Supporting Information

Photoredox-catalysed arylamination of non-anomeric exoglycals with aryl sulfinamides *via* radical Smiles rearrangement

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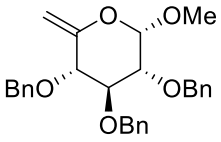
1. General Information

Commercial reagents were purchased from Aldrich Chemical, 3A, Alfa Aesar, TCI, Strem, Acros, Energy Chemical, J&K Chemical, Innochem and were used as received. All catalytic reactions were run in dried glassware. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz),^{13}C NMR (101 MHz) and ^{19}F (376 MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High Resolution Mass spectra were performed on Agilent 1260 Series (ESI Source). Optical rotations were measured on an automatic polarimeter with $[\alpha]_D^{25}$ values; concentration (c) is in g/100 mL.

2. Numbering and structure of all substrates



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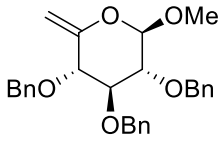

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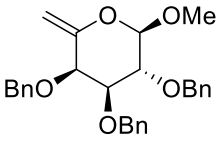

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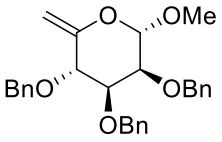

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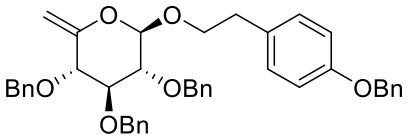

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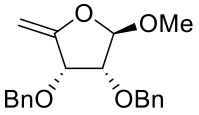

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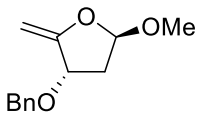

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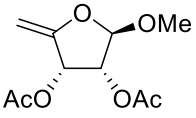

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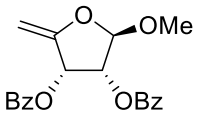

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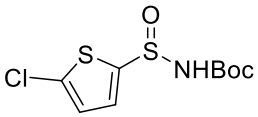

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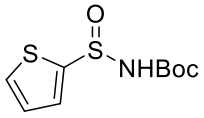

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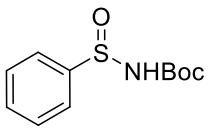

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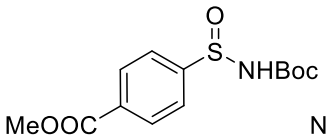

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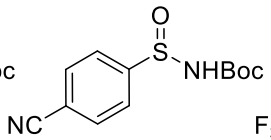

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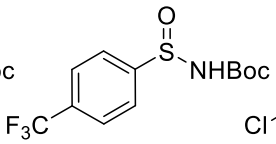

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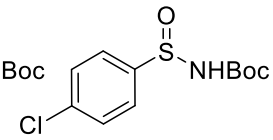

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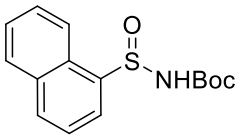

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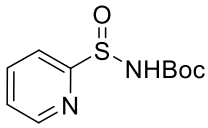

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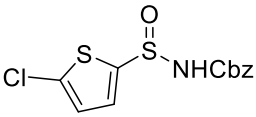

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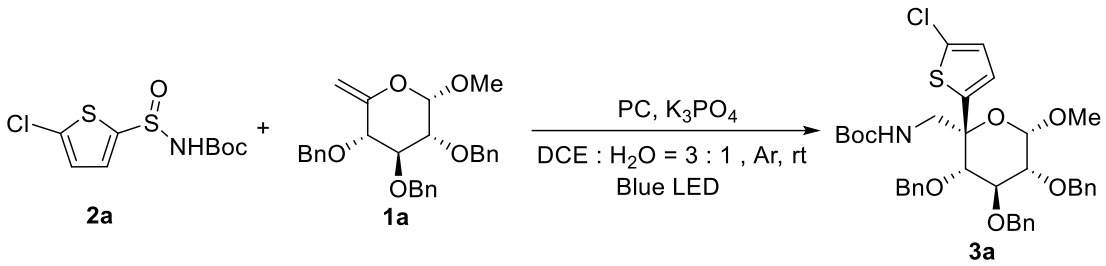
3. Optimization of conditions

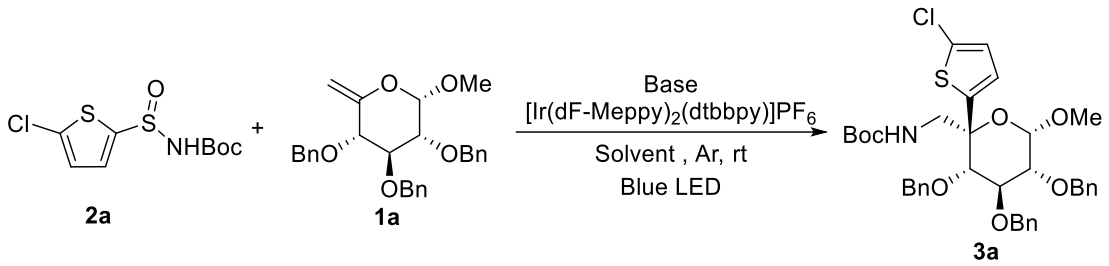
Table S1. The screening of PC [a]



Entry	Photocatalyst	yield/%[b]
1	$[Ir(ppy)_2(dtbbpy)]PF_6$	48
2	$[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$	36
3	$[Ir(dFCF_3ppy)_2(5,5'\text{-}dCF_3bpy)]PF_6$	29
4	$[Ir(dF\text{-}Meppy)_2(dtbbpy)]PF_6$	49
13	4CzIPN	48

[a] Reaction conditions: A solution of **1a** (0.225 mmol), **2a** (0.15 mmol), PC (2 mol%) and K_3PO_4 (0.225 mmol) in solvent (1.5 mL) was irradiated by 90 W blue LEDs for 17 hours under Ar atmosphere. [b] Isolated yield.

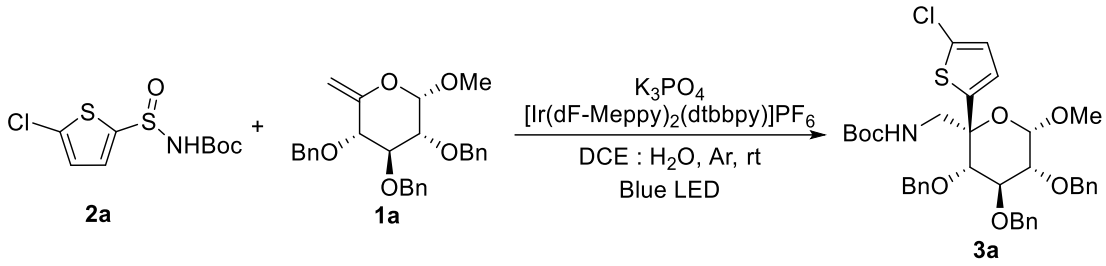
Table S2. The screening of solvent and base [a]



Entry	Base	Solvent	yield/%[b]
1	K_3PO_4	MeCN/H_2O(v/v = 3:1）	11
2	K_3PO_4	DCM/H_2O(v/v = 3:1）	48
3	K_3PO_4	THF/H_2O(v/v = 3:1）	15
4	K_3PO_4	DCE/H_2O(v/v = 10:1）	42
5	K_3PO_4	DCE/H_2O(v/v = 5:1）	46
6	K_3PO_4	DCE/H_2O(v/v = 2:1）	56
7	K_3PO_4	DCE/H_2O(v/v = 1:1）	51
8	K_2CO_3	DCE/H_2O(v/v = 2:1）	34
9	Cs_2CO_3	DCE/H_2O(v/v = 2:1）	40
10	KO*t*Bu	DCE/H_2O(v/v = 2:1）	26

[a] Reaction conditions: A solution of **1a** (0.225 mmol), **2a** (0.15 mmol), [Ir(dF-Meppy)$_2$(dtbbpy)]PF_6 (2 mol%) and Base (0.225 mmol) in solvent (1.5 mL) was irradiated by 90 W blue LEDs for 17 hours under Ar atmosphere. [b] Isolated yield.

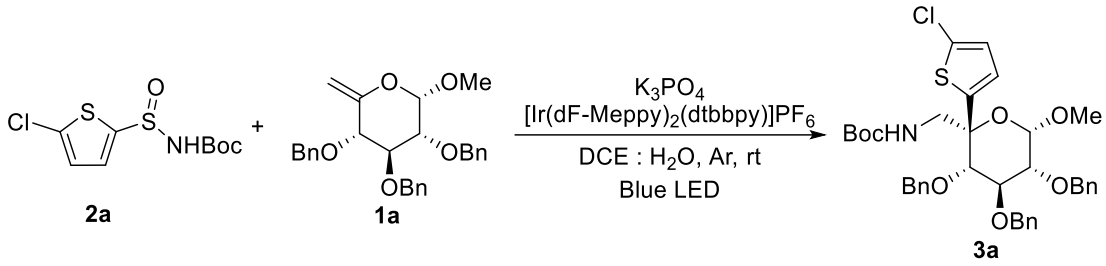
Table S3. The screening of reaction concentration [a]



Entry	DCE:H_2O	yield/%[b]
1	1.2 mL: 0.6 mL	56
2	0.66 mL: 0.33 mL	56
3	0.5 mL: 0.25 mL	49
4	0.6 mL: 0.4 mL	56
5	0. 5 mL: 0.5 mL	56
6	0.4 mL: 0.6 mL	57
7	0.3 mL: 0.7 mL	57

[a] Reaction conditions: A solution of **1a** (0.225 mmol), **2a** (0.15 mmol), [Ir(dF-Meppy)$_2$(dtbbpy)]PF_6 (2 mol%) and K_3PO_4 (0.225 mmol) in solvent (1 mL) was irradiated by 90 W blue LEDs for 17 hours under Ar atmosphere. [b] Isolated yield.

Table S4 The screening of other conditions [a]



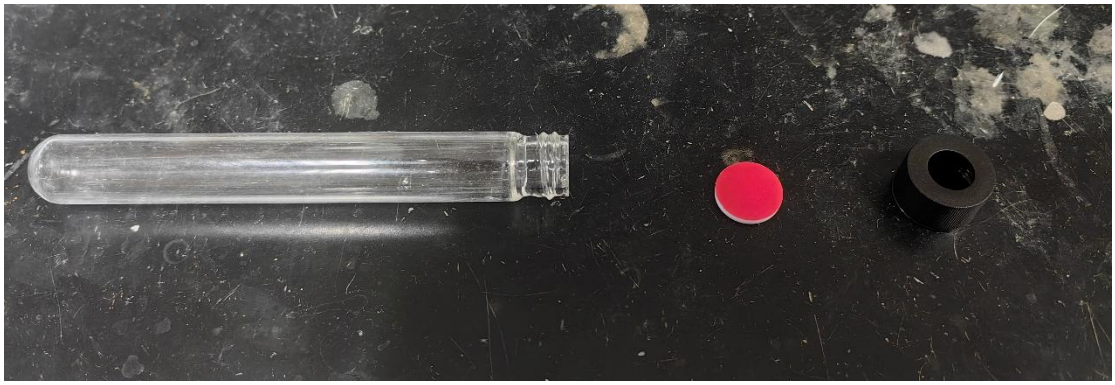
2a **1a** **3a**

Entry	K_3PO_4 (n equiv)	DCE:H_2O	yield/%[b]
1	2.0	0.4 mL: 0.6 mL	56
2	2.5	0.4 mL: 0.6 mL	58
3[c]	2.5	0.4 mL: 0.6 mL	68
4	2.0	0.3 mL: 0.7 mL	57
5	2.5	0.3 mL: 0.7 mL	57
6[c]	2.5	0.3 mL: 0.7 mL	59
7[d]	1.5	0.4 mL: 0.6 mL	47
8[e]	2.5	0.4 mL: 0.6 mL	37
9[f]	2.5	0.4 mL: 0.6 mL	0
10[g]	2.5	0.4 mL: 0.6 mL	0

[a] Reaction conditions: A solution of **1a** (0.225 mmol), **2a** (0.15 mmol), [Ir(dF-Meppy)$_2$(dtbbpy)]PF_6 (2 mol%) and K_3PO_4 (0.225 mmol) in solvent (1 mL) was irradiated by 90 W blue LEDs for 17 hours under Ar atmosphere. [b] Isolated yield. [c]**1a** (0.3 mmol, 2.0 equiv). [d]**2a** (0.1 mmol, 1.0 equiv) and **1a** (0.15 mmol, 1.5 equiv). [e]**2a** (0.1 mmol, 1.0 equiv) and **1a** (0.2 mmol, 2.0 equiv). [f]No PC. [g]No Light.

4. Reaction setup

Medium-sized screw-cap test tubes (8 mL) were used for all 0.1 mmol scale reactions: Fisher13 x 100 mm tubes (Cat. No. 14-959-35C). Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)



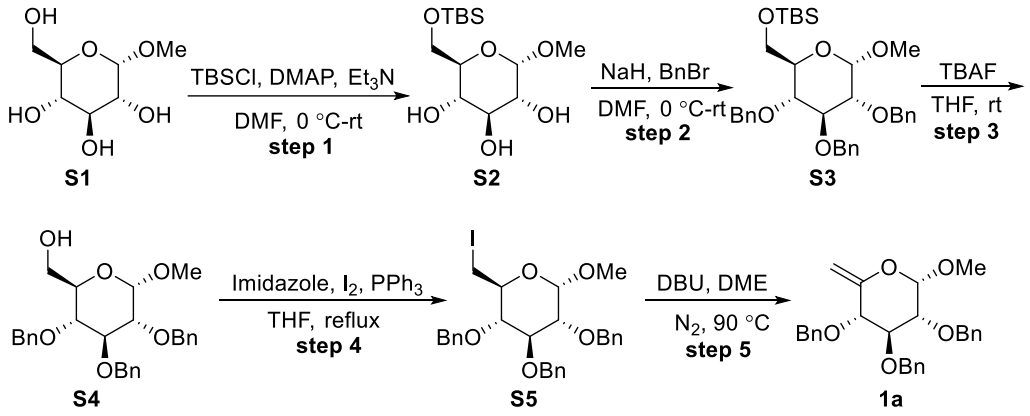
Light source: Kessil® A360W E-SERIES TUNA BLUE. The distance between the tube and the lamp was about 10 cm (two fans was added)

Figure S1. The reaction setup

5. Substrate preparation

5.1 General procedure A

Glycals **1a-1i** were synthesized according to the literatures.[1-4] Taking **1a** as an example:



Step 1:

To a 100 mL flask was added **S1** (20 mmol, 1.0 equiv), DMAP (4 mmol, 0.2 equiv) and DMF (0.5 M), in which Et_3N (40 mmol, 2.0 equiv) was injected using a syringe. The flask was cooled in an ice bath, and then TBSCl (24 mmol, 1.2 equiv) was added in portion. The system was warmed up to room temperature and monitored by TLC. After 18 h, the system was diluted with H_2O and extract with EA for third times. The organic layer was combined, washed with saturated NaCl, dried with Na_2SO_4 and evaporated. The residue needed to be thoroughly vacuumed for the removal of relevant silicon containing part, after which **S2** was collected as white solid or colorless oil.

Step 2:

To a 250 mL flask was added **S2** (20 mmol, 1.0 equiv) and DMF (0.25 M), then the flask was cooled in an ice bath, and NaH (80 mmol, 4.0 equiv) was added in portion. After 10 minutes, BnBr (80 mmol, 4.0 equiv) was added dropwise using a syringe. The system was warmed up to room temperature and stirred overnight. After total consumption of **S2**, the system was diluted with H_2O and quenched with saturated NH_4Cl. The water layer was extracted with EA for third times. The organic layer was combined, washed with saturated NaCl, dried with Na_2SO_4 and evaporated. The residue was purified by chromatography (PE:EA = 20:1) to get **S3** was collected as white solid.

Step 3:

S3 (10 mmol) was added in a 50 mL flask and dissolved with 20 mL TBAF (1M in THF). The reaction system was stirred overnight, monitored by TLC and was evaporated under reduced pressure. The residue was purified by flash chromatography to get **S4** as white solid.

Step 4:

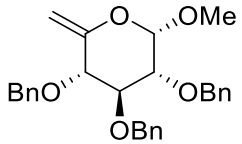
To a two-neck bottle was added **S4** (10 mmol, 1.0 equiv), imidazole (20 mmol, 2.0 equiv), PPh_3 (15 mmol, 1.5 equiv) and THF (0.2 M). The system set with condenser was refluxed at 70℃. I_2 (15 mmol, 1.5 equiv) was added dropwise through a syringe as 1M solution in THF. The reaction was stirred overnight and monitored by TLC. After completion, the reaction was cooled down to room temperature, added 50 mL Et_2O and cooled to -20℃. The mixture was filtered, then the filtrate was Sequentially washed with 10% $Na_2S_2O_3$, H_2O and saturated NaCl. The organic phase was evaporated under reduced pressure and purified by flash chromatography to get **S5**.

Step 5:

S5 (10 mmol, 1.0 equiv) was dissolved in 1,2-Dimethoxyethane (0.3 M) in a 100 mL flask, and DBU (30 mmol, 3.0 equiv) was added via a syringe. The reaction was stirred at 90℃ for 5 h. The system was evaporated under reduced pressure, and was purified by flash chromatography to get **1a**.

5.2 Glycal substrates characterization

(2S,3R,4S,5S)-3,4,5-tris(benzyloxy)-2-methoxy-6-methylenetetrahydro-2H-pyran

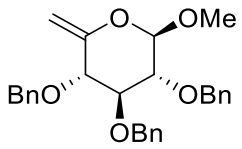


1a

According to the **general procedure A**, **1a** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = - 22.0 (c 1.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 15H), 5.02 – 4.60 (m, 9H),

4.15 – 3.83 (m, 2H), 3.61 (dd, *J* = 9.1, 3.4 Hz, 1H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 138.8, 138.2, 138.1, 128.6, 128.5, 128.5, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 99.2, 97.0, 81.3, 79.6, 79.4, 75.9, 74.6, 73.7, 55.6. HRMS (ESI) m/z: [M + Na] $^+$ Calcd for $C_{28}H_{30}NaO_5^+$ 469.1985; Found 469.1989.

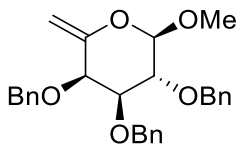
(2R,3R,4S,5S)-3,4,5-tris(benzyloxy)-2-methoxy-6-methylenetetrahydro-2H-pyran



1b

According to the **general procedure A**, **1b** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = - 46.1 (c 1.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 15H), 4.82 – 4.73 (m, 5H), 4.72 – 4.65 (m, 3H), 4.63 (d, *J* = 6.2 Hz, 1H), 4.08 (dt, *J* = 7.6, 1.5 Hz, 1H), 3.70 – 3.62 (m, 1H), 3.58 (s, 3H), 3.57 (m, *J* = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 138.4, 138.3, 138.0, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 104.1, 94.7, 82.2, 81.6, 78.4, 74.4, 74.0, 73.2, 57.0. HRMS (ESI) m/z: [M + Na] $^+$ Calcd for $C_{28}H_{30}NaO_5^+$ 469.1986; Found 469.1988.

(2S,3R,4S,5R)-3,4,5-tris(benzyloxy)-2-methoxy-6-methylenetetrahydro-2H-pyran

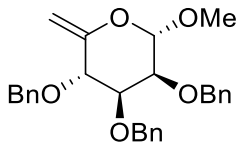


1c

According to the **general procedure A**, **1c** was obtained as colorless liquid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = - 3.6 (c 0.88, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 15H), 4.83 (m 4H), 4.63 (s, 2H), 4.50 – 4.42 (m, 3H), 4.11 – 3.93 (m, 2H), 3.63 (s, 3H), 3.58 (dd, *J* = 9.2, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 138.8, 138.3, 138.0, 128.4, 128.4,

128.3, 128.2, 128.0, 127.8, 127.7, 127.7, 105.5, 100.3, 78.6, 75.0, 73.3, 72.2, 69.5, 57.2. HRMS (ESI) m/z: [M + Na] $^+$ Calcd for $C_{37}H_{42}ClNNaO_7S^+$ 702.2263; Found 702.2260.

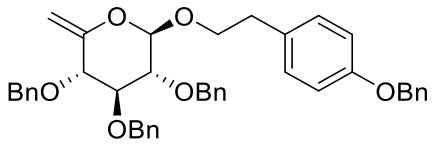
(2S,3S,4S,5S)-3,4,5-tris(benzyloxy)-2-methoxy-6-methylenetetrahydro-2H-pyran



1d

According to the **general procedure A**, **1d** was obtained as semi solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = + 35.6 (c 0.92, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 9H), 4.90 – 4.76 (m, 8H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.43 (dt, *J* = 8.7, 1.7 Hz, 1H), 4.06 – 3.84 (m, 2H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 138.6, 138.3, 128.4, 128.4, 127.9, 127.8, 127.8, 127.6, 127.6, 100.9, 96.7, 78.7, 76.6, 75.8, 73.6, 73.3, 73.0, 55.5. HRMS (ESI) m/z: [M + Na] $^+$ Calcd for $C_{28}H_{30}NaO_5^+$ 469.1985; Found 469.1992.

(2R,3R,4S,5S)-3,4,5-tris(benzyloxy)-2-(4-(benzyloxy) phenethoxy)-6-methylenetetrahydro-2H-pyran

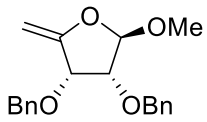


1e

According to the **general procedure A**, **1e** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = - 27.7 (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.22 (m, 20H), 7.20 – 7.12 (m, 2H), 6.93 – 6.84 (m, 2H), 4.99 (s, 2H), 4.79 – 4.53 (m, 9H), 4.16 (dt, *J* = 9.5, 6.8 Hz, 1H), 4.03 (dt, *J* = 7.8, 1.5 Hz, 1H), 3.76 (dt, *J* = 9.7, 7.3 Hz, 1H), 3.63 (t, *J* = 7.4 Hz, 1H), 3.56 (t, *J* = 6.7 Hz, 1H), 2.91 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 154.1, 138.5, 138.4, 138.0, 137.3, 131.0, 130.0, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 114.9, 103.1, 94.8, 82.4, 81.8, 78.5, 74.5, 74.1, 73.2,

70.8, 70.1, 35.4. HRMS (ESI) m/z: [M + H] $^{+}$ Calcd for $C_{28}H_{29}NO_9$ 524.1915; Found 524.1919.

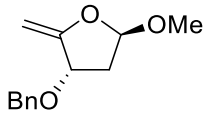
(2R,3R,4S)-3,4-bis(benzyloxy)-2-methoxy-5-methylenetetrahydrofuran



1f

According to the **general procedure A**, **1f** was obtained as slurry solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = - 62.8 (c 2.68, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 10H), 5.13 (d, *J* = 2.3 Hz, 1H), 4.63 (dd, *J* = 11.4, 2.8 Hz, 4H), 4.52 (t, *J* = 1.9 Hz, 1H), 4.37 (dt, *J* = 4.8, 1.5 Hz, 1H), 4.25 (t, *J* = 1.7 Hz, 1H), 3.82 (dd, *J* = 4.7, 2.4 Hz, 1H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 137.7, 137.5, 128.5, 128.2, 128.0, 128.0, 127.9, 106.9, 85.1, 78.8, 76.0, 72.3, 71.6, 56.5. HRMS (ESI) m/z: [M + Na] $^{+}$ Calcd for $C_{20}H_{22}NaO_4^{+}$ 349.1410; Found 349.1410.

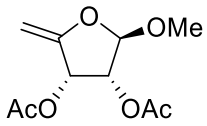
(3S,5R)-3-(benzyloxy)-5-methoxy-2-methylenetetrahydrofuran



1g

According to the **general procedure A**, **1g** was obtained as colorless liquid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = - 63.8 (c 3.54, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 5.33 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 4.57 – 4.47 (m, 3H), 4.22 (t, *J* = 1.5 Hz, 1H), 3.45 (s, 3H), 2.27 – 2.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 138.0, 128.6, 127.9, 127.9, 106.0, 84.6, 76.6, 71.0, 56.4, 38.5. HRMS (ESI) m/z: [M + H] $^{+}$ Calcd for $C_{13}H_{17}O_3^{+}$ 221.1173; Found 221.1171.

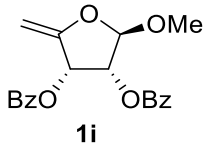
(2R,3R,4S)-2-methoxy-5-methylenetetrahydrofuran-3,4-diyl diacetate



1h

According to the **general procedure A**, **1h** was obtained as colorless liquid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = + 45.2 (c 2.68, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.75 (m, 1H), 5.15 (dt, *J* = 5.0, 0.9 Hz, 1H), 5.05 (d, *J* = 1.2 Hz, 1H), 4.52 (td, *J* = 2.4, 0.7 Hz, 1H), 4.15 (t, *J* = 2.1 Hz, 1H), 3.42 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 169.7, 156.7, 106.0, 85.2, 73.2, 69.6, 56.2, 20.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}NaO_6^+$ 253.0683; Found 253.0688.

(2R,3R,4S)-2-methoxy-5-methylenetetrahydrofuran-3,4-diyl dibenzoate

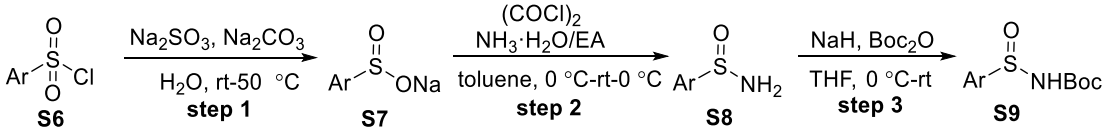


1i

According to the **general procedure A**, **1i** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 10:1 - 5:1. $[\alpha]_D^{25}$ = + 81.9 (c 0.86, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (ddd, *J* = 8.7, 5.3, 1.5 Hz, 4H), 7.64 – 7.48 (m, 2H), 7.37 (m, 4H), 6.17 (dt, *J* = 4.0, 2.0 Hz, 1H), 5.57 (d, *J* = 5.1 Hz, 1H), 5.30 (s, 1H), 4.66 (t, *J* = 2.4 Hz, 1H), 4.33 (t, *J* = 2.1 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.4, 157.1, 133.6, 133.5, 130.0, 129.9, 129.7, 129.2, 128.6, 128.5, 106.3, 85.7, 73.8, 70.3, 56.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}NaO_6^+$ 377.0996; Found 377.0999.

5.3 General procedure B

Aryl sulfinamides **2a**-**2j** were synthesized according to the literatures.[5,6]



Step 1:

In a 50 M flask, Na_2SO_3 (15 mol, 1.5 equiv) and Na_2CO_3 (20 mmol, 2.0 equiv) were dissolved in H_2O (0.5 M). The system was heated to 50℃, and **S6** (10 mmol, 1.0 equiv) was added in one portion. After stirring overnight, the reaction was evaporated under reduced pressure, and toluene was used to remove H_2O. The residue was fully dried, then 30 mL ethanol was added together with sufficient stirring. The mixture was filtered and repeated for 3 times. The organic layer was combined and concentrated to get **S7** as white solid.

Step 2:

S7 (1.2 equiv) and Toluene (0.25 M) was added to a flask under inert atmosphere and was cooled using an ice bath. Oxalyl chloride (1.0 equiv) was added dropwise for 2 minutes, then the reaction was stirred at 0℃ for 1 h and room temperature for 1 h. Next, the reaction was cooled to 0℃, added NH_4OH/EA (*v*:*v* = 1:1, 10 equiv) under open air and stirred vigorously for 15 minutes. The mixture was transferred to a funnel, added H_2O (5 ml/mmol) and EA (5 ml/mmol) and extracted with EA for 3 times. The organic layer was combined, washed with saturated NaCl, dried with Na_2SO_4 and evaporated under reduced pressure to get **S8**.

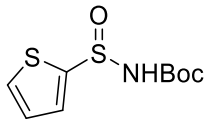
Step 3:

S8 (10 mmol, 1.0 equiv, 0.8 M solution in THF) was added dropwise to a solution of NaH (20 mmol, 2.0 equiv) in THF (0.4 M) at 0 ℃. After 5 minutes, a solution of Boc_2O (11 mmol, 1.1 equiv) in THF (2 M) was added dropwise, and the reaction was stirred at 0℃ for 1 h and at room temperature until completion. The system was cooled back to 0℃, quenched with 5 mL saturated NH_4Cl, and added EA/half satuated NH_4Cl (*v*:*v*= 1:1). EA was used to extracted twice, and the organic phase was combined, washed with saturated $NaHCO_3$, dried and evaporated under reduced pressure. The crude **S9** was purified by flash chromatography as white powder.

5.4 Aryl sulfinamide substrates characterization

Characterizations of aryl sulfinamide **2a**, **2c**, **2f**, **2g**, **2h, 2j** were consistent with the data reported by literatures.[5,6]

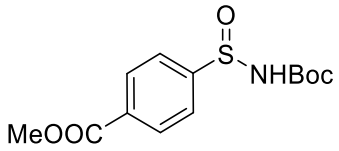
tert-butyl (thiophen-2-ylsulfonyl) carbamate



2b

According to the **general procedure B**, **2b** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 2:1. $[\alpha]_D^{25}$ = + 2.4 (c 0.86, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.51 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.11 – 7.07 (m, 1H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 146.0, 131.6, 129.8, 128.1, 84.1, 28.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{13}NNaO_3S_2^+$ 270.0230; Found 270.0226.

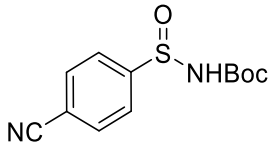
methyl 4-(N-(tert-butoxycarbonyl) sulfamoyl) benzoate



2d

According to the **general procedure B**, **2d** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 11.6 (c 0.38, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.15 (m, 2H), 7.82 (dd, *J* = 8.6, 2.7 Hz, 2H), 3.96 (s, *J* = 2.0 Hz, 2H), 1.51 (s, *J* = 2.6 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 152.4, 148.5, 133.5, 130.6, 125.2, 84.2, 52.7, 28.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}NO_5^+$ 300.0901; Found 300.0902.

tert-butyl ((4-cyanophenyl) sulfonyl) carbamate

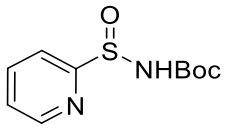


2e

According to the **general procedure B**, **2e** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 14.7 (c 0.30,

$CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.80 (m, 4H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 148.9, 133.1, 126.1, 117.6, 115.9, 84.6, 28.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}N_2NaO_3^+$ 289.0618; Found 289.0617.

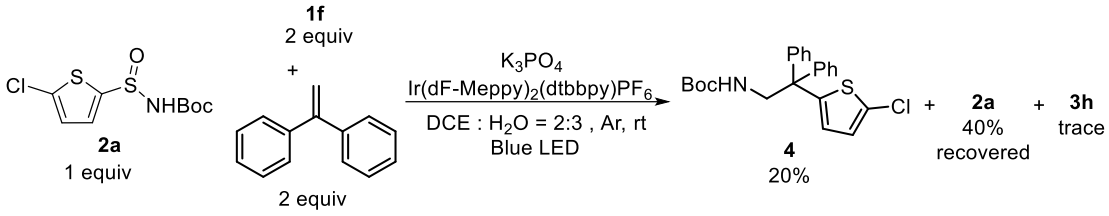
tert-butyl (pyridin-2-ylsulfonyl) carbamate



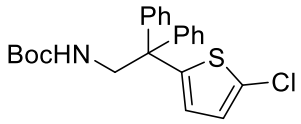
2h

According to the **general procedure B**, **2h** was obtained as white solid. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 11.7 (c 0.36, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.70 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 8.03 – 7.92 (m, 2H), 7.61 – 7.56 (m, 1H), 7.49 (ddd, *J* = 7.2, 4.7, 1.6 Hz, 1H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 152.6, 150.1, 138.6, 126.3, 121.9, 83.8, 28.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{15}N_2O_3S^+$ 243.0798; Found 243.0795.

6. Mechanism study



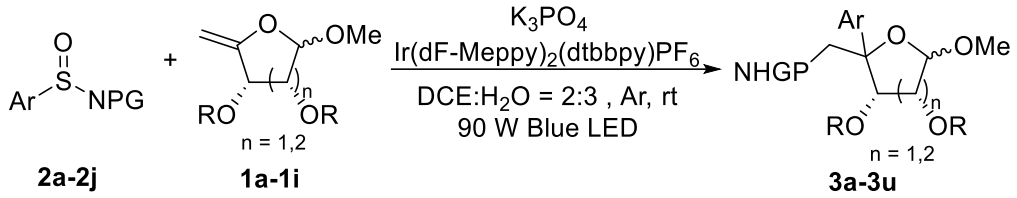
Ayl sulfamide **2a** (0.15 mmol, 1.0 equiv)**,** glycal **1f** (0.3 mmol, 2.0 equiv), K_3PO_4 (0.375 mmol, 2.5 equiv) and $[Ir(dF\text{-}Meppy)_2(dtbbpy)]PF_6$ (2 mol%, 1.8 mg) were added to an 8 mL screw-cap tube equipped with a magnetic stirring bar. The tube was changed with Argon for three times, then 1,1-diphenylethylene (0.3 mmol, 2.0 equiv) was injected through a microsyringe. The 90 W blue LED was applied to the tube at room temperature for 12 h. After TLC completion, it was extracted with DCM, washed with brine and dried. The residue was concentrated and purified by flash chromatography to afford radical capture product **4** (12.4 mg, 20%) and recovered **2a** (17 mg, 40%).



4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 6H), 7.21 – 7.13 (m, 4H), 6.72 (d, J = 3.9 Hz, 1H), 6.42 (d, J = 3.9 Hz, 1H), 4.46 (m, 1H),4.28 (d, J = 6.2 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 144.5, 129.8, 128.8, 128.6, 127.4, 126.7, 125.0, 80.0, 55.6, 49.6, 28.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{24}ClNNaO_2S^+$ 436.1109; Found 436.1106.

7. General procedure C for synthesis of products

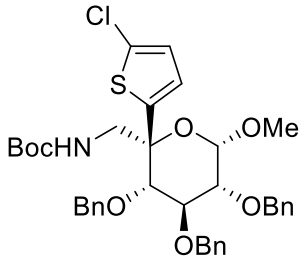


2a-2j **1a-1i** **3a-3u**

Ayl sulfamide **2** (0.15 mmol, 1.0 equiv)**,** glycal **1** (0.3 mmol, 2.0 equiv), K_3PO_4 (0.375 mmol, 2.5 equiv) and $[Ir(dF\text{-}Meppy)_2(dtbbpy)]PF_6$ (2 mol%, 1.8 mg) were added to an 8 mL screw-cap tube equipped with a magnetic stirring bar. The tube was changed with Argon for three times, and 90 W blue LEDs was applied to the tube at room temperature for 17-48 h. After TLC completion, it was extracted with DCM, washed with brine and dried. The residue was concentrated and purified by flash chromatography to afford product **3a-3u**.

8. Product characterization

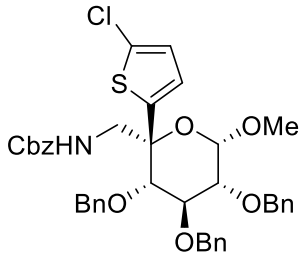
tert-butyl (((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-(5-chlorothiophen-2-yl)-6-methoxytetrahydro-2H-pyran-2-yl) methyl) carbamate



3a

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2a** (0.15 mmol, 42 mg), **3a** (69 mg, 68%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1, reaction time = 18 h. $[\alpha]_D^{25}$ = + 13.1 (c 0.81, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.20 (m, 13H), 7.21 – 7.15 (m, 2H), 6.81 (d, *J* = 3.9 Hz, 1H), 6.68 (d, *J* = 3.9 Hz, 1H), 4.92 (d, *J* = 10.7 Hz, 1H), 4.86 – 4.71 (m, 4H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.29 (d, *J* = 10.9 Hz, 1H), 4.11 (t, *J* = 9.7 Hz, 1H), 4.04 (dd, *J* = 14.1, 6.1 Hz, 1H), 3.87 (dd, *J* = 14.1, 4.8 Hz, 1H), 3.61 (dd, *J* = 9.8, 4.1 Hz, 1H), 3.56 (d, *J* = 9.7 Hz, 1H), 3.52 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 145.2, 138.4, 138.1, 138.0, 129.6, 128.7, 128.5, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 125.9, 123.9, 101.0, 85.6, 81.1, 80.2, 79.2, 78.5, 76.2, 75.9, 73.8, 58.3, 44.3, 28.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{42}ClNNaO_7S^+$ 702.2263; Found 702.2263.

