Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Late-Stage C(sp^2) and C(sp^3)−H Glycosylation towards *C*-Aryl/Alkyl Glycopeptides：Mechanistic Insights and Fluorescence Labeling

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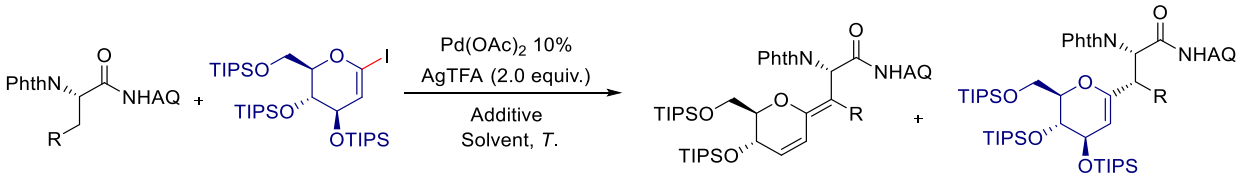
General Remarks

Catalytic reactions were performed under a N_2 atmosphere using pre-dried glassware and standard Schlenk techniques. 1,4-Dioxane was dried over Na and freshly distilled under N_2. The following starting materials were synthesized according to previous described methods: The 8-aminoquinoline (AQ) amide substrates[1] and triazolyldimethylmethyl (TAM) amide substrates[2] as well as phenylalanine and alanine-containing peptides.[2] 1-Iodo glycals were synthesized according to literature procedures.[3] Other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR. Flash chromatography: Merck silica gel 60 (40– 63 μm). NMR: Spectra were recorded on a Varian Mercury Vx 300, Varian VNMRS 300, Varian Inova 500, Varian Inova 600, Bruker Avance III 400, Bruker Avance III HD 400 and a Bruker Avance III HD 500 instrument in the solvent indicated; chemical shifts (δ) are provided in ppm. IR spectra were recorded on a Bruker FT-IR alpha-P device. EI-MS was recorded on Joel AccuTof at 70 eV. ESI-MS was recorded on Bruker Daltonic micrOTOF. High resolution mass spectrometry (HR-MS) was recorded on micrOTOF, Bruker Daltonic. Melting points (m.p.) were measured on Stuart® melting point apparatus SMP3, Barloworld Scientific, values are uncorrected.

Optimization of the Reaction Condition

Table S1. Optimization of C–H Glycosylation.[a]



1 R = H, Ph **2a** **3'** **3**

Entry	Additive	*T*/℃	Sol./mL	3'/%	3/%
1	-	130	PhMe	58[a]	-
2	-	130	*o*-Xylene	42	-
3	-	130	DCE	49	-
4	-	130	1,4-dioxane	74	
5	-	130	CH_3CN	41	-
6	**-**	**100**	**1,4-dioxane**	**79**	
7	-	40	1,4-dioxane	20	69
8	**-**	**40**	**1,4-dioxane**	**-**	**85[b]**
9	K_2CO_3	40	1,4-dioxane	-	82[c]
10	$(BnO)_2PO_2H$	40	1,4-dioxane	-	27
11	-	40	1,4-dioxane	-	Trace[d]
12	K_2CO_3	60	1,4-dioxane	-	38
13	**K_2CO_3/BQ**	**60**	**1,4-dioxane**	**-**	**93[e]**
14	K_2CO_3/Ac-Gly-OH	60	1,4-dioxane		88

[a] Reaction conditions: **1** (0.10 mmol), **2** (111 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol %), AgTFA (44 mg, 0.2 mmol), toluene (1.0 mL) at 130 °C, 16 h. [b] Reaction time 8 h. [c] Addition of K_2CO_3 (13.8 mg, 0.10 mmol) [d] R = Ph. [d] Addition of BQ (5.4 mg, 50 mol %), K_2CO_3 (13.8 mg, 0.10 mmol).

General Procedures

General Procedure A: C(sp^3)–H Glycosylation with TAM^{Bn}.

Amide (0.1 mmol), $Pd(TFA)_2$ (3.3 mg, 10 mol %), Ag_2CO_3 (55 mg, 0.2 mmol), 1-$AdCO_2H$ (5.4 mg, 30 mol %) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, 1-iodo glycal **2** (0.15 mmol) in 1,4-dioxane (0.5 mL) was added. The tube was sealed and heated at 80 °C for 10 h (for glycosylation of peptides: 16 h). After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product.

General procedure B: C(sp^2)–H Glycosylation with TAM^{Bu}.

Amide (0.1 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol %), Ag_2CO_3 (55 mg, 0.2 mmol), were added to an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, 1-iodo glycal **2a** (0.15 mmol) in 1,4-dioxane (0.5 mL) was added. The tube was sealed and heated at 80 °C for 10 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product.

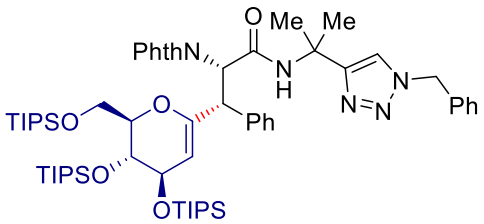
General procedure C: Primary C(sp^3)–H Glycosylation with AQ.

Amide (0.1 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol %), AgTFA (44 mg, 0.2 mmol) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, 1- iodo glycal **2** (0.15 mmol) in dioxane (1.0 mL) was added. The tube was sealed and heated at 40 °C for 8 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product.

General procedure D: Secondary C(sp^3)–H Glycosylation with AQ.

Amide (0.1 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol %), AgTFA (44 mg, 0.2 mmol), K_2CO_3 (13.8 mg, 0.1 mmol), BQ (5.4 mg, 50 mol %) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, 1-iodo glycal **2** (0.15 mmol) in dioxane (1.0 mL) was added. The tube was sealed and heated at 60 °C for 8 h. After cooling to ambient temperature, the resulting reaction mixture was diluted with CH_2Cl_2 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel yielded the product.

Characterization Data of Products



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-((2*S*,3*S*,4*S*)-3,4-bis{(triisopropylsilyl)oxy-2-[((triisopropylsilyl)oxy)methyl]-3,4-dihydro-2*H*-pyran-6-yl}-2- (1,3-dioxoisoindolin-2-yl)-3-phenylpropanamide (3a)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**1a**) (49 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3a** (105 mg, 95%, d.r. > 20:1).

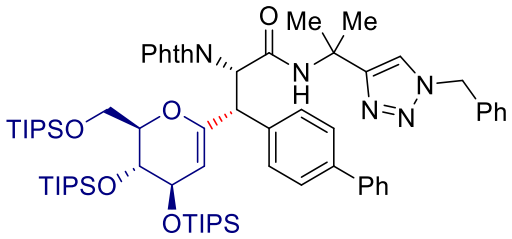
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.56 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.44 (s, 1H), 7.33 – 7.25 (m, 3H), 7.26 – 7.17 (m, 4H), 7.04 (d, *J* = 5.6 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 5.49 (d, *J* = 11.8 Hz, 1H), 5.41 (s, 2H), 5.06 (d, *J* = 5.4, 1H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.35 (t, *J* = 6.6 Hz, 1H), 4.10 (t, *J* = 2.0 Hz, 1H), 4.06 – 3.93 (m, 3H), 1.76 (s, 3H), 1.73 (s, 3H), 1.11 – 1.04 (m, 42H), 0.91 – 0.78 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.7 (C_q), 153.1 (C_q), 151.4 (C_q), 138.5 (C_q), 135.0 (C_q), 133.7 (CH), 131.4 (C_q), 128.9 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.9 (CH), 126.8 (CH), 123.2 (CH), 121.0 (CH), 98.8 (CH), 80.9 (CH), 69.5 (CH), 66.7 (CH), 61.2 (CH_2), 55.4 (CH), 53.9 (CH_2), 52.1 (C_q), 50.1 (CH), 28.7 (CH_3), 28.0 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3053, 2943, 2867, 1716, 1264, 895, 737, 705 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1128 (85) $[M+Na]^+$, 1106 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{62}H_{95}N_5NaO_7Si_3^+$ $[M+Na]^+$:1128.6432, found: 1128.6436.



***N*-((*R*)-[1,1'-Biphenyl]-4-yl((2*R*,3*R*,4*R*)-3,4-bis((triisopropylsilyl)oxy)-2{[(triisopropylsilyl)oxy)methyl]-3,4-dihydro-2*H*-pyran-6-yl}methyl)-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)acetamide (3b)**

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**1b**) (57 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3b** (73 mg, 62%, d.r. > 20:1).

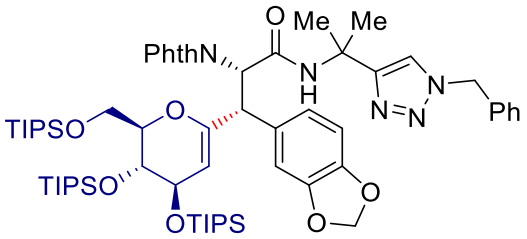
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.55 (t, *J* = 5.4, 3.1 Hz, 2H), 7.44 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.24 (m, 8H), 7.21 (dd, *J* = 7.2, 2.2 Hz, 2H) 7.04 (s, 1H), 5.55 (d, *J* = 11.8 Hz, 1H), 5.41 (s, 2H), 5.10 (d, *J* = 5.3 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.37 (t, *J* = 6.8 Hz, 1H), 4.10 (m, 1H), 4.04 (d, *J* = 6.8 Hz, 2H), 4.00 (d, *J* = 5.3 Hz, 1H), 1.78 (s, 3H), 1.74 (s, 3H), 1.11 – 1.04 (m, 42H), 0.90 – 0.81 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.7 (C_q), 153.1 (C_q), 151.4 (C_q), 140.8 (C_q), 139.4 (C_q), 137.7 (C_q), 135.0 (C_q), 133.7 (CH), 131.4 (C_q), 128.9 (CH), 128.5 (CH), 128.5 (CH), 128.3 (CH), 127.9 (CH), 126.9 (CH), 126.7 (CH), 126.6 (CH), 123.2 (CH), 120.9 (CH), 98.8 (CH), 80.9 (CH), 69.4 (CH), 66.7 (CH), 61.2 (CH_2), 55.2 (CH), 53.9 (CH_2), 52.2 (C_q), 49.9 (CH), 28.6 (CH_3), 28.1 (CH_3), 18.24 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3018, 2943, 2866, 1715, 1387, 1215, 908, 751, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1204 (100) $[M+Na]^+$, 1182 (80) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{68}H_{100}N_5O_7Si_3^+$ $[M+H]^+$: 1182.6925, found: 1182.6914.



(2*S*,3*S*)-3-(Benzo[d][1,3]dioxol-5-yl)-*N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-{(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2 [((triisopropylsilyl)oxy)methyl]-3,4-dihydro-2*H*-pyran-6-yl}-2-(1,3-dioxoisoindolin-2-yl)propenamide (3c)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**1c**) (54 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3c** (75 mg, 65%, d.r. > 20:1).

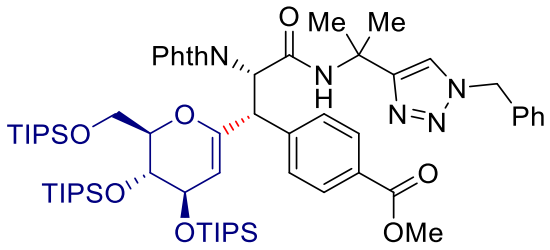
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 – 7.65 (m, 2H), 7.62 – 7.59 (m, 2H), 7.42 (s, 1H), 7.33 – 7.25 (m, 3H), 7.23 – 7.15 (m, 2H), 6.98 (s, 1H), 6.79 (s, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 5.74 (m, 2H), 5.51 – 5.27 (m, 3H), 5.03 (d, *J* = 5.3 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.43 – 4.30 (m, 1H), 4.10 (s, 1H), 4.03 – 3.92 (m, 3H), 1.74 (s, 3H), 1.72 (s, 3H), 1.14 – 0.99 (m, 42H), 0.94 – 0.87 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.6 (C_q), 153.1 (C_q), 151.5 (C_q), 147.0 (C_q), 146.3 (C_q), 135.0 (C_q), 133.8 (CH), 132.5 (C_q), 131.4 (C_q), 128.9 (CH), 128.3 (CH), 127.9 (CH), 123.3 (CH), 121.6 (CH), 120.9 (CH), 108.6 (CH), 107.6 (CH), 100.6 (CH_2), 98.6 (CH), 80.9 (CH), 69.4 (CH), 66.7 (CH), 61.2 (CH_2), 55.4 (CH), 53.9 (CH_2), 52.1 (C_q), 49.7 (CH), 28.6 (CH_3), 28.0 (CH_3), 18.2 (CH_3) , 18.19 (CH_3), 18.1 (CH_3), 18.02 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.30 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3019, 2867, 1715, 1385, 1264, 1215, 908, 754, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1172 (100) $[M+Na]^+$, 1150 (75) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{63}H_{95}N_5NaO_9Si_3^+$ $[M+Na]^+$: 1172.6330, found: 1172.6319.



Methyl 4-[(1*S*,2*S*)-3-{[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]amino}-1-{(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl}-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]benzoate (3d)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**1d**) (28 mg, 0.05 mmol) and 1-iodo glycal **2a** (55 mg, 0.08 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3d** (30 mg, 51%, d.r. > 20:1).

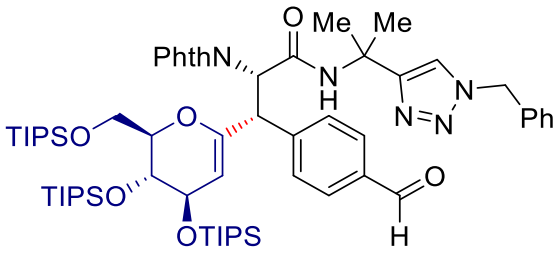
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (dd, J = 8.3 Hz, 2H), 7.66 – 7.53 (m, 4H), 7.40 (s, 1H), 7.37 – 7.27 (m, 5H), 7.22 – 7.16 (m, 2H), 6.95 (s, 1H), 5.52 (d, J = 11.9 Hz, 1H), 5.40 (s, 2H), 5.08 (dd, J = 5.4, 1.4 Hz, 1H), 4.69 (d, J = 11.9 Hz, 1H), 4.34 (t, J = 6.7 Hz, 1H), 4.13 – 3.91 (m, 4H), 3.79 (s, 3H), 1.76 (s, 3H), 1.71 (s, 3H), 1.13 – 0.98 (m, 42H), 0.93 – 0.73 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7 (C_q), 166.9 (C_q), 166.3 (C_q), 153.0 (C_q), 150.6 (C_q), 143.9 (C_q), 134.9 (C_q), 133.9 (CH), 131.3 (C_q), 129.4 (C_q), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 123.3 (CH), 120.8 (CH), 99.3 (CH), 81.1 (CH), 69.4 (CH), 66.6 (CH), 61.2 (CH), 54.9 (CH), 53.9 (CH_2), 52.2 (CH), 51.9 (CH_3), 50.1 (CH), 28.4 (CH_3), 28.2 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.2 (CH), 12.1 (CH)

IR (ATR): $\tilde{\nu}$ = 2865, 1718, 1463, 1382, 1279, 1062, 883, 757, 681 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1186 (100) $[M+Na]^+$, 1164 (10) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{97}N_5NaO_9Si_3^+$ $[M+Na]^+$: 1186.6486, found: 1186.6486.



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-(4-formylphenyl)propenamide (3e)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**1e**) (52 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3e** (63 mg, 56%, d.r. >20:1).

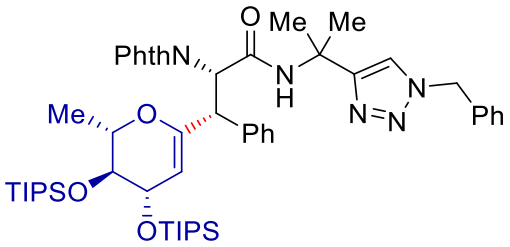
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 7.66 – 7.61 (m, 2H), 7.60 – 7.54 (m, 4H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 (s, 1H), 7.32 – 7.24 (m, 3H), 7.23 – 7.16 (m, 2H), 6.92 (s, 1H), 5.54 (d, *J* = 11.8 Hz, 1H), 5.40 (s, 2H), 5.10 (d, *J* = 5.4 Hz, 1H), 4.74 (d, *J* = 11.8 Hz, 1H), 4.35 (t, *J* = 6.3 Hz, 1H), 4.11 – 4.04 (m, 2H), 4.02 – 3.93 (m, 2H), 1.76 (s, 3H), 1.71 (s, 3H), 1.07 (m, *J* = 7.8 Hz, 42H), 0.83 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.8 (CH), 167.7 (C_q), 166.2 (C_q), 153.0 (C_q), 150.2 (C_q), 145.7 (C_q), 135.1 (C_q), 134.9 (C_q), 133.9 (CH), 131.2 (C_q), 129.5 (CH), 128.9 (CH), 128.9 (CH), 128.4 (CH), 127.9 (CH), 123.3 (CH), 120.8 (CH), 99.5 (CH), 81.1 (CH), 69.3 (CH), 66.5 (CH), 61.2 (CH_2), 54.8 (CH), 53.9 (CH_2), 52.2 (C_q), 50.2 (CH), 28.3 (CH_3), 28.2(CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.2 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 3020, 1714, 1265, 1216, 909, 755, 706, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1156 (100) $[M+Na]^+$, 1134 (15) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{63}H_{95}N_5NaO_8Si_3^+$ $[M+Na]^+$: 1156.6381, found: 1156.6374.



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-{(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl}-3-phenylpropanamide (3f)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**1a**) (49 mg, 0.10 mmol) and 1-iodo glycal **2b** (85 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3f** (80 mg, 86%, d.r. > 20:1).

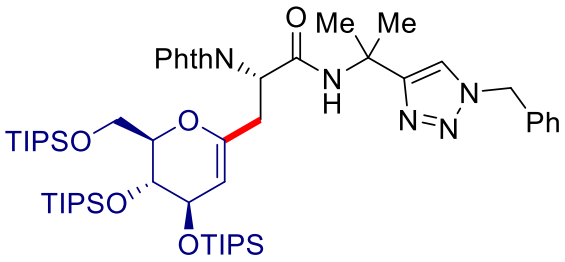
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 – 7.72 (m, 2H), 7.69 – 7.63 (m, 3H), 7.45 – 7.41 (m, 3H), 7.40 – 7.36 (m, 2H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.26 (s, 1H), 7.17 (dd, *J* = 7.3 Hz, 2H), 7.10 (dd, *J* = 7.3 Hz, 1H), 5.61 (d, *J* = 11.4 Hz, 1H), 5.56 (s, 2H), 5.28 (d, *J* = 4.3 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H), 4.49 (dt, *J* = 7.0 Hz, 1H), 4.23 (d, *J* = 4.3 Hz, 1H), 3.94 (q, *J* = 1.8 Hz, 1H), 1.86 (s, 3H), 1.82 (s, 3H), 1.18 – 1.02 (m, 45H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.8 (C_q), 153.0 (C_q), 151.2 (C_q), 138.0 (C_q), 135.0 (C_q), 133.7 (CH), 131.5 (C_q), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 126.9 (CH), 123.1 (CH), 121.1 (CH), 100.7 (CH), 75.8 (CH), 74.0 (CH), 67.3 (CH), 53.9 (CH_2), 53.5 (CH), 52.4 (C_q), 51.3 (CH), 29.0 (CH_3), 27.6 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 15.2 (CH_3), 12.5 (CH), 12.5 (CH).

IR (ATR): $\tilde{\nu}$ = 3054, 2867, 1715, 1386, 1265, 1092, 884, 737, 705 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 956 (100) $[M+Na]^+$, 934 (40) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{75}N_5NaO_6Si_2^+$ $[M+Na]^+$: 956.5148, found: 956.5129.



(*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4 bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (3g)

The general procedure **A** was followed using Phth-Ala-TAM^{Bn} (**1f**) (42 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3g** (91 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.43 (s, 1H), 7.38 – 7.28 (m, 3H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.24 (m, 1H), 7.07 (s, 1H), 5.45 (s, 2H), 5.00 (t, *J* = 8.0, 6.0 Hz, 1H), 4.76 (dd, *J* = 5.4, 1.3 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.01 (d, *J* = 2.0 Hz, 1H), 3.95 – 3.88 (m, 2H), 3.85 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.08 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.96 (dd, *J* = 14.8, 6.0 Hz, 1H), 1.72 (s, 3H), 1.71 (s, 3H), 1.07 – 0.97 (m, 42H), 0.98 – 0.90 (m, 21H).

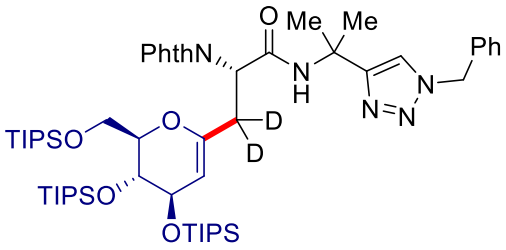
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.5 (C_q), 153.2 (C_q), 149.2 (C_q), 134.8 (C_q), 133.8 (CH), 132.0 (C_q), 128.9 (CH), 128.4 (CH), 128.0 (CH), 123.3 (CH), 120.6 (CH), 99.1 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 54.0 (CH_2), 53.1 (CH), 52.0 (C_q), 35.0 (CH_2), 28.4 (CH_3), 27.9 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.3 (CH), 11.9 (CH).

(1 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 2867, 2012, 1716, 1384, 1265, 1054, 895, 737, 705 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1052 (100) $[M+Na]^+$, 1030 (25) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{56}H_{91}N_5NaO_7Si_3^+$ $[M+Na]^+$: 1052.6119, found: 1052.6120.



(*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (3h)

The general procedure **A** was followed using Phth*N*-[**D$_3$**]-Ala-TAM^{Bn} (**[D$_3$]-1f**) (42 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3h** (93 mg, 91%).

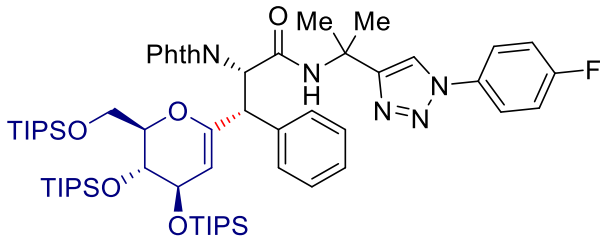
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.42 (s, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.21 (m, 2H), 7.06 (s, 1H), 5.45 (s, 2H), 4.98 (s, 1H), 4.75 (d, *J* = 4.4 Hz, 1H), 4.24 (dt, *J* = 7.0, 3.8 Hz, 1H), 4.00 (d, *J* = 2.0 Hz, 1H), 3.95 – 3.81 (m, 3H), 1.71 (s, 3H), 1.70 (s, 3H), 1.05 – 0.97 (m, 42H), 0.96 – 0.91 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9 (C_q), 167.5 (C_q), 153.2 (C_q), 149.2 (C_q), 134.8 (C_q), 133.8 (CH), 132.0 (C_q), 128.9 (CH), 128.4 (CH), 128.0 (CH), 123.3 (CH), 120.6 (CH), 99.1 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 54.0 (CH_2), 53.0 (CH), 52.0(C_q), 28.4 (CH_3), 27.8 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.3 (CH), 11.9 (CH). (2 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 2945, 2866, 1716, 1387, 1265, 1215, 909, 754, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1054 (100) $[M+Na]^+$, 1032 (20) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{56}H_{89}D_2N_5NaO_7Si_3^+$ $[M+Na]^+$: 1054.6244, found: 1054.6244.



(2*S*,3*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-*N*-{2-[1-(4-fluorophenyl)-1*H*-1,2,3-triazol-4-yl]propan-2-yl}-3-phenylpropanamide (3i)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**1g**) (50 mg, 0.05 mmol) and 1-iodo glycal **2a** (55 mg, 0.08 mmol), AgOAc (17 mg, 0.1 mmol). After 10 h at 60 °C, purification by column chromatography (*n*-hexane/EtOAc 5:1) yielded **3i** (41 mg, 74%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.72 (dd, *J* = 9.0, 4.6 Hz, 2H), 7.63 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.56 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 5.57 (d, *J* = 11.5 Hz, 1H), 5.11 (dd, *J* = 5.4, 1.4 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.39 (t, *J* = 6.6 Hz, 1H), 4.12 (d, *J* = 1.8 Hz, 1H), 4.09 – 3.97 (m, 3H), 1.82 (s, 3H), 1.82 (s, 3H), 1.30 – 1.00 (m, 42H), 0.98 – 0.78 (m, 21H).

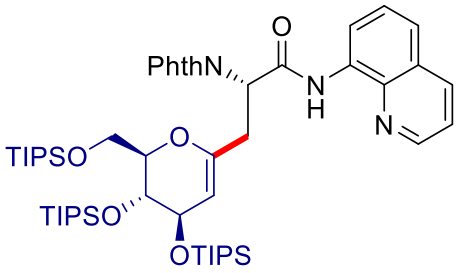
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.0 (C_q), 167.0 (C_q), 162.1 (d, $^1J_{C-F}$ = 247.9 Hz, C_q), 153.5 (C_q), 151.6 (C_q), 138.5 (C_q), 133.8 (CH), 133.6 (d, $^4J_{C-F}$ = 3.2 Hz, C_q), 131.4 (C_q), 128.0 (CH), 128.0 (CH), 126.9 (CH), 123.1 (CH), 122.1 (d, $^3J_{C-F}$ = 8.5 Hz, CH), 119.4 (CH), 116.3 (d, $^2J_{C-F}$ = 23.0 Hz, CH), 99.0 (CH), 81.1 (CH), 69.4 (CH), 66.7 (CH), 61.2 (CH_2), 55.1 (CH), 52.4 (C_q), 50.3 (CH), 29.2 (CH_3), 27.8 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.04 (CH_3), 18.0 (CH_3), 17.96 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

^{19}F NMR (282 MHz, $CDCl_3$): δ: = -113.32 (s).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1714, 1516, 1463, 1383, 1234, 1043, 882, 755, 683 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1132 (100) $[M+Na]^+$, 1110 (85) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{61}H_{92}FN_5NaO_7Si_3^+$ $[M+Na]^+$: 1132.6181, found: 1132.6170.



(*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)propenamide (3j)

The general procedure **C** was followed using Phth-Ala-AQ (**1h**) (35 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3j** (81 mg, 85%).

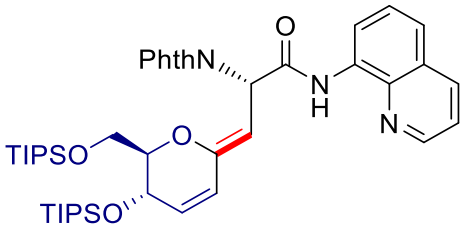
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1H), 8.75 – 8.56 (m, 2H), 8.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.48 (m, 2H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.51 (dd, *J* = 11.2, 4.6 Hz, 1H), 4.82 (d, *J* = 5.1 Hz, 1H), 4.28 (t, *J* = 5.9 Hz, 1H), 4.01 (t, *J* = 2.0 Hz, 1H), 3.95 (dd, *J* = 10.9, 7.0 Hz, 1H), 3.89 (m, 2H), 3.53 (dd, *J* = 14.6, 11.2 Hz, 1H), 3.17 (dd, *J* = 14.6, 4.6 Hz, 1H), 1.08 – 1.04 (m, 21H), 1.02 – 0.98 (m, 21H), 0.95 – 0.87 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.84 (C_q), 166.78 (C_q), 148.94 (C_q), 148.20 (CH), 138.47 (C_q), 136.13 (CH), 133.98 (C_q), 133.81 (CH), 132.07 (C_q), 127.77 (C_q), 127.18 (CH), 123.40 (CH), 121.81 (CH), 121.52 (CH), 116.76 (CH), 98.97 (CH), 81.14 (CH), 69.34 (CH), 66.20 (CH), 62.16 (CH_2), 52.91 (CH), 33.78 (CH_2), 18.13 (CH_3), 18.09 (CH_3), 18.00 ($2CH_3$), 17.94 (CH_3), 17.93 (CH_3), 12.40 (CH), 12.33 (CH), 12.01 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 2943, 1720, 1532, 1464, 1384, 1264, 1060, 883, 738 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 980 (100) $[M+Na]^+$, 958 (40) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{83}N_3NaO_7Si_3^+$ $[M+Na]^+$: 980.5431, found: 980.5426.



(*S*,*Z*)-2-(1,3-Dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)-3-[(5*S*,6*R*)-5-[(triisopropylsilyl)oxy]-6-{[(triisopropylsilyl)oxy]methyl}-5,6-dihydro-2*H*-pyran-2-ylidene]propenamide (3j')

The general procedure **C** was followed using Phth-Ala-AQ **(1h)** (35 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 8 h at 100 °C, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3j'** (62 mg, 79%).

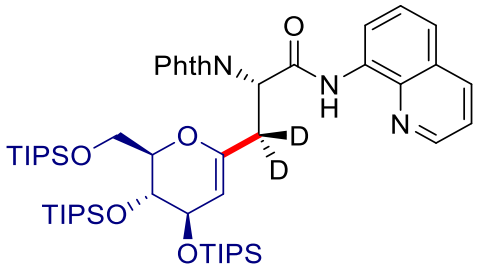
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.63 (s, 1H), 8.72 – 8.66 (m, 2H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.48 (m, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.31 (d, *J* = 9.4 Hz, 1H), 6.20 (dd, *J* = 10.0, 1.4 Hz, 1H), 6.13 (dd, *J* = 10.0, 2.6 Hz, 1H), 5.51 (d, *J* = 9.4 Hz, 1H), 4.80 (d, *J* = 6.6 Hz, 1H), 4.07 – 3.96 (m, 2H), 3.90 (dd, *J* = 7.3, 2.6 Hz, 1H), 1.26 – 0.97 (m, 21H), 0.94 – 0.76 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 165.8 (C_q), 152.3 (C_q), 148.0 (CH), 138.8 (C_q), 136.0 (CH), 134.2 (C_q), 133.9 (CH), 132.4 (CH), 132.2 (C_q), 127.8 (C_q), 127.3 (CH), 123.4 (CH), 122.7 (CH), 121.6 (CH), 121.4 (CH), 116.4 (CH), 100.5 (CH), 81.0 (CH), 63.3 (CH), 62.1 (CH_2), 50.3 (CH), 18.12 (CH_3) , 18.1 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 12.6 (CH), 11.8 (CH).

IR (ATR): $\tilde{\nu}$ = 3004, 1711, 1420, 1359, 1220, 1092, 902, 530 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 806 (100) $[M+Na]^+$, 784 (70) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{61}N_3NaO_6Si_2^+$ $[M+Na]^+$: 806.3991, found: 806.3987.



(*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)propenamide (3k)

The general procedure **D** was followed using Phth-[$\mathbf{D_3}$]Ala-AQ (**[$\mathbf{D_3}$]-1h**) (35 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3k** (76 mg, 79%).

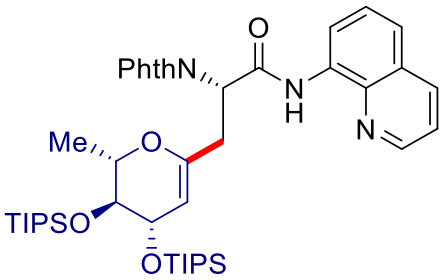
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1H), 8.72 – 8.66 (m, 2H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.48 (d, *J* = 4.5 Hz, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.50 (s, 1H), 4.81 (dd, *J* = 5.2, 1.4 Hz, 1H), 4.28 (dt, *J* = 9.0, 3.4 Hz, 1H), 4.00 (d, *J* = 1.9 Hz, 1H), 3.95 (dd, *J* = 10.9, 7.1 Hz, 1H), 3.91 – 3.86 (m, 2H), 1.06 (m, 21H), 1.00 (m, 21H), 0.94 – 0.88 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9 (C_q), 166.8 (C_q), 148.9 (C_q), 148.2 (CH), 138.5 (C_q), 136.1 (CH), 134.0 (C_q), 133.8 (CH), 132.1 (C_q), 127.8 (C_q), 127.2 (CH), 123.4 (CH), 121.8 (CH), 121.5 (CH), 116.8 (CH), 99.0 (CH), 81.2 (CH), 69.4 (CH), 66.2 (CH), 62.2 (CH_2), 52.8 (CH), 18.2 (CH_3), 18.1 (CH_3), 18.0 ($2CH_3$), 17.96 (CH_3), 17.9 (CH_3), 12.4 (CH_3), 12.3 (CH_3), 12.0 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2866, 2254, 1720, 1531, 1464, 1382, 905, 730, 650 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 982 (55) $[M+Na]^+$, 960 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{53}H_{82}D_2N_3O_7Si_3^+$ $[M+H]^+$:960.5737, found: 960.5723.



(*S*)-2-(1,3-Dioxoisoindolin-2-yl)-3-[(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl]-*N*-(quinolin-8-yl)propenamide (3l)

The general procedure **C** was followed using Phth*N*-Ala-AQ (**1h**) (35 mg, 0.10 mmol) and 1-iodo glycal **2b** (85 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3l** (41 mg, 52%).

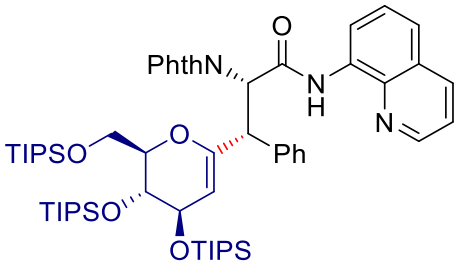
^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.33 (s, 1H), 8.70 (dd, *J* = 5.5, 3.6 Hz, 1H), 8.64 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.49 (s, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.52 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.76 (d, *J* = 5.1 Hz, 1H), 4.35 (dtd, *J* = 7.1, 5.1, 1.9 Hz, 1H), 4.07 – 3.89 (m, 1H), 3.82 (d, *J* = 1.9 Hz, 1H), 3.43 (dd, *J* = 14.5, 11.5 Hz, 1H), 3.16 (dd, *J* = 14.5, 4.5, Hz, 1H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.06 – 0.95 (m, 21H), 0.89 – 0.80 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8 (C_q), 166.8 (C_q), 148.2 (CH), 147.7 (C_q), 138.5 (C_q), 136.2 (C_q), 133.9 (CH), 131.9 (C_q), 127.8 (C_q), 127.3 (CH), 123.5 (CH), 121.8 (CH), 121.5 (CH), 116.7 (CH), 99.4 (CH), 75.2 (CH) , 72.8 (CH), 66.6 (CH), 52.7 (CH), 33.8 (CH_2), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 15.7 (CH_3), 12.6 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2948, 1718, 1535, 1464, 1388, 1262, 885, 740 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 808 (30) $[M+Na]^+$, 786 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{44}H_{64}N_3O_6Si_2^+$ $[M+H]^+$: 786.4328, found: 786.4312.



(2*S*,3*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-phenyl-*N*-(quinolin-8-yl)propenamide (3m)

The general procedure **D** was followed using Phth*N*-Phe-AQ (**1i**) (42 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3m** (96 mg, 93%, d.r. = 10:1).

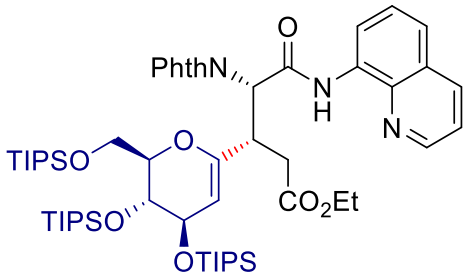
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.51 (s, 1H), 8.90 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.82 (dd, *J* = 5.4, 3.7 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.58 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.49 (s, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.45 (m, 3H), 7.11 (m, 2H), 7.04 (m, 1H), 5.85 (d, *J* = 12.1 Hz, 1H), 5.22 – 5.01 (m, 2H), 4.29 (dt, *J* = 7.8, 4.0 Hz, 1H), 4.17 (d, *J* = 1.9 Hz, 1H), 4.03 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.99 (dt, *J* = 4.7, 1.9 Hz, 1H), 3.71 (dd, *J* = 10.2, 5.8 Hz, 1H), 1.02 – 0.83 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 165.1 (C_q), 151.2 (C_q), 148.4 (CH), 138.7 (C_q), 138.6 (C_q), 135.9 (CH), 134.4 (C_q), 133.8 (CH), 131.3 (C_q) 128.2 (CH), 128.1 (CH), 127.8 (C_q), 127.2 (CH), 126.8 (CH), 123.3 (CH), 121.6 (CH), 121.4 (CH), 117.1 (CH), 99.0 (CH), 80.5 (CH), 69.2 (CH), 66.7 (CH), 60.8 (CH_2), 57.1 (CH), 48.7 (CH), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.93 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 12.3 (CH), 11.7 (CH). (1 CH resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum)

IR (ATR): $\tilde{\nu}$ = 3019, 2022, 1719, 1530, 1215, 750, 1215, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1056 (75) $[M+Na]^+$, 1034 (50) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{59}H_{87}N_3NaO_7Si_3^+$ $[M+Na]^+$: 1056.5744, found: 1056.5738.



Ethyl (3*S*,4*S*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-4-(1,3-dioxoisoindolin-2-yl)-5-oxo-5-(quinolin-8-ylamino)pentanoate (3n)

The general procedure **D** was followed using Phth-Glu(OEt)-AQ (**1j**) (43 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3n** (96 mg, 92%, d.r. = 6:1).

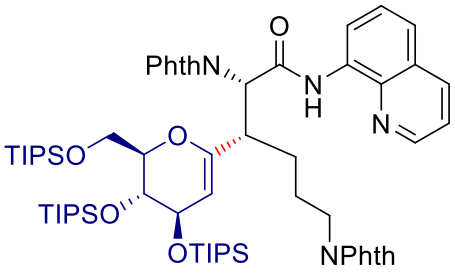
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.47 (s, 1H), 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 6.8, 2.3 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.51 – 7.37 (m, 3H), 5.39 (d, *J* = 11.5 Hz, 1H), 5.11 (d, *J* = 5.2 Hz, 1H), 4.30 (dd, *J* = 11.5, 6.0 Hz, 1H), 4.27 – 4.23 (m, 1H), 4.21 – 4.07 (m, 1H), 4.06 – 3.91 (m, 2H), 3.93 – 3.77 (m, 2H), 3.71 (dd, *J* = 10.3, 5.8 Hz, 1H), 2.70 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.48 (dd, *J* = 16.2, 6.0 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.07 – 0.95 (m, 21H), 0.92 – 0.77 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1 (C_q), 167.7 (C_q), 164.6 (C_q), 150.2 (C_q), 148.4 (CH), 138.7 (C_q), 135.9 (CH), 134.3 (C_q), 134.1 (CH), 131.7 (C_q), 127.8 (C_q), 127.2 (CH), 123.6 (CH), 121.6 (CH), 121.4 (CH), 117.1 (CH), 100.0 (CH), 80.3 (CH), 69.3 (CH), 66.5 (CH), 60.8 (CH_2), 60.4 (CH_2), 57.2 (CH), 39.5 (CH), 35.7 (CH_2), 18.1 (CH_3), 18.1 ($2CH_3$), 18.0 (CH_3), 17.93 (CH_3), 17.9 (CH_3), 13.9 (CH_3), 12.4 (CH), 12.2 (CH), 11.8 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019,2317, 2182, 1722, 1530, 1214, 751, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1066 (100) $[M+Na]^+$, 1044 (55) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{57}H_{89}N_3NaO_9Si_3^+$ $[M+Na]^+$:1066.5799, found: 1066.5794.



(2*S*,3*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2,6-bis(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)hexanamide (3o)

The general procedure **D** was followed using Phth-Lys(Phth)-AQ (**1k**) (27 mg, 0.05 mmol) and 1-iodo glycal **2a** (55 mg, 0.08 mmol). After 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3o** (53 mg, 92%, d.r. = 6:1).

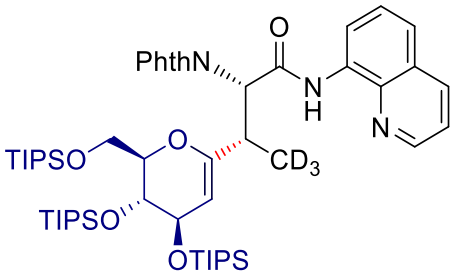
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 1H), 8.88 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.71 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.73 – 7.68 (m, 2H), 7.68 – 7.62 (m, 4H), 7.48 – 7.38 (m, 3H), 5.29 (d, *J* = 11.2 Hz, 1H), 5.07 (d, *J* = 5.2 Hz, 1H), 4.25 (t, *J* = 7.1 Hz, 1H), 4.16 (d, *J* = 1.9 Hz, 1H), 4.05 – 3.91 (m, 2H), 3.79 (td, *J* = 11.2, 3.8 Hz, 1H), 3.70 (dd, *J* = 10.1, 5.7 Hz, 1H), 3.59 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.73 (m, 2H), 1.74 – 1.58 (m, 2H), 1.00 – 0.92 (m, 21H), 0.90 – 0.77 (m, 42H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.0 (C_q), 167.9 (C_q), 165.1 (C_q), 149.3 (C_q), 148.4 (CH), 138.8 (C_q), 135.9 (CH), 134.3 (C_q), 134.0 (CH), 133.5 (CH), 132.1 (C_q), 131.6 (C_q), 127.8 (C_q), 127.2 (CH), 123.5 (CH), 122.9 (CH), 121.5 (CH), 121.4 (CH), 117.1 (CH), 101.2 (CH), 80.1 (CH), 69.4 (CH), 66.4 (CH), 60.8 (CH_2), 58.1 (CH), 42.2 (CH), 37.7 (CH_2), 26.1 (CH_2), 25.4 (CH_2), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.2 (CH), 11.8 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 2399, 1716, 1530 1214, 751, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1167 (100) $[M+Na]^+$, 1145 (20) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{64}H_{92}N_4NaO_9Si_3^+$ $[M+Na]^+$: 1167.6064, found: 1167.6064.



(2*S*,3*S*)-3-[(2*R*,3*R*,4*R*)-3,4-Bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-*N*-(quinolin-8-yl)butanamide (3p)

The general procedure **D** was followed using **1l** (36 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 8 h, Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded inseparable diastereomers **3p** (87 mg, 90%, d.r. = 4:1).

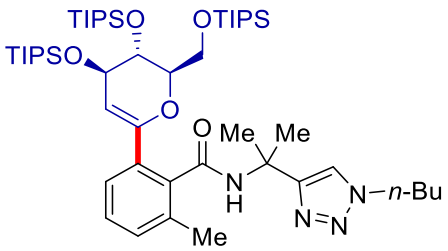
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.48 (s, 1H), 8.97 – 8.80 (m, 1H), 8.78 – 8.62 (m, 1H), 8.20 – 8.01 (m, 1H), 7.90 – 7.76 (m, 2H), 7.72 – 7.59 (m, 2H), 7.52 – 7.32 (m, 3H), 5.32 – 5.14 (m, 1H), 5.04 – 4.79 (m, 1H), 4.31 – 4.11 (m, 2H), 4.07 – 3.93 (m, 2H), 3.88 (d, *J* = 11.9 Hz, 1H), 3.79 – 3.69 (m, 1H), 1.09 – 0.94 (m, 21H), 0.92 – 0.77 (m, 42H)

^{13}C NMR (101 MHz, $CDCl_3$): the major isomer: δ = 168.0 (C_q), 165.5 (C_q), 152.8 (C_q), 148.4 (CH), 138.8 (C_q), 135.9 (CH), 134.3 (C_q), 134.1 (CH), 131.7 (C_q), 127.8 (C_q), 127.2 (CH), 123.5 (CH), 121.6 (CH), 121.3 (CH), 117.2 (CH), 98.2 (CH), 80.3 (CH), 69.4 (CH), 66.6 (CH), 61.0 (CH_2), 58.7 (CH), 37.4 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9(CH_3), 12.5 (CH), 12.2 (CH), 11.8 (CH). the minor isomer: **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.7 (C_q), 166.8 (C_q), 152.6 (C_q), 148.5 (CH), 138.6 (C_q), 136.1 (CH), 134.3 (C_q), 133.7 (CH), 131.9 (C_q), 127.8 (C_q), 127.1 (CH), 123.4 (CH), 121.9 (CH), 121.6 (CH), 117.0 (CH), 98.3 (CH), 80.6 (CH), 69.7 (CH), 66.2 (CH), 61.7 (CH_2), 58.4 (CH), 37.3 (CH), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.5 (CH), 12.2 (CH), 11.8 (CH).

IR (ATR): $\tilde{\nu}$ = 3019, 2867, 1719, 1531, 1381, 1215, 751, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 997 (100) $[M+Na]^+$, 975 (70) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{54}H_{82}D_3N_3NaO_7Si_3^+$ $[M+Na]^+$: 997.5776, found: 997.5773.



2-({2*R*,3*R*,4*R*}-3,4-Bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-*N*-[2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-6-methylbenzamide (5a)

The general procedure **B** was followed using phenyl-TAM^{Bn} (**4a**) (30 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 9:1 → 8:2) yielded **5a** (87 mg, 95%).

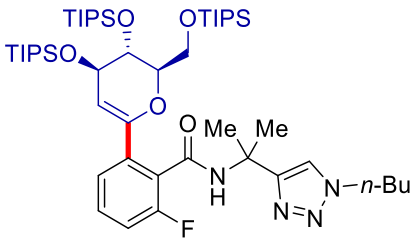
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.21 (dd, J = 7.7, 7.7 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 6.22 (s, 1H), 5.44 (d, J = 4.4 Hz, 1H), 4.42 (dd, J = 8.2, 4.4 Hz, 1H), 4.32 (t, J = 7.3 Hz, 2H), 4.23 – 4.06 (m, 3H), 3.84 (dd, J = 11.2, 4.3 Hz, 1H), 2.20 (s, 3H), 1.94 – 1.81 (m, 5H), 1.73 (s, 3H), 1.43 – 1.30 (m, 2H), 1.11 – 1.01 (m, 63H), 0.95 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.2 (C_q), 153.0 (C_q), 148.1 (C_q), 135.7 (C_q), 135.0 (C_q), 133.4 (C_q), 130.1 (CH), 128.1 (CH), 126.3 (CH), 120.5 (CH), 101.7 (CH), 81.0 (CH), 71.1 (CH), 67.1 (CH), 60.9 (CH_2), 51.6 (C_q), 50.0 (CH_2), 32.3 (CH_2), 28.4 (CH_3), 26.9 (CH_3), 19.7 (CH_2), 18.9 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 13.5 (CH_3), 12.5 (CH), 12.3 (CH), 12.0 (CH). (1 CH_3 resonance of the TIPS group is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1660, 1462, 1383, 1050, 1012, 881, 680 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 936 (100) $[M+Na]^+$, 913 (62) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{50}H_{93}N_4O_5Si_3$ $[M+H]^+$: 913.6448 found: 913.6441.



2-({2*R*,3*R*,4*R*}-3,4-Bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-*N*-[2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-6-fluorobenzamide (5b)

The general procedure **A** was followed using phenyl-TAM^{Bn} (**4b**) (30 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **5b** (85 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (s, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.32 (ddd, J = 7.9, 7.4, 5.8 Hz, 1H), 7.05 (dd, J = 9.1, 7.4 Hz, 1H), 6.26 (s, 1H), 5.52 (d, J = 4.6 Hz, 1H), 4.45 (dd, J = 7.9, 4.6 Hz, 1H), 4.34 (t, J = 7.4 Hz, 2H), 4.22 – 4.10 (m, 3H), 3.87 (dd, J = 11.3, 4.4 Hz, 1H), 1.96 – 1.85 (m, 5H), 1.74 (s, 3H), 1.40 (tq, J = 7.9, 7.4 Hz, 2H), 1.14 – 1.02 (m, 63H), 0.98 (t, J = 7.4 Hz, 3H).

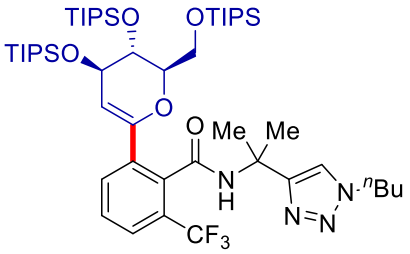
^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.3 (C_q), 159.3 (d, $^{1}J_{C\text{-}F}$ = 245.5 Hz, C_q), 153.0 (C_q), 147.2 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz, C_q), 135.8 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz, C_q), 129.8 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz, CH) 124.4 (d, $^{2}J_{C\text{-}F}$ = 19.9 Hz, C_q), 124.4 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz, CH), 120.3 (d, $^{7}J_{C\text{-}F}$ = 2.9 Hz, CH), 115.4 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz, CH), 102.3 (CH), 81.2 (CH), 70.6 (CH), 66.8 (CH), 60.9 (CH_2), 52.7 (C_q), 50.0 (CH_2), 32.2, (CH_2) 29.1 (CH_3), 27.3 (CH_3), 19.7 (CH_2), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 13.5 (CH_3), 12.5 (CH), 12.4 (CH), 12.0 (CH).

^{19}F NMR (282 MHz, $CDCl_3$): δ = -117.5 (s).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1673, 1508, 1461, 1082, 1052, 881, 758, 679 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 940 (100) $[M+Na]^+$, 917 (55) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{49}H_{90}N_4O_5Si_3F$ $[M+H]^+$: 917.6198 found: 917.6188.



2-[{2*R*,3*R*,4*R*}-3,4-Bis{(triisopropylsilyl)oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-*N*-[2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-6-(trifluoromethyl)benzamide (5c)

The general procedure **B** was followed using phenyl-TAM^{Bn} (**4c**) (35 mg, 0.10 mmol) and 1-iodo-glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **5c** (91 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.59 (s, 1H), 7.46 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.45 (s, 1H), 5.55 (d, *J* = 4.6 Hz, 1H), 4.47 – 4.41 (m, 1H), 4.40 – 4.22 (m, 3H), 4.17 (d, *J* = 4.7 Hz, 1H), 4.08 (s, 1H), 3.81 (d, *J* = 11.3 Hz, 1H), 1.94 – 1.85 (m, 5H), 1.79 (s, 3H), 1.39 (tq, *J* = 7.5, 7.5 Hz, 2H), 1.14 – 1.07 (m, 63H), 0.98 (t, *J* = 7.5 Hz, 3H).

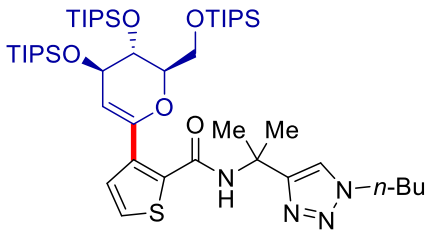
^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.6 (C_q), 152.7 (C_q), 146.5 (C_q), 135.8 (C_q), 133.9 (q, $^3J_{C\text{-}F}$ = 1.6 Hz, C_q), 133.5 (CH), 128.5 (CH), 127.4 (q, $^2J_{C\text{-}F}$ = 31.3 Hz, C_q), 126.0 (q, $^3J_{C\text{-}F}$ = 4.9 Hz, CH), 123.7 (q, $^1J_{C\text{-}F}$ = 274.4 Hz, C_q), 120.2 (CH), 103.4 (CH), 81.2 (CH), 71.1 (CH), 66.9 (CH), 60.6 (CH_2), 52.7 (C_q), 50.0 (CH_2), 32.2 (CH_2), 28.2 (CH_3), 27.2 (CH_3), 19.7 (CH_2), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 13.4 (CH_3), 12.4 (CH), 12.3 (CH), 11.9 (CH).

^{19}F NMR (377 MHz, $CDCl_3$): δ = - 58.48 (s).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1664, 1320, 1133, 1075, 1058, 881, 734, 673 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 990 (100) $[M+Na]^+$, 967 (34) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{50}H_{90}N_4O_5Si_3F_3$ $[M+H]^+$: 967.6166 found: 967.6150.



3-({2*R*,3*R*,4*R*}-3,4-Bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-*N*-[2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]thiophene-2-carboxamide (5d)

The general procedure **B** was followed using thiophene-TAM^{Bn} (**4d**) (29 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 8:1 → 7:2) yielded **5d** (79 mg, 87%).

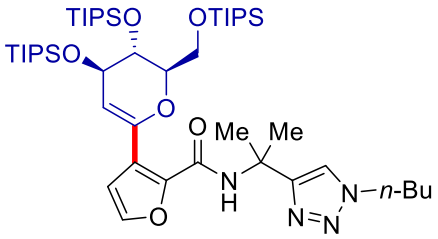
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.54 (s, 1H), 7.34 (d, J = 5.1 Hz, 1H), 7.11 (d, J = 5.1 Hz, 1H), 5.38 (d, J = 5.0 Hz, 1H), 4.58 – 4.49 (m, 1H), 4.28 (t, J = 7.4 Hz, 2H), 4.24 – 4.12 (m, 3H), 3.91 (dd, J = 11.4, 3.8 Hz, 1H), 1.94 – 1.76 (m, 8H), 1.37 (q, J = 7.6 Hz, 2H), 1.15 – 0.96 (m, 63H), 0.95 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.0 (C_q), 152.5 (C_q), 146.6 (C_q), 138.7 (C_q), 134.6 (C_q), 130.3 (CH), 128.2 (CH), 121.0 (CH), 102.7 (CH), 82.2 (CH), 69.5 (CH), 65.8 (CH), 61.7 (CH_2), 51.8 (C_q), 49.9 (CH_2), 32.2 (CH_2), 28.8 (CH_3), 28.6 (CH_3), 19.8 (CH_2), 18.1 (CH_3), 18.1 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 13.5 (CH_3), 12.5 (CH), 12.4 (CH), 11.9 (CH). (2 CH_3 resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1649, 1462, 1300, 1060, 1012, 881, 680 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 928 (100) $[M+Na]^+$, 905 (23) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{47}H_{89}N_4O_5Si_3S$ $[M+H]^+$: 905.5856 found: 905.5857.



