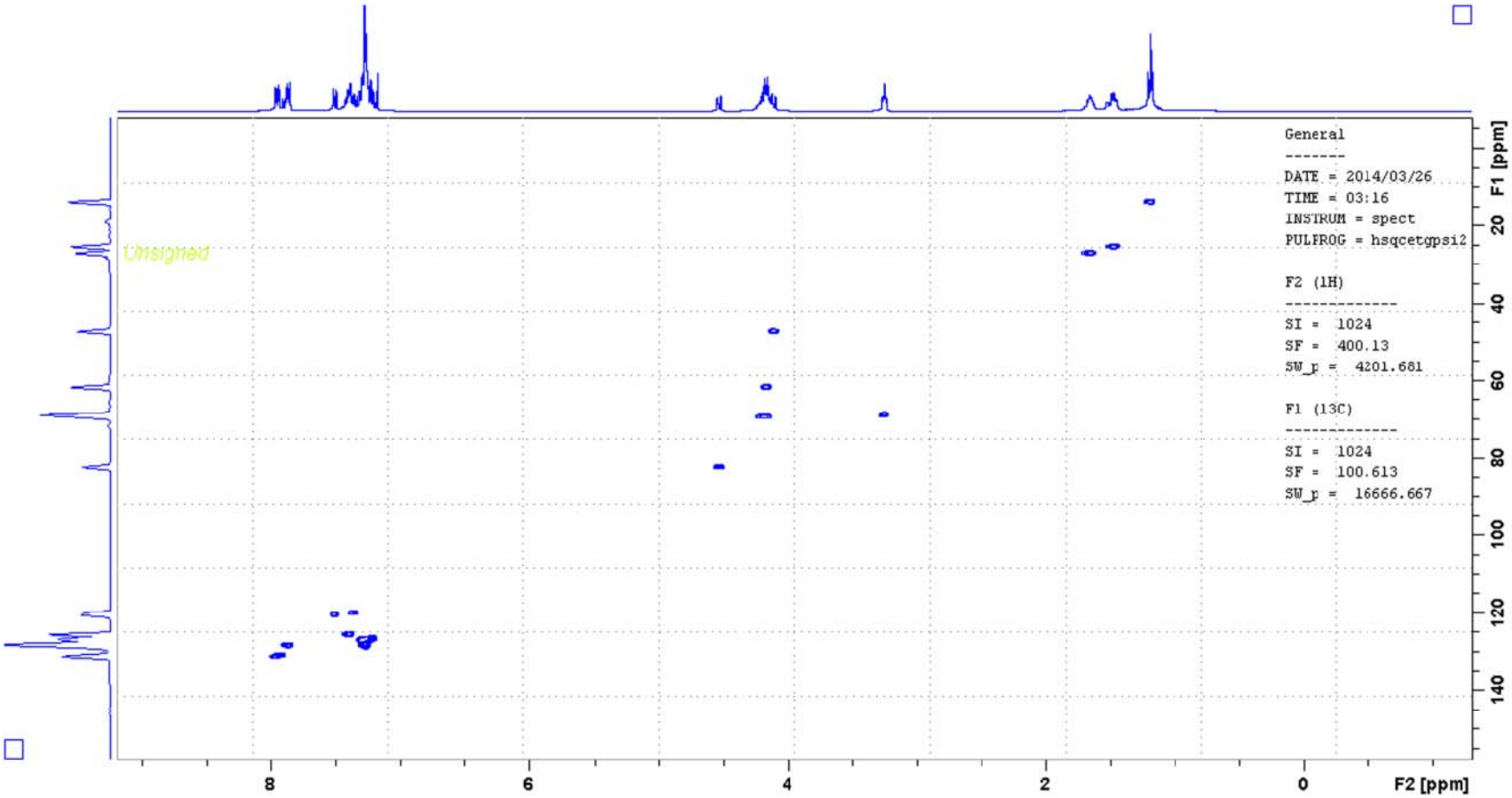
^{1}H NMR spectrum of **5a**



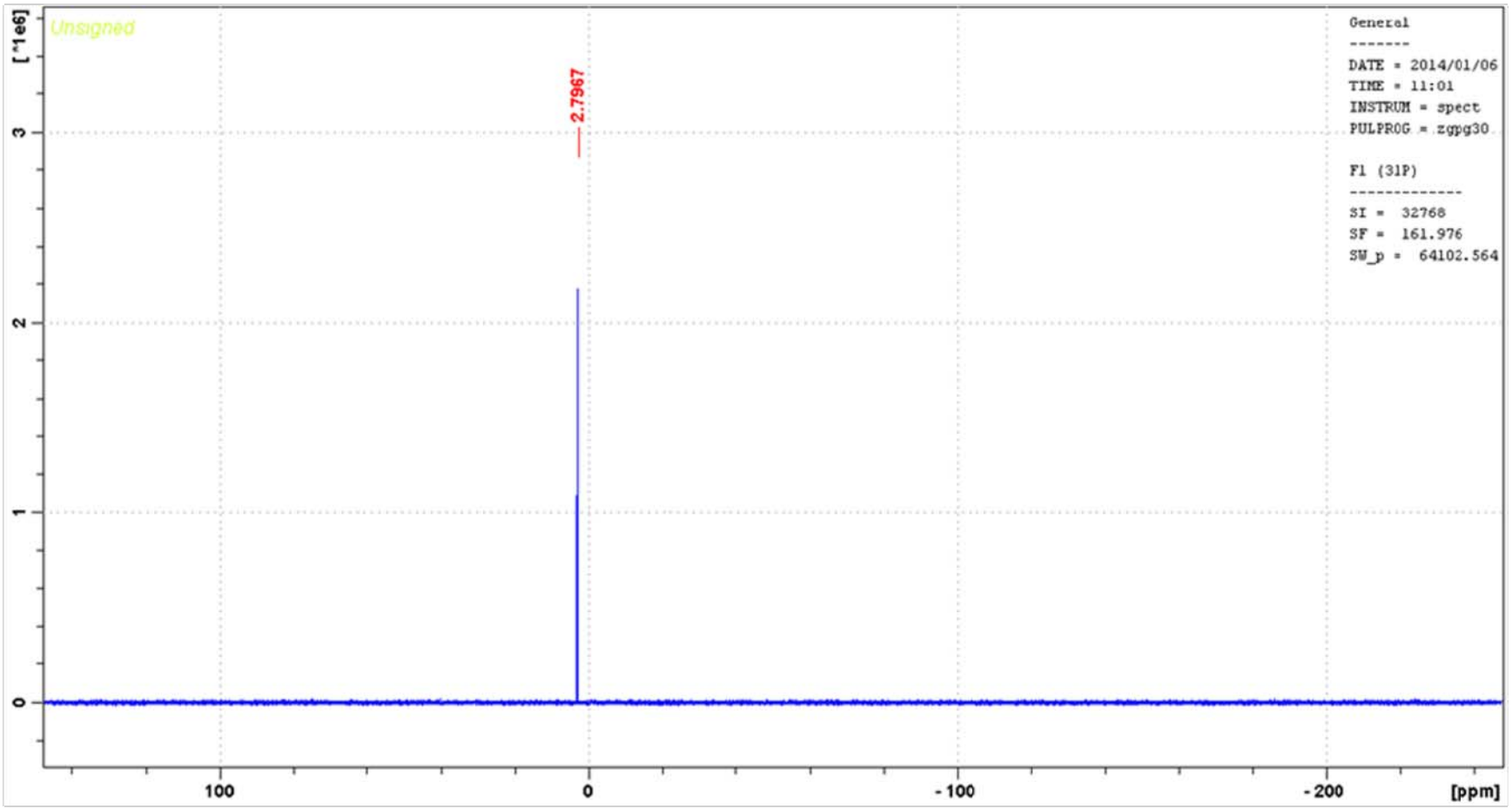
^{13}C NMR spectrum of **5a**



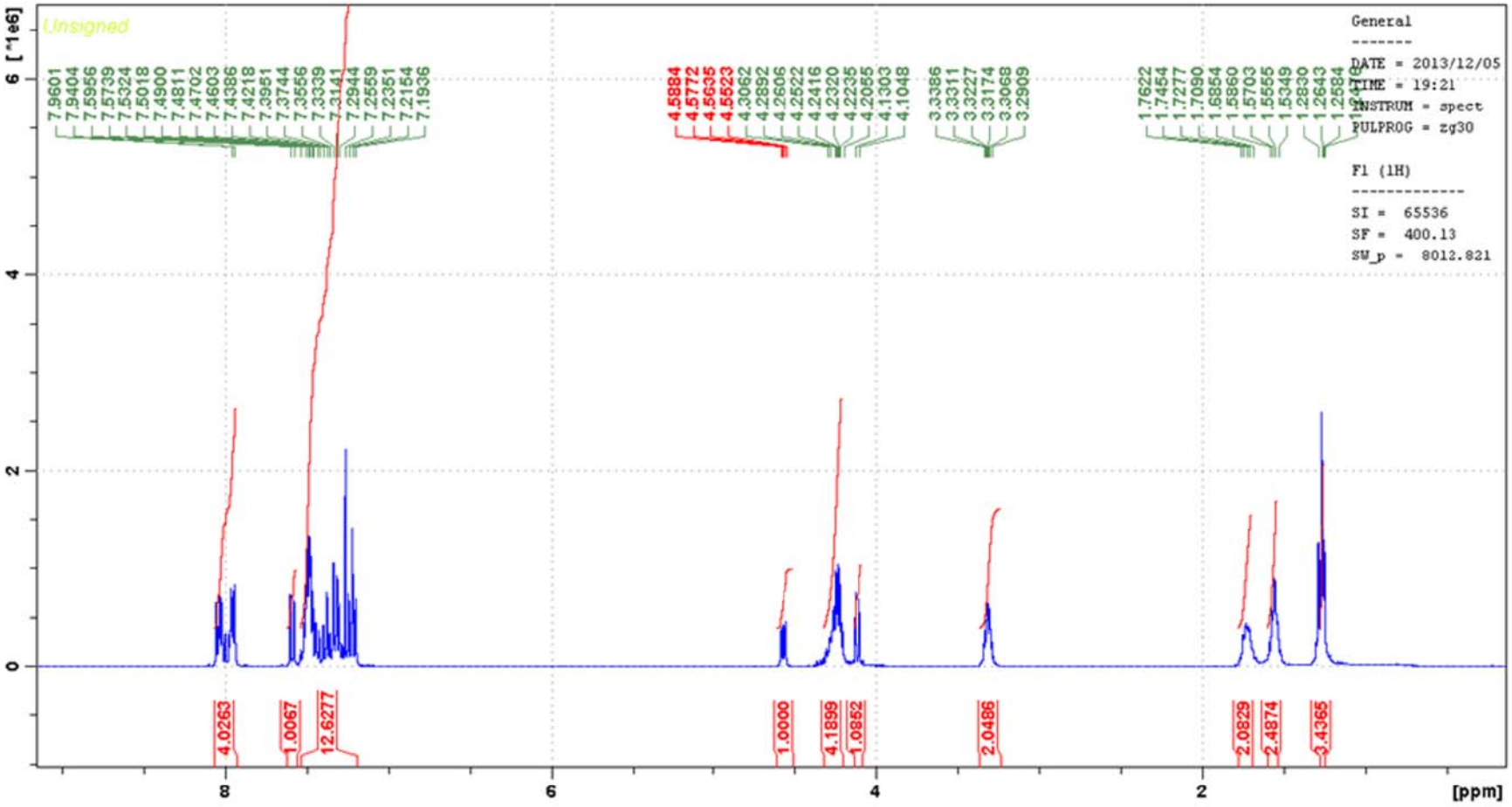
HSQC spectrum of **5a**



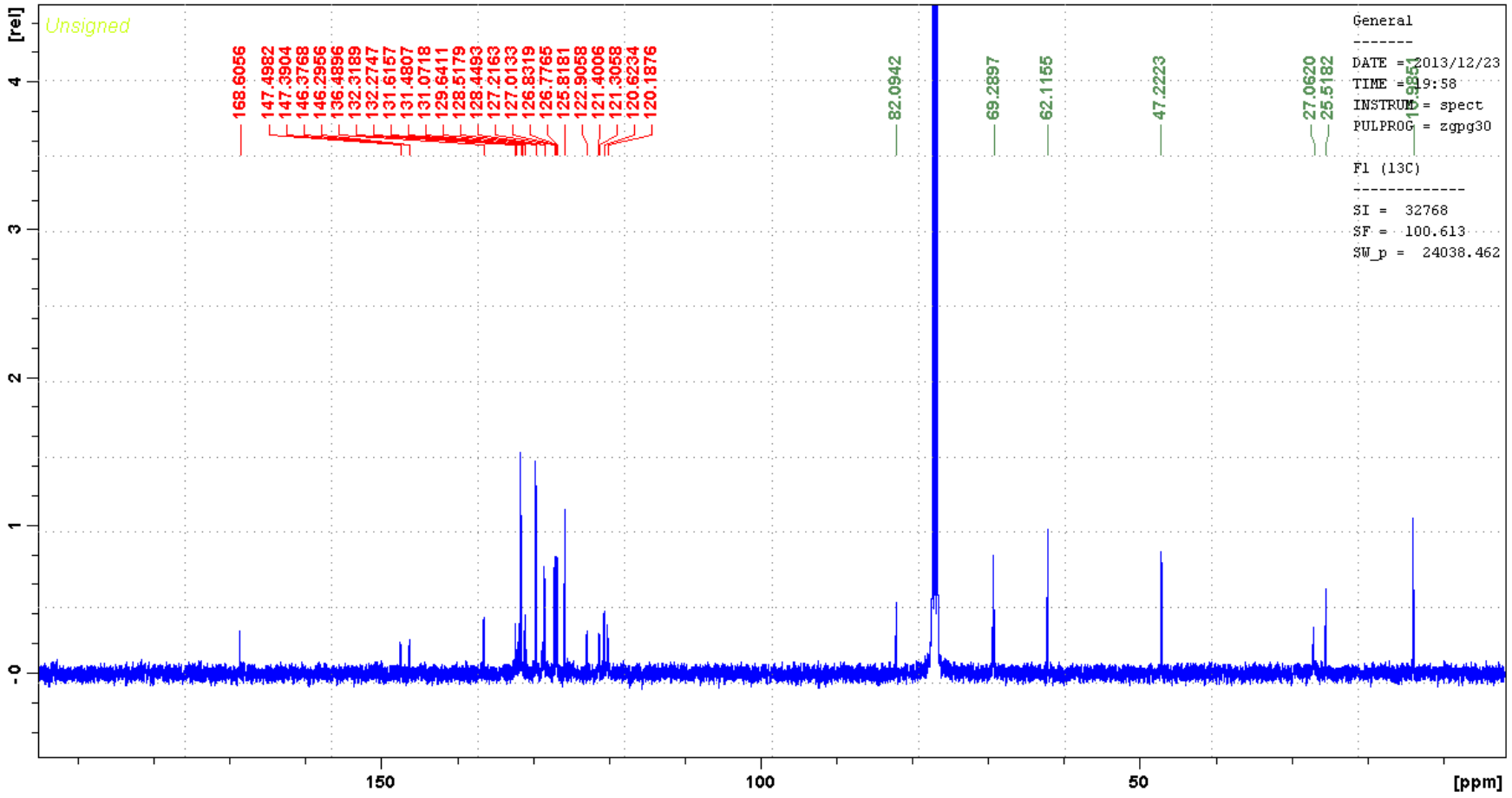
