SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Table S1. Assignments of signals from ^{1}H and ^{13}C NMR spectra (in CD_3OD) of DiNAC-PTS-catechol (**5**) and TriNAC-PTS-catechol (**6**).

Figure S1. ^{1}H NMR spectrum (in CD_3OD) of TriNAC-PTS-catechol (**6**). A signal for HCOOH appeared at 8.07 ppm.

Figure S2. ^{1}H NMR spectrum (in CD_3OD) of DiNAC-PTS-catechol (**5**). A signal for HCOOH appeared at 8.07 ppm.

Figure S3. ^{1}H NMR spectrum (in CD_3OD) of PTS-catechol (**4**).

Figure S4. ^{13}C-NMR spectrum (in CD_3OD) of DiNAC-PTS-catechol (**5**).

Figure S5. ^{13}C-NMR spectrum (in CD_3OD) of TriNAC-PTS-catechol (**6**).

Figure S6. ^{13}C-NMR spectrum (in CD_3OD) of PTS-catechol (**4**).

Figure S7. 2D DQF-COSY of DiNAC-PTS-catechol (**5**).

Figure S8. 2D DQF- COSY of TriNAC-PTS-catechol (**6**).

Figure S9. 2D DQF-COSY of PTS-catechol (**4**).

Figure S10. 2D HMBC of DiNAC-PTS-catechol (**5**).

Figure S11. 2D HMBC of TriNAC-PTS-catechol (**6**).

Figure S12. 2D HMBC of PTS-catechol (**4**).

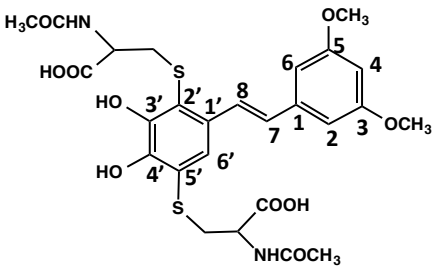
Figure S13. 2D HMQC of DiNAC-PTS-catechol (**5**).

Figure S14. 2D HMQC of TriNAC-PTS-catechol (**6**).

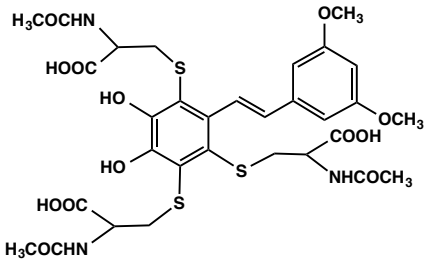
Figure S15. 2D HMQC of PTS-catechol (**4**).

Figure S16. Tyrosinase-dependent cytotoxicity against **(a)** PTS (**2**), **(b)** RES (**1**), and **(c)** 4SCAP in human tyrosinase-expressing 293T cells (hTYR-293T cells). Viability of TYR- or mock-transfected cells treated with the indicated concentrations of compounds for 2 h were assessed. Data represent means ± SD (n = 3 wells). Similar results were obtained in two or three experiments.

Table S1. Assignments of signals from ^{1}H and ^{13}C NMR spectra (in CD_3OD) of DiNAC-PTS- catechol (**5**) and TriNAC-PTS-catechol (**6**). Chemical shifts were referenced to the solvent signals (3.30 ppm for ^{1}H or 49.0 ppm for ^{13}C).



DiNAC-PTS-catechol (**5**)



TriNAC-PTS-catechol (**6**)

Position	DiNAC-PTS-catechol (**5**)			TriNAC-PTS-catechol (**6**)		
	δ_H	Mult., *J* (Hz)	δ_C	δ_H	Mult., *J* (Hz)	δ_C
1			141			141
2	6.73	d, J = 2.0	106	6.72	d, J = 2.0	106
3			162			163
4	6.40	dd, J = 2.2, 2.4	101	6.41	dd, J = 2.2, 2.2	101
5			162			163
6	6.73	d, J = 2.0	106	6.72	d, J = 2.0	106
7	6.97	d, J = 16.4	130	6.55	d, J = 16.0	129
8	7.71	d, J = 16.0	128	7.34	d, J = 16.4	127
1'			134			137
2'			123			121
3'			148			142
4'			146			142
5'			123			121
6'	7.35	s	122			119
(2'-NAC)						
COOH			174			174
α	4.37	dd, J = 4.2, 4.6	54.5	4.32	dd, J = 4.4, 4.4	54.0
β	3.20	dd, J = 8.4, 14.0	37.0	3.40	dd, J = 4.4, 13.6	38.3
β	3.02	dd, J = 8.4, 13.6	37.0	3.01	dd, J = 8.6, 10.6	38.3
COMe			172			173
COMe	1.84[a]	s	22.4	1.79[b]	s	22.4
(5'-NAC)						
COOH			174			174
α	4.60	dd, J = 4.2, 4.2	53.9	4.53	dd, J = 4.6, 7.8	54.0
β	3.47	dd, J = 4.4, 14.4	35.8	3.45	dd, J = 4.4, 14.0	36.9
β	3.36	dd, J = 4.4, 14.0	35.8	3.30	m	36.9
COMe			172			172
COMe	1.95[a]	s	22.4	1.82[b]	s	22.4
(6'-NAC)						
COOH						174
α				4.28	dd, J = 4.0, 8.4	54.0
β				3.30	m	39.5
β				3.05	dd, J = 9.2, 10.0	39.5
COMe						173
COMe				1.97[b]	s	22.4
-OMe	3.82	s	55.8	3.82	s	55.8
-OMe	3.82	s	55.8	3.83	s	55.8

a, b: interchangeable within the same sign.

Figure S1. ^{1}H-NMR spectrum of TriNAC-PTS-catechol (**6**).

