Supporting Information

Facile and Efficient Synthesis of Carbohybrids as Stereodivergent Drug-like Small Molecules

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1. Material and methods:

All reactions were performed either in oven-dried glassware or microwave vessel. All reactions were monitored by thin-layer chromatography (TLC) using pre-coated glass-backed plates (silica gel 60 F_{254} 0.25mm), and components were visualized by observation under UV light (254 and 365 nm) or by treating the plates with $Ce(SO_4)_2$ (1% in 2N H_2SO_4) solution, followed by heating. Solvents used for reactions were dried by standard drying methods. Solvent used for chromatography and organic reagents were purchased from commercial venders and used without further purification unless otherwise mentioned. Optical rotations were determined on automated polarimeter using 1 dm cells at 28 ºC in $CHCl_3$. Concentrations were in g/100 mL. NMR spectra were recorded on 500 MHz FT-NMR spectrophotometer at 500 MHz (^{1}H) and 125 MHz (^{13}C) respectively. Chemical shifts were reported in ppm relative to the reference peak TMS, 0.00 ppm (^{1}H) and $CDCl_3$, 77.2 ppm (^{13}C) unless otherwise stated. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublets of doublet); ddd (doublet of doublet of doublet); dt (doublets of triplet); td (triplets of doublet); brs (broad singlet), etc. Coupling constants were reported in Hz. The high resolution mass spectrometric analyses were conducted at the Mass Spectrometry Laboratory by direct injection for fast atomic bombardment (FAB). Microwave reactions were performed using automated CEM Discover Benchmate and temperature was maintained by controlled air cooling. Microwave reaction condition is given in experimental procedure section. The products were purified by column chromatography on silica gel (230–400 mesh).

2. General experimental procedures:

a) Synthesis of 5 under thermal condition in EtOH:

To a stirred solution of 2-*C*-formyl glucal **1** (110 mg, 0.250 mmol) in anhydrous ethanol, 3-aminopyrazole **3a** (31.1 mg, 0.375 mmol, 1.5 equiv.) was added and resulting mixture was refluxed for 6 h (TLC). Resulting product mixture was concentrated in vacuum and purified by flash column chromatography to obtained pure product **5** (79 mg) in 62% yield.

b) Synthesis of 5 and 6 using base K_2CO_3 in EtOH:THF (1:1):

To a stirred suspension of K_2CO_3 (172.5 mg, 1.25 mmol, 5.0 equiv.) in EtOH (2.0 mL), 2-*C*-formyl glucal **1** (110 mg, 0.250 mmol) and 3-aminopyrazole **3a** (31.1 mg, 0.375 mmol, 1.5 equiv.) in THF (2.0 mL) was added and resulting mixture was heated at 80 ºC for 8 h (TLC). Resulting reaction mixture was concentrated in vacuum and subjected to flash column chromatography purification to obtained pure product **5** (79 mg) in 62% yield. When the similar reaction condition was applied using 2-*C*-formyl glucal **1** (110 mg, 0.250 mmol) and 3-amino-1,2,4-triazole **4a** (31.5 mg, 0.375 mmol, 1.5 equiv.), the reaction was completed in 12 h (TLC) and desired compound **6** (82.5 mg) was isolated in 65 % yield.

c) Synthesis of 5 and 6 using glacial AcOH as solvent at room temperature:

To a stirred solution of 2-*C*-formyl glucal **1** (110 mg, 0.250 mmol) in glacial acetic acid (3 mL), 3-aminopyrazole **3a** (31.1 mg, 0.375 mmol, 1.5 equiv.) was added and resulting mixture was stirred at room temperature for 1 h (TLC). Resulting product mixture was diluted with EtOAc (20 mL) then neutralized by saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer extracted with EtOAc (3 × 5 mL). The combined organic layer washed with brine, and dried over anhydrous Na_2SO_4. The crude product obtained after evaporation of solvent was chromatographed to yield pure compound **5** (91.5 mg) in 72% yield. Similar procedure was applied using 2-*C*-formyl glucal **1** (110 mg, 0.250 mmol) and 3-amino-1,2,4-triazole **4a** (31.5 mg, 0.375 mmol, 1.5 equiv.), reaction was completed in 24 h (TLC) and provided desired compound **6** (29.2 mg) in 23 % isolable yield with some highly polar mass.

d) Synthesis of 5 under microwave irradiation in Toluene:

A mixture of 2-*C*-formyl glucal **1** (110 mg, 0.250 mmol) and 3-aminopyrazole **3a** (31.1 mg, 0.375 mmol, 1.5 equiv.) dissolved in dry toluene (2.0 mL) was heated in capped microwave vessel under microwave irradiation (250 W, 110 ºC) for 20 min. Controlled air cooling was applied to maintain the temperature. Resulting yellow mixture was concentrated in vacuo and subjected to flash column chromatography to obtain desired compound **5** (108 mg) in 85% isolable yield. When toluene:AcOH (10:1) solvent system used in the same reaction, it was completed in 10 min and given almost same isolable yield of **5** (110.5 mg, 87%).

e) Synthesis of 5 and 6 under microwave irradiation in glacial AcOH:

A mixture of 2-*C*-formyl glucal **1** (110 mg, 0.250 mmol) and 3-aminopyrazole **3a** (31.1 mg, 0.375 mmol, 1.5 equiv.) dissolved in glacial AcOH (1.5 mL) was heated in capped microwave vessel under microwave irradiation (200 W, 110 ºC) for 5 min. Controlled air cooling was applied to maintain the temperature. Resulting product mixture was diluted with EtOAc (15 mL) and neutralized by saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was concentrated in vacuo and purified by flash column chromatography to yield desired compound **5** (118 mg) in 93% yield. All other compounds **7–15** were synthesized by the condensation of 2-*C*-formyl glycals **1–2** with respective 3-aminopyrazole **3b–e** under same reaction procedure.

Similar reaction protocol was applied when 2-*C*-formyl glycals **1–2** were reacted with 3-amino-1,2,4-triazoles **4a–c**. The desired products **6**, **16–20** were obtained in good isolable yield (76~90%) after 15–20 min of microwave irradiation (200 W, 110 ºC). Traces of respective acetylated product were observed in crude ^{1}H NMR spectra as well as in LC/MS spectra of crude products. We observed greater than 99% regioselectivity in all the cases for the synthesis of triazolo[1,5-a]pyrimidines from their crude ^{1}H NMR spectra and LC/MS of crude product.

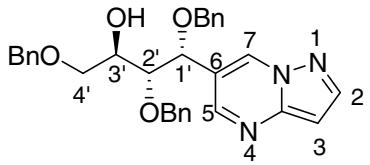
f) Glycosidation: synthesis of 21 and 22:

2,3,4,6-Tetra-*O*-acetyl-glucopyranosyl bromide (158 mg, 0.384 mmol, 1.5 equiv.) and glycosyl acceptor **7** (150 mg, 0.256 mmol) were placed in a aluminium foil covered RB flask in CH_2Cl_2 (3 mL) along with 100 mg of 4 Å molecular sieves under nitrogen atmosphere and cooled to 0 ºC. AgOTf (98.6 mg, 0.384 mmol, 1.5 equiv.) in dry toluene (1.5 mL) was added dropwise within 10 min. After 4 h of stirring at 0 ºC, the reaction was quenched by the addition of iPr_2NEt (1 mL) and stirred for additional 10 min. The reaction mixture was filtered through Celite®, and the filtrate was concentrated in vacuo. The crude mixture was chromatographed to obtain β-glycosidated product **21** (173 mg) in 74% yield as major product along with some minor undesired product. Similarly β-glycosidated product **22** was obtained from **12** in 73% of isolable yield.

To a stirred solution of compound **21** (235 mg, 0.256 mmol) in ethanol (4 mL) at 70 ºC, 1,4-cyclohexadiene (0.57 mL, 6.144 mmol, 24.0 equiv.) and $Pd(OH)_2$ (140 mg, 0.6 equiv./weight) was added in 3–4 installment on every 4 h. After 24 h, the reaction mixture was filtered through Celite®. The filtrate was concentrated to obtain crude product. The crude product was chromatographed in short column using MeOH:CH_2Cl_2

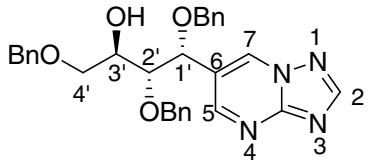
solvent system to obtain debenzylated product **23** (98 mg) in 59% yield. Similarly, debenzylated product **24** was obtained in 60% yield starting from compound **22**.

3. Physiochemical and Spectral data of all compounds



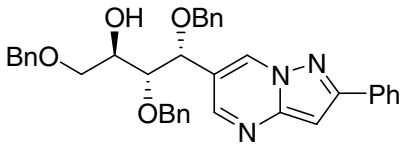
5

Compound 5. Amorphous solid, $[\alpha]_D^{28}$ –37.73 (*c* 0.343, $CHCl_3$); TLC: R_f = 0.27 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.0 Hz, 1H), 8.42 (d, *J* = 2.5 Hz, 1H), 8.11 (d, *J* = 2.5 Hz, 1H), 7.34–7.25 (m, 10H), 7.06–7.05 (m, 3H), 6.95 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.69 (d, *J* = 2.0 Hz, 1H), 4.77 (d, *J* = 2.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.53 (brs, 2H), 4.42 (d, *J* = 11.0 Hz, 1H), 4.32 (d, *J* = 11.5 Hz, 1H), 4.14 (d, *J* = 11.0 Hz, 1H), 4.06 (m, 1H), 3.68-3.67 (m, 2H), 3.62 (dd, *J* = 8.0, 2.5 Hz, 1H), 2.62 (brd, *J* = 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 148.3, 145.2, 137.6, 137.0, 136.8, 134.0, 128.8, 128.7, 128.5, 128.3, 128.2, 119.5, 97.0, 80.9, 76.0, 74.5, 73.7, 72.0, 70.7, 70.0; FAB HRMS *m/z* calcd for $C_{31}H_{31}N_3O_4$ $[M+H]^+$: 510.2393; Found: 510.2393.



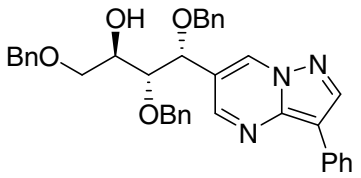
6

Compound 6. Amorphous solid, $[\alpha]_D^{28}$ –50.56 (*c* 0.396, $CHCl_3$); TLC: R_f = 0.33 (4:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.0 Hz, 1H), 8.61 (d, *J* = 2.0 Hz, 1H), 8.46 (s, 1H), 7.35–7.24 (m, 10H), 7.01–6.98 (m, 3H), 6.88 (dd, *J* = 7.5, 1.0 Hz, 2H), 4.88 (d, *J* = 2.5 Hz, 1H), 4.57–4.54 (m, 3H), 4.47 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.09 (d, *J* = 11.5 Hz, 1H), 4.06 (m, 1H), 3.74–3.72 (m, 2H), 3.63 (dd, *J* = 8.5, 2.5 Hz, 1H), 2.64 (brd, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 155.0, 137.6, 136.7, 136.5, 134.9, 128.9, 128.8, 128.6, 128.5, 128.37, 128.3, 128.1, 122.9, 104.9, 80.6, 75.8, 74.4, 73.8, 72.5, 70.6, 70.0; FAB HRMS *m/z* calcd for $C_{30}H_{30}N_4O_4$ $[M+H]^+$: 511.2345; Found: 511.2350.



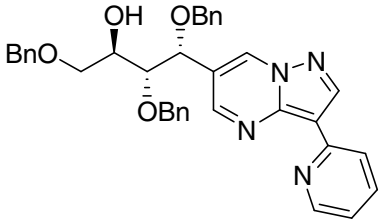
7

Compound 7. Amorphous solid, $[\alpha]_D^{28}$ –44.06 (*c* 0.413, $CHCl_3$); TLC: R_f = 0.37 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (brs, 1H), 8.39 (d, *J* = 2.0 Hz, 1H), 8.01 (dd, *J* = 9.0, 1.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.35–7.24 (m, 10H), 7.07–7.06 (m, 3H), 6.99 (dd, *J* = 7.0, 3.0 Hz, 2H), 6.97 (s, 1H), 4.77 (d, *J* = 3.0 Hz, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.53 (brs, 2H), 4.45 (d, *J* = 11.0 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 4.19 (d, *J* = 11.0 Hz, 1H), 4.06 (m, 1H), 3.70–3.67 (m, 2H), 3.64 (dd, *J* = 8.0, 2.7 Hz, 1H), 2.53 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 149.8, 149.6, 137.8, 137.1, 137.0, 133.8, 133.0, 129.1, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 126.7, 119.5, 93.7, 81.1, 76.2, 74.6, 73.8, 71.9, 70.8, 70.1; FAB HRMS *m/z* calcd for $C_{37}H_{35}N_3O_4$ $[M+H]^+$: 586.2706; Found: 586.2712.



8

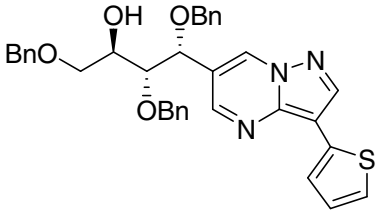
Compound 8. Amorphous solid, $[\alpha]_D^{28}$ –54.10 (*c* 0.356, $CHCl_3$); TLC: R_f = 0.38 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.0 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 8.42 (s, 1H), 8.03 (brd, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.35–7.23 (m, 11H), 7.04–7.02 (m, 3H), 6.95 (dd, *J* = 7.5, 2.5 Hz, 2H), 4.78 (d, *J* = 3.0 Hz, 1H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.53 (brs, 2H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.18 (d, *J* = 11.5 Hz, 1H), 4.07 (m, 1H), 3.70–3.67 (m, 2H), 3.65 (dd, *J* = 7.5, 2.5 Hz, 1H), 2.58 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 144.7, 142.9, 137.7, 137.0, 136.9, 134.3, 132.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 126.5, 119.9, 111.0, 81.0, 76.1, 74.5, 73.8, 72.0, 70.8, 70.1; FAB HRMS *m/z* calcd for $C_{37}H_{35}N_3O_4$ $[M+H]^+$: 586.2706; Found: 586.2712.



9

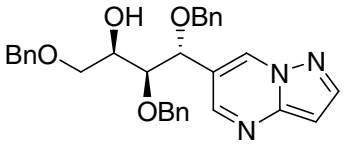
Compound 9. Amorphous solid, $[\alpha]_D^{28}$ –61.72 (*c* 0.366, $CHCl_3$); TLC: R_f = 0.42 (4:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.65 (m, 1H), 8.55 (d, *J* = 2.0 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 8.41 (brd, *J* = 8.0 Hz, 1H), 7.76 (dt, *J* = 8.0, 1.5

Hz, 1H), 7.35–7.25 (m, 10H), 7.14 (ddd, J = 7.0 Hz, J = 5.0, 1.5 Hz, 1H), 7.03–6.99 (m, 3H), 6.95 (dd, J = 7.5, 2.5 Hz, 2H), 4.81 (d, J = 3.0 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 4.54 (brs, 2H), 4.46 (d, J = 11.0 Hz, 1H), 4.36 (d, J = 11.5 Hz, 1H), 4.16 (d, J = 11.0 Hz, 1H), 4.08 (m, 1H), 3.72–3.68 (m, 2H), 3.65 (dd, J = 7.7, 2.0 Hz, 1H), 2.71 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.66, 150.4, 149.6, 145.2, 144.7, 137.7, 137.0, 136.7, 134.5, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 121.3, 121.1, 120.1, 111.2, 81.0, 76.0, 74.5, 73.8, 72.1, 70.8, 70.0; FAB HRMS *m/z* calcd for $C_{36}H_{34}N_4O_4$ $[M+H]^+$: 587.2658; Found: 587.2662.



10

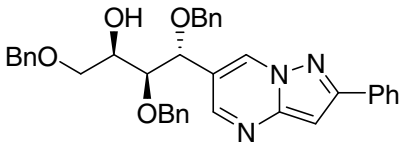
Compound 10. Amorphous solid, $[\alpha]_D^{28}$ –62.88 (*c* 0.390, $CHCl_3$); TLC: R_f = 0.42 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 1.5 Hz, 1H), 8.46 (d, J = 2.0 Hz, 1H), 8.32 (s, 1H), 7.55 (dd, J = 3.5, 1.0 Hz, 1H), 7.35–7.26 (m, 11H), 7.13 (dd, J = 5.2, 3.5 Hz, 1H), 7.03–7.01 (m, 3H), 6.95 (dd, J = 7.0, 3.0 Hz, 2H), 4.78 (d, J = 3.0 Hz, 1H), 4.59 (d, J = 11.5 Hz, 1H), 4.53 (brs, 2H), 4.45 (d, J = 11.5 Hz, 1H), 4.34 (d, J = 11.5 Hz, 1H), 4.16 (d, J = 11.5 Hz, 1H), 4.06 (m, 1H), 3.69–3.68 (m, 2H), 3.64 (dd, J = 8.0, 3.0 Hz, 1H), 2.56 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 144.0, 142.3, 137.7, 136.9, 136.8, 134.1, 133.6, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 123.6, 123.3, 120.1, 106.6, 81.0, 76.1, 74.6, 73.8, 72.1, 70.8, 70.1; FAB HRMS *m/z* calcd for $C_{35}H_{33}N_3O_4S$ $[M+H]^+$: 592.2270; Found: 592.2275.



11

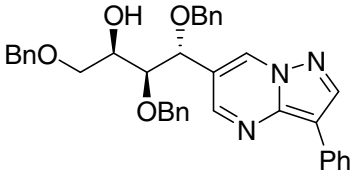
Compound 11. Amorphous solid, $[\alpha]_D^{28}$ –14.08 (*c* 0.333, $CHCl_3$); TLC: R_f = 0.14 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, J = 1.5 Hz, 1H), 8.45 (d, J = 1.5 Hz, 1H), 8.11 (d, J = 2.5 Hz, 1H), 7.35–7.24 (m, 10H), 7.10–7.04 (m, 3H), 6.88 (dd, J = 8.0, 1.5 Hz, 2H), 6.70 (d, J = 2.0 Hz, 1H), 4.60 (d, J = 8.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 11.5 Hz, 1H), 4.36 (brd, J = 11.5 Hz, 2H),

4.18 (m, 1H), 4.11 (d, J = 11.0 Hz, 1H), 3.75 (dd, J = 8.0, 2.0 Hz, 1H), 3.61 (dd, J = 9.5, 5.5 Hz, 1H), 3.53 (dd, J = 9.5, 6.5 Hz, 1H), 2.55 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 148.4, 145.3, 137.8, 137.0, 136.6, 134.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 120.1, 97.0, 80.7, 76.7, 74.8, 73.7, 71.7, 71.0, 69.4; FAB HRMS *m/z* calcd for $C_{31}H_{31}N_3O_4$ $[M+H]^+$: 510.2393; Found: 510.2388.



12

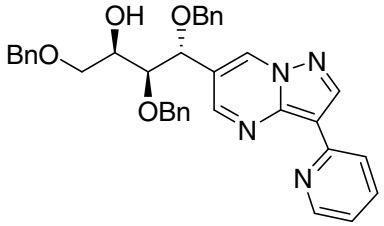
Compound 12. Amorphous solid, $[\alpha]_D^{28}$ –15.90 (*c* 0.423, $CHCl_3$); TLC: R_f = 0.43 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, J = 2.0 Hz, 1H), 8.42 (d, J = 2.0 Hz, 1H), 8.00 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (m, 1H), 7.35–7.23 (m, 10H), 7.07–7.05 (m, 3H), 6.98 (s, 1H), 6.91 (dd, J = 7.5, 2.0 Hz, 2H), 4.59 (d, J = 8.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.38 (d, J = 11.5 Hz, 1H), 4.37 (d, J = 11.5 Hz, 1H), 4.18 (m, 1H), 4.15 (d, J = 11.0 Hz, 1H), 3.76 (dd, J = 8.0, 2.5 Hz, 1H), 3.61 (dd, J = 9.5, 5.5 Hz, 1H), 3.53 (dd, J = 9.5, 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 150.1, 149.6, 137.9, 137.1, 136.8, 133.9, 132.9, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 126.7, 120.1, 93.8, 81.0, 76.8, 75.0, 73.8, 71.8, 71.1, 69.5; FAB HRMS *m/z* calcd for $C_{37}H_{35}N_3O_4$ $[M+H]^+$: 586.2706; Found: 586.2704.



13

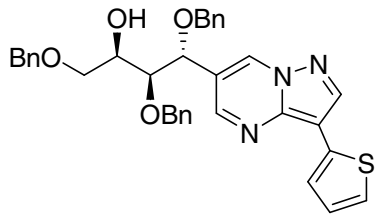
Compound 13. Amorphous solid, $[\alpha]_D^{28}$ –15.90 (*c* 0.416, $CHCl_3$); TLC: R_f = 0.42 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (dd, J = 7.5, 2.0 Hz, 2H), 8.41 (s, 1H), 8.04 (d, J = 1.5 Hz, 1H), 8.03 (d, J = 1.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.34–7.23 (m, 11H), 7.04–7.02 (m, 3H), 6.89 (dd, J = 7.5, 2.0 Hz, 2H), 4.60 (d, J = 8.0 Hz, 1H), 4.56 (d, J = 11.5 Hz, 1H), 4.51 (d, J = 11.5 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 11.5 Hz, 1H), 4.37 (d, J = 11.5 Hz, 1H), 4.20 (dt, J = 6.0, 2.0 Hz, 1H), 4.15 (d, J = 11.5 Hz, 1H), 3.78 (dd, J = 8.0, 2.0 Hz, 1H), 3.62 (dd, J = 9.5, 6.0 Hz, 1H), 3.54 (dd, J = 9.5,

6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 144.7, 143.0, 137.8, 137.0, 136.7, 134.3, 132.0, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 126.8, 126.5, 120.4, 111.0, 80.8, 76.8, 74.9, 73.8, 71.8, 71.1, 69.5; FAB HRMS *m/z* calcd for $C_{37}H_{35}N_3O_4$ $[M+H]^+$: 586.2706; Found: 586.2700.



14

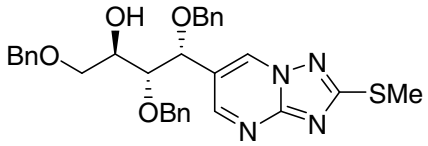
Compound 14. Amorphous solid, $[\alpha]_D^{28}$ –15.63 (*c* 0.446, $CHCl_3$); TLC: R_f = 0.72 (4:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.66 (brd, *J* = 5.0 Hz, 1H), 8.57 (d, *J* = 2.0 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 8.41 (brd, *J* = 8.5 Hz, 1H), 7.77 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.36–7.24 (m, 10H), 7.15 (m, 1H), 7.03–7.00 (m, 3H), 6.88 (dd, *J* = 7.5, 2.0 Hz, 2H), 4.62 (d, *J* = 8.5 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.21 (dt, *J* = 6.5, 2.0 Hz, 1H), 4.14 (d, *J* = 11.5 Hz, 1H), 3.79 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.63 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.55 (dd, *J* = 9.5, 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 150.8, 149.7, 145.3, 144.9, 137.9, 137.0, 136.8, 136.7, 134.7, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 121.4, 121.3, 120.7, 111.3, 80.8, 76.8, 75.0, 73.8, 71.9, 71.1, 69.5; FAB HRMS *m/z* calcd for $C_{36}H_{34}N_4O_4$ $[M+H]^+$: 587.2658; Found: 587.2647.



15

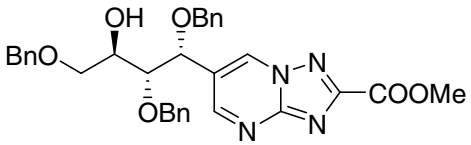
Compound 15. Amorphous solid, $[\alpha]_D^{28}$ –15.64 (*c* 0.380, $CHCl_3$); TLC: R_f = 0.42 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.0 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 8.32 (s, 1H), 7.55 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.34–7.23 (m, 11H), 7.13 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.04–7.02 (m, 3H), 6.88 (dd, *J* = 7.7, 2.0 Hz, 2H), 4.59 (d, *J* = 8.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.0 Hz, 1H), 4.36 (d, *J* = 11.5 Hz, 1H), 4.19 (dt, *J* = 6.0, 2.0 Hz, 1H), 4.14 (d, *J* = 11.0 Hz, 1H), 3.77 (dd, *J* = 8.0 Hz and *J* = 2.0 Hz, 1H), 3.62 (dd, *J* = 9.5, 6.0 Hz, 1H),

3.54 (dd, J = 9.5, 6.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 144.0, 142.4, 137.8, 137.0, 136.6, 134.2, 133.5, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 123.7, 123.3, 120.6, 106.7, 80.7, 76.7, 74.9, 73.8, 71.8, 71.1, 69.4; FAB HRMS *m/z* calcd for $C_{35}H_{33}N_3O_4S$ $[M+H]^{+\cdot}$: 592.2270; Found: 592.2266.