^{31}P NMR spectrum of **5a**



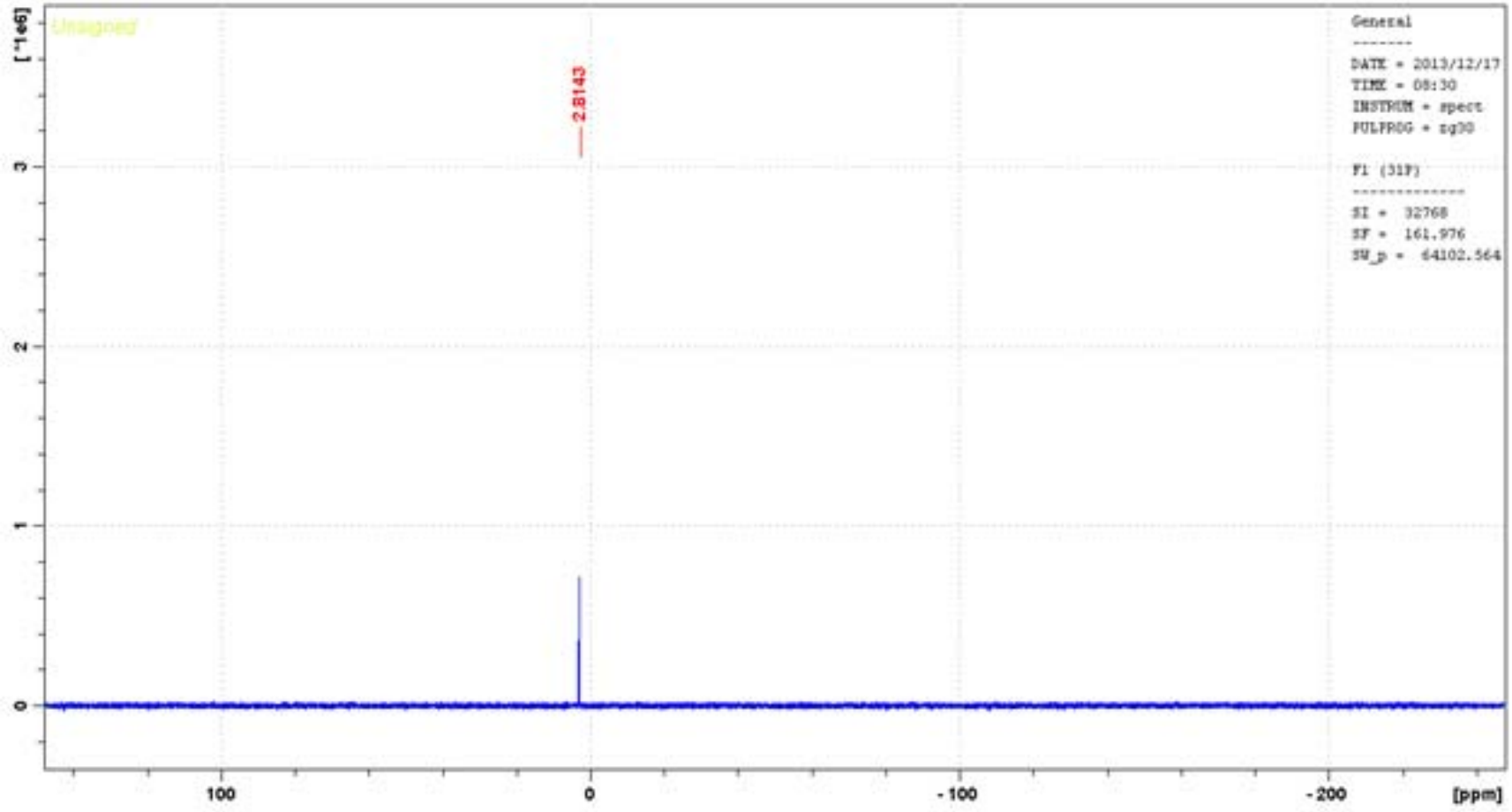
^{1}H NMR spectrum of **5b**



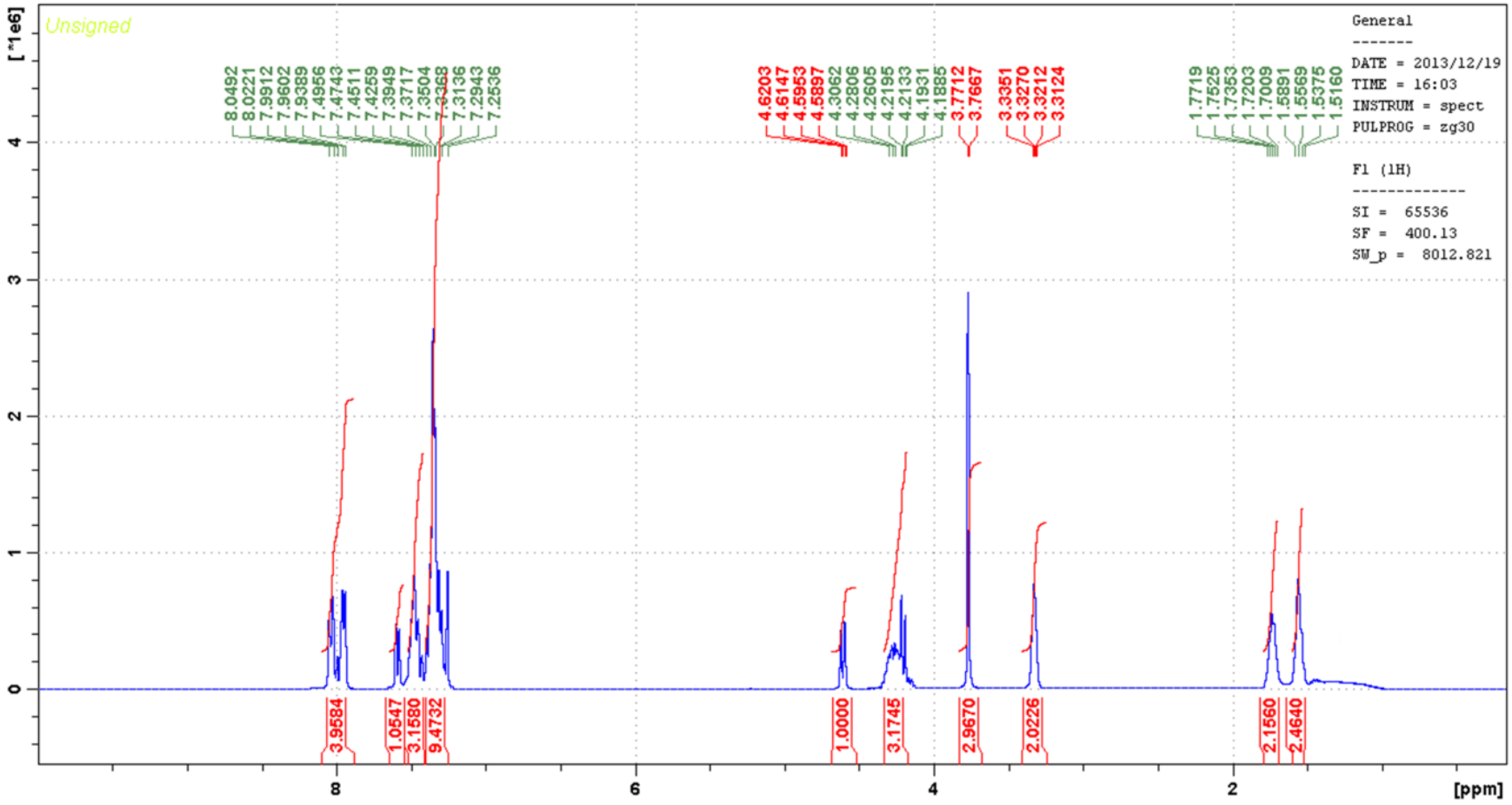
^{13}C NMR spectrum of **5b**



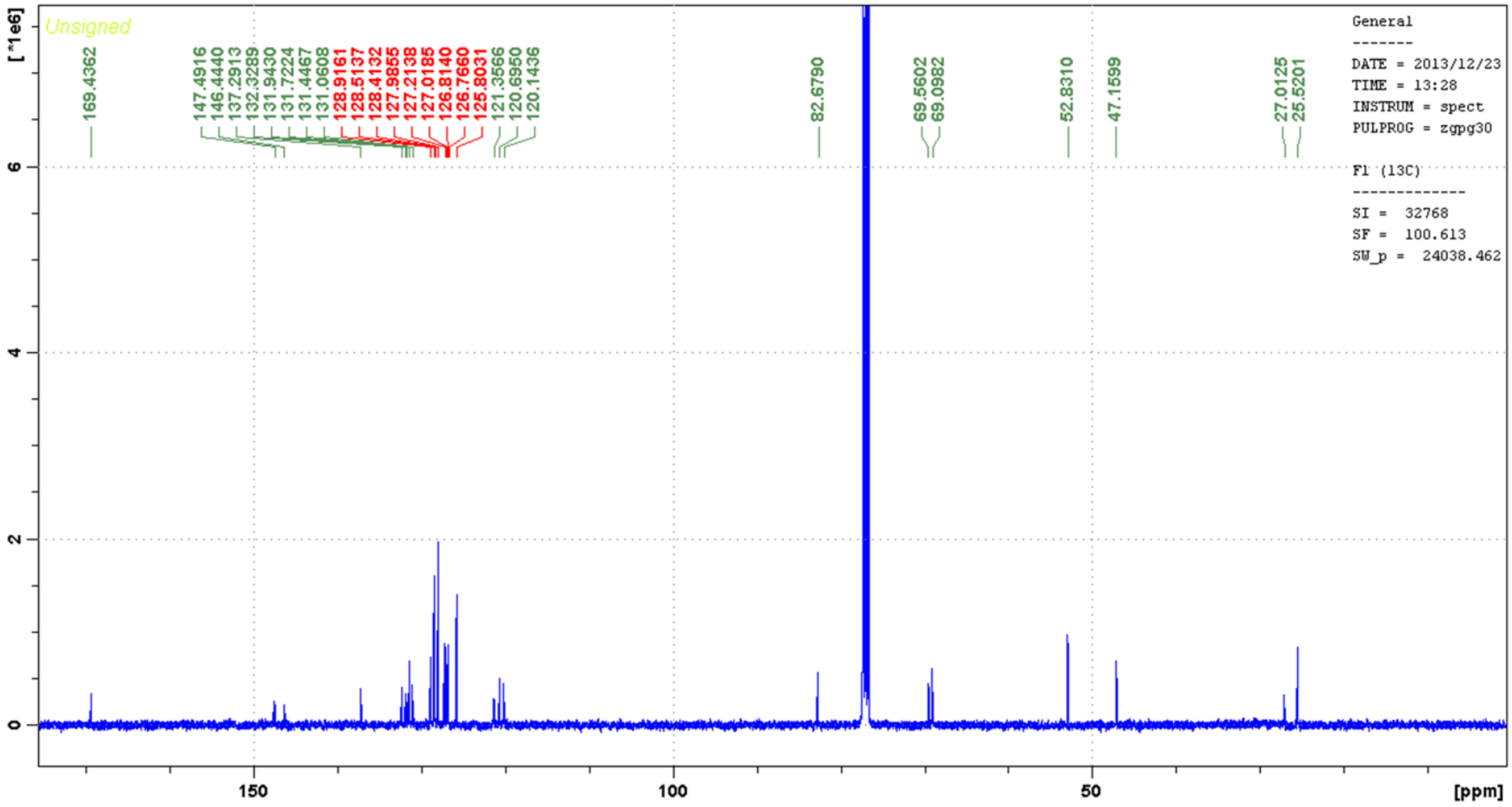