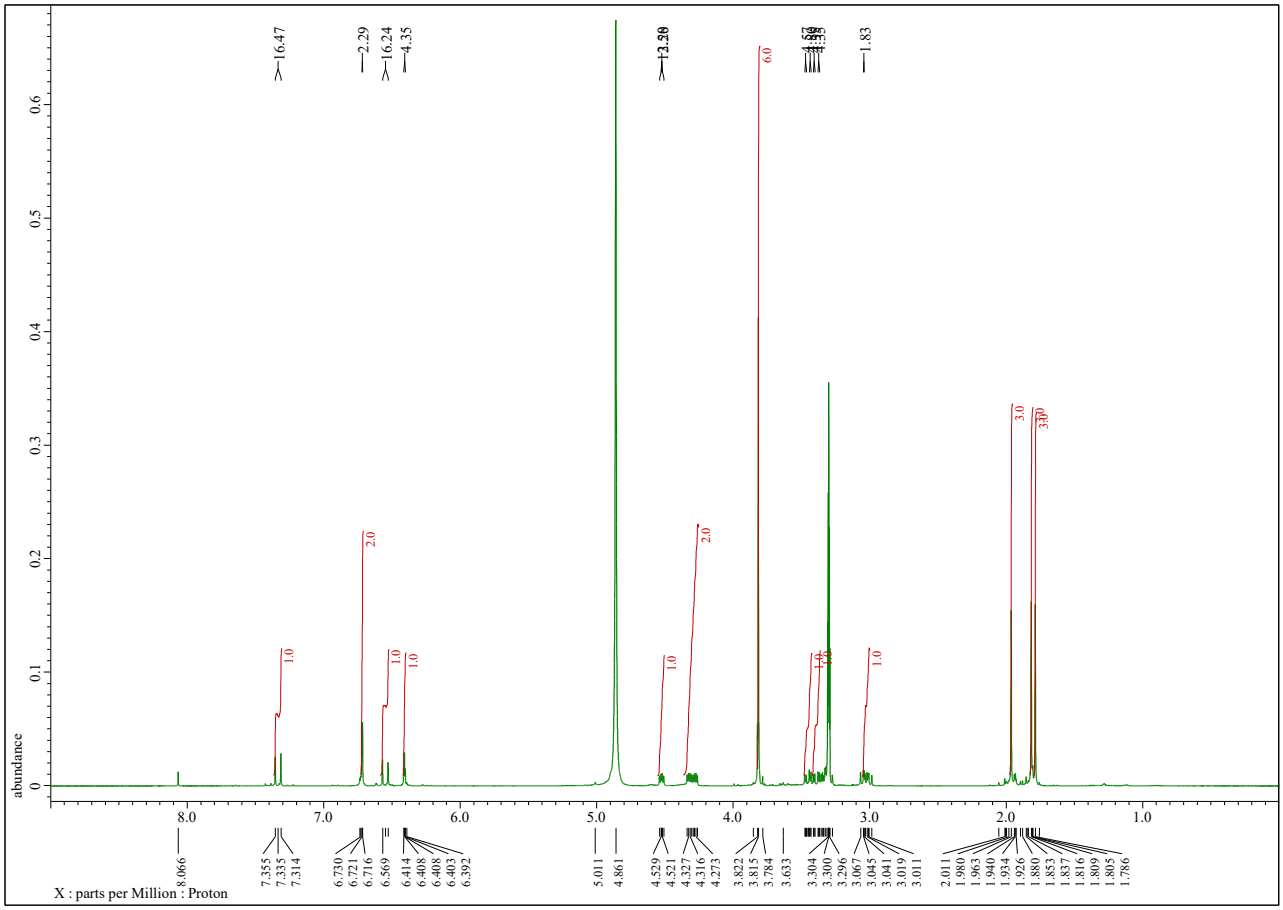


Figure S2. ^{1}H-NMR spectrum of DiNAC-PTS-catechol (**5**).

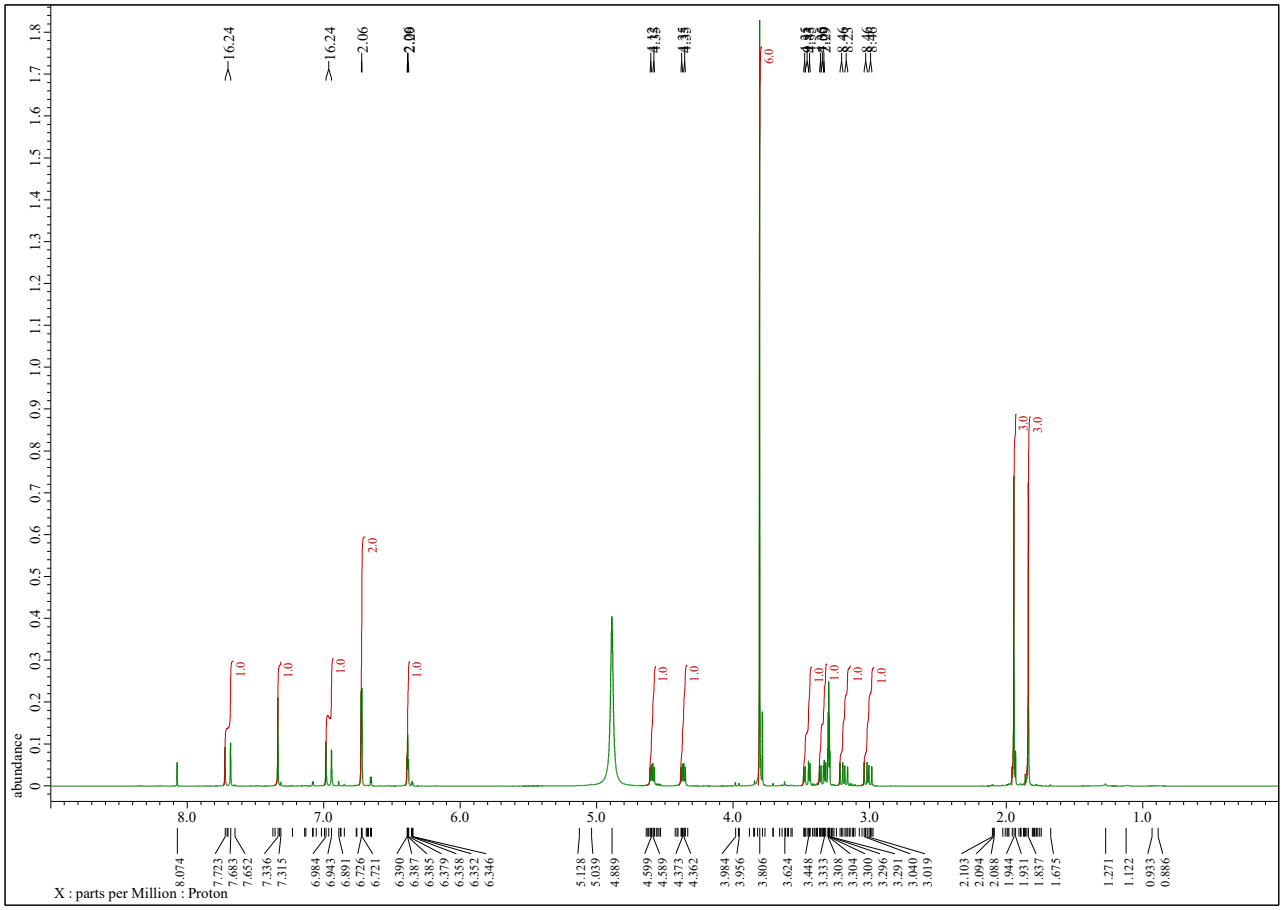


Figure S3. ^{1}H-NMR spectrum of PTS-catechol (**4**).