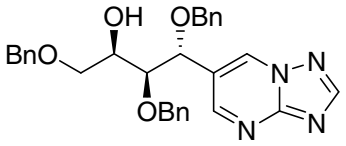
16

Compound 16. Amorphous solid, $[\alpha]_D^{28}$ –50.86 (*c* 0.333, $CHCl_3$); TLC: R_f = 0.25 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, J = 2.0 Hz, 1H), 8.48 (d, J = 2.0 Hz, 1H), 7.35–7.23 (m, 10H), 7.06–7.01 (m, 3H), 6.91 (brd, J = 6.5 Hz, 2H), 4.84 (d, J = 2.0 Hz, 1H), 4.54 (brt, J = 11.5 Hz, 3H), 4.46 (d, J = 11.5 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 4.08 (d, J = 11.5 Hz, 1H), 4.04 (m, 1H), 3.73–3.69 (m, 2H), 3.61 (dd, J = 8.0, 2.5 Hz, 1H), 2.72 (s, 3H), 2.68 (d, J = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 155.7, 154.0, 137.6, 136.8, 136.7, 133.8, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 121.7, 81.0, 75.7, 74.5, 73.8, 72.3, 70.7, 70.0, 14.1; FAB HRMS *m/z* calcd for $C_{31}H_{32}N_4O_4S$ $[M+H]^+$: 557.2223; Found: 557.2225.



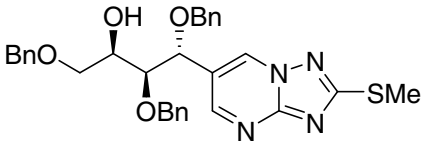
17

Compound 17. Amorphous solid, $[\alpha]_D^{28}$ –42.82 (*c* 0.403, $CHCl_3$); TLC: R_f = 0.37 (4:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 2.5 Hz, 1H), 8.59 (d, J = 2.0 Hz, 1H), 7.33–7.21 (m, 10H), 6.94–6.91 (m, 3H), 6.84 (dd, J = 7.0, 2.0 Hz, 2H), 4.89 (d, J = 2.0 Hz, 1H), 4.58-4.55 (m, 2H), 4.52 (d, J = 11.0 Hz, 1H), 4.47 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 4.09 (s, 3H), 4.06 (m, 1H), 4.05 (d, J = 11.5 Hz, 1H), 3.76-3.71 (m, 2H), 3.63 (dd, J = 8.0, 2.5 Hz, 1H), 2.61 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 157.2, 156.5, 155.0, 137.5, 136.6, 136.5, 135.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.0, 125.1, 80.4, 75.7, 74.3, 73.8, 72.9, 70.5, 70.0, 53.5; FAB HRMS *m/z* calcd for $C_{32}H_{32}N_4O_6$ $[M+H]^+$: 569.2400; Found: 569.2393.



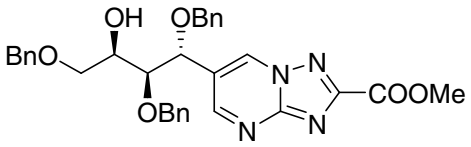
18

Compound 18. Amorphous solid, $[\alpha]_D^{28}$ –13.39 (*c* 0.393, $CHCl_3$); TLC: R_f = 0.36 (4:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.0 Hz, 1H), 8.58 (d, *J* = 2.0 Hz, 1H), 8.46 (s, 1H), 7.36–7.21 (m, 10H), 7.05–6.99 (m, 3H), 6.84 (brd, *J* = 7.0 Hz, 2H), 4.67 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.46–4.38 (m, 3H), 4.19 (m, 1H), 4.10 (d, *J* = 11.5 Hz, 1H), 3.77 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.66 (dd, *J* = 9.5, 5.5 Hz, 1H), 3.56 (dd, *J* = 9.5, 7.0 Hz, 1H), 2.54 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 155.6, 155.0, 137.7, 136.7, 136.4, 134.7, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2 123.4, 80.5, 76.4, 74.8, 73.8, 72.2, 71.0, 69.3; FAB HRMS *m/z* calcd for $C_{30}H_{30}N_4O_4$ $[M+H]^+$: 511.2345; Found: 511.2350.



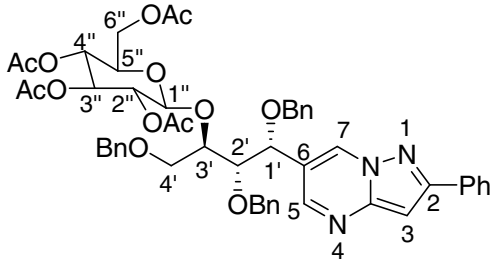
19

Compound 19. Amorphous solid, $[\alpha]_D^{28}$ –20.39 (*c* 0.366, $CHCl_3$); TLC: R_f = 0.26 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.0 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 7.34–7.21 (m, 10H), 7.08–7.03 (m, 3H), 6.86 (brd, *J* = 6.5 Hz, 2H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.5 Hz, 1H), 4.37 (d, *J* = 11.5 Hz, 1H), 4.16 (m, 1H), 4.09 (d, *J* = 11.0 Hz, 1H), 3.73 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.63 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.54 (dd, *J* = 9.5, 7.0 Hz, 1H), 2.72 (s, 3H), 2.50 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 155.7, 154.6, 137.7, 136.8, 136.5, 133.4, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 122.3, 80.7, 76.3, 74.8, 73.8, 72.1, 71.0, 69.3, 14.1; FAB HRMS *m/z* calcd for $C_{31}H_{32}N_4O_4S$ $[M+H]^+$: 557.2223; Found: 557.2224.



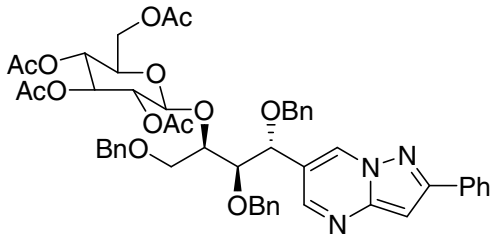
20

Compound 20. Amorphous solid, $[\alpha]_D^{28}$ –13.88 (*c* 0.416, $CHCl_3$); TLC: R_f = 0.38 (4:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.5 Hz, 1H), 8.57 (d, *J* = 2.5 Hz, 1H), 7.35–7.19 (m, 10H), 7.00–6.96 (m, 3H), 6.83 (dd, *J* = 7.5, 1.5 Hz, 2H), 4.70 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.46–4.43 (m, 3H), 4.20 (m, 1H), 4.10 (s, 3H), 4.10 (d, *J* = 11.5 Hz, 1H), 3.77 (dd, *J* = 8.5 Hz and *J* = 2.0 Hz, 1H), 3.67 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.56 (dd, *J* = 9.5, 7.0 Hz, 1H), 2.52 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 157.2, 155.0, 137.6, 136.5, 136.2, 134.8, 128.7, 128.6, 128.5, 128.2, 128.1, 125.5, 80.3, 76.2, 74.8, 73.8, 72.5, 70.8, 69.2, 53.4; FAB HRMS *m/z* calcd for $C_{32}H_{32}N_4O_6$ $[M+H]^+$: 569.2400; Found: 569.2405.



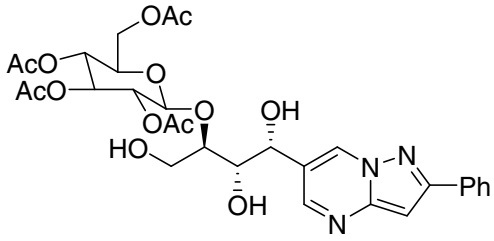
21

Compound 21. Amorphous solid, $[\alpha]_D^{28}$ –28.60 (*c* 0.363, $CHCl_3$); TLC: R_f = 0.54 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.0 Hz, 1H), 8.41 (d, *J* = 2.0 Hz, 1H), 8.00 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.48 (t, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.35–7.25 (m, 10H), 7.10–7.05 (m, 5H), 6.96 (s, 1H), 5.19 (t, *J* = 9.5 Hz, 1H), 5.07 (t, *J* = 10.0 Hz, 1H), 4.99 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.76 (d, *J* = 8.5 Hz, 1H), 4.71 (d, *J* = 4.0 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.50–4.47 (m, 2H), 4.45 (d, *J* = 11.5 Hz, 1H), 4..32 (d, *J* = 11.5 Hz, 1H), 4.22 (m, 1H), 4.16 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.99 (dd, *J* = 12.5, 2.0 Hz, 1H), 3.88 (m, 1H), 3.86 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.63 (dd, *J* = 11.0, 5.5 Hz, 1H), 3.55 (ddd, *J* = 10.0, 4.5, 2.5 Hz, 1H), 2.01, 2.00, 1.97, 1.96 (4s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 170.4, 169.4, 169.5, 156.6, 149.8, 149.6, 137.9, 137.4, 133.9, 133.0, 129.2, 129.0, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 119.8, 99.6, 93.7, 81.9, 77.8, 77.1, 75.0, 73.7, 72.9, 72.1, 71.8, 71.7, 69.3, 68.4, 61.7, 20.9, 20.81, 20.80 (4 × OCO*C*H_3); FAB HRMS *m/z* calcd for $C_{51}H_{53}N_3O_{13}$ $[M+ H]^+$: 916.3657; Found: 916.3657.



22

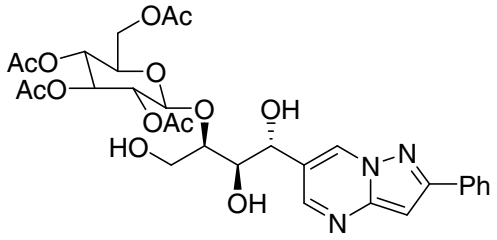
Compound 22. Amorphous solid, $[\alpha]_D^{28}$ + 6.96 (*c* 0.340, $CHCl_3$); TLC: R_f = 0.53 (1:1, EtOAc:hexane, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.0 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 8.00 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.35–7.25 (m, 10H), 7.12–7.09 (m, 3H), 6.98 (dd, *J* = 7.5, 3.0 Hz, 2H), 6.96 (s, 1H), 5.19 (t, *J* = 9.5 Hz, 1H), 5.11 (t, *J* = 9.5 Hz, 1H), 5.00 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.84 (d, *J* = 8.0 Hz, 1H), 4.72 (d, *J* = 7.5 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.44-4.41 (m, 3H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.21 (d, *J* = 11.5 Hz, 1H), 4.16 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.90 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.87 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.57–3.54 (m, 3H), 2.01, 2.00, 1.95, 1.94 (4s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 170.4, 169.5, 169.3, 156.5, 150.5, 149.6, 137.8, 137.5, 137.3, 134.1, 133.0, 129.1, 129.0, 128.7, 128.6, 128.3, 128.2, 128.0, 127.9, 127.3, 126.6, 120.1, 100.4, 93.6, 81.0, 77.0, 76.3, 74.6, 73.8, 72.9, 72.1, 71.7, 70.0, 68.2, 61.6, 20.9, 20.84, 20.82 (4 × OCO*C*H_3); FAB HRMS *m/z* calcd for $C_{51}H_{53}N_3O_{13}$ $[M+H]^+$: 916.3657; Found: 916.3655.



23

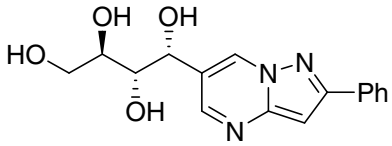
Compound 23. Amorphous solid, $[\alpha]_D^{28}$ –76.28 (*c* 0.400, $CHCl_3$); TLC: R_f = 0.40 (1:19, MeOH: CH_2Cl_2, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 1.0 Hz, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 7.90 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.46 (m, 1H), 6.85 (s, 1H), 5.23 (t, *J* = 9.5 Hz, 1H), 5.16 (brd, *J* = 3.5 Hz, 1H), 5.04 (t, *J* = 9.5 Hz, 1H), 5.01 (dd, *J* = 10.0, 8.0 Hz, 1H), 4.79 (d, *J* = 8.0 Hz, 1H), 4.42 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.03 (dd, *J* = 12.5, 6.0 Hz, 1H), 3.95–3.87 (m, 3H), 3.81–3.75 (m, 2H), 3.72–3.69 (m, 2H), 2.09 (brs, 6H), 2.05, 2.01 (2s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 170.3, 169.7, 169.5, 156.5, 149.0, 133.0, 132.7, 129.3, 129.1, 126.8, 122.5, 101.2, 93.6, 80.2, 77.4, 73.7,

72.7, 72.4, 71.6, 68.5, 67.2, 63.4, 62.0, 20.9, 20.8, 20.7; FAB HRMS *m/z* calcd for $C_{30}H_{35}N_3O_{13}$ $[M+H]^+$: 646.2248; Found: 646.2242.



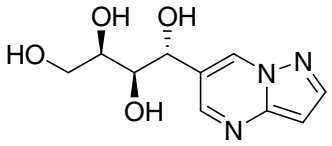
24

Compound 24. Amorphous solid, $[\alpha]_D^{28}$ –12.26 (*c* 0.666, $CHCl_3$); TLC: R_f = 0.40 (1:19, MeOH: CH_2Cl_2, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.0 Hz, 1H), 8.50 (d, *J* = 2.0 Hz, 1H), 7.92 (brd, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 5.25 (t, *J* = 9.5 Hz, 1H), 5.06 (t, *J* = 9.5 Hz, 1H), 5.05 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 4.73 (dd, *J* = 8.0, 5.7 Hz, 1H), 4.40 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.22 (m, 1H), 4.03 (dd, *J* = 12.5, 6.0 Hz, 1H), 4.02 (m, 1H), 3.86–3.85 (m, 2H), 3.76 (m, 1H), 3.68 (m, 1H), 2.07, 2.05 (2s, 6H), 2.02 (brs, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.3, 170.0, 169.5, 156.5, 150.0, 133.1, 132.7, 129.3, 129.0, 126.7, 123.0, 101.2, 93.5, 78.8, 75.2, 72.6, 72.4, 71.6, 69.1, 68.7, 63.0, 62.1, 20.9, 20.8, 20.7; FAB HRMS *m/z* calcd for $C_{30}H_{35}N_3O_{13}$ $[M+H]^+$: 646.2248; Found: 646.2245.



25

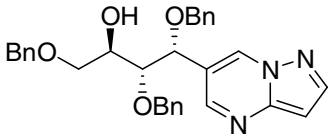
Compound 25. Amorphous solid, TLC: R_f = 0.52 (1:4, MeOH:CH_2Cl_2, v/v); ^{1}H NMR (500 MHz, DMSO-d_6 ,δ = 2.54 ppm) δ 8.09 (brs, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.24 (brd, *J* = 7.0 Hz, 2H), 6.70 (t, *J* = 7.7 Hz, 2H), 6.63 (t, *J* = 8.0 Hz, 1H), 6.39 (s, 1H), 4.62 (d, *J* = 6.5 Hz, 1H), 4.23 (d, *J* = 5.0 Hz, 1H), 3.97 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 5.5 Hz, 1H), 3.62 (t, *J* = 5.5 Hz, 1H), 2.86–2.80 (m, 2H), 2.69-2.65 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.3, 150.9, 149.2, 133.3, 129.5, 126.7, 125.8, 93.2, 74.7, 72.1, 68.5, 64.1; FAB HRMS *m/z* calcd for $C_{16}H_{17}N_3O_4$ $[M+H]^+$: 316.1297; Found: 316.1293.



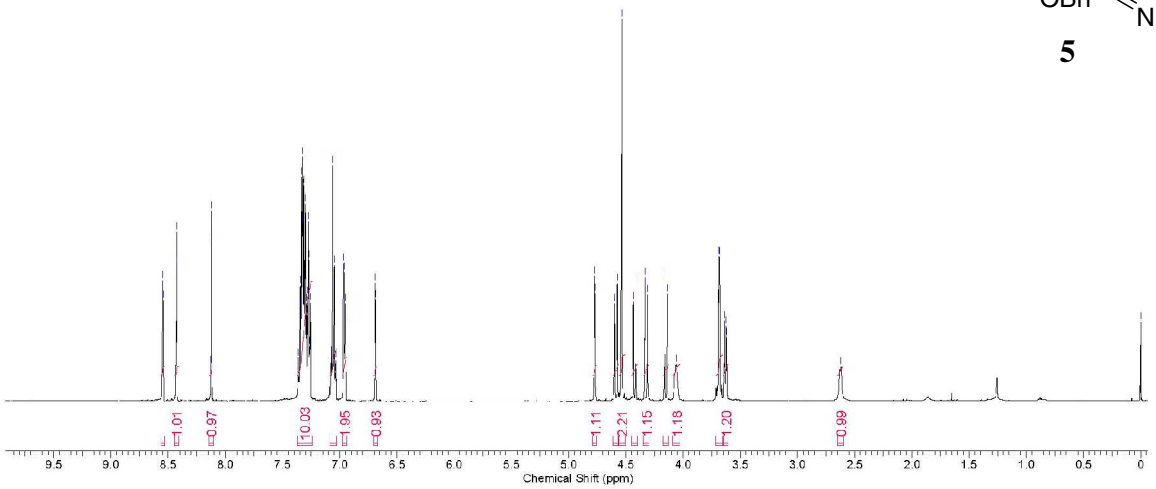
26

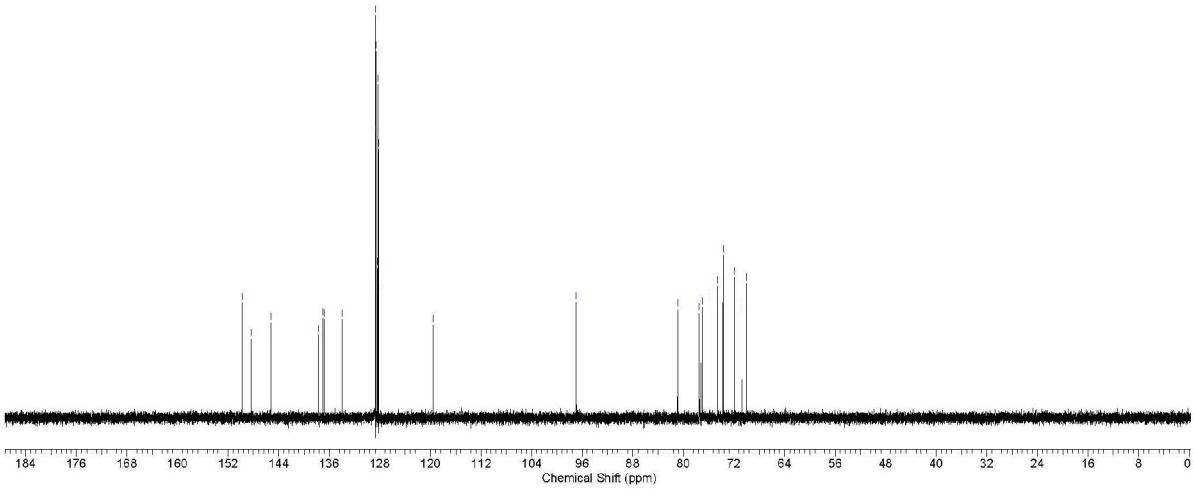
Compound 26. Amorphous solid, TLC: R_f = 0.40 (1:4, MeOH:CH_2Cl_2, v/v); ^{1}H NMR (500 MHz, $CDCl_3$:CD_3OD) δ 8.81 (brs, 1H), 8.62 (brs, 1H), 8.10 (d, *J* = 2.5 Hz, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 4.81 (d, *J* = 8.5 Hz, 1H), 4.03 (m, 1H), 3.72–3.68 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD) δ 147.5, 144.5, 124.0, 96.0, 74.1, 70.1, 69.5, 63.7; FAB HRMS *m/z* calcd for $C_{10}H_{13}N_3O_4$ $[M+H]^+$: 240.0984; Found: 240.0976.

4. Copies of ^{1}H and ^{13}C NMR spectra of all compounds:



5



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8.617
8.613
8.470
7.338
7.332
7.322
7.304
7.290
7.282
7.261
7.258
6.988
6.898
6.895
4.882
4.877
4.571
4.565
4.548
4.482
4.459
4.393
4.389
4.103
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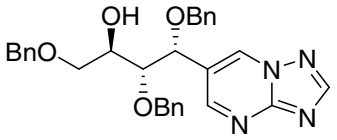
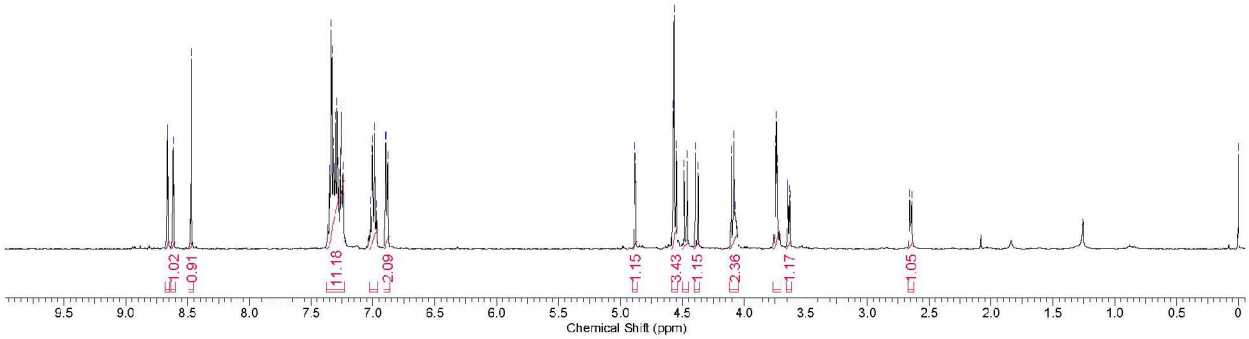
4.072
3.741
3.734
3.727
3.647
3.631
2.656
2.642
0.000


OH
OBn
BnO
OBn
N
N
N
N

6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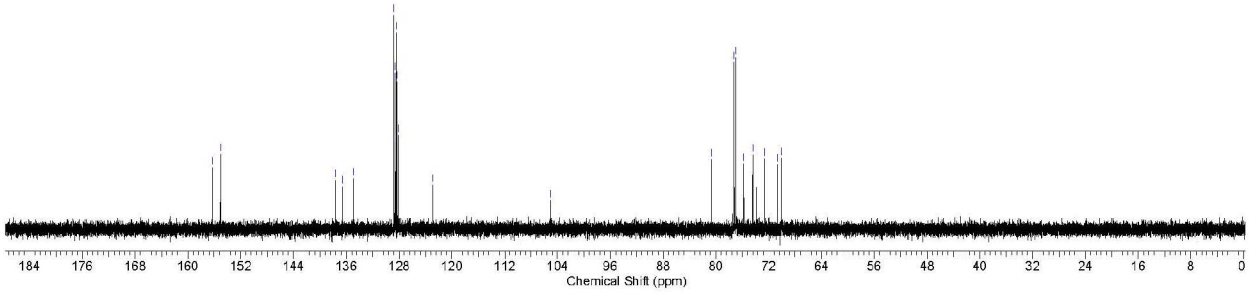
2.09
1.15
3.43
1.15
2.36
1.17
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