^{31}P NMR spectrum of **5b**



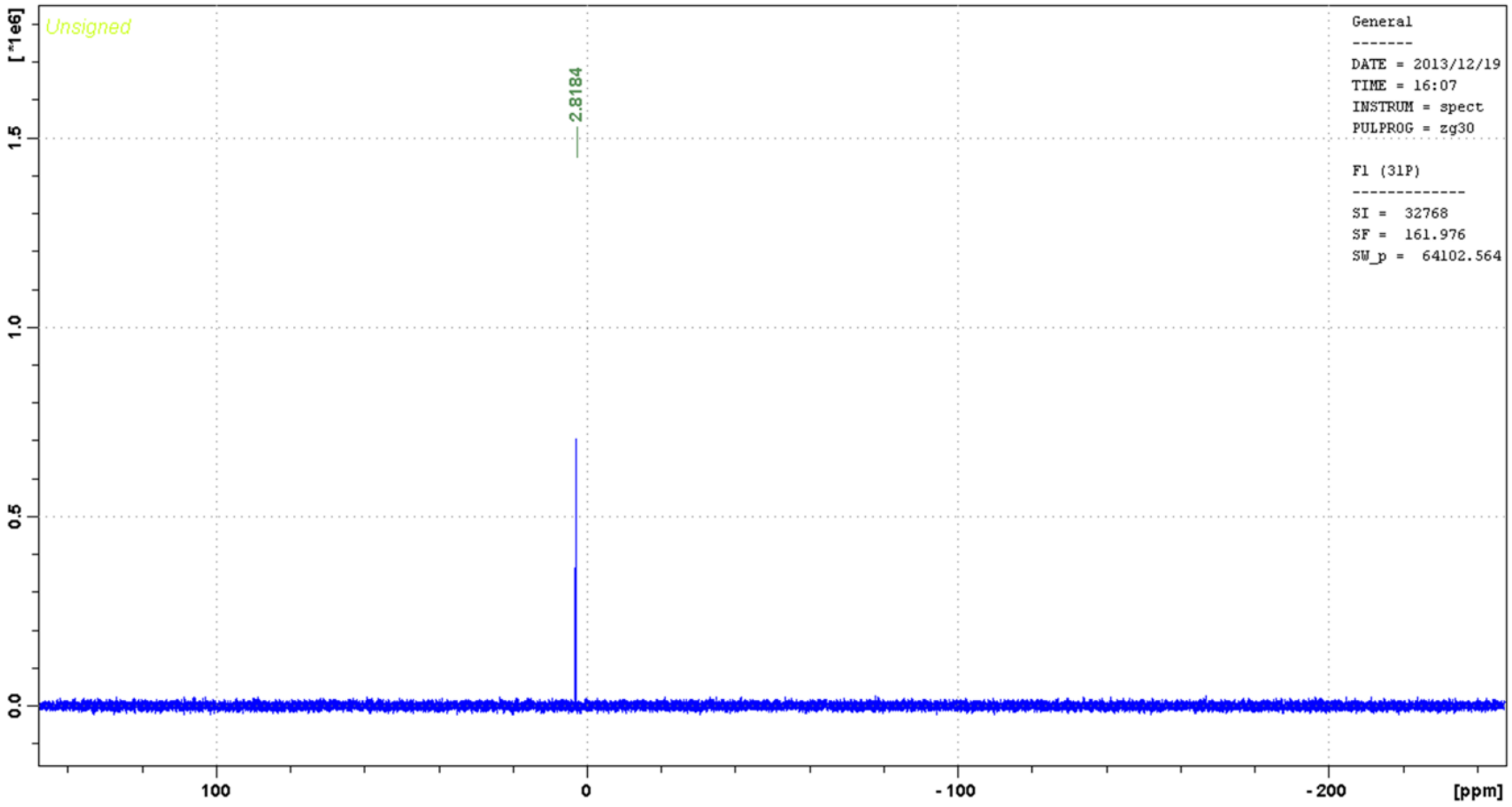
^{1}H NMR spectrum of **5c**



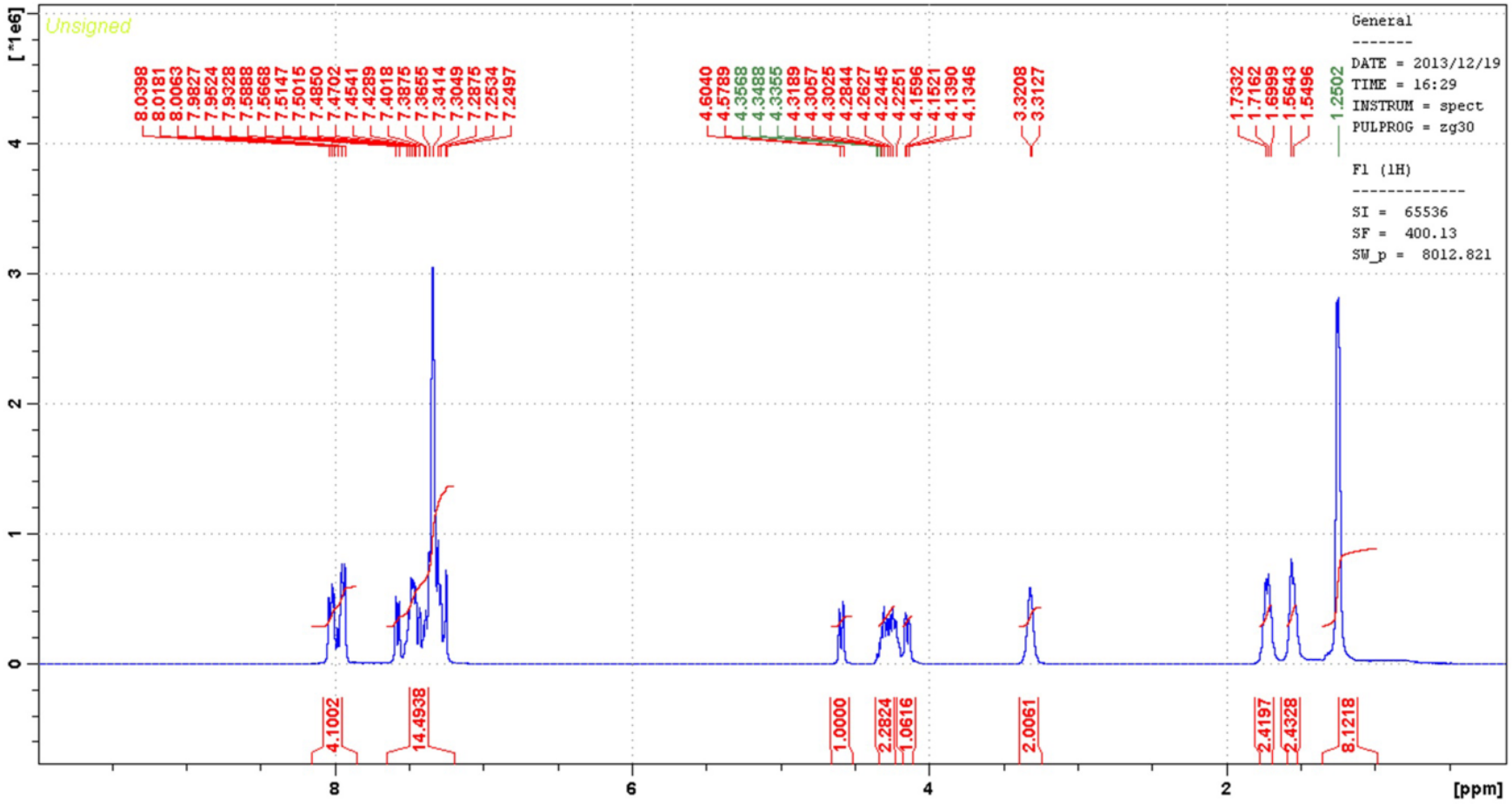
^{13}C NMR spectrum of **5c**



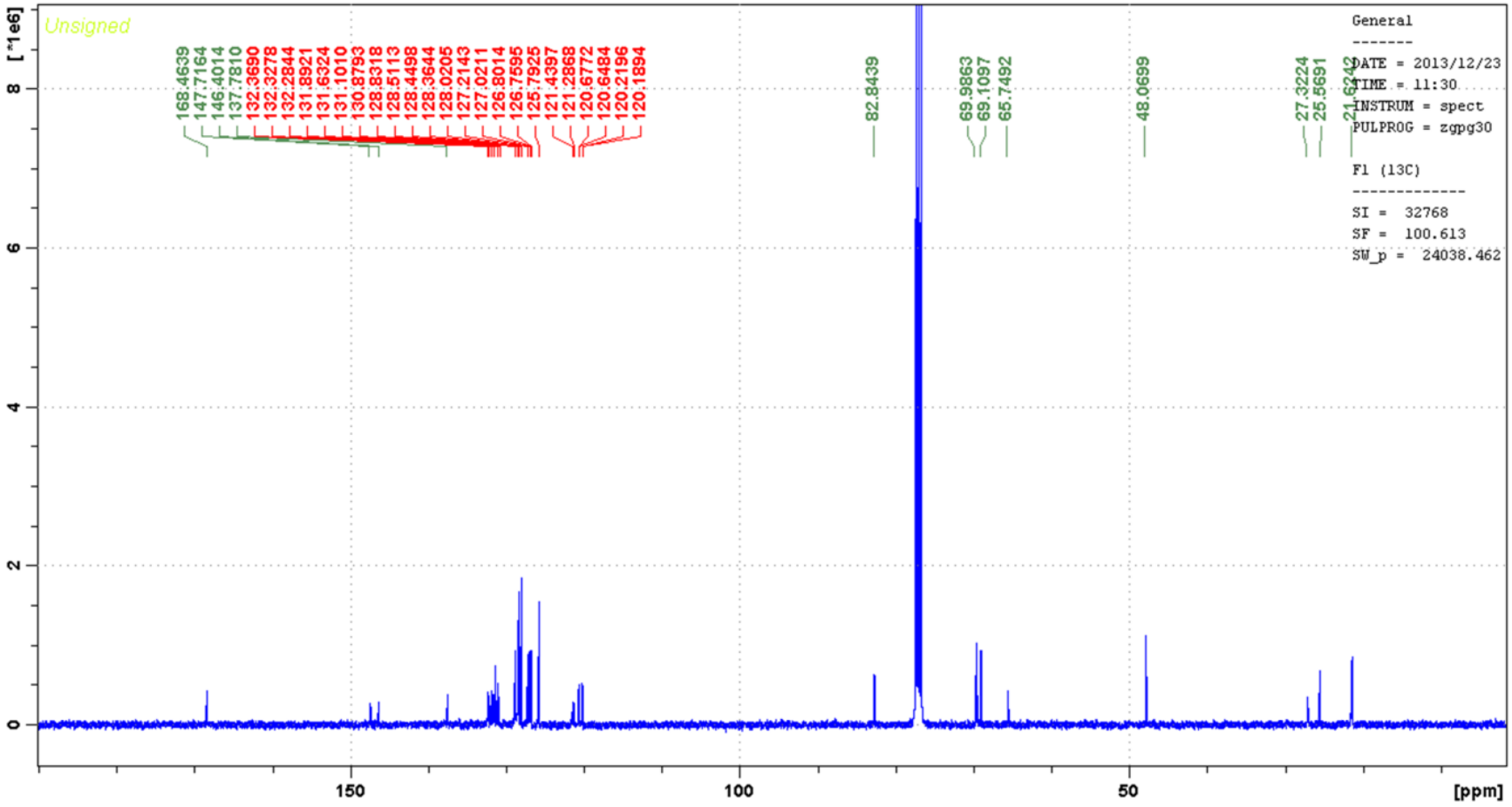
^{31}P NMR spectrum of **5c**