3-({2*R*,3*R*,4*R*}-3,4-Bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-*N*-[2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]furan-2-carboxamide (5e)

The general procedure **B** was followed using furan-TAM^{Bn} (**4e**) (28 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 9:1 → 8:2) yielded **5e** (48 mg, 54%).

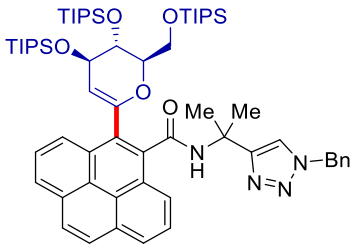
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 7.56 (s, 1H), 7.40 (d, *J* = 1.8 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 5.57 (dd, *J* = 5.4, 1.5 Hz, 1H), 4.57 – 4.43 (m, 1H), 4.26 (t, *J* = 7.4 Hz, 2H), 4.20 – 4.07 (m, 3H), 3.85 (dd, *J* = 11.5, 3.5 Hz, 1H), 1.92 – 1.77 (m, 8H), 1.35 (tq, *J* = 7.4, 7.4 Hz, 2H), 1.10 – 0.96 (m, 63H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.8 (C_q), 152.7 (C_q), 143.6 (C_q), 143.4 (C_q), 143.0 (CH), 122.8 (C_q), 121.2 (CH), 111.8 (CH), 102.2 (CH), 82.3 (CH), 69.3 (CH), 65.6 (CH), 61.8 (CH_2), 51.6 (C_q), 49.9 (CH_2), 32.3 (CH_2), 28.6 (CH_3), 28.5 (CH_3), 19.8 (CH_2), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 13.5 (CH_3), 12.5 (CH), 12.4 (CH), 11.9 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1670, 1462, 1095, 1058, 881, 755, 679 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 912 (100) $[M+Na]^+$, 889 (22) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{47}H_{89}N_4O_6Si_3$ $[M+H]^+$: 889.6084 found: 889.6089.



***N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-5-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]pyrene-4-carboxamide (4f)**

The general procedure **B** was followed using pyrene-TAM^{Bn} (**1cf**) (44 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **4f** (83 mg, 79%).

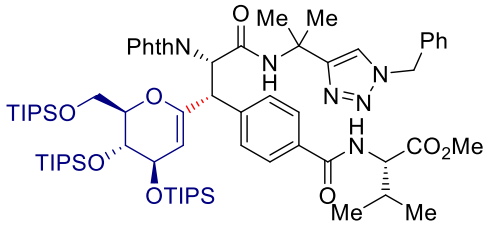
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 8.15 (dd, *J* = 7.4 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.95 (m, 2H), 7.65 (s, 1H), 7.43 – 7.38 (m, 3H), 7.37 – 7.33 (m, 2H), 6.48 (s, 1H), 5.77 (d, *J* = 3.9 Hz, 1H), 5.59 (s,1H), 5.58 (s, 1H), 4.66 – 4.56 (m, 1H), 4.41 (dd, *J* = 11.4, 8.5 Hz, 1H), 4.29 (d, *J* = 4.4 Hz, 1H), 4.17 – 4.16 (m, 1H), 3.91 (dd, *J* = 11.4, 3.5 Hz, 1H), 2.04 (s, 3H), 1.78 (s, 3H), 1.37 – 0.92 (m, 63H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1 (C_q), 153.7 (C_q), 148.1 (C_q), 134.9 (C_q), 131.2 (C_q), 131.1 (C_q), 131.0 (C_q), 130.8 (C_q), 130.6 (C_q), 129.1 (CH), 128.6 (CH), 128.5 (CH), 128.3(C_q), 128.2 (CH), 128.1 (CH), 127.3 (CH), 126.2 (CH), 125.4 (CH), 125.3 (CH), 125.0 (CH), 124.6 (CH), 124.3 (C_q), 124.2 (C_q), 120.6 (CH), 103.3 (CH), 81.7 (CH), 71.3 (CH), 67.2 (CH), 61.1 (CH_2), 54.2 (CH_2), 52.1 (C_q), 28.8 (CH_3), 26.8 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 12.5 (CH), 12.4 (CH), 12.1 (CH).). (3 CH_3 resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 1716, 1215, 908, 752, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1079 (100) $[M+Na]^+$, 1057 (40) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{62}H_{92}N_4NaO_5Si_3^+$ $[M+Na]^+$: 1079.6268, found: 1079.6252.



Methyl {4-[(1*S*,2*S*)-3-({2-[1-benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-1-({2*R*,3*R*,4*R*}-3,4-bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]benzoyl}-*L*-valinate (7a)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**6a**) (65 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1 mL). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 2:1) yielded **7a** (78 mg, 62%, d.r. >20 :1).

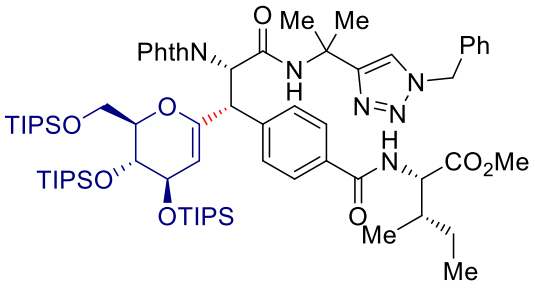
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 – 7.57 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.24 – 7.17 (m, 2H), 6.96 (s, 1H), 6.41 (d, *J* = 8.6 Hz, 1H), 5.56 (d, *J* = 11.8 Hz, 1H), 5.42 (s, 2H), 5.10 (d, *J* = 5.3 Hz, 1H), 4.79 – 4.60 (m, 2H), 4.45 – 4.26 (m, 1H), 4.15 – 3.93 (m, 4H), 3.74 (s, 3H), 2.28 – 2.17 (m, 1H), 1.78 (s, 3H), 1.73 (s, 3H), 1.14 – 1.05 (m, 42H), 0.93 (t, *J* = 7.2 Hz, 6H), 0.88 – 0.83 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.5 (C_q), 167.8 (C_q), 166.8 (C_q), 166.4 (C_q), 153.0 (C_q), 150.6 (C_q), 142.8 (C_q), 134.9 (C_q), 133.9 (CH), 132.5 (C_q), 131.3 (C_q), 128.9 (CH), 128.4 (CH), 128.4 (CH), 127.9 (CH), 126.8 (CH), 123.4 (CH), 120.9 (CH), 99.2 (CH), 81.1 (CH), 69.3 (CH), 66.6 (CH), 61.2 (CH_2), 57.2 (CH), 54.8 (CH), 53.9 (CH_2), 52.2 (C_q), 52.2 (CH_3), 50.0 (CH), 31.6 (CH), 28.4 (CH_3), 28.2 (CH_3), 18.9 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 12.4 (CH), 12.3 (CH), 12.2 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2865, 2197, 1717, 1464, 1383, 1102, 1060, 681 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1286 (81) $[M+Na]^+$, 1263(92) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{69}H_{107}N_6O_{10}Si_3$ $[M+H]^+$: 1263.7351 found: 1263.7335.



Methyl {4-[(1*R*,2*R*)-3-({2-[1-benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-1-({2*R*,3*R*,4*R*}-3,4-bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-3-oxopropyl]benzoyl}-*L*-isoleucinate (7b).

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**6b**) (67 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1.0 mL). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 2:1) yielded **7b** (65 mg, 51%, d.r. >20 :1).

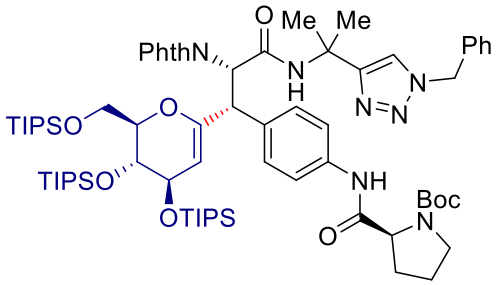
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.56 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.25 – 7.17 (m, 2H), 6.96 (s, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 5.56 (d, *J* = 11.9 Hz, 1H), 5.42 (s, 2H), 5.10 (d, *J* = 5.4 Hz, 1H), 4.79 – 4.64 (m, 2H), 4.43 – 4.28 (m, 1H), 4.14 – 3.92 (m, 4H), 3.74 (s, 3H), 1.99 – 1.90 (m, 1H), 1.78 (s, 3H), 1.73 (s, 3H), 1.52 – 1.42 (m, 1H), 1.24 – 1.16 (m, 1H), 1.15 – 1.03 (m, 42H), 0.97 – 0.88 (m, 6H), 0.88 – 0.80 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4 (C_q), 167.7 (C_q), 166.6 (C_q), 166.4 (C_q), 153.0 (C_q), 150.6 (C_q), 142.7 (C_q), 134.9 (C_q), 133.9 (CH), 132.4 (C_q), 131.2 (C_q), 128.9 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 126.8 (CH), 123.4 (CH), 120.8 (CH), 99.1 (CH), 81.0 (CH), 69.3 (CH), 66.6 (CH), 61.2 (CH_2), 56.5 (CH), 54.8 (CH), 53.9 (CH_2), 52.2 (C_q), 52.1 (CH_3), 50.0 (CH), 38.2 (CH), 28.4 (CH_3), 28.2 (CH_3), 25.2 (CH_2), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 15.4 (CH_3), 12.3 (CH), 12.2 (CH), 12.1 (CH), 11.5 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1717, 16651, 1462, 1382, 1095, 1052, 882, 682 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1300 (84) $[M+Na]^+$, 1277 (100) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{70}H_{109}N_6O_{10}Si_3$ $[M+H]^+$: 1277.7507 found: 1277.7483.



***tert*-Butyl (*S*)-2-([4-{(1*s*,2*s*)-3-([2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]amino)-1-({2*R*,3*R*,4*R*}-3,4-bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]phenyl}carbamoyl)pyrrolidine-1-carboxylate (7c)**

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**6c**) (71 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1 mL). After 16 h, purification by column chromatography (hexane/EtOAc 2:1 → 1:1) yielded **7c** (106 mg, 80%, d.r. >20 :1).

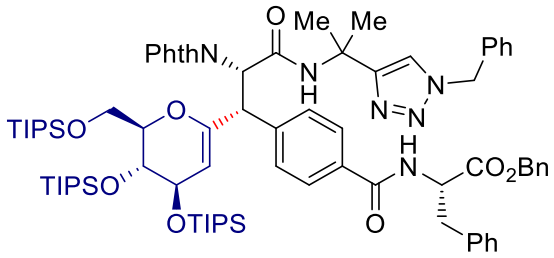
^{1}H NMR (600 MHz, DMSO-d_6, 100 °C): δ = 9.27 (s, 1H), 7.74 – 7.71 (m, 3H), 7.70 – 7.66 (m, 2H), 7.37 (s, 1H), 7.35 – 7.27 (m, 3H), 7.25 (d, J = 8.6 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.06 – 7.03 (m, 2H), 5.48 (s, 2H), 5.28 (d, J = 11.4 Hz, 1H), 5.01 (dd, J = 5.2, 1.5 Hz, 1H), 4.52 (d, J = 11.4 Hz, 1H), 4.24 (ddt, J = 7.6, 6.0, 1.8 Hz, 1H), 4.18 (dd, J = 1.8, 1.8 Hz, 1H), 4.13 (dd, J = 8.4, 4.1 Hz, 1H), 4.11 – 4.05 (m, 1H), 4.04 (dt, J = 4.4, 1.8 Hz, 1H), 3.74 (dd, J = 10.7, 5.6 Hz, 1H), 3.38 (ddd, J = 10.2, 7.5, 5.6 Hz, 1H), 3.32 (dt, J = 10.2, 6.7 Hz, 1H), 2.14 – 2.05 (m, 1H), 1.89 – 1.71 (m, 3H), 1.66 (s, 3H), 1.61 (s, 3H), 1.24 (s, 9H), 1.10 – 1.07 (m, 21H), 1.05 – 1.01 (m, 21H), 0.98 – 0.94 (m, 21H).

^{13}C NMR (151 MHz, DMSO-d_6, 100 °C): δ = 170.2 (C_q), 166.5 (C_q), 164.9 (C_q), 152.9 (C_q), 152.6 (C_q), 151.6 (C_q), 137.3 (C_q), 135.3 (C_q), 133.8 (CH), 132.8 (C_q), 130.4 (C_q), 128.0 (CH), 127.6 (CH), 127.3 (CH), 127.2 (CH), 122.3 (CH), 120.3 (CH), 117.9 (CH), 96.9 (CH), 80.2 (CH), 78.0 (C_q), 69.3 (CH), 66.2 (CH), 60.9 (CH_2), 59.8 (CH), 54.5 (CH), 52.4 (CH_2), 51.1 (C_q), 47.8 (CH), 46.0 (CH_2), 29.9 (CH_2), 27.6 (CH_3), 27.5 (CH_3), 27.3 (CH_3), 22.8 (CH_2), 17.4 (CH_3), 17.4 (CH_3), 17.2 (CH_3), 17.2 (CH_3), 17.2 (CH_3), 17.2 (CH_3), 11.5 (CH), 11.5 (CH), 11.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2943, 2865, 1708, 1526, 1383, 1098, 1052, 1026, 882, 715, 679 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1341 (100) $[M+Na]^+$, 1318 (7) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{72}H_{112}N_7O_{10}Si_3$ $[M+H]^+$: 1318.7773 found: 1318.7750.



Benzyl {4-[(1*S*,2*S*)-3-({2-[1-benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-1-({2*R*,3*R*,4*R*}-3,4-bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]benzoyl}-*L*-phenylalaninate (7d)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**6d**) (77 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1.0 mL). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 2:1 → 1:1) yielded **7d** (69 mg, 50%, d.r. >20 :1).

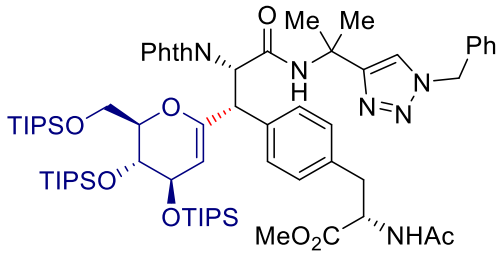
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.54 (m, 4H), 7.47 – 7.40 (m, 3H), 7.39 – 7.27 (m, 10H), 7.25 – 7.14 (m, 5H), 7.01 – 6.92 (m, 3H), 6.42 – 6.31 (m, 1H), 5.54 (d, *J* = 12.1 Hz, 1H), 5.42 (s, 2H), 5.27 – 4.97 (m, 4H), 4.72 (dd, *J* = 12.1, 1.9 Hz, 1H), 4.41 – 4.30 (m, 1H), 4.17 – 3.91 (m, 4H), 3.34 – 3.03 (m, 2H), 1.78 (s, 3H), 1.74 (s, 3H), 1.14 – 1.06 (m, 42H), 0.87 – 0.83 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3 (C_q), 167.7 (C_q), 166.4 (C_q), 166.3 (C_q), 153.0 (C_q), 150.5 (C_q), 142.7 (C_q), 135.6 (C_q), 135.0 (C_q), 134.9 (C_q), 133.9 (CH), 132.2 (C_q), 131.2 (C_q), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.0 (CH), 126.7 (CH), 123.3 (CH), 120.8 (CH), 99.2 (CH), 81.0 (CH), 69.3 (CH), 67.3 (CH_2), 66.6 (CH), 61.1 (CH_2), 54.9 (CH), 53.9 (CH_2), 53.3 (CH), 52.2 (C_q), 50.0 (CH), 37.8 (CH_2), 28.3 (CH_3), 28.2 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 12.3 (CH), 12.2 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1715, 1664, 1461, 1050, 881, 718, 681 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1411 (100) $[M+Na]^+$, 1387 (33) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{79}H_{111}N_6O_{10}Si_3$ $[M+H]^+$: 1387.7664 found: 1387.7636.



Methyl (*S*)-2-acetamido-3-{4-[(1*S*,2*S*)-3-{[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]amino}-1-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]phenyl}propanoate (7e)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**6e**) (64 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:2) yielded **7e** (40 mg, 32 %, d.r. >20 :1).

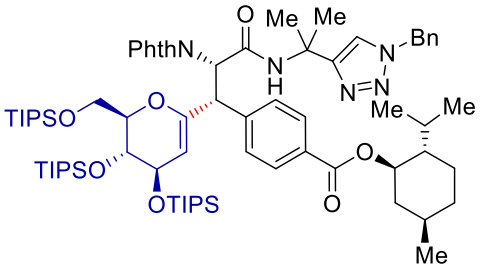
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.59 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.42 (s, 1H), 7.33 – 7.25 (m, 3H), 7.20 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.00 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 2H), 5.51 (d, *J* = 7.7 Hz, 1H), 5.45 (d, *J* = 11.7 Hz, 1H), 5.40 (s, 2H), 5.03 (dd, *J* = 5.4, 1.4 Hz, 1H), 4.63 (dt, *J* = 7.7, 5.8 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.33 (tt, *J* = 6.5, 1.9 Hz, 1H), 4.09 (q, *J* = 1.8 Hz, 1H), 4.05 – 3.99 (m, 2H), 3.97 (dq, *J* = 5.2, 1.8 Hz, 1H), 3.43 (s, 3H), 2.89 (dd, *J* = 14.1, 5.8 Hz, 1H), 2.83 (dd, *J* = 14.1, 5.8 Hz, 1H), 1.77 (s, 3H), 1.74 (s, 3H), 1.71 (s, 3H), 1.12 – 0.99 (m, 42H), 0.91 – 0.84 (m, 21H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.5 (C_q), 169.2 (C_q), 167.7 (C_q), 166.4 (C_q), 153.0 (C_q), 151.1 (C_q), 137.5 (C_q), 134.9 (C_q), 134.2 (C_q), 133.7 (CH), 131.3 (C_q), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 123.2 (CH), 120.9 (CH), 99.0 (CH), 80.9 (CH), 69.5 (CH), 66.7 (CH), 61.2 (CH_2), 55.4 (CH), 53.9 (CH_2), 52.8 (CH), 52.1 (C_q), 51.9 (CH_3), 49.7 (CH), 37.1 (CH_2), 28.5 (CH_3), 28.0 (CH_3), 22.9 (CH_3), 18.23 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.02 (CH_3), 18.0 (CH_3), 17.95 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 1717, 1669, 1514, 1463, 1383, 1215, 1051, 883, 682 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1271 (100) $[M+Na]^+$, 1249 (10) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{68}H_{104}N_6NaO_{10}Si_3^+$ $[M+Na]^+$: 1271.7014, found: 1271.7006.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-[(1*S*,2*S*)-3-({2-[1-benzyl-1*H*-1,2,3-triazol-4-yl]propan-2-yl}amino)-1-({2*R*,3*R*,4*R*}-3,4-bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl]benzoate (7f)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**6f**) (68 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1.0 mL). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 4:1) yielded **7f** (82 mg, 64%, d.r. >20 :1).

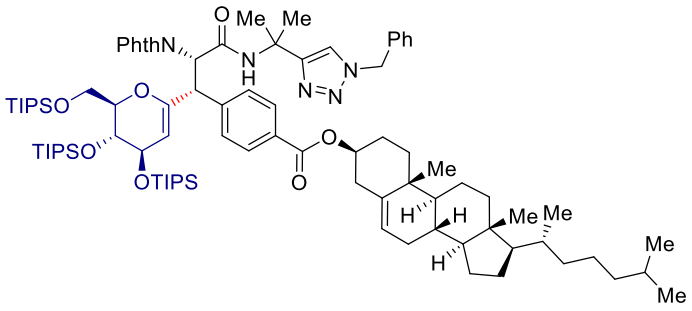
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.64 (m, 2H), 7.64 – 7.58 (m, 2H), 7.42 (s, 1H), 7.37 – 7.29 (m, 5H), 7.24 – 7.19 (m, 2H), 6.97 (s, 1H), 5.56 (d, *J* = 11.9 Hz, 1H), 5.42 (s, 2H), 5.10 (dd, *J* = 5.5, 1.4 Hz, 1H), 4.81 (ddd, *J* = 10.8, 10.8, 4.3 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.36 (ddd, *J* = 7.8, 4.9, 3.1 Hz, 1H), 4.13 – 4.05 (m, 2H), 4.02 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.97 (dd, *J* = 4.9, 2.5 Hz, 1H), 2.03 (dd, *J* = 12.0, 4.2 Hz, 1H), 1.90 (dtd, *J* = 13.9, 7.2, 2.8 Hz, 1H), 1.78 (s, 3H), 1.75 – 1.65 (m, 5H), 1.57 – 1.42 (m, 2H), 1.13 – 1.06 (m, 42H), 1.03 – 0.98 (m, 1H), 0.93 – 0.82 (m, 29H), 0.72 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7 (C_q), 166.4 (C_q), 165.9 (C_q), 153.0 (C_q), 150.6 (C_q), 143.7 (C_q), 134.9 (C_q), 133.8 (CH), 131.3 (C_q), 129.3 (C_q), 129.3 (CH), 128.9 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 123.3 (CH), 120.8 (CH), 99.1 (CH), 81.0 (CH), 74.5 (CH), 69.3 (CH), 66.6 (CH), 61.2 (CH_2), 54.8 (CH), 53.9 (CH_2), 52.2 (C_q), 50.1 (CH), 47.1 (CH), 40.9 (CH_2), 34.2 (CH_2), 31.3 (CH), 28.4 (CH_3), 28.2 (CH_3), 26.2 (CH), 23.4 (CH_2), 22.0 (CH_3), 20.8 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 16.3 (CH_3), 12.3 (CH), 12.2 (CH), 12.1 (CH).

IR (ATR): $\tilde{\nu}$ = 2942, 2865, 1714, 1462, 1382, 1274, 1107, 1049, 882, 717, 657 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1311 (100) $[M+Na]^+$, 1288 (7) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{73}H_{114}N_5O_9Si_3$ $[M+H]^+$: 1288.7919 found: 1288.7885.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-[(*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4- ((1*S*,2*S*)-3-((2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl)amino)-1-({2*R*,3*R*,4*R*}-3,4- bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6- yl)-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropyl)benzoate (7g)

The general procedure **A** was followed using Phth-Phe-TAM^{Bn} (**6g**) (91 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1.0 mL). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 7:3) yielded **7g** (101 mg, 67%, d.r. >20 :1).

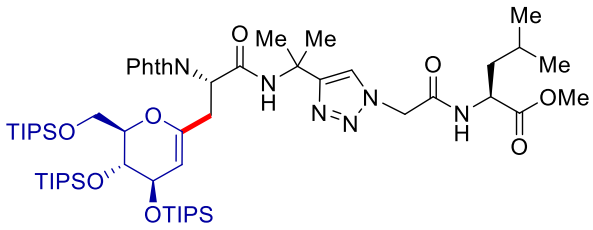
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.60 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.43 (s, 1H), 7.36 – 7.29 (m, 5H), 7.25 – 7.19 (m, 2H), 6.98 (s, 1H), 5.55 (d, *J* = 11.9 Hz, 1H), 5.43 (s, 2H), 5.40 – 5.36 (m, 1H), 5.10 (dd, *J* = 5.6, 1.5 Hz, 1H), 4.81 – 4.67 (m, 2H), 4.35 (dddd, *J* = 7.1, 6.7, 3.2, 3.2 Hz, 1H), 4.14 – 4.06 (m, 1H), 4.06 – 3.93 (m, 1H), 2.38 (d, *J* = 8.2 Hz, 2H), 2.03 (dt, *J* = 12.7, 3.2 Hz, 2H), 1.98 – 1.82 (m, 5H), 1.78 (s, 3H), 1.74 (s, 3H), 1.66 – 1.43 (m, 8H), 1.43 – 1.32 (m, 4H), 1.25 – 1.14 (m, 5H), 1.11 – 1.07 (m, 43H), 1.05 (s, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.91 – 0.85 (m, 28H), 0.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7 (C_q), 166.4 (C_q), 165.8 (C_q), 153.0 (C_q), 150.7 (C_q), 143.8 (C_q), 139.6 (C_q), 135.0 (C_q), 133.9 (CH), 131.3 (C_q), 129.4 (CH), 129.4 (C_q), 128.9 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 123.3 (CH), 122.7 (CH), 120.9 (CH), 99.1 (CH), 81.1 (CH), 74.2 (CH), 69.4 (CH), 66.6 (CH), 61.2 (CH_2), 56.7 (CH), 56.1 (CH), 54.8 (CH), 53.9 (CH_2), 52.2 (C_q), 50.1 (CH), 50.0 (CH), 42.3 (C_q), 39.7 (CH_2), 39.5 (CH_2), 38.2 (CH_2), 37.0 (CH_2), 36.6 (C_q), 36.2 (CH_2), 35.8 (CH), 31.9 (CH), 31.9 (CH_2), 28.4 (CH_3), 28.2 (CH_2), 28.2 (CH_3), 28.0 (CH_2), 27.8 (CH), 24.3 (CH_2), 23.8 (CH_2), 22.8 (CH_3), 22.6 (CH_3), 21.0 (CH_2), 19.3 (CH_3), 18.7 (CH_3), 18.2 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH), 11.9 (CH_3).

IR (ATR): $\tilde{\nu}$ = 2941, 2865, 1716, 1464, 1272, 1050, 882, 717, 681 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1542 (100) $[M+Na]^+$, 1519 (30) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{90}H_{140}N_5O_9Si_3$ $[M+H]^+$: 1519.9985 found: 1519.9961.



Methyl (2-{4-[2-((*S*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2-yl)propanamido)propan-2-yl]-1*H*-1,2,3-triazol-1-yl}acetyl)-*L*-leucinate (9a)

The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Leu-OMe (**8a**) (51 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:1) yielded **9a** (81 mg, 72%)

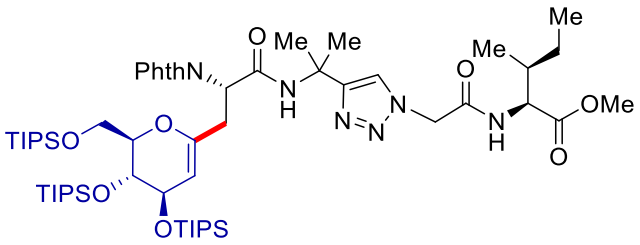
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 (s, 1H), 7.02 (s, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 5.24 – 4.88 (m, 3H), 4.75 (d, *J* = 5.0 Hz, 1H), 4.55 (t, *J* = 6.2 Hz, 1H), 4.24 (t, *J* = 5.0 Hz, 1H), 4.14 – 3.96 (m, 1H), 3.93 – 3.83 (m, 3H), 3.68 (s, 3H), 3.05 (dd, *J* = 14.9, 5.9 Hz, 1H), 2.96 (dd, *J* = 14.9, 5.9 Hz, 1H), 1.74 (s, 3H), 1.72 (s, 3H), 1.61 – 1.45 (m, 3H), 1.08 – 0.91 (m, 63H), 0.87 – 0.81 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4 (C_q), 167.8 (C_q), 167.7 (C_q), 165.2 (C_q), 153.3 (C_q), 149.2 (C_q), 133.9 (CH), 131.9 (C_q), 123.4 (CH), 122.6 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 53.0 (CH), 52.8 (CH_2), 52.3 (CH_3), 51.8 (C_q), 51.1 (CH), 40.8 (CH_2), 34.9 (CH_2), 28.3 (CH_3), 28.0 (CH_3), 24.8 (CH), 22.6 (CH_3), 21.7 (CH_3), 18.11 (CH_3), 18.1 (CH_3), 17.97 (CH_3), 12.3 (CH), 11.9 (CH).). (3 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum):

IR (ATR): $\tilde{\nu}$ = 2943, 1714, 1661, 1384, 1056, 881, 731, 680 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1147 (100) $[M+Na]^+$, 1125 (5) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{100}N_6NaO_{10}Si_3^+$ $[M+Na]^+$: 1147.6701, found: 1147.6697.



Methyl (2-{4-[2-((*S*)-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-2-(1,3-dioxoisoindolin-2- yl)propanamido)propan-2-yl]-1*H*-1,2,3-triazol-1-yl}acetyl)-*L*-isoleucinate (9b)

The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Ile-Ome (**8b**) (51 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:2) yielded 9**b** (74 mg, 65%).

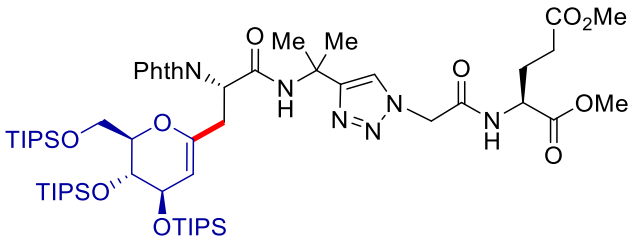
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.68 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.62 (s, 1H), 7.06 (s, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.11 – 4.92 (m, 3H), 4.76 (d, *J* = 4.7 Hz, 1H), 4.49 (dd, *J* = 8.4, 4.9 Hz, 1H), 4.25 (td, *J* = 5.1, 2.6 Hz, 1H), 4.01 (d, *J* = 1.9 Hz, 1H), 3.96 – 3.82 (m, 3H), 3.68 (s, 3H), 3.06 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.97 (dd, *J* = 14.8, 6.2 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.73 (s, 6H), 1.39 – 1.20 (m, 2H), 1.06 – 0.92 (m, 63H), 0.86 – 0.74 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ= 171.3 (C_q), 167.9 (C_q), 167.7 (C_q), 165.1 (C_q), 153.4 (C_q), 149.2 (C_q), 133.9 (CH), 131.92 (C_q), 123.4 (CH), 122.5 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 56.7 (CH), 53.1 (CH), 52.8 (CH_2), 52.1 (CH_3), 51.8 (C_q), 37.5 (CH), 35.0 (CH_2), 28.4 (CH_3), 27.9 (CH_3), 25.0 (CH_2), 18.1 (CH_3), 18.1 (CH_3), 18.0 ($4CH_3$), 15.3 (CH_3), 12.3 (CH), 11.9 (CH), 11.4 (CH).

IR (ATR): $\tilde{\nu}$ = 3019, 1716, 1665, 1215, 908, 753, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1147 (100) $[M+Na]^+$, 1125 (15) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{100}N_6NaO_{10}Si_3^+$ $[M+Na]^+$: 1147.6701, found: 1147.6686.



Dimethyl [2-(4-{2-[(*R*)-3-((2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2-yl)propanamido]propan-2-yl}-1*H*-1,2,3-triazol-1-yl)acetyl]-*L*-glutamate (9c)

The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Glu(OMe)-OMe (**8c**) (53 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:2) yielded **9c** (72 mg, 62%).

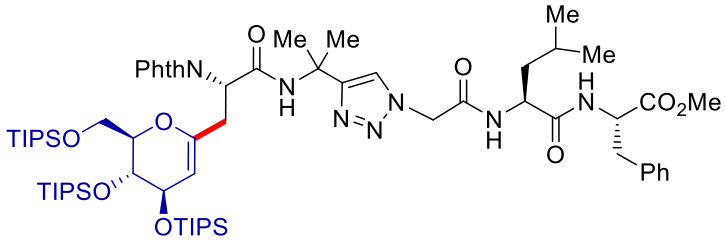
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.63 (s, 1H), 7.01 (s, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.07 – 4.89 (m, 3H), 4.75 (d, *J* = 5.1 Hz, 1H), 4.54 (q, *J* = 7.7, 6.8 Hz, 1H), 4.27 – 4.20 (m, 1H), 4.08 – 3.96 (m, 1H), 3.93 – 3.82 (m, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.06 (dd, *J* = 15.0, 8.1 Hz, 1H), 2.95 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.39 – 2.24 (m, 2H), 2.14 (dq, *J* = 13.8, 6.8 Hz, 1H), 1.94 (dq, *J* = 13.8, 7.7 Hz, 1H), 1.74 (s, 6H), 1.11 – 1.01 (m, 21H), 1.00 – 0.97 (m, 21H), 0.96 – 0.91 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0 (C_q), 171.3 (C_q), 167.9 (C_q), 167.7 (C_q), 165.4 (C_q), 153.3 (C_q), 149.2 (C_q), 133.9 (CH), 131.9 (C_q), 123.4 (CH), 122.5 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 53.0 (CH), 52.7 (CH_2), 52.6 (CH_3), 52.0 (CH), 51.9 (CH_3), 51.8 (C_q), 34.8 (CH_2), 29.8 (CH_2), 28.3 (CH_3), 27.9 (CH_3), 26.6 (CH_2), 18.11 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 12.3 (CH), 11.9 (CH).). (3 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3019, 1716, 1663, 1215, 908, 752, 669 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1177 (100) $[M+Na]^+$, 1155 (5) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{58}H_{98}N_6NaO_{12}Si_3^+$ $[M+Na]^+$: 1177.6443, found: 1177.6436.



Methyl [2-(4-{2-[(*S*)-3-({2*R*,3*R*,4*R*}-3,4-bis{[triisopropylsilyl]oxy}-2- {[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2- yl)propanamido]propan-2-yl}-1*H*-1,2,3-triazol-1-yl)acetyl]-*L*-leucyl-*L*-phenylalaninate (9d)

The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Leu-Phe-OMe (**8d**) (66 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1.0 mL). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 → 1:2) yielded **9d** (79 mg, 62%).

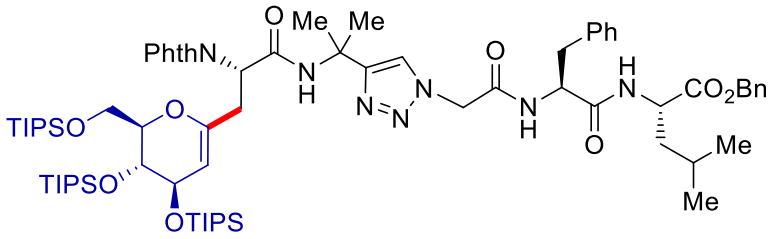
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.68 – 7.64 (m, 2H), 7.58 (s, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.16 (m, 1H), 7.11 – 7.05 (m, 2H), 6.98 (s, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 4.98 (dd, *J* = 8.2, 5.8 Hz, 1H), 4.89 (s, 2H), 4.78 (ddd, *J* = 8.0, 6.7, 5.7 Hz, 1H), 4.73 (dd, *J* = 5.3, 1.4 Hz, 1H), 4.32 (td, *J* = 8.5, 6.0 Hz, 1H), 4.22 (ddt, *J* = 7.2, 5.6, 1.9 Hz, 1H), 4.02 – 3.97 (m, 1H), 3.91 – 3.81 (m, 3H), 3.68 (s, 3H), 3.11 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.07 – 2.98 (m, 2H), 2.93 (dd, *J* = 14.8, 5.8 Hz, 1H), 1.71 (s, 3H), 1.70 (s, 3H), 1.54 (ddd, *J* = 13.5, s7.4, 5.8 Hz, 1H), 1.48 – 1.37 (m, 2H), 1.03 – 1.00 (m, 21H), 0.98 – 0.97 (m, 21H), 0.95 – 0.91 (m, 21H), 0.80 (d, *J* = 6.4 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.7 (C_q), 170.8 (C_q), 167.9 (C_q), 167.7 (C_q), 165.4 (C_q), 153.2 (C_q), 149.1 (C_q), 135.7 (C_q), 133.9 (CH), 131.9 (C_q), 129.2 (CH), 128.5 (CH), 127.1 (CH), 123.4 (CH), 122.7 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 66.0 (CH), 61.8 (CH_2), 53.1 (CH), 53.0 (CH), 52.6 (CH_2), 52.3 (CH), 52.2 (CH_3), 51.7 (C_q), 40.2 (CH_2), 37.7 (CH_2), 34.8 (CH_2), 28.3 (CH_3), 27.8 (CH_3), 24.6 (CH), 22.6 (CH_3), 21.9 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.3 (CH), 11.9 (CH) (1 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3263, 2942, 2865, 1718, 1660, 1556, 1381, 1051, 881, 679 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1295 (100) $[M+Na]^+$, 1272 (2) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{67}H_{1100}N_7O_{11}Si_3$ $[M+H]^+$: 1272.7566 found: 1272.7537.



Benzyl [2-(4-{2-[(*S*)-3-({2*R*,3*R*,4*R*}-3,4-bis{[triisopropylsilyl]oxy}-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-2-(1,3-dioxoisoindolin-2- yl)propanamido]propan-2-yl}-1*H*-1,2,3-triazol-1-yl)acetyl]-*L*-phenylalanyl-*L*-leucinate (9e)

The general procedure **A** was followed using Phth-Ala-Tzl-Gly-Phe-Leu-OBn (**8e**) (74 mg, 0.10 mmol) and 1-iodo glycal **2a** (111 mg, 0.15 mmol) in 1,4-dioxane (1 mL). After 16 h, purification by column chromatography (*n*-hexane/EtOAc 3:2 → 2:3) yielded **9e** (68 mg, 50%).

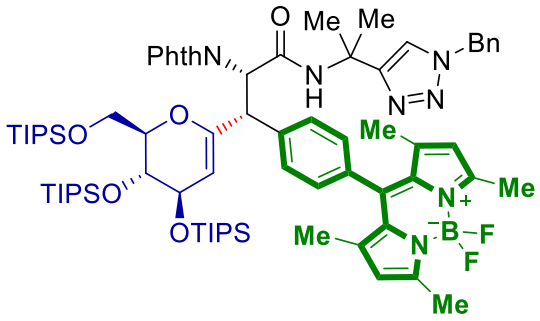
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 5.5 Hz, 2H), 7.66 (dd, *J* = 5.5 Hz, 2H), 7.54 (s, 1H), 7.40 – 7.28 (m, 5H), 7.24 – 7.14 (m, 3H), 7.06 (d, *J* = 7.1 Hz, 2H), 7.01 (s, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 6.22 (d, *J* = 8.1 Hz, 1H), 5.12 (s, 2H), 5.01 (dd, *J* = 8.2, 5.8 Hz, 1H), 4.92 (d, *J* = 16.8 Hz, 1H), 4.87 (d, *J* = 16.8 Hz, 1H), 4.75 (d, *J* = 5.1 Hz, 1H), 4.65 – 4.42 (m, 2H), 4.25 (t, *J* = 6.2 Hz, 1H), 4.02 (s, 1H), 3.95 – 3.81 (m, 3H), 3.08 (dd, *J* = 14.8, 8.3 Hz, 1H), 3.02 – 2.88 (m, 3H), 1.76 – 1.68 (s, 6H), 1.61 – 1.51 (m, 1H), 1.51 – 1.40 (m, 2H), 1.06 – 1.02 (m, 21H), 1.00 (s, 21H), 0.96 – 0.91 (m, 21H), 0.88 – 0.78 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1 (C_q), 169.7 (C_q), 167.8 (C_q), 167.7 (C_q), 165.2 (C_q), 153.2 (C_q), 149.1 (C_q), 136.0 (C_q), 135.3 (C_q), 133.9 (CH), 131.9 (C_q), 129.2 (CH), 128.6 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.0 (CH), 123.4 (CH), 122.5 (CH), 99.2 (CH), 81.4 (CH), 69.1 (CH), 67.0 (CH_2), 66.0 (CH), 61.8 (CH_2), 54.9 (CH), 53.0 (CH), 52.6 (CH_2), 51.7 (C_q), 51.0 (CH), 41.2 (CH_2), 37.6 (CH_2), 34.9 (CH_2), 28.4 (CH_3), 27.7 (CH_3), 24.7 (CH), 22.6 (CH_3), 21.8 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3), 12.3 (CH), 11.9 (CH). (2 CH_3 and 1 CH resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

IR (ATR): $\tilde{\nu}$ = 3307, 2942, 2866, 1716, 1651, 1463, 1383, 881, 730, 680 cm^{-1}.

MS (ESI) *m/z* (relative intensity): 1371 (100) $[M+Na]^+$, 1348 (2) $[M+H]^+$.

HR-MS (ESI): *m/z* calcd for $C_{73}H_{114}N_7O_{11}Si_3$ $[M+H]^+$: 1348.7879 found: 1348.7852.



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-((2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl)-3-[4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (11a)

The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**10a**) (74 mg, 0.10 mmol) and 1-iodo glycal **2a** (110 mg, 0.15 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:1) yielded **11a** (111 mg, 84%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.60 (m, 4H), 7.45 (d, J = 7.8 Hz, 2H), 7.41 (s, 1H), 7.35 – 7.28 (m, 3H), 7.20 (dd, J = 6.8, 2.7 Hz, 2H), 7.05 – 6.93 (m, 3H), 5.82 (s, 2H), 5.46 (d, J = 11.7 Hz, 1H), 5.41 (s, 2H), 5.01 (d, J = 5.0 Hz, 1H), 4.67 (d, J = 11.7 Hz, 1H), 4.40 (t, J = 7.1 Hz, 1H), 4.25 – 4.21 (m, 1H), 4.16 (t, J = 10.5, 7.1 Hz, 1H), 4.03 (d, J = 5.0 Hz, 1H), 3.93 (t, J = 10.5, 7.1 Hz, 1H), 2.48 (s, 6H), 1.75 (s, 3H), 1.71 (s, 3H), 1.11 – 1.05 (m, 42H), 1.02 – 0.98 (m, 21H), 0.86 (s, 6H).

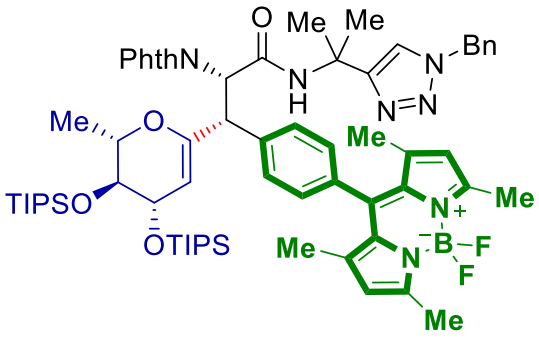
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 155.2 (C_q), 153.0 (C_q), 151.0 (C_q), 142.8 (C_q), 141.5 (C_q), 140.4 (C_q), 134.9 (C_q), 134.0 (CH), 133.6 (C_q), 131.3 (C_q), 131.2 (C_q), 129.2 (CH), 128.9 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 123.4 (CH), 121.0 (CH), 120.7 (CH), 99.8 (CH), 80.9 (CH), 69.6 (CH), 66.8 (CH), 61.0 (CH_2), 56.0 (CH), 53.9 (CH_2), 52.0 (C_q), 49.2 (CH), 28.5 (CH_3), 27.9 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1(CH_3), 14.5 (CH_3), 13.9 (CH_3), 12.5 (CH), 12.4 (CH), 12.1 (CH). (2 CH_3 resonances of the TIPS groups are missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

^{19}F NMR (282 MHz, $CDCl_3$): δ = -146.41 (dd, $J_{B\text{-}F}$ = 68.8, 32.4 Hz).

IR (ATR): $\tilde{\nu}$ = 2946, 1717, 1544, 1510, 1382, 1214, 984, 883, 751, 668 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1374 (100) $[M+Na]^+$, 1352 (55) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{75}H_{108}BF_2N_7NaO_7Si_3^+$ $[M+Na]^+$: 1374.7584, found: 1374.7546.



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl]-2-(1,3-dioxoisoindolin-2-yl)-3-{(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl}propenamide (11b)

The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**10b**) (37 mg, 0.05 mmol) and 1-iodo glycal **2b** (43 mg, 0.08 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:1) yielded **11b** (55 mg, 93%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.68 (m, 1H), 7.68 – 7.58 (m, 3H), 7.57 – 7.47 (m, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.25 (m, 5H), 7.19 (s, 1H), 7.02 (d, *J* = 7.7 Hz, 2H), 5.80 (s, 2H), 5.58 (d, *J* = 11.2 Hz, 1H), 5.45 (s, 2H), 5.29 (d, *J* = 4.3 Hz, 1H), 4.59 (d, *J* = 11.2 Hz, 1H), 4.50 (d, *J* = 7.4 Hz, 1H), 4.12 (d, *J* = 4.3 Hz, 1H), 3.88 (s, 1H), 2.47 (s, 6H), 1.75 (s, 3H), 1.72 (s, 3H), 1.18 – 0.92 (m, 48H), 0.75 (s, 3H).

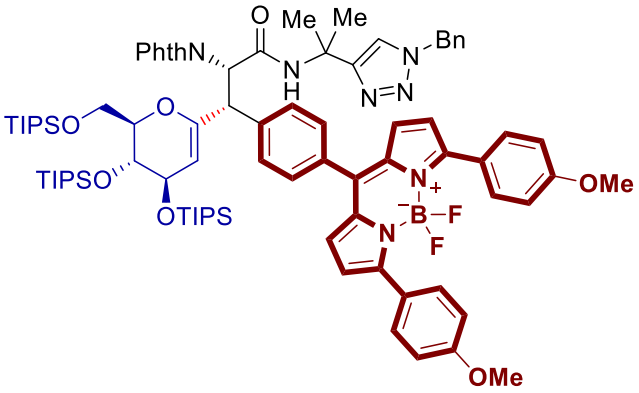
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.5 (C_q), 166.5 (C_q), 155.3 (C_q), 152.9 (C_q), 150.2 (C_q), 142.7 (C_q), 141.2 (C_q), 139.5 (C_q), 135.0 (C_q), 133.8 (CH), 133.7 (C_q), 131.5 (C_q), 131.2 (C_q), 129.5 (CH), 128.4 (CH), 128.0 (CH), 127.4 (CH), 123.4 (CH), 123.1 (CH), 121.1 (CH), 121.0 (CH), 101.7 (CH), 75.7 (CH), 73.7 (CH), 66.8 (CH), 53.9 (CH_2), 52.7 (CH), 52.50 (C_q), 51.9 (CH), 28.9 (CH_3), 27.6 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 15.0 (CH_3), 14.5 (CH_3), 13.4 (CH_3), 12.5 (CH), 12.4 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).-

^{19}F NMR (377 MHz, $CDCl_3$): δ = -146.42 (dd, $J_{B\text{-}F}$ = 65.6, 30.6 Hz).

IR (ATR): $\tilde{\nu}$ = 2866, 1715, 1545, 1511, 1214, 983, 883, 751, 668 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1202 (100) $[M+Na]^+$, 1180 (30) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{66}H_{88}BF_2N_7NaO_6Si_2^+$ $[M+Na]^+$ 1202.6299, found: 1202.6285.



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-3- {4-[5,5-difluoro-3,7-bis(4-methoxyphenyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl]phenyl}-2-(1,3-dioxoisoindolin-2-yl)propenamide (11c).

The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**10c**) (45 mg, 0.10 mmol) and 1-iodo glycal **2a** (55 mg, 0.08 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:3) yielded **11c** (43 mg, 57%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.8 Hz, 4H), 7.68 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.62 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.48 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.26 – 7.23 (m, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.99 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 4H), 6.42 (d, *J* = 4.3 Hz, 2H), 6.18 (d, *J* = 4.3 Hz, 2H), 5.57 (d, *J* = 11.4 Hz, 1H), 5.45 (s, 2H), 5.14 (d, *J* = 5.2 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.46 (t, *J* = 6.5 Hz, 1H), 4.18 (t, *J* = 1.9 Hz, 1H), 4.11 (d, *J* = 6.5 Hz, 2H), 4.04 (m, 1H), 3.84 (s, 6H), 1.79 (s, 3H), 1.76 (s, 3H), 1.14 – 1.07 (m, 42H), 1.04 – 0.87 (m, 21H).

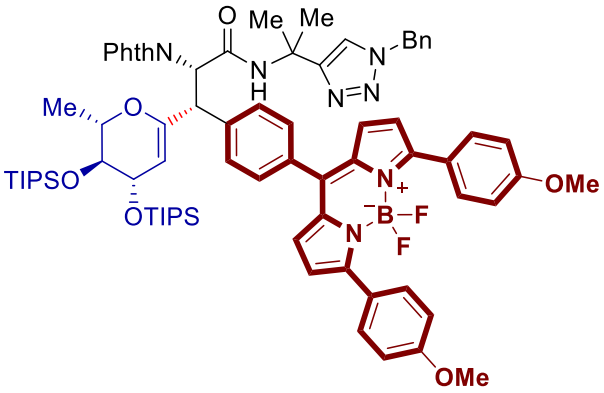
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 160.7 (C_q), 158.0 (C_q), 153.1 (C_q), 150.4 (C_q), 142.1 (C_q), 140.8 (C_q), 136.0 (C_q), 134.9 (C_q), 134.0 (CH), 133.0 (C_q), 131.1 (C_q), 131.01 (C_q), 131.0 (CH), 130.0 (CH), 129.9 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 125.1 (C_q), 123.2 (CH), 120.9 (CH), 120.1 (CH), 113.7 (CH), 99.6 (CH), 81.1 (CH), 69.5 (CH), 66.6 (CH), 61.2 (CH_2), 55.3 (CH_3), 53.9 (CH_2), 52.1 (C_q), 50.2 (CH), 28.5 (CH_3), 28.0 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.05 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

^{19}F NMR (377 MHz, $CDCl_3$): δ = -133.08 (dd, $J_{B\text{-}F}$ = 64.8, 32.1 Hz).

IR (ATR): $\tilde{\nu}$ = 2923, 1717, 1550, 1466, 1214, 1142, 1071, 749, 668 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1530 (100) $[M+Na]^+$, 1508 (40) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{85}H_{112}BF_2N_7NaO_9Si_3^+$ $[M+Na]^+$: 1530.7796, found: 1530.7785.



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-{4-[5,5-difluoro-3,7-bis(4-methoxyphenyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl]phenyl}-2-(1,3-dioxoisoindolin-2-yl)-3-{(2*S*,3*S*,4*S*)-2-methyl-3,4-bis[(triisopropylsilyl)oxy]-3,4-dihydro-2*H*-pyran-6-yl}propenamide (11d)

The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**10d**) (40 mg, 0.045 mmol) and 1-iodo glycal **2b** (38 mg, 0.067 mmol). After 10 h, purification by column chromatography (*n*-hexane/EtOAc 1:3) yielded **11d** (58 mg, 97%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.5 Hz, 4H), 7.73 – 7.67 (m, 2H), 7.67 – 7.60 (m, 2H), 7.56 (s, 1H), 7.46 – 7.22 (m, 9H), 7.09 (s, 1H), 6.93 (d, J = 8.5 Hz, 4H), 6.45 (d, J = 4.4 Hz, 2H), 6.22 (d, J = 4.4 Hz, 2H), 5.54 (d, J = 11.2 Hz, 1H), 5.48 (s, 2H), 5.27 (d, J = 4.7 Hz, 1H), 4.62 (d, J = 11.2 Hz, 1H), 4.46 (d, J = 7.4 Hz, 1H), 4.19 (d, J = 4.7 Hz, 1H), 3.91 (s, 1H), 3.84 (s, 6H), 1.78 (s, 3H), 1.76 (s, 3H), 1.18 (d, J = 6.9 Hz, 3H), 1.10 – 0.98 (m, 42H).

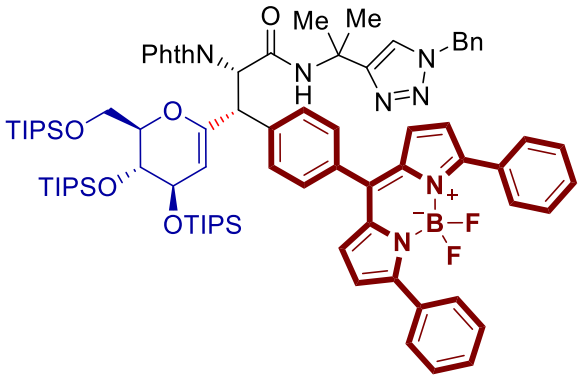
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 166.3 (C_q), 160.7 (C_q), 158.1 (C_q), 153.0 (C_q), 150.5 (C_q), 141.9 (C_q), 140.4 (C_q), 136.0 (C_q), 135.0 (C_q), 134.0 (CH), 133.2 (C_q), 131.3 (C_q), 131.0 (CH), 129.9 (CH), 129.8 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 125.1 (C_q), 123.2 (CH), 121.0 (CH), 120.2 (CH), 113.8 (CH), 100.8 (CH), 75.9 (CH), 73.6 (CH), 67.1 (CH), 55.2 (CH_3), 54.0 (CH_2), 53.6 (CH), 52.4(C_q), 50.9 (CH), 28.72 (CH_3), 27.7 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 15.6 (CH_3), 12.5 (CH), 12.5 (CH). (1 CH_3 resonance of the TIPS groups is missing due to overlap, the overlap was verified by analysis of the HSQC spectrum).

^{19}F NMR (377 MHz, $CDCl_3$): δ = -133.10 (dd, $J_{B\text{-}F}$ = 64.9, 32.3 Hz).

IR (ATR): $\tilde{\nu}$ = 2940, 1715, 1547, 1464, 1255, 1137, 1057, 883, 794, 718, 681 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 1358 (100) $[M+Na]^+$, 1336 (35) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{76}H_{92}BF_2N_7NaO_8Si_2^+$ $[M+Na]^+$:1358.6512, found: 1358.6506.