156.307
155.048
137.633
136.729
134.938
128.949
128.805
128.642
128.364
128.331
128.146
122.952
104.989
80.685
77.505
77.250
76.995
75.829
74.411
73.871
72.532
70.687
70.073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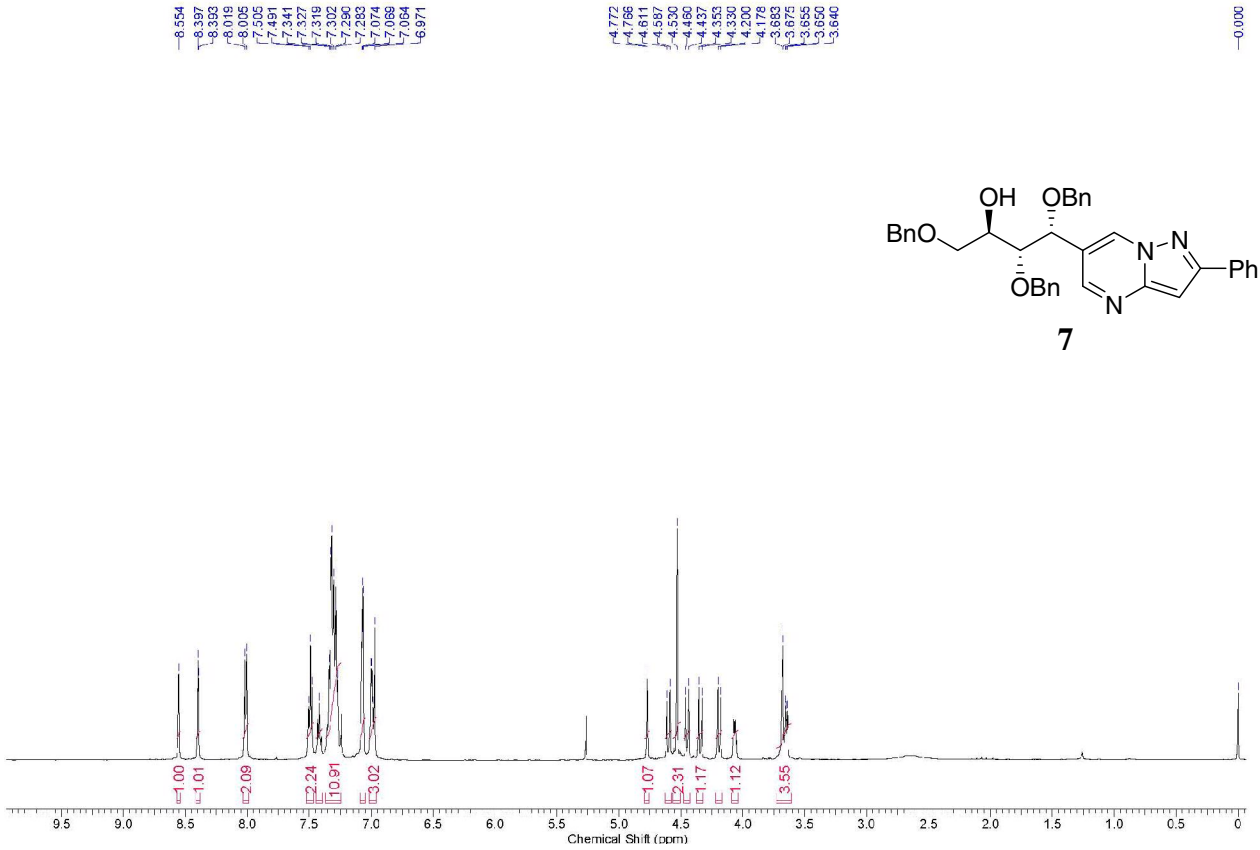
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)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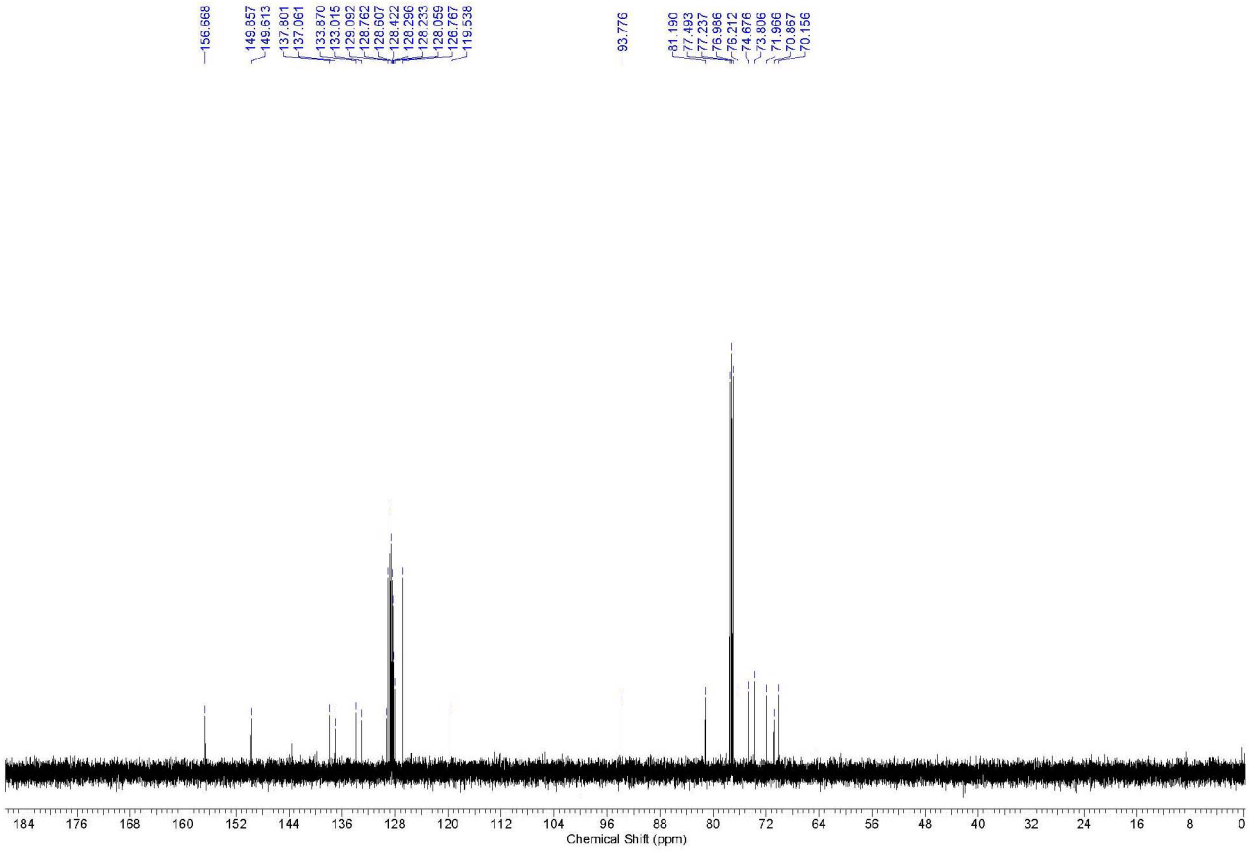
8.005
7.505
7.491
7.344
7.327
7.319
7.302
7.290
7.283
7.074
7.069
7.064
6.971
4.772
4.766
4.611
4.587
4.530
4.460
4.437
4.353
4.330
4.200
4.178
3.683
3.675
3.655
3.650
3.640
0.000
OH
OBn
BnO
OBn
N
N
Ph
N
7
1.00
1.01
2.09
2.24
10.91
3.02
1.07
2.31
1.17
1.12
3.55
Chemical Shift (ppm)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133.015
129.092
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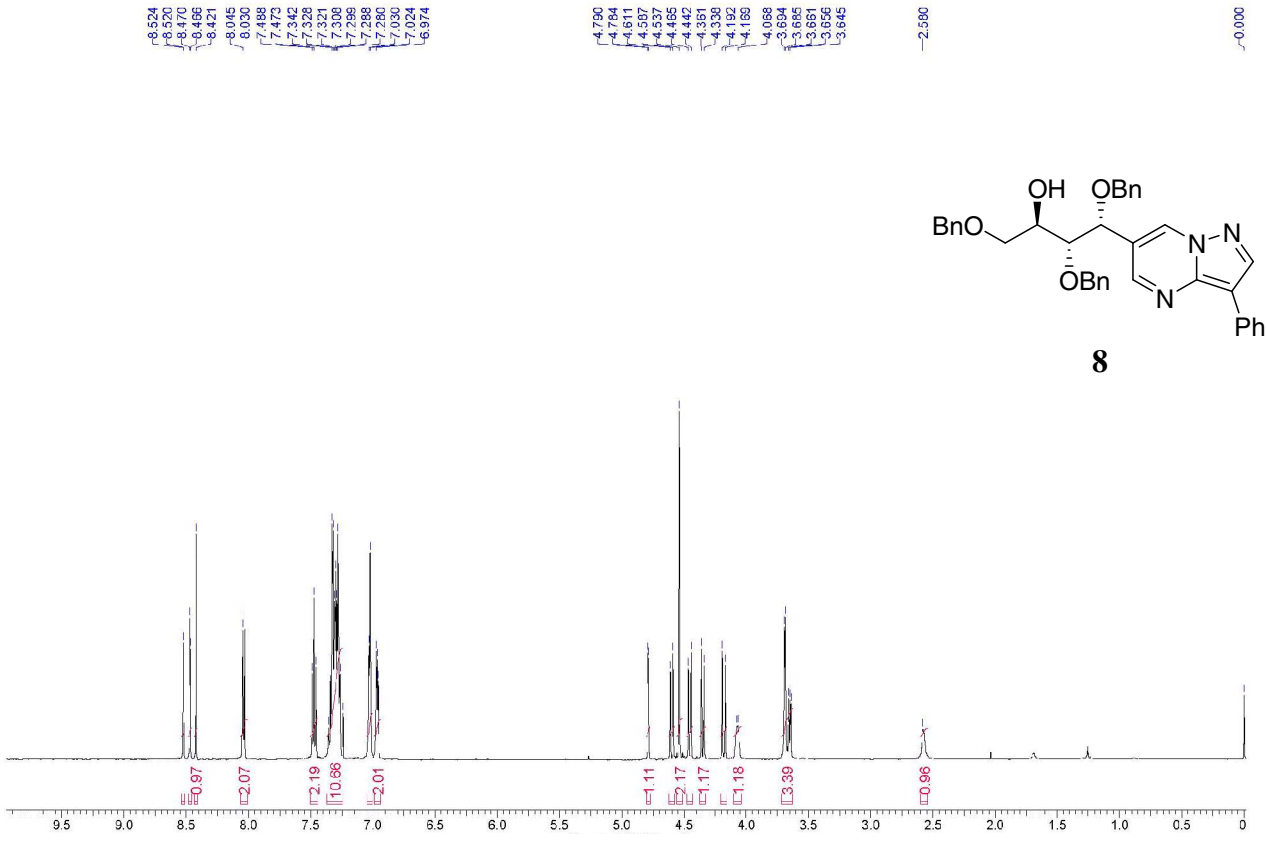
128.607
128.422
128.296
128.233
128.059
126.767
119.538
93.776
81.190
77.493
77.237
76.986
76.212
74.676
73.806
71.966
70.867
70.156
Chemical Shift (ppm)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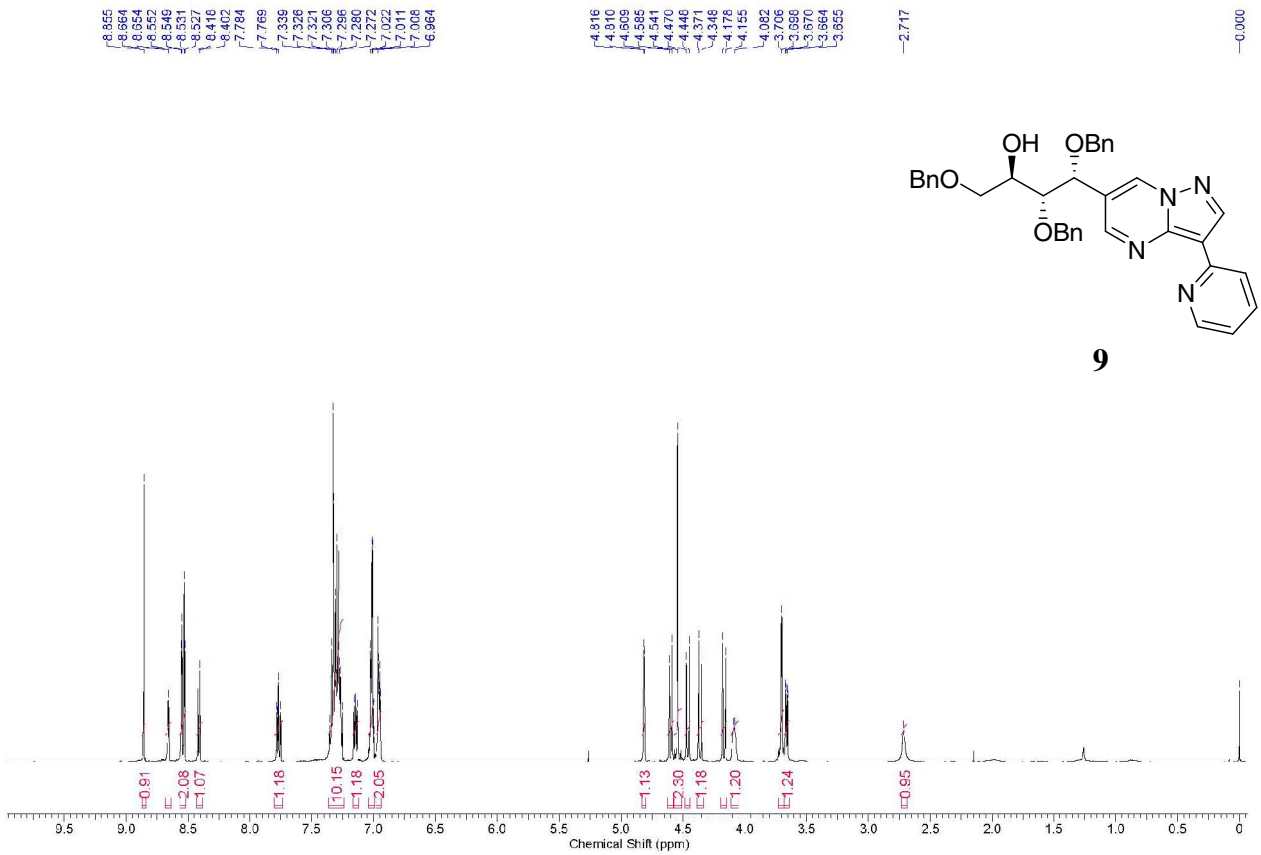
7.342
7.328
7.321
7.308
7.299
7.288
7.280
7.030
7.024
6.974
4.790
4.784
4.611
4.587
4.537
4.485
4.442
4.361
4.338
4.192
4.168
4.068
3.694
3.685
3.661
3.656
3.645
2.580
0.000
OH
OBn
BnO
OBn
N
N
N
Ph
0.97
2.07
2.19
10.86
2.01
1.11
2.17
1.17
1.18
3.39
0.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
148.761
144.691
142.911
137.755
129.030
126.779
126.734
126.564
126.434
126.323
126.264
126.212
126.502
119.866
111.000
80.981
77.502
77.250
76.995
76.128
74.555
73.771
72.053
70.035
70.139
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

8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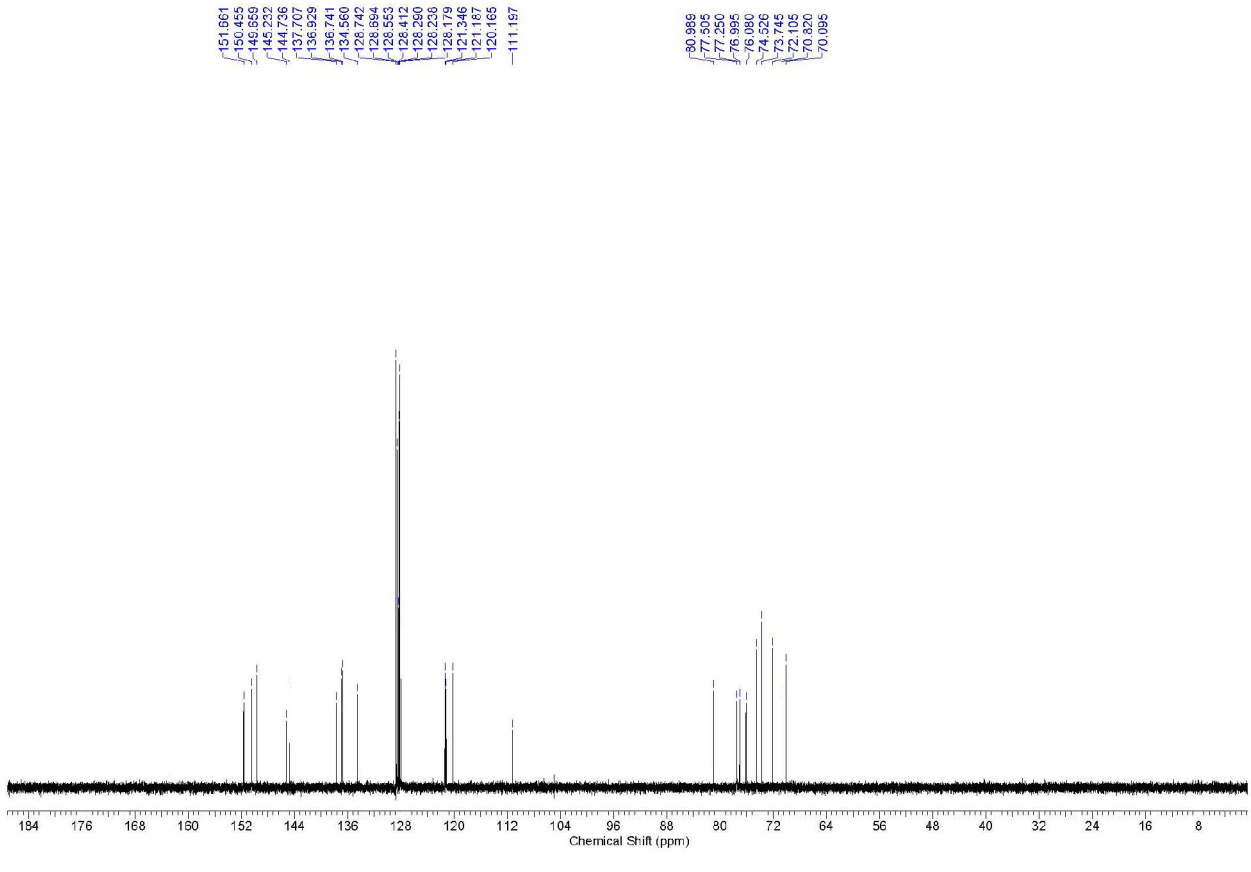
7.321
7.306
7.296
7.280
7.272
7.022
7.011
7.008
6.964
4.816
4.810
4.609
4.585
4.541
4.470
4.446
4.371
4.348
4.178
4.155
4.082
3.706
3.698
3.670
3.664
3.655
2.717
0.000
0.91
2.08
1.07
1.18
0.15
1.18
2.05
1.13
2.30
1.18
1.20
1.24
0.85
Chemical Shift (ppm)

OH
OBn
BnO
OBn
N
N
N

9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128.412
128.290
128.236
128.179
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121.187
120.165
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76.080
74.526
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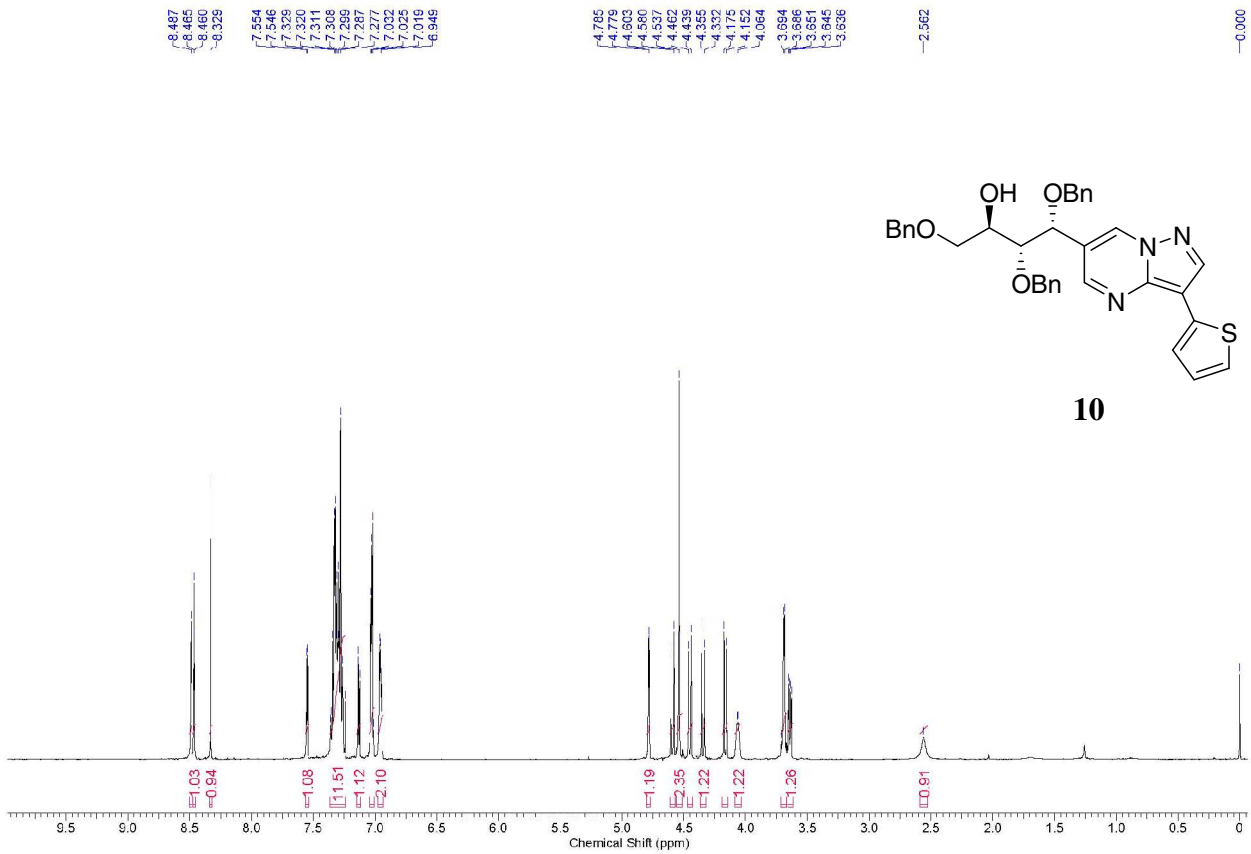
72.105
70.820
70.095
Chemical Shift (ppm)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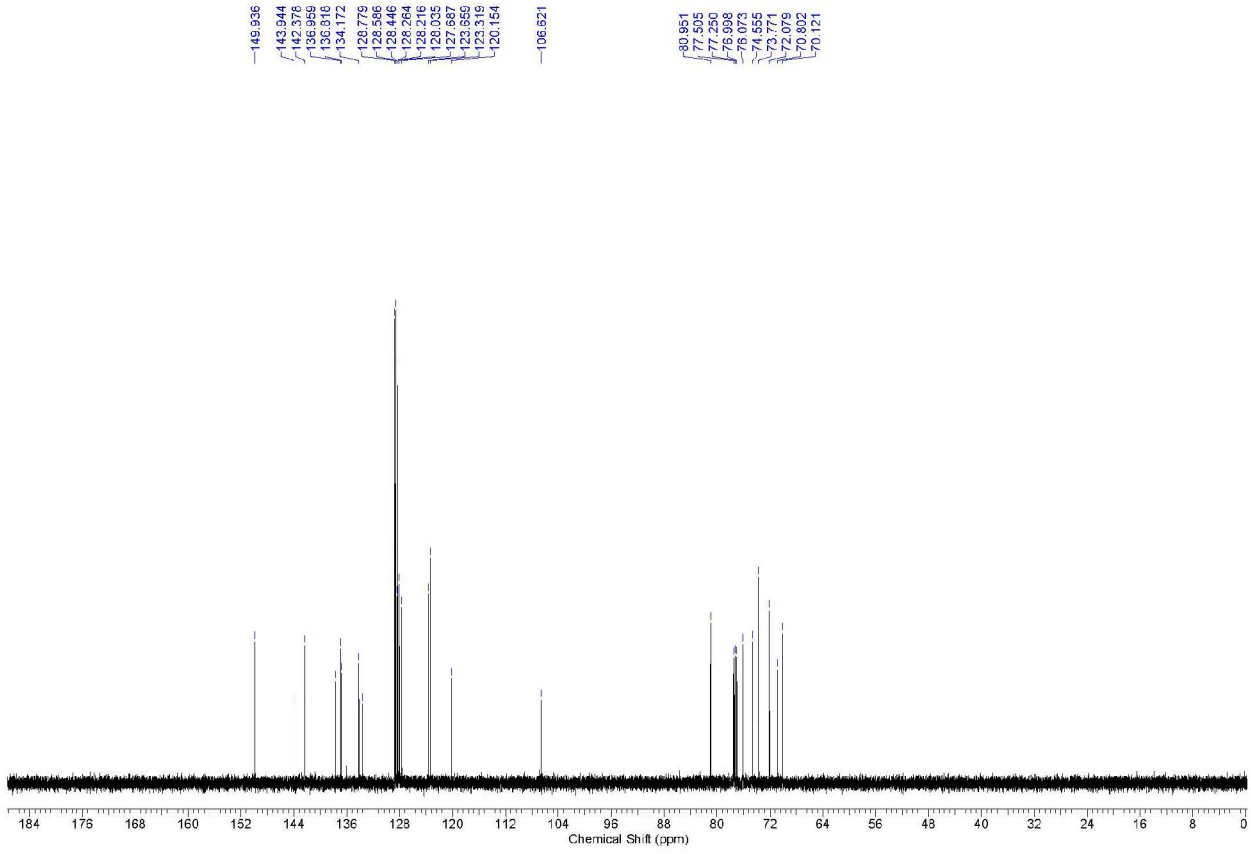
7.025
7.019
6.949
4.785
4.779
4.603
4.580
4.537
4.462
4.428
4.355
4.332
4.175
4.152
4.064
3.694
3.686
3.651
3.645
3.636
2.562
0.000
OH
OBn
BnO
OBn
N
N
N
S
1.03
0.94
1.08
1.51
1.12
2.10
1.19
2.35
1.22
1.22
1.26
0.91
Chemical Shift (ppm)

