The Supporting Information

Nickel-Catalyzed Negishi Cross-Couplings of 6-Chloropurines with Organozinc Halides at Room Temperature

Dong-Chao Wang,[a] Hong-Ying Niu,[b] Gui-Rong Qu,[a]* Lei Liang, [a] Xue-Jiao Wei,[a] Yang Zhang,[a] and Hai-Ming Guo[a]*

[a] *College of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions of Ministry of Education, Henan Normal University, Xinxiang 453007, China. Fax: +86-3733329276; E-mail: guguir@sina.com; guohm518@hotmail.com*

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

General.....**S1**
Experiments.....**S2**
Characterization of compounds.....**S2**
References.....**S5**
Copies of 1H and 13C NMR spectra.....**S6**

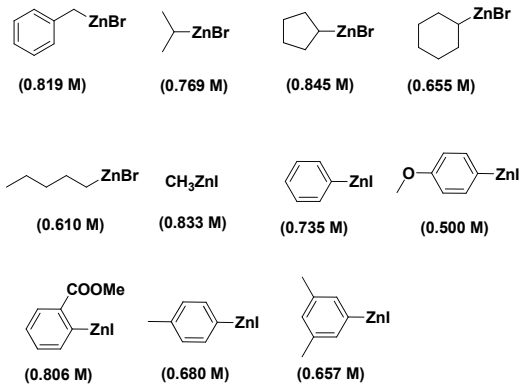
General

All reactions were carried out in oven-dried 10-mL round-bottom flask filled nitrogen, and monitored by thin layer chromatography (TLC). All reagents were reagent grade quality and purchased from commercial sources unless otherwise indicated. Organozinc halides in THF were prepared according to literature procedures[1,2] and determined by iodometric titration using Knochel's procedure. Anhydrous THF were freshly distilled from sodium/ benzophenone before used. LiCl was received from Aldrich. 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 $CDCl_3$. 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.

Experiments

Preparations of organozinc halides[1,2]:

Anhydrous LiCl (20 mmol) was placed in an oven-dried 100 mL Schlenck tube equipped with a magnetic stir bar. The vessel was heated with alcohol burner for 20 min under high vacuum and backfilled with N_2 after cooling to room temperature. Zinc powder (60 mmol, 3 equiv) was added, the mixture of Zn and LiCl was heated again for 10-20 min by alcohol burner and backfilled with N_2 after cooling to room temperature. THF (20 mL) was added via syringe and Zn was activated by and $BrCH_2CH_2Br$ (5 mol %) and Me_3SiCl (1 mol %). The alkyl or aryl zinc halides (20 mmol) was added neat at the room temperature. The reaction mixture was stirred at 50 ℃ over night and the organozinc reagent was determined by iodometric titration using Knochel's procedure.



General Procedure for the Reaction of $Ni(acac)_2$-Catalyzed Negishi:

To an oven-dried 10 mL round-bottom flask equipped with a magnetic stir bar, was added 9-benzyl-6-chloropurine **1a** (0.1 mmol, 24.4 mg), $Ni(acac)_2$ (1.5 mg, 5 mol %). The flask sealed with threaded stopper was evacuated and backfilled with N_2 (this process was repeated for 3 times), and then THF (1 mL) were added via syringe. The solution was stirred for 5 min at room temperature and benzylzinc bromide in THF **2a** (1.5 eq, 0.19 mL) was added slowly via syringe. The mixture was stirred at room temperature until **1a** disappeared as monitored by TLC. The reaction mixture was quenched with saturated NH_4Cl solution (2 mL) and extracted with ethyl acetate (10 mL). The organic were dried over Na_2SO_4, filtered and concentrated under vacuum. The resulted residue was purified by flash chromatography over silica gel (ethyl acetate / petroleum ether) to give the desired product **3a** (98%).

Characterization of compounds

Compound 3a[3]: Colourless crystal, m.p. 85-87 ℃. ^{1}H NMR ($CDCl_3$) δ 8.92 (s, 1H), 8.02(s, 1H), 8.47 (d, J =7.2Hz, 2H), 7.27-7.37 (m, 7H), 7.19 (t, J = 7.2Hz, 1H), 5.41 (s, 2H), 4.53 (s, 2H). ^{13}C NMR($CDCl_3$) δ 160.7, 152.8, 151.2, 143.9, 137.8, 135.0, 132.4, 129.3, 129.1, 128.6, 128.5, 127.9, 126.6, 47.3, 39.4.

Compound 3b: Colourless syrup. ^{1}H NMR ($CDCl_3$) δ 8.89 (s, 1H), 8.28(s, 1H), 7.44 (d, J = 7.6Hz, 2H), 7.26 (t, J = 7.6Hz, 2H), 7.18 (t, J = 7.2Hz, 1H), 5.77 (dd, J = 2.8, 6.2Hz, 1H), 4.52 (s, 2H), 4.14-4.17(m, 1H), 3.74-3.81(m, 1H), 2.01-2.13(m, 3H), 1.63.-1.80(m, 3H). ^{13}C NMR($CDCl_3$) δ 106.7, 152.6, 150.4, 142.0, 137.7, 132.4, 129.3, 128.5, 126.6, 107.0, 81.9, 68.9, 58.3, 39.4, 31.7, 24.8, 22.8. HRMS calcd for $C_{17}H_{19}N_4O$ $[M+H]^+$ 295.1559, found 295.1558.

Compound 3c: Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 8.88 (s, 1H), 8.05(s, 1H), 7.46 (d, J = 7.6Hz, 2H), 7.28 (t, J = 7.4Hz, 2H), 7.19 (t, J = 7.0 Hz, 1H), 4.52 (s, 2H), 4.25 (t, J = 7.2Hz, 2H), 1.84-1.92(m, 2H), 1.32-1.41(m, 2H), 0.95(t, J = 7.2Hz, 3H). ^{13}C NMR($CDCl_3$) δ 160.5, 152.4, 151.2, 144.1, 137.9, 132.5, 129.3, 128.5, 126.6, 43.7, 39.5, 31.9, 19.9, 13.5. HRMS calcd for $C_{16}H_{19}N_4$ $[M+H]^+$ 267.1610, found 267.1611.

Compound 3d: Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 8.88 (s, 1H), 8.04(s, 1H), 7.46 (d, J = 7.6Hz, 2H), 7.27 (t, J = 7.6Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 4.52 (s, 2H), 4.20 (t, J = 7.6Hz, 2H), 1.88-1.97(m, 2H), 0.96(t, J = 7.4Hz, 3H). ^{13}C NMR($CDCl_3$) δ 160.5, 152.5, 151.2, 144.2, 137.9, 132.5, 129.3, 128.5, 126.6, 45.6, 39.5, 23.3, 11.24. HRMS calcd for $C_{15}H_{17}N_4$ $[M+H]^+$ 253.1453, found 253.1452.

Compound 3e[4]**:**Pale yellow crystal, m.p. 117-118 ℃. ^{1}H NMR ($CDCl_3$) δ 8.90 (s, 1H), 8.20(s, 1H), 7.46 (d, J = 7.6Hz, 2H), 7.29 (t, J = 7.6Hz, 2H), 7.20 (t, J = 7.2Hz, 1H), 6.23(d, J = 5.6Hz, 1H), 5.97(t, J = 5.4Hz, 1H), 5.68(t, J = 5.0Hz, 1H), 4.52(s, 2H), 4.42-4.46 (m, 2H),4.35-4.39 (m, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H). ^{13}C NMR($CDCl_3$) δ 170.3, 169.5, 169.3, 161.3, 152.8, 150.7, 142.5, 137.5, 133.1, 129.3, 128.6, 126.7, 86.3, 80.3, 72.9, 70.6, 63.0, 39.5, 30.9, 29.7, 20.7, 20.5, 20.3.

Compound 3f: Pale yellow syrup. ^{1}H NMR ($CDCl_3$) δ 8.19 (s, 1H), 7.48 (d, J = 7.2Hz, 2H), 7.29 (t, J = 7.6Hz, 2H), 7.21 (t, J = 7.4Hz, 1H), 6.22(d, J = 5.6Hz, 1H), 5.79(t, J = 5.6Hz, 1H), 5.59(t, J = 4.8Hz, 1H), 4.47(s, 2H), 4.45 (t, J = 3.8Hz, 1H),4.39 (d, J = 3.6Hz, 2H), 2.16 (s,3H), 2.14 (s, 3H), 2.07 (s, 3H). ^{13}C NMR($CDCl_3$) δ 170.3, 169.6, 169.4, 163.5, 154.4, 152.4, 142.7,

136.8, 132.0, 129.4, 128.7, 126.9, 85.8, 80.6, 73.1, 70.6, 63.0, 58.5, 39.6, 20.8, 20.5, 20.4, 18.5. HRMS calcd for $C_{23}H_{23}ClN_4NaO_7$ $[M+Na]^+$ 525.1153, found 525.1154.

Compound 3h: Pale yellow syrup. ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 1H), 7.46 (d, J = 7.2Hz, 2H), 7.38 (d, J = 7.2Hz, 2H), 7.24-7.29 (m, 4H), 7.17-7.21 (m, 2H), 6.05(d, J = 4.4Hz, 1H), 5.95(t, J = 5.0Hz, 1H), 5.62 (t, J = 5.6Hz, 1H), 4.47(s, 2H), 4.36-4.40 (m, 3H),4.28 (dd, J =12.2 3.4Hz, 1H), 4.03-4.08 (m, 1H), 2.15 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H). ^{13}C NMR($CDCl_3$) δ 170.3, 169.4, 169.3, 164.4, 161.1, 151.0, 142.5, 138.6, 137.7, 131.2, 129.4, 129.3, 128.4, 128.3, 126.6, 126.3, 87.1, 80.0, 73.1, 70.7, 63.4, 45.7, 39.7, 20.7, 20.6, 20.5. HRMS calcd for $C_{30}H_{30}N_4NaO_7$ $[M+Na]^+$ 581.2012, found 581.2015.

Compound 3g: Pale yellow syrup. ^{1}H NMR ($CDCl_3$) δ 8.19 (s, 1H), 7.49 (d, J = 7.2Hz, 2H), 7.28 (t, J = 7.2Hz, 2H), 7.21 (t, J = 7.4Hz, 1H), 5.64(s, 2H), 4.78(s, 2H), 4.17(t, J = 4.6Hz, 2H), 3.76(t, J = 4.6Hz, 2H), 1.99 (s, 3H). ^{13}C NMR($CDCl_3$) δ 170.8, 163.3, 154.6, 153.1, 144.7, 136.8, 131.2, 129.4, 128.6, 126.9, 72.8, 68.1, 62.8, 58.4 39.6, 20.8, 18.4. HRMS calcd for $C_{17}H_{17}ClN_4NaO_3$ $[M+Na]^+$ 383.0887, found 383.0886.

Compound 3i: Pale yellow syrup. ^{1}H NMR ($CDCl_3$) δ 8.09 (s, 1H), 7.48 (d, J = 7.2Hz, 2H), 7.37 (d, J = 7.2Hz, 2H), 7.24-7.28 (m, 4H), 7.17-7.21(m, 2H), 5.61(s, 2H), 4.49(s 2 H), 4.35(s, 2H), 4.11 (t, J = 4.6Hz, 2H),3.70 (t, J = 4.6Hz, 2H), 1.97 (s, 3H). ^{13}C NMR($CDCl_3$) δ 170.8, 164.5, 160.7, 152.1, 143.7, 138.9, 137.8, 130.1, 129.4, 129.2, 128.4, 128.2, 126.5, 126.3, 72.4, 67.9, 62.8, 58.4, 45.7, 39.6, 29.7, 20.7, 18.5. HRMS calcd for $C_{24}H_{24}N_4NaO_3$ $[M+Na]^+$ 439.1746, found 439.1748.

Compound 3j[5]: Yellow crystal, m.p. 74-76 ℃. ^{1}H NMR ($CDCl_3$) δ 8.89 (s, 1H), 8.03(s, 1H), 7.29-7.37 (m, 5H), 5.44 (s, 2H), 2.87 (s, 3H). ^{13}C NMR($CDCl_3$) δ 159.3, 152.5, 150.6, 143.5, 135.1, 132.9, 129.1, 128.6, 127.8, 47.2, 19.4.

Compound 3k[6]: Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 8.91 (s, 1H), 7.99(s, 1H), 7.29-7.38 (m, 5H), 5.43 (s, 2H), 3.19 (t, J = 7.8Hz, 2H), 1.85-1.93(m, 2H), 1.32-1.43(m, 4H), 0.88 (t, J = 7.0Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 163.2.152.6, 150.8, 143.4, 135.2, 132.4, 129.1, 128.5, 127.9, 47.2, 33.2, 31.8, 28.2, 22.4, 13.9.

Compound 3l: Colourless oil. ^{1}H NMR ($CDCl_3$) δ 8.93 (s, 1H), 7.99(s, 1H), 7.30-7.38 (m, 5H), 5.43 (s, 2H), 3.85-3.93 (m, 1H), 2.12-2.18 (m, 2H), 2.01-2.10 (m, 2H), 1.89-1.97 (m, 2H), 1.75-1.79 (m, 2H). ^{13}C NMR($CDCl_3$) δ 166.4, 152.8, 150.6, 143.3, 135.2, 132.1, 129.1, 128.6,

127.9, 58.4, 47.2, 42.6, 32.8, 26.3, 18.5. HRMS calcd for $C_{17}H_{19}N_4$ $[M+H]^+$ 279.1610, found 279.1608.

Compound 3m: Colourless oil. ^{1}H NMR ($CDCl_3$) δ 8.92 (s, 1H), 7.99(s, 1H), 7.34 (m, 5H), 5.42 (s, 2H), 3.45 (m, 1H), 1.75-1.98 (m, 7H), 1.33-1.52 (m, 3H). ^{13}C NMR($CDCl_3$) δ 166.6, 152.7, 150.9, 143.2, 135.2, 131.6, 129.1, 128.5, 127.8, 47.2, 41.7, 31.3, 26.2, 25.9. HRMS calcd for $C_{18}H_{21}N_4$ $[M+H]^+$ 293.1766, found 293.1765.

Compound 3n: Colourless oil. ^{1}H NMR ($CDCl_3$) δ 8.94 (s, 1H), 8.00(s, 1H), 7.31-7.37 (m, 5H), 5.44 (s, 2H), 3.76-3.82 (m, 1H), 1.45 (d, J = 6.8Hz, 6H). ^{13}C NMR($CDCl_3$) δ 167.4, 152.7, 150.8, 143.3, 135.2, 131.4, 129.1, 128.6, 127.9, 58.4, 47.2, 31.6, 21.2, 18.4. HRMS calcd for $C_{15}H_{17}N_4$ $[M+H]^+$ 253.1453, found 253.1454.

Compound 3o: Colourless oil. ^{1}H NMR ($CDCl_3$) δ 8.92 (s, 1H), 8.00(s, 1H), 7.32-7.37 (m, 5H), 5.44 (s, 2H), 3.18 (t, J = 7.8Hz, 2H), 1.89-1.99 (m, 2H), 1.03 (t, J = 7.4Hz, 3H). ^{13}C NMR($CDCl_3$) δ 163.0, 152.6, 150.8, 143.5, 135.2, 132.6, 129.1, 128.6, 127.9, 47.3, 35.2, 21.9, 14.2. HRMS calcd for $C_{15}H_{17}N_4$ $[M+H]^+$ 253.1453, found 253.1454.

Compound 5a[3]: Colourless crystal, m.p. 118-119 ℃. ^{1}H NMR ($CDCl_3$) δ 9.06 (s, 1H), 8.78(d, J =7.2Hz, 2H), 8.10 (s, 1H), 7.50-7.59 (m, 3H), 7.32-7.37 (m, 5H), 5.48 (s, 2H). ^{13}C NMR($CDCl_3$) δ 154.9, 152.6, 152.5, 144.1, 135.6, 135.2, 130.9, 129.8, 129.1, 128.6, 128.5, 127.8, 47.3.

Compound 5b[3]: Colourless crystal, m.p. 158-160 ℃. ^{1}H NMR ($CDCl_3$) δ 9.00 (s, 1H), 8.81(d, J =8.8Hz, 2H), 8.07 (s, 1H), 7.32-7.37 (m, 5H), 7.08 (d, J = 8.8Hz, 2H), 5.48 (s, 2H), 3.90(s, 3H). ^{13}C NMR($CDCl_3$) δ 162.0, 154.6, 152.5, 152.3, 143.6, 135.3, 131.5, 130.4, 129.1, 128.5, 128.3, 127.8, 114.1, 55.4, 47.2.