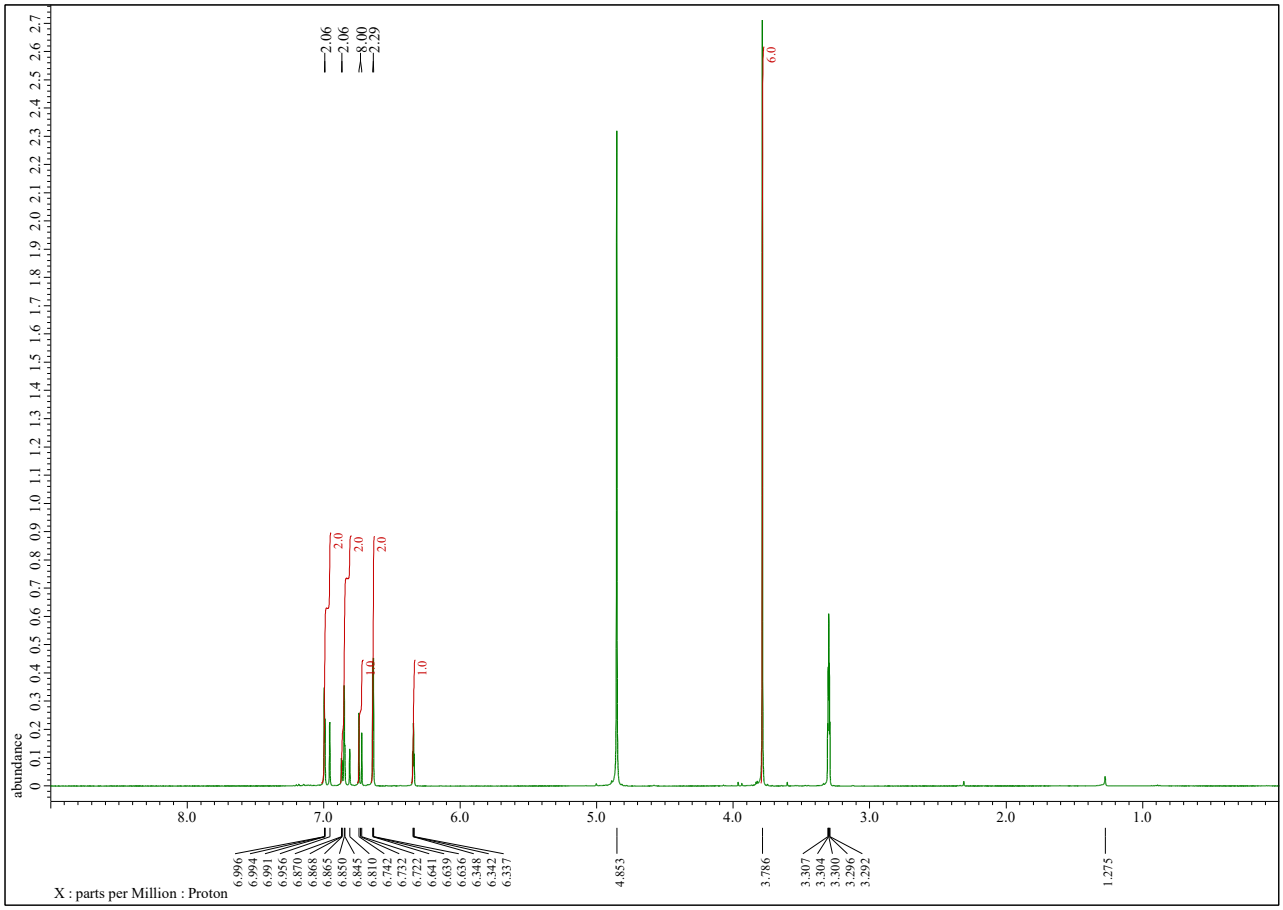


Figure S4. ^{13}C-NMR spectrum of DiNAC-PTS-catechol (**5**).

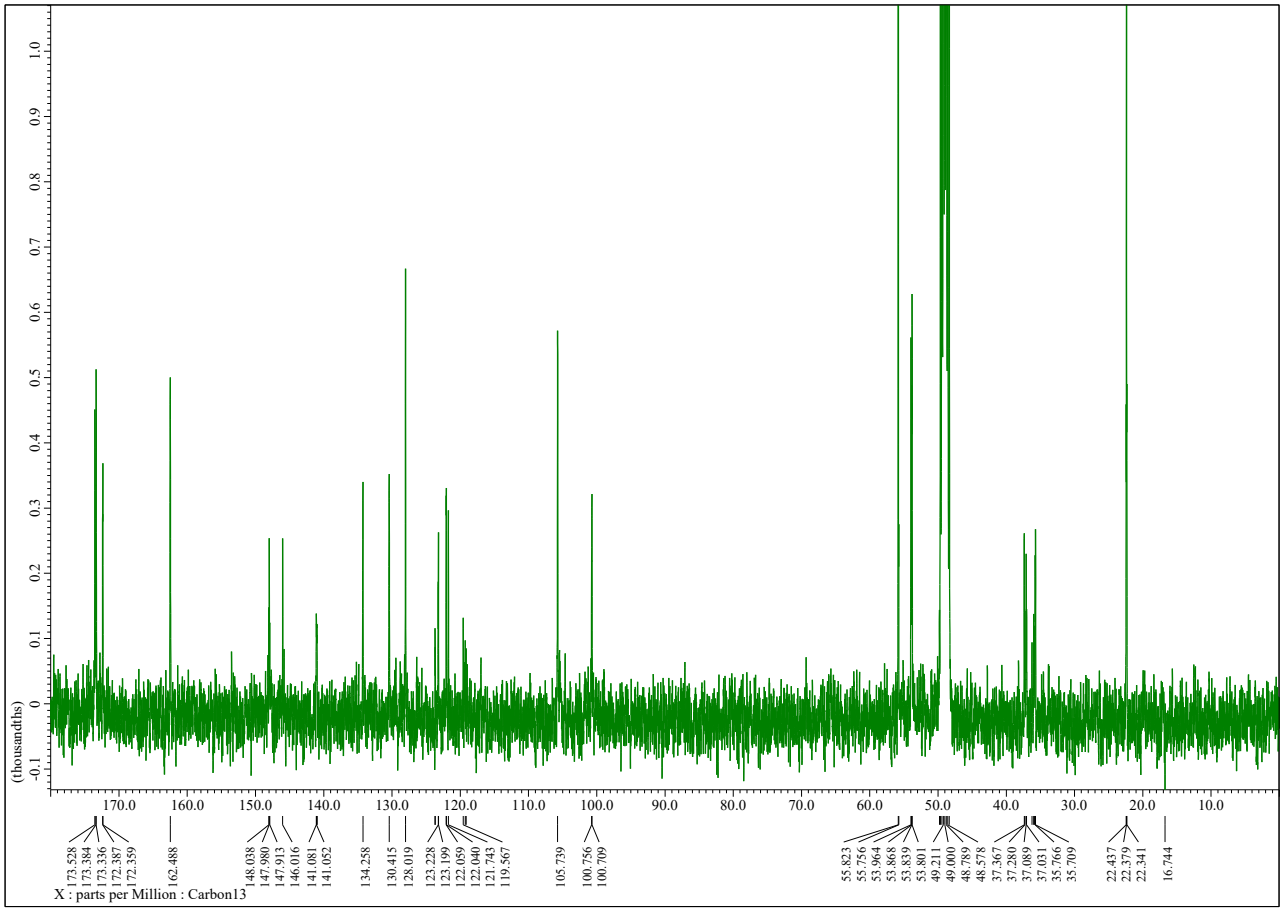


Figure S5. ^{13}C-NMR spectrum of TriNAC-PTS-catechol (**6**).

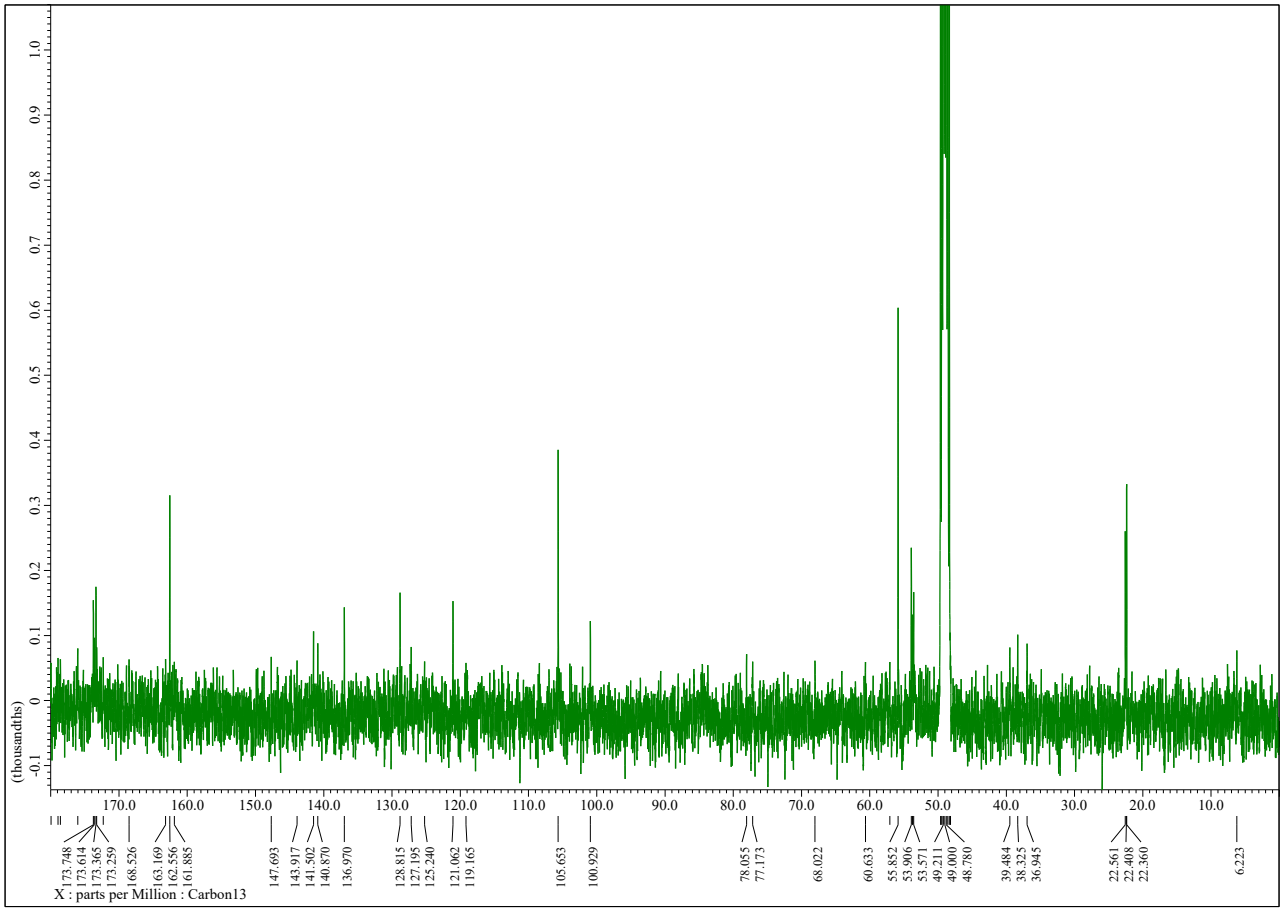


Figure S6. ^{13}C-NMR of PTS-catechol (**4**).

