Supporting Information

Direct Synthesis of 6-Arylpurines by Reaction of 6-Chloropurines with Activated Aromatics

Hai-Ming Guo,* [†] Pu Li,[†] Hong-Ying Niu,[‡] Dong-Chao Wang,[†] and Gui-Rong Qu*,[†]

[†] College of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions of Ministry of Education, Henan Normal University, Xinxiang 453007, Henan, China,
Fax: +86 373 3329276
E-mail: ghm@henannu.edu.cn; guguir@sina.com

[‡] School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453003, China

General: Melting points were recorded with a micro melting point apparatus and uncorrected. NMR spectra were recorded with a 400 NMR spectrometer for ^{1}H-NMR, 100 MHz for ^{13}C-NMR. Proton chemical shifts δ were given in ppm relative to tetramethylsilane (0.00 ppm) in $CDCl_3$ or to the residual proton signals of the deuterated solvent DMSO-d_6 (2.50 ppm). High resolution mass spectra were taken with a 3000 mass spectrometer, using Waters Q-TofMS/MS system. For column chromatography 200-300 mesh silica gel (GF254) was used as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

Typical Experimental Procedure for the Reaction of Purines with 1-naphthol in Conventional Heating Bath.

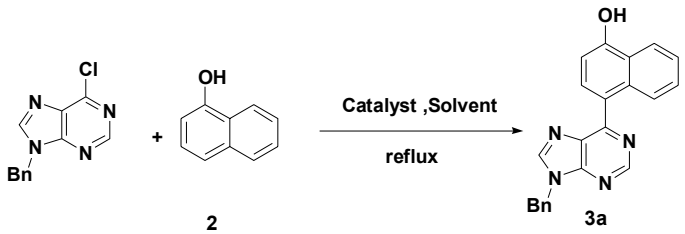
Purine base **1a** (0.5 mmol) and 1,2-dichloroethane (5 mL) were put in a 25 mL glass vial equipped with a small magnetic stirring bar. To this was added 1-naphthol **2** (1 mmol) and anhydrous $AlCl_3$ (1.5 mmol). The reaction mixture was stirred in oiling heating bath at reflux temperature for 0.5 hour. Then the vial was cooled to room temperature, and the mixture was poured into water (20 mL), stirred for 15 min, and then extracted with ethyl acetate (3×10 mL). The organic layers were collected, combined, washed with water (3×10 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The resulted residue was purified by column chromatography over silica gel (dichloroethane/ethyl acetate) to give the desired products.

The optimization of reaction conditions

At the outset of the study, we investigated the direct arylation of 9-Bn-6-chloropurine with 1-naphthol in the presence of anhydrous $AlCl_3$ in 1,2-dichloroethane at reflux temperature. To our delight, the direct arylation proceeded successfully to produce the desired product **3a** in 50% yield in 0.5 hour (Table 1, entry 1). For comparison purpose,

other common Lewis acids (entries 1-7) were tested for the direct arylation reaction. As shown in Table 1, it was observed that anhydrous $AlCl_3$ was far more effective than others such as $ZnCl_2$, $FeCl_3$, $SnCl_2$, $CuCl_2$, CuCl, or $ZnBr_2$.

Table 1 The optimization of reaction conditions[a]



2 3a

entry	solvent	catalyst (mol%)	time/h	Yields[b] (%)
1	1,2-dichloroethane	$AlCl_3$ (200)	0.5	50
2	1,2-dichloroethane	$ZnCl_2$ (200)	20	10
3	1,2-dichloroethane	$FeCl_3$ (200)	24	Trace
4	1,2-dichloroethane	$SnCl_2$ (200)	24	20
5	1,2-dichloroethane	$CuCl_2$ (200)	18	NR
6	1,2-dichloroethane	CuCl (200)	18	NR
7	1,2-dichloroethane	$ZnBr_2$ (200)	24	Trace
8	dichloromethane	$AlCl_3$ (200)	1	40
9	trichloromethane	$AlCl_3$ (200)	1	38
10	CH_3CN	$AlCl_3$ (200)	1	35
11	THF	$AlCl_3$ (200)	10	NR
12	Toluene	$AlCl_3$ (200)	12	35
13	DMF[c]	$AlCl_3$ (200)	12	Trace
14	DMSO[c]	$AlCl_3$ (200)	10	Trace
15	1,2-dichloroethane	$AlCl_3$ (50)	24	NR
16	1,2-dichloroethane	$AlCl_3$ (100)	24	24
17	1,2-dichloroethane	$AlCl_3$ (200)	5	50
18	1,2-dichloroethane	$AlCl_3$ (300)	0.5	75
19	1,2-dichloroethane	$AlCl_3$ (400)	0.5	76

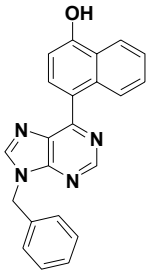
[a]Reaction conditions: 9-Bn-6-chloropurine (0.5 mmol), 1-naphthol (1 mmol), catalyst, 1,2-dichloroethane (5 mL). [b]Isolated yields based on nucleobases. [c]Reaction temperature: 85 °C.

With anhydrous $AlCl_3$ as the best catalyst for the direct arylation, we then tried to screen a variety of solvents (Table 1, entries 1, 8-14). It was found that 1,2-dichloroethane was more effective than other solvents, so 1,2-dichloroethane was chosen as the best solvent.

The effect of the amount of $AlCl_3$ on the reaction was also studied. It was found that no product was observed when using 50 mol% anhydrous $AlCl_3$ (entry 15). With increasing catalyst amount, the yields increased. When the amount of anhydrous $AlCl_3$ was 3 equiv based on purine base, the product **3a** was obtained in 75% isolated (entry 18). No significant change was observed by increasing the catalyst amount from 3 to 4 equiv based on purine base (entry 19) (76%).

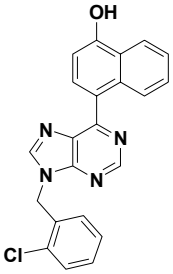
Characterization of compounds

4-(9-benzyl-9H-purin-6-yl)naphthalen-1-ol (3a)



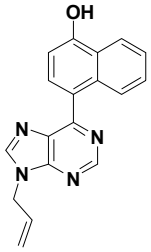
Light yellow powder, mp 282-284 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 10.76 (s, 1H), 9.03 (s, 1H), 8.71 (s, 1H), 8.45 (t, *J*= 5.6 Hz, 1H), 8.26 (t, *J*= 2.8 Hz, 1H), 8.04 (d, *J*= 8.0 Hz, 1H), 7.49 (t, *J*= 4.0 Hz, 2H), 7.41 (d, *J*= 8.0 Hz, 2H), 7.36 (t, *J*= 4.0 Hz, 2H), 7.30 (d, *J*= 8.0 Hz, 1H), 7.05 (d, *J*= 8.0 Hz, 1H), 5.55 (s, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 156.34, 154.9, 151.3, 151.2, 145.5, 136.1, 131.6, 131.5, 131.2, 128.3, 127.5, 127.3, 126.3, 125.3, 124.3, 124.2, 122.4, 121.8, 106.9, 46.0. HRMS: calcd for $C_{22}H_{17}N_4O$ [M + H^+] 353.1402, found 353.1403.

4-(9-(2-chlorobenzyl)-9H-purin-6-yl)naphthalen-1-ol (3b)



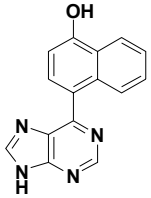
Yellow powder, mp 284-286 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 10.80 (s, 1H), 8.64 (s, 1H), 8.49-8.47 (m, 1H), 8.28-8.26 (m, 1H), 8.07 (d, *J*= 8.0 Hz, 1H), 7.53-7.48 (m, 3H), 7.36-7.29 (m, 2H), 7.18 (d, *J*= 8.0 Hz, 1H), 7.06 (d, *J*= 8.0 Hz, 1H), 5.65 (s, 1H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 156.4, 155.0, 151.4, 151.2, 145.7, 133.1, 131.7, 131.6, 131.0, 129.4, 129.2, 129.1, 127.2, 126.4, 125.3, 124.3, 124.2, 122.3, 121.8, 107.0, 44.1. HRMS: calcd for $C_{22}H_{16}ClN_4O$ [M + H^+] 387.1013, found 387.1012.

4-(9-allyl-9H-purin-6-yl)naphthalen-1-ol (3c)



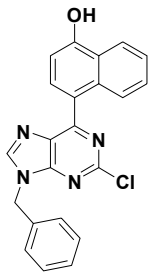
Light yellow powder, mp 265-267 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 10.73 (s, 1H), 9.02 (s, 1H), 8.56 (s, 1H), 8.45-8.43 (m, 1H), 8.27-8.25 (m, 1H), 8.04 (d, *J*= 8.0 Hz, 1H), 7.51-7.58 (m, 1H), 7.04 (d, *J*= 8.0 Hz, 1H), 5.25 (d, *J*= 9.6 Hz, 1H), 5.14 (d, *J*= 16.0 Hz, 1H), 4.97 (d, *J*= 8.0 Hz, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 156.3, 154.9, 151.2, 151.1, 145.4, 132.5, 131.6, 131.5, 131.1, 126.3, 125.3, 124.3, 124.2, 122.4, 121.8, 117.5, 107.0, 44.8, 30.2. HRMS: calcd for $C_{18}H_{15}N_4O$ [M + H^+] 303.1246, found 303.1247.

4-(9H-purin-6-yl)naphthalen-1-ol (3d)



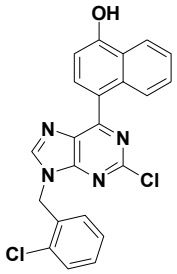
Brown powder, mp 255-257 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 13.54 (s, 1H), 10.72 (s, 1H), 9.00 (s, 1H). 8.56 (s, 1H), 8.27-8.25 (m, 1H), 8.00 (s, 1H), 7.51-7.49 (m, 2H), 7.04 (d, *J*= 8.0 Hz, 1H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 160.3, 154.7, 152.7, 151.1, 146.7, 143.8, 131.3, 126.3, 125.3, 124.3, 122.7, 121.8, 107.0. HRMS: calcd for $C_{15}H_{11}N_4O$ [M + H^+] 263.0933, found 263.0933.

4-(9-benzyl-2-chloro-9H-purin-6-yl)naphthalen-1-ol (3e)



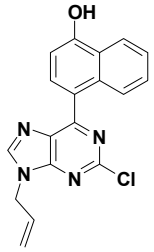
Yellow powder, mp 250-252 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 8.73 (s, 1H), 8.45 (d, *J*= 8.0 Hz, 1H), 8.26 (t, *J*= 2.4 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J*= 4.0 Hz, 2H), 7.38 (d, *J*= 4.0 Hz, 5H), 7.33-7.32 (m, 1H), 5.52 (s, 1H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 158.2, 155.7, 153.0, 151.8, 146.4, 135.7, 132.3, 131.5, 130.5, 128.4, 127.6, 126.8, 125.0, 124.5, 124.2, 121.9, 121.0, 107.0, 46.1. HRMS: calcd for $C_{22}H_{16}ClN_4O$ [M + H^+] 387.1013, found 387.1015.

4-(9-(2-chlorobenzyl)-2-chloro-9H-purin-6-yl)naphthalen-1-ol (3f)



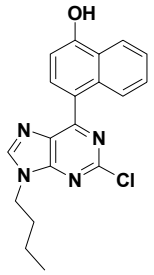
Yellow powder, mp 212-212 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 10.94 (s, 1H), 8.64 (s, 1H), 8.51 (d, *J*= 8.0 Hz, 1H), 8.28 (d, *J*= 8.0 Hz, 1H), 8.15 (d, *J*= 8.0 Hz, 1H), 7.53 (s, 3H), 7.36-7.31 (m, 2H), 7.15 (d, *J*= 8.0 Hz, 1H), 7.07 (d, *J*= 8.0 Hz, 1H), 5.58 (s, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 158.3, 155.8, 153.2, 151.9, 146.5, 132.7, 132.5, 131.7, 131.5, 130.4, 129.5, 129.2, 129.0, 127.3, 126.8, 125.0, 124.5, 124.3, 121.9, 121.0, 107.1, 44.3. HRMS: calcd for $C_{22}H_{15}Cl_2N_4O$ [M + H^+] 421.0623, found 421.0625.

4-(9-allyl-2-chloro-9H-purin-6-yl)naphthalen-1-ol (3g)



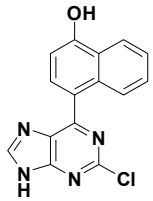
Yellow powder, mp 273-275 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 10.90 (s, 1H), 8.60 (s, 1H), 8.46-8.44 (m, 1H), 8.28-8.25 (m, 1H), 8.10 (d, *J*= 8 Hz, 1H), 7.55-7.51 (m, 2H), 7.05 (d, *J* = 8 Hz, 1H), 6.13-6.09 (m, 1H), 5.26 (d, *J*= 8.0 Hz, 1H), 5.15 (d, *J*= 16.0 Hz, 1H), 4.92 (d, *J*= 8.0 Hz, 1H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 158.1, 155.7, 153.0, 146.4, 132.3, 132.1, 131.5, 130.4, 126.7, 125.0, 124.5, 124.2, 121.9, 121.1, 117.7, 107.0, 45.0, 30.2. HRMS: calcd for $C_{18}H_{14}ClN_4O$ [M + H$^+$] 337.0856, found 337.0854.

4-(9-butyl-2-chloro-9H-purin-6-yl)naphthalen-1-ol (3h)



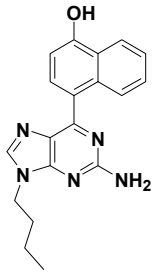
White powder, mp 272-274 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 10.89 (s, 1H), 8.63 (s, 1H), 8.46-8.43 (m, 1H), 8.27-8.25 (m, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.55-7.50 (m, 2H), 7.04 (d, *J* = 8 Hz, 1H), 4.26 (t, *J*= 8.0 Hz, 2H), 1.88-1.84 (m, 2H), 1.34-1.28 (m, 2H), 0.92 (t, *J*= 8.0 Hz, 3H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 158.0, 155.6, 153.2, 151.6, 146.6, 132.2, 131.5, 130.5, 126.7, 125.0, 124.5, 124.2, 121.9, 121.2, 107.0, 42.7, 30.6, 18.9, 12.9. HRMS: calcd for $C_{19}H_{18}ClN_4O$ [M + H$^+$] 353.1169, found 353.1169.

4-(2-chloro-9H-purin-6-yl)naphthalen-1-ol (3i)



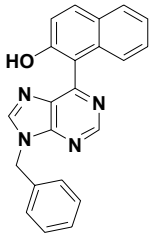
Yellow powder, mp 274-276 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 13.63 (s, 1H), 10.87 (s, 1H), 8.63 (s, 1H), 8.27 (t, *J*= 8.0 Hz, 2H), 8.27-8.17 (m, 1H), 7.53 (s, 1H), 7.05 (d, 1H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 155.4, 151.7, 131.3, 126.8, 124.6, 124.2, 121.9, 121.4, 107.6, 48.1. HRMS: calcd for $C_{15}H_{10}ClN_4O$ [M + H^+] 297.0543, found 297.0544.