Compound 5c[7]: Colourless crystal, m.p. 125-127 ℃. ^{1}H NMR ($CDCl_3$) δ 9.04 (s, 1H), 8.70(d, J =8.4Hz, 2H), 8.09 (s, 1H), 7.32-7.38 (m, 7H), 5.49 (s, 2H), 2.45(s, 3H). ^{13}C NMR($CDCl_3$) δ 155.0, 152.6, 152.4, 143.9, 141.4, 135.2, 132.9, 130.7, 129.7, 129.4, 129.1, 128.5, 127.8, 47.2, 21.6.

Compound 5d: Yellow oil. ^{1}H NMR ($CDCl_3$) δ 9.05 (s, 1H), 8.06 (s, 1H), 8.04 (d, J =7.6Hz, 1H), 7.92 (d, J =7.6Hz, 1H), 7.63-7.67(m, 1H), 7.54-7.57 (m, 1H), 7.29-7.38 (m, 5H), 5.47 (s, 2H), 3.64(s, 3H). ^{13}C NMR($CDCl_3$) δ 168.7, 156.8, 152.3, 151.7, 144.6, 135.5, 135.1, 132.3, 131.7, 131.3, 131.2, 129.9, 129.8, 129.2, 128.6, 127.9, 52.2, 47.4, 30.9. HRMS calcd for $C_{20}H_{17}N_4O_2$

$[M+H]^+$ 345.1352, found 345.1354.

Compound 5e: Yellow crystal, m.p. 121-123 ℃. ^{1}H NMR ($CDCl_3$) δ 9.05 (s, 1H), 8.39 (s, 2H), 8.10 (s, 1H), 7.31-7.39 (m, 5H), 7.17(s, 1H), 5.49 (s, 2H), 2.45(s, 6H). ^{13}C NMR($CDCl_3$) δ 206.9, 155.3, 152.5, 152.4, 144.0, 138.2, 135.5, 135.2, 132.8, 130.9, 129.1, 128.5, 127.8, 127.5, 107.0, 47.2, 30.9, 21.5. HRMS calcd for $C_{20}H_{19}N_4$ $[M+H]^+$ 315.1610, found 315.1606.

References

(1) Krasovskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 6040.

(2) Han, C.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 7532.

(3) L.-L. Gundersen, A. K. Bakkestuen, A. J. Aasen, H. Øverås, F. Rise, *Tetrahedron* **1994**, *50*, 9743.

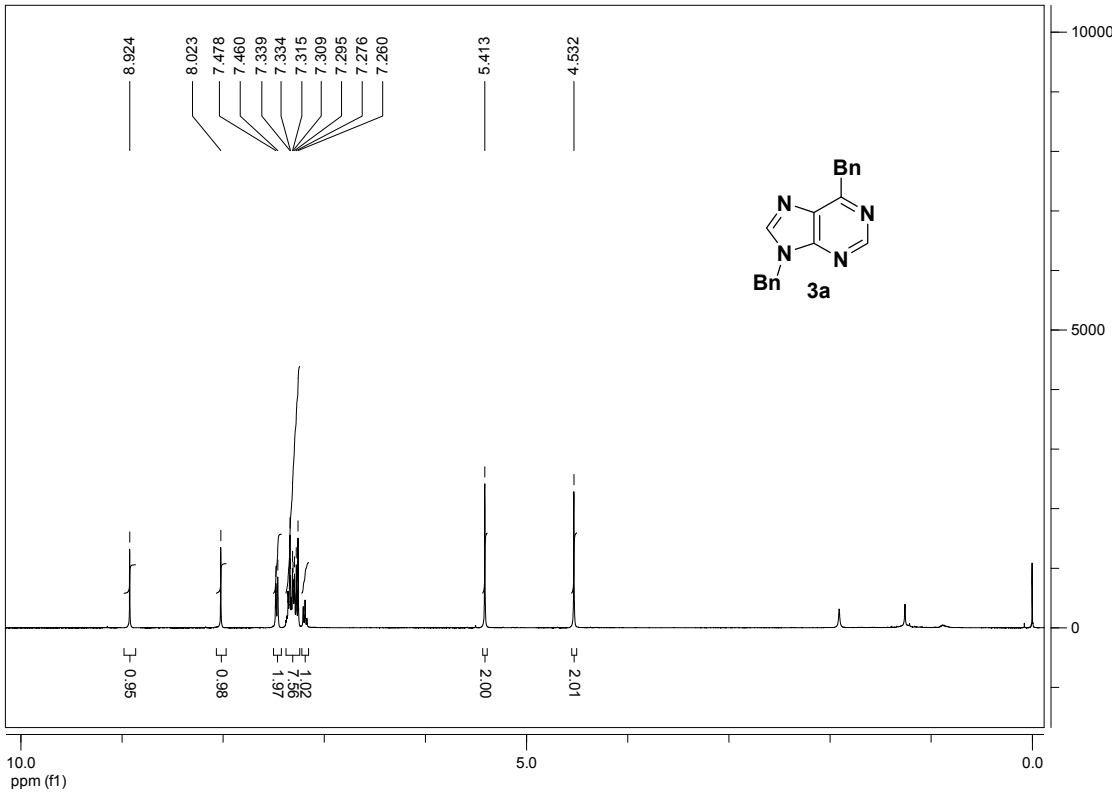
(4) a) M. Hocek, P. Šilhár, I. Shih, E. Mabery, R. Mackman, *Bioorg. Med. Chem. Lett*. **2006**, *16*, 5290.
b) M. Hocek, A. Holý, I. Votruba, H. Dvořáková, *Collect. Czech. Chem. Commun*. **2001**, *66*, 483.

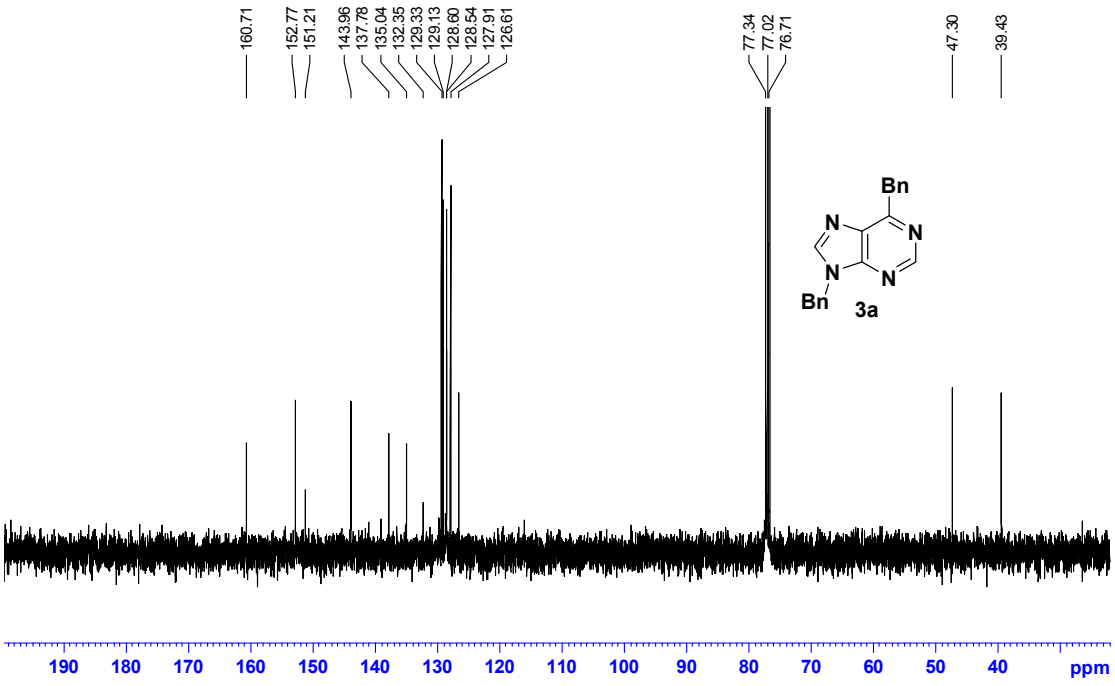
(5) G. -R. Qu, Z. -J. Mao, H. -Y. Niu, D. -C. Wang, C. Xia, H. -M. Guo, *Org. Lett.* **2009**, *11*, 1745.

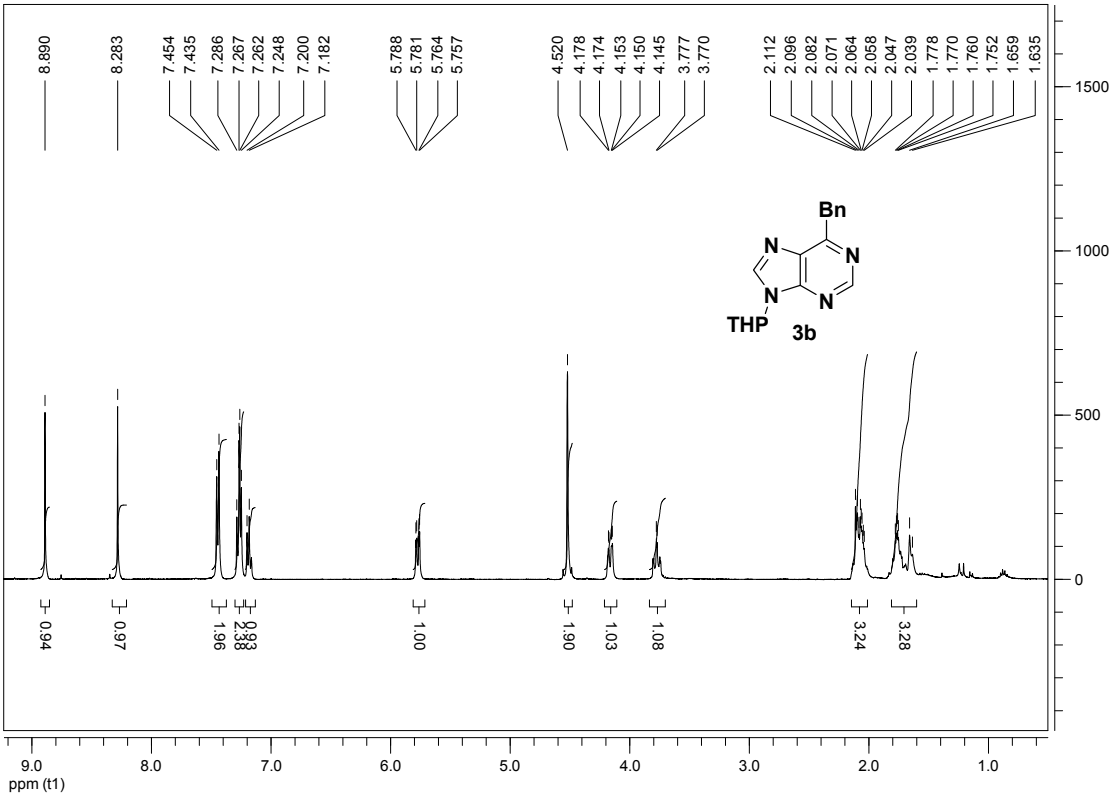
(6) H.-M. Guo, Y. Zhang, H.-Y. Niu, D.-C. Wang, Z.-L. Chu, G.-R. Qu, *Org. Biomol. Chem.*, **2011**, *9*, 2065

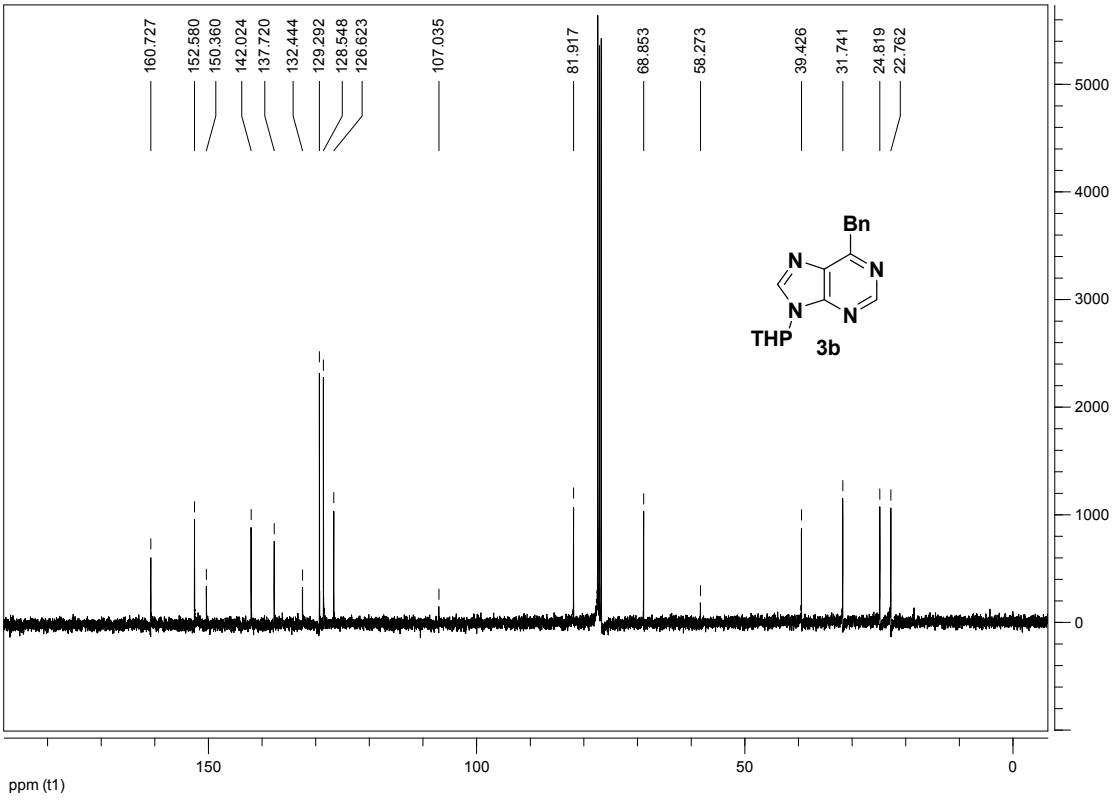
(7) M. Brændvang L.-L. Gundersen, *Bioorg. Med. Chem.* **2005**, *13*, 6360