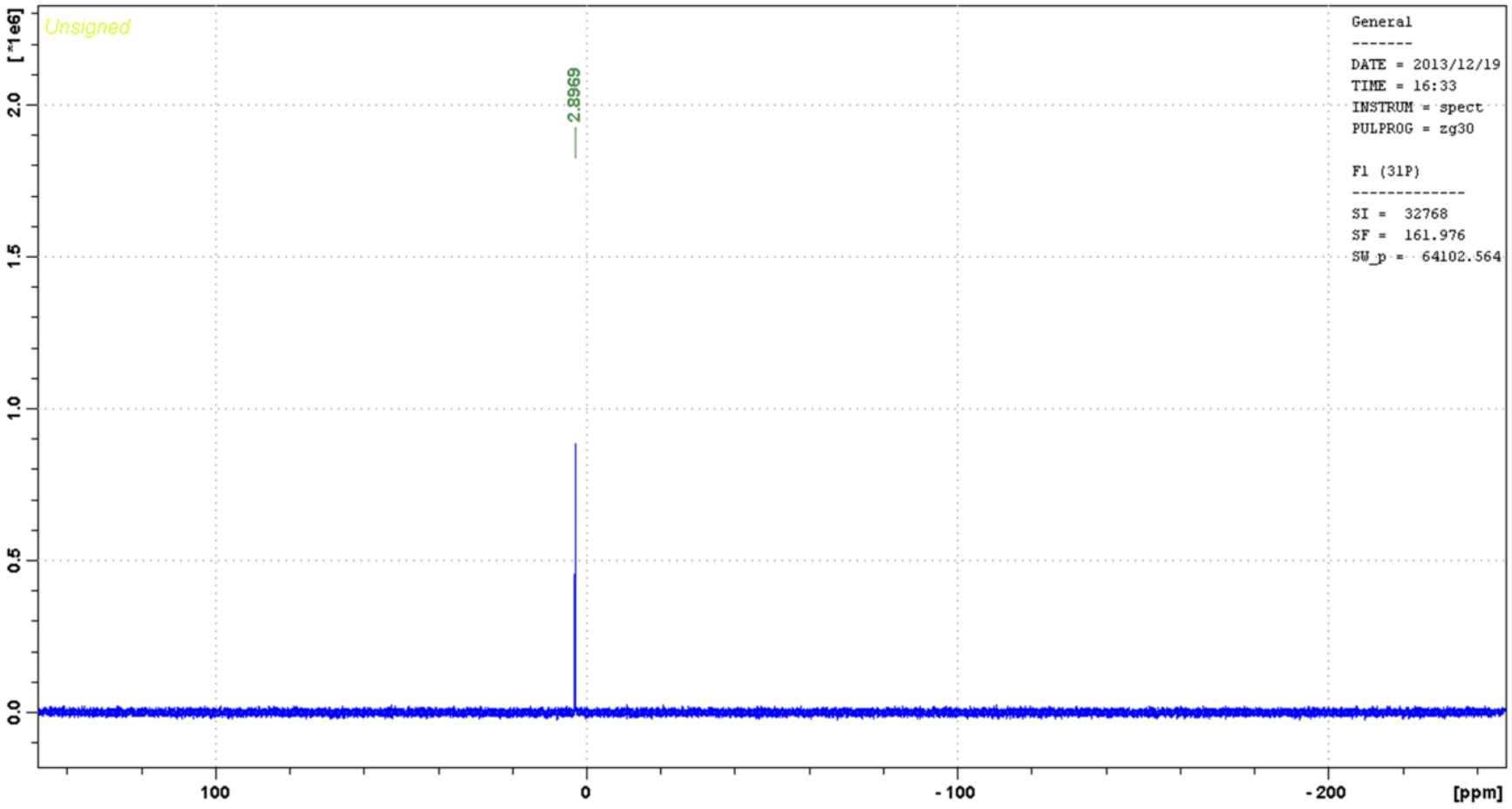
^{1}H NMR spectrum of **5d**



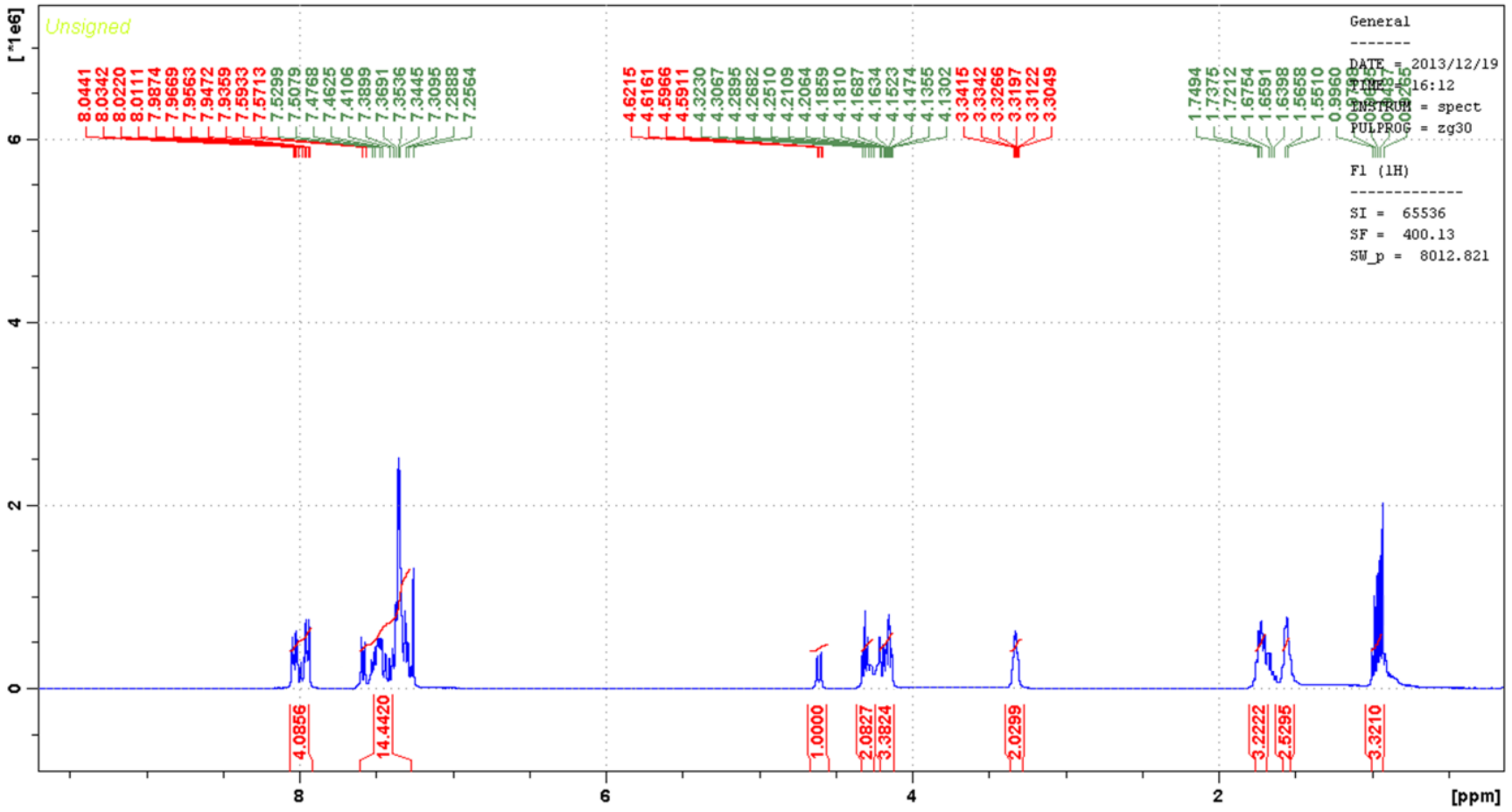
^{13}C NMR spectrum of **5d**



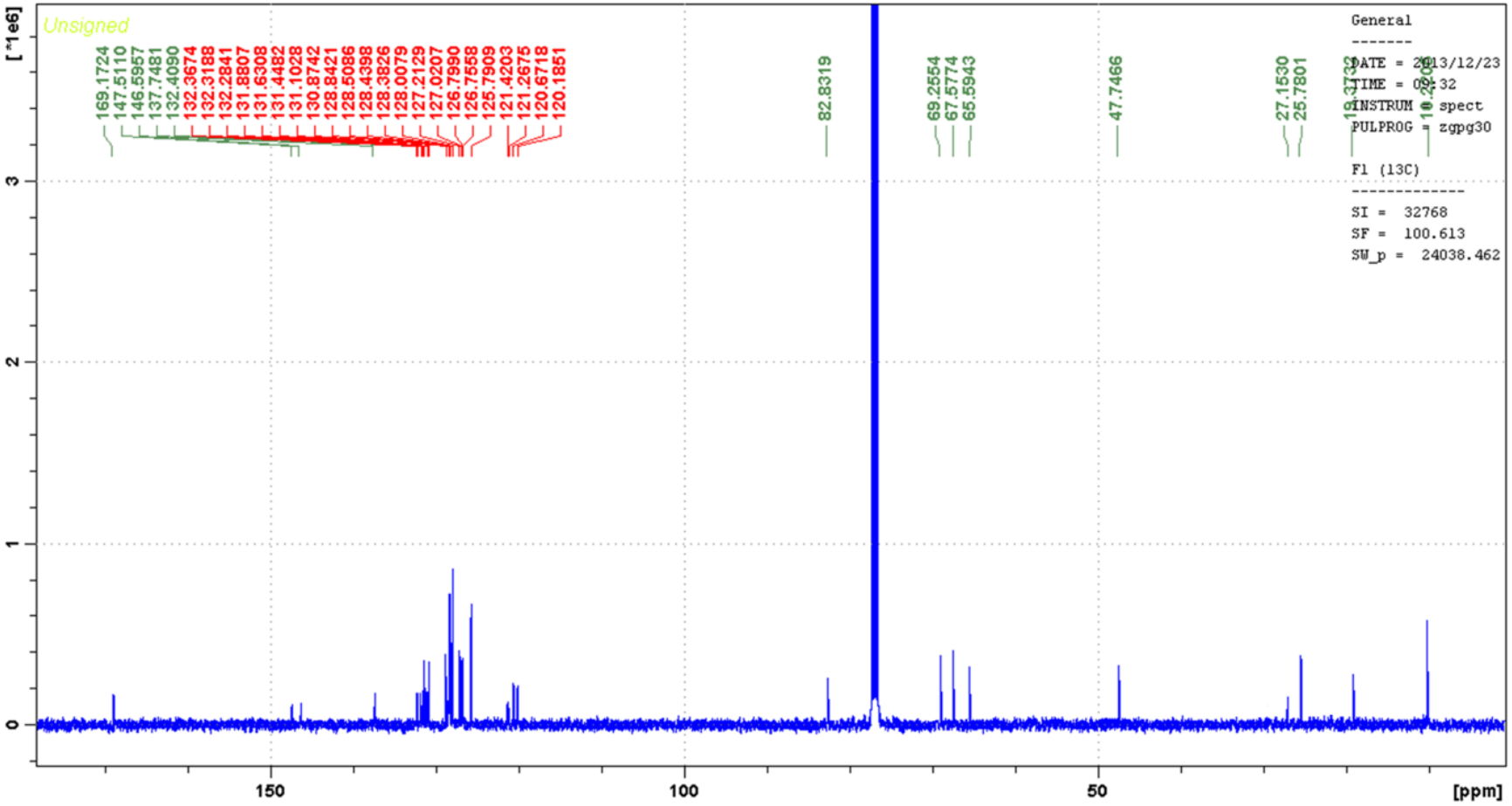
^{31}P NMR spectrum of **5d**



