Supporting information

Synthesis of 5-Aryl-3-*C*-Glycosyl- and Unsymmetrical 3,5-Diaryl-1,2,4-Triazoles from Alkylidene-Amidrazones

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Contents

SYNTHETIC PROCEDURES AND COMPOUND CHARACTERIZATION 2

O-Peracylated *N*-[*C*-(β-D-glycopyranosyl)methylideneamino]guanidine **(8)** and N^1-[*C*-(β-D-glycopyranosyl)methylidene]arenecarboxamidrazones **(9-13)** 2

N^1-Arylidene-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidrazones **(18-20)** 12

Transformation of N^1-arylidene-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)form-amidrazones **(18-20)** by PIDA 17

O-Peracylated *N*-arenecarboximidoyl-*C*-(β-D-glycopyranosyl)carbohydrazonoyl bromides **(24-29)** 18

O-peracylated 5-(β-D-glycopyranosyl)-3-substituted-1,2,4-triazoles **(21, 30-33)** 26

N^1-arylidene-arenecarboxamidrazones **(35, 36)** 29

3,5-disubstituted-1,2,4-triazoles **(39, 40)** 39

ANALYSIS OF REACTION MIXTURES BY LCMS 47

REFERENCES 52

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SYNTHETIC PROCEDURES AND COMPOUND CHARACTERIZATION

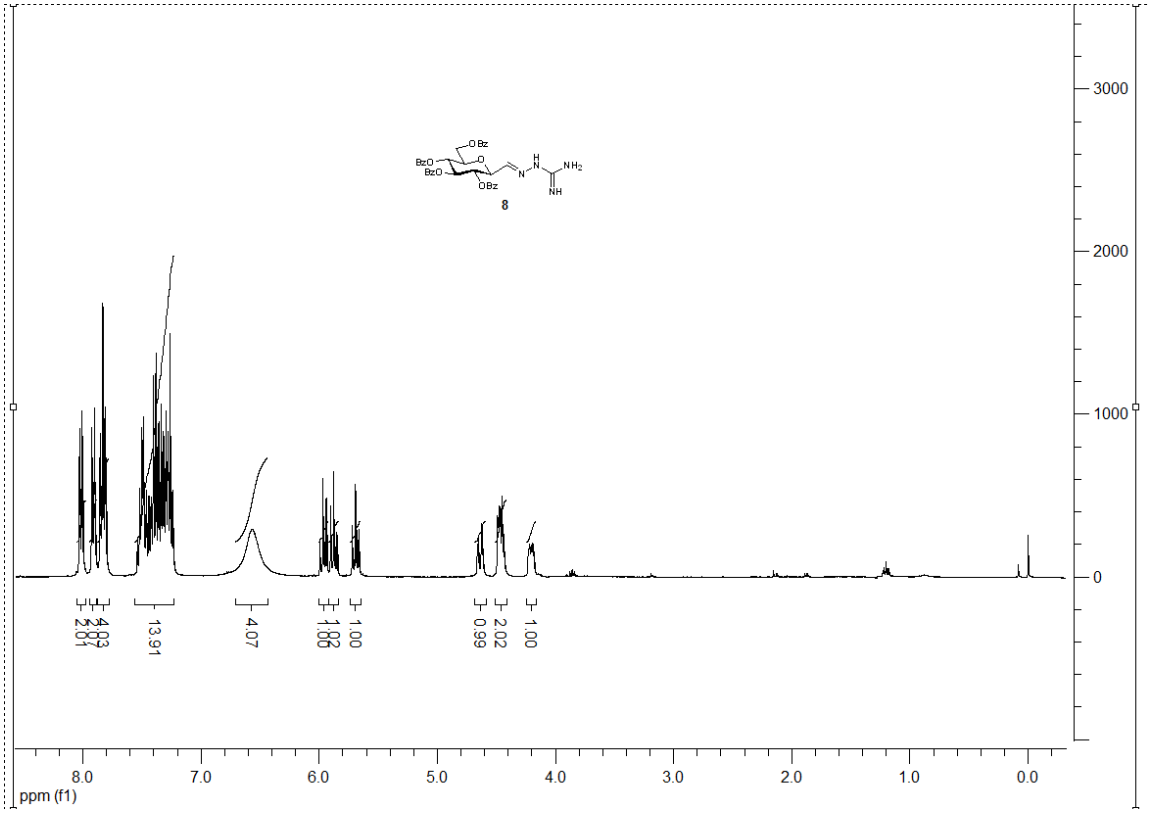
General procedure I for the synthesis of *O*-peracylated *N*-[*C*-(β-D-glycopyranosyl)methylideneamino]guanidine (8) and N^1-[*C*-(β-D-glycopyranosyl)methylidene]arenecarboxamidrazones (9-13)

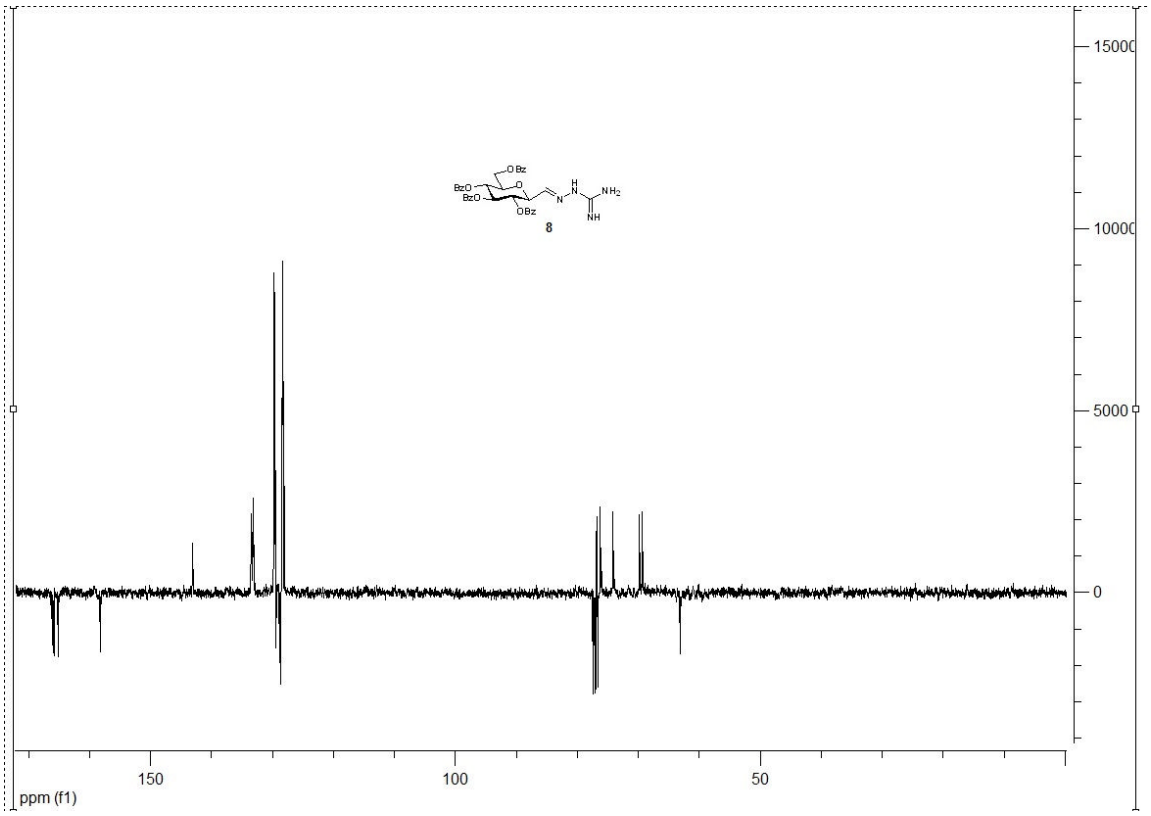
Aminoguanidine × H_2CO_3 (**4**, 0.50 mmol) or an arenecarboxamidrazone (**5-7**, 0.50 mmol) was dissolved in a mixture of pyridine (1.5 mL) and H_2O (0.9 mL), and stirred for 20 min at rt. Then AcOH (0.9 mL), Raney-Ni (0.38 g, from an aqueous suspension, Merck), NaH_2PO_2 (0.20 g, 2.27 mmol), and the corresponding *O*-peracylated β-D-glycopyranosyl cyanide (**1-3**, 0.25 mmol) were added to the mixture. The reaction mixture was vigorously stirred and heated at 40 °C. When the reaction was complete (TLC, EtOAc/hexane = 1:2) the insoluble materials were filtered off with suction, and washed with CH_2Cl_2 (10 mL). The organic layer of the filtrate was separated, washed with H_2O (2 x 6 mL), dried ($MgSO_4$), and evaporated *in vacuo,* traces of pyridine were removed by repeated co-evaporations with toluene. The residue was purified by column chromatography.

N-[*C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)methylideneamino]guanidine (8)

Prepared from **1**[1] (3.00 g, 4.95 mmol) and aminoguanidine × H_2CO_3 (**4**, 1.35 g, 9.90 mmol) according to **General procedure I**. Purified by column chromatography ($CHCl_3$/MeOH = 16:1) to yield **8** as a brownish amorphous solid (2.1 g, 64%). R_f 0.22 ($CHCl_3$/MeOH = 16:1); $[\alpha]_D$ = +45 (c 0.58, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.99 (m, 2 H, Ar), 7.94-7.89 (m, 2 H, Ar), 7.87-7.80 (m, 4 H, Ar), 7.55-7.23 (m, 13 H, Ar, CH=N), 6.58 (br s, 4 H, 2 × NH, NH_2), 5.97, 5.88, 5.69 (3 pseudo t, J = 9.6, 10.0 Hz in each H-2, H-3, H-4, 3 H), 4.64 (dd, J = 2.9, 12.2 Hz, 1 H, H-6a), 4.48 (dd, J = 4.3, 9.5 Hz, 1 H, H-1), 4.46 (dd, J = 5.0, 12.2 Hz, 1 H, H-6b), 4.18-4.23 (m, 1 H, H-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 165.9, 165.8, 165.1 (CO), 158.2 (C=NH), 143.1 (CH=N), 133.5-128.3 (Ar), 76.8, 76.2, 74.1, 69.8,

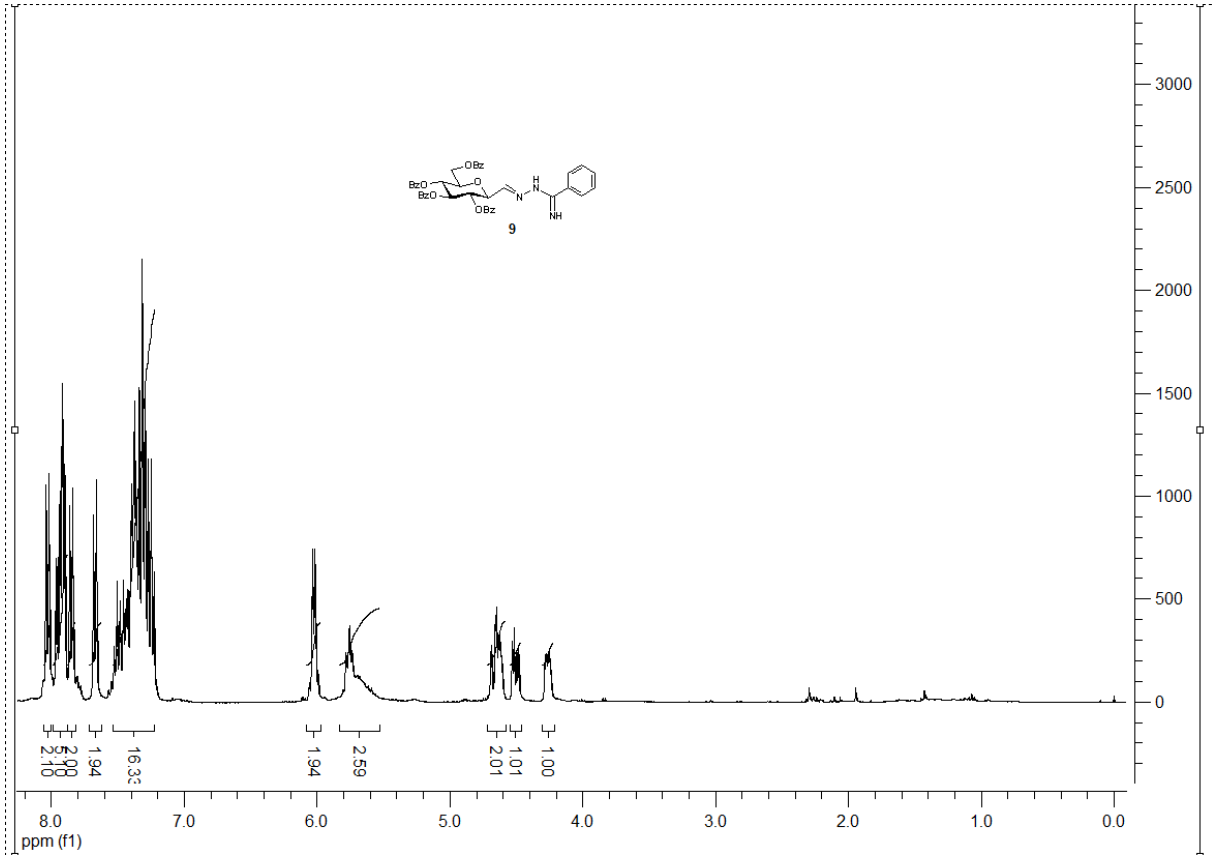
69.4 (C-1-C-5), 63.1 (C-6) ppm. Anal. Calcd. for $C_{36}H_{32}N_4O_9$ (664.66): C, 65.05, H, 4.85; N, 8.43. Found: C, 65.14; H, 4.93; N, 8.39.

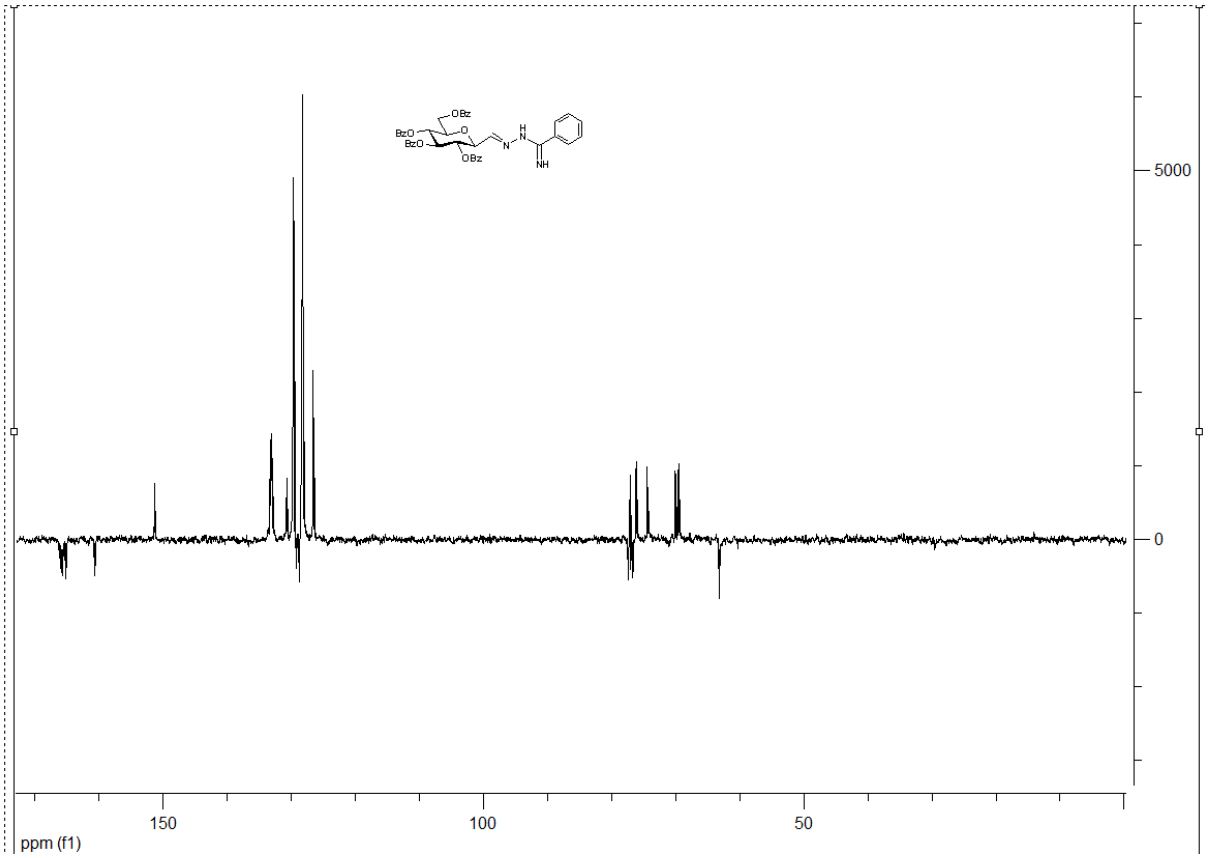




***N*^{1}-[C-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)methylidene]benzamidrazone (9)**

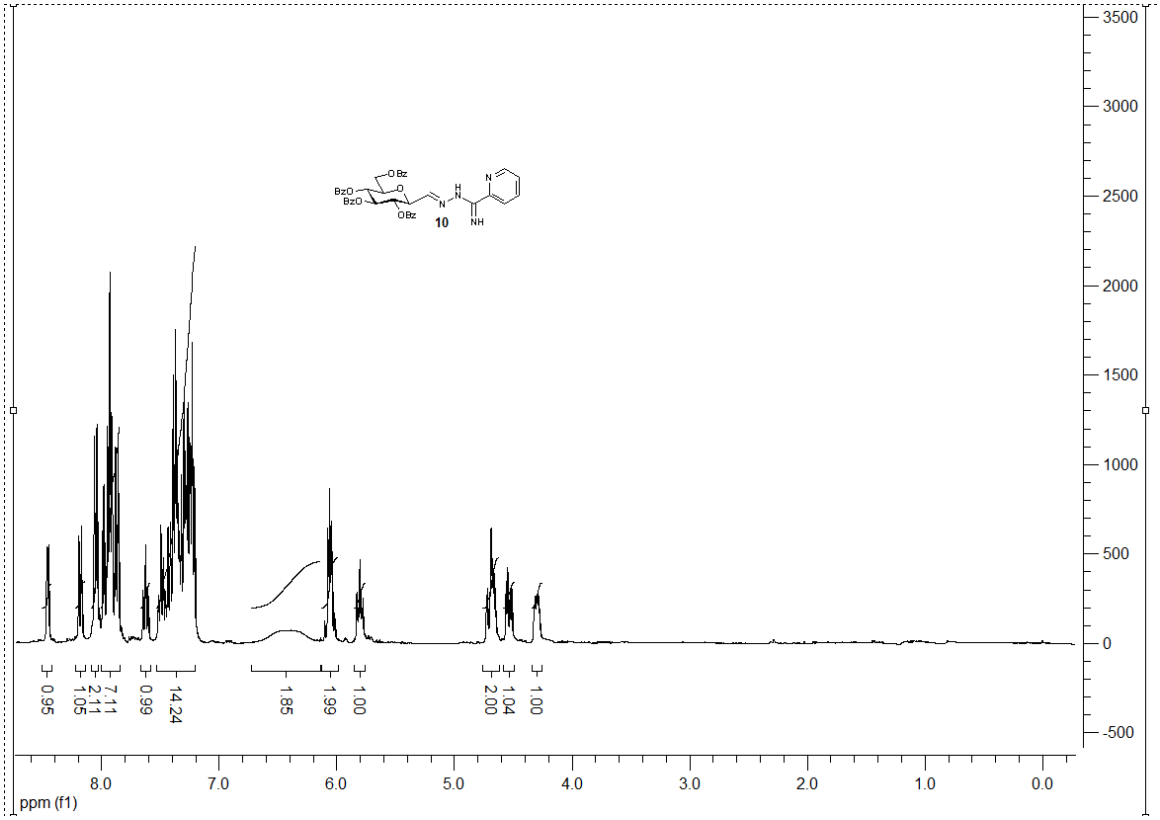
Prepared from **1**[1] (2.52 g, 4.16 mmol) and benzamidrazone (**5**, 1.12 g, 8.32 mmol) according to **General procedure I**. Purified by column chromatography (EtOAc/hexane = 1:2) to yield the title compound **9** as a white amorphous solid (1.45 g, 48%). R_f 0.50 (EtOAc/hexane = 2:3); $[\alpha]_D$ = +16 (c 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.23 (m, 26 H, Ar, CH=N), 6.06-5.99 (strongly coupled m, 2 H, H-2 and/or H-3 and/or H-4), 5.80-5.58 (m, 3 H, H-2 or H-3 or H-4, NH_2), 4.67 (dd, J = 2.8, 12.3 Hz, 1 H, H-6a), 4.62 (dd, J = 2.7, 9.4 Hz, 1 H, H-1), 4.50 (dd, J = 5.0, 12.3 Hz, 1 H, H-6b), 4.26 (ddd, J = 2.8, 5.0, 9.2 Hz, 1 H, H-5) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 165.8, 165.6, 165.1 (CO), 160.6 (C=NH), 151.3 (CH=N), 133.3-126.5 (Ar), 77.1, 76.1, 74.4, 70.0, 69.5 (C-1-C-5), 63.1 (C-6) ppm. Anal. Calcd. for $C_{42}H_{35}N_3O_9$ (725.74): C, 69.51; H, 4.86; N, 5.79. Found: C, 69.41; H, 4.76; N, 5.71.