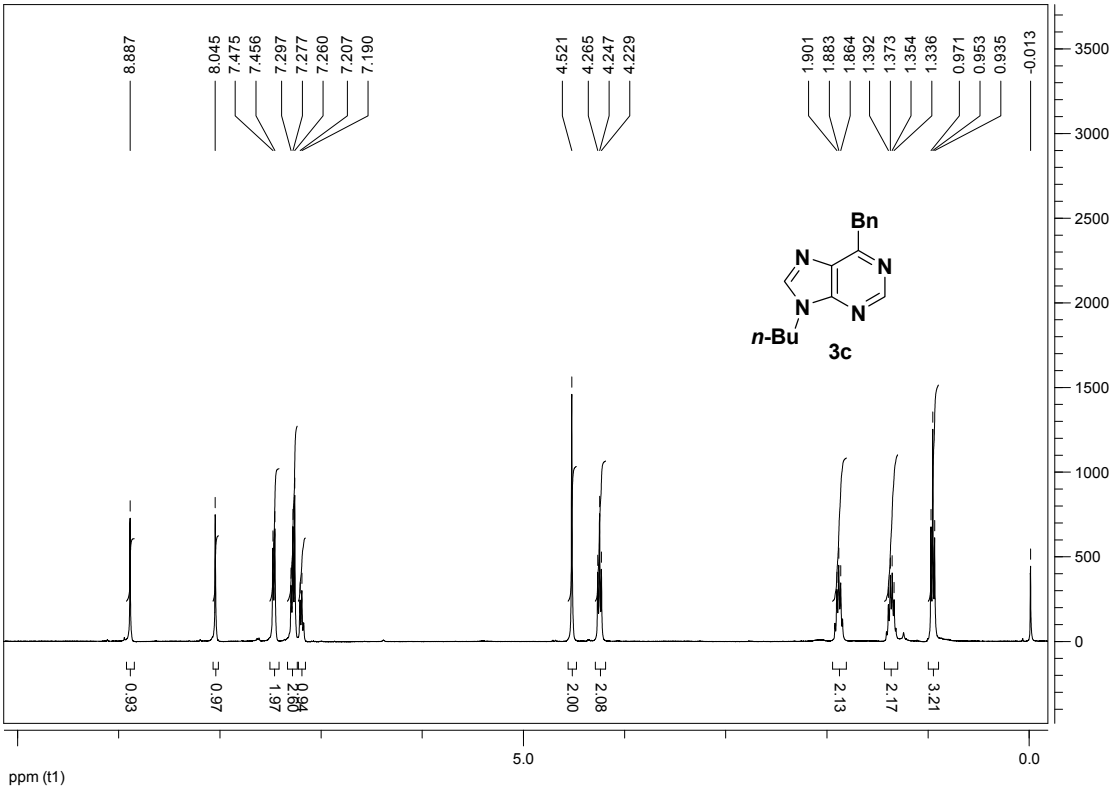
Copies of ^{1}H and ^{13}C NMR spectra

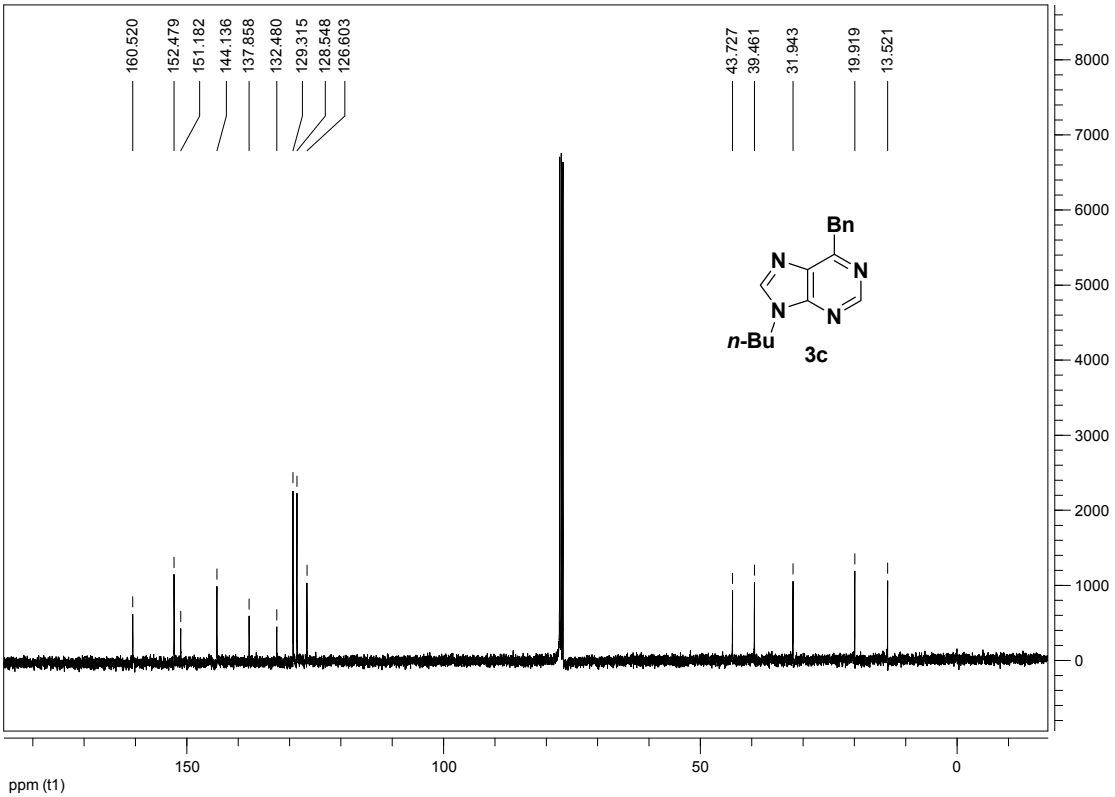


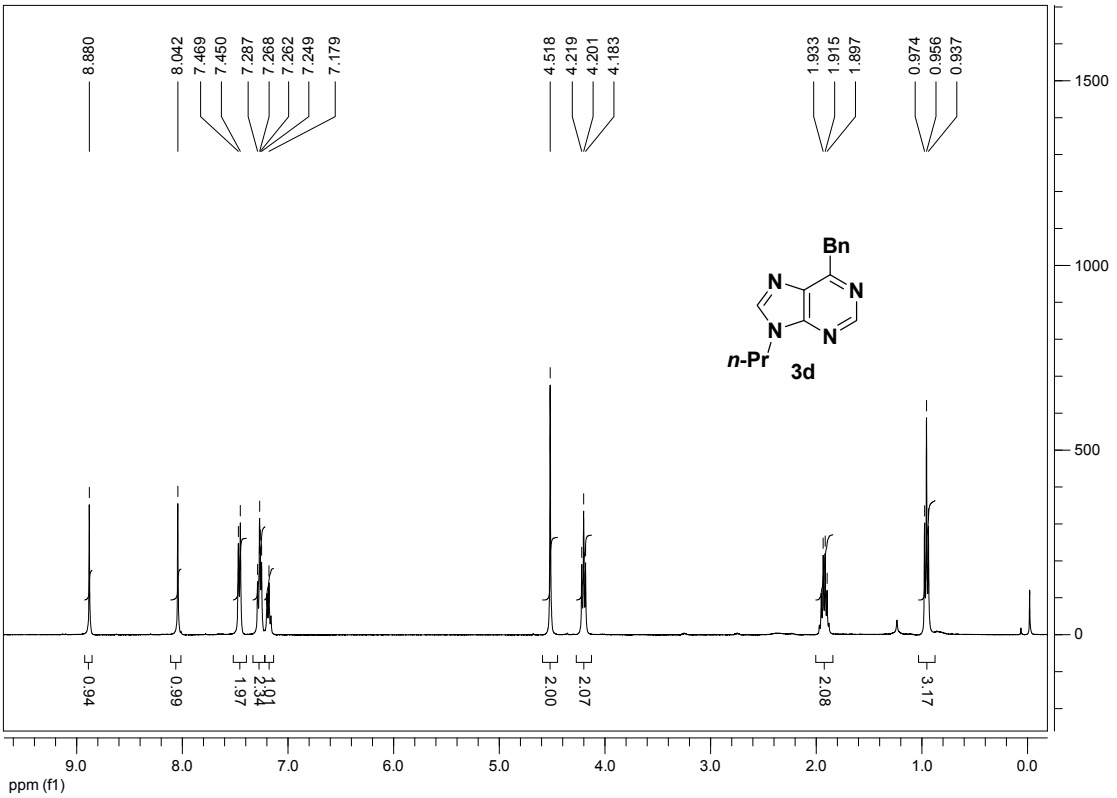


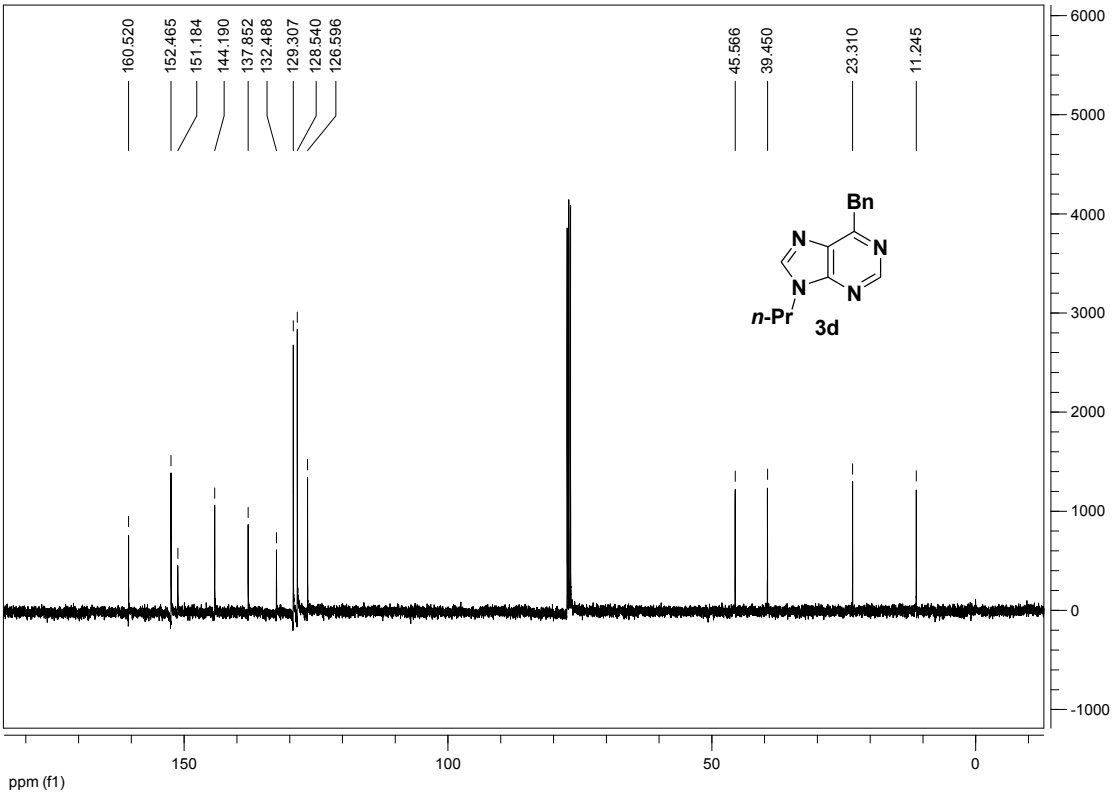


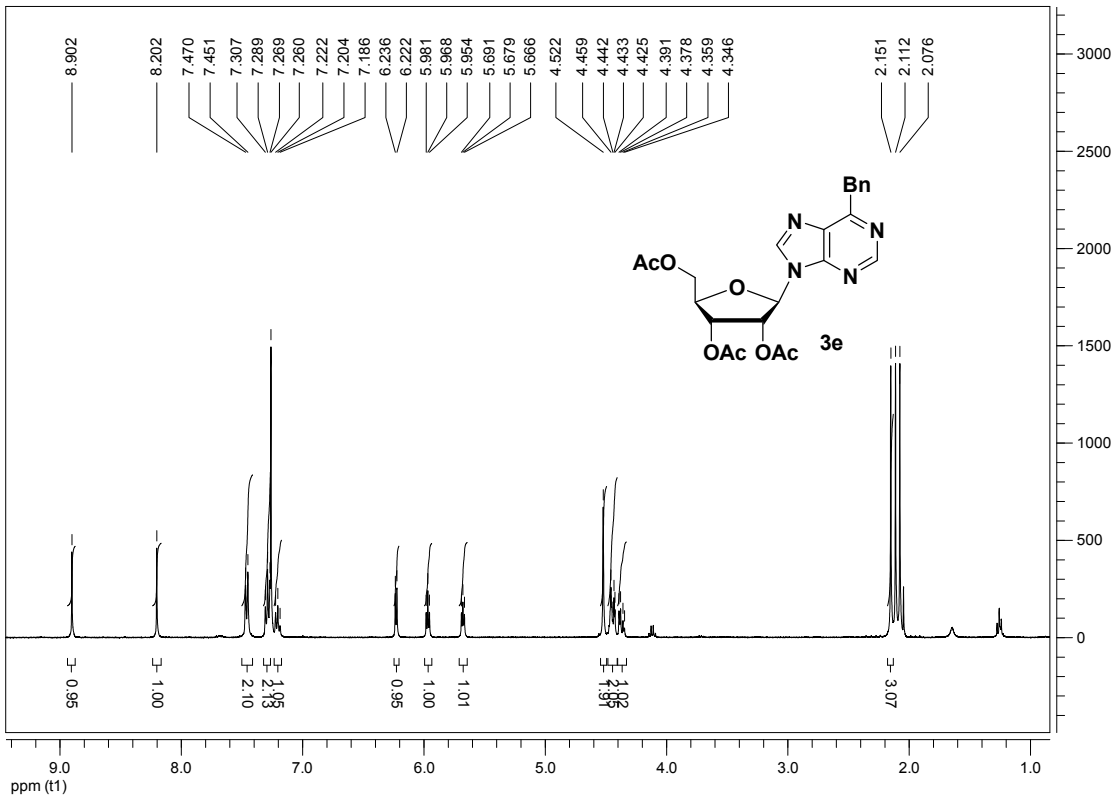


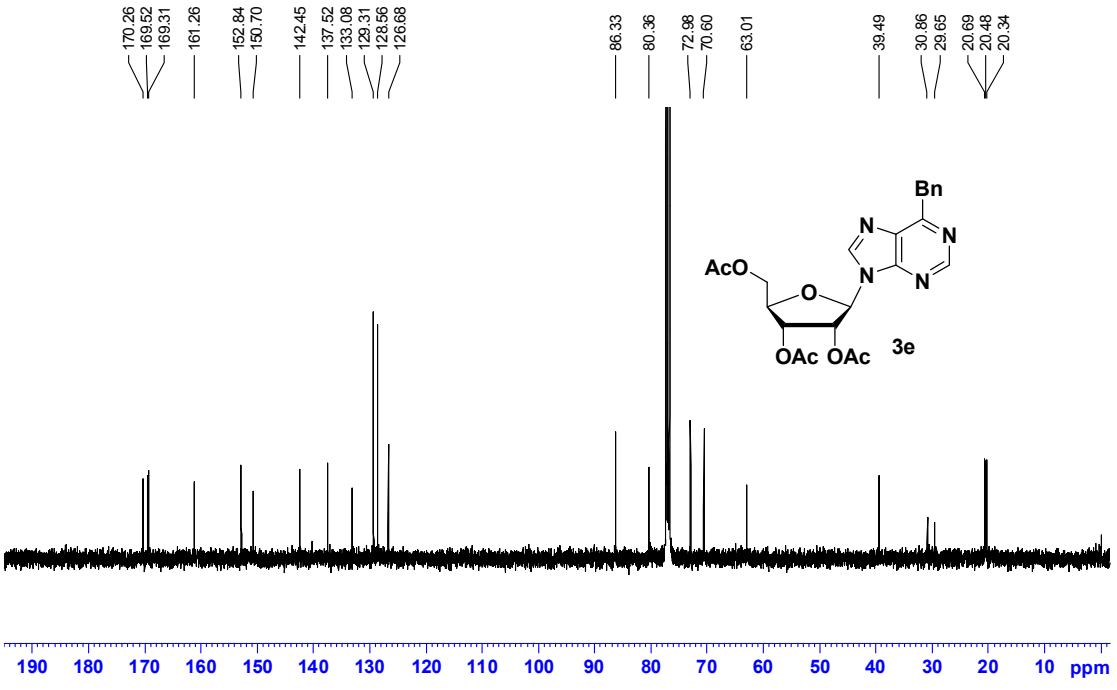


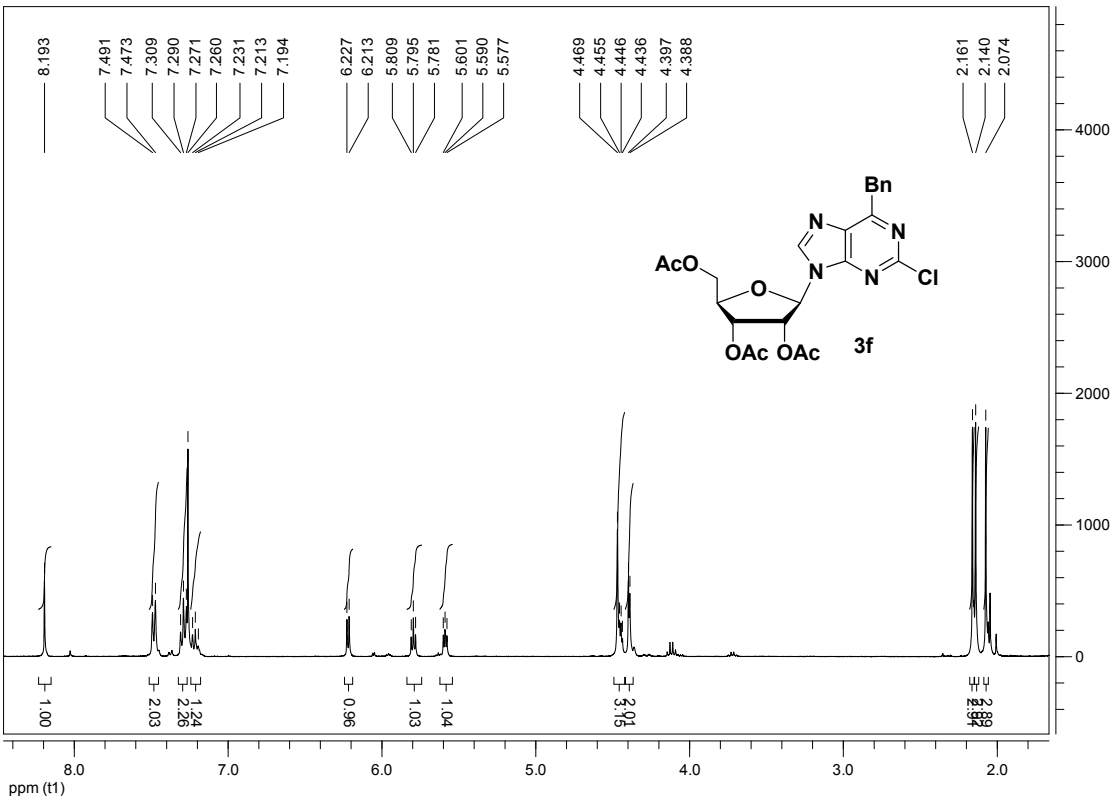


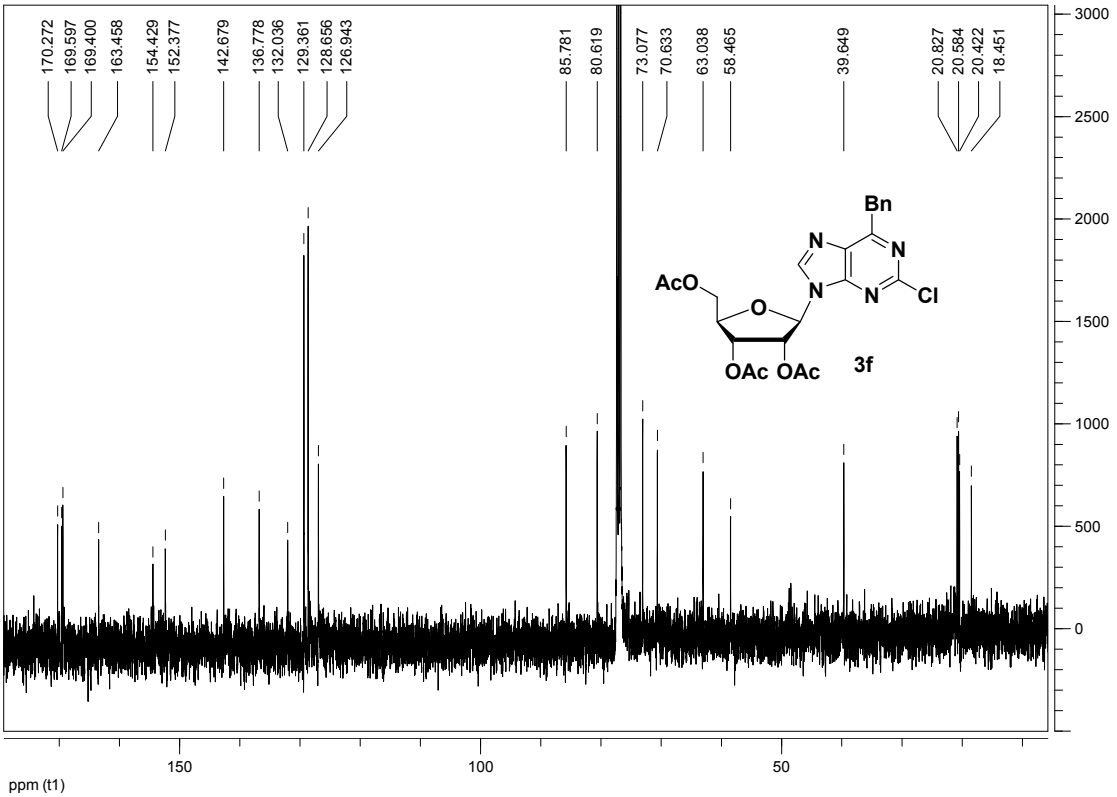