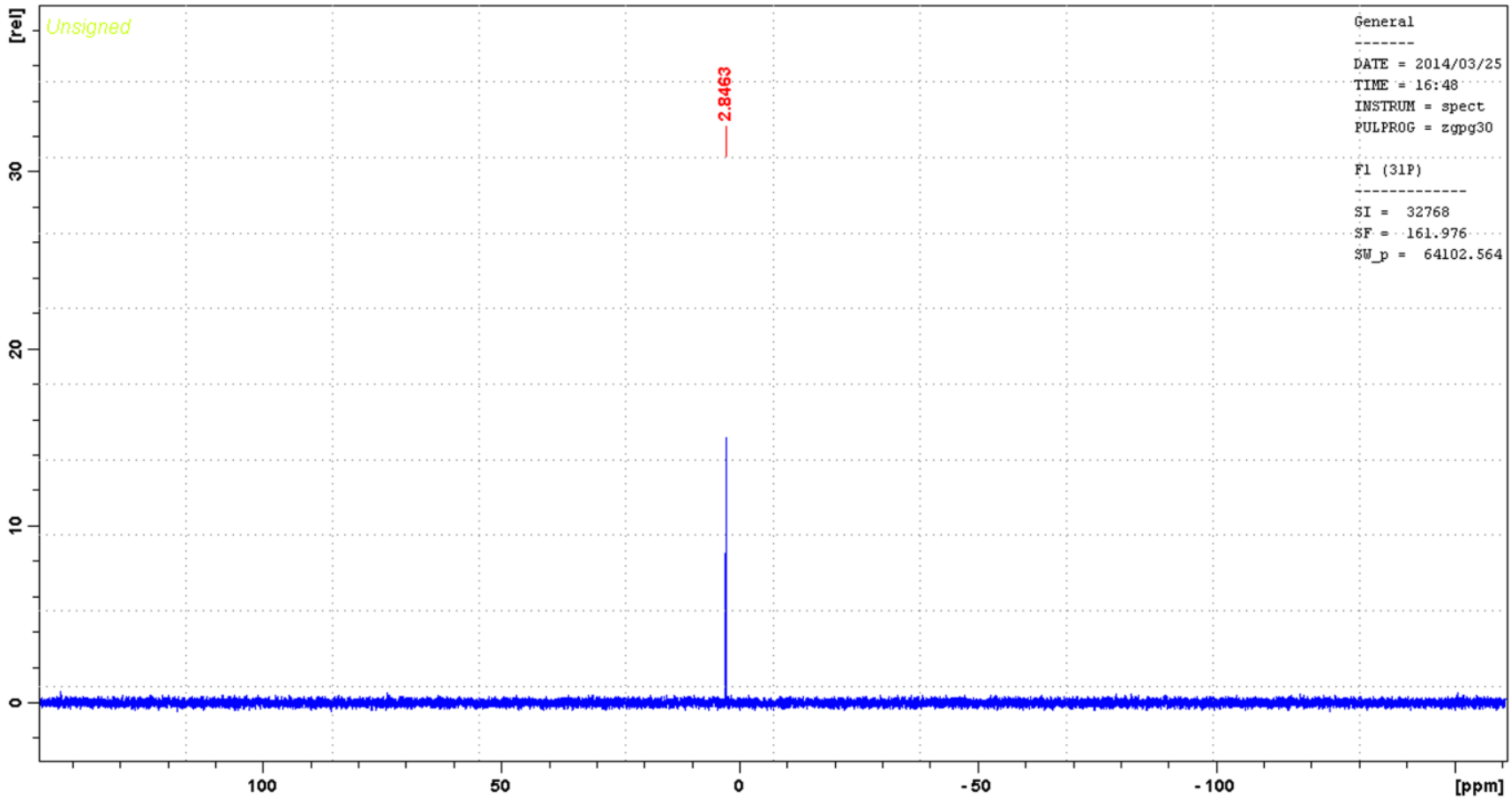
^{1}H NMR spectrum of **5e**



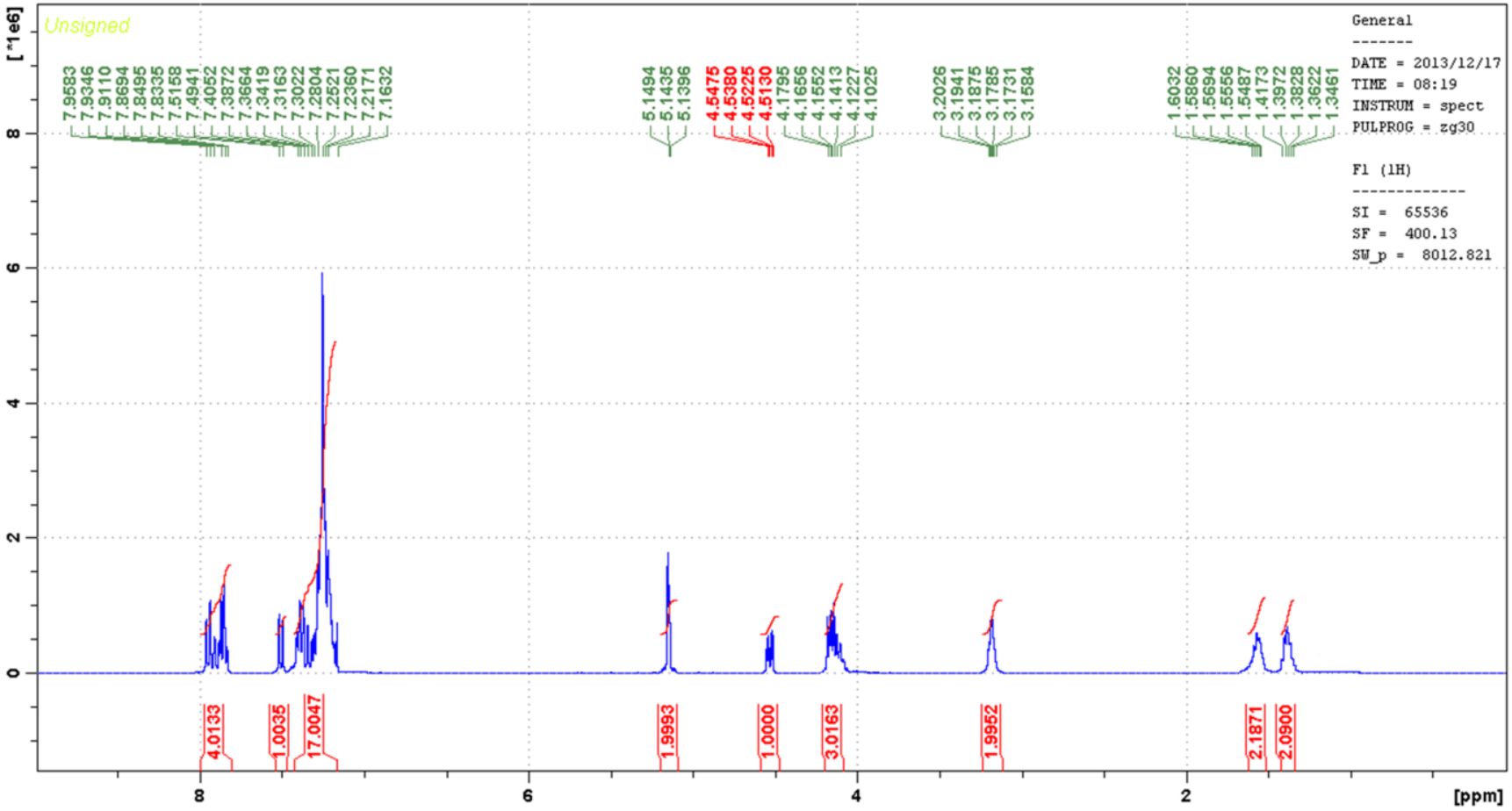
^{13}C NMR spectrum of **5e**



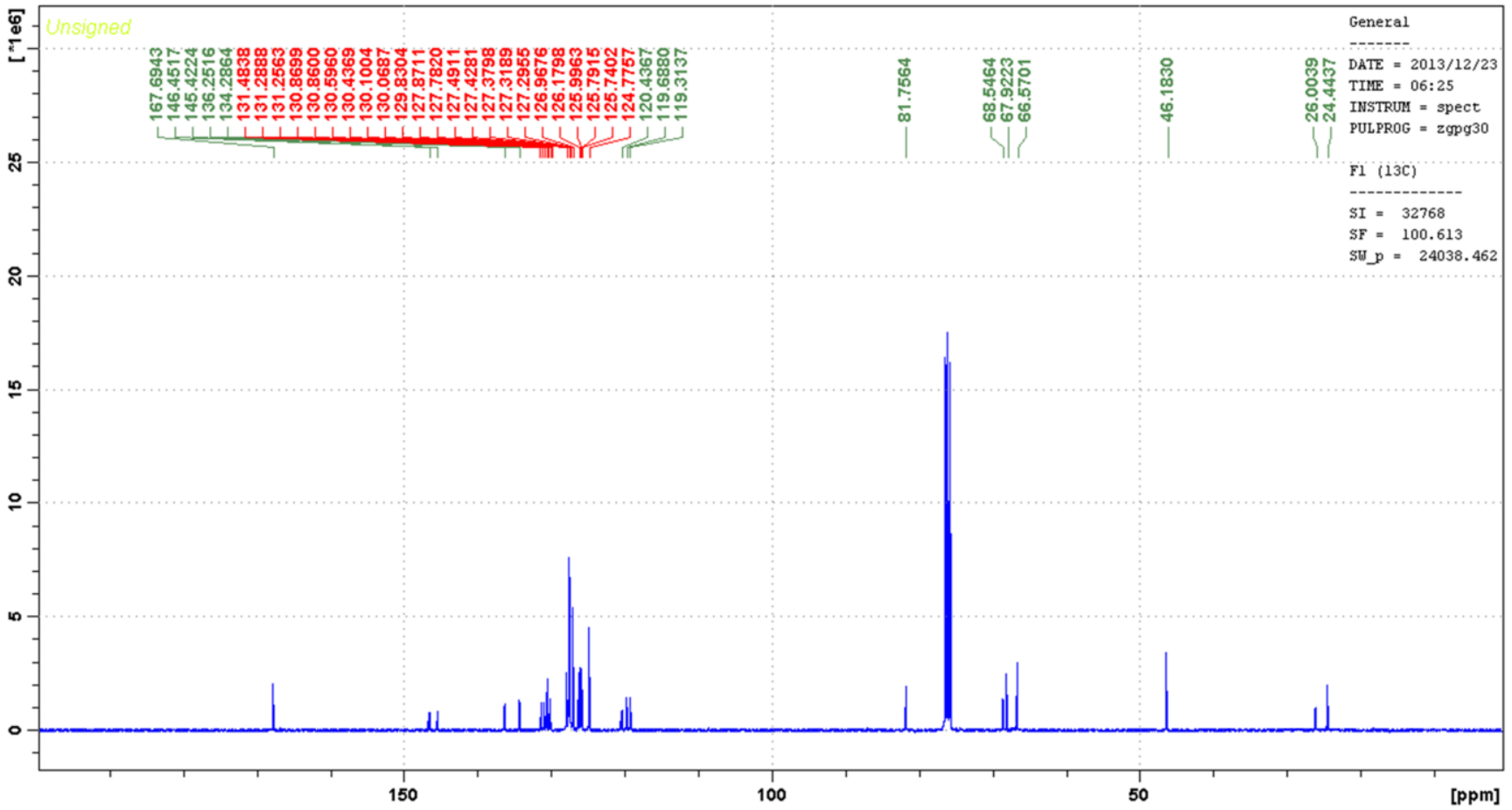
^{31}P NMR spectrum of **5e**



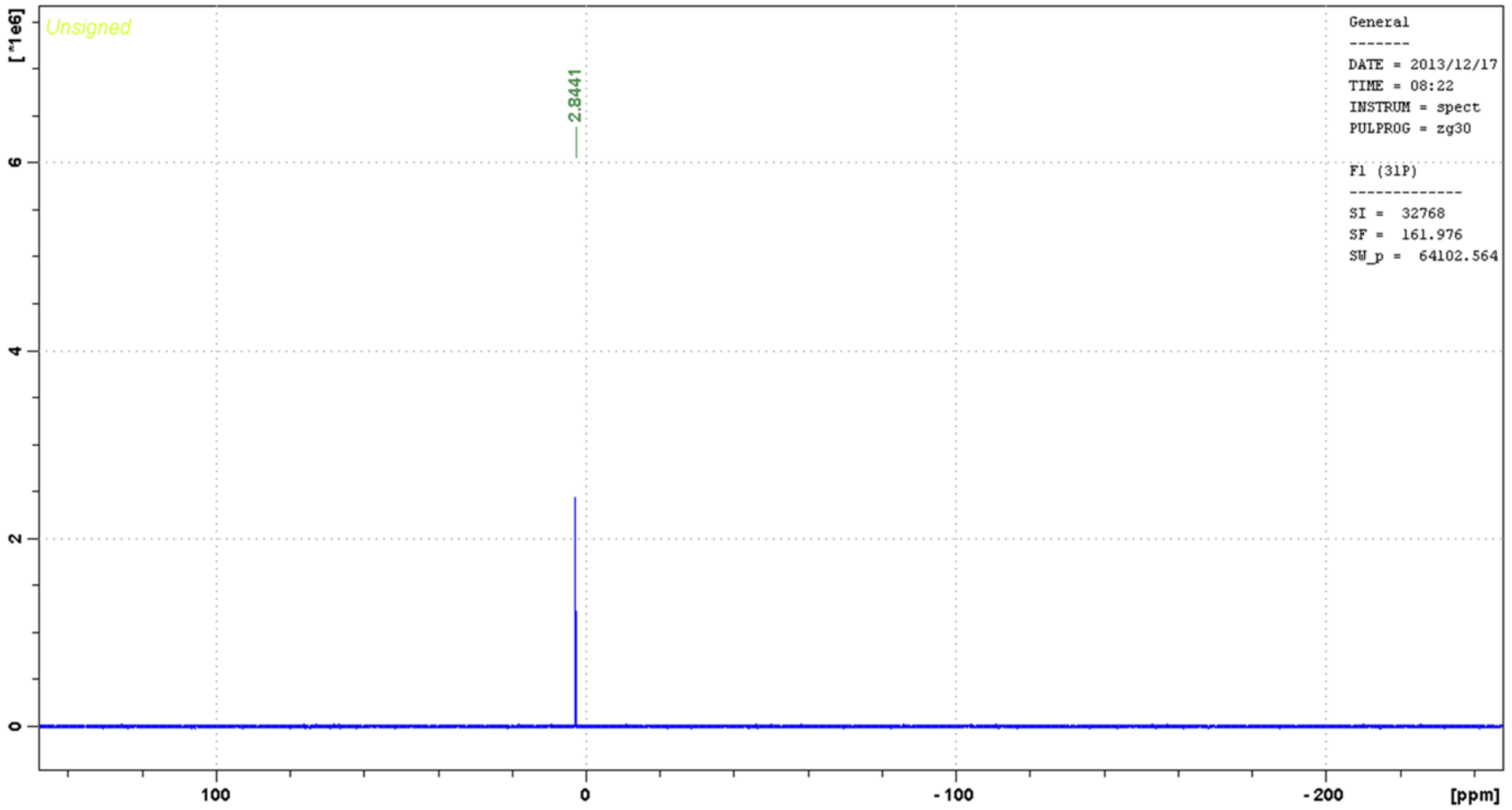