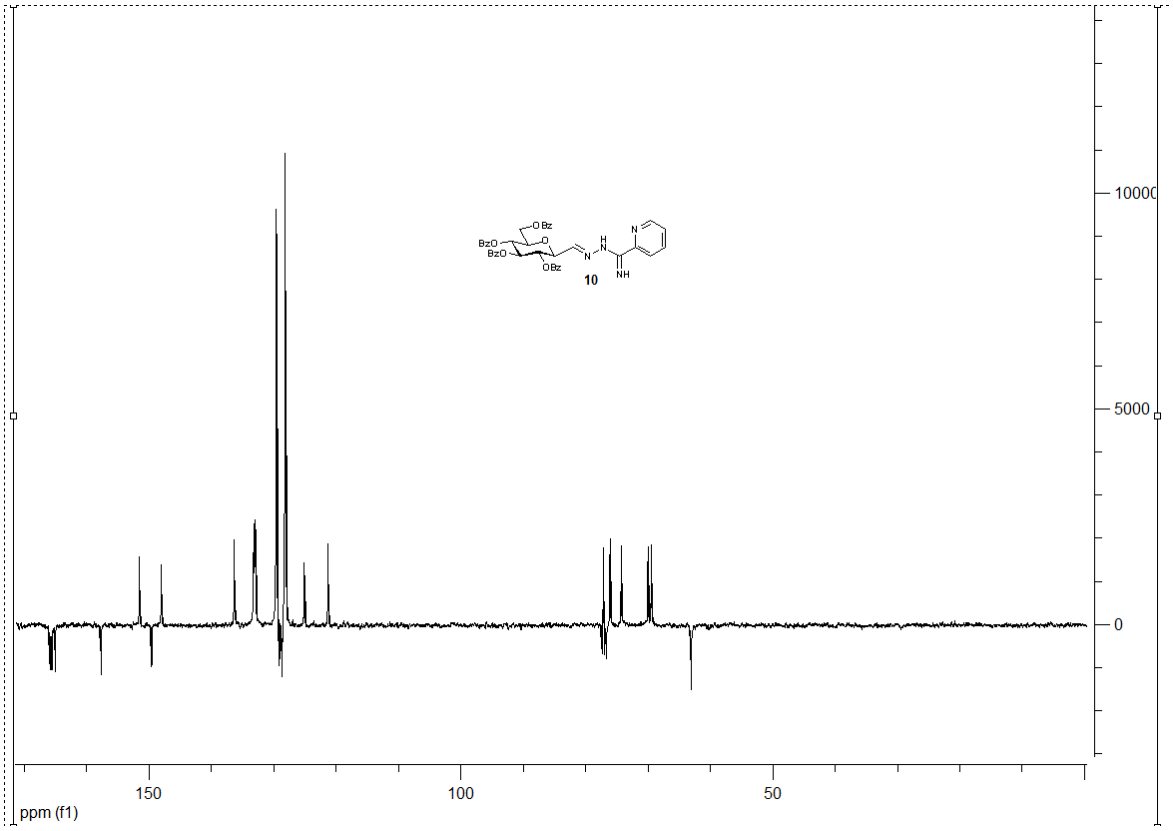




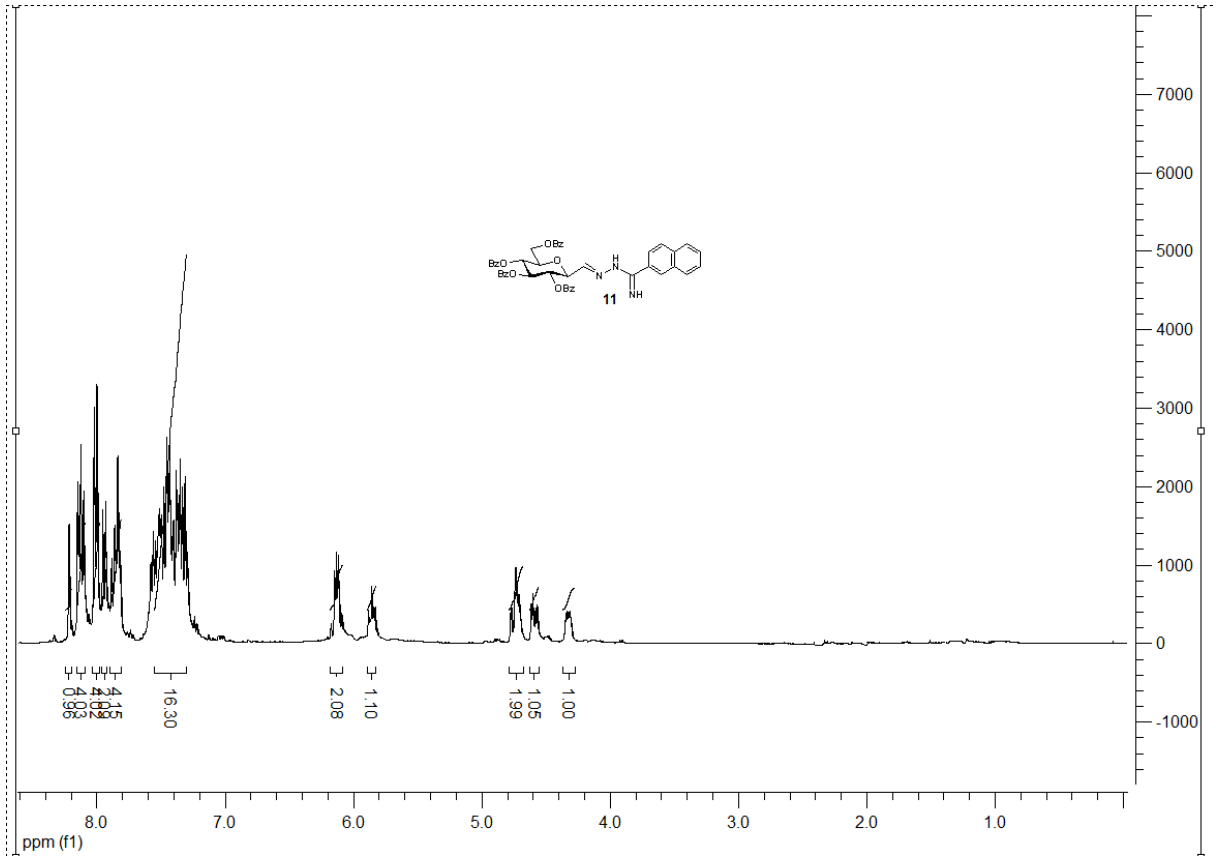
***N*^{1}-[*C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)methylidene]pyridine-2-carboxamidrazone (10)** Prepared from **1**[1] (2.00 g, 3.31 mmol) and pyridine-2-carboxamidrazone (**6**, 0.90 g, 6.62 mmol) according to **General procedure I**. Purified by column chromatography (EtOAc/hexane = 1:1) to yield the title compound **10** as a white amorphous solid (1.18 g, 49%). R_f 0.55 (EtOAc/hexane = 1:1); $[\alpha]_D$ = +59 (c 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.45-7.21 (m, 25 H, Ar, CH=N), 6.43 (br s, 2 H, NH_2), 6.10-6.02 (strongly coupled m, 2 H, H-2 and/or H-3 and/or H-4), 5.80 (pseudo t, J = 9.3, 9.6 Hz, 1 H, H-2 or H-3 or H-4), 4.70 (dd, J = 3.0, 12.2 Hz, 1 H, H-6a), 4.66 (dd, J = 4.2, 9.6 Hz, 1 H, H-1), 4.54 (dd, J = 5.4, 12.2 Hz, 1 H, H-6b), 4.30 (ddd, J = 3.0, 5.1, 9.9 Hz, 1 H, H-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 165.7, 165.5, 165.0 (CO), 157.7 (C=NH), 151.5 (CH=N), 149.6, 148.0, 136.3-121.3 (Ar), 77.1, 76.1, 74.3, 70.0, 69.4 (C-1-C-5), 63.0 (C-6)

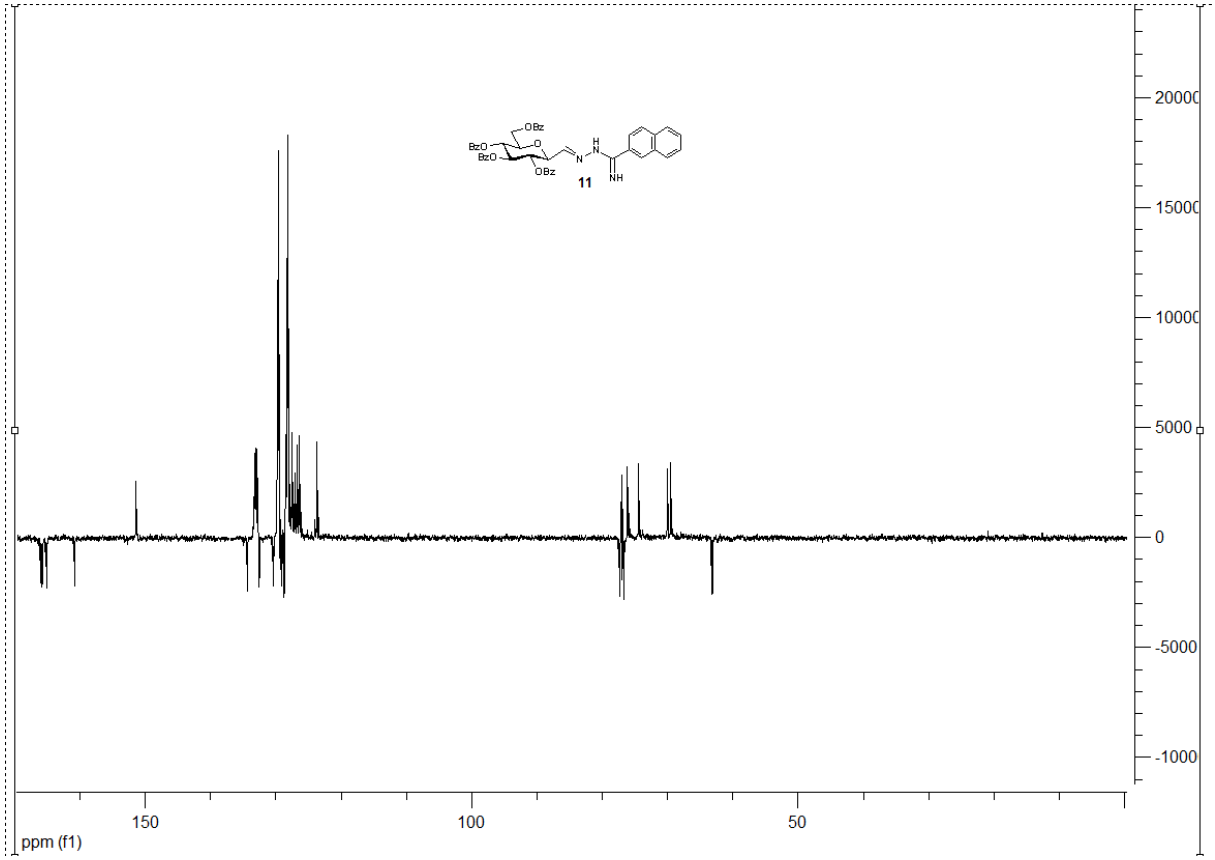
ppm. Anal. Calcd. for $C_{41}H_{34}N_4O_9$ (726.73): C, 67.76, H, 4.72; N, 7.71. Found: C, 67.65; H, 4.62; N, 7.61.





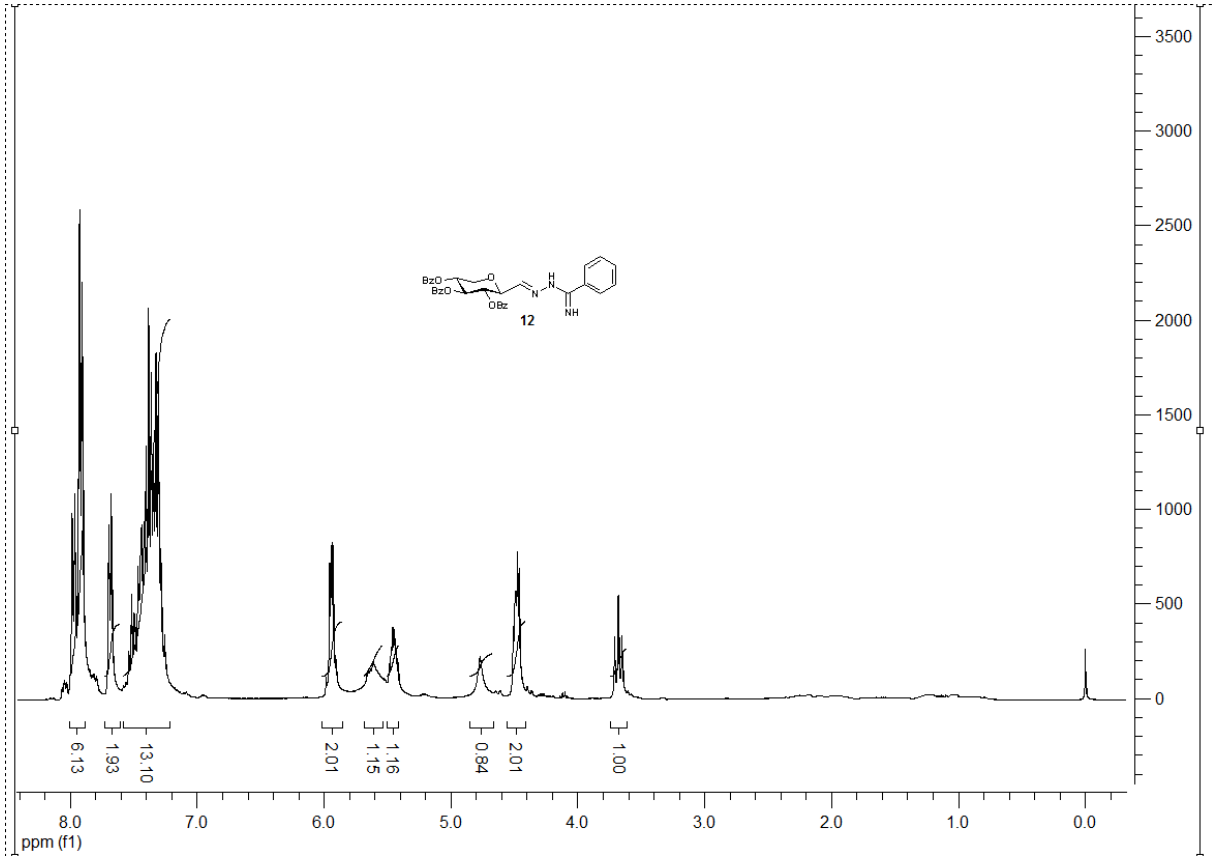
***N*^{1}-[*C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)methylidene]naphthalene-2-carboxamidrazone (11)** Prepared from **1**[1] (1.54 g, 2.55 mmol) and naphthalene-2-carboxamidrazone (**7**, 0.96 g, 5.10 mmol) according to **General procedure I**. Purified by column chromatography (EtOAc/hexane = 1:2) to yield the title compound **11** as a white amorphous solid (1.00 g, 51%). R_f 0.44 (EtOAc/hexane = 1:2); $[\alpha]_D$ = +1 (c 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13-7.21 (m, 28 H, Ar, CH=N), 6.09-6.01 (m, 2 H, H-2 and/or H-3 and/or H-4), around 6 (very br s, NH_2), 5.77 (pseudo t, J = 9.6 Hz, 1 H, H-2 or H-3 or H-4), 4.67 (dd, J = 2.7, 12.2 Hz, 1 H, H-6a), 4.63 (dd, J = 4.3, 9.1 Hz, 1 H, H-1), 4.51 (dd, J = 4.9, 12.2 Hz, 1 H, H-6b), 4.24 (ddd, J = 2.7, 4.5, 9.5 Hz, 1 H, H-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 165.9, 165.7, 165.1 (CO), 160.8 (C=NH), 151.4 (CH=N), 134.3-123.7 (Ar), 77.1, 76.1, 74.4, 70.0, 69.5 (C-1-C-5), 63.1 (C-6) ppm. Anal. Calcd. for $C_{46}H_{37}N_3O_9$ (775.80): C, 71.22; H, 4.81; N, 5.42. Found: C, 71.11; H, 4.72; N, 5.51.





***N*^{1}-[*C*-(2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl)methylidene]benzamidrazone (12)**

Prepared from **2**[2] (1.00 g, 2.12 mmol) and benzamidrazone (**5**, 0.58 g, 4.3 mmol) according to **General procedure I**. Purified by column chromatography (EtOAc/hexane = 2:3) to yield the title compound **12** as a white amorphous solid (0.76 g, 65%). R_f 0.31 (EtOAc/hexane = 2:3); $[\alpha]_D$ = –4 (c 0.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12-7.23 (m, 21 H, Ar, CH=N), 5.96, 5.93 (2 pseudo t, J = 9.1, 9.6 Hz, 2 H, H-2, H-3), 5.61 (br s, 1 H, NH), 5.44 (ddd, J = 5.3, 9.4, 9.7 Hz, 1 H, H-4), 4.77 (br s, 1 H, NH), 4.53-4.41 (m, 2 H, H-1, H-5a), 3.68 (pseudo t, J = 10.5 Hz, 1 H, H-5b) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 165.7, 165.5 (CO), 160.6 (C=NH), 151.9 (CH=N), 133.5-126.6 (Ar), 77.5, 73.7, 70.0, 69.9 (C-1-C-4), 66.9 (C-5) ppm. Anal. Calcd. for $C_{34}H_{29}N_3O_7$ (591.61): C, 69.03, H, 4.94; N, 7.10. Found: C, 69.15; H, 5.07; N, 7.00.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OBz
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H
NH
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13.10
2.01
1.15
1.16
0.84
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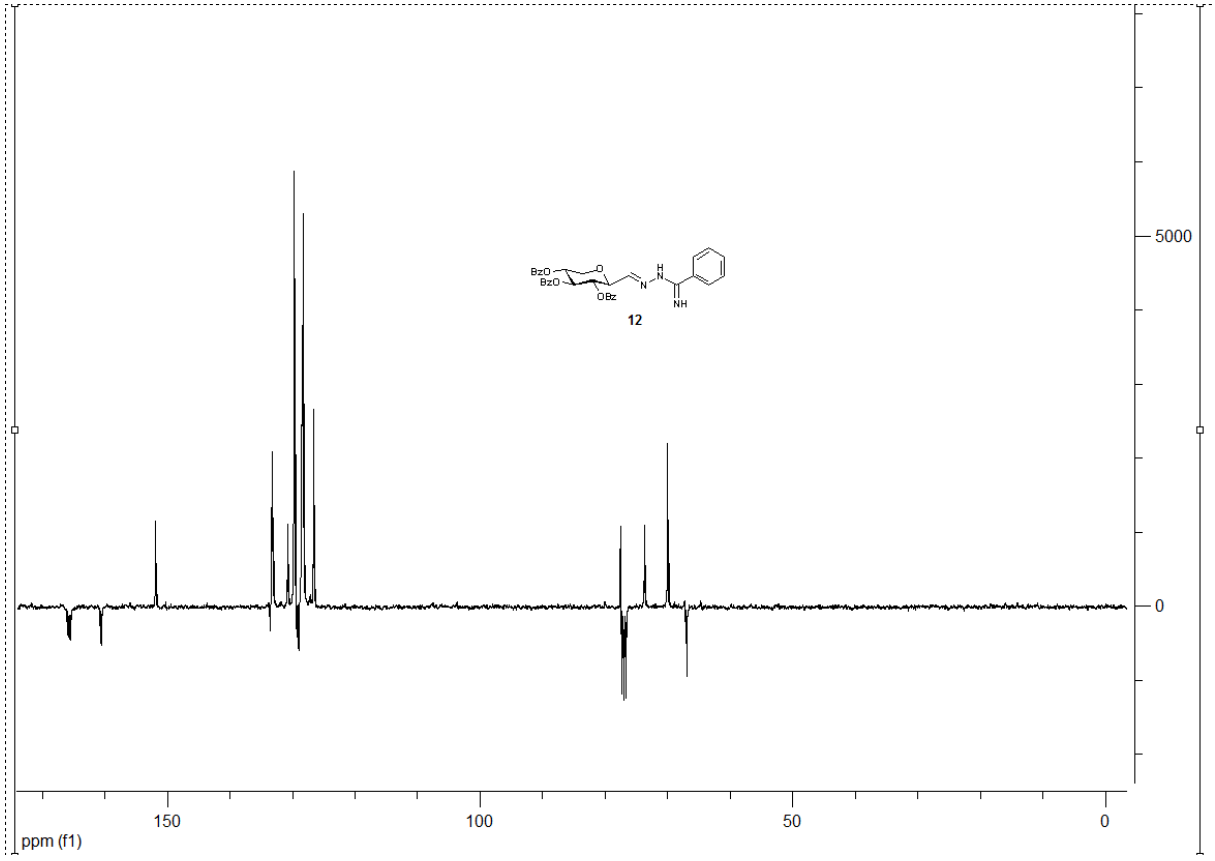
2.0
1.0
0.0
ppm (f1)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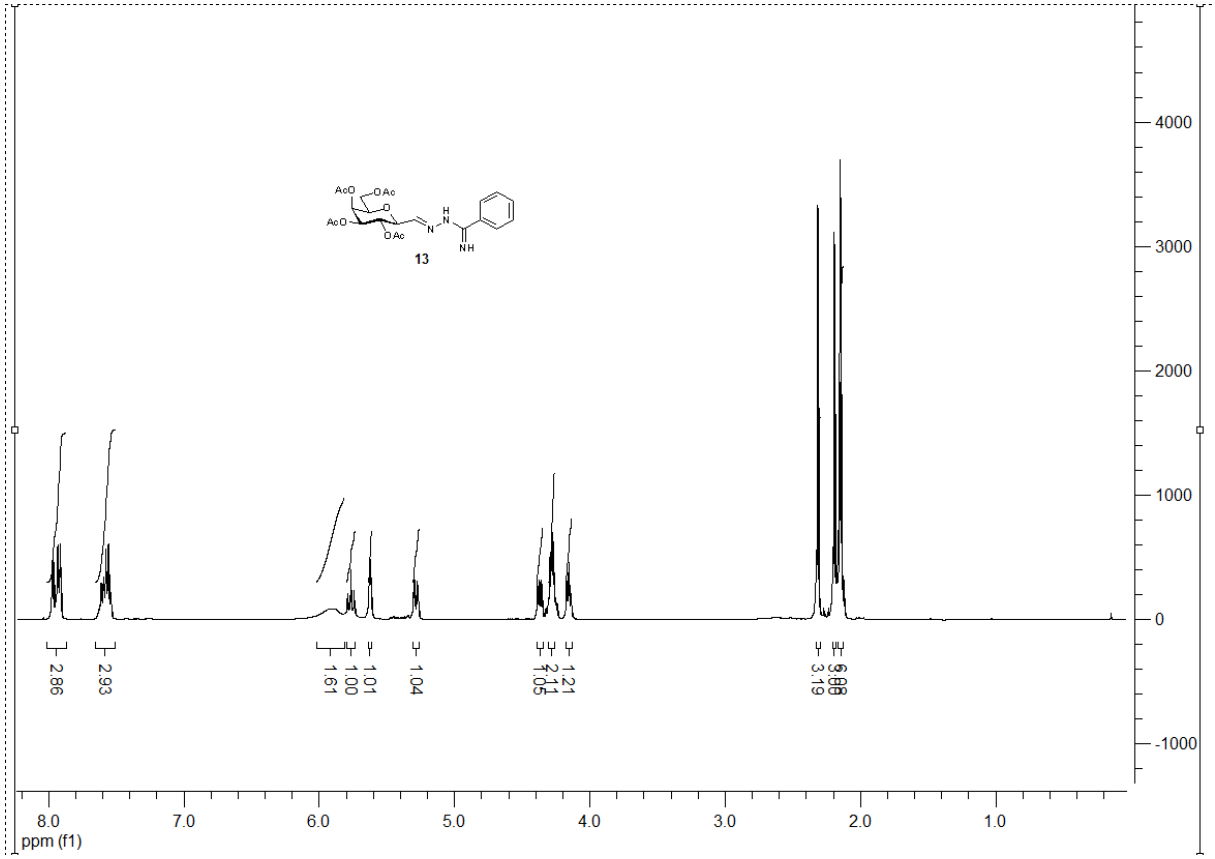
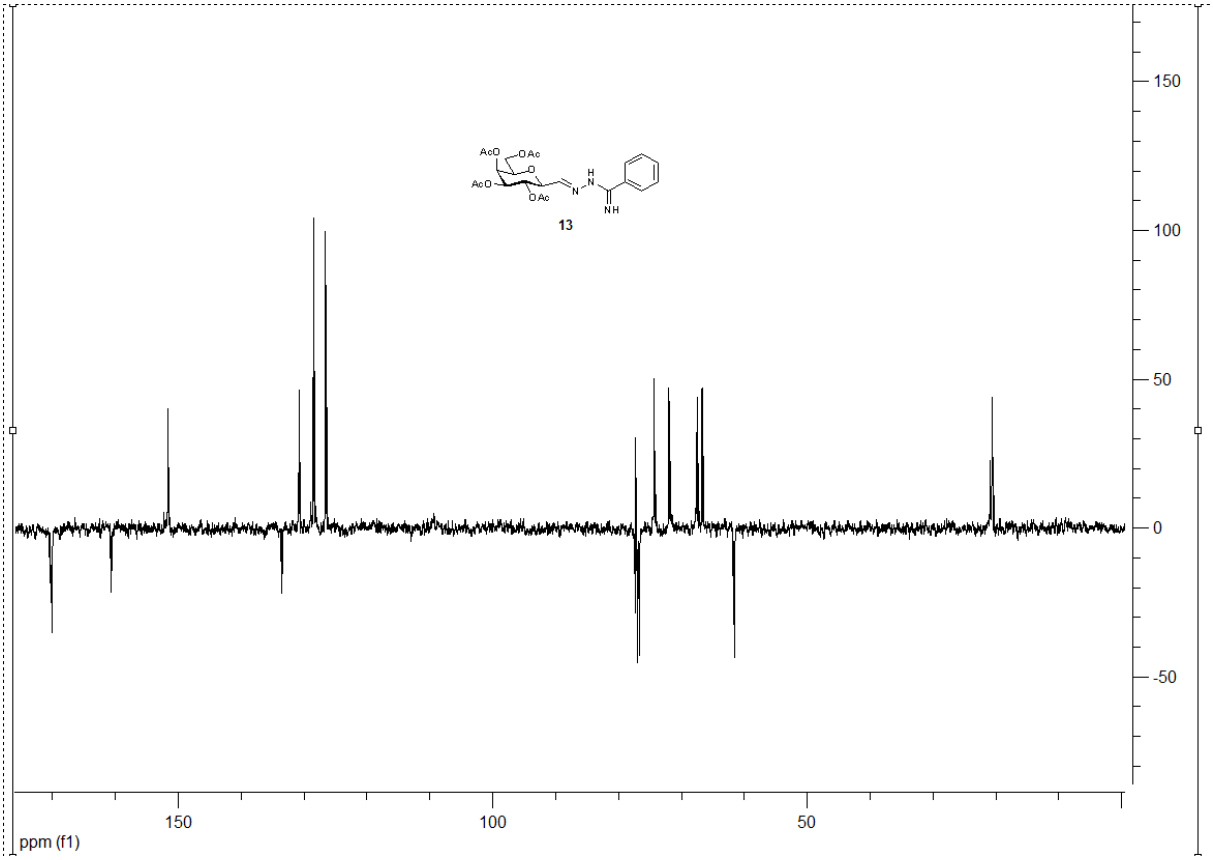
ppm (f1)