(2*S*,3*S*)-*N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-3-[(2*R*,3*R*,4*R*)-3,4-bis[(triisopropylsilyl)oxy]-2-{[(triisopropylsilyl)oxy]methyl}-3,4-dihydro-2*H*-pyran-6-yl]-3-[4-(5,5-difluoro-3,7-diphenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)phenyl]-2-(1,3-dioxoisoindolin-2-yl)propenamide (11e)

The general procedure **A** was followed using Phth-Ala^{BODYPY}-TAM^{Bn} (**10e**) (56 mg, 0.067 mmol) and 1-iodo glycal **2a** (74 mg, 0.10 mmol). After 10 h, purification by column chromatography (n-hexane/EtOAc 1:1) yielded **11e** (70 mg, 72%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 – 7.78 (m, 4H), 7.72 – 7.67 (m, 2H), 7.66 – 7.60 (m, 2H), 7.49 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.37 (m, 7H), 7.35 – 7.30 (m, 3H), 7.26 – 7.19 (m, 3H), 7.01 (s, 1H), 6.46 (d, *J* = 4.3 Hz, 2H), 6.25 (d, *J* = 4.3 Hz, 2H), 5.60 (d, *J* = 11.3 Hz, 1H), 5.45 (s, 2H), 5.17 (d, *J* = 5.2 Hz, 1H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.48 (d, *J* = 6.7 Hz, 1H), 4.19 (s, 1H), 4.13 (d, *J* = 6.7 Hz, 2H), 4.06 (d, *J* = 5.2 Hz, 1H), 1.81 (s, 3H), 1.77 (s, 3H), 1.19 – 1.05 (m, 42H), 0.98 – 0.91 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 166.0 (C_q), 158.6 (C_q), 153.1 (C_q), 150.4 (C_q), 143.8 (C_q), 141.1 (C_q), 136.1 (C_q), 134.9 (C_q), 134.0 (CH), 132.8 (C_q), 132.5 (C_q), 131.1 (C_q), 130.3 (CH), 130.0 (CH), 129.4 (CH), 129.4 (CH), 129.3 (CH), 128.9 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 123.2 (CH), 120.9 (CH), 120.5 (CH), 99.6 (CH), 81.1 (CH), 69.4 (CH), 66.6 (CH), 61.2 (CH_2), 55.2 (CH), 53.9 (CH_2), 52.1 (C_q), 50.2 (CH), 28.5 (CH_3), 28.0 (CH_3), 18.3 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.1 (CH_3), 18.03 (CH_3), 18.0 (CH_3), 12.4 (CH), 12.3 (CH), 12.1 (CH).

^{19}F NMR (377 MHz, $CDCl_3$): δ = -132.60 (dd, $J_{B\text{-}F}$ = 63.9, 32.1 Hz).

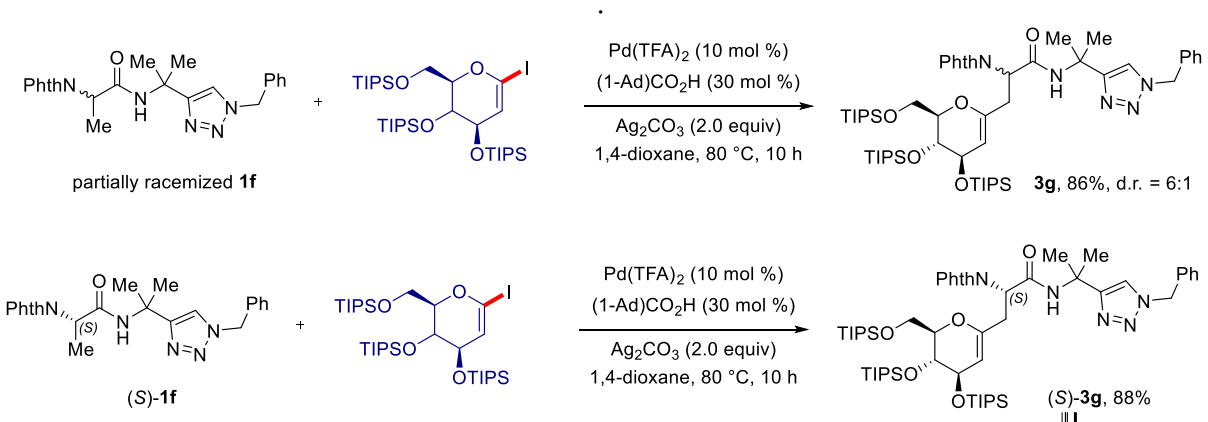
IR (ATR): $\tilde{\nu}$ = 2941, 1717, 1546, 1467, 1274, 1068, 998, 882,718, 683 cm^{-1}.

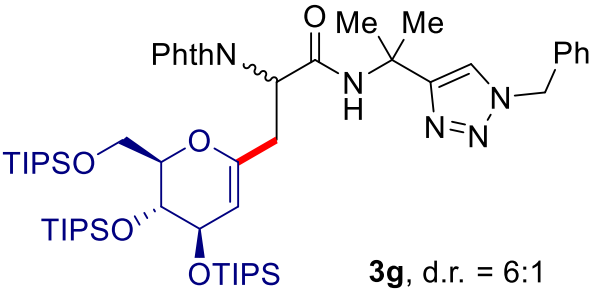
MS (ESI) *m*/*z* (relative intensity): 1470 (100) $[M+Na]^+$, 1448 (50) $[M+H]^+$.

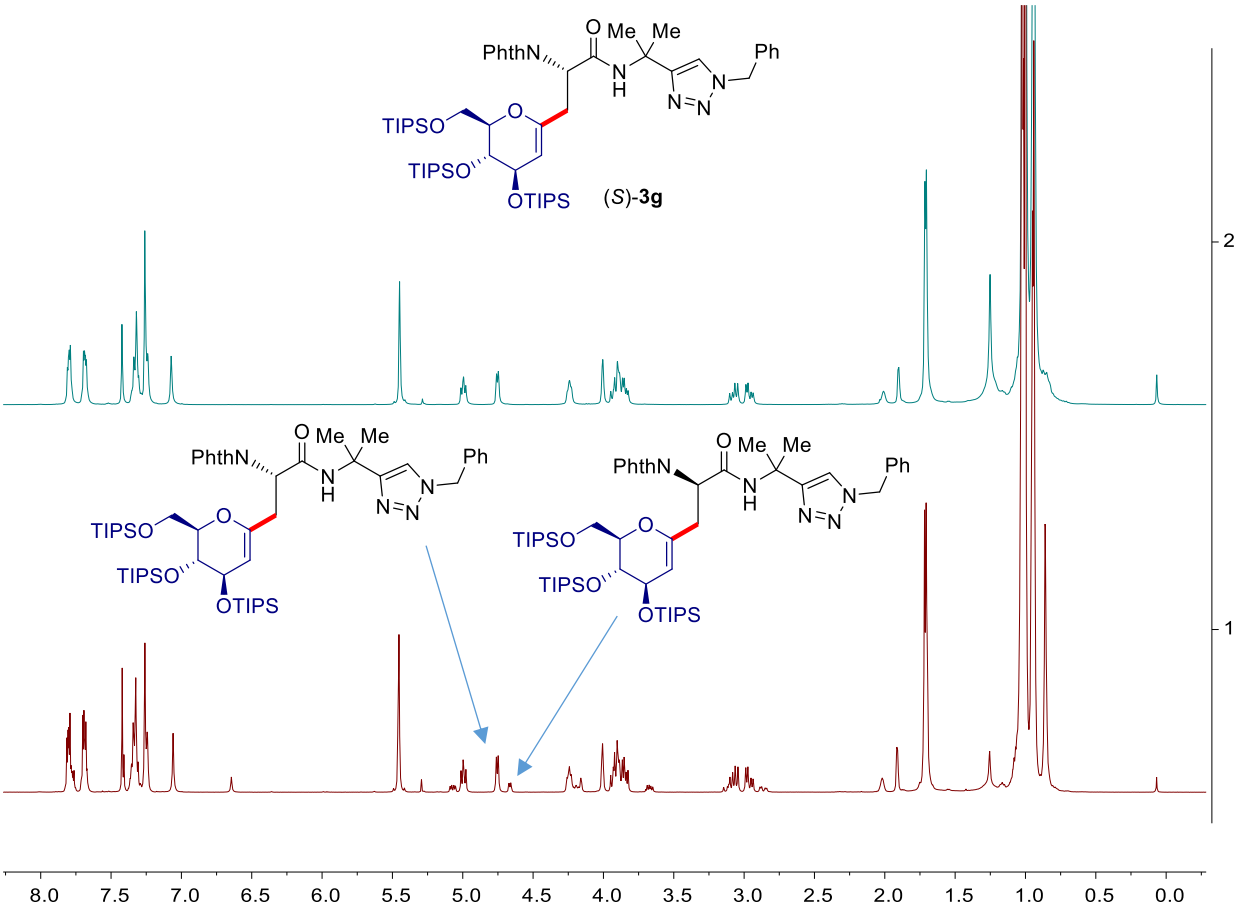
HR-MS (ESI): *m*/*z* calcd for $C_{83}H_{109}BF_2N_7O_7Si_3^+$ $[M+H]^+$: 1448.7765, found: 1448.7748.

Studies on Potential Racemization

Substrates (*S*)-**1f**, partially racemized **1f** were subjected to the C–H glycosylation reaction under the optimized reaction conditions. ^{1}H NMR analysis of the obtained products showed that no racemization occurred during the C–H glycosylation process.

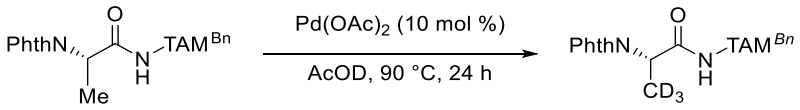





PhthN
O
Me
Me
N
H
Ph
N
N=N
TIPSO
O
TIPSO
OTIPS
(S)-3g
2
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

Mechanistic Investigations

H/D Exchange

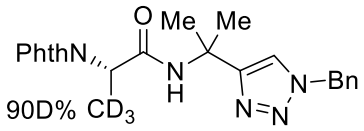


1f **[D_3]-1f,** 90D%

A solution of alanine substrate **1f** (417 mg, 1.0 mmol) and $Pd(OAc)_2$ (22 mg, 10 mol%) in deuterated acetic acid (AcOD) (3.0 mL) was stirred at 90 ºC for 24 h. Then, the reaction was filtrated and concentrated. This procedure was repeated twice. The product was purified by column chromatography (*n*-hexane/EtOAc 1:1), yielding deuterated alanine substrate **[D]-1f** in 94% yield with 90D%. The deuterium incorporation was determined by ^{1}H NMR spectroscopy.

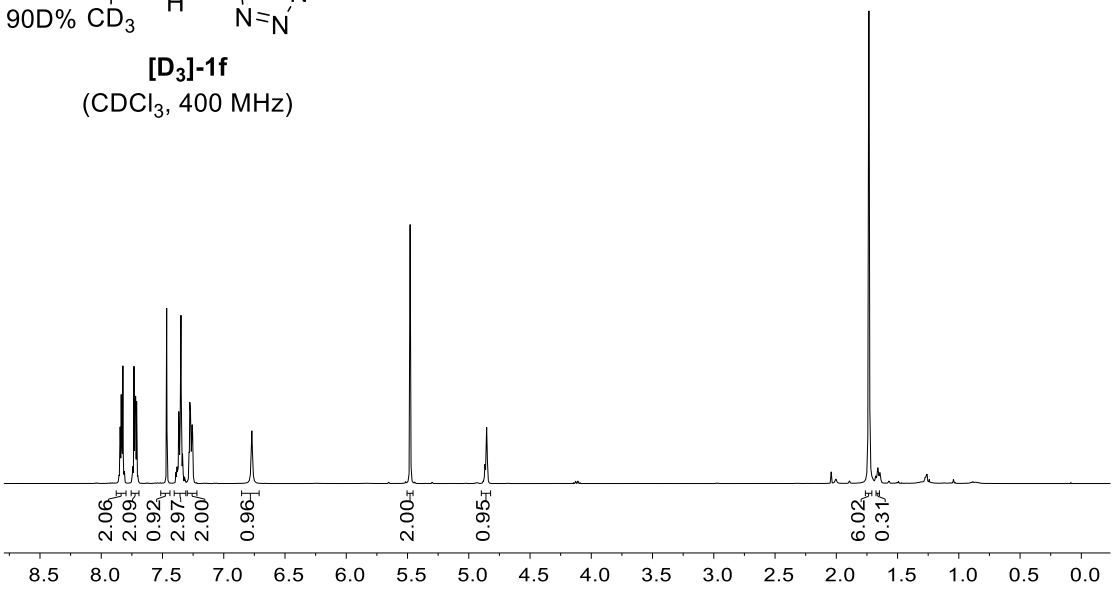
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.47 (s, 1H), 7.40 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 6.77 (s, 1H), 5.48 (s, 2H), 4.85 (s, 1H), 1.73 (s, 6H).

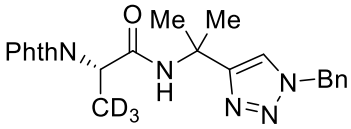
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.1 (C_q), 167.7 (C_q), 153.4 (C_q), 134.6 (C_q), 134.1 (CH), 131.8 (C_q), 129.0 (CH), 128.5 (CH), 128.0 (CH), 123.4 (CH), 120.3 (CH), 54.0 (CH_2), 51.9 (C_q), 49.5 (CH), 27.9 (CH_3), 27.8 (CH_3).



[D_3]-1f

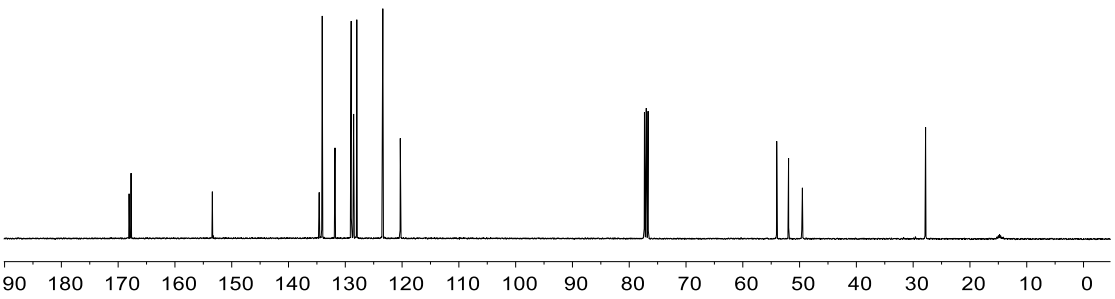
($CDCl_3$, 400 MHz)



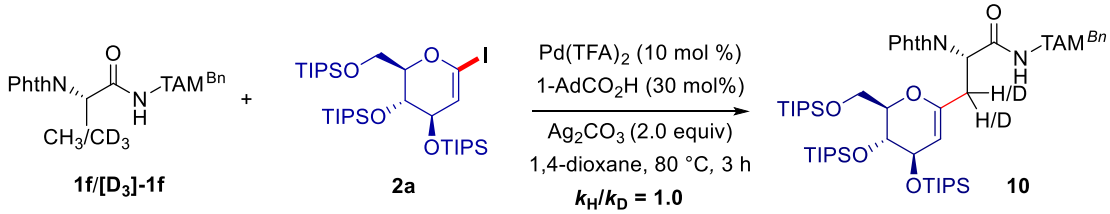


[D_3]-1f

($CDCl_3$, 101 MHz)

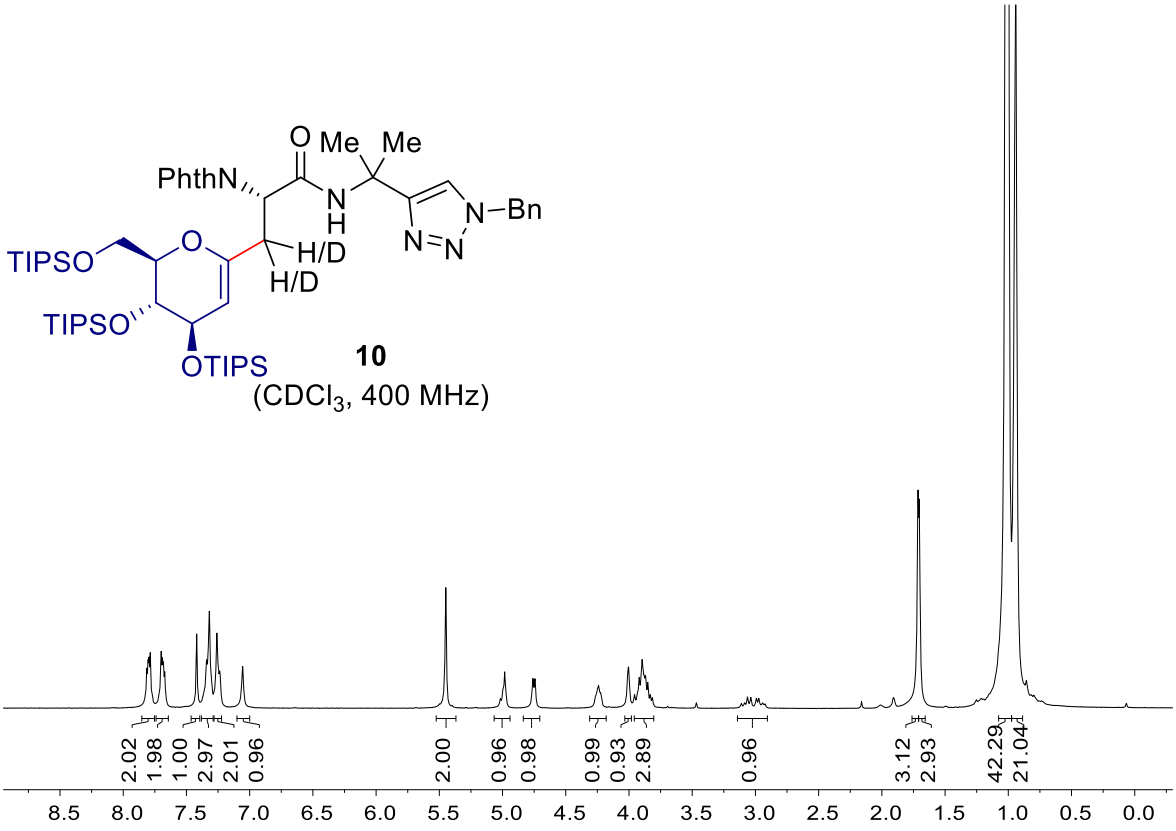


Kinetic Isotope Effect



Deuterated substrate **[D_3]-1f** (21 mg, 0.05 mmol) and non-deuterated substrate **1f** (21 mg, 0.05 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol %), Ag_2CO_3 (55 mg, 0.1 mmol), and (1-Ad)CO_2H (5.4 mg, 30 mol %) were placed in an oven-dried Schlenk tube. The mixture was evacuated and purged with N_2 three times. Then, a solution of 1-iodo glycal **2a** (110 mg, 0.15 mmol) in 1,4-dioxane (0.5 mL) was added. The resulting reaction mixture was stirred at 80 ºC for 3 h. After cooling to ambient temperature, the mixture was diluted with CH_2Cl_2 (10 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel isolated the product **10** in 87%yield. A k_H/k_D = 1.0 was determined by ^{1}H NMR spectroscopy.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (dd, J = 5.5, 3.1 Hz, 2H), 7.69 (dd, J = 5.5, 3.1 Hz, 2H), 7.42 (s, 1H), 7.37 – 7.28 (m, 3H), 7.28 – 7.21 (m, 2H), 7.06 (s, 1H), 5.45 (s, 2H), 5.01 – 4.95 (m, 1H), 4.75 (d, J = 5.2 Hz, 1H), 4.24 (t, J = 5.4 Hz, 1H), 4.11 – 3.96 (m, 1H), 3.98 – 3.76 (m, 3H), 3.14 – 2.89 (m, 1H), 1.71 (s, 3H), 1.70 (s, 3H), 1.01 (m, 42H), 0.94 (m, 21H).



Computational Data

All calculations were performed using Gaussian 16, Revision A.03 package.[4] All structures were optimized in gas phase at the ωB97X-D[5] level of theory. The basis set BS(I) was used for the geometry optimizations and frequency calculations. BS(I) consists of the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LANL2DZ) for the Pd, Ag, and I atoms,[6] supplemented with one polarization shell per atom: Pd (f = 1.472), Ag (f = 1.611) and I (d = 0.289),[7] whereas all-electron basis set 6-31G(d) was used for all other atoms. Analytical frequency calculations were carried out at the same level of theory in order to identify all stationary points as either intermediates (no imaginary frequencies) or transition states (only one imaginary frequency). The Gibbs free energy was then refined through single point calculations at the same functional with a larger basis set BS(II): SDD[8] for the Pd, Ag, and I atoms and 6-311++g(d,p) on non-metallic centers.[9] This was carried out in the presence of solvent through the SMD[10] method with a dielectric constant of ε = 2.2099 that corresponds to 1,4-dioxane. All reported energies are free energies at a concentration of 1 M and a temperature of 298.15 K. All the 3D molecular structures of the species were generated by using the CYLview program.[11] Non-covalent interactions were localized and visualized through the use of the Multiwfn 3.7[12] and VMD 1.9.3 program.[13]

Table S2. Calculated electronic energies and Gibbs free energies for all structures in the present work (all in Hartree).

Structure	Electronic Energy	Gibbs Free Energy
I1	-4073.301109	-4072.433903
TS1-2	-4073.270692	-4072.407190
I2	-4073.313391	-4072.443994
TS2-3	-4073.289849	-4072.421870
I3	-4073.383054	-4072.513377
SI-1	-1974.861765	-1974.373880
SI-TS1-2	-1974.821533	-1974.336310
SI-2	-1974.864196	-1974.374450
I1'	-3517.966294	-3517.105769

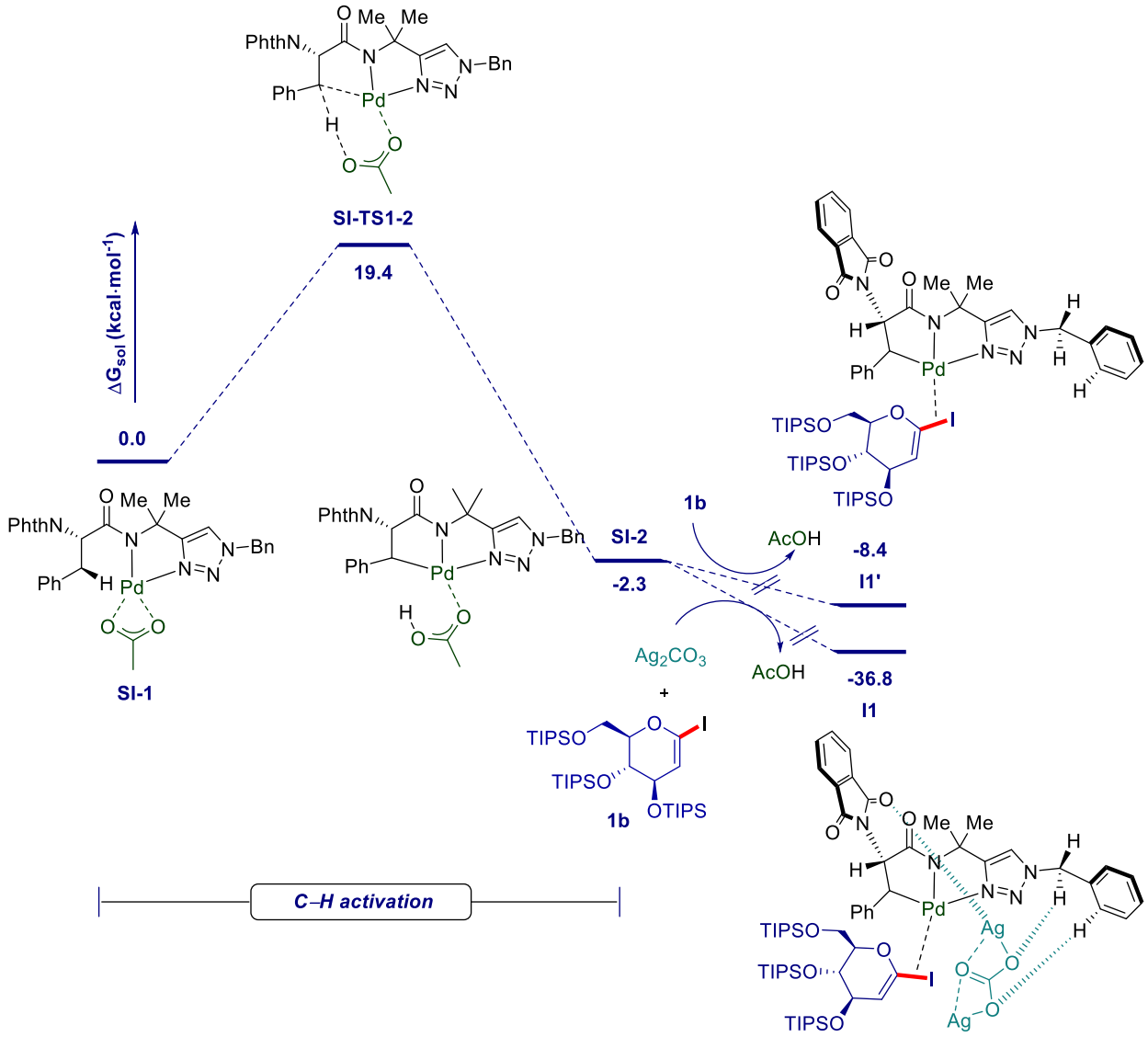


Figure S1. Relative Gibbs free energies in kcal·mol^{-1} for the C−H bond activation. (A similar barrier of 18.3 kcal·mol^{-1} is obtained by the benchmark calculation at the B3LYP-D3/6-311++G(d,p), SDD(Pd, I, Ag) + SMD(1,4-dioxane)// B3LYP-D3/6-31G(d), LANL2DZ(Pd, I, Ag) level of theory.)

The formation of complex **I1** from intermediate **SI-2** involves the exchange of coordinated acetic acid with Ag_2CO_3. Since the dissolution of Ag_2CO_3 from solid Ag_2CO_3, as employed in the experiments, can only be insufficiently described using standard DFT methods, this process was not calculated and dissolved Ag_2CO_3 was assumed in the calculations.

Cartesian coordinates of the optimized structures

I1

Lowest frequency = 10.35 cm^{-1}

Charge = 0, Multiplicity = 1

125

C	2.773618	6.900016	-10.454354
C	3.846067	6.688476	-9.579215
C	4.592705	5.515567	-9.731309
C	4.265976	4.574548	-10.702971
C	3.181126	4.789769	-11.547874
C	2.437253	5.960720	-11.422177
C	4.269699	7.718796	-8.574602
C	4.730393	8.995267	-9.287624
C	4.829466	10.234626	-8.394959
O	5.384085	11.249861	-8.806575
N	5.976632	8.795545	-10.005926
C	6.063095	8.822275	-11.412701
C	7.510022	8.652164	-11.728285
C	8.202863	8.564008	-10.526911
C	7.215672	8.666247	-9.418630
C	9.575602	8.405548	-10.487706
C	10.244040	8.337808	-11.713440
C	9.548326	8.426394	-12.921343
C	8.159729	8.586625	-12.946188
O	5.128198	8.957656	-12.160938
O	7.460737	8.625650	-8.221045
N	4.204409	10.042343	-7.214771
Pd	3.085156	8.349225	-7.003311
C	3.917652	11.200499	-6.341591
C	5.197570	11.910534	-5.868240

C	2.977793	12.188416	-7.060231
C	3.206062	10.643312	-5.141281
C	3.173038	11.057496	-3.832390
N	2.397144	10.152022	-3.206294
N	1.965742	9.219348	-4.040408
N	2.453633	9.520184	-5.219142
C	2.124835	10.008480	-1.770663
C	2.920522	10.990988	-0.950838
C	4.300478	10.807078	-0.807457
C	5.040391	11.725921	-0.070612
C	4.414611	12.818265	0.529280
C	3.041663	12.999034	0.387832
C	2.296591	12.087414	-0.356561
H	4.003451	9.257215	-10.063731
H	3.663517	11.861935	-3.312150
H	7.608507	8.658704	-13.877744
H	10.097548	8.371153	-13.856085
H	11.322512	8.215414	-11.728511
H	10.105616	8.340173	-9.543347
H	1.049293	10.138006	-1.621814
H	2.405198	8.983205	-1.518902
H	2.728045	13.024970	-6.398883
H	3.466696	12.577373	-7.956534
H	2.047231	11.686670	-7.346288
H	4.933511	12.804652	-5.290852
H	5.782043	11.248710	-5.219703
H	5.786465	12.218193	-6.732463
H	1.224550	12.229896	-0.473426
H	2.550547	13.848728	0.852792
H	4.998197	13.529982	1.106246

H	6.111980	11.586121	0.033774
H	4.773327	9.955341	-1.299641
H	5.440179	5.339311	-9.073365
H	4.861479	3.671244	-10.798998
H	2.922399	4.055861	-12.305232
H	1.597904	6.148848	-12.085235
H	2.195762	7.816285	-10.373991
H	5.099315	7.312262	-7.982773
C	5.328477	8.368642	-3.701953
O	5.046628	7.545798	-4.689312
O	6.210576	9.269779	-3.879208
Ag	3.159833	6.809502	-3.523999
Ag	6.477806	8.750637	-6.113197
O	4.668361	8.243068	-2.598743
C	-0.797408	7.482249	-6.120398
C	0.137347	8.071063	-7.191113
C	1.310952	7.155013	-7.493619
C	1.913376	6.514933	-6.433995
C	-0.069450	6.573284	-5.112563
H	1.433925	6.799769	-8.508499
I	3.085391	4.727624	-6.556034
O	1.378307	6.661647	-5.187698
H	-0.298070	6.927736	-4.107468
H	-1.535403	6.873932	-6.655191
H	0.516970	8.995227	-6.739604
C	-0.456797	5.100481	-5.263883
H	0.067028	4.507789	-4.503402
H	-0.121600	4.743293	-6.249256
O	-1.415993	8.558862	-5.463361
O	-0.591410	8.331603	-8.360940

O	-1.846505	4.977037	-5.112472
Si	-2.779402	3.987161	-6.106493
Si	-3.060627	8.680531	-5.139522
Si	-0.611654	9.859534	-9.078366
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H	-3.065062	11.160106	-5.447879
H	-4.361512	10.643498	-4.353285
H	-2.688593	10.714780	-3.778771
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H	-4.624453	7.529380	-3.579325
H	-3.202132	6.519423	-3.912862
H	-3.080788	7.883470	-2.787053
C	-4.024214	8.251600	-6.696429
H	-5.090834	8.469738	-6.566576
H	-3.659646	8.830596	-7.552389
H	-3.935964	7.190765	-6.955792
C	-4.541010	4.302746	-5.564061
H	-4.670281	4.062623	-4.503194
H	-4.818584	5.353146	-5.703230
H	-5.245023	3.688956	-6.137532
C	-2.509525	4.460926	-7.906869
H	-2.782331	5.502319	-8.111647
H	-1.466815	4.327385	-8.218715
H	-3.123069	3.824997	-8.556507
C	-2.276543	2.198239	-5.843981
H	-2.864872	1.525178	-6.478618
H	-1.219586	2.040884	-6.089554
H	-2.426965	1.895676	-4.801877
C	-1.156501	11.134345	-7.812827
H	-2.212167	10.987405	-7.560017

H	-0.584310	11.069452	-6.880738
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C	-1.864250	9.703054	-10.458992
H	-1.959030	10.645940	-11.009930
H	-1.567300	8.926345	-11.172009
H	-2.853071	9.440111	-10.067474
C	1.089922	10.293561	-9.746391
H	1.179049	11.371497	-9.925477
H	1.880466	10.018221	-9.037459
H	1.291987	9.784518	-10.695574

TS1-2

Lowest frequency = -117.94 cm^{-1}

Charge = 0, Multiplicity = 1

125

C	3.636685	5.965799	-9.477965
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C	5.293198	5.374284	-7.827946
C	5.297815	4.067767	-8.294921
C	4.463014	3.699171	-9.350370
C	3.643200	4.653761	-9.944918
C	4.450023	7.690468	-7.787720
C	4.055146	8.896579	-8.623060
C	3.718120	10.130558	-7.757496
O	3.490674	11.214959	-8.287122
N	5.076447	9.251831	-9.600879
C	4.939543	9.049323	-10.985691
C	6.169977	9.616476	-11.604029
C	6.964224	10.128664	-10.586092
C	6.264101	9.893394	-9.295668

C	8.184469	10.724785	-10.844151
C	8.587990	10.794999	-12.180599
C	7.789283	10.280838	-13.204651
C	6.558387	9.678105	-12.928849
O	4.001163	8.513828	-11.524882
O	6.665342	10.199195	-8.183896
N	3.705671	9.823589	-6.442427
Pd	3.379539	7.826775	-6.049169
C	3.165763	10.766228	-5.435652
C	3.980195	12.065239	-5.391500
C	1.681100	11.066488	-5.708442
C	3.308532	10.024402	-4.128193
C	3.888085	10.338541	-2.924061
N	3.843356	9.193681	-2.206795
N	3.276434	8.216998	-2.898746
N	2.948060	8.716160	-4.058782
C	4.487741	8.868197	-0.922959
C	5.236153	10.048796	-0.363739
C	6.470872	10.401331	-0.920227
C	7.161179	11.500878	-0.419431
C	6.634876	12.245575	0.635277
C	5.407469	11.893911	1.190112
C	4.708594	10.798990	0.687334
H	3.151691	8.688149	-9.203756
H	4.353478	11.234052	-2.548910
H	5.929777	9.274293	-13.715339
H	8.132373	10.351060	-14.232102
H	9.538657	11.256443	-12.428586
H	8.796863	11.120245	-10.040773
H	3.705737	8.524029	-0.241186

H	5.174151	8.048768	-1.163329
H	1.280217	11.737029	-4.940758
H	1.576077	11.544901	-6.685572
H	1.098608	10.140758	-5.690846
H	3.591559	12.731020	-4.612689
H	5.034662	11.857755	-5.166484
H	3.918855	12.569504	-6.356334
H	3.748462	10.523815	1.118116
H	4.993502	12.470033	2.012472
H	7.181720	13.099434	1.025235
H	8.118417	11.773605	-0.854018
H	6.863021	9.828795	-1.762709
H	5.928200	5.668233	-6.993795
H	5.955482	3.334001	-7.837834
H	4.464588	2.676936	-9.717097
H	3.010654	4.381910	-10.784929
H	3.022256	6.702455	-9.986288
H	5.418530	7.858088	-7.308351
C	6.427752	7.881460	-3.867801
O	6.049015	7.447637	-5.047514
O	6.951298	9.049821	-3.778975
Ag	4.585183	5.951730	-3.907482
Ag	6.434631	9.695115	-5.888386
O	6.210724	7.146359	-2.836986
C	-1.357411	8.132215	-6.967052
C	-0.178514	8.230261	-7.962109
C	0.870116	7.186258	-7.654476
C	1.212146	7.103383	-6.366599
C	-0.920629	7.612194	-5.582674
H	1.351325	6.623785	-8.441587

I	2.321327	5.204348	-5.609557
O	0.517108	7.691633	-5.394943
H	-1.315957	8.277702	-4.815329
H	-2.056867	7.407918	-7.401677
H	0.266975	9.226717	-7.802546
C	-1.370840	6.178158	-5.304210
H	-1.018301	5.877980	-4.309901
H	-0.906860	5.507401	-6.042248
O	-1.952439	9.401916	-6.865410
O	-0.645404	8.082075	-9.273822
O	-2.774186	6.124018	-5.363765
Si	-3.570822	4.823516	-6.078168
Si	-3.600211	9.661080	-6.639727
Si	-0.633713	9.315170	-10.426676
C	-3.848794	11.494410	-6.922958
H	-3.656030	11.777369	-7.962164
H	-4.876224	11.786165	-6.675196
H	-3.173965	12.076232	-6.285367
C	-4.112323	9.201108	-4.893436
H	-5.184348	9.382949	-4.747703
H	-3.917872	8.142040	-4.692402
H	-3.571033	9.799445	-4.151131
C	-4.566809	8.623869	-7.875180
H	-5.624537	8.912742	-7.878207
H	-4.180232	8.741971	-8.893384
H	-4.517745	7.559904	-7.621302
C	-5.388395	5.160258	-5.794103
H	-5.614661	5.179476	-4.722588
H	-5.689008	6.125311	-6.215652
H	-6.008914	4.383856	-6.256176

C	-3.139553	4.760539	-7.907206
H	-3.501283	5.643641	-8.445429
H	-2.056723	4.701006	-8.070387
H	-3.588143	3.877276	-8.377464
C	-3.026423	3.232454	-5.242226
H	-3.535728	2.365416	-5.678990
H	-1.947898	3.067980	-5.351020
H	-3.255705	3.252503	-4.171069
C	-1.768854	10.718170	-9.914663
H	-2.811840	10.390619	-9.849539
H	-1.481028	11.113821	-8.935295
H	-1.714978	11.536213	-10.643208
C	-1.260974	8.474310	-11.977437
H	-1.327974	9.186295	-12.808186
H	-0.591112	7.663392	-12.282677
H	-2.257322	8.047660	-11.818047
C	1.098228	9.982995	-10.662532
H	1.082352	10.779412	-11.417481
H	1.525787	10.425605	-9.754345
H	1.787362	9.212672	-11.024101

I2

Lowest frequency = 11.86 cm^{-1}

Charge = 0, Multiplicity = 1

125

C	2.046231	6.981680	-8.786635
C	3.179435	6.701734	-8.013581
C	3.602756	5.371561	-7.904517
C	2.918869	4.347679	-8.548493
C	1.797138	4.639274	-9.319517

C	1.366859	5.958833	-9.437996
C	3.987281	7.758908	-7.346474
C	4.281997	8.982196	-8.209388
C	4.758582	10.208813	-7.416611
O	5.354675	11.122998	-7.986188
N	5.158022	8.701136	-9.332159
C	4.674583	8.775656	-10.663303
C	5.851307	8.538146	-11.538572
C	6.962491	8.378717	-10.721146
C	6.518955	8.501909	-9.308848
C	8.222718	8.148769	-11.240894
C	8.333206	8.082949	-12.632658
C	7.215662	8.243688	-13.455279
C	5.947242	8.476501	-12.915936
O	3.529274	8.995625	-10.964478
O	7.247669	8.419270	-8.328380
N	4.395692	10.149539	-6.125369
Pd	3.360887	8.528701	-5.520968
C	4.524109	11.309311	-5.215339
C	5.985478	11.781606	-5.106433
C	3.618462	12.462339	-5.686629
C	4.076083	10.845649	-3.850877
C	4.378583	11.294165	-2.588215
N	3.717276	10.456606	-1.759584
N	3.040540	9.539548	-2.432570
N	3.253905	9.781128	-3.693810
C	3.734214	10.422157	-0.297522
C	5.085700	10.809587	0.254526
C	6.238379	10.146556	-0.181288
C	7.475445	10.511746	0.338814

C	7.571994	11.523635	1.293411
C	6.424974	12.181515	1.726298
C	5.183695	11.828135	1.201393
H	3.359837	9.293936	-8.703186
H	5.020512	12.078008	-2.221889
H	5.072528	8.605120	-13.544357
H	7.336674	8.187647	-14.532462
H	9.304106	7.904875	-13.083923
H	9.084172	8.027646	-10.592883
H	2.950072	11.088034	0.075694
H	3.465374	9.396557	-0.032016
H	3.705922	13.313229	-5.002703
H	3.924027	12.782330	-6.686579
H	2.575162	12.138971	-5.712580
H	6.034342	12.673773	-4.471316
H	6.603179	11.000368	-4.652913
H	6.363310	12.041999	-6.095694
H	4.288100	12.348549	1.533395
H	6.493585	12.973960	2.465580
H	8.541793	11.801775	1.695717
H	8.367983	10.000805	-0.008952
H	6.171301	9.364706	-0.940337
H	4.469637	5.141203	-7.290714
H	3.260896	3.322446	-8.445145
H	1.257767	3.843665	-9.824851
H	0.494919	6.193295	-10.040293
H	1.687525	8.002336	-8.878296
H	4.908541	7.330284	-6.943454
C	6.045124	8.190736	-3.685687
O	5.328572	7.720641	-4.687880

O	7.136040	8.806691	-3.946544
Ag	3.823524	6.823650	-2.603726
Ag	7.171703	8.674317	-6.119600
O	5.670152	8.011519	-2.476208
C	-1.017987	10.286249	-6.654500
C	0.202913	11.055074	-7.162782
C	1.450884	10.214642	-7.134447
C	1.647729	9.394416	-6.104630
C	-0.660160	9.168158	-5.654743
H	2.198272	10.424311	-7.879342
I	2.113201	6.187457	-4.653955
O	0.698646	9.219044	-5.167338
H	-1.268281	9.309410	-4.760675
H	-1.459883	9.816781	-7.539339
H	0.332137	11.908179	-6.476463
C	-0.904787	7.771289	-6.232736
H	-0.760928	7.025466	-5.445929
H	-0.154398	7.576042	-7.014410
O	-1.920432	11.199922	-6.075926
O	-0.085960	11.524938	-8.459493
O	-2.223033	7.694388	-6.729238
Si	-2.557245	6.963843	-8.203044
Si	-3.532123	11.342571	-6.518170
Si	0.716336	12.785236	-9.224709
C	-4.022116	13.067333	-5.972338
H	-3.454123	13.826193	-6.521760
H	-5.089074	13.249267	-6.147179
H	-3.827475	13.210280	-4.903882
C	-4.555943	10.035438	-5.643713
H	-5.596285	10.041893	-5.991602

H	-4.135693	9.041545	-5.836117
H	-4.562450	10.196079	-4.559562
C	-3.700416	11.165701	-8.383726
H	-4.616225	11.653877	-8.737515
H	-2.844545	11.624194	-8.892144
H	-3.747487	10.115793	-8.690858
C	-4.421653	7.026028	-8.362118
H	-4.898653	6.448981	-7.562549
H	-4.792495	8.054707	-8.296189
H	-4.750255	6.610367	-9.321786
C	-1.722773	7.934728	-9.584971
H	-2.217903	8.895231	-9.762742
H	-0.676183	8.158709	-9.348793
H	-1.738638	7.372484	-10.526686
C	-1.933160	5.193007	-8.174067
H	-2.075234	4.704588	-9.145852
H	-0.864638	5.147359	-7.934359
H	-2.471054	4.606840	-7.420564
C	0.927227	14.218364	-8.026208
H	-0.030747	14.499937	-7.574392
H	1.623457	13.974961	-7.215706
H	1.326677	15.096486	-8.547416
C	-0.417887	13.243275	-10.643747
H	0.008219	14.049291	-11.252218
H	-0.584598	12.380277	-11.297768
H	-1.393472	13.576945	-10.273441
C	2.388786	12.235720	-9.885702
H	2.775364	12.981071	-10.592245
H	3.150856	12.113754	-9.106754
H	2.306652	11.284423	-10.424585

TS2-3

Lowest frequency = -263.98 cm^{-1}

Charge = 0, Multiplicity = 1

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C	8.667172	9.537750	-8.146986
C	8.389411	10.114172	-6.898400
C	8.485025	9.337256	-5.734818
C	8.844541	7.997474	-5.823146
C	9.115171	7.430721	-7.065844
C	9.037872	8.205010	-8.226249
C	7.997191	11.513132	-6.732550
C	8.428144	12.602944	-7.703968
C	7.820697	13.980176	-7.351581
O	8.180889	14.952891	-8.015167
N	9.877529	12.725899	-7.801042
C	10.559680	12.341882	-8.985234
C	11.961272	12.802754	-8.819646
C	12.050644	13.471372	-7.606617
C	10.712962	13.444439	-6.966013
C	13.237501	14.027780	-7.165961
C	14.350522	13.889378	-7.999523
C	14.260373	13.217675	-9.221459
C	13.054125	12.659733	-9.653895
O	10.055413	11.767102	-9.916168
O	10.417106	13.965714	-5.902598
N	6.971383	13.964042	-6.309801
Pd	5.903095	12.279595	-5.771955
H	8.117277	12.359686	-8.721153
H	12.971306	12.137933	-10.601195

H	15.144306	13.129422	-9.845097
H	15.302711	14.311260	-7.694139
H	13.295734	14.549319	-6.216594
H	8.283780	9.800050	-4.769375
H	8.913956	7.397432	-4.921427
H	9.392616	6.382883	-7.134473
H	9.257457	7.761525	-9.192765
H	8.593583	10.133859	-9.050922
H	8.139077	11.807958	-5.689512
C	5.452255	10.083364	-10.023593
C	5.397545	11.614445	-9.998658
C	5.677659	12.144318	-8.615905
C	6.008196	11.334928	-7.594906
C	4.990318	9.516006	-8.680009
H	5.768937	13.217133	-8.517541
I	4.306916	10.286130	-4.831239
O	5.861476	10.004668	-7.657972
H	3.968981	9.862405	-8.460093
H	6.511238	9.808148	-10.141025
H	4.403185	11.919097	-10.354505
C	5.091463	7.996174	-8.530600
H	4.981703	7.775672	-7.459528
H	6.100125	7.685223	-8.826789
O	4.665331	9.594361	-11.072279
O	6.415459	12.105280	-10.851466
O	4.169246	7.276295	-9.301757
Si	2.514424	7.214280	-9.019572
Si	5.266140	8.669545	-12.340353
Si	6.481676	13.625987	-11.573831
C	6.155943	9.799159	-13.547035

H	6.921629	10.382941	-13.023383
H	6.642302	9.232426	-14.349848
H	5.456625	10.507720	-14.004096
C	3.747080	7.893030	-13.109214
H	4.003374	7.297467	-13.992856
H	3.255894	7.234447	-12.385286
H	3.024936	8.657878	-13.415241
C	6.450848	7.354480	-11.709942
H	6.838294	6.761156	-12.546926
H	7.314044	7.787768	-11.190561
H	5.931815	6.682980	-11.018543
C	1.941793	5.664836	-9.905590
H	2.139448	5.720009	-10.981738
H	2.456147	4.779919	-9.515980
H	0.863643	5.516394	-9.773155
C	2.201804	7.097115	-7.170866
H	2.701298	6.226315	-6.731384
H	2.556697	7.988913	-6.640272
H	1.127779	7.004379	-6.970041
C	1.650720	8.728132	-9.726565
H	0.590835	8.517918	-9.914357
H	1.700345	9.583279	-9.042392
H	2.119561	9.030583	-10.668544
C	5.736126	13.497289	-13.292442
H	6.321325	12.821185	-13.924513
H	4.712044	13.108137	-13.247950
H	5.701905	14.477373	-13.782969
C	8.295670	14.078712	-11.613990
H	8.910435	13.247014	-11.972376
H	8.474841	14.946582	-12.259634

H	8.625433	14.338185	-10.600651
C	5.545131	14.905538	-10.559604
H	6.125272	15.171907	-9.668470
H	5.413141	15.819716	-11.150778
H	4.548914	14.571241	-10.247045
C	6.421376	15.216495	-5.737776
C	7.465363	16.335282	-5.608410
C	5.216492	15.700449	-6.560892
C	5.984373	14.804113	-4.354576
C	6.061010	15.356009	-3.099187
N	5.584022	14.396103	-2.271090
N	5.226337	13.315861	-2.933327
N	5.469197	13.561385	-4.187711
C	5.571069	14.344313	-0.796129
C	6.190018	15.580386	-0.201714
C	7.582363	15.673892	-0.109208
C	8.161666	16.825068	0.416230
C	7.362541	17.881127	0.851691
C	5.976053	17.788536	0.760600
C	5.392144	16.639992	0.232384
H	6.437937	16.295287	-2.731155
H	4.528386	14.226758	-0.489786
H	6.134416	13.436643	-0.544595
H	4.760303	16.581760	-6.097742
H	5.548099	15.965310	-7.568707
H	4.457774	14.914039	-6.631807
H	7.031350	17.168530	-5.044839
H	8.354098	15.982953	-5.071931
H	7.775234	16.688465	-6.589740
H	4.309326	16.564775	0.161574

H	5.349703	18.607270	1.102226
H	7.820018	18.775399	1.265237
H	9.242958	16.895111	0.490576
H	8.186372	14.842736	-0.473109
C	7.973976	12.211159	-2.137503
O	8.043141	11.661843	-3.318643
O	8.592593	13.326928	-1.934052
Ag	5.920539	10.532998	-2.604648
Ag	9.235945	13.614337	-4.025320
O	7.252970	11.681013	-1.219956

I3

Lowest frequency = 11.27 cm^{-1}

Charge = 0, Multiplicity = 1

125

C	10.505680	9.639399	-8.405054
C	9.845584	10.155477	-7.287430
C	9.902478	9.468957	-6.075143
C	10.632039	8.285886	-5.976878
C	11.300531	7.780796	-7.088168
C	11.233022	8.458435	-8.304449
C	9.031486	11.434801	-7.364330
C	9.812953	12.637925	-7.933425
C	9.290400	14.061123	-7.591252
O	10.034438	14.993245	-7.889641
N	11.220619	12.602882	-7.580978
C	12.218539	12.460259	-8.571897
C	13.517218	12.604128	-7.863832
C	13.245942	12.859798	-6.525994
C	11.771185	12.886180	-6.353096

C	14.255492	13.042640	-5.599676
C	15.569807	12.959232	-6.067950
C	15.843088	12.702511	-7.413512
C	14.811906	12.519501	-8.339436
O	12.001050	12.258140	-9.740227
O	11.172967	13.120237	-5.312788
N	8.117952	14.146945	-6.927393
Pd	6.397819	13.017102	-7.305844
H	9.836966	12.563405	-9.025463
H	15.011658	12.321032	-9.386962
H	16.875323	12.645088	-7.744204
H	16.393881	13.096609	-5.375055
H	14.032065	13.242369	-4.557104
H	9.341663	9.848051	-5.222787
H	10.669648	7.756023	-5.029713
H	11.868612	6.858469	-7.010506
H	11.747908	8.067069	-9.176943
H	10.466809	10.167020	-9.355176
H	8.684734	11.652689	-6.348109
C	6.468621	10.026854	-10.290309
C	6.315526	11.544229	-10.208625
C	7.225468	12.078489	-9.108003
C	7.777009	11.194963	-8.181520
C	6.329843	9.418682	-8.895051
H	7.838090	12.908527	-9.442456
I	3.907752	11.922923	-7.468719
O	7.298105	9.984071	-7.987482
H	5.338336	9.657654	-8.501538
H	7.483628	9.814879	-10.668016
H	5.260728	11.740820	-9.994827

C	6.590513	7.912091	-8.800080
H	6.803781	7.693255	-7.744676
H	7.491801	7.665407	-9.373424
O	5.473587	9.494134	-11.109824
O	6.695717	12.117006	-11.433489
O	5.535160	7.129585	-9.282683
Si	4.012154	7.047833	-8.567573
Si	5.766569	8.656945	-12.539899
Si	5.814153	13.419097	-12.043032
C	6.279064	9.865274	-13.882971
H	7.139493	10.459844	-13.557814
H	6.549964	9.339849	-14.806595
H	5.467157	10.563291	-14.115964
C	4.138802	7.828899	-12.944331
H	4.159214	7.379508	-13.943836
H	3.924925	7.036067	-12.219580
H	3.314385	8.549648	-12.913501
C	7.119319	7.380485	-12.278849
H	7.285524	6.809829	-13.200450
H	8.078432	7.833453	-12.001352
H	6.824781	6.680749	-11.489532
C	3.438464	5.282307	-8.817271
H	3.442122	5.020890	-9.881530
H	4.090632	4.573938	-8.295605
H	2.417178	5.144643	-8.443390
C	4.173715	7.461776	-6.737055
H	4.874155	6.795133	-6.221586
H	4.518433	8.493627	-6.585420
H	3.199884	7.373026	-6.241500
C	2.818222	8.236558	-9.391238

H	1.869757	8.266153	-8.840887
H	3.214823	9.255485	-9.437200
H	2.602737	7.927332	-10.419324
C	6.662016	13.856734	-13.650462
H	7.708364	14.131730	-13.479924
H	6.645163	13.005439	-14.339682
H	6.166459	14.701246	-14.142800
C	5.882587	14.820960	-10.791258
H	6.914423	15.123078	-10.576169
H	5.341202	15.704127	-11.150534
H	5.419751	14.515552	-9.843603
C	4.028904	12.901236	-12.307601
H	3.531209	12.660181	-11.361178
H	3.458319	13.708360	-12.782457
H	3.964219	12.016151	-12.949342
C	7.747299	15.467900	-6.342498
C	8.894082	16.147741	-5.577862
C	7.192482	16.416613	-7.417830
C	6.678878	15.100298	-5.350537
C	6.405460	15.390621	-4.037131
N	5.377465	14.570298	-3.709770
N	5.012592	13.814512	-4.722399
N	5.798214	14.137942	-5.710112
C	4.776117	14.293854	-2.390524
C	5.398830	15.144992	-1.317470
C	6.613319	14.751182	-0.746592
C	7.206609	15.547930	0.228305
C	6.595992	16.731959	0.638947
C	5.386354	17.124523	0.071595
C	4.791119	16.332281	-0.906601