^{1}H NMR spectrum of **5f**



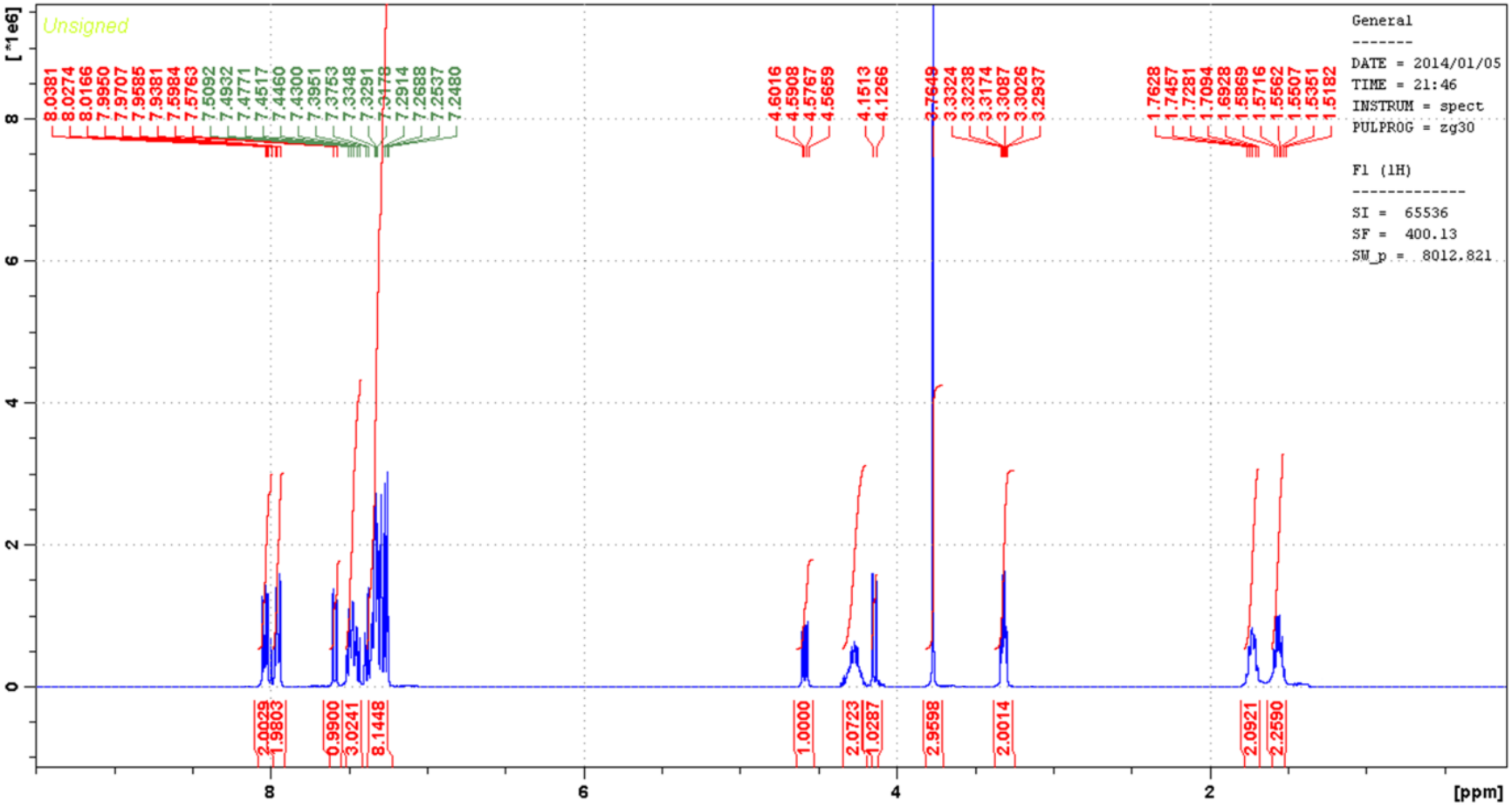
^{13}C NMR spectrum of **5f**



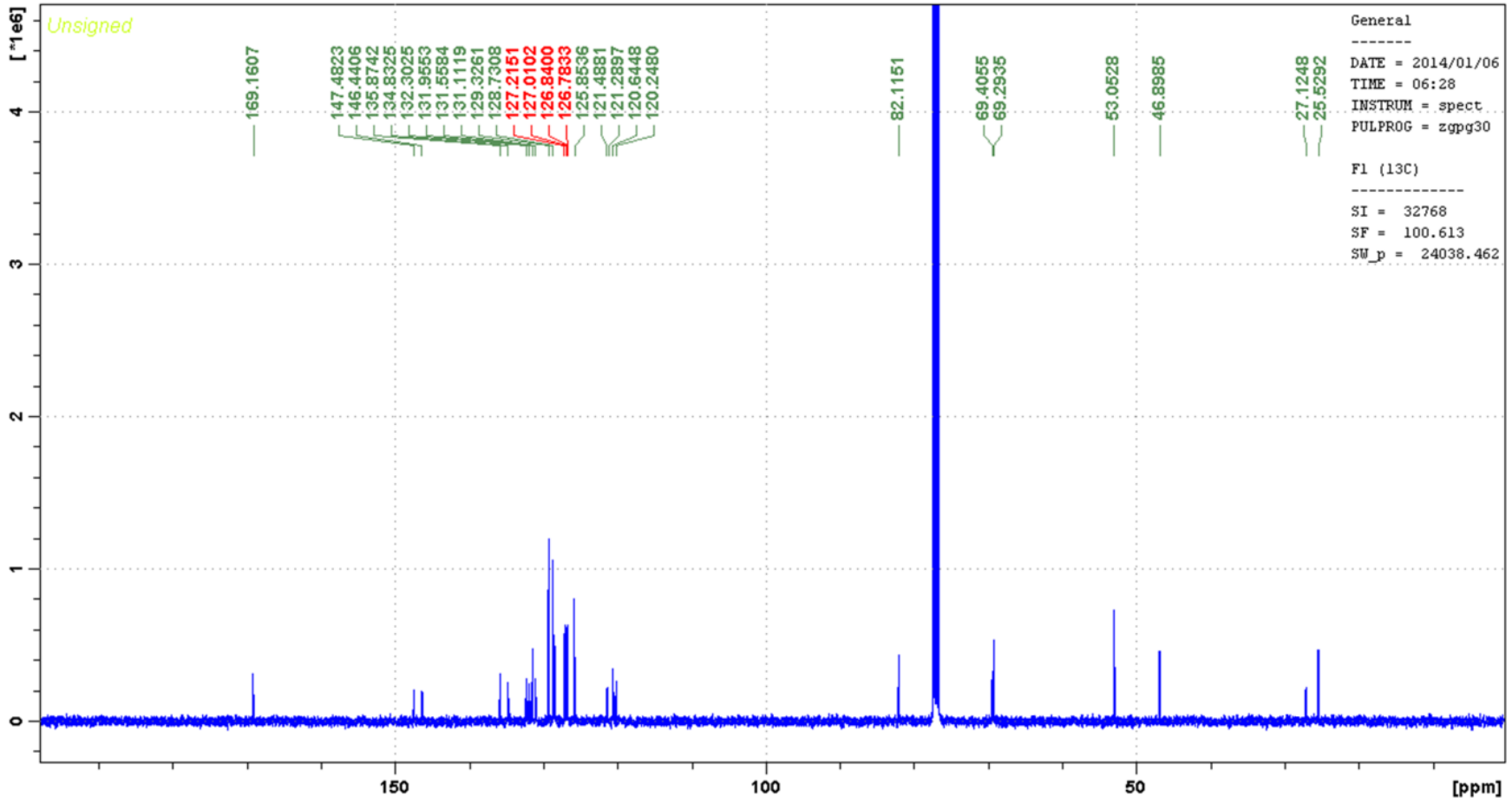
^{31}P NMR spectrum of **5f**



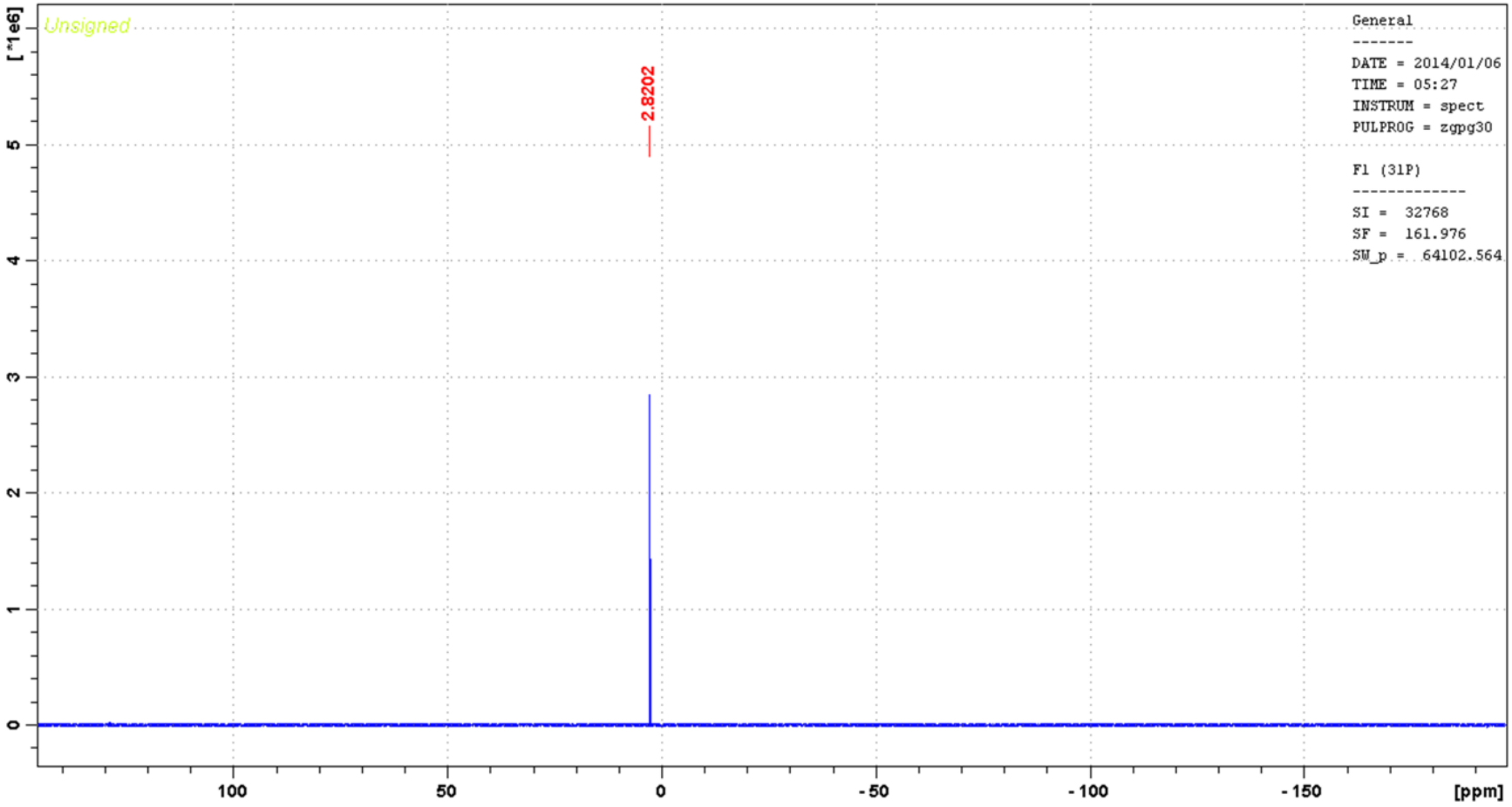