4-(2-amino-9-butyl-9H-purin-6-yl)naphthalen-1-ol (3j)



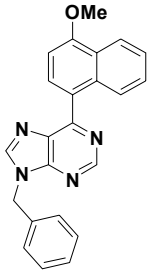
White powder, mp 285-287 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 10.56 (s, 1H), 8.37-8.35 (m, 1H), 8.23-8.20 (m, 1H), 8.04 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.48-7.43 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 4.07 (t, *J*= 8.0 Hz, 2H), 1.83-1.76 (m, 2H), 1.32-1.27 (m, 2H), 0.91 (t, *J*= 7.6 Hz, 3H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 159.6, 157.3, 154.2, 153.2, 141.6, 131.6, 130.2, 125.9, 125.7, 124.9, 124.1, 123.5, 121.6, 106.8, 41.8, 30.8, 18.9, 13.0. HRMS: calcd for $C_{19}H_{20}N_5O$ [M + H^+] 334.1668, found 334.1667.

1-(9-benzyl-9H-purin-6-yl)naphthalen-2-ol (4a)



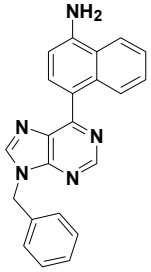
Light yellow powder mp 244-245 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 9.79 (s, 1H), 9.07 (s, 1H), 8.65 (s, 1H), 7.93 (d, *J*= 8.0 Hz, 1H), 7.86 (t, *J*= 8.0 Hz, 1H), 7.46 (d, *J*= 8.0 Hz, 2H), 7.38 (t, *J*= 8.0 Hz, 2H), 7.33-7.25 (m, 4H), 7.15 (s, 1H), 5.55 (s, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 154.9, 152.7, 151.6, 150.8, 145.6, 136.1, 133.0, 132.2, 130.1, 128.4, 127.5, 127.1, 126.0, 123.5, 122.3, 118.0, 115.0, 46.1. HRMS: calcd for $C_{22}H_{17}N_4O$ [M + H^+] 353.1402 found 353.1401

9-benzyl-6-(4-methoxynaphthalen-1-yl)-9H-purine (4b)



White powder, mp 197-198 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 9.07 (s, 1H), 8.75 (s, 1H), 8.44 (d, *J*= 8.0 Hz, 1H), 8.28-8.26 (m, 1H), 8.11 (d, *J*= 8.0 Hz, 1H), 7.56-7.50 (m, 2H), 7.43 (d, *J*= 8.0 Hz, 2H), 7.35 (t, *J*= 8.0 Hz, 2H), 7.30 (d, *J*= 8.0 Hz, 1H), 7.15 (d, *J*= 8.0 Hz, 1H), 5.56 (s, 2H), 4.05 (s, 3H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 156.0, 155.9, 151.3, 151.2, 145.7, 136.1, 131.3, 131.1, 128.3 127.5, 127.3, 126.5, 125.4, 125.0, 124.6, 124.0, 121.2, 103.3, 55.4, 46.0. HRMS: calcd for $C_{23}H_{19}N_4O$ [M + H^+] 367.1559, found 367.1558.

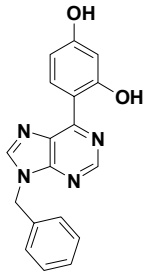
4-(9-benzyl-9H-purin-6-yl)naphthalen-1-amine (4c)



Yellow powder, mp 238-240 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 8.96 (s, 1H), 8.67 (s, 1H), 8.65 (d, *J*= 1.6 Hz, 1H), 8.18 (d, *J*= 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.45-7.39 (m,

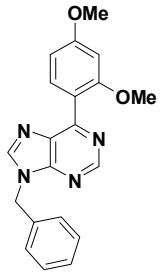
4H), 7.35 (t, *J*= 8.0 Hz, 2H), 7.30 (t, *J*= 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.38 (s, 2H), 5.53 (s, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 156.9, 151.0, 147.2, 144.8, 136.3, 132.8, 131.6, 130.6, 128.3, 127.4, 127.3, 125.9, 125.7, 123.4, 122.1, 121.8, 118.3, 105.9, 46.0. HRMS: calcd for $C_{22}H_{18}N_5$ [M + H$^+$] 352.1562, found 352.1561.

4-(9-benzyl-9H-purin-6-yl)benzene-1,3-diol (4e)



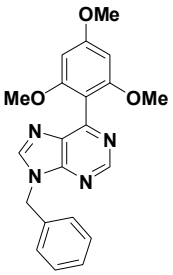
Yellow powder, mp 250-253 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 14.60 (s, 1H), 9.24 (d, *J*= 8.0 Hz, 1H), 8.88 (s, 1H), 8.80 (s, 1H), 7.36-7.30 (m, 5H), 6.50 (d, *J*= 4.0 Hz, 1H), 6.46 (d, *J*= 4.0 Hz, 1H), 5.54 (s, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 162.9, 162.0, 153.9, 150.6, 149.1, 145.2, 136.0, 133.2, 128.3, 127.5, 127.2, 127.0, 108.5, 107.6, 102.8, 46.0. HRMS: calcd for $C_{18}H_{15}N_4O_2$ [M + H $^+$] 319.1195 found 319.1195.

9-benzyl-6-(2,4-dimethoxyphenyl)-9H-purine (4f)



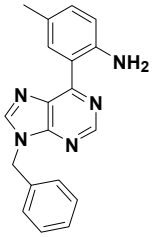
Yellow powder, mp 125-127 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 8.91 (s, 1H), 8.65 (s, 1H), 7.53-7.51 (d, *J* = 8.0 Hz, 1H), 7.40-7.29 (m, 5H), 6.73 (s, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.50 (s, 2H), 3.84 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) 161.6, 158.3, 154.9, 151.3, 150.1, 145.1, 136.2, 132.0, 131.2, 128.3, 127.3, 117.3, 104.7, 98.4, 55.2, 55.0, 46.0. HRMS: calcd for $C_{20}H_{19}N_4O_2$ [M + H$^+$] 347.1508, found 347.1508.

9-benzyl-6-(2,4,6-trimethoxyphenyl)-9H-purine (4g)



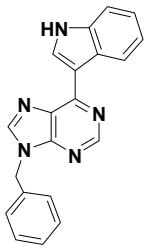
White powder, mp 251-253 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 8.91 (s, 1H), 8.61 (s, 1H), 7.45 (d. *J*= 8.0 Hz, 2H), 7.36 (t, *J*= 4.0 Hz, 2H), 7.31 (t, *J*= 8.0 Hz, 1H), 6.35 (s, 2H), 5.49 (s, 2H), 3.85 (s, 3H), 3.58 (s, 6H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 161.5, 158.1, 153.7, 151.3, 150.3, 145.2, 136.1, 133.1, 128.3, 127.6, 106.1, 90.5, 55.2, 55.0, 46.1. HRMS: calcd for $C_{21}H_{21}N_4O_3$ [M + H$^+$] 377.1614, found 377.1614.

2-(9-benzyl-9H-purin-6-yl)-4-methylbenzenamine (4h)



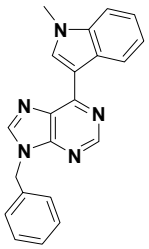
Yellow powder, mp 171-173 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 9.80 (s, 1H), 8.42 (s, 1H), 8.37 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.36-7.30 (m, 4H), 7.29-7.26 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 2H), 2.07 (s, 3H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 151.6, 149.0, 141.1, 136.6, 136.5, 131.0, 128.3, 128.2, 127.3, 127.1, 120.4, 119.1, 45.8, 20.0. HRMS: calcd for $C_{19}H_{18}N_5$ [M + H$^+$] 316.1562, found 316.1562.

9-benzyl-6-(1H-indol-3-yl)-9H-purine (4i)



Yellow powder, mp 178-180 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 11.93 (s, 1H), 9.00 (s, 1H), 8.89 (s, 1H), 8.81 (d, *J* = 8.0 Hz, 1H), 8.65 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.37-7.26 (m, 5H), 7.25-7.22 (m, 2H), 5.52 (s, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 152.7, 151.8, 149.9, 144.0, 136.4, 136.2, 132.3, 128.3, 128.0, 127.4, 125.3, 122.2, 121.9, 120.4, 111.6, 110.1, 45.8. HRMS: calcd for $C_{20}H_{16}N_5$ [M + H$^+$] 326.1406, found 326.1405.

9-benzyl-6-(1-methyl-1H-indol-3-yl)-9H-purine (4j)



Yellow powder, mp 167-169 ^{o}C ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 8.96 (s, 1H), 8.87 (s, 1H), 8.81 (d, *J* = 8.0 Hz, 2H), 8.69 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.39-7.33 (m, 4H), 7.30-7.23 (m, 3H), 5.51 (s, 2H), 3.96 (s, 3H). ^{13}C NMR (DMSO-d$_6$, 100 MHz) δ 152.2, 151.8, 149.9, 144.0, 136.8, 136.4, 135.9, 128.3, 127.8, 127.4, 127.1, 125.7, 122.4, 122.0, 120.7, 109.9, 109.8, 15.9, 32.7. HRMS: calcd for $C_{21}H_{18}N_5$ [M + H$^+$] 340.1562, found 340.1562.

X-Ray structure of 3b

Repeated attempts to crystallize compound **3a, 4a, 4b, 4c, 4e, 4i,** and **4j** were unsuccessful, but we found that crystal of **3b** could be grown under carefully defined conditions involving very slow evaporation of solutions in methanol(???). The crystal of **3b** proved that the substitution reaction occurred on the para-position of hydroxyl group of 1-naphthol and gave 4-[9-(2-Chloro-benzyl)-9H-purin-6-yl]-naphthalen-1-ol (**3b**). (Fig.1)

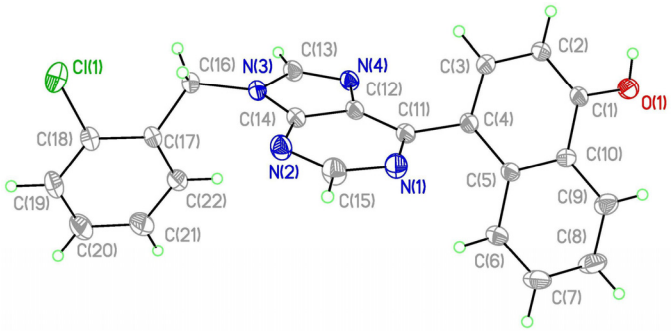
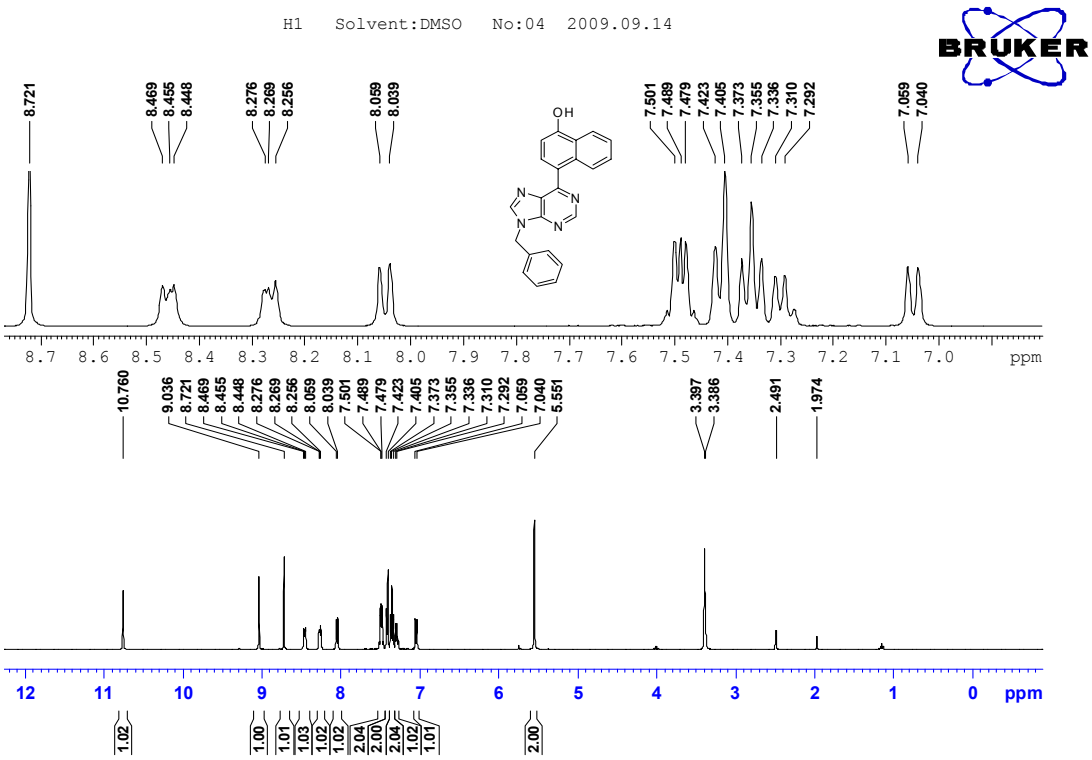
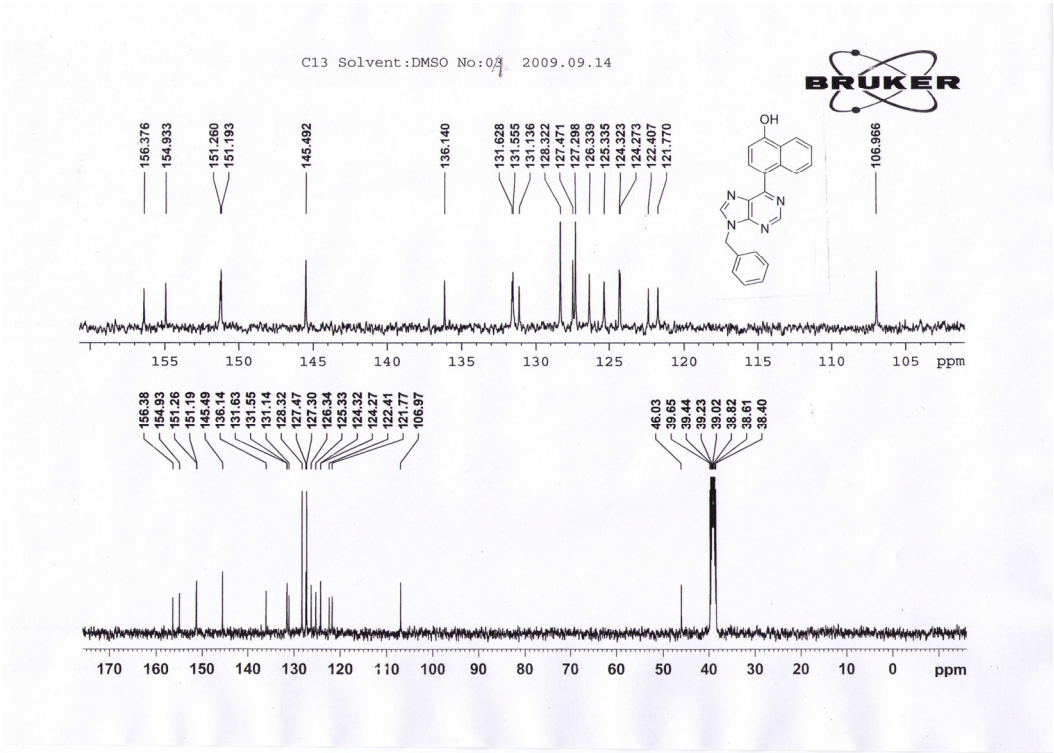