10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128.446
128.264
128.216
128.035
127.687
123.859
123.319
120.154
106.621
80.951
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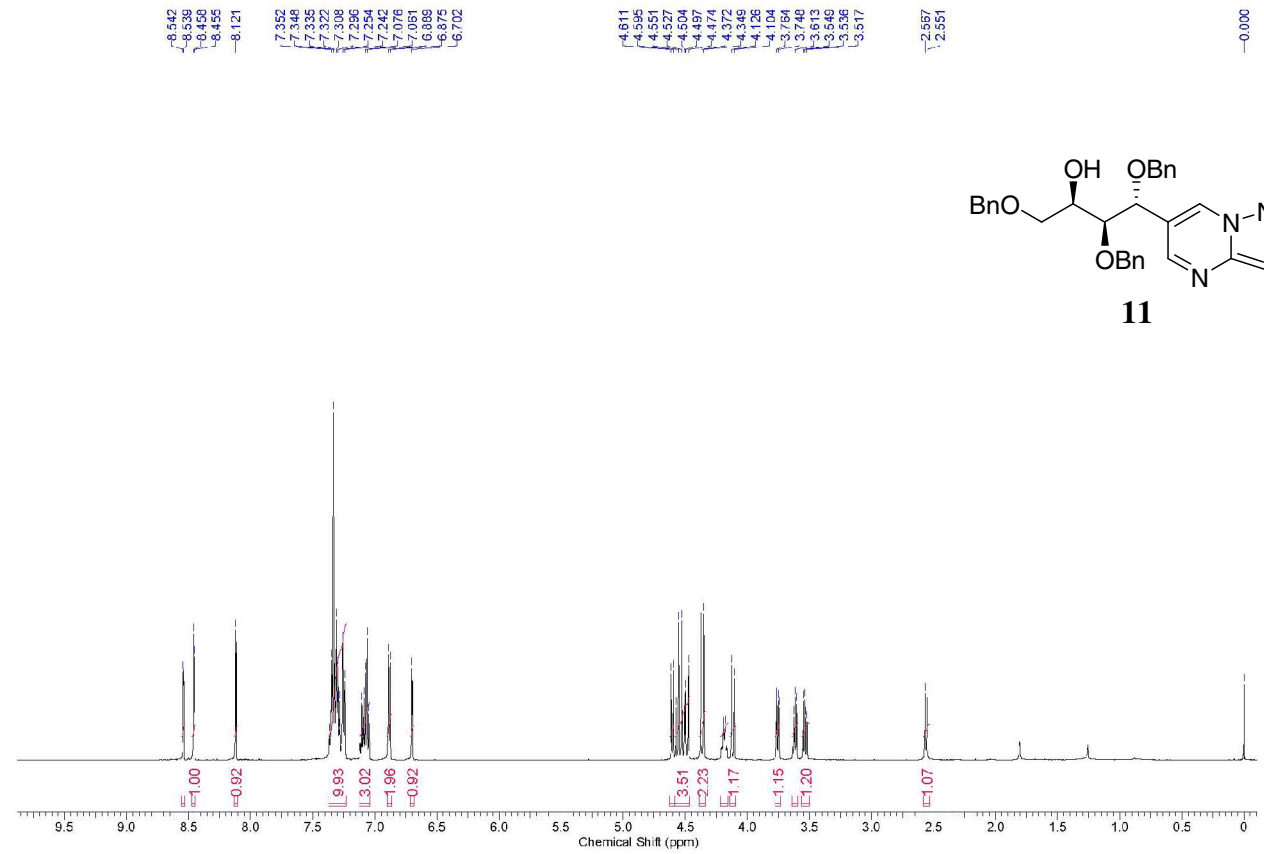
77.250
76.998
76.073
74.555
73.771
72.079
70.802
70.121
Chemical Shift (ppm)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7.061
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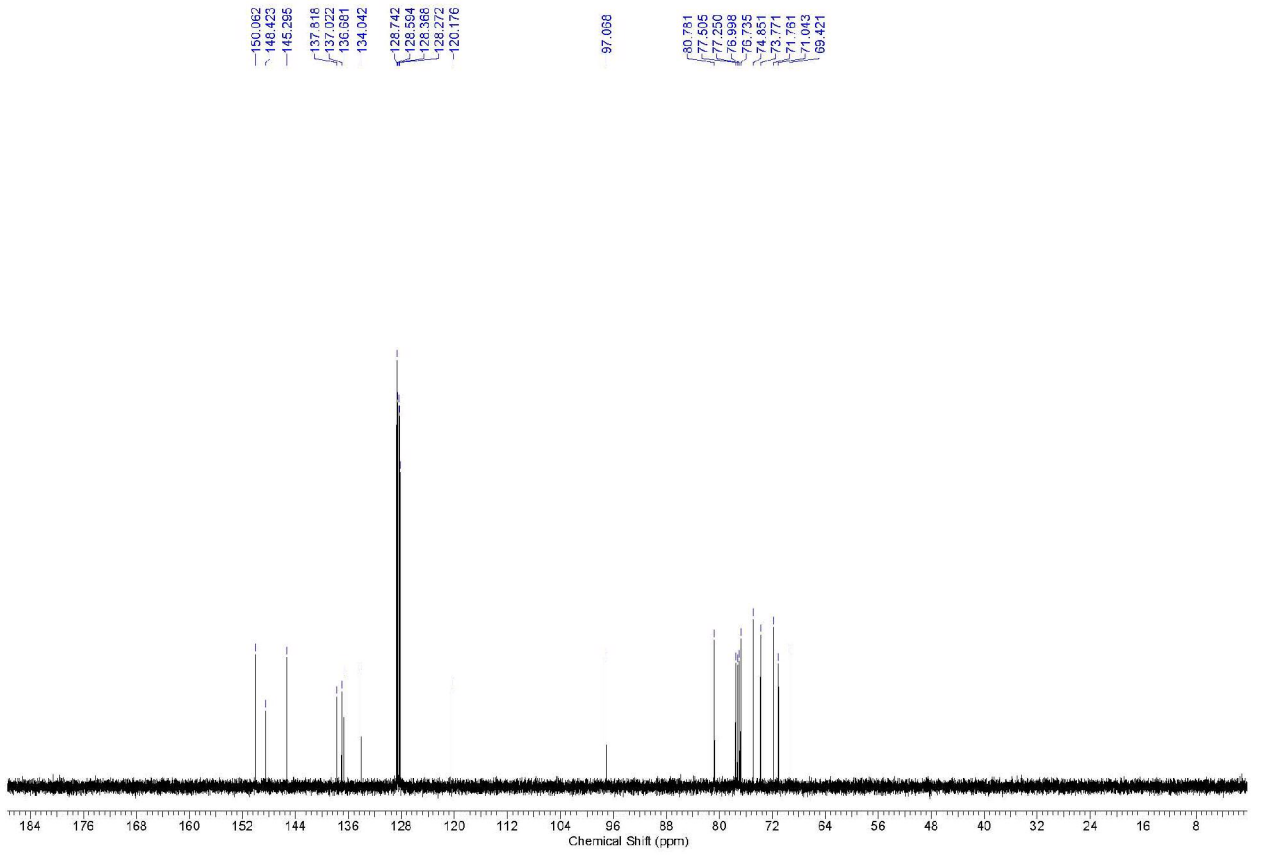
6.875
6.702
4.611
4.595
4.551
4.527
4.504
4.497
4.474
4.372
4.349
4.126
4.104
3.764
3.740
3.613
3.549
3.536
3.517
2.567
2.551
0.000
1.00
0.92
9.93
3.02
1.96
0.92
3.51
2.23
1.17
1.15
1.20
1.07
Chemical Shift (ppm)

OH
OBn
BnO
OBn
N
N
N

11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128.368
128.272
120.176
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80.781
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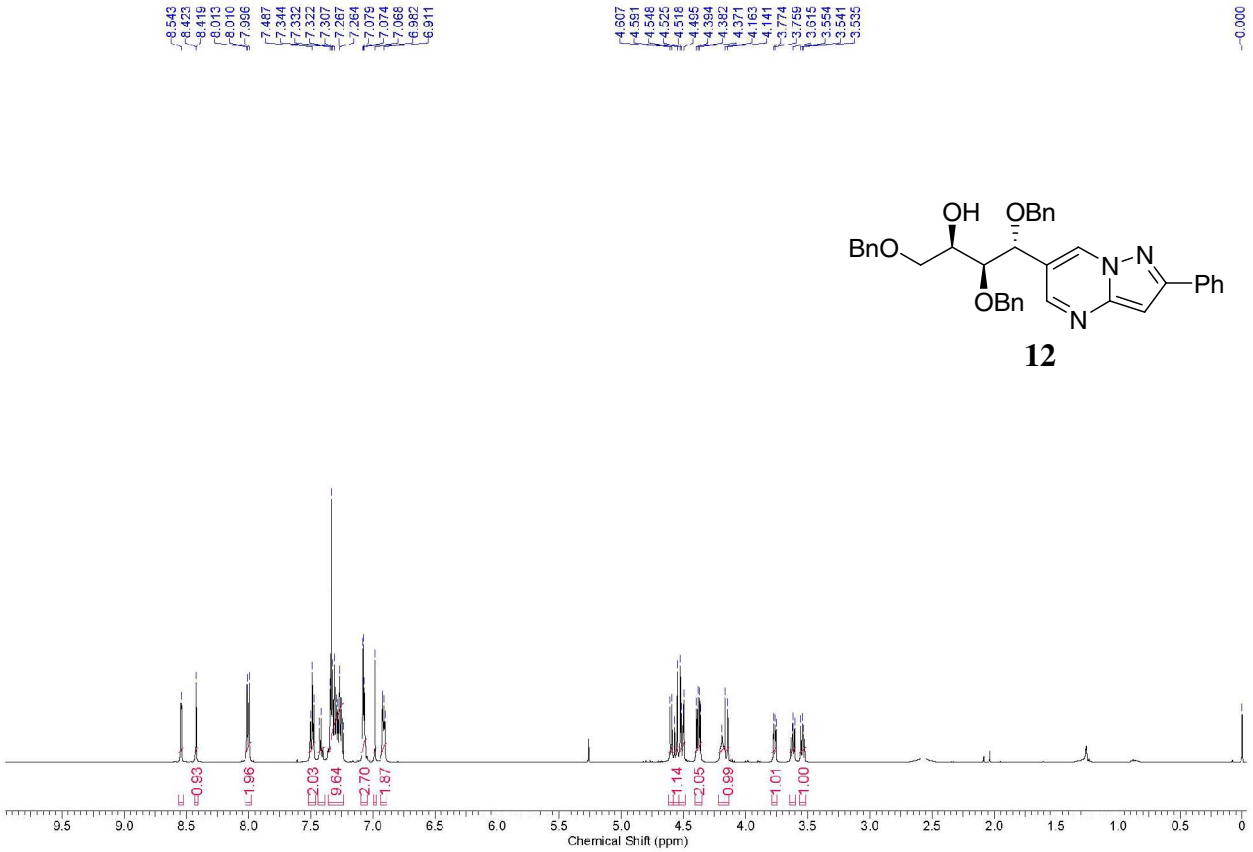
77.250
76.998
76.735
74.851
73.771
71.761
71.043
69.421
Chemical Shift (ppm)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7.264
7.079
7.074
7.068
6.982
6.911
4.607
4.591
4.548
4.525
4.518
4.495
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4.382
4.371
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4.141
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3.759
3.615
3.554
3.541
3.535
0.000
OH
OBn
BnO
OBn
N
N
Ph
N
12
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2.70
1.87
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0.99
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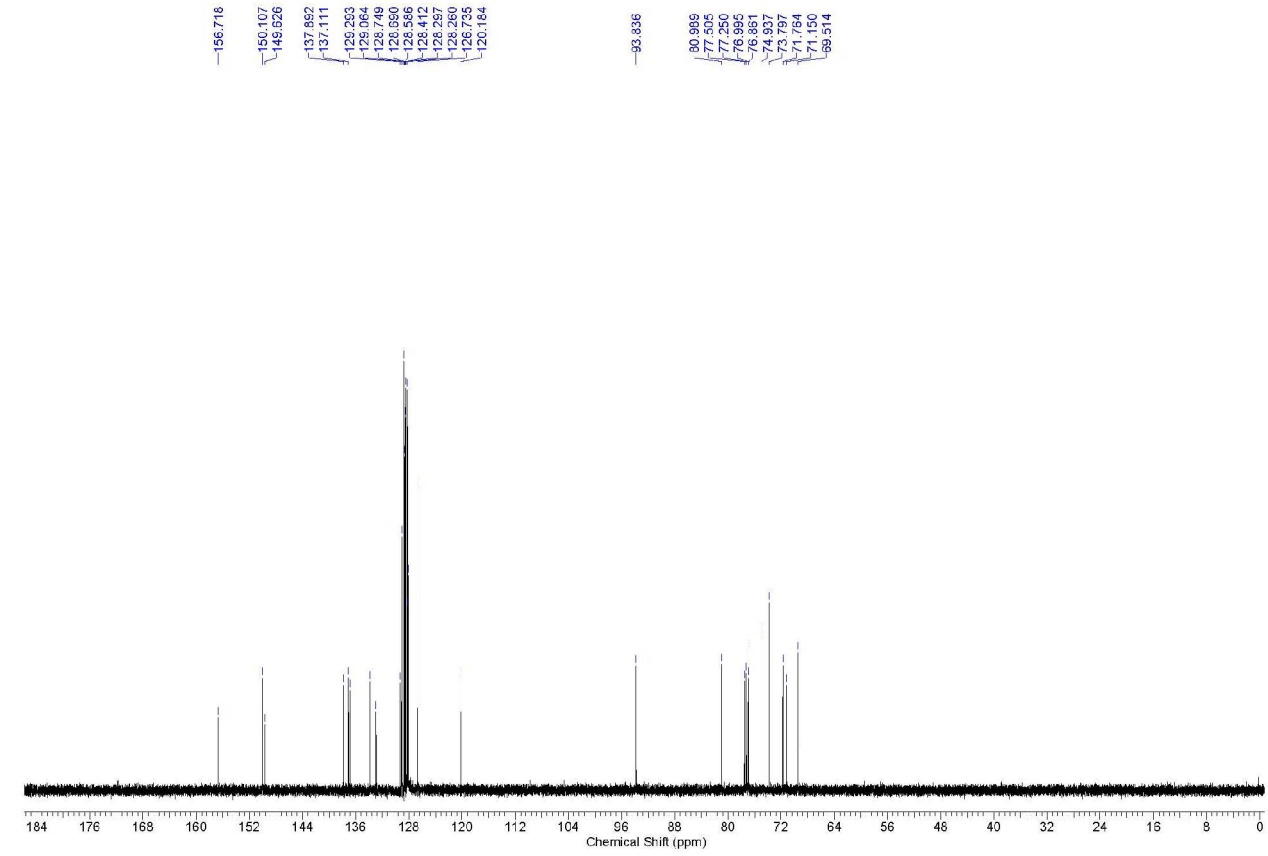
1.00
Chemical Shift (ppm)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128.749
128.690
128.566
128.412
126.257
126.260
126.735
120.184
93.836
80.989
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77.250
76.995
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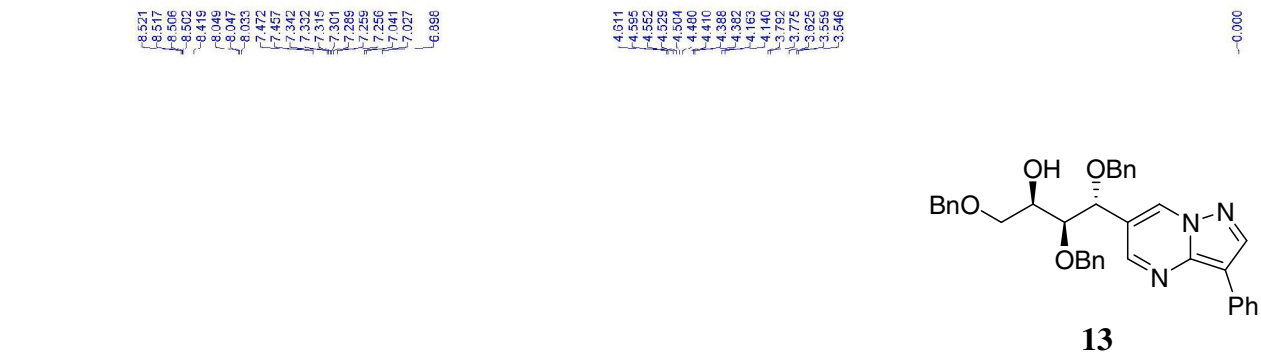
74.937
73.797
71.764
71.150
69.514
Chemical Shift (ppm)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8.047
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7.315
7.301
7.289
7.259
7.256
7.041
7.027
6.898
4.611
4.595
4.552
4.529
4.504
4.480
4.410
4.388
4.382
4.163
4.140
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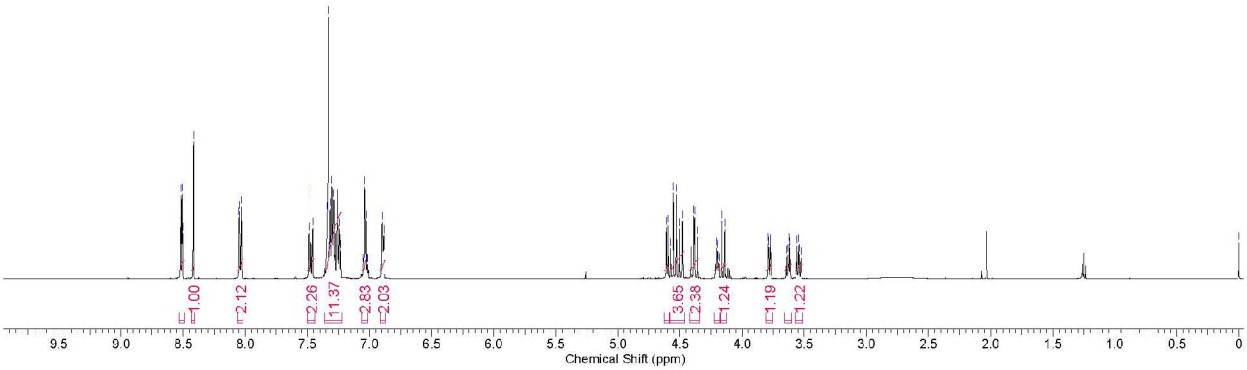
0.000

OH
OBn
BnO
OBn
N
N
Ph

13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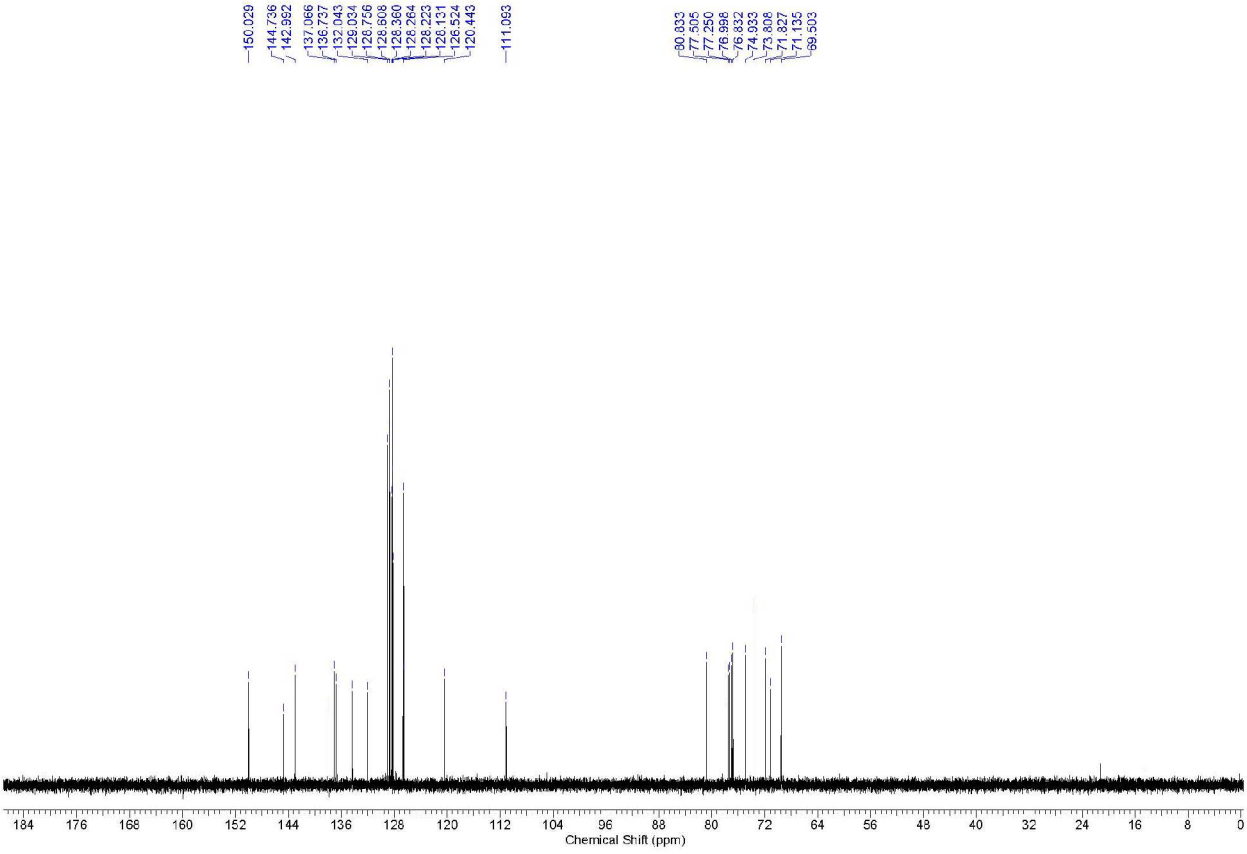
2.03
3.65
2.38
1.24
1.19
1.22
Chemical Shift (ppm)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136.737
132.043
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126.131
126.524
120.443
111.093
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77.250
76.998
76.832
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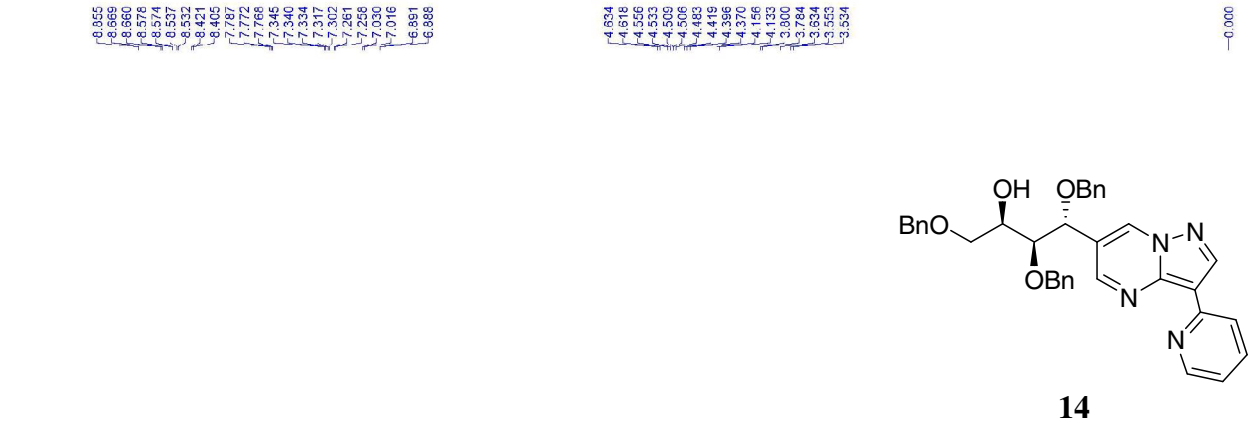
73.806
71.827
71.135
69.503
Chemical Shift (ppm)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7.302
7.261
7.258
7.030
7.016
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6.888
4.634
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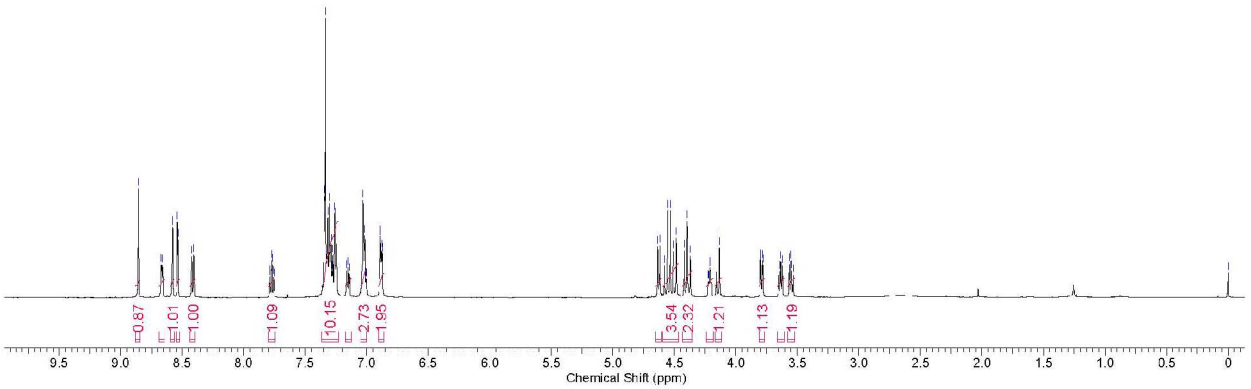
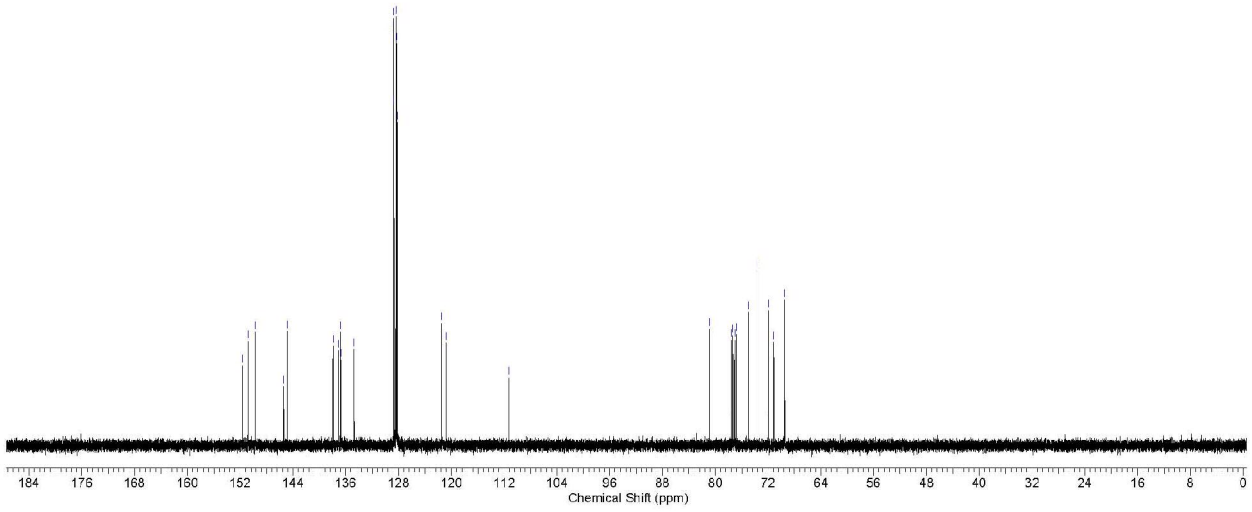
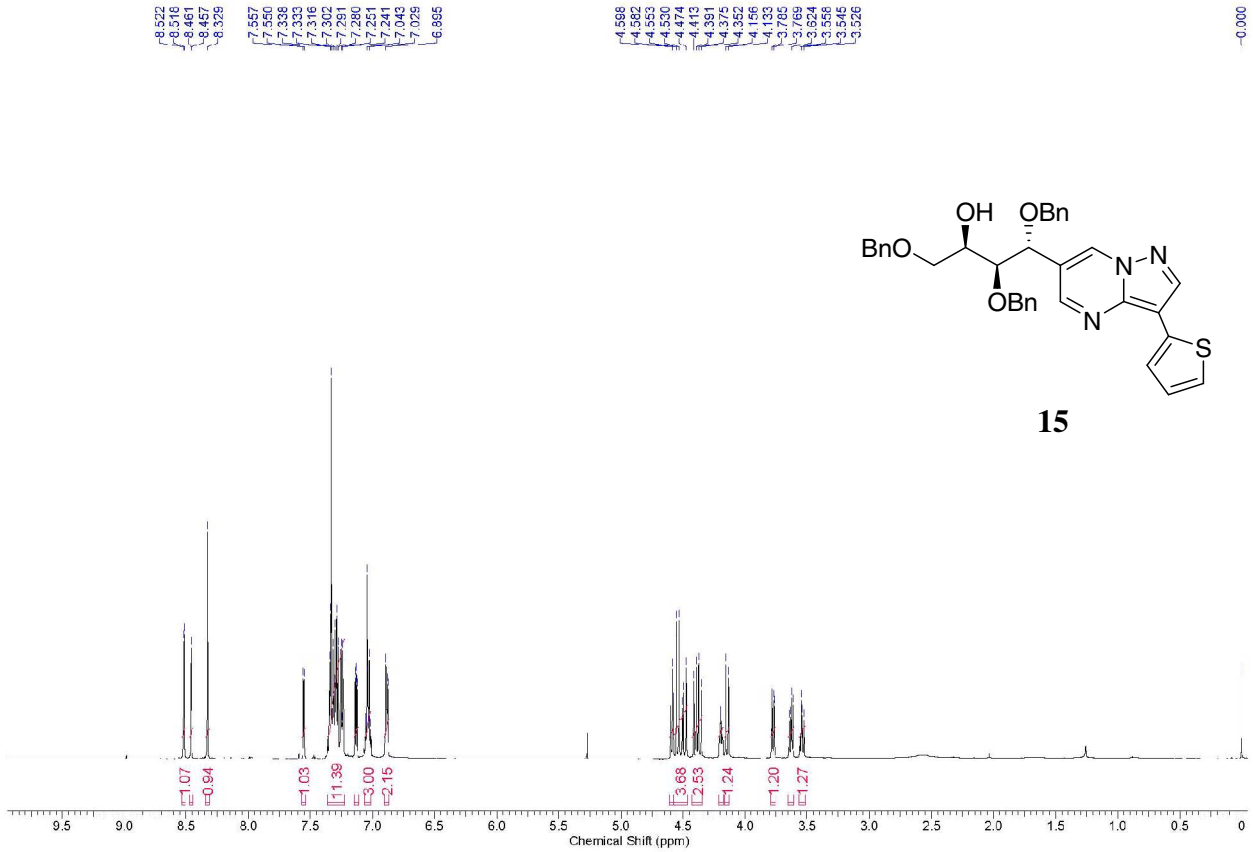
4.556
4.533
4.509
4.506
4.483
4.419
4.396
4.370
4.156
4.133
3.800
3.784
3.634
3.553
3.534
0.000
OH
OBn
BnO
OBn
N
N
N
N