^{1}H NMR spectrum of **5g**



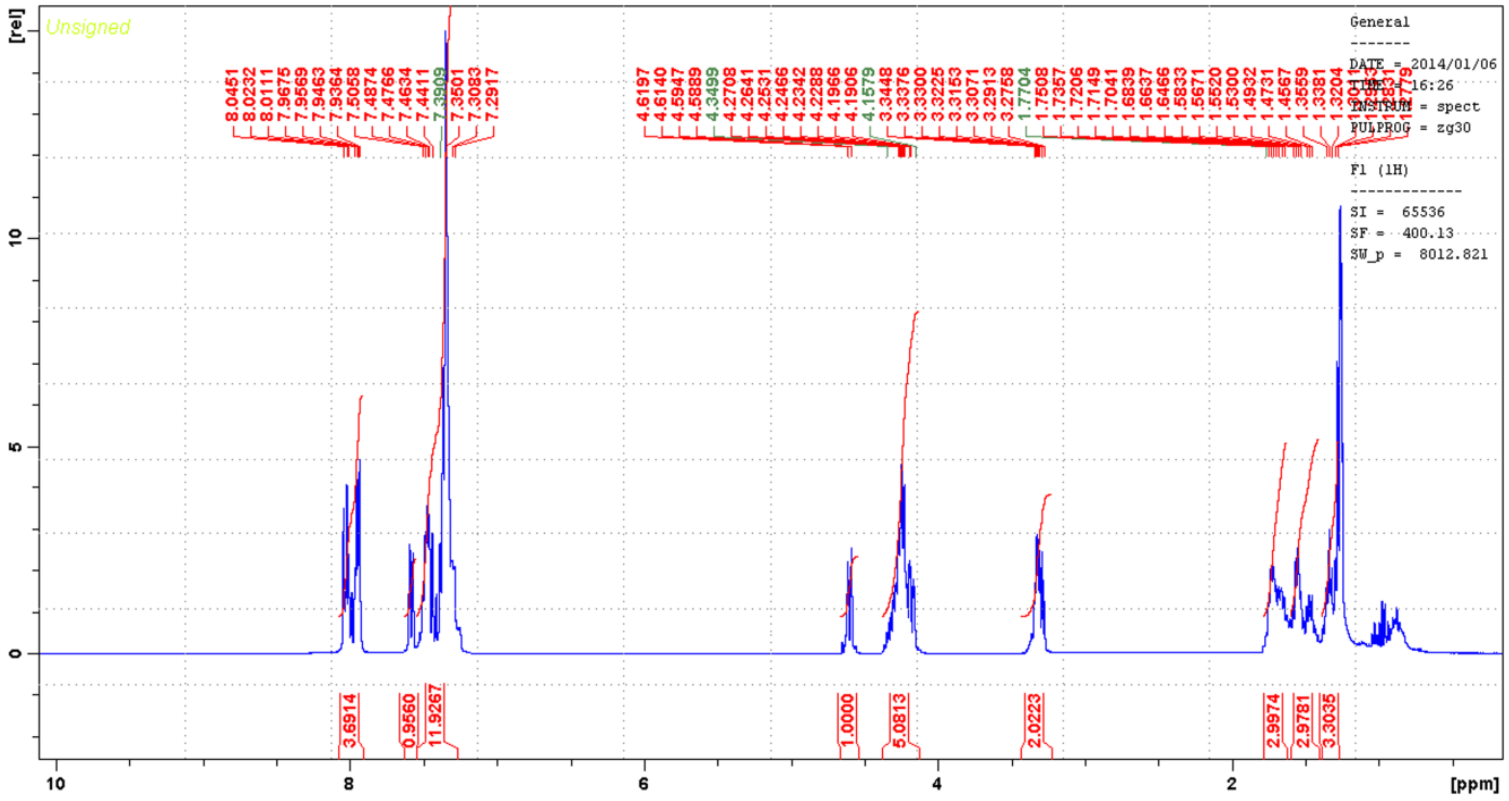
^{13}C NMR spectrum of **5g**



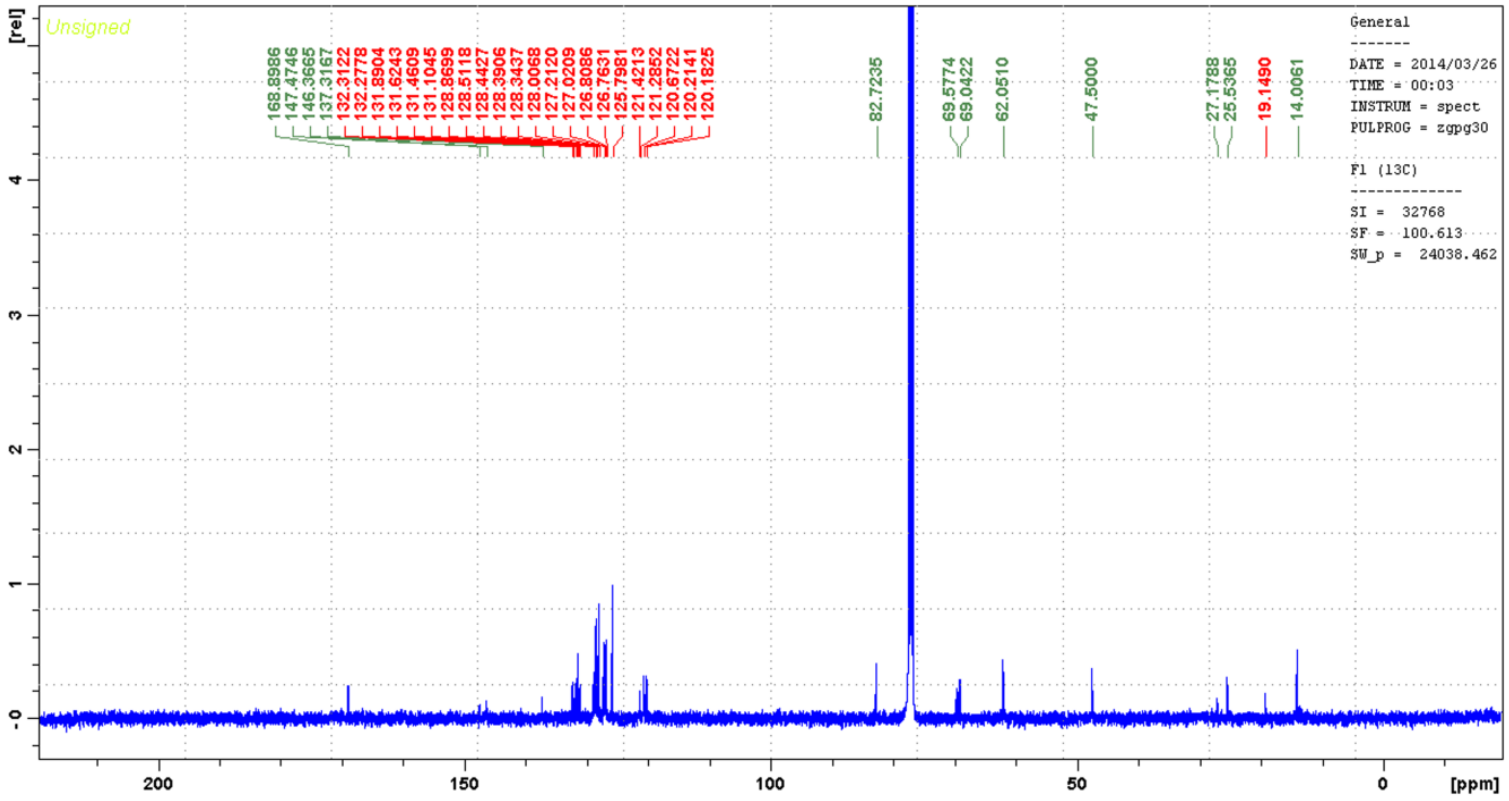
^{31}P NMR spectrum of **5g**



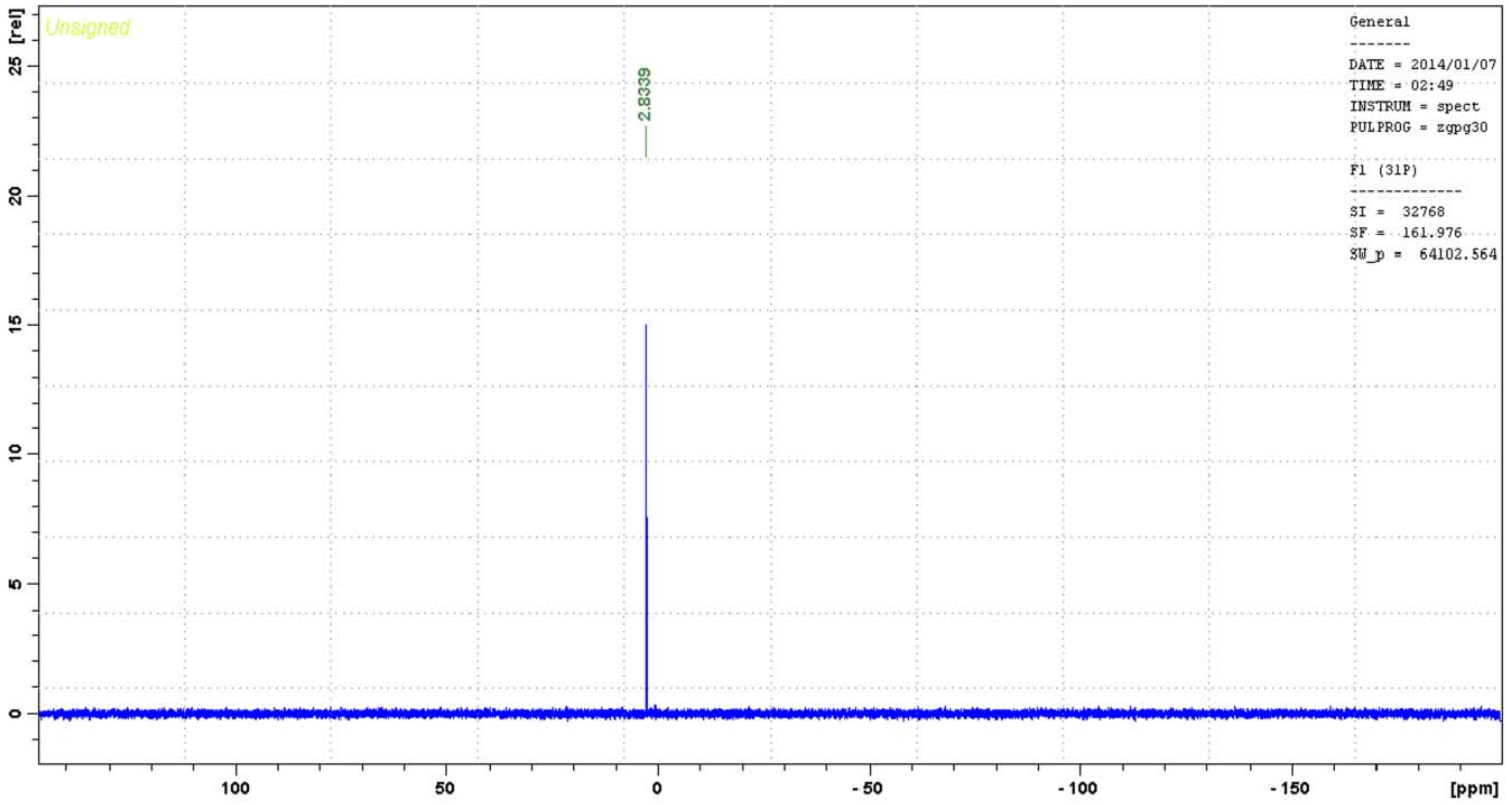
^{1}H NMR spectrum of **5h**