***N*^{1}-[*C*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)methylidene]benzamidrazone (13)**

Prepared from **3**[3, 4] (1.00 g, 2.80 mmol) and benzamidrazone (**5**, 0.76 g, 5.6 mmol) according to **General procedure I**. Purified by column chromatography (EtOAc/hexane = 2:3) to yield the title compound **13** as a white amorphous solid (0.86 g, 64%). R_f 0.28 (EtOAc/hexane = 1:1); $[\alpha]_D$ = +20 (c 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.37 (m, 6 H, Ar, CH=N), 5.77 (br s, 2 H, NH_2), 5.62 (pseudo t, J = 9.9 Hz, 1 H, H-2), 5.47 (d, J = 3.1 Hz, 1 H, H-4), 5.13 (dd, J = 3.4, 10.1 Hz, 1 H, H-3), 4.22 (dd, J = 4.6, 9.9 Hz, 1 H, H-1), 4.16-4.08 (m, 2 H, H-6a, H-6b), 4.00 (m, 1 H, H-5), 2.17, 2.05, 2.01, 2.00 (4 s, 12 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 170.2, 170.1 (CO), 160.6 (C=NH), 151.6 (CH=N), 133.5, 130.8, 128.5, 126.6 (Ar), 77.3, 74.3, 72.0, 67.5, 66.7 (C-1–C-5), 63.1 (C-6) ppm. Anal. Calcd. for $C_{22}H_{27}N_3O_9$ (477.46): C, 55.34, H, 5.70; N, 8.80. Found: C, 55.47; H, 5.83; N, 8.92.

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N
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100
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0
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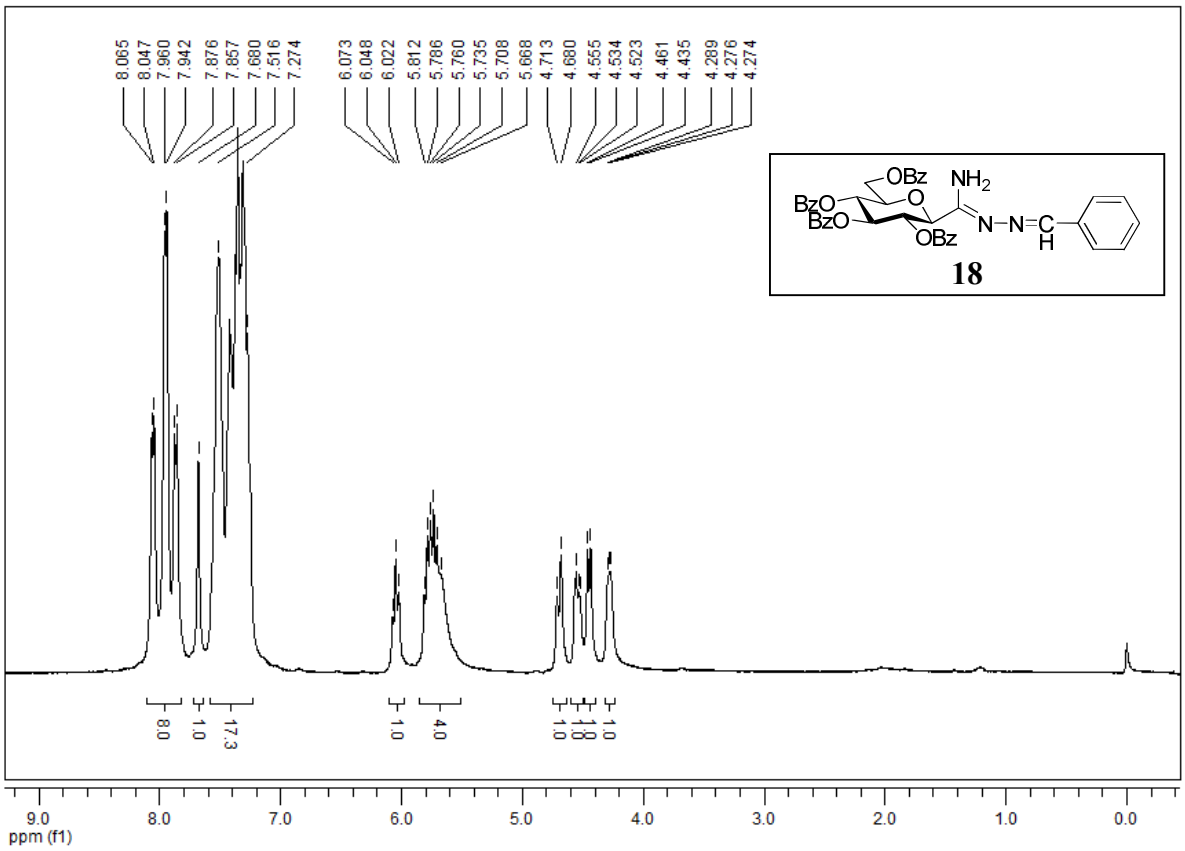
150
100
50
ppm (f1)

General procedure II for the synthesis of N^1-arylidene-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidrazones (18-20)

C-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidrazone[5] (**14**, 1.0 g, 1.57 mmol) and the corresponding aromatic aldehyde (**15-17**, 1.1 equiv.) was heated in dry EtOH (20 mL) at reflux temperature, and the reaction was monitored by TLC (EtOAc/hexane = 1:1). After total consumption of the starting formamidrazone the product was separated either by filtration or by column chromatography.

N^1-Benzylidene-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidrazone (18)

Prepared from formamidrazone **14** (1.2 g, 1.88 mmol) and benzaldehyde (**15**, 0.21 mL, 2.07 mmol) according to **General procedure II**. Reaction time: 2 h. The product precipitated from the hot reaction mixture, was filtered, and used without further purification. Yield: 0.94 g (69%), white solid. Mp: 161-162 °C; $[\alpha]_D$ = +3 (c 0.50, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.07-7.86 (8H, m, Ar), 7.68 (1H, s, =CH), 7.52-7.27 (16H, m, Ar), 6.05, 5.79, 5.74 (3 x 1H, 3 pseudo t, J = 9.2, 9.2 Hz in each, H-2, H-3, H-4), 5.67 (2H, br s, NH_2), 4.70 (1H, dd, J = 11.9, < 1 Hz, H-6a), 4.54 (1H, dd, J = 11.9, 5.3 Hz, H-6b), 4.52 (1H, d, J = 9.9 Hz, H-1), 4.28 (1H, ddd, J = 9.2, 5.3, < 1 Hz, H-5); ^{13}C NMR (90 MHz, $CDCl_3$): δ = 166.1, 165.7, 165.3, 165.2 (C=O), 156.6 (C=N), 156.1 (=CH), 134.7-127.8 (Ar), 77.3, 76.4, 73.5, 70.5, 69.2 (C-1 – C-5), 62.9 (C-6). MS-ESI (m/z): calcd for $C_{42}H_{36}N_3O_9^+$ $[M+H]^+$: 726.24. Found: 726.7.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5.708
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4.680
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4.534
4.523
4.461
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4.289
4.276
4.274
8.0
1.0
17.3
1.0
4.0
1.0
1.0
1.0
1.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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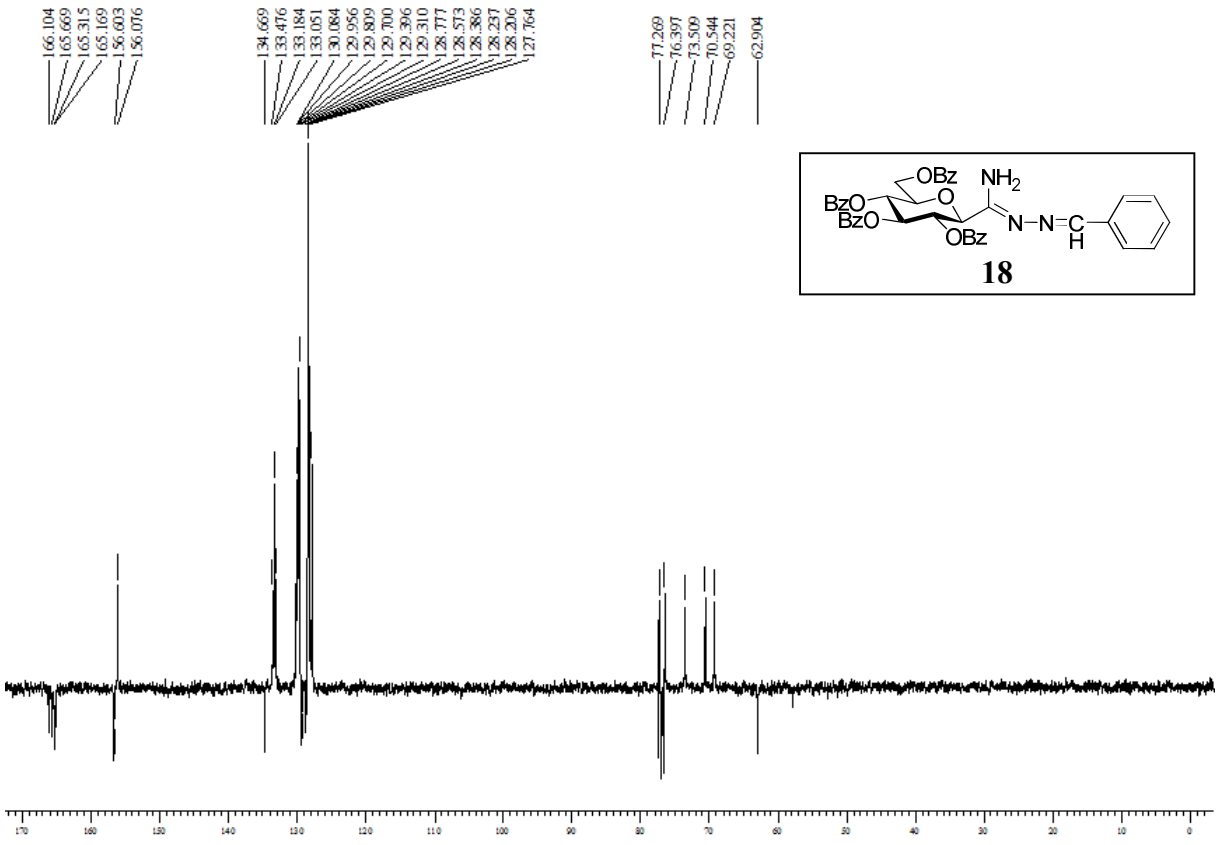
BzO
BzO
O
OBz
N–N=C
H
18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128.386
128.237
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127.764
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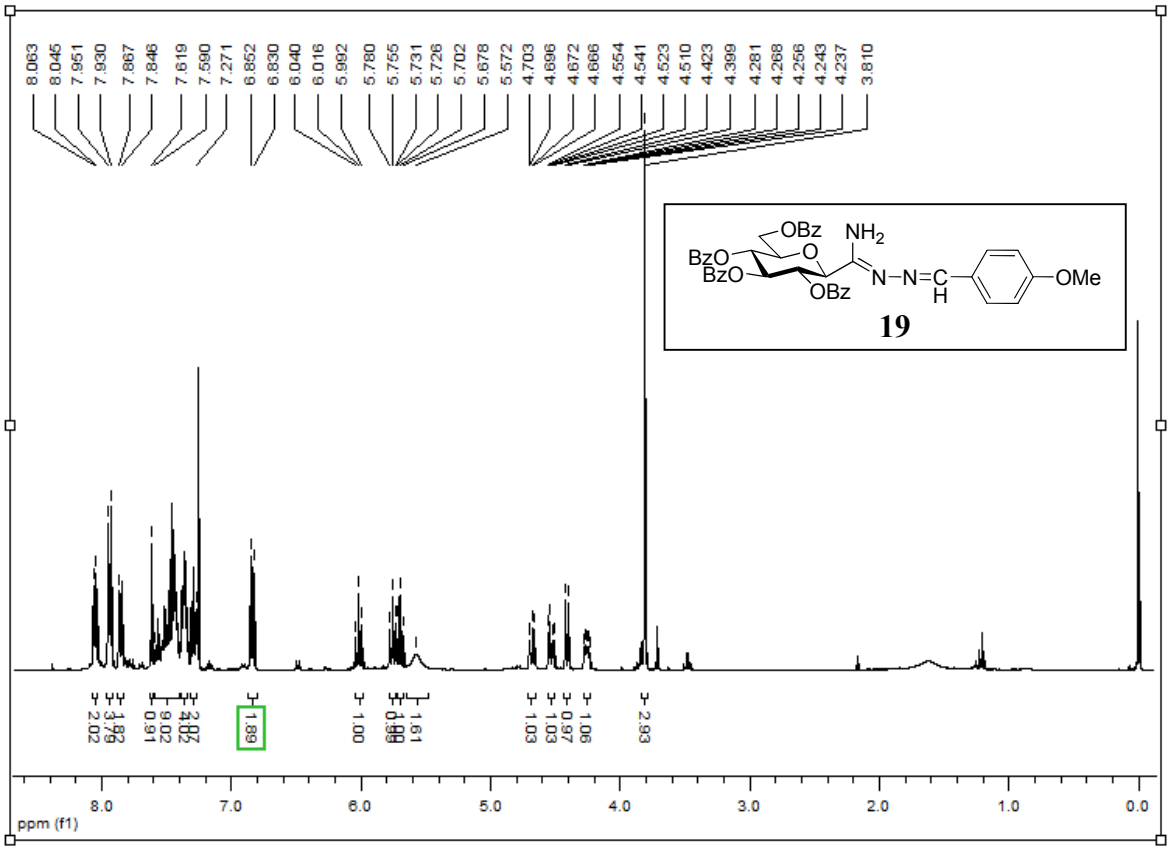
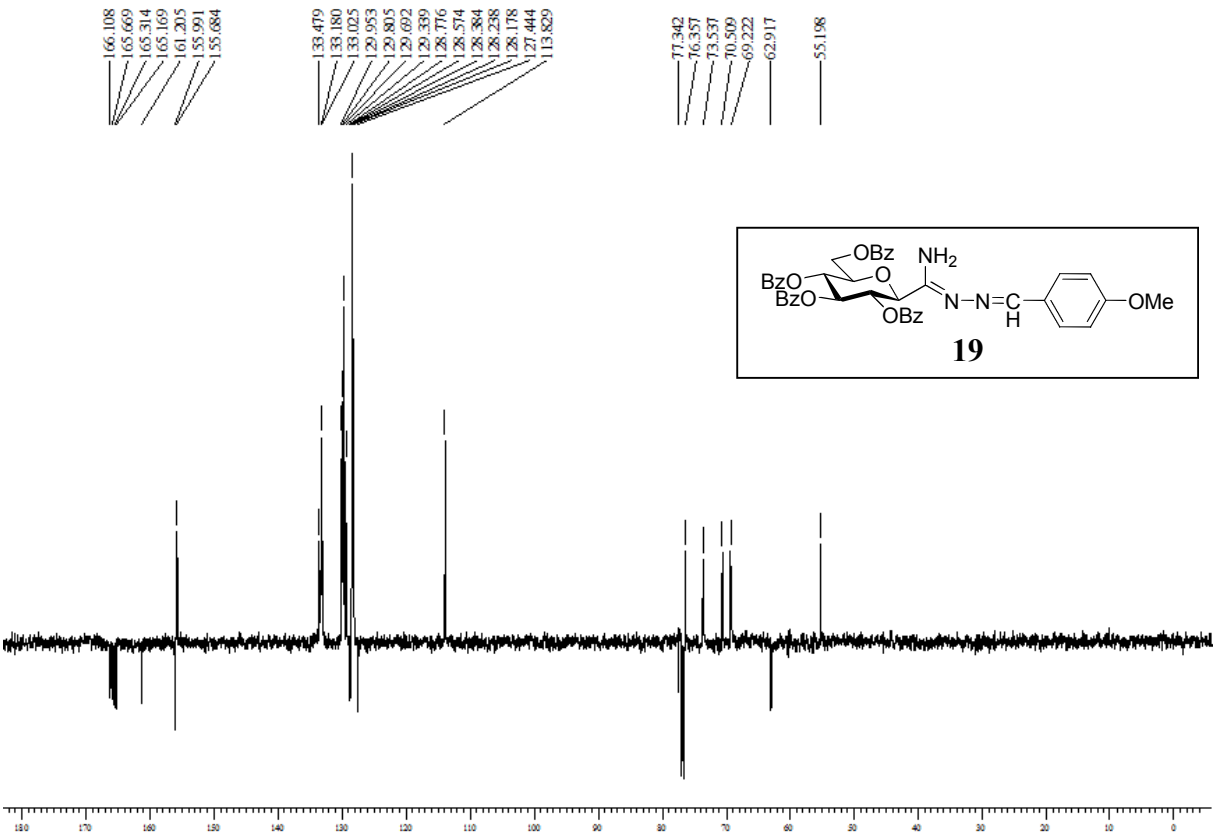
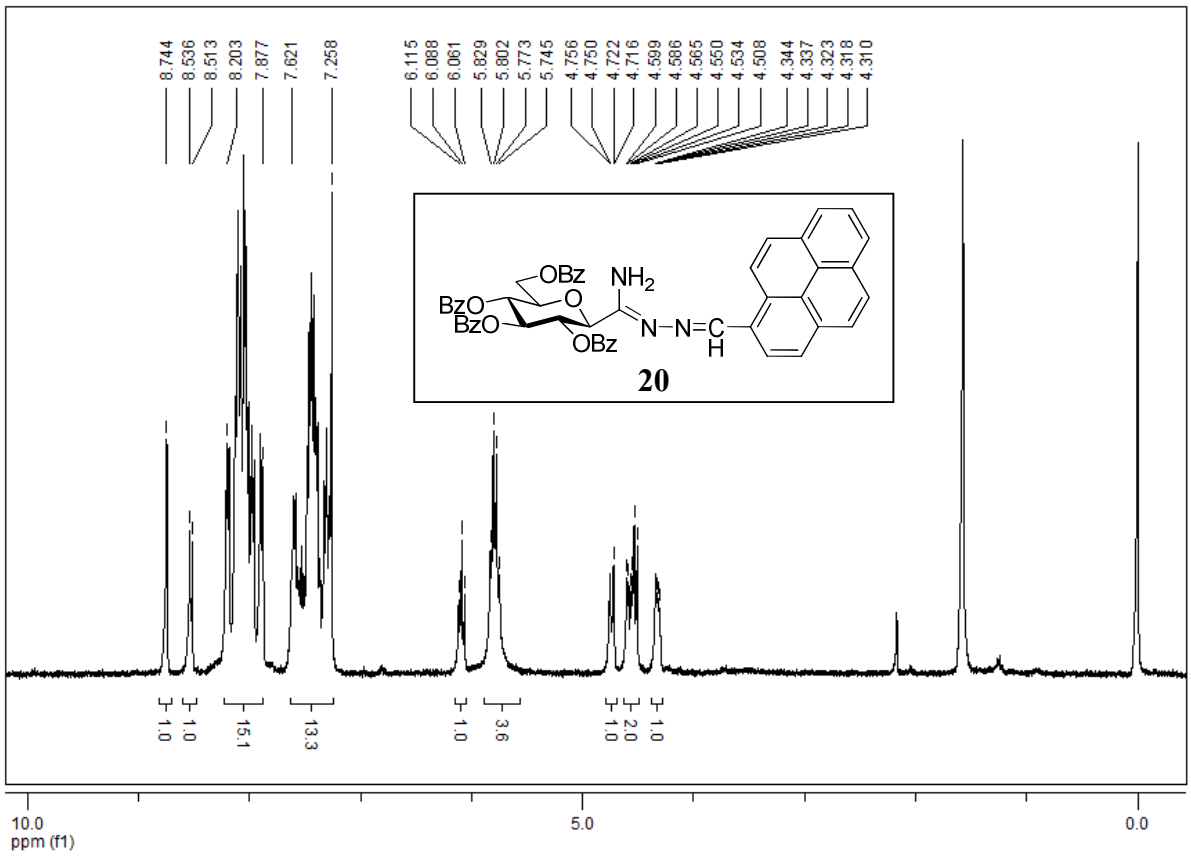
76.397
73.509
70.544
69.221
62.904
OBz
NH2
BzO
BzO
O
OBz
N–N=C
H
18

***N*^{1}-(4-Methoxybenzylidene)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-formamidrazone (19)** Prepared from formamidrazone **14** (0.5 g, 0.78 mmol) and *p*-anisaldehyde (**16**, 105 µL, 0.86 mmol) according to **General procedure II**. Reaction time: 4 h. Purified by column chromatography (EtOAc/hexane = 2:3) to give 0.45 g (76%) colourless syrup. R_f: 0.55 (EtOAc/hexane = 2:3); $[\alpha]_D = -10$ (c 0.50, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.06-7.85 (8H, m, Ar), 7.62 (1H, s, =CH), 7.59-7.27 (14H, m, Ar), 6.84 (2H, d, J = 8.6 Hz, Ar), 6.02, 5.76, 5.70 (3 x 1H, 3 pseudo t, J = 9.9, 9.2 Hz in each, H-2, H-3, H-4), 5.57 (2H, br s, NH_2), 4.68 (1H, dd, J = 11.9, 2.6 Hz, H-6a), 4.53 (1H, dd, J = 11.9, 5.3 Hz, H-6b), 4.41 (1H, d, J = 9.9 Hz, H-1), 4.26 (1H, ddd, J = 9.9, 5.3, 2.6 Hz, H-5), 3.81 (3H, s, OMe); ^{13}C NMR (90 MHz, $CDCl_3$): δ = 166.1, 165.7, 165.3, 165.2 (C=O), 161.2, 156.0 (Ar, C=N), 155.7 (=CH), 133.5-127.4, 113.8 (Ar), 77.3, 76.4, 73.5, 70.5, 69.2 (C-1–C-5), 62.9 (C-6), 55.2 (OMe). MS-ESI (m/z): calcd for $C_{43}H_{37}N_3O_{10}$ $[M]^+$: 755.25. Found: 755.3.