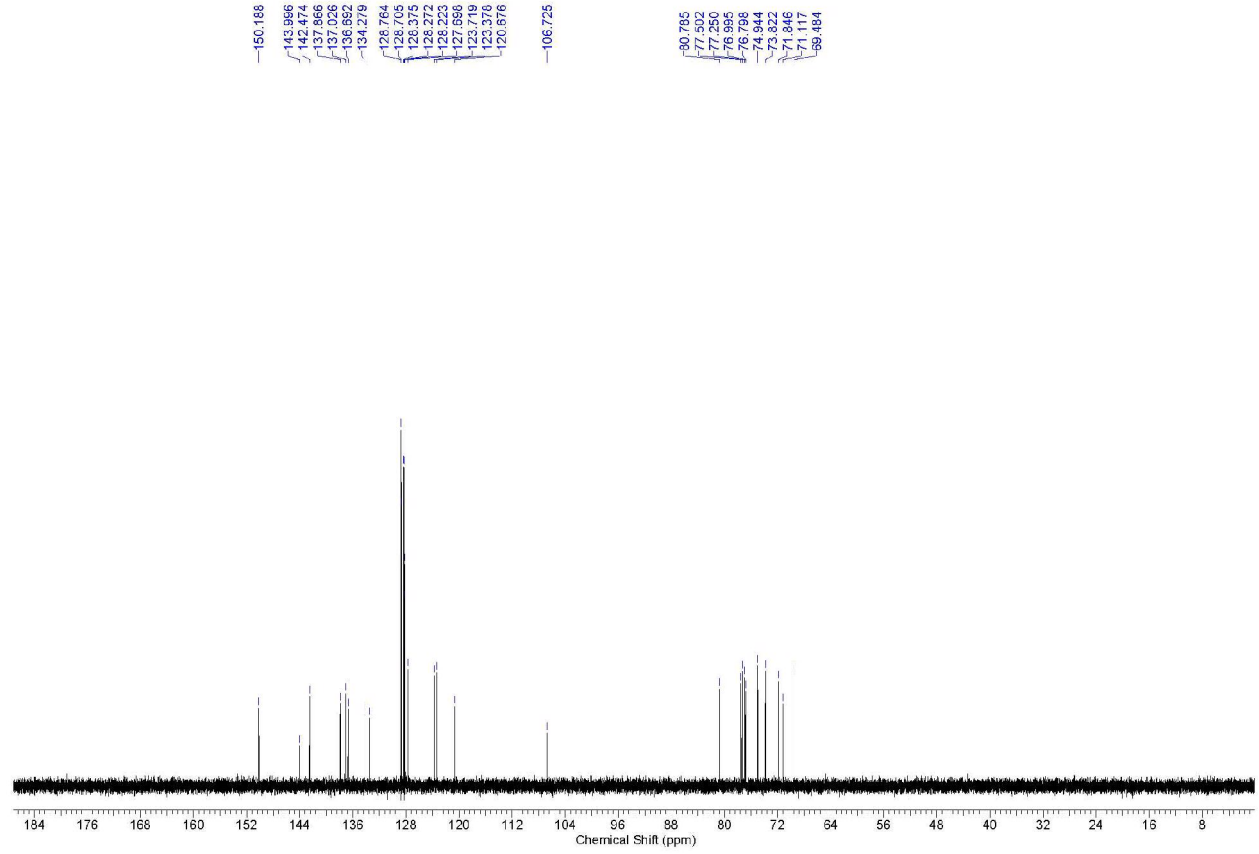
14

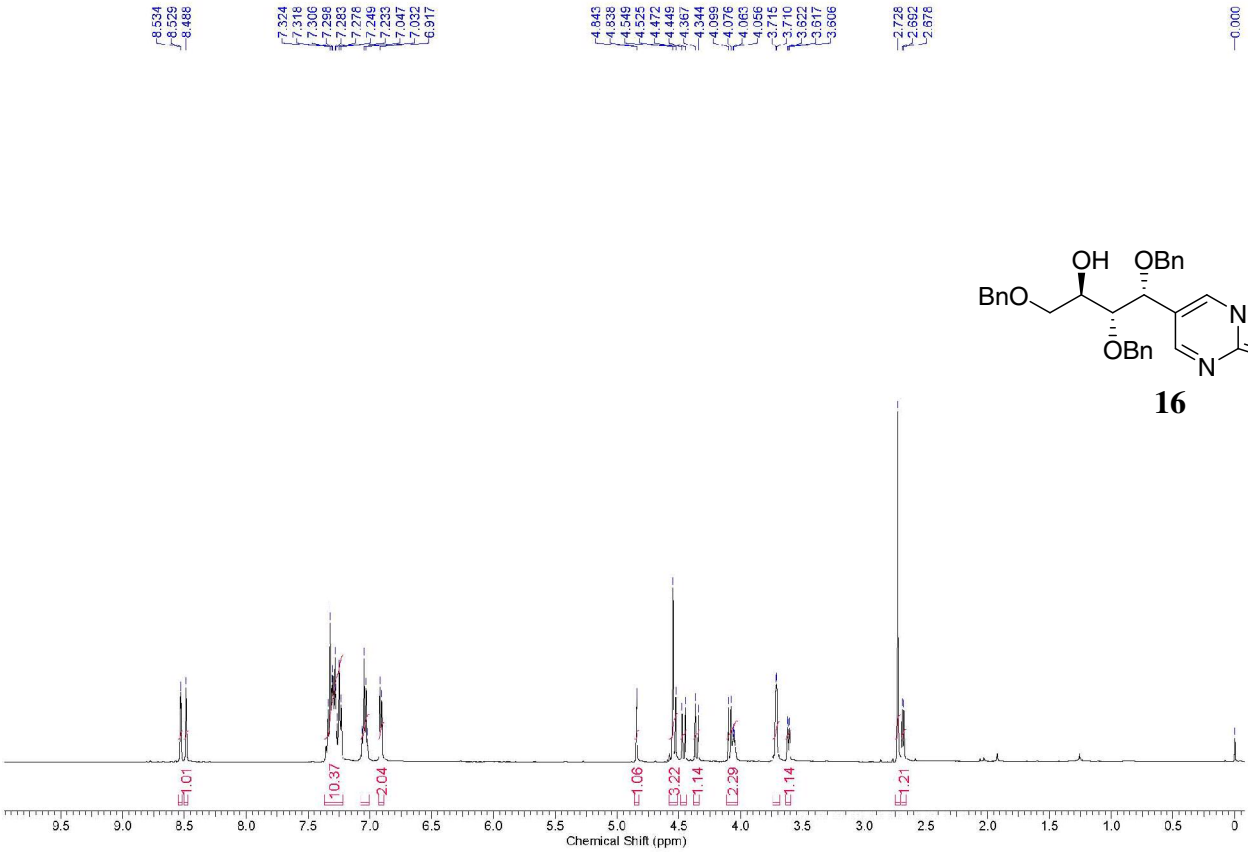

0.87
1.01
1.00
1.09
10.15
2.73
1.95
3.54
2.32
1.21
1.13
1.19
Chemical Shift (ppm)


151.684
150.759
149.740
145.360
144.914
137.910
137.077
136.852
134.768
128.819
128.753
126.668
126.416
126.279
126.156
121.468
121.316
120.776
111.348
80.889
77.579
77.328
77.072
76.826
75.011
73.871
71.961
71.172
69.529


Chemical Shift (ppm)

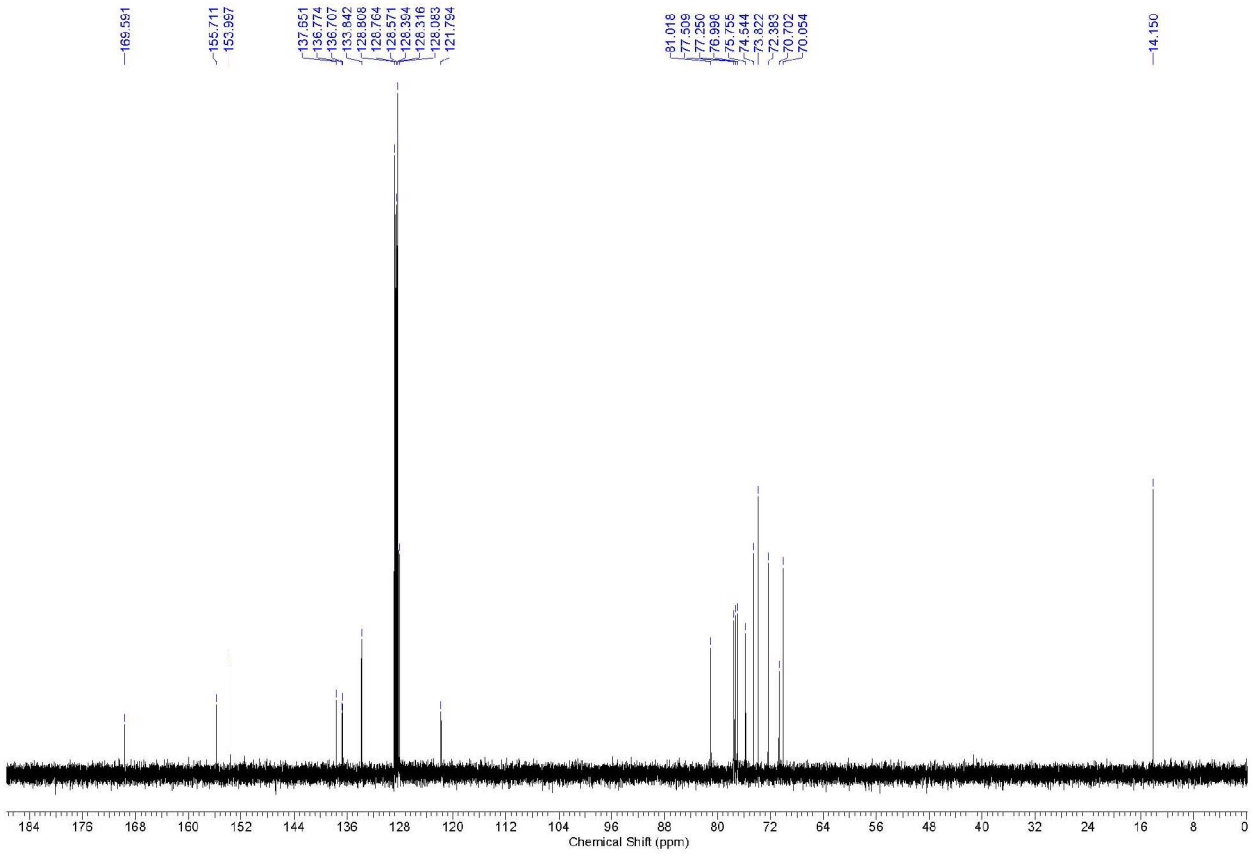

8.522
8.516
8.461
8.457
8.329
7.557
7.556
7.338
7.333
7.316
7.302
7.291
7.280
7.251
7.241
7.043
7.029
6.895
4.598
4.582
4.553
4.530
4.474
4.413
4.391
4.375
4.352
4.156
4.133
3.785
3.769
3.624
3.556
3.545
3.526
0.000
OH
OBn
BnO
OBn
N
N
N
S
15
1.07
0.94
1.03
1.39
3.00
2.15
3.68
2.53
1.24
1.20
1.27
Chemical Shift (ppm)


150.188
143.966
142.474
137.866
137.026
136.892
134.279
126.764
126.705
126.375
126.272
126.223
127.656
123.719
123.376
120.676
106.725
80.785
77.502
77.250
76.995
76.798
74.944
73.822
71.846
71.117
69.484
Chemical Shift (ppm)

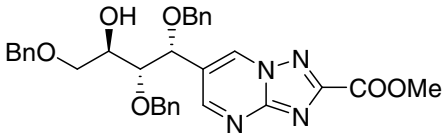

8.534
8.529
8.488
7.324
7.318
7.306
7.298
7.288
7.283
7.278
7.249
7.233
7.047
7.032
6.917
4.843
4.838
4.549
4.525
4.472
4.449
4.367
4.344
4.089
4.076
4.063
4.056
3.715
3.710
3.622
3.617
3.606
2.728
2.692
2.676
0.000
1.01
10.37
2.04
1.06
3.22
1.14
2.29
1.14
1.21
Chemical Shift (ppm)

OH
OBn
BnO
OBn
N
N
N
N
SMe

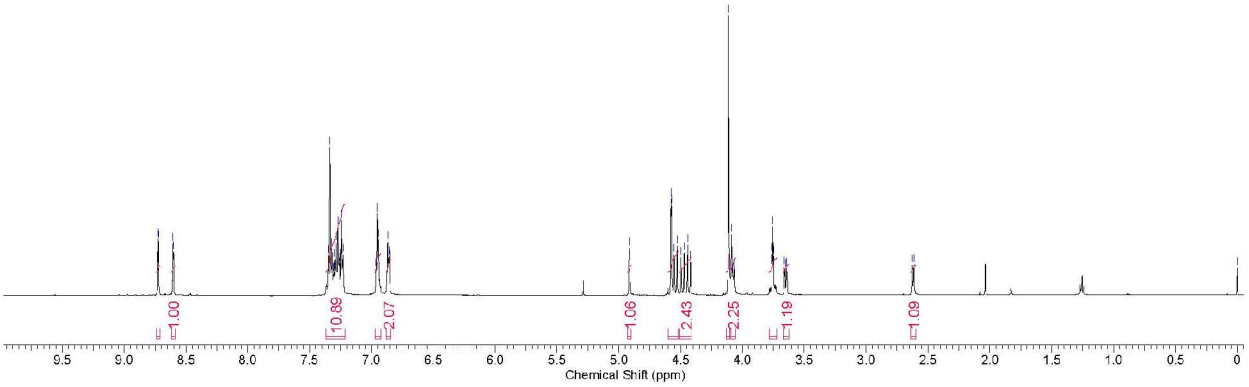
16


169.591
155.711
153.957
137.651
136.774
136.707
133.842
128.808
126.764
128.571
128.354
126.316
128.083
121.754
81.018
77.509
77.250
76.998
75.755
74.544
73.822
72.383
70.702
70.054
14.150
Chemical Shift (ppm)

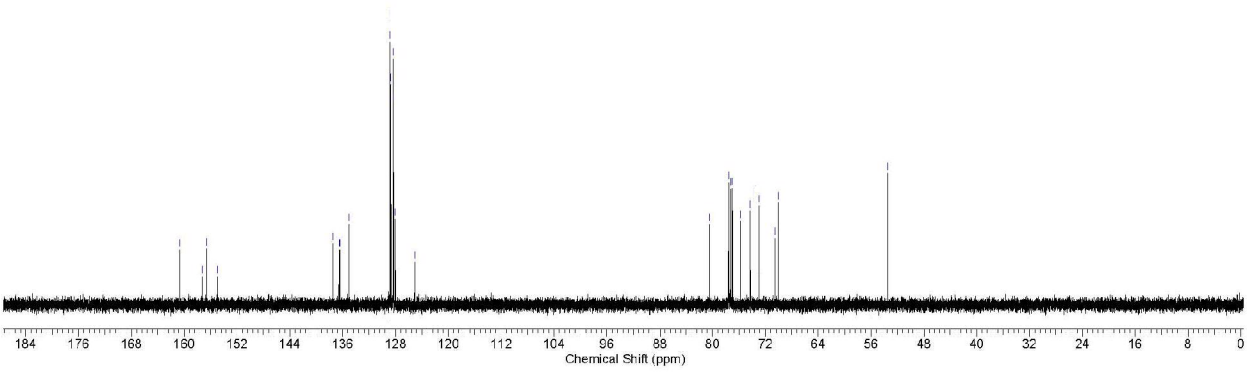

8.725
8.720
8.605
8.601
7.348
7.335
7.319
7.285
7.270
7.249
7.244
7.229
6.956
6.953
6.942
6.868
4.915
4.911
4.578
4.574
4.551
4.528
4.496
4.472
4.443
4.419
4.111
4.088
4.065
3.762
3.755
3.748
3.660
2.628
2.613
0.000


OH
OBn
BnO
OBn
N
N
N
N
COOMe

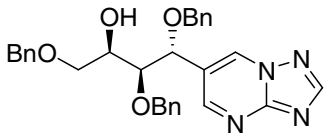
17


1.00
10.89
2.07
1.06
2.43
2.25
1.19
1.09
Chemical Shift (ppm)

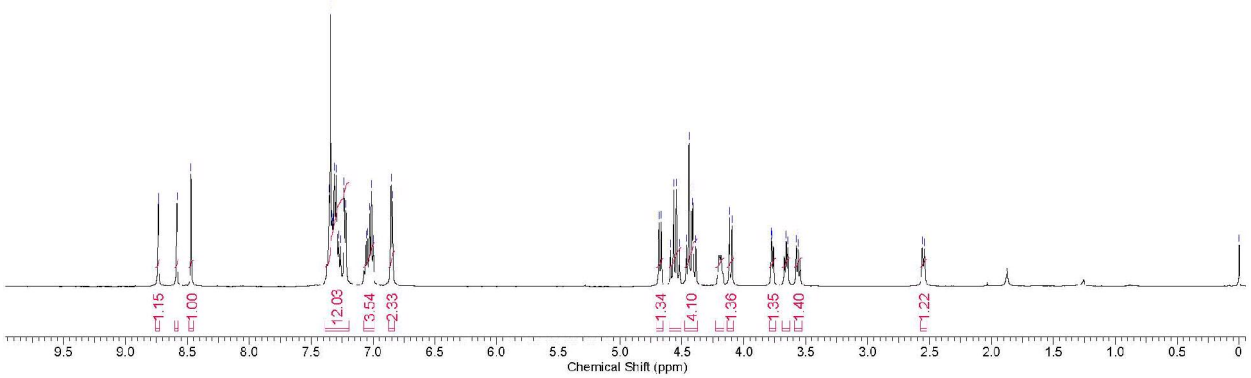

160.641
157.228
156.536
154.989
137.536
136.485
135.038
128.838
126.793
128.668
128.342
128.305
128.064
125.116
80.481
77.505
77.250
76.995
75.777
74.304
73.356
72.945
70.547
70.028
53.520


Chemical Shift (ppm)

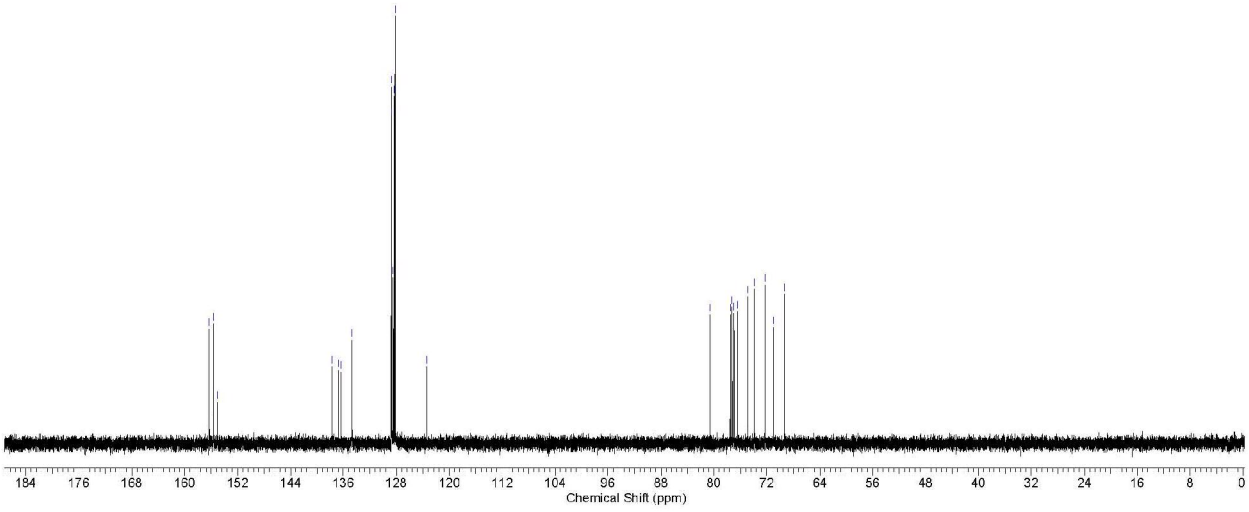

8.734
8.730
8.584
8.466
7.352
7.340
7.328
7.311
7.296
7.287
7.231
7.217
7.025
7.010
6.853
6.839
4.686
4.670
4.570
4.546
4.466
4.443
4.420
4.411
4.119
4.086
3.780
3.776
3.764
3.760
3.657
3.579
3.565
2.559
2.543
0.000