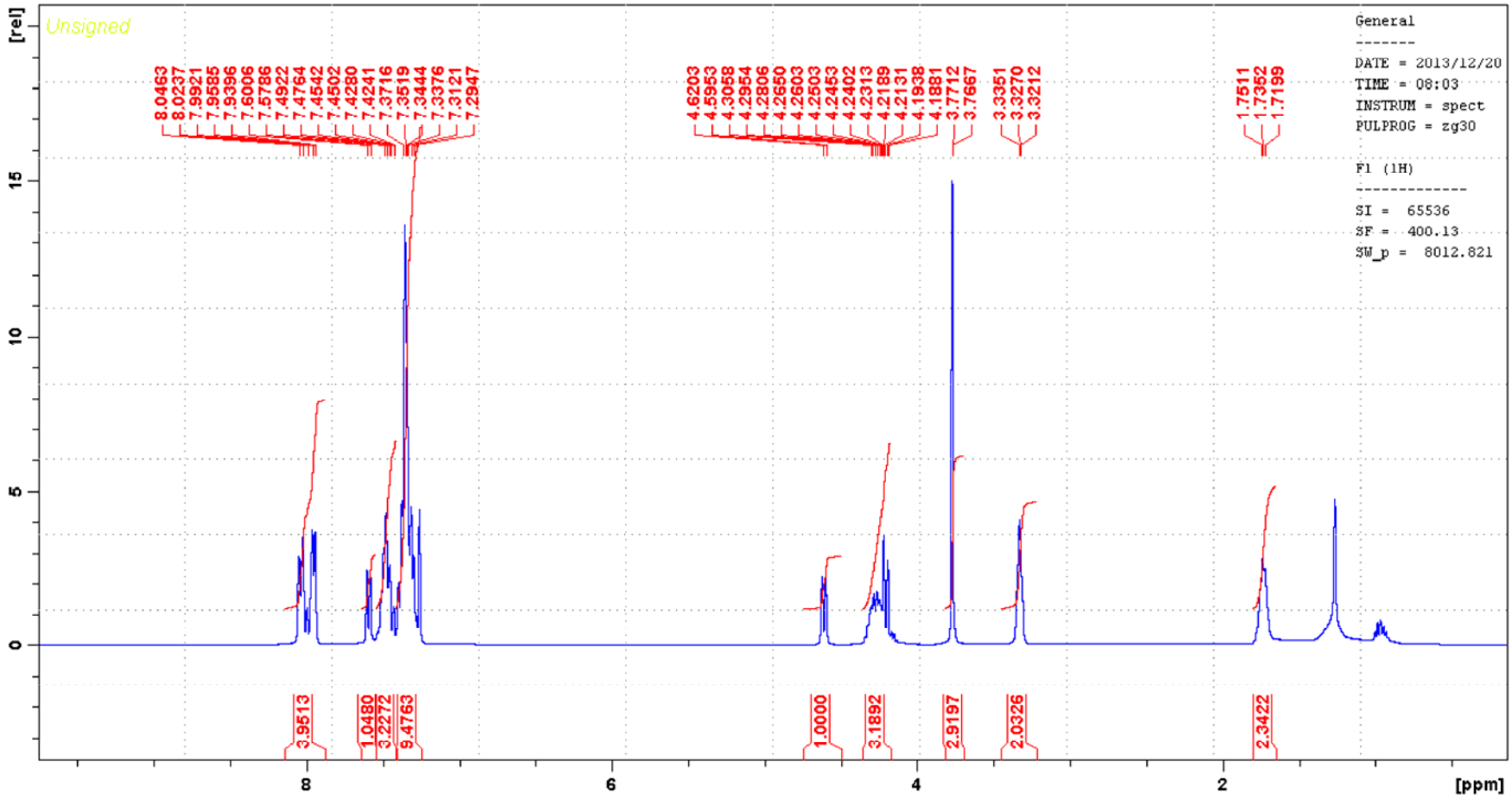
^{13}C NMR spectrum of **5h**



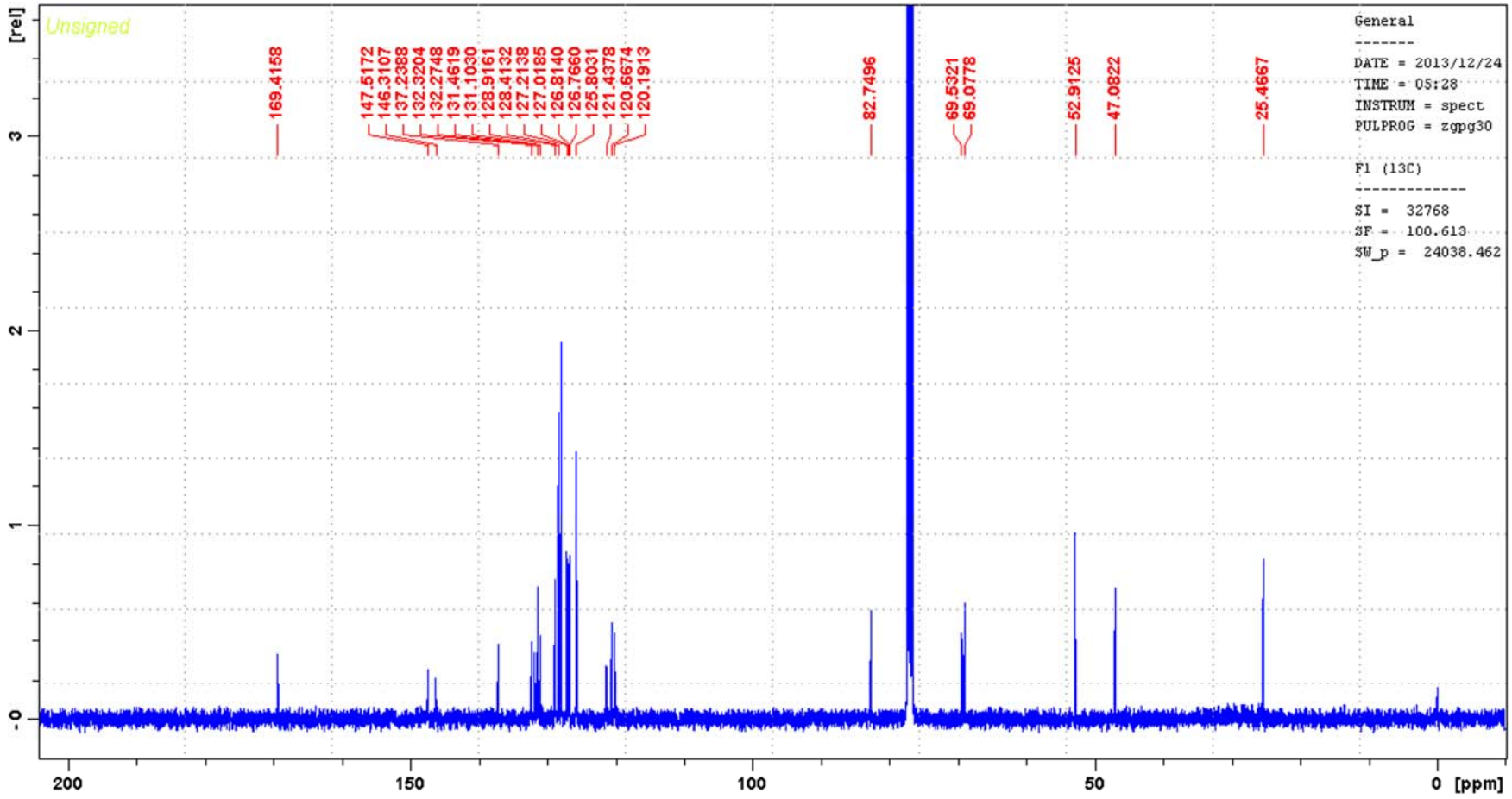
^{31}P NMR spectrum of **5h**



^{1}H NMR spectrum of **5i**



^{13}C NMR spectrum of **5i**



^{31}P NMR spectrum of **5i**