Fig. 1. X-Ray structure of **3b.**

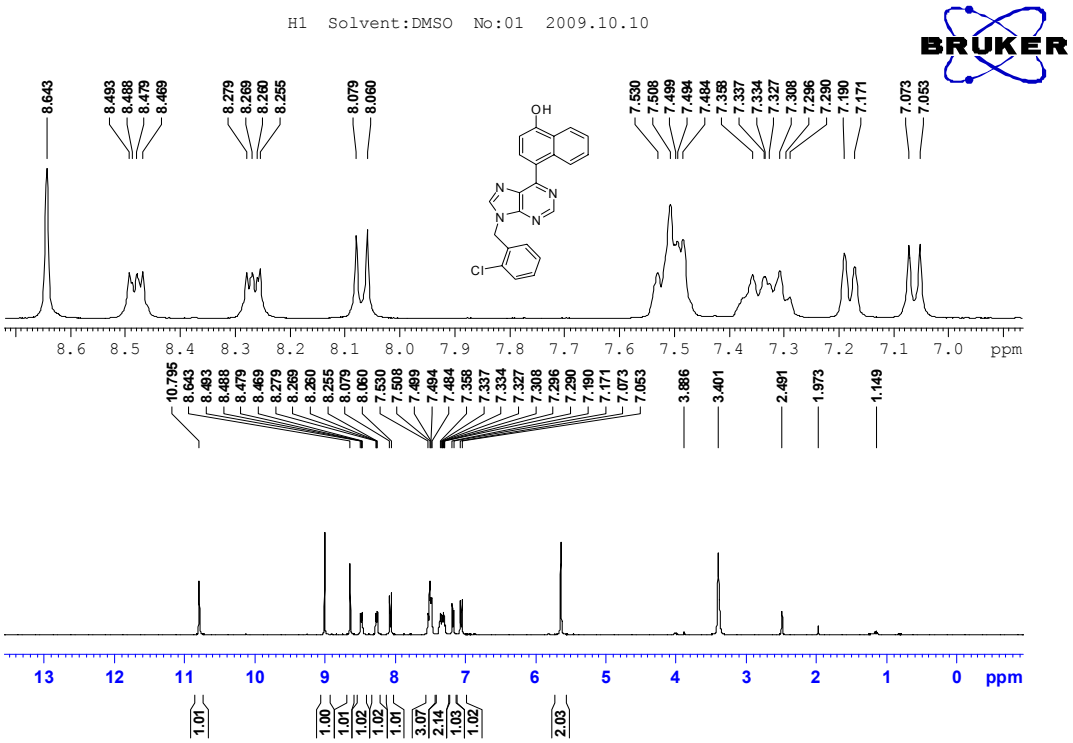
^{1}H NMR of compound **3a**



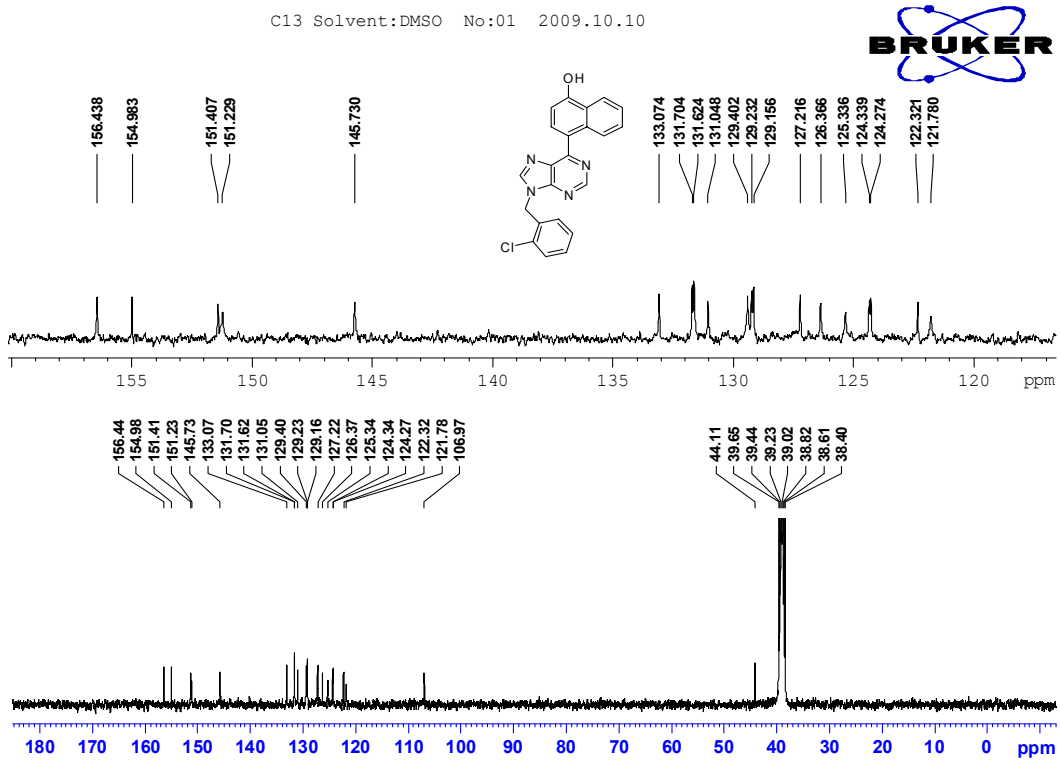
^{13}C NMR of compound **3a**



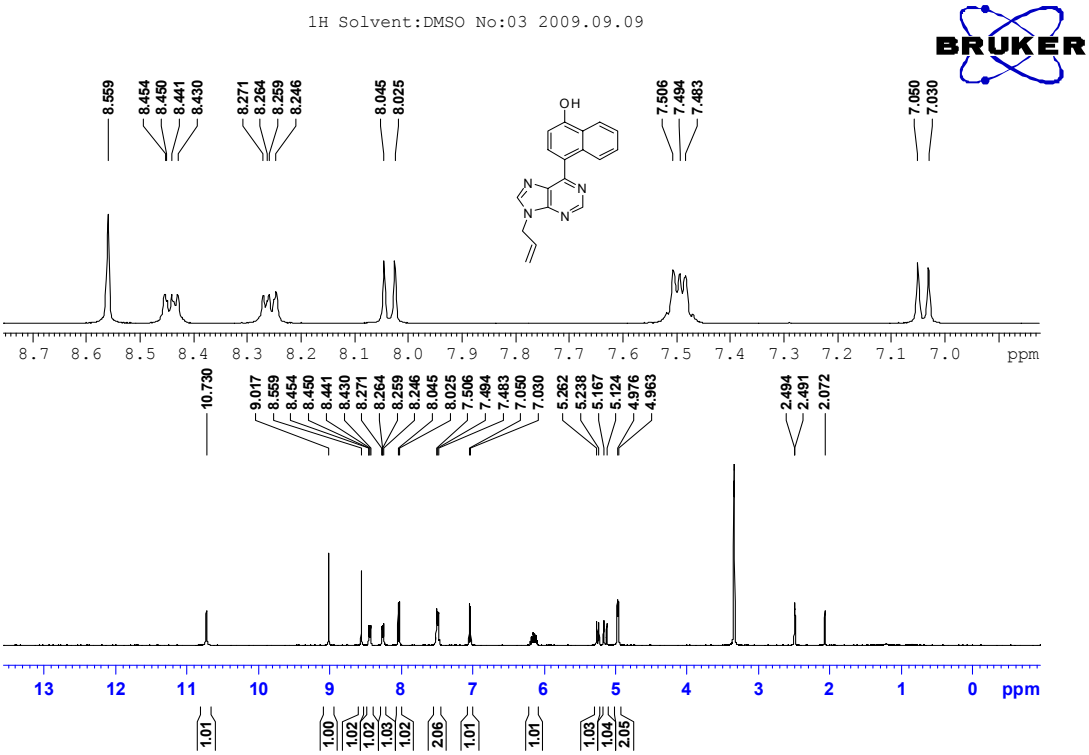
^{1}H NMR of compound **3b**



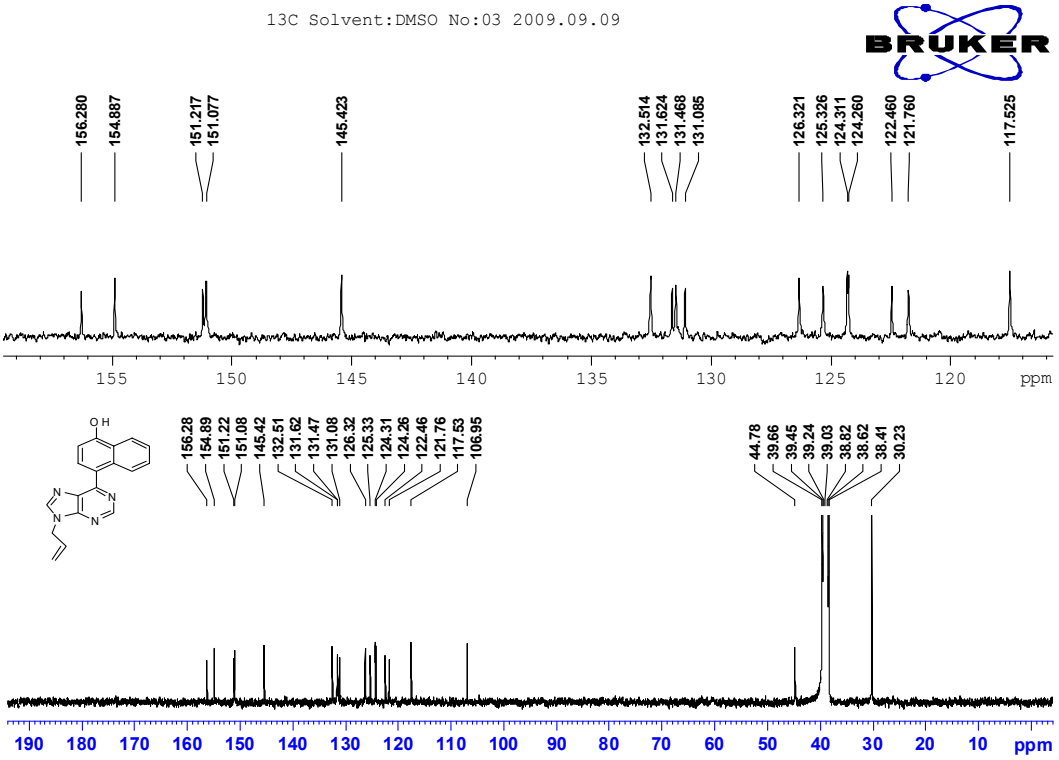
^{13}C NMR of compound **3b**



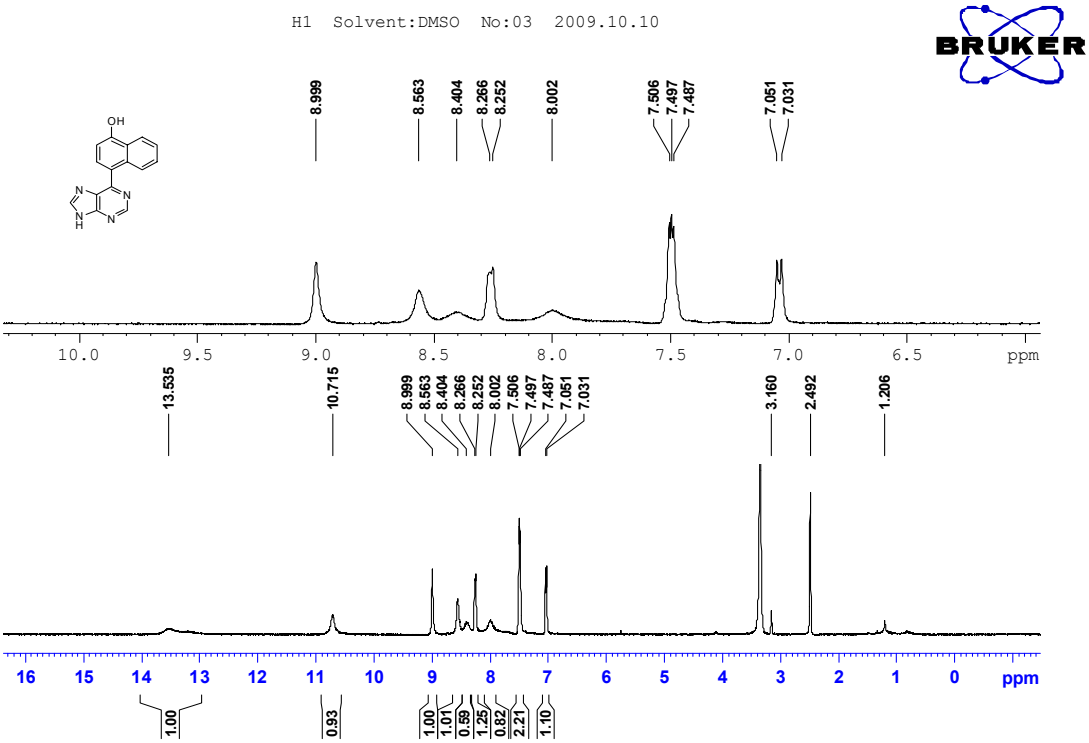
^{1}H NMR of compound **3c**



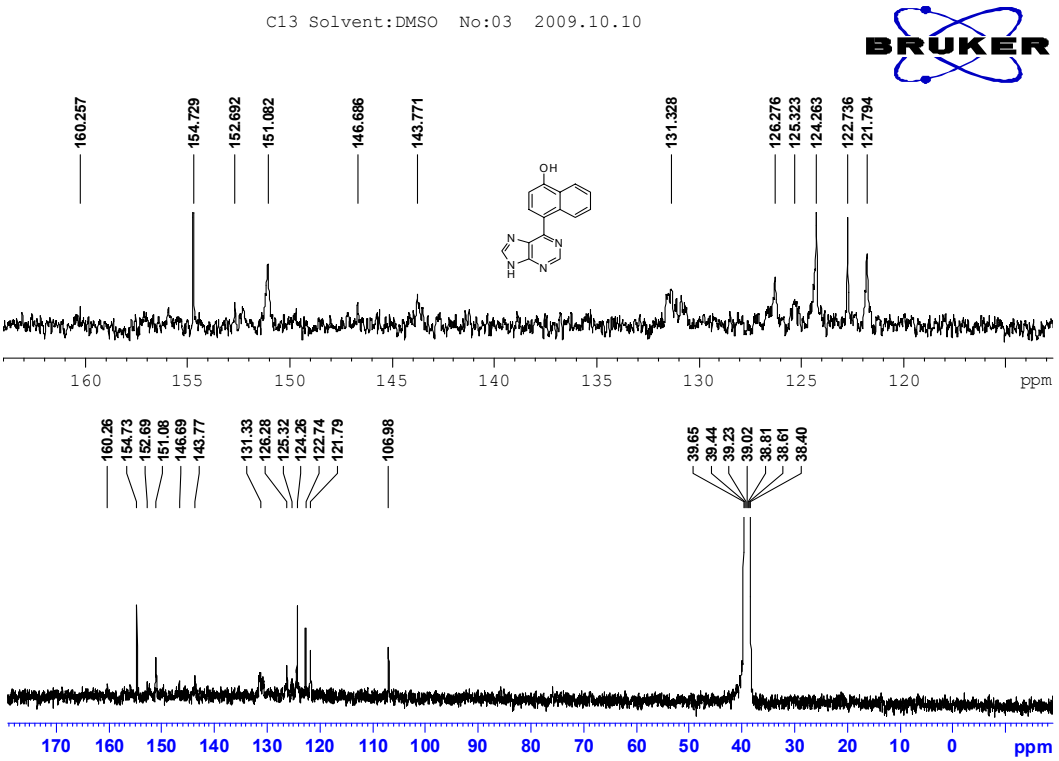