8.880
8.042
7.469
7.450
7.287
7.268
7.262
7.249
7.179
4.518
4.219
4.201
4.183
1.933
1.915
1.897
0.974
0.956
0.937
Bn
N
N
N
N
n-Pr
3d
0.94
0.99
1.97
2.34
2.01
2.00
2.07
2.08
3.17
ppm (f1)

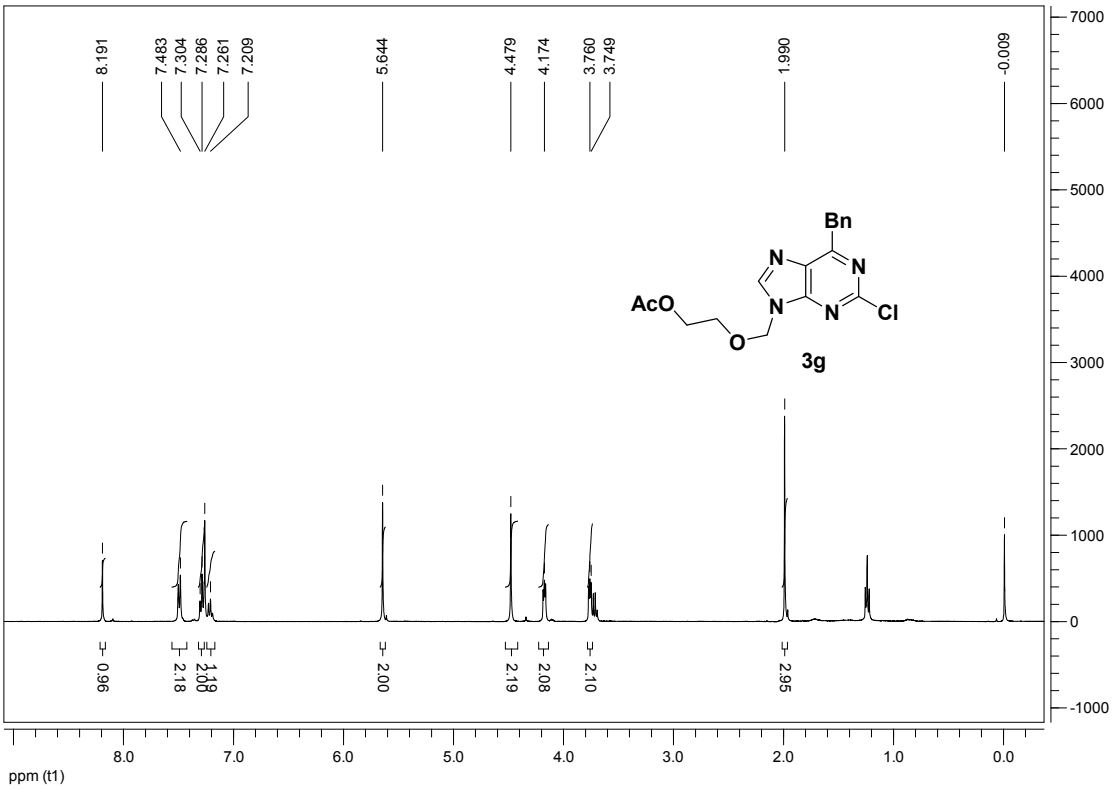

160.520
152.465
151.184
144.190
137.852
132.488
129.307
128.540
126.596
45.566
39.450
23.310
11.245
Bn
N
N
N
N
n-Pr
3d
ppm (f1)