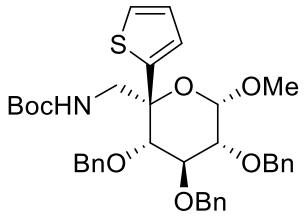
benzyl (((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-(5-chlorothiophen-2-yl)-6-methoxytetrahydro-2H-pyran-2-yl) methyl) carbamate



3b

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2j** (0.15 mmol, 47 mg), **3b** (68 mg, 63%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 1.0 (c 1.60, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.08 (m, 20H), 6.78 (d, *J* = 3.9 Hz, 1H), 6.65 (d, *J* = 3.9 Hz, 1H), 5.01 (s, 2H), 4.98 – 4.94 (m, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.85 – 4.72 (m, 4H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.27 (d, *J* = 10.9 Hz, 1H), 4.17 – 4.05 (m, 2H), 3.92 (dd, *J* = 14.1, 4.3 Hz, 1H), 3.60 (dd, *J* = 9.8, 4.0 Hz, 1H), 3.55 (d, *J* = 9.7 Hz, 1H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 144.9, 138.1, 137.8, 136.7, 129.7, 128.7, 128.6, 128.5, 128.5, 128.2, 128.1, 128.1, 128.1, 127.9, 127.8, 127.6, 126.1, 123.9, 101.1, 85.4, 81.1, 80.2, 78.5, 76.3, 75.9, 73.9, 66.7, 58.4, 44.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{40}ClNNaO_7S^+$ 736.2106; Found 736.2116.

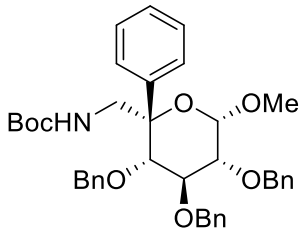
tert-butyl (((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-2-(thiophen-2-yl) tetrahydro-2H-pyran-2-yl) methyl) carbamate



3c

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2b** (0.15 mmol, 37 mg), **3c** (53 mg, 55%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 8.1 (c 3.08, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 16H), 7.08 (d, *J* = 3.8 Hz, 1H), 6.90 (dd, *J* = 5.3, 3.5 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.87 – 4.70 (m, 4H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.24 – 4.06 (m, 3H), 3.96 (dd, *J* = 13.8, 5.0 Hz, 1H), 3.69 – 3.59 (m, 2H), 3.54 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 146.7, 138.5, 138.2, 138.2, 128.7, 128.5, 128.4, 128.1, 128.1, 127.8, 127.6, 127.4, 126.9, 125.2, 124.7, 101.0, 86.2, 81.1, 80.3, 79.0, 78.6, 76.1, 75.9, 73.8, 58.1, 44.7, 28.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{43}NNaO_7S^+$ 668.2652; Found 668.2656.

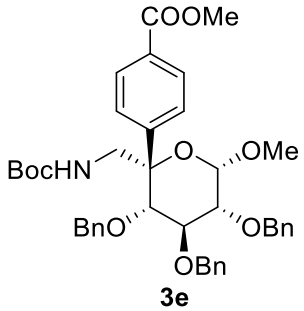
tert-butyl (((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-2-phenyltetrahydro-2H-pyran-2-yl) methyl) carbamate



3d

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2c** (0.15 mmol, 36 mg), **3d** (43 mg, 45%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 6.1 (c 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.45 – 7.20 (m, 16H), 7.12 (dd, *J* = 7.6, 1.9 Hz, 2H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.91 – 4.76 (m, 3H), 4.71 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.56 (d, *J* = 4.8 Hz, 1H), 4.31 – 4.13 (m, 2H), 4.03 – 3.90 (m, 2H), 3.67 (dd, *J* = 9.8, 4.1 Hz, 1H), 3.55 (s, 3H), 3.51 (d, *J* = 9.7 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 142.1, 138.6, 138.3, 138.1, 128.7, 128.5, 128.4, 128.1, 127.8, 127.6, 126.4, 101.2, 86.2, 81.6, 80.4, 79.0, 78.7, 76.0, 75.9, 73.8, 58.1, 43.0, 28.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{46}NO_7^+$ 640.3269; Found 640.3266.

methyl 4-((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-2-(((tert-butoxycarbonyl) amino) methyl)-6-methoxytetrahydro-2H-pyran-2-yl) benzoate

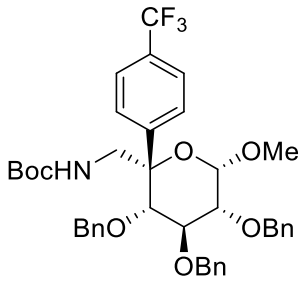


3e

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2d** (0.15 mmol, 45 mg), **3e** (50 mg, 48%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 35.4 (c 0.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.51 – 7.20 (m,

13H), 7.17 – 7.08 (m, 2H), 5.04 – 4.76 (m, 3H), 4.69 (t, *J* = 11.0 Hz, 2H), 4.51 (dd, *J* = 6.9, 3.4 Hz, 1H), 4.28 (dd, *J* = 14.1, 7.1 Hz, 1H), 4.18 (t, *J* = 9.7 Hz, 1H), 4.06 – 3.86 (m, 2H), 3.91 (s, 3H), 3.66 (dd, *J* = 9.8, 4.1 Hz, 1H), 3.56 (s, 3H), 3.46 (d, *J* = 9.5 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 155.9, 147.3, 138.5, 137.8, 129.5, 128.7, 128.5, 128.5, 128.5, 128.2, 128.2, 128.1, 127.8, 127.7, 127.6, 126.4, 101.2, 85.6, 81.7, 80.3, 78.7, 76.1, 75.9, 73.8, 58.2, 52.3, 43.1, 28.4. HRMS (ESI) m/z: [M + H] $^+$ Calcd for $C_{41}H_{48}NO_9^+$ 698.3324; Found 698.3325.

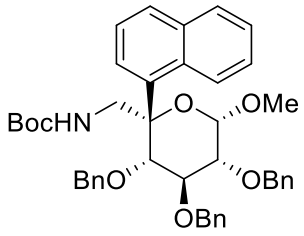
tert-butyl (((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-2-(4-(trifluoromethyl) phenyl) tetrahydro-2H-pyran-2-yl) methyl) carbamate



3f

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2f** (0.15 mmol, 46 mg), **3f** (45 mg, 42%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 1.0 (c 0.56, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.20 (m, 13H), 7.10 (dd, *J* = 7.0, 2.6 Hz, 2H), 5.06 – 4.65 (m, 6H), 4.50 (m, 1H), 4.33 – 4.15 (m, 2H), 4.04 (d, *J* = 11.0 Hz, 1H), 3.94 (dd, *J* = 14.1, 3.4 Hz, 1H), 3.65 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.56 (s, 3H), 3.51 – 3.44 (m, 1H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 146.1, 138.4, 138.2, 137.8, 129.7, 128.7, 128.6, 128.5, 128.2, 128.2, 128.1, 127.9, 127.8, 127.6, 126.8, 125.1, 124.3 (J_1 = 271.8 Hz), 101.2, 85.3, 81.6, 80.3, 79.3, 78.7, 76.0, 75.9, 73.8, 58.3, 53.6, 43.3, 29.8, 28.4, 0.1. HRMS (ESI) m/z: [M + H] $^+$ Calcd for $C_{40}H_{45}F_3NO_7^+$ 708.3143; Found 708.3137.

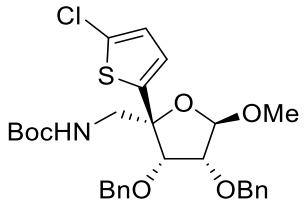
tert-butyl (((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-2-(naphthalen-1-yl) tetrahydro-2H-pyran-2-yl) methyl) carbamate



3g

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2h** (0.15 mmol, 45 mg), **3g** (47 mg, 45%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 30.0 (c 0.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.85 – 7.75 (m, 3H), 7.65 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.55 – 7.17 (m, 14H), 7.14 – 7.04 (m, 2H), 5.00 – 4.93 (m, 2H), 4.92 – 4.79 (m, 2H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 4.3 Hz, 1H), 4.37 (dd, *J* = 13.9, 6.5 Hz, 1H), 4.23 (t, *J* = 9.8 Hz, 1H), 4.07 (dd, *J* = 14.0, 3.9 Hz, 1H), 3.91 (d, *J* = 10.8 Hz, 1H), 3.73 (dd, *J* = 9.8, 4.1 Hz, 1H), 3.59 (m, *J* = 103.8, 9.4 Hz, 4H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 139.4, 138.6, 138.0, 133.2, 132.9, 128.7, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 126.3, 126.1, 125.6, 124.3, 101.3, 86.1, 81.7, 80.5, 78.7, 76.1, 76.0, 73.8, 58.1, 43.1, 28.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{43}H_{48}NO_7^+$ 690.3426; Found 690.3425.

tert-butyl (((2S,3S,4R,5R)-3,4-bis(benzyloxy)-2-(5-chlorothiophen-2-yl)-5-methoxytetrahydrofuran-2-yl) methyl) carbamate

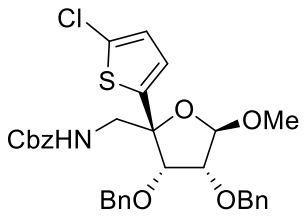


3h

According to the **general procedure C** from **1f** (0.3 mmol, 98 mg) and **2a** (0.15 mmol, 42 mg), **3h** (74 mg, 88%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 18.6 (c 1.74, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 10H), 6.72 (m, 2H), 5.21 (dd, *J* = 8.5, 3.9 Hz, 1H), 4.98 (s, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.64 – 4.56 (m, 2H), 4.50 (d, *J* = 11.6 Hz, 1H),

4.33 (d, *J* = 4.9 Hz, 1H), 3.95 (d, *J* = 5.0 Hz, 1H), 3.86 (dd, *J* = 14.1, 8.4 Hz, 1H), 3.67 (dd, *J* = 14.0, 3.7 Hz, 1H), 3.41 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 147.4, 137.5, 137.4, 128.6, 128.1, 128.1, 127.9, 127.9, 125.9, 122.5, 106.5, 85.7, 85.1, 80.8, 78.9, 73.3, 73.1, 56.0, 46.7, 28.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{34}ClNNaO_6S^+$ 582.1688; Found 582.1692.

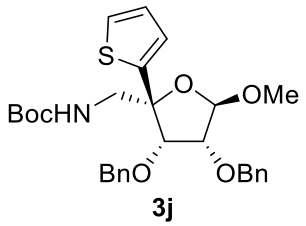
benzyl (((2S,3S,4R,5R)-3,4-bis(benzyloxy)-2-(5-chlorothiophen-2-yl)-5-methoxytetrahydrofuran-2-yl) methyl) carbamate



3i

According to the **general procedure C** from **1f** (0.3 mmol, 98 mg) and **2j** (0.15 mmol, 47 mg), **3i** (66 mg, 74%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 14.8 (c 2.82, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) (**major isomer**) δ 7.40 – 7.25 (m, 15H), 6.71 (d, *J* = 0.8 Hz, 2H), 5.56 (dd, *J* = 8.4, 3.6 Hz, 1H), 5.02 (m, 3H), 4.74 – 4.45 (m, 4 H), 4.35 (d, *J* = 4.9 Hz, 1H), 4.00 – 3.87 (m, 2H), 3.76 (dd, *J* = 14.1, 3.5 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.4, 137.3, 137.3, 137.1, 128.7, 128.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.9, 126.0, 122.3, 106.4, 85.6, 84.9, 80.6, 73.3, 73.1, 66.4, 56.0, 47.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{33}ClNO_6S^+$ 594.1712; Found 594.1711.

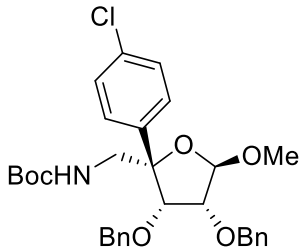
tert-butyl (((2S,3S,4R,5R)-3,4-bis(benzyloxy)-2-(4-chlorophenyl)-5-methoxytetrahydrofuran-2-yl) methyl) carbamate



3j

According to the **general procedure C** from **1f** (0.3 mmol, 98 mg) and **2b** (0.15 mmol, 37 mg), **3j** (51 mg, 65%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 8.5 (c 2.28, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$)(**major isomer**) δ 7.41 – 7.27 (m, 10H), 7.18 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.02 – 6.82 (m, 2H), 5.32 (dd, *J* = 8.2, 3.8 Hz, 1H), 5.03 (s, 1H), 4.74 – 4.47 (m, 5H), 4.41 (d, *J* = 4.9 Hz, 1H), 3.97 (d, *J* = 5.0 Hz, 1H), 3.89 (dd, *J* = 14.1, 8.2 Hz, 1H), 3.71 (dd, *J* = 14.1, 3.8 Hz, 1H), 3.42 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 148.8, 137.6, 137.5, 128.6, 128.6, 128.2, 128.0, 127.9, 127.8, 126.8, 124.1, 123.2, 106.4, 85.9, 85.4, 81.0, 78.7, 73.3, 73.0, 55.8, 47.1, 28.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{36}NO_6S^+$ 526.2258; Found 526.2257.

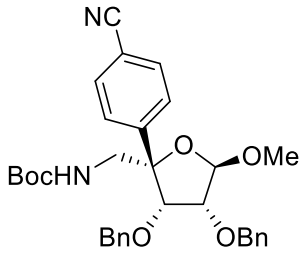
tert-butyl (((2S,3S,4R,5R)-3,4-bis(benzyloxy)-2-(4-chlorophenyl)-5-methoxytetrahydrofuran-2-yl) methyl) carbamate



3k

According to the **general procedure C** from **1f** (0.3 mmol, 98 mg) and **2g** (0.15 mmol, 41 mg), **3k** (48 mg, 58%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 39.9 (c 0.74, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) (**major isomer**) δ 7.55 – 7.29 (m, 12H), 7.29 – 7.02 (m, 2H), 5.29 (dd, *J* = 8.7, 3.5 Hz, 1H) , 5.05 (s, 1H), 4.79 – 4.41 (m, 4H), 4.28 (d, *J* = 5.0 Hz, 1H), 3.94 (d, *J* = 5.0 Hz, 1H), 3.72 (dd, *J* = 13.9, 8.6 Hz, 1H), 3.53 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.34 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 143.4, 137.6, 137.5, 133.0, 128.7, 128.6, 128.2, 128.1, 128.1, 127.9, 127.9, 126.6, 106.0, 86.6, 84.4, 80.4, 78.7, 72.9, 72.9, 55.7, 47.3, 28.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{37}ClNO_6^+$ 554.2304; Found 554.2302.

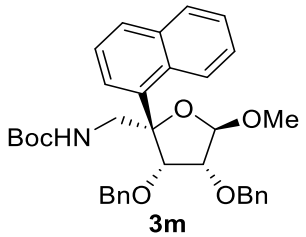
tert-butyl (((2S,3S,4R,5R)-3,4-bis(benzyloxy)-2-(4-cyanophenyl)-5-methoxytetrahydrofuran-2-yl) methyl) carbamate



3l

According to the **general procedure C** from **1f** (0.3 mmol, 98 mg) and **2e** (0.15 mmol, 40 mg), **3l** (48 mg, 59%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 45.8 (c 0.51, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) (**major isomer**) δ 7.59 – 7.49 (m, 4H), 7.41 – 7.27 (m, 10H), 5.26 – 5.18 (m, 1H), 5.04 (s, 1H), 4.77 – 4.41 (m, 4H), 4.25 (d, *J* = 5.0 Hz, 1H), 3.94 (d, *J* = 5.0 Hz, 1H), 3.77 (dd, *J* = 14.2, 8.7 Hz, 1H), 3.55 (dd, *J* = 14.1, 3.7 Hz, 1H), 3.33 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 150.2, 137.4, 137.2, 128.7, 128.7, 128.3, 128.2, 128.0, 128.0, 125.9, 119.0, 111.0, 106.0, 86.5, 84.0, 8f0.2, 78.9, 73.0, 72.9, 55.8, 47.1, 28.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{37}N_2O_6^+$ 545.2647; Found 545.2646.

tert-butyl (((2S,3S,4R,5R)-3,4-bis(benzyloxy)-5-methoxy-2-(naphthalen-1-yl) tetrahydrofuran-2-yl) methyl) carbamate

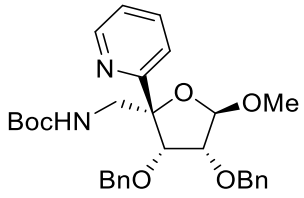


3m

According to the **general procedure C** from **1f** (0.3 mmol, 98 mg) and **2h** (0.15 mmol, 44 mg), **3m** (47 mg, 55%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 61.3 (c 1.44, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) (**major isomer**) δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.84 – 7.75 (m, 3H), 7.61 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.50 – 7.30 (m, 12H), 5.45 (dd, *J* = 8.3, 3.4 Hz, 1H), 5.15

(s, 1H), 4.94 – 4.51 (m, 4H), 4.48 (d, *J* = 5.0 Hz, 1H), 4.01 (d, *J* = 5.1 Hz, 1H), 3.85 (dd, *J* = 14.1, 8.3 Hz, 1H), 3.66 (dd, *J* = 14.1, 3.4 Hz, 1H), 3.40 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 142.3, 137.6, 133.1, 132.7, 128.6, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 127.7, 127.6, 126.0, 125.8, 123.8, 123.5, 106.0, 87.1, 84.4, 80.6, 78.5, 72.9, 72.9, 55.7, 47.4, 28.4. HRMS (ESI) m/z: [M + H] $^+$ Calcd for $C_{35}H_{40}NO_6^+$ 570.2851; Found 570.2847.

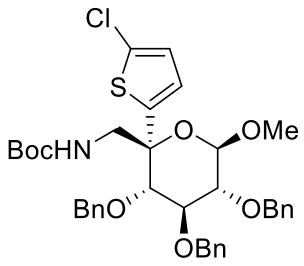
tert-butyl (((2R,3S,4R,5R)-3,4-bis(benzyloxy)-5-methoxy-2-(pyridin-2-yl) tetrahydrofuran-2-yl) methyl) carbamate



3n

According to the **general procedure C** from **1f** (0.3 mmol, 98 mg) and **2i** (0.15 mmol, 36 mg), **3n** (51 mg, 65%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 2.4 (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) (**major isomer**)δ 8.55 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.46 – 7.39 (m, 2H), 7.37 – 7.28 (m, 8H), 7.15 (td, *J* = 5.1, 3.2 Hz, 1H), 5.45 (dd, *J* = 8.1, 3.9 Hz, 1H), 5.05 (d, *J* = 1.8 Hz, 1H), 4.86 (m, 2H), 4.77 (d, *J* = 5.0 Hz, 1H), 4.66 (s, 2H), 3.92 – 3.70 (m, 2H), 3.57 (dd, *J* = 13.8, 3.8 Hz, 1H), 3.28 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 156.4, 148.5, 139.3, 138.5, 138.0, 136.2, 129.6, 128.5, 128.5, 128.1, 127.9, 127.8, 127.8, 126.5, 123.7, 122.2, 121.0, 106.6, 88.2, 82.8, 81.7, 78.5, 73.3, 73.2, 55.8, 46.8, 28.5. HRMS (ESI) m/z: [M + H] $^+$ Calcd for $C_{30}H_{37}N_2O_6^+$ 521.2647; Found 521.2645.

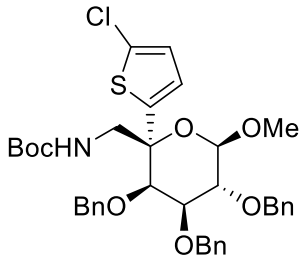
tert-butyl (((3S,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-(5-chlorothiophen-2-yl)-6-methoxytetrahydro-2H-pyran-2-yl) methyl) carbamate



3o

According to the **general procedure C** from **1a** (0.3 mmol, 134 mg) and **2a** (0.15 mmol, 42 mg), **3o** (47 mg, 46%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 42.7 (c 1.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.19 (m, 15H), 7.09 (d, *J* = 3.9 Hz, 1H), 6.77 (d, *J* = 3.9 Hz, 1H), 5.07 (d, *J* = 6.5 Hz, 1H), 4.95 – 4.76 (m, 5H), 4.70 (d, *J* = 11.0 Hz, 1H), 4.59 (d, *J* = 7.9 Hz, 1H), 3.94 – 3.82 (m, 3H), 3.60 (s, 3H), 3.43 (t, *J* = 8.3 Hz, 1H), 3.32 – 3.23 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 139.7, 138.4, 138.3, 138.3, 131.1, 128.6, 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 126.7, 125.5, 101.0, 82.7, 81.4, 79.7, 79.1, 76.4, 75.1, 57.3, 49.6, 28.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{43}ClNO_7S^+$ 680.2444; Found 680.2448.

tert-butyl (((2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-2-(5-chlorothiophen-2-yl)-6-methoxytetrahydro-2H-pyran-2-yl) methyl) carbamate

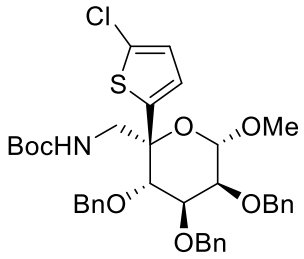


3p

According to the **general procedure C** from **1c** (0.3 mmol, 134 mg) and **2a** (0.15 mmol, 42 mg), **3p** (75 mg, 74%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 53.2 (c 4.66, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 15H), 6.66 (d, *J* = 3.8 Hz, 1H), 6.22 (d, *J* = 3.9 Hz, 1H), 5.08 (d, *J* = 11.1 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 2H), 4.78 – 4.71 (m, 2H), 4.70 – 4.63 (m, 2H), 4.35 – 4.27 (m, 1H), 3.98 (d, *J* = 2.6 Hz, 1H), 3.91 (dd, *J* = 9.8, 7.6 Hz,

1H), 3.76 (dd, *J* = 9.7, 2.6 Hz, 1H), 3.62 (s, 3H), 3.57 – 3.41 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 141.6, 138.6, 138.5, 137.9, 130.4, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.7, 125.9, 124.2, 102.3, 79.7, 79.2, 78.8, 77.4, 77.1, 75.0, 73.9, 57.2, 48.3, 28.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{42}ClNNaO_7S^+$ 702.2263; Found 702.2260.

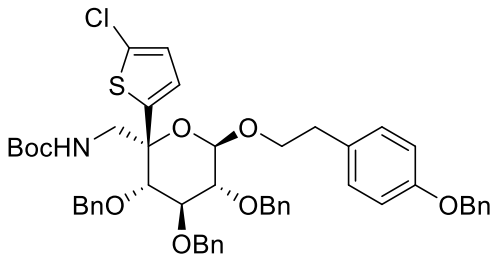
tert-butyl (((2S,3S,4S,5S,6S)-3,4,5-tris(benzyloxy)-2-(5-chlorothiophen-2-yl)-6-methoxytetrahydro-2H-pyran-2-yl) methyl) carbamate



3q

According to the **general procedure C** from **1d** (0.3 mmol, 134 mg) and **2a** (0.15 mmol, 42 mg), **3q** (61 mg, 60%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 24.1 (c 2.88, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.08 (m, 15H), 6.81 (d, *J* = 3.9 Hz, 1H), 6.73 (d, *J* = 3.9 Hz, 1H), 4.87 (d, *J* = 2.9 Hz, 1H), 4.85 – 4.68 (m, 4H), 4.62 (m, *J* = 1.8 Hz, 2H), 4.37 (d, *J* = 11.2 Hz, 1H), 4.16 (d, *J* = 9.4 Hz, 1H), 4.06 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.96 (dd, *J* = 13.9, 5.8 Hz, 1H), 3.86 – 3.74 (m, 2H), 3.46 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 145.5, 138.4, 138.3, 138.1, 129.5, 128.5, 128.4, 128.1, 127.8, 127.7, 127.6, 125.8, 123.5, 101.5, 81.2, 80.8, 79.2, 76.2, 75.9, 75.8, 73.1, 72.7, 57.1, 45.1, 28.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{42}ClNNaO_7S^+$ 702.2263; Found 702.2268.

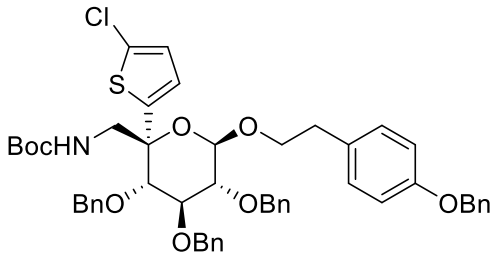
tert-butyl (((2S,3S,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-(4-(benzyloxy) phenethoxy)-2-(5-chlorothiophen-2-yl) tetrahydro-2H-pyran-2-yl) methyl) carbamate



3r

According to the **general procedure C** from **1e** (0.3 mmol, 192 mg) and **2a** (0.15 mmol, 42 mg), **3r** (38 mg, 41%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 2.0 (c 1.85, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.02 (m, 22H), 6.91 – 6.83 (m, 2H), 6.81 – 6.72 (m, 2H), 4.98 (s, 2H), 4.94 (d, *J* = 7.9 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 4.71 (d, *J* = 10.9 Hz, 1H), 4.61 (d, *J* = 11.2 Hz, 1H), 4.42 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.29 (d, *J* = 11.1 Hz, 1H), 4.09 (dt, *J* = 9.8, 6.7 Hz, 1H), 4.01 (dd, *J* = 14.9, 8.2 Hz, 1H), 3.87 (t, *J* = 9.5 Hz, 1H), 3.76 (dt, *J* = 9.5, 7.4 Hz, 1H), 3.68 (dd, *J* = 15.0, 3.5 Hz, 1H), 3.59 (d, *J* = 9.5 Hz, 1H), 3.49 (t, *J* = 8.6 Hz, 1H), 2.91 (t, *J* = 7.1 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 156.0, 144.7, 138.7, 138.3, 138.1, 137.3, 131.0, 130.1, 130.0, 128.7, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 127.6, 127.4, 125.9, 123.4, 114.9, 99.6, 84.7, 82.7, 81.8, 79.8, 78.4, 75.9, 74.7, 70.9, 70.1, 40.5, 35.6, 28.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{55}ClNO_8S^+$ 876.3332; Found 876.3336.

tert-butyl (((2R,3S,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-(4-(benzyloxy) phenethoxy)-2-(5-chlorothiophen-2-yl) tetrahydro-2H-pyran-2-yl) methyl) carbamate

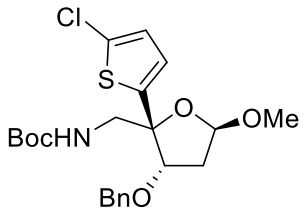


3r'

According to the **general procedure C** from **1e** (0.3 mmol, 192 mg) and **2a** (0.15 mmol, 42 mg), **3r'** (25 mg, 28%) was obtained as colorless oil. Flash column chromatography

eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 35.0 (c 3.17, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.16 (m, 22H), 7.08 (d, *J* = 4.0 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.77 (d, *J* = 3.9 Hz, 1H), 5.09 – 5.01 (m, 1H), 4.99 (d, *J* = 2.6 Hz, 2H), 4.97 – 4.89 (m, 1H), 4.89 – 4.76 (m, 3H), 4.73 – 4.66 (m, 2H), 4.60 (d, *J* = 11.0 Hz, 1H), 4.19 (dt, *J* = 9.5, 6.5 Hz, 1H), 3.89 (d, *J* = 8.9 Hz, 3H), 3.76 (q, *J* = 7.5 Hz, 1H), 3.44 (t, *J* = 8.3 Hz, 1H), 3.35 – 3.23 (m, 1H), 2.93 (m, *J* = 7.0, 2.8 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 155.5, 139.8, 138.4, 138.2, 137.2, 131.0, 130.8, 130.0, 128.7, 128.5, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 126.8, 125.5, 115.0, 99.8, 82.7, 81.4, 79.7, 79.1, 77.4, 76.3, 76.1, 75.0, 71.1, 70.1, 49.7, 35.6, 28.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{55}ClNO_8S^+$ 876.3332; Found 876.3329.

tert-butyl (((2S,3S,5R)-3-(benzyloxy)-2-(5-chlorothiophen-2-yl)-5-methoxytetrahydrofuran-2-yl) methyl) carbamate

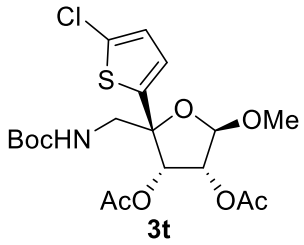


3s

According to the **general procedure C** from **1g** (0.3 mmol, 66 mg) and **2a** (0.15 mmol, 42 mg), **3s** (54 mg, 80%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 17.4 (c 4.71, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, *J* = 7.2, 6.5 Hz, 5H), 6.72 (m, *J* = 3.9 Hz, 2H), 5.10 (dd, *J* = 5.1, 1.8 Hz, 1H), 4.92 – 4.84 (m, 1H), 4.56 (m, *J* = 11.8 Hz, 2H), 4.48 – 4.40 (m, 1H), 3.74 (dd, *J* = 14.2, 7.8 Hz, 1H), 3.46 (dd, *J* = 14.1, 4.8 Hz, 1H), 3.42 (s, 3H), 2.28 (ddd, *J* = 12.9, 6.7, 1.6 Hz, 1H), 2.16 (ddd, *J* = 13.2, 8.5, 5.2 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 147.2, 137.6, 128.9, 128.7, 128.1, 127.7, 126.0, 122.6, 104.3, 85.9, 85.2, 79.3, 72.9, 55.8, 46.4, 38.8, 28.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}ClNO_5S^+$ 454.1450; Found 454.1448.

(2S,3S,4R,5R)-2-(((tert-butoxycarbonyl) amino) methyl)-2-(5-chlorothiophen-2-

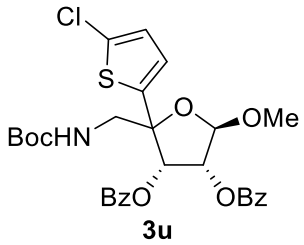
yl)-5-methoxytetrahydrofuran-3,4-diyl diacetate



3t

According to the **general procedure C** from **1h** (0.3 mmol, 69 mg) and **2a** (0.15 mmol, 42 mg), **3t** (56 mg, 80%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = - 41.7 (c 2.58, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 6.75 (t, *J* = 2.9 Hz, 2H), 5.68 (d, *J* = 5.1 Hz, 1H), 5.26 (dd, *J* = 5.1, 1.9 Hz, 1H), 5.02 (d, *J* = 2.0 Hz, 1H), 4.77 (dd, *J* = 7.9, 4.5 Hz, 1H), 3.72 (dd, *J* = 14.0, 7.9 Hz, 1H), 3.49 (dd, *J* = 14.1, 4.5 Hz, 1H), 3.44 (s, 3H), 2.10 (s, 6H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 155.7, 145.0, 129.9, 126.2, 123.2, 106.4, 85.4, 79.6, 76.4, 75.5, 56.4, 46.6, 28.4, 20.7, 20.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{26}ClNNaO_8S^+$ 486.0960; Found 486.0968.

(2S,3S,4R,5R)-2-(((tert-butoxycarbonyl) amino) methyl)-2-(5-chlorothiophen-2-yl)-5-methoxytetrahydrofuran-3,4-diyl dibenzoate



3u

According to the **general procedure C** from **1i** (0.3 mmol, 106 mg) and **2a** (0.15 mmol, 42 mg), **3u** (69 mg, 78%) was obtained as colorless oil. Flash column chromatography eluent, Petroleum ether: ethyl acetate = 5:1. $[\alpha]_D^{25}$ = + 40.5 (c 6.26, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 10.0, 7.5, 1.4 Hz, 4H), 7.55 (td, *J* = 7.3, 1.3 Hz, 2H), 7.39 (td, *J* = 8.1, 6.4 Hz, 4H), 6.87 (d, *J* = 3.9 Hz, 1H), 6.78 (d, *J* = 3.9 Hz, 1H), 6.02 (d, *J* = 5.1 Hz, 1H), 5.67 (dd, *J* = 5.1, 1.5 Hz, 1H), 5.26 (d, *J* = 1.3 Hz, 1H), 4.92 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.98 (dd, *J* = 13.9, 8.3 Hz, 1H), 3.85 (dd, *J* = 13.9, 3.9 Hz,

1H), 3.55 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 165.0, 155.9, 144.9, 133.8, 133.7, 129.9, 129.9, 129.8, 129.0, 128.7, 128.7, 126.3, 123.4, 106.6, 85.8, 79.6, 77.6, 76.1, 56.5, 46.9, 28.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{30}ClNNaO_8S^+$ 610.1273; Found 610.1277.

9. References

(1) L. Somsák, *Chem. Rev.*, 2001, **101**, 81-136.

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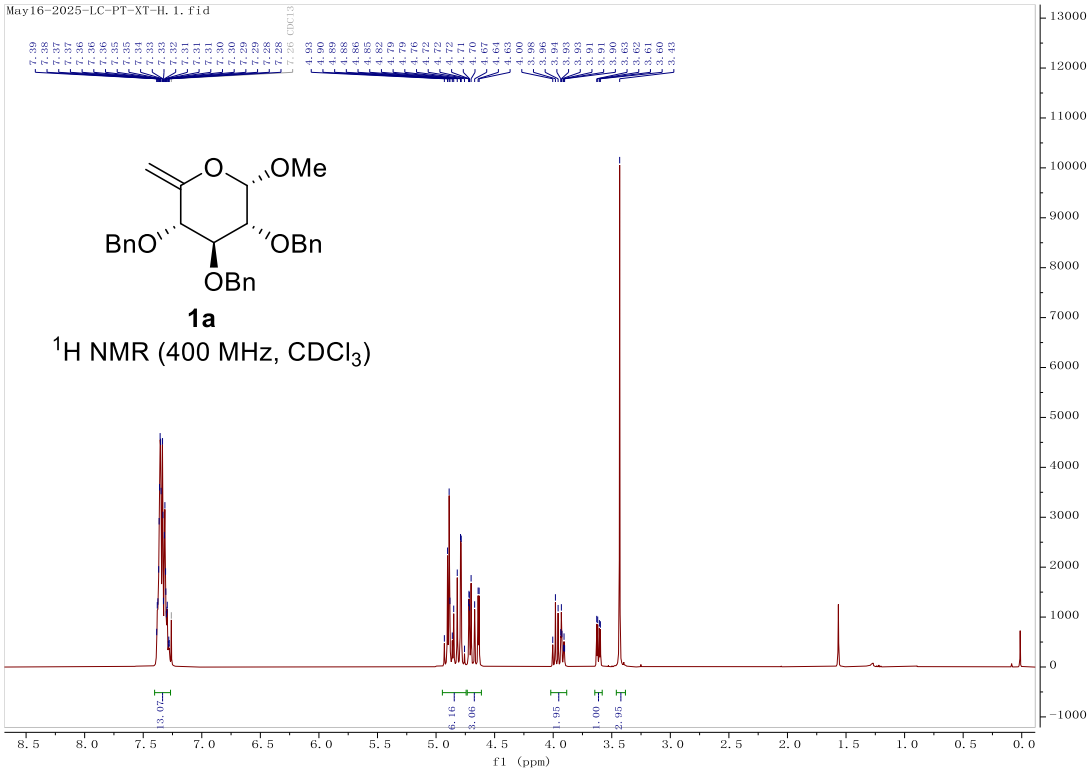
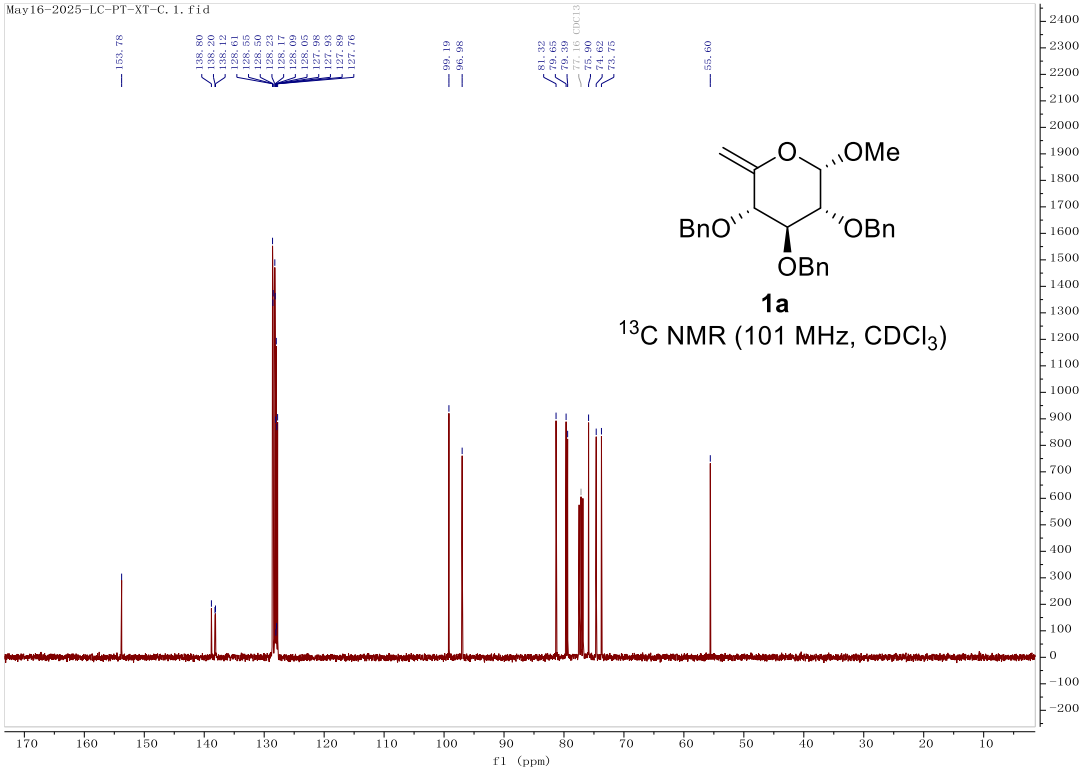
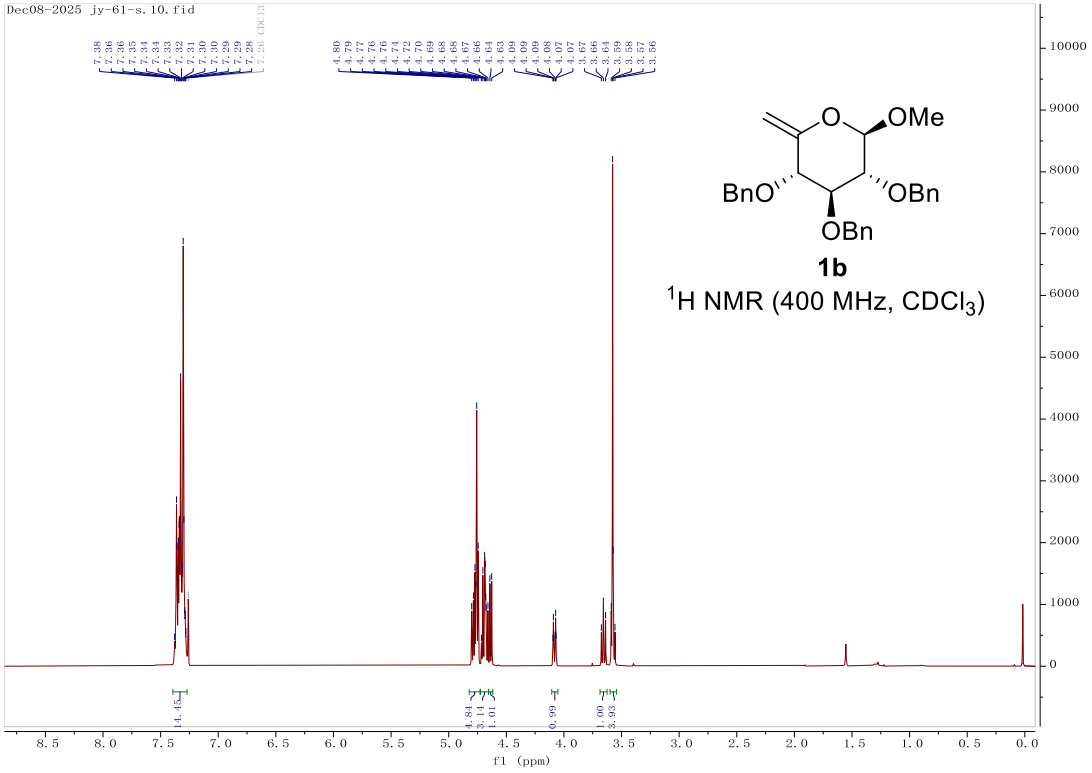
10. NMR spectra data for the products



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OBn
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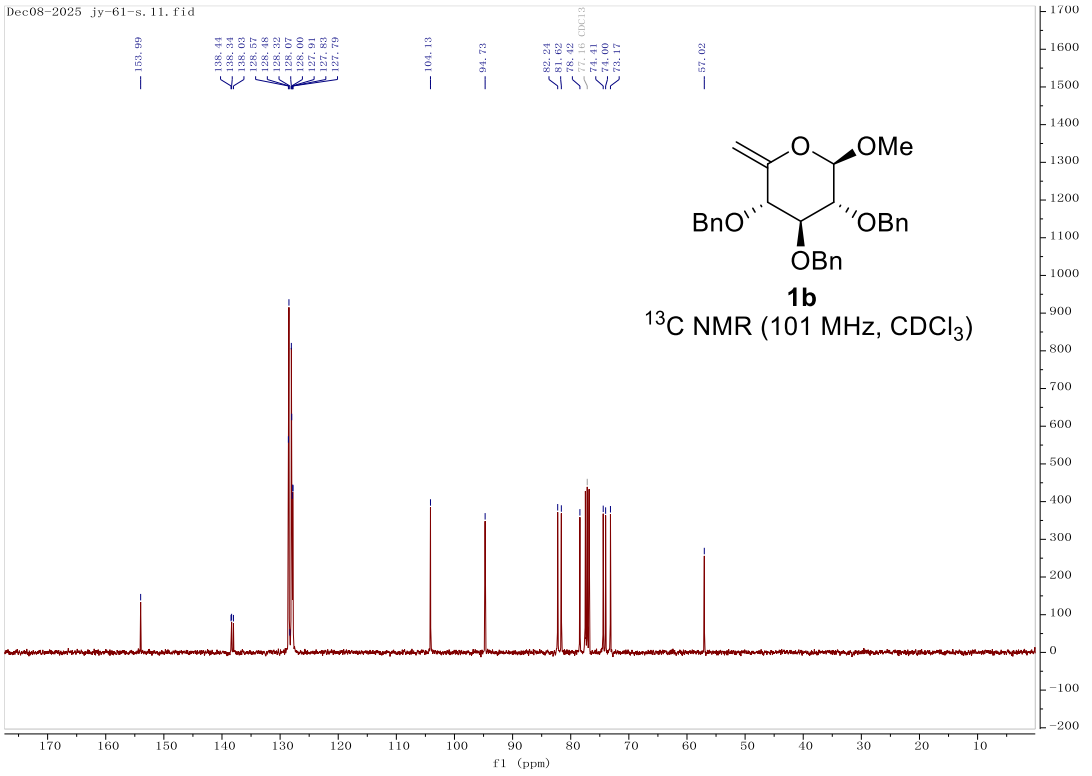
f1 (ppm)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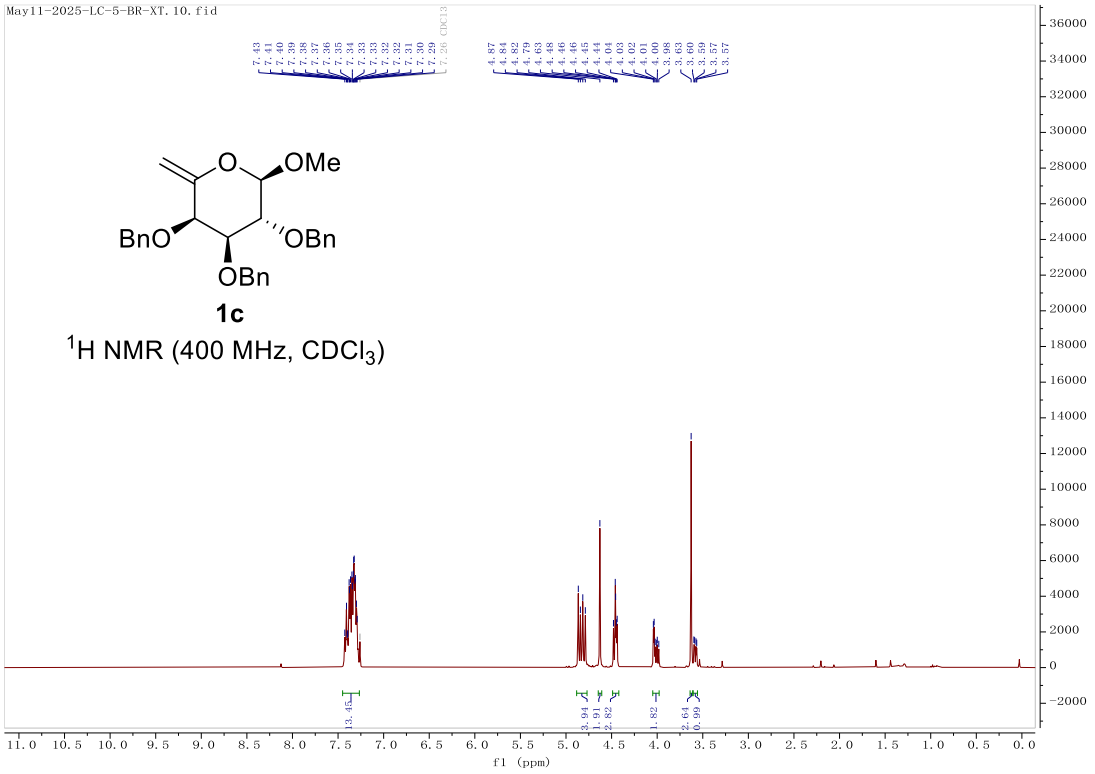
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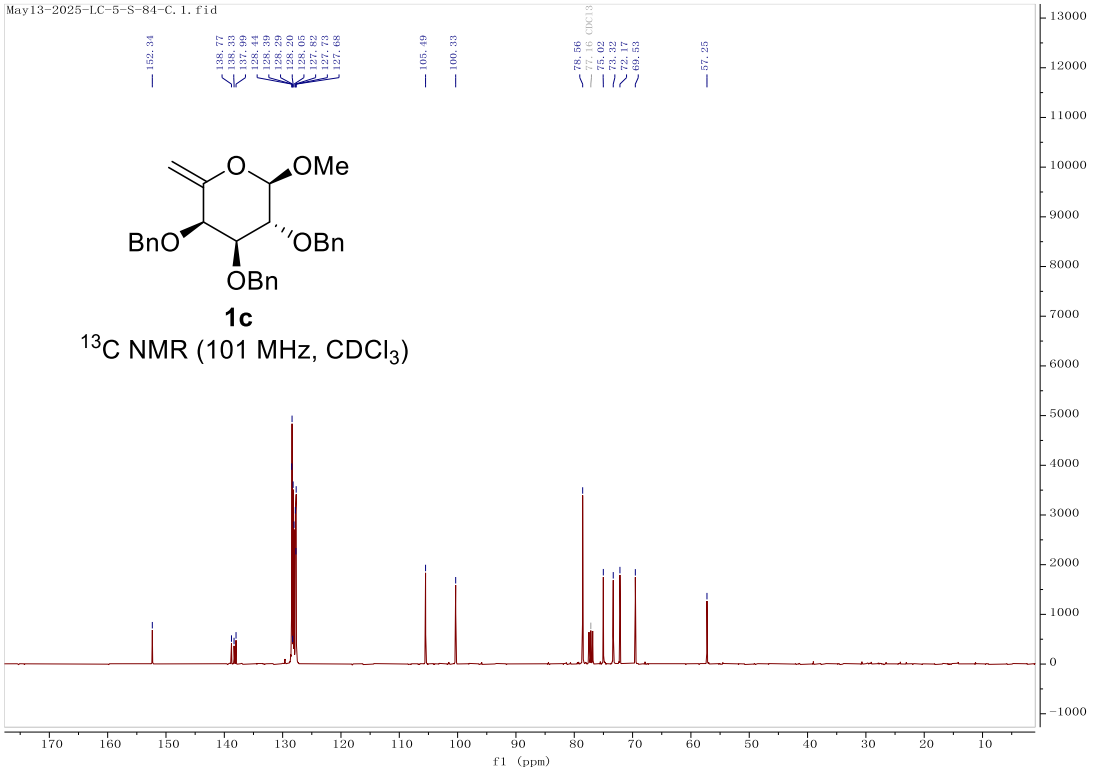
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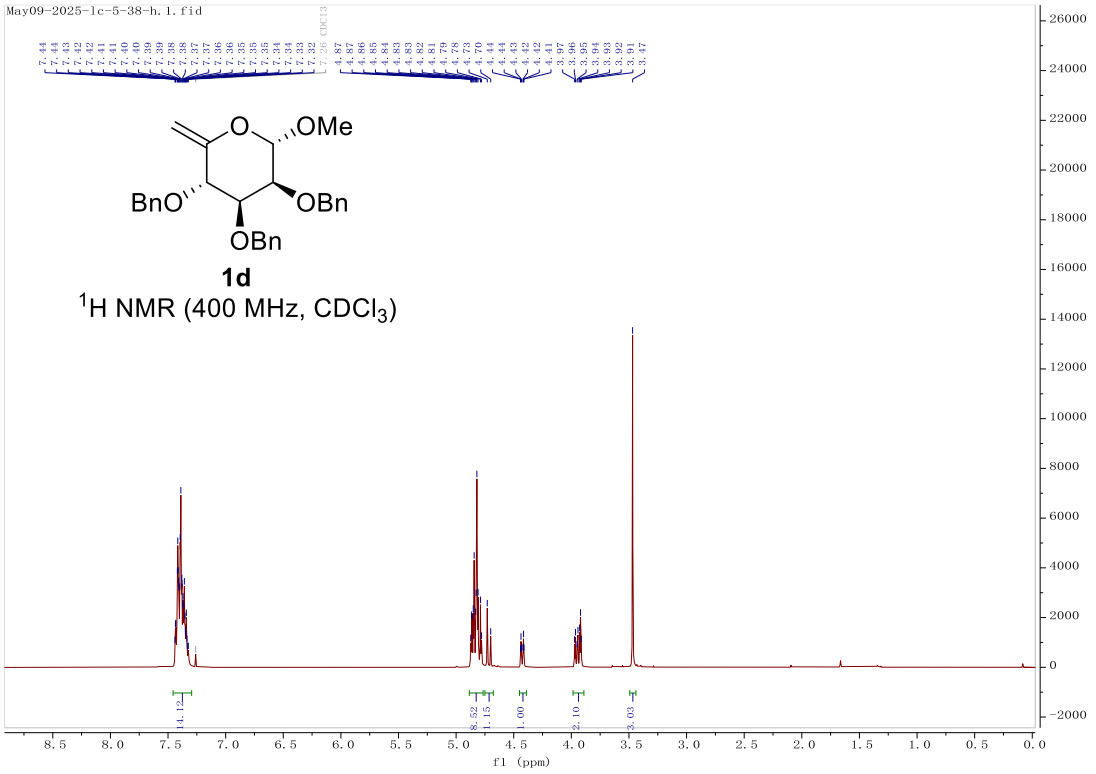
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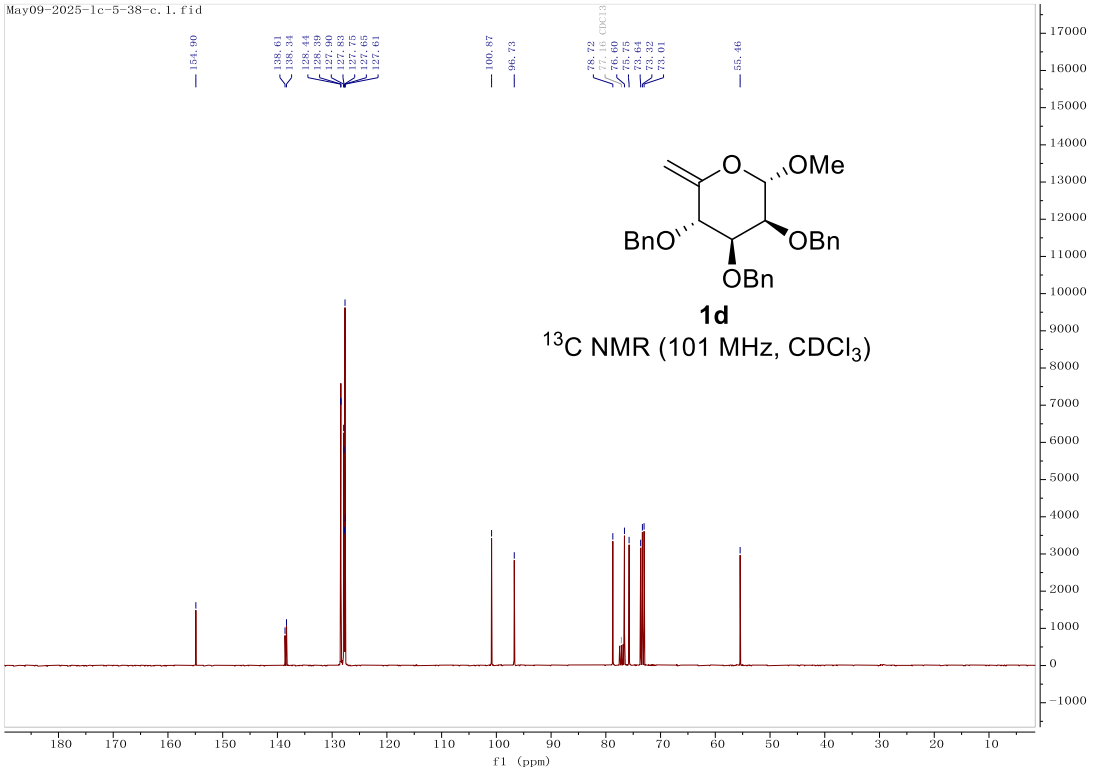
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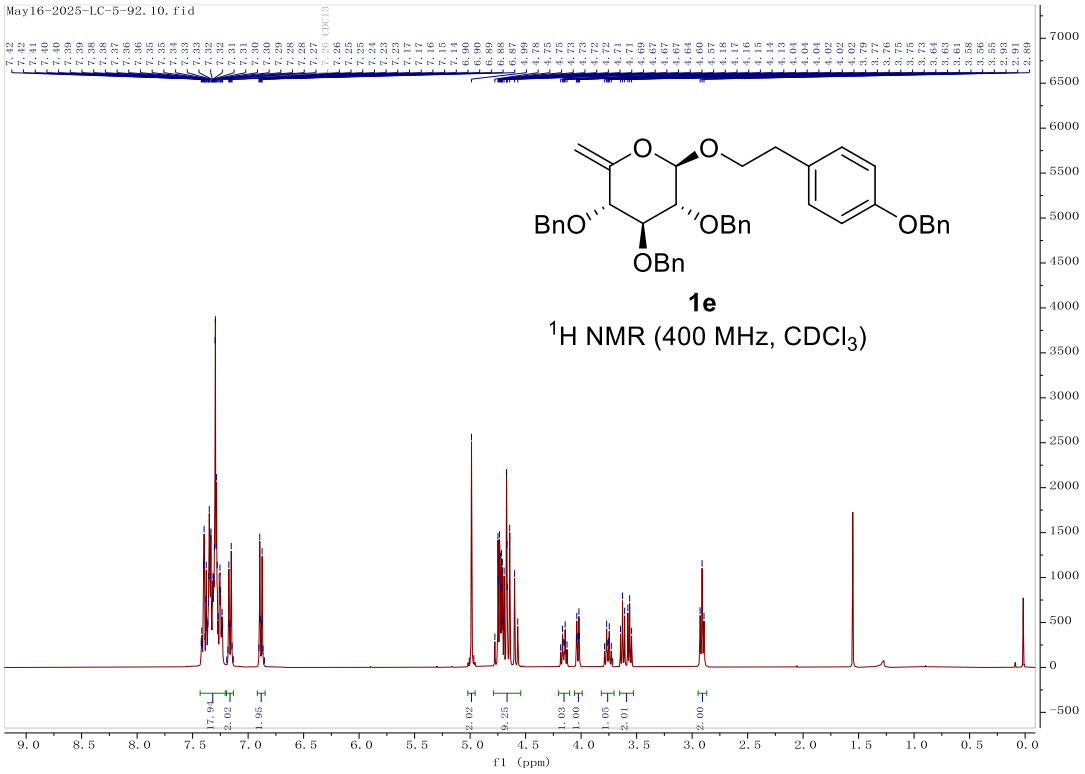
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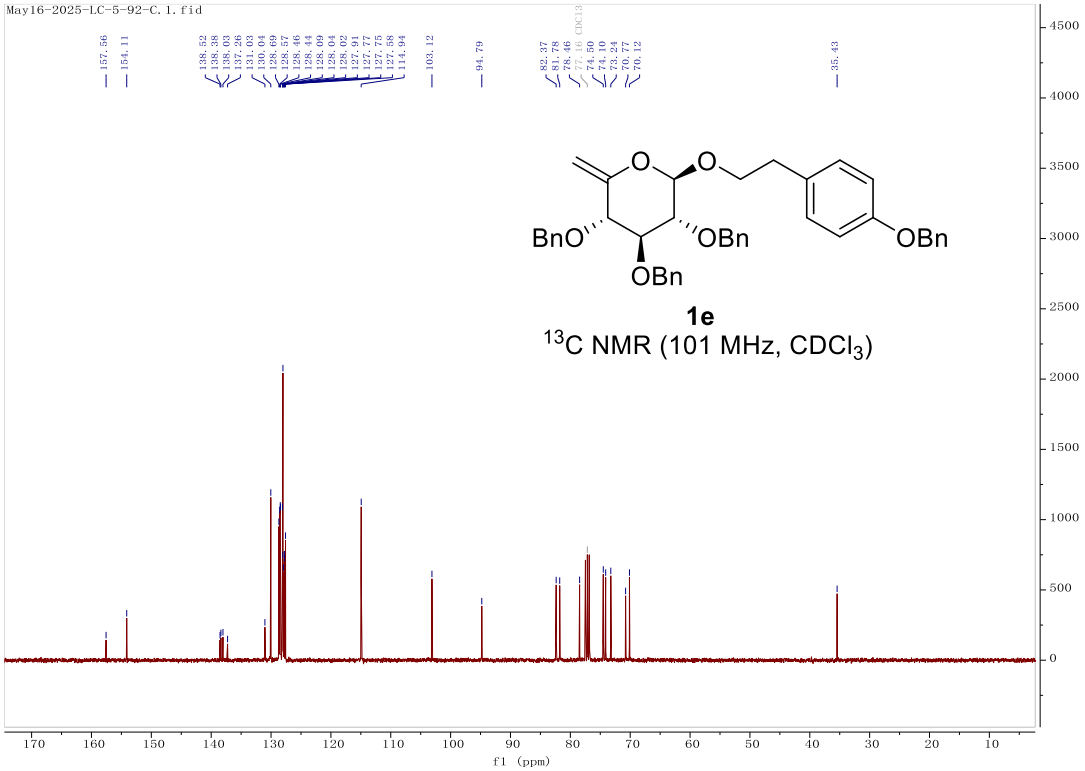
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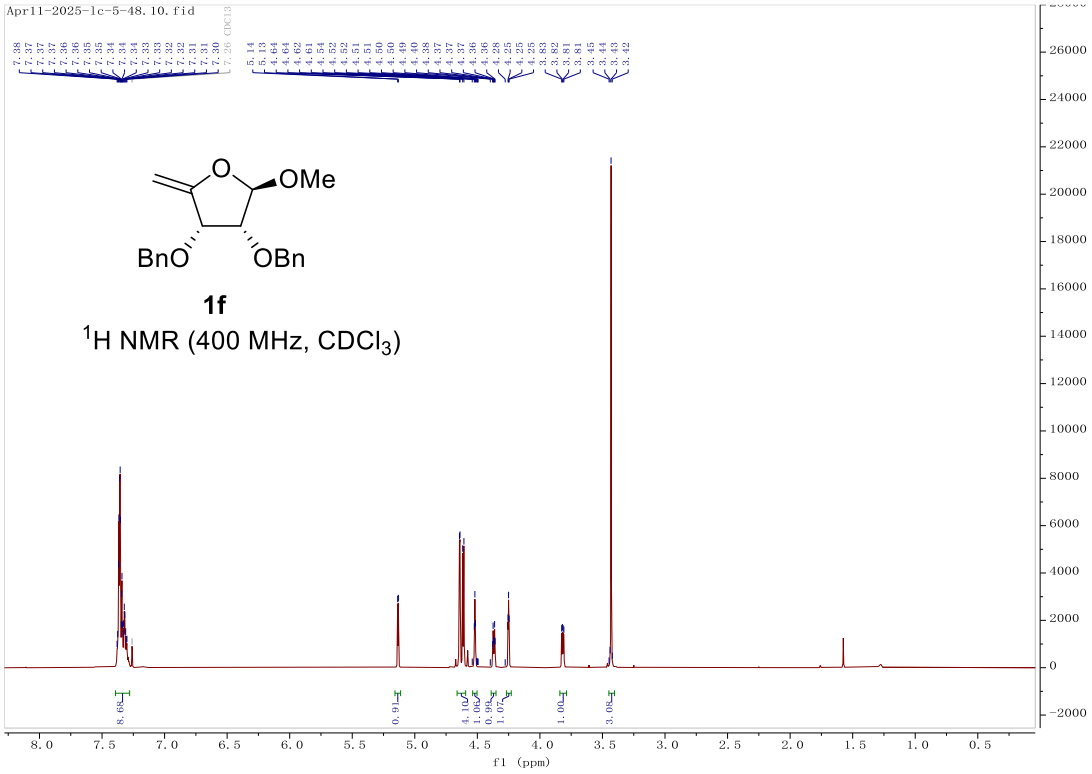
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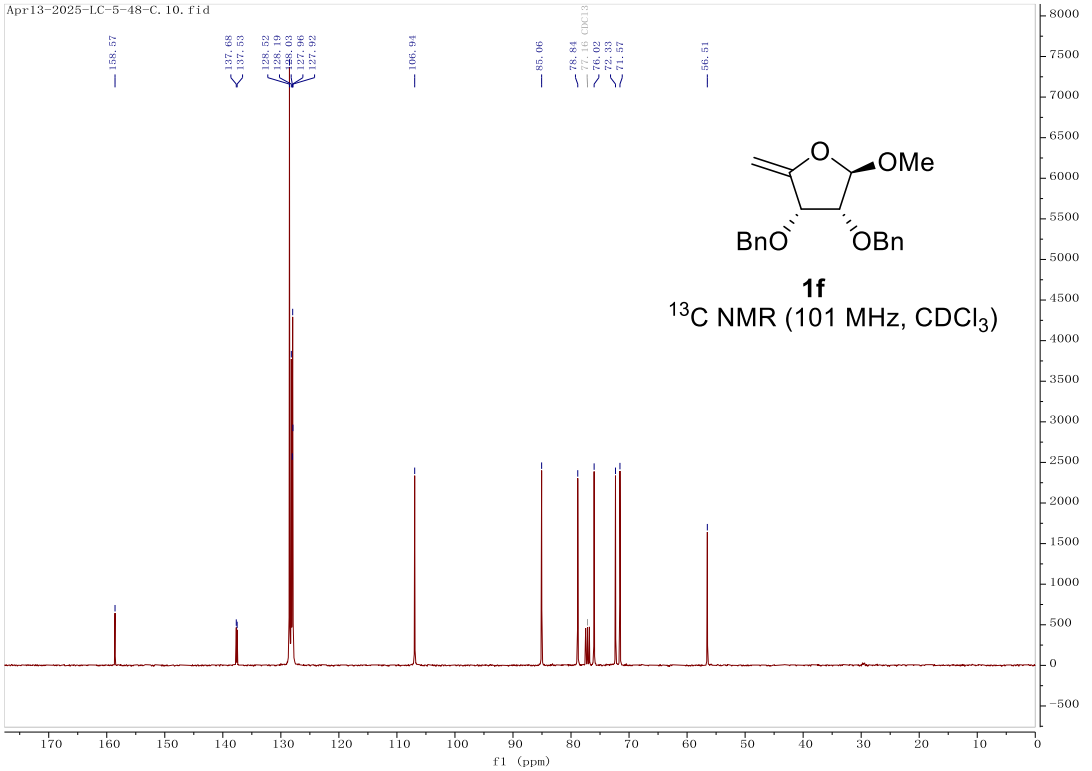
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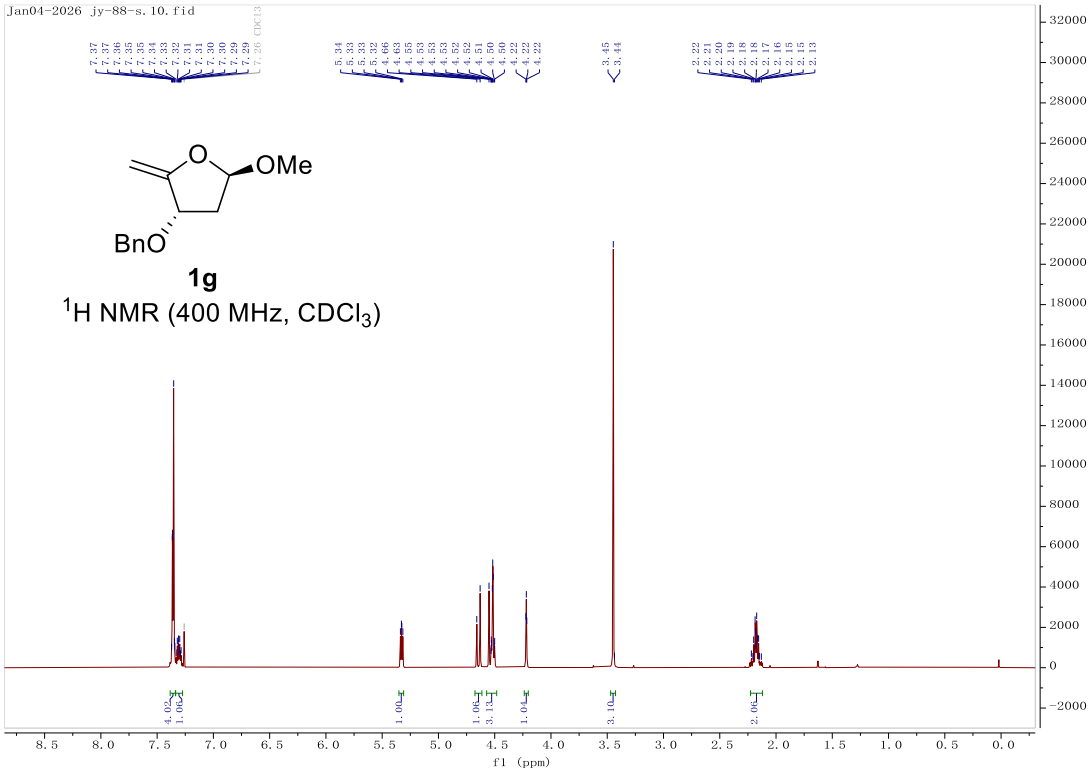
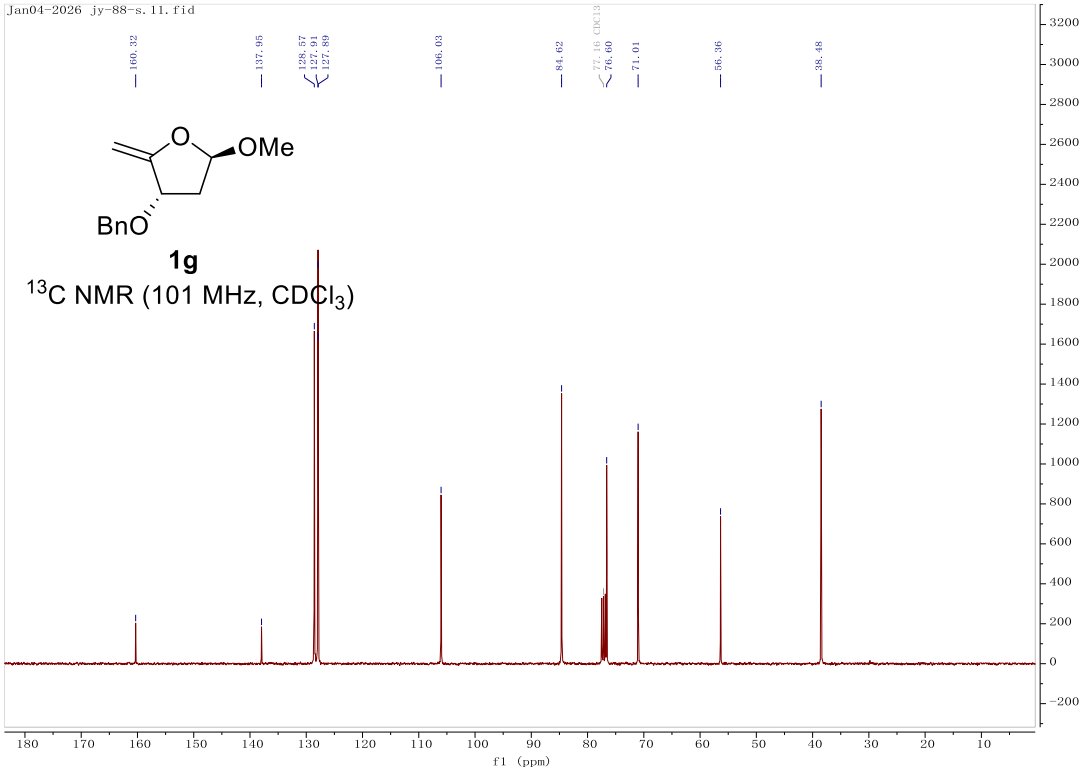
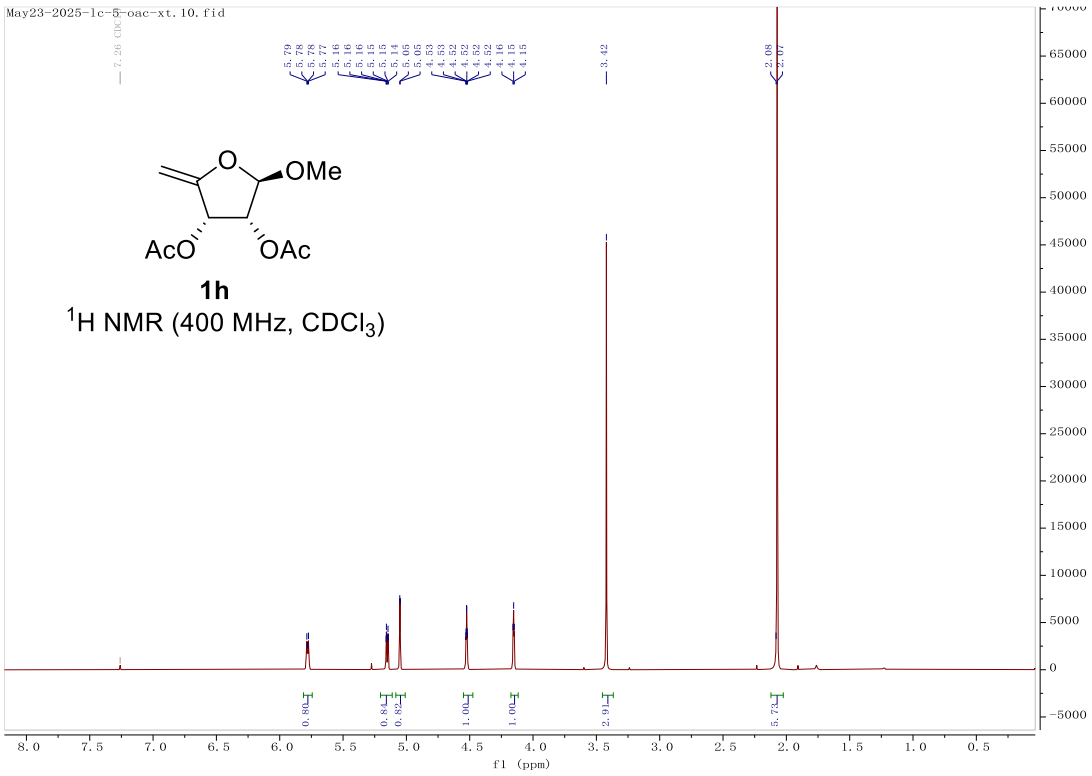
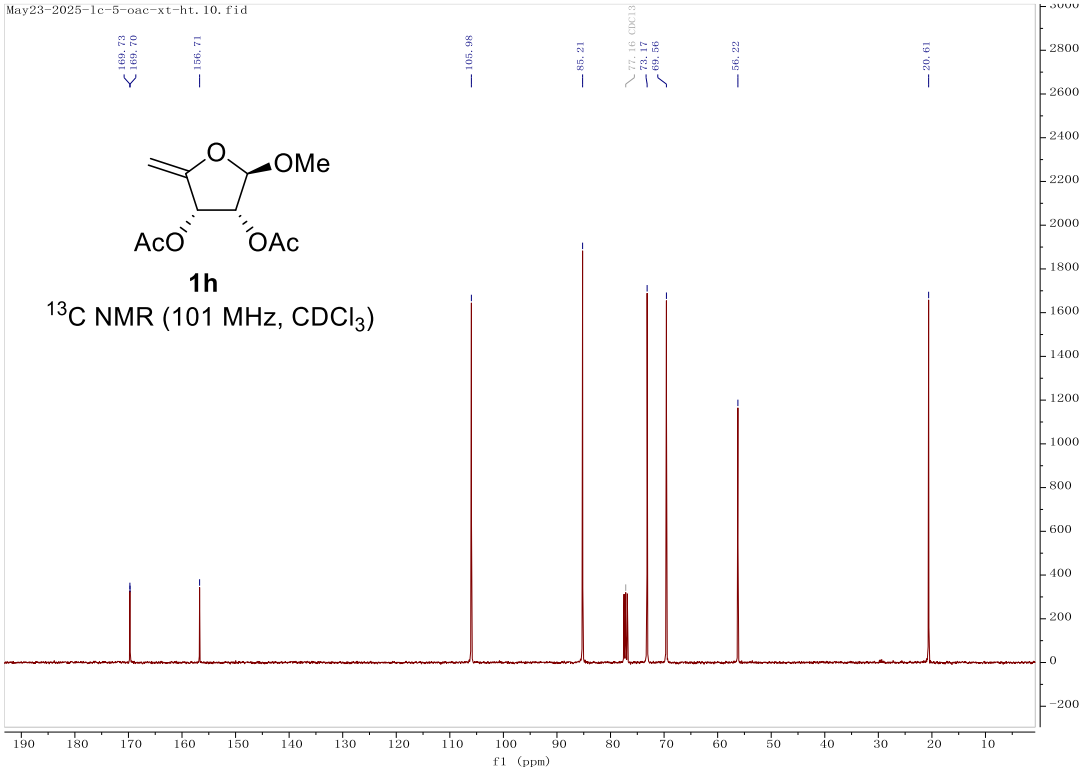
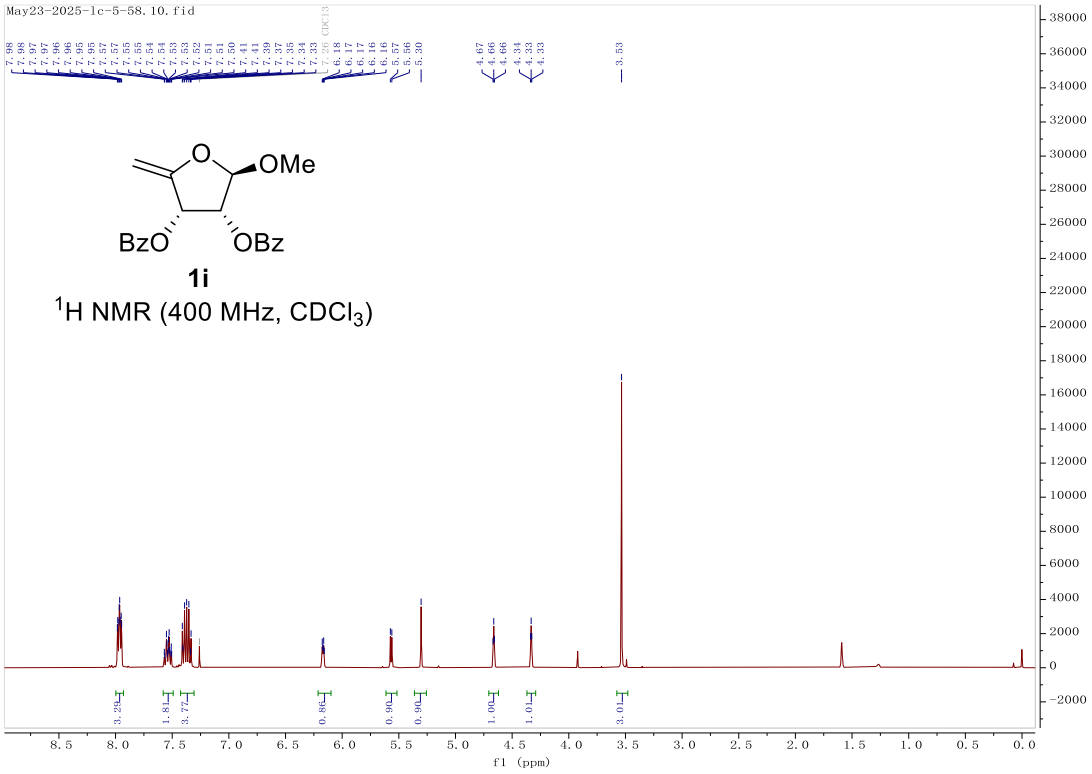
13C NMR (101 MHz, CDCl3)
f1 (ppm)

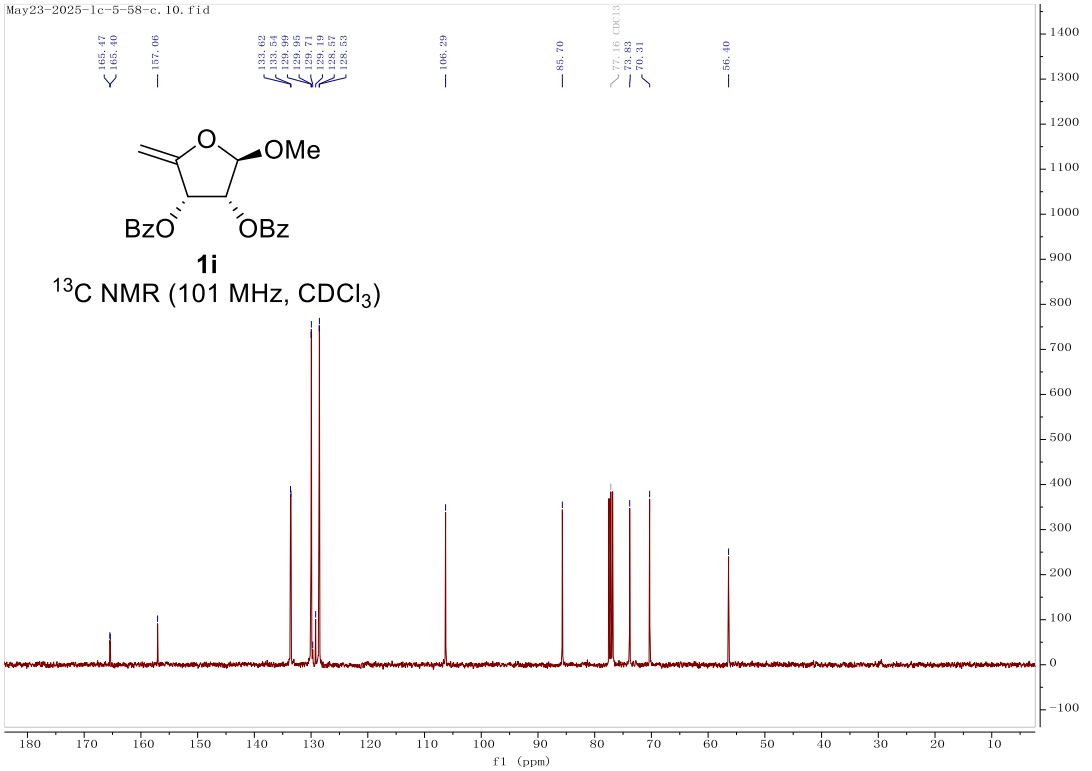

Jan04-2026 jy-88-s.10.fid
OMe
BnO
1g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

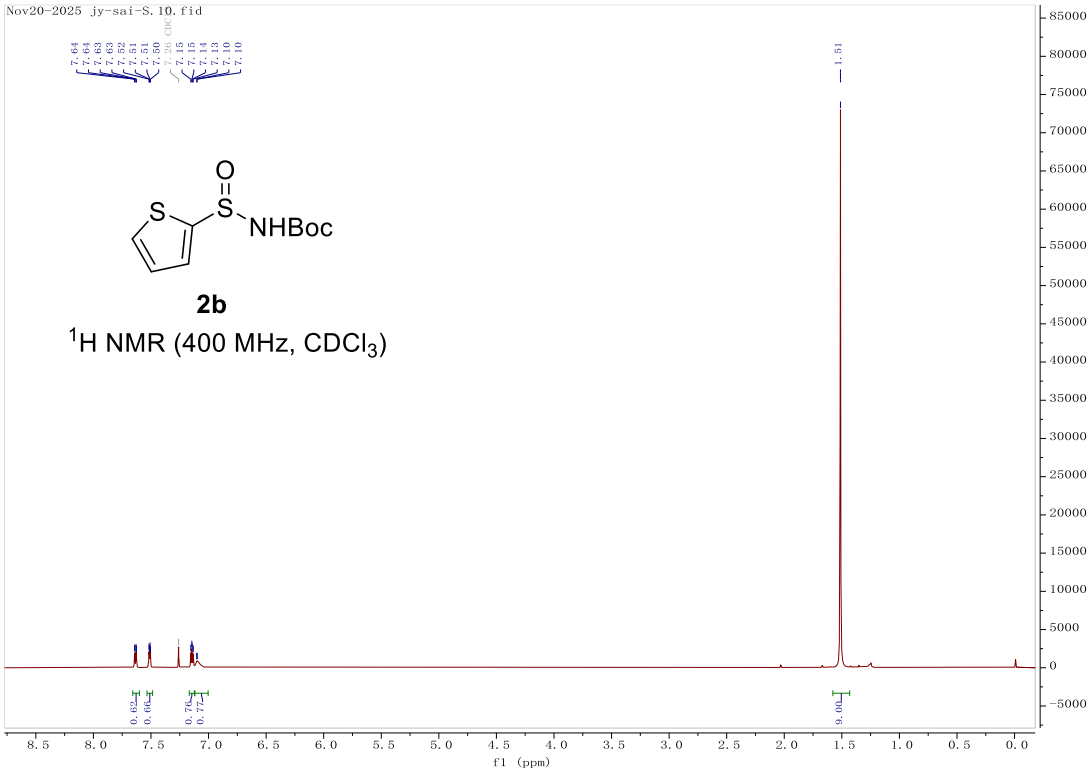

Jan04-2026 jy-88-s.11.fid
OMe
BnO
1g
13C NMR (101 MHz, CDCl3)
f1 (ppm)


May23-2025-lc-5-oac-xt.10.fid
OMe
AcO
OAc
1h
1H NMR (400 MHz, CDCl3)
f1 (ppm)


May23-2025-lc-5-oac-xt-ht.10.fid
OMe
AcO
OAc
1h
13C NMR (101 MHz, CDCl3)
f1 (ppm)

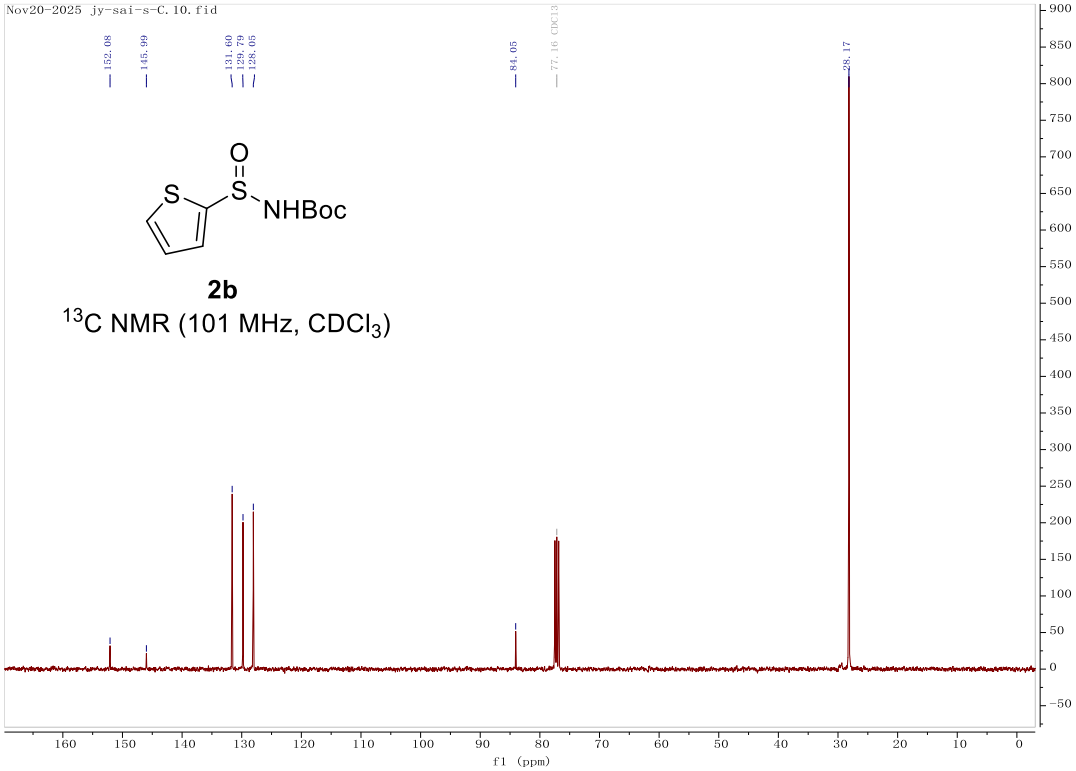

May23-2025-lc-5-58.10.fid
OMe
BzO
OBz
1i
1H NMR (400 MHz, CDCl3)
f1 (ppm)


May23-2025-lc-5-58-c.10.fid
OMe
BzO
OBz
1i
13C NMR (101 MHz, CDCl3)
f1 (ppm)



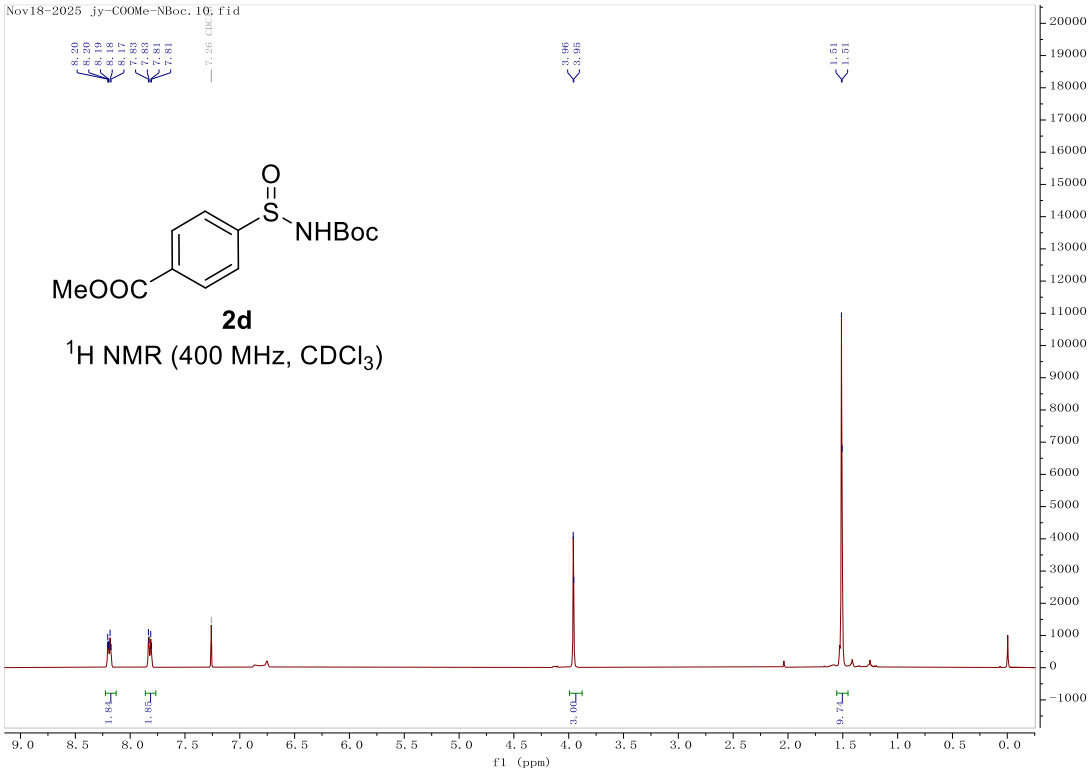
2b

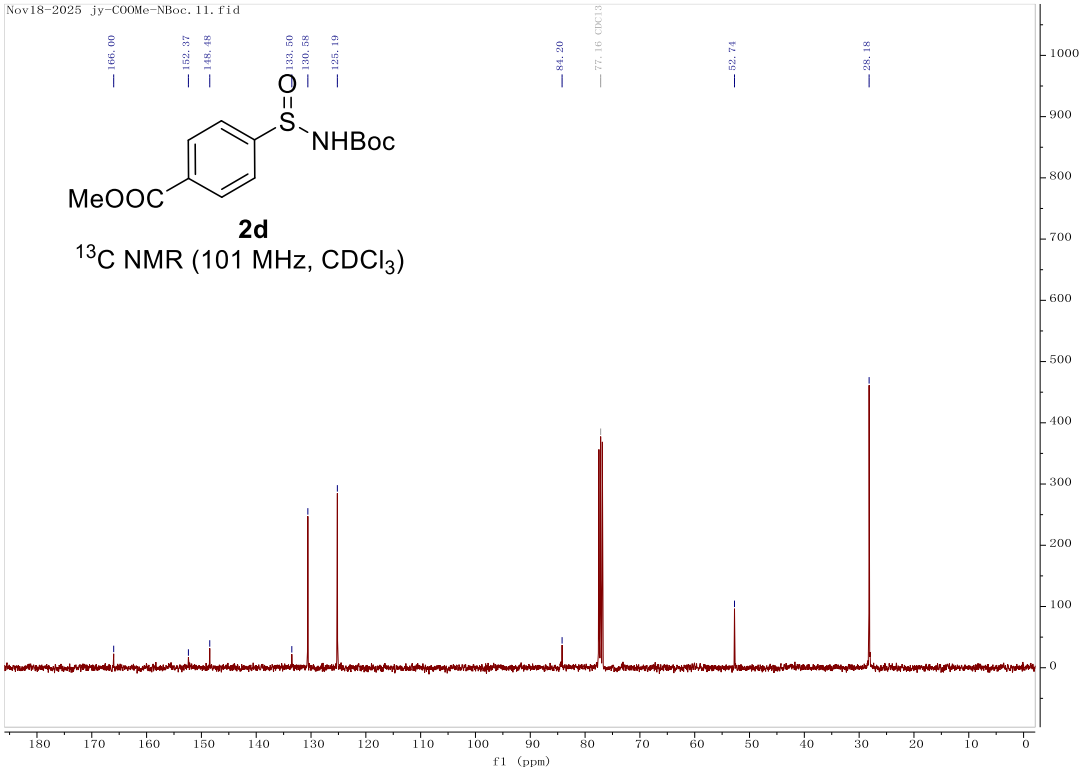
^{1}H NMR (400 MHz, $CDCl_3$)

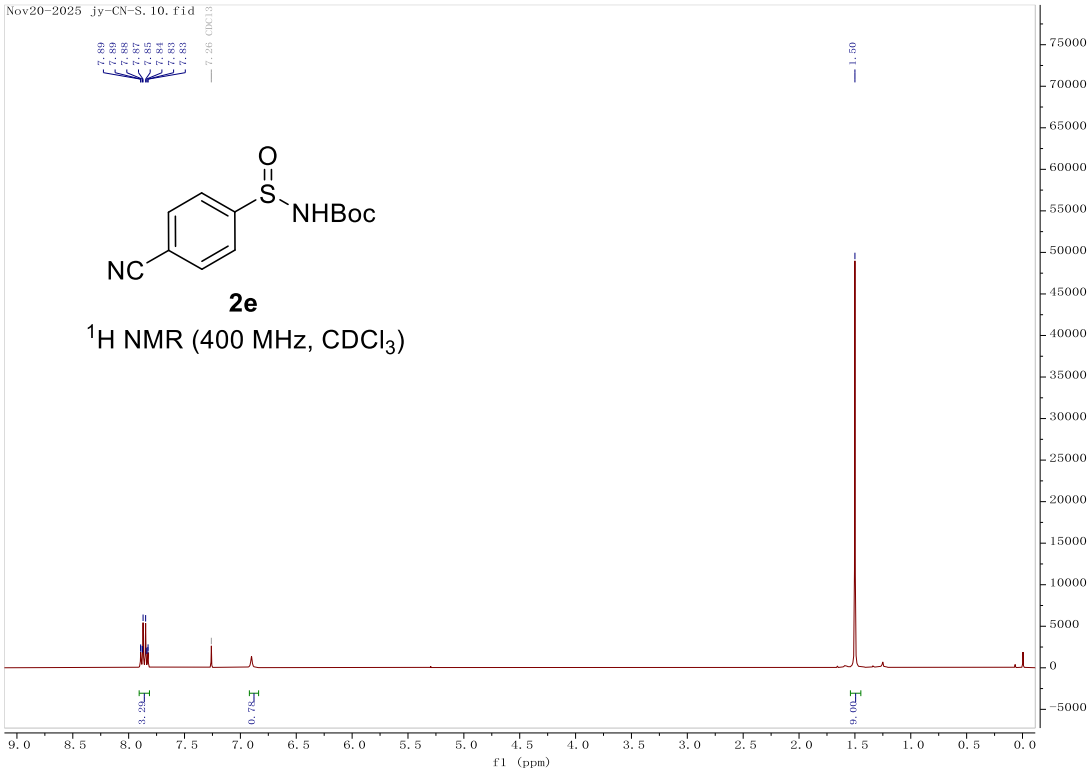


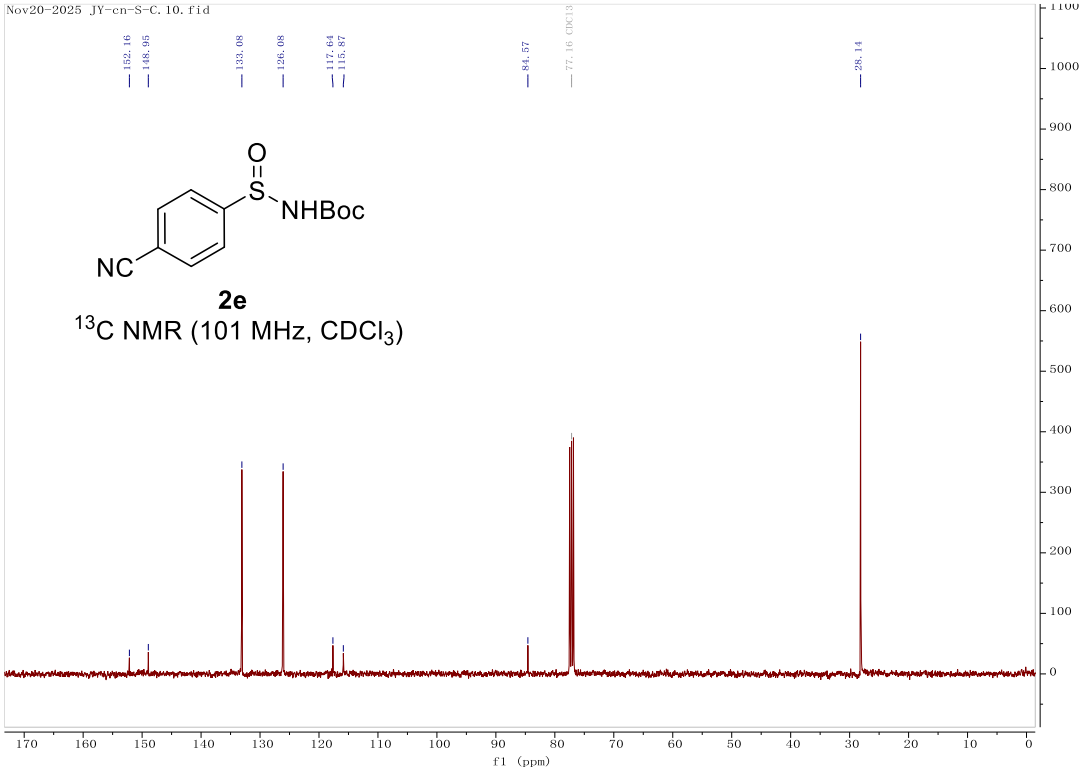
2b

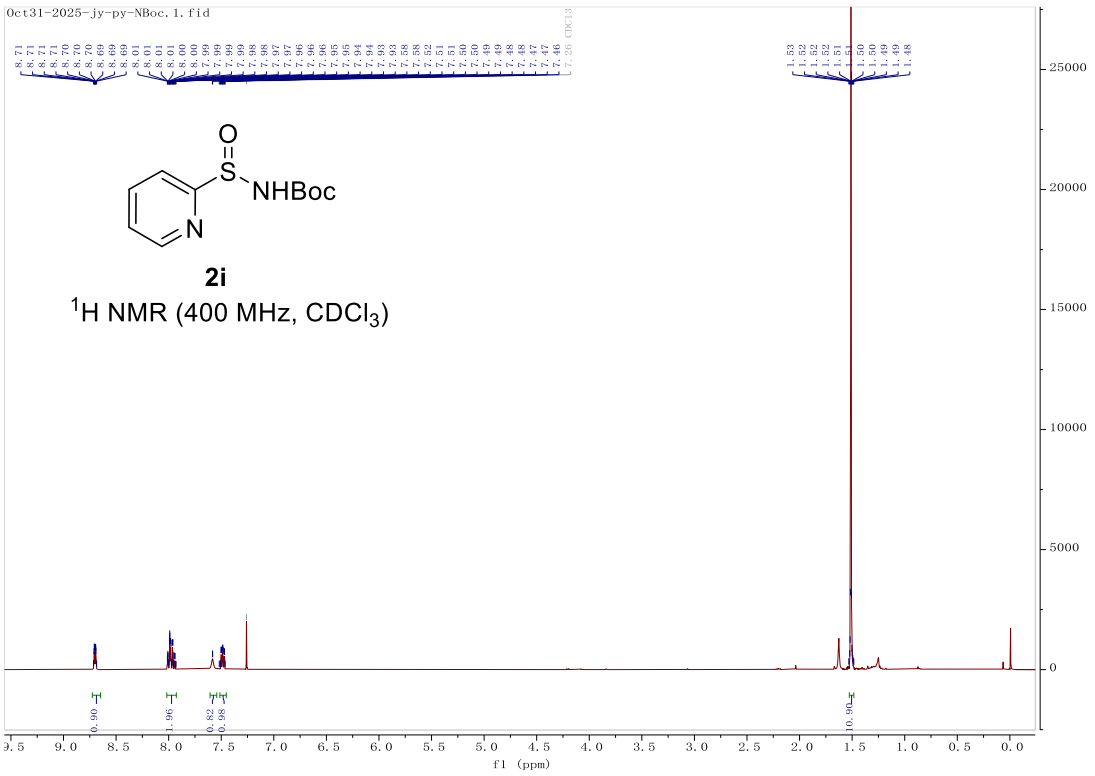
^{13}C NMR (101 MHz, $CDCl_3$)

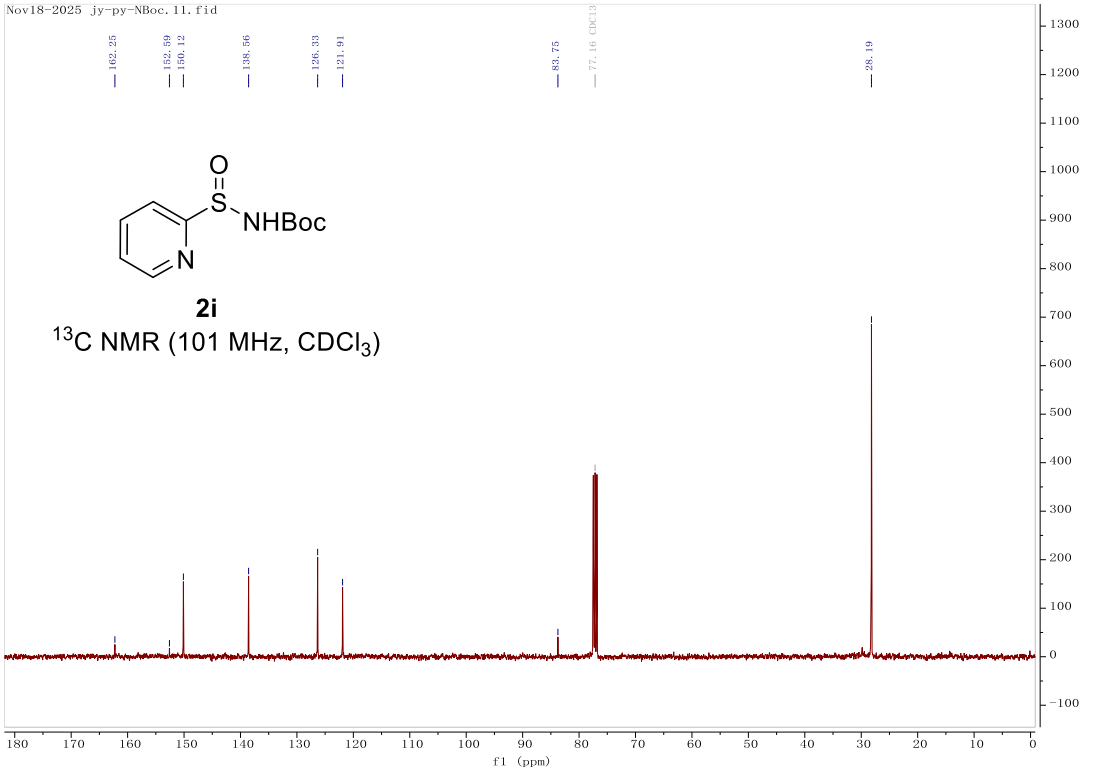

Nov18-2025 jy-COOMe-NBoc.10.fid
8.20
8.20
8.19
8.18
8.17
7.83
7.83
7.81
7.81
7.26 CDCl3
3.96
3.95
1.61
1.61
O
S
NHBoc
MeOOC
2d
1H NMR (400 MHz, CDCl3)
1.84
1.86
3.00
9.74
f1 (ppm)

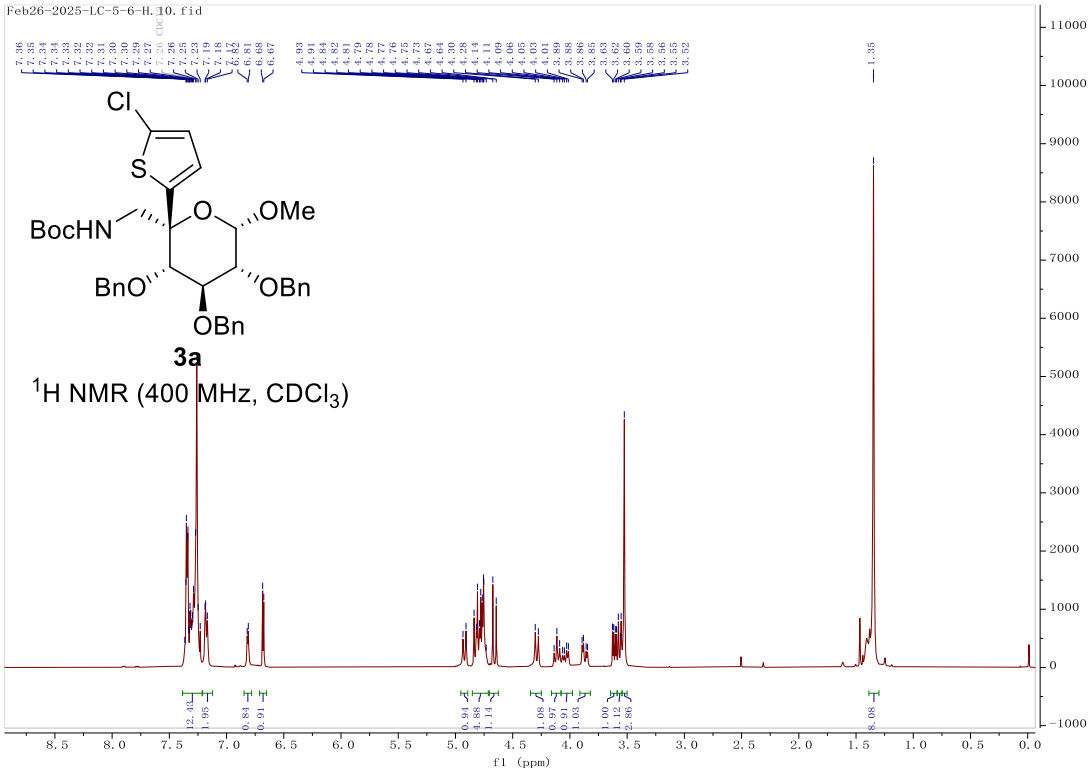

Nov18-2025 jy-COOMe-NBoc.11.fid
166.00
152.37
148.48
133.50
130.58
125.19
84.20
77.16 CDCl3
52.74
28.18
O
S
NHBoc
MeOOC
2d
13C NMR (101 MHz, CDCl3)
f1 (ppm)

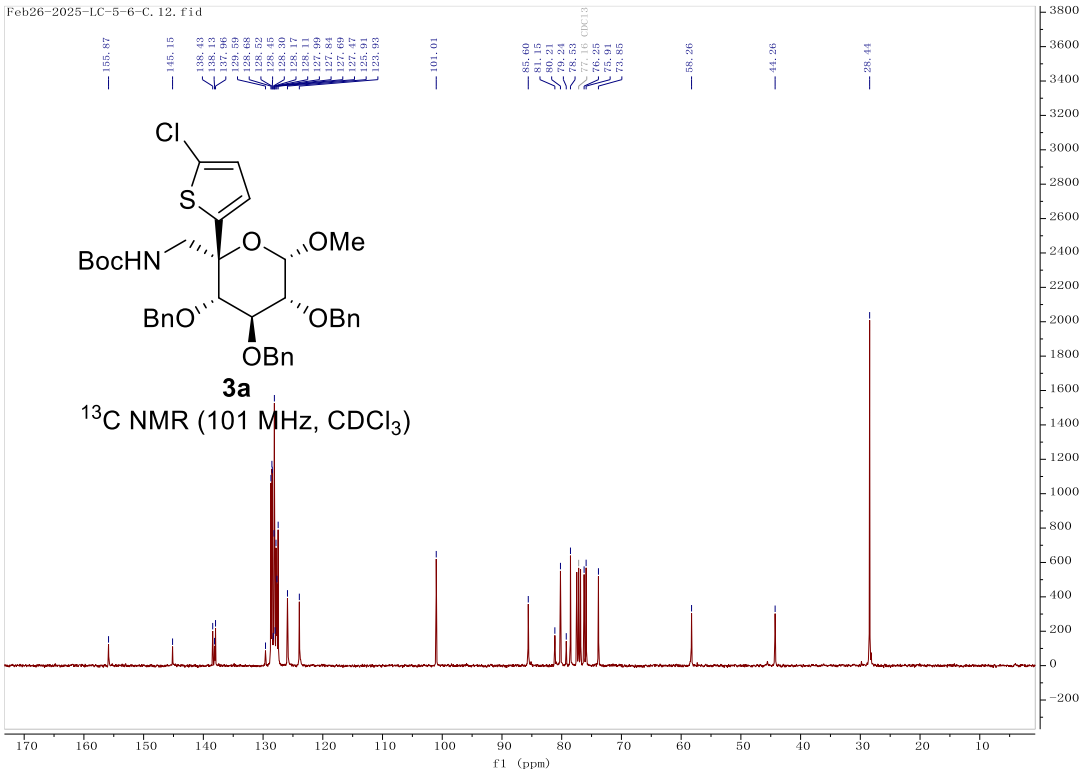

Nov20-2025 jy-CN-S.10.fid
7.89
7.89
7.88
7.87
7.85
7.84
7.83
7.83
7.26 CDCl3
1.50
O
S
NHBoc
NC
2e
1H NMR (400 MHz, CDCl3)
3.29
0.78
9.00
f1 (ppm)

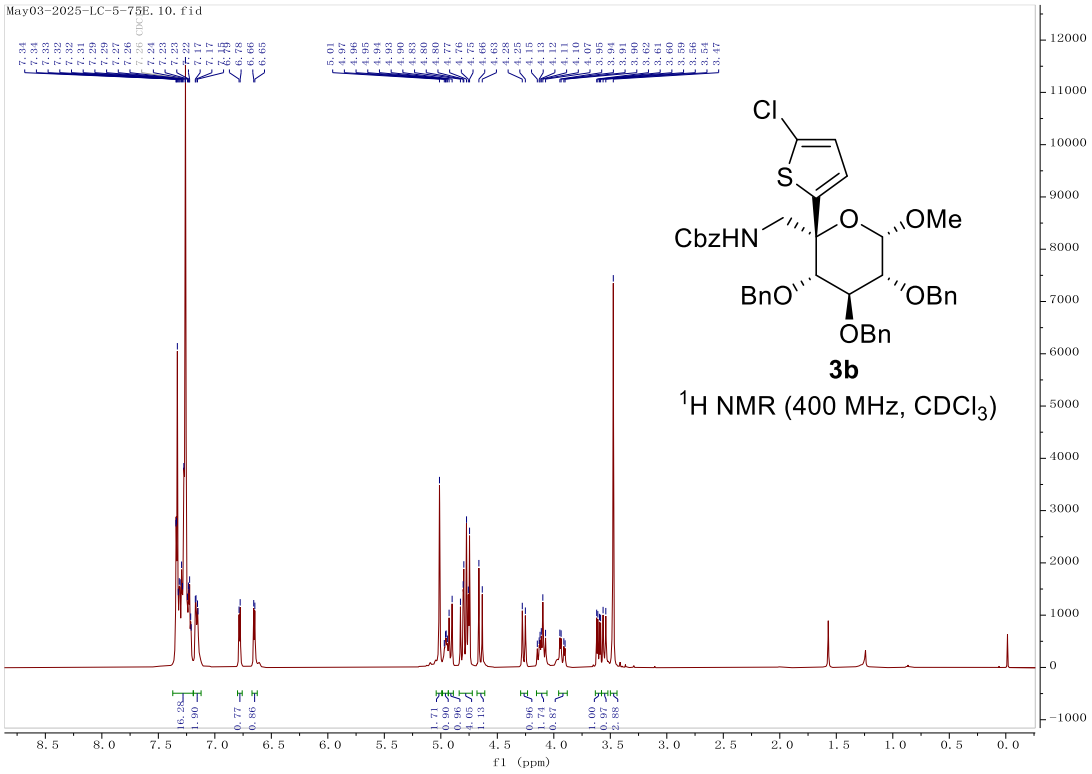

Nov20-2025 JY-cn-S-C.10.fid
152.16
148.95
133.08
126.08
117.64
115.87
84.57
77.16 CDCl3
28.14
O
S
NHBoc
NC
2e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

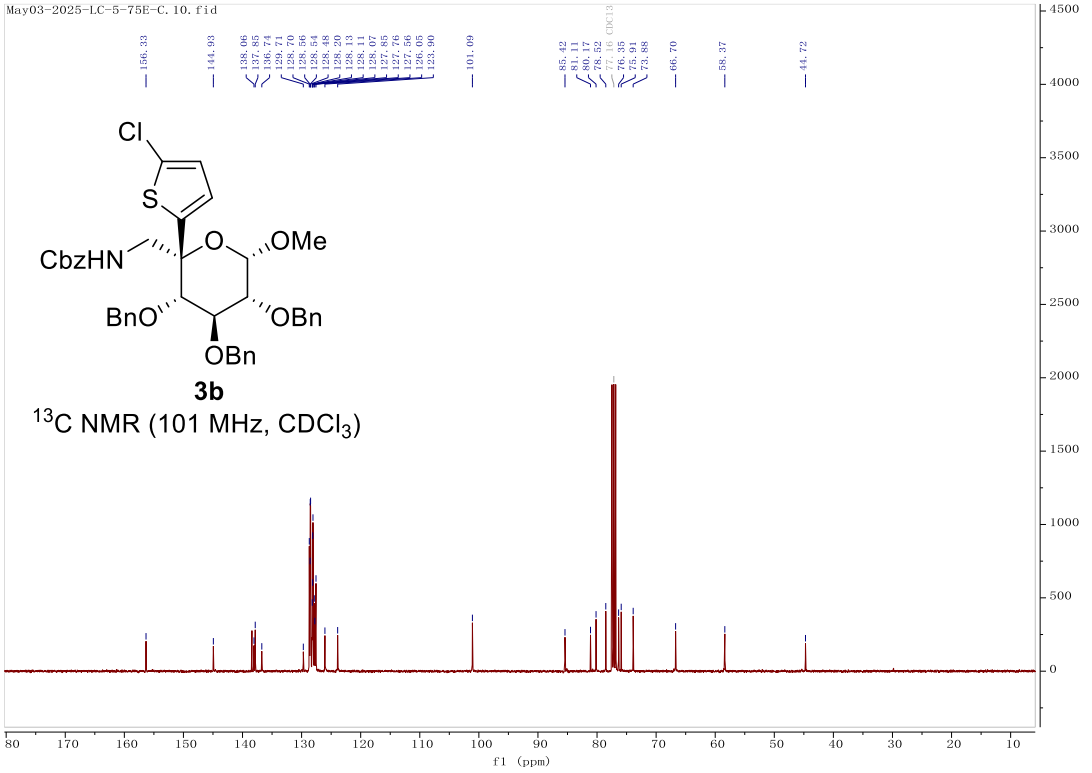

Oct31-2025-jy-py-NBoc.1.fid
O
S
NHBoc
N
2i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

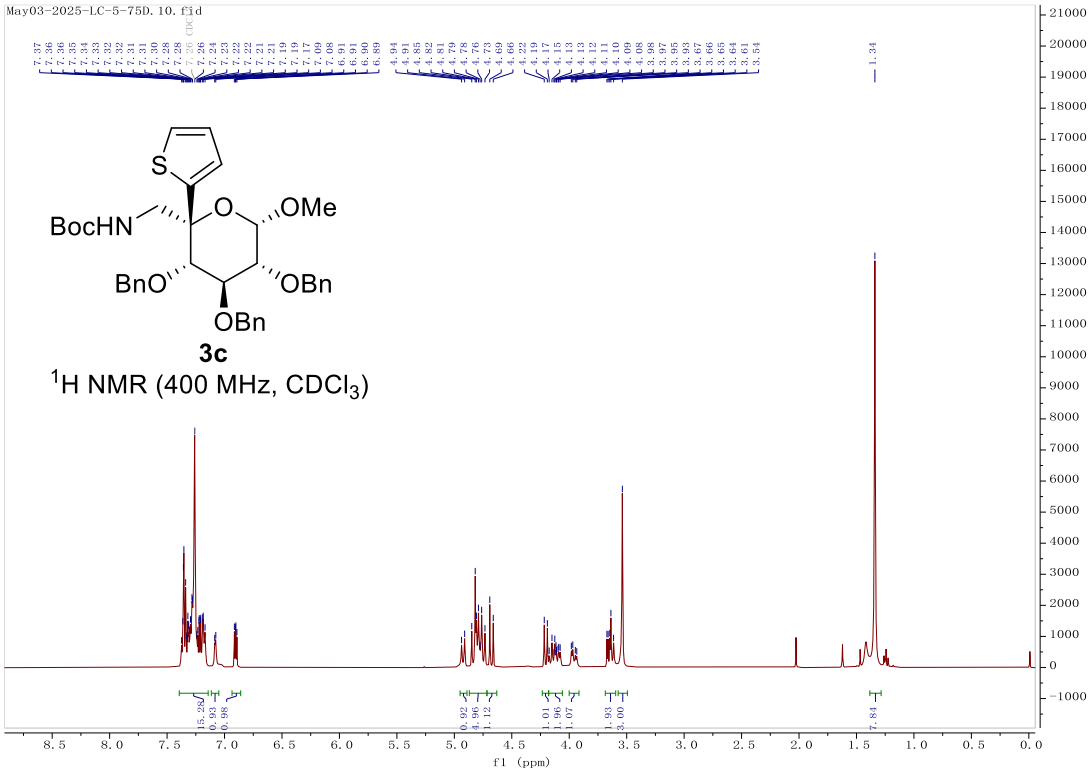

Nov18-2025 jy-py-NBoc.11.fid
162.25
152.59
150.12
138.56
126.33
121.91
83.75
77.16 CDCl3
28.19
O
S
NHBoc
N
2i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

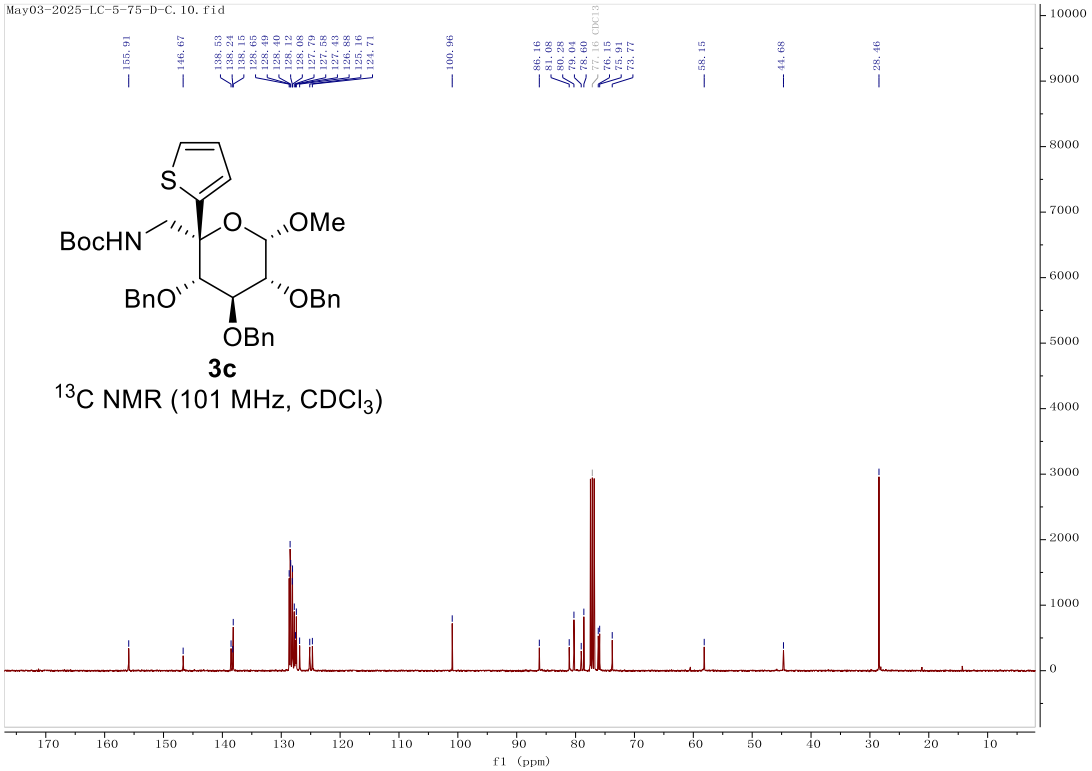

Feb26-2025-LC-5-6-H.10.fid
Cl
S
O
OMe
BocHN
BnO
OBn
OBn
3a
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Feb26-2025-LC-5-6-C.12.fid
Cl
S
O
OMe
BocHN
BnO
OBn
OBn
3a
13C NMR (101 MHz, CDCl3)
f1 (ppm)


May03-2025-LC-5-75E.10.fid
Cl
S
O
OMe
CbzHN
BnO
OBn
OBn
3b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


May03-2025-LC-5-75E-C.10.fid
Cl
S
O
OMe
CbzHN
BnO
OBn
OBn
3b
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


May03-2025-LC-5-75D.10.fid
BocHN
BnO
OBn
OBn
OMe
3c
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)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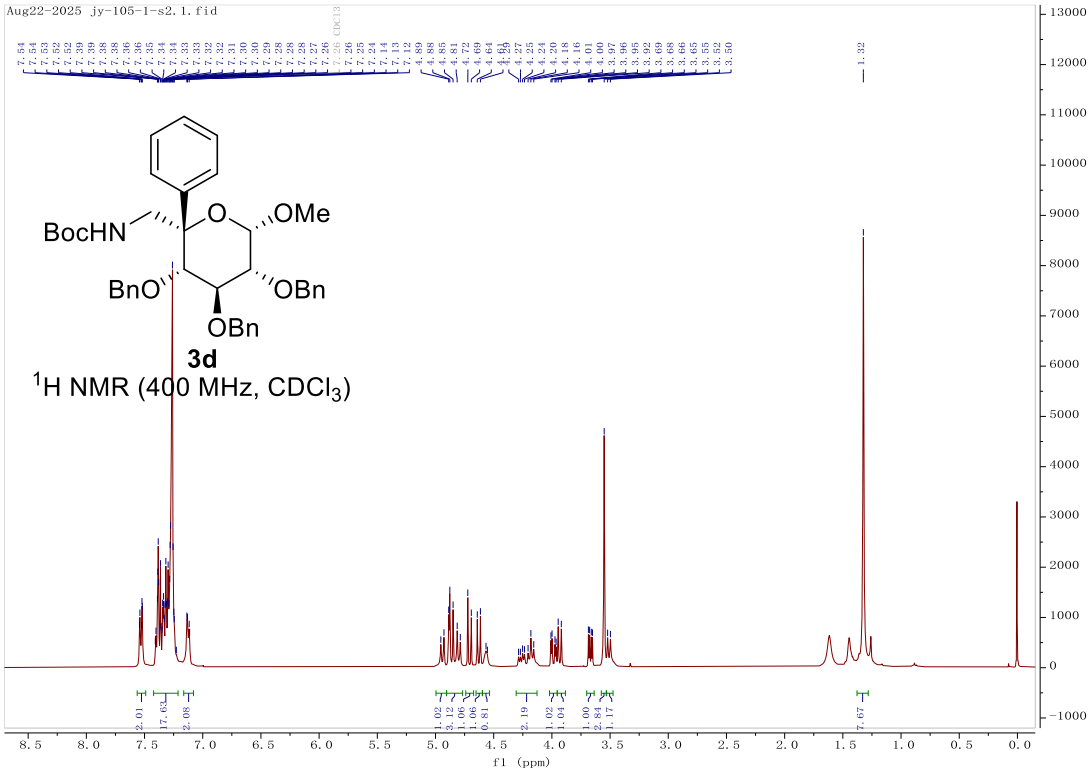
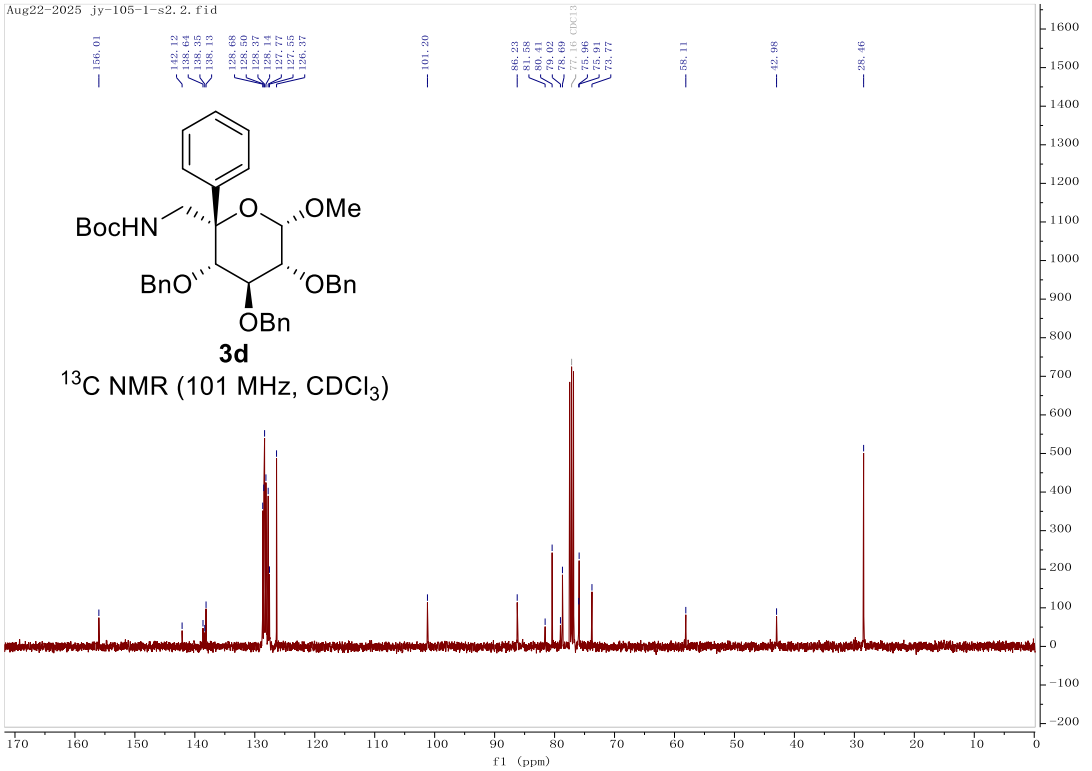
BocHN
BnO
OBn
OBn
OMe
3c
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


Aug22-2025 jy-105-1-s2.1.fid
BocHN
O
OMe
BnO
OBn
OBn
3d
1H NMR (400 MHz, CDCl3)
f1 (ppm)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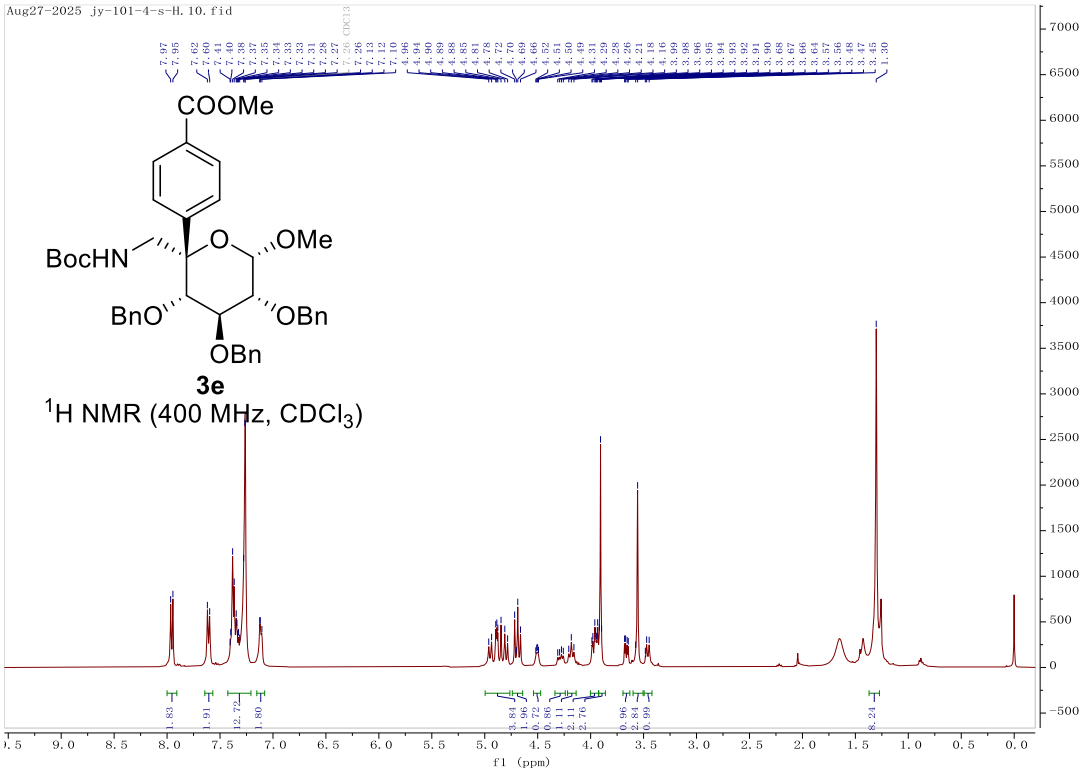
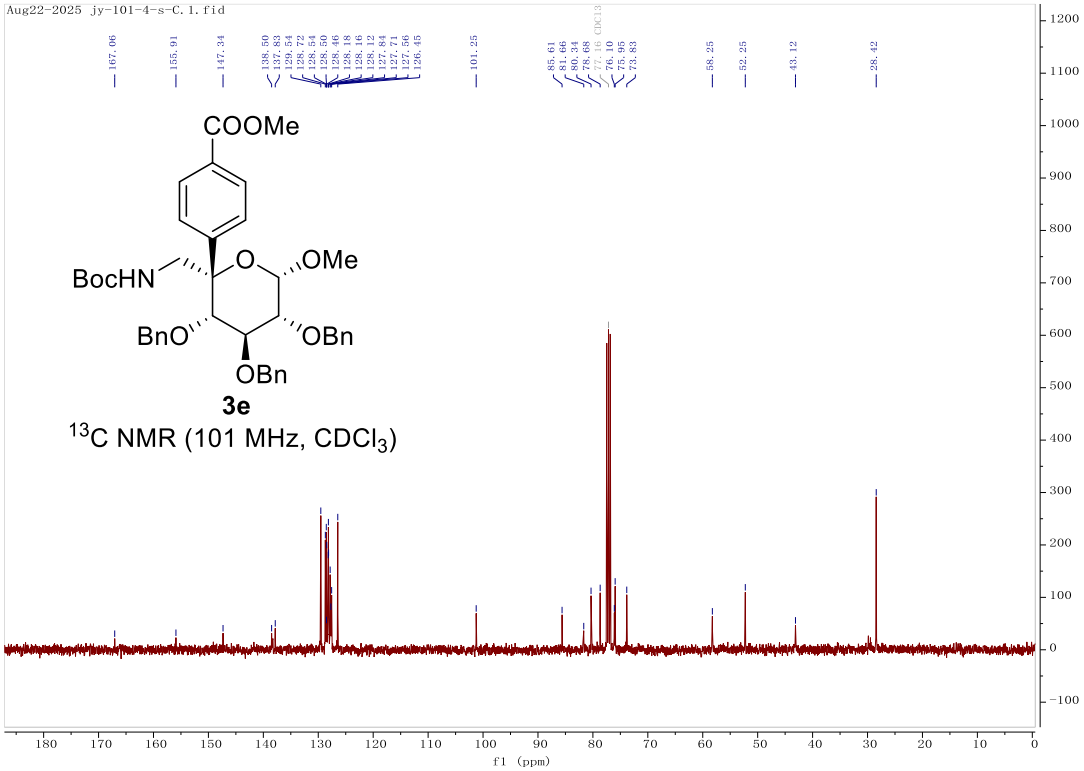
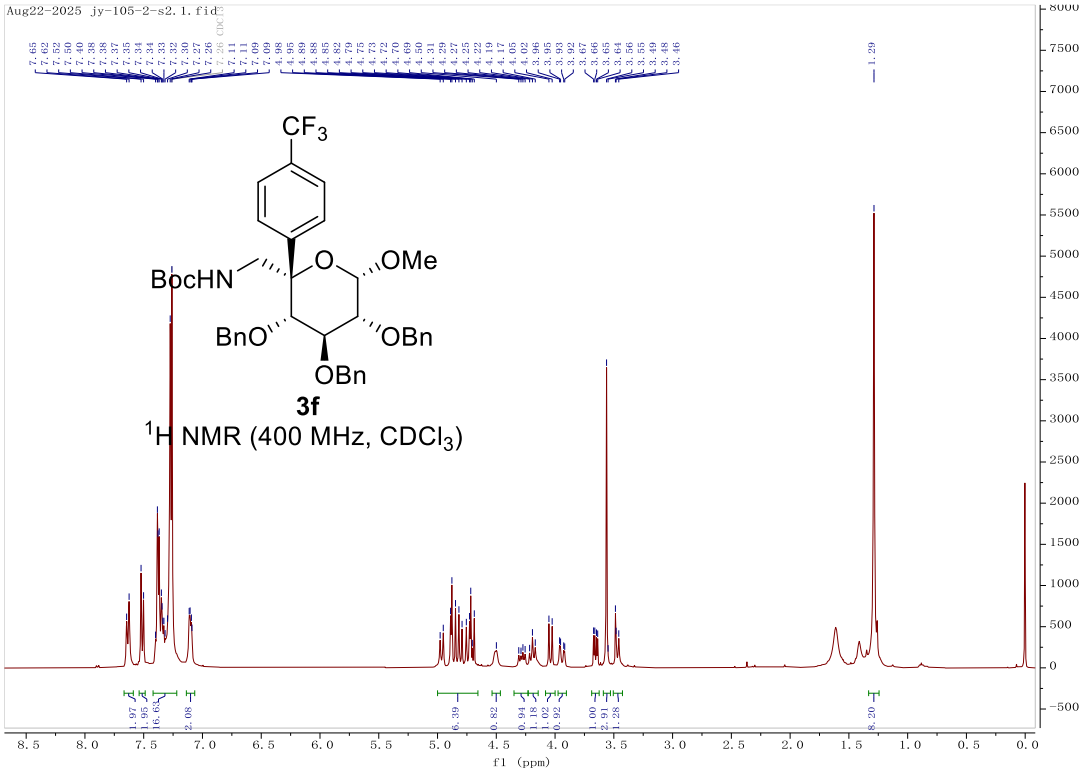
O
OMe
BnO
OBn
OBn
3d
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Aug27-2025 jy-101-4-s-H.10.fid
COOMe
BocHN
O
OMe
BnO
OBn
OBn
3e
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Aug22-2025 jy-101-4-s-C.1.fid
COOMe
BocHN
O
OMe
BnO
OBn
OBn
3e
13C NMR (101 MHz, CDCl3)
f1 (ppm)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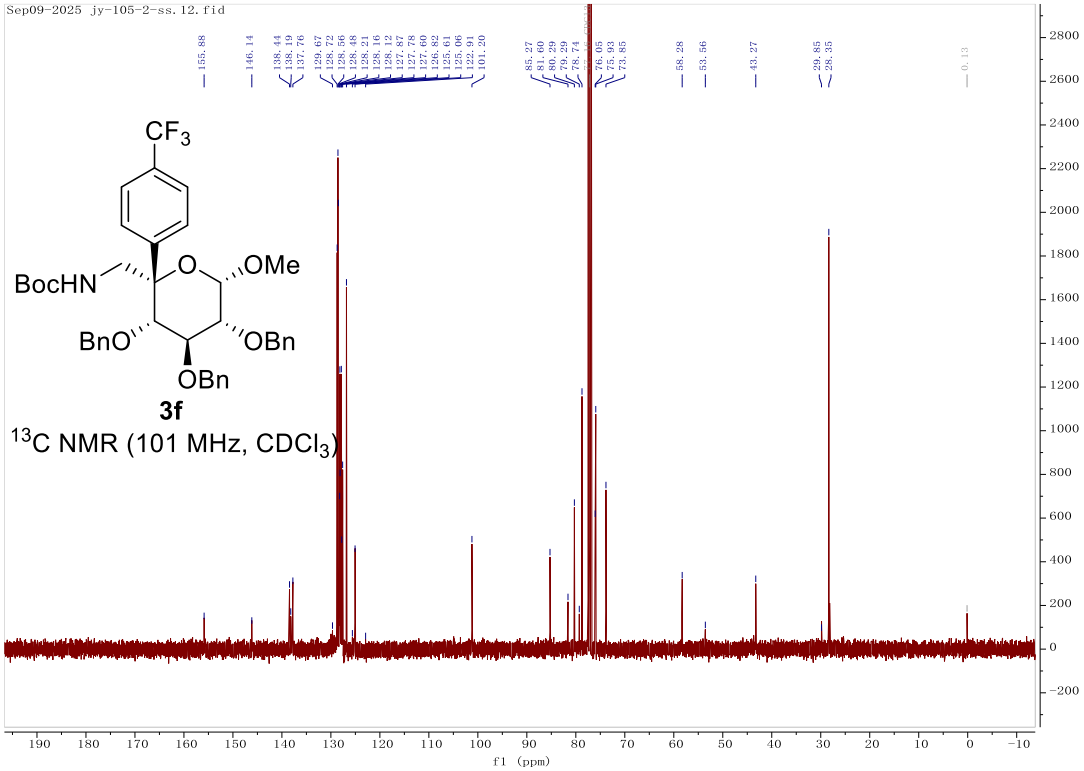
BocHN
O
OMe
BnO
OBn
OBn
3f
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Sep09-2025 jy-105-2-ss.12.fid
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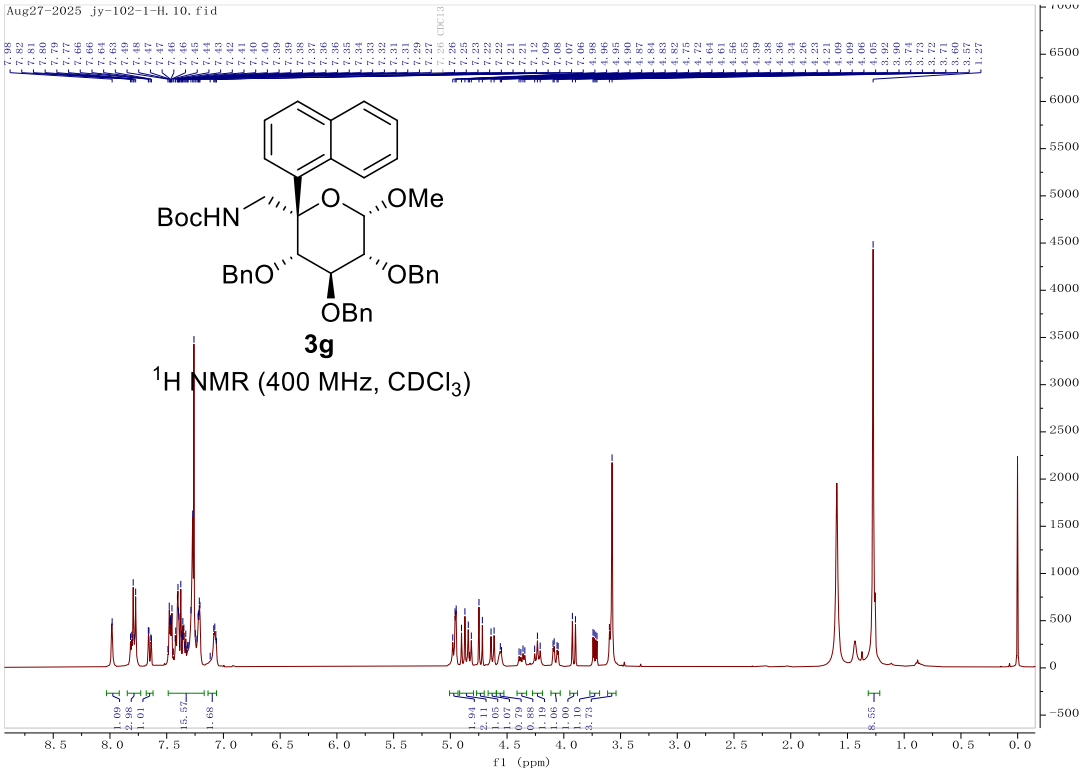
BocHN
O
OMe
BnO
OBn
OBn
3f
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Aug27-2025 jy-102-1-H. 10. fid
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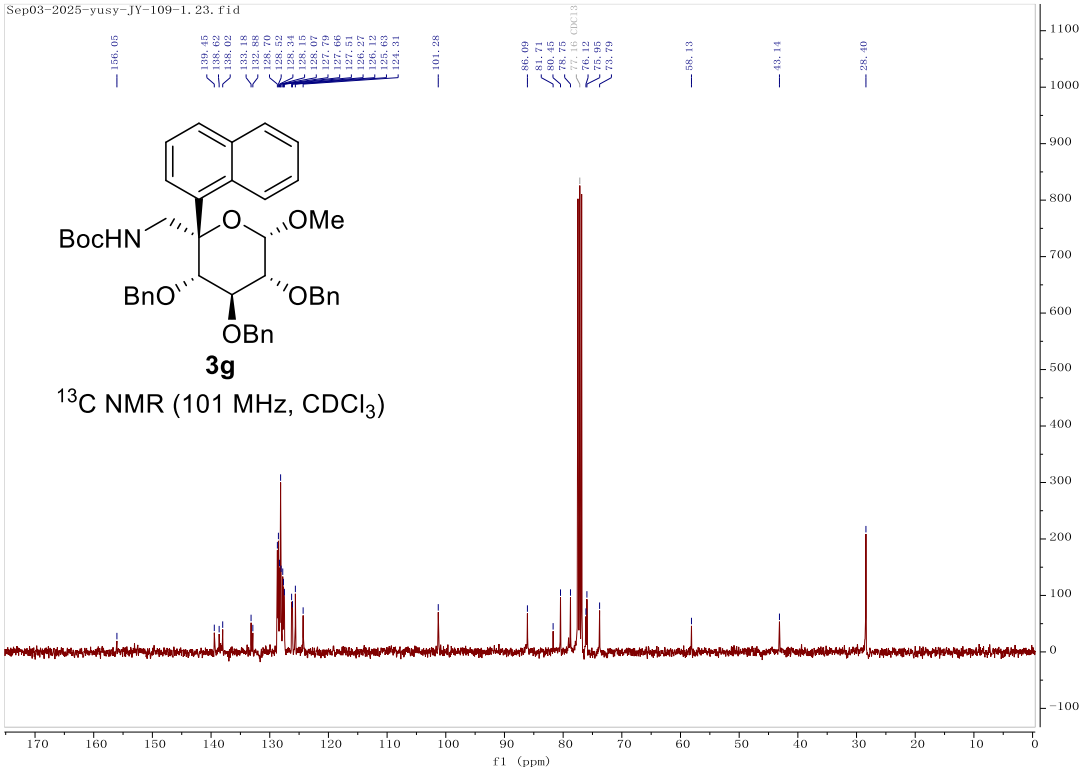
O
OMe
BnO
OBn
OBn
3g
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Sep03-2025-yusy-JY-109-1. 23. fid
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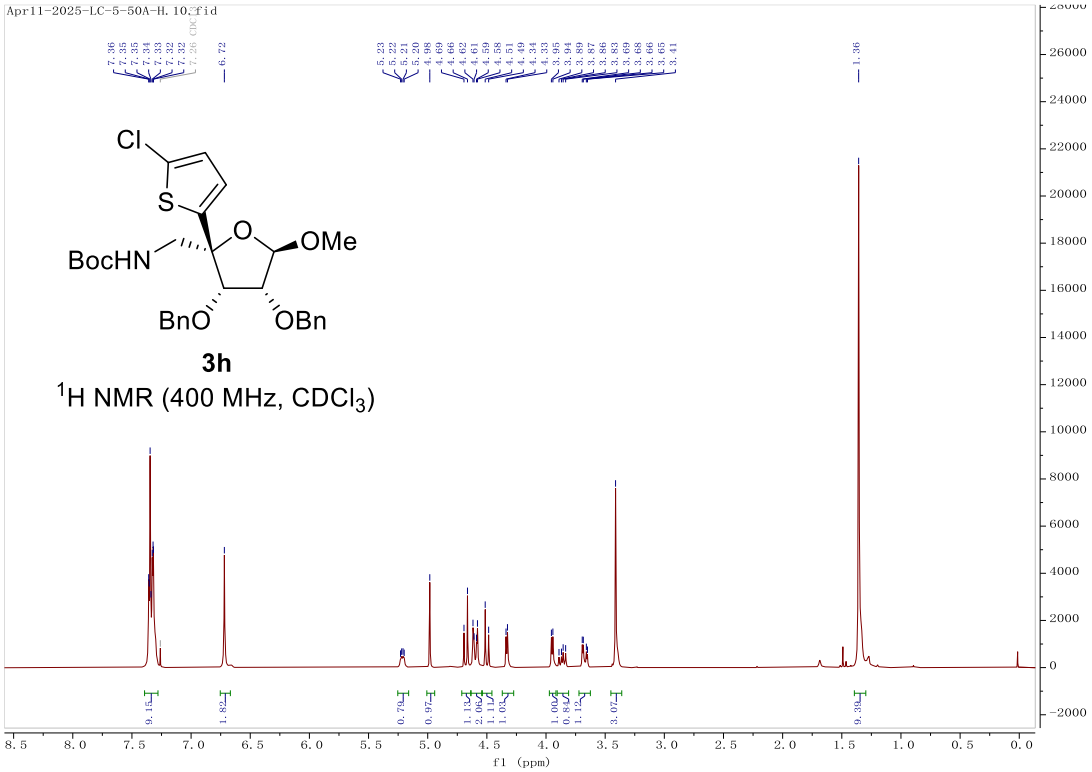
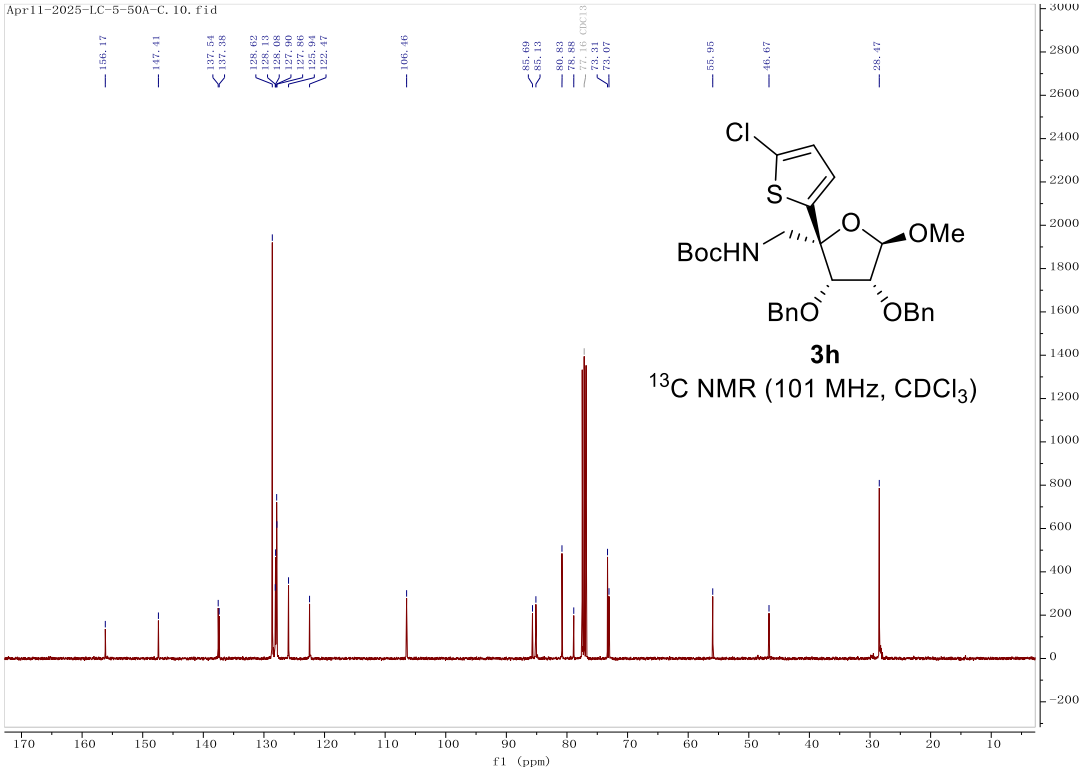
O
OMe
BnO
OBn
OBn
3g
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


Apr11-2025-LC-5-50A-H.10.fid
Cl
S
O
OMe
BocHN
BnO
OBn
3h
1H NMR (400 MHz, CDCl3)
f1 (ppm)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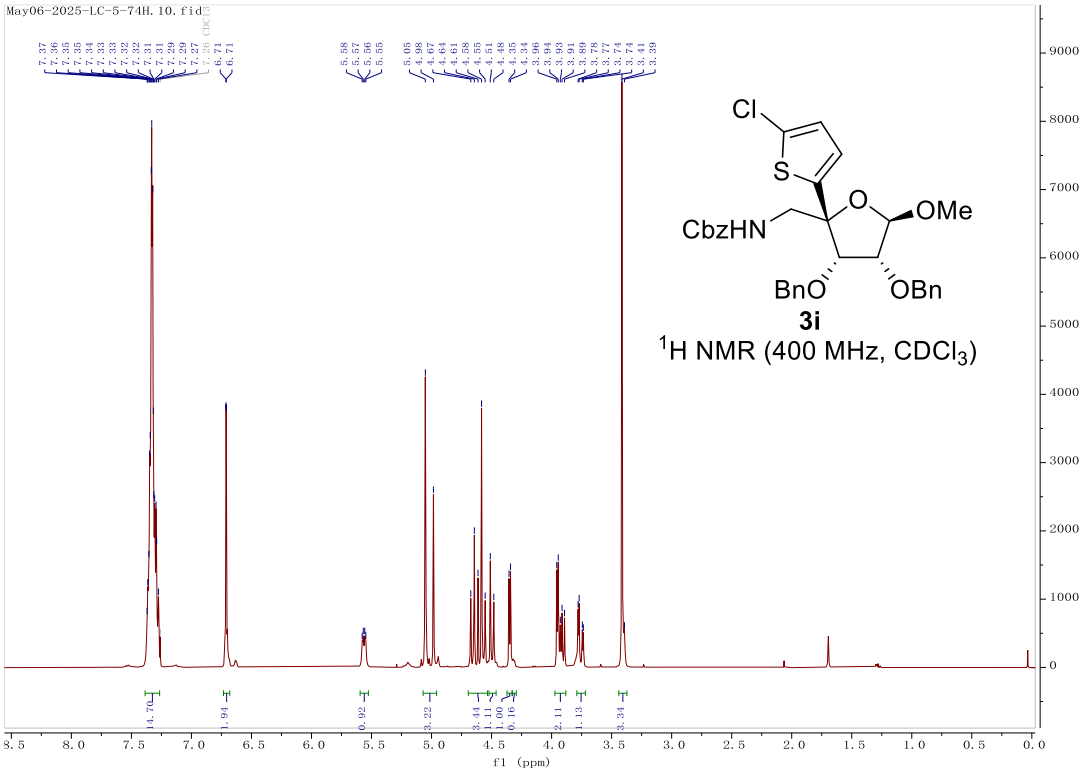
S
O
OMe
BocHN
BnO
OBn
3h
13C NMR (101 MHz, CDCl3)
f1 (ppm)


May06-2025-LC-5-74H.10.fid
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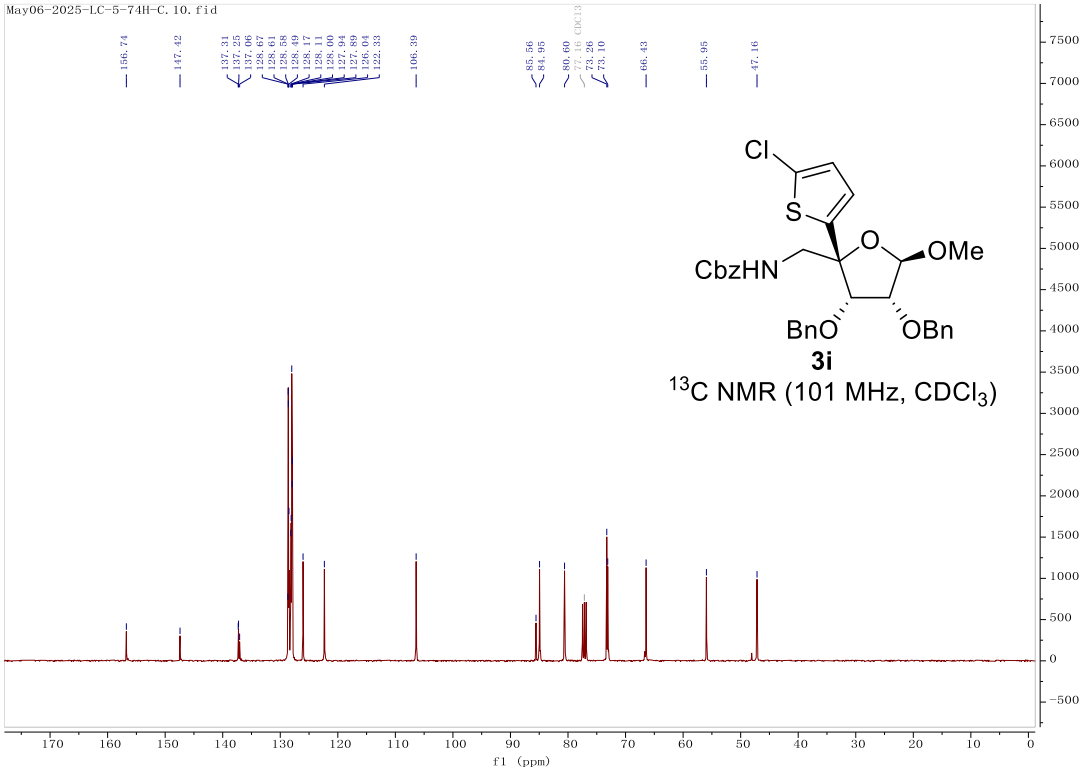
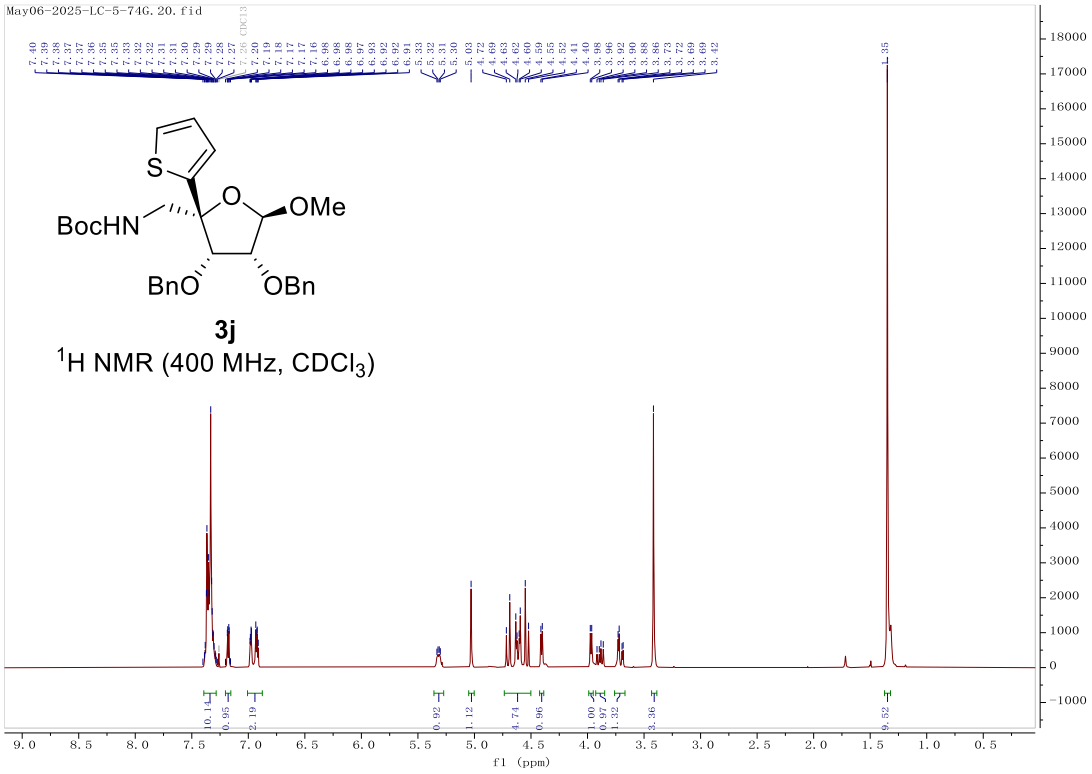
S
O
OMe
CbzHN
BnO
OBn
3i
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


May06-2025-LC-5-74H-C.10.fid
Cl
S
O
OMe
CbzHN
BnO
OBn
3i
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)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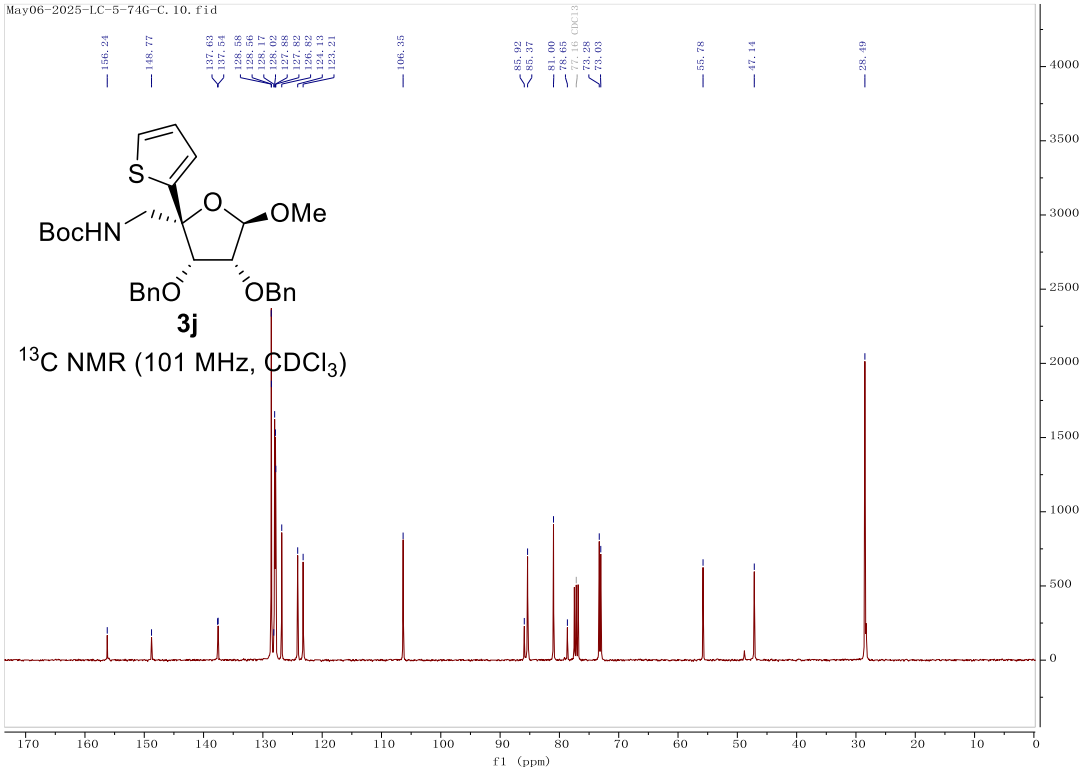
BocHN
OMe
BnO
OBn
3j
1H NMR (400 MHz, CDCl3)
f1 (ppm)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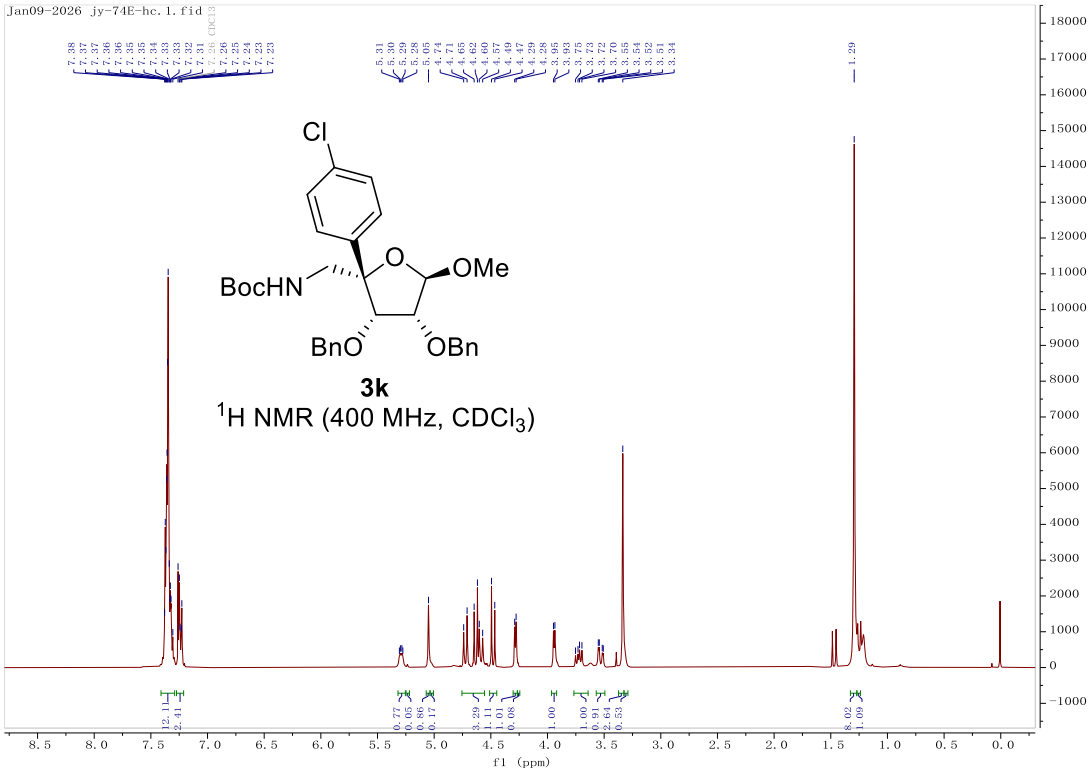
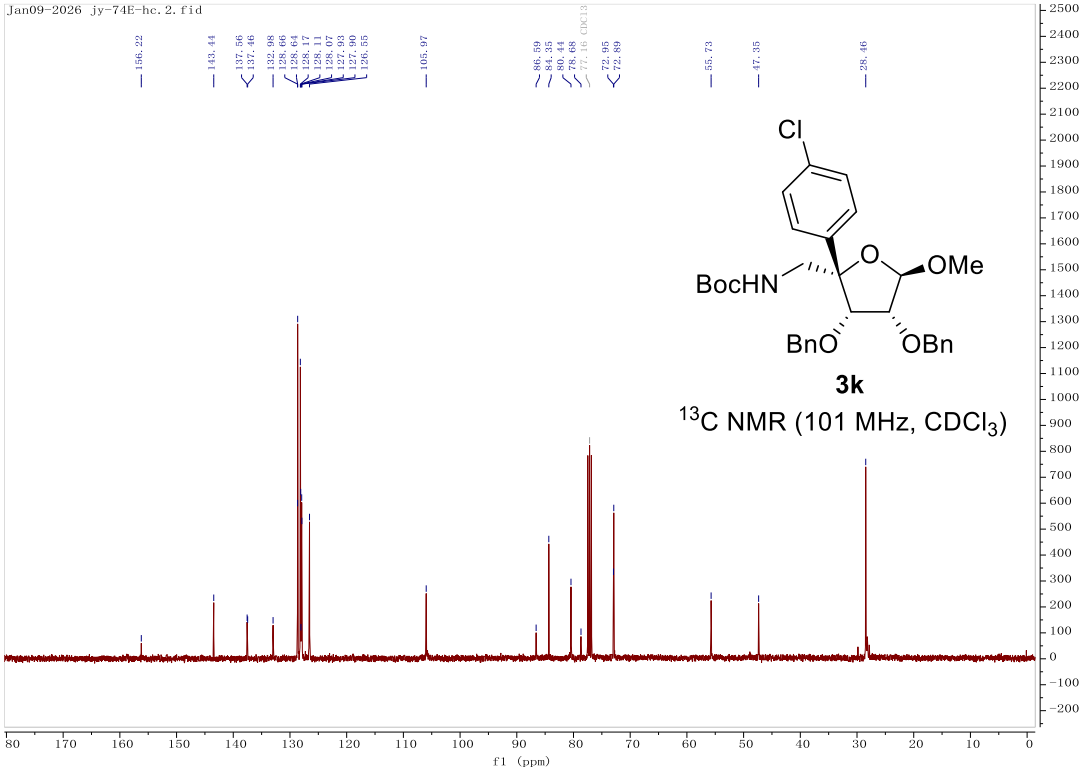
BocHN
OMe
BnO
OBn
3j
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Jan09-2026 jy-74E-hc.1.fid
Cl
O
OMe
BocHN
BnO
OBn
3k
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Jan09-2026 jy-74E-hc.2.fid
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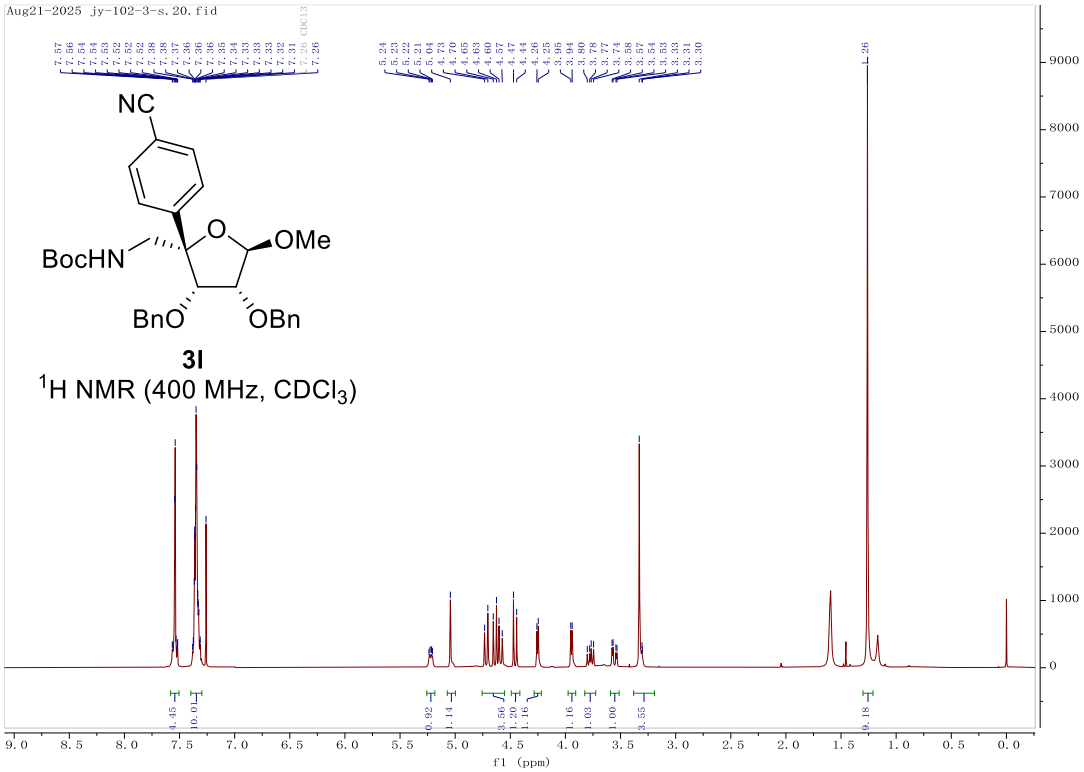
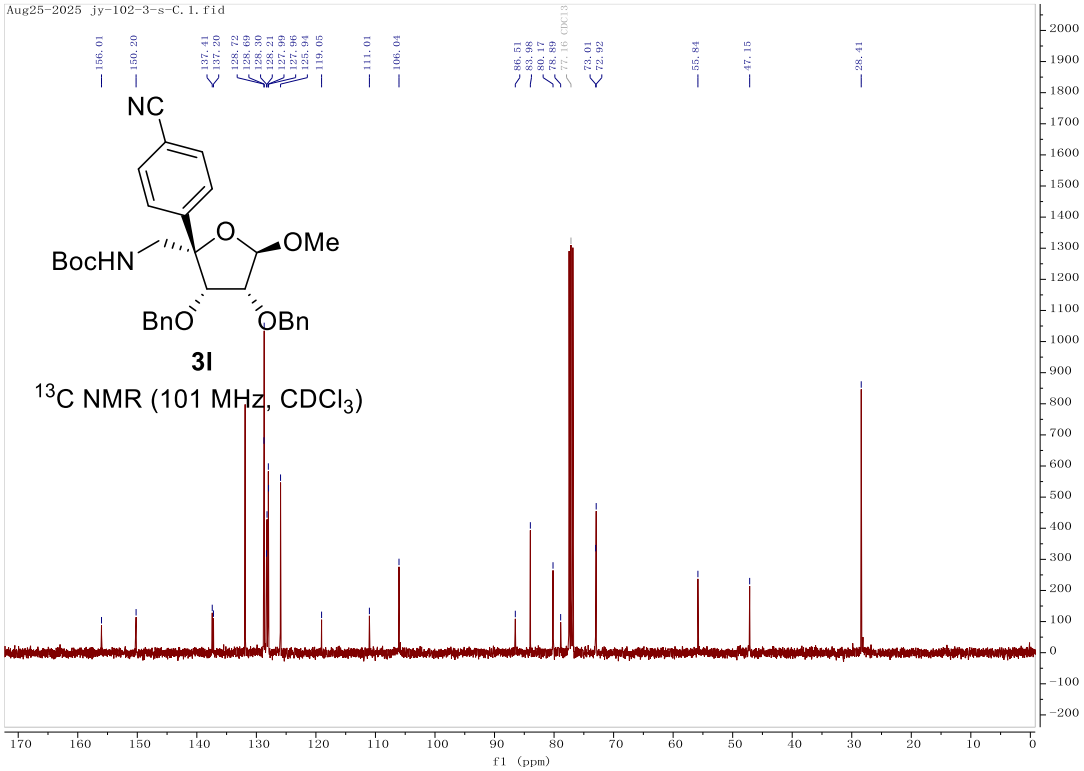
OMe
BocHN
BnO
OBn
3k
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Aug21-2025 jy-102-3-s.20.fid
NC
BocHN
O
OMe
BnO
OBn
3l
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Aug25-2025 jy-102-3-s-C.1.fid
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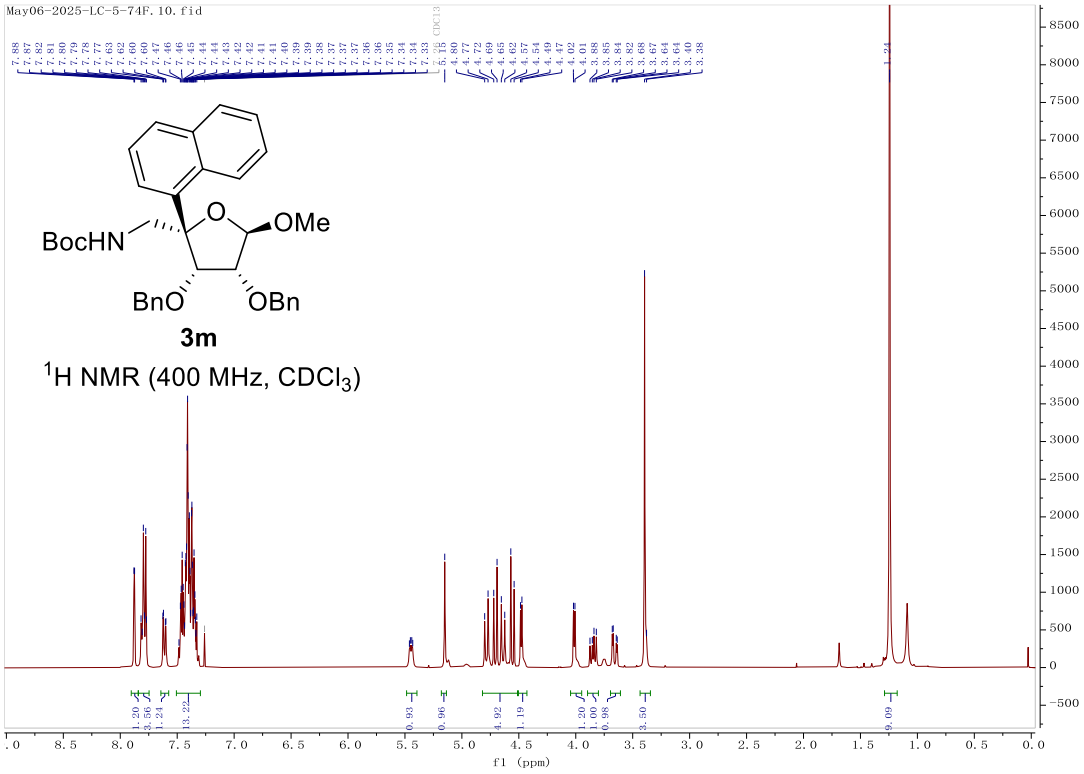
BocHN
O
OMe
BnO
OBn
3l
13C NMR (101 MHz, CDCl3)
f1 (ppm)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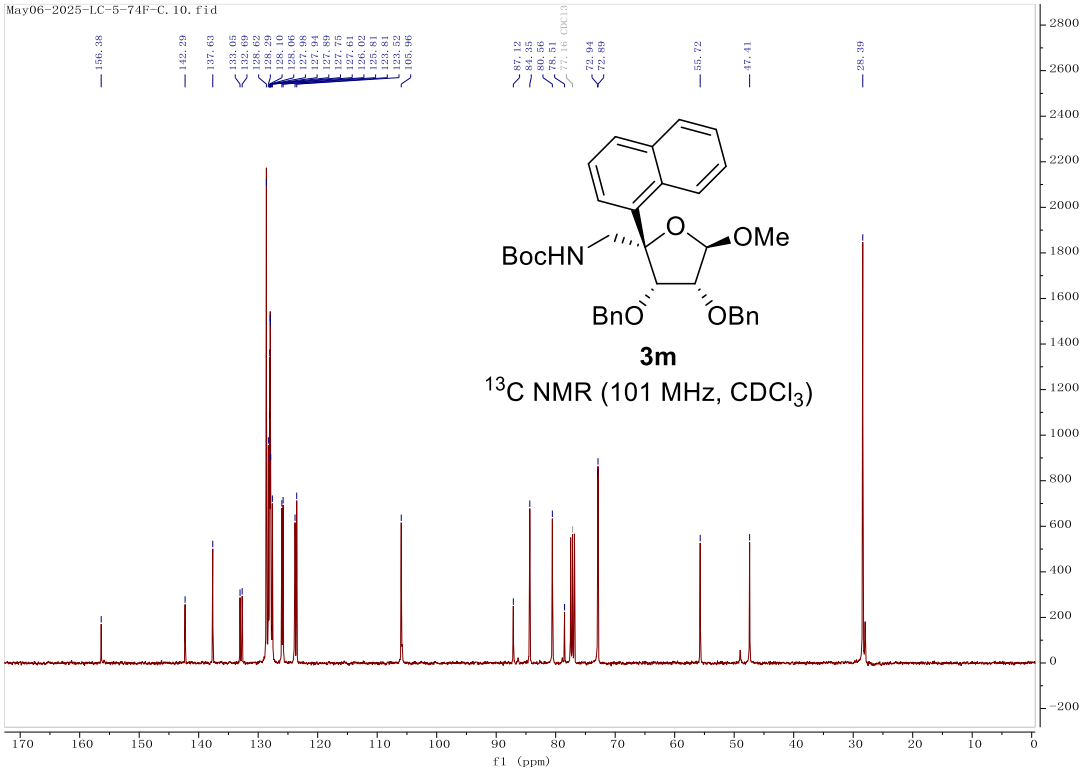
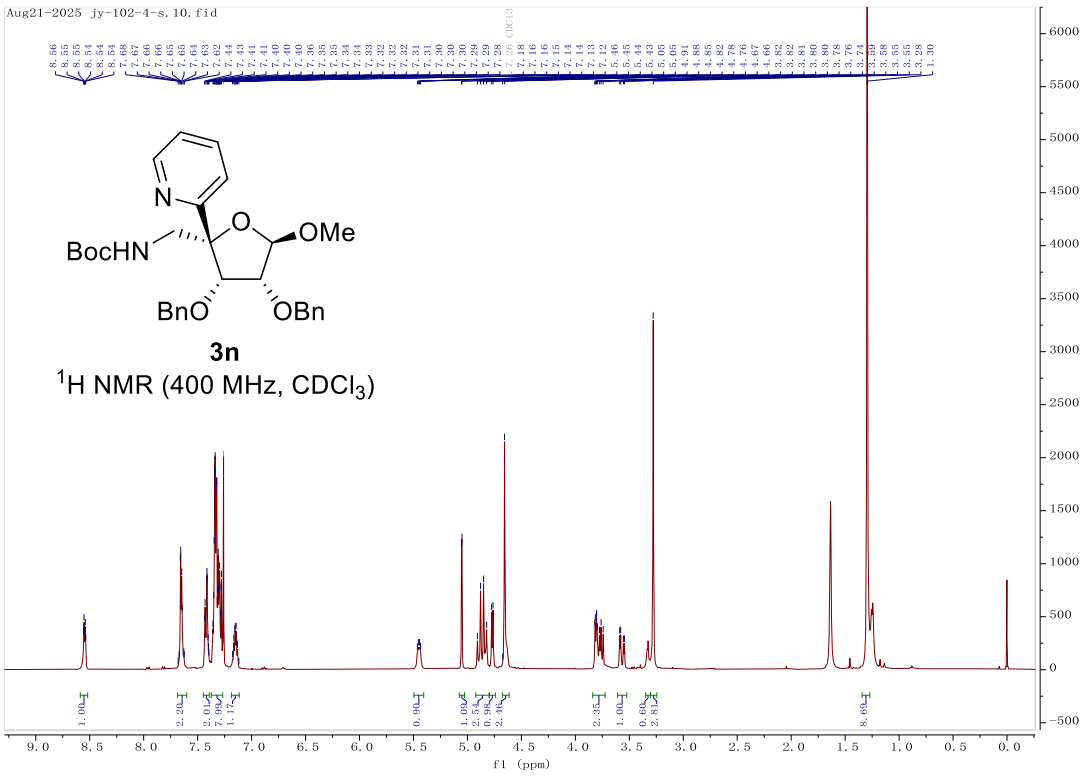
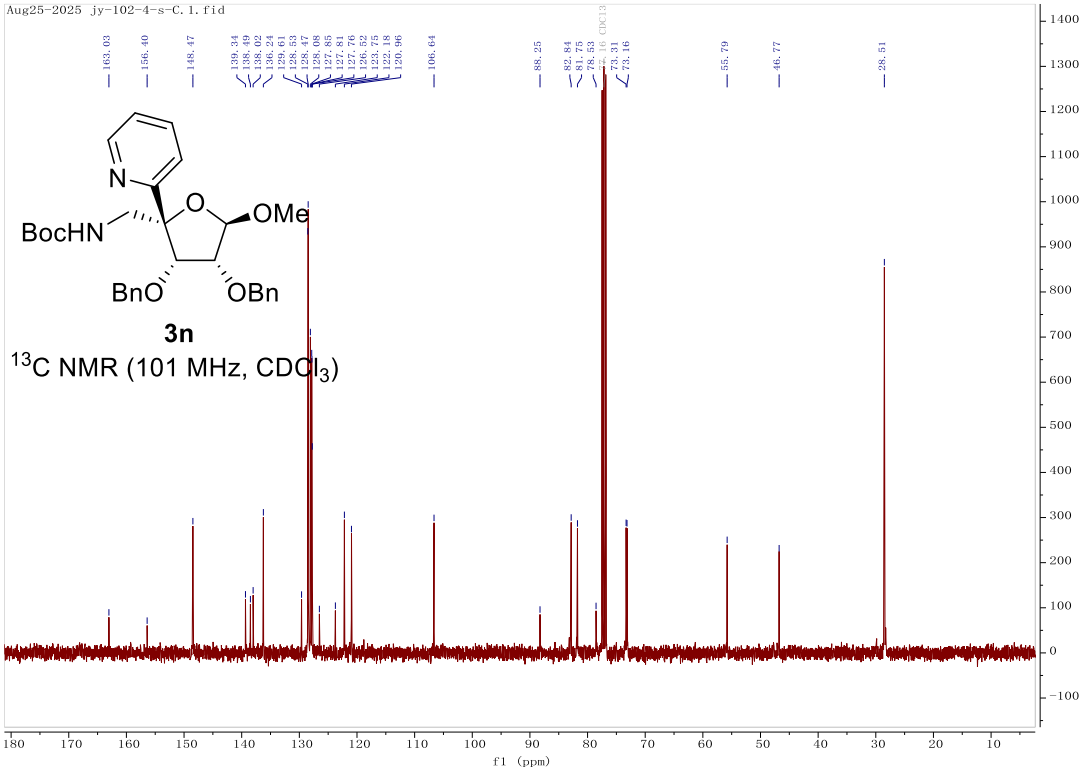
BocHN
OMe
BnO
OBn
3m
1H NMR (400 MHz, CDCl3)
f1 (ppm)


May06-2025-LC-5-74F-C.10.fid
BocHN
OMe
BnO
OBn
3m
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Aug21-2025 jy-102-4-s.10.fid
BocHN
OMe
BnO
OBn
3n
1H NMR (400 MHz, CDCl3)
f1 (ppm)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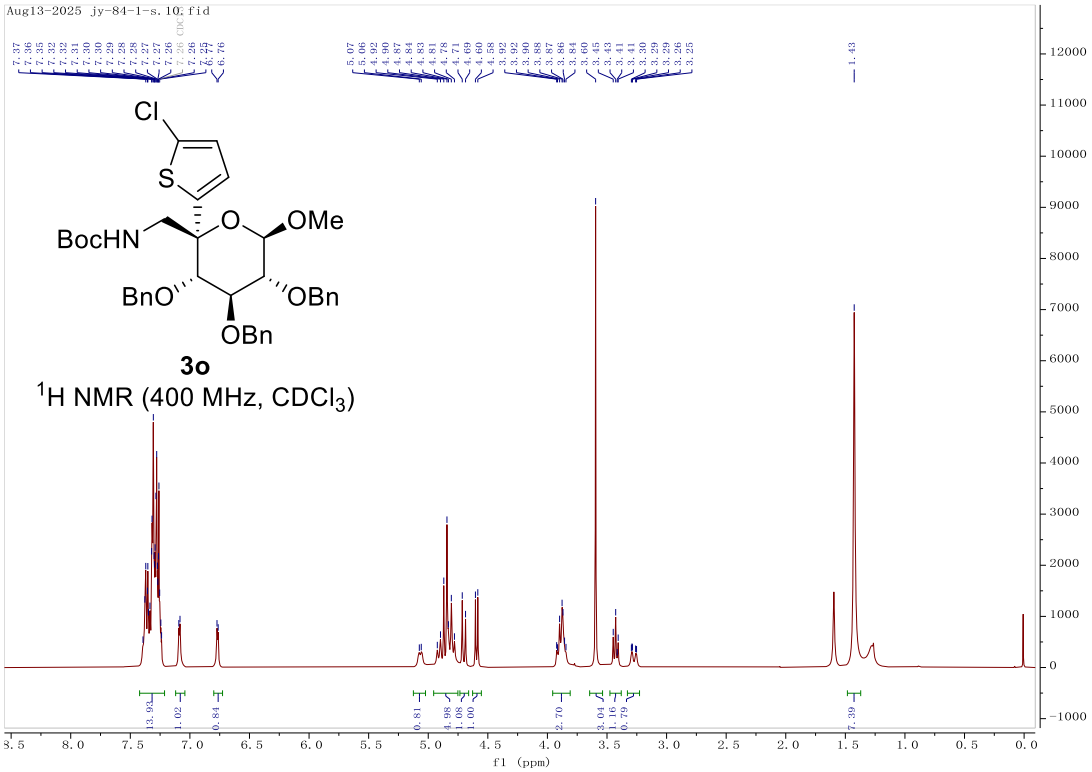
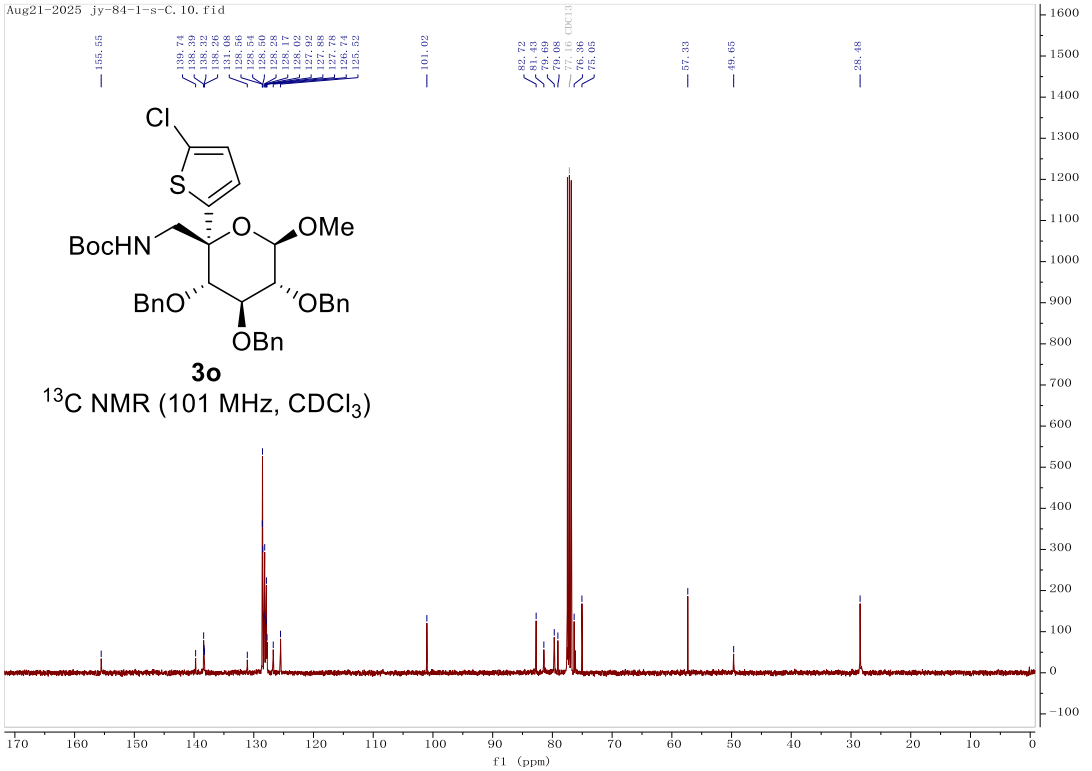
BocHN
OMe
BnO
OBn
3n
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Aug13-2025 jy-84-1-s.10.fid
Cl
S
BocHN
O
OMe
BnO
OBn
OBn
3o
1H NMR (400 MHz, CDCl3)
f1 (ppm)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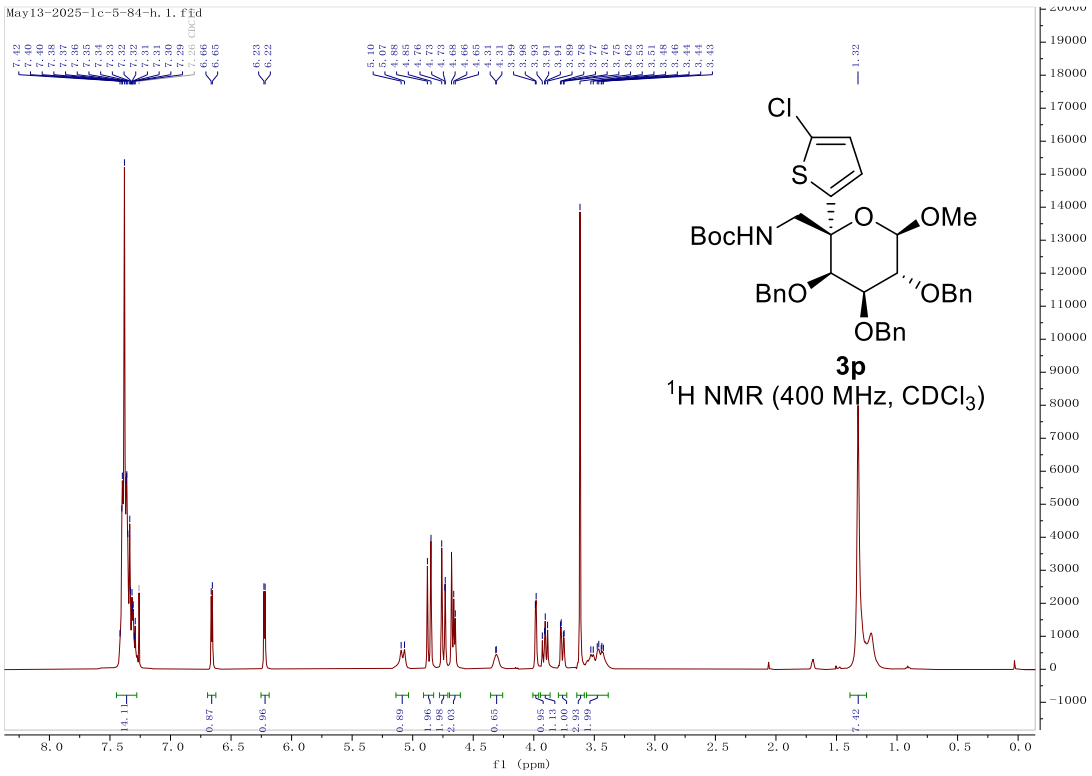
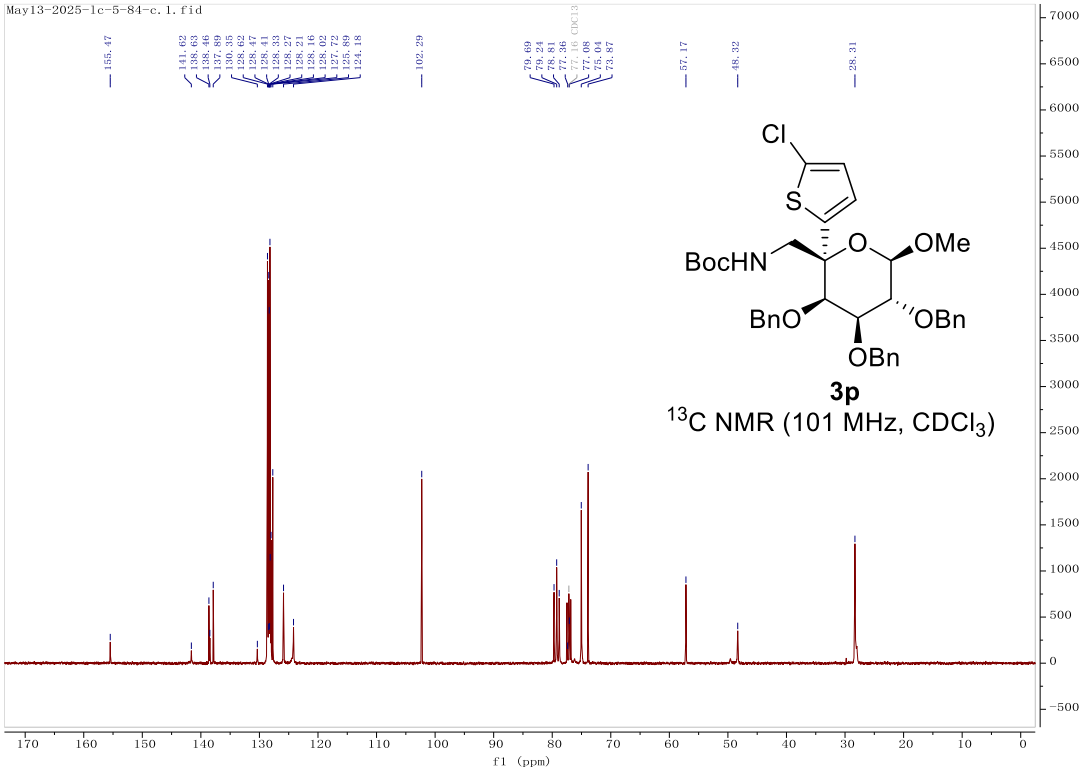
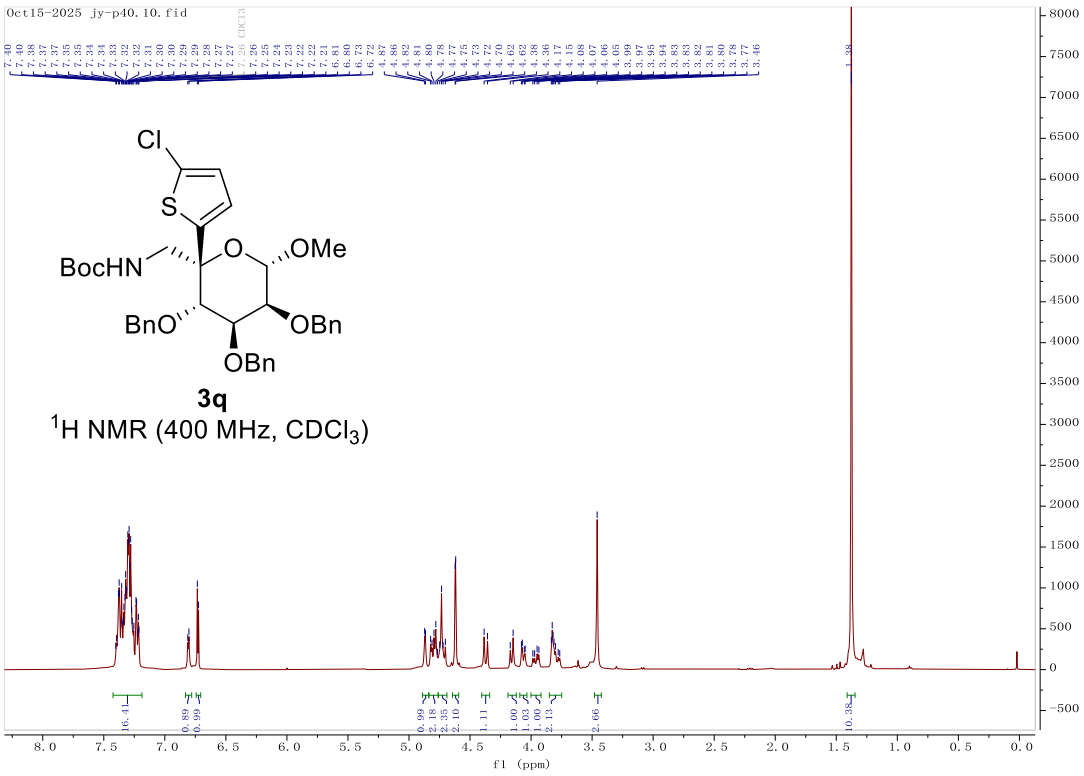
Cl
S
BocHN
O
OMe
BnO
OBn
OBn
3o
13C NMR (101 MHz, CDCl3)
f1 (ppm)


May13-2025-lc-5-84-h.1.fid
Cl
S
O
OMe
BocHN
BnO
OBn
OBn
3p
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


May13-2025-lc-5-84-c.1.fid
Cl
S
O
OMe
BocHN
BnO
OBn
OBn
3p
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


Oct15-2025 jy-p40.10.fid
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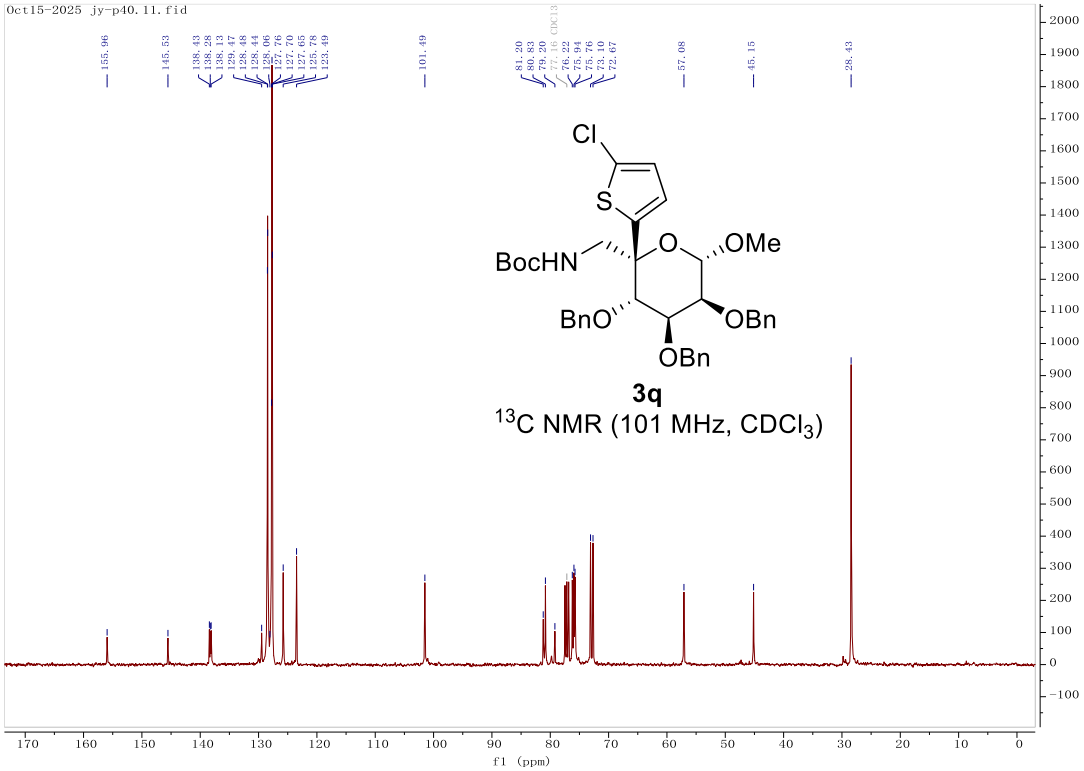
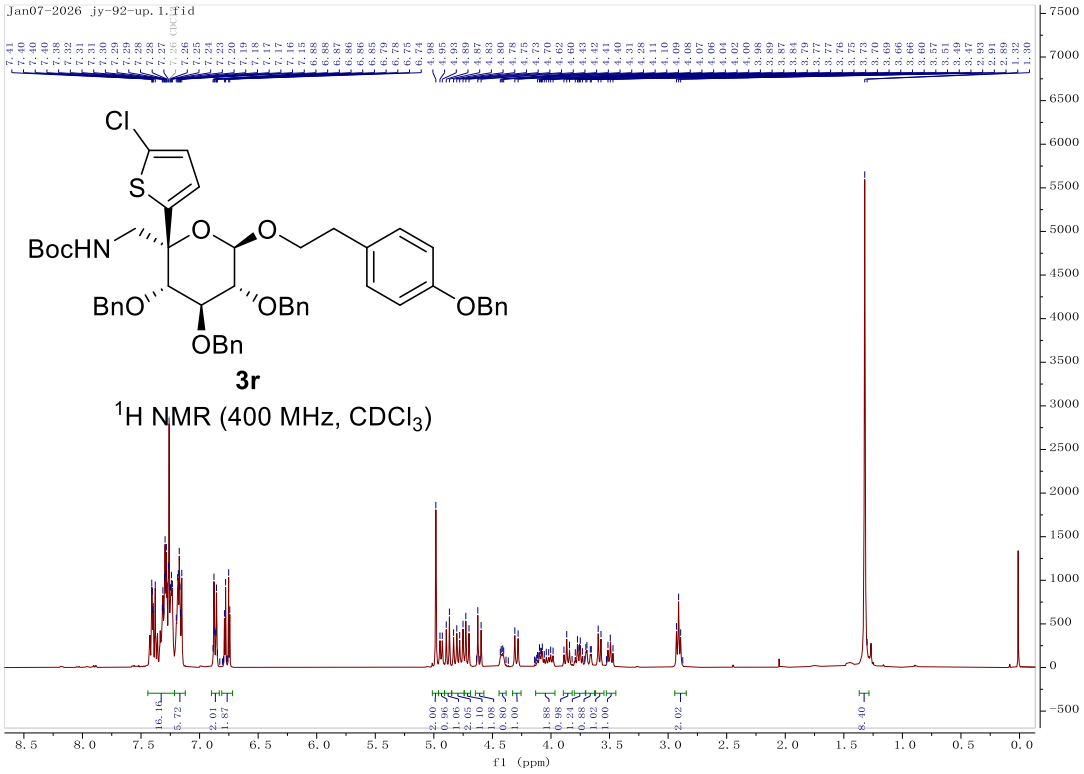
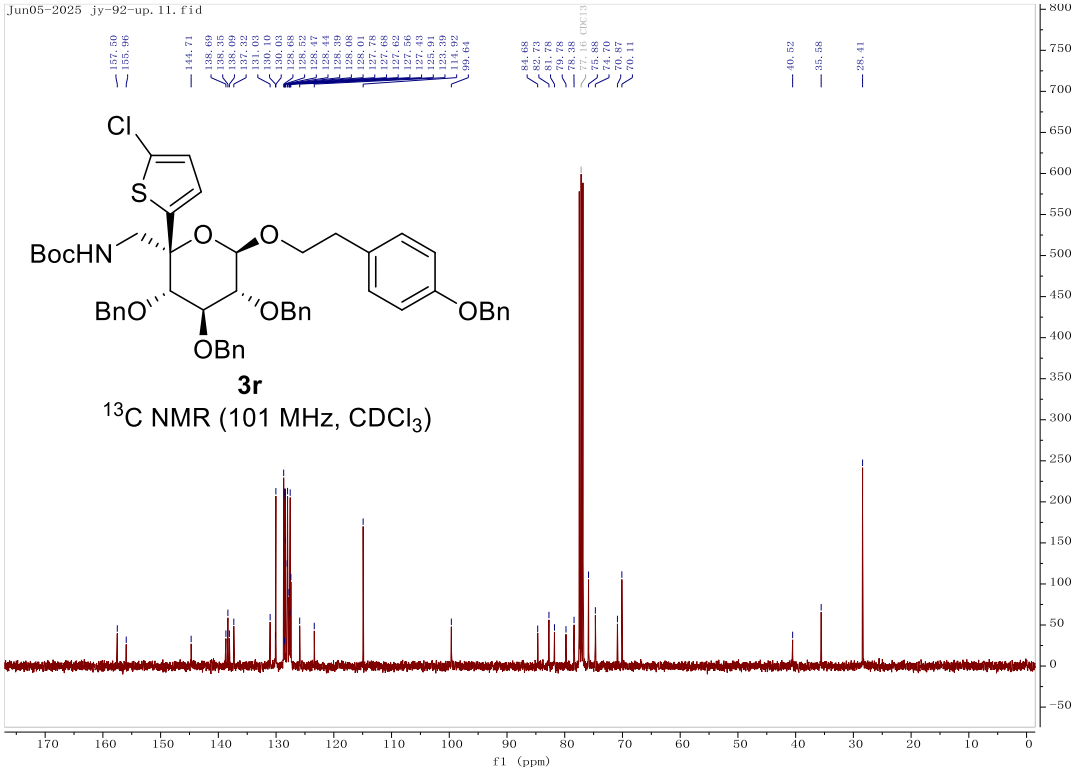
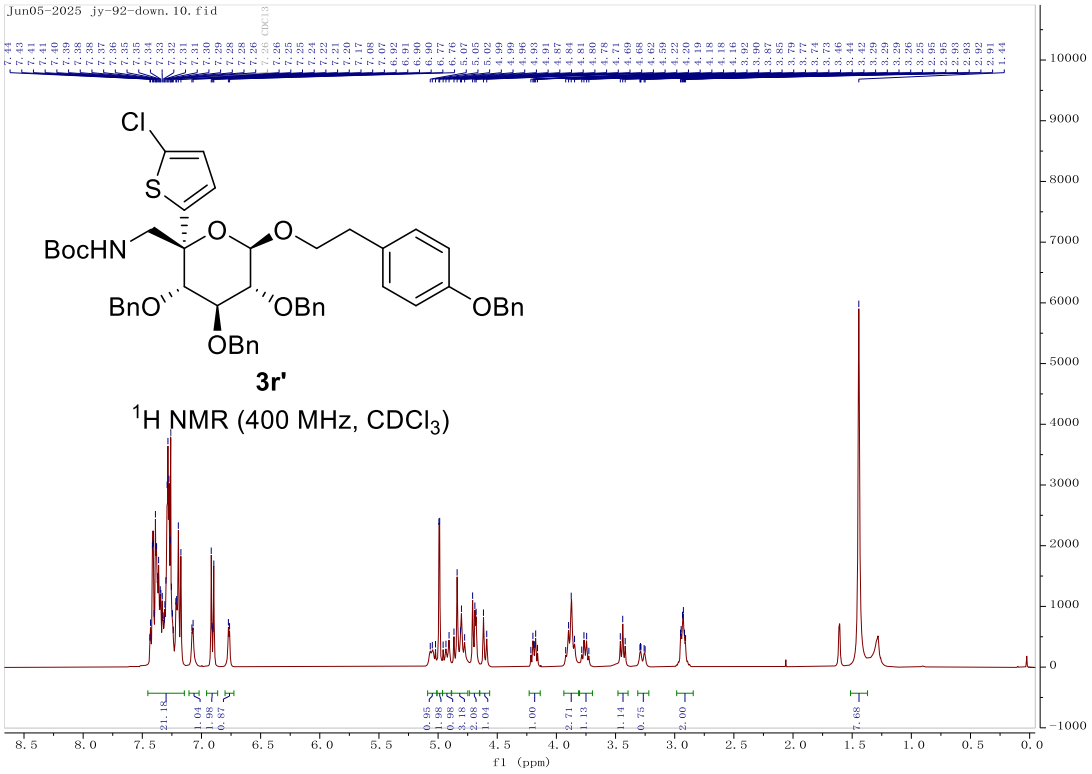
S
BocHN
O
OMe
BnO
OBn
OBn
3q
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Oct15-2025 jy-p40.11.fid
Cl
S
BocHN
O
OMe
BnO
OBn
OBn
3q
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Jan07-2026 jy-92-up.1.fid
Cl
S
BocHN
O
O
BnO
OBn
OBn
OBn
3r
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Jun05-2025 jy-92-up.11.fid
Cl
S
BocHN
O
O
BnO
OBn
OBn
OBn
3r
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Jun05-2025 jy-92-down.10.fid
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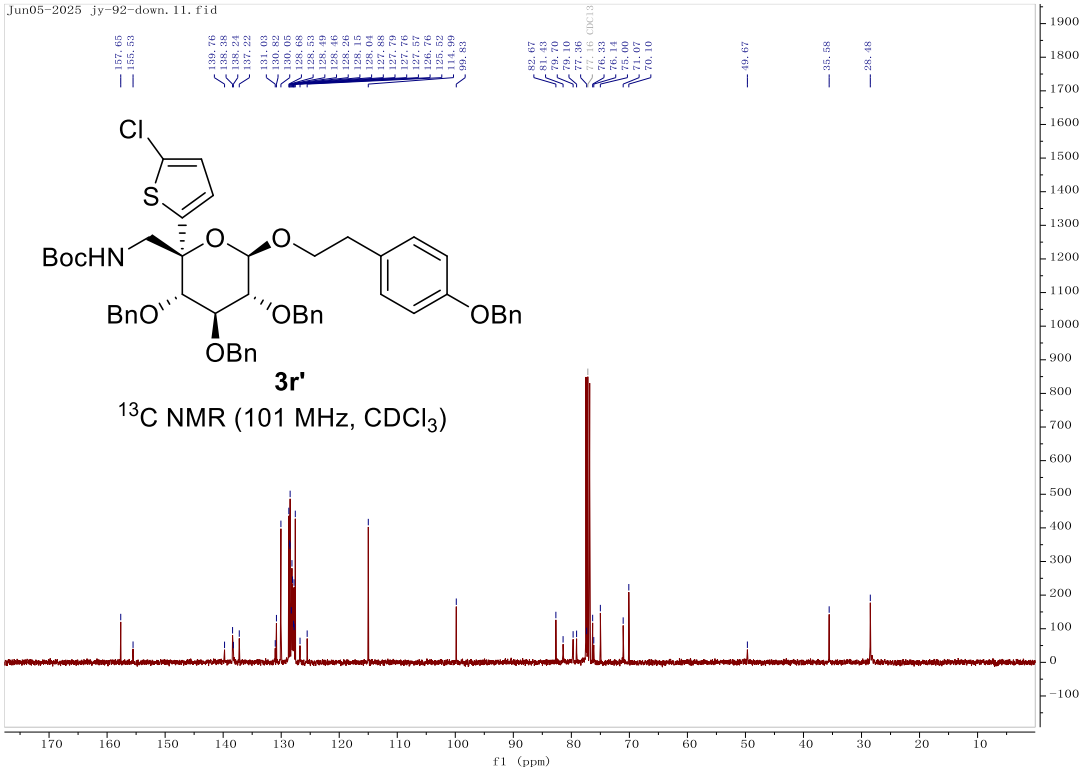
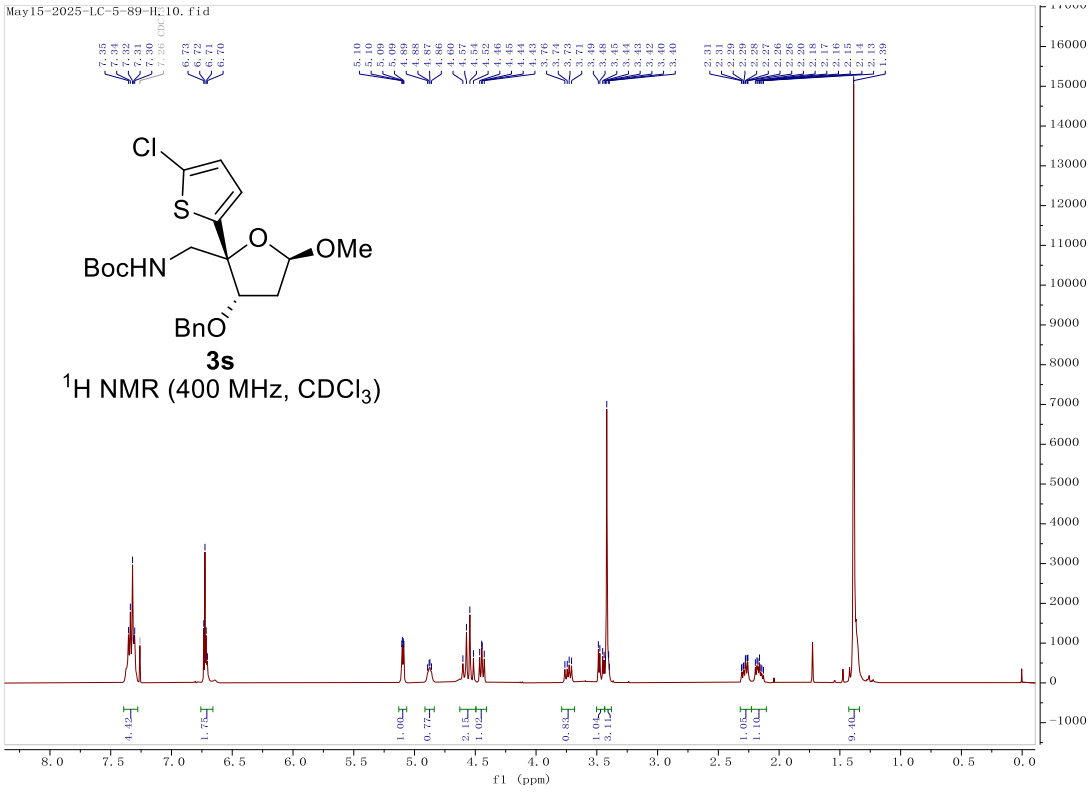
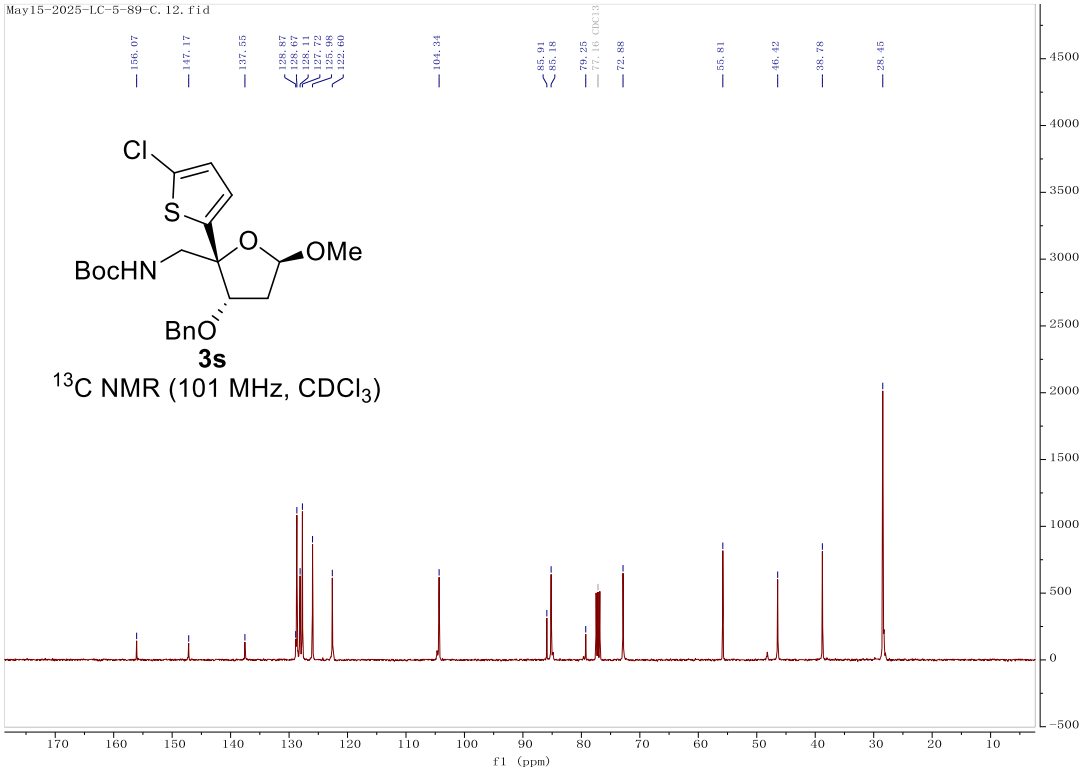
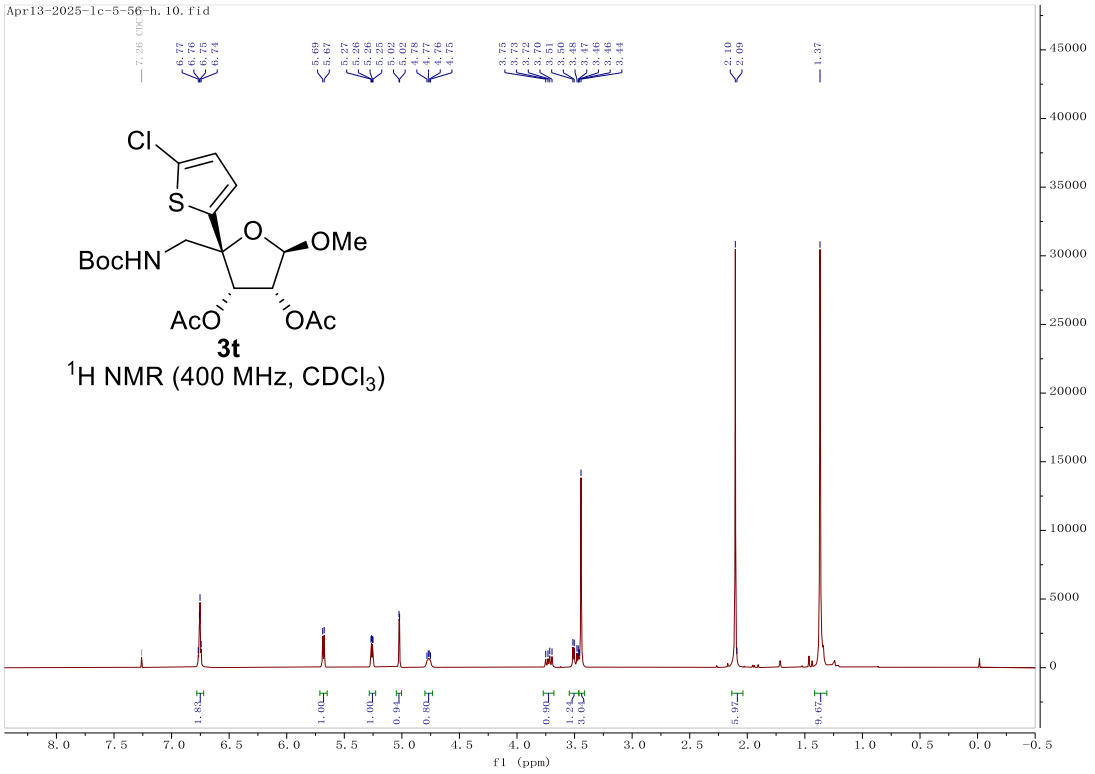
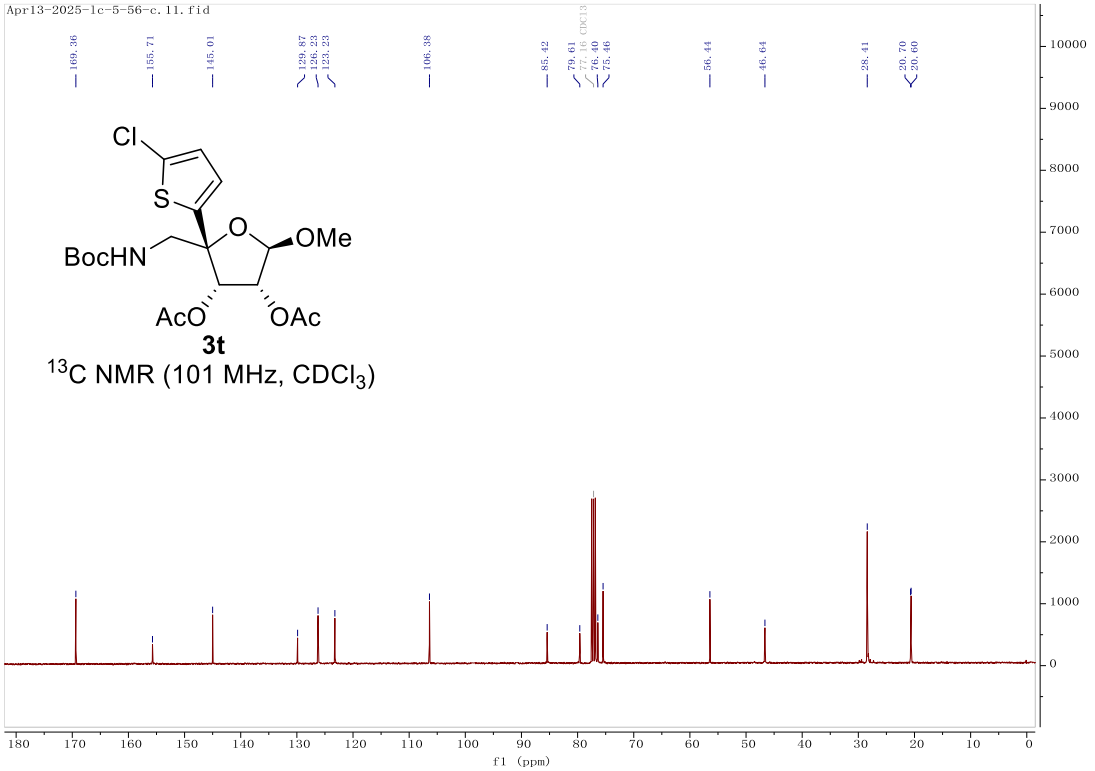
S
BocHN
O
O
BnO
OBn
OBn
OBn
3r'
1H NMR (400 MHz, CDCl3)
f1 (ppm)

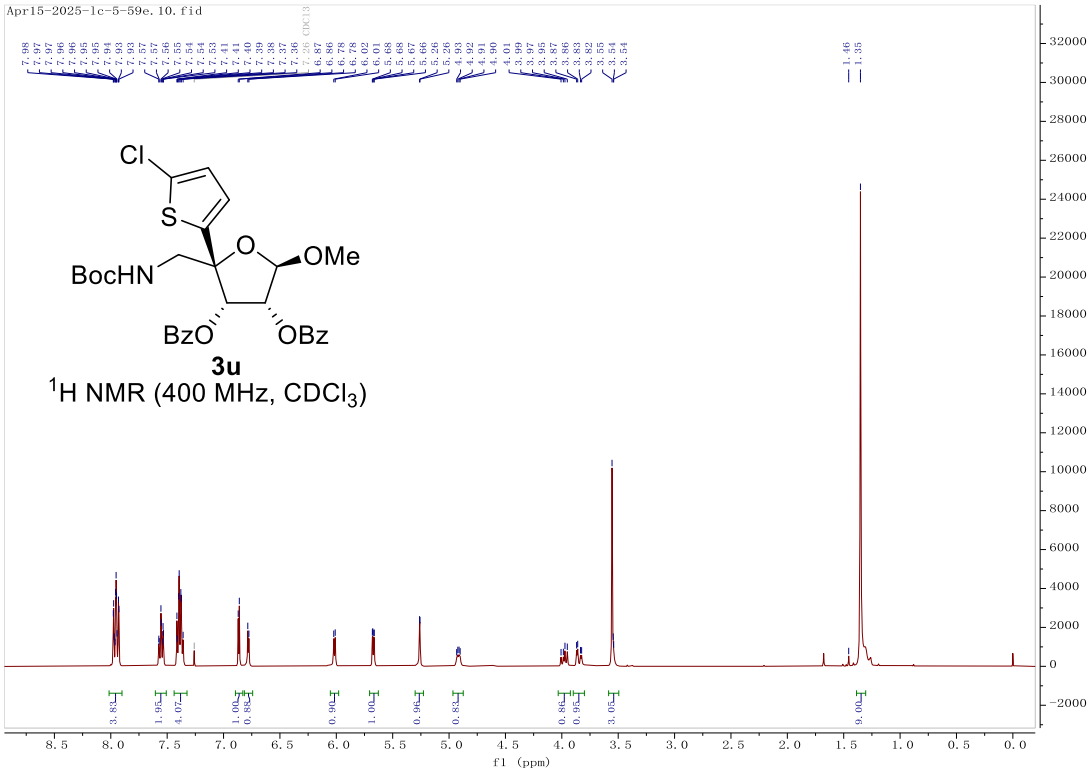

Jun05-2025 jy-92-down.11.fid
Cl
S
BocHN
O
O
BnO
OBn
OBn
OBn
3r'
13C NMR (101 MHz, CDCl3)
f1 (ppm)

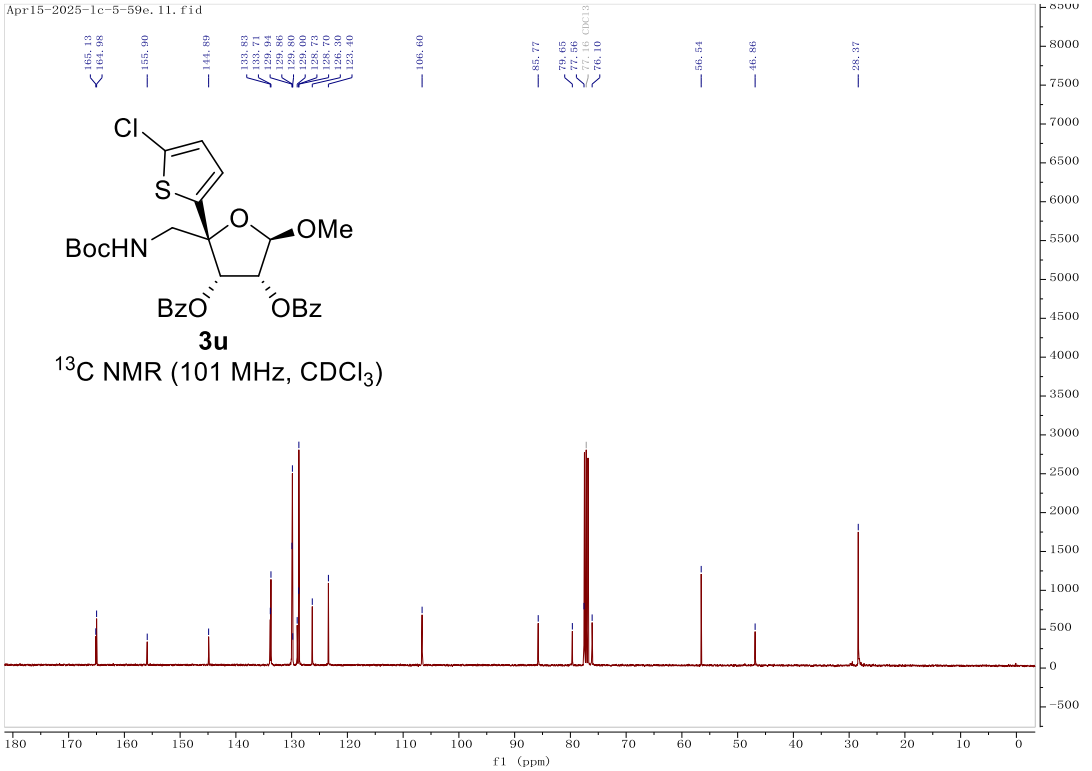

May15-2025-LC-5-89-H.10.fid
Cl
S
O
OMe
BocHN
BnO
3s
1H NMR (400 MHz, CDCl3)
f1 (ppm)

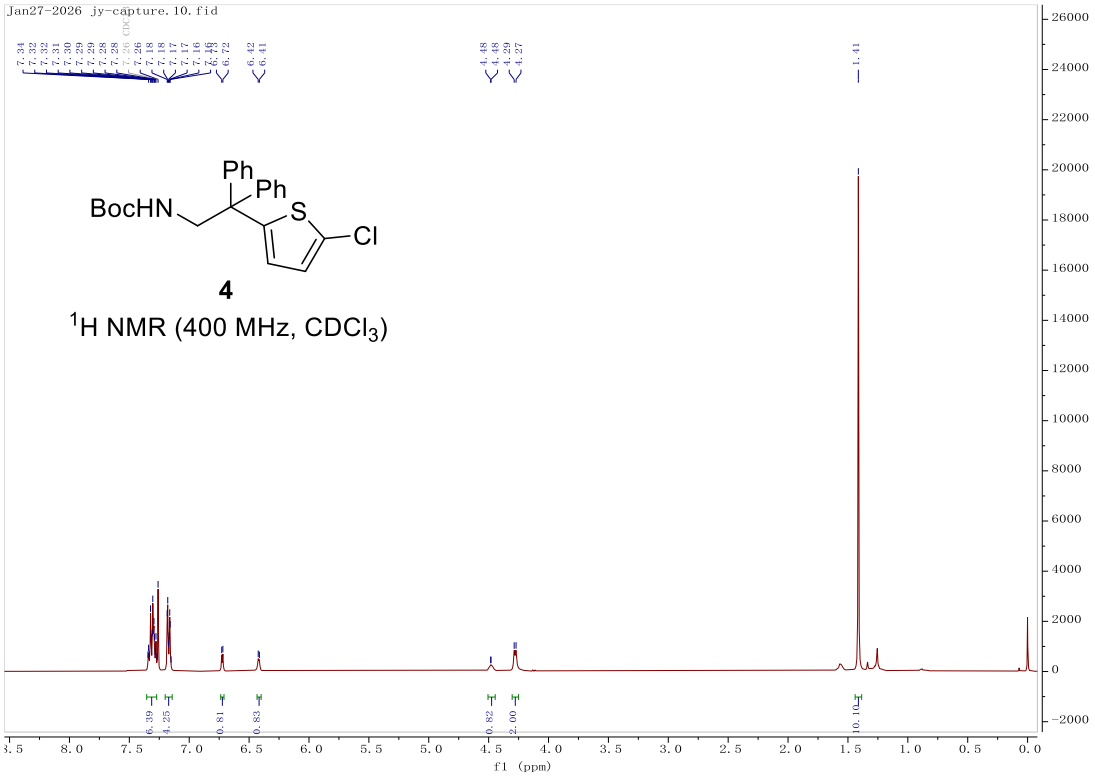

May15-2025-LC-5-89-C.12.fid
Cl
S
O
OMe
BocHN
BnO
3s
13C NMR (101 MHz, CDCl3)
f1 (ppm)

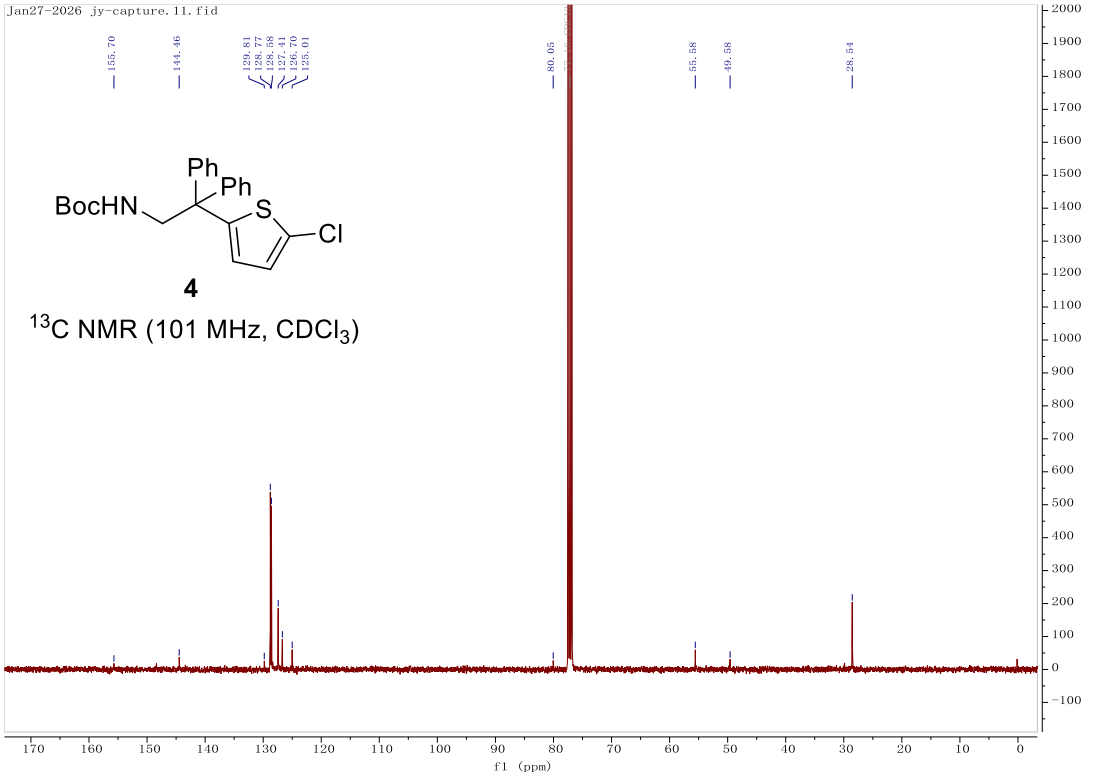

Apr13-2025-lc-5-56-h.10.fid
Cl
S
O
OMe
BocHN
AcO
OAc
3t
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Apr13-2025-lc-5-56-c.11.fid
Cl
S
O
OMe
BocHN
AcO
OAc
3t
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

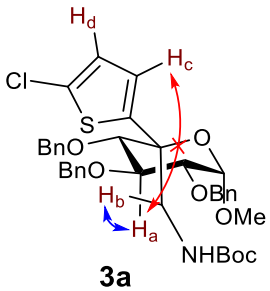

Apr15-2025-lc-5-59e.10.fid
Cl
S
O
OMe
BocHN
BzO
OBz
3u
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Apr15-2025-lc-5-59e.11.fid
Cl
S
O
OMe
BocHN
BzO
OBz
3u
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Jan27-2026 jy-capture.10.fid
Ph
Ph
BocHN
S
Cl
4
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Jan27-2026 jy-capture.11.fid
Ph
Ph
BocHN
S
Cl
4
13C NMR (101 MHz, CDCl3)
f1 (ppm)

11. Stereochemistry assignment

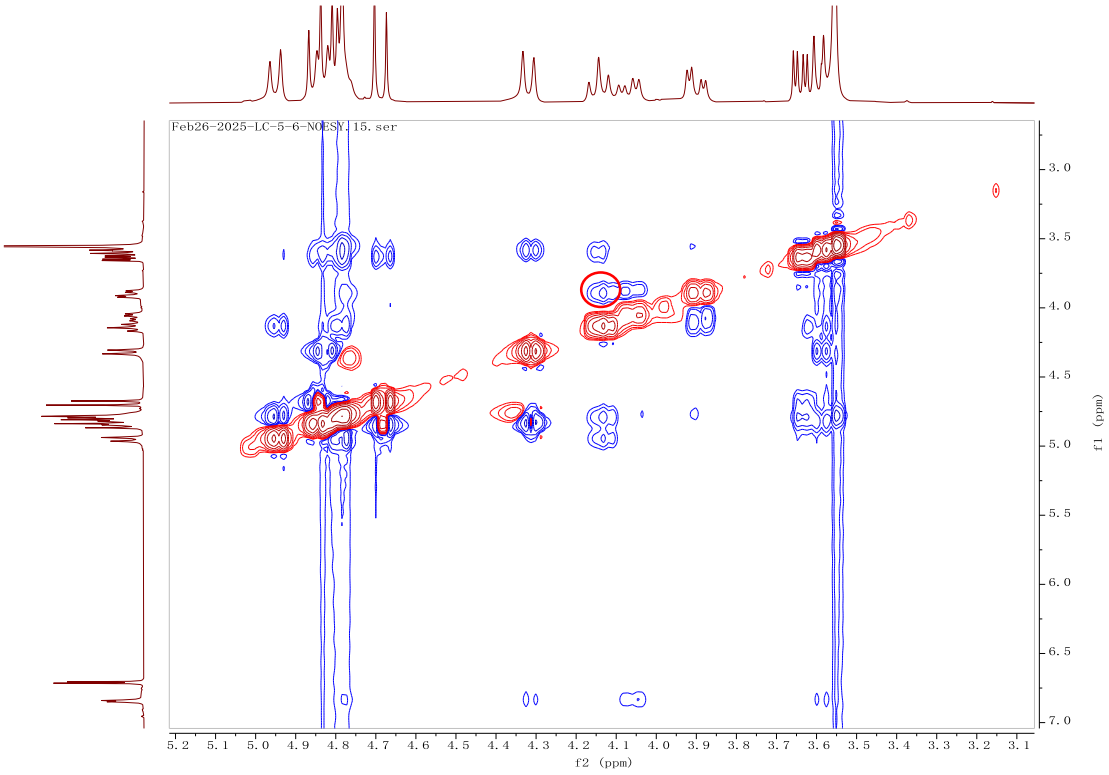


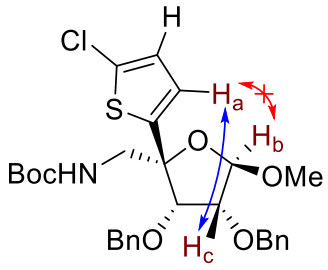
3a

NOESY NMR (400 MHz, $CDCl_3$)

NOESY colleration

No NOESY colleration



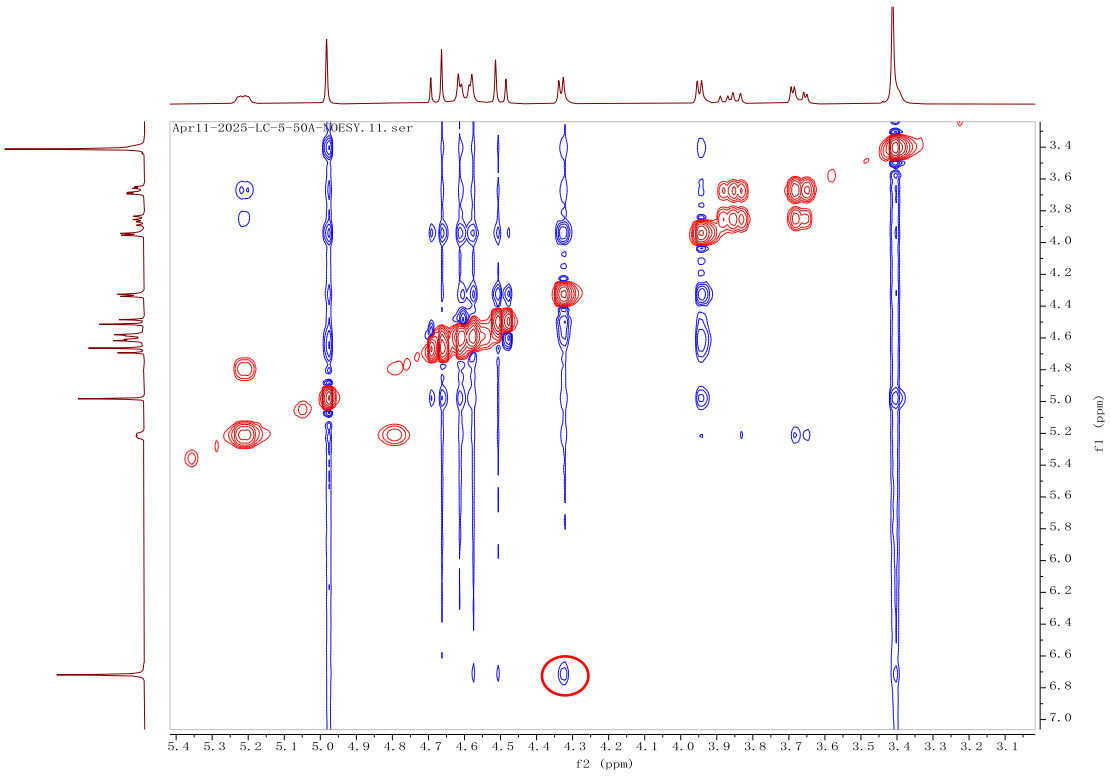


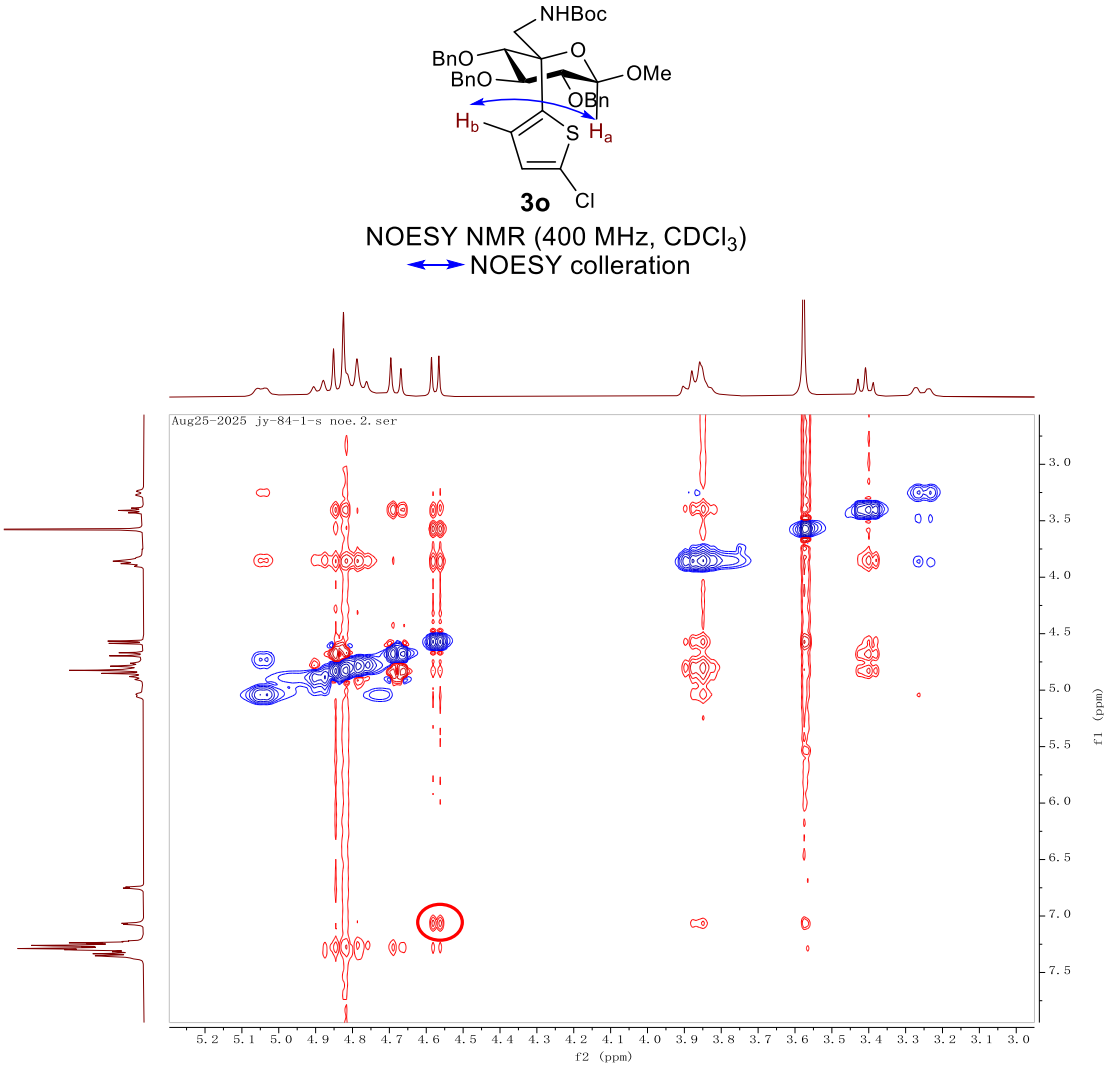
3h

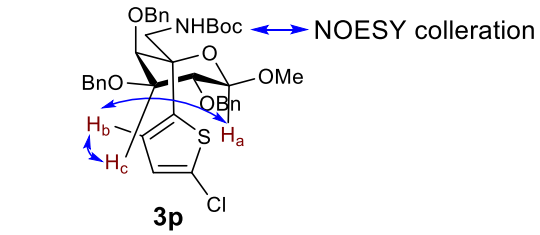
NOESY NMR (400 MHz, $CDCl_3$)

NOESY colleration

No NOESY colleration

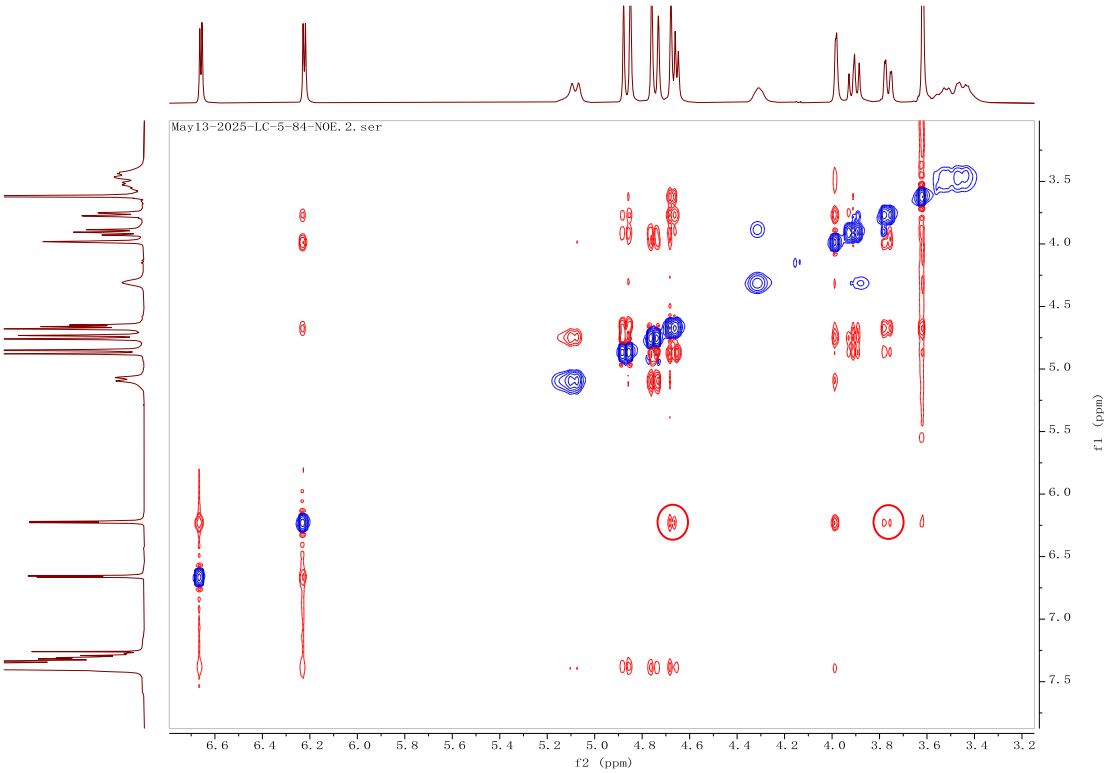


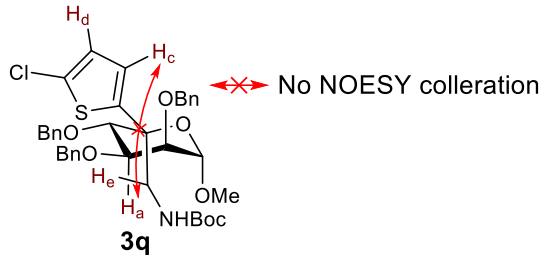

NHBoc
BnO
BnO
O
OMe
OBn
Hb
S
Ha
Cl
3o
NOESY NMR (400 MHz, CDCl3)
NOESY colleration
Aug25-2025 jy-84-1-s noe.2.ser
f2 (ppm)
f1 (ppm)



3p

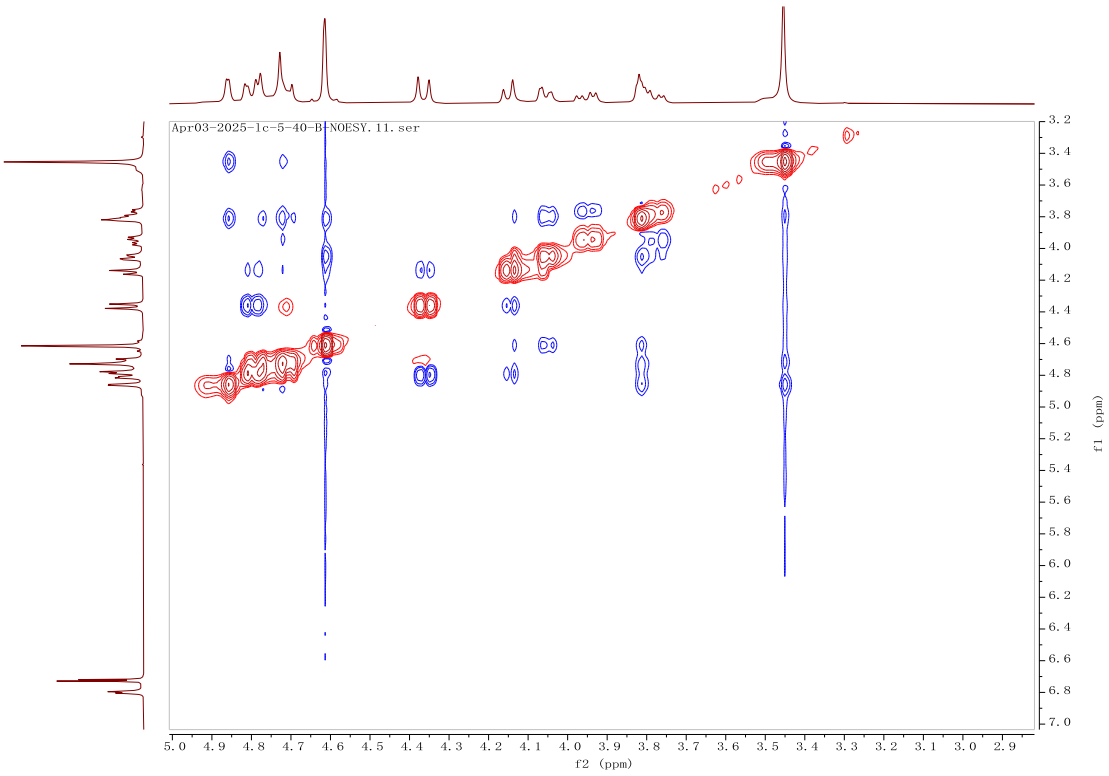
NOESY NMR (400 MHz, $CDCl_3$)

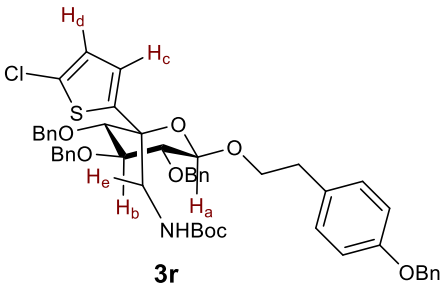




3q

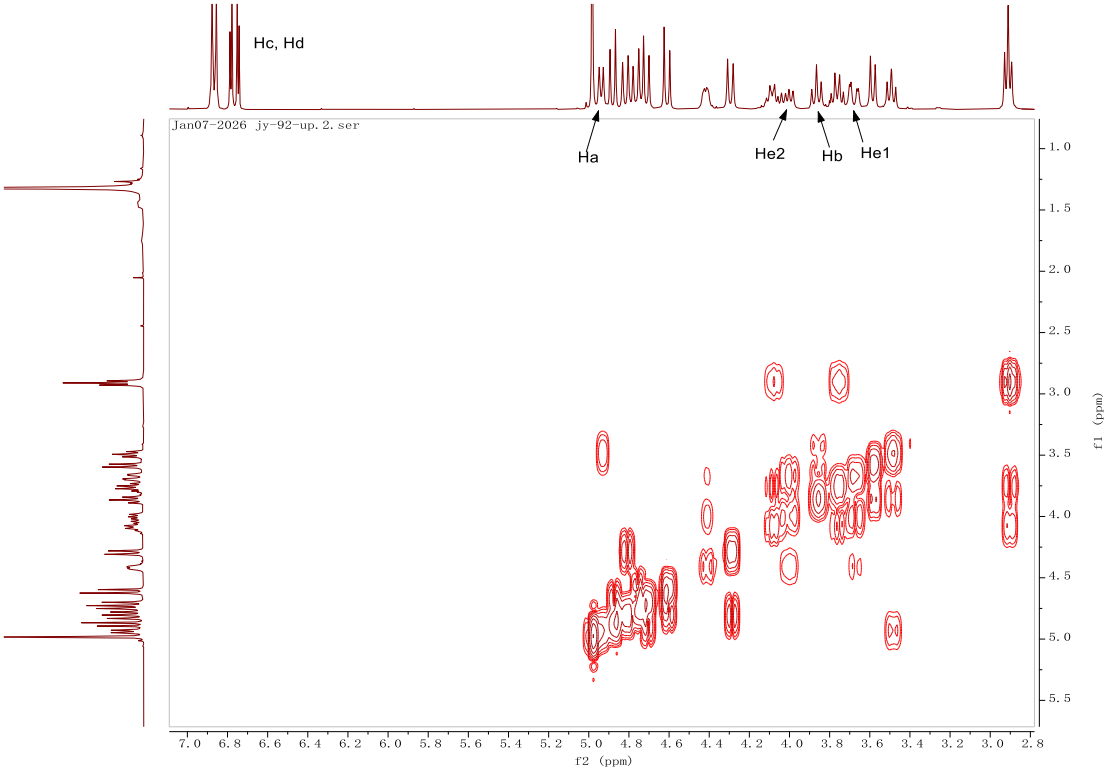
NOESY NMR (400 MHz, $CDCl_3$)

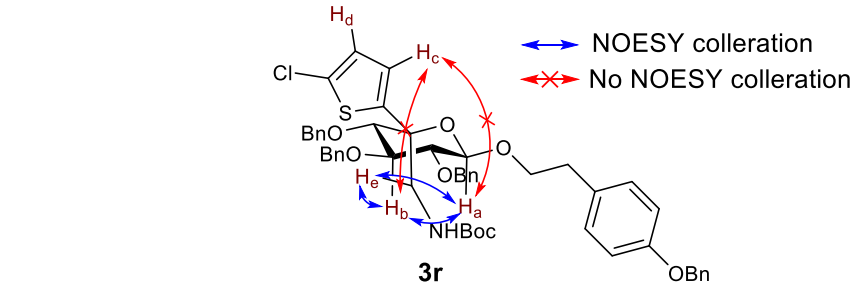




3r

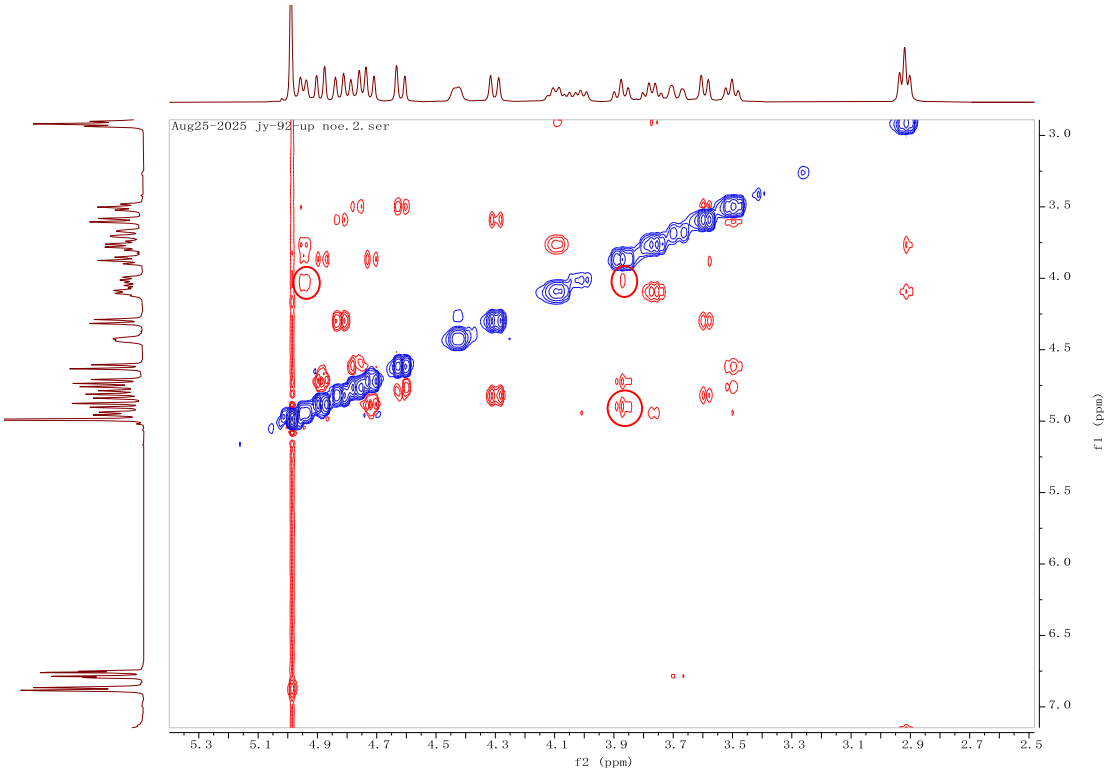
^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$)

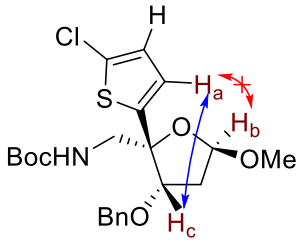




3r

NOESY NMR (400 MHz, $CDCl_3$)



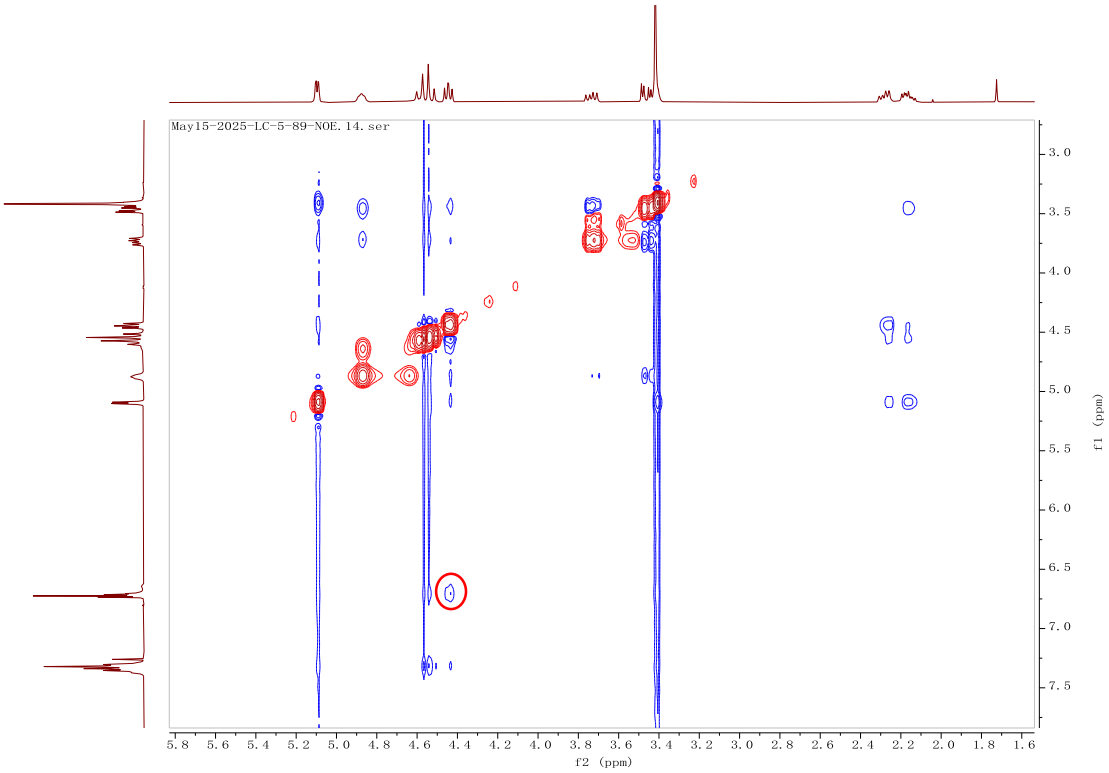


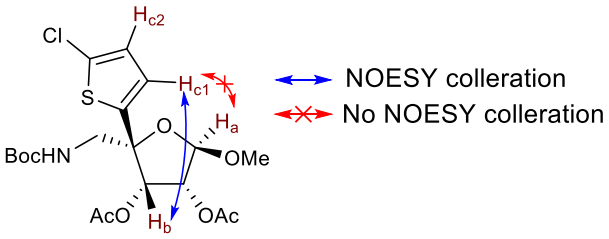
3s

NOESY NMR (400 MHz, $CDCl_3$)

NOESY colleration

No NOESY colleration





3t

NOESY NMR (400 MHz, $CDCl_3$)