^{13}C NMR of compound **3c**



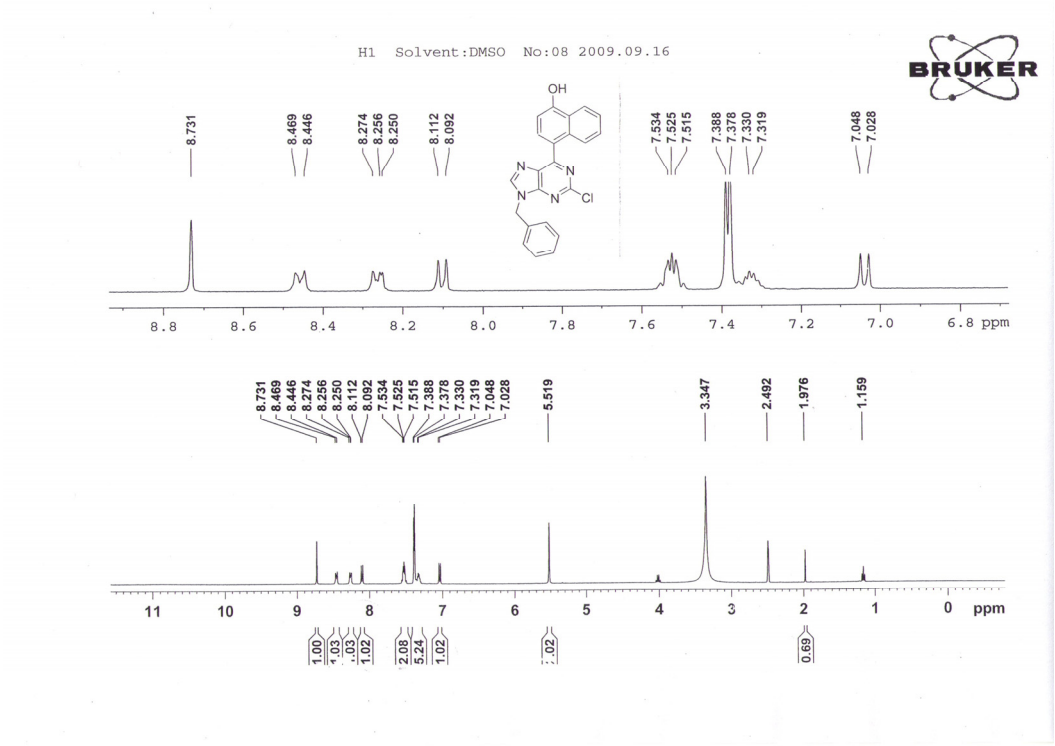
^{1}H NMR of compound **3d**



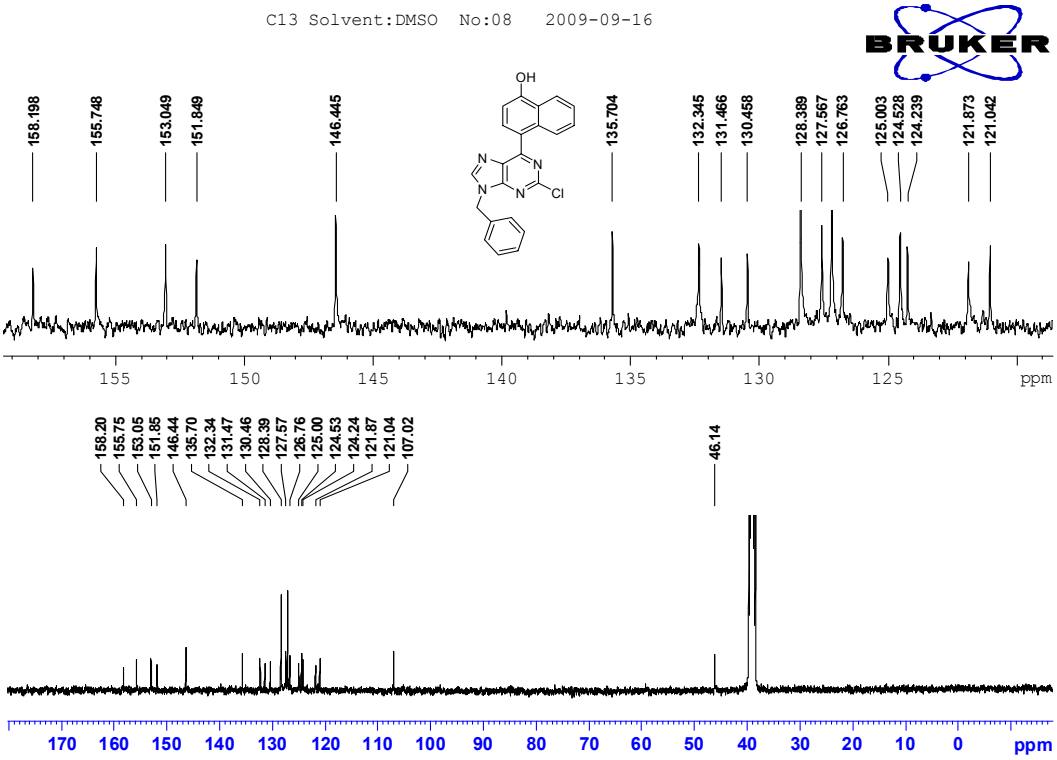
^{13}C NMR of compound **3d**



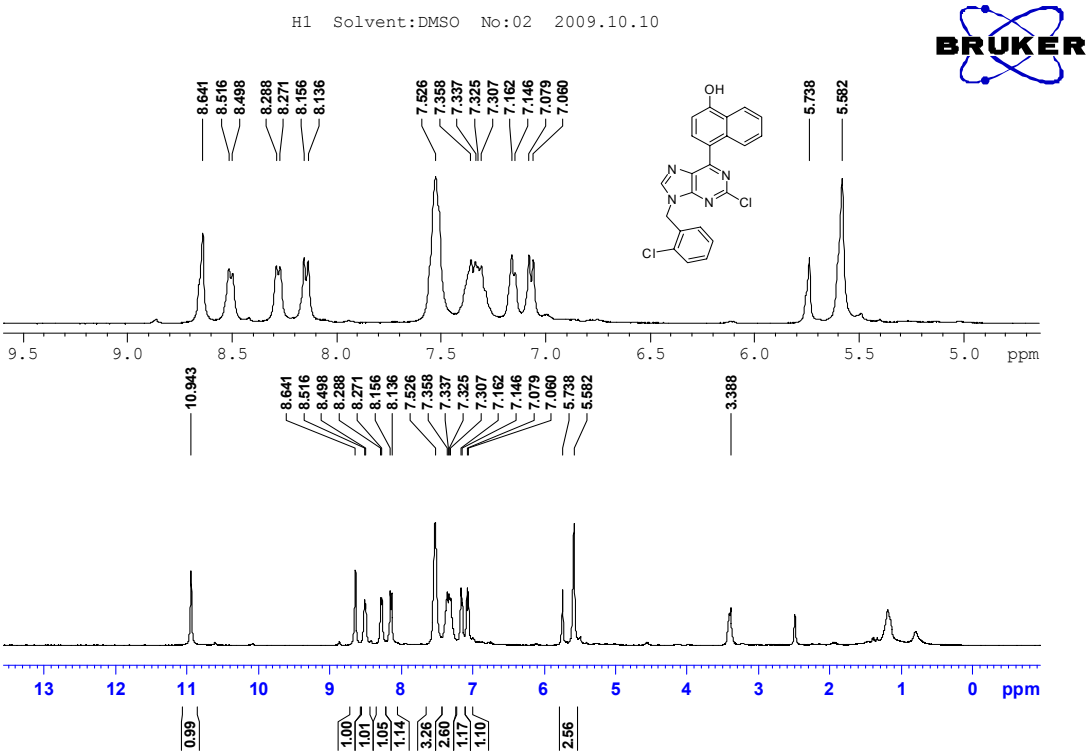
^{1}H NMR of compound **3e**



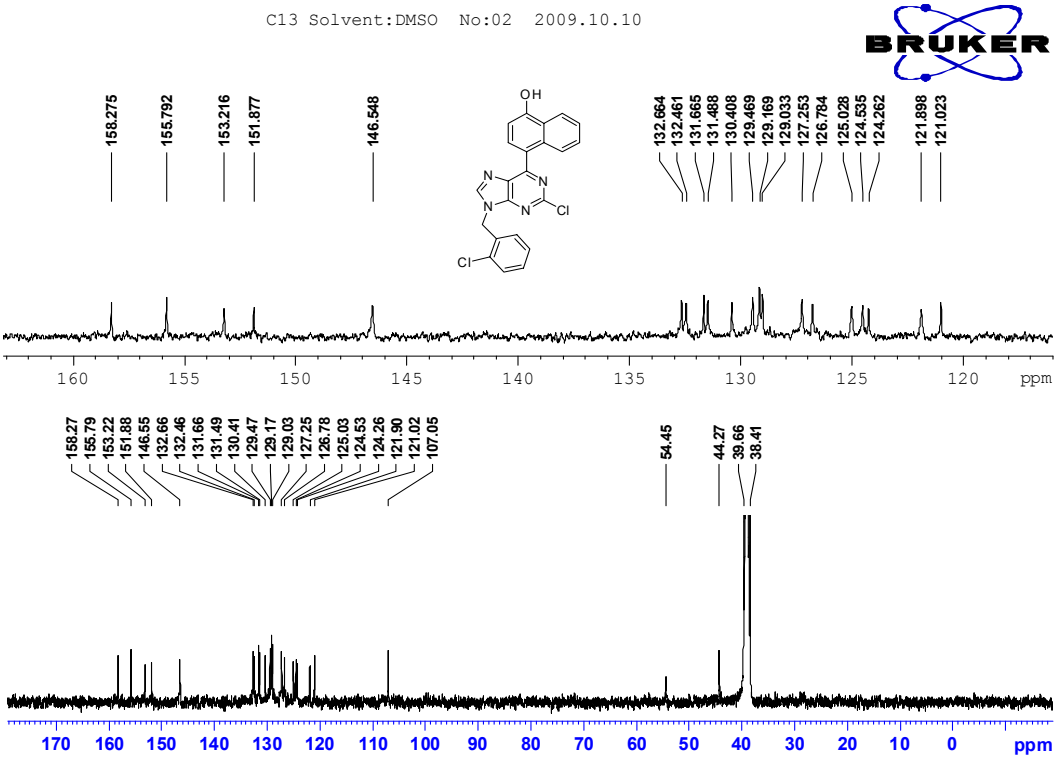
^{13}C NMR of compound **3e**



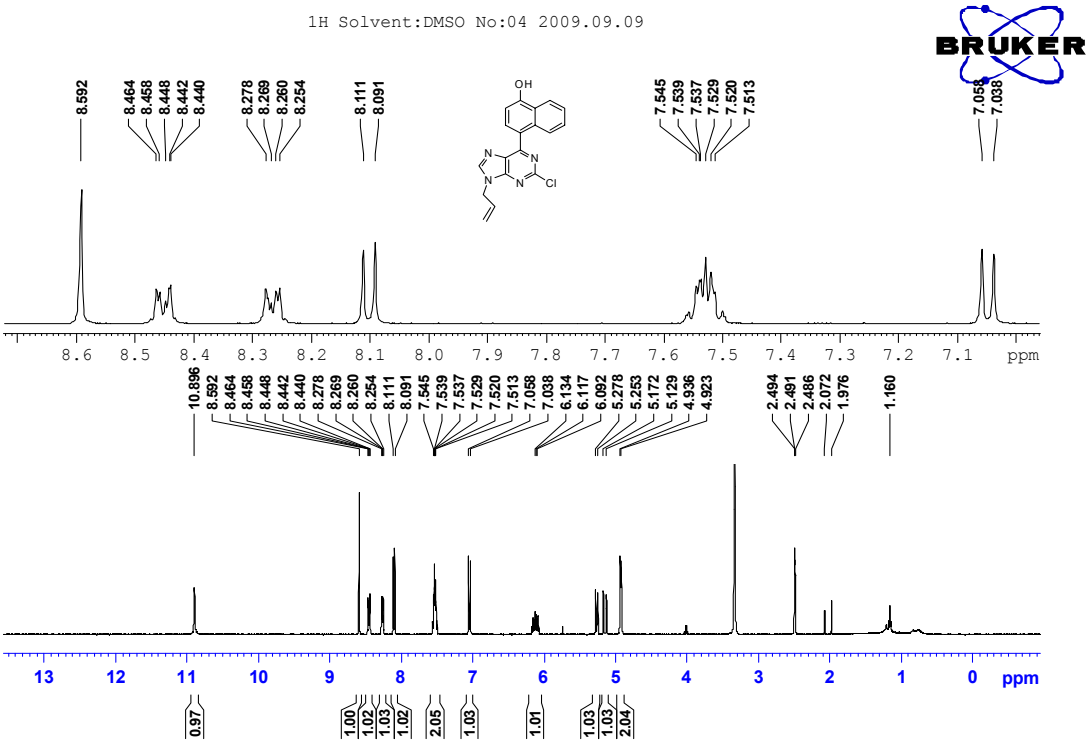
^{1}H NMR of compound **3f**



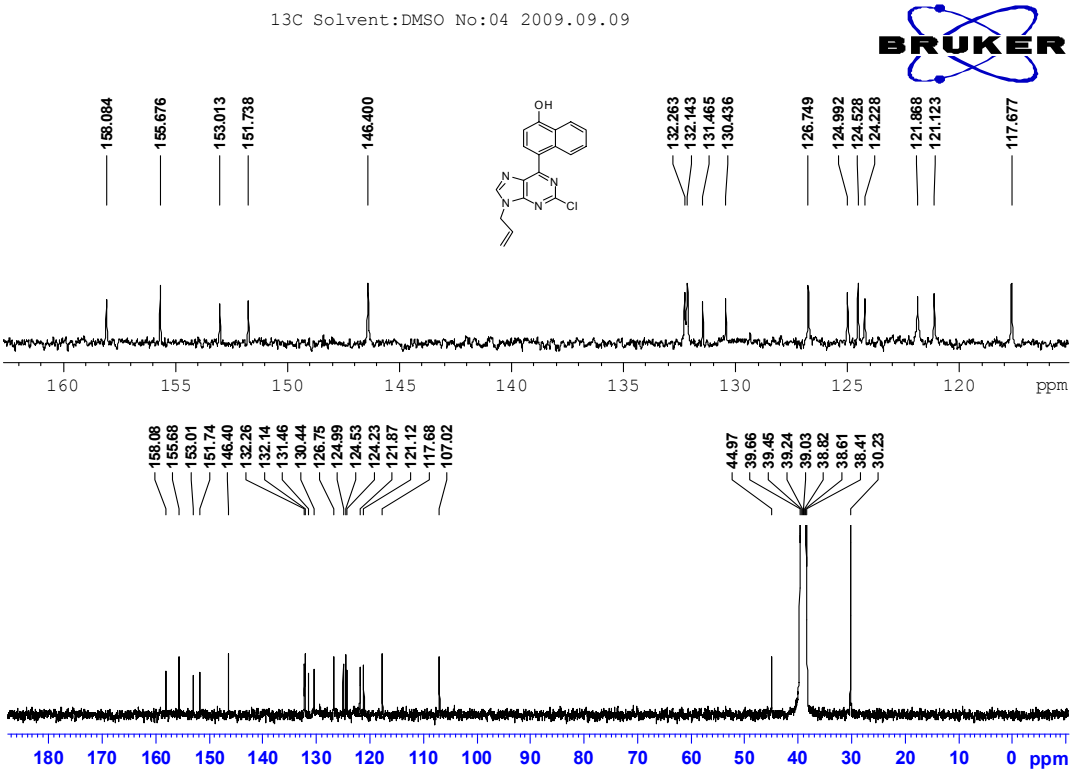