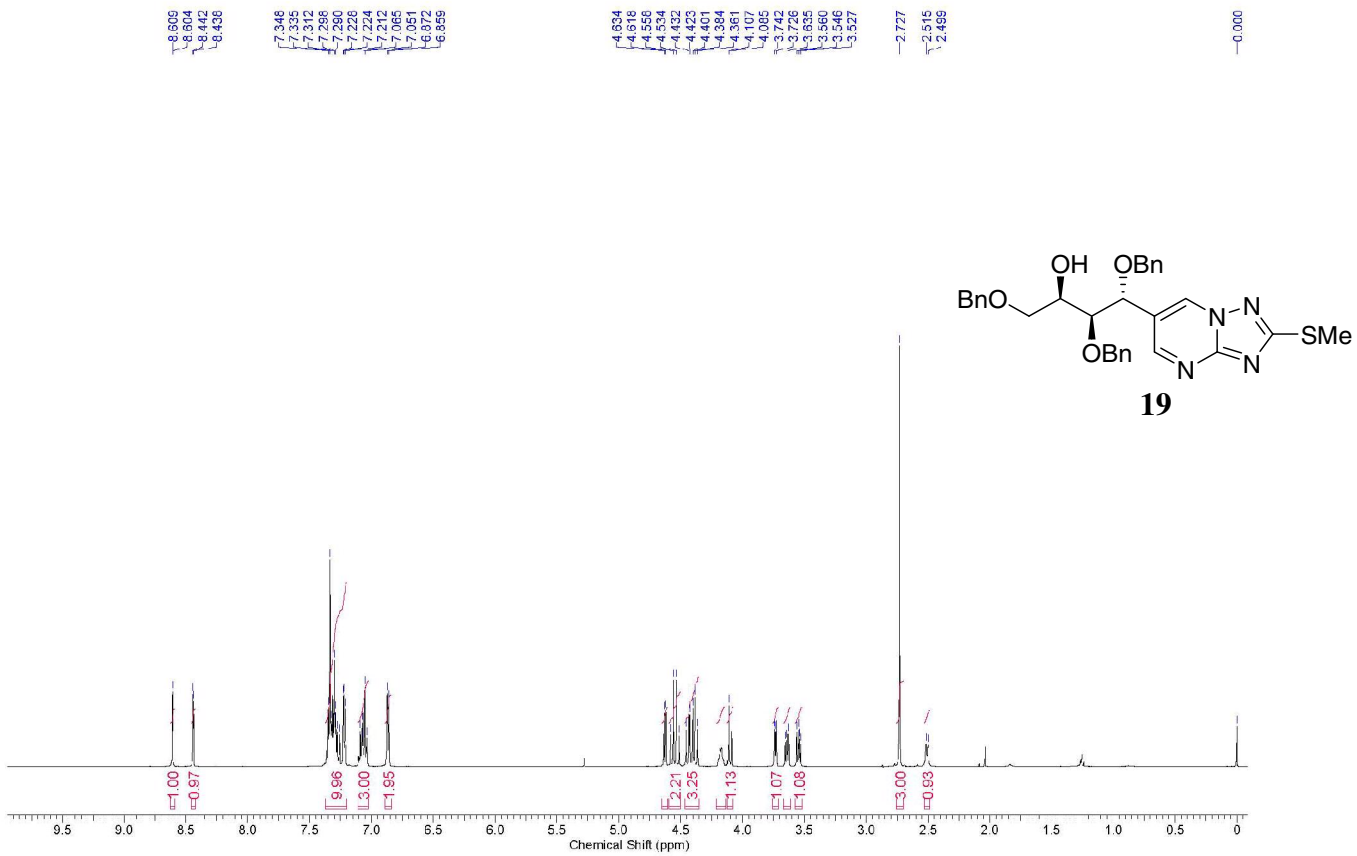

OH
OBn
BnO
OBn
N
N
N
N

18

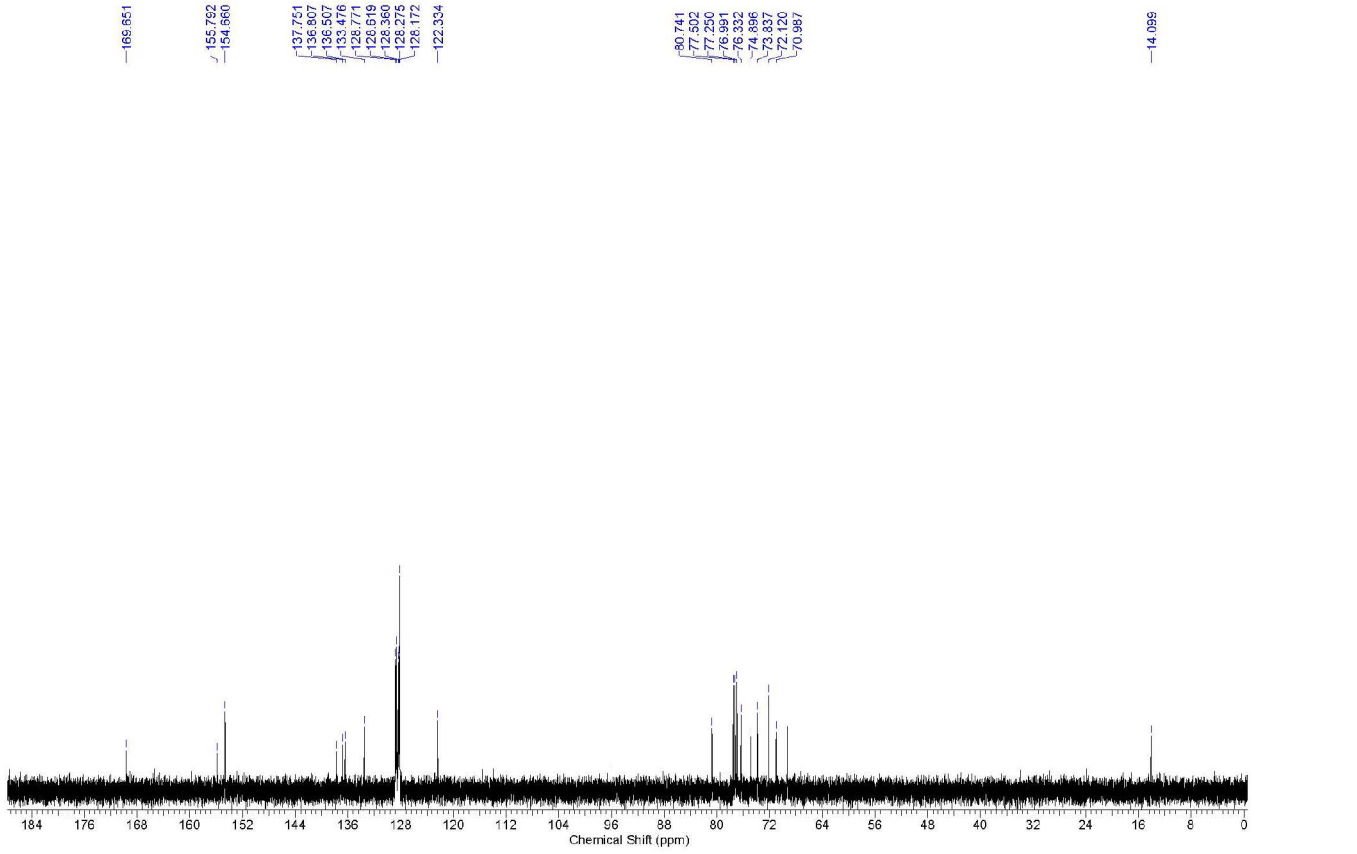

1.15
1.00
12.03
3.54
2.33
1.34
4.10
1.36
1.35
1.40
1.22
Chemical Shift (ppm)


156.296
155.629
155.096
137.725
136.759
136.419
134.727
128.793
128.723
128.656
126.457
126.301
128.205
123.448
80.596
77.505
77.250
76.998
76.413
74.877
73.871
72.290
70.991
69.358

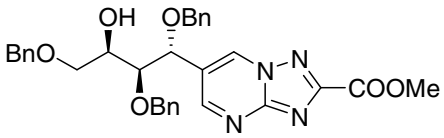

Chemical Shift (ppm)


8.609
8.604
8.442
8.436
7.346
7.335
7.312
7.286
7.280
7.226
7.224
7.212
7.065
7.051
6.872
6.859
4.634
4.616
4.556
4.534
4.432
4.423
4.401
4.384
4.361
4.107
4.085
3.742
3.726
3.635
3.560
3.546
3.527
2.727
2.515
2.499
0.000
OH
OBn
BnO
OBn
N
N
N
N
SMe
1.00
0.97
9.96
3.00
1.95
2.21
3.25
1.13
1.07
1.08
3.00
0.93
Chemical Shift (ppm)

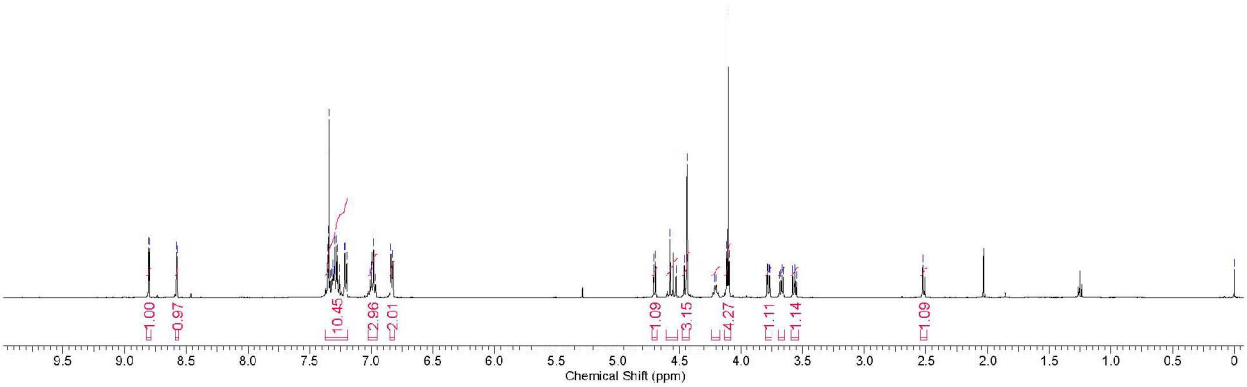
19


166.651
155.762
154.660
137.751
136.807
136.507
133.476
128.771
128.619
128.360
128.275
126.172
122.334
80.741
77.502
77.250
76.991
76.332
74.896
73.837
72.120
70.987
14.099
Chemical Shift (ppm)

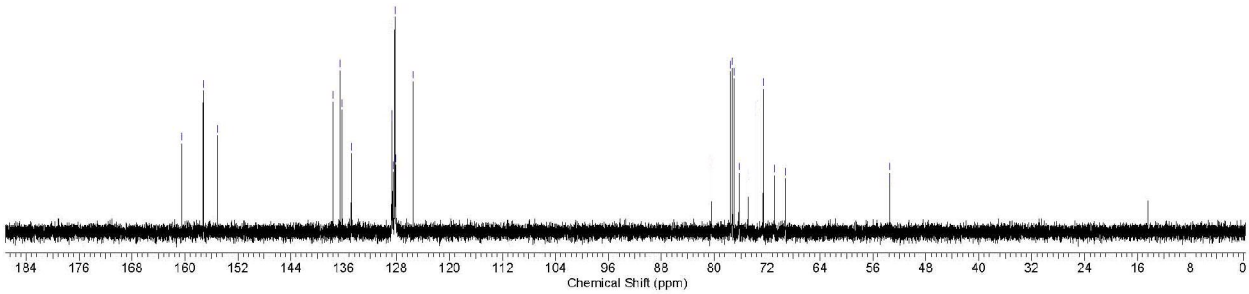
8.804
8.799
8.575
8.571
7.353
7.345
7.340
7.294
7.280
7.272
7.215
7.212
6.992
6.978
6.839
6.824
4.709
4.692
4.599
4.576
4.551
4.462
4.436
4.118
4.105
4.095
3.786
3.784
3.772
3.768
3.669
3.581
3.567
2.527
2.510
0.000

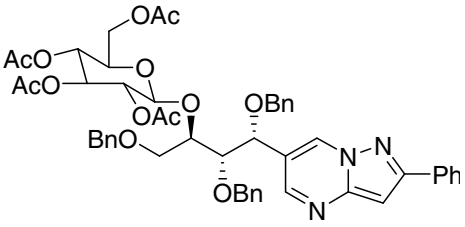


20

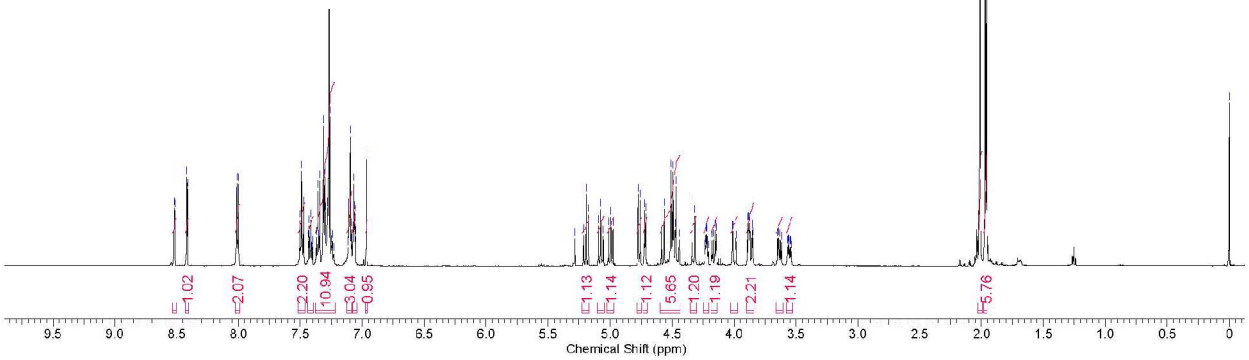


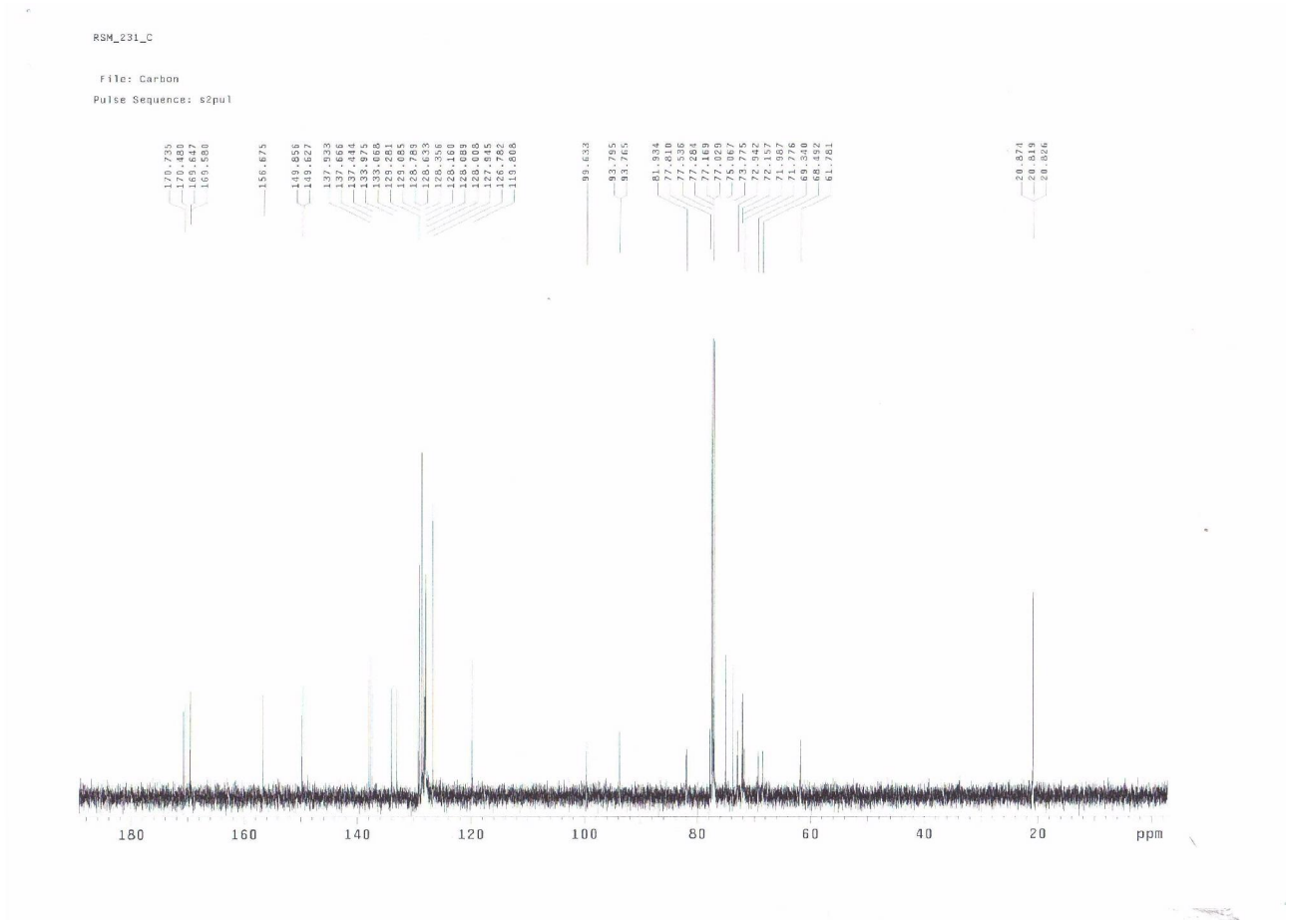
160.541
157.203
155.048
137.614
136.544
136.252
134.808
128.764
126.671
126.501
126.275
126.131
125.510
80.337
77.505
77.250
76.995
76.236
74.826
73.841
72.553
70.861
69.277
53.483
53.427

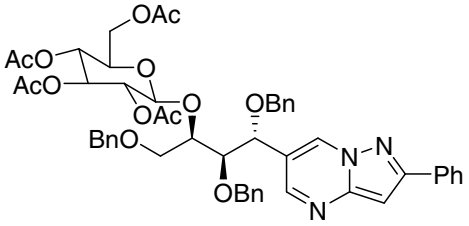



OAc
AcO
AcO
O
OAc
O
OBn
BnO
N
N
Ph
OBn
N

21

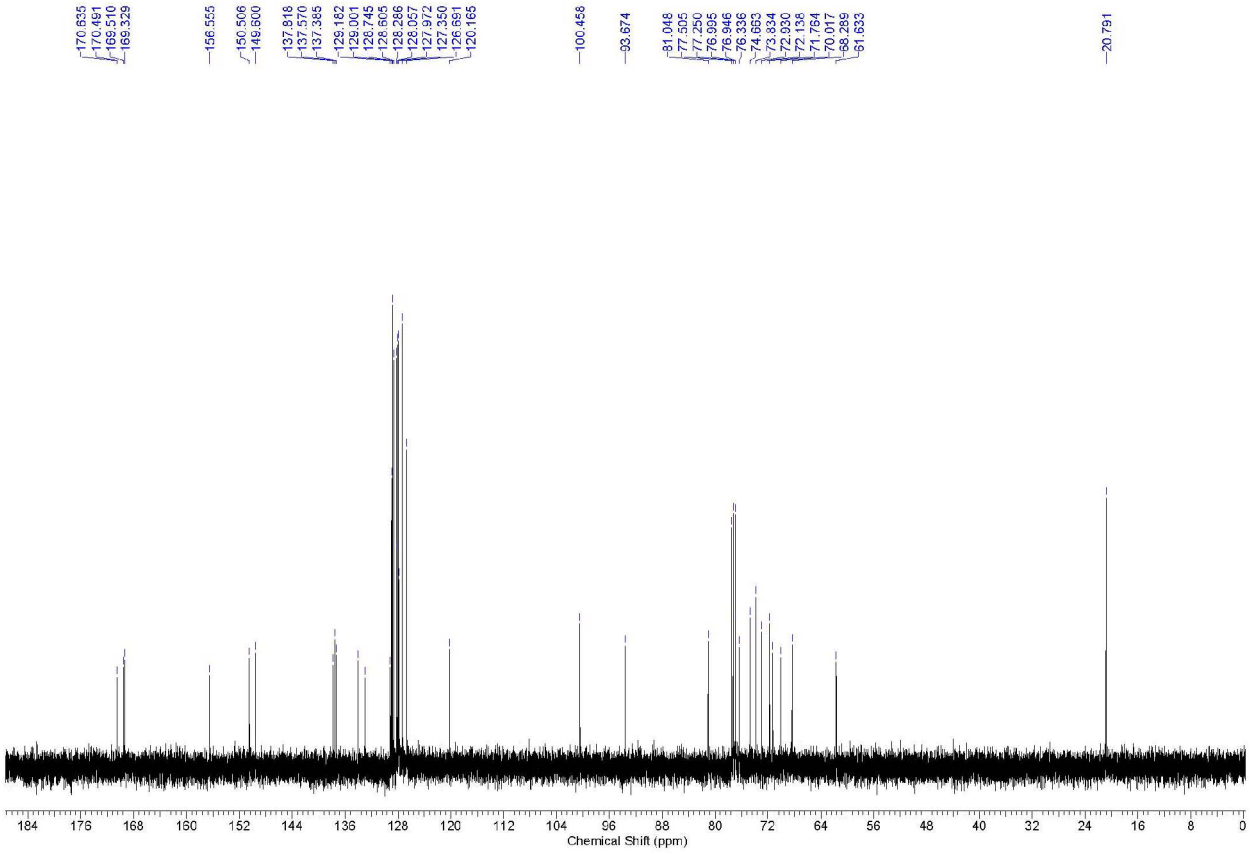

1.02
2.07
2.20
10.94
3.04
0.95
1.13
1.14
1.12
5.65
1.20
1.19
2.21
1.14
5.76
Chemical Shift (ppm)

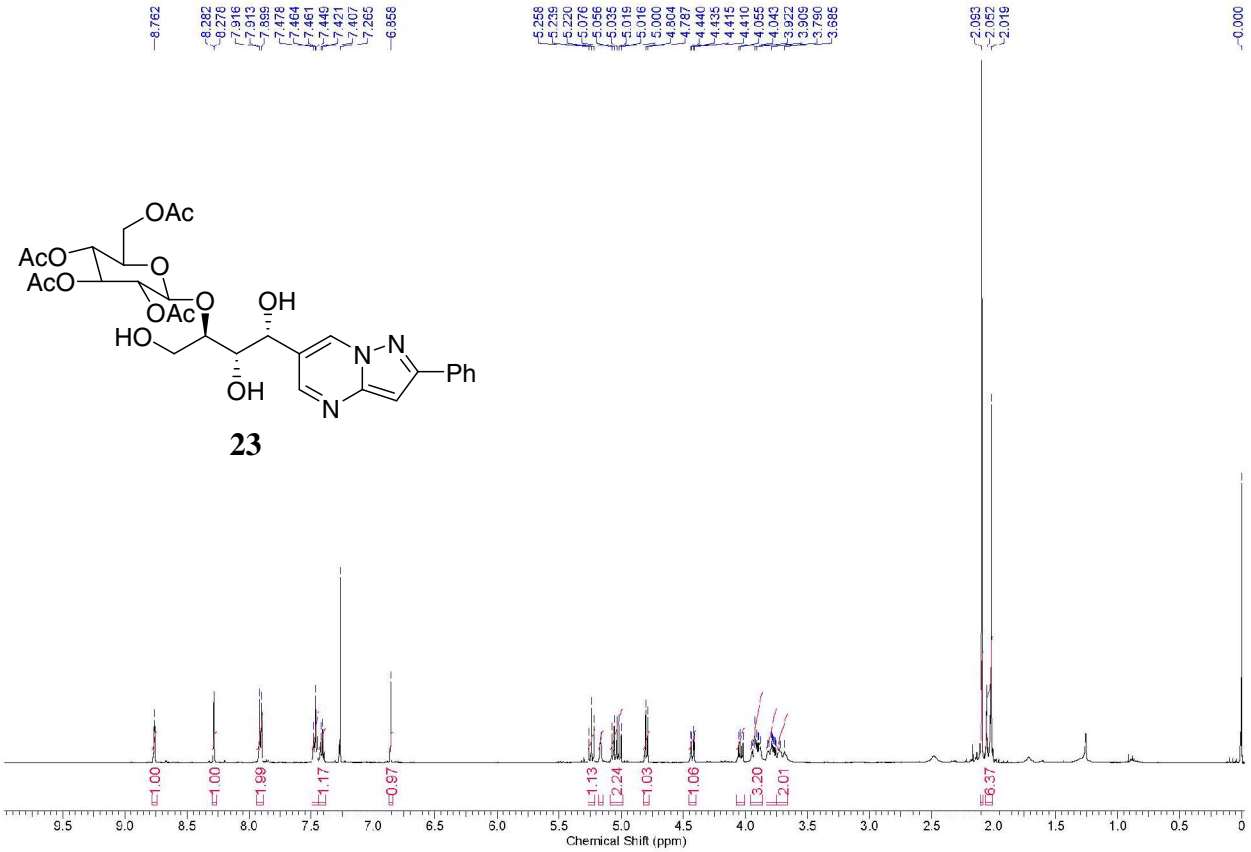

RSM_231_C
File: Carbon
Pulse Sequence: s2pul
ppm

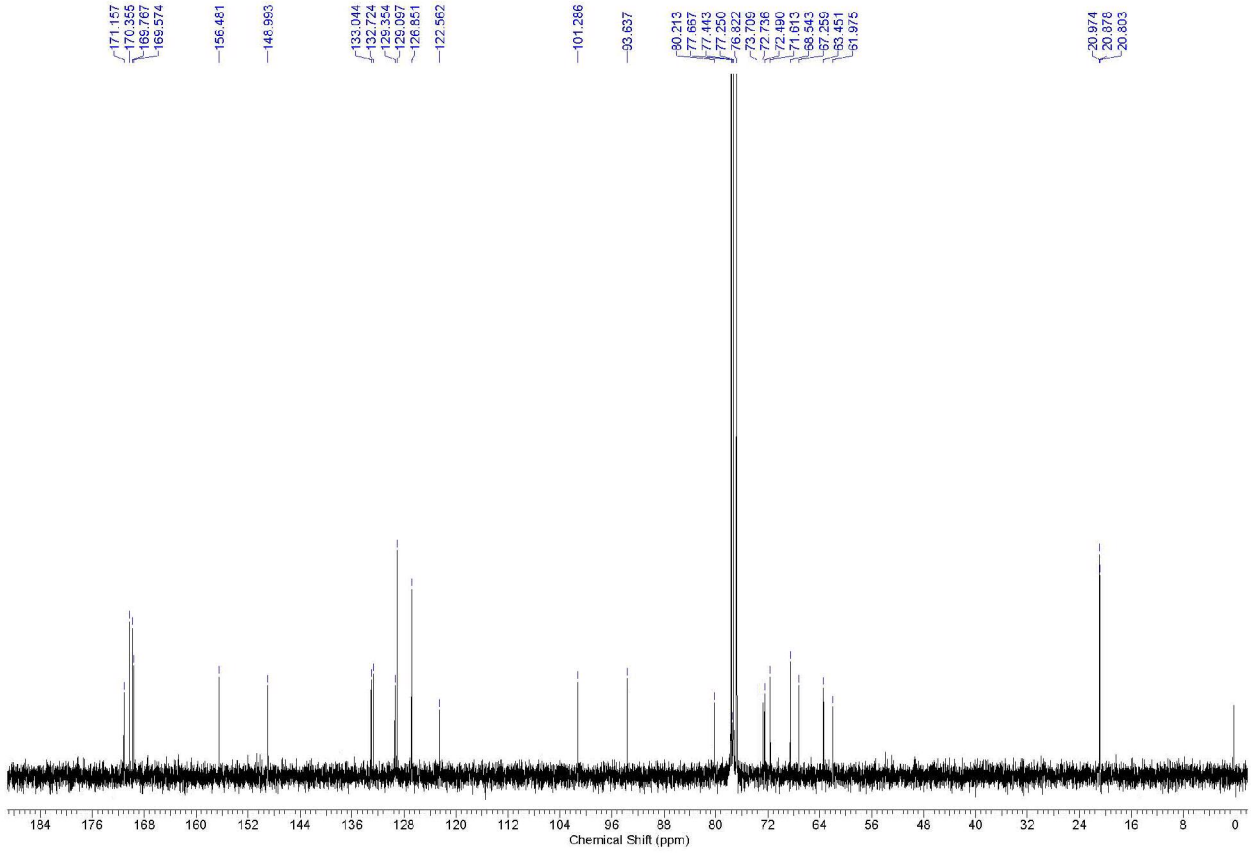

OAc
AcO
AcO
O
OAc
O
OBn
BnO
N
N
Ph
OBn
N

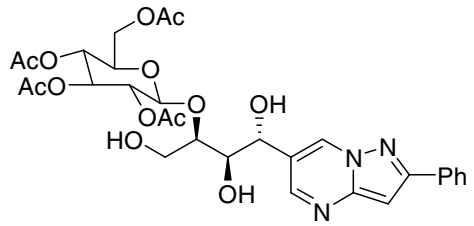
22

Chemical Shift (ppm)