H	6.863640	16.051025	-3.320550
H	3.703389	14.480436	-2.484529
H	4.951031	13.222921	-2.227614
H	6.872539	17.363663	-6.970000
H	7.975011	16.616462	-8.154172
H	6.333093	15.966737	-7.925508
H	8.495916	17.007921	-5.028217
H	9.346732	15.460808	-4.852369
H	9.669129	16.487966	-6.260564
H	3.845776	16.636314	-1.350439
H	4.905480	18.044293	0.391201
H	7.061270	17.347576	1.403533
H	8.148242	15.239275	0.672989
H	7.081251	13.831656	-1.097936
C	6.927651	11.711697	-3.400406
O	7.373803	11.326572	-4.570765
O	7.657632	12.514974	-2.699693
Ag	5.110697	10.843474	-5.163574
Ag	9.198494	12.898801	-4.229062
O	5.771503	11.338827	-3.010432

SI-1

Lowest frequency = 3.43 cm^{-1}

Charge = 0, Multiplicity = 1

71

C	5.461626	4.985697	-9.208371
C	6.340587	5.999801	-8.815168
C	7.685456	5.898170	-9.173656
C	8.147088	4.803399	-9.901444
C	7.265944	3.796922	-10.284482

C	5.919684	3.893391	-9.937069
C	5.832564	7.199205	-8.050301
C	4.912816	8.085609	-8.916670
C	4.512077	9.410446	-8.229870
O	4.761153	10.472485	-8.797053
N	5.525399	8.394941	-10.190142
C	4.835189	8.262709	-11.396721
C	5.746413	8.802408	-12.447949
C	6.898866	9.258736	-11.823792
C	6.765502	9.014593	-10.356375
C	7.938959	9.819390	-12.541862
C	7.783550	9.912835	-13.927277
C	6.622792	9.453755	-14.555457
C	5.579995	8.887056	-13.818106
O	3.726154	7.798043	-11.527710
O	7.570328	9.261153	-9.486658
N	3.947485	9.319356	-6.996748
Pd	2.875153	7.743312	-6.332785
O	2.676804	6.358071	-7.877961
C	2.020536	5.583746	-7.105235
C	1.567543	4.242495	-7.588851
C	3.759494	10.585555	-6.247364
C	5.082070	11.355550	-6.077353
C	2.673934	11.474034	-6.885716
C	3.291878	10.165993	-4.884598
C	3.179625	10.769088	-3.656623
N	2.651354	9.814618	-2.850084
N	2.443568	8.677451	-3.494032
N	2.829584	8.904879	-4.717002
C	2.357664	9.904083	-1.420916

C	3.589747	10.265715	-0.626415
C	4.707512	9.427642	-0.657930
C	5.849102	9.759143	0.060980
C	5.881756	10.928600	0.820392
C	4.771122	11.764882	0.855790
C	3.628010	11.435138	0.129744
O	1.799573	5.982654	-5.922622
H	4.008761	7.523776	-9.164848
H	3.441850	11.750036	-3.294660
H	4.673274	8.526334	-14.292547
H	6.531966	9.540270	-15.634058
H	8.576049	10.349173	-14.527887
H	8.834583	10.171828	-12.040842
H	1.563550	10.642792	-1.279911
H	1.965143	8.922228	-1.146780
H	2.502154	12.371683	-6.280021
H	2.999800	11.768214	-7.884081
H	1.733006	10.919339	-6.965055
H	4.930600	12.222236	-5.422777
H	5.838855	10.704284	-5.629363
H	5.439236	11.701193	-7.046019
H	2.761449	12.091524	0.156489
H	4.792424	12.676839	1.444316
H	6.774216	11.185960	1.382379
H	6.714645	9.104767	0.031051
H	4.681729	8.517422	-1.252363
H	8.370456	6.693421	-8.891992
H	9.197290	4.740743	-10.172707
H	7.623706	2.944019	-10.854257
H	5.223425	3.115639	-10.238990

H	4.409385	5.071188	-8.949421
H	6.668477	7.798789	-7.683173
H	5.258101	6.868741	-7.179461
H	2.432916	3.571909	-7.625440
H	0.818966	3.826222	-6.913324
H	1.168566	4.331451	-8.602084

SI-TS1-2

Lowest frequency = -1442.81 cm^{-1}

Charge = 0, Multiplicity = 1

71

C	4.092960	6.295406	-10.591093
C	4.835246	6.268512	-9.407296
C	5.480551	5.083254	-9.046187
C	5.391804	3.949783	-9.848193
C	4.660763	3.988621	-11.032269
C	4.015819	5.166813	-11.400171
C	4.940005	7.465550	-8.484058
C	4.936964	8.840278	-9.161559
C	5.323903	9.991042	-8.201398
O	5.792102	11.032882	-8.655485
N	5.815496	8.894435	-10.309212
C	5.404663	9.305300	-11.577150
C	6.647044	9.373137	-12.400903
C	7.722798	9.034404	-11.589627
C	7.200066	8.744129	-10.222213
C	9.016418	9.003707	-12.076232
C	9.202068	9.329739	-13.422363
C	8.120230	9.670503	-14.238042
C	6.816969	9.696195	-13.734427

O	4.262182	9.529060	-11.908142
O	7.813259	8.429938	-9.227167
N	5.063448	9.726081	-6.909085
Pd	4.391617	7.940403	-6.392981
O	3.539515	6.108584	-5.896746
C	2.677056	5.786096	-6.767471
C	1.842246	4.556631	-6.532596
C	5.344434	10.721552	-5.862193
C	6.855292	11.002420	-5.770123
C	4.553672	12.021348	-6.098831
C	4.875056	10.100444	-4.572488
C	4.807168	10.544914	-3.275596
N	4.282580	9.505565	-2.580963
N	4.021710	8.468145	-3.362046
N	4.383854	8.832651	-4.558207
C	3.964854	9.442062	-1.156576
C	3.011345	10.541452	-0.753342
C	3.383181	11.490410	0.196378
C	2.499829	12.505921	0.558475
C	1.244188	12.578589	-0.035000
C	0.869452	11.633052	-0.989438
C	1.748071	10.617705	-1.345946
O	2.508639	6.429108	-7.844889
H	3.940627	9.081382	-9.548590
H	5.058711	11.483561	-2.808703
H	5.968056	9.959538	-14.356701
H	8.297362	9.919557	-15.279916
H	10.202818	9.319143	-13.843427
H	9.847872	8.737570	-11.431997
H	3.535507	8.449434	-1.002512

H	4.899866	9.502278	-0.592127
H	4.728529	12.730927	-5.281641
H	4.874666	12.471358	-7.038974
H	3.482267	11.804517	-6.152807
H	7.069972	11.708811	-4.959567
H	7.399922	10.071829	-5.583446
H	7.195337	11.427036	-6.716279
H	1.458283	9.881346	-2.091797
H	-0.109882	11.687435	-1.454579
H	0.556297	13.371054	0.243284
H	2.796618	13.240365	1.300785
H	4.365666	11.436727	0.659362
H	6.059021	5.052086	-8.125782
H	5.903632	3.038754	-9.551175
H	4.595629	3.108264	-11.664965
H	3.442153	5.209153	-12.321514
H	3.572210	7.199941	-10.891159
H	5.910393	7.345735	-7.985989
H	3.645702	7.130286	-8.001250
H	0.806949	4.749640	-6.822207
H	2.224882	3.758592	-7.177452
H	1.898793	4.239223	-5.491026

SI-2

Lowest frequency = 12.27 cm^{-1}

Charge = 0, Multiplicity = 1

71

C	3.734350	6.543693	-10.047624
C	4.823466	6.386307	-9.179663
C	5.295918	5.083327	-8.957877

C	4.697716	3.982303	-9.559165
C	3.605145	4.155902	-10.408539
C	3.133539	5.442622	-10.652092
C	5.478331	7.523360	-8.463350
C	5.405568	8.891312	-9.137128
C	5.801958	10.011042	-8.159780
O	6.350400	11.042065	-8.539626
N	6.171971	8.981349	-10.361427
C	5.612442	9.364922	-11.579391
C	6.756414	9.496279	-12.528931
C	7.926938	9.221388	-11.833546
C	7.565815	8.898148	-10.420092
C	9.163419	9.264530	-12.450544
C	9.191315	9.599710	-13.806900
C	8.013799	9.876387	-14.506128
C	6.769867	9.827312	-13.871406
O	4.432043	9.537524	-11.789723
O	8.298939	8.598219	-9.506627
N	5.396226	9.700223	-6.913101
Pd	4.820017	7.838817	-6.556176
O	4.155271	5.809945	-6.199633
C	3.040132	5.466341	-6.583679
C	2.558648	4.053683	-6.522587
C	5.596693	10.624899	-5.791613
C	7.099155	10.824551	-5.515437
C	4.907704	11.976002	-6.058151
C	4.954310	9.988349	-4.580412
C	4.725587	10.462479	-3.311358
N	4.127776	9.435846	-2.661033
N	3.975843	8.378426	-3.450464

N	4.477689	8.713769	-4.604637
C	3.655617	9.391945	-1.281849
C	2.703884	10.525220	-0.979555
C	2.983729	11.433055	0.039368
C	2.101714	12.476700	0.314225
C	0.939418	12.619788	-0.435805
C	0.657353	11.716384	-1.460348
C	1.534278	10.673078	-1.729891
O	2.173819	6.305935	-7.119020
H	4.377350	9.121483	-9.433443
H	4.911943	11.413795	-2.839276
H	5.847843	10.040878	-14.402054
H	8.068666	10.134472	-15.559401
H	10.142753	9.647377	-14.328010
H	10.070290	9.048347	-11.895435
H	3.175576	8.416307	-1.173433
H	4.523053	9.420112	-0.615502
H	5.024040	12.645699	-5.197826
H	5.356934	12.441747	-6.936245
H	3.839544	11.822966	-6.241652
H	7.254810	11.489245	-4.657323
H	7.572587	9.860189	-5.305831
H	7.566766	11.262896	-6.399478
H	1.317744	9.970389	-2.530970
H	-0.248358	11.826001	-2.048778
H	0.253257	13.434558	-0.225978
H	2.327617	13.178748	1.110937
H	3.894233	11.325791	0.624070
H	6.142122	4.941234	-8.290468
H	5.090667	2.986611	-9.370939

H	3.138308	3.299498	-10.886565
H	2.294106	5.596198	-11.324233
H	3.356933	7.534900	-10.280636
H	6.530479	7.283241	-8.273456
H	2.620032	7.177823	-7.206787
H	1.500988	4.013886	-6.254774
H	2.678251	3.627350	-7.524949
H	3.163624	3.486490	-5.815853

I1'

Lowest frequency = 10.86 cm^{-1}

Charge = 0, Multiplicity = 1

119

C	6.641608	9.312249	-9.237262
C	7.953697	9.734101	-8.983828
C	8.935402	8.748156	-8.822671
C	8.617276	7.395513	-8.885289
C	7.303830	6.994274	-9.120446
C	6.318500	7.962044	-9.303934
C	8.302657	11.178924	-8.824817
C	7.736885	12.103930	-9.905540
C	7.591525	13.552901	-9.418476
O	7.681456	14.510698	-10.180834
N	8.469842	12.051107	-11.151162
C	7.853172	11.793489	-12.377710
C	8.902897	12.022208	-13.414224
C	10.059267	12.444061	-12.770787
C	9.787059	12.489008	-11.302380
C	11.212090	12.742496	-13.473418
C	11.169036	12.604746	-14.863319

C	10.005708	12.180530	-15.510515
C	8.847345	11.880925	-14.788692
O	6.702607	11.451692	-12.528884
O	10.536853	12.808859	-10.408469
N	7.269359	13.565614	-8.108649
Pd	7.651543	11.925903	-7.041989
C	6.972079	14.819763	-7.403207
C	8.226167	15.710652	-7.325245
C	5.809809	15.570005	-8.077090
C	6.550317	14.433961	-6.003502
C	5.872157	15.107978	-5.015469
N	5.817183	14.238599	-3.977527
N	6.401597	13.086125	-4.276583
N	6.847231	13.209377	-5.493167
C	5.117015	14.373647	-2.702662
C	3.672519	13.939691	-2.798108
C	2.651767	14.887766	-2.841421
C	1.322708	14.486097	-2.950629
C	1.010766	13.131667	-3.022638
C	2.026941	12.177751	-2.983990
C	3.353862	12.581448	-2.868972
H	6.721474	11.791910	-10.172592
H	5.428394	16.089495	-4.971367
H	7.936639	11.552483	-15.278658
H	10.003625	12.084385	-16.592072
H	12.052523	12.831872	-15.452329
H	12.108052	13.073022	-12.958334
H	5.672216	13.760364	-1.989851
H	5.198898	15.418975	-2.394349
H	5.567210	16.483809	-7.521417

H	6.095307	15.838989	-9.094697
H	4.920790	14.932994	-8.111086
H	8.018706	16.631608	-6.767720
H	9.037101	15.170498	-6.826472
H	8.542818	15.965138	-8.339123
H	4.148845	11.838679	-2.854445
H	1.790308	11.121036	-3.071276
H	-0.023979	12.817082	-3.116691
H	0.533661	15.231230	-2.982781
H	2.893715	15.946770	-2.786872
H	9.962432	9.053266	-8.634618
H	9.398429	6.651934	-8.753581
H	7.051857	5.938799	-9.172842
H	5.292350	7.665498	-9.502839
H	5.856563	10.050031	-9.375243
H	9.387502	11.316519	-8.768230
C	2.993291	9.025081	-5.206822
C	3.438888	10.362133	-5.815814
C	4.904893	10.275595	-6.140611
C	5.678218	9.789416	-5.179644
C	4.016761	8.487622	-4.180833
H	5.290814	10.598015	-7.097559
I	7.795015	9.714581	-5.347019
O	5.193104	9.319803	-4.018049
H	3.539066	8.493230	-3.200825
H	2.929711	8.315986	-6.041102
H	3.287996	11.136733	-5.052086
C	4.505958	7.082602	-4.529802
H	5.151710	6.713040	-3.723705
H	5.115326	7.152205	-5.445020

O	1.752418	9.139710	-4.563362
O	2.642768	10.636213	-6.939332
O	3.395569	6.239827	-4.697924
Si	3.332534	5.051995	-5.883129
Si	0.240123	8.890577	-5.254132
Si	2.598595	12.134434	-7.716280
C	-0.645854	10.546871	-5.229218
H	0.014423	11.329204	-5.618694
H	-1.558537	10.532806	-5.836162
H	-0.928597	10.821243	-4.206170
C	-0.646274	7.655462	-4.155553
H	-1.660596	7.451933	-4.519214
H	-0.097071	6.707629	-4.126246
H	-0.726385	8.024825	-3.127068
C	0.386382	8.218260	-6.999034
H	-0.609983	8.112650	-7.444544
H	0.978356	8.890121	-7.627832
H	0.858282	7.229283	-7.012066
C	1.596274	4.362549	-5.777387
H	1.404643	3.946253	-4.782440
H	0.847325	5.140007	-5.963403
H	1.441872	3.564421	-6.512551
C	3.682267	5.813499	-7.566713
H	2.970424	6.608650	-7.816151
H	4.689749	6.242889	-7.617701
H	3.614667	5.048827	-8.350165
C	4.618916	3.732230	-5.520141
H	4.594546	2.938005	-6.275631
H	5.631100	4.153832	-5.519239
H	4.446723	3.271413	-4.541246

C	2.813838	13.491383	-6.437069
H	2.057929	13.440253	-5.645642
H	3.799260	13.423069	-5.961549
H	2.746624	14.478774	-6.909021
C	0.917738	12.180144	-8.541800
H	0.805575	13.083254	-9.152784
H	0.791946	11.314715	-9.202289
H	0.104332	12.162401	-7.808950
C	3.953256	12.255435	-9.008625
H	3.806468	13.141949	-9.638087
H	4.948682	12.352326	-8.557844
H	3.950425	11.383591	-9.673215

Reference

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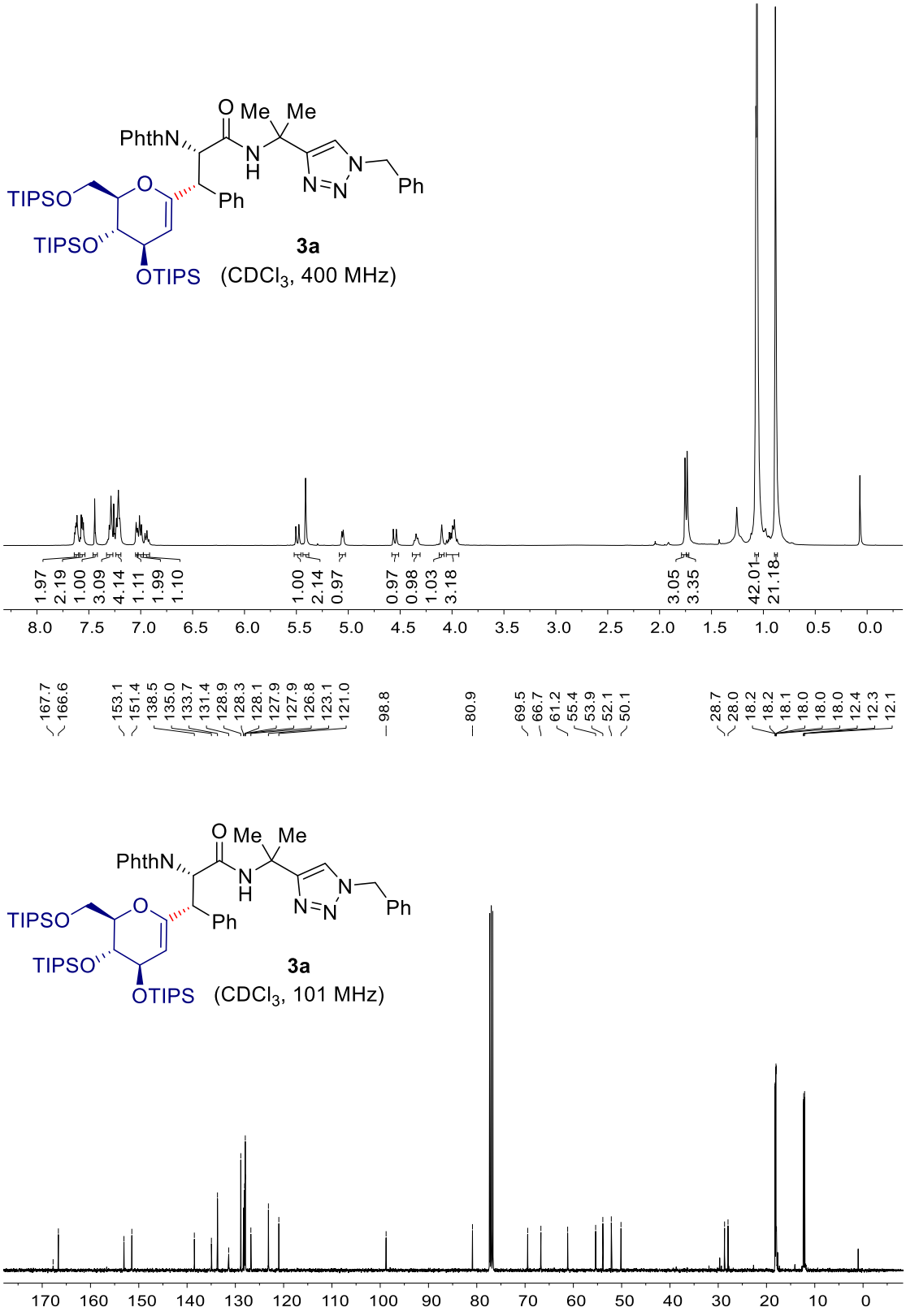
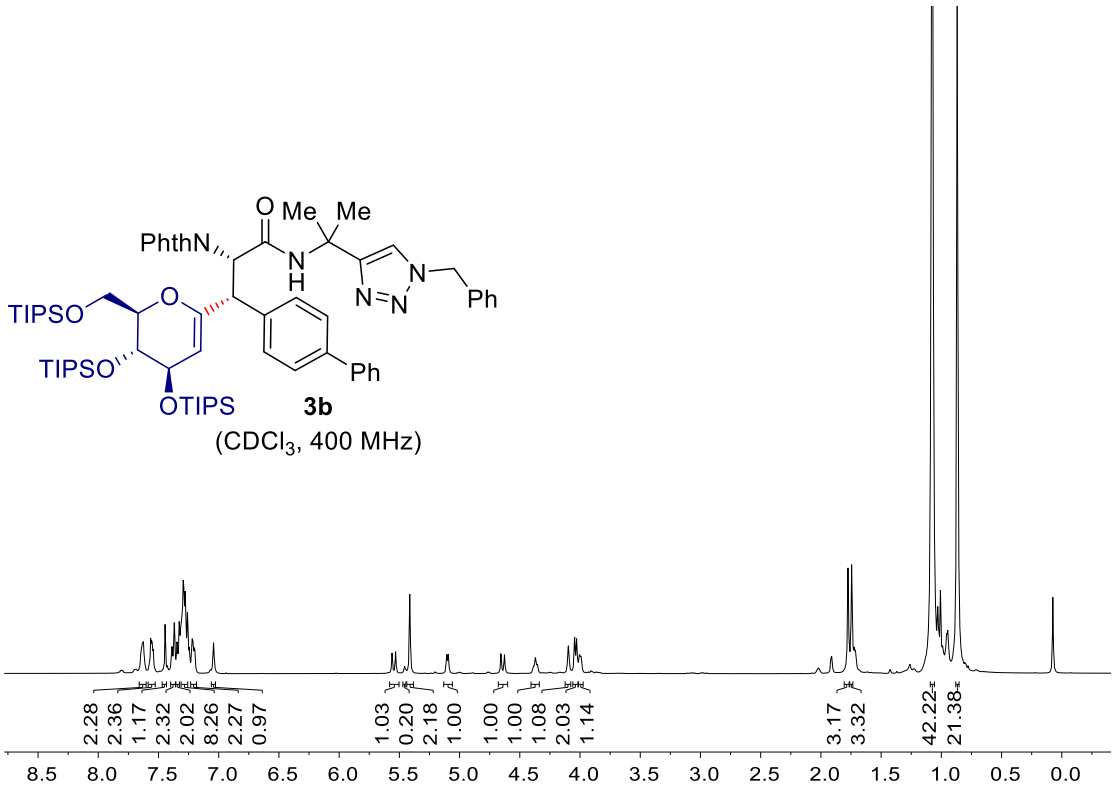
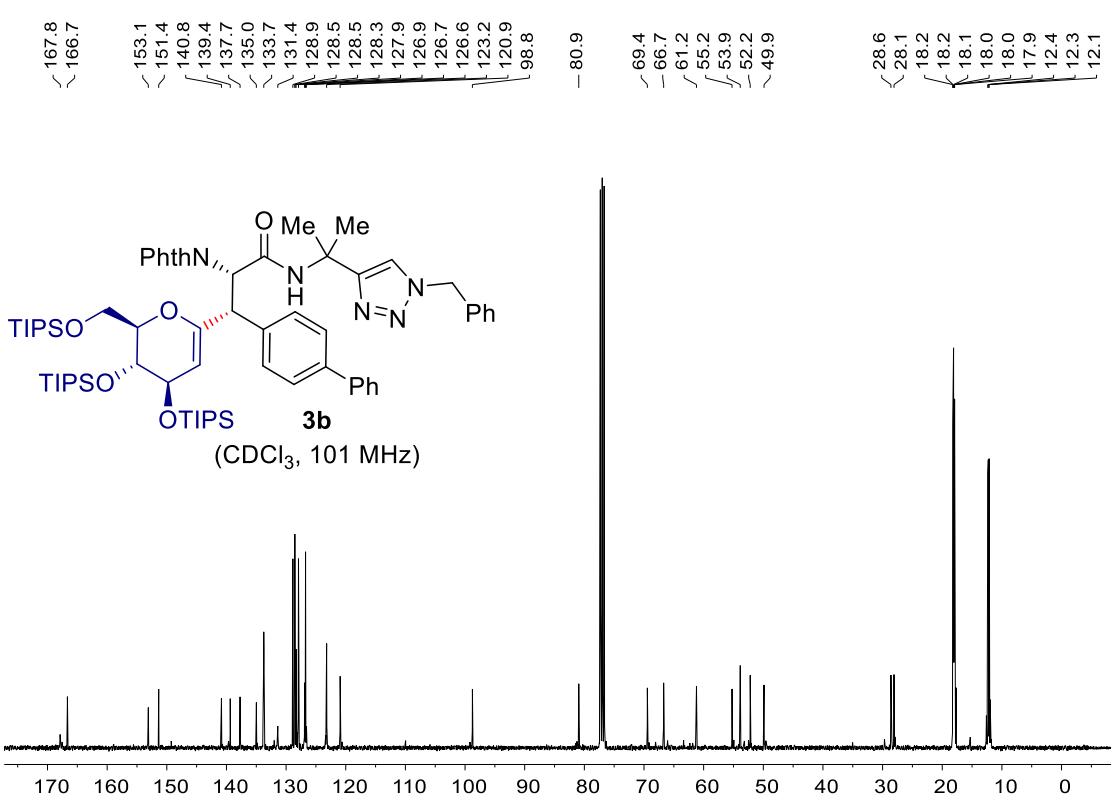
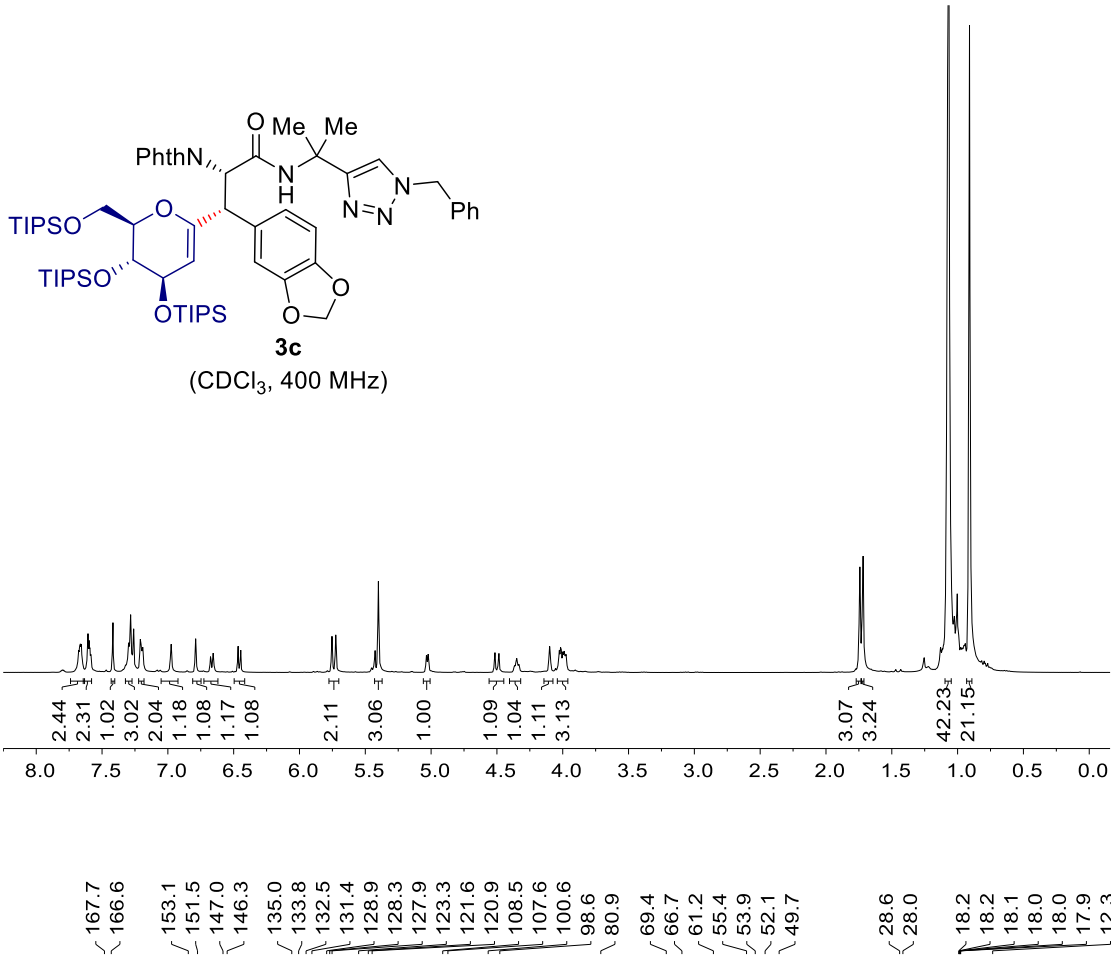
^{1}H-, ^{13}C- and ^{19}F-NMR Spectra



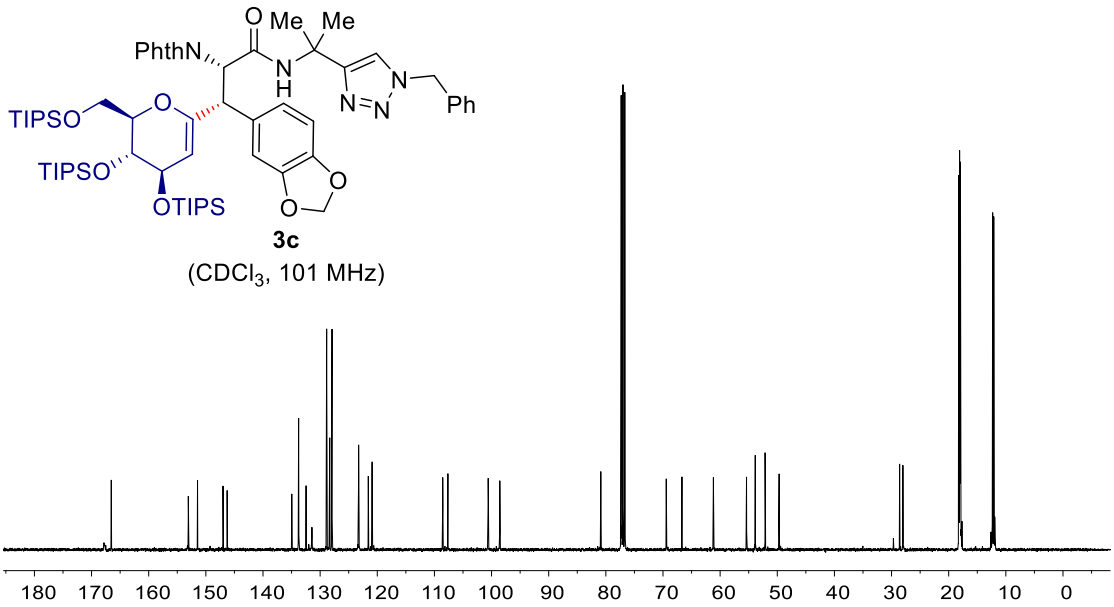

O
Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
Ph
OTIPS
3b
(CDCl3, 400 MHz)
2.28
2.36
1.17
2.32
2.02
8.26
2.27
0.97
1.03
0.20
2.18
1.00
1.00
1.00
1.08
2.03
1.14
3.17
3.32
42.22
21.38
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.8
166.7
153.1
151.4
140.8
139.4
137.7
135.0
133.7
131.4
128.9
128.5
128.5
128.3
127.9
126.9
126.7
126.6
123.2
120.9
98.8
80.9
69.4
66.7
61.2
55.2
53.9
52.2
49.9
28.6
28.1
18.2
18.2
18.1
18.0
18.0
17.9
12.4
12.3
12.1
O
Me
Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
Ph
OTIPS
3b
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



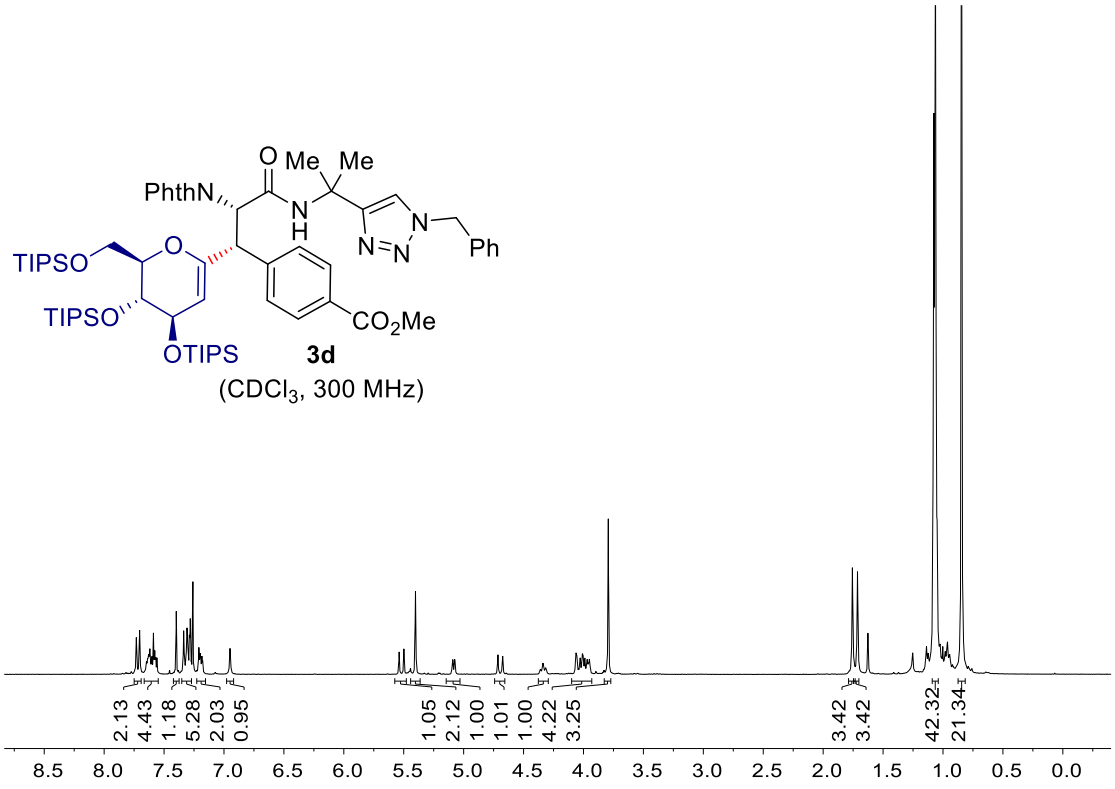
3c

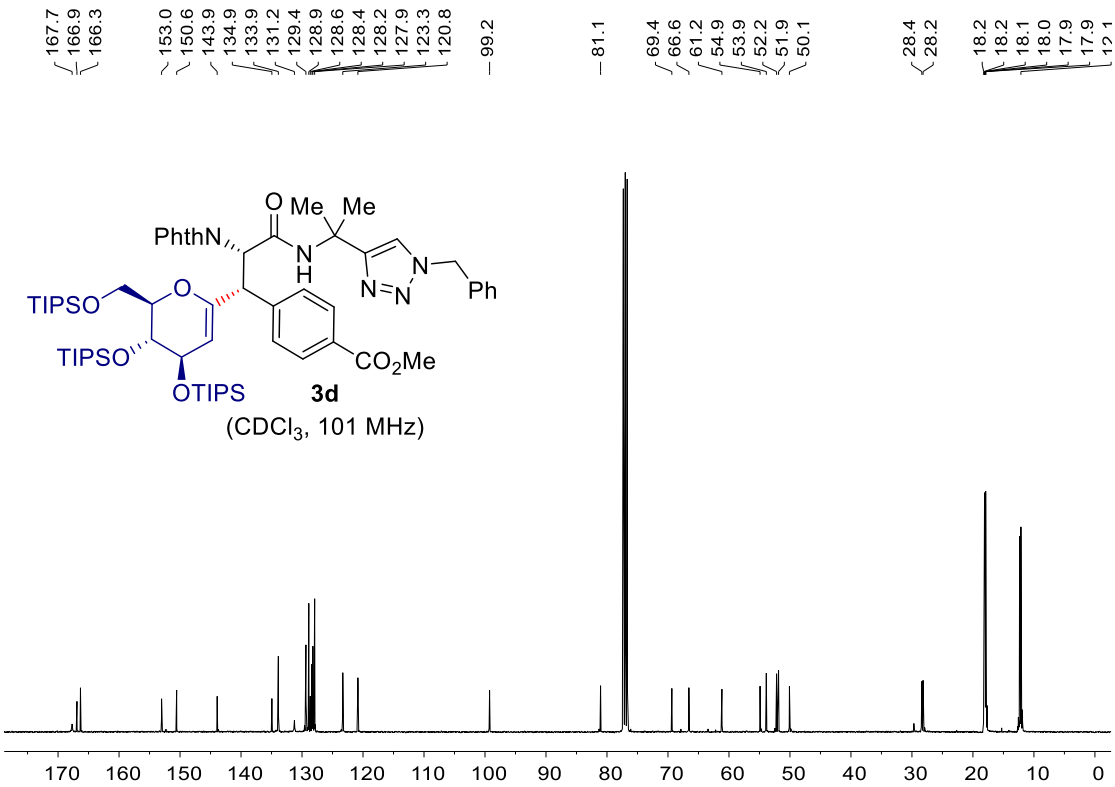
($CDCl_3$, 400 MHz)

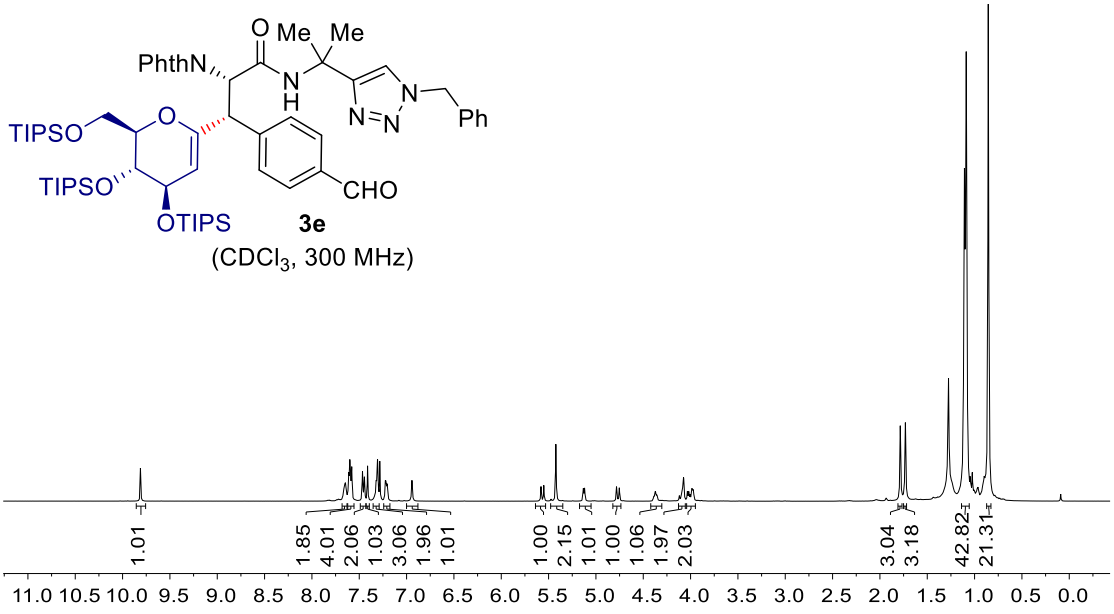


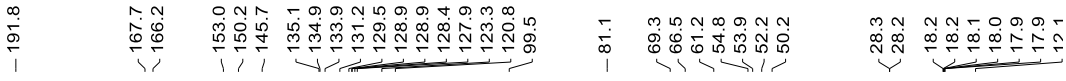
3c

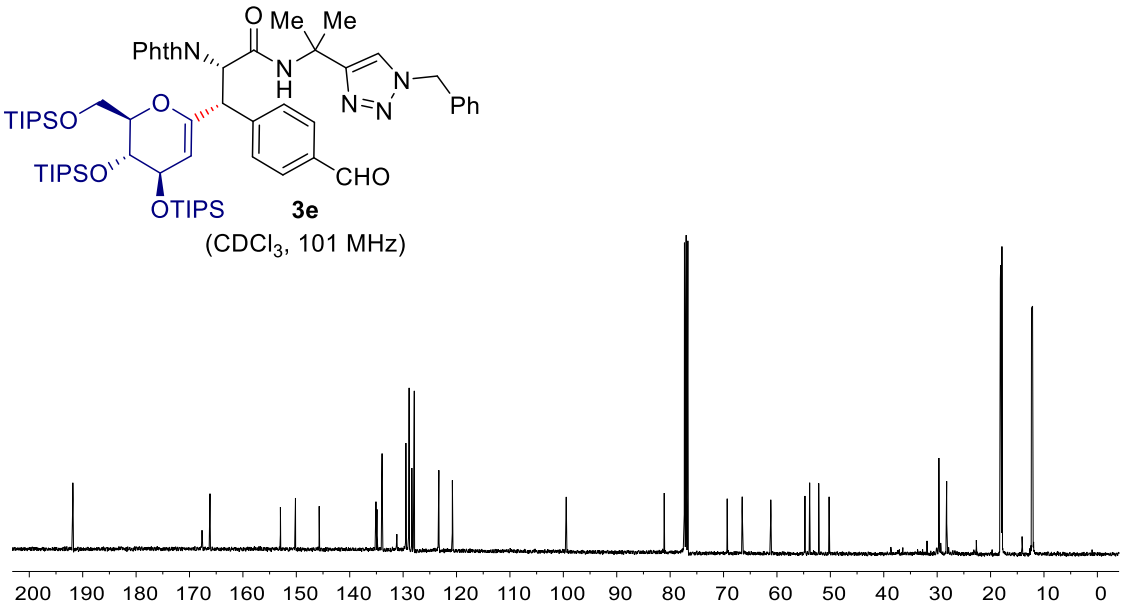
($CDCl_3$, 101 MHz)

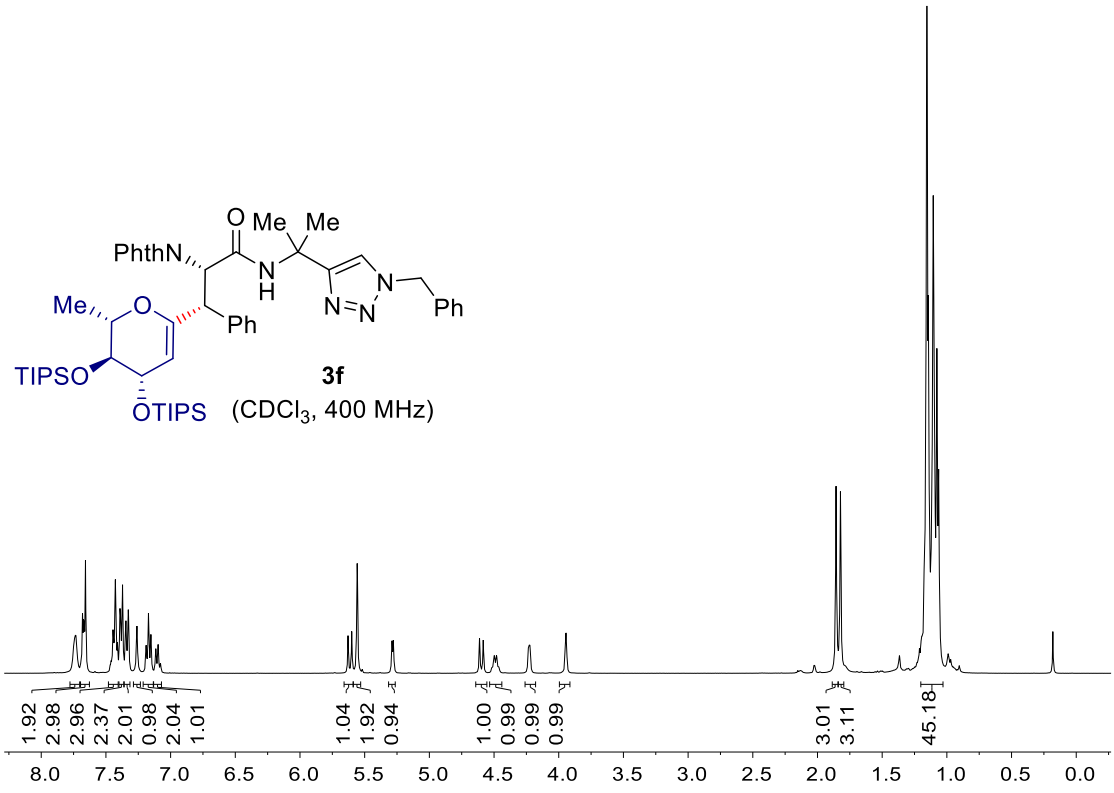

PhthN
O
Me
Me
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
CO2Me
3d
(CDCl3, 300 MHz)
2.13
4.43
1.18
5.28
2.03
0.95
1.05
2.12
1.00
1.01
1.00
4.22
3.25
3.42
3.42
42.32
21.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


PhthN
O
Me
Me
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
CO2Me
3d
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

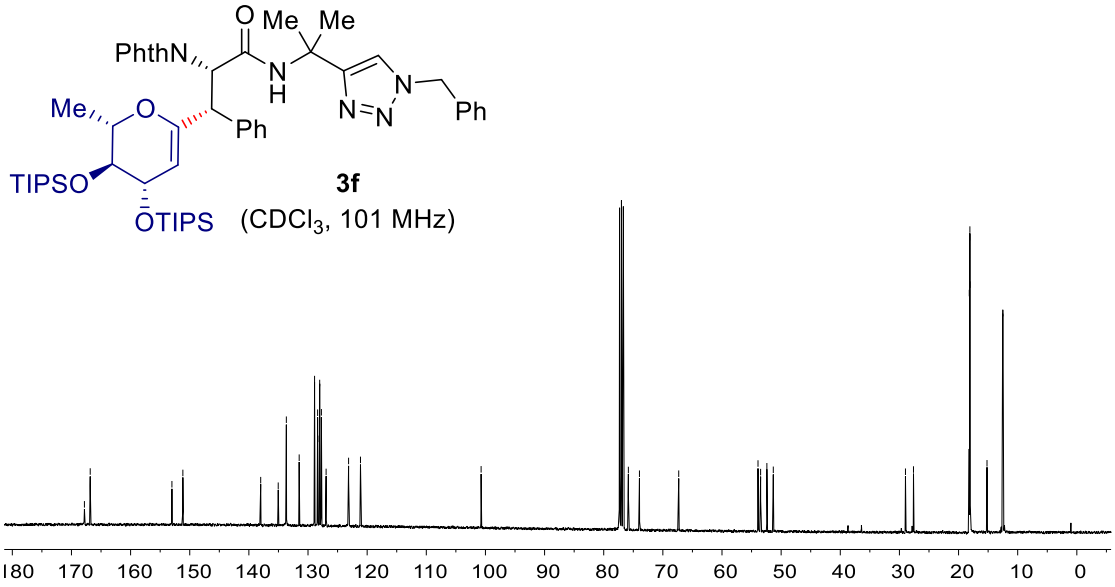

O Me Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
CHO
3e
(CDCl3, 300 MHz)
1.01
1.85
4.01
2.06
1.03
3.06
1.96
1.01
1.00
2.15
1.01
1.00
1.06
1.97
2.03
3.04
3.18
42.82
21.31
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

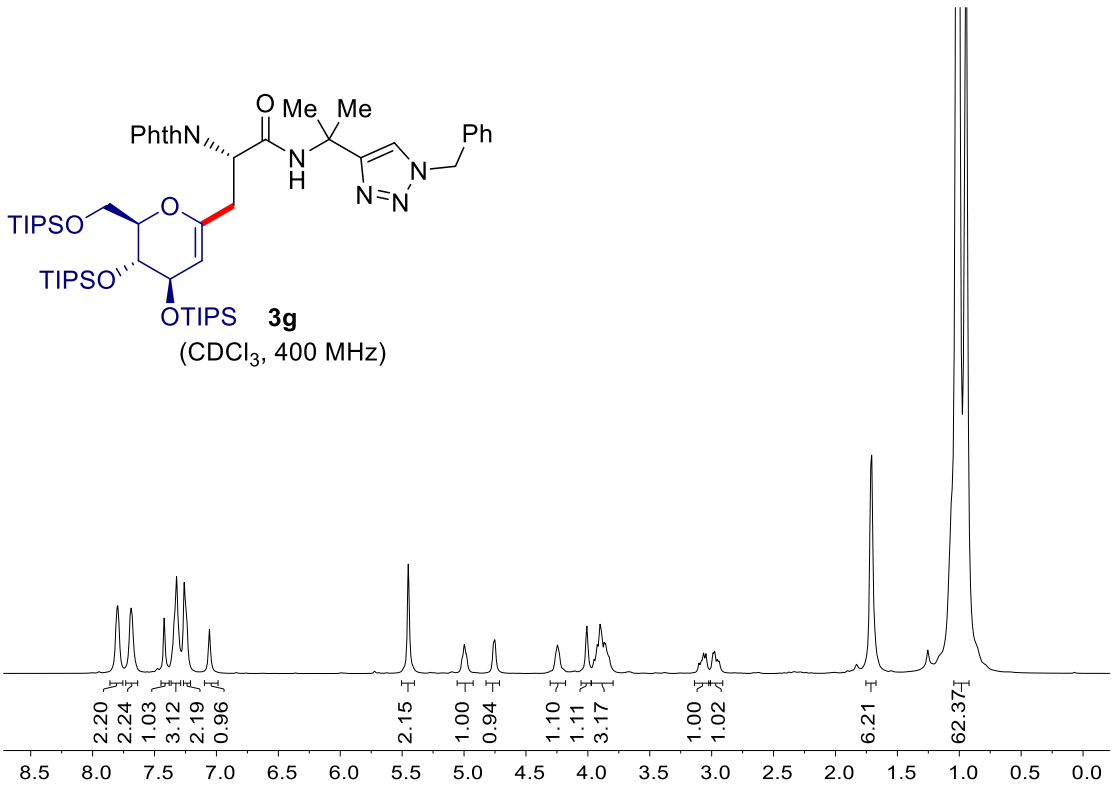

191.8
167.7
166.2
153.0
150.2
145.7
135.1
134.9
133.9
131.2
129.5
128.9
128.9
128.4
127.9
123.3
120.8
99.5
81.1
69.3
66.5
61.2
54.8
53.9
52.2
50.2
28.3
28.2
18.2
18.2
18.1
18.0
17.9
17.9
13.1

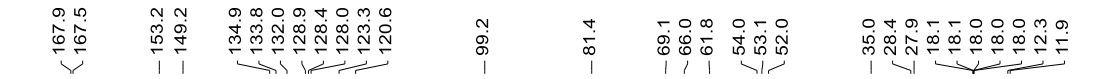

O Me Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
CHO
3e
(CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


O Me Me
PhthN
N
H
N
N=N
Ph
Me
O
Ph
TIPSO
OTIPS
3f
(CDCl3, 400 MHz)
1.92
2.98
2.96
2.37
2.01
0.98
2.04
1.01
1.04
1.92
0.94
1.00
0.99
0.99
0.99
3.01
3.11
45.18
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
0.0


167.8
166.8
153.0
151.2
138.0
135.0
133.7
131.5
128.9
128.4
128.3
128.0
127.7
126.9
123.1
121.1
100.7
75.8
74.0
67.3
53.9
53.5
52.4
51.3
29.0
27.6
18.2
18.1
18.1
18.0
15.2
12.5
12.5


O Me Me
PhthN
N
H
N
N=N
Ph
Me
O
Ph
TIPSO
OTIPS
3f
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


PhthN
O
Me
Me
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
3g
(CDCl3, 400 MHz)
2.20
2.24
1.03
3.12
2.19
0.96
2.15
1.00
0.94
1.10
1.11
3.17
1.00
1.02
6.21
62.37
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
0.0