^{13}C NMR of compound **3f**



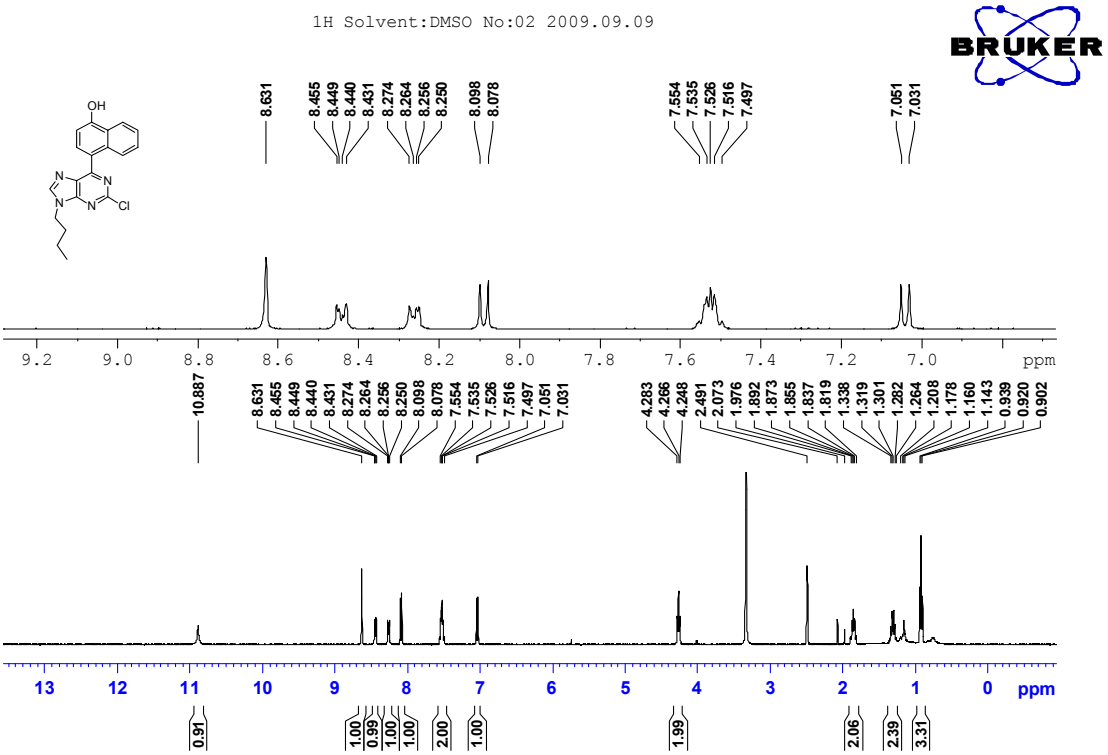
^{1}H NMR of compound **3g**



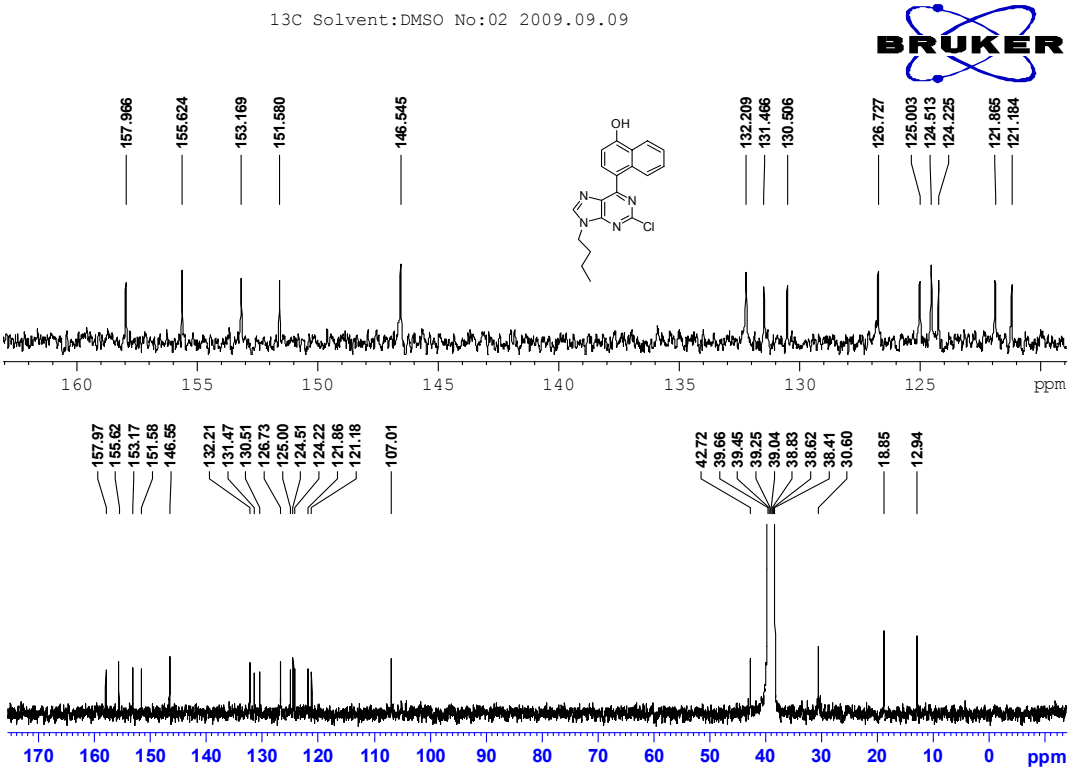
^{13}C NMR of compound **3g**



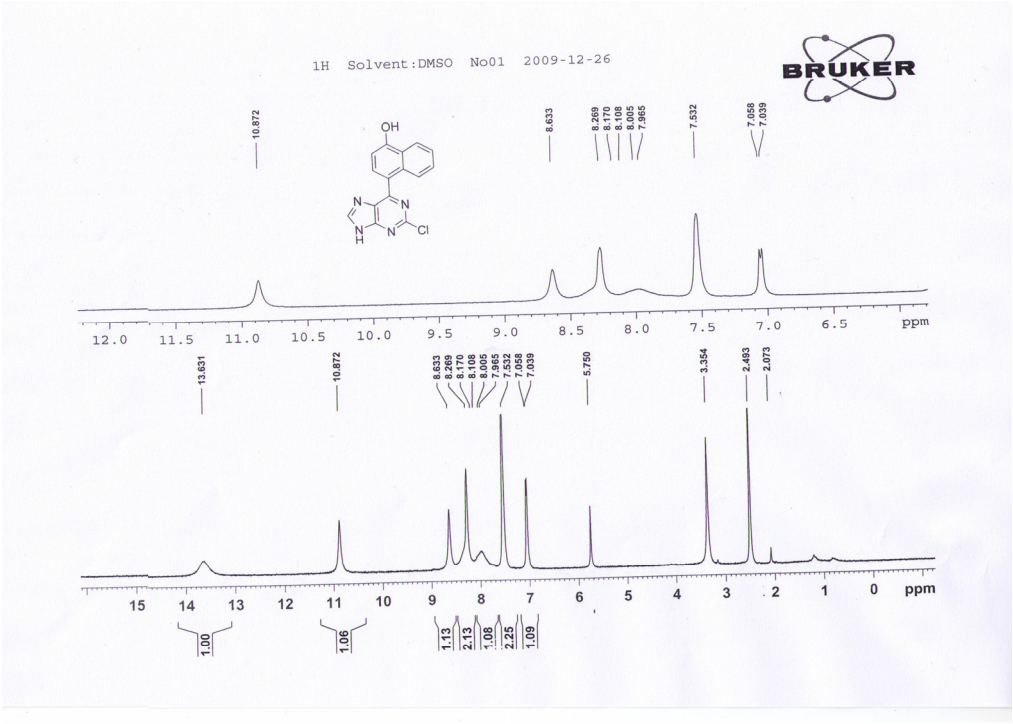
^{1}H NMR of compound **3h**



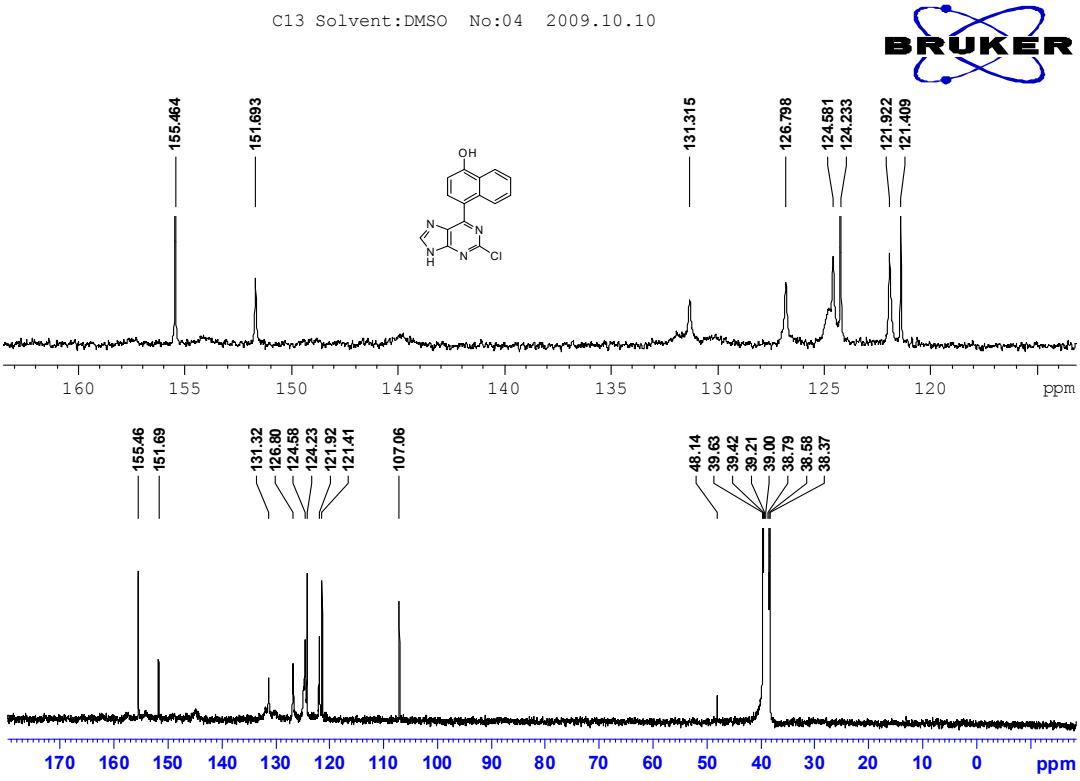
^{13}C NMR of compound **3h**



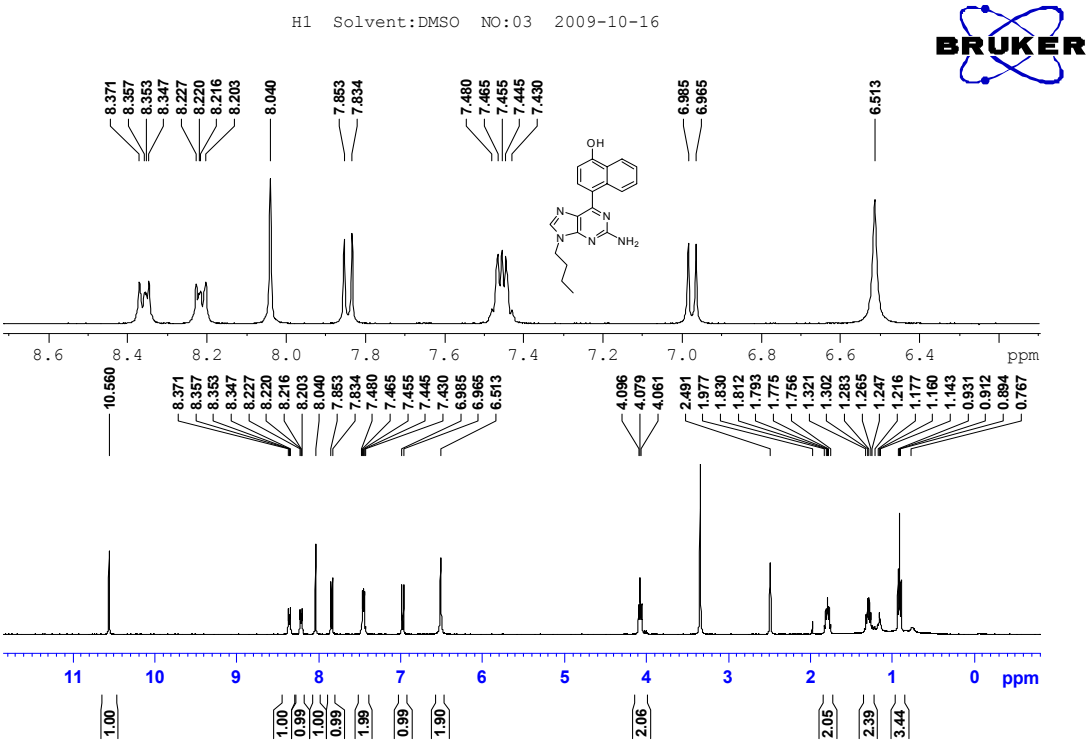
^{1}H NMR of compound **3i**



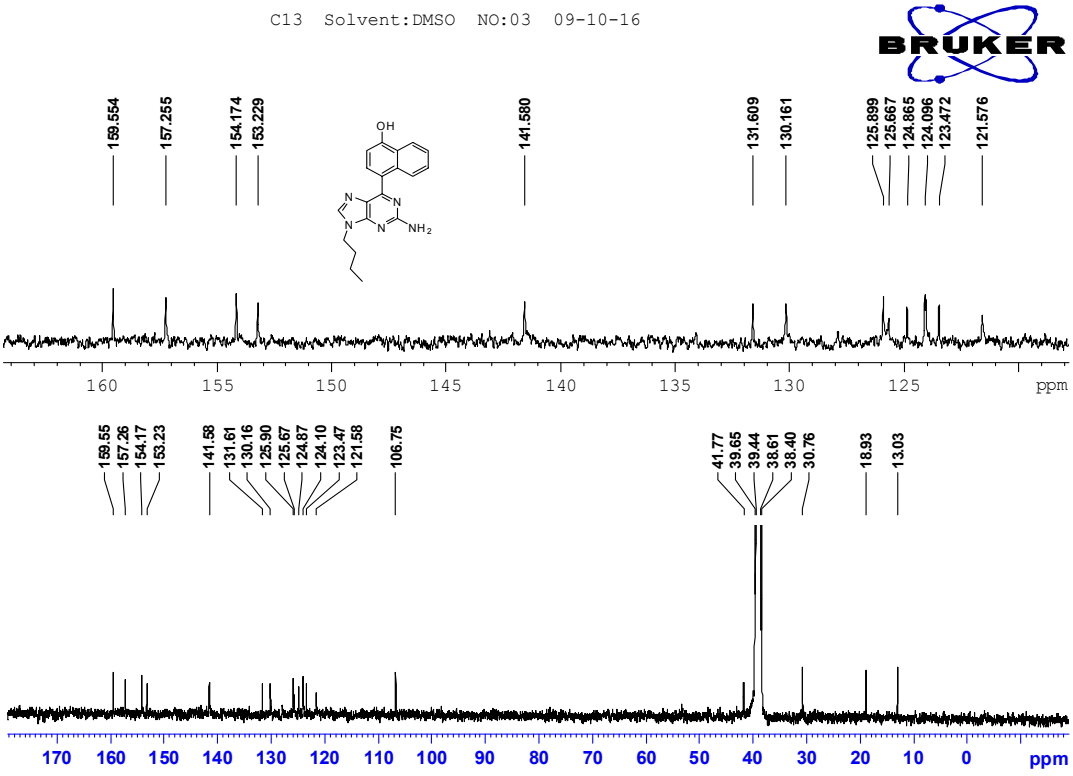
^{13}C NMR of compound **3i**