***N*^{1}-(Pyren-1-ylmethylidene)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-formamidrazone (20)** Prepared from formamidrazone **14** (1.0 g, 1.57 mmol) and pyrene-1-carbaldehyde (**17**, 0.40 g, 1.73 mmol) according to **General procedure II**. Reaction time: 1 h. The product precipitated from the hot reaction mixture, was filtered, and used without further purification. Yield: 0.95 g (71%), yellow solid. Mp: 139-141 °C; $[\alpha]_D$ = +84 (c 0.50, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.74 (1H, s, Ar), 8.53 (1H, d, J = 8.6 Hz, Ar), 8.20-7.26 (28H, m, Ar, =CH), 6.09 (1H, pseudo t, J = 9.2, 9.2 Hz, H-2 or H-3 or H-4), 5.83-5.75 (4H, m, H-2 and/or H-3 and/or H-4, NH_2), 4.74 (1H, dd, J = 11.9, 2.6 Hz, H-6a), 4.58 (1H, dd, J = 11.9, 5.3 Hz, H-6b), 4.52 (1H, d, J = 9.9 Hz, H-1), 4.32 (1H, ddd, J = 9.2, 5.3, 2.6 Hz, H-5); ^{13}C NMR (90 MHz, $CDCl_3$): δ = 166.1, 165.7, 165.4, 165.2 (C=O), 156.7 (C=N), 154.1 (=CH), 133.5-122.3 (Ar), 77.2, 76.4, 73.5, 70.7, 69.3 (C-1 – C-5), 62.9 (C-6). MS-ESI (m/z): calcd for $C_{52}H_{40}N_3O_9^+$ $[M+H]^+$: 850.27. Found: 850.7.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4.599
4.586
4.565
4.550
4.534
4.508
4.344
4.337
4.323
4.318
4.310
1.0
1.0
15.1
13.3
1.0
3.6
1.0
2.0
1.0
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NH2
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O
BzO
OBz
N–N=C
H
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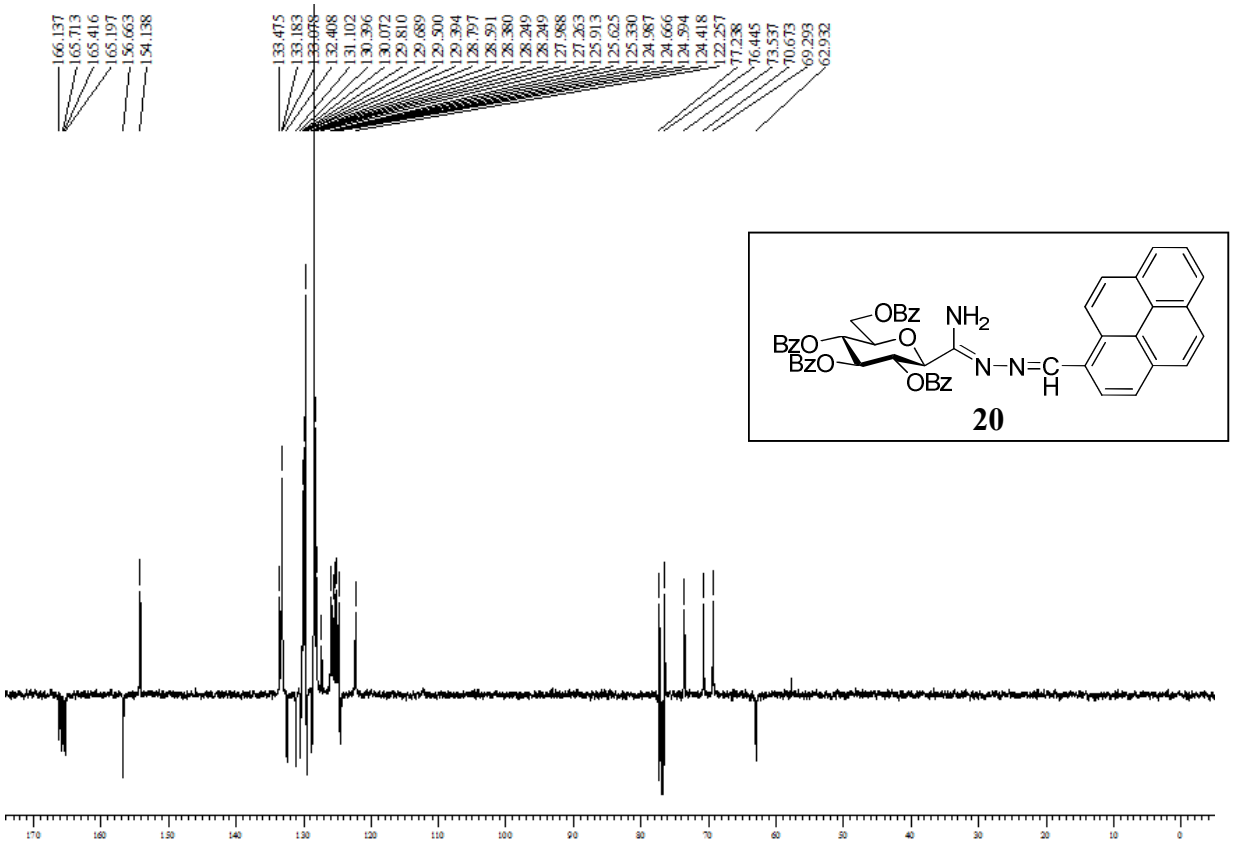
ppm (f1)
5.0
0.0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129.810
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129.500
129.394
128.797
128.591
128.380
128.249
128.249
127.588
127.263
125.913
125.625
125.330
124.987
124.666
124.594
124.418
122.257
77.238
76.445
73.537
70.673
69.293
62.932
OBz
NH2
BzO
O
BzO
OBz
N–N=C
H
20

General procedure III for the transformation of *N*^{1}-arylidene-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formamidrazones (18-20) by PIDA

To a solution of the corresponding arylidene amidrazone (**18-20**, 0.10 g) in dry CH_2Cl_2 (3 mL) PIDA (2 equiv.) was added and the reaction mixture was stirred at rt. After disappearance of the starting material monitored by TLC (EtOAc/hexane = 1:1) the mixture was diluted with CH_2Cl_2 (15 mL), extracted with water (10 mL), satd aq $NaHCO_3$ solution (10 mL), and then with water (10 mL). The organic phase was dried over $MgSO_4$, filtered the solvent was evaporated under reduced pressure. The resulting products were separated by column chromatography.

3-(4-Methoxyphenyl)-5-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-triazole 22

From formamidrazone **19** according to **General procedure III**. Reaction time: 2 d. Purified by column chromatography (EtOAc/hexane = 2:3) to give cyanide **1** as the first then the title compound **22** as the second fraction.

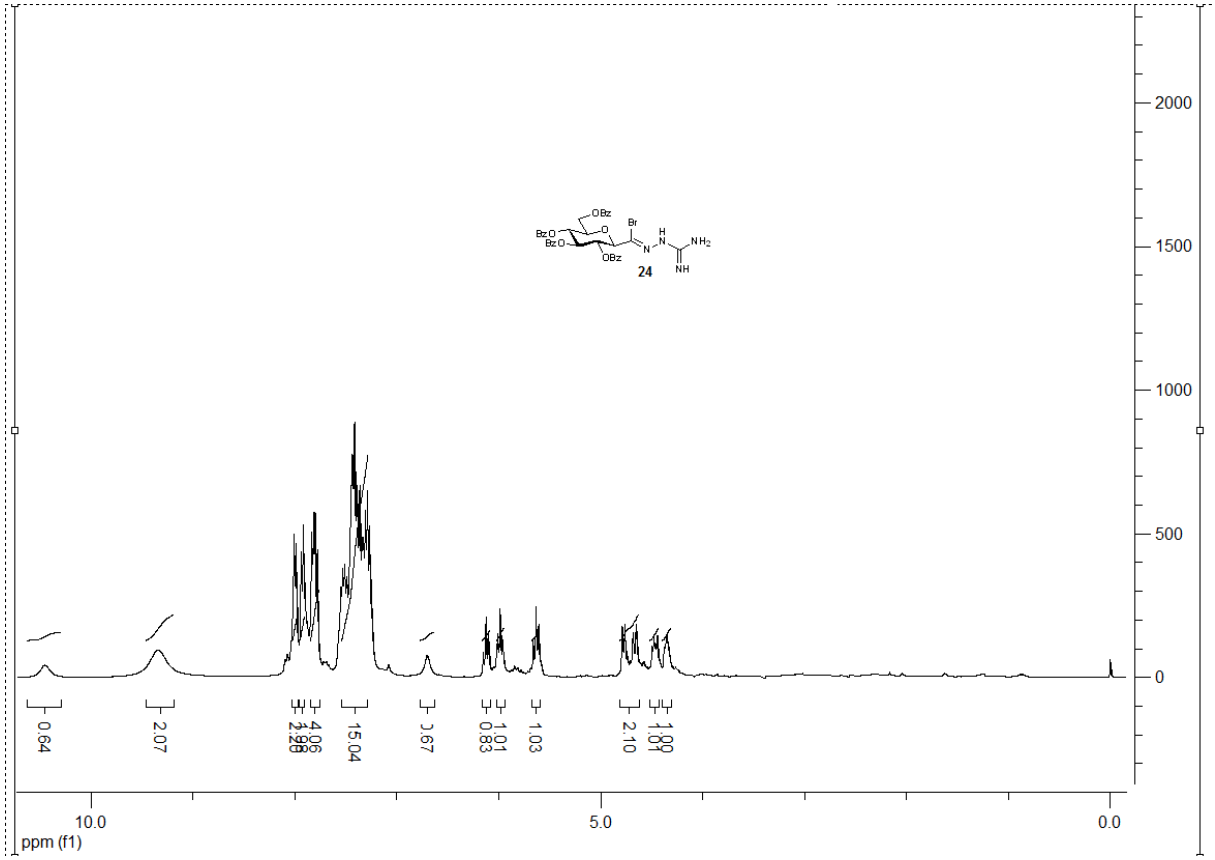
Compound **1**: Yield: 60 mg (75%). ^{1}H and ^{13}C NMR data correspond to the reported spectra.[1]

Compound **22**: Yield: 13 mg (13%) colourless syrup. R_f: 0.38 (EtOAc/hexane = 1:1); $[\alpha]_D$ = –4 (c 0.45, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.95-7.20 (22H, m, Ar), 6.84 (2H, d, J = 7.9 Hz, Ar), 6.02, 6.09, 5.93 (3 x 1H, 3 pseudo t, J = 9.9, 9.2 Hz in each, H-2, H-3, H-4), 5.24 (1H, d, J = 9.9 Hz, H-1), 4.66 (1H, dd, J = 12.6, 2.6 Hz, H-6a), 4.57 (1H, dd, J = 12.6, 4.6 Hz, H-6b), 4.42 (1H, d, J = 9.2, 4.6, 2.6 Hz, H-5) 3.79 (3H, s, OMe); MS-ESI (m/z): calcd for $C_{43}H_{36}N_3O_{10}^+$ $[M+H]^+$: 754.23. Found: 754.7.

General procedure IV for the synthesis of *O*-peracylated *N*-arenecarboximidoyl-*C*-(β-D-glycopyranosyl)carbohydrazonoyl bromides (24-29)

An alkylidene amidrazone (**8-13**, 0.28 mmol) was dissolved in CH_2Cl_2 (4 mL), then *N*-bromosuccinimide (0.05 g, 0.28 mmol) was added. The mixture was stirred at rt. When the reaction was complete (TLC, EtOAc/hexane = 1:2) the solvent was evaporated, and the residue was purified by column chromatography.

***N*-Aminocarboximidoyl-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)carbo-hydrazonoyl bromide (24)** Prepared from **8** (0.60 g, 0.90 mmol) and NBS (0.18 g, 0.99 mmol) according to **General procedure IV**. Purified by column chromatography ($CHCl_3$/methanol = 12:1) to yield the title compound **24** as a yellow amorphous solid (0.20 g, 30%). R_f 0.40 ($CHCl_3$/methanol = 12:1); $[\alpha]_D$ = +21 (c 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.45 (br s, 1 H, NH), 9.35 (br s, 2 H, NH_2), 8.04-7.23 (m, 20 H, Ar), 6.70 (br s, 1 H, NH), 6.12, 5.98, 5.63 (3 pseudo t, 3 H, J = 9.5 Hz, 3 H, H-2, H-3, H-4), 4.77 (d, J = 9.4 Hz, 1 H, H-1), 4.66 (dd, J = 1, 12.1 Hz, 1 H, H-6a), 4.53 (dd, J = 6.4, 12.1 Hz, 1 H, H-6b), 4.32 (m, 1 H, H-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 165.9, 165.7, 165.1 (CO), 155.4 (C=NH), 147.3 (C(=N)Br), 133.6-128.2 (Ar), 76.5, 74.0, 73.0, 69.2, 68.6 (C-1-C-5), 63.2 (C-6) ppm. Anal. Calcd. for $C_{36}H_{31}N_4O_9Br$ (743.56): C, 58.56, H, 4.20; N, 7.53. Found: C, 58.47; H, 4.09; N, 7.65.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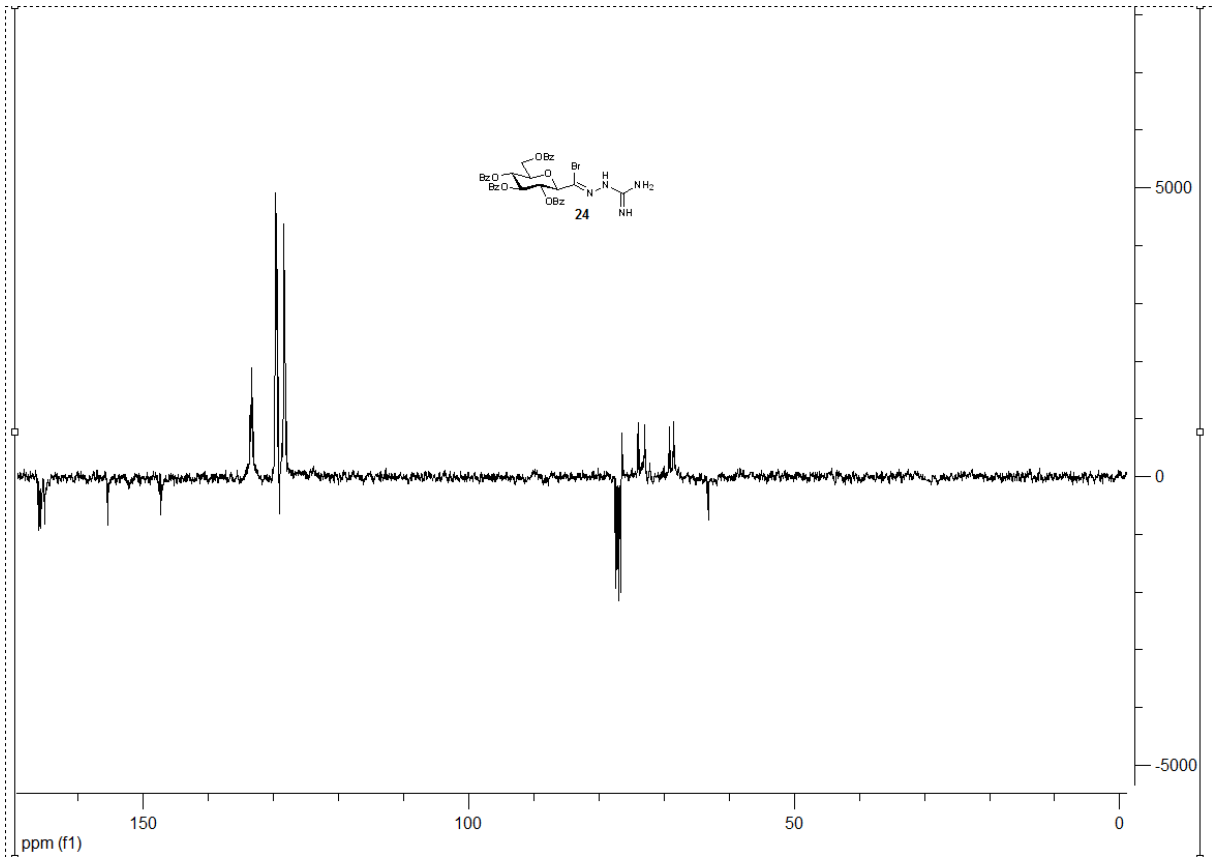
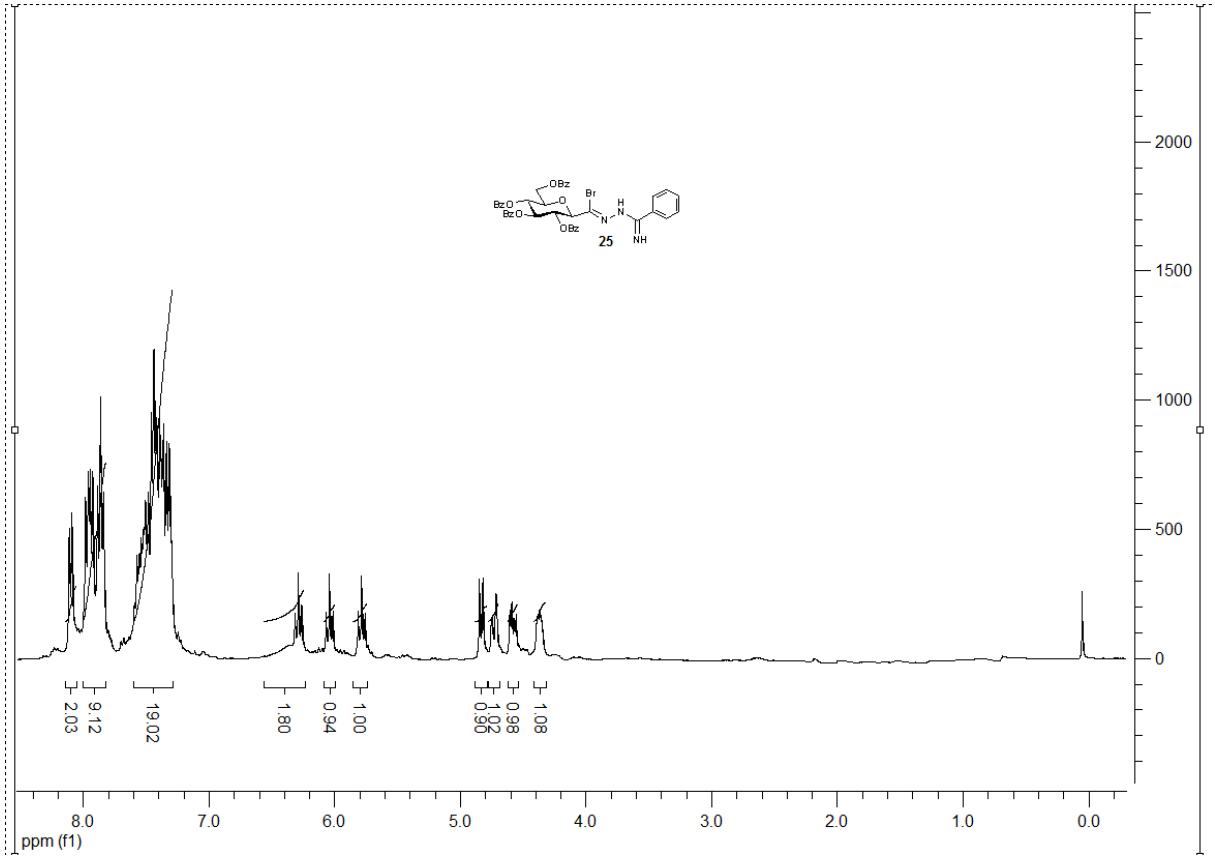
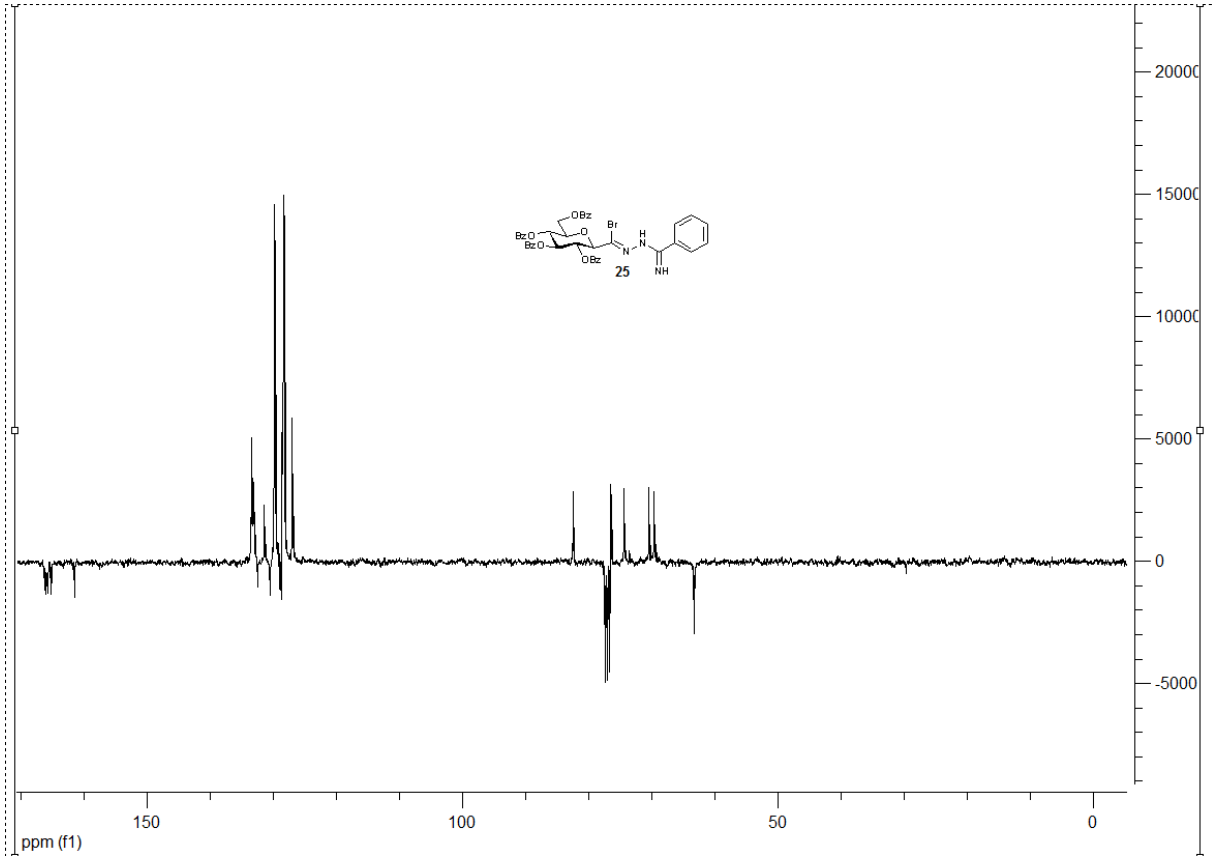
2.07
4.06
2.98
15.04
3.67
1.01
0.83
1.03
2.10
1.01
1.00
10.0
5.0
0.0
ppm (f1)