167.9
167.5
153.2
149.2
134.9
133.8
132.0
128.9
128.4
128.0
123.3
120.6
99.2
81.4
69.1
66.0
61.8
54.0
53.1
52.0
35.0
28.4
27.9
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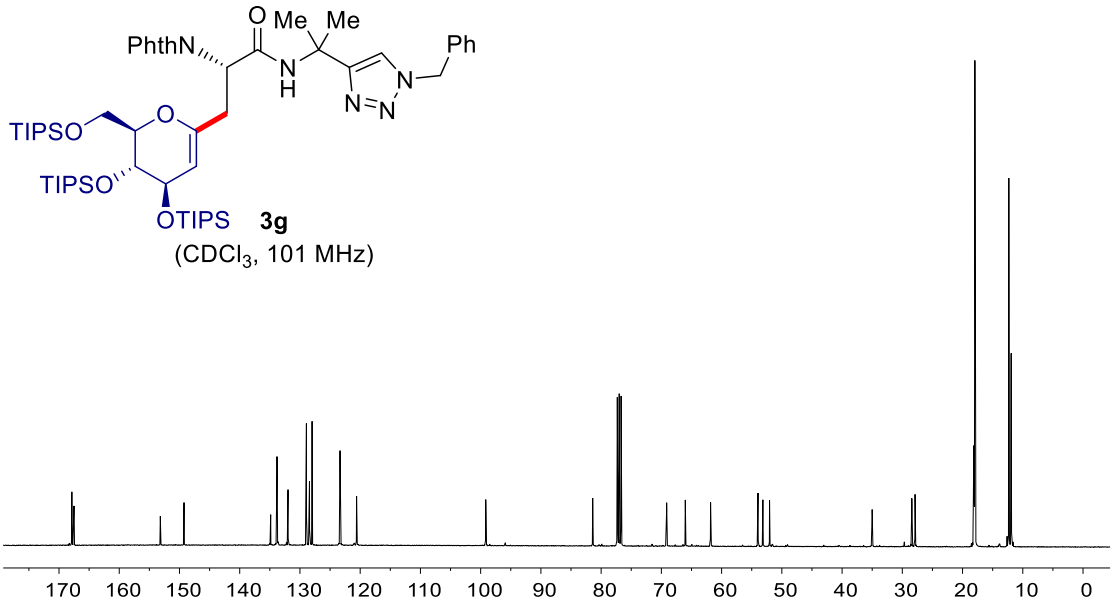
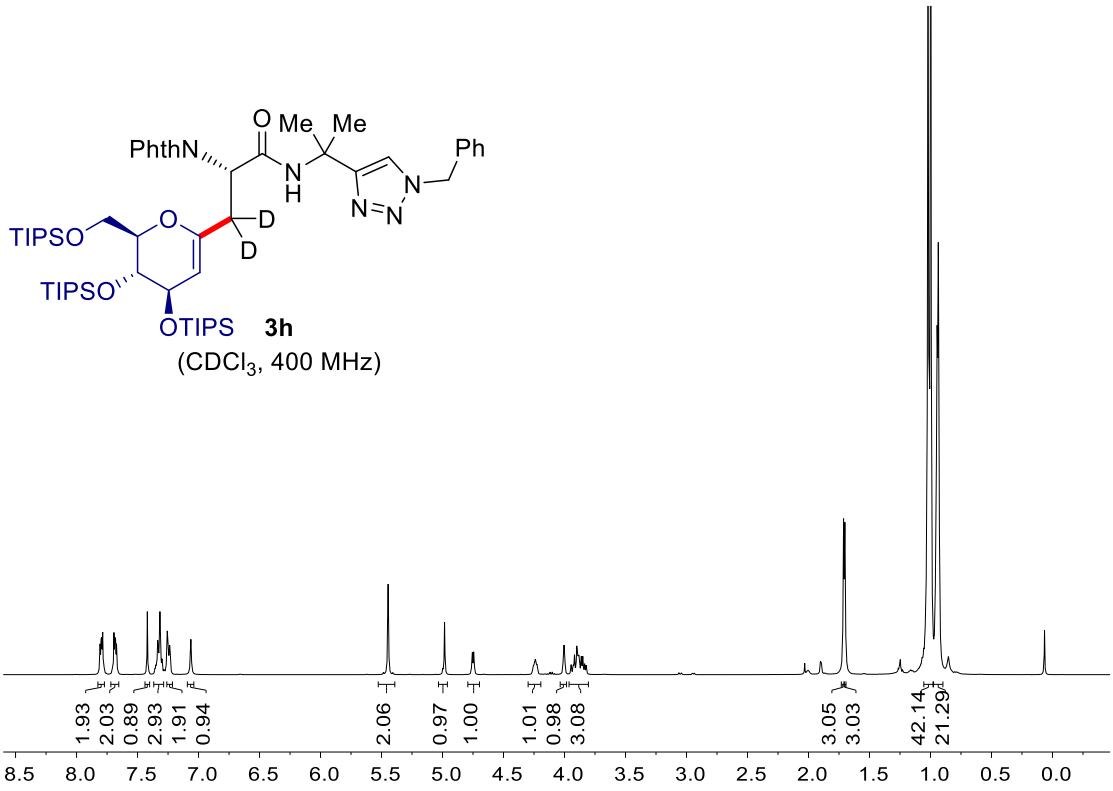
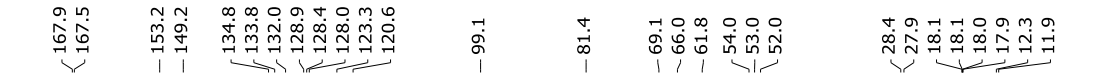
18.0
18.0
18.0
18.0
12.3
11.9

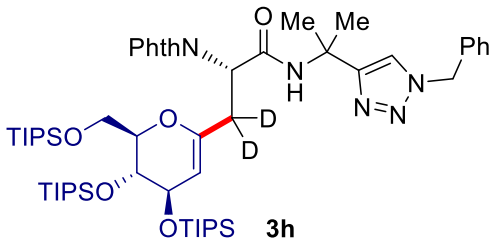

PhthN
O
Me
Me
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
3g
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



3h

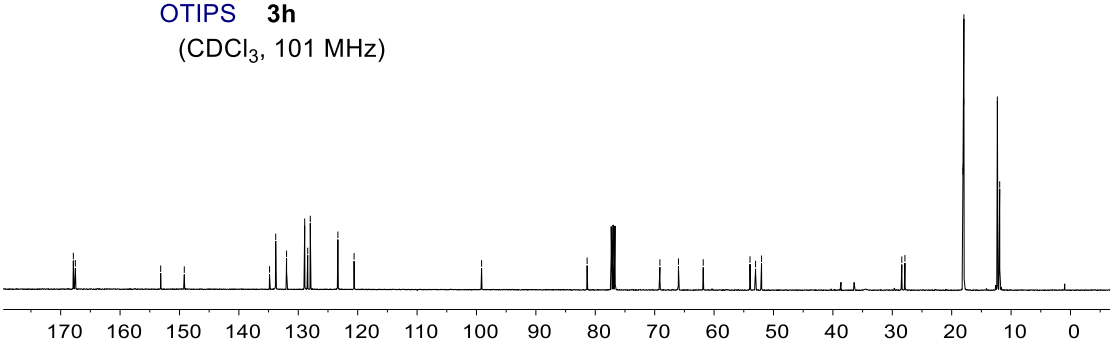
($CDCl_3$, 400 MHz)

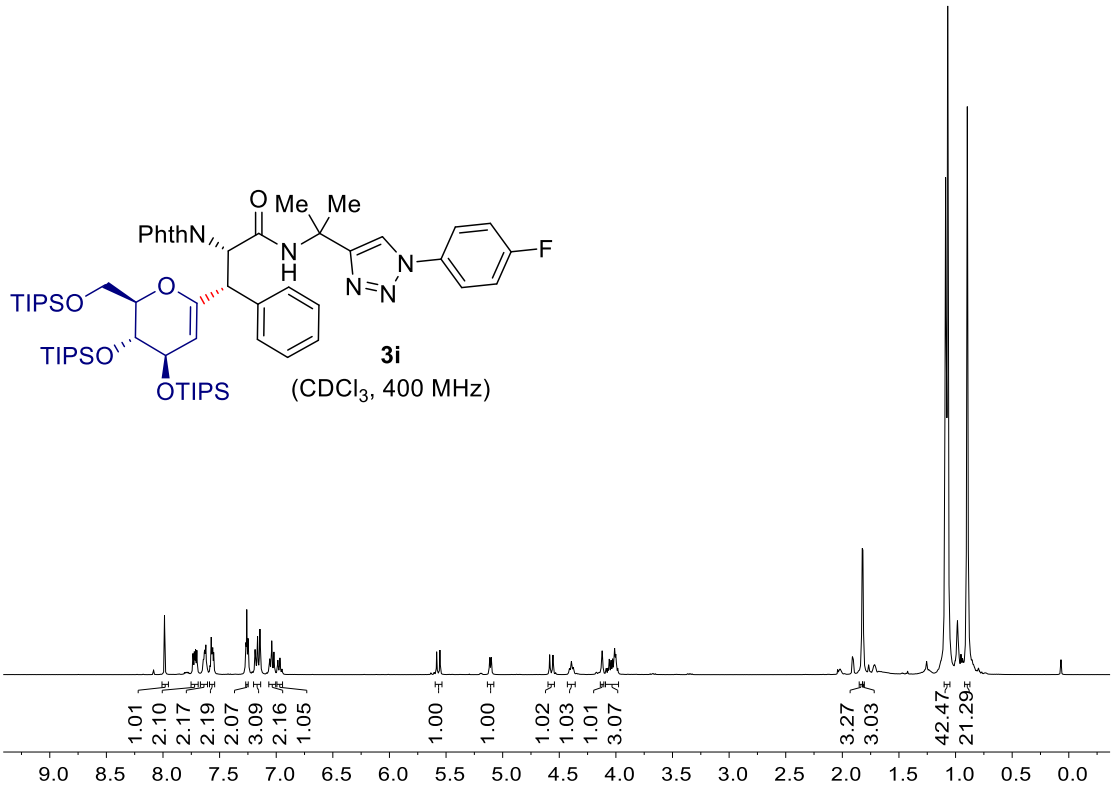


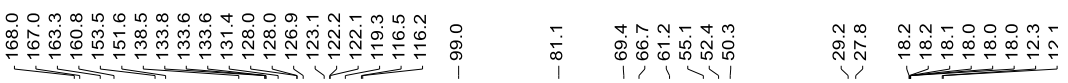


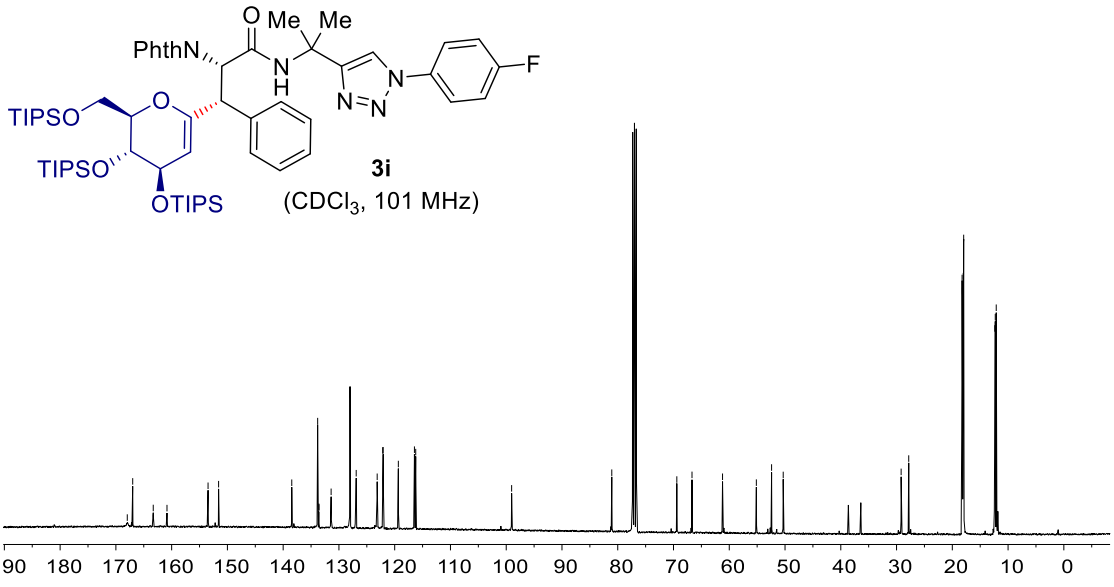
3h

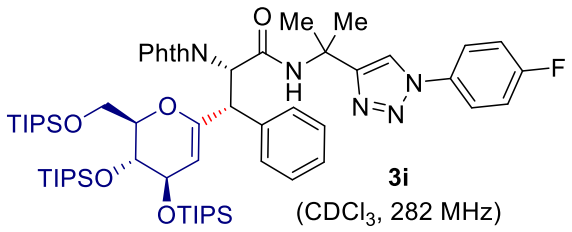
($CDCl_3$, 101 MHz)




O
Me
Me
PhthN
N
H
N
N=N
F
TIPSO
O
TIPSO
OTIPS
3i
(CDCl3, 400 MHz)
1.01
2.10
2.17
2.19
2.07
3.09
2.16
1.05
1.00
1.00
1.02
1.03
1.01
3.07
3.27
3.03
42.47
21.29
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
0.0

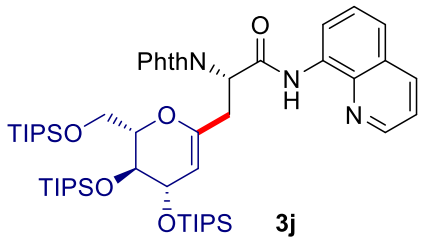

168.0
167.0
163.3
160.8
153.5
151.6
138.5
133.8
133.6
133.6
131.4
128.0
128.0
126.9
123.1
122.2
122.1
119.3
116.5
116.2
99.0
81.1
69.4
66.7
61.2
55.1
52.4
50.3
29.2
27.8
18.2
18.2
18.1
18.0
18.0
18.0
12.3
12.1


O
Me
Me
PhthN
N
H
N
N=N
F
TIPSO
O
TIPSO
OTIPS
3i
(CDCl3, 101 MHz)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



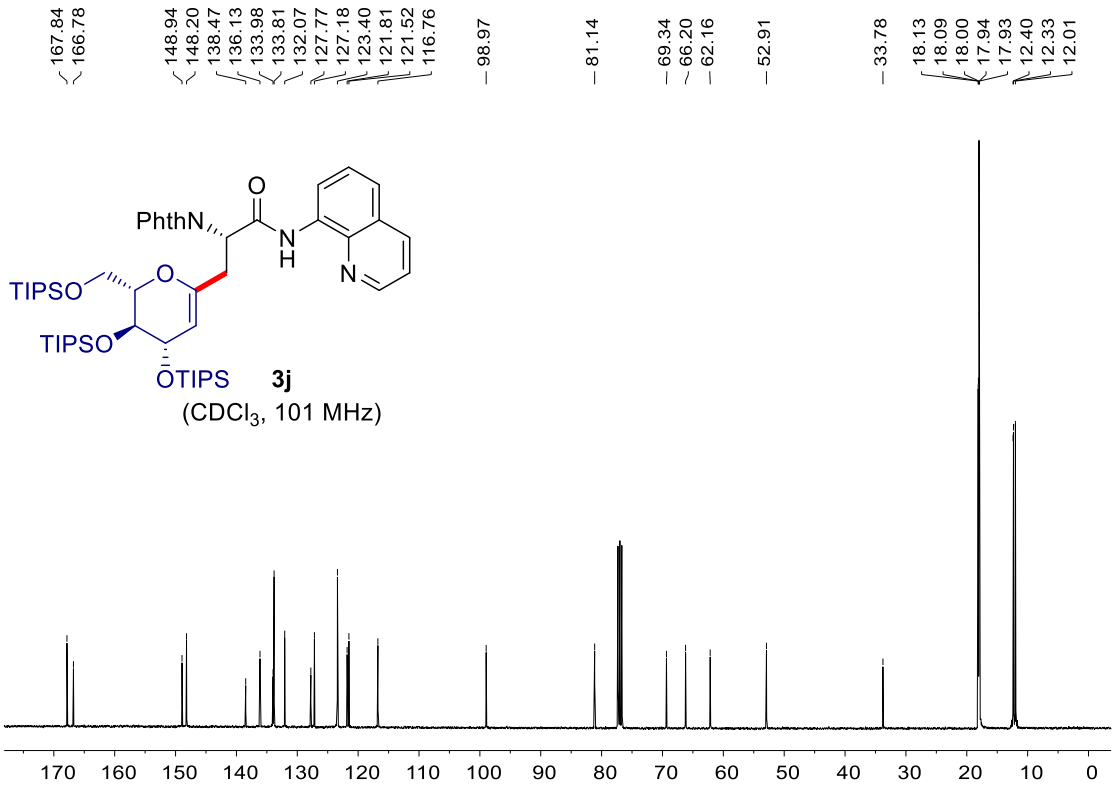
3i

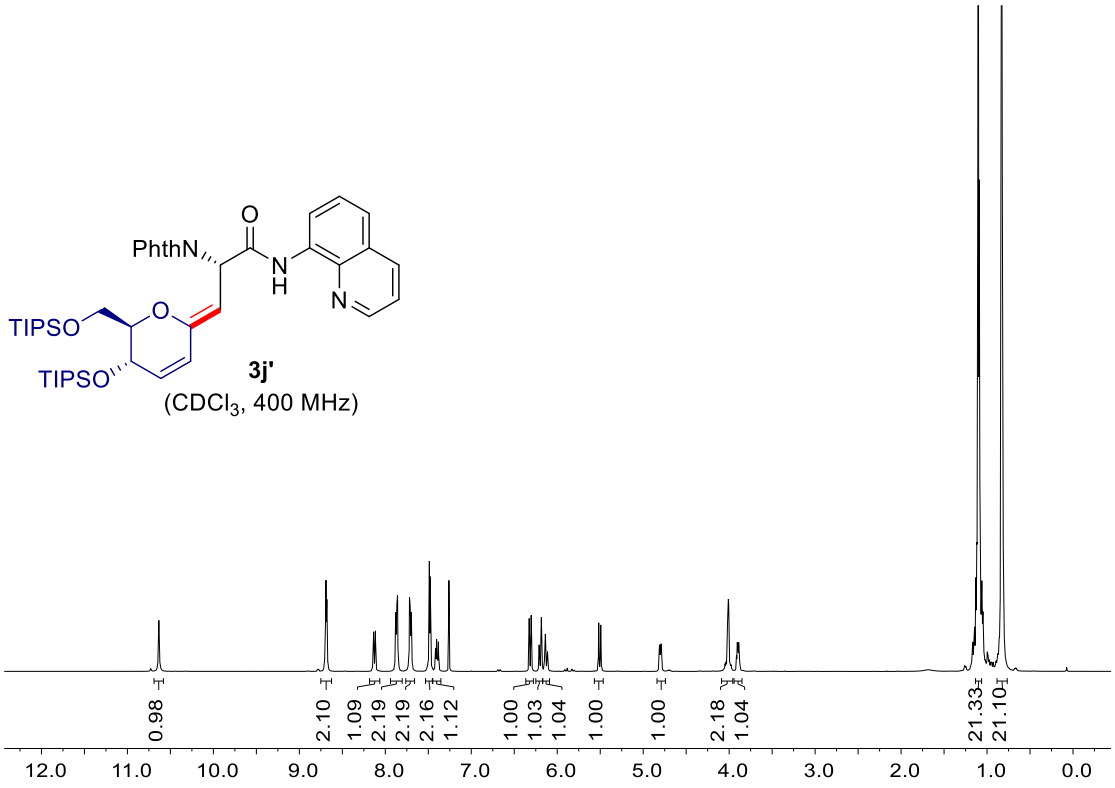
($CDCl_3$, 282 MHz)

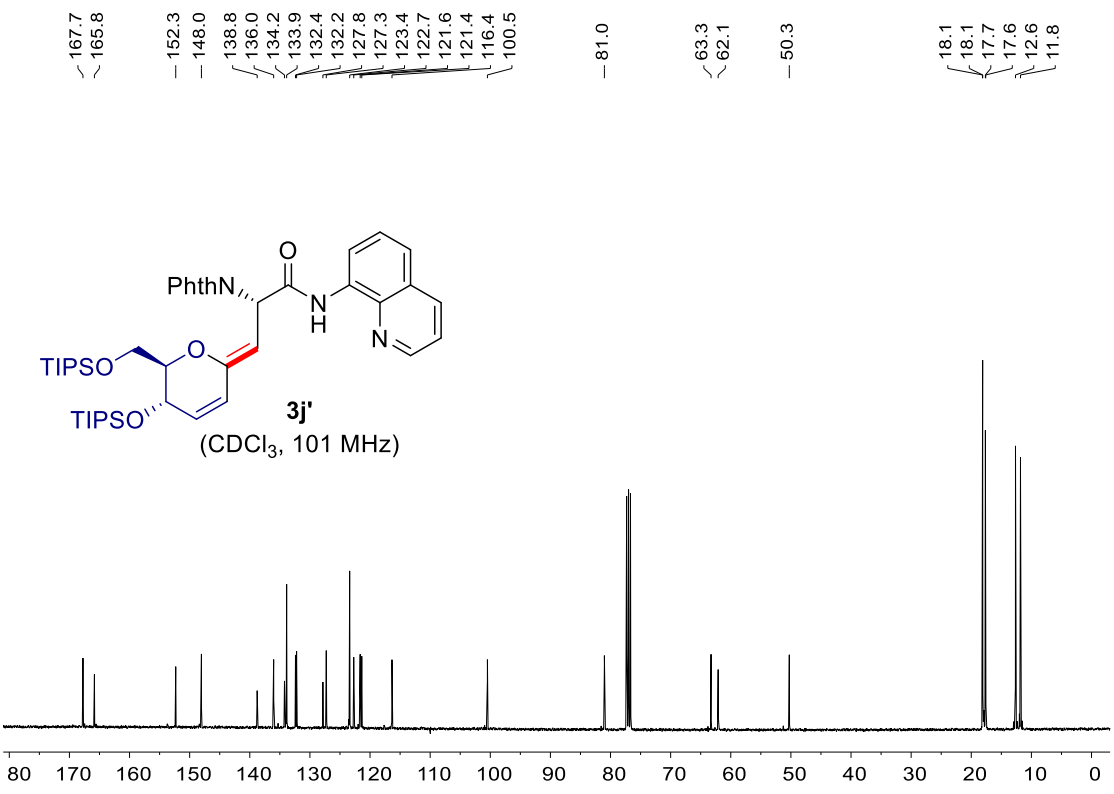


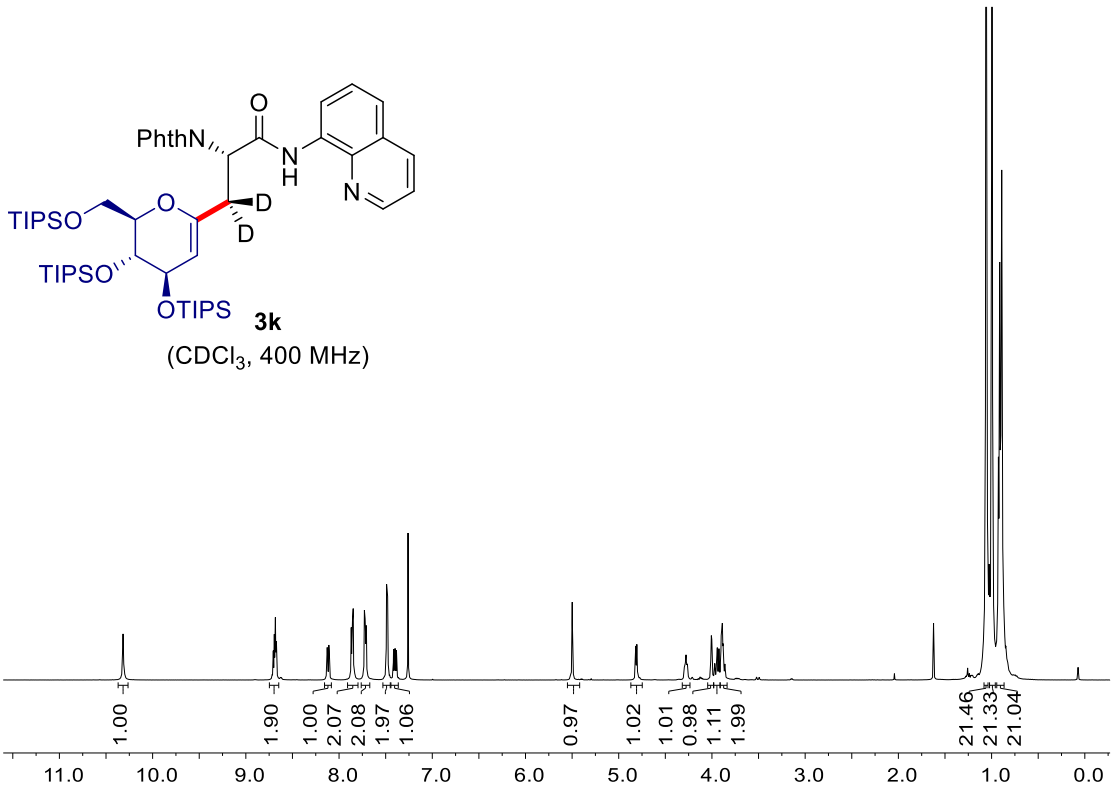
3j

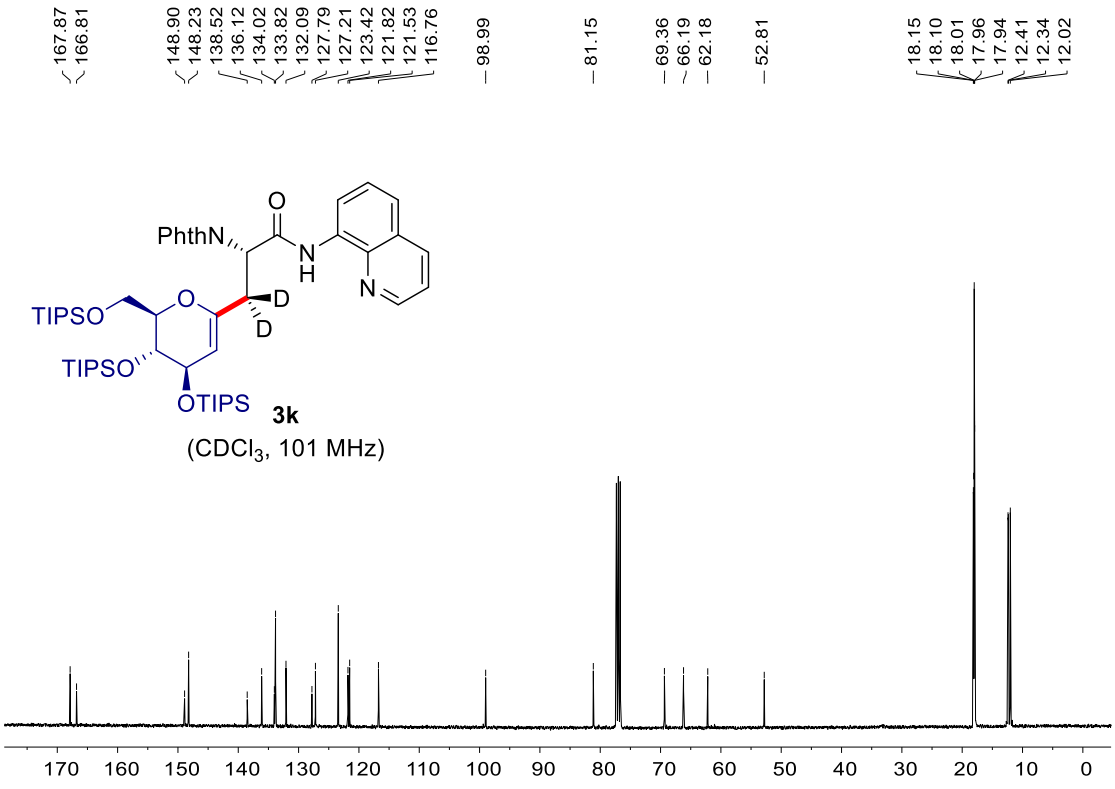
($CDCl_3$, 400 MHz)

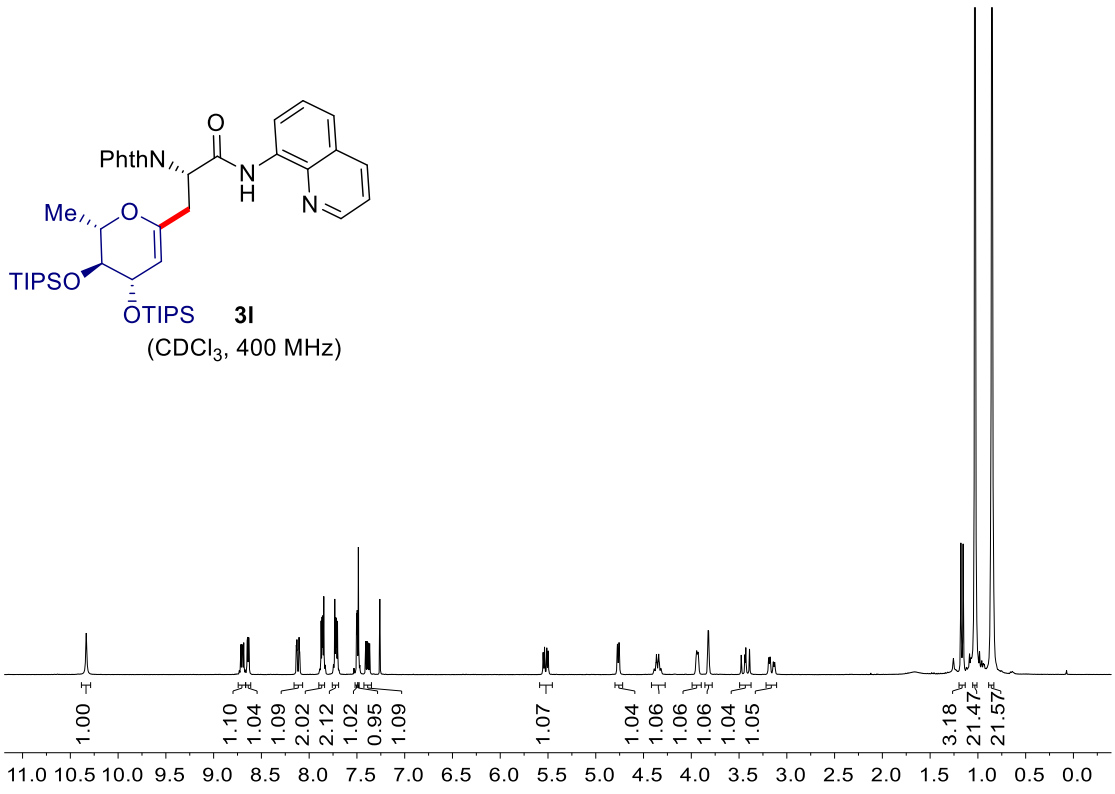

167.84
166.78
148.94
148.20
138.47
136.13
133.98
133.81
132.07
127.77
127.18
123.40
121.81
121.52
116.76
98.97
81.14
69.34
66.20
62.16
52.91
33.78
18.13
18.09
18.00
17.94
17.93
12.40
12.33
12.01
PhthN
O
N
H
N
O
TIPSO
TIPSO
OTIPS
3j
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

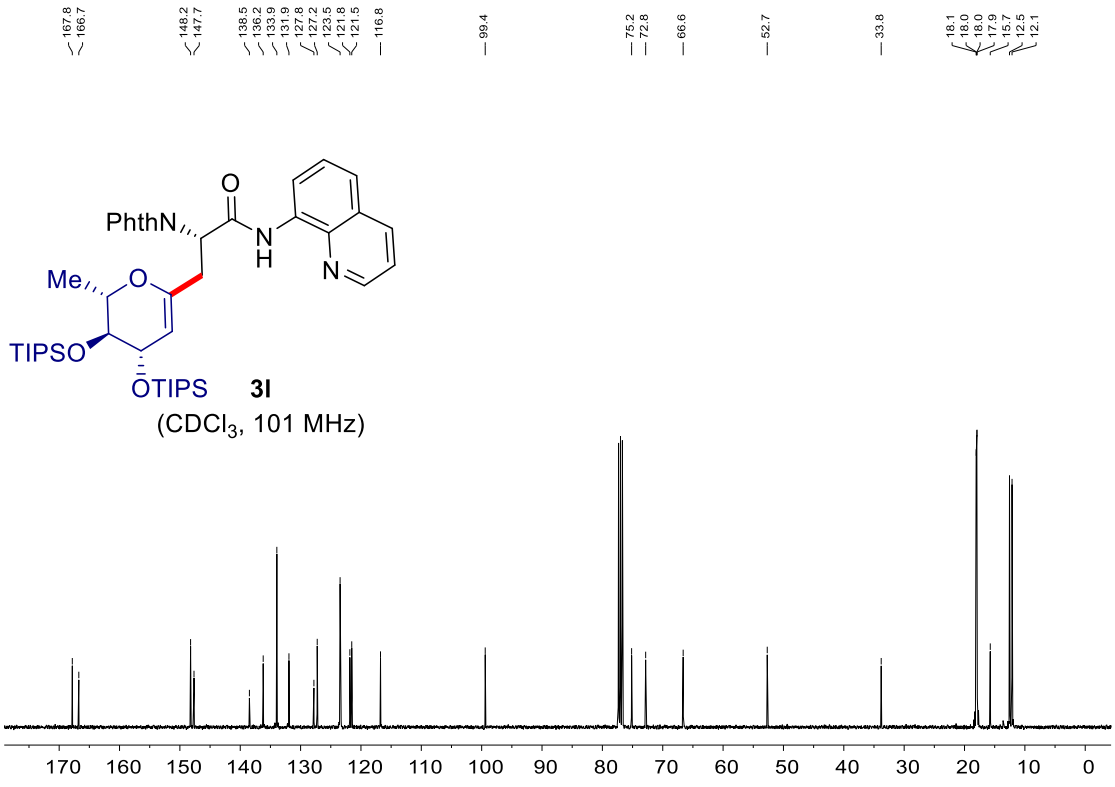

PhthN
O
N
H
N
O
TIPSO
TIPSO
3j'
(CDCl3, 400 MHz)
0.98
2.10
1.09
2.19
2.19
2.16
1.12
1.00
1.03
1.04
1.00
1.00
2.18
1.04
21.33
21.10
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

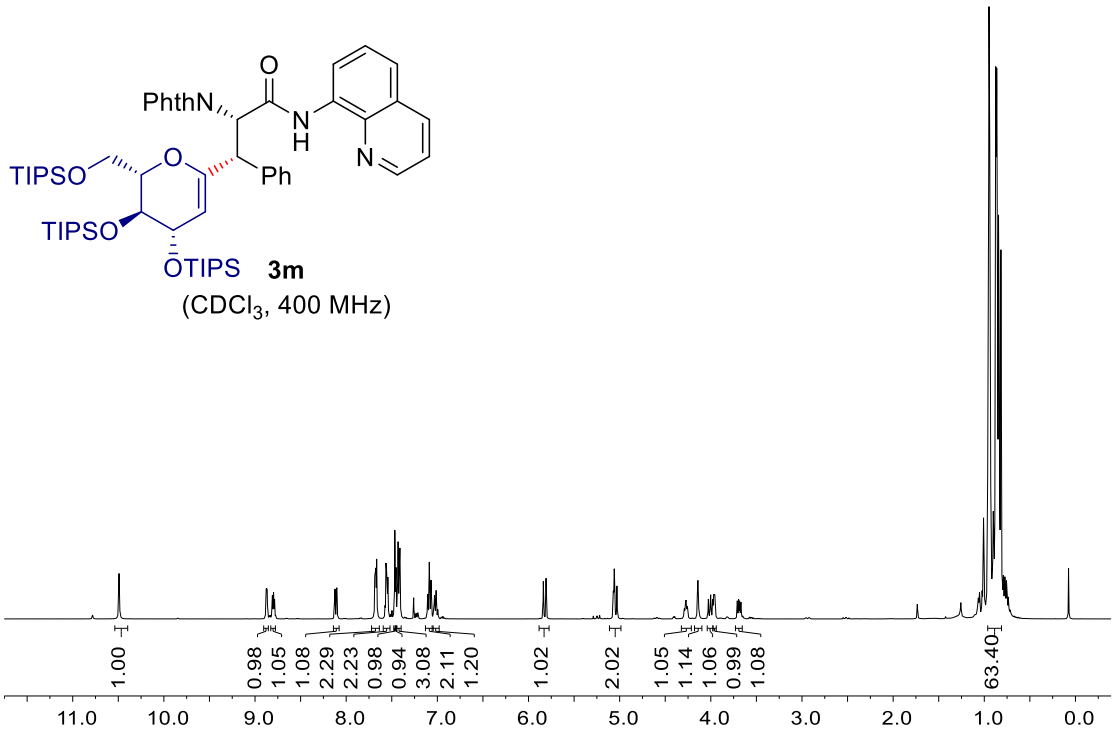

167.7
165.8
152.3
148.0
138.8
136.0
134.2
133.9
132.4
132.2
127.8
127.3
123.4
122.7
121.6
121.4
116.4
100.5
81.0
63.3
62.1
50.3
18.1
18.1
17.7
17.6
12.6
11.8
PhthN
O
N
H
N
TIPSO
O
TIPSO
3j'
(CDCl3, 101 MHz)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

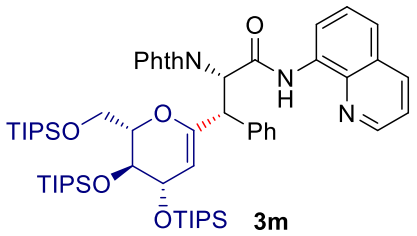

PhthN
O
N
H
N
D
D
TIPSO
O
TIPSO
OTIPS
3k
(CDCl3, 400 MHz)
1.00
1.90
1.00
2.07
2.08
1.97
1.06
0.97
1.02
1.01
0.98
1.11
1.99
21.46
21.33
21.04
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


167.87
166.81
148.90
148.23
138.52
136.12
134.02
133.82
132.09
127.79
127.21
123.42
121.82
121.53
116.76
98.99
81.15
69.36
66.19
62.18
52.81
18.15
18.10
18.01
17.96
17.94
12.41
12.34
12.02
PhthN
O
N
H
N
D
D
O
TIPSO
TIPSO
OTIPS
3k
(CDCl3, 101 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


PhthN
O
N
H
N
Me
O
TIPSO
OTIPS
3l
(CDCl3, 400 MHz)
1.00
1.10
1.04
1.09
2.02
2.12
1.02
0.95
1.09
1.07
1.04
1.06
1.06
1.06
1.04
1.05
3.18
21.47
21.57
11.0 10.5 10.0 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 0.0

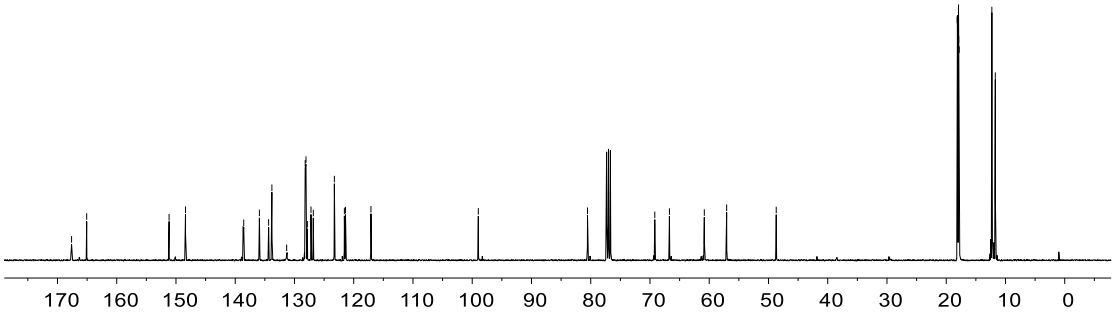

167.8
166.7
148.2
147.7
138.5
136.2
133.9
131.9
127.8
127.2
123.5
121.8
121.5
116.8
99.4
75.2
72.8
66.6
52.7
33.8
18.1
18.0
18.0
17.9
15.7
12.5
12.1
PhthN
O
N
H
N
Me
O
TIPSO
OTIPS
3l
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

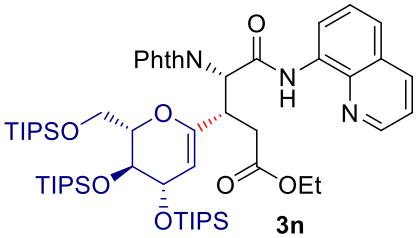

PhthN
O
N
H
N
Ph
TIPSO
O
TIPSO
OTIPS
3m
(CDCl3, 400 MHz)
1.00
0.98
1.05
1.08
2.29
2.23
0.98
0.94
3.08
2.11
1.20
1.02
2.02
1.05
1.14
1.06
0.99
1.08
63.40
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



3m

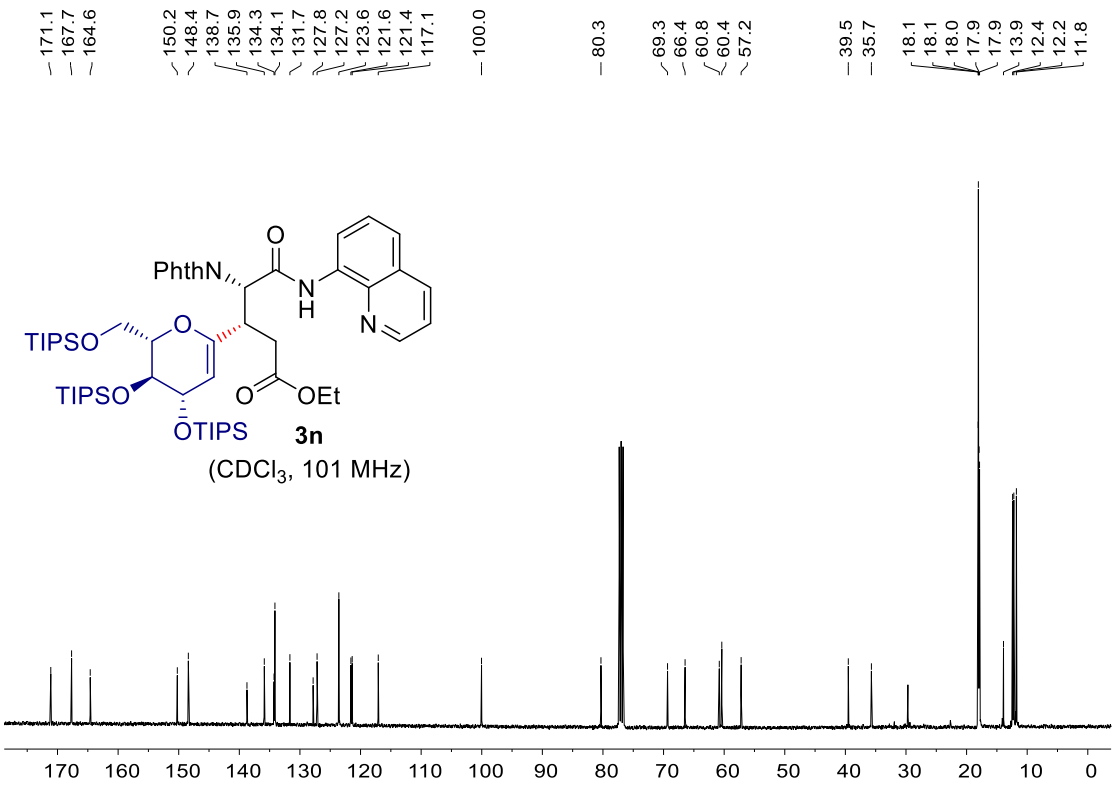
($CDCl_3$, 101 MHz)

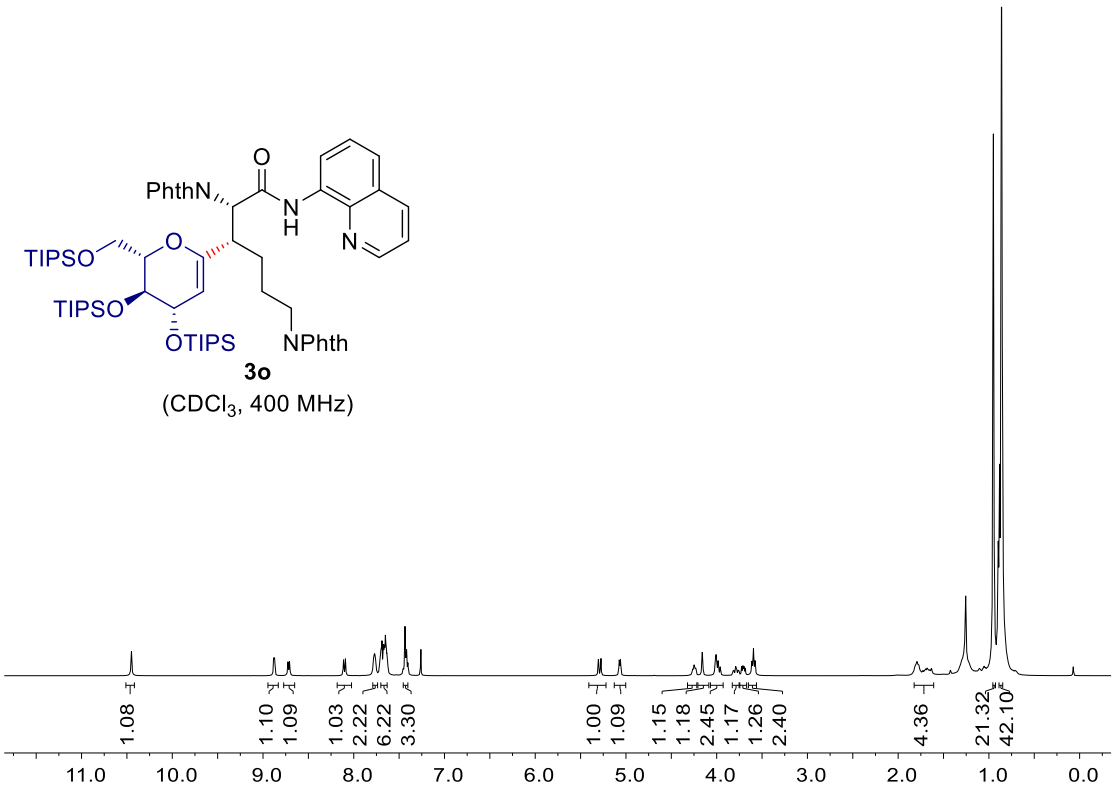


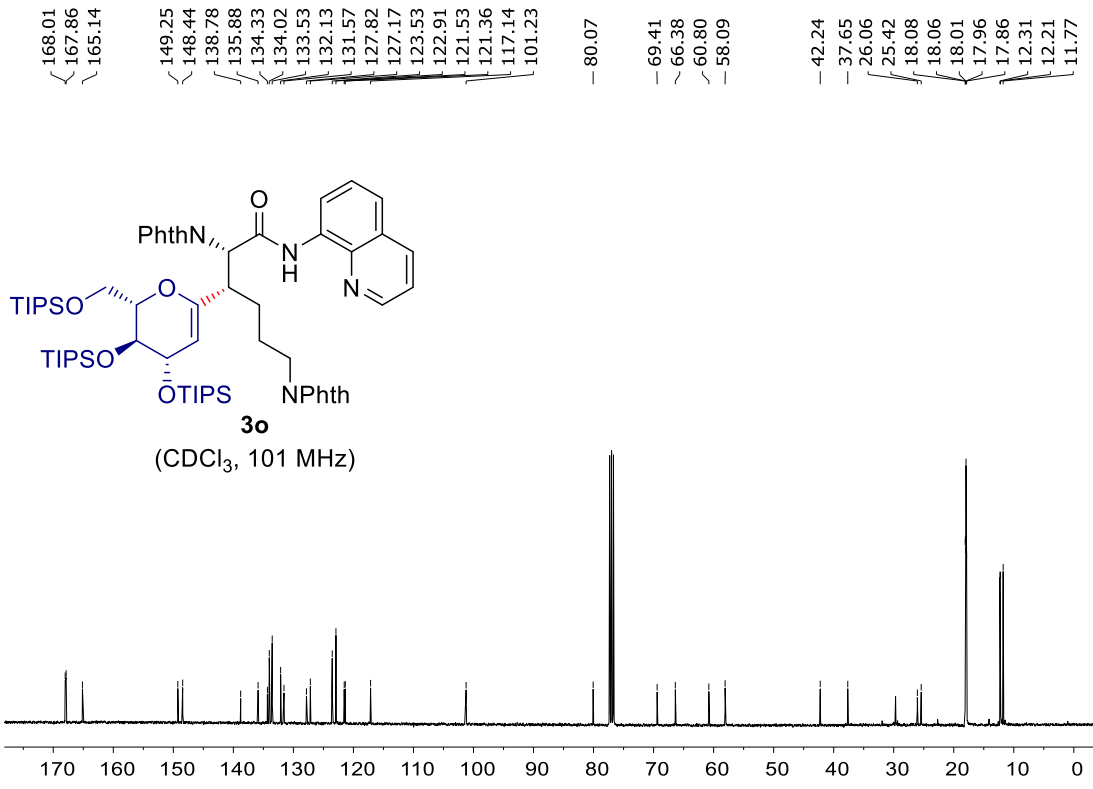


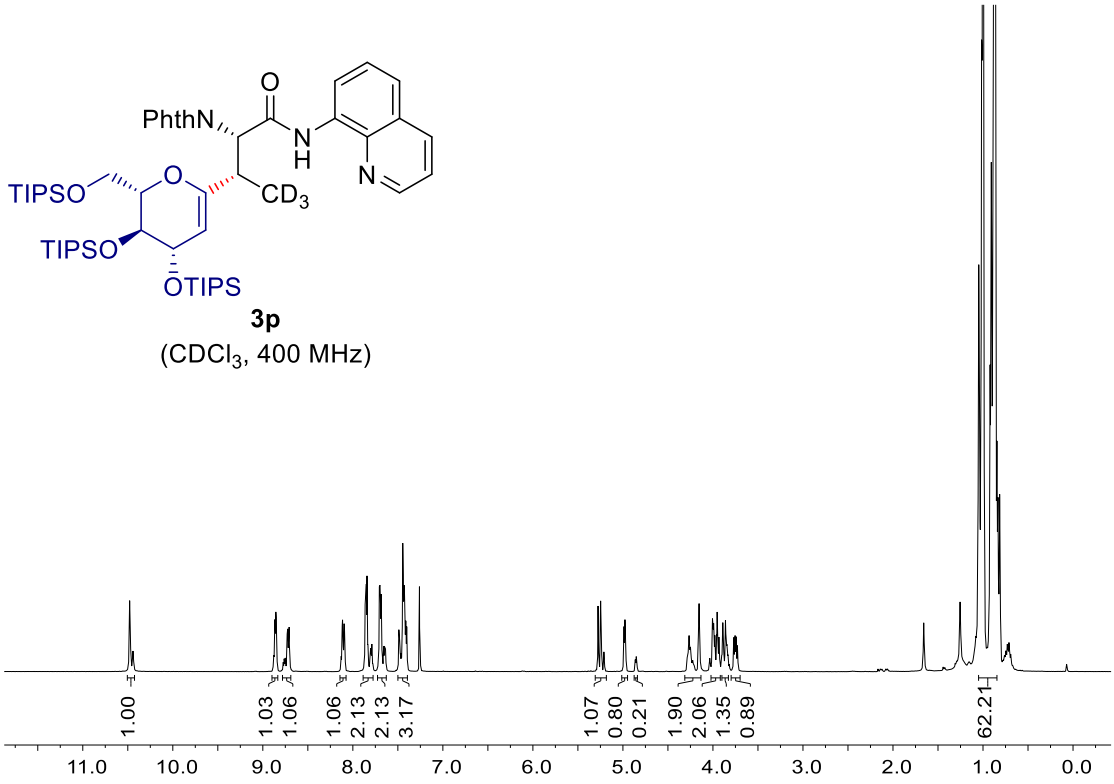
3n

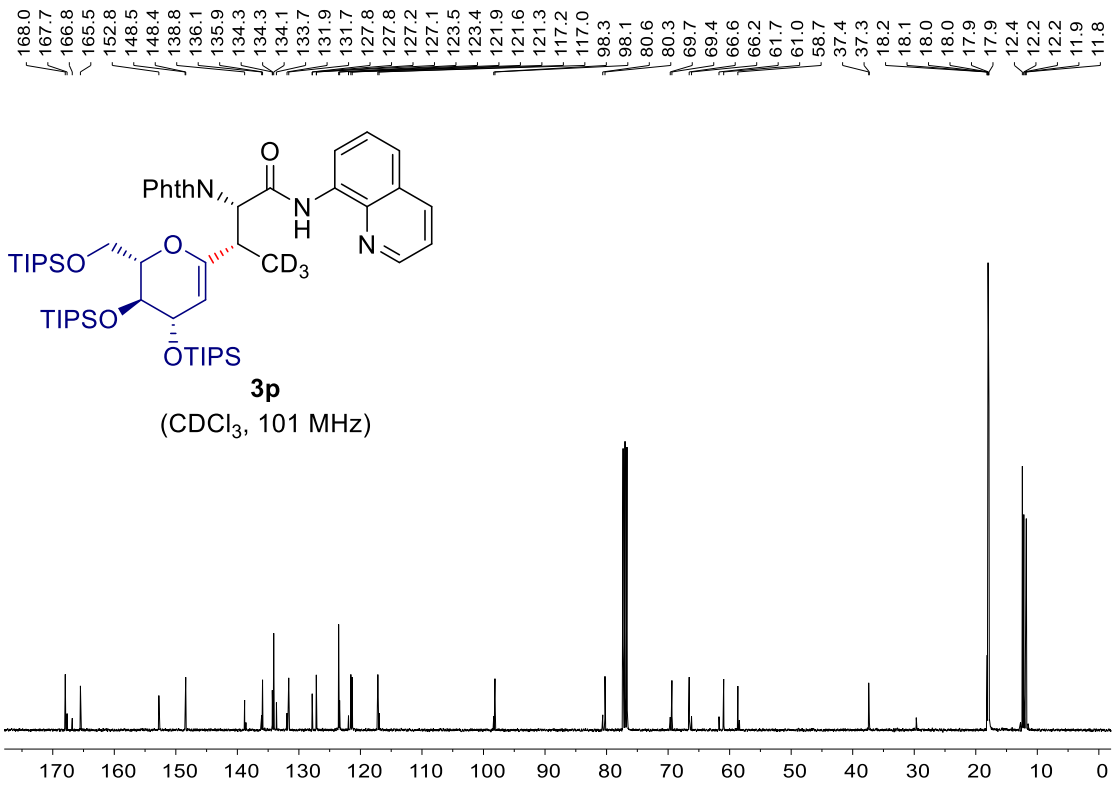
($CDCl_3$, 400 MHz)