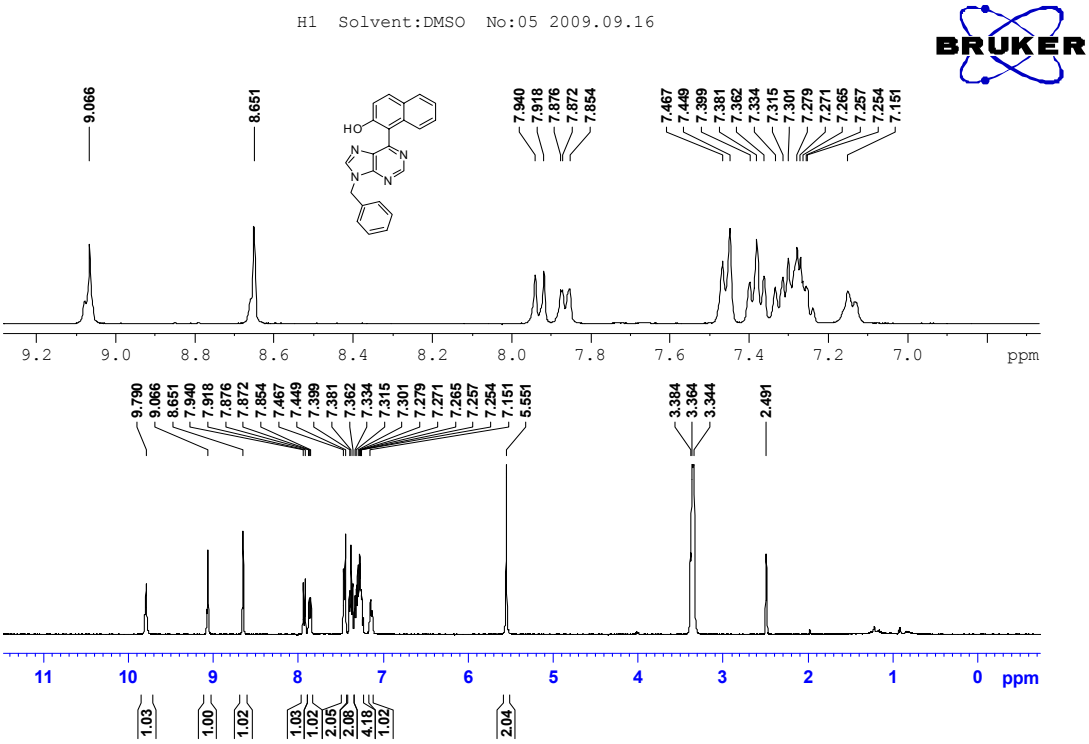
^{1}H NMR of compound **3j**



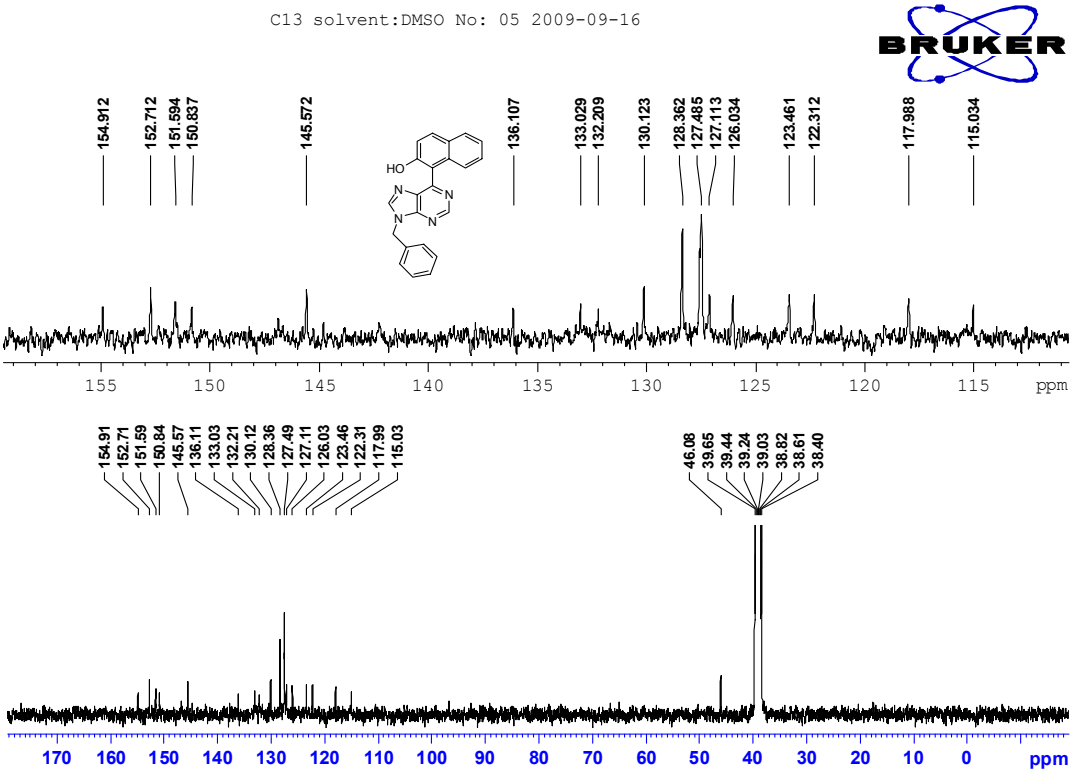
^{13}C NMR of compound **3j**



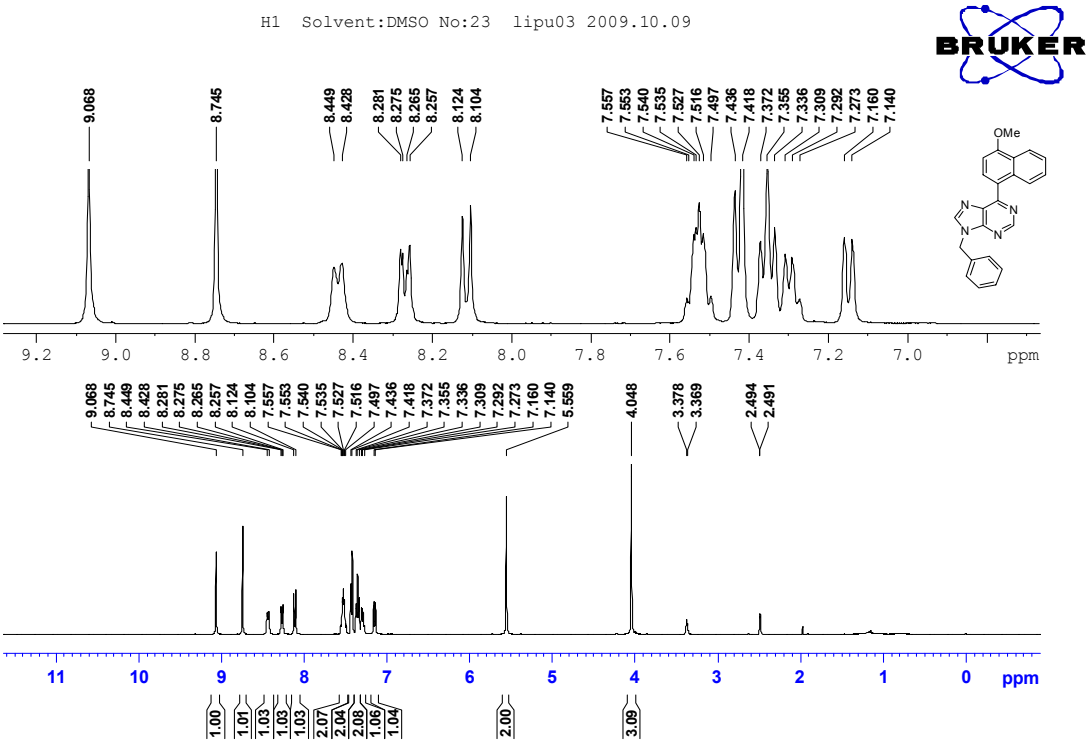
^{1}H NMR of compound **4a**



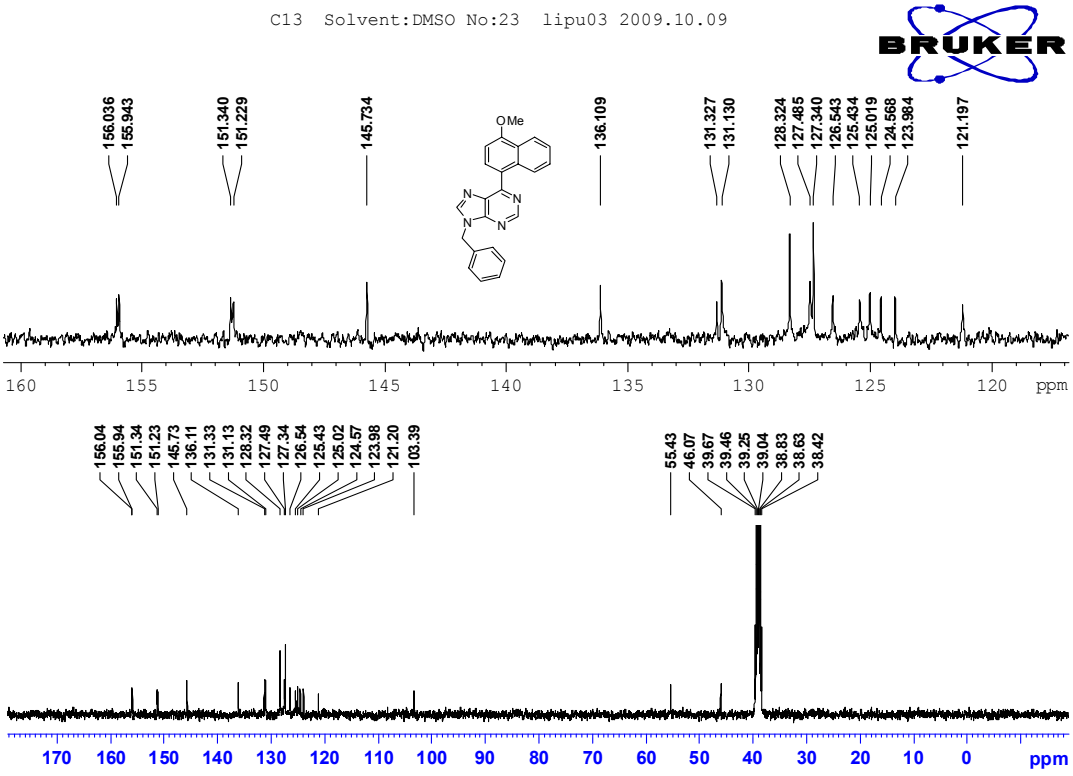
^{13}C NMR of compound **4a**



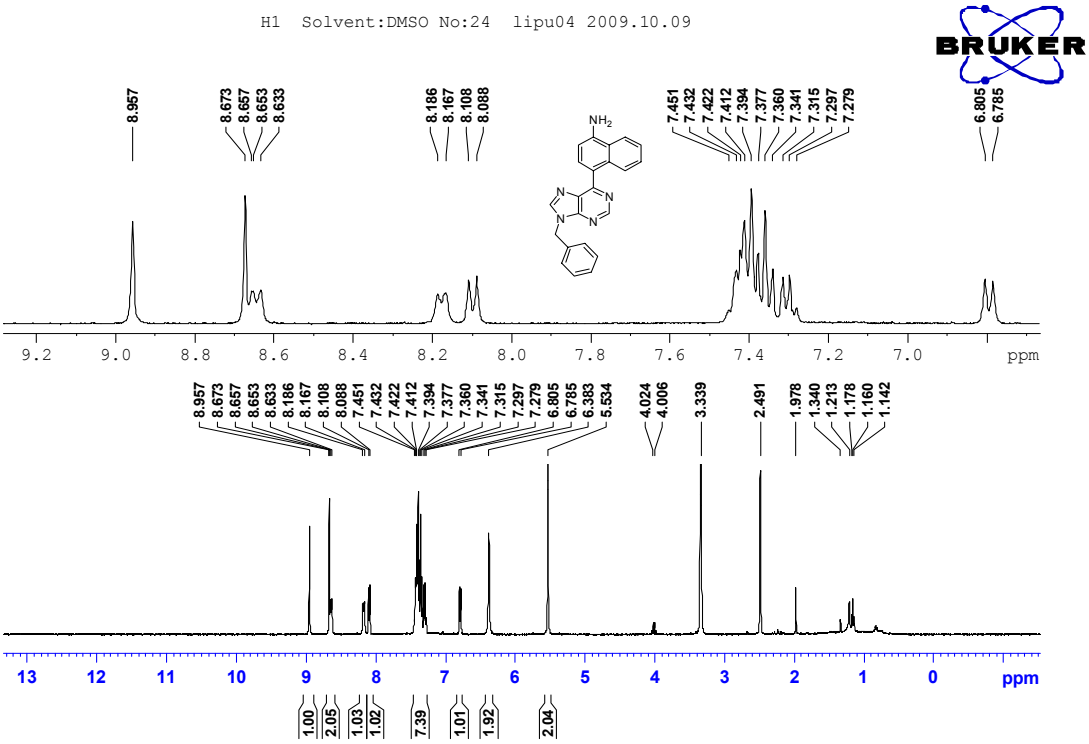
^{1}H NMR of compound **4b**



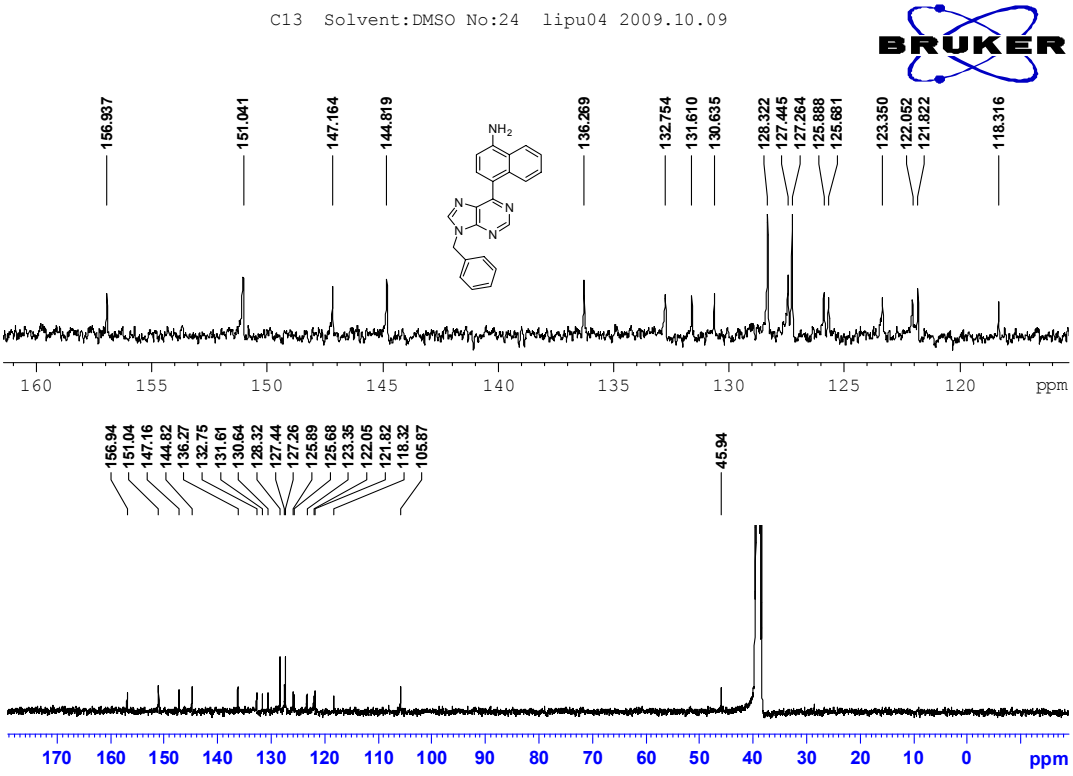
^{13}C NMR of compound **4b**



