Halogenated *β*, *γ*-methylene- and ethylidene-dGTP-DNA ternary complexes with DNA polymerase *β*: structural evidence for stereospecific binding of the fluoro analogues

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For detailed synthesis and analytical data for compounds **1-9**, **15**, **16** see *Biochemistry* **2008**, *47,* 870-879 and *JACS* **2007**, *129,* 15412-15413.

Supporting Information

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Table S1. Summary of HPLC peak retention and eluting buffer data for β,γ-methylene bisphosphonate dGTP analogues **1 - 16**

(Column specifications and other HPLC information are given in the main article. See also: *Biochemistry* **2008**, *47,* 870-879 and *JACS* **2007**, *129,* 15412-15413.

Compound (#)	CXY	Retention time (column)	Buffer
dGMP	------	3.5 min (C-18)	0.1N TEAB (2% CH_3CN)
	------	8 min (SAX)	0-100% 0.5M TEAB gradient
dGMP-Morph	------	5.5 min (C-18)	0.1N TEAB (2% CH_3CN)
	------	5 min (SAX)	0-100% 0.5M TEAB gradient
dGMP-MBP (**1**)	CH_2	16 min (SAX)	0-100% 0.5M TEAB gradient
dGMP-DFBP (**2**)	CF_2	17 min (SAX)	0-100% 0.5M TEAB gradient
dGMP-MFBP (**3**/**4**)	CHF	13 min (SAX)	0-100% 0.5M LiCl gradient
dGMP-DCBP (**5**)	CCl_2	16 min (SAX)	0-100% 0.5M TEAB gradient
dGMP-MCBP (**6**/**7**)	CHCl	17 min (SAX)	0-100% 0.5M TEAB gradient
dGMP-MBBP (**8**/**9**)	CHBr	13 min (SAX)	0-100% 0.5M LiCl gradient
dGMP-EBP (**10**/**11**)	$CH(CH_3)$	12 min (SAX)	0-100% 0.5M LiCl gradient
dGMP-DMBP (**12**)	$C(CH_3)_2$	11 min (SAX)	0-100% 0.5M LiCl gradient
dGMP-FMBP (**13**/**14**)	$CF(CH_3)$	13 min (SAX)	0-100% 0.5M LiCl gradient
dGMP-FClBP (**15**/**16**)	CFCl	12 min (SAX)	0-100% 0.5M LiCl gradient

Figures S1-S6: HPLC analysis

Reaction mixtures were analyzed by injecting 2-3 μL into the indicated column. The relative intensities of the weaker spectra have been increased up to 3- fold to aid in peak comparisons. The HPLC data were visualized using either Chromplot v1.2 (Rainin) or EZStart v7.4 (Shimadzu).

Figure S1. HPLC analysis (SAX) of the conversion of dGMP-Morph to **10/11**.

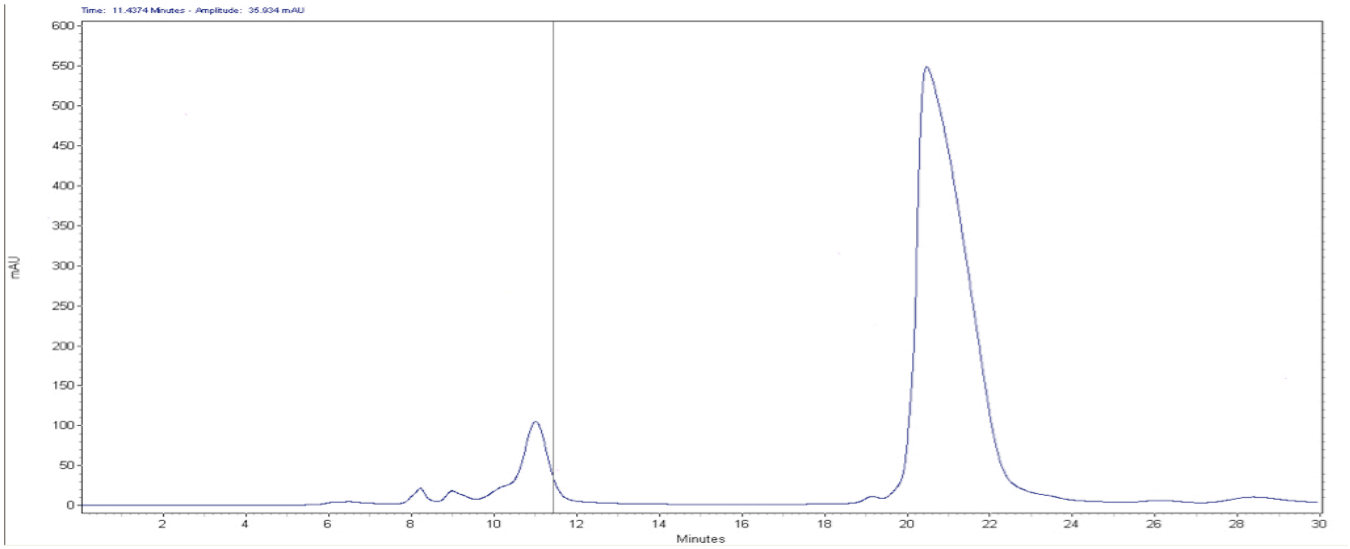


Figure S2. HPLC analysis (SAX) of **10/11** after dual-pass prep. HPLC.