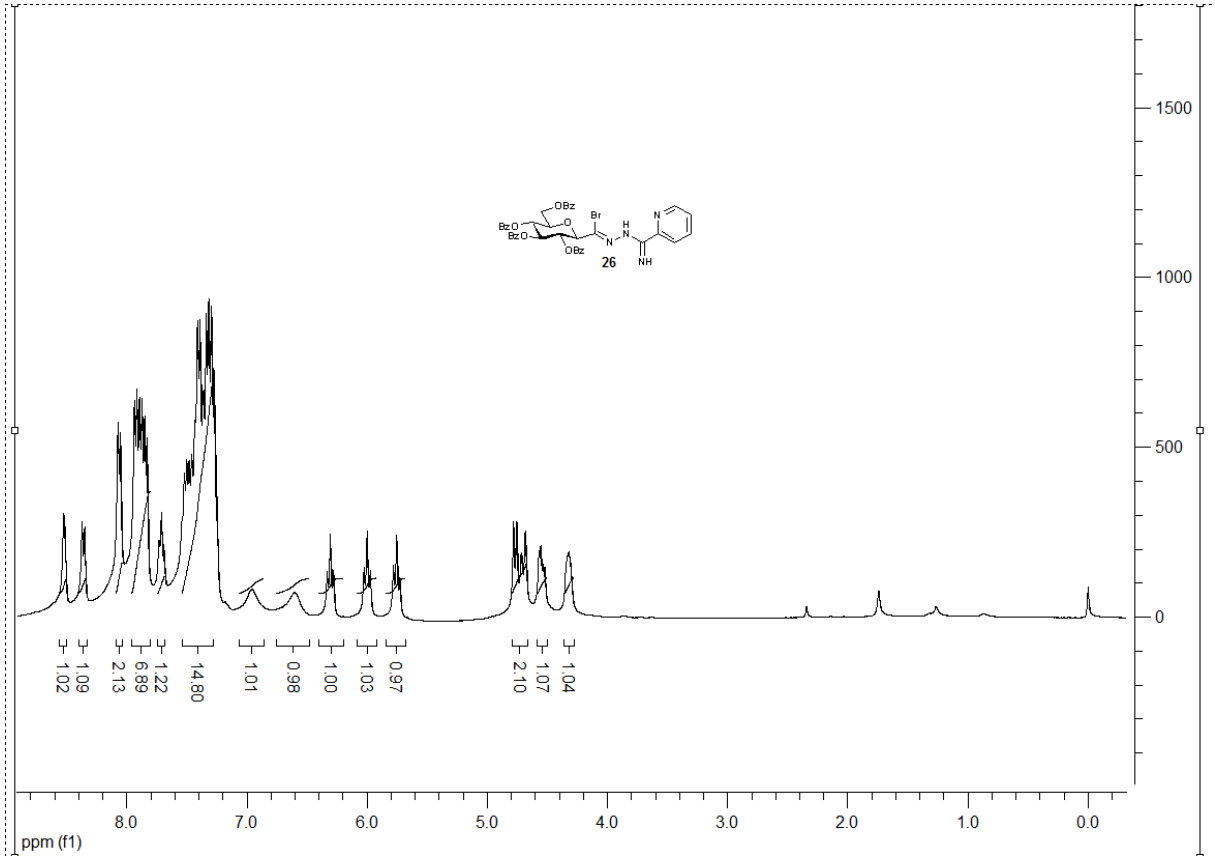

24
5000
0
-5000
150
100
50
0
ppm (f1)

***N*-Benzenecarboximidoyl-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)carbohydrazonoyl bromide (25)** Prepared from **9** (0.40 g, 0.55 mmol) and NBS (0.10 g, 0.55 mmol) according to **General procedure IV**. Purified by column chromatography (EtOAc/hexane = 1:2) to yield the title compound **25** as a white amorphous solid (0.33 g, 74%). R_f 0.30 (EtOAc/hexane = 1:2); $[\alpha]_D$ = +30 (c 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-7.24 (m, 26 H, Ar, NH), 6.30 (brs, 1 H, NH), 6.24, 5.99, 5.73 (3 pseudo t, J = 9.6 Hz, 3 H, H-2, H-3, H-4), 4.78 (d, J = 9.6 Hz, 1 H, H-1), 4.68 (dd, J = 2.5, 12.2 Hz, 1 H, H-6a), 4.53 (dd, J = 5.6, 12.2 Hz, 1 H, H-6b), 4.32 (ddd, J = 2.5, 5.6, 9.6 Hz, 1 H, H-5) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 166.0, 165.8, 165.2 (CO), 161.5 (C=NH), 133.4-127.0 (Ar, C(=N)Br), 82.3, 76.5, 74.3, 70.4, 69.6 (C-1-C-5), 63.2 (C-6) ppm. Anal. Calcd. for $C_{42}H_{34}N_3O_9Br$ (804.64): C, 62.69, H, 4.26; N, 5.22. Found: C, 62.59; H, 4.15; N, 5.10.





***N*-(Pyridine-2-carboximidoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-carbohydrazonoyl bromide (26)** Prepared from **10** (0.15 g, 0.21 mmol) and NBS (0.09 g, 0.41 mmol) according to **General procedure IV**. Purified by column chromatography (EtOAc/toluene = 1:8) to yield the title compound **26** as a white amorphous solid (0.11 g, 64%). R_f 0.50 (EtOAc/toluene = 1:8); $[\alpha]_D$ = +55 (c 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52-7.25 (m, 24 H, Ar), 6. 96 (1 br s, 1 H, NH), 6.60 (1 br s, 1 H, NH), 6.30, 6.00, 5.75 (3 pseudo t, J = 9.4, 9.6 Hz, 3 H, H-2, H-3, H-4), 4.76 (d, J = 9.6 Hz, 1 H, H-1), 4.70 (dd, J = 1.0, 12.2 Hz, 1 H, H-6a), 4.54 (dd, J = 5.3, 12.0 Hz, 1 H, H-6b), 4.41-4.18 (m, 1 H, H-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 165.9, 165.8, 165.1 (CO), 158.8 (C=NH), 149.1, 148.2, 136.7, 133.4-122.3 (Ar, C(=N)Br), 82.4, 76.5, 74.4, 70.4, 69.6 (C-1-C-5), 63.2 (C-6) ppm. Anal. Calcd. for $C_{41}H_{34}N_3O_9Br$ (805.63): C, 64.12, H, 4.13; N, 6.95. Found: C, 64.24; H, 4.26; N, 6.83.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BzO
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HN
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OBz
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1.09
2.13
6.89
1.22
14.80
1.01
0.98
1.00
1.03
0.97
2.10
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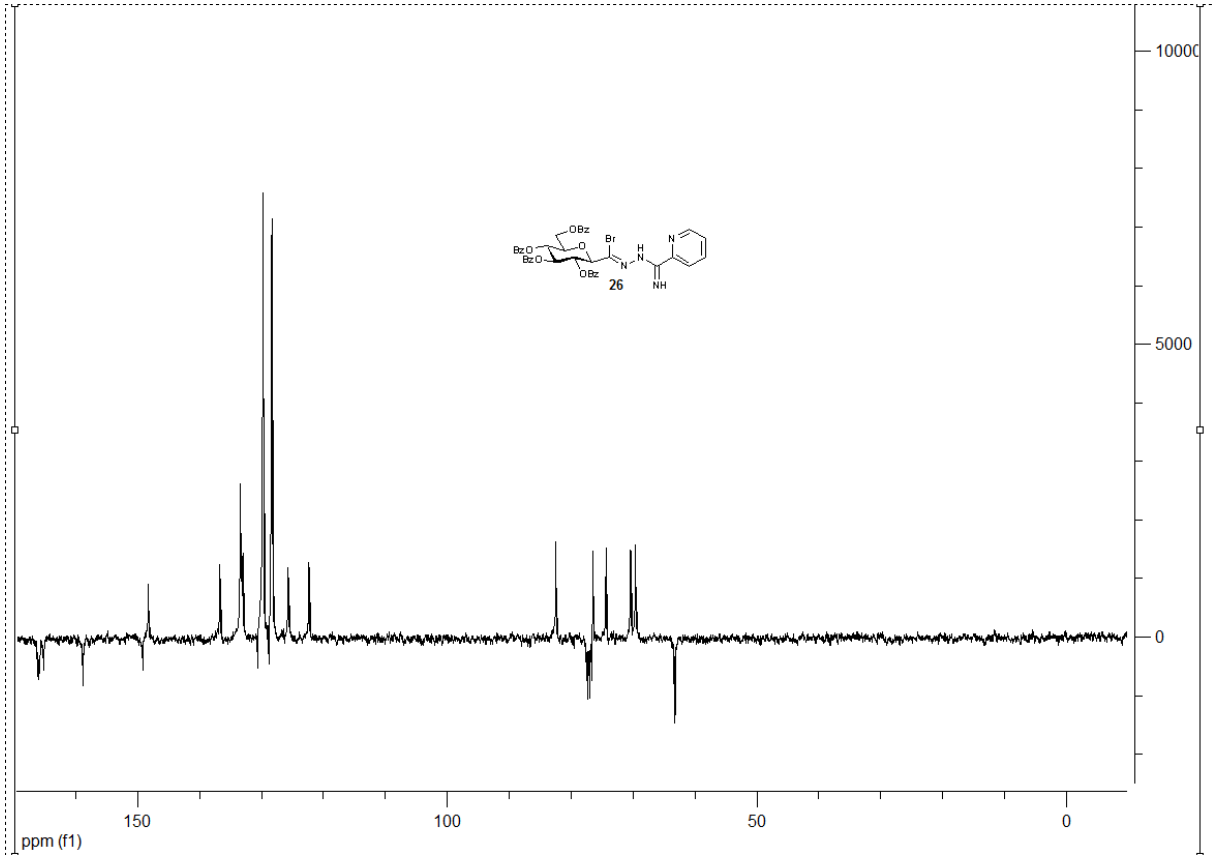
0.0
ppm (f1)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BzO
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OBz
NH
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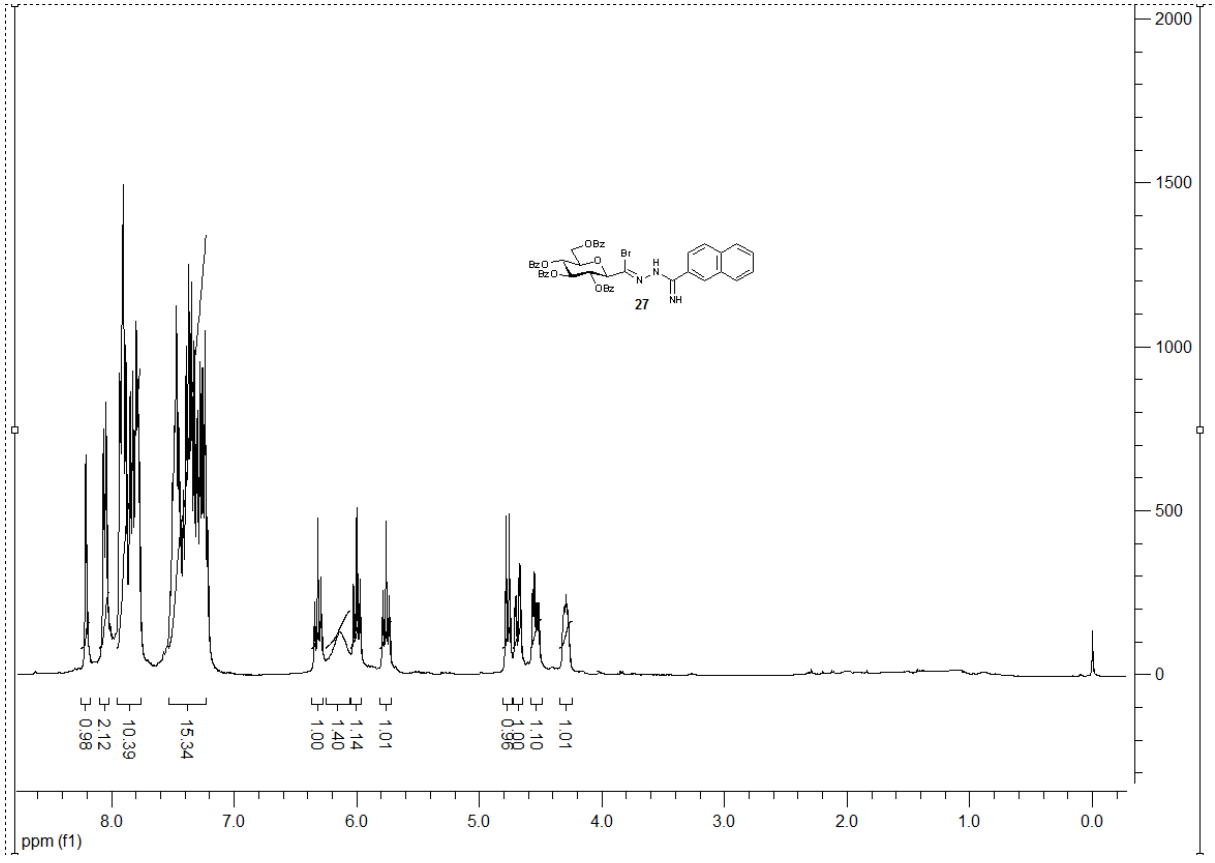
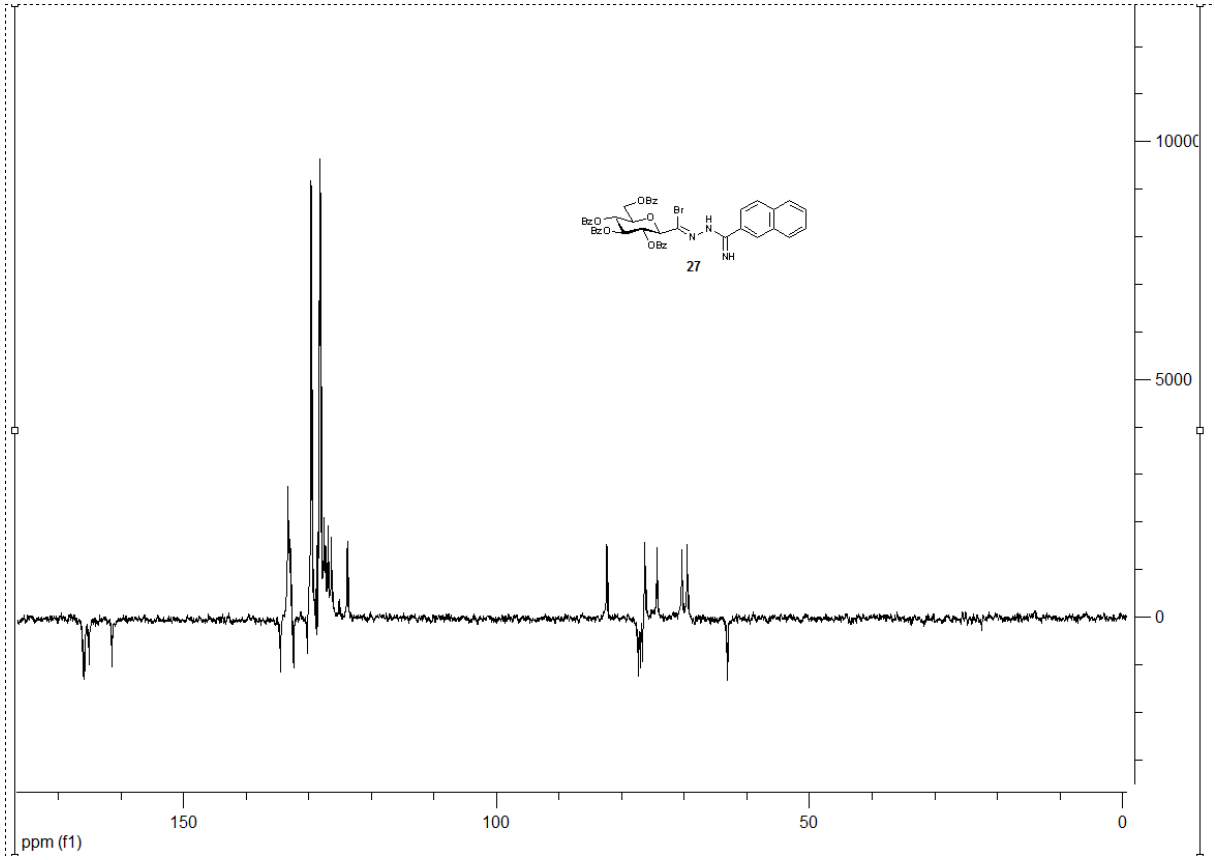
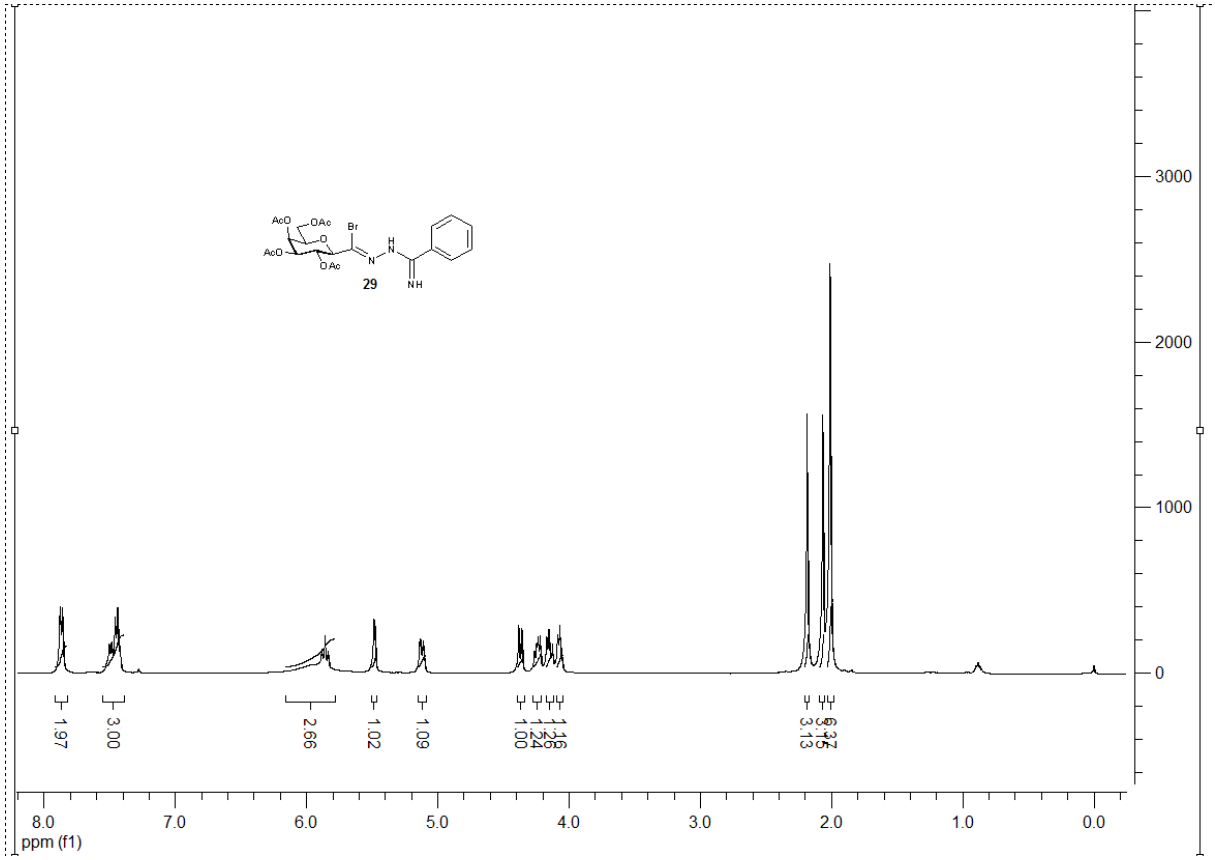
0
150
100
50
0
ppm (f1)

***N*-(Naphthalene-2-carboximidoyl)-*C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)carbohydrazonoyl bromide (27)** Prepared from **11** (0.30 g, 0.39 mmol) and NBS (0.08 g, 0.39 mmol) according to **General procedure IV**. Purified by column chromatography (EtOAc/hexane = 1:2) to yield the title compound **27** as a pale yellow amorphous solid (0.23 g, 70%). R_f 0.40 (EtOAc/hexane = 1:2); $[\alpha]_D$ = +17 (c 0.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-7.21 (m, 28 H, Ar, NH), 6.31 (pseudo t, J = 9.5, 9.7 Hz, 1 H, H-2 or H-3 or H-4), 6.14 (brs, 1 H, NH), 6.00, 5.76 (2 pseudo t, J = 9.6, 9.8 Hz, 2 H, H-2 and/or H-3 and/or H-4), 4.77 (d, J = 9.8 Hz, 1 H, H-1), 4.69 (dd, J = 2.4, 12.2 Hz, 1 H, H-6a), 4.54 (dd, J = 5.2, 12.2 Hz, 1 H, H-6b), 4.29 (ddd, J = 2.4, 5.2, 9.6 Hz, 1 H, H-5) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ= 166.0, 165.9, 165.8, 165.1 (CO), 161.4 (C=NH), 134.5-123.8 (Ar, C(=N)Br), 82.4, 76.3, 74.4, 70.4, 69.5 (C-1-C-5), 63.1 (C-6) ppm. ESI-MS (positive mode) m/z calcd. for $C_{46}H_{37}N_3O_9Br^+$ (854.171) $[M+H]^+$, Found: 854.168, 856.167.