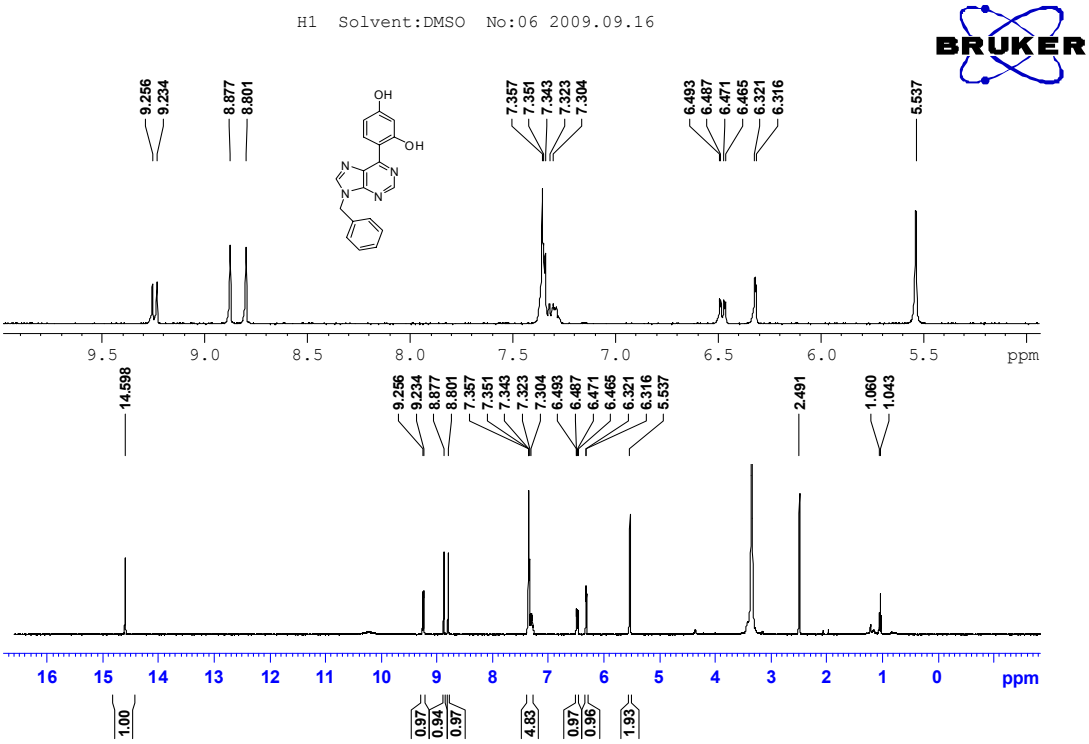
^{1}H NMR of compound **4c**



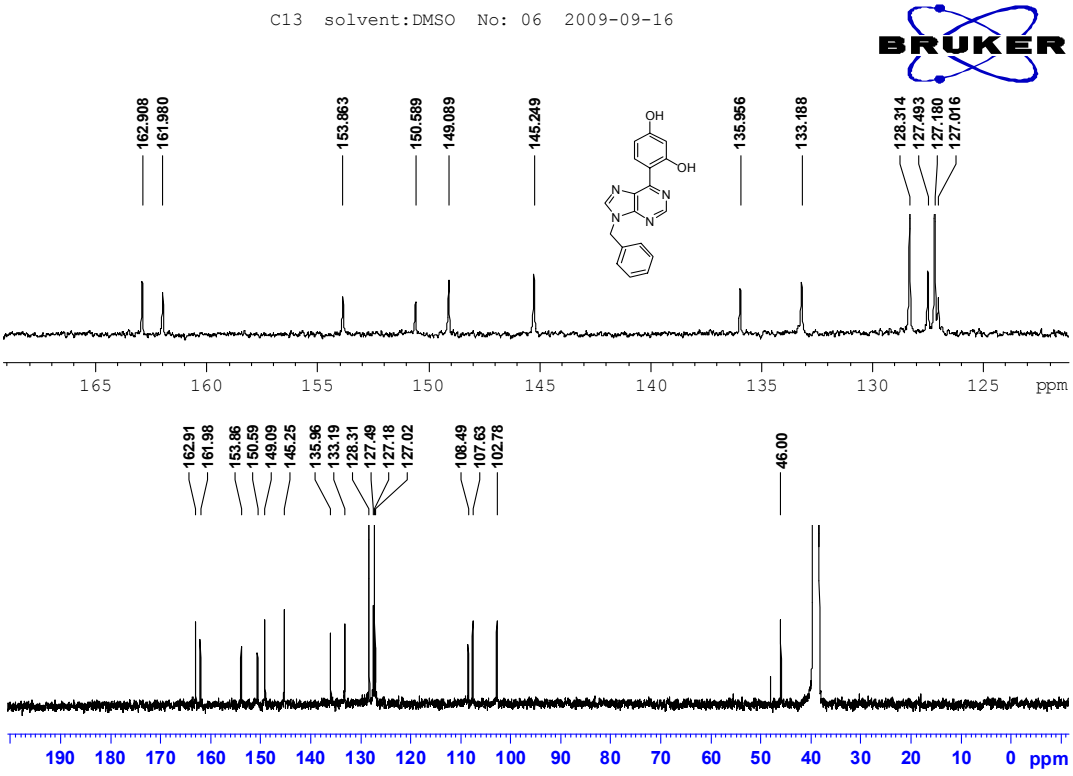
^{13}C NMR of compound **4c**



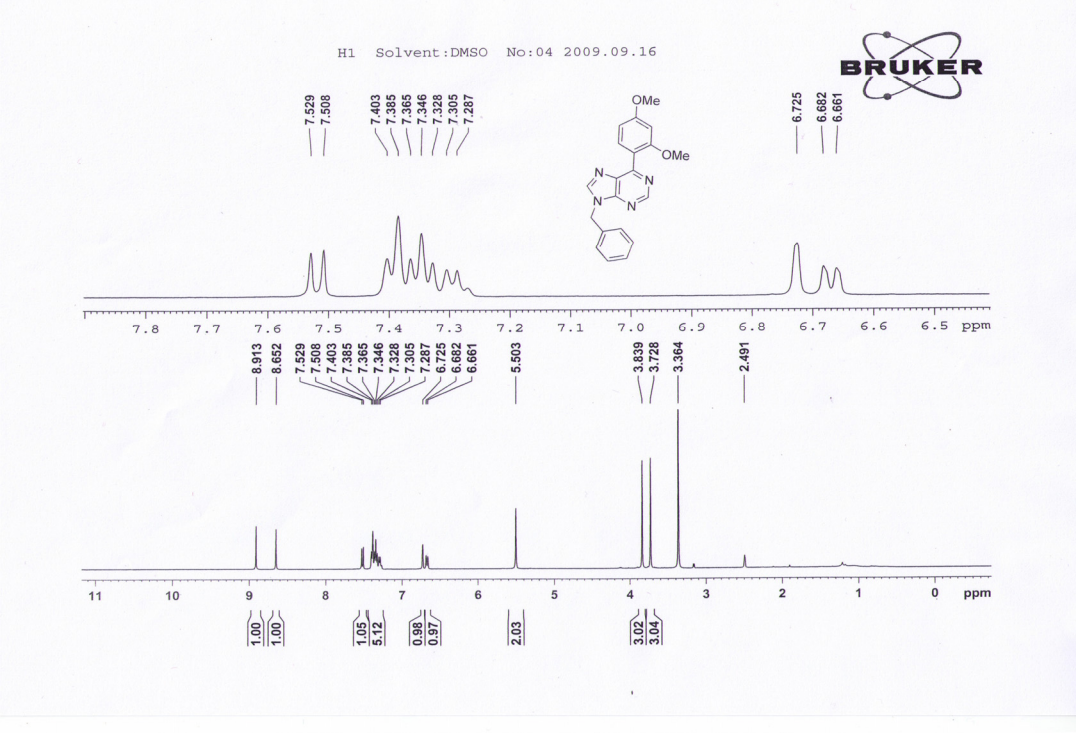
^{1}H NMR of compound **4e**



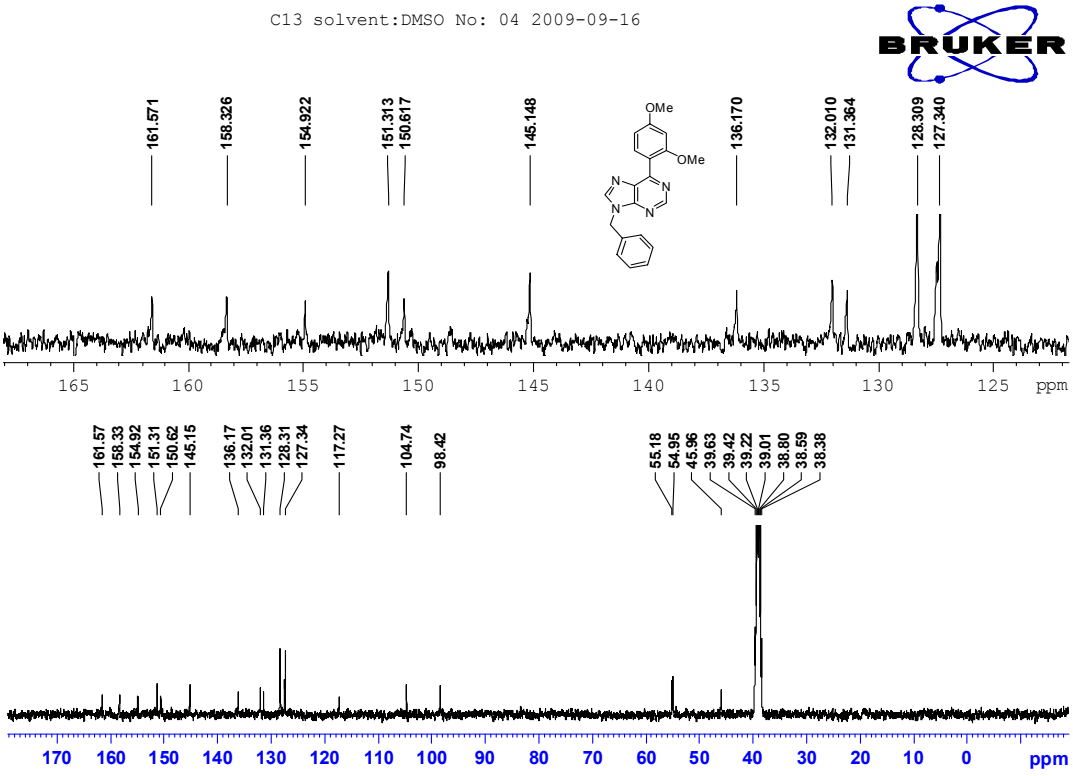
^{13}C NMR of compound **4e**



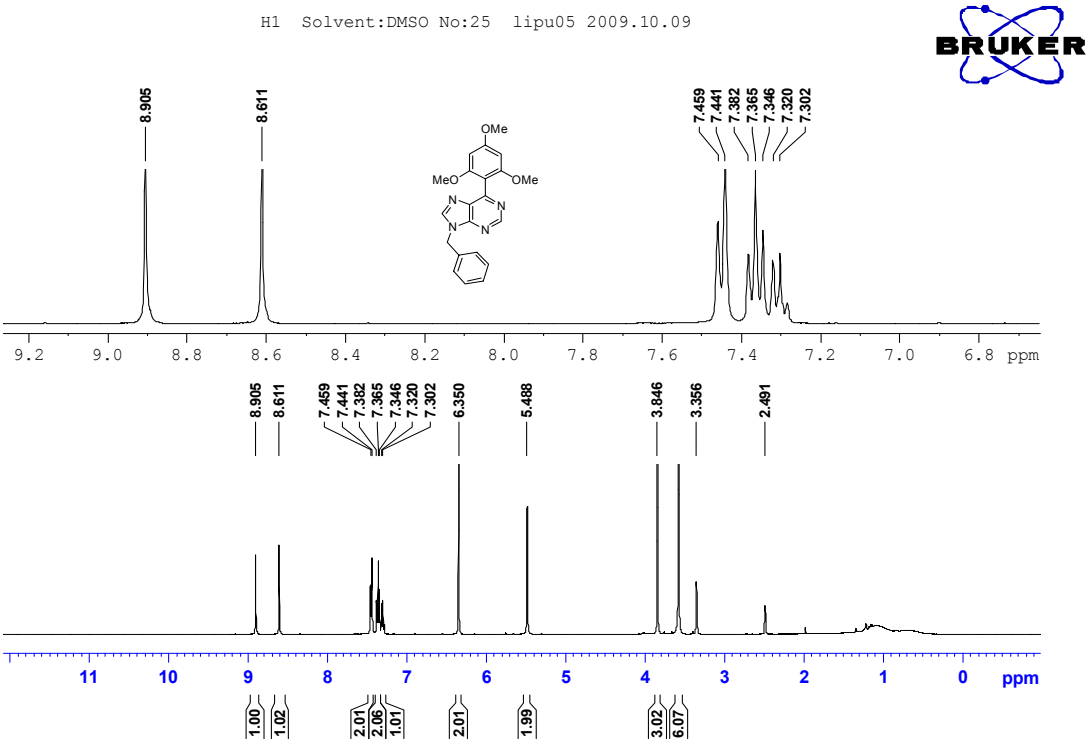
^{1}H NMR of compound **4f**



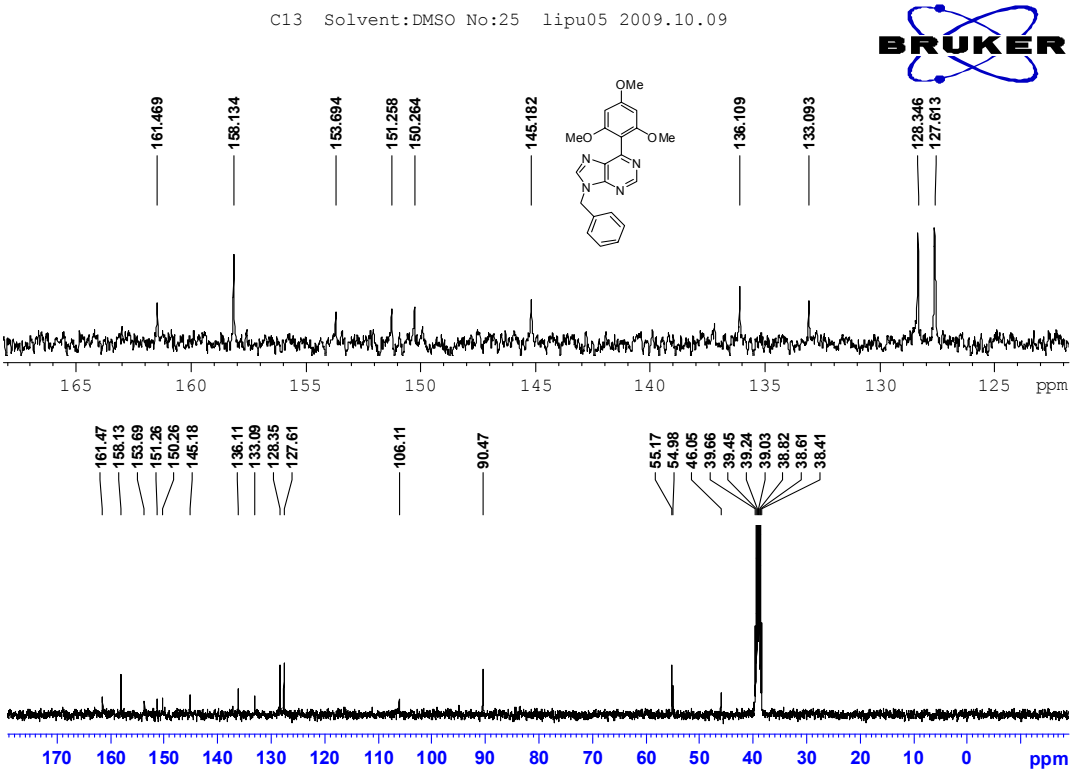
^{13}C NMR of compound **4f**