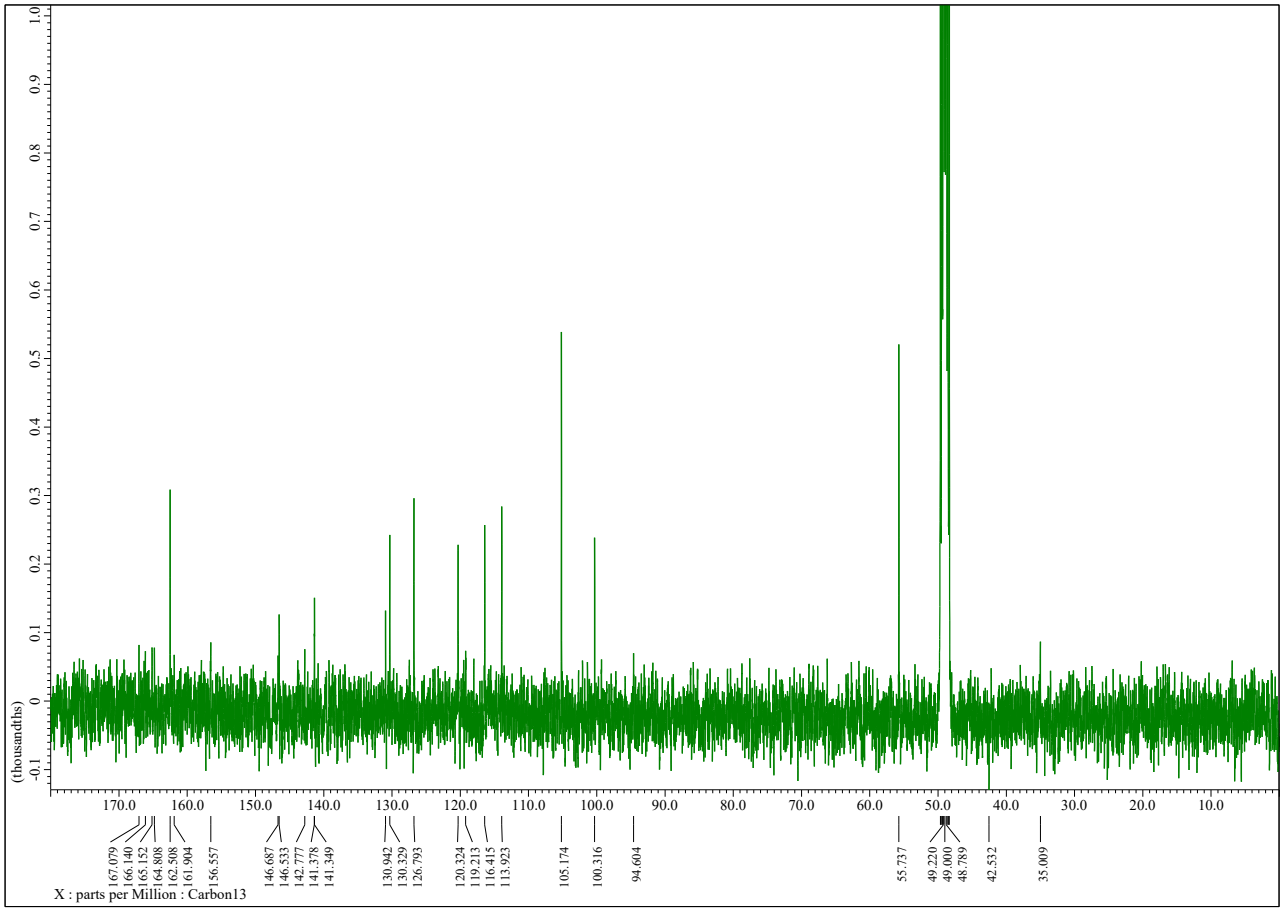


Figure S7. COSY of DiNAC-PTS-catechol (**5**).

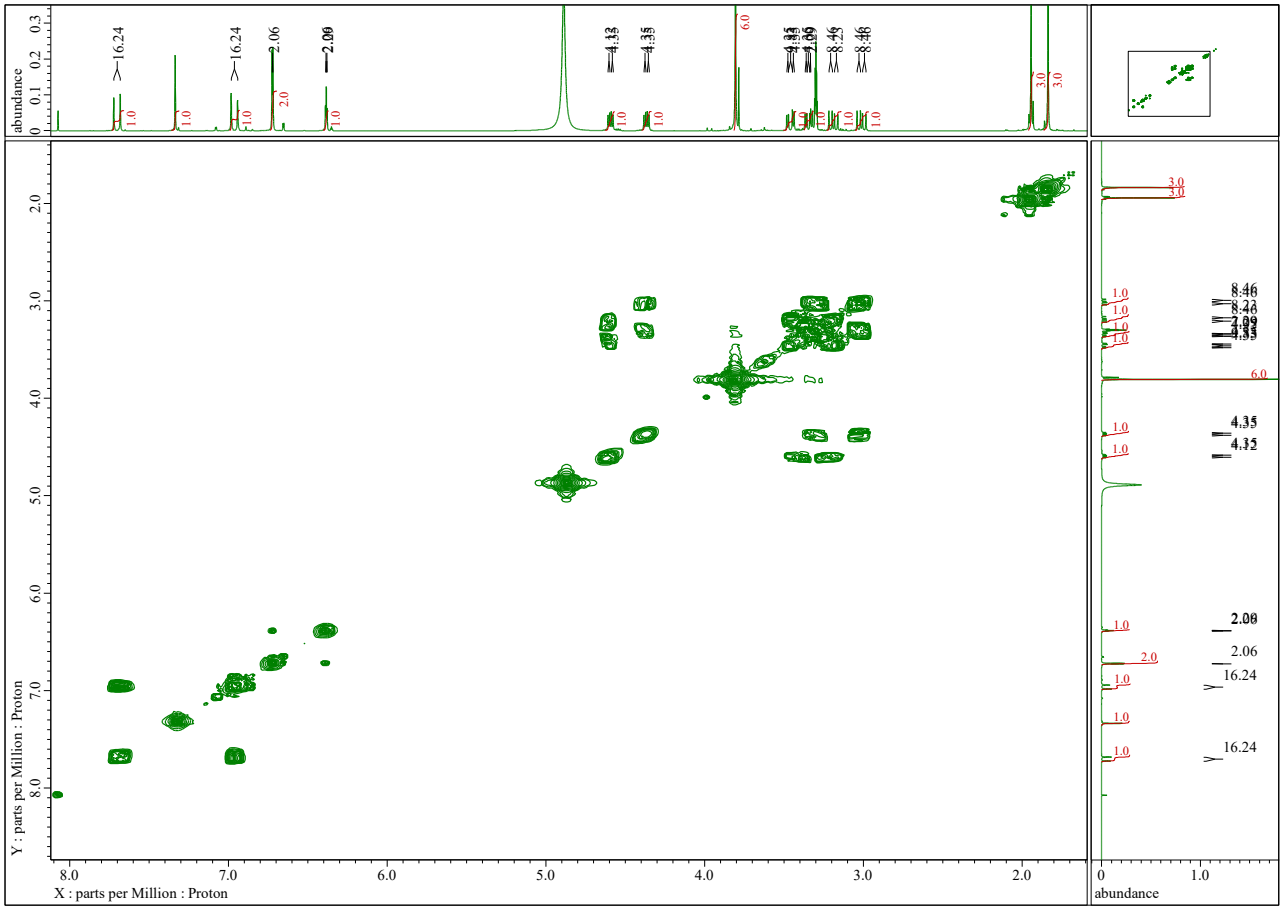


Figure S8. COSY of TriNAC-PTS-catechol (**6**).