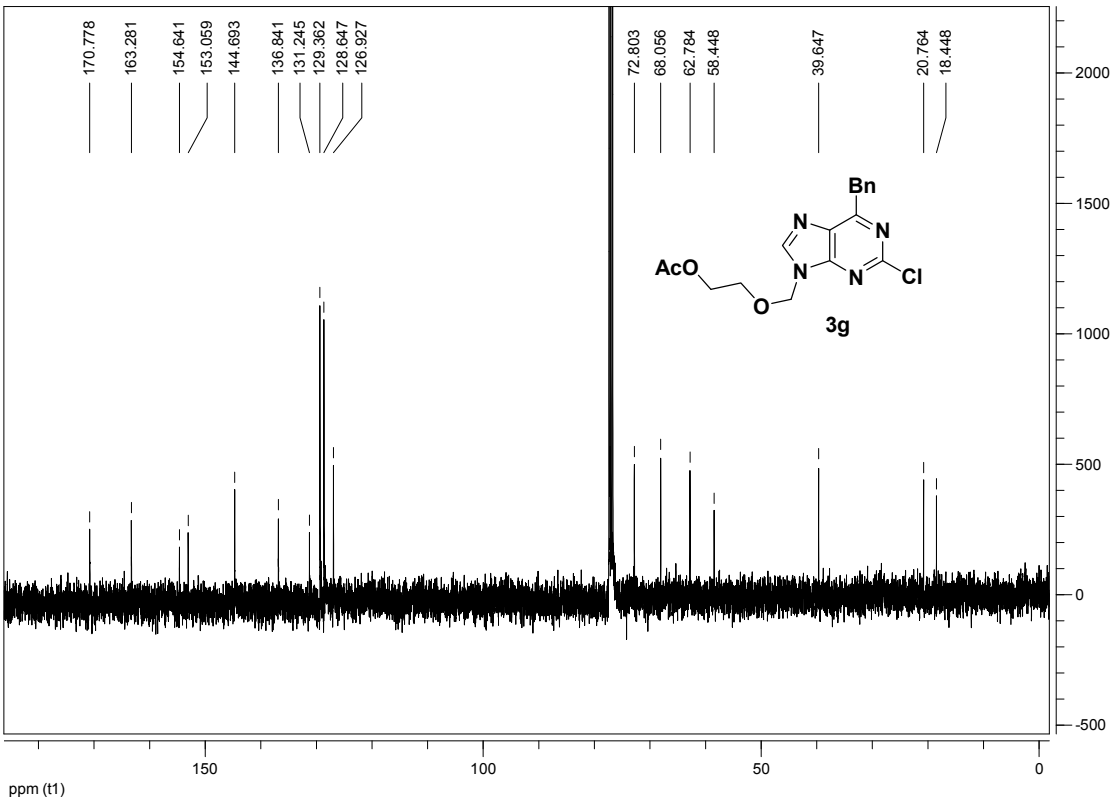


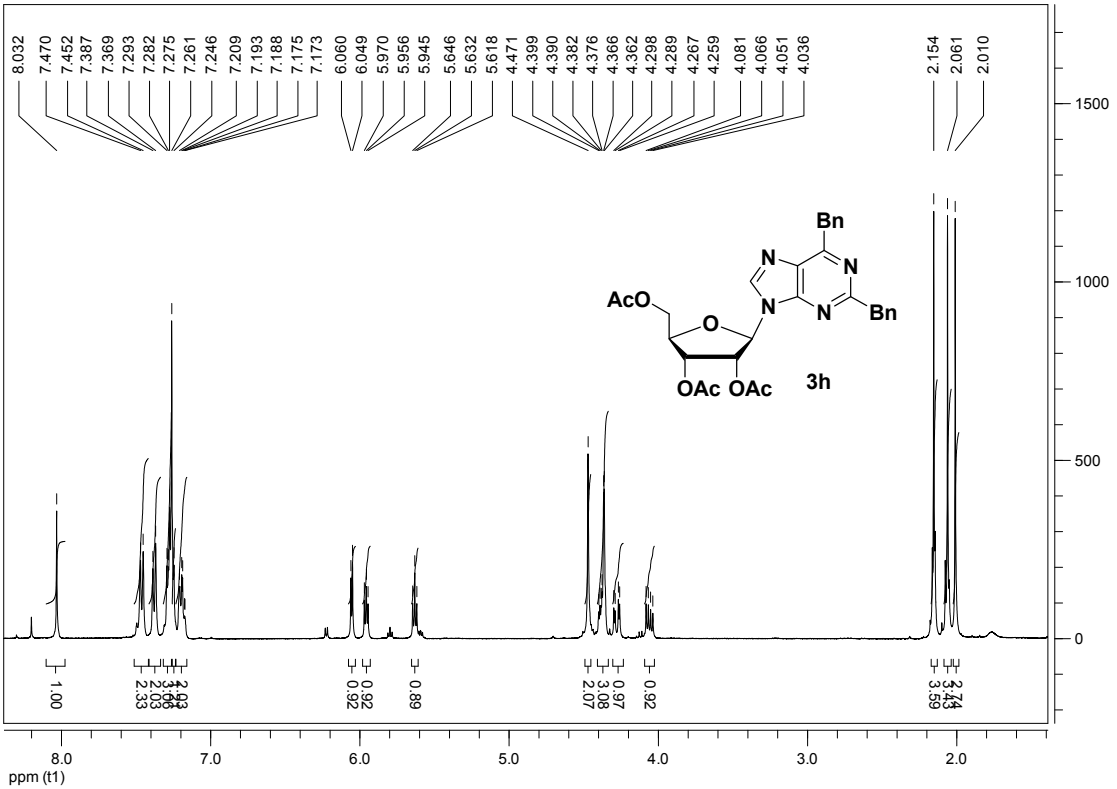


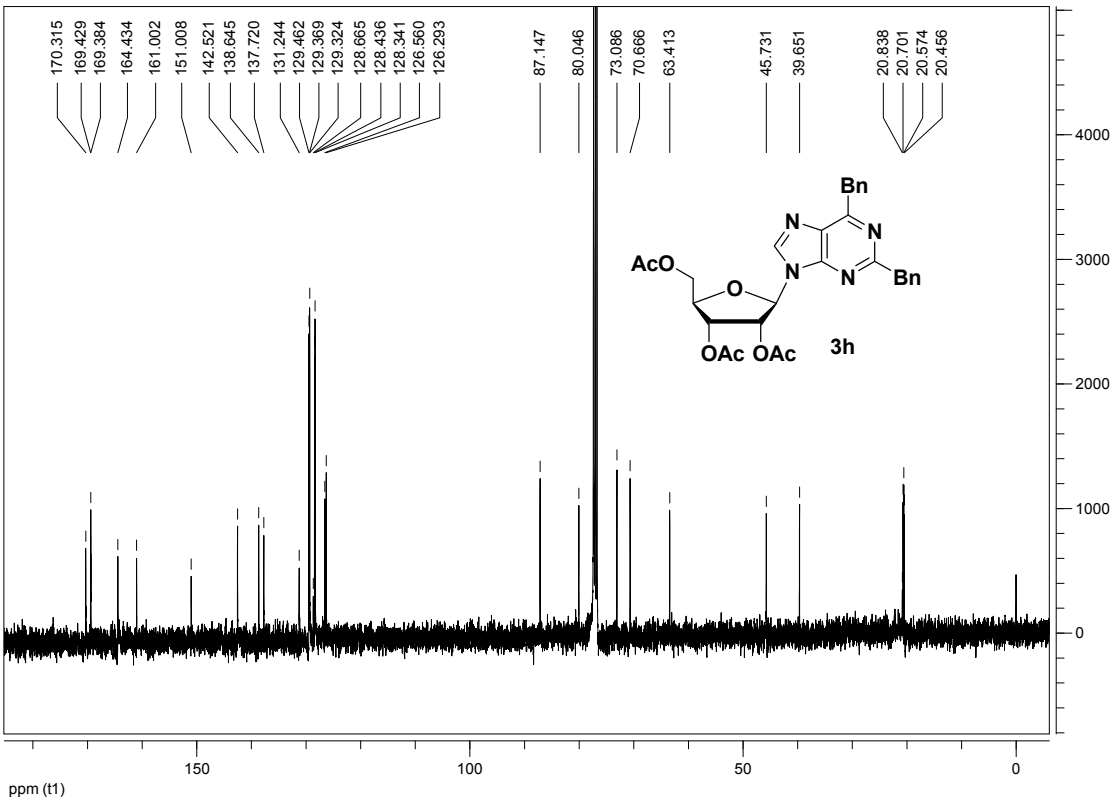


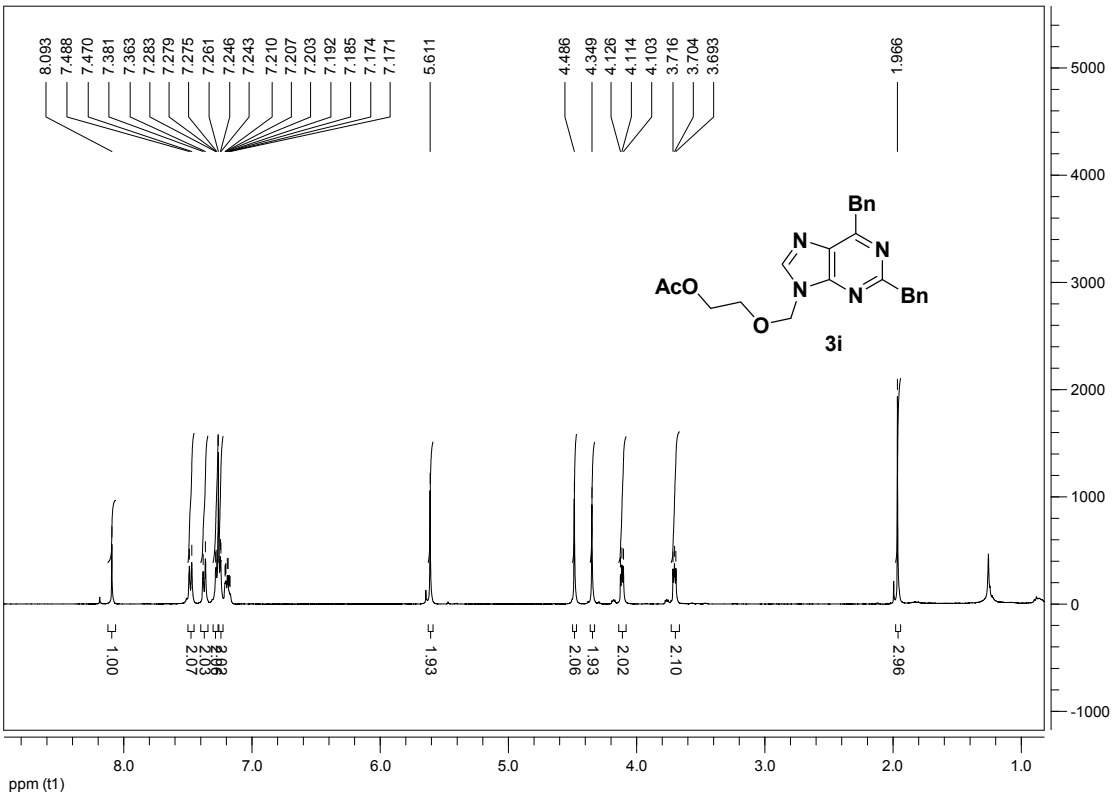


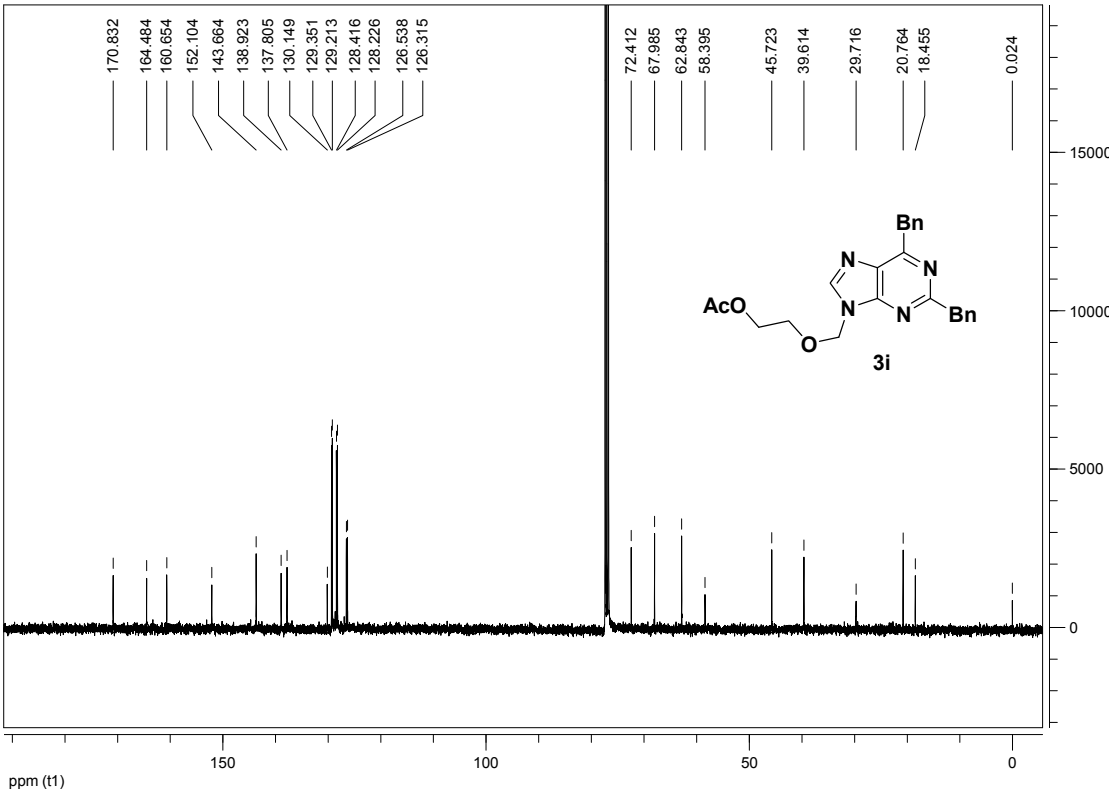


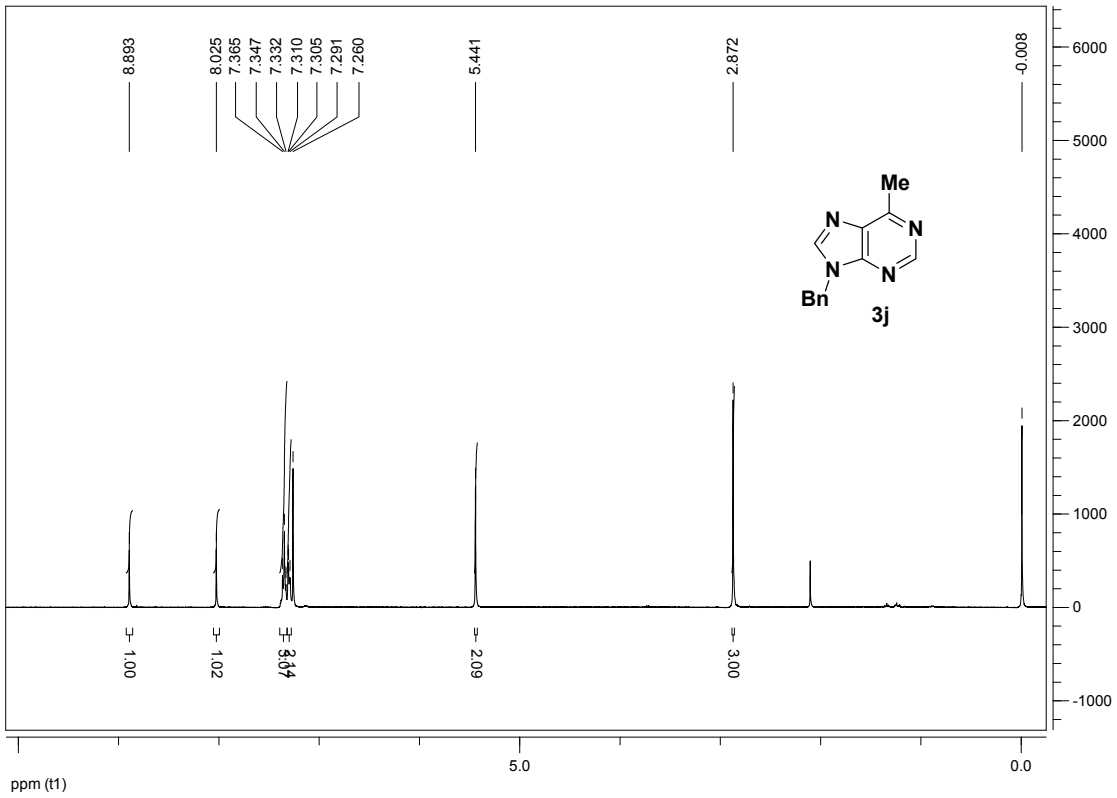


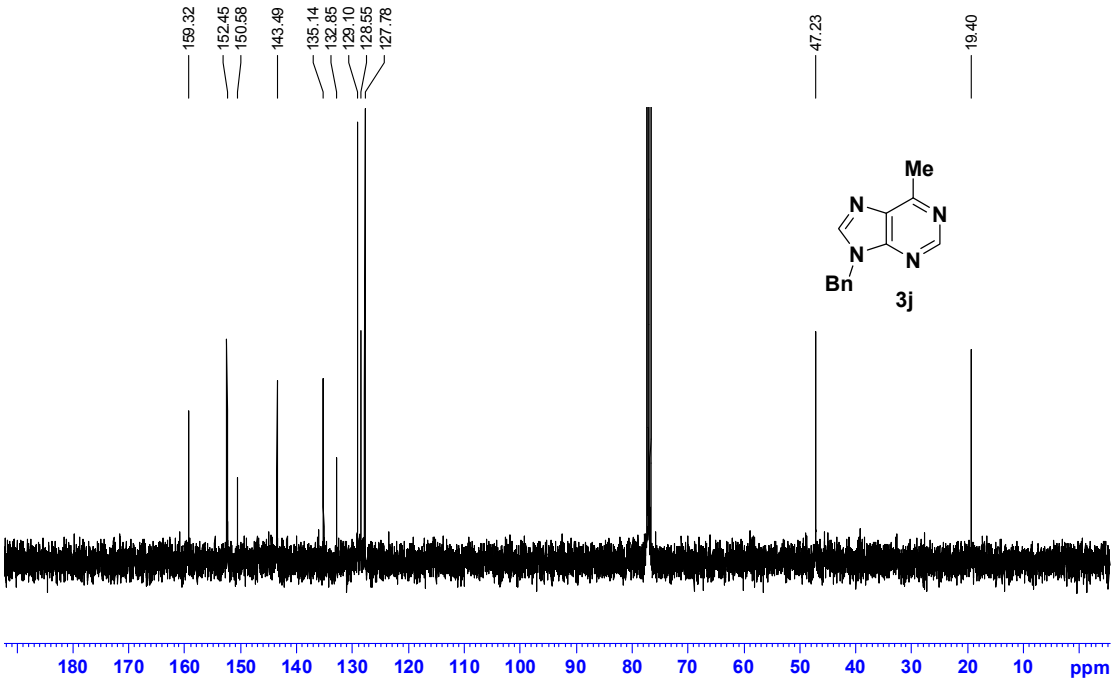


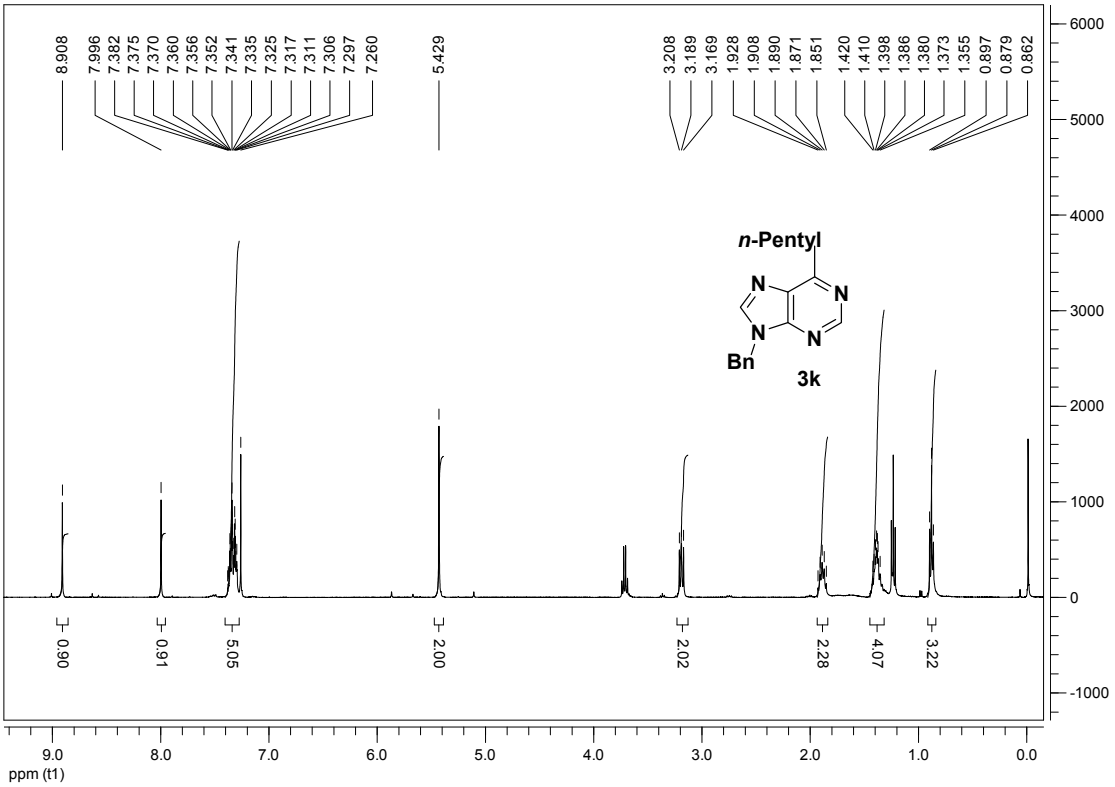


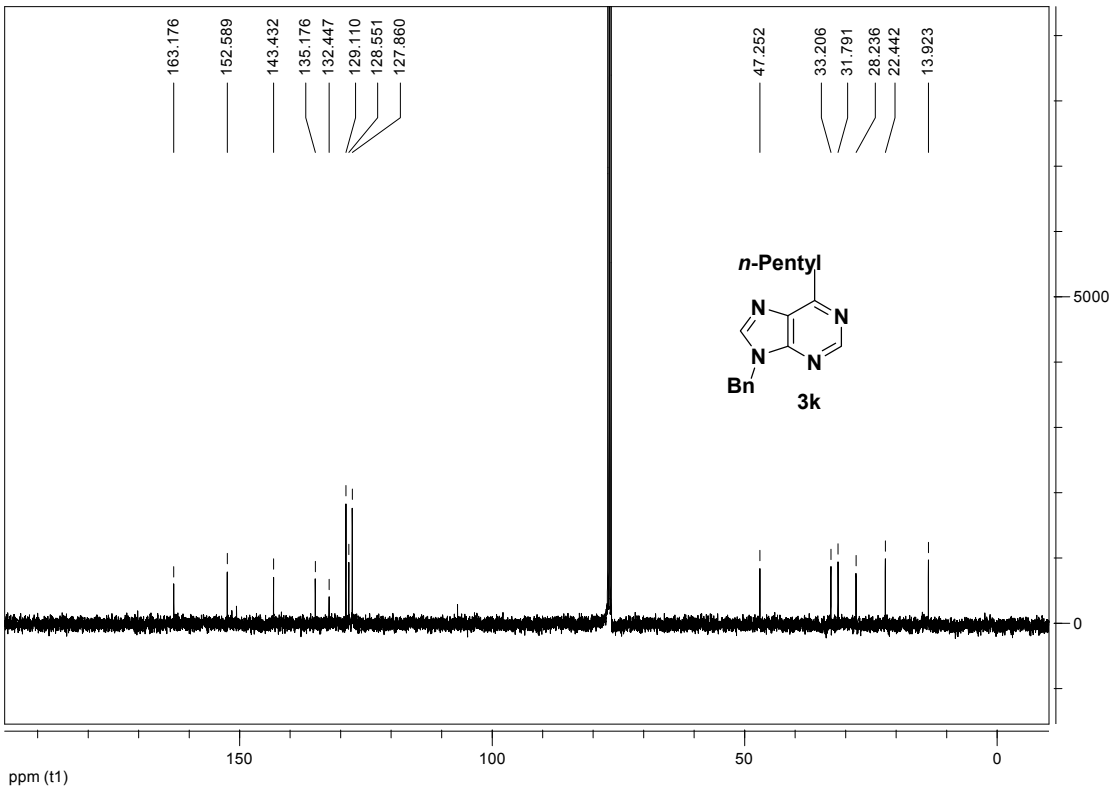


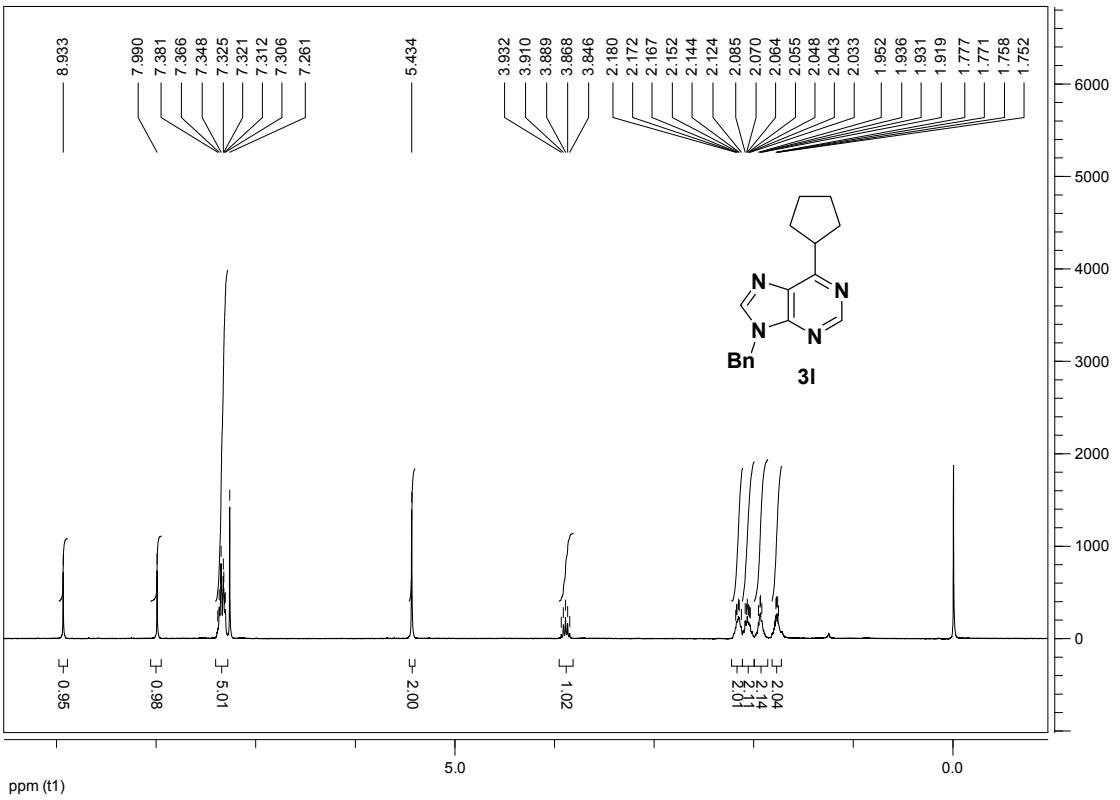


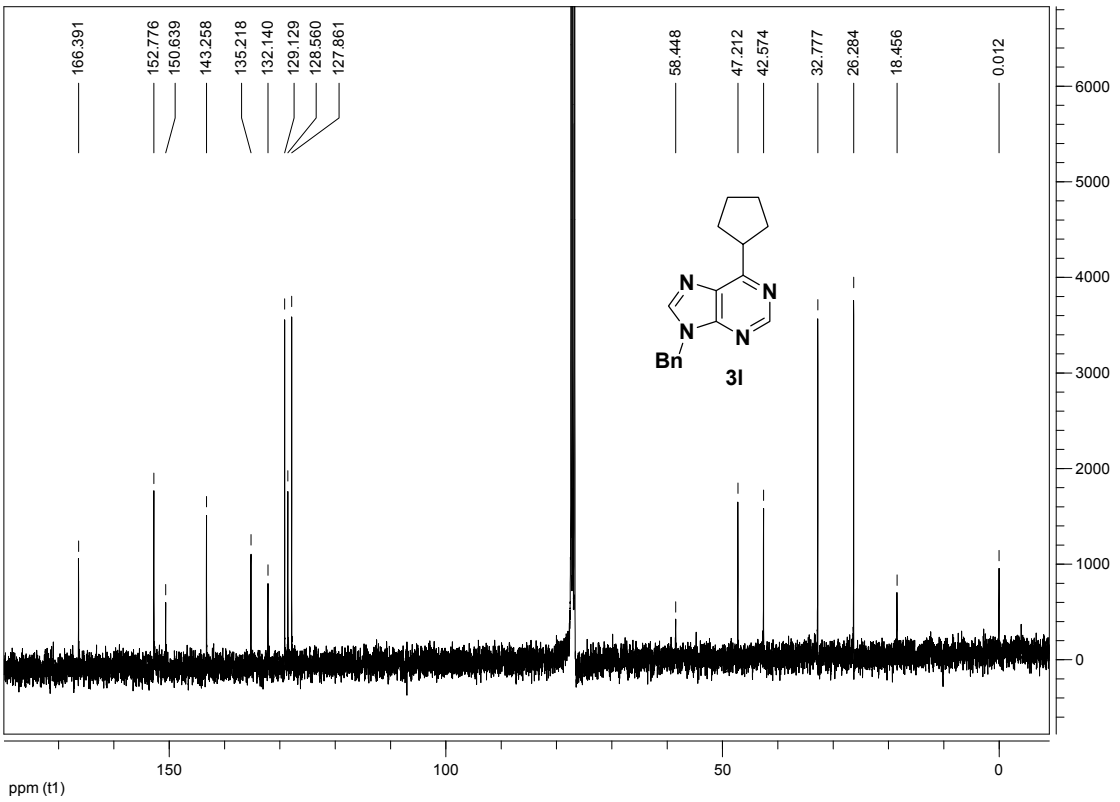

8.893
8.025
7.365
7.347
7.332
7.310
7.305
7.291
7.260
5.441
2.872
-0.008
Me
N
N
N
N
Bn
3j
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.02
3.14
3.07
2.09
3.00
5.0
0.0
ppm (t1)

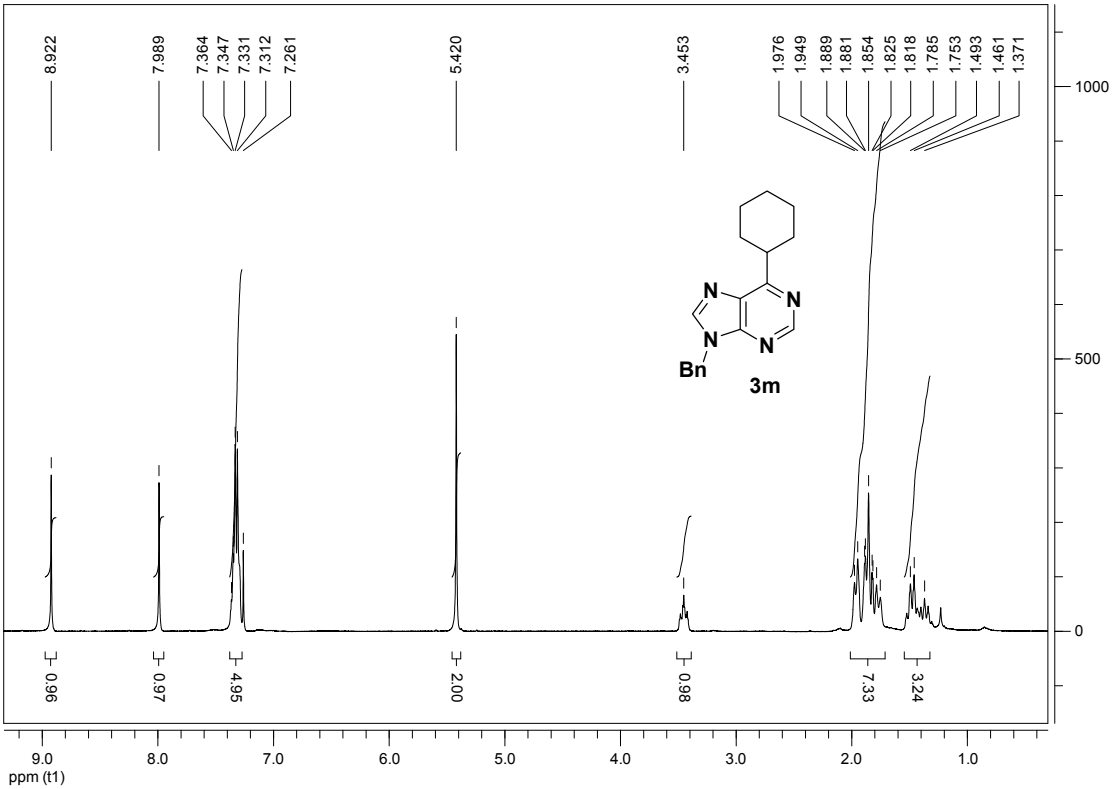

159.32
152.45
150.58
143.49
135.14
132.85
129.10
128.55
127.78
47.23
19.40
Me
N
N
N
N
Bn
3j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

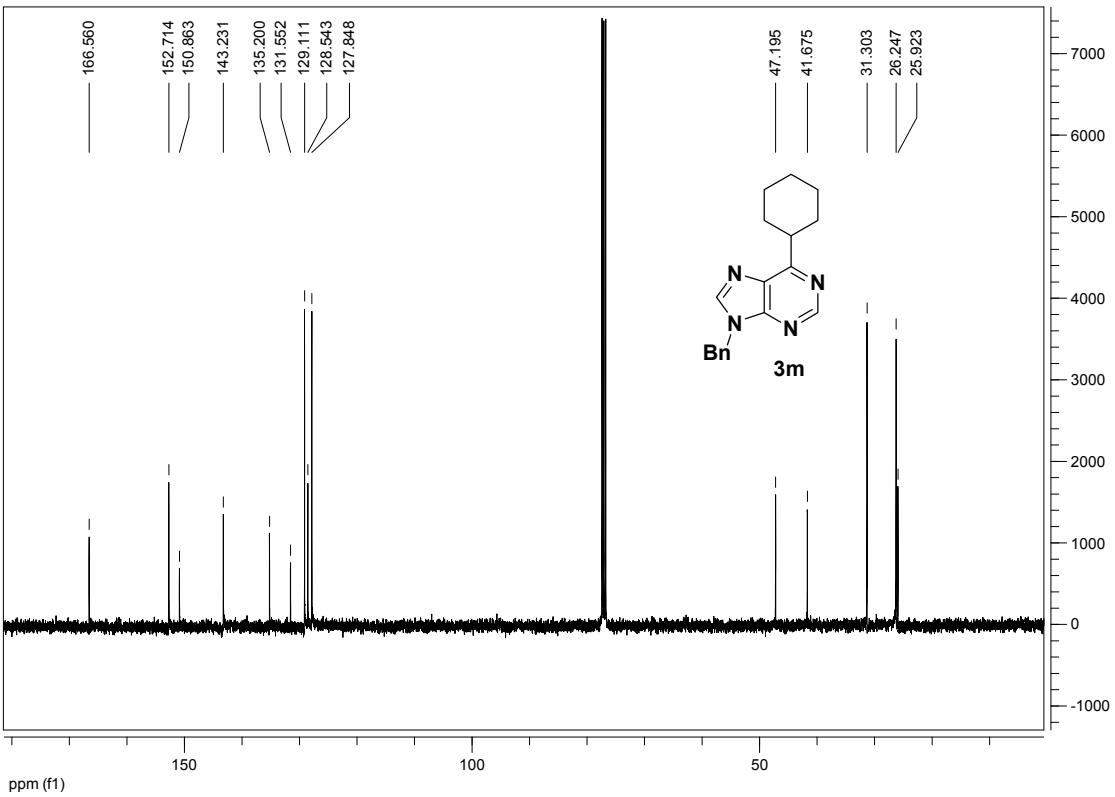


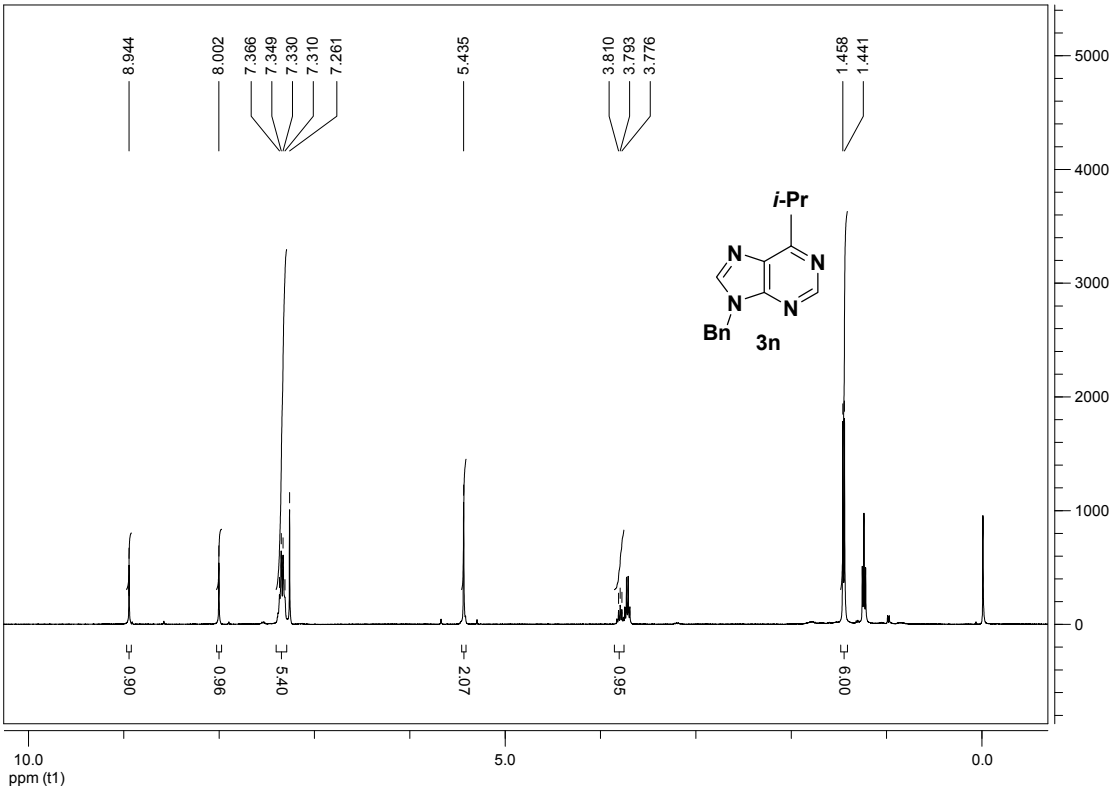


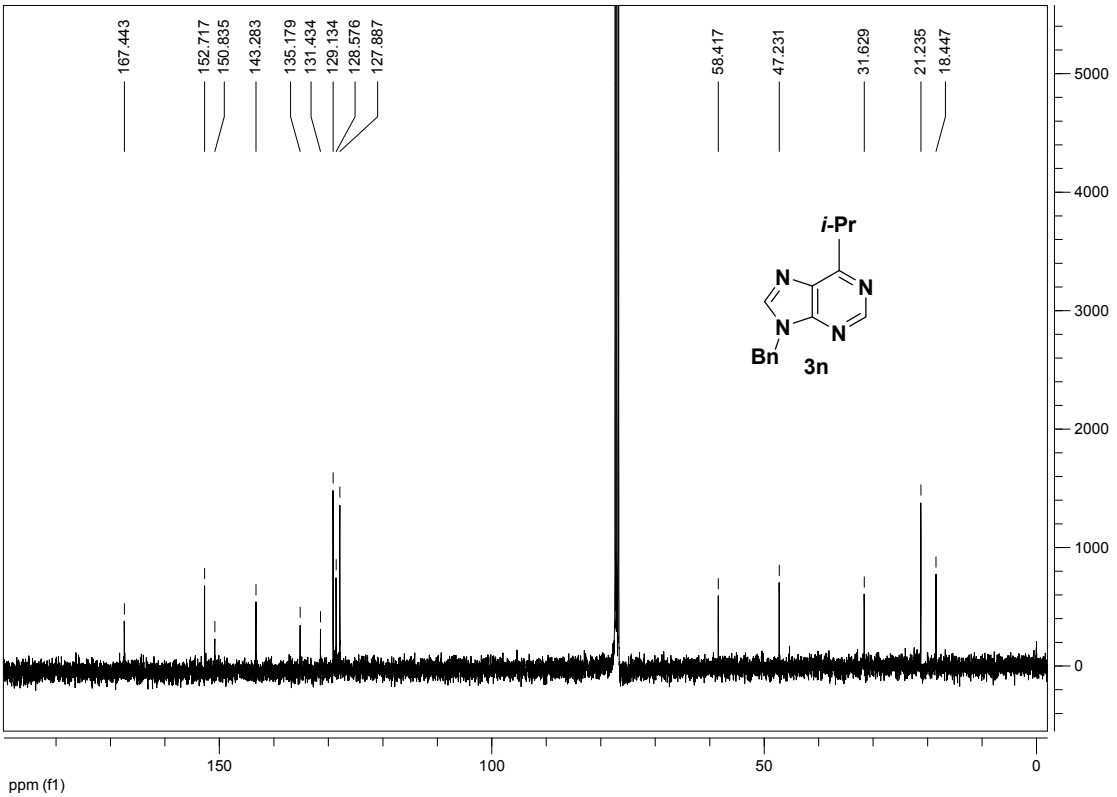


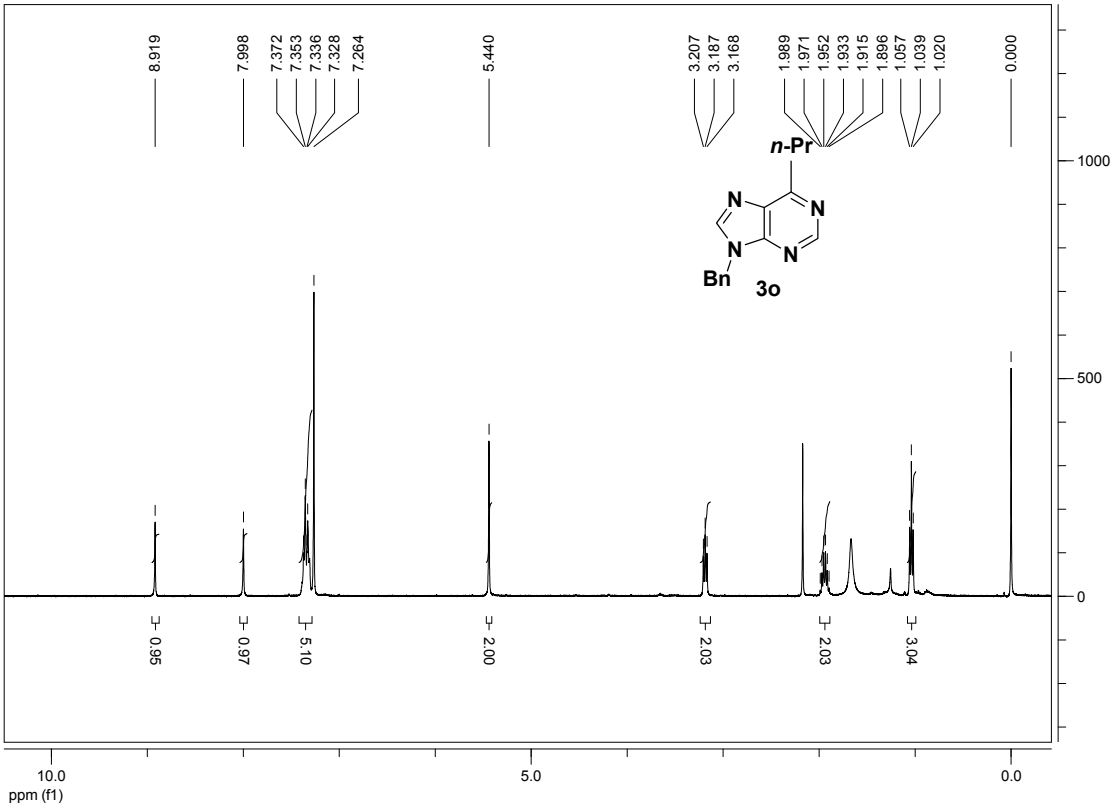


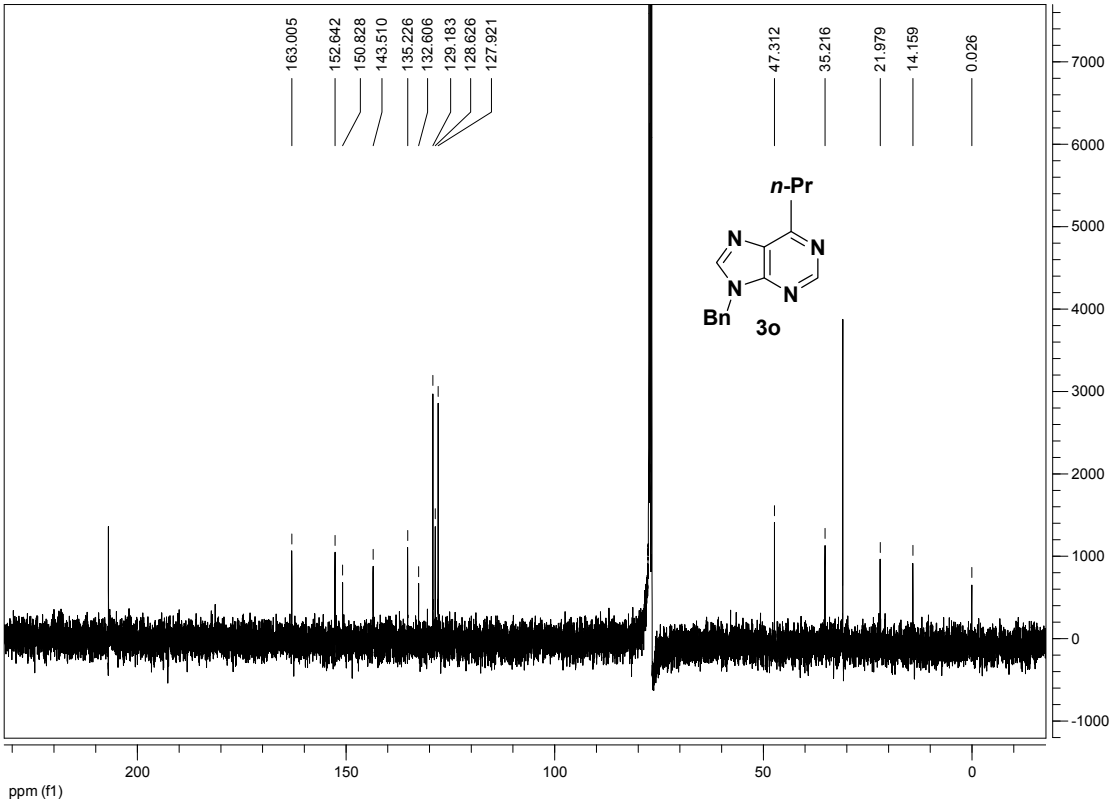

8.922
7.989
7.364
7.347
7.331
7.312
7.261
5.420
3.453
1.976
1.949
1.889
1.881
1.854
1.825
1.818
1.785
1.753
1.493
1.461
1.371
N
N
N
N
Bn
3m
0.96
0.97
4.96
2.00
0.98
7.33
3.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
1000
500
0

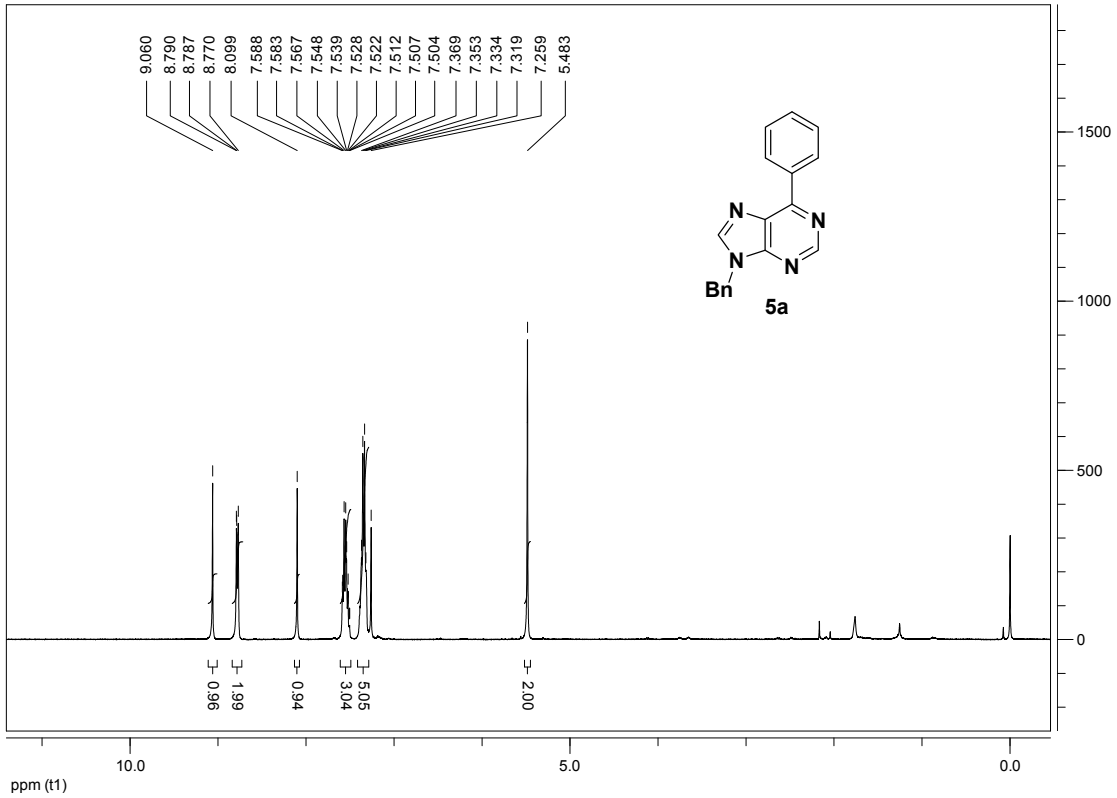

166.560
152.714
150.863
143.231
135.200
131.552
129.111
128.543
127.848
47.195
41.675
31.303
26.247
25.923
N
N
N
N
Bn
3m
150
100
50
ppm (f1)
7000
6000
5000
4000
3000
2000
1000
0
-1000

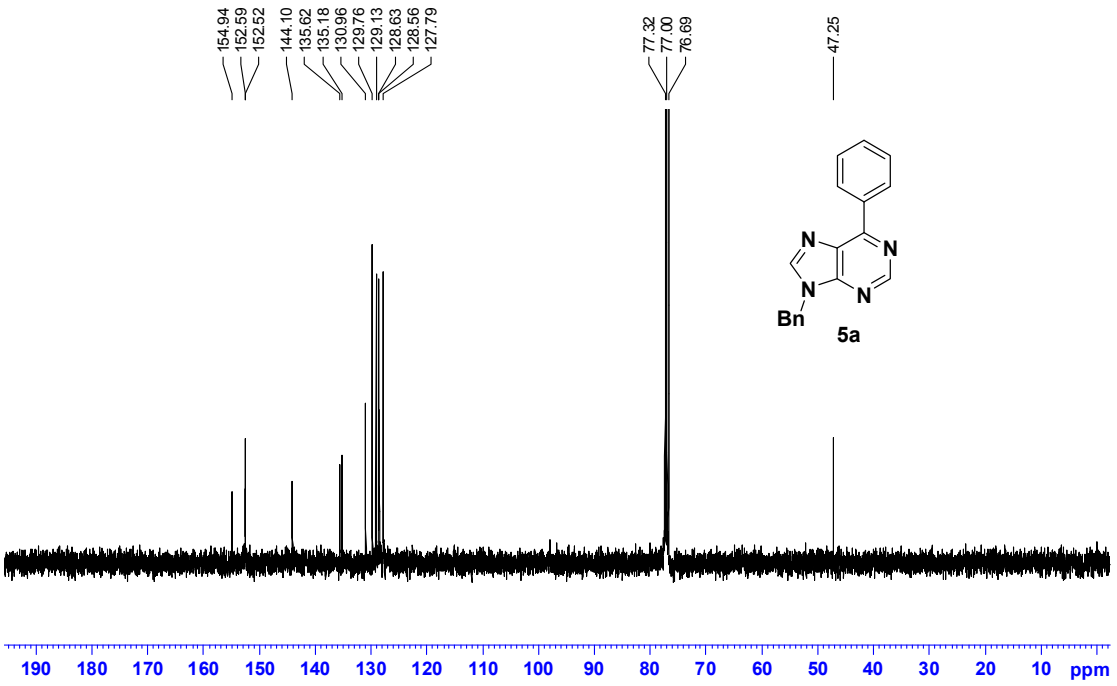


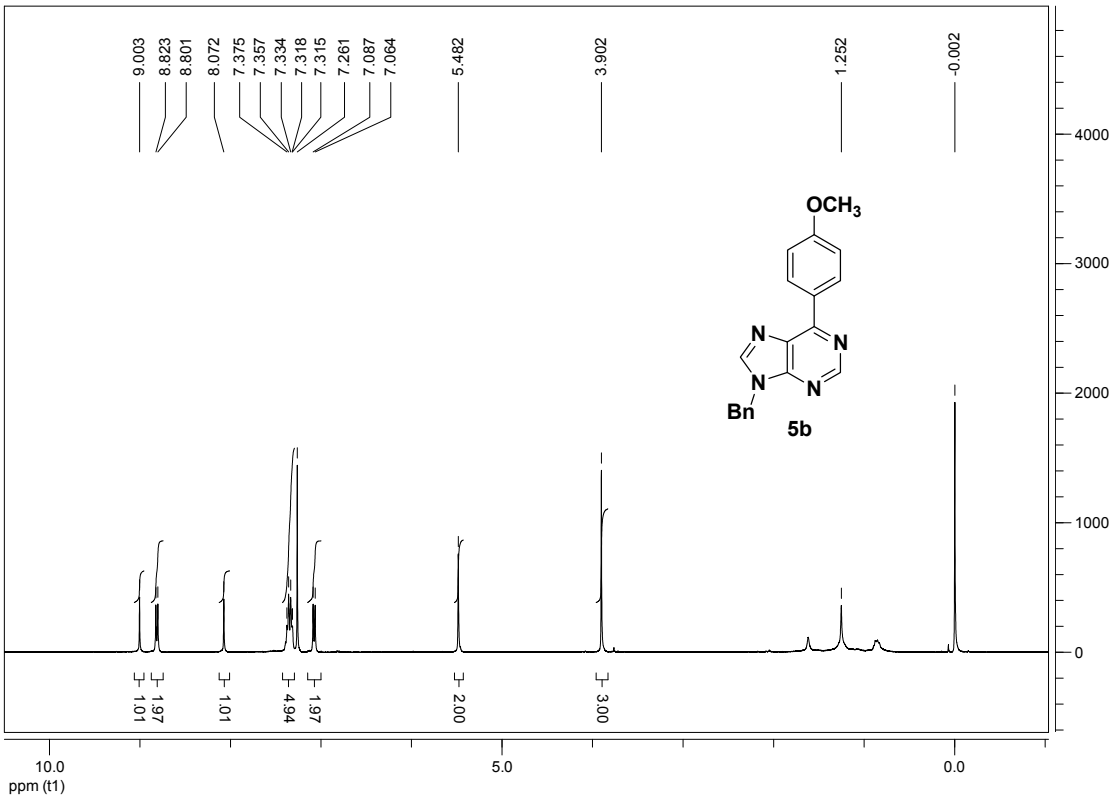


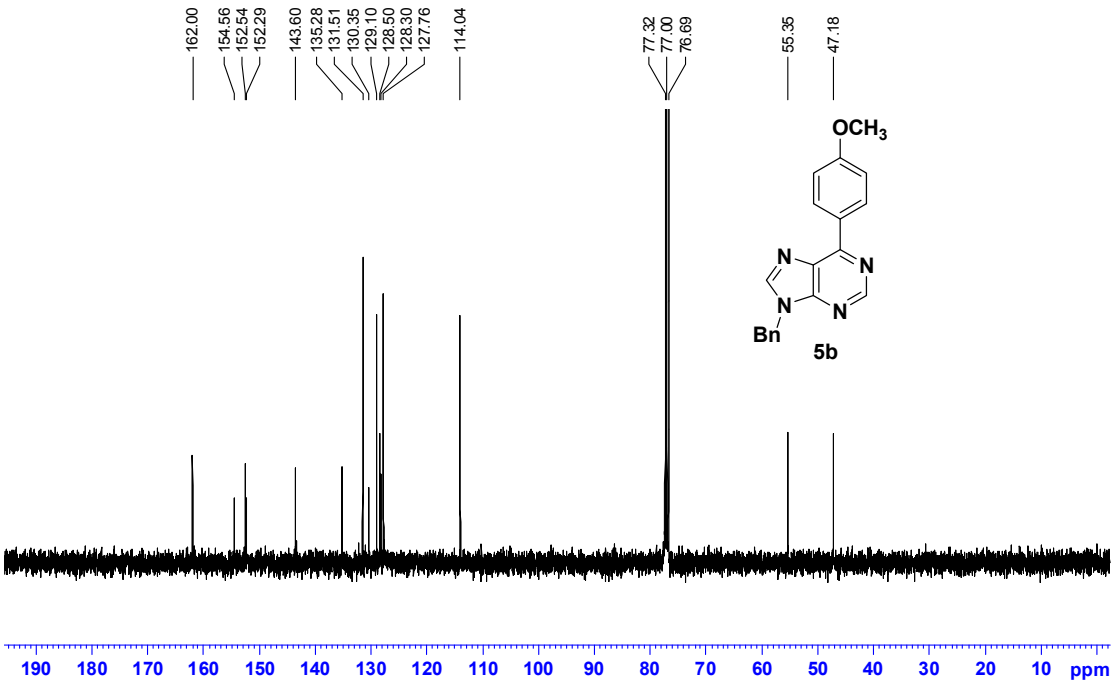


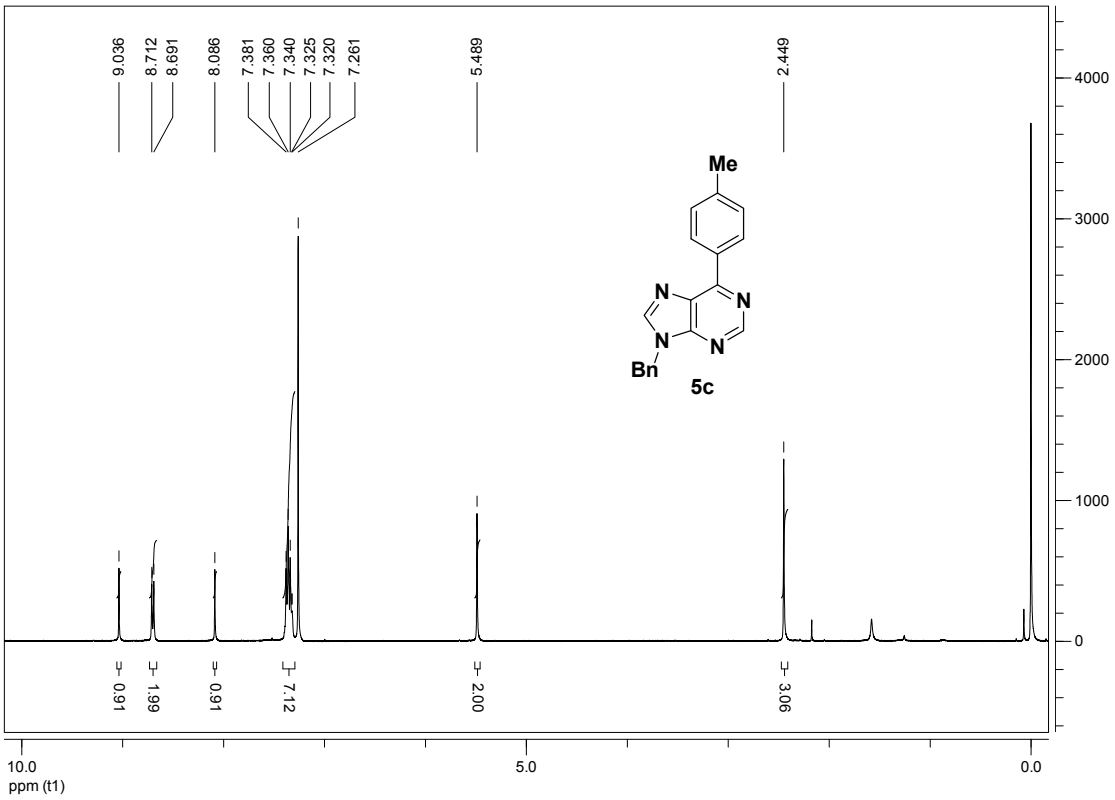


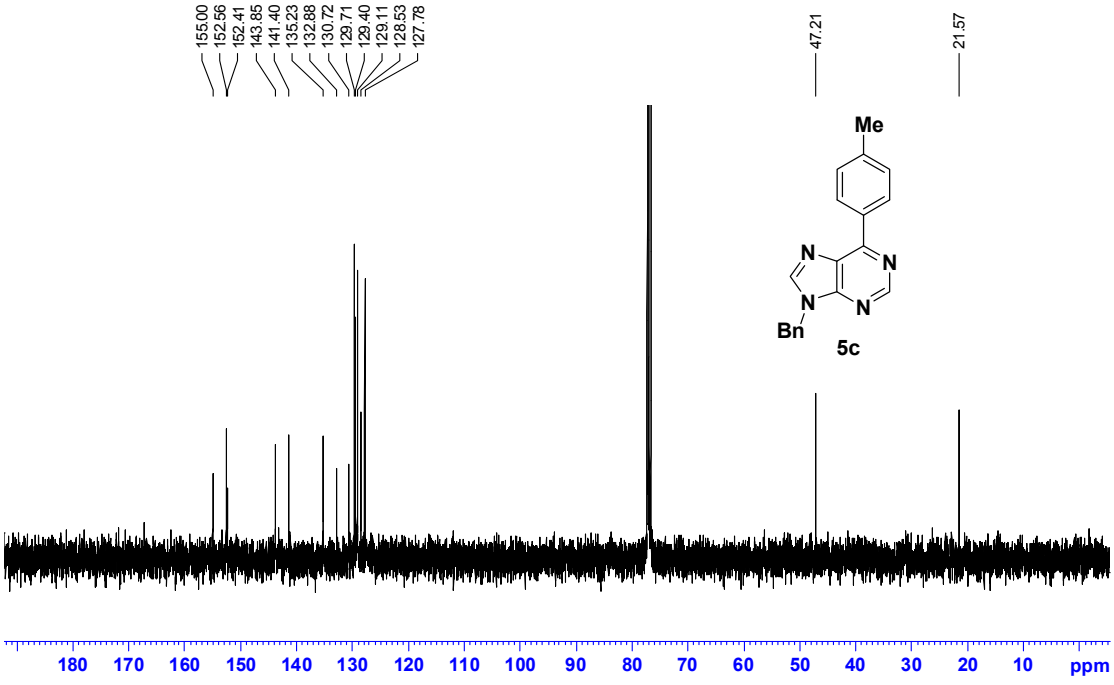


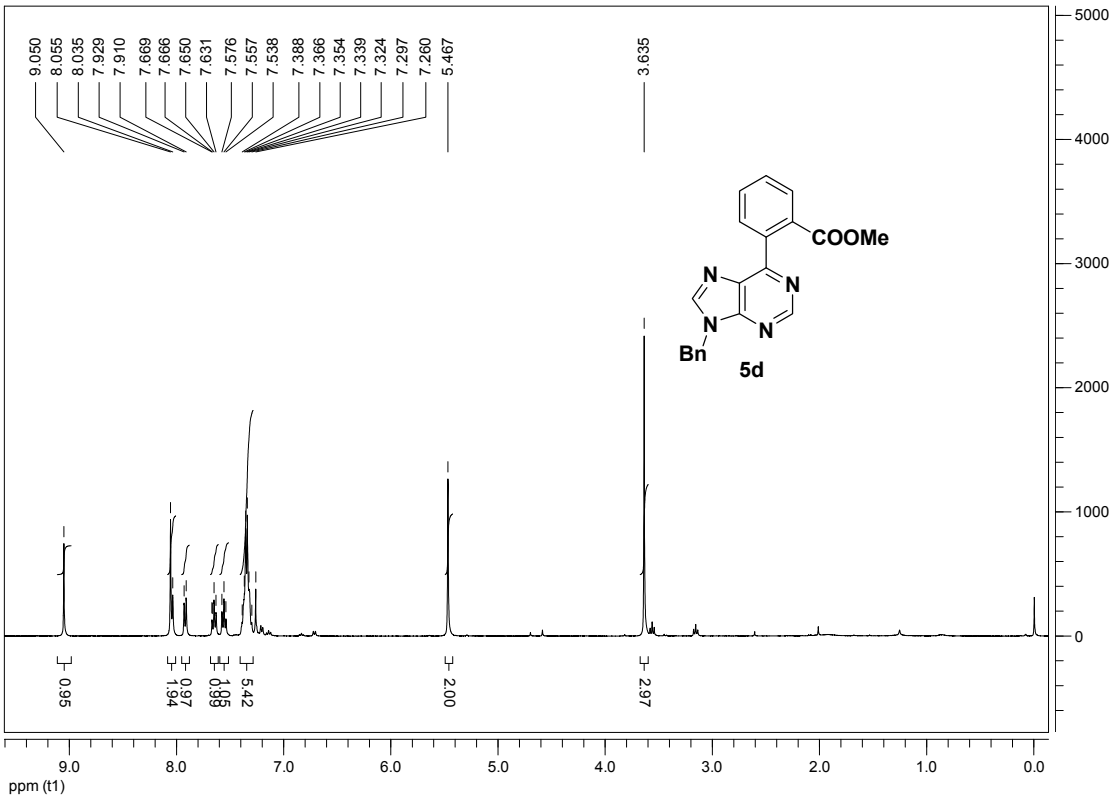


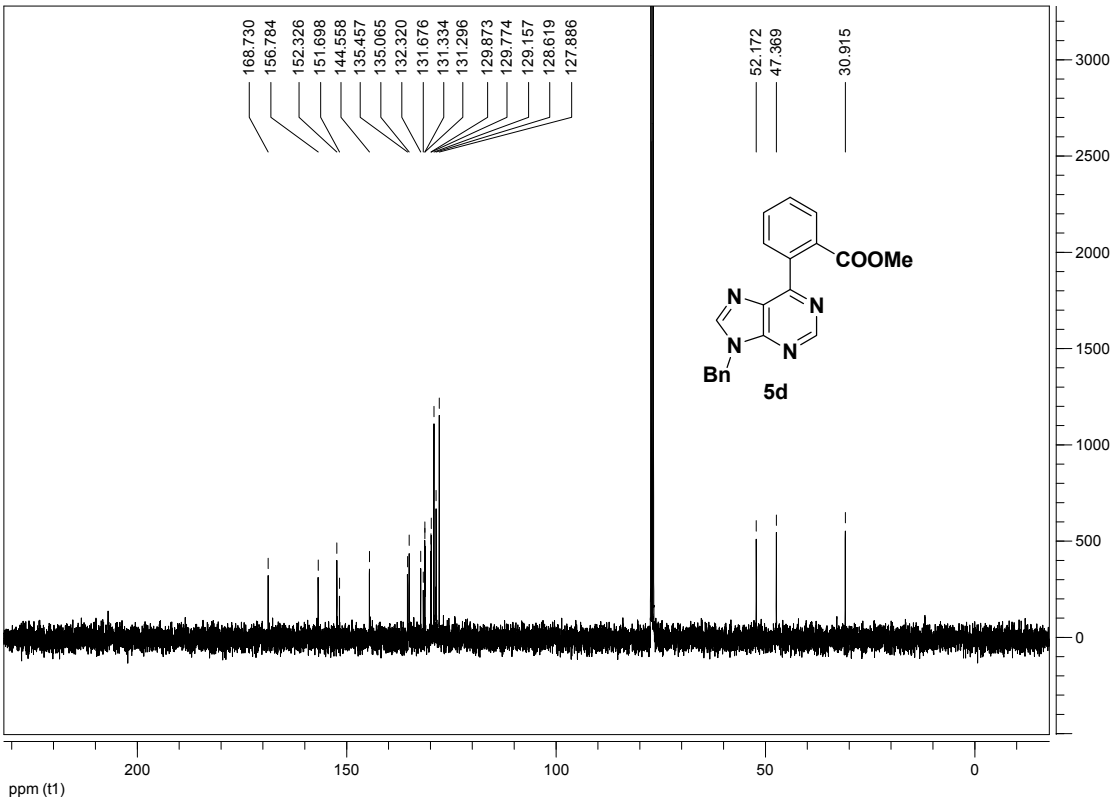


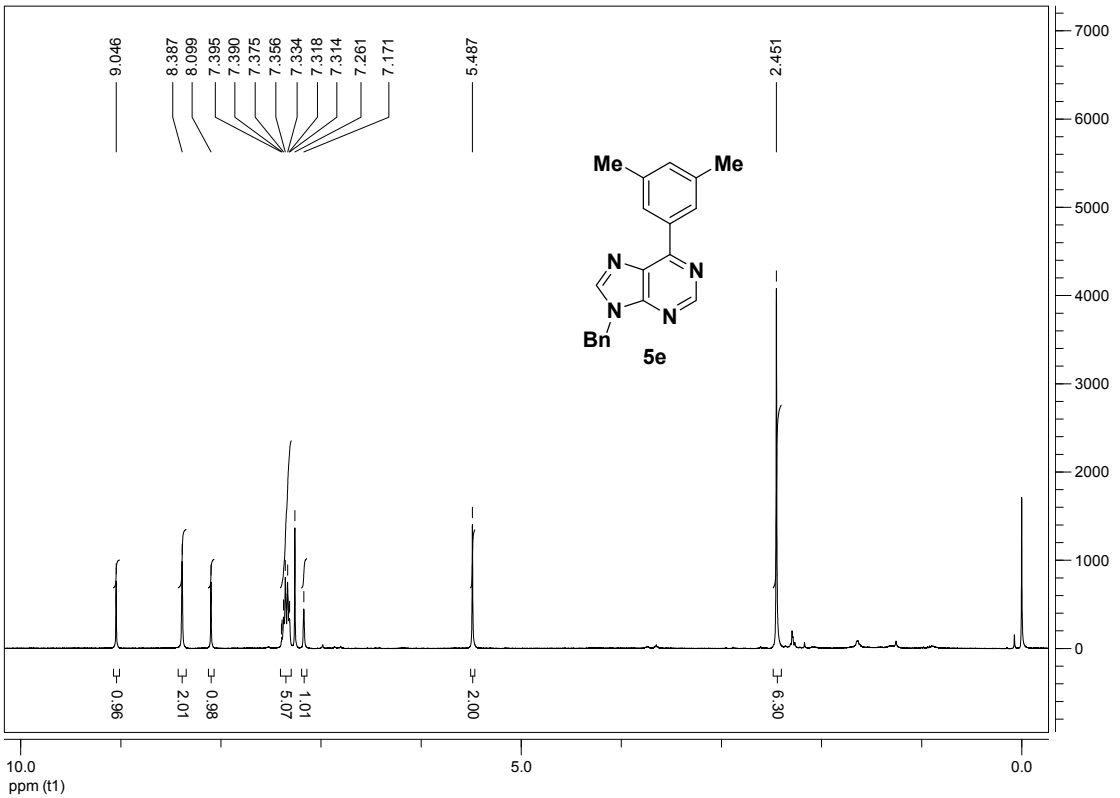


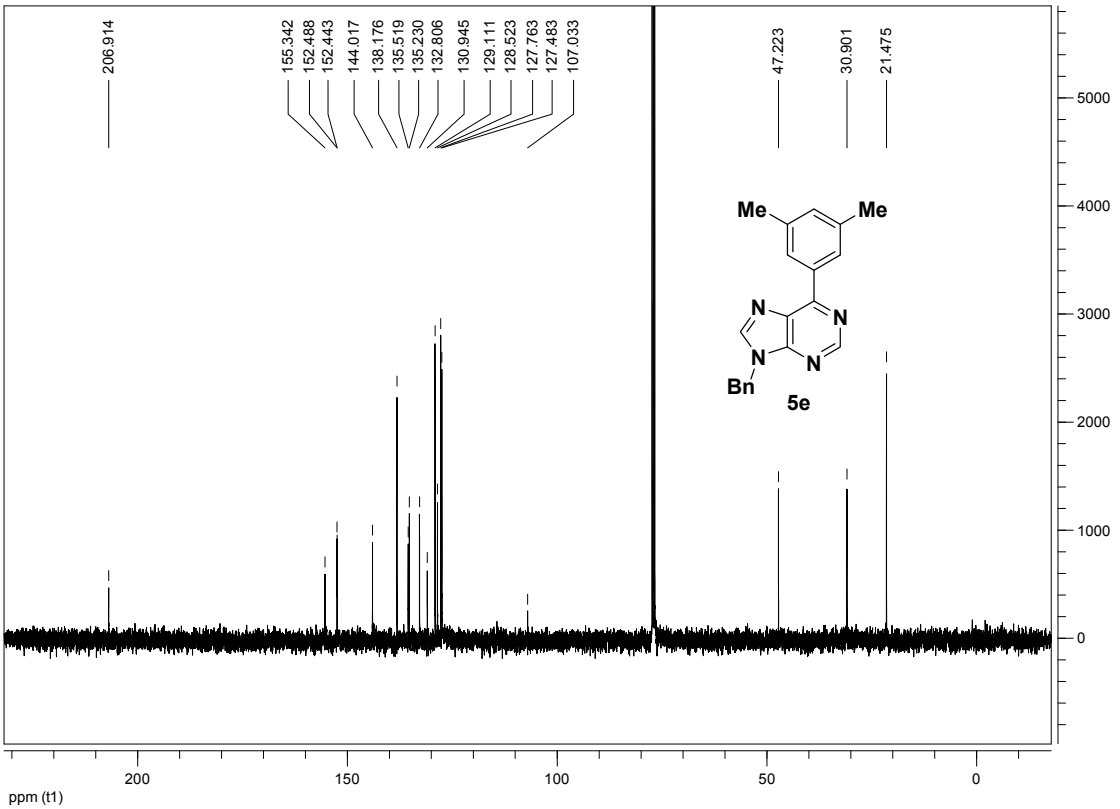





9.050
8.055
8.035
7.929
7.910
7.669
7.666
7.650
7.631
7.576
7.557
7.538
7.388
7.366
7.354
7.339
7.324
7.297
7.260
5.467
3.635
COOMe
N
N
N
N
Bn
5d
0.95
1.94
0.97
0.88
1.05
5.42
2.00
2.97
ppm (t1)


168.730
156.784
152.326
151.698
144.558
135.457
135.065
132.320
131.676
131.334
131.296
129.873
129.774
129.157
128.619
127.886
52.172
47.369
30.915
COOMe
N
N
N
N
Bn
5d
ppm (t1)


9.046
8.387
8.099
7.395
7.390
7.375
7.356
7.334
7.318
7.314
7.261
7.171
5.487
2.451
Me
Me
N
N
N
N
Bn
5e
0.96
2.01
0.98
5.07
1.01
2.00
6.30
7000
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (t1)


206.914
155.342
152.488
152.443
144.017
138.176
135.519
135.230
132.806
130.945
129.111
128.523
127.763
127.483
107.033
47.223
30.901
21.475
Me
Me
N
N
N
N
Bn
5e
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)