***N*-Benzenecarboximidoyl-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)carbohydrazonoyl bromide (29)** Prepared from **13** (0.35 g, 0.73 mmol) and NBS (0.13 g, 0.73 mmol) according to **General procedure IV**. Purified by column chromatography (EtOAc/hexane = 1:1) to yield the title compound **29** as a white amorphous solid (0.27 g, 66%). R_f 0.40 (EtOAc/hexane = 1:1); $[\alpha]_D = -8$ (c 0.85, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.3 Hz, 2 H, Ar), 7.56-7.38 (m, 3 H, Ar), 5.93 (very br s, NH_2), 5.86 (pseudo t, J = 9.8 Hz, 1 H, H-2), 5.47 (d, J = 2.6 Hz, 1 H, H-4), 5.11 (dd, J = 3.1, 10.0 Hz, 1 H, H-3), 4.36 (d, J = 9.6 Hz, 1 H, H-1), 4.24 (dd, J = 6.8, 11.1 Hz, 1 H, H-6a), 4.15 (dd, J = 6.5, 11.1 Hz, 1 H, H-6b), 4.07 (pt, J = 6.5 Hz, 1 H, H-5), 2.19, 2.07, 2.01 (3 s, 12 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 170.3, 170.2, 170.1 (CO), 161.5 (C=NH), 132.7, 131.4, 130.9, 128.6, 127.0 (Ar), 82.5, 74.7, 72.1, 67.3 (C-1-C-5), 61.9 (C-6) ppm. Anal. Calcd. for $C_{22}H_{26}N_3O_9Br$ (556.36): C, 47.49, H, 4.71; N, 7.55. Found: C, 47.39; H, 4.63; N, 7.63.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AcO
OAc
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H
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NH
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1000
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1.02
1.09
1.00
3.13
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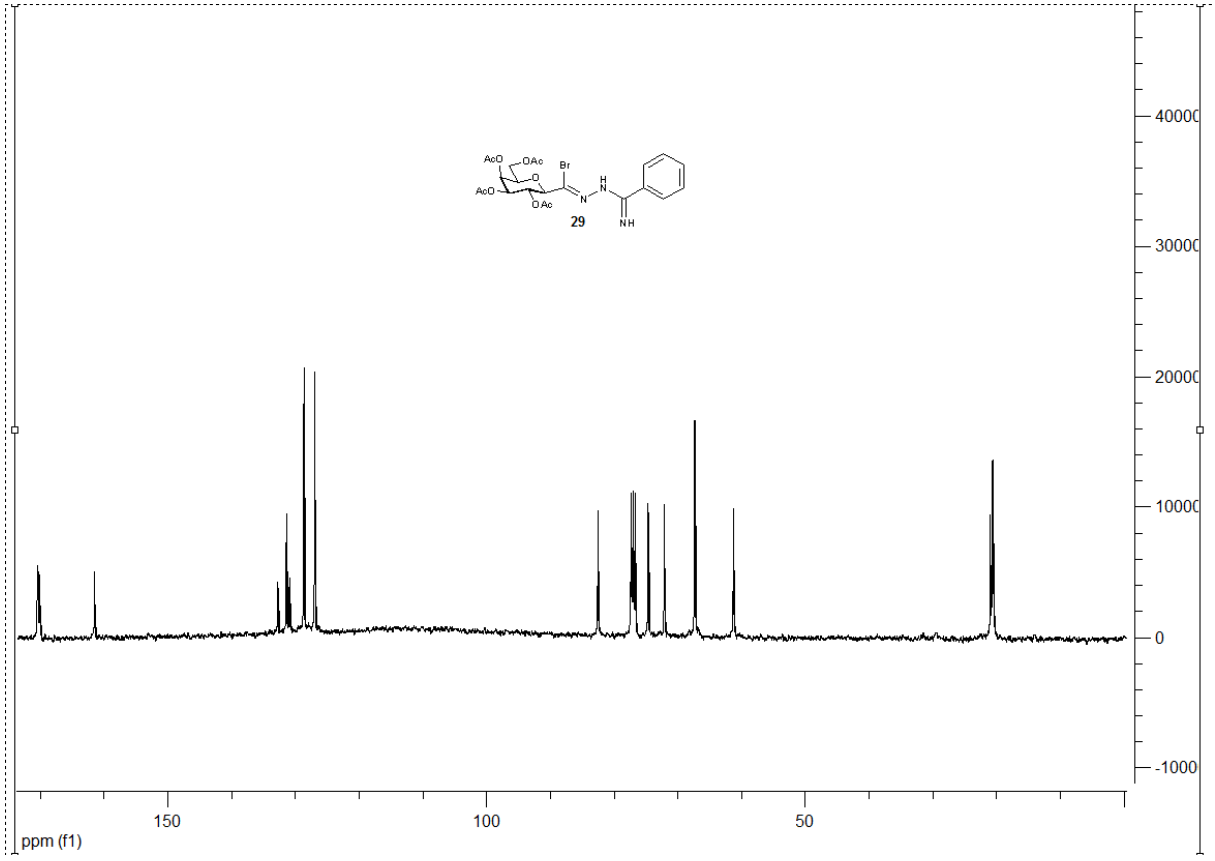
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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OAc
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O
AcO
OAc
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H
N
NH
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30000
20000
10000
0
-1000
150
100
50
ppm (f1)

General procedure V for the synthesis of *O*-peracylated 5-(β-D-glycopyranosyl)-3-substituted-1,2,4-triazoles (21, 30-33)

A carbohydrazonoyl bromide (**24-29**, 0.14 mmol) was dissolved in glacial AcOH (3 mL), then NH_4OAc (0.012 g, 0.15 mmol) was added. The mixture was stirred and heated at 110 °C. When the reaction was complete (TLC, EtOAc/toluene = 2:7) the mixture was diluted with H_2O (6 mL), and washed with CH_2Cl_2 (3 x 7 mL). The organic layer was separated and washed with cold, saturated $NaHCO_3$ solution (8 mL), and H_2O (8 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography.

General procedure VI for the synthesis of *O*-peracylated 5-(β-D-glycopyranosyl)-3-substituted-1,2,4-triazoles (21, 30)

A carbohydrazonoyl bromide (**24-26**, 0.10 mmol) was dissolved in anhydrous pyridine (6 mL). The mixture was stirred and heated at 110 °C. The reaction was monitored by TLC (EtOAc/toluene = 1:3). When the reaction was complete the solvent was evaporated under reduced pressure. The residue was purified by column chromatography.

3-Phenyl-5-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-triazole (21) Prepared from **25** (0.04 g, 0.05 mmol) according to **General procedure V**. Purified by column chromatography (EtOAc/toluene = 1:3) to yield the title compound **21** as a white solid (0.021 g, 56%).

Prepared from **25** (0.1 g, 0.12 mmol) according to **General procedure VI**. Purified by column chromatography (EtOAc/toluene = 1:3) to yield the title compound **21** as a white solid (0.05 g, 58%).

Characterization data correspond to the lit. values.[5] The original spectra are available in the supporting information of that publication at http://dx.doi.org/10.1016/j.tet.2013.09.099.

3-(Pyridin-2-yl)-5-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-triazole (30):

Prepared from **26** (0.25 g, 0.31 mmol) according to **General procedure V**. Purified by column chromatography (EtOAc/toluene = 1:3) to yield the title compound **30** as a white solid(0.07 g, 32%).

Prepared from **26** (0.11 g, 0.10 mmol) according to **General procedure VI**. Purified by column chromatography (EtOAc-toluene 1:3) to yield the title compound **30** as a white solid (0.05 g, 53%).

Characterization data correspond to the lit. values.[5] The original spectra are available in the supporting information of that publication at http://dx.doi.org/10.1016/j.tet.2013.09.099.

3-(Naphthalen-2-yl)-5-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2,4-triazole (31)

Prepared from **27** (0.12 g, 0.14 mmol) according to **General procedure V**. Purified by column chromatography (EtOAc/toluene = 2:7) to yield the title compound **31** as a white solid (0.06 g, 55%).

Characterization data correspond to the lit. values.[5] The original spectra are available in the supporting information of that publication at http://dx.doi.org/10.1016/j.tet.2013.09.099.

3-Phenyl-5-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-1,2,4-triazole (32) Prepared from **28** (crude product,0.23 g, 0.35 mmol) according to **General procedure V**. Purified by column chromatography (EtOAc/hexane = 2:3) to yield the title compound **32** as a white solid (0.07 g, 32%). m.p. 173-175 °C; $[\alpha]_D$ = –48 (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.60 (s, 1 H, NH-triazole), 8.08-7.76 (m, 8 H, Ar), 7.50-7.20 (m, 12 H, Ar), 6.15-5.97 (m, 2 H, H-2, H-3), 5.62-5.47 (m, 1 H, H-4), 5.06 (d, J = 9.1 Hz, 1 H, H-1), 4.52 (dd, J = 5.4, 11.3 Hz, 1 H, H-5a), 3.76 (pseudo t, J = 10.6 Hz, 1 H, H-5b) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

165.9, 165.5, 165.3 (CO), 158.2, 158.0 (C-3-, C-5-triazole), 133.4-126.5 (Ar), 74.5, 73.6, 71.2, 70.0 (C-1-C-4), 67.2 (C-5) ppm. Anal. Calcd. for $C_{34}H_{27}N_3O_7$ (589.59): C, 69.26; H, 4.62; N, 7.13. Found: C, 69.11; H, 4.51; N, 7.23.

3-Phenyl-5-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1,2,4-triazole (33) Prepared from **29** (0.13 g, 0.23 mmol) according to **General procedure V**. Purified by column chromatography (EtOAc/hexane = 2:3) to yield the title compound **33** as a colourless amorphous solid (0.07 g, 64%). R_f 0.22 (EtOAc/hexane = 1:1); $[\alpha]_D$ = +22 (c 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-7.94 (m, 2 H, Ar), 7.44-7.36 (m, 3 H, Ar), 5.73 (pseudo t, J = 10.0 Hz, 1 H, H-2), 5.54 (d, J = 3.3 Hz, 1 H, H-4), 5.25 (dd, J = 3.1, 10.0 Hz, 1 H, H-3), 4.81 (d, J = 9.9 Hz, 1 H, H-1), 4.17-4.13 (m, 3 H, H-5, H-6a, H-6b), 2.08, 2.01, 1.96 (3 s, 12 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.1, 170.0 (CO), 158.0, 157.5 (C-3-, C-5-triazole), 130.0, 128.7, 128.0, 126.4 (Ar), 74.9, 74.0, 71.9, 67.9, 67.4 (C-1-C-5), 61.5 (C-6) ppm. Anal. Calcd. for $C_{22}H_{25}N_3O_9$ (475.45): C, 55.58; H, 5.30; N, 8.84. Found: C, 55.41; H, 5.19; N, 8.93.

General procedure VII for the synthesis of N^1-arylidene-benzamidrazones (35)

Ethylbenzimidate (**34**, 1.01 mmol) was dissolved in dry EtOH (10mL), and the corresponding aryl hydrazone (1.01 mmol) was added. The reaction mixture was stirred and heated at reflux temperature overnight. The reaction was monitored by TLC (EtOAc/hexane = 1:3). When the reaction was complete the solvent was evaporated under reduced pressure, and the residue was crystallized from ethanol-hexane mixture.

General procedure VIII for the synthesis of N^1-arylidene-arenecarboxamidrazones (35, 36)

An arenecarboxamidrazone (**5**[5] or **6**[6], 1.1 mmol) was dissolved in dry EtOH (8 mL), and the corresponding aromatic aldehyde (1.21 mmol) was added. The reaction mixture was stirred and heated at reflux temperature. The reaction was monitored by TLC (EtOAc/hexane = 1:2). When the reaction was complete the solvent was evaporated under reduced pressure, and the residue was crystallized from ethanol-hexane mixture.

***N^1*-(4-Fluorobenzylidene)-benzamidrazone (35a)** Prepared from ethylbenzimidate (**34**, 0.15 g, 1.01 mmol) and 4-fluorobenzaldehyde hydrazone (0.14 g, 1.01 mmol) according to **General procedure VII** to yield **35a** as a white solid (0.21 g, 86%).

Prepared from benzamidrazone (**5**, 0.30 g, 2.22 mmol) and 4-fluorobenzaldehyde (0.26 mL, 2.44 mmol) according to **General procedure VIII** to yield **35a** as a white solid (0.50 g, 93%). m.p. 158-160 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.46 (s, 1 H, CH=N), 8.18-7.80 (m, 4 H, Ar), 7.68-7.20 (m, 5 H, Ar), 7.10 (brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 163.4 (d, J = 246.4 Hz, Ar), 159.3 (C=NH), 152.4 (CH=N), 134.3, 132.7, 130.7, 130.2 (d, J = 8.0 Hz), 128.6, 127.2, 116.0 (d, J = 21.6 Hz) (Ar) ppm. Anal. Calcd. for $C_{14}H_{12}N_3F$ (241.26): C, 69.70; H, 5.01; N, 17.42. Found: C, 69.82; H, 5.14; N, 17.30.

***N*^{1}-(3-Chlorobenzylidene)-benzamidrazone (35b):** Prepared from benzamidrazone (**5**,0.30 g, 2.22 mmol) and 3-chlorobenzaldehyde (0.28mL, 2.44 mmol) according to **General procedure VIII** to yield **35b** as a white solid (0.46 g, 81%). m.p. 136-138 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.44 (s, 1 H, CH=N), 8.09 (s, 1 H, Ar), 7.96 (d, *J* = 6.8 Hz, 2 H, Ar), 7.86-7.75 (m, 1 H, Ar), 7.54-7.36 (m, 5 H, Ar), 7.21 (brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 159.3 (C=NH), 151.4 (CH=N), 137.9, 133.7, 133.5, 130.3, 130.2, 129.1, 128.1, 126.8, 126.6, 126.5 (Ar) ppm. Anal. Calcd. for $C_{14}H_{12}N_3Cl$ (257.72): C, 65.25; H, 4.69; N, 16.30. Found: C, 65.12; H, 4.79; N, 16.19.

***N*^{1}-(4-Bromobenzylidene)-benzamidrazone (35c):** Prepared from ethylbenzimidate (**34**, 0.15 g, 1.01 mmol) and 4-bromobenzaldehyde hydrazone (0.20 g, 1.01 mmol) according to **General procedure VII** to yield **35c** as a white solid (0.12 g, 39%).

Prepared from benzamidrazone (**5**, 0.20 g, 1.48 mmol) and 4-bromobenzaldehyde (0.30g, 1.63 mmol) according to **General procedure VIII** to yield **35c** as a white solid (0.38 g, 85%). m.p. 154-156 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.43 (s, 1 H, CH=N), 7.95 (d, *J* = 6.5 Hz, 2 H, Ar), 7.87 (d, *J* = 8.0 Hz, 2 H, Ar), 7.62 (d, *J* = 8.0 Hz, 2 H, Ar), 7.54-7.40 (m, 3 H, Ar), 7.14 (brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ159.0 (C=NH), 151.8 (CH=N),134.9, 133.7, 131.4, 130.3, 129.5, 128.1, 126.7, 122.8 (Ar) ppm. Anal. Calcd. for $C_{14}H_{12}N_3Br$ (302.17): C, 55.65; H, 4.00; N, 13.91. Found: C, 55.55; H, 4.11; N, 13.98.

***N*^{1}-(4-Methylbenzylidene)-benzamidrazone (35d):** Prepared from benzamidrazone (**5**, 0.30 g, 2.22 mmol) and 4-methylbenzaldehyde (0.29 mL, 2.44 mmol) according to **General procedure VIII** to yield **35d** as a white solid (0.43 g, 82%). m.p. 197-199 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.41 (s, 1 H, CH=N), 7.96 (dd, *J* = 1.3, 7.5 Hz, 2 H, Ar), 7.78 (d, *J* =

8.0 Hz, 2 H, Ar), 7.49-7.40 (m, 3 H, Ar), 7.24 (d, *J* = 8.0 Hz, 2 H, Ar), 6.97 (brs, 2 H, 2 NH), 2.35 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 158.4 (C=NH), 153.1 (CH=N), 139.3, 133.8, 132.8, 130.1, 129.1, 128.0, 127.6, 126.6 (Ar), 20.98 (CH_3) ppm. Anal. Calcd. for $C_{15}H_{15}N_3$ (237.3): C, 75.92; H, 6.37; N, 17.71. Found: C, 75.80; H, 6.25; N, 17.82.

***N*^{1}-(4-Methylthiobenzylidene)-benzamidrazone (35e):** Prepared from benzamidrazone (**5**, 0.15 g, 1.11 mmol) and 4-methylthiobenzaldehyde (0.16 mL, 1.22 mmol) according to **General procedure VIII** to yield **35e** as a white solid (0.24 g, 80%). m.p. 189-191 °C; ^1H NMR (400 MHz, DMSO-d6): δ = 8.39 (s, 1 H, CH=N), 7.93 (d, *J* = 6.7 Hz, 2 H, Ar), 7.82 (d, *J* = 7.8 Hz, 2 H, Ar), 7.51-7.37 (m, 3 H, Ar), 7.27 (d, *J* = 7.8 Hz, 2 H, Ar), 7.02 (brs, 2 H, 2 NH), 2.50 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 158.4 (C=NH), 152.6 (CH=N), 140.2, 133.8, 132.1, 130.2, 128.1, 126.6, 125.4 (Ar), 14.3 (CH_3) ppm. Anal. Calcd. for $C_{15}H_{15}N_3S$ (269.36): C, 66.88; H, 5.61; N, 15.60. Found: C, 66.81; H, 5.69; N, 15.68.

***N*^{1}-(4-Methoxybenzylidene)-benzamidrazone (35f):** Prepared from ethylbenzimidate (**34**, 0.15 g, 1.01 mmol) and 4-methoxybenzaldehyde hydrazone (0.15 g, 1.01 mmol) according to **General procedure VII** to yield **35f** as a white solid (0.12 g, 47%).
Prepared from benzamidrazone (**5**, 0.30 g, 2.22 mmol) and 4-methoxybenzaldehyde (0.30mL, 2.44 mmol) according to **General procedure VIII** to yield **35f** as a white solid (0.51 g, 90%). m.p. 143-145 °C; ^1H NMR (400 MHz, DMSO-d6): δ = 8.40 (s, 1 H, CH=N), 8.10-7.70 (m, 4 H, Ar), 7.60-7.30 (m, 3 H, Ar), 7.15-6.73 (m, 4 H, Ar, 2 NH), 3.81 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.5, 158.0 (C=NH, C-OMe), 152.8 (CH=N), 133.9, 130.0, 129.2, 128.2, 128.0, 126.5, 114.0 (Ar), 55.2 (CH_3) ppm. Anal. Calcd. for $C_{15}H_{15}N_3O$ (253.3): C, 71.13; H, 5.97; N, 16.59. Found: C, 71.01; H, 6.09; N, 16.47.

***N*^{1}-(4-Nitrobenzylidene)-benzamidrazone (35g):** Prepared from ethylbenzimidate (**34**, 0.15 g, 1.01 mmol) and 4-nitrobenzaldehyde hydrazone (0.17 g, 1.01 mmol) according to **General procedure VII** to yield **35g** as an orange solid (0.16 g, 59%).

Prepared from benzamidrazone (**5**, 0.15 g, 1.11 mmol) and 4-nitrobenzaldehyde (0.18 g, 1.22 mmol) according to **General procedure VIII** to yield **35g** as an orange solid (0.28 g, 94%). m.p. 195-198 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.56 (s, 1 H, CH=N), 8.26 (d, J = 8.7 Hz, 2 H, Ar), 8.18 (d, J = 8.7 Hz, 2 H, Ar), 7.98 (d, J = 7.5 Hz, 2 H, Ar), 7.55-7.42 (m, 3 H, Ar), 7.38 (brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.7 (C=NH), 151.2 (CH=N), 148.0, 142.6, 134.0, 131.1, 128.9, 128.7, 127.4, 124.2 (Ar) ppm. Anal. Calcd. for $C_{14}H_{12}N_4O_2$ (268.27): C, 62.68; H, 4.51; N, 20.88. Found: C, 62.80; H, 4.63; N, 20.99.

***N*^{1}-(4-Cyanobenzylidene)-benzamidrazone (35h):** Prepared from ethylbenzimidate (**34**, 0.15 g, 1.01 mmol) and 4-cyanobenzaldehyde hydrazone (0.15 g, 1.01 mmol) according to **General procedure VII** to yield **35h** as a white solid (0.21 g, 84%).

Prepared from benzamidrazone (**5**, 0.20 g, 1.48 mmol) and 4-cyanobenzaldehyde (0.21g, 1.63 mmol) according to **General procedure VIII** to yield **35h** as a white solid (0.29 g, 78%). m.p. 190-192 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.50 (s, 1 H, CH=N), 8.10 (d, J = 7.9 Hz, 2 H, Ar), 7.97 (d, J = 6.9 Hz, 2 H, Ar), 7.87 (d, J = 7.9 Hz, 2 H, Ar), 7.55-7.40 (m, 3 H, Ar), 7.35 (brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 159.9 (C=NH), 151.2 (CH=N), 140.1, 133.4, 132.4, 130.6, 128.2, 126.9, 118.9 (Ar), 111.2 (CN) ppm. Anal. Calcd. for $C_{15}H_{12}N_4$ (248.28): C, 72.56; H, 4.87; N, 22.57. Found: C, 72.49; H, 4.96; N, 22.65.

***N*^{1}-(4-Acetamidobenzylidene)-benzamidrazone (35i):** Prepared from ethylbenzimidate (**34**, 0.15 g, 1.01 mmol) and 4-acetamidobenzaldehyde hydrazone (0.18 g, 1.01 mmol) according to **General procedure VII** to yield **35i** as a white solid (0.21 g, 74%).

Prepared from benzamidrazone (**5**, 0.15 g, 1.11 mmol) and 4-acetamidobenzaldehyde (0.20 g, 1.22 mmol) according to **General procedure VIII** to yield **35i** as a white solid (0.25 g, 82%). m.p. 199-202 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 10.11 (s, 1 H, NH), 8.38 (s, 1 H, CH=N), 7.95 (d, J = 6.4 Hz, 2 H, Ar), 7.82 (d, J = 8.2 Hz, 2 H, Ar), 7.65 (d, J = 8.1 Hz, 2 H, Ar), 7.51-7.39 (m, 3 H, Ar), 7.00 (brs, 2 H, 2 NH), 2.07 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 168.9 (CO), 158.8 (C=NH), 153.3 (CH=N), 141.1, 134.4, 130.8, 130.6, 128.8, 128.6, 127.1, 119.2 (Ar), 24.6 (CH_3) ppm. Anal. Calcd. for $C_{16}H_{16}N_4O$ (280.32): C, 68.55; H, 5.75; N, 19.99. Found: C, 68.48; H, 5.69; N, 19.91.

***N*^{1}-(4-Hydroxybenzylidene)-benzamidrazone (35j):** Prepared from benzamidrazone (**5**, 0.20 g, 1.48 mmol) and 4-hydroxybenzaldehyde (0.20 g, 1.63 mmol) according to **General procedure VIII** to yield **35j** (0.33 g, 93%) as a yellow solid. m.p. 179-182 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 9.87 (s, 1 H, OH), 8.35 (s, 1 H, CH=N), 7.93 (d, J = 6.4 Hz, 2 H, Ar), 7.72 (d, J = 8.3 Hz, 2 H, Ar), 7.51-7.35 (m, 3 H, Ar), 6.89 (brs, 2 H, 2 NH), 6.82 (d, J = 8.3 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 159.6, 158.2 (C=NH, C-OH), 153.8 (CH=N), 134.5, 130.5, 129.9, 128.6, 127.2, 127.0, 115.9 (Ar) ppm. Anal. Calcd. for $C_{14}H_{13}N_3O$ (239.27): C, 70.28; H, 5.48; N, 17.56. Found: C, 70.40; H, 5.56; N, 17.49.

***N*^{1}-[(Pyridin-4-yl)methylidene]-benzamidrazone (35k):** Prepared from benzamidrazone (**5**, 0.10 g, 0.74 mmol) and 4-pyridinecarboxaldehyde (0.077 mL, 0.81 mmol) according to **General procedure VIII** to yield **35k** as a yellow solid (0.13 g, 77%). m.p. 169-172 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.62 (s, 2 H, Ar), 8.43 (s, 1 H, CH=N), 7.97 (d, J = 7.0 Hz, 2 H, Ar), 7.90-7.81 (m, 2 H, Ar), 7.56-7.39 (m, 3 H, Ar), 7.32 (brs, 2 H, 2 NH). ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.6 (C=NH), 151.2 (CH=N), 150.4, 143.1, 134.0, 131.1, 128.7,

127.4, 122.0 (Ar) ppm. Anal. Calcd. for $C_{13}H_{12}N_4$ (224.26): C, 69.62; H, 5.39; N, 24.98. Found: C, 69.74; H, 5.28; N, 25.09.