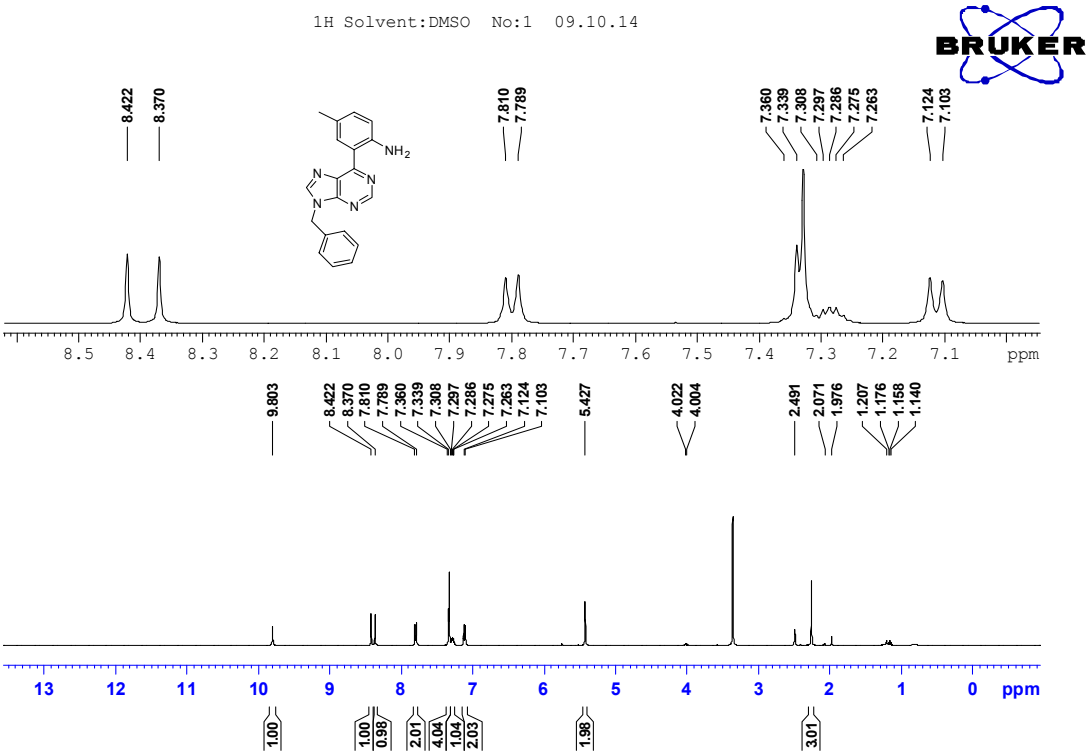
^{1}H NMR of compound **4g**



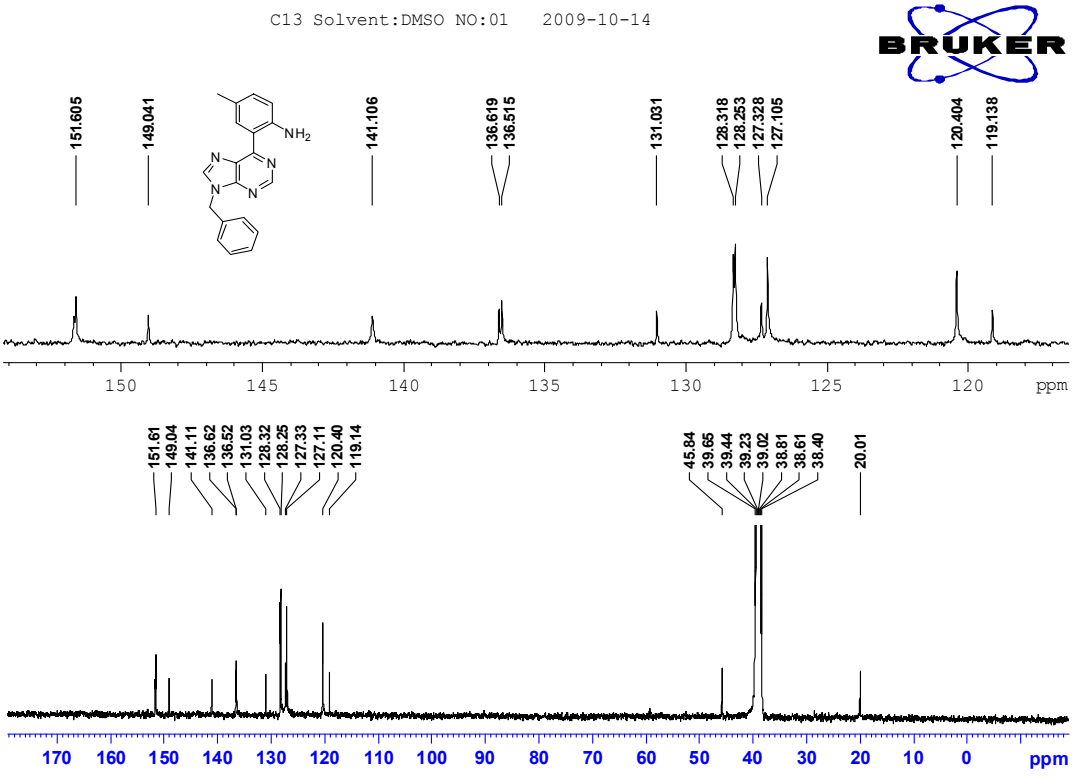
^{13}C NMR of compound **4g**



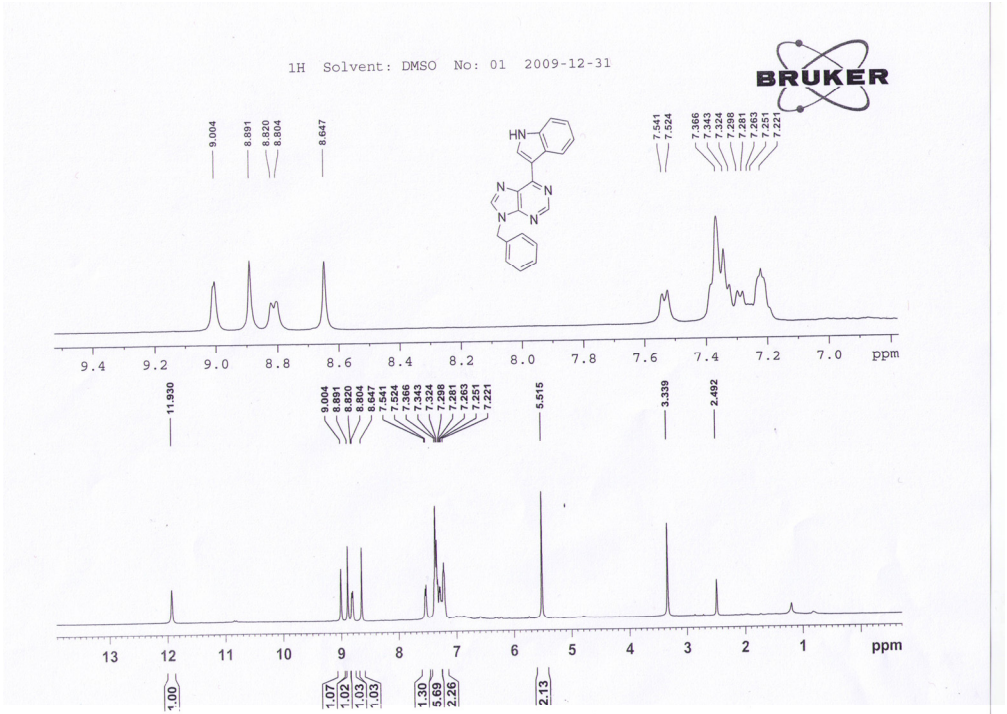
^{1}H NMR of compound **4h**



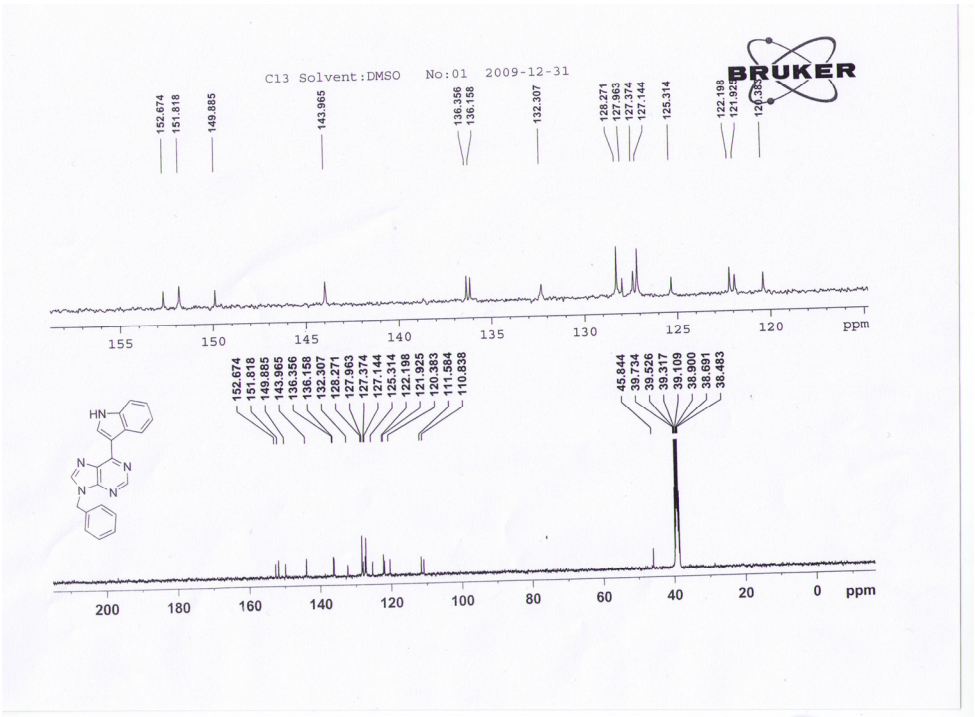
^{13}C NMR of compound **4h**



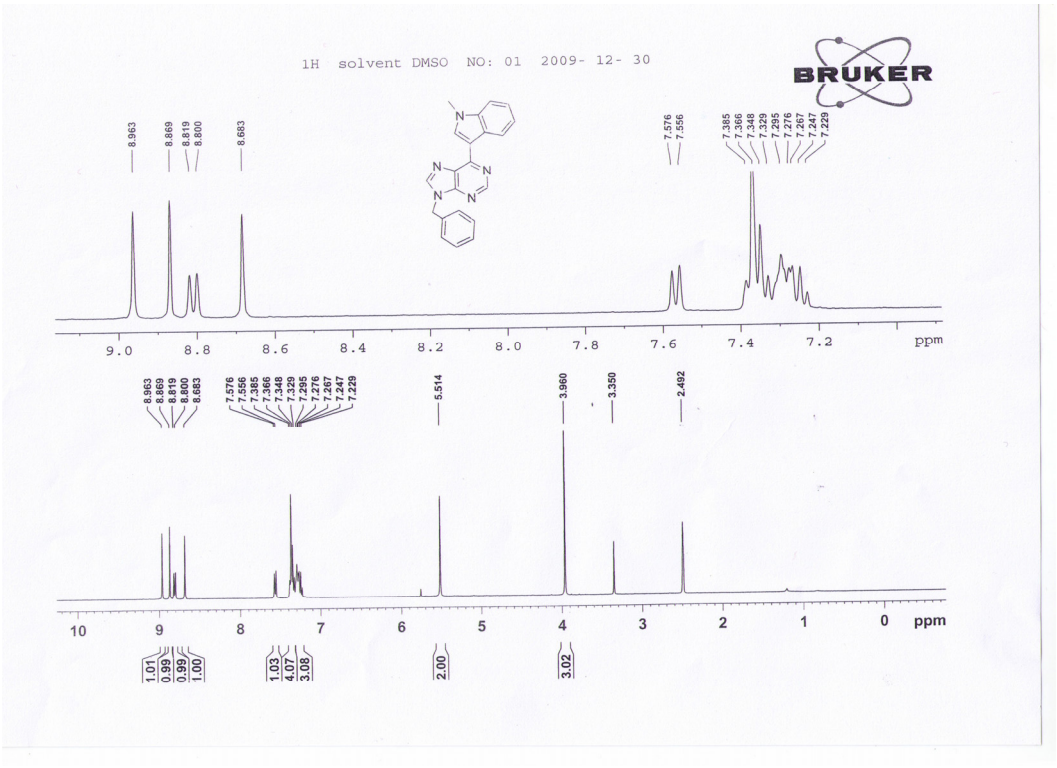
^{1}H NMR of compound **4i**



^{13}C NMR of compound **4i**



^{1}H NMR of compound **4j**



^{13}C NMR of compound **4j**