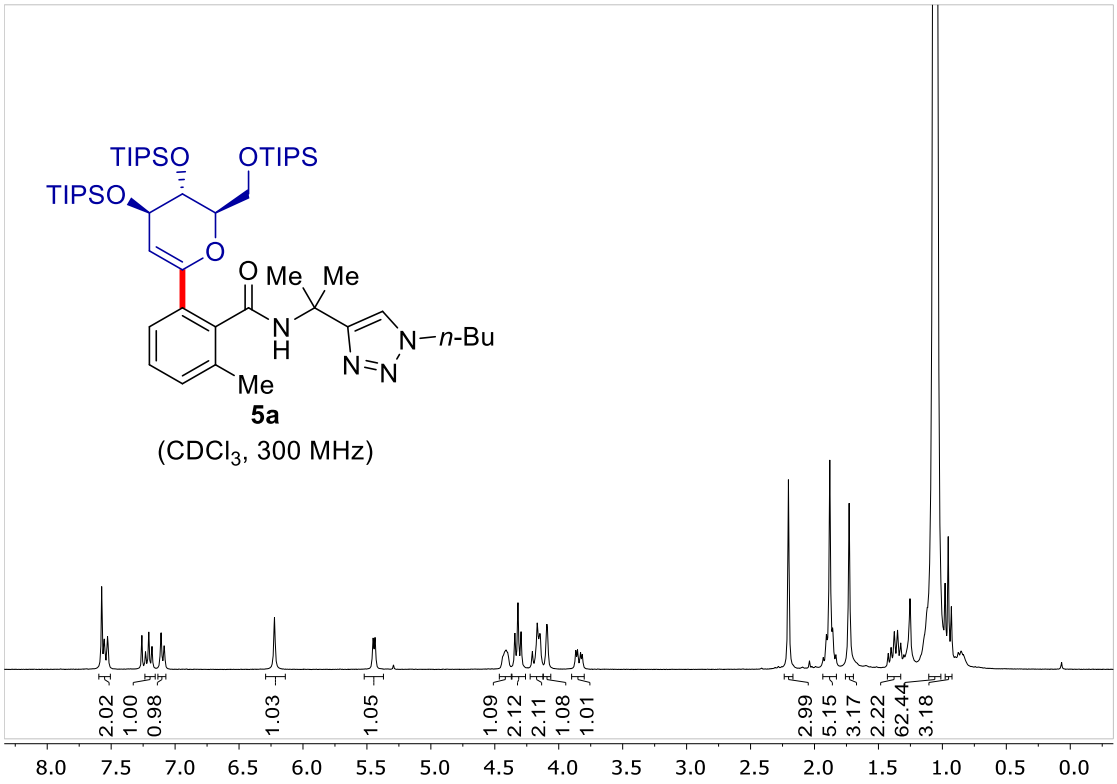

171.1
167.7
164.6
150.2
148.4
138.7
135.9
134.3
134.1
131.7
127.8
127.2
123.6
121.6
121.4
117.1
100.0
80.3
69.3
66.4
60.8
60.4
57.2
39.5
35.7
18.1
18.1
18.0
17.9
17.9
13.9
12.4
12.2
11.8
PhthN
O
N
H
N
TIPSO
O
TIPSO
O
OEt
OTIPS
3n
(CDCl3, 101 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

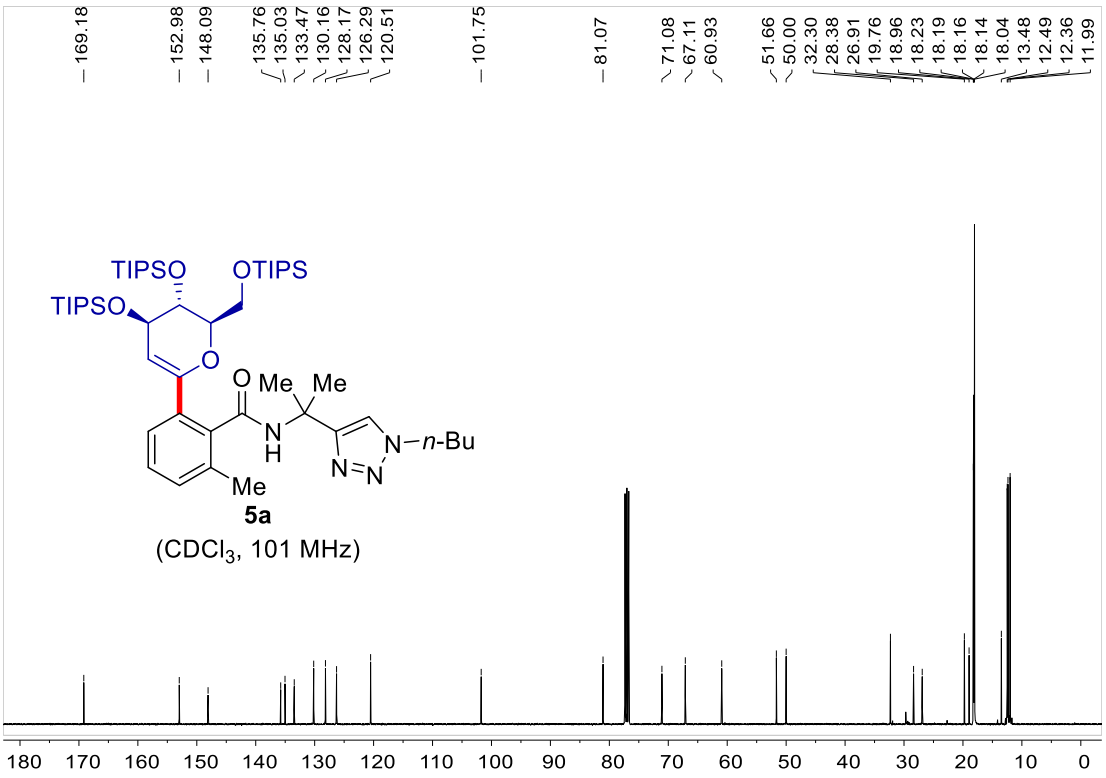

PhthN
O
N
H
N
TIPSO
O
TIPSO
OTIPS
NPhth
3o
(CDCl3, 400 MHz)
1.08
1.10
1.09
1.03
2.22
6.22
3.30
1.00
1.09
1.15
1.18
2.45
1.17
1.26
2.40
4.36
21.32
42.10
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

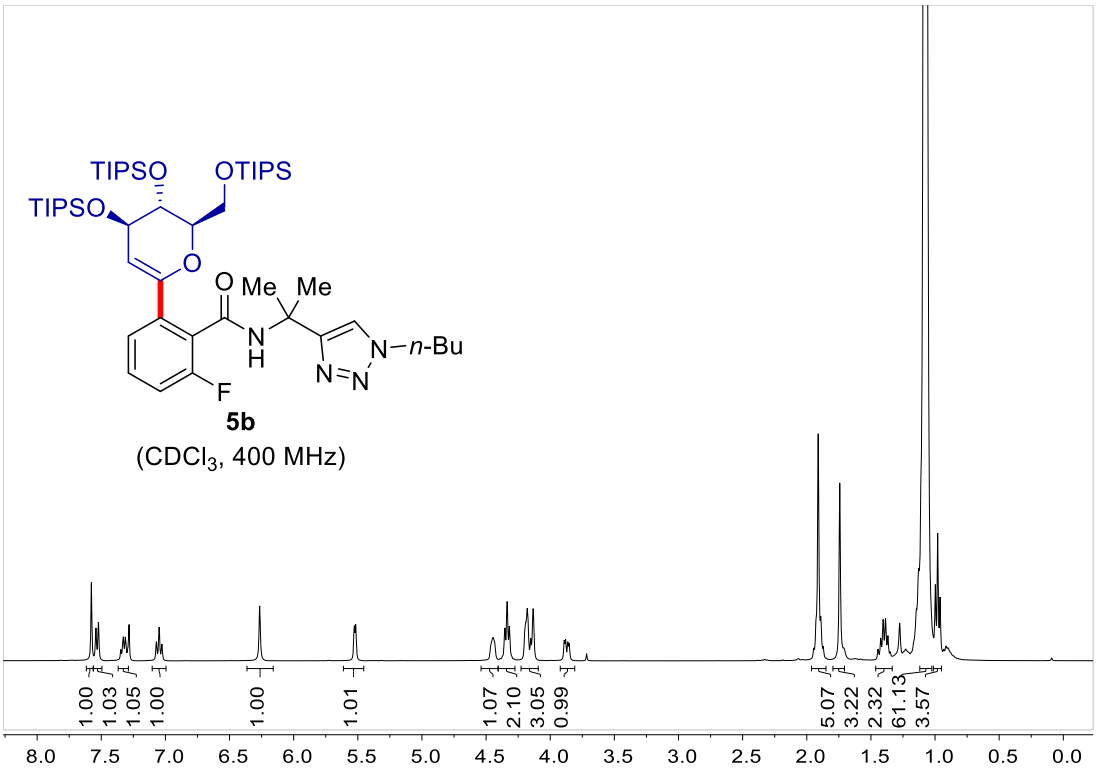

168.01
167.86
165.14
149.25
148.44
138.78
135.88
134.33
134.02
133.53
132.13
131.57
127.82
127.17
123.53
122.91
121.53
121.36
117.14
101.23
80.07
69.41
66.38
60.80
58.09
42.24
37.65
26.06
25.42
18.08
18.06
18.01
17.96
17.86
12.31
12.21
11.77
PhthN
O
N
H
N
TIPSO
O
TIPSO
OTIPS
NPhth
3o
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

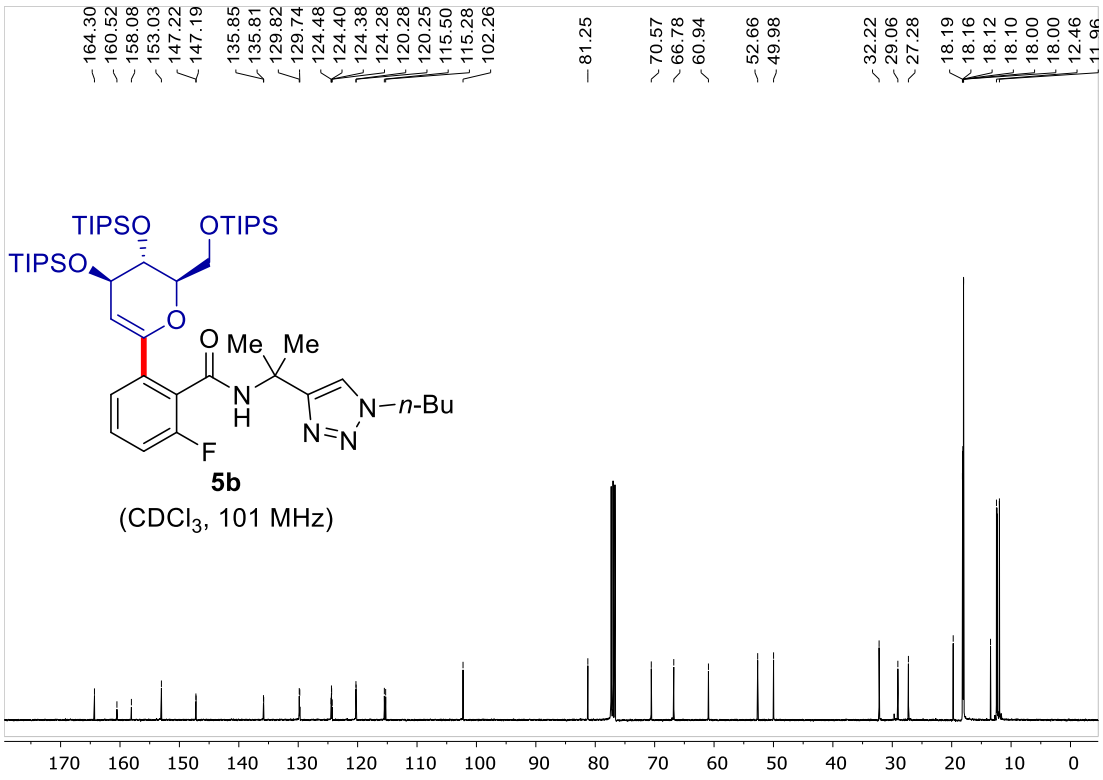

PhthN
O
N
H
N
TIPSO
O
CD3
TIPSO
OTIPS
3p
(CDCl3, 400 MHz)
1.00
1.03
1.06
1.06
2.13
2.13
3.17
1.07
0.80
0.21
1.90
2.06
1.35
0.89
62.21
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


168.0
167.7
166.8
165.5
152.8
148.5
148.4
138.8
136.1
135.9
134.3
134.3
134.1
133.7
131.9
131.7
127.8
127.8
127.2
127.1
123.5
123.4
121.9
121.6
121.3
117.2
117.0
98.3
98.1
80.6
80.3
69.7
69.4
66.6
66.2
61.7
61.0
58.7
37.4
37.3
18.2
18.1
18.0
18.0
17.9
17.9
12.4
12.2
12.2
11.9
11.8
PhthN
O
N
H
N
TIPSO
O
CD3
TIPSO
OTIPS
3p
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


TIPSO
OTIPS
TIPSO
O
O
Me
Me
N
H
N
N
n-Bu
Me
5a
(CDCl3, 300 MHz)
2.02
1.00
0.98
1.03
1.05
1.09
2.12
2.11
1.08
1.01
2.99
5.15
3.17
2.22
62.44
3.18
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
0.0

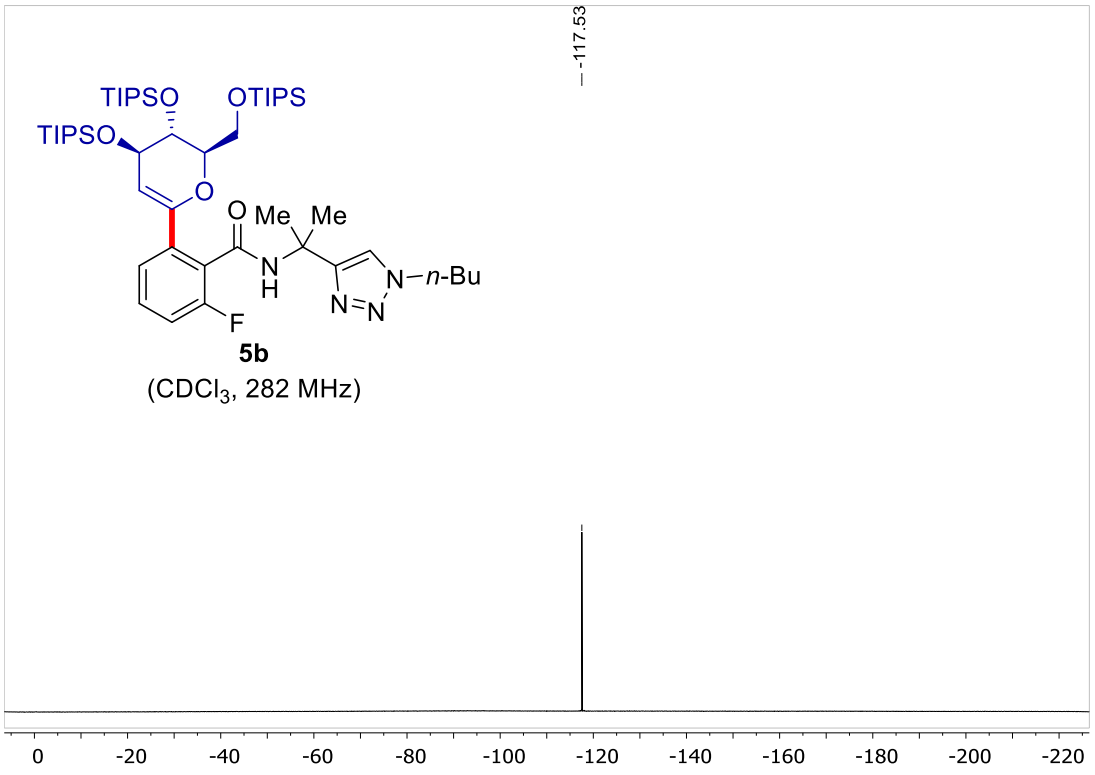

169.18
152.98
148.09
135.76
135.03
133.47
130.16
128.17
126.29
120.51
101.75
81.07
71.08
67.11
60.93
51.66
50.00
32.30
28.38
26.91
19.76
18.96
18.23
18.19
18.16
18.14
18.04
13.48
12.49
12.36
11.99
TIPSO
OTIPS
TIPSO
O
O
Me
Me
N
H
N
N
N–n-Bu
Me
5a
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


TIPSO
OTIPS
TIPSO
O
O
Me
Me
N
H
N
N
N–n-Bu
F
5b
(CDCl3, 400 MHz)
1.00
1.03
1.05
1.00
1.00
1.01
1.07
2.10
3.05
0.99
5.07
3.22
2.32
61.13
3.57
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
0.0



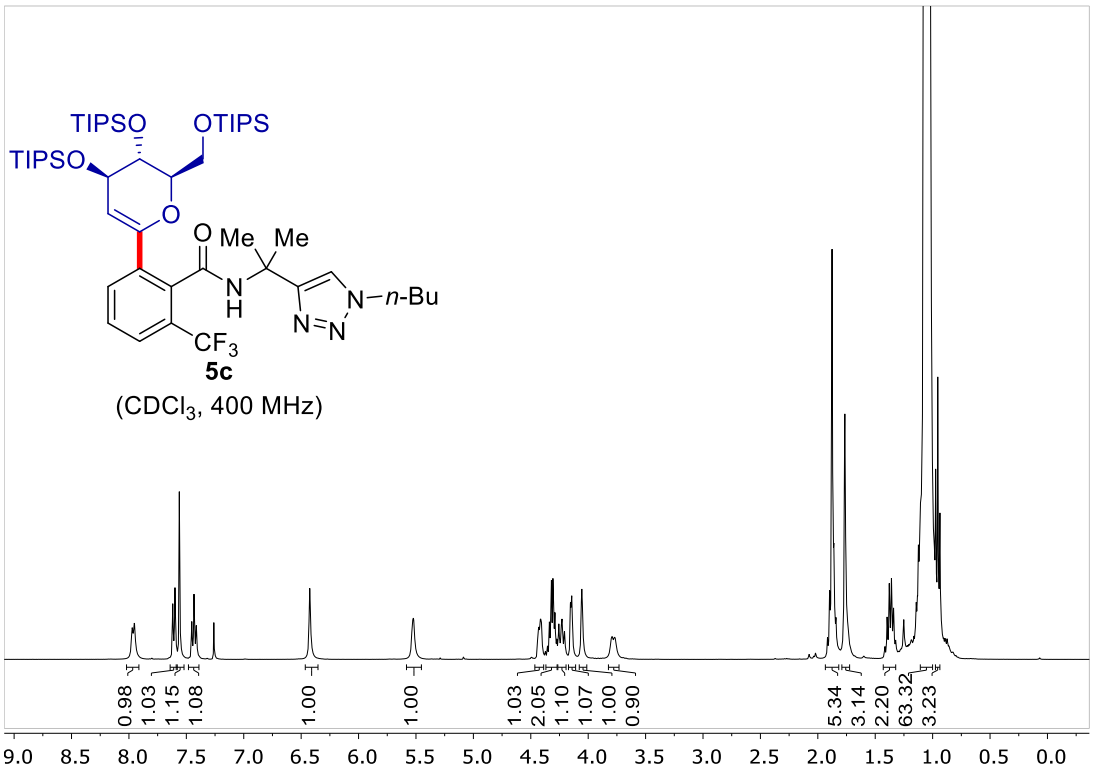
5b

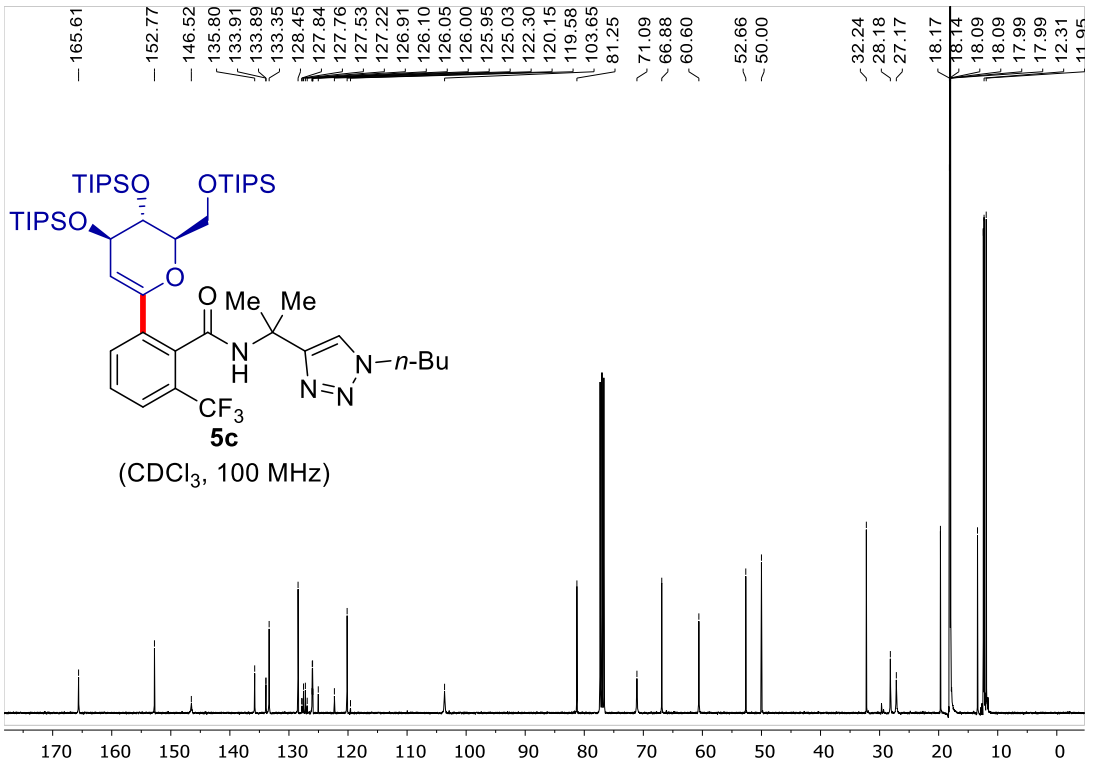
($CDCl_3$, 101 MHz)

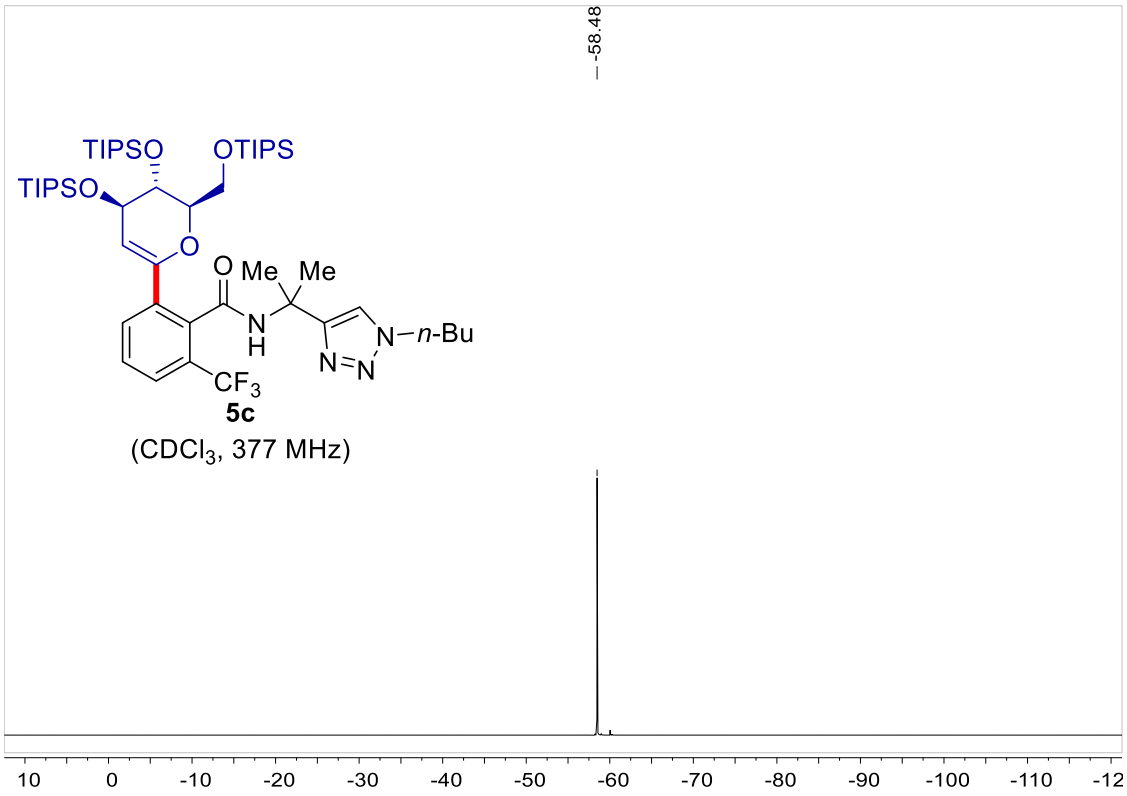


5b

($CDCl_3$, 282 MHz)

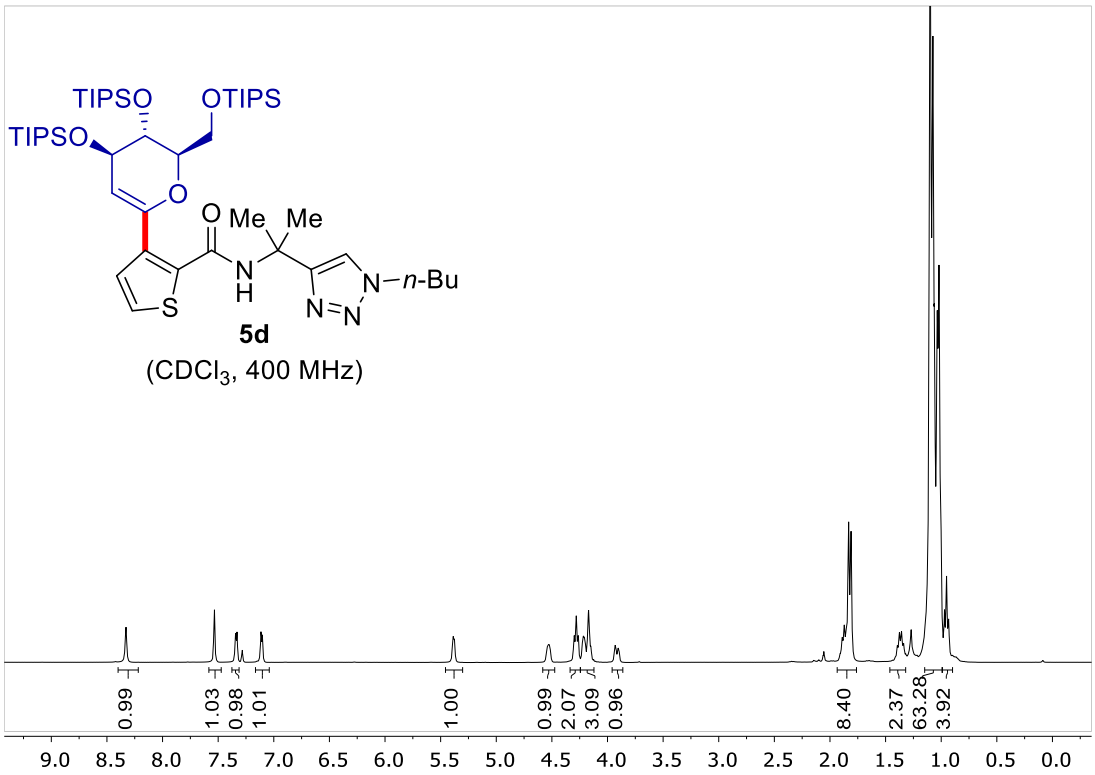

TIPSO
OTIPS
TIPSO
O
O Me Me
N
H
N
N=N
N–n-Bu
CF3
5c
(CDCl3, 400 MHz)
0.98 1.03 1.15 1.08 1.00 1.00 1.03 2.05 1.10 1.07 1.00 0.90 5.34 3.14 2.20 63.32 3.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


165.61 152.77 146.52 135.80 133.91 133.89 133.35 128.45 127.84 127.76 127.53 127.22 126.91 126.10 126.05 126.00 125.95 125.03 122.30 120.15 119.58 103.65 81.25 71.09 66.88 60.60 52.66 50.00 32.24 28.18 27.17 18.17 18.14 18.09 18.09 17.99 17.99 12.31 11.95
TIPSO
OTIPS
TIPSO
O
O Me Me
N
H
N
N=N
N–n-Bu
CF3
5c
(CDCl3, 100 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



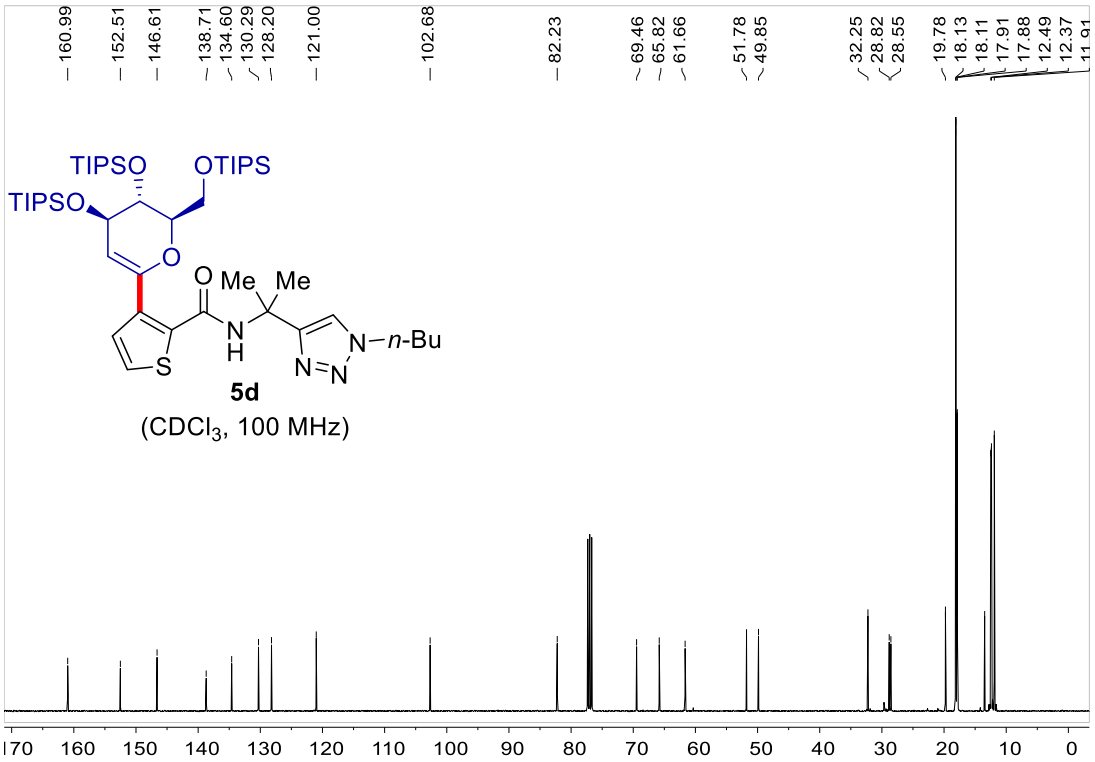
5c

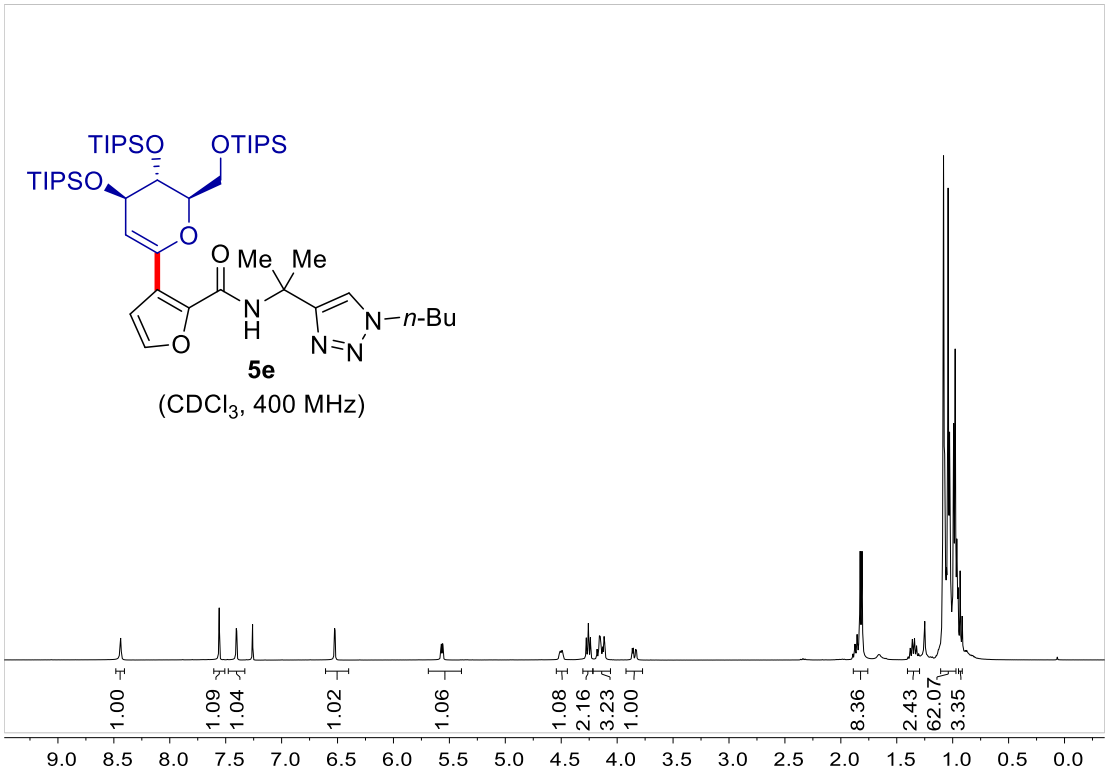
($CDCl_3$, 377 MHz)

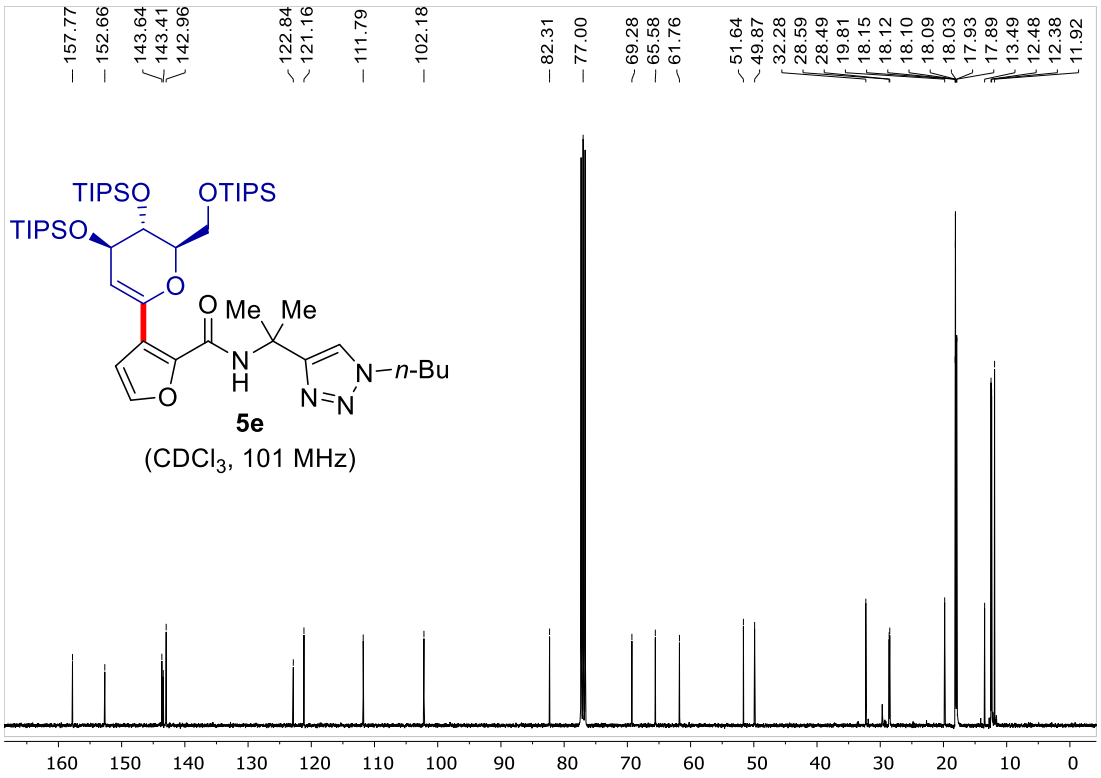


5d

($CDCl_3$, 400 MHz)

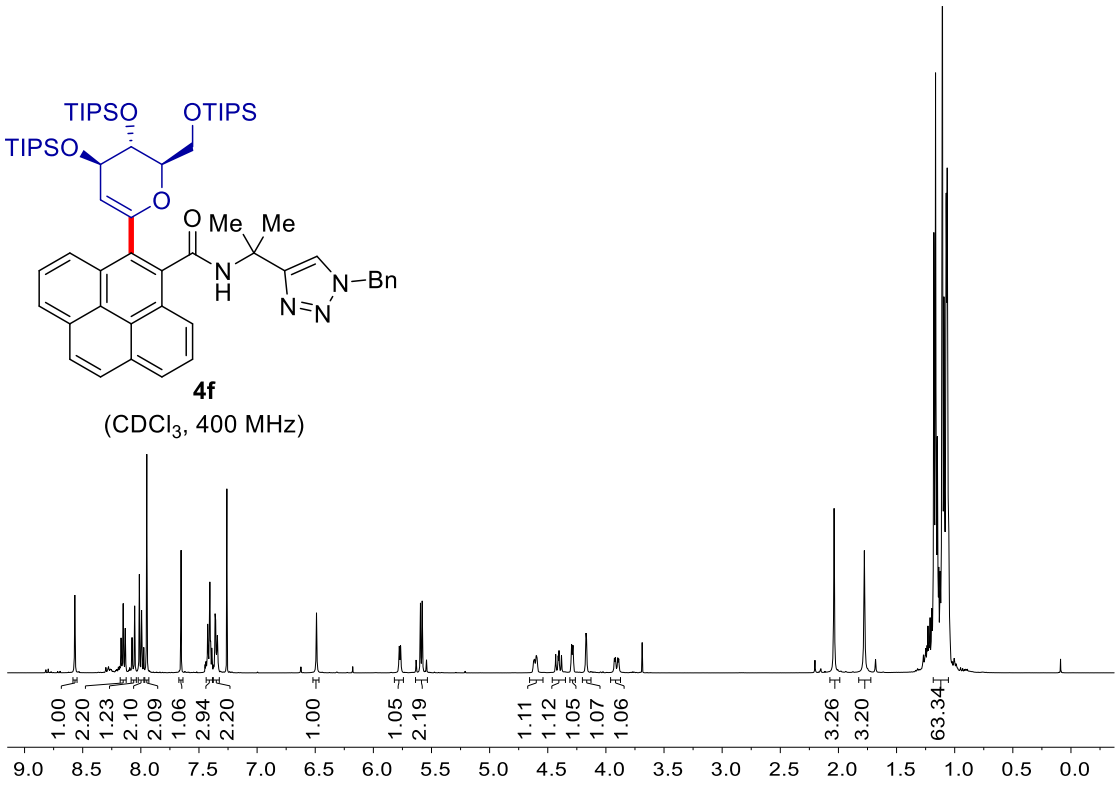

160.99
152.51
146.61
138.71
134.60
130.29
128.20
121.00
102.68
82.23
69.46
65.82
61.66
51.78
49.85
32.25
28.82
28.55
19.78
18.13
18.11
17.91
17.88
12.49
12.37
11.91
TIPSO
OTIPS
TIPSO
O
O
Me
Me
N
H
N
N
N–n-Bu
S
5d
(CDCl3, 100 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


TIPSO
OTIPS
TIPSO
O
O
Me
Me
N
H
N
N
N–n-Bu
O
5e
(CDCl3, 400 MHz)
1.00
1.09
1.04
1.02
1.06
1.08
2.16
3.23
1.00
8.36
2.43
62.07
3.35
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
0.0



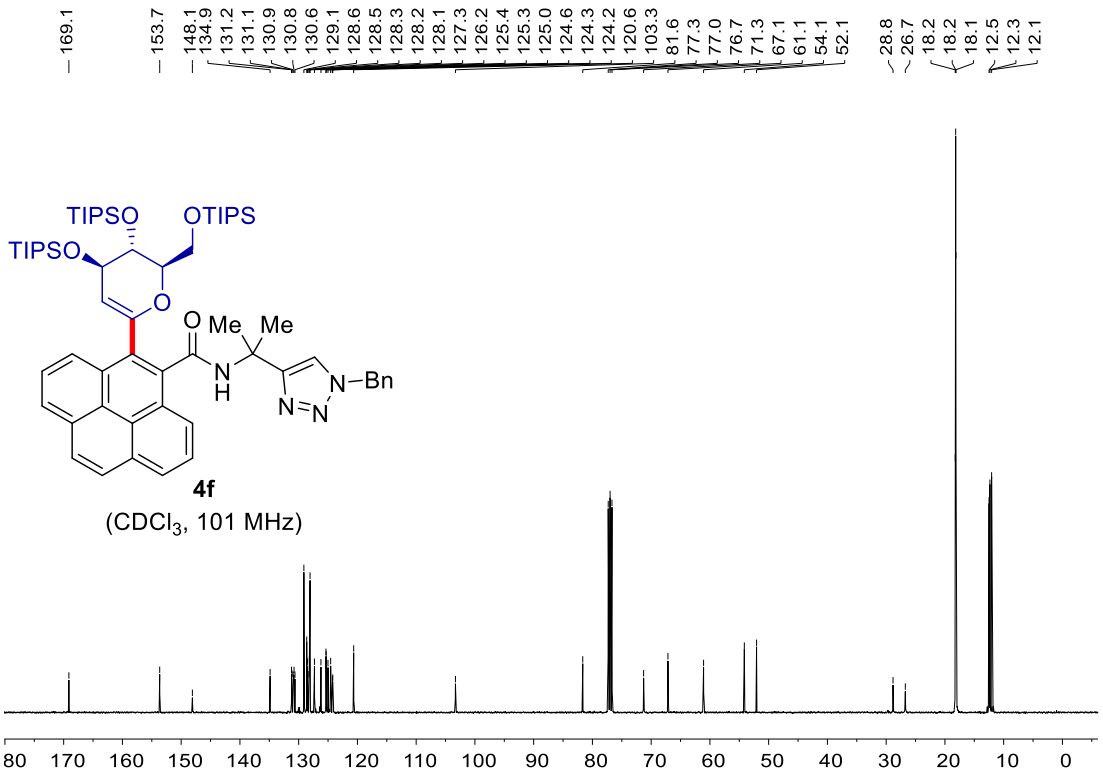
5e

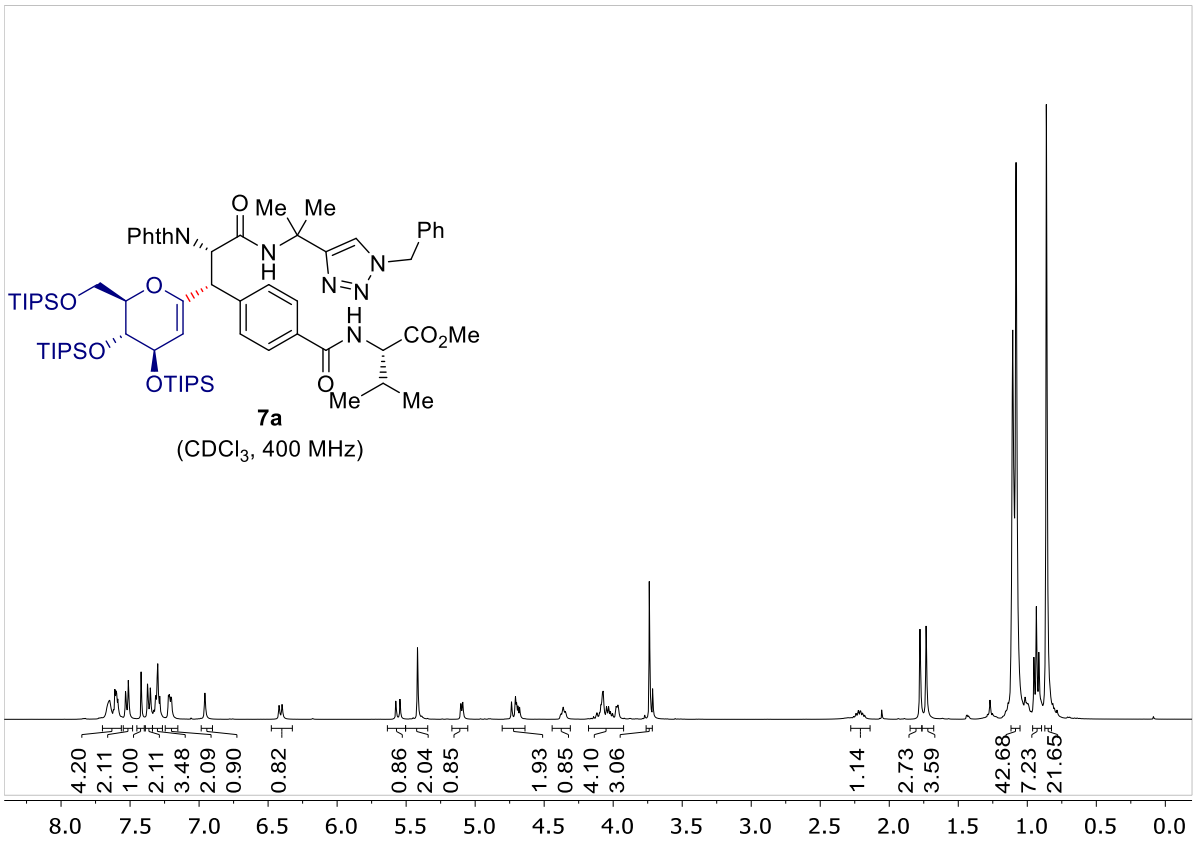
($CDCl_3$, 101 MHz)

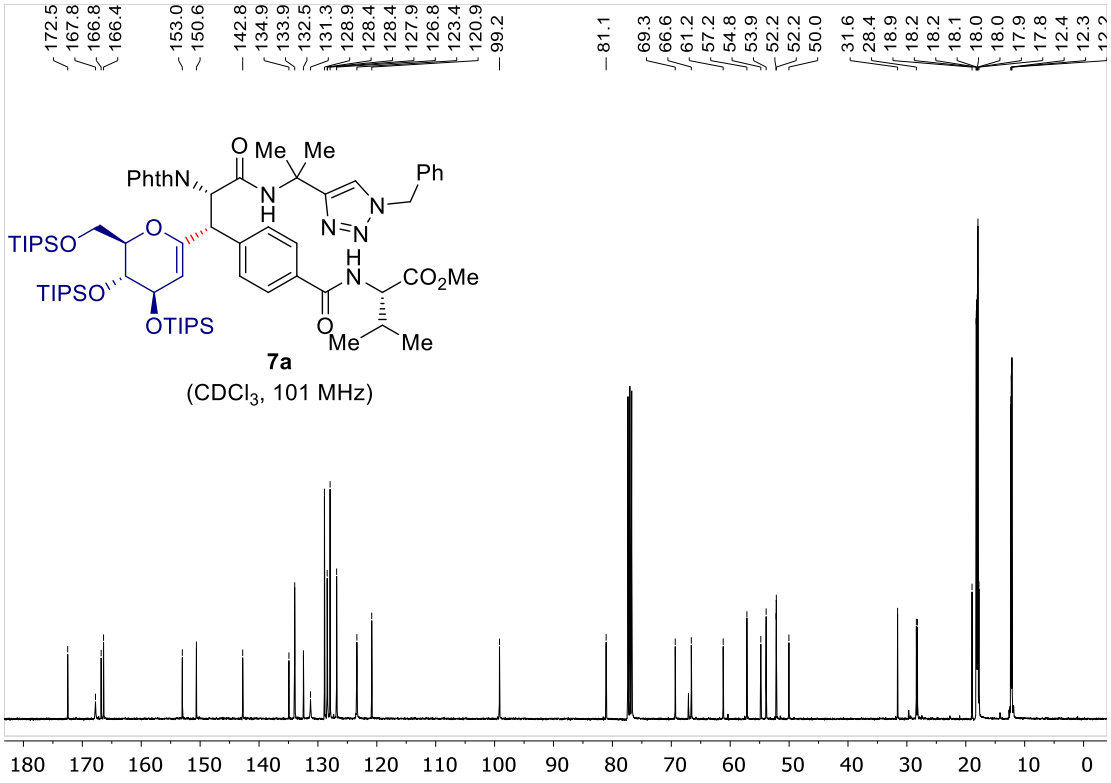


4f

($CDCl_3$, 400 MHz)

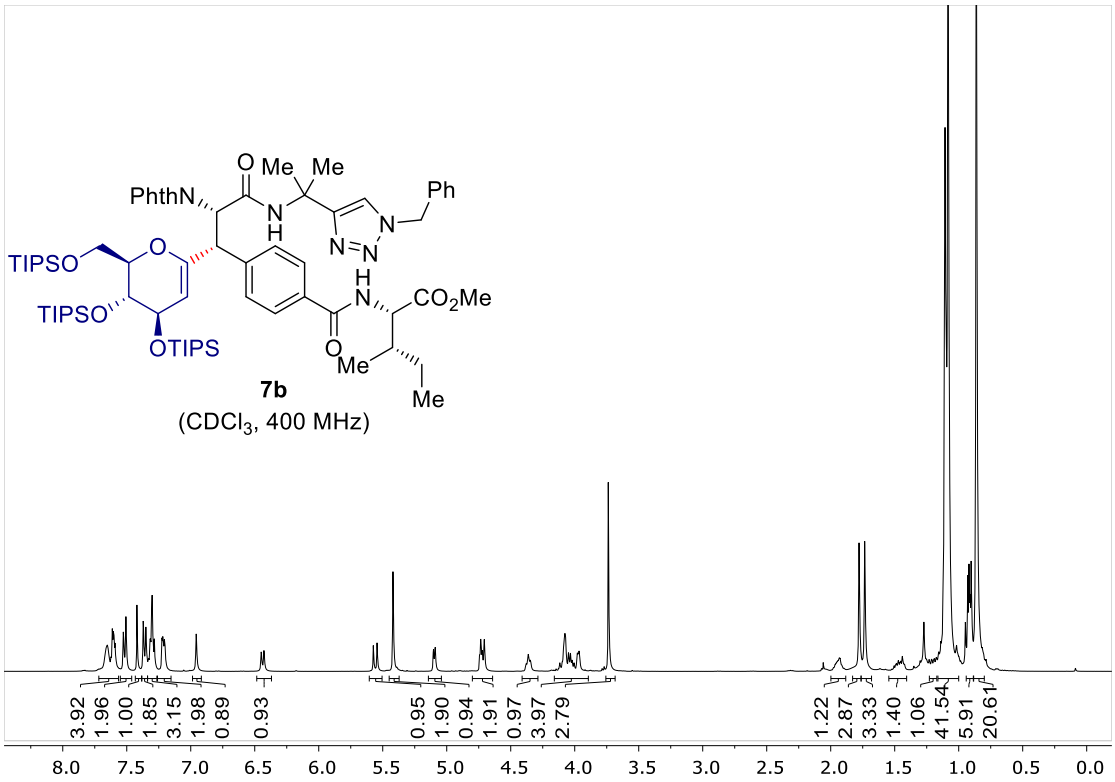

169.1
153.7
148.1
134.9
131.2
131.1
130.9
130.8
130.6
129.1
128.6
128.5
128.3
128.2
128.1
127.3
126.2
125.4
125.3
125.0
124.6
124.3
124.2
120.6
103.3
81.6
77.3
77.0
76.7
71.3
67.1
61.1
54.1
52.1
28.8
26.7
18.2
18.2
18.1
12.5
12.3
12.1
TIPSO
OTIPS
TIPSO
O
O Me Me
N
H
N
N=N
N–Bn
4f
(CDCl3, 101 MHz)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


O Me Me
PhthN
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
H
N
CO2Me
O
Me
Me
7a
(CDCl3, 400 MHz)
4.20
2.11
1.00
2.11
3.48
2.09
0.90
0.82
0.86
2.04
0.85
1.93
0.85
4.10
3.06
1.14
2.73
3.59
42.68
7.23
21.65
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 0.0