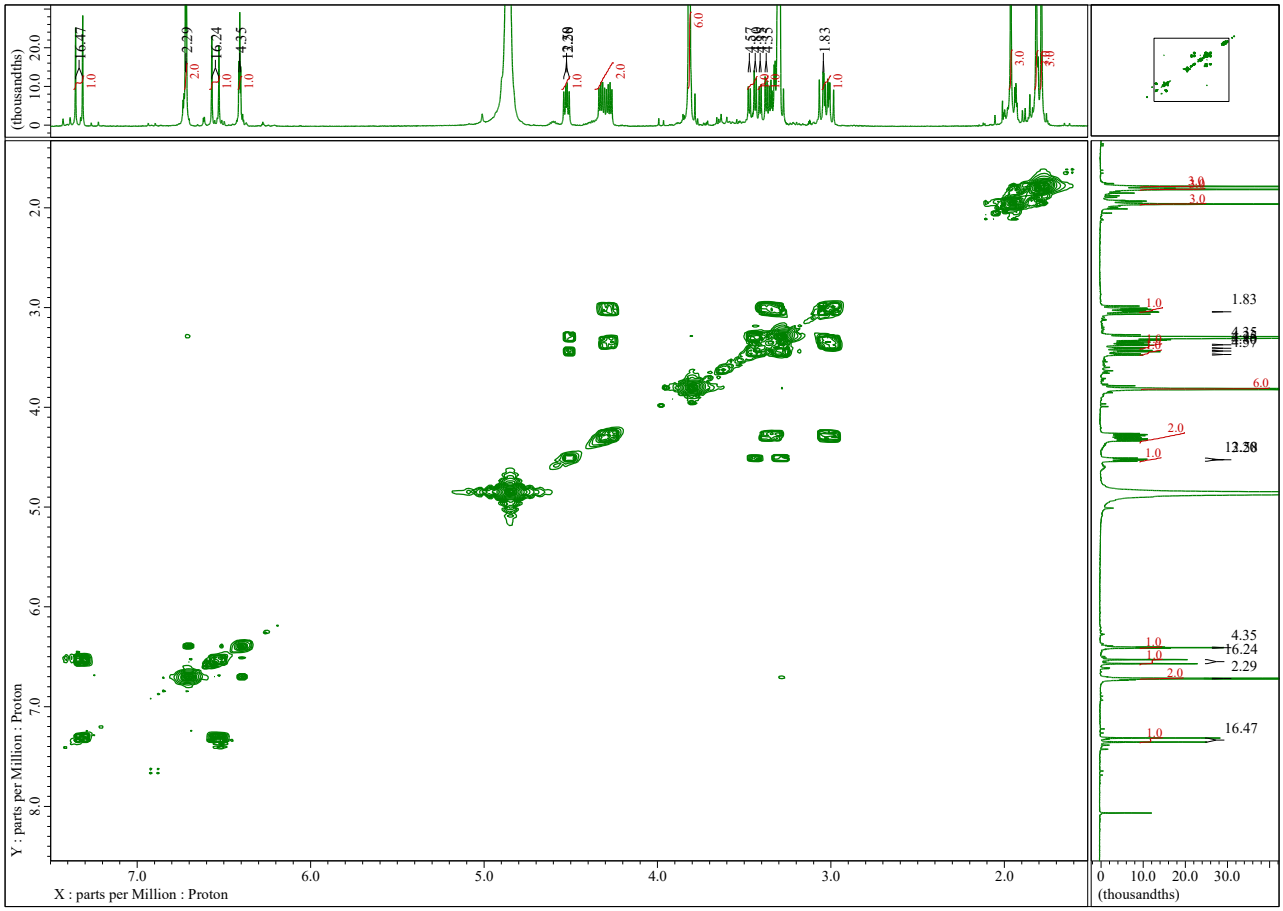


Figure S9. COSY of PTS-catechol (**4**).

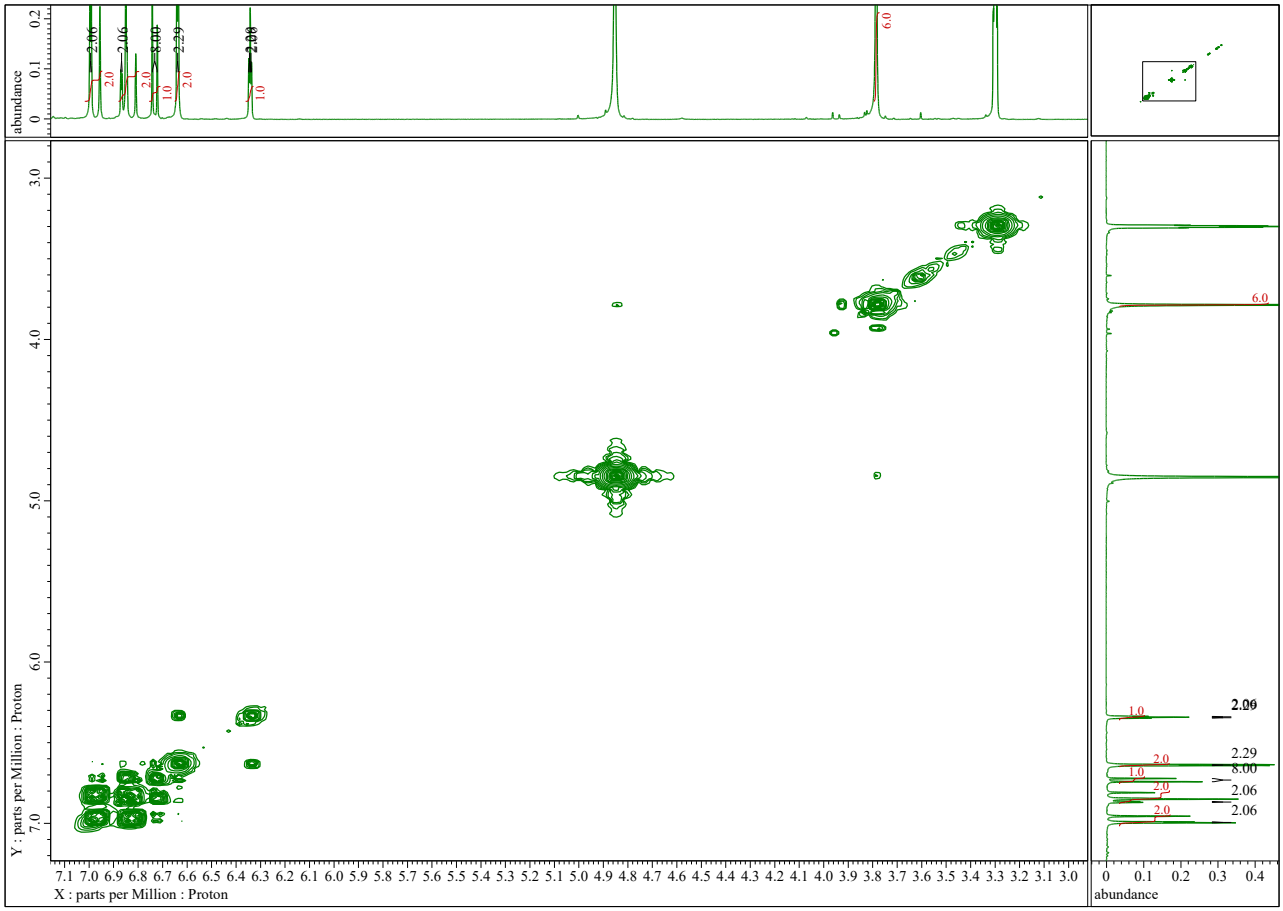


Figure S10. HMBC of DiNAC-PTS-catechol (**5**).