Chemical Shift (ppm)

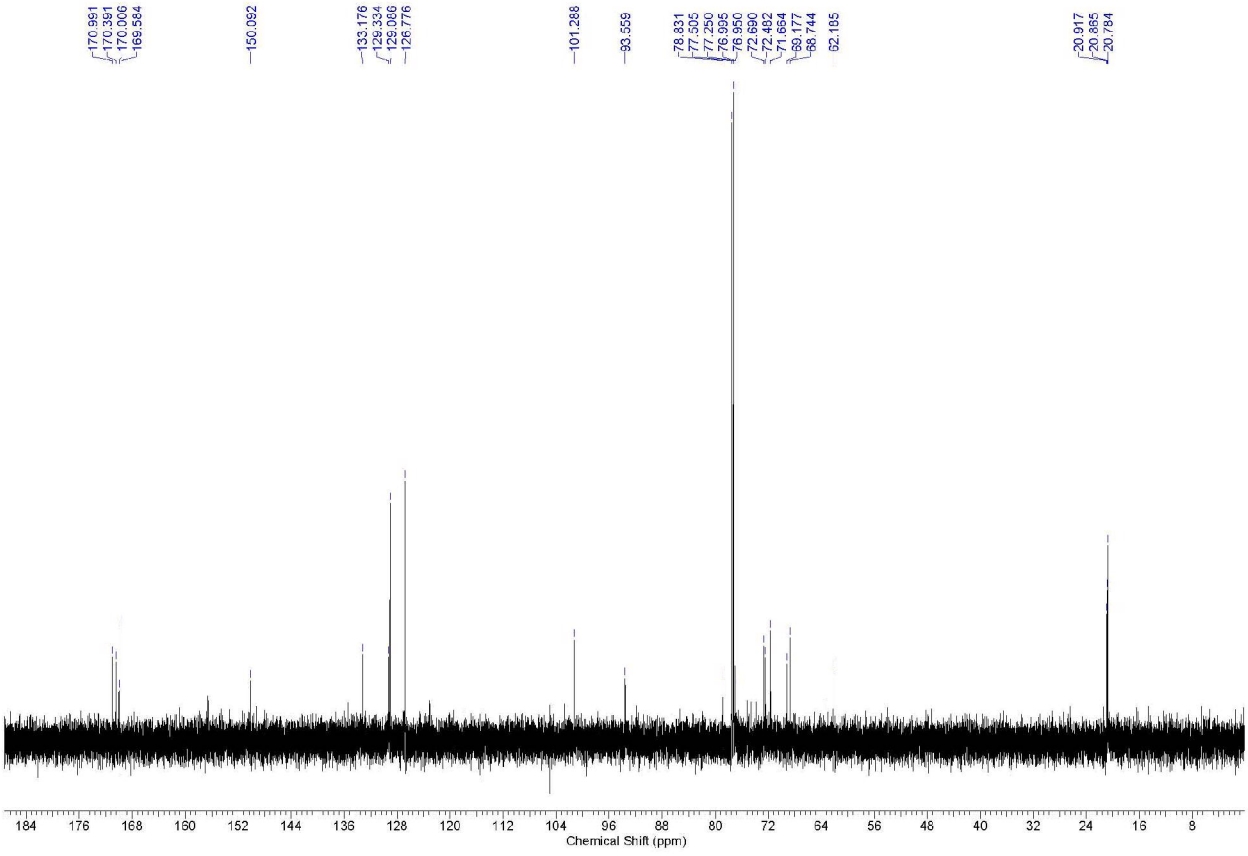

8.762
8.282
8.278
7.916
7.913
7.899
7.478
7.464
7.461
7.449
7.421
7.407
7.265
6.858
5.258
5.239
5.220
5.076
5.056
5.035
5.019
5.016
5.000
4.804
4.787
4.440
4.435
4.415
4.410
4.055
4.043
3.922
3.909
3.790
3.685
2.093
2.052
2.019
0.000
OAc
AcO
AcO
O
OAc
O
OH
HO
OH
N
N
Ph
N
23
1.00
1.00
1.99
1.17
0.97
1.13
2.24
1.03
1.06
3.20
2.01
6.37
Chemical Shift (ppm)

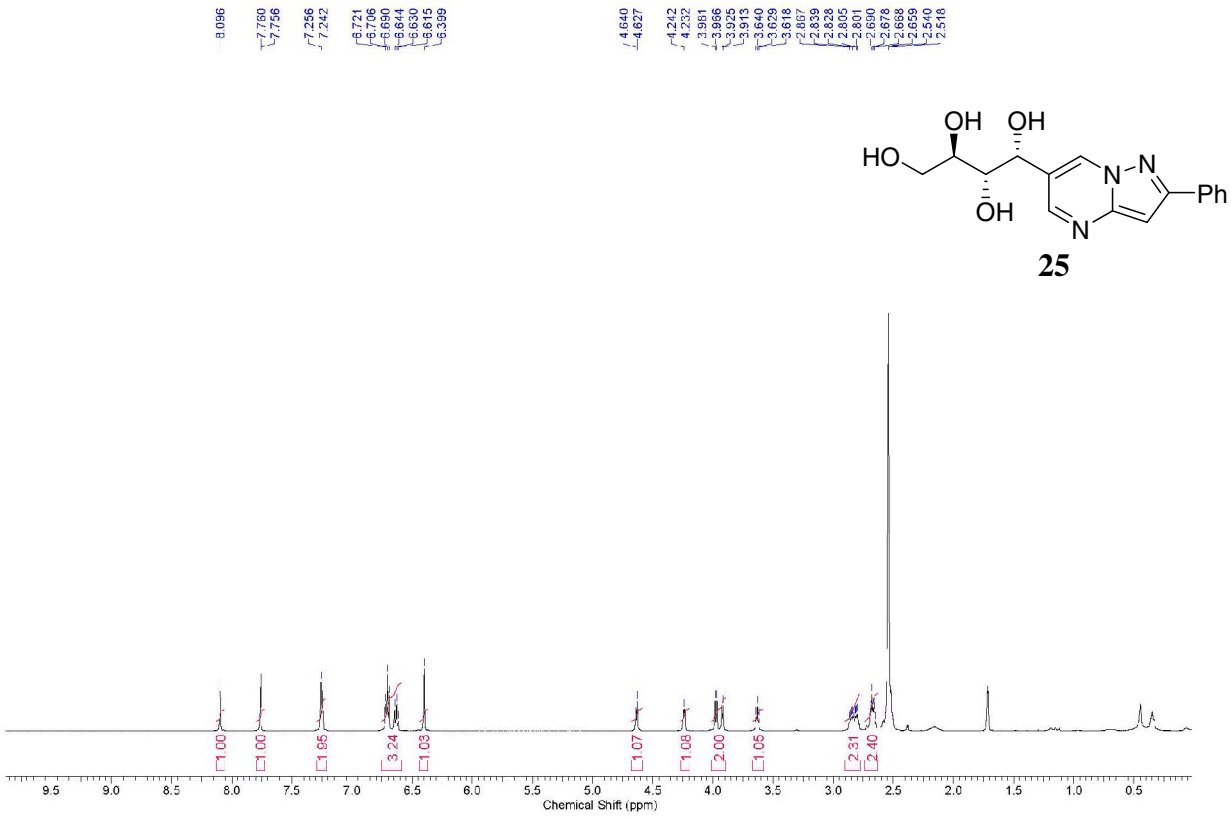

171.157
170.355
169.767
169.574
156.481
148.993
133.044
132.724
129.354
129.057
126.851
122.562
101.286
93.637
80.213
77.667
77.443
77.250
76.822
73.709
72.736
72.490
71.813
68.543
67.259
63.451
61.975
20.974
20.876
20.803
Chemical Shift (ppm)


OAc
AcO
AcO
O
OAc
O
OH
HO
OH
N
N
Ph
N

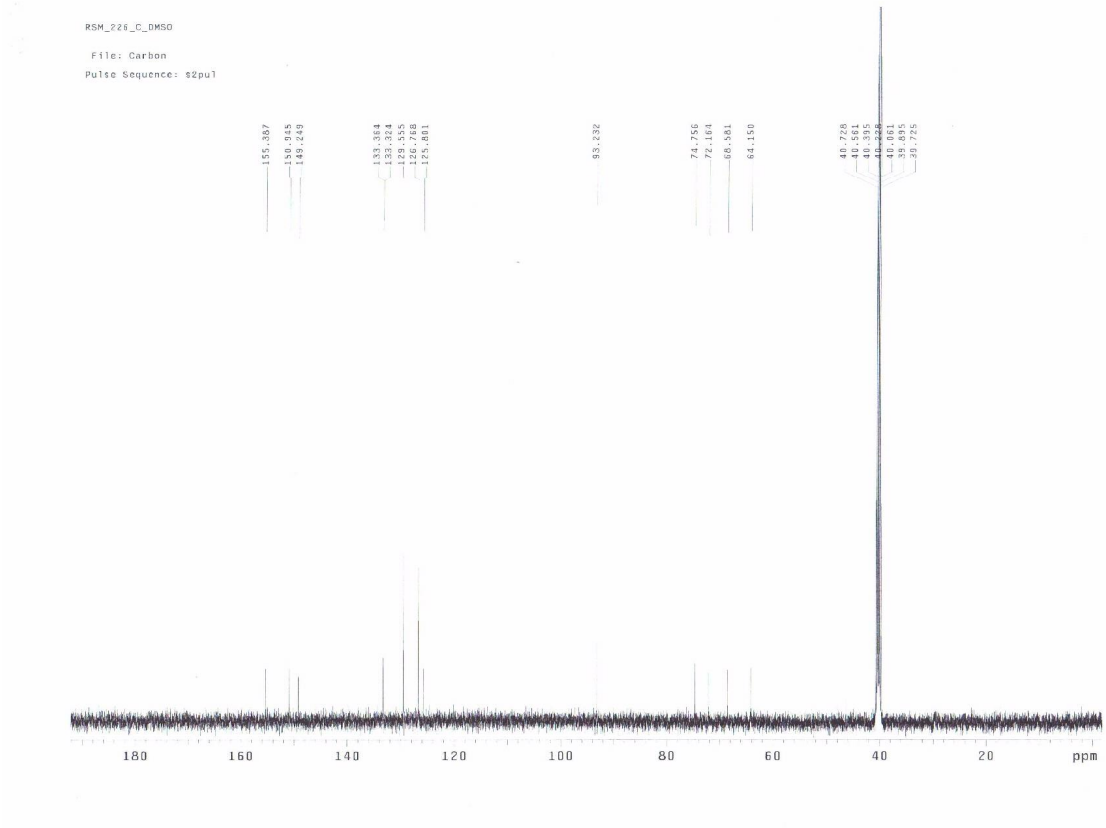
24

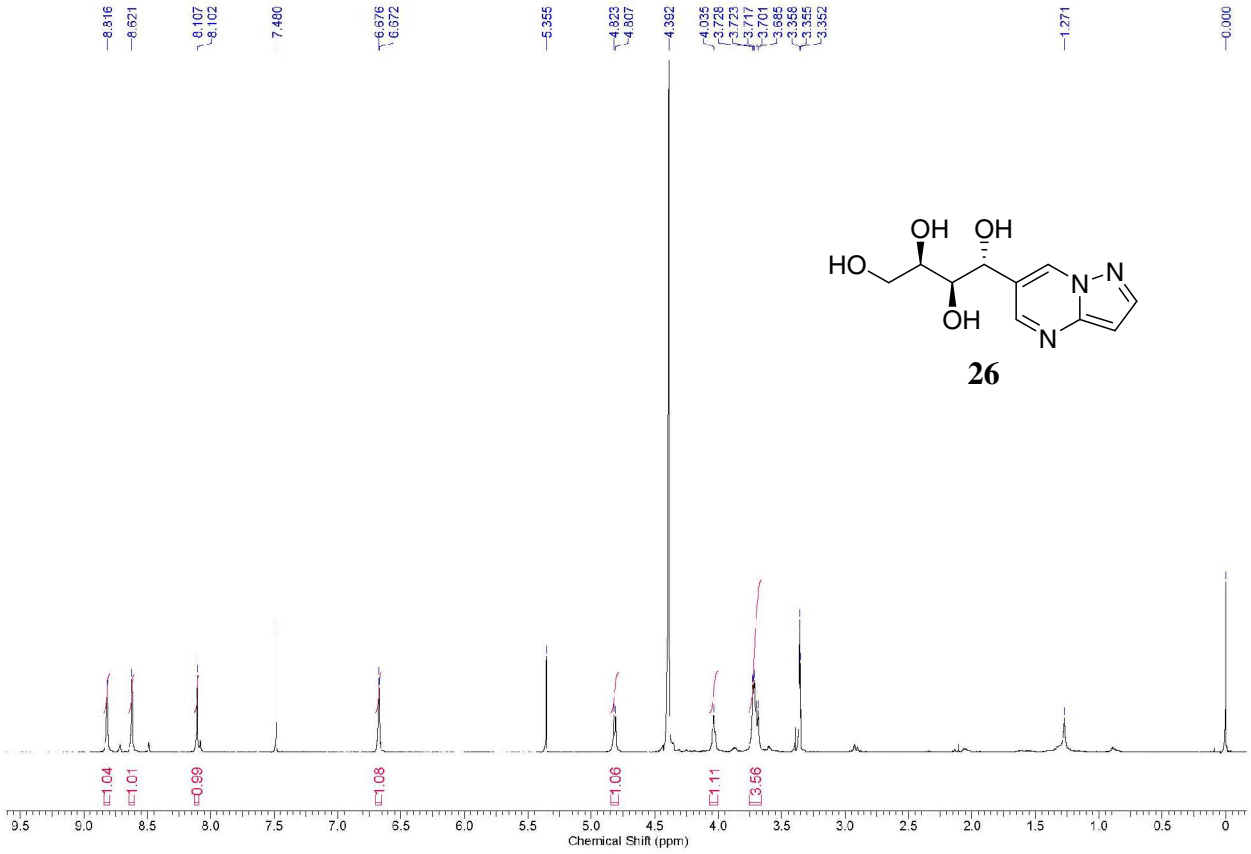
8.733
8.503
8.498
7.928
7.925
7.920
7.911
7.472
7.468
7.458
7.442
7.413
7.402
7.398
7.275
7.266
6.869
5.253
5.234
5.084
5.069
5.064
5.053
5.050
5.045
5.034
4.822
4.806
4.391
4.227
4.224
4.025
4.020
4.012
3.863
3.852
3.761
3.677
2.075
2.051
2.022
0.000
1.00
0.96
2.10
1.25
0.97
1.23
2.27
1.14
1.09
1.20
2.08
2.12
1.25
6.84


170.991
170.391
170.006
169.584
150.092
133.176
129.334
129.066
126.776
101.288
93.559
78.831
77.505
77.250
76.995
76.950
72.690
72.492
71.664
69.177
68.744
62.185
20.917
20.865
20.784
Chemical Shift (ppm)


8.096
7.760
7.756
7.256
7.242
6.721
6.706
6.690
6.644
6.630
6.615
6.399
4.640
4.627
4.242
4.232
3.961
3.966
3.925
3.913
3.640
3.629
3.618
2.867
2.839
2.828
2.805
2.801
2.690
2.678
2.668
2.659
2.540
2.518
OH
OH
HO
OH
N
N
Ph
1.00
1.00
1.95
3.24
1.03
1.07
1.08
2.00
1.05
2.31
2.40
Chemical Shift (ppm)

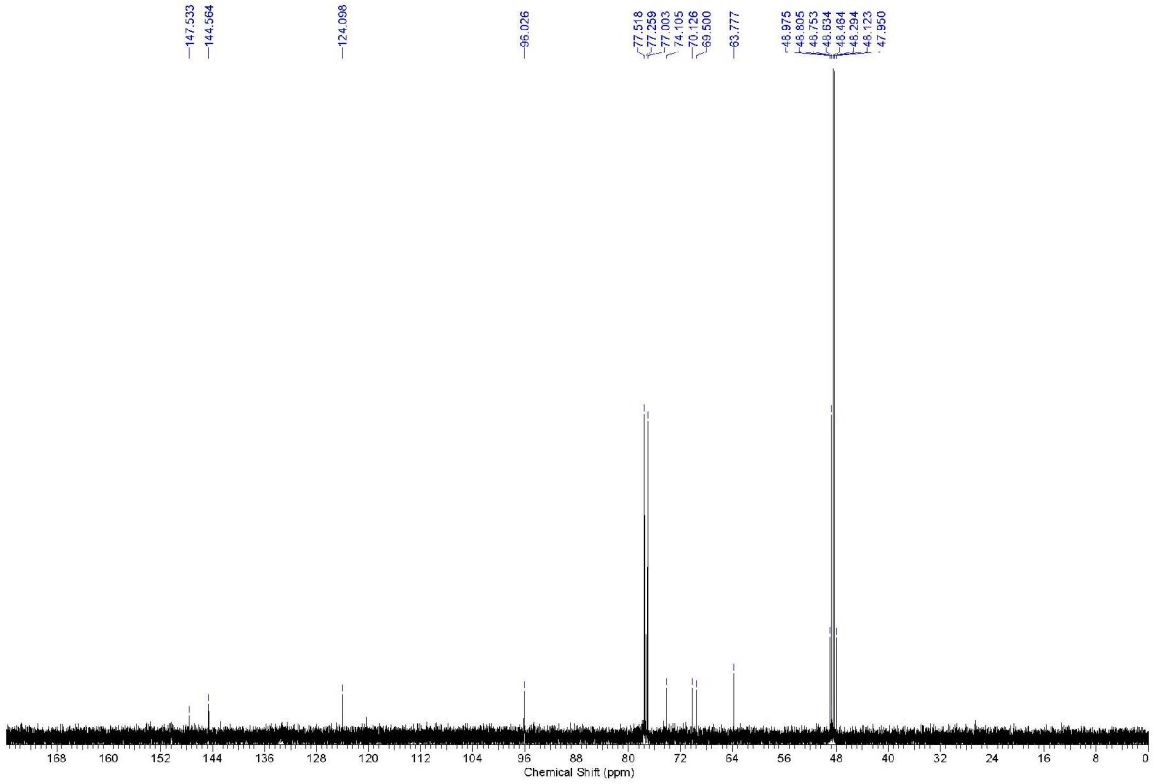
25


RSM_226_C_DMSO
File: Carbon
Pulse Sequence: s2pul
155.367
150.945
149.249
133.364
133.324
128.555
126.768
125.801
83.232
74.756
72.164
68.561
64.150
40.728
40.561
40.395
40.228
40.061
39.895
39.725
ppm

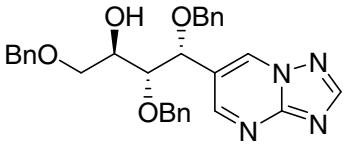

8.816
8.621
8.107
8.102
7.480
6.676
6.672
5.355
4.823
4.807
4.392
4.035
3.728
3.723
3.717
3.701
3.685
3.358
3.355
3.352
1.271
0.000
1.04
1.01
0.99
1.08
1.06
1.11
3.56
Chemical Shift (ppm)

OH
OH
HO
OH
N
N
N

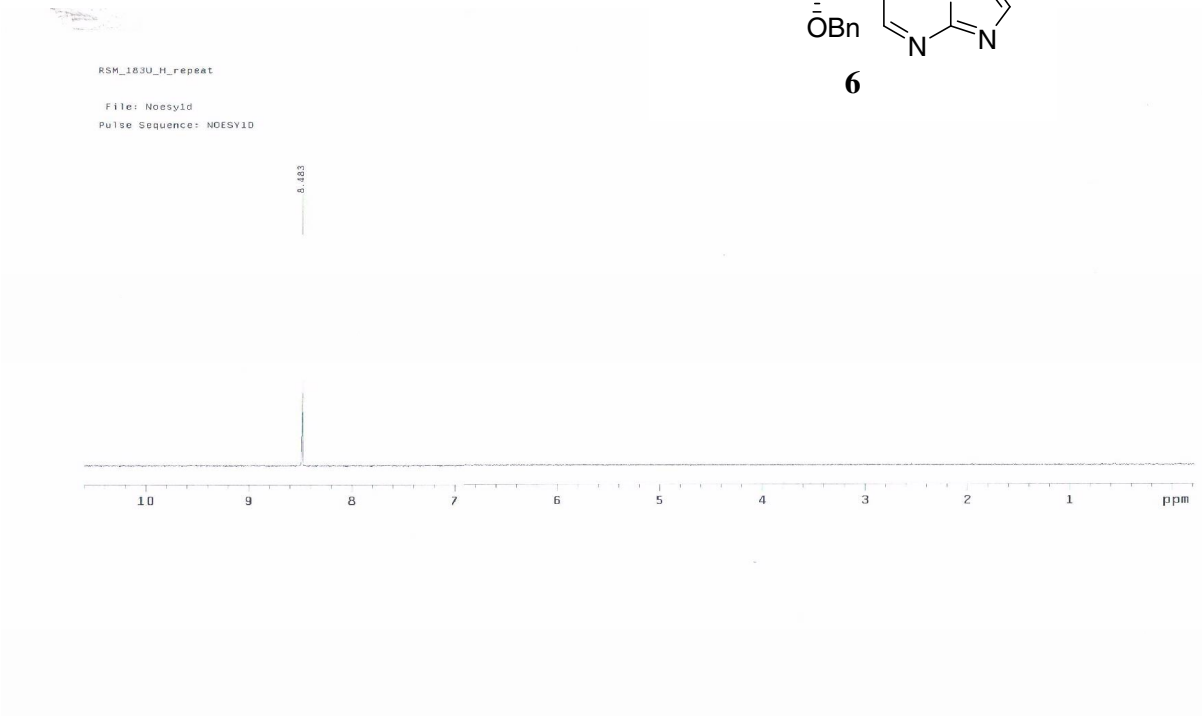
26


147.533
144.564
124.098
96.026
77.518
77.259
77.003
74.105
70.126
69.500
63.777
48.975
48.805
48.753
48.634
48.484
48.294
48.123
47.950
Chemical Shift (ppm)