***N*^{1}-(4-Fluorobenzylidene)-pyridine-2-carboxamidrazone (36a):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.13 g, 0.92 mmol) and 4-fluorobenzaldehyde (0.11 mL, 1.01 mmol) according to **General procedure VIII** to yield **36a** as a white solid (0.20 g, 75%). m.p. 115-117 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.65 (d, J = 3.9 Hz, 1 H, Ar), 8.49 (s, 1 H, CH=N), 8.23 (d, J = 7.8 Hz, 1 H, Ar), 8.04-7.88 (m, 3 H, Ar), 7.57-7.48 (m, 1 H, Ar), 7.33-7.23 (m, 2 H, Ar), 7.11 (brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 163.0 (d, J = 247.9 Hz, Ar), 156.5 (C=NH), 152.8 (CH=N), 150.2, 148.4, 136.9, 131.9, 129.9 (d, J = 8.2 Hz), 125.3, 121.0, 119.4, 115.6, 115.5 (d, J = 21.7 Hz) (Ar) ppm. Anal. Calcd. for $C_{13}H_{11}N_4F$ (242.25): C, 64.45; H, 4.58; N, 23.13. Found: C, 64.38; H, 4.51; N, 23.23.

***N*^{1}-(3-Chlorobenzylidene)-pyridine-2-carboxamidrazone (36b):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.15 g, 1.10 mmol) and 3-chlorobenzaldehyde (0.14 mL, 1.21 mmol) according to **General procedure VIII** to yield **36b** as a white solid (0.19 g, 61%). m.p. 70-72 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ= 8.67 (d, J = 4.4 Hz, 1 H, Ar), 8.48 (s, 1 H, CH=N), 8.24 (d, J = 7.9 Hz, 1 H, Ar), 8.12 (s, 1 H, Ar), 7.97-7.88 (m, 1 H, Ar), 7.87-7.78 (m, 1 H, Ar), 7.58-7.50 (m, 1 H, Ar), 7.49-7.50 (m, 2 H, Ar),7.38, 7.15 (2 brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 157.0 (C=NH), 152.4 (CH=N), 150.1, 148.5, 137.6, 136.9, 133.5, 130.3, 129.3, 126.8, 126.7, 125.4, 121.1 (Ar) ppm. Anal. Calcd. for $C_{13}H_{11}N_4Cl$ (258.71): C, 60.35; H, 4.29; N, 21.66. Found: C, 60.46; H, 4.38; N, 21.74.

***N*^{1}-(4-Bromobenzylidene)-pyridine-2-carboxamidrazone (36c):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.15 g, 1.10 mmol) and 4-bromobenzaldehyde (0.22

g, 1.21 mmol) according to **General procedure VIII** to yield **36c** as a white solid (0.30 g, 85%). m.p. 145-148 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.66 (bs, 1 H, Ar), 8.47 (s, 1 H, CH=N), 8.23 (d, J = 6.6 Hz, 1 H, Ar), 7.97-7.83 (m, 3 H, Ar), 7.64 (d, J = 6.5 Hz, 2 H, Ar), 7.56-7.47 (m, 1 H, Ar), 7.16 (brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 156.7 (C=NH), 152.8 (CH=N), 150.1, 148.4, 136.9, 134.6, 131.4, 129.6, 125.3, 123.0, 121.0 (Ar) ppm. Anal. Calcd. for $C_{13}H_{11}N_4Br$ (303.16): C, 51.50; H, 3.66; N, 18.48. Found: C, 51.59; H, 3.72; N, 18.56.

***N*^{1}-(4-Methylbenzylidene)-pyridine-2-carboxamidrazone (36d):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.30 g, 2.22 mmol) and 4-methylbenzaldehyde (0.29 mL, 2.43 mmol) according to **General procedure VIII** to yield **36d** as a white solid (0.39 g, 74%). m.p. 119-121 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.66 (bs, 1 H, Ar), 8.47 (s, 1 H, CH=N), 8.24 (d, J = 6.6 Hz, 1 H, Ar), 8.00-7.65 (m, 3 H, Ar), 7.60-7.40 (m, 1 H, Ar), 7.38-7.19 (m, 2 H, Ar), 7.05 (brs, 2 H, 2 NH), 2.34 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 156.2 (C=NH), 154.1 (CH=N), 150.3, 148.4, 139.6, 136.8, 132.6, 129.1, 127.8, 125.3, 121.0 (Ar), 21.0 (CH_3) ppm. Anal. Calcd. for $C_{14}H_{14}N_4$ (238.29): C, 70.57; H, 5.92; N, 23.51. Found: C, 70.65; H, 5.83; N, 23.59.

***N*^{1}-(4-(Methylthiobenzylidene)-pyridine-2-carboxamidrazone (36e):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.18 g, 1.32 mmol) and 4-methylthiobenzaldehyde (0.19 mL, 1.46 mmol) according to **General procedure VIII** to yield **5i** as a yellow solid (0.29 g, 82%). m.p. 151-153 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.67 (d, J = 4.0 Hz, 1 H, Ar), 8.45 (s, 1 H, CH=N), 8.22 (d, J = 7.4 Hz, 1 H, Ar), 7.96-7.90 (m, 1 H, Ar), 7.87 (d, J = 8.3 Hz, 2 H, Ar), 7.60-7.48 (m, 1 H, Ar), 7.30 (d, J = 8.3 Hz, 2 H, Ar), 7.06 (brs, 2 H, 2 NH), 2.52 (s, 3 H, SCH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 156.25 (C=NH), 153.7

(CH=N), 150.3, 148.4, 140.6, 136.9, 131.8, 128.2, 125.4, 125.3, 121.0 (Ar), 14.2 (SCH_3) ppm. Anal. Calcd. for $C_{14}H_{14}N_4S$ (270.35): C, 62.20; H, 5.22; N, 20.72. Found: C, 62.28; H, 5.31; N, 20.83.

***N*^{1}-(4-Methoxybenzylidene)-pyridine-2-carboxamidrazone (36f):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.15 g, 1.10 mmol) and 4-methoxybenzaldehyde (0.15 mL, 1.21 mmol) and according to **General procedure VIII** to yield **36f** as a white solid (0.22 g, 79%). m.p. 112-113 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.66 (d, J = 4.5 Hz, 1 H, Ar), 8.44 (s, 1 H, CH=N), 8.23 (d, J = 7.9 Hz, 1 H, Ar), 7.96-7.83 (m, 3 H, Ar), 7.56-7.48 (m, 1 H, Ar), 7.09-6.95 (m, 4 H, Ar, 2 NH), 3.81 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.5, 155.7 (C-OMe, C=NH), 153.6 (CH=N), 150.1, 148.2, 136.6, 129.2, 127.7, 125.0, 120.6, 113.8 (Ar), 55.0 (CH_3) ppm. Anal. Calcd. for $C_{14}H_{14}N_4O$ (254.29): C, 66.13; H, 5.55; N, 22.03. Found: C, 66.21; H, 5.62; N, 22.13.

***N*^{1}-(4-Nitrobenzylidene)-pyridine-2-carboxamidrazone (36g):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.15 g, 1.10 mmol) and 4-nitrobenzaldehyde (0.18 g, 1.21 mmol) according to **General procedure VIII** to yield **36g** as an orange solid (0.26 g, 87%). m.p. 218-220 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.67 (d, J = 4.3 Hz, 1 H, Ar), 8.60 (s, 1 H, CH=N), 8.32-8.18 (m, 5 H, Ar), 8.01-7.90 (m, 1 H, Ar), 7.60-7.53 (m, 1 H, Ar), 7.50, 7.33 (2 brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 157.8 (C=NH), 151.7 (CH=N), 150.0, 148.6, 147.6, 141.7, 137.1, 128.6, 125.7, 123.7, 121.4 (Ar) ppm. Anal. Calcd. for $C_{13}H_{11}N_5O_2$ (269.26): C, 57.99; H, 4.12; N, 26.01. Found: C, 58.09; H, 4.19; N, 26.11.

***N*^{1}-(4-Cyanobenzylidene)-pyridine-2-carboxamidrazone (36h):** Prepared from pyridinecarboximidic acid, hydrazide (**6**, 0.23 g, 1.69 mmol) and 4-cyanobenzaldehyde (0.24 g, 1.86 mmol) according to **General procedure VIII** to yield **36h** as a white solid (0.34 g, 81%). m.p. 192-194 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ 8.67 (brs, 1 H, Ar), 8.55 (s, 1 H, CH=N), 8.24 (d, J = 7.6 Hz, 1 H, Ar), 8.13 (d, J = 7.4 Hz, 2 H, Ar), 7.98-7.75 (m, 3 H, Ar), 7.60-7.50 (m, 1 H, Ar), 7.43, 7.27 (2 brs, 2 H, 2 NH) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 157.5 (C=NH), 152.2 (CH=N), 150.0, 148.5, 139.8, 137.0, 132.3, 128.2, 125.5, 121.3, 118.8 (Ar), 111.5 (CN) ppm. Anal. Calcd. for $C_{14}H_{11}N_5$ (249.27): C, 67.46; H, 4.45; N, 28.10. Found: C, 67.37; H, 4.52; N, 28.18.

***N*^{1}-(4-Acetamidobenzylidene)-pyridine-2-carboxamidrazone (36i):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.30 g, 2.21 mmol) and 4-acetamidobenzaldehyde (0.40 g, 2.43 mmol) according to **General procedure VIII** to yield **36i** as a white solid (0.62 g, 95%). m.p. 193-195 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 10.12 (s, 1 H, NH), 8.65 (d, J = 4.4 Hz, 1 H, Ar), 8.42 (s, 1 H, CH=N), 8.22 (d, J = 7.9 Hz, 1 H, Ar), 7.95-7.87 (m, 1 H, Ar), 7.84 (d, J = 8.5 Hz, 2 H, Ar), 7.65 (d, J = 8.5 Hz, 2 H, Ar), 7.55-7.47 (m, 1 H, Ar), 7.01 (brs, 2 H, 2 NH), 2.07 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 168.4 (CO), 156.1 (C=NH), 153.7 (CH=N), 150.3, 148.4, 140.8, 136.8, 130.0, 128.4, 125.2, 120.9, 118.6 (Ar), 24.1 (CH_3). Anal. Calcd. for $C_{15}H_{15}N_5O$ (281.31): C, 64.04; H, 5.37; N, 24.90. Found: C, 64.11; H, 5.31; N, 24.98.

***N*^{1}-[(Pyridin-4-yl)methylidene]-pyridine-2-carboxamidrazone (36j):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.10 g, 0.74 mmol) and 4-pyridinecarboxaldehyde (0.077 mL, 0.81 mmol) according to **General procedure VIII** to yield **36j** as a yellow solid

(0.26 g, 81%). m.p. 152-155 °C (lit.[7] m.p. 151 °C); NMR data correspond to the literature values.[7]

***N*^{1}-(4-Hydroxybenzylidene)-pyridine-2-carboxamidrazone (36k):** Prepared from pyridinecarboximidic acid hydrazide (**6**, 0.18 g, 1.32 mmol) and 4-hydroxybenzaldehyde (0.18 g, 1.46 mmol) according to **General procedure VIII** to yield **36k** as a yellow solid (0.27 g, 79%). m.p. 195-197 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 9.92 (s, 1 H, OH), 8.64 (d, J = 4.7 Hz, 1 H, Ar), 8.39 (s, 1 H, CH=N), 8.27-8.17 (m, 1 H, Ar), 7.96-7.86 (m, 1 H, Ar), 7.74 (d, J = 8.5 Hz, 2 H, Ar), 7.57-7.47 (m, 1 H, Ar), 6.88 (brs, 2 H, 2 NH), 6.83 (d, J = 8.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 159.3, 155.7 (C=NH, C-OH), 154.3 (CH=N), 150.4, 148.4, 136.8, 129.6, 126.4, 125.1, 120.8, 115.4 (Ar) ppm. Anal. Calcd. for $C_{13}H_{12}N_4O$ (240.26): C, 64.99; H, 5.03; N, 23.32. Found: C, 64.90; H, 5.11; N, 23.41.

General procedure IX for the synthesis of asymmetric 3,5-disubstituted-1,2,4-triazoles (39, 40)

An arylidene amidazone (**35** or **36**, 0.331 mmol) was dissolved in CH_2Cl_2 (10 mL), and NBS (0.059 g, 0.331 mmol) was added. The reaction mixture was stirred at room temperature. When the reaction was complete (TLC, EtOAc/hexane = 1:3) the solvent was evaporated under reduced pressure.The crude product was dissolved in glacial acetic acid (8 mL), then ammonium acetate (0.028 g, 0.364 mmol) was added. The reaction mixture was stirred and heated at 110 °C overnight. When the reaction was complete (TLC, EtOAc/toluene = 1:3) the mixture was diluted with H_2O (30 mL), and washed with EtOAc (4 x 15 mL). The organic layer was separated, and washed with water (15 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc/hexane = 1:2).

General procedure X for the synthesis of asymmetric 3,5-disubstituted-1,2,4-triazoles(39, 40)

An arylidene amidazone (**35** or **36**, 0.83 mmol) and ammonium acetate (0.13 g, 0.1.66 mmol) was dissolved in glacial AcOH (16 mL), then NBS (0.148 g, 0.83 mmol) was added. The mixture was stirred and heated at 110 °C overnight. When the reaction was complete (TLC, EtOAc/toluene = 1:3) the mixture was diluted with H_2O (30 mL), and washed with EtOAc (4 x 15 mL). The organic layer was separated, and washed with water (15 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc/hexane = 1:2).

3-(4-Fluorophenyl)-5-phenyl-1,2,4-triazole (39a) and 4-(4-fluorobenzylidene-amino)-3-(4-fluorophenyl)-5-phenyl-1,2,4-triazole (41a): Prepared from **35a** (0.10 g, 0.41 mmol) according to **General procedure IX**. Purified by column chromatography (EtOAc/hexane = 1:2) to yield **39a** as a white solid (0.022 g, 22%) and **41a** as a white amorphous solid (0.021 g, 14%).

Prepared from **35a** (0.20 g, 0.83 mmol) according to **General procedure X** to yield **39a** as a white solid (0.135 g, 68%).

39a: m.p. 220-222 °C (lit.[8] m.p. 208-211 °C); ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.55 (brs, 1 H, NH), 8.35-7.92 (m, 4 H, Ar), 7.70-7.06 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 163.1 (d, J = 246.7 Hz, Ar), 160.6, 155.0 (C-3-, C-5-triazole), 129.7, 128.9, 128.2, 126.0, 115.8 (d, J = 21.6 Hz) (Ar) ppm. ESI-MS (positive mode) m/z calcd. for $C_{14}H_{10}N_3F$ (239.25), Found: 239.1 $[M]^+$.

41a: R_f: 0.2 (EtOAc/hexane = 1:2); ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.56 (s, 1 H, CH=N), 8.21-7.91 (m, 3 H, Ar), 7.90-7.71 (m, 3 H, Ar), 7.58-7.31 (m, 4 H, Ar), 7.21-6.96 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6) δ = 165.4 (d, J = 251.4 Hz, Ar), 165.0 (d, J = 246.5 Hz, Ar), 159.7 (C-3-, C-5-triazol), 154.7 (CH=N), 133.7-126.4 (Ar), 115.7 (d, J = 21.9 Hz) (Ar) ppm. ESI-MS (positive mode) m/z calcd. for $C_{21}H_{14}N_4F_2$ (360.36), Found: 360.1 $[M]^+$.

3-(3-Chlorophenyl)-5-phenyl-1,2,4-triazole (39b): Prepared from **35b** (0.10 g, 0.39 mmol) according to **General procedure IX** to yield **39b** as a white solid (0.034 g, 34%).

Prepared from **35b** (0.20 g, 0.78 mmol) according to **General procedure X** to yield **39b** as a white solid (128 mg, 64%). m.p. 219-220 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.58 (s, 1 H, NH), 8.13-7.90 (m, 4 H, Ar), 7.54-7.35 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-

d6): δ = 160.1, 155.4 (C-3-, C-5-triazole), 133.6, 130.8, 129.8, 128.9, 126.0, 125.5, 124.4 (Ar) ppm. ESI-MS (positive mode) m/z calcd. for $C_{14}H_{10}N_3Cl$ (255.70), Found: 255.1 $[M]^+$.

3-(4-Bromophenyl)-5-phenyl-1,2,4-triazole (39c): Prepared from **35c** (0.10 g, 0.33 mmol) according to **General procedure IX** to yield **39c** as a white solid (22 mg, 22%).
Prepared from **35c** (0.10 g, 0.33 mmol) according to **General procedure X** to yield **39c** as a white solid (0.06 g,60%). m.p. 255-257 °C (lit.[9] m.p. 249-251 °C); ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.60 (s, 1 H, NH), 8.25-7.98 (m, 4 H, Ar), 7.81-7.68 (m, 2 H, Ar), 7.57-7.48 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 161.8, 156.0 (C-3-, C-5-triazole), 132.9, 130.9, 130.0, 129.0, 127.1, 123.7 (Ar) ppm. ESI-MS (positive mode) m/z calcd. for $C_{14}H_{10}N_3Br$ (300.15), Found: 300.0 $[M]^+$.

3-(4-Methylphenyl)-5-phenyl-1,2,4-triazole (39d) and 4-(4-methylbenzylidene-amino)-3-(4-methylphenyl)-5-phenyl-1,2,4-triazole (41d): Prepared from **35d** (0.10 g, 0.42 mmol) according to **General procedure IX**. Purified by column chromatography (EtOAc/hexane = 1:2) to yield **39d** as a white solid (17 mg, 17%) and **41d** as a white amorphous solid (0.056 g, 38%).
Prepared from **35d** (0.05 g, 0.21 mmol) according to **General procedure X** to yield **39d** as a white solid (25 mg, 50%).
39d: m.p. 178-181 °C (lit.[10] m.p. 180-183 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.49 (s, 1 H, NH), 7.94 (d, J = 8.0 Hz, 2 H, Ar), 7.82 (d, J = 8.1 Hz, 2 H, Ar), 7.35-7.25 (m, 3 H, Ar), 7.08 (d, J = 8.3 Hz, 2 H, Ar), 2.31 (3H, s, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 162.0, 155.6 (C-3-, C-5-triazole), 140.4, 138.7, 131.9, 129.9, 129.3, 129.2, 126.5, 125.1 (Ar), 21.4 (CH_3) ppm. ESI-MS (positive mode) m/z calcd. for $C_{15}H_{13}N_3$ (235.28), Found: 235.1 $[M]^+$.

41d: R_f: 0.2 (EtOAc/hexane = 1:2); m.p. 175-178 °C (lit.[11] m.p. 178-179 °C); ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 8.57 (s, 1 H, CH=N), 7.84 (d, J = 7.4 Hz, 2 H, Ar), 7.71-7.67 (m, 4 H, Ar), 7.54-7.43 (m, 3 H, Ar), 7.38-7.26 (m, 4 H, Ar), 2.36, 2.32 (2 s, 6 H, CH_3). ^{13}C NMR (100 MHz, DMSO-d6): δ (ppm) = 171.0 (CH=N), 150.1, 150.0 (C-3-, C-5-triazole), 144.0, 139.4 (C-OMe), 129.8-123.5 (Ar), 21.2, 21.0 (CH_3). ESI-MS (positive mode) m/z calcd. for $C_{23}H_{20}N_4$ (352.43), Found: 352.2 $[M]^+$.

3-(4-Methylthiophenyl)-5-phenyl-1,2,4-triazole (39e): Prepared from **35e** (0.10 g, 0.37 mmol) according to **General procedure IX** to yield **39e** as a white solid (0.03 g, 30%). Prepared from **35e** (0.10 g, 0.37 mmol) according to **General procedure X** to yield **39e** as a white solid (0.06 g, 61%). m.p. 173-175 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.42 (s, 1 H, NH), 8.08 (d, J = 7.4 Hz, 2 H, Ar), 8.01 (d, J = 8.2 Hz, 2 H, Ar), 7.57-7.45 (m, 3 H, Ar), 7.41 (d, J = 8.2 Hz, 2 H, Ar), 2.53 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 158.3, 157.9 (C-3-, C-5-triazole), 140.2, 129.5, 128.8, 126.3, 125.9, 125.7 (Ar), 14.3 (CH_3) ppm. ESI-MS (positive mode) m/z calcd. for $C_{15}H_{13}N_3S$ (267.35), Found: 267.1 $[M]^+$.

3-(4-Methoxyphenyl)-5-phenyl-1,2,4-triazole (39f): Prepared from **35f** (0.10 g, 0.40 mmol) according to **General procedure X** to yield **39f** as a white solid (0.06 g, 60%). m.p. 158-160 °C (lit.[12] m.p. 154-156 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.70 (s, 1 H, NH), 8.00-7.91 (m, 2 H, Ar), 7.94 (d, J = 8.8 Hz, 2 H, Ar), 7.38-7.22 (m, 3 H, Ar), 6.79 (d, J = 8.8 Hz, 2 H, Ar), 3.77 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 160.0, 158.8 (C-OMe, C-3-, C-5-triazole), 129.7, 129.0, 128.7, 128.0, 126.5, 120.8, 114.1 (Ar), 55.2 (CH_3) ppm. ESI-MS (positive mode) m/z calcd. for $C_{15}H_{13}N_3O$ (251.28), Found: 251.1 $[M]^+$.

3-(4-Nitrophenyl)-5-phenyl-1,2,4-triazole (39g): Prepared from **35g** (0.15 g, 0.56 mmol) according to **General procedure X** to yield **39g** as a white solid (0.05 g, 34%). m.p. 226-228 °C (lit.[13] m.p. 231-234 °C); ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.75 (brs, 1 H, NH), 8.40-8.26 (m, 4 H, Ar), 8.08 (d, J = 7.0 Hz, 2 H, Ar), 7.61-7.45 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 158.4, 157.0 (C-3-, C-5-triazole), 147.6, 136.2, 130.2, 129.0, 127.6, 126.8, 126.1, 124.1 (Ar) ppm.

3-(4-Cyanophenyl)-5-phenyl-1,2,4-triazole (39h): Prepared from **35h** (0.20 g, 0.81 mmol) according to **General procedure X** to yield **39h** as a white solid (0.070 g, 35%). m.p. 237-239 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.78 (s, 1 H, NH), 8.24 (d, J = 8.1 Hz, 2 H, Ar), 8.14-7.86 (m, 4 H, Ar), 7.64-7.40 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.1, 155.5 (C-3-, C-5-triazole), 135.4, 132.8, 130.4, 129.0, 126.4, 126.1, 118.6 (Ar), 111.3 (CN) ppm. Anal. Calcd. for $C_{15}H_{10}N_4$ (246.27): C, 73.16; H, 4.09; N, 22.75. Found: C, 73.25; H, 4.22; N, 22.86.