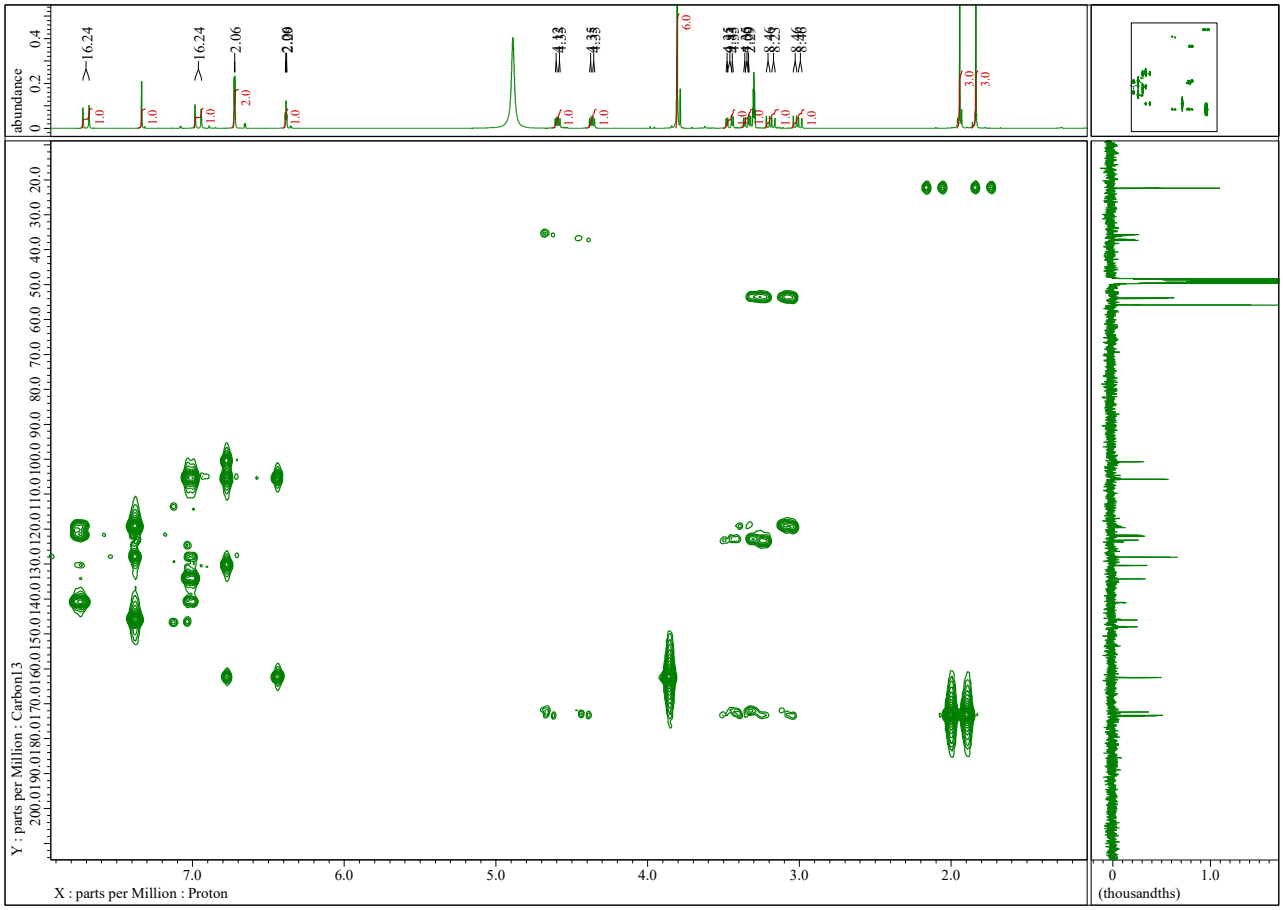


Figure S11. HMBC of TriNAC-PTS-catechol (**6**).

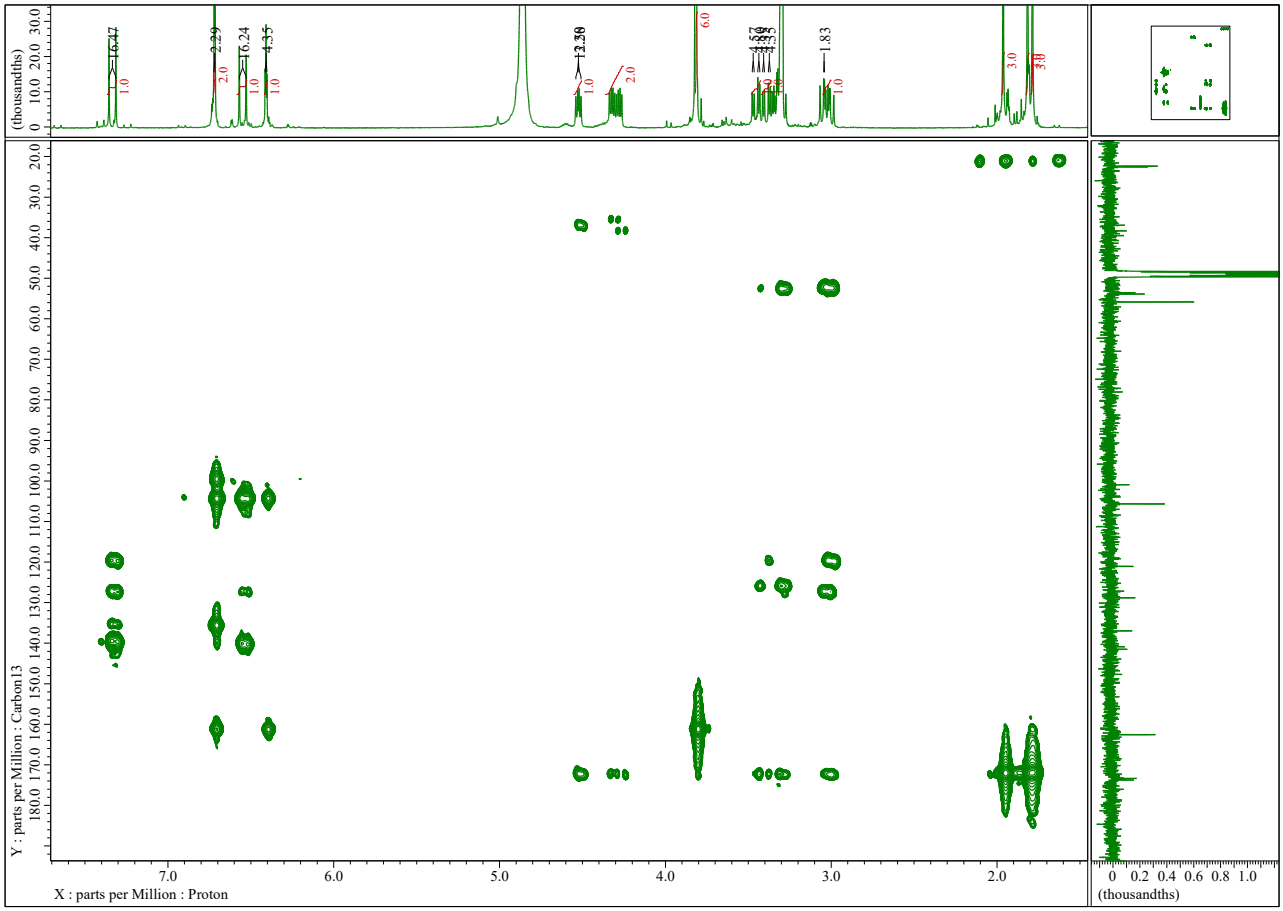


Figure S12. HMBC of PTS-catechol (**4**).

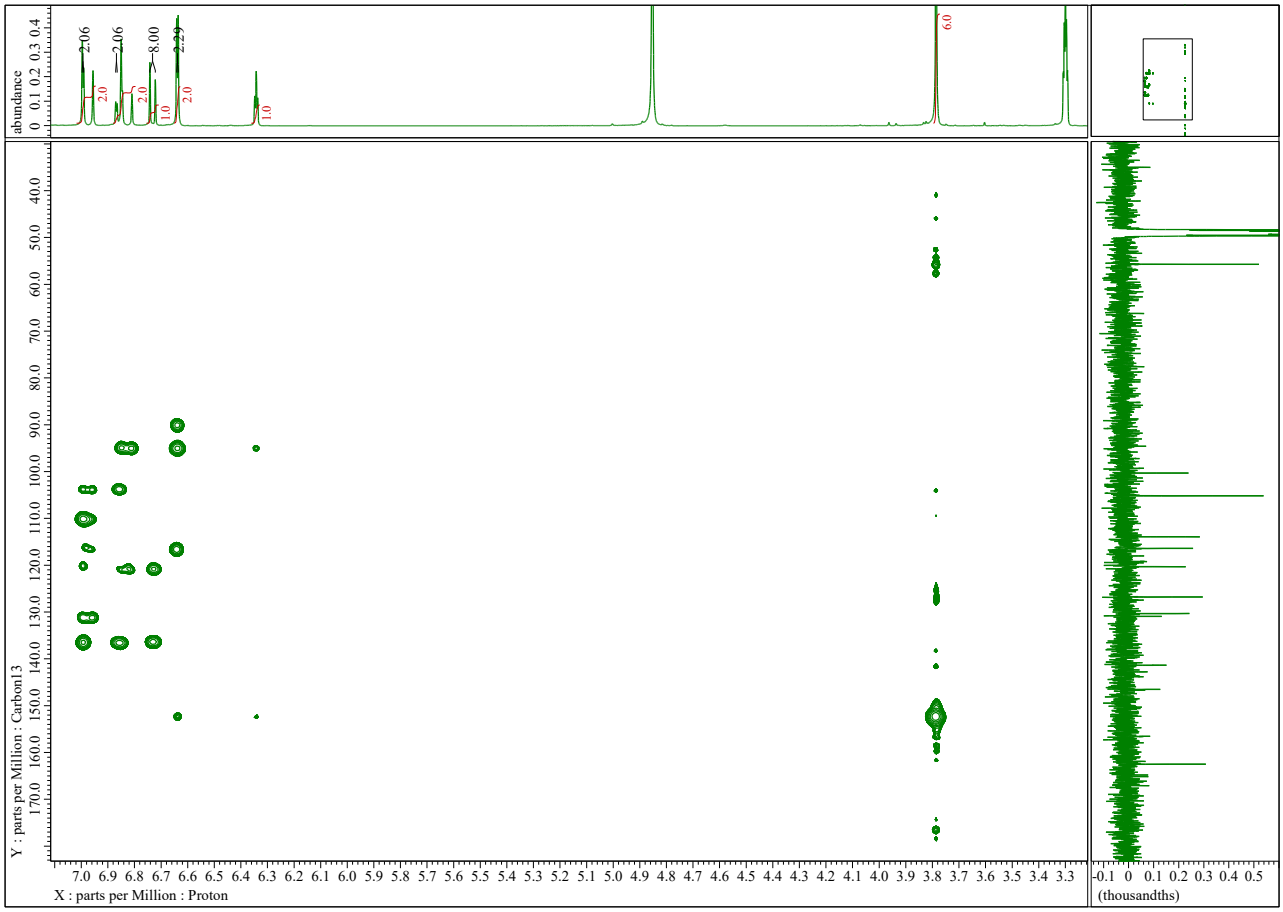


Figure S13. HMQC of DiNAC-PTS-catechol (**5**).

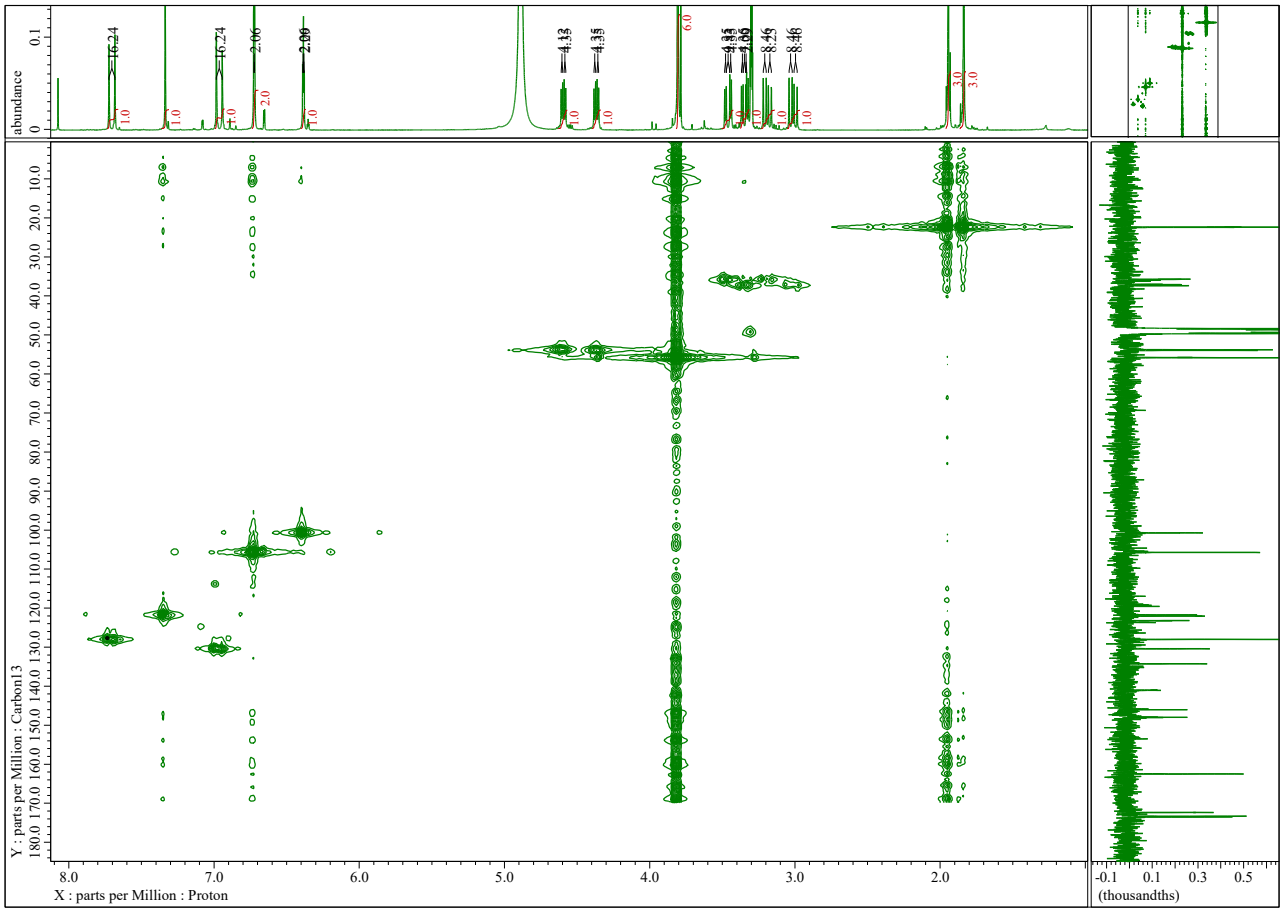


Figure S14. HMQC of TriNAC-PTS-catechol (**6**).

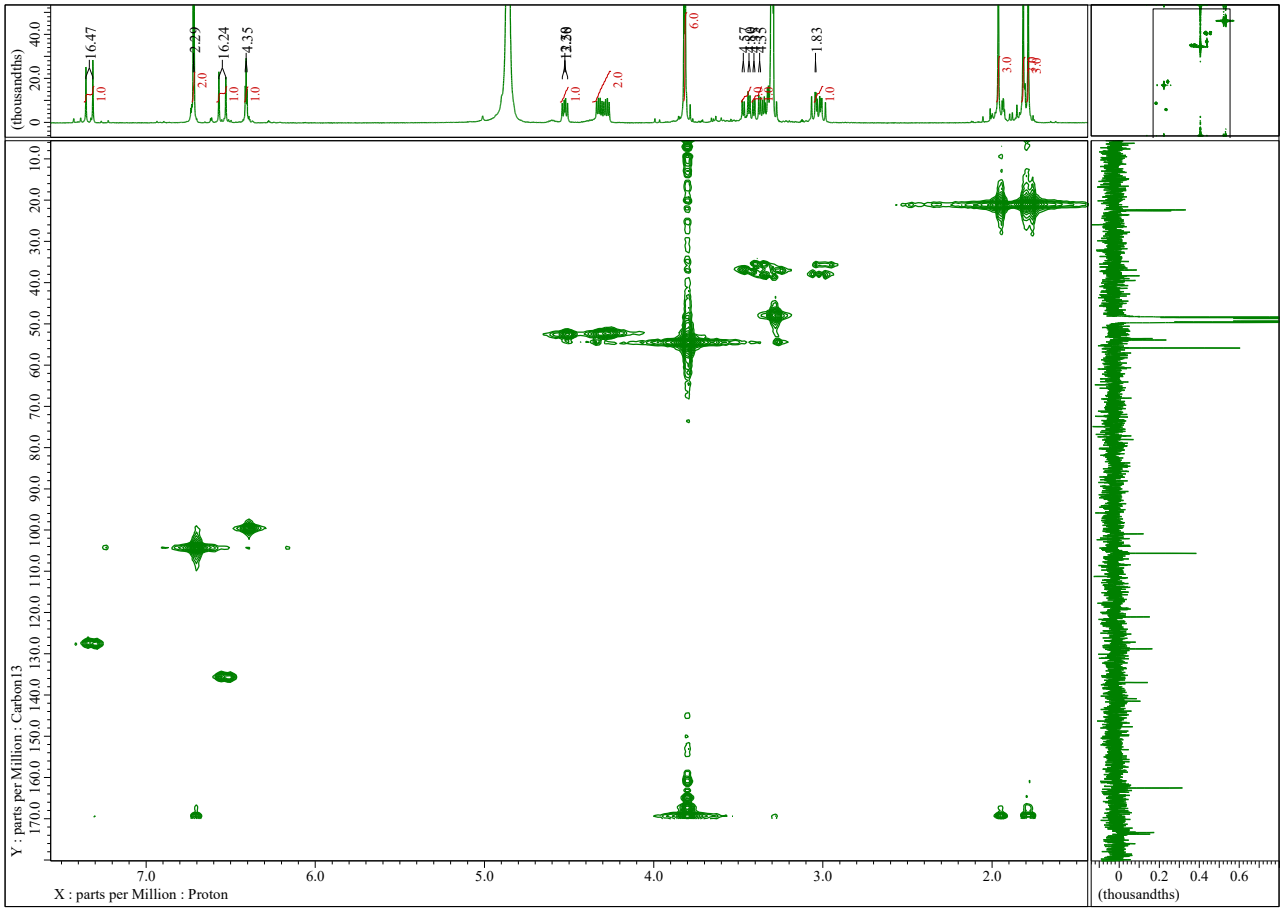


Figure S15. HMQC of PTS-catechol (**4**).

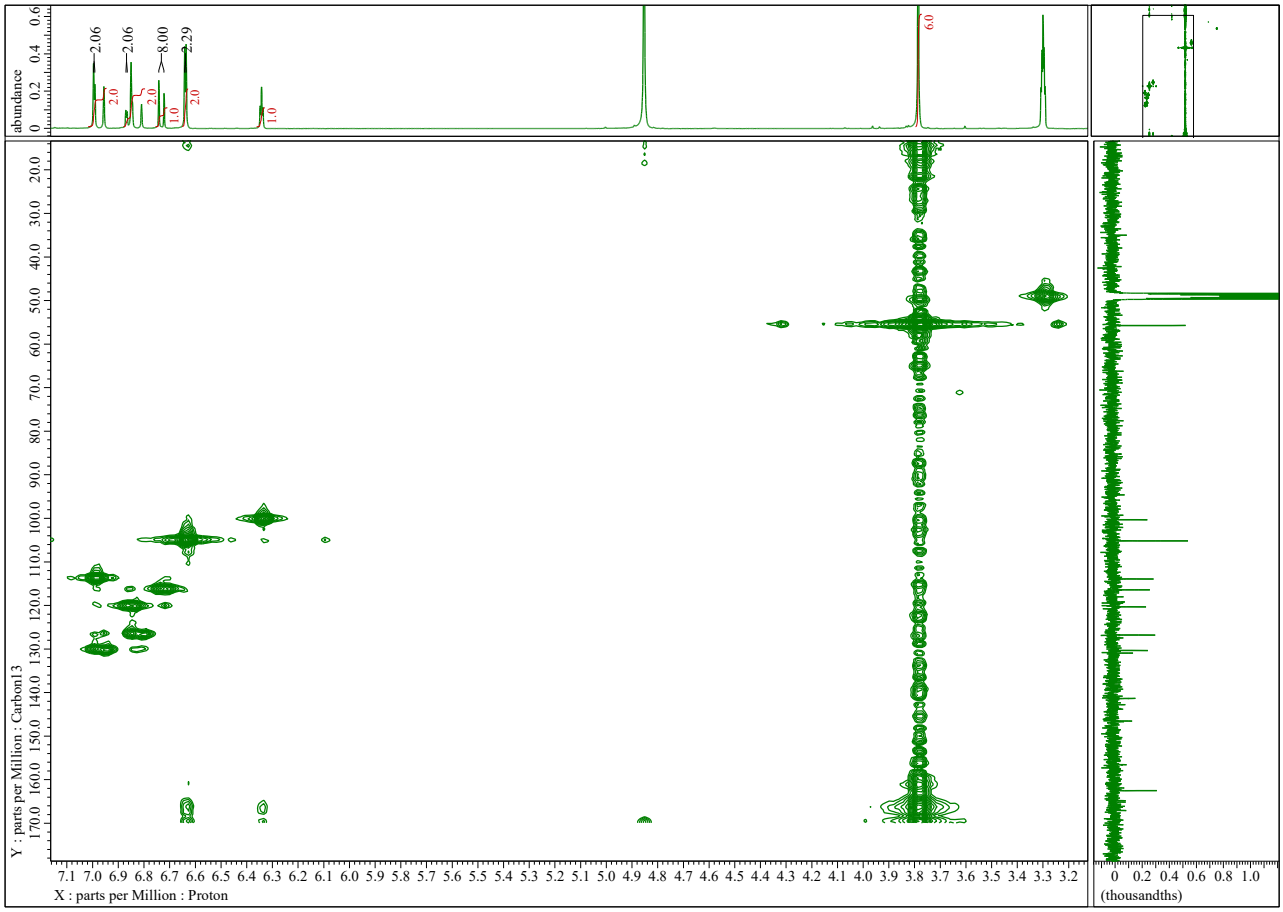


Figure S16. Tyrosinase-dependent cytotoxicity against **(a)** PTS (**2**), **(b)** RES (**1**), and **(c)** 4SCAP in human tyrosinase-expressing 293T cells (hTYR-293T cells). Viability of TYR- or mock-transfected cells treated with the indicated concentrations of compounds for 2 h were assessed. Data represent means ± SD (n = 3 wells). Results are representative of two or three independent experiments.