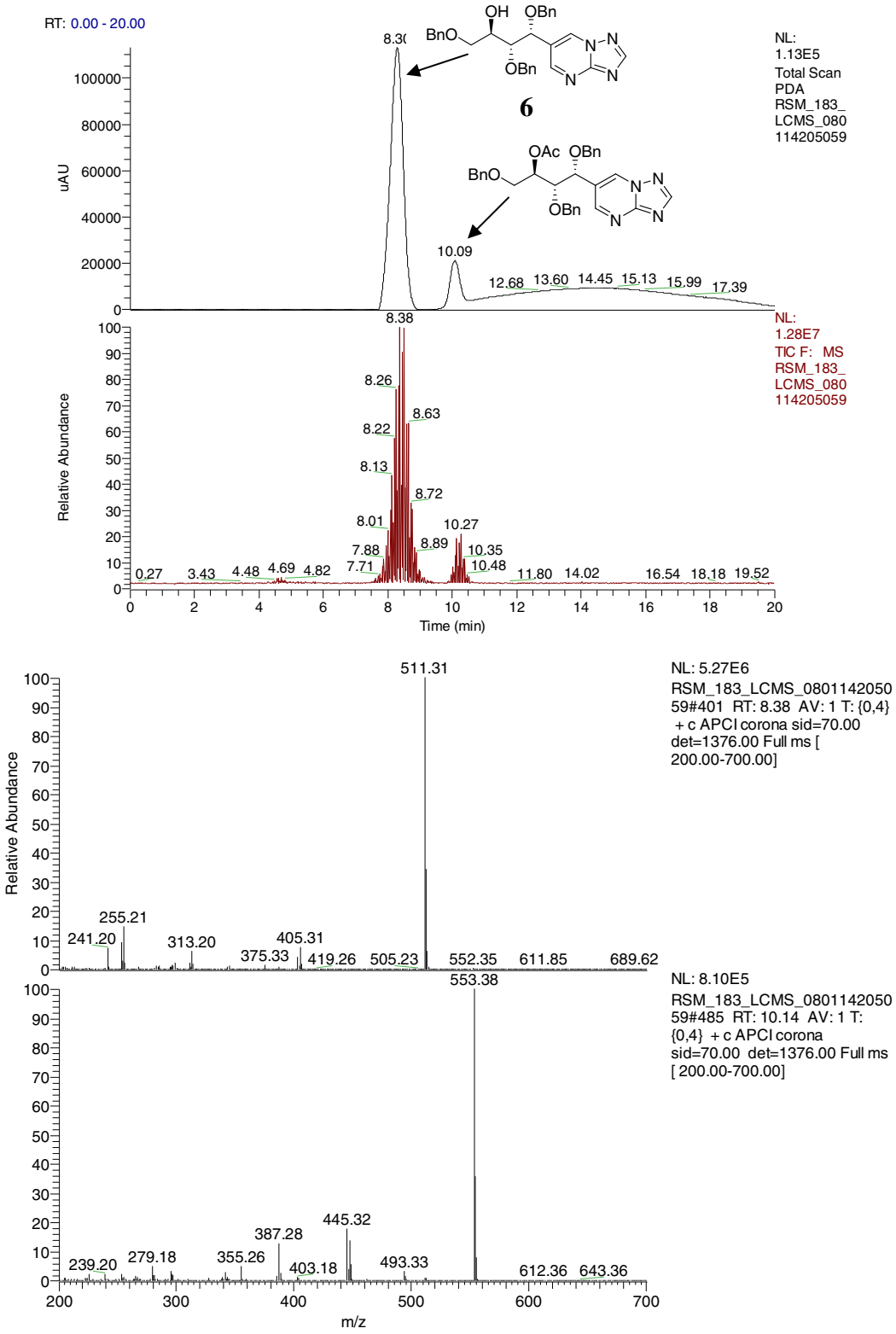
5. Crude NOE Spectra of 6:



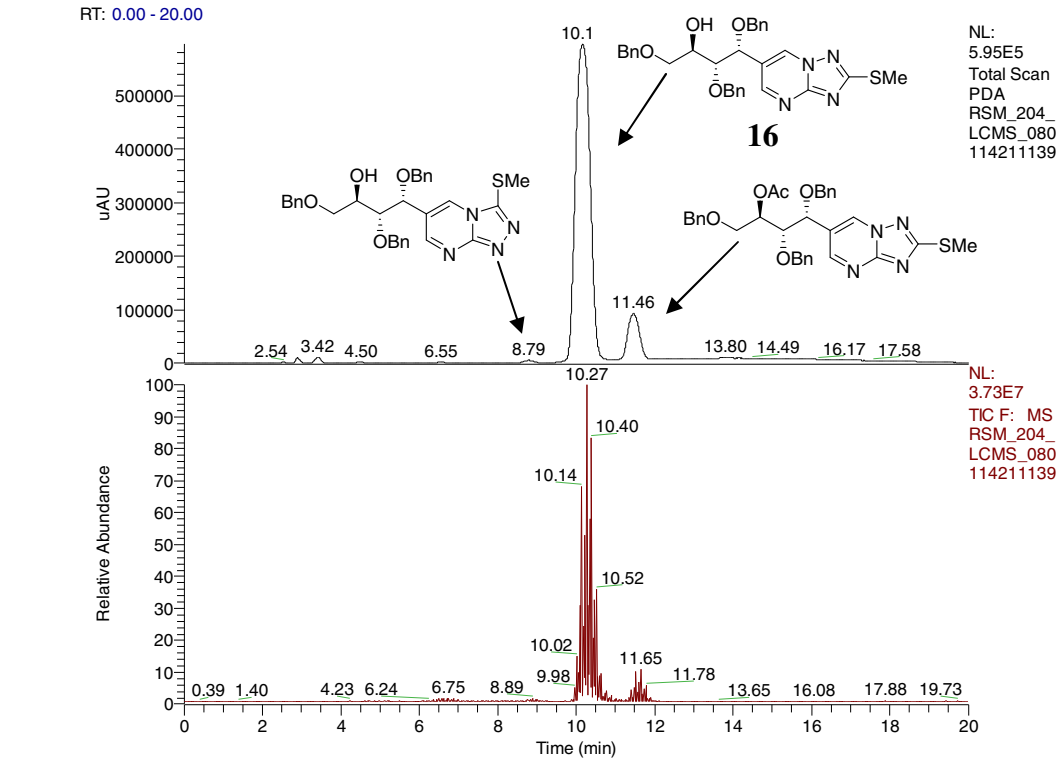
6

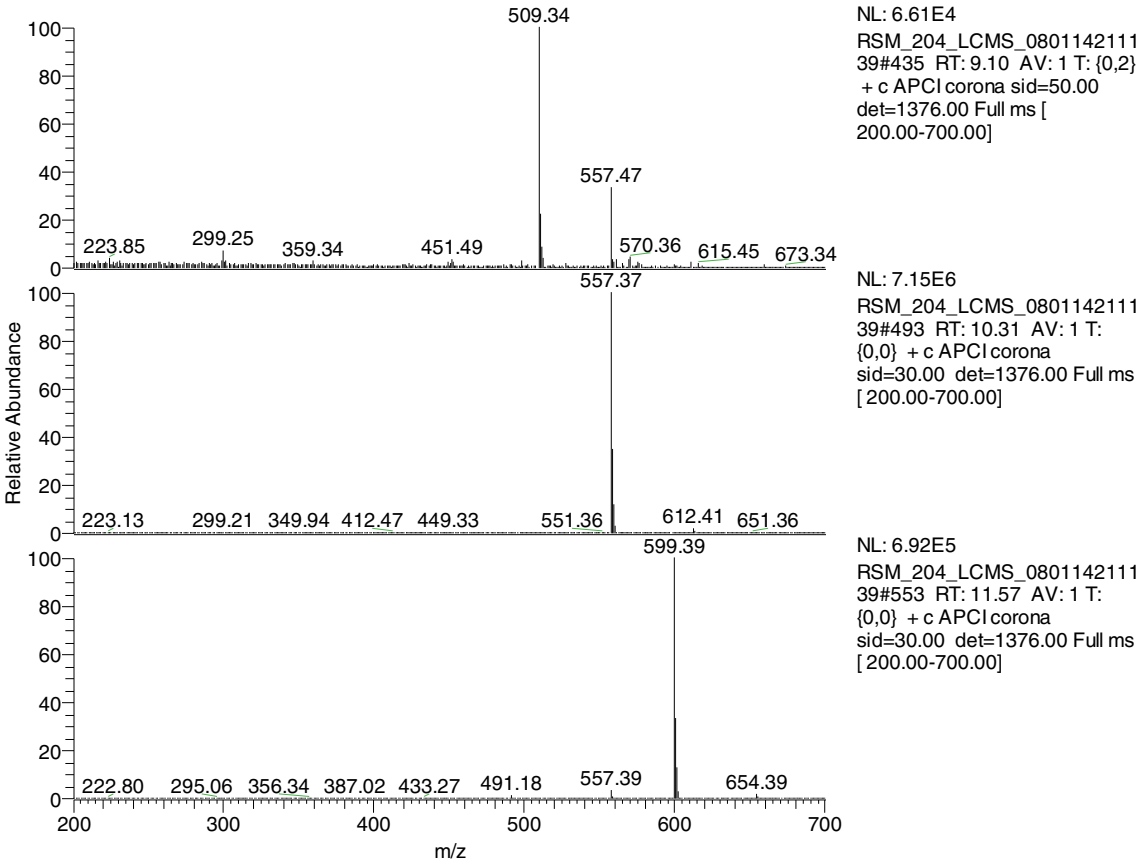


6. Crude LCMS data of 6, 16–20 compounds:

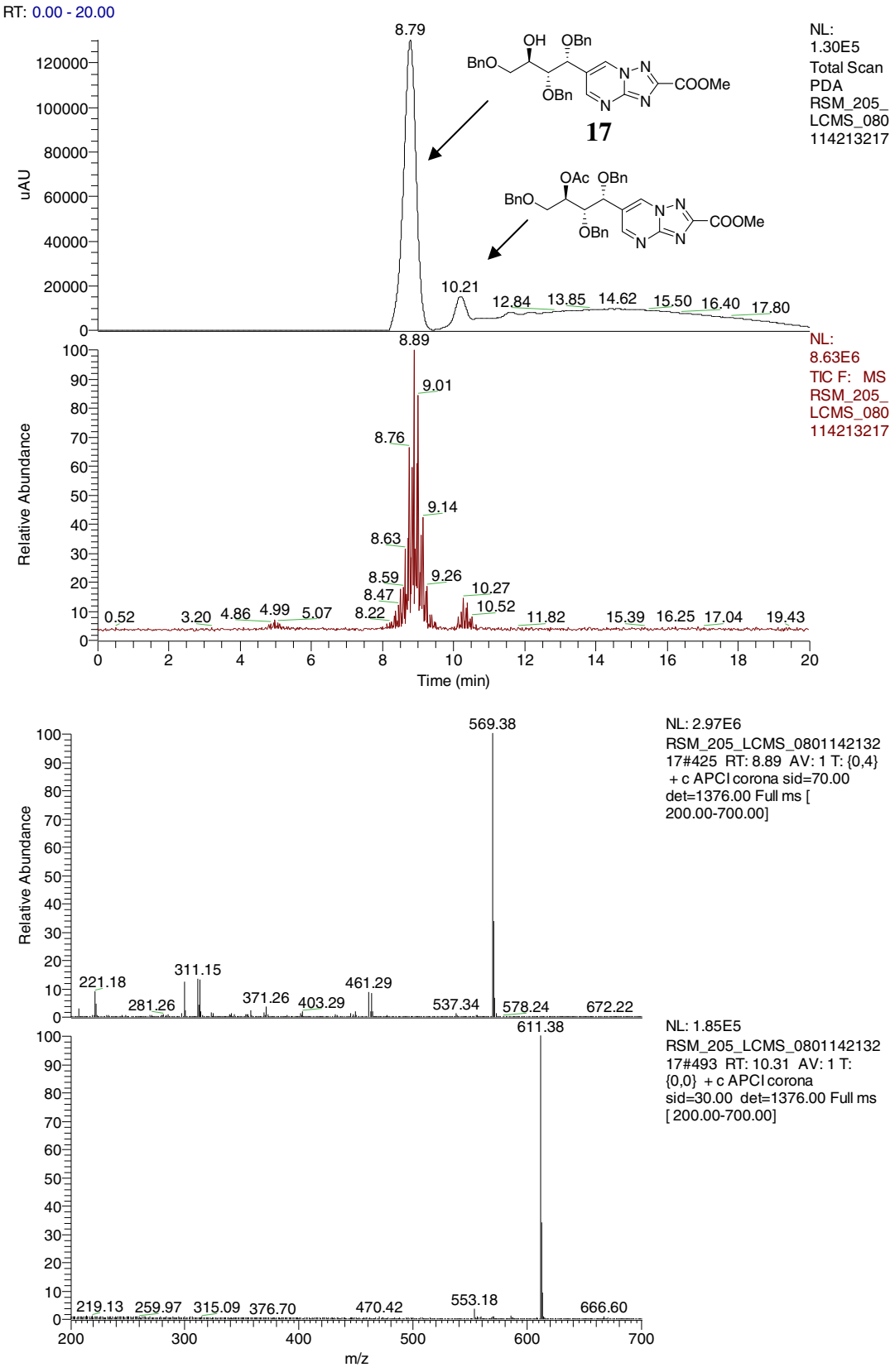


LCMS data of crude sample of compound **6**

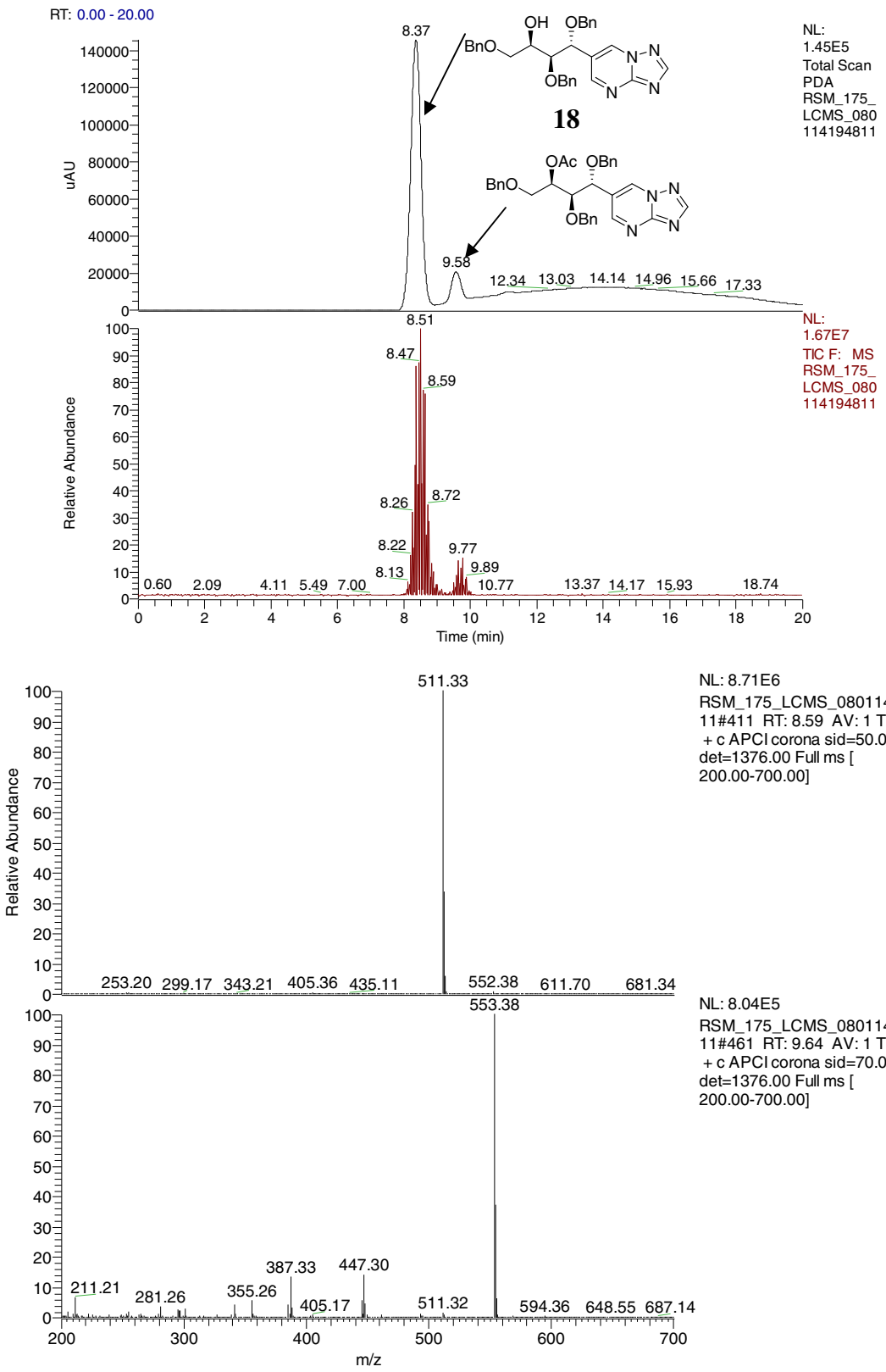




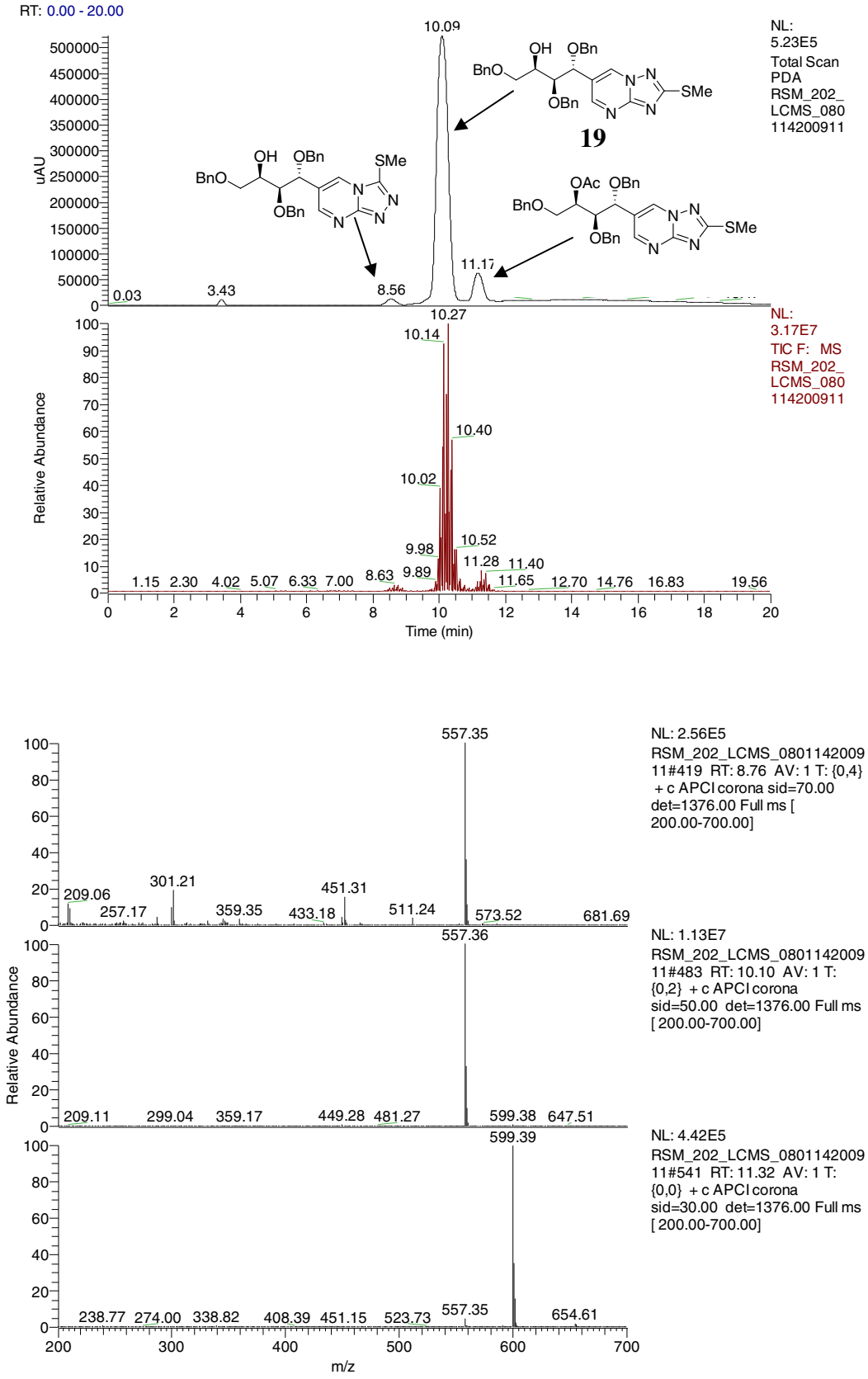
LCMS data of crude sample of compound **16**



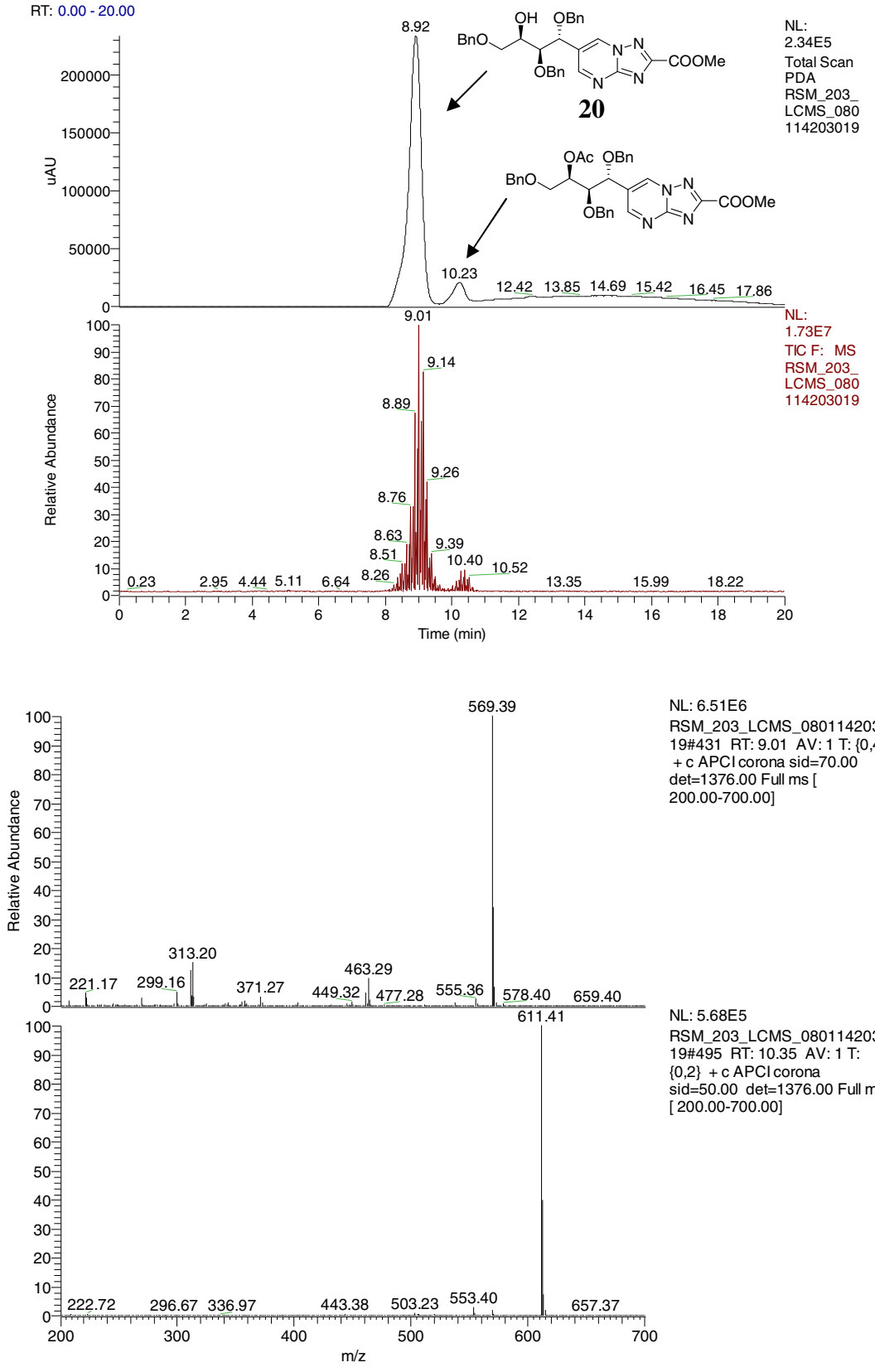
LCMS data of crude sample of compound **17**



LCMS data of crude sample of compound **18**



LCMS data of crude sample of compound **19**



LCMS data of crude sample of compound **20**