3-(4-Acetamidophenyl)-5-phenyl-1,2,4-triazole (39i): Prepared from **35i** (0.10 g, 0.34 mmol) according to **General procedure X** to yield **39i** as a white solid (0.056 g, 56%). m.p. 264-266 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 10.33 (s, 1 H, NH), 8.25-7.99 (m, 2 H, Ar), 8.04 (d, J = 7.5 Hz, 2 H, Ar), 7.80 (d, J = 7.3 Hz, 2 H, Ar), 7.64-7.10 (m, 4 H, Ar, NH), 2.09 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 168.7 (CO), 156.8, 156.1 (C-3-, C-5-triazole), 141.4, 130.3, 129.0, 127.4, 127.2, 126.4, 121.2, 119.0 (Ar), 24.1 (CH_3) ppm. Anal. Calcd. for $C_{16}H_{14}N_4O$ (278.31): C, 69.05; H, 5.07; N, 20.13. Found: C, 69.15; H, 5.14; N, 20.22.

3-(4-Pyridyl)-5-phenyl-1,2,4-triazole (39j): Prepared from **35j** (0.20 g, 0.89 mmol) according to **General procedure X** to yield **39j** as a white solid (0.08 g, 40%). m.p. 242-244 °C (lit.[14] m.p. 244 °C); ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.85 (s, 1 H, NH), 8.81-8.63 (m, 2 H, Ar), 8.08 (d, J = 7.0 Hz, 2 H, Ar), 8.00 (d, J = 4.2 Hz, 2 H, Ar), 7.60-7.48 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 160.0, 156.1 (C-3-, C-5-triazole), 150.8, 138.7, 130.9, 129.5, 126.7, 120.6 (Ar) ppm. ESI-MS (positive mode) m/z calcd. for $C_{13}H_{10}N_4$ (222.25), Found: 222.1 $[M]^+$.

3-(4-Fluorophenyl)-5-(2-pyridyl)-1,2,4-triazole (40a): Prepared from **36a** (0.12 g, 0.50 mmol) according to **General procedure X** to yield **40a** as a white solid (0.07 g, 59%). m.p. 239-241 °C (lit.[14] m.p. 241-243 °C);^{1}H NMR (400 MHz, DMSO-d6): δ = 14.83 (s, 1 H, NH), 8.72 (s, 1 H, Ar), 8.34-7.87 (m, 4 H, Ar), 7.68-7.20 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 162.7 (d, J = 245.9 Hz, Ar), 160.6, 154.8 (C-3-, C-5-triazole), 149.5, 146.3, 137.6, 128.0 (d, J = 7.6 Hz), 127.2, 124.9, 121.3, 115.7 (d, J = 21.7 Hz, Ar) ppm.

3-(3-Chlorophenyl)-5-(2-pyridyl)-1,2,4-triazole (40b): Prepared from **36b** (0.13 g, 0.50 mmol) according to **General procedure X** to yield **40b** as a white solid (0.058 g, 45%). m.p. 214-216 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.97 (s, 1 H, NH), 8.73 (s, 1 H, Ar), 8.26-7.95 (m, 4 H, Ar), 7.62-7.46 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.3, 154.8 (C-3-, C-5-triazole), 149.5, 145.9, 137.8, 133.5, 133.1, 130.7, 128.8, 125.3, 125.2, 124.3, 121.4 (Ar) ppm. Anal. Calcd. for $C_{13}H_9N_4Cl$ (256.69): C, 60.83; H, 3.53; N, 21.83. Found: C, 60.91; H, 3.63; N, 21.91.

3-(4-Bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (40c): Prepared from **36c** (0.20 g, 0.66 mmol) according to **General procedure X** to yield **40c** as a white solid (0.08 g, 40%). m.p.

279-281 °C (lit.[15] m.p. 230-231 °C); ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.92 (s, 1 H, NH), 8.72 (s, 1 H, Ar), 8.23-7.95 (m, 4 H, Ar), 7.75-7.62 (m, 2 H, Ar), 7.61-7.47 (m, 1 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.7, 154.7 (C-3-, C-5-triazole), 149.5, 146.0, 137.8, 131.7, 130.3, 127.7, 125.1, 122.3, 121.3 (Ar) ppm.

3-(4-Methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (40d): Prepared from **36d** (0.20 g, 0.84 mmol) according to **General procedure X** to yield **40d** as a white solid (0.115 g, 50%). m.p. 202-205 °C (lit.[14] m.p. 203-204 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.75 (s, 1 H, NH), 8.71 (s, 1 H, Ar), 8.16 (d, 1 H, J = 6.5 Hz, Ar), 8.07-7.90 (m, 3 H, Ar), 7.60-7.45 (m, 1 H, Ar), 7.40-7.21 (m, 2 H, Ar), 2.35 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 161.7, 154.4 (C-3, C-5-triazole), 149.5, 146.2, 138.4, 137.8, 129.3, 128.4, 125.8, 125.0, 121.3 (Ar), 22.0 (CH_3).

3-(4-Methanesulfinylphenyl)-5-(2-pyridyl)-1,2,4-triazole (40e): Prepared from **36e** (0.10 g, 0.37 mmol) according to **General procedure X** to yield **40e** as a white solid (0.056 g, 53%). m.p. 171-173 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.98 (s, 1 H, NH), 8.73 (s, 1 H, Ar), 8.28 (d, J = 8.0 Hz, 2 H, Ar), 8.19 (d, J = 7.6 Hz, 1 H, Ar), 8.07-7.98 (m, 1 H, Ar), 7.81 (d, J = 7.4 Hz, 2 H, Ar), 7.60-7.51 (m, 1 H, Ar), 2.80 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ 160.8, 154.8 (C-3-, C-5-triazole), 149.5, 146.9, 145.9, 137.8, 133.2, 126.4, 125.2, 124.1, 121.4 (Ar), 43.1 (CH_3) ppm. ESI-MS (positive mode) m/z calcd. for $C_{14}H_{13}N_4OS^+$ (285.34), Found: 285.2 $[M+H]^+$.

3-(4-Methoxyphenyl)-5-(2-pyridyl)-1,2,4-triazole (40f): Prepared from **36f** (0.15 g, 0.59 mmol) according to **General procedure X** to yield **40f** as a white solid (0.086 g, 58%). m.p. 188-191 °C (lit.[14] m.p. 183-185 °C); ^{1}H NMR (400 MHz, DMSO-d6): δ = 14.67 (s, 1 H, NH),

8.71 (brs, 1 H, Ar), 8.22-7.90 (m, 4 H, Ar), 7.61-7.41 (m, 1 H, Ar), 7.17-6.95 (m, 2 H, Ar), 3.81 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 160.1, 154.3 (C-OMe, C-3-, C-5-triazole), 149.4, 146.2, 137.5, 127.3, 124.7, 123.7, 121.3, 114.1 (Ar), 55.1 (CH_3) ppm.

3-(4-Cyanophenyl)-5-(2-pyridyl)-1,2,4-triazole (40h): Prepared from **36h** (0.15 g, 0.60 mmol) according to **General procedure X** to yield **40h** as a white solid (0.060 g, 40%). m.p. 240-243 °C; ^1H NMR (400 MHz, DMSO-d6): δ = 14.93 (s, 1 H, NH), 8.73 (s, 1 H, Ar), 8.22-7.95 (m, 4 H, Ar), 7.77-7.48 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 160.7, 154.7 (C-3-, C-5-triazole), 149.5, 145.9, 137.8, 131.7, 130.3, 127.8, 125.1, 122.3, 121.3 (Ar), 107.8 (CN) ppm. Anal. Calcd. for $C_{14}H_9N_5$ (247.25): C, 68.01; H, 3.67; N, 28.32. Found: C, 68.11; H, 3.76; N, 28.41.

3-(4-Acetamidophenyl)-5-(2-pyridyl)-1,2,4-triazole (40i): Prepared from **36i** (0.15 g, 0.53 mmol) according to **General procedure X** to yield **40i** as a white solid (0.091 g, 61%). m.p. 290-292 °C; ^1H NMR (400 MHz, DMSO-d6): δ = 14.74 (s, 1 H, NH), 10.11 (s, 1 H, NH), 8.71 (s, 1 H, Ar), 8.15 (d, J = 7.5 Hz, 1 H, Ar), 8.08-7.94 (m, 3 H, Ar), 7.76-7.65 (m, 2 H, Ar), 7.59-7.46 (m, 1 H, Ar), 2.08 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ = 168.4 (CO), 161.5, 154.4 (C-3-, C-5-triazole), 149.5, 146.2, 140.1, 137.8, 130.3, 126.4, 125.0, 121.3, 118.8 (Ar), 24.0 (CH_3) ppm. Anal. Calcd. for $C_{15}H_{13}N_5O$ (279.30): C, 64.51; H, 4.69; N, 25.07. Found: C, 64.61; H, 4.76; N, 25.16.

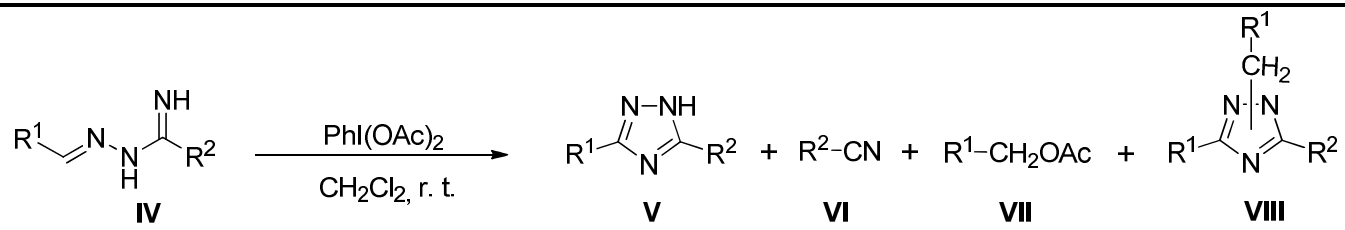
3-(4-Pyridyl)-5-(2-pyridyl)-1,2,4-triazole (40j): Prepared from **36j** (0.15 g, 0.67 mmol) according to **General procedure X** to yield **40j** as a white solid (0.045 g, 30%). m.p. 268-270 °C (lit.[16] m.p. 260-261 °C); ^1H NMR (400 MHz, DMSO-d6): δ = 15.15 (s, 1 H, NH), 8.95-8.65 (m, 3 H, Ar), 8.35-7.81 (m, 4 H, Ar), 7.70-7.40 (m, 1 H, Ar) ppm. ^{13}C NMR (100 MHz,

DMSO-d6): δ = 159.8, 156.0 (C-3-, C-5-triazole), 150.9, 150.1, 146.5, 138.4, 125.8, 122.0, 120.5 (Ar) ppm.

ANALYSIS OF REACTION MIXTURES BY LCMS

LC was performed on a Hypersil Gold (50 x 2.1mm, 1.9 μm, with precolumn filter, Thermo Electron Corp., San Jose, CA, USA) column, using an Accela HPLC system (Thermo Electron Corp., San Jose, CA, USA) eluted with a gradient of acetonitrile (A) and water (B) containing 0.1% (V/V) formic acid each. The gradient was from 10% of A (hold for 1 min) to 90% A over 12 min, hold for 6 min and return to initial conditions and hold for 2 min to equilibrate the column. The LC system was coupled with a Thermo LTQ XL mass spectrometer (Thermo Electron Corp., San Jose, CA, USA) operated in a full scan positive ion ESI mode (m/z range was 150-2000 Da). The ion injection time was set to 100 ms. ESI parameters were a spray voltage of 5 kV, a capillary temperature of 300°C, a sheath gas flow of 20 units N_2 and an auxiliary gas flow of 10 ubuts N_2. The tray temperature was set to 20°C and the column oven was set to 30 °C to perform the optimal retention of the compounds in the reaction mixtures. The injection amount was 1 μL for each sample, the total concentration of all compounds in the samples was 50 ppm.

Table S1. Reactions of sugar derived *N*^{1}-alkylidene-amidrazones with PIDA[a] - detailed product analysis



IV **V** **VI** **VII** **VIII**

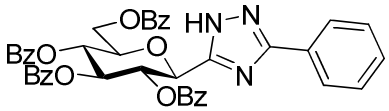
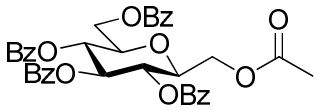
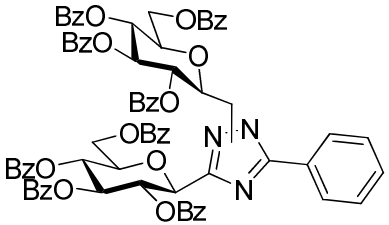
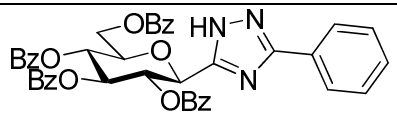
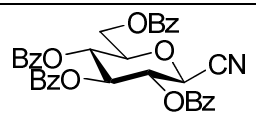
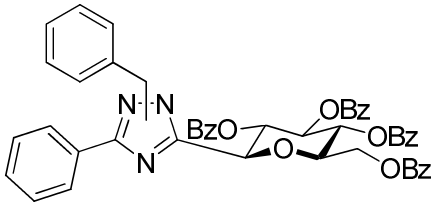
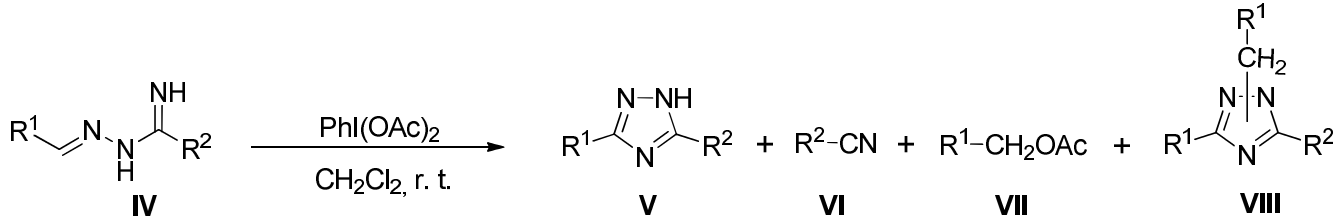
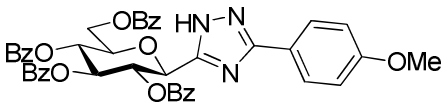
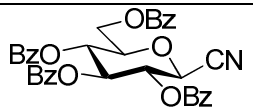
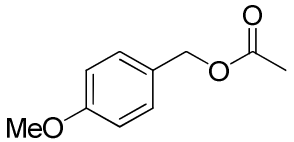
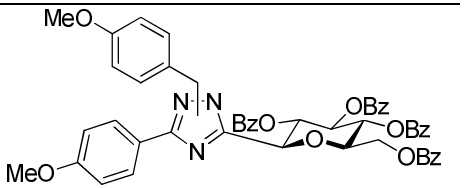
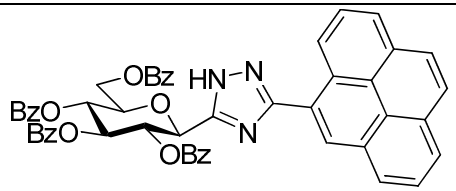
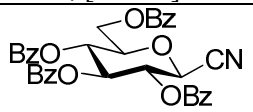
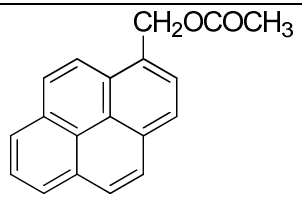
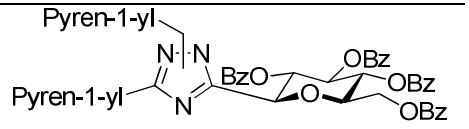
Entry	Starting compd (type **IV**)	R^1	R^2	Detected compounds			
				V	**VI**	**VII**	**VIII**
1.	**9**	Bz_4-β-D-Glcp	Ph	 **21** Calcd. for $C_{42}H_{33}N_3O_9$ (723.22) Found: 724.3, $[M+H]^+$; 1446.8, $[2M+H]^+$; 1468.9, $[2M+Na]^+$	Ph-CN not detected[b]	 Calcd. for $C_{37}H_{32}O_{11}$ (652.19) Found: 653.8, $[M+H]^+$; 670.5, $[M+H_2O]^+$	 Calcd. for $C_{77}H_{61}N_3O_{18}$ (1315.40) Found: 1316.4, $[M+H]^+$
2.	**18**	Ph	Bz_4-β-D-Glcp	 **21** Calcd. for $C_{42}H_{33}N_3O_9$ (723.22) Found: 724.7, $[M+H]^+$; 1447.3, $[2M+H]^+$	 **1** Calcd. for $C_{35}H_{27}NO_9$ (605.17) Found: 606.0, $[M+H]^+$; 623.2, $[M+H_2O]^+$ 628.2, $[M+Na]^+$	Ph-CH_2-OAc not detected[b]	 Calcd. for $C_{49}H_{39}N_3O_9$ (813.27) Found: 814.3, $[M+H]^+$

Table S1. *continued*



IV **V** **VI** **VII** **VIII**

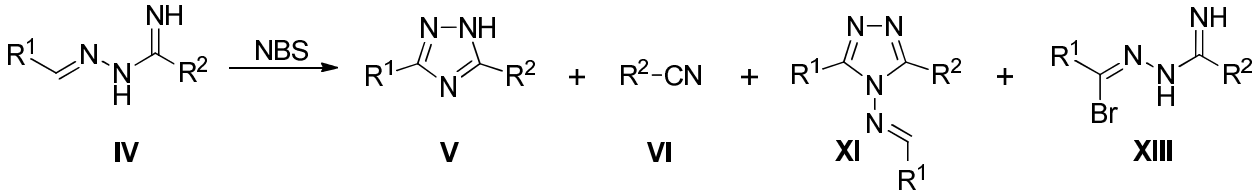
Detected compounds

Entry	Starting compd (type **IV**)	R^1	R^2	**V**	**VI**	**VII**	**VIII**
3.	**19**	4-MeO-Ph	Bz_4-β-D-Glcp	 **22** Calcd. for $C_{43}H_{35}N_3O_{10}$ (753.23) Found: 754.7, $[M+H]^+$; 1507.1, $[2M+H]^+$	 **1** Calcd. for $C_{35}H_{27}NO_9$ (605.17) Found: 605.9, $[M+H]^+$; 623.2, $[M+H_2O]^+$; 628.2, $[M+Na]^+$	 Calcd. for $C_{10}H_{13}O_3$ (180.08) Found: 120.9, $[M-AcO]^+$	 Calcd. for $C_{51}H_{43}N_3O_{11}$ (873.29) Found: 874.4, $[M+H]^+$; 896.3, $[M+Na]^+$
4.	**20**	Pyren-1-yl	Bz_4-β-D-Glcp	 Calcd. for $C_{52}H_{37}N_3O_9$ (847.25) Found: 848.3, $[M+H]^+$; 1695.8, $[2M+H]^+$	 **1** Calcd. for $C_{35}H_{27}NO_9$ (605.17) Found: 605.9, $[M+H]^+$; 623.2, $[M+H_2O]^+$; 628.3, $[M+Na]^+$	 **23** Calcd. for $C_{14}H_{19}O_2$ (274.10) Found: 215.1, $[M-AcO]^+$	 Calcd. for $C_{69}H_{47}N_3O_9$ (1061.33) Found: 1062.3, $[M+H]^+$; 1084.3, $[M+Na]^+$

[a]Roman numbers denote compound types and are identical with those in mechanistic Scheme 6.

[b]The compound can be present in the mixture, but was not detected due to its low molecular weight.

Table S3. LC-MS analysis of reaction mixtures of sugar derived N^1-alkylidene-amidrazones with NBS[a]



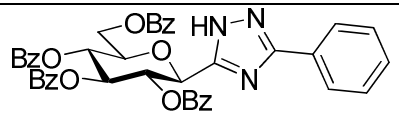
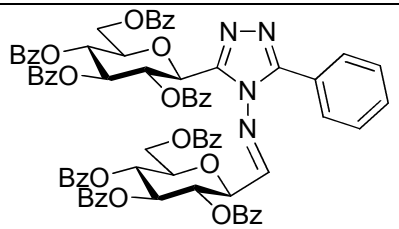
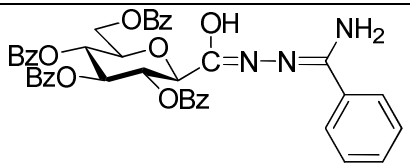
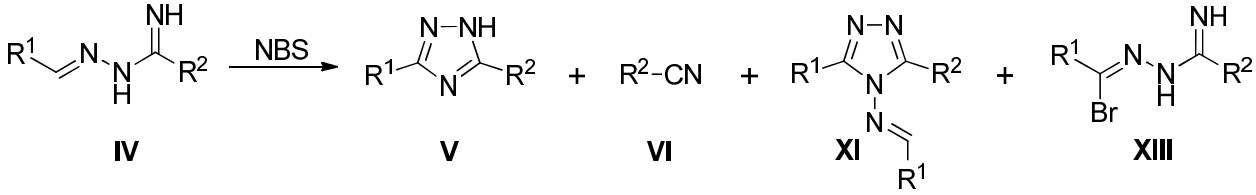
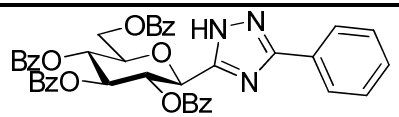
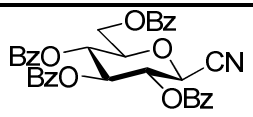
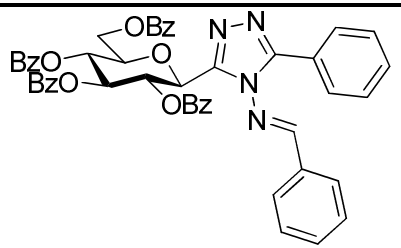
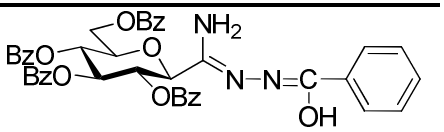
Entry	Starting compd (type **IV**)	R^1	R^2	Detected compounds			
				V	**VI**	**XI**	**XIII**
1.	**9**	Bz4-β-D-Glcp	Ph	 **21** Calcd. for $C_{42}H_{33}N_3O_9$ (723.22) Found: 724.5 $[M+H]^+$	Ph-CN not detected[b]	 Calcd. for $C_{77}H_{60}N_4O_{18}$ (1328.39) Found: 1329.5 $[M+H]^+$ 1351.4 $[M+Na]^+$	 **25** Calcd. for $C_{42}H_{35}N_3O_{10}$ (741.23) Found: 742.8 $[M+H]^+$

Table S3. *continued*



Entry	Starting compd (type **IV**)	R^1	R^2	Detected compounds **V**	**VI**	**XI**	**XIII**
2.	**18**	Ph	Bz_4-β-D-Glcp	 **21** Calcd. for $C_{42}H_{33}N_3O_9$ (723.22) Found: 724.9 $[M+H]^+$ 746.6 $[M+Na]^+$ 1447.4 $[2M+H]^+$	 **1** Calcd. for $C_{35}H_{27}NO_9$ (605.17) Found: 606.1 $[M+H]^+$ 623.2 $[M+H_2O]^+$ 628.3 $[M+Na]^+$	 Calcd. for $C_{49}H_{38}N_4O_9$ (826.26) Found: 827.5 $[M+H]^+$ 849.7 $[M+Na]^+$	 Calcd. for $C_{42}H_{35}N_3O_{10}$ (741.23) Found: 742.2 $[M+H]^+$

[a]Roman numbers denote compound types and are identical with those in mechanistic Scheme 8.

[b]The compound can be present in the mixture, but was not detected due to its low molecular weight.

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