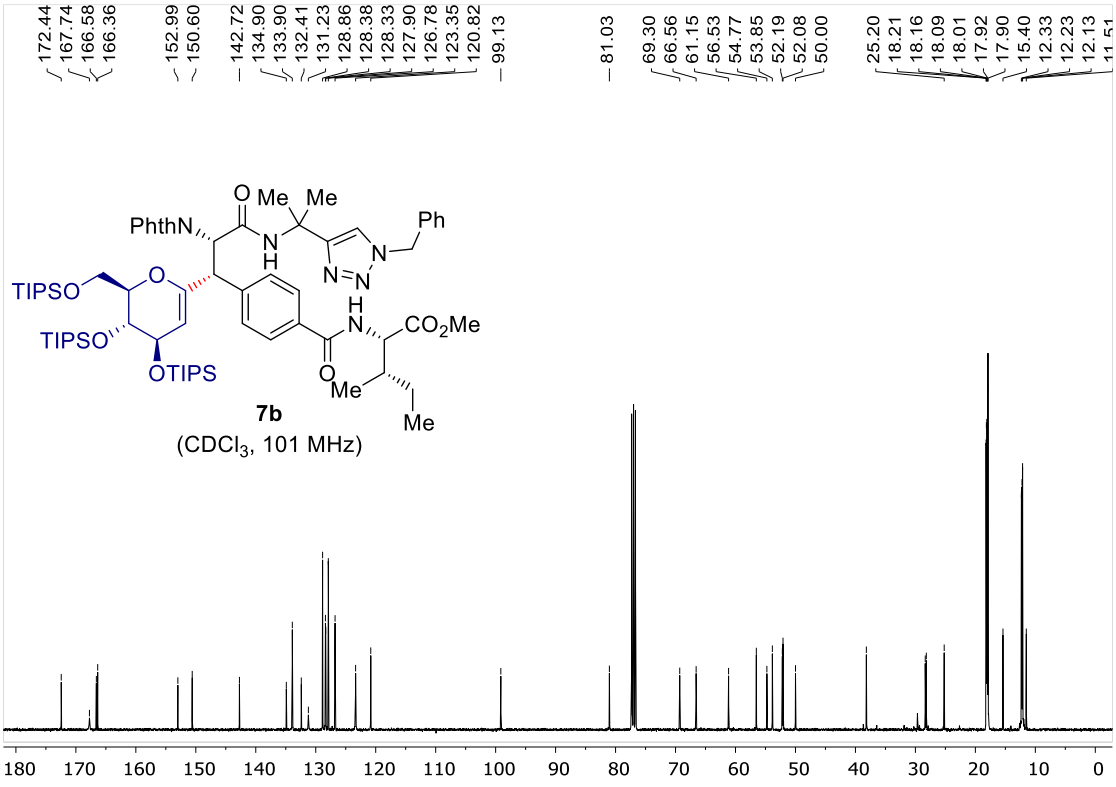
7a

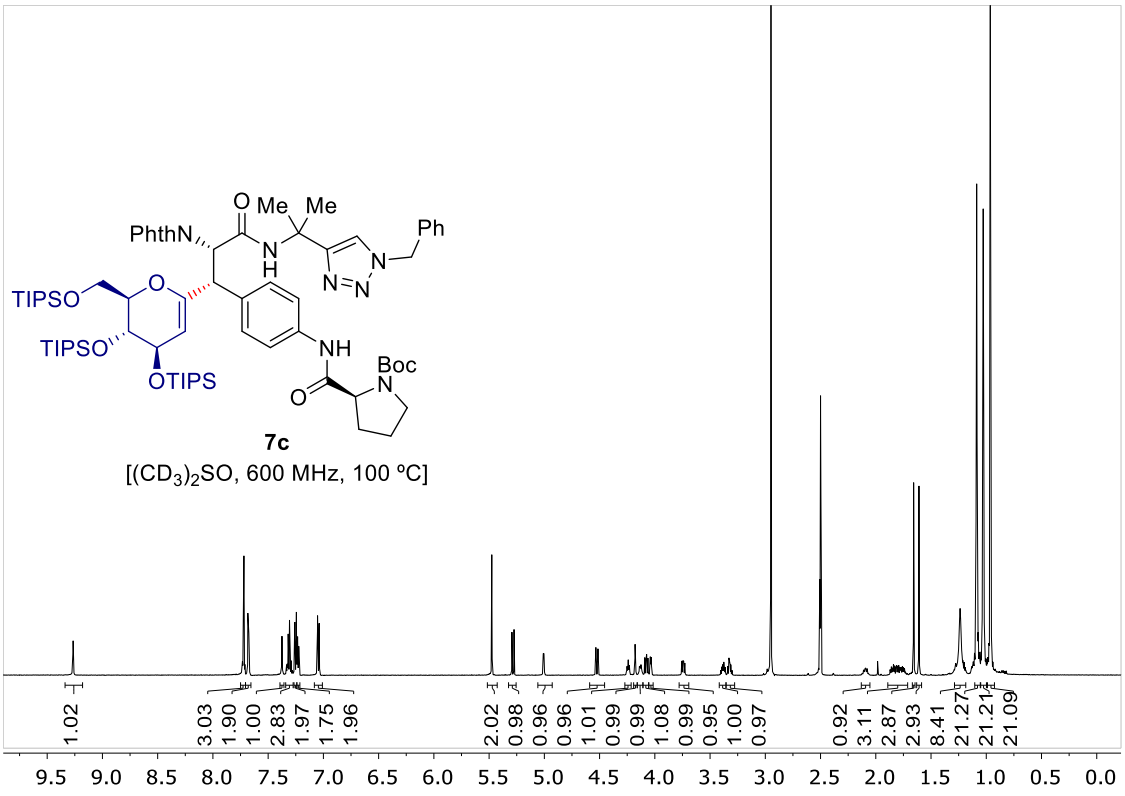
($CDCl_3$, 101 MHz)

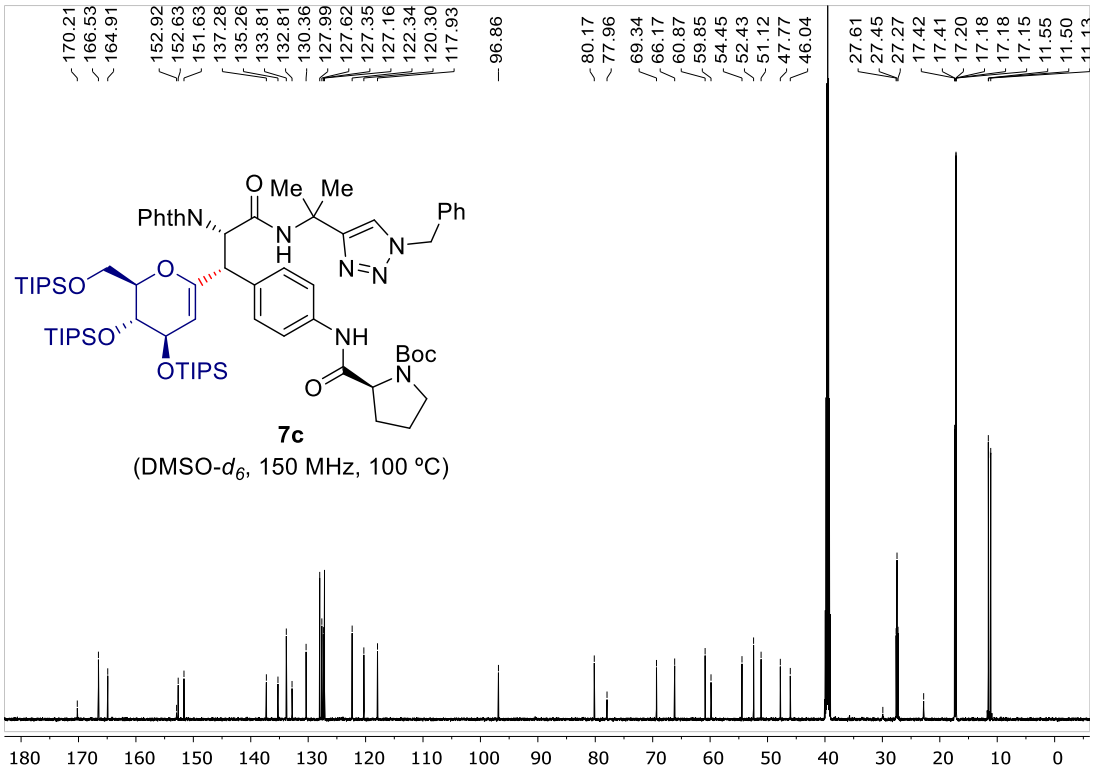


7b

($CDCl_3$, 400 MHz)

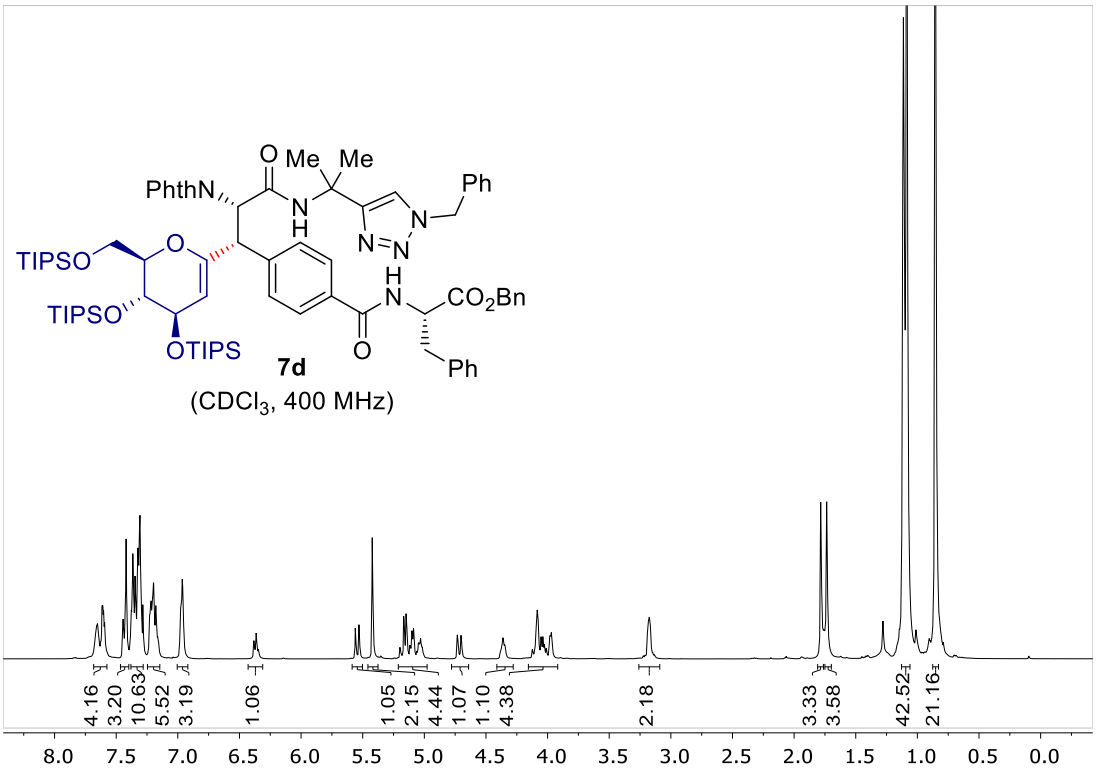

172.44
167.74
166.58
166.36
152.99
150.60
142.72
134.90
133.90
132.41
131.23
128.86
128.38
128.33
127.90
126.78
123.35
120.82
99.13
81.03
69.30
66.56
61.15
56.53
54.77
53.85
52.19
52.08
50.00
25.20
18.21
18.16
18.09
18.01
17.92
17.90
15.40
12.33
12.23
12.13
PhthN
O
Me
Me
N
H
Ph
N
N
TIPSO
O
TIPSO
OTIPS
H
N
CO2Me
O
Me
Me
7b
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


PhthN
O
Me
Me
N
H
Ph
N
N
TIPSO
O
TIPSO
OTIPS
NH
Boc
N
O
7c
[(CD3)2SO, 600 MHz, 100 °C]
1.02
3.03
1.90
1.00
2.83
1.97
1.75
1.96
2.02
0.98
0.96
0.96
1.01
0.99
0.99
1.08
0.99
0.95
1.00
0.97
0.92
3.11
2.87
2.93
8.41
21.27
21.21
21.09
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
0.0



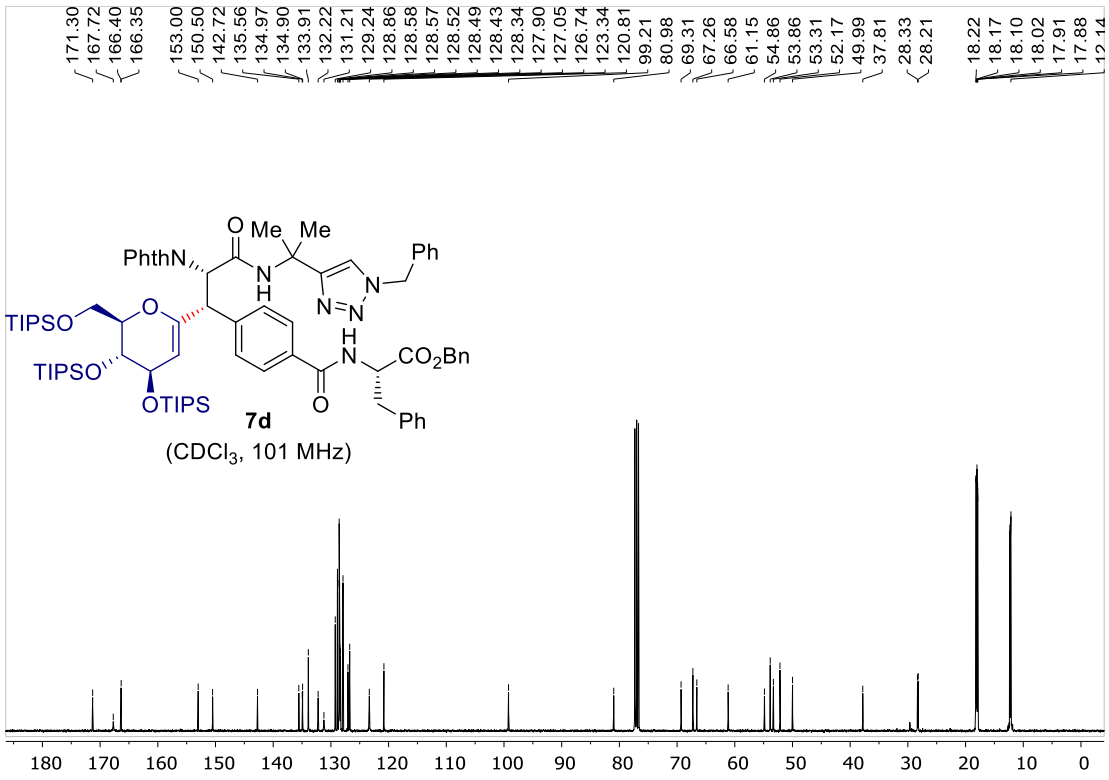
7c

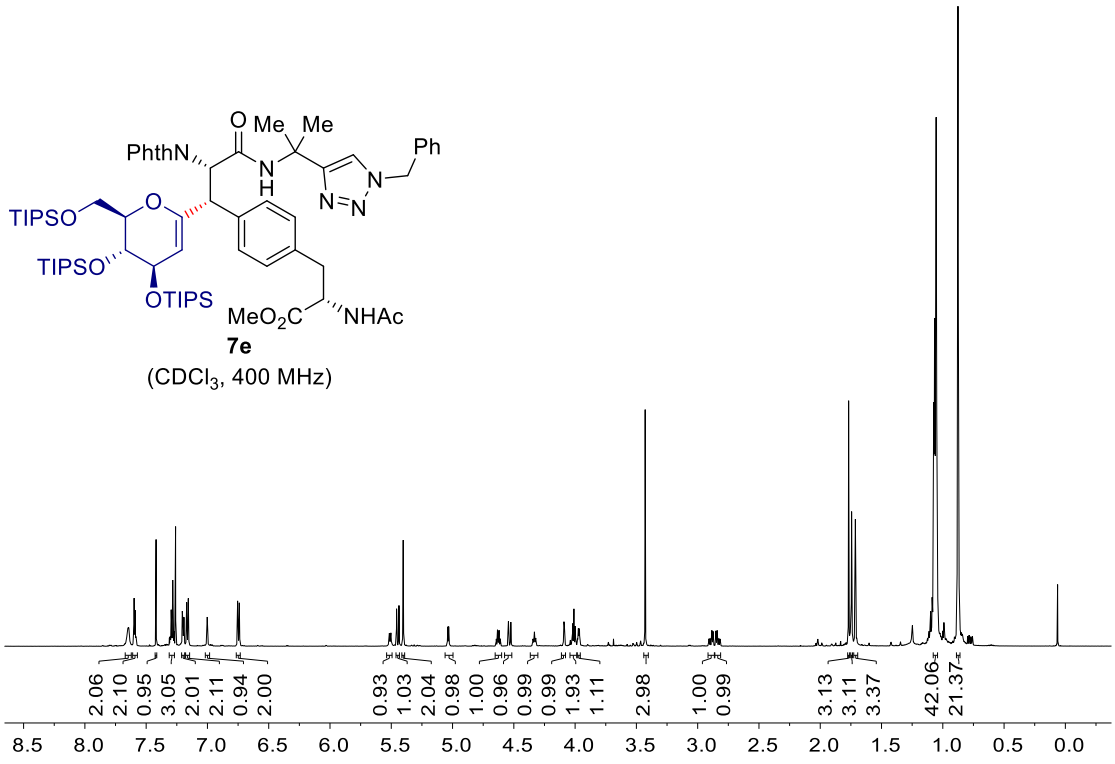
(DMSO-d_6, 150 MHz, 100 ºC)

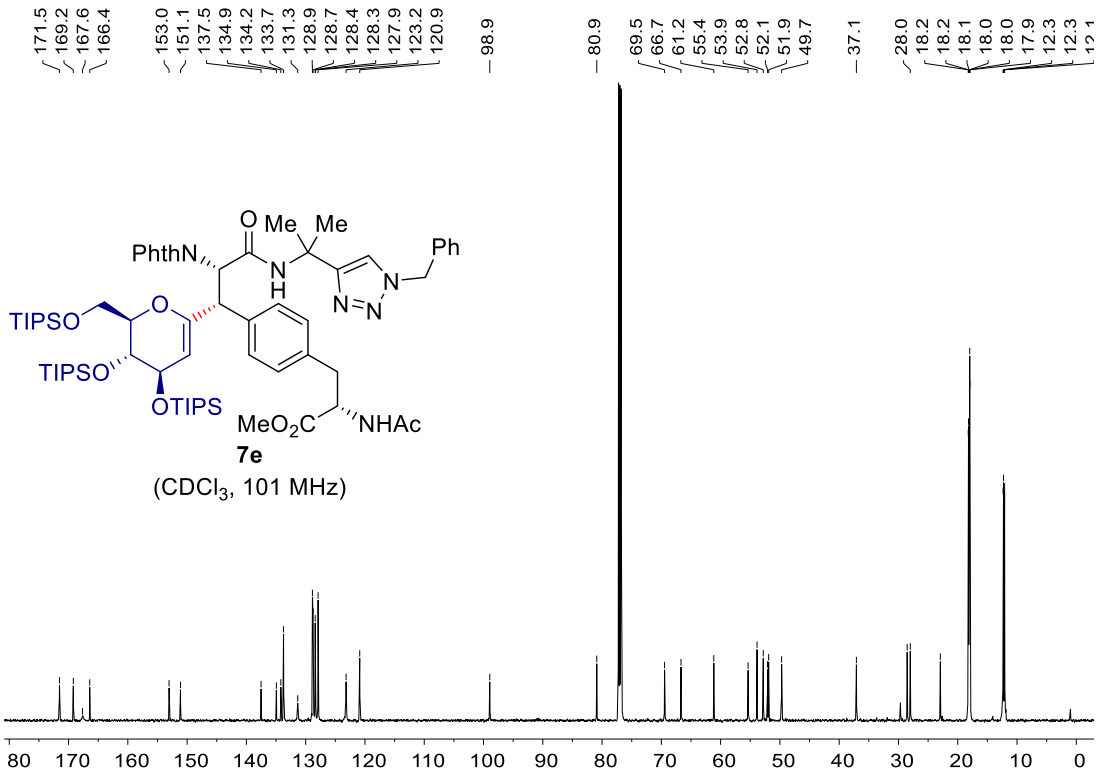


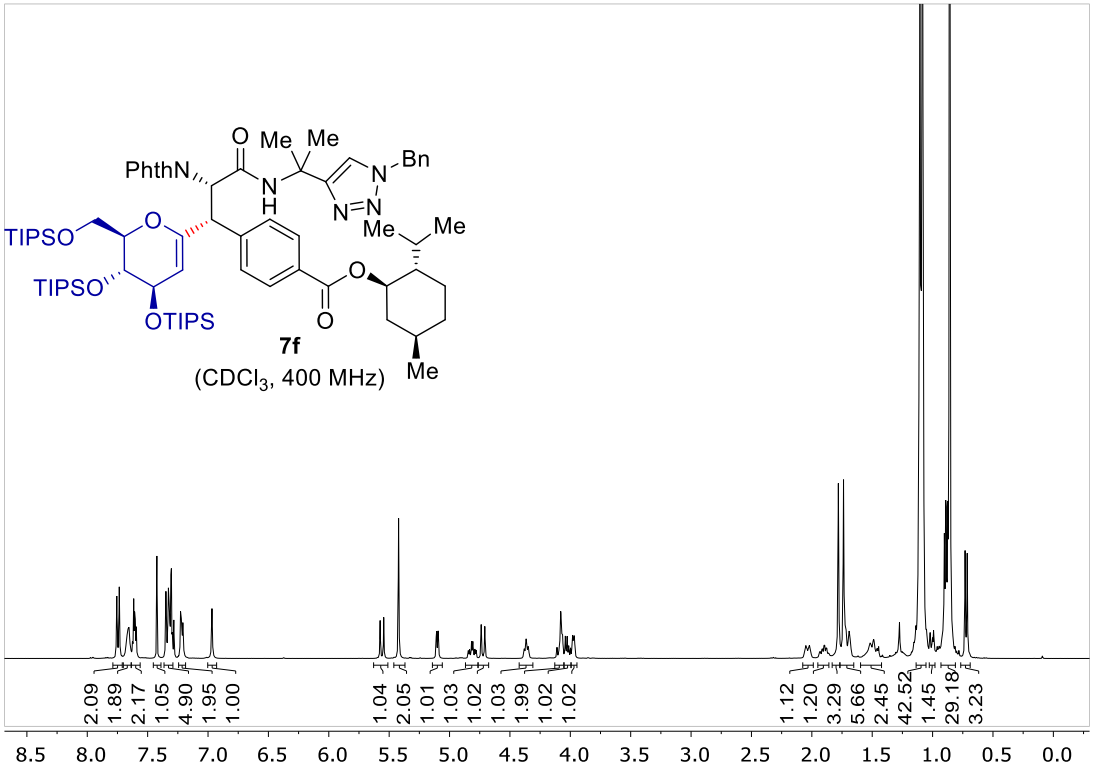
7d

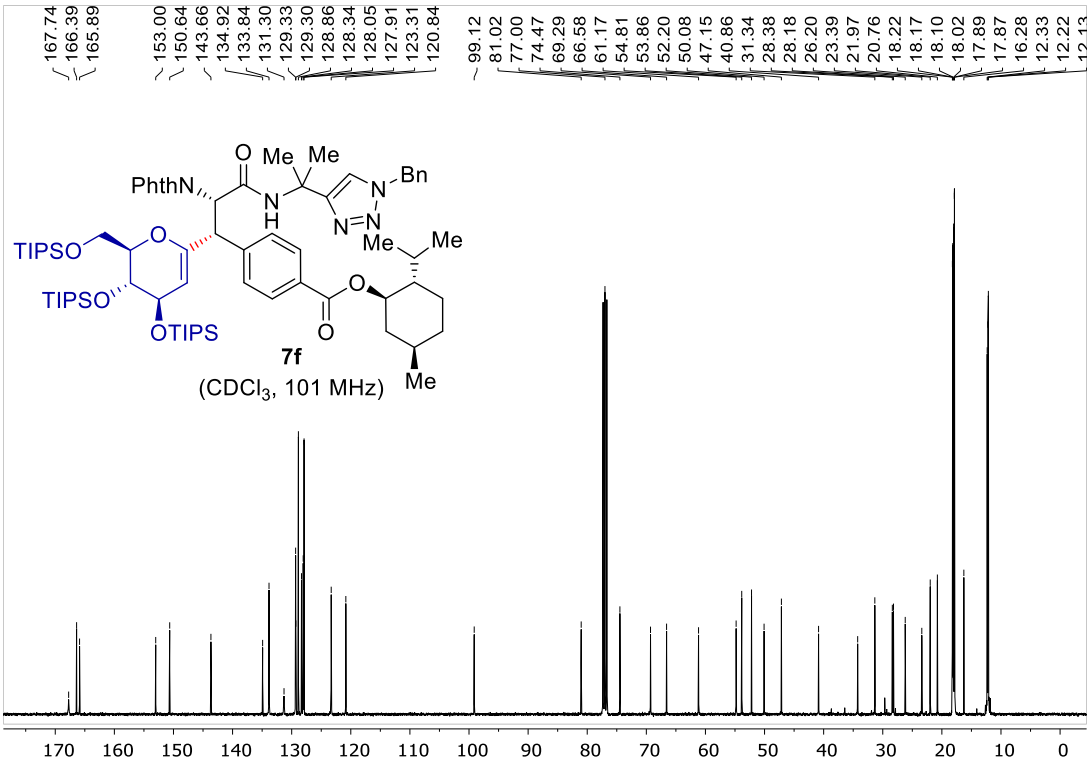
($CDCl_3$, 400 MHz)

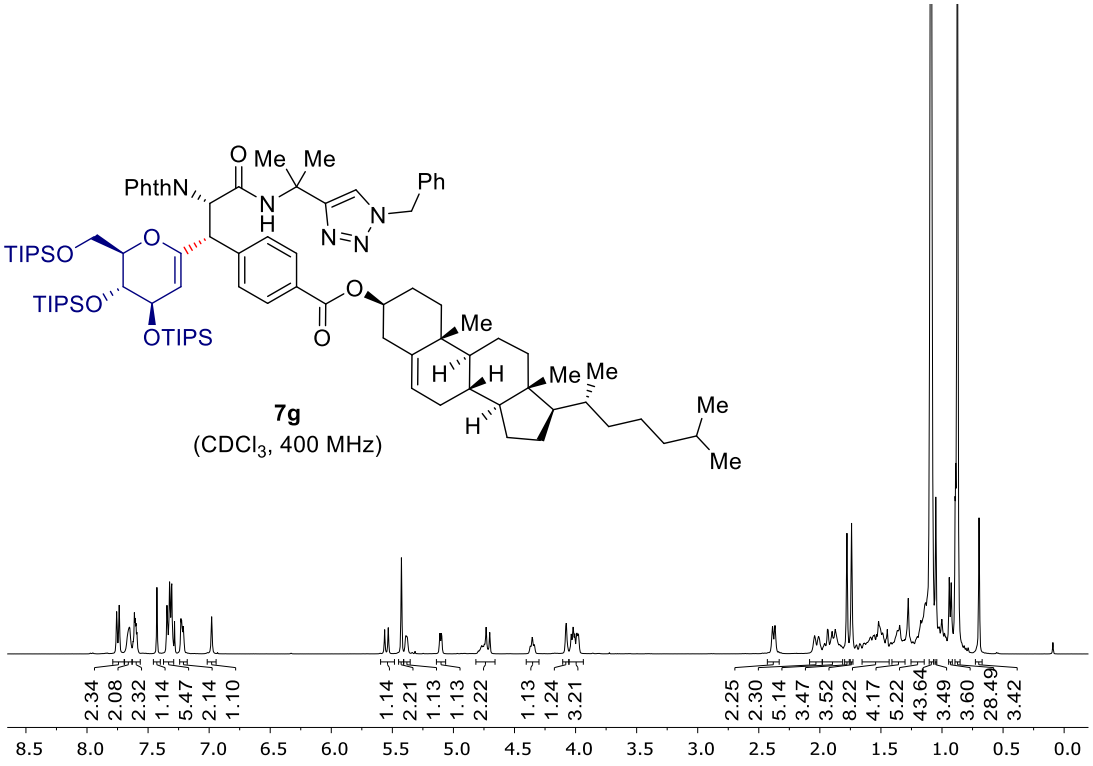

171.30
167.72
166.40
166.35
153.00
150.50
142.72
135.56
134.97
134.90
133.91
132.22
131.21
129.24
128.86
128.58
128.57
128.52
128.49
128.43
128.34
127.90
127.05
126.74
123.34
120.81
99.21
80.98
69.31
67.26
66.58
61.15
54.86
53.86
53.31
52.17
49.99
37.81
28.33
28.21
18.22
18.17
18.10
18.02
17.91
17.88
12.14
O
Me
Me
PhthN
N
H
Ph
N
N=N
TIPSO
O
H
N
CO2Bn
TIPSO
O
Ph
OTIPS
7d
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

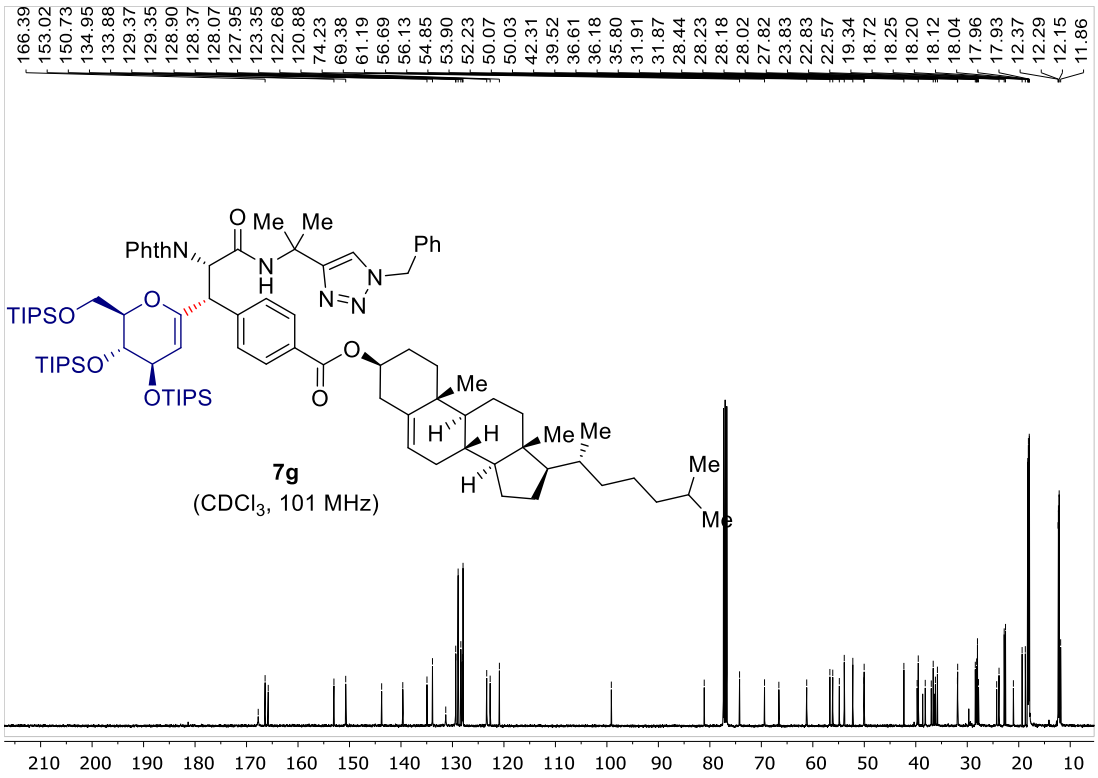

O
Me
Me
PhthN
N
H
Ph
N
N=N
TIPSO
O
TIPSO
OTIPS
MeO2C
NHAc
7e
(CDCl3, 400 MHz)
2.06
2.10
0.95
3.05
2.01
2.11
0.94
2.00
0.93
1.03
2.04
0.98
1.00
0.96
0.99
0.99
1.93
1.11
2.98
1.00
0.99
3.13
3.11
3.37
42.06
21.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

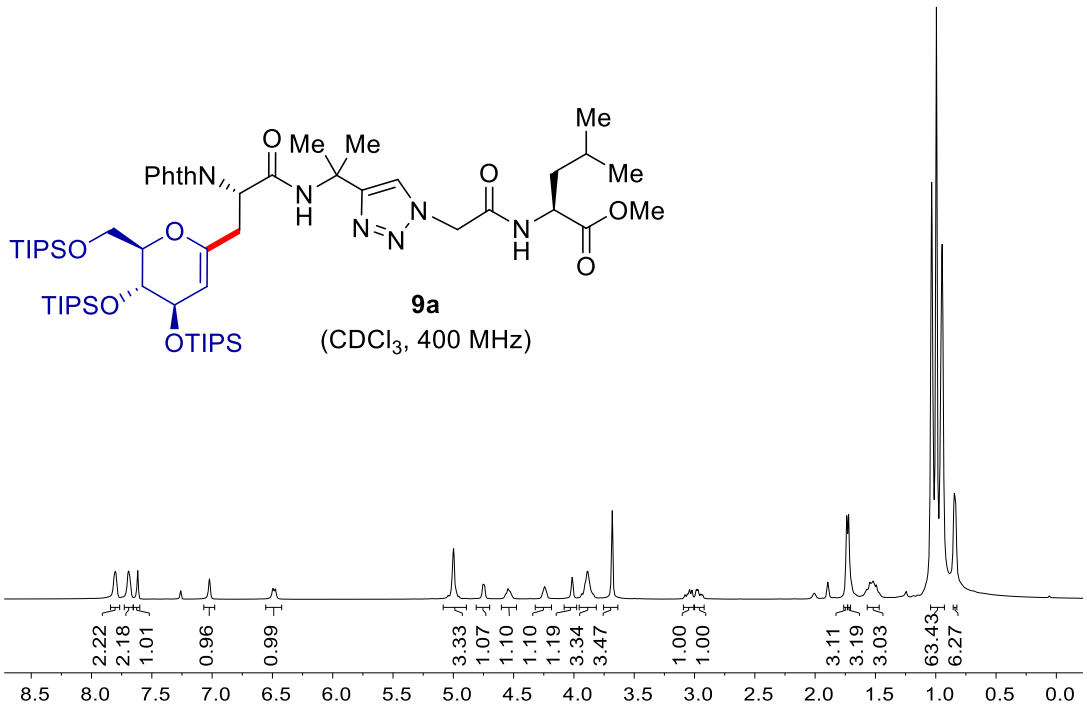

171.5
169.2
167.6
166.4
153.0
151.1
137.5
134.9
134.2
133.7
131.3
128.9
128.7
128.4
128.3
127.9
123.2
120.9
98.9
80.9
69.5
66.7
61.2
55.4
53.9
52.8
52.1
51.9
49.7
37.1
28.0
18.2
18.2
18.1
18.0
18.0
17.9
12.3
12.3
12.1
PhthN
O
Me
Me
N
H
N
N=N
Ph
TIPSO
O
TIPSO
OTIPS
MeO2C
NHAc
7e
(CDCl3, 101 MHz)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

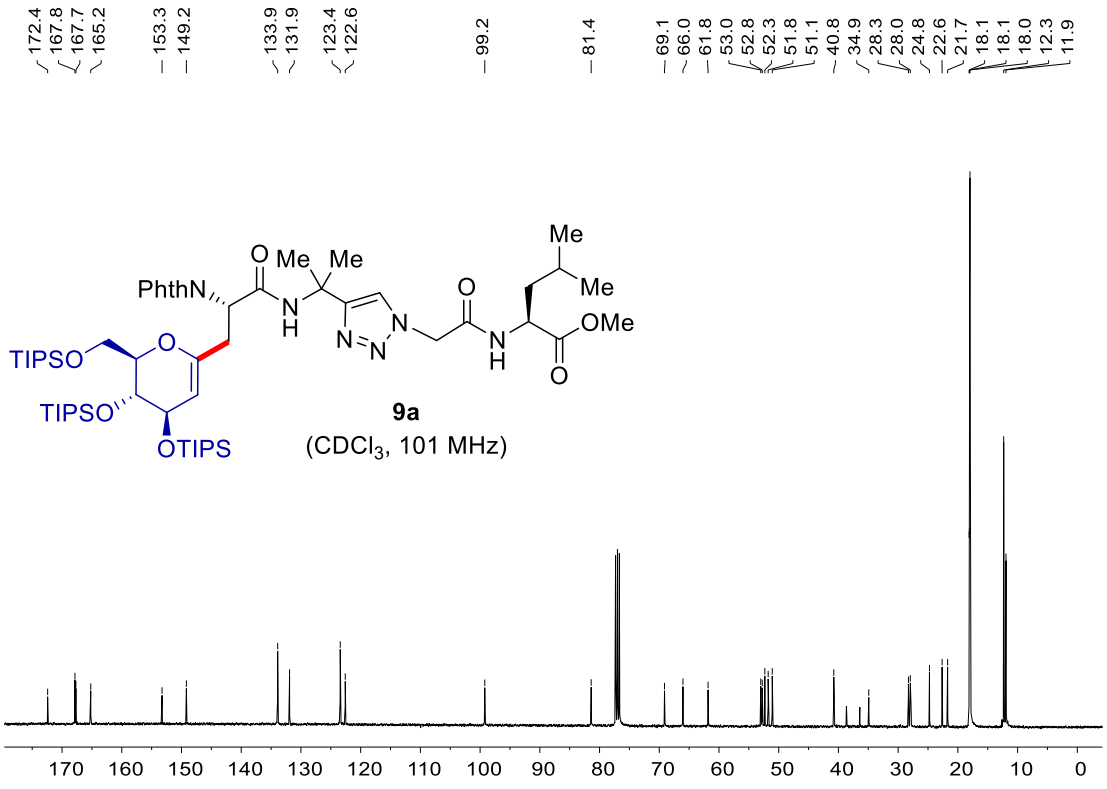

PhthN
O
Me
Me
N
H
N
Bn
N=N
Me
Me
TIPSO
O
TIPSO
OTIPS
O
O
Me
7f
(CDCl3, 400 MHz)
2.09
1.89
2.17
1.05
4.90
1.95
1.00
1.04
2.05
1.01
1.03
1.02
1.03
1.99
1.02
1.02
1.12
1.20
3.29
5.66
2.45
42.52
1.45
29.18
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

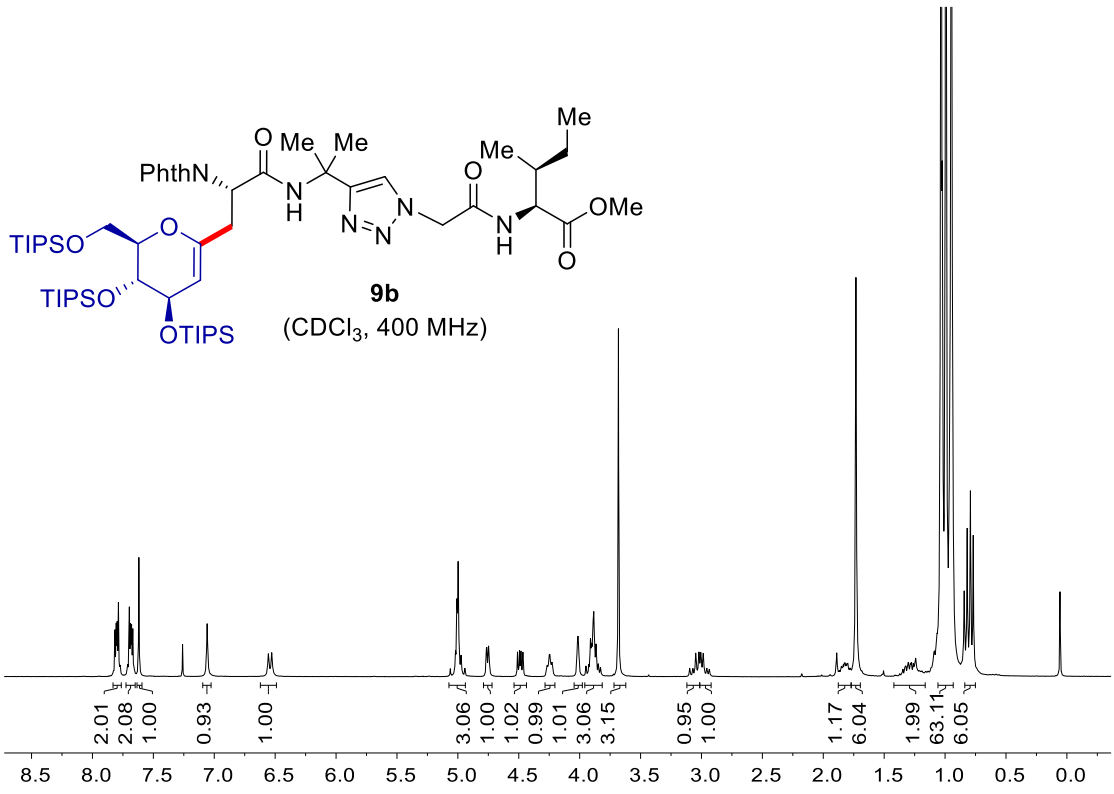

7f
(CDCl3, 101 MHz)

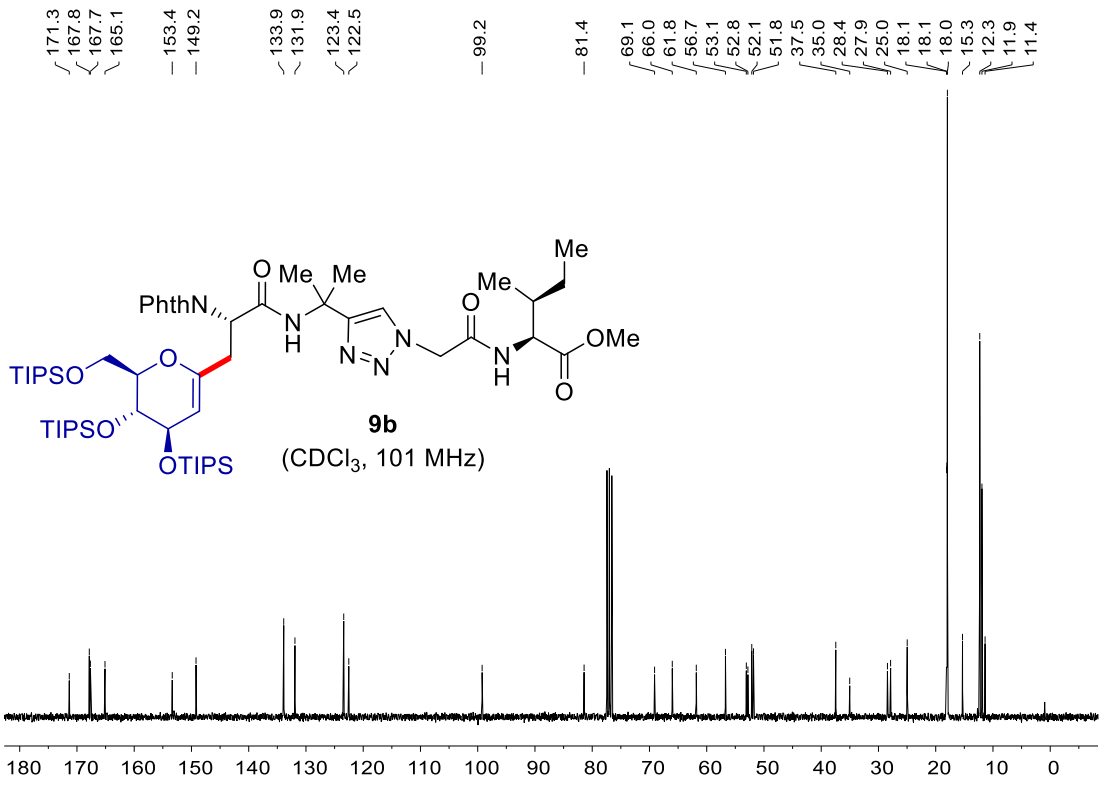

7g
(CDCl3, 400 MHz)

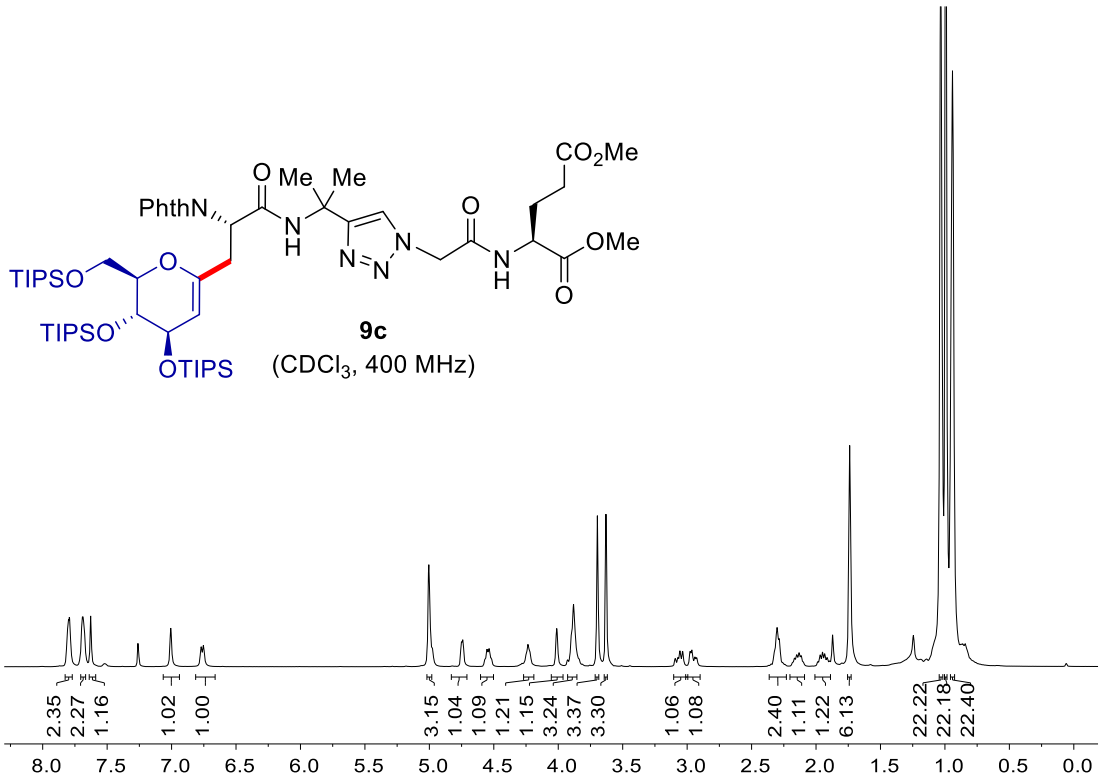

166.39
153.02
150.73
134.95
133.88
129.37
129.35
128.90
128.37
128.07
127.95
123.35
122.68
120.88
74.23
69.38
61.19
56.69
56.13
54.85
53.90
52.23
50.07
50.03
42.31
39.52
36.61
36.18
35.80
31.91
31.87
28.44
28.23
28.18
28.02
27.82
23.83
22.83
22.57
19.34
18.72
18.25
18.20
18.12
18.04
17.96
17.93
12.37
12.29
12.15
11.86
PhthN
O
Me
Me
N
H
Ph
N
N=N
TIPSO
O
TIPSO
OTIPS
O
O
Me
H
H
Me
Me
H
Me
Me
7g
(CDCl3, 101 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

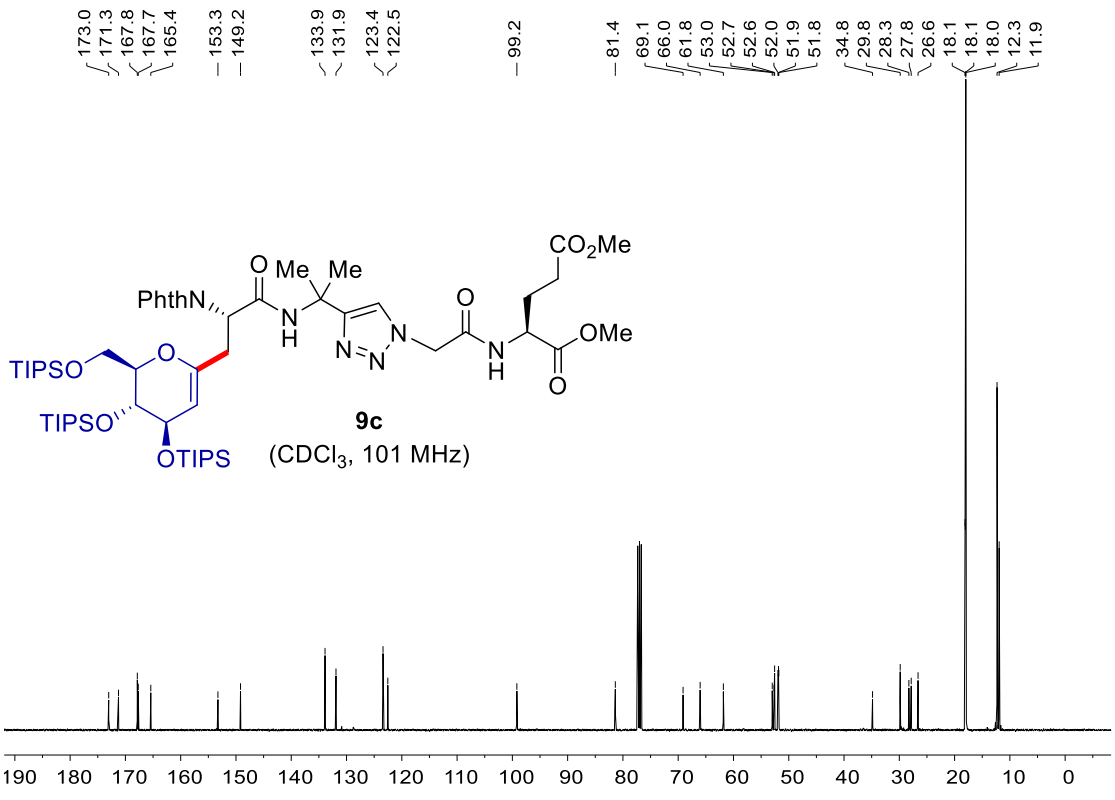

PhthN
O
Me
Me
N
H
N
N=N
O
N
H
Me
Me
OMe
O
TIPSO
O
TIPSO
OTIPS
9a
(CDCl3, 400 MHz)
2.22
2.18
1.01
0.96
0.99
3.33
1.07
1.10
1.10
1.19
3.34
3.47
1.00
1.00
3.11
3.19
3.03
63.43
6.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

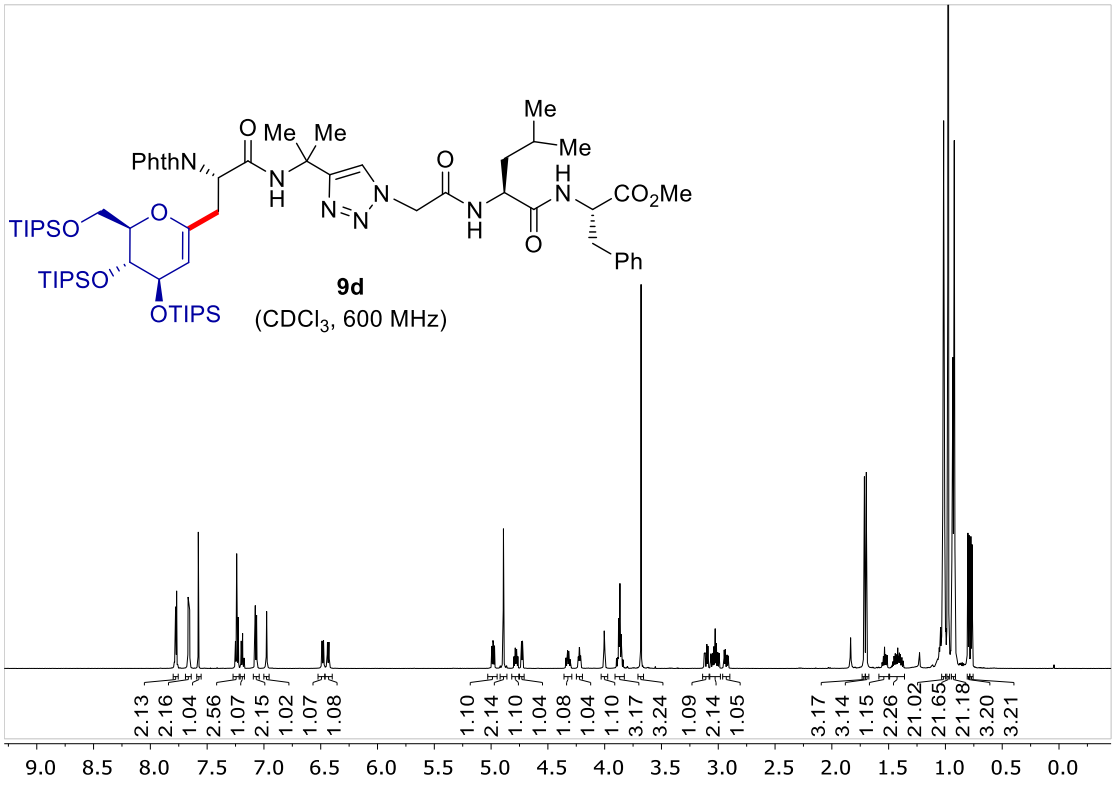

172.4
167.8
167.7
165.2
153.3
149.2
133.9
131.9
123.4
122.6
99.2
81.4
69.1
66.0
61.8
53.0
52.8
52.3
51.8
51.1
40.8
34.9
28.3
28.0
24.8
22.6
21.7
18.1
18.1
18.0
12.3
11.9
PhthN
O
Me
Me
N
H
N
N
N
O
N
H
Me
Me
OMe
O
TIPSO
O
TIPSO
OTIPS
9a
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