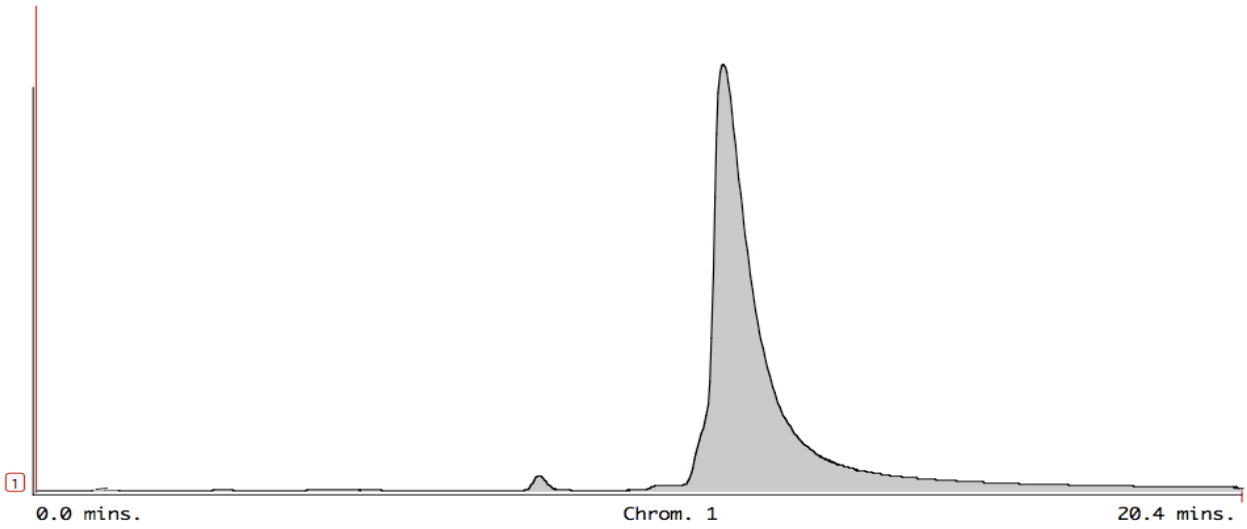


Figure S3. HPLC analysis (SAX) of the conversion of dGMP-Morph to **12.**

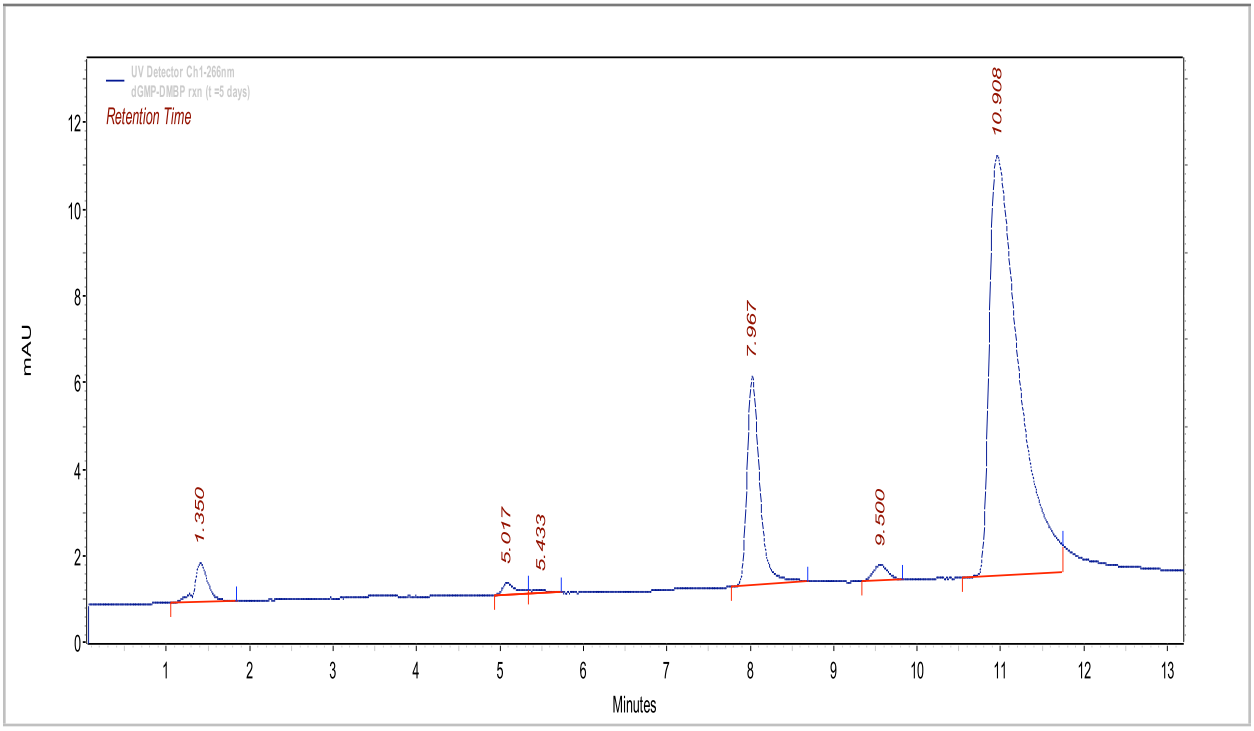


Figure S4. HPLC analysis (SAX) of **12** after dual-pass prep. HPLC.

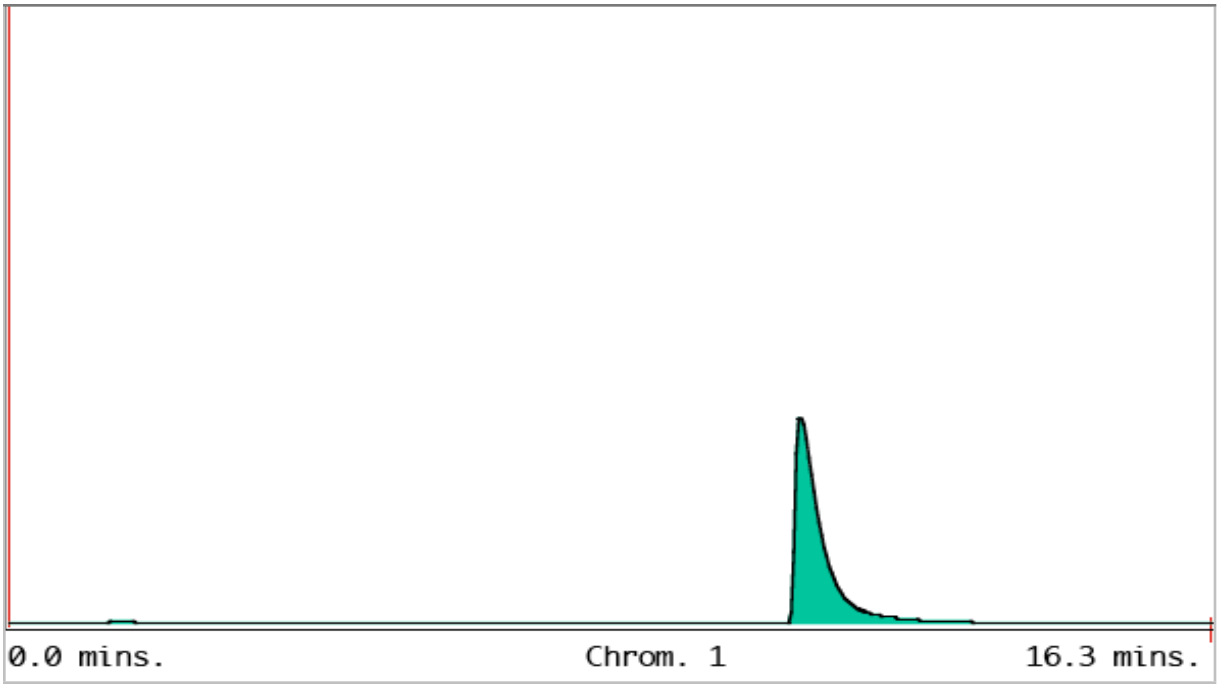


Figure S5. HPLC analysis (SAX) of the conversion of **dGMP-Morph** to **13**/**14**.

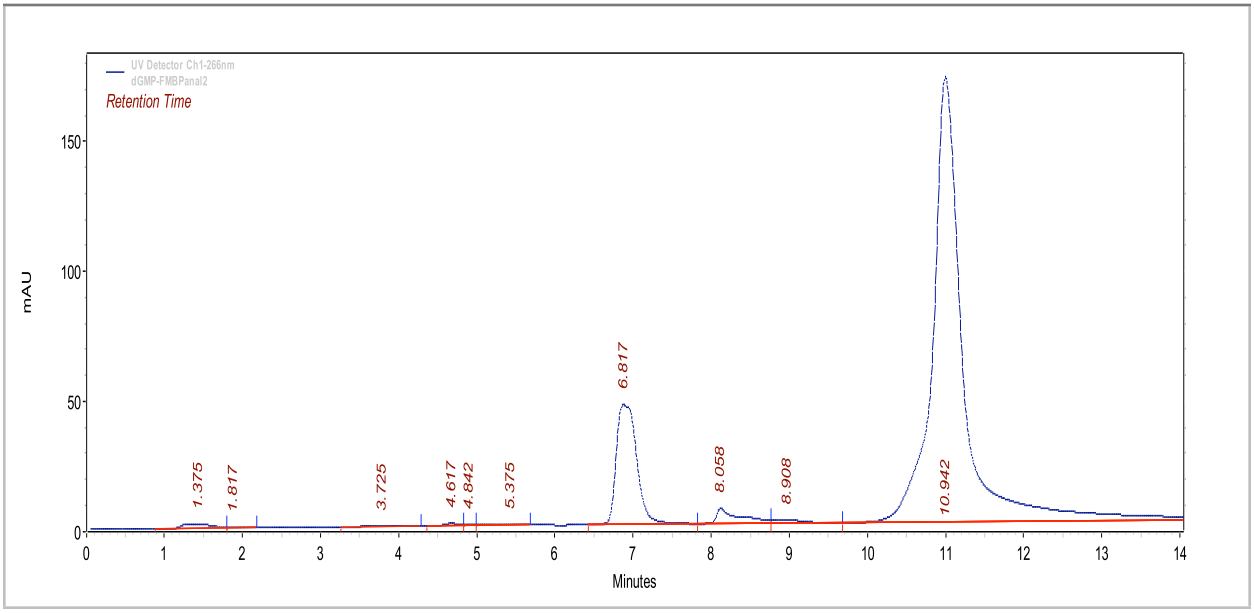
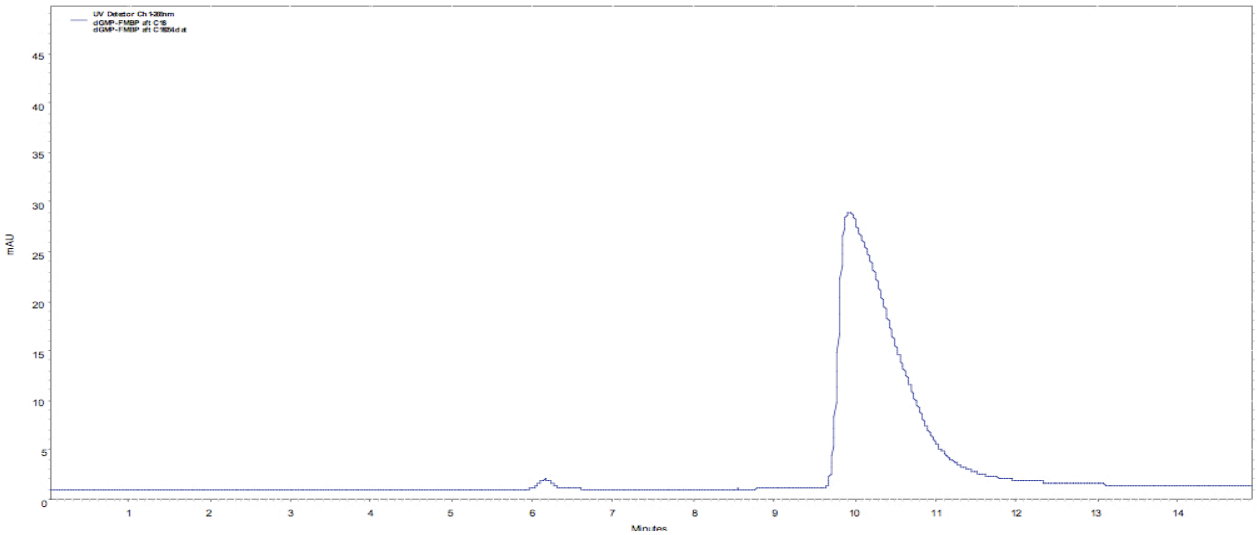


Figure S6. HPLC analysis (SAX) of **13**/**14** after dual-pass prep. HPLC.



MS Analysis of *β,γ*-methylene analogues of dGTP

Figure S7. HRMS dGMP-EBP, **10/11**

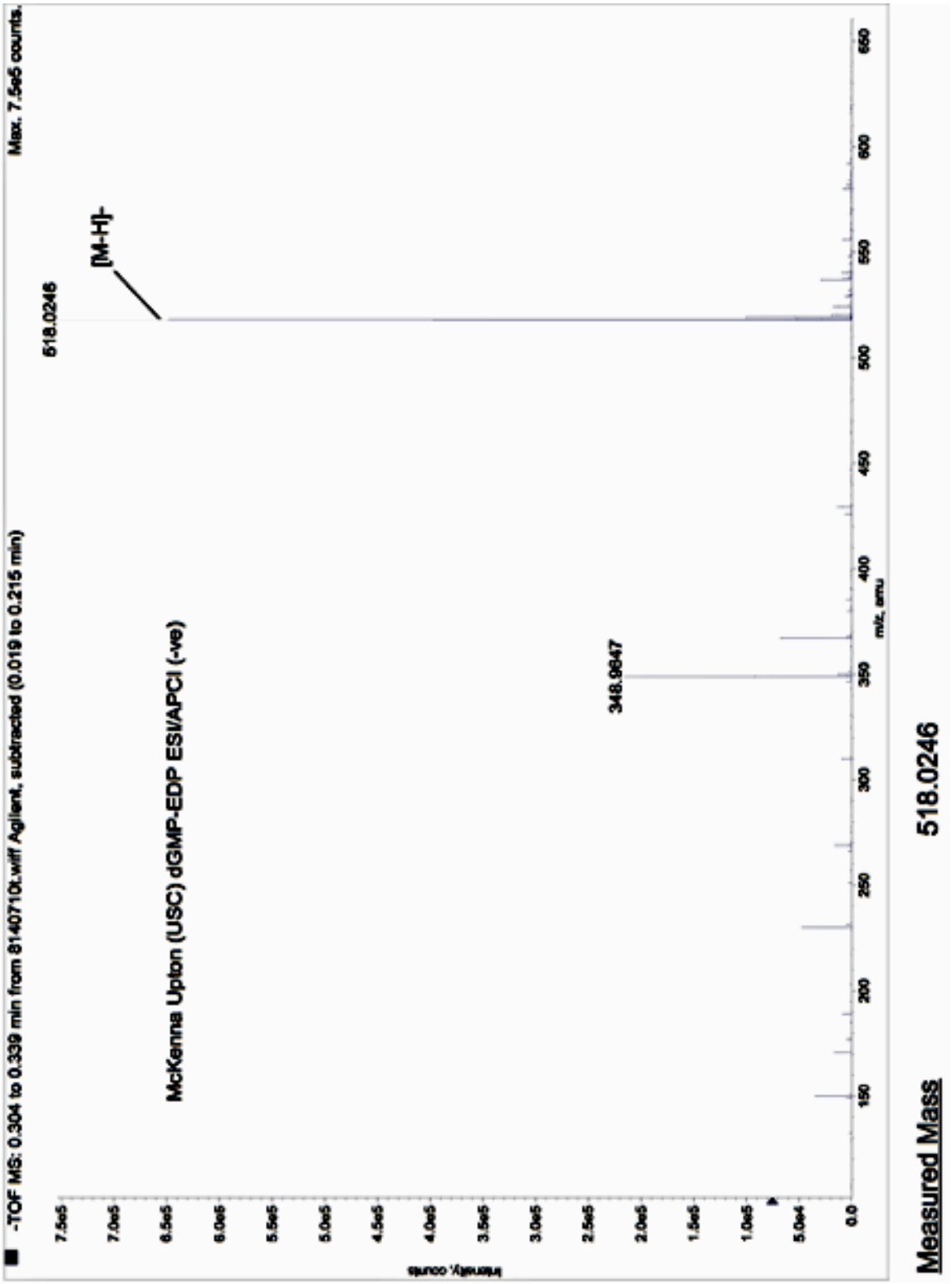


Figure S8. HRMS dGMP-DMBP, **12**

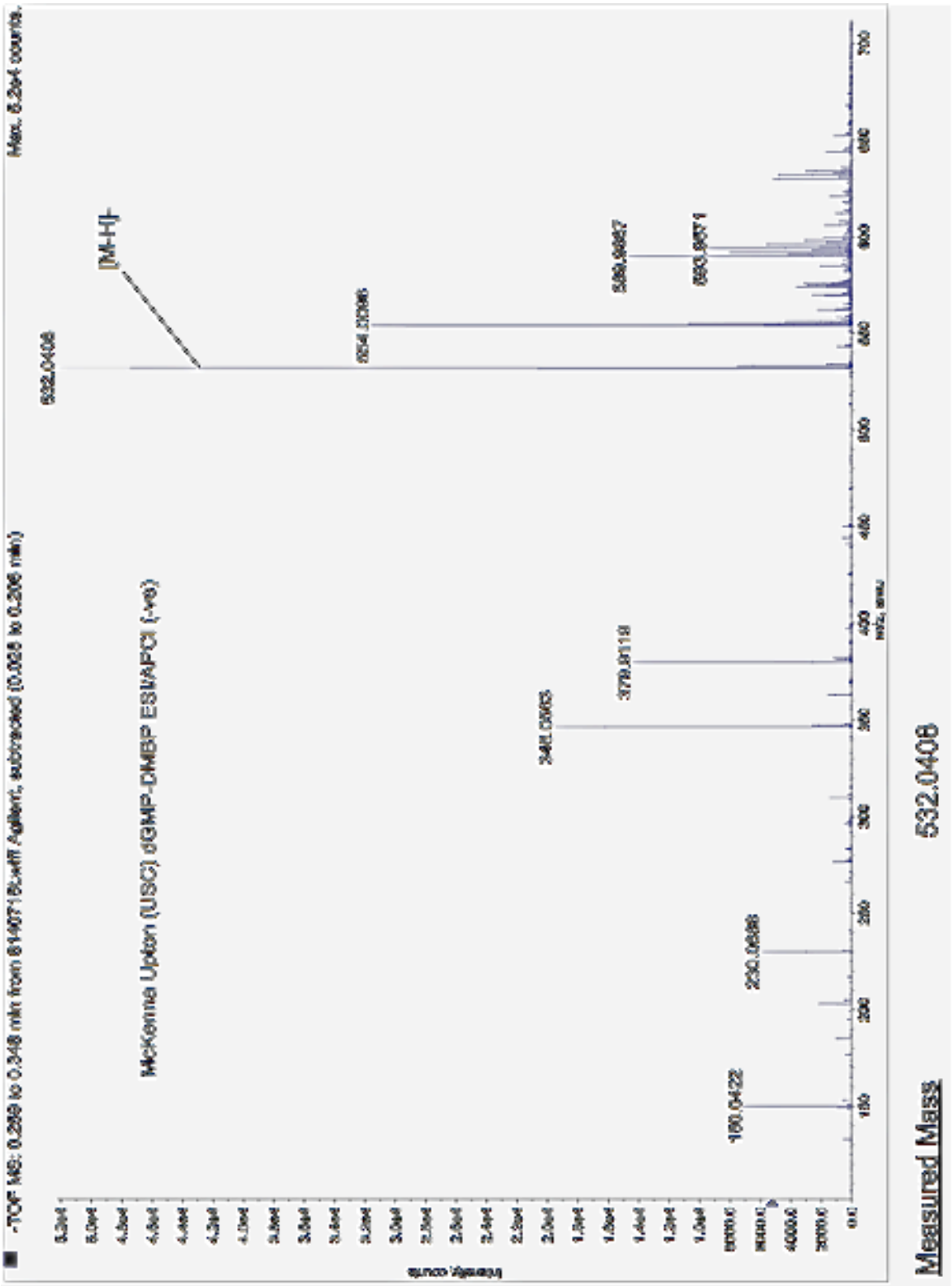
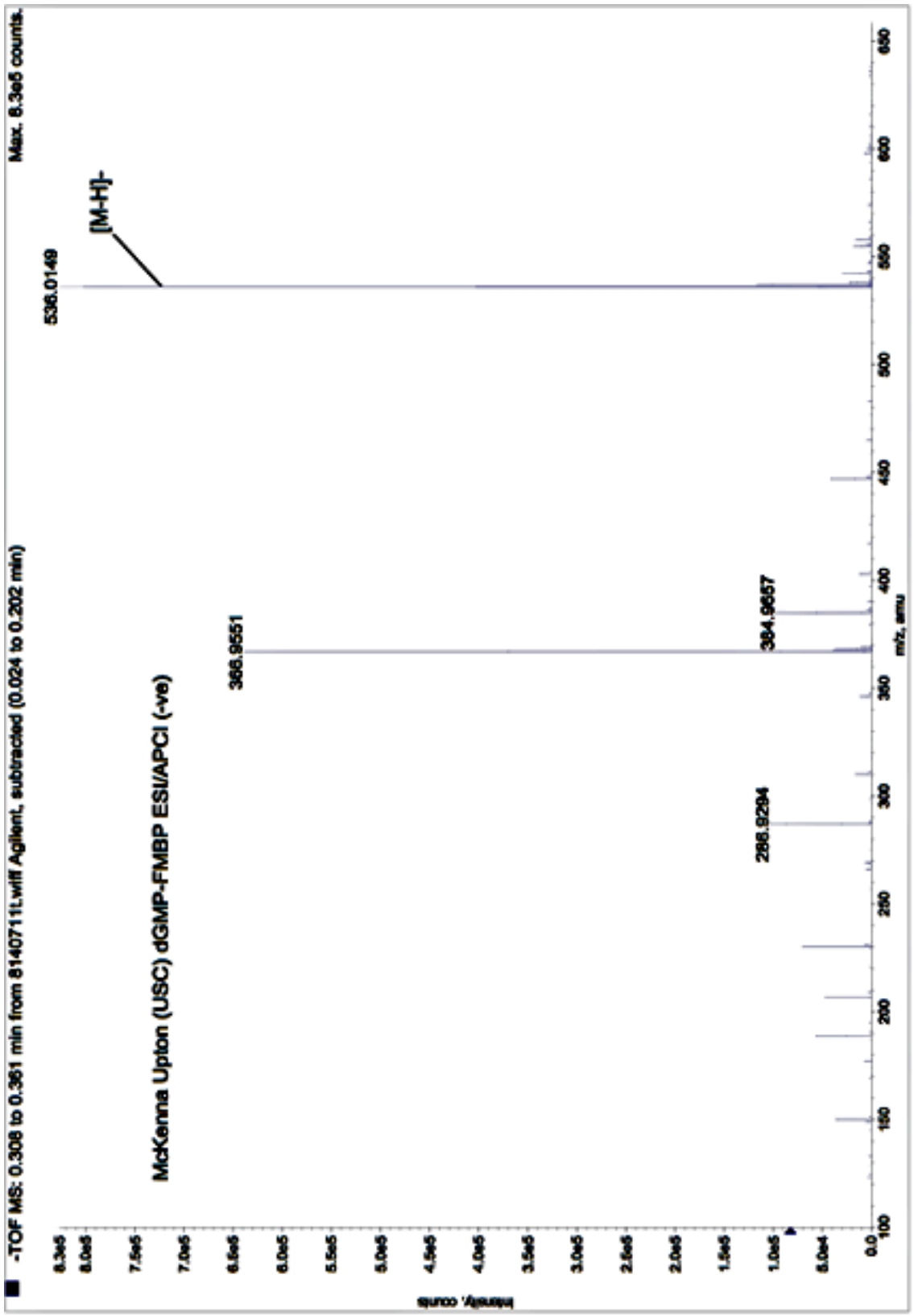


Figure S9. HRMS dGMP-FMBP, **13/14**



NMR Analysis of *β,γ*-methylene analogues of dGTP

NOTE All compounds are isolated as the triethylammonium salt after dual-pass HPLC

Figure S10. ^{1}H NMR of dGMP-*β,γ*-EBP, **10/11**

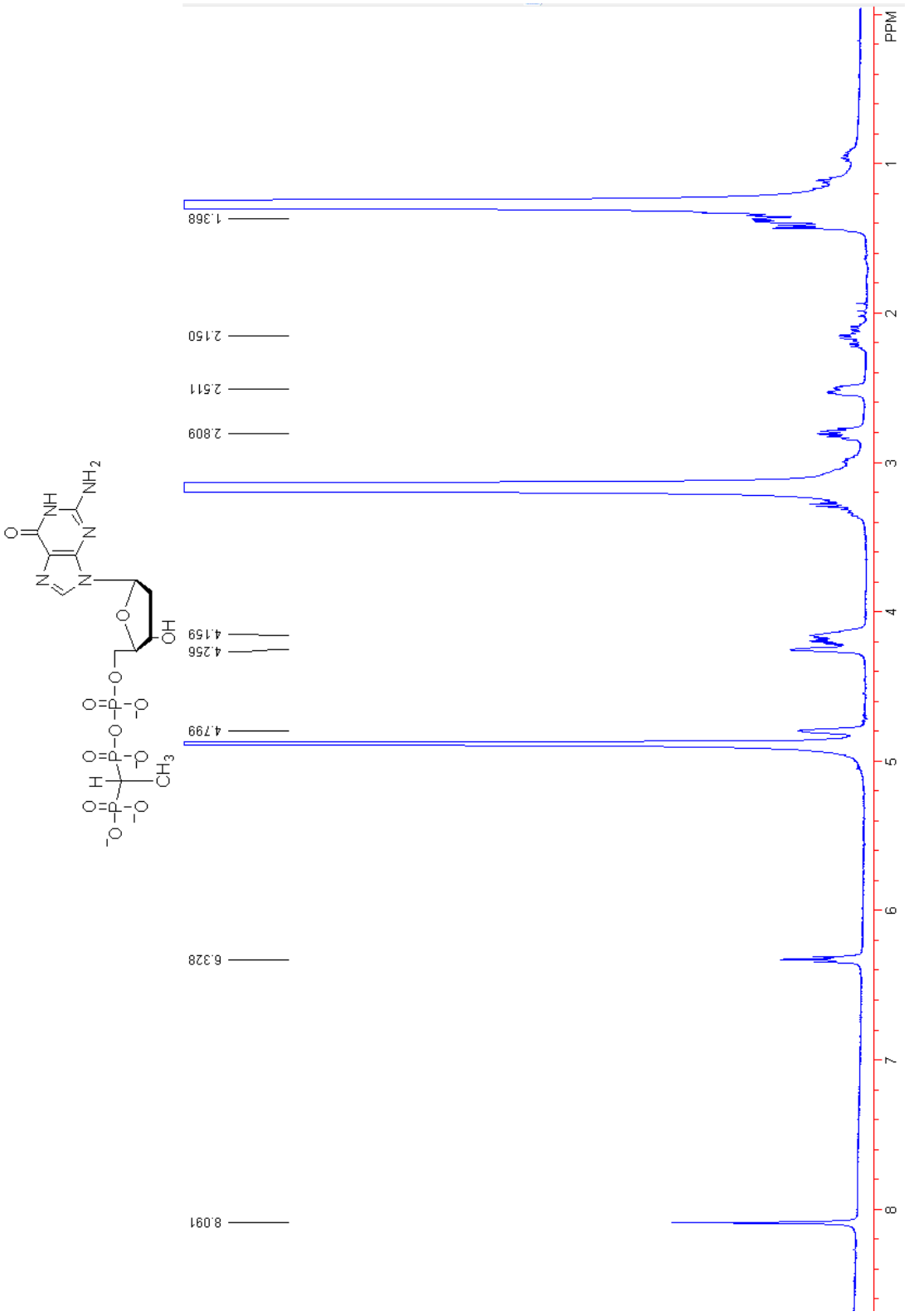


Figure S11. ^{31}P NMR of dGMP-*β,γ*-EBP, **10/11** (^{1}H decoupled)

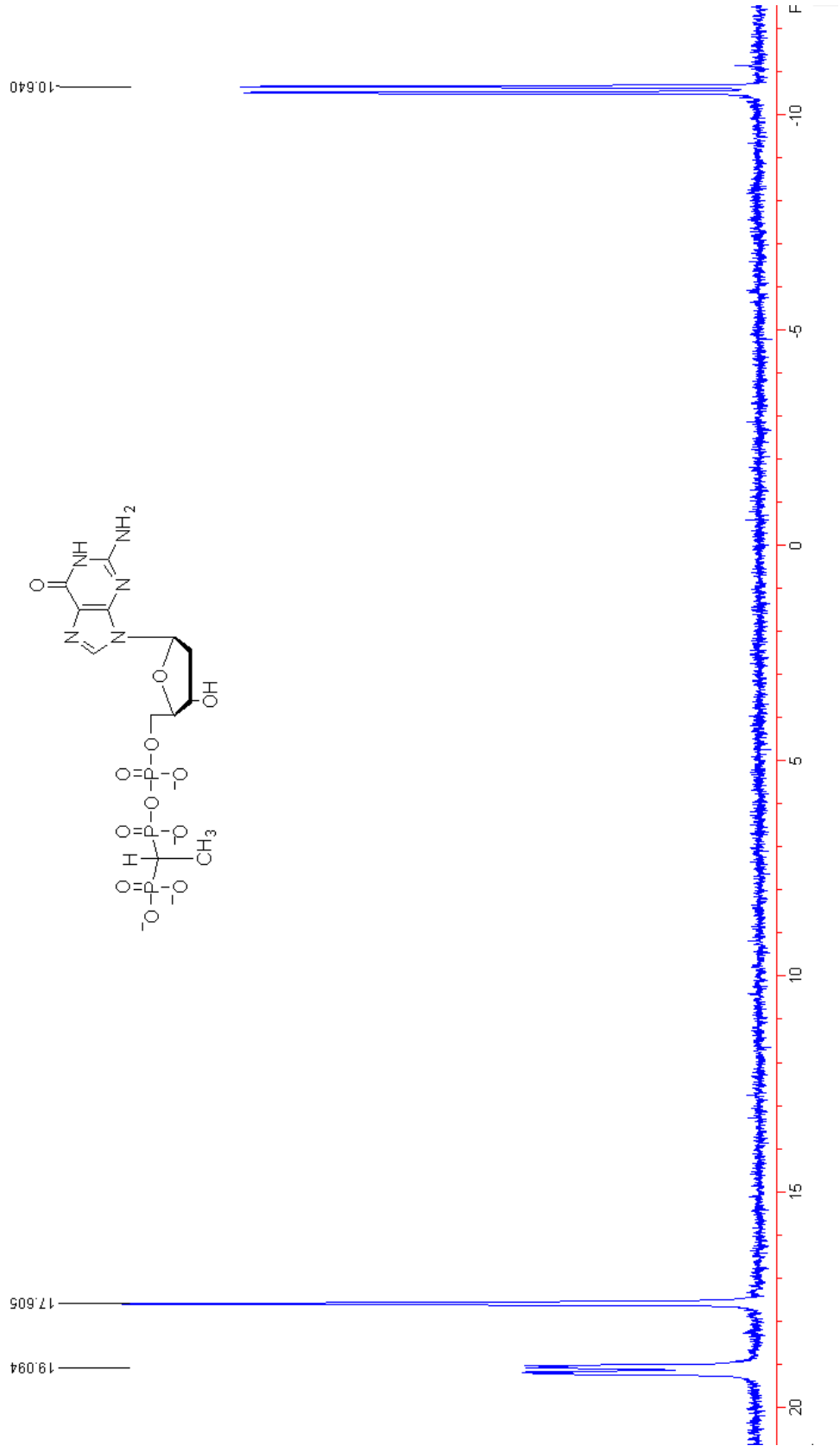


Figure S12. ^{1}H NMR of dGMP-*β,γ*-DMBP, **12**

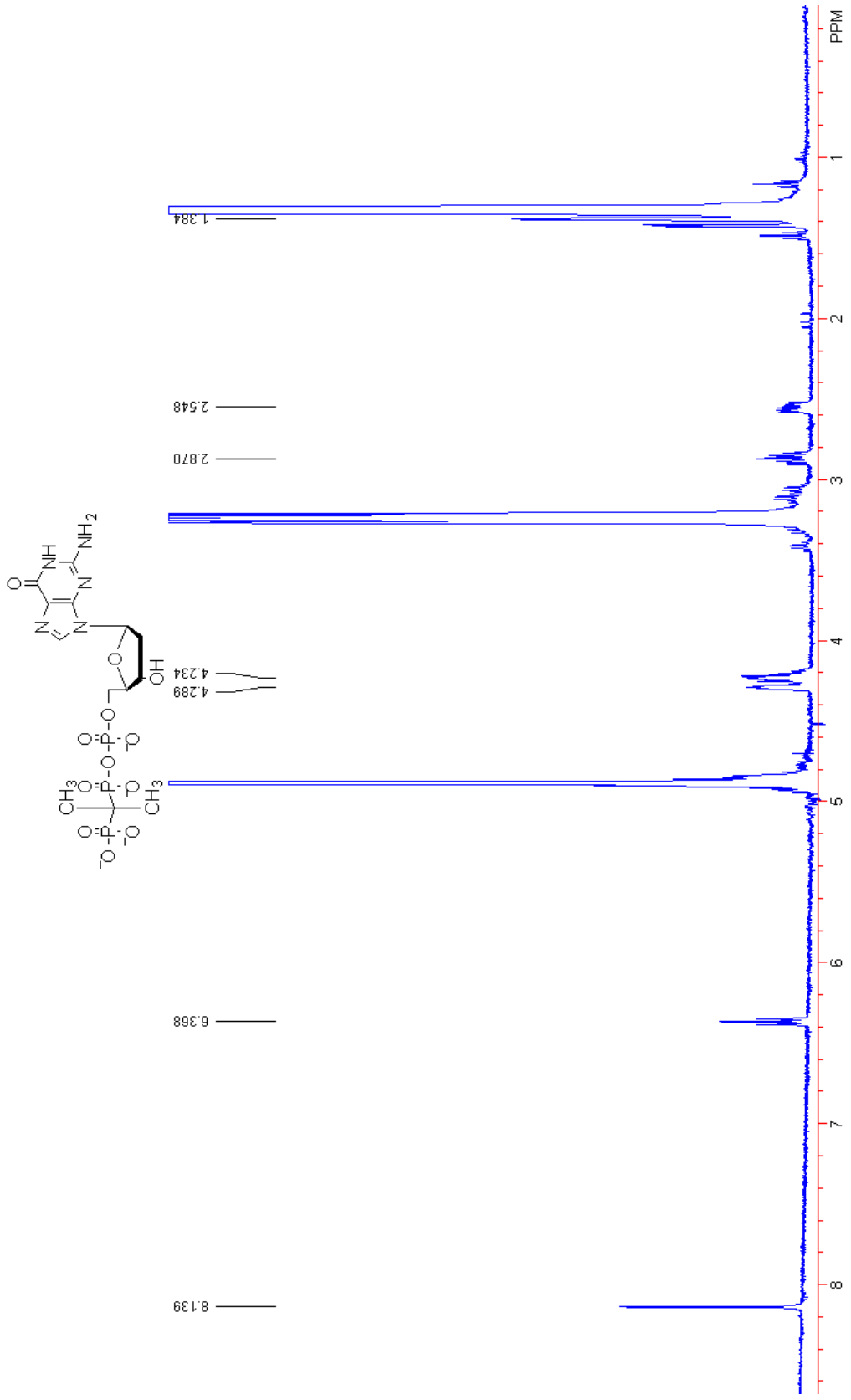


Figure S13. ^{31}P NMR of dGMP-β,γ-DMBP, **12** (^{1}H decoupled)

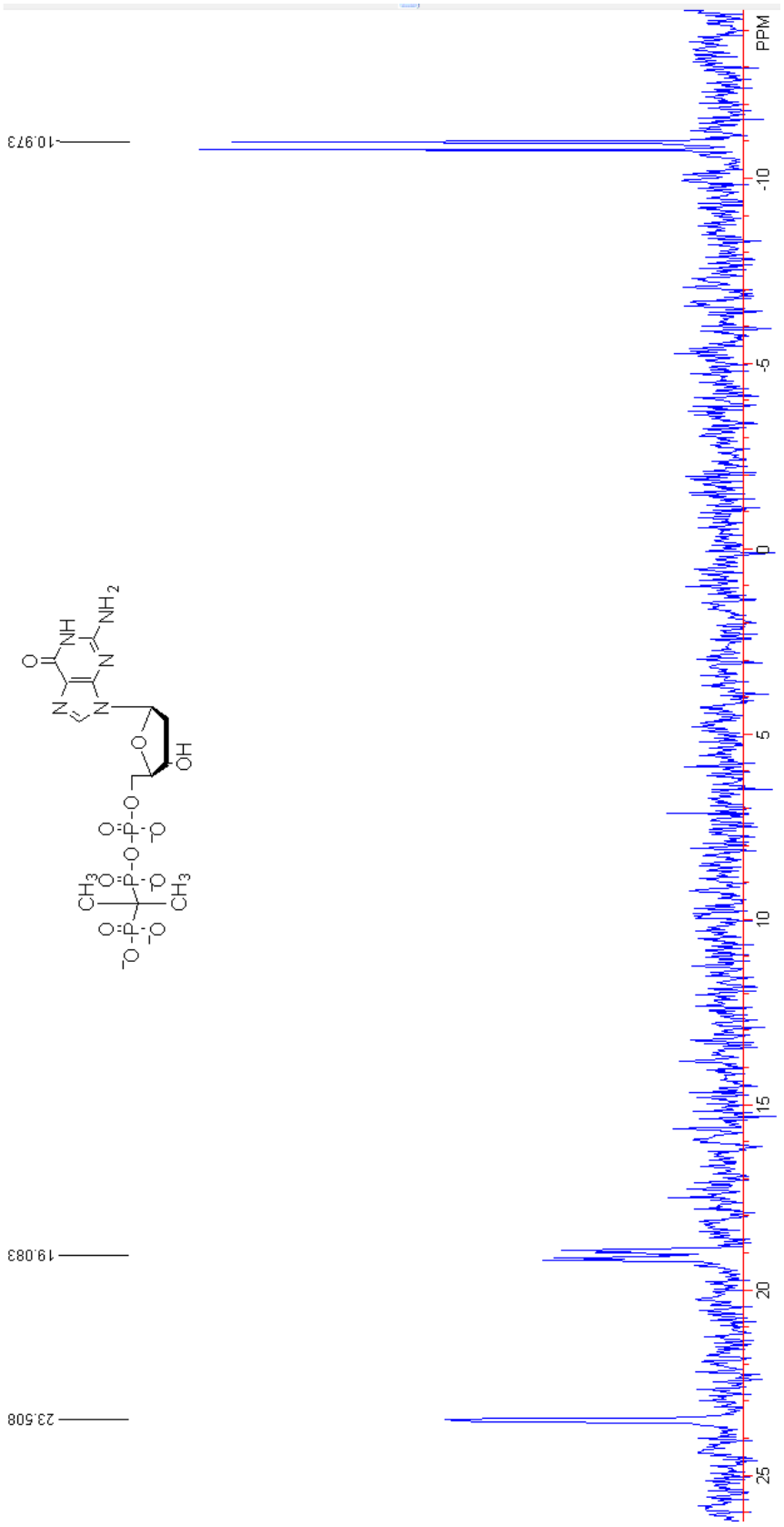


Figure S14. ^{1}H NMR of dGMP-*β,γ*-FMBP, **13/14**

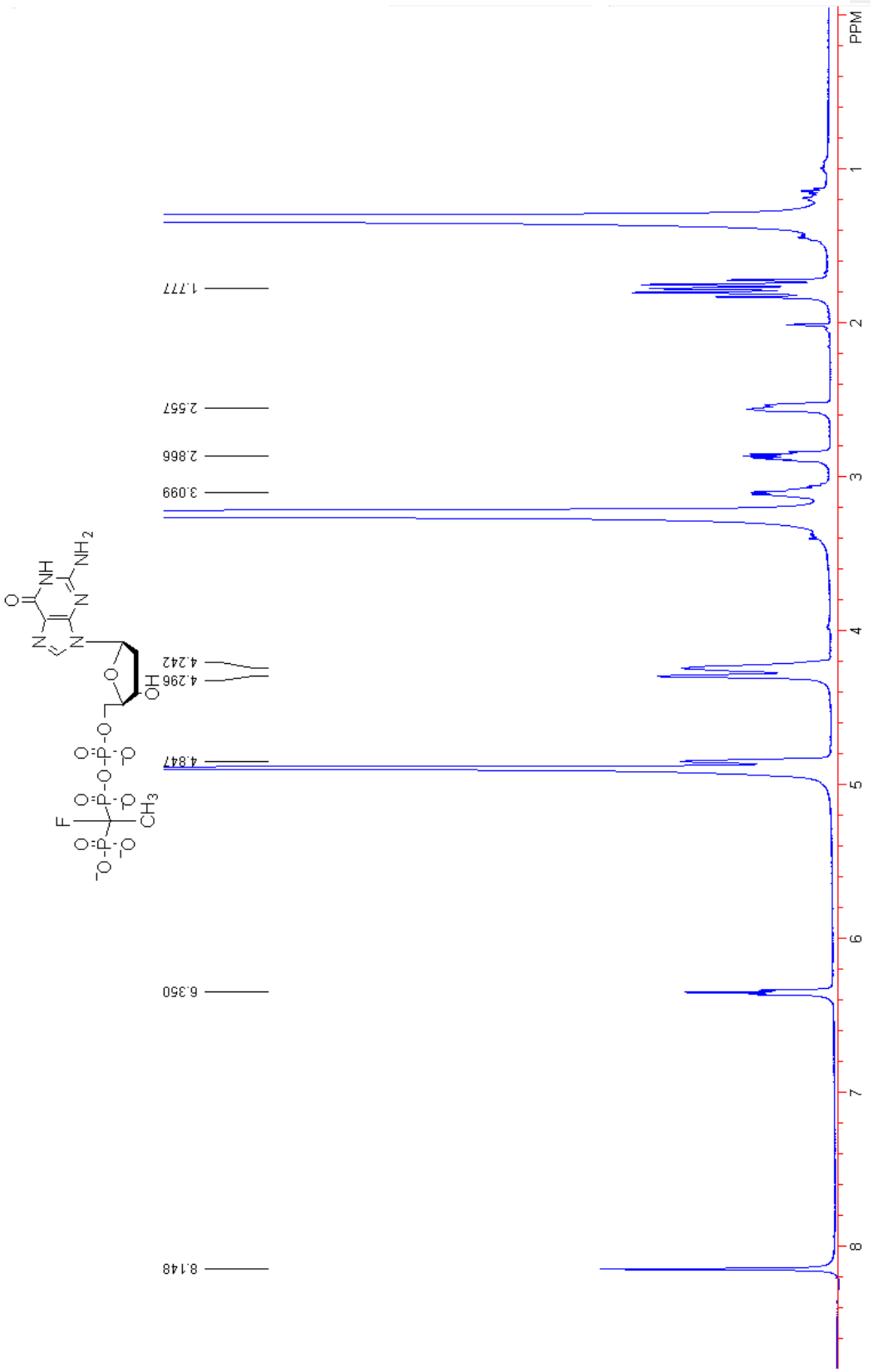


Figure S15. ^{31}P NMR of dGMP-β,γ-FMBP, **13/14** (^{1}H decoupled)

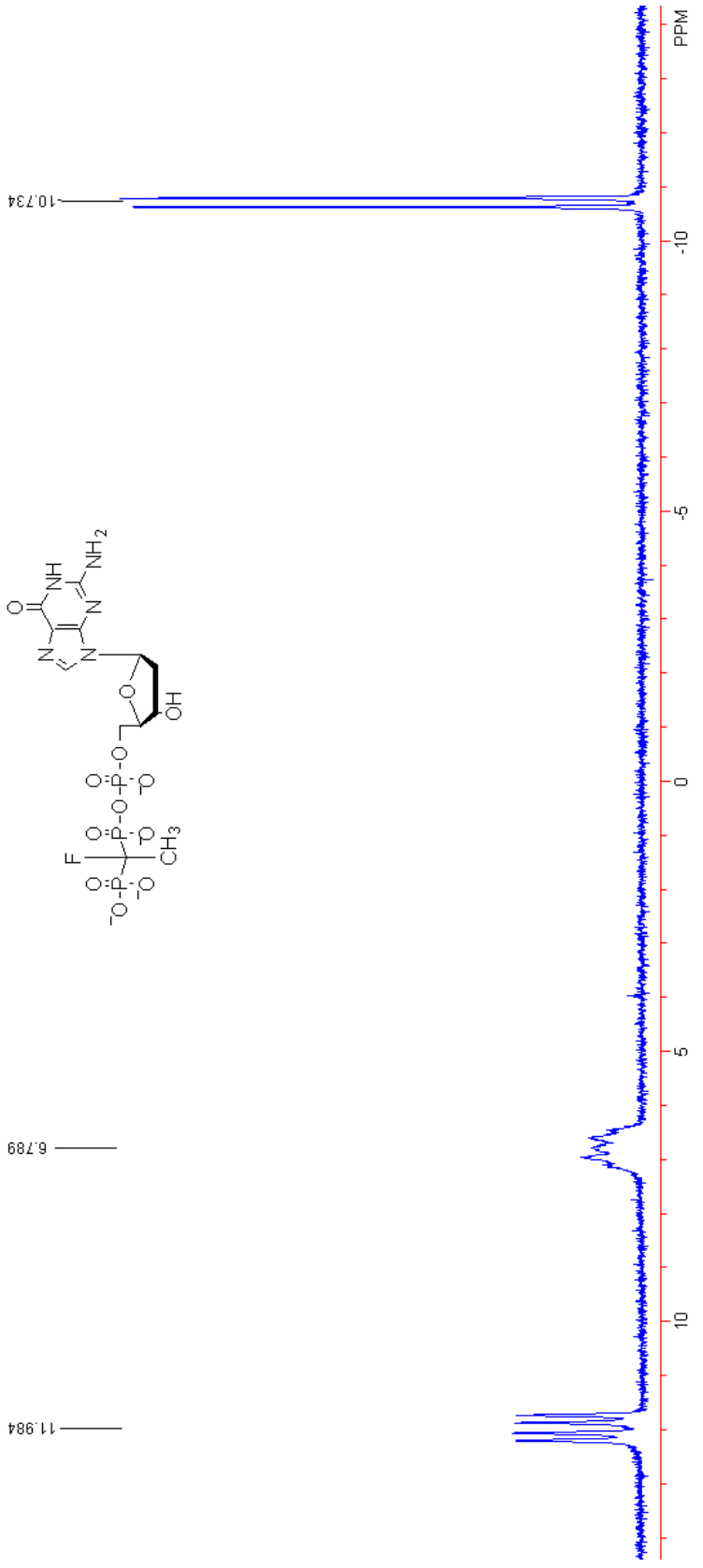


Figure S16. ^{19}F NMR of dGMP-*β,γ*-FMBP, **13/14**