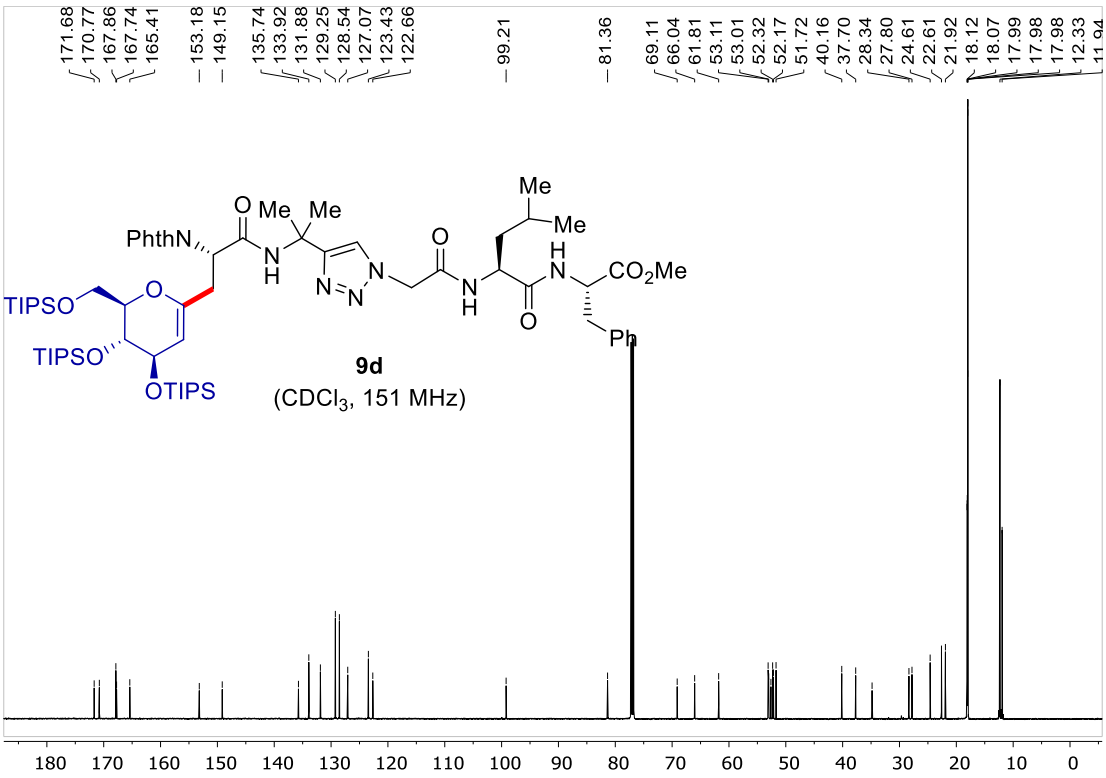

PhthN
O
Me
Me
N
H
N
N
N
O
N
H
Me
Me
OMe
O
TIPSO
O
TIPSO
OTIPS
9b
(CDCl3, 400 MHz)
2.01
2.08
1.00
0.93
1.00
3.06
1.00
1.02
0.99
1.01
3.06
3.15
0.95
1.00
1.17
6.04
1.99
63.11
6.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

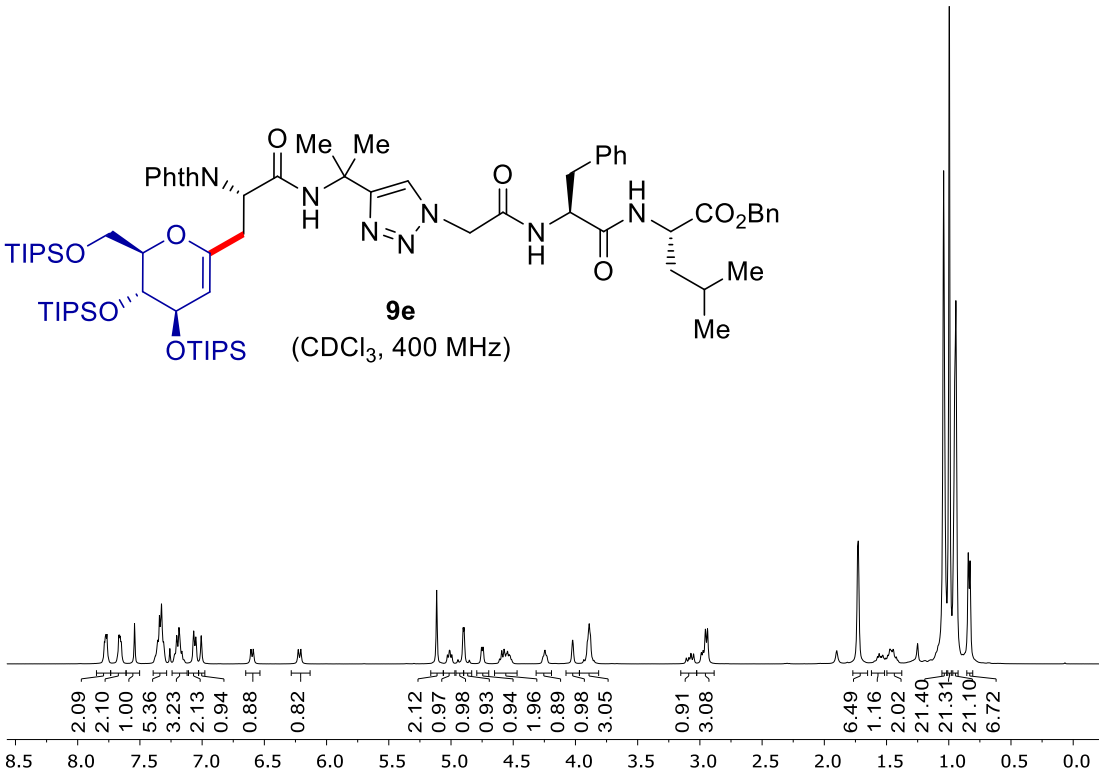

171.3
167.8
167.7
165.1
153.4
149.2
133.9
131.9
123.4
122.5
99.2
81.4
69.1
66.0
61.8
56.7
53.1
52.8
52.1
51.8
37.5
35.0
28.4
27.9
25.0
18.1
18.1
18.0
15.3
12.3
11.9
11.4
PhthN
TIPSO
TIPSO
OTIPS
Me
Me
Me
OMe
9b
(CDCl3, 101 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

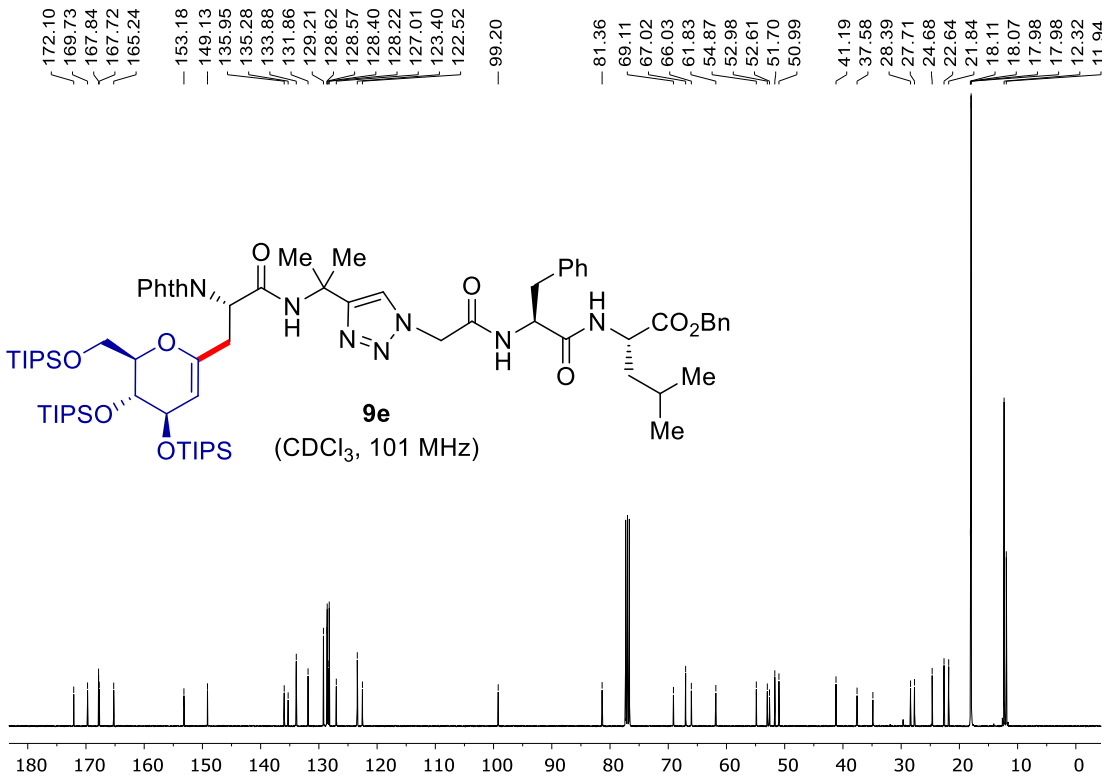

CO2Me
PhthN
TIPSO
TIPSO
OTIPS
Me
Me
OMe
9c
(CDCl3, 400 MHz)
2.35
2.27
1.16
1.02
1.00
3.15
1.04
1.09
1.21
1.15
3.24
3.37
3.30
1.06
1.08
2.40
1.11
1.22
6.13
22.22
22.18
22.40
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

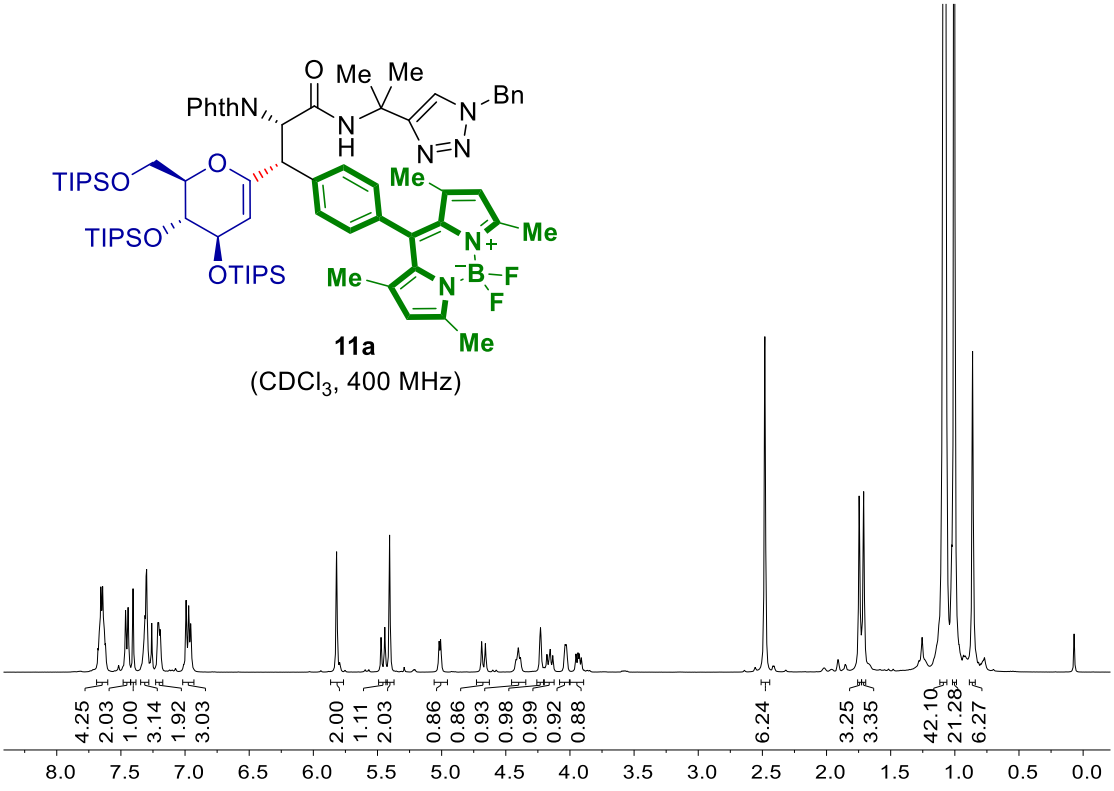

173.0
171.3
167.8
167.7
165.4
153.3
149.2
133.9
131.9
123.4
122.5
99.2
81.4
69.1
66.0
61.8
53.0
52.7
52.6
52.0
51.9
51.8
34.8
29.8
28.3
27.8
26.6
18.1
18.1
18.0
12.3
11.9
CO2Me
O
Me
Me
PhthN
N
H
O
N
N
N
O
N
H
OMe
O
TIPSO
O
TIPSO
OTIPS
9c
(CDCl3, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

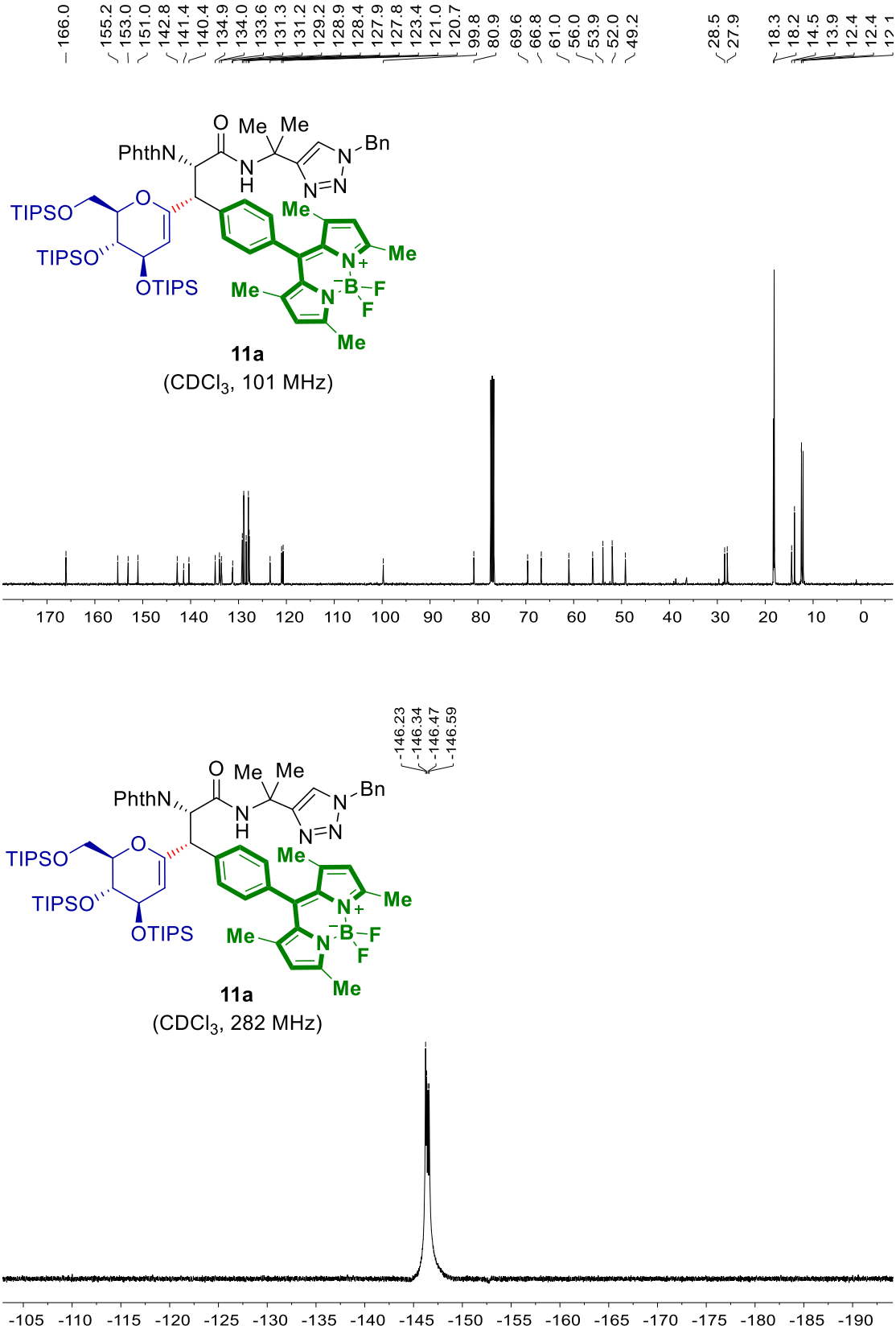

Me
Me
O
Me
Me
PhthN
N
H
O
N
N
N
O
N
H
H
N
CO2Me
O
Ph
TIPSO
O
TIPSO
OTIPS
9d
(CDCl3, 600 MHz)
2.13
2.16
1.04
2.56
1.07
2.15
1.02
1.07
1.08
1.10
2.14
1.10
1.04
1.08
1.04
1.10
3.17
3.24
1.09
2.14
1.05
3.17
3.14
1.15
2.26
21.02
21.65
21.18
3.20
3.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

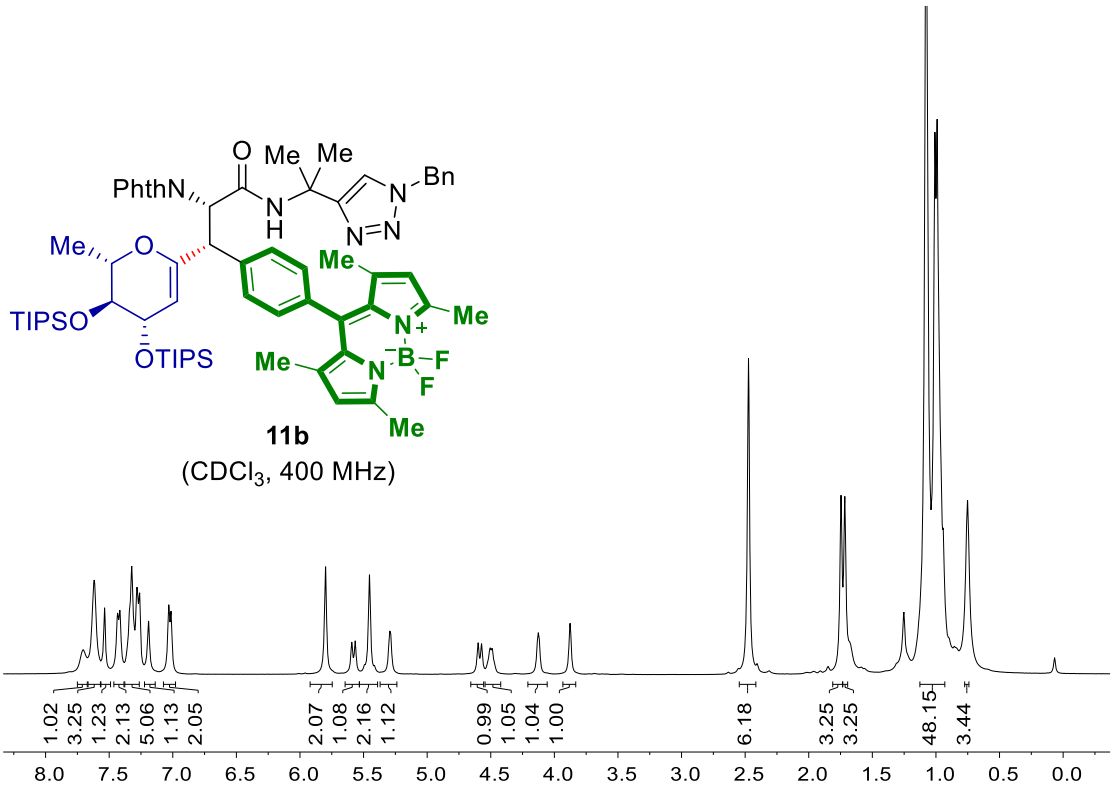

171.68
170.77
167.86
167.74
165.41
153.18
149.15
135.74
133.92
131.88
129.25
128.54
127.07
123.43
122.66
99.21
81.36
69.11
66.04
61.81
53.11
53.01
52.32
52.17
51.72
40.16
37.70
28.34
27.80
24.61
22.61
21.92
18.12
18.07
17.99
17.98
17.98
12.33
11.94
PhthN
O
Me
Me
N
H
N
N
N
O
N
H
Me
Me
H
N
CO2Me
O
Ph
TIPSO
O
TIPSO
OTIPS
9d
(CDCl3, 151 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


PhthN
O
Me
Me
N
H
N
N
N
O
N
H
Ph
H
N
CO2Bn
O
Me
Me
TIPSO
O
TIPSO
OTIPS
9e
(CDCl3, 400 MHz)
2.09
2.10
1.00
5.36
3.23
2.13
0.94
0.88
0.82
2.12
0.97
0.98
0.93
0.94
1.96
0.89
0.98
3.05
0.91
3.08
6.49
1.16
2.02
21.40
21.31
21.10
6.72
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
0.0


172.10
169.73
167.84
167.72
165.24
153.18
149.13
135.95
135.28
133.88
131.86
129.21
128.62
128.57
128.40
128.22
127.01
123.40
122.52
99.20
81.36
69.11
67.02
66.03
61.83
54.87
52.98
52.61
51.70
50.99
41.19
37.58
28.39
27.71
24.68
22.64
21.84
18.11
18.07
17.98
17.98
12.32
11.94
PhthN
O
Me
Me
N
H
N
N
N
O
N
H
Ph
H
N
CO2Bn
O
Me
Me
TIPSO
O
TIPSO
OTIPS
9e
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

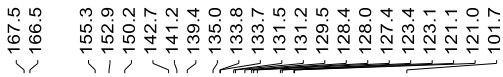

PhthN
O
Me
Me
N
H
N
N
N
Bn
TIPSO
O
TIPSO
OTIPS
Me
Me
N+
Me
N
B
F
F
Me
11a
(CDCl3, 400 MHz)
4.25
2.03
1.00
3.14
1.92
3.03
2.00
1.11
2.03
0.86
0.86
0.93
0.98
0.99
0.92
0.88
6.24
3.25
3.35
42.10
21.28
6.27
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

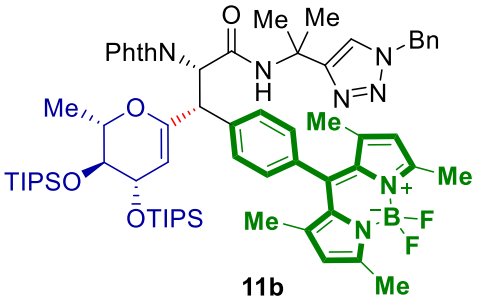

166.0
155.2
153.0
151.0
142.8
141.4
140.4
134.9
134.0
133.6
131.3
131.2
129.2
128.9
128.4
127.9
127.8
123.4
121.0
120.7
99.8
80.9
69.6
66.8
61.0
56.0
53.9
52.0
49.2
28.5
27.9
18.3
18.2
14.5
13.9
12.4
12.4
PhthN
O
Me
Me
N
H
N
Bn
N=N
TIPSO
O
TIPSO
OTIPS
Me
Me
N+
Me
N
B
F
F
Me
11a
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-146.23
-146.34
-146.47
-146.59
PhthN
O
Me
Me
N
H
N
Bn
N=N
TIPSO
O
TIPSO
OTIPS
Me
Me
N+
Me
N
B
F
F
Me
11a
(CDCl3, 282 MHz)
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190



11b

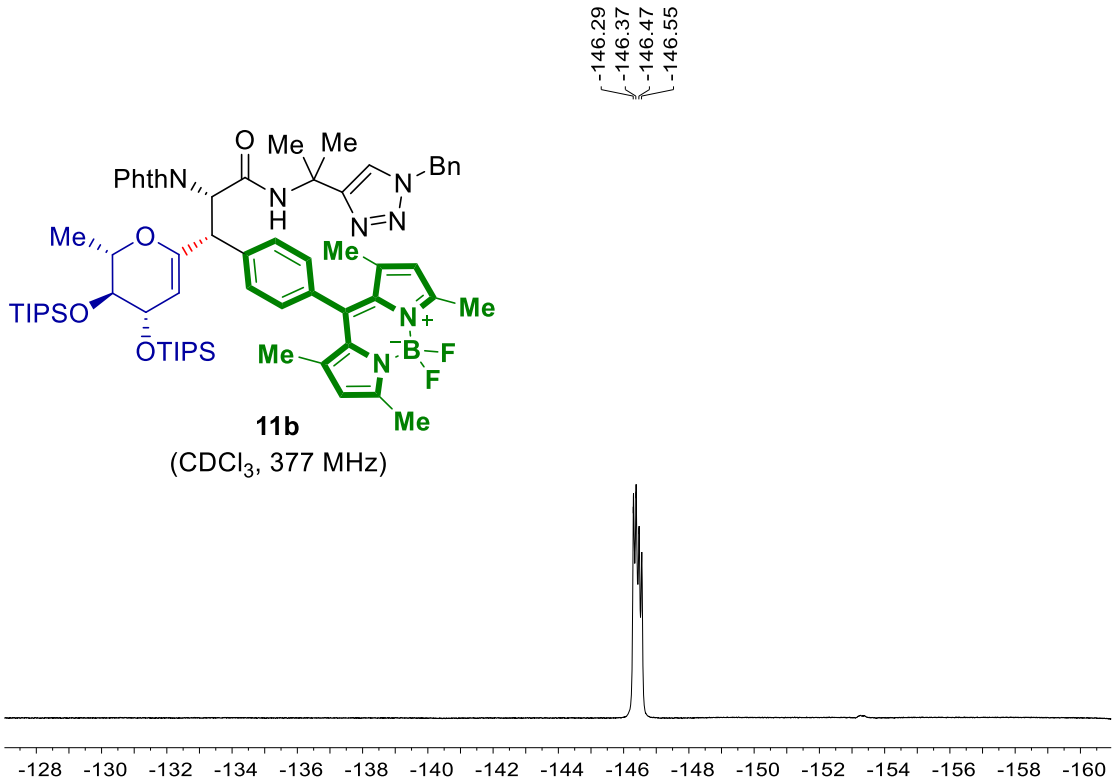
($CDCl_3$, 400 MHz)





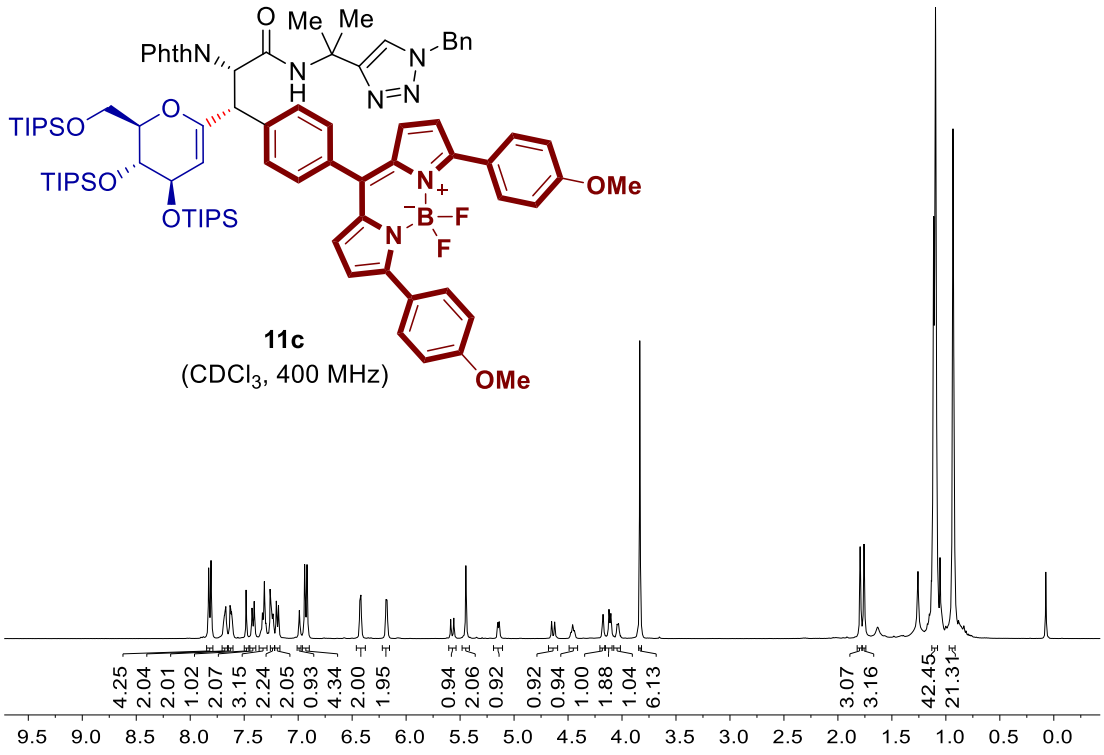
11b

($CDCl_3$, 101 MHz)



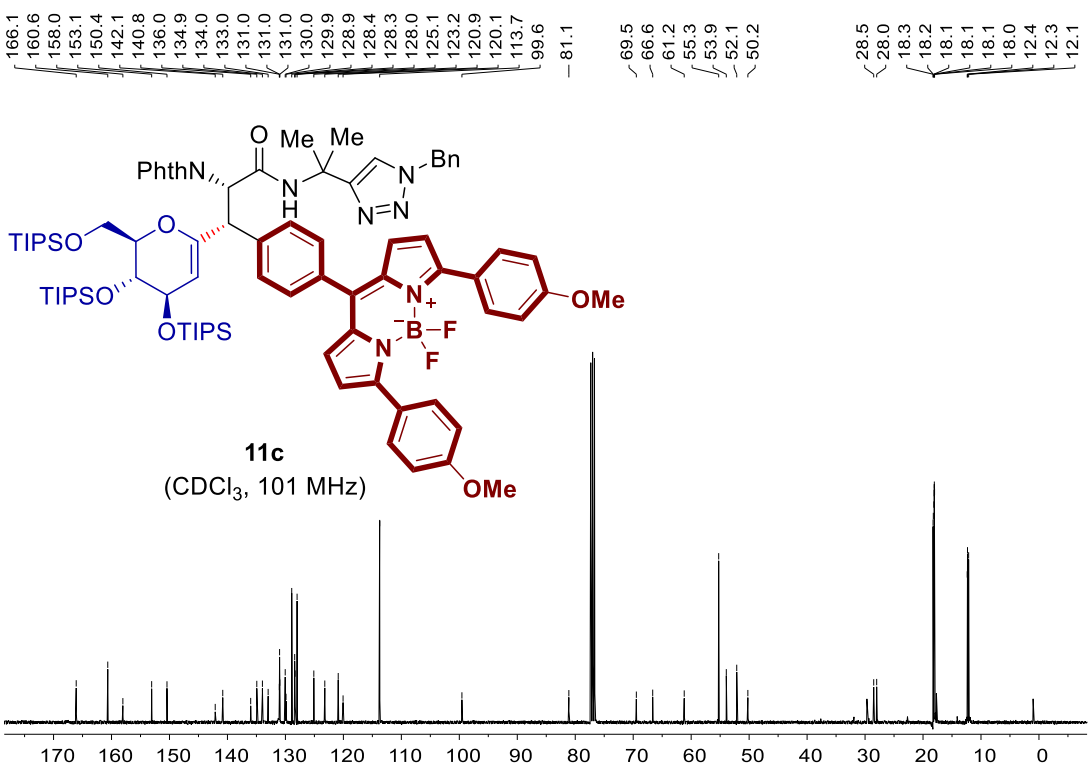
11b

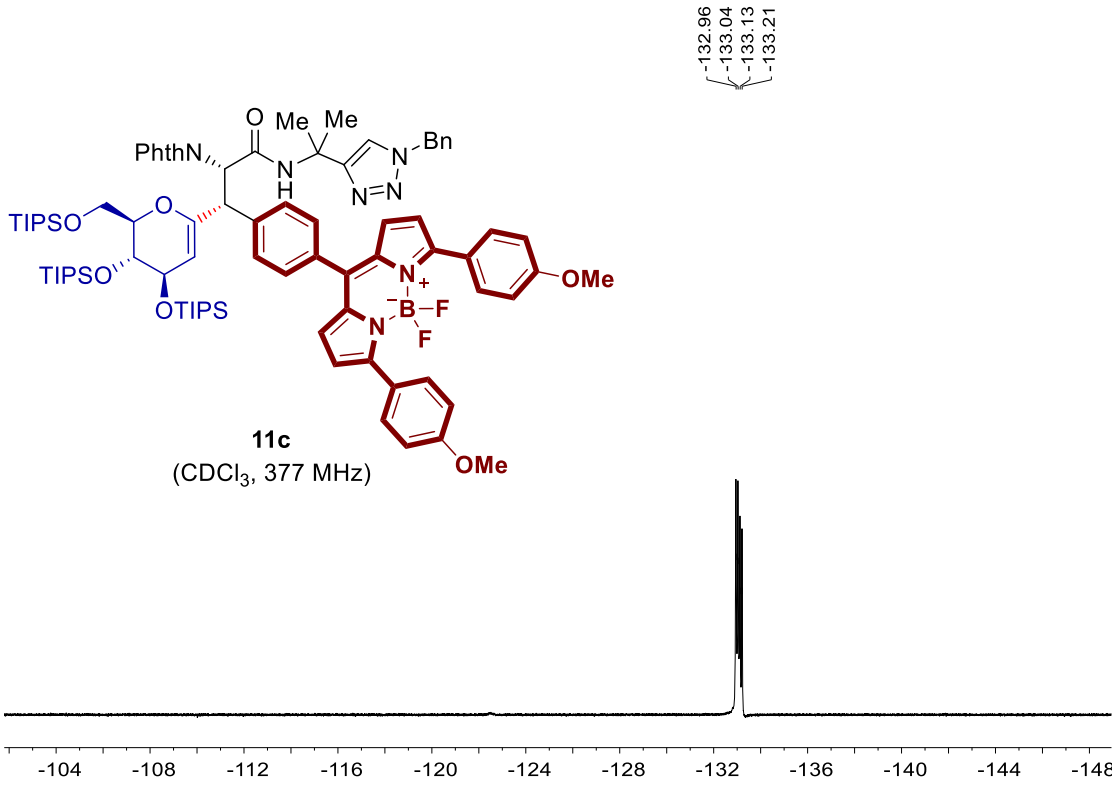
($CDCl_3$, 377 MHz)

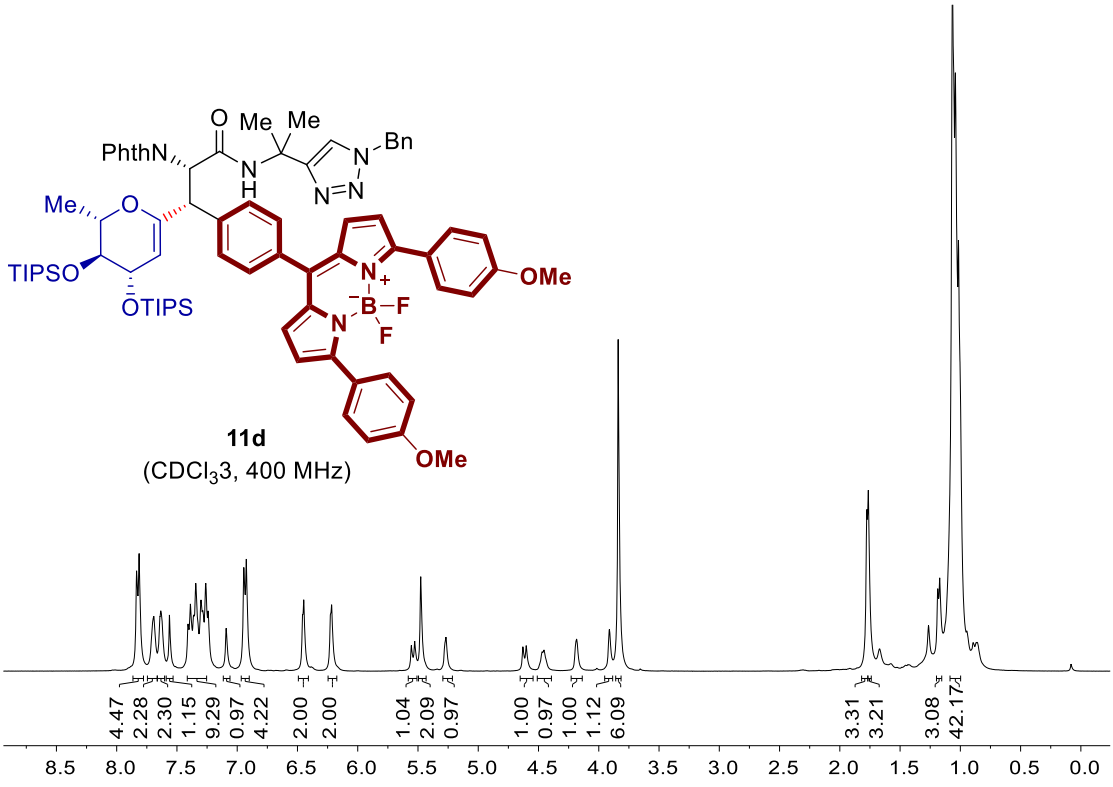


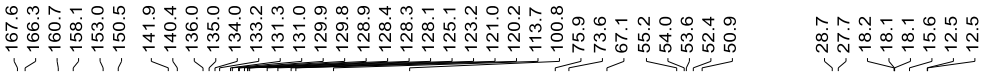
11c

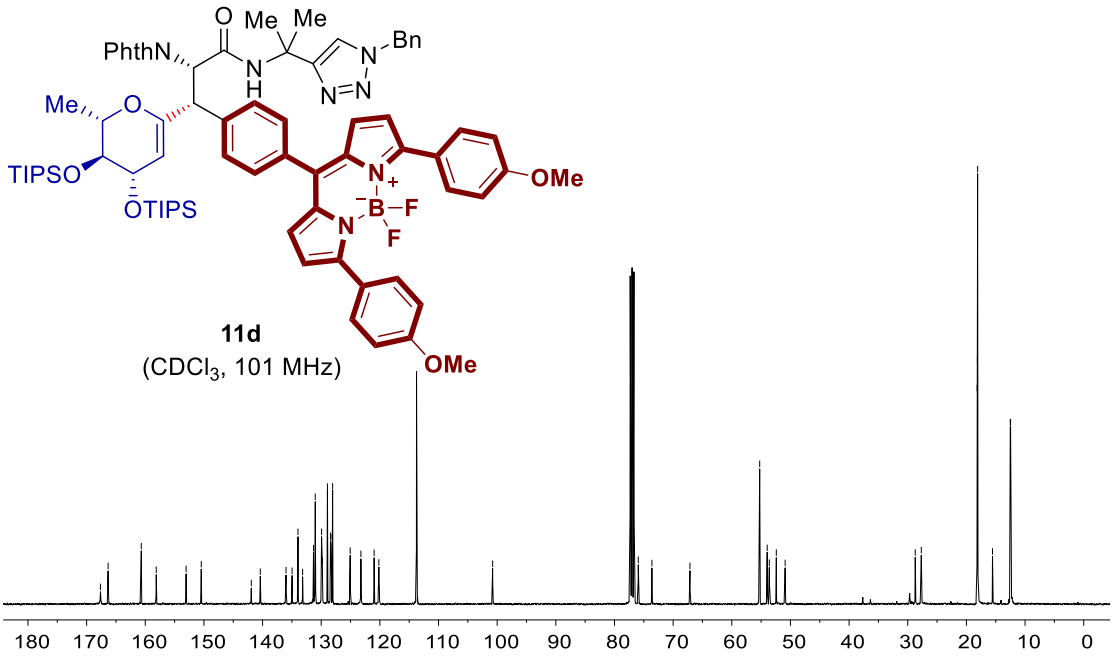
($CDCl_3$, 400 MHz)

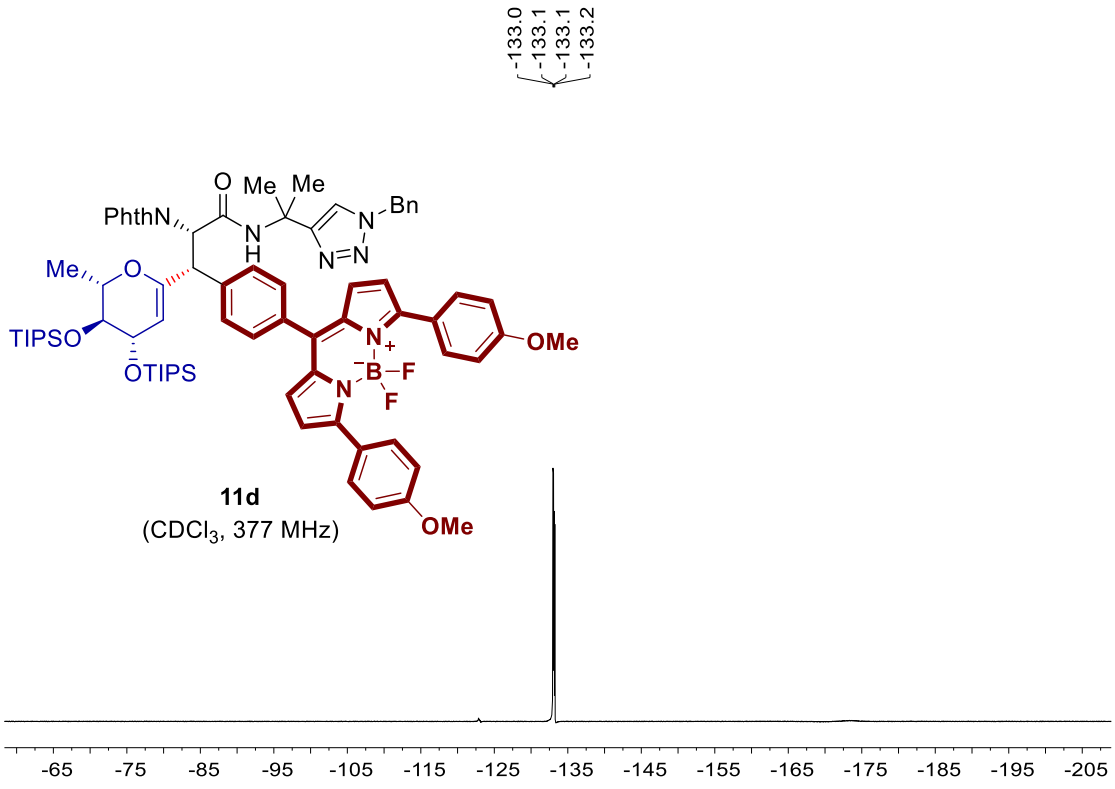

166.1
160.6
158.0
153.1
150.4
142.1
140.8
136.0
134.9
134.0
133.0
131.0
131.0
131.0
130.0
129.9
128.9
128.4
128.3
128.0
125.1
123.2
120.9
120.1
113.7
99.6
81.1
69.5
66.6
61.2
55.3
53.9
52.1
50.2
28.5
28.0
18.3
18.2
18.1
18.1
18.1
18.0
12.4
12.3
12.1
O
Me
Me
PhthN
N
H
N
N=N
Bn
TIPSO
O
TIPSO
OTIPS
N+
B−F
F
N
OMe
OMe
11c
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

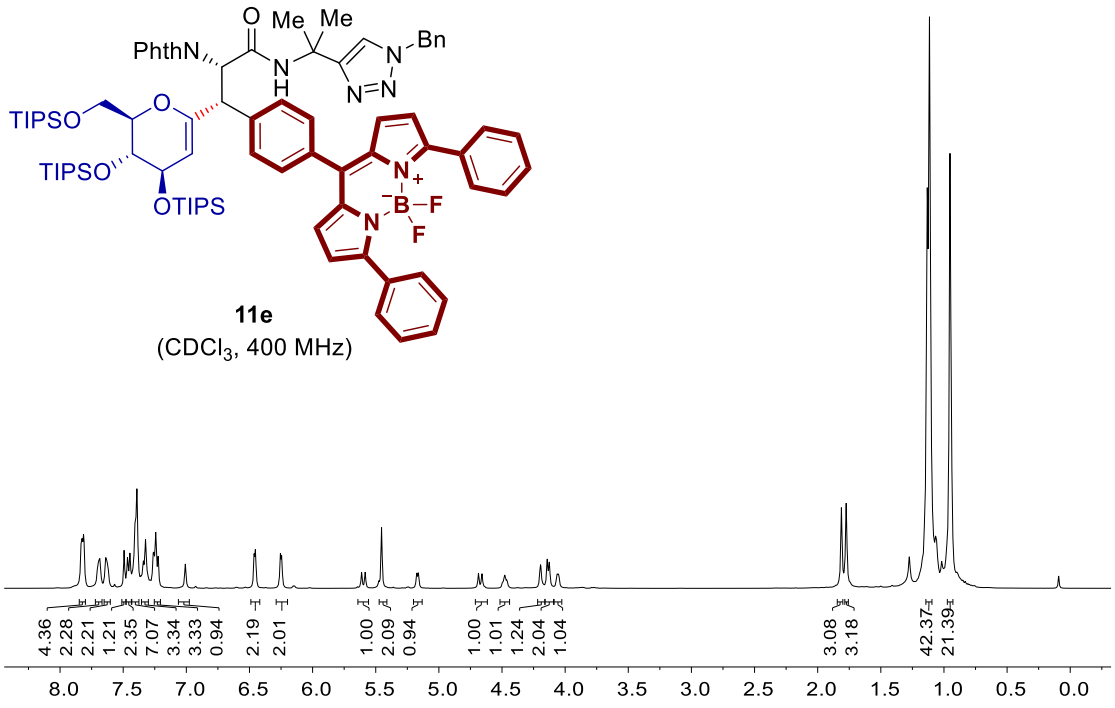

-132.96
-133.04
-133.13
-133.21
O
Me
Me
PhthN
N
H
N
N=N
Bn
TIPSO
O
TIPSO
OTIPS
N+
B−F
F
N
OMe
OMe
11c
(CDCl3, 377 MHz)
-104
-108
-112
-116
-120
-124
-128
-132
-136
-140
-144
-148

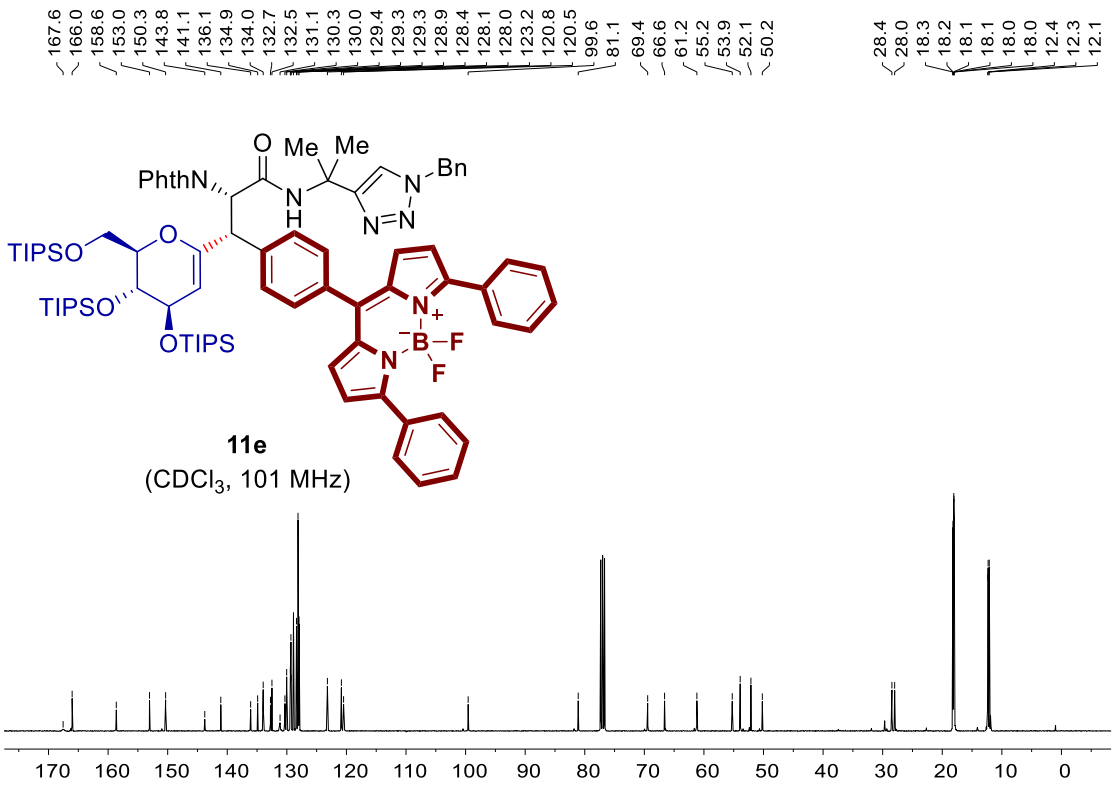

PhthN
O
Me
Me
N
H
N
N=N
Bn
Me
O
TIPSO
OTIPS
N+
B
F
F
N
OMe
OMe
11d
(CDCl3 3, 400 MHz)
4.47
2.28
2.30
1.15
9.29
0.97
4.22
2.00
2.00
1.04
2.09
0.97
1.00
0.97
1.00
1.12
6.09
3.31
3.21
3.08
42.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

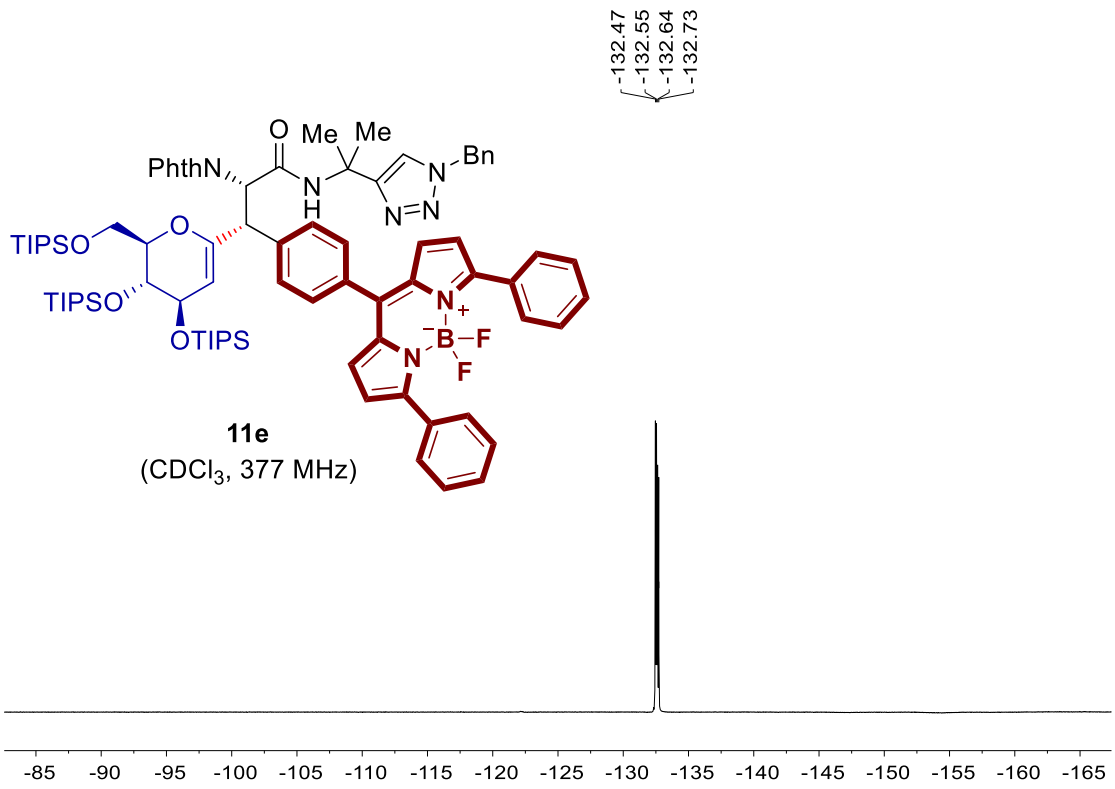

167.6
166.3
160.7
158.1
153.0
150.5
141.9
140.4
136.0
135.0
134.0
133.2
131.3
131.0
129.9
129.8
128.9
128.4
128.3
128.1
125.1
123.2
121.0
120.2
113.7
100.8
75.9
73.6
67.1
55.2
54.0
53.6
52.4
50.9
28.7
27.7
18.2
18.1
18.1
15.6
12.5
12.5


PhthN
O
Me
Me
N
H
N
N=N
Bn
Me
O
TIPSO
OTIPS
N+
B
F
F
N
OMe
OMe
11d
(CDCl3, 101 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-133.0
-133.1
-133.1
-133.2
PhthN
O
Me
Me
N
H
N
N=N
Bn
Me
O
TIPSO
OTIPS
N+
B−F
F
N
OMe
OMe
11d
(CDCl3, 377 MHz)
-65
-75
-85
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
-195
-205


PhthN
O
Me
Me
N
H
N
N=N
Bn
TIPSO
O
TIPSO
OTIPS
N+
B−F
F
N
11e
(CDCl3, 400 MHz)
4.36
2.28
2.21
1.21
2.35
7.07
3.34
3.33
0.94
2.19
2.01
1.00
2.09
0.94
1.00
1.01
1.24
2.04
1.04
3.08
3.18
42.37
21.39
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
0.0


167.6
166.0
158.6
153.0
150.3
143.8
141.1
136.1
134.9
134.0
132.7
132.5
131.1
130.3
130.0
129.4
129.3
129.3
128.9
128.4
128.1
128.0
123.2
120.8
120.5
99.6
81.1
69.4
66.6
61.2
55.2
53.9
52.1
50.2
28.4
28.0
18.3
18.2
18.1
18.1
18.0
18.0
12.4
12.3
12.1
O
Me
Me
PhthN
N
H
N
N=N
Bn
TIPSO
O
TIPSO
OTIPS
N+
B
F
F
N
11e
(CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-132.47
-132.55
-132.64
-132.73
O
Me
Me
PhthN
N
H
N
N=N
Bn
TIPSO
O
TIPSO
OTIPS
N+
B
F
F
N
11e
(CDCl3, 377 